Electronic Supplementary Information (ESI)

1, 8-Naphthalimide-based highly blue-emissive fluorophore induced by bromine atom: reversible thermochromism and vapochromism characteristics

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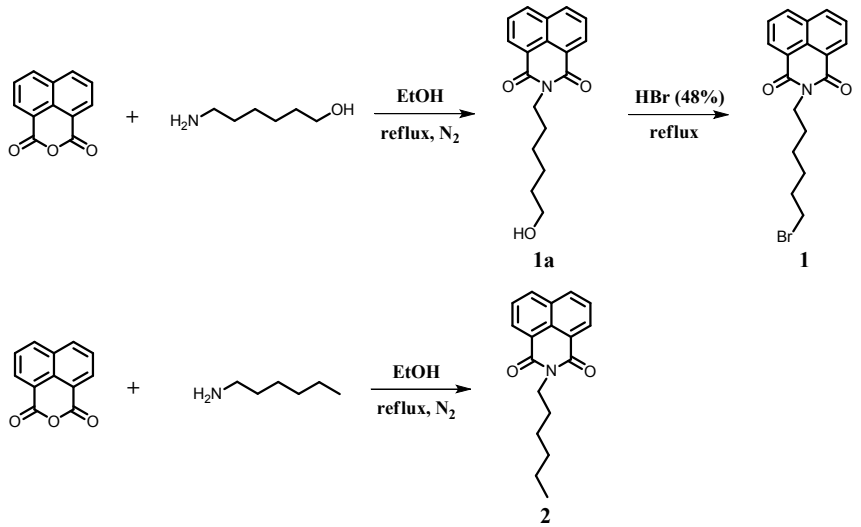
Contents

1. Experimental Section

Materials and measurements

The starting materials 1, 8-naphthalic anhydride, hexylamine, 6-amino-1-hexanol and hydrobromic acid 48% purchased from Alfa Aesar were used as received. ultra-pure water was used in the experiments. All other reagents were purchased as analytical-grade from Shen Shi Hua Gong Company (China) and used without further purification. ^{1}H NMR (400 MHz) and ^{13}C NMR (100.6 MHz) spectra were collected on American Varian Mercury Plus 400 spectrometer (400 MHz). ^{1}H NMR spectra are reported as followed: chemical shift in ppm (δ) relative to the chemical shift of TMS at 0.00 ppm, integration, multiplicities (s=singlet, d=doublet, t=triplet, m=multiplet), and coupling constant (Hz). ^{13}C NMR chemical shifts reported in ppm (δ) relative to the central line of triplet for $CDCl_3$ at 77 ppm. EI-MS was obtained using Thermo scientific DSQⅡ. Elemental analyses (C, H, N) were performed by the Microanalytical Services, College of Chemistry, CCNU. UV-Vis spectra were obtained on U-3310 UV Spectrophotometer. Fluorescence spectra were recorded on a Fluoromax-P luminescence spectrometer (HORIBA JOBIN YVON INC.). the absolute fluorescence quantum yield was measured by Edinburgh Instruments FLS900. The X-ray crystal-structure determinations of compounds **1** and **2** were obtained on a Bruker APEX DUO CCD system.



Scheme S1. Synthesis of the compounds **1** and **2**

General procedure for the synthesis

Synthesis of **1a:** A mixture of 1, 8-naphthalic anhydride (10.1 mmol, 2.0 g), 6-amino-1-hexanol (11.1 mmol) were stirred in EtOH (50 ml) for 4 hours under an argon atmosphere at 78℃. After completion of present reaction, the mixture was extracted with dichloromethane (3×20 mL). The combined organic layers were washed with brine, dried (Na_2SO_4), and concentrated in vacuo. The residues were purified by column chromatography, affording the expected white solid product in a yield of 90.1%. ^{1}H NMR (400 MH_Z, $CDCl_3$): δ (ppm)= 8.59 (d, J= 4 Hz, 2H), 8.20 (d, J= 8 Hz, 2H), 7.75 (t, J= 8 Hz, 2H), 4.18 (t, J= 8 Hz, 2H), 3.64 (d, J= 8 Hz, 2H), 1.87-1.59 (m, 5H), 1.46 (t, J= 4 Hz, 4H). ^{13}C NMR (100 MH_Z, $CDCl_3$): δ (ppm)= 163.97, 133.70, 131.25, 130.96, 127.76, 126.71, 122.30, 62.48, 40.06, 32.43, 27.82, 26.57, 25.18. EI-MS: m/z= 297.30$[M]^+$. Anal. Calcd. for $C_{18}H_{19}NO_3$: C, 72.71; H, 6.44; N, 4.71. Found: C, 72.75; H, 6.40; N, 4.74.

Synthesis of **1:** A mixture of **1a** (6.7 mmol, 2.0 g), hydrobromic acid 48% (33.6 mmol) were stirred for 12 hours at 126℃. After completion of present reaction, the mixture was extracted with dichloromethane (3×20 mL). The combined organic layers were washed with brine, dried (Na_2SO_4), and concentrated in vacuo. The residues were purified by column chromatography, affording the expected white solid product in a yield of 87.0%. ^{1}H NMR (400 MH_Z, $CDCl_3$): δ (ppm)= 8.60 (d, J= 8Hz, 2H), 8.22 (d, J= 8 Hz, 2H), 7.76 (t, J= 8 Hz, 2H), 4.19 (t, J= 8 Hz, 2H), 3.42 (t, J= 6 Hz, 2H), 1.92-1.85 (m, 2H), 1.80-1.72 (m, 2H), 1.54-1.44 (m, 4H). ^{13}C NMR (100 MH_Z, $CDCl_3$): δ (ppm)= 164.11, 133.85, 131.46, 131.13, 128.02, 126.86, 122.55, 40.19, 33.86, 32.61, 27.83, 26.22. EI-MS: m/z= 359.24$[M]^+$. Anal. Calcd. for $C_{18}H_{18}BrNO_2$: C, 60.01; H, 5.04; N, 3.89. Found: C, 60.04; H, 5.00; N, 3.84.

Compounds **2** was prepared by procedures described in the corresponding literature.[1]

Crystallographic Details

Single crystals of compounds **1** and **2** suitable for X-ray analysis were obtained by slow diffusion of *n*-hexane into a solution of dichloromethane containing small amounts of **1** and **2**. Crystals of **1** and **2** with approximate dimensions of 0.10 × 0.10 × 0.10 mm^3 for **1** and **2** were mounted on a glass fiber for diffraction experiment. Intensity data were collected on a Nonius Kappa CCD diffractometer with Mo Kα radiation (0.71073 Å) at room temperature. The structures were solved by a combination of direct methods (SHELXS-97)[2] and Fourier difference techniques and refined by full-matrix least-squares (SHELXL-97)[3]. All non-H atoms were refined anisotropically. The hydrogen atoms were placed in the ideal positions and refined as riding atoms. Further crystal datas of **1** and **2** are summarized in Table S1 and S2. Bond distances and angles of **1** and **2** are given in Table S3 and S4. Crystallographic datas for compounds **1** and **2** in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplemental publication CCDC 1014213 (compound **1**), CCDC 1014214 (compound **2**).

2. References

1. S. Asaoka, N. Takeda, T. Lyoda, A. R. Cook and J. R. Miller. *J. Am. Chem. Soc*. 2008; **130**: 11912.

2. G. M. Sheldrick, SHELXS-97: Program for crystal structure solution, University of Götingen, Götingen, Germany, **1997**.

3. G. M. Sheldrick, SHELXL-97: Program for crystal structure refinement, University of Götingen, Götingen, Germany, **1997**.

3. Fig. S1

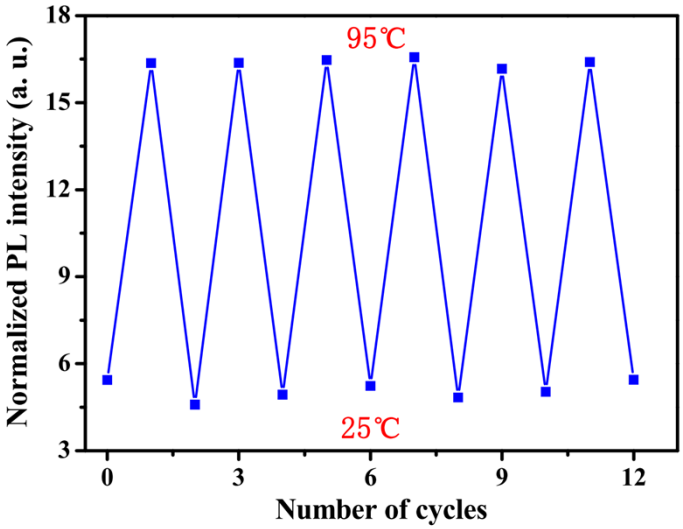


Fig. S1 Reversible temperature-dependence of the PL of **1** at 457 nm.

4. Table S1-S4

Table S1. Structure determination summary for the compound **1**.

Empirical formula	C_{18} $H_{18}BrNO_2$
Formula weight	360.24
Temperature (K)	298(2)
Crystal system	Orthorhombic
Space group	Pca2(1)
a (Å)	24.404(4)
b (Å)	4.7162(9)
c (Å)	14.206(3)
α (deg)	90
β (deg)	90
γ (deg)	90
V (Å^3)	1635.1(5)
Z	4
Absorption coefficient (mm^{-1})	2.520
F (000)	736

Theta range for data collection (deg)	2.20 to 31.59
Index ranges	-35<=h<=35, -6<=k<=6, -20<=l<=17
Reflections collected/unique	16467/5002 (R_{int}= 0.0428)
Final R indices [I>2sigma(I)]	R_1= 0.0404, wR_2= 0.0976
R indices (all data)	R_1= 0.0831, wR_2= 0.1118
Goodness-of-fit on F^2	0.972
Largest difference peak and hole(e $Å^{-3}$)	0.367, -0.431

Table S2. Structure determination summary for the compound **2**.

Empirical formula	C_{18} $H_{19}NO_2$
Formula weight	281.34
Temperature (K)	298(2)
Crystal system	Monoclinic
Space group	P2(1)/n
a (Å)	8.2418(14)
b (Å)	16.336(3)
c (Å)	11.3610(19)
α (deg)	90
β (deg)	103.266(3)
γ (deg)	90
V ($Å^3$)	1488.8(4)
Z	4
Absorption coefficient (mm^{-1})	0.082
F (000)	600
Theta range for data collection (deg)	2.22 to 25.99
Index ranges	-10<=h<=10, -20<=k<=20, -13<=l<=14
Reflections collected/unique	11160/2930 (R_{int}= 0.0346)
Final R indices [I>2sigma(I)]	R_1= 0.0569, wR_2= 0.1592
R indices (all data)	R_1= 0.0689, wR_2= 0.1744
Goodness-of-fit on F^2	1.036
Largest difference peak and hole(e $Å^{-3}$)	0.625, -0.295

Table S3. Bond lengths [Å] and angles [°] of **1**.

Br(1)-C(18)	1.948(3)	C(16)-H(16B)	0.9700
C(1)-O(1)	1.206(3)	C(17)-C(18)	1.495(4)
C(1)-N(1)	1.398(4)	C(17)-H(17A)	0.9700
C(1)-C(2)	1.481(4)	C(17)-H(17B)	0.9700
C(2)-C(3)	1.362(4)	C(18)-H(18A)	0.9700
C(2)-C(12)	1.405(4)	C(18)-H(18B)	0.9700
C(3)-C(4)	1.404(5)		
C(3)-H(3)	0.9300	O(1)-C(1)-N(1)	120.0(3)
C(4)-C(5)	1.355(5)	O(1)-C(1)-C(2)	123.1(3)
C(4)-H(4)	0.9300	N(1)-C(1)-C(2)	116.9(2)
C(5)-C(6)	1.411(4)	C(3)-C(2)-C(12)	120.2(3)
C(5)-H(5)	0.9300	C(3)-C(2)-C(1)	119.7(3)
C(6)-C(7)	1.416(4)	C(12)-C(2)-C(1)	120.2(2)
C(6)-C(12)	1.421(4)	C(2)-C(3)-C(4)	120.2(3)
C(7)-C(8)	1.353(5)	C(2)-C(3)-H(3)	119.9
C(7)-H(7)	0.9300	C(4)-C(3)-H(3)	119.9
C(8)-C(9)	1.393(4)	C(5)-C(4)-C(3)	121.0(3)
C(8)-H(8)	0.9300	C(5)-C(4)-H(4)	119.5
C(9)-C(10)	1.379(4)	C(3)-C(4)-H(4)	119.5
C(9)-H(9)	0.9300	C(4)-C(5)-C(6)	120.6(3)
C(10)-C(12)	1.408(4)	C(4)-C(5)-H(5)	119.7
C(10)-C(11)	1.475(3)	C(6)-C(5)-H(5)	119.7
C(11)-O(2)	1.213(3)	C(5)-C(6)-C(7)	123.4(3)
C(11)-N(1)	1.399(4)	C(5)-C(6)-C(12)	118.2(3)
C(13)-N(1)	1.468(3)	C(7)-C(6)-C(12)	118.4(2)
C(13)-C(14)	1.512(4)	C(8)-C(7)-C(6)	121.1(3)
C(13)-H(13A)	0.9700	C(8)-C(7)-H(7)	119.5
C(13)-H(13B)	0.9700	C(6)-C(7)-H(7)	119.5
C(14)-C(15)	1.520(4)	C(7)-C(8)-C(9)	120.6(3)
C(14)-H(14A)	0.9700	C(7)-C(8)-H(8)	119.7
C(14)-H(14B)	0.9700	C(9)-C(8)-H(8)	119.7
C(15)-C(16)	1.525(4)	C(10)-C(9)-C(8)	120.7(3)
C(15)-H(15A)	0.9700	C(10)-C(9)-H(9)	119.7
C(15)-H(15B)	0.9700	C(8)-C(9)-H(9)	119.7
C(16)-C(17)	1.510(4)	C(9)-C(10)-C(12)	119.8(2)
C(16)-H(16A)	0.9700	C(9)-C(10)-C(11)	119.8(2)

C(12)-C(10)-C(11)	120.4(2)	C(16)-C(15)-H(15B)	109.0
O(2)-C(11)-N(1)	120.4(2)	H(15A)-C(15)-H(15B)	107.8
O(2)-C(11)-C(10)	122.7(2)	C(17)-C(16)-C(15)	112.5(2)
N(1)-C(11)-C(10)	116.9(2)	C(17)-C(16)-H(16A)	109.1
C(2)-C(12)-C(10)	120.8(2)	C(15)-C(16)-H(16A)	109.1
C(2)-C(12)-C(6)	119.8(2)	C(17)-C(16)-H(16B)	109.1
C(10)-C(12)-C(6)	119.4(2)	C(15)-C(16)-H(16B)	109.1
N(1)-C(13)-C(14)	111.7(2)	H(16A)-C(16)-H(16B)	107.8
N(1)-C(13)-H(13A)	109.3	C(18)-C(17)-C(16)	115.3(3)
C(14)-C(13)-H(13A)	109.3	C(18)-C(17)-H(17A)	108.5
N(1)-C(13)-H(13B)	109.3	C(16)-C(17)-H(17A)	108.5
C(14)-C(13)-H(13B)	109.3	C(18)-C(17)-H(17B)	108.5
H(13A)-C(13)-H(13B)	107.9	C(16)-C(17)-H(17B)	108.5
C(13)-C(14)-C(15)	112.7(2)	H(17A)-C(17)-H(17B)	107.5
C(13)-C(14)-H(14A)	109.1	C(17)-C(18)-Br(1)	112.8(2)
C(15)-C(14)-H(14A)	109.1	C(17)-C(18)-H(18A)	109.0
C(13)-C(14)-H(14B)	109.1	Br(1)-C(18)-H(18A)	109.0
C(15)-C(14)-H(14B)	109.1	C(17)-C(18)-H(18B)	109.0
H(14A)-C(14)-H(14B)	107.8	Br(1)-C(18)-H(18B)	109.0
C(14)-C(15)-C(16)	113.1(2)	H(18A)-C(18)-H(18B)	107.8
C(14)-C(15)-H(15A)	109.0	C(1)-N(1)-C(11)	124.8(2)
C(16)-C(15)-H(15A)	109.0	C(1)-N(1)-C(13)	118.0(2)
C(14)-C(15)-H(15B)	109.0	C(11)-N(1)-C(13)	117.0(2)

Table S4. Bond lengths [Å] and angles [^{o}] of **2**.

C(1)-O(1)	1.215(2)	C(6)-C(11)	1.413(3)
C(1)-N(1)	1.393(2)	C(6)-C(7)	1.417(2)
C(1)-C(2)	1.472(2)	C(7)-C(8)	1.406(2)
C(2)-C(3)	1.373(3)	C(8)-C(9)	1.378(2)
C(2)-C(7)	1.413(2)	C(8)-C(12)	1.474(3)
C(3)-C(4)	1.407(3)	C(9)-C(10)	1.403(3)
C(3)-H(3)	0.9300	C(9)-H(9)	0.9300
C(4)-C(5)	1.355(3)	C(10)-C(11)	1.356(3)
C(4)-H(4)	0.9300	C(10)-H(10)	0.9300
C(5)-C(6)	1.411(3)	C(11)-H(11)	0.9300
C(5)-H(5)	0.9300	C(12)-O(2)	1.214(2)

C(12)-N(1)	1.398(2)	C(11)-C(6)-C(7)	117.96(19)
C(13)-N(1)	1.476(2)	C(8)-C(7)-C(2)	120.68(15)
C(13)-C(14)	1.502(3)	C(8)-C(7)-C(6)	119.99(16)
C(13)-H(13A)	0.9700	C(2)-C(7)-C(6)	119.32(17)
C(13)-H(13B)	0.9700	C(9)-C(8)-C(7)	120.28(17)
C(14)-C(15)	1.523(3)	C(9)-C(8)-C(12)	119.46(17)
C(14)-H(14A)	0.9700	C(7)-C(8)-C(12)	120.26(15)
C(14)-H(14B)	0.9700	C(8)-C(9)-C(10)	119.6(2)
C(15)-C(16)	1.542(3)	C(8)-C(9)-H(9)	120.2
C(15)-H(15A)	0.9700	C(10)-C(9)-H(9)	120.2
C(15)-H(15B)	0.9700	C(11)-C(10)-C(9)	120.96(19)
C(16)-C(17)	1.493(3)	C(11)-C(10)-H(10)	119.5
C(16)-H(16A)	0.9700	C(9)-C(10)-H(10)	119.5
C(16)-H(16B)	0.9700	C(10)-C(11)-C(6)	121.17(19)
C(17)-C(18)	1.493(3)	C(10)-C(11)-H(11)	119.4
C(17)-H(17A)	0.9700	C(6)-C(11)-H(11)	119.4
C(17)-H(17B)	0.9700	O(2)-C(12)-N(1)	120.01(17)
C(18)-H(18A)	0.9600	O(2)-C(12)-C(8)	123.17(17)
C(18)-H(18B)	0.9600	N(1)-C(12)-C(8)	116.81(15)
C(18)-H(18C)	0.9600	N(1)-C(13)-C(14)	112.10(16)
		N(1)-C(13)-H(13A)	109.2
O(1)-C(1)-N(1)	120.17(16)	C(14)-C(13)-H(13A)	109.2
O(1)-C(1)-C(2)	122.70(17)	N(1)-C(13)-H(13B)	109.2
N(1)-C(1)-C(2)	117.12(15)	C(14)-C(13)-H(13B)	109.2
C(3)-C(2)-C(7)	120.02(16)	H(13A)-C(13)-H(13B)	107.9
C(3)-C(2)-C(1)	119.96(16)	C(13)-C(14)-C(15)	112.45(17)
C(7)-C(2)-C(1)	120.02(16)	C(13)-C(14)-H(14A)	109.1
C(2)-C(3)-C(4)	120.31(19)	C(15)-C(14)-H(14A)	109.1
C(2)-C(3)-H(3)	119.8	C(13)-C(14)-H(14B)	109.1
C(4)-C(3)-H(3)	119.8	C(15)-C(14)-H(14B)	109.1
C(5)-C(4)-C(3)	120.64(19)	H(14A)-C(14)-H(14B)	107.8
C(5)-C(4)-H(4)	119.7	C(14)-C(15)-C(16)	111.89(17)
C(3)-C(4)-H(4)	119.7	C(14)-C(15)-H(15A)	109.2
C(4)-C(5)-C(6)	120.81(18)	C(16)-C(15)-H(15A)	109.2
C(4)-C(5)-H(5)	119.6	C(14)-C(15)-H(15B)	109.2
C(6)-C(5)-H(5)	119.6	C(16)-C(15)-H(15B)	109.2
C(5)-C(6)-C(11)	123.14(18)	H(15A)-C(15)-H(15B)	107.9
C(5)-C(6)-C(7)	118.90(18)	C(17)-C(16)-C(15)	114.96(18)

C(17)-C(16)-H(16A)	108.5	H(17A)-C(17)-H(17B)	107.8
C(15)-C(16)-H(16A)	108.5	C(17)-C(18)-H(18A)	109.5
C(17)-C(16)-H(16B)	108.5	C(17)-C(18)-H(18B)	109.5
C(15)-C(16)-H(16B)	108.5	H(18A)-C(18)-H(18B)	109.5
H(16A)-C(16)-H(16B)	107.5	C(17)-C(18)-H(18C)	109.5
C(18)-C(17)-C(16)	112.7(2)	H(18A)-C(18)-H(18C)	109.5
C(18)-C(17)-H(17A)	109.0	H(18B)-C(18)-H(18C)	109.5
C(16)-C(17)-H(17A)	109.0	C(1)-N(1)-C(12)	124.96(14)
C(18)-C(17)-H(17B)	109.0	C(1)-N(1)-C(13)	118.38(15)
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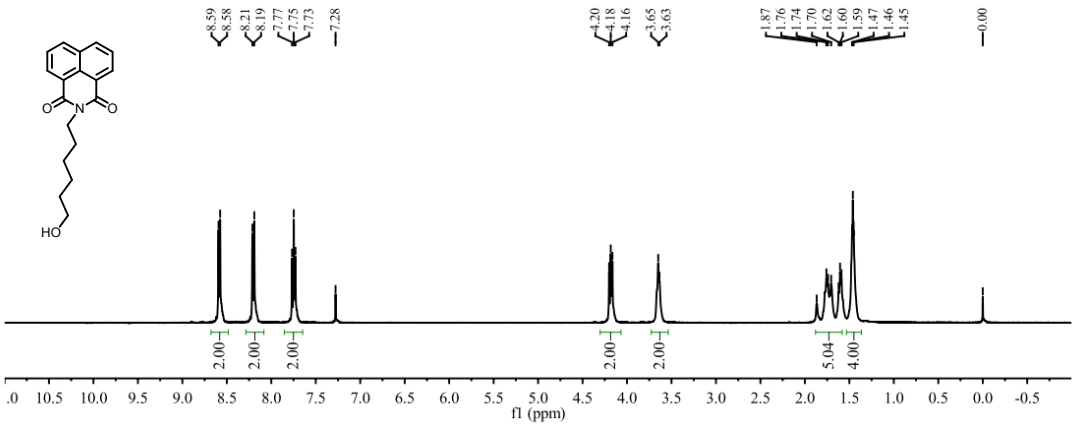
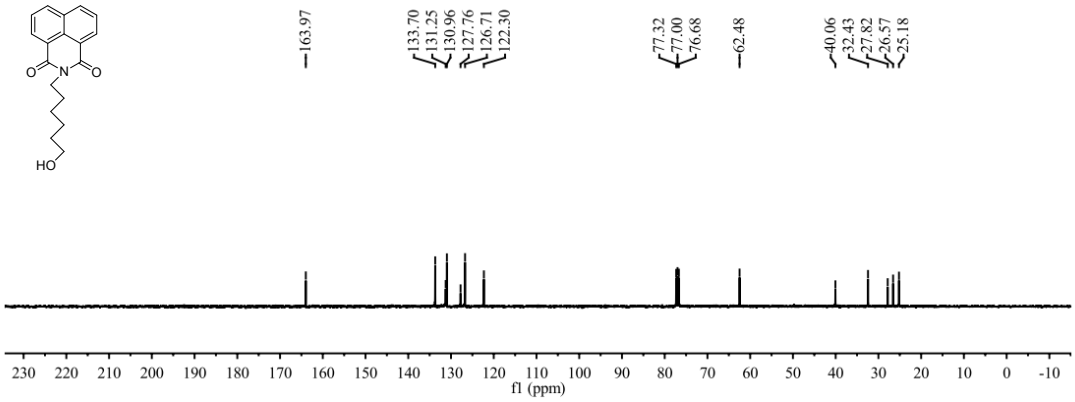
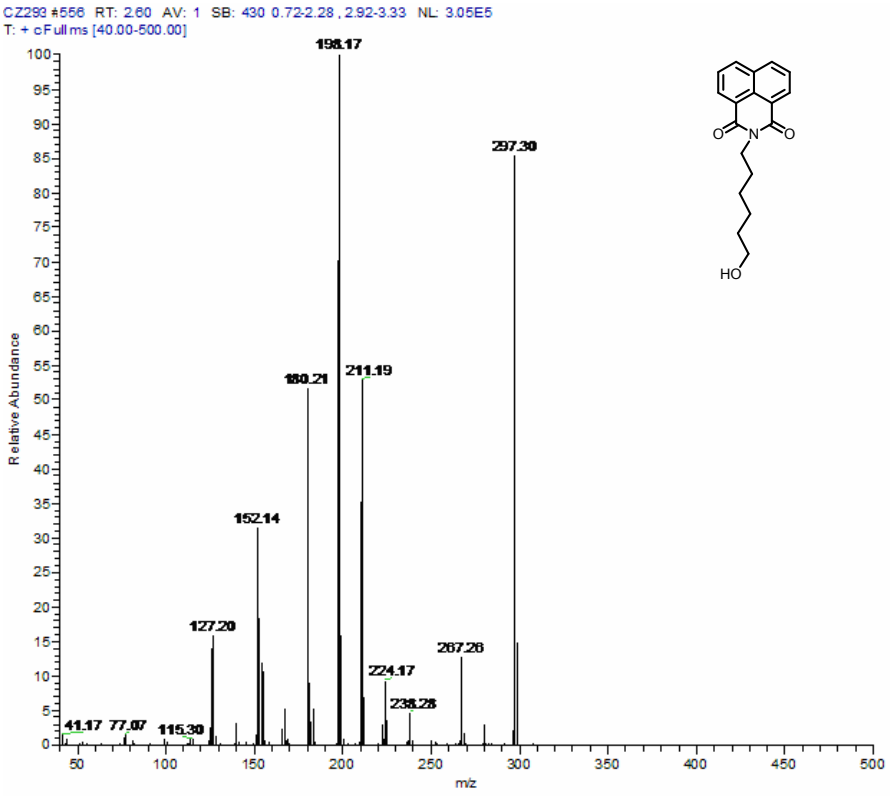
5. Copies of NMR spectra and Mass spectra



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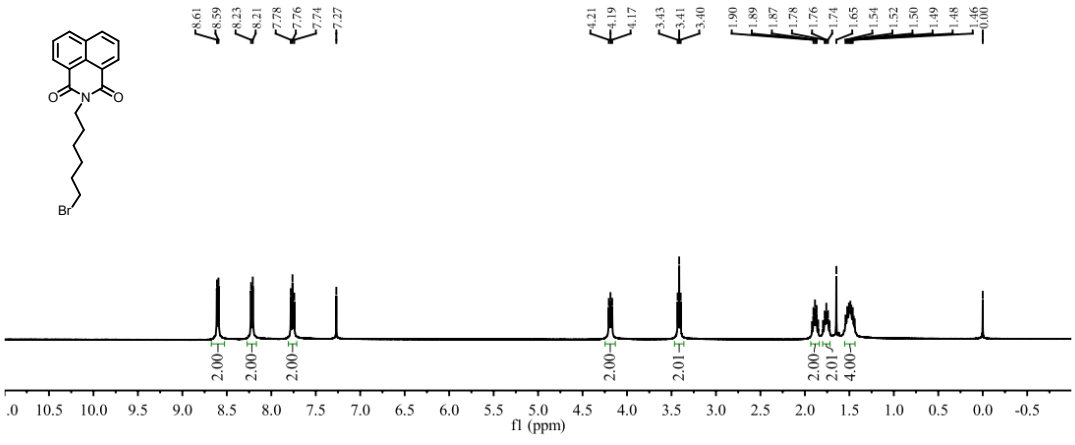
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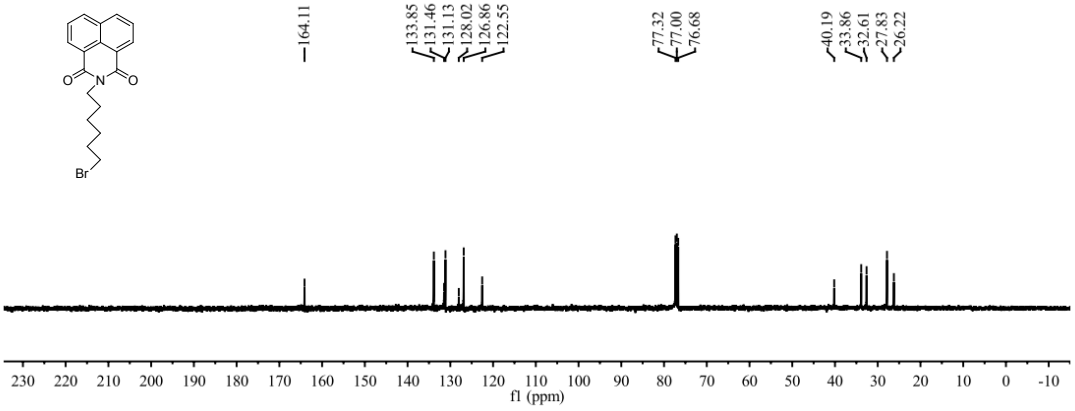
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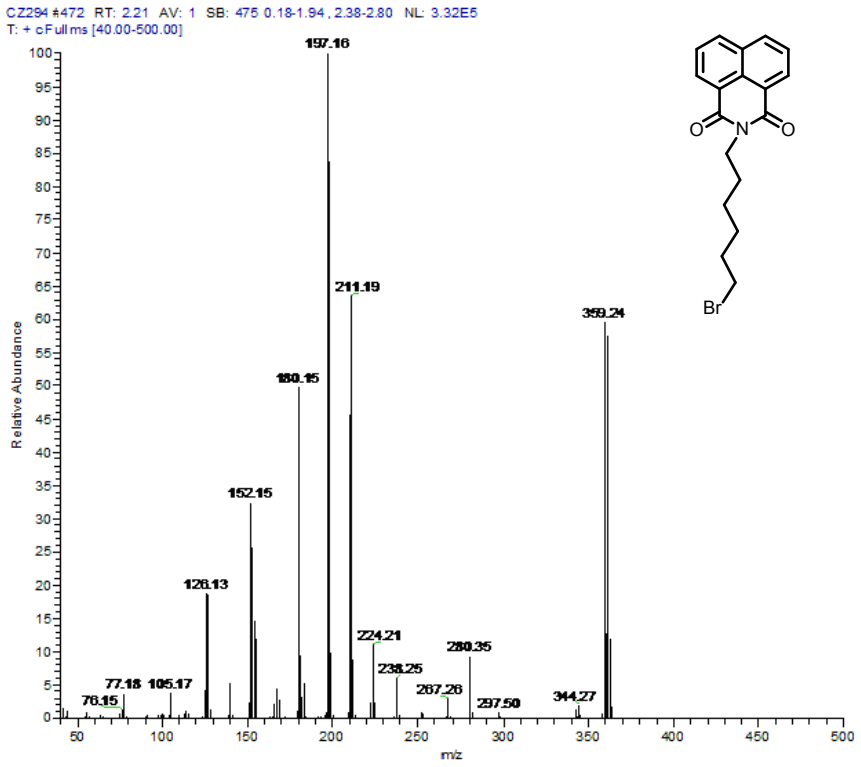
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197.16
211.19
359.24
180.15
152.15
126.13
224.21
280.35
238.25
267.26
297.50
344.27
77.18
105.17
76.15
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