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Efficient and versatile mechanochromic luminescence of phenanthroimidazolylbenzothiadiazoles: tricolor switching and directional control over the chromism

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1. Solvatofluorochromism of phenanthroimidazolylbenzothiadiazole 1a

Bathochromic shifts in maximum emission wavelengths were observed for **1a** with increasing the polarity of solvents (Fig. S1).

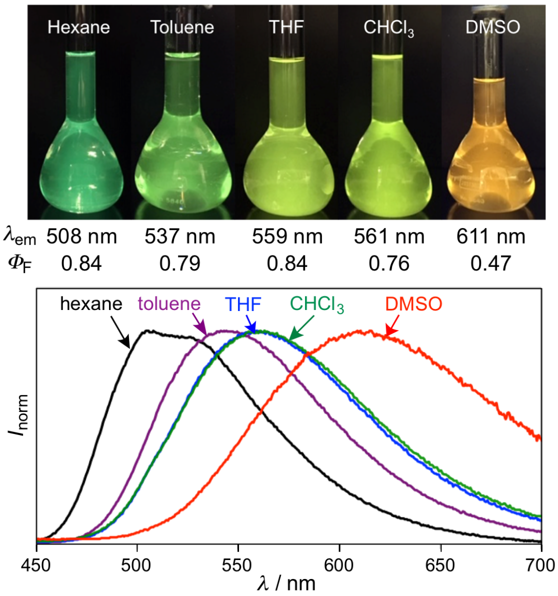


Fig. S1 Photographs and normalized fluorescence spectra of **1a** in hexane, toluene, THF, $CHCl_3$, or DMSO (1.0×10^{-5} M) irradiated with UV light.

2. Single-crystal X-ray diffraction analyses

*X-ray analysis of **1a***

A single crystal of **1a** was obtained from vapor diffusion of hexane into a chloroform solution of **1a** and was mounted on a glass fiber. All measurements were made on a Rigaku XtaLAB P200 diffractometer using multi-layer mirror monochromated Cu-Kα radiation (λ = 1.54184 Å). The data were collected at a temperature of -50 ± 1 °C to a maximum 2θ value of 152.9°. A total of 4040 oscillation images were collected. The crystal-to-detector distance was 29.00 mm. Readout was performed in the 0.172 mm pixel mode.

Of the 35863 reflections that were collected, 4434 were unique (R_{int} = 0.0694); equivalent reflections were merged. Data were collected and processed using CrysAlisPro (Rigaku Oxford Diffraction).[1] The linear absorption coefficient, μ, for Cu-Kα radiation is 14.302 cm^{-1}. An empirical absorption correction was applied which resulted in transmission factors ranging from 0.044 to 0.813. The data were corrected for Lorentz and polarization effects.

The structure was solved by direct methods (SIR2011)[2] and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined using the riding model. All calculations were performed using the CrystalStructure[3] crystallographic software package except for refinement, which was performed using SHELXL Version 2014/7.[4]

Crystal data for **1a** (CCDC 1886938): $C_{33}H_{20}N_4S$, M = 504.61, monoclinic, a = 11.56239(16) Å, b = 10.33576(16) Å, c = 20.3081(3) Å, β = 95.3214(12)°, V = 2416.48(6) Å^3, space group $P2_1/c$ (no. 14), Z = 4, D_c = 1.387 g cm^{-3}, $F(000)$ = 1048.00, T = 223(1) K, μ(Cu-Kα) = 14.302 cm^{-1}, 35863 reflections measured, 4434 independent (R_{int} = 0.0694). The final refinement converged to R_1 = 0.0426 for $I > 2.0\sigma(I)$, wR_2 = 0.1157 for all data.

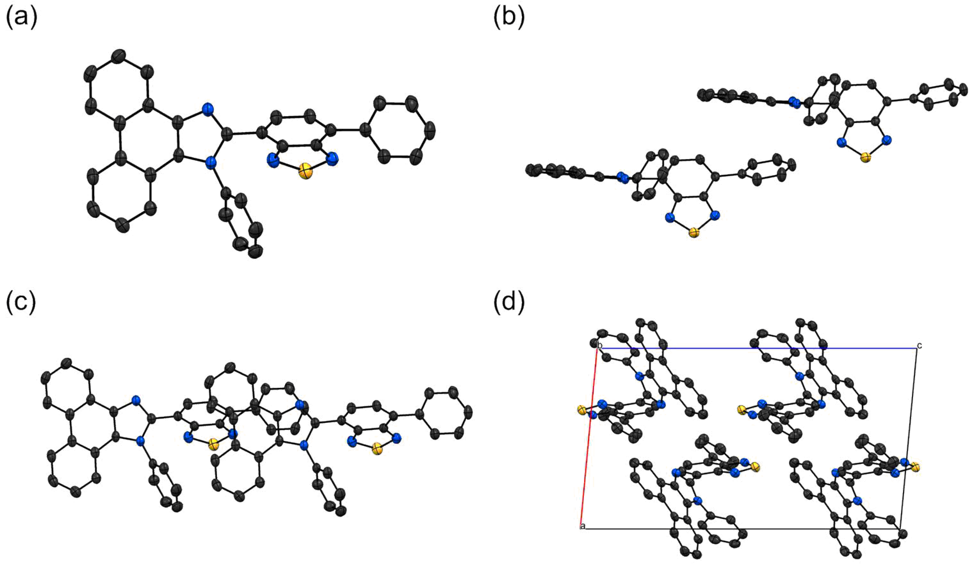


Fig. S2 The molecular structure of **1a** with atomic displacement parameters set at 50% probability (Color code: gray = C, red = O, blue = N, yellow = S). All hydrogen atoms are omitted for clarity. (a) Front view. (b) Side view of neighbouring two molecules. (c) Front view of neighbouring two molecules. (d) Unit cell structure viewed along b-axis.

*X-ray analysis of **1b***

A single crystal of **1b** was obtained from vapor diffusion of hexane into a chloroform solution of **1b** and was mounted on a glass fiber. All measurements were made on a Rigaku XtaLAB P200 diffractometer using graphite monochromated Cu-Kα radiation (λ = 1.54184 Å). The data were collected at a temperature of –50 ± 1 °C to a maximum 2θ value of 152.9°. A total of 6446 oscillation images were collected. The crystal-to-detector distance was 40.00 mm. Readout was performed in the 0.172 mm pixel mode.

Of the 61336 reflections that were collected, 9290 were unique (R_{int} = 0.0741); equivalent reflections were merged. Data were collected and processed using CrysAlisPro (Rigaku Oxford Diffraction).[1] The linear absorption coefficient, μ, for Cu-Kα radiation is 13.734 cm^{-1}. An empirical absorption correction was applied which resulted in transmission factors ranging from 0.313 to 0.771. The data were corrected for Lorentz and polarization effects.

The structure was solved by direct methods (SIR2011)[2] and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined using the riding model. All calculations were performed using the CrystalStructure[3] crystallographic software package except for refinement, which was performed using SHELXL Version 2014/7.[4]

Crystal data for **1b** (CCDC 1886939): $C_{34}H_{22}N_4S$, M = 518.64, triclinic, a = 11.68960(7) Å, b = 15.16518(10) Å, c = 16.54421(10) Å, α = 106.7151(6)°, β = 97.5581(5)°, γ = 110.4272(6)°, V = 2542.92(3) Å^3, space group P-1 (no. 2), Z = 4, D_c = 1.355 g cm^{-3}, F(000) = 1080.00, T = 223(1) K, μ(Cu-Kα) = 13.734 cm^{-1}, 61336 reflections measured, 9290 independent (R_{int} = 0.0741). The final refinement converged to R_1 = 0.0461 for $I > 2.0\sigma(I)$, wR_2 = 0.1301 for all data.

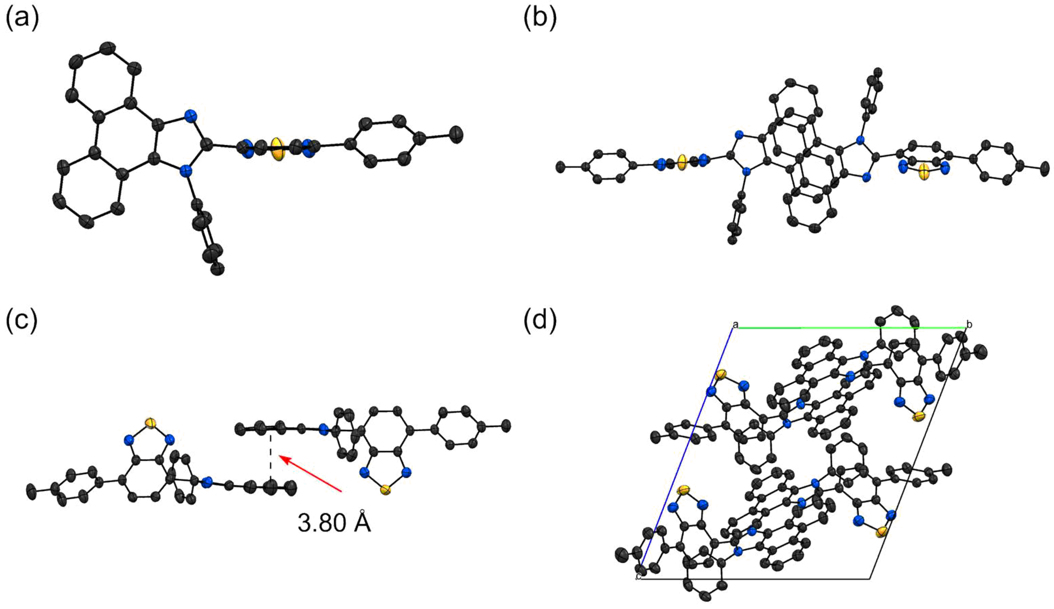


Fig. S3 The molecular structure of **1b** with atomic displacement parameters set at 50% probability (Color code: gray = C, red = O, blue = N, yellow = S). All hydrogen atoms are omitted for clarity. (a) Front view. (b) Front view of neighbouring two molecules. (c) Side view of neighbouring two molecules. (d) Unit cell structure viewed along a-axis.

X-ray analysis of ***1c***

A single crystal of **1c** was obtained from vapor diffusion of hexane into a chloroform solution of **1c** and was mounted on a glass fiber. All measurements were made on a Rigaku XtaLAB P200 diffractometer using multi-layer mirror monochromated Cu-Kα radiation (λ = 1.54184 Å). The data were collected at a temperature of -50 ± 1 °C to a maximum 2θ value of 152.8°. A total of 1778 oscillation images were collected. The crystal-to-detector distance was 29.00 mm. Readout was performed in the 0.172 mm pixel mode.

Of the 15869 reflections that were collected, 3641 were unique (R_{int} = 0.0358); equivalent reflections were merged. Data were collected and processed using CrysAlisPro (Rigaku Oxford Diffraction).[1] The linear absorption coefficient, μ, for Cu-Kα radiation is 14.341 cm^{-1}. An empirical absorption correction was applied which resulted in transmission factors ranging from 0.636 to 0.929. The data were corrected for Lorentz and polarization effects.

The structure was solved by direct methods (SIR2011)[2] and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined using the riding model. All calculations were performed using the CrystalStructure[3] crystallographic software package except for refinement, which was performed using SHELXL Version 2014/7.[4]

Crystal data for **1c** (CCDC 1886940): $C_{34}H_{22}N_4OS$, M = 534.63, orthorhombic, a = 19.24398(15) Å, b = 21.13245(17) Å, c = 6.19786(5) Å, V = 2520.50(3) Å^3, space group $Pna2_1$ (no. 33), Z = 4, D_c = 1.409 g cm^{-3}, $F(000)$ = 1112.00, T = 223(1) K, μ(Cu-Kα) = 14.341 cm^{-1}, 15869 reflections measured, 3641 independent (R_{int} = 0.0358). The final refinement converged to R_1 = 0.0309 for $I > 2.0\sigma(I)$, wR_2 = 0.0814 for all data.

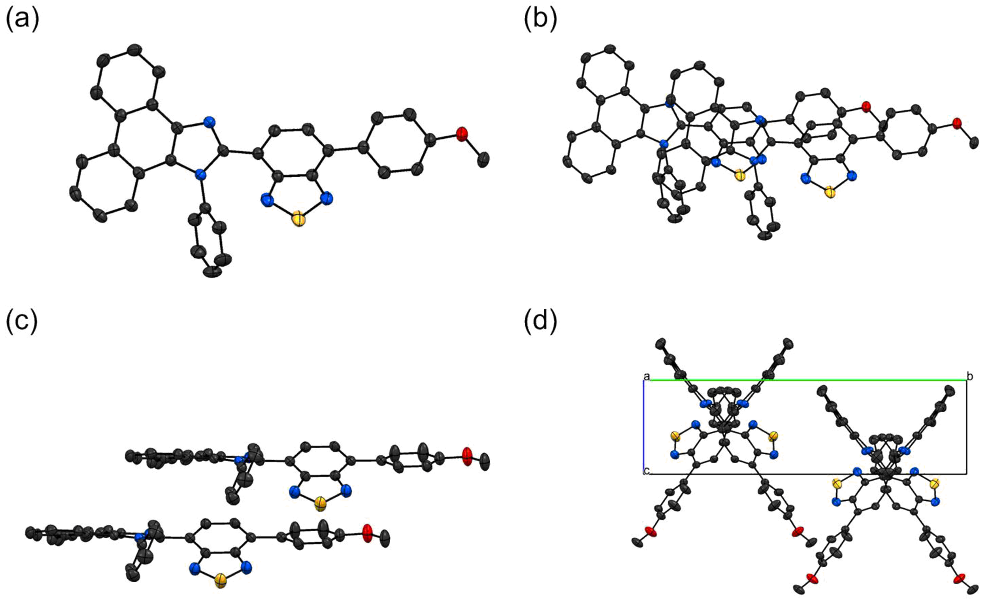


Fig. S4 The molecular structure of **1c** with atomic displacement parameters set at 50% probability (Color code: gray = C, red = O, blue = N, yellow = S). All hydrogen atoms are omitted for clarity. (a) Front view. (b) Front view of neighbouring two molecules. (c) Side view of neighbouring two molecules. (d) Unit cell structure viewed along a-axis.

X-ray analysis of ***1d***

A single crystal of **1d** was obtained from vapor diffusion of hexane into a chloroform solution of **1d** and was mounted on a glass fiber. All measurements were made on a Rigaku XtaLAB P200 diffractometer using graphite monochromated Cu-Kα radiation (λ = 1.54184 Å). The data were collected at a temperature of –50 ± 1 °C to a maximum 2θ value of 153.1°. A total of 3480 oscillation images were collected. The crystal-to-detector distance was 40.00 mm. Readout was performed in the 0.172 mm pixel mode.

Of the 34979 reflections that were collected, 5081 were unique (R_{int} = 0.0585); equivalent reflections were merged. Data were collected and processed using CrysAlisPro (Rigaku Oxford Diffraction).[1] The linear absorption coefficient, μ, for Cu-Kα radiation is 13.140 cm^{-1}. An empirical absorption correction was applied which resulted in transmission factors ranging from 0.336 to 0.778. The data were corrected for Lorentz and polarization effects.

The structure was solved by direct methods (SIR2011)[2] and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined using the riding model. All calculations were performed using the CrystalStructure[3] crystallographic software package except for refinement, which was performed using SHELXL Version 2014/7.[4]

Crystal data for **1d** (CCDC 1886941): $C_{35}H_{24}N_4OS$, M = 548.66, monoclinic, a = 15.39674(12) Å, b = 10.80897(7) Å, c = 17.32088(15) Å, β = 105.4259(9)°, V = 2778.75(4) Å^3, space group $P2_1/n$ (no. 14), Z = 4, D_c = 1.311 g cm^{-3}, F(000) = 1144.00, T = 223(1) K, μ(Cu-Kα) = 13.140 cm^{-1}, 34979 reflections measured, 5081 independent (R_{int} = 0.0585). The final refinement converged to R_1 = 0.0435 for $I > 2.0\sigma(I)$, wR_2 = 0.1215 for all data.

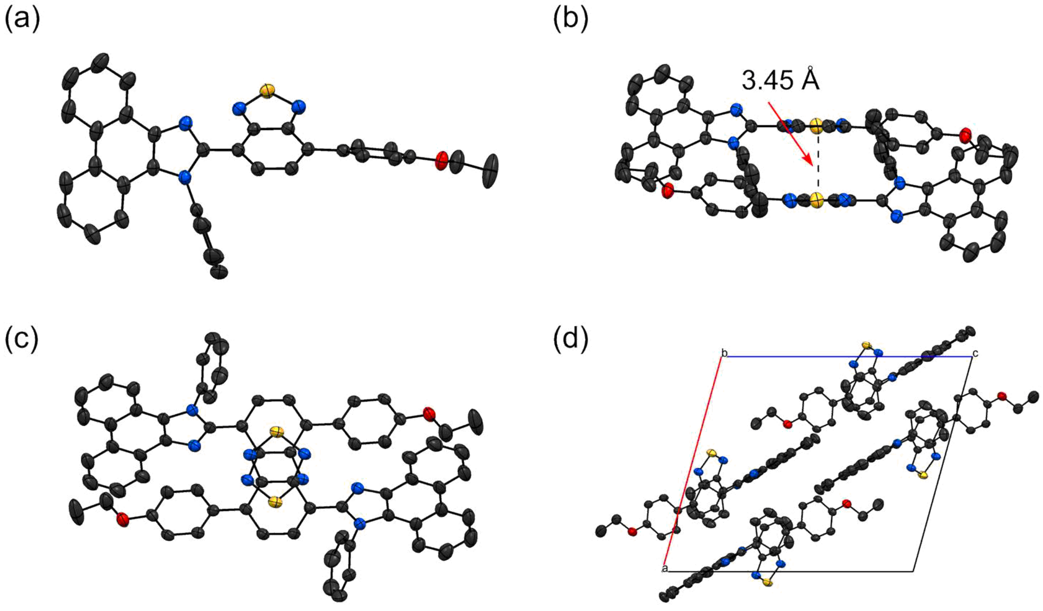


Fig. S5 The molecular structure of **1d** with atomic displacement parameters set at 50% probability (Color code: gray = C, red = O, blue = N, yellow = S). All hydrogen atoms are omitted for clarity. (a) Front view. (b) Side view of neighbouring two molecules. (c) Top view of neighbouring two molecules. (d) Unit cell structure viewed along b-axis.

*X-ray analysis of **1e***

A single crystal of **1e** was obtained from vapor diffusion of hexane into a chloroform solution of **1e** and was mounted on a glass fiber. All measurements were made on a Rigaku XtaLAB P200 diffractometer using graphite monochromated Cu-Kα radiation (λ = 1.54184 Å). The data were collected at a temperature of -50 ± 1 °C to a maximum 2θ value of 159.1°. A total of 2976 oscillation images were collected. The crystal-to-detector distance was 40.00 mm. Readout was performed in the 0.172 mm pixel mode.

Of the 25114 reflections that were collected, 4474 were unique (R_{int} = 0.0450); equivalent reflections were merged. Data were collected and processed using CrysAlisPro (Rigaku Oxford Diffraction).[1] The linear absorption coefficient, μ, for Cu-Kα radiation is 14.932 cm^{-1}. An empirical absorption correction was applied which resulted in transmission factors ranging from 0.484 to 0.813. The data were corrected for Lorentz and polarization effects.

The structure was solved by direct methods (SIR2011)[2] and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined using the riding model. All calculations were performed using the CrystalStructure[3] crystallographic software package except for refinement, which was performed using SHELXL Version 2014/7.[4]

Crystal data for **1e** (CCDC 1886942): $C_{33}H_{19}FN_4S$, M = 522.60, monoclinic, a = 9.7866(3) Å, b = 16.2397(5) Å, c = 15.7471(5) Å, β = 102.022(3)°, V = 2447.82(13) Å^3, space group $P2_1/n$ (no. 14), Z = 4, D_c = 1.418 g cm^{-3}, $F(000)$ = 1080.00, T = 223(1) K, μ(Cu-Kα) = 14.932 cm^{-1}, 25114 reflections measured, 4474 independent (R_{int} = 0.0450). The final refinement converged to R_1 = 0.0390 for $I > 2.0\sigma(I)$, wR_2 = 0.1073 for all data.

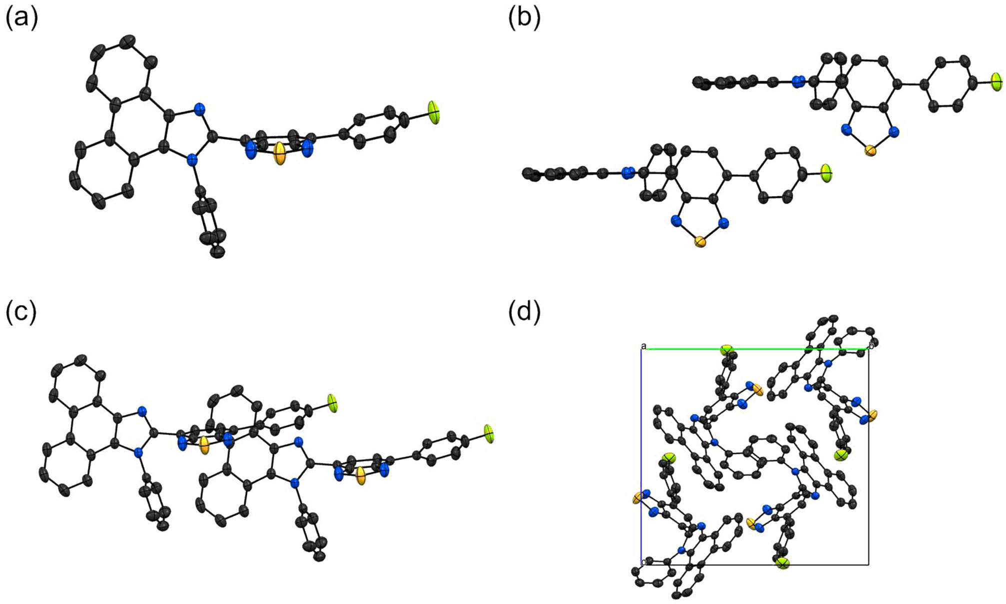


Fig. S6 The molecular structure of **1e** with atomic displacement parameters set at 50% probability (Color code: gray = C, red = O, blue = N, yellow = S, green = F). All hydrogen atoms are omitted for clarity. (a) Front view. (b) Side view of neighbouring two molecules. (c) Front view of neighbouring two molecules. (d) Unit cell structure viewed along a-axis.

*X-ray analysis of **1f***

A single crystal of **1f** was obtained from vapor diffusion of hexane into a chloroform solution of **1f** and was mounted on a glass fiber. All measurements were made on a Rigaku XtaLAB P200 diffractometer using graphite monochromated Cu-Kα radiation (λ = 1.54184 Å). The data were collected at a temperature of −50 ± 1 °C to a maximum 2θ value of 153.8°. A total of 2936 oscillation images were collected. The crystal-to-detector distance was 40.00 mm. Readout was performed in the 0.172 mm pixel mode.

Of the 28440 reflections that were collected, 8231 were unique (R_{int} = 0.0668); equivalent reflections were merged. Data were collected and processed using CrysAlisPro (Rigaku Oxford Diffraction).[1] The linear absorption coefficient, μ, for Cu-Kα radiation is 15.097 cm^{-1}. An empirical absorption correction was applied which resulted in transmission factors ranging from 0.132 to 0.470. The data were corrected for Lorentz and polarization effects.

The structure was solved by direct methods (SIR2011)[2] and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined using the riding model. All calculations were performed using the CrystalStructure[3] crystallographic software package except for refinement, which was performed using SHELXL Version 2014/7.[4]

Crystal data for **1f** (CCDC 1886943): $C_{34}H_{19}F_3N_4S$, M = 572.61, monoclinic, a = 10.20299(16) Å, b = 15.8241(2) Å, c = 16.8045(3) Å, β = 93.1817(15)°, V = 2708.96(7) Å^3, space group Pc (no. 7), Z = 4, D_c = 1.404 g cm^{-3}, $F(000)$ = 1176.00, T = 223(1) K, μ(Cu-Kα) = 15.097 cm^{-1}, 28440 reflections measured, 8231 independent (R_{int} = 0.0668). The final refinement converged to R_1 = 0.0633 for $I > 2.0\sigma(I)$, wR_2 = 0.1793 for all data.

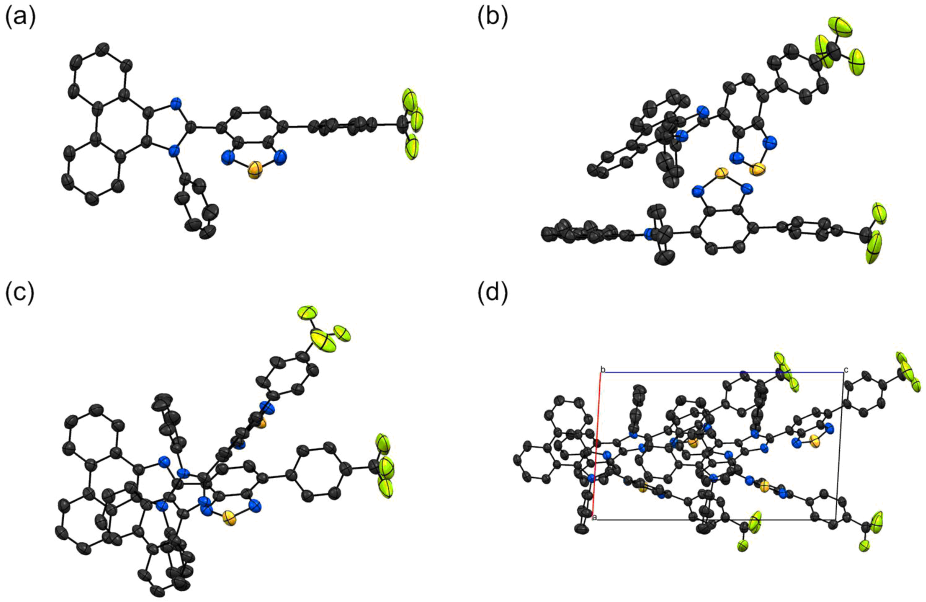


Fig. S7 The molecular structure of **1f** with atomic displacement parameters set at 50% probability (Color code: gray = C, red = O, blue = N, yellow = S, green = F). All hydrogen atoms are omitted for clarity. (a) Front view. (b) Side view of neighbouring two molecules. (c) Front view of neighbouring two molecules. (d) Unit cell structure viewed along b-axis.

Determination of bend angle

As a representable example, the definition and determination for the bend angle of benzothiadiazole ring in crystalline **1e** is shown in Fig. 8. The bend angle is defined as the dihedral angle of two planes of both sides of benzothiadiazole ring, in which one is defined by three carbons C15, C17, and C21, and the other is by C18, C20, and C22.

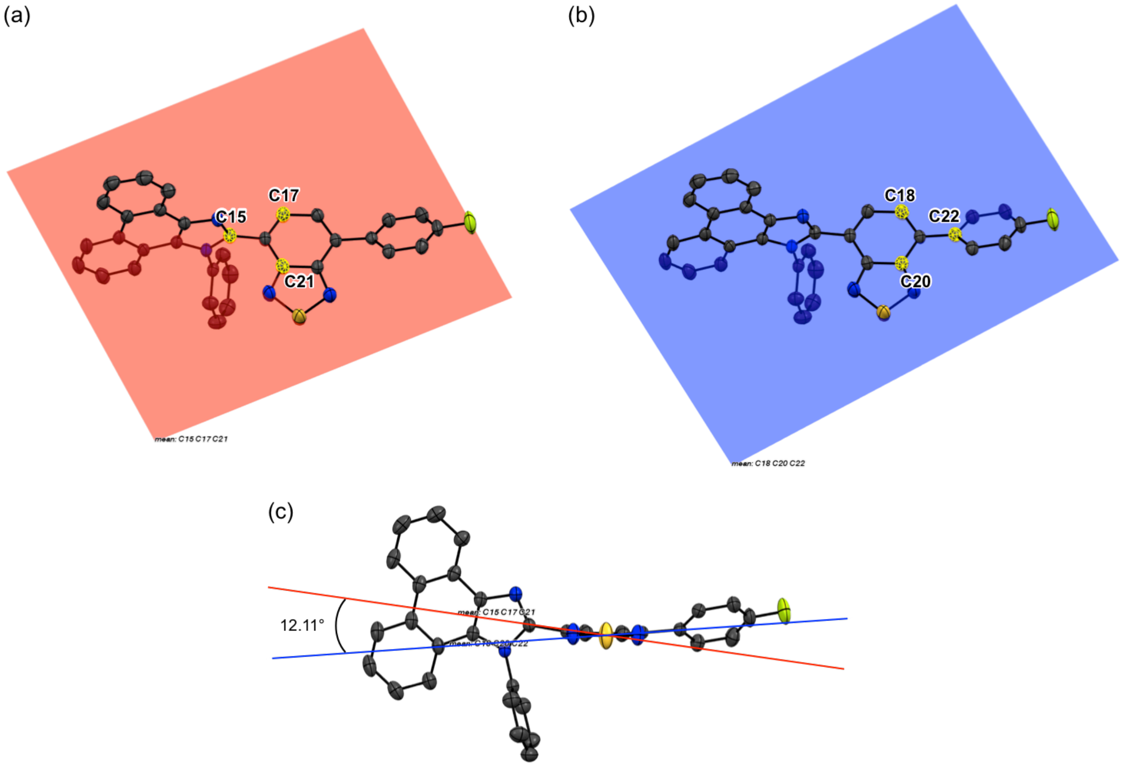


Fig. S8 Determination for bend angle of benzothiadiazole ring in **1e** (Color code: gray = C, red = O, blue = N, yellow = S, green = F). (a,b) Molecular structure with two planes created by C15, C17, and C21 as well as C18, C20, and C22, respectively. (c) Front view of molecular structure with dihedral angle of two planes.

3. Theoretical calculations

Experimental absorption maxima and the results of DFT and TD-DFT calculations are shown in Table S1.

Table S1 Experimental absorption maxima and calculated absorption properties of X-ray structures for **1a**–**f**.

Compd	Absorption in toluene λ_{abs} (nm)	Calcd absorption λ_{abs} (nm)	Transition from HOMO to LUMO	Oscillator strength	HOMO (eV)	LUMO (eV)	Dipole moment (D)
1a	414	369	0.642	0.339	–6.48	–1.27	3.98
1b-1	413	361	0.605	0.370	–6.46	–1.14	4.67
1b-2	413	340	0.687	0.003	–6.51	–1.18	4.75
1c	419	406	0.665	0.626	–6.26	–1.24	4.06
1d	417	377	0.655	0.586	–6.38	–1.04	5.74
1e	416	349	0.652	0.110	–6.59	–1.32	4.10
1f-1	420	373	0.658	0.361	–6.54	–1.43	4.10
1f-2	420	371	0.654	0.366	–6.61	–1.45	3.99

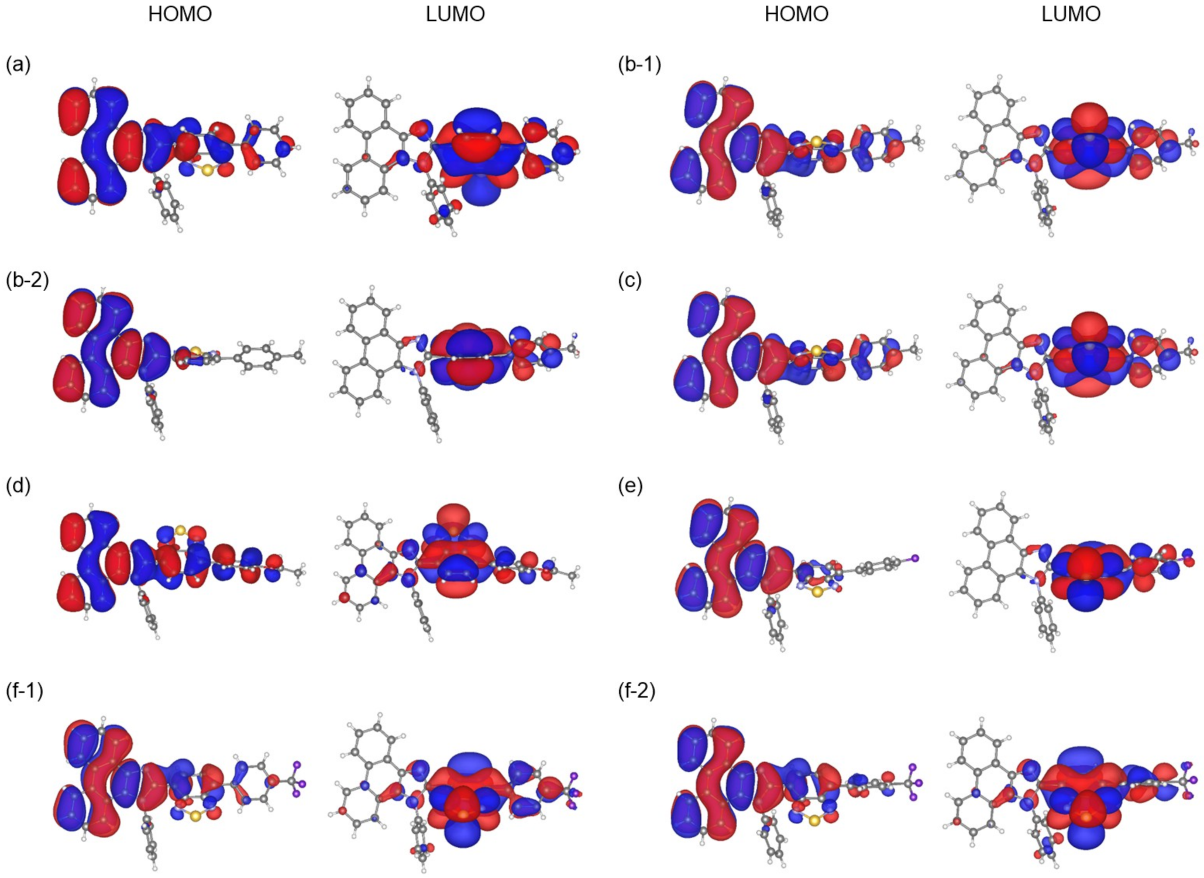
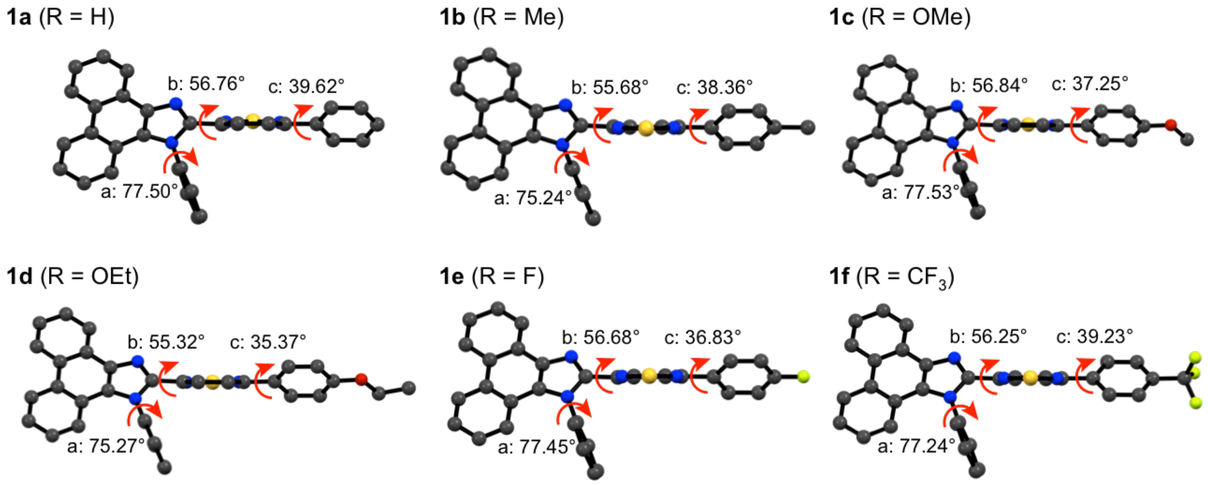


Fig. S9 HOMO and LUMO of **1a** (a), **1b** (b), **1c** (c), **1d** (d), **1e** (e), and **1f** (f) calculated at the CAM-B3LYP/6-31G(d) level. The structures are drawn by VESTA.[5]

An optimization of the molecular structures of **1a**–**f** was carried out by DFT calculations at the CAM-B3LYP/6-31G(d) level of theory, using the single-crystal X-ray diffraction structures as the initial geometry. The molecular conformations and absorption properties for optimized structures of **1a**–**f** obtained by DFT and TD-DFT calculations are shown in Tables S2 and S3.

Table S2 Sum of the dihedral angles (a–c) of adjacent (hetero)aryl groups and bend angles of the benzothiadiazole rings for optimized structures of **1a**–**f**.



Compd	a (°)	b (°)	c (°)	a+b+c (°)[a]	Bend angle (°)[b]	Calcd absorption λ_{abs} (nm)[c]
1a	77.50	56.76	39.62	173.88	0.43	373
1b-1	75.24	55.68	38.36	169.28	1.76	368
1b-2	77.49	56.80	38.91	173.20	0.46	374
1c	77.53	56.84	37.25	171.62	0.57	380
1d	75.27	55.32	35.37	165.96	2.84	374
1e	77.45	56.68	36.83	170.96	0.58	376
1f-1	77.24	56.25	39.23	172.72	0.44	379
1f-2	77.24	56.38	37.19	170.81	0.45	379

[a] Sum of the dihedral angles a–c. [b] Bend angles of the benzothiadiazole rings (Fig. S8). [c] Maximum absorption wavelength calculated at the CAM-B3LYP/6-31G(d) level of theory.

Table S3 Calculated absorption properties of optimized structures for **1a**–**f**.

Compd	Absorption in toluene λ_{abs} (nm)	Calcd absorption λ_{abs} (nm)	Transition from HOMO to LUMO	Oscillator strength	HOMO (eV)	LUMO (eV)	Dipole moment (D)
1a	414	373	0.641	0.392	–6.50	–1.30	3.66
1b-1	413	368	0.634	0.475	–6.47	–1.17	5.06
1b-2	413	374	0.633	0.433	–6.48	–1.27	3.89
1c	419	380	0.624	0.471	–6.44	–1.24	4.97
1d	417	374	0.631	0.530	–6.42	–1.13	5.41
1e	416	376	0.643	0.388	–6.54	–1.38	3.25
1f-1	420	379	0.656	0.391	–6.61	–1.51	3.90
1f-2	420	379	0.657	0.385	–6.61	–1.52	3.69

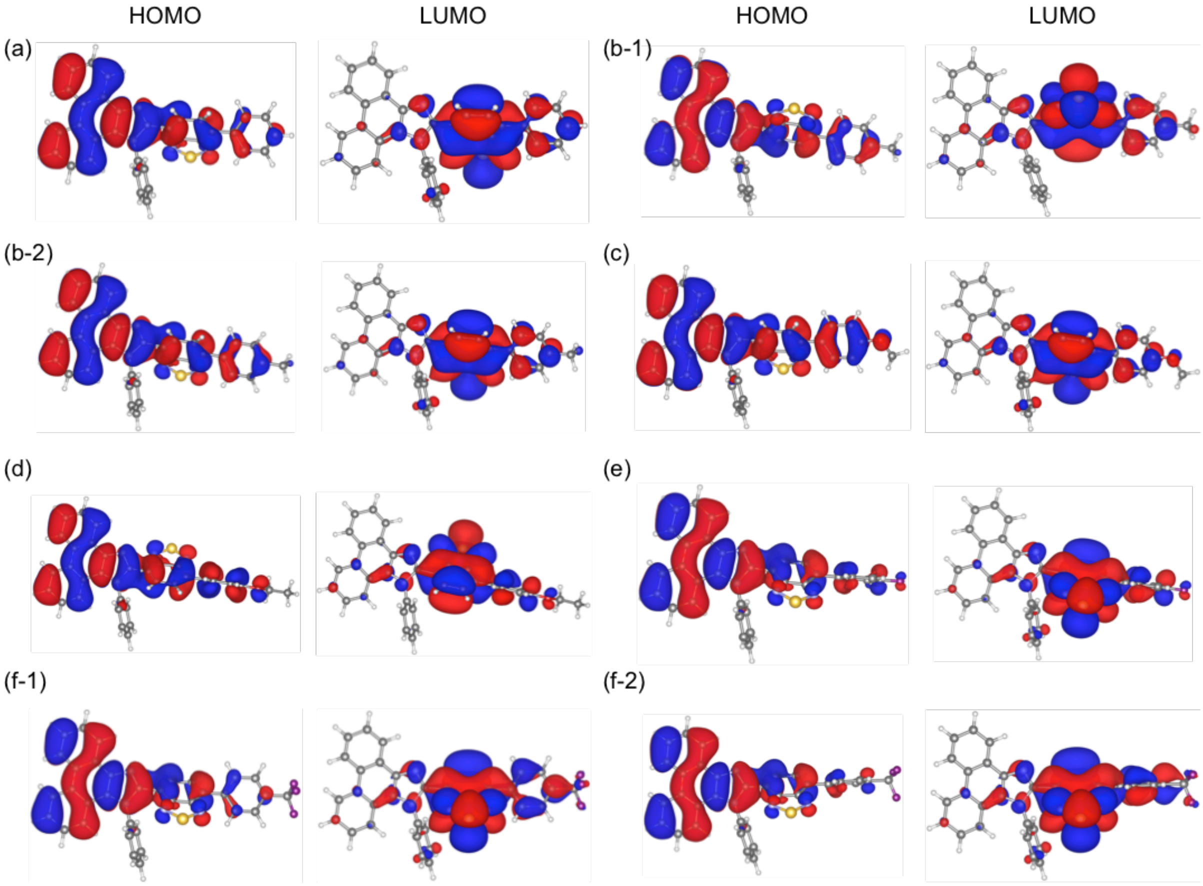


Fig. S10 HOMO and LUMO of optimized structures for **1a** (a), **1b** (b), **1c** (c), **1d** (d), **1e** (e), and **1f** (f) calculated at the CAM-B3LYP/6-31G(d) level. The structures are drawn by VESTA.[5]

4. Absorption spectra

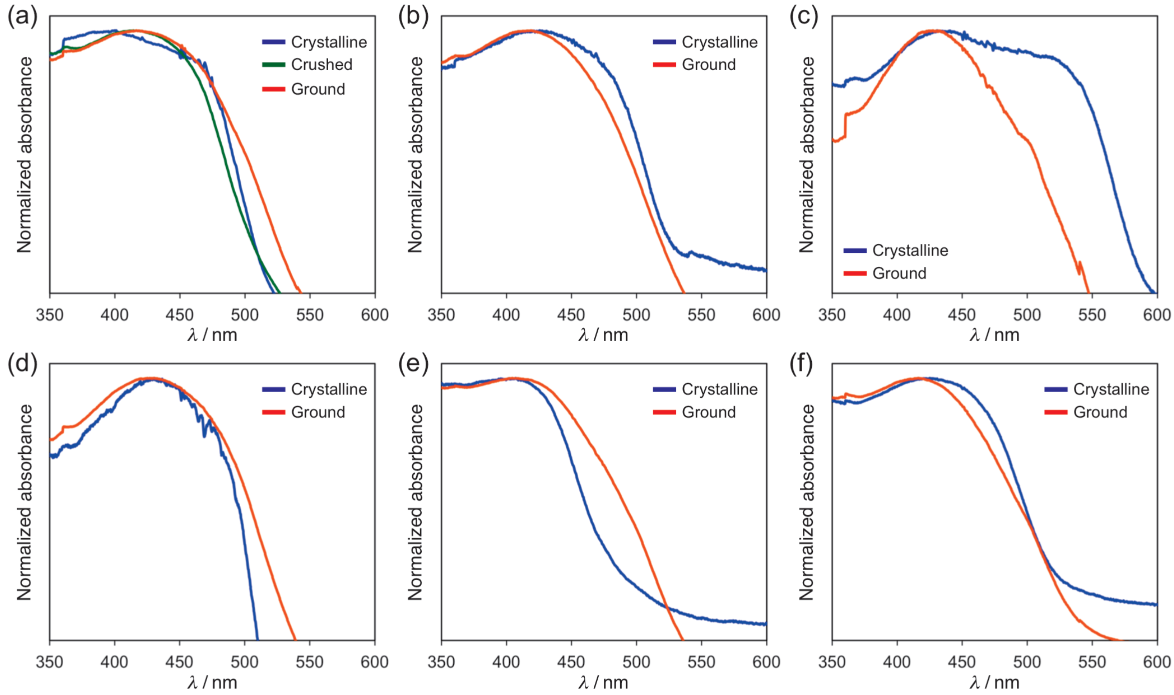


Fig. S11 Solid-state absorption spectra of **1a** (a), **1b** (b), **1c** (c), **1d** (d), **1e** (e), and **1f** (f).

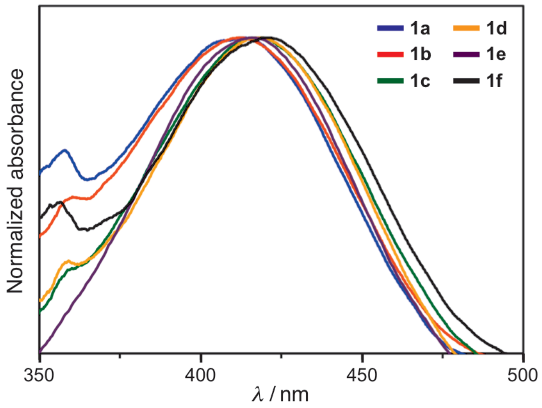
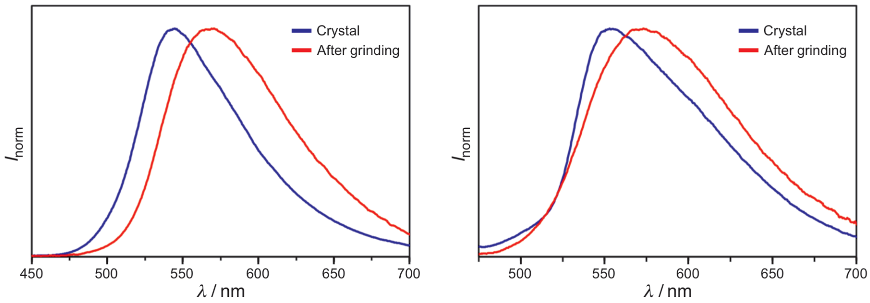


Fig. S12 Normalized UV-vis absorption spectra of **1a–f** in toluene.

5. Fluorescence spectra for the mechanochromic luminescence

Fluorescence spectra showed significant shifts in maximum emission wavelengths for **1b** and **1d**–**f** after grinding (Fig. S13).

(a) **1b** (R = Me) (b) **1d** (R = OEt)



(c) **1e** (R = F) (d) **1f** (R = CF_3)

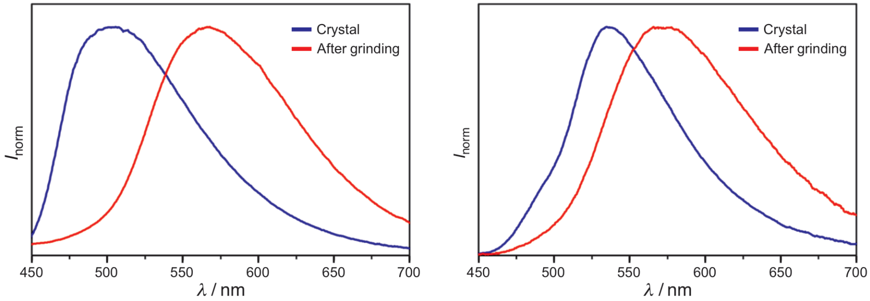
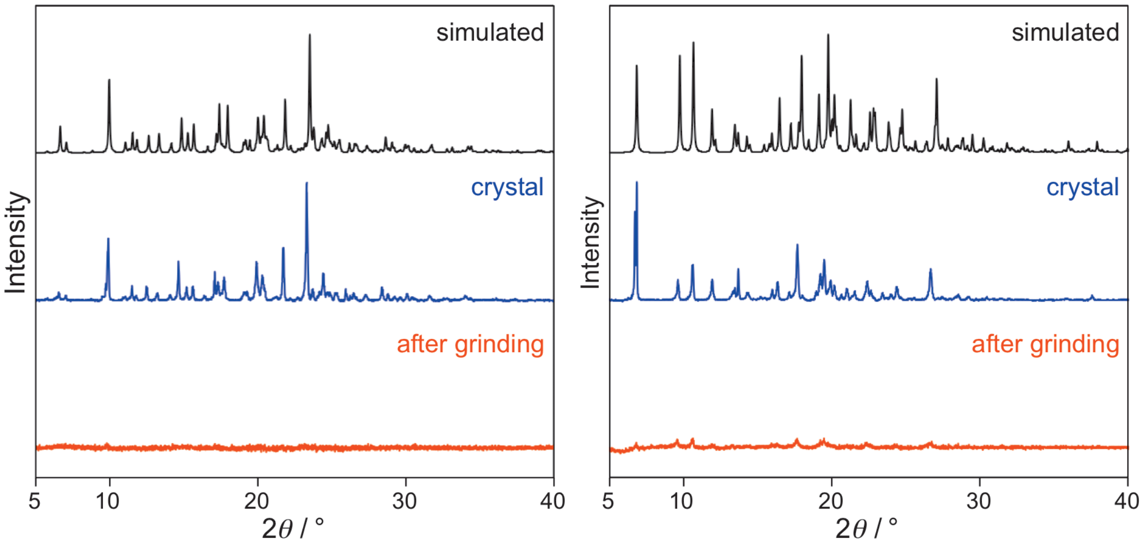


Fig. S13 Fluorescence spectra for MCL of **1b** (a), **1d** (b), **1e** (c), and **1f** (d) irradiated with UV light at 365 nm. Blue lines: crystalline samples. Red lines: ground samples.

6. Powder X-ray diffraction analyses

Powder X-ray diffraction patterns for **1b, 1d–f** showed that the crystal structures of powdered samples were identical to those of their single crystals and became amorphous upon grinding.

(a) **1b** (R = Me) (b) **1d** (R = OEt)



(c) **1e** (R = F) (d) **1f** (R = CF_3)

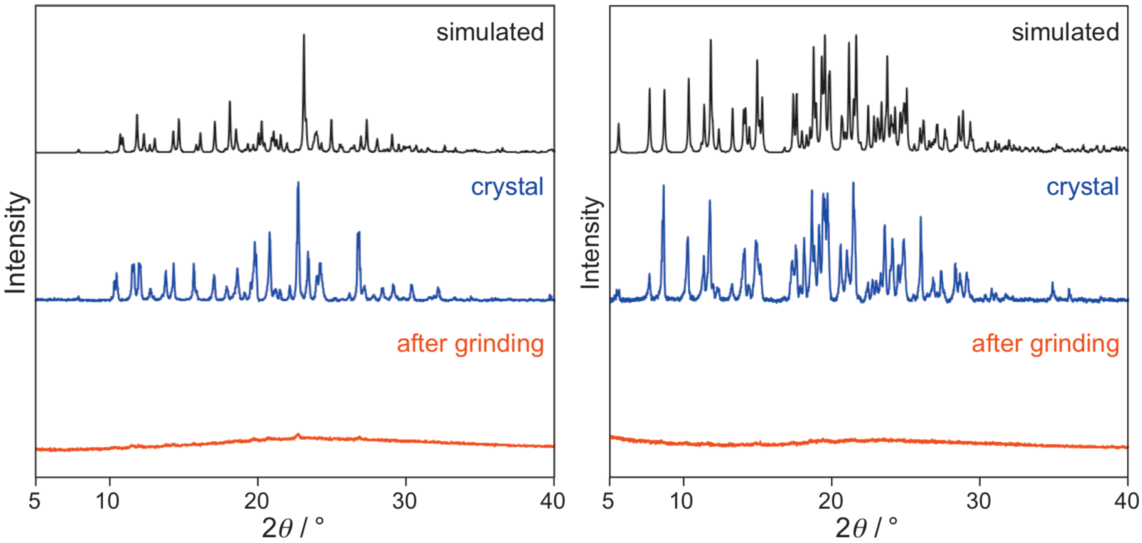


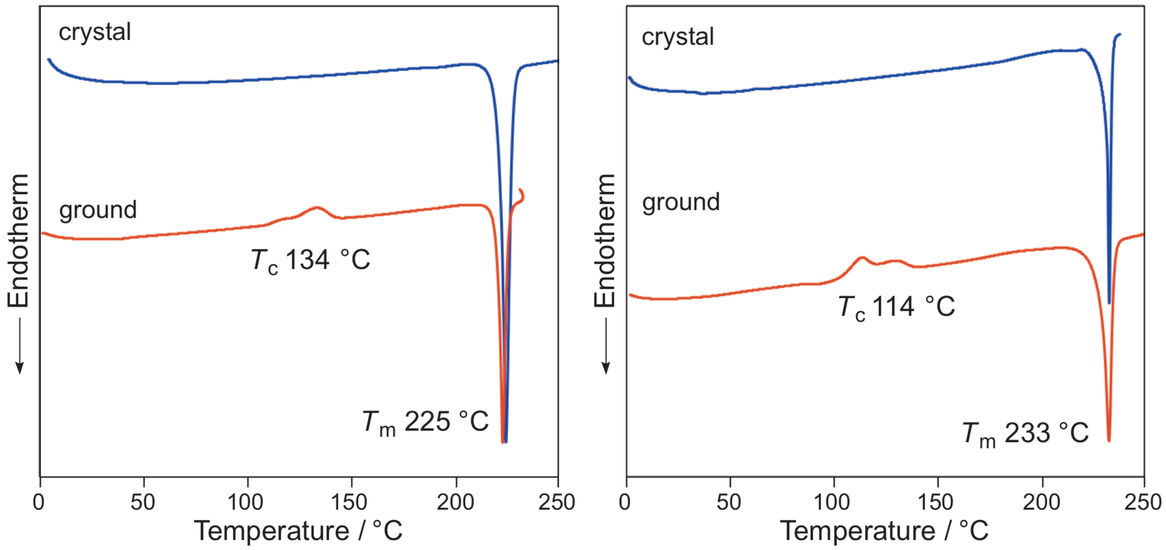
Fig. S14 PXRD patterns for **1b** (a), **1d** (b), **1e** (c), and **1f** (d). Black lines: Simulated PXRD patterns calculated from the single-crystal structure. Blue lines: Experimental PXRD patterns of the powdered crystalline samples. Red lines: Experimental PXRD patterns of the ground samples.

7. Differential scanning calorimetry (DSC) analyses

In the DSC thermograms of **1b** and **1d**–**1f**, melting points (T_m) were observed for crystalline samples and cold crystallization transition peaks (T_c) were observed for their ground samples.

(a) DSC scans of **1b**

(b) DSC scans of **1d**



(c) DSC scans of **1e**

(d) DSC scans of **1f**

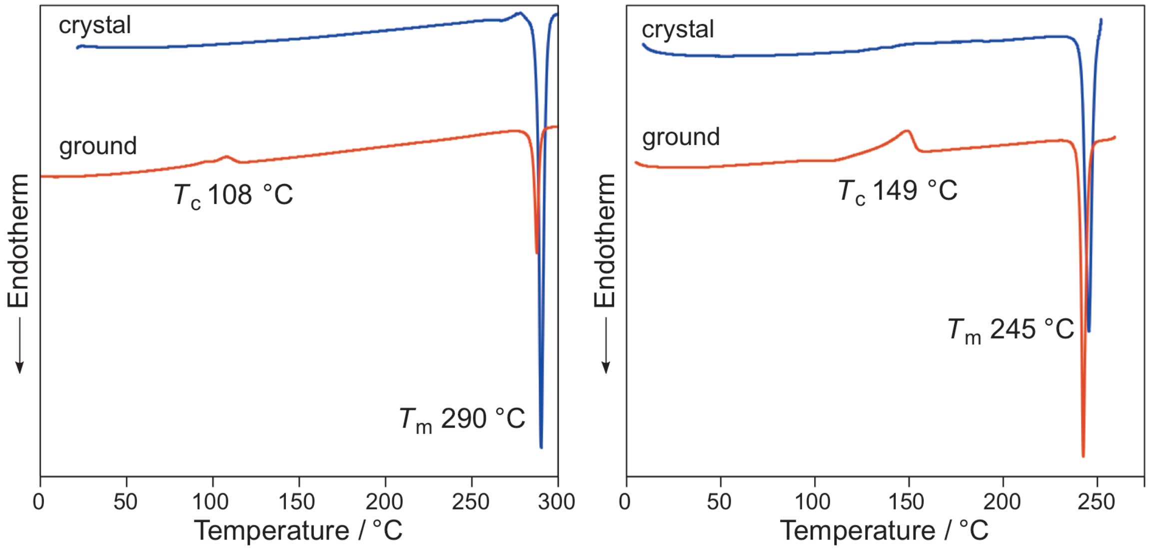


Fig. S15 DSC thermograms for **1b** (a), **1d** (b), **1e** (c), and **1f** (d). Blue lines: Powdered crystalline samples. Red lines: Ground samples. T_c and T_m values are noted near the corresponding peaks.

8. Single-particle-level observation of 1a–f by fluorescence microscope

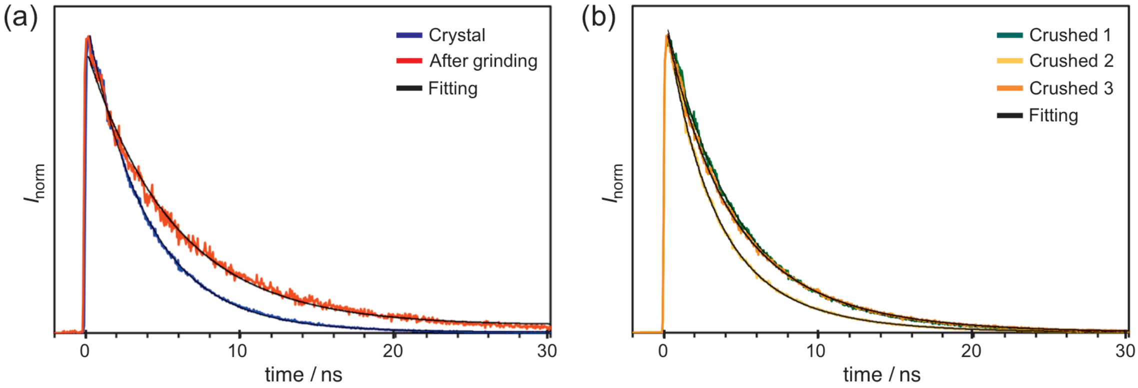


Fig. S16 (a) Decay profiles observed for crystalline (blue line) and amorphous (red line: after grinding) **1a** by single-particle fluorescence imaging. The black lines indicate single-exponential curves fitted to the time profiles. (b) Decay profiles observed for crushed 1 (green line), crushed 2 (yellow line), and crushed 3 (orange line) of **1a** by single-particle fluorescence imaging. The black lines indicate bi-exponential curves fitted to the time profiles.

Table S4 Determination of intensity-weighted mean fluorescence lifetime <τ> for crystalline and ground **1a**–**f** by single-particle fluorescence imaging[a]

Compd.	State	a_1	τ_1 (ns)	a_2	τ_2 (ns)	f_1	f_2	<τ> (ns)
1a	Crystalline	1.07	3.88					3.88
	Ground	0.94	5.62					5.62
1b	Crystalline	1.03	4.96					4.96
	Ground	1.01	5.61					5.61
1c	Crystalline	1.09	4.20					4.20
	Ground	0.96	5.81					5.81
1d	Crystalline	1.10	2.58					2.58
	Ground	0.37	1.77	0.69	5.36	0.15	0.85	4.82
1e	Crystalline	1.06	5.00					5.00
	Ground	0.98	6.00					6.00
1f	Crystalline	1.05	3.20					3.20
	Ground	0.35	2.07	0.70	6.33	0.14	0.86	5.73

[a] $<\tau> = (a_1\tau_1^2+a_2\tau_2^2)/(a_1\tau_1+a_2\tau_2)$. $f_n = a_n\tau_n/(a_1\tau_1+a_2\tau_2)$.

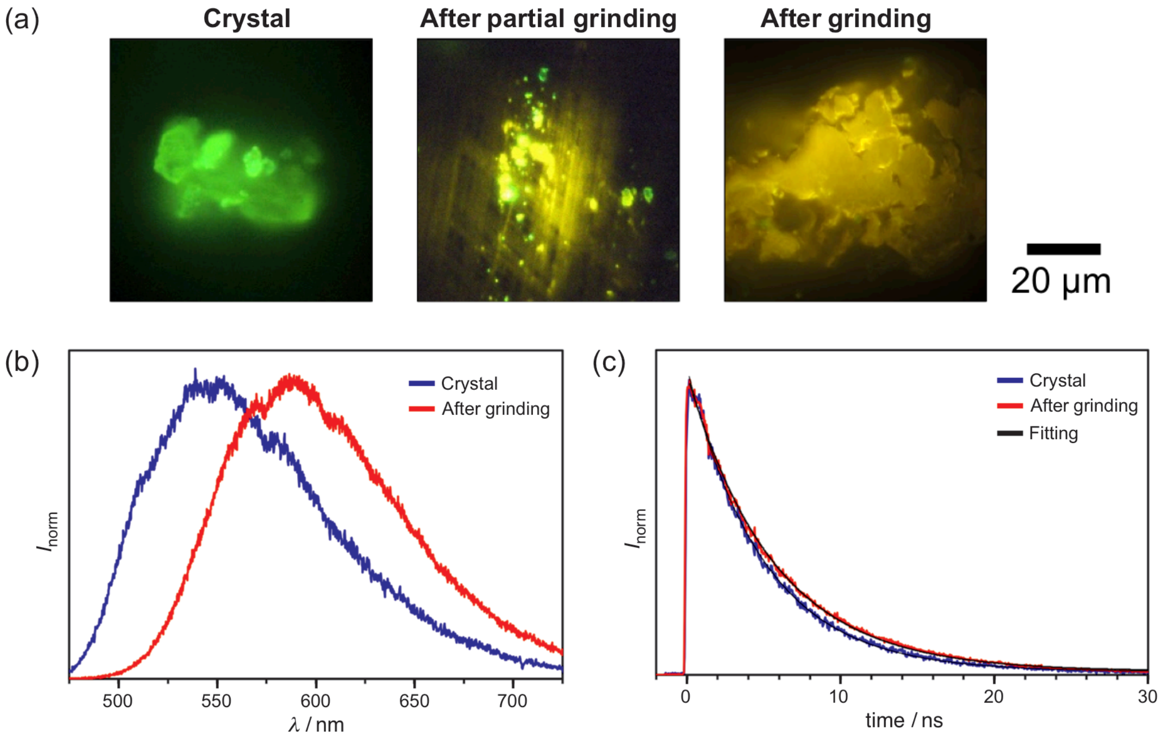


Fig. S17 Photographs (a), fluorescence spectra (b), and decay profiles (c) observed for crystalline (blue lines) and amorphous (red lines: after grinding) **1b** by single-particle fluorescence imaging. The black lines indicate single-exponential curves fitted to the time profiles.

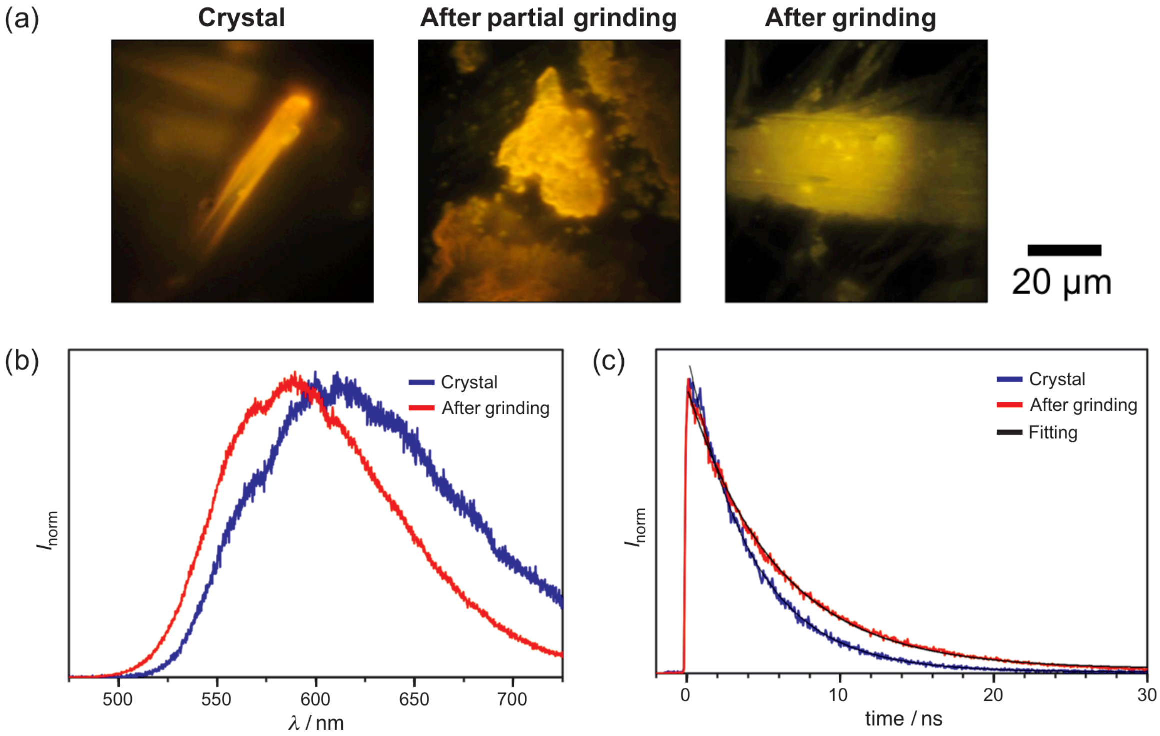


Fig. S18 Photographs (a), fluorescence spectra (b), and decay profiles (c) observed for crystalline (blue lines) and amorphous (red lines; after grinding) **1c** by single-particle fluorescence imaging. The black lines indicate single-exponential curves fitted to the time profiles.

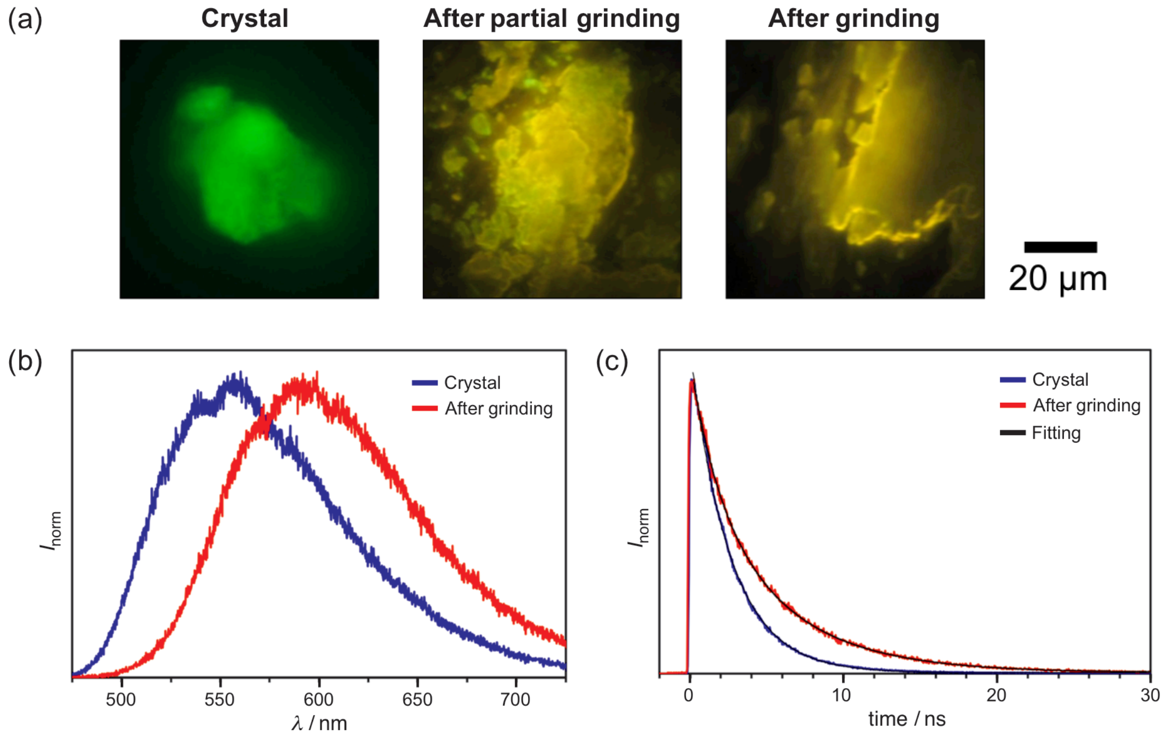


Fig. S19 Photographs (a), fluorescence spectra (b), and decay profiles (c) observed for crystalline (blue lines) and amorphous (red lines; after grinding) **1d** by single-particle fluorescence imaging. The black lines indicate single- and bi-exponential curves fitted to the time profiles.

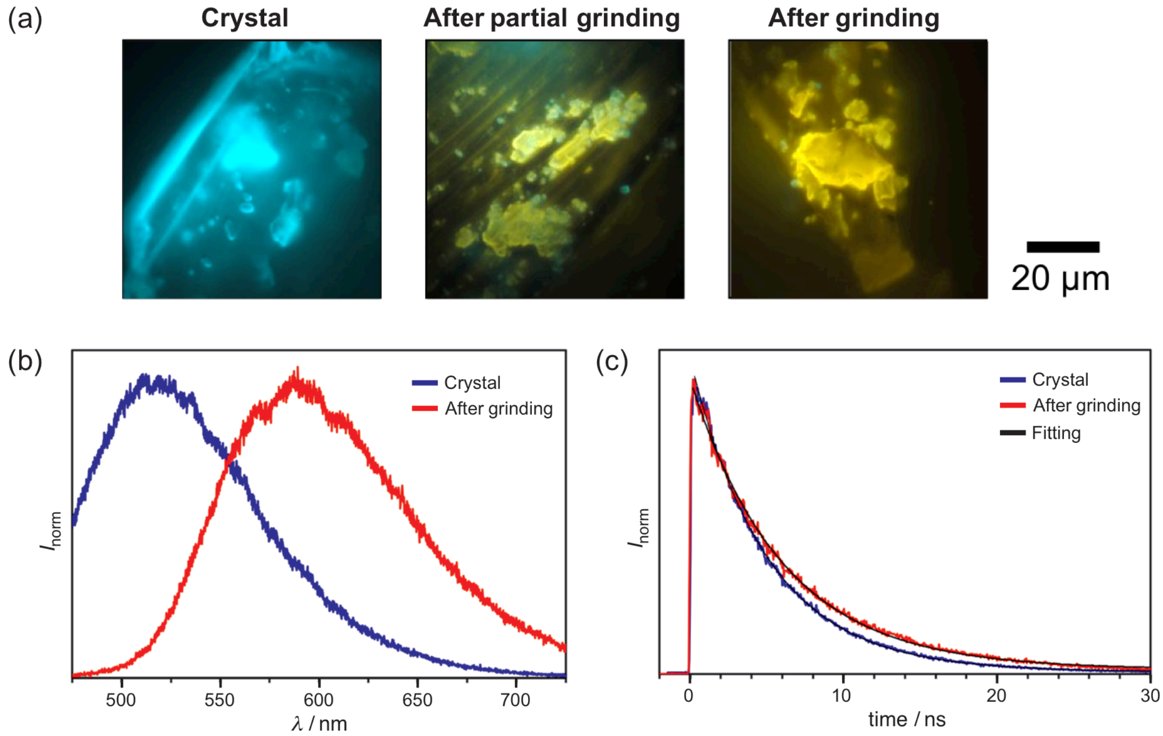


Fig. S20 Photographs (a), fluorescence spectra (b), and decay profiles (c) observed for crystalline (blue lines) and amorphous (red lines; after grinding) **1e** by single-particle fluorescence imaging. The black lines indicate single-exponential curves fitted to the time profiles.

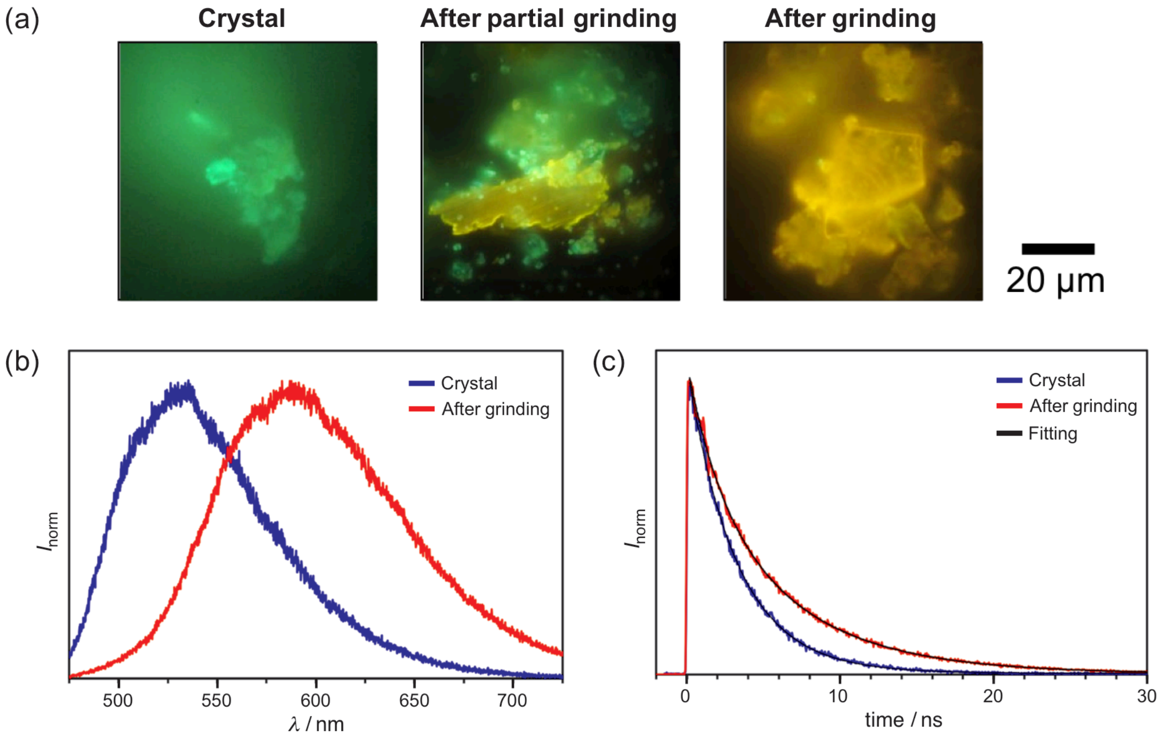


Fig. S21 Photographs (a), fluorescence spectra (b), and decay profiles (c) observed for crystalline (blue lines) and amorphous (red lines; after grinding) **1f** by single-particle fluorescence imaging. The black lines indicate single- and bi-exponential curves fitted to the time profiles.

9. References

1) CrysAlisPro: Data Collection and Processing Software, Rigaku Corporation (2015). Tokyo 196-8666, Japan.
2) SIR2011: M. C. Burla, R. Caliandro, M. Camalli, B. Carrozzini, G. L. Cascarano, C. Giacovazzo, M. Mallamo, A. Mazzone, G. Polidori and R. Spagna, *J. Appl. Cryst.*, 2012, **45**, 357.
3) CrystalStructure 4.2.5: Crystal Structure Analysis Package, Rigaku Corporation (2000-2017). Tokyo 196-8666, Japan.
4) SHELXL Version 2014/7: G. M. Sheldrick, *Acta Cryst.*, 2008, **A64**, 112.
5) K. Momma and F. Izumi, *J. Appl. Crystallogr.*, 2011, **44**, 1272.

^{1}H NMR (500 MHz, in $CDCl_3$)

Acquisition Time (sec)	3.1719	**Comment**	299 0.8	**D**	3.827959	**D1**	3.827959	**DE**	6
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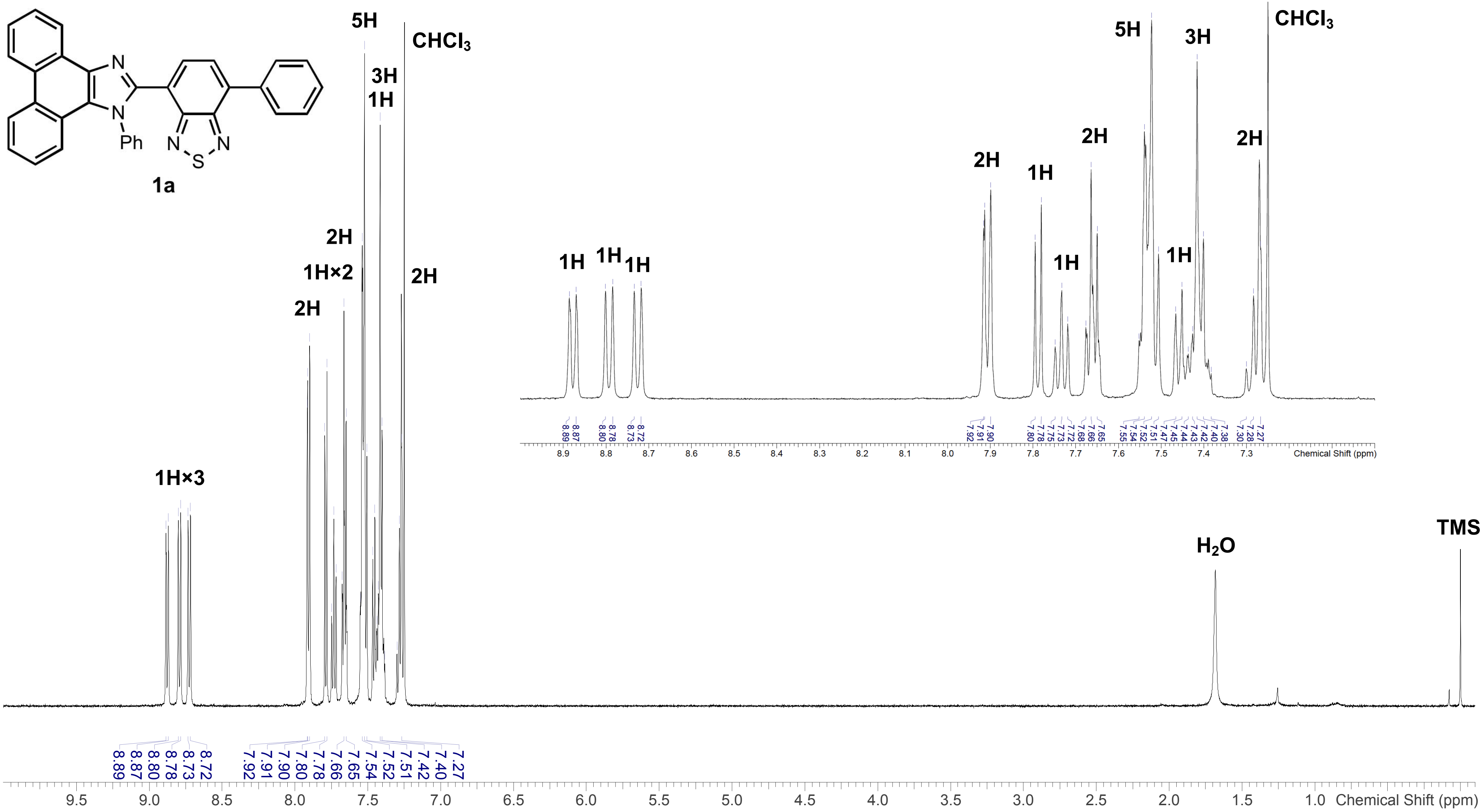
Original Points Count	32768	**Owner**	root	**PC**	1	**PROBHD**	<5 mm BBO BB-1H Z-GRD Z859001/0006 >		
PULPROG	<zg30>	**Points Count**	32768	**Pulse Sequence**	zg30	**Receiver Gain**	287.40	**SF**	500.130006648269
SFO1	500.133088507478			**SI**	32768	**SSB**	0	**SW(cyclical) (Hz)**	10330.58
SWH	10330.5785123967			**Solvent**	CHLOROFORM-d			**Spectrum Offset (Hz)**	3070.5063
Spectrum Type	standard	**Sweep Width (Hz)**	10330.26	**TD**	65536	**TD0**	1	**TE**	298.1
Temperature (degree C)	25.100	**WDW**	1						



^{13}C NMR (126 MHz, in $CDCl_3$)

Acquisition Time (sec)	1.0912	**Comment**	1f	**D**	0.00345	**D1**	2	**DE**	6
DS	4	**Date**	05 Jul 2018 10:54:35			**Date Stamp**	05 Jul 2018 10:54:35		
File Name	C:¥Users¥Asami-Lab¥Desktop¥1¥PDATA¥1¥1r			**Frequency (MHz)**	125.7578	**GB**	0	**INSTRUM**	<spect>
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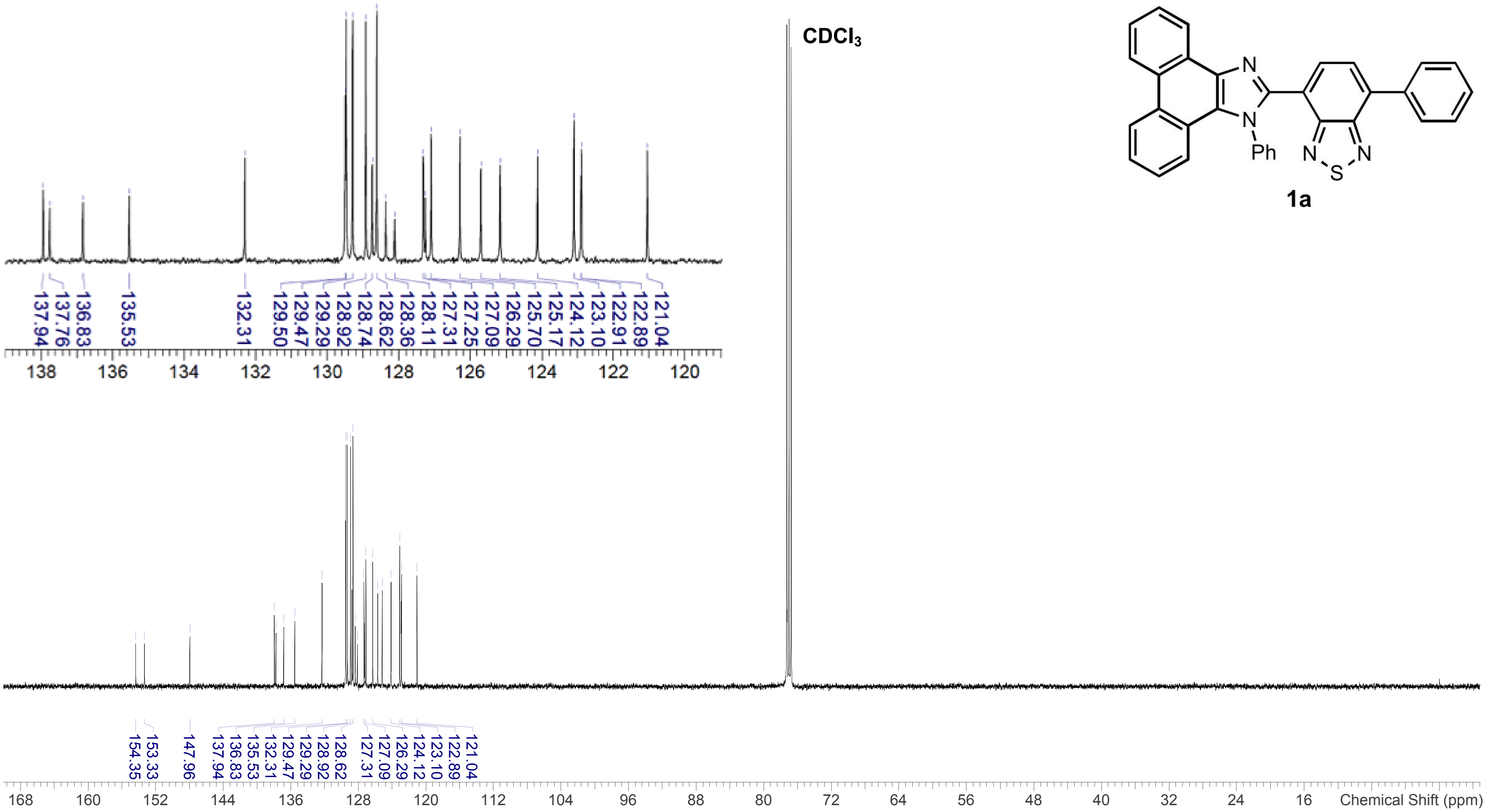
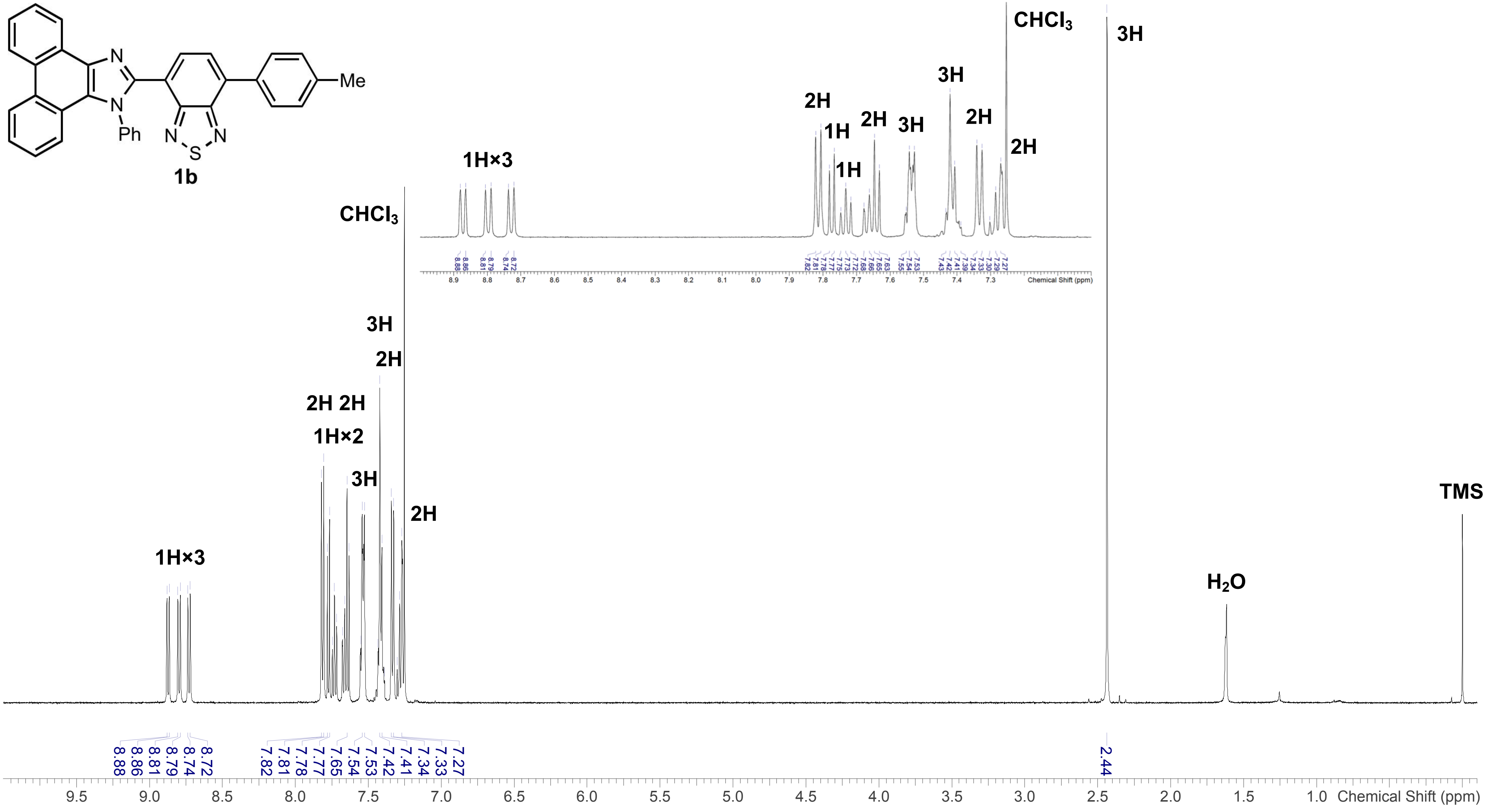
Original Points Count	32768	**Owner**	root	**PC**	1.4	**PROBHD**	<5 mm BBO BB-1H Z-GRD Z859001/0006 >		
PULPROG	<zgpg30>	**Points Count**	32768	**Pulse Sequence**	zgpg30	**Receiver Gain**	3251.00	**SF**	125.757789
SFO1	125.770364304853			**SI**	32768	**SSB**	0	**SW(cyclical) (Hz)**	30030.03
SWH	30030.03003003			**Solvent**	CHLOROFORM-d			**Spectrum Offset (Hz)**	12569.6924
Spectrum Type	standard	**Sweep Width (Hz)**	30029.11	**TD**	65536	**TD0**	1	**TE**	299.2
Temperature (degree C)	26.200	**WDW**	1						



1a

^{1}H NMR (500 MHz, in $CDCl_3$)

Acquisition Time (sec)	3.1719	**Comment**	rvp419 column1			**D**	3.827959	**D1**	3.827959
DE	6	**DS**	2	**Date**	16 Nov 2018 18:15:13			**Date Stamp**	16 Nov 2018 18:15:13
File Name	C:¥Users¥Asami-Lab¥Desktop¥sna157 MePh HNMR 20181116¥1¥PDATA¥1¥1r					**Frequency (MHz)**	500.1300	**GB**	0
INSTRUM	<spect>	**LB**	0.1	**NS**	8	**Nucleus**	1H	**Number of Transients**	8
Origin	spect	**Original Points Count**	32768	**Owner**	root	**PC**	1		
PROBHD	<5 mm BBO BB-1H Z-GRD Z859001/0006 >			**PULPROG**	<zg30>	**Points Count**	32768	**Pulse Sequence**	zg30
Receiver Gain	362.00	**SF**	500.130006648269			**SFO1**	500.133088507478		
SI	32768	**SSB**	0	**SW(cyclical) (Hz)**	10330.58	**SWH**	10330.5785123967		
Solvent	CHLOROFORM-d			**Spectrum Offset (Hz)**	3072.1069	**Spectrum Type**	standard	**Sweep Width (Hz)**	10330.26
TD	65536	**TD0**	1	**TE**	297.3	**Temperature (degree C)**	24.300	**WDW**	1



1b

^{13}C NMR (126 MHz, in CDCl$_3$)

Acquisition Time (sec)	1.0912	**D**	0.00345	**D1**	2	**DE**	6	**DS**	4
Date	10 Nov 2017 16:21:56			**Date Stamp**	10 Nov 2017 16:21:56				
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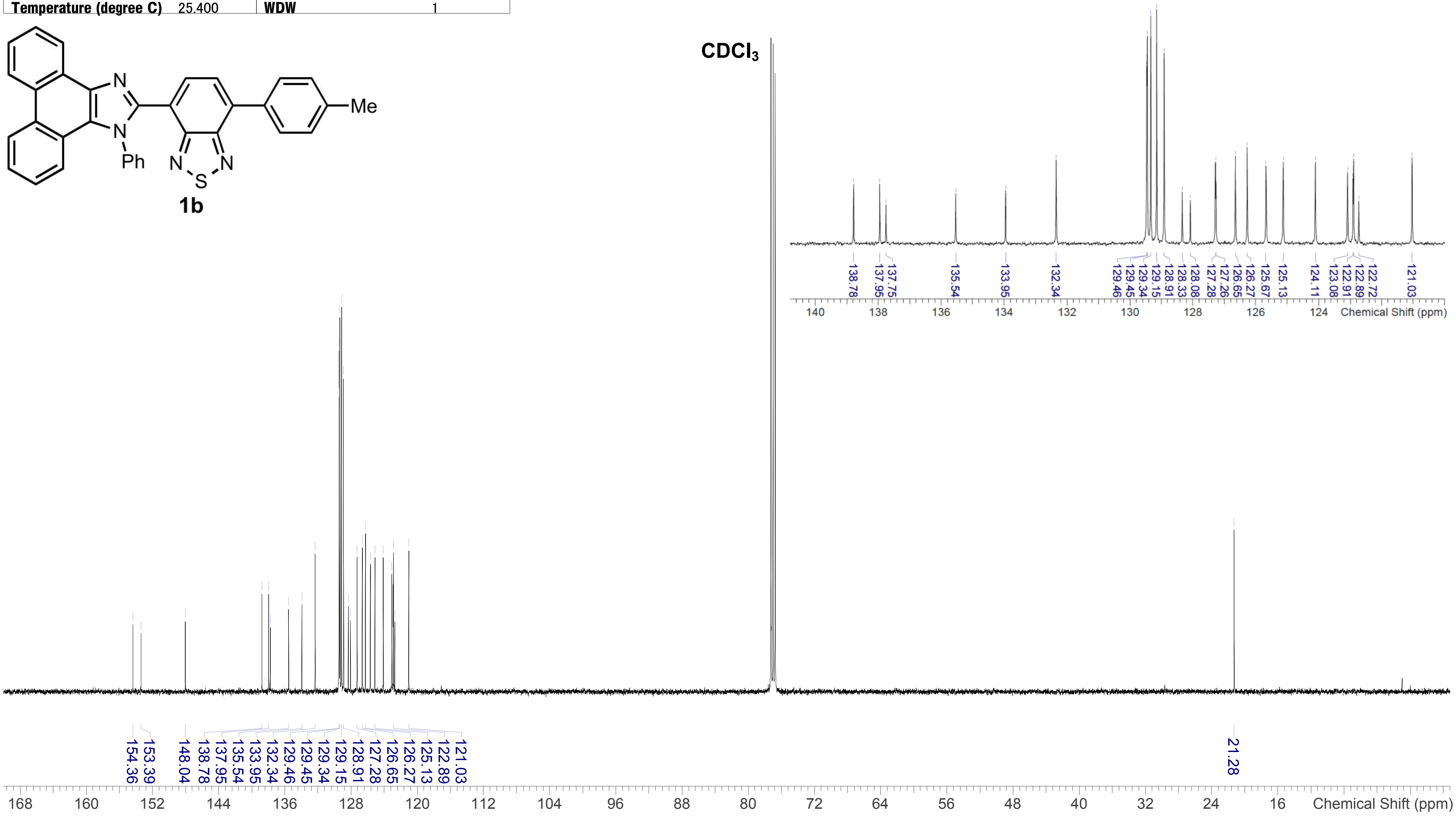
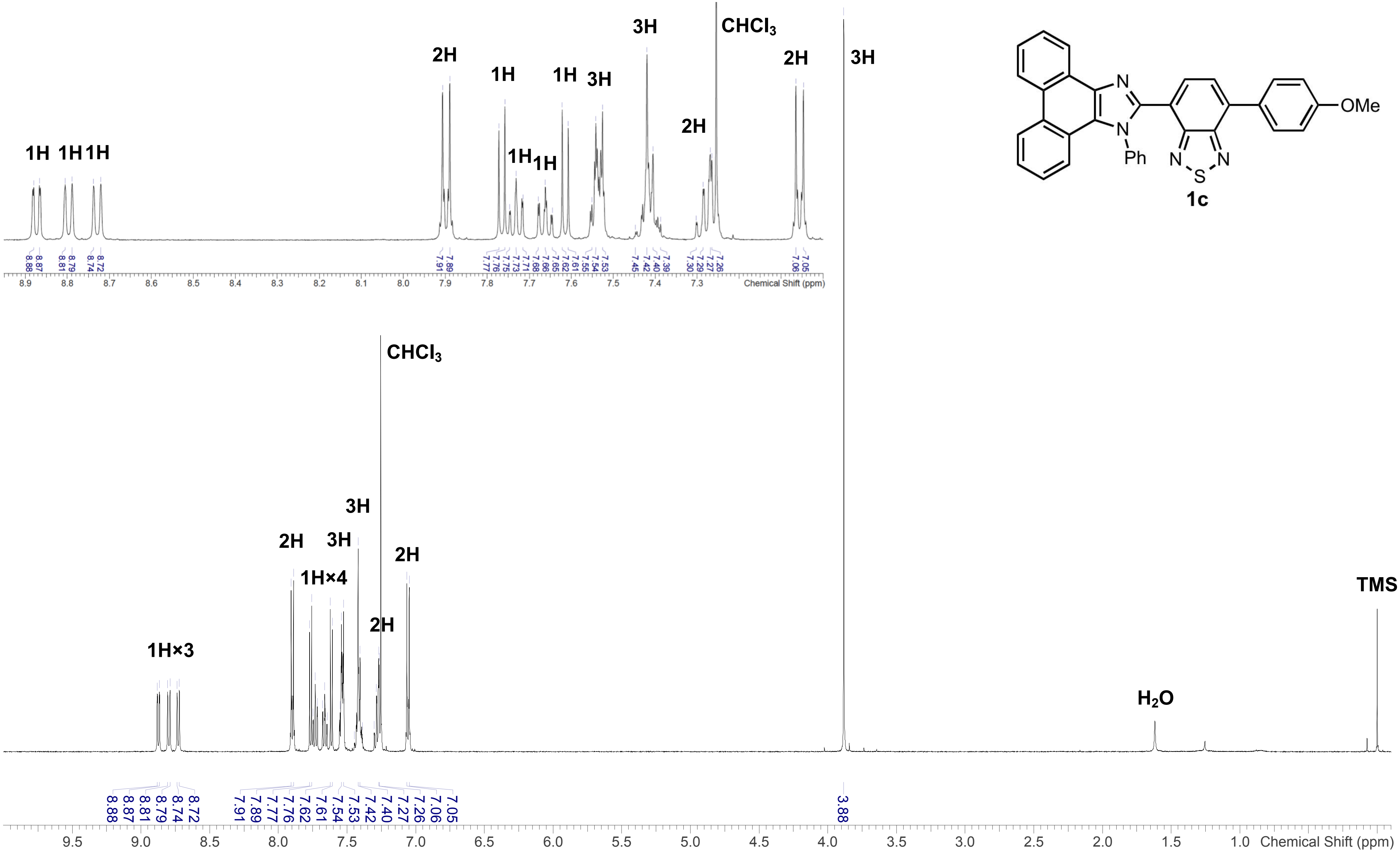
Original Points Count	32768	**Owner**	root	**PC**	1.4	**PROBHD**	<5 mm BBO BB-1H Z-GRD Z859001/0006 >		
PULPROG	<zgpg30>	**Points Count**	32768	**Pulse Sequence**	zgpg30	**Receiver Gain**	6502.00	**SF**	125.757789
SFO1	125.770364304853			**SI**	32768	**SSB**	0	**SW(cyclical) (Hz)**	30030.03
SWH	30030.03003003			**Solvent**	CHLOROFORM-d			**Spectrum Offset (Hz)**	12567.8574
Spectrum Type	standard	**Sweep Width (Hz)**	30029.11	**TD**	65536	**TD0**	1	**TE**	298.4
Temperature (degree C)	25.400	**WDW**	1						



^{1}H NMR (500 MHz, in $CDCl_3$)

Acquisition Time (sec)	3.1719	**Comment**	1125-1+H	**Date**	13 Apr 2018 17:21:20			**Date Stamp**	13 Apr 2018 17:21:20
File Name	C:¥Users¥Asamilab2¥Desktop¥1¥PDATA¥1¥1r			**Frequency (MHz)**	500.1331	**Nucleus**	1H	**Number of Transients**	8
Origin	spect	**Original Points Count**	32768	**Owner**	root	**Points Count**	32768	**Pulse Sequence**	zg30
Receiver Gain	362.00	**SW(cyclical) (Hz)**	10330.58	**Solvent**	CHLOROFORM-d			**Spectrum Offset (Hz)**	3072.7227
Spectrum Type	STANDARD	**Sweep Width (Hz)**	10330.26	**Temperature (degree C)**	24.600				



^{13}C NMR (126 MHz, in CDCl$_3$)

Acquisition Time (sec)	1.0912	**D**	0.00345	**D1**	2	**DE**	6	**DS**	4
Date	13 Apr 2018 18:19:25			**Date Stamp**	13 Apr 2018 18:19:25				
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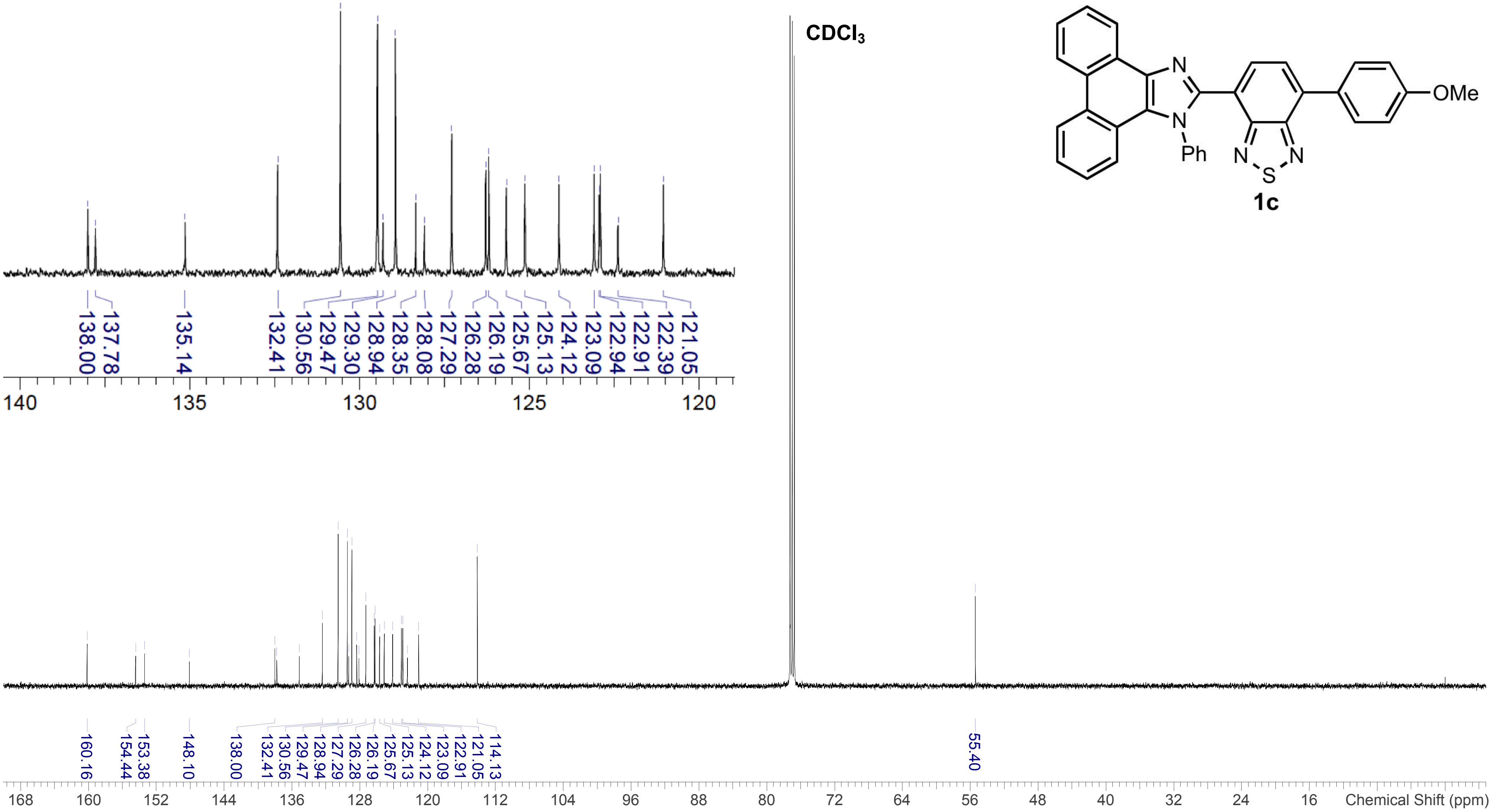
Original Points Count	32768	**Owner**	root	**PC**	1.4	**PROBHD**	<5 mm BBO BB-1H Z-GRD Z859001/0006 >		
PULPROG	<zgpg30>	**Points Count**	32768	**Pulse Sequence**	zgpg30	**Receiver Gain**	3251.00	**SF**	125.757789
SFO1	125.770364304853			**SI**	32768	**SSB**	0	**SW(cyclical) (Hz)**	30030.03
SWH	30030.03003003			**Solvent**	CHLOROFORM-d			**Spectrum Offset (Hz)**	12571.5225
Spectrum Type	standard	**Sweep Width (Hz)**	30029.11	**TD**	65536	**TD0**	1	**TE**	298.4
Temperature (degree C)	25.400	**WDW**	1						



1c

^{1}H NMR (500 MHz, in $CDCl_3$)

Acquisition Time (sec)	3.1719	**Comment**	274 5	**D**	3.827959	**D1**	3.827959	**DE**	6
DS	2	**Date**	29 Dec 2017 18:10:22			**Date Stamp**	29 Dec 2017 18:10:22		
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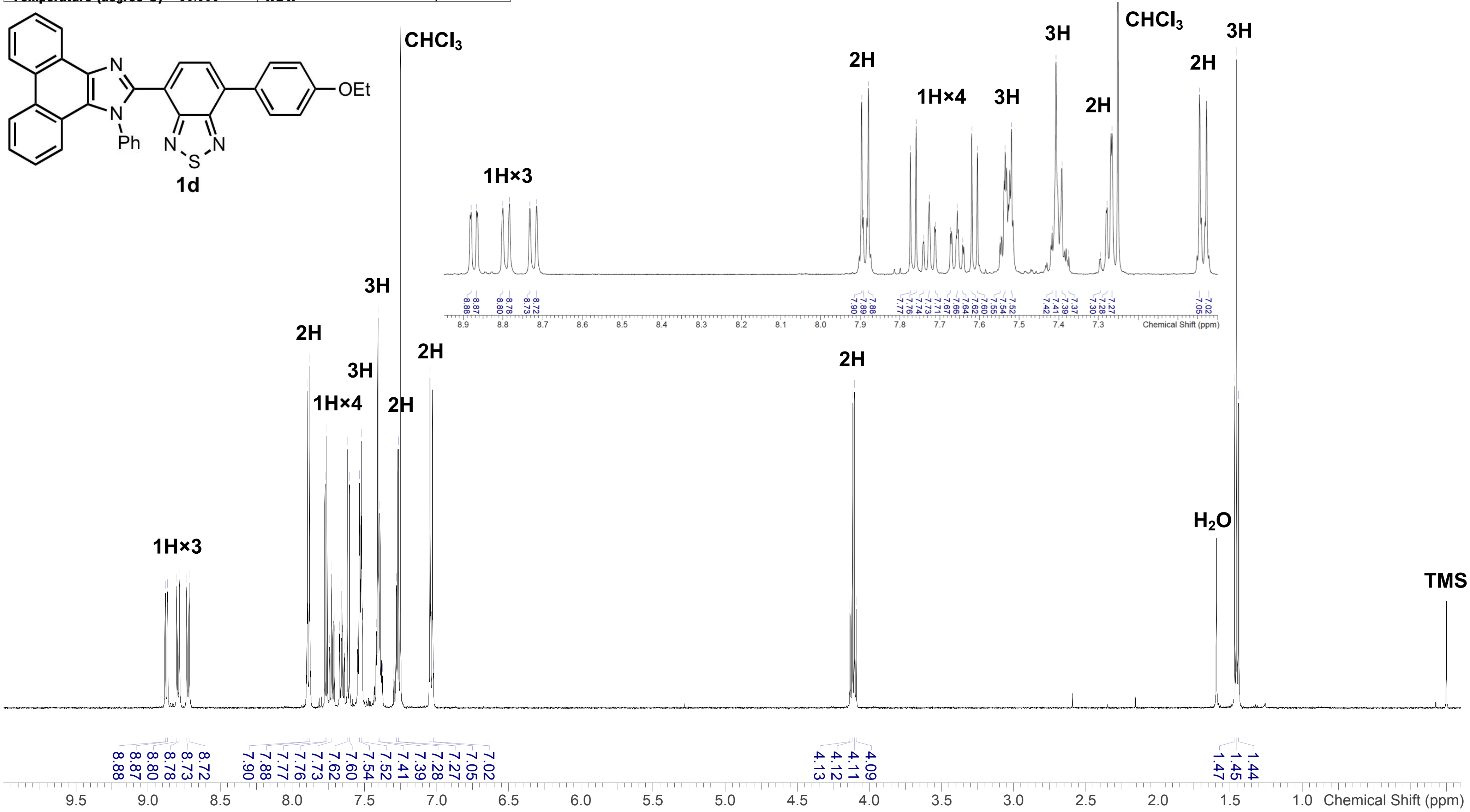
Original Points Count	32768	**Owner**	root	**PC**	1	**PROBHD**	<5 mm BBO BB-1H Z-GRD Z859001/0006 >		
PULPROG	<zg30>	**Points Count**	32768	**Pulse Sequence**	zg30	**Receiver Gain**	362.00	**SF**	500.130006648269
SFO1	500.133088507478			**SI**	32768	**SSB**	0	**SW(cyclical) (Hz)**	10330.58
SWH	10330.5785123967			**Solvent**	CHLOROFORM-d			**Spectrum Offset (Hz)**	3071.1565
Spectrum Type	standard	**Sweep Width (Hz)**	10330.26	**TD**	65536	**TD0**	1	**TE**	303.6
Temperature (degree C)	30.600	**WDW**	1						

1d



^{13}C NMR (126 MHz, in CDCl$_3$)

Acquisition Time (sec)	1.0912	**Comment**	272 0.6	**D**	0.00345	**D1**	2	**DE**	6
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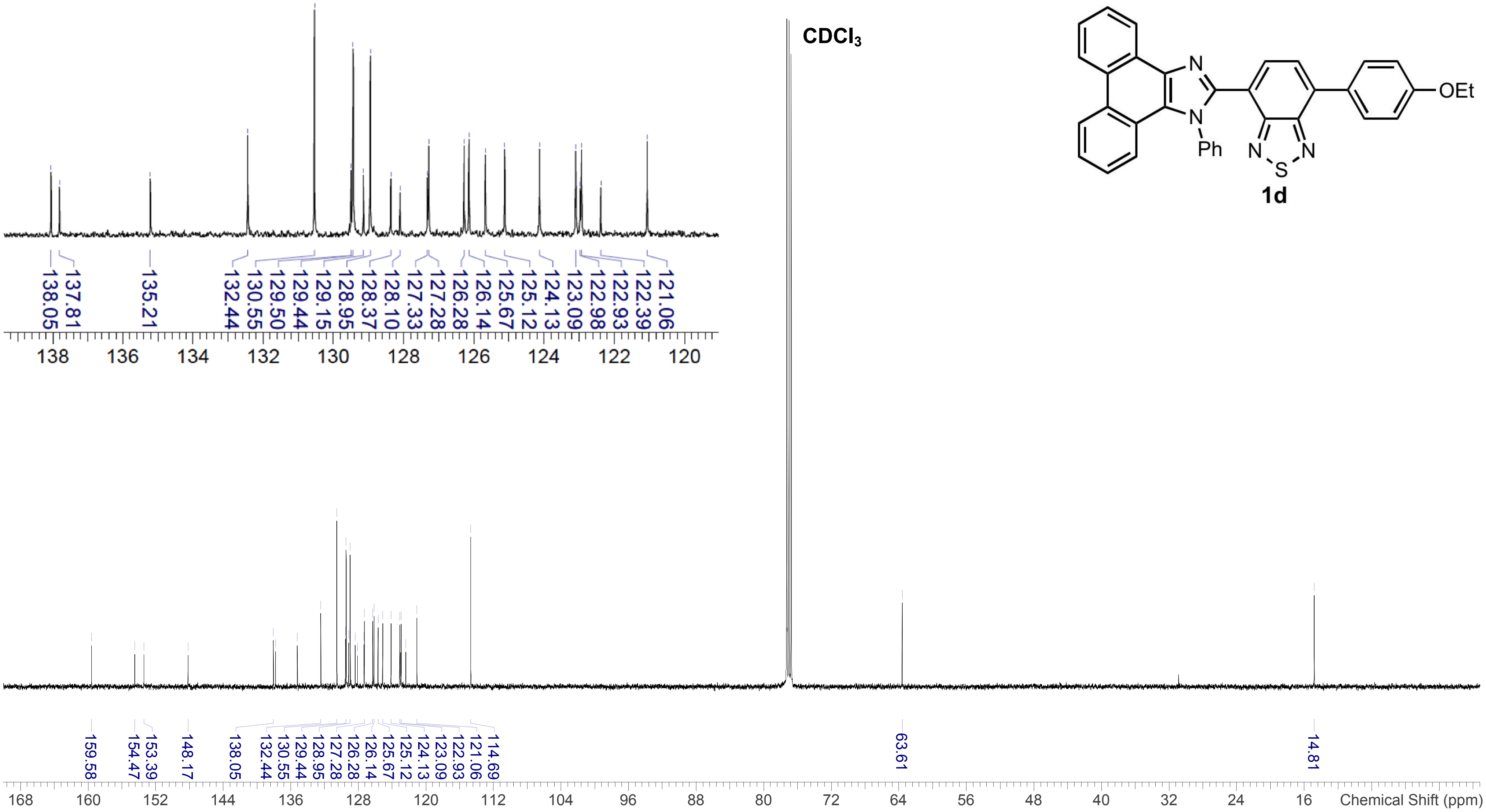
LB	1	**NS**	1024	**Nucleus**	13C	**Number of Transients**	1024	**Origin**	spect
Original Points Count	32768	**Owner**	root	**PC**	1.4	**PROBHD**	〈5 mm BBO BB-1H Z-GRD Z859001/0006 〉		
PULPROG	〈zgpg30〉	**Points Count**	32768	**Pulse Sequence**	zgpg30	**Receiver Gain**	5792.60	**SF**	125.757789
SFO1	125.770364304853			**SI**	32768	**SSB**	0	**SW(cyclical) (Hz)**	30030.03
SWH	30030.03003003			**Solvent**	CHLOROFORM-d			**Spectrum Offset (Hz)**	12573.3564
Spectrum Type	standard	**Sweep Width (Hz)**	30029.11	**TD**	65536	**TD0**	1	**TE**	304
Temperature (degree C)	31.000	**WDW**	1						



1d

^{1}H NMR (500 MHz, in $CDCl_3$)

Acquisition Time (sec)	3.1719	**Comment**	1125-5+H	**D**	3.827959	**D1**	3.827959	**DE**	6
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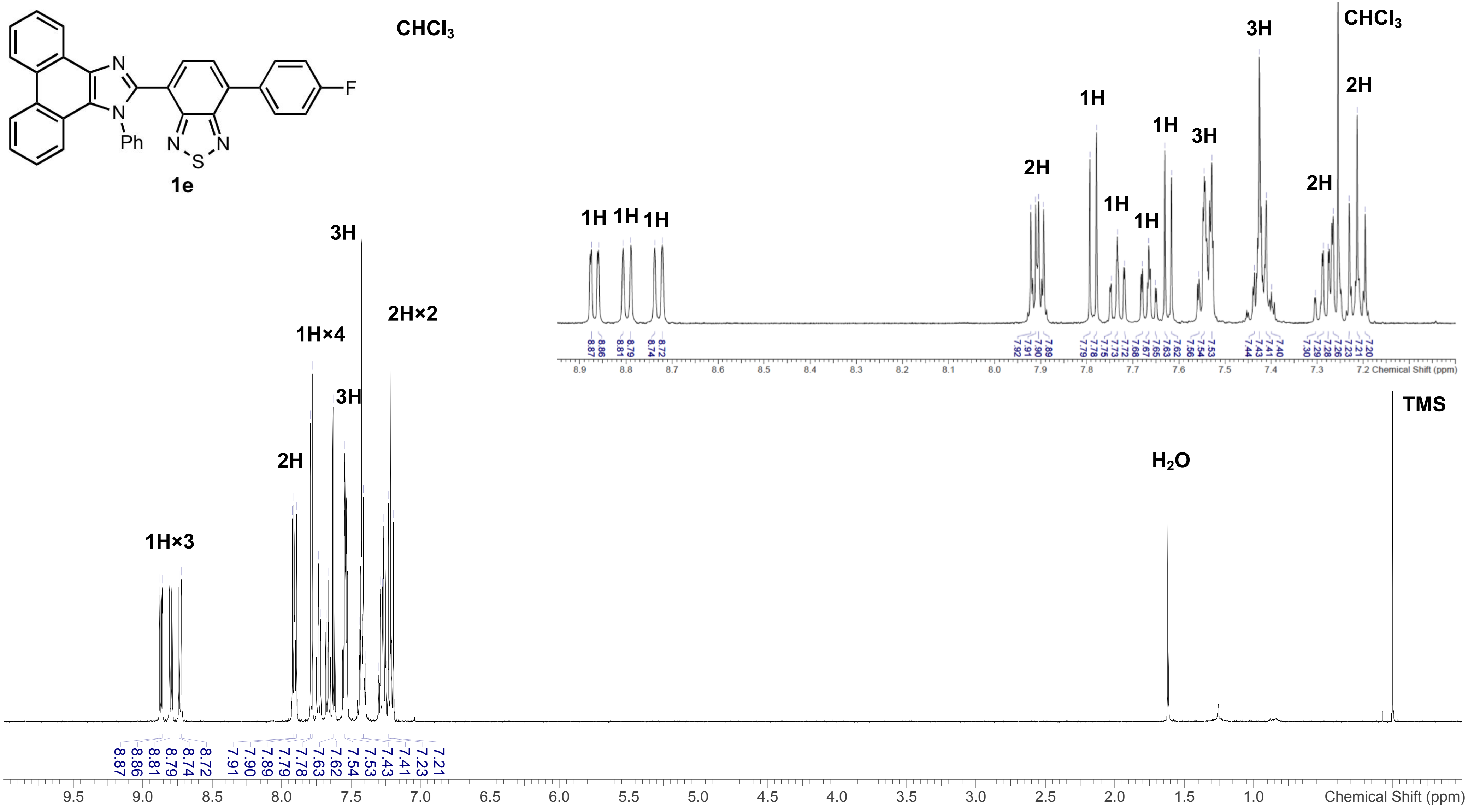
Original Points Count	32768	**Owner**	root	**PC**	1	**PROBHD**	<5 mm BBO BB-1H Z-GRD Z859001/0006 >		
PULPROG	<zg30>	**Points Count**	32768	**Pulse Sequence**	zg30	**Receiver Gain**	406.40	**SF**	500.130006648269
SFO1	500.133088507478			**SI**	32768	**SSB**	0	**SW(cyclical) (Hz)**	10330.58
SWH	10330.5785123967			**Solvent**	CHLOROFORM-d			**Spectrum Offset (Hz)**	3072.7070
Spectrum Type	standard	**Sweep Width (Hz)**	10330.26	**TD**	65536	**TD0**	1	**TE**	297.7
Temperature (degree C)	24.700	**WDW**	1						



1e

^{13}C NMR (126 MHz, in CDCl$_3$)

Acquisition Time (sec)	1.0912	**D**	0.00345	**D1**	2	**DE**	6	**DS**	4
Date	14 Dec 2018 15:05:20			**Date Stamp**	14 Dec 2018 15:05:20				
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Original Points Count	32768	**Owner**	root	**PC**	1.4	**PROBHD**	<5 mm BBO BB-1H Z-GRD Z859001/0006 >		
PULPROG	<zgpg30>	**Points Count**	32768	**Pulse Sequence**	zgpg30	**Receiver Gain**	3251.00	**SF**	125.757789
SFO1	125.770364304853			**SI**	32768	**SSB**	0	**SW(cyclical) (Hz)**	30030.03
SWH	30030.03003003			**Solvent**	CHLOROFORM-d			**Spectrum Offset (Hz)**	12572.4346
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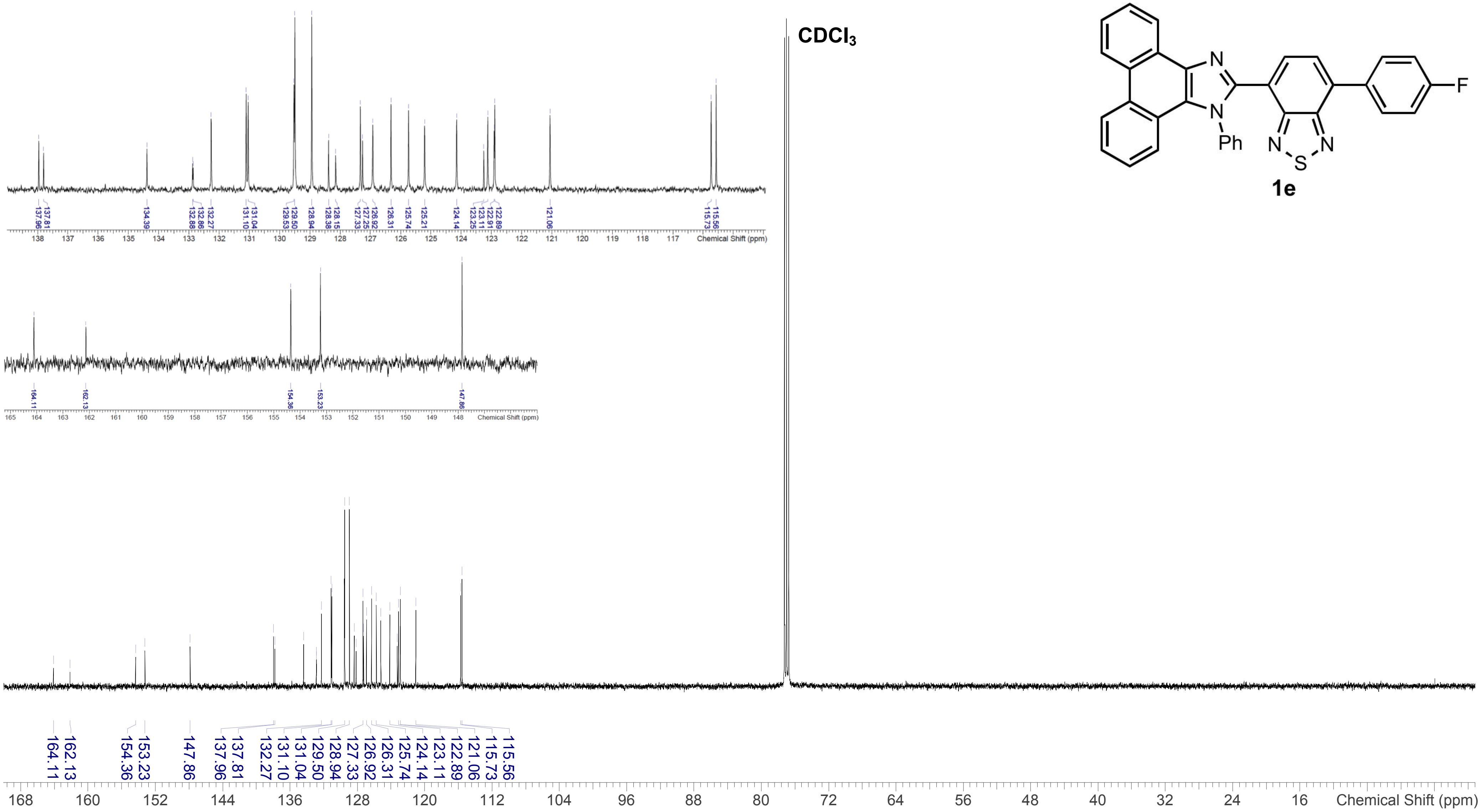
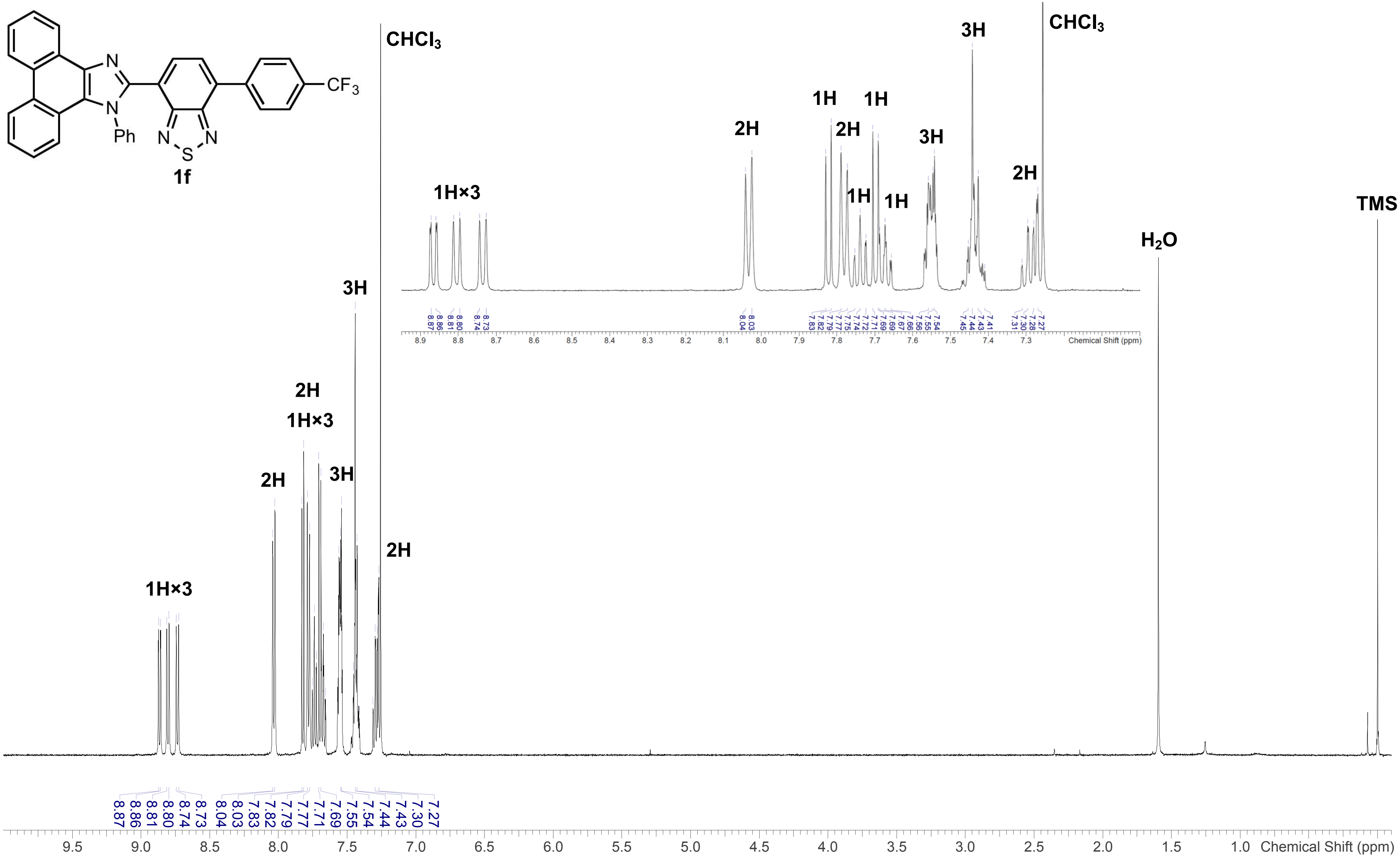
Temperature (degree C)	25.600	**WDW**	1						



1e

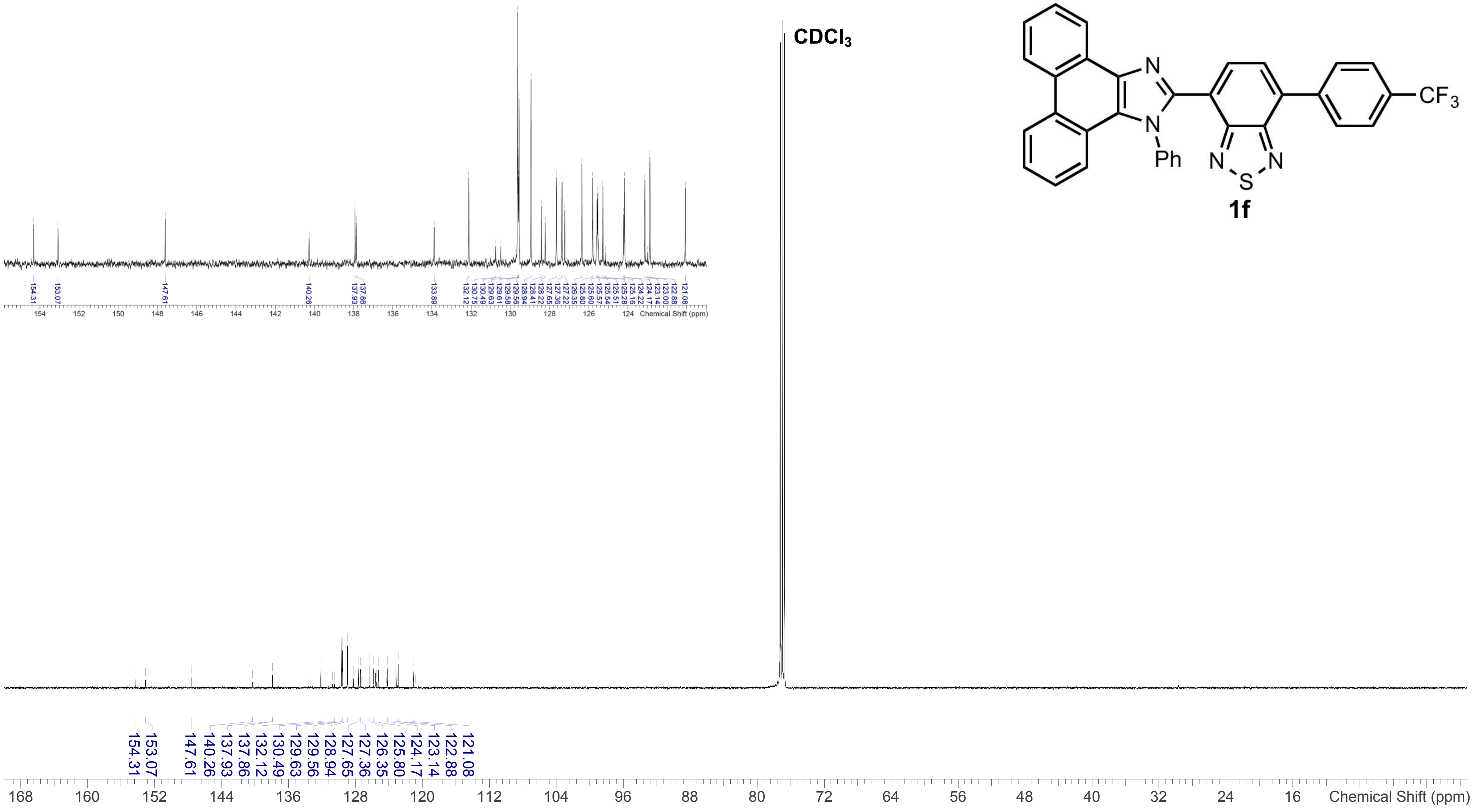
^{1}H NMR (500 MHz, in $CDCl_3$)

Acquisition Time (sec)	3.1719	**Comment**	ST245-step1, cdcl3			**Date**	06 Oct 2017 17:49:04		
Date Stamp	06 Oct 2017 17:49:04			**File Name**	C:¥Users¥Asamilab2¥Desktop¥1¥PDATA¥1¥1r			**Frequency (MHz)**	500.1331
Nucleus	1H	**Number of Transients**	8	**Origin**	spect	**Original Points Count**	32768	**Owner**	root
Points Count	32768	**Pulse Sequence**	zg30	**Receiver Gain**	512.00	**SW(cyclical) (Hz)**	10330.58	**Solvent**	CHLOROFORM-d
Spectrum Offset (Hz)	3073.6685	**Spectrum Type**	STANDARD	**Sweep Width (Hz)**	10330.26	**Temperature (degree C)**	24.600		



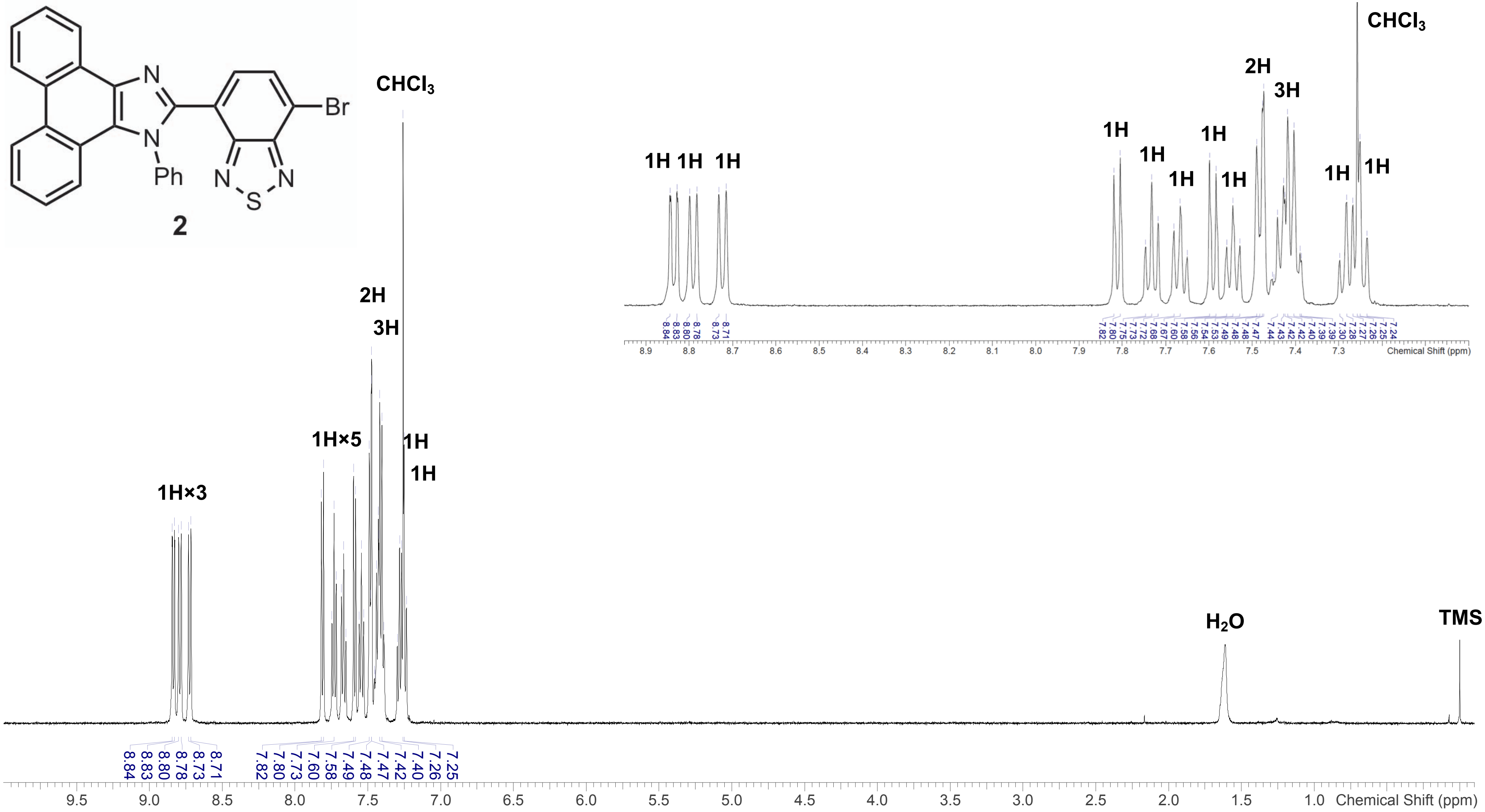
^{13}C NMR (126 MHz, in $CDCl_3$)

Acquisition Time (sec)	1.0912	**Comment**	272 0.6	**D**	0.00345	**D1**	2	**DE**	6
DS	4	**Date**	26 Dec 2018 04:21:16			**Date Stamp**	26 Dec 2018 04:21:16		
File Name	C:¥Users¥Asami-Lab¥Desktop¥1¥PDATA¥1¥1r			**Frequency (MHz)**	125.7578	**GB**	0	**INSTRUM**	〈spect〉
LB	1	**NS**	8192	**Nucleus**	13C	**Number of Transients**	8192	**Origin**	spect
Original Points Count	32768	**Owner**	root	**PC**	1.4	**PROBHD**	〈5 mm BBO BB-1H Z-GRD Z859001/0006 〉		
PULPROG	〈zgpg30〉	**Points Count**	32768	**Pulse Sequence**	zgpg30	**Receiver Gain**	2580.30	**SF**	125.757789
SFO1	125.770364304853			**SI**	32768	**SSB**	0	**SW(cyclical) (Hz)**	30030.03
SWH	30030.03003003			**Solvent**	CHLOROFORM-d			**Spectrum Offset (Hz)**	12573.3525
Spectrum Type	standard	**Sweep Width (Hz)**	30029.11	**TD**	65536	**TD0**	1	**TE**	298.9
Temperature (degree C)	25.900	**WDW**	1						



^{1}H NMR (500 MHz, in $CDCl_3$)

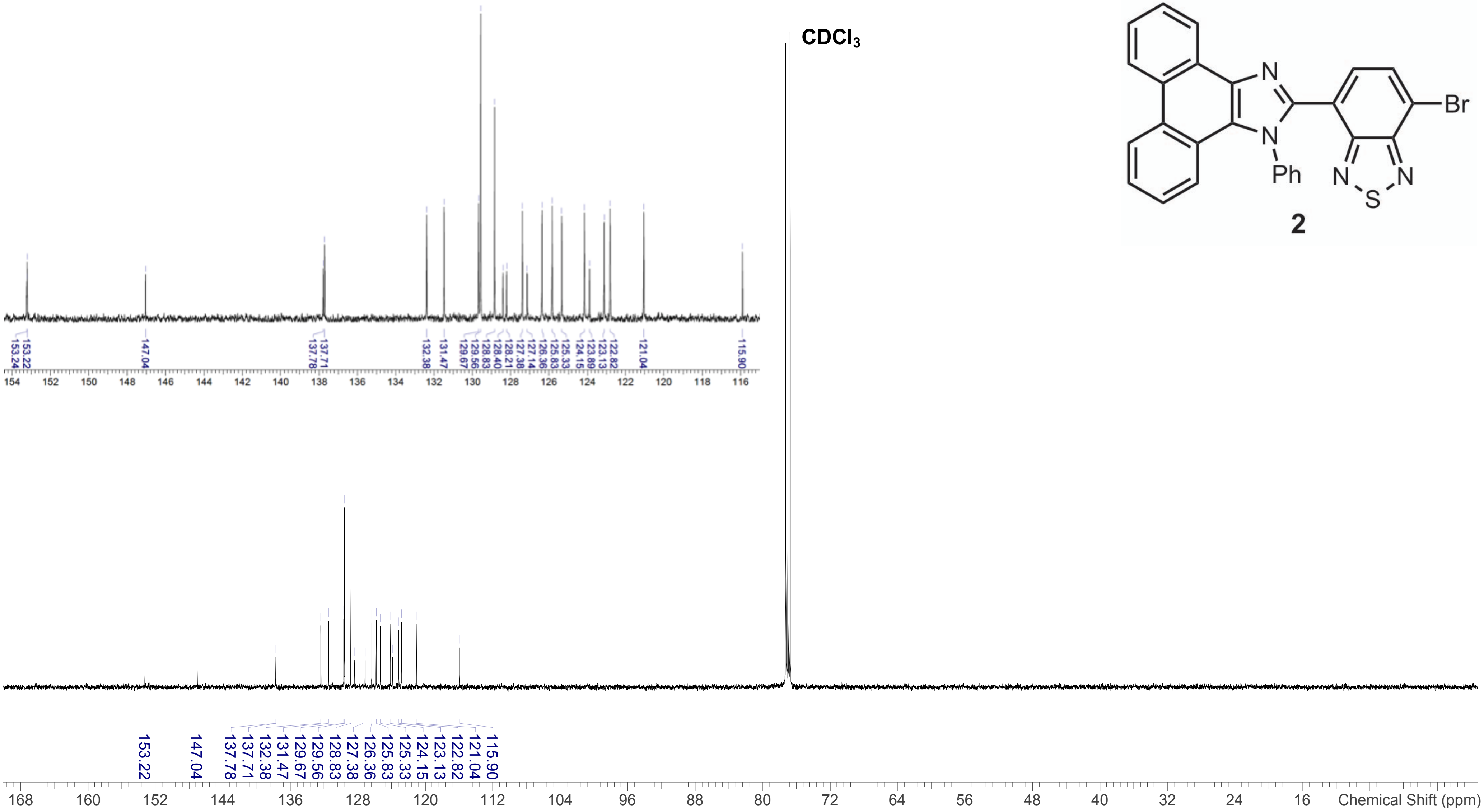
Acquisition Time (sec)	3.1719	**Comment**	dist4	**D**	3.827959	**D1**	3.827959	**DE**	6
DS	2	**Date**	06 Apr 2018 10:15:50			**Date Stamp**	06 Apr 2018 10:15:50		
File Name	C:¥Users¥Asami-Lab¥Desktop¥sna81 Br HNMR 20180406¥1¥PDATA¥1¥1r					**Frequency (MHz)**	500.1300	**GB**	0
INSTRUM	<spect>	**LB**	0.1	**NS**	8	**Nucleus**	1H	**Number of Transients**	8
Origin	spect	**Original Points Count**	32768	**Owner**	root	**PC**	1		
PROBHD	<5 mm BBO BB-1H Z-GRD Z859001/0006 >			**PULPROG**	<zg30>	**Points Count**	32768	**Pulse Sequence**	zg30
Receiver Gain	456.10	**SF**	500.130006648269			**SFO1**	500.133088507478		
SI	32768	**SSB**	0	**SW(cyclical) (Hz)**	10330.58	**SWH**	10330.5785123967		
Solvent	CHLOROFORM-d			**Spectrum Offset (Hz)**	3074.3074	**Spectrum Type**	standard	**Sweep Width (Hz)**	10330.26
TD	65536	**TD0**	1	**TE**	297.6	**Temperature (degree C)**	24.600	**WDW**	1



2

^{13}C NMR (126 MHz, in CDCl$_3$)

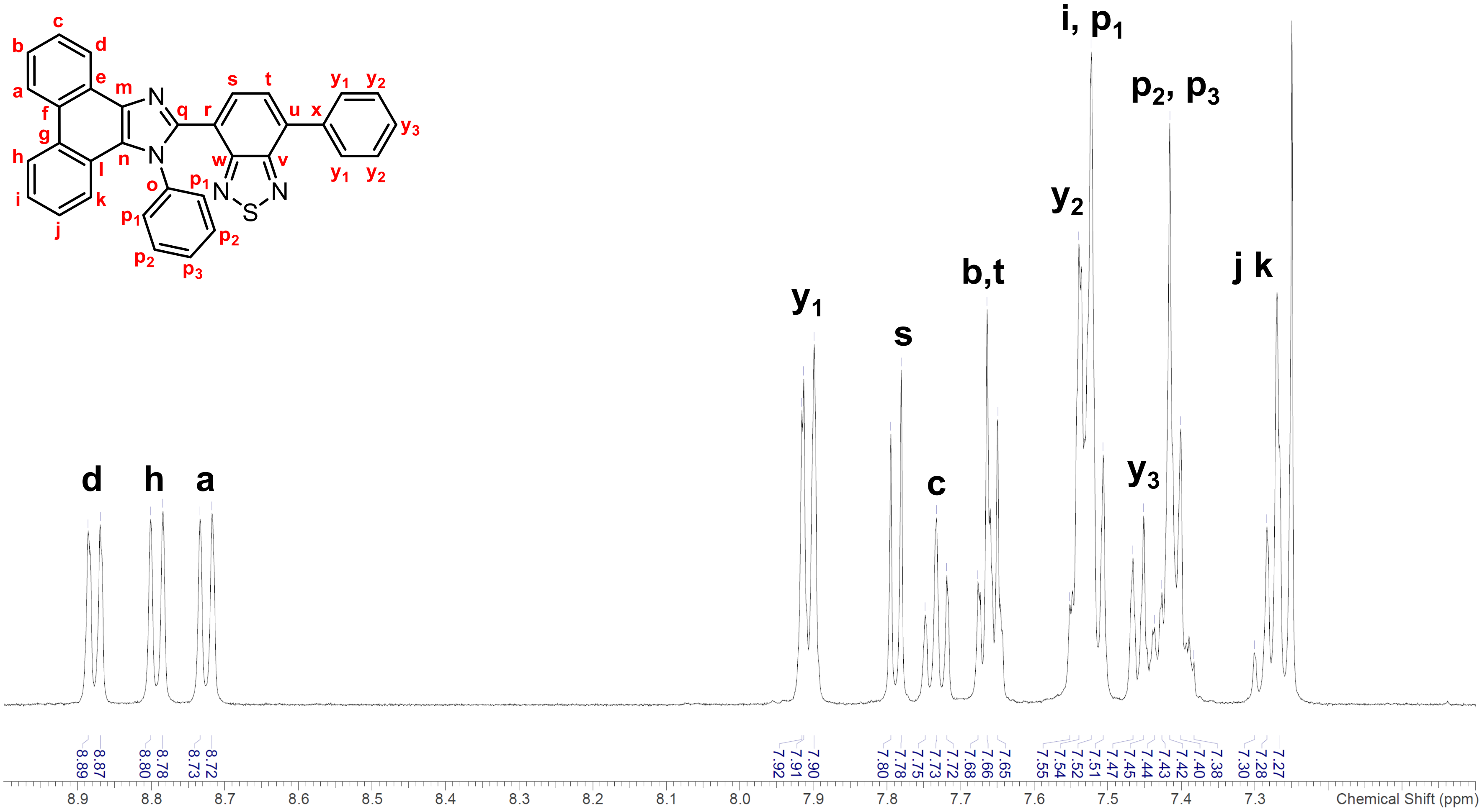
Acquisition Time (sec)	1.0912	**D**	0.00345	**D1**	2	**DE**	6	**DS**	4
Date	07 Apr 2018 11:04:21			**Date Stamp**	07 Apr 2018 11:04:21				
File Name	C:¥Users¥Asami-Lab¥Desktop¥10¥PDATA¥1¥1r			**Frequency (MHz)**	125.7578	**GB**	0	**INSTRUM**	<spect>
LB	1	**NS**	1024	**Nucleus**	13C	**Number of Transients**	1024	**Origin**	spect
Original Points Count	32768	**Owner**	root	**PC**	1.4	**PROBHD**	<5 mm BBO BB-1H Z-GRD Z859001/0006 >		
PULPROG	<zgpg30>	**Points Count**	32768	**Pulse Sequence**	zgpg30	**Receiver Gain**	5160.60	**SF**	125.757789
SFO1	125.770364304853			**SI**	32768	**SSB**	0	**SW(cyclical) (Hz)**	30030.03
SWH	30030.03003003			**Solvent**	CHLOROFORM-d			**Spectrum Offset (Hz)**	12571.5166
Spectrum Type	standard	**Sweep Width (Hz)**	30029.11	**TD**	65536	**TD0**	1	**TE**	298.3
Temperature (degree C)	25.300	**WDW**	1						



2

Partial ^{1}H NMR spectrum of **1a** (500 MHz, in $CDCl_3$, rt)

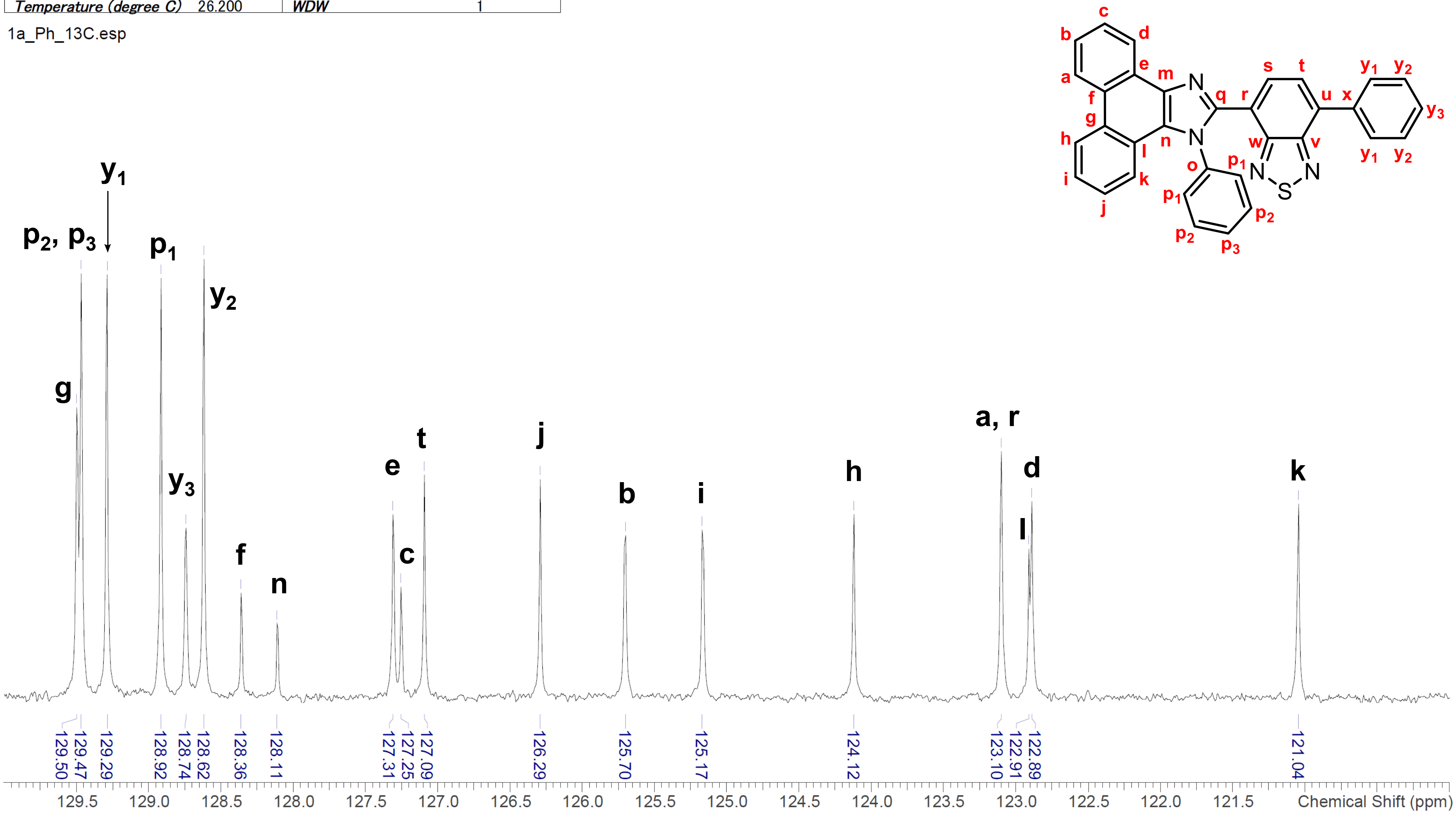
Acquisition Time (sec)	3.1719	*Comment*	299 0.8	*D*	3.827959	*D1*	3.827959	*DE*	6
DS	2	*Date*	05 Jul 2018 09:55:50			*Date Stamp*	05 Jul 2018 09:55:50		
File Name	C:¥Users¥Asami-Lab¥Desktop¥1¥PDATA¥1¥1r			*Frequency (MHz)*	500.1300	*GB*	0	*INSTRUM*	<spect>
LB	0.1	*NS*	8	*Nucleus*	1H	*Number of Transients*	8	*Origin*	spect
Original Points Count	32768	*Owner*	root	*PC*	1	*PROBHD*	<5 mm BBO BB-1H Z-GRD Z859001/0006 >		
PULPROG	<zg30>	*Points Count*	32768	*Pulse Sequence*	zg30	*Receiver Gain*	287.40	*SF*	500.130006648269
SFO1	500.133088507478			*SI*	32768	*SSB*	0	*SW(cyclical) (Hz)*	10330.58
SWH	10330.5785123967			*Solvent*	CHLOROFORM-d			*Spectrum Offset (Hz)*	3070.5063
Spectrum Type	standard	*Sweep Width (Hz)*	10330.26	*TD*	65536	*TD0*	1	*TE*	298.1
Temperature (degree C)	25.100	*WDW*	1						



Partial ^{13}C NMR spectrum of **1a** (126 MHz, in $CDCl_3$, rt)

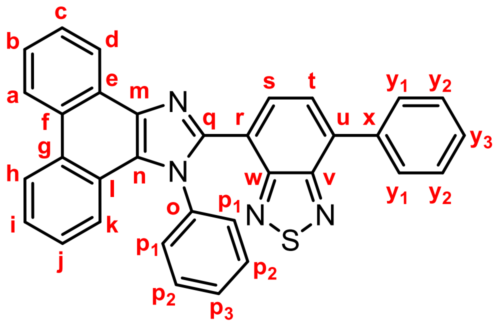
Acquisition Time (sec)	1.0912	*Comment*	1f	*D*	0.00345	*D1*	2	*DE*	6
DS	4	*Date*	05 Jul 2018 10:54:35			*Date Stamp*	05 Jul 2018 10:54:35		
File Name	C:¥Users¥Asami-Lab¥Desktop¥1¥PDATA¥1¥1r			*Frequency (MHz)*	125.7578	*GB*	0	*INSTRUM*	<spect>
LB	1	*NS*	1024	*Nucleus*	13C	*Number of Transients*	1024	*Origin*	spect
Original Points Count	32768	*Owner*	root	*PC*	1.4	*PROBHD*	<5 mm BBO BB-1H Z-GRD Z859001/0006 >		
PULPROG	<zgpg30>	*Points Count*	32768	*Pulse Sequence*	zgpg30	*Receiver Gain*	3251.00	*SF*	125.757789
SFO1	125.770364304853			*SI*	32768	*SSB*	0	*SW(cyclical) (Hz)*	30030.03
SWH	30030.03003003			*Solvent*	CHLOROFORM-d			*Spectrum Offset (Hz)*	12569.6924
Spectrum Type	standard	*Sweep Width (Hz)*	30029.11	*TD*	65536	*TD0*	1	*TE*	299.2
Temperature (degree C)	26.200	*WDW*	1						

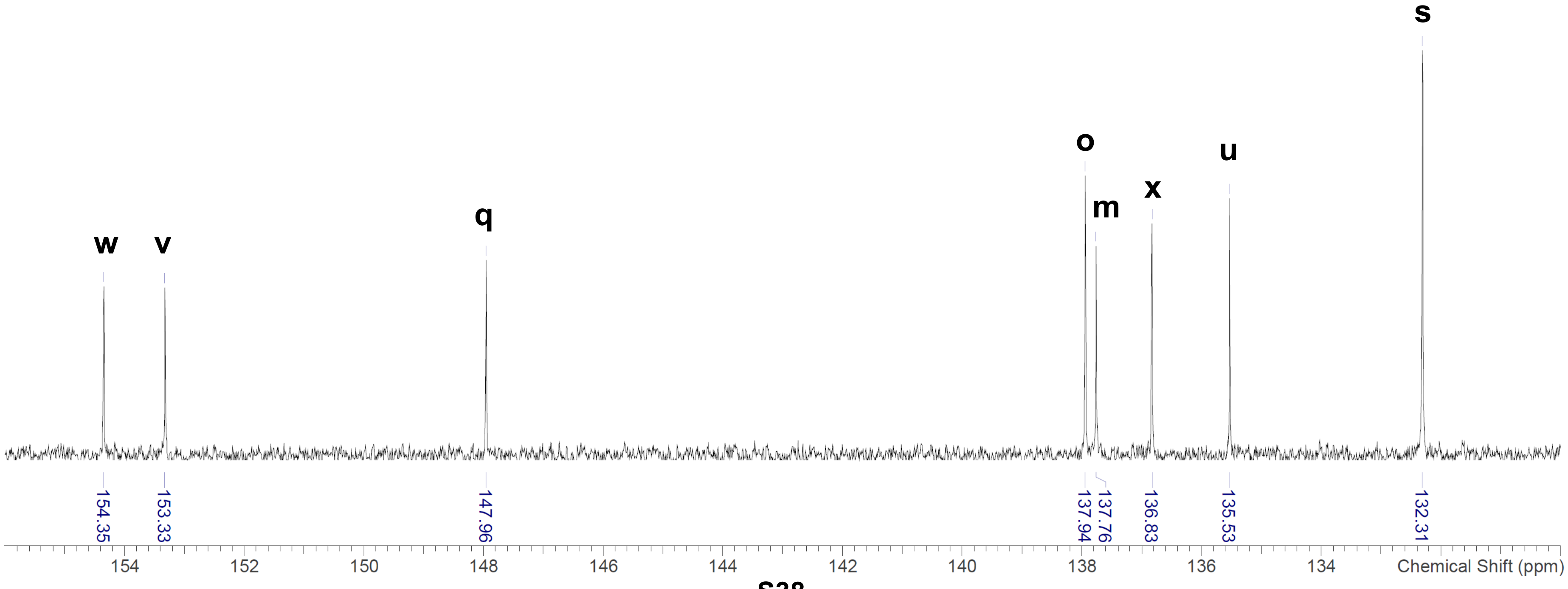
1a_Ph_13C.esp



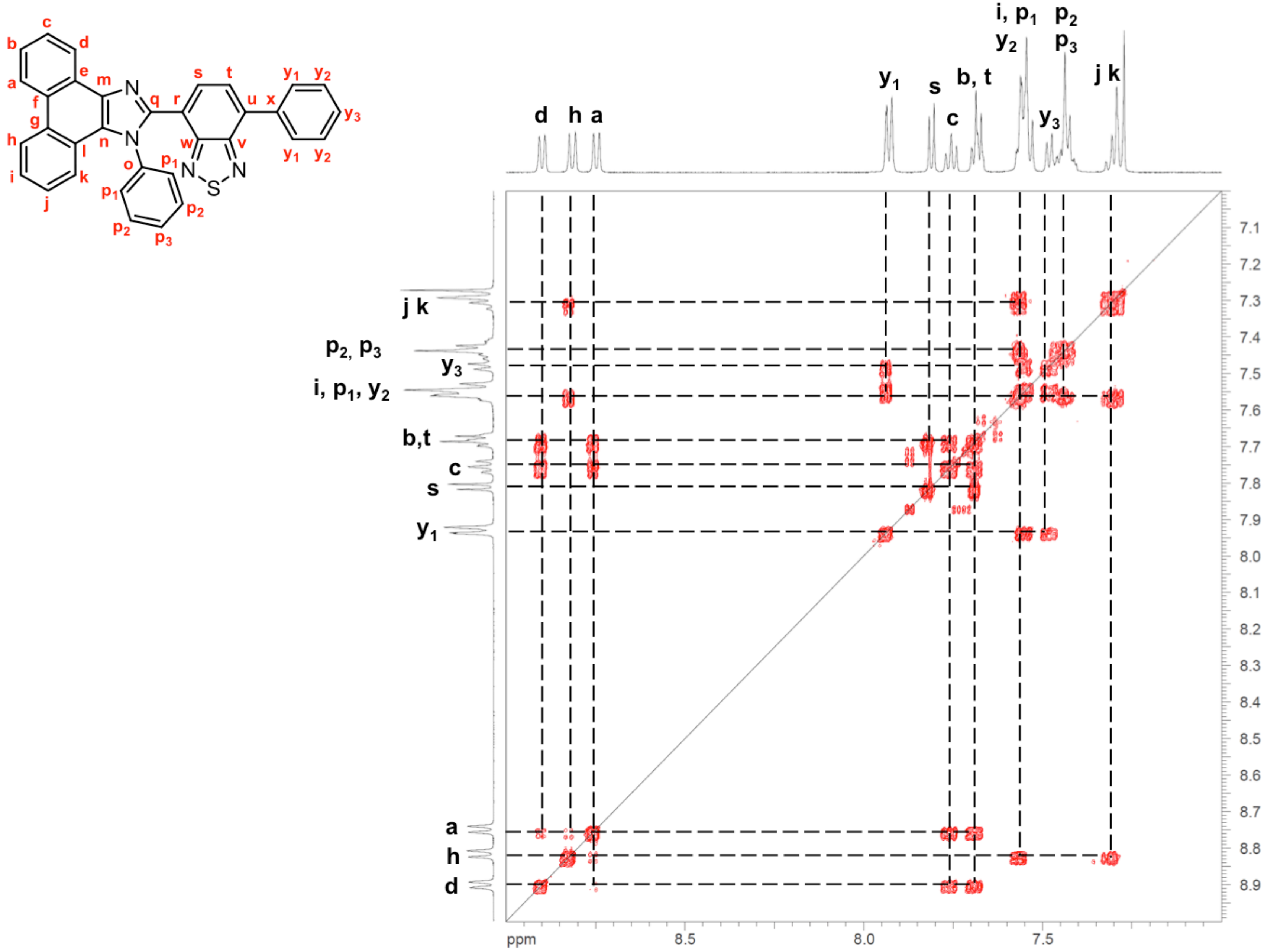
Partial ^{13}C NMR spectrum of **1a** (126 MHz, in $CDCl_3$, rt)

Acquisition Time (sec)	1.0912	*Comment*	1f	*D*	0.00345	*D1*	2	*DE*	6
DS	4	*Date*	05 Jul 2018 10:54:35			*Date Stamp*	05 Jul 2018 10:54:35		
File Name	C:¥Users¥Asami-Lab¥Desktop¥1¥PDATA¥1¥1r			*Frequency (MHz)*	125.7578	*GB*	0	*INSTRUM*	<spect>
LB	1	*NS*	1024	*Nucleus*	13C	*Number of Transients*	1024	*Origin*	spect
Original Points Count	32768	*Owner*	root	*PC*	1.4	*PROBHD*	<5 mm BBO BB-1H Z-GRD Z859001/0006 >		
PULPROG	<zgpg30>	*Points Count*	32768	*Pulse Sequence*	zgpg30	*Receiver Gain*	3251.00	*SF*	125.757789
SFO1	125.770364304853			*SI*	32768	*SSB*	0	*SW(cyclical) (Hz)*	30030.03
SWH	30030.03003003			*Solvent*	CHLOROFORM-d			*Spectrum Offset (Hz)*	12569.6924
Spectrum Type	standard	*Sweep Width (Hz)*	30029.11	*TD*	65536	*TD0*	1	*TE*	299.2
Temperature (degree C)	26.200	*WDW*	1						

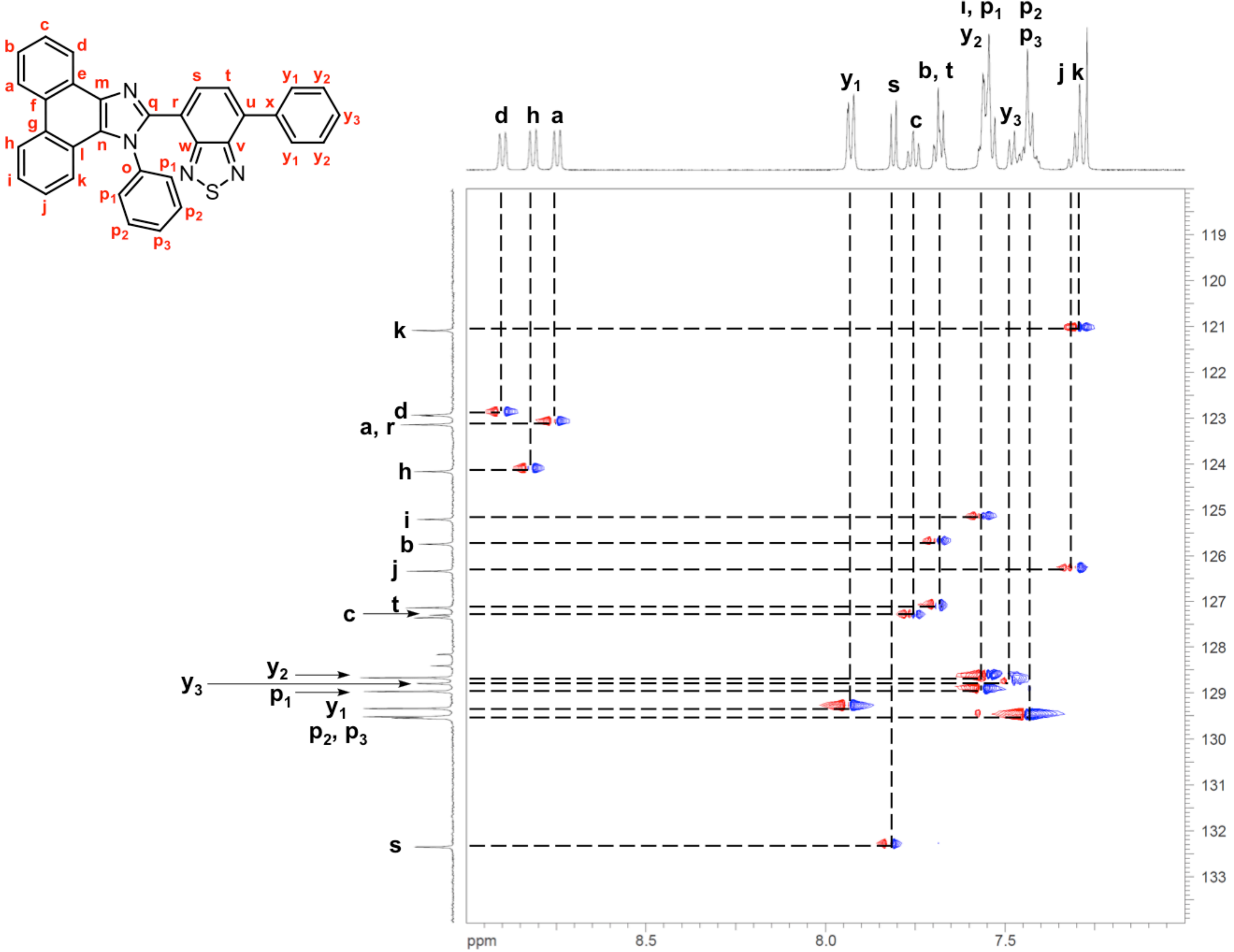




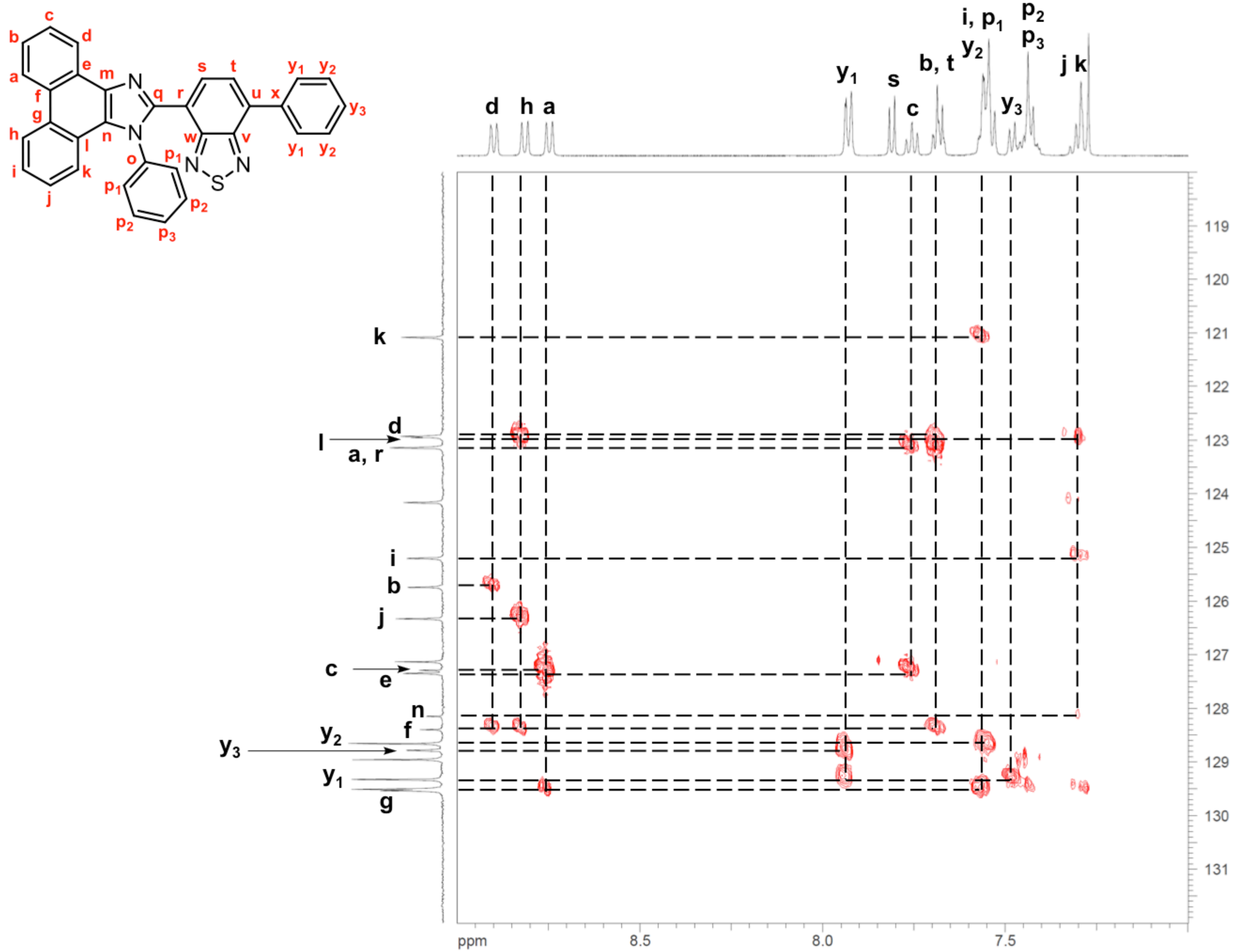
Partial COSY spectrum of **1a** (500 MHz, in CDCl$_3$, rt)



Partial HSQC spectrum of **1a** (500 MHz, in $CDCl_3$, rt)



Partial HMBC spectrum of **1a** (500 MHz, in $CDCl_3$, rt)



Partial HMBC spectrum of **1a** (500 MHz, in $CDCl_3$, rt)