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# CARBENE-FUNCTIONALIZED COMPOSITE MATERIALS

## RELATED APPLICATIONS

This application is related to U.S. Provisional Patent Application No. 61/867,466, filed on August 19, 2013, and U.S. Provisional Patent Application No. 62/018,782, filed on June 30, 2014.

61/867,466, filed on August 19, 2013, and U.S. Provisional Patent Application No. 62/018,782, filed on June 30, 2014.

## FIELD OF THE INVENTION

The present invention relates to the field of composite materials, more specifically to the use of carbene-functionalized composite materials.

60000 F. Davis et al. Organometallics 30, 6713 (2011) and NHC-based cross-coupling catalysts [E. A. B

catalysts such as the Grubbs second generation metathesis catalyst [R. M. Thomas, et al.



each R<sup>o</sup> is independently H, halogen, the substituent X-L-Z as defined above, C<sub>1</sub>-C<sub>10</sub> alkyl, C<sub>10</sub>-C<sub>20</sub> alkyl, C<sub>1</sub>-C<sub>10</sub> alkenyl, C<sub>10</sub>-C<sub>20</sub> alkenyl, C<sub>1</sub>-C<sub>10</sub> alkynyl, or C<sub>10</sub>-C<sub>20</sub> alkynyl,

[REDACTED]

[REDACTED]

[REDACTED]

[REDACTED]

[REDACTED]

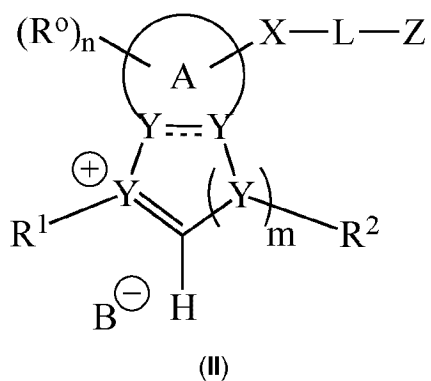
[REDACTED]

[REDACTED]

$Y^2$  and  $Y^3$  are independently C or a heteroatom, and the dashed line represents an

optional double bond;

$R^1$  and  $R^2$  are independently absent, at least one less unit of chlorine, H, O, C



wherein:

n is an integer from 1 to 8, or from 1 to 4;

m is an integer from 0 to 4;

B is a counter ion that optionally acts as a base;

A is absent, an aliphatic cycle, a heterocycle, an aromatic ring, a fused aromatic ring



conjugated diene, thiol, or thioester, each of which is optionally substituted;

each  $X^1$  is independently H, halogen, alkyl, alkoxy, or aryl;

each  $D^0$  is independently H, halogen, alkyl, alkoxy, or aryl; each  $D^1$  is independently H, halogen, alkyl, alkoxy, or aryl;

wherein:

m is an integer from 0 to 4;

R is a substituent that optionally acts as a base;

$\gamma^1$  and  $\gamma^2$  are independently O or a heteroatom;

$\gamma^1$  and  $\gamma^2$  are independently O or a heteroatom, and the dashed line is an optional

wherein:

$n$  is an integer from 1 to 4, or alternatively 1 to 9;

$m$  is an integer from 0 to 4;

$G$  is a perhalogenated alkyl, perhalogenated alkenyl, perhalogenated alkynyl, a perhalogenated aryl, or  $OR'$ , wherein  $R'$  is an aliphatic group, for example, an alkyl group.

$R'$  is absent or aliphatic cyclic, a heterocycle, an aromatic ring, a fused aromatic ring

C-alkenyl, C-alkenyl, C-alkenyl, cyclic aliphatic moieties, and heteroaryl ether

thioether, amine, sulfonamide, sulfoxide, or sulfinic acid, each of which is optionally

Y<sup>2</sup> and Y<sup>3</sup> are independently C or a heteroatom, and the dashed line represents an

optional double bond;

R<sup>1</sup> and R<sup>2</sup> are independently absent, at least one lone pair of electrons, H, C, O,

alkenyl, C, C, alkenyl, C, C, alkenyl, C, C, alkenyl, C, C, alkenyl, C, C, alkenyl,

material forms at least part of an analytical instrument. In another embodiment, the metal

alkyl, C<sub>10</sub>-C<sub>20</sub> alkenyl, C<sub>10</sub>-C<sub>20</sub> alkynyl, C<sub>10</sub>-C<sub>20</sub> alkoxy, C<sub>6</sub>-C<sub>20</sub> cyclic aliphatic moiety,  
aryl, ether, thioether, sulfoxide, sulfone, each of which is optionally

R<sup>1</sup> and R<sup>2</sup> are independently absent, at least one lone pair of electrons, H, C<sub>10</sub>-C<sub>20</sub>

alkyl, C<sub>10</sub>-C<sub>20</sub> alkylidene, C<sub>10</sub>-C<sub>20</sub> alkenyl, C<sub>10</sub>-C<sub>20</sub> alkenylidene, cyclic aliphatic moieties, and other thiol

wherein the substituents are substituted with one or more substituents



m is an integer from 0 to 4;

\_\_\_\_\_

\_\_\_\_\_

\_\_\_\_\_

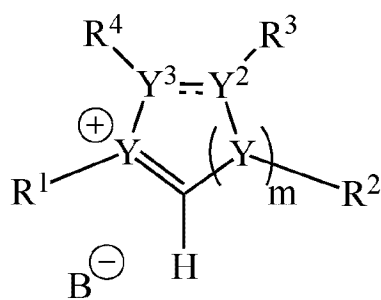
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In accordance with another embodiment, the carbene precursor is of formula Va



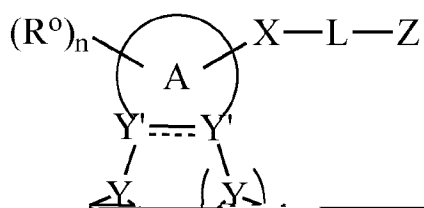
wherein:

m is an integer from 0 to 4;

B is a counter ion that optionally acts as a base;

each Y is independently C or a heteroatom;

Y2 and Y3 are independently C or a heteroatom, and the dashed line is an optional



G

(VI)

wherein:

$n$  is an integer from 1 to 4, or alternatively from 1 to 0

(i)

$m$  is an integer from 0 to 4;

$Q$  is a non-halogenated alkyl, non-halogenated allyl, non-halogenated alkynyl, non-halogenated alkoxy, or

each R<sup>o</sup> is independently H, halogen, the substituent X-L-Z as defined above, C<sub>10</sub>-C<sub>20</sub> alkyl, C<sub>10</sub>-C<sub>20</sub> alkenyl, C<sub>10</sub>-C<sub>20</sub> alkynyl, C<sub>10</sub>-C<sub>20</sub> alkoxy, C<sub>6</sub>-C<sub>20</sub> cyclic aliphatic moiety, aryl, ether, thioether, polyether, or polythioether, each of which is optionally substituted, or two of R<sup>o</sup> together with the atoms to which they are attached are

[REDACTED]

[REDACTED]

[REDACTED]

[REDACTED]

[REDACTED]

connected to form a cycle which is optionally substituted, and

[REDACTED]

[REDACTED]

[REDACTED]

[REDACTED]

$Y^2$  and  $Y^3$  are independently C or a heteroatom, and the dashed line represents an

optional double bond;

optional double bond;

$R^1$  and  $R^2$  are independently absent, at least one lone pair of electrons, H, C, O,

or N

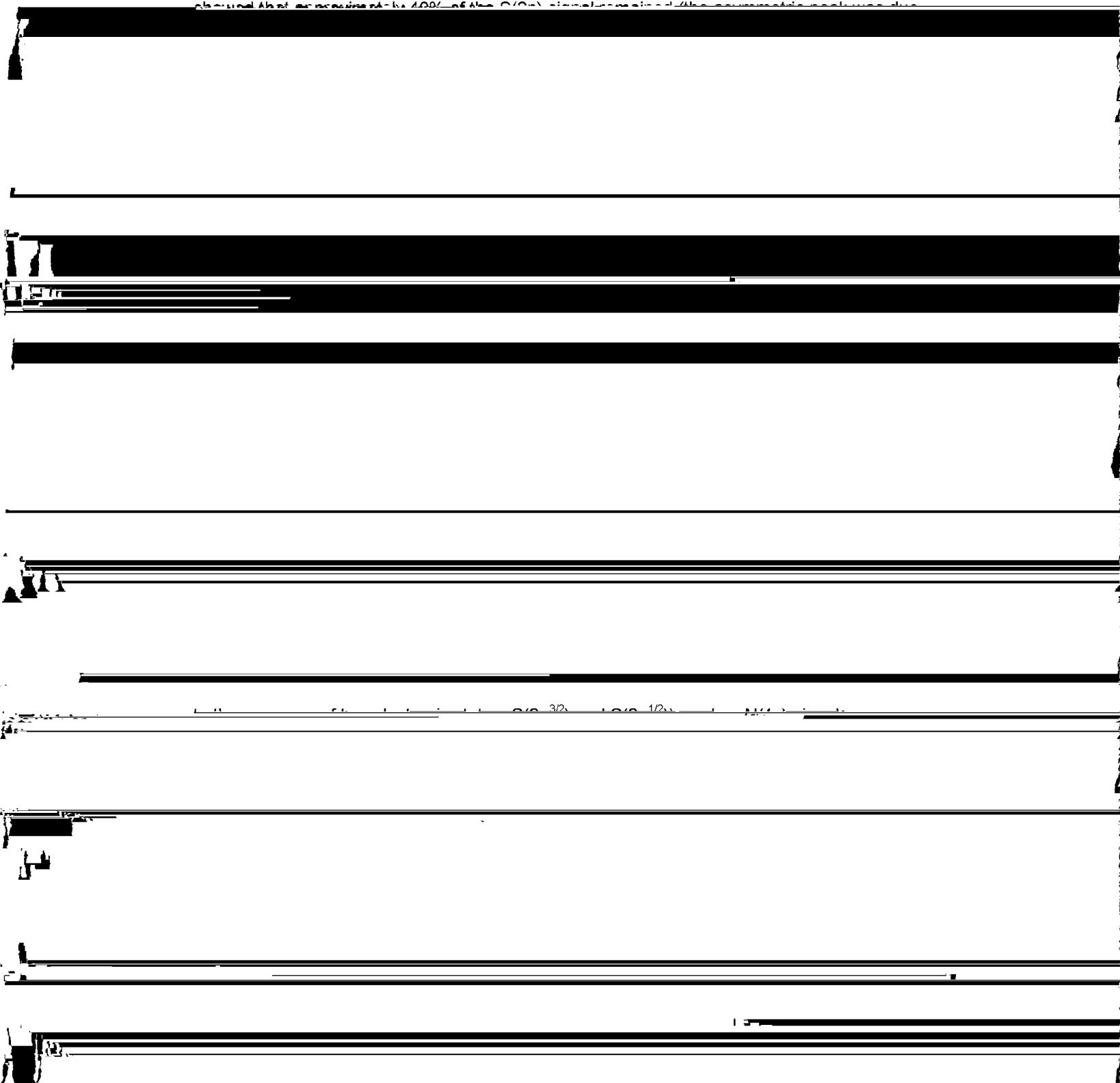
Table 2 presents results of stability tests of a representative NDC on Au(111). For most of

these XPS spectra, there is a high degree of overlap, suggesting no change following

exposure to the stated conditions. In the C(1s) spectra on the left line, the inner spectrum

Figure 2B depicts an STM image of the monolayer prepared from the carbonate salt of ~~MLC-1 on Au(111) demonstrating highly ordered self assembly. A repeating lattice unit is~~

Figure 3D depicts representative XPS data for the treatment of dodecanethiol-protected Au(111) surfaces with solutions of NHC-1 for 24 h at room temperature; the XPS spectra showed that approximately 40% of the S(2p) signal remained after the treatment process due





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Figure 9 depicts XRD data of films of MHC 4 on Au(111) before (left peak) and after 24h

soaking in water (right peak) for 24h and showed decomposition

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Figure 17A depicts SPR data from a commercial HPA chip in PBS buffer;

Figure 17B depicts SPR data from a NHC-16 carbene chip in PBS buffer;

Figure 17C depicts a plot of absorbance versus time for an experiment of the type of NHC

...tion. A "substituent" is an atom or group of bonded atoms that can be considered to

...tion. A "substituent" is an atom or group of bonded atoms that can be considered to

...bond which can be unsubstituted or optionally substituted with one or more substituents

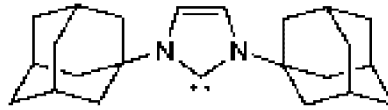
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are not limited to azetidines, oxetanones, thietanones, piperidines, piperazines, morpholines, pyrrolidines,

azetidiny, azetidionyl, oxetanyl, thietanyl, piperidinyl, piperazinyl, morpholinyl, pyrrolyl

oxazolones, thiazolidones, diazolidones, tetrahydroimidazolidones, hexahydroimidazolidones, tetrahydroimidazoles, imidazoles,



As would be well appreciated by a worker skilled in the art, there are many alternative

retains its useful properties on the timescale of its expected usefulness in the presence of



air, moisture or heat, and under the expected conditions of application. This chemical  
stability may be defined relative to other self-assembled monolayer-functionalized surfaces

[REDACTED]

[REDACTED]

circuits and/or instruments that use sensors to receive and respond to signals and/or

[REDACTED]

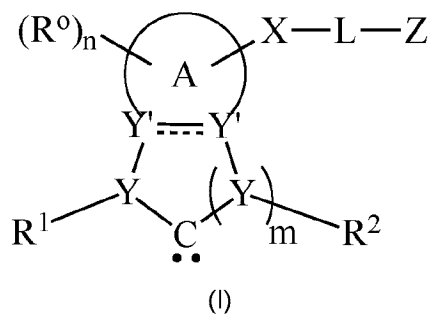
[REDACTED]

[REDACTED]





more carbenes of formula I



n is an integer from 1 to 8, or from 1 to 4;



$X^1$  and  $X^2$  are independently  $C$  or a heteroatom

$X^2$  and  $X^3$  are independently  $C$  or a heteroatom, and the dashed line represents a

optional double bond;

$D^1$  and  $D^2$  are independently absent, or each represents a lone pair of electrons,  $H$ ,  $C$ ,  $O$

(II)

wherein:

n is an integer from 1 to 8, or from 1 to 4;

m is an integer from 0 to 4;

*This is a continuation that originally acts as a base*

*A is chosen as alpha-beta-gamma-delta-epsilon-zeta-eta-theta-iota-kappa-lambda-mu-nu-xi-omicron-pi-rho-sigma-tau-psi-omega*

connected to form a cycle, or heterocycle, each of which is optionally substituted; and

R<sup>1</sup> and R<sup>2</sup> are independently absent, at least one lone pair of electrons, H, C<sub>1</sub>-C<sub>10</sub>



A substituted heterocyclic ring system, a heterocyclic ring system, a fused heterocyclic ring

system, a heterocyclic ring, and/or fused heterocyclic ring system, each of

which is optionally substituted;



attached as indicated to form a complete and coherent document.

optionally substituted;

wherein when A is absent or non-existent, the dashed line represents an optional

polyether, or polythioether, each of which is optionally substituted; or, any one of R<sup>3</sup>  
or R<sup>4</sup> with any one of R<sup>1</sup> or R<sup>2</sup> together with the atoms to which they are attached

activating or deactivating the metal surface to make it reactive or unreactive to a selected

[REDACTED]

[REDACTED]

reagent or combination of reagents, or by displacing existing chemical groups or moieties

[REDACTED]

One method to functionalize gold, and to a lesser degree silver and copper, is to

White et al., *Journal of Electroanalytical Chemistry*, 1984, 171, 1-11

as Au-C bond can be a poor conductor; here compared to certain Au-C bonding

parisipational, L.M. Carreira, et al., *J. Am. Chem. Soc.* 129, 5040 (2007); see also

hydrocarbon-based compound to a metal via a carbon-metal bond, particularly one discent

thiols, remained, however.

The stability of these carbene SAM functionalized metal surfaces has been

ordered NHC film was inferred from NEXAFS C K-edge spectroscopy, but no stability studies were performed and no potential for derivatization illustrated. With respect to

be used to aid in collecting functional information, and to help in identifying both control and non-control surfaces. For

[REDACTED]

[REDACTED]

[REDACTED]

[REDACTED]

[REDACTED]

[REDACTED]

[REDACTED]

[REDACTED]



continued by the oxidation of gold metal through dissolution in aqua regia. Aqua regia was

prepared as a mixture of concentrated nitric and hydrochloric acid (1:3 ratio v/v). Gold wire was dissolved in an appropriate volume of aqua regia solution such that no solid remained.

Careful evaporation of the solution after 24 hours yielded chloroauric acid tetrahydrate as a

iridium tips were used for all experiments. GXSM [Zahl, P., *et al. J. Vac. Sci. Tech. B* 28, C4E39 (2010)] was used as control software using the Signal Ranger A810 DSP and Nanonis HVA4 high-voltage amplifier.

**EXAMPLE 1. CRYSTALLINITY MEASUREMENTS**

**EXAMPLE 1A. Comparison of 4.0-Diameter 4.0-Micrometer Cu Nanoparticles with 1.0-Micrometer**

To a solution of 4-oxo-2-nitrobenzal (640 mg, 4 mmol) and 4,4'-dibromo

dodecane (9.624 g, 8 mmol) in anhydrous acetonitrile (40 mL), potassium carbonate (550

mg, 8 mmol) was added. The mixture was stirred at 80 °C for 2 h under argon. The solvent

into 25 mL of a saturated solution of NaHCO<sub>3</sub> in water and centrifuged. The desired product

was extracted from precipitate with CHCl<sub>3</sub> (3 x 25 mL). Yield 237 mg (69 %). ES-MS (m/z)  
for C<sub>16</sub>H<sub>20</sub>N<sub>2</sub>O: 343.2387 Calc.: 343.2372 <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>) δ (ppm): 8.06 (s, 1H, N-

CH=N), 7.44 (d, 1H, *J*<sub>HH</sub> = 8.5 Hz, ArH), 7.05 (s, 1H, ArH), 6.78 (d, 1H, *J*<sub>HH</sub> = 7.9 Hz, ArH),  
3.95 (t, 2H, *J*<sub>HH</sub> = 6.5 Hz, -O-CH<sub>2</sub>), 3.28 (m, 2H, *J*<sub>HH</sub> = 6.8 Hz, N<sub>3</sub>-CH<sub>2</sub>), 1.70 (m, 2H), 1.50 (m,  
2H), 1.41 (m, br, 2H), 1.23 (m, br, 14H). <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>) δ (ppm): 154.88 (s, N-CH=N),  
141.39 (s, C), 137.78 (s, C), 133.45 (s, C), 116.27 (s, Ar), 111.75 (s, Ar), 98.19 (s, Ar)

was dissolved in toluene and filtered through Celite. The filtrate was concentrated under reduced pressure to give a solid.

[REDACTED]

functionalization.

**EXAMPLE 1D. Four step synthesis of 5-(dodecyloxy)-1,3-diisopropyl-1H-benzo[d]imidazol-3-ium hydrogen carbonate (NHC-1 hydrogen carbonate salt):**

(i) 4-(dodecyloxy)-2-nitroaniline:

To a solution of 4-amine-2-nitrophenol (1.540 g, 10 mmol) and 1-bromododecane (9.730 g

[REDACTED]

(iii) 5-(dodecyloxy)-1,3-diisopropyl-1H-benzo[d]imidazol-3-ium iodide:

To a solution of 5-(dodecyloxy)-1H-benzo[d]imidazole (100 mg, 0.4 mmol) and

[REDACTED]

[REDACTED]

[REDACTED]

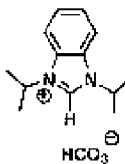
2.3 0.02 (20% 1 mmol) in acetonitrile (50 mL) + iodine (1.4 g, 0.5 mL, 0.5 mmol)

[REDACTED]

[REDACTED]

[REDACTED]

EXAMPLE 1E. General Experimental Protocol for benzimidazole carbonate synthesis



Preparation of LiBr·RIMY(H)/HCO<sub>3</sub><sup>⊖</sup> ("carbonate salt of NHC 1"):

[REDACTED]

A similar procedure to Tetay, Fàbregas, M. et al. / *Am. Chem. Soc.* 2010, 132 (15)

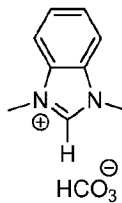
6376-6784 and Fàbregas, M. et al. / *Org. Chem.* 2012, 77 (20), 40425-40444 was followed

[REDACTED]

[REDACTED]

EXAMPLE 15 Synthesis of 4,6-Dimethylimidazo[1,2-a]pyridine Hydrochloride

EXAMPLE 15





Each carbon was found to react with Au surface after simple room temperature immersion

(5 Au/112) or Au nanoparticles in solution of the carbon or the corresponding carbonate

showed an increase in the amount of the surface area of the C4 layer that

demonstrating thermal and oxidative stability. A large fraction of the surface even remained

different IMed ICG gold deposition methods were investigated: (1) IMed ICG (4 mg) was

[REDACTED]

[REDACTED]

[REDACTED]

[REDACTED]

[REDACTED]

[REDACTED]

[REDACTED]

glycolized in wet methanol under air and a gold silt was completely submersed into the

[REDACTED]

[REDACTED]

**EXAMPLE 5. NANOPARTICLES STUDIES****EXAMPLE 5A. Preparation of Gold Nanoparticles**

Chloroauric acid tetrahydrate (50 mg, 0.180 mmol) in water (5.4 mL) was added to a

solution of tetraoctylammonium bromide (167 mg, 0.306 mmol) in toluene (3.06 mL). The resulting mixture was stirred vigorously until the aqueous layer became colorless. Following

mixture was stirred vigorously for 20 min. 0.5 mM of dodecyl sulfide was added to the reaction mixture and it was stirred for a further 20 minutes. A aqueous solution of NaOH

To construct the face centered cubic (fcc) unit cell of gold was optimized according

a method described below. Resulting lattice constant was 4.107 Å, which is in good

to gold via three-fold hollow (tetrahedral) sites [H. Häkkinen, *Nature Chem.* **4**, 443 (2012)],  
with a reported binding energy of 127 kJ/mol [D. J. Lavrich, *et al. J. Phys. Chem. B* **102**,  
2450 (1998)]. However, with respect to the current DFT studies, the calculations indicated

(Figures 2A and 2B) showed no evidence of islands. However, islands were clearly present

in the STM image of Ni/Cu<sub>2</sub>S on Au(111) (see Figure 5). The density of defect regions was



**EXAMPLE 9. SPR EXPERIMENTS WITH NHC-16 AND COMPARISON TO COMMERCIAL "HPA" CHIP**

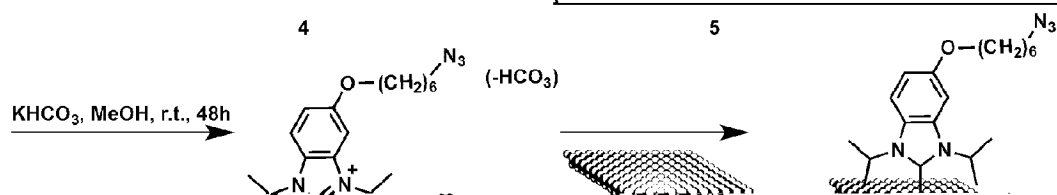
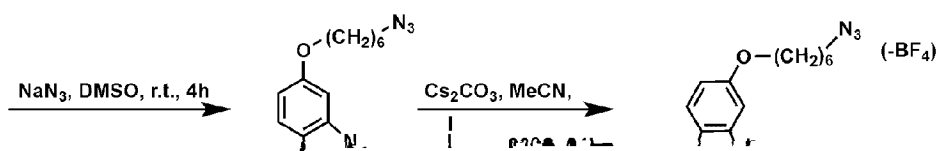
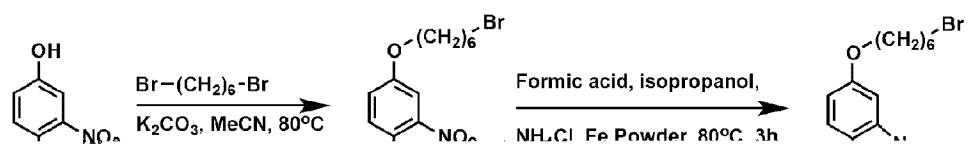
A Surface Plasmon Resonance (SPR) chip was prepared by depositing a NHC-16 self-assembled monolayer on a blank Au chip (blank Au available from Biacore, General Electric, Pittsburgh, PA, USA). The resulting chip was consequently coated with a hydrophobic layer, which can be used to form a model lipid layer on its surface. Such a lipid

ship in this regard. See Tables 5A and 5B for comparison data between the LIDA chip and

performance of all conditions that the carbon chip outperforms the commercial IRA chip in

conclusion: first, the magnitude of the reduction in alcohol labeling is after the

Scheme 1:



Compound 2 (1.0 mmol) was dissolved in 10 ml of dry acetonitrile and

•

Compound 1 (1.0 mmol) was dissolved in a dry round bottom flask under Ar (c) 30 ml of dry acetonitrile

was added to the flask and the mixture was stirred until all of compound 1 had dissolved. 2



NHC-9 was made by placing diphenyliodonium tetrafluoroborate salt (0.037g) and  $\text{Cr}_2\text{SO}_4$  (0.8 mg, 5 mol%) in a vial and dissolving them in 2 ml of dimethylformamide (DMF).

NHC-9 was then added to the solution and the vial was cooled with a TFEI QM® cap. The

EXAMPLE 12. WATER OXIDATION STUDIES USING CERIUM AMMONIUM NITRATE

UV-VIS ABSORBANCE DETECTION

These experiments are intended to demonstrate that Ni(II)-terminated metal samples

are capable of oxidizing water. A sacrificial oxidant, cerium ammonium nitrate ("CAN"), was used both to complete the oxidation cycle and to track the progress of reaction by monitoring



100 °C for 24 h. After this time, the samples were cooled to room temperature

pinged with benzene (2 x 5 ml), ether (2 x 5 ml), and ethanol (2 x 5 ml), dried under a

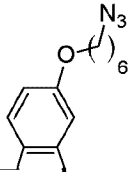
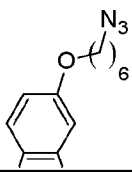
nitrogen gas stream, and analysed by XPS. The samples treated at 100°C showed no  
discernible change, while the samples treated at 180°C showed decomposition (see Figure

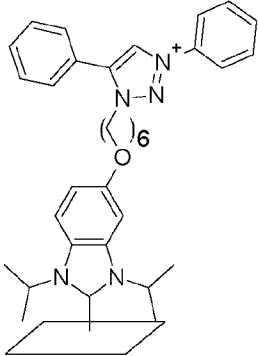
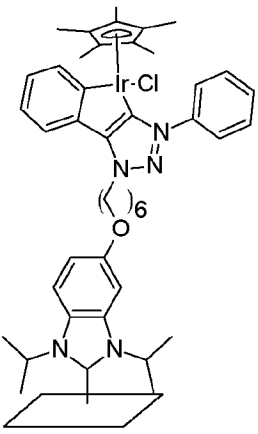
TABLE 1: Structural information for NHCs on metal.

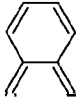
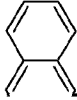
Nickname	Structure	Name of NHC/alk	Prepared from
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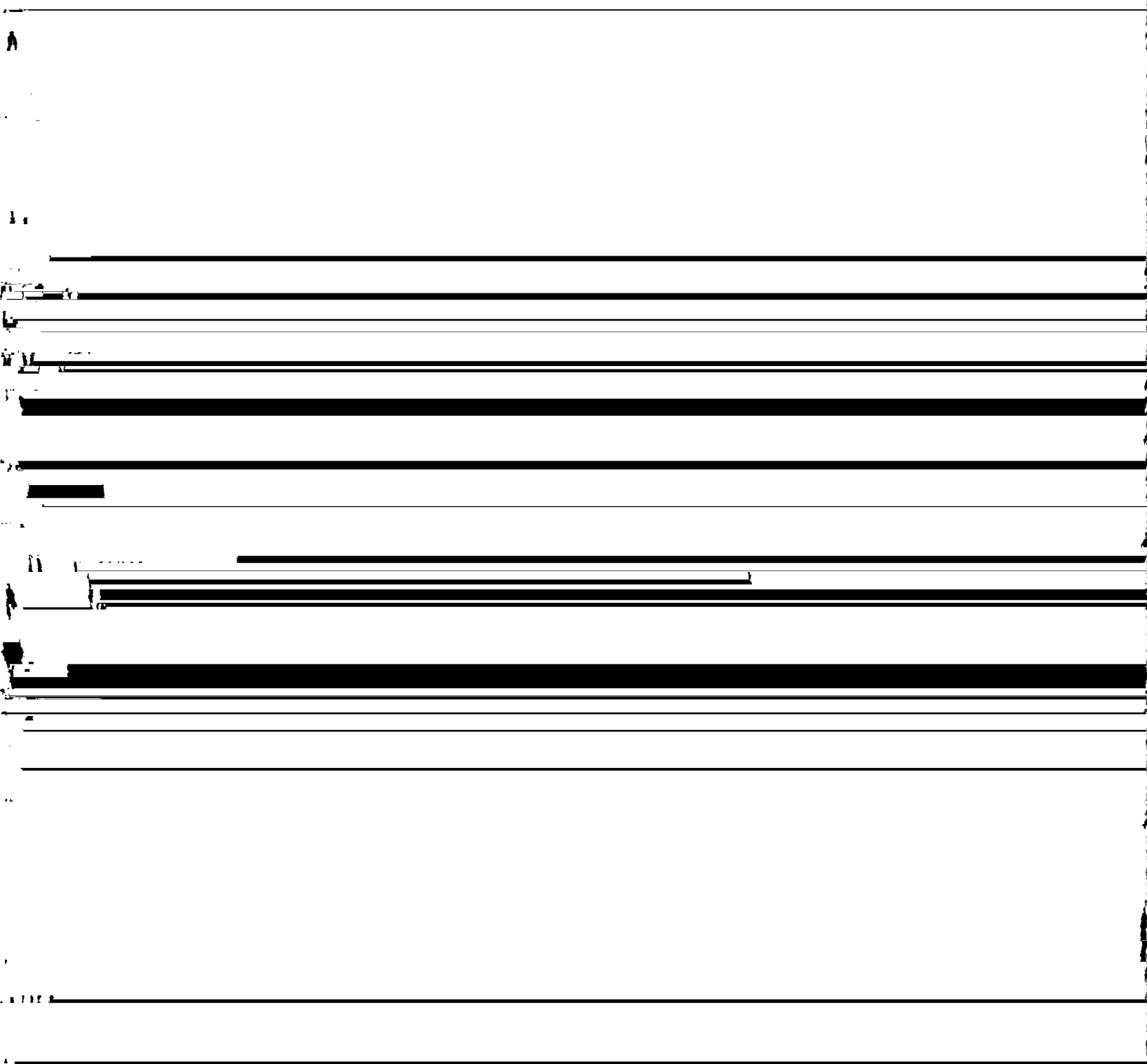
[The table content is almost entirely obscured by heavy black redaction bars.]

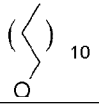
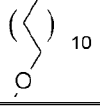


NHC-7		5-(6-azidohexyloxy)-1,3-diisopropyl-2,3-dihydro-1H-	
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<p>NHC-9</p>			
<p>NHC-10</p>			

Monolayer prep'd using budesonide		1,3-diisopropyl- naphtho[2,3- d]imidazolium	
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Monolayer		5-(dodecyloxy)-1,3-	
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[REDACTED]

[REDACTED]

[REDACTED]

[REDACTED]

**TABLE 2A: XPS data for products obtained by reacting NHCs with Au(111) surfaces and Au nanoparticles**

Carbene NHC on GOLD	N:C ratio (XPS)		
	Expected	Found	
		Au(111)	Au <sub>NP</sub>
NHC-1	2:13	2:14	2:13
NHC-2	3:20	3:21	3:22



**TABLE 3: Stability Tests of Self-Assembled Monolayers: Films of NHC-1 deposited on Au(111) from its hydrogen carbonate precursor before and after exposure to listed conditions.**

Conditions	Au(111) Spectra	C(1s) Spectra
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	— Starting — H <sub>2</sub> O, 100°C, 24h	— Starting
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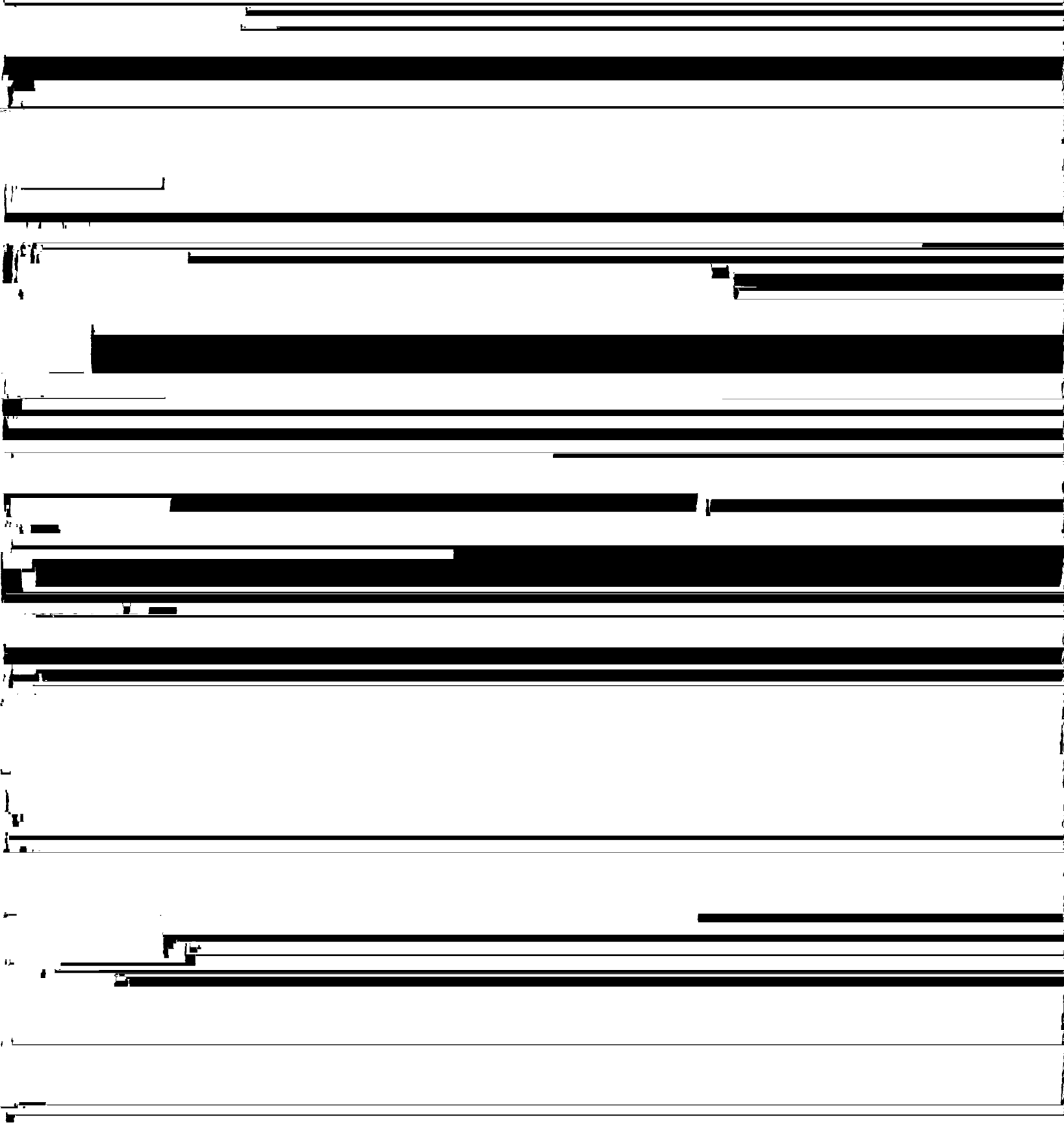


TABLE 4: Characterization of NHC-1-substituted Pd nanoparticles.

Pd		Stabilizing			
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		804±33	563±40	516±40	212±12
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[REDACTED]

[REDACTED]

[REDACTED]

[REDACTED]

[REDACTED]

[REDACTED]

[REDACTED]

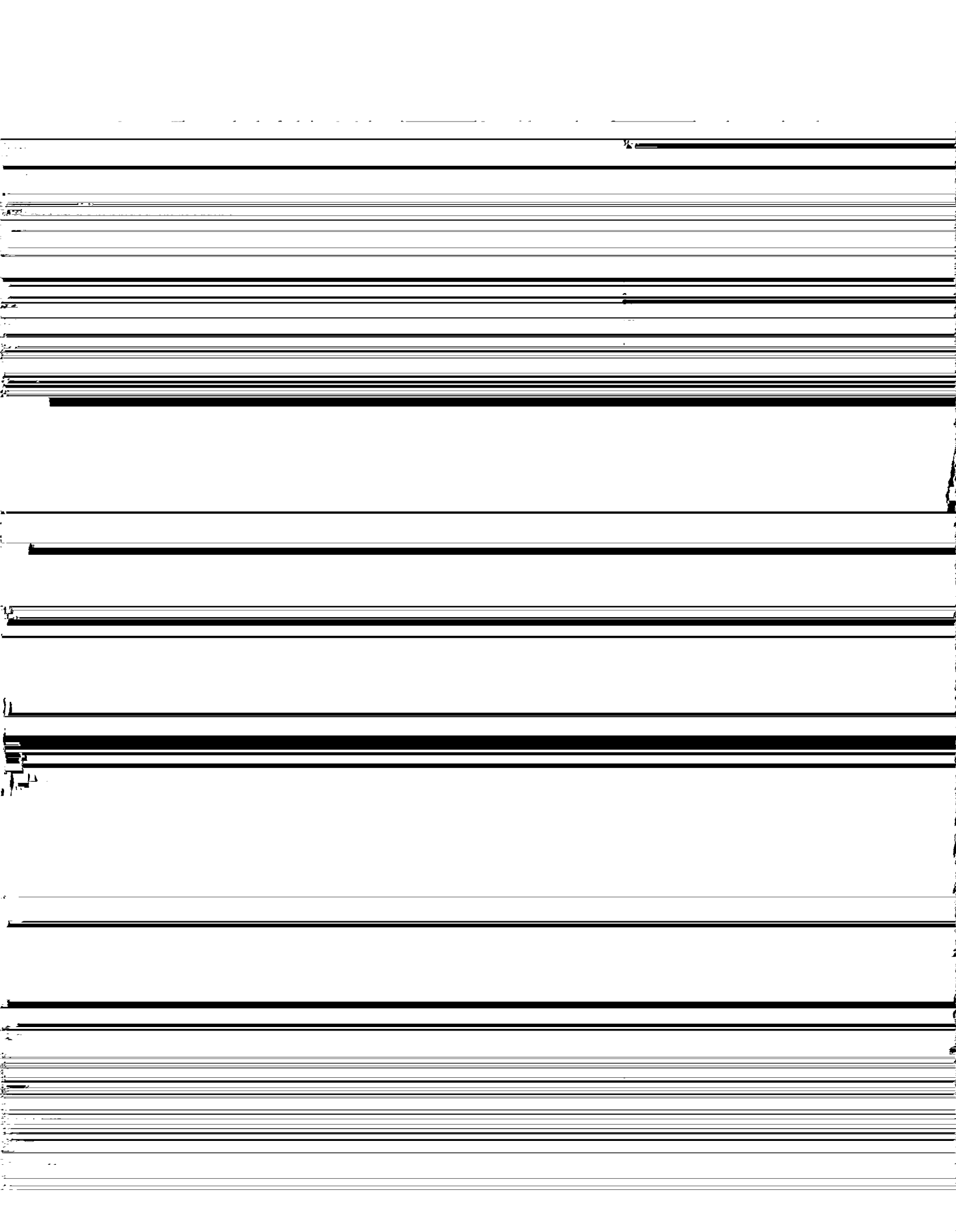
[REDACTED]

All publications, patents and patent applications mentioned herein are indicative of the level of skill of those skilled in the art to which this invention pertains.

many ways. Such variations are not to be regarded as a departure from the spirit and scope of the invention, and although modifications are possible to one skilled in the art are

1,3-dihydro-1,3-bis(isopropyl)-2H-benzimidazol-2-ylidene

is a catalyst for the polymerization of acrylonitrile in the presence of a metal selected from



15. Use of the carbene-functionalized composite of any one of claims 1 – 6 or of the carbene-functionalized composite prepared by the method of any one of claims 7-12 for:



> < > <

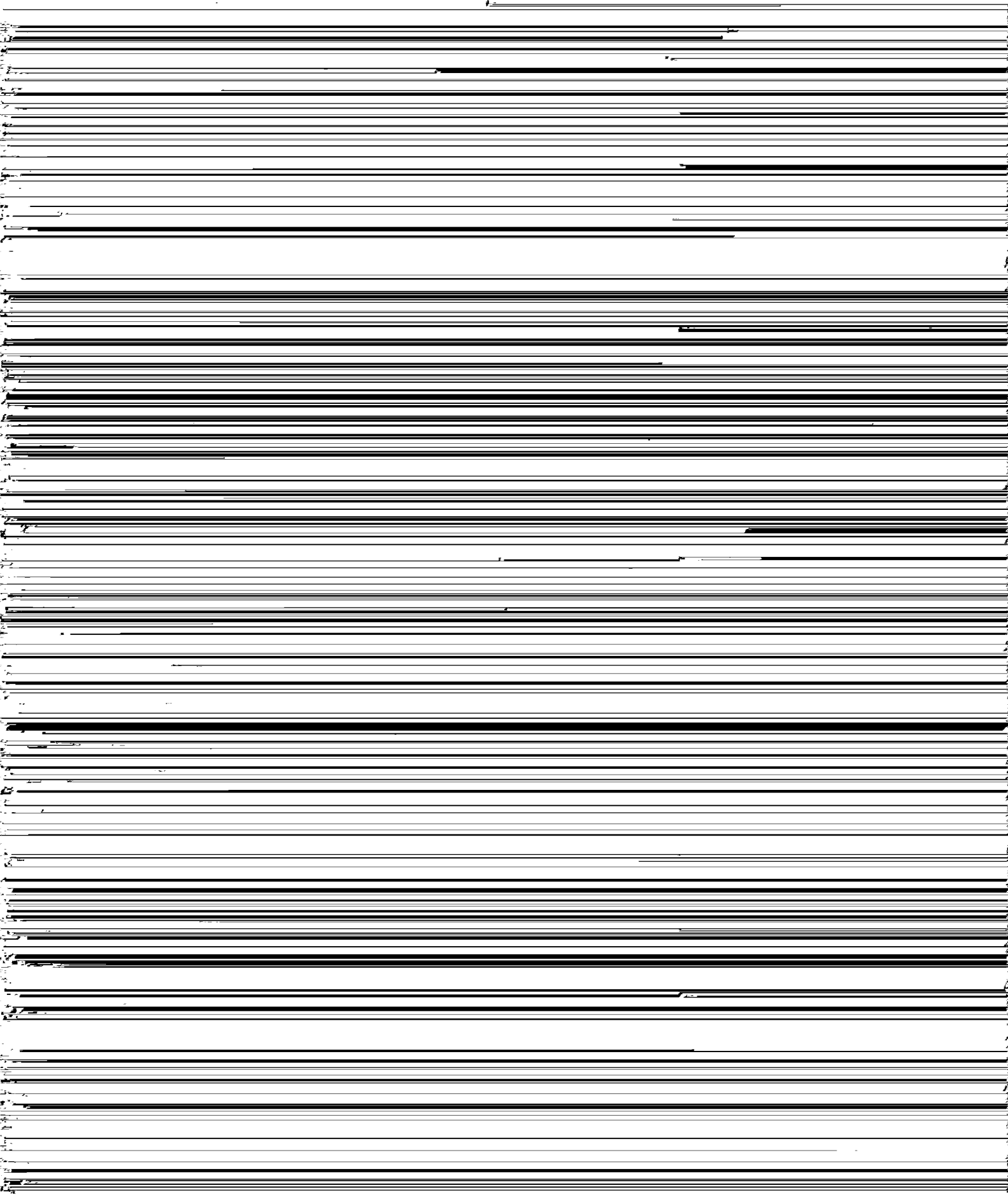
S(C...H...)

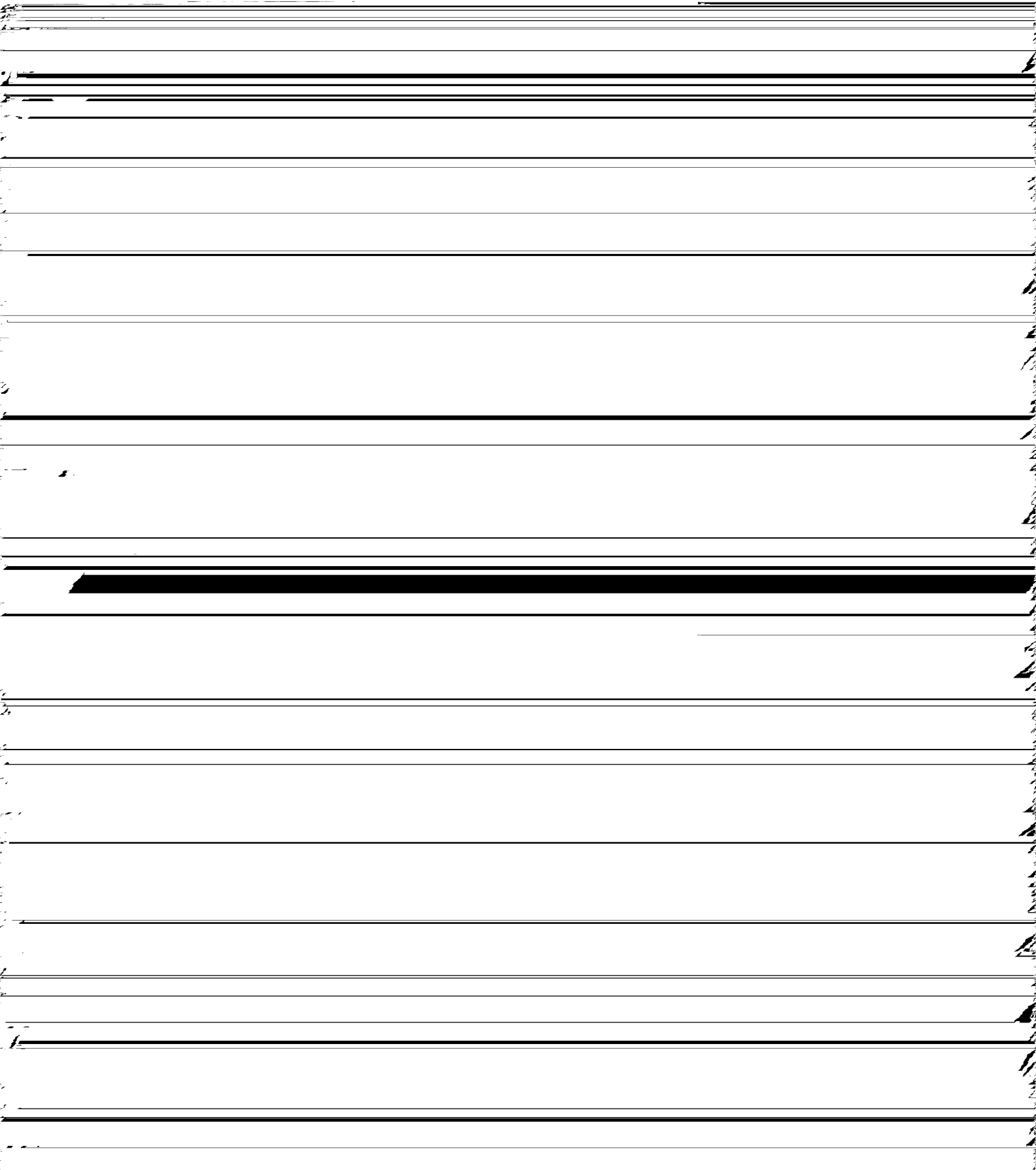
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N(1s)

C(1s)

S(2p)

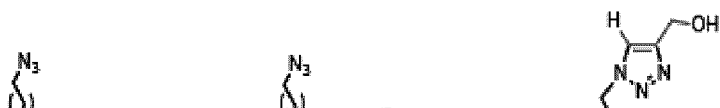




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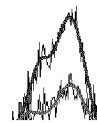
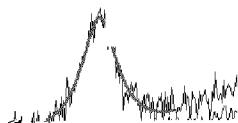


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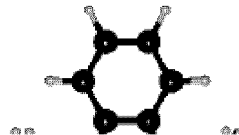
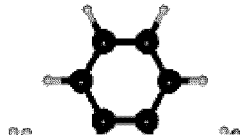
N(1s)

C(1s)

S(2p)



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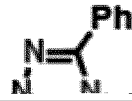
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N(1s)

C(1s)



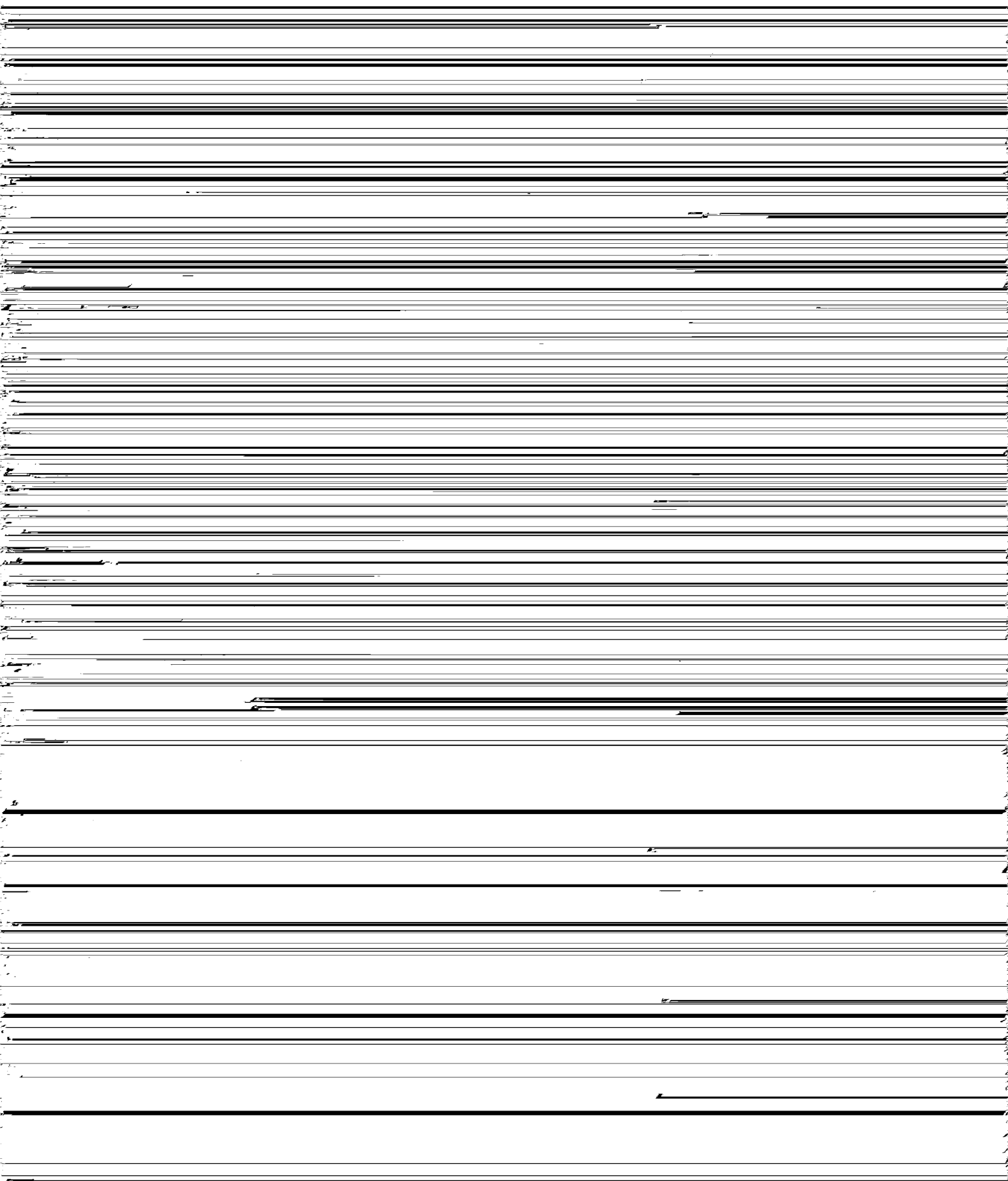
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N(1s)

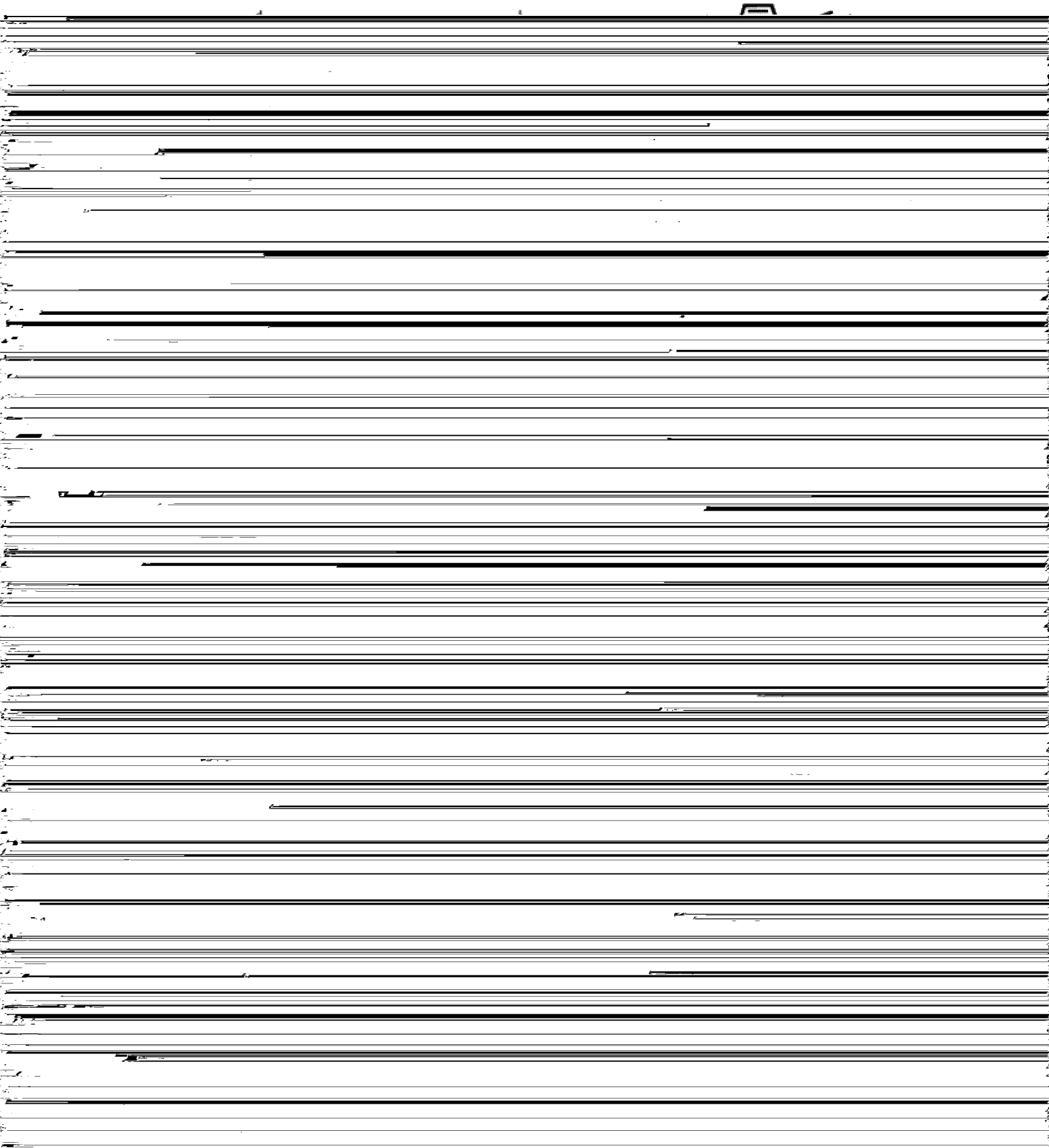
C(1s)



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N(1s)

C(1s)



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N 1s

C 1s

WA

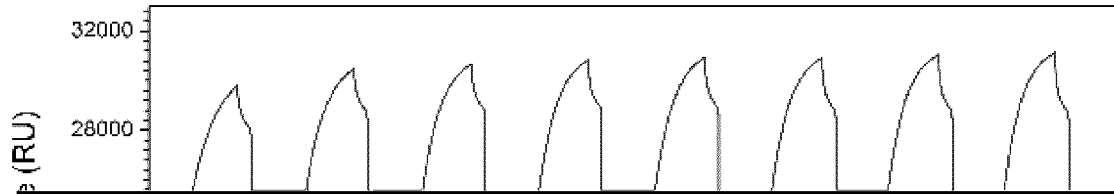
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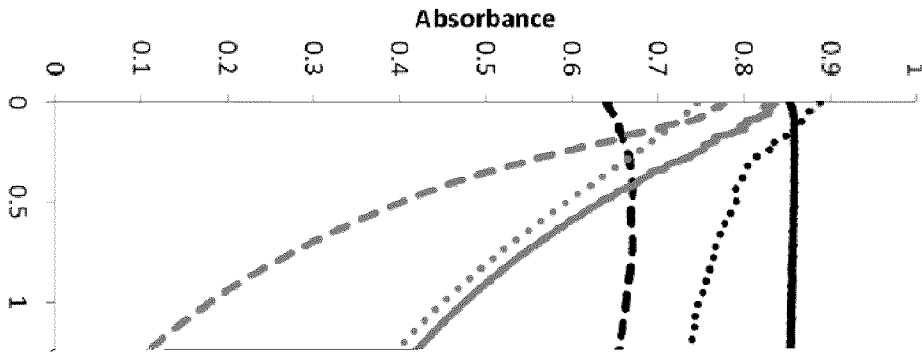




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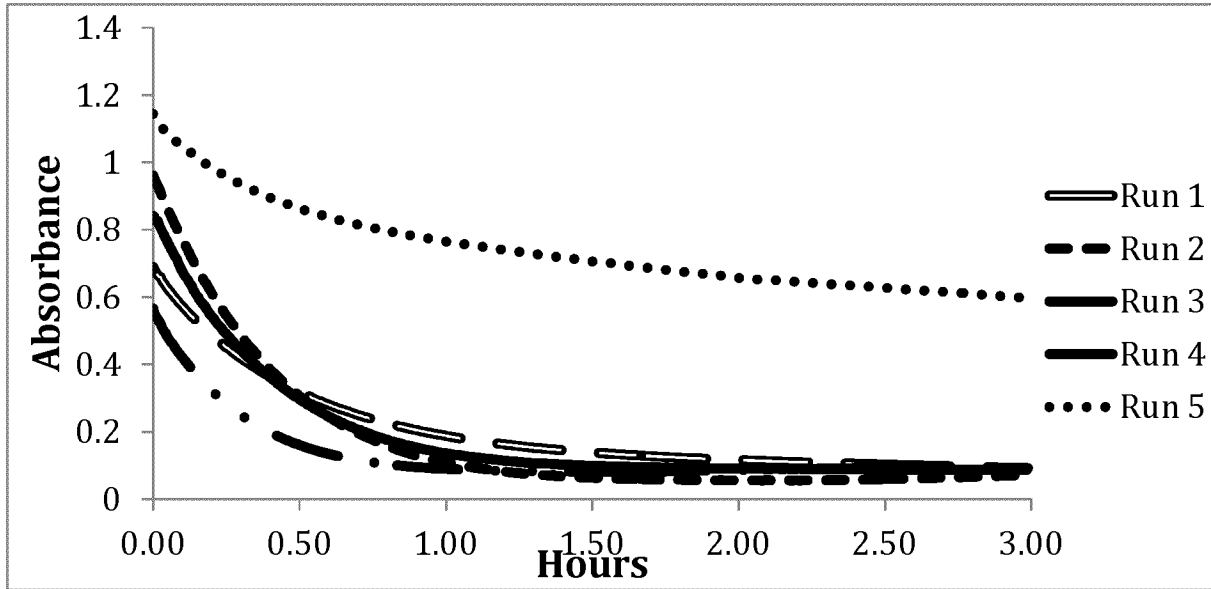


Fig. 18B

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	<p>Pd 3d</p>	<p>N 1s</p>
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Starting



Starting

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