Enantioselective [2+2] photocycloaddition of quinolone using C_1-symmetric chiral phosphoric acid as a visible-light photocatalyst

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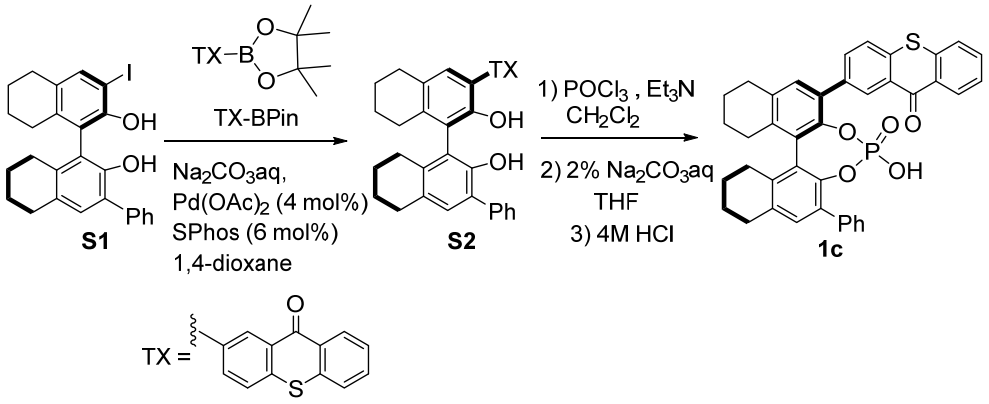
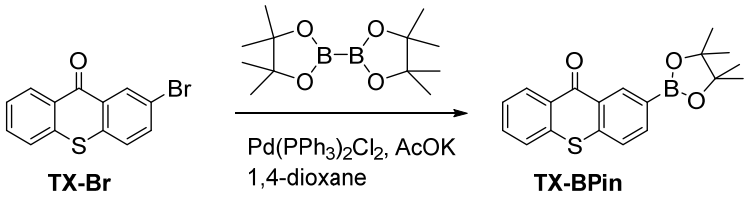
1. Preparation of chiral phosphoric acid and quinolone

General Method

Internal references for ^{1}H NMR spectra were 0.0 ppm (Me_4Si) for $CDCl_3$ and $(CD_3)_2CO$ (2.05 ppm). Chemical shifts for ^{13}C NMR spectra were referenced to $CDCl_3$ (77.0 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. 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).

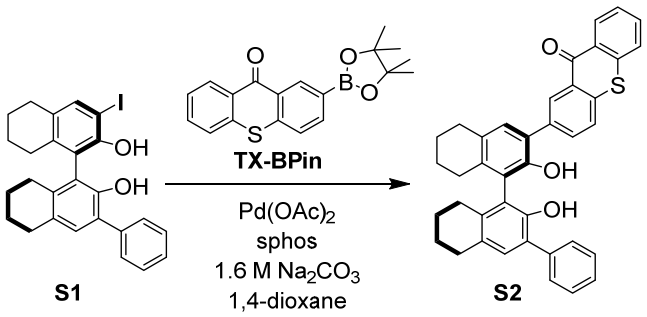
Preparation of chiral phosphoric acid 1c



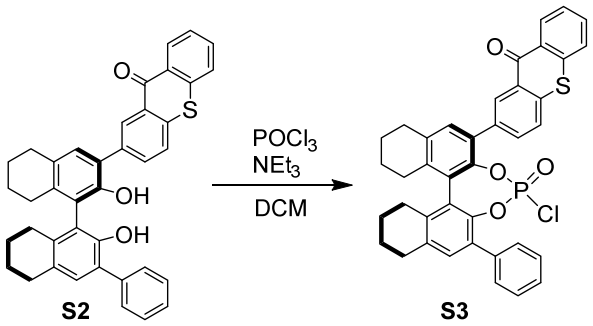


TX-Br[1] (0.23 g, 0.78 mmol), bis(pinacolato)diboron (0.26 g, 1.0 mmol) and AcOK(0.49 g, 5.0 mmol) were dissolved in 1,4-dioxane (7.8 mL). After degas by freeze-pump-thaw cycles, and $Pd(PPh_3)_2Cl_2$ (22.0 mg, 3 mol%) was added to the

mixture under N_2-atmosphere. The suspension was stirred at 100 °C for 23 h. After cooling, EtOAc was added and filtered. The filtrate was evaporated and washed by hexane to give **TX-BPin**[2] (0.22 g, 86% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.06 (s, 1 H), 8.64 (d, *J* = 8.1 Hz, 1 H), 7.99 (d, *J* = 8.1 Hz, 1 H), 7.64-7.53 (m, 3 H), 7.48 (ddd, *J* = 8.0, 6.9, 1.0 Hz, 1 H), 1.38 (s, 12 H).

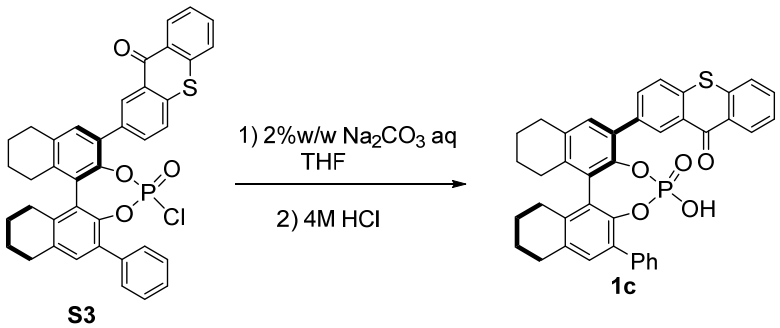


S1[3] (100 mg, 0.20 mmol), **TX-BPin** (90.1 mg, 0.27 mmol) and Na_2CO_3 (1.55 M in H_2O, 0.5 mL) were dissolved in 1,4-dioxane (2.0 mL). After degas by freeze-pump-thaw cycles, and $Pd(OAc)_2$ (1.9 mg, 4 mol%) and 2-dicyclohexylphosphino-2',6'-dimethoxybiphenyl (SPhos) (5.0 mg, 6 mol%) were added to the mixture under N_2-atmosphere.[4] After the mixture was stirred at 105 °C for 15 h, the organic layer was separated, diluted with $CHCl_3$, washed with H_2O as well as with brine and dried with Na_2SO_4, filtered, and evaporated. The residue was purified by column chromatography (SiO_2, hexane:EtOAc = 1:6) to give **S2** (109 mg, 0.19 mmol, 93% yield) as a yellow solid. mp 164 °C. $[\alpha]^{22}_D$ –105.5 (*c* = 0.83, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.87 (d, *J* = 1.8 Hz, 1 H), 8.65 (d, *J* = 8.1 Hz, 1 H), 8.00 (dd, *J* = 8.1, 1.8 Hz, 1 H), 7.65-7.57 (m, 5 H), 7.52-7.45 (m, 1 H), 7.44 (t, *J* = 7.6 Hz, 2 H), 7.37-7.31 (m, 1 H), 7.30 (s, 1 H), 7.17 (s, 1 H), 4.94 (s, 2 H), 2.87-2.78 (m, 4 H), 2.48-2.36 (m, 2 H), 2.33-2.22 (m, 2 H), 1.87-1.67 (m, 8 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 180.0, 148.3, 148.2, 137.7, 137.3, 137.2, 136.8, 136.6, 135.6, 133.6, 132.1, 132.0, 131.7, 130.6, 130.4, 129.9 (x3), 129.3, 129.2 (x2), 128.4 (x2), 127.2, 126.3 (x2), 126.0, 125.6, 124.3, 120.6, 119.4, 29.2 (x2), 27.2, 27.2, 23.05, 23.02 (x3). HRMS (ESI+) *m*/*z* calcd for $C_{39}H_{32}O_3S$, $[M+Na]^+$ 603.19650, found 603.19644.



S2 S3

To a solution of **S2** (283 mg, 0.49 mmol) and Et_3N (0.35 mL, 2.5 mmol) in CH_2Cl_2 (3.0 mL) was slowly added $POCl_3$ (0.22 mL, 2.4 mmol) at 0 °C. The reaction mixture was stirred for 44 h at room temperature, quenched with H_2O, then extracted with CH_2Cl_2. The combined 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 column chromatography (SiO_2, benzene:EtOAc:hexane = 1:6:1) to give **S3** (183 mg, 0.28 mmol, 57% yield) as a colorless solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.78 (d, J = 2.2 Hz, minor-1 H), 8.75 (d, J = 2.2 Hz, major-1 H), 8.67 (d, J = 8.4 Hz, minor-1 H), 8.65 (d, J = 8.5 Hz, major-1 H), 8.08 (dd, J = 8.5, 2.2 Hz, major-1 H), 7.92 (dd, J = 8.4, 2.2 Hz, minor-1 H), 7.70-7.24 (m, 11 H), 3.01-2.86 (m, 4 H), 2.83-2.68 (m, 2 H), 2.52-2.34 (m, 2 H), 1.96-1.83 (m, 6 H), 1.78-1.66 (m, 2 H). HRMS (ESI+) *m*/*z* calcd for $C_{39}H_{30}O_4ClPS$, $[M+H]^+$ 661.13623, found 661.13637.



S3 1c

To a solution of the phosphoryl chloride (67.5 mg, 0.10 mmol) in THF (2.5 mL) was added Na_2CO_3 (2% w/w in H_2O, 2.3 mL). After heating at 85 °C for 18 h, the reaction mixture was neutralized by 1M HCl and extracted with CH_2Cl_2 (3 times). The combined organic layers were washed with H_2O and brine, dried over Na_2SO_4, filtered, and concentrated in vacuo. The crude product was dissolved in CH_2Cl_2, washed with 4M HCl and water, and concentrated in vacuo to give **1c** (42 mg, 64 μmol, 64% yield) as a yellow solid. mp 215-220 °C. $[\alpha]^{22}_D$ –161.0 (c = 1.14, $CHCl_3$). ^{1}H NMR (400 MHz, $(CD_3)_2CO$) δ 8.72 (d, J =

2.0 Hz, 1 H), 8.54 (d, *J* = 8.1 Hz, 1 H), 8.13 (dd, *J* = 8.1, 2.0 Hz, 1 H), 7.81-7.73 (m, 3 H), 7.68-7.63 (m, 2 H), 7.60-7.54 (m, 1 H), 7.41-7.34 (m, 3 H), 7.34-7.27 (m, 1 H), 7.24 (s, 1 H), 3.03-2.87 (m, 4 H), 2.87-2.75 (m, 2 H), 2.45-2.30 (m, 2 H), 1.94-1.82 (m, 6 H), 1.74-1.62 (m, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 179.9, 143.2 (d, *J* = 7.3 Hz), 143.1 (d, *J* = 9.4 Hz), 138.1, 137.3, 137.2, 137.0, 136.0, 135.5, 135.3 (d, *J* = 2.7 Hz), 135.2, 133.7, 131.9, 131.6 (d, *J* = 3.3 Hz), 131.3, 131.2, 130.1, 129.9 (d, *J* = 3.3 Hz), 129.7, 129.4 (x2), 128.8, 128.7, 128.0 (x2), 127.2, 127.0 (x2), 125.9, 125.7, 125.6, 29.2, 29.1, 27.9, 27.8, 22.6 (x2), 22.5 (x2). HRMS (ESI+) *m*/*z* calcd for $C_{39}H_{31}O_5PS$, $[M+H]^+$ 643.17041, found 643.17026.

Preparation of quinolone 2

Quinolones **2a**-**e**,**g**-**j** were prepared according to reported procedures and the spectral data were in the agreement with the published data (**2a**,**e**,[5] **2b**,[3] **2c**,**d**,[6] **2g**,**h**,**i**,[7] **3j**[8]. Quinolone **2f** and hydroquinolone H_2-**2f** were purchased from chemical company.

2. Characterization of the complex of chiral phosphoric acid and quinolone using NMR measurements and DFT calculations

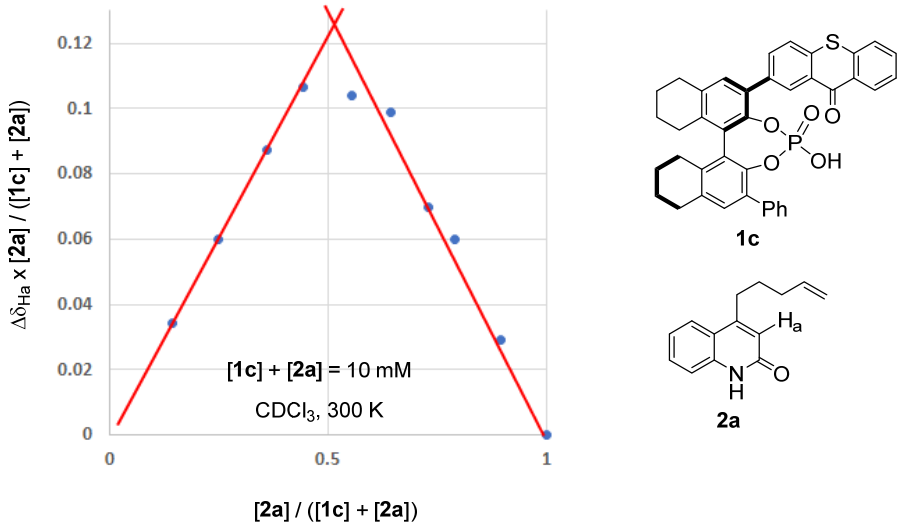


Fig. S1 Stoichiometry determination in the complexation of phosphoric acid **1c** and quinolone **2a** by Job's method.

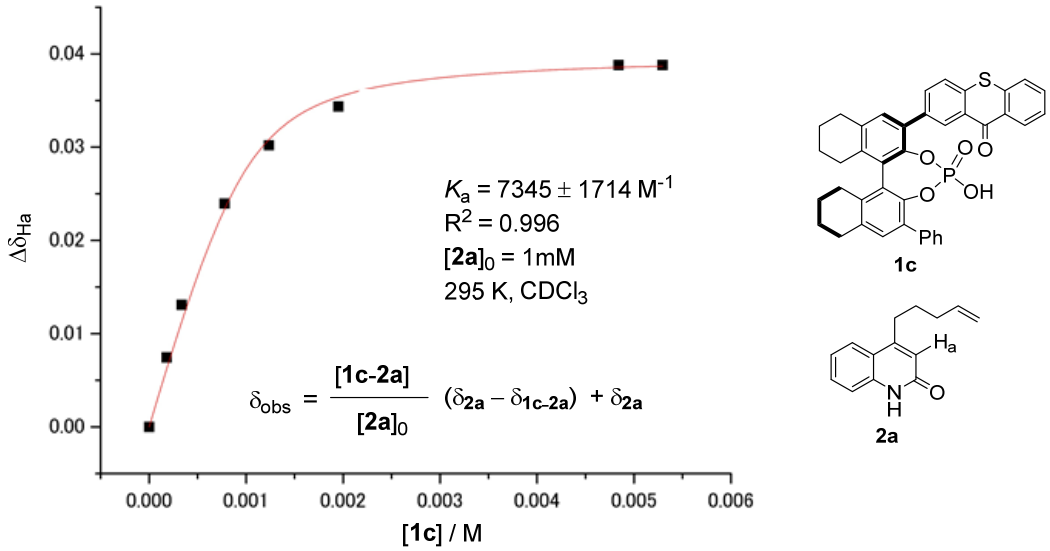


Fig. S2 Determination of the association constant for the formation of the 1:1 complex of **1c** and **2a** via ^{1}H NMR titration experiment.

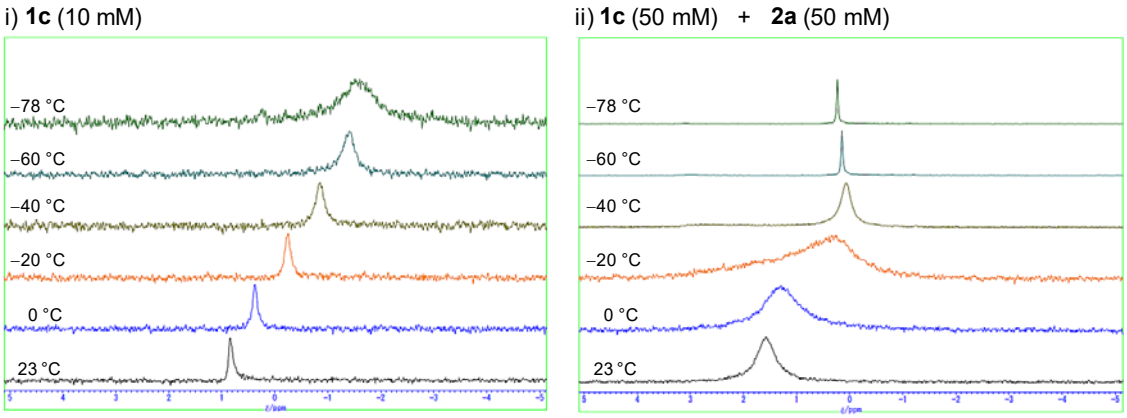


Fig. S3 VT–^{31}P NMR spectra of (i) phosphoric acid **1c** (10 mM) and (ii) a mixture of **1c** and **2a** (**1c**: 50 mM, **2a**: 50 mM) in CD_2Cl_2.

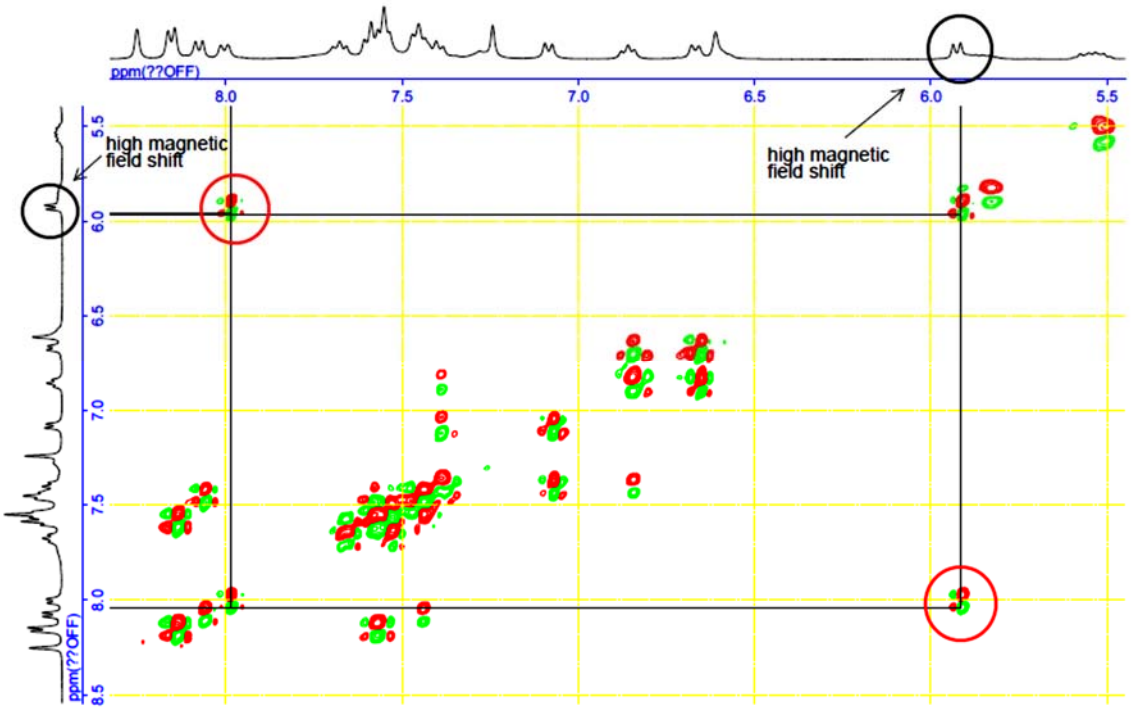


Fig. S4 ^{1}H-^{1}H dqf–COSY spectrum of a mixture of **1c** (10 mM) and **2a** (10 mM) in CD_2Cl_2 at –78 °C.

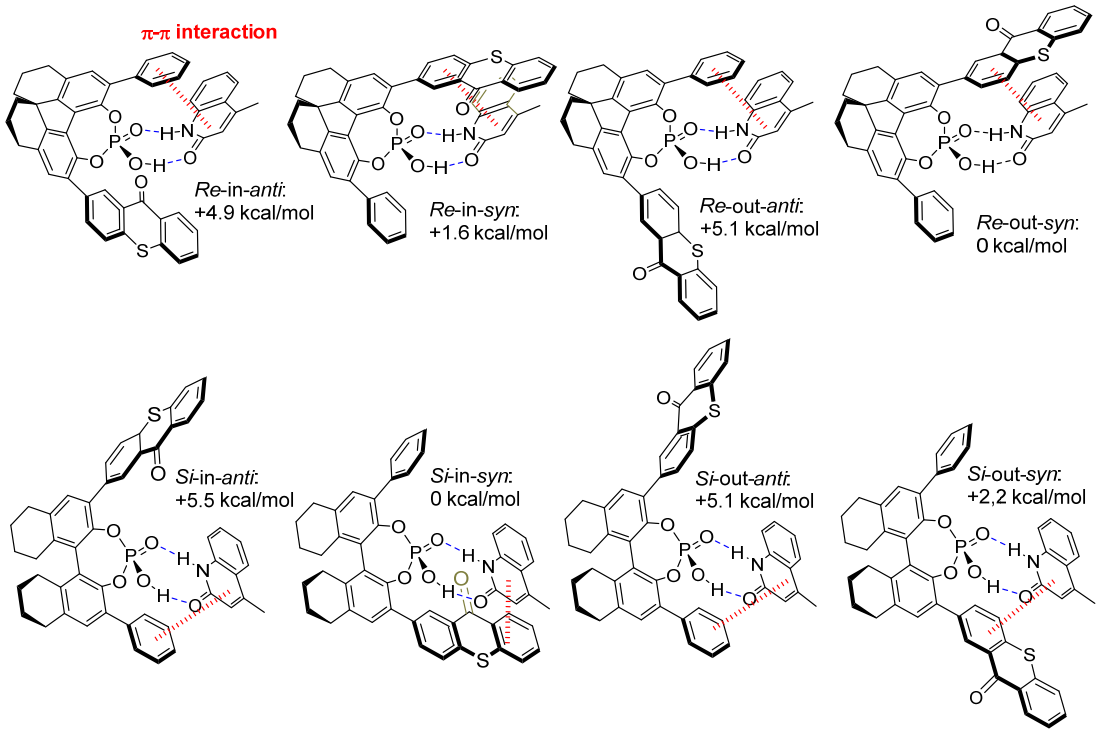


Fig. S5 Schematic structures and relative Gibbs energies at 195.15 K of the 1:1 complex of 4-methyl quinolinone and phosphoric acid **1c** at M06-2X/6-311+(d,p)/SMD(CH_2Cl_2)//M06-2X/6-31G(d,p) level of theory.

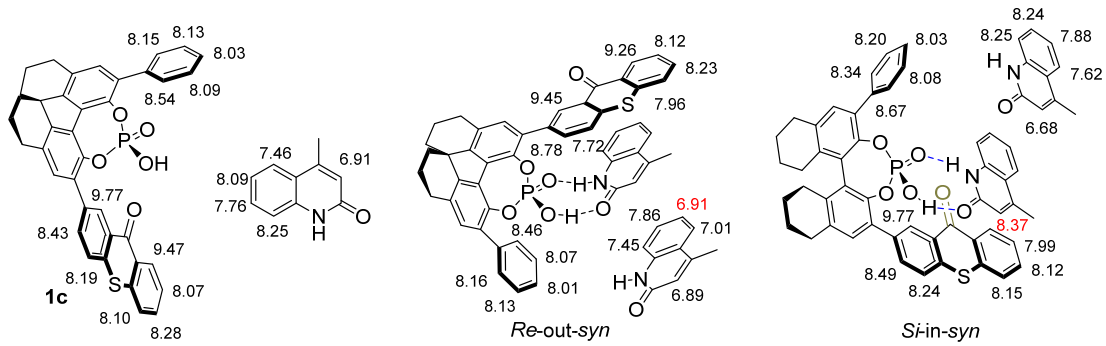


Fig. S6 Speculated ^{1}H NMR chemical shift using the GIAO method at M06-2X/6-31G(d,p) of phosphoric acid **1c**, 4-methyl quinolinone, and 1:1 complexes of **1c** and 4-methyl quinolinone *Re*-out-*syn* and *Si*-in-*syn*. .

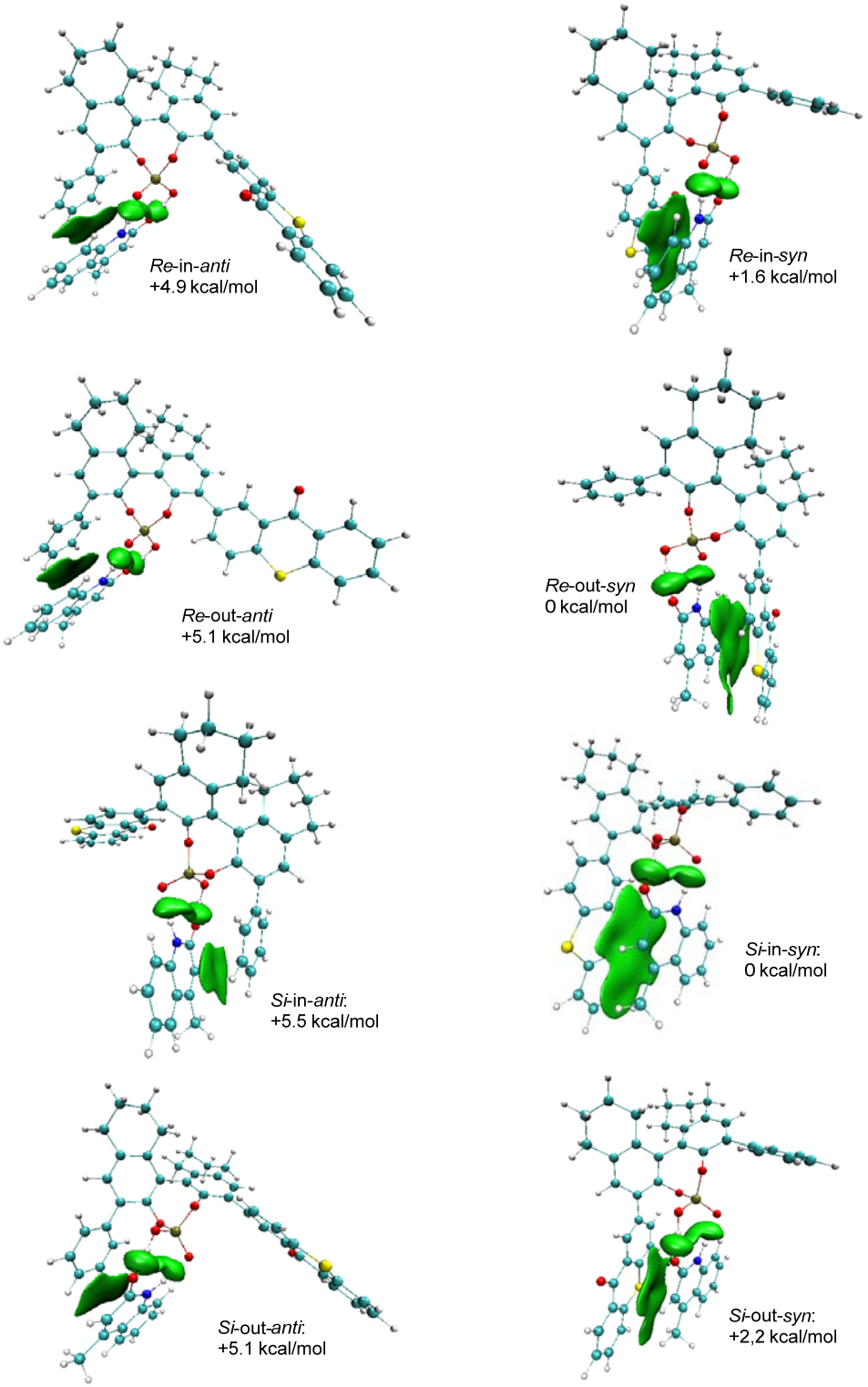


Fig. S7 Nonbonding interactions visualized by IGMplot (δg^{inter} = 0.01 a.u., -0.1 a.u. < ρsign(λ_2) < 0.1 a.u.) of the 1:1 complex of 4-methyl quinolinone and phosphoric acid **1c**.

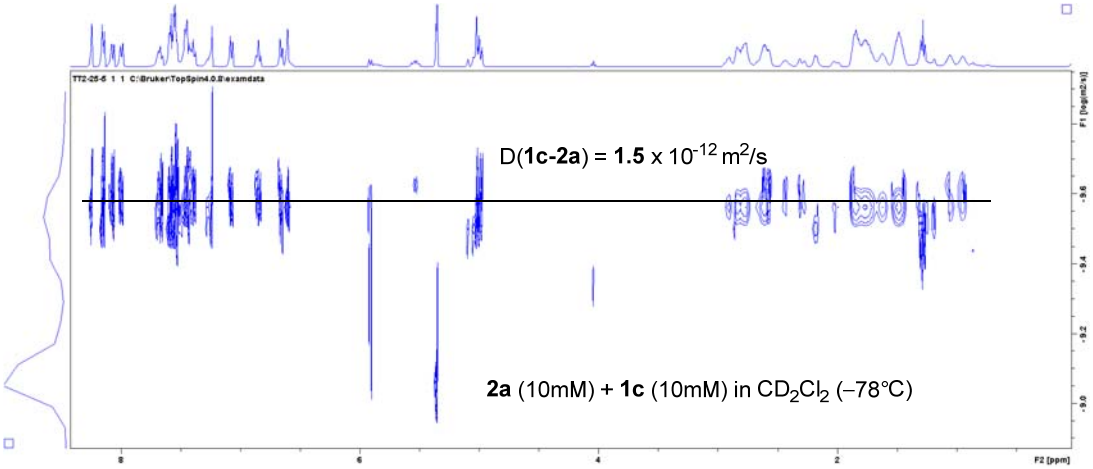


Fig. S8 DOSY measurement of a mixture of **1c** (10 mM) and **2a** (10 mM) in CD_2Cl_2 at –78 °C.

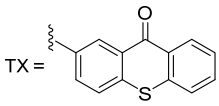
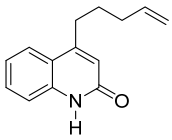
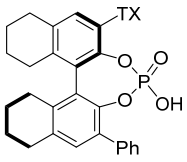
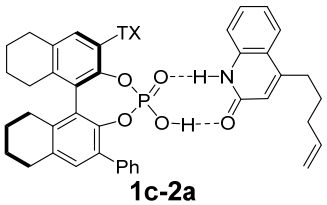
TX = 	**2a** 	**1c** 	**1c-2a** 
Diffusion coefficient (^{1}H NMR, 10 mM, CD_2Cl_2, –78 °C)	D = **8.1** x 10^{-12} m^2/s	D = **2.2** x 10^{-12} m^2/s	D(**1c-2a**) = **1.5** x 10^{-12} m^2/s
Molar volume (B3LYP/6-31G*)	**181** cm^3	Monomer : **457** cm^3 Dimer: **850** cm^3	**593** cm^3

Fig. S9 Diffusion coefficient in CD_2Cl_2 (10 mM) at –78 °C and molar volume calculated at the B3LYP/6-31G* level of theory of **1c**, **2a** and the 1:1 complex of **1c** and **2a**.

3. Estimation of triplet energy of chiral phosphoric acid and quinolone using DFT calculations and phosphorescence measurement

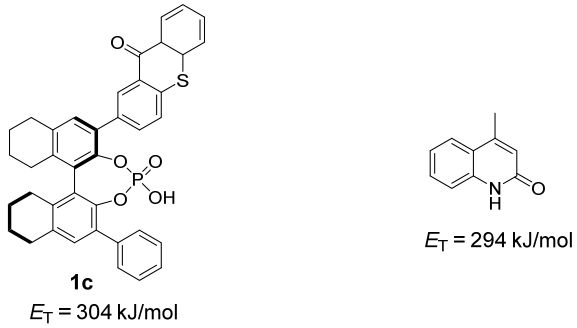


Fig. S10 Triplet energy calculated at the M06-2X/6-31G* (d,p) level of theory of phosphoric acid **1c** and 4-methyl quinolone.

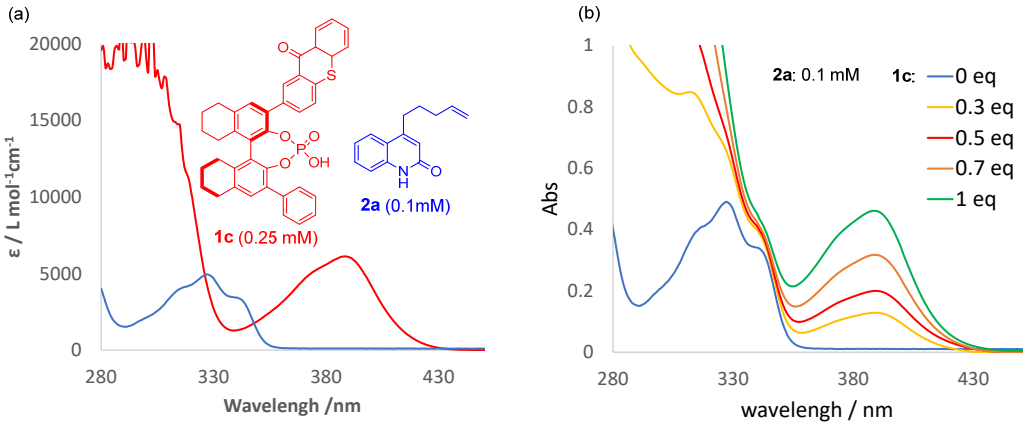


Fig. S11 UV/Vis spectra of (a) phosphoric acid **1c** (0.25 mM, red), quinolone **2a** (0.1 mM, blue) and (c) a mixture of **1c** and **2a** in CH_2Cl_2 at 20 °C.

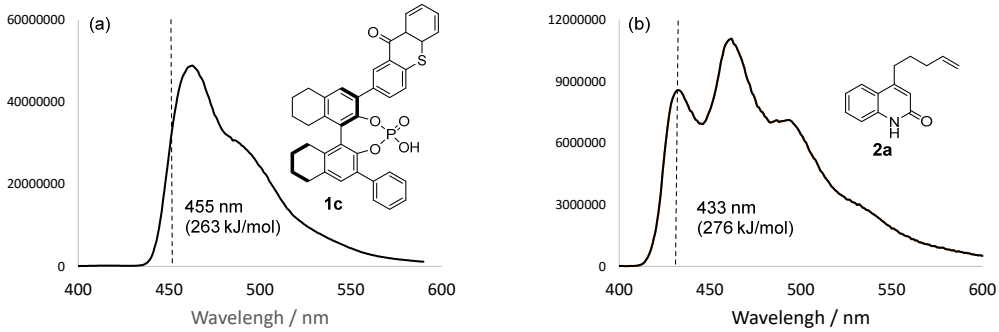
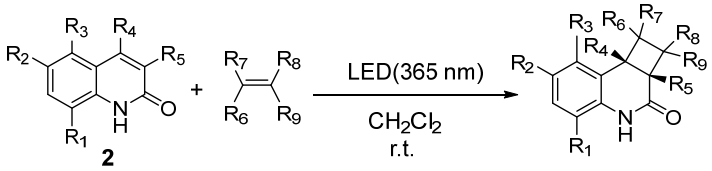


Fig. S12 Phosphorescence spectra of (a) phosphoric acid **1a** (0.14 mM, λ_{ex} = 385 nm) and (b) quinolone **2a** (0.02 mM, λ_{ex} = 322 nm) in 2-methyl tetrahydrofuran at 77 K.

4. Photochemical reactions

The photochemical reactions were carried out using dichloromethane (spectroscopic grade) which was stored over molecular sieves 4 Å and degassed by five times freeze-pump-thaw cycles before use. The light source used was a commercially available UV-LED (365 or 405 nm) from ARK TECH.

Typical precedure of preparation of racemic cycloadduct 3



A solution of quinolone **2** (0.10 mmol) and 2,3-dimethyl-2-butene (in the case of the intermolecular photocycloaddition) in CH_2Cl_2 (20 mL) was degassed by freeze-pump thaw and irradiated at r.t. by 405 nm LED lamp (Fig. S13). After the appropriate irradiation time, solvent was removed by reduced pressure evaporation and the crude product was purified by silicagel column chromatography (hexane:AcOEt = 1:1) to give cycloadduct **3**.

Typical precedure of [2+2] photocycloaddition of quinolone 2 catalyzed by phosphoric acid 1c

A solution of quinolone **2** (0.10 mmol), CPA **1c** (6.4 mg, 10.0 μmol; dried in vacuo at 50 °C for 3 h before use) and 2,3–dimethyl 2–butene (in the case of the intermolecular photocycloaddition) in CH_2Cl_2 (20 mL) was degassed by freeze-pump thaw, cooled to –78 °C and irradiated by 405 nm LED lamp (Fig. S13). After the appropriate irradiation time, solvent was removed by reduced pressure evaporation and the crude product was purified by silicagel column chromatography (hexane hexane:AcOEt = 1:1) to give cycloadduct **3**.

Reaction Apparatus

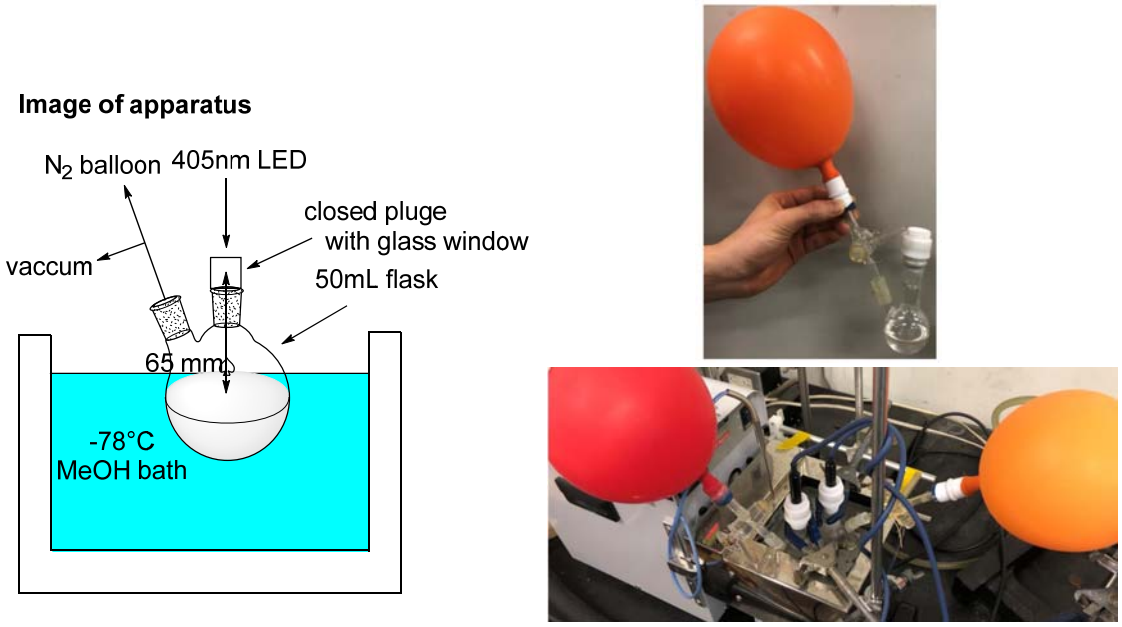
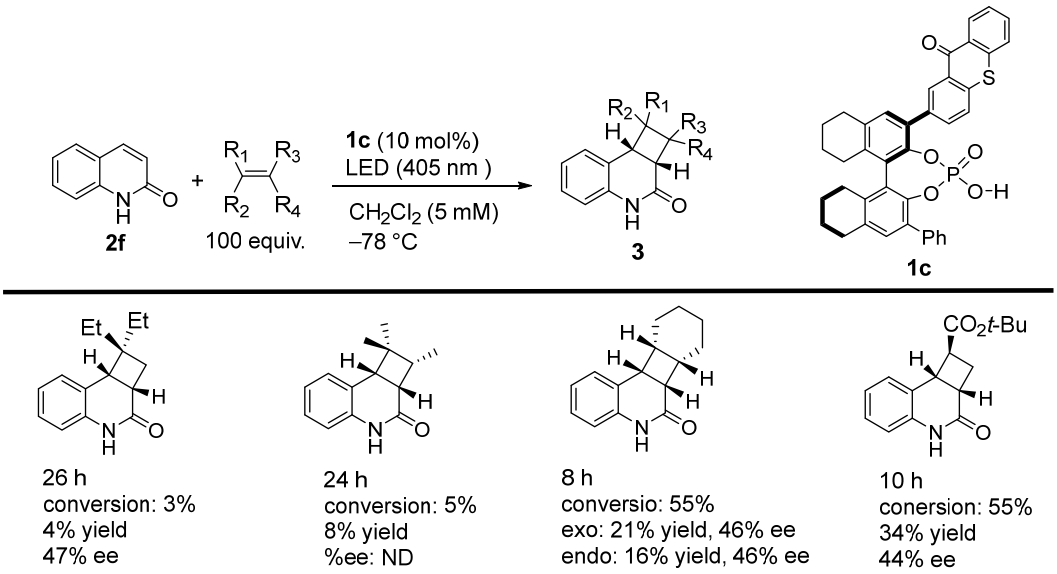


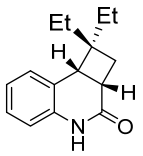
Fig. S13 Reaction Apparatus

Table S1. Scope of alkene in the intermolecular photocycloaddition of quinolone 2f[a]

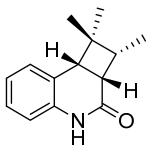


[a] The reactions were conducted with quinolone **2** (0.1 mmol), CPA **1c** (10 mol%) and 2,3-dimethyl 2-butene (10 mmol) in CH_2Cl_2 (20 mL) at –78 °C. The chemical yield were determined from the isolated cycloadduct. The enantiomeric excess were determined by chiral stationary phase HPLC analysis. ND = not determined.

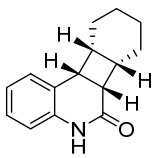
Characterization of cycloadducts



white solid. mp 131-133 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (s, 1 H), 7.12 (td, *J* = 7.2, 2.9 Hz, 1 H), 6.96 (m, 2 H), 6.64 (d, *J* = 7.2 Hz, 1 H), 3.58 (d, *J* = 10.1 Hz, 1 H), 3.34 (td, *J* = 10.1, 5.5 Hz 1 H), 2.32 (dd, *J* = 12.1, 10.1 Hz, 1 H) 2.17 (ddd, *J* = 12.1, 5.5, 0.82 Hz, 1 H), 1.67-1.58 (m, 2 H), 1.29-1.13 (m, 2 H), 0.92 (t, *J* = 7.6 Hz, 3 H), 0.61 (t, *J* = 7.3 Hz, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.7, 137.5, 129.5, 127.5, 122.8, 121.1, 115.6, 46.9, 44.2, 37.5, 31.7, 31.4, 25.8, 8.3, 6.9. HRMS (ESI+) *m*/*z* calcd for $C_{15}H_{19}NO$, $[M+H]^+$ 230.15394, found 230.15413.

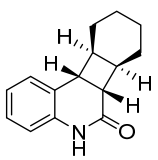


white solid. mp102-103 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (s, 1 H), 7.13 (td, *J* = 7.6, 1.6 Hz, 1 H), 6.96 (m, 2 H), 6.64 (d, *J* = 7.6 Hz, 1 H), 3.37 (d, *J* = 9.5 Hz, 1 H), 2.94 (dd, *J* = 9.5, 7.4 Hz, 1 H), 2.43-2.35 (m, 1 H) 1.20 (s, 3 H), 1.17 (d, *J* = 7.1 Hz, 3 H), 0.83 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.1, 137.0, 129.9, 127.5, 122.9, 121.5, 115.7, 45.7, 44.0, 43.2, 40.5, 25.7, 24.5, 15.3. HRMS (ESI+) *m*/*z* calcd for $C_{14}H_{17}NO$, $[M+H]^+$ 216.13829, found 216.13837.



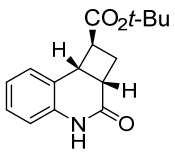
endo

white solid. mp 185 °C. 1H NMR (400 MHz, $CDCl_3$) δ 8.66 (s, 1 H), 7.12 (td, *J* = 7.4, 1.4 Hz, 1 H), 7.00 (d, *J* = 7.4 Hz , 1 H), 6.95 (td, *J* = 7.4, 0.3 Hz, 1 H), 6.74 (d, *J* = 7.4 Hz, 1 H), 3.88 (t, *J* = 9.1 Hz, 1 H), 3.38 (t, *J* = 9.7 Hz, 1 H), 3.09-3.00 (m, 1 H), 2.88-2.77 (m, 1 H), 1.88-1.78 (m, 1 H), 1.61-1.51 (m, 1 H), 1.41-1.19 (m, 5 H), 1.13-1.01 (m, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.3, 137.6, 128.6, 127.4, 123.0, 122.3, 115.4, 39.3, 38.6, 37.6, 36.4, 23.6, 23.4, 22.1, 21.7. HRMS (ESI+) *m*/*z* calcd for $C_{15}H_{17}ON$, $[M+Na]^+$ 250.12024, found 250.12041.



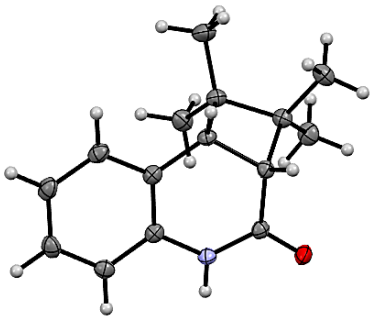
exo

white solid. mp 177 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (s, 1 H), 7.13 (td, *J* = 7.7, 1.0 Hz, 1 H), 7.06 (d, *J* = 7.7 Hz, 1 H), 6.97 (td, *J* = 7.7, 0.8 Hz, 1 H), 6.66 (d, *J* = 7.7 Hz, 1 H), 3.48 (t, *J* = 7.3 Hz, 1 H), 3.08 (dd, *J* = 8.0, 5.1 Hz, 1 H), 2.85-2.76 (m, 1 H), 2.61-2.52 (m, 1 H), 1.94-1.83 (m, 1 H), 1.76-1.67 (m, 1 H), 1.67-1.58 (m, 4 H), 1.46-1.37 (m, 1 H), 1.37-1.26 (m, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.3, 136.6, 128.0, 127.4, 124.7, 123.2, 115.4, 41.7, 41.0, 38.8, 38.3, 27.9, 26.7, 22.6, 22.3. HRMS (ESI+) *m*/*z* calcd for $C_{15}H_{17}NO$, $[M+H]^+$ 228.13829, found 228.13838.



white solid. mp 143 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (s, 1 H), 7.18 (t, J = 7.6 Hz, 1 H), 7.12 (d, J = 7.6 Hz, 1 H), 6.99 (t, J = 7.6 Hz, 1 H), 6.68 (d, J = 7.6 Hz, 1 H), 3.94 (t, J = 8.8 Hz, 1 H), 3.31-3.23 (m, 1 H), 3.23 (q, J = 9.2 Hz, 1 H), 2.81 (dt, J = 12.0, 9.2 Hz, 1 H), 2.58 (ddd, J = 12.0, 9.2, 3.2 Hz, 1 H), 1.48 (s, 9 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.2, 172.7, 136.8, 128.2, 127.8, 123.5, 122.7, 116.0, 80.9, 45.9, 40.1, 34.5, 29.1, 28.1 (x3). HRMS (ESI+) calcd for *m*/*z* $C_{16}H_{19}NO_3$ $[M+Na]^+$ 296.12571, found 296.12589.

5. X-ray crystallography data



ORTEP drawing of **3f** with thermal ellipsoids at 50% probability level.

Identification code	Olex2
Empirical formula	$C_{15}H_{19}NO$
Formula weight	229.31
Temperature	100 K
Wavelength	1.54184 Å [Cu-Kα]
Crystal system	orthorhombi
Space group	P 21 21 21
Unit cell dimensions	a = 7.11510(10) Å α = 90°
	b = 8.44480(10) Å β = 90°
	c = 21.3264(2) Å γ = 90°
Volume	1281.41(3) Å^3
Z	4
Density (calculated)	1.189 Mg/m^3
Absorption coefficient	0.574 mm^{-1}
F(000)	496
Crystal size	0.08 x 0.07 x 0.03 mm^3
Data collection range	4.07 ≤ θ ≤ 76.2
Index ranges	-8 ≤ h ≤ 8, -10 ≤ k ≤ 10, -26 ≤ l ≤ 26
Reflections collected	35155
Independent reflections	20763 [R(int) = 0.0348]
Completeness to theta = 30.90	100%
Absorption correction	Empirical
Max. and min. transmission	n/a
Refinement method	SHELXL

Data / restraints / parameters	2676 / 0 / 158
Goodness-of-fit on F^2	1.020
Final R indices [$I>2\sigma(I)$]	$R_1 = 0.0295$, $wR_2 = 0.0765$
R indices (all data)	$R_1 = 0.0304$, $wR_2 = 0.0773$
Absolute structure parameter	0.05(6)
Largest diff. peak and hole	0.147 and -0.177 e.Å^{-3}
Extinction coefficient	n/a

6. Details of laser flash photolysis experiments

To measure the triplet-triplet absorbance spectrum of the 1:1 complex of phosphoric acid **1c** and quinolone **2f** , a mixture of phosphoric acid **1c** (1.3 mM) and quinolone **2f** (0.13 mM) in dichloromethane was used for the laser flash photolysis experiments. Based on the binding constant between phosphoric acid **1c** and quinolone **2a** ($K_{a\_1c\text{-}2a}$ = 7345), 89% of phosphoric acid **1c** bind with quinolone **2f** to form the 1:1 complex at 25 °C in the mixture. The mixture was placed in a 1 x 1 cm quartz cell and deoxygenated by argon purging for 20 min. Kinetic traces at varying probe wavelength (340-800 nm) were recorded at –78 °C after pulsed laser excitation (Nd:YAG laser, 355 nm, 4-6 ns pulse length, ca. 7mJ/pluse). From these kinetic traces, the transient absorption spectra show in Fig. 7a were constructed. The triplet of the thioxanthone chromophore on the 1:1 complex has a broad transient absorption spectrum around 540 to 740 nm. Absorbance decay trace was monitored at 600 nm and fitted to a mono-exponential function to determine the life time (Fig. 7b).

On the quenching experiment, the laser flash photolysis experiments was carried out after the addition of appropriated amounts of 2,3-dimethyl 2-butene to the mixture of phosphoric acid **1c** and quinolone **2f**. The resulting observed rate constant (k_{obs}) was plotted against the concentration of 2,3-dimethyl 2-butene. The bimolecular quenching rate constant (k_q) was obtained from the slope of this plot (Fig. S19).

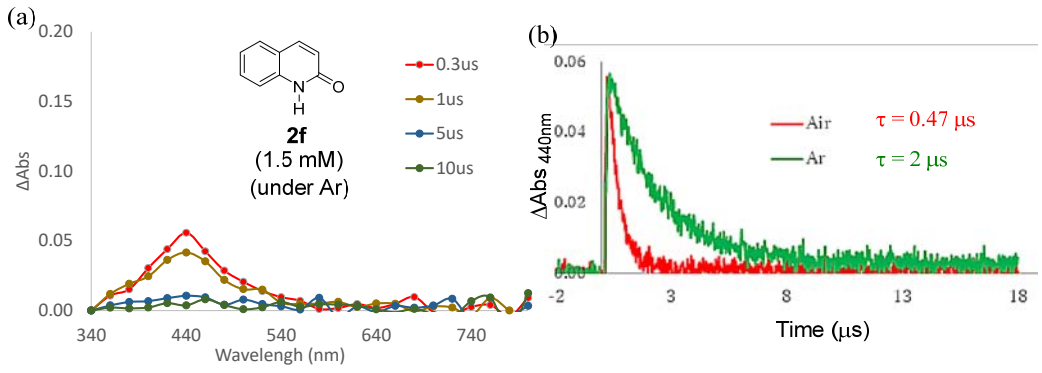


Fig. S14 (a) Transient absorption spectra of quinolone **2f** (1.5 mM) in Ar saturated CH_2Cl_2 at –78 °C, and (b) the decay cube at 440 nm under Ar (green) and under air (red).

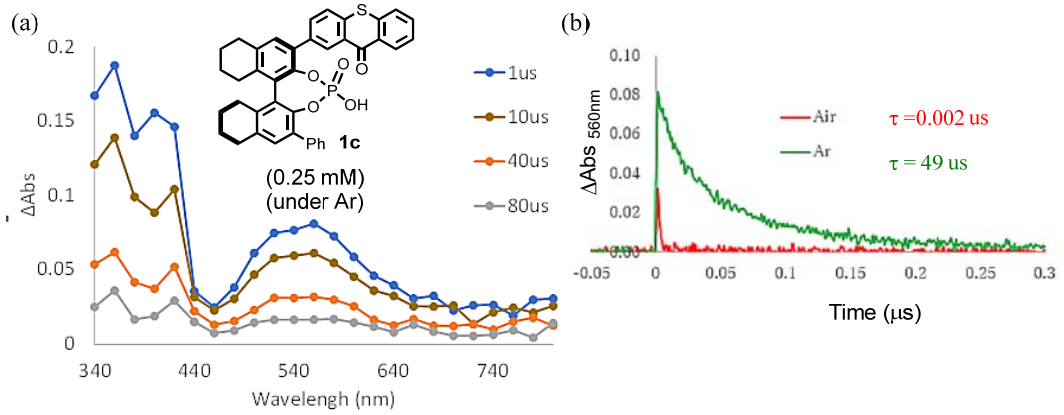


Fig. S15 (a) Transient absorption spectra of phosphoric acid **1c** (0.25 mM) in Ar saturated CH_2Cl_2 at –78 °C, and (b) the decay cube at 560 nm under Ar (green) and under air (red).

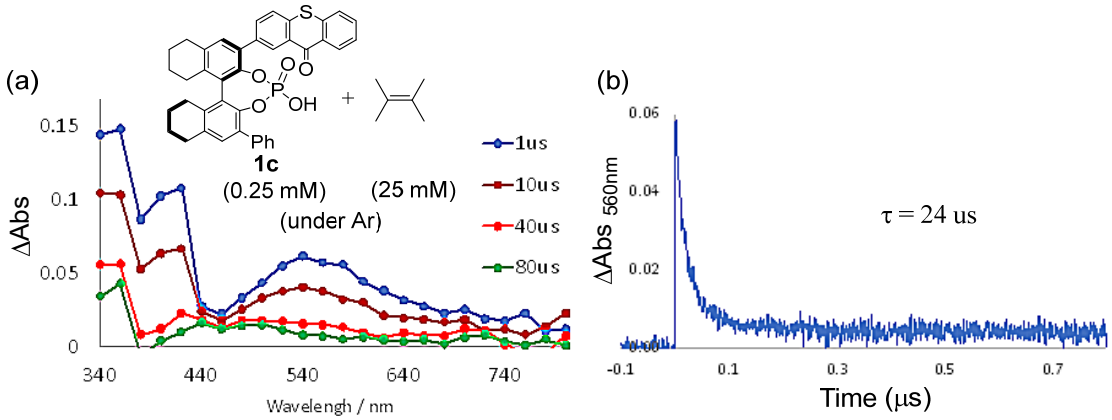


Fig. S16 (a) Transient absorption spectra of a mixture of phosphoric acid **1c** (0.25 mM) and 2,3-dimethyl 2-butene (25 mM) in Ar saturated CH_2Cl_2 at –78 °C, and (b) the decay cube at 560 nm under Ar.

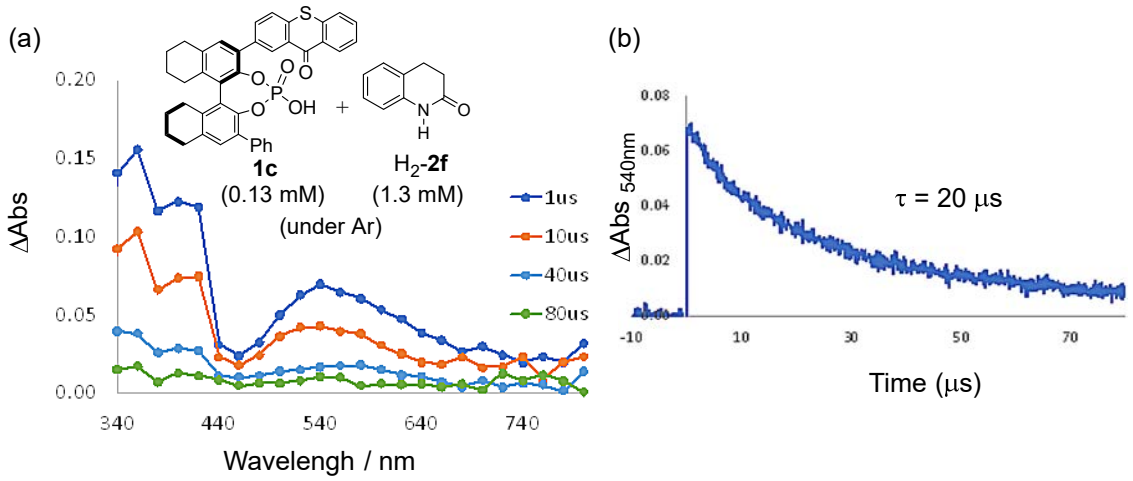


Fig. S17 (a) Transient absorption spectra of a mixture of phosphoric acid **1c** (0.13 mM) and hydroquinolone H_2-**2f** (1.3 mM) in Ar saturated CH_2Cl_2 at –78 °C, and (b) the decay cube at 540 nm under Ar.

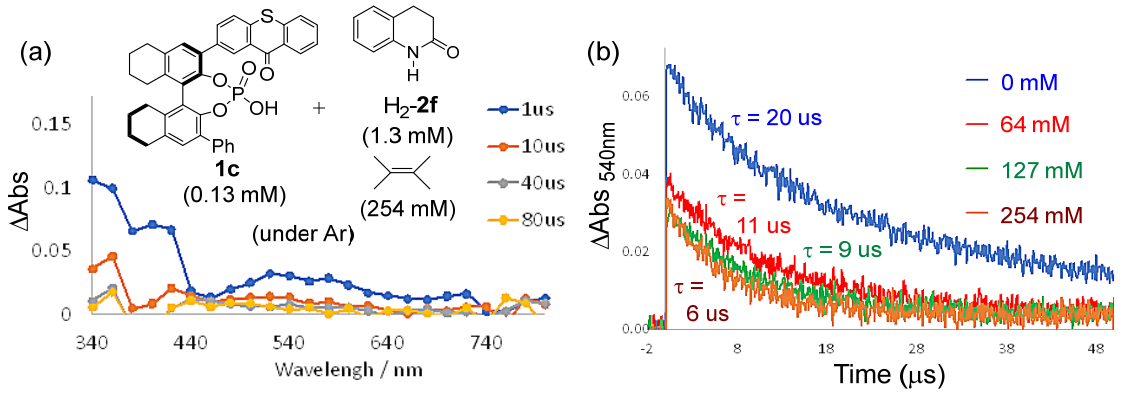


Fig. S18 (a) Transient absorption spectra of a mixture of phosphoric acid **1c** (0.13 mM), H_2-**2f** (1.3 mM) and 2,3-dimethyl 2-butene (254 mM) in Ar saturated CH_2Cl_2 at –78 °C, and (b) the decay cube at 540 nm under Ar in the presence of varying concentration of 2,3-dimethyl 2-butene.

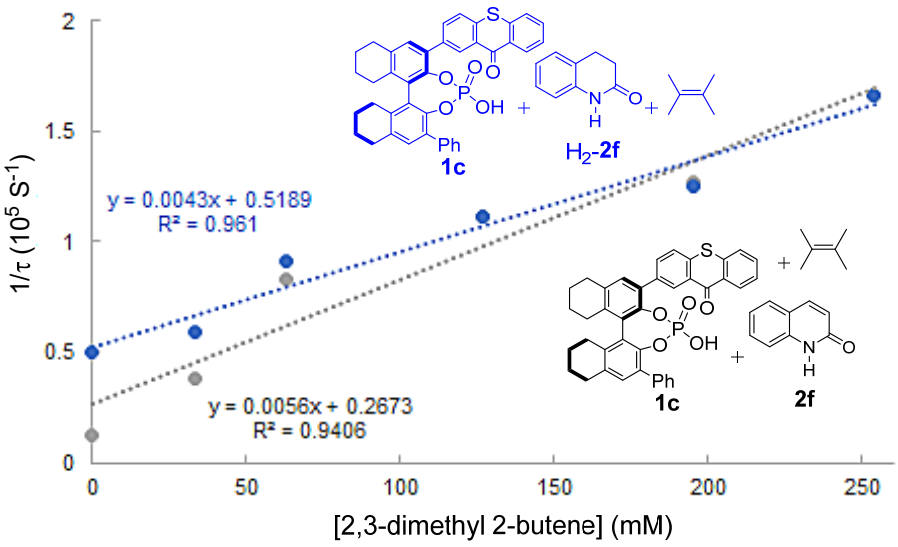


Fig. S19 The Stern–Volmer plot $k_{obs} = k_d + k_q$[2,3-dimethyl 2-butene] for the quenching reaction of the 1:1 complex of phosphoric acid **1c** and (a) quinolone **2f** (black) and (b) hydroquinolone H_2-**2f** (blue) in Ar saturated CH_2Cl_2 at –78 °C. In the study for the 1:1 complex of **1c** and **2f**, the concentration of 2,3-dimethyl 2-butene reacted with the triplet stat of **2f** was not considered.

7. DFT calculations on the intramolecular [2+2] photocycloaddition

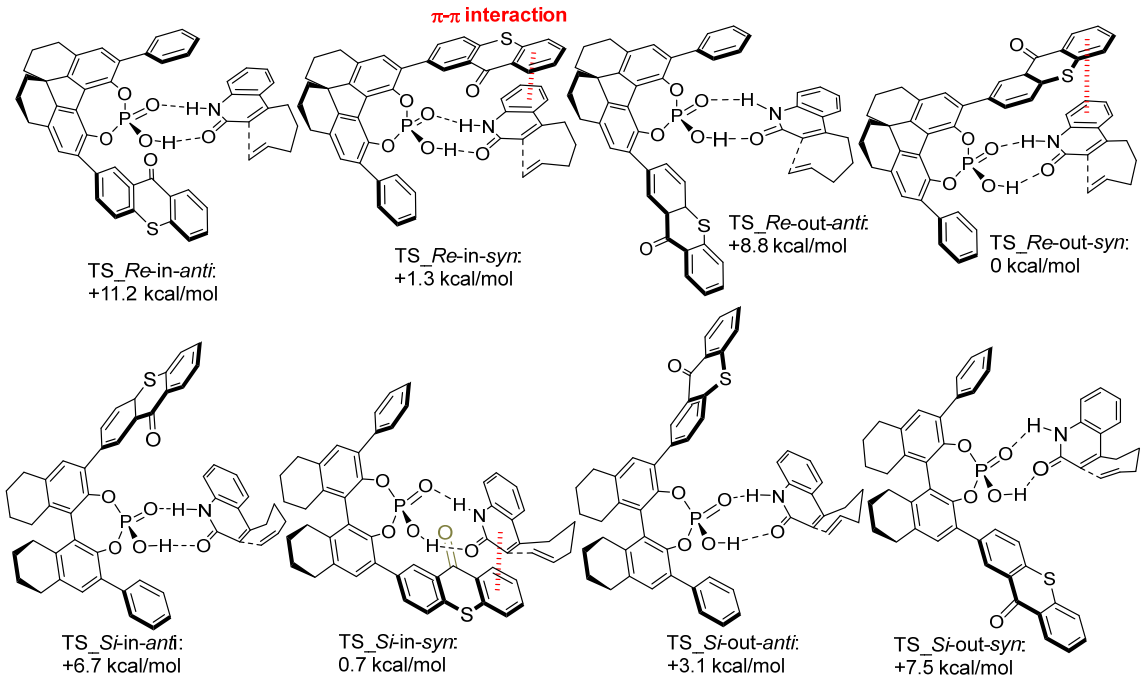


Fig. S20 Schematic structures and relative Gibbs energies at 195.15 K of possible transition states on the intermolecular [2+2] photocycloaddition of quinolone **2a** catalyzed by phosphoric acid **1c** at M06-2X-D3/6-311+(d,p)/SMD(CH_2Cl_2)//M06-2X/6-31G(d,p) level of theory.

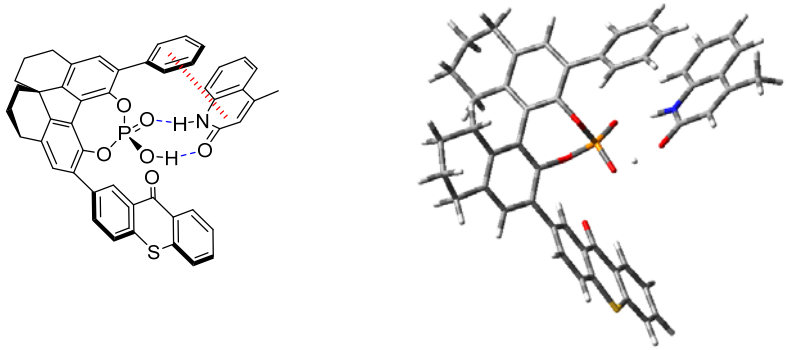
8. Computational details

All the computational studies were carried out by means of the Gaussian 16 package.[9] The 1 : 1 complexes of 4-methyl quinolinone and phosphoric acids **1c** were optimized by M06-2X/6-31G(d,p) level of theory.[10] To get more accurate energies, free energies at 195.15 K were estimated in conjunction with the single-point energies of the optimized structures with 6-311+(d,p) and the frequencies computed with 6-31G(d,p). Truhlar's quasiharmonic approximation was used to correct for errors in the estimation of vibrational entropies by setting all positive frequencies below 100 cm^{-1} to 100 cm^{-1}.[11] Solvent corrections in CH_2Cl_2, which was used experimentally, were evaluated with SMD solvent model,[12] by the single-point energy calculation of the above optimized structures at the same level of theory.

NMR chemical shift calculations were performed at M06-2X/6-31G(d,p) level of theory, using the GIAO method.[13] Analysis of non-covalent interaction (NCI) were conducted by using IGMPlot package[14] and the NCI surfaces were visualized with the VMD program.[15]

Computational data: Cartesian coordinates, energies of the 1:1 complex of 4-methyl quinolinone and phosphoric acid 1c (Figs. S6 and S7)

Re*-in-*anti



RM06-2X/6-31G(d,p) (a.u.)
Imaginary Freq = 0
Electronic Energy (EE) = -3136.192032
Zero-point Energy Correction = 0.786279
Thermal Correction to Energy = 0.833205

Thermal Correction to Enthalpy = 0.834149
Thermal Correction to Free Energy = 0.70299
EE + Zero-point Energy = -3135.405753
EE + Thermal Energy Correction = -3135.358827
EE + Thermal Enthalpy Correction = -3135.357883
EE + Thermal Free Energy Correction = -3135.489042
Truhlar's quasiharmonic corrected Gibbs energy (at 195.15 K) = -3135.439892

E_{sp} (RM06-2X/6-311+G(d,p)/SMD (CH_2Cl_2)) = -3136.883099

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-3.313030	1.382155	0.522335
2	1	0	-4.796358	2.012868	1.927806
3	6	0	-3.812006	2.222749	1.515203
4	6	0	-1.332061	2.829573	0.422925
5	6	0	-3.088906	3.307503	2.016125
6	6	0	-2.063509	1.721921	-0.000293
7	6	0	-1.823907	3.607096	1.489127
8	6	0	0.956393	2.125583	-0.277904
9	6	0	-0.033978	3.110510	-0.264345
10	6	0	2.404767	3.537005	-1.525110
11	6	0	0.179808	4.307052	-0.979186
12	6	0	2.194212	2.311513	-0.897498
13	6	0	1.423693	4.525614	-1.589234
14	1	0	3.369504	3.721611	-1.992687
15	8	0	-1.467495	0.890614	-0.941296
16	8	0	0.704665	0.907698	0.343020
17	15	0	-0.362196	-0.109452	-0.301421
18	8	0	-0.904743	-1.012154	0.742566
19	6	0	-4.054694	0.178141	0.069843
20	6	0	-5.534825	-2.058032	-0.755081
21	6	0	-4.722838	-0.622132	1.004079
22	6	0	-4.126649	-0.168770	-1.285668

23	6	0	-4.860732	-1.278355	-1.692109
24	6	0	-5.461170	-1.728398	0.595660
25	1	0	-4.640686	-0.384038	2.060639
26	1	0	-3.606326	0.433997	-2.021352
27	1	0	-5.956012	-2.351322	1.334713
28	6	0	3.235194	1.255903	-0.925157
29	6	0	5.270573	-0.682969	-1.021546
30	6	0	3.590957	0.540896	0.210960
31	6	0	3.915938	0.982460	-2.123101
32	6	0	4.915065	0.029754	-2.174721
33	6	0	4.606776	-0.424153	0.183911
34	1	0	3.096438	0.714411	1.160191
35	1	0	3.634822	1.513477	-3.027589
36	1	0	5.421821	-0.178314	-3.112216
37	6	0	1.748552	5.822540	-2.305869
38	6	0	-0.957433	5.291880	-1.190378
39	1	0	-1.603595	5.344092	-0.312419
40	6	0	-3.715593	4.152225	3.109889
41	1	0	-4.288778	3.505511	3.782202
42	6	0	-0.955037	4.675353	2.127620
43	1	0	-0.333527	5.173815	1.380396
44	1	0	2.395035	5.608953	-3.163311
45	1	0	-0.251695	4.164849	2.800341
46	1	0	-4.442707	4.832745	2.645850
47	1	0	2.338410	6.453529	-1.626999
48	1	0	-1.589778	4.889782	-1.994724
49	6	0	-1.758442	5.695737	2.929569
50	1	0	-2.347400	6.323022	2.246579
51	1	0	-1.076934	6.360377	3.468738
52	6	0	-2.698222	4.977426	3.894192
53	1	0	-3.217161	5.689453	4.542873
54	1	0	-2.108732	4.318497	4.543786
55	6	0	-0.478500	6.686943	-1.584024
56	1	0	-1.338529	7.309460	-1.848231
57	1	0	0.013034	7.164380	-0.725552
58	6	0	0.507985	6.595683	-2.744599

59	1	0	0.026976	6.079366	-3.584752
60	1	0	0.794207	7.590588	-3.098503
61	1	0	-5.298123	-6.397873	-0.008198
62	6	0	-4.653842	-5.658952	0.457230
63	6	0	-2.998292	-3.758054	1.673030
64	6	0	-3.810413	-4.871325	-0.350854
65	6	0	-4.668912	-5.501299	1.828451
66	6	0	-3.832745	-4.547781	2.435433
67	6	0	-2.990915	-3.915885	0.277234
68	1	0	-5.322228	-6.115260	2.438575
69	1	0	-3.845484	-4.427959	3.513830
70	1	0	-2.358839	-2.999566	2.115243
71	6	0	-3.760362	-4.965402	-1.795738
72	6	0	-2.939622	-4.136857	-2.489179
73	1	0	-2.871821	-4.169534	-3.570587
74	6	0	-2.103618	-3.149954	-1.834560
75	7	0	-2.177809	-3.107480	-0.482057
76	8	0	-1.358269	-2.381746	-2.484741
77	6	0	-4.626532	-5.968187	-2.504359
78	1	0	-5.685269	-5.777405	-2.300535
79	1	0	-4.405872	-6.983926	-2.162327
80	1	0	-1.642316	-2.369547	0.011219
81	8	0	0.283425	-0.760268	-1.550291
82	1	0	-0.367428	-1.475039	-1.967056
83	1	0	-4.469811	-5.924510	-3.582718
84	6	0	4.919183	-1.108306	1.467901
85	8	0	4.331565	-0.799809	2.491200
86	16	0	6.554247	-1.863721	-1.217199
87	1	0	-6.101889	-2.928268	-1.072416
88	1	0	-4.903402	-1.534937	-2.746300
89	6	0	6.708991	-2.570049	0.382219
90	6	0	7.121291	-3.818462	2.850101
91	6	0	7.666568	-3.587593	0.509825
92	6	0	5.956495	-2.176260	1.494921
93	6	0	6.179070	-2.815653	2.724557
94	6	0	7.868487	-4.203771	1.731739

95	1	0	8.245970	-3.887664	-0.358221
96	1	0	5.579607	-2.486797	3.566347
97	1	0	8.611561	-4.990227	1.816234
98	1	0	7.280483	-4.303300	3.806963

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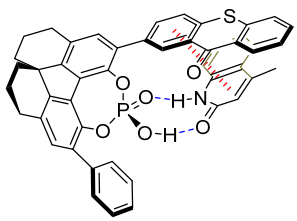
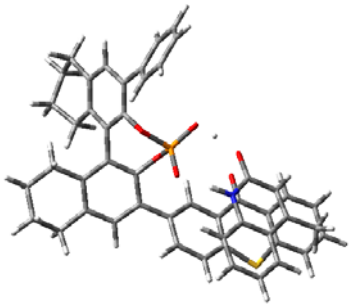




RM06-2X/6-31G(d,p) (a.u.)
Imaginary Freq = 0
Electronic Energy (EE) = -3136.198205
Zero-point Energy Correction = 0.786455
Thermal Correction to Energy = 0.833142
Thermal Correction to Enthalpy = 0.834086
Thermal Correction to Free Energy = 0.705358
EE + Zero-point Energy = -3135.411750
EE + Thermal Energy Correction = -3135.365063
EE + Thermal Enthalpy Correction = -3135.364119
EE + Thermal Free Energy Correction = -3135.492848
Truhlar's quasiharmonic corrected Gibbs energy (at 195.15 K) = -3135.445739

E_{sp} (RM06-2X/6-311+G(d,p)/SMD (CH_2Cl_2)) = -3136.888751

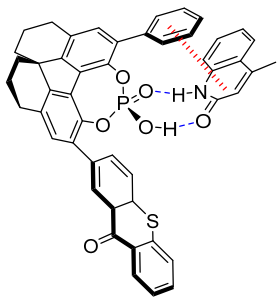
Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.510216	-2.190151	-0.387799

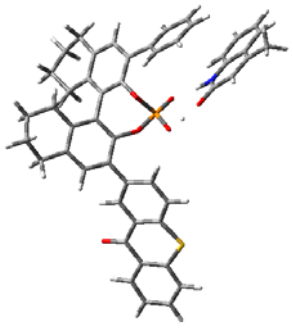
2	1	0	0.267763	-4.166291	-1.174183
3	6	0	0.984022	-3.390104	-0.913274
4	6	0	2.845113	-1.463932	-0.171578
5	6	0	2.342509	-3.627238	-1.134726
6	6	0	1.476645	-1.248513	-0.029674
7	6	0	3.288317	-2.651360	-0.786291
8	6	0	3.657409	0.898254	-0.202228
9	6	0	3.772337	-0.395023	0.313848
10	6	0	5.451570	1.647935	1.158487
11	6	0	4.697884	-0.640473	1.348899
12	6	0	4.491480	1.946827	0.194062
13	6	0	5.558897	0.390605	1.751213
14	1	0	6.134153	2.435894	1.468363
15	8	0	1.072998	0.001190	0.418282
16	8	0	2.676012	1.157416	-1.154850
17	15	0	1.121372	1.125253	-0.751126
18	8	0	0.299395	0.777575	-1.937327
19	6	0	-0.941479	-1.927343	-0.230398
20	6	0	-3.720375	-1.635880	0.126577
21	6	0	-1.847708	-2.360105	-1.213684
22	6	0	-1.455057	-1.297516	0.899326
23	6	0	-2.834053	-1.143967	1.093229
24	6	0	-3.213105	-2.219809	-1.042132
25	1	0	-1.467868	-2.800664	-2.130762
26	1	0	-0.802800	-0.915027	1.676122
27	1	0	-3.897660	-2.550525	-1.818363
28	6	0	4.364921	3.321980	-0.350287
29	6	0	4.213558	5.940012	-1.338907
30	6	0	4.204498	3.556194	-1.720900
31	6	0	4.443553	4.417522	0.515846
32	6	0	4.368355	5.717086	0.026010
33	6	0	4.131452	4.855691	-2.209104
34	1	0	4.141969	2.715055	-2.402421
35	1	0	4.540682	4.243678	1.583437
36	1	0	4.421451	6.555409	0.713213
37	1	0	4.010951	5.021719	-3.274835

38	1	0	4.151944	6.953267	-1.722684
39	6	0	6.627434	0.176584	2.806706
40	6	0	4.681689	-1.960395	2.101126
41	1	0	4.454207	-2.794061	1.434216
42	6	0	2.756629	-4.961921	-1.725766
43	1	0	2.008389	-5.280506	-2.458977
44	6	0	4.748486	-2.822714	-1.163143
45	1	0	5.400894	-2.360850	-0.418920
46	1	0	6.740894	1.092696	3.395277
47	1	0	4.914266	-2.255983	-2.090146
48	1	0	2.740213	-5.713762	-0.924852
49	1	0	7.588553	0.017318	2.298790
50	1	0	3.844663	-1.918804	2.812464
51	6	0	5.137740	-4.280416	-1.394641
52	1	0	5.133631	-4.821039	-0.438437
53	1	0	6.157290	-4.331860	-1.787973
54	6	0	4.148499	-4.938811	-2.352504
55	1	0	4.460555	-5.956979	-2.603429
56	1	0	4.123404	-4.368242	-3.289305
57	6	0	5.973812	-2.230489	2.867923
58	1	0	5.851215	-3.121328	3.491151
59	1	0	6.786454	-2.442123	2.159754
60	6	0	6.345543	-1.017001	3.714810
61	1	0	5.512937	-0.781404	4.389303
62	1	0	7.218828	-1.224897	4.340306
63	1	0	-6.676939	0.715241	-2.568470
64	6	0	-5.625629	0.597255	-2.809489
65	6	0	-2.918764	0.278684	-3.439569
66	6	0	-4.655129	1.050319	-1.894679
67	6	0	-5.255780	0.001921	-3.998413
68	6	0	-3.894159	-0.155097	-4.312269
69	6	0	-3.299401	0.880252	-2.227541
70	1	0	-6.014628	-0.342711	-4.692201
71	1	0	-3.606489	-0.621650	-5.248815
72	1	0	-1.859905	0.161747	-3.652446
73	6	0	-4.971401	1.655484	-0.614883

74	6	0	-3.961539	2.028405	0.212623
75	1	0	-4.151219	2.473196	1.183483
76	6	0	-2.565887	1.874755	-0.149844
77	7	0	-2.322626	1.299383	-1.354161
78	8	0	-1.640926	2.245793	0.606041
79	6	0	-6.405480	1.876349	-0.226177
80	1	0	-6.981363	0.950939	-0.318626
81	1	0	-6.867416	2.622889	-0.880932
82	1	0	-1.334721	1.136571	-1.622794
83	8	0	0.775041	2.429380	0.007939
84	1	0	-0.240363	2.417168	0.276725
85	1	0	-6.477684	2.220287	0.807386
86	6	0	-3.264742	-0.450806	2.339306
87	8	0	-2.440211	-0.045368	3.138828
88	16	0	-5.469014	-1.617069	0.282301
89	6	0	-5.739961	-0.751686	1.784242
90	6	0	-6.387958	0.671903	4.102801
91	6	0	-4.719476	-0.256862	2.604428
92	6	0	-7.082576	-0.549124	2.139960
93	6	0	-7.401164	0.156905	3.286694
94	6	0	-5.065290	0.456800	3.762227
95	1	0	-7.869322	-0.945030	1.503656
96	1	0	-8.443438	0.309858	3.547496
97	1	0	-4.250098	0.827362	4.374392
98	1	0	-6.638564	1.228273	4.999271

Re*-out-*anti





RM06-2X/6-31G(d,p) (a.u.)
Imaginary Freq = 0
Electronic Energy (EE) = -3136.195033
Zero-point Energy Correction = 0.786166
Thermal Correction to Energy = 0.832909
Thermal Correction to Enthalpy = 0.833853
Thermal Correction to Free Energy = 0.70399
EE + Zero-point Energy = -3135.408867
EE + Thermal Energy Correction = -3135.362124
EE + Thermal Enthalpy Correction = -3135.361180
EE + Thermal Free Energy Correction = -3135.491043
Truhlar's quasiharmonic corrected Gibbs energy (at 195.15 K) = -3135.443035

E_{sp} (RM06-2X/6-311+G(d,p)/SMD (CH_2Cl_2)) = -3136.882769

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-3.264561	1.957451	0.282277
2	1	0	-4.538263	3.075904	1.585481
3	6	0	-3.525568	2.968362	1.203351
4	6	0	-0.946539	2.765951	0.187692
5	6	0	-2.532135	3.829488	1.675667
6	6	0	-1.957504	1.895338	-0.205196
7	6	0	-1.220631	3.718499	1.191224
8	6	0	1.089833	1.412032	-0.373079
9	6	0	0.399055	2.625380	-0.451110
10	6	0	2.984630	2.387023	-1.432888
11	6	0	0.977906	3.699171	-1.162563
12	6	0	2.407078	1.274943	-0.825841
13	6	0	2.289420	3.577710	-1.639049
14	1	0	4.004833	2.301371	-1.799565
15	8	0	-1.598326	0.861200	-1.063678
16	8	0	0.499065	0.317406	0.250620

17	15	0	-0.860684	-0.351596	-0.287025
18	8	0	-1.641963	-0.905216	0.847432
19	6	0	-4.303716	0.977346	-0.121539
20	6	0	-6.320661	-0.830519	-0.851784
21	6	0	-5.187254	0.465820	0.836219
22	6	0	-4.437620	0.557622	-1.451742
23	6	0	-5.438053	-0.339323	-1.811113
24	6	0	-6.191541	-0.426648	0.474217
25	1	0	-5.065615	0.752762	1.876731
26	1	0	-3.755902	0.936683	-2.204550
27	1	0	-5.523798	-0.658944	-2.845227
28	6	0	3.205838	0.037114	-0.639071
29	6	0	4.806133	-2.253441	-0.312083
30	6	0	2.711203	-1.237117	-0.970402
31	6	0	4.501550	0.133378	-0.151514
32	6	0	5.317750	-0.994068	0.018799
33	6	0	3.499075	-2.360594	-0.809151
34	1	0	1.709532	-1.345112	-1.371155
35	1	0	4.922056	1.093360	0.130866
36	1	0	3.104754	-3.337192	-1.073701
37	6	0	2.996435	4.713177	-2.354837
38	6	0	0.155695	4.932073	-1.499068
39	1	0	-0.533182	5.181291	-0.690212
40	6	0	-2.919238	4.884585	2.695018
41	1	0	-3.676132	4.472994	3.370667
42	6	0	-0.099492	4.532458	1.812358
43	1	0	0.657851	4.789587	1.069206
44	1	0	3.631400	4.300525	-3.145380
45	1	0	0.410660	3.883177	2.537668
46	1	0	-3.402640	5.715936	2.163747
47	1	0	3.674375	5.200540	-1.640922
48	1	0	-0.481443	4.673964	-2.356909
49	6	0	-0.596183	5.785783	2.528379
50	1	0	-0.957903	6.514540	1.790151
51	1	0	0.233589	6.256550	3.063784
52	6	0	-1.730744	5.427652	3.483993

53	1	0	-2.040059	6.296531	4.072550
54	1	0	-1.376820	4.667274	4.191273
55	6	0	1.011330	6.142830	-1.862257
56	1	0	0.367904	6.954071	-2.215777
57	1	0	1.530412	6.510572	-0.966584
58	6	0	2.039991	5.758840	-2.921428
59	1	0	1.518413	5.349707	-3.795728
60	1	0	2.602453	6.633361	-3.261624
61	1	0	-7.346682	-4.929795	0.759093
62	6	0	-6.520461	-4.329432	1.125888
63	6	0	-4.395780	-2.781974	2.088272
64	6	0	-5.513883	-3.918784	0.229473
65	6	0	-6.466379	-3.977482	2.459342
66	6	0	-5.395255	-3.203145	2.939558
67	6	0	-4.458315	-3.135364	0.730161
68	1	0	-7.247620	-4.300809	3.138345
69	1	0	-5.355147	-2.930439	3.989016
70	1	0	-3.568714	-2.165725	2.428996
71	6	0	-5.517412	-4.231116	-1.184871
72	6	0	-4.521098	-3.755513	-1.974229
73	1	0	-4.484252	-3.959695	-3.038119
74	6	0	-3.444325	-2.941861	-1.450110
75	7	0	-3.476155	-2.686075	-0.121910
76	8	0	-2.533106	-2.500222	-2.192454
77	6	0	-6.630276	-5.061374	-1.759097
78	1	0	-7.596651	-4.569104	-1.608672
79	1	0	-6.681037	-6.037839	-1.267938
80	1	0	-2.750612	-2.058026	0.274531
81	8	0	-0.503850	-1.331465	-1.433692
82	1	0	-1.370445	-1.866567	-1.770876
83	1	0	-6.486368	-5.218951	-2.828531
84	6	0	6.686120	-0.762482	0.549944
85	16	0	5.694484	-3.758307	-0.154787
86	8	0	7.066887	0.368934	0.806410
87	6	0	7.245817	-3.251999	0.490565
88	6	0	9.779309	-2.659343	1.517218

89	6	0	7.591395	-1.923586	0.767308
90	6	0	8.171927	-4.279069	0.729096
91	6	0	9.424064	-3.983499	1.236844
92	6	0	8.868109	-1.647916	1.282182
93	1	0	7.896751	-5.306946	0.512260
94	1	0	10.130068	-4.787830	1.416845
95	1	0	9.103650	-0.609027	1.485446
96	1	0	10.761482	-2.429995	1.915657
97	1	0	-7.096026	-1.537489	-1.132501
98	1	0	-6.853134	-0.833206	1.233766

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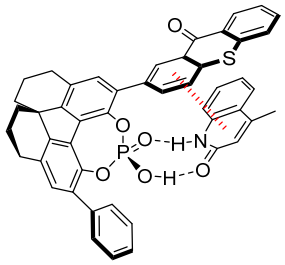
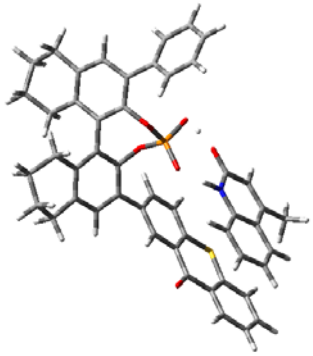




RM06-2X/6-31G(d,p) (a.u.)
Electronic Energy (EE) = -3136.202365
Zero-point Energy Correction = 0.786642
Thermal Correction to Energy = 0.833168
Thermal Correction to Enthalpy = 0.834112
Thermal Correction to Free Energy = 0.706862
EE + Zero-point Energy = -3135.415723
EE + Thermal Energy Correction = -3135.369197
EE + Thermal Enthalpy Correction = -3135.368253
EE + Thermal Free Energy Correction = -3135.495503
Truhlar's quasiharmonic corrected Gibbs energy (at 195.15 K) = -3135.449763

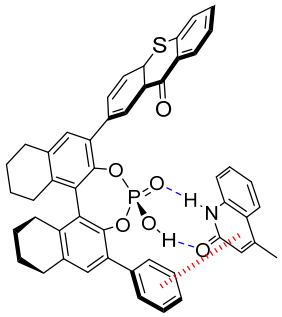
E_{sp} (RM06-2X/6-311+G(d,p)/SMD (CH_2Cl_2)) = -3136.891426

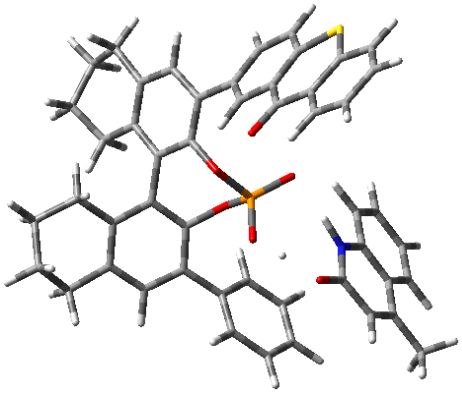
Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.522553	-2.052624	0.289943
2	1	0	-0.074891	-4.002630	-0.356639
3	6	0	0.752496	-3.300251	-0.284353
4	6	0	2.898252	-1.544843	-0.058474
5	6	0	1.998400	-3.668136	-0.797132
6	6	0	1.625259	-1.203740	0.390712
7	6	0	3.080545	-2.778601	-0.713756
8	6	0	3.859207	0.736122	-0.386964
9	6	0	3.996659	-0.549958	0.142981
10	6	0	5.987891	1.358047	0.459852
11	6	0	5.127017	-0.850326	0.930259
12	6	0	4.844813	1.717517	-0.251548
13	6	0	6.140089	0.110157	1.062315
14	1	0	6.786224	2.090161	0.557225
15	8	0	1.443660	0.085873	0.875104
16	8	0	2.698600	1.056397	-1.085352
17	15	0	1.289904	1.173981	-0.320680
18	8	0	0.176006	0.873640	-1.252474
19	6	0	-0.828647	-1.627770	0.729677
20	6	0	-3.418966	-0.927283	1.582647
21	6	0	-1.942220	-1.931962	-0.041701
22	6	0	-1.027507	-0.926793	1.934225
23	6	0	-2.298921	-0.583841	2.353644
24	6	0	-3.240964	-1.596580	0.365700
25	1	0	-1.837252	-2.432697	-0.998985
26	1	0	-0.174101	-0.650372	2.542635
27	1	0	-2.433000	-0.042261	3.285622
28	6	0	4.696392	3.087453	-0.803861
29	6	0	4.513717	5.690430	-1.827235
30	6	0	4.213993	3.310026	-2.098888
31	6	0	5.080503	4.187646	-0.029917

32	6	0	4.990201	5.479561	-0.536815
33	6	0	4.125954	4.601912	-2.604709
34	1	0	3.912622	2.465778	-2.708936
35	1	0	5.430558	4.025672	0.985302
36	1	0	5.284180	6.322180	0.080805
37	1	0	3.753558	4.758452	-3.612008
38	1	0	4.439932	6.697939	-2.223763
39	6	0	7.418985	-0.173842	1.827301
40	6	0	5.193917	-2.145420	1.721829
41	1	0	4.736899	-2.970148	1.171971
42	6	0	2.145207	-5.044647	-1.418304
43	1	0	1.220459	-5.303867	-1.943791
44	6	0	4.389147	-3.089670	-1.417190
45	1	0	5.237504	-2.676929	-0.866947
46	1	0	7.749333	0.740959	2.329935
47	1	0	4.376131	-2.556614	-2.378269
48	1	0	2.253407	-5.778474	-0.607853
49	1	0	8.205555	-0.426793	1.103191
50	1	0	4.571309	-2.011395	2.617900
51	6	0	4.586760	-4.580629	-1.678215
52	1	0	4.762450	-5.102691	-0.727808
53	1	0	5.476435	-4.731753	-2.296705
54	6	0	3.346750	-5.160919	-2.352855
55	1	0	3.502227	-6.207688	-2.630422
56	1	0	3.150375	-4.606715	-3.279109
57	6	0	6.611681	-2.512888	2.152355
58	1	0	6.579595	-3.375861	2.824173
59	1	0	7.198949	-2.810815	1.273189
60	6	0	7.281716	-1.319238	2.826494
61	1	0	6.668844	-0.997239	3.677714
62	1	0	8.265427	-1.590115	3.221450
63	1	0	-6.741605	2.145736	-0.619170
64	6	0	-5.802207	1.793478	-1.032813
65	6	0	-3.393722	0.835766	-2.090492
66	6	0	-4.608028	2.000329	-0.313248
67	6	0	-5.790453	1.134212	-2.244863

68	6	0	-4.581333	0.641823	-2.765541
69	6	0	-3.402886	1.530139	-0.869038
70	1	0	-6.718006	0.972509	-2.782739
71	1	0	-4.578048	0.094247	-3.702056
72	1	0	-2.449151	0.459448	-2.472884
73	6	0	-4.548472	2.664516	0.972808
74	6	0	-3.346202	2.846907	1.575791
75	1	0	-3.256067	3.340873	2.536431
76	6	0	-2.105347	2.407273	0.972586
77	7	0	-2.214349	1.748252	-0.207925
78	8	0	-0.995814	2.612974	1.517823
79	6	0	-5.822038	3.120572	1.623308
80	1	0	-6.505461	2.272747	1.743077
81	1	0	-6.330094	3.868520	1.006573
82	1	0	-1.341149	1.398256	-0.642556
83	8	0	1.250827	2.523320	0.439432
84	1	0	0.314168	2.629028	0.898628
85	1	0	-5.626408	3.553018	2.605169
86	6	0	-4.350321	-1.955778	-0.555921
87	8	0	-4.124069	-2.555675	-1.594844
88	16	0	-4.980361	-0.496914	2.257757
89	6	0	-6.100345	-0.895933	0.969662
90	6	0	-8.047674	-1.445120	-0.962423
91	6	0	-5.740238	-1.549374	-0.214494
92	6	0	-7.436360	-0.519747	1.181853
93	6	0	-8.397292	-0.788887	0.222761
94	6	0	-6.732921	-1.818514	-1.168768
95	1	0	-7.710308	-0.020479	2.107371
96	1	0	-9.425819	-0.490426	0.398987
97	1	0	-6.418749	-2.323179	-2.076263
98	1	0	-8.802324	-1.658932	-1.711501

Si*-in-*anti





RM06-2X/6-31G(d,p) (a.u.)
Imaginary Freq = 0
Electronic Energy (EE) = -3136.189627
Zero-point Energy Correction = 0.786019
Thermal Correction to Energy = 0.833069
Thermal Correction to Enthalpy = 0.834013
Thermal Correction to Free Energy = 0.701393
EE + Zero-point Energy = -3135.403608
EE + Thermal Energy Correction = -3135.356558
EE + Thermal Enthalpy Correction = -3135.355614
EE + Thermal Free Energy Correction = -3135.488234
Truhlar's quasiharmonic corrected Gibbs energy (at 195.15 K) = -3135.437634

E_{sp} (RM06-2X/6-311+G(d,p)/SMD (CH_2Cl_2)) = -3136.882110

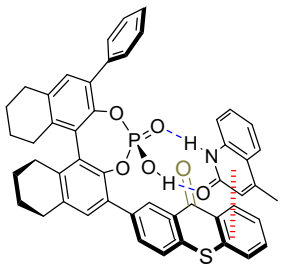
Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.780499	2.246328	1.236780
2	1	0	-2.657185	3.509317	2.722266
3	6	0	-1.777250	3.334511	2.106944
4	6	0	0.437866	2.954515	0.476678
5	6	0	-0.688317	4.196740	2.227729
6	6	0	-0.647923	2.076244	0.436053
7	6	0	0.445381	3.995383	1.427088

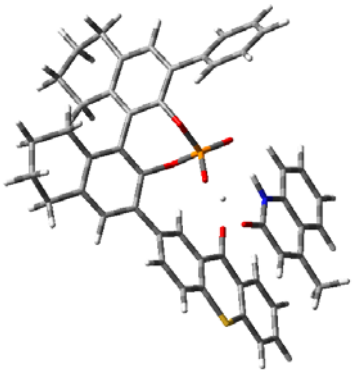
8	6	0	2.237715	1.474162	-0.346316
9	6	0	1.598796	2.707946	-0.431068
10	6	0	3.807679	2.102095	-2.006398
11	6	0	2.035641	3.638012	-1.395157
12	6	0	3.348729	1.133609	-1.118526
13	6	0	3.166582	3.333091	-2.167122
14	1	0	4.684056	1.880207	-2.611603
15	8	0	-0.602281	0.995283	-0.433939
16	8	0	1.686997	0.515290	0.494071
17	15	0	0.384090	-0.241268	-0.107834
18	8	0	-0.075949	-1.234408	0.892616
19	6	0	-2.930184	1.310539	1.197978
20	6	0	-5.159431	-0.405294	1.184169
21	6	0	-3.516642	0.878161	2.399030
22	6	0	-3.479727	0.867184	0.001917
23	6	0	-4.593598	0.017345	-0.024884
24	6	0	-4.610451	0.034252	2.396360
25	1	0	-3.087545	1.195102	3.344844
26	1	0	-3.065709	1.172999	-0.952369
27	1	0	-5.042674	-0.300868	3.334390
28	6	0	3.967834	-0.211886	-1.023446
29	6	0	5.174818	-2.734730	-0.872580
30	6	0	4.274329	-0.781505	0.218702
31	6	0	4.258409	-0.931174	-2.186985
32	6	0	4.857580	-2.184765	-2.112184
33	6	0	4.878858	-2.031968	0.293632
34	1	0	4.037542	-0.236418	1.126578
35	1	0	3.986801	-0.510708	-3.150607
36	1	0	5.067072	-2.736671	-3.023040
37	1	0	5.111548	-2.462466	1.263762
38	1	0	5.641902	-3.713511	-0.813621
39	6	0	3.734522	4.318497	-3.171483
40	6	0	1.225640	4.890864	-1.676765
41	1	0	0.782221	5.286482	-0.760342
42	6	0	-0.779856	5.347261	3.212366
43	1	0	-1.344440	5.024869	4.093353

44	6	0	1.704290	4.811278	1.665747
45	1	0	2.248959	4.978585	0.734807
46	1	0	4.124568	3.769389	-4.034666
47	1	0	2.373041	4.201290	2.289665
48	1	0	-1.367649	6.151662	2.749383
49	1	0	4.597291	4.820648	-2.712471
50	1	0	0.376494	4.594387	-2.308358
51	6	0	1.434930	6.136398	2.374097
52	1	0	0.906740	6.818225	1.693945
53	1	0	2.384376	6.614154	2.633572
54	6	0	0.582478	5.902920	3.618045
55	1	0	0.453491	6.828282	4.187373
56	1	0	1.094149	5.187992	4.274581
57	6	0	2.028165	5.971043	-2.397160
58	1	0	1.364687	6.791052	-2.687569
59	1	0	2.780043	6.390802	-1.715040
60	6	0	2.727212	5.375827	-3.616315
61	1	0	1.975899	4.918631	-4.272093
62	1	0	3.233995	6.151596	-4.198110
63	1	0	4.703273	-6.351815	2.055307
64	6	0	4.038277	-5.511648	2.226861
65	6	0	2.326790	-3.345945	2.686681
66	6	0	3.281111	-5.001361	1.154971
67	6	0	3.947192	-4.954601	3.487144
68	6	0	3.084551	-3.869333	3.714499
69	6	0	2.430048	-3.908176	1.404542
70	1	0	4.539763	-5.355270	4.302081
71	1	0	3.014648	-3.434220	4.705930
72	1	0	1.660816	-2.500438	2.834205
73	6	0	3.340137	-5.528191	-0.194558
74	6	0	2.633567	-4.917923	-1.177382
75	1	0	2.670605	-5.254333	-2.207131
76	6	0	1.810627	-3.752011	-0.925326
77	7	0	1.701675	-3.363175	0.371291
78	8	0	1.215526	-3.144465	-1.841511
79	6	0	4.211187	-6.716127	-0.489954

80	1	0	5.260078	-6.491711	-0.268771
81	1	0	4.134455	-7.002609	-1.539406
82	1	0	1.024314	-2.617331	0.599885
83	8	0	0.720479	-0.750303	-1.527641
84	1	0	0.885326	-1.788234	-1.650890
85	1	0	3.923982	-7.573336	0.126444
86	6	0	-5.110652	-0.372059	-1.364974
87	16	0	-6.545474	-1.473690	1.314707
88	6	0	-6.936086	-1.844824	-0.356127
89	6	0	-7.727242	-2.556377	-2.941814
90	6	0	-8.009249	-2.727387	-0.550433
91	6	0	-6.258215	-1.316155	-1.460799
92	6	0	-6.671158	-1.686189	-2.750285
93	6	0	-8.398631	-3.077973	-1.830744
94	1	0	-8.529635	-3.133725	0.311744
95	1	0	-6.124676	-1.259364	-3.584107
96	1	0	-9.229371	-3.762895	-1.966931
97	1	0	-8.033024	-2.833596	-3.944638
98	8	0	-4.599857	0.075416	-2.377915

Si*-in-*syn





RM06-2X/6-31G(d,p) (a.u.)
Imaginary Freq = 0
Electronic Energy (EE) = -3136.202085

Zero-point Energy Correction = 0.787068
Thermal Correction to Energy = 0.833393
Thermal Correction to Enthalpy = 0.834337
Thermal Correction to Free Energy = 0.70807
EE + Zero-point Energy = -3135.415017
EE + Thermal Energy Correction = -3135.368692
EE + Thermal Enthalpy Correction = -3135.367748
EE + Thermal Free Energy Correction = -3135.494016
Truhlar's quasiharmonic corrected Gibbs energy (at 195.15 K) = -3135.449065

E_{sp} (RM06-2X/6-311+G(d,p)/SMD (CH_2Cl_2)) = -3136.891817

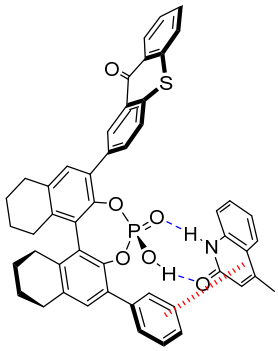
Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	4.236572	2.074396	-0.101021
2	1	0	5.682758	2.976359	1.187107
3	6	0	5.113160	2.072695	0.982652
4	6	0	3.738652	-0.269683	0.418336
5	6	0	5.274165	0.970525	1.821469
6	6	0	3.554889	0.880635	-0.352522
7	6	0	4.563624	-0.209459	1.559032
8	6	0	1.604851	-1.443321	-0.027318
9	6	0	2.995343	-1.510486	0.042938
10	6	0	1.474921	-3.738196	-0.609213
11	6	0	3.644536	-2.712236	-0.300603
12	6	0	0.807212	-2.538469	-0.367840
13	6	0	2.865992	-3.841786	-0.593626
14	1	0	0.889030	-4.626454	-0.834542
15	8	0	2.645348	0.831383	-1.405260
16	8	0	1.008625	-0.213712	0.201859
17	15	0	1.075489	0.838203	-1.034588
18	8	0	0.496067	2.122985	-0.576257
19	6	0	4.038137	3.299398	-0.915122
20	6	0	3.747019	5.651288	-2.411551

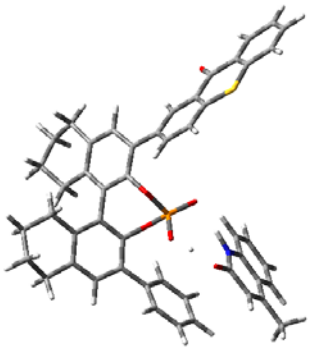
21	6	0	3.937687	4.541787	-0.280169
22	6	0	3.985216	3.250639	-2.313010
23	6	0	3.842368	4.418747	-3.053059
24	6	0	3.793470	5.709301	-1.021894
25	1	0	3.949820	4.585254	0.804888
26	1	0	4.060195	2.293398	-2.816974
27	1	0	3.806325	4.365483	-4.136422
28	1	0	3.708263	6.663926	-0.512572
29	1	0	3.631641	6.560897	-2.992157
30	6	0	-0.665968	-2.440348	-0.515907
31	6	0	-3.472953	-2.444362	-0.764291
32	6	0	-1.460076	-1.684731	0.340714
33	6	0	-1.305292	-3.160288	-1.540786
34	6	0	-2.681264	-3.168727	-1.663601
35	6	0	-2.857568	-1.673470	0.228592
36	1	0	-1.021797	-1.086740	1.131417
37	1	0	-0.705031	-3.714157	-2.255685
38	1	0	-3.153170	-3.740828	-2.456633
39	6	0	3.495202	-5.192515	-0.878948
40	6	0	5.153385	-2.757264	-0.462242
41	1	0	5.646213	-2.102823	0.259448
42	6	0	6.241988	1.079818	2.984727
43	1	0	6.202767	2.094977	3.392900
44	6	0	4.593065	-1.358819	2.551578
45	1	0	4.509723	-2.321687	2.043774
46	1	0	2.896839	-5.719433	-1.629384
47	1	0	3.689324	-1.276281	3.171803
48	1	0	7.261766	0.943916	2.599190
49	1	0	3.441583	-5.797996	0.036252
50	1	0	5.386798	-2.333053	-1.449055
51	6	0	5.821426	-1.335510	3.457498
52	1	0	6.717781	-1.580643	2.871651
53	1	0	5.723249	-2.103743	4.230354
54	6	0	5.987109	0.047851	4.080009
55	1	0	6.808961	0.059585	4.802186
56	1	0	5.071955	0.306466	4.627191

57	6	0	5.720769	-4.172161	-0.382568
58	1	0	6.785775	-4.156442	-0.632510
59	1	0	5.636932	-4.546915	0.646611
60	6	0	4.952823	-5.097485	-1.322379
61	1	0	5.004304	-4.695562	-2.341947
62	1	0	5.400647	-6.095472	-1.346133
63	1	0	-6.326555	2.887097	1.049900
64	6	0	-5.246832	2.995153	1.071102
65	6	0	-2.461146	3.267138	1.141659
66	6	0	-4.467924	2.307376	0.120335
67	6	0	-4.651214	3.792205	2.027071
68	6	0	-3.252678	3.927582	2.057175
69	6	0	-3.069602	2.451103	0.175614
70	1	0	-5.261041	4.315328	2.755508
71	1	0	-2.788068	4.553911	2.811480
72	1	0	-1.378118	3.345694	1.153368
73	6	0	-5.025115	1.446820	-0.902397
74	6	0	-4.189315	0.785968	-1.744786
75	1	0	-4.560553	0.120244	-2.515580
76	6	0	-2.750541	0.917478	-1.665144
77	7	0	-2.276794	1.770256	-0.723669
78	8	0	-1.991472	0.274630	-2.427948
79	6	0	-6.513825	1.291689	-1.013288
80	1	0	-6.939051	0.966361	-0.058675
81	1	0	-6.769718	0.553030	-1.775088
82	1	0	-1.257118	1.930379	-0.670206
83	8	0	0.458658	0.163933	-2.280750
84	1	0	-0.601475	0.243027	-2.350936
85	1	0	-6.979721	2.246607	-1.277864
86	6	0	-3.605847	-0.811787	1.182098
87	8	0	-3.013268	-0.033871	1.911952
88	16	0	-5.211473	-2.570932	-0.987132
89	6	0	-5.862485	-1.705203	0.393254
90	6	0	-7.101074	-0.281773	2.457684
91	6	0	-7.252669	-1.781225	0.570208
92	6	0	-5.089233	-0.928394	1.264432

93	6	0	-5.729474	-0.212716	2.287907
94	6	0	-7.862715	-1.080704	1.596601
95	1	0	-7.844301	-2.394120	-0.103353
96	1	0	-5.102958	0.396410	2.931268
97	1	0	-8.937855	-1.152023	1.726248
98	1	0	-7.581621	0.272468	3.256634

Si*-out-*anti





RM06-2X/6-31G(d,p) (a.u.)
Imaginary Freq = 0
Electronic Energy (EE) = -3136.191573
Zero-point Energy Correction = 0.786232
Thermal Correction to Energy = 0.833227
Thermal Correction to Enthalpy = 0.834171
Thermal Correction to Free Energy = 0.701868
EE + Zero-point Energy = -3135.405341
EE + Thermal Energy Correction = -3135.358346
EE + Thermal Enthalpy Correction = -3135.357402
EE + Thermal Free Energy Correction = -3135.489706
Truhlar's quasiharmonic corrected Gibbs energy (at 195.15 K) = -3135.439396

E_{sp} (RM06-2X/6-311+G(d,p)/SMD (CH_2Cl_2)) = -3136.882829

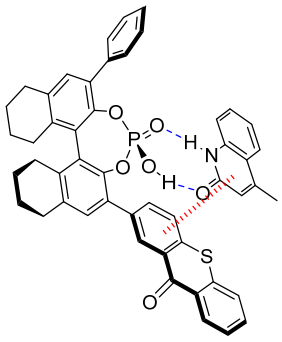
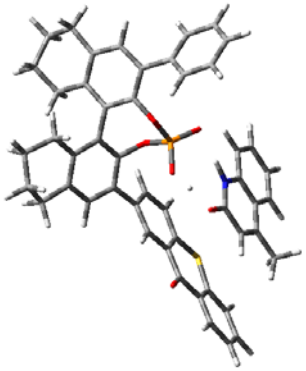
Center	Atomic	Atomic	Coordinates (Angstroms)		

Number	Number	Type	X	Y	Z
1	6	0	1.654605	-2.374190	0.047283
2	1	0	2.952206	-3.607856	1.214840
3	6	0	1.916466	-3.388106	0.966880
4	6	0	-0.729065	-2.896568	0.280811
5	6	0	0.905048	-4.113756	1.593991
6	6	0	0.313069	-2.149722	-0.274761
7	6	0	-0.435397	-3.851438	1.275281
8	6	0	-2.596609	-1.292876	0.053186
9	6	0	-2.134356	-2.593427	-0.127907
10	6	0	-4.742433	-1.870789	-0.768368
11	6	0	-2.987833	-3.542370	-0.725474
12	6	0	-3.897048	-0.891703	-0.255158
13	6	0	-4.309198	-3.174856	-1.020855
14	1	0	-5.770483	-1.601784	-1.001286
15	8	0	0.004411	-1.146460	-1.186127
16	8	0	-1.688227	-0.335586	0.486948
17	15	0	-0.693156	0.215761	-0.667823
18	8	0	0.188946	1.247752	-0.072415
19	6	0	2.760200	-1.564248	-0.519847
20	6	0	4.914142	-0.077809	-1.556947
21	6	0	3.814592	-1.169897	0.291393
22	6	0	2.796771	-1.198860	-1.878446
23	6	0	3.853560	-0.470214	-2.386986
24	6	0	4.898982	-0.432245	-0.203781
25	1	0	3.824013	-1.406764	1.350343
26	1	0	1.986873	-1.494260	-2.535396
27	6	0	-4.326742	0.519193	-0.088310
28	6	0	-5.184569	3.168419	0.215659
29	6	0	-4.053827	1.225584	1.089971
30	6	0	-5.019332	1.164715	-1.117725
31	6	0	-5.445931	2.480482	-0.966748
32	6	0	-4.483769	2.539619	1.242706
33	1	0	-3.503934	0.737251	1.887670
34	1	0	-5.198820	0.634707	-2.048341

35	1	0	-5.973084	2.972077	-1.778323
36	1	0	-4.264542	3.076476	2.161502
37	1	0	-5.515917	4.196002	0.333566
38	6	0	-5.302529	-4.167508	-1.595444
39	6	0	-2.452120	-4.897765	-1.150982
40	1	0	-1.706116	-5.265120	-0.442904
41	6	0	1.296762	-5.186083	2.592928
42	1	0	2.183698	-4.858539	3.144618
43	6	0	-1.551493	-4.500418	2.075657
44	1	0	-2.432716	-4.676104	1.456116
45	1	0	-5.967064	-3.649544	-2.294652
46	1	0	-1.869719	-3.773419	2.836432
47	1	0	1.596651	-6.083695	2.034944
48	1	0	-5.940727	-4.529740	-0.777735
49	1	0	-1.911366	-4.752262	-2.096762
50	6	0	-1.119483	-5.789164	2.770567
51	1	0	-0.953528	-6.575187	2.021401
52	1	0	-1.920603	-6.137846	3.429121
53	6	0	0.169595	-5.556149	3.553236
54	1	0	0.447213	-6.443621	4.129674
55	1	0	0.011278	-4.741218	4.270598
56	6	0	-3.552092	-5.934763	-1.362390
57	1	0	-3.122669	-6.846003	-1.789258
58	1	0	-3.993183	-6.209073	-0.394472
59	6	0	-4.638557	-5.364930	-2.270334
60	1	0	-4.184307	-5.050745	-3.218324
61	1	0	-5.390828	-6.122758	-2.508795
62	1	0	-3.291730	7.012942	2.143496
63	6	0	-2.675098	6.120094	2.152249
64	6	0	-1.078845	3.821394	2.191908
65	6	0	-2.478185	5.405791	0.954673
66	6	0	-2.097096	5.696641	3.332519
67	6	0	-1.293802	4.544028	3.347672
68	6	0	-1.676990	4.249106	0.996066
69	1	0	-2.260482	6.254592	4.247810
70	1	0	-0.839349	4.215054	4.276265

71	1	0	-0.469341	2.922206	2.179580
72	6	0	-3.063043	5.787362	-0.315721
73	6	0	-2.877475	4.992383	-1.398252
74	1	0	-3.320825	5.218202	-2.361266
75	6	0	-2.105229	3.768565	-1.331964
76	7	0	-1.490021	3.509663	-0.150296
77	8	0	-1.990959	2.997942	-2.311076
78	6	0	-3.895099	7.035083	-0.405029
79	1	0	-4.765833	6.968048	0.255825
80	1	0	-4.248236	7.194428	-1.424449
81	1	0	-0.832394	2.713900	-0.106769
82	8	0	-1.533880	0.614950	-1.902147
83	1	0	-1.687097	1.649810	-2.080909
84	1	0	-3.317765	7.911670	-0.096025
85	16	0	6.190978	0.845662	-2.327561
86	6	0	7.308376	1.173171	-1.014530
87	6	0	9.216333	1.803722	0.930926
88	6	0	7.130618	0.733266	0.302804
89	6	0	8.442564	1.927314	-1.352517
90	6	0	9.384619	2.237917	-0.388641
91	6	0	8.100218	1.060831	1.263888
92	1	0	10.256620	2.822432	-0.663839
93	1	0	7.932333	0.704760	2.274383
94	1	0	9.955886	2.049018	1.685194
95	6	0	5.967313	-0.071774	0.764652
96	1	0	3.867183	-0.197641	-3.437936
97	1	0	8.573157	2.265568	-2.376133
98	8	0	5.893944	-0.432214	1.928796

Si*-out-*syn

RM06-2X/6-31G(d,p) (a.u.)
Imaginary Freq = 0
Electronic Energy (EE) = -3136.196368
Zero-point Energy Correction = 0.786515
Thermal Correction to Energy = 0.833107
Thermal Correction to Enthalpy = 0.834051
Thermal Correction to Free Energy = 0.705336
EE + Zero-point Energy = -3135.409853
EE + Thermal Energy Correction = -3135.363261
EE + Thermal Enthalpy Correction = -3135.362316
EE + Thermal Free Energy Correction = -3135.491031
Truhlar's quasiharmonic corrected Gibbs energy (at 195.15 K) = -3135.443794

E_{sp} (RM06-2X/6-311+G(d,p)/SMD (CH_2Cl_2)) = -3136.887849

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	4.684788	1.709519	-0.416377
2	1	0	6.526301	2.303807	0.487836
3	6	0	5.771065	1.522889	0.436385
4	6	0	3.902713	-0.518967	0.241772
5	6	0	5.920397	0.387634	1.231630
6	6	0	3.755576	0.666708	-0.484182
7	6	0	4.966976	-0.637676	1.158457
8	6	0	1.552699	-1.265898	0.375913

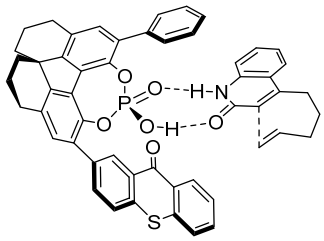
9	6	0	2.874398	-1.593722	0.095273
10	6	0	0.830814	-3.479896	-0.071602
11	6	0	3.167478	-2.895830	-0.358860
12	6	0	0.504206	-2.182738	0.307273
13	6	0	2.135297	-3.844378	-0.418375
14	1	0	0.040357	-4.225449	-0.123333
15	8	0	2.656604	0.810164	-1.321174
16	8	0	1.248535	0.065190	0.629389
17	15	0	1.166748	0.966588	-0.721713
18	8	0	0.712396	2.327025	-0.345843
19	6	0	4.536966	2.970346	-1.186331
20	6	0	4.359742	5.373430	-2.618829
21	6	0	4.812463	4.193803	-0.566216
22	6	0	4.166396	2.967991	-2.536271
23	6	0	4.080829	4.160964	-3.244760
24	6	0	4.724726	5.386614	-1.275982
25	1	0	5.076150	4.206969	0.487302
26	1	0	3.949861	2.026704	-3.028859
27	1	0	3.795588	4.142573	-4.291701
28	1	0	4.933823	6.327282	-0.776597
29	1	0	4.287855	6.303166	-3.173998
30	6	0	-0.887274	-1.759154	0.598605
31	6	0	-3.538097	-1.071563	1.235054
32	6	0	-1.186653	-1.048321	1.776132
33	6	0	-1.924858	-2.054976	-0.272868
34	6	0	-3.254553	-1.719022	0.026565
35	6	0	-2.488106	-0.712277	2.093618
36	1	0	-0.381305	-0.771865	2.448546
37	1	0	-1.733656	-2.540053	-1.224871
38	6	0	2.395238	-5.279901	-0.835342
39	6	0	4.549613	-3.227761	-0.891908
40	1	0	5.323635	-2.703526	-0.327095
41	6	0	7.134063	0.291127	2.136912
42	1	0	7.374657	1.286045	2.525477
43	6	0	5.017542	-1.799852	2.135683
44	1	0	4.649338	-2.719439	1.677175

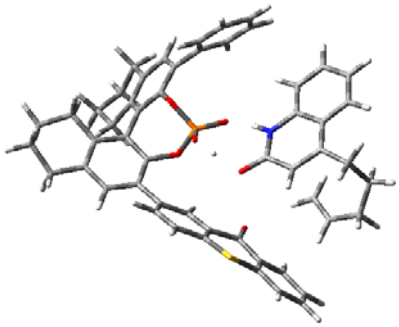
45	1	0	1.536976	-5.650406	-1.405141
46	1	0	4.310445	-1.574621	2.946847
47	1	0	7.995475	-0.016616	1.528424
48	1	0	2.451131	-5.897793	0.071441
49	1	0	4.609172	-2.825545	-1.912970
50	6	0	6.404829	-2.019993	2.733539
51	1	0	7.083049	-2.405704	1.960390
52	1	0	6.350119	-2.778799	3.519906
53	6	0	6.955908	-0.705736	3.278749
54	1	0	7.909830	-0.860339	3.791820
55	1	0	6.253010	-0.301245	4.017891
56	6	0	4.830324	-4.727607	-0.930748
57	1	0	5.781350	-4.911576	-1.439308
58	1	0	4.932859	-5.111672	0.093311
59	6	0	3.685782	-5.454088	-1.631924
60	1	0	3.558798	-5.035569	-2.638025
61	1	0	3.908565	-6.518565	-1.751308
62	1	0	-5.924360	3.367687	1.813219
63	6	0	-4.839930	3.365533	1.782019
64	6	0	-2.042695	3.374046	1.711421
65	6	0	-4.182655	2.678960	0.743296
66	6	0	-4.123119	4.031414	2.755867
67	6	0	-2.719006	4.034800	2.716425
68	6	0	-2.775771	2.693309	0.726190
69	1	0	-4.643579	4.554184	3.550675
70	1	0	-2.158465	4.561637	3.481551
71	1	0	-0.957794	3.364205	1.655832
72	6	0	-4.873853	1.963008	-0.312891
73	6	0	-4.149581	1.294377	-1.245671
74	1	0	-4.619625	0.733318	-2.046423
75	6	0	-2.701302	1.297346	-1.244726
76	7	0	-2.098260	2.032714	-0.276972
77	8	0	-2.039656	0.667760	-2.100664
78	6	0	-6.374013	1.984638	-0.370709
79	1	0	-6.806277	1.671240	0.583922
80	1	0	-6.743677	1.311773	-1.147278

81	1	0	-1.073403	2.156832	-0.313678
82	8	0	0.339517	0.198123	-1.774580
83	1	0	-0.688330	0.446932	-1.918007
84	1	0	-6.730653	2.998629	-0.580306
85	16	0	-5.153599	-0.693831	1.806940
86	6	0	-6.185689	-1.214679	0.489167
87	6	0	-7.995752	-1.868159	-1.540801
88	6	0	-5.715698	-1.753380	-0.714397
89	6	0	-7.564507	-1.032649	0.682115
90	6	0	-8.458011	-1.354214	-0.323749
91	6	0	-6.640363	-2.070970	-1.722074
92	1	0	-9.520638	-1.203750	-0.162826
93	1	0	-6.243344	-2.486197	-2.642111
94	1	0	-8.696514	-2.116126	-2.330362
95	1	0	-2.705628	-0.179290	3.014650
96	1	0	-7.922439	-0.628240	1.624970
97	6	0	-4.281504	-2.049441	-0.995724
98	8	0	-3.961333	-2.563361	-2.053877

Cartesian coordinates, energies of the transition state of the intramolecular [2+2] photocycloaddition of 2a catalyzed by phosphoric acid 1c (Fig. S20)

TS_*Re*-in-*anti*





UB3LYP-D3/6-31G(d,p) (a.u.)
Imaginary Freq = 1: -273.96 cm-1

Electronic Energy (EE) = -3293.281543
Zero-point Energy Correction = 0.867403
Thermal Correction to Energy = 0.918403
Thermal Correction to Enthalpy = 0.919347
Thermal Correction to Free Energy = 0.780368
EE + Zero-point Energy = -3292.414140
EE + Thermal Energy Correction = -3292.363140
EE + Thermal Enthalpy Correction = -3292.36296
EE + Thermal Free Energy Correction = -3292.501175
Truhlar's quasiharmonic corrected Gibbs energy (at 195.15 K) = -3292.450196

E_{sp} (UM06-2X-D3/6-311+G(2d,2p)/SMD (CH_2Cl_2)) = -3292.884732

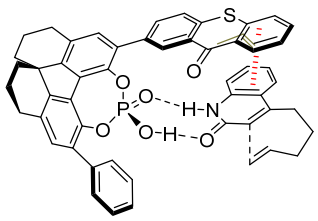
Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	3.720763	2.595779	0.148814
2	1	0	4.985995	3.829388	1.356298
3	6	0	4.750240	2.807300	1.071418
4	6	0	4.189634	0.183105	0.322109
5	6	0	5.456508	1.759238	1.667724
6	6	0	3.482789	1.265633	-0.220051
7	6	0	5.153189	0.427995	1.325136
8	6	0	2.489314	-1.601138	0.000141
9	6	0	3.824103	-1.195134	-0.133949
10	6	0	2.972837	-3.694281	-1.023407
11	6	0	4.740274	-2.050261	-0.785049
12	6	0	2.016676	-2.830767	-0.477809
13	6	0	4.312272	-3.331720	-1.182784
14	1	0	2.652050	-4.674962	-1.365672
15	8	0	2.433705	0.985222	-1.108440
16	8	0	1.586599	-0.702357	0.570855
17	15	0	1.055703	0.517100	-0.377173
18	8	0	0.380267	1.541094	0.462903
19	6	0	2.870721	3.714274	-0.332571

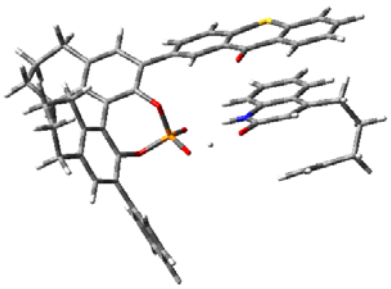
20	6	0	1.210399	5.825583	-1.175511
21	6	0	2.399093	4.667647	0.583551
22	6	0	2.497760	3.838755	-1.680656
23	6	0	1.674636	4.883433	-2.096035
24	6	0	1.578436	5.715070	0.166481
25	1	0	2.650717	4.563280	1.634368
26	1	0	2.847120	3.106588	-2.399367
27	1	0	1.214641	6.435547	0.893654
28	6	0	0.566686	-3.138475	-0.549135
29	6	0	-2.203202	-3.601355	-0.856544
30	6	0	-0.328813	-2.833804	0.474191
31	6	0	0.045355	-3.692493	-1.736518
32	6	0	-1.311019	-3.924449	-1.889713
33	6	0	-1.710410	-3.049801	0.339610
34	1	0	0.013412	-2.389774	1.399786
35	1	0	0.715401	-3.908746	-2.562287
36	1	0	-1.686465	-4.339057	-2.820649
37	6	0	5.276051	-4.341999	-1.783938
38	6	0	6.122354	-1.550944	-1.180329
39	1	0	6.525510	-0.863228	-0.435584
40	6	0	6.552337	2.093983	2.666841
41	1	0	6.276192	2.995556	3.225524
42	6	0	5.748840	-0.722691	2.123122
43	1	0	5.893502	-1.606593	1.499636
44	1	0	4.746680	-4.966511	-2.512746
45	1	0	4.997951	-1.017955	2.870826
46	1	0	7.462165	2.353769	2.105584
47	1	0	5.603647	-5.023094	-0.984561
48	1	0	5.996855	-0.946788	-2.091185
49	6	0	7.050607	-0.358247	2.843116
50	1	0	7.858356	-0.236393	2.107872
51	1	0	7.346519	-1.178338	3.506643
52	6	0	6.876969	0.945178	3.626837
53	1	0	7.778549	1.182568	4.202399
54	1	0	6.058759	0.824335	4.349194
55	6	0	7.122584	-2.675701	-1.463672

56	1	0	8.044657	-2.252466	-1.877188
57	1	0	7.395169	-3.173395	-0.522574
58	6	0	6.512956	-3.701875	-2.421947
59	1	0	6.229144	-3.198611	-3.355878
60	1	0	7.241134	-4.476960	-2.685464
61	8	0	0.259933	-0.085518	-1.578857
62	1	0	-0.757190	-0.200637	-1.365506
63	6	0	-2.578265	-2.642044	1.471073
64	8	0	-2.129341	-1.979396	2.406085
65	16	0	-3.915034	-3.867339	-1.191458
66	1	0	0.558973	6.631546	-1.500163
67	1	0	1.391776	4.960133	-3.141770
68	6	0	-4.675551	-3.621042	0.379142
69	6	0	-6.041645	-3.294433	2.806995
70	6	0	-6.031938	-3.981239	0.485723
71	6	0	-4.004524	-3.075119	1.489348
72	6	0	-4.711590	-2.921174	2.697139
73	6	0	-6.704680	-3.822802	1.689659
74	1	0	-6.546074	-4.399437	-0.374888
75	1	0	-4.171704	-2.492434	3.534118
76	1	0	-7.747815	-4.116282	1.761310
77	1	0	-6.567513	-3.173307	3.748530
78	6	0	-3.916499	5.765085	-0.365627
79	6	0	-2.548274	5.594341	-0.120900
80	6	0	-1.979260	4.312432	-0.188666
81	6	0	-2.767126	3.215049	-0.502062
82	6	0	-4.178303	3.351430	-0.768840
83	6	0	-4.714678	4.674763	-0.679236
84	7	0	-2.172499	1.948919	-0.548528
85	6	0	-2.822792	0.803436	-0.907583
86	6	0	-4.245361	0.889515	-1.068715
87	6	0	-4.939817	2.203902	-1.061523
88	8	0	-2.194185	-0.284147	-1.059043
89	6	0	-7.306840	0.684910	0.735347
90	6	0	-4.806399	0.442399	1.226214
91	6	0	-6.048068	-0.080238	1.028621

92	1	0	-4.360064	6.754757	-0.308095
93	1	0	-1.919728	6.444486	0.124176
94	1	0	-0.920372	4.167923	0.003062
95	1	0	-5.773501	4.825618	-0.857676
96	1	0	-1.202648	1.863403	-0.214985
97	1	0	-3.971565	-0.200895	1.482439
98	1	0	-4.654393	1.506688	1.370656
99	1	0	-7.917985	0.702677	1.652980
100	6	0	-6.436050	2.219325	-1.168340
101	1	0	-6.763962	3.137643	-1.667297
102	1	0	-4.722849	0.028848	-1.520956
103	1	0	-6.148859	-1.161911	1.034472
104	6	0	-7.172952	2.118302	0.200366
105	1	0	-8.185624	2.525074	0.088823
106	1	0	-6.661510	2.760872	0.926319
107	1	0	-7.900590	0.097845	0.019851
108	1	0	-6.769761	1.390701	-1.807081

TS_*Re*-in-*syn*





UB3LYP-D3/6-31G(d,p) (a.u.)
Imaginary Freq = 1: -114.48 cm-1
Electronic Energy (EE) = -3293.294322
Zero-point Energy Correction = 0.867098
Thermal Correction to Energy = 0.918301
Thermal Correction to Enthalpy = 0.919246
Thermal Correction to Free Energy = 0.778636
EE + Zero-point Energy = -3292.427224

EE + Thermal Energy Correction = -3292.376020
EE + Thermal Enthalpy Correction = -3292.375076
EE + Thermal Free Energy Correction = -3292.515685
Truhlar's quasiharmonic corrected Gibbs energy (at 195.15 K) = -3292.463277

E_{sp} (UM06-2X-D3/6-311+G(2d,2p)/SMD (CH_2Cl_2)) = -3292.900339

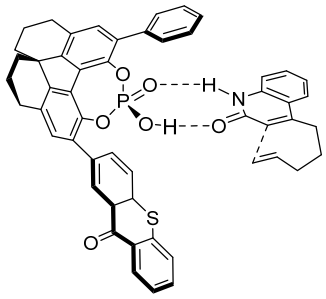
Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	1.571709	-2.604995	-0.305635
2	1	0	1.854415	-4.603153	-1.030823
3	6	0	2.344242	-3.659463	-0.805430
4	6	0	3.648112	-1.287594	-0.156522
5	6	0	3.714545	-3.542973	-1.052307
6	6	0	2.268000	-1.433465	0.024747
7	6	0	4.376244	-2.334812	-0.764103
8	6	0	3.816353	1.200473	-0.309931
9	6	0	4.282776	0.005118	0.253125
10	6	0	5.424763	2.458838	0.908546
11	6	0	5.288351	0.062165	1.246029
12	6	0	4.367861	2.452118	-0.006713
13	6	0	5.877403	1.302947	1.549420
14	1	0	5.897179	3.409007	1.143380
15	8	0	1.568052	-0.329905	0.512933
16	8	0	2.727705	1.145132	-1.191810
17	15	0	1.255962	0.846112	-0.581163
18	8	0	0.308681	0.442221	-1.656429
19	6	0	0.095039	-2.708557	-0.211725
20	6	0	-2.723751	-2.927628	-0.109335
21	6	0	-0.621750	-3.408078	-1.206371
22	6	0	-0.636239	-2.123027	0.820145
23	6	0	-2.037623	-2.207303	0.885505
24	6	0	-1.999443	-3.524738	-1.154814
25	1	0	-0.087664	-3.839258	-2.046928

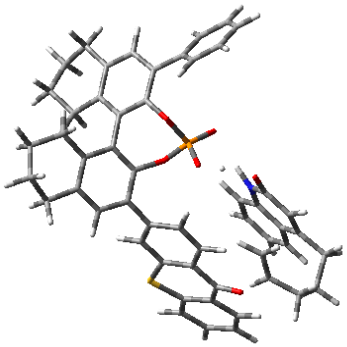
26	1	0	-0.144943	-1.564706	1.605354
27	1	0	-2.527214	-4.055018	-1.941797
28	6	0	3.848181	3.718169	-0.581332
29	6	0	2.915473	6.155644	-1.633649
30	6	0	3.546117	3.839981	-1.947355
31	6	0	3.669702	4.837399	0.246941
32	6	0	3.208394	6.045341	-0.273781
33	6	0	3.085483	5.047934	-2.466752
34	1	0	3.673672	2.983957	-2.599732
35	1	0	3.869769	4.747958	1.310357
36	1	0	3.068163	6.896993	0.385748
37	1	0	2.859631	5.123993	-3.526516
38	1	0	2.552545	7.095101	-2.040465
39	6	0	7.022012	1.423027	2.542725
40	6	0	5.634954	-1.170858	2.068661
41	1	0	5.594159	-2.078024	1.463756
42	6	0	4.459898	-4.746661	-1.606709
43	1	0	3.803399	-5.305316	-2.283759
44	6	0	5.814411	-2.121880	-1.212076
45	1	0	6.353545	-1.473851	-0.519155
46	1	0	6.944991	2.377471	3.075952
47	1	0	5.777449	-1.563147	-2.159062
48	1	0	4.682731	-5.427946	-0.772255
49	1	0	7.965414	1.467871	1.978585
50	1	0	4.840557	-1.290627	2.820130
51	6	0	6.585467	-3.426518	-1.433904
52	1	0	6.789959	-3.904004	-0.465442
53	1	0	7.556799	-3.207075	-1.890655
54	6	0	5.771734	-4.382983	-2.309203
55	1	0	6.339792	-5.292529	-2.533775
56	1	0	5.554900	-3.895996	-3.269344
57	6	0	6.986001	-1.071498	2.783378
58	1	0	7.103092	-1.919455	3.467237
59	1	0	7.799286	-1.141644	2.047460
60	6	0	7.095454	0.257775	3.533968
61	1	0	6.271206	0.332902	4.255676

62	1	0	8.027733	0.312118	4.107002
63	8	0	0.869225	2.063130	0.314935
64	1	0	-0.122808	2.037384	0.625802
65	6	0	-2.705309	-1.492002	2.004455
66	8	0	-2.041680	-0.869914	2.832946
67	16	0	-4.469156	-3.139021	-0.157555
68	6	0	-5.036529	-2.212211	1.224490
69	6	0	-6.143311	-0.778985	3.366496
70	6	0	-4.190592	-1.518905	2.110562
71	6	0	-6.430729	-2.185613	1.418474
72	6	0	-6.975635	-1.480077	2.480823
73	6	0	-4.772152	-0.803007	3.175799
74	1	0	-7.078190	-2.721192	0.730160
75	1	0	-8.052776	-1.470101	2.619582
76	1	0	-4.095476	-0.277296	3.840452
77	1	0	-6.571250	-0.224738	4.195808
78	6	0	-5.389772	-0.941065	-3.010491
79	6	0	-4.049188	-1.090351	-3.385173
80	6	0	-3.037754	-0.493002	-2.619580
81	6	0	-3.360578	0.248801	-1.491151
82	6	0	-4.726571	0.421133	-1.076941
83	6	0	-5.723085	-0.206249	-1.882123
84	7	0	-2.330168	0.847318	-0.757374
85	6	0	-2.506673	1.520129	0.419517
86	6	0	-3.863646	1.707159	0.856785
87	6	0	-5.007806	1.189639	0.073127
88	8	0	-1.534101	1.983307	1.069642
89	6	0	-7.131879	2.551499	-0.309009
90	6	0	-6.422932	3.919242	-0.257871
91	6	0	-3.913128	4.089214	-0.018349
92	6	0	-5.017826	3.850898	-0.772259
93	1	0	-6.174134	-1.408301	-3.598382
94	1	0	-3.785160	-1.667349	-4.265650
95	1	0	-1.991733	-0.605700	-2.887972
96	1	0	-6.763984	-0.115417	-1.592672
97	1	0	-1.369428	0.712092	-1.097964

98	1	0	-7.181606	2.209358	-1.349633
99	1	0	-8.166637	2.661765	0.039691
100	1	0	-6.424857	4.297772	0.772158
101	1	0	-3.994016	4.453582	1.001196
102	1	0	-2.914522	4.053650	-0.438240
103	1	0	-7.000972	4.633197	-0.862199
104	6	0	-6.405327	1.482586	0.540263
105	1	0	-7.002163	0.562468	0.536303
106	1	0	-6.376591	1.815067	1.584365
107	1	0	-4.001911	2.039748	1.876887
108	1	0	-4.893861	3.541671	-1.808726

TS_*Re*-out-*anti*





UB3LYP-D3/6-31G(d,p) (a.u.)
Imaginary Freq = 1: -166.77 cm-1
Electronic Energy (EE) = -3293.287404
Zero-point Energy Correction = 0.867658
Thermal Correction to Energy = 0.918686
Thermal Correction to Enthalpy = 0.91963
Thermal Correction to Free Energy = 0.780124
EE + Zero-point Energy = -3292.419746
EE + Thermal Energy Correction = -3292.368718
EE + Thermal Enthalpy Correction = -3292.367774
EE + Thermal Free Energy Correction = -3292.507281

E_{sp} (UM06-2X-D3/6-311+G(2d,2p)/SMD (CH_2Cl_2)) = -3292.889071

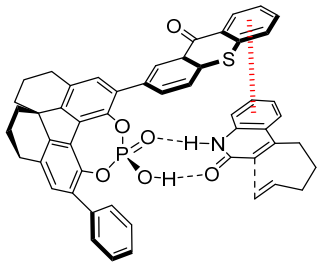
Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-4.900644	1.661428	-0.891021
2	1	0	-6.454504	1.575208	-2.358161
3	6	0	-5.779075	0.986872	-1.742845
4	6	0	-4.118874	-0.539097	-0.106413
5	6	0	-5.805835	-0.406145	-1.852602
6	6	0	-4.077119	0.858653	-0.089884
7	6	0	-4.954463	-1.186935	-1.050279
8	6	0	-1.831293	-1.123524	0.705841
9	6	0	-3.214206	-1.317986	0.797566
10	6	0	-1.424826	-3.018048	2.101676
11	6	0	-3.702621	-2.284698	1.710586
12	6	0	-0.911314	-1.990933	1.311278
13	6	0	-2.796188	-3.146965	2.352086
14	1	0	-0.729530	-3.707856	2.573476
15	8	0	-3.149873	1.476490	0.756080
16	8	0	-1.333984	-0.094759	-0.085258
17	15	0	-1.592274	1.475010	0.298878
18	8	0	-1.181317	2.295444	-0.868476
19	6	0	-4.834805	3.144098	-0.878065
20	6	0	-4.769754	5.956584	-0.900537
21	6	0	-4.863707	3.853876	-2.088827
22	6	0	-4.768426	3.868673	0.323172
23	6	0	-4.737307	5.261390	0.309965
24	6	0	-4.832073	5.247280	-2.100533
25	1	0	-4.883614	3.305585	-3.025807
26	1	0	-4.741581	3.335918	1.266665
27	1	0	-4.844461	5.777836	-3.048240
28	6	0	0.545057	-1.855858	1.046039
29	6	0	3.286661	-1.594107	0.402509
30	6	0	1.220365	-2.887137	0.394696
31	6	0	1.248918	-0.684394	1.384715

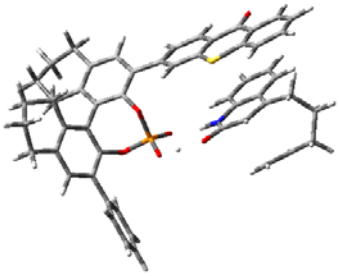
32	6	0	2.588106	-0.570235	1.070471
33	6	0	2.576714	-2.757692	0.053760
34	1	0	0.672279	-3.778795	0.104363
35	1	0	0.727308	0.128233	1.874211
36	1	0	3.128903	0.336938	1.297181
37	6	0	-3.264802	-4.259729	3.276631
38	6	0	-5.182256	-2.326829	2.063475
39	1	0	-5.800551	-2.078363	1.199061
40	6	0	-6.786038	-1.035070	-2.830230
41	1	0	-6.893134	-0.386881	-3.707421
42	6	0	-4.841267	-2.686116	-1.293843
43	1	0	-4.655485	-3.229703	-0.366985
44	1	0	-2.552817	-4.373847	4.102111
45	1	0	-3.940871	-2.845780	-1.905667
46	1	0	-7.777409	-1.064965	-2.354396
47	1	0	-3.232318	-5.206800	2.717847
48	1	0	-5.363328	-1.520498	2.789403
49	6	0	-6.049692	-3.286110	-2.018900
50	1	0	-6.913231	-3.308619	-1.339541
51	1	0	-5.834211	-4.325108	-2.291941
52	6	0	-6.399683	-2.454542	-3.254434
53	1	0	-7.218454	-2.912579	-3.820298
54	1	0	-5.529442	-2.417671	-3.923281
55	6	0	-5.625701	-3.657513	2.677567
56	1	0	-6.658315	-3.573510	3.033580
57	1	0	-5.617452	-4.441451	1.907248
58	6	0	-4.683341	-4.053831	3.816911
59	1	0	-4.679623	-3.257526	4.573022
60	1	0	-5.028133	-4.965866	4.316396
61	8	0	-0.886539	1.789968	1.662492
62	1	0	-0.202002	2.581749	1.595775
63	16	0	3.289052	-4.110126	-0.831183
64	6	0	4.716143	-1.367423	0.091689
65	1	0	-4.739803	7.042233	-0.908134
66	1	0	-4.687265	5.805094	1.248870
67	6	0	5.410684	-2.277124	-0.852712

68	6	0	6.859185	-3.890310	-2.637495
69	6	0	6.689990	-1.894575	-1.301081
70	6	0	4.866590	-3.488582	-1.320362
71	6	0	5.602170	-4.292262	-2.210087
72	6	0	7.409006	-2.682109	-2.184108
73	1	0	7.084268	-0.957368	-0.925532
74	1	0	5.177873	-5.225854	-2.568108
75	1	0	8.391255	-2.367996	-2.522609
76	1	0	7.413293	-4.516634	-3.330271
77	8	0	5.322903	-0.412795	0.586861
78	6	0	4.771653	0.836122	-2.627874
79	6	0	3.445305	0.442390	-2.840902
80	6	0	2.418858	0.991051	-2.055800
81	6	0	2.714269	1.912895	-1.063636
82	6	0	4.068775	2.321569	-0.799714
83	6	0	5.078104	1.753981	-1.635246
84	7	0	1.671834	2.430039	-0.281850
85	6	0	1.849345	3.251347	0.799802
86	6	0	3.189254	3.691267	1.069660
87	6	0	4.331141	3.230819	0.245479
88	8	0	0.870613	3.574664	1.528980
89	6	0	6.607789	2.834218	1.376697
90	6	0	6.067957	2.620276	2.806484
91	6	0	3.573364	2.432031	3.189746
92	6	0	4.759959	1.896829	2.792164
93	1	0	5.568097	0.406031	-3.226815
94	1	0	3.203789	-0.287195	-3.606779
95	1	0	1.385921	0.688645	-2.201620
96	1	0	6.112128	2.031888	-1.468800
97	1	0	0.707454	2.300229	-0.603486
98	1	0	6.684996	1.861935	0.877625
99	1	0	7.617716	3.260842	1.430129
100	1	0	5.975585	3.585321	3.321676
101	1	0	3.526457	3.382082	3.712883
102	1	0	2.651365	1.861507	3.157651
103	1	0	6.804215	2.023667	3.363810

104	6	0	5.703757	3.771234	0.537460
105	1	0	6.221625	3.993720	-0.404218
106	1	0	5.609336	4.728499	1.066608
107	1	0	3.286796	4.572206	1.689941
108	1	0	4.786075	0.905965	2.347723

TS_*Re*-out-*syn*





UB3LYP-D3/6-31G(d,p) (a.u.)
Imaginary Freq = 1: -185.01 cm-1
Electronic Energy (EE) = -3293.298497
Zero-point Energy Correction = 0.867565
Thermal Correction to Energy = 0.918495
Thermal Correction to Enthalpy = 0.919439
Thermal Correction to Free Energy = 0.781254
EE + Zero-point Energy = -3292.430932
EE + Thermal Energy Correction = -3292.380002
EE + Thermal Enthalpy Correction = -3292.379058
EE + Thermal Free Energy Correction = -3292.517243

E_{sp} (UM06-2X-D3/6-311+G(2d,2p)/SMD (CH_2Cl_2)) = -3292.902850

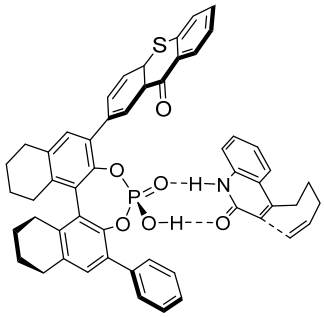
Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	1.269459	-2.459601	-0.445679
2	1	0	1.345269	-4.471230	-1.186816

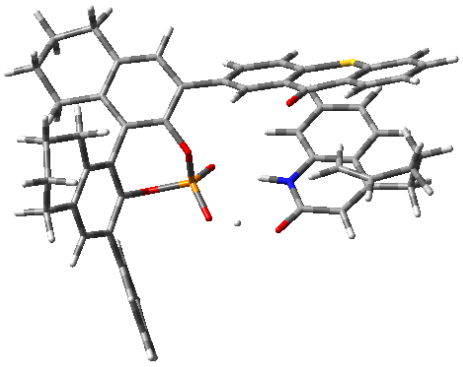
3	6	0	1.931255	-3.590015	-0.942346
4	6	0	3.483968	-1.406722	-0.199764
5	6	0	3.311184	-3.632536	-1.151310
6	6	0	2.088510	-1.377695	-0.084789
7	6	0	4.102902	-2.522049	-0.806767
8	6	0	4.007061	1.036388	-0.235659
9	6	0	4.265219	-0.230813	0.299780
10	6	0	5.687265	2.013073	1.132363
11	6	0	5.204045	-0.352963	1.350939
12	6	0	4.703058	2.187718	0.154879
13	6	0	5.934811	0.782271	1.745730
14	1	0	6.269030	2.878542	1.438284
15	8	0	1.512315	-0.197896	0.387068
16	8	0	2.982890	1.158827	-1.184320
17	15	0	1.448180	1.046780	-0.681142
18	8	0	0.534259	0.806733	-1.831254
19	6	0	-0.210611	-2.447691	-0.329856
20	6	0	-3.036572	-2.612493	-0.050892
21	6	0	-0.996802	-3.166588	-1.257895
22	6	0	-0.867620	-1.786180	0.712346
23	6	0	-2.261654	-1.855067	0.846592
24	6	0	-2.367722	-3.253332	-1.109514
25	1	0	-0.519981	-3.644842	-2.106436
26	1	0	-0.292901	-1.218583	1.433467
27	1	0	-2.975653	-3.809872	-1.813169
28	6	0	4.402116	3.533031	-0.394866
29	6	0	3.886859	6.111540	-1.396281
30	6	0	4.207604	3.741801	-1.769875
31	6	0	4.328949	4.637865	0.468041
32	6	0	4.074375	5.915591	-0.027460
33	6	0	3.953749	5.019508	-2.263959
34	1	0	4.256593	2.898899	-2.449404
35	1	0	4.446763	4.485771	1.536649
36	1	0	4.012313	6.756038	0.657880
37	1	0	3.808580	5.162174	-3.330890
38	1	0	3.684702	7.105906	-1.783658

39	6	0	7.016746	0.706178	2.811042
40	6	0	5.330986	-1.654755	2.129848
41	1	0	5.215302	-2.522009	1.477852
42	6	0	3.923609	-4.905392	-1.714059
43	1	0	3.233138	-5.356755	-2.435669
44	6	0	5.575690	-2.481348	-1.184144
45	1	0	6.157306	-1.923756	-0.448070
46	1	0	7.033362	1.641142	3.382671
47	1	0	5.653219	-1.898611	-2.113982
48	1	0	4.021072	-5.632189	-0.894150
49	1	0	7.993008	0.642758	2.308047
50	1	0	4.478457	-1.701206	2.823623
51	6	0	6.186805	-3.867153	-1.412141
52	1	0	6.285257	-4.390218	-0.450659
53	1	0	7.197852	-3.760791	-1.820232
54	6	0	5.300786	-4.691204	-2.349722
55	1	0	5.760728	-5.658834	-2.578410
56	1	0	5.189773	-4.156720	-3.302564
57	6	0	6.631953	-1.766807	2.930585
58	1	0	6.589289	-2.649133	3.578680
59	1	0	7.476314	-1.917505	2.243491
60	6	0	6.866429	-0.495130	3.748970
61	1	0	6.012502	-0.336068	4.420936
62	1	0	7.756469	-0.590604	4.380670
63	8	0	1.166791	2.272642	0.238587
64	1	0	0.156877	2.387075	0.490676
65	6	0	-5.253723	-2.120835	1.144094
66	6	0	-6.817714	-0.959020	3.171555
67	6	0	-4.658176	-1.311081	2.129533
68	6	0	-6.645821	-2.327624	1.196967
69	6	0	-7.424832	-1.757843	2.190924
70	6	0	-5.449230	-0.736696	3.142001
71	1	0	-7.077958	-2.955296	0.425419
72	1	0	-8.496085	-1.931093	2.213168
73	1	0	-4.981599	-0.115930	3.901040
74	1	0	-7.415987	-0.509184	3.958307

75	6	0	-5.044030	-0.940876	-2.805369
76	6	0	-3.730818	-0.944399	-3.287842
77	6	0	-2.744824	-0.183610	-2.644583
78	6	0	-3.069318	0.572083	-1.526785
79	6	0	-4.409196	0.612822	-1.014303
80	6	0	-5.378368	-0.178512	-1.695629
81	7	0	-2.060280	1.303241	-0.888409
82	6	0	-2.222101	1.978639	0.286143
83	6	0	-3.567874	2.102326	0.777308
84	6	0	-4.694058	1.418629	0.111907
85	8	0	-1.244447	2.497051	0.892519
86	6	0	-6.967639	2.526983	-0.196136
87	6	0	-6.395895	3.957255	-0.275083
88	6	0	-3.897957	4.352511	-0.202224
89	6	0	-5.024914	3.986981	-0.876756
90	1	0	-5.801221	-1.554324	-3.281870
91	1	0	-3.465379	-1.545324	-4.151445
92	1	0	-1.714407	-0.197570	-2.986036
93	1	0	-6.393341	-0.207205	-1.317011
94	1	0	-1.111172	1.205736	-1.269509
95	1	0	-7.049929	2.113863	-1.208474
96	1	0	-7.983297	2.559633	0.218261
97	1	0	-6.372582	4.400570	0.728638
98	1	0	-3.953927	4.782365	0.793148
99	1	0	-2.931195	4.395238	-0.690630
100	1	0	-7.077646	4.571606	-0.880692
101	6	0	-6.082977	1.590491	0.658985
102	1	0	-6.579378	0.617039	0.744432
103	1	0	-6.026063	1.989074	1.678844
104	1	0	-3.676654	2.472308	1.788627
105	1	0	-4.934619	3.632911	-1.902072
106	6	0	-4.505052	-2.791585	0.044974
107	8	0	-5.101661	-3.503771	-0.763568
108	16	0	-2.937720	-0.937080	2.193742

TS_*Si*-in-*anti*





UB3LYP-D3/6-31G(d,p) (a.u.)
Imaginary Freq = 1: -161.32 cm-1
Electronic Energy (EE) = -3293.286216
Zero-point Energy Correction = 0.86683
Thermal Correction to Energy = 0.918112
Thermal Correction to Enthalpy = 0.919056
Thermal Correction to Free Energy = 0.778865
EE + Zero-point Energy = -3292.419387
EE + Thermal Energy Correction = -3292.368105
EE + Thermal Enthalpy Correction = -3292.367160
EE + Thermal Free Energy Correction = -3292.507351

E_{sp} (UM06-2X-D3/6-311+G(2d,2p)/SMD (CH_2Cl_2)) = -3292.891346

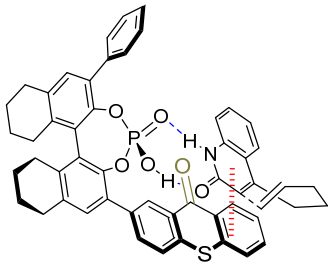
Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	1.114685	-2.304570	-0.850962
2	1	0	1.076618	-4.118438	-1.985859
3	6	0	1.715559	-3.360784	-1.538679
4	6	0	3.362027	-1.453971	-0.345111
5	6	0	3.101969	-3.461900	-1.691698
6	6	0	1.967834	-1.358230	-0.274776
7	6	0	3.940137	-2.492406	-1.109923

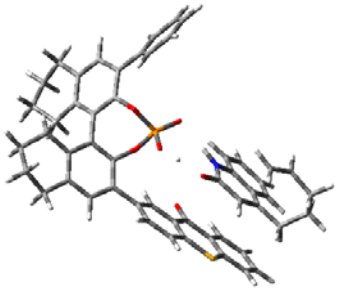
8	6	0	3.991040	0.934711	-0.037765
9	6	0	4.177496	-0.401401	0.336487
10	6	0	5.652992	1.646379	1.505741
11	6	0	5.066424	-0.703282	1.392644
12	6	0	4.716500	1.992231	0.526145
13	6	0	5.826902	0.335980	1.958624
14	1	0	6.256070	2.437330	1.943780
15	8	0	1.414137	-0.229652	0.336859
16	8	0	3.015906	1.220394	-1.000985
17	15	0	1.449312	1.124825	-0.584948
18	8	0	0.600325	1.063824	-1.807096
19	6	0	-0.361497	-2.178223	-0.769654
20	6	0	-3.171645	-2.027657	-0.644848
21	6	0	-1.138701	-2.195689	-1.942628
22	6	0	-1.015124	-2.072127	0.454257
23	6	0	-2.417469	-2.014047	0.544734
24	6	0	-2.520277	-2.114351	-1.885363
25	1	0	-0.642305	-2.250761	-2.906199
26	1	0	-0.454367	-2.048527	1.381147
27	1	0	-3.101408	-2.096476	-2.801160
28	6	0	4.490864	3.410099	0.150219
29	6	0	4.111025	6.117432	-0.516362
30	6	0	4.356458	3.805817	-1.190522
31	6	0	4.427404	4.394344	1.149134
32	6	0	4.239873	5.735686	0.819600
33	6	0	4.169486	5.146880	-1.518603
34	1	0	4.398460	3.057896	-1.973743
35	1	0	4.498731	4.098419	2.191377
36	1	0	4.183265	6.480664	1.608070
37	1	0	4.069491	5.434420	-2.561271
38	1	0	3.960101	7.161557	-0.774617
39	6	0	6.861683	0.069651	3.040016
40	6	0	5.104675	-2.100003	1.995490
41	1	0	4.974627	-2.866863	1.229790
42	6	0	3.665046	-4.642051	-2.466890
43	1	0	2.983427	-4.901038	-3.285336

44	6	0	5.431508	-2.484825	-1.412383
45	1	0	6.006350	-2.129158	-0.555565
46	1	0	6.894822	0.918923	3.732037
47	1	0	5.597263	-1.735725	-2.200636
48	1	0	3.682107	-5.517011	-1.800349
49	1	0	7.853742	0.027491	2.566453
50	1	0	4.225024	-2.194469	2.649244
51	6	0	5.967905	-3.838112	-1.888598
52	1	0	5.988241	-4.544509	-1.047029
53	1	0	7.002116	-3.723682	-2.231408
54	6	0	5.080340	-4.401611	-3.001006
55	1	0	5.492630	-5.334749	-3.400517
56	1	0	5.045606	-3.685100	-3.832511
57	6	0	6.367715	-2.378248	2.816169
58	1	0	6.262438	-3.334556	3.340345
59	1	0	7.231133	-2.477509	2.143486
60	6	0	6.623764	-1.236858	3.803353
61	1	0	5.751616	-1.127512	4.461642
62	1	0	7.483456	-1.456512	4.446106
63	8	0	1.169213	2.254627	0.449981
64	1	0	0.213964	2.664045	0.410925
65	6	0	-3.012437	-1.972835	1.906960
66	16	0	-4.931285	-1.910542	-0.701964
67	6	0	-5.404100	-2.026947	0.991372
68	6	0	-6.362394	-2.138684	3.623478
69	6	0	-6.788633	-2.067909	1.243019
70	6	0	-4.493280	-2.039184	2.064246
71	6	0	-5.000083	-2.094234	3.376637
72	6	0	-7.260954	-2.126477	2.545792
73	1	0	-7.486145	-2.056673	0.410422
74	1	0	-4.276558	-2.093562	4.184211
75	1	0	-8.331325	-2.162826	2.725484
76	1	0	-6.732229	-2.183799	4.642869
77	8	0	-2.291122	-1.902543	2.901062
78	6	0	-5.060777	0.624032	-3.797896
79	6	0	-3.720702	0.400188	-4.138139

80	6	0	-2.696458	0.897714	-3.312148
81	6	0	-3.003943	1.616734	-2.168756
82	6	0	-4.374228	1.892882	-1.802160
83	6	0	-5.383627	1.348503	-2.660749
84	7	0	-1.963487	2.052676	-1.340912
85	6	0	-2.137262	2.809958	-0.215913
86	6	0	-3.488884	3.101334	0.166147
87	6	0	-4.643232	2.631160	-0.639125
88	8	0	-1.157633	3.195096	0.478118
89	6	0	-6.524048	1.557650	0.730142
90	6	0	-6.085256	1.540448	2.202028
91	6	0	-3.621800	1.133523	1.668347
92	6	0	-4.612035	1.544729	2.495282
93	1	0	-5.854142	0.231080	-4.426718
94	1	0	-3.465208	-0.159449	-5.032364
95	1	0	-1.653111	0.703236	-3.540908
96	1	0	-6.425972	1.507942	-2.409685
97	1	0	-1.006492	1.759770	-1.579534
98	1	0	-6.196511	0.647890	0.218012
99	1	0	-7.620877	1.540541	0.716231
100	1	0	-6.537910	2.400908	2.714234
101	1	0	-2.586387	1.145039	1.990155
102	1	0	-3.834588	0.617854	0.738617
103	1	0	-6.520617	0.653470	2.688434
104	6	0	-6.025473	2.794385	-0.076803
105	1	0	-6.736044	2.983594	-0.889299
106	1	0	-6.061294	3.679844	0.570542
107	1	0	-3.623156	3.848123	0.937376
108	1	0	-4.327942	1.937462	3.470610

TS_*Si*in-*syn*





UB3LYP-D3/6-31G(d,p) (a.u.)
Imaginary Freq = 1: -170.15 cm-1
Electronic Energy (EE) = -3293.295261
Zero-point Energy Correction = 0.867297
Thermal Correction to Energy = 0.918406
Thermal Correction to Enthalpy = 0.91935
Thermal Correction to Free Energy = 0.779754
EE + Zero-point Energy = -3292.427963
EE + Thermal Energy Correction = -3292.376855
EE + Thermal Enthalpy Correction = -3292.37591
EE + Thermal Free Energy Correction = -3292.515507

E_{sp} (UM06-2X-D3/6-311+G(2d,2p)/SMD (CH_2Cl_2)) = -3292.901503

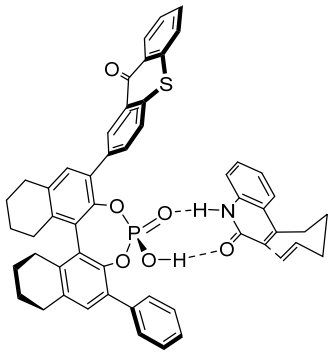
Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	4.432207	2.347145	0.398102
2	1	0	5.897478	3.048487	1.790397
3	6	0	5.407021	2.167623	1.384652
4	6	0	4.228416	-0.103508	0.289400
5	6	0	5.758631	0.910518	1.881885
6	6	0	3.854920	1.182327	-0.126140
7	6	0	5.148999	-0.241710	1.353654
8	6	0	2.183263	-1.386931	-0.278910
9	6	0	3.575030	-1.290093	-0.347065
10	6	0	2.206167	-3.463284	-1.439071

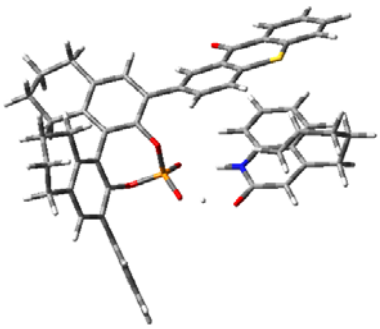
11	6	0	4.292534	-2.277919	-1.059927
12	6	0	1.462890	-2.461642	-0.812232
13	6	0	3.595562	-3.382894	-1.584375
14	1	0	1.681423	-4.323495	-1.847677
15	8	0	2.859508	1.309067	-1.100954
16	8	0	1.476632	-0.315747	0.270045
17	15	0	1.315098	0.980229	-0.715330
18	8	0	0.531994	2.024293	-0.001556
19	6	0	4.025250	3.709433	-0.029396
20	6	0	3.316000	6.323132	-0.795085
21	6	0	3.835790	4.714479	0.932479
22	6	0	3.848324	4.036473	-1.383792
23	6	0	3.498504	5.331200	-1.760794
24	6	0	3.484879	6.009347	0.553963
25	1	0	3.940787	4.468876	1.984980
26	1	0	3.987001	3.271775	-2.139081
27	1	0	3.368882	5.565944	-2.813393
28	1	0	3.333684	6.769997	1.314543
29	1	0	3.038944	7.330603	-1.091682
30	6	0	-0.018578	-2.487061	-0.762497
31	6	0	-2.837250	-2.526962	-0.690519
32	6	0	-0.710377	-2.207196	0.414017
33	6	0	-0.766968	-2.778260	-1.918589
34	6	0	-2.152095	-2.796764	-1.886250
35	6	0	-2.112862	-2.224870	0.478076
36	1	0	-0.178472	-1.962338	1.324708
37	1	0	-0.250102	-2.961351	-2.855116
38	1	0	-2.710119	-3.006568	-2.793933
39	6	0	4.318969	-4.518222	-2.290921
40	6	0	5.769092	-2.082643	-1.370668
41	1	0	6.286373	-1.597233	-0.541170
42	6	0	6.819951	0.827458	2.967193
43	1	0	6.735828	1.697332	3.628648
44	6	0	5.378224	-1.597243	2.007119
45	1	0	5.354266	-2.403243	1.271997
46	1	0	3.684551	-4.914011	-3.092424

47	1	0	4.519566	-1.786087	2.668372
48	1	0	7.808339	0.905463	2.490526
49	1	0	4.449635	-5.342968	-1.574750
50	1	0	5.831472	-1.369194	-2.205632
51	6	0	6.667226	-1.670624	2.831270
52	1	0	7.536216	-1.674280	2.158435
53	1	0	6.693727	-2.613498	3.388655
54	6	0	6.764433	-0.471313	3.777127
55	1	0	7.646500	-0.547954	4.422527
56	1	0	5.885828	-0.459850	4.435825
57	6	0	6.488434	-3.375947	-1.765148
58	1	0	7.499534	-3.142460	-2.116465
59	1	0	6.599373	-4.021101	-0.882443
60	6	0	5.692469	-4.120275	-2.840014
61	1	0	5.566782	-3.466024	-3.713013
62	1	0	6.229974	-5.011125	-3.183353
63	8	0	0.782052	0.492326	-2.100469
64	1	0	-0.246618	0.572473	-2.234928
65	6	0	-2.734914	-1.931182	1.798362
66	8	0	-2.031654	-1.660543	2.769955
67	16	0	-4.598450	-2.578944	-0.772916
68	6	0	-5.104734	-2.260384	0.884459
69	6	0	-6.112759	-1.774953	3.453615
70	6	0	-6.491405	-2.280989	1.118740
71	6	0	-4.215592	-1.988371	1.941065
72	6	0	-4.747436	-1.748927	3.221479
73	6	0	-6.988379	-2.039025	2.392439
74	1	0	-7.172271	-2.495765	0.300005
75	1	0	-4.040553	-1.532344	4.013940
76	1	0	-8.061204	-2.061528	2.560052
77	1	0	-6.501421	-1.585506	4.449075
78	6	0	-4.824601	1.640768	2.902484
79	6	0	-3.449297	1.840130	3.071473
80	6	0	-2.584919	1.715833	1.975928
81	6	0	-3.088985	1.396594	0.722370
82	6	0	-4.493699	1.175021	0.516611

83	6	0	-5.337045	1.314885	1.655890
84	7	0	-2.203848	1.290341	-0.358701
85	6	0	-2.554275	0.823115	-1.593764
86	6	0	-3.958355	0.637479	-1.840329
87	6	0	-4.960026	0.839988	-0.775037
88	8	0	-1.693007	0.601633	-2.486568
89	6	0	-7.197144	1.982438	-1.212272
90	6	0	-6.654447	2.877556	-2.344747
91	6	0	-4.202912	2.837790	-2.967929
92	6	0	-5.213604	3.234307	-2.144465
93	1	0	-5.495035	1.725021	3.752178
94	1	0	-3.043845	2.082345	4.048156
95	1	0	-1.514539	1.857012	2.090816
96	1	0	-6.399459	1.129825	1.549469
97	1	0	-1.225646	1.561974	-0.201410
98	1	0	-7.126976	2.522046	-0.260362
99	1	0	-8.261279	1.776342	-1.384618
100	1	0	-6.782282	2.369742	-3.309231
101	1	0	-4.408669	2.336402	-3.908675
102	1	0	-3.178519	3.151935	-2.804066
103	1	0	-7.259449	3.794834	-2.383394
104	6	0	-6.415837	0.653129	-1.095966
105	1	0	-6.893027	0.031537	-0.327401
106	1	0	-6.510793	0.101454	-2.039265
107	1	0	-4.221003	0.091258	-2.736788
108	1	0	-4.971565	3.800423	-1.246865

TS_*Si*-out-*anti*





UB3LYP-D3/6-31G(d,p) (a.u.)
Imaginary Freq = 1: -115.02 cm-1
Temperature = 298.15
Pressure = 1
Frequencies scaled by = 1
Electronic Energy (EE) = -3293.294
Zero-point Energy Correction = 0.867322
Thermal Correction to Energy = 0.918461
Thermal Correction to Enthalpy = 0.919405
Thermal Correction to Free Energy = 0.779685
EE + Zero-point Energy = -3292.4267
EE + Thermal Energy Correction = -3292.3756
EE + Thermal Enthalpy Correction = -3292.3746
EE + Thermal Free Energy Correction = -3292.5143

E_{sp} (UM06-2X-D3/6-311+G(2d,2p)/SMD (CH_2Cl_2)) = -3292.897729

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
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4	6	0	3.263659	-1.642456	0.099157
5	6	0	2.580530	-3.916162	-0.415557
6	6	0	1.927138	-1.336923	0.380842

7	6	0	3.589234	-2.936387	-0.366397
8	6	0	4.134746	0.615998	-0.494824
9	6	0	4.286320	-0.560220	0.248691
10	6	0	6.140195	1.508463	0.416881
11	6	0	5.354588	-0.658564	1.169430
12	6	0	5.046936	1.677861	-0.438499
13	6	0	6.300258	0.381266	1.227054
14	1	0	6.885387	2.298200	0.463152
15	8	0	1.612074	-0.007280	0.680993
16	8	0	3.002473	0.740282	-1.309001
17	15	0	1.563052	1.003803	-0.608921
18	8	0	0.465333	0.721774	-1.573759
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22	6	0	-0.874709	-1.140446	1.712748
23	6	0	-2.204630	-0.910620	2.024574
24	6	0	-2.898131	-2.293882	0.150091
25	1	0	-1.318192	-3.118277	-1.011990
26	1	0	-0.100076	-0.688706	2.320888
27	6	0	4.860894	2.936483	-1.202639
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29	6	0	4.474334	2.930142	-2.552766
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31	6	0	4.947375	5.366699	-1.280437
32	6	0	4.329806	4.125127	-3.254330
33	1	0	4.287231	1.985257	-3.049482
34	1	0	5.362389	4.192527	0.474106
35	1	0	5.121600	6.312644	-0.775737
36	1	0	4.031855	4.100487	-4.298530
37	1	0	4.447621	6.278052	-3.170539
38	6	0	7.518983	0.303070	2.132551
39	6	0	5.411286	-1.803912	2.170246
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42	1	0	2.019066	-5.759272	-1.370310

43	6	0	4.973903	-3.230310	-0.923873
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45	1	0	7.768136	1.305749	2.498387
46	1	0	5.008080	-2.809204	-1.939529
47	1	0	2.979249	-5.956387	0.083198
48	1	0	8.379045	-0.019416	1.527237
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53	6	0	4.156851	-5.490745	-1.659956
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55	1	0	3.990346	-5.084898	-2.666620
56	6	0	6.795272	-2.003291	2.795549
57	1	0	6.729913	-2.736212	3.607315
58	1	0	7.482474	-2.419635	2.045821
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76	1	0	-7.650930	-1.104203	1.442782
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80	6	0	-3.096438	0.410350	-2.004539
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85	6	0	-1.680217	3.239127	-0.123465
86	6	0	-2.878531	3.874590	0.351361
87	6	0	-4.218391	3.319826	0.054168
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90	6	0	-5.082677	3.139632	3.002911
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99	1	0	-6.971089	3.784756	2.143924
100	1	0	-4.813624	4.136709	3.374001
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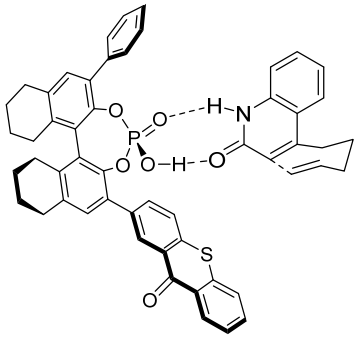
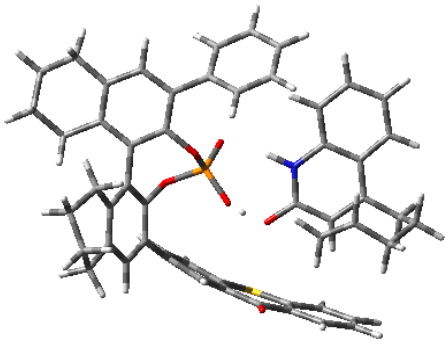
TS_*Si*-out-*syn*





UB3LYP-D3/6-31G(d,p) (a.u.)
Imaginary Freq = 1: -136.48 cm-1
Electronic Energy (EE) = -3293.291135
Zero-point Energy Correction = 0.867935
Thermal Correction to Energy = 0.91875
Thermal Correction to Enthalpy = 0.919694
Thermal Correction to Free Energy = 0.78159
EE + Zero-point Energy = -3292.423200
EE + Thermal Energy Correction = -3292.372385
EE + Thermal Enthalpy Correction = -3292.371441
EE + Thermal Free Energy Correction = -3292.509545

E_{sp} (UM06-2X-D3/6-311+G(2d,2p)/SMD (CH_2Cl_2)) = -3292.891446

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
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4	6	0	-4.159339	0.178749	-0.023813
5	6	0	-5.802347	1.816673	-0.742953
6	6	0	-3.270805	1.232007	0.231802
7	6	0	-5.426074	0.470716	-0.575459
8	6	0	-2.525667	-1.651446	-0.421670
9	6	0	-3.686076	-1.218480	0.230212

10	6	0	-2.621073	-3.762013	0.680642
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12	6	0	-1.958812	-2.912936	-0.204882
13	6	0	-3.770703	-3.365538	1.373126
14	1	0	-2.202307	-4.748049	0.865034
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16	8	0	-1.855856	-0.749510	-1.259365
17	15	0	-0.960247	0.395009	-0.511271
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23	6	0	-0.858817	4.759967	1.503834
24	6	0	-1.601149	5.735281	-0.574167
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27	1	0	-0.210694	4.778305	2.374996
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30	6	0	-0.630527	-3.229588	-0.792571
31	6	0	1.965305	-3.388587	-1.861765
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33	6	0	0.476219	-3.340693	0.041251
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35	6	0	0.848518	-3.357059	-2.712466
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37	1	0	0.361162	-3.279090	1.116941
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39	6	0	-5.399421	-1.550967	2.086130
40	1	0	-6.059421	-0.864707	1.553111
41	6	0	-7.186365	2.199910	-1.241896
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43	6	0	-6.313080	-0.645963	-1.105855
44	1	0	-6.232575	-1.543180	-0.489607
45	1	0	-3.653792	-4.985673	2.781850

46	1	0	-5.913850	-0.935479	-2.089239
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53	6	0	-7.882912	1.085686	-2.029393
54	1	0	-8.928885	1.355375	-2.212701
55	1	0	-7.404995	0.972329	-3.011614
56	6	0	-6.216698	-2.658406	2.758061
57	1	0	-6.889135	-2.218451	3.502802
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60	1	0	-4.642845	-3.190199	4.133801
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62	8	0	0.125967	-0.316632	0.369334
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65	6	0	4.657443	-3.057821	-1.324204
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69	6	0	6.949763	-2.568299	-0.701344
70	6	0	5.286608	-2.902530	1.007606
71	1	0	7.972869	-2.350009	-0.992691
72	1	0	4.980946	-2.963287	2.046338
73	1	0	7.351001	-2.476598	1.423676
74	1	0	0.989581	-3.346206	-3.789182
75	1	0	6.267191	-2.737350	-2.730548
76	6	0	2.892725	-3.291320	0.514582
77	8	0	2.662240	-3.296183	1.725501
78	6	0	4.051837	5.479102	-0.104616
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82	6	0	4.253459	3.031717	-0.140994
83	6	0	4.803360	4.325712	0.082647
84	7	0	2.295505	1.738787	-0.858467
85	6	0	2.915105	0.533492	-0.678715
86	6	0	4.253813	0.554322	-0.181852
87	6	0	4.955473	1.822616	0.088773
88	8	0	2.285758	-0.545319	-0.883887
89	6	0	6.464151	1.982829	2.138480
90	6	0	5.597168	0.983616	2.929594
91	6	0	3.352239	0.130864	2.113859
92	6	0	4.142287	1.129498	2.606868
93	1	0	4.503402	6.449879	0.076736
94	1	0	2.123131	6.287245	-0.657321
95	1	0	1.103089	4.058295	-1.072050
96	1	0	5.834124	4.408300	0.410155
97	1	0	1.325617	1.715940	-1.194230
98	1	0	6.136561	3.003461	2.371601
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108	1	0	3.715118	2.121971	2.739434

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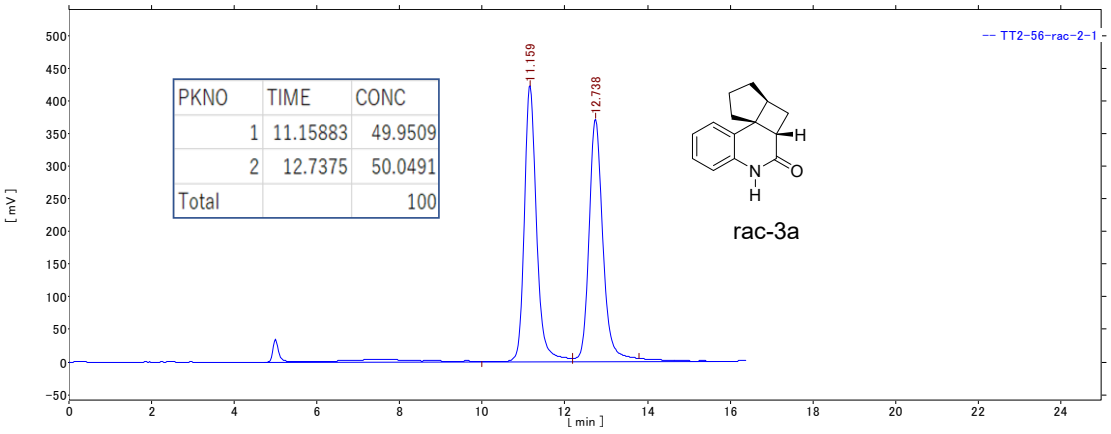
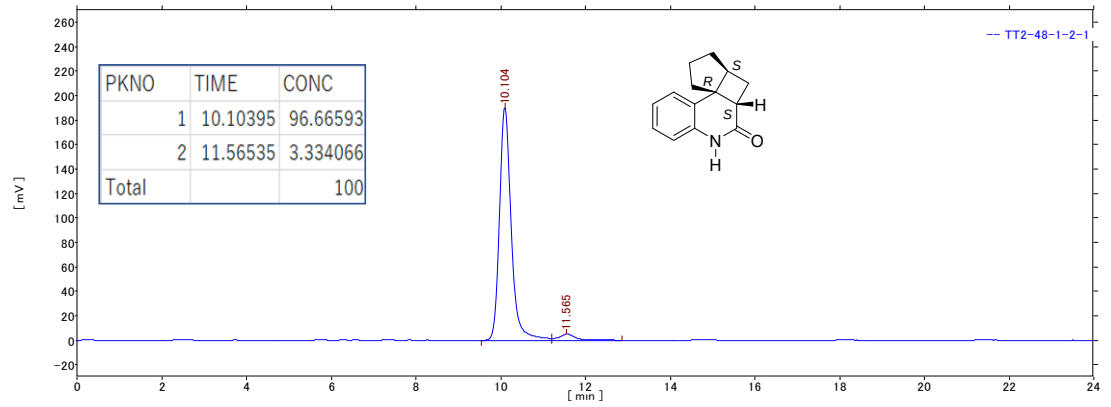
10. HPLC traces

3a: Chiralpak IC, hexane:EtOH=20:1, 1.5 ml/min, 254 nm

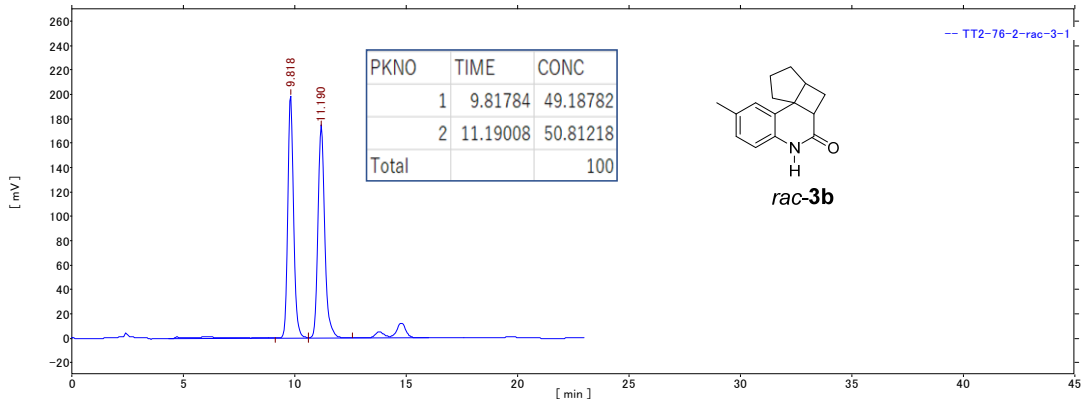


rac-3a

96% ee



3b: Chiralpak IC, hexane:EtOH=20:1, 1.5 ml/min, 254 nm



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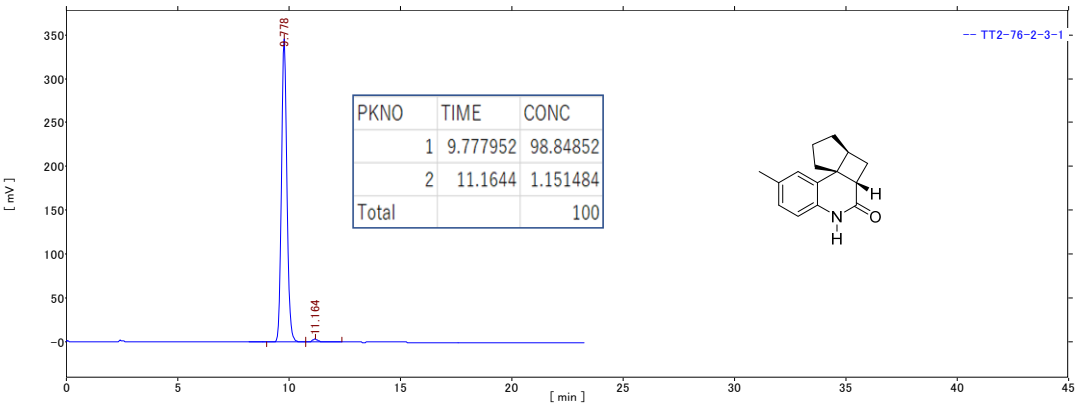
Total		100

rac-**3b**

97% ee



PKNO	TIME	CONC
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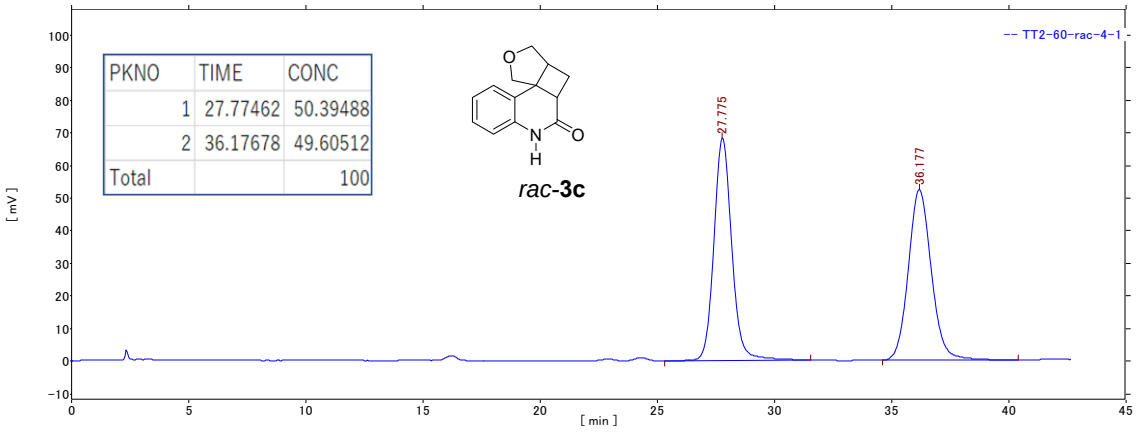
2	11.1644	1.151484
Total		100

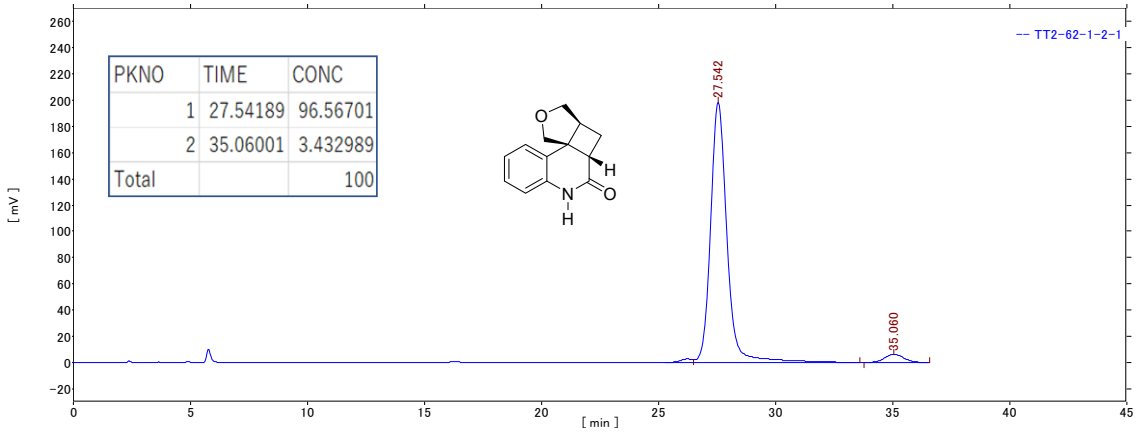
3c: Chiralpak IC, hexane:EtOH=20:1, 1.5 ml/min, 254 nm



PKNO	TIME	CONC
1	27.77462	50.39488
2	36.17678	49.60512
Total		100

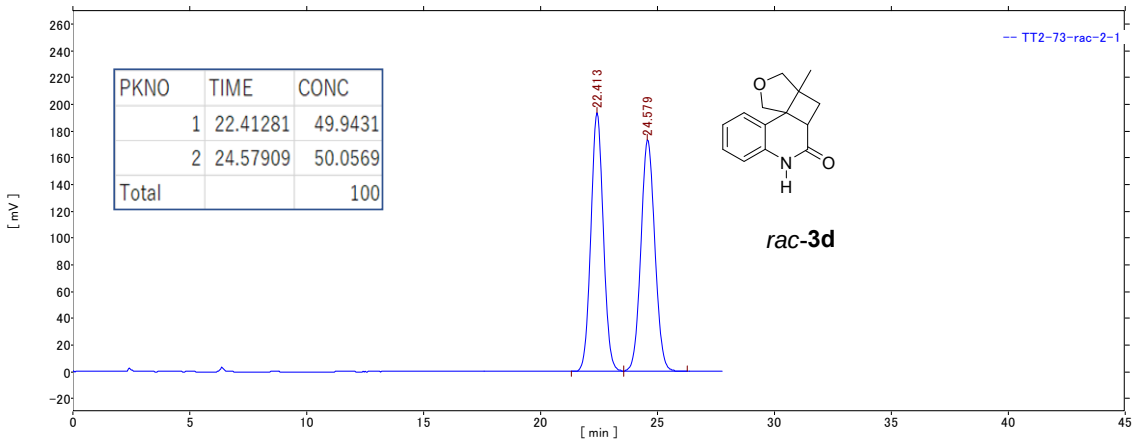
rac-**3c**

94% ee



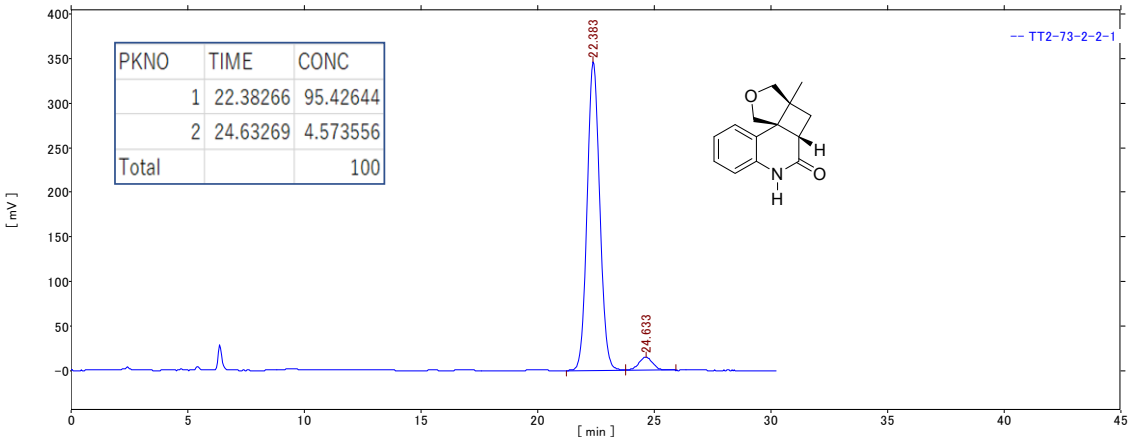
PKNO	TIME	CONC
1	27.54189	96.56701
2	35.06001	3.432989
Total		100

3d: Chiralpak IC, hexane:EtOH=20:1, 1.5 ml/min, 254 nm

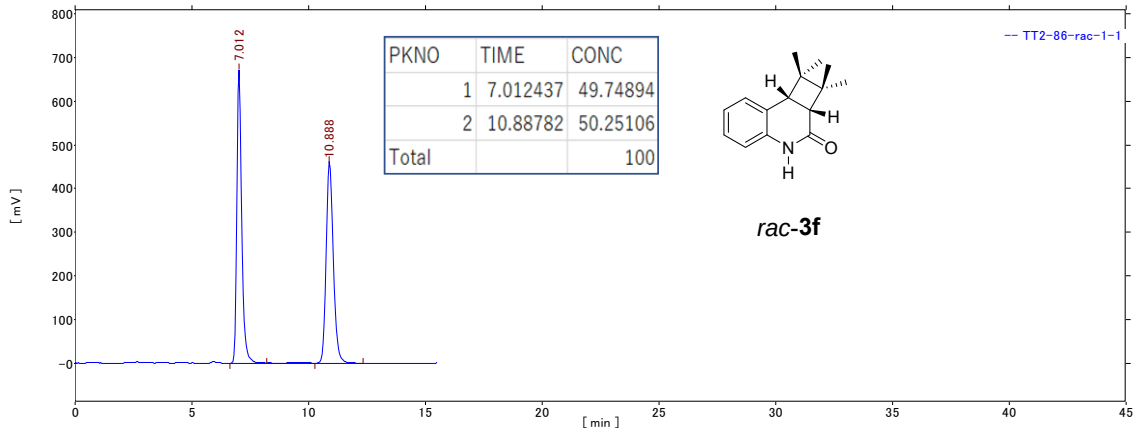


rac-**3d**

91% ee



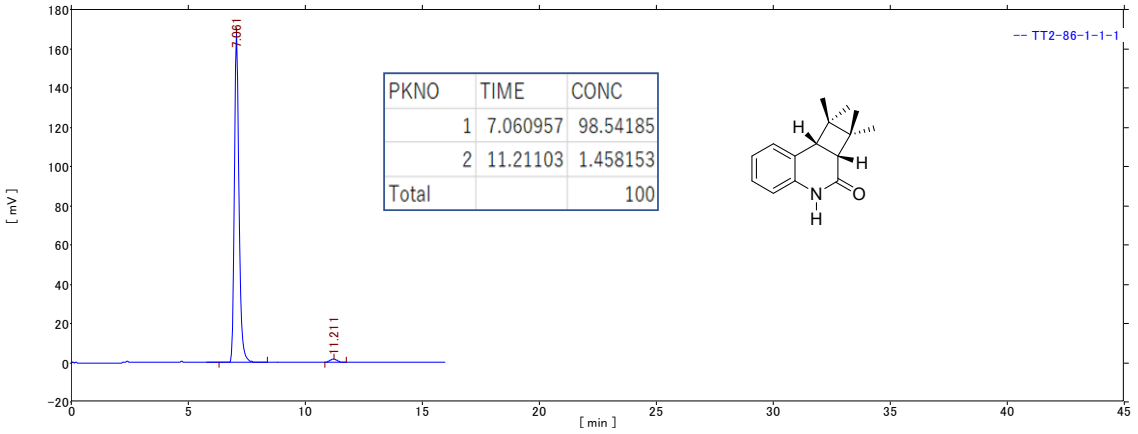
3f: Chiralpak IC, hexane:EtOH=20:1, 1.5 ml/min, 254 nm



PKNO	TIME	CONC
1	7.012437	49.74894
2	10.88782	50.25106
Total		100

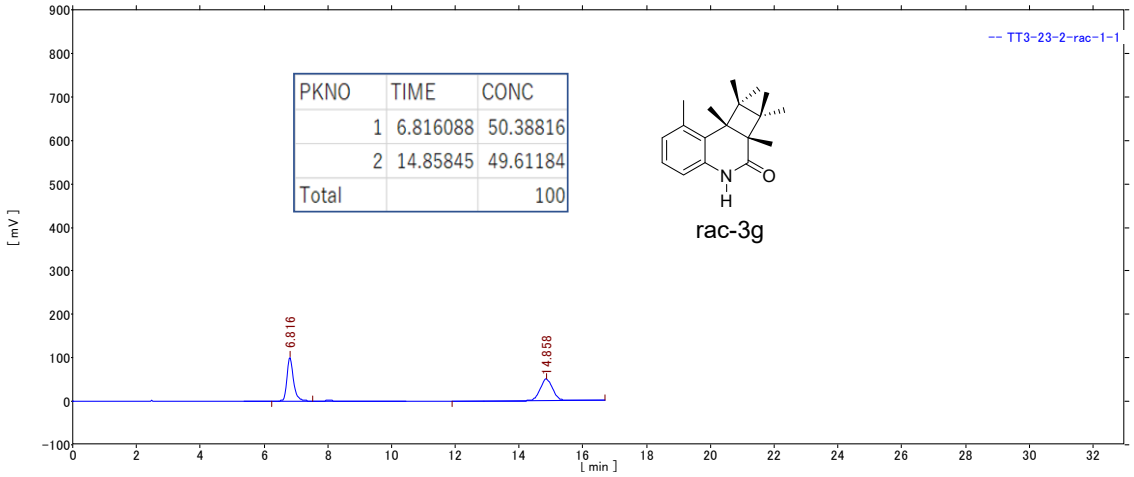
rac-**3f**

97% ee



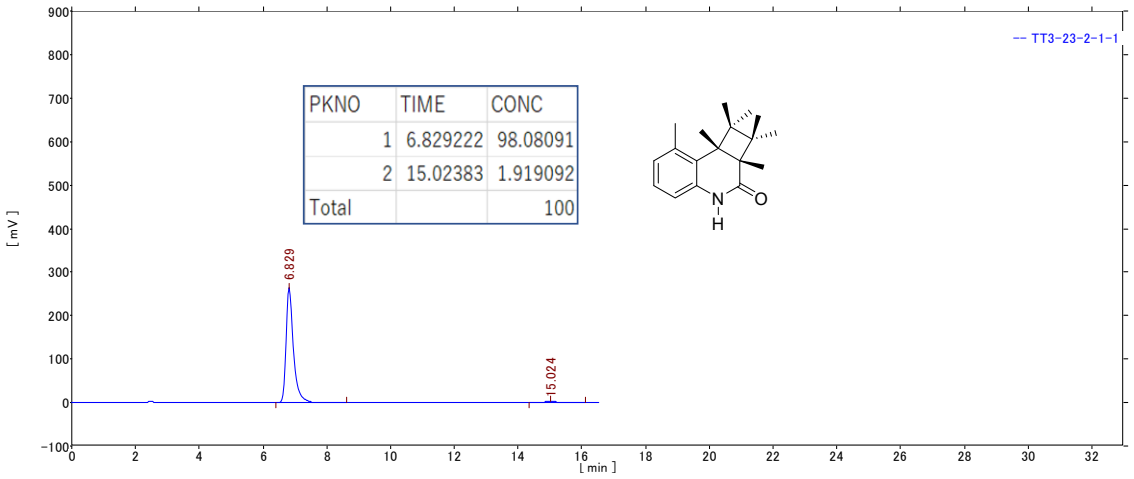
PKNO	TIME	CONC
1	7.060957	98.54185
2	11.21103	1.458153
Total		100

3g: Chiralpak IC, hexane:EtOH=20:1, 1.5 ml/min, 254 nm

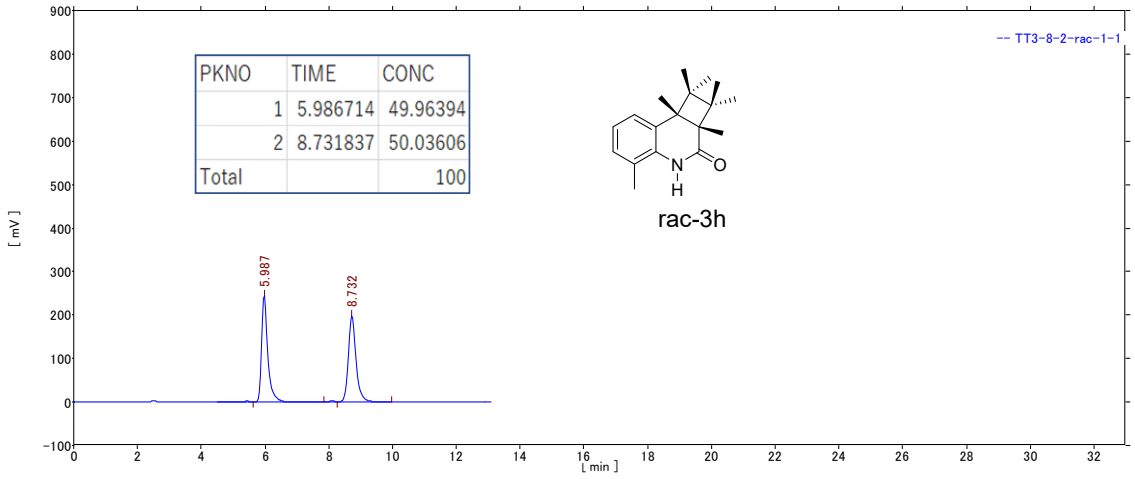


rac-3g

98% ee

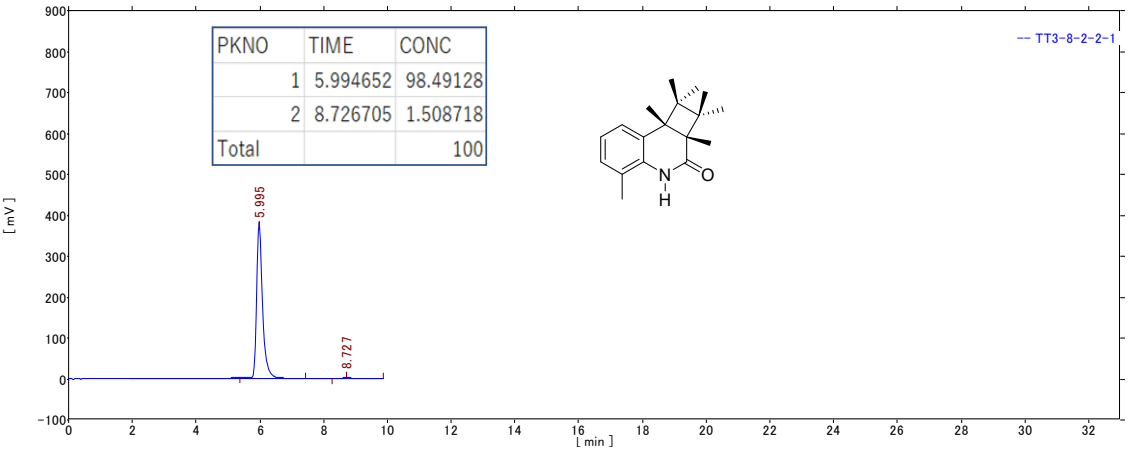


3h: Chiralpak IC, hexane:EtOH=20:1, 1.5 ml/min, 254 nm

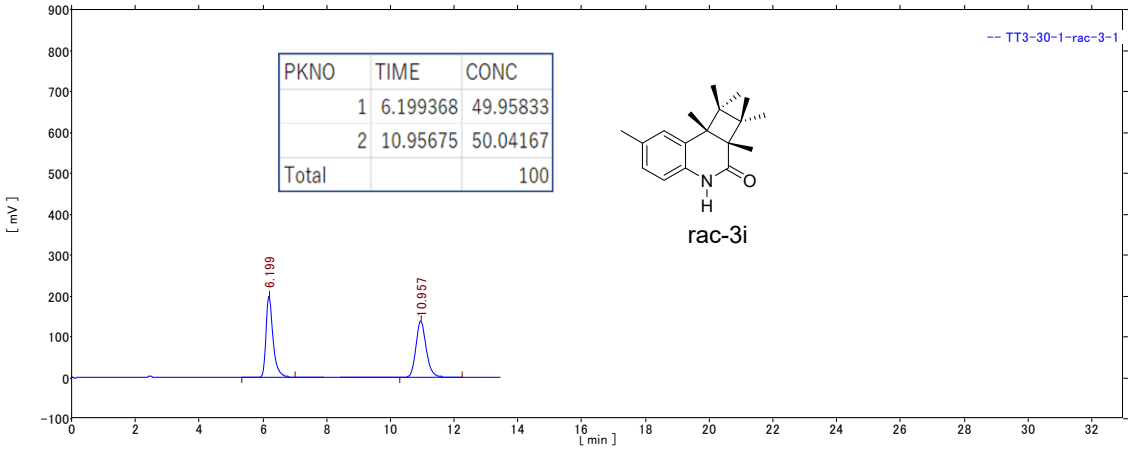


rac-3h

97% ee

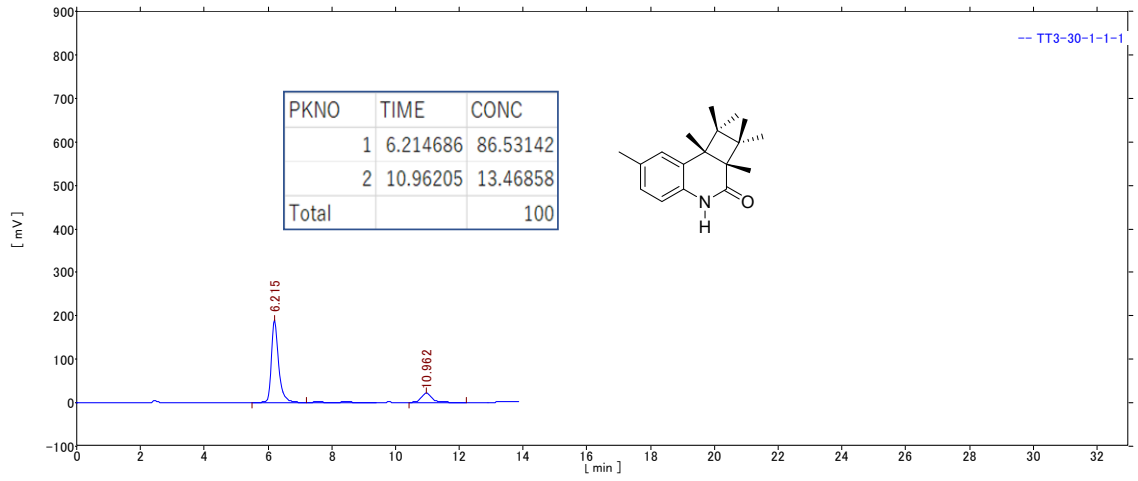


3i: Chiralpak IC, hexane:EtOH=20:1, 1.5 ml/min, 254 nm

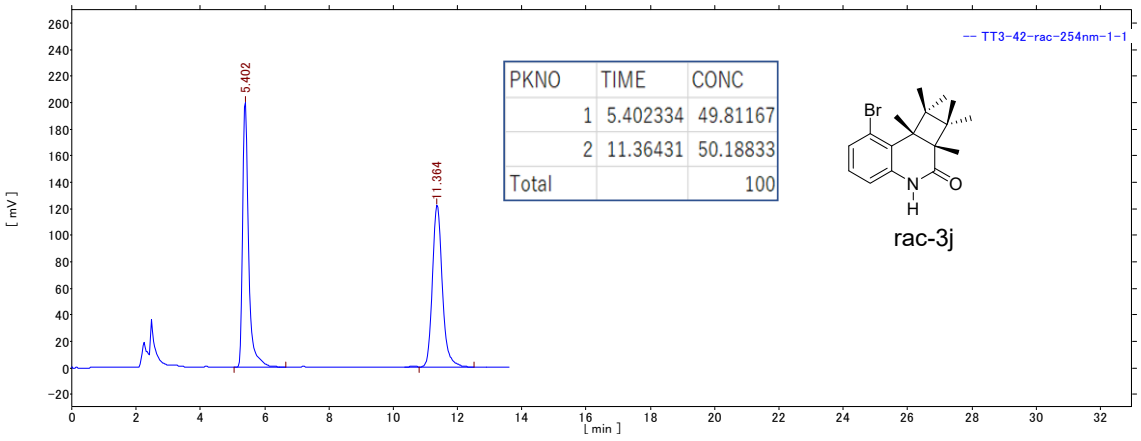


rac-3i

73% ee



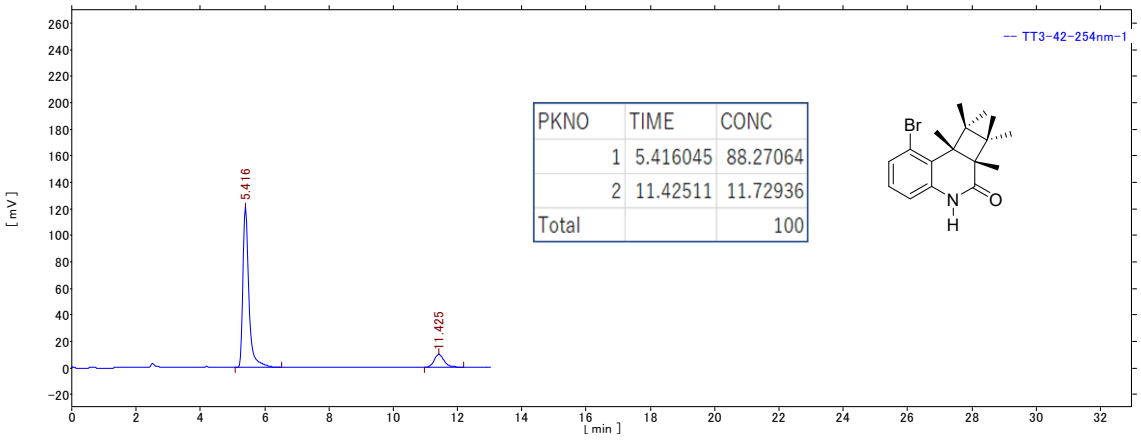
3j: Chiralpak IC, hexane:EtOH=20:1, 1.5 ml/min, 254 nm



PKNO	TIME	CONC
1	5.402334	49.81167
2	11.36431	50.18833
Total		100

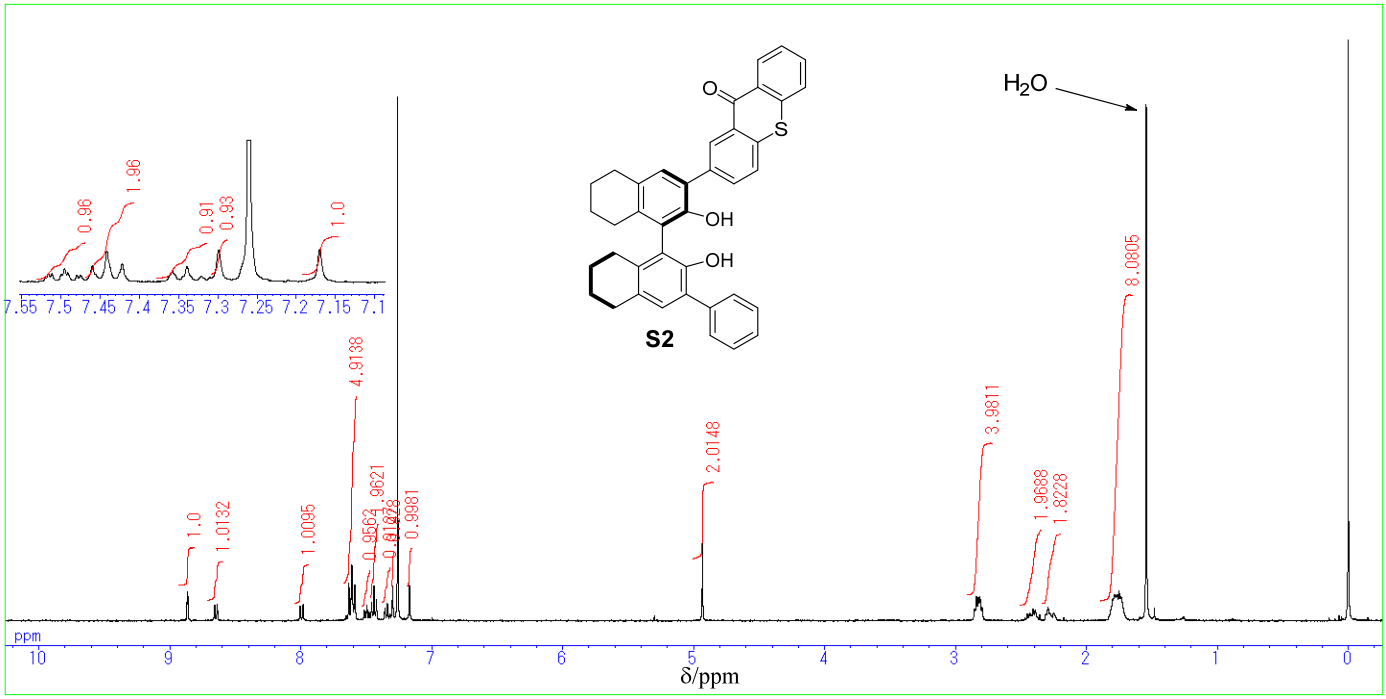
rac-3j

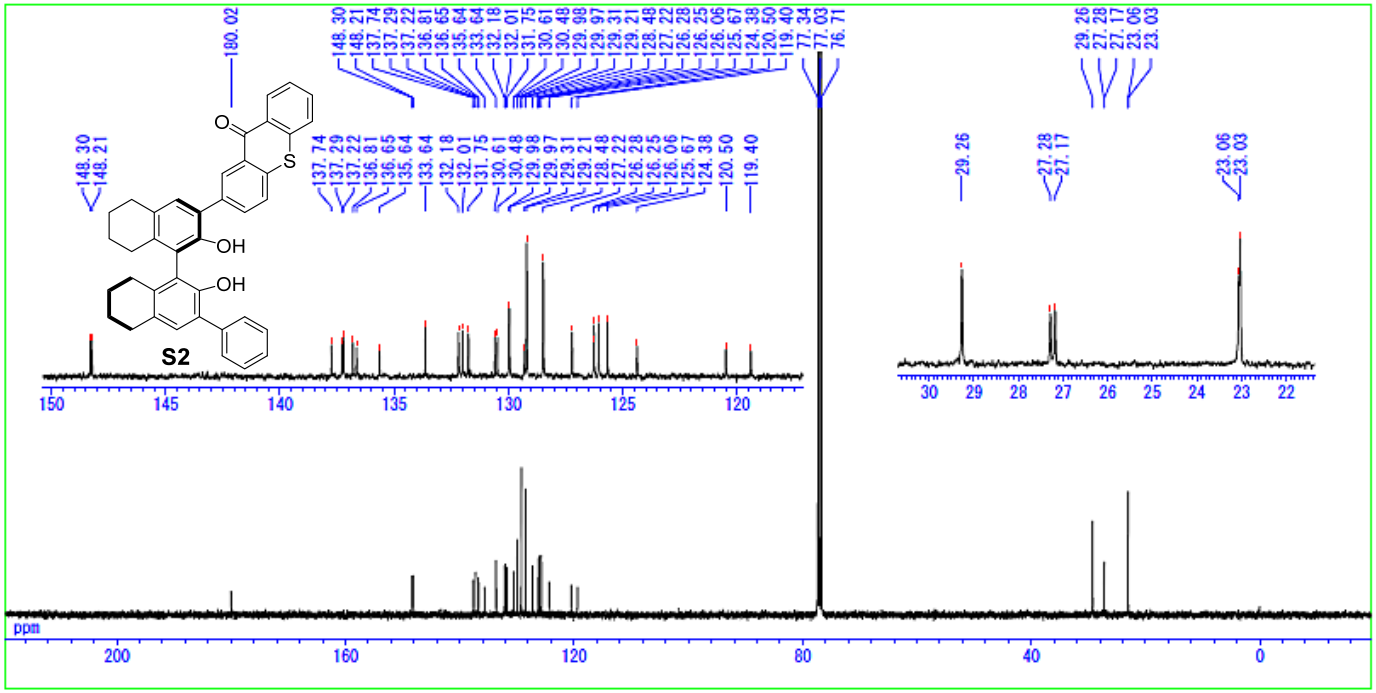
75% ee

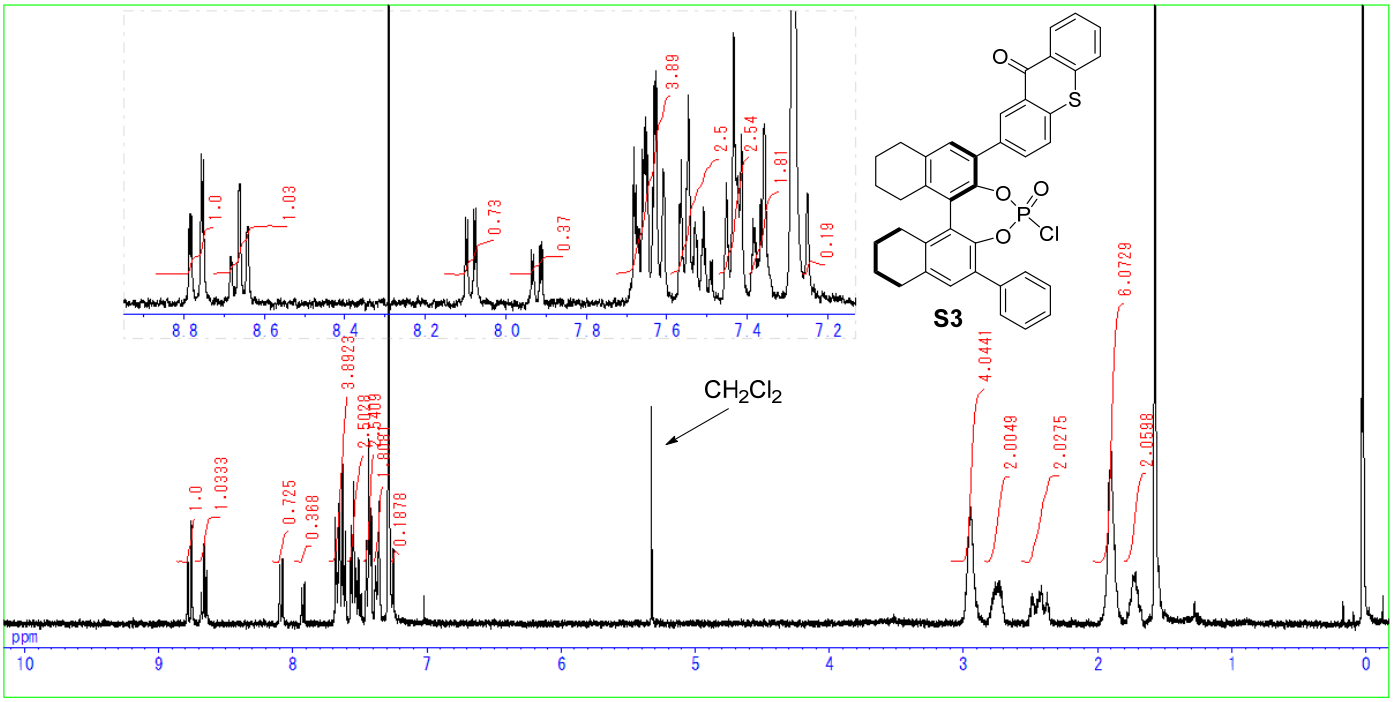


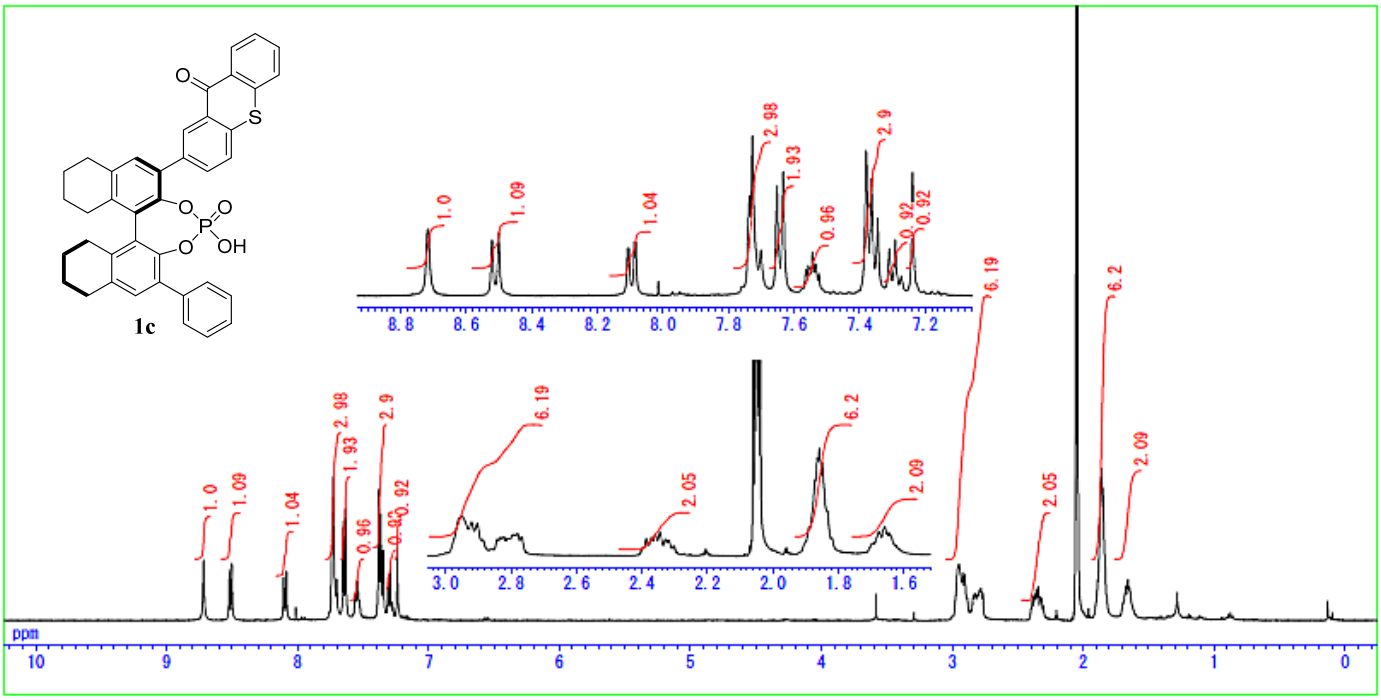
PKNO	TIME	CONC
1	5.416045	88.27064
2	11.42511	11.72936
Total		100

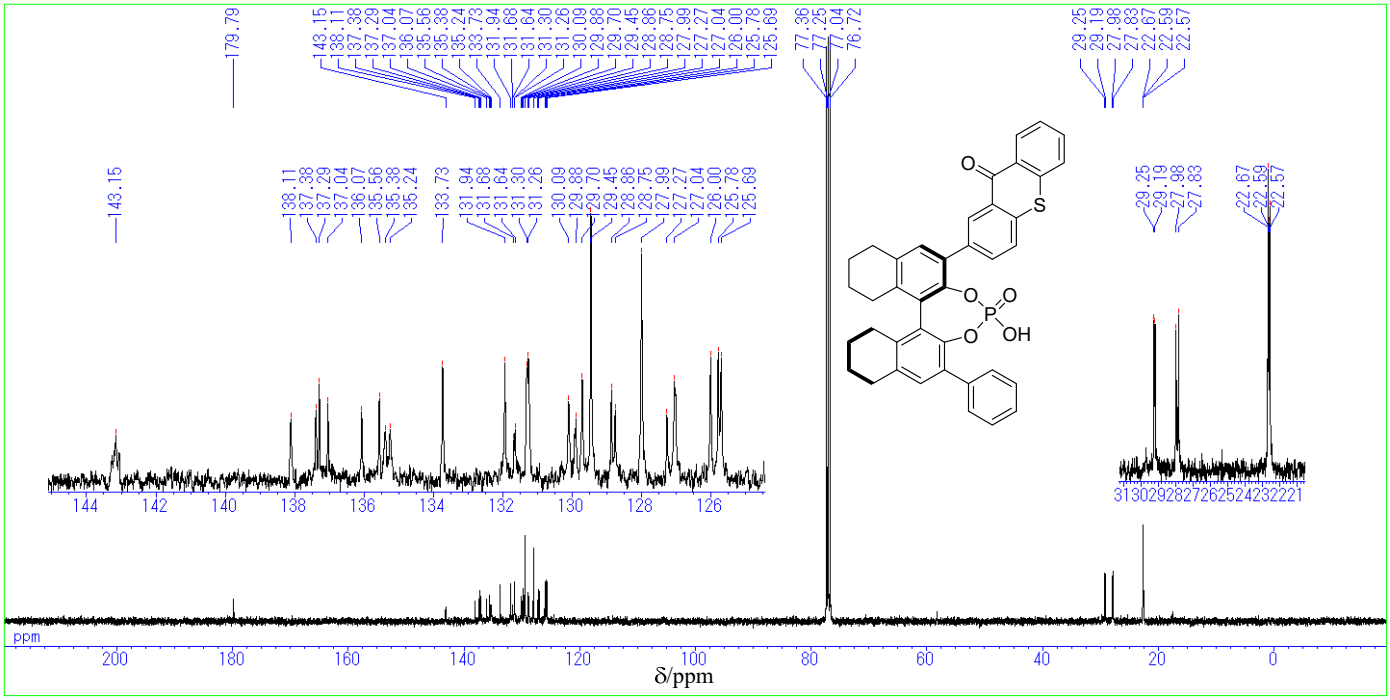
11. NMR Spectra of New Compounds

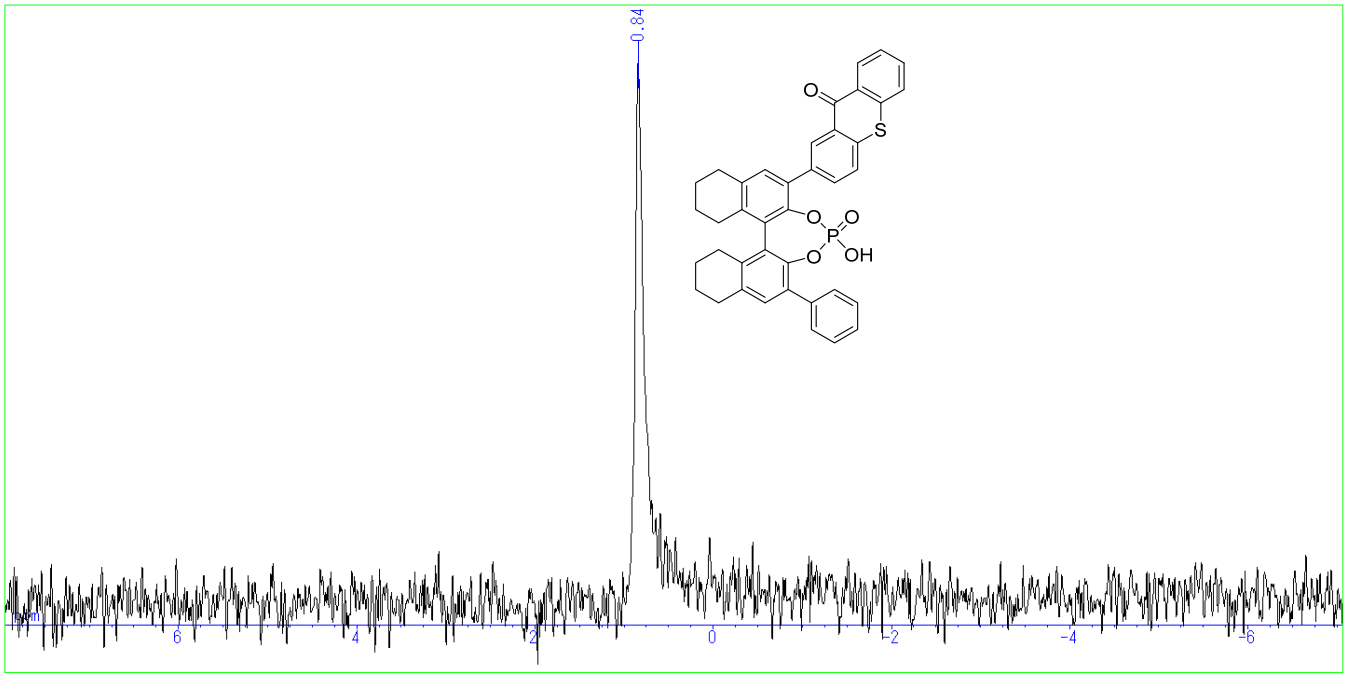


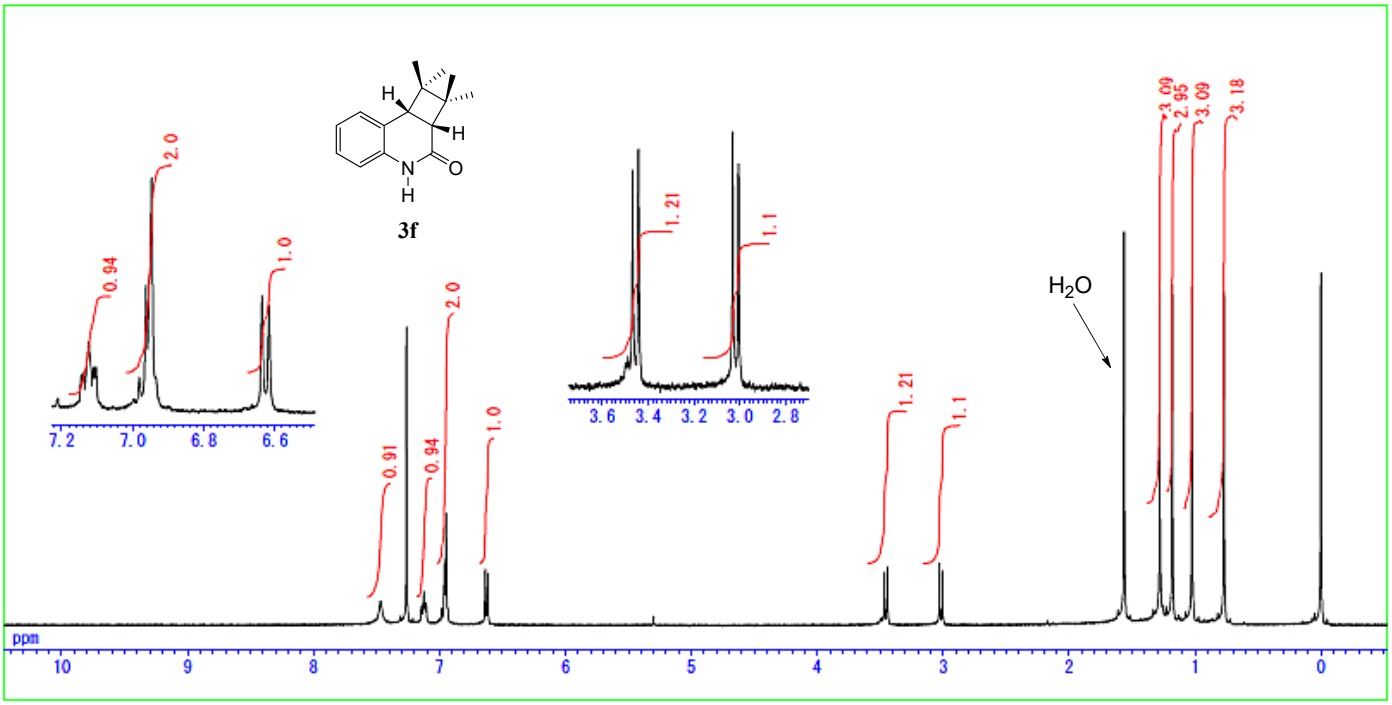


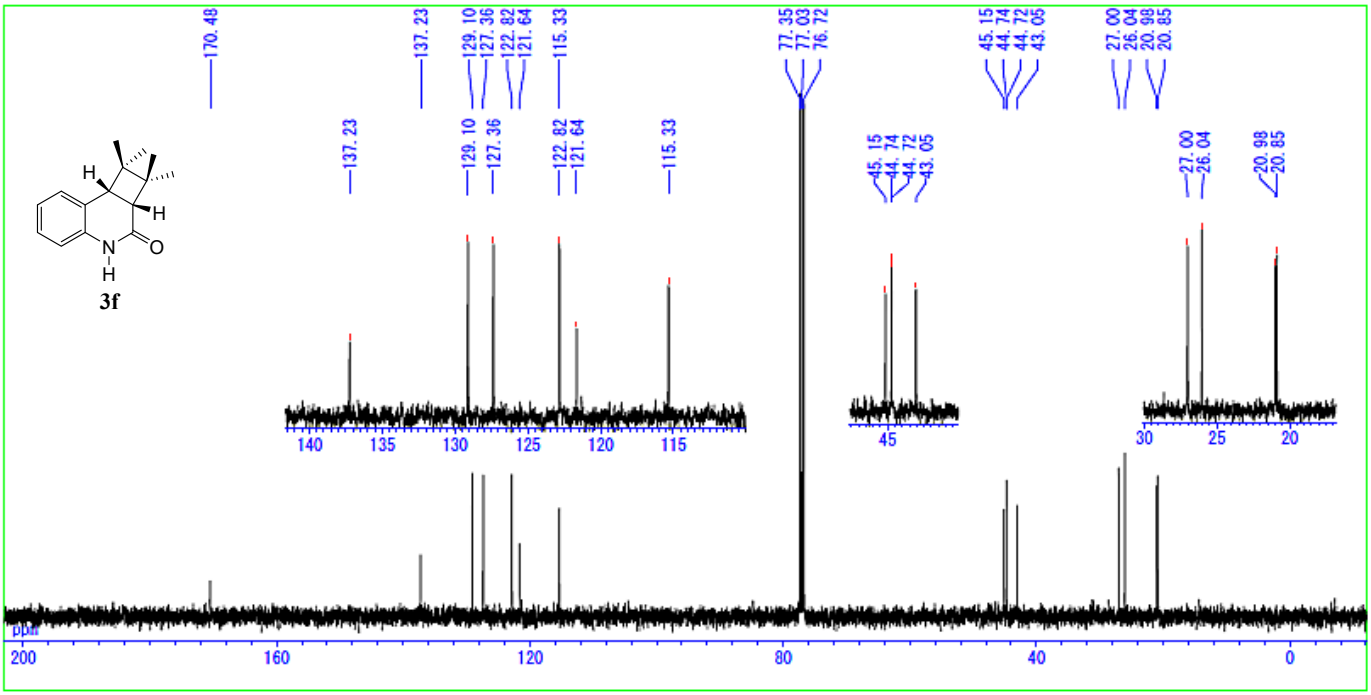

S3
CH2Cl2
ppm

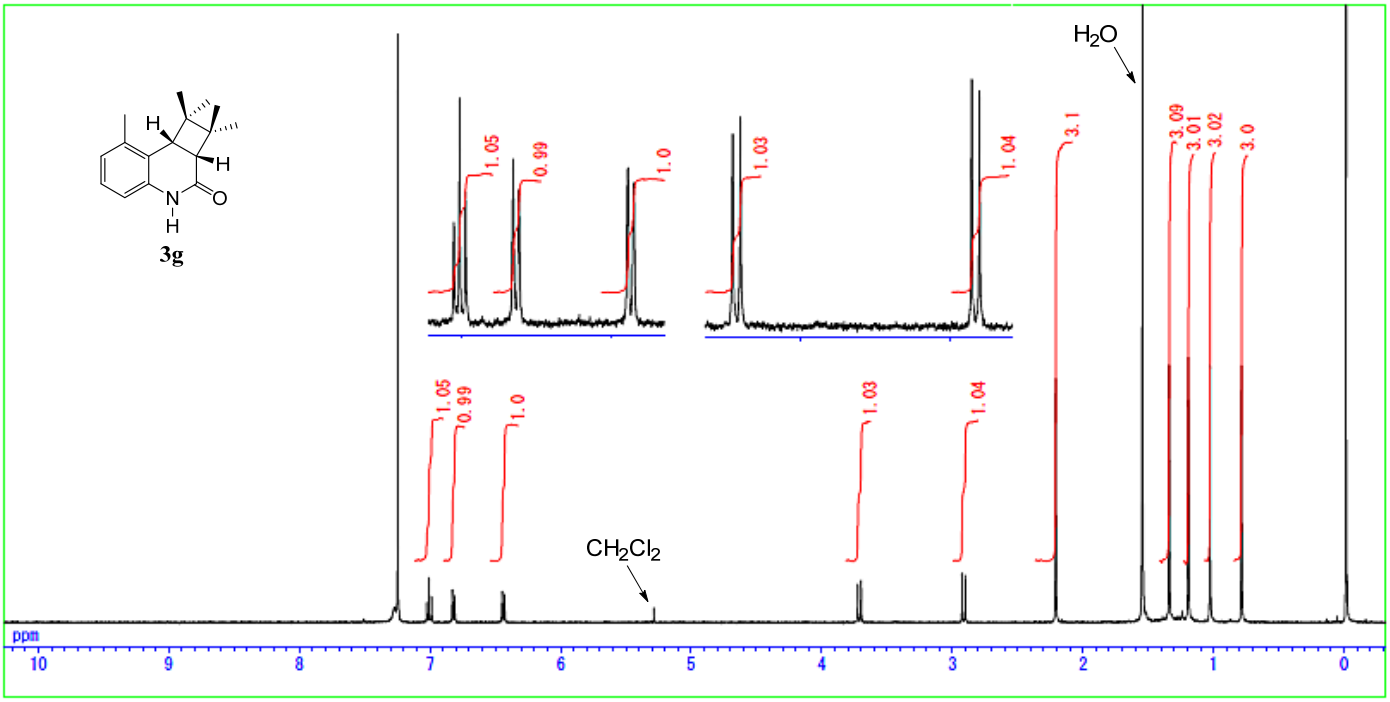

1c
ppm

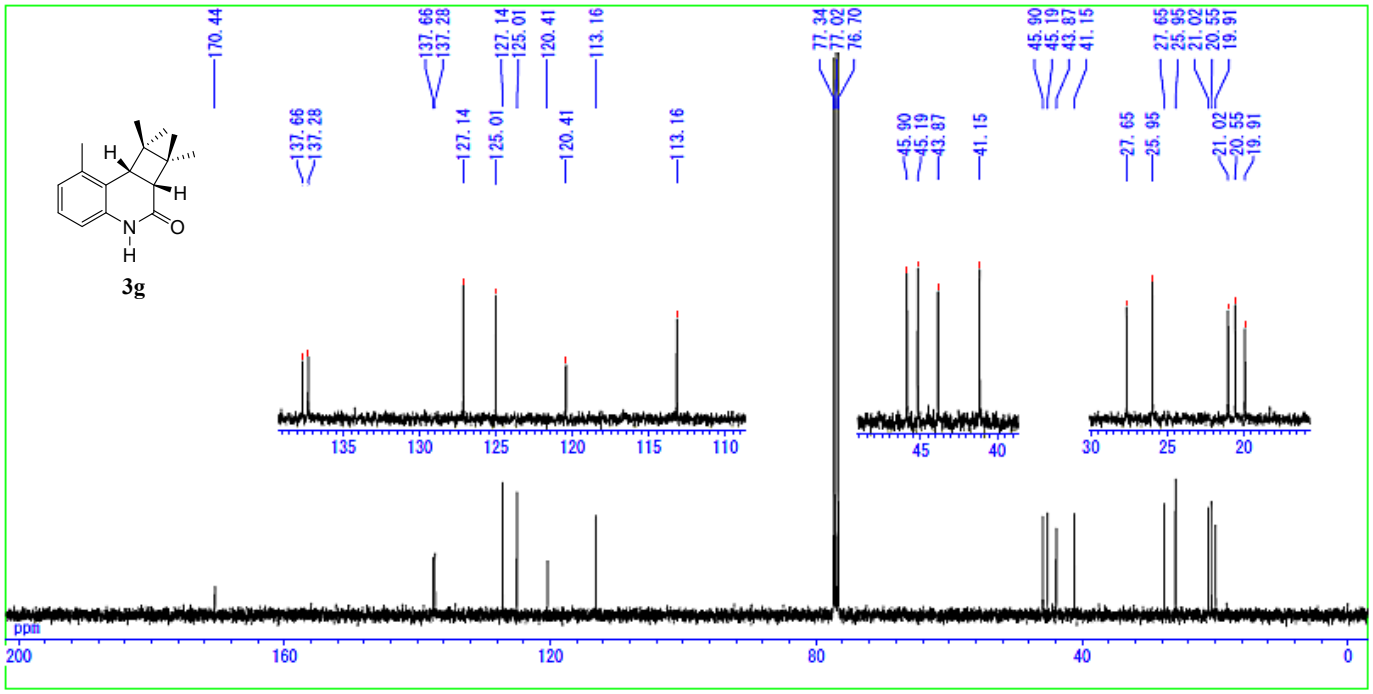

ppm
δ/ppm

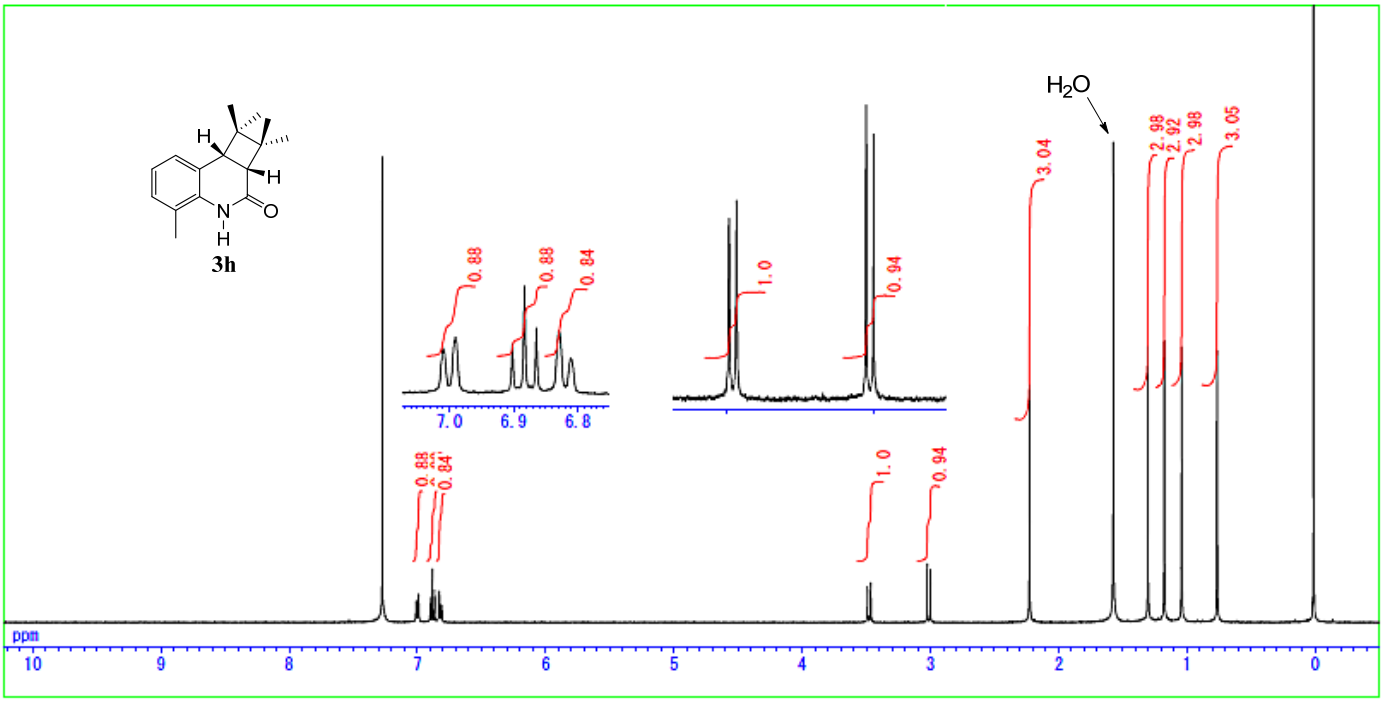

0.84
O
S
O
O
P
O
OH
ppm
6
4
2
0
-2
-4
-6

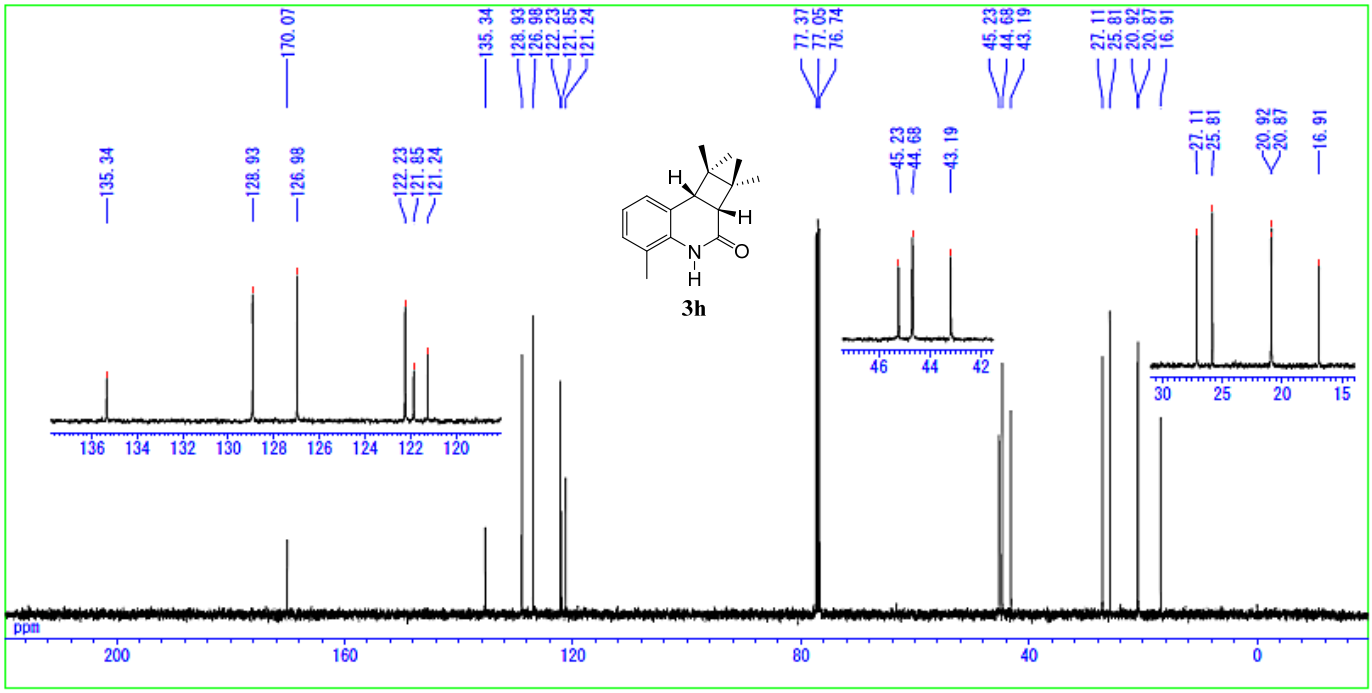

3f
H2O
ppm

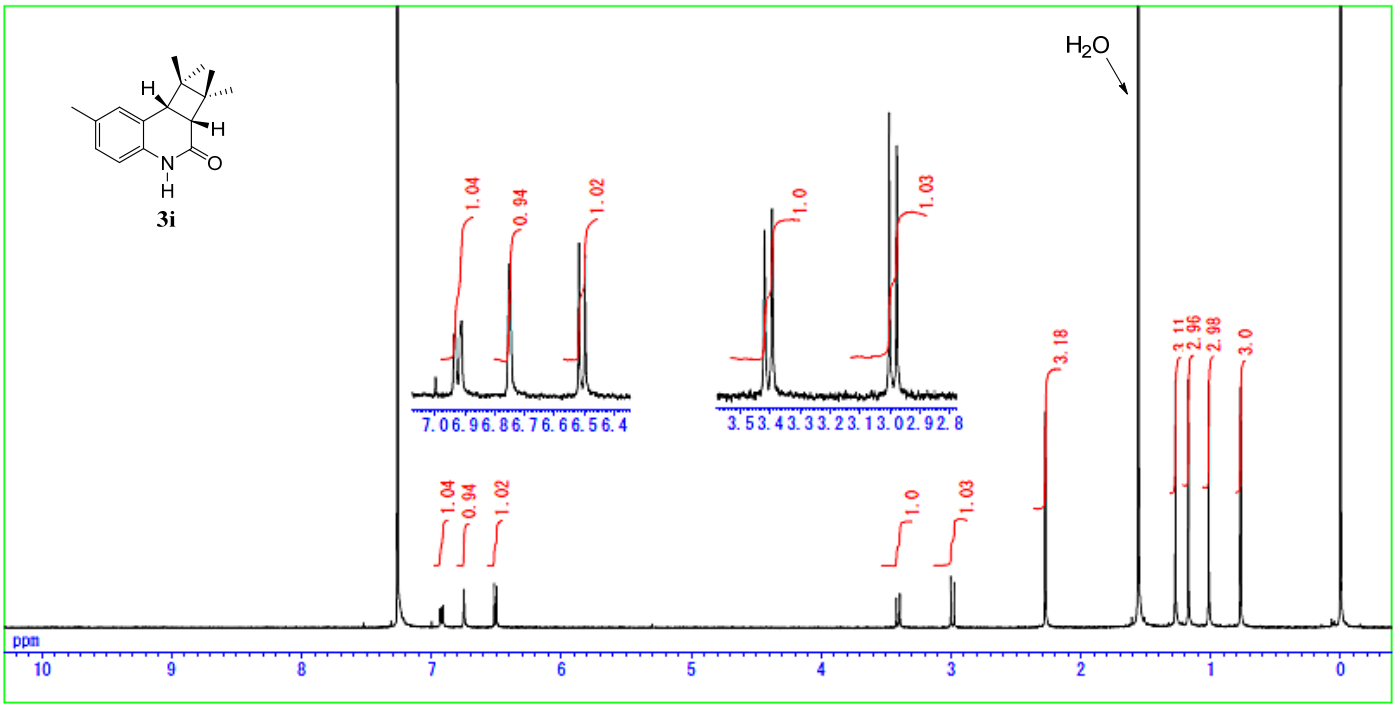

3f
ppm

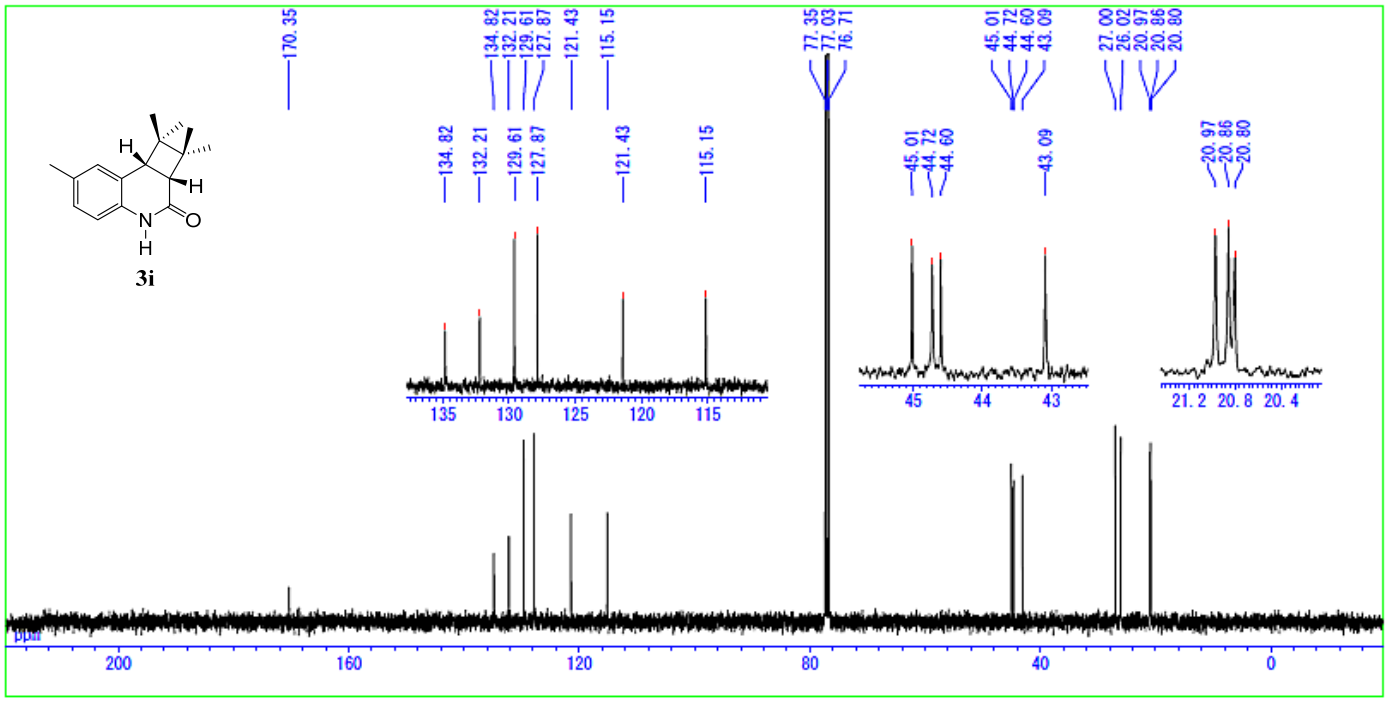

H
H
N
H
O
3g
H2O
CH2Cl2
1.05
0.99
1.0
1.03
1.04
3.1
3.09
3.01
3.02
3.0
ppm
10
9
8
7
6
5
4
3
2
1
0

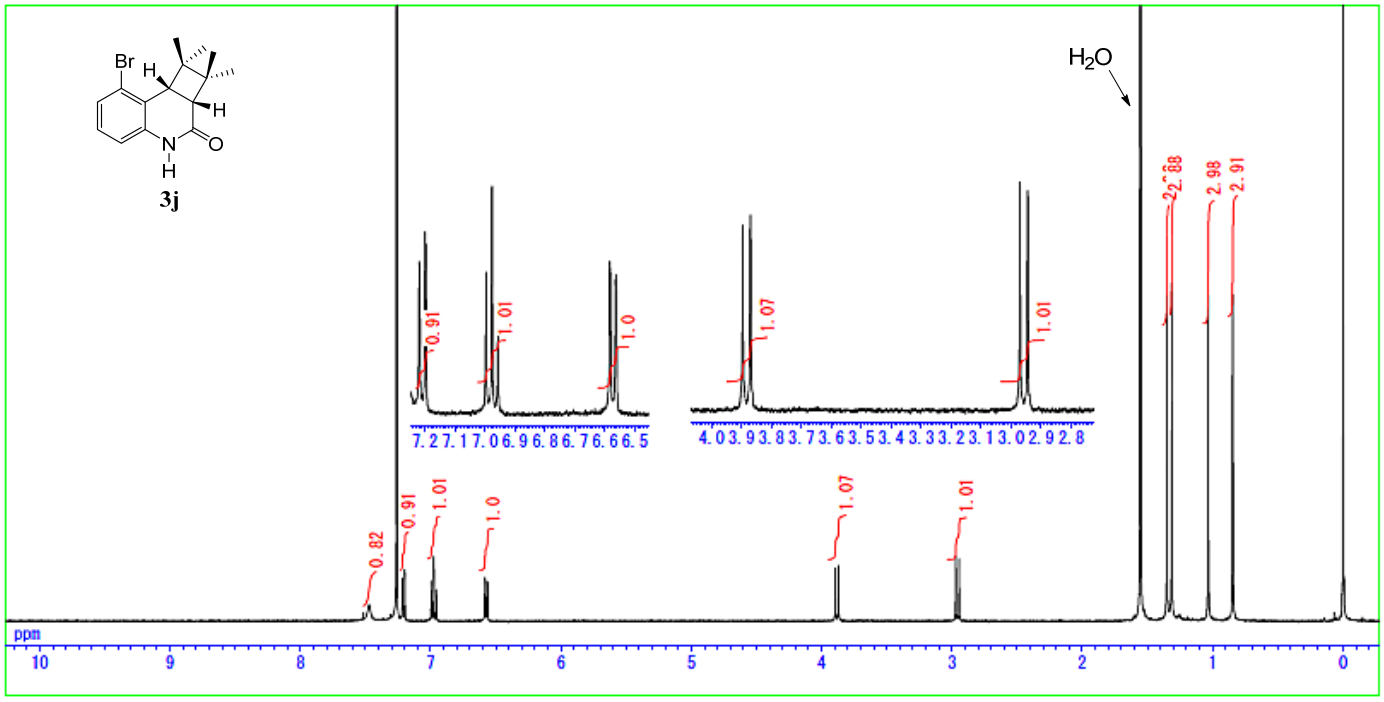

H
H
N
H
O
3g
170.44
137.66
137.28
127.14
125.01
120.41
113.16
77.34
77.02
76.70
45.90
45.19
43.87
41.15
27.65
25.95
21.02
20.55
19.91
135
130
125
120
115
110
45
40
30
25
20
ppm
200
160
120
80
40
0

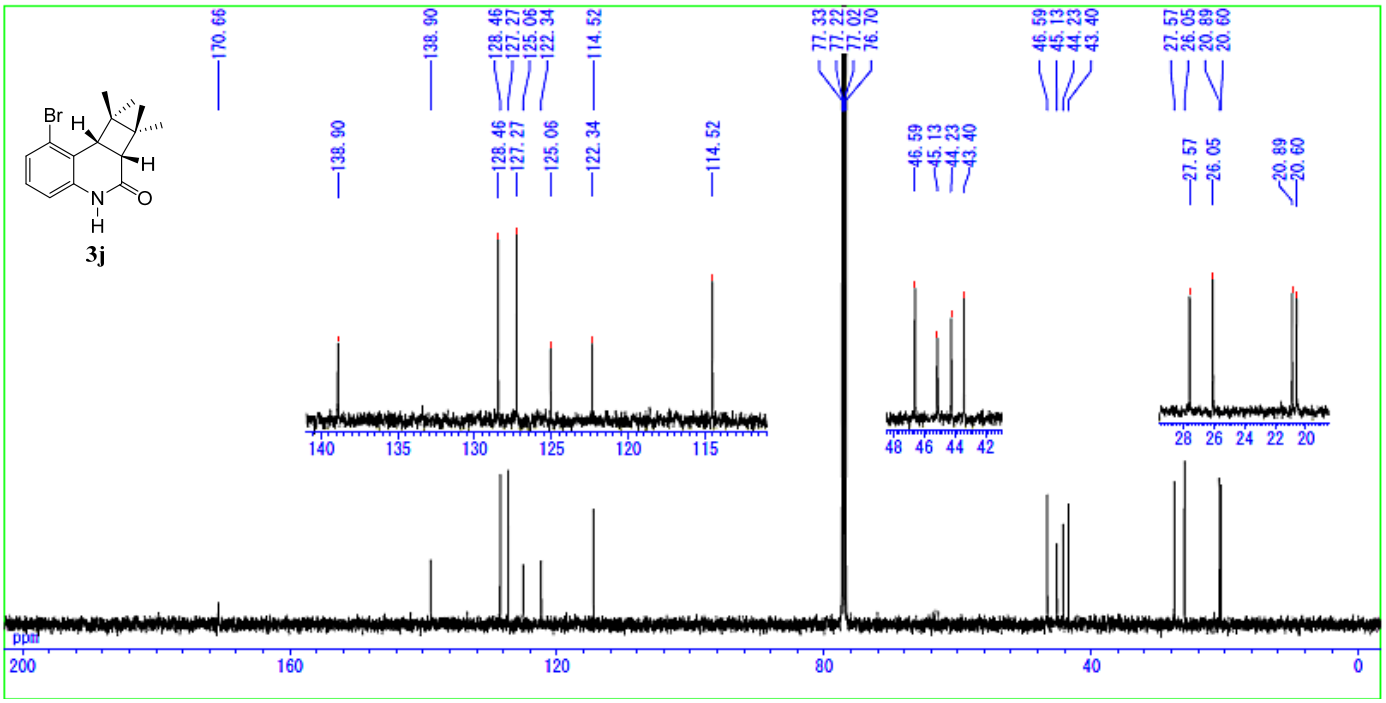

3h
H2O
0.88
0.88
0.84
1.0
0.94
3.04
2.98
2.92
2.98
3.05
ppm

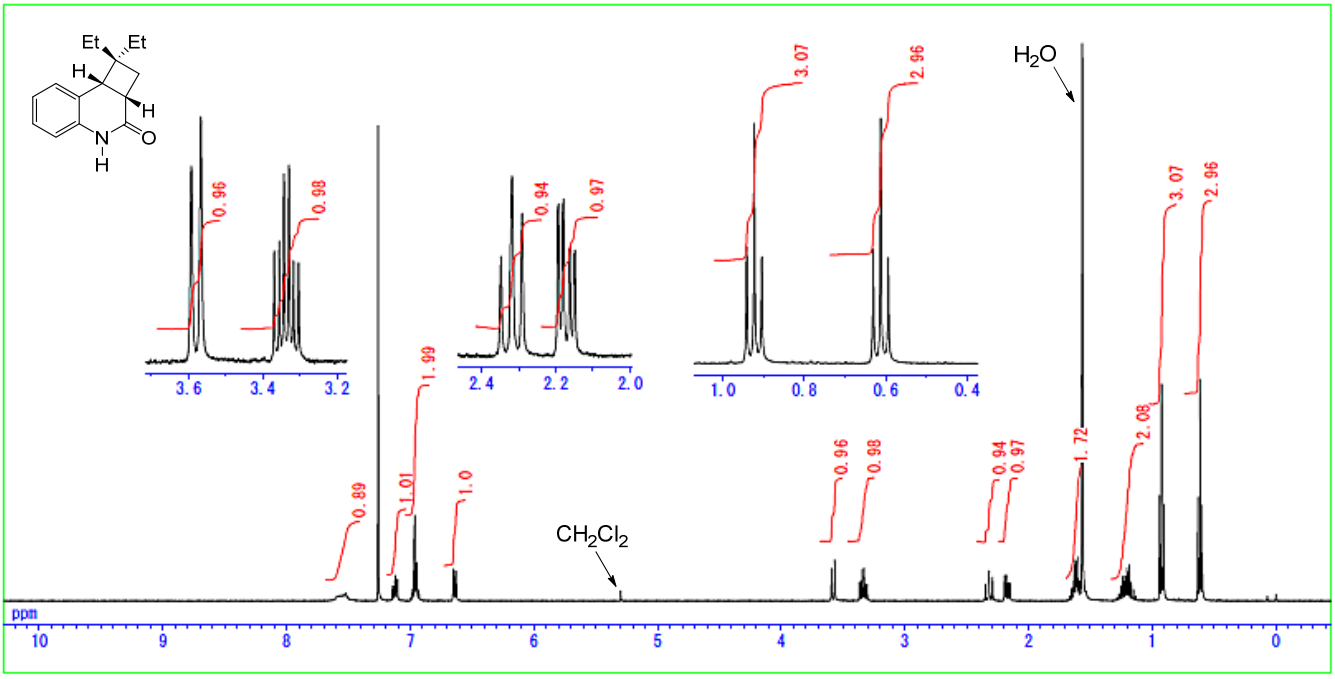

3h
170.07
135.34
128.93
126.98
122.23
121.85
121.24
77.37
77.05
76.74
45.23
44.68
43.19
27.11
25.81
20.92
20.87
16.91
ppm

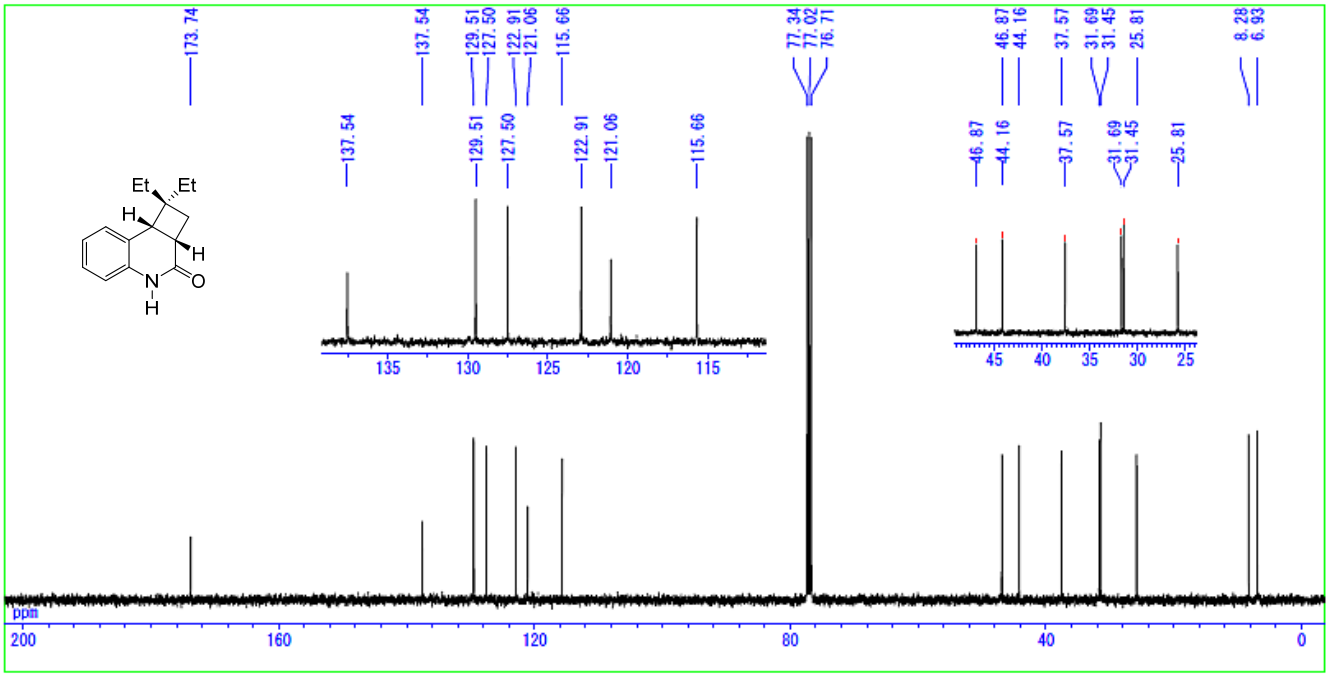

H
H
N
H
O
3i
H2O
1.04
0.94
1.02
1.0
1.03
3.18
3.11
2.96
2.98
3.0
ppm
10
9
8
7
6
5
4
3
2
1
0

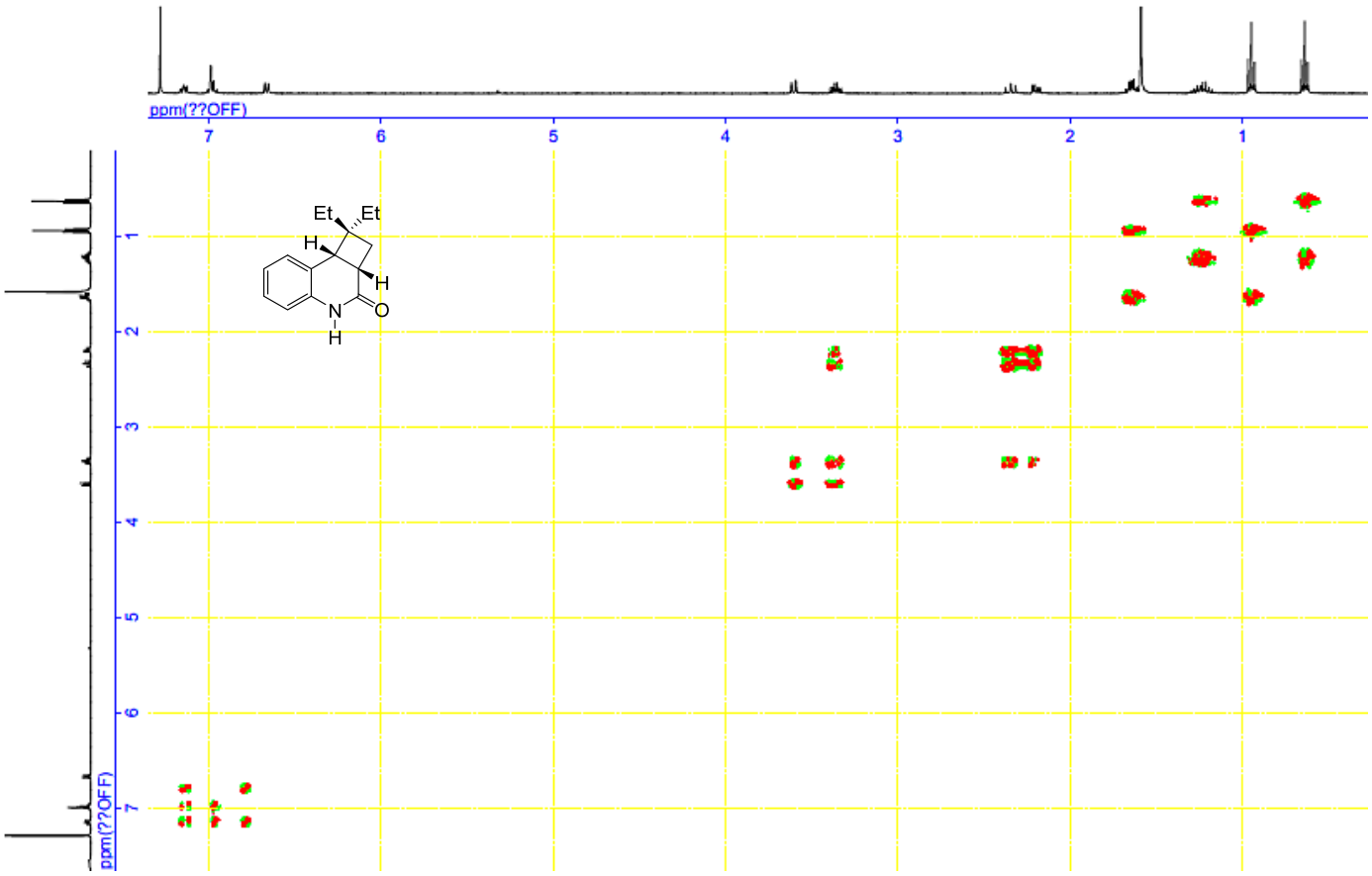

H
H
N
H
O
3i
170.35
134.82
132.21
129.61
127.87
121.43
115.15
77.35
77.03
76.71
45.01
44.72
44.60
43.09
27.00
26.02
20.97
20.86
20.80
ppm
200
160
120
80
40
0

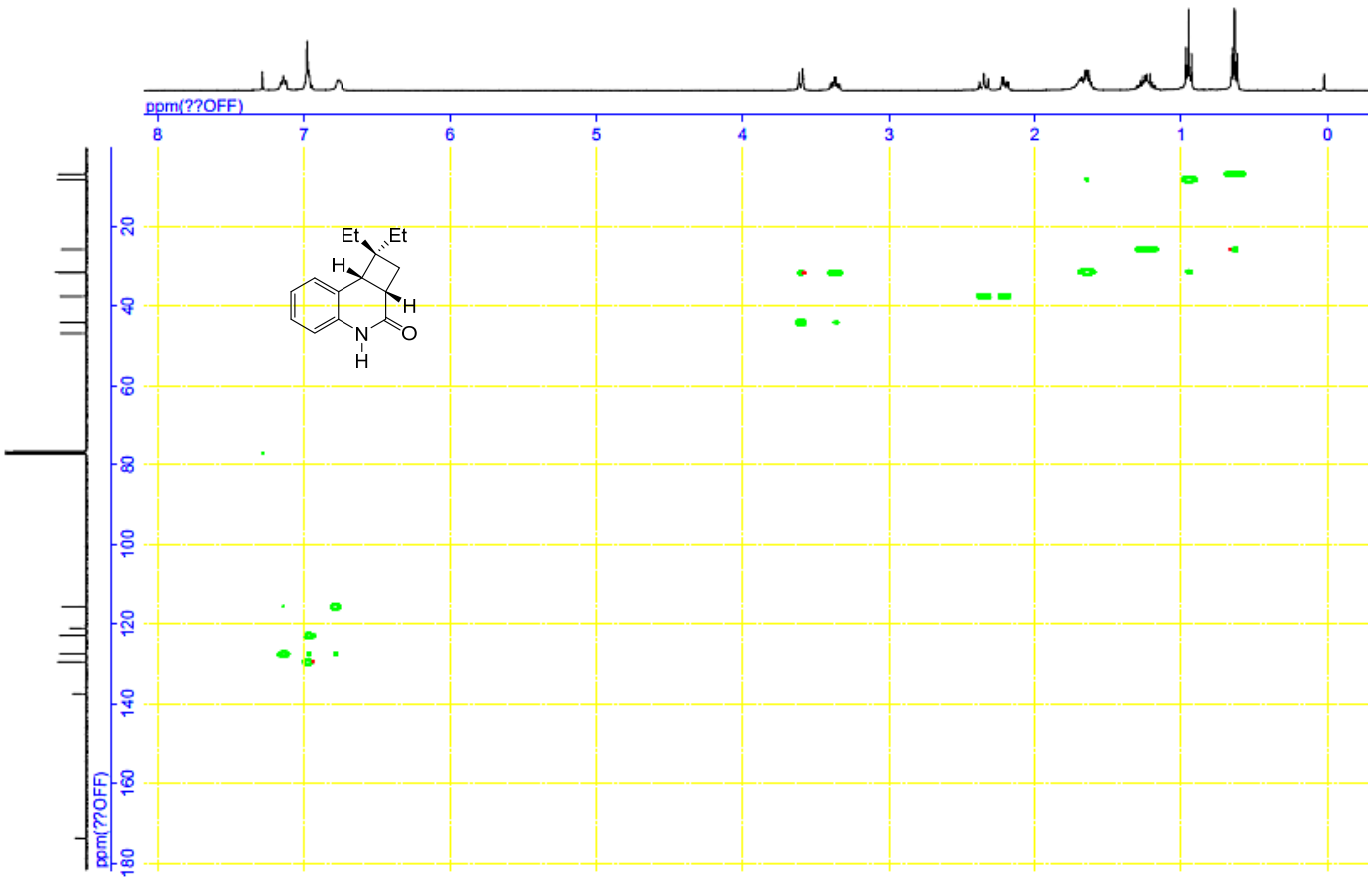

Br
H
H
N
H
O
3j
H2O
2.88
2.98
2.91
0.91
1.01
1.0
1.07
1.01
0.82
0.91
1.01
1.0
1.07
1.01
ppm
10
9
8
7
6
5
4
3
2
1
0

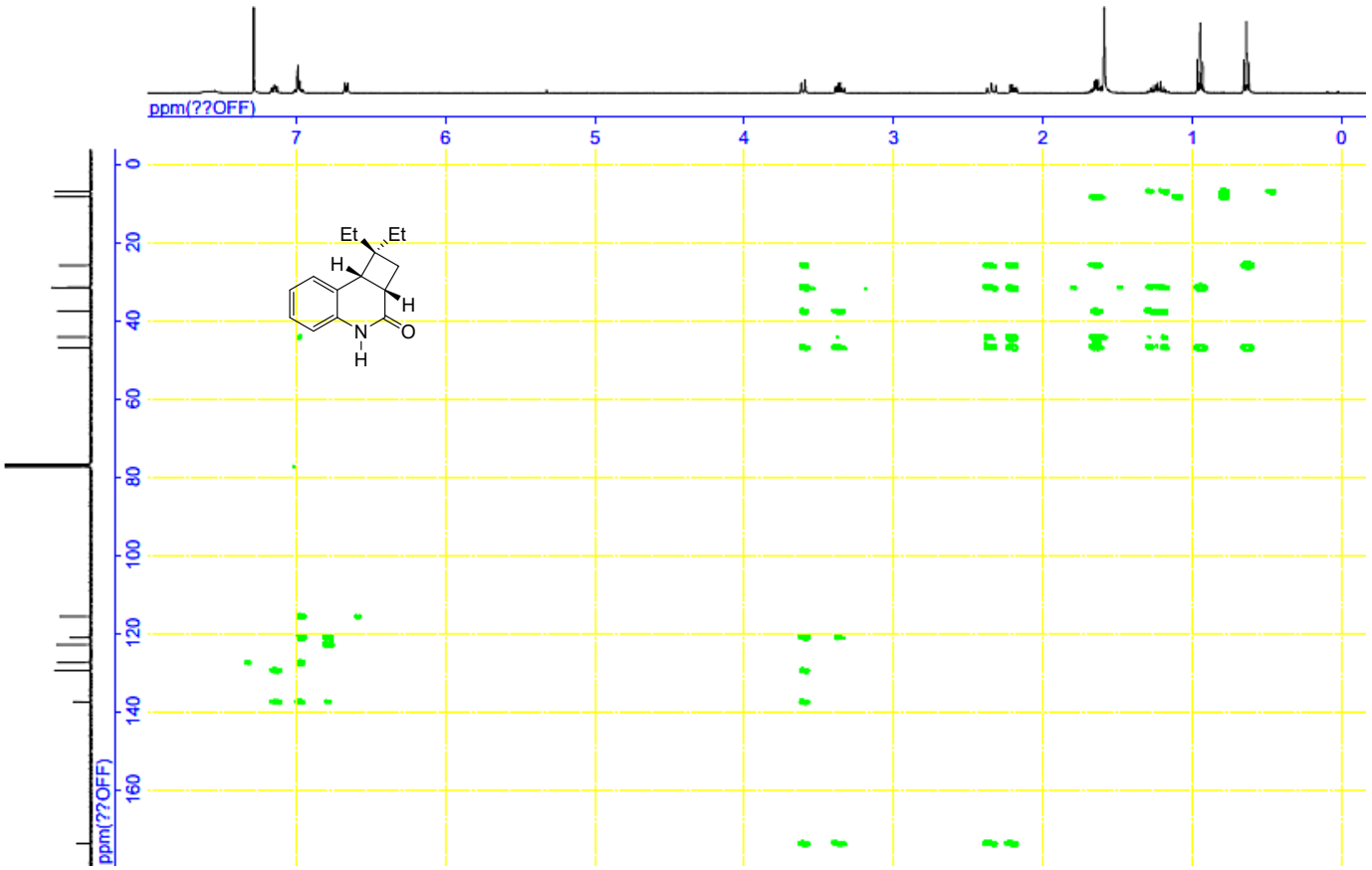

170.66
138.90
128.46
127.27
125.06
122.34
114.52
77.33
77.22
77.02
76.70
46.59
45.13
44.23
43.40
27.57
26.05
20.89
20.60
Br
H
H
N
H
O
3j
ppm
200
160
120
80
40
0

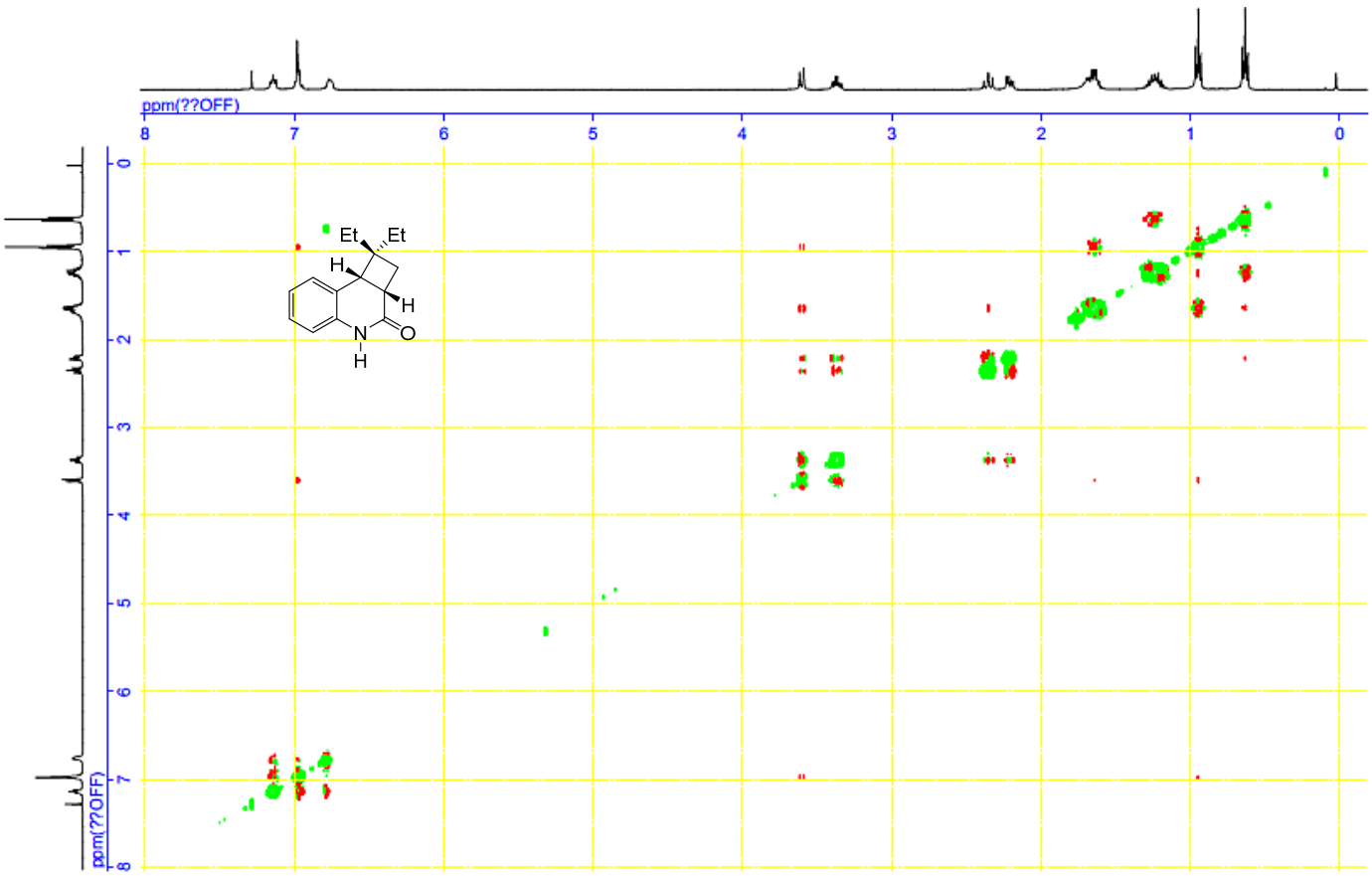

Et
Et
H
H
N
H
O
0.96
0.98
0.94
0.97
3.07
2.96
H2O
1.99
1.01
1.0
0.89
CH2Cl2
1.72
2.08
ppm


173.74
137.54
129.51
127.50
122.91
121.06
115.66
77.34
77.02
76.71
46.87
44.16
37.57
31.69
31.45
25.81
8.28
6.93
Et
Et
H
H
N
H
O
ppm


ppm(??OFF)
7
6
5
4
3
2
1
Et
Et
H
H
N
H
O
ppm(??OFF)
1
2
3
4
5
6
7


ppm(??OFF)
8
7
6
5
4
3
2
1
0
Et
Et
H
H
N
H
O
ppm(??OFF)
20
40
60
80
100
120
140
160
180


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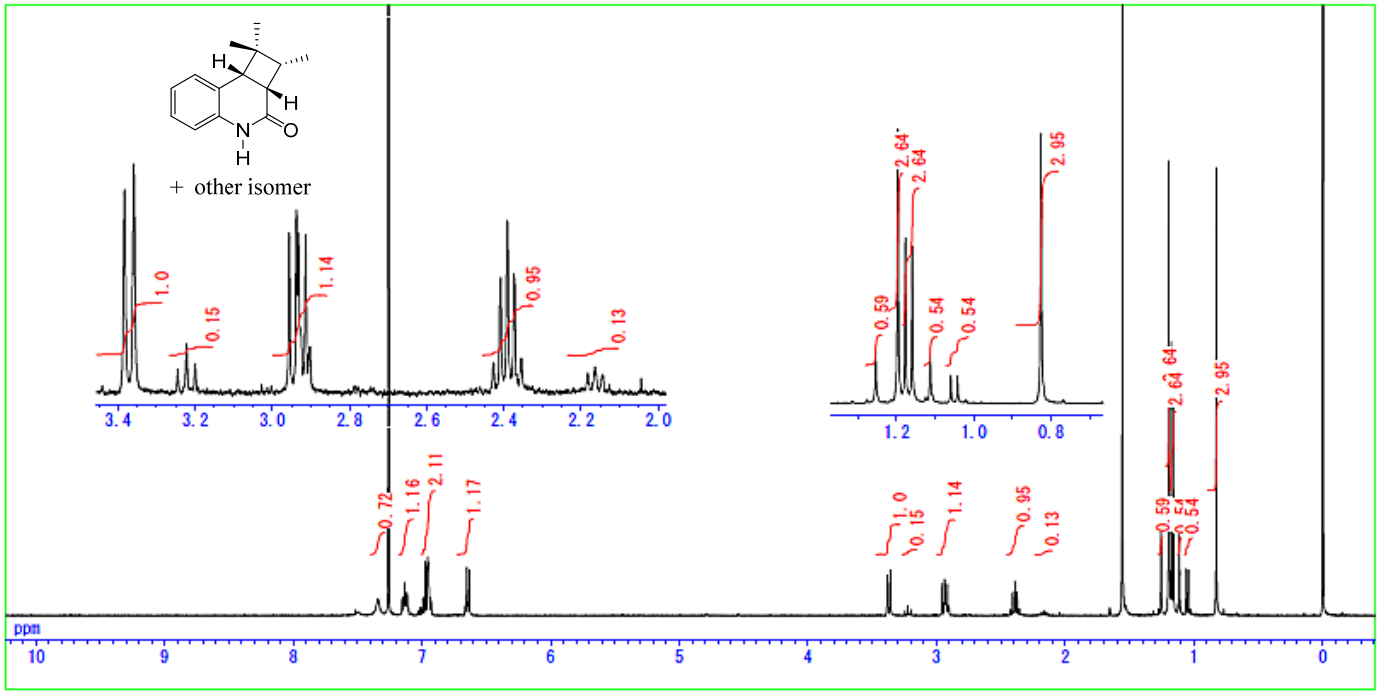
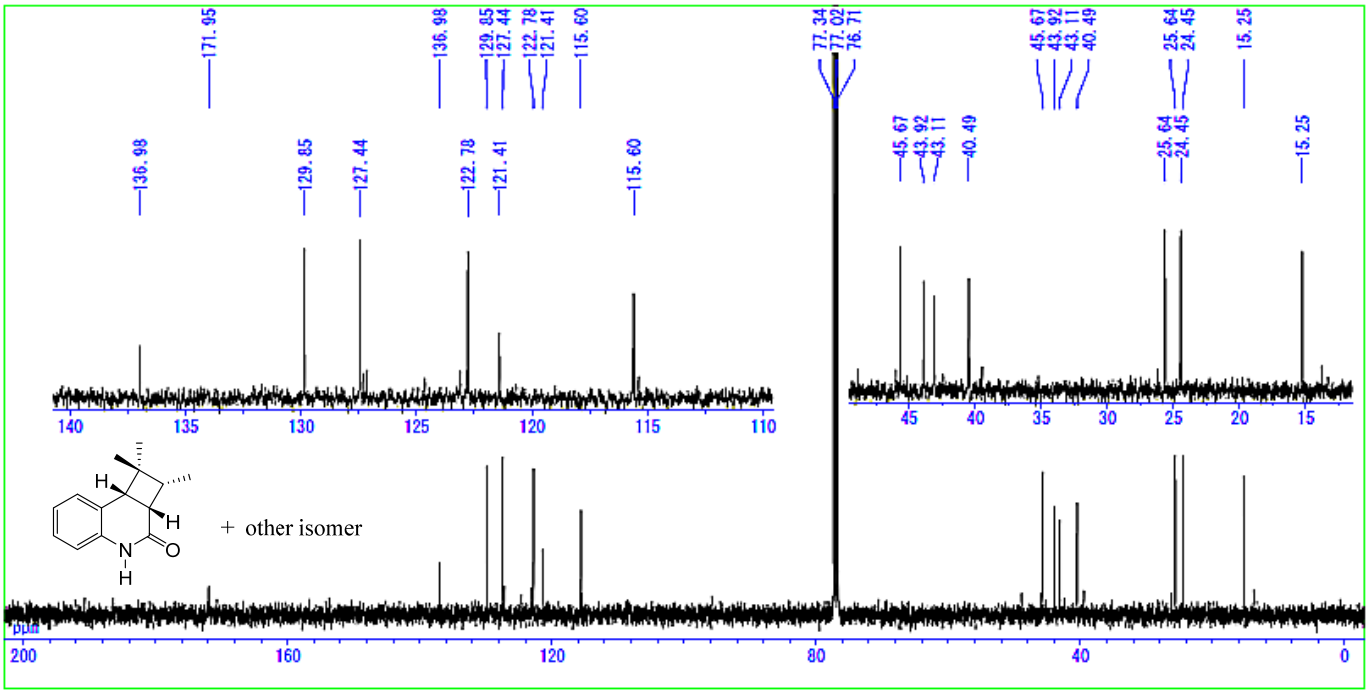
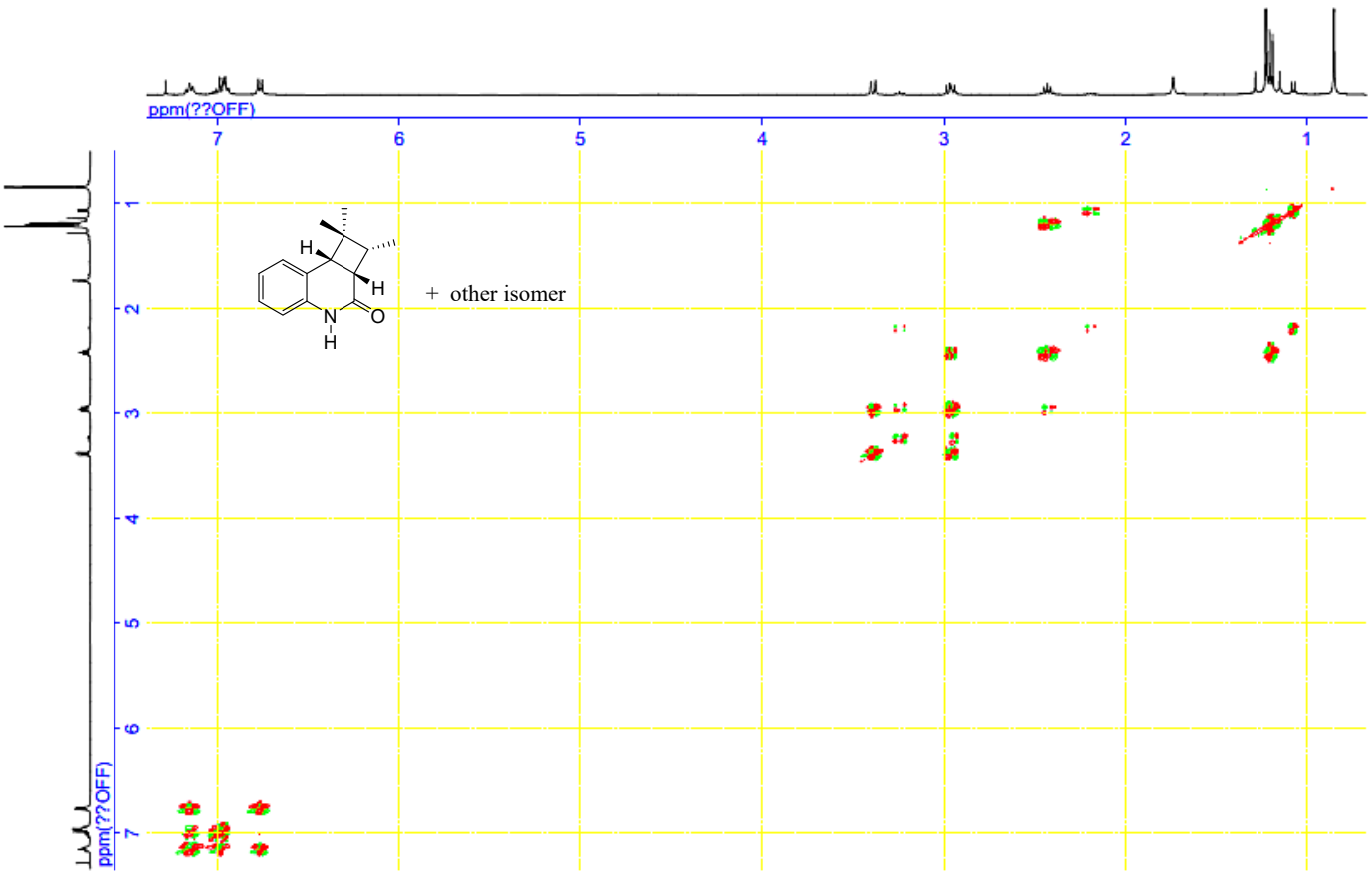
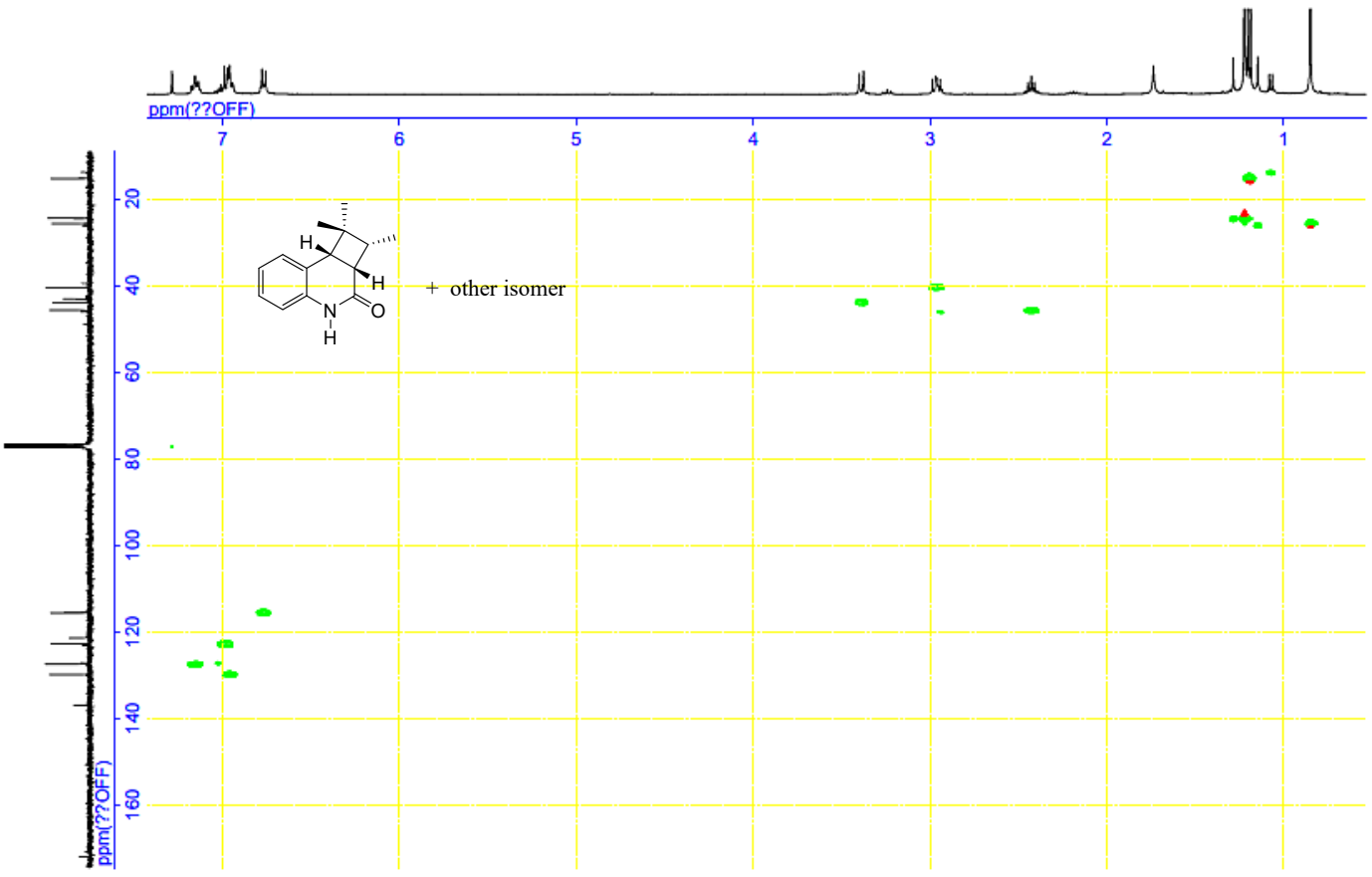
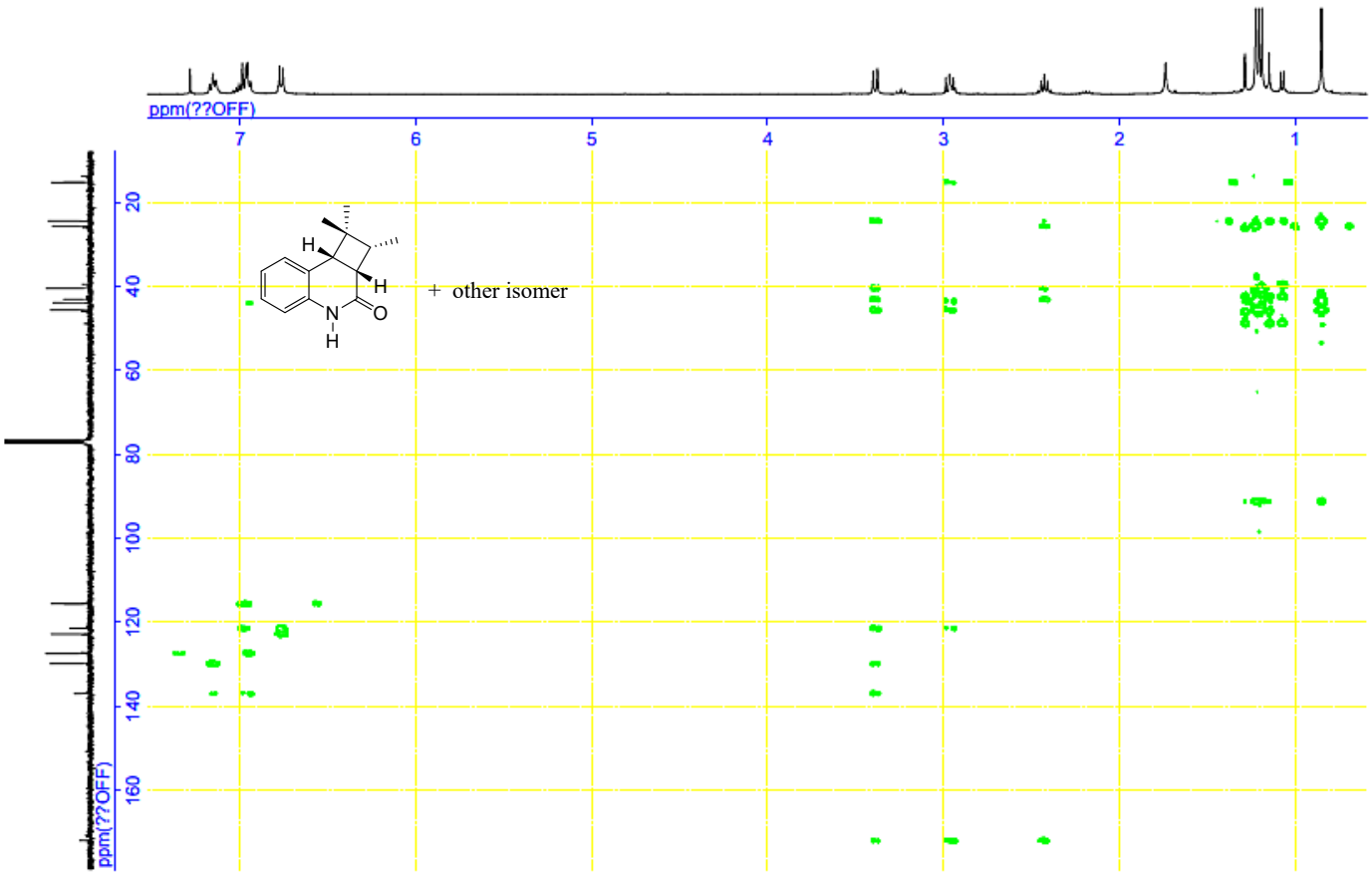
8
7
6
5
4
3
2
1
0
0
1
2
3
4
5
6
7
8
ppm(??OFF)
Et
Et
H
H
N
H
O

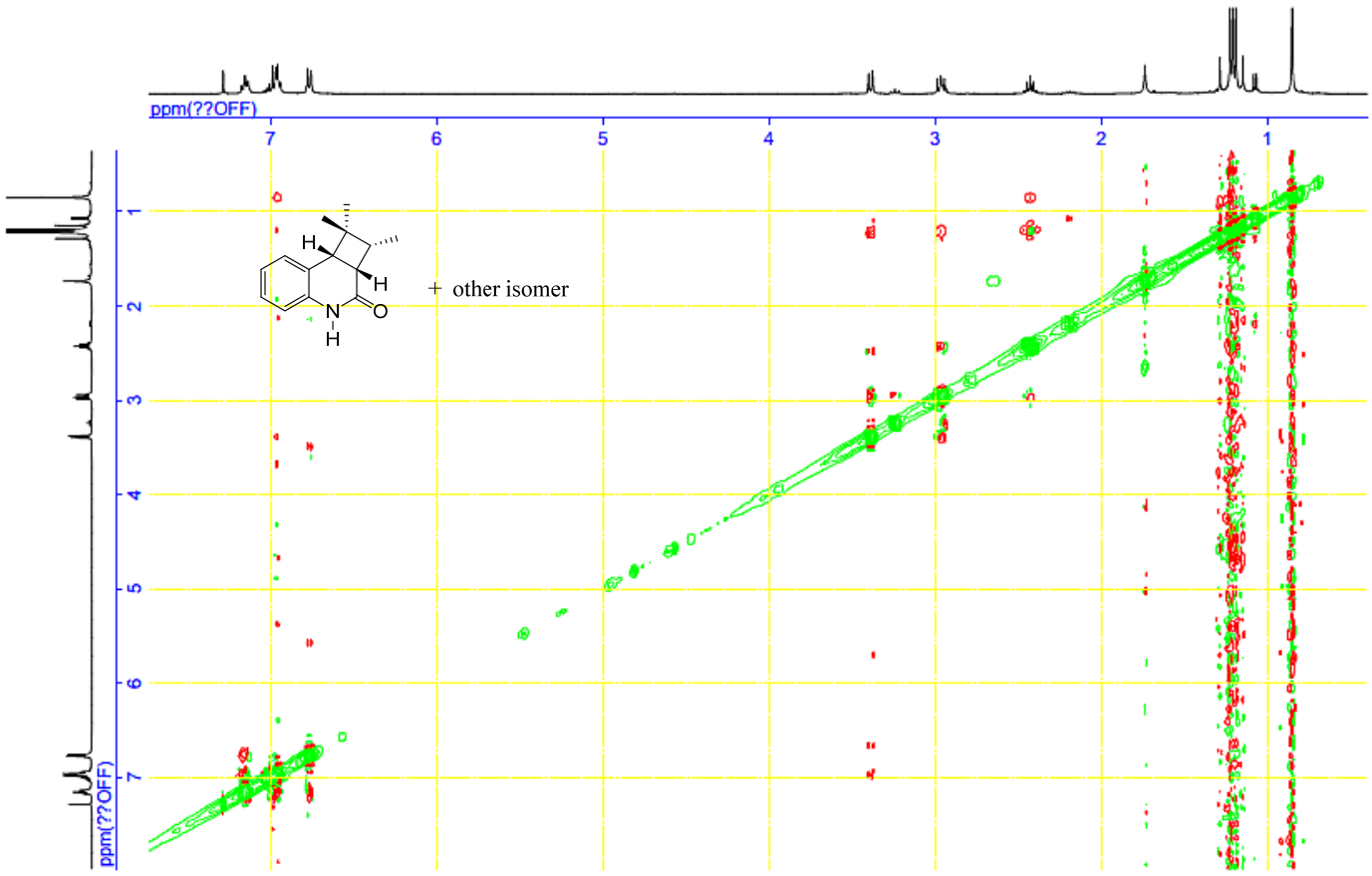

+ other isomer
ppm

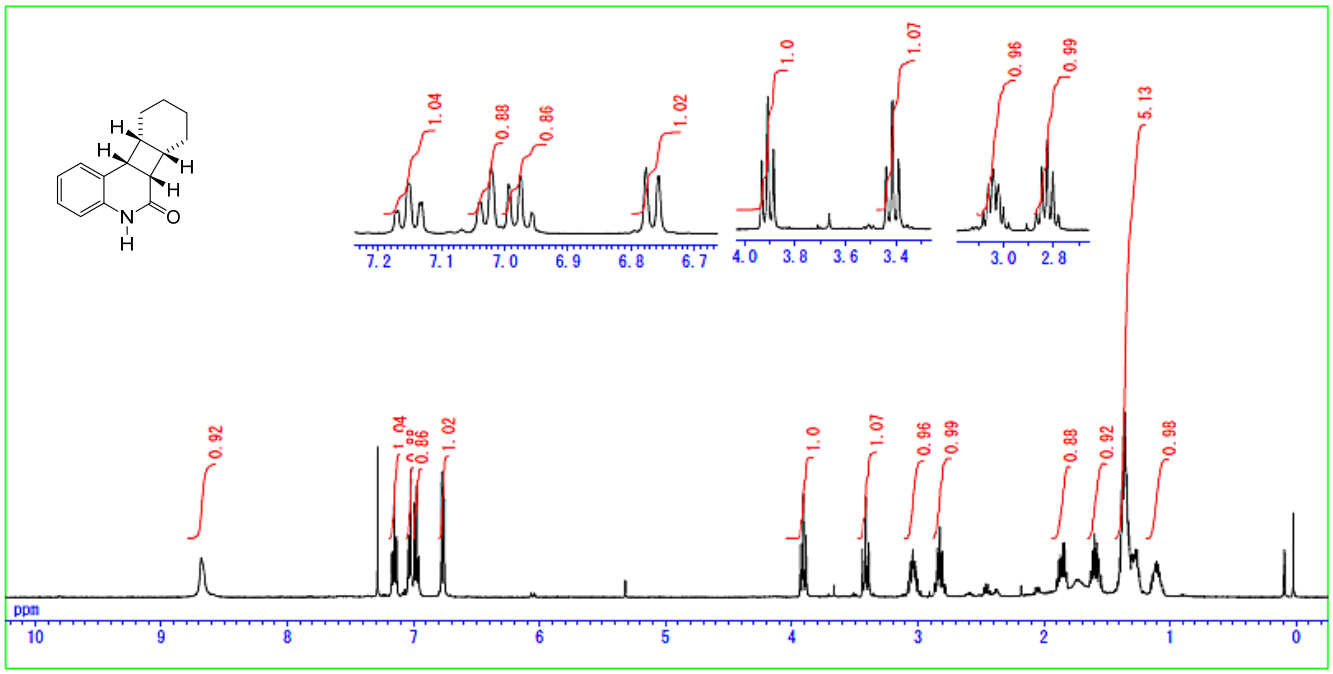

+ other isomer
ppm

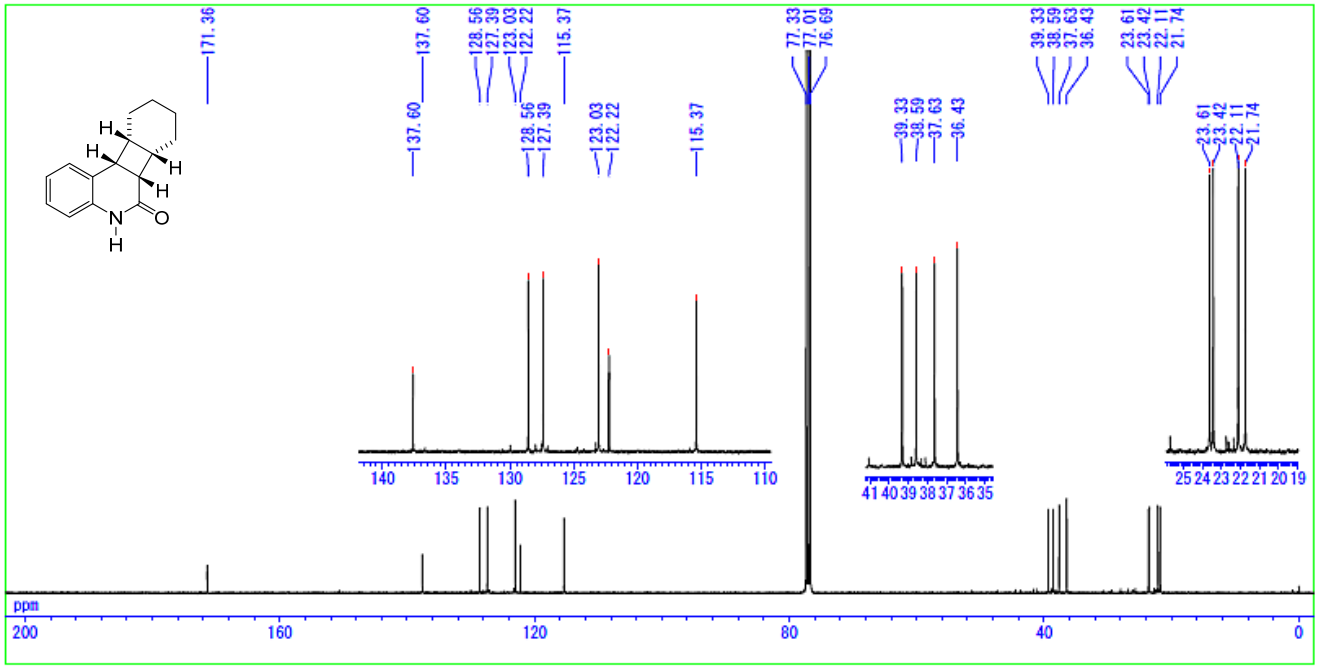

ppm(??OFF)
+ other isomer

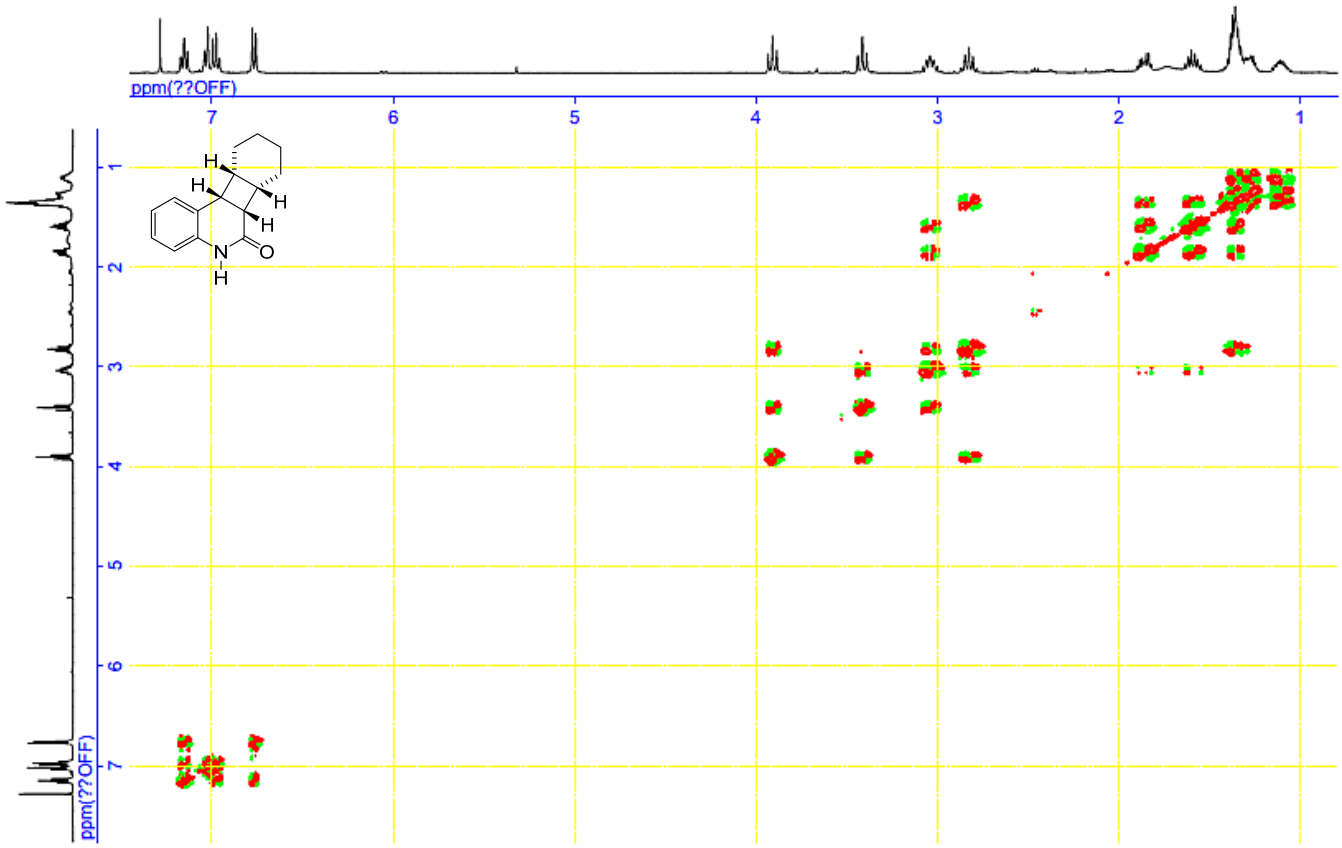

ppm(??OFF)
+ other isomer


ppm(??OFF)
+ other isomer


ppm(??OFF)
+ other isomer


1.04
0.88
0.86
1.02
1.0
1.07
0.96
0.99
5.13
0.92
0.98
ppm


171.36
137.60
128.56
127.39
123.03
122.22
115.37
77.33
77.01
76.69
39.33
38.59
37.63
36.43
23.61
23.42
22.11
21.74
ppm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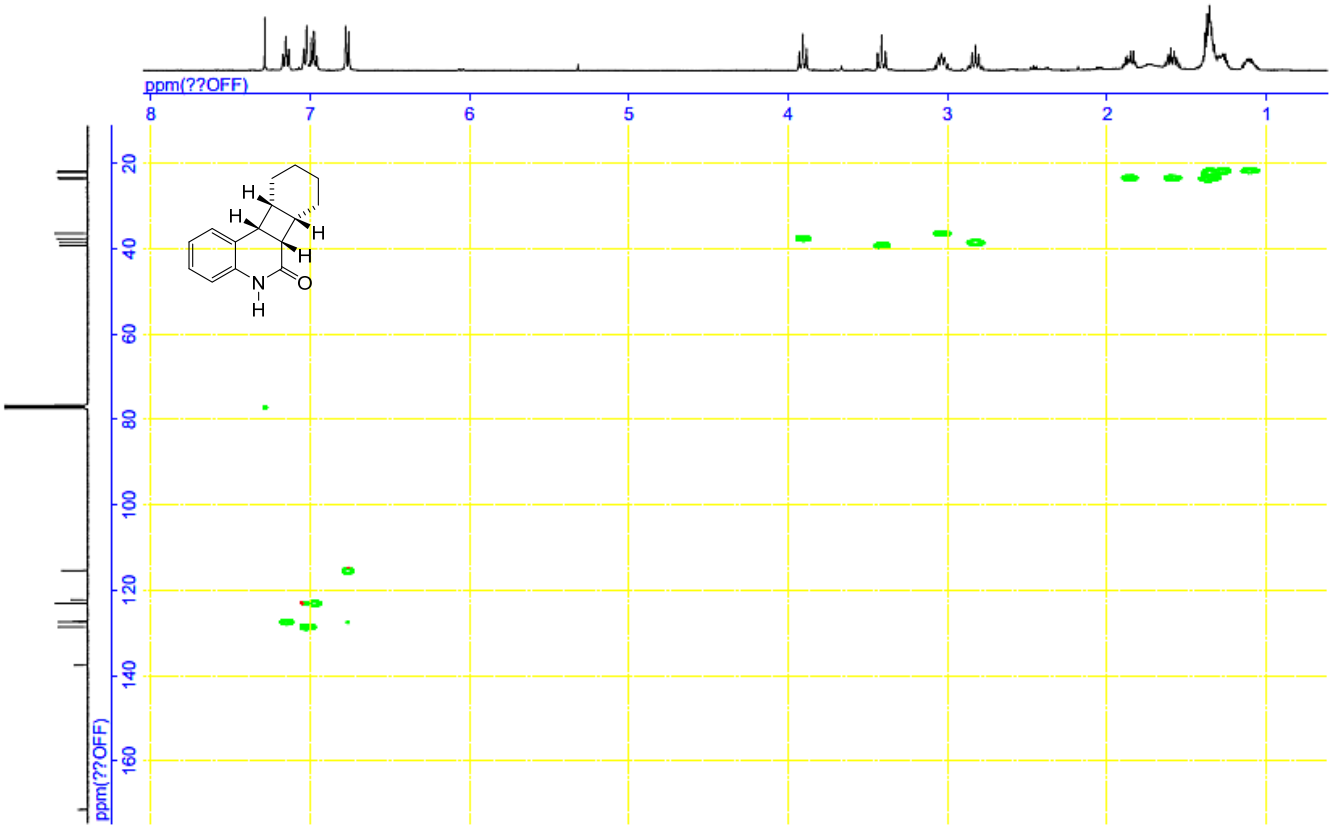
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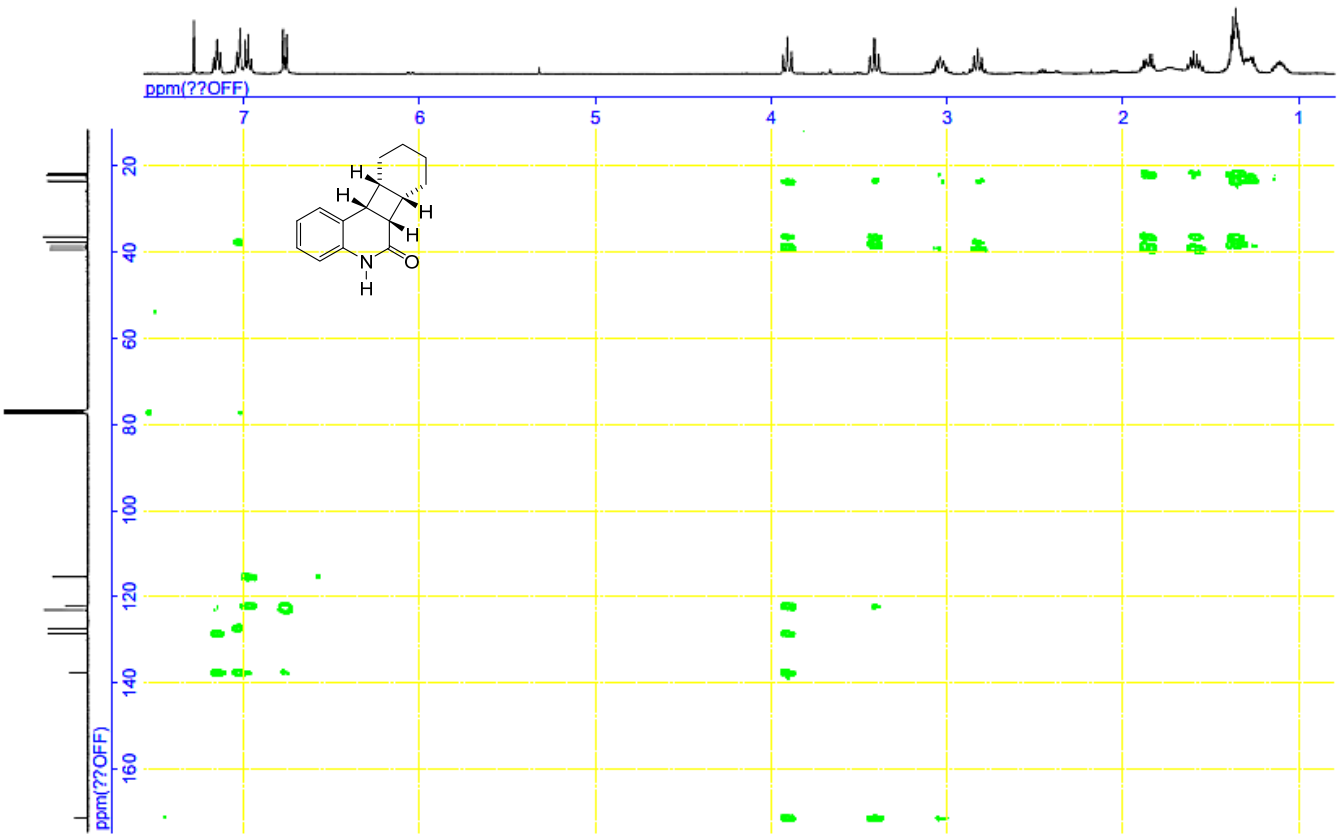
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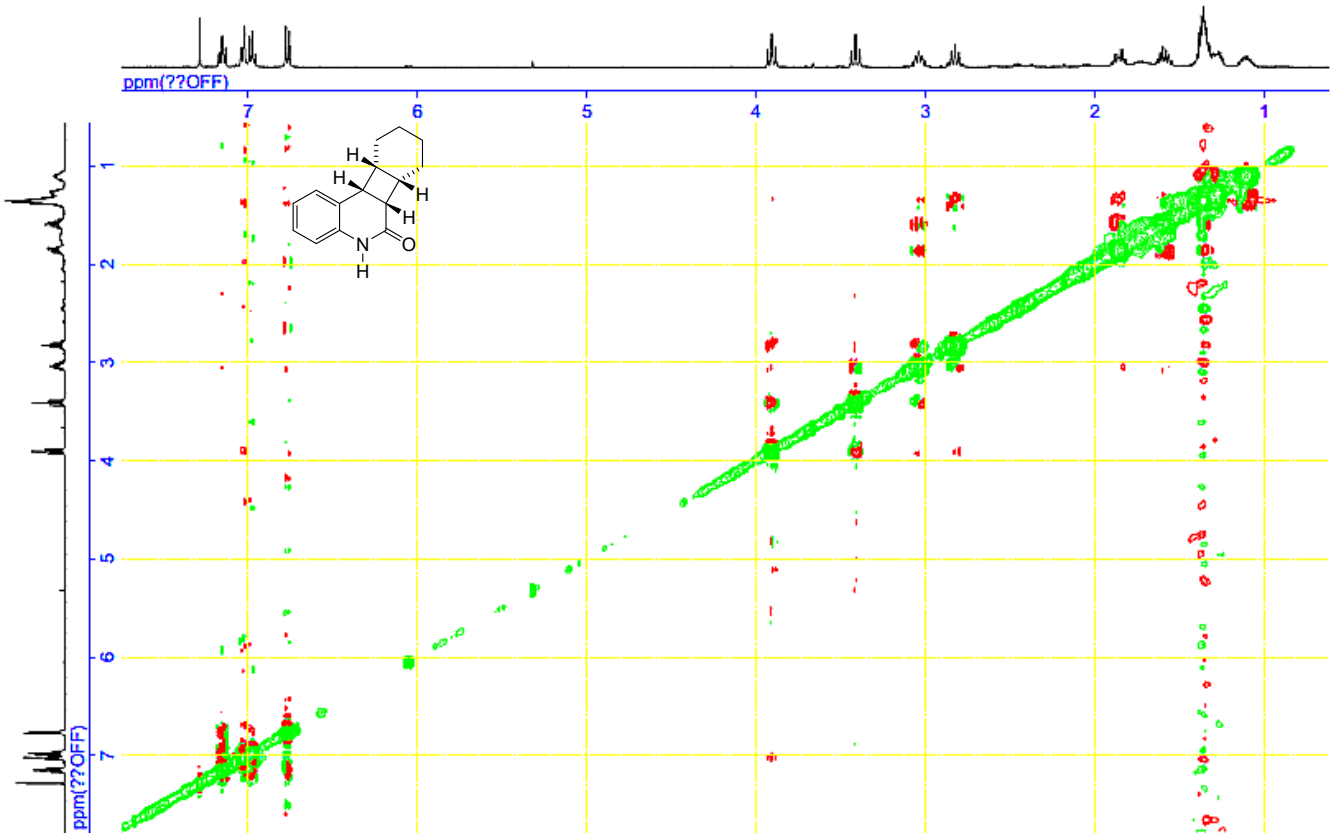
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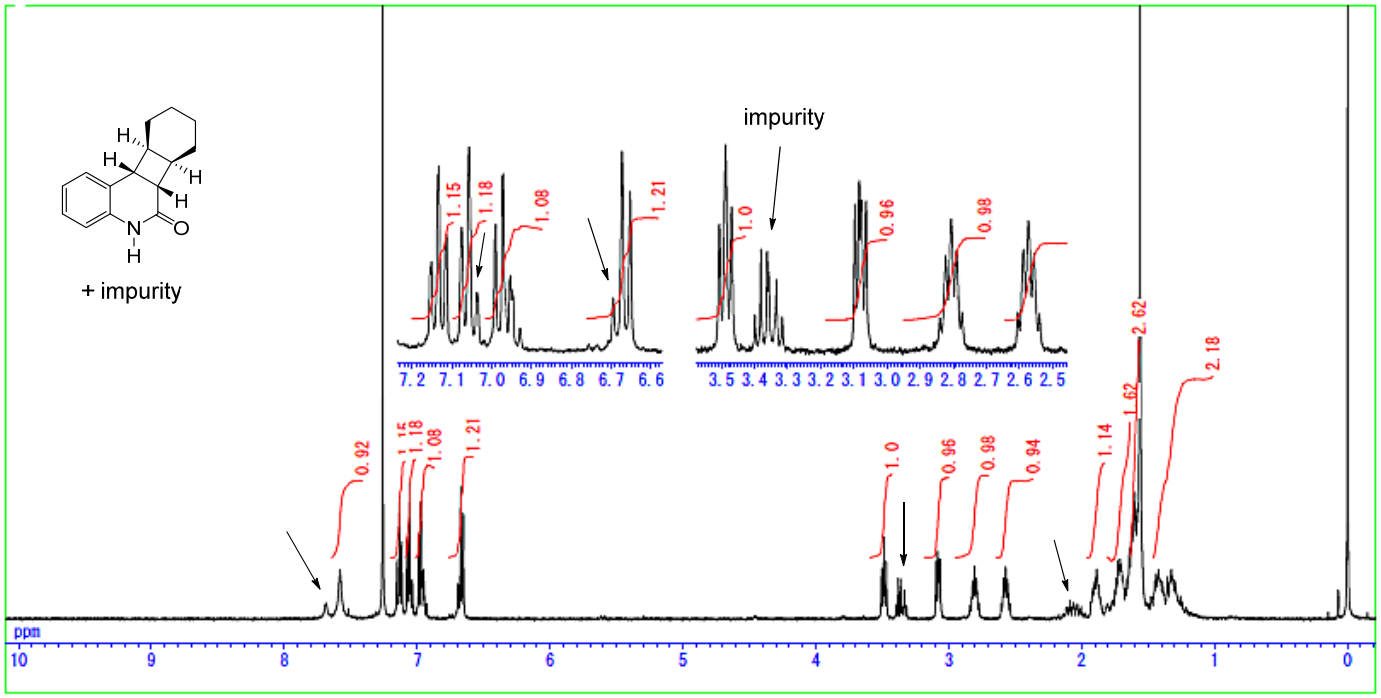
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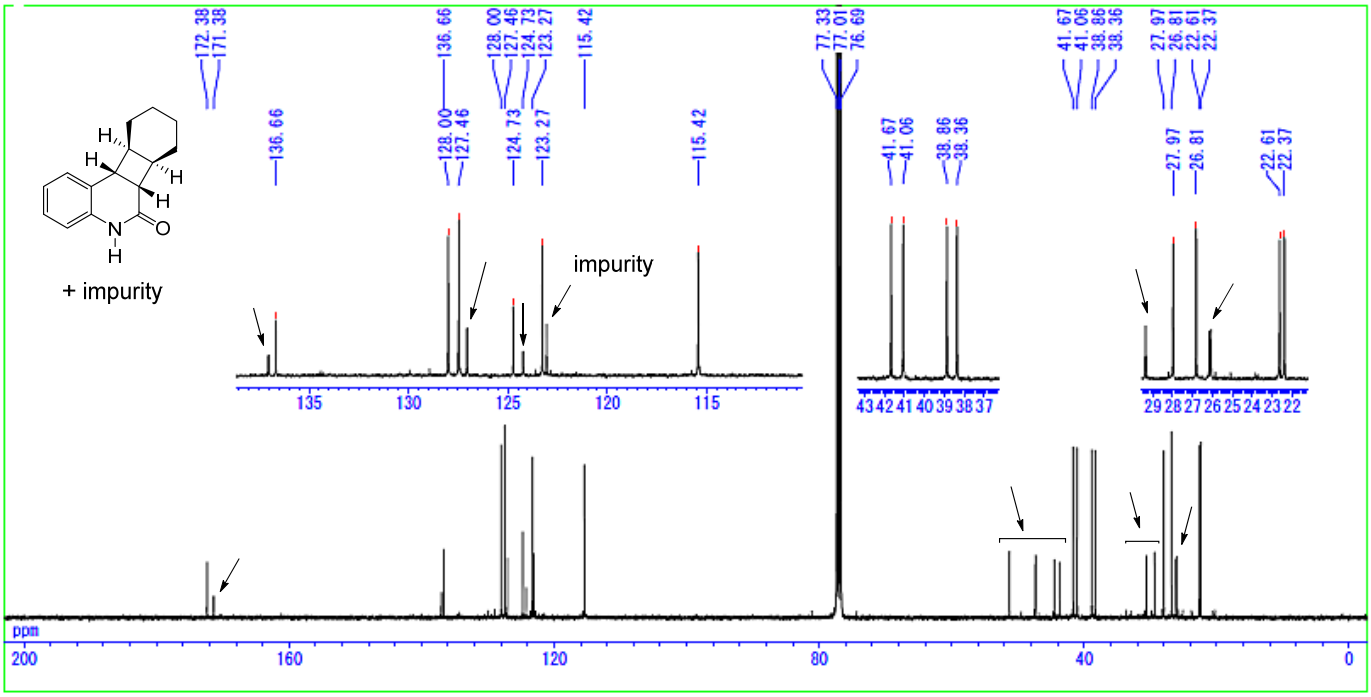
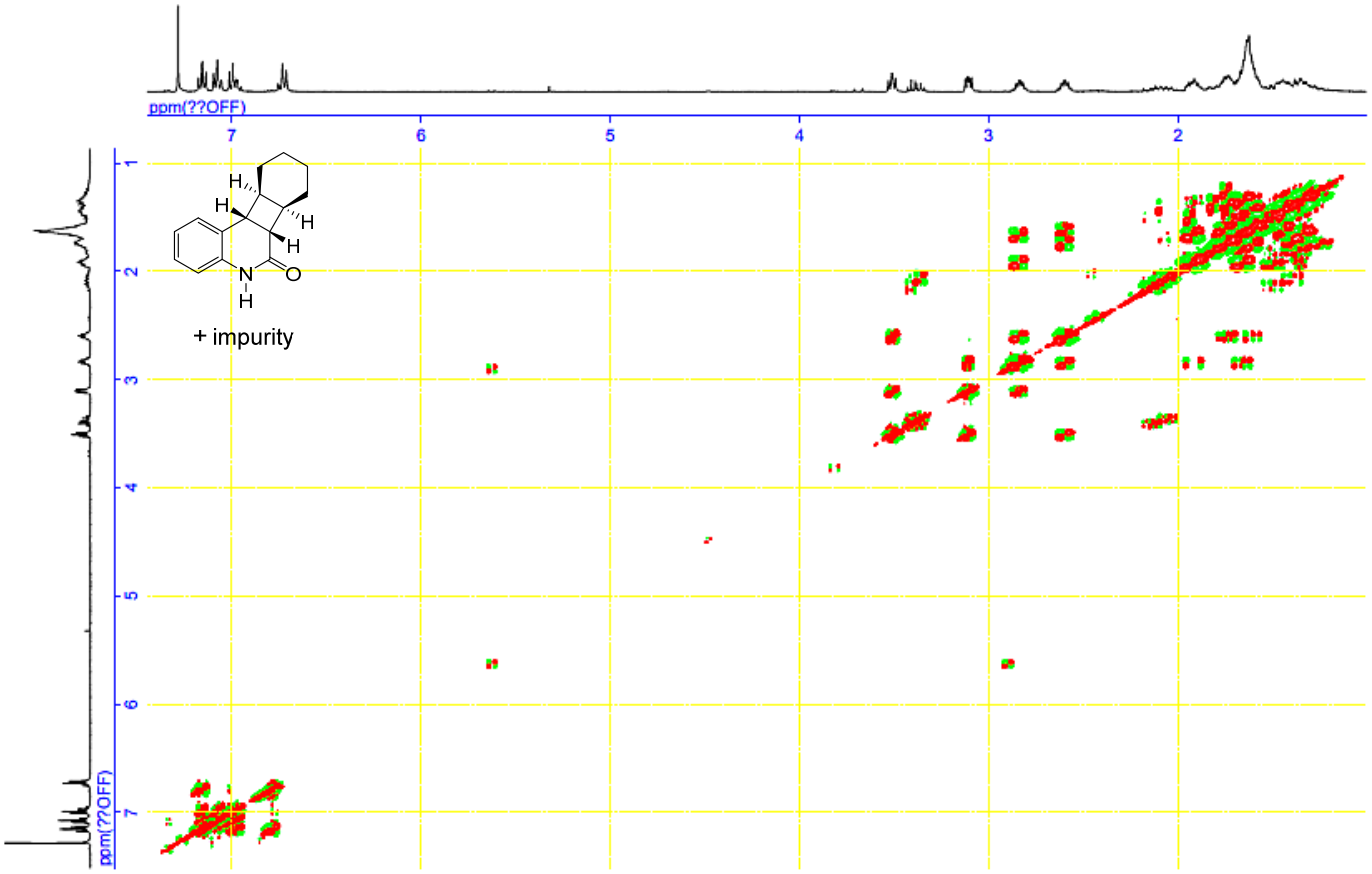
impurity
ppm


+ impurity
impurity
ppm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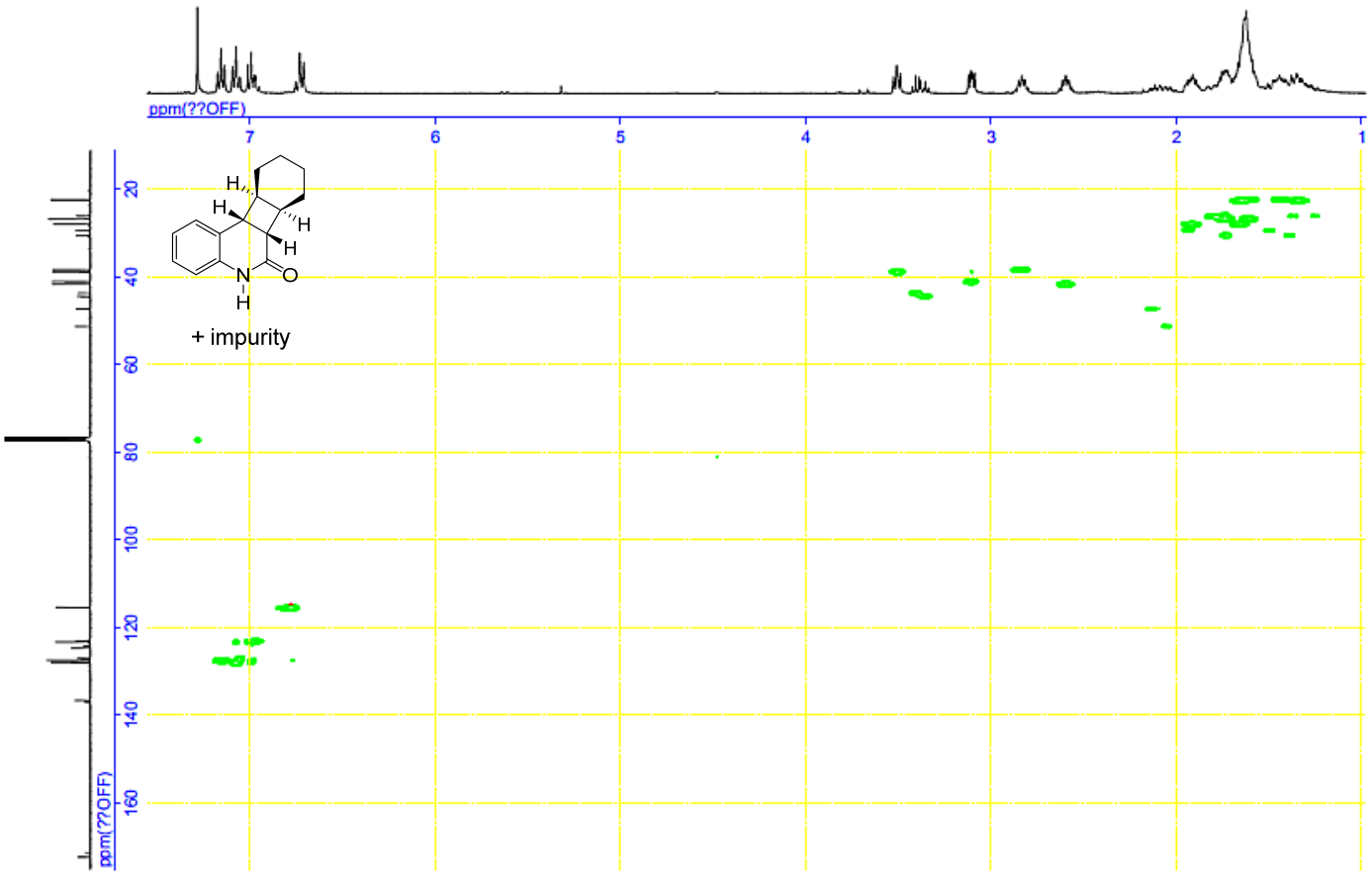
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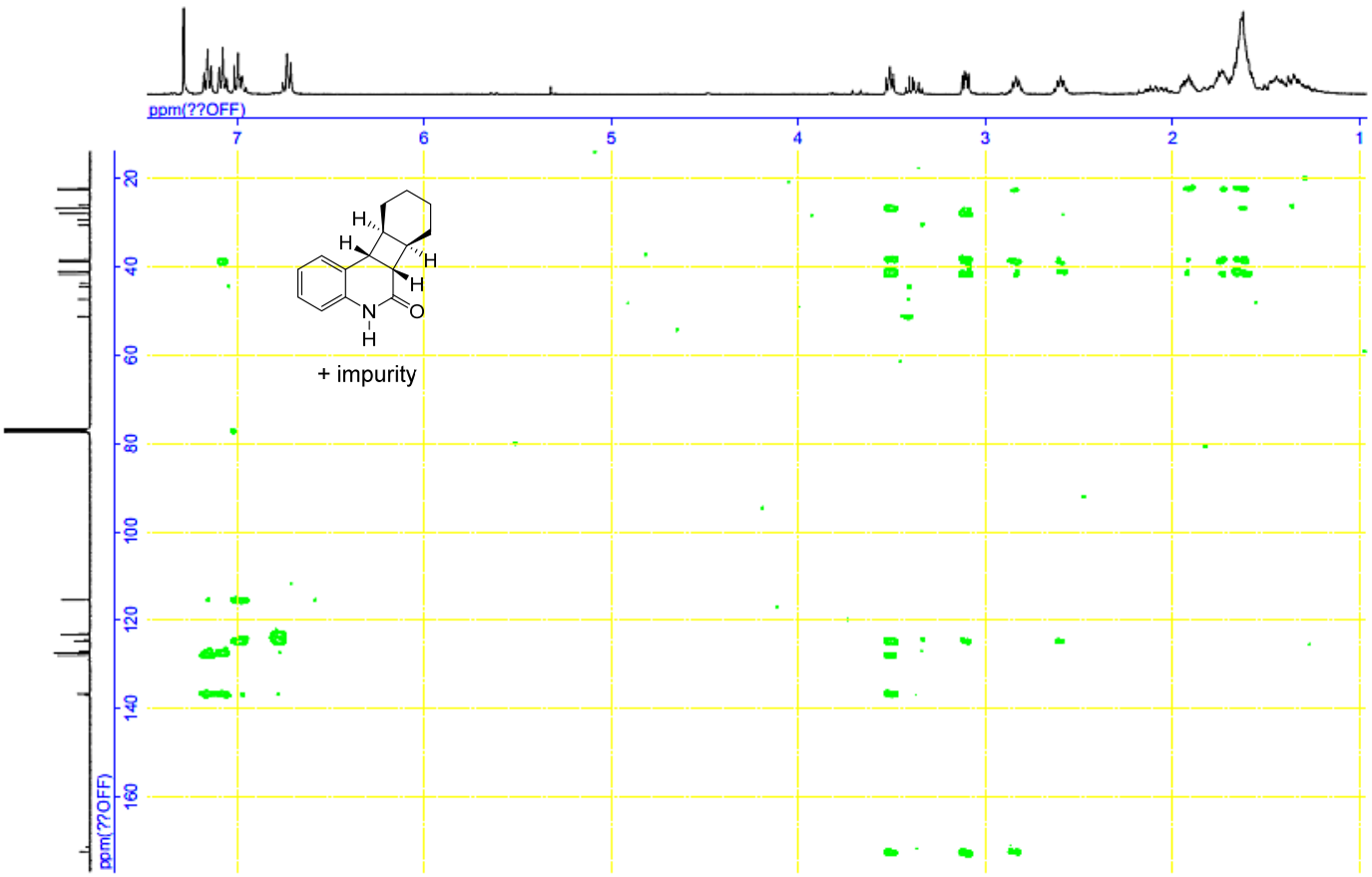
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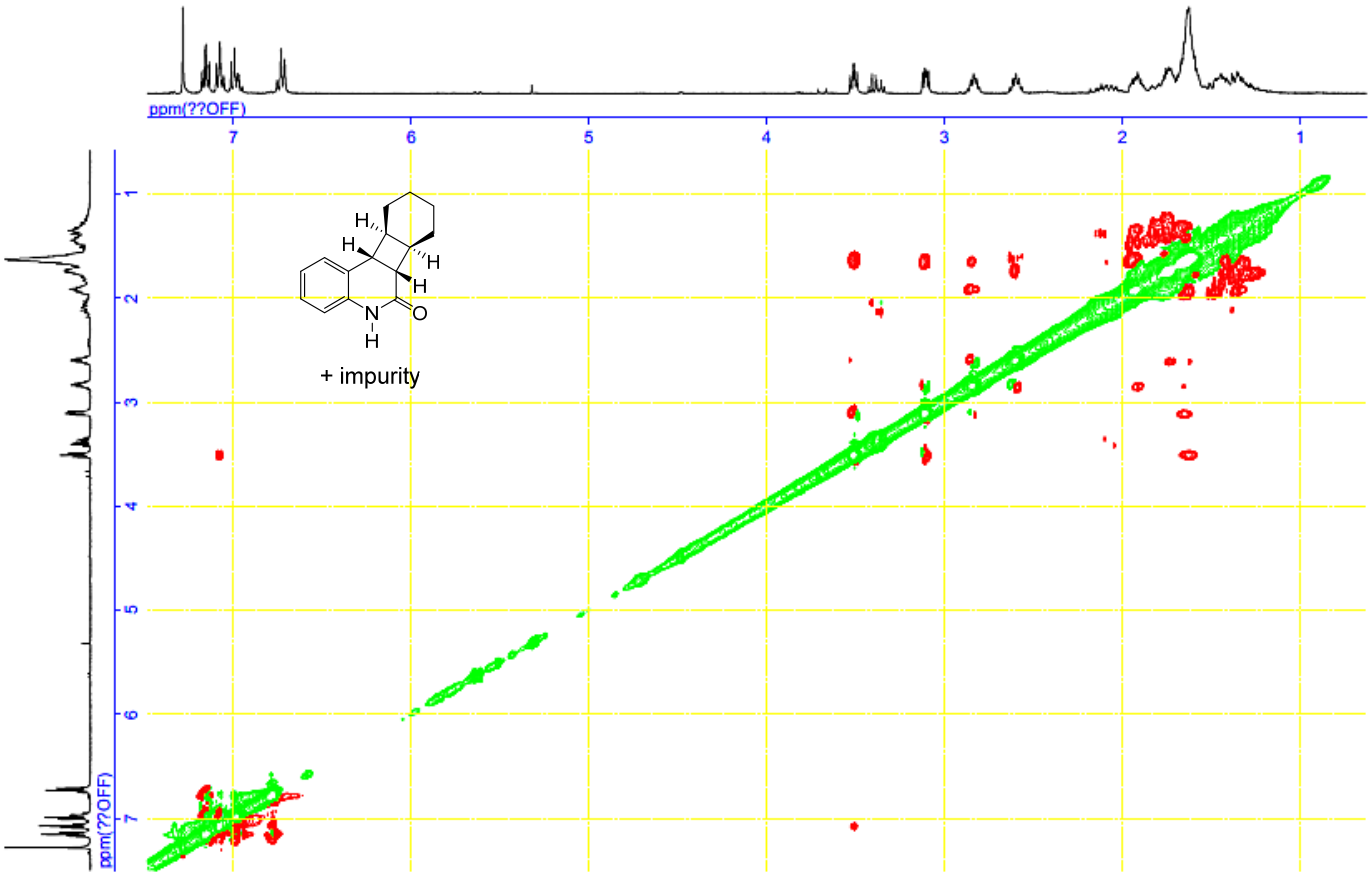
H
H
H
N
H
O
+ impurity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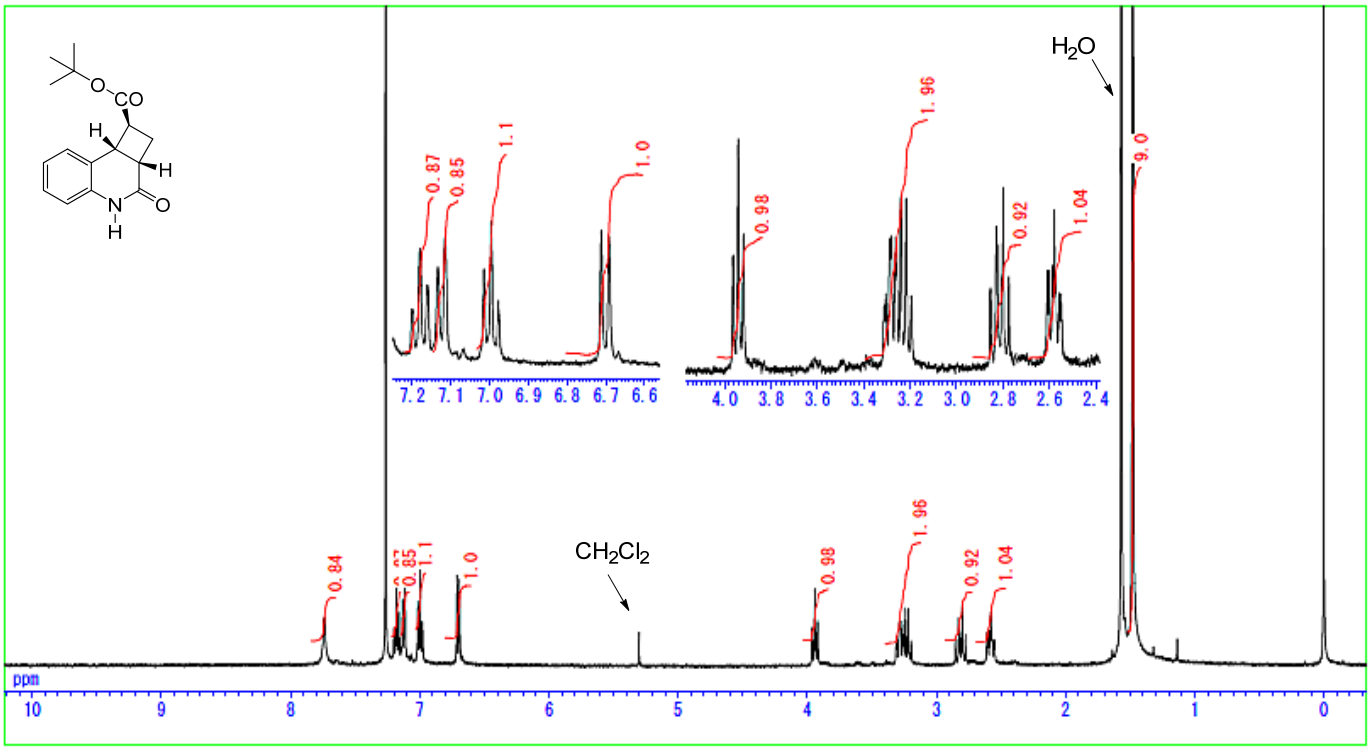
H
H
H
N
H
O
+ impurity


H2O
CH2Cl2
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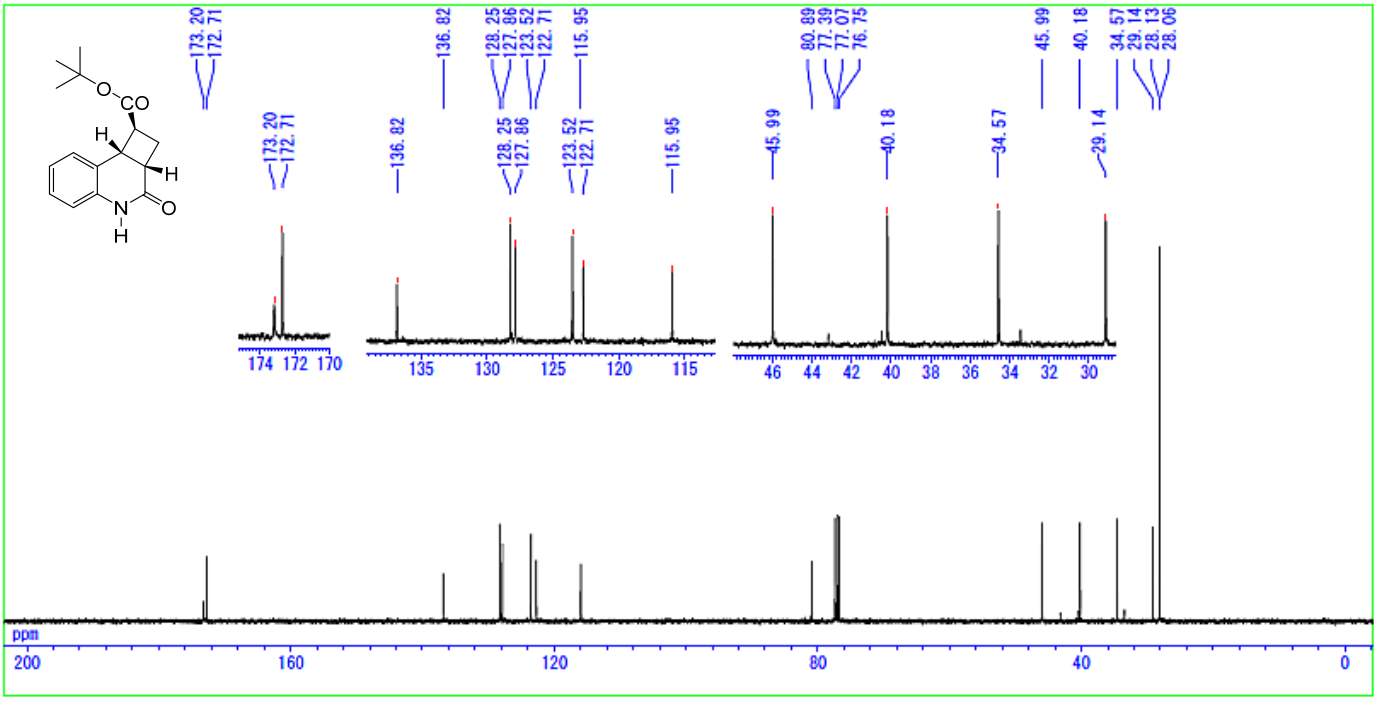
0.87
0.85
1.1
1.0
0.98
1.96
0.92
1.04
9.0
ppm


173.20
172.71
136.82
128.25
127.86
123.52
122.71
115.95
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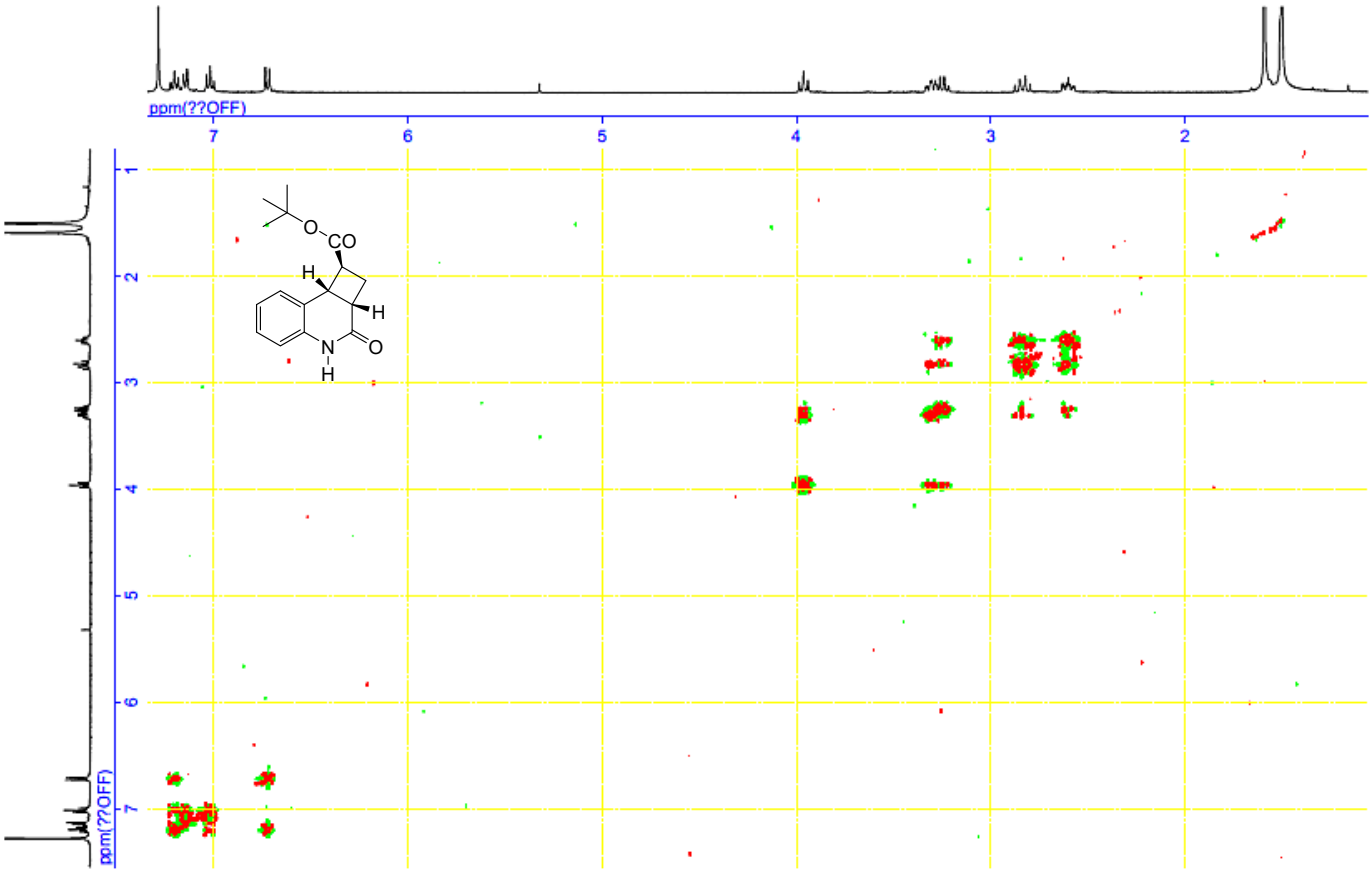
77.39
77.07
76.75
45.99
40.18
34.57
29.14
28.13
28.06
ppm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2
3
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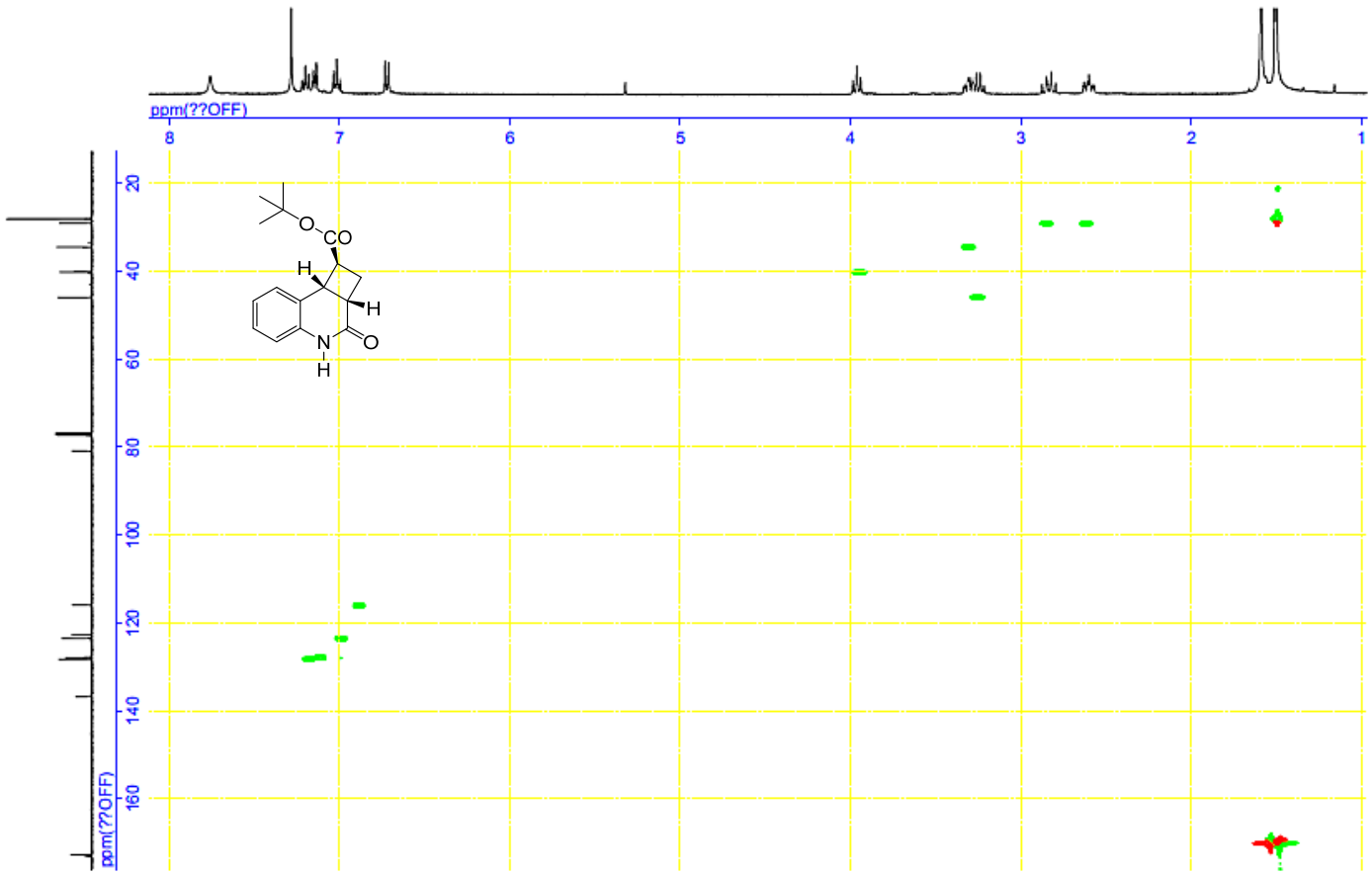
5
6
7
ppm(??OFF)
O
CO
H
H
N
H
O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ppm(??OFF)
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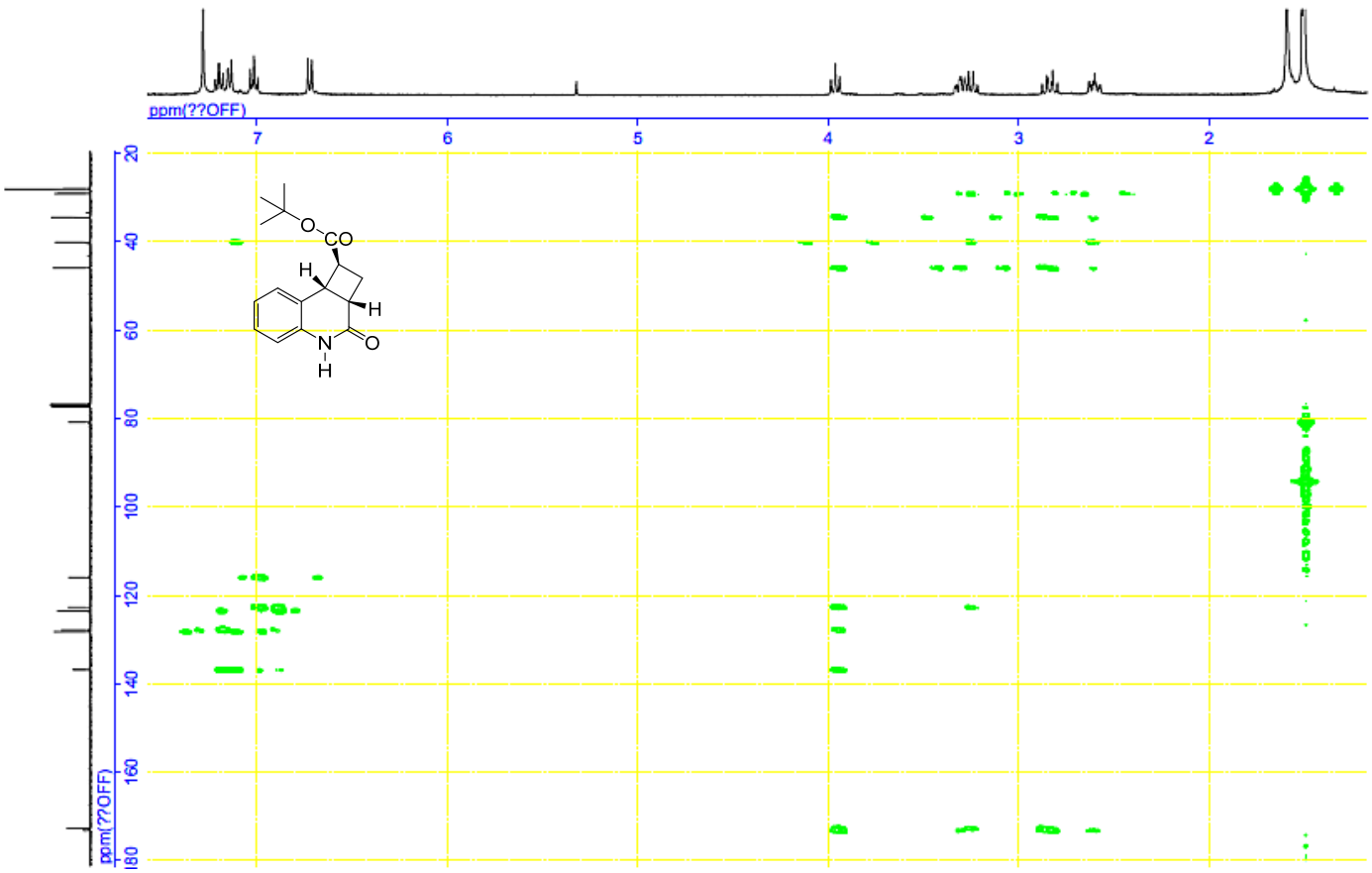
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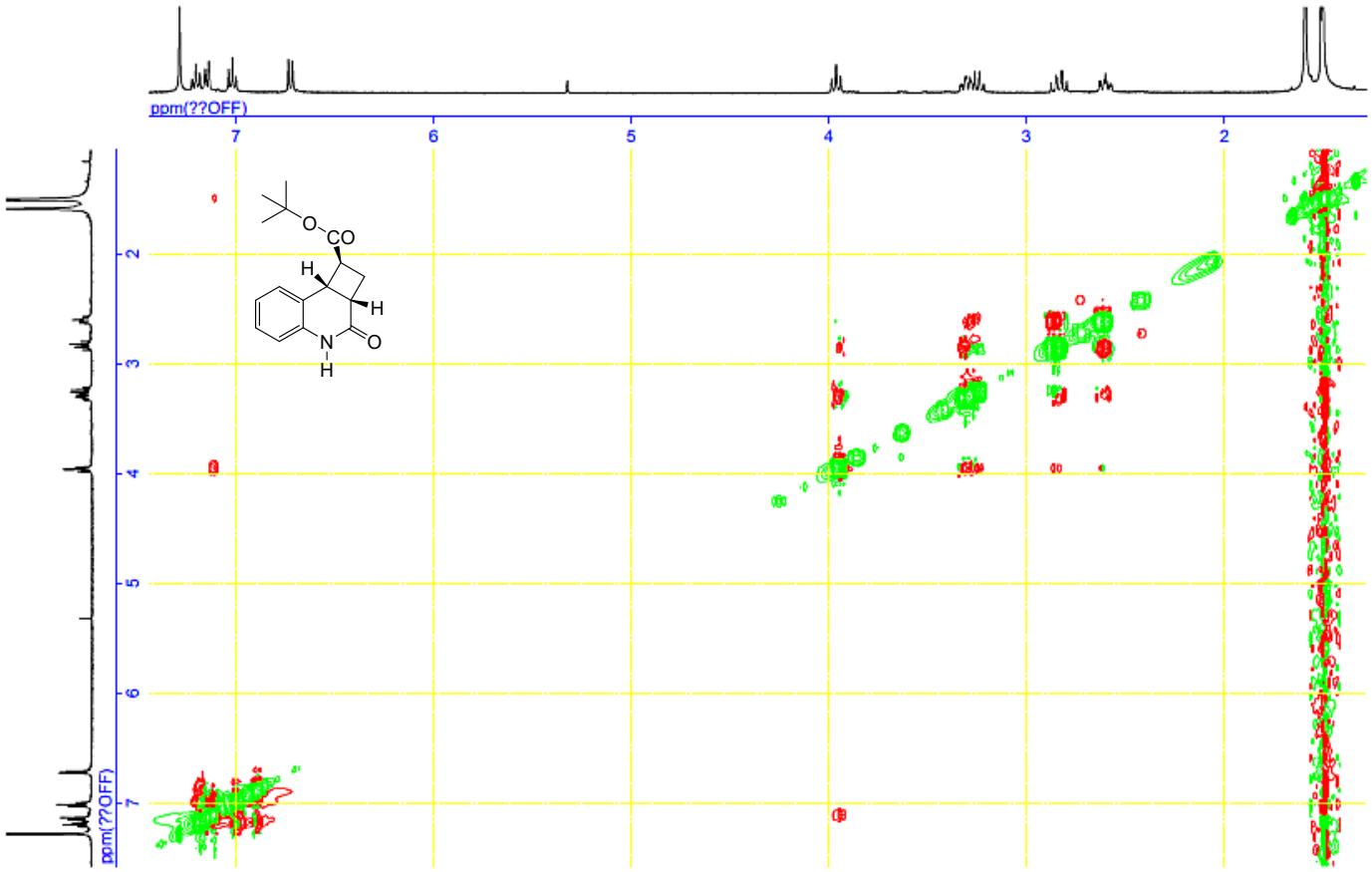
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ppm(??OFF)
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CO
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