

Supporting information

Non-Conjugated Alkyl Chains Engineering to Tune Condensed State Photophysical and Supramolecular Assembly Properties

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1. Experimental Section

1.1. Materials and Instrumentations

Reagents and starting materials, including 1,8-naphthalic anhydride, and various n-amines (methyl, ethyl, propyl, butyl, pentyl, and hexyl), were sourced from Sigma Aldrich (INDIA) in reagent-grade quality. HPLC-grade solvents were procured from Fisher Scientific Ltd. and RANKEM. Nuclear magnetic resonance (NMR) spectra, encompassing both ^1H and ^{13}C , were obtained using a Bruker Avance 400 MHz spectrometer, where the residual solvent signal acted as an internal reference. Electro spray ionization mass (ESI-MS) spectra were recorded on a Waters (Micro mass MS-Technologies) Q-ToF MS Analyzer spectrometer. UV/visible (UV/vis) and photoluminescence (PL) spectra were documented employing a Perkin-Elmer Model Lambda-750 spectrophotometer and a Horiba Fluoromax-4 spectrofluorometer, respectively. All measurements were executed at 298 K using 4 mm quartz cuvettes. A DeltaDiode-375 laser diode emitting at 375 nm served as the excitation source for both UV/visible and photoluminescence experiments. The zeta potential and hydrodynamic radius of the materials were assessed using a Malvern Zetasizer instrument. Field emission scanning electron microscopy (FESEM) images were captured using a Sigma Carl ZEISS field emission scanning electron microscope. Single crystal data were acquired employing a Bruker SMART APEX diffractometer, featuring a CCD area detector.

1.2. Synthesis of NC derivatives

In this experimental endeavour, 1,8-naphthalic anhydride (5 mmol) was meticulously dissolved in 20 mL of ethanol. Subsequently, various n-amines (methyl, ethyl, propyl, butyl, pentyl, and hexyl) (5.2 mmol) were added at room temperature, inducing a carefully monitored reaction. The ensuing suspension underwent robust stirring and was subjected to a controlled heating regime at 85°C for 18 hrs. Following the heating phase, the mixture underwent a gradual cooling process, initially to room temperature and then further cooled to 5 °C for 1 hour, facilitating the meticulous recrystallization of naphthalimide congeners (**NC**). Post-recrystallization, the solvent was effectively separated through filtration, leaving behind the purified **NC** in the form of a

visually striking light white crystalline solid. The overall yield of this process was noteworthy, achieving an impressive 85%.

Characterization data for 1H-benzo[de]isoquinoline-1,3(2H)-dione (NC0): ^1H NMR (400 MHz, CDCl_3) δ 7.72 (t,1H), 8.18 (d,2H), 8.53 (d,2H). ^{13}C NMR (100 MHz, CDCl_3) δ 122.66, 126.76, 131.05, 134.76, 135.73, 135.73, 164.34. HRMS: calculated for $\text{C}_{12}\text{H}_7\text{NO}_2$: 197.0477 [M], Found: 198.0551 [M+H] $^+$

Characterization data for 2-methyl-1H-benzo[de]isoquinoline-1,3(2H)-dione (NC1): ^1H NMR (400 MHz, CDCl_3) δ 3.87 (t,3H), 7.26 (t,2H), 8.23 (d,2H), 8.62 (d,2H). ^{13}C NMR (100 MHz, CDCl_3) δ 27.26, 122.61, 126.72, 128.40, 131.42, 131.73, 134.44, 164.33. HRMS: calculated for $\text{C}_{13}\text{H}_9\text{NO}_2$: 211.0633 [M], Found: 212.0708[M+H] $^+$

Characterization data for 2-ethyl-1H-benzo[de]isoquinoline-1,3(2H)-dione (NC2): ^1H NMR (400 MHz, CDCl_3) 0.51 (t, 3H), 4.51 (q, 2H), 7.26 (t,2H), 8.23 (d,2H), 8.62 (d,2H). ^{13}C NMR (100 MHz, CDCl_3) δ 13.38, 36.51, 122.76, 126.91, 131.13, 131.57, 133.86, 164.02. HRMS: calculated for $\text{C}_{14}\text{H}_{11}\text{NO}_2$: 225.0790 [M], Found: 248.0687[M+Na] $^+$

Characterization data for 2-propyl-1H-benzo[de]isoquinoline-1,3(2H)-dione (NC3): ^1H NMR (400 MHz, CDCl_3) δ 0.60 (t, 2H), 1.96 (m, 2H), 4.60 (t, 2H), 7.26 (t,2H), 8.23 (d,2H), 8.62 (d,2H). ^{13}C NMR (100 MHz, CDCl_3) δ 11.51, 22.26, 42.37, 122.65, 127.71, 129.08, 131.04, 134.46, 165.02. HRMS: calculated for $\text{C}_{15}\text{H}_{13}\text{NO}_2$: 239.0946 [M], Found: 262.0850 [M+Na] $^+$

Characterization data for 2-butyl-1H-benzo[de]isoquinoline-1,3(2H)-dione (NC4): ^1H NMR (400 MHz, CDCl_3) δ 0.77 (t, 3H), 1.3 (t, 2H), 1.99 (t, 2H), 4.56 (t, 2H), 7.26 (t,2H), 8.23 (d,2H), 8.62 (d,2H). (^{13}C NMR (100 MHz, CDCl_3) δ 13.48, 20.21, 30.27, 40.34, 122.35, 127.04, 128.70, 131.42, 132.11, 134.07, 164.34. RMS: calculated for $\text{C}_{16}\text{H}_{15}\text{NO}_2$: 253.1103 [M], Found: 254.1193 [M+H] $^+$

Characterization data for 2-pentyl-1H-benzo[de]isoquinoline-1,3(2H)-dione (NC5): ^1H NMR (400 MHz, CDCl_3) δ 0.83 (t, 3H), 1.33 (t,4H), 2.97 (m, 2H), 4.57 (t, 2H), 7.26 (t,2H), 8.23 (d,2H), 8.62 (d,2H). ^{13}C NMR (100 MHz, CDCl_3) δ 13.86, 22.93, 27.93, 29.27, 40.72, 122.64, 127.34, 128.01, 130.74, 132.11, 133.76, 163.96. HRMS: calculated for $\text{C}_{17}\text{H}_{17}\text{NO}_2$: 267.1259 [M], Found: 290.1153 [M+Na] $^+$

Characterization data for 2-hexyl-1H-benzo[de]isoquinoline-1,3(2H)-dione (NC6): ^1H NMR (400 MHz, CDCl_3) δ 0.89 (t, 3H), 1.35 (m, 5H), 1.76 (t, 2H), 7.26 (t, 2H), 8.23 (d, 2H), 8.62 (d, 2H). ^{13}C NMR (100 MHz, CDCl_3) δ 13.86, 22.59, 26.58, 28.30, 31.94, 40.33, 122.34, 126.05, 127.73, 131.43, 132.11, 134.08, 163.96. HRMS: calculated for $\text{C}_{18}\text{H}_{19}\text{NO}_2$: 281.1416 [M], Found: 282.1371 [M+H] $^+$

1.3. Preparation of the Test Solution

Stock solutions of **NC** materials, denoted as **NC0**, **NC1**, **NC2**, **NC3**, **NC4**, **NC5**, and **NC6**, respectively, were formulated in dimethyl sulfoxide (DMSO) at a standardized concentration of 20 mM. To explore the aggregation behavior, test solutions were meticulously crafted at a concentration of 20 μM by adjusting the water fraction in DMSO. Prior to spectrum recording, the prepared solutions underwent thorough agitation at room temperature, ensuring optimal mixing and dispersion of the compounds. This procedural step was imperative to uphold uniformity and precision in subsequent measurements.

1.4. Preparation of FESEM samples:

To conduct morphological analysis of supramolecular self-assembly via FESEM, a diluted suspension of **NC** derivatives (20 μM) was prepared using a mixture of 99.8% water and 0.2% EtOH. Subsequently, this suspension was drop-casted onto an aluminum foil-coated glass surface. The samples underwent overnight air drying at room temperature before being subjected to analysis.

1.5. Theoretical Studies

The electronic characteristics of **NC** derivatives were assessed via density functional theory (DFT) calculations, employing the B3LYP hybrid functional within the Gaussian 16 package. Ground state optimized geometries for each derivative were computed, and the electron density along with the energy levels of the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) were determined. The calculations were performed using the 6-31G basis set, known for its ability to yield accurate results within a computationally efficient

timeframe. The computational studies for all the derivatives were conducted using computational DFT in both their gaseous state and EtOH solvent state

1.6. Photoluminescence quantum Yield Calculations:

The fluorescence quantum yields (Φ_{PL}) of **NC** derivatives were assessed by comparing their fluorescence to that of Quinine sulfate ($\Phi_r = 0.57$ in 0.1 M H_2SO_4) as a standard, utilizing a specific formula:

$$\Phi_{PL} = \Phi_r (A_r F_s / A_s F_r) (\eta_s^2 / \eta_r^2) \quad (S1)$$

In this equation, the subscripts "s" and "r" denote the sample and reference, respectively. The symbols Φ represent the quantum yield, A signifies absorbance, F indicates relative integrated fluorescence intensity, and η represents the refractive index.

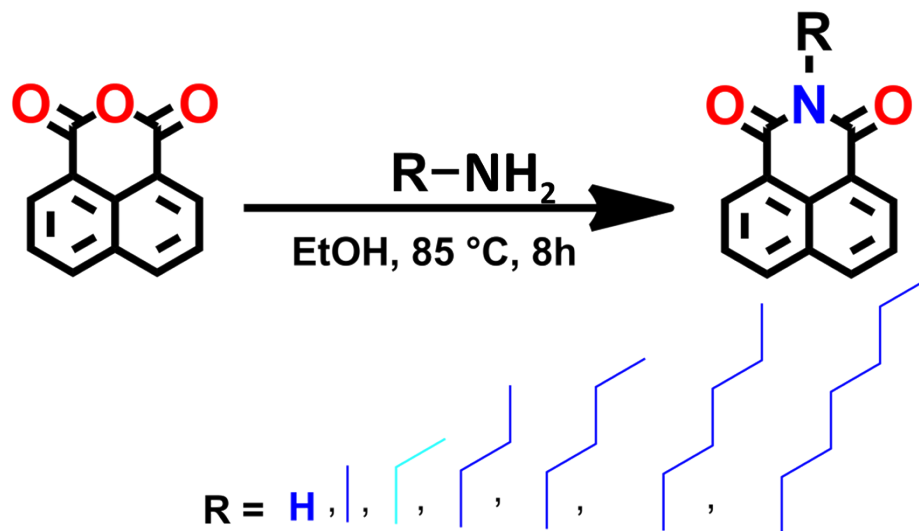
1.7. Powder X-ray Diffraction:

To prepare the PXRD sample, the final estimated NC derivatives obtained via recrystallization process in EtOH solvent was dried and grounded properly to ensure that all the grains were randomly oriented. The resulted powders were placed on the sample holder and bombarded with the X-ray beam generated from a copper source and the diffracted beams were collected at different angles ranging from 2°-50° (2 θ). The PXRD experiment was performed using 9KW Powder X-Ray Diffraction System made by Rigaku Technologies.

1.8. Single-Crystal X-ray Diffraction and structure analysis

The well-grown crystals of NC derivatives were collected from ethanol solvent. The good quality crystal having minimal defect was selected under microscope. The selected crystal was placed on the loop and mounted in front of X-Ray beam. The diffracted signals were collected at the Bruker APEX-II CCD detector from various angles. Later, all the frames were analysed and integrated in APEX 4 software and the data refinement was performed using SHELX software to obtain the final structure.

Synthetic Route



Scheme S1. The synthetic approach is used for the preparation of NC derivatives.

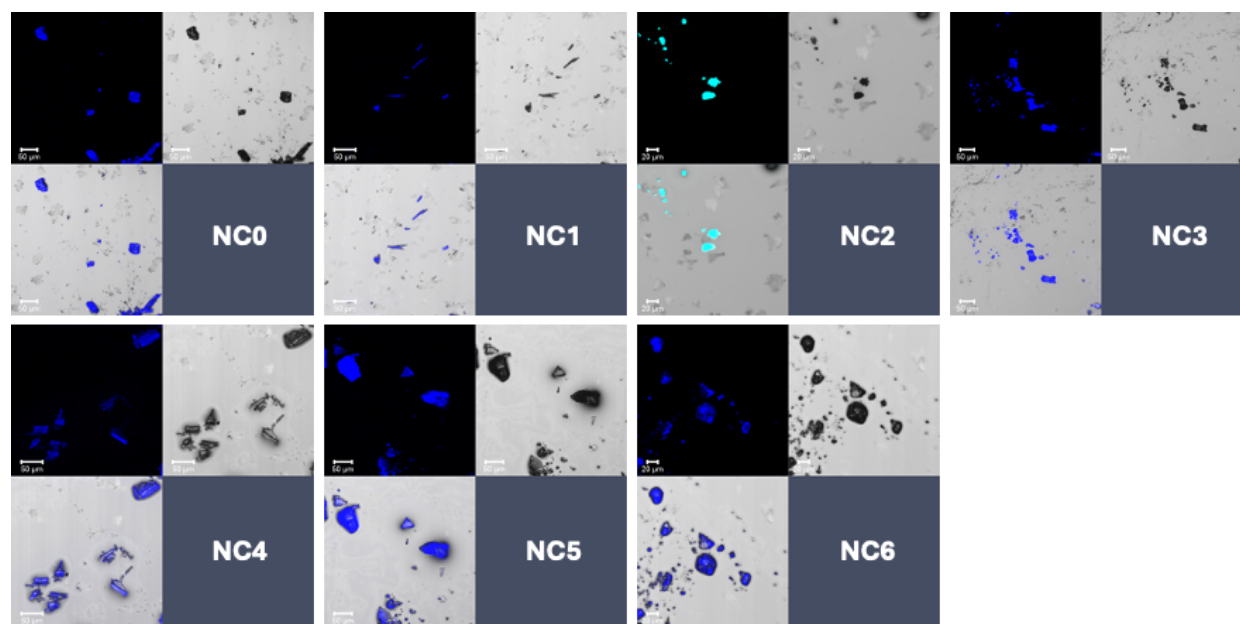


Figure S1. Microscopic luminescence images of the NC derivatives. Scale bar: 20 μM for NC2 and NC6, 50 μM for rest.

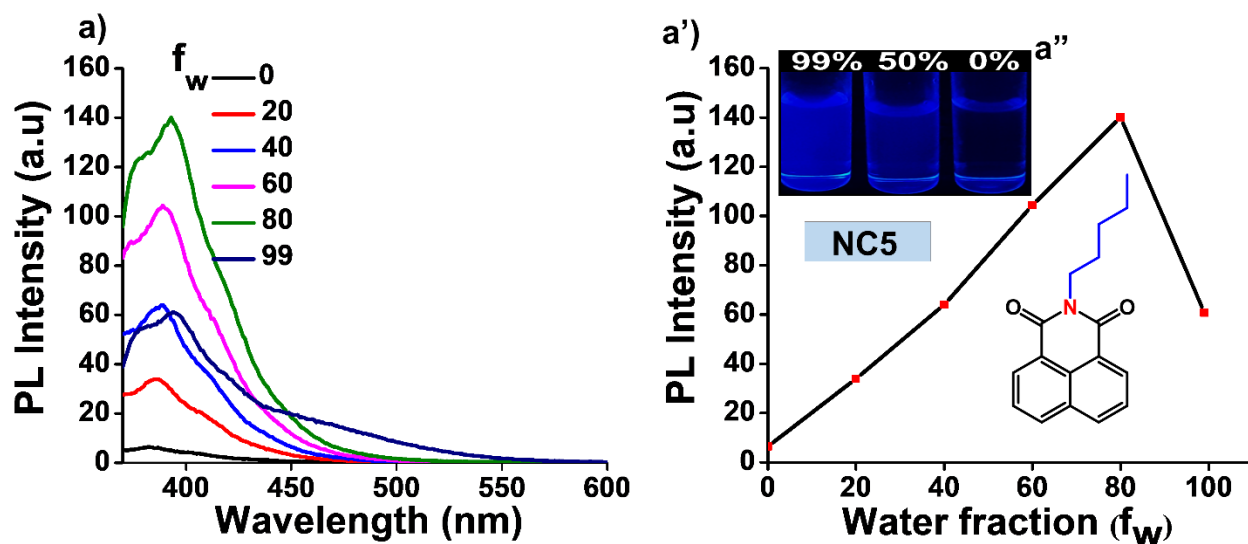


Figure S2. (a) The photoluminescence spectra of the **NC5** at various f_w in EtOH (20 μ M, excited at 360 nm). (a') plots of $\lambda_{\text{emi,max}}$ variation against water fraction (f_w). (a'') digital photograph of the **NC5** luminogen at 0%, 50%, and 99.8% f_w in EtOH under 365 nm UV exposure. Inset: chemical structure of the **NC5** derivative.

Table S1. CIE coordinates for the **NC** derivatives in aggregated and solid state.

Materials	Aggregated		Solid	
	X	Y	X	Y
NC0	0.1511	0.0347	0.2092	0.2121
NC1	0.159	0.0212	0.1705	0.1518
NC2	0.1608	0.0182	0.2096	0.4137
NC3	0.1609	0.018	0.1852	0.2289
NC4	0.1609	0.018	0.1761	0.1455
NC5	0.1605	0.0187	0.1597	0.1893
NC6	0.1595	0.0203	0.1506	0.1741

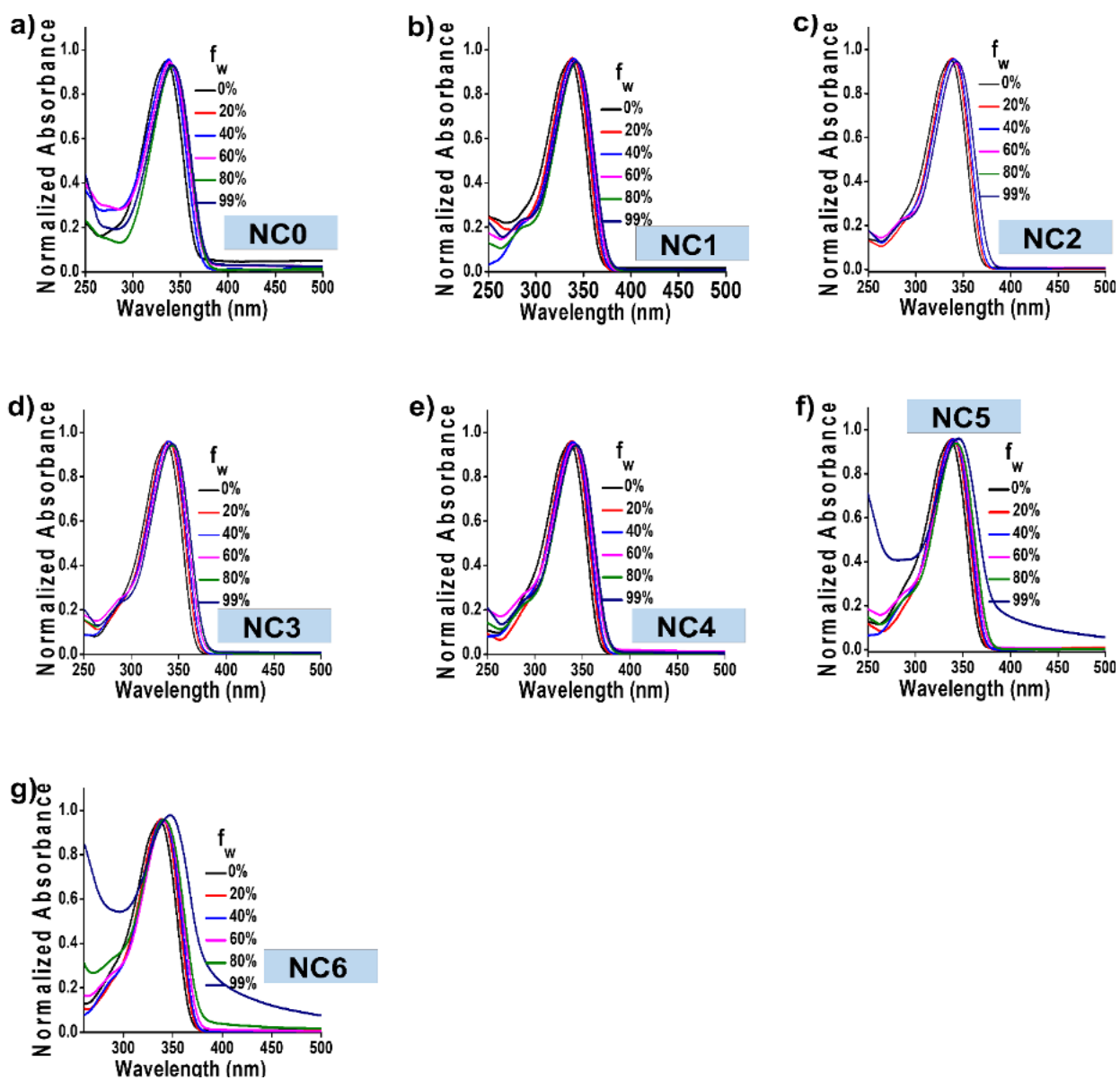


Figure S3. The Normalized absorption spectra of all the NC derivatives in their solution state (in EtOH, 20 μM).

Table S2. Photophysical data for the **NC** derivatives.

Materials	Solvent ^[a]	$\lambda_{\text{abs.max}}$ (nm)	A	$\Delta\lambda$	$\lambda_{\text{em.max}}$ (nm)	Φ_{FL} ^[b]
NC0	0%	332, 340	0.044034	3	389 ^[c] , 397 ^[d] ,422 ^[e]	0.25
	99%	343	0.058154			
NC1	0%	332,342	0.2027	1	389 ^[c] , 397 ^[d] ,452 ^[e]	0.22
	99%	343	0.197575			
NC2	0%	332,342	0.363396	1	389 ^[c] , 397 ^[d] ,504 ^[e]	0.20
	99%	343	0.364819			
NC3	0%	332,343	0.344832	1	389 ^[c] , 397 ^[d] ,459 ^[e]	0.19
	99%	344	0.256517			
NC4	0%	332,343	0.377468	1	389 ^[c] , 397 ^[d] ,435 ^[e]	0.18
	99%	344	0.275808			
NC5	0%	332,343	0.332407	1	389 ^[c] , 397 &460 ^[d] ,468 ^[e]	0.20
	99%	344	0.252016			
NC6	0%	332,343	0.320951	1	389 ^[c] , 397 &460 ^[d] ,464 ^[e]	0.23
	99%	344	0.235997			

A, $\Delta\lambda$, are the absorbance and wavelength maxima shifts in their absorption. [a] Various water fractions (f_w) in EtOH. [b] Photoluminescence quantum yields in the aggregated-state were determined in this study using quinine sulfate as the standard reference (0.1 M H₂SO₄, λ_{ex} =350 nm, Φ_{FL} = 57.7%). [c], [d], and [e] are the wavelength maxima at their solution, aggregated and solid state, respectively.

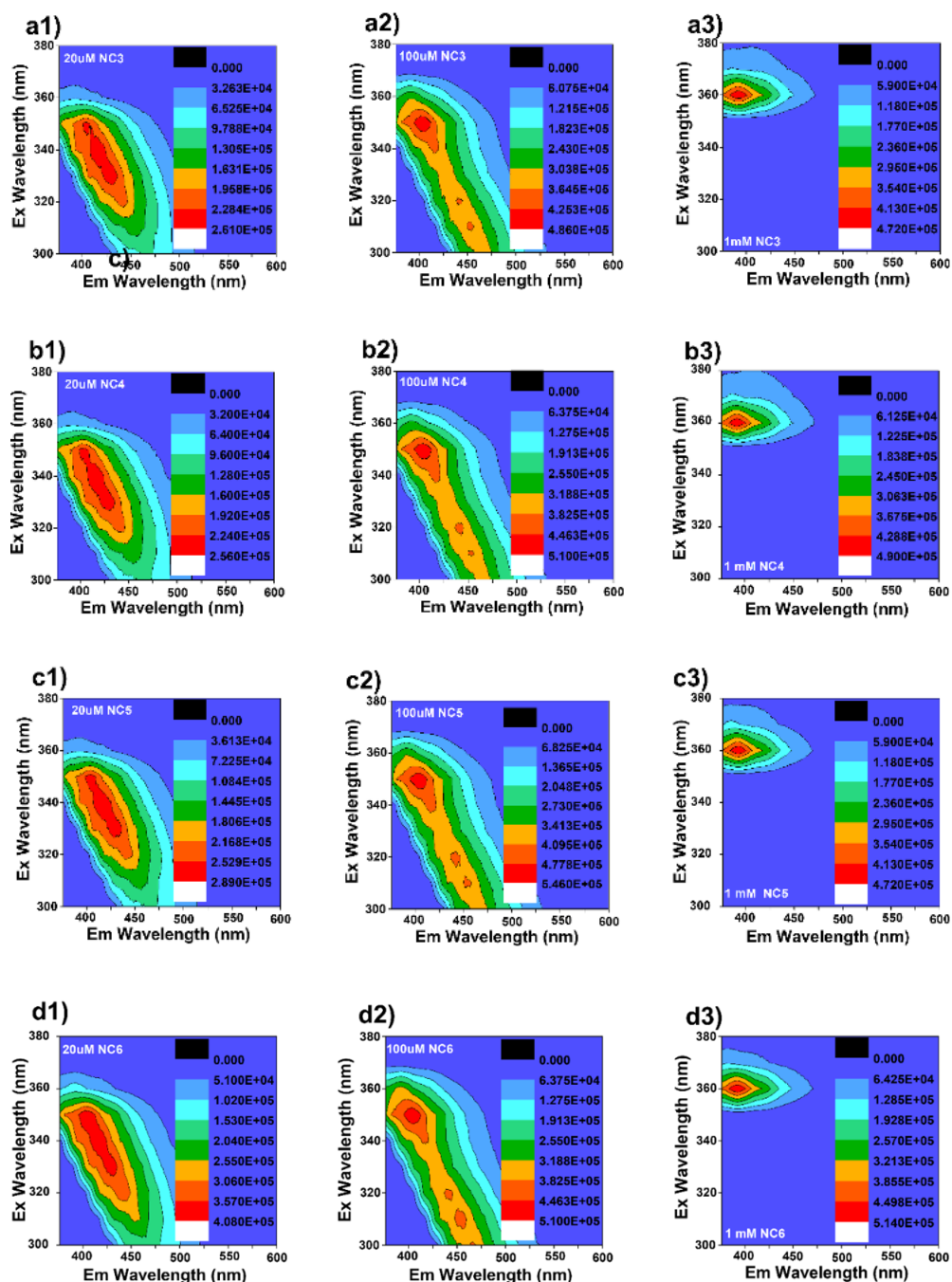


Figure S4. (a-d) 2D contour projections of the EEM spectra were obtained for **NC3**, **NC4**, **NC5**, and **NC6** derivatives, respectively, each at different concentrations (left: 20 μM (a1-d1); middle: 100 μM (a2-d2); right: 1 mM (a3-d3)) in EtOH. The emission spectra were collected from 390 to 600 nm by exciting the molecules from 300 to 380 nm at 10 nm increments.

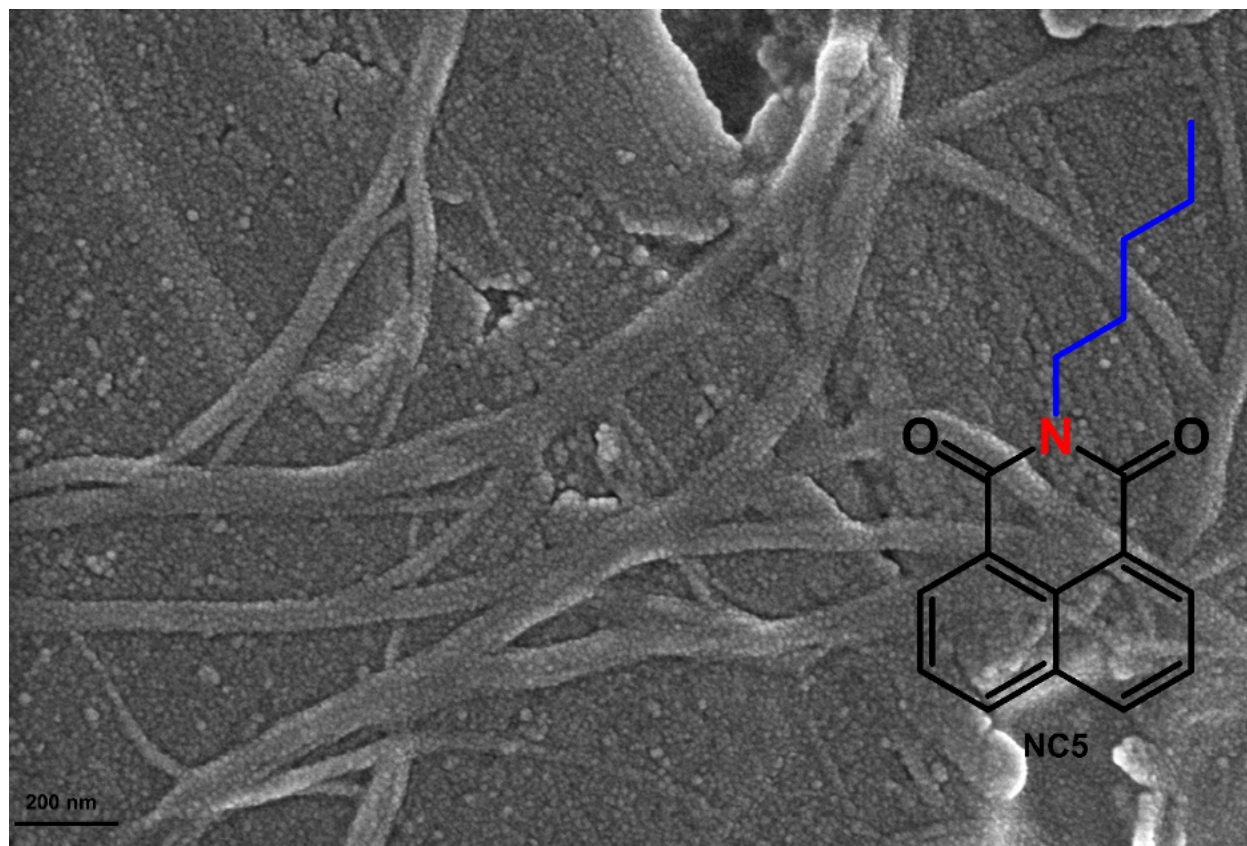


Figure S5. (a-g) FESEM images capture the nano fibrils formation of **NC5** luminogen at 99.8% f_w in EtOH (20 μ M). The nano-ribbon assembly was achieved through a straightforward drop-casting technique, followed by room temperature drying, as illustrated in Figure 4h.

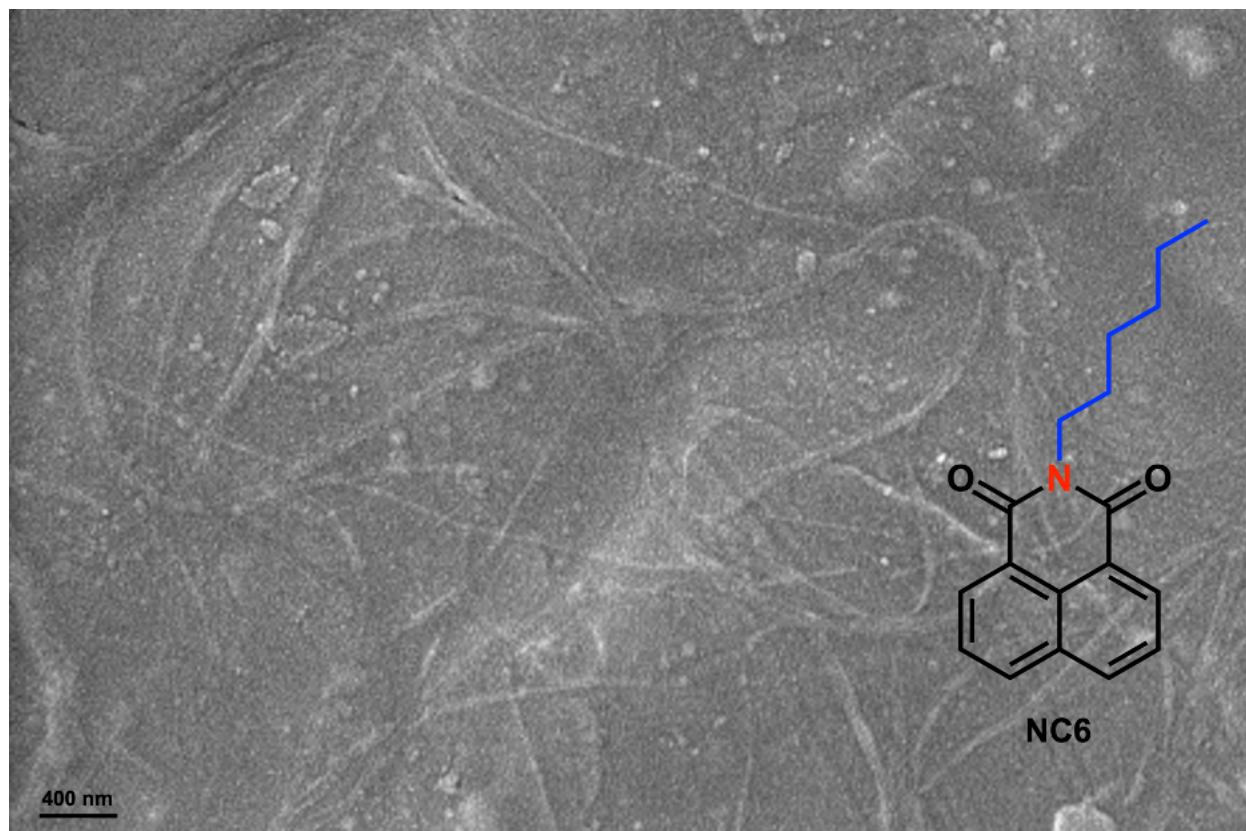


Figure S6. (a-g) FESEM images showcase the nano fibrils structures formed by **NC6** luminogen at 99.8% f_w in EtOH (20 μ M). The nano-ribbon assembly was achieved through a simple drop-casting technique followed by room temperature drying, as outlined in Figure 4h.

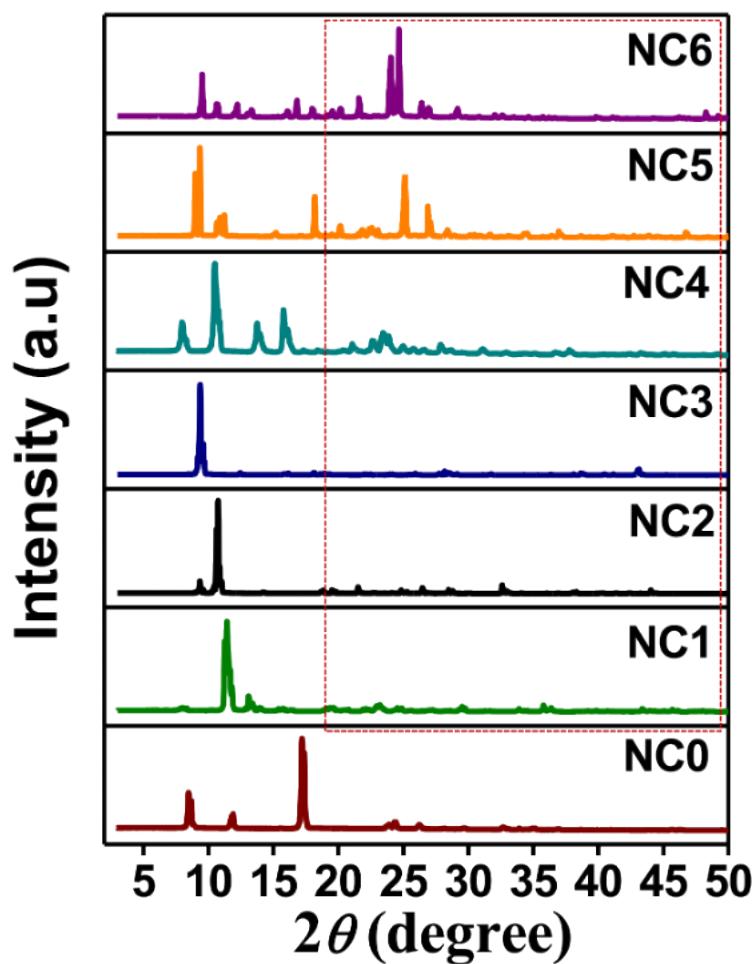


Figure S7. Merged PXRD pattern for all the **NC** derivatives. The red dotted box area represents the distinctive interchain hydrophobic interactions facilitated by the specific alkyl chain interactions.

Crystallographic Details

Table S3. SC-XRD Data and Parameters for NC crystals.

Compound code	NC0	NC1	NC2	NC3
CCDC	2374545	2374523	2374524	2374525
Empirical Formula	C ₁₂ H ₇ N O ₂	C ₂₆ H ₁₈ N ₂ O ₄	C ₁₄ H ₁₁ N O ₂	C ₁₅ H ₁₃ N O ₂
Formula Weight	197.19	422.42	225.24	239.26
Temperature	295 K	295K	297 K	296 K
Wavelength	0.71073	0.71073	0.71073	0.71073

Crystal System	monoclinic	monoclinic	monoclinic	monoclinic
Space Group	P 21/n	P 1 21/c 1	C 2/c	P 21/c
Unit Cell Dimension	a=11.0018(7) b=5.4073(3) c=15.6669(10) alpha=90 beta=108.949(2) gamma=90	a= 18.691(2) b= 3.8980(5) c= 26.717(3) alpha=90 beta= 90.349(4) gamma=90	a=7.0702(13) b=18.754(4) c=16.522(3) alpha=90 beta=96.935(5) gamma=90	a=9.3455(9) b=6.8284(6) c=19.0394(17) alpha=90 beta=97.030(3) gamma=90
Volume	881.52(9)	1946.5(4)	2174.7(7)	1205.86(19)
Z	4	4	8	4
Absorption coefficient	0.103	0.099	0.093	0.088
F (000)	408.0	880.0	944.0	504.0
Theta range for data collection	3.917-24.992	1.326- 25.102	3.099-25.000	2.156-26.496
Index Range	-13<=h<=13, -6<=k<=6, -18<=l<=18	-22<=h<=22, -4<=k<=4, -31<=l<=31	-8<=h<=8, -22<=k<=22, -19<=l<=19	-11<=h<=11, -8<=k<=8, -23<=l<=23
Reflections Collected/unique	19135/1541 (R _{int} = 0.0328)	36220 /3476 (R _{int} = 0.0671)	18987/1914 (R _{int} = 0.0531)	36769/ 2505 (R _{int} = 0.0531)
Goodness-of-fit on F2	1.406	1.185	1.339	1.041
Final R indices [I>2σ(I)]	R1 = 0.0394, ωR2 = 0.1405	R1 = 0.0832, ωR2 = 0.1479	R1 = 0.0546, ωR2 = 0.1631	R1 = 0.0599, ωR2 = 0.1612
R indices (all data)	R1 = 0.0460, ωR2 = 0.1625	R1 = 0.1300, ωR2 = 0.1689	R1 = 0.0788, ωR2 = 0.1948	R1 = 0.0879, ωR2 = 0.1911
Largest difference peak and hole (e Å ⁻³)	0.167, -0.192	0.171, -0.198	0.136, -0.208	0.314, -0.374

Compound code	NC4	NC5	NC6
CCDC	2374526	2374522	2374529

Empirical Formula	C16 H15 N O2	C17 H17 N O2	C18 H19 N O2
Formula Weight	253.29	267.31	281.34
Temperature	296 K	296 K	297 K
Wavelength	0.71073	0.71073	0.71073
Crystal System	orthorhombic	triclinic	monoclinic
Space Group	P 21 21 21	P -1	P 21/n
Unit Cell Dimension	a= 4.7154(10) b= 12.531(3) c= 22.215(4) alpha=90 beta=90 gamma=90	a=9.639(3) b=9.806(3) c=14.785(4) alpha=89.903(9) beta=89.916(9) gamma=81.105(9)	a=8.2305(4) b=16.3481(9) c=11.3549(6) alpha=90 beta=103.2440(10) gamma=90
Volume	1312.7(5)	1380.6(7)	1487.20(13)
Z	4	4	4
Absorption coefficient	0.085	0.084	0.082
F (000)	536.0	568	600.0
Theta range for data collection	1.833-24.990	1.377- 25.000	2.777-24.992
Index Range	-5<=h<=5, -14<=k<=14, -26<=l<=26	-11<=h<=11, -11<=k<=11, -17<=l<=17	-9<=h<=9, -19<=k<=19, -13<=l<=13
Reflections Collected/unique	42762/2319 (R _{int} = 0.0876)	56551/4856 (R _{int} = 0.0689)	39731/2597 (R _{int} = 0.0464)
Goodness-of-fit on F2	1.045	1.141	1.064
Final R indices [I>2σ(I)]	R1 = 0.0471, ωR2 = 0.1090	R1 = 0.0595, ωR2 = 0.1643	R1 = 0.0542, ωR2 = 0.1431
R indices (all data)	R1 = 0.0647, ωR2 = 0.1213	R1 = 0.0897, ωR2 = 0.1966	R1 = 0.0638, ωR2 = 0.1575
Largest difference peak and hole (e Å ⁻³)	0.118, -0.149	0.385, -0.274	0.574, -0.220

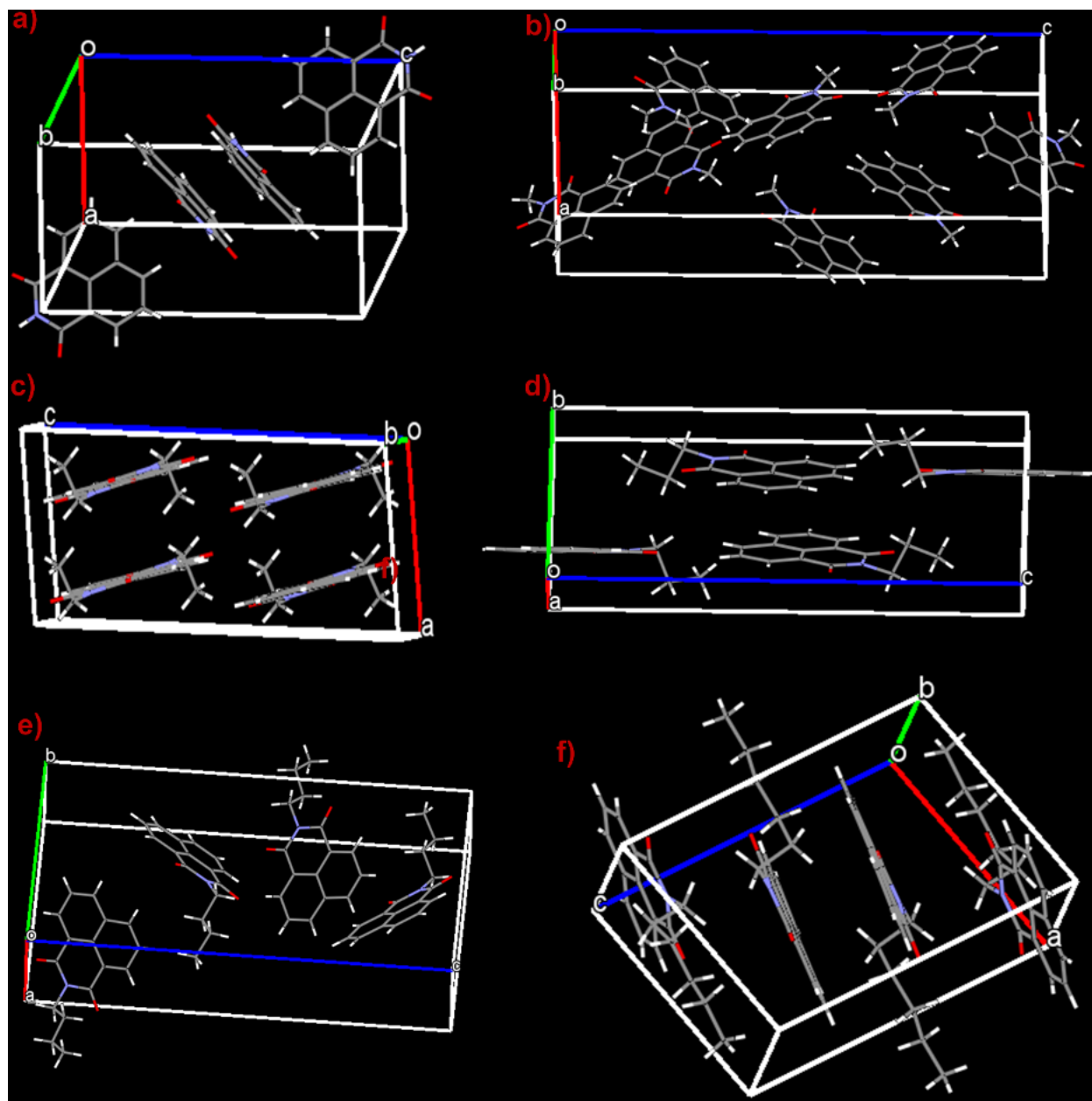


Figure S8. The single crystal unit cells of NC derivatives, namely (a) NC0, (b) NC1, (c) NC2, (d) NC3, (e) NC4, and (f) NC5.

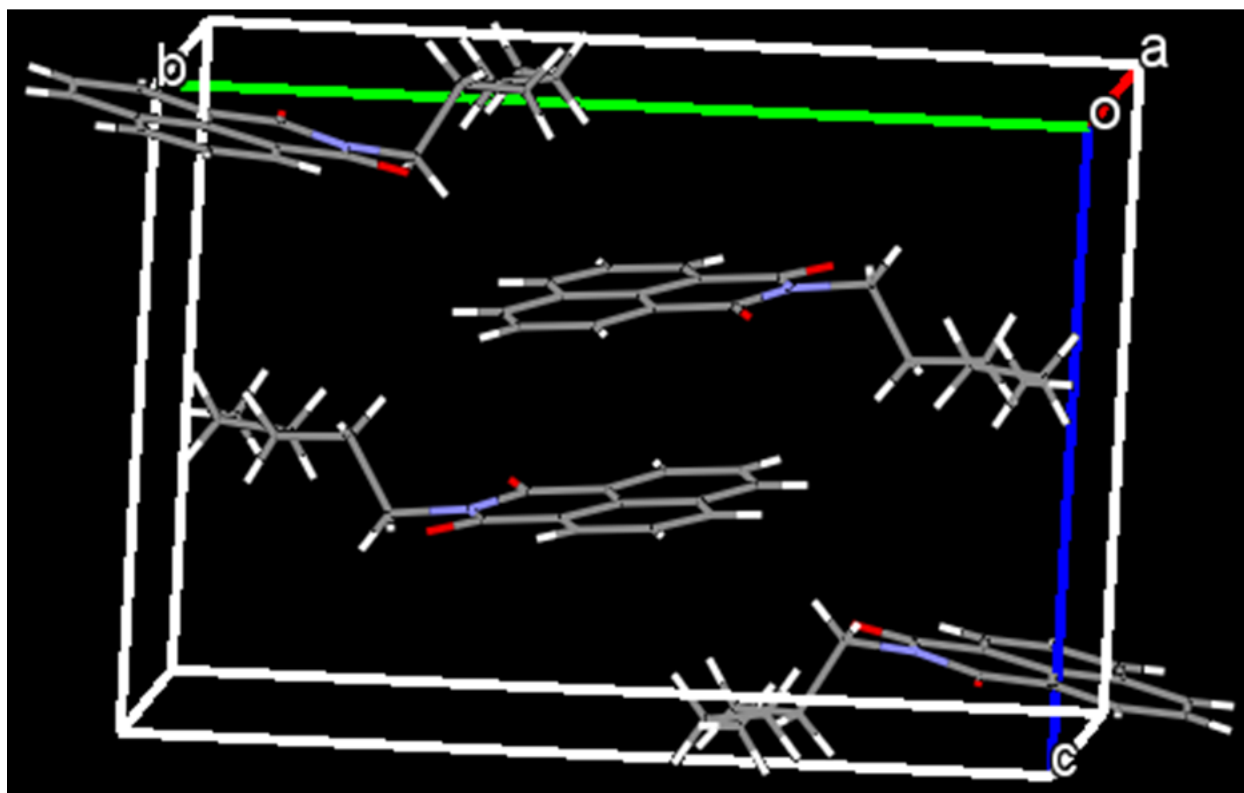


Figure S9. The single crystal unit cell of NC6.

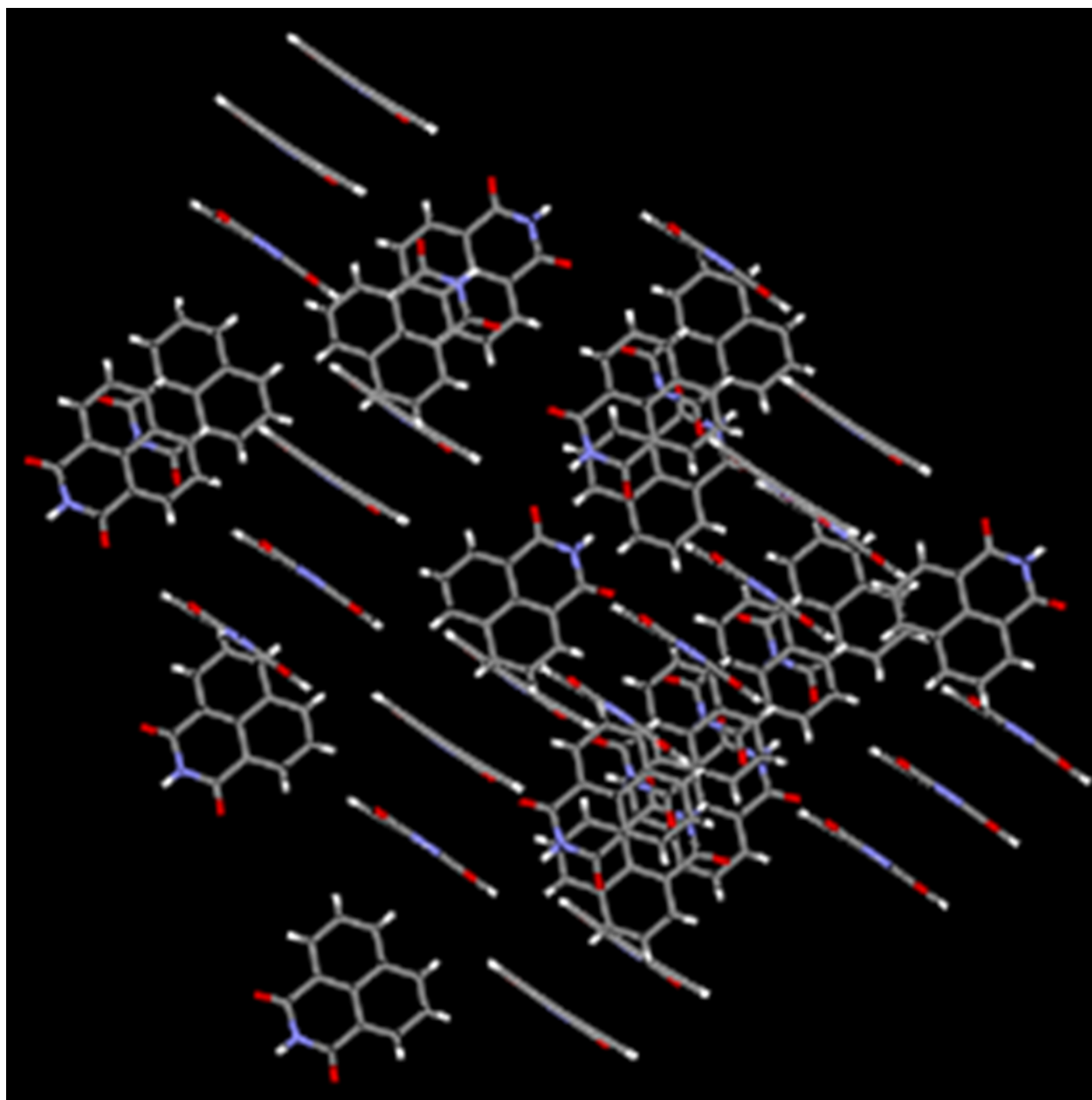


Figure S10. The single crystal packing diagram of **NCO** illustrates the arrangement perturbation in the naphthalimide through a simple structural modification without the alkyl chain.

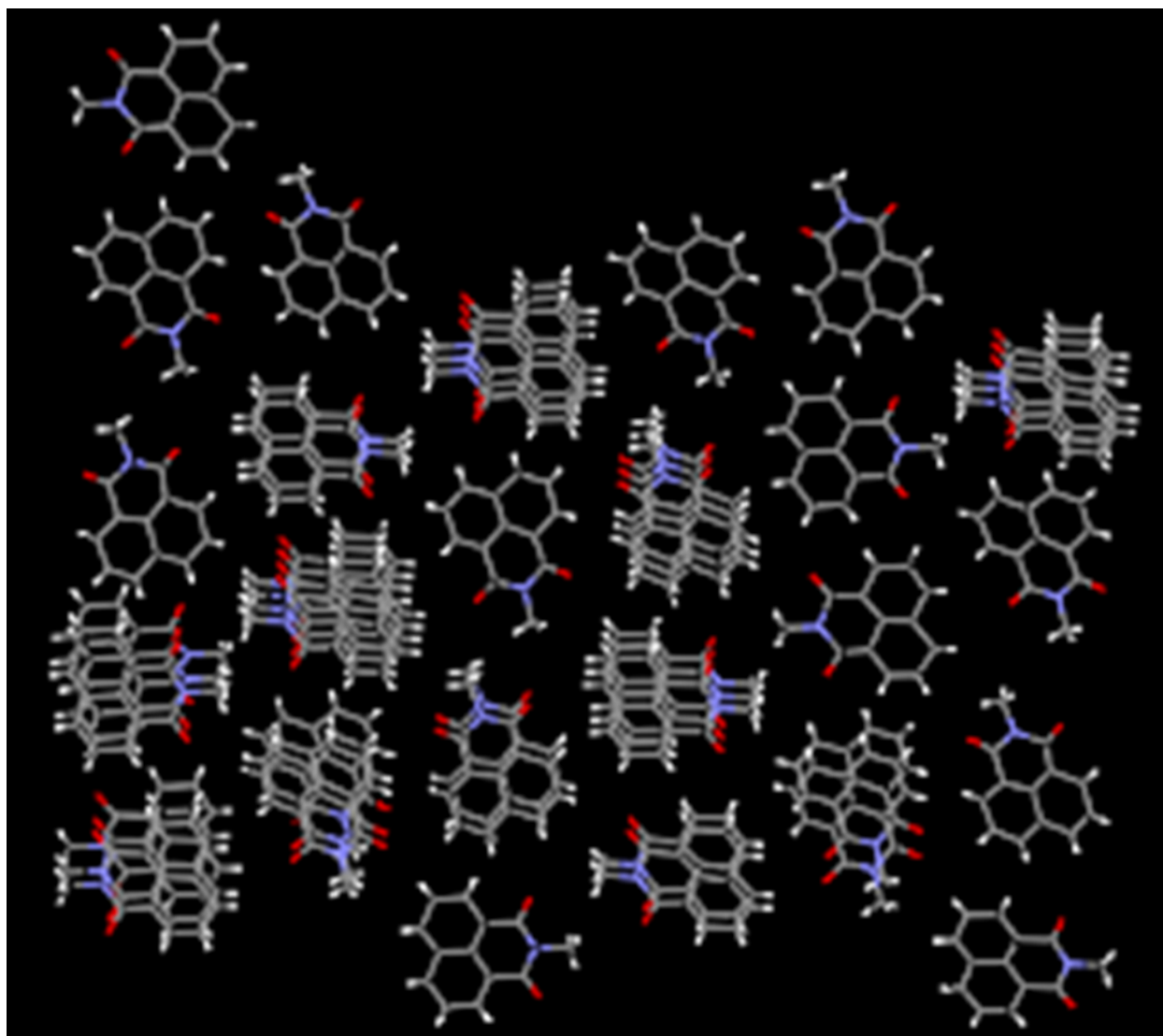


Figure S11. The single crystal packing diagram of **NC1** reveals the arrangement perturbation in the naphthalimide through a simple structural modification.

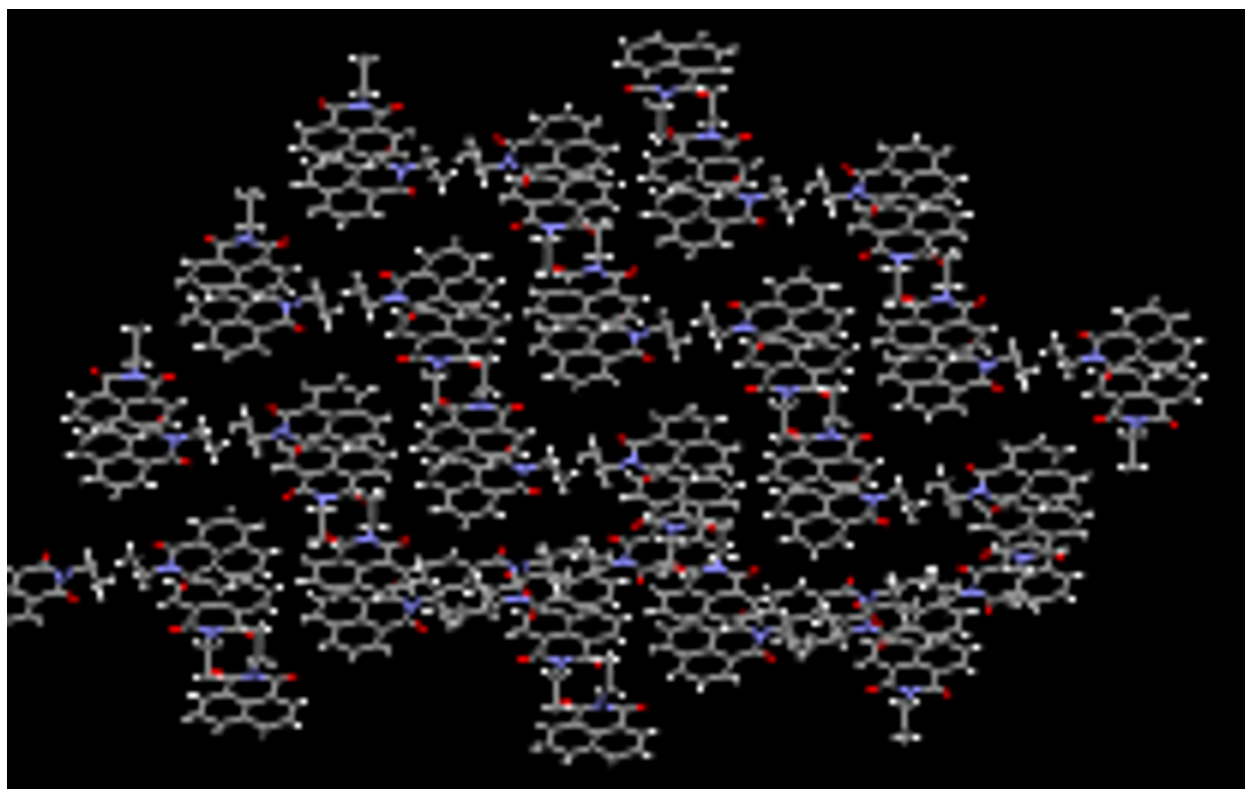


Figure S12. The single crystal packing diagram of **NC2** highlights the arrangement perturbation in the naphthalimide through a straightforward structural modification.

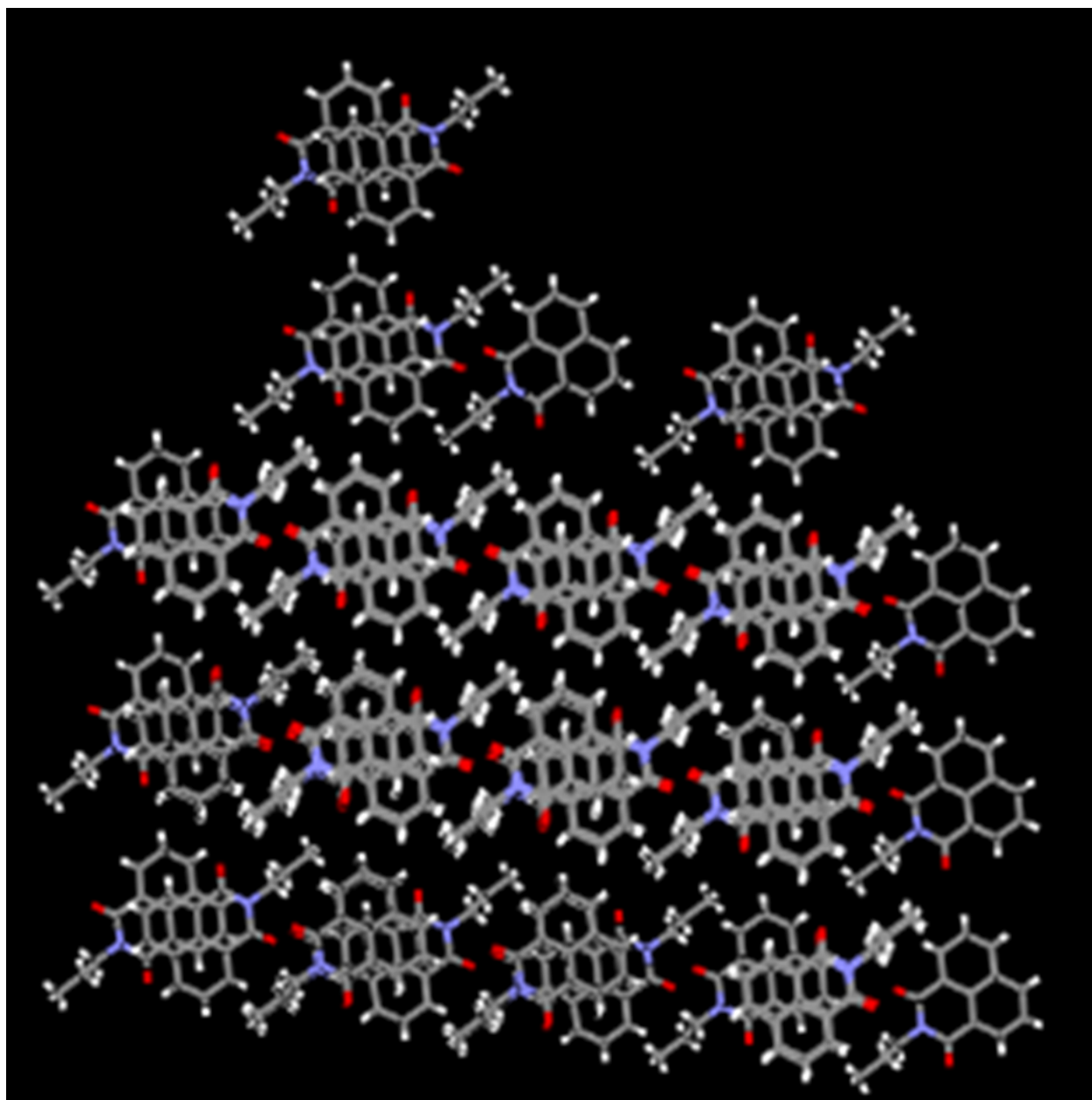


Figure S13. The single crystal packing diagram of **NC3** illustrates the arrangement perturbation in the naphthalimide through a simple structural modification.

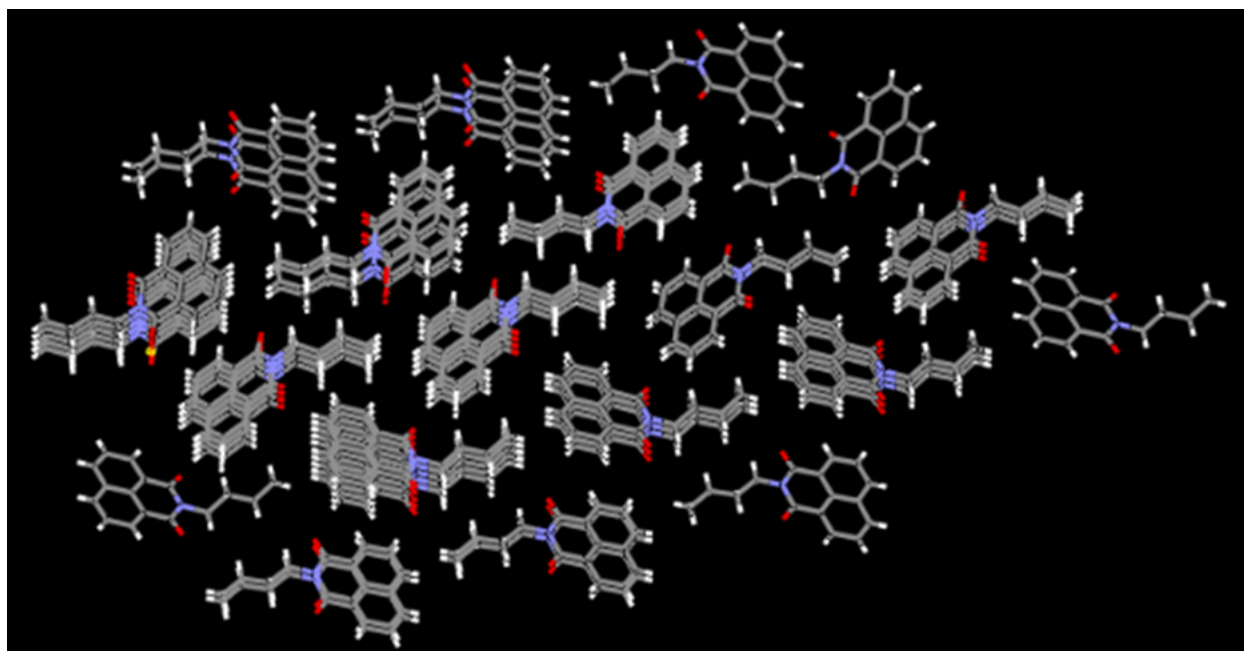


Figure S14. The single crystal packing diagram of **NC4** shows the arrangement perturbation in the naphthalimide through a simple structural modification.

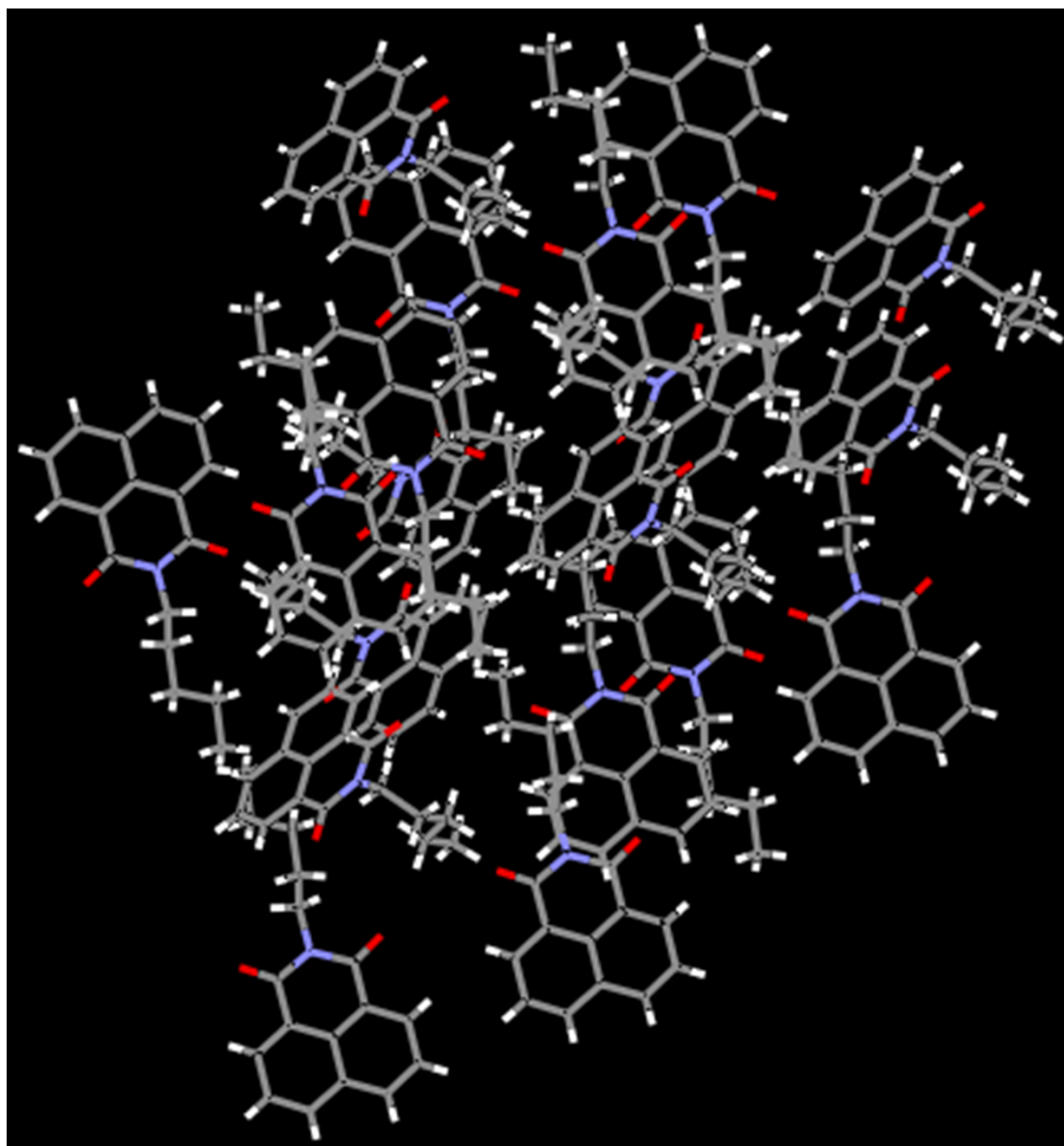


Figure S15. The single crystal packing diagram of **NC5** demonstrates the arrangement perturbation in the naphthalimide through a simple structural modification.

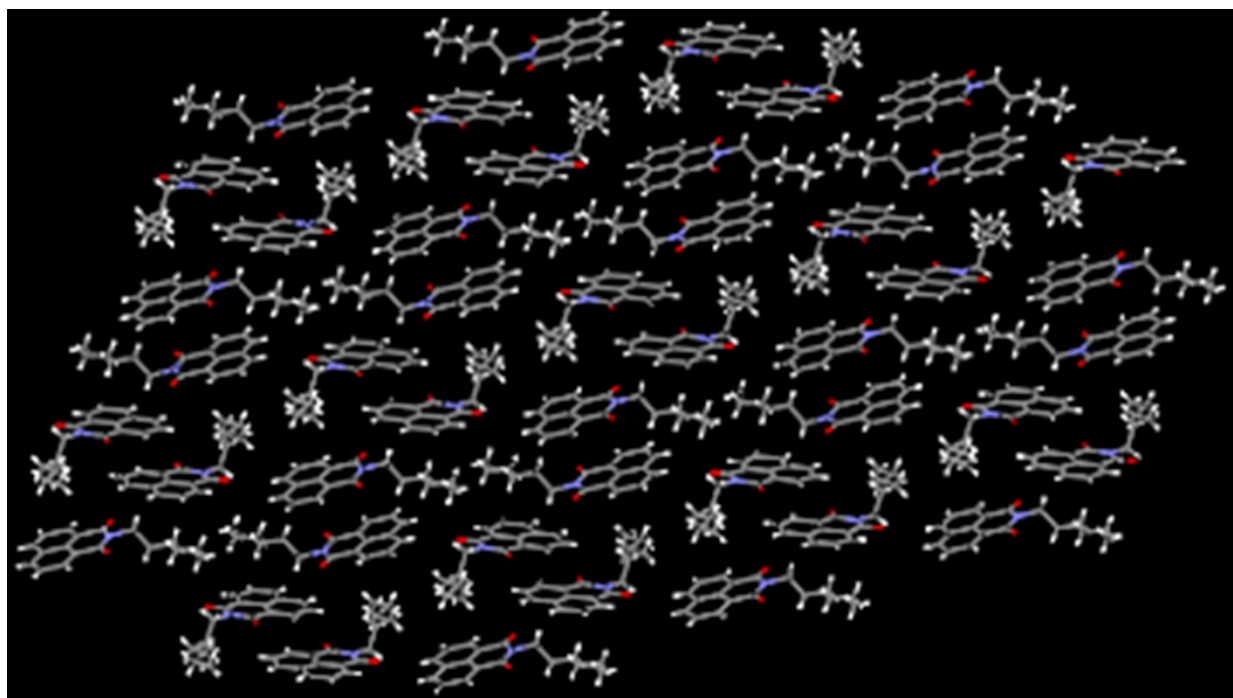


Figure S16. The single crystal packing diagram of **NC6** illustrates the arrangement perturbation in the naphthalimide through a simple structural modification.

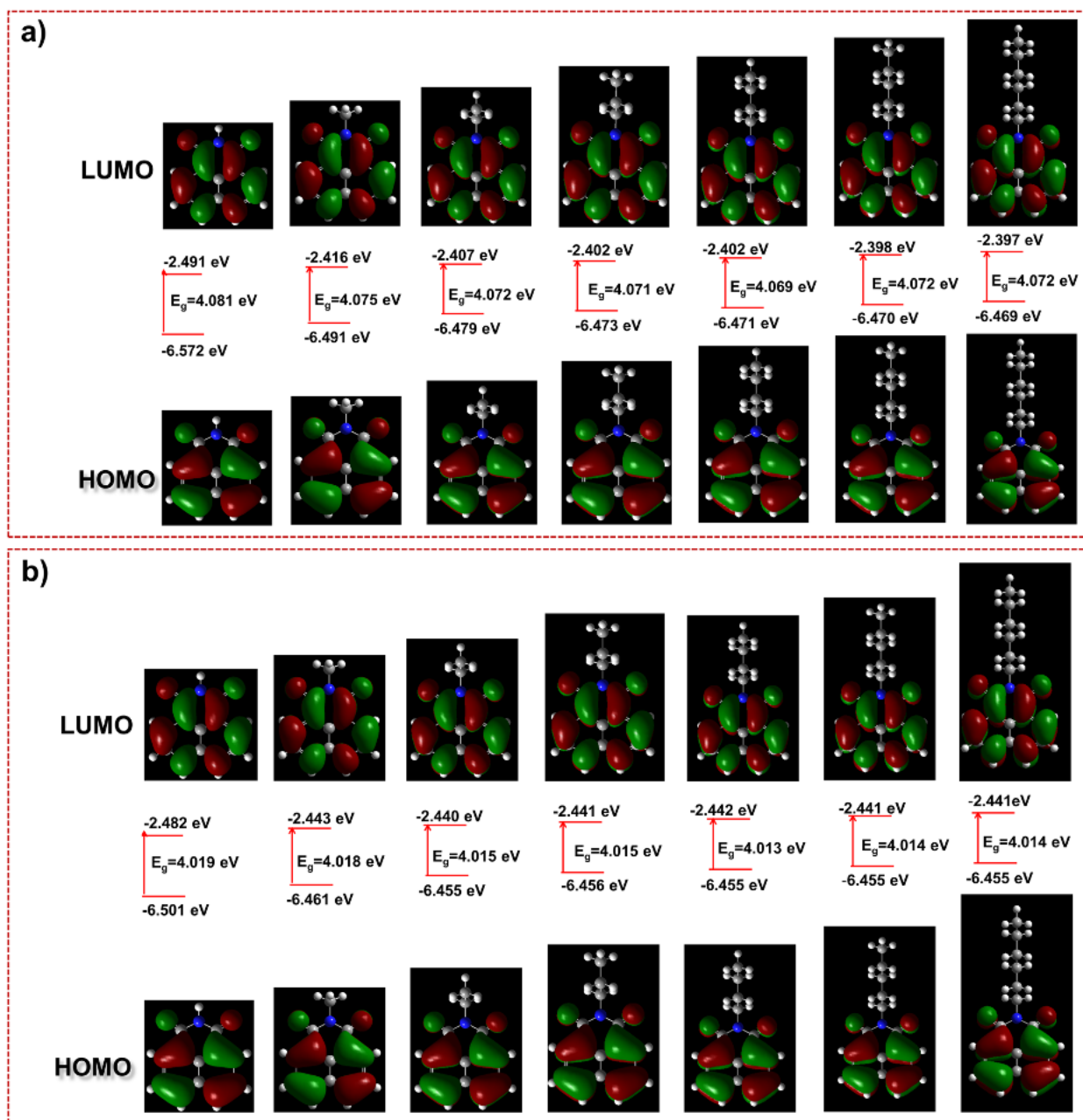
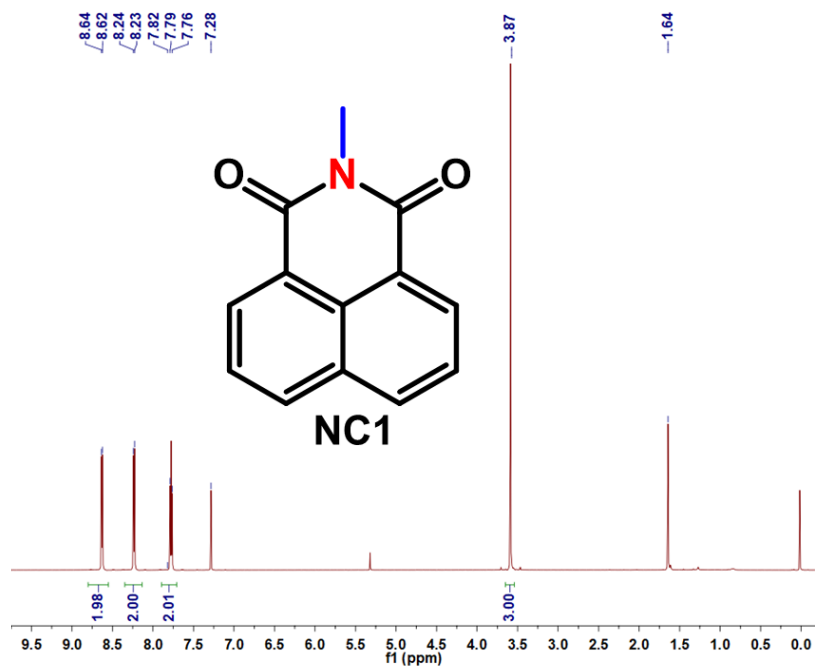
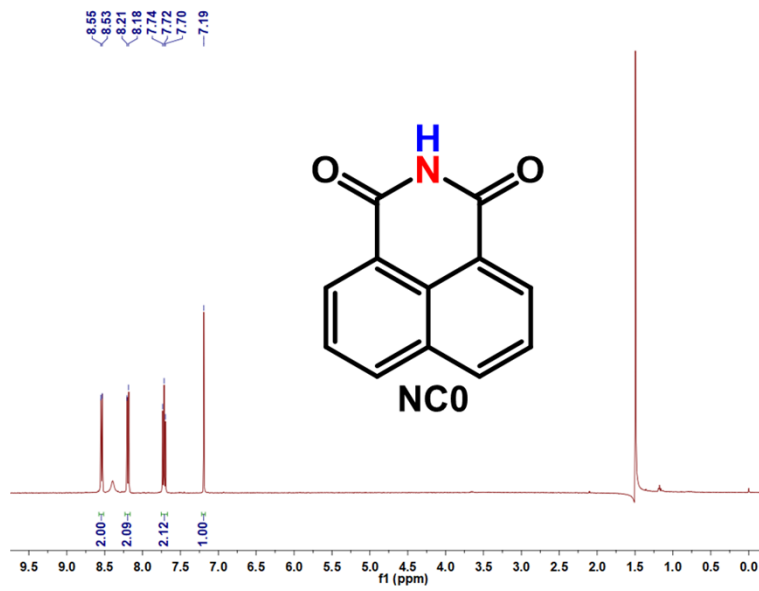
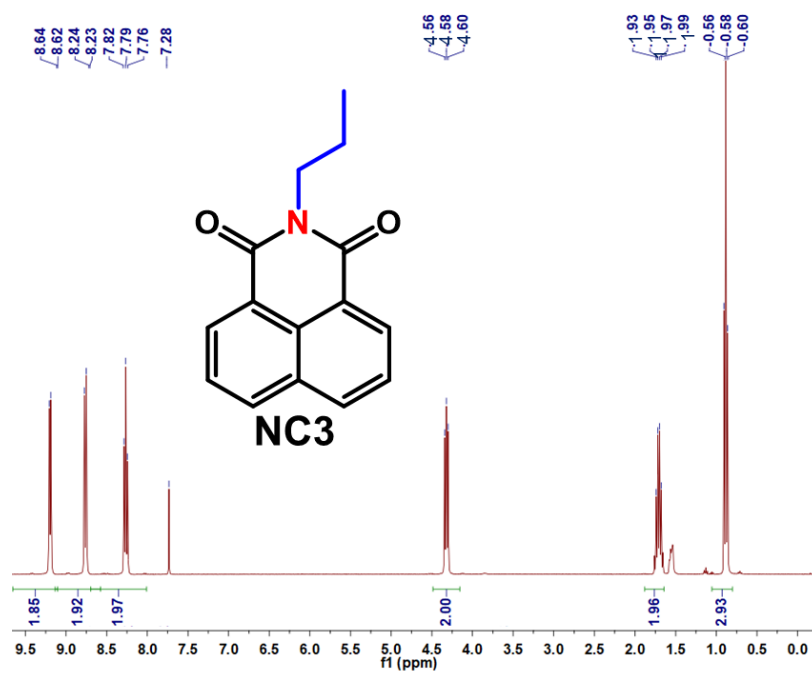
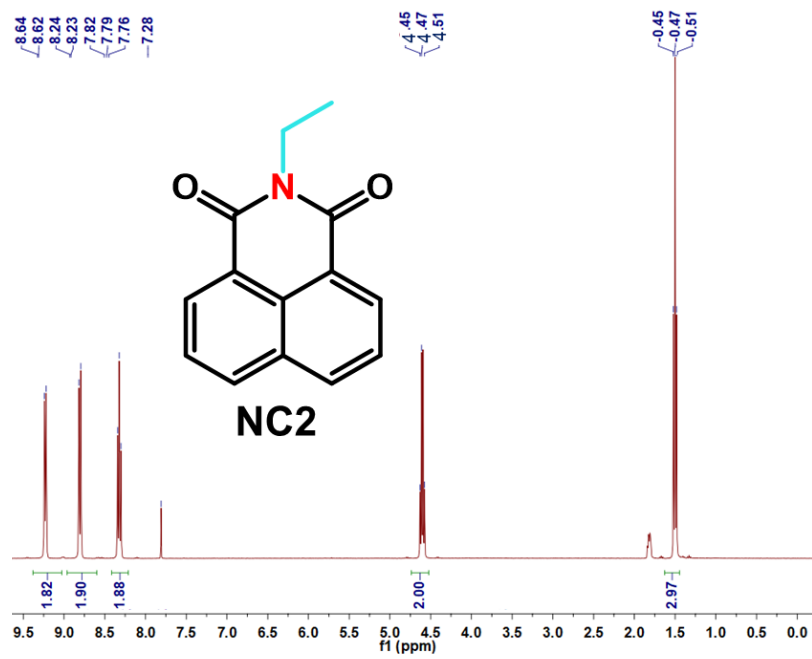


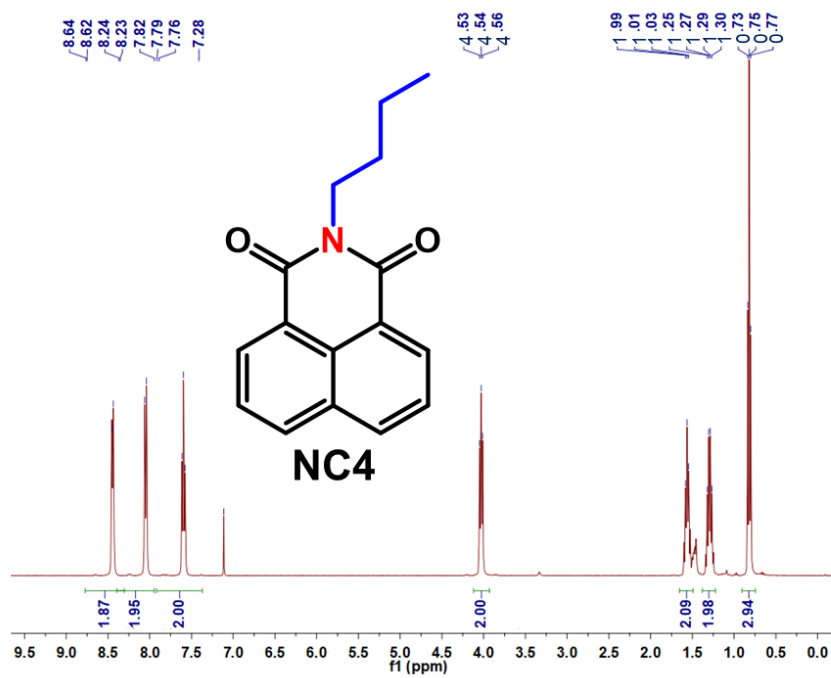
Figure S17. Optimized structures and HOMO/LUMO electron density of the NC derivatives were computed in both (a) gaseous state and (b) solvent state. The calculations were performed using time-dependent density functional theory with the B3LYP exchange functional, employing 6-31G* basis sets in the Gaussian 09 program.

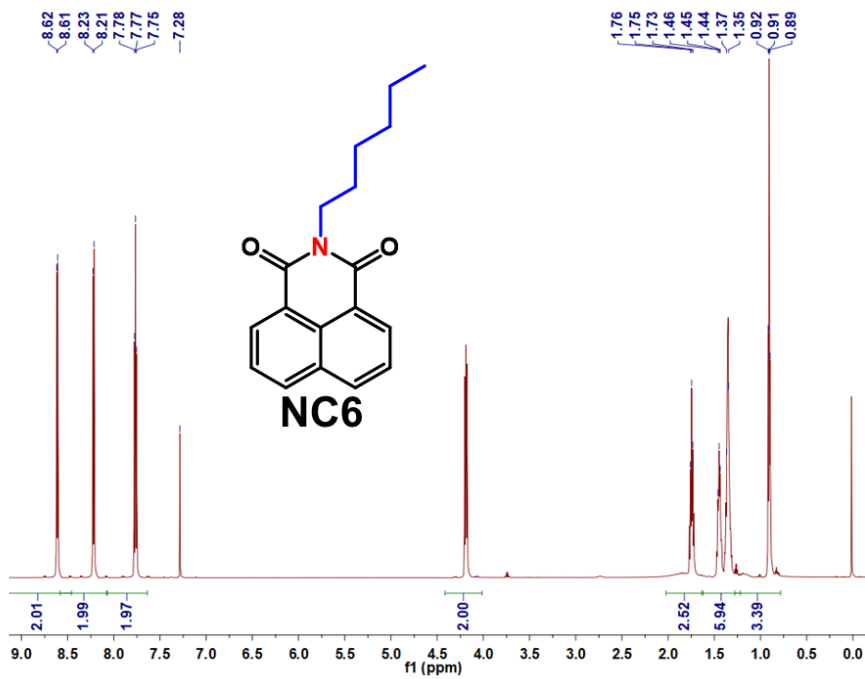
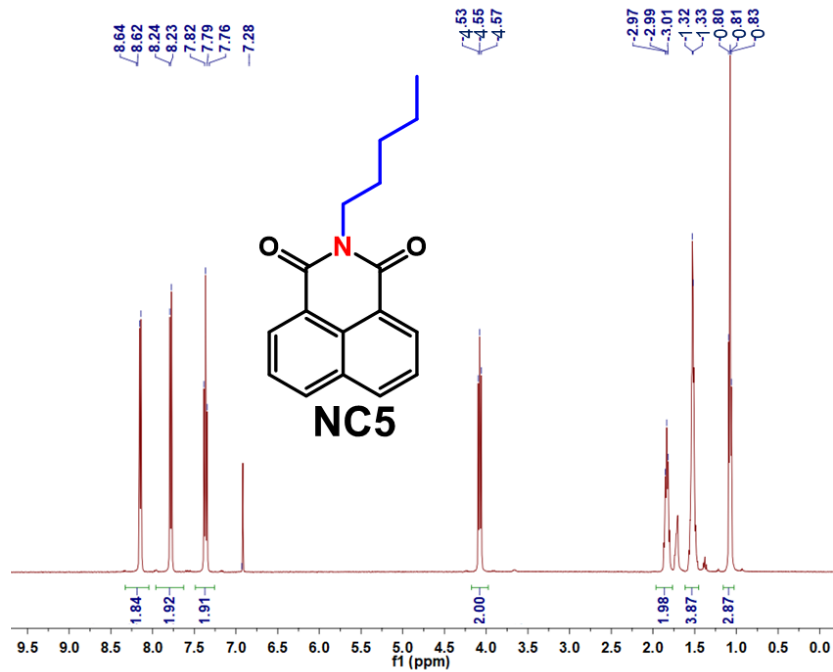
2. Supporting Characterization Figures

¹H NMR Spectra

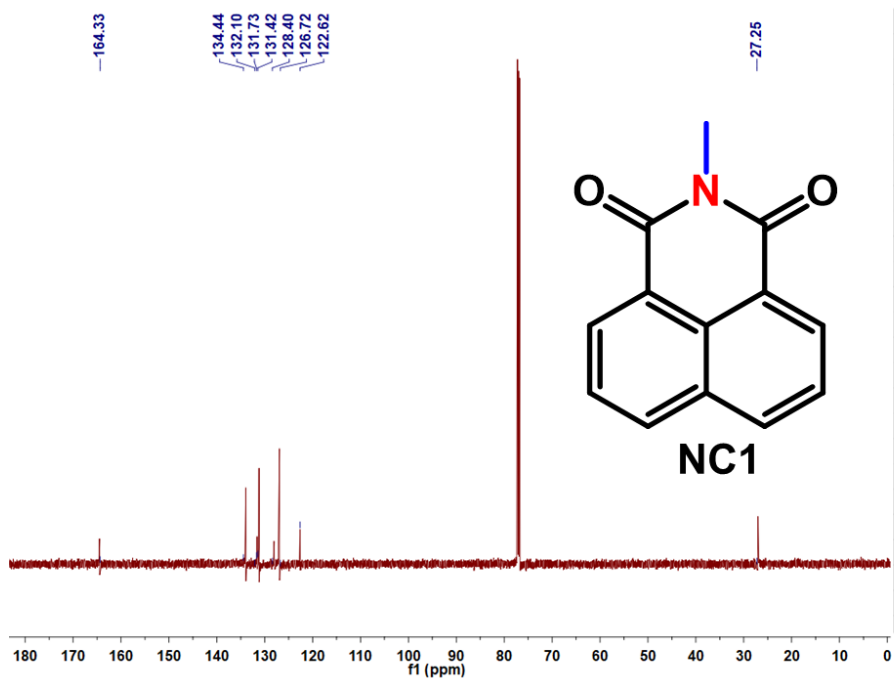
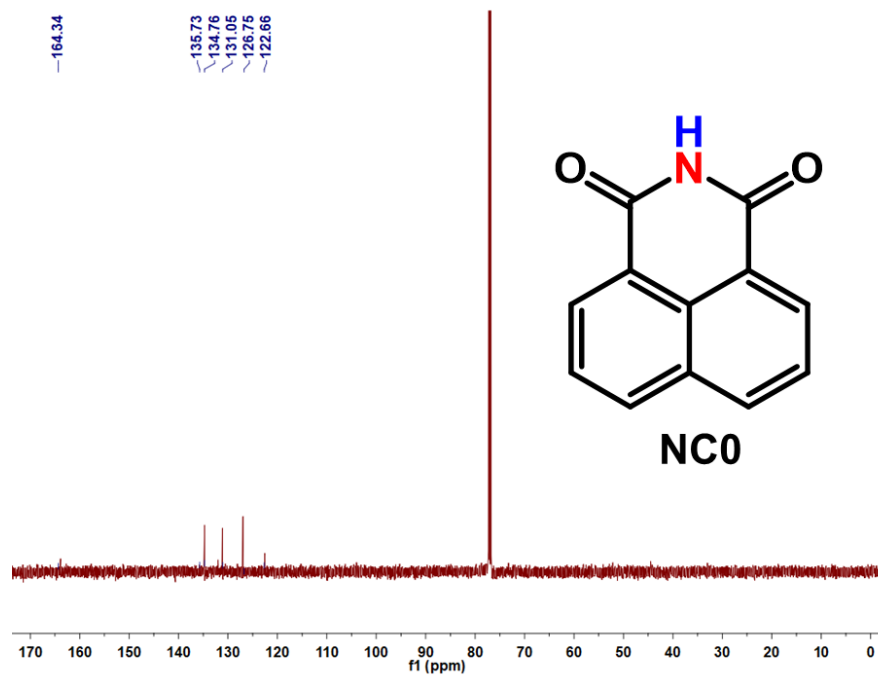


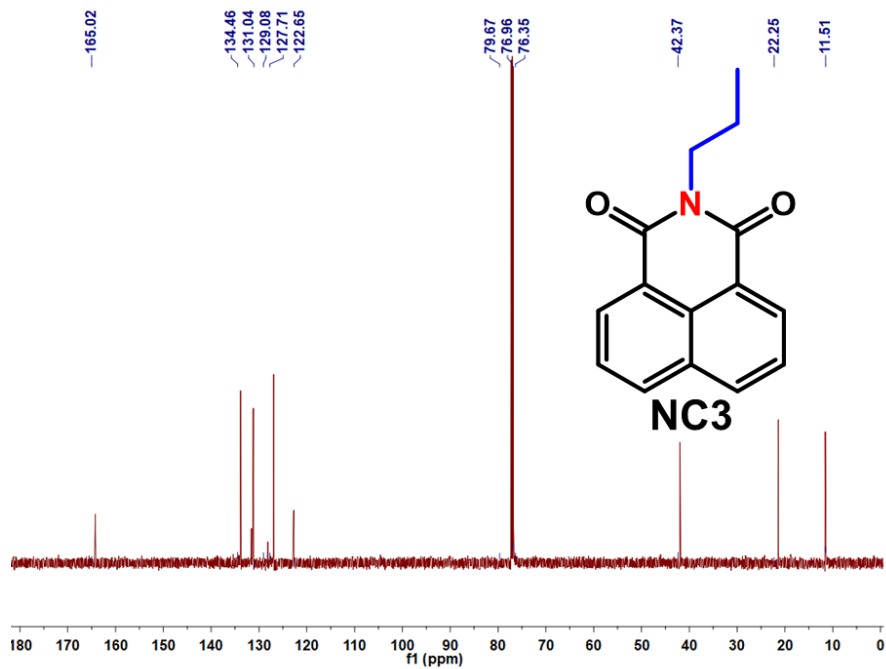
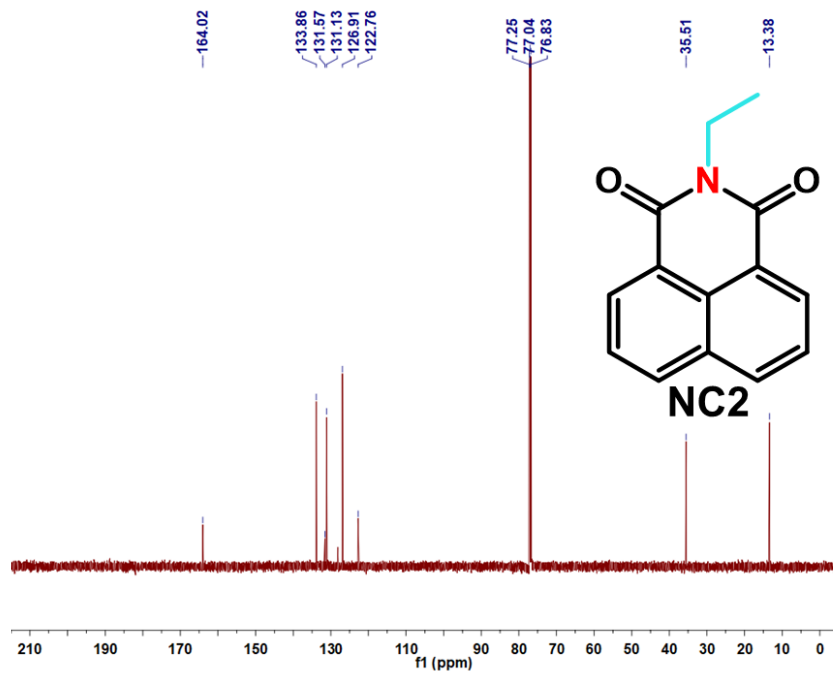


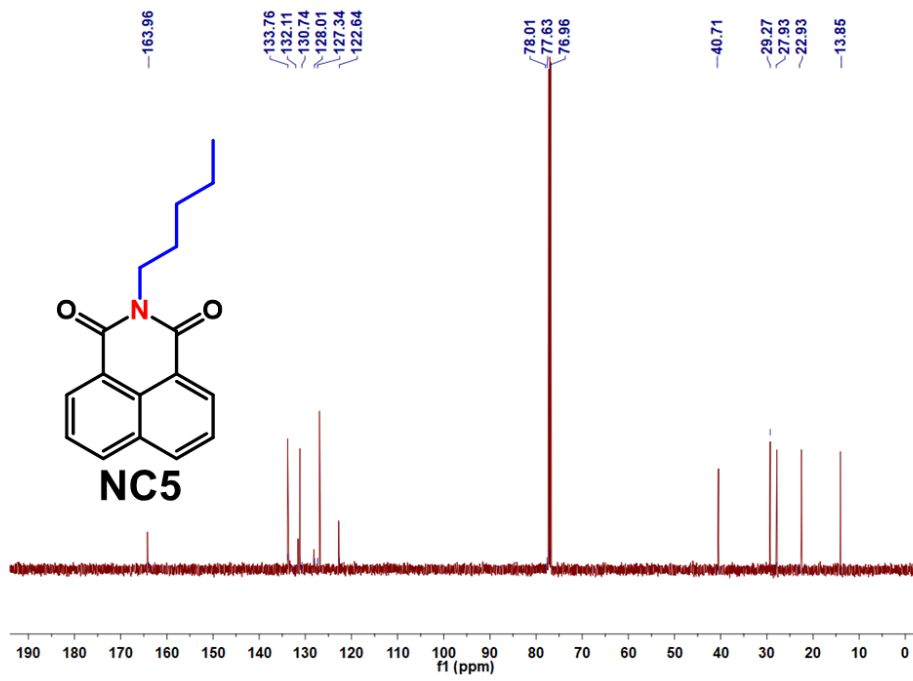
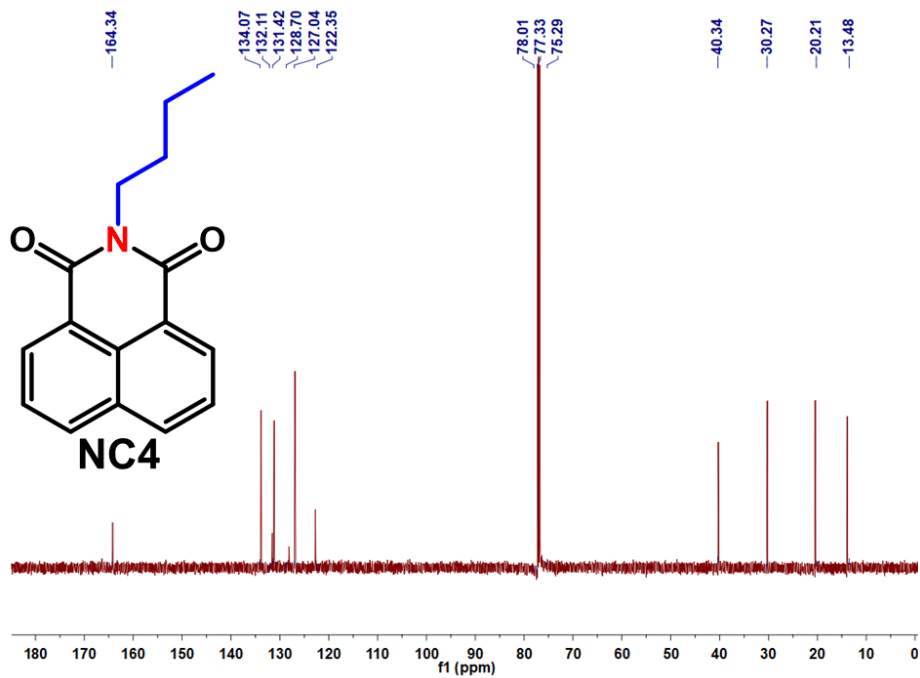


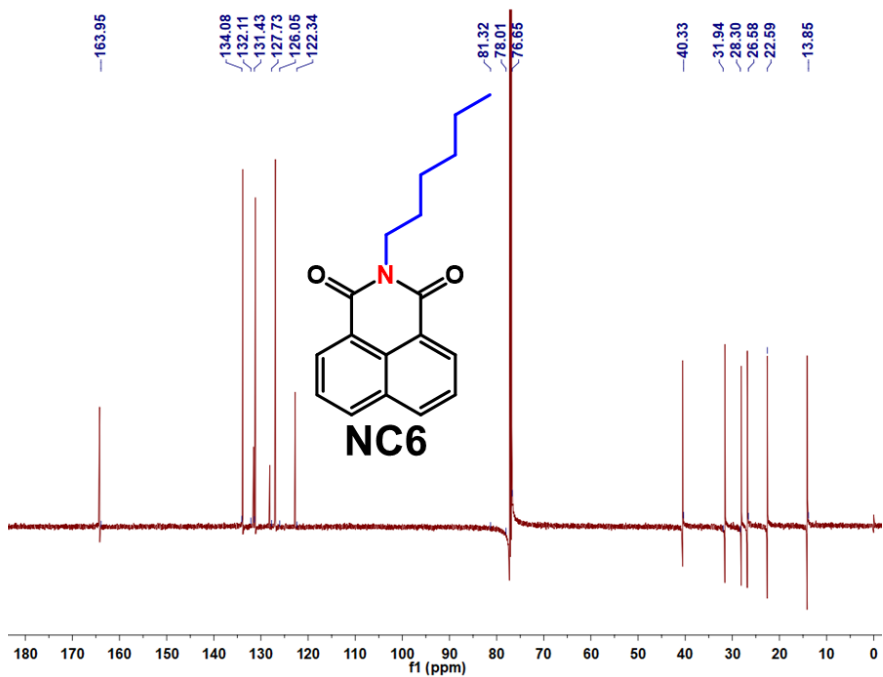


¹³C NMR Spectra

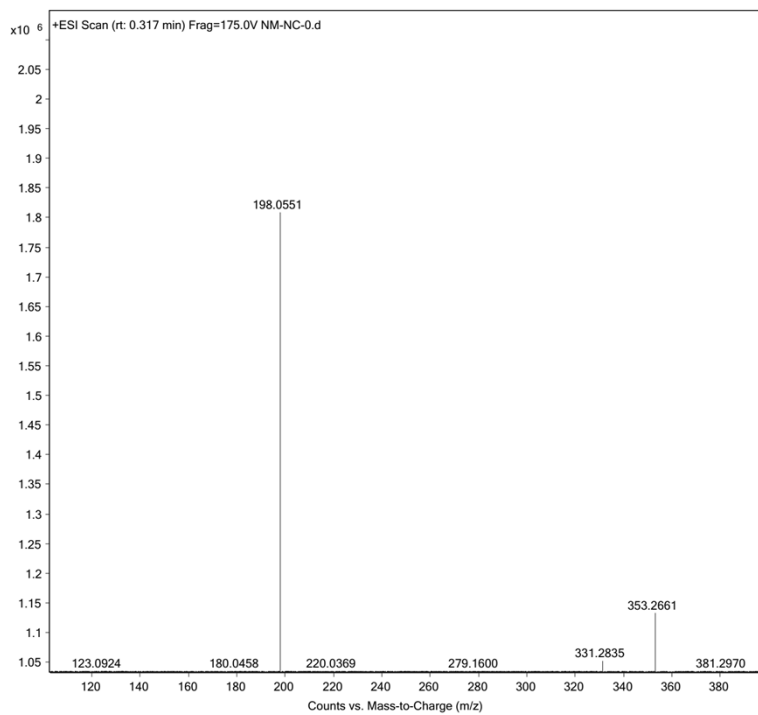




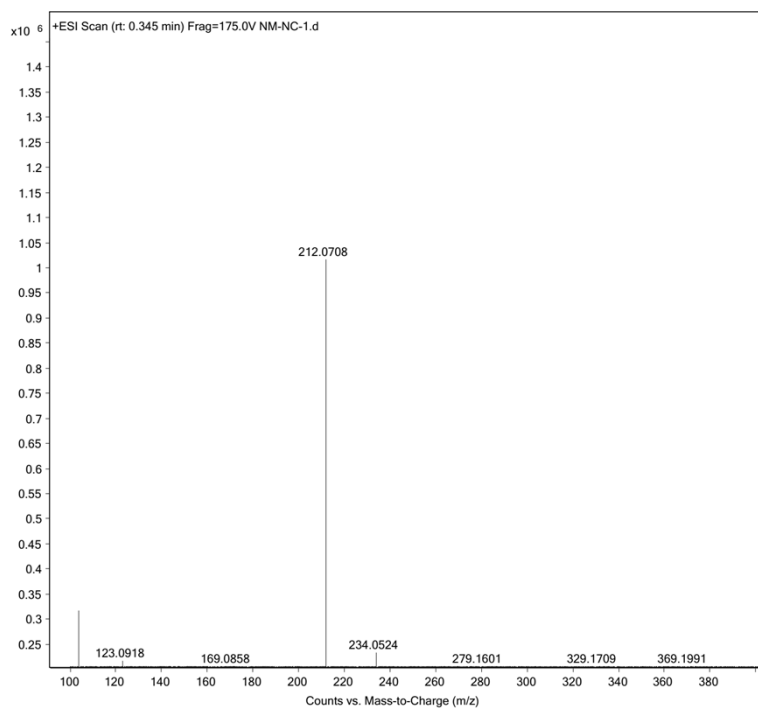




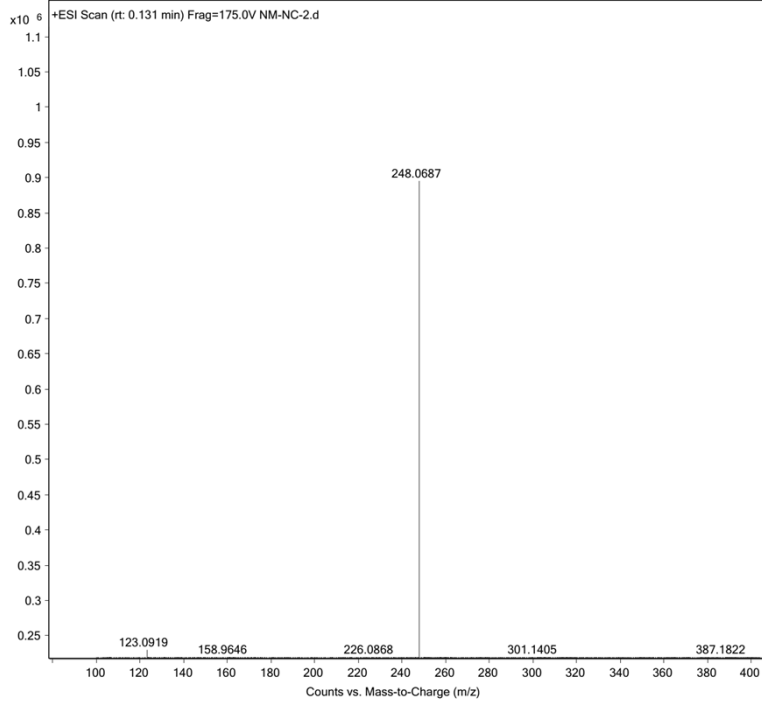
HRMS Spectra



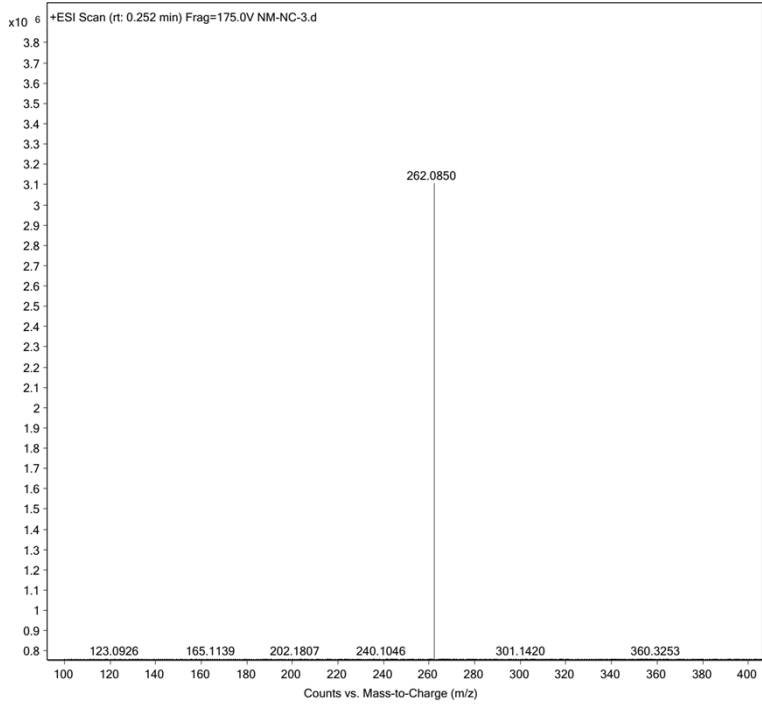
Mass spectra of NCO



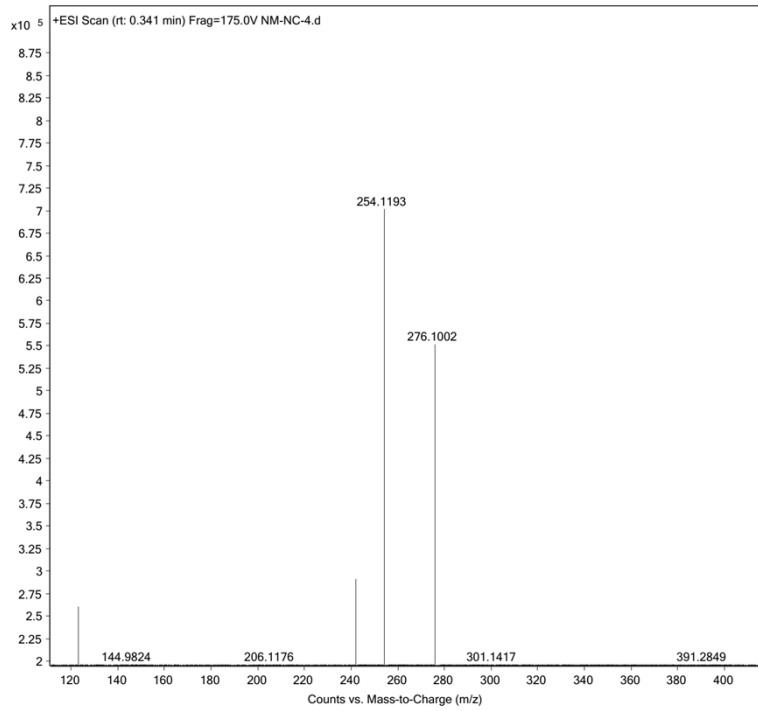
Mass spectra of NC1



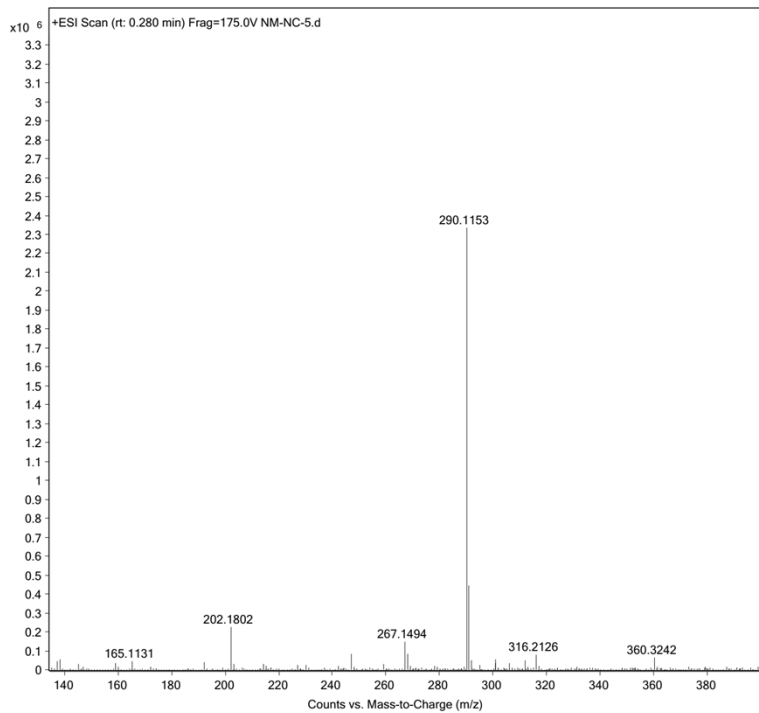
Mass spectra of NC2



Mass spectra of NC3



Mass spectra of NC4



Mass spectra of NC5

References

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