Electronic Supplementary Information

Facile synthesis of picenes incorporating imide moieties at the both edges of the molecule and their application to *n*-channel field-effect transistors

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Contents

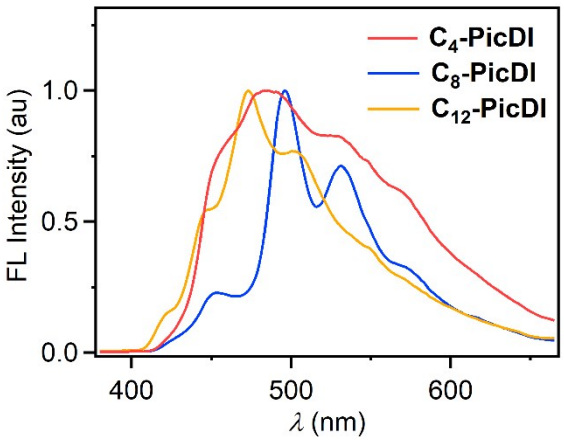


Fig. S1 Fluorescence spectra of **C_n-PicDI**s in the solid state.

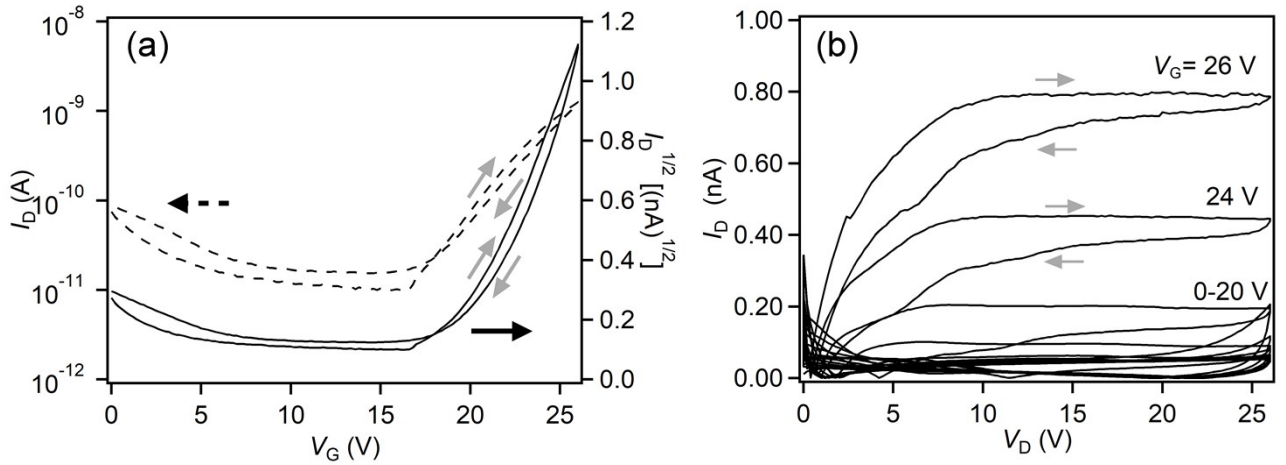


Fig. S2 Transfer (a) and output (b) curves of **C_4-PicDI** thin-film FETs with ZrO_2 gate dielectric. This FET refers to device #2 in Table S1.

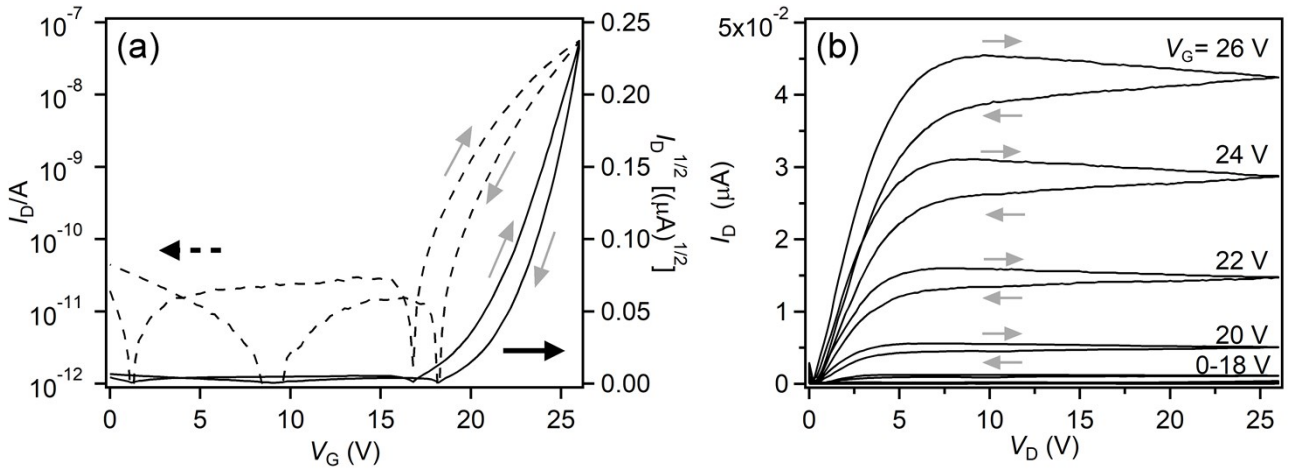


Fig. S3 Transfer (a) and output (b) curves of **C_{12}-PicDI** thin-film FETs with ZrO_2 gate dielectric. This FET refers to device #5 in Table S2.

Table S1 FET parameters of **C_4-PicDI** thin-film FET with ZrO_2 gate dielectric. The parameters were determined from the forward transfer curves [a]

sample	μ ($cm^2\ V^{-1}\ s^{-1}$)	$\lvert V_{th}\rvert$ (V)	on/off	S (V/decade)
#1	2.4×10^{-4}	19.4	1.3×10^2	4.1
#2	2.7×10^{-4}	20.0	1.2×10^2	3.9
#3	1.2×10^{-4}	17.7	0.45×10^2	5.3
#4	0.75×10^{-4}	17.8	1.2×10^2	4.1
average	$2(1)\times10^{-4}$	19(1)	$1.0(4) \times 10^2$	4.3(7)

[a] The parameters were determined from the forward transfer curves.

Table S2 FET parameters of **C_{12}-PicDI** thin-film FET with ZrO_2 gate dielectric. The parameters were determined from the forward transfer curves [a]

sample	μ ($cm^2\ V^{-1}\ s^{-1}$)	$\lvert V_{th}\rvert$ (V)	on/off	S (V/decade)
#1	1.5×10^{-2}	17.9	11×10^4	1.0
#2	0.97×10^{-2}	18.0	11×10^4	1.7
#3	1.1×10^{-2}	18.2	1.5×10^4	1.2
#4	1.8×10^{-2}	20.2	0.56×10^4	2.1
#5	1.9×10^{-2}	20.5	3.3×10^4	1.6
#6	1.4×10^{-2}	20.1	3.3×10^4	1.8
#7	1.5×10^{-2}	19.5	4.2×10^4	1.4
#8	1.3×10^{-2}	20.9	2.0×10^4	1.7
average	$1.4(3) \times 10^{-2}$	19(1)	$5(4) \times 10^4$	1.6(4)

[a] The parameters were determined from the forward transfer curves.

Experimental

General Information

^{1}H and ^{13}C NMR spectra were recorded on VARIAN NMR System 600 (600 MHz) and VARIAN 400-MR (400 MHz) and JEOL JNM-ECZ600R (600 MHz) spectrometers. IR spectra were recorded on a JASCO FT/IR-460 Plus spectrophotometer. Absorption spectra in solution were respectively obtained on a JASCO V-530 UV-VIS spectrophotometers. Absorption spectra of thin films of **C_n-PicDI**s, formed on a quartz substrate by thermal deposition under 10^{-7} Torr, were collected with a JASCO V-670 iRM EX spectorophotometer. Fluorescence spectra were collected on a JASCO FP-6300 spectrofluorometer.

Elemental analyses were measured on a PERKIN-ELMER 2400II CHN-S analyzer at the Micro Elemental Analysis Laboratory of Okayama University. High-resolution mass spectra (FAB) were recorded on a JEOL JMS-700 MStation spectrometer at Institute for Materials Chemistry and Engineering, Kyushu University.

Photoelectron yield spectroscopy (PYS) of the films of **C_n-PicDI**s was measured at room temperature using a PYS spectrometer (Bunko-keiki BIP-KV201). For the measurement of the PYS spectra, a 60-nm film of **C_n-PicDI**s was formed on a SiO_2/Si substrate.

The X-ray diffraction (XRD) patterns of thin films of **C_n-PicDI**s were measured with CuKα radiation (wavelength λ = 1.5418 Å) using a RIGAKU SMARTLAB-PRO at room temperature. For the XRD measurements, a 60-nm thin-film of **C_n-PicDI**s was formed on the SiO_2/Si substrate by thermal deposition under 10^{-7} Torr.

FET device fabrication and measurements of FET characteristics

60 nm thick thin-films of **C_n-PicDI**s were formed for an active layer on solid gate dielectrics of 150 nm thick ZrO_2 by a thermal deposition of **C_n-PicDI**s under a vacuum of 10^{-7} Torr. The surface of ZrO_2 was covered with 50 nm thick parylene. The ZrO_2 / Si substrates were heated at 100°C during the thermal deposition of **C_8-PicDI** and **C_{12}-PicDI**, and at 80°C during the thermal deposition of **C_4-PicDI**. The above temperatures are the general ones in heating the substrate of FETs with phenacene derivatives, and without heating the substrate, the device did not operate. The shape of the thin film

was determined by use of a metal mask. 3 nm thick 2,3,5,6-tetrafluoro-7,7,8,8-teracyano-quinodimethane (F4TCNQ) was deposited on the **C_n-PicDI**s' thin films under vacuum of 10^{-7} Torr, and the source and drain electrodes were formed by the thermal deposition of Au under vacuum of 10^{-7} Torr. The device structure is top-contact bottom-gate type.

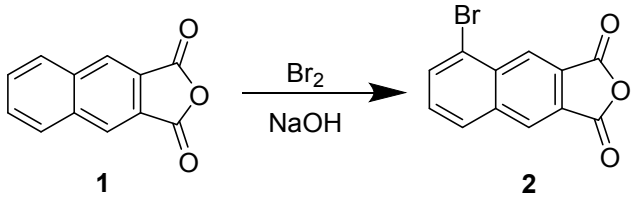
All measurements were made in two-terminal measurement mode at room temperature with an Agilent B1500A semiconductor parametric analyzer; the FET characteristics in FET devices were measured in an Ar-filled glove box. The measured transfer curves were analyzed to determine the FET parameters (μ, threshold voltage (V_{th}), on/off ratio and subthreshold swing (S)) using the general formula for a saturation regime:

$$I_D = \frac{\mu W C_o}{2L}(V_G - V_{th})^2,$$

where I_D, V_G, V_{th}, W, L and C_o refer to drain current, gate voltage, threshold voltage, channel width, channel length and capacitance per area of gate dielectric, respectively; the value of drain voltage, V_D, was fixed to 26 V in the measurement of the transfer curve. The capacitance, C_o, was determined by extrapolation of the capacitance recorded at 20 Hz –1.0 kHz to 0 Hz with an AC amplitude of 1 V using LCR meter (Agilent E4980A). The C_o value for the employed ZrO_2 gate dielectric was 3.89×10^{-8} F cm^{-2}. The condition for a saturation regime, $V_D > V_G - V_{th}$, was completely satisfied in the analysis of the transfer curve. The saturation was completely recorded in the output characteristics of all FET devices fabricated in this study.

Materials

4-Bromo-2,3-naphthalenedicarboxylic anhydride 2

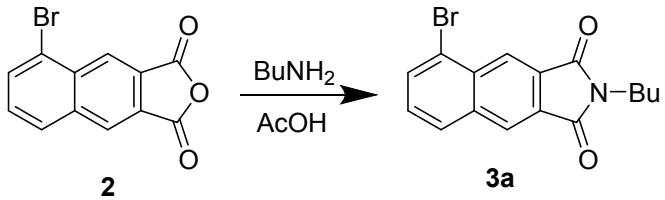


1 **2**

Compound **2** was prepared according to the method reported for bromination of phthalic anhydride.[S1] To a mixture of naphthalene-2,3-dicarboxylic anhydride **1** (2.0 g, 10.1 mmol) in aqueous NaOH (1

M, 20 ml) was dropwise added Br_2 (1 mL, 19.4 mmol). The reaction mixture was refluxed for *ca*. 16 h. After being cooled to room temperature, the solid formed was collected by suction filtration. The obtained solid was dissolved in a 1 : 1 mixture of MeOH and H_2O (40 ml) and acidified to pH 1.5 with conc. HCl. The resulting mixture was extracted with ether (4 × 60 ml) and the combined extracts were washed with $Na_2S_2O_3$ aq., dried over Na_2SO_4, and concentrated. The residue was recrystallized from MeCN to afford anhydride **2** (719 mg, 26%) as colorless crystals, mp 214–216°C. ^{1}H NMR (600 MHz, $CDCl_3$), δ_H 9.00 (s, 1H), 8.55 (s, 1H), 8.14–8.08 (m, 2H), 7.66 (dd, *J* = 8.1, 7.7 Hz, 1H), ^{13}C NMR (151 MHz, $CDCl_3$), δ_C 162.71, 162.60, 137.66, 135.28, 134.65, 130.88, 130.41, 128.27, 127.78, 127.31, 126.88, 125.51. IR (neat) ν_{max} 1837, 1793 (C=O), 1236, 1182 (CO) cm^{-1}. HRMS (FAB, *m/z*, MH^+) Calcd. for $C_{12}H_6{}^{79}BrO_3$: 276.9500. Found: 276.9503.

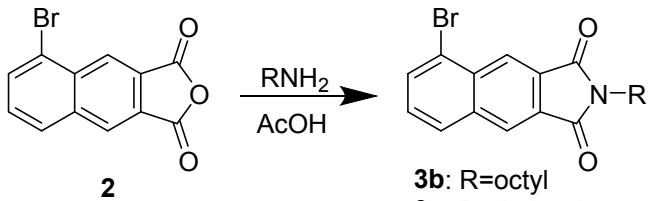
_N_-Butyl-4-bromonaphthalene-2,3-dicarboximide 3a



2 **3a**

To a solution of anhydride **2** (76 mg, 0.27 mmol) in acetic acid (2 mL) was added butylamine (50 µl mL, 0.50 mmol) and the mixture was refluxed for 17 h. After being cooled to r.t., the reaction mixture was poured into ice water (100 ml) and extracted with AcOEt (100 ml). The organic layer was washed with $NaHCO_3$ aq., dried over $MgSO_4$, and concentrated. The residue was chromatographed on silica gel (AcOEt) followed by recrystallization from a $CHCl_3$-hexane mixture to afford imide **3a** (79 mg, 87%) as colorless needle, mp 123–124°C. ^{1}H NMR (400 MHz, $CDCl_3$), δ_H 8.77 (s, 1H), 8.31 (s, 1H), 8.01(d, *J* = 8.3 Hz, 1H), 7.98 (dd, *J* = 7.5, 1.0 Hz, 1H), 7.53 (t, *J* = 7.9 Hz, 1H), 3.77(t, *J* = 7.3 Hz, 2H), 1.75–1.67 (m, 2H), 1.40 (sext, *J* = 7.5 Hz, 2H), 0.97 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (100MHz, $CDCl_3$), δ_C 167.89, 167.82, 137.02, 134.51, 133.30, 130.15, 129.49, 129.30, 128.80, 125.26, 124.87, 124.26, 38.36, 30.69, 20.28, 13.81. IR (neat) ν_{max} 1696 (C=O), 1400 (C-N) cm^{-1}. Anal. Calcd. for $C_{16}H_{14}BrNO_2$: C, 57.85; H, 4.25; N, 4.22. Found: C, 57.95; H, 4.08; N, 4.13.

***N*-octyl-4-bromonaphthalene-2,3-dicarboximide 3b and *N*-dodecyl-4-bromonaphthalene-2,3-dicarboximide 3c**



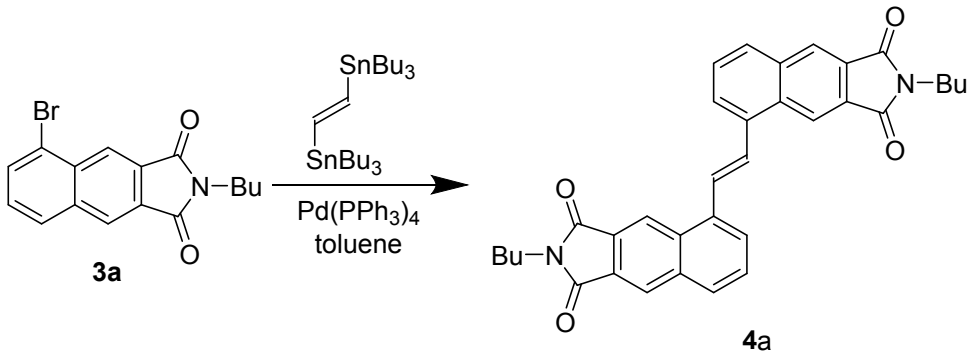
2 **3b**: R=octyl
3c: R=dodecyl

Compounds **3b** and **3c** were obtained via the same procedure for preparation of **3a** by using octylamine and dodecylamine, respectively.

3b: (yield: 83%). Colorless needles, mp 107–108°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ_H 8.77 (s, 1H), 8.31 (s, 1H), 8.01 (d, J = 8.3 Hz, 1H), 7.98 (dd, J = 7.5, 1.1 Hz, 1H), 7.53 (dd, J = 8.1, 7.6 Hz, 1H), 3.76 (t, J = 7.3 Hz, 2H), 1.72 (quin, J = 7.3 Hz, 2H), 1.41–1.18 (m, 10H), 0.87 (t, J = 6.9 Hz, 3H). ^{13}C NMR (100MHz, $CDCl_3$), δ_C 167.89, 167.82, 137.00, 134.49, 133.29, 130.15, 129.49, 129.28, 128.78, 125.25, 124.88, 124.26, 38.62, 31.91, 29.31 (two lines overlap), 28.66, 27.05, 22.77, 14.23. IR (neat) ν_{max} 2921 (C-H), 1693 (C=O), 1400 (C-N) cm^{-1}. Anal. Calcd. for $C_{20}H_{22}BrNO_2$: C, 61.86; H, 5.71; N, 3.61. Found: C, 61.86; H, 5.65; N, 3.56.

3c (yield: 89%). Colorless needles, mp 104–105°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ_H 8.78 (s, 1H), 8.31 (s, 1H), 8.01 (d, J = 8.3 Hz, 1H), 7.98 (dd, J = 7.5, 1.0 Hz, 1H), 7.53 (t, J = 7.8 Hz, 1H), 3.76 (t, J = 7.3 Hz, 2H), 1.72 (quin, J = 7.4 Hz, 2H), 1.41–1.18 (m, 18H), 0.87 (t, J = 6.9 Hz, 3H). ^{13}C NMR (100MHz, $CDCl_3$), δ_C 167.91, 167.84, 137.02, 134.51, 133.30, 130.16, 129.51, 129.30, 128.79, 125.27, 124.89, 124.28, 38.64, 32.05, 29.77, 29.76, 29.71, 29.64, 29.49, 29.36, 28.66, 27.06, 22.83, 14.28. IR (neat) ν_{max} 2920 (C-H), 1693 (C=O), 1400 (C-N) cm^{-1}. Anal. Calcd. for $C_{24}H_{30}BrNO_2$: C, 64.86; H, 6.80; N, 3.15. Found: C, 64.85; H, 6.79; N, 3.10.

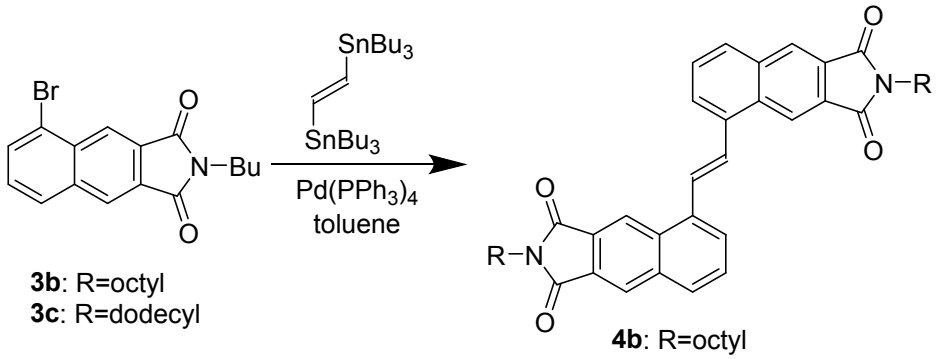
(*E*)-1,2-Bis(2-butyl-1,3-dihydro-1,3-dioxobenzo[*f*]-2*H*-isoindol-5-yl)ethene 4a



A round flask containing a solution of compound **3a** (483.6 mg, 1.44 mmol) and (*E*)-1,2-bis(tributylstannyl)ethene (411 mg, 0.7 mmol) in 15 ml toluene was deaerated by three evacuation-argon-refill cycles. $Pd(PPh_3)_4$ (63 mg, 3 mol%) was added to the mixture. The mixture was further purged with argon. The resulting solution was refluxed overnight. After being cooled to r.t., the solvent was removed and the residue was chromatographed on silica gel using a hexane-AcOEt mixture (5:1). The obtained crude product was recrystallized from a MeOH-$CHCl_3$ mixture to afford compound **4a** (312 mg, 84%) as yellow crystals, mp ＞300℃. ^{1}H NMR (600 MHz, $CDCl_3$): δ_H 8.72 (s, 1H), 8.38 (s, 1H), 8.10 (d, J = 7.3 Hz, 1H), 8,08 (d, J = 8.3 Hz, 1H) 7.99 (s, 1H), 7.79 (dd, J = 8.2, 7.4 Hz, 1H), 3.77 (t, J = 7.3 Hz, 2H), 1.75–1.67 (m, 2H), 1.40 (sext, J = 7.5 Hz, 2H), 0.96 (t, J = 7.4 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$): δ_C 168.40, 168.17, 137.29, 136.06, 133.55, 130.89, 129.61, 129.17, 128.32, 128.07, 127.37, 125.36, 120.53, 38.30, 30.74, 20.29, 13.81. IR (neat) ν_{max} 2378 (C-H), 1703 (C=C), 1489, 1338, 1057 cm^{-1}. Anal. Calcd. for $C_{34}H_{30}N_2O_4$: C, 76.96; H, 5.70; N, 5.28%. Found: C, 76.75; H, 5.33; N, 5.20%.

(*E*)-1,2-Bis(2-octyl-1,3-dihydro-1,3-dioxobenzo[*f*]-2*H*-isoindol-5-yl)ethene 4b and (*E*)-1,2-bis(2-dodecyl-1,3-dihydro-1,3-dioxobenzo[*f*]-2*H*-isoindol-5-yl)ethene 4c

Compounds **4b** and **4c** were obtained via the same procedure for preparation of **4a** by using substrates **3b** and **3c**, respectively.



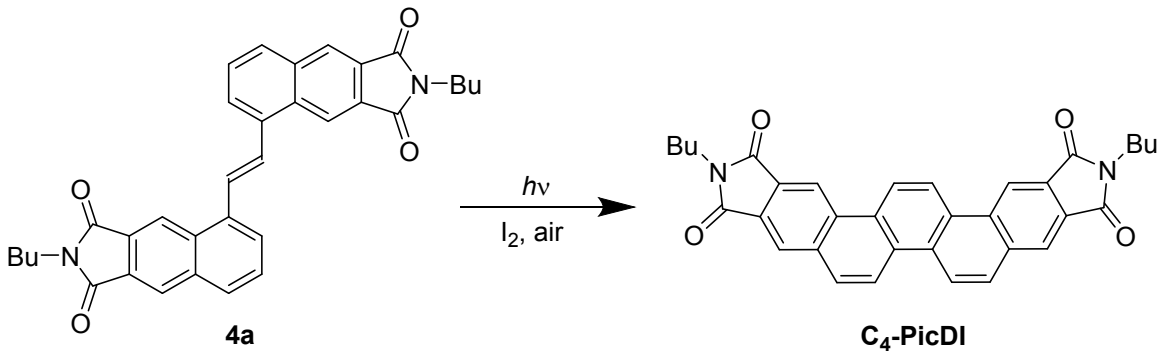
3b: R=octyl
3c: R=dodecyl

4b: R=octyl
4c: R=dodecyl

4b: (yield: 79%). Yellow crystals, mp 260–261°C. ^{1}H NMR (600 MHz, $CDCl_3$) δ_H 8.73 (s, 1H), 8.39 (s, 1H), 8.10 (d, J = 7.3 Hz, 1H), 8.08 (d, J = 8.3 Hz, 1H), 8.00 (s, 1H), 7.79 (dd, J = 8.0, 7.3 Hz, 1H), 3.75 (t, J = 7.4 Hz, 2H), 1.71 (quin, J = 7.4 Hz, 2H), 1.42–1.19 (m, 10H), 0.86 (t, J = 7.0 Hz, 3H). ^{13}C NMR (151MHz, $CDCl_3$) δ_C 168.41, 168.16, 137.28, 136.06, 133.54, 130.89, 129.59, 129.17, 128.32, 128.07, 127.37, 125.38, 120.53, 38.57, 31.91, 29.32 (two lines overlap), 28.71, 27.07, 22.77, 14.23. IR (neat) ν_{max} 2924 (C-H), 1764, 1707 (C=O), 1384 (C-N) cm^{-1}. Anal. Calcd. for $C_{42}H_{46}N_2O_4$: C, 78.47; H, 7.21; N, 4.36. Found: C, 78.62; H, 7.15; N, 4.37.

4c: (yield: 88%). Yellow crystals, mp 237–239°C. ^{1}H NMR (600 MHz, $CDCl_3$) δ_H 8.72 (s, 1H), 8.38 (s, 1H), 8.09 (d, J = 7.4 Hz, 1H), 8.07 (d, J = 8.1 Hz, 1H), 7.99 (s, 1H), 7.79 (t, J = 7.7 Hz, 1H), 3.75 (t, J = 7.4 Hz, 2H), 1.71 (quin, J = 7.3 Hz, 2H), 1.39–1.18 (m, 18H), 0.86 (t, J = 7.0 Hz, 3H). ^{13}C NMR (151MHz, $CDCl_3$) δ_C 168.40, 168.16, 137.29, 136.07, 133.56, 130.89, 129.60, 129.17, 128.34, 128.09, 127.37, 125.37, 120.52, 38.58, 32.05, 29.77, 29.76, 29.71, 29.65, 29.48, 29.37, 28.71, 27.08, 22.82, 14.26. IR (neat) ν_{max} 2921 (C-H), 1766, 1710 (C=O), 1384 (C-N) cm^{-1}. Anal. Calcd. for $C_{50}H_{62}N_2O_4$: C, 79.54; H, 8.28; N, 3.71. Found: C, 79.55; H, 8.33; N, 3.77.

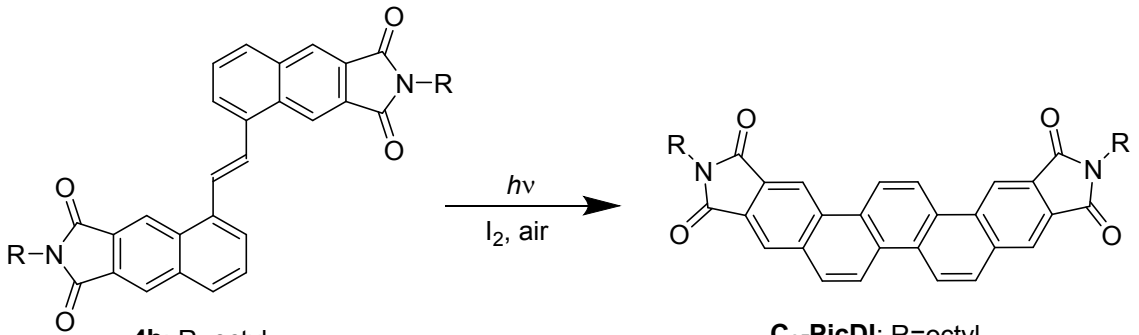
N,*N*'-Dibutylpicene-2,3,10,11-tetracarboxydiimide C_4-PicDI



4a **C_4-PicDI**

A solution of compound **4a** (217 mg, 0.4 mmol) and iodine (10 mg, 10 mol%) in 400 mL CH_2Cl_2 was purged with air and irradiated with black-light lamps (352 nm, 6 ×15 W) until TLC analysis revealed the complete consumption of **4a**. The solvent was removed under reduced pressure and the residue was dissolved in CH_2Cl_2 (100 ml). The solution was washed with saturated $Na_2S_2O_3$ solution 3 times, dried over $MgSO_4$, and concentrated. The residue was recrystallized from chlorobenzene to afford **C_4-PicDI** as pale yellow solid (130 mg, 60%), mp > 300°C. ^{1}H NMR (600 MHz, $CDCl_3$) δ_H 9.32 (s, 1H), 9.07 (s, 1H), 8.98 (d, J = 9.2 Hz, 1H), 8.48 (s, 1H), 8.25 (d, J = 9.0 Hz, 1H), 3.82 (t, J = 7.4 Hz, 2H), 1.80–1.72 (m, 2H), 1.45 (sext, J = 7.5 Hz, 2H), 1.00 (t, J = 7.4 Hz, 3H). ^{13}C NMR (151 MHz, 50°C) δ_H 168.44, 168.16, 135.38, 133.72, 130.48, 130.20, 129.68, 129.59, 129.06, 124.83, 124.58, 123.37, 119.62, 38.436, 30.852, 20.354, 13.77. IR (neat) ν_{max} 2912 (C-H), 1736 (C=C), 1261, 1120, 781cm^{-1}. Anal. Calcd. for $C_{34}H_{28}N_2O_4$: C, 77.25; H, 5.34; N, 5.16%. Found: C, 77.55; H, 5.06; N, 5.16%.

_N_,_N_'-Dioctyl-picene-2,3,10,11-tetracarboxydiimide C_8-PicDI and _N_,_N_'-Didodecyl-picene-2,3,10,11-tetracarboxydiimide C_{12}-PicDI



4b: R=octyl
4c: R=dodecyl

C_8-PicDI: R=octyl
C_{12}-PicDI: R=dodecyl

C_8-PicDI and **C_{12}-PicDI** were prepared by the same procedure for the synthesis of **C_4-PicDI** by using

4b and **4c**, respectively.

C_8-PicDI (yield: 54%). Pale yellow solid, mp >300°C. ^{1}H NMR (600 MHz, $CDCl_3$) δ_H 9.08 (s, 1H), 8.88 (d, *J* = 9.4 Hz, 1H), 8.80 (s, 1H), 8.35 (s, 1H), 8.16 (d, *J* = 9.0 Hz, 1H), 3.77 (t, *J* = 7.5 Hz, 2H), 1.76 (quin, J = 7.4 Hz, 2H), 1.44–1.22 (m, 10H), 0.88 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ_C 168.33, 167.99, 135.01, 133.25, 129.99, 129.78, 129.27, 129.18, 128.90, 124.64, 124.33, 122.95, 119.29, 38.61, 31.95, 29.36 (two lines overlap), 28.78, 27.13, 22.80, 14.25. IR (neat) ν_{max} 2924 (C-H), 1763, 1711 (C=O), 1388 (C-N) cm^{-1}, HRMS (FAB, *m/z*, M^+) Calcd. for $C_{42}H_{44}N_2O_4$: 640.3301. Found: 640.3277.

C_{12}-PicDI (yield: 82%). Pale yellow solid, mp >300°C. ^{1}H NMR (600 MHz, $CDCl_3$) δ_H 9.11 (s, 1H), 8.89 (d, *J* = 9.4 Hz, 1H), 8.84 (s, 1H), 8.37 (s, 1H), 8.18 (d, *J* = 9.0 Hz, 1H), 3.78 (t, *J* = 7.4 Hz, 2H), 1.75 (quin, *J* = 7.4 Hz, 2H), 1.43–1.18 (m, 18H), 0.86 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ_C 168.36, 168.03, 135.02, 133.26, 130.00, 129.80, 129.25, 129.17, 128.91, 124.66, 124.36, 122.98, 119.33, 38.61, 32.06, 29.80, 29.78, 29.75, 29.70, 29.51, 29.40, 28.78, 27.13, 22.84, 14.29. IR (neat) ν_{max} 2917 (C-H), 1765, 1698 (C=O), 1391 (C-N) cm^{-1}. Anal. Calcd. for $C_{50}H_{60}N_2O_4$: C, 79.75; H, 8.03; N, 3.72. Found: C, 79.64; H, 8.03; N, 3.74.

Theoretical calculations

Theoretical calculations were performed by using GAUSSIAN 09 Revision C. 01 package.[S2] The ground-state geometry of picene and **C_n-PicDI**s (n = 4, 8, 12) were optimized by density functional theory (DFT) using B3LYP functional[S3,S4] with 6-31+G(d) basis set. The optimized atomic coordinates were listed in Tables S3–S6.

The inclined angles (Fig. 3(b)) were evaluated by using the calculated geometries of **C_n-PicDI**s.

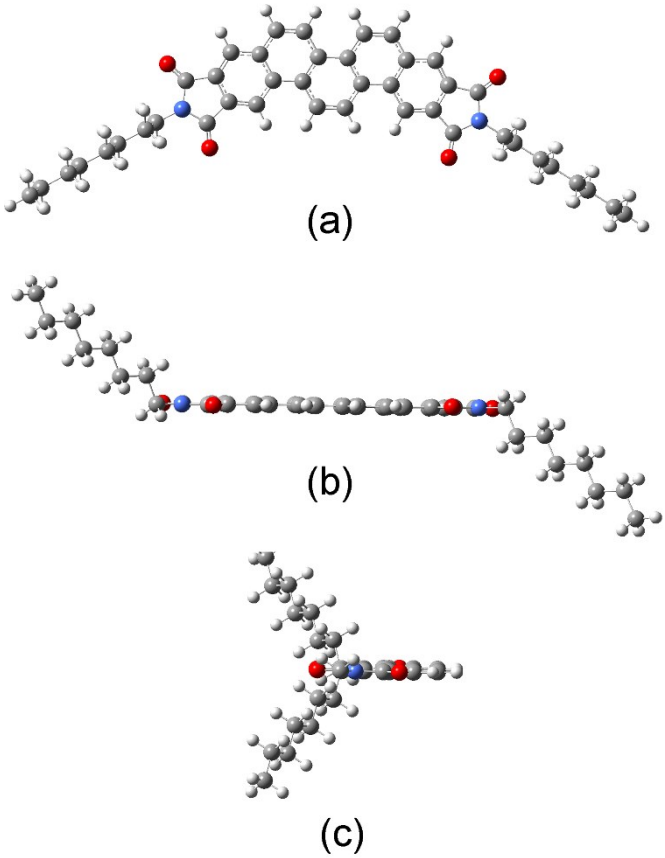


Fig. S4 Calculated molecular structure of **C_8-PicDI**: (a) Top view; (b), (c) side views.

Calculated coordinates

Table S3 Optimized ground state geometry of picene
(Total energy −846.85214037 au)

atom	x	y (angstrom)	z
C	0.00000000	5.73131500	-0.38378400
C	0.00000000	5.00891100	0.79315700
C	0.00000000	3.59200300	0.77954500
C	0.00000000	2.89201600	-0.46367200

C	0.00000000	3.66410500	-1.65365600
C	0.00000000	5.04741700	-1.61725500
C	0.00000000	2.84216600	1.99623700
C	0.00000000	1.43653500	-0.45925800
C	0.00000000	0.72458700	0.77019000
C	0.00000000	1.47746500	1.99196300
C	0.00000000	-0.72458700	0.77019000
C	0.00000000	-1.43653500	-0.45925800
C	0.00000000	-0.68528200	-1.66739000
C	0.00000000	0.68528200	-1.66739000
H	0.00000000	3.38299300	2.94003900
H	0.00000000	6.81793900	-0.36230000
H	0.00000000	5.52081500	1.75312100
H	0.00000000	3.17492400	-2.62138000
H	0.00000000	5.60939600	-2.54772100
H	0.00000000	0.96232100	2.94479200
H	0.00000000	-1.19700300	-2.62299700
H	0.00000000	1.19700300	-2.62299700
C	0.00000000	-1.47746500	1.99196300
C	0.00000000	-2.84216600	1.99623700
H	0.00000000	-3.38299300	2.94003900
C	0.00000000	-3.59200300	0.77954500
C	0.00000000	-2.89201600	-0.46367200
H	0.00000000	-0.96232100	2.94479200
C	0.00000000	-5.00891100	0.79315700
C	0.00000000	-5.73131500	-0.38378400
H	0.00000000	-6.81793900	-0.36230000
C	0.00000000	-5.04741700	-1.61725500
H	0.00000000	-5.60939600	-2.54772100
C	0.00000000	-3.66410500	-1.65365600
H	0.00000000	-3.17492400	-2.62138000
H	0.00000000	-5.52081500	1.75312100

Table S4 Optimized ground state geometry of **C_4-PicDI** (Total energy −1723.10764212 au)

atom	x	y	z
		(angstrom)	
C	0.02161300	-5.69925600	0.90722400
C	0.03274800	-5.01352500	2.09485900
C	0.02456500	-3.59044300	2.05776700
C	0.00773400	-2.88805500	0.80800100
C	-0.00701800	-3.64432000	-0.39910000
C	-0.00009100	-5.01570500	-0.32580500
C	0.03228100	-2.84140400	3.27220300
C	0.00406300	-1.43527100	0.81356900
C	0.00552800	-0.72503600	2.04548500
C	0.02103100	-1.47501400	3.26603900
C	-0.00552800	0.72503600	2.04548500
C	-0.00406300	1.43527100	0.81356900
C	-0.00084500	0.68465300	-0.39721600
C	0.00084500	-0.68465300	-0.39721600
H	0.04664000	-3.38051700	4.21563700
H	0.04660400	-5.53038400	3.05059000
H	-0.02582300	-3.16519400	-1.37062500
H	0.02783700	-0.96174000	4.21937800
H	-0.00235300	1.19308000	-1.35370500
H	0.00235300	-1.19308000	-1.35370500

C	-0.02103100	1.47501400	3.26603900
C	-0.03228100	2.84140400	3.27220300
H	-0.04664000	3.38051700	4.21563700
C	-0.02456500	3.59044300	2.05776700
C	-0.00773400	2.88805500	0.80800100
H	-0.02783700	0.96174000	4.21937800
C	-0.03274800	5.01352500	2.09485900
C	-0.02161300	5.69925600	0.90722400
C	0.00009100	5.01570500	-0.32580500
C	0.00701800	3.64432000	-0.39910000
H	0.02582300	3.16519400	-1.37062500
H	-0.04660400	5.53038400	3.05059000
C	-0.02305200	7.16042200	0.62236100
C	0.02305200	-7.16042200	0.62236100
C	0.01678300	6.03298500	-1.41211900
C	-0.01678300	-6.03298500	-1.41211900
O	-0.03527100	8.09739700	1.40612400
O	0.03527100	-8.09739700	1.40612400
O	0.04595400	5.86675100	-2.62214600
O	-0.04595400	-5.86675100	-2.62214600
N	-0.00084500	7.28194100	-0.77424000
N	0.00084500	-7.28194100	-0.77424000
C	0.00230100	8.56059300	-1.48363300
H	0.52476400	9.27836100	-0.84467700
H	0.58990600	8.41968700	-2.39556600
C	-0.00230100	-8.56059300	-1.48363300
H	-0.52476400	-9.27836100	-0.84467700
H	-0.58990600	-8.41968700	-2.39556600
C	-1.40862300	9.06160800	-1.82103900
H	-1.91949900	8.30791700	-2.43492400
H	-1.98488700	9.16427400	-0.89176300
C	1.40862300	-9.06160800	-1.82103900
H	1.91949900	-8.30791700	-2.43492400
H	1.98488700	-9.16427400	-0.89176300
C	-1.38051700	10.40348800	-2.56492500
H	-0.86125000	11.15047800	-1.94775200
H	-0.78891500	10.29650800	-3.48531700
C	1.38051700	-10.40348800	-2.56492500
H	0.86125000	-11.15047800	-1.94775200
H	0.78891500	-10.29650800	-3.48531700
C	-2.78204300	10.91680200	-2.91606800
H	-3.38795500	11.06213800	-2.01257700
H	-2.73183100	11.87698100	-3.44313400
H	-3.31268500	10.20694800	-3.56333600
C	2.78204300	-10.91680200	-2.91606800
H	3.38795500	-11.06213800	-2.01257700
H	2.73183100	-11.87698100	-3.44313400
H	3.31268500	-10.20694800	-3.56333600

Table S5 Optimized ground state geometry of **C_8-PicDI** (Total energy −2037.60841182 au)

atom	x	y (angstrom)	z
C	-0.47341131	-5.67960103	0.90722406
C	-0.40276718	-4.99742773	2.09485906

C	-0.28733401	-3.57901153	2.05776706
C	-0.24310368	-2.87781551	0.80800106
C	-0.32347655	-3.62994221	-0.39909994
C	-0.43567143	-4.99674765	-0.32580494
C	-0.21459809	-2.83347250	3.27220306
C	-0.12059614	-1.43020136	0.81356906
C	-0.05745746	-0.72277687	2.04548506
C	-0.10714366	-1.47126777	3.26603906
C	0.05745746	0.72277687	2.04548506
C	0.12059614	1.43020136	0.81356906
C	0.05861577	0.68213975	-0.39721594
C	-0.05861577	-0.68213975	-0.39721594
H	-0.24711173	-3.37179570	4.21563706
H	-0.43384931	-5.51353733	3.05059006
H	-0.30060159	-3.15099327	-1.37062494
H	-0.05578892	-0.96052398	4.21937806
H	0.10126699	1.18877686	-1.35370494
H	-0.10126699	-1.18877686	-1.35370494
C	0.10714366	1.47126777	3.26603906
C	0.21459809	2.83347250	3.27220306
H	0.24711173	3.37179570	4.21563706
C	0.28733401	3.57901153	2.05776706
C	0.24310368	2.87781551	0.80800106
H	0.05578892	0.96052398	4.21937806
C	0.40276718	4.99742773	2.09485906
C	0.47341131	5.67960103	0.90722406
C	0.43567143	4.99674765	-0.32580494
C	0.32347655	3.62994221	-0.39909994
H	0.30060159	3.15099327	-1.37062494
H	0.43384931	5.51353733	3.05059006
C	0.59887034	7.13537167	0.62236106
C	-0.59887034	-7.13537167	0.62236106
C	0.54064440	6.00873475	-1.41211894
C	-0.54064440	-6.00873475	-1.41211894
O	0.66806758	8.06986790	1.40612406
O	-0.66806758	-8.06986790	1.40612406
O	0.55526887	5.84059548	-2.62214594
O	-0.55526887	-5.84059548	-2.62214594
N	0.63154656	7.25450304	-0.77423994
N	-0.63154656	-7.25450304	-0.77423994
C	0.74572314	8.52805106	-1.48363294
H	1.32854566	9.19773486	-0.84467694
H	1.31887140	8.33664780	-2.39556594
C	-0.74572314	-8.52805106	-1.48363294
H	-1.32854566	-9.19773486	-0.84467694
H	-1.31887140	-8.33664780	-2.39556594
C	-0.61636052	9.14970262	-1.82103894
H	-1.19075949	8.44322528	-2.43492394
H	-1.18153152	9.30202546	-0.89176294
C	0.61636052	-9.14970262	-1.82103894
H	1.19075949	-8.44322528	-2.43492394
H	1.18153152	-9.30202546	-0.89176294
C	-0.47182731	10.48407215	-2.56492494
H	0.11034903	11.18314510	-1.94775194
H	0.10824910	10.32611960	-3.48531694
C	0.47182731	-10.48407215	-2.56492494
H	-0.11034903	-11.18314510	-1.94775194
H	-0.10824910	-10.32611960	-3.48531694
C	-1.82348039	11.11716009	-2.91606794
H	-2.41448177	11.31456645	-2.01257694
H	-2.41376373	10.45607068	-3.56333594
C	1.82348039	-11.11716009	-2.91606794

H	2.41448177	-11.31456645	-2.01257694
H	2.41376373	-10.45607068	-3.56333594
C	-1.63610994	12.45450948	-3.65633067
C	-2.95374783	13.17486972	-3.77925613
H	-1.20705086	12.24195252	-4.66541572
H	-0.90029393	13.07256557	-3.08699140
C	-2.80160485	14.49578502	-4.50381631
H	-3.68656952	12.52911434	-4.33168731
H	-3.36631970	13.37635828	-2.75533983
C	-4.11928047	15.21610210	-4.62678626
H	-2.06880918	15.14153074	-3.95139563
H	-2.37467888	14.31332684	-5.52538384
H	-3.98359925	16.18593516	-5.16340840
H	-4.85504236	14.59790081	-5.19603670
H	-4.54837700	15.42834722	-3.61763185
C	1.63610994	-12.45450948	-3.65633067
C	2.94590862	-13.19427286	-3.74221845
H	1.23669090	-12.23967426	-4.67703389
H	0.87677321	-13.05968715	-3.10430398
C	2.79357836	-14.51563772	-4.46591906
H	3.70221294	-12.56129064	-4.27751756
H	3.32862112	-13.39774590	-2.70715920
C	4.10341654	-15.25535867	-4.55185046
H	2.03730047	-15.14861070	-3.93062979
H	2.39618043	-14.33097680	-5.49893998
H	3.96772976	-16.22519378	-5.08846749
H	4.86269896	-14.65003469	-5.10379027
H	4.50287574	-15.46988235	-3.53107802

Table S6 Optimized ground state geometry of **C_{12}-PicDI** (Total energy −2037.60841182 au)

atom	x	y (angstrom)	z
C	0.01038400	5.70074800	-2.74700600
C	0.01500000	5.01495300	-3.93484700
C	0.01017000	3.59254500	-3.89903800
C	0.00178100	2.88858500	-2.64998000
C	-0.00629900	3.64452700	-1.44343900
C	-0.00177700	5.01582400	-1.51580300
C	0.01310600	2.84226800	-5.11299900
C	0.00082600	1.43562600	-2.65708900
C	0.00197200	0.72485500	-3.88810400
C	0.00795200	1.47654000	-5.10776400
C	-0.00197200	-0.72485500	-3.88810400
C	-0.00082600	-1.43562600	-2.65708900
C	0.00009400	-0.68452100	-1.44718500
C	-0.00009400	0.68452100	-1.44718500
H	0.01913200	3.38227000	-6.05653200
H	0.02191800	5.53670800	-4.88830100
H	-0.01702500	3.16957100	-0.46948400
H	0.00979300	0.96281800	-6.06120100
H	-0.00054300	-1.19478500	-0.49137700
H	0.00054300	1.19478500	-0.49137700
C	-0.00795200	-1.47654000	-5.10776400
C	-0.01310600	-2.84226800	-5.11299900
H	-0.01913200	-3.38227000	-6.05653200
C	-0.01017000	-3.59254500	-3.89903800

C	-0.00178100	-2.88858500	-2.64998000
H	-0.00979300	-0.96281800	-6.06120100
C	-0.01500000	-5.01495300	-3.93484700
C	-0.01038400	-5.70074800	-2.74700600
C	0.00177700	-5.01582400	-1.51580300
C	0.00629900	-3.64452700	-1.44343900
H	0.01702500	-3.16957100	-0.46948400
H	-0.02191800	-5.53670800	-4.88830100
C	-0.01391400	-7.16520000	-2.46254000
C	0.01391400	7.16520000	-2.46254000
C	0.01017000	-6.03037800	-0.42320500
C	-0.01017000	6.03037800	-0.42320500
O	-0.02084800	-8.09861200	-3.24465200
O	0.02084800	8.09861200	-3.24465200
O	0.02779600	-5.85863000	0.78259100
O	-0.02779600	5.85863000	0.78259100
N	-0.00082600	-7.28097200	-1.06266200
N	0.00082600	7.28097200	-1.06266200
C	-0.00752500	-8.55572800	-0.34902700
H	0.50800200	-9.28015800	-0.98663800
H	0.57735400	-8.41284400	0.56486500
C	0.00752500	8.55572800	-0.34902700
H	-0.50800200	9.28015800	-0.98663800
H	-0.57735400	8.41284400	0.56486500
C	-1.42280100	-9.04370200	-0.00968900
H	-1.93148000	-8.27229400	0.58342200
H	-1.99148200	-9.16463800	-0.94135800
C	1.42280100	9.04370200	-0.00968900
H	1.93148000	8.27229400	0.58342200
H	1.99148200	9.16463800	-0.94135800
C	-1.40579200	-10.36657800	0.76757200
H	-0.88576800	-11.13362600	0.17416200
H	-0.81831100	-10.23846400	1.68922600
C	1.40579200	10.36657800	0.76757200
H	0.88576800	11.13362600	0.17416200
H	0.81831100	10.23846400	1.68922600
C	-2.80952800	-10.87152400	1.13022300
H	-3.39400800	-11.01169900	0.20842000
H	-3.33317400	-10.09660900	1.71007800
C	2.80952800	10.87152400	1.13022300
H	3.39400800	11.01169900	0.20842000
H	3.33317400	10.09660900	1.71007800
C	-2.80016500	-12.18145500	1.93018400
C	-4.20272600	-12.68360700	2.30039300
H	-2.21219200	-12.03926800	2.84975100
H	-2.27759600	-12.95781300	1.35080600
C	-4.19393700	-13.98461600	3.11500600
H	-4.72766600	-11.90259100	2.87137900
H	-4.78863200	-12.83473100	1.38090200
C	-5.59596400	-14.48381300	3.49111000
H	-3.67123000	-14.76713600	2.54399200
H	-3.60545300	-13.83288100	4.03281200
H	-6.11994700	-13.69869100	4.05739900
H	-6.18347800	-14.64106400	2.57363000
C	2.80016500	12.18145500	1.93018400
C	4.20272600	12.68360700	2.30039300
H	2.21219200	12.03926800	2.84975100
H	2.27759600	12.95781300	1.35080600
C	4.19393700	13.98461600	3.11500600
H	4.72766600	11.90259100	2.87137900
H	4.78863200	12.83473100	1.38090200
C	5.59596400	14.48381300	3.49111000

H	3.67123000	14.76713600	2.54399200
H	3.60545300	13.83288100	4.03281200
H	6.11994700	13.69869100	4.05739900
H	6.18347800	14.64106400	2.57363000
C	5.58692200	15.77946800	4.31426400
C	6.98855300	16.27679100	4.69377900
H	4.99798500	15.62199700	5.23083800
H	5.06441900	16.56558000	3.74791800
C	6.98081500	17.57026800	5.52030800
H	7.51230800	15.49031900	5.25869300
H	7.57773800	16.43691200	3.77764400
C	8.38554900	18.05821100	5.89475800
H	6.45878000	18.35698800	4.95612300
H	6.39309600	17.41076600	6.43621900
H	8.34557700	18.98289700	6.48324000
H	8.92042500	17.30705700	6.49039300
H	8.98722300	18.25920900	4.99880000
C	-5.58692200	-15.77946800	4.31426400
C	-6.98855300	-16.27679100	4.69377900
H	-4.99798500	-15.62199700	5.23083800
H	-5.06441900	-16.56558000	3.74791800
C	-6.98081500	-17.57026800	5.52030800
H	-7.51230800	-15.49031900	5.25869300
H	-7.57773800	-16.43691200	3.77764400
C	-8.38554900	-18.05821100	5.89475800
H	-6.45878000	-18.35698800	4.95612300
H	-6.39309600	-17.41076600	6.43621900
H	-8.34557700	-18.98289700	6.48324000
H	-8.92042500	-17.30705700	6.49039300
H	-8.98722300	-18.25920900	4.99880000

Additional References

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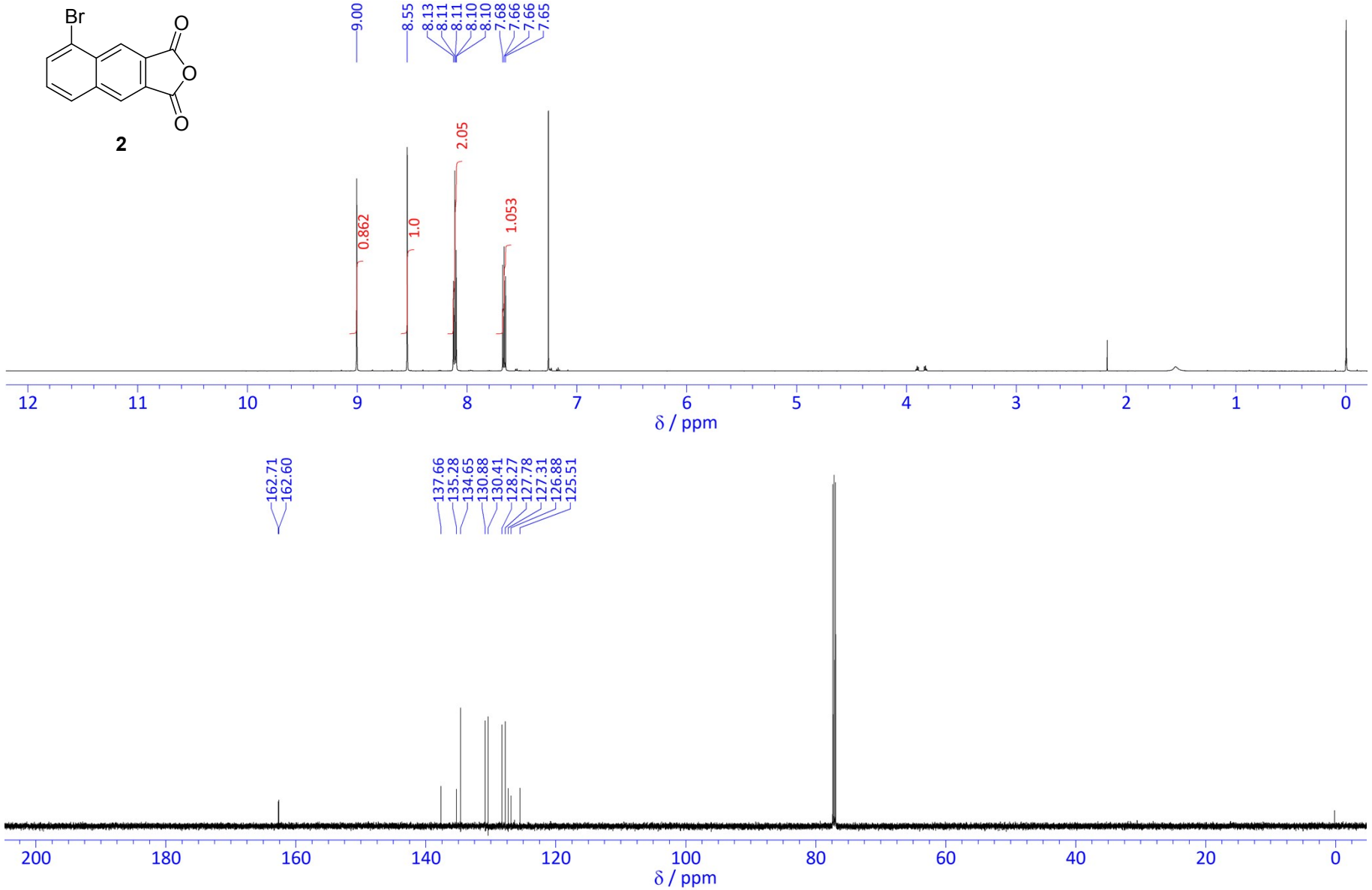

Fig. S5 ^{1}H (600 MHz, upper) and ^{13}C (151 MHz, lower) NMR spectra of compound **2** in $CDCl_3$.

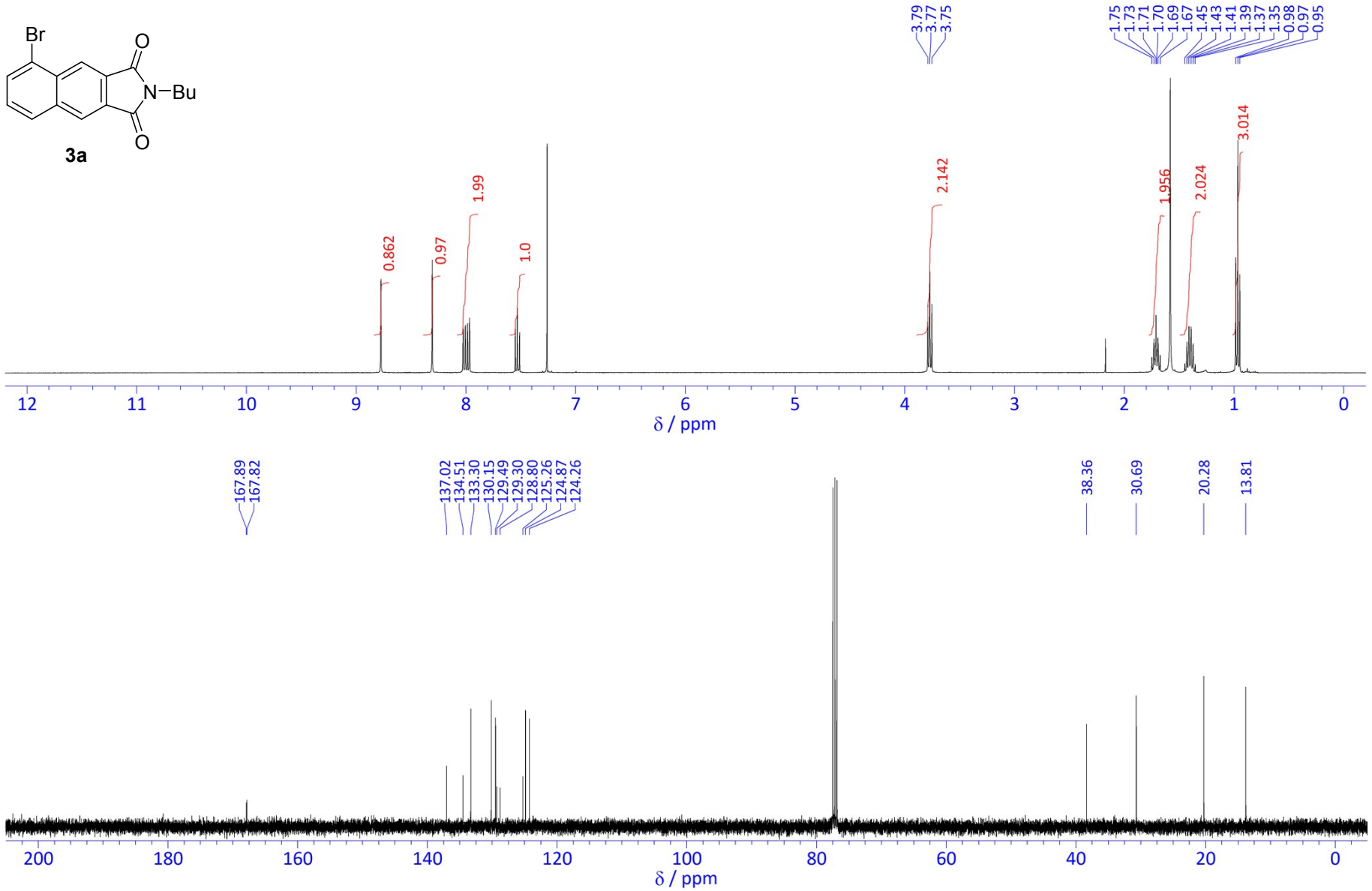

Fig. S6 ^{1}H (400 MHz, upper) and ^{13}C (100 MHz, lower) NMR spectra of compound **3a** in $CDCl_3$.

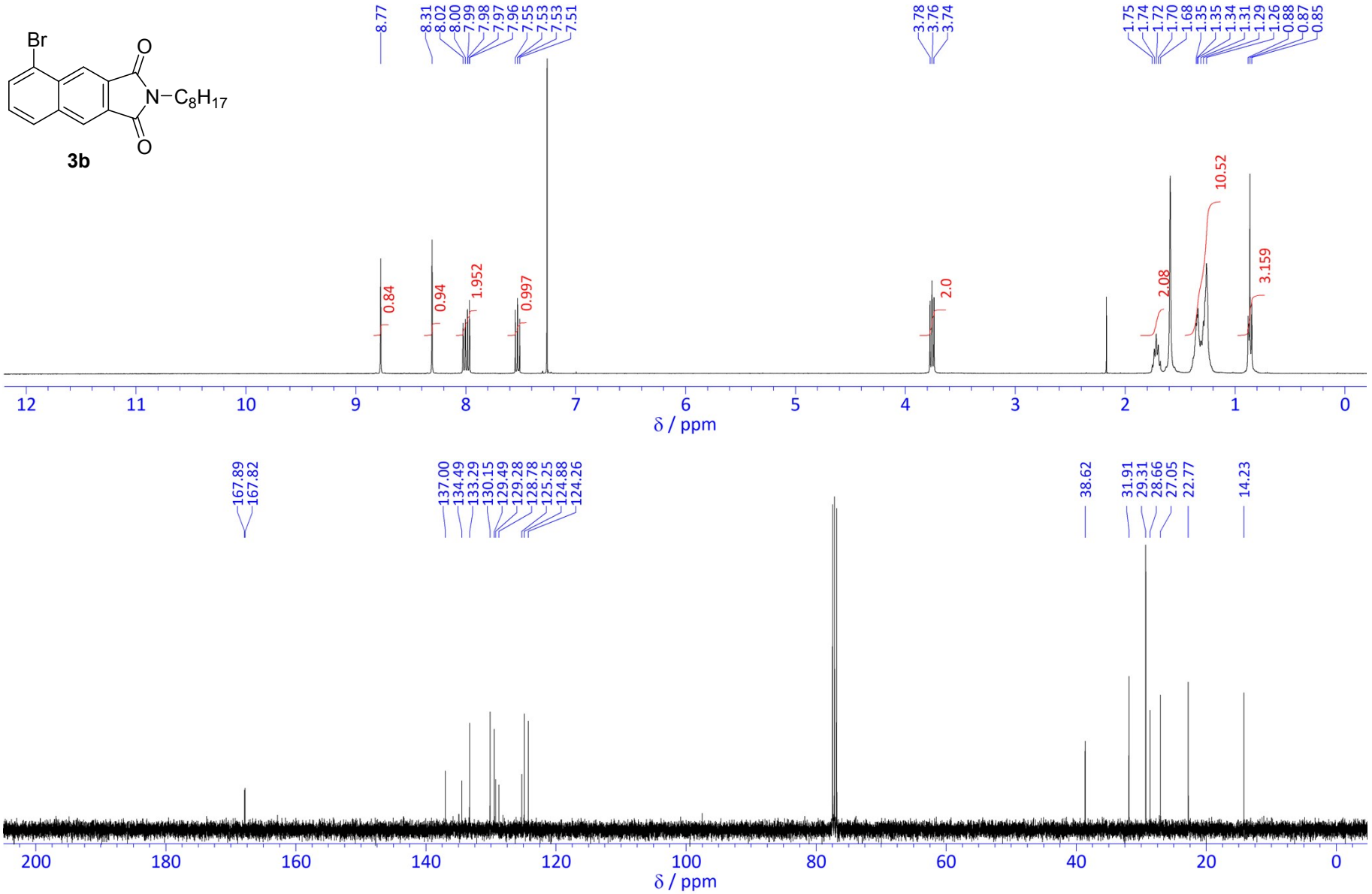

Fig. S7 ^{1}H (400 MHz, upper) and ^{13}C (100 MHz, lower) NMR spectra of compound **3b** in $CDCl_3$.

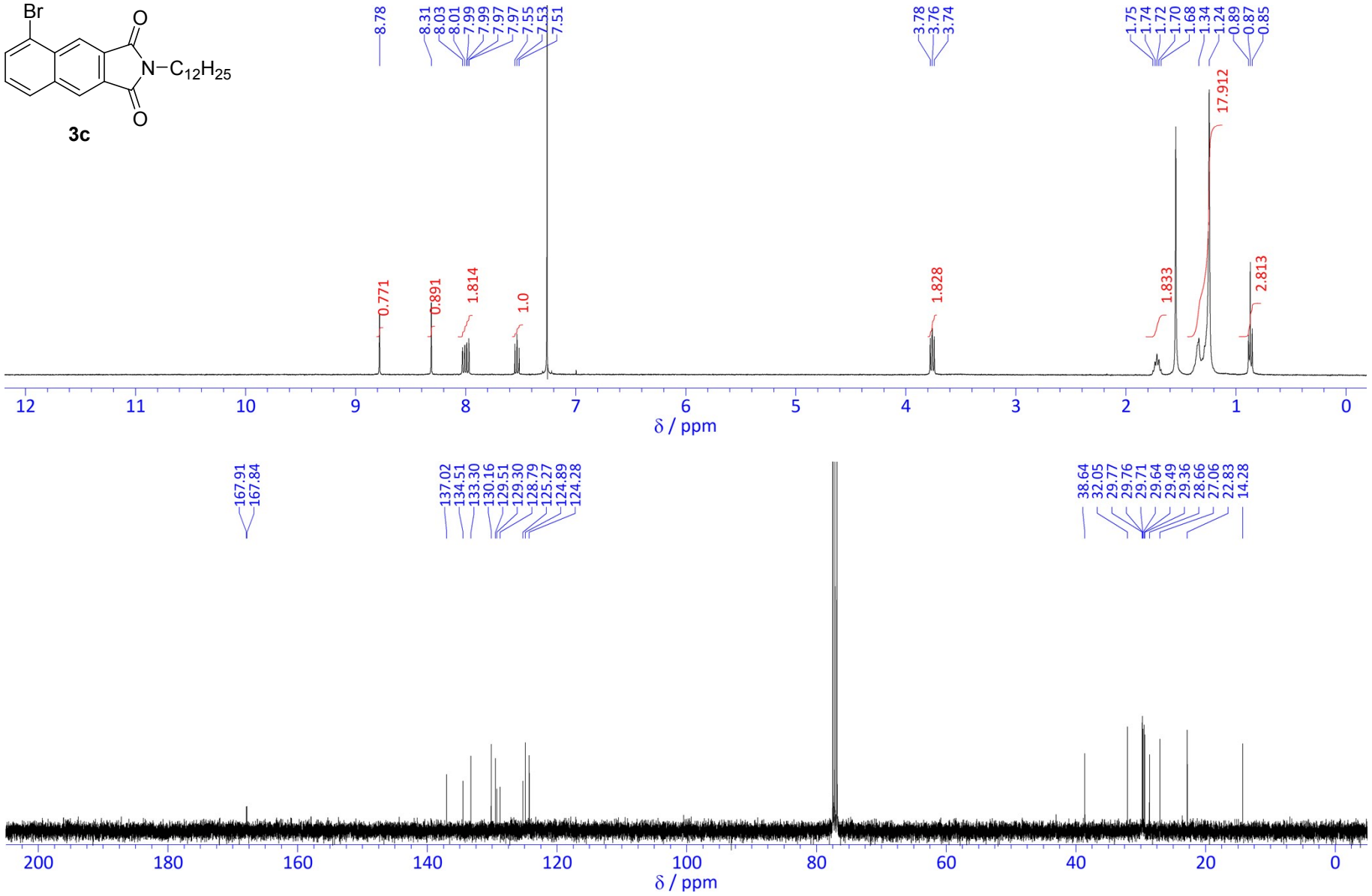

Fig. S8 ^{1}H (400 MHz, upper) and ^{13}C (100 MHz, lower) NMR spectra of compound **3c** in $CDCl_3$.

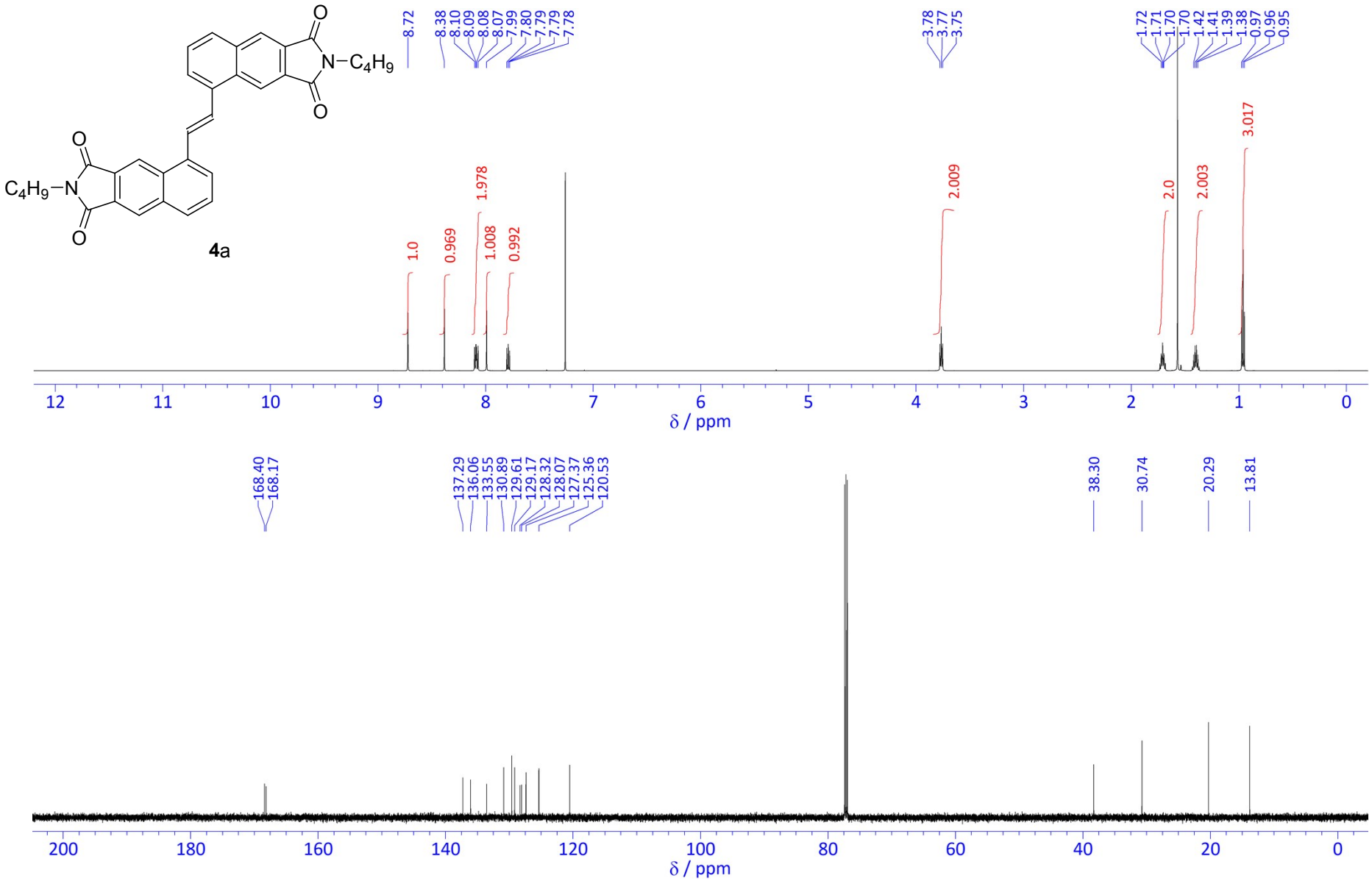

Fig. S9 ^{1}H (600 MHz, upper) and ^{13}C (151 MHz, lower) NMR spectra of compound **4a** in $CDCl_3$.

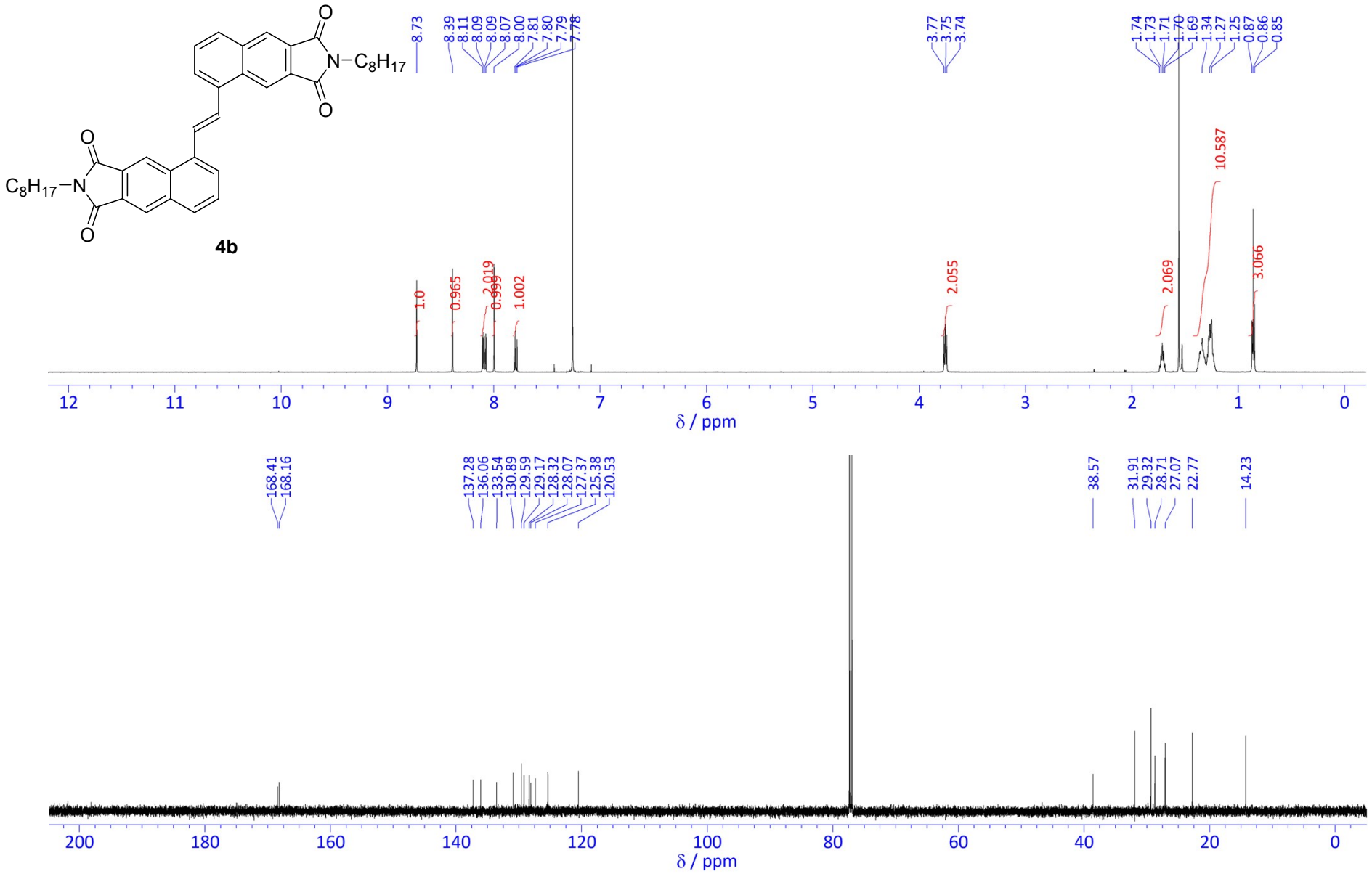

Fig. S10 ^{1}H (600 MHz, upper) and ^{13}C (151 MHz, lower) NMR spectra of compound **4b** in $CDCl_3$.

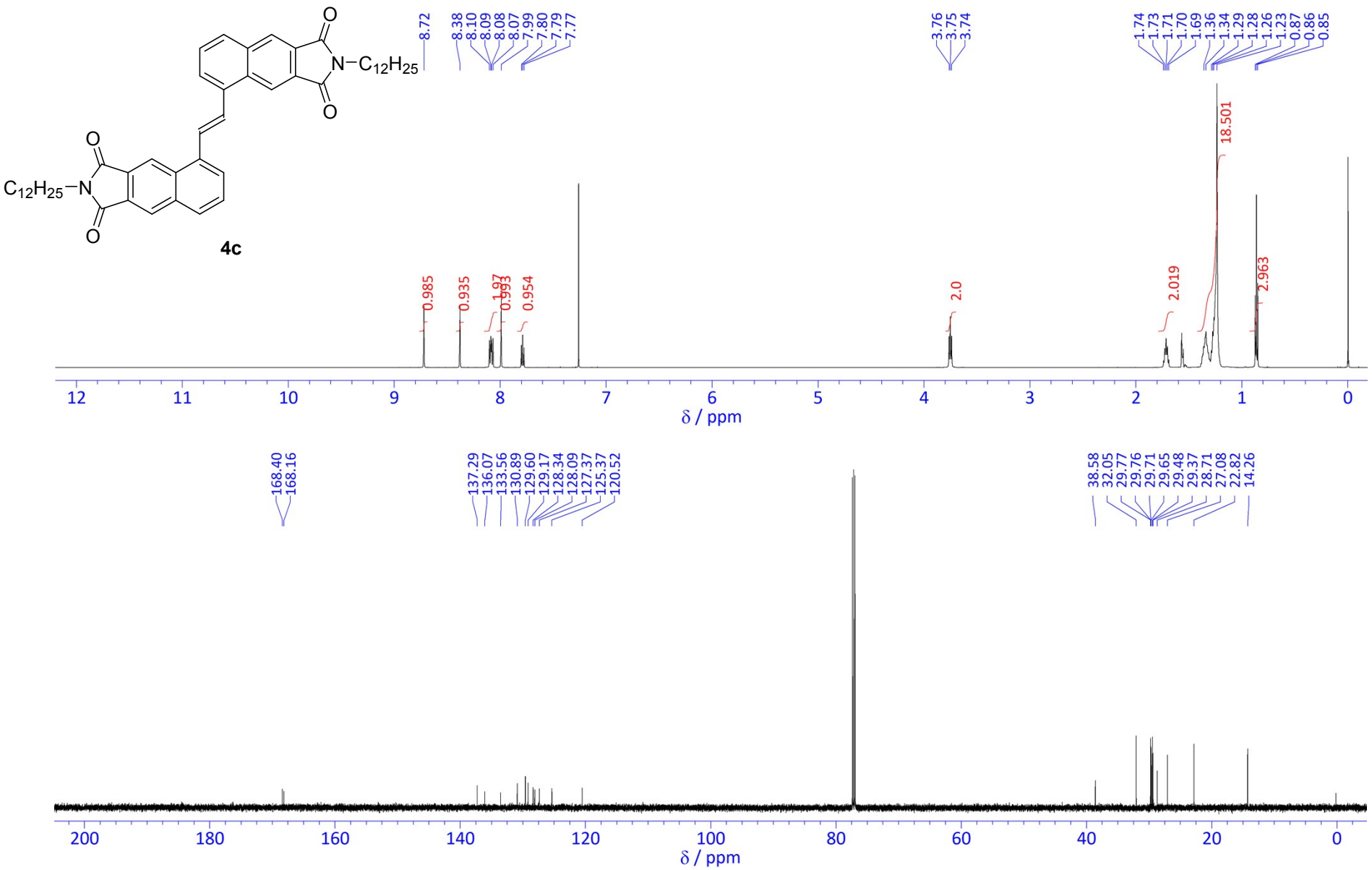

Fig. S11 ^{1}H (600 MHz, upper) and ^{13}C (151 MHz, lower) NMR spectra of compound **4c** in $CDCl_3$.

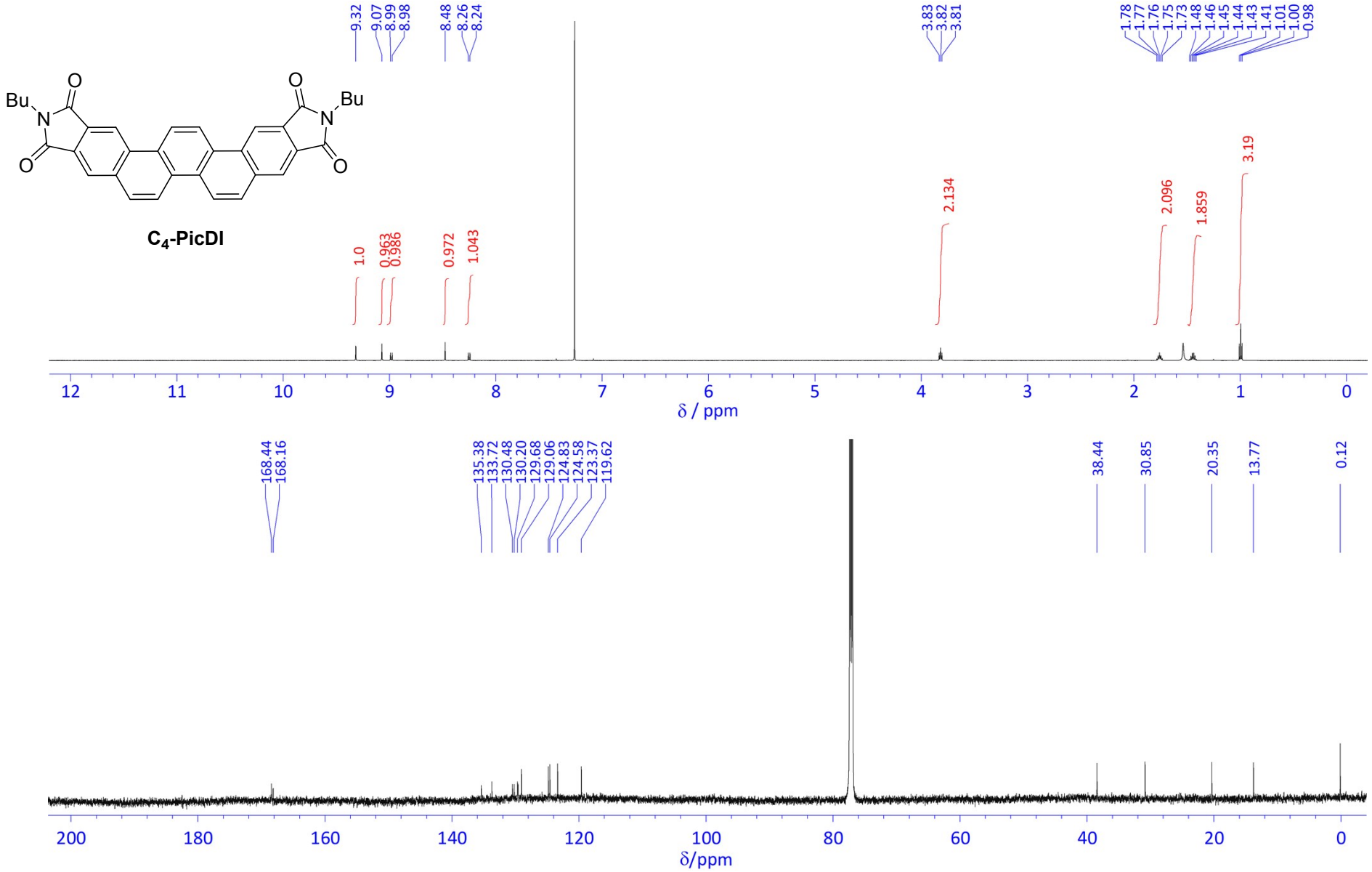

Fig. S12 ^{1}H (600 MHz) and ^{13}C (151 MHz, 50°C, lower) NMR spectra of **C_4-PicDI** in $CDCl_3$.

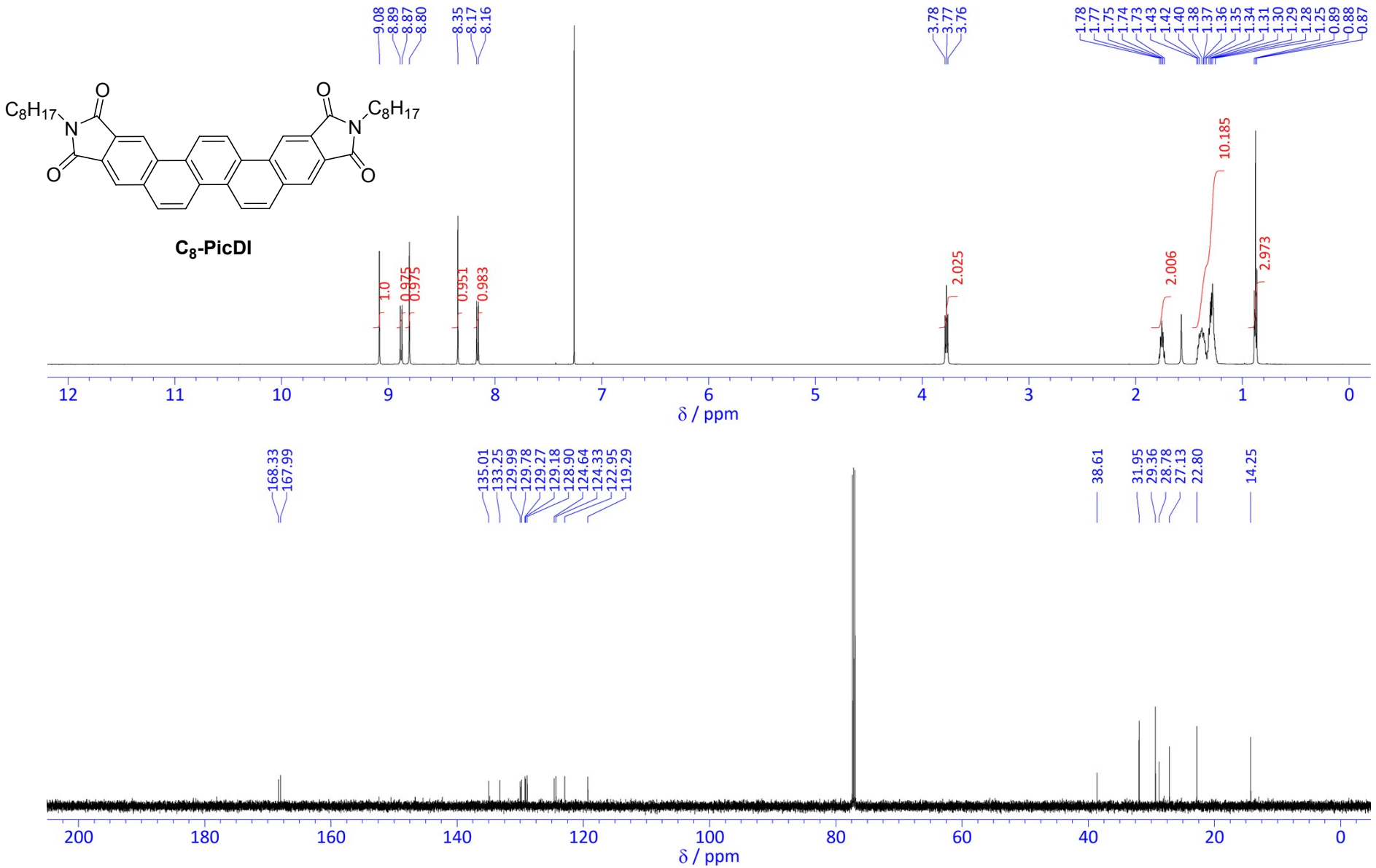

Fig. S13 ^{1}H (600 MHz, upper) and ^{13}C (151 MHz, lower) NMR spectra of **C_8-PicDI** in $CDCl_3$.

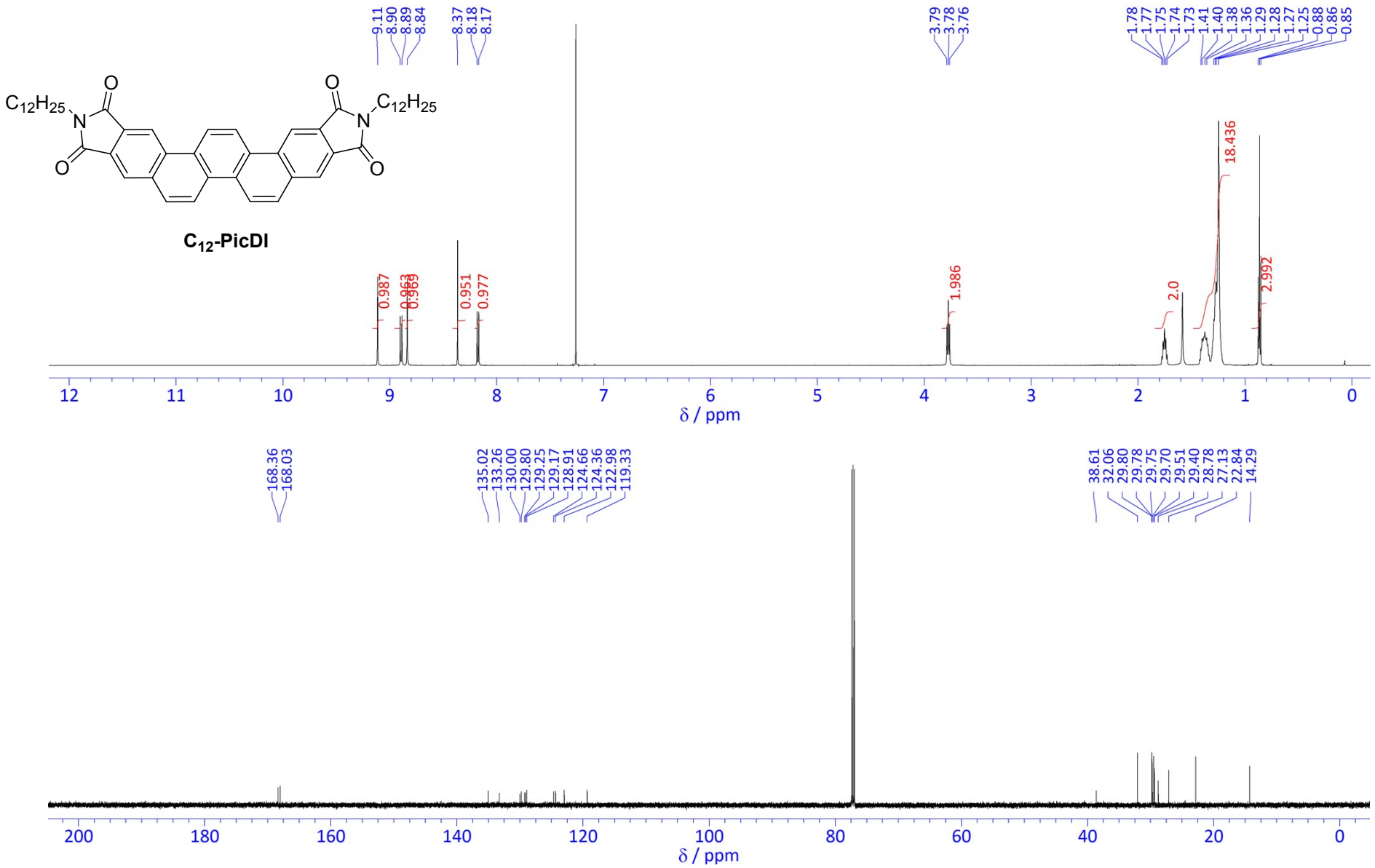

Fig. S14 ^{1}H (600 MHz, upper) and ^{13}C (151 MHz, lower) NMR spectra of **C_{12}-PicDI** in $CDCl_3$.