Enantioselective intramolecular [2+2] photocycloaddition using phosphoric acid as a chiral template

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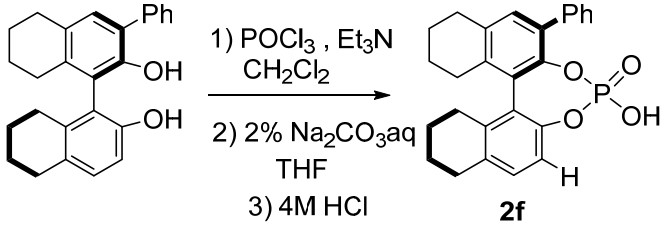
General Method

Internal references for ^{1}H NMR spectra were 0.0 ppm (Me_4Si) for $CDCl_3$ and CD_3OD (3.31 ppm). Chemical shifts for ^{13}C NMR spectra were referenced to $CDCl_3$ (77.0 ppm) and CD_3OD (49.86 ppm). Chemical shift for ^{31}P NMR spectra were reported on the basis on 85% H_3PO_4 (0.0 ppm) as an external standard. High resolution mass spectral (HRMS) data were recorded with a LTQ Orbitrap trap mass spectrometer using electrospray ionization (ESI) method. The enantiomeric excess (ee) of the products was determined by high performance liquid chromatography (HPLC) analysis on Chiralpak IC column (0.46 × 25 cm). Optical rotations were measured on a digital polarimeter with a 0.1 dm cell at room temperature. All reactions involving air- and moisture-sensitive reagents were carried out under N_2. All reactions were monitored by analytical thin-layer chromatography (TLC), which was visualized by ultraviolet light (254 nm).

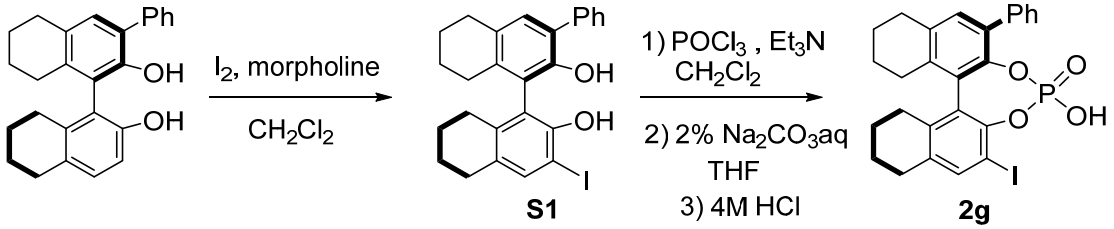
Typical precedure of preparation of chiral phosphoric acid 2

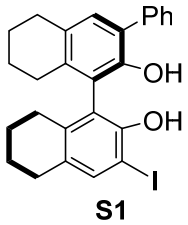


(*R*)-5,5',6,6',7,7',8,8'-Octahydro-3-phenyl-[1,1'-Binaphthalene]-2,2'-diol[1] (97.7 mg, 0.26 mmol) was dissolved in CH_2Cl_2 (1.5 mL). To the mixture was added Et_3N (0.3 mL, 2.16 mmol) and $POCl_3$ (0.2 mL, 2.15 mmol) at 0 °C. After the addition, the mixture was allowed to warm up to room temperature. After the stirring at room temperature for 18 h, the reaction mixture quenched with H_2O, then extracted with CH_2Cl_2. The organic layer were washed with H_2O and brine, dried over Na_2SO_4, filtered, and concentrated in vacuo. The crude product was purified by silica gel column chromatography (hexane/EtOAc = 10:1). After work up, the reaction mixture was dissolved in THF (4.0 mL) and 2% Na_2CO_3 aq (5.0 mL) and refluxed for 21 h at 110 °C. After the refluxing, THF was remove by evaporation and the reaction mixture was neutralized by 1N HCl, then extracted with CH_2Cl_2. The organic layer were washed with H_2O and brine, dried over Na_2SO_4, filtered, and concentrated in vacuo. The crude product was purified by silica gel column chromatography (CH_2Cl_2/MeOH = 10 : 1). The resultant solid was dissolved in CH_2Cl_2, The

organic layer was washed with 4N HCl and water, and concentrated in vacuo to give the title compound in 80% yield as a colorless solid. mp 171-173 °C. $[\alpha]^{26}_{D}$ –164.5 (*c* = 1.00, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (d, *J* = 7.5 Hz, 2 H), 7.32 (t, *J* = 7.5 Hz, 2 H), 7.24 (t, *J* = 7.5 Hz, 1 H), 7.16 (s, 1 H), 7.10 (d, *J* = 8.2 Hz, 1 H), 7.01 (d, *J* = 8.2 Hz, 1 H), 2.93-2.74 (m, 4 H), 2.74-2.62 (m, 2 H), 2.39-2.23 (m, 2 H), 1.87-1.72 (m, 6 H), 1.67-1.52 (m, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.1 (d, *J* = 9.0 Hz), 142.9 (d, *J* = 9.2 Hz), 138.3, 137.6, 137.0, 135.6 (d, *J* = 2.0 Hz), 135.4 (d, *J* = 2.2 Hz), 131.7 (d, *J* = 3.5 Hz), 131.2, 130.1, 129.5 (x2), 128.1 (x2), 127.2, 126.6, 126.3, 118.1 (d, *J* = 3.5 Hz), 29.2 (x2), 27.9 (x2), 22.6, 22.5 (x2), 22.4. ^{31}P NMR (160 MHz, $CDCl_3$) δ 2.28. HRMS (ESI+) *m*/*z* calcd for $C_{26}H_{26}O_4P$ $[M+H]^+$ 433.15632, found 433.15628.

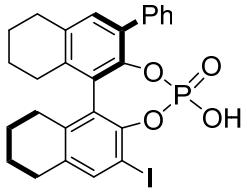
Preparation of chiral phosphoric acid 2g[2]





(*R*)-5,5',6,6',7,7',8,8'-Octahydro-3-phenyl-[1,1'-Binaphthalene]-2,2'-diol (250 mg, 0.68 mmol), and I_2 (186 mg, 0.73 mmol) were dissolved in CH_2Cl_2 (4.0 mL). To the mixture with stirring, was added morpholine (0.33 ml, 3.8 mmol) at room temperature. The reaction mixture was stirred for 23 h at room temperature. After being stirring, the reaction mixture quenched with sat. $Na_2S_2O_3$, then extracted with CH_2Cl_2. The organic layer were washed with H_2O and brine, dried over Na_2SO_4, filtered, and concentrated in vacuo. The combined crude product was purified by silica gel column chromatography (hexane/EtOAc = 5 : 1) to give **S1** in 86% yield as a colorless solid. mp 117-118 °C. $[\alpha]^{25}_{D}$ –4.4 (*c* = 1.00, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (d, *J* = 7.4 Hz, 2 H), 7.53 (s, 1 H), 7.43 (t, *J* = 7.4 Hz, 2 H), 7.33 (t, *J* = 7.4 Hz, 1 H), 7.13 (s, 1 H), 5.12 (s, 1 H), 4.77 (s, 1 H), 2.79 (t, *J* = 6.5 Hz, 2 H), 2.73 (t, *J* = 6.1 Hz, 2 H), 2.40-2.28 (m, 2 H), 2.23-2.11 (m, 2 H), 1.82-1.62 (m, 8 H). ^{13}C

NMR (100 MHz, $CDCl_3$) δ 150.3, 147.7, 139.4, 138.0, 137.7, 136.3, 132.5, 131.7, 130.2, 129.2 (x2), 128.6 (x2), 127.3, 126.2, 120.5, 120.3, 80.5, 29.2, 28.9, 27.1 (x2), 23.0 (x2), 22.8, 22.7. HRMS (ESI+) *m*/*z* calcd for $C_{26}H_{25}IO_2$ $[M+Na]^+$ 519.07914, found 519.07898.

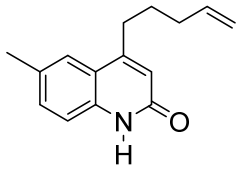


2g

(*R*)-5,5',6,6',7,7',8,8'-Octahydro-3-iodo-3'-phenyl-[1,1'-Binaphthalene]-2,2'-diol **S1** (199 mg, 0.40 mmol) was dissolved in CH_2Cl_2 (1.5 mL). To the mixture was added Et_3N (0.3 mL, 2.16 mmol) and $POCl_3$ (0.2 mL, 2.15 mmol) at 0 °C. After the addition, the mixture was allowed to warm up to room temperature. After being stirring at room temperature for 23 h, the reaction mixture was quenched with H_2O, then extracted with CH_2Cl_2. The organic layer was washed with H_2O and brine, dried over Na_2SO_4, filtered, and concentrated in vacuo. The crude product was purified by silica gel column chromatography (hexane/EtOAc = 10 : 1). The resultant solid was dissolved in THF (5.0 mL) and 2% Na_2CO_3 aq (10 ml) and refluxed for 21 h at 110 °C. After the refluxing, THF was remove by evaporation and the reaction mixture was neutralized by 1N HCl, and then extracted with CH_2Cl_2. The organic layer was washed with H_2O and brine, dried over Na_2SO_4, filtered, and concentrated in vacuo. The crude product was purified by silica gel column chromatography (CH_2Cl_2/MeOH = 10 : 1). The resultant solid was extracted with CH_2Cl_2, and the organic layer was washed with 4N HCl and water, and concentrated in vacuo to give the title compound in 77% yield as a colorless solid. mp 233-234 °C. $[\alpha]^{28}_D$ –216.0 (*c* = 1.00, $CHCl_3$). ^1H NMR (400 MHz, CD_3OD) δ 7.64 (s, 1 H), 7.61 (d, *J* = 7.9 Hz, 2 H), 7.39 (t, *J* = 7.9 Hz, 2 H), 7.31 (t, *J* = 7.9 Hz, 1 H), 7.21 (s, 1 H), 2.74-2.30 (m, 4 H), 2.73-2.62 (m, 2 H), 2.29-2.18 (m, 2 H), 1.88-1.72 (m, 6 H), 1.66-1.52 (m, 2 H). ^{13}C NMR (100 MHz, CD_3OD) δ 146.6 (d, *J* = 9.0 Hz), 143.4 (d, *J* = 9.0 Hz), 139.0, 138.5, 137.3, 137.0, 136.9, 135.1, 131.9 (d, *J* = 2.9 Hz), 131.1, 129.3 (x2), 127.7 (x2), 127.5, 126.9 (x2), 85.0 (d, *J* = 4.2 Hz), 28.6, 28.3, 27.4, 27.3, 22.3, 22.2, 22.1, 22.0. ^{31}P NMR (160 MHz, CD_3OD) δ –0.68. HRMS (ESI+) *m*/*z* calcd for $C_{26}H_{24}IO_4P$ $[M+Na]^+$ 581.03491, found 581.03522.

Preparation of quinolinone 3a-c,e-g

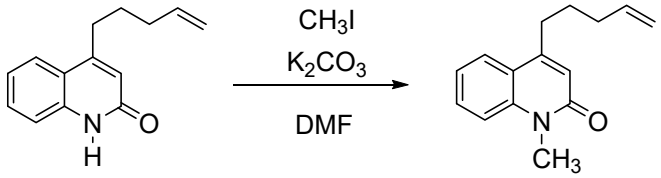
Quinolinones **3a**,**c**[3a], **e-g**[3b] were prepared according to reported procedures. Quinolinone **3b** was prepared from 4,8-Dimethyl-2-quinoline[3c].



3b

mp 138-139 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.14 (br, 1 H), 7.48 (s, 1 H), 7.32 (dd, J = 8.3, 1.5 Hz), 7.2 (d, J = 8.3 Hz, 1 H), 6.56 (s, 1 H), 5.92-5.81 (m, 1 H), 5.13-5.02 (m, 2 H), 2.85 (t, J = 7.8 Hz, 2 H), 2.44 (s, 3 H), 2.25-2.17 (m, 2 H), 1.89-1.78 (m, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.5, 152.6, 137.8, 136.3, 132.0, 131.7, 124.0, 119.7, 119.6, 116.3, 115.5, 33.3, 31.5, 27.8, 21.2. HRMS (ESI+) calcd for $C_{15}H_{18}NO$ $[M+H]^+$ 228.13829, found 228.13837.

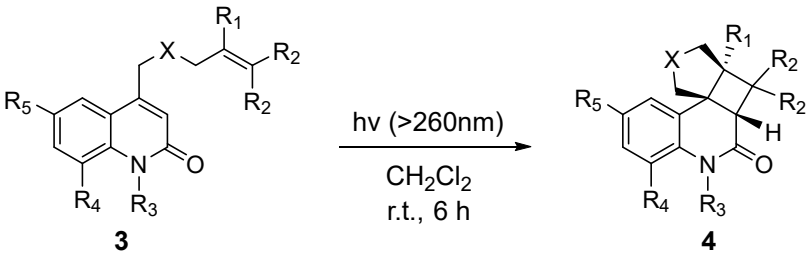
Preparation of quinolinone 3d[4]



3a **3d**

Quniolinone **3a** (206 mg, 0.98 mmol) and K_2CO_3 (808 mg, 5.85 mmol) were mixed in DMF (5.0 mL) under N_2. To the suspension was added iodomethane (0.5 mL, 8.0 mmol) and stirred at room temperature for 20 h. After the stirring, the mixture was concentrated in vacuo and added water, then extracted with diethyl ether. The organic layer were washed with sat. $NaHCO_3$ and brine, dried over Na_2SO_4, filtered, and concentrated in vacuo. The crude product was purified by silica gel column chromatography (hexane/EtOAc = 1 : 1) to give **3d** in 83% yield as as a white solid. mp 40 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, J = 8.0 Hz, 1 H), 7.60 (t, J = 7.8 Hz, 1 H), 7.39 (d, J = 8.4 Hz, 1 H), 7.26 (t, J = 7.6 Hz, 1 H), 6.61 (s, 1 H), 5.92-5.78 (m, 1 H), 5.12-4.99 (m, 2 H) ,3.72 (s, 3 H), 2.83 (t, J = 7.8 Hz, 2 H), 2.25-2.16 (m, 2 H), 1.86-1.76 (m, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.2, 150.0, 140.1, 137.8, 130.3, 124.9, 121.8, 120.6, 120.2, 115.5, 114.6, 33.4, 31.3, 29.2, 27.9. HRMS (ESI+) m/z calcd for $C_{15}H_{17}NO$ $[M+Na]^+$ 250.12024, found 250.12041.

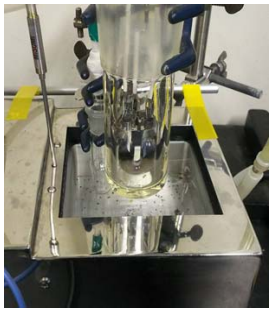
Typical precedure of preparation of racemic cycloadduct 4



Quinolinone derivative **3** (25 μmol) were dissolved in CH_2Cl_2 (0.25 mL, degassed by N_2 bubbling) in NMR tube (under N_2 gas, septum sealed). The solution was irradiated by 100 W high pressure mercury lamp. After 6 hours irradiation, the solvent was removed by reduced pressure and the crude was purified by silica gel column chromatography to give racemic cycloadduct **4**.

Reaction Apparatus

100 W High pressure Hg-lamp



Pyrex test tube and lamp

Image of apparatus

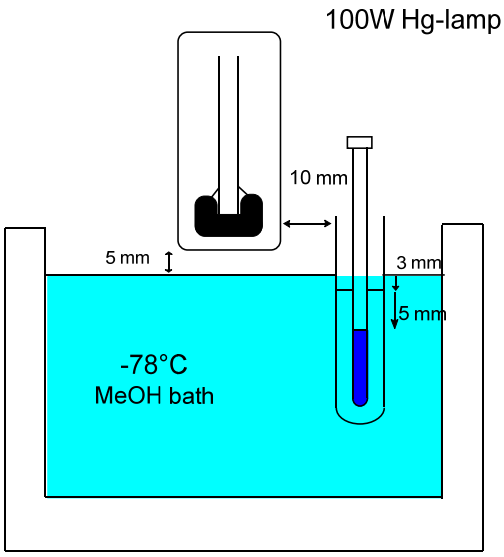


Fig. S1 Reaction apparatus.

Characterization of the complex of phosphoric acid 2a and quinolinone 3a using NMR measurements and DFT calculations

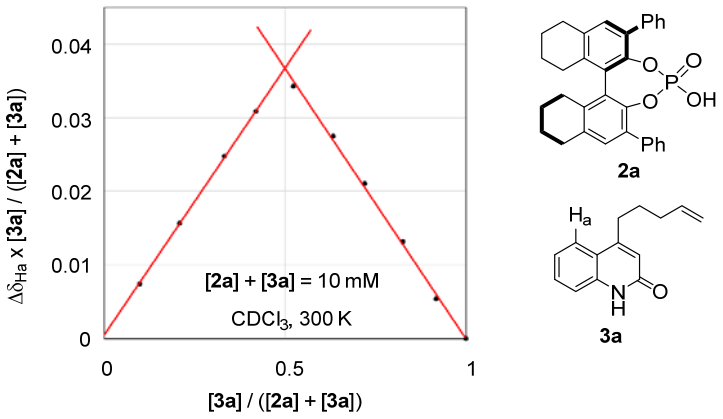


Fig. S2 Stoichiometry determination in the complexation of **2a** and **3a** by Job's method.

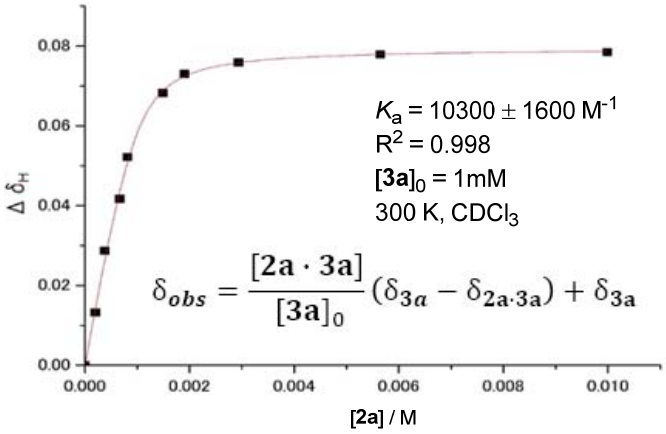


Fig. S3 Determination of the association constant for the formation of the 1:1 complex of **2a** and **3a** via ^{1}H NMR titration experiment.

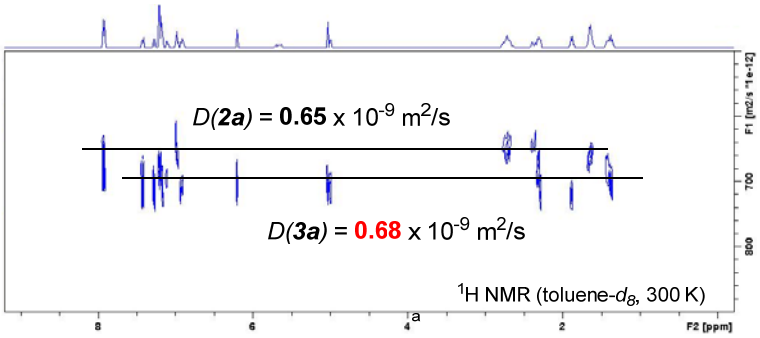


Fig. S4 Determination of the association constant for the formation of the 1:1 complex of **2a** and **3a** via DOSY measurement in ^{1}H NMR titration experiment.

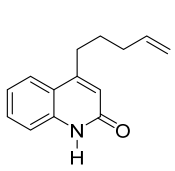
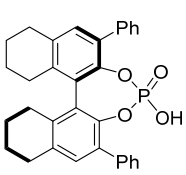
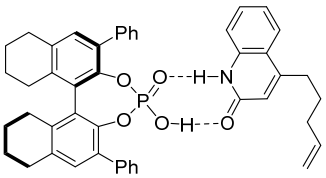
	 **3a**	 **2a**	 **2a=3a**
Diffusion coefficient (^{1}H NMR, 10 mM, toluene-d_8, 300 K)	D = **0.98** x 10^{-9} m^2/s	D = **0.46** x 10^{-9} m^2/s	D(**2a**) = **0.65** x 10^{-9} m^2/s D(**3a**) = **0.68** x 10^{-9} m^2/s
Molar volume (B3LYP/6-31G*)	**290 Å^3**	Monomer : **554 Å^3** Dimer: **1240 Å^3**	**721 Å^3**

Fig. S5 Diffusion coefficient in toluene-d_8 (10 mM) at 300 K and molar volume calculated at the B3LYP/6-31G* level of theory of **2a**, **3a** and the 1:1 complex of **2a** and **3a**.

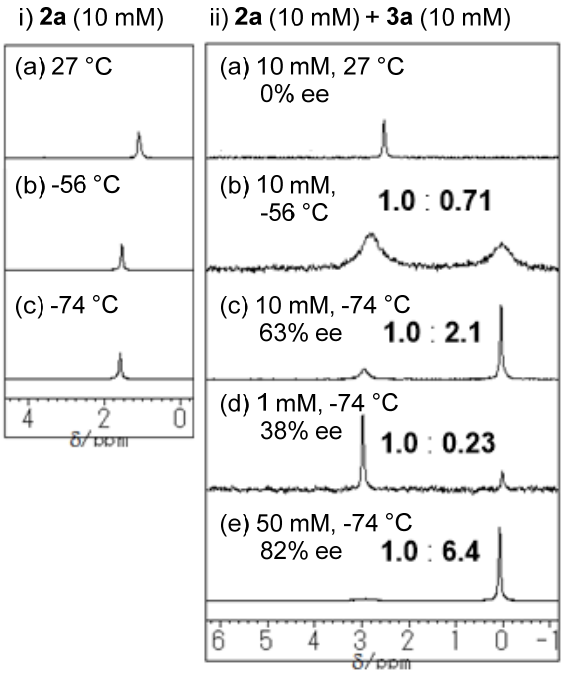


Fig. S6 ^{31}P NMR spectra of (i) phosphoric acid **2a** and (ii) a mixture of **2a** and **3a** (**2a**/**3a** = 1:1) in CD_2Cl_2 at several conditions.

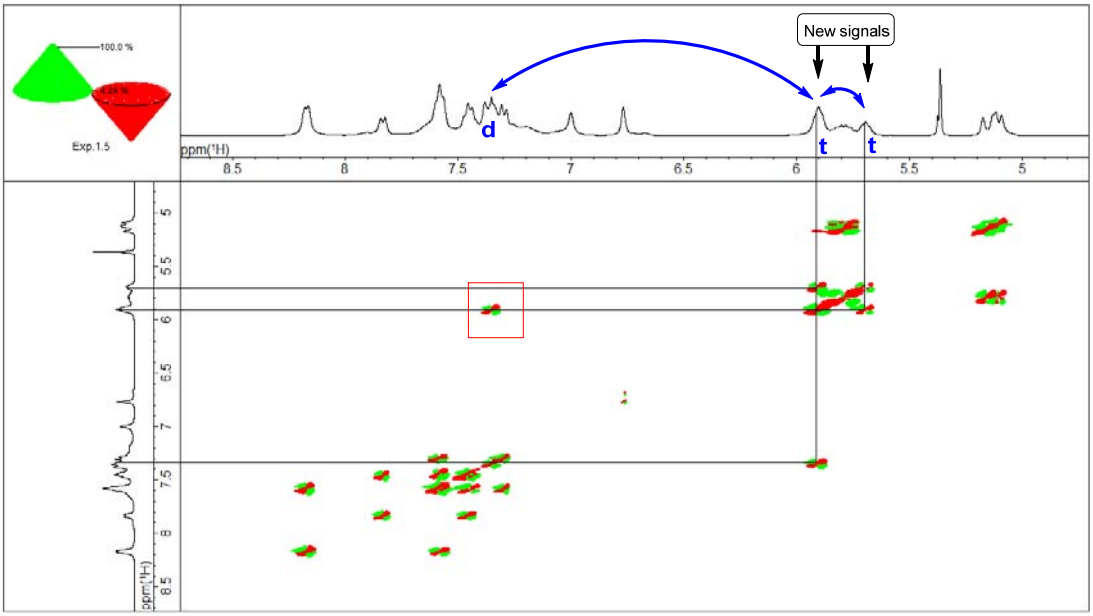


Fig. S7 ^{1}H-^{1}H DQF-COSY spectrum of a mixture of **2a** and **3a** (50 mM, **2a**/**3a** = 1:1) in CD_2Cl_2 at -74 °C.

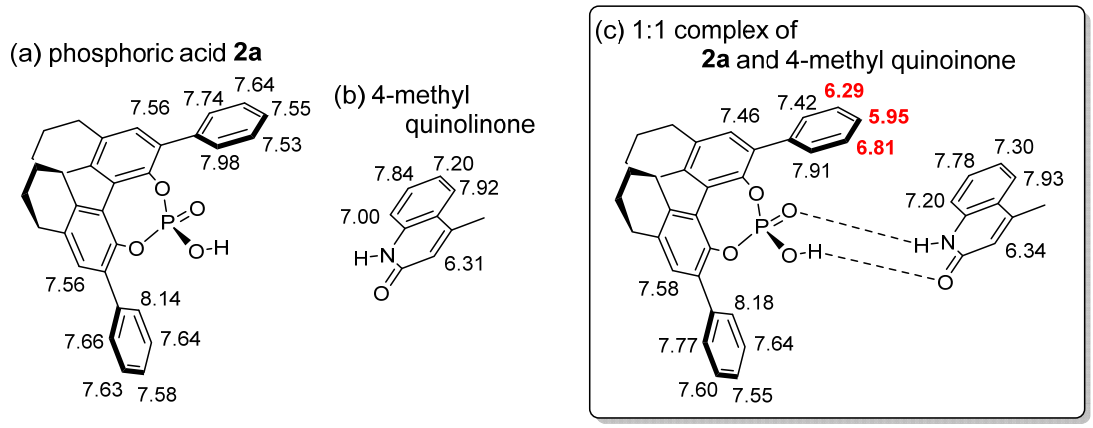
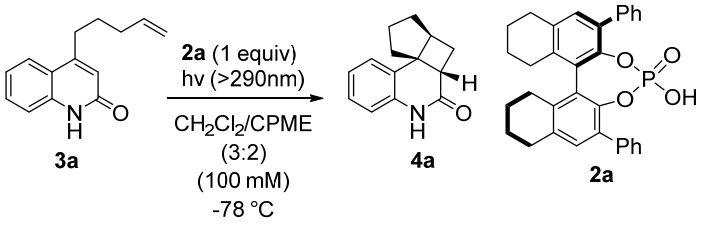


Fig. S8 Speculated ^{1}H NMR chemical shift using the GAIO method at HF/6-31G(d) of (a) phosphoric acid **2a**, (b) 4-methyl quinolinone, and (c) *Re*-form of the 1:1 complex of **2a** and 4-methyl quinolinone.

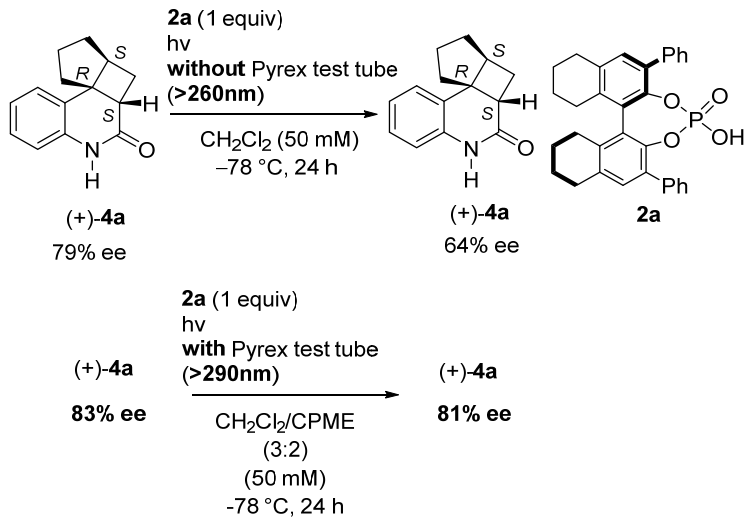
Optimization of reaction conditions

Table S1 Time profile of the photocycloaddition of **3a** using **2a**[a]



irradiation time	**3a** : **4a**[b]	ee (%)[c]
1 h	90 : 10	59
7.5 h	56 : 44	83
12 h	43 : 57	85
18 h	29 : 71	88
24 h	17 : 83	87
40 h	14 : 86	84

[a] All reactions were conducted at a substrate concentration of 100 mM with 1.0 equiv of phosphoric acid **2a** in CH_2Cl_2 at –78 °C. [b] Determined by ^{1}H NMR measurement of crude product. [c] Determined by chiral stationary phase HPLC analysis.



Scheme S1 Recombination of the cyclobutane ring on **4a** under the photocycloaddition conditions.

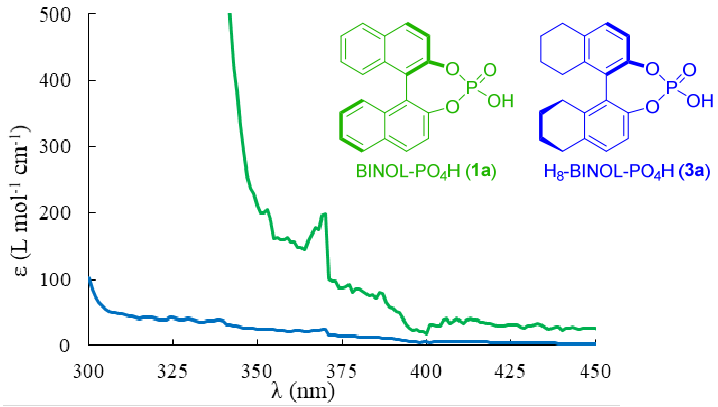
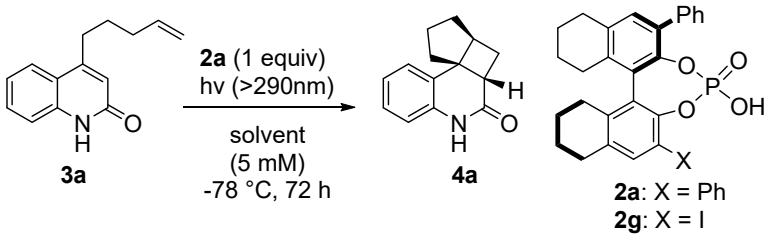


Fig. S9 UV Absorption spectra of BINOL- and H_8-BINOL-PO_4H in benzene.

Table S2 Screening of solvent in the photocycloaddition using **2a**[a]



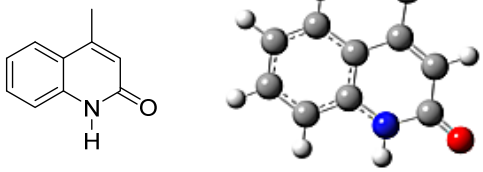
Entry	solvent	yield (%)[b]	ee (%)[c]
1[d,e]	toluene	94	33
2[d]	CH_2Cl_2	95	67
3[d]	acetone	>95	35
4[d]	THF	>95	7
5[d]	MTBE	61	68
6[f]	CPME	>95	60

[a] All reactions were conducted at a substrate concentration of 5 mM with 1.0 equiv of phosphoric acid **2a** at –78 °C. [b] Isolated yield. [c] Determined by chiral stationary phase HPLC analysis. [d] A mixture of **2a** and **2g** (**2a**/**2g** = 9:1) was used for the reaction as a chiral template. [e] The reaction mixture was irradiated for 48 h. [f] A 10 mM solution of **3a** in CPME was used for the reaction. MTBE = methyl *tert*-butyl ether. CPME = cyclopentyl methyl ether.

Computational data: Cartesian coordinates, energies in Figs. 6 and S7.[5]

The relative Gibbs energies in Fig. 6 were estimated after the correction of basis set superposition errors (BSSE)[6] using the counterpoise method.[7,8]

4-Methyl quinolinone



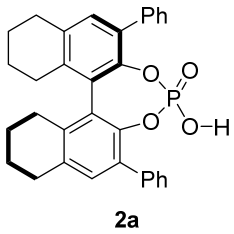
RB3LYP/6-31G(d)
empirical dispersion=gd3

Number of Imaginary Frequencies = 0
Zero-point correction = 0.169179 a.u.
Thermal correction to Energy = 0.178475 a.u.
Thermal correction to Enthalpy= 0.179419 a.u.
Thermal correction to Gibbs Free Energy = 0.134850 a.u.
Sum of electronic and zero-point Energies = -516.337496 a.u.
Sum of electronic and thermal Energies = -516.328199 a.u.
Sum of electronic and thermal Enthalpies = -516.327255 a.u.
Sum of electronic and thermal Free Energies = -516.371825 a.u.

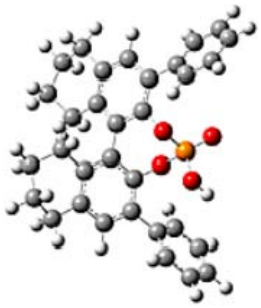
Center Number	Atomic Number	Forces (Hartrees/Bohr) X	Y	Z
1	1	-0.000000604	-0.000006947	0.000006888
2	6	0.000003024	0.000036410	-0.000012194
3	6	0.000003487	-0.000019335	0.000018755
4	6	-0.000076583	-0.000003227	-0.000022522
5	6	0.000014382	-0.000024199	0.000015646
6	6	-0.000015704	0.000008871	-0.000015585
7	6	0.000126605	0.000091546	-0.000028091
8	1	-0.000002622	0.000002960	-0.000004220
9	1	0.000008636	0.000002921	0.000004120
10	1	-0.000000771	0.000002207	-0.000004736
11	6	0.000029521	-0.000083219	0.000014231
12	6	0.000063811	0.000026755	0.000037435
13	1	-0.000009961	0.000003919	0.000000583
14	6	-0.000091033	0.000042319	-0.000125286
15	7	-0.000111081	-0.000102778	0.000088576
16	8	0.000037937	0.000020110	0.000005196
17	6	-0.000010043	0.000017182	0.000003715
18	1	-0.000002506	-0.000002299	-0.000000531
19	1	0.000005219	0.000000907	0.000002061

20	1	0.000031735	-0.000012214	0.000015557
21	1	-0.000003449	-0.000001886	0.000000405

Phosphoric acid 2a



2a



RB3LYP/6-31G(d)
empirical dispersion=gd3

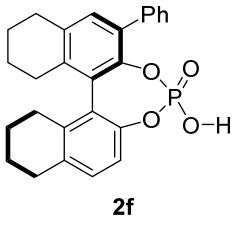
Number of Imaginary Frequencies = 0
Zero-point correction = 0.540188 a.u.
Thermal correction to Energy = 0.570319 a.u.
Thermal correction to Enthalpy = 0.571264 a.u.
Thermal correction to Gibbs Free Energy = 0.478768 a.u.
Sum of electronic and zero-point Energies = -1878.783638 a.u.
Sum of electronic and thermal Energies = -1878.753507 a.u.
Sum of electronic and thermal Enthalpies = -1878.752563 a.u.
Sum of electronic and thermal Free Energies = -1878.845058 a.u.

Center Number	Atomic Number	Forces (Hartrees/Bohr) X	Y	Z
1	6	0.000005721	0.000000382	0.000001943
2	1	0.000000609	0.000000970	0.000000645
3	6	-0.000000405	-0.000004594	0.000003769
4	6	-0.000001135	-0.000003314	0.000002960
5	6	-0.000006987	0.000003935	0.000001474
6	6	-0.000002442	0.000002719	0.000003116

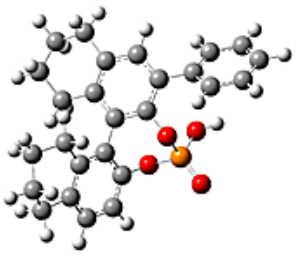
7	6	0.000007354	0.000005134	-0.000002759
8	6	0.000009531	0.000002563	-0.000005214
9	6	-0.000004276	-0.000004857	-0.000004479
10	6	-0.000001144	-0.000002179	-0.000003503
11	6	0.000000089	-0.000000572	0.000004139
12	6	-0.000006127	-0.000001307	0.000001652
13	6	0.000008152	0.000001002	-0.000000578
14	1	-0.000000250	0.000000910	-0.000001657
15	8	-0.000002520	-0.000006892	-0.000016727
16	8	-0.000001380	-0.000006034	0.000011966
17	15	0.000006638	0.000016081	0.000002060
18	8	0.000005018	-0.000000287	0.000001901
19	8	-0.000004225	-0.000001963	0.000005431
20	1	-0.000000679	-0.000000593	-0.000003097
21	6	-0.000001852	0.000002089	-0.000001410
22	6	0.000000540	0.000000472	0.000002287
23	6	0.000000052	0.000001207	0.000002135
24	6	-0.000000187	0.000001694	0.000000801
25	6	-0.000000092	0.000001370	0.000001477
26	6	0.000000397	0.000001707	0.000001172
27	1	0.000000712	0.000001606	0.000001057
28	1	-0.000000883	0.000000818	0.000000821
29	1	-0.000000283	0.000001290	0.000001324
30	1	0.000000991	0.000001531	0.000001803
31	1	0.000000726	0.000001550	0.000001849
32	6	0.000001093	0.000002163	-0.000000223
33	6	0.000000588	-0.000000730	-0.000001010
34	6	0.000001454	-0.000002466	-0.000002020
35	6	-0.000001131	-0.000000721	-0.000001419
36	6	0.000000645	-0.000001165	-0.000001563
37	6	0.000001762	-0.000000817	-0.000000020
38	1	0.000000269	-0.000001363	-0.000000125
39	1	0.000000204	-0.000002396	-0.000000720
40	1	0.000000923	-0.000001163	-0.000000912
41	1	0.000001731	-0.000001115	-0.000000570
42	1	0.000001568	-0.000001503	-0.000000780

43	6	-0.000003052	0.000002410	-0.000000125
44	6	-0.000001168	-0.000001079	-0.000003378
45	1	-0.000000050	-0.000000798	0.000000642
46	6	0.000001595	-0.000000620	0.000001028
47	1	-0.000000159	0.000000633	0.000000344
48	6	-0.000001565	-0.000002305	-0.000001072
49	1	-0.000000105	0.000000082	0.000000448
50	1	0.000000251	-0.000001720	0.000000240
51	1	-0.000000811	-0.000000268	0.000000628
52	1	-0.000000546	0.000000572	0.000000203
53	1	-0.000002527	-0.000002355	-0.000001494
54	1	-0.000001927	0.000000831	0.000000259
55	6	0.000000404	-0.000000563	0.000000131
56	1	-0.000000679	0.000000088	0.000000260
57	1	-0.000000292	-0.000000370	-0.000000179
58	6	-0.000001183	0.000001138	0.000000323
59	1	-0.000000226	0.000000460	0.000000348
60	1	0.000000486	-0.000000397	0.000000713
61	6	-0.000002119	0.000001856	0.000000953
62	1	-0.000001910	0.000000358	-0.000000715
63	1	-0.000001058	-0.000000909	-0.000001573
64	6	-0.000000739	-0.000002021	-0.000003089
65	1	-0.000001273	0.000000302	-0.000000467
66	1	-0.000002119	-0.000000493	-0.000001420

Phosphoric acid 2f



2f



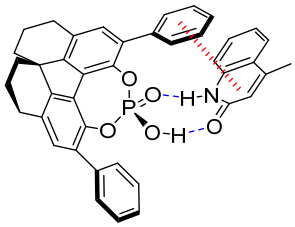
RB3LYP/6-31G(d)
empirical dispersion=gd3

Number of Imaginary Frequencies = 0
Zero-point correction = 0.458985 a.u.
Thermal correction to Energy = 0.484364 a.u.
Thermal correction to Enthalpy = 0.485308 a.u.
Thermal correction to Gibbs Free Energy = 0.403662 a.u.
Sum of electronic and zero-point Energies = -1647.797836 a.u.
Sum of electronic and thermal Energies = -1647.772457 a.u.
Sum of electronic and thermal Enthalpies = -1647.771513 a.u.
Sum of electronic and thermal Free Energies = -1647.853159 a.u.

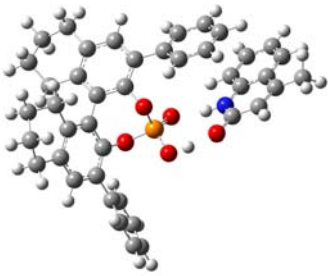
Center Number	Atomic Number	Forces (Hartrees/Bohr) X	Y	Z
1	6	-0.000005155	-0.000002296	0.000002432
2	1	-0.000002315	0.000001496	0.000003679
3	6	0.000001362	-0.000002074	-0.000000656
4	6	0.000003500	-0.000000853	-0.000002101
5	6	0.000001951	0.000007181	0.000003640
6	6	-0.000004298	0.000003762	0.000007072
7	6	-0.000007885	-0.000001697	0.000001245
8	6	-0.000006253	-0.000004090	-0.000001377
9	6	0.000004497	-0.000004076	0.000002110
10	6	0.000004096	-0.000005592	0.000000389
11	6	0.000000493	0.000004431	-0.000001330
12	6	0.000004306	0.000007271	-0.000001923
13	6	-0.000005435	-0.000002729	-0.000004390
14	1	0.000000819	-0.000000518	-0.000002267
15	8	0.000003685	-0.000004552	0.000002300
16	8	0.000000350	0.000001945	0.000002155
17	15	-0.000005863	-0.000001578	0.000001397
18	8	-0.000003142	-0.000001596	0.000002246
19	8	0.000000570	-0.000002267	-0.000000400
20	1	-0.000001156	-0.000003063	0.000002089
21	6	-0.000000968	-0.000001309	0.000001747
22	6	0.000000370	-0.000000862	-0.000000423

23	6	0.000001439	-0.000001769	0.000000816
24	6	-0.000001148	-0.000001844	-0.000000868
25	6	0.000000882	-0.000004176	0.000000180
26	6	-0.000002062	-0.000001272	0.000000688
27	1	-0.000000559	0.000000619	0.000000893
28	1	0.000000791	-0.000003329	-0.000001309
29	1	-0.000000073	-0.000003742	-0.000000955
30	1	-0.000000735	-0.000000563	0.000001225
31	1	-0.000000804	-0.000003056	0.000000421
32	6	0.000002797	0.000000475	-0.000002497
33	6	0.000001153	-0.000001301	-0.000000951
34	1	0.000000743	0.000000289	-0.000001308
35	6	-0.000001801	0.000001597	0.000001358
36	1	-0.000001178	0.000003194	0.000002917
37	6	0.000001454	0.000002229	0.000001109
38	1	0.000000829	0.000002155	-0.000001147
39	1	0.000001823	-0.000001843	-0.000004077
40	1	0.000000371	0.000003179	0.000000543
41	1	-0.000000640	0.000002592	0.000001892
42	1	0.000002685	-0.000000092	-0.000003549
43	1	0.000000469	-0.000000822	-0.000001387
44	6	0.000000571	0.000002643	-0.000000128
45	1	0.000000414	0.000003267	-0.000000289
46	1	0.000000736	0.000004227	-0.000000452
47	6	-0.000000112	0.000005244	0.000001578
48	1	-0.000000260	0.000004735	0.000001404
49	1	-0.000000564	0.000004123	0.000001571
50	6	0.000002000	0.000000685	-0.000002872
51	1	0.000001616	-0.000000062	-0.000002682
52	1	0.000001706	0.000000608	-0.000002660
53	6	0.000001542	-0.000001603	-0.000002937
54	1	0.000001692	-0.000001779	-0.000003217
55	1	0.000002465	-0.000000905	-0.000004166
56	1	-0.000001770	-0.000000635	0.000003220

Re-form of the 1:1 complex of 2a with 4-methyl quinolinone



Re-form of complex of **2a**
with 4-methyl quinolinone



RB3LYP/6-31G(d)
empirical dispersion=gd3

Number of Imaginary Frequencies = 0
Zero-point correction = 0.710995 a.u.
Thermal correction to Energy = 0.751411 a.u.
Thermal correction to Enthalpy = 0.752355 a.u.
Thermal correction to Gibbs Free Energy = 0.636504 a.u.
Sum of electronic and zero-point Energies = -2395.171721 a.u.
Sum of electronic and thermal Energies = -2395.131305 a.u.
Sum of electronic and thermal Enthalpies = -2395.130361 a.u.
Sum of electronic and thermal Free Energies = -2395.246212 a.u.
BSSE energy = 0.010665237821 a.u.

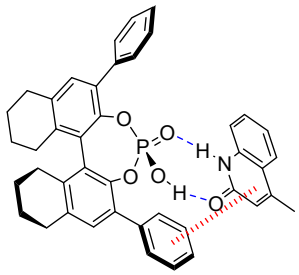
Center Number	Atomic Number	Forces (Hartrees/Bohr) X	Y	Z
1	6	0.000001089	-0.000001306	0.000000760
2	1	0.000000310	-0.000000079	-0.000001352
3	6	-0.000000781	0.000000265	-0.000000777
4	6	-0.000000317	-0.000001435	-0.000000991
5	6	0.000000645	-0.000000264	-0.000000008
6	6	-0.000001581	0.000005542	0.000002136
7	6	-0.000001236	0.000002283	0.000001065
8	6	-0.000002920	0.000004455	0.000003589
9	6	-0.000000138	0.000000403	-0.000001493
10	6	0.000000639	0.000000961	0.000000188

11	6	0.000001393	-0.000000721	-0.000000039
12	6	-0.000000289	0.000000243	0.000000921
13	6	0.000000081	-0.000000911	0.000001258
14	1	0.000000291	-0.000000013	0.000001206
15	8	0.000001387	-0.000004574	-0.000005603
16	8	0.000001844	-0.000006445	-0.000004449
17	15	-0.000000809	0.000010634	0.000008581
18	8	0.000001780	-0.000001437	-0.000001616
19	6	-0.000002253	0.000000136	-0.000002454
20	6	0.000000266	-0.000000112	-0.000001773
21	6	-0.000000570	-0.000000333	-0.000000237
22	6	0.000001545	-0.000001675	0.000001494
23	6	-0.000001048	-0.000000408	-0.000000844
24	6	0.000000391	-0.000001465	0.000000251
25	1	-0.000000704	-0.000000173	-0.000001032
26	1	0.000000498	-0.000000764	-0.000000430
27	1	-0.000000154	-0.000000878	-0.000000307
28	1	-0.000000549	-0.000000253	-0.000001468
29	1	-0.000000113	-0.000001060	-0.000000591
30	6	0.000000971	0.000001339	0.000001631
31	6	0.000000640	0.000000075	0.000001524
32	6	0.000000042	0.000000243	-0.000000441
33	6	-0.000000085	-0.000000047	0.000000959
34	6	0.000000531	0.000000728	0.000001585
35	6	0.000000237	0.000000837	0.000001431
36	1	-0.000000018	0.000001901	0.000000922
37	1	0.000000652	-0.000000010	0.000001170
38	1	0.000000777	0.000000222	0.000001475
39	1	0.000000298	0.000001012	0.000001137
40	1	0.000000540	0.000000828	0.000001504
41	6	-0.000000269	-0.000000335	0.000001299
42	6	-0.000000241	0.000000203	-0.000000420
43	1	0.000001246	0.000000097	0.000000139
44	6	-0.000000093	0.000000153	-0.000000732
45	1	-0.000000580	0.000000584	-0.000001208
46	6	-0.000000509	0.000000547	0.000000192

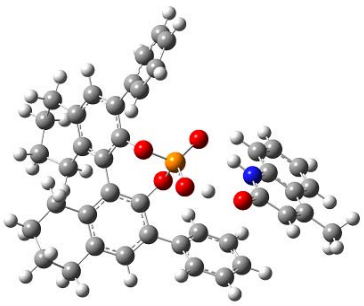
47	1	0.000000302	0.000000675	-0.000000193
48	1	0.000000875	-0.000000270	0.000001685
49	1	-0.000000330	0.000000756	-0.000000520
50	1	-0.000000342	0.000000496	-0.000001071
51	1	0.000000895	0.000001243	0.000000287
52	1	-0.000000551	0.000000503	0.000001023
53	6	-0.000000033	0.000001012	-0.000001023
54	1	-0.000000456	0.000000512	-0.000000157
55	1	-0.000000387	0.000000895	-0.000000113
56	6	-0.000001073	0.000000811	-0.000000628
57	1	-0.000000521	0.000000736	-0.000000952
58	1	-0.000000444	0.000000926	-0.000000554
59	6	-0.000000348	-0.000000635	0.000000507
60	1	-0.000000287	-0.000000016	0.000000168
61	1	0.000000272	0.000000276	-0.000000160
62	6	0.000000938	0.000000417	0.000000339
63	1	-0.000000037	-0.000000653	0.000000579
64	1	0.000000127	0.000000034	0.000000295
65	1	-0.000000060	-0.000000738	-0.000000597
66	6	-0.000000229	-0.000001562	-0.000000663
67	6	-0.000001153	-0.000000313	0.000000901
68	6	0.000001132	0.000003428	0.000001249
69	6	-0.000001606	-0.000001029	-0.000000945
70	6	0.000001379	0.000000952	-0.000001781
71	6	0.000000150	-0.000001791	-0.000002056
72	1	0.000000283	0.000000404	-0.000000875
73	1	-0.000001113	-0.000000426	-0.000000095
74	1	-0.000000185	0.000000226	-0.000000548
75	6	-0.000002187	-0.000006325	-0.000001694
76	6	-0.000001053	0.000000760	0.000001757
77	1	0.000000174	-0.000001702	0.000000190
78	6	0.000005229	-0.000004951	0.000003777
79	7	0.000002100	0.000004083	0.000000819
80	8	-0.000005349	0.000003840	-0.000008773
81	6	0.000001645	-0.000002820	0.000003148
82	1	-0.000000050	-0.000000200	-0.000002067

83	1	-0.000002007	-0.000000317	-0.000002680
84	1	-0.000002569	0.000000031	-0.000000226
85	8	-0.000007068	-0.000005265	-0.000000315
86	1	0.000007802	-0.000004076	0.000003822
87	1	0.000003299	0.000001076	-0.000000011

Si-form of the 1:1 complex of 2a with 4-methyl quinolinone



Si-form of complex of **2a**
with 4-methyl quinolinone



RB3LYP/6-31G(d)
empirical dispersion=gd3

Number of Imaginary Frequencies = 0
Zero-point correction =0.710880 a.u.
Thermal correction to Energy = 0.751341 a.u.
Thermal correction to Enthalpy = 0.752285 a.u.
Thermal correction to Gibbs Free Energy = 0.635746 a.u
Sum of electronic and zero-point Energies = -2395.170177 a.u.
Sum of electronic and thermal Energies = -2395.129716 a.u.
Sum of electronic and thermal Enthalpies = -2395.128772 a.u.
Sum of electronic and thermal Free Energies = -2395.245310 a.u.
BSSE energy = 0.009609387408 a.u.

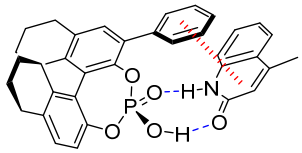
Center Number	Atomic Number	Forces (Hartrees/Bohr) X	Y	Z
1	6	-0.000000885	0.000002151	-0.000001734

2	1	-0.000000445	0.000000937	-0.000001078
3	6	-0.000000549	0.000000829	-0.000000474
4	6	-0.000000428	0.000000463	-0.000000143
5	6	-0.000000720	-0.000000449	-0.000000007
6	6	0.000000407	-0.000002160	-0.000002113
7	6	0.000000086	0.000002062	0.000001020
8	6	0.000001285	0.000000939	0.000000236
9	6	-0.000001704	0.000000598	0.000001078
10	6	-0.000001580	0.000000012	0.000002194
11	6	0.000000711	-0.000002184	0.000000258
12	6	0.000001253	-0.000001660	0.000000736
13	6	0.000003349	0.000002303	0.000002005
14	1	0.000001263	0.000000002	0.000002012
15	8	-0.000005059	0.000000675	0.000005120
16	8	0.000001095	0.000000194	0.000002878
17	15	0.000006252	-0.000002233	-0.000007685
18	8	-0.000001719	0.000000866	-0.000001052
19	6	0.000000081	-0.000001202	-0.000001049
20	6	-0.000001029	-0.000000635	-0.000002960
21	6	-0.000000616	0.000000550	-0.000001680
22	6	-0.000000711	-0.000000600	-0.000001297
23	6	-0.000000444	-0.000000998	-0.000001538
24	6	-0.000000945	-0.000000324	-0.000002085
25	1	-0.000001362	0.000000964	-0.000001830
26	1	-0.000000082	-0.000000501	-0.000001034
27	1	-0.000000317	-0.000001630	-0.000001818
28	1	-0.000001328	0.000000052	-0.000002601
29	1	-0.000000879	-0.000001171	-0.000002616
30	6	0.000000226	-0.000001226	-0.000000676
31	6	-0.000000017	-0.000000362	0.000000613
32	6	0.000001648	-0.000000027	0.000000599
33	6	-0.000000159	-0.000001218	0.000000753
34	6	0.000002226	-0.000000986	0.000000870
35	6	-0.000000938	-0.000000711	0.000000303
36	1	-0.000000276	0.000000405	0.000000586
37	1	0.000001114	-0.000001011	0.000001660

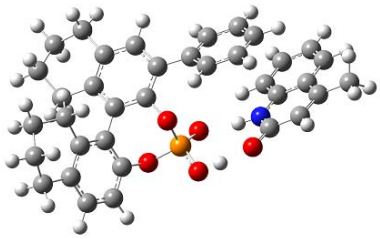
38	1	0.000000988	-0.000001462	0.000000960
39	1	0.000000106	0.000000111	0.000000437
40	1	0.000000398	-0.000000765	0.000000033
41	6	0.000000783	-0.000000731	0.000002335
42	6	0.000000831	0.000001083	0.000000983
43	1	0.000000463	0.000000481	0.000001631
44	6	0.000000034	0.000001965	0.000000155
45	1	-0.000001494	0.000002070	-0.000000044
46	6	-0.000000508	0.000001848	0.000000356
47	1	-0.000000401	0.000001387	0.000001226
48	1	0.000001386	-0.000000018	0.000002486
49	1	-0.000000027	0.000001706	0.000001033
50	1	-0.000001140	0.000002579	0.000000244
51	1	0.000001016	0.000000241	0.000002402
52	1	0.000000769	0.000000119	0.000001825
53	6	0.000000225	0.000002433	0.000001416
54	1	-0.000000489	0.000002061	0.000001176
55	1	-0.000000251	0.000002373	0.000001399
56	6	-0.000000558	0.000002231	-0.000000504
57	1	-0.000001017	0.000002899	0.000000493
58	1	-0.000000981	0.000002515	0.000000685
59	6	0.000000310	0.000000493	0.000001899
60	1	0.000000890	0.000000366	0.000002125
61	1	0.000000759	0.000000962	0.000002406
62	6	0.000001343	0.000000193	0.000002910
63	1	0.000001106	-0.000000359	0.000002001
64	1	0.000001591	-0.000000001	0.000002894
65	1	-0.000000453	-0.000000069	-0.000000979
66	6	-0.000000626	-0.000001797	-0.000001380
67	6	0.000000160	-0.000000873	-0.000000734
68	6	-0.000001408	0.000000626	-0.000002570
69	6	-0.000000349	-0.000000144	-0.000001051
70	6	-0.000001325	0.000001004	-0.000002092
71	6	0.000000797	-0.000000789	0.000000213
72	1	-0.000001188	0.000000693	-0.000001930
73	1	-0.000000738	0.000000021	-0.000001466

74	1	-0.000000582	0.000000496	-0.000001646
75	6	-0.000001817	-0.000002503	0.000000293
76	6	0.000002795	-0.000000572	-0.000002464
77	1	0.000000614	-0.000003337	0.000000465
78	6	0.000000016	-0.000001755	0.000002351
79	7	-0.000000097	0.000000091	-0.000002719
80	8	0.000000884	-0.000003724	-0.000006798
81	6	0.000003688	-0.000004389	-0.000001764
82	1	-0.000000162	-0.000000791	0.000000047
83	1	-0.000000201	-0.000000904	-0.000001274
84	1	-0.000000661	0.000000439	-0.000000082
85	8	0.000002845	0.000000150	0.000002455
86	1	-0.000004465	-0.000001137	0.000001771
87	1	-0.000002666	-0.000000233	-0.000001057

_Re_-form of the 1:1 complex of 2f with 4-methyl quinolinone



Re-form of complex of **2f**
with 4-methyl quinolinone



RB3LYP/6-31G(d)
empirical dispersion=gd3

Number of Imaginary Frequencies = 0
Zero-point correction = 0.630050 a.u.
Thermal correction to Energy = 0.665591 a.u.
Thermal correction to Enthalpy = 0.666535 a.u.
Thermal correction to Gibbs Free Energy = 0.562168 a.u.
Sum of electronic and zero-point Energies = -2164.185543 a.u.
Sum of electronic and thermal Energies = -2164.150002 a.u
Sum of electronic and thermal Enthalpies = -2164.149058 a.u.
Sum of electronic and thermal Free Energies = -2164.253425 a.u.

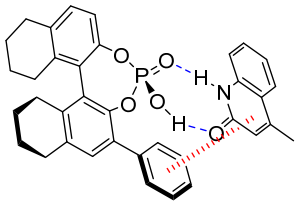
BSSE energy = 0.010759701044 a.u.

Center Number	Atomic Number	Forces (Hartrees/Bohr) X	Y	Z
1	8	-0.000010391	-0.000000469	0.000010472
2	1	0.000011497	0.000003504	-0.000010426
3	1	-0.000000446	-0.000001602	0.000005387
4	6	-0.000000875	-0.000006566	-0.000003215
5	1	0.000002567	0.000000261	-0.000003278
6	6	-0.000010230	0.000005958	-0.000001630
7	6	-0.000006016	0.000005876	-0.000001411
8	6	0.000009330	0.000007079	-0.000000056
9	6	0.000004990	0.000011859	-0.000000608
10	6	-0.000004255	-0.000017594	-0.000000696
11	6	-0.000008644	0.000000846	0.000012452
12	6	0.000002170	-0.000000368	0.000000086
13	6	-0.000000441	-0.000004324	0.000003657
14	6	0.000000284	-0.000005988	0.000000675
15	6	-0.000000513	-0.000005681	0.000000759
16	6	0.000000083	0.000001634	0.000006337
17	1	-0.000000148	-0.000001209	0.000006588
18	8	0.000006092	-0.000006121	0.000003886
19	8	0.000014157	0.000004108	0.000000289
20	15	-0.000003861	-0.000007776	0.000012249
21	8	-0.000005380	0.000004826	-0.000012109
22	6	0.000003778	-0.000009470	0.000002661
23	6	-0.000001379	0.000001440	0.000001111
24	6	0.000002678	0.000003010	-0.000007554
25	6	-0.000005069	0.000007459	-0.000004344
26	6	0.000005329	0.000004138	0.000001102
27	6	-0.000004738	0.000003499	-0.000003097
28	1	-0.000003157	0.000000836	-0.000002646
29	1	-0.000002222	0.000001619	-0.000001088
30	1	0.000000648	0.000003744	-0.000001046

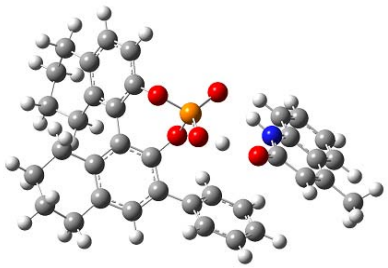
31	1	-0.000001001	0.000001707	-0.000003074
32	1	-0.000001280	0.000003457	-0.000002652
33	6	-0.000001542	-0.000000938	0.000007369
34	6	0.000000876	0.000002825	0.000002863
35	1	0.000002033	0.000002836	0.000000155
36	6	-0.000000604	-0.000002333	-0.000002352
37	1	-0.000000674	-0.000000479	-0.000002863
38	6	-0.000000117	0.000001609	0.000002162
39	1	-0.000000277	-0.000001515	0.000001553
40	1	0.000000967	-0.000000892	0.000006649
41	1	-0.000001171	-0.000002487	-0.000000814
42	1	-0.000000943	0.000000376	-0.000002241
43	1	0.000000892	-0.000001136	0.000005888
44	1	0.000001486	0.000000809	0.000002620
45	6	-0.000000252	-0.000001830	-0.000000653
46	1	0.000000210	-0.000000319	-0.000000982
47	1	-0.000001112	-0.000002729	-0.000000653
48	6	-0.000001033	-0.000001767	-0.000003516
49	1	-0.000001749	-0.000001011	-0.000002715
50	1	-0.000001822	-0.000002825	-0.000001824
51	6	0.000000553	0.000000360	0.000002401
52	1	0.000000855	0.000002574	0.000003266
53	1	0.000001077	-0.000000091	0.000004025
54	6	0.000001923	0.000001991	0.000003116
55	1	0.000002121	0.000001282	0.000005068
56	1	0.000001234	0.000000570	0.000005802
57	1	0.000000290	-0.000000354	0.000000695
58	6	0.000003764	0.000009548	-0.000010363
59	6	0.000003136	0.000012711	-0.000010896
60	6	0.000003943	-0.000009265	-0.000001487
61	6	0.000006613	-0.000007358	0.000006205
62	6	-0.000012546	-0.000011008	-0.000008075
63	6	-0.000002901	-0.000023628	0.000000522
64	1	-0.000001452	-0.000000102	-0.000006678
65	1	-0.000001161	-0.000001638	-0.000004812
66	1	-0.000001445	-0.000002041	-0.000001355

67	6	-0.000000826	0.000007514	-0.000013631
68	6	-0.000013333	0.000004024	0.000007136
69	1	0.000001435	0.000003285	-0.000001672
70	6	0.000011793	0.000007069	-0.000003718
71	7	0.000005680	0.000008147	0.000010171
72	8	-0.000004655	-0.000005613	0.000001510
73	6	0.000020648	-0.000007021	-0.000017397
74	1	0.000002069	0.000008554	0.000001727
75	1	-0.000001630	0.000006415	0.000002147
76	1	-0.000008606	-0.000007233	0.000000868
77	1	-0.000007301	0.000003426	0.000006001

_Si_-form of the 1:1 complex of 2f with 4-methyl quinolinone



_Si_-form of complex of **2f**
with 4-methyl quinolinone



RB3LYP/6-31G(d)
empirical dispersion=gd3

Number of Imaginary Frequencies = 0
Zero-point correction = 0.629980 a.u.
Thermal correction to Energy = 0.665543 a.u.
Thermal correction to Enthalpy = 0.666488 a.u.
Thermal correction to Gibbs Free Energy = 0.561471 a.u.
Sum of electronic and zero-point Energies = -2164.183974 a.u
Sum of electronic and thermal Energies = -2164.148410 a.u.
Sum of electronic and thermal Enthalpies = -2164.147466 a.u.
Sum of electronic and thermal Free Energies = -2164.252483 a.u.
BSSE energy = 0.009609387408 a.u.

Center Number	Atomic Number	Forces (Hartrees/Bohr) X	Y	Z
1	6	0.000002225	-0.000003021	0.000003068
2	1	-0.000001273	-0.000000696	0.000003877
3	6	-0.000004524	0.000000301	0.000003488
4	6	-0.000001377	0.000000419	0.000000100
5	6	0.000000715	0.000002716	-0.000001528
6	6	-0.000001920	0.000003135	-0.000002191
7	6	0.000003697	-0.000006134	0.000001360
8	6	0.000013917	0.000005871	-0.000002786
9	6	-0.000008652	-0.000001966	0.000002108
10	6	-0.000002715	-0.000002765	0.000005913
11	6	0.000003852	0.000005371	-0.000001960
12	6	-0.000001476	0.000003010	-0.000002066
13	6	0.000008452	-0.000001816	0.000001635
14	1	0.000004120	-0.000001449	-0.000004244
15	8	-0.000006831	-0.000003446	0.000004842
16	8	0.000006842	-0.000004427	0.000002440
17	15	0.000006974	-0.000005540	0.000010675
18	8	-0.000000928	0.000002754	0.000002831
19	6	0.000000667	0.000000969	0.000002969
20	6	0.000000803	0.000005439	-0.000001501
21	6	-0.000009722	-0.000009628	-0.000007456
22	6	0.000001784	0.000002657	-0.000006307
23	6	0.000002545	-0.000001846	0.000001181
24	6	0.000005701	0.000002247	-0.000001873
25	1	-0.000004830	0.000007793	-0.000003704
26	1	0.000000444	0.000001762	-0.000001314
27	1	0.000000707	0.000002737	-0.000004074
28	1	-0.000000103	-0.000001387	-0.000001566
29	1	0.000000601	0.000000777	-0.000002022
30	6	-0.000003474	-0.000002796	-0.000004258
31	6	-0.000001122	-0.000002324	0.000004299
32	1	0.000001060	-0.000000368	-0.000000056

33	6	-0.000000333	-0.000003165	0.000004014
34	1	-0.000002140	-0.000002091	0.000002005
35	6	-0.000003716	-0.000001737	0.000002453
36	1	-0.000000765	-0.000002172	-0.000000481
37	1	0.000001987	-0.000000595	-0.000002593
38	1	-0.000000034	-0.000002414	0.000000876
39	1	-0.000002156	-0.000002520	0.000002372
40	1	0.000002369	-0.000001521	-0.000000075
41	1	0.000000654	-0.000002120	-0.000001687
42	6	0.000001072	-0.000002676	-0.000000736
43	1	0.000000355	-0.000001883	0.000002871
44	1	-0.000000190	-0.000004094	0.000001495
45	6	-0.000001916	-0.000001880	0.000003240
46	1	-0.000001078	-0.000003195	0.000002587
47	1	-0.000000659	-0.000002662	0.000002215
48	6	-0.000000485	-0.000001537	-0.000001023
49	1	0.000000804	-0.000001242	0.000000412
50	1	0.000000589	-0.000002282	-0.000000111
51	6	0.000003581	0.000000073	0.000000149
52	1	0.000000354	-0.000000851	-0.000001073
53	1	0.000002231	-0.000002873	-0.000001397
54	1	0.000000216	0.000002841	-0.000005403
55	6	-0.000002402	-0.000005629	0.000006299
56	6	-0.000001736	-0.000005832	-0.000002225
57	6	0.000010765	0.000004293	0.000006823
58	6	-0.000001947	0.000006431	-0.000004625
59	6	0.000003603	0.000004779	0.000001729
60	6	-0.000003419	-0.000006721	0.000002927
61	1	-0.000001427	-0.000000257	0.000002154
62	1	-0.000002338	-0.000001318	0.000001304
63	1	-0.000000917	0.000001155	0.000002252
64	6	0.000001693	-0.000004919	-0.000002726
65	6	0.000016885	-0.000004073	-0.000006496
66	1	0.000000575	0.000001273	-0.000001570
67	6	0.000007116	0.000011721	-0.000028025
68	7	0.000000161	0.000008640	0.000013636

69	8	-0.000031505	0.000000073	0.000035380
70	6	-0.000023186	-0.000013515	0.000004770
71	1	0.000004594	0.000007256	-0.000002731
72	1	-0.000006320	0.000005505	-0.000003833
73	1	-0.000010162	0.000002956	-0.000018602
74	8	-0.000024426	0.000006200	-0.000030682
75	1	0.000038494	0.000000920	0.000011648
76	1	-0.000001609	0.000001039	0.000002102
77	1	0.000010606	0.000022268	-0.000001496

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Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski and D. J. Fox, Gaussian, Inc., Wallingford CT, 2009.
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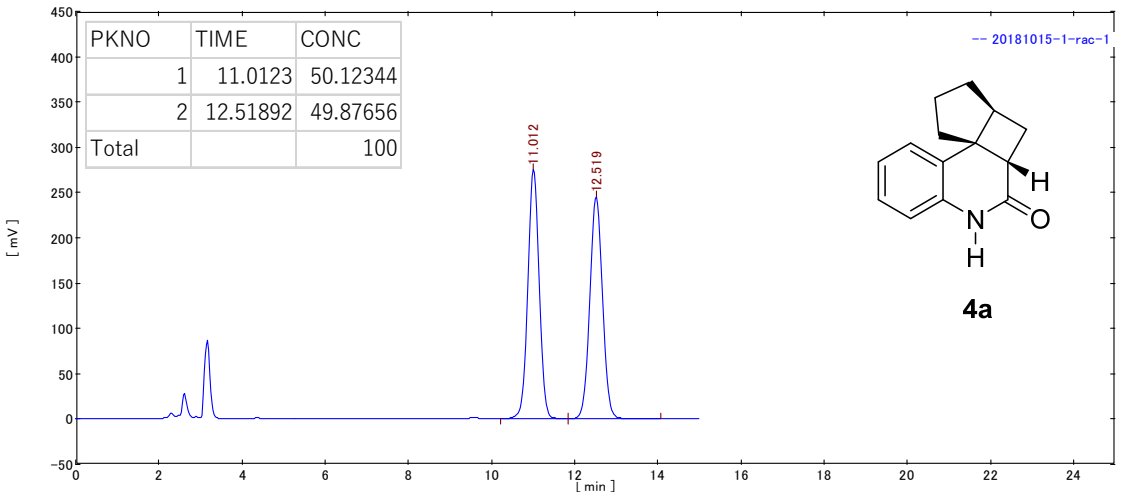
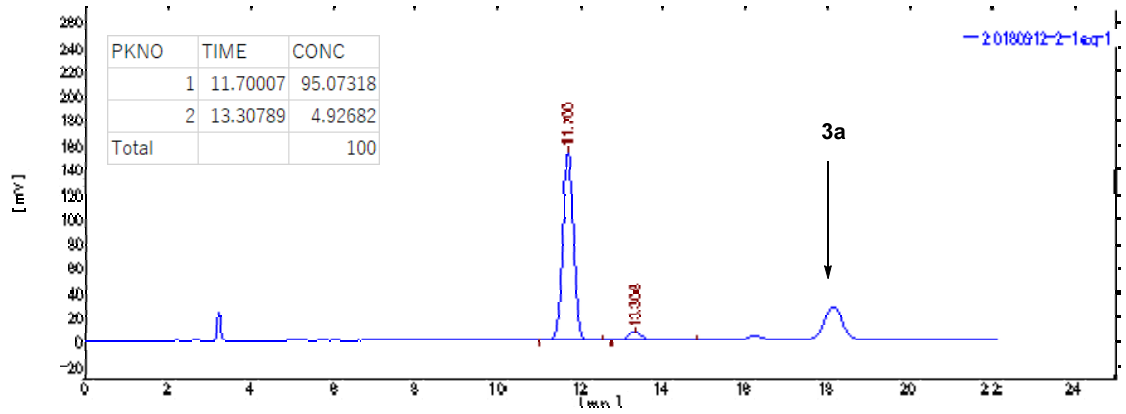
8. The stability order was not influenced by the corrections.

HPLC traces

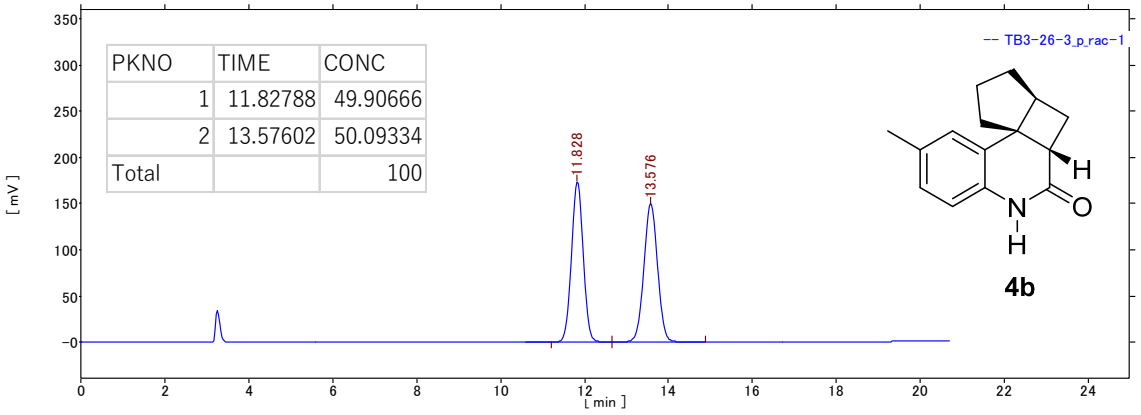
rac-**4a**：Chiralpak IC, hexane:EtOH=20:1, 1.5 ml/min, 254 nm



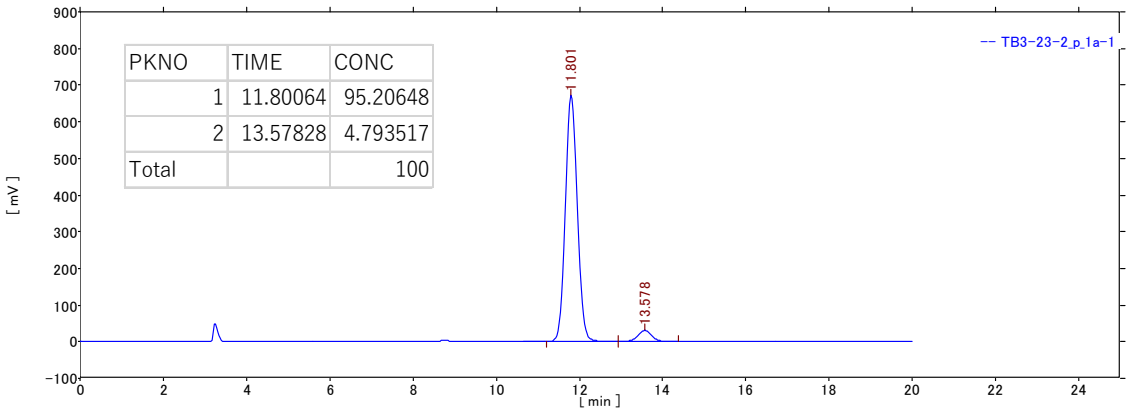
4a: 90% ee



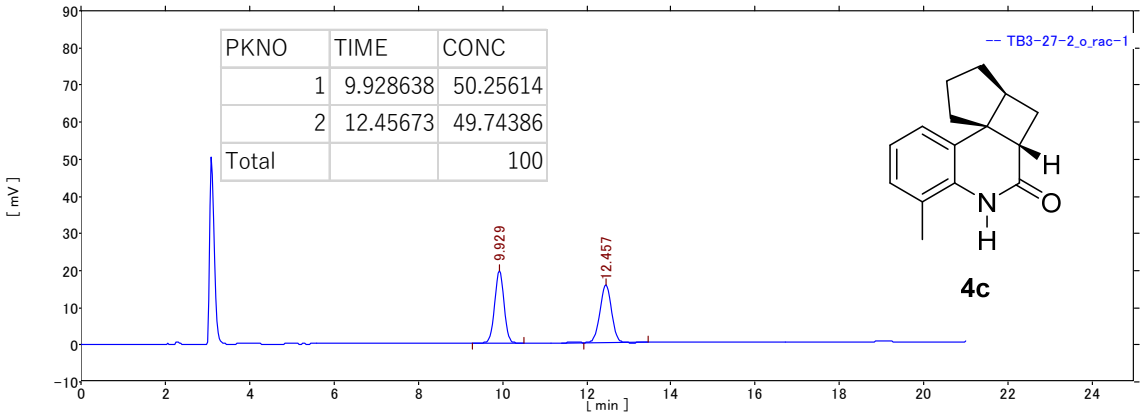
rac-**4b** : Chiralpak IC, hexane:EtOH=20:1, 1.5 ml/min, 254 nm



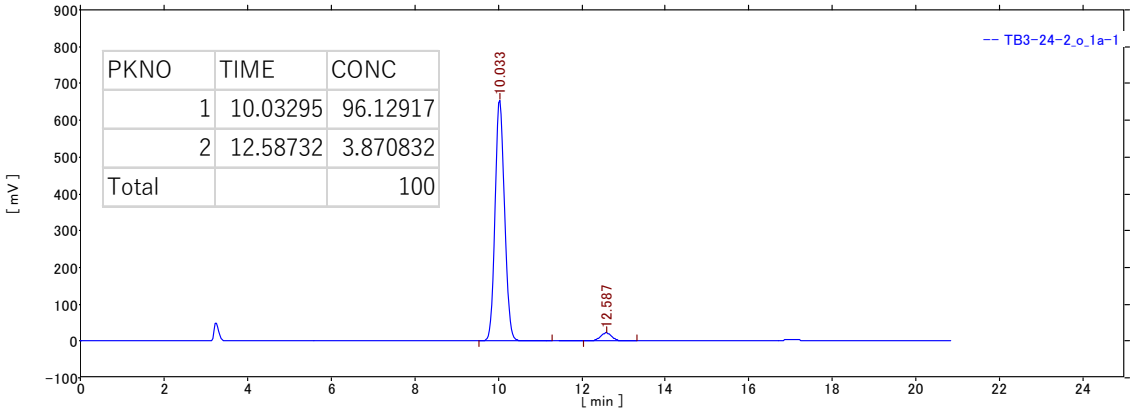
4b: 90% ee



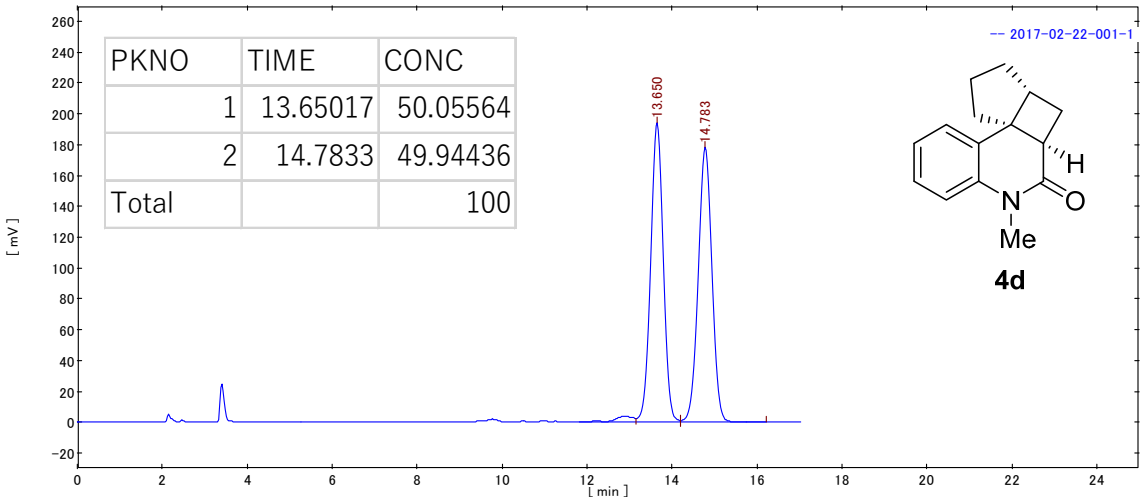
rac-**4c** : Chiralpak IC, hexane:EtOH=20:1, 1.5 ml/min, 254 nm



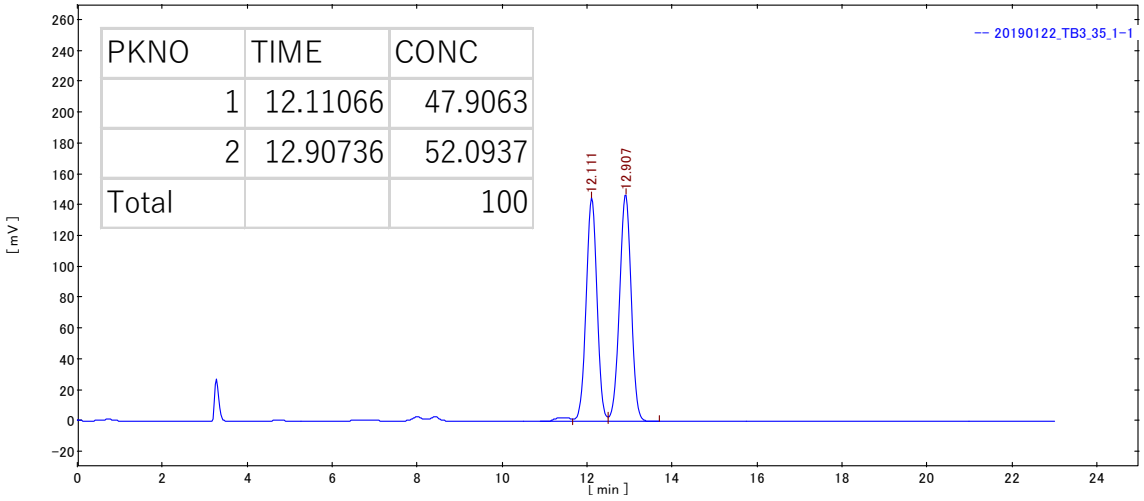
4c: 92% ee



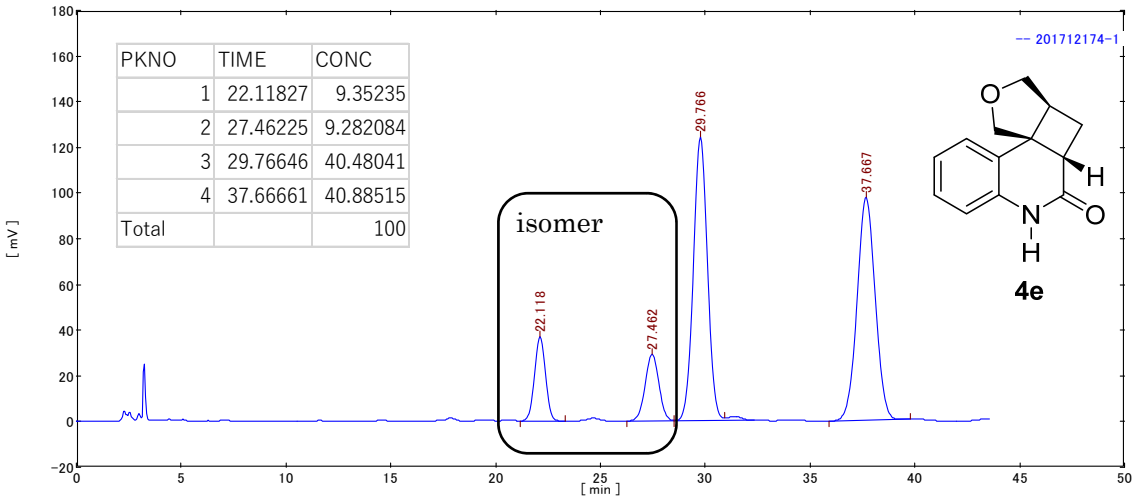
rac-**4d** : Chiralpak IC, hexane:EtOH=20:1, 1.5 ml/min, 254 nm



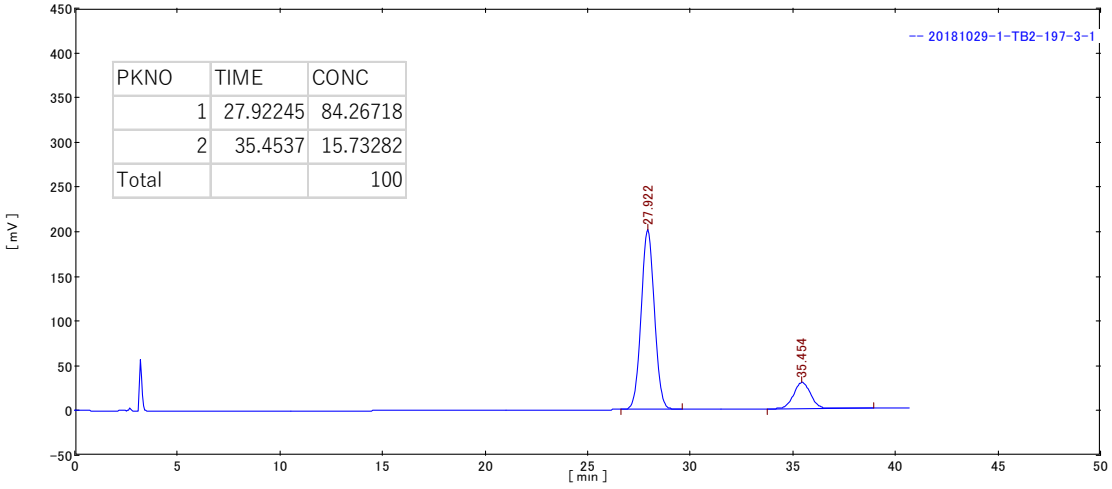
4d: 4% ee



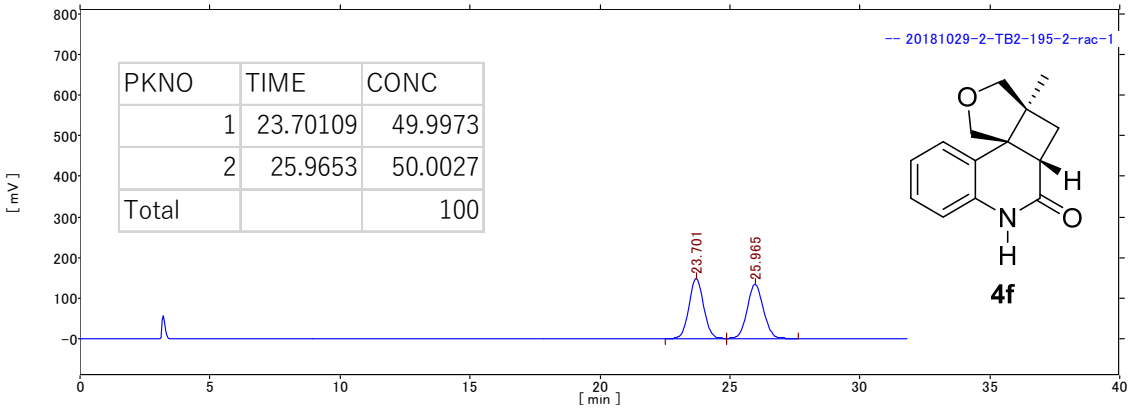
rac-**4e**: Chiralpak IC, hexane:EtOH=20:1, 1.5 ml/min, 254 nm



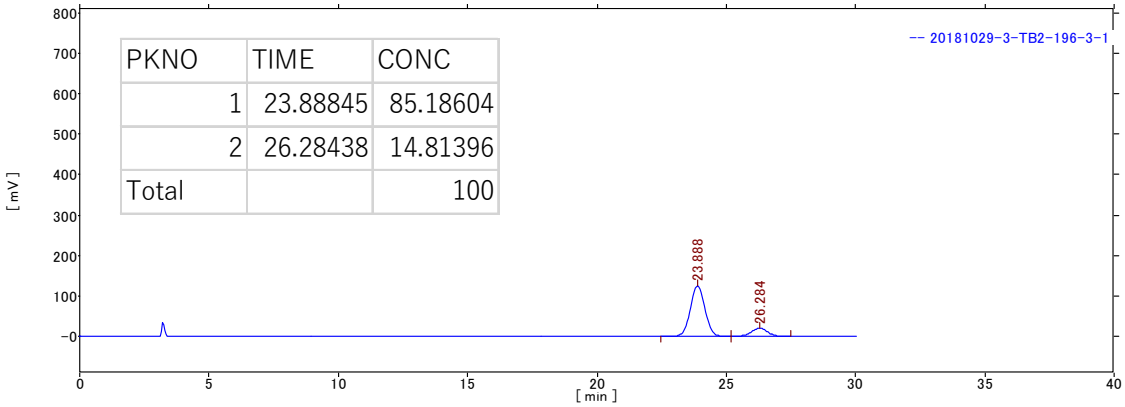
4e: 69% ee



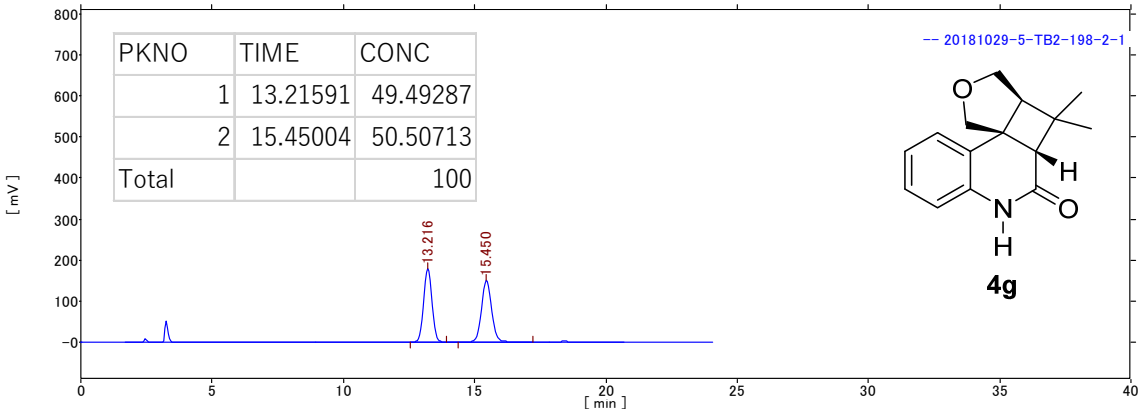
rac-**4f**: Chiralpak IC, hexane:EtOH=20:1, 1.5 ml/min, 254 nm



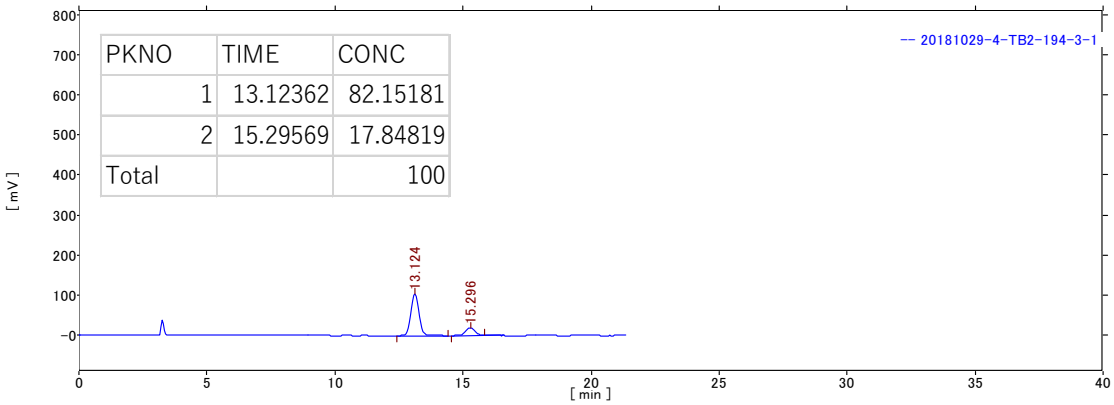
4f: 70% ee



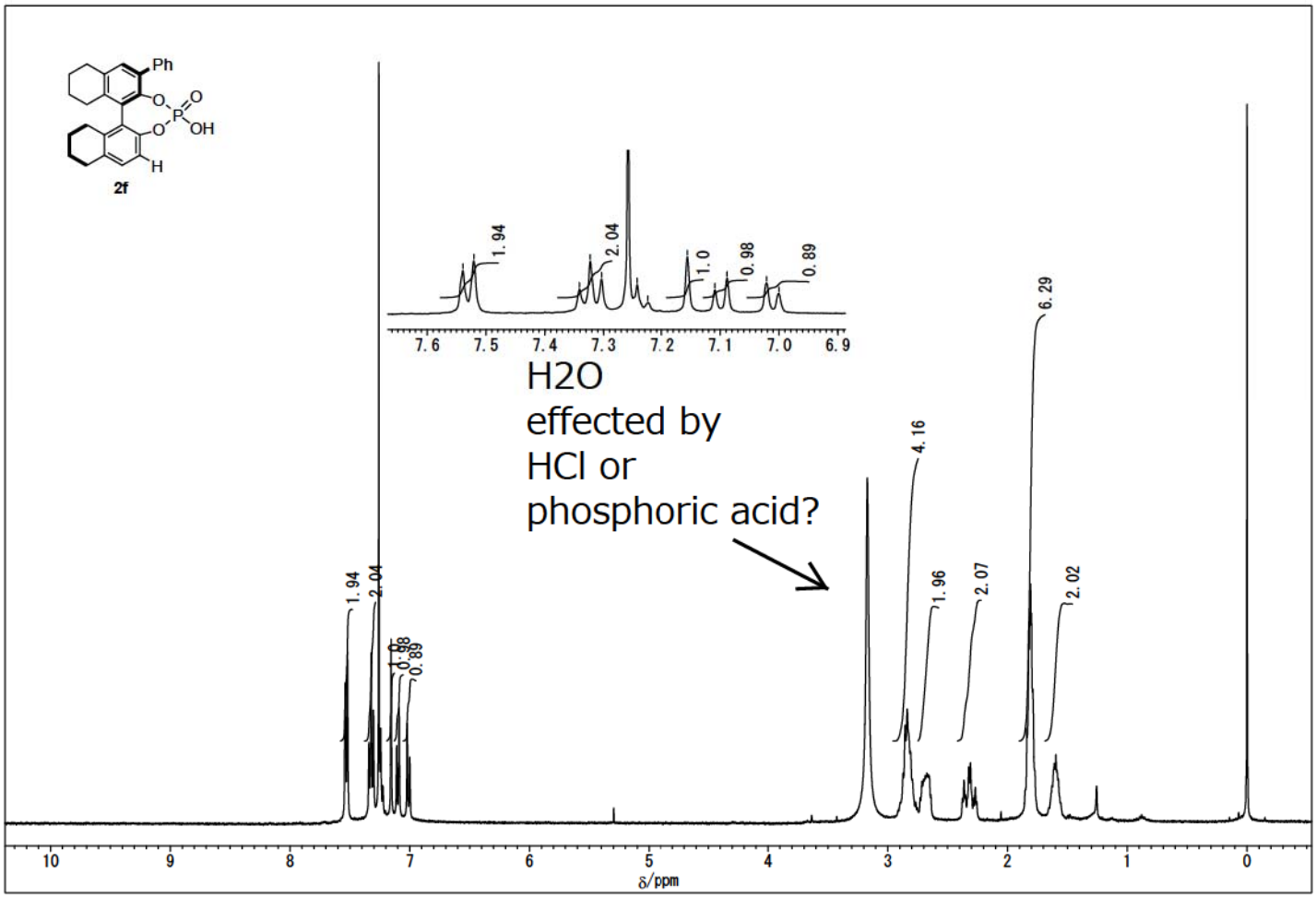
rac-**4g**: Chiralpak IC, hexane:EtOH=20:1, 1.5 ml/min, 254 nm

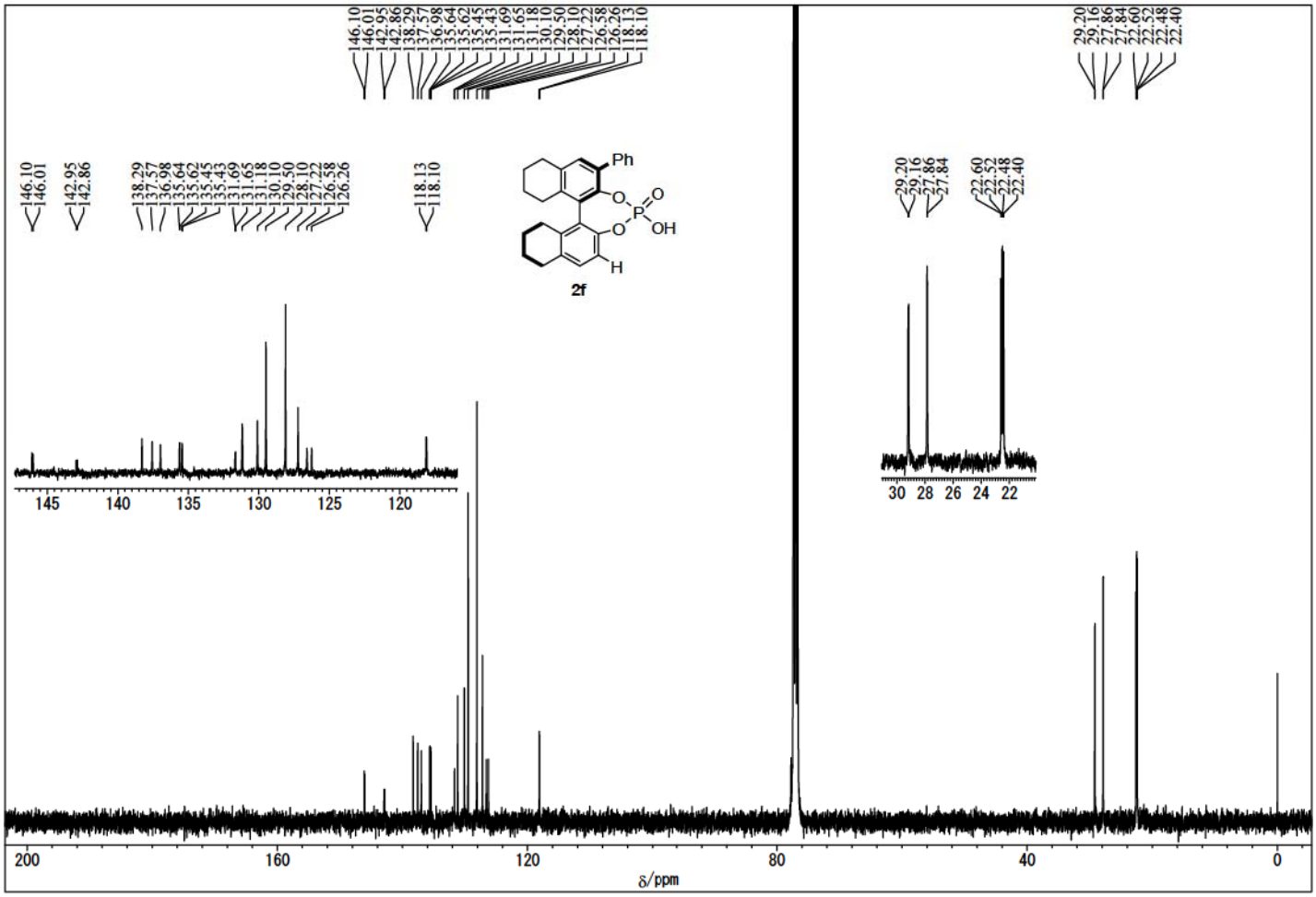


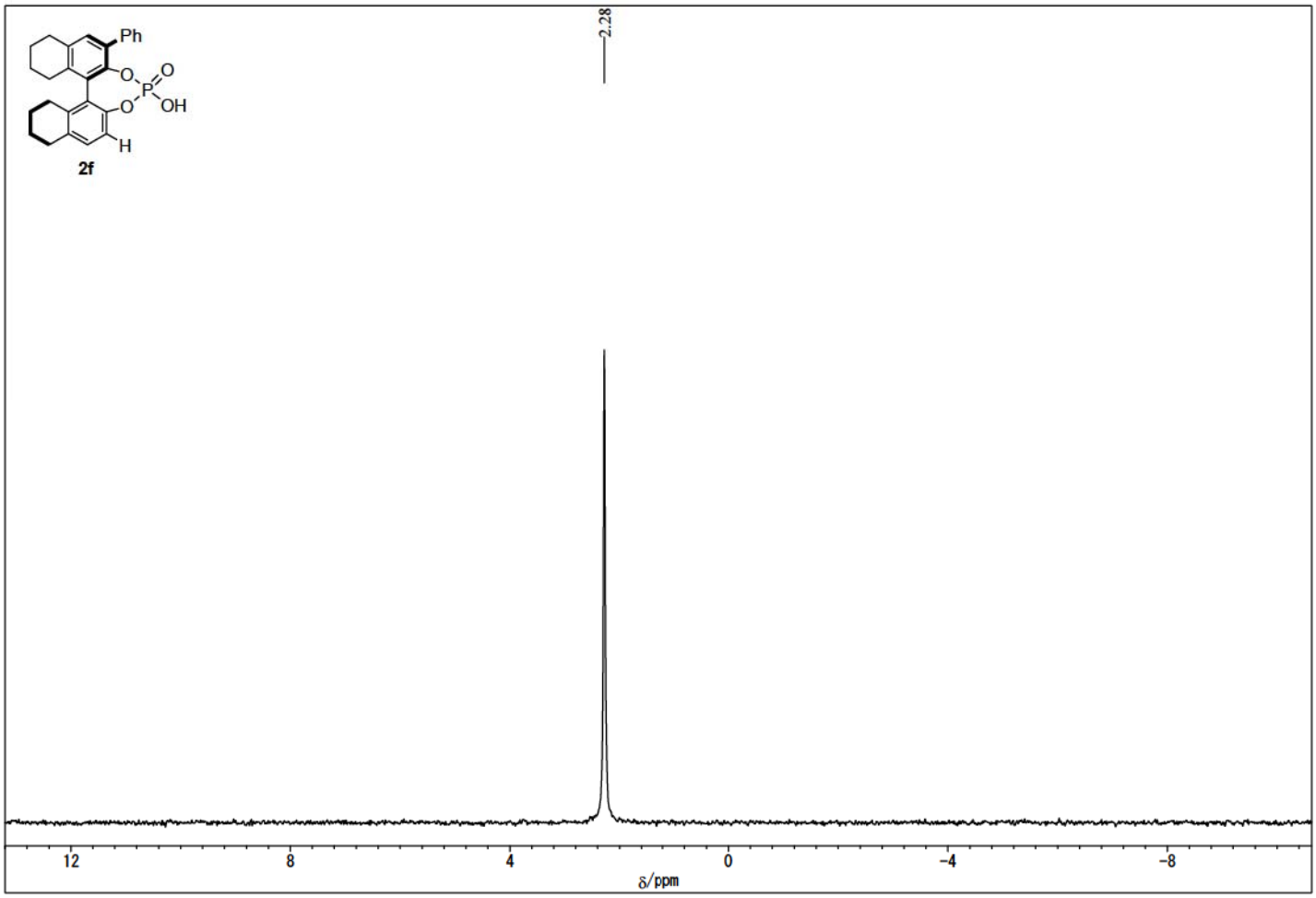
4g: 64% ee

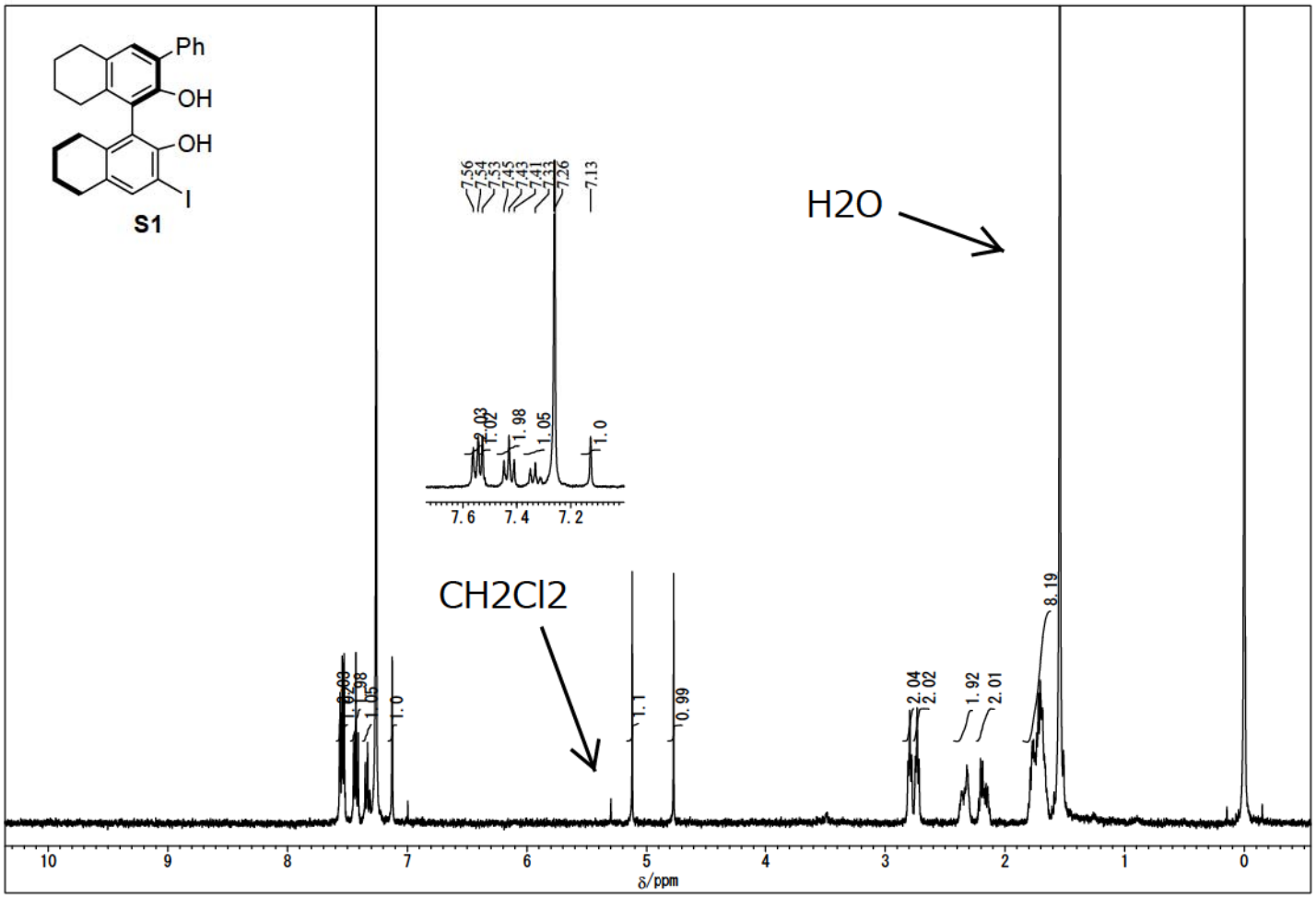


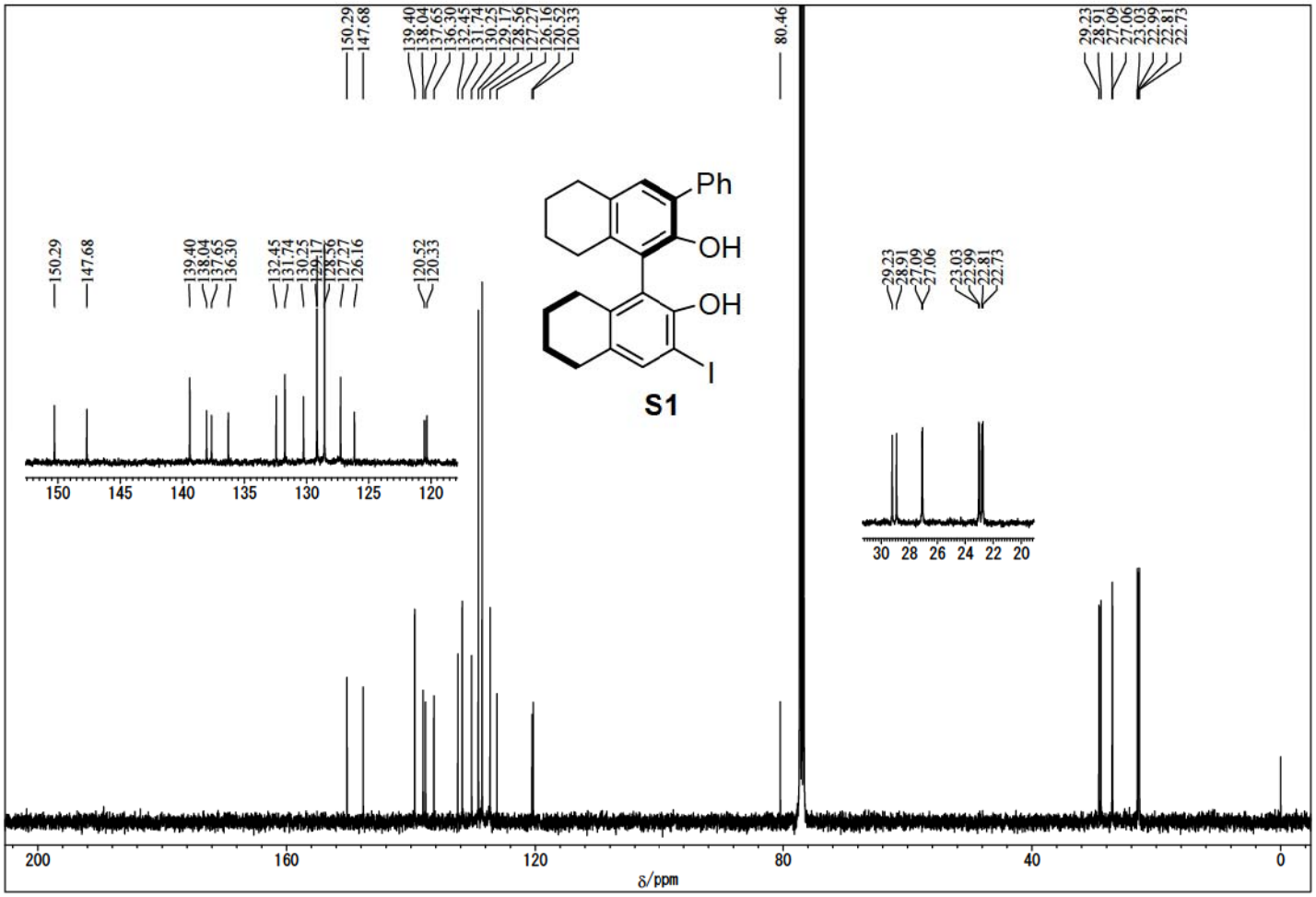
NMR Spectra of New Compounds

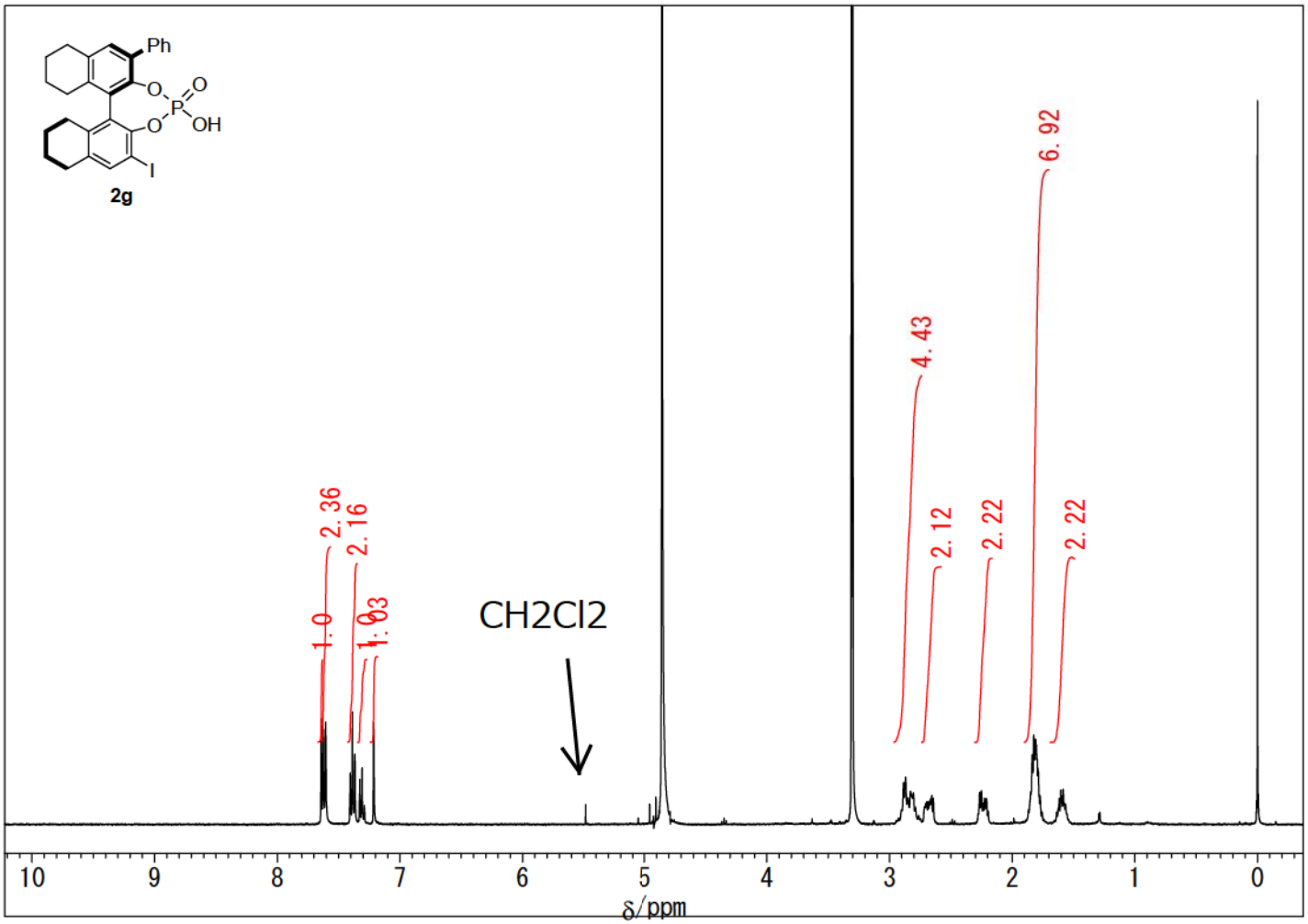

Ph
O
P
O
OH
H
2f
1.94
2.04
1.0
0.98
0.89
7.6
7.5
7.4
7.3
7.2
7.1
7.0
6.9
H2O
effected by
HCl or
phosphoric acid?
6.29
4.16
1.96
2.07
2.02
1.94
2.04
1.0
0.98
0.89
10
9
8
7
6
5
4
3
2
1
0
δ/ppm

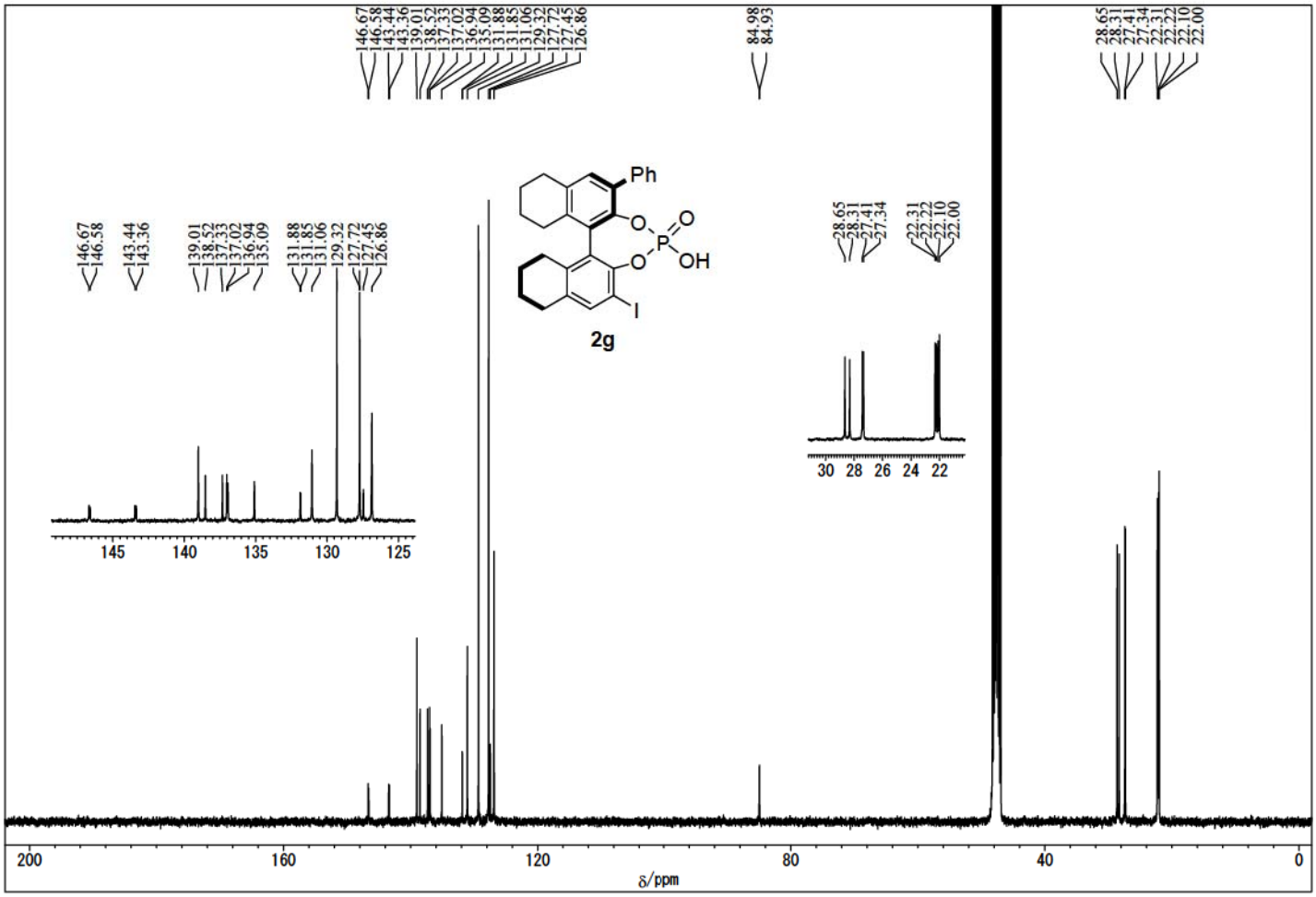

146.10
146.01
142.95
142.86
138.29
137.57
136.98
135.64
135.62
135.45
135.43
131.69
131.65
131.18
130.10
129.50
128.10
127.22
126.58
126.26
118.13
118.10
29.20
29.16
27.86
27.84
22.60
22.52
22.48
22.40
Ph
O
P
O
OH
H
2f
145
140
135
130
125
120
30
28
26
24
22
200
160
120
80
40
0
δ/ppm

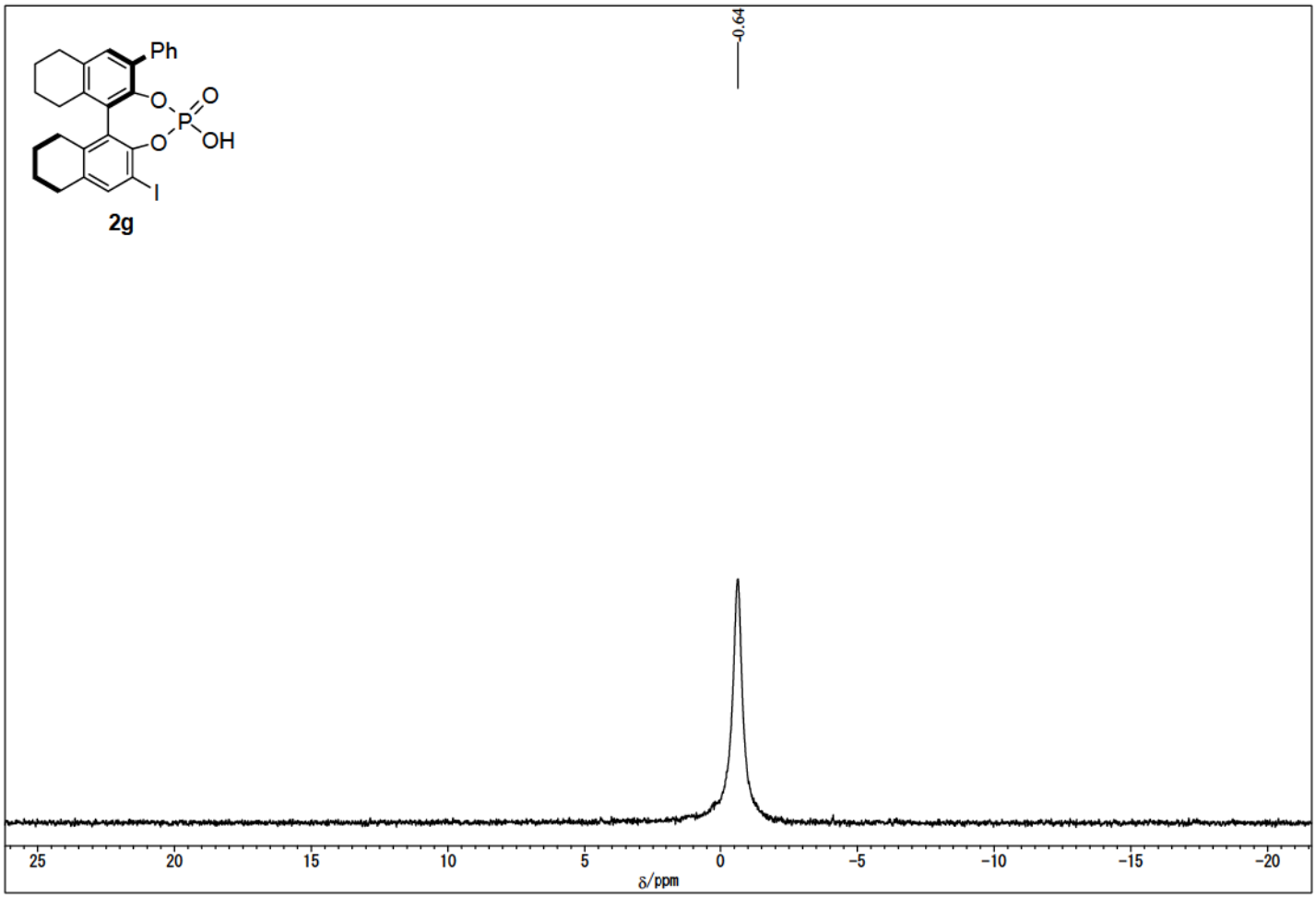

Ph
O
O
P
O
OH
H
2f
2.28
12
8
4
0
-4
-8
δ/ppm

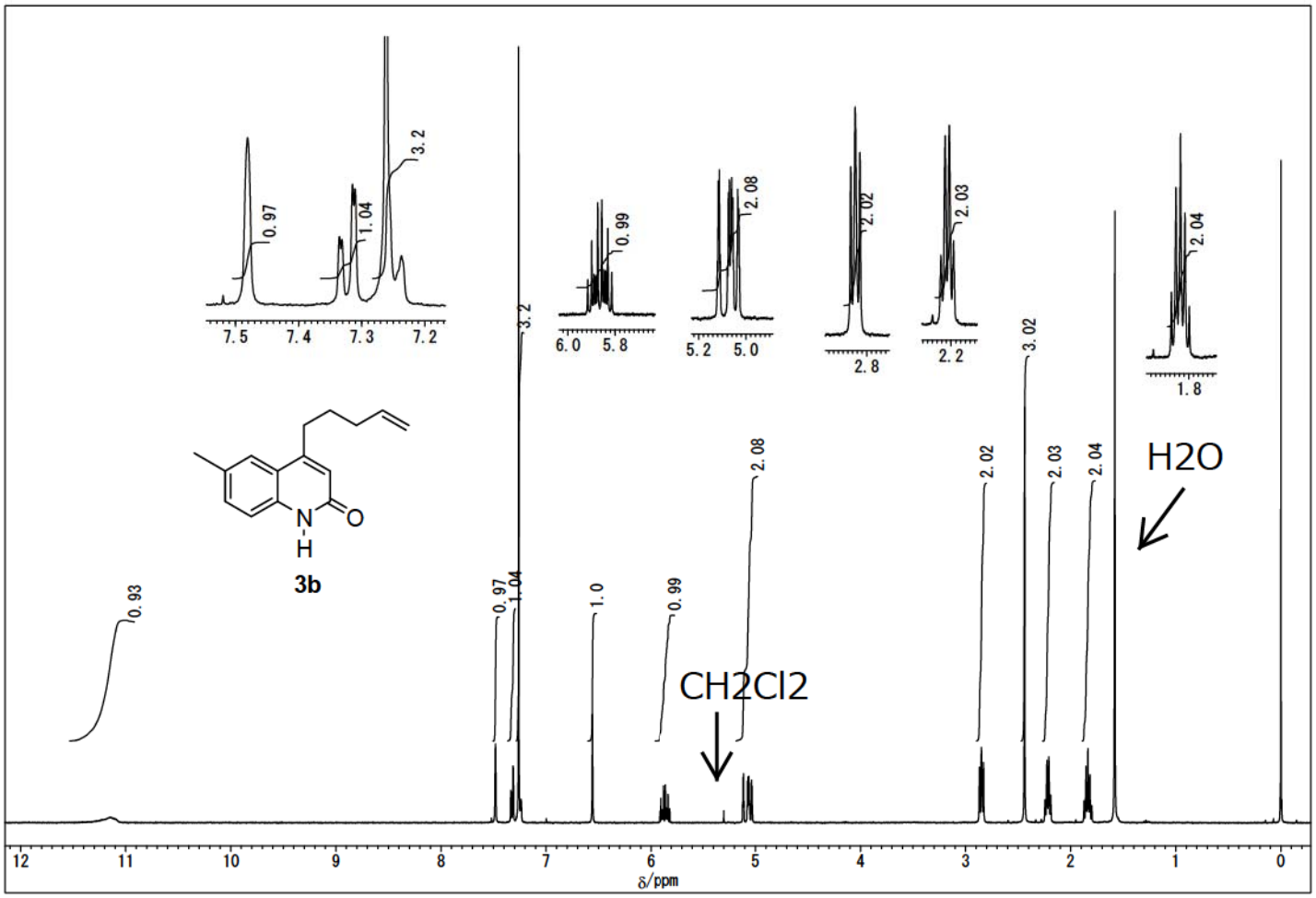

Ph
OH
OH
I
S1
H2O
CH2Cl2
δ/ppm

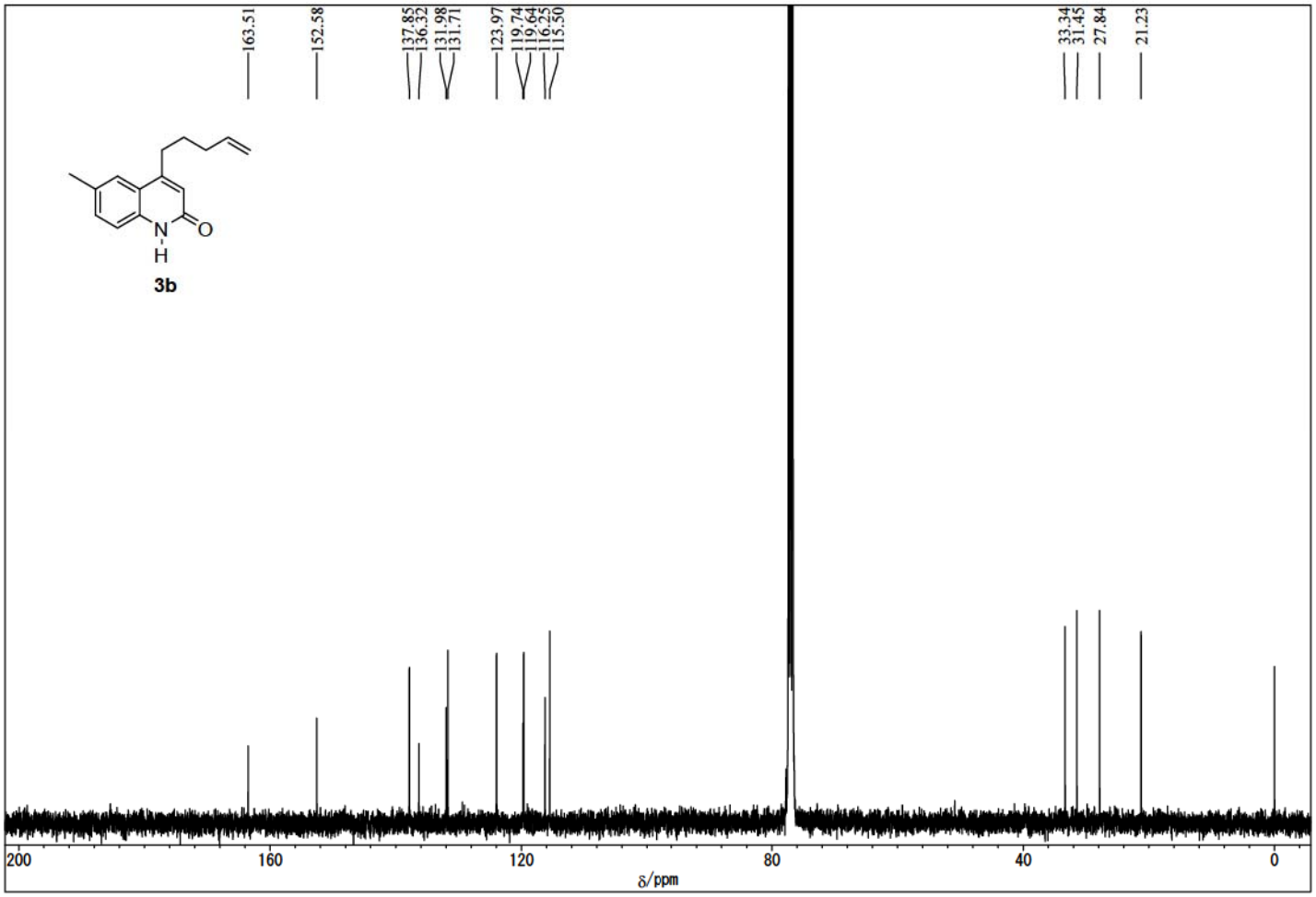

Ph
OH
OH
I
S1
δ/ppm

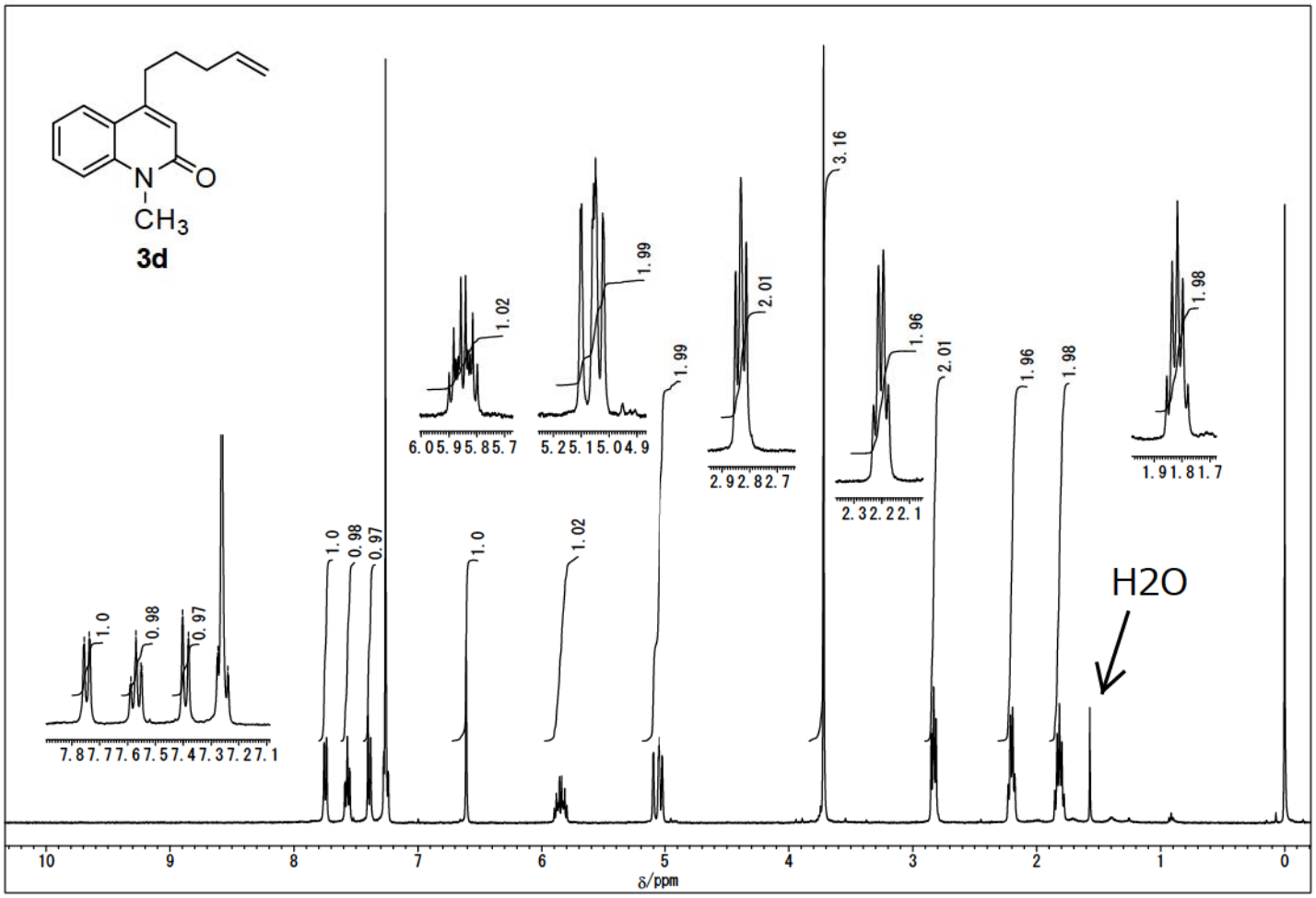

Ph
O
P
O
OH
O
I
2g
6.92
4.43
2.36
2.16
2.12
2.22
2.22
1.0
1.03
CH2Cl2
10
9
8
7
6
5
4
3
2
1
0
δ/ppm

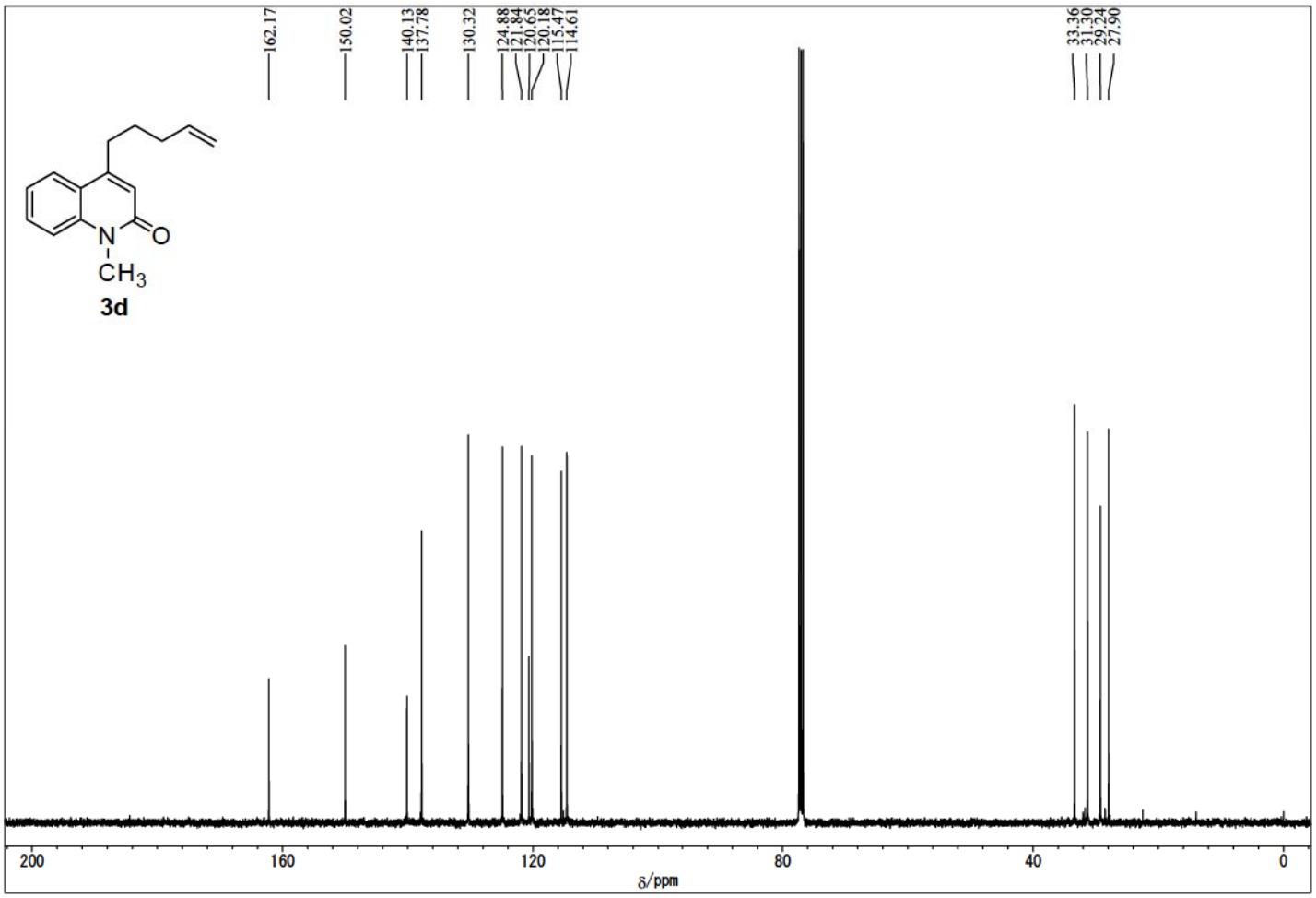

146.67
146.58
143.44
143.36
139.01
138.52
137.33
137.02
136.94
135.09
131.88
131.85
131.06
129.32
127.72
127.45
126.86
84.98
84.93
28.65
28.31
27.41
27.34
22.31
22.22
22.10
22.00
Ph
O
P
O
OH
O
I
2g
200
160
120
80
40
0
δ/ppm

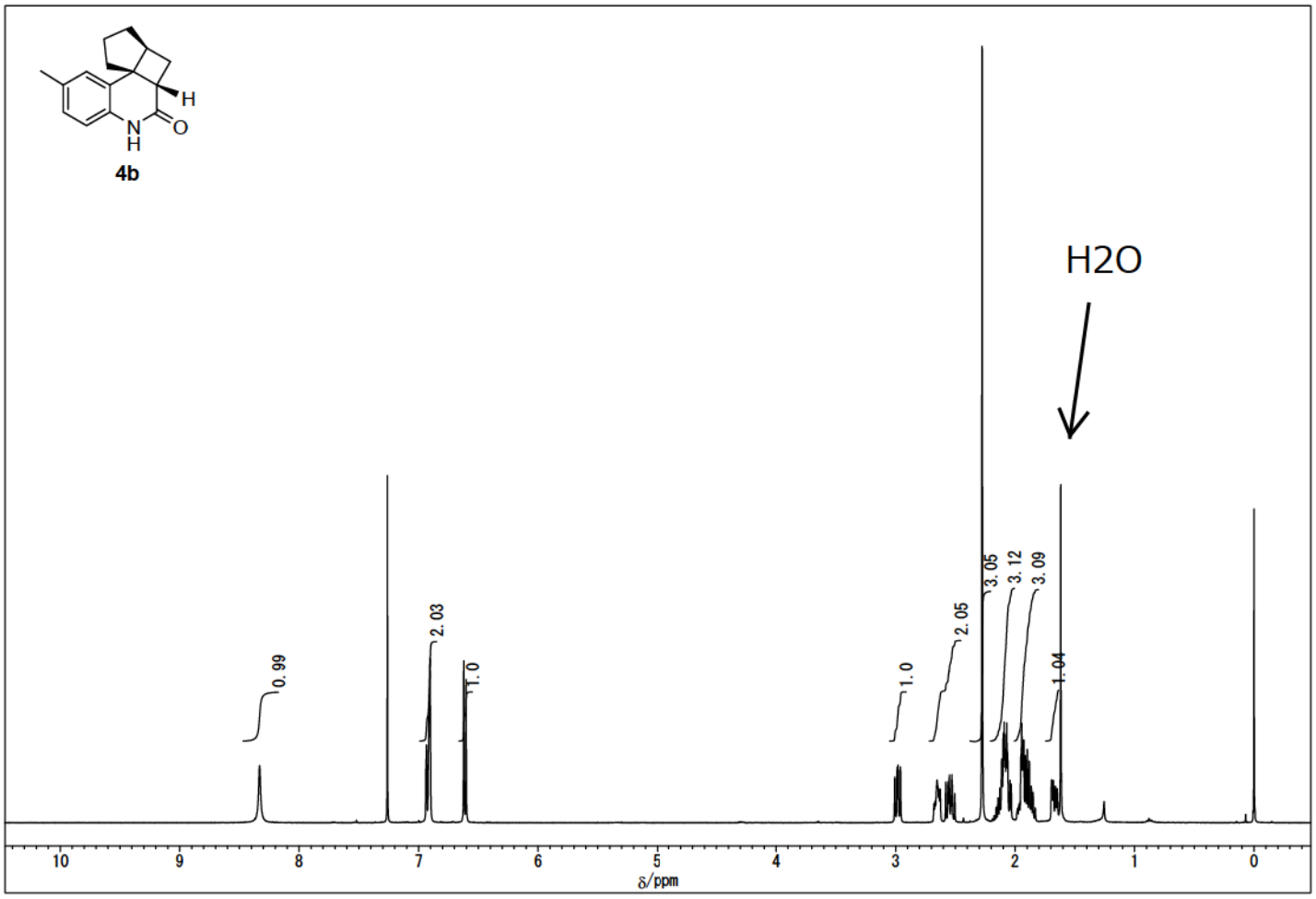

Ph
O
P
O
O
OH
I
2g
0.64
25
20
15
10
5
0
-5
-10
-15
-20
δ/ppm

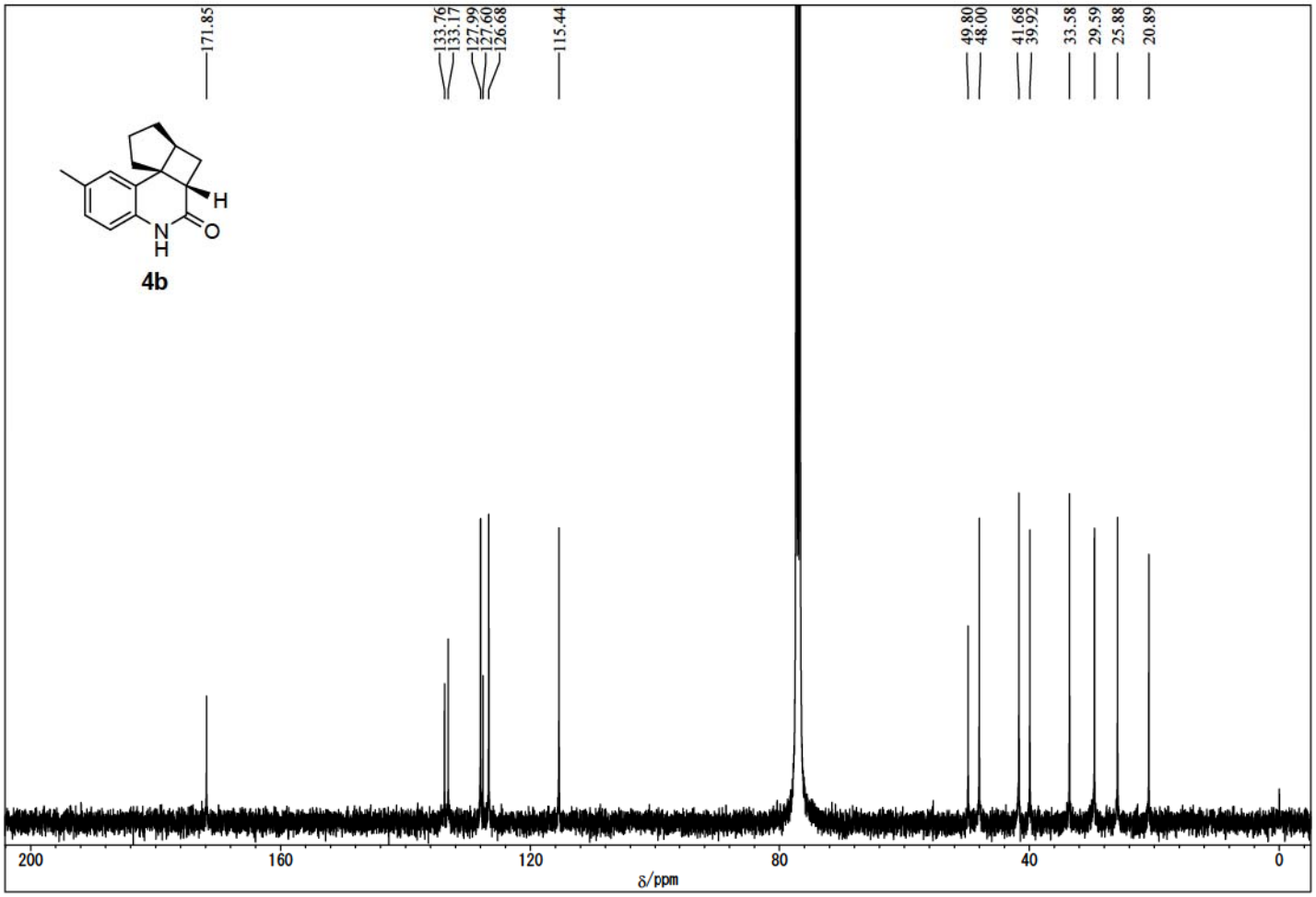

0.93
0.97
1.04
3.2
1.0
0.99
2.08
2.02
3.02
2.03
2.04
H2O
CH2Cl2
3b
δ/ppm

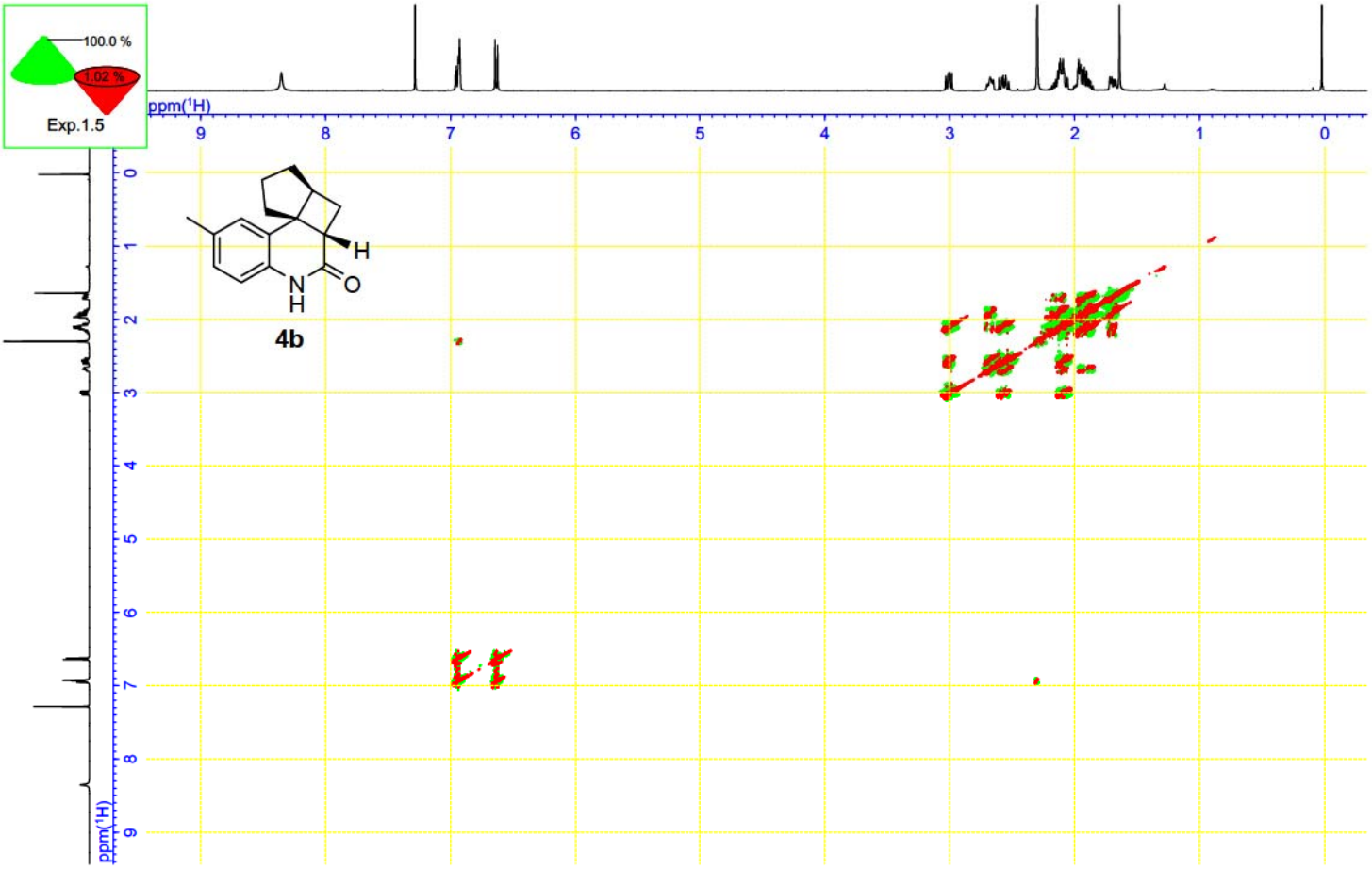

163.51
152.58
137.85
136.32
131.98
131.71
123.97
119.74
119.64
116.25
115.50
33.34
31.45
27.84
21.23
3b
δ/ppm

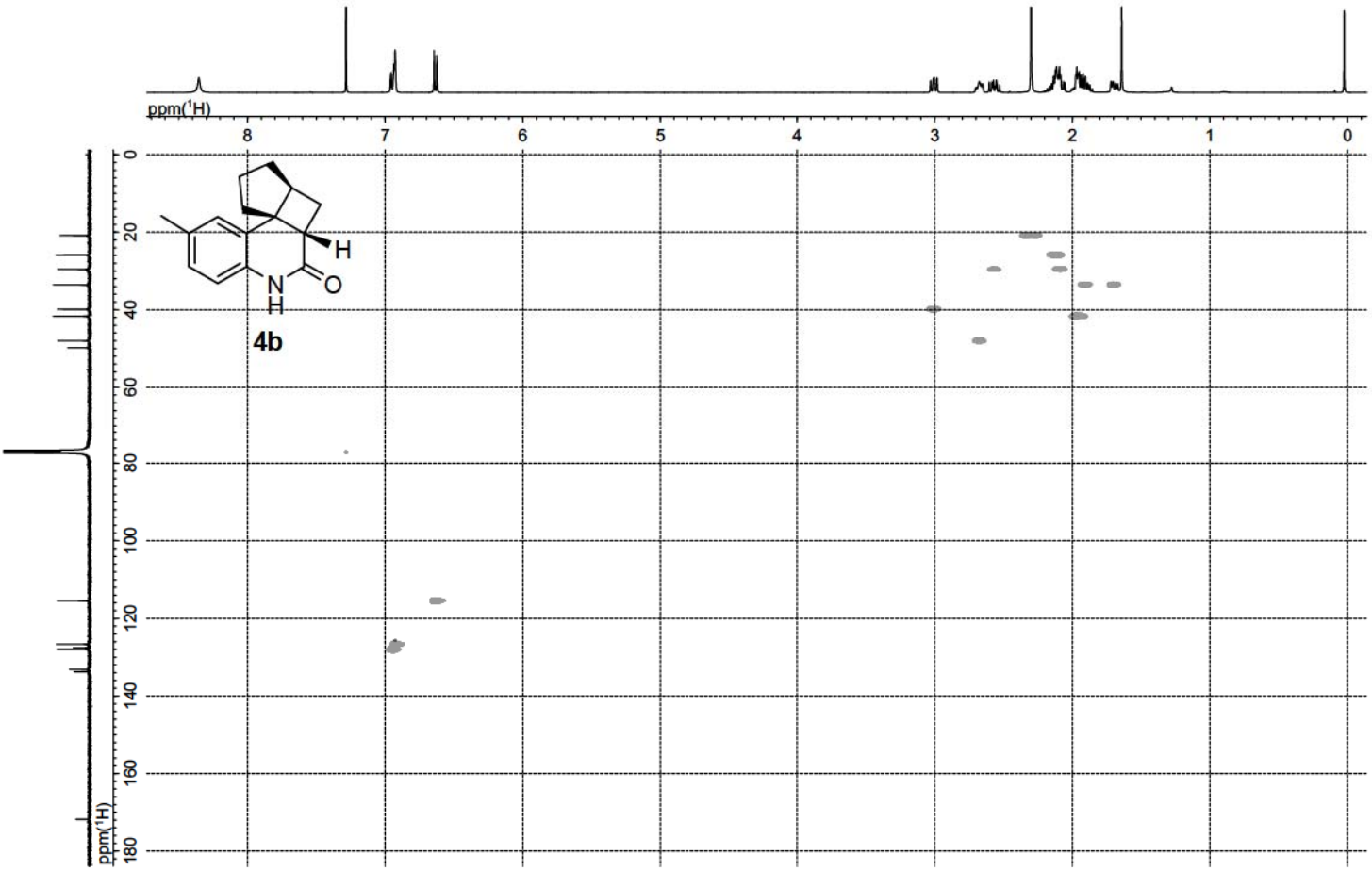

3d
H2O
δ/ppm

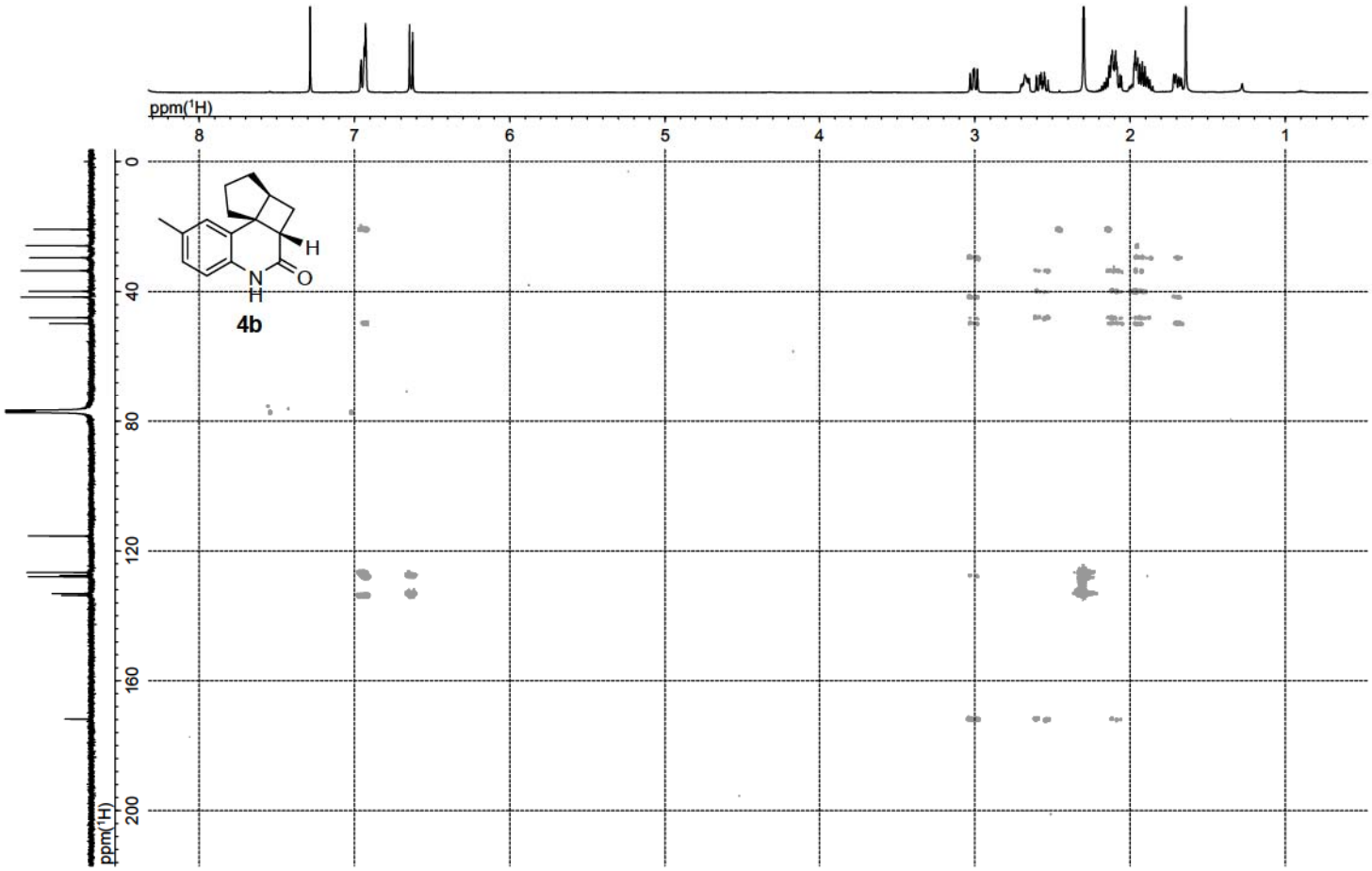

162.17
150.02
140.13
137.78
130.32
124.88
121.84
120.65
120.18
115.47
114.61
33.36
31.30
29.24
27.90
3d
δ/ppm

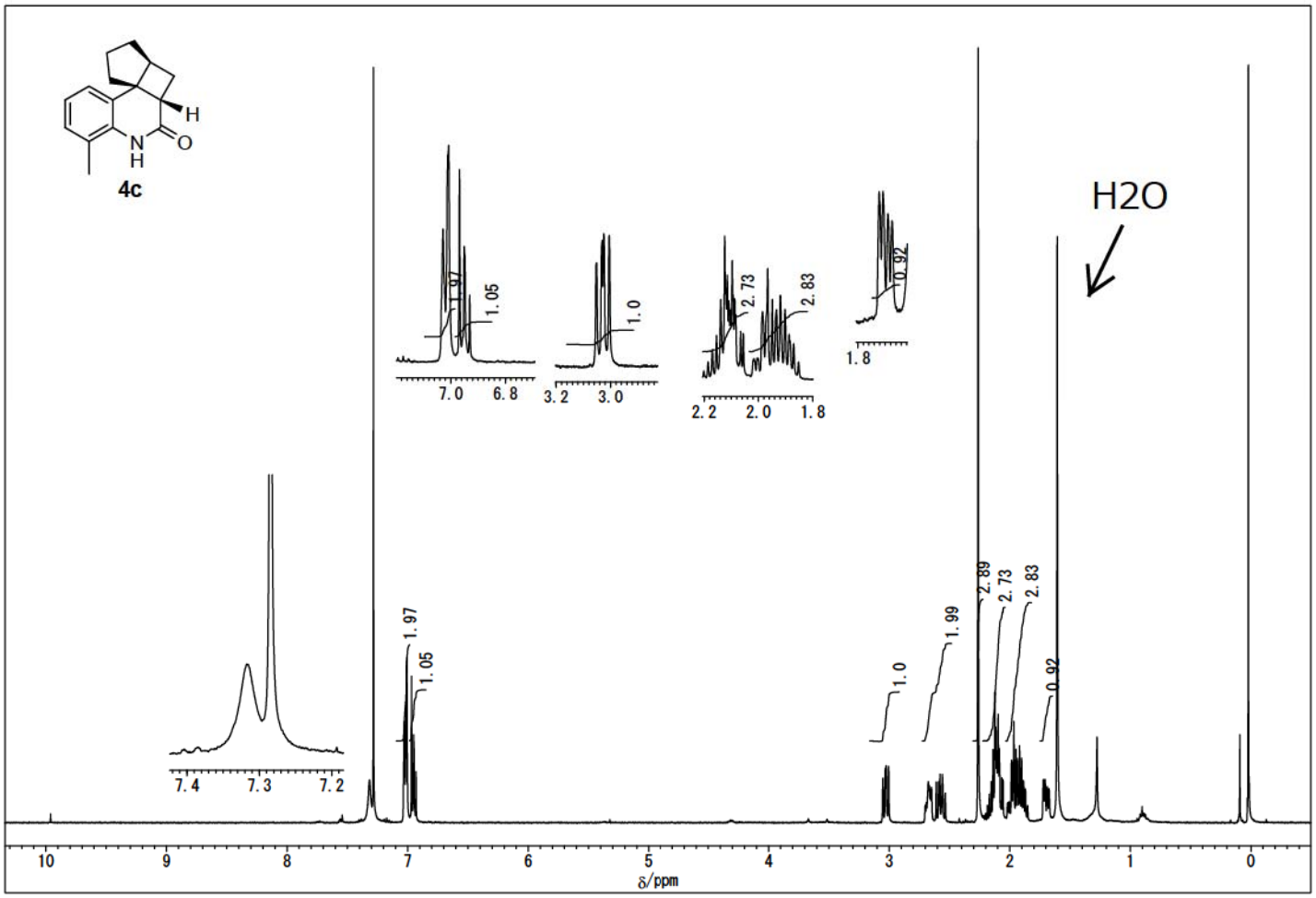

4b
H2O
0.99
2.03
1.0
1.0
2.05
3.05
3.12
3.09
1.04
10
9
8
7
6
5
4
3
2
1
0
δ/ppm

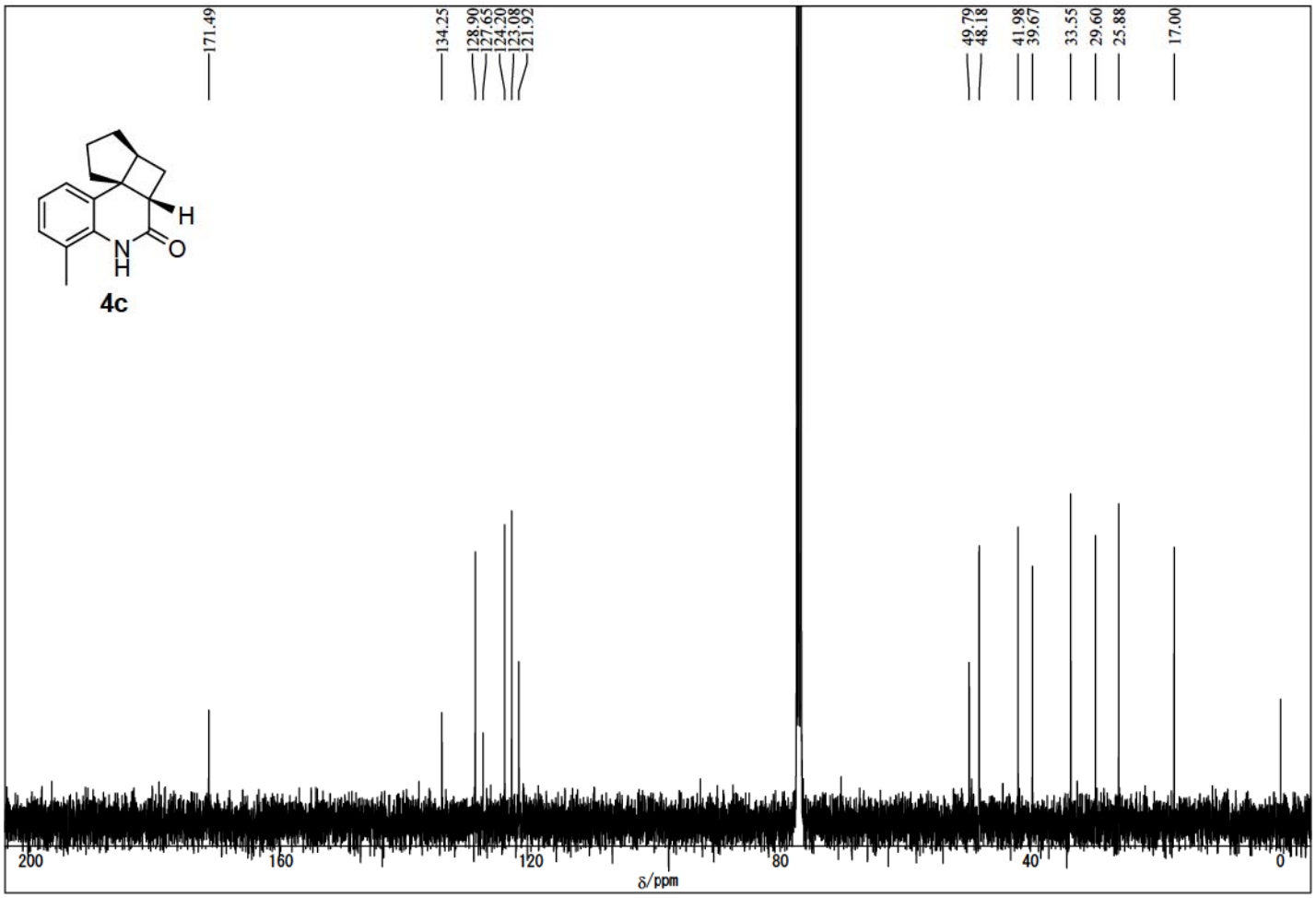

171.85
133.76
133.17
127.99
127.60
126.68
115.44
49.80
48.00
41.68
39.92
33.58
29.59
25.88
20.89
4b
200
160
120
80
40
0
δ/ppm

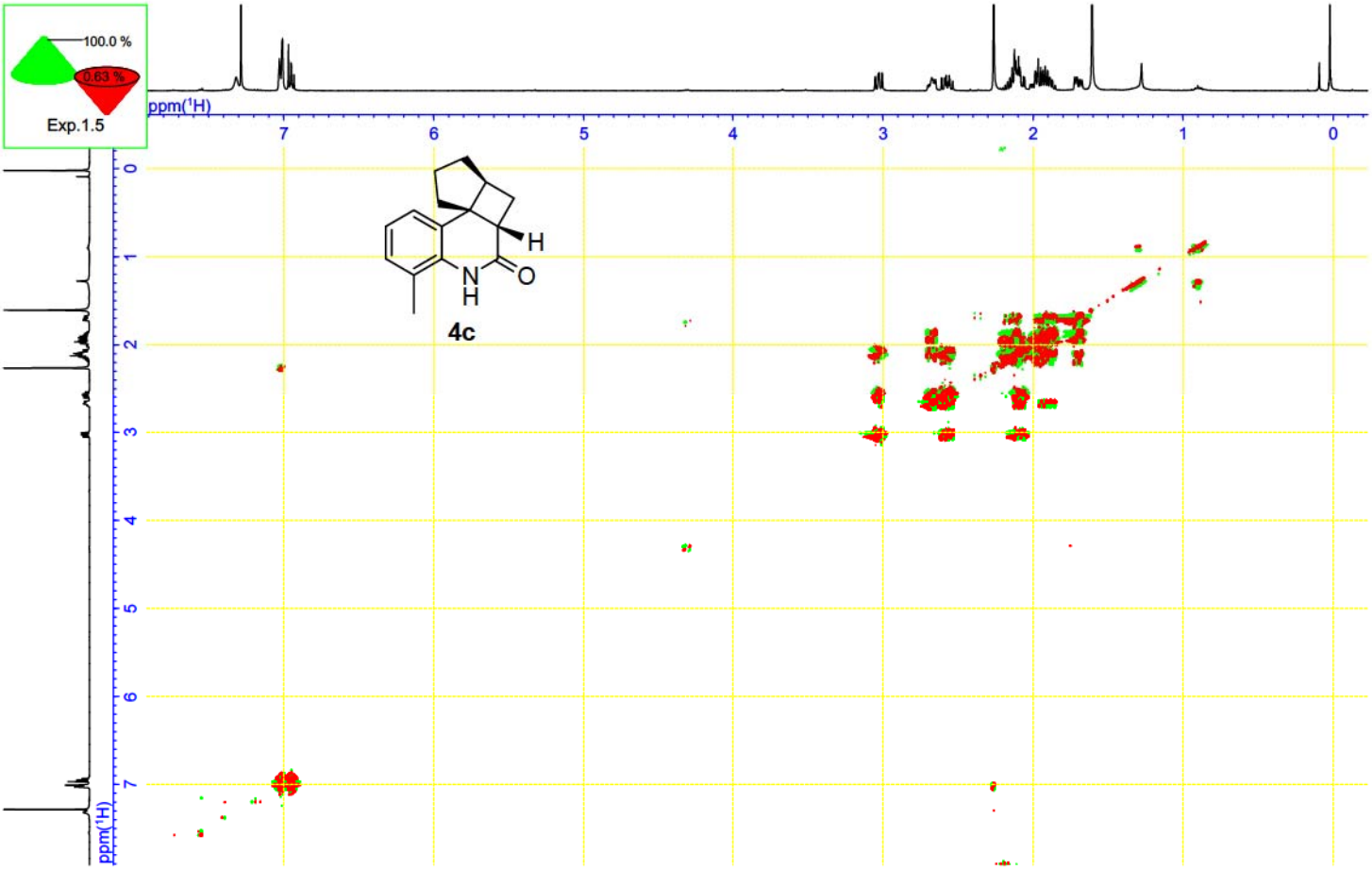

100.0 %
1.02 %
Exp.1.5
ppm(¹H)
4b

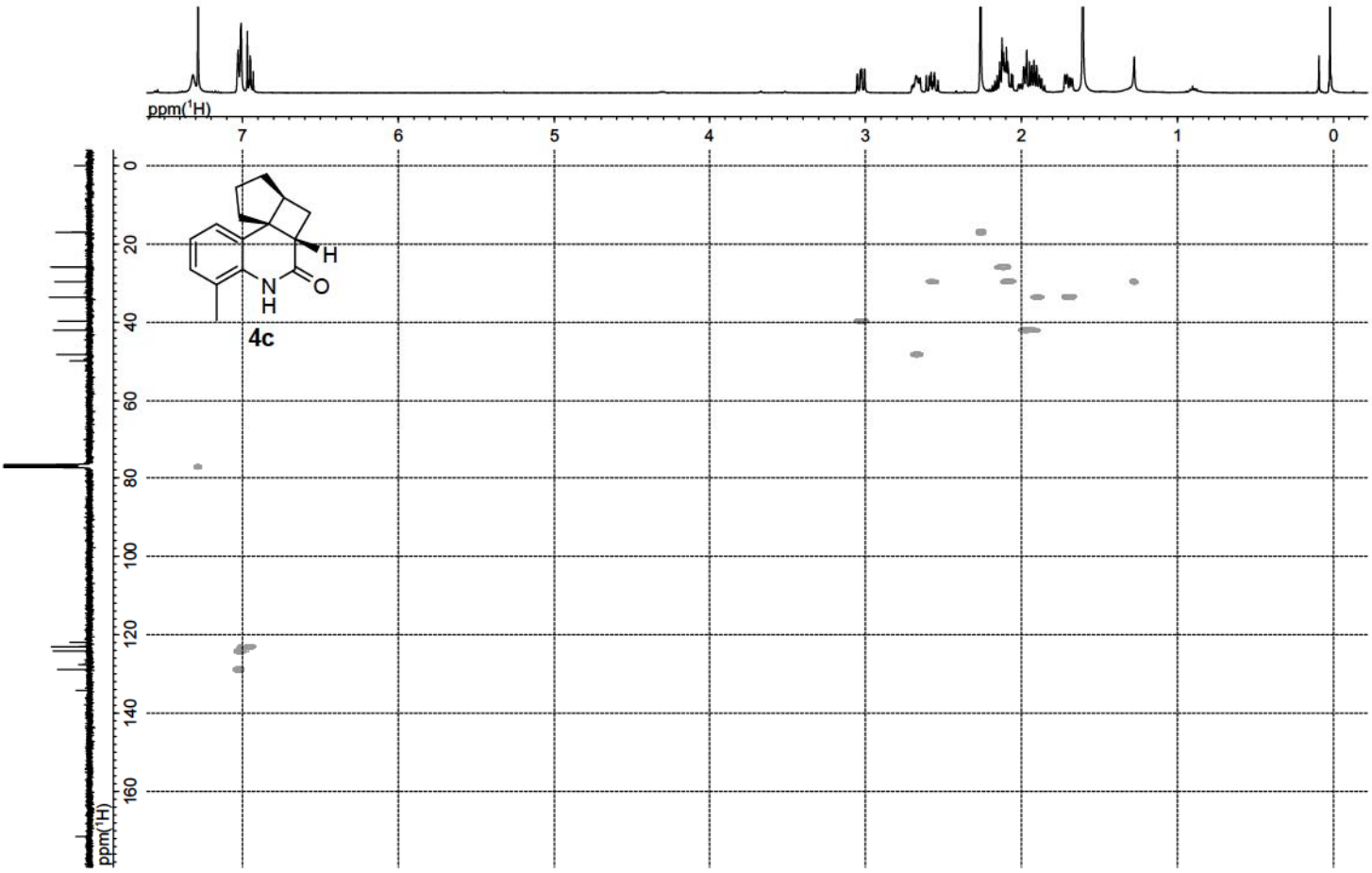

ppm(¹H)
4b

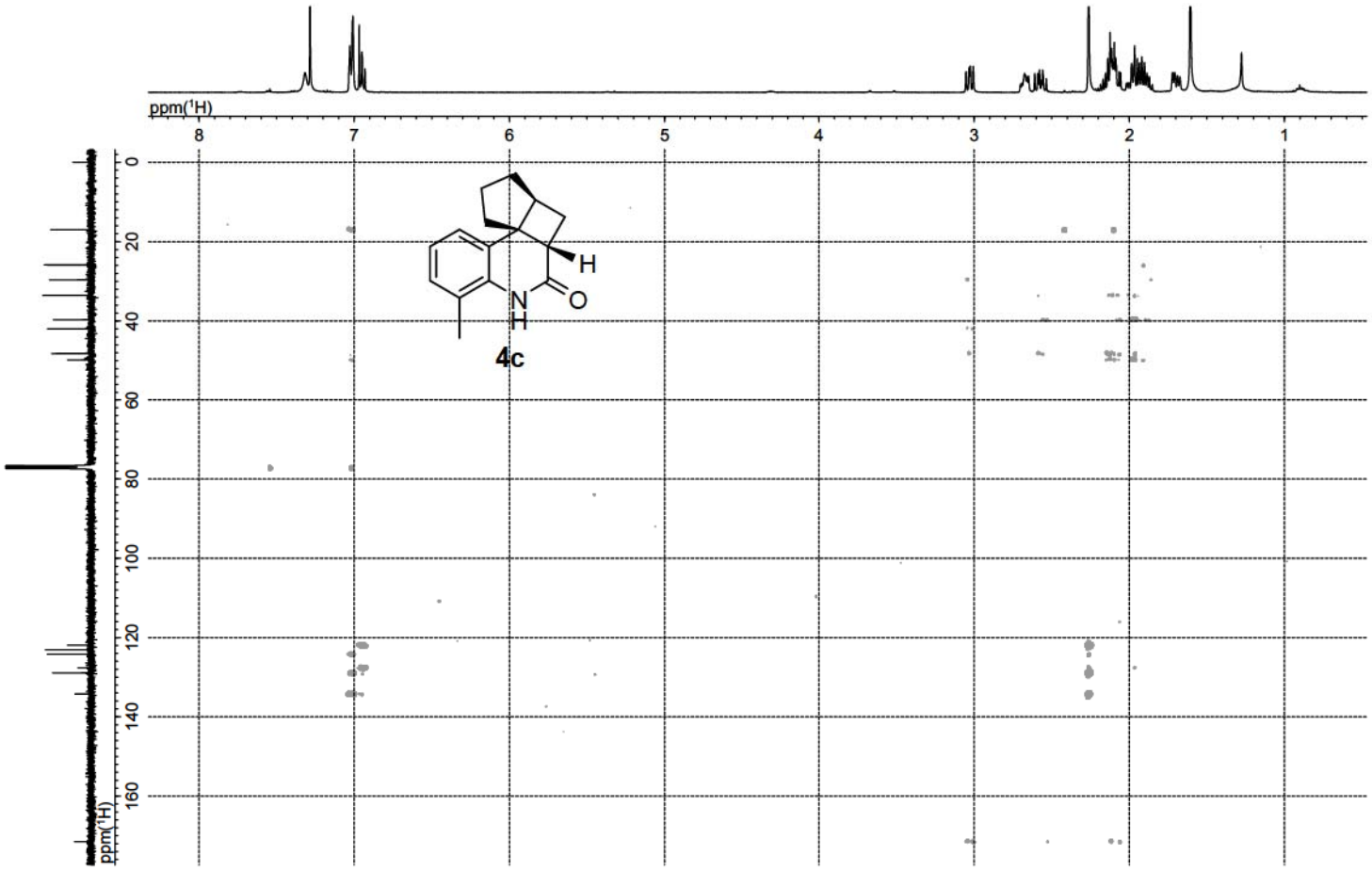

ppm(¹H)
8
7
6
5
4
3
2
1
0
40
80
120
160
200
ppm(¹H)
H
N
H
O
4b

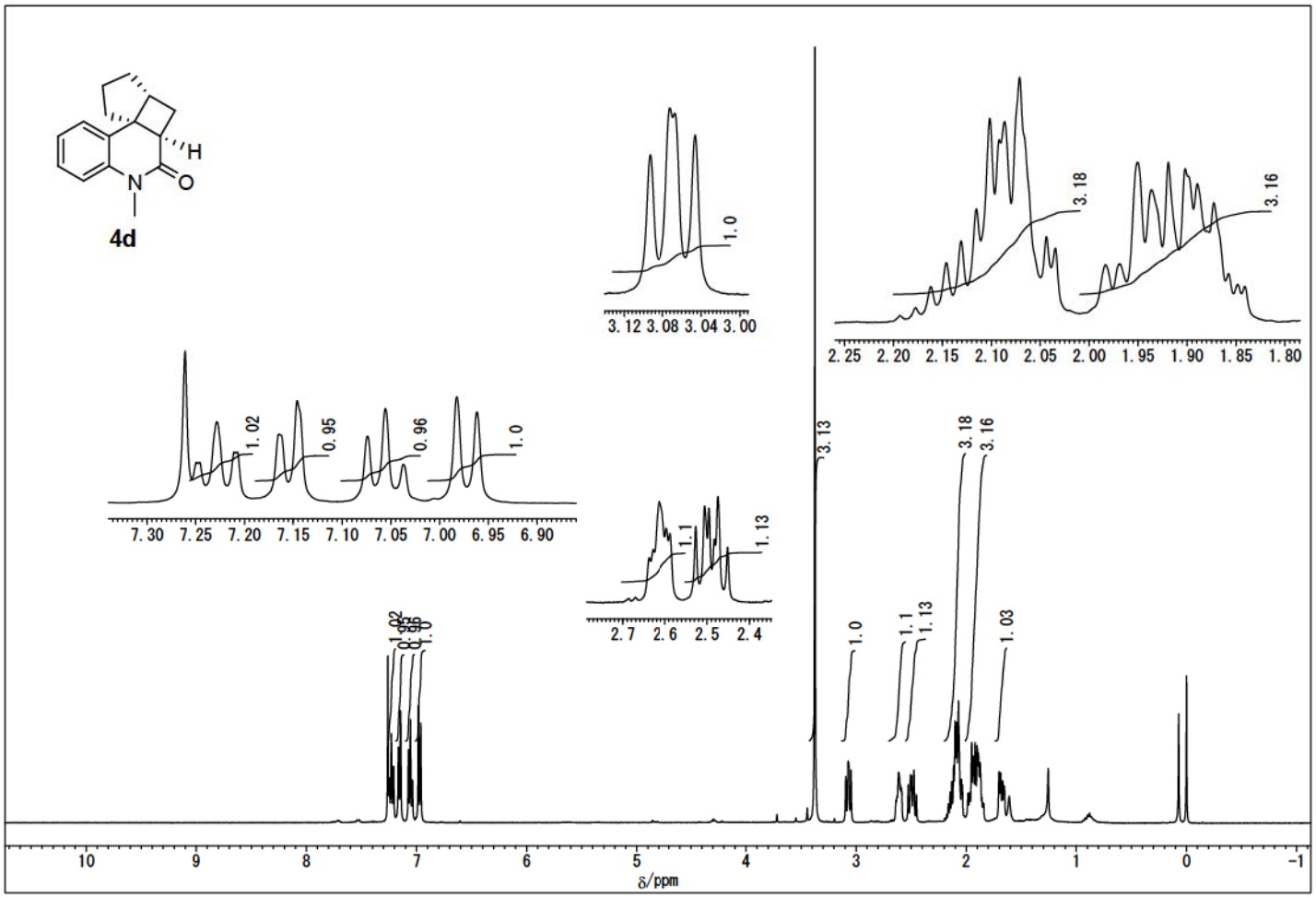

4c
H2O
1.97
1.05
1.0
1.99
2.89
2.73
2.83
0.92
δ/ppm

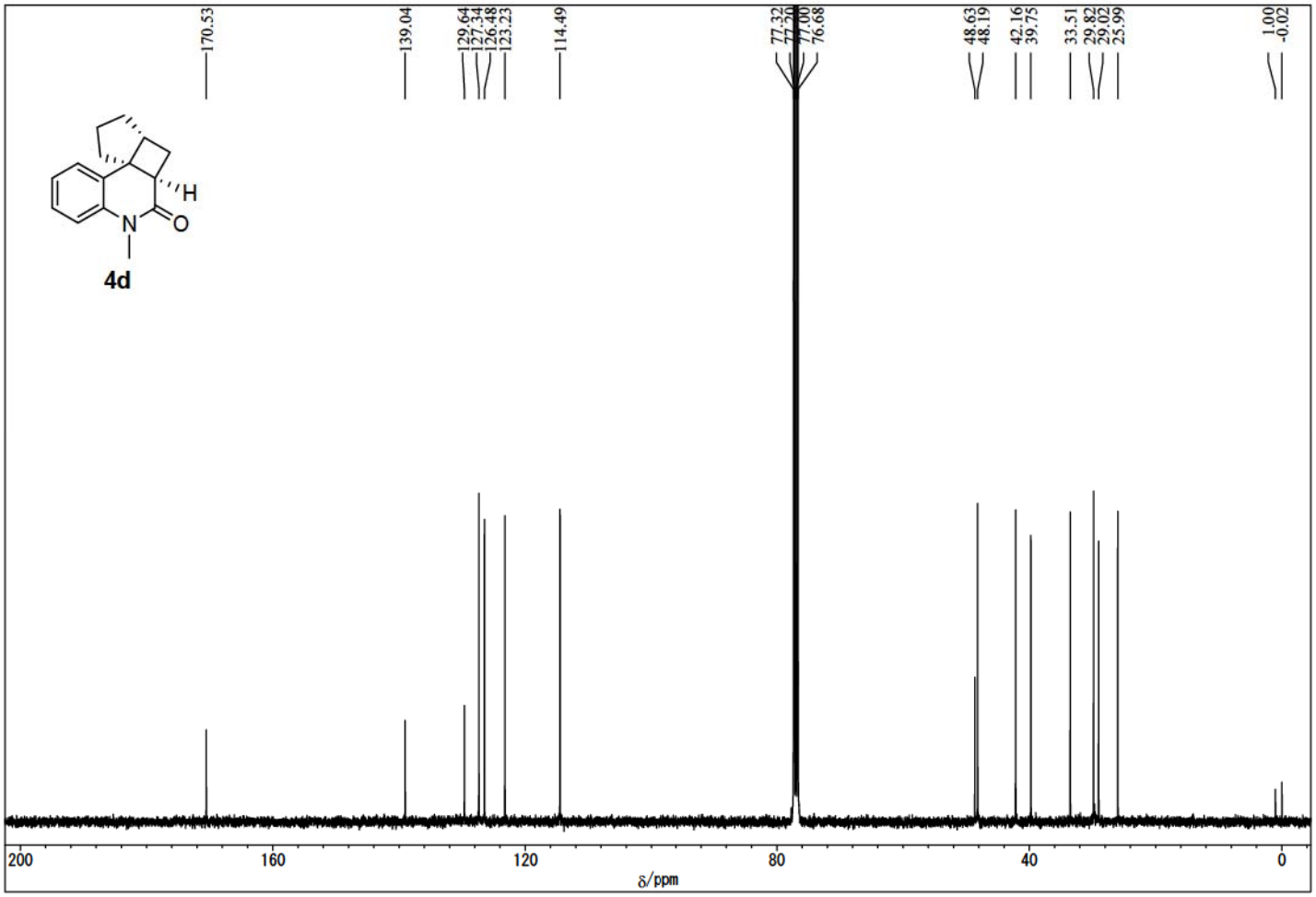

171.49
134.25
128.90
127.65
124.20
123.08
121.92
49.79
48.18
41.98
39.67
33.55
29.60
25.88
17.00
4c
δ/ppm

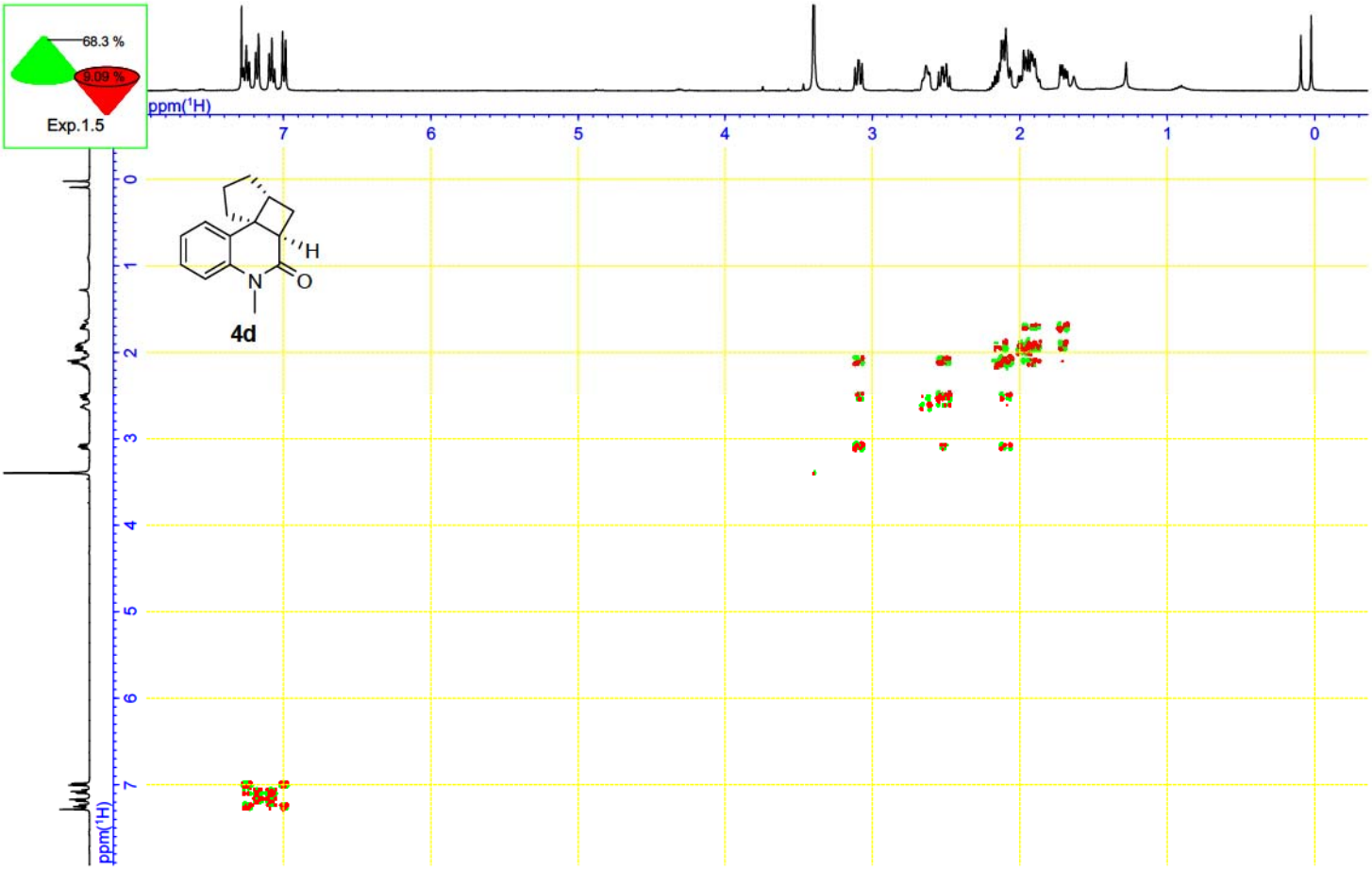

100.0 %
0.63 %
Exp.1.5
ppm(¹H)
4c

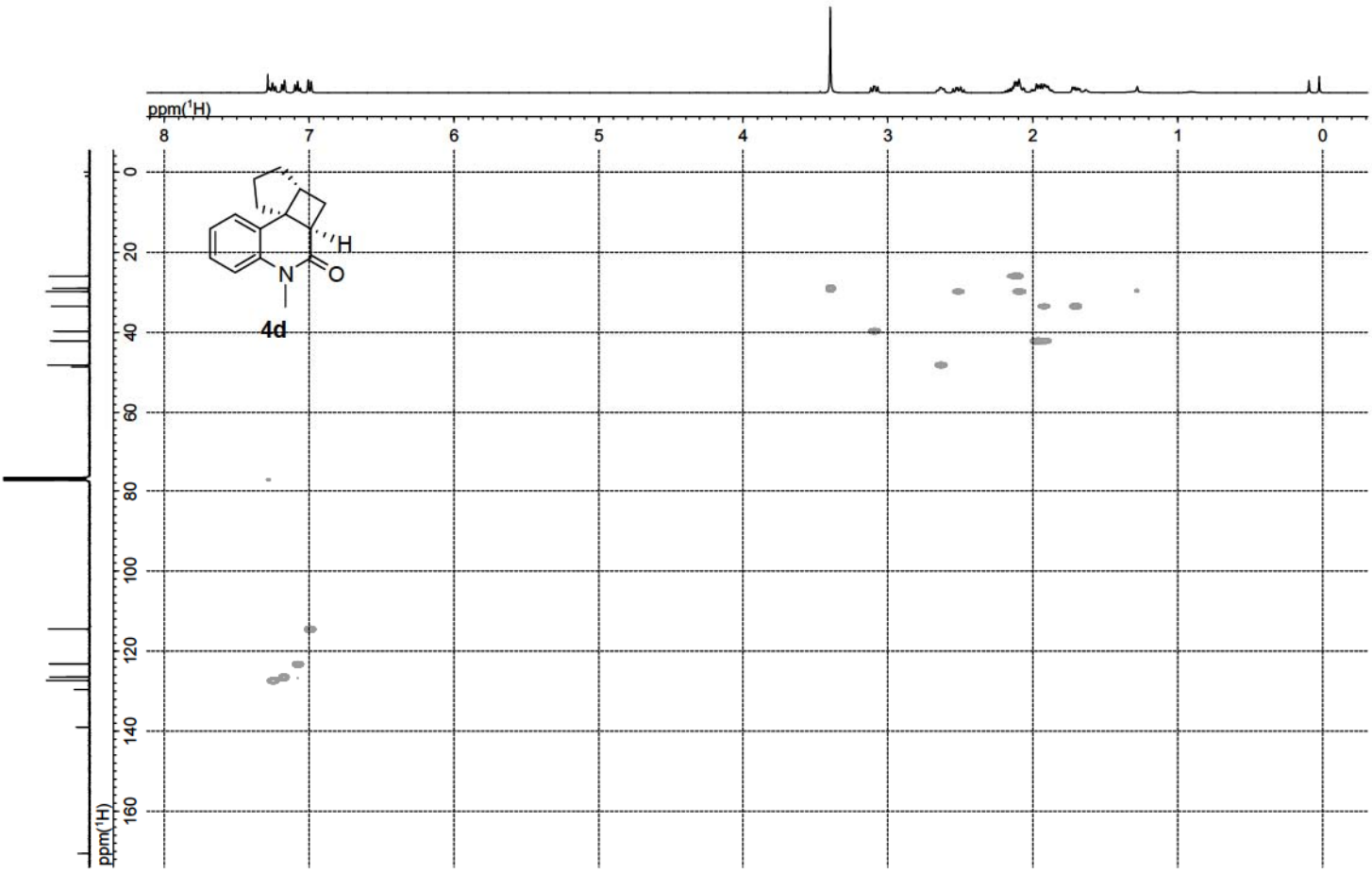

ppm(¹H)
4c

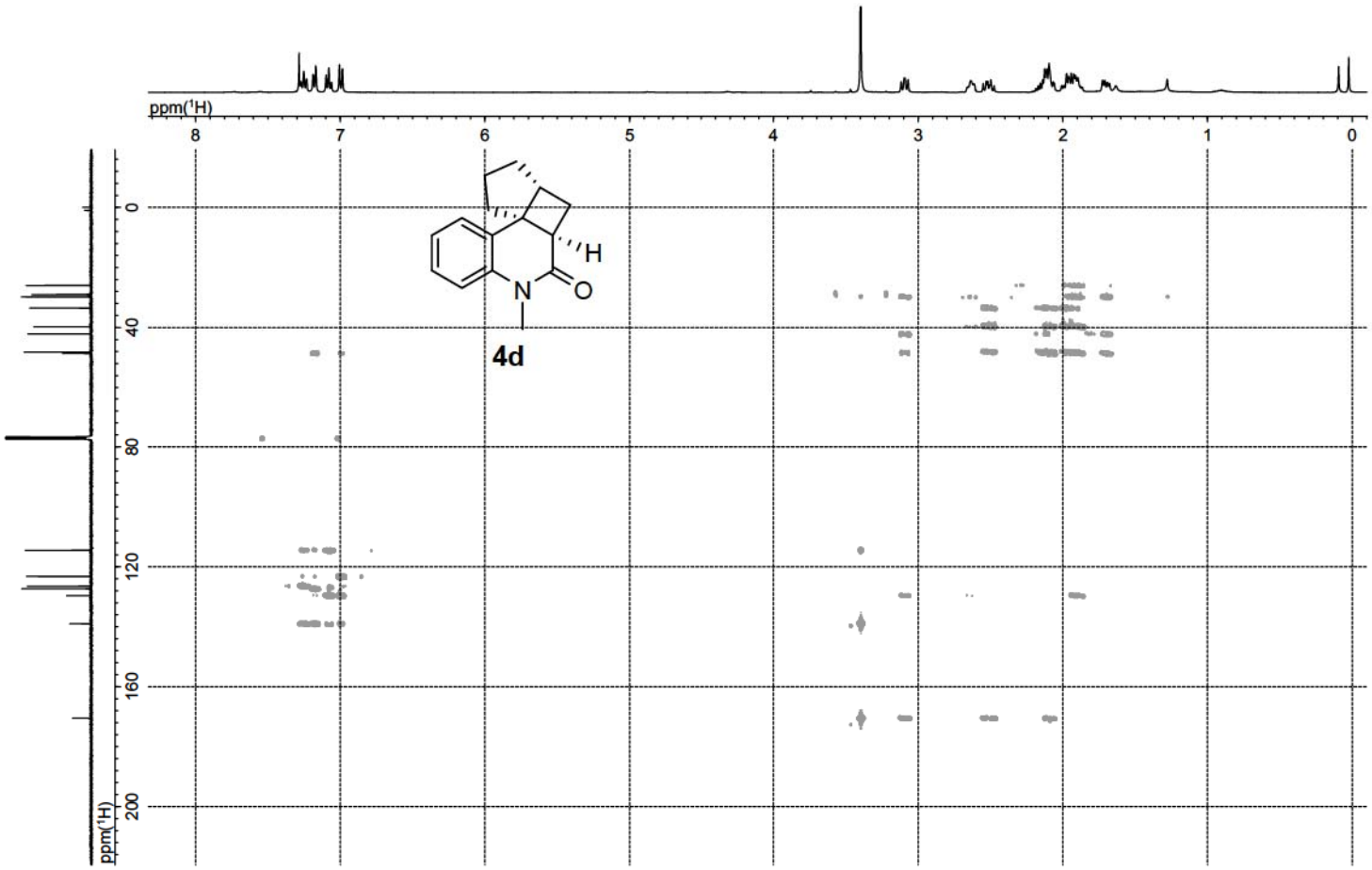

ppm(¹H)
8
7
6
5
4
3
2
1
0
20
40
60
80
100
120
140
160
ppm(¹H)
H
N
H
O
4c


4d
δ/ppm


4d
δ/ppm


68.3 %
9.09 %
Exp.1.5
ppm(¹H)
4d


ppm(¹H)
4d


ppm(¹H)
8
7
6
5
4
3
2
1
0
0
40
80
120
160
200
ppm(¹H)
H
N
O
4d