

## Supplementary Information

# Heavy-Atom-Free $\pi$ -Twisted Photosensitizers for Fluorescence Bioimaging and Photodynamic Therapy

*Darío Puchán Sánchez,<sup>†a</sup> Korentin Morice<sup>†a</sup> Monika G. Mutovska,<sup>b</sup> Lhoussain Khrouz,<sup>c</sup> Pierre Josse,<sup>a</sup> Magali Allain,<sup>a</sup> Frédéric Gohier,<sup>a</sup> Philippe Blanchard,<sup>a</sup> Cyrille Monnereau,<sup>c</sup> Tangui Le Bahers,<sup>c,d</sup> Nasim Sabouri,<sup>e</sup> Yulian Zagranyski,<sup>b\*</sup> Clement Cabanetos<sup>a\*</sup> and Marco Deiana<sup>e,f\*</sup>*

<sup>a)</sup> Univ Angers, CNRS, MOLTECH-ANJOU, SFR MATRIX, F-49000 Angers, France

<sup>b)</sup> Faculty of Chemistry and Pharmacy, University of Sofia, 1 James Bourchier blvd., 1164 Sofia, Bulgaria

<sup>c)</sup> ENS de Lyon, CNRS, Laboratoire de Chimie UMR 5182, F-69342 Lyon, France

<sup>d)</sup> Institut Universitaire de France, 5 rue Descartes, 75005 Paris, France

<sup>e)</sup> Department of Medical Biochemistry and Biophysics, Umeå University, SE-901 87, Umeå, Sweden

<sup>f)</sup> Institute of Advanced Materials, Faculty of Chemistry, Wrocław University of Science and Technology, 50-370 Wrocław, Poland

† These authors contributed equally.

Corresponding Authors

\*Clement Cabanetos, E-mail: clement.cabanetos@univ-angers.fr

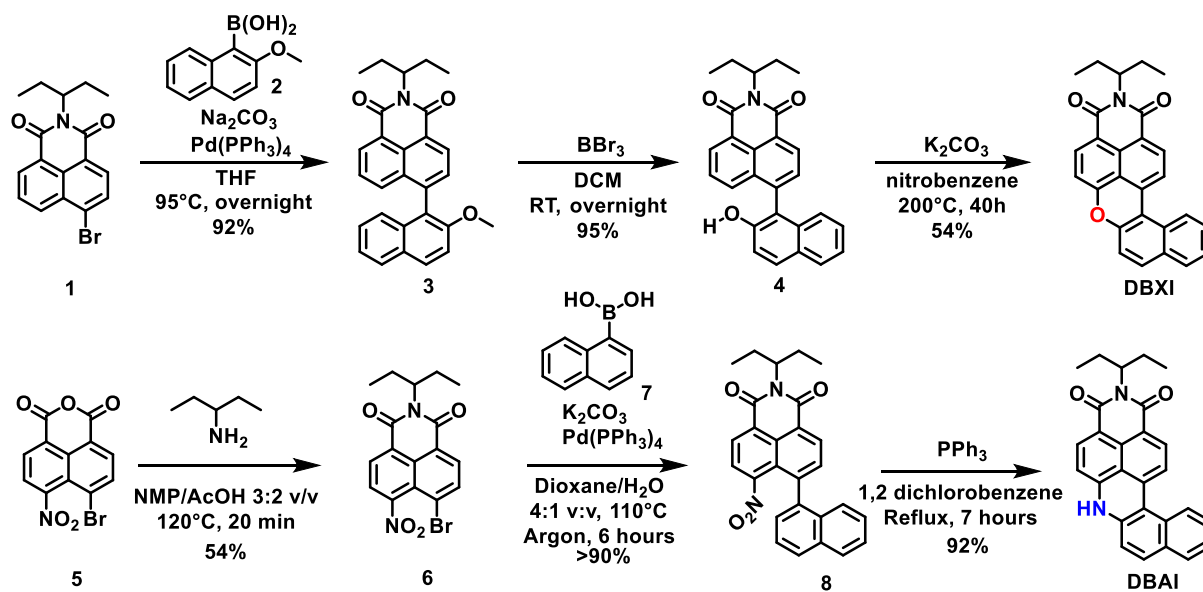
\*Yulian Zagranyski, E-mail: zagranyskiyulian@gmail.com

\*Marco Deiana, E-mail: m.deiana@pwr.edu.pl

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## Synthetic procedures



**1** was synthesized according to a reported procedure.<sup>1</sup>

## Spectral data

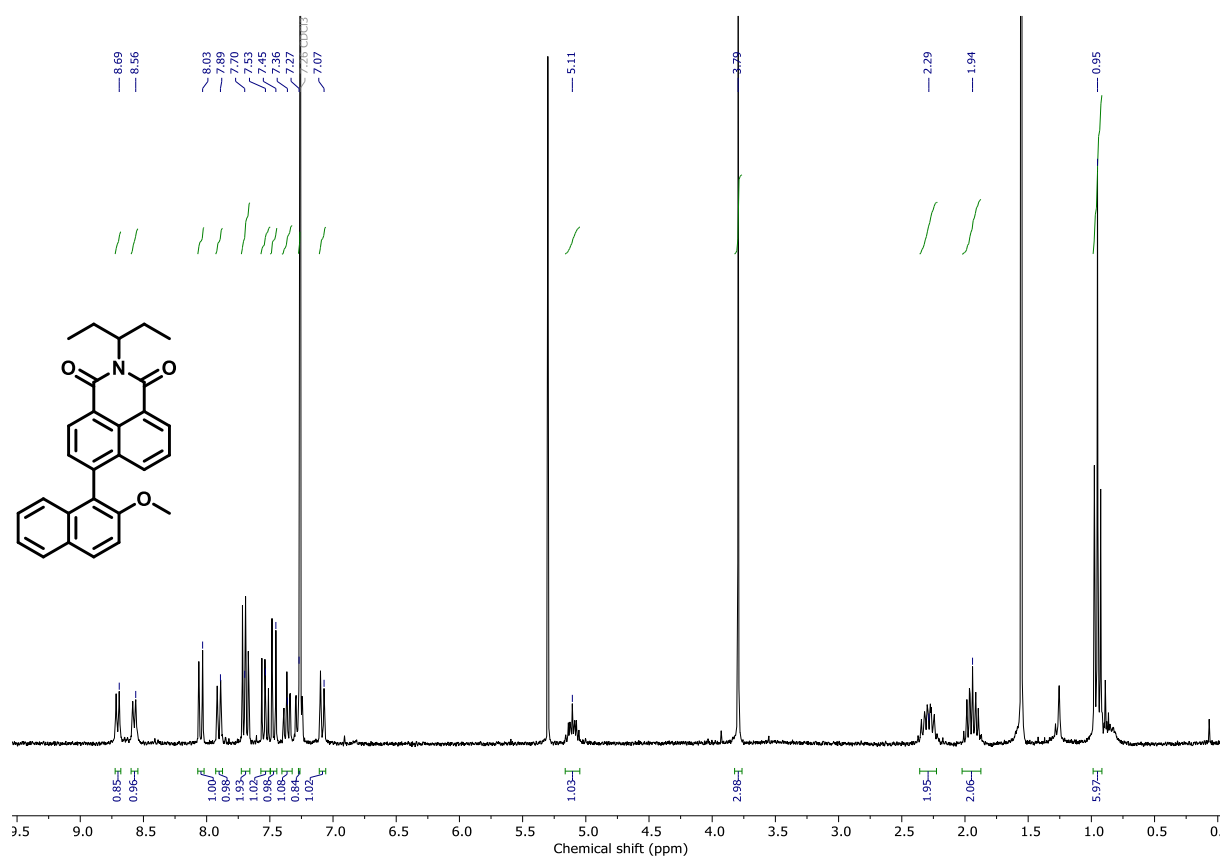
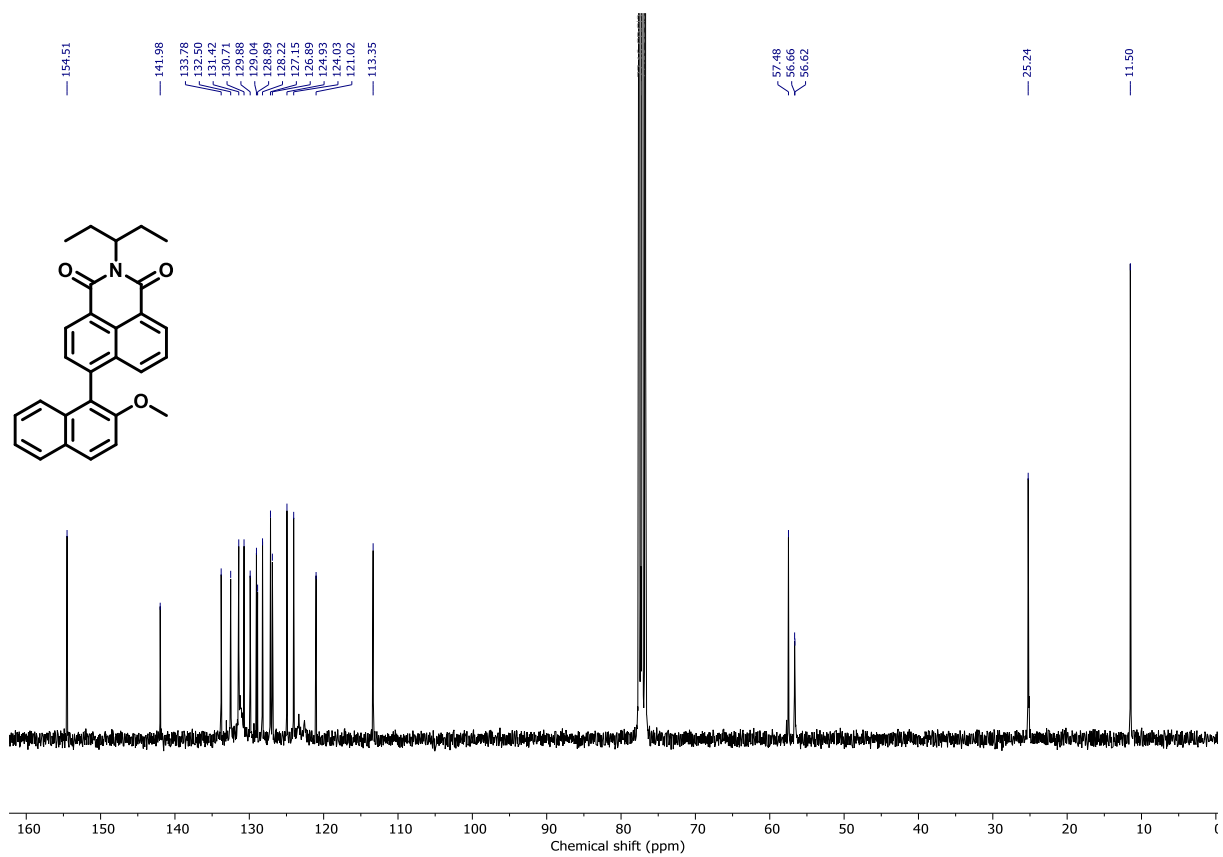
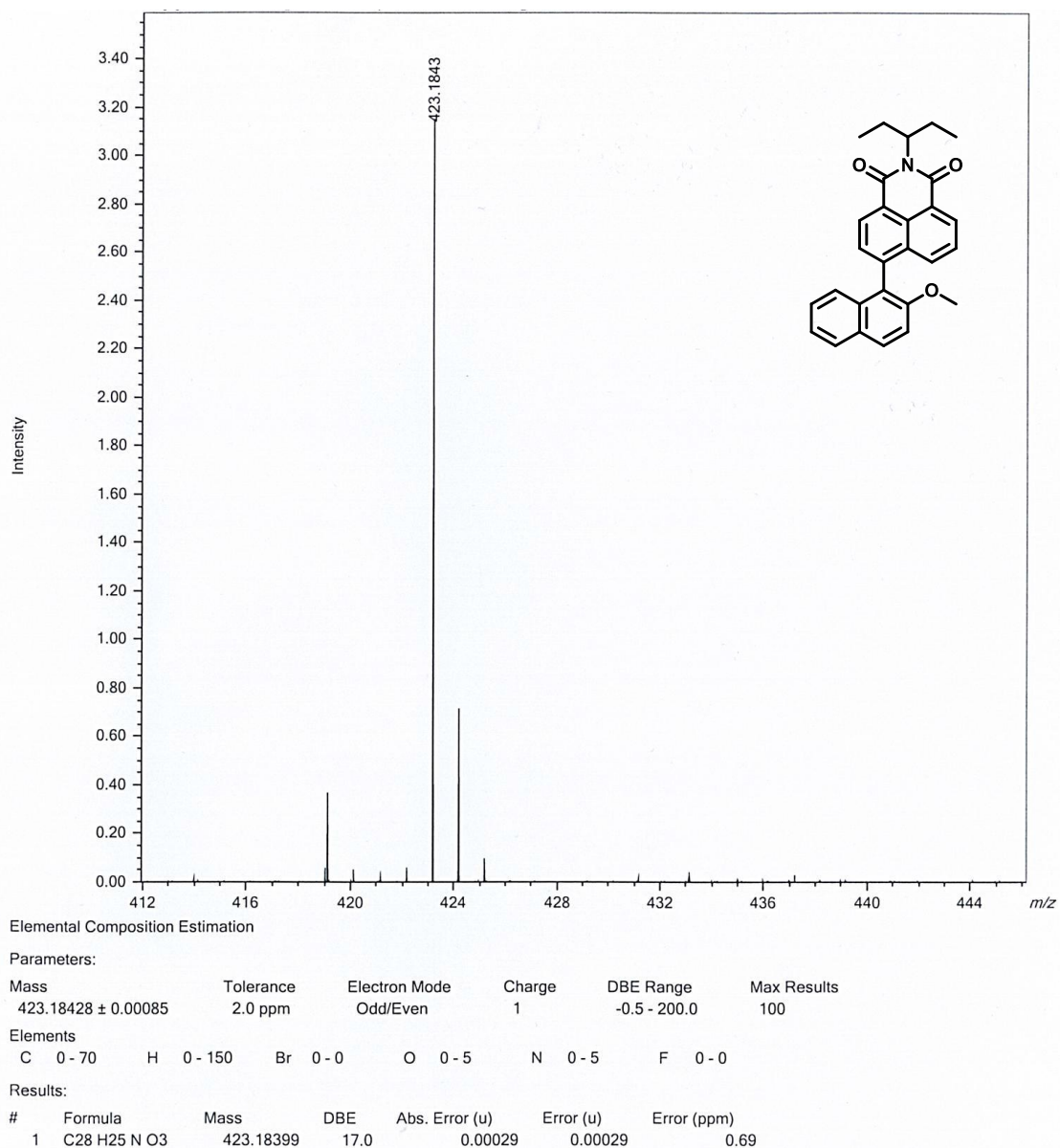


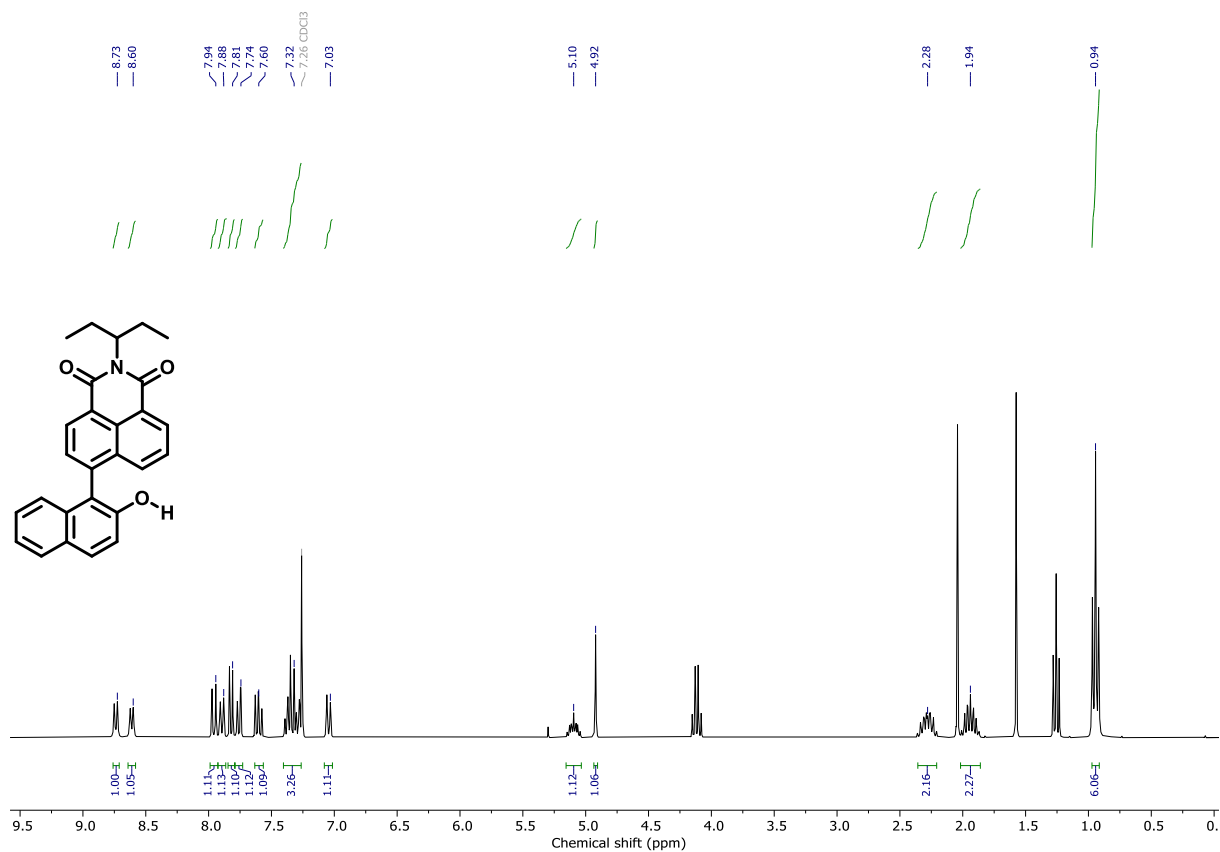
Figure S1. <sup>1</sup>H NMR spectrum (CDCl<sub>3</sub>) of **2**



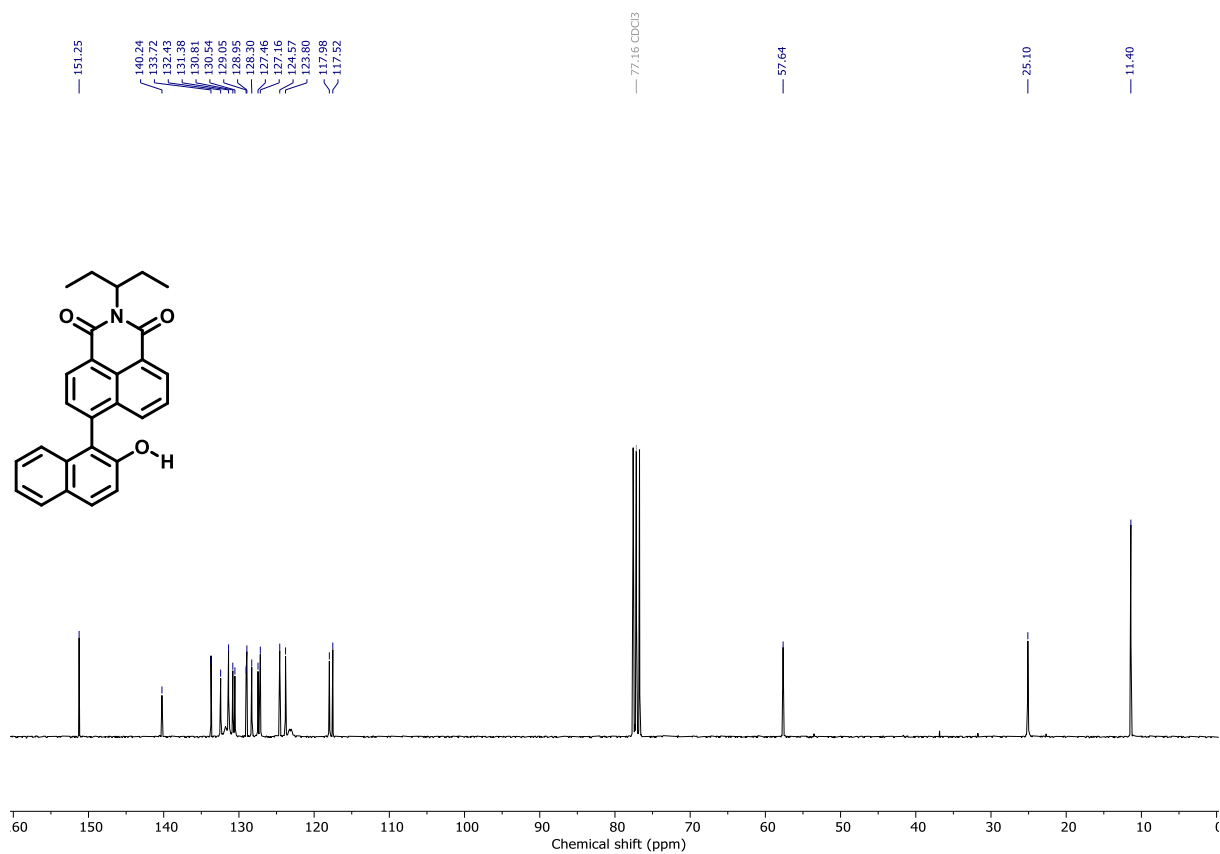
**Figure S2.**  $^{13}\text{C}$  NMR spectrum (CDCl<sub>3</sub>) of 2



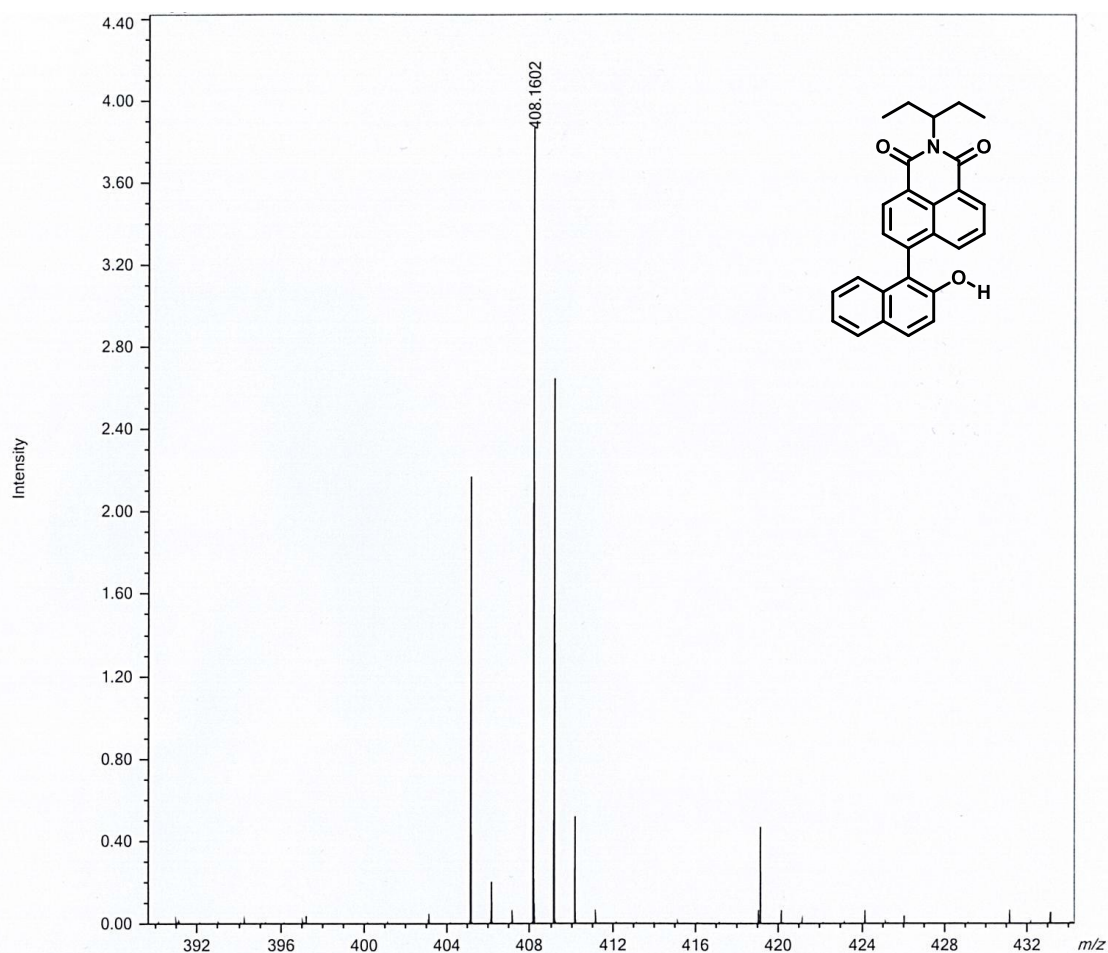
**Figure S3.** HRMS spectrum (MALDI-TOF) of **2**



**Figure S4.**  $^1\text{H}$  NMR spectrum ( $\text{CDCl}_3$ ) of **3**



**Figure S5.**  $^{13}\text{C}$  NMR spectrum ( $\text{CDCl}_3$ ) of **3**



Elemental Composition Estimation

Parameters:

Mass	Tolerance	Electron Mode	Charge	DBE Range	Max Results
408.16018 ± 0.00082	2.0 ppm	Odd/Even	1	-0.5 - 200.0	100

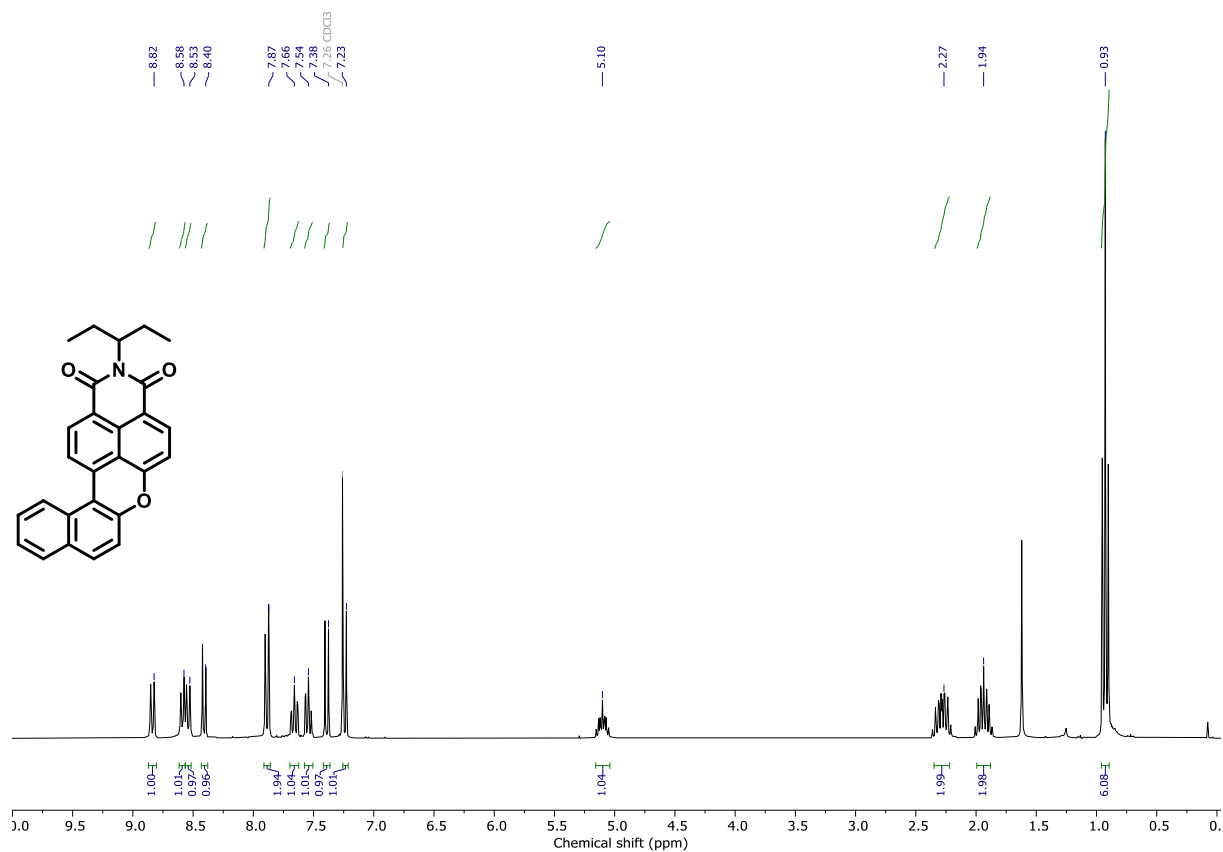
Elements

C	H	Br	O	N	F
0 - 70	0 - 150	0 - 0	0 - 5	0 - 5	0 - 0

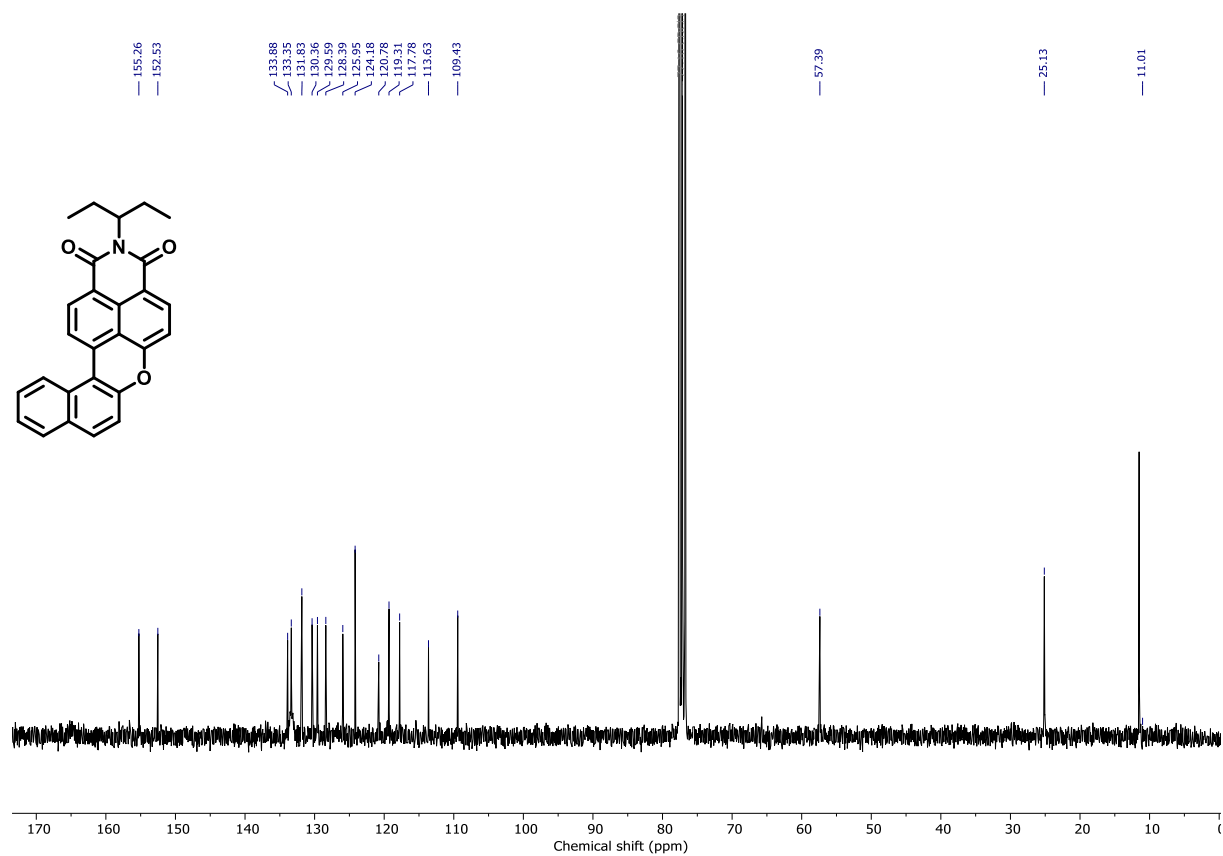
Results:

#	Formula	Mass	DBE	Abs. Error (u)	Error (u)	Error (ppm)
1	C <sub>27</sub> H <sub>22</sub> N <sub>1</sub> O <sub>3</sub>	408.16052	17.5	0.00033	-0.00033	-0.82

**Figure S6.** HRMS spectrum (MALDI-TOF) of **3**

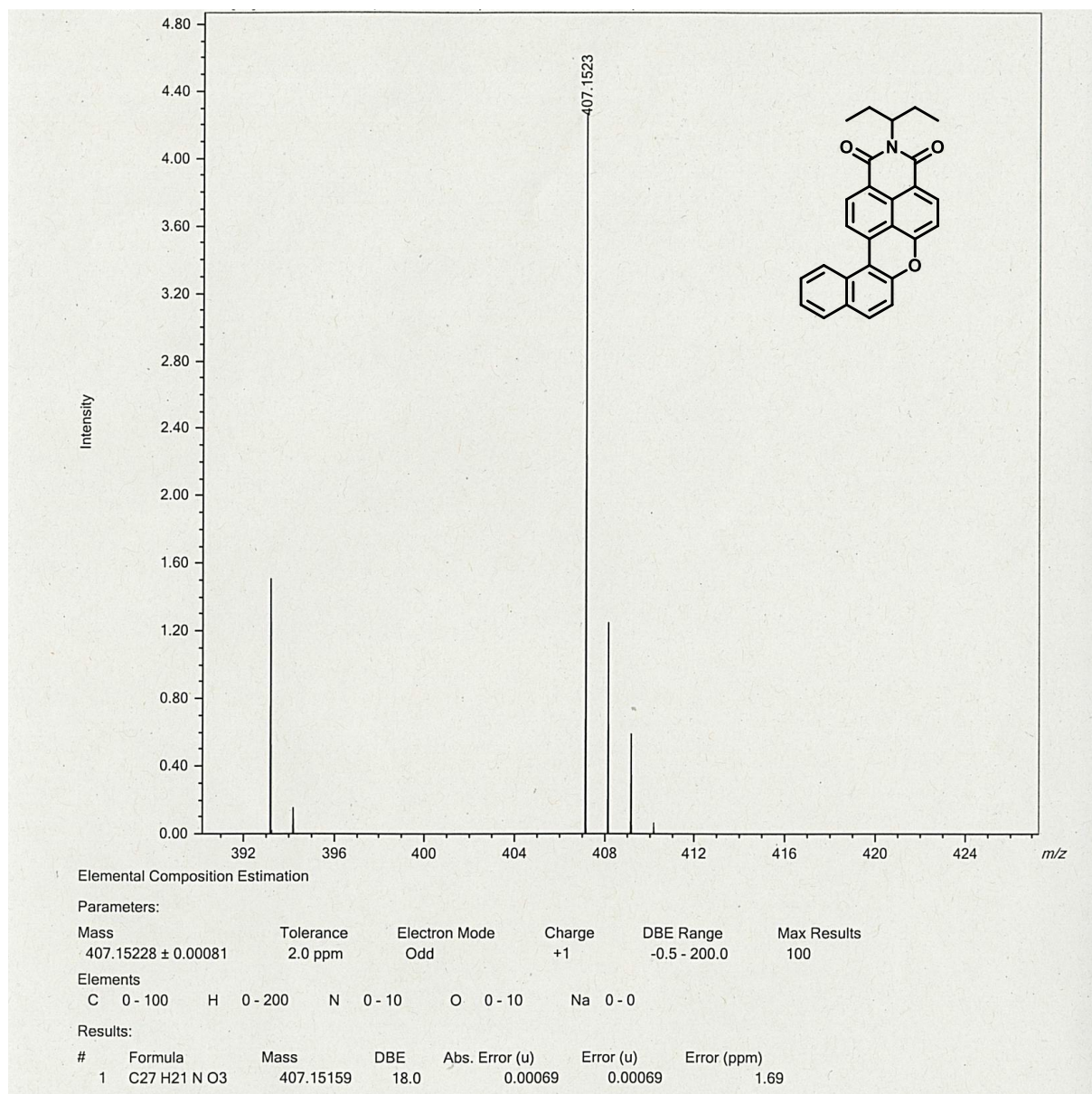


**Figure S7.** <sup>1</sup>H NMR spectrum (CDCl<sub>3</sub>) of DBXI

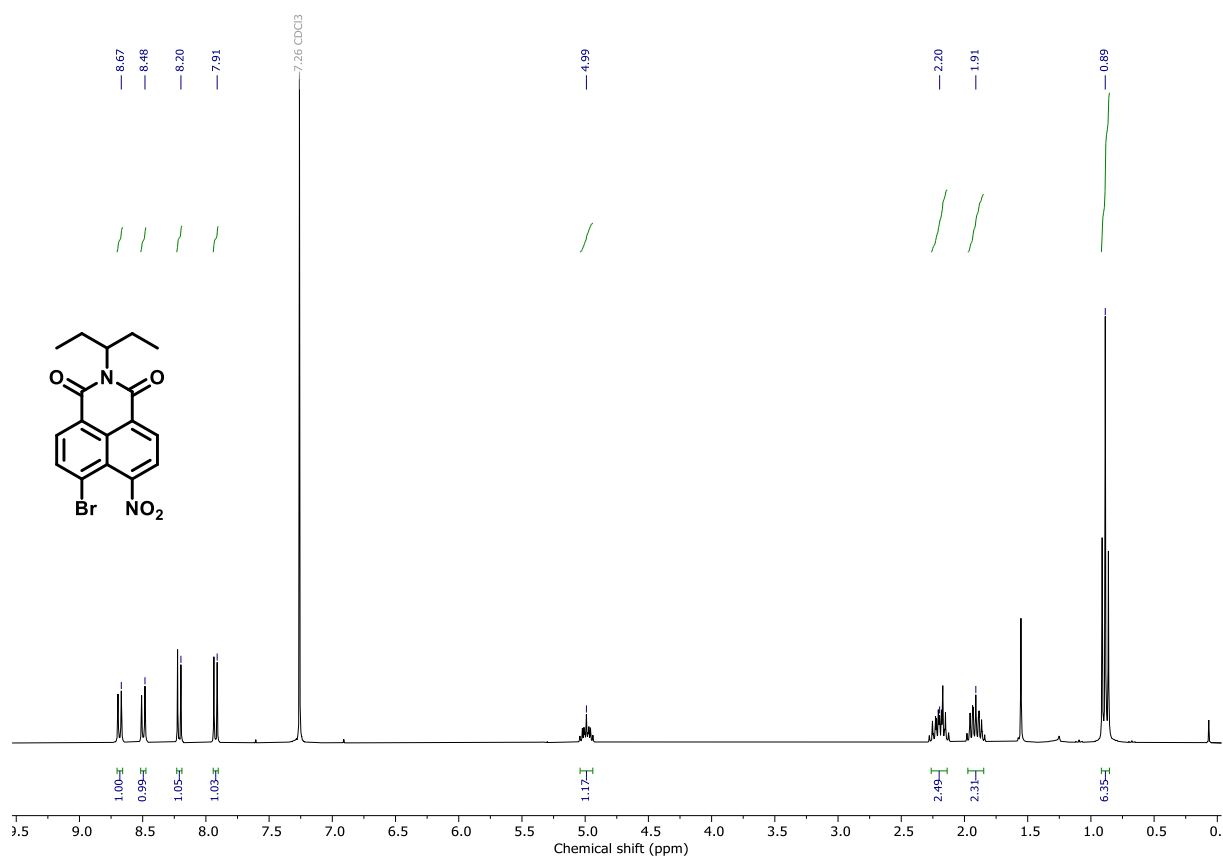


**Figure S8.** <sup>13</sup>C NMR spectrum (CDCl<sub>3</sub>) of DBXI

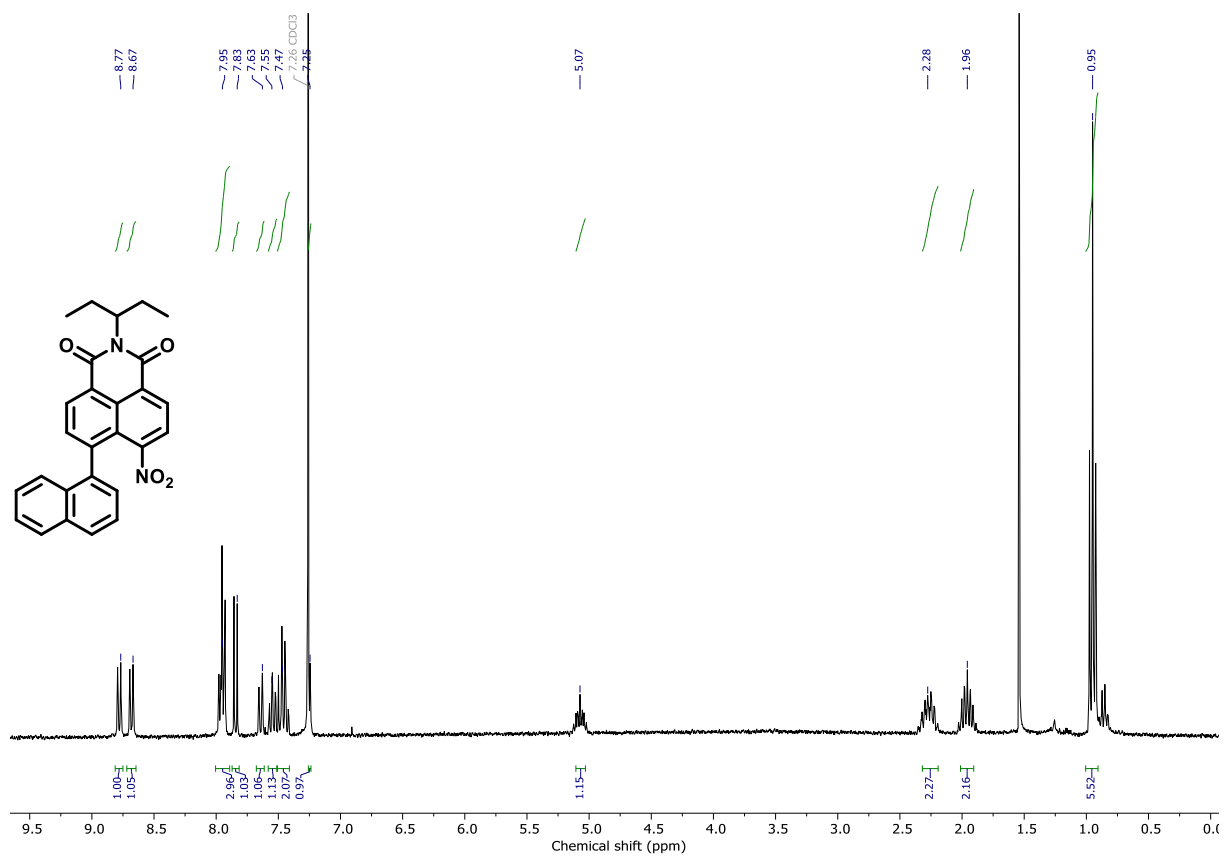




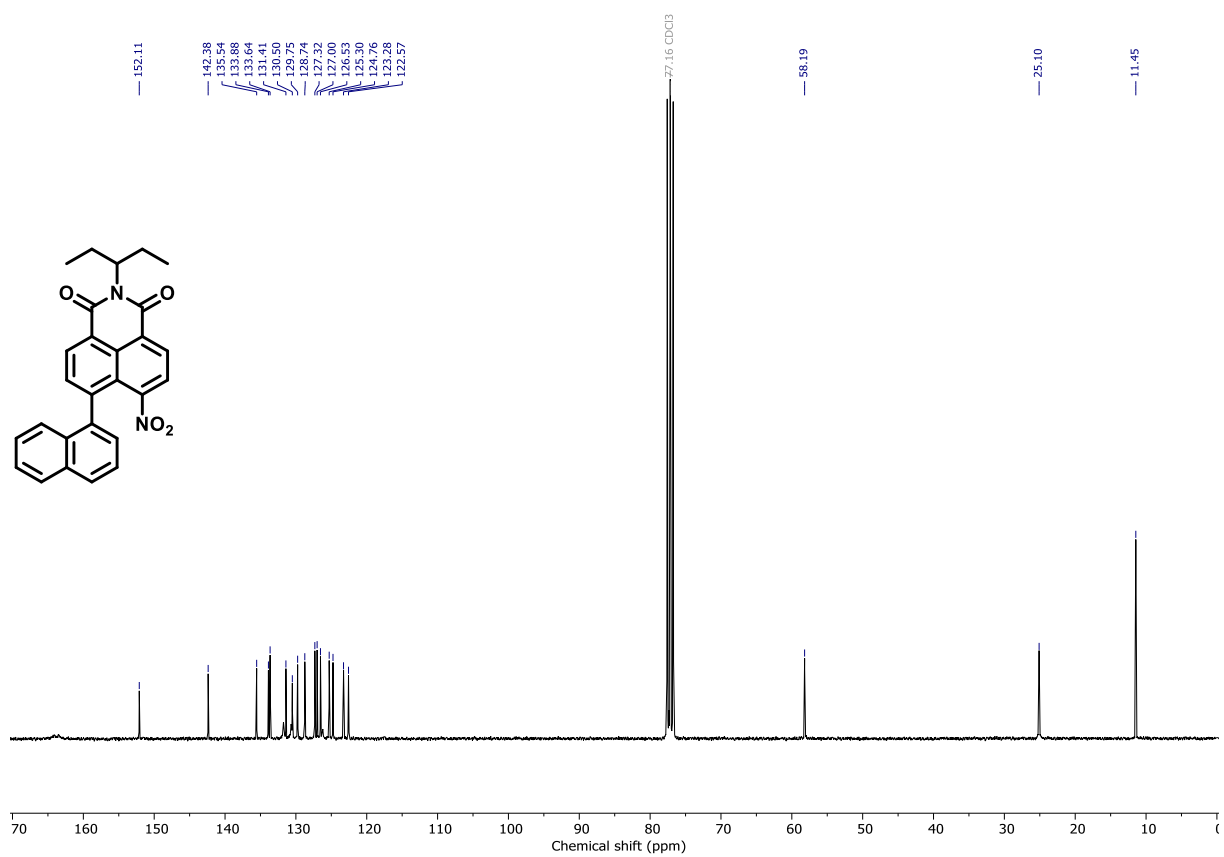
**Figure S9.** HRMS spectrum (MALDI-TOF) of DBXI



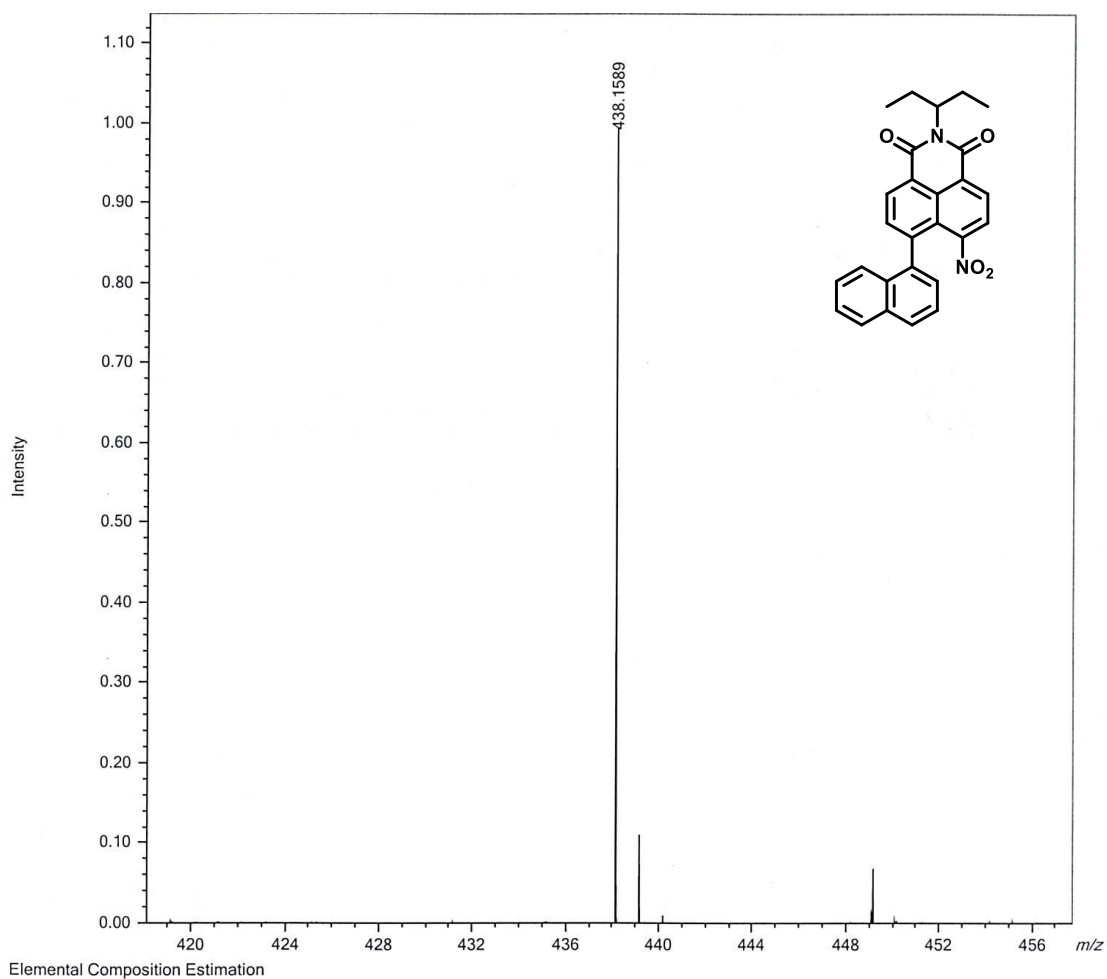
**Figure S10.**  $^1\text{H}$  NMR spectrum ( $\text{CDCl}_3$ ) of **5**



**Figure S11.**  $^1\text{H}$  NMR spectrum ( $\text{CDCl}_3$ ) of **6**



**Figure S12.**  $^{13}\text{C}$  NMR spectrum (CDCl<sub>3</sub>) of **6**



Parameters:

Mass	Tolerance	Electron Mode	Charge	DBE Range	Max Results
438.15889 ± 0.00131	3.0 ppm	Odd	1	-0.5 - 200.0	100

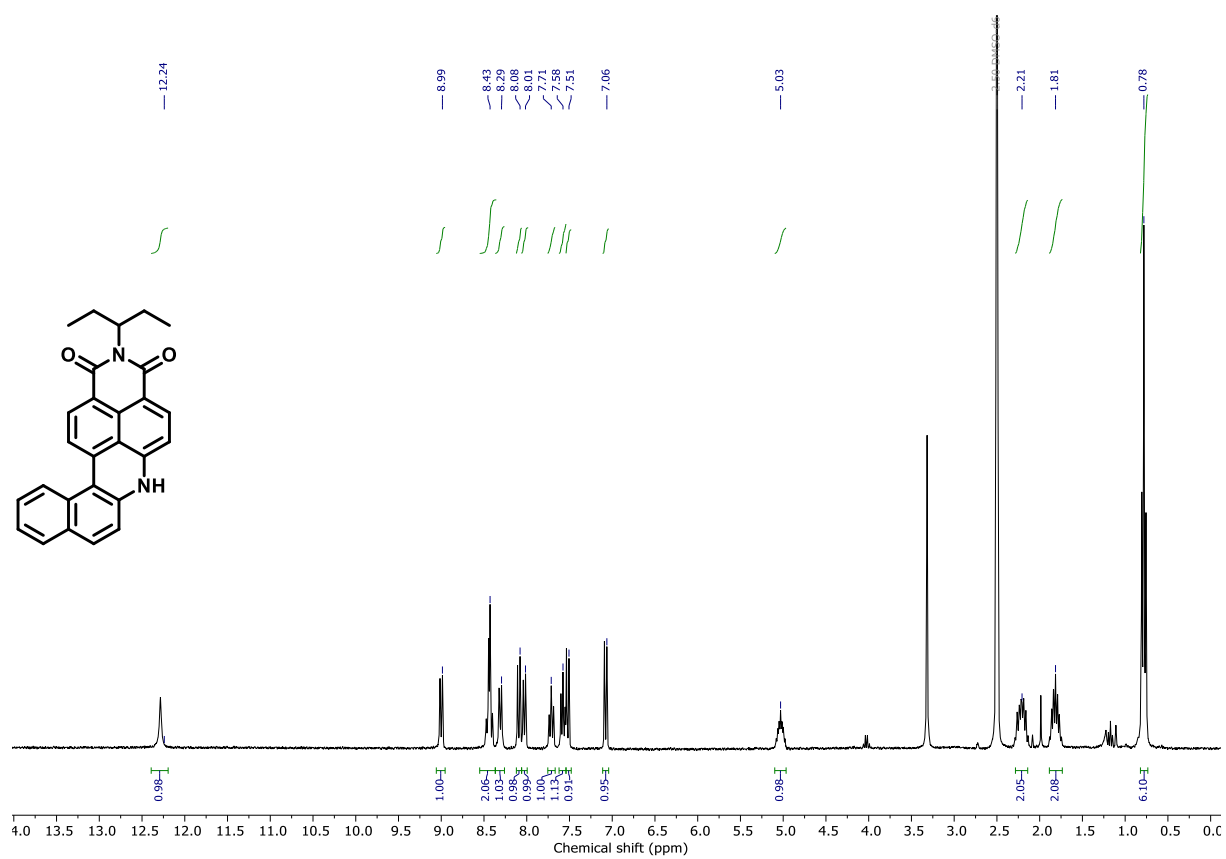
Elements

C	H	S	O	Na	N	Br
0 - 30	0 - 30	0 - 0	0 - 5	0 - 0	0 - 5	0 - 0

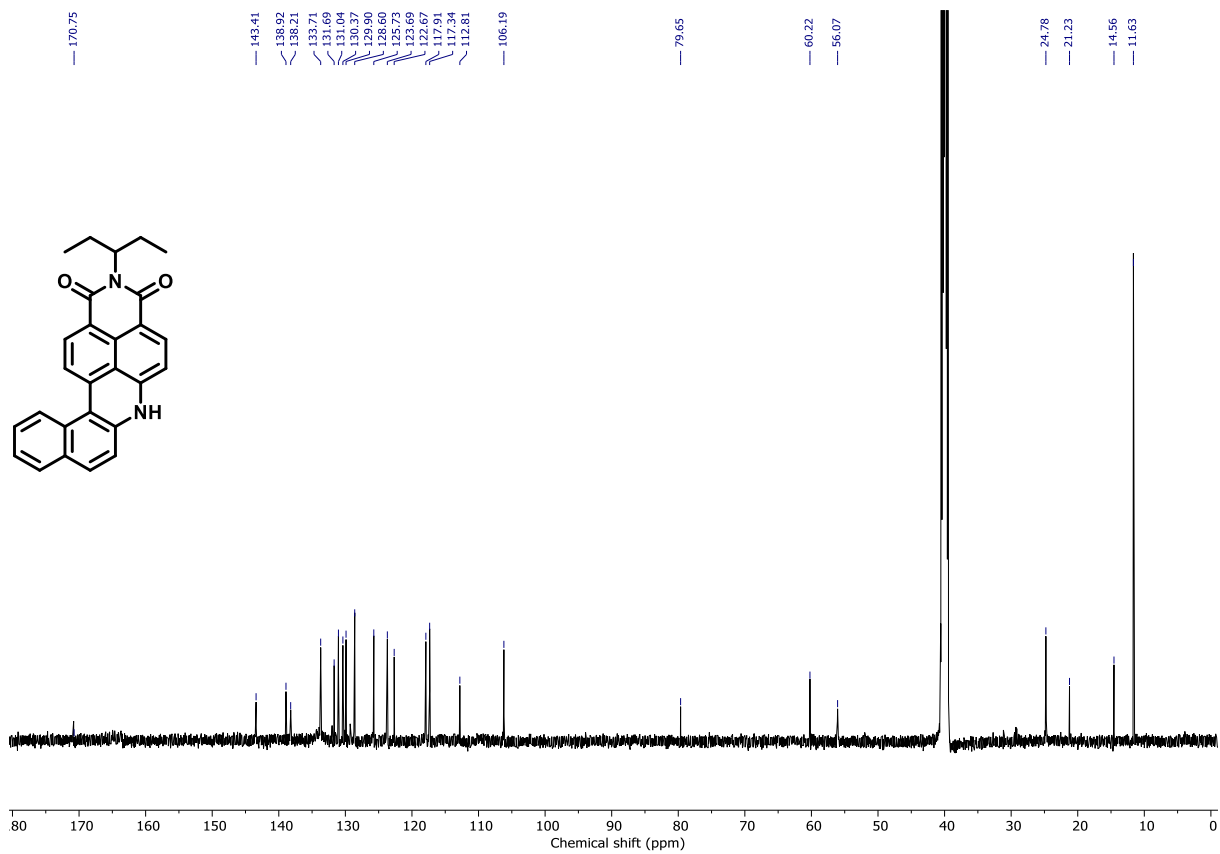
Results:

#	Formula	Mass	DBE	Abs. Error (u)	Error (u)	Error (ppm)
1	C <sub>27</sub> H <sub>22</sub> N <sub>2</sub> O <sub>4</sub>	438.15851	18.0	0.00038	0.00038	0.88

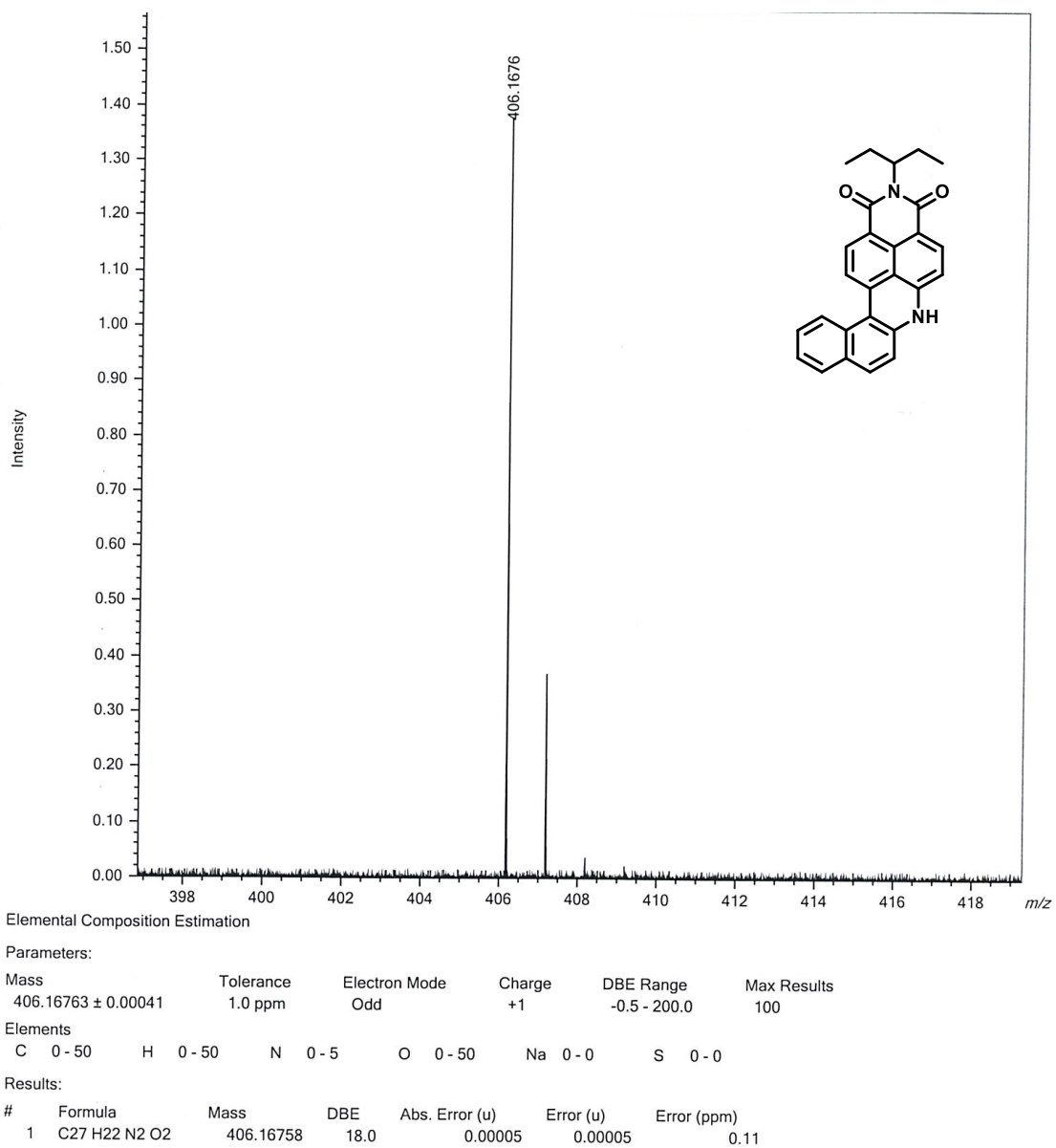
**Figure S13.** HRMS spectrum (MALDI-TOF) of **6**



**Figure S14.** <sup>1</sup>H NMR spectrum (CDCl<sub>3</sub>) of DBAI



**Figure S15.**  $^{13}\text{C}$  NMR spectrum ( $\text{CDCl}_3$ ) of *DBAI*



**Figure S16.** HRMS spectrum (MALDI-TOF) of DBAI



## Crystallographic data

**Table S1.** X-Ray single crystal diffraction data for DBI, DBXI, DBAI.

Crystal	DBI	DBXI	DBAI
Formula	C <sub>27</sub> H <sub>21</sub> NO <sub>2</sub> S	C <sub>27</sub> H <sub>21</sub> NO <sub>3</sub>	C <sub>27</sub> H <sub>24</sub> N <sub>2</sub> O <sub>3</sub>
Molecular Weight	423.51	407.45	424.48
Temperature (K)	150	200	200
Crystal system	Orthorhombic	Triclinic	Triclinic
Space group	<i>P</i> 2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub>	<i>P</i> -1	<i>P</i> -1
a (Å)	7.4412(2)	7.394(1)	8.116(1)
b (Å)	8.0589(3)	11.029(1)	11.003(1)
c (Å)	33.526(1)	12.950(2)	11.670(1)
α (°)	90	103.47(1)	87.387(9)
β (°)	90	92.67(1)	84.33(1)
γ (°)	90	108.59(1)	87.188(9)
V (Å <sup>3</sup> )	2010.5(1)	965.1(3)	1034.8(2)
Z	4	2	2
Crystal color	Orange	Yellow	Orange
Crystal size (mm <sup>3</sup> )	0.161x0.135x0.032	0.294x0.129x0.019	0.123x0.066x0.033
D <sub>c</sub> (g cm <sup>-3</sup> )	1.399	1.402	1.362
μ (mm <sup>-1</sup> )	1.630	0.731	0.715
F(000)	888	428	448
Transmission (min/max)	0.904/1.000	0.798/1.000	0.692/1.000
θ (min/max) (°)	2.636 / 72.412	3.54 / 74.589	3.81 / 72.338
Data collected	7476	6318	7015
Data unique	3803	3626	3889
Data observed	3613	1848	2367
R (int)	0.0276	0.0809	0.0639
Nb of parameters	294	295	313
R <sub>1</sub> [I > 2σ(I)]	0.0546	0.0684	0.0921
wR <sub>2</sub> [I > 2σ(I)]	0.1353	0.1518	0.02343
R <sub>1</sub> [all data]	0.0574	0.1251	0.1251
wR <sub>2</sub> [all data]	0.1370	0.1964	0.2753
GOF on F <sup>2</sup>	1.130	0.976	1.038
Largest peak in final: difference (e Å <sup>-3</sup> )	0.486/-0.400	0.259/-0.233	0.388/-0.331

## References

(1) Josse, P.; Morice, K.; Puchán Sánchez, D.; Ghanem, T.; Boixel, J.; Blanchard, P.; Cabanetos, C. Revisiting the synthesis of the benzothioxanthene imide five decades later. *New Journal of Chemistry* **2022**, *46* (18), 8393-8397. DOI: 10.1039/D2NJ00955B.