

## Electronic Supplementary Information for

### Evaluating the thermal behaviour of benzimidazolylidene sources for thin-film applications

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# 1. General Considerations

## 1.1. Materials

Unless otherwise stated, all solvents and reagents were obtained from Sigma-Aldrich and used without further purification. Compounds benzNHC<sup>iPr</sup> and (benzNHC<sup>Et</sup>)<sub>2</sub> were prepared via deprotonation of their iodide salt precursors<sup>1</sup> following previously established methods,<sup>2, 3</sup> and manipulated under an inert nitrogen or argon atmosphere using standard Schlenk and dry box techniques. Tetrahydrofuran (THF) used for the synthesis of benzNHC<sup>iPr</sup> and (benzNHC<sup>Et</sup>)<sub>2</sub> was dried over sodium/benzophenone and distilled prior to use. Carbene benzNHC<sup>iPr</sup> was purified by vacuum distillation (70 °C, 5 mTorr) prior to all kinetic and thermal analyses. Following an existing method,<sup>4</sup> benzNHC<sup>iPr</sup>•H<sub>2</sub>CO<sub>3</sub> was prepared from the precursor iodide salt using HCO<sub>3</sub><sup>-</sup> anion exchange resin and complete exchange of I<sup>-</sup> for HCO<sub>3</sub><sup>-</sup> was verified by elemental analysis prior to use.

Unless otherwise stated, all NMR solvents were obtained from Sigma-Aldrich and used without further purification. Benzene-*d*<sub>6</sub> (C<sub>6</sub>D<sub>6</sub>) (≥ 99.6 atom % D, anhydrous, Aldrich 570680) used for kinetics measurements was degassed by three freeze-pump-thaw cycles and then stored under inert atmosphere over activated 4 Å molecular sieves prior to use.

Cu films were fabricated using a commercial thermal evaporator from Angstrom engineering that is housed in an N<sub>2</sub> glovebox. Cu shot (99.999%) was used as the Cu source. The Si substrate wafers were used as received (mechanical grade Si purchased from University wafer). Copper surfaces were cleaned by submerging into 50 °C *glacial* acetic acid (99.99 %, trace metal analysis, Sigma-Aldrich) for 10 minutes then drying with argon 5.0.<sup>5</sup> Freshly cleaned copper surfaces were functionalized with NHCs by subliming 10 mg of benzNHC<sup>iPr</sup> or benzNHC<sup>iPr</sup>•H<sub>2</sub>CO<sub>3</sub> at 373 K for 1 minute under static vacuum, followed by a 5 seconds of dynamic vacuum. A thin film of **1a** was prepared by submerging a clean Cu wafer in a 10 mM solution of **1a** in 1,2-dichloroethane (99%+, HPLC grade, Alfa Aesar) for 24 h, then drying with argon 5.0.

## 1.2. Instrumentation

<sup>1</sup>H, and <sup>13</sup>C{<sup>1</sup>H} NMR spectra were recorded at either Queen's University using a Bruker Avance 400 MHz spectrometer at 298 K or at Carleton University using a Bruker Avance 300 MHz spectrometer at 298K. Chemical shifts (δ) are reported in parts per million (ppm) and are referenced to residual protonated (<sup>1</sup>H) or deuterated (<sup>13</sup>C{<sup>1</sup>H}) solvent signals.<sup>6</sup> Coupling constants (*J*) are reported as absolute values. All NMR data were processed and displayed using Bruker TopSpin software.

Elemental analyses were performed at Queen's University using Flash 2000 CHNS-O analyzer.

Thermogravimetric analysis (TGA) of benzNHC<sup>iPr</sup>, **1a** and (benzNHC<sup>Et</sup>)<sub>2</sub> was performed at Carleton University using TA Instruments Q500 instrument which was housed in a nitrogen-filled MBraun glovebox. The purge gas during TGA experiments was nitrogen gas of (99.999 %, 5.0). In a typical TGA experiment 10 ± 2 mg of analyte was placed in a platinum pan whose mass was monitored by the instrument during the analysis. Temperature ramp analyses were performed at a ramp rate of 10 °C min<sup>-1</sup>.

TGA of benzNHC<sup>iPr</sup>•H<sub>2</sub>CO<sub>3</sub> was performed at Queen's University using a TA Instruments Q500 instrument. The purge gas during TGA experiments was argon 5.0. In a typical TGA

experiment,  $10 \pm 2$  mg of  $\text{benzNHC}^{i\text{Pr}} \cdot \text{H}_2\text{CO}_3$  was placed in a platinum pan whose mass was monitored by the instrument during the analysis. Temperature ramp analyses were performed at a ramp rate of  $5 \text{ }^\circ\text{C min}^{-1}$ .

Differential scanning calorimetry was performed at Carleton University using a TA Instruments Q10 instrument with a purge gas of nitrogen (99.998 %, 4.8). Samples intended for DSC were hermetically sealed in aluminum pans in a nitrogen-filled glovebox. Due to the volatile nature of the analytes, mass loadings greater than 1.000 mg often lead to a rupturing of the sample pans. Thus, small mass loadings of  $0.300 \pm 0.200$  mg were used for typical DSC experiment. Temperature ramp analyses were performed at a ramp rate of  $10 \text{ }^\circ\text{C min}^{-1}$ .

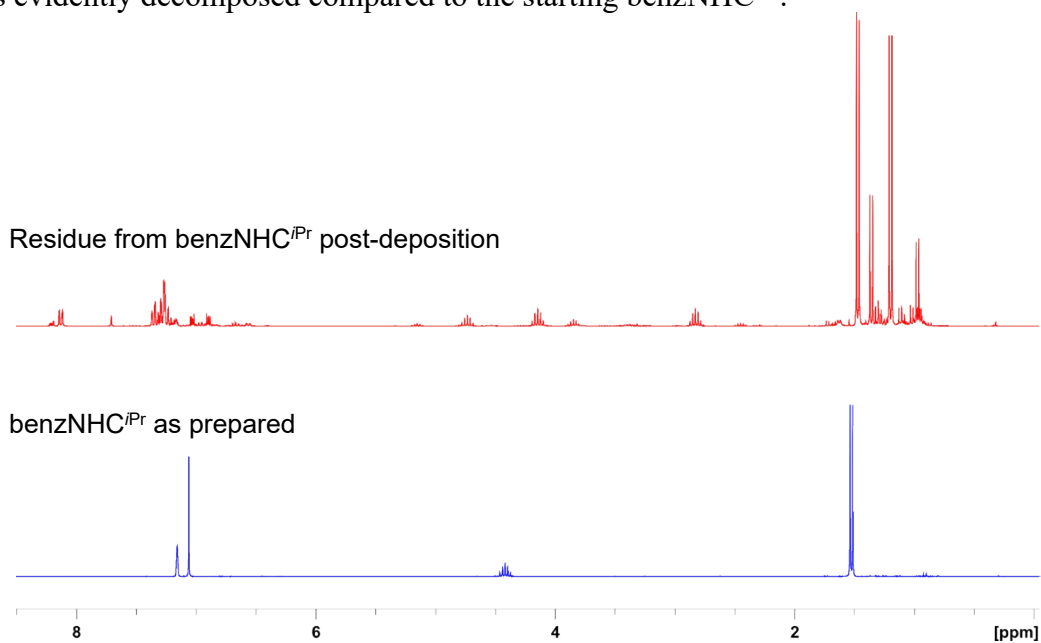
All single crystal X-ray diffraction measurements were made using a Bruker AXS D8 Venture Duo diffractometer with  $\text{Mo K}_\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ) generated by a high brilliance Incoatec Ims microfocus tube equipped with a HELIOS multilayer mirror optics (power:  $50 \text{ kV} \times 1 \text{ mA}$ ). Data were recorded with a Bruker AXS PHOTON II Charge-Integrating Pixel Array Detector (CPAD) (frame size:  $768 \times 1024$ ).

X-ray photoelectron spectroscopy (XPS) measurements were performed at Queen's University using a Kratos Axis Nova ultrahigh vacuum (UHV) surface analysis instrument using  $\text{Al K}_\alpha$  X-rays (1486.6 eV). Survey spectra were collected at a pass energy of 160 eV and high-resolution element scans were collected at a pass energy of 20 eV. In all cases, the C 1s peak at 284.8 eV was used as a reference for binding energy corrections.<sup>7</sup> A Shirley type background correction was used to fit all spectra and quantification.

## 2. Thermolysis reactions

### 2.1. Qualitative $^1\text{H}$ NMR analysis of $\text{benzNHC}^{i\text{Pr}}$ residue after vapour deposition

After flash-depositing neat  $\text{benzNHC}^{i\text{Pr}}$  at 373 K onto a Cu wafer, the colourless carbene solid changed to an orange coloured oil. The residue obtained was analyzed by  $^1\text{H}$  NMR spectroscopy and has evidently decomposed compared to the starting  $\text{benzNHC}^{i\text{Pr}}$ .



**Figure S1.**  $^1\text{H}$  NMR (300 MHz,  $\text{C}_6\text{D}_6$ ) of  $\text{benzNHC}^{i\text{Pr}}$  after heating to 373 K.

## 2.2. Thermal decomposition of benzNHC<sup>*i*Pr</sup>

A small vial was charged with pale yellow crystalline carbene benzNHC<sup>*i*Pr</sup> (200 mg, 1 mmol, 1 eq.) and transferred to a stainless steel Parr vessel. The Parr vessel was sealed and transferred to a sand bath preheated to between 453 - 483 K for 4 hours. After cooling to room temperature, the Parr vessel was opened to air to reveal a dark brown coloured oil, of which 180 mg was collected and purified by column chromatography using a hexanes/ethyl acetate gradient. 1,2-diisopropylbenzimidazole (**1a**) was isolated as a pale yellow coloured solid. Yield: 78 mg (39 %).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 7.78–7.74 (m, 1H, aromatic C-H), 7.52–7.48 (m, 1H, aromatic C-H), 7.22–7.16 (m, 2H, aromatic C-H), 4.75 (sept, 1H, <sup>3</sup>J<sub>HH</sub> = 7.0 Hz, NCH-(CH<sub>3</sub>)<sub>2</sub>), 3.22 (sept, 1H, <sup>3</sup>J<sub>HH</sub> = 7.0 Hz, CCH-(CH<sub>3</sub>)<sub>2</sub>), 1.66 (d, 6H, <sup>3</sup>J<sub>HH</sub> = 7.0 Hz, NCH-(CH<sub>3</sub>)<sub>2</sub>), 1.45 ppm (d, 6H, <sup>3</sup>J<sub>HH</sub> = 7.0 Hz, CCH-(CH<sub>3</sub>)<sub>2</sub>).

<sup>13</sup>C {<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>) δ: 159.1, 143.4, 133.4, 121.6, 121.4, 119.8, 111.7, 47.3, 27.0, 21.8, 21.5 ppm. Anal. Calc. for C<sub>13</sub>H<sub>18</sub>N<sub>2</sub>: C, 77.18 %; H, 8.97 %; N, 13.85. Found: C, 76.76 %; H, 8.94 %; N, 13.80 %.

1-isopropylbenzimidazole (**1b**) was isolated as a pale yellow coloured oil. Yield: 34 mg (21 %). Spectroscopic data for **1b** were consistent with previous literature reports.<sup>8</sup>

## 2.3. Mixed thermal decomposition of benzNHC<sup>*i*Pr</sup> and (benzNHC<sup>Et</sup>)<sub>2</sub>

The same thermal decomposition procedure as above was repeated using benzNHC<sup>*i*Pr</sup> (103 mg, 0.5 mmol, 1.0 eq.) and yellow coloured (benzNHC<sup>Et</sup>)<sub>2</sub> (88 mg, 0.5 mmol, 1.0 eq.). A dark brown coloured oil was obtained which was not purified further. The <sup>1</sup>H NMR spectrum was complex, however ESI-MS contained mass peaks corresponding to crossover products with both Et and *i*Pr groups.

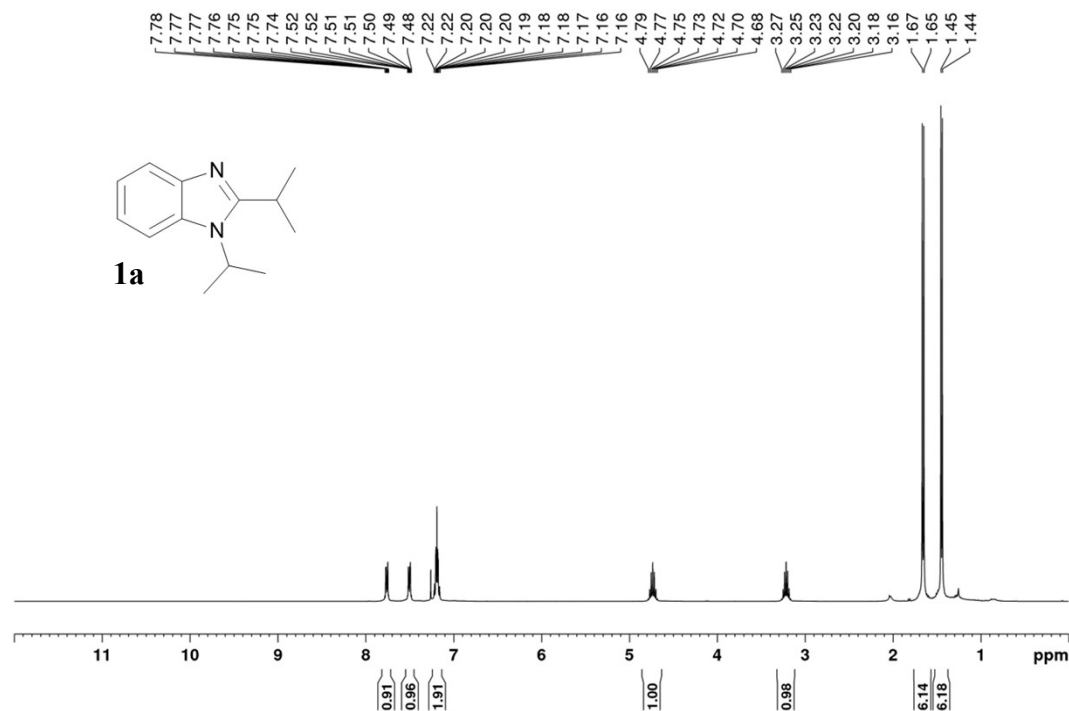


Figure S2. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectrum of **1a**.

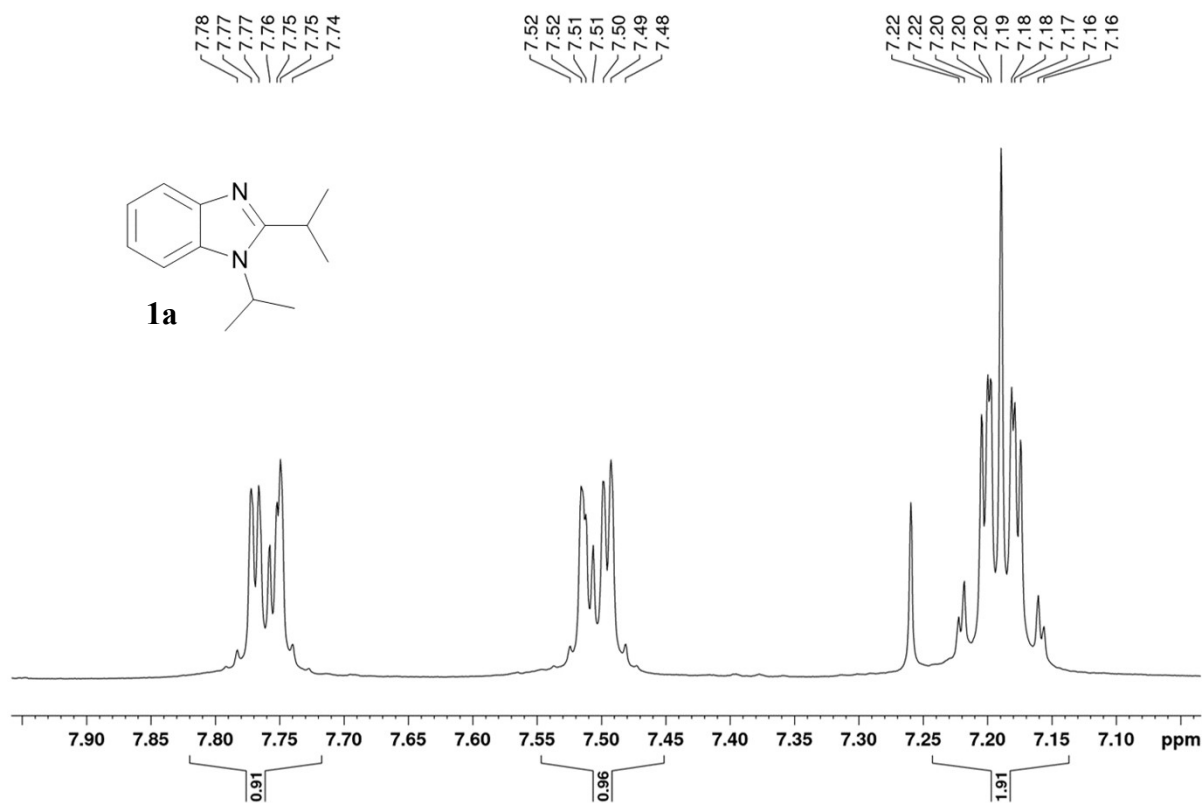


Figure S3. Zoomed in aromatic region for <sup>1</sup>H NMR spectrum of **1a**.

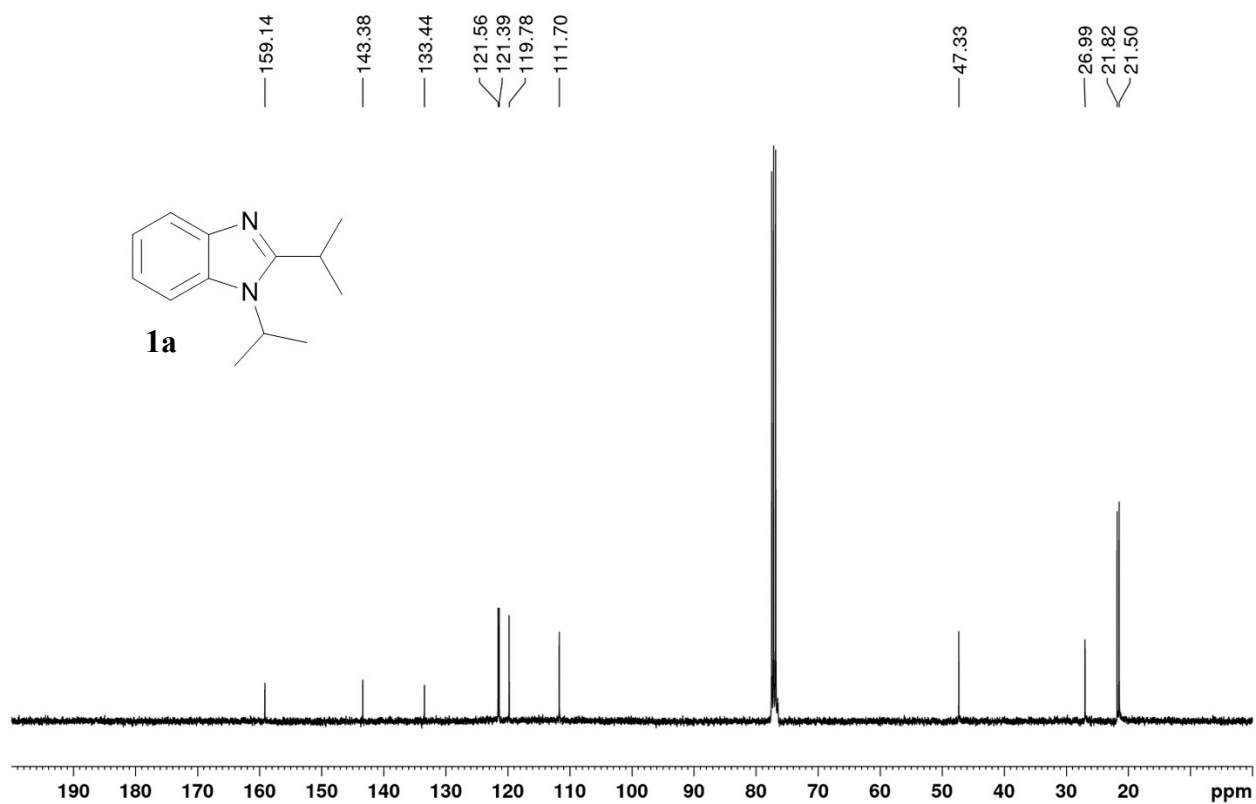
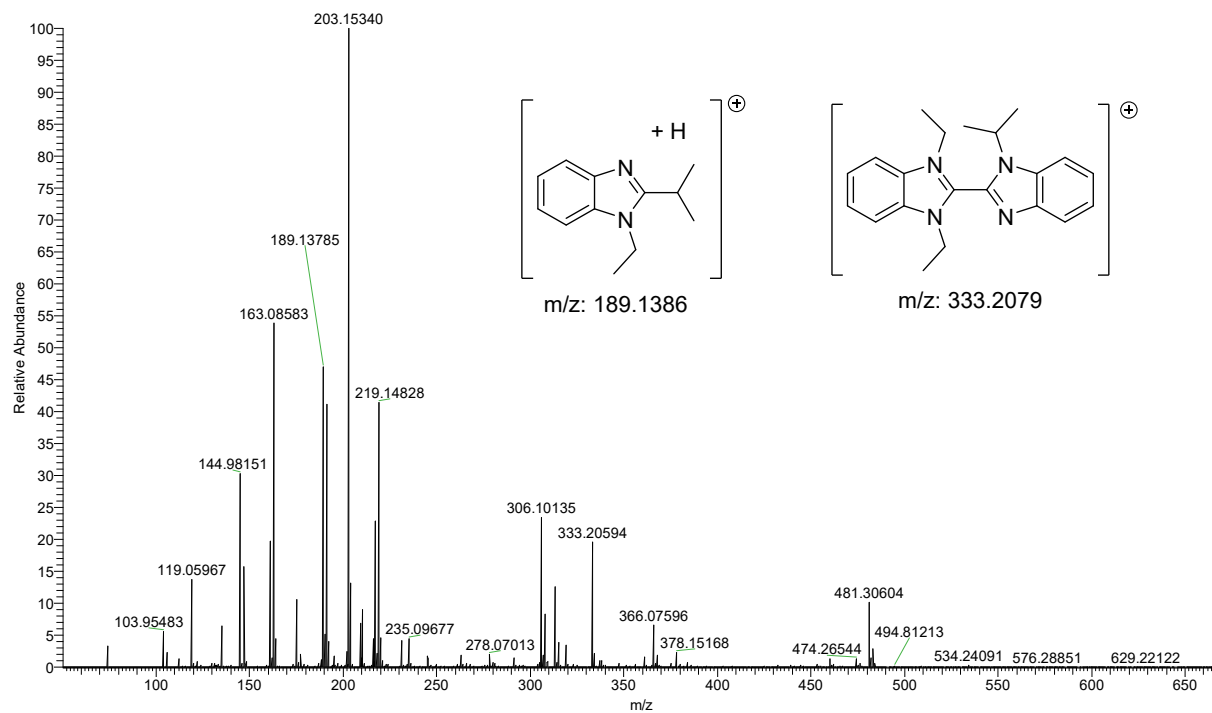
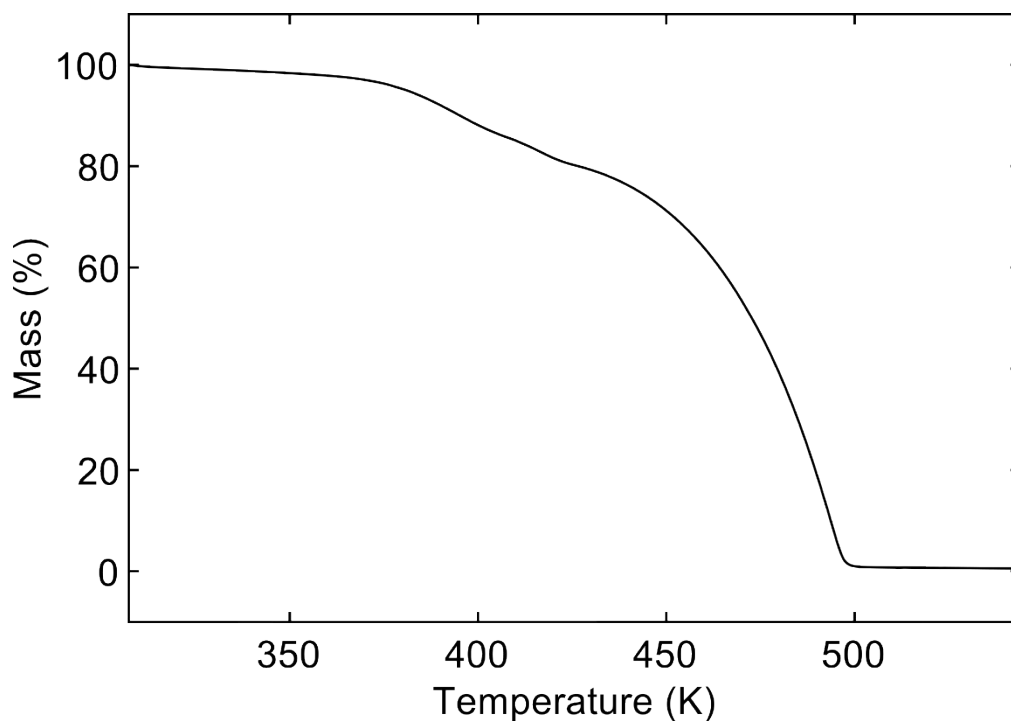


Figure S4. <sup>13</sup>C {<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>) spectrum of **1a** in CDCl<sub>3</sub>.

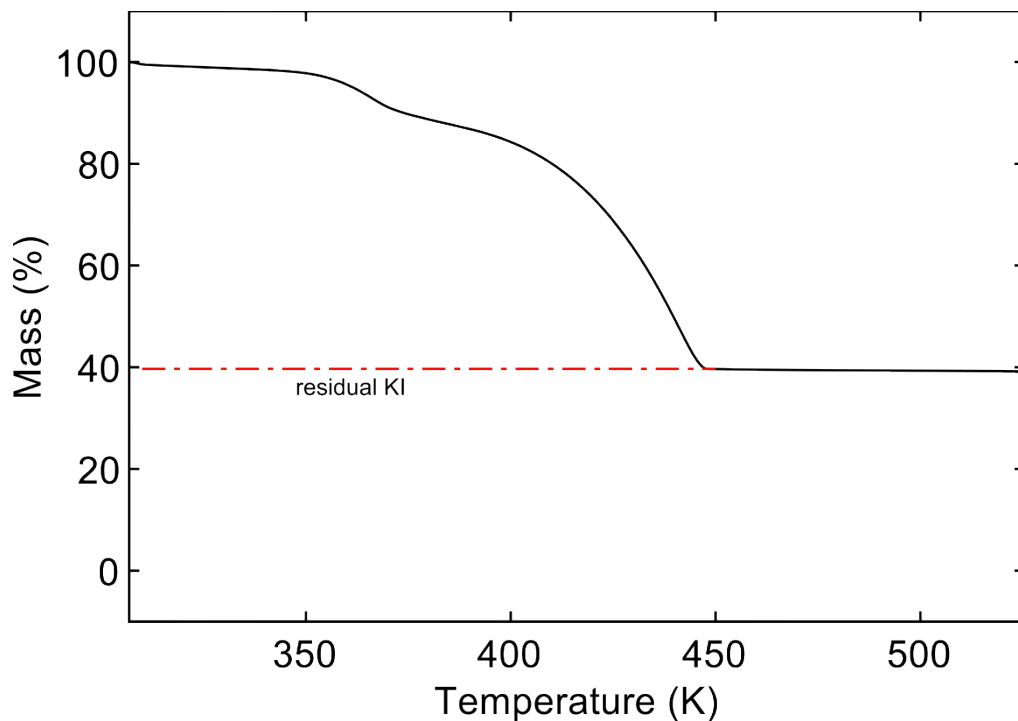


**Figure S5.** ESI-MS for mixed thermal decomposition of benzNHC<sup>i</sup>Pr and (benzNHC<sup>Et</sup>)<sub>2</sub>. [M+H]<sup>+</sup> for crossover products of interest were found at  $m/z = 189.1378$  and  $333.2059$ .

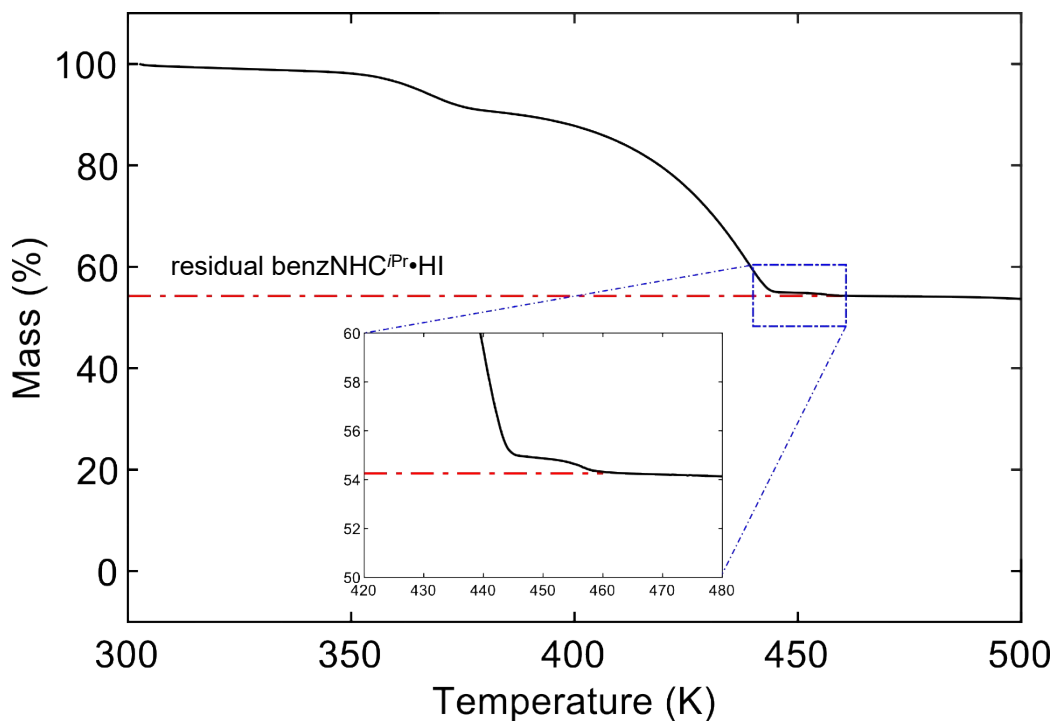
### 3. Thermogravimetric Analysis



**Figure S6.** TGA curve for hydrogen carbonate salt benzNHC<sup>i</sup>Pr·H<sub>2</sub>CO<sub>3</sub>. Sample loading: 11.8120 mg. Heating rate: 50 °C min<sup>-1</sup>.



**Figure S7.** TGA curve for hydrogen carbonate salt  $\text{benzNHC}^{i\text{Pr}}\cdot\text{H}_2\text{CO}_3$  mixed with KI (1:1 molar ratio). Sample loading: 18.2980 mg (11.3 mg  $\text{benzNHC}^{i\text{Pr}}\cdot\text{H}_2\text{CO}_3$ , 7.0 mg KI (99.99%); theoretical 38.5 % KI by weight).



**Figure S8.** TGA curve for hydrogen carbonate salt  $\text{benzNHC}^{i\text{Pr}}\cdot\text{H}_2\text{CO}_3$  mixed with its benzimidazolium iodide salt precursor ( $\text{benzNHC}^{i\text{Pr}}\cdot\text{HI}$ , 1:1 molar ratio). Sample loading: 25.0930 mg (11.1 mg  $\text{benzNHC}^{i\text{Pr}}\cdot\text{H}_2\text{CO}_3$ , 14.0 mg  $\text{benzNHC}^{i\text{Pr}}\cdot\text{HI}$ ; theoretical 56 %  $\text{benzNHC}^{i\text{Pr}}\cdot\text{HI}$  by weight).

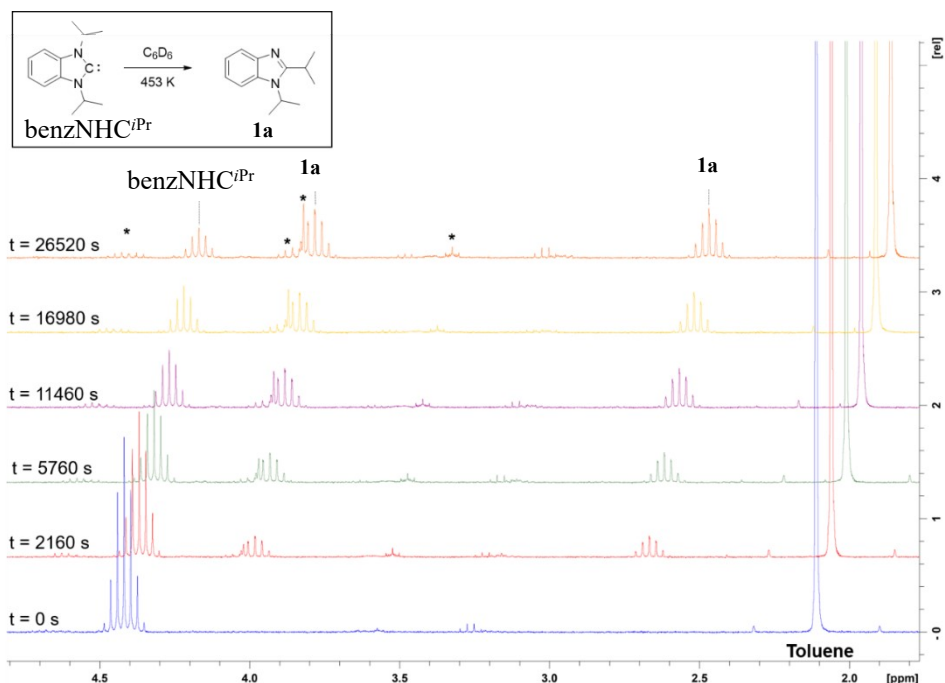
## 4. Kinetics Measurements

In a nitrogen-filled glovebox, a 0.072 M solution of benzNHC<sup>*i*Pr</sup> and 0.086 M toluene (as an internal standard) in C<sub>6</sub>D<sub>6</sub> was prepared. A thick-walled NMR tube (Aldrich NORS5500HW7) was filled with 200 μL of the above solution and then flame sealed under vacuum. An initial spectrum was recorded, and then the tube was then placed in a nitrogen-purged bottle, to prevent hydrolysis, which was itself preheated in an oven at the desired temperature. <sup>1</sup>H NMR spectra of the solution of benzNHC<sup>*i*Pr</sup> were recorded at room temperature by removing the NMR tube from the oven. The concentration of benzNHC<sup>*i*Pr</sup> over time was calculated by comparing the integration of the methine proton of the isopropyl group at 4.42 ppm with the methyl resonance of toluene at 2.11 ppm because these were well isolated from other interfering resonances.

**Table S1.** Summary of kinetic measurements completed using <sup>1</sup>H NMR spectroscopy.

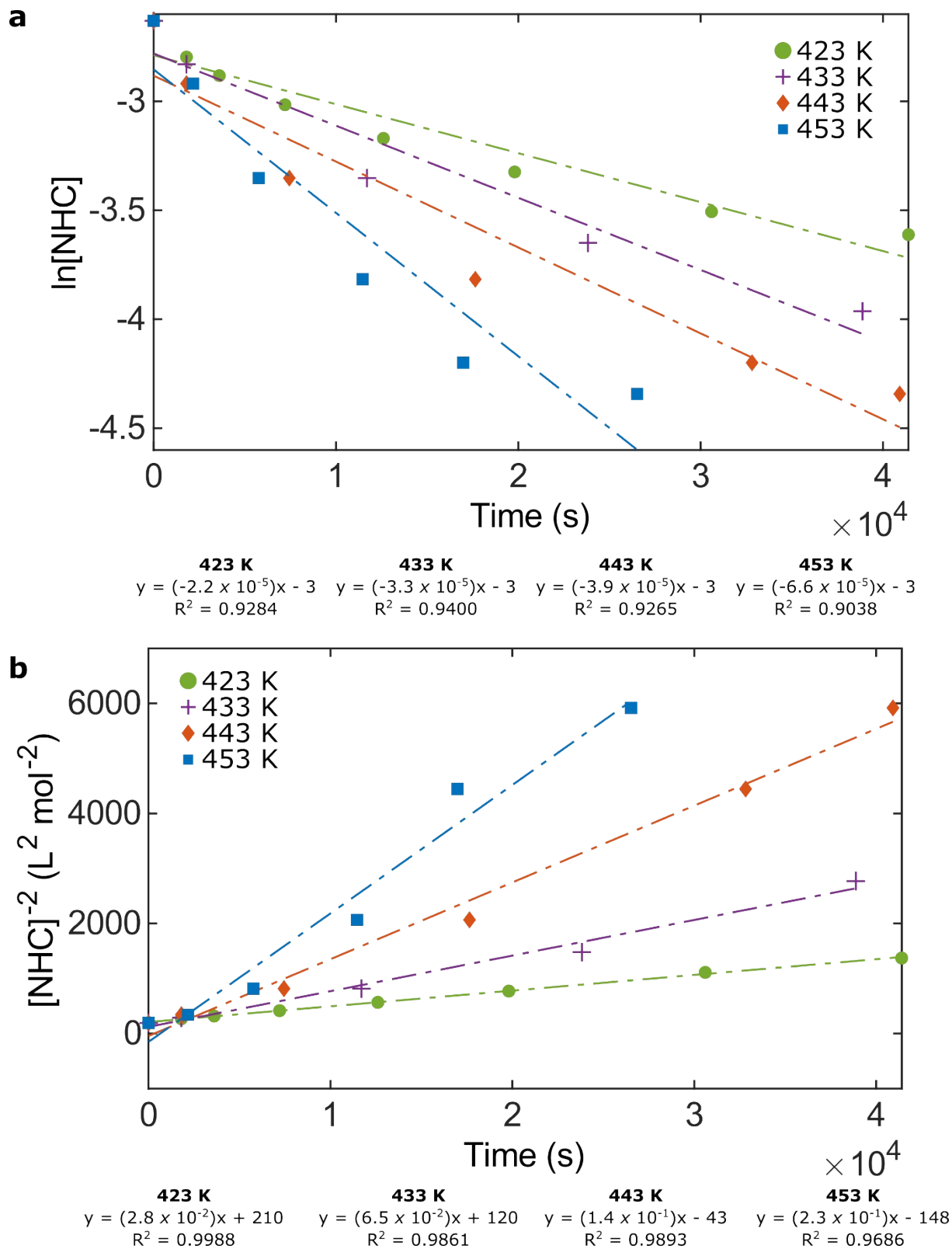
423 K		433 K		443 K		453 K	
Time (s)	[NHC] (M)	Time (s)	[NHC] (M)	Time (s)	[NHC] (M)	Time (s)	[NHC] (M)
0	0.072	0	0.072	0	0.072	0	0.072
1800	0.061	1800	0.059	1800	0.054	2160	0.054
3600	0.056	11700	0.035	7440	0.035	5760	0.035
7200	0.049	23820	0.026	17640	0.022	11460	0.022
12600	0.042	38880	0.019	32820	0.015	16980	0.015
19800	0.036			40920	0.013	26520	0.013
30600	0.030						
41400	0.027						

$k = 5.5 \times 10^{-4} \text{ L mol}^{-1} \text{ s}^{-1}$   $k = 1.0 \times 10^{-3} \text{ L mol}^{-1} \text{ s}^{-1}$   $k = 1.5 \times 10^{-3} \text{ L mol}^{-1} \text{ s}^{-1}$   $k = 2.5 \times 10^{-3} \text{ L mol}^{-1} \text{ s}^{-1}$



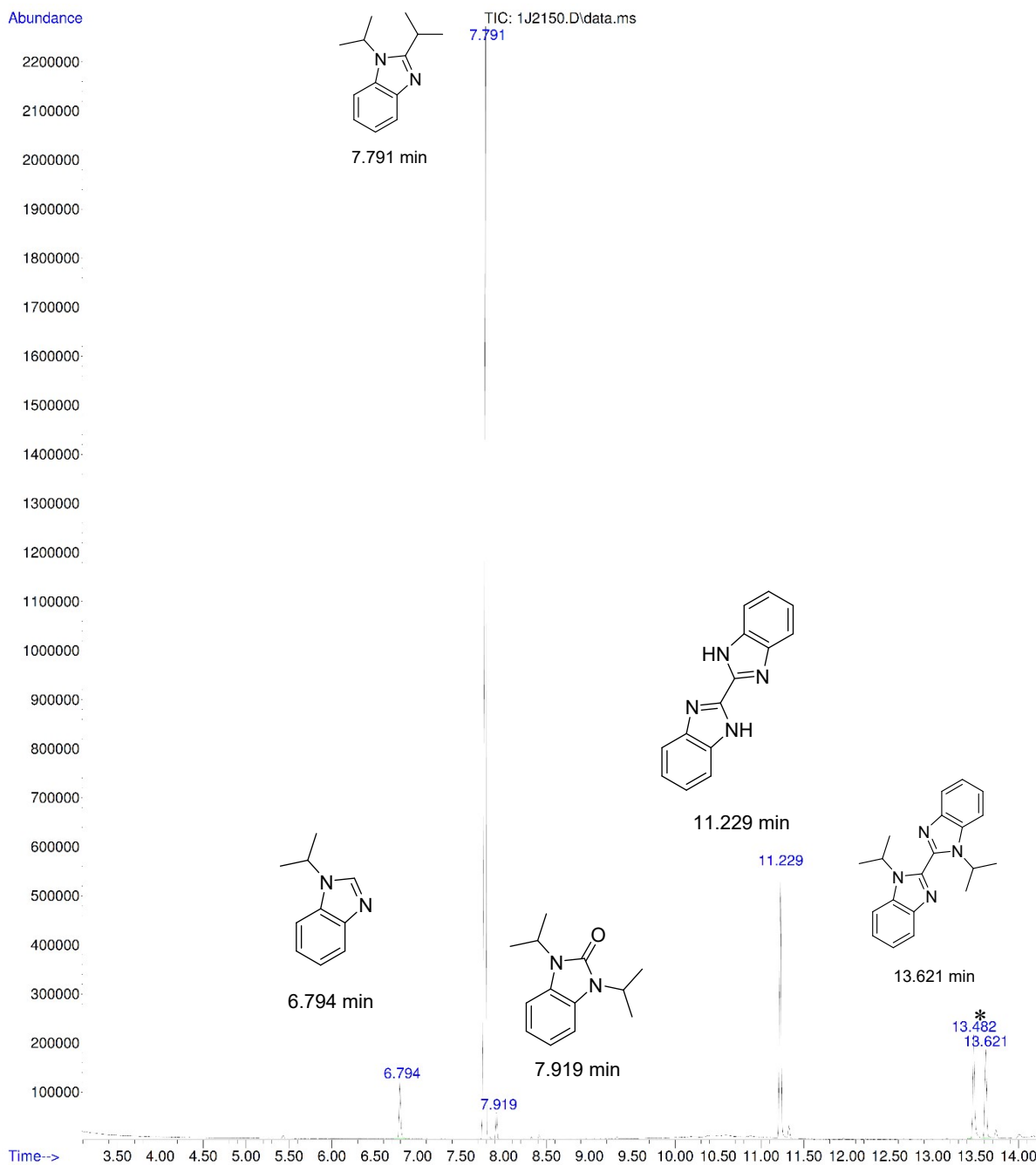
**Figure S9.** Representative <sup>1</sup>H NMR thermolysis experiment for benzNHC<sup>*i*Pr</sup> at 453 K (0.072 M in C<sub>6</sub>D<sub>6</sub>, toluene internal standard). Times correspond to the reaction duration. \*Other minor decomposition products.



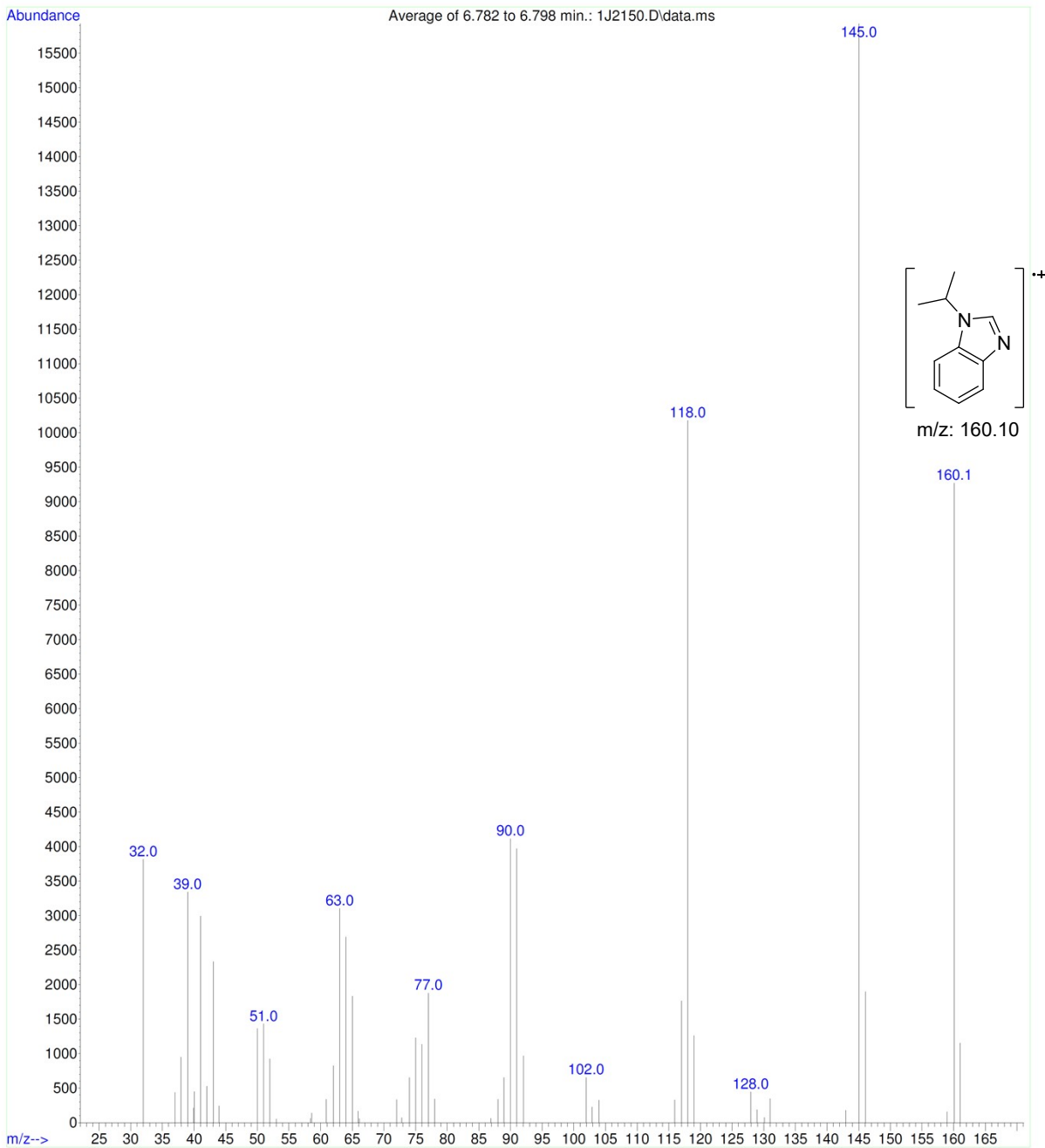


**Figure S10.** (a) First and (b) third order reaction plots for the thermolysis of benzNHC<sup>Pr</sup>. Lines of best fit at each temperature are given below each plot.

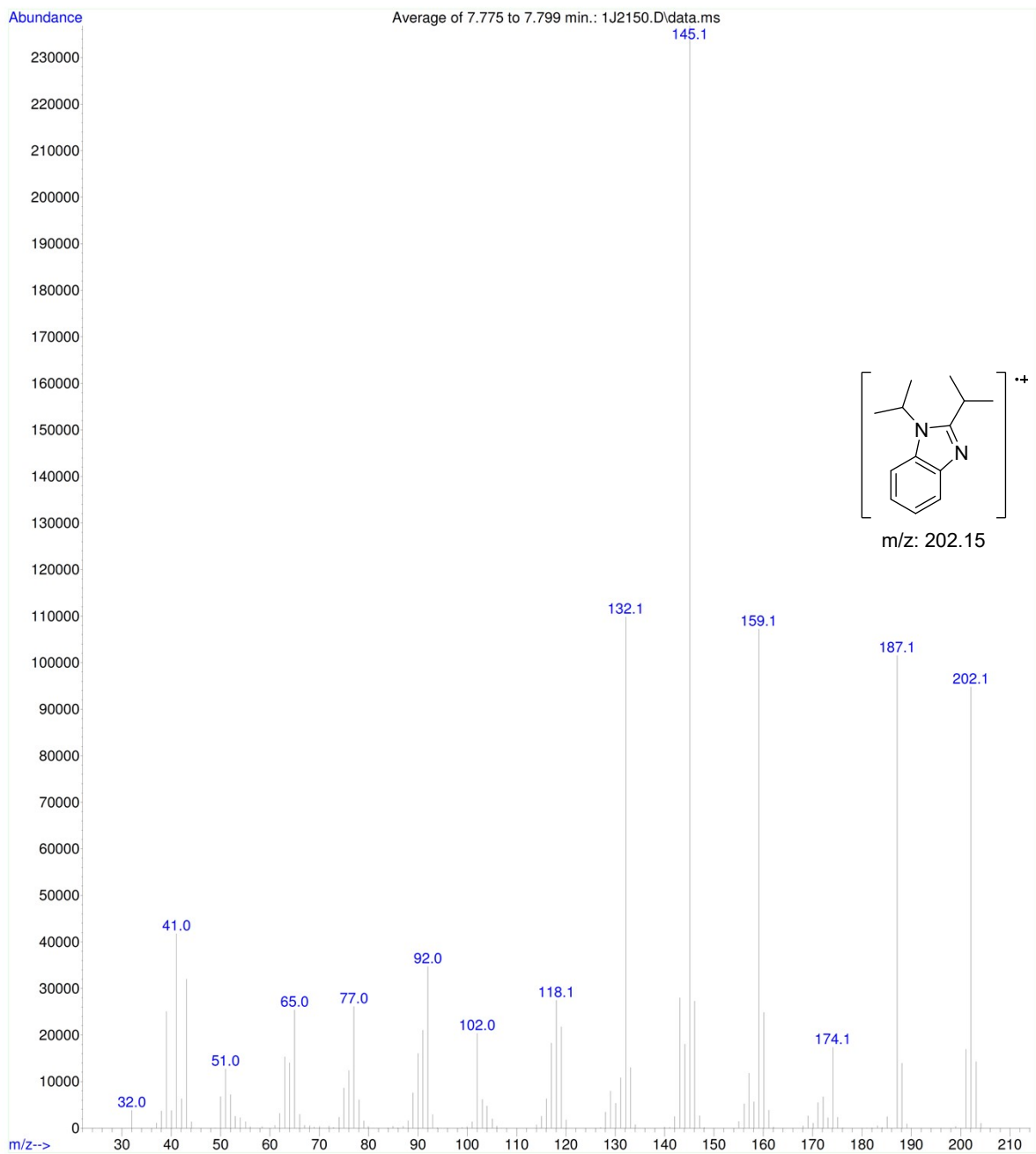
## 5. GC-MS Measurements



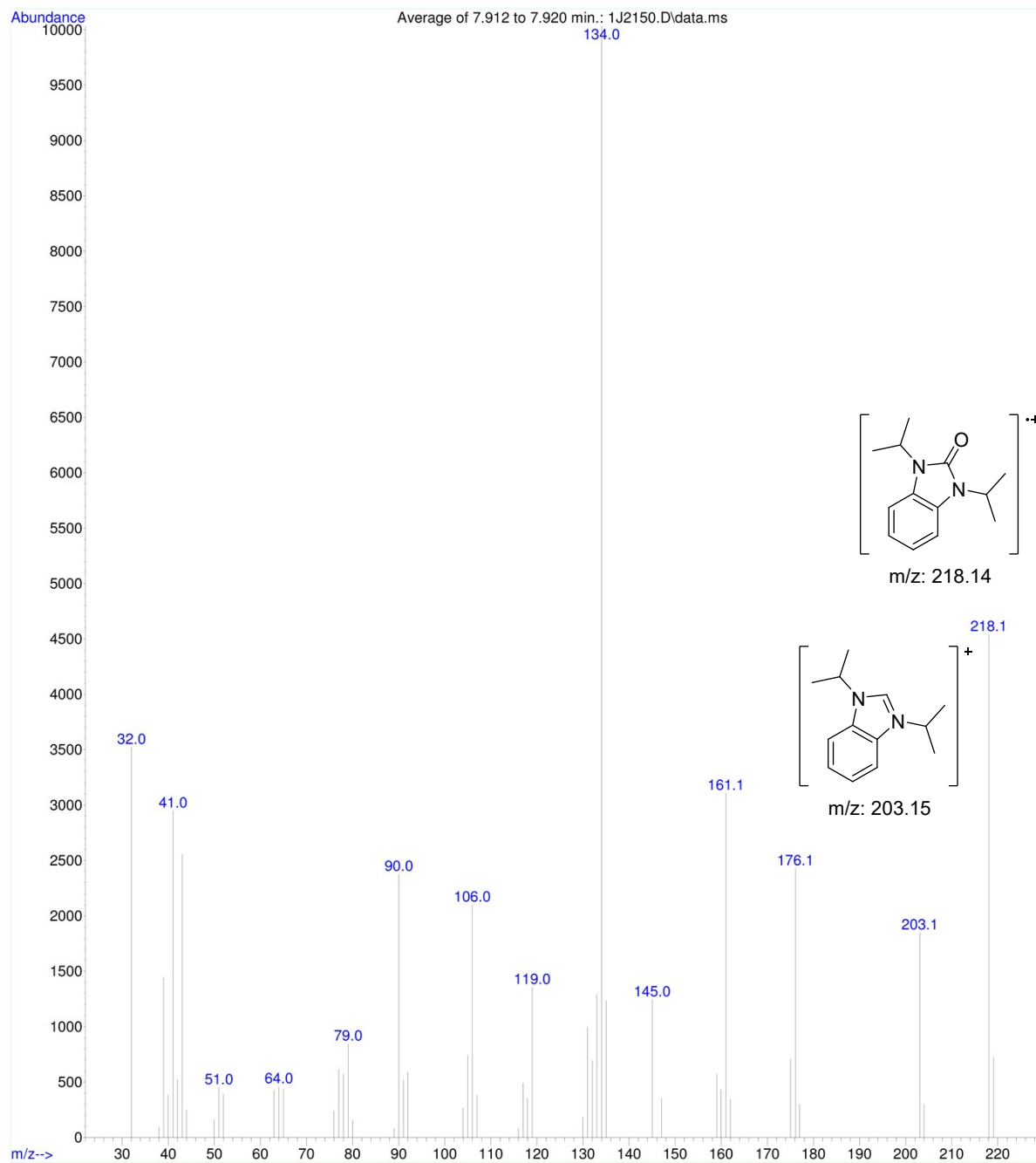
**Figure S11.** Representative chromatogram obtained from GC-MS measurements. Sampled from kinetics measurement completed at 423 K. \*Unidentifiable decomposition product.



**Figure S12.** MS for  $t = 6.794$  min.  $[M]^+$  peak correlates with 1-isopropylbenzimidazole (**1b**).



**Figure S13.** MS for  $t = 7.791$  min.  $[M]^+$  peak correlates with 1,2-disopropylbenzimidazole (**1a**).



**Figure S14.** MS for  $t = 7.919$  min.  $[M]^+$  peak correlates with 1,3-disopropylbenzimidazol-2-one.

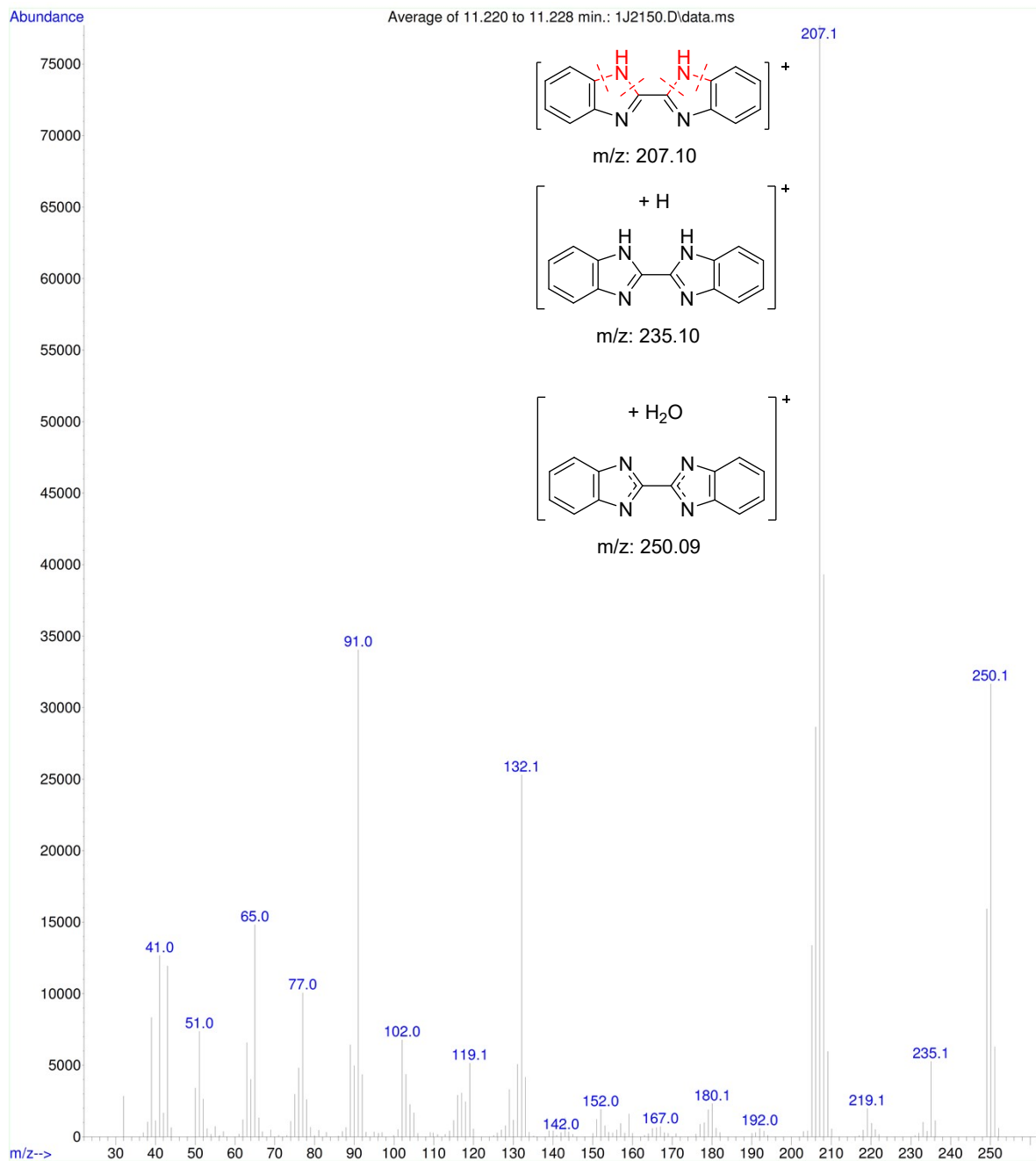


Figure S15. MS for  $t = 11.229$  min.  $[M+O]^+$  and  $[M+H]^+$  peaks correlate with 2,2'-bibenzimidazole (**2b**).

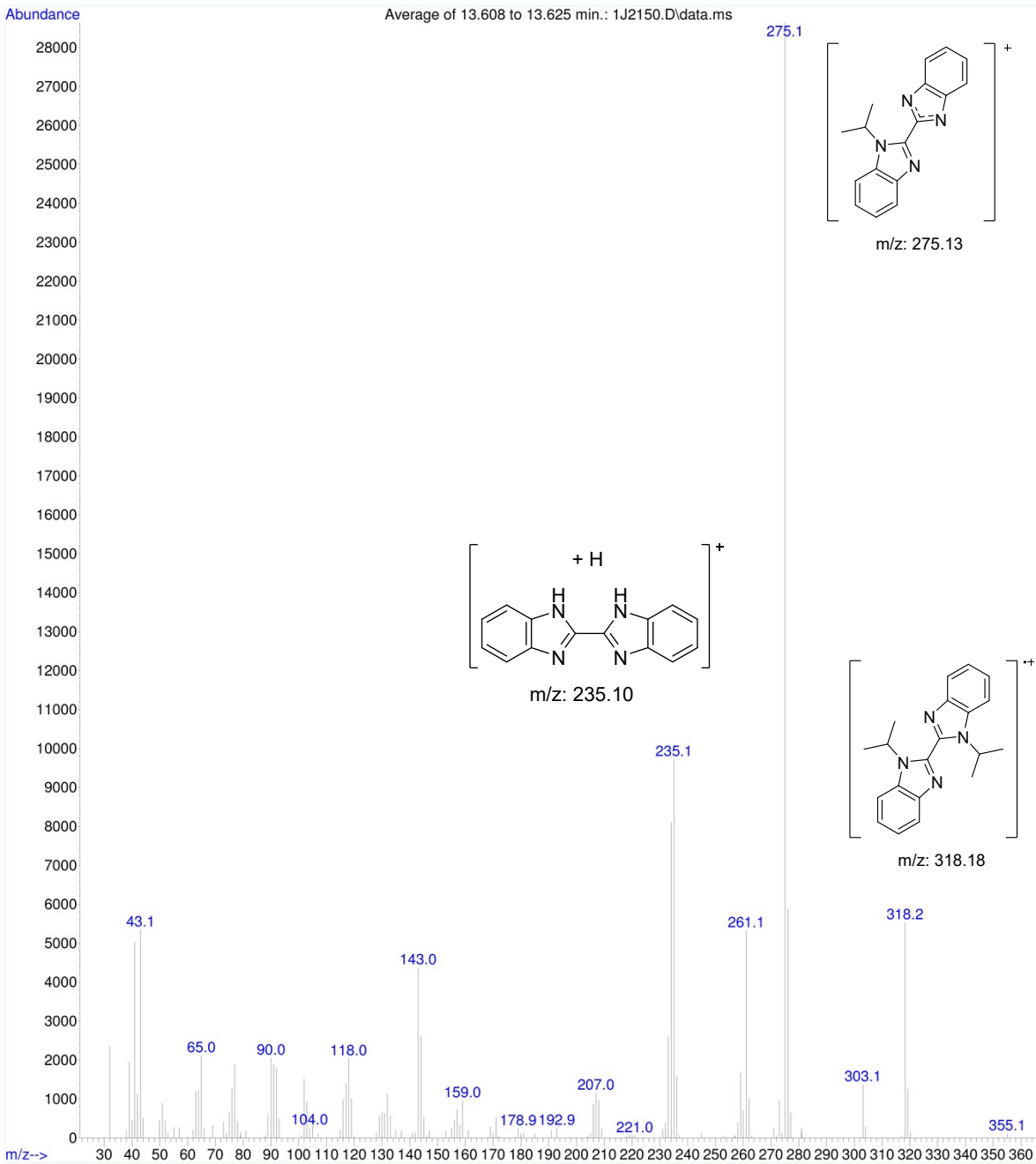


Figure S16. MS for  $t = 13.621$  min.  $[M]^+$  peak correlates with 1,1'-diisopropyl-2,2'-bibenzimidazole (**2a**).

## 6. Surface characterisation using XPS

Table S2. Summary of XPS data

Region	Atomic Percentage			
	Bare Cu	benzNHC <sup>iPr</sup>	<b>1a</b>	benzNHC <sup>iPr</sup> •H <sub>2</sub> CO <sub>3</sub>
Cu 2p	60.13	1.42	2.04	47.27
C 1s	28.23	83.96	73.85	33.01
N 1s	–	11.22	15.05	2.85
O 1s	11.12	3.38	9.06	16.86

### 6.1. Bare Cu (blank)

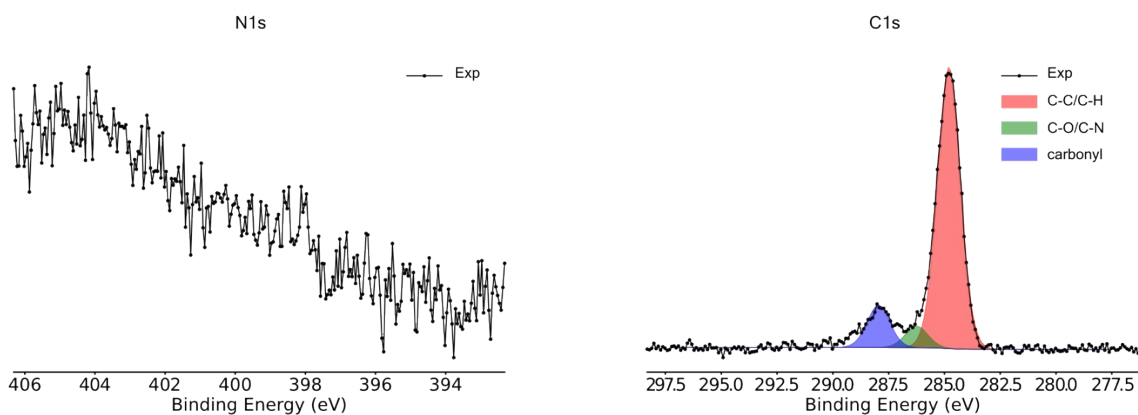


Figure S17. High-resolution N 1s and C 1s XPS data for copper blank.

### 6.2. benzNHC<sup>iPr</sup> on Cu

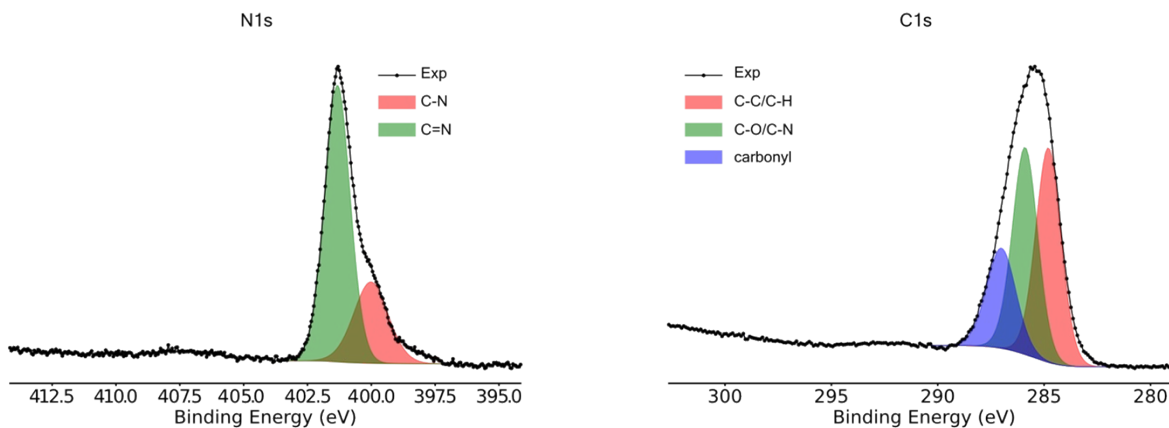


Figure S18. High-resolution N 1s and C 1s XPS data for copper treated with benzNHC<sup>iPr</sup>.



### 6.3. 1a on Cu

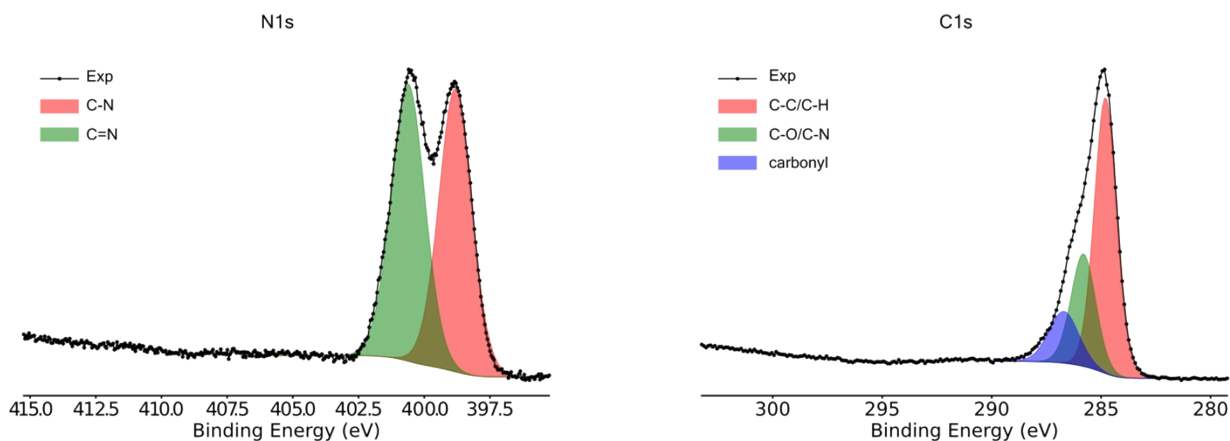


Figure S19. High-resolution N 1s and C 1s XPS data for copper treated with **1a**.

### 6.4. benzNHC<sup>iPr</sup>•H<sub>2</sub>CO<sub>3</sub> on Cu

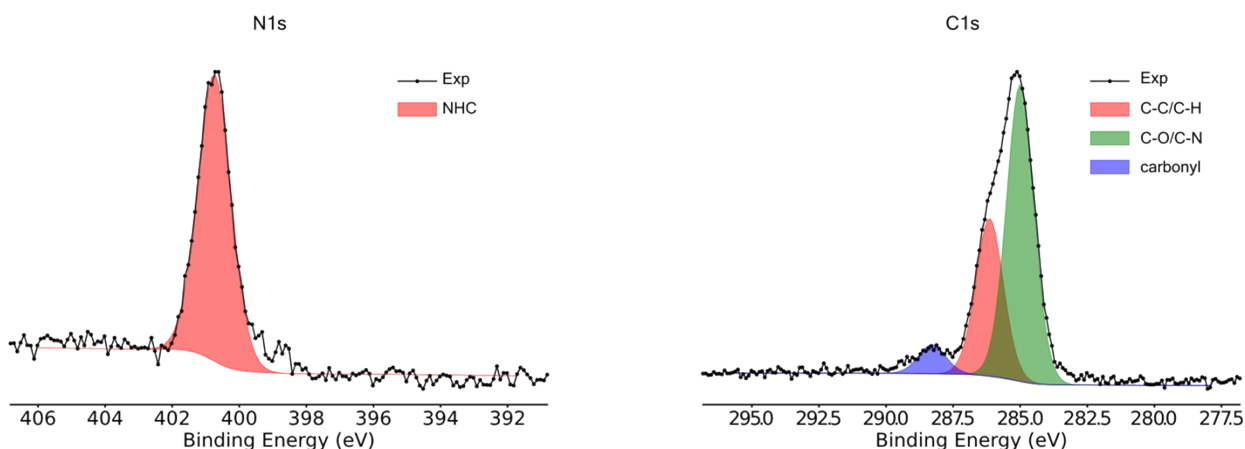


Figure S20. High-resolution N 1s and C 1s XPS data for copper treated with benzNHC<sup>iPr</sup>•H<sub>2</sub>CO<sub>3</sub>.

## 7. X-ray Crystallography

### 7.1. Summary

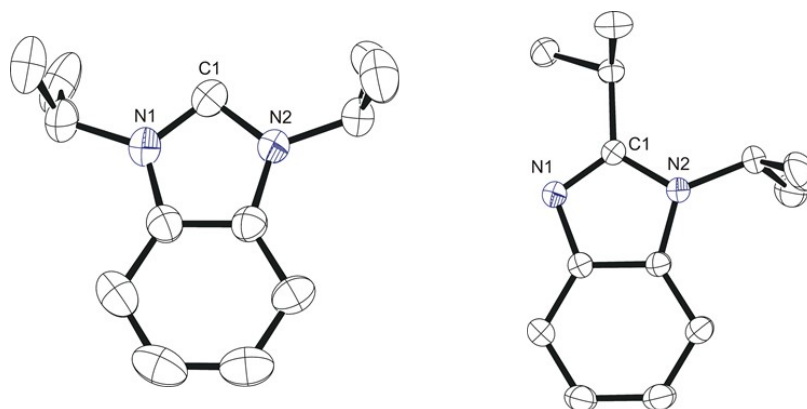
A clear colourless block-like specimen of benzNHC<sup>iPr</sup>, 0.166 mm x 0.148 mm x 0.107 mm, was obtained by sublimation of benzNHC<sup>iPr</sup> (70 °C, 5 mTorr) and then single crystals for diffraction were then grown from the sublimed materials using saturated anhydrous toluene solutions at -35°C. The resulting crystals were examined using single crystal X-ray diffraction. A total of 623 frames were collected for a total exposure time of 2.60 hours.

A clear colourless block-like specimen of **1a**, 0.441 mm x 0.416 mm x 0.403 mm, was obtained by sublimation of **1a** (100 °C, 5 mTorr) and then single crystals for diffraction were then grown from the sublimed materials using saturated anhydrous toluene solutions at -35°C. The resulting crystals were examined using single crystal X-ray diffraction. A total of 2310 frames were collected for a total exposure time of 6.42 hours.

For each crystal structure determination, the frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm,<sup>9</sup> and corrected for absorption effects using the Multi-Scan method (SADABS),<sup>10,11</sup> as implemented in APEX3.<sup>12</sup> The structures of benzNHC<sup>i</sup>Pr and **1a** were solved using direct methods *via* SHELXT,<sup>13</sup> and refined using SHELXL.<sup>14</sup> All atoms were refined anisotropically, except hydrogen atoms which were refined isotropically. Hydrogen atoms were placed in idealized geometries and positioned relative to the atoms in which they were attached using a riding model. Molecular graphics were rendered using ORTEP-3.<sup>15</sup>

**Table S3.** Summary of crystallographic data for benzNHC<sup>i</sup>Pr and **1a**.

Compound reference	benzNHC <sup>i</sup> Pr	<b>1a</b>
CCDC Number	2151982	2151983
Chemical formula	C <sub>13</sub> H <sub>18</sub> N <sub>2</sub>	C <sub>13</sub> H <sub>18</sub> N <sub>2</sub>
Formula Mass	202.29	202.29
Crystal system	Monoclinic	Triclinic
<i>a</i> /Å	8.7704(8)	10.5854(3)
<i>b</i> /Å	16.1245(16)	10.8589(3)
<i>c</i> /Å	8.6071(9)	12.3706(4)
<i>α</i> /°	90	100.0750(10)
<i>β</i> /°	92.294(3)	114.9280(10)
<i>γ</i> /°	90	106.0140(10)
Unit cell volume/Å <sup>3</sup>	1216.2(2)	1168.22(6)
Temperature/K	180(2)	180(2)
Space group	Cc	<b>PError!</b>
No. of formula units per unit cell, Z	4	4
No. of reflections measured	18978	49405
No. of independent reflections	2491	5733
<i>R</i> <sub>int</sub>	0.0479	0.0289
Final <i>R</i> <sub>1</sub> values ( <i>I</i> > 2σ( <i>I</i> ))	0.0415	0.0414
Final <i>wR</i> ( <i>F</i> <sup>2</sup> ) values ( <i>I</i> > 2σ( <i>I</i> ))	0.0973	0.1058
Final <i>R</i> <sub>1</sub> values (all data)	0.0494	0.0441
Final <i>wR</i> ( <i>F</i> <sup>2</sup> ) values (all data)	0.1033	0.1083
Goodness of fit on <i>F</i> <sup>2</sup>	1.087	1.048



**Figure S21.** Molecular structures for benzNHC<sup>i</sup>Pr and **1a**. Thermal ellipsoids are shown at 50% probability and hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°) for benzNHC<sup>i</sup>Pr: N1-C1 1.372(3), N2-C1 1.363(4), N2-C1-N1 103.5(2). Selected bond lengths (Å) and angles (°) for **1a**: N1-C1 1.3187(9), N2-C1 1.3766(9), N1-C1-N2 113.37(6).

## 8. References

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