Electronic Supplementary Material (ESI) for ChemComm.

Electronic Supplementary Information

Luminescent mechanochromism of a chiral complex: Distinct crystal structure and color changes of racemic and homochiral gold(I)-isocyanide complexes with a binaphthyl moiety

Mingoo Jin, Tomohiro Seki* and Hajime Ito*

Division of Applied Chemistry and Frontier Chemistry Center (FCC), Faculty of Engineering,
Hokkaido University, Sapporo, Hokkaido 060-8628, Japan

seki@eng.hokudai.ac.jp; hajito@eng.hokudai.ac.jp

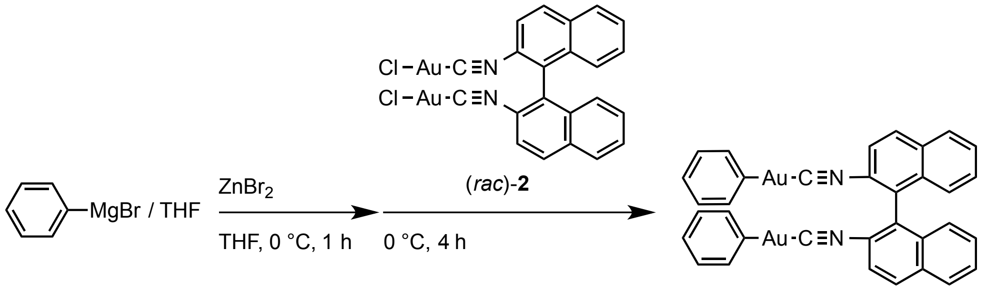
Contents

1. General

All commercially available reagents and solvents are of reagent grade and were used without further purification unless otherwise noted. Solvents for the synthesis were purchased from commercial suppliers, degassed by three freeze-pump-thaw cycles and further dried over molecular sieves (4 Å). NMR spectra were recorded on a JEOL JNM-ECX400P or JNM-ECS400 spectrometer (^{1}H: 400 MHz; ^{13}C: 99.5 MHz) using tetramethylsilane and $CDCl_3$ as internal standards, respectively. Emission spectra were recorded on a Hitachi F-7000 spectrometer. The emission quantum yields of the solid samples were recorded on a Hamamatsu Quantaurus-QY spectrometer with an integrating sphere. Emission lifetime measurements were recorded on a Hamamatsu Quantaurus-Tau spectrometer. Elemental analyses and low- and high resolution mass spectra were recorded at Global Facility Center, Creative Research Institution, Hokkaido University. Photographs were obtained using Olympus BX51 or SZX7 microscopes with Olympus DP72, Nikon D5100 or RICOH CX1 digital cameras. Thermal gravimetric analysis profiles were recorded on Bruker TG-DTA2010SAT.

2. Synthesis of (*rac*)-1 and (*S*)-1

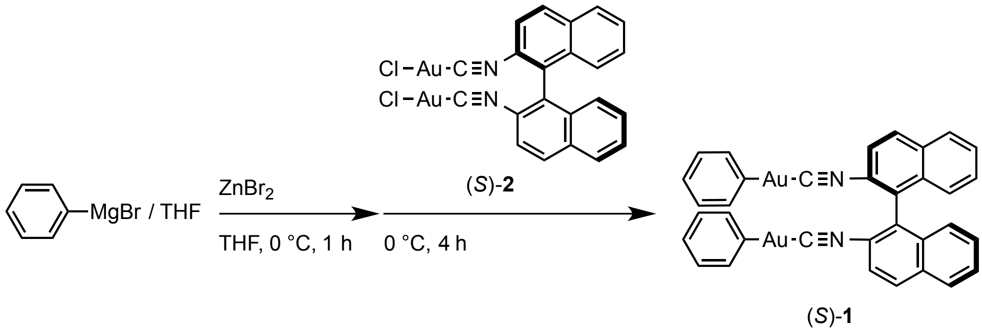
*Synthesis of (rac)-***1**.



(*rac*)-**1**

A powder of zinc bromide (0.067 g, 0.30 mol) was placed in an oven-dried two-neck flask. The flask was connected to a vacuum/nitrogen manifold through a rubber tube. It was evacuated and then backfilled with nitrogen. This cycle was repeated three times. THF (1.0 mL) was then added in the flask through the rubber septum using a syringe, and stirred at 0 °C. A phenylmagnesium bromide reagent in THF (0.400 ml, 0.30 mmol, 0.75 M) was then added to the reaction mixture using a syringe, and stirred at 0 °C for 1 h. Then, a solid of (*rac*)-**2**[1] (0.076 g, 0.10 mmol) was added and the mixture was stirred at 0 °C. After the reaction completion was monitored by TLC analysis, the reaction mixture was quenched by the addition of a phosphate buffer solution and then extracted with CH_2Cl_2 three times and washed with H_2O and brine. The organic layers were collected and dried over $MgSO_4$. After filtration, the solvent was removed *in vacuo*. Further purification by flash column chromatography (SiO_2, CH_2Cl_2/hexane = 1:1) gave an analytically pure orange solid of (*rac*)-**1** (0.060 g, 0.070 mmol, 70 %). ^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.00–7.06 (m, 2H), 7.17–7.20 (m, 6H), 7.29 (d, *J* = 8.0 Hz, 4H), 7.52 (t, *J* = 7.8 Hz, 2H), 7.71–7.75 (m, 4H), 8.09 (d, *J* = 8.4 Hz, 2H), 8.20 (d, *J* = 8.4 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 122.7 (*C*), 123.2 (*C*H), 126.0 (*C*H), 126.2 (*C*H), 127.5 (*C*H), 129.2 (*C*H), 129.3 (*C*H), 129.3 (*C*H), 131.0 (*C*), 131.6 (*C*), 132.1 (*C*H), 133.8 (*C*), 140.6 (*C*H), 162.5 (*C*), 164.6 (*C*H). MS-ESI (*m*/*z*): $[M+Na]^+$ calculated for $C_{34}H_{22}Au_2N_2Na^+$, 875.11140; found, 875.10117. Anal. Calcd for $C_{34}H_{22}Au_2N_2$: C, 47.90; H, 2.60; N, 3.29. Found: C, 48.48; H, 2.74; N, 3.10.

*Synthesis of (S)-***1**.



(*S*)-**1** was prepared from (*S*)-**2**[1] (0.145, 0.20 mmol) according to the procedure similar to that described for the preparation of (*rac*)-**1**. Yield: 74 % (0.127g, 0.149 mmol, orange solid).

^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.01–7.06 (m, 2H), 7.16–7.20 (m, 6H), 7.30 (dd, *J* = 1.6, 8.0 Hz, 4H), 7.52 (t, *J* = 7.8 Hz, 2H), 7.71–7.75 (m, 4H) 8.09 (d, *J* = 8.0 Hz, 2H), 8.19 (d, *J* = 8.8 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 122.7 (*C*), 123.3 (*C*H), 126.0 (*C*H), 126.1 (*C*H), 127.5 (*C*H), 129.2 (*C*H), 129.3 (*C*H), 129.3 (*C*H), 131.0 (*C*), 131.6 (*C*), 132.0 (*C*H), 133.8 (*C*), 140.6 (*C*H), 162.5 (*C*), 164.4 (*C*). MS-ESI (*m*/*z*): [M+Na]$^+$ calculated for $C_{34}H_{22}Au_2N_2Na^+$, 875.11140; found, 875.10117. Anal. Calcd. for $C_{34}H_{22}Au_2N_2$: C, 47.90; H, 2.60; N, 3.29. Found: C, 48.23; H, 2.75; N, 3.09.

*Preparation of the single crystals of (rac)-**1G** and (S)-**1G***: The resulting solid was dissolved in CH_2Cl_2 in a vial and hexane was carefully layered for crystallization and allowed to stand at room temperature to give CH_2Cl_2 included crystals (*rac*)-**1G** and (*S*)-**1G**.

3. TGA profiles

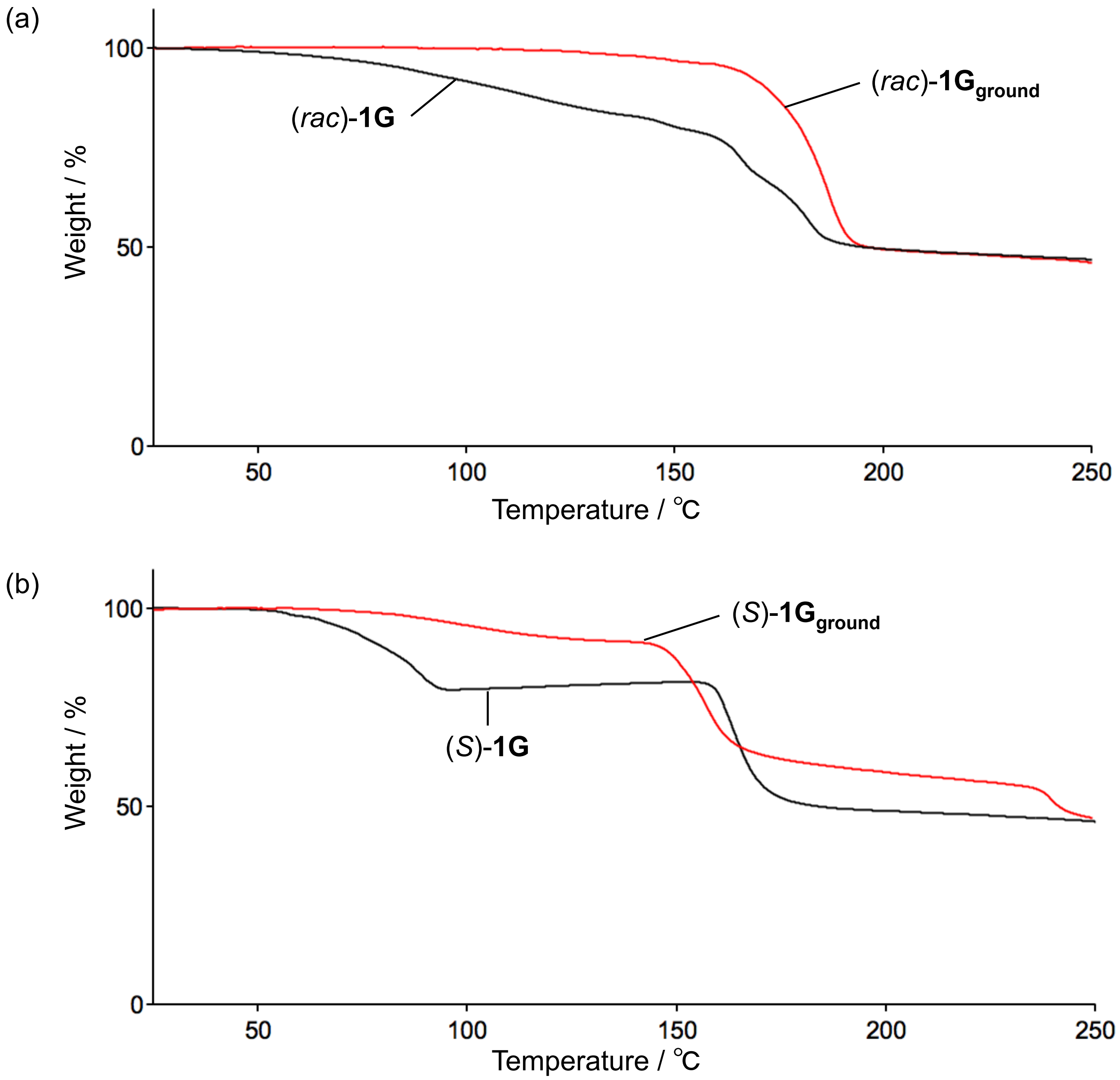


Fig. S1 TGA profiles of (*rac*)-**1G** [black line in (a)], (*rac*)-**1G**$_{\textbf{ground}}$ [red line in (a)], (*S*)-**1G** [black line in (b)], and (*S*)-**1G**$_{\textbf{ground}}$ [red line in (b)] at heating rates of 5 °C min^{-1}.

4. NMR spectra and elemental analysis

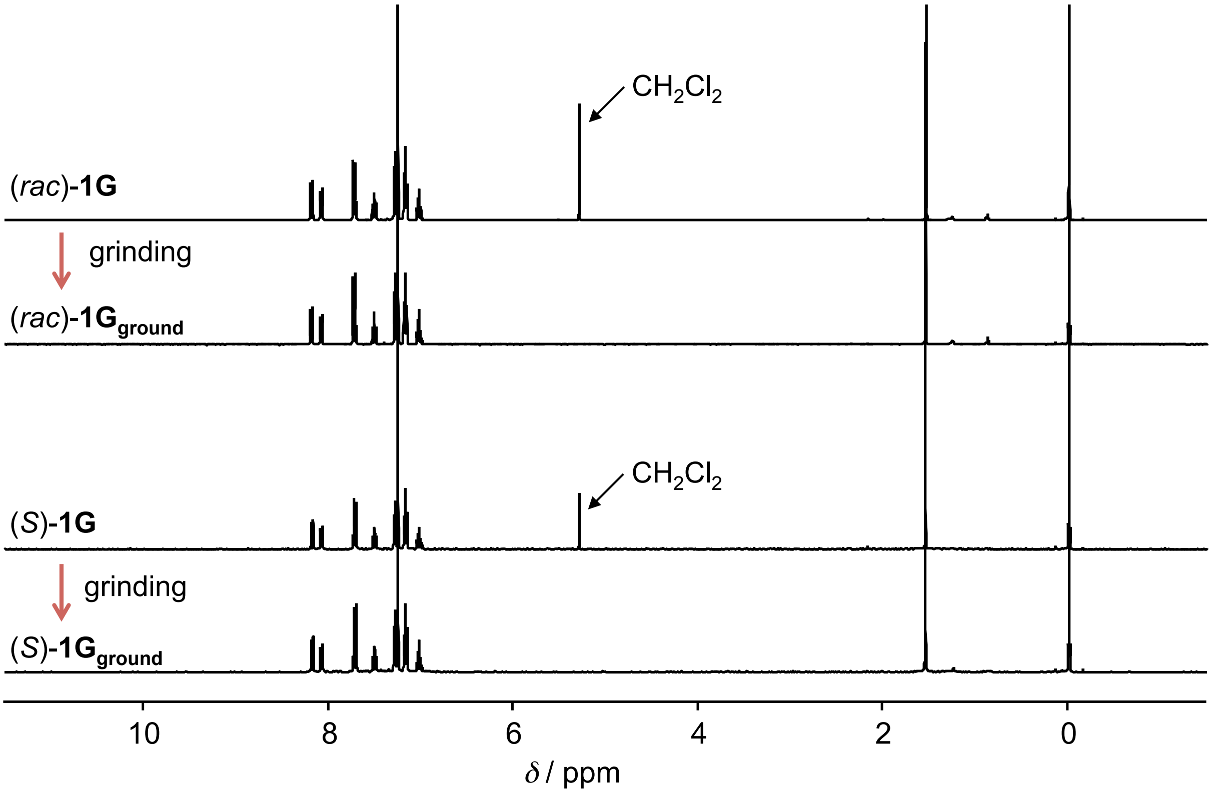


Fig. S2 ^{1}H NMR spectra of (*rac*)-**1G**, (*rac*)-**1G$_{ground}$**, (*S*)-**1G**, and (*S*)-**1G$_{ground}$** dissolved in $CDCl_3$.

Table S1 Elemental analyses of the ground powders (*rac*)-**1G$_{ground}$** and (*S*)-**1G$_{ground}$**.

	C	H	N
Calculated for **1** ($C_{34}H_{22}Au_2N_2$)	47.90	2.60	3.29
(*rac*)-**1G$_{ground}$**	48.23	2.73	3.08
(*S*)-**1G$_{ground}$**	47.46	2.55	3.21

5. Crystal structures of (*rac*)-1G and (*S*)-1G

Single crystal X-ray structural analyses were carried out on a Rigaku R-AXIS RAPID diffractometer using graphite monochromated Mo-K_α radiation. The structure was solved by direct methods and expanded using Fourier techniques. Non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined using the riding model. All calculations were performed using the CrystalStructure crystallographic software package except for refinement, which was performed using SHELXL-2013.[3]

Table S2 Summary of X-ray crystallographic data for (*rac*)-**1G** and (*S*)-**1G**.

Crystal	(*rac*)-**1G**	(*S*)-**1G**
CCDC Name	1472283	1472333
Empirical Formula	$C_{34.25}H_{22.5}Au_2Cl_{0.5}N_2$	$C_{34.5}H_{23}Au_2ClN_2$
Formula Weight	873.73	894.96
Crystal System	orthorhombic	orthorhombic
Crystal Size / mm	0.165 × 0.131 × 0.072	0.362 × 0.091 × 0.036
a / Å	13.0435(4)	13.3962(12)
b / Å	18.7272(7)	19.3637(16)
c / Å	23.6159(9)	22.587(2)
α / °	90	90
β / °	90	90
γ / °	90	90
V / Å^3	5768.6(4)	5859.0(9)
Space Group	*Pbcn* (#60)	$P2_12_12_1$ (#19)
Z value	8	8
Dcalc / g·cm^{-3}	2.012	2.029
Temperature / K	123	123
$2\theta_{max}$ / °	52.0	52.0
μ (MoK$_\alpha$) / cm^{-1}	102.685	101.568
No. of Reflections Measured	Total : 46284 Unique : 5667 (R_{int} = 0.0887)	Total : 5525 Unique : 2516 (R_{int} = 0.0574)
Residuals: R_1 (I > 2.00σ (I)) / %	3.80	6.43
Residuals: wR_2 (All reflections) / %	7.49	13.83
Goodness of Fit (GOF)	1.061	1.052
Maximum peak in Final Diff. Map / Å^3	0.85 e$^-$	1.67 e$^-$
Minimum peak in Final Diff. Map / Å^3	–1.19 e$^-$	–1.75 e$^-$
Flack Parameter	-	0.004 (15)

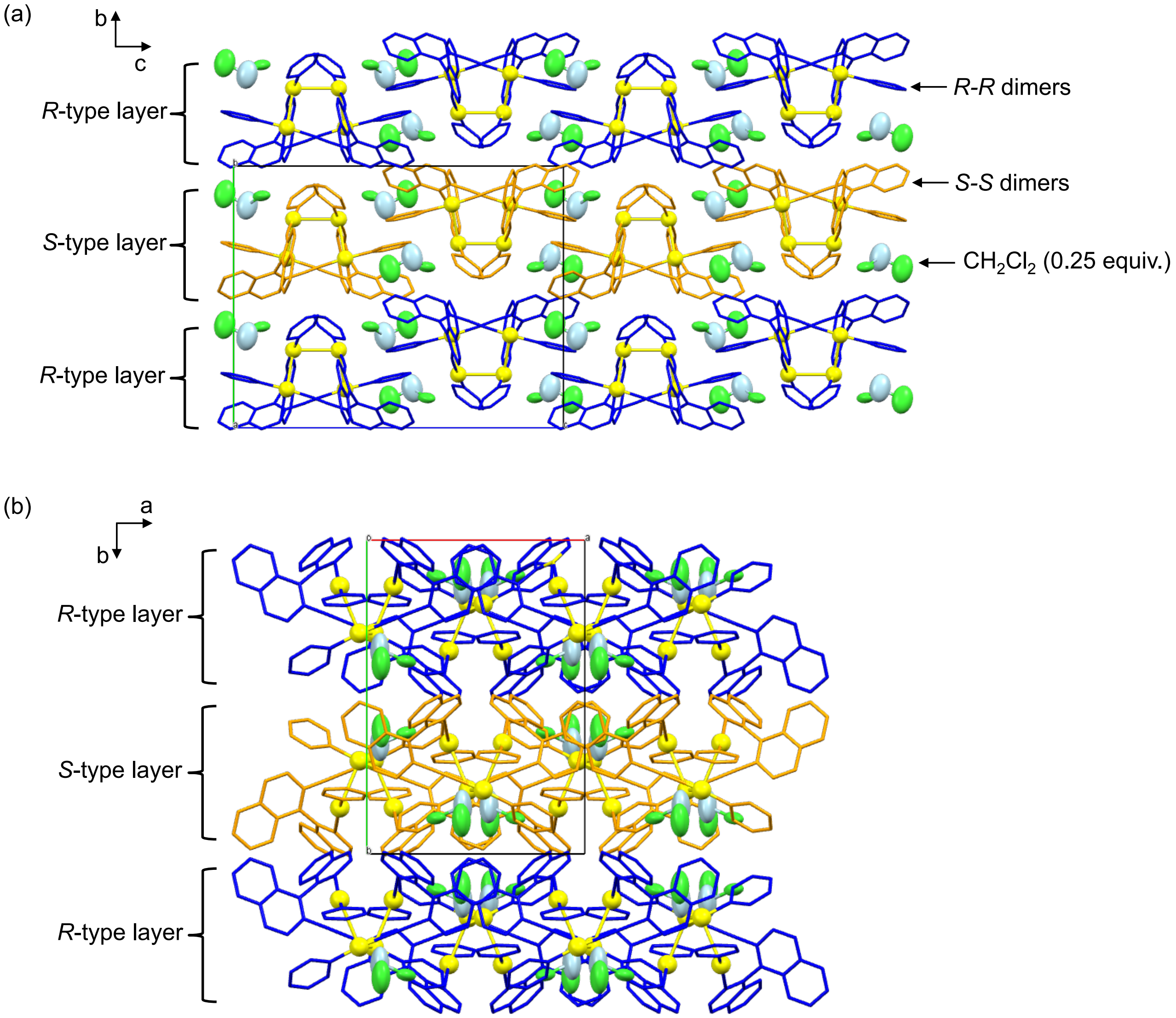


Fig. S3 Single crystal structure of (*rac*)-**1G**. Packing structure of (*rac*)-**1G** viewed along *a* axis (a) and *c* axis (b). All the H atoms were omitted for clarity

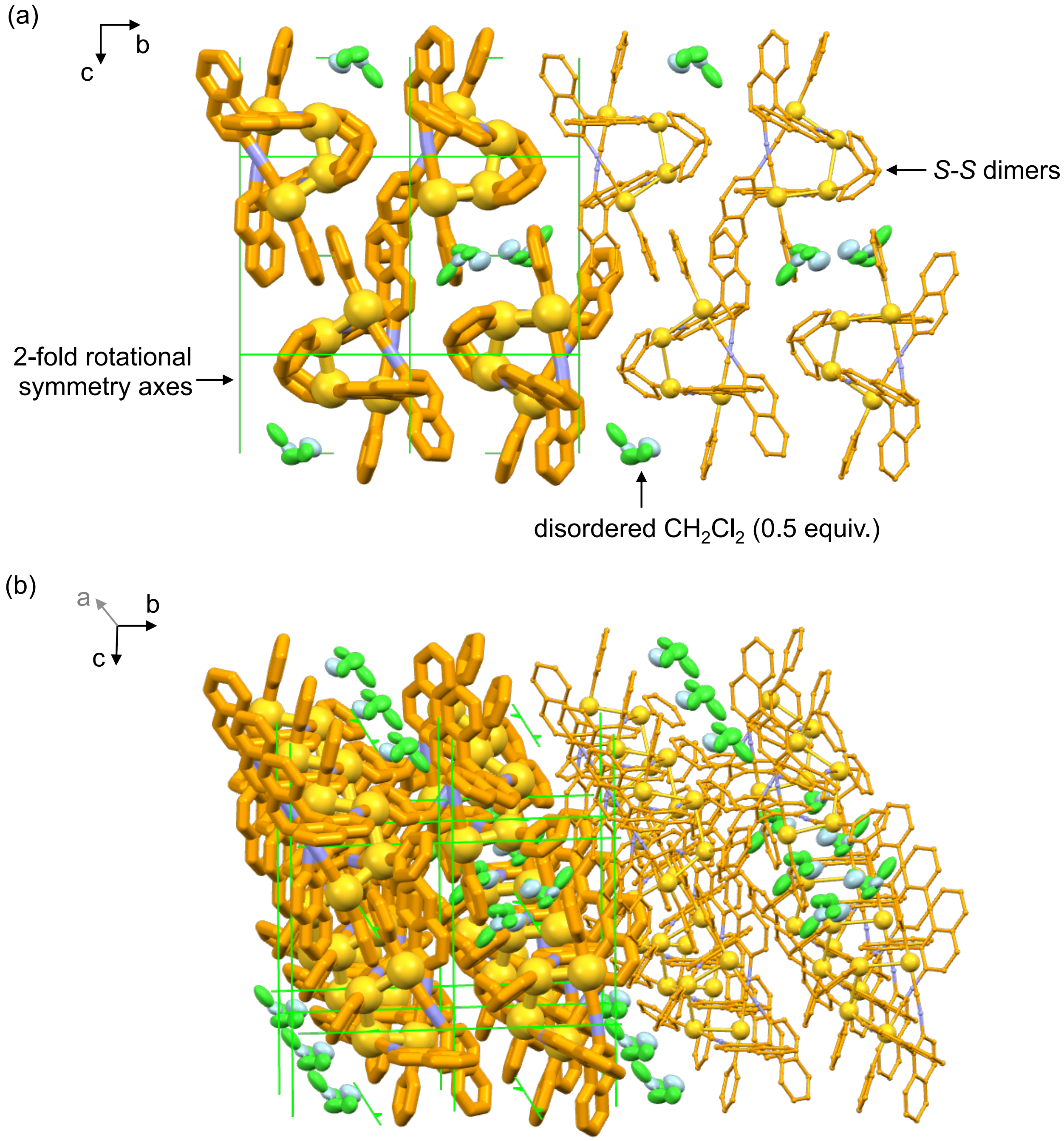


Fig. S4 Single crystal structure of (*S*)-**1G**. (a) Packing structure of (*S*)-**1G** viewed along *a* axis. (b) Packing structure of (*S*)-**1G**. Light green lines denote 2-fold rotational symmetry axes. All the H atoms were omitted for clarity.

6. The CH_2Cl_2 release by heating under vacuum from (*rac*)-1G and (*S*)-1G

No emission color change takes place when CH_2Cl_2 was released from (*rac*)-**1G** and (*S*)-**1G** by heating under vacuum, rather than mechanical stimulation. The CH_2Cl_2 molecules included in both crystals of (*rac*)-**1G** and (*S*)-**1G** (Fig. S5) can be released under vacuum at 65 ºC for 1 h which is confirmed by ^{1}H-NMR studies (Fig. S6). During this procedure for releasing CH_2Cl_2, molecular arrangements of both complexes are unchanged, which are confirmed by intact PXRD patterns (Fig. S7). The emission spectra of (*rac*)-**1G** and (*S*)-**1G** after releasing CH_2Cl_2 by above procedure were almost identical to those containing CH_2Cl_2 (Fig. S8). These results indicate that mechanoinduced emission color changes of these complexes are caused by the phase transition into amorphous phase rather than just by the release of included CH_2Cl_2 molecules.

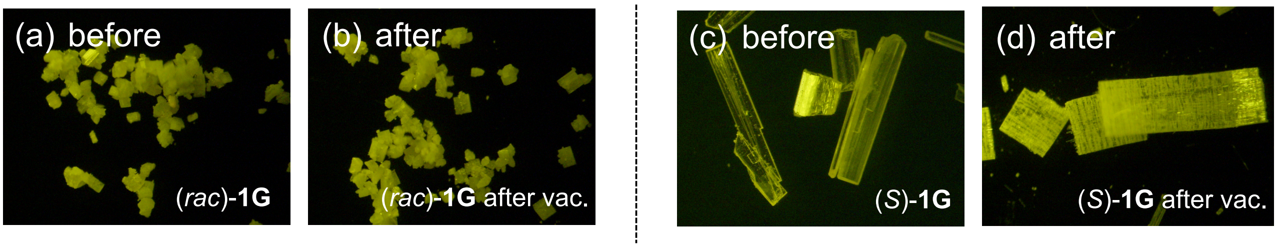


Fig. S5 Photographs of (a) (*rac*)-**1G** and (c) (*S*)-**1G** crystals and the corresponding crystals of (b) (*rac*)-**1G** and (d) (*S*)-**1G** obtained after heated at 65 ºC for 1h under vacuum. These photographs were taken under UV irradiation at 367 nm at room temperature under air.

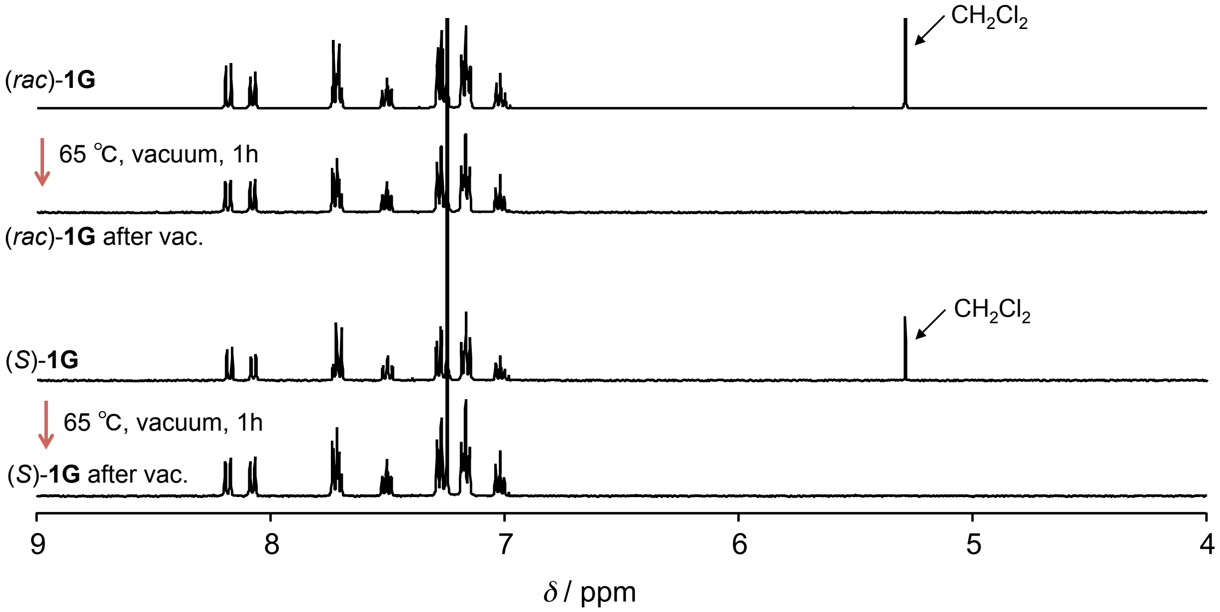
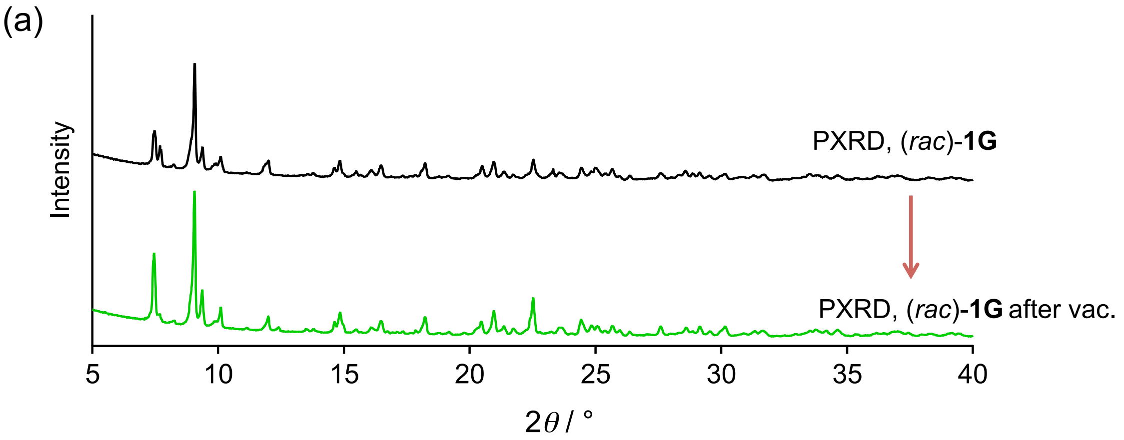


Fig. S6 ^{1}H-NMR spectra of (a) (*rac*)-**1G** obtained before and after heating at 65 ºC for 1h and (b) (*S*)-**1G** obtained before and after heating at 65 ºC for 1h dissolved in $CDCl_3$.



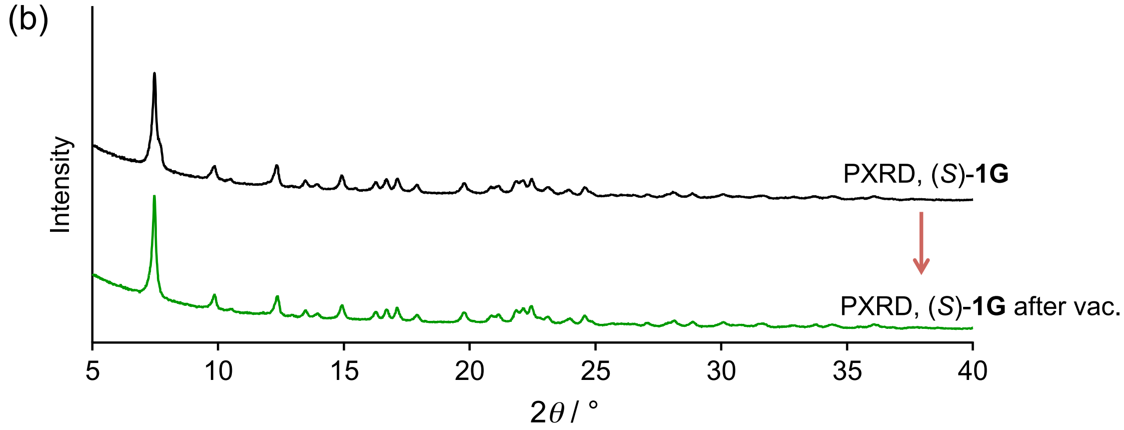


Fig. S7 PXRD patterns of (a) (*rac*)-**1G** before (black line) and after heating at 65 ºC for 1h (yellowish green line) and (b) (*S*)-**1G** before (black line) and after heating at 65 ºC for 1h (green line).

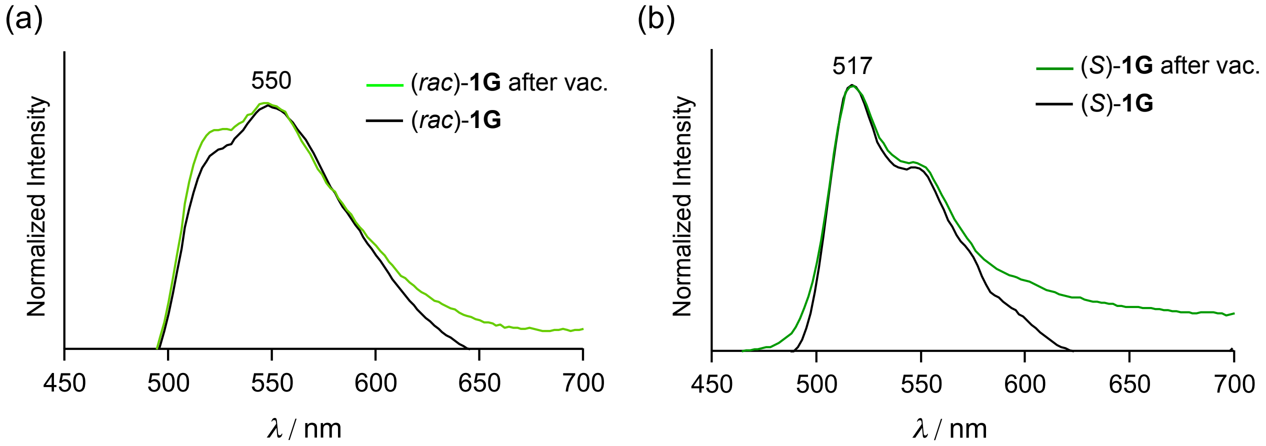


Fig. S8 Emission spectra of a (a) (*rac*)-**1G** before (black line) and after heating at 65 ºC for 1h (light green line) and (b) (*S*)-**1G** before (black line) and after heating at 65 ºC for 1h (green line). Excitation wavelength is 365 nm.

7. Photophysical properties of each solid phase

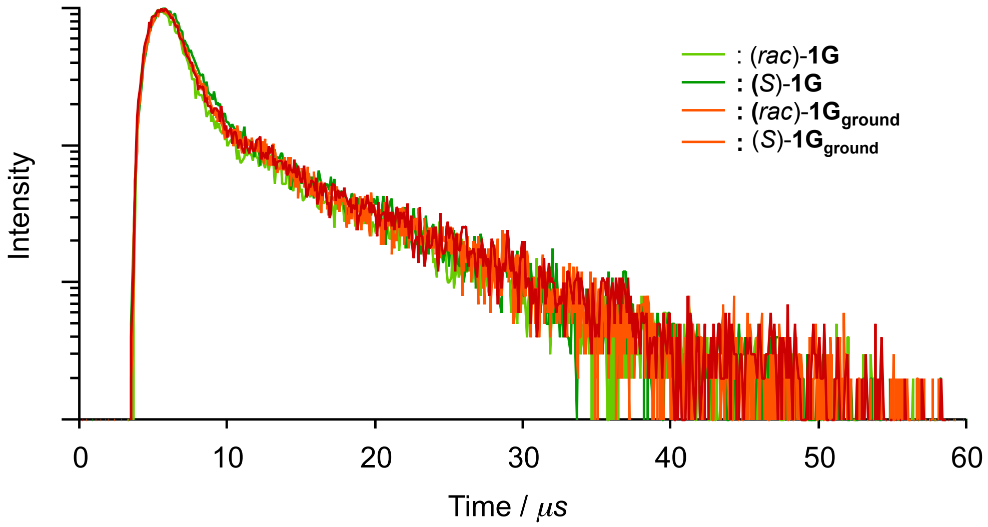


Fig. S9 Emission decay profiles of (*rac*)-**1G** (λ_{em} = 546 nm), (*S*)-**1G** (λ_{em} = 517 nm), (*rac*)-**1G$_{ground}$** (λ_{em} = 664 nm), and (*S*)-**1G$_{ground}$** (λ_{em} = 664 nm). Excitation wavelength is 370 nm.

Table S3. Photophysical properties of (*rac*)-**1G**, (*S*)-**1G**, (*rac*)-**1G$_{ground}$**, and (*S*)-**1G$_{ground}$**

	Φ_{em} / -	τ_{av} / μs^{e,f} (λ_{em} / nm)	τ_1 / μs^{e} (A / -)	τ_2 / μs^{e} (A / -)
(*rac*)-**1G**	0.081^{a}	5.34 (546)	1.40 (0.90)	10.11 (0.10)
(*S*)-**1G**	0.023^{b}	5.34 (517)	1.60 (0.87)	9.60 (0.13)
(*rac*)-**1G$_{ground}$**	0.21^{c}	5.10 (664)	1.41 (0.87)	8.86 (0.14)
(*S*)-**1G$_{ground}$**	0.13^{d}	5.36 (664)	1.38 (0.87)	9.37 (0.13)

$^{a}\lambda_{ex}$ = 454 nm. $^{b}\lambda_{ex}$ = 458 nm. $^{c}\lambda_{ex}$ = 449 nm. $^{d}\lambda_{ex}$ = 445 nm. $^{e}\lambda_{ex}$ = 370 nm. $^{f}\tau_{av} = (A_1\tau_1^2 + A_2\tau_2^2 + \cdots) / (A_1\tau_1 + A_2\tau_2 + \cdots)$. Emission decay were fitted by tail fitting.

8. Optical properties of solution phase

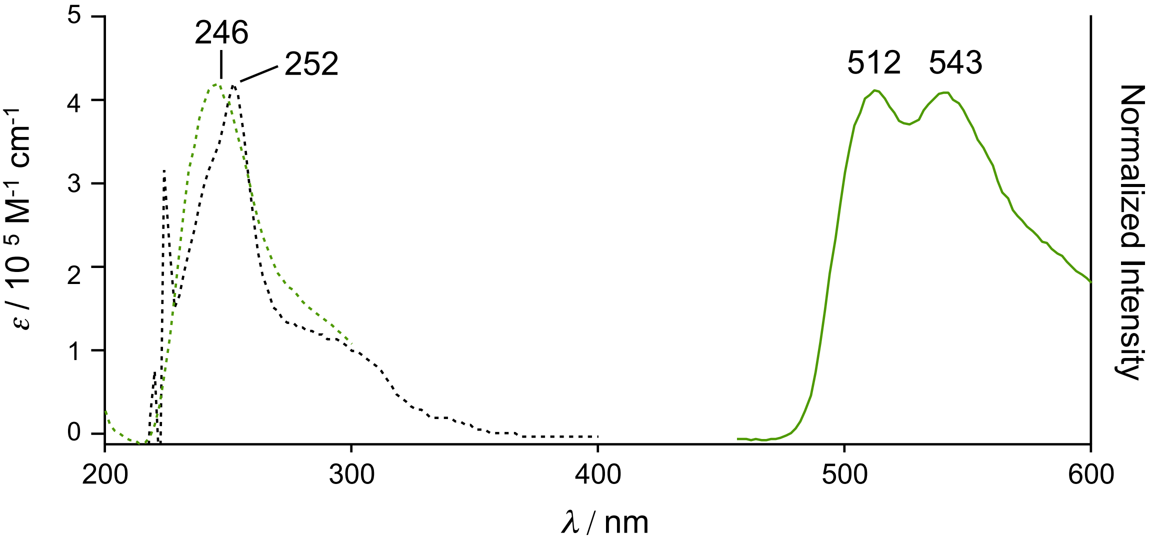


Fig. S10 UV/vis absorption (black dashed line), excitation (green dashed line, λ_{em} = 512 nm), and emission spectra (green solid line, λ_{ex} = 246 nm) of (*rac*)-**1** in CH_2Cl_2 ($c = 2.8 \times 10^{-5}$ M) at room temperature.

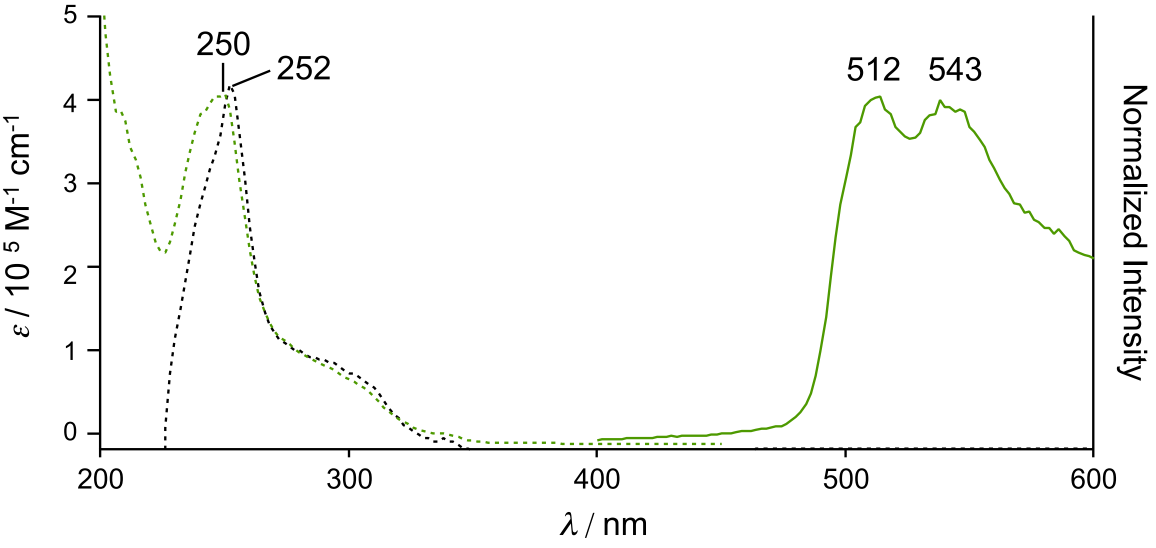


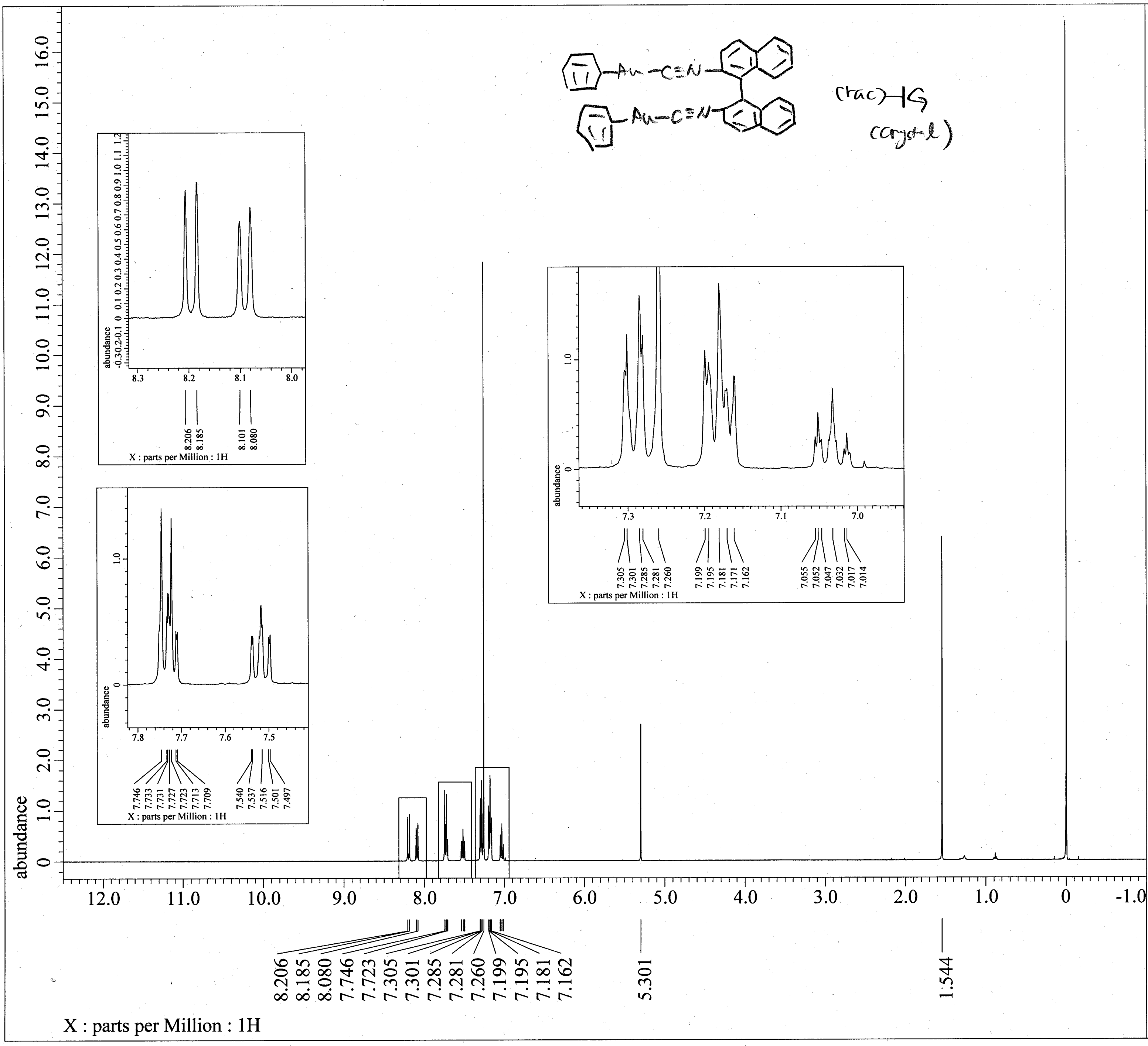
Fig. S11 UV/vis absorption (black dashed line), excitation (green dashed line, λ_{em} = 512 nm), and emission spectra (green solid line, λ_{ex} = 250 nm) of (*S*)-**1** in CH_2Cl_2 ($c = 3.2 \times 10^{-5}$ M) at room temperature.

9. References

1. C. Bartolome, D. Garcia-Cuadrado, Z. Ramiro and P. Espinet, *Inorg. Chem.*, 2010, **49**, 9758–9764.

2. http://www.ccdc.cam.ac.uk/free_services/mercury/downloads/Mercury_3.0/

3. Sheldrick, G. M. SHELXL-2013, Program for the Refinement of Crystal Structures; University of Göttingen, Göttingen, Germany, **2013**.



(rac)-1G
(crystal)

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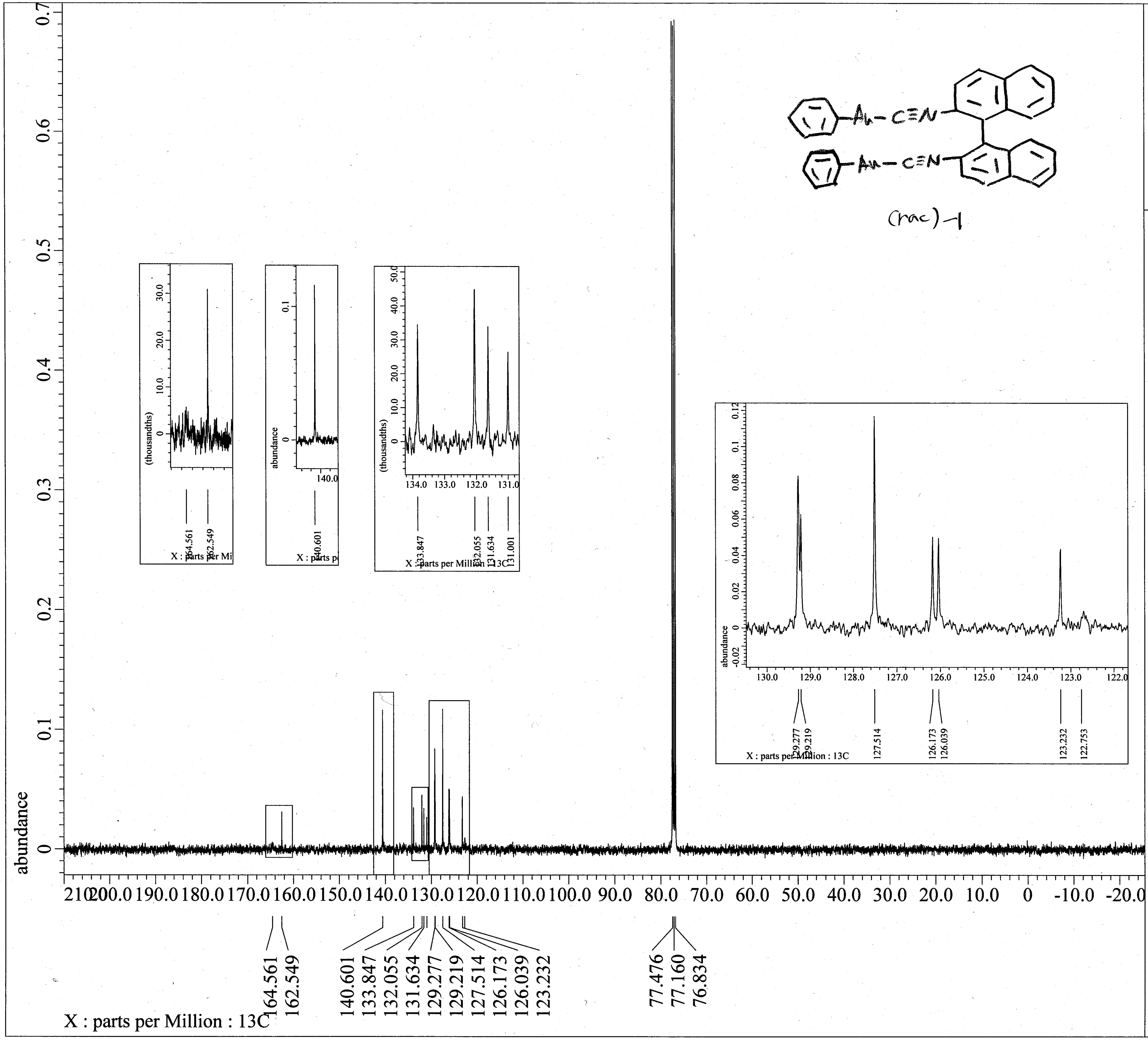

(rac)-1

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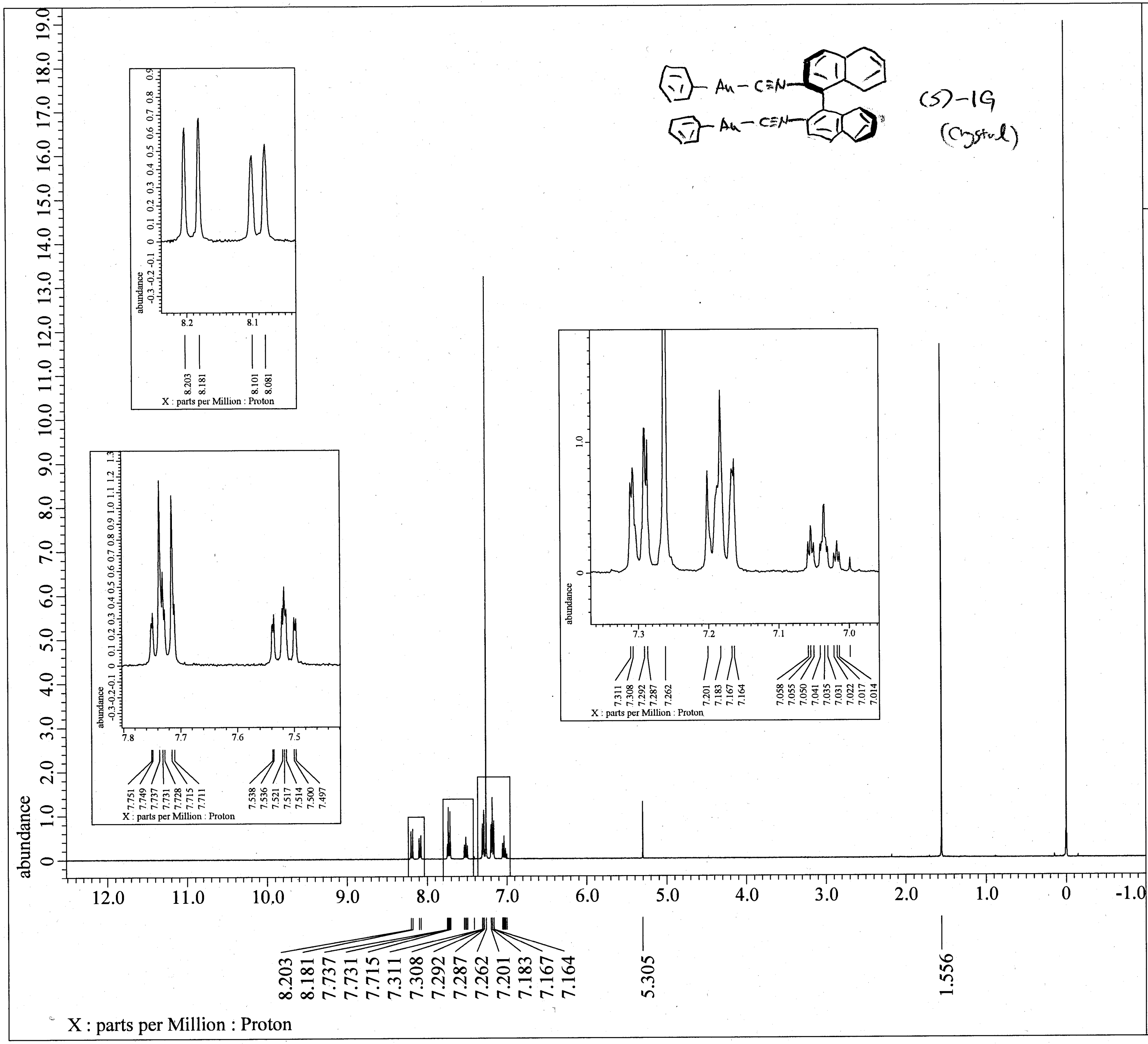

(S)-1G
(Crystal)

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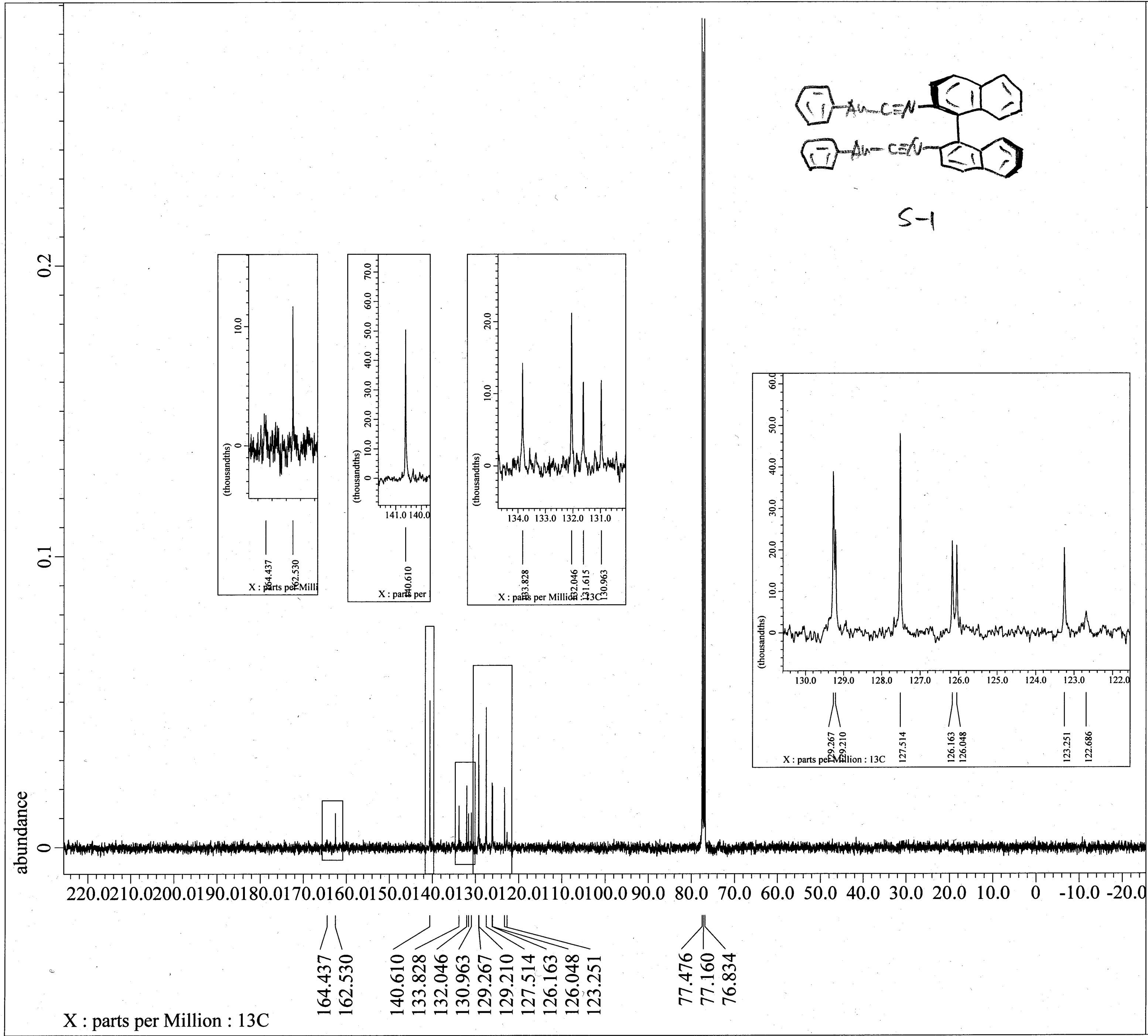
Initial_Wait        = 1[s]
```



S-1

```
---- PROCESSING PARAMETERS ----
dc_balance( 0, FALSE )
sexp( 2.0[Hz], 0.0[s] )
trapezoid3( 0[%], 80[%], 100[%] )
zerofill( 1 )
fft( 1, TRUE, TRUE )
machinephase
ppm

以下に由来:: BNP-S-1-13C-6.jdf
```

```
Filename            = BNP-S-1-13C-9.jdf
Author              = element
Experiment          = single_pulse_dec
Sample_Id           = S#489445
Solvent             = CHLOROFORM-D
Creation_Time       =  8-APR-2016 14:02:10
Revision_Time       = 17-APR-2016 14:49:20
Current_Time        = 17-APR-2016 14:50:17

Comment             = single pulse decoupled gat
Data_Format         = 1D COMPLEX
Dim_Size            = 26214
Dim_Title           = 13C
Dim_Units           = [ppm]
Dimensions          = X
Site                = ECX 400P
Spectrometer        = DELTA2_NMR

Field_Strength      = 9.2982153[T] (400[MHz])
X_Acq_Duration      = 1.048576[s]
X_Domain            = 13C
X_Freq              = 99.54517646[MHz]
X_Offset            = 100[ppm]
X_Points            = 32768
X_Prescans          = 4
X_Resolution        = 0.95367432[Hz]
X_Sweep             = 31.25[kHz]
Irr_Domain          = 1H
Irr_Freq            = 395.88430144[MHz]
Irr_Offset          = 5[ppm]
Clipped             = FALSE
Scans               = 500
Total_Scans         = 500

Relaxation_Delay    = 2[s]
Recvr_Gain          = 48
Temp_Get            = 21.3[dC]
X_90_Width          = 9.3[us]
X_Acq_Time          = 1.048576[s]
X_Angle             = 30[deg]
X_Atn               = 3.4[dB]
X_Pulse             = 3.1[us]
Irr_Atn_Dec         = 20.20655[dB]
Irr_Atn_Noe         = 20.20655[dB]
Irr_Noise           = WALTZ
Decoupling          = TRUE
Initial_Wait        = 1[s]
Noe                 = TRUE
Noe_Time            = 2[s]
Repetition_Time     = 3.048576[s]
```