Relationship between Crystal Structure, Crystal Morphology, and Mechanochromic Luminescence of Triphenylimidazolylbenzothiadiazole Derivatives

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1. Powder X-ray diffraction analyses

As diffraction peaks were observed by powder X-ray diffraction (PXRD) measurement, the powdered precipitates of **1b**–**d** and **1f** obtained from toluene should be the aggregates of microcrystals. The intensity of diffraction patterns of **1b**–**d** and **1f** decreased after grinding, which indicates the amorphization of the crystalline structures in response to mechanical stimuli (Figure S1).

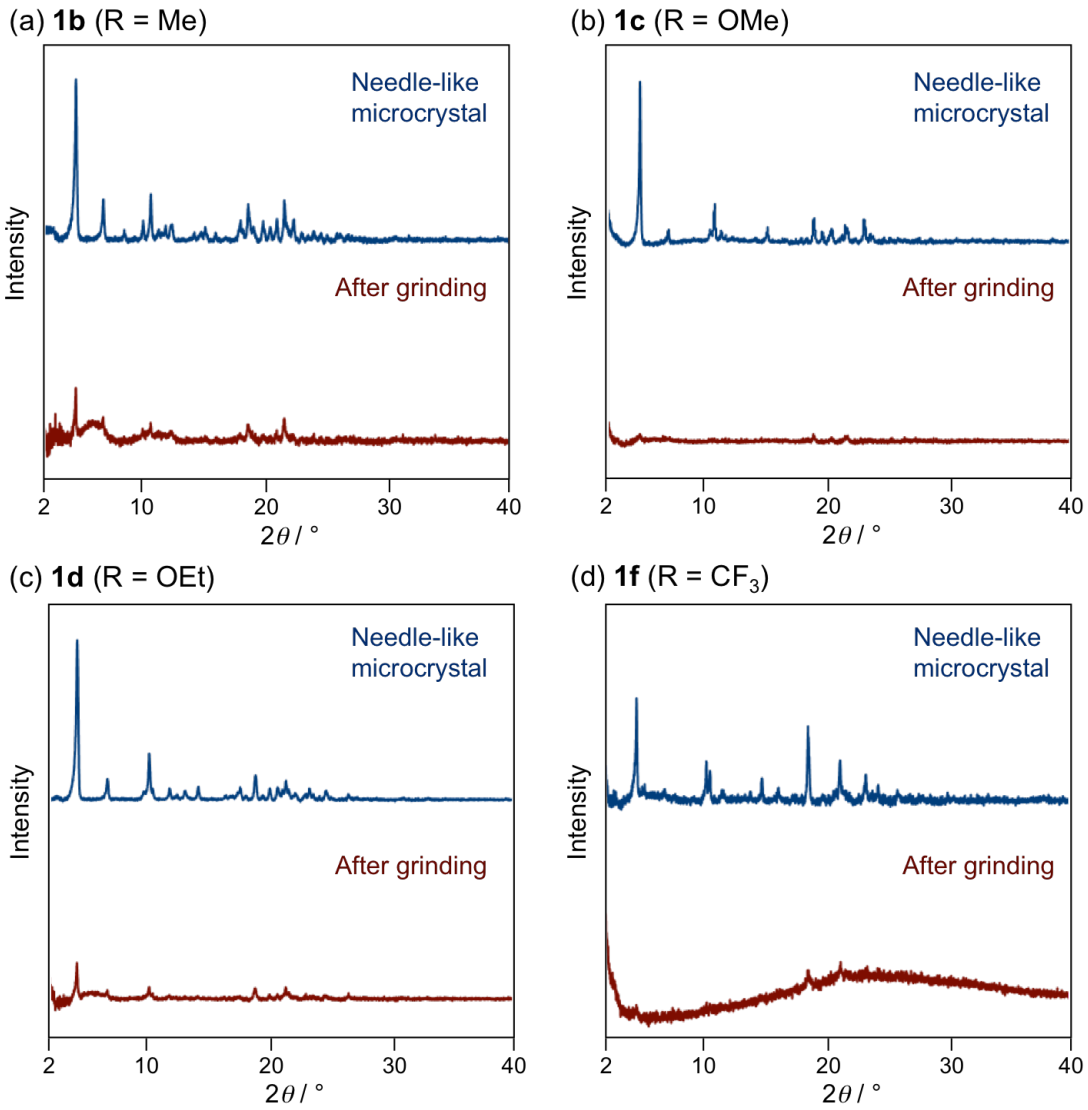

Figure S1. PXRD patterns for **1b** (a), **1c** (b), **1d** (c), and **1f** (d). Experimental patterns of the powdered precipitates obtained from toluene (blue). Experimental patterns of the samples after grinding (red).

PXRD patterns of **1a** and **1e** showed that the crystal structures of plate-like crystalline samples prepared from toluene solutions were identical to those of their single crystals prepared from $CHCl_3$/hexane. The intensity of diffraction patterns of **1a** and **1e** decreased after grinding and recovered after heating (Figure S2).

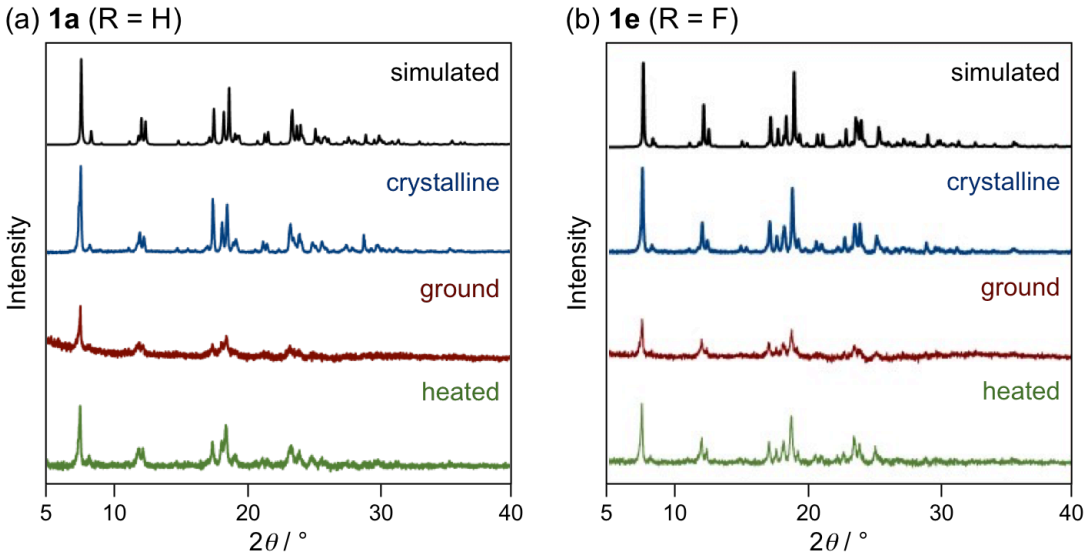

Figure S2. PXRD patterns for the MCL of **1a** (a) and **1e** (b). Simulated patterns calculated from the single-crystal X-ray diffraction structures prepared from $CHCl_3$/hexane (black). Experimental patterns of the samples prepared by recrystallization from toluene (blue), after grinding (red), and after heating (green).

2. Fluorescence spectra of crystalline 1a–f before and after grinding

Fluorescence spectra showed significant shifts in maximum emission wavelengths of plate-like crystals **1a** and **1e** after grinding, whereas slight shifts or broadening of spectra were observed for needle-like crystals **1b**–**d** and **1f** after grinding (Figure S3).

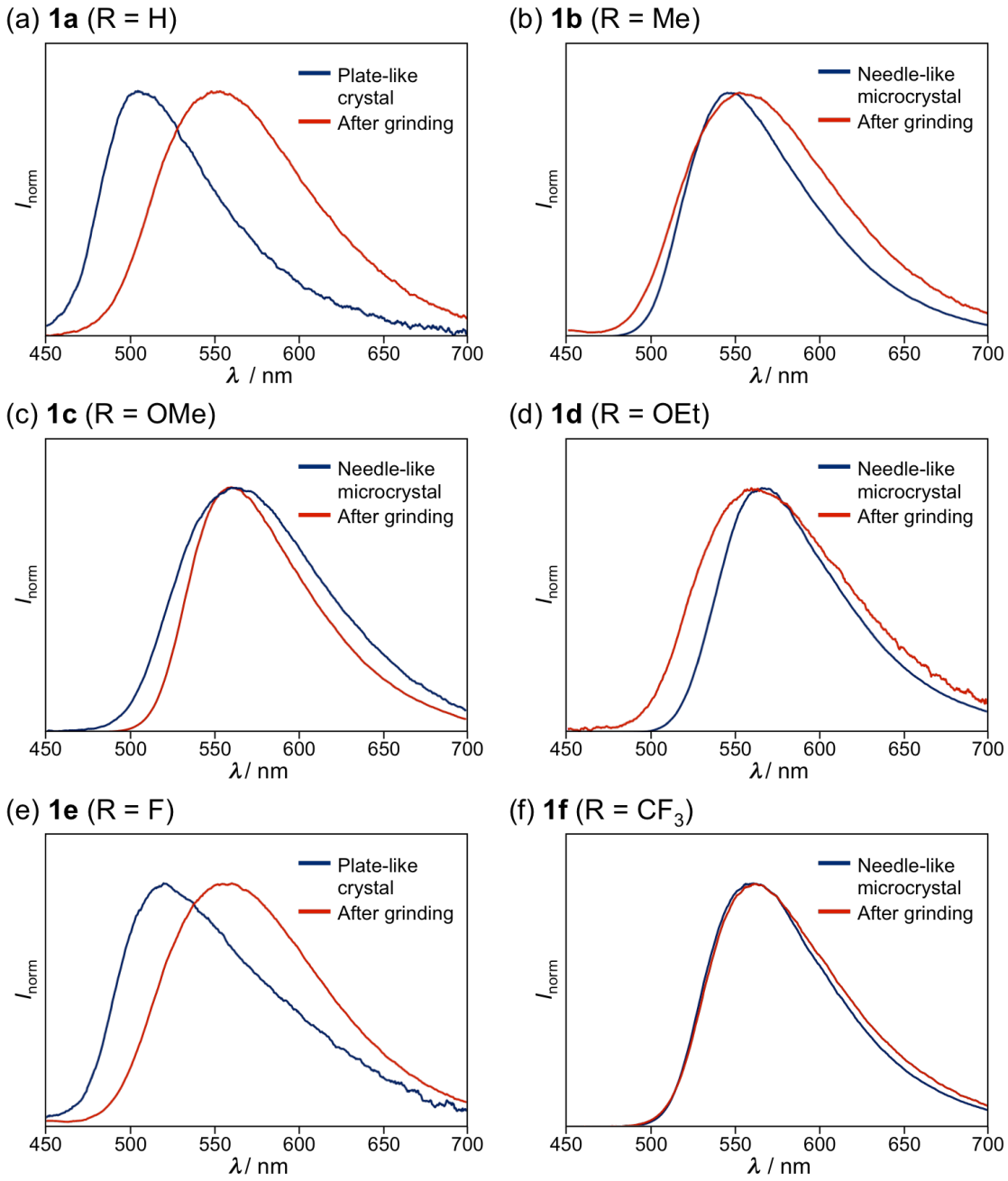

Figure S3. Fluorescence spectra for crystalline (blue) and ground (red) **1a** (a), **1b** (b), **1c** (c), **1d** (d), **1e** (e), and **1f** (f) irradiated with UV light at 365 nm.

3. Differential scanning calorimetry (DSC) analyses

The DSC thermograms of plate-like crystals **1a** and **1e** showed endothermic peak that corresponds to their melting points (**1a**: T_m = 257 °C; **1e**: T_m = 231 °C). Cold crystallization transition peaks (T_c) were observed for ground samples of **1a** (74 °C) and **1e** (94 °C). (Figure S4).

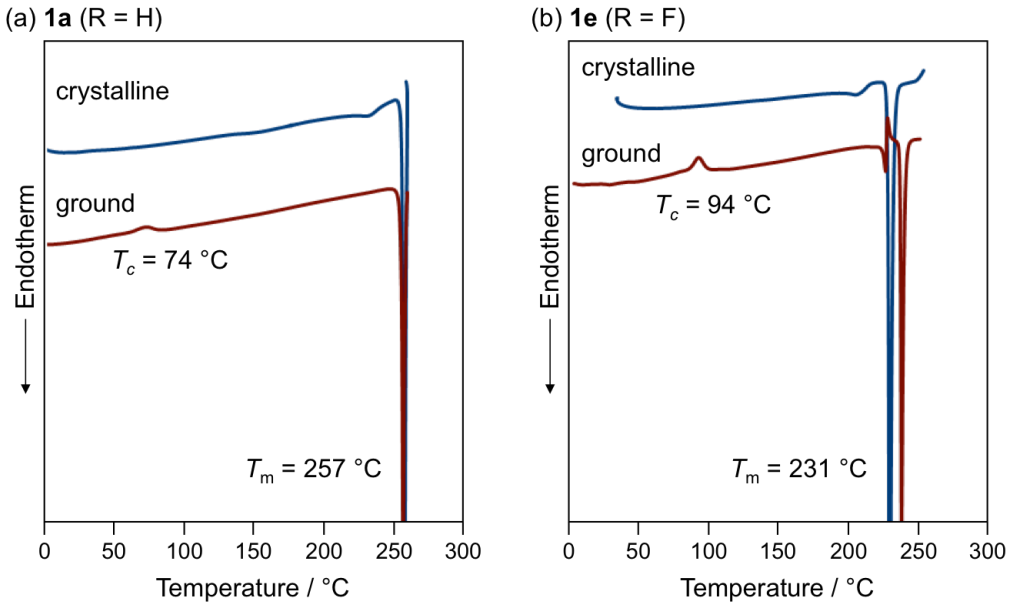

Figure S4. DSC thermograms for **1a** (a) and **1e** (b).

4. 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 153.0°. A total of 5604 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 26524 reflections that were collected, 4598 were unique (R_{int} = 0.0353); 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 13.728 cm^{-1}. An empirical absorption correction was applied which resulted in transmission factors ranging from 0.645 to 0.830. The data were corrected for Lorentz and polarization effects.

The structure was solved by direct methods (SIR92)[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** (CCDC1984811): $C_{33}H_{22}N_4S$, M = 506.62, triclinic, a = 10.22254(9) Å, b = 10.98801(10) Å, c = 12.00679(9) Å, α = 110.8577(7)°, β = 92.4058(7)°, γ = 90.1529(7)°, V = 1258.951(19) Å^3, space group P-1 (no. 2), Z = 2, D_c = 1.336 g cm^{-3}, F(000) = 528.00, T = 223(1) K, μ(Cu-Kα) = 13.728 cm^{-1}, 26524 reflections measured, 4598 independent (R_{int} = 0.0353). The final refinement converged to R_1 = 0.0331 for $I > 2.0\sigma(I)$, wR_2 = 0.0907 for all data.

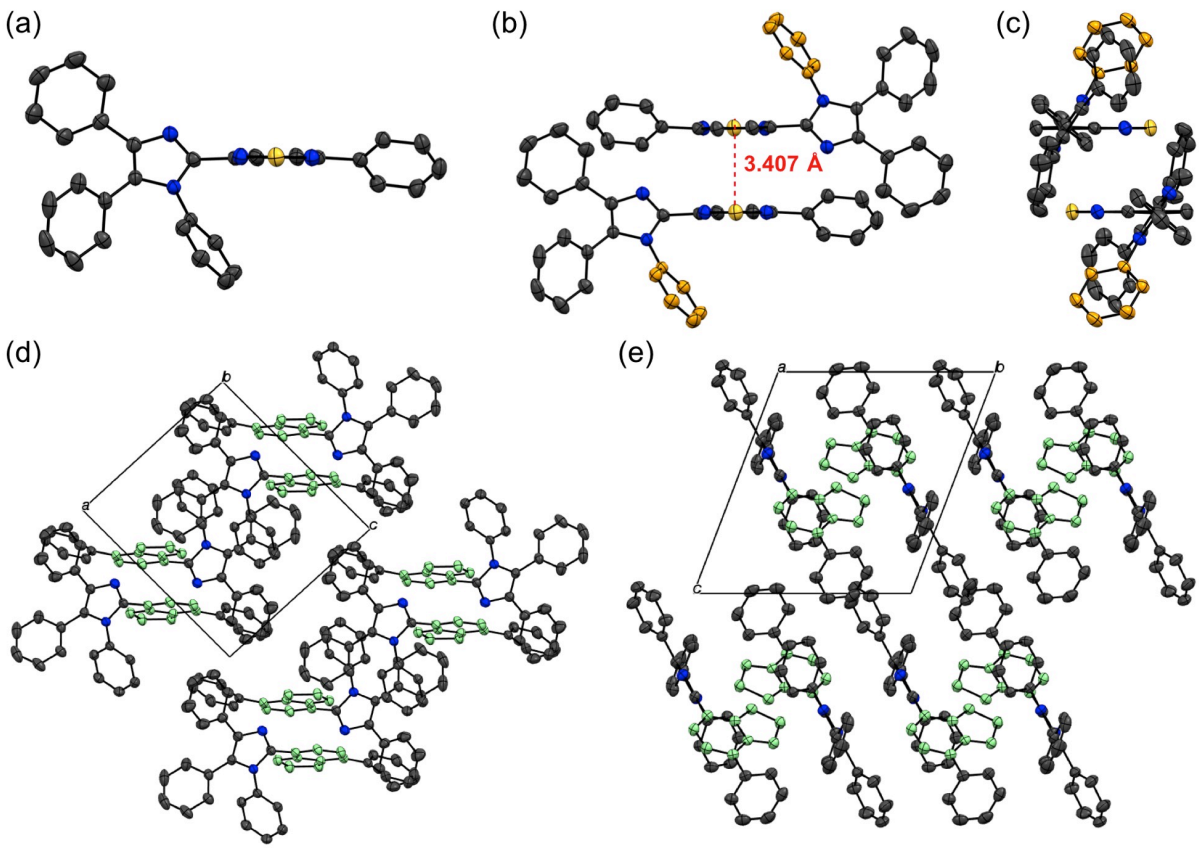

Figure S5. Molecular structures of **1a** in crystalline state with atomic displacement parameters set at 50% probability (Color code: gray and orange = C; blue = N; yellow = S; red = O; green = stacked benzothiadiazole rings). All hydrogen atoms are omitted for clarity. (a) Molecular structure. (b) Front view for molecular structures of adjacent two molecules. (c) Side view for molecular structures of adjacent two molecules. (d) Packing structure viewed along *b*-axis. (e) Packing structure viewed along *a*-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 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 153.4°. A total of 5908 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 27438 reflections that were collected, 4709 were unique (R_{int} = 0.1352); 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 14.193 cm^{-1}. An empirical absorption correction was applied which resulted in transmission factors ranging from 0.440 to 0.898. 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** (CCDC1984812): $C_{33}H_{21}FN_4S$, M = 524.61, triclinic, a = 10.25600(12) Å, b = 11.01019(14) Å, c = 12.04356(15) Å, α = 108.3702(11)°, β = 93.4257(10)°, γ = 90.4464(10), V = 1287.85(3) Å^3, space group P-1 (no. 2), Z = 2, D_c = 1.353 g cm^{-3}, F(000) = 544.00, T = 223(1) K, μ(Cu-Kα) = 14.193 cm^{-1}, 27438 reflections measured, 4709 independent (R_{int} = 0.1352). The final refinement converged to R_1 = 0.0547 for $I > 2.0\sigma(I)$, wR_2 = 0.1566 for all data.

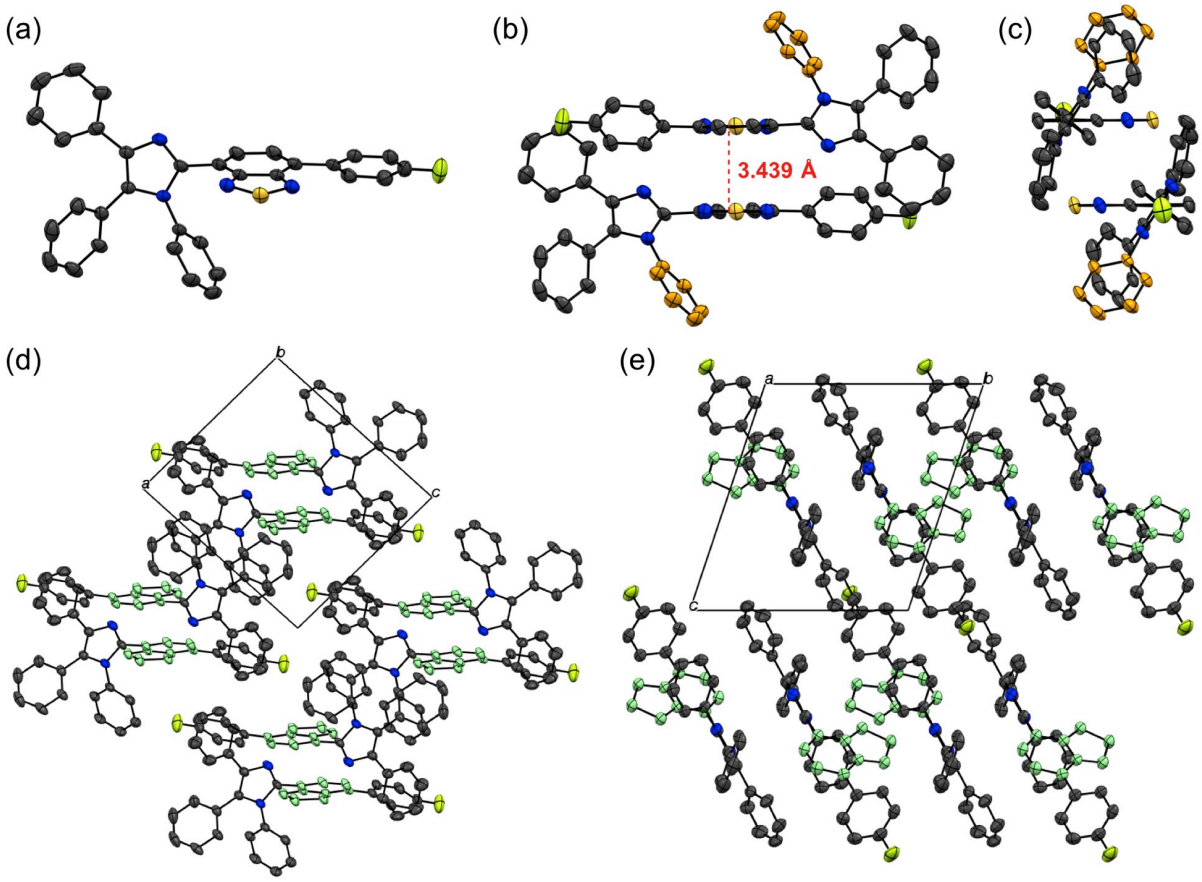

Figure S6. Molecular structures of **1e** in crystalline state with atomic displacement parameters set at 50% probability (Color code: gray and orange = C; blue = N; yellow = S; red = O; yellow green = F; green = stacked benzothiadiazole rings). All hydrogen atoms are omitted for clarity. (a) Molecular structure. (b) Front view for molecular structures of adjacent two molecules. (c) Side view for molecular structures of adjacent two molecules. (d) Packing structure viewed along *b*-axis. (e) Packing structure viewed along *a*-axis.

5. Theoretical calculations

Table S1. Calculated absorption properties of triphenylimidazolylbenzothiadiazole derivatives.

Compd	Calcd absorption λ_{abs} (nm)	Transition from HOMO to LUMO	Oscillator strength	HOMO (eV)	LUMO (eV)	Dipole moment (D)
1a	364.72	0.64133	0.2708	–6.57	–1.20	3.786358
1a (opt)	369.18	0.64004	0.3707	–6.59	–1.22	3.333850
1d-1	424.81	0.66767	0.4608	–6.37	–1.38	3.631136
1d-1 (opt)	377.15	0.64620	0.4506	–6.49	–1.14	3.988018
1d-2	414.51	0.67109	0.5391	–6.29	–1.27	7.408554
1d-2 (opt)	369.01	0.64238	0.4682	–6.49	–1.06	5.955150
1e	369.36	0.64685	0.2531	–6.59	–1.30	3.551846
1e (opt)	372.50	0.64148	0.3732	–6.62	–1.29	3.588022

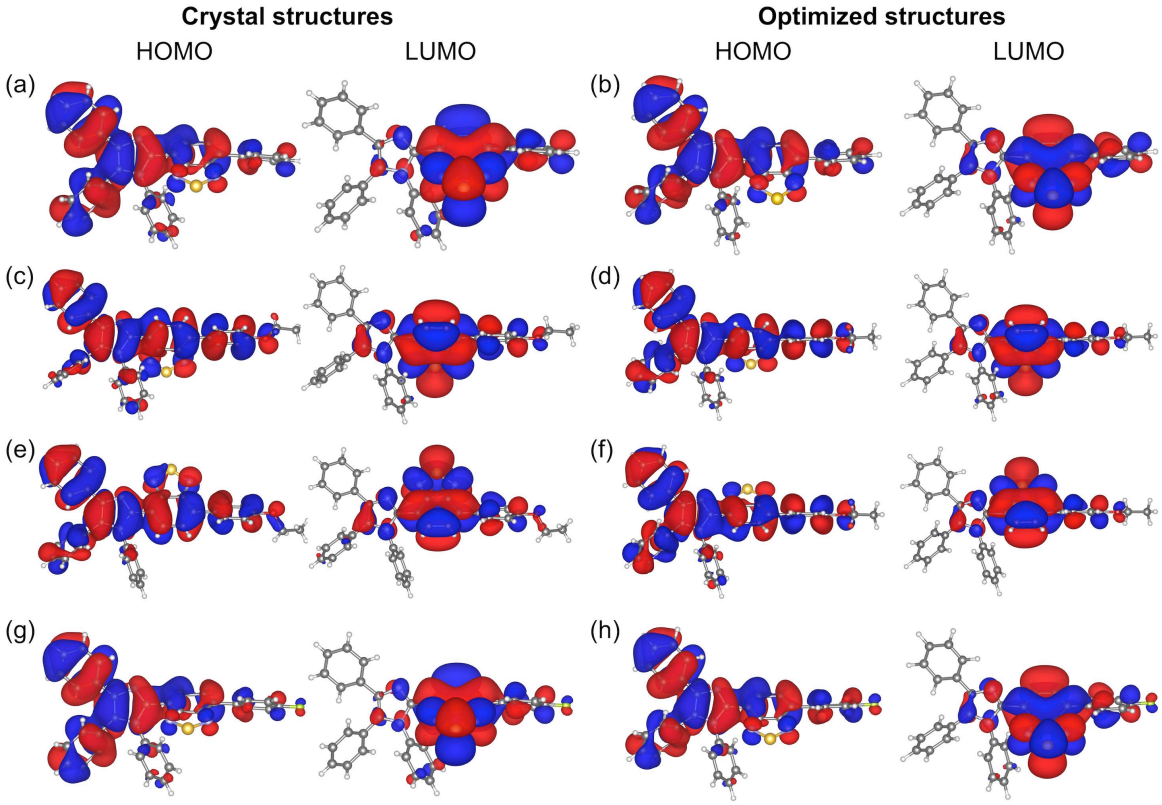

Figure S7. HOMO and LUMO for crystal structures (a, c, e, and g) and optimized structures (b, d, f, and h) of **1a** (a and b), **1d-1** (c and d), **1d-2** (e and f), and **1e** (g and h) calculated at the CAM-B3LYP/6-31G(d) level. The structures are drawn by VESTA.[5]

6. Solid-state absorption spectra of 1a–f before and after grinding

Significant shifts in the absorption spectra were observed for plate-like crystals **1a** and **1e** after grinding, whereas those of needle-like crystals **1b**–**d** and **1f** were almost unchanged after grinding (Figure S8).

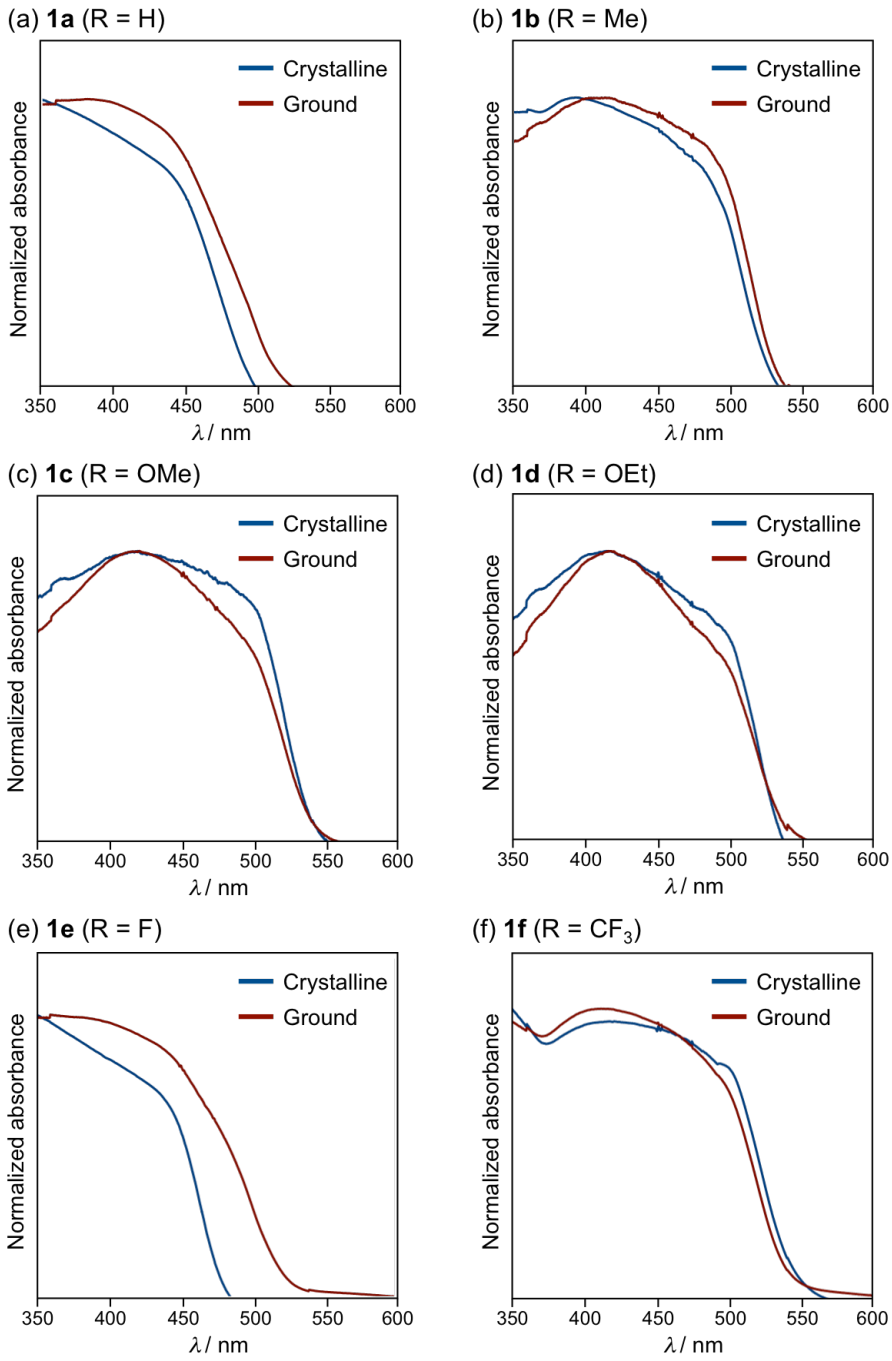

Figure S8. Solid-state absorption spectra for crystalline (blue) and ground (red) **1a** (a), **1b** (b), **1c** (c), **1d** (d), **1e** (e), and **1f** (f).

7. References

1) CrysAlisPro: Data Collection and Processing Software, Rigaku Corporation (2015). Tokyo 196-8666, Japan.

2) a) Altomare, A.; Cascarano, G.; Giacovazzo, C.; Guagliardi, A. Completion and Refinement of Crystal Structures with *SIR*92. *J. Appl. Cryst.* **1993**, *26*, 343–350. b) Burla, M. C.; Caliandro, R.; Camalli, M.; Carrozzini, B.; Cascarano, G. L.; Giacovazzo, C.; Mallamo, M.; Mazzone, A.; Polidori, G.; Spagna, R. *SIR2011*: A New Package for Crystal Structure Determination and Refinement. *J. Appl. Cryst.* **2012**, *45*, 357–361.

3) CrystalStructure 4.2.5: Crystal Structure Analysis Package, Rigaku Corporation (2000-2017). Tokyo 196-8666, Japan.

4) Sheldrick, G. M. A Short History of *SHELX*. *Acta Cryst.* **2008**, *A64*, 112–122.

5) Momma, K.; Izumi, F. *VESTA3* for Three-Dimentional Visualization of Crystal, Volumetric and Morphology Data. *J. Appl. Crystallogr.* **2011**, *44*, 1272–1276.

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

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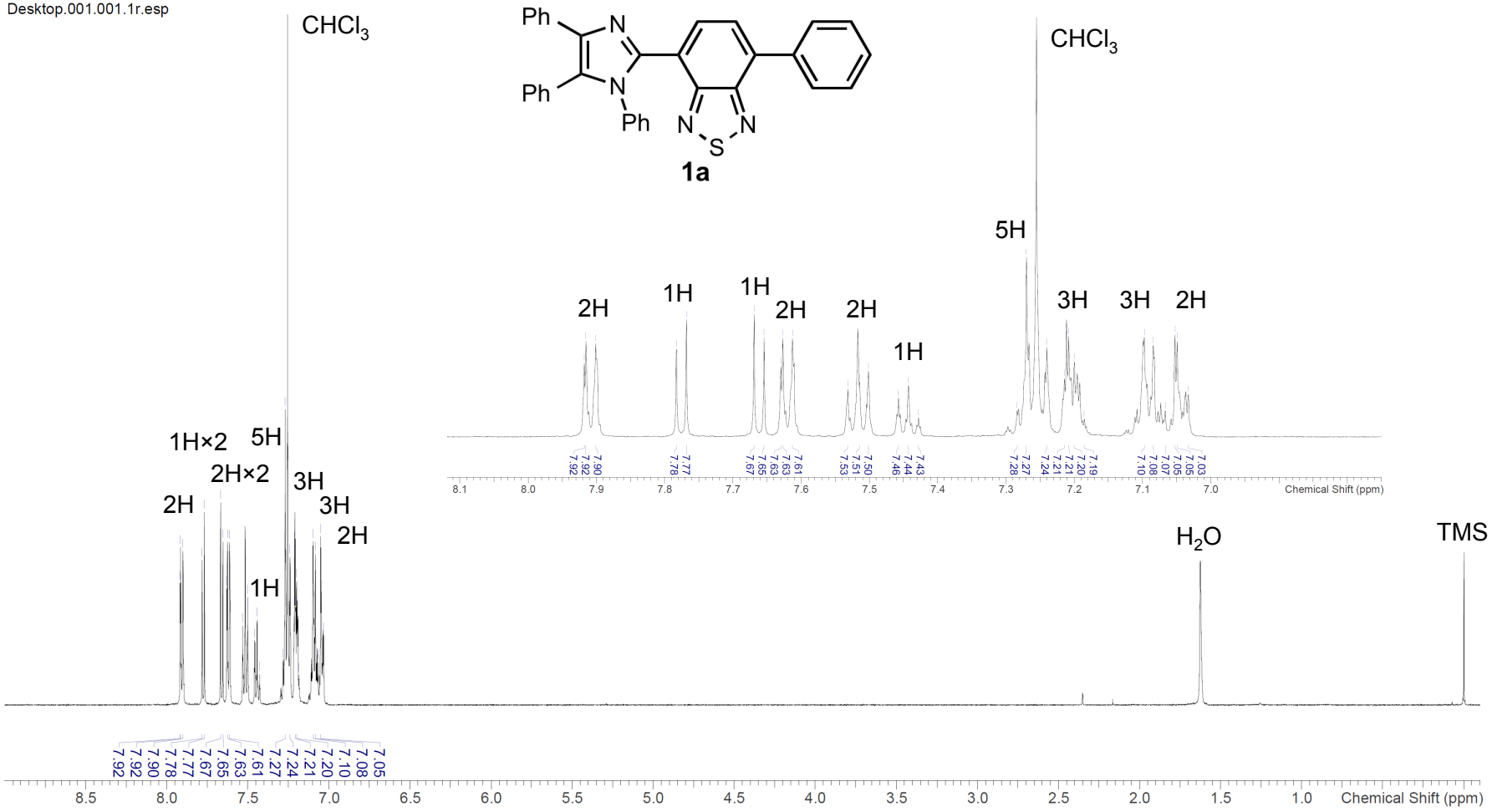

^{13}C NMR spectrum of **1a** (126 MHz, in $CDCl_3$)

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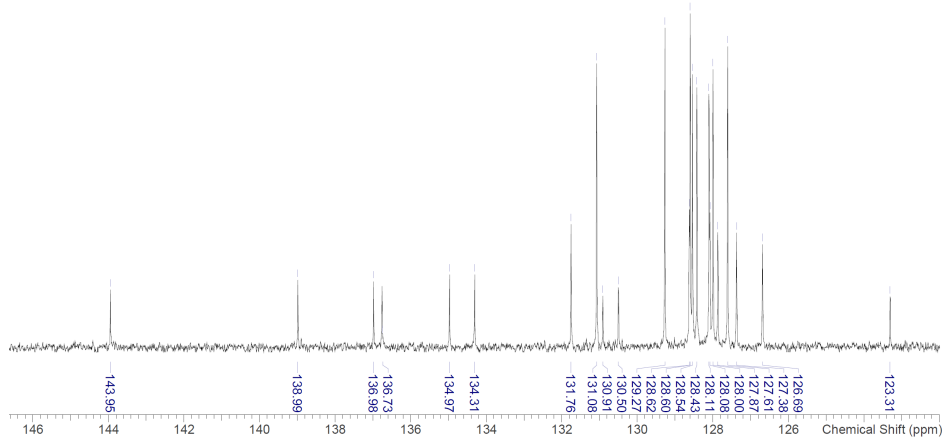
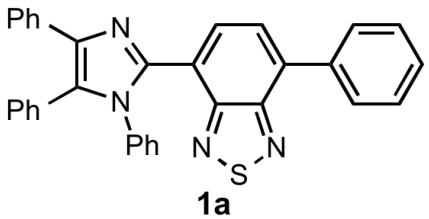
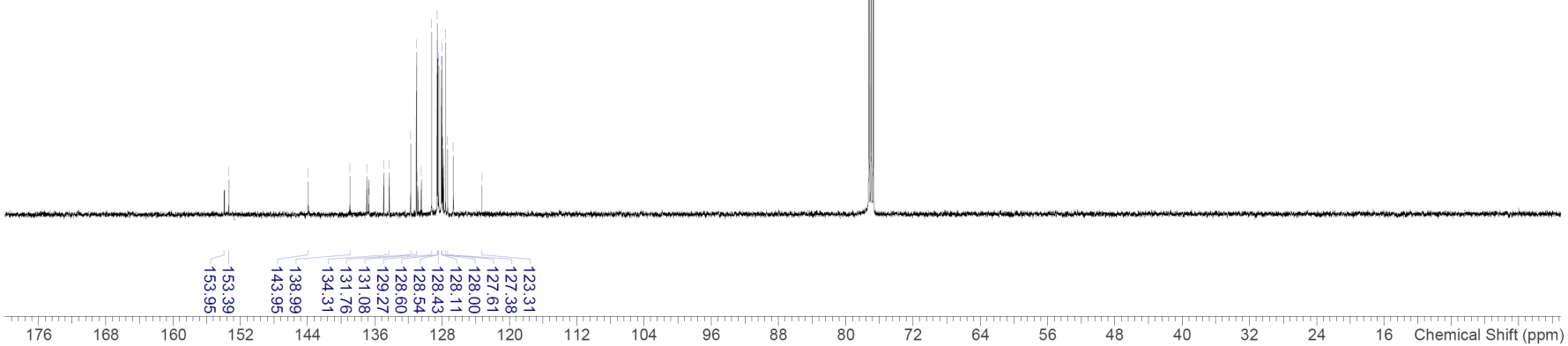


$CDCl_3$



1a



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

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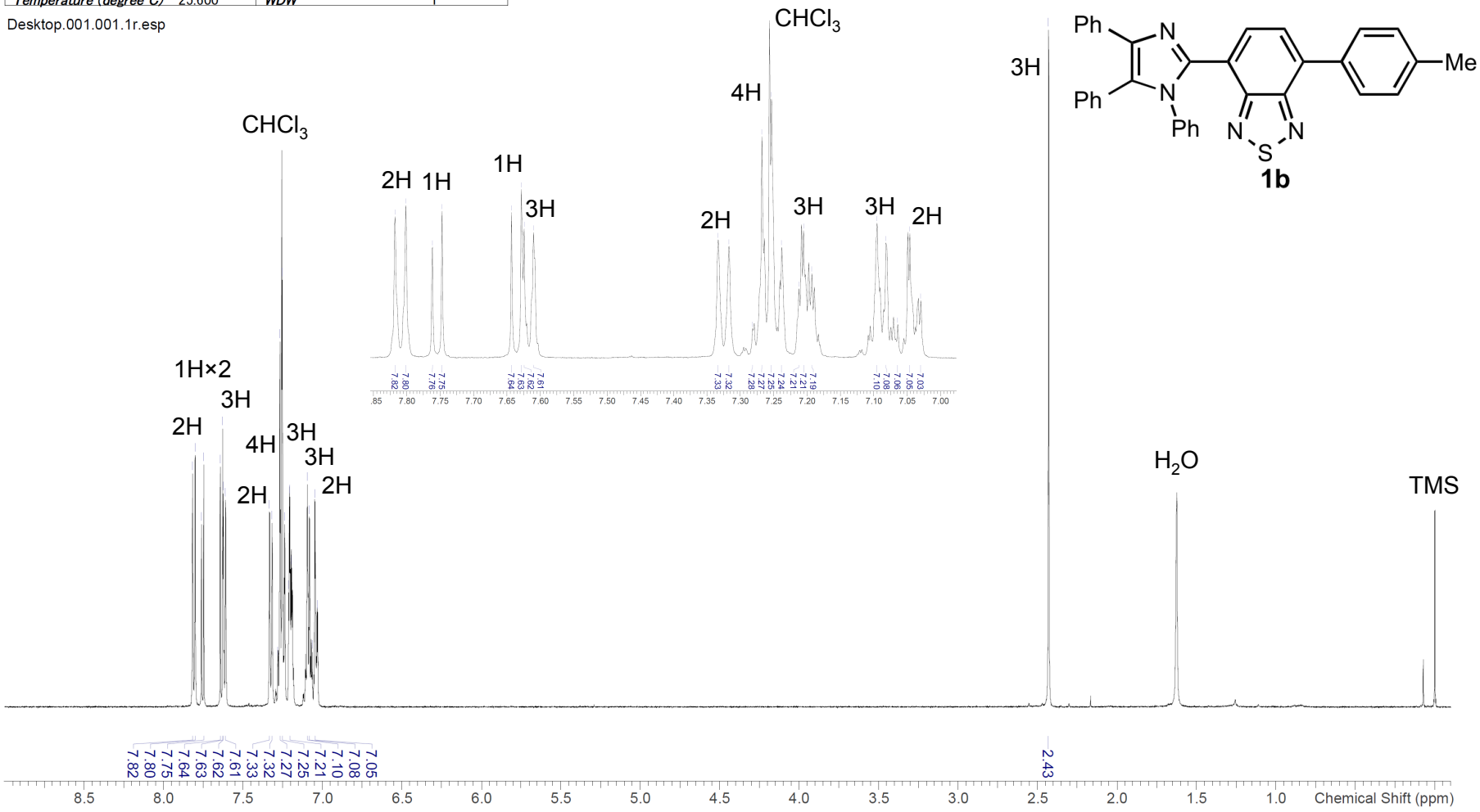

^{13}C NMR spectrum of **1b** (126 MHz, in $CDCl_3$)

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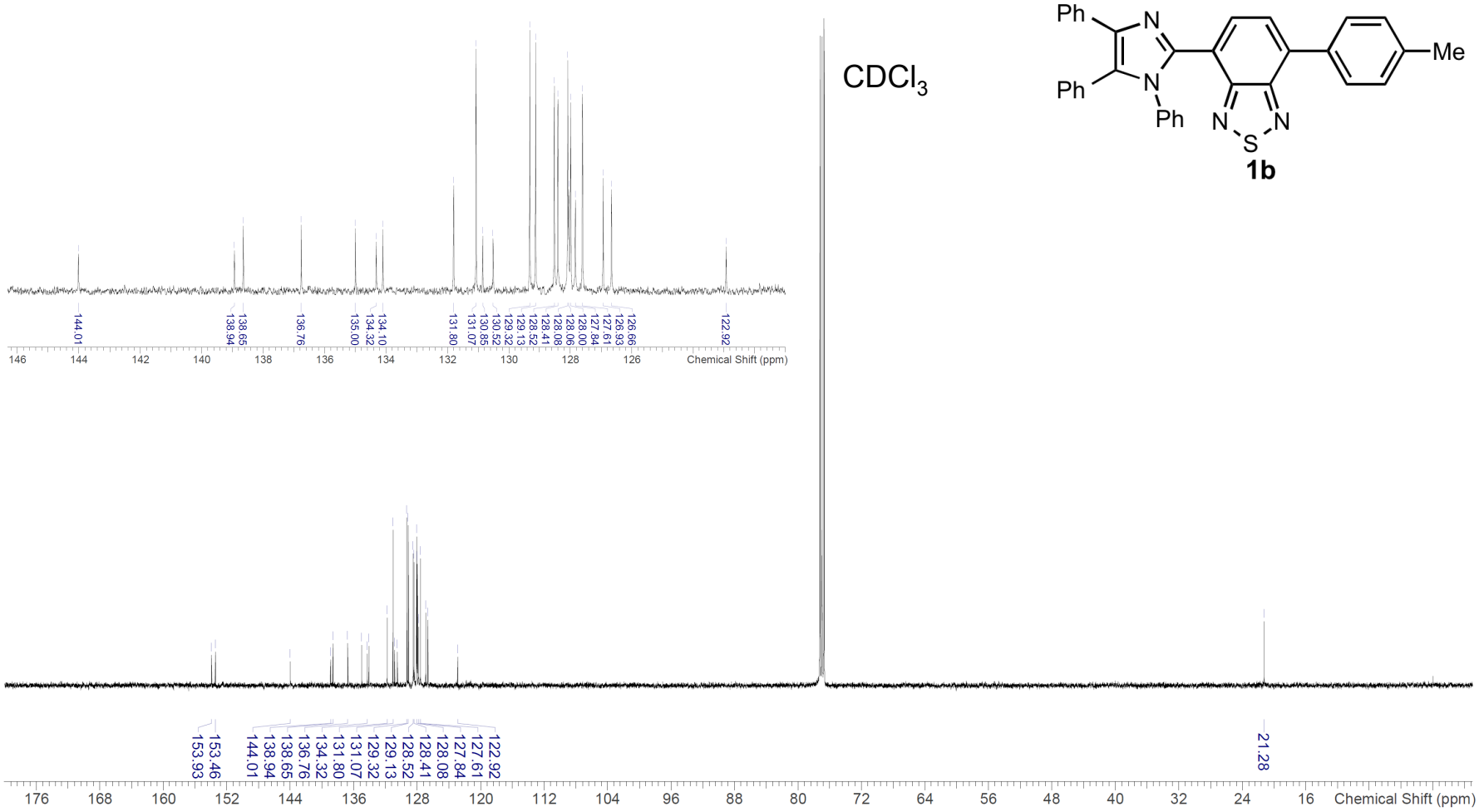

^{1}H NMR spectrum of **1c** (500 MHz, in $CDCl_3$)

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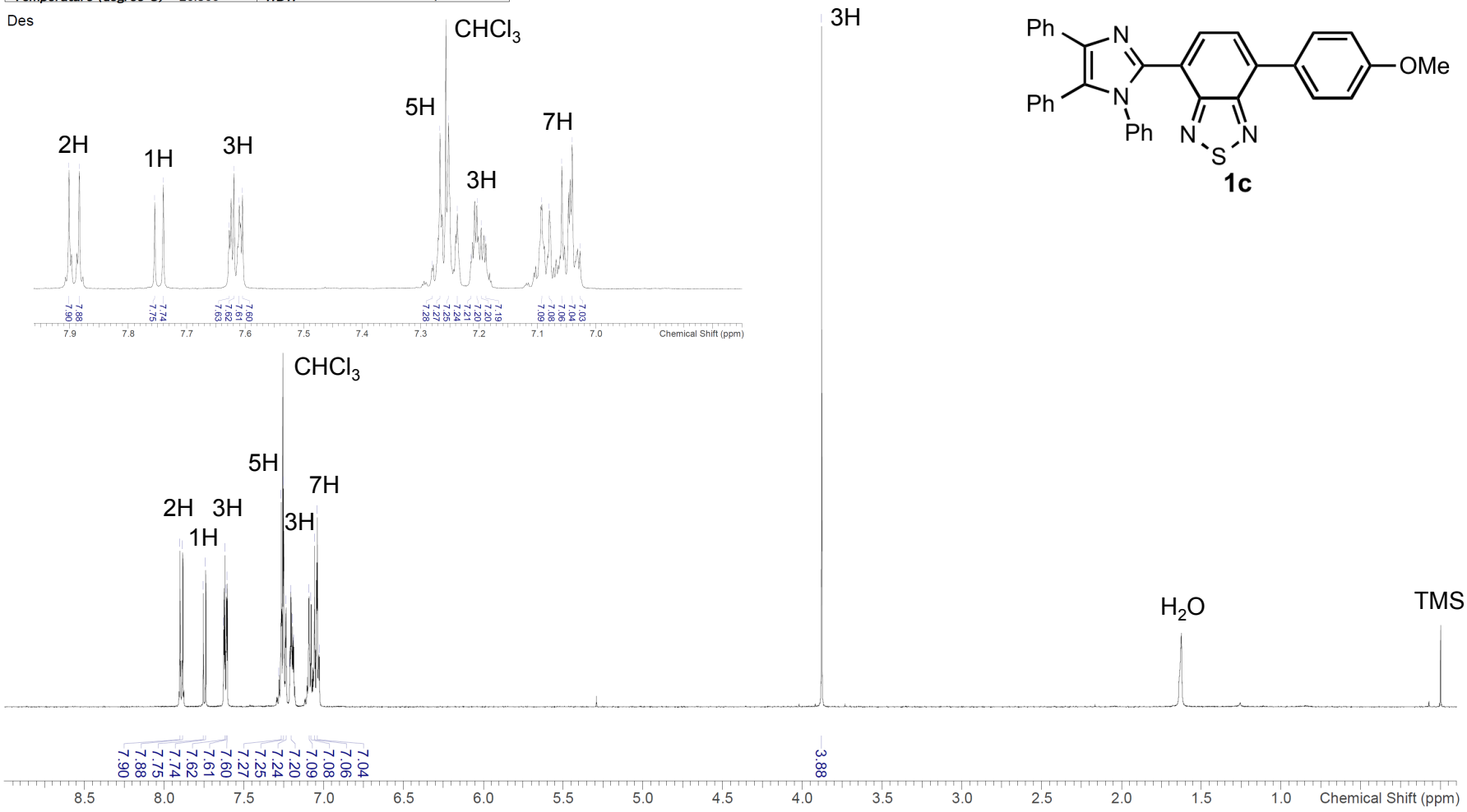

^{13}C NMR spectrum of **1c** (126 MHz, in $CDCl_3$)

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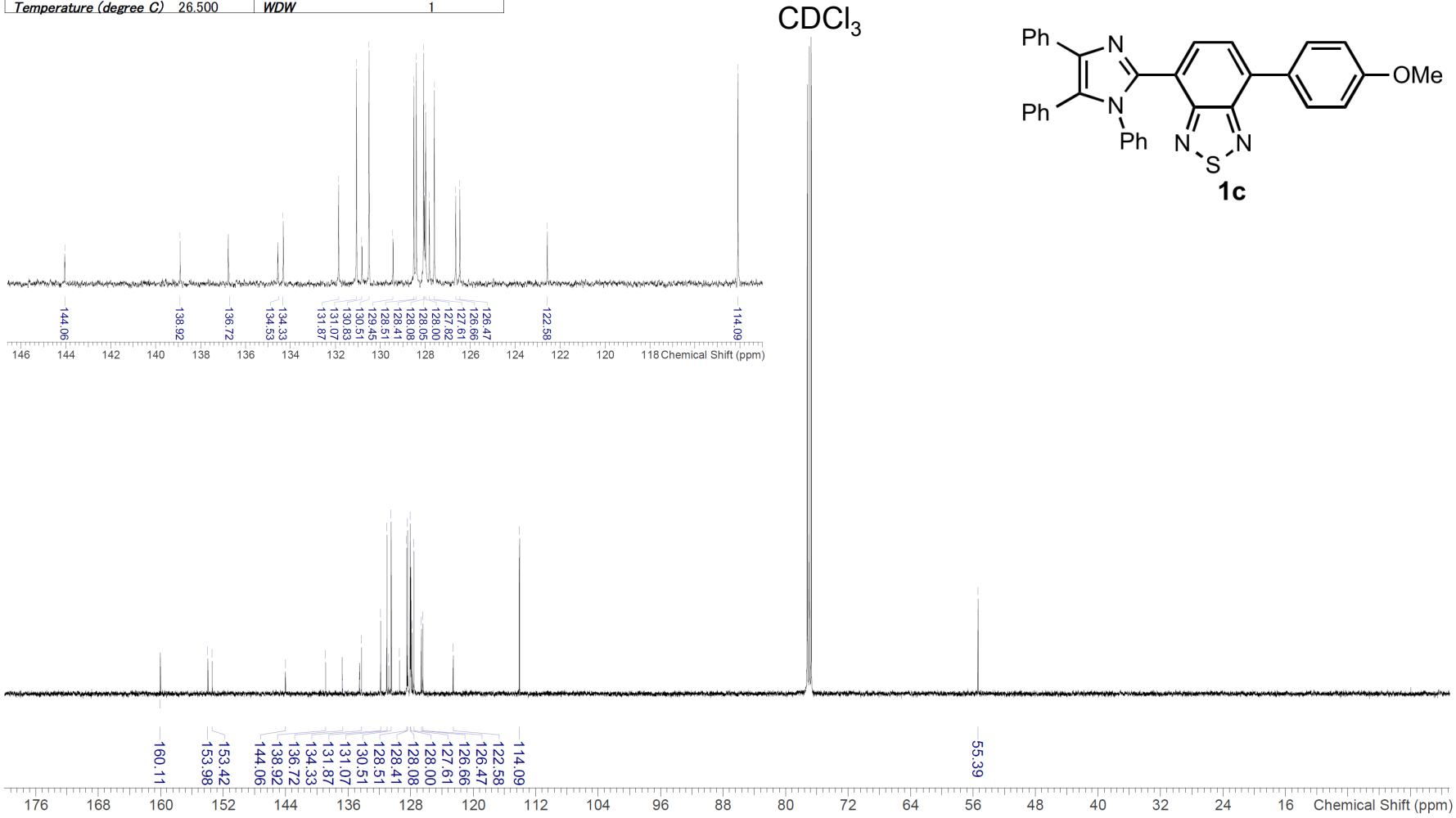

1c

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

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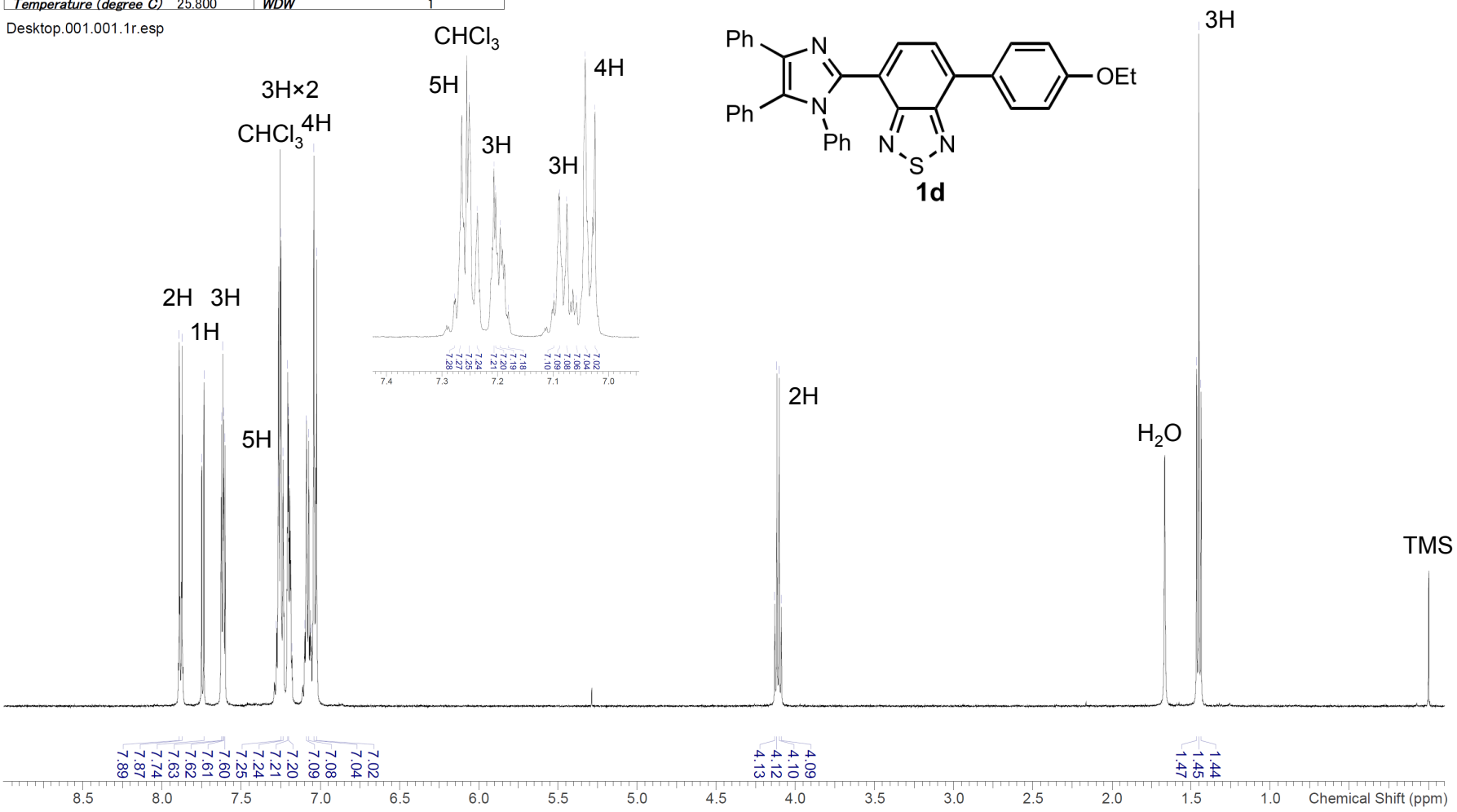
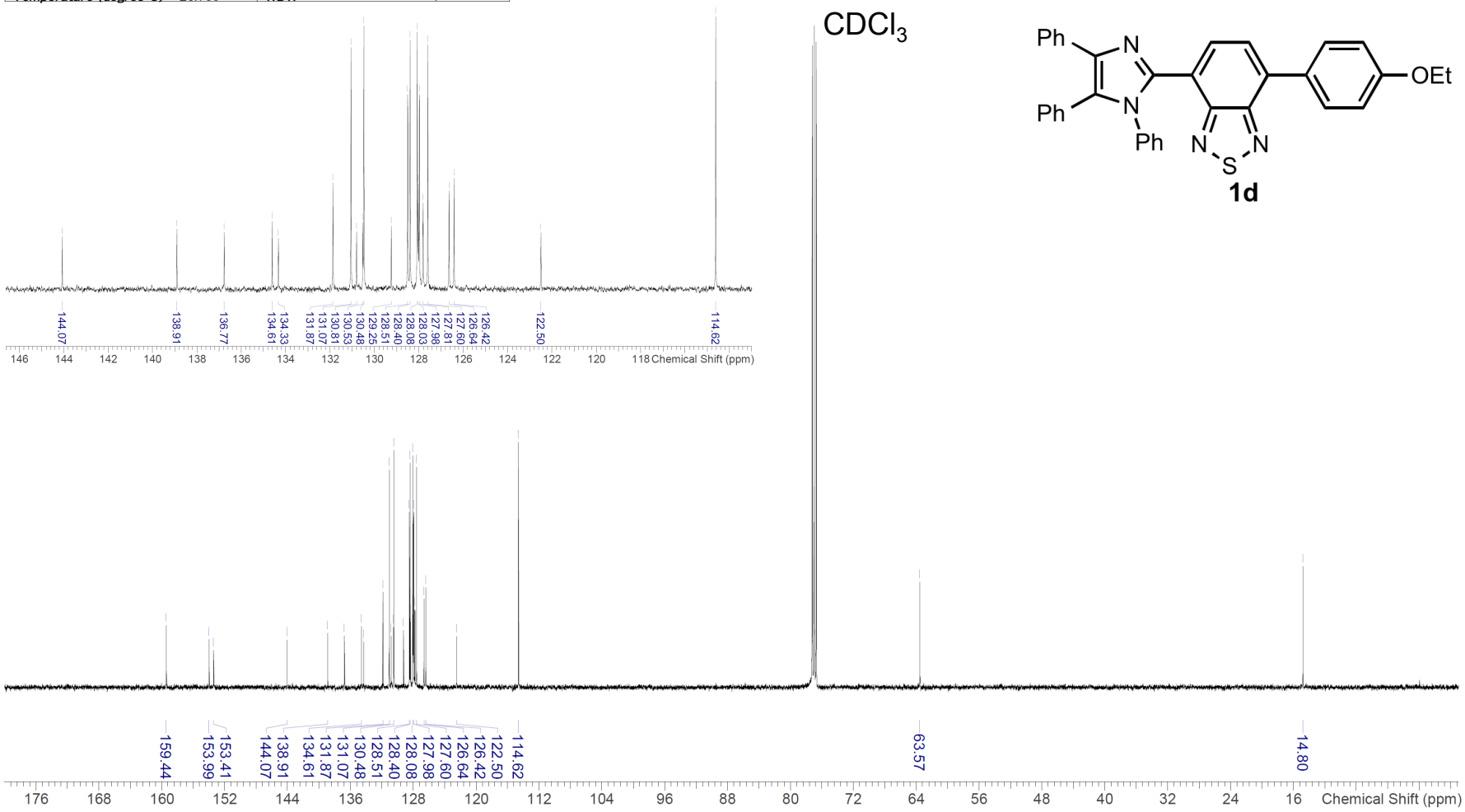
Original Points Count	32768	*Owner*	root	*PC*	1	*PROBHD*	<5 mm BBO BB-1H Z-GRD Z859001/0006 >		
PULPROG	<zg30>	*Points Count*	32768	*Pulse Sequence*	zg30	*Receiver Gain*	181.00	*SF*	500.130006648269
SFO1	500.133088507478			*SI*	32768	*SSB*	0	*SW(cyclical) (Hz)*	10330.58
SWH	10330.5785123967			*Solvent*	CHLOROFORM-d			*Spectrum Offset (Hz)*	3073.3572
Spectrum Type	standard	*Sweep Width (Hz)*	10330.26	*TD*	65536	*TD0*	1	*TE*	298.8
Temperature (degree C)	25.800	*WDW*	1						

Desktop.001.001.1r.esp



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

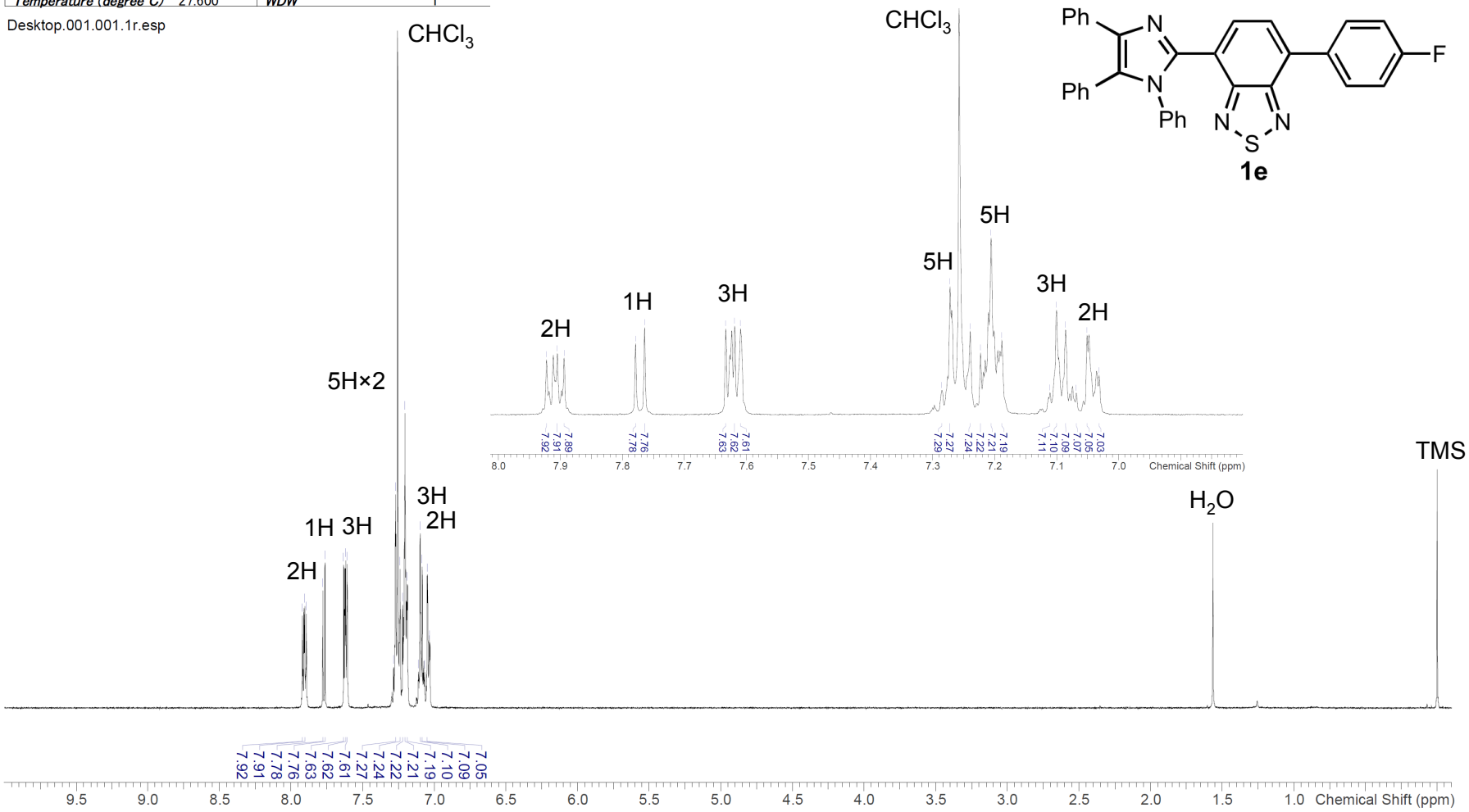
Acquisition Time (sec)	1.0912	*D*	0.00345	*D1*	2	*DE*	6	*DS*	4
Date	31 Jul 2018 19:02:16			*Date Stamp*	31 Jul 2018 19:02:16				
File Name	C:¥Users¥Asami-Lab¥Desktop¥1¥PDATA¥1¥1r			*Frequency (MHz)*	125.7578	*GB*	0	*INSTRUM*	<spect>
LB	1	*NS*	1024	*Nucleus*	13C	*Number of Transients*	1024	*Origin*	spect
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*	1824.60	*SF*	125.757789
SFO1	125.770364304853			*SI*	32768	*SSB*	0	*SW(cyclical) (Hz)*	30030.03
SWH	30030.03003003			*Solvent*	CHLOROFORM-d			*Spectrum Offset (Hz)*	12570.6113
Spectrum Type	standard	*Sweep Width (Hz)*	30029.11	*TD*	65536	*TD0*	1	*TE*	299.7
Temperature (degree C)	26.700	*WDW*	1						



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

Acquisition Time (sec)	3.1719	*Comment*	1125-2++H	*D*	3.827959	*D1*	3.827959	*DE*	6
DS	2	*Date*	17 Jan 2019 12:12:59			*Date Stamp*	17 Jan 2019 12:12:59		
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*	574.70	*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*	300.6
Temperature (degree C)	27.600	*WDW*	1						

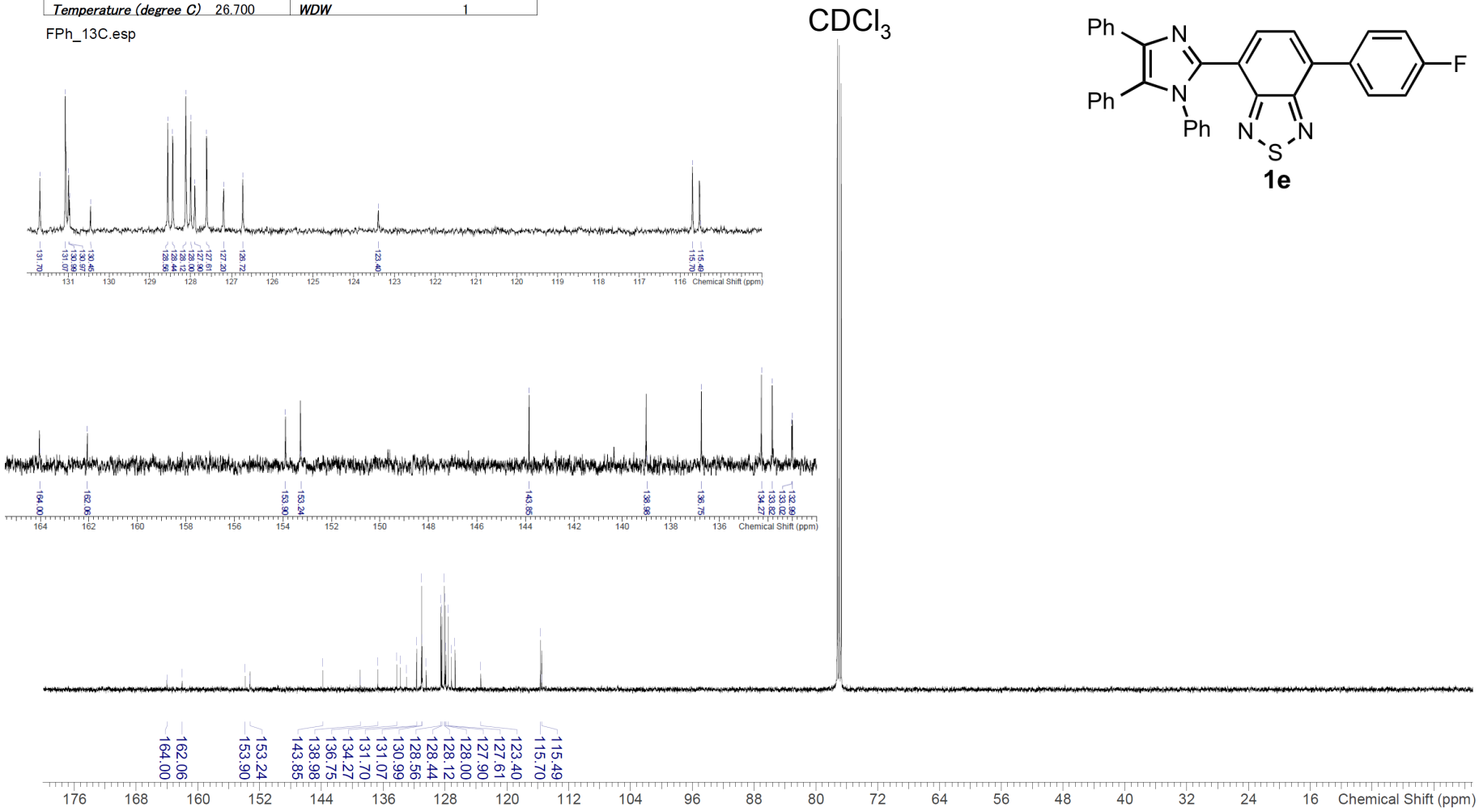
Desktop.001.001.1r.esp



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

Acquisition Time (sec)	1.0912	*Comment*	1f	*D*	0.00345	*D1*	2	*DE*	6
DS	4	*Date*	18 Jul 2018 10:59:13			*Date Stamp*	18 Jul 2018 10:59:13		
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*	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*	299.7
Temperature (degree C)	26.700	*WDW*	1						

FPh_13C.esp

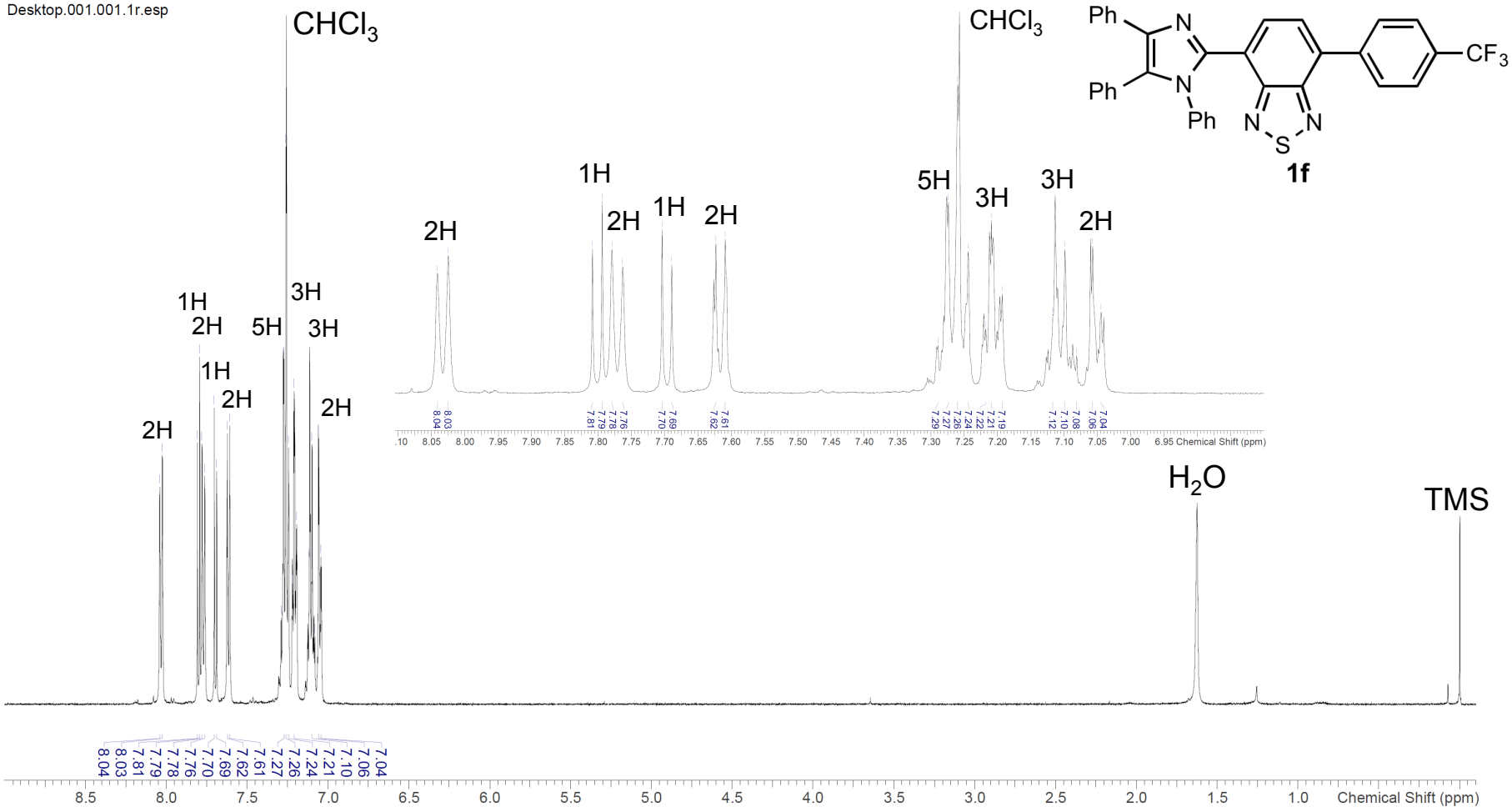


1e

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

Acquisition Time (sec)	3.1719	*Comment*	1,4-diazabicyclo[2.2.2]octane			*D*	3.827959	*D1*	3.827959
DE	6	*DS*	2	*Date*	11 Jul 2018 13:13:52			*Date Stamp*	11 Jul 2018 13:13:52
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*	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)*	3074.3074
Spectrum Type	standard	*Sweep Width (Hz)*	10330.26	*TD*	65536	*TD0*	1	*TE*	298.9
Temperature (degree C)	25.900	*WDW*	1						

Desktop.001.001.1r.esp



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

Acquisition Time (sec)	1.0912	*D*	0.00345	*D1*	2	*DE*	6	*DS*	4
Date	11 Jul 2018 14:12:05			*Date Stamp*	11 Jul 2018 14:12:05				
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*	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)*	12572.4346
Spectrum Type	standard	*Sweep Width (Hz)*	30029.11	*TD*	65536	*TD0*	1	*TE*	299.7
Temperature (degree C)	26.700	*WDW*	1