Solvates of a dianisyl-substituted donor–acceptor-type benzothiadiazole: mechanochromic, vapochromic, and acid-responsive multicolor luminescence

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1. Fluorescence spectra of 1 in solution
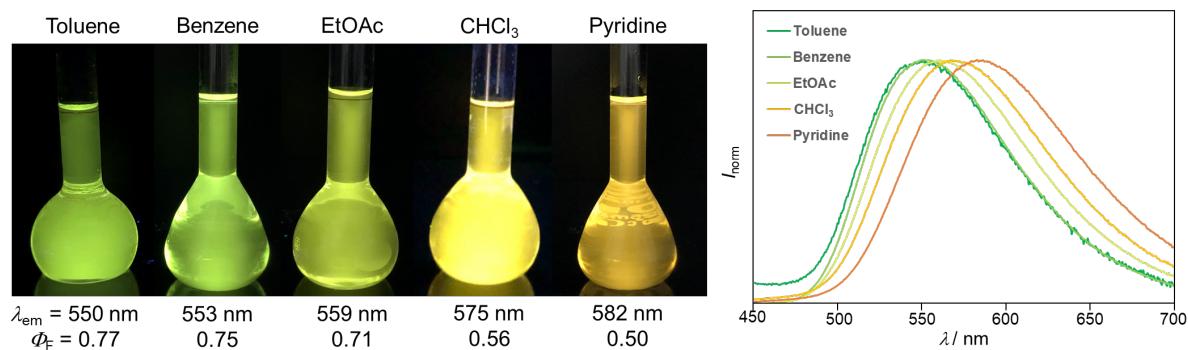

Fig. S1 Photographs and fluorescence spectra of **1** in solvents (λ_{ex} = 365 nm).

2. Single-crystal X-ray diffraction analyses

**Table S1.** Selected crystallographic data of 1 and 1•Solvent

|	1•CHCl$_3$	1•Benzene	1•Pyridine	1•EtOAc	1•Toluene	1
Empirical formula	C$_{35}$H$_{24}$N$_4$O$_2$S•CHCl$_3$	C$_{35}$H$_{24}$N$_4$O$_2$S•C$_6$H$_6$	C$_{35}$H$_{24}$N$_4$O$_2$S•C$_5$H$_5$N	C$_{35}$H$_{24}$N$_4$O$_2$S (+solvent)	C$_{35}$H$_{24}$N$_4$O$_2$S•C$_7$H$_8$	C$_{35}$H$_{24}$N$_4$O$_2$S
Formula weight	684.04	642.75	643.76	564.66	656.80	564.66
Temperature / K	223	223.15	223	223	223	223
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic	triclinic	triclinic
Space group	$P2_1/c$ (#14)	$C2/c$ (#15)	$C2/c$ (#15)	$P2_1/c$ (#14)	P-1 (#2)	P-1 (#2)
a / Å	13.6322(2)	27.8666(4)	27.6505(2)	13.2848(2)	11.62224(9)	12.20306(9)
b / Å	22.3975(3)	10.41560(10)	10.34767(8)	21.9654(3)	14.66776(11)	21.16656(17)
c / Å	10.78060(19)	23.2099(4)	23.2526(2)	10.92692(17)	21.05256(16)	22.98109(18)
α / °	90.0000	90.0000	90.0000	90.0000	100.6593(6)	69.0121(7)
β / °	111.601(2)	108.110(2)	108.4906(10)	111.8702(18)	91.6602(6)	87.5755(6)
γ / °	90.0000	90.0000	90.0000	90.0000	109.9863(7)	87.6112(6)
V / Å^3	3060.44(9)	6402.89(17)	6309.54(9)	2959.06(8)	3297.98(5)	5534.93(8)
Z	4	8	8	4	4	8
D_{calcd} / g cm^{-3}	1.484	1.334	1.355	1.267	1.323	1.355
μ / mm^{-1}	3.691	1.246	1.275	1.275	1.221	1.363
$F(000)$	1408.00	2688.00	2688.00	1176.00	1376.00	2352.00
Crystal size / mm^3	0.700 × 0.500 × 0.010	0.7 × 0.5 × 0.01	0.700 × 0.500 × 0.010	0.100 × 0.010 × 0.010	0.300 × 0.200 × 0.100	0.200 × 0.100 × 0.010
Radiation	CuKα (λ = 1.54184 Å)	CuKα (λ = 1.54184 Å)	CuKα (λ = 1.54184 Å)	CuKα (λ = 1.54184 Å)	CuKα (λ = 1.54184 Å)	CuKα (λ = 1.54184 Å)
2θ range for data collection / °	7.894 to 136.486	8.016 to 146.42	8.018 to 136.474	9.606 to 136.500	8.136 to 136.464	7.852 to 136.494
Index ranges	−16 ≤ h ≤ 16	−33 ≤ h ≤ 31	−33 ≤ h ≤ 31	−13 ≤ h ≤ 15	−13 ≤ h ≤ 14	−14 ≤ h ≤ 14
	−26 ≤ k ≤ 20	−12 ≤ k ≤ 12	−12 ≤ k ≤ 6	−26 ≤ k ≤ 25	−17 ≤ k ≤ 17	−23 ≤ k ≤ 25
	−12 ≤ l ≤ 10	−25 ≤ l ≤ 28	−27 ≤ l ≤ 28	−13 ≤ l ≤ 13	−25 ≤ l ≤ 22	−18 ≤ l ≤ 27
Reflections collected	18142	17502	19744	18511	46430	73764
Independent reflections	5603 [R_{int} = 0.0580]	6248 [R_{int} = 0.0459]	5778 [R_{int} = 0.0247]	5402 [R_{int} = 0.0288]	12036 [R_{int} = 0.0567]	20185 [R_{int} = 0.0323]
Data / restraints / parameters	5603/0/415	6248/0/401	5778/0/433	5402/0/379	12036/0/883	20185/0/1513
Goodness-of-fit on F^2	1.066	1.071	1.052	1.057	1.065	1.037
Final R indexes [$I > 2\sigma$ (I)]	R_1 = 0.0436, wR_2 = 0.1219	R_1 = 0.0533, wR_2 = 0.1488	R_1 = 0.0425, wR_2 = 0.1126	R_1 = 0.0425, wR_2 = 0.1081	R_1 = 0.0491, wR_2 = 0.1362	R_1 = 0.0608, wR_2 = 0.1731
Final R indexes [all data]	R_1 = 0.0470, wR_2 = 0.1252	R_1 = 0.0570, wR_2 = 0.1521	R_1 = 0.0449, wR_2 = 0.1145	R_1 = 0.0458, wR_2 = 0.1106	R_1 = 0.0533, wR_2 = 0.1400	R_1 = 0.0670, wR_2 = 0.1783
Largest diff. peak/hole / eÅ^{-3}	0.26/−0.42	0.35/−0.43	0.48/−0.53	0.30/−0.54	0.54/−0.39	1.77/−0.61
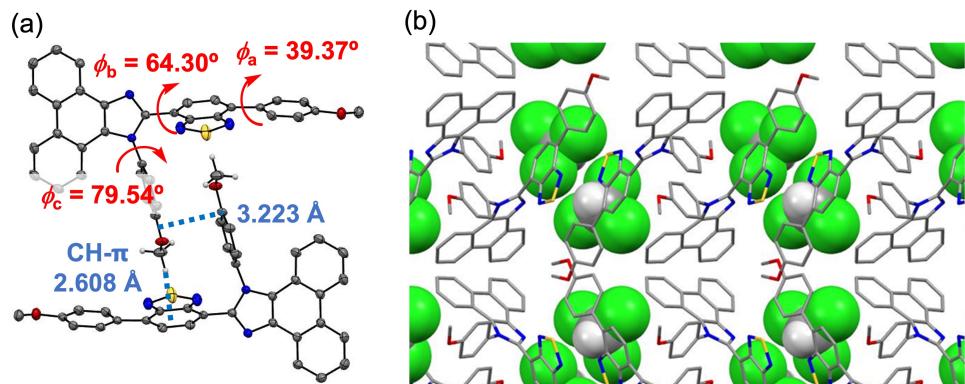
Fig. S2 The crystal structure of **1·CHCl₃** (Color code: gray = C, red = O, blue = N, yellow = S, green = Cl). (a) Adjacent two molecules with atomic displacement parameters set at 50% probability. (b) Packing structure. Solvate molecules are represented with space-filling model.
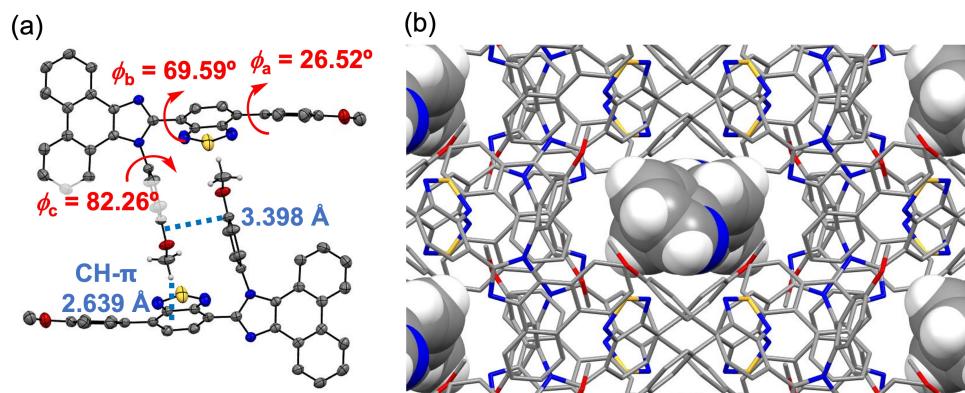

Fig. S3 The crystal structure of **1·Pyridine** (Color code: gray = C, red = O, blue = N, yellow = S). (a) Adjacent two molecules with atomic displacement parameters set at 50% probability. (b) Packing structure viewed along *c*-axis. Solvate molecules are represented with space-filling model.
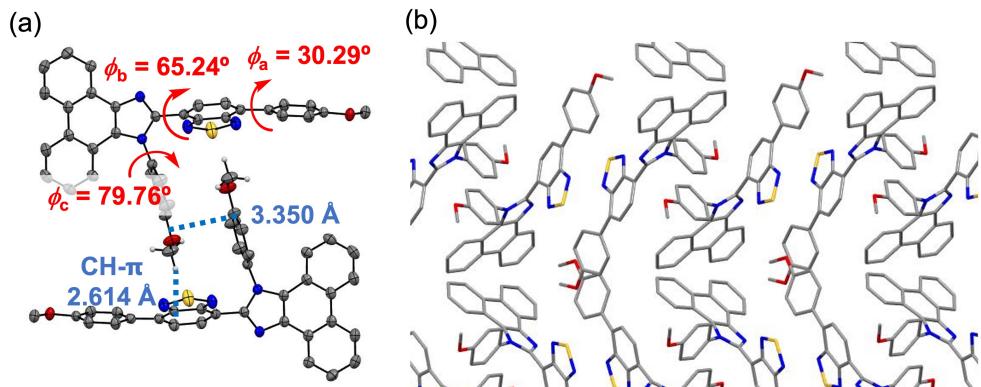
Fig. S4 The crystal structure of **1•EtOAc** (Color code: gray = C, red = O, blue = N, yellow = S). (a) Adjacent two molecules with atomic displacement parameters set at 50% probability. (b) Packing structure viewed along *c*-axis.
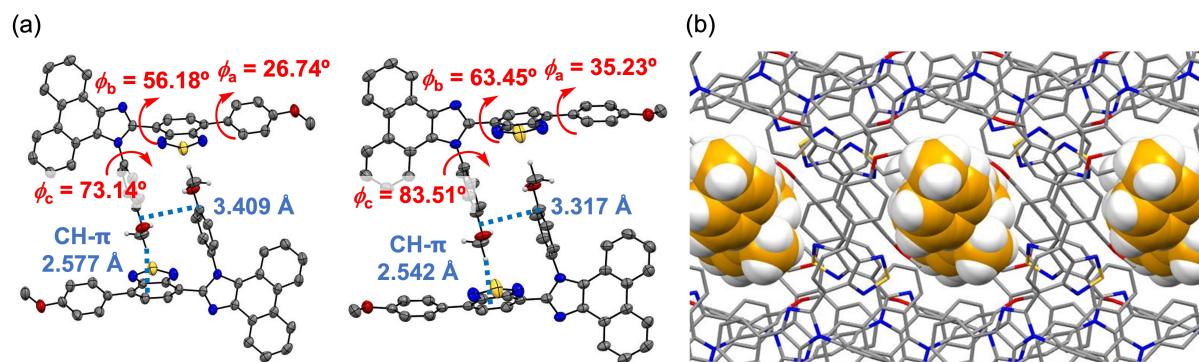

Fig. S5 The crystal structure of **1•Toluene** (Color code: gray = C, red = O, blue = N, yellow = S). (a) Adjacent two molecules with atomic displacement parameters set at 50% probability. Crystallographically independent two pairs are shown. (b) Packing structure viewed along *c*-axis. Solvate molecules are represented with space-filling model. Carbon atoms of solvate molecules are shown in orange.
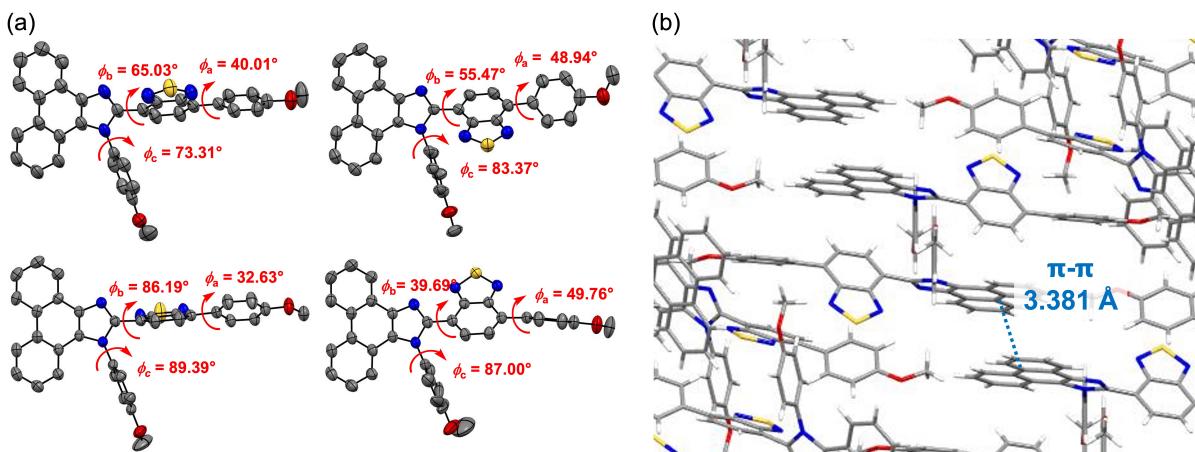
Fig. S6 The crystal structure of **1** with atomic displacement parameters set at 50% probability (Color code: gray = C, red = O, blue = N, yellow = S). (a) Four crystallographically independent molecules of **1**. (b) Packing structure of **1**.

3. Absorption spectra for crystalline 1 and 1•Solvent
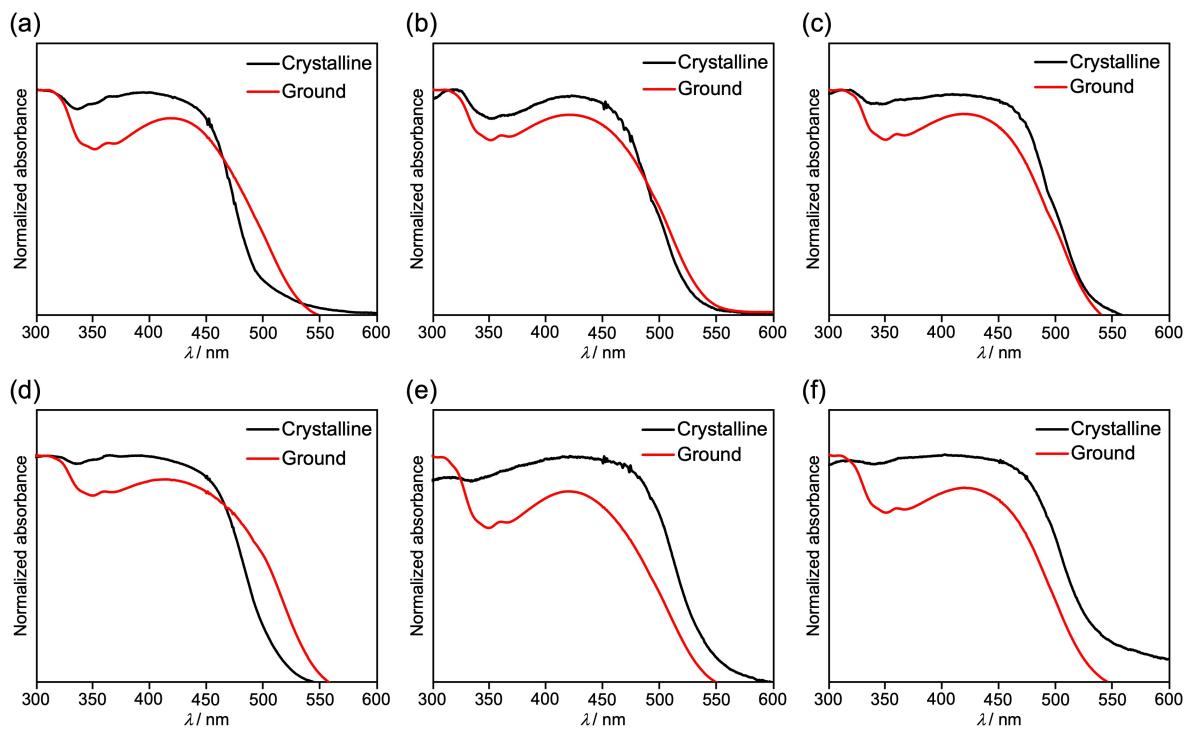
Fig. S7 Solid-state absorption spectra of **1•CHCl₃** (a), **1•Benzene** (b), **1•Pyridine** (c), **1•EtOAc** (d), **1•Toluene** (e), and **1** (f).

4. Theoretical calculations

Table S2 Experimental fluorescence maxima and calculated absorption properties of X-ray structures for **1** and **1•Solvent**.

Compd.	Crystalline λ_{em} (nm)	Calcd λ_{abs} (nm)	Transition from HOMO to LUMO	Oscillator strength	HOMO (eV)	LUMO (eV)	Dipole moment (D)
1•CHCl₃	508	373	0.622	0.390	–6.37	–1.17	5.03
1•Benzene	521	379	0.607	0.422	–6.36	–1.19	5.20
1•Pyridine	522	377	0.607	0.408	–6.37	–1.20	5.23
1•EtOAc	524	381	0.614	0.428	–6.36	–1.20	5.25
1•Toluene	565	382	0.624	0.471	–6.35	–1.18	5.23
1	550	371	0.640	0.396	–6.42	–1.17	3.34
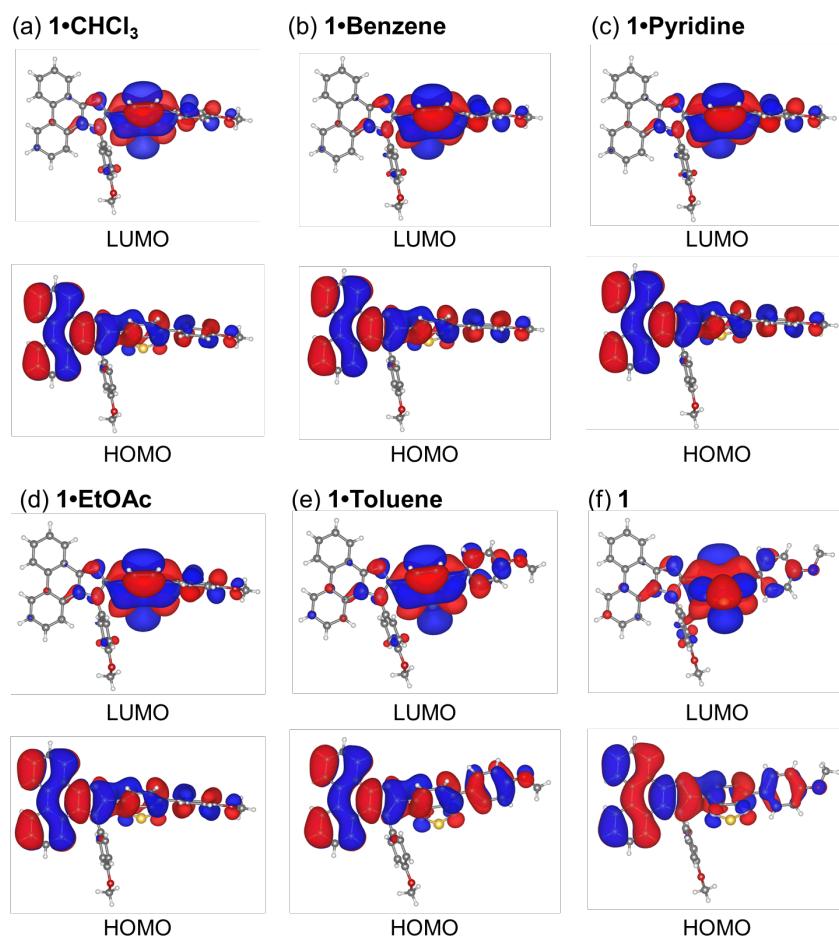
Fig. S8 HOMO and LUMO of **1** in crystalline **1•CHCl₃** (a), **1•Benzene** (b), **1•Pyridine** (c), **1•EtOAc** (d), **1•Toluene** (e), and **1** (f) calculated at the CAM-B3LYP/6-31G(d) level. The structures are drawn by VESTA.[1]

5. Fluorescence spectra for the MCL of 1•Solvent

λ_{em} = 521 nm
Φ_F = 0.83

λ_{em} = 576 nm
Φ_F = 0.81

λ_{em} = 552 nm
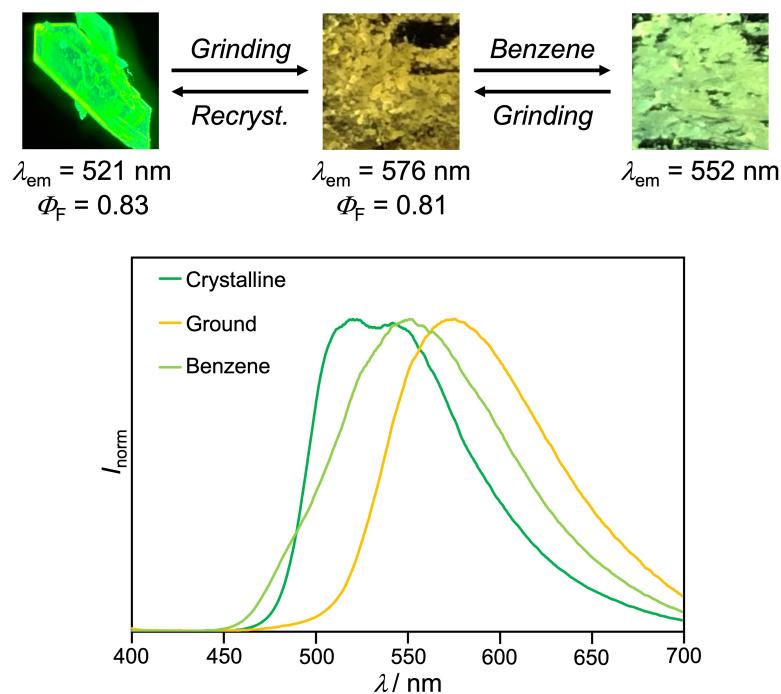
Fig. S9 Photographs and fluorescence spectra for the MCL of **1•Benzene**.

λ_{em} = 508 nm
Φ_F = 0.67

λ_{em} = 569 nm
Φ_F = 0.72

λ_{em} = 509 nm
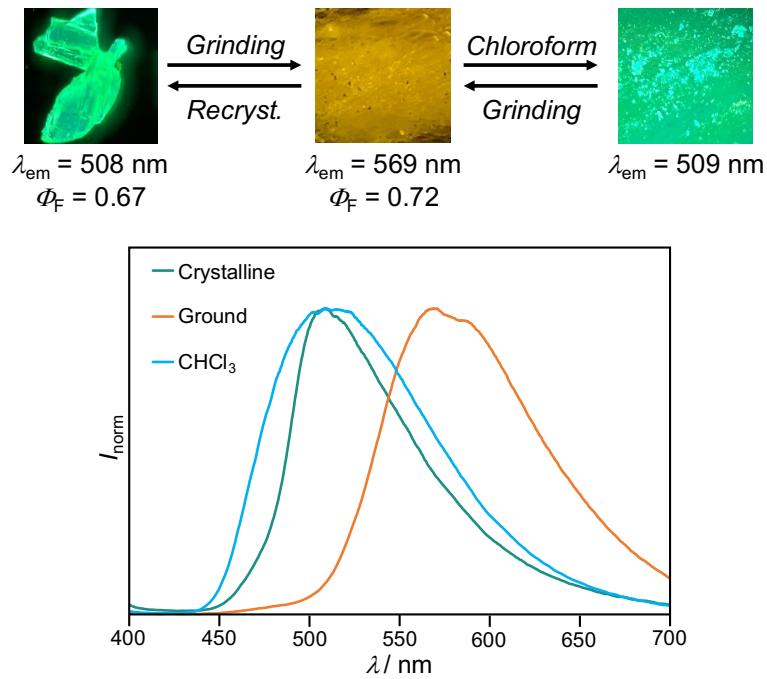
**Fig. S10** Photographs and fluorescence spectra for the MCL of **1•CHCl₃**.
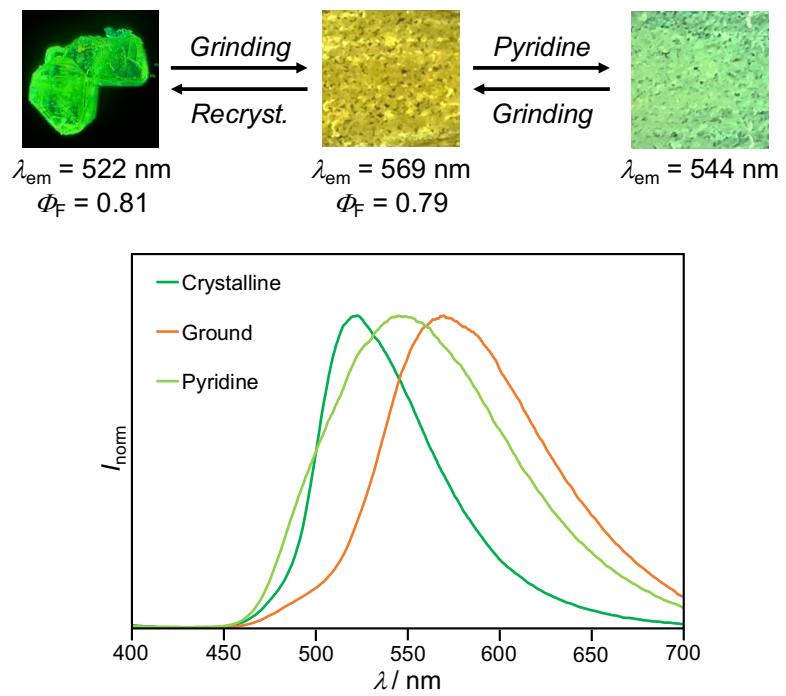
Fig. S11 Photographs and fluorescence spectra for the MCL of **1•Pyridine**.
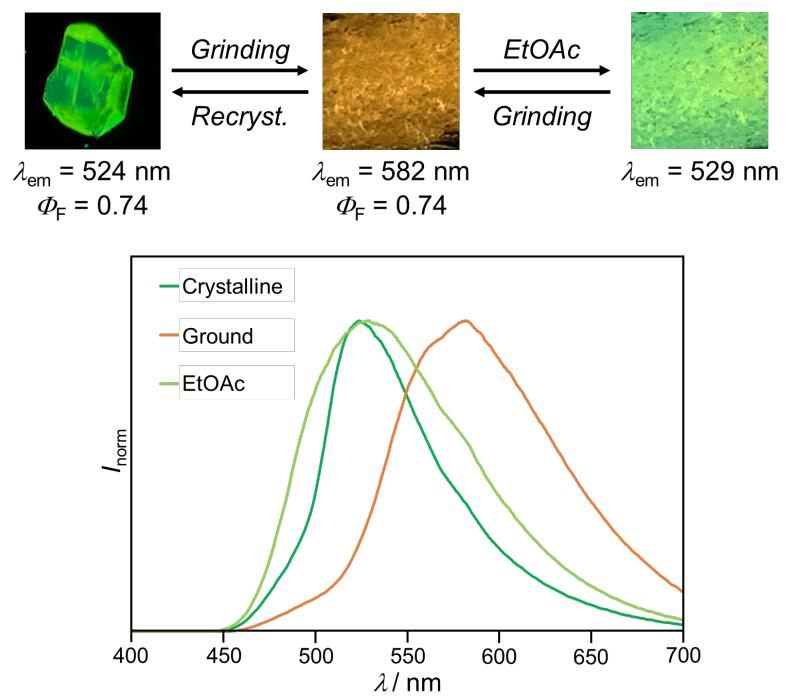

Fig. S12 Photographs and fluorescence spectra for the MCL of **1•EtOAc**.

λ_{em} = 565 nm λ_{em} = 543 nm λ_{em} = 576 nm
Φ_F = 0.76 Φ_F = 0.74
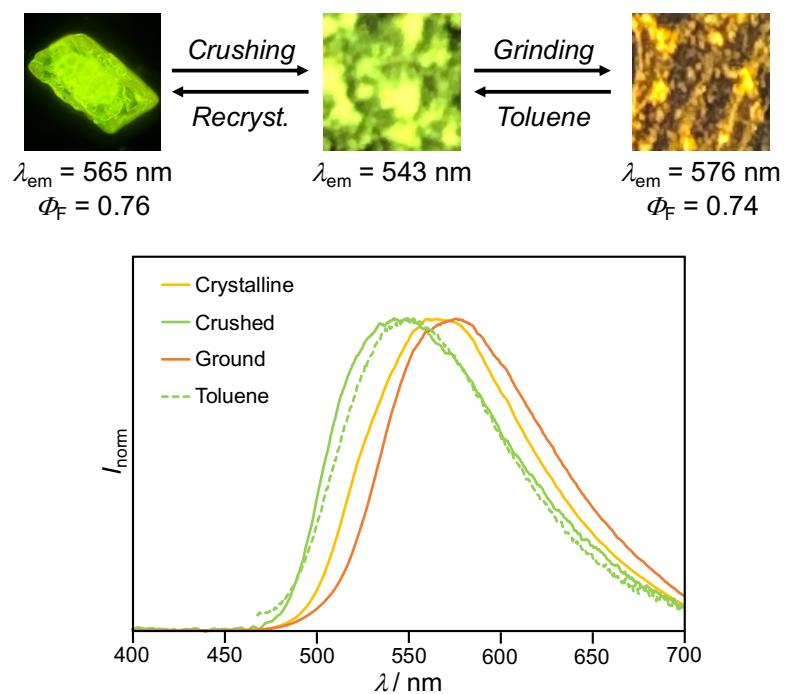
Fig. S13 Photographs and fluorescence spectra for the MCL of **1•Toluene**.

6. Powder X-ray diffraction (PXRD) patterns for the MCL of 1•Solvent
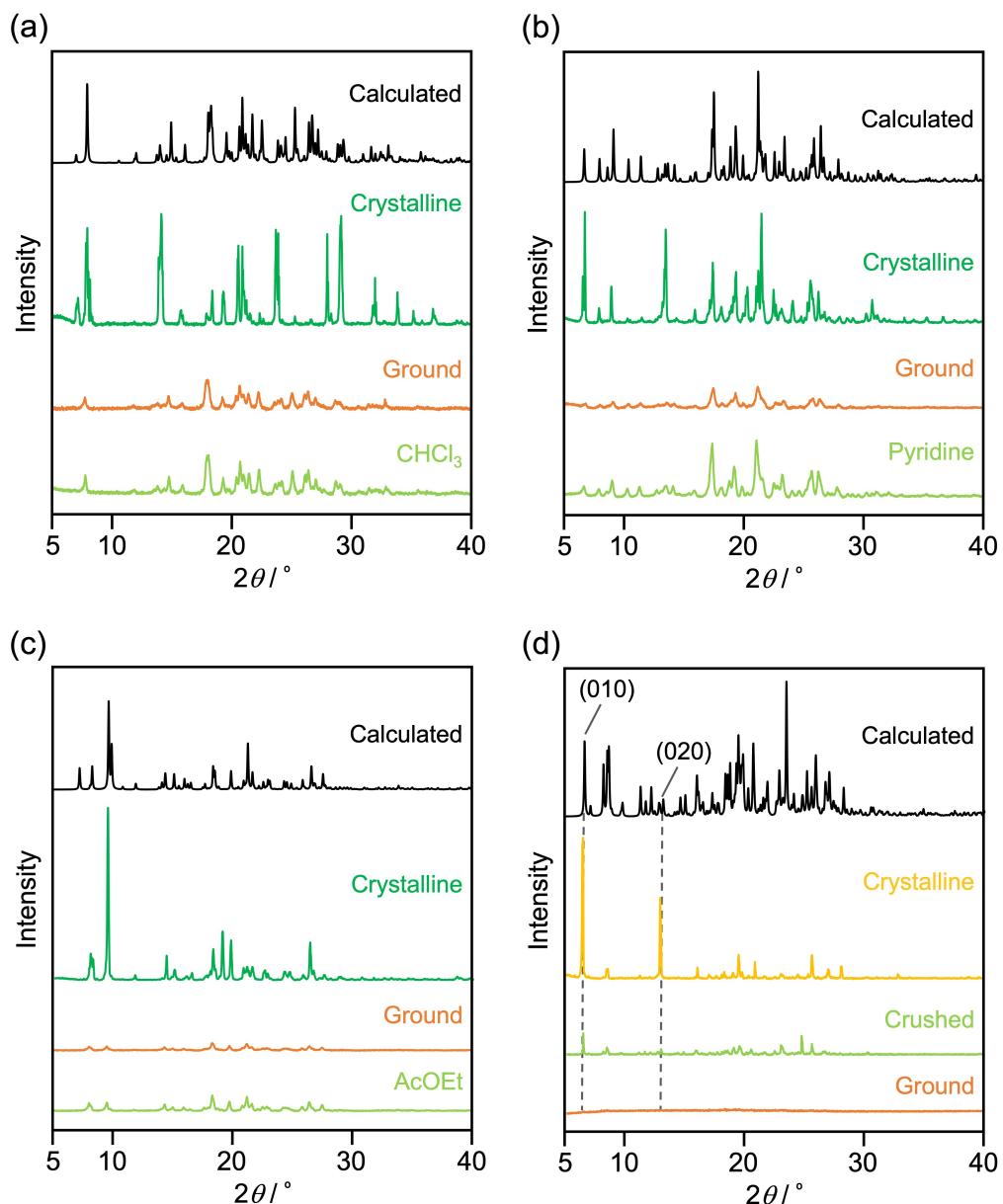

Fig. S14 PXRD patterns for **1•CHCl₃** (a), **1•Pyridine** (b), **1•EtOAc** (c), and **1•Toluene** (d). (a–c) Black lines: Simulated PXRD patterns calculated from the single-crystal structure. Green lines: Experimental PXRD patterns of the powdered crystalline samples. Orange lines: Experimental PXRD patterns of the ground samples. Yellow-green lines: Experimental PXRD patterns of the solvent-exposed samples. (d) Black line: Simulated PXRD patterns calculated from the single-crystal structure. Yellow line: Experimental PXRD patterns of the powdered crystalline sample. Yellow-green line: Experimental PXRD patterns of the crushed sample. Orange line: Experimental PXRD patterns of the ground sample.

7. ¹H NMR spectra of 1•Benzene
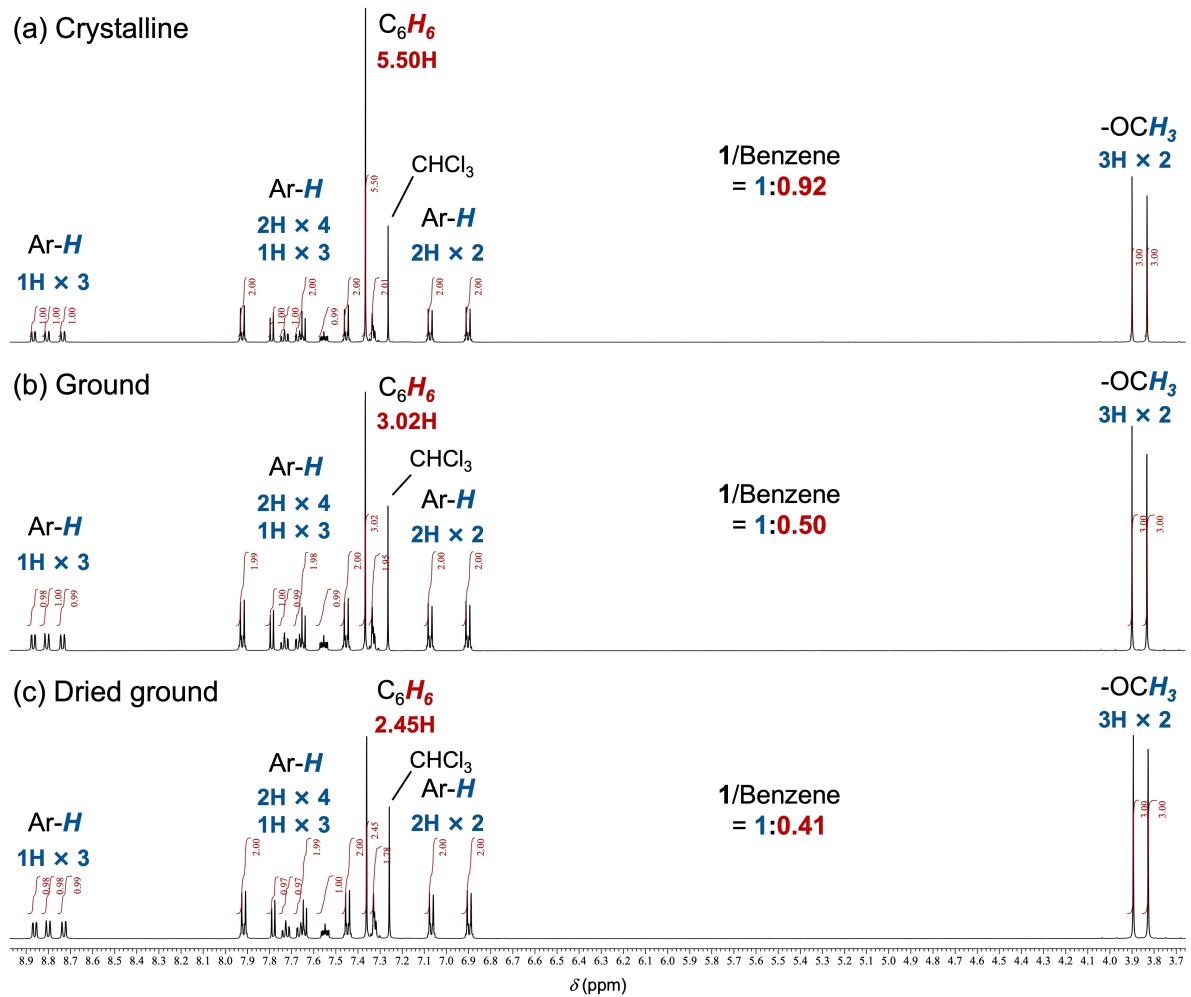
Fig. S15 ¹H NMR spectra (500 MHz, in CDCl$_3$, rt) of (a) crystalline **1•Benzene**, (b) ground **1•Benzene**, and (c) ground **1•Benzene** after drying in vacuo for 6 h.

## 8. Supplemental data for the acid-responsive luminescence of 1•Pyridine
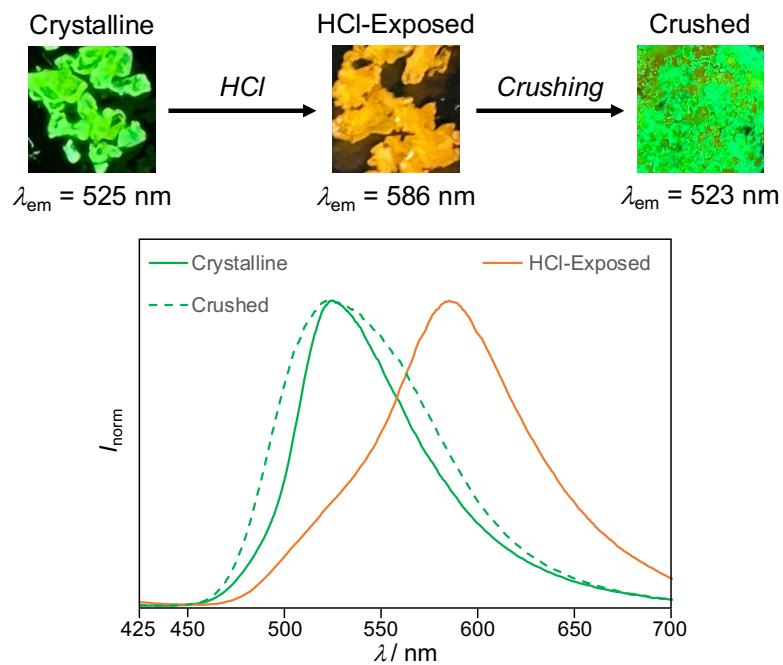
Fig. S16 Photographs and fluorescence spectra for acid-responsive luminescence of **1•Pyridine**.
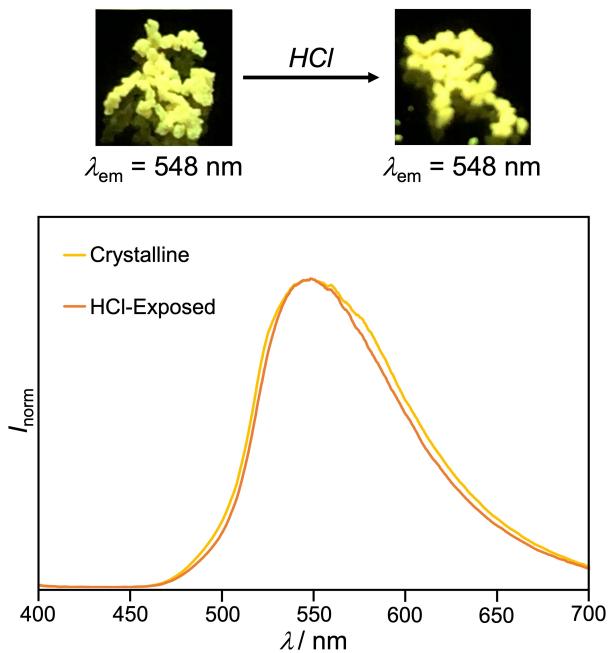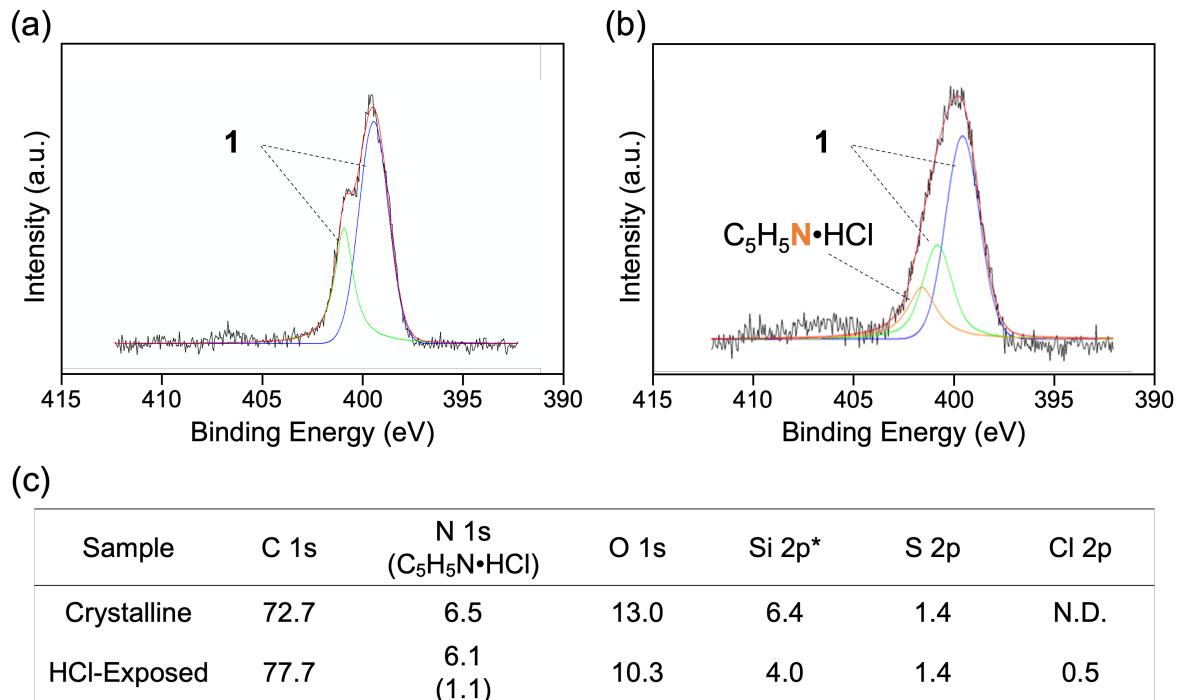

Fig. S17 Photographs and fluorescence spectra for crystalline **1** and acid-exposed **1**.

X-ray photoelectron spectroscopy (XPS) suggested the presence of pyridine hydrochloride on the surface of HCl-exposed **1•Pyridine** (Fig. S18). Surface pyridine molecules should have volatilized from crystalline **1•Pyridine** prior to XPS measurement under high vacuum conditions (Fig. S18a), while a broad N 1s peak that should correspond to protonated pyridine salts was detected for the HCl-exposed sample (Fig. S18b). In addition, Cl 2p was detected for HCl-exposed **1•Pyridine** (Fig. S18c).

| Sample	C 1s	N 1s (C$_5$H$_5$N•HCl)	O 1s	Si 2p*	S 2p	Cl 2p
Crystalline	72.7	6.5	13.0	6.4	1.4	N.D.
HCl-Exposed	77.7	6.1 (1.1)	10.3	4.0	1.4	0.5

*Derived from contamination.

Fig. S18 N 1s XPS spectra of crystalline **1•Pyridine** (a) and HCl-exposed **1•Pyridine** (b). (c) Atomic percentages (%) of the elements calculated from the XPS spectra of crystalline and HCl-exposed **1•Pyridine**.
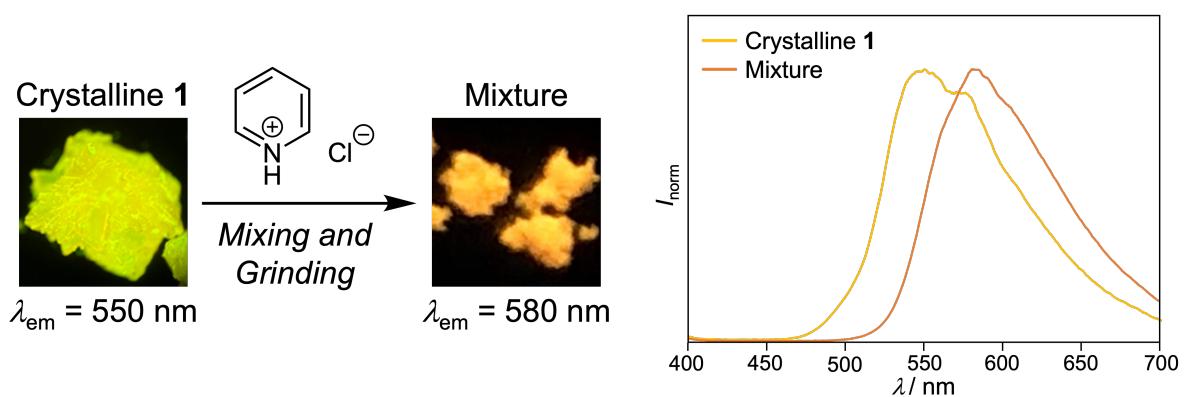
Fig. S19 Photographs and fluorescence spectra for crystalline **1** and mixture of **1** and pyridine hydrochloride.
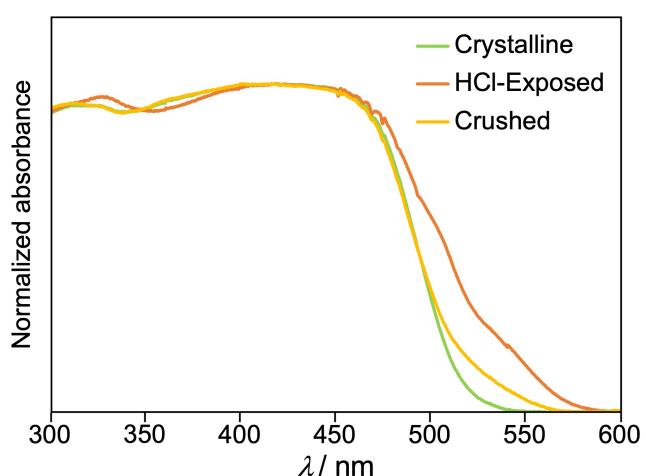
Fig. S20 Solid-state absorption spectra of crystalline, HCl-exposed, and crushed **1·Pyridine**.
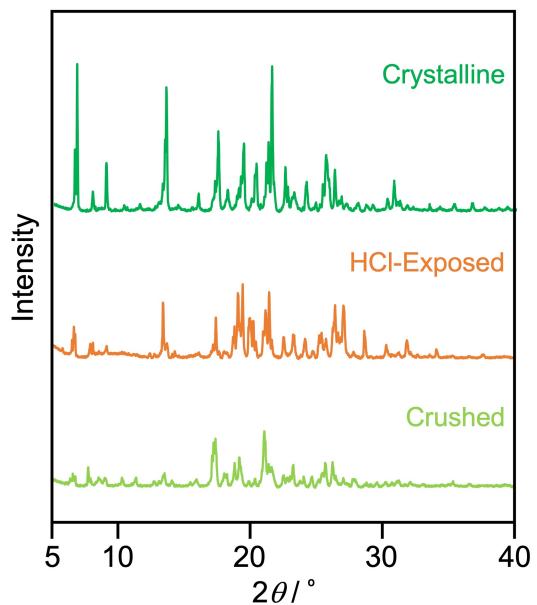
Fig. S21 PXRD patterns of **1·Pyridine**. Green line: Experimental PXRD pattern of the powdered crystalline sample. Orange line: Experimental PXRD pattern of the HCl-exposed sample. Yellow-green line: Experimental PXRD pattern of the crushed samples.
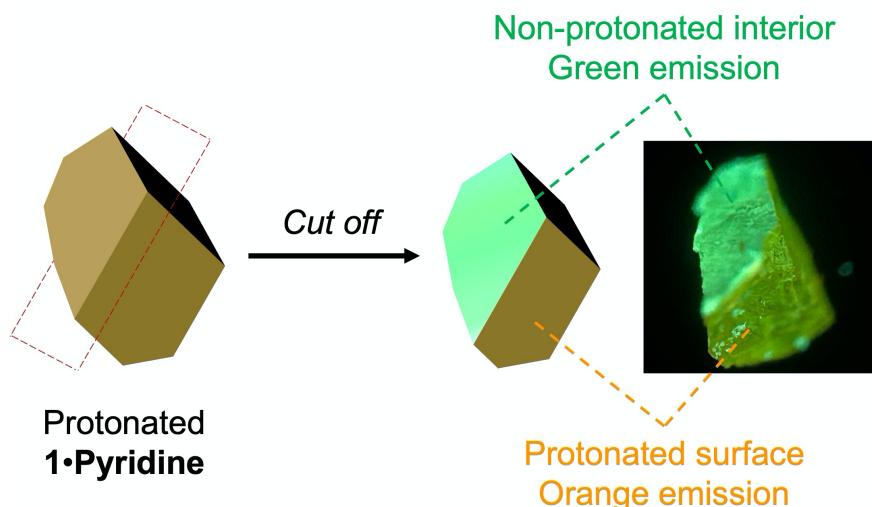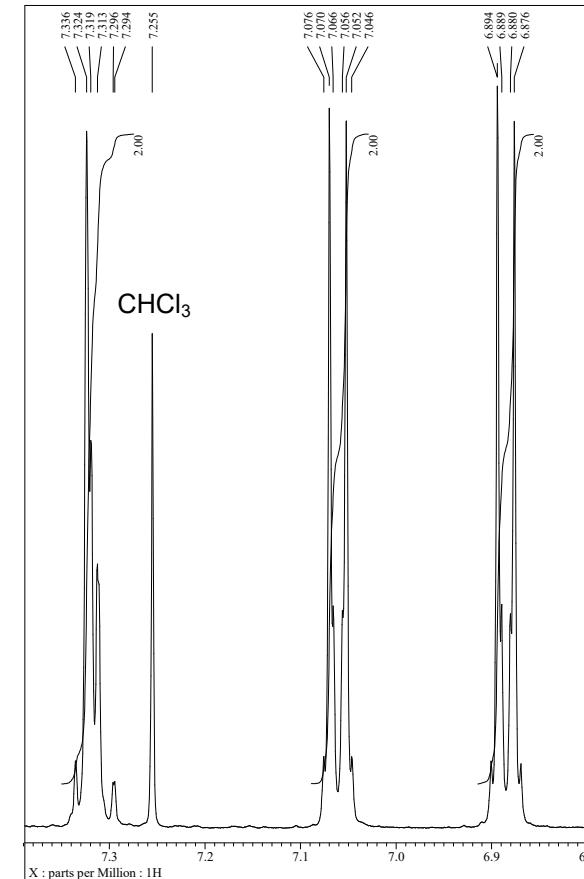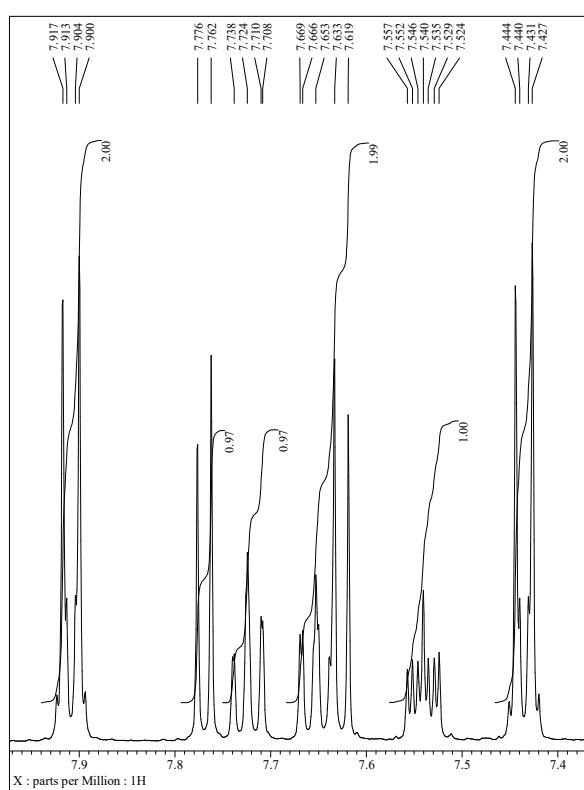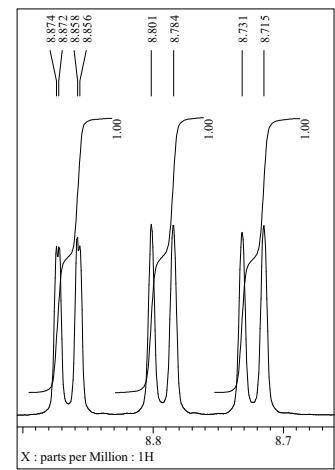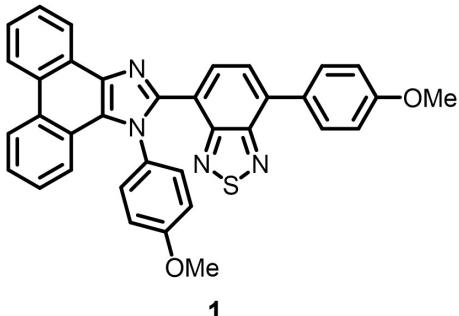

Fig. S22 Schematic diagram and photograph for the cutting process of HCl-exposed **1·Pyridiine**.
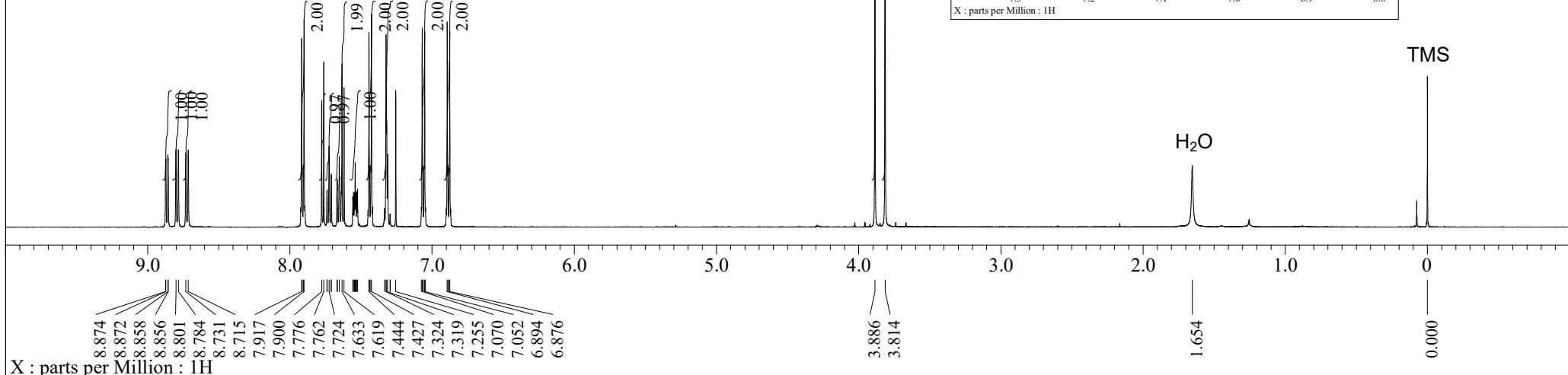
Reference

1) K. Momma and F. Izumi, *J. Appl. Crystallogr.*, 2011, **44**, 1272.
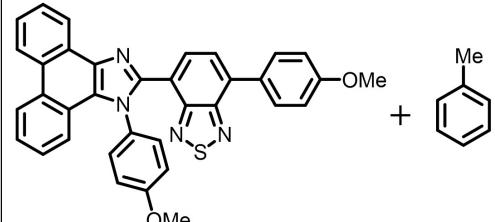
¹H NMR spectrum of 1 (500 MHz, CDCl₃, rt)
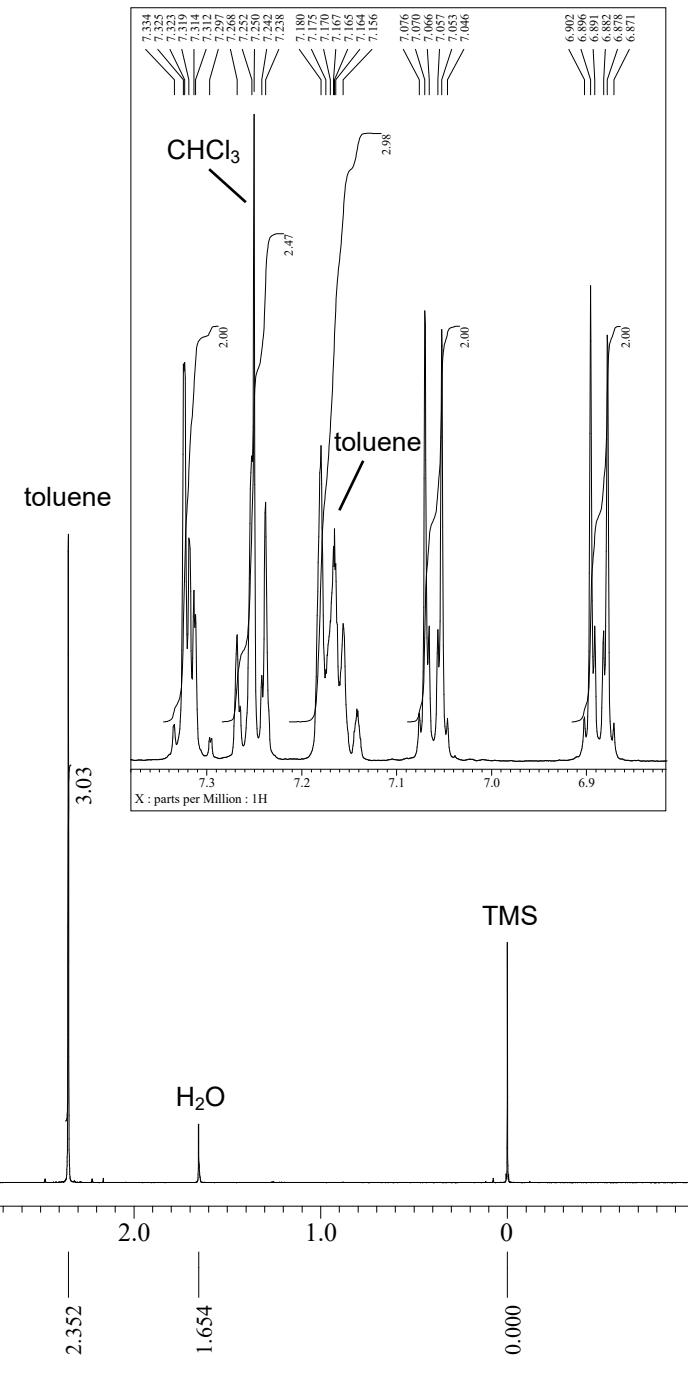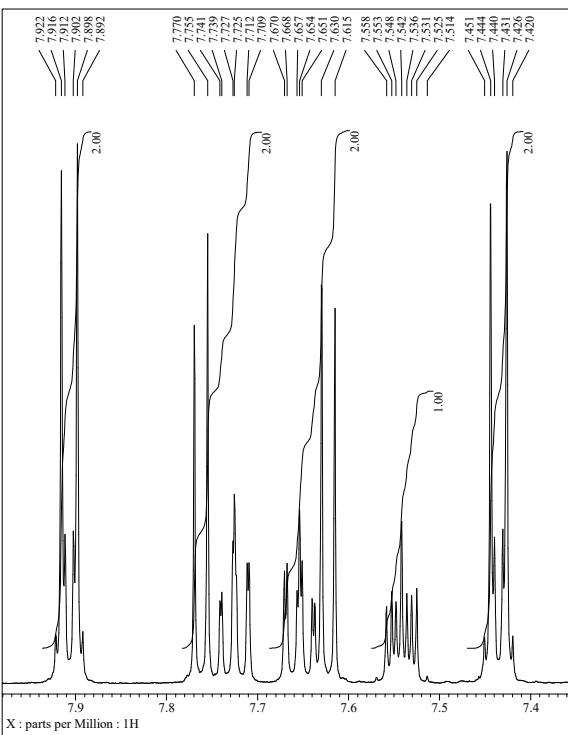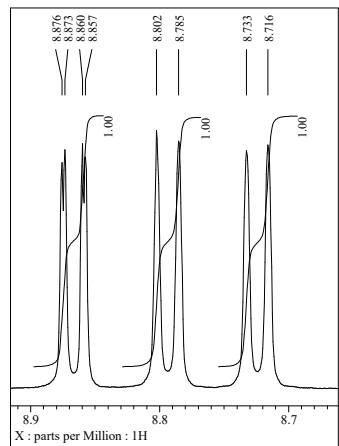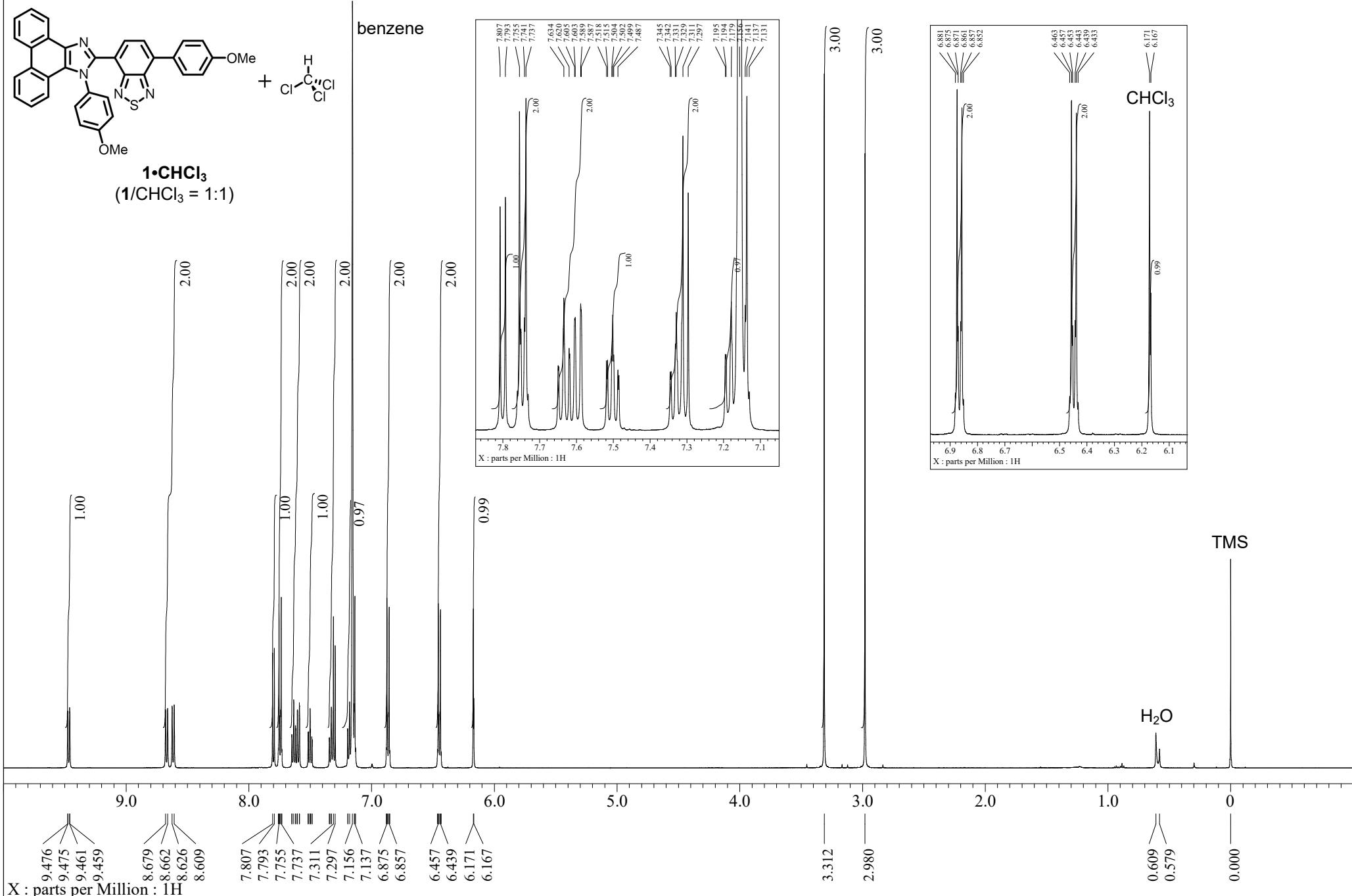
# ¹H NMR spectrum of **1•Toluene** (500 MHz, CDCl$_3$, rt)
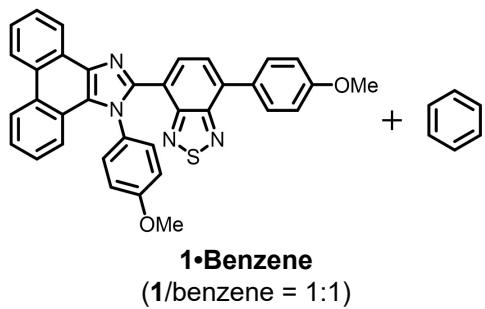
^{1}H NMR spectrum of **1•CHCl$_3$** (500 MHz, C$_6$D$_6$, rt)
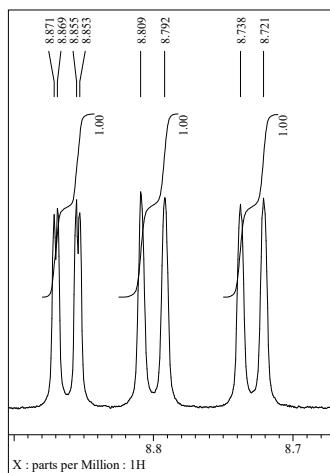
¹H NMR spectrum of **1•Benzene** (500 MHz, CDCl₃, rt)
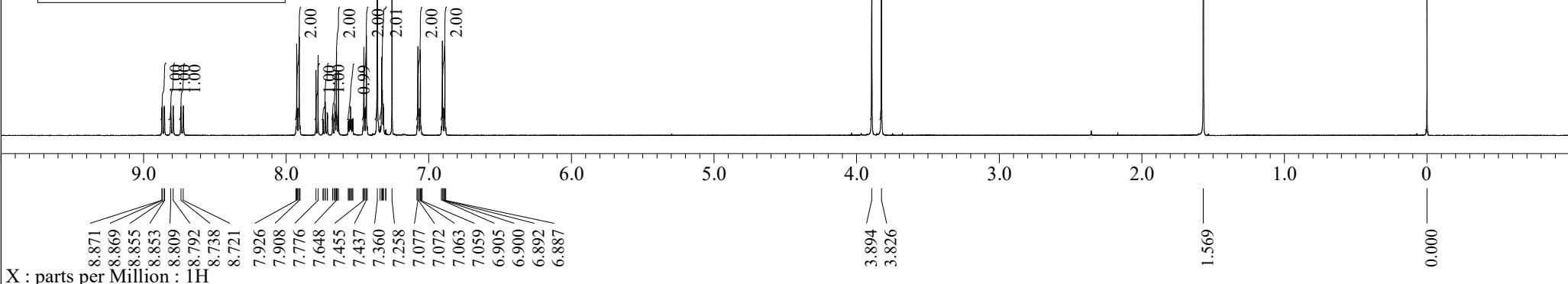
1•Benzene
(**1**/benzene = 1:1)
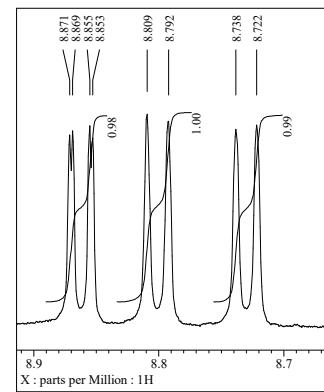
^{1}H NMR spectrum of ground **1•Benzene** (500 MHz, CDCl$_3$, rt)
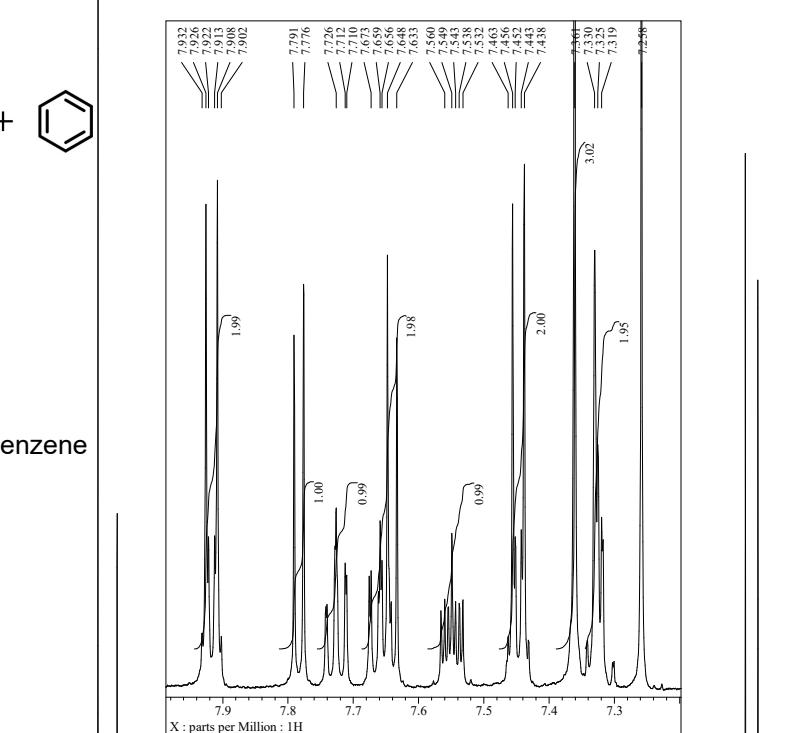
1•Benzene
(1/benzene = 1:0.5)

benzene

CHCl$_3$

H$_2$O

TMS
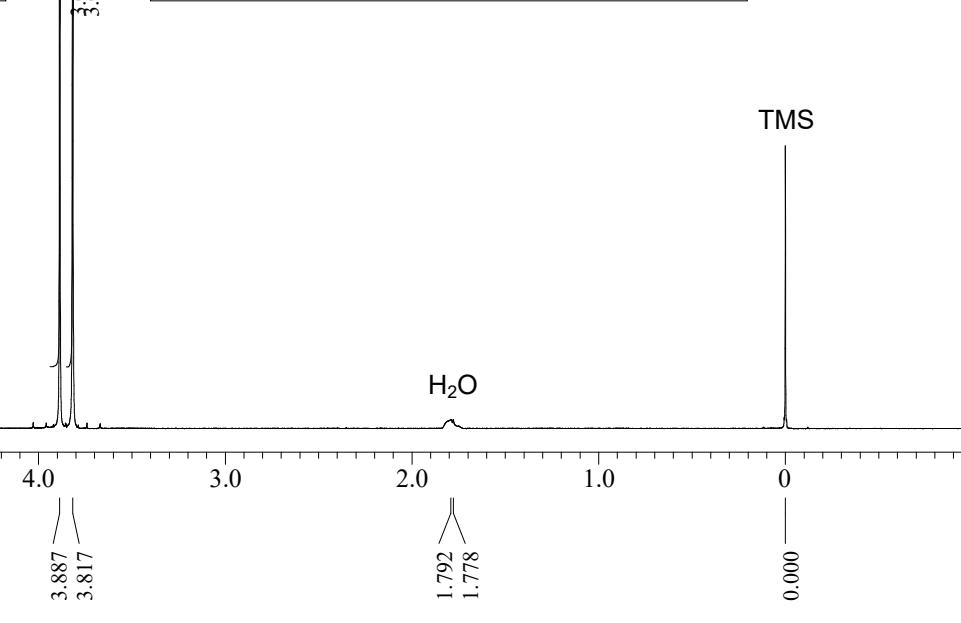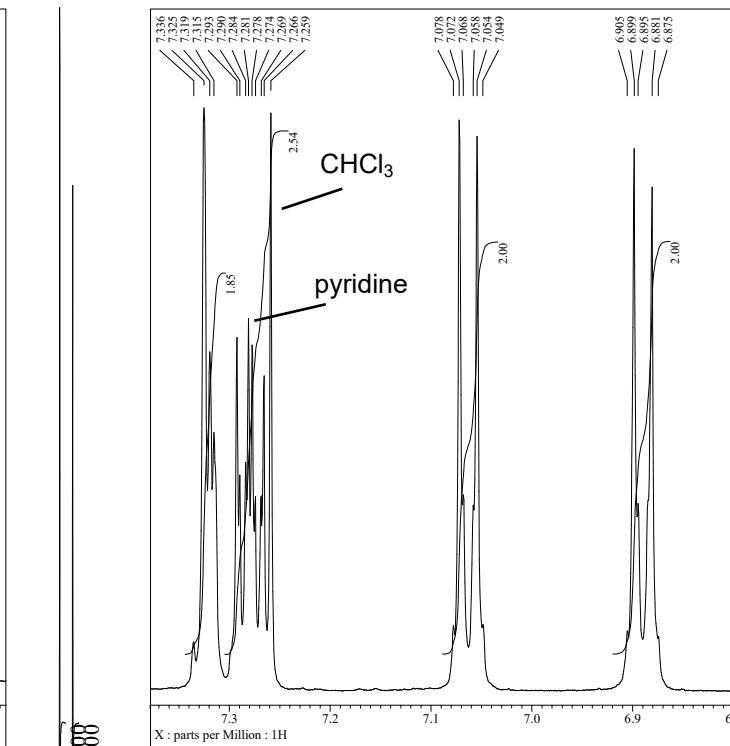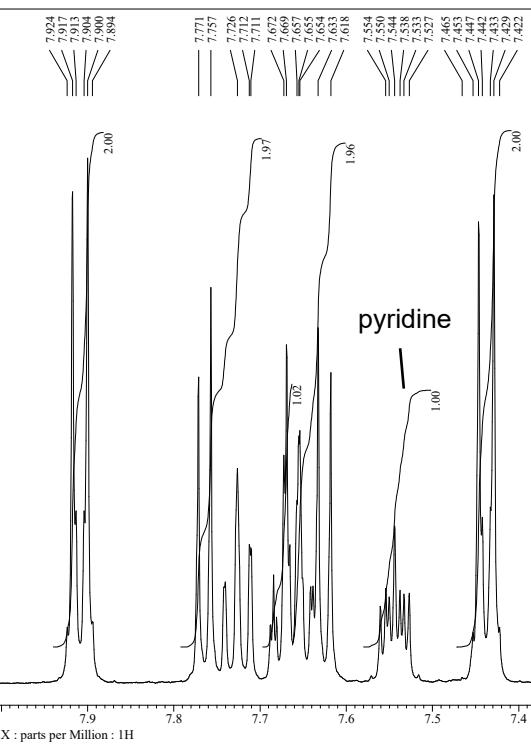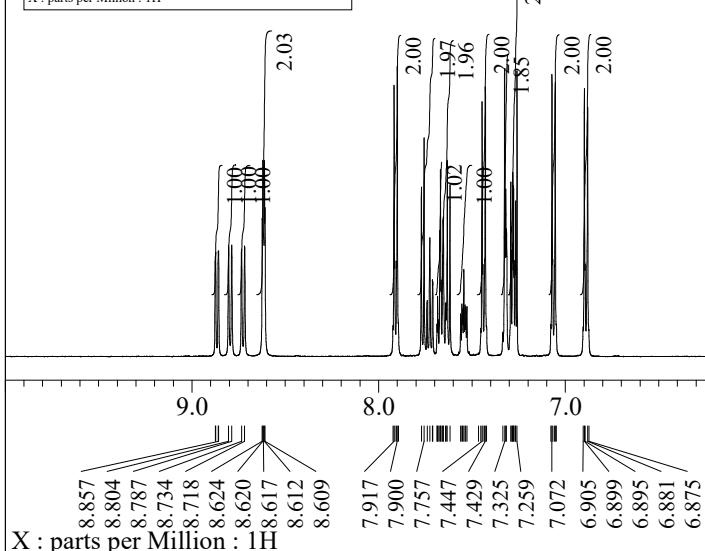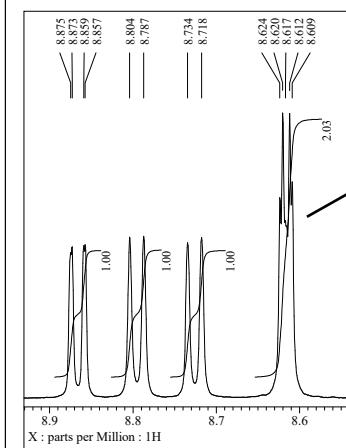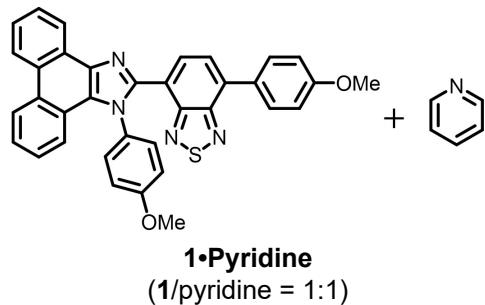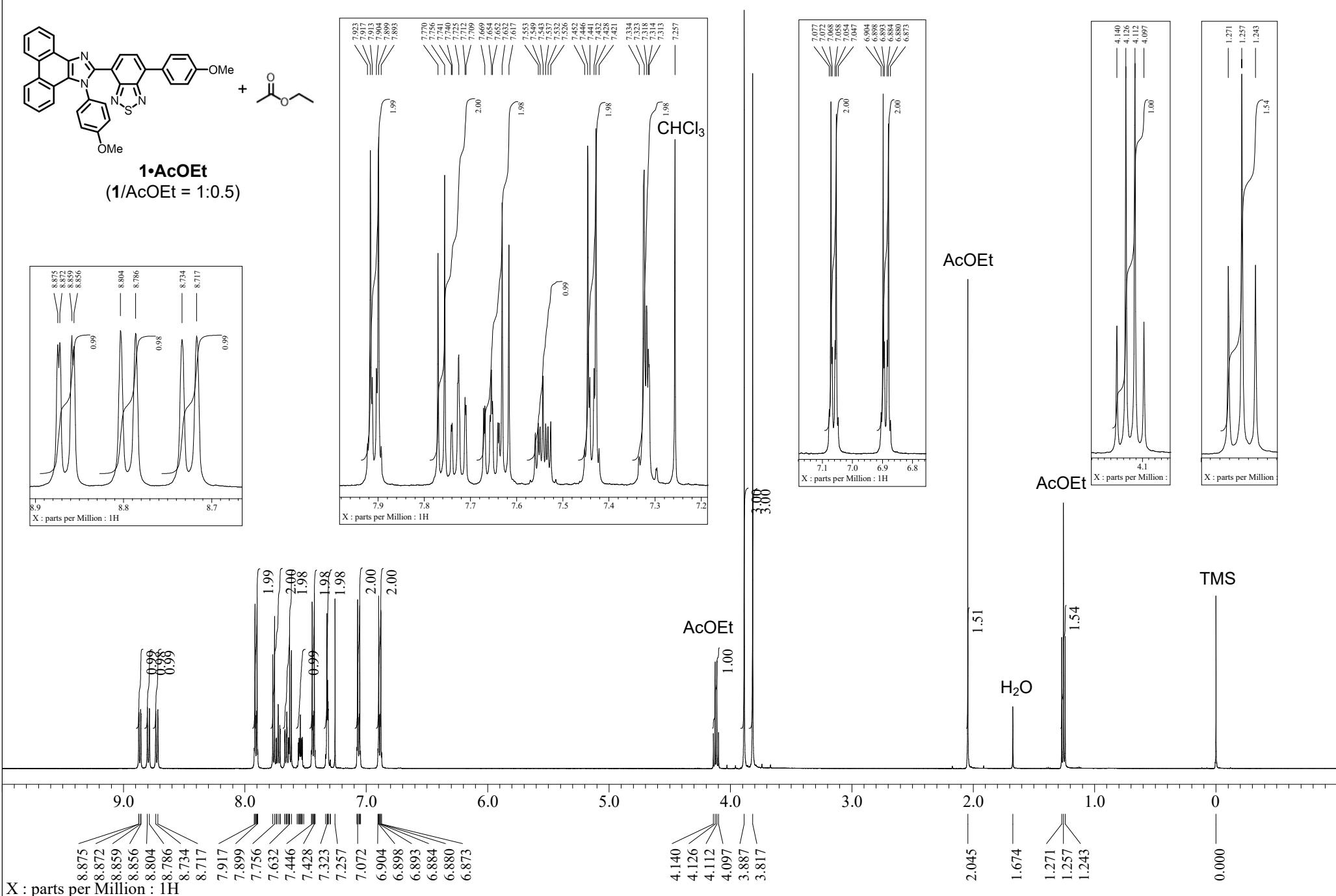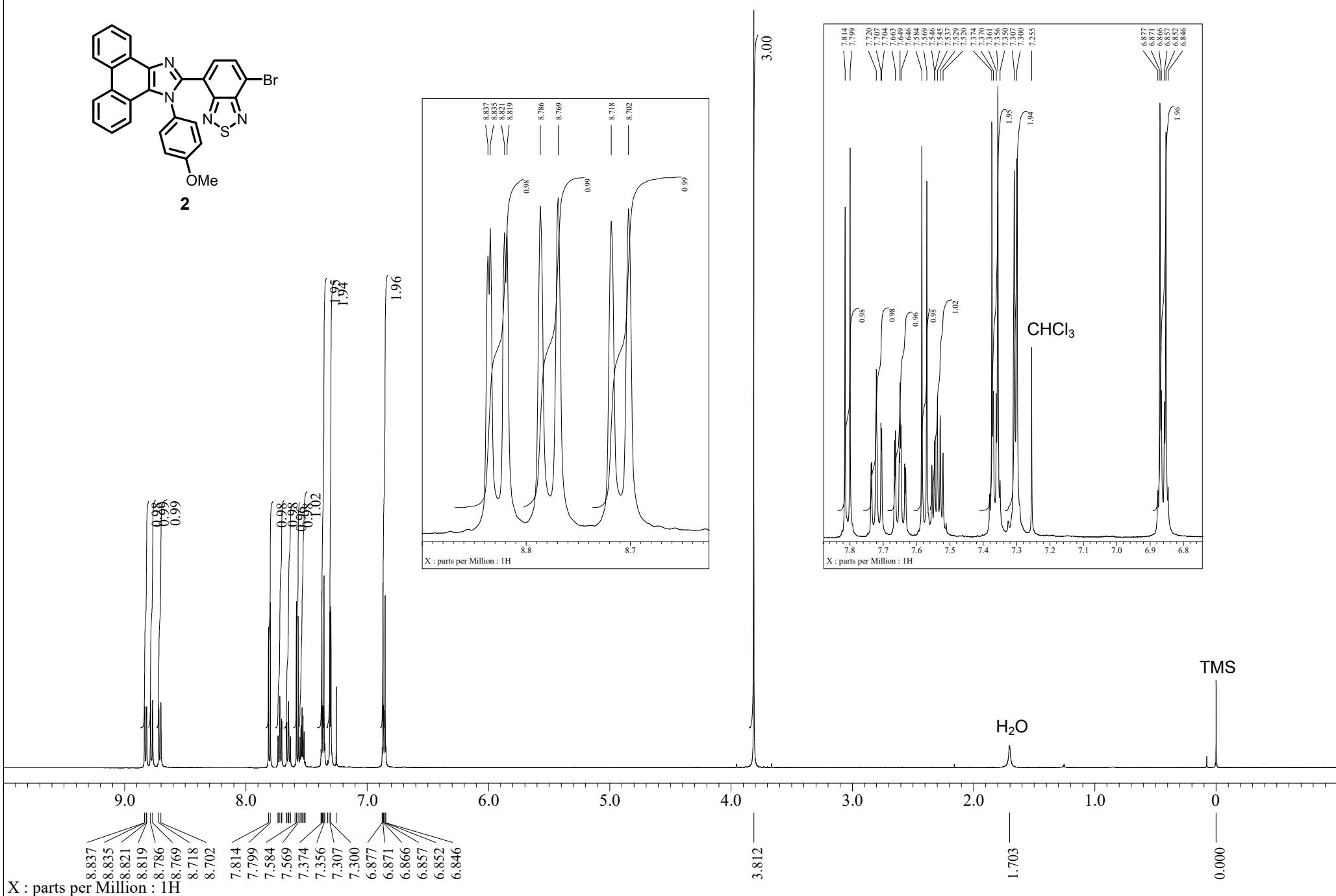
^{1}H NMR spectrum of **1•Pyridine** (500 MHz, CDCl$_3$, rt)
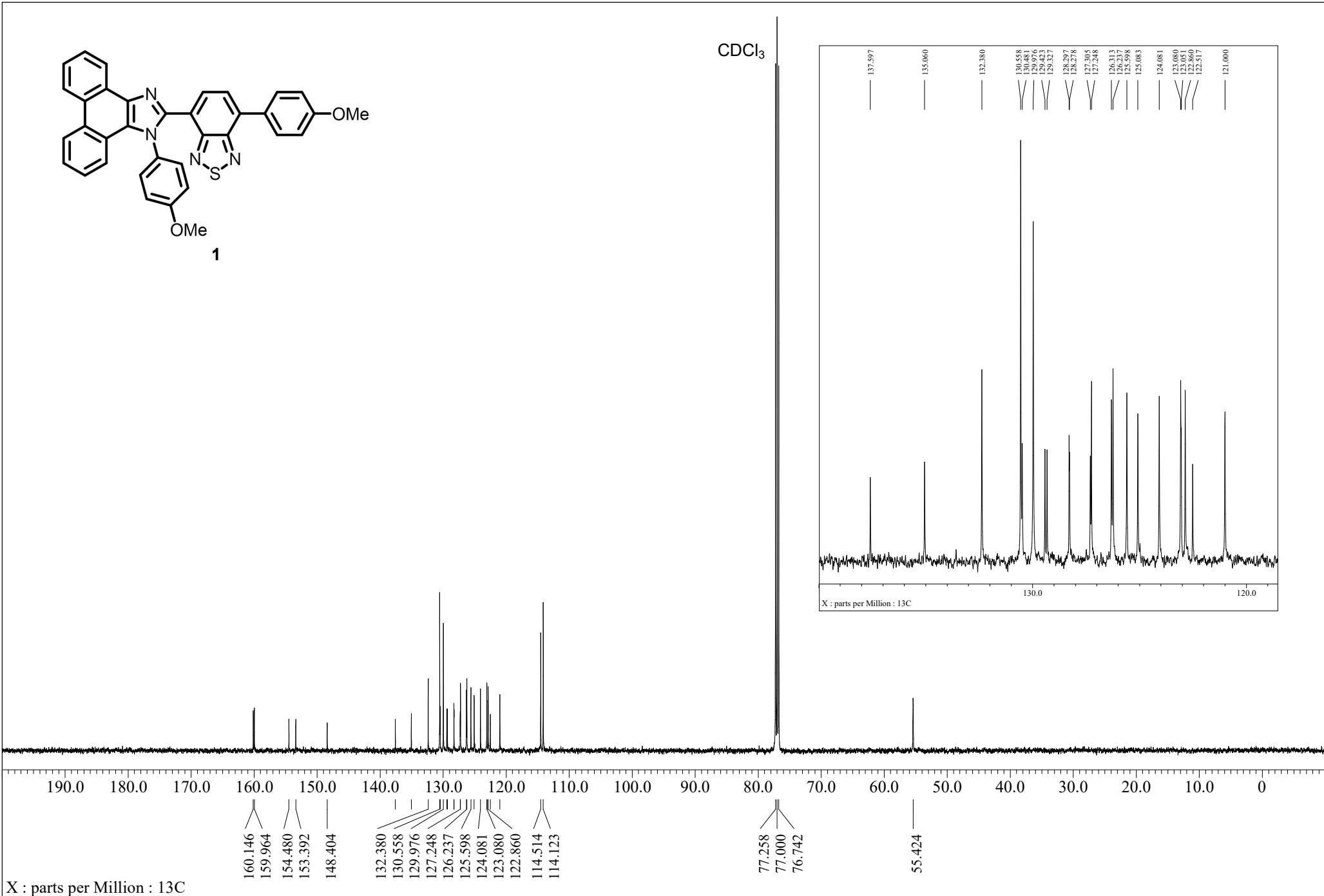
# ^{1}H NMR spectrum of **1•AcOEt** (500 MHz, CDCl$_3$, rt)

**1•AcOEt**

(**1**/AcOEt = 1:0.5)

¹H NMR spectrum of **2** (500 MHz, CDCl₃, rt)

^{13}C NMR spectrum of **1** (126 MHz, CDCl$_3$, rt)

CDCl$_3$

Inset peaks: 137.597, 135.060, 132.380, 130.558, 130.481, 129.976, 129.423, 129.327, 128.297, 128.278, 127.305, 127.248, 126.313, 126.237, 125.598, 125.083, 124.081, 123.080, 123.051, 122.860, 122.517, 121.000

X : parts per Million : 13C

Peak labels: 160.146, 159.964, 154.480, 153.392, 148.404, 132.380, 130.558, 129.976, 127.248, 126.237, 125.598, 124.081, 123.080, 122.860, 114.514, 114.123, 77.258, 77.000, 76.742, 55.424

X : parts per Million : 13C

S25

^{13}C NMR spectrum of **2** (126 MHz, CDCl$_3$, rt)

CDCl$_3$

X : parts per Million : 13C