Electronic Supplementary Information

Fluorescence behaviour of 2-, 3- and 4-amino-1,8-naphthalimides: Effects of the substitution positions of the amino functionality on the photophysical properties

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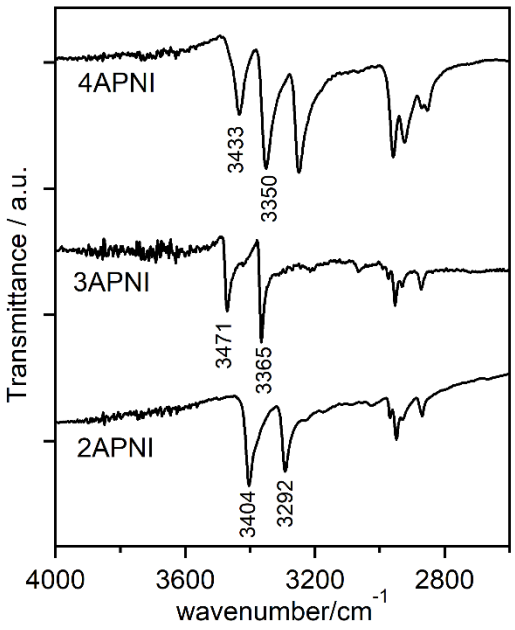


Fig. S1 FT-IR spectra ($\nu_{N\text{-}H}$ absorption) of **APNI**s in the solid state.

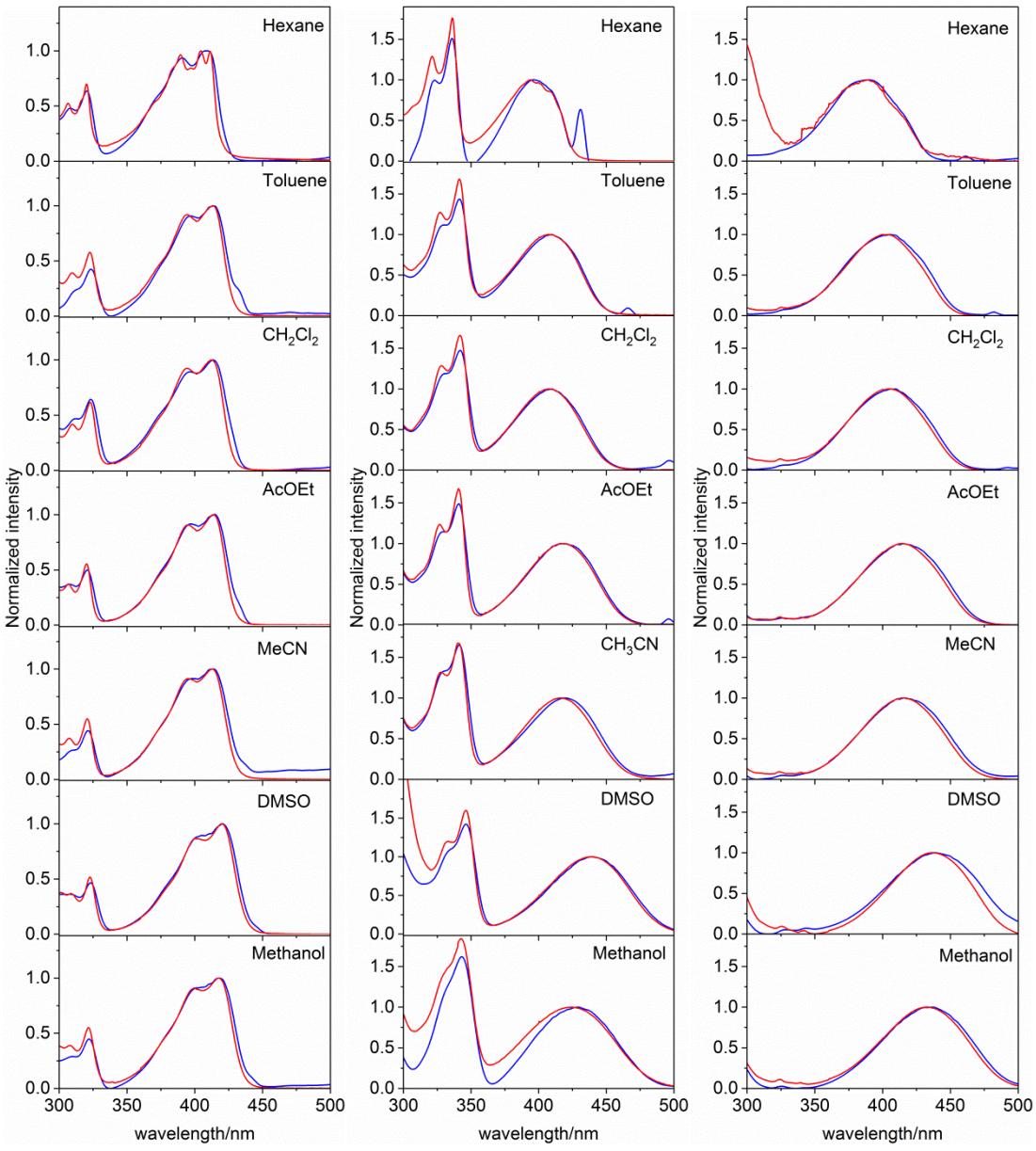


Fig. S2 Absorption (red) and fluorescence excitation (blue) spectra of **2APNI** (a), **3APNI** (b) and **4APNI** (c) in various solvents.

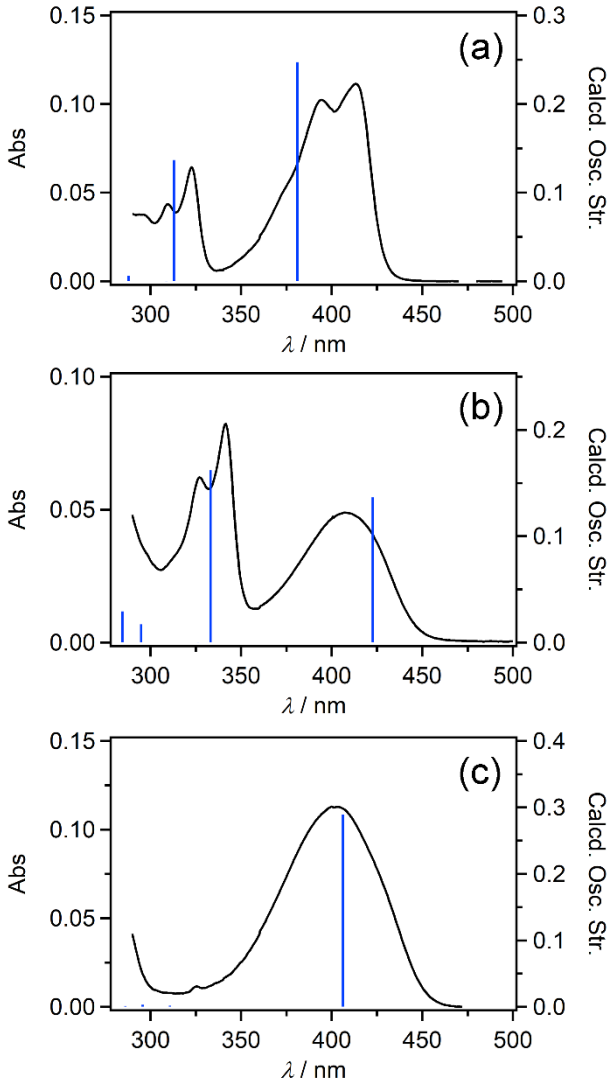


Fig. S3 Electronic absorption spectra of **2APNI** (a), **3APNI** (b) and **4APNI** (c) in toluene. The vertical bars display wavelengths and oscillator strengths for electronic transition of **ANPI**s in toluene calculated at the TD-B3LYP/6-31+G(d) level.

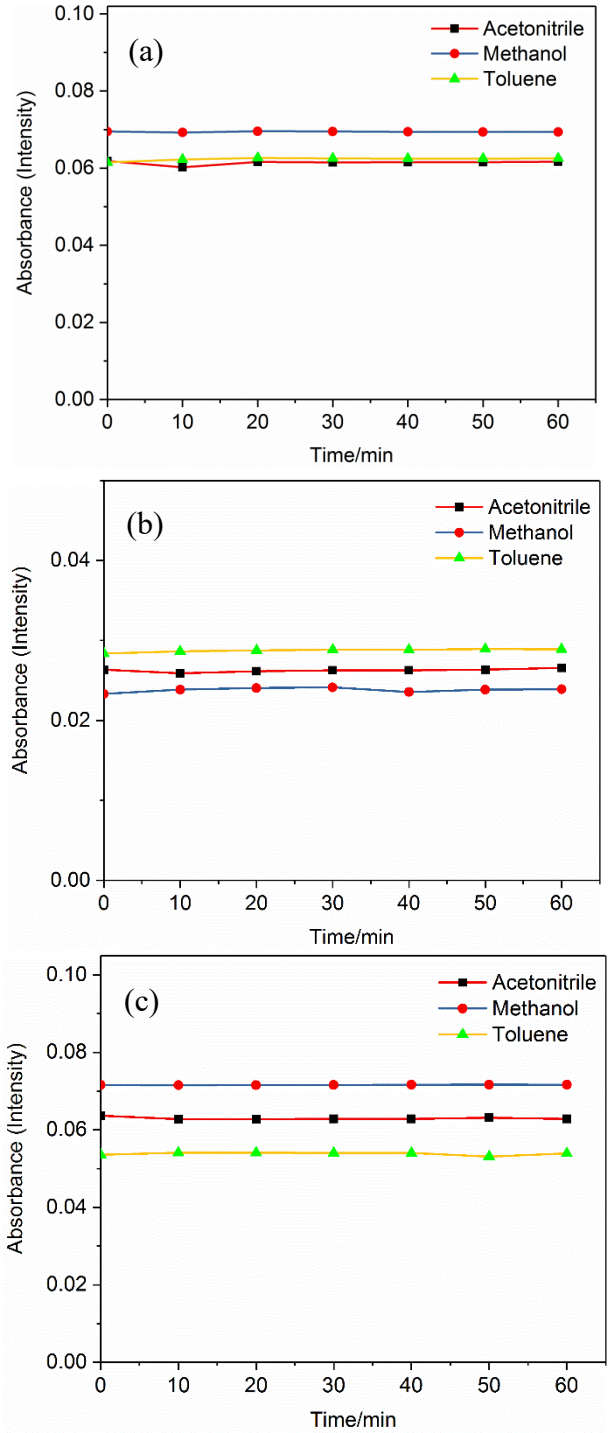
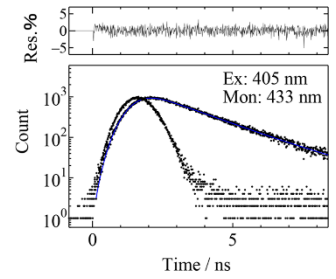


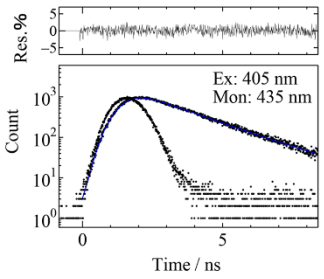
Fig. S4 Absorption spectral changes of **2APNI** (a), **3APNI** (b) and **4APNI** (c) during photoirradiation in toluene, MeCN and MeOH at λ_{max}^{Abs}. (cf. Table 2). The solutions of **APNI**s were irradiated with a Xe-lamp of the fluorescence spectrophotometer under the conditions for fluorescence measurements and the absorption spectra were collected with 10-minutes of interval in 0–60 min of time course. The absorbance at the λ_{max}^{Abs}.was plotted as a function of irradiation time.



Decay profile of fluorescence of 2–18–ANI in toluene at 295 K

τ_f = 1.71 ns

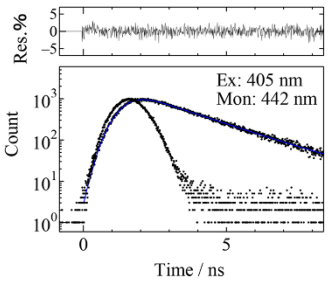
(a) **2APNI** in toluene



Decay profile of fluorescence of 2–18–ANI in acetonitrile at 295 K

τ_f = 1.74 ns

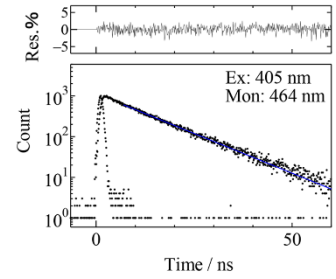
(b) **2APNI** in MeCN



Decay profile of fluorescence of 2–18–ANI in methanol at 295 K

τ_f = 1.86 ns

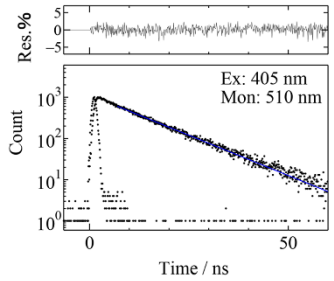
(c) **2APNI** in MeOH



Decay profile of fluorescence of 3–18–ANI in toluene at 295 K

τ_f =11.7 ns

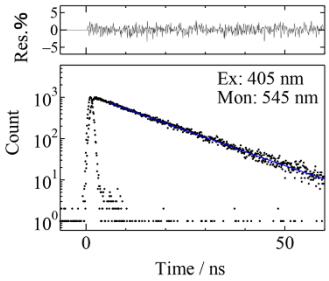
(d) **3APNI** in toluene



Decay profile of fluorescence of 3–18–ANI in acetonitrile at 295 K

τ_f =17.7 ns

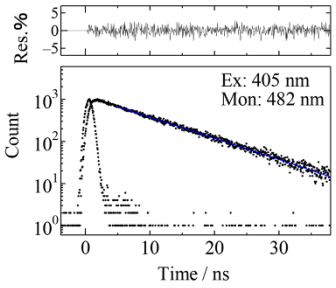
(e) **3APNI** in MeCN



Decay profile of fluorescence of 3–18–ANI in methanol at 295 K

τ_f =12.4 ns

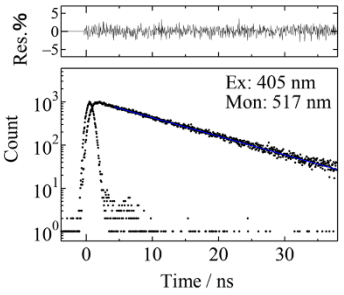
(f) **3APNI** in MeOH



Decay profile of fluorescence of 4–18–ANI in toluene at 295 K

τ_f =8.74 ns

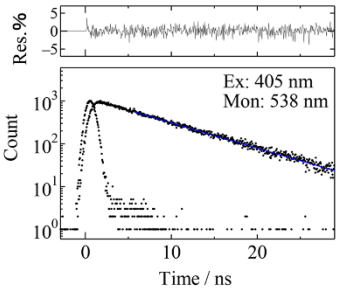
(g) **4APNI** in toluene



Decay profile of fluorescence of 4–18–ANI in acetonitrile at 295 K

τ_f =10.1 ns

(h) **4APNI** in MeCN



Decay profile of fluorescence of 4–18–ANI in methanol at 295 K

τ_f =7.28 ns

(i) **4APNI** in MeOH

Fig. S5 Fluorescence decay profiles for **APNI**s.

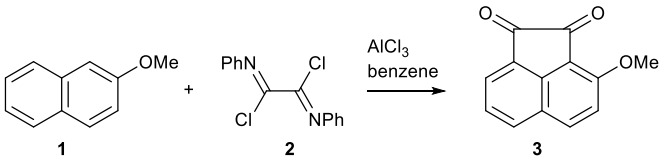
Experimental

Instruments

^{1}H and ^{13}C NMR spectra were collected on VARIAN Mercury 300 (300 MHz), VARIAN 400MR (400 MHz) or VARIAN NMR System 600 (600 MHz) spectrometers. IR spectra were measured using a SHIMADZU IR Prestige-21 spectrophotometer. Elemental analyses were performed using Perkin-Elmer 2400II CHN-S analyzer at the Micro Elemental Analysis Laboratory of Okayama University. Absorption spectra were recorded on JASCO V-530 spectrophotometers. Fluorescence spectra were obtained on a JASCO 5300 spectrophotometer. Spectroscopic grade solvents were used for the absorption and the fluorescence measurements. The fluorescence quantum yields (Φ_F) were measured in solution using coumarin 153 as a standard (Φ_F = 0.56 in acetonitrile)[1]. Fluorescence lifetimes (τ_F) were determined with a Hamamatsu Photonics Tau time-correlated single-photon counting fluorimeter system.

Materials

3-Methoxy-1, 2-acenaphthylenedione (3)[2,3]

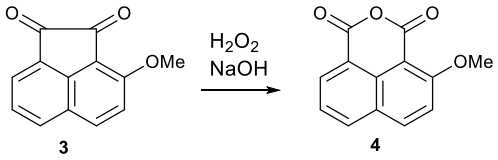


1 2 3

A solution of oxalyl chloride (330 mg, 5 mmol) in dry toluene (10 mL) was dropwise added to the solution of aniline (475 mg, 5 mmol) in dry toluene (10 mL) at room temperature. The mixture was stirred for 2 h. Then, PCl_5 (1.05 g, 5.5 mmol) was added and the resulting mixture was refluxed until no further gas evolved. The resulting yellow solution was concentrated under reduced pressure. Hexane (100 mL) was added to the residue and the precipitate formed was filtered off. The filtrate was concentrated under reduced pressure and the residue (bright yellow solid of *N,N'*-diphenyloxalimidoyl dichloride **2**) was used directly without further purification.[3] A solution of dichloride **2** and 2-methoxynaphthalene (403 mg, 2.5 mmol) in dry benzene (10 mL) was added to a mixture of aluminum trichloride (1 g, 7.5 mmol) in benzene (2 ml). The mixture was stirred at room temperature overnight. The resulting mixture was poured into ice water, extracted with $CHCl_3$, and washed with brine and water. The organic layer was dried

over anhydrous sodium sulfate and concentrated under reduced pressure. The residue was triturated with saturated sodium bisulfite solution, and acidified with concentrated hydrochloric acid to precipitate the product. The solid formed was collected, washed with water, and dried. Compound **3** was obtained as yellow solid (258 mg, 49%). Mp 207–210°C (lit.[4] 224–226°C). ^{1}H NMR (400 MHz, $CDCl_3$) δ_H = 8.21 (d, *J* = 9.2 Hz, 1H), 8.12 (dd, *J* = 8.4, 0.8 Hz, 1H), 8.01 (dd, *J* = 7.2, 0.8 Hz, 1H), 7.63 (dd, *J* = 8.4, 7.2 Hz, 1H), 7.45 (d, *J* = 9.2 Hz, 1H), 4.23 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ_C = 188.3, 184.7, 155.7, 147.9, 135.7, 132.7, 126.6, 126.0, 125.9, 123.0, 116.9, 112.9, 57.9 ppm. IR (neat) ν_{max} 1734 (C=O), 1709, 1258 (Ar-O-C) cm^{-1}.

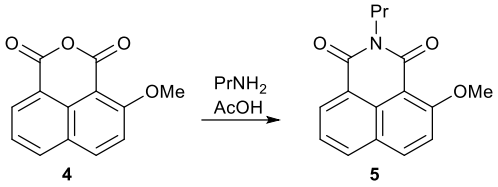
2-Methoxy-1,8-naphthalic anhydride (4)[4]



3 4

To a solution of of 3-methoxy-1, 2-acenaphthylenedione **3** (101 mg, 0.47 mmol) in ethanol (2 mL) was slowly added 4 M aqueous sodium hydroxide (5.5 mL) and 30% hydrogen peroxide (5.5 mL) at room temperature. After the mixture was stirred for 1 h, the resulting mixture was acidified with 6 M aqueous sulfuric acid with ice cooling and extracted with $CHCl_3$ (20 ml). The extract was washed with brine and water, dried over anhydrous sodium sulfate and concentrated under reduced pressure. The residue recrystallized from ethanol to afford compound **4** as white needles (109 mg, 94%). Mp 270–273°C (lit.[4] = 261–262°C). ^{1}H NMR (600 MHz, DMSO-d_6) δ_H = 8.52 (d, *J* = 9.6 Hz, 1H), 8.45 (dd, *J* = 7.2, 1.2 Hz, 1H), 8.43 (dd, J = 8.4, 1.2 Hz, 1H), 7.78 (d, *J* = 9.0 Hz, 1H), 7.71 (dd, *J* = 8.4, 7.2 Hz, 1H), 4.14 (s, 3H). ^{13}C NMR (151 MHz, DMSO-d_6) δ_C =164.1, 161.3, 156.7, 138.3, 135.8, 133.0, 131.8, 126.2, 124.8, 117.5, 115.7, 102.2, 57.2 ppm. IR (neat) ν_{max} 2961 (C-H), 1757 (C=O), 1260 (Ar-O-C), 999 (C-O) cm^{-1}.

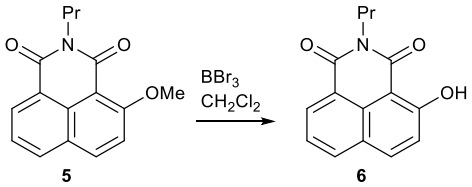
2-Methoxy-*N*-propyl-1,8-naphthalimide (5)



4 5

A solution of 2-methoxy-1,8-naphthalic anhydride **4** (456 mg, 2.0 mmol) and propylamine (1.2 g, 20 mmol) in acetic acid (10 mL) was heated at 130 °C overnight under nitrogen atmosphere. The resulting mixture was poured into ice water, and extracted with $CHCl_3$ (20 ml). The extract was washed with brine and water, dried over anhydrous sodium sulfate, and concentrated under reduced pressure. The residue was purified by silica-gel column chromatography (hexane : AcOEt = 3 : 1) to give colorless solid of **5** (532 mg, 99%). Mp 153–154.5°C. ^{1}H NMR (600 MHz, $CDCl_3$) δ_H = 8.59 (dd, *J* = 7.2, 1.2 Hz, 1H), 8.15 (d, *J* = 9.0 Hz, 1H), 8.07 (dd, *J* = 7.8, 1.2 Hz, 1H), 7.58 (dd, *J* = 7.8, 7.2 Hz, 1H), 7.45 (d, *J* = 9.0 Hz, 1H), 4.18 (s, 3H), 4.14–4.11 (m, 2H), 1.78–1.72 (m, 2H), 1.00 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ_C = 164.0, 163.1, 162.6, 136.4, 134.0, 132.1, 130.1, 126.5, 124.6, 121.9, 114.5, 107.3, 57.0, 41.9, 21.4, 11.7 ppm. IR (neat) ν_{max} 2963 (C-H), 1688 (C=O), 1641, 1269 (Ar-O-C) cm^{-1}. Anal. Calcd for $C_{16}H_{15}NO_3$: C, 71.36; H, 5.61; N, 5.20%. Found: C, 71.23; H, 5.59; N, 5.11%.

2-Methoxy-*N*-propyl-1,8-naphthalimide (6)

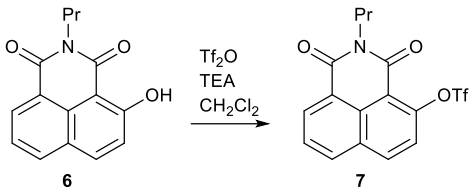


5 6

A solution of boron tribromide (5 mL) in dichloromethane (1 M) was added to a solution of *N*-propyl-2-methoxy-1,8-naphthalimide **5** (1.27 g, 4.7 mmol) in dry dichloromethane (15 mL) through a syringe in ice water bath under nitrogen atmosphere. After the mixture was stirred for 1 h at room temperature, the mixture was poured into ice water, and extracted with $CHCl_3$. The extract was washed with brine and water dried ($MgSO_4$), and concentrated under reduced pressure. The residue was purified by silica-gel column chromatography (hexane : AcOEt = 10 : 1) to give compound **6** as yellow needles (1.12 g, 93%). Mp 163–164°C. ^{1}H NMR (600 MHz, $CDCl_3$) δ_H 13.11 (s, 1H), 8.57 (dd, *J* = 7.8, 1.2 Hz, 1H), 8.11-8.03 (m, 2H), 7.60 (t, *J* = 7.8 Hz, 1H), 7.28 (d, *J* = 9.6 Hz, 1H), 4.17-4.12 (m, 2H), 1.82–1.72 (m, 2H), 1.02 (t, *J* = 7.4

Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ_C 169.2, 165.5, 163.8, 137.0, 134.4, 131.8, 129.0, 126.1, 124.6, 121.0, 120.5, 102.1, 41.6, 21.4, 11.6 ppm. IR (neat) ν_{max} 2961 (C-H), 1680 (C=O), 1634, 1204(C-O) cm^{-1}. Anal. Calcd for $C_{15}H_{13}NO_3$: C, 70.58; H, 5.13; N, 5.49%. Found: C, 70.37; H, 5.10; N, 5.40%.

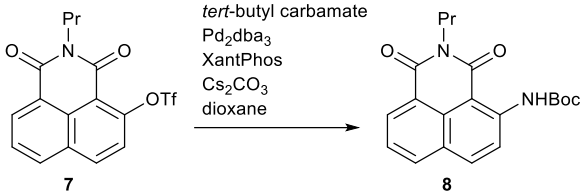
2-Trifluoromethanesulfonyloxy-*N*-propyl-1,8-naphthalimide (7)



6 7

A mixture of triethylamine (468 mg, 4.6 mmol) and trifluoromethanesulfonic anhydride (1.3 g, 4.6 mmol) was added to the solution of *N*-propyl-2-hydroxy-1,8-naphthalimide **6** (983 mg, 3.85 mmol) in dry dichloromethane (10 mL) in ice water bath. After the mixture was stirred overnight at room temperature, the mixture was concentrated under reduced pressure. The residue was purified by silica-gel column chromatography (hexane : AcOEt = 5 : 1) to give compound **7** as colorless needles (1.32 g, 88%). Mp. 122–123°C. ^{1}H NMR (600 MHz, $CDCl_3$) δ_H = 8.74 (dd, *J* = 7.8, 1.2 Hz, 1H), 8.30 (d, *J* = 9.6 Hz, 1H), 8.25 (dd, *J* = 8.4, 1.2 Hz, 1H), 7.86 (dd, *J* =7.8, 7.2 Hz, 1H), 7.55 (d, *J* = 9.0 Hz, 1H), 4.20–4.15 (m, 2H), 1.82–1.72 (m, 2H), 1.01 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ_C = 163.0, 161.4, 149.8, 136.1, 134.0, 133.0, 130.8, 128.8, 128.1, 123.3, 122.5, 120.0, 117.8, 115.0, 42.2, 21.3, 11.5 ppm. IR (neat) ν_{max} 2972 (C-H), 1705 (C=O), 1655, 1366 (SO_2), 1206(C-O) cm^{-1}. Anal. Calcd for $C_{16}H_{12}F_3NO_5S$: C, 49.62; H, 3.12; N, 3.62%. Found: C, 49.45; H, 3.08; N, 3.53%.

2-*tert*-Butoxycarbonylamino-*N*-propyl-1,8-naphthalimide (8)

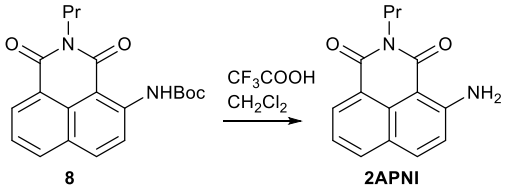


7 8

A mixture of 2-trifluoromethanesulfonyloxy-*N*-propyl-1,8-naphthalimide **7** (387 mg, 1.0 mmol), *tert*-butyl carbamate (176 mg, 1.5 mmol), Pd_2dba_3 (23 mg, 0.025 mmol), 9,9-dimethyl-4,5-bis(diphenylphosphino)xanthene (46 mg, 0.08 mmol) and cesium carbonate (970 mg, 3.0

mmol) were put in a flask. Under an argon atmosphere, dry dioxane (5 mL) was added through a syringe and the mixture was heated at 110 °C for 20 h. After cooling to room temperature, the mixture was concentrated under reduced pressure. The residue was separated by silica-gel column chromatography (hexane : AcOEt = 10 : 1) followed by recrystallization from hexane to afford compound **8** (227 mg, 64 %). Mp 191–192°C. ^{1}H NMR (600 MHz, $CDCl_3$) δ_H = 12.04 (s, 1H), 8.91 (d, *J* = 9.0 Hz, 1H), 8.60 (d, *J* = 7.2 Hz, 1H), 8.08 (t, *J* = 7.8, 1.2 Hz, 2H), 7.61 (t, *J* = 7.8, 7.2 Hz, 1H), 4.18–4.12 (m, 2H), 1.76 (t, *J* = 7.5 Hz, 2H), 1.59 (s, 9H), 1.03 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ_C = 167.0, 163.7, 152.9, 146.8, 135.9, 134.3, 132.0, 129.1, 127.0, 124.8, 121.4, 119.4, 103.1, 81.8, 42.0, 28.4, 21.4, 11.7 ppm. IR (neat) ν_{max} 2963 (C-H), 1736 (C=O), 1684, 1638, 1157(C-O-C) cm^{-1}. Anal. Calcd for $C_{20}H_{22}N_2O_4$: C, 67.78; H, 6.26; N, 7.90%. Found: C, 67.56; H, 6.33; N, 7.84%.

2-Amino-*N*-propyl-1,8-naphthalimide (2APNI)

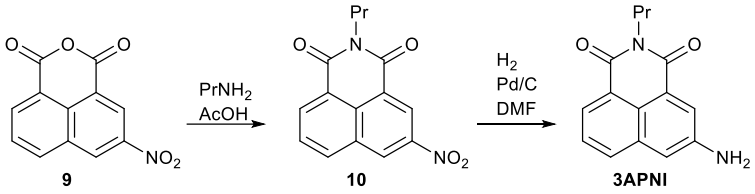


8 **2APNI**

To a solution of 2-butoxycarbonylamino-*N*-propyl-1,8-naphthalimide **8** (187 mg, 0.53 mmol) in CH_2Cl_2 (5 mL) was slowly added trifluoroacetic acid (5 mL) in ice-water bath under nitrogen atmosphere. The mixture was stirred for 2 h at room temperature, then diluted with $CHCl_3$. The resulting mixture was successively washed with saturated sodium bicarbonate, 0.1 M aqueous sodium hydroxide and water. The organic layer was dried over anhydrous sodium sulfate and concentrated under reduced pressure. The residue was purified by silica-gel column chromatography (hexane: AcOEt = 3 : 1) to give **2APNI** as yellow needles (83 mg, 61 %). Mp 217–218°C. ^{1}H NMR (300 MHz, acetone-d_6) δ_H = 9.16 (s, 2H), 8.41 (dd, *J* = 7.8, 1.5 Hz, 1H), 8.08 (dd, *J* = 7.8, 1.2 Hz, 1H), 7.97 (d, *J* = 9.0 Hz, 1H), 7.47 (t, *J* = 7.8 Hz, 1H), 7.23 (d, *J* = 9.0 Hz, 1H), 4.16–4.05 (m, 2H), 1.71 (m, 2H), 0.96 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ_C = 166.6, 164.4, 153.2, 135.5, 133.9, 131.3, 130.5, 125.3, 122.9, 120.5, 120.1, 98.4, 41.6, 21.5, 11.8 ppm. IR (neat) ν_{max} 3404 (N-H), 3292, 2949 (C-H), 1738 (C=O), 1636, 1346

(C_{Ar}-N) cm^{-1}. Anal. Calcd for $C_{15}H_{14}N_2O_2$: C, 70.85; H, 5.55; N, 11.02. Found: C, 70.63; H, 5.48; N, 10.88.

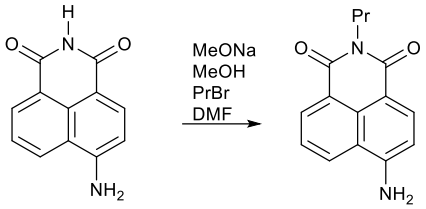
3-Amino-*N*-propyl-1,8-naphthalimide (3APNI)



A mixture of 3-nitro-1,8-naphthalic anhydride **9** (486.4 mg, 2.0 mmol) and propylamine (0.5 mL, 6.0 mmol) in acetic acid (10 mL) was was refluxed for 6 h. The mixture was poured into ice water and the precipitate formed was collected, washed with water, and dried at room temperature to give compound **10** as yellow solid (520 mg, 93%). Mp 172–175°C (lit.[5] 166–167°C). ^{1}H NMR (400 MHz, $CDCl_3$) δ_H = 9.32 (d, *J* = 2.0 Hz, 1H), 9.13 (d, *J* = 2.4 Hz, 1H), 8.78 (dd, *J* = 7.2, 1.2 Hz, 1H), 8.42 (dd, *J* = 8.4, 1.2 Hz 1H), 7.94 (dd, *J* = 8.4, 7.2 Hz, 1H), 4.19–4.15 (m, 2H), 1.83–1.75 (m, 2H), 1.03 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ_C = 163.6, 162.9, 146.8, 135.9, 134.9, 131.4, 130.7, 129.5, 129.3, 125.2, 124.7, 123.7, 42.8, 21.8, 11.9 ppm. IR (neat) ν_{max} 2954 (C-H), 1701 (C=O), 1659, 1350 (NO_2) cm^{-1}.

A solution of 3-nitro-*N*-propyl-1,8-naphthalimide **10** (500 mg, 1.8 mmol) in DMF (50 mL) was stirred under H_2 in the presence of 10% Pd/C (192 mg, 0.18 mmol) for 5 h. The catalyst was filtered off and the filtrate was concentrated under reduced pressure. The residue was purified by silica-gel column chromatography ($CHCl_3$: CH_3OH = 100 : 1) to give compound **14** as yellow solid. The crude product was recrystallized from a chloroform/hexane mixture to give yellow needles of **3APNI** (290 mg, 64 %). Mp 206–209°C (lit.[6] 202–203°C) ^{1}H NMR (400 MHz, $CDCl_3$) δ_H = 8.30 (dd, *J* = 7.2, 1.2 Hz, 1H), 8.02 (d, *J* = 2.3 Hz, 1H), 7.91 (dd, *J* = 8.3, 1.1 Hz, 1H), 7.59 (t, *J* = 7.6 Hz, 1H), 7.29 (d, *J* = 2.4 Hz, 1H), 4.17 (br, 2H), 4.14–4.10 (m, 2H), 1.79–1.70 (m, 2H), 1.00 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ_C = 164.5, 164.2, 145.2, 133.4, 131.6, 127.4, 127.2, 123.7, 122.6, 122.5, 122.0, 113.9, 41.9, 21.4, 11.5 ppm. IR (neat) ν_{max} 3472 (N-H), 3366, 2953 (C-H), 1686 (C=O), 1641, 1383 cm^{-1}.

4-Amino-*N*-propyl-1,8-naphthalimide (4APNI)



11 **4APNI**

A solution of sodium methoxide (216 mg, 4.0 mmol) in methanol (4 mL) was dropwise added to a solution of 4-amino-1,8-naphthalimide **11** (424 mg, 2.0 mmol) in DMF (20 mL). The mixture was stirred at room temperature for 1 h. To the mixture was added 1-bromopropane (369 mg, 3.0 mmol) The resulting reaction mixture was stirred at room temperature for another 5 h, then poured into ice water. The precipitate formed was collected, washed with water, and dried at room temperature to give yellow solid. The crude product was purified by silica-gel column chromatography (hexane : AcOEt = 1 : 1) to give **4APNI** as orange crystals (310 mg, 61%). Mp 258–261°C (lit.[7] = 258.5°C). ^{1}H NMR (400 MHz, $CDCl_3$) δ_H = 8.60 (d, *J* = 7.2 Hz, 1H), 8.42 (d, *J* = 8.0 Hz, 1H), 8.10 (d, *J* = 8.0 Hz, 1H), 7.66 (t, *J* = 8.4, 7.6 Hz, 1H), 6.89 (d, *J* = 8.4 Hz, 1H), 4.93 (br, 2H), 4.14–4.11 (m, 2H), 1.80–1.71 (m, 2H), 1.00 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ_C = 164.7, 164.2, 149.0, 133.9, 131.6, 130.0, 126.8, 125.2, 123.4, 120.3, 112.5, 109.7, 41.9, 21.6, 11.7 ppm. IR (neat) ν_{max} 3433 (N-H), 3350, 2959 (C-H), 1672 (C=O), 1632, 1375 cm^{-1}.

Theoretical calculations

Theoretical calculations were performed by using GAUSSIAN 09 Revision C. 01 package.[8] The molecular geometries of **APNI**s were optimized at the PBE0/6-311G+(d,g) level. Vertical electronic transitions were calculated at the TD-PBE0/6-311G+(d,g) level using the ground-state structures optimized by PBE0/6-311G+(d,g) level. Solvent effects of toluene were considered by polarizable continuum model to compare the calculated transitions with the experimental spectra. The optimized geometries are shown in Table S1–S6.

Table S1 Optimized coordinate of **2APNI** (PBE0/6-311+G(d,p) in vacuum).
Total energy -839.31423786 a.u.

Atomic Type	Coordinates (Angstroms) X	Y	Z
C	2.56914300	-2.79646900	0.13637700
C	3.32454100	-1.64463900	0.22608400
C	2.72168400	-0.37781900	0.15371900
C	1.31566700	-0.28011100	-0.01593600
C	0.56316500	-1.47002400	-0.10544000
C	1.18482000	-2.70440900	-0.02839200
H	3.04501100	-3.76902800	0.19383800
H	4.40165400	-1.70439300	0.35478400
C	3.46640500	0.82911600	0.24379000
C	0.67745100	0.98260900	-0.09097700
H	0.56535800	-3.59186500	-0.10036300
C	1.44449000	2.15947400	0.00456400
C	2.85842300	2.04304300	0.17274500
C	-0.89671900	-1.41982200	-0.28020100
C	-0.76654000	1.05159600	-0.26463100
O	-1.38892600	2.11236600	-0.32412800
O	-1.59219700	-2.41585700	-0.34771900
C	-2.91463500	-0.07570100	-0.55273600
H	-3.12221100	0.82738000	-1.12791600
H	-3.20385100	-0.95265700	-1.13370100
C	-3.66774700	-0.04757500	0.77080400
H	-3.33219300	0.81871800	1.35074800
H	-3.40976400	-0.94526100	1.34245300
C	-5.17246600	0.01881300	0.55513900
H	-5.70686100	0.03634200	1.50870300
H	-5.45545600	0.91923400	0.00013000
H	-5.53083600	-0.84812900	-0.00937200
N	-1.46434300	-0.14878100	-0.37170300
H	4.54340800	0.77128300	0.37222300
H	3.44437300	2.95465000	0.24417200
N	0.89393600	3.38505500	-0.05807000
H	-0.11239300	3.44465400	-0.17453500
H	1.46950700	4.20459400	0.01257300

Table S2 Optimized coordinate of **2APNI** (PBE0/6-311+G(d,p), CPCM toluene).
Total energy -839.32099530 a.u.

Atomic Type	Coordinates (Angstroms) X	Y	Z
C	2.56914800	-2.79760200	0.13582400

C	3.32388300	-1.64388200	0.22651500
C	2.71969100	-0.37834800	0.15436800
C	1.31365600	-0.28073700	-0.01597200
C	0.56172200	-1.47119100	-0.10569800
C	1.18574700	-2.70625700	-0.02903900
H	3.04581500	-3.76965900	0.19286200
H	4.40075400	-1.70248600	0.35566200
C	3.46634700	0.82896000	0.24587200
C	0.67566500	0.98275200	-0.09175400
H	0.57136300	-3.59698300	-0.10104200
C	1.44532400	2.16064300	0.00387600
C	2.86005100	2.04301600	0.17452000
C	-0.89602000	-1.41940700	-0.27962000
C	-0.76538000	1.04999600	-0.26561000
O	-1.39120800	2.11036900	-0.32792000
O	-1.59351800	-2.41815900	-0.34889000
C	-2.91533000	-0.07785200	-0.55045700
H	-3.12299700	0.82210900	-1.12988900
H	-3.20677200	-0.95406000	-1.13087600
C	-3.66946400	-0.04444400	0.77246700
H	-3.33266800	0.82173900	1.35180400
H	-3.41401500	-0.93977600	1.34898400
C	-5.17392700	0.02478800	0.55531100
H	-5.70826300	0.04582600	1.50877600
H	-5.45378300	0.92443400	-0.00244300
H	-5.53342200	-0.84249800	-0.00794600
N	-1.46461500	-0.15175300	-0.36969600
H	4.54289900	0.76968600	0.37567200
H	3.44539300	2.95447400	0.24725200
N	0.90152400	3.38669200	-0.06020600
H	-0.10248500	3.45756600	-0.17826300
H	1.48095000	4.20476900	0.00962300

Table S3 Optimized coordinate of **3APNI** (PBE0/6-311+G(d,p) in vacuum).
Total energy -839.31423786 a.u.

Atomic Type	Coordinates (Angstroms) X	Y	Z
C	-2.02578600	3.07021400	0.16054200
C	-2.92598400	2.03316900	0.22466600
C	-2.49327500	0.68841800	0.12959200
C	-1.10392900	0.44646400	-0.03507600
C	-0.19741400	1.52341300	-0.09841000
C	-0.65210000	2.82046600	-0.00049200
H	-2.37613500	4.09417200	0.23592700
H	-3.98536900	2.23632100	0.35066600

C	-3.37895400	-0.40697200	0.18881600
C	-0.64909200	-0.88476800	-0.13202000
H	0.06630100	3.63090500	-0.05040100
C	-1.53136200	-1.93394700	-0.06462400
C	-2.91931600	-1.70890500	0.09402100
H	-1.13837400	-2.94397800	-0.13386800
C	1.24878000	1.26757200	-0.26666600
C	0.79322400	-1.16917700	-0.30437700
O	1.22979500	-2.30067900	-0.38055100
O	2.07140500	2.15984800	-0.30937100
C	3.07322700	-0.33434200	-0.55188100
H	3.16018100	-1.24523200	-1.14583800
H	3.48945300	0.50512300	-1.11043300
C	3.79792600	-0.49753100	0.77785700
H	3.33419100	-1.31867300	1.33444500
H	3.66412400	0.41560300	1.36717500
C	5.27972900	-0.77597700	0.57334300
H	5.79470000	-0.89395600	1.53031500
H	5.43468200	-1.69441700	-0.00209500
H	5.76664300	0.04276600	0.03370500
N	1.64388500	-0.06829900	-0.38229900
H	-4.44127900	-0.21620300	0.31644700
N	-3.77008600	-2.79351700	0.20768900
H	-4.74630600	-2.62074200	0.03012600
H	-3.44304400	-3.66091500	-0.18627300

Table S4 Optimized coordinate of **3APNI** (PBE0/6-311+G(d,p), CPCM toluene). Total energy -839.32099530 a.u.

Atomic Type	Coordinates (Angstroms) X	Y	Z
C	-2.02794600	3.07023500	0.15919400
C	-2.92716500	2.03186300	0.22333200
C	-2.49245600	0.68705500	0.12905300
C	-1.10264300	0.44573700	-0.03483400
C	-0.19702600	1.52371100	-0.09818700
C	-0.65400900	2.82101200	-0.00102000
H	-2.37881300	4.09390500	0.23364400
H	-3.98679000	2.23349600	0.34827100
C	-3.37953800	-0.40695100	0.18846900
C	-0.64837900	-0.88575700	-0.13165100
H	0.05946500	3.63558600	-0.05066200
C	-1.53232700	-1.93497300	-0.06523100
C	-2.92114000	-1.71076700	0.09378100
H	-1.14588100	-2.94697500	-0.13636400
C	1.24691200	1.26685000	-0.26602500

C	0.79260300	-1.16691200	-0.30258900
O	1.23394200	-2.29908800	-0.37832200
O	2.07250300	2.15998800	-0.30997000
C	3.07361600	-0.33302800	-0.55060700
H	3.16137900	-1.24198300	-1.14682600
H	3.48992300	0.50448900	-1.11141700
C	3.80021200	-0.49677900	0.77806800
H	3.33654900	-1.31615400	1.33730400
H	3.66833100	0.41546100	1.36922200
C	5.28136000	-0.77726000	0.57099000
H	5.79690800	-0.89554800	1.52757600
H	5.43362200	-1.69585200	-0.00490500
H	5.76804400	0.04061300	0.02984400
N	1.64372000	-0.06706300	-0.38025500
H	-4.44154100	-0.21502400	0.31408100
N	-3.77109200	-2.79343600	0.20892700
H	-4.74742700	-2.61946300	0.02876000
H	-3.44615800	-3.66048200	-0.18935700

Table S5 Optimized coordinate of **4APNI** (PBE0/6-311+G(d,p) in vacuum).
Total energy -839.31423786 a.u.

Atomic Type	Coordinates (Angstroms) X	Y	Z
C	-2.26079900	2.67648600	0.13991200
C	-3.04594500	1.54763800	0.20326500
C	-2.48329500	0.25811800	0.09620500
C	-1.07415400	0.14702300	-0.05568900
C	-0.28916000	1.31898700	-0.12124900
C	-0.87418800	2.56279300	-0.02834700
H	-2.71478400	3.65726000	0.22902800
H	-4.11308800	1.66813600	0.36023100
C	-3.26437400	-0.94241700	0.13981600
C	-0.45567400	-1.11830700	-0.12985100
H	-0.23723400	3.43896500	-0.08053200
C	-1.23541300	-2.25534500	-0.05341200
C	-2.61993300	-2.17147400	0.07581500
H	-0.74431300	-3.22104900	-0.10823800
H	-3.21060600	-3.08168000	0.11834100
C	1.17933500	1.22849700	-0.28508700
C	0.99826800	-1.24113800	-0.28452800
O	1.57115000	-2.31326400	-0.33560100
O	1.88664800	2.21641900	-0.33963100
C	3.17400600	-0.15035600	-0.54134900
H	3.36661400	-1.06223500	-1.10826300
H	3.49246700	0.71519700	-1.12441900

N	-4.62702000	-0.87976500	0.29218000
H	-5.10474600	-0.05450800	-0.02785700
H	-5.13730600	-1.73201200	0.12761900
C	3.90920300	-0.19058100	0.79191000
H	3.54368700	-1.04564100	1.37028700
H	3.66710500	0.71583900	1.35679300
C	5.41434700	-0.29682400	0.59618100
H	5.93588900	-0.32264000	1.55661600
H	5.68062200	-1.20758800	0.05004500
H	5.80226700	0.55721500	0.03144900
N	1.72383200	-0.04724500	-0.37943700

Table S6 Optimized coordinate of **2APNI** (PBE0/6-311+G(d,p), CPCM toluene). Total energy -839.32099530 a.u.

Atomic Type	Coordinates (Angstroms) X	Y	Z
C	-2.26316700	2.67775300	0.13411100
C	-3.04710000	1.54698000	0.19609700
C	-2.48268400	0.25830200	0.09455200
C	-1.07306900	0.14747000	-0.05659800
C	-0.28896800	1.32060800	-0.12060100
C	-0.87664000	2.56468300	-0.02875400
H	-2.71905400	3.65788500	0.21745500
H	-4.11547700	1.66879900	0.34084700
C	-3.26610600	-0.94370000	0.14227500
C	-0.45372900	-1.11758700	-0.13347700
H	-0.24494900	3.44451800	-0.07944100
C	-1.23687700	-2.25585800	-0.05978700
C	-2.61864300	-2.17485700	0.07344300
H	-0.75078200	-3.22380700	-0.11746700
H	-3.20837100	-3.08506700	0.11643700
C	1.17707900	1.22932800	-0.28248100
C	0.99600600	-1.23752600	-0.28730400
O	1.57434500	-2.31043400	-0.34547500
O	1.88804300	2.21843200	-0.33582200
C	3.17391600	-0.14720400	-0.53764900
H	3.36799800	-1.05453900	-1.11071600
H	3.49384500	0.71909500	-1.11821600
N	-4.62077500	-0.88666500	0.29966500
H	-5.11341100	-0.04966700	0.03876200
H	-5.14021000	-1.73649800	0.15096700
C	3.90951600	-0.19428100	0.79530700
H	3.54363900	-1.05060800	1.37159900
H	3.66821800	0.70839500	1.36652900
C	5.41459500	-0.30079400	0.59850700

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 H    5.93568100      -0.33132700    1.55901300
 H    5.67950500      -1.20911500    0.04765800
 H    5.80253200       0.55536000    0.03700400
 N    1.72319600      -0.04438000   -0.37622200
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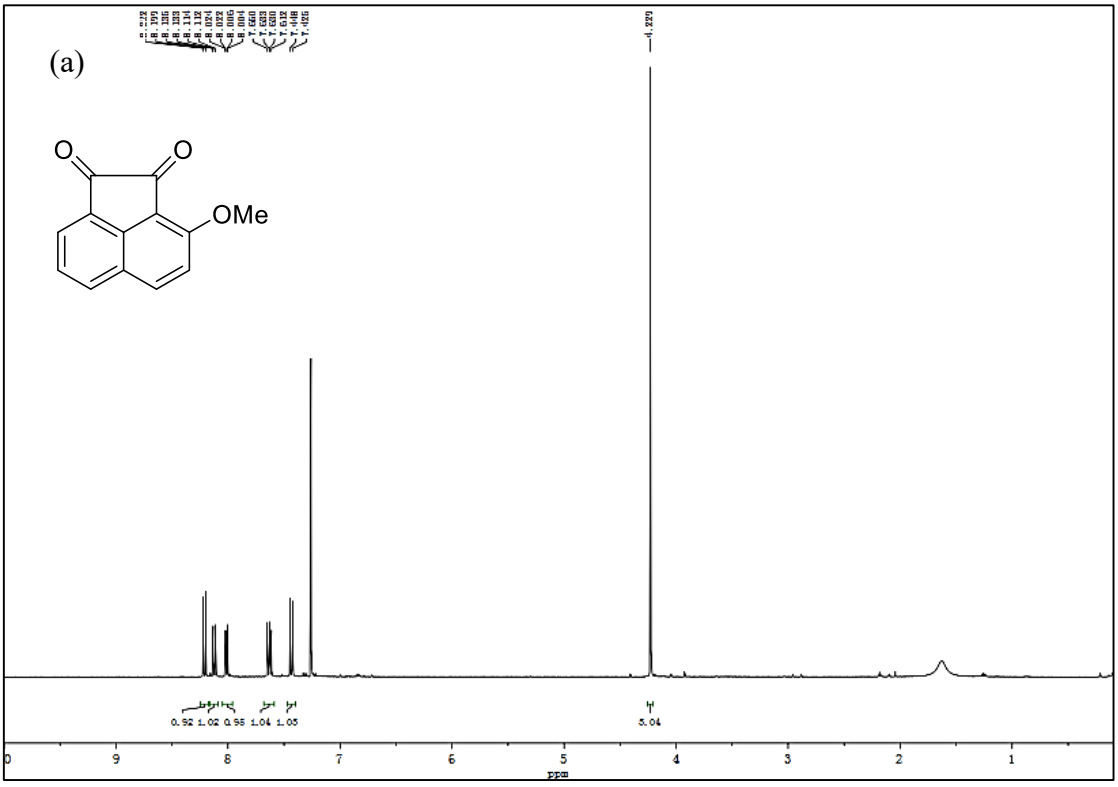
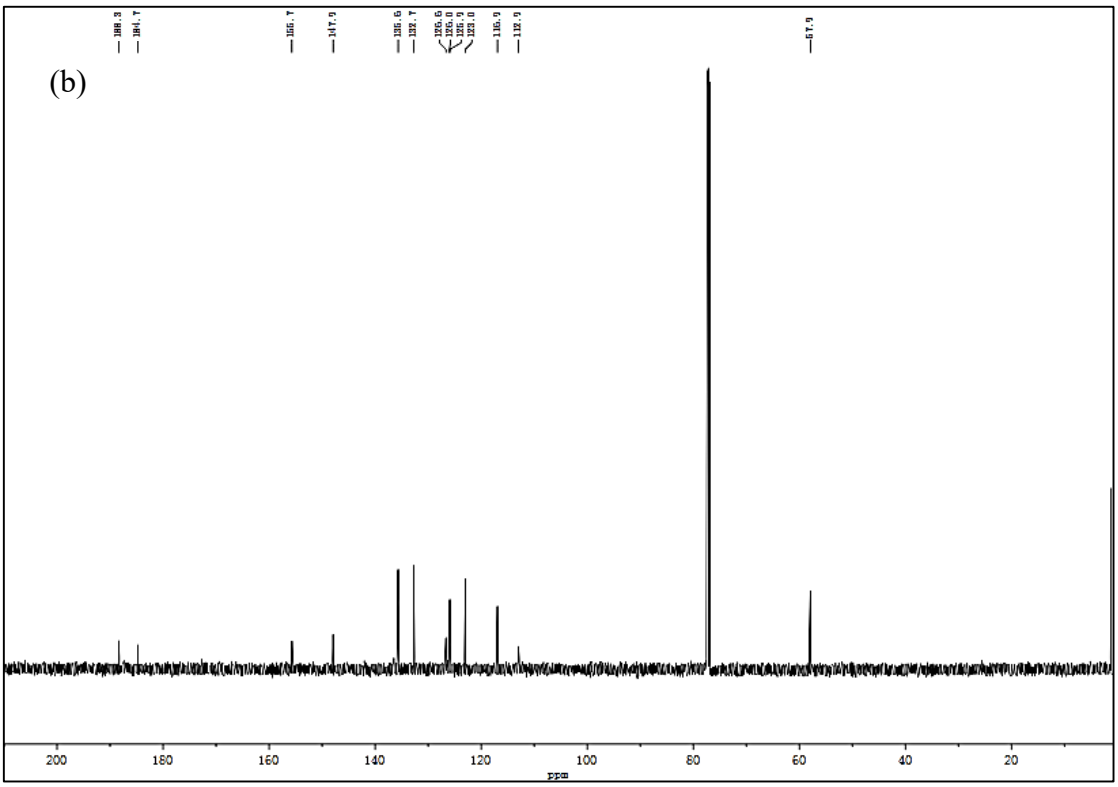
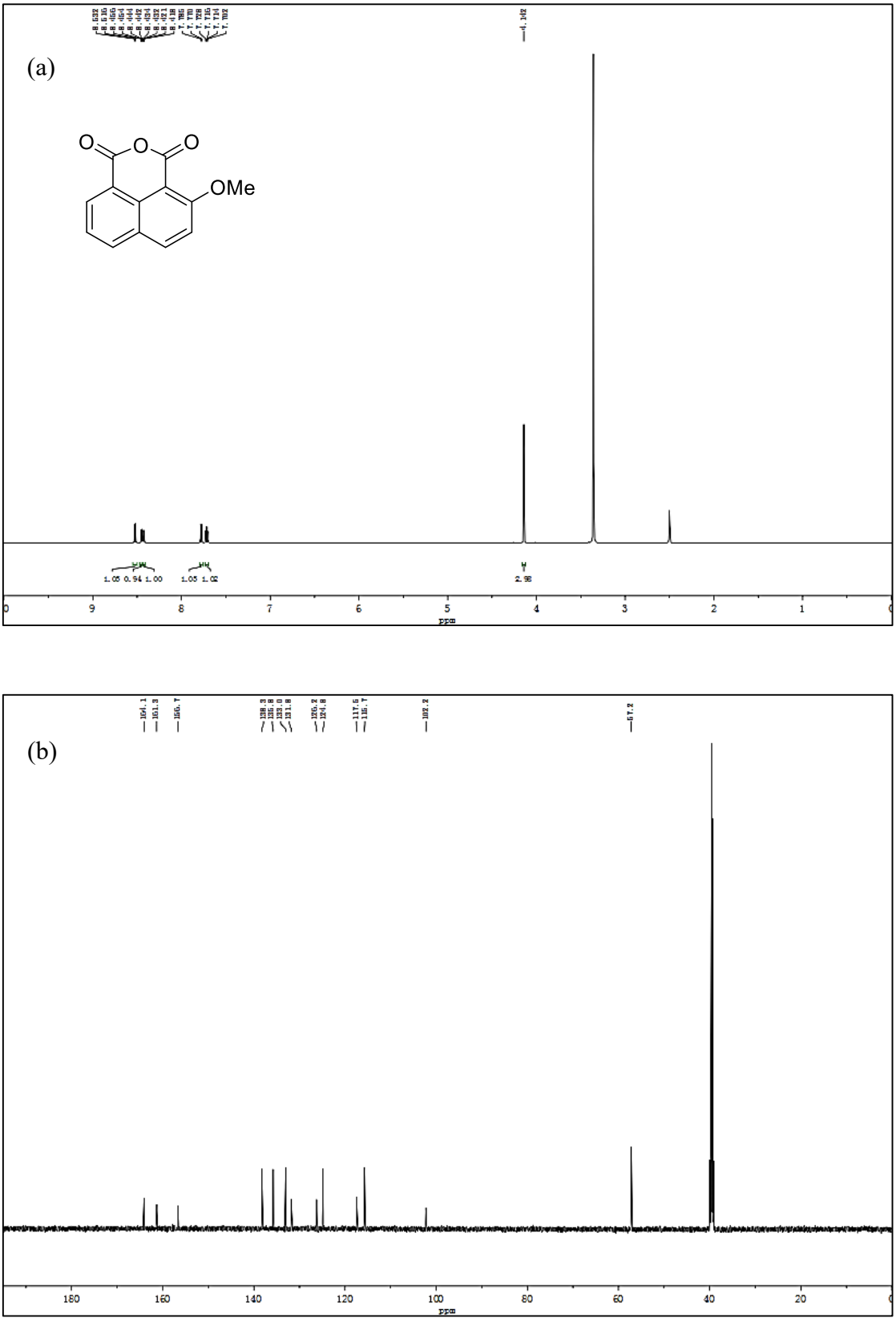
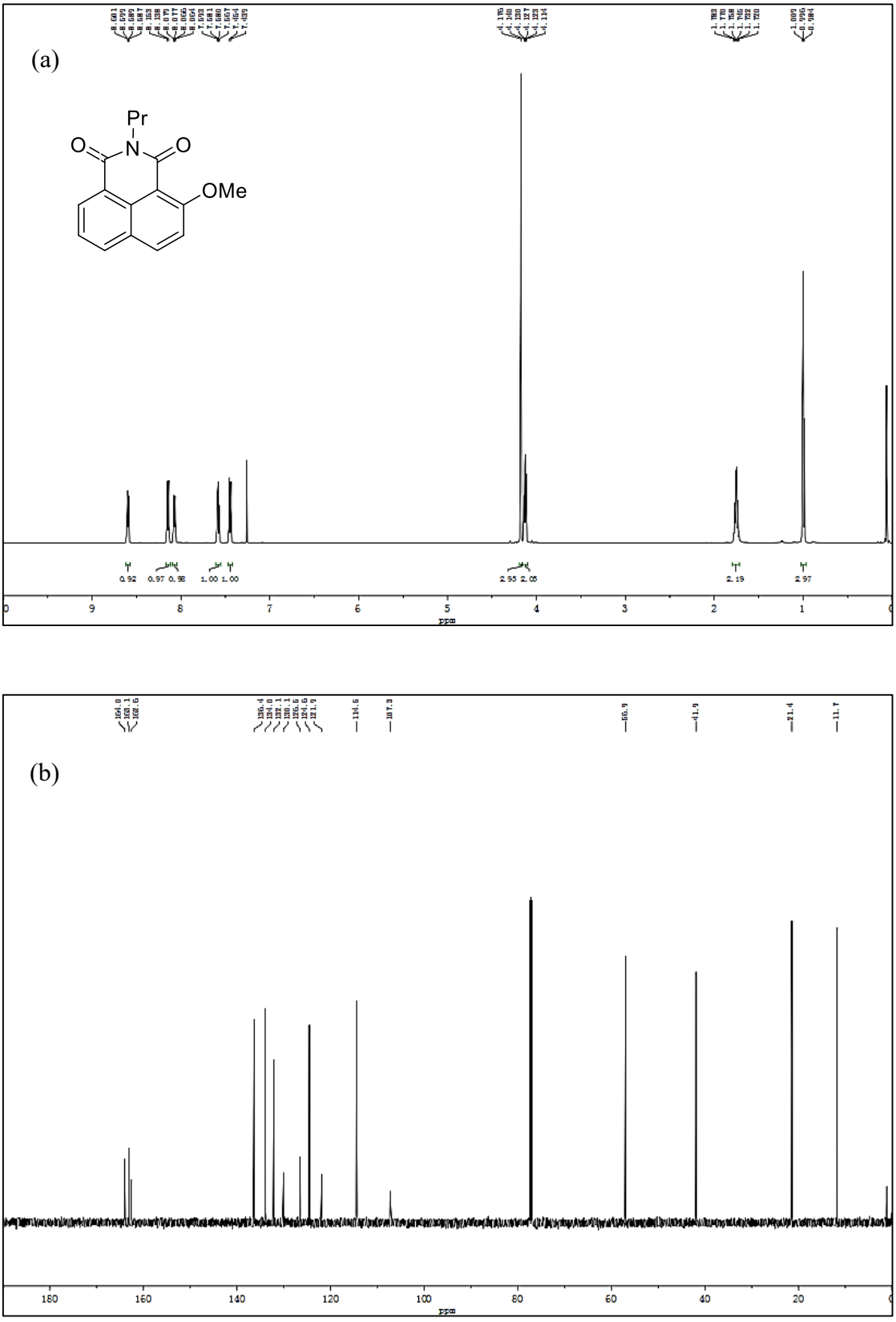




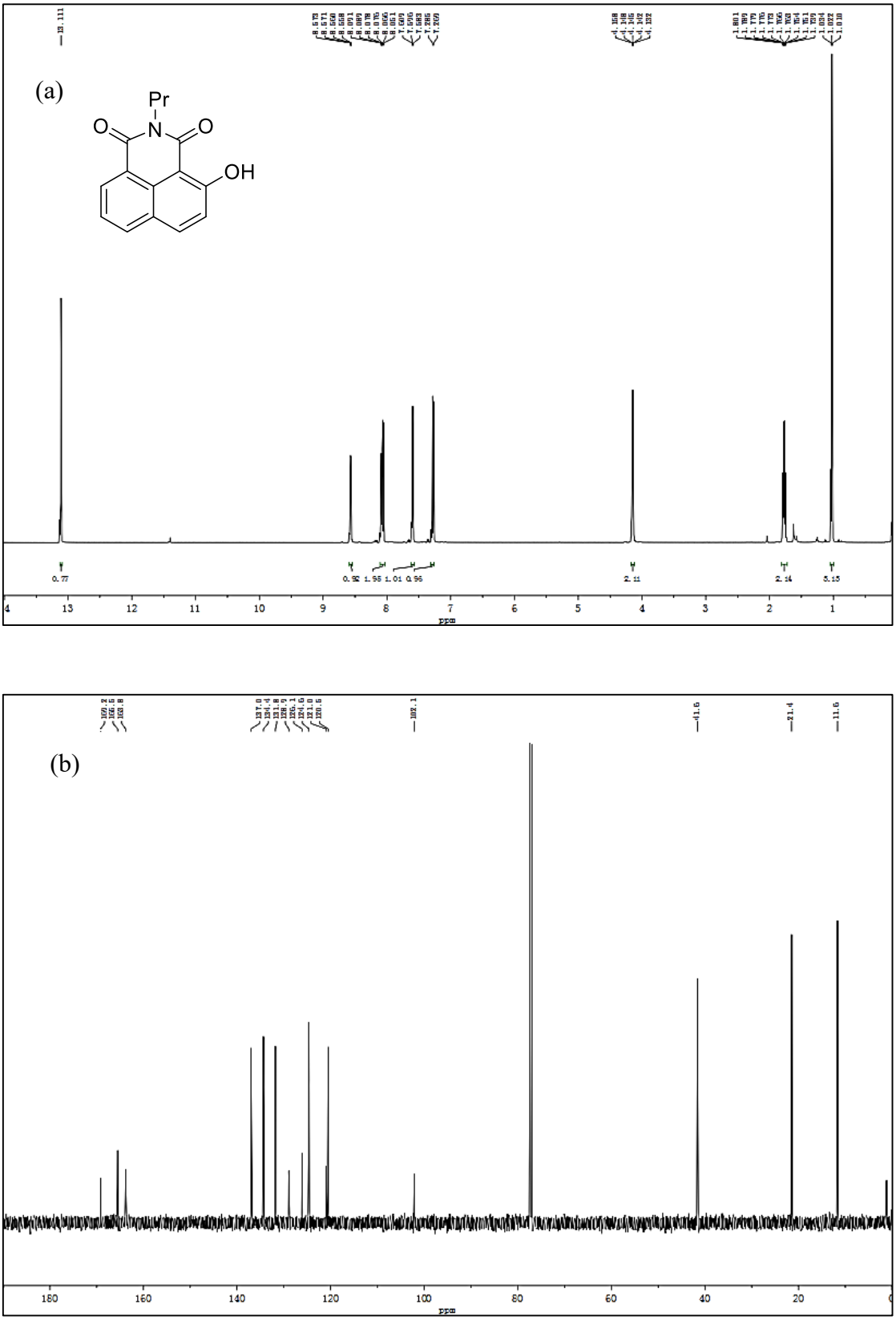
(a) ^{1}H NMR (400 MHz) and (b) ^{13}C NMR (151 MHz) spectra of 3-methoxy-1,2-acenaphthylenedione **3** ($CDCl_3$).



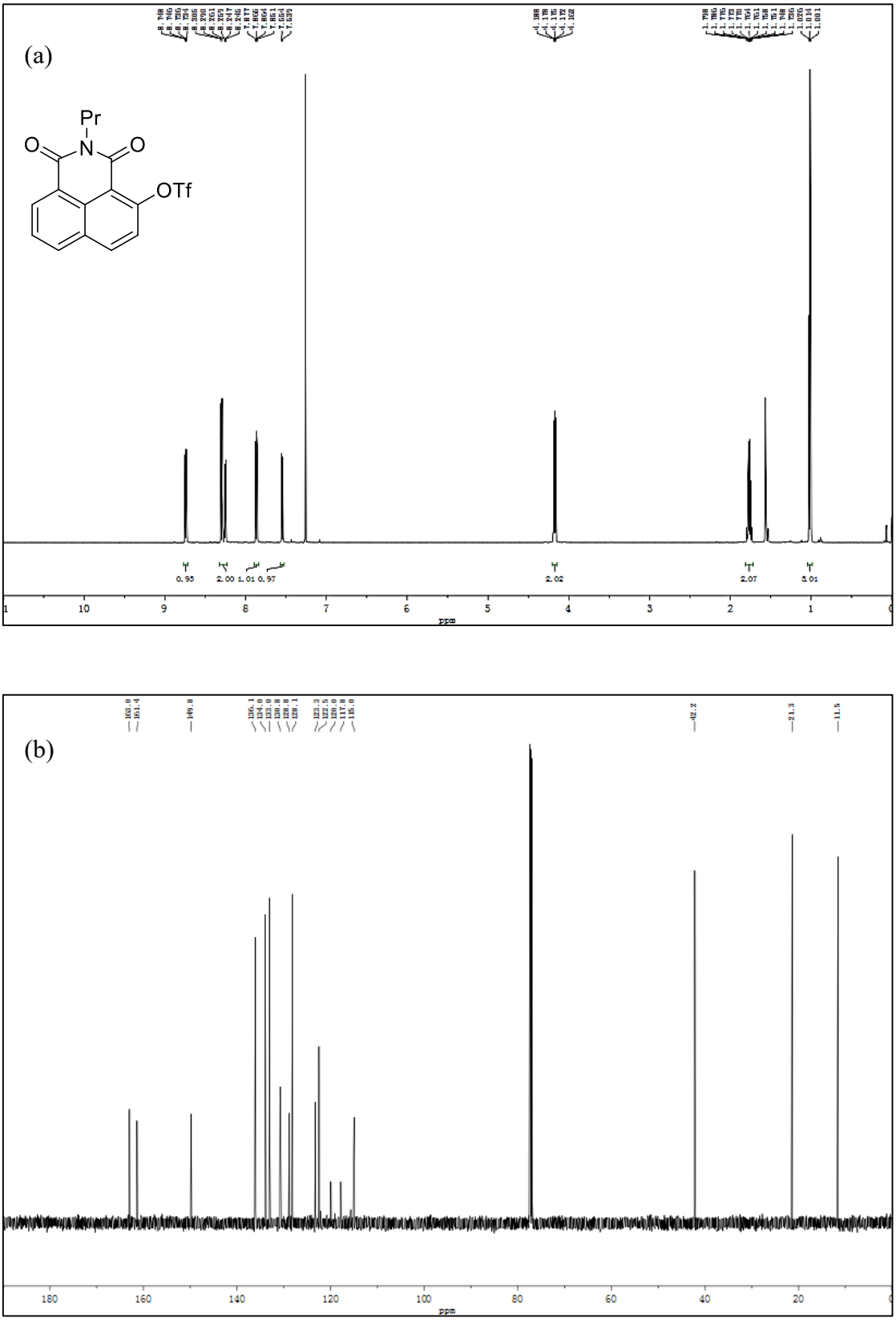
(a) ^{1}H NMR (600 MHz) and (b) ^{13}C NMR (151 MHz) spectra of 2-methoxy-1,8-naphthalic anhydride **4** (DMSO-d_6).



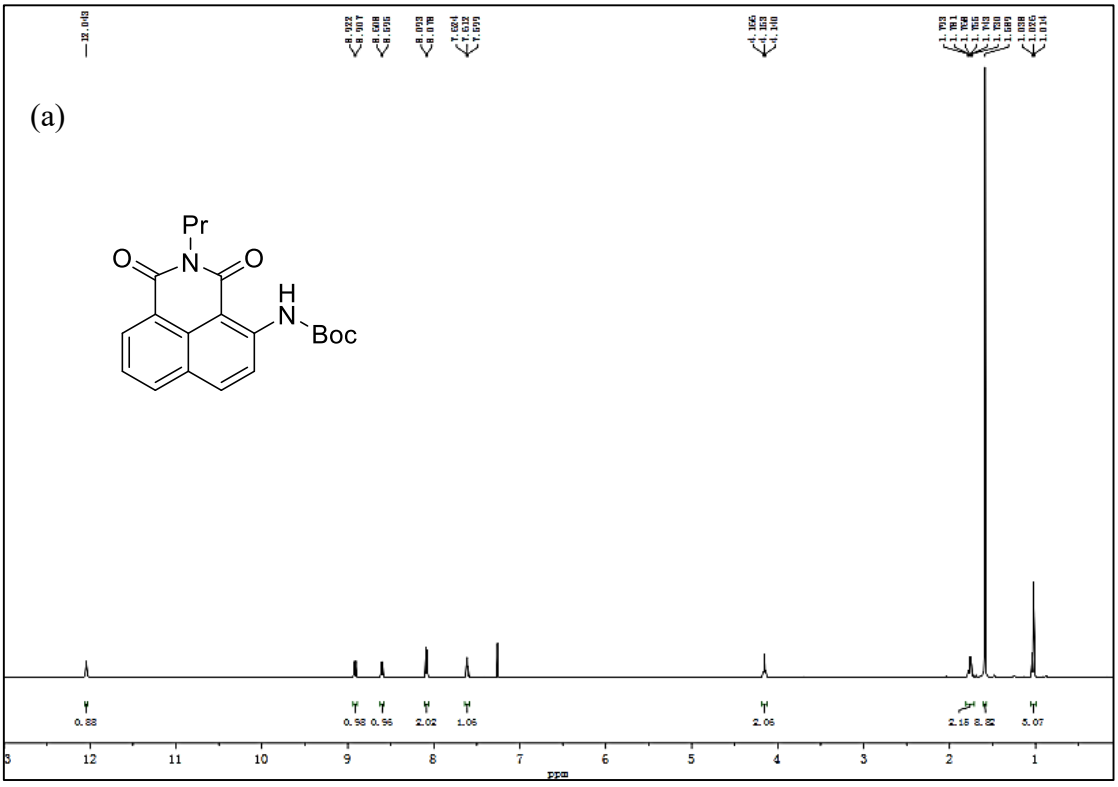
(a) ^{1}H NMR (600 MHz) and (b) ^{13}C NMR (151 MHz) spectra of 2-methoxy-*N*-propyl-1,8-naphthalimide **5** ($CDCl_3$).

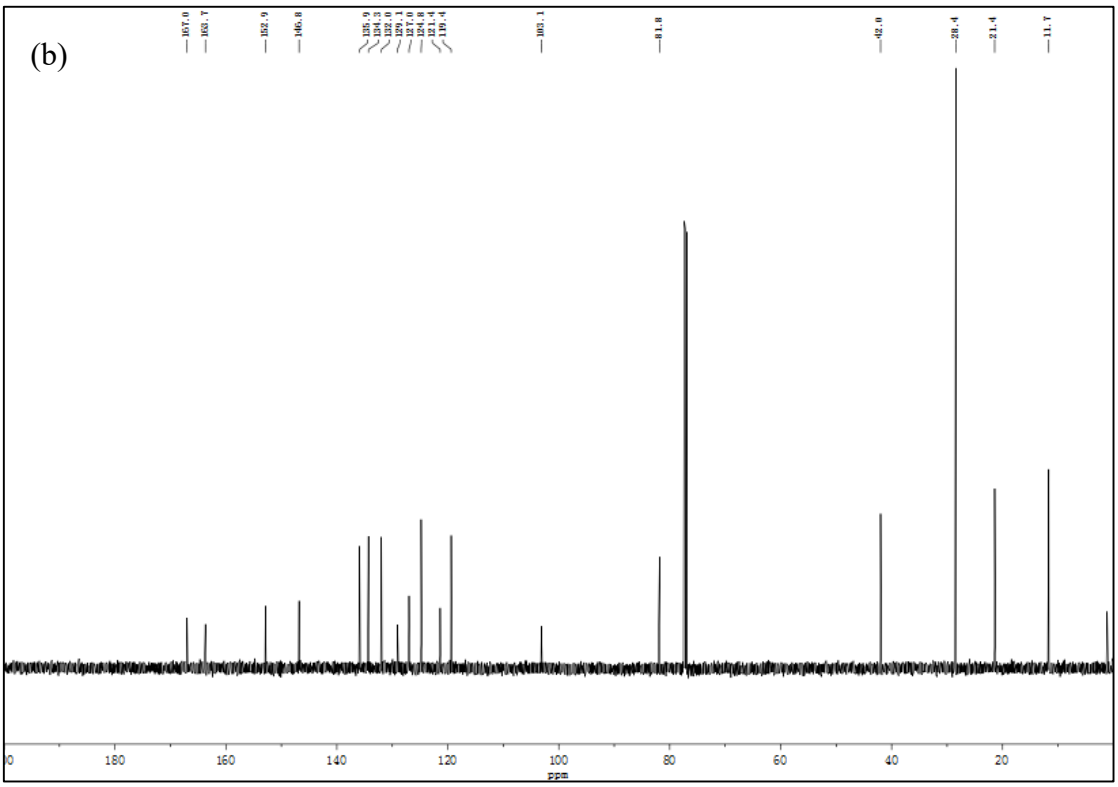


(a) ^{1}H NMR (600 MHz) and (b) ^{13}C NMR (151 MHz) spectra of 2-hydroxy-*N*-propyl-1,8-naphthalimide **6** ($CDCl_3$).

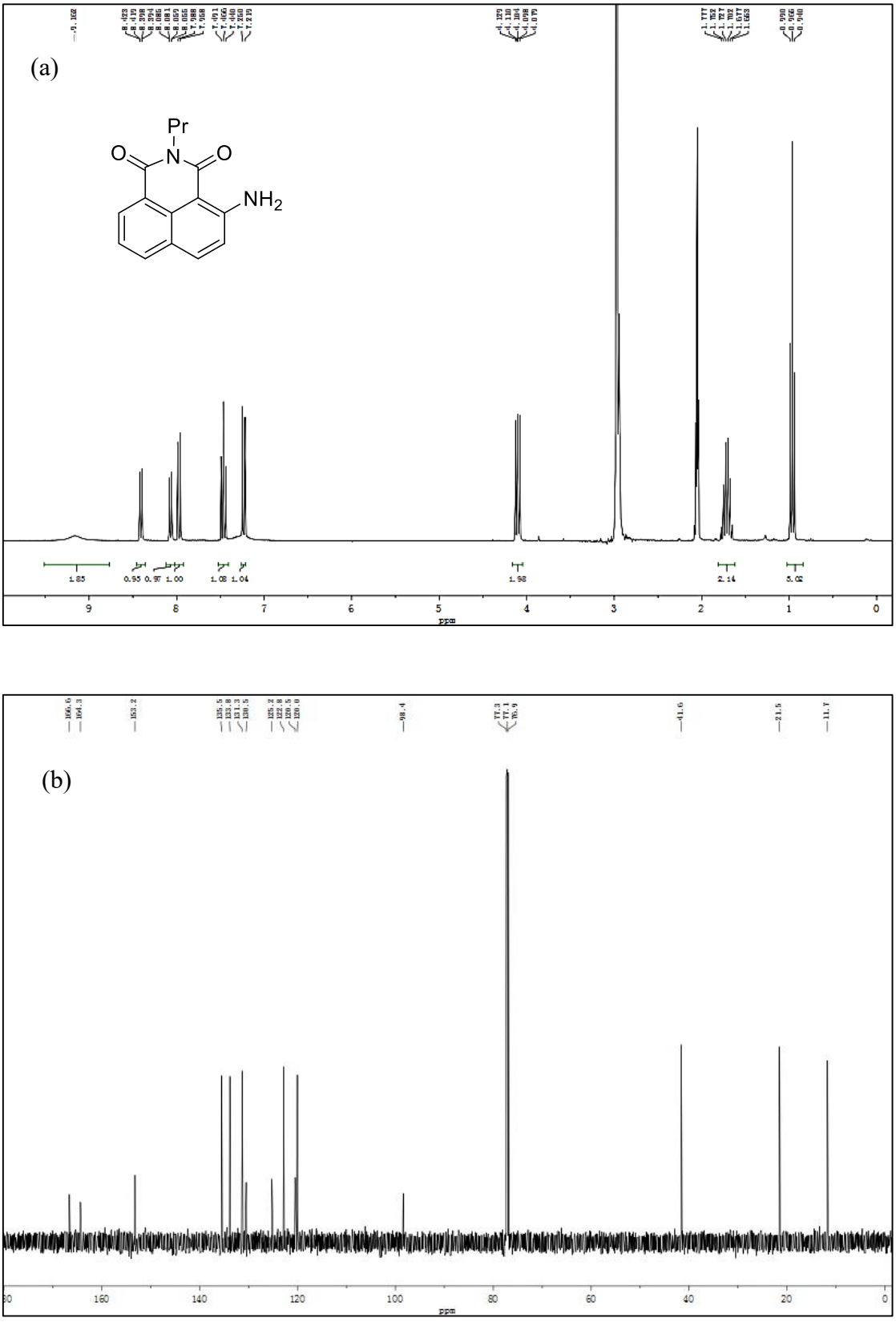


(a) ^{1}H NMR (600 MHz) and (b) ^{13}C NMR (151 MHz) spectra of 2-(trifluoromethanesulfonyloxy)-*N*-propyl-1,8-naphthalimide **7** ($CDCl_3$).

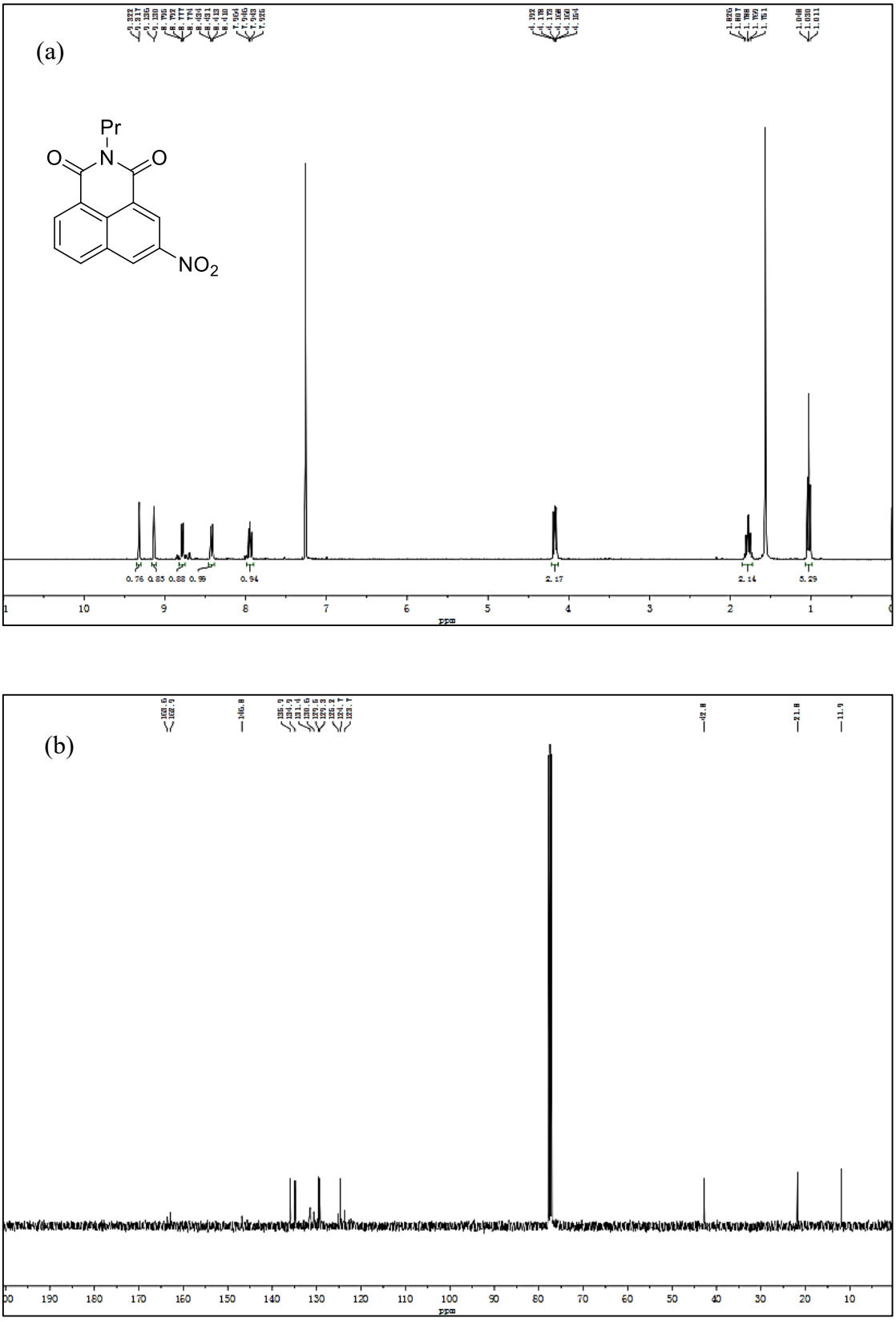




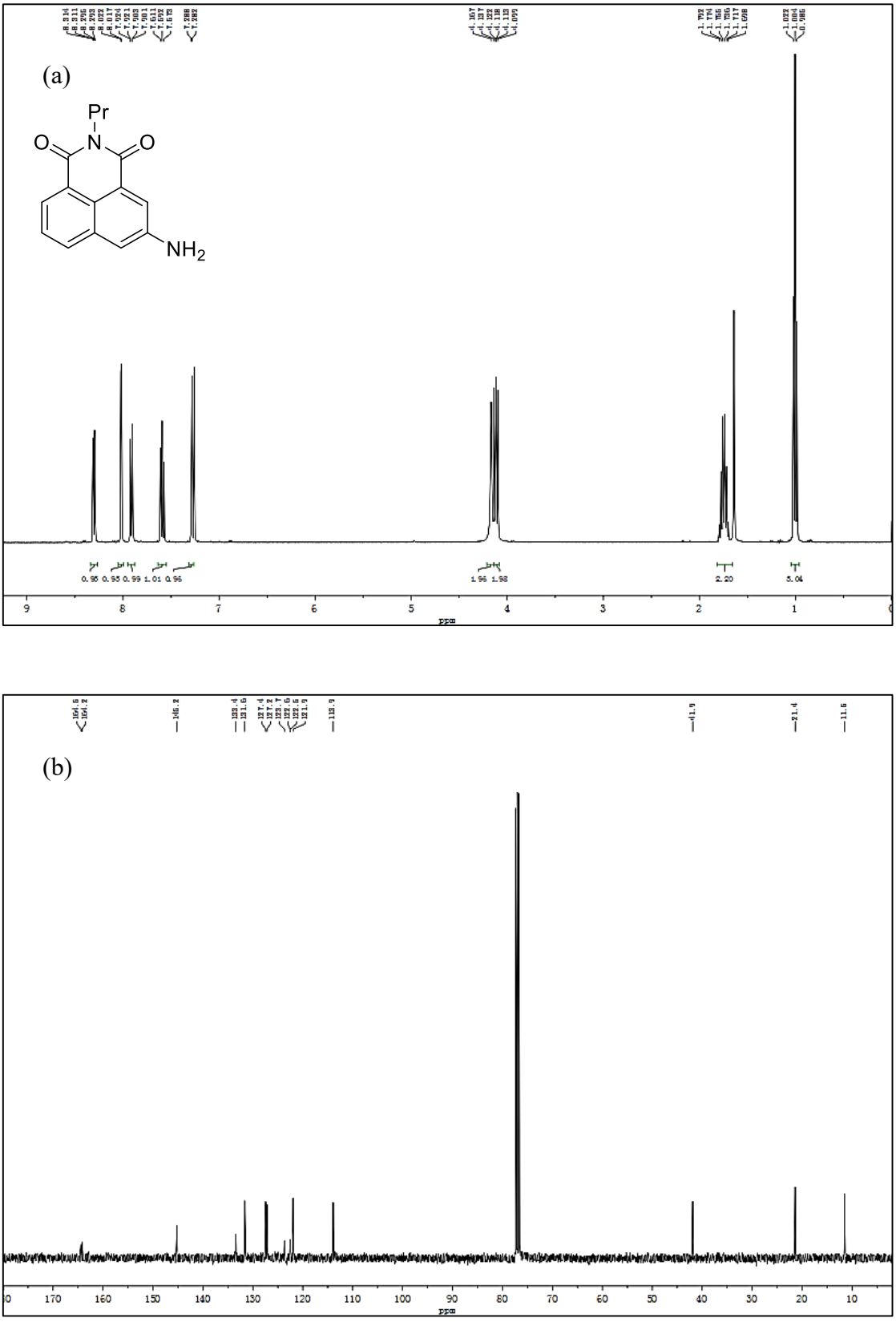
(a) ^{1}H NMR (600 MHz) and (b) ^{13}C NMR (151 MHz) spectra of 2-[(*tert*-butoxycarbonyl)amino]-*N*-propyl-1,8-naphthalimide **8** ($CDCl_3$).



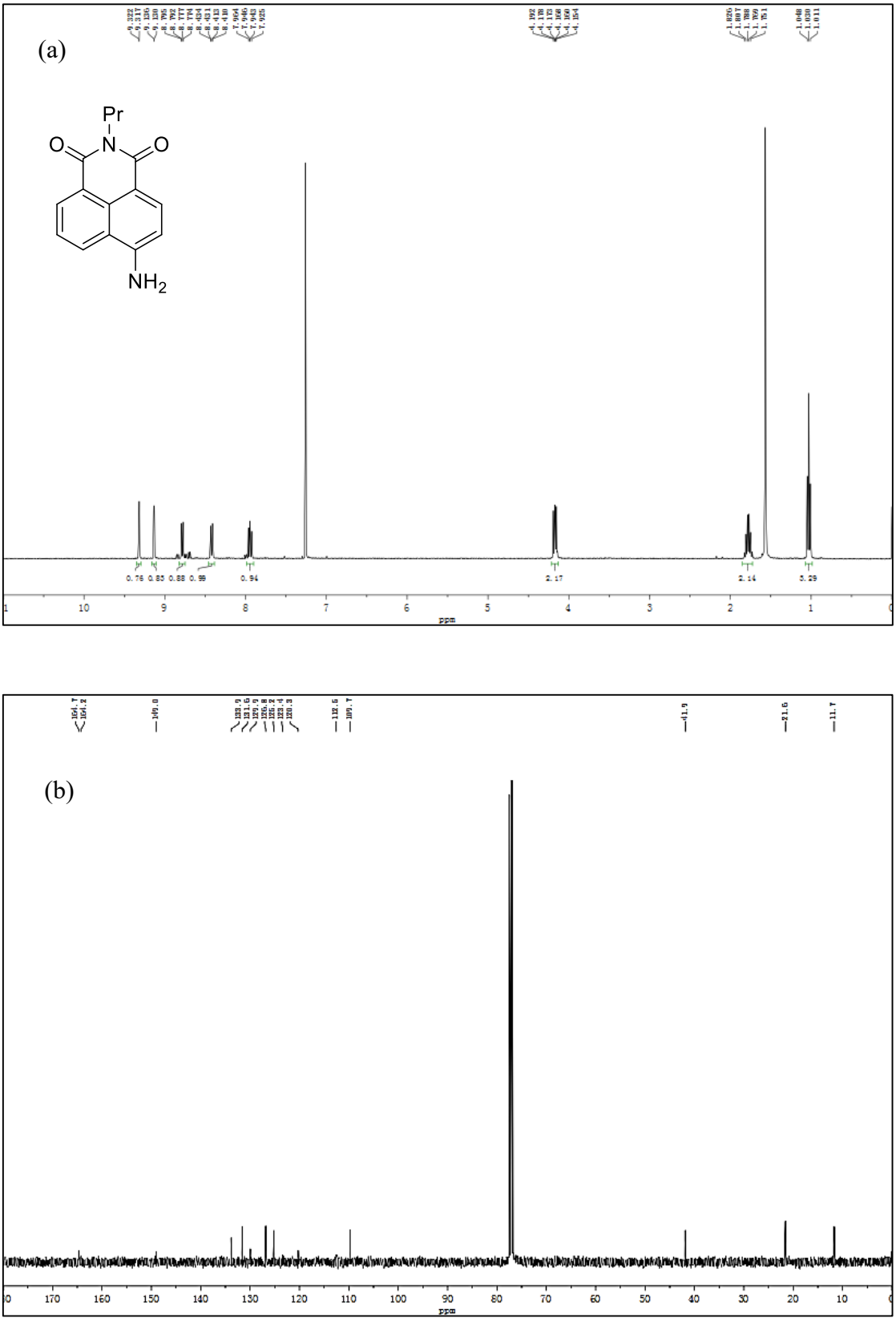
(a) ^{1}H NMR (300 MHz, actone-d_6) and (b) ^{13}C NMR (151 MHz, $CDCl_3$) spectra of **2APNI**.



(a) ^{1}H NMR (400 MHz) and (b) ^{13}C NMR (100 MHz) spectra of 3-nitro-*N*-propyl-1,8-naphthalimide **10** ($CDCl_3$)



(a) ^{1}H NMR (400 MHz) and (b) ^{13}C NMR (100 MHz) spectra of **3APNI** ($CDCl_3$).



(a) ^{1}H NMR (400 MHz) and (b) ^{13}C NMR (100 MHz) spectra of **4APNI** ($CDCl_3$).