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# Tunable mechanochromic luminescence of 2-alkyl-4-(pyren-1-yl)thiophenes: controlling the self-recovering properties and the range of chromism

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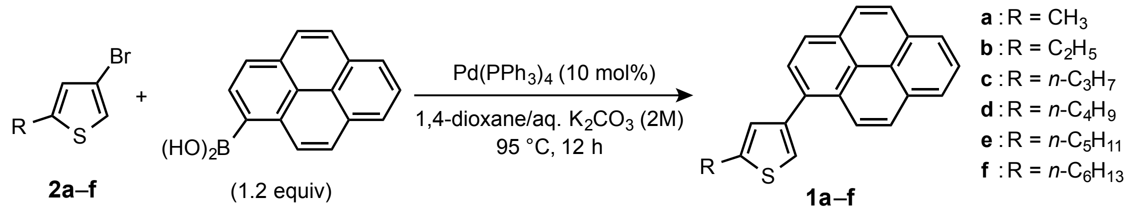
## 1. General

All air-sensitive experiments were carried out under an argon atmosphere unless otherwise noted. IR spectra were recorded on a Nicolet iS10 FT-IR spectrometer. $^{1}$H and $^{13}$C NMR spectra were recorded on a JEOL ECA500 spectrometer using tetramethylsilane as an internal standard. A miniature fiber-optic spectrometer (FLAME-S-XR1-ES, Ocean Optics) and a handy UV lamp (365 nm, LUV-6, AS ONE) were used for the measurements of mechanochromic luminescence. Fluorescence spectra were measured on a JASCO FP-8300 fluorescence spectrometer. The absolute fluorescence quantum yields were determined using a 100 mm $\phi$ integrating sphere JASCO ILF-835. Powder X-ray diffraction (PXRD) measurements were performed on a Rigaku SmartLab system using CuK$\alpha$ radiation. Differential scanning calorimetry (DSC) data were recorded on a Shimadzu DSC-60 plus (heating rate: 10 °C min$^{-1}$). Melting points were determined on a Stuart melting point apparatus SMP3 and uncorrected. High-resolution electrospray ionization (HRMS-ESI) mass spectra were recorded on a Hitachi Nano Frontier LD spectrometer. Elemental analyses were carried out on a Vario EL III Elemental analyzer. Silica gel 60 N (spherical, neutral, 63–210 μm) was used for column chromatography. TLC analyses were done on silicagel 60 F$_{254}$-precoated aluminum backed sheets (E. Merck). 2-Alkyl-4-bromothiophenes (**2a**–**f**) were synthesized according to the literature procedure.[1] Other reagents and solvents were commercially available and were used as received.

The theoretical calculations were performed using the Gaussian 16 program.[2] The six lowest singlet–singlet transitions of **1a**–**f** except **1d** were calculated using time-dependent density functional theory (TD-DFT) calculations at the B3LYP/6-31G(d) level of theory. The molecular structures, obtained from the single-crystal X-ray diffraction analysis, were used as a starting point.

## 2. Synthesis of 2-alkyl-4-(pyren-1-yl)thiophene derivatives



**Scheme S1** Synthesis of 2-alkyl-4-(pyren-1-yl)thiophene derivatives **1a**–**f**

*Typical experimental procedure (**1a**, Scheme S1)*

To a stirred solution of 1-bromopyrene (2.4 mmol, 675 mg) in THF (15.0 mL), a hexane solution of *n*-BuLi (2.6 M, 3.6 mmol, 1.4 mL) was added dropwise through a syringe at –78 ºC. To the mixture was added dropwise triisopropyl borate (4.8 mmol, 1.10 mL) at –78 ºC, and the reaction mixture was gradually warmed to room temperature and stirred at room temperature for 24 h. To the reaction mixture was added 2 M aqueous HCl, and the organic layer was separated. The aqueous layer was extracted with ethyl acetate three times, and the combined organic layer was washed with water and brine, and dried over anhydrous $Na_2SO_4$. After removal of the solvent under reduced pressure, crude pyrene-1-boronic acid was dissolved in 1,4-dioxane (15.0 mL). To the solution were added 4-bromo-2-methylthiophene (**2a**, 2.0 mmol, 354 mg) and 2 M aqueous $K_2CO_3$ (4.0 mL), and the mixture was degassed under ultrasonic irradiation. To the mixture was added $Pd(PPh_3)_4$ (0.20 mmol, 231 mg), and the mixture was further degassed under ultrasonic irradiation. After the mixture was stirred at 95 ºC for 12 h, water and dichloromethane were added to the mixture. The organic layer was separated and the aqueous layer was extracted with dichloromethane three times. The combined organic layer was washed with water and brine, and dried over anhydrous $Na_2SO_4$. After removal of the solvent under reduced pressure, crude product was purified with silica-gel column chromatography twice (hexane/toluene = 10:1 then hexane) to give 2-methyl-4-(pyren-1-yl)thiophene (**1a**, 311 mg, 52%) as white solid.

### 2-Methyl-4-(pyren-1-yl)thiophene (1a)

Crystalline powder of **1a** was obtained by recrystallization from AcOEt/$CH_3CN$ = 2:1; White solid; M.p. 88–90 ºC; IR (KBr): $\nu_{max}$ 3088, 3042, 2944, 2914, 1654, 1602, 1508, 1458, 1199, 1148, 968, 840, 757, 722 $cm^{-1}$; $^1H$ NMR (500 MHz, $CDCl_3$): $\delta$ (ppm) 8.34 (d, $J$ = 9.2 Hz, 1H), 8.14–8.12 (m, 3H), 8.03–7.96 (m, 5H), 7.23 (s, 1H), 7.08 (s, 1H), 2.61 (s, 3H); $^{13}C$ NMR (126 MHz, $CDCl_3$): $\delta$ (ppm) 141.4, 139.8, 132.8, 131.4, 131.0, 130.5, 128.6, 128.3, 127.40, 127.36 (2C), 127.3, 125.9, 125.3, 125.03, 124.95, 124.85, 124.76, 124.6, 121.7, 15.4; Anal. Calcd for $C_{21}H_{14}S$: C, 84.53; H, 4.73; S, 10.74. Found: C, 84.54; H, 4.61; S, 10.41. Crystal data for **1a** (CCDC 1947301): $C_{21}H_{14}S$, $M$ = 298.40, triclinic, $a$ = 7.6239(3) Å, $b$ = 7.7590(2) Å, $c$ = 25.3429(9) Å, $\alpha$ =93.231(3)°, $\beta$ = 93.462(3)°, $\gamma$ = 91.842(3)°, $V$ = 1493.06(9) Å$^3$, space group $P1$ (no. 1), $Z$ = 4, $D_c$ = 1.327 g cm$^{-3}$, $F$(000) = 624.00, $T$ = 223(1) K, $\mu$(Cu-K$\alpha$) = 18.391 cm$^{-1}$, 15874 reflections measured, 7028 independent ($R_{\mathrm{int}}$ = 0.0531). The final refinement converged to $R_1$ = 0.1215 for $I > 2.0\sigma(I)$, w$R_2$ = 0.3754 for all data.

### 2-Ethyl-4-(pyren-1-yl)thiophene (1b)

Crystalline powder of **1b** was obtained by recrystallizations from AcOEt/$CH_3CN$ = 2:1; White solid; M.p. 91–92 ºC; IR (KBr): $\nu_{\max}$ 3086, 3047, 2969, 2932, 1601, 1507, 1457, 1193, 843, 757, 723 cm$^{-1}$; $^1$H NMR (500 MHz, $CDCl_3$): $\delta$ (ppm) 8.35 (d, $J$ = 9.2 Hz, 1H), 8.15–8.12 (m, 3H), 8.03–7.95 (m, 5H), 7.26 (s, 1H), 7.11 (s, 1H), 2.96 (q, $J$ = 7.5 Hz, 2H), 1.41 (t, $J$ = 7.5 Hz, 3H); $^{13}$C NMR (126 MHz, $CDCl_3$): $\delta$ (ppm) 147.5, 141.2, 132.9, 131.5, 131.0, 130.5, 128.6, 127.40 (2C), 127.37, 127.3, 126.4, 125.9, 125.3, 125.03, 124.97, 124.9, 124.7, 124.6, 121.3, 23.5, 16.0; HRMS-ESI (m/z): [M + H]$^+$ calcd for $C_{22}H_{17}S$, 313.1046; found, 313.1047. Crystal data for **1b** (CCDC 1947302): $C_{44}H_{32}S_2$, $M$ = 624.86, monoclinic, $a$ = 8.32033(14) Å, $b$ = 7.16490(12) Å, $c$ = 53.8962(7) Å, $\beta$ = 93.3805(13)°, $V$ = 3207.40(9) Å$^3$, space group $P2_1/c$ (no. 14), $Z$ = 4, $D_c$ = 1.294 g cm$^{-3}$, $F$(000) = 1312.00, $T$ = 223(1) K, $\mu$(Cu-K$\alpha$) = 17.350 cm$^{-1}$, 16899 reflections measured, 5854 independent ($R_{\mathrm{int}}$ = 0.0296). The final refinement converged to $R_1$ = 0.0811 for $I > 2.0\sigma(I)$, w$R_2$ = 0.2095 for all data.

### 2-Propyl-4-(pyren-1-yl)thiophene (1c)

Crystalline powder of **1c** was obtained by recrystallizations from $CH_3CN$; White solid; M.p. 67–69 ºC; IR (KBr): $\nu_{\max}$ 3081, 3039, 2957, 2927, 2870, 1601, 1508, 1460, 1191, 847, 759, 722 cm$^{-1}$; $^1$H NMR (500 MHz, $CDCl_3$): $\delta$ (ppm) 8.37 (d, $J$ = 9.2 Hz, 1H), 8.19–8.16 (m, 3H), 8.07–8.00 (m, 5H), 7.29 (s, 1H), 7.13 (s, 1H), 2.93 (t, $J$ = 7.7 Hz, 2H), 1.85–1.81 (m, 2H), 1.08 (t, $J$ = 7.5 Hz, 3H); $^{13}$C NMR (126 MHz, $CDCl_3$): $\delta$ (ppm) 145.7, 141.1, 132.9, 131.5, 131.0, 130.4, 128.6, 127.4 (3C), 127.3, 127.2, 125.9, 125.3, 125.02, 124.98, 124.9, 124.7, 124.6, 121.4, 32.2, 25.0, 13.8; Anal. Calcd for $C_{23}H_{18}S$: C, 84.62; H, 5.56; S, 9.82. Found: C, 84.74; H, 5.51; S, 9.71. Crystal data for **1c** (CCDC 1947303): $C_{23}H_{18}S$, $M$ = 326.46, orthorhombic, $a$ = 7.65747(11) Å, $b$ = 14.0292(2) Å, $c$ = 15.4998(2) Å, $V$ = 1665.12(4) Å$^3$, space group $P2_12_12_1$ (no. 19), $Z$ = 4, $D_c$ = 1.302 g cm$^{-3}$, $F$(000) = 688.00, $T$ = 223(1) K, $\mu$(Cu-K$\alpha$) = 16.929 cm$^{-1}$, 7128 reflections measured, 2959 independent ($R_{\mathrm{int}}$ = 0.0302). The final refinement converged to $R_1$ = 0.0351 for $I > 2.0\sigma(I)$, w$R_2$ = 0.0926 for all data.

### 2-Butyl-4-(pyren-1-yl)thiophene (1d)

Crystalline powder of **1d** was obtained by recrystallizations from MeOH; White solid; M.p. 34–36 ºC;

IR (KBr): $\nu_{max}$ 3039, 2956, 2930, 2871, 2858, 1508, 1464, 1190, 841, 755, 720 cm$^{-1}$; $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ (ppm) 8.37 (d, $J$ = 9.2 Hz, 1H), 8.18–8.15 (m, 3H), 8.06–7.98 (m, 5H), 7.28 (s, 1H), 7.12 (s, 1H), 2.94 (t, $J$ = 7.7 Hz, 2H), 1.81–1.75 (m, 2H), 1.51–1.47 (m, 2H), 1.00 (t, $J$ = 7.5 Hz, 3H); $^{13}$C NMR (126 MHz, CDCl$_3$): $\delta$ (ppm) 146.0, 141.1, 132.9, 131.5, 131.0, 130.5, 128.6, 127.4 (3C), 127.3, 127.1, 126.0, 125.3, 125.04, 124.99, 124.9, 124.8, 124.6, 121.4, 33.9, 29.9, 22.3, 13.9; HRMS-ESI (m/z): [M + H]$^+$ calcd for $C_{24}H_{21}S$, 341.1359; found, 341.1329.

**2-Pentyl-4-(pyren-1-yl)thiophene (1e)**

Crystalline powder of **1e** was obtained by recrystallizations from AcOEt/CH$_3$CN = 2:1; White solid; M.p. 53–55 ºC; IR (KBr): $\nu_{max}$ 3098, 3036, 2945, 2928, 2864, 1601, 1509, 1467, 1203, 1187, 1147, 838, 794, 752, 717 cm$^{-1}$; $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ (ppm) 8.36 (d, $J$ = 9.2 Hz, 1H), 8.15–8.12 (m, 3H), 8.04–7.96 (m, 5H), 7.26 (s, 1H), 7.11 (s, 1H), 2.92 (t, $J$ = 7.6 Hz, 2H), 1.81–1.75 (m, 2H), 1.45–1.38 (m, 4H), 0.94 (t, $J$ = 6.7 Hz, 3H); $^{13}$C NMR (126 MHz, CDCl$_3$): $\delta$ (ppm) 146.0, 141.1, 132.9, 131.5, 131.0, 130.4, 128.6, 127.4 (3C), 127.3, 127.1, 125.9, 125.3, 125.01, 124.98, 124.9, 124.7, 124.6, 121.4, 31.43, 31.40, 30.2, 22.5, 14.1; HRMS-ESI (m/z): [M + H]$^+$ calcd for $C_{25}H_{23}S$, 355.1515; found, 355.1507. Crystal data for **1e** (CCDC 1947304): $C_{25}H_{22}S$, $M$ = 354.51, triclinic, $a$ = 8.77664(13) Å, $b$ = 9.33669(16) Å, $c$ = 12.0593(2) Å, $\alpha$ = 93.6123(14)°, $\beta$ = 106.3533(14)°, $\gamma$ = 99.6734(13)°, $V$ = 928.36(3) Å$^3$, space group $P$-1 (no. 2), $Z$ = 2, $D_c$ = 1.268 g cm$^{-3}$, $F$(000) = 376.00, $T$ = 223(1) K, $\mu$(Cu-K$\alpha$) = 15.575 cm$^{-1}$, 9050 reflections measured, 3389 independent ($R_{int}$ = 0.0295). The final refinement converged to $R_1$ = 0.0339 for $I > 2.0\sigma(I)$, w$R_2$ = 0.0968 for all data.

**2-Hexyl-4-(pyren-1-yl)thiophene (1f)**

Crystalline powder of **1f** was obtained by recrystallizations from CH$_3$CN; White solid; M.p. 55–57 ºC; IR (KBr): $\nu_{max}$ 3100, 3038, 2946, 2917, 2853, 1602, 1583, 1509, 1471, 1186, 1148, 843, 770, 720 cm$^{-1}$; $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ (ppm) 8.36 (d, $J$ = 9.2 Hz, 1H), 8.17–8.14 (m, 3H), 8.05–7.97 (m, 5H), 7.27 (s, 1H), 7.11 (s, 1H), 2.92 (t, $J$ = 7.7 Hz, 2H), 1.81–1.75 (m, 2H), 1.47–1.42 (m, 2H), 1.37–1.34 (m, 4H), 0.91 (t, $J$ = 6.9 Hz, 3H); $^{13}$C NMR (126 MHz, CDCl$_3$): $\delta$ (ppm) 146.0, 141.1, 132.9, 131.5, 131.0, 130.4, 128.6, 127.4 (3C), 127.3, 127.1, 126.0, 125.3, 125.02, 124.98, 124.9, 124.8, 124.6, 121.4, 31.7, 31.6, 30.2, 28.9, 22.6, 14.1; HRMS-ESI (m/z): [M + H]$^+$ calcd for $C_{26}H_{25}S$, 369.1672; found, 369.1648. Crystal data for **1f** (CCDC 1947305): $C_{26}H_{24}S$, $M$ = 368.54, monoclinic, $a$ = 8.71844(12) Å, $b$ = 10.13255(17) Å, $c$ = 22.2883(3) Å, $\beta$ = 91.7546(13)°, $V$ = 1968.03(5) Å$^3$, space group $P2_1/c$ (no. 14), $Z$ = 4, $D_c$ = 1.244 g cm$^{-3}$, $F$(000) = 784.00, $T$ = 223(1) K, $\mu$(Cu-K$\alpha$) = 14.880 cm$^{-1}$, 13816 reflections measured, 3608 independent ($R_{int}$ = 0.0447). The final refinement converged to $R_1$ = 0.0388 for $I > 2.0\sigma(I)$, w$R_2$ = 0.1087 for all data.

## 3. Single-crystal X-ray diffraction analyses

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

A single crystal of **1a** was obtained from natural evaporation of a methanol solution of **1a** at 5 °C and was mounted on a glass fiber. All measurements were made on a Rigaku XtaLAB P200 diffractometer using multi-layer mirror monochromated Cu-K$\alpha$ radiation ($\lambda$ = 1.54184 Å). The data were collected at a temperature of –50 ± 1 °C to a maximum 2$\theta$ value of 149.8°. A total of 3004 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 15874 reflections that were collected, 7028 were unique ($R_{\mathrm{int}}$ = 0.0531); equivalent reflections were merged. Data were collected and processed using CrysAlisPro (Rigaku Oxford Diffraction).[3] The linear absorption coefficient, $\mu$, for Cu-K$\alpha$ radiation is 18.391 cm$^{-1}$. An empirical absorption correction was applied which resulted in transmission factors ranging from 0.227 to 0.593. The data were corrected for Lorentz and polarization effects.

The structure was solved by direct methods (SIR2011)[4] 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[5] crystallographic software package except for refinement, which was performed using SHELXL Version 2014/7.[6]

Crystal data for **1a** (CCDC 1947301): $C_{21}H_{14}S$, $M$ = 298.40, triclinic, $a$ = 7.6239(3) Å, $b$ = 7.7590(2) Å, $c$ = 25.3429(9) Å, $\alpha$ =93.231(3)°, $\beta$ = 93.462(3)°, $\gamma$ = 91.842(3)°, $V$ = 1493.06(9) Å$^3$, space group $P$1 (no. 1), $Z$ = 4, $D_c$ = 1.327 g cm$^{-3}$, $F$(000) = 624.00, $T$ = 223(1) K, $\mu$(Cu-K$\alpha$) = 18.391 cm$^{-1}$, 15874 reflections measured, 7028 independent ($R_{\mathrm{int}}$ = 0.0531). The final refinement converged to $R_1$ = 0.1215 for $I > 2.0\sigma(I)$, w$R_2$ = 0.3754 for all data.

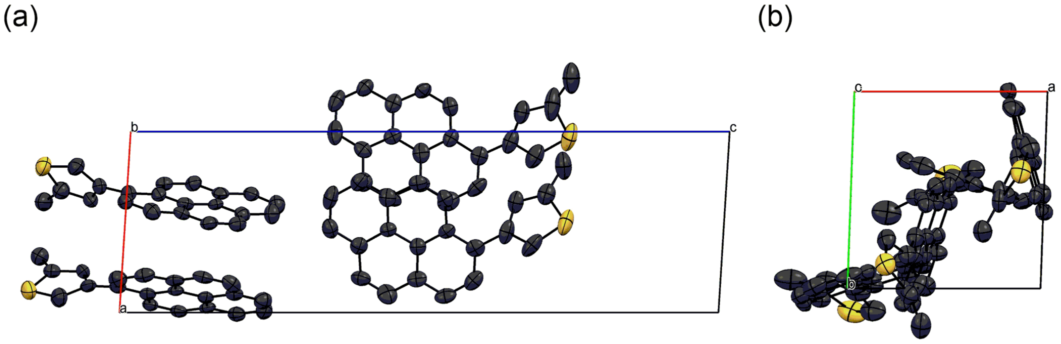


**Fig. S1** The molecular structure of **1a** with atomic displacement parameters set at 50% probability (Color code: gray = C, yellow = S). All hydrogen atoms are omitted for clarity. (a) Unit cell structure viewed along $b$-axis. (b) Unit cell structure viewed along $c$-axis.

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

A single crystal of **1b** was obtained from natural evaporation of an acetonitrile solution of **1b** at 5 °C and was mounted on a glass fiber. All measurements were made on a Rigaku XtaLAB P200 diffractometer using multi-layer mirror monochromated Cu-K$\alpha$ radiation ($\lambda$ = 1.54184 Å). The data were collected at a temperature of $-50 \pm 1$ °C to a maximum $2\theta$ value of 146.5°. A total of 1482 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 16899 reflections that were collected, 5854 were unique ($R_{\mathrm{int}}$ = 0.0296); equivalent reflections were merged. Data were collected and processed using CrysAlisPro (Rigaku Oxford Diffraction).[3] The linear absorption coefficient, $\mu$, for Cu-K$\alpha$ radiation is 17.350 cm$^{-1}$. An empirical absorption correction was applied which resulted in transmission factors ranging from 0.420 to 0.679. The data were corrected for Lorentz and polarization effects.

The structure was solved by direct methods (SIR2011)[4] 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[5] crystallographic software package except for refinement, which was performed using SHELXL Version 2014/7.[6]

Crystal data for **1b** (CCDC 1947302): $C_{44}H_{32}S_2$, $M$ = 624.86, monoclinic, $a$ = 8.32033(14) Å, $b$ = 7.16490(12) Å, $c$ = 53.8962(7) Å, $\beta$ = 93.3805(13)°, $V$ = 3207.40(9) Å$^3$, space group $P2_1/c$ (no. 14), $Z$ = 4, $D_c$ = 1.294 g cm$^{-3}$, $F(000)$ = 1312.00, $T$ = 223(1) K, $\mu$(Cu-K$\alpha$) = 17.350 cm$^{-1}$, 16899 reflections measured, 5854 independent ($R_{\mathrm{int}}$ = 0.0296). The final refinement converged to $R_1$ = 0.0811 for $I > 2.0\sigma(I)$, w$R_2$ = 0.2095 for all data.

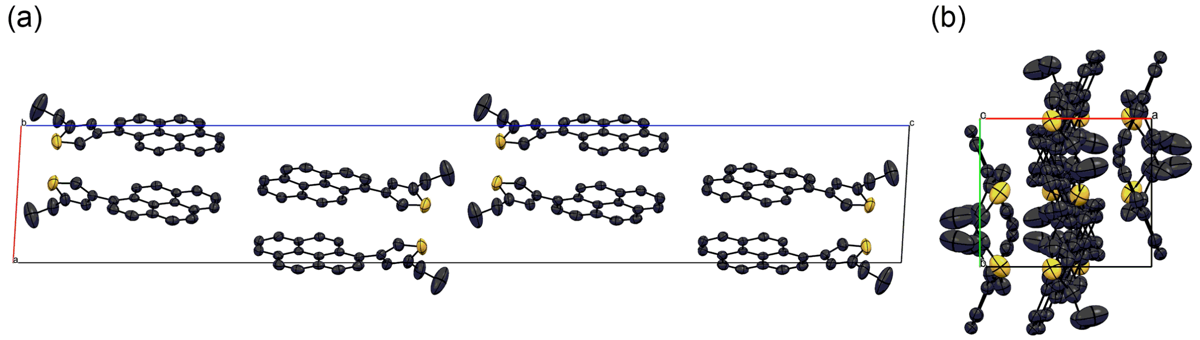


**Fig. S2** The molecular structure of **1b** with atomic displacement parameters set at 50% probability (Color code: gray = C, yellow = S). All hydrogen atoms are omitted for clarity. (a) Unit cell structure viewed along $a$-axis. (b) Unit cell structure viewed along $c$-axis.

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

A single crystal of **1c** was obtained by cooling a hot acetonitrile 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-K$\alpha$ radiation ($\lambda$ = 1.54184 Å). The data were collected at a temperature of −50 ± 1 °C to a maximum $2\theta$ value of 146.2°. A total of 1162 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 7128 reflections that were collected, 2959 were unique ($R_{\text{int}}$ = 0.0302); equivalent reflections were merged. Data were collected and processed using CrysAlisPro (Rigaku Oxford Diffraction).[3] The linear absorption coefficient, $\mu$, for Cu-K$\alpha$ radiation is 16.929 cm$^{-1}$. An empirical absorption correction was applied which resulted in transmission factors ranging from 0.638 to 0.805. The data were corrected for Lorentz and polarization effects.

The structure was solved by direct methods (SIR2011)[4] 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[5] crystallographic software package except for refinement, which was performed using SHELXL Version 2014/7.[6]

Crystal data for **1c** (CCDC 1947303): $C_{23}H_{18}S$, $M$ = 326.46, orthorhombic, $a$ = 7.65747(11) Å, $b$ = 14.0292(2) Å, $c$ = 15.4998(2) Å, $V$ = 1665.12(4) Å$^3$, space group $P2_12_12_1$ (no. 19), $Z$ = 4, $D_c$ = 1.302 g cm$^{-3}$, $F(000)$ = 688.00, $T$ = 223(1) K, $\mu$(Cu-K$\alpha$) = 16.929 cm$^{-1}$, 7128 reflections measured, 2959 independent ($R_{\text{int}}$ = 0.0302). The final refinement converged to $R_1$ = 0.0351 for $I > 2.0\sigma(I)$, w$R_2$ = 0.0926 for all data.

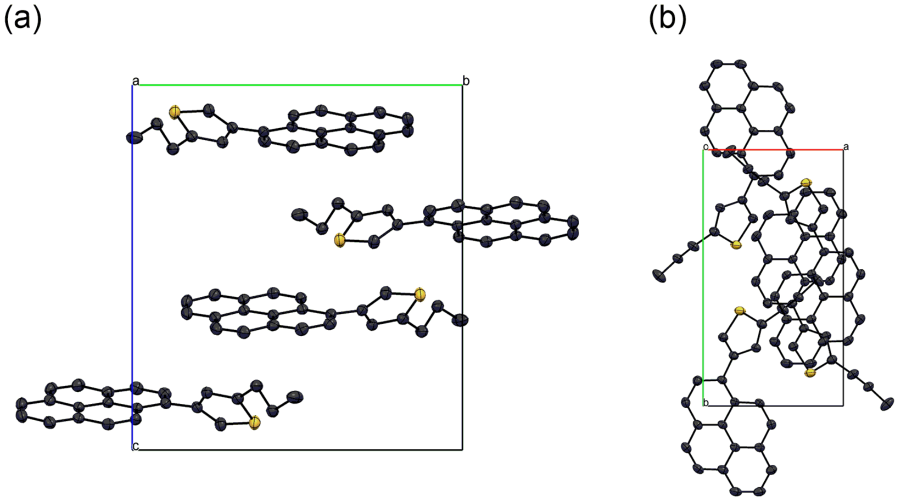


**Fig. S3** The molecular structure of **1c** with atomic displacement parameters set at 50% probability (Color code: gray = C, yellow = S). All hydrogen atoms are omitted for clarity. (a) Unit cell structure viewed along *a*-axis. (b) Unit cell structure viewed along *c*-axis.

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

A single crystal of **1e** was obtained from natural evaporation of an acetonitrile solution of **1e** at 5 °C and was mounted on a glass fiber. All measurements were made on a Rigaku XtaLAB P200 diffractometer using multi-layer mirror monochromated Cu-K$\alpha$ radiation ($\lambda$ = 1.54184 Å). The data were collected at a temperature of –50 ± 1 °C to a maximum 2$\theta$ value of 145.9°. A total of 2440 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 9050 reflections that were collected, 3389 were unique ($R_{\mathrm{int}}$ = 0.0295); equivalent reflections were merged. Data were collected and processed using CrysAlisPro (Rigaku Oxford Diffraction).[3] The linear absorption coefficient, $\mu$, for Cu-K$\alpha$ radiation is 15.575 cm$^{-1}$. An empirical absorption correction was applied which resulted in transmission factors ranging from 0.690 to 0.843. The data were corrected for Lorentz and polarization effects.

The structure was solved by direct methods (SIR2011)[4] 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[5] crystallographic software package except for refinement, which was performed using SHELXL Version 2014/7.[6]

Crystal data for **1e** (CCDC 1947304): $C_{25}H_{22}S$, $M$ = 354.51, triclinic, $a$ = 8.77664(13) Å, $b$ = 9.33669(16) Å, $c$ = 12.0593(2) Å, $\alpha$ = 93.6123(14)°, $\beta$ = 106.3533(14)°, $\gamma$ = 99.6734(13)°, $V$ = 928.36(3) Å$^3$, space group $P$-1 (no. 2), $Z$ = 2, $D_c$ = 1.268 g cm$^{-3}$, $F$(000) = 376.00, $T$ = 223(1) K, $\mu$(Cu-K$\alpha$) = 15.575 cm$^{-1}$, 9050 reflections measured, 3389 independent ($R_{\mathrm{int}}$ = 0.0295). The final refinement converged to $R_1$ = 0.0339 for $I > 2.0\sigma(I)$, w$R_2$ = 0.0968 for all data.

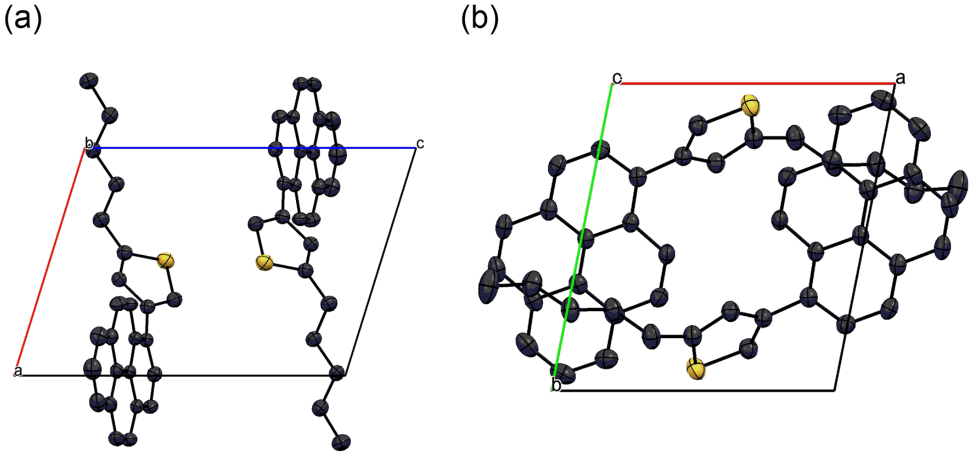


**Fig. S4** The molecular structure of **1e** with atomic displacement parameters set at 50% probability (Color code: gray = C, yellow = S). All hydrogen atoms are omitted for clarity. (a) Unit cell structure viewed along *b*-axis. (b) Unit cell structure viewed along *c*-axis.

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

A single crystal of **1f** was obtained from natural evaporation of an acetonitrile solution of **1f** at 5 °C and was mounted on a glass fiber. All measurements were made on a Rigaku XtaLAB P200 diffractometer using multi-layer mirror monochromated Cu-K$\alpha$ radiation ($\lambda$ = 1.54184 Å). The data were collected at a temperature of –50 ± 1 °C to a maximum $2\theta$ value of 150.1°. A total of 2044 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 13816 reflections that were collected, 3608 were unique ($R_{\mathrm{int}}$ = 0.0447); equivalent reflections were merged. Data were collected and processed using CrysAlisPro (Rigaku Oxford Diffraction).[3] The linear absorption coefficient, $\mu$, for Cu-K$\alpha$ radiation is 14.880 cm$^{-1}$. An empirical absorption correction was applied which resulted in transmission factors ranging from 0.469 to 0.828. The data were corrected for Lorentz and polarization effects.

The structure was solved by direct methods (SIR2011)[4] 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[5] crystallographic software package except for refinement, which was performed using SHELXL Version 2014/7.[6]

Crystal data for **1f** (CCDC 1947305): $C_{26}H_{24}S$, $M$ = 368.54, monoclinic, $a$ = 8.71844(12) Å, $b$ = 10.13255(17) Å, $c$ = 22.2883(3) Å, $\beta$ = 91.7546(13)°, $V$ = 1968.03(5) Å$^3$, space group $P2_1/c$ (no. 14), $Z$ = 4, $D_c$ = 1.244 g cm$^{-3}$, $F(000)$ = 784.00, $T$ = 223(1) K, $\mu$(Cu-K$\alpha$) = 14.880 cm$^{-1}$, 13816 reflections measured, 3608 independent ($R_{\mathrm{int}}$ = 0.0447). The final refinement converged to $R_1$ = 0.0388 for $I > 2.0\sigma(I)$, w$R_2$ = 0.1087 for all data.

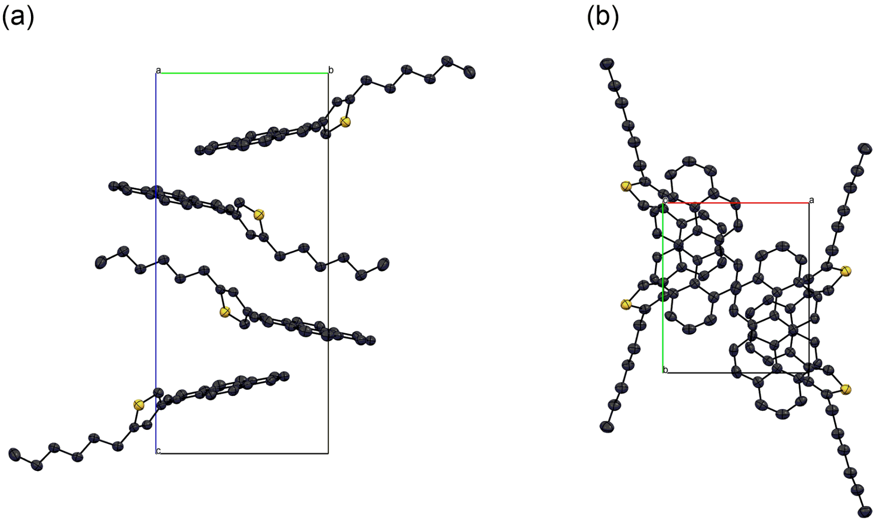


**Fig. S5** The molecular structure of **1f** with atomic displacement parameters set at 50% probability (Color code: gray = C, yellow = S). All hydrogen atoms are omitted for clarity. (a) Unit cell structure viewed along *a*-axis. (b) Unit cell structure viewed along *c*-axis.

## 4. Theoretical calculations

Based on the single-crystal X-ray diffraction structures, absorption wavelengths of **1a**–**f** except **1d** were calculated by time-dependent density functional theory (TD-DFT) at the B3LYP/6-31G(d) level of theory (Table S1). Calculated HOMO and LUMO of **1a**–**f** except **1d** are shown in Fig. S6.

**Table S1** Experimental absorption maxima and calculated absorption properties of **1a**–**f** except **1d**.

| Compd | Calcd absorption $\lambda_{abs}$ (nm) | Transition from HOMO to LUMO | Oscillator strength | HOMO (eV) | LUMO (eV) | Dipole moment (D) |
|---|---|---|---|---|---|---|
| **1a** | 358.08 | 0.67787 | 0.4378 | –5.12 | –1.48 | 0.909426 |
| **1b** | 343.72 | 0.67334 | 0.4076 | –5.20 | –1.40 | 0.968558 |
| **1c** | 350.12 | 0.67626 | 0.4261 | –5.15 | –1.43 | 0.885961 |
| **1e** | 352.90 | 0.67775 | 0.4436 | –5.14 | –1.45 | 0.948442 |
| **1f** | 347.43 | 0.67554 | 0.4313 | –5.14 | –1.38 | 1.087808 |

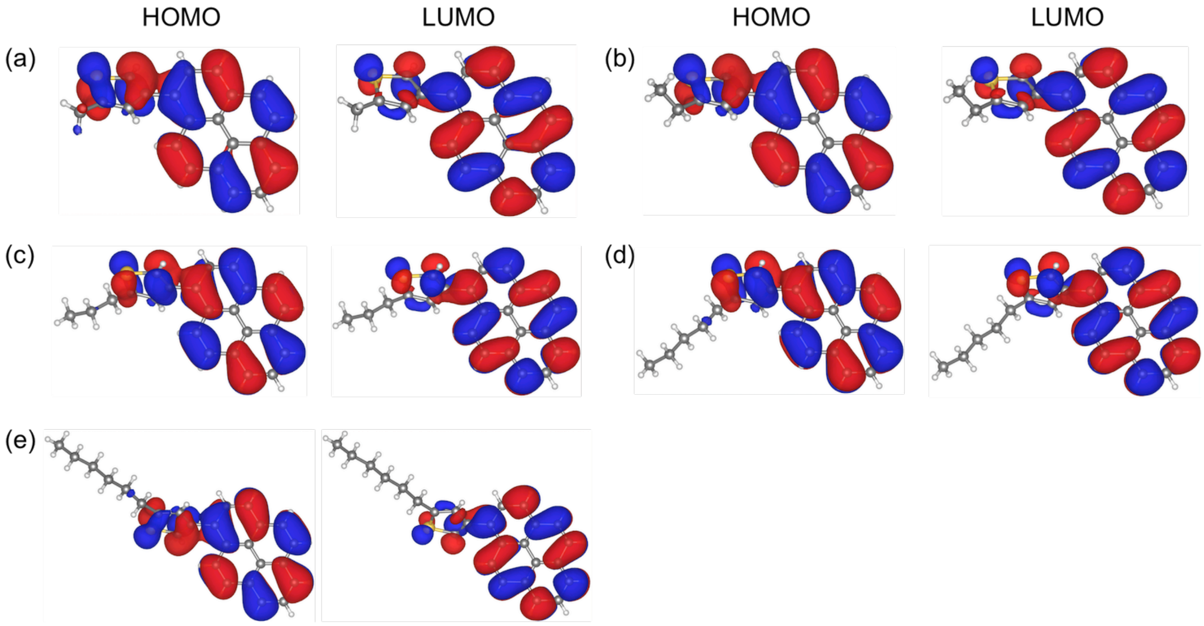


**Fig. S6** HOMO and LUMO of **1a** (a), **1b** (b), **1c** (c), **1e** (d), and **1f** (e) calculated at the B3LYP/6-31G(d) level. The structures are drawn by VESTA.[7]

## 5. Excitation spectra for the mechanochromic luminescence of 1

Excitation spectra of crystalline and ground samples of **1a–f** measured at their maximum emission wavelengths showed that maximum excitation wavelengths shifted bathochromically after grinding (Fig. S7). These results indicate that the bathochromically shifted emission of ground samples should be attributed to the formation of static excimers upon grinding.

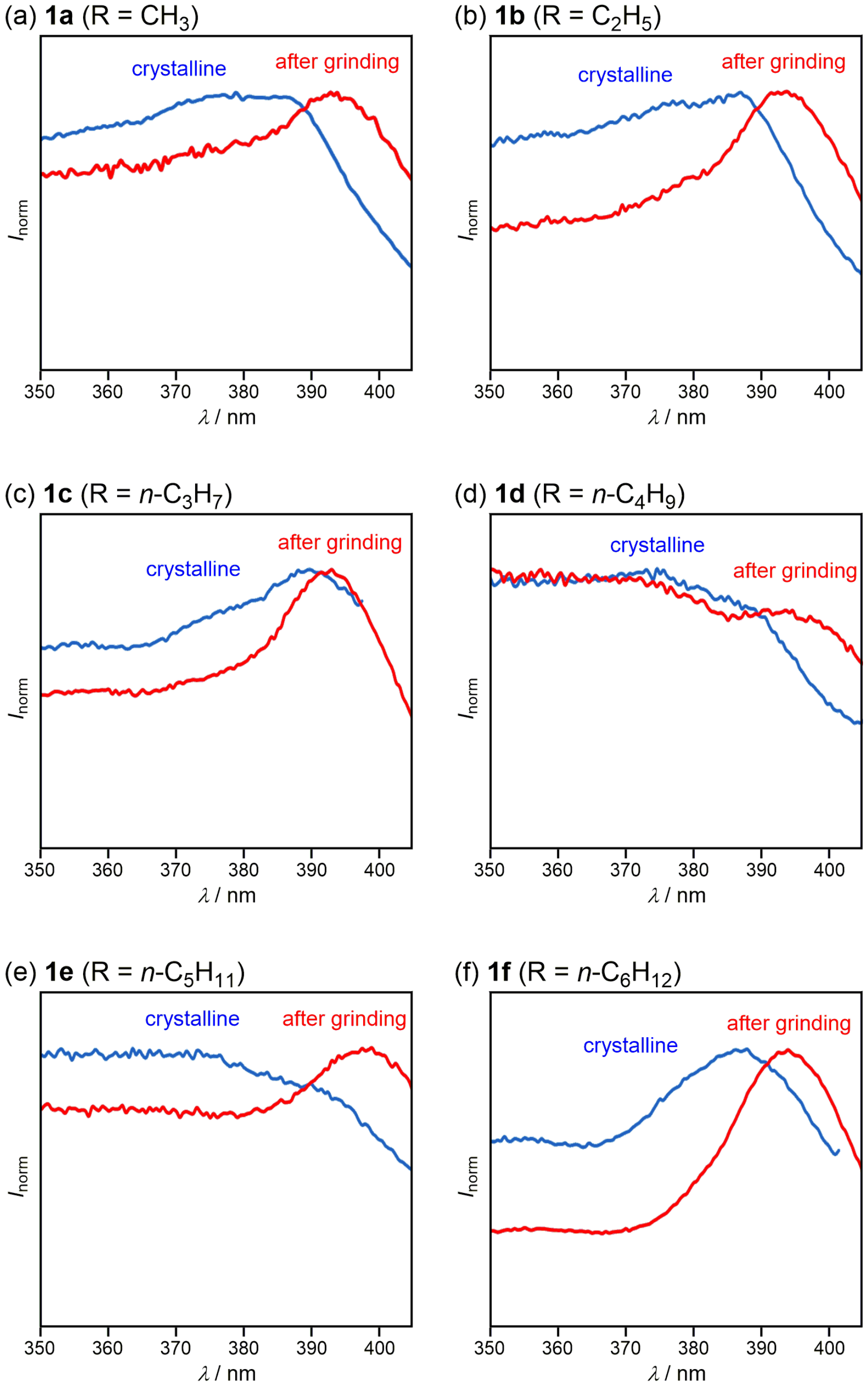

(a) **1a** (R = $CH_3$)
(b) **1b** (R = $C_2H_5$)
(c) **1c** (R = $n$-$C_3H_7$)
(d) **1d** (R = $n$-$C_4H_9$)
(e) **1e** (R = $n$-$C_5H_{11}$)
(f) **1f** (R = $n$-$C_6H_{12}$)

**Fig. S7** Excitation spectra of crystalline and ground **1a** (a), **1b** (b), **1c** (c), **1d** (d), **1e** (e), and **1f** (f).

## 6. Fluorescence spectra for the mechanochromic luminescence of 1

Fluorescence spectra showed significant shifts in maximum emission wavelengths of **1b**–**e** after grinding crystalline samples. For **1c**–**e**, a slightly blue-shifted emission band with a shoulder peak was observed within 5 s after standing the ground sample under room temperature (Fig. S8).

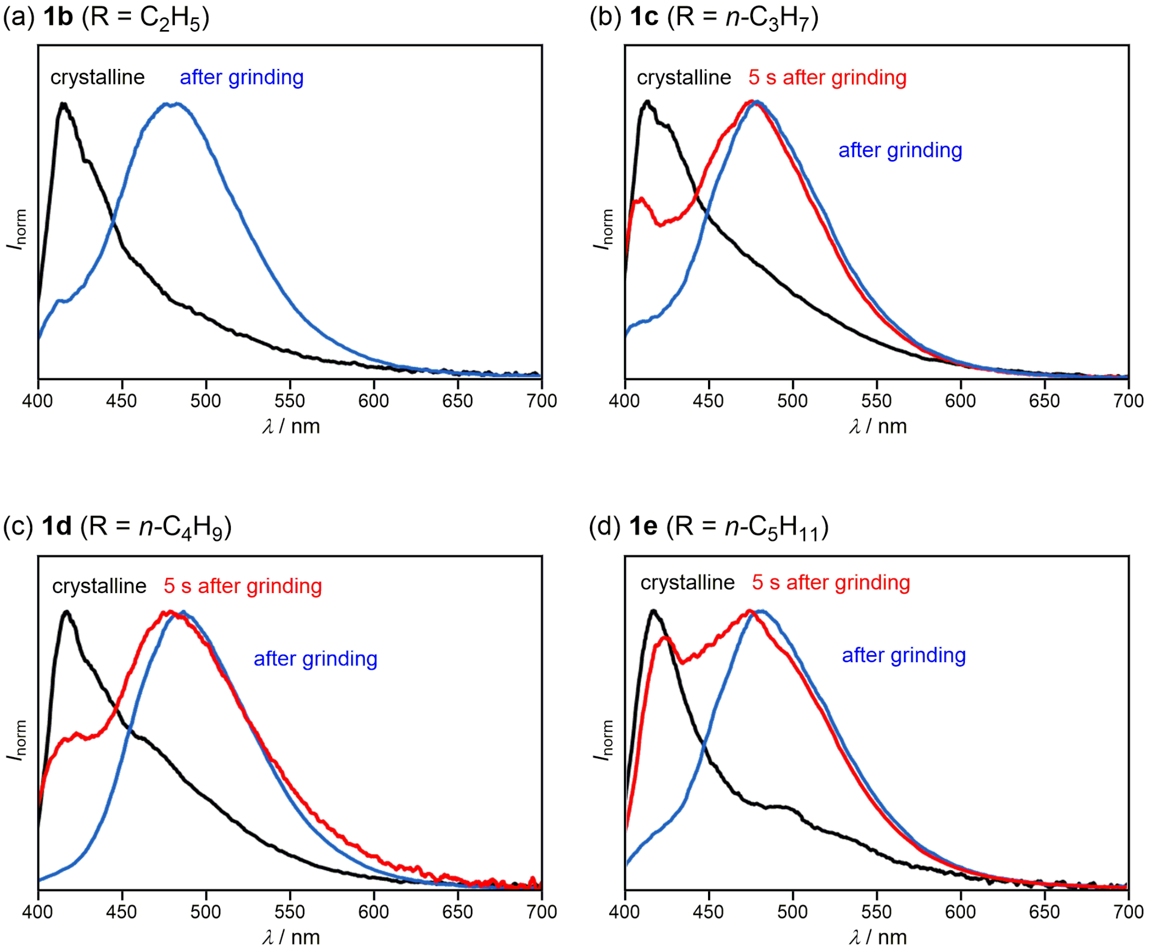
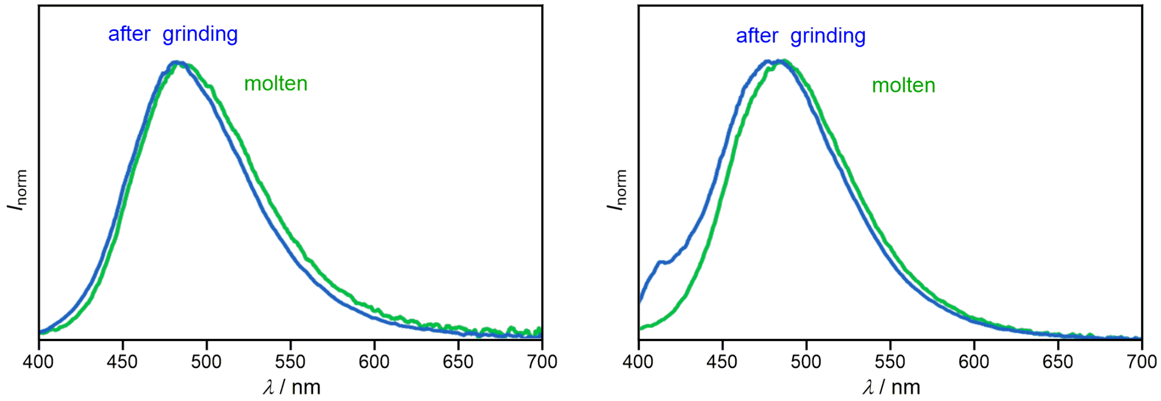
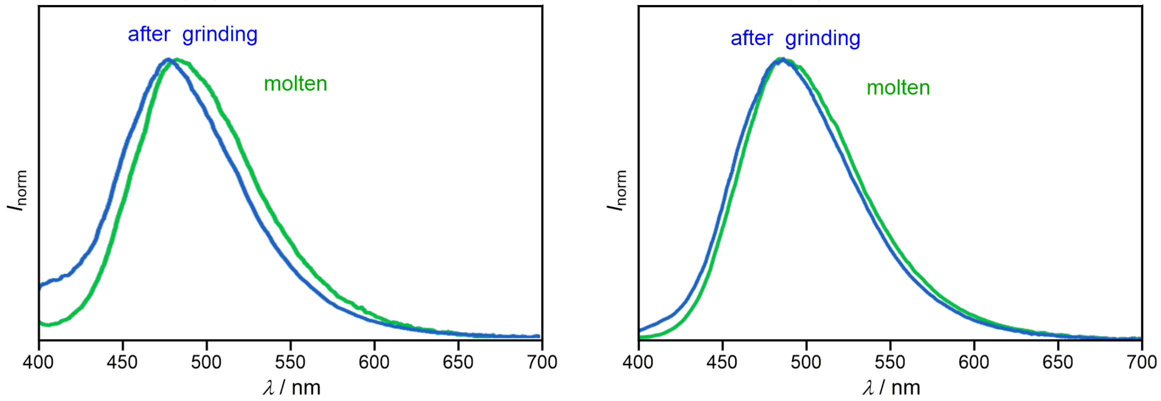


**Fig. S8** Fluorescence spectra for MCL of **1b** (a), **1c** (b), **1d** (c), and **1e** (d) irradiated with UV light at 365 nm.

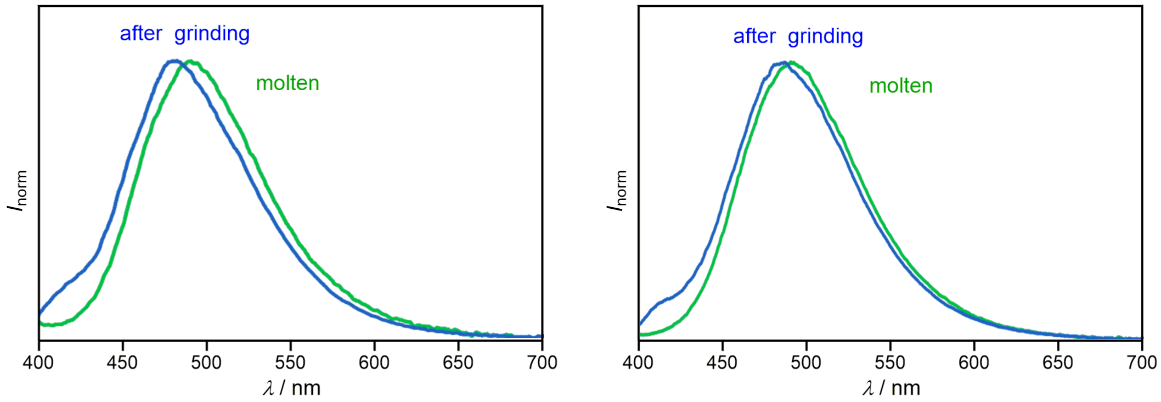
Fluorescence spectra of molten **1a–f** were in good agreement with those of the mechanically changed states (Fig. S9).


(a) **1a** (R = $CH_3$)

(b) **1b** (R = $C_2H_5$)


(c) **1c** (R = $n$-$C_3H_7$)

(d) **1d** (R = $n$-$C_4H_9$)


(e) **1e** (R = $n$-$C_5H_{11}$)

(f) **1f** (R = $n$-$C_6H_{13}$)

**Fig. S9** Fluorescence spectra for **1a** (a), **1b** (b), **1c** (c), **1d** (d), **1e** (e), and **1f** (f) irradiated with UV light at 365 nm.

## 7. Powder X-ray diffraction analyses of 1

Powder X-ray diffraction (PXRD) patterns of **1a**–**f** except **1d** showed that the crystal structures of powdered samples were identical to those of their single crystals. The intensity of diffraction patterns of **1b** decreased after grinding and recovered after heating. Partial self-recovery of crystallinity was observed for ground samples of **1c**–**e**. The intensity of diffraction patterns of **1c** and **1e** recovered after exposure to solvent, whereas the diffraction peaks of ground **1d** were unchanged after heating or exposure to solvent (Fig. S10).

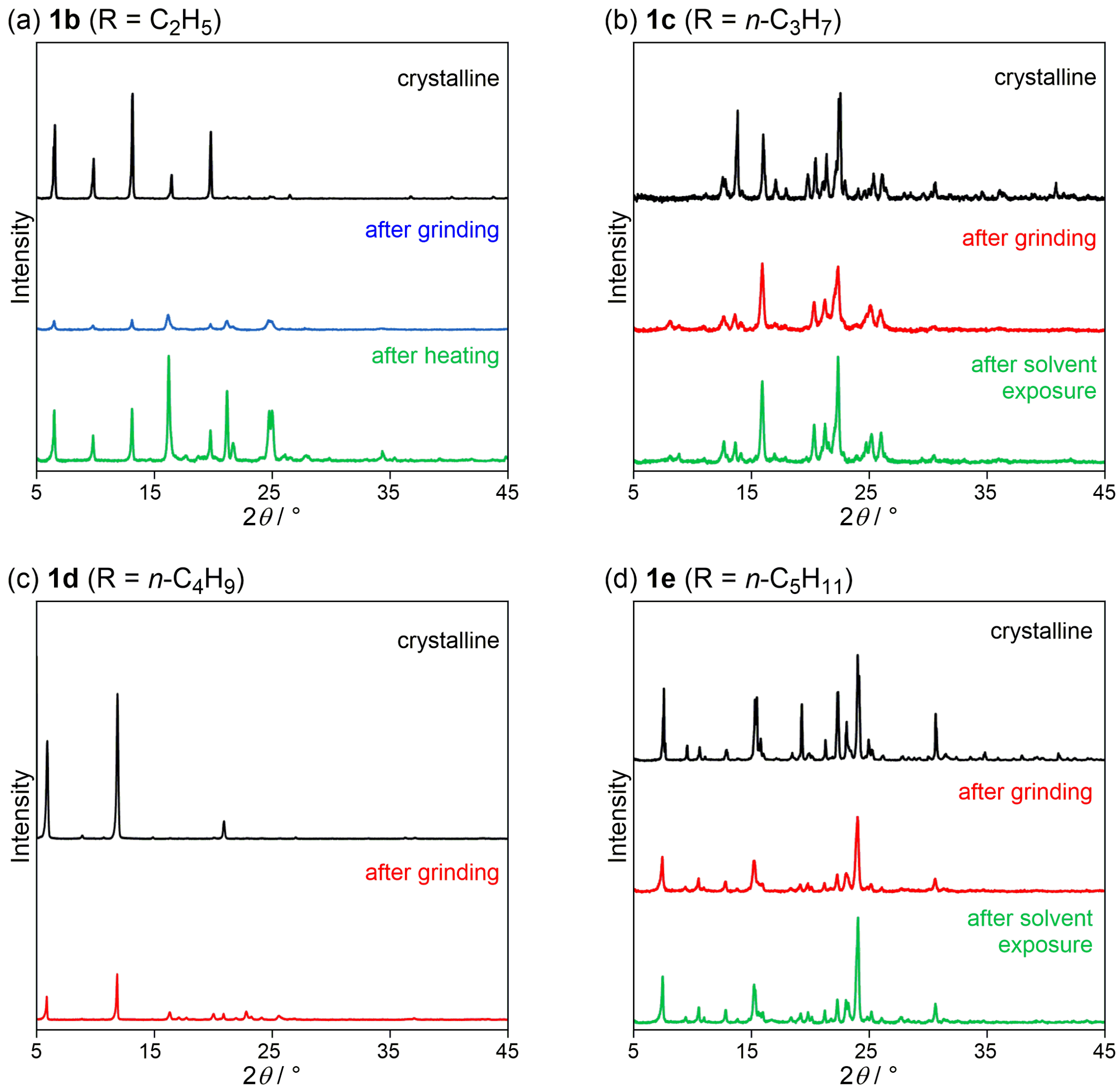


**Fig. S10** PXRD patterns for **1b** (a), **1c** (b), **1d** (c), and **1e** (d).

## 8. Differential scanning calorimetry (DSC) analyses

The DSC thermograms of powdered crystalline **1a** and **1b** showed only one endothermic peak that corresponds to their melting points ($T_m$). Cold crystallization transition peaks ($T_c$) were observed for molten **1a** and **1b** during the second heating or cooling process, respectively (Fig. S11).

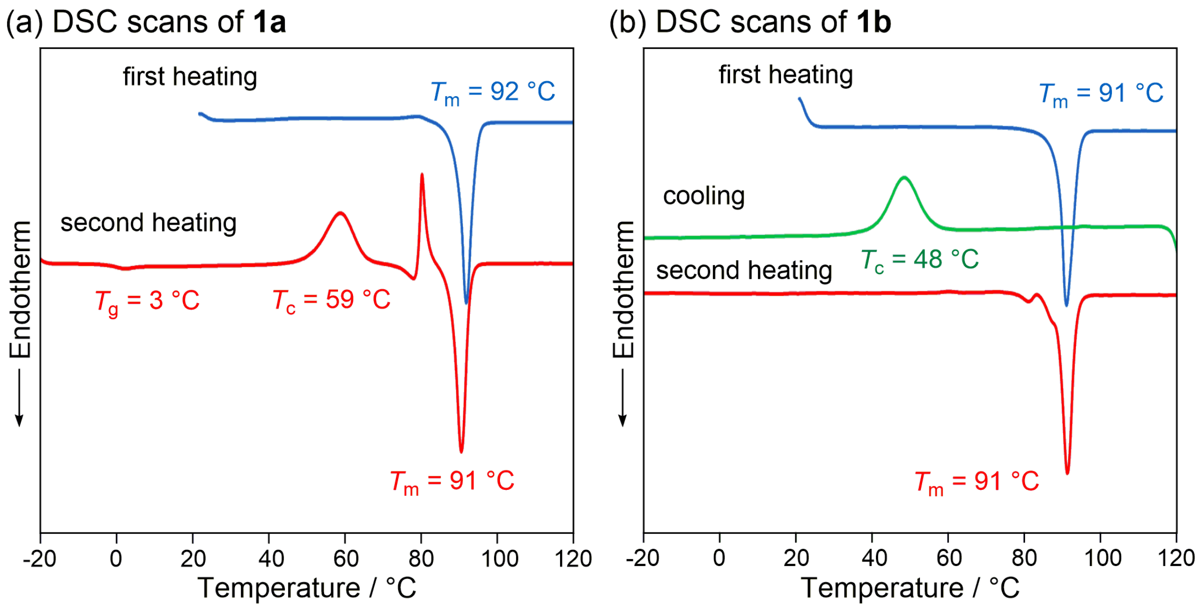
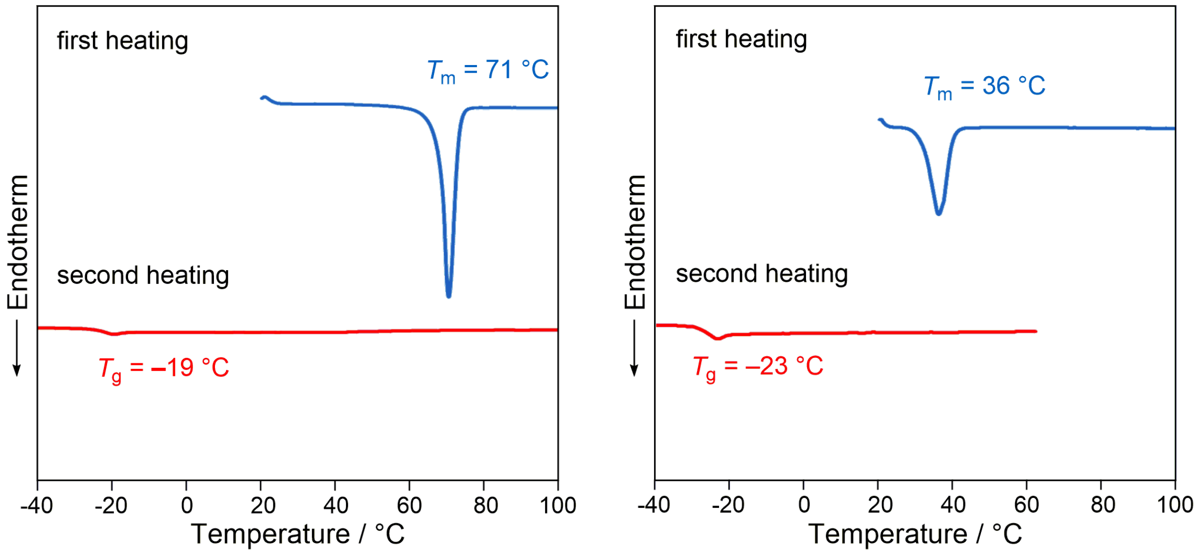
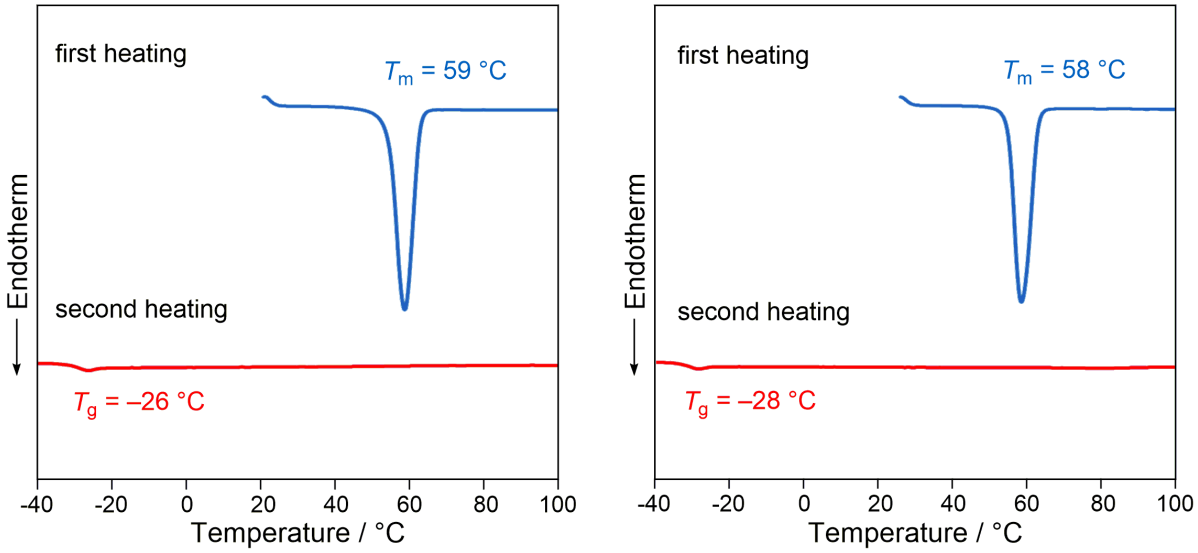


**Fig. S11** DSC thermograms for **1a** (a) and **1b** (b).

The DSC thermograms of powdered crystalline **1c**–**f** also showed only one endothermic peak that corresponds to their $T_m$. Molten samples of **1c**–**f** exhibited glass-transition steps ($T_g$) below room temperature (Fig. S12).


(a) **1c** (R = $n$-$C_3H_7$)

(b) **1d** (R = $n$-$C_4H_9$)


(c) **1e** (R = $n$-$C_5H_{11}$)

(b) **1f** (R = $n$-$C_6H_{13}$)

**Fig. S12** DSC thermograms for **1c** (a), **1d** (b), **1e** (c), and **1f** (d).

## 9. Fluorescence spectra for the mechanochromic luminescence of 1/DMQA

As-prepared two-component dyes **1/DMQA** exhibited green emission. The behavior of the ground orange-emissive states of **1a**–**f**/DMQA depends on the length of the alkyl chain in **1a**–**f** (Fig. S13).

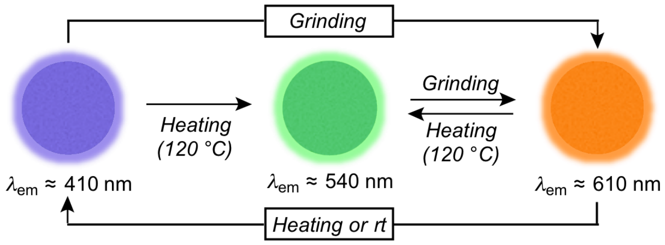


**Fig. 13** Schematic illustration for the MCL of **1/DMQA**

Two-component dyes **1a/DMQA** and **1b/DMQA** exhibited high-contrast MCL between violet and orange (Fig. S14 and S15). The orange-emissive states were recovered to the violet-emissive states after heating.

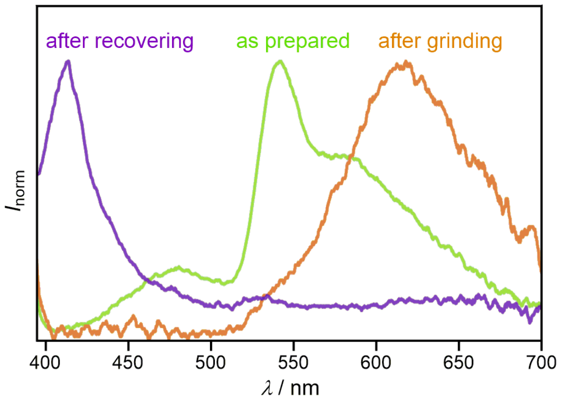


**Fig. S14** Fluorescence spectra for the MCL of **1a/DMQA** irradiated with UV light at 365 nm.

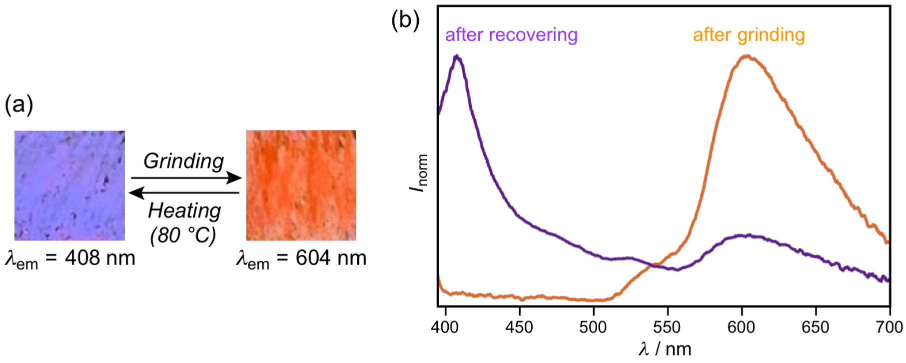


**Fig. S15** Photographs (a) and fluorescence spectra (b) for the MCL of **1b/DMQA** irradiated with UV light at 365 nm.

Orange-emissive state of **1c**/**DMQA** changed to another state with two emission maxima (Fig. S16c). This intermediate state changed to violet-emissive state on heating (Fig. S16a and S16b).

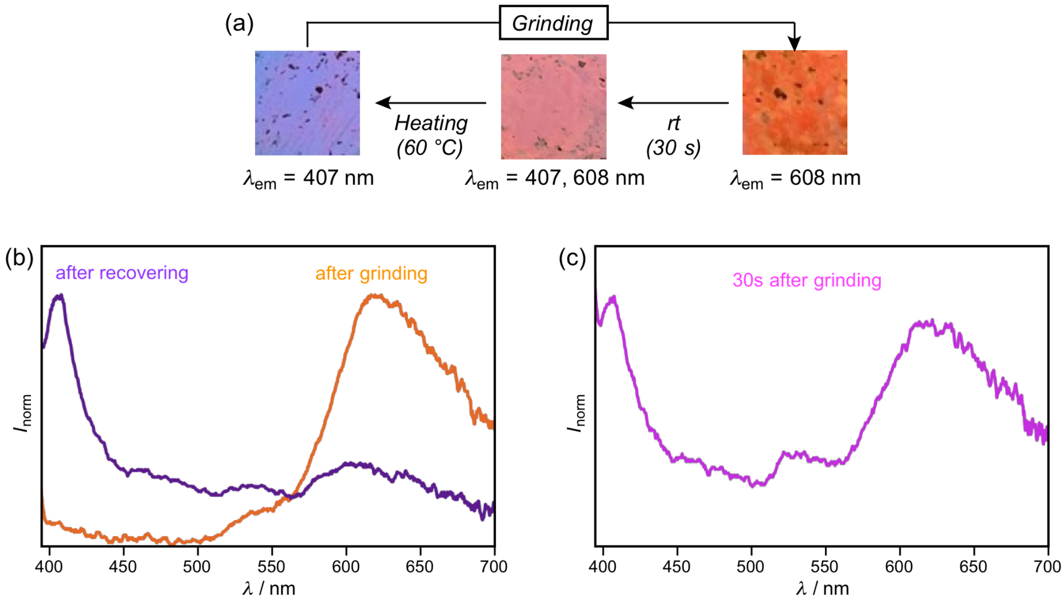


**Fig. S16** Photographs (a) and fluorescence spectra (b,c) for the MCL of **1c**/**DMQA** irradiated with UV light at 365 nm.

Orange-emissive state of **1d**/**DMQA** did not change to violet-emissive state after standing at room temperature or even by heating or exposure to solvents (Fig. S17).

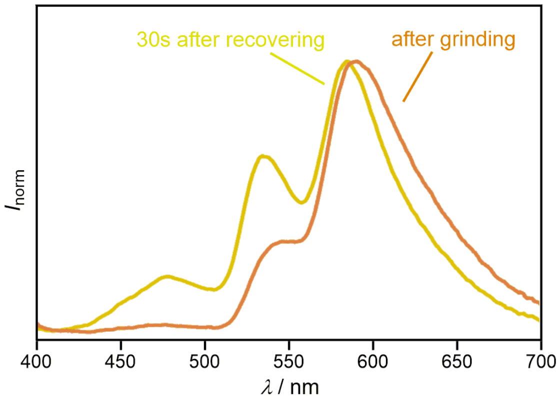


**Fig. S17** Fluorescence spectra for **1d**/**DMQA** irradiated with UV light at 365 nm.

The two-component dye **1e**/**DMQA** exhibited self-recovering MCL between violet and orange (Fig. S18a and S18b). The orange-emissive state of **1e**/**DMQA** gradually changed to violet-emissive state under room temperature for 30 min (Fig. S18c).

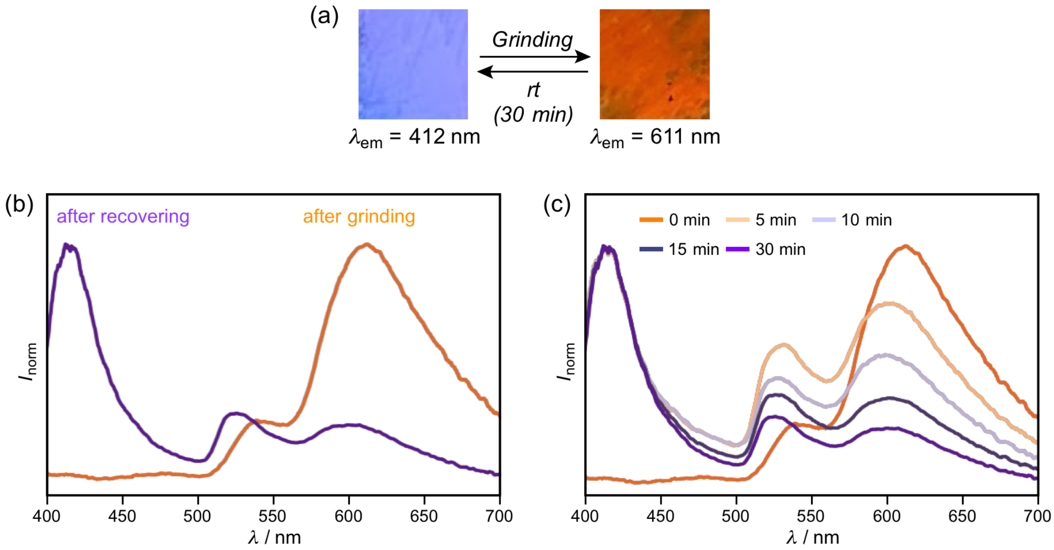


**Fig. S18** Photographs (a) and fluorescence spectra (b,c) for the MCL of **1e**/**DMQA** irradiated with UV light at 365 nm.

The maximum emission wavelengths of the self-recovering MCL of **1f**/**DMQA** were observed within experimental errors during five grinding–self-recovering cycles (Fig. S19).

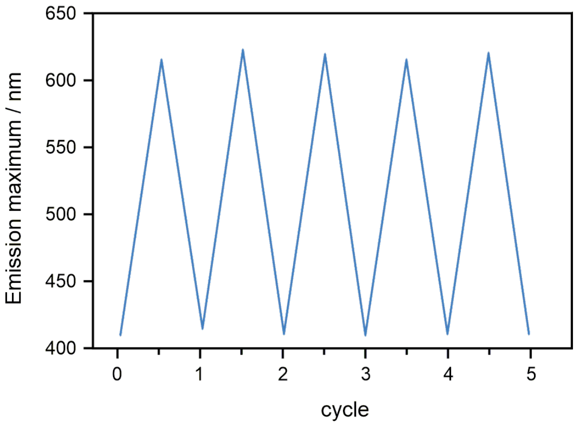


**Fig. S19** Plots of the emission maxima during five grinding–self-recovering cycles.

## 10. Powder X-ray diffraction analyses of 1/DMQA

The PXRD data for two-component dyes **1a-e/DMQA** are shown in Fig. S20.

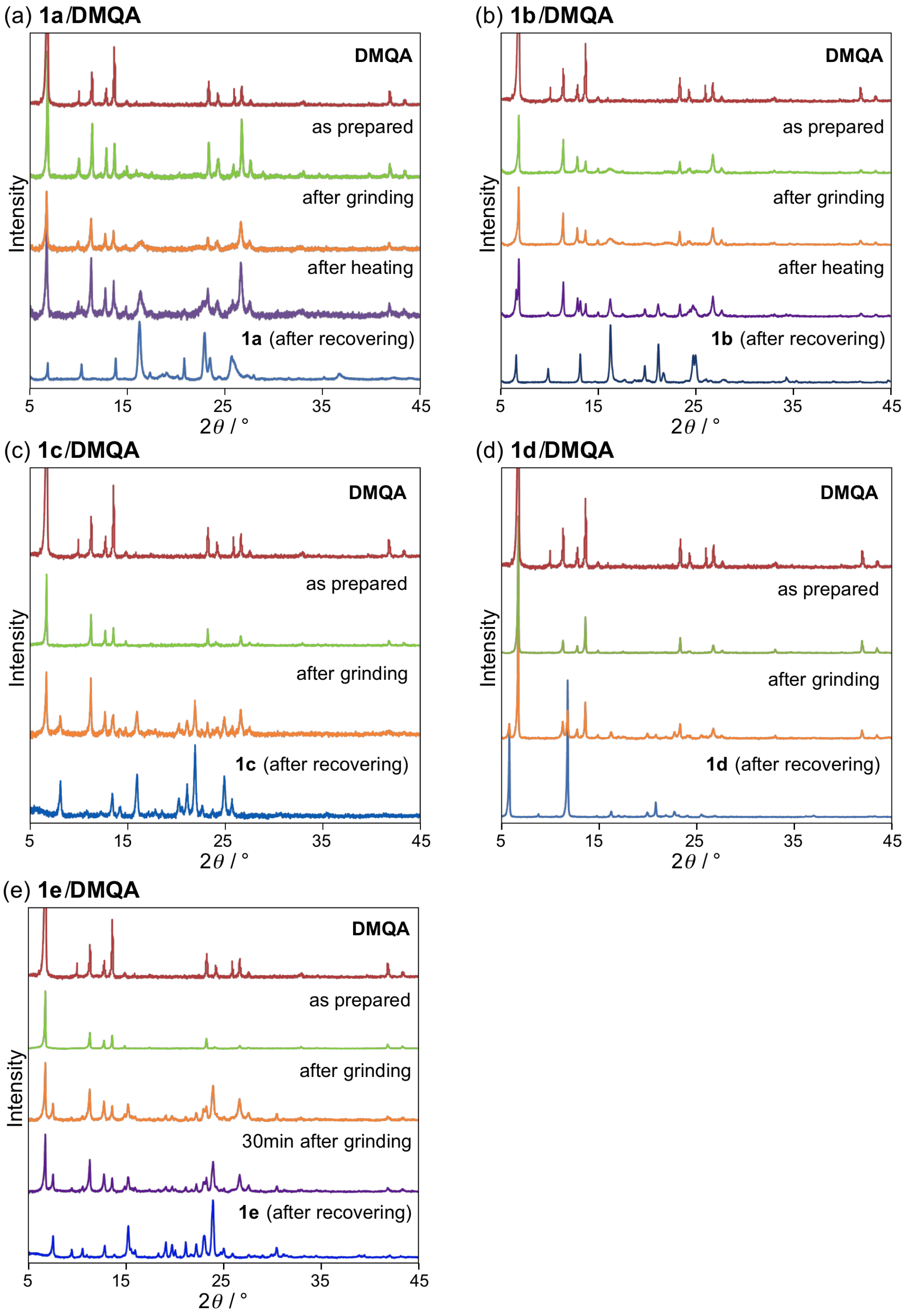


**Fig. S20** PXRD patterns for **1a/DMQA** (a), **1b/DMQA** (b), **1c/DMQA** (c), **1d/DMQA** (d), and **1e/DMQA** (e).

## 11. References

1) D. Mari, N. Miyagawa, K. Okano and A. Mori, *J. Org. Chem.*, 2018, **83**, 14126.

2) Gaussian 16, Revision A.03, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman and D. J. Fox, Gaussian, Inc., Wallingford CT, 2016.

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

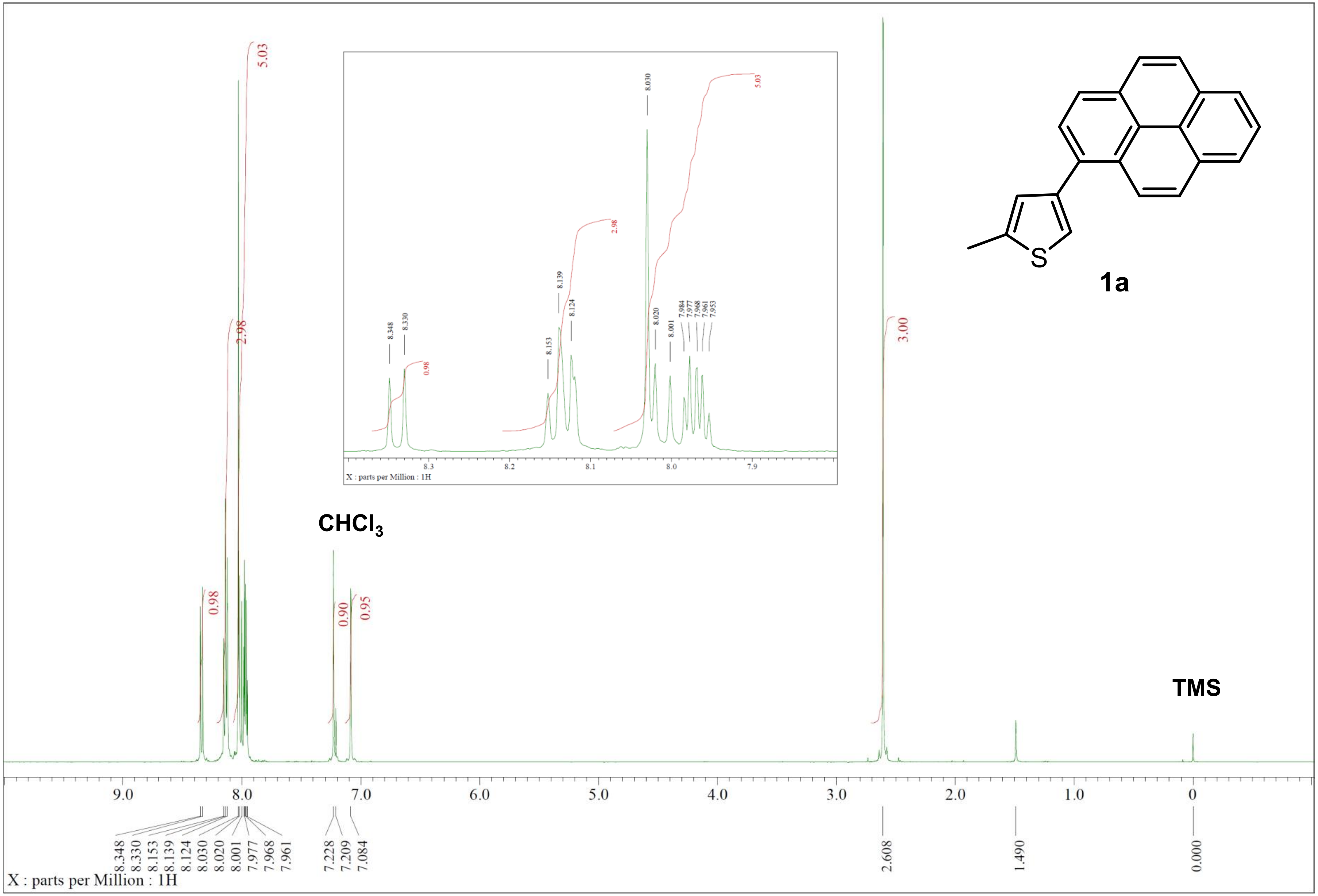
4) SIR2011: M. C. Burla, R. Caliandro, M. Camalli, B. Carrozzini, G. L. Cascarano, C. Giacovazzo, M. Mallamo, A. Mazzone, G. Polidori and R. Spagna, *J. Appl. Cryst.*, 2012, **45**, 357.

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

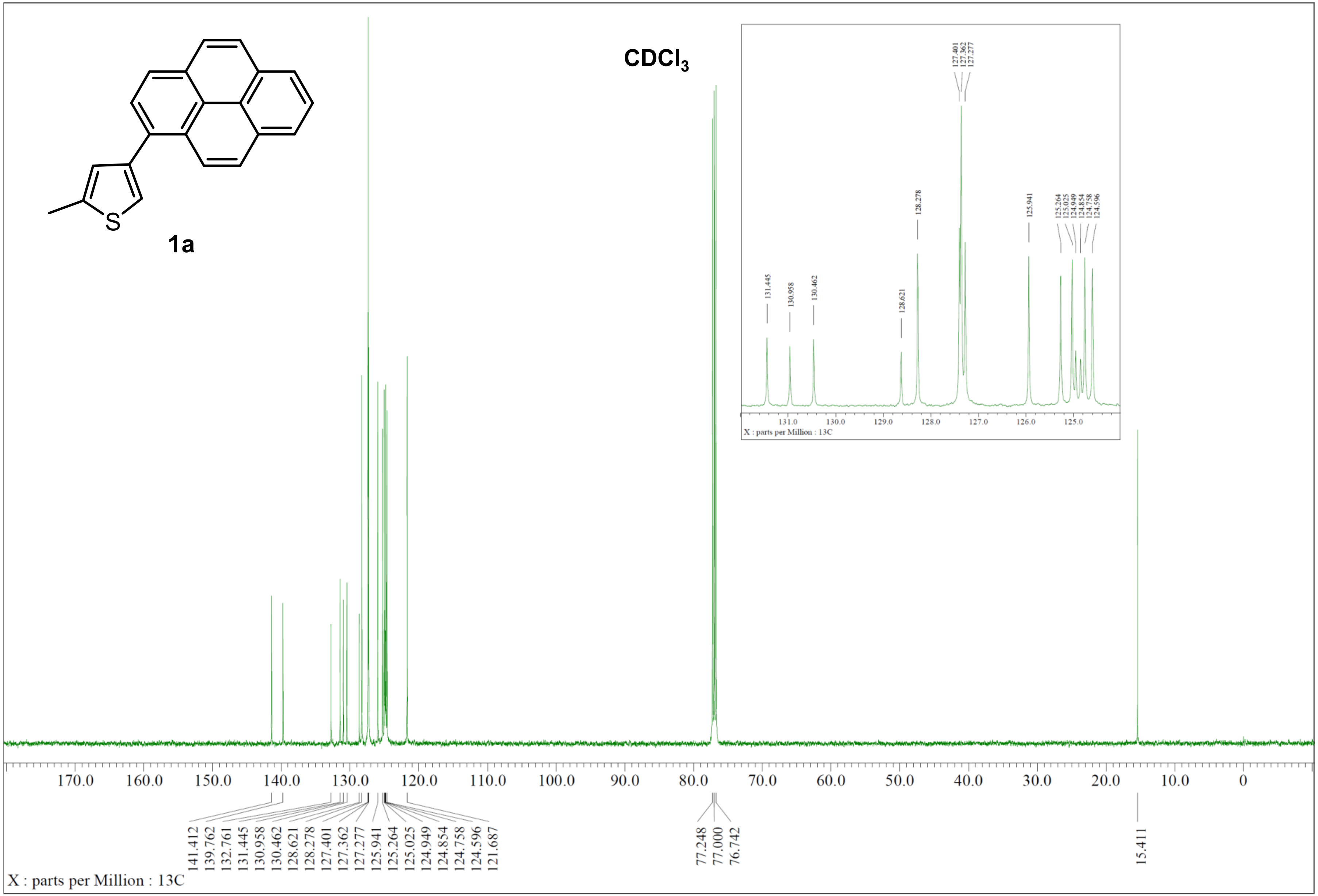
6) SHELXL Version 2014/7: G. M. Sheldrick, *Acta Cryst.*, 2008, **A64**, 112.

7) K. Momma and F. Izumi, *J. Appl. Crystallogr.*, 2011, **44**, 1272.

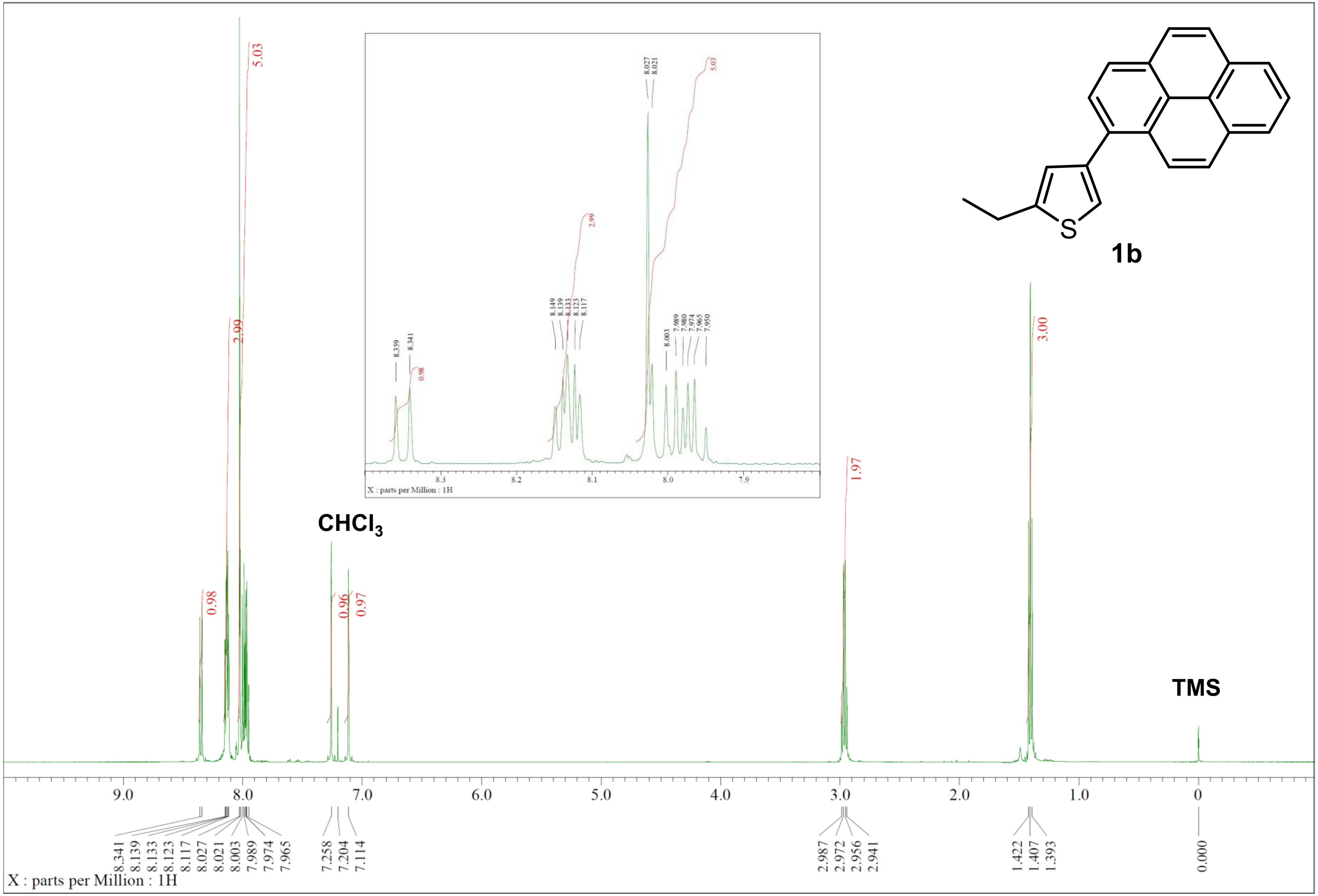
# $^1$H NMR spectrum of 1a (500 MHz, in $CDCl_3$, rt)



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



# $^1$H NMR spectrum of 1b (500 MHz, in $CDCl_3$, rt)



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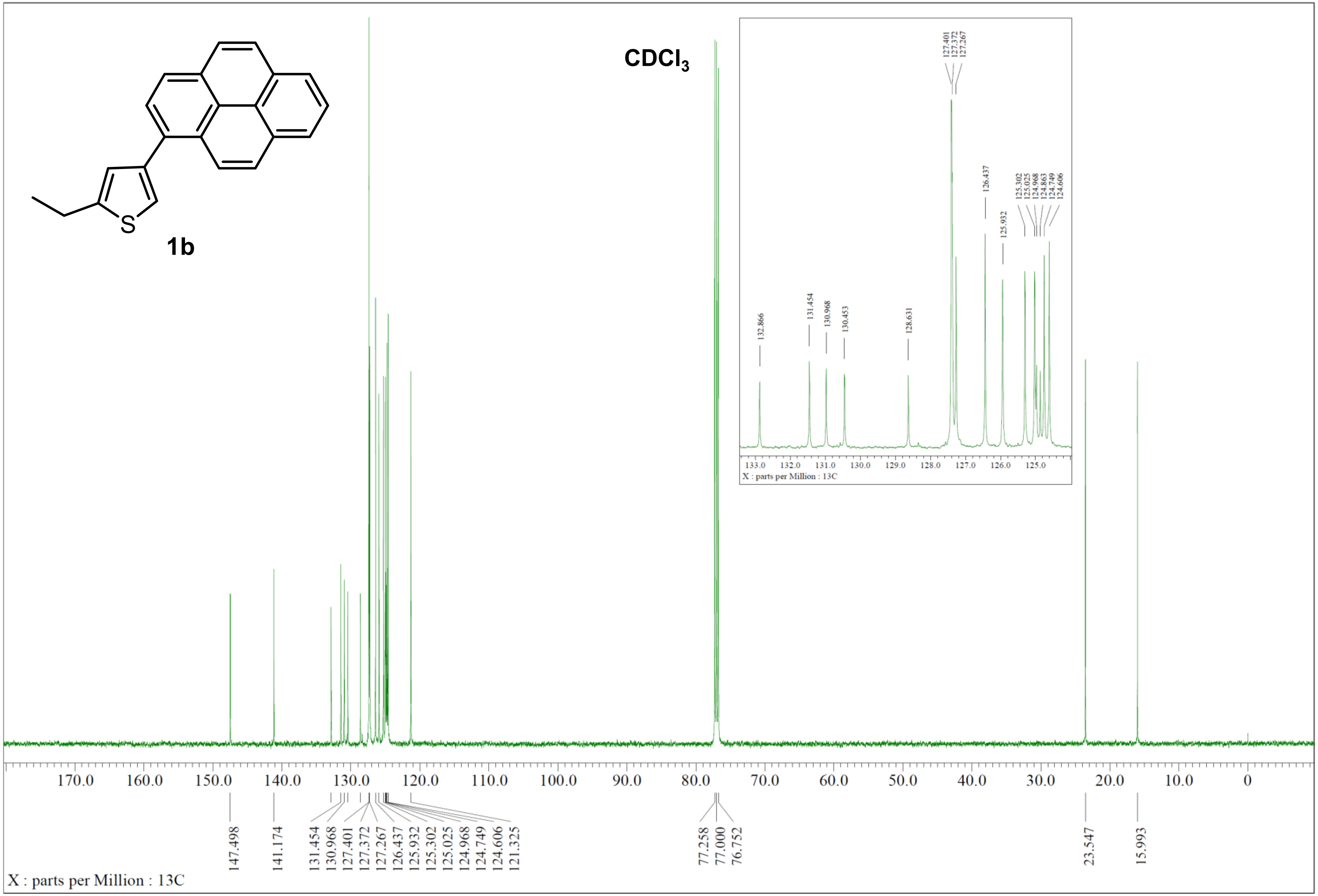
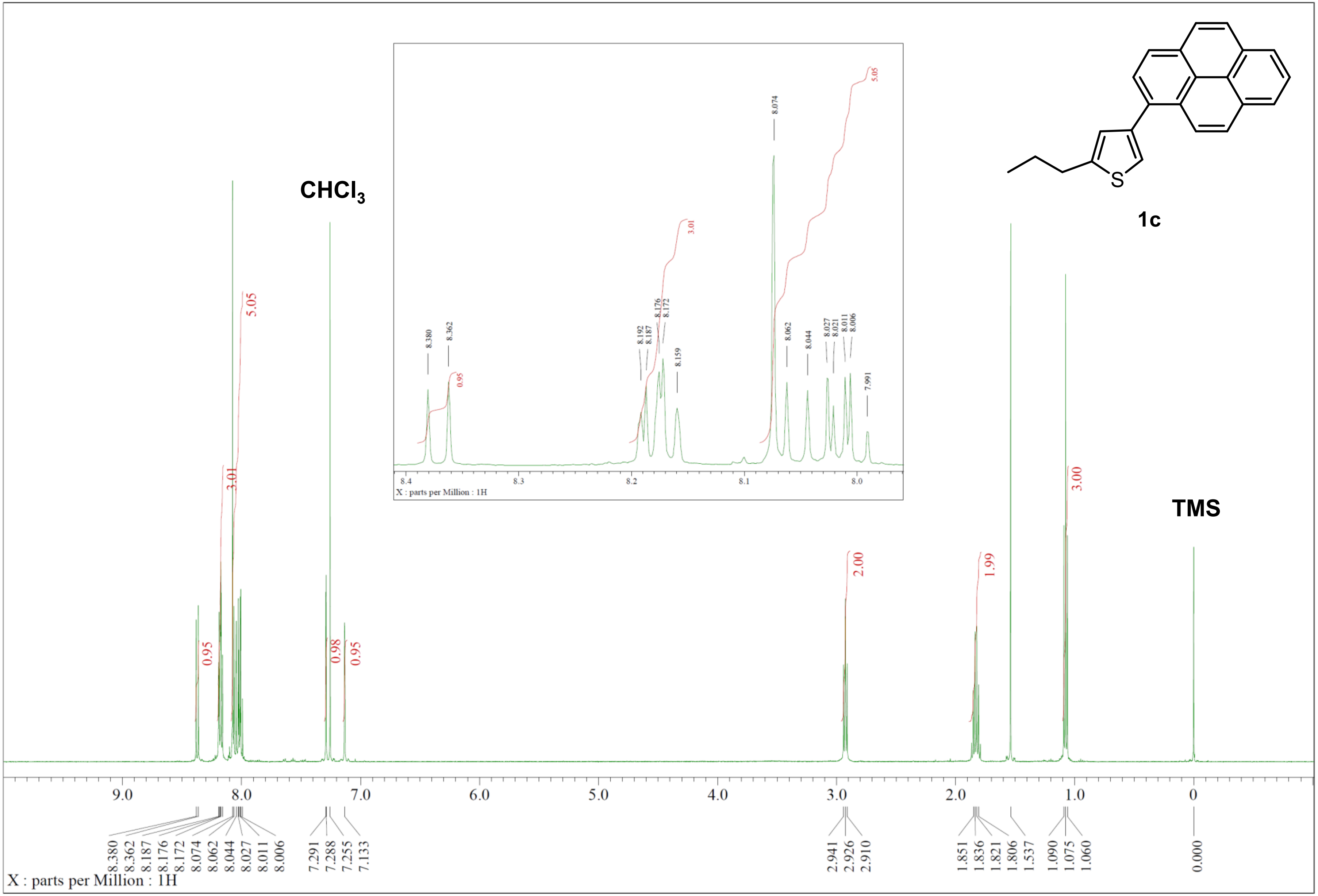
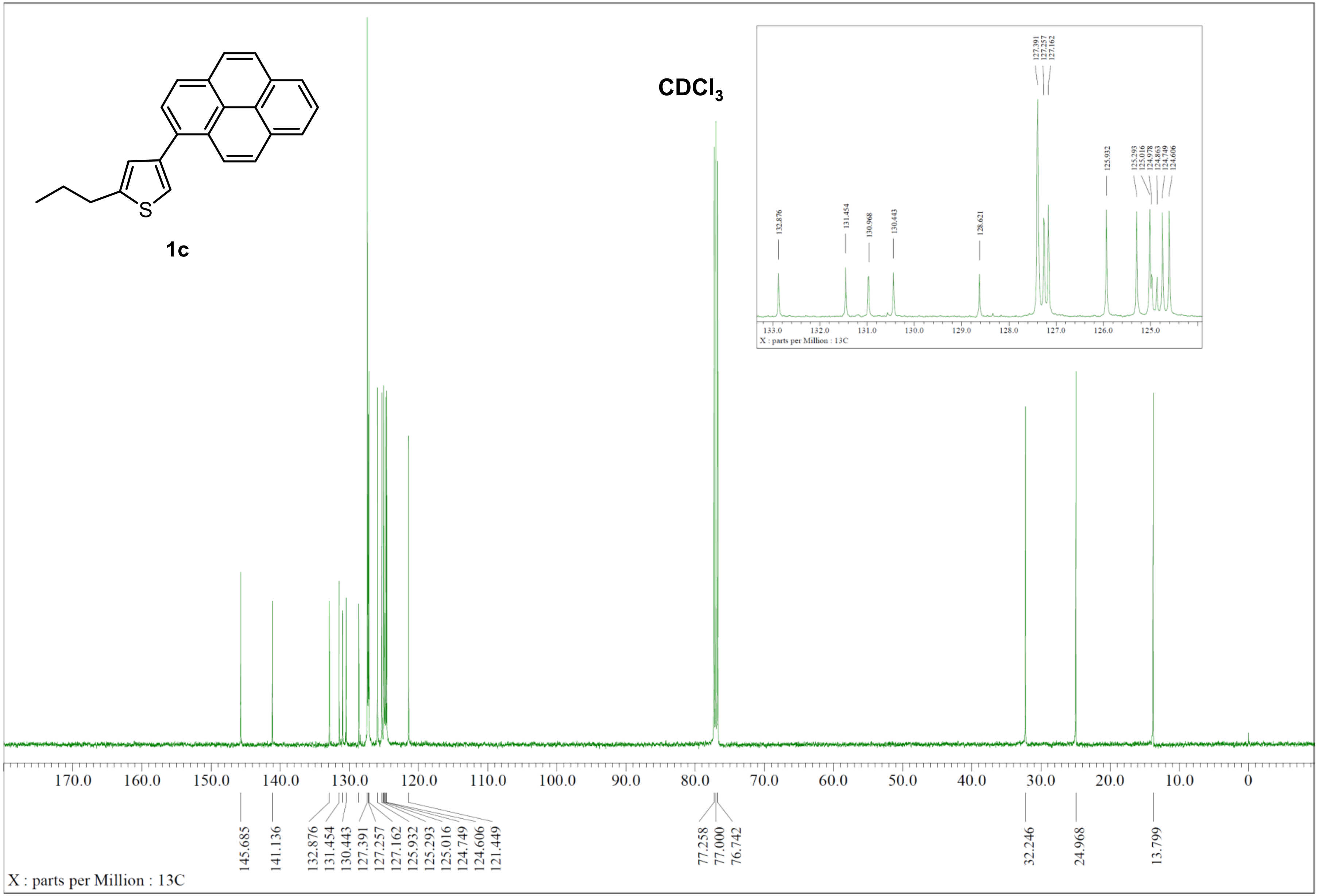


# $^1H$ NMR spectrum of 1c (500 MHz, in $CDCl_3$, rt)

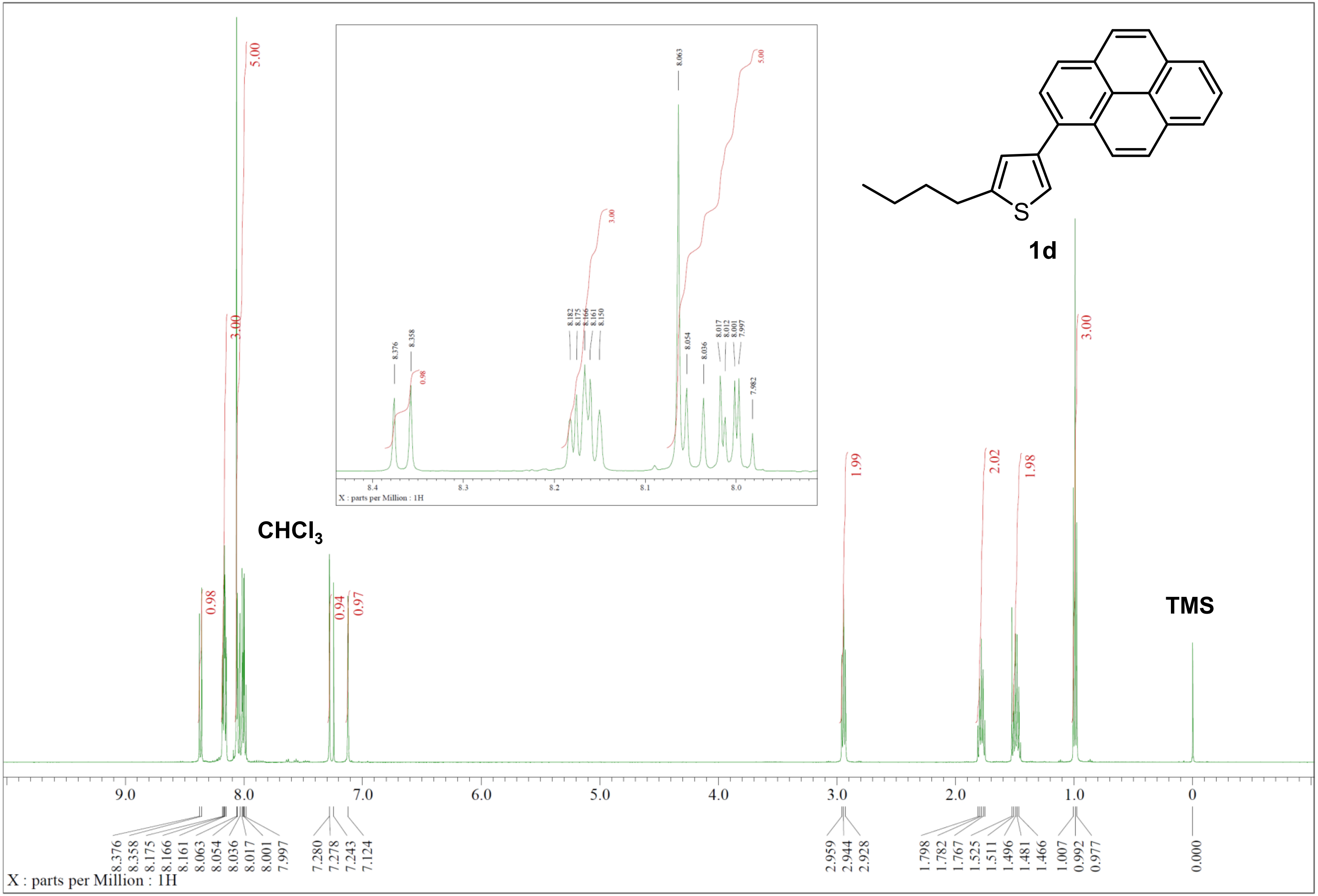


# $^{13}C$ NMR spectrum of 1c (126 MHz, in $CDCl_3$, rt)



**1c**

# $^1$H NMR spectrum of 1d (500 MHz, in $CDCl_3$, rt)



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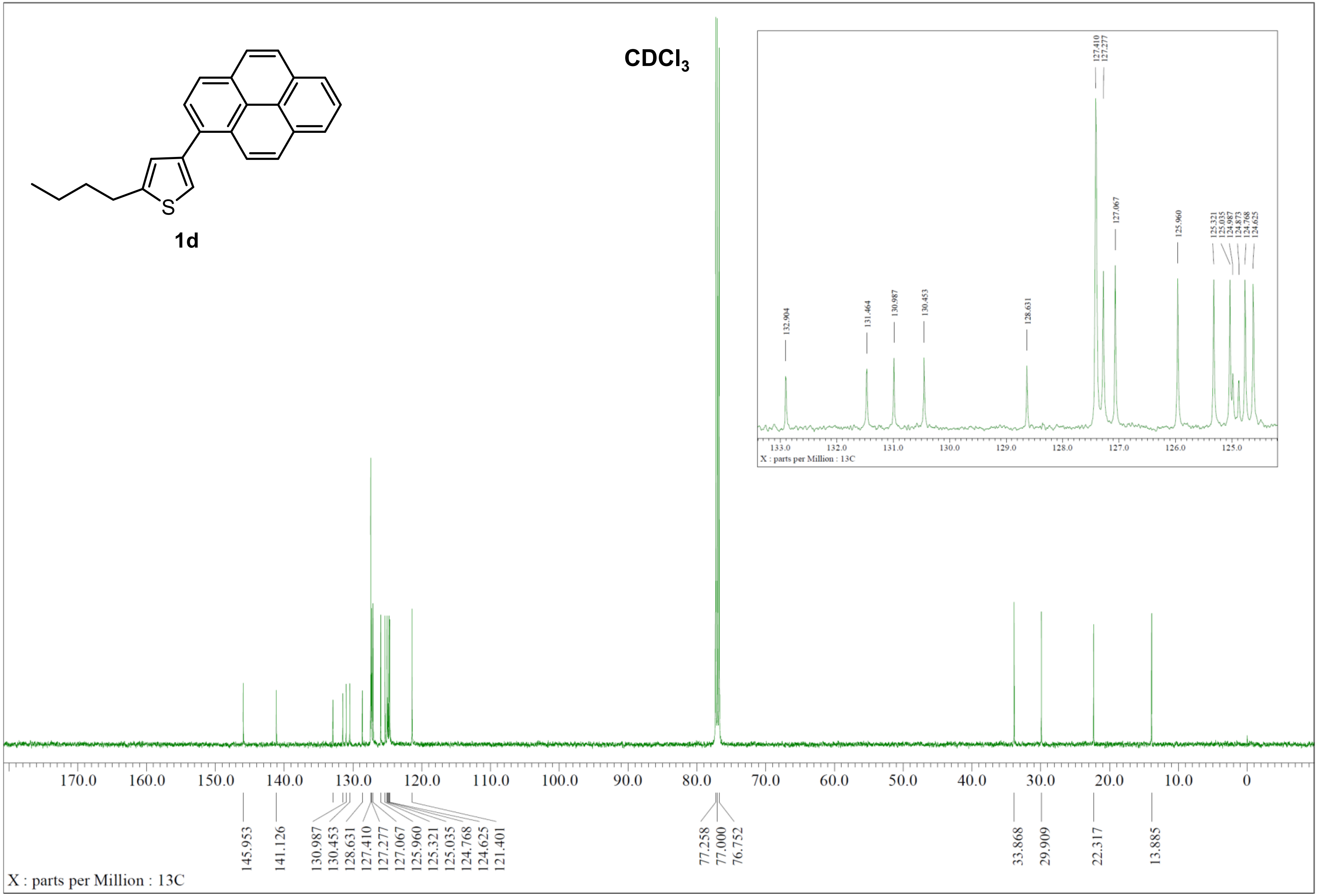
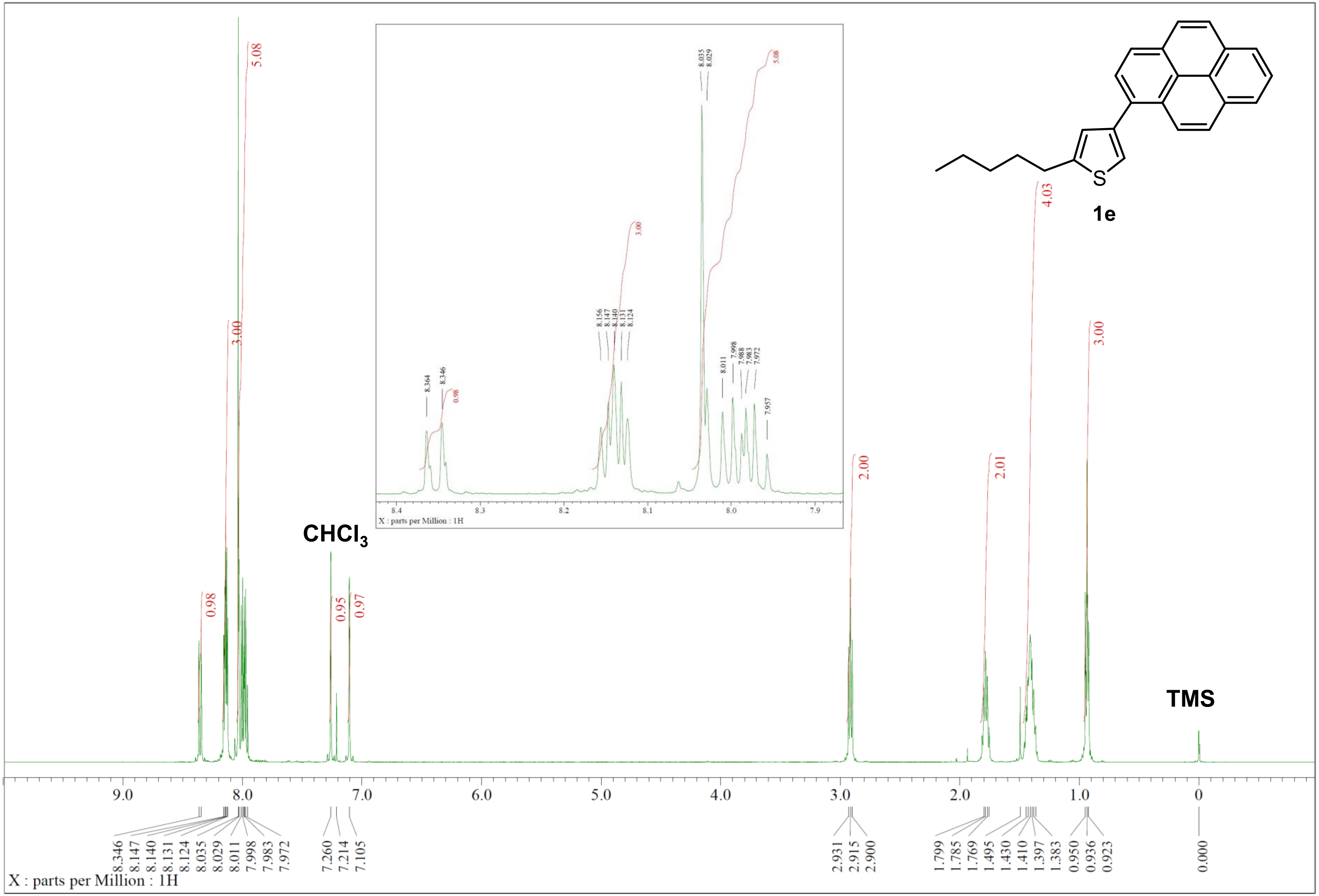
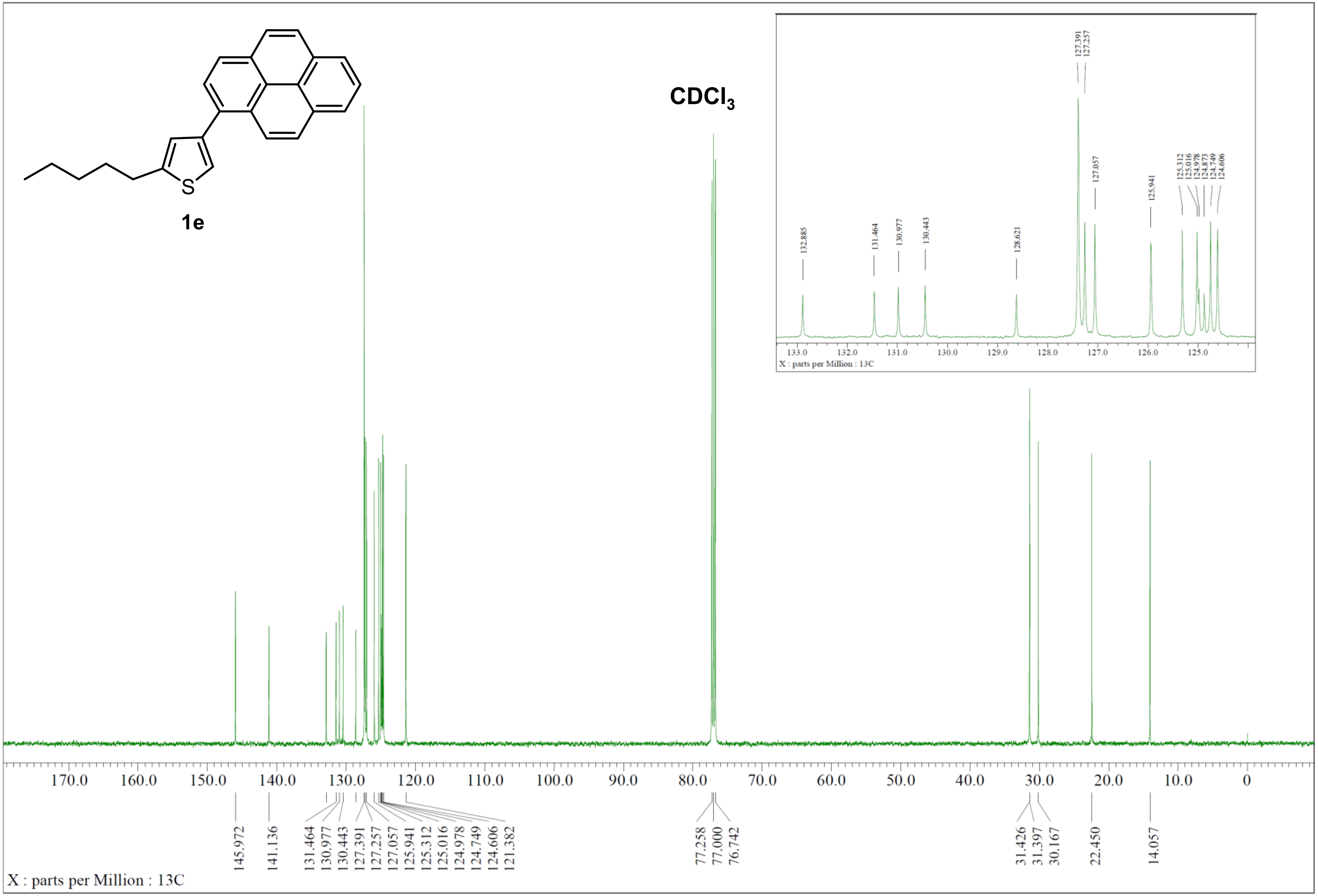


# $^1$H NMR spectrum of 1e (500 MHz, in $CDCl_3$, rt)

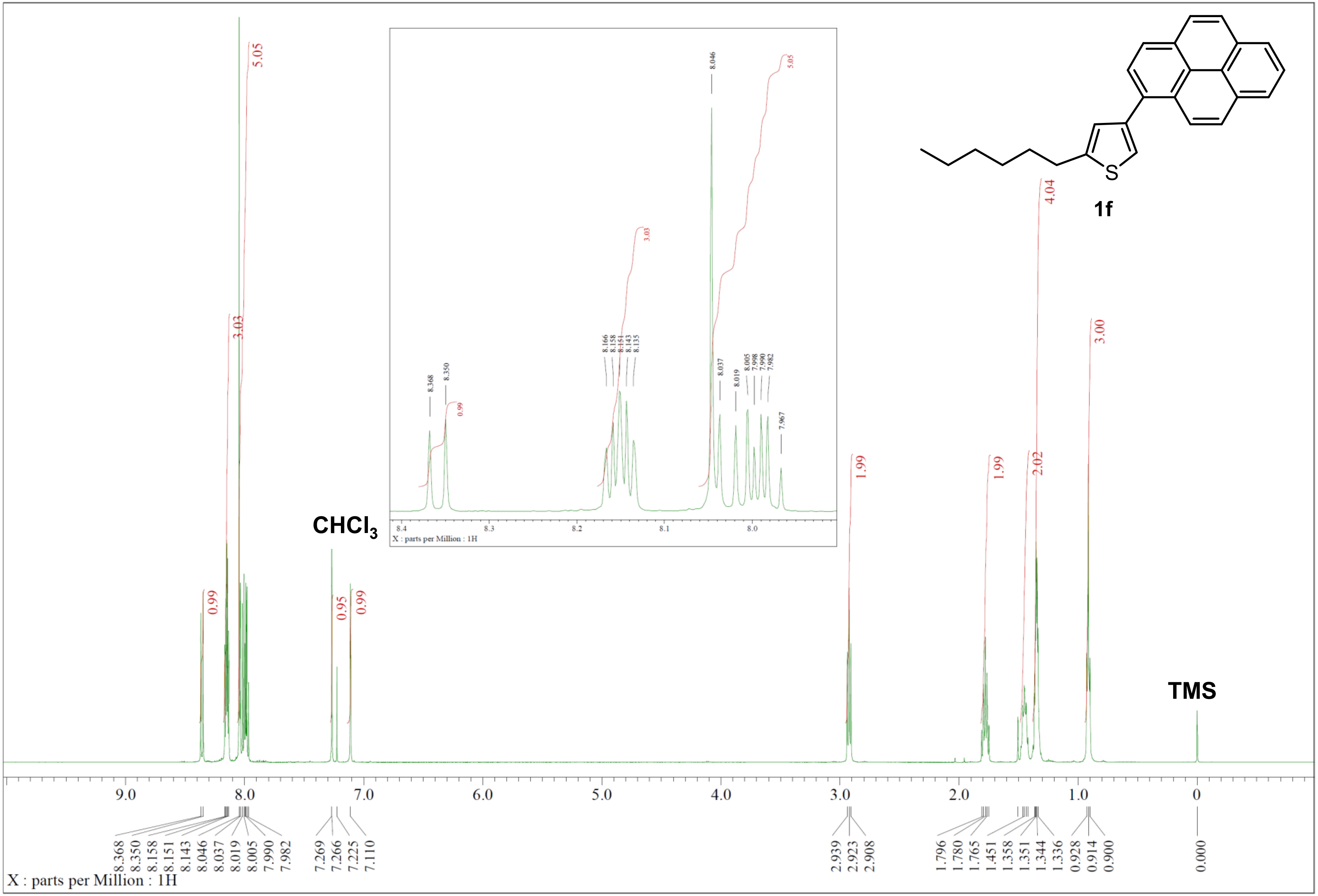


# $^{13}$C NMR spectrum of 1e (126 MHz, in $CDCl_3$, rt)



1e

# $^1$H NMR spectrum of 1f (500 MHz, in $CDCl_3$, rt)



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