Electronic Supplementary Material (ESI) for Chemical Science.


# Supplementary Information for

## Ambiphilicity of Ring-Expanded *N*-Heterocyclic Carbenes

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# I. General Considerations

All manipulations were performed using standard glovebox and Schlenk techniques. Glassware was dried in an oven overnight at 150 °C or flame-dried, and solvent were dried and degassed before use. Benzene, THF, diethyl ether, and n-pentane were freshly distilled over Na metal. Hexanes, dichloromethane, and chloroform were freshly distilled over $CaH_2$.

**NMR Characterization**: Deuterium-labeled solvents were purchased from Cambridge Isotope Laboratories. NMR: Multinuclear NMR data were recorded on a Varian INOVA 500 MHz or a Bruker Avance 300 MHz at UCSD. Chemical shifts (δ) are reported in parts per million (ppm) and are referenced to residual solvent signals ($^1$H, $^{13}$C). Coupling constants J are given in hertz (Hz). NMR multiplicities are abbreviated as follows: s = singlet, d = doublet, t = triplet, q = quartet, sext = sextet, sept = septet, m = multiplet, br = broad. All spectra were recorded at 298 K unless otherwise noted.

# II. Synthesis and Characterization of Iminiums and Carbenes

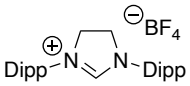
## A. Literature procedures

Iminium precursors and the corresponding carbenes were prepared according to known literature procedures: **NHC-5,**[1] **NHC-6**,[2] **NHC-7**,[3] and **NHC-8** and $^{Mes}$**NHC-8**[4].

## B. Characterizations

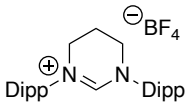
### B.1. Carbene Iminium Precursors

**NHC-5.HBF$_4$ (NHC-5$^H$):** $^1$H NMR (300 MHz, $CDCl_3$) δ = 8.49 (s, 1H), 7.44 (t, 2H, J=7.8Hz), 7.25 (d, 4H, J=7.8Hz), 4.80 (s, 4H), 2.97 (sept, 4H, J=6.9Hz), 1.36 (d, 12H, J=6.9Hz), 1.23 (d, 12H, J=6.9Hz) $^{13}$C{$^1$H} NMR (125 MHz, $CDCl_3$) δ = 158.8, 146.5, 131.9, 129.5, 125.3, 55.4, 29.0, 25.3, 23.5.



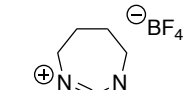
**NHC-5$^H$**

**NHC-6.HBF$_4$ (NHC-6$^H$):** $^1$H NMR (500 MHz, $CDCl_3$) δ = 7.56 (s, 1H), 7.42 (t, 2H, J=7.8Hz), 7.24 (d, 4H, J=7.8Hz), 4.22 (t, 4H), 3.01 (dt, 4H), 2.74 (br m, 2H), 1.35 (d, 12H, J=6.8Hz), 1.20 (d, 12H, J=6.8Hz) $^{13}$C{$^1$H} NMR (125 MHz, $CDCl_3$) δ = 153.3, 146.1, 136.1, 131.6, 125.4, 48.9, 28.7, 24.7, 24.6, 19.2.



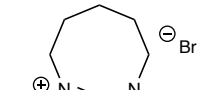
**NHC-6$^H$**

**NHC-7.HBF$_4$ (NHC-7$^H$):** $^1$H NMR (500 MHz, $CDCl_3$) δ = 7.42 (t, 2H, J=7.8Hz), 7.30 (s, 1H), 7.25 (d, 4H, J=7.8Hz), 4.68 (br s, 4H), 3.21 (dt, 4H, J=6.8Hz), 2.64 (br s, 4H), 1.39 (d, 12H, J=6.8Hz), 1.24 (d, 12H, J=6.8Hz) $^{13}$C{$^1$H} NMR (125 MHz, $CDCl_3$) δ = 157.5, 145.3, 139.2, 131.3, 125.7, 56.2, 28.8, 24.8, 24.6, 24.4.



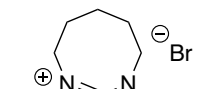
**NHC-7$^H$**

**NHC-8.HBr (NHC-8$^H$):** $^1$H NMR (400 MHz, $CDCl_3$) δ = 7.47 (s, 1H), 7.36 (t, 2H, J=7.7Hz), 7.20 (d, 4H, J=7.7Hz), 4.83 (br s, 4H), 3.24 (dt, 4H, J=6.8Hz), 2.30 (br s, 4H), 2.12 (br s, 2H), 1.34 (d, 12H, J=6.8Hz), 1.21 (d, 12H, J=6.8Hz) $^{13}$C{$^1$H} NMR (100 MHz, $CDCl_3$) δ = 157.03, 144.79, 141.05, 130.75, 125.55, 55.13, 28.74, 27.67, 25.17, 24.94, 21.46.



**NHC-8$^H$**

**$^{Mes}$NHC-8.HBr ($^{Mes}$NHC-8$^H$):** $^1$H NMR (400 MHz, $CDCl_3$) δ = 7.39 (s, 1H), 6.93 (s, 4H), 4.81 (m, 4H), 2.41 (s, 12H), 2.29 (m, 4H), 2.26 (s, 6H), 2.13 (m, 2H), 1.34 (d, 12H, J=6.8Hz), 1.21 (d, 12H, J=6.8Hz) $^{13}$C{$^1$H} NMR (100 MHz, $CDCl_3$) δ = 158.8, 141.9, 140.1, 133.7, 130.5, 53.9, 28.4, 21.0, 20.9, 18.9.

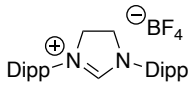


**$^{Mes}$NHC-8$^H$**

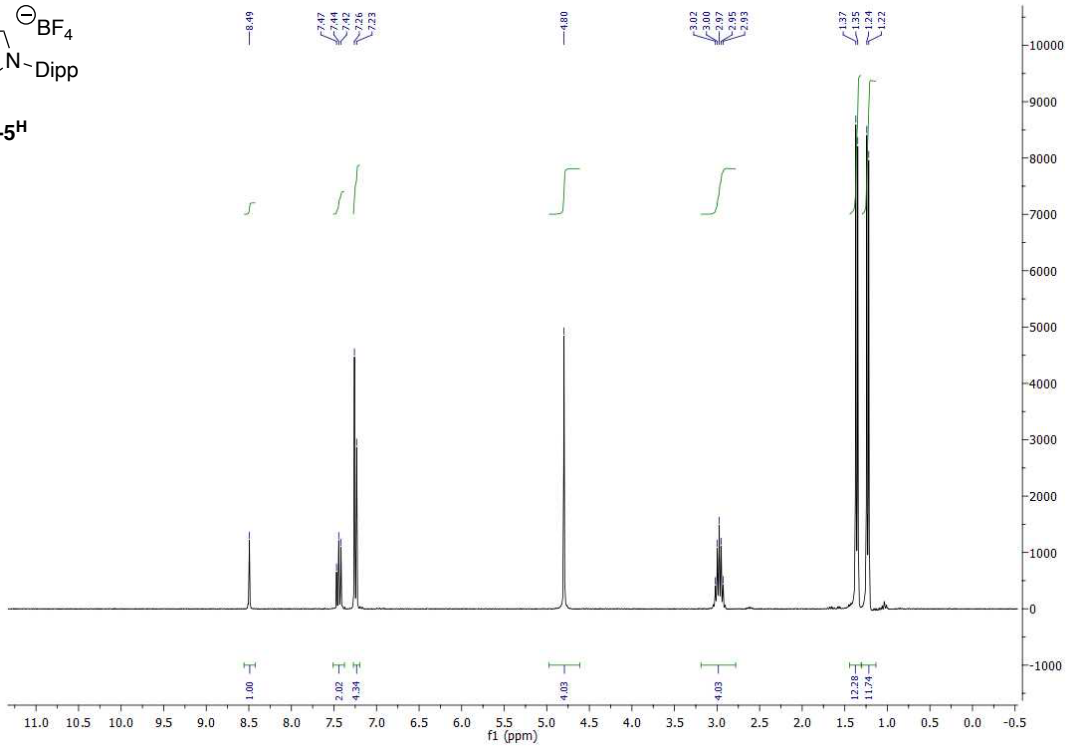
## B.2. Carbene Iminium Precursors NMR Spectra

**NHC-5.HBF$_4$ (NHC-5$^H$)**

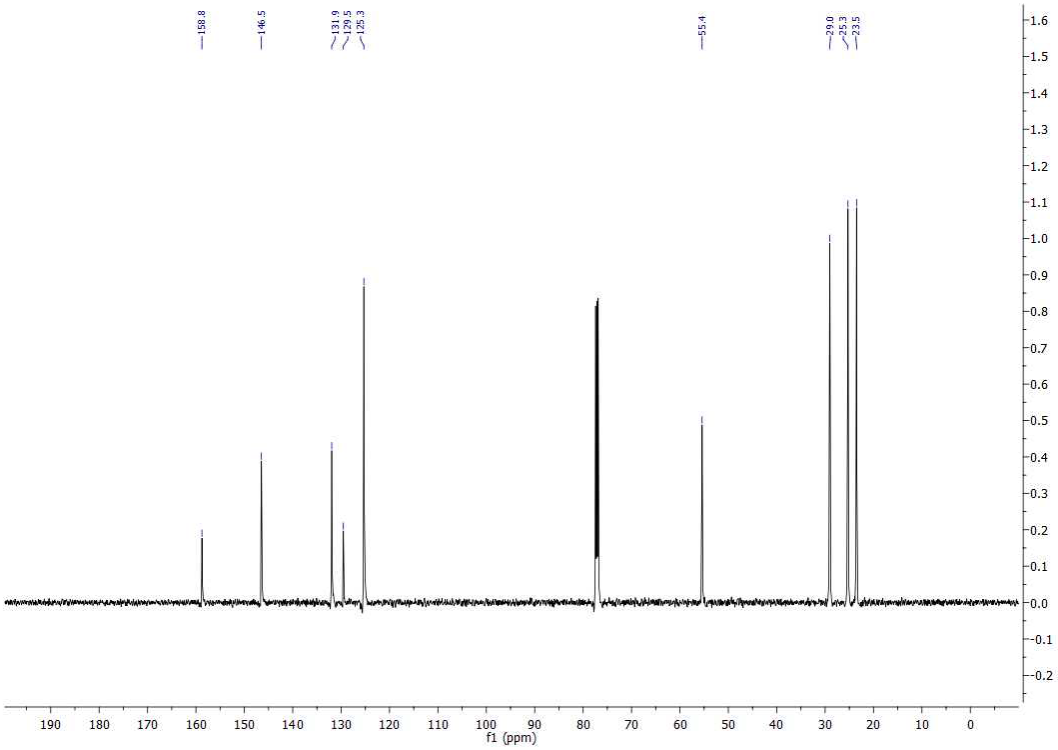
**$^1$H**




**NHC-5$^H$**

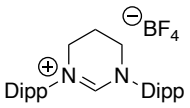



**$^{13}$C{$^1$H}**



## NHC-6.HBF$_4$ (NHC-6$^H$)

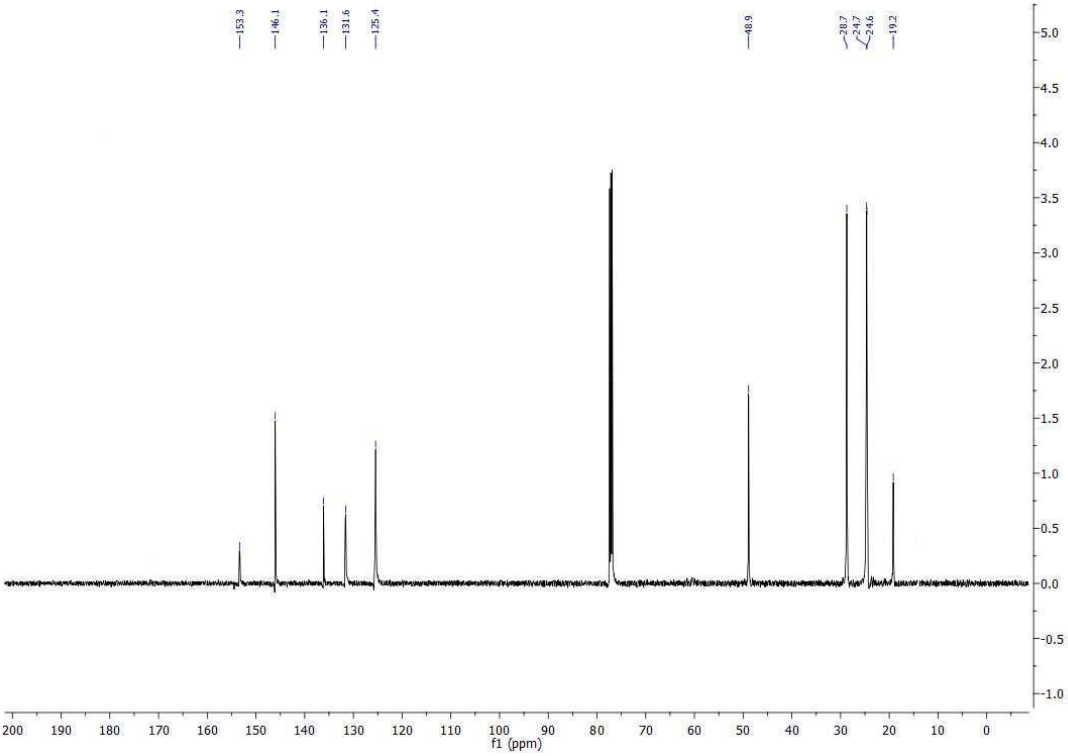
### $^1$H




NHC-6$^H$

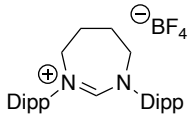



### $^{13}$C{$^1$H}



**NHC-7.HBF$_4$ (NHC-7$^H$)**

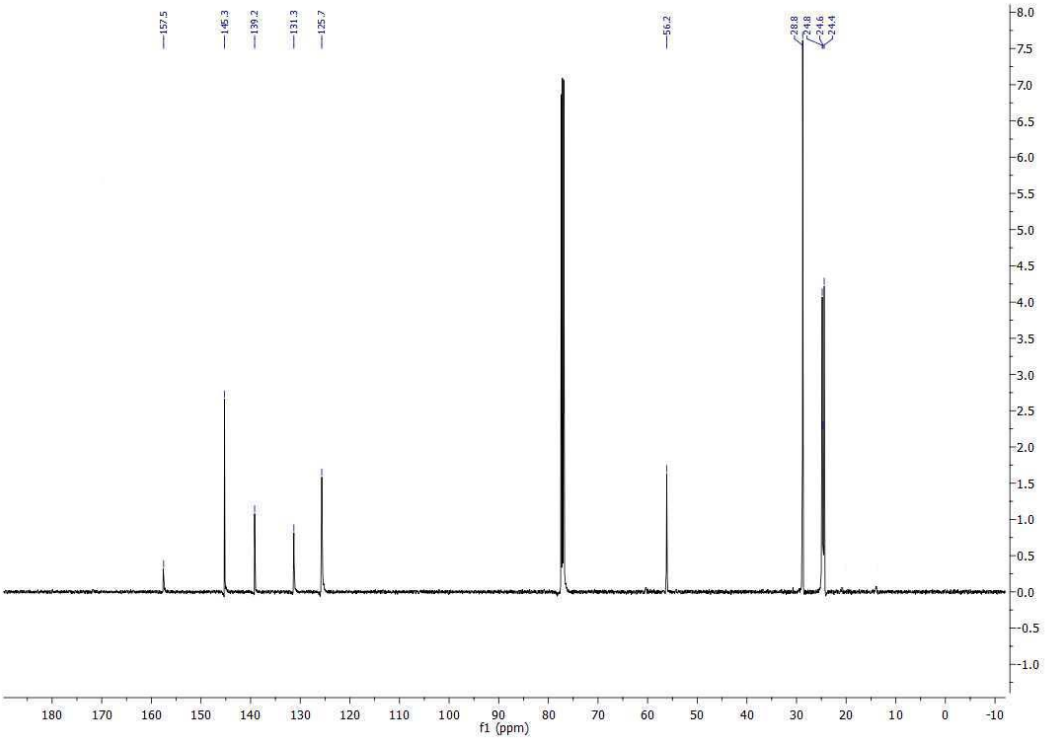
**$^1$H**




**NHC-7$^H$**

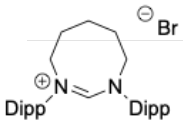



**$^{13}$C{$^1$H}**



## NHC-8.HBr (NHC-8$^{H}$)

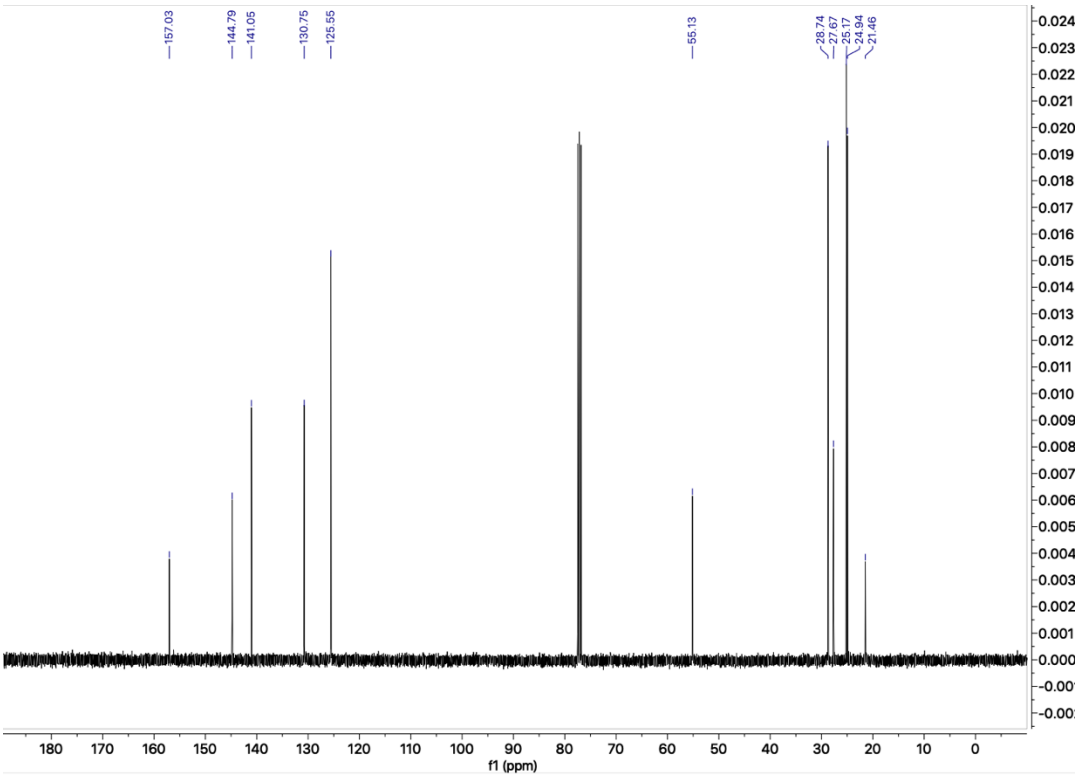
**$^{1}$H**




NHC-8$^{H}$

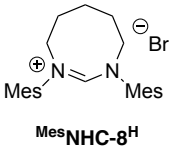



**$^{13}$C{$^{1}$H}**



**$^{Mes}$NHC-8.HBr ($^{Mes}$NHC-8$^{H}$)**

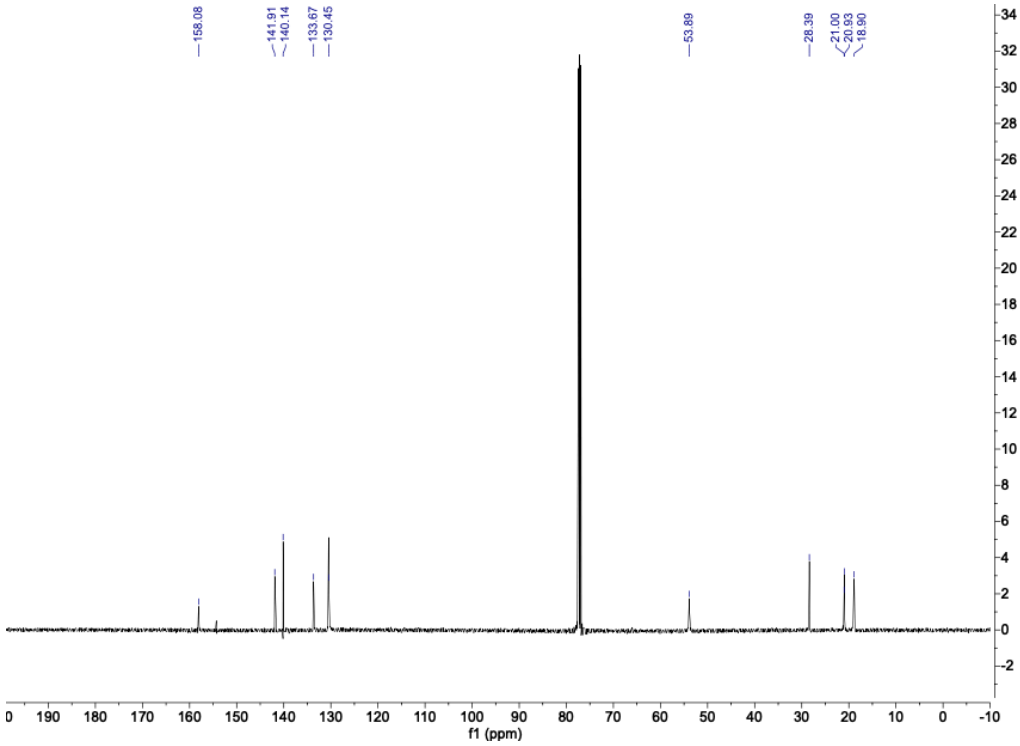
**$^{1}$H**




**$^{Mes}$NHC-8$^{H}$**

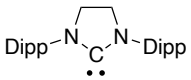



**$^{13}$C{$^{1}$H}**



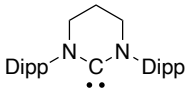
## B.3. Free Carbenes

**NHC-5:** $^{1}$H NMR (500 MHz, $C_6D_6$) δ = 7.28 (t, 2H, J=7.5Hz), 7.19 (d, 4H, J=7.5Hz), 3.34 (s, 4H), 3.27 (sept, 4H, J=6.6Hz), 1.34 (d, 12H, J=6.5Hz), 1.28 (d, 12H, J=6.5Hz) $^{13}C\{^{1}H\}$ NMR (125 MHz, $C_6D_6$) δ = 244.6, 147.5, 139.5, 128.3, 124.0, 53.3, 28.4, 24.9, 23.1.



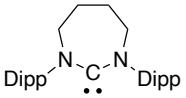
**NHC-5**

**NHC-6:** $^{1}$H NMR (500 MHz, $C_6D_6$) δ = 7.25 (dd, 2H, J=7.5Hz), 7.17 (d, 4H, J=7.5Hz), 3.39 (sept, 4H, J=7.0Hz), 2.84 (t, 4H, J=6.0Hz), 1.71 (t, 2H, J=6.0Hz), 1.29 (d, 12H, J=7.0Hz), 1.28 (d, 12H, J=7.0Hz) $^{13}C\{^{1}H\}$ NMR (125 MHz, $C_6D_6$) δ = 245.6, 146.2, 145.5, 127.6, 124.1, 43.9, 28.1, 24.6, 23.9, 21.4.



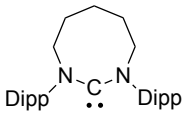
**NHC-6**

**NHC-7:** $^{1}$H NMR (500 MHz, $C_6D_6$) δ = 7.23 (dd, 4H, J=7.5Hz), 7.15 (d, 4H, J=7.5Hz), 3.56 (sept, 4H, J=7.0Hz), 3.48 (dd, 4H, J=5.5Hz), 1.80 (dd, 4H, J=5.5Hz), 1.29 (d, 12H, J=7.0Hz), 1.25 (d, 12H, J=7.0Hz) $^{13}C\{^{1}H\}$ NMR (125 MHz, $C_6D_6$) δ = 261.0, 148.2, 145.6, 127.1, 124.1, 52.8, 28.2, 26.0, 24.3, 24.0.



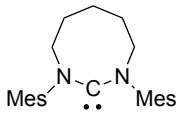
**NHC-7**

**NHC-8:** $^{1}$H NMR (500 MHz, $C_6D_6$) δ = 7.23 (t, 2H, J=7.6Hz), 7.14-7.16 (m, 4H), 3.56 (m, 8H), 1.87 (m, 2H), 1.54 (m, 4H), 1.28 (d, 12H, J=7.0Hz), 1.22 (d, 12H, J=7.0Hz), 0.14 (s, HHMDS) $^{13}C\{^{1}H\}$ NMR (125 MHz, $C_6D_6$) δ = 255.0, 149.5, 145.0, 126.7, 124.4, 52.1, 29.0, 28.5, 25.2, 24.7, 22.5, 7.21 (HHMDS). *Contains trace hexamethyl-disilazane (HHMDS).*



**NHC-8**

**$^{Mes}$NHC-8:** $^{1}$H NMR (500 MHz, $C_6D_6$) δ 6.87 (s, 4H), 3.37 (m, 4H), 2.33 (s, 12H), 2.22 (s, 6H), 1.80 (m, 2H), 1.47 – 1.37 (m, 4H), 0.14 (s, HHMDS) $^{13}C\{^{1}H\}$ NMR (126 MHz, $C_6D_6$) δ 250.5, 149.6, 135.2, 134.0, 130.0, 50.8, 29.6, 21.8, 21.0, 19.2, 7.3. *Contains trace hexamethyl-disilazane (HHMDS).*

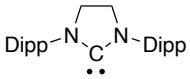


**$^{Mes}$NHC-8**

## B.4. Free Carbene NMR Spectra

**NHC-5**

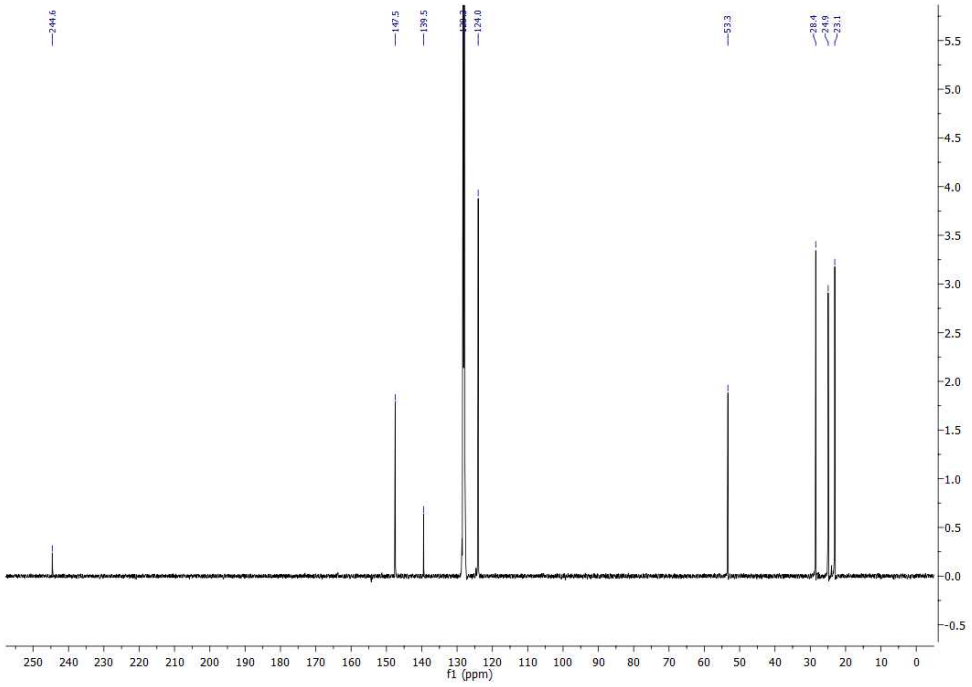
**$^{1}$H**




**NHC-5**

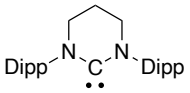



**$^{13}$C{$^{1}$H}**



## NHC-6

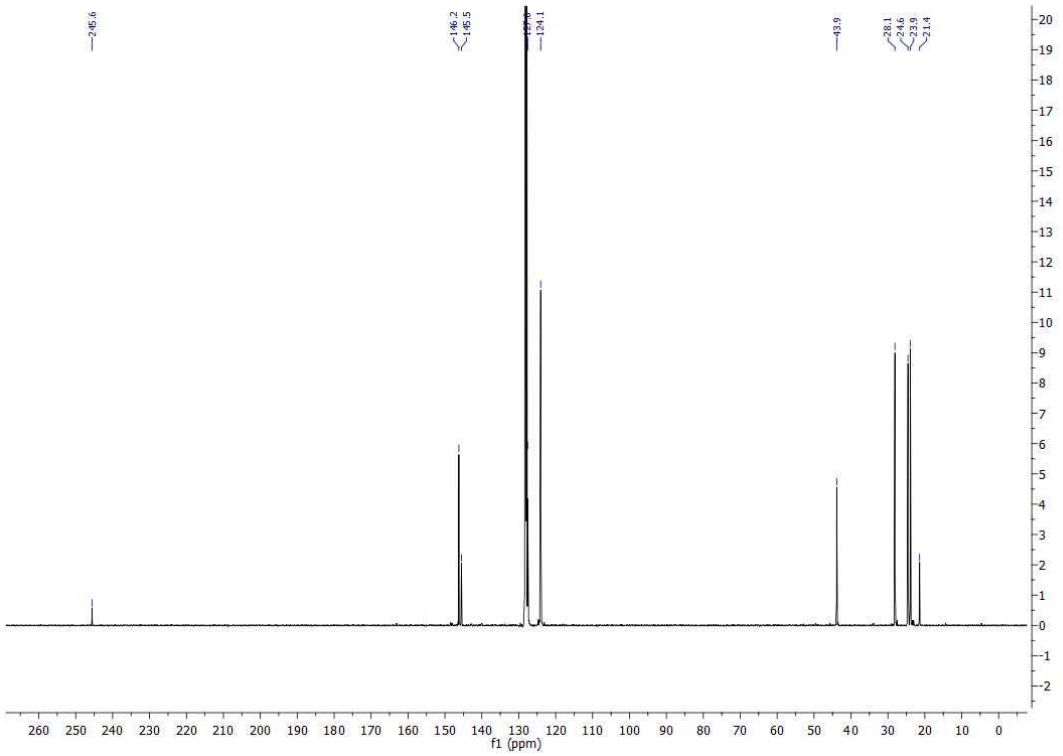
### $^{1}H$




**NHC-6**

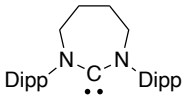



### $^{13}C\{^{1}H\}$



**NHC-7**

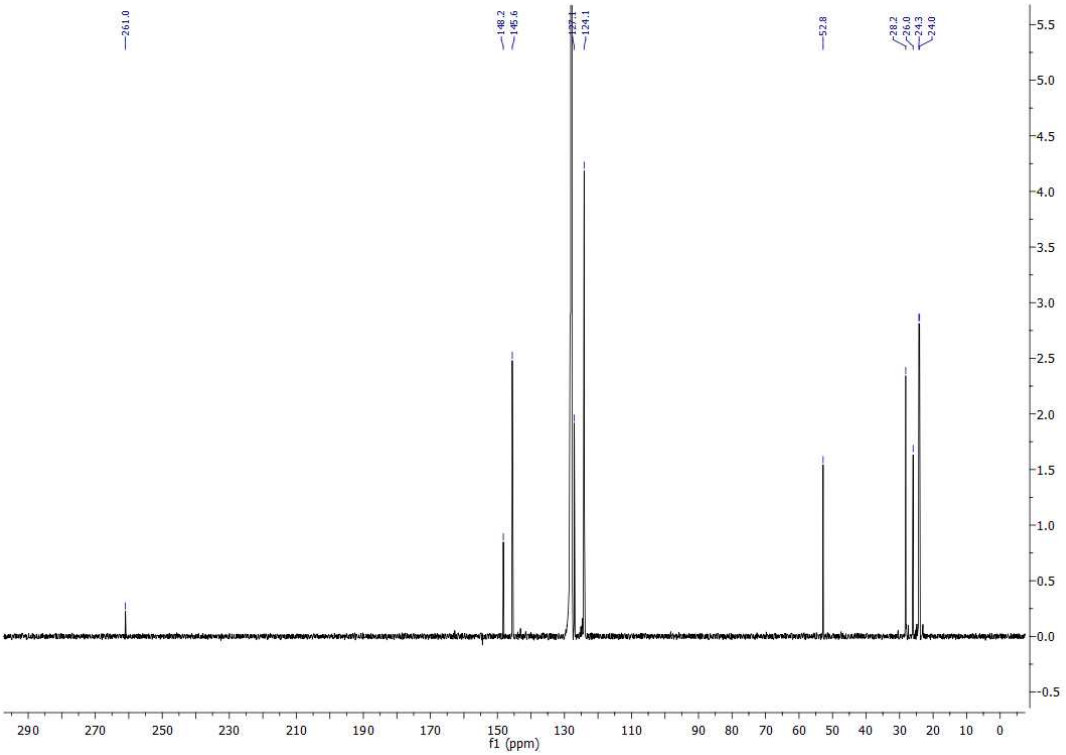
**$^{1}H$**




**NHC-7**

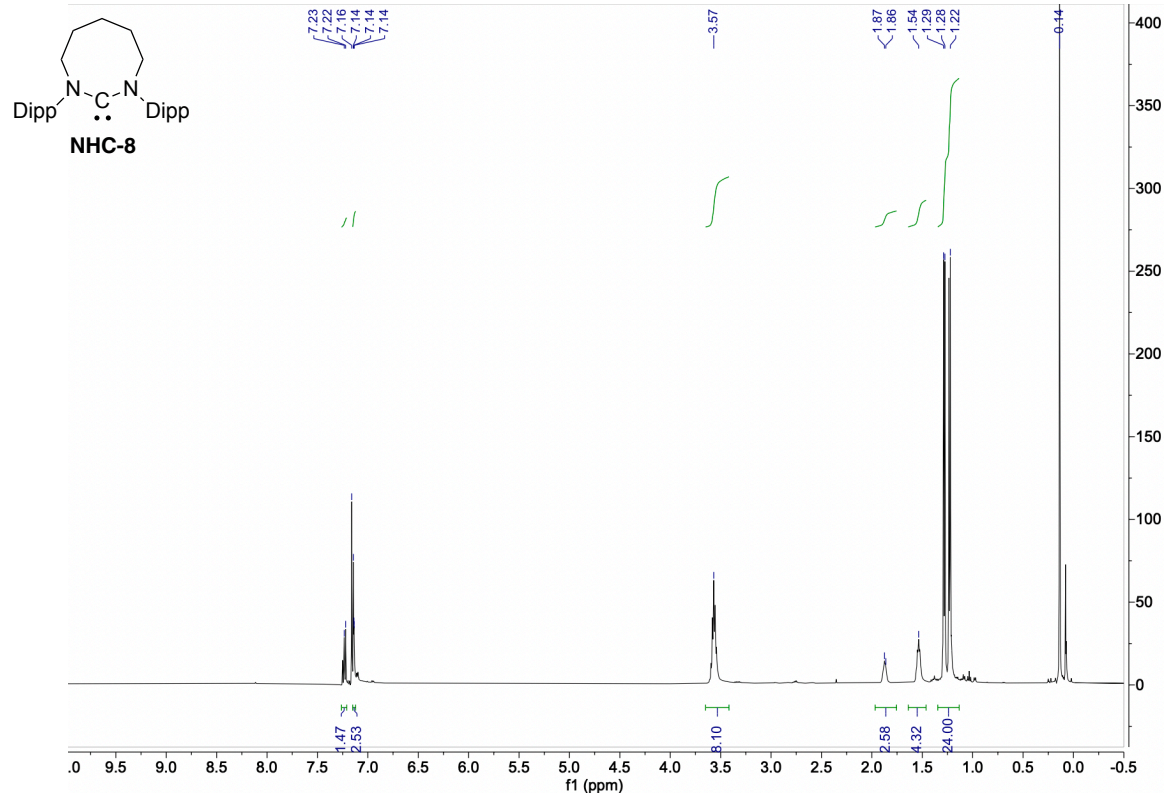



**$^{13}C\{^{1}H\}$**

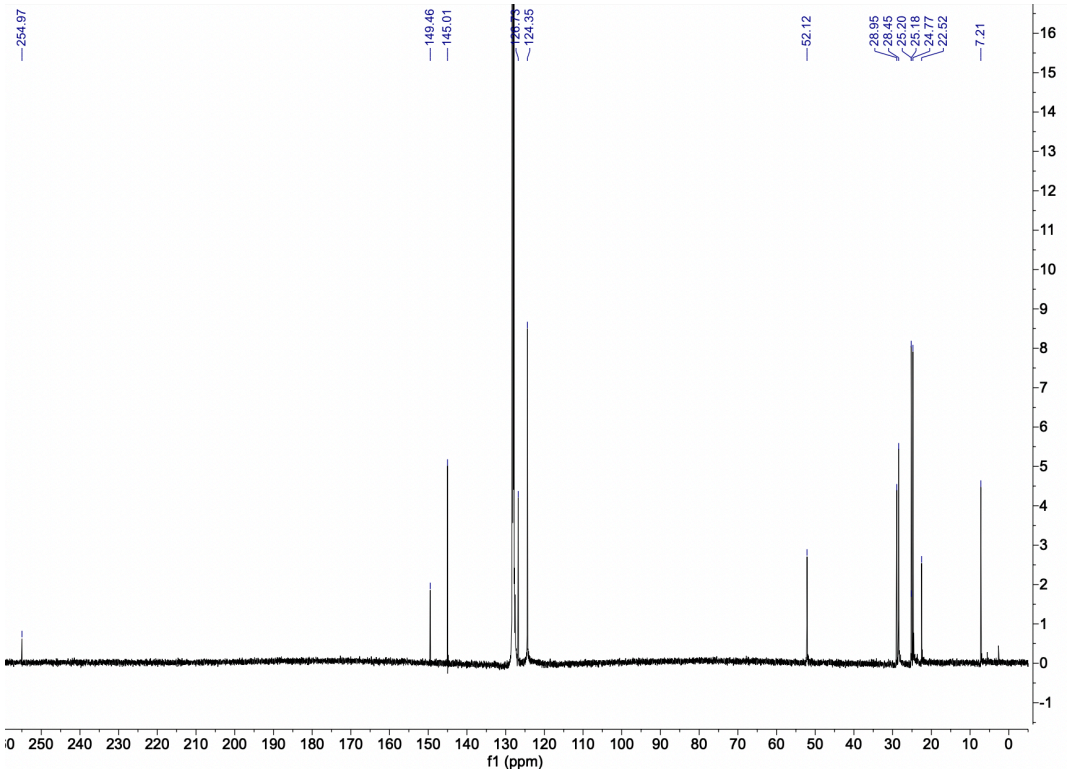


## NHC-8

### $^{1}H$

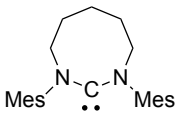



### $^{13}C\{^{1}H\}$

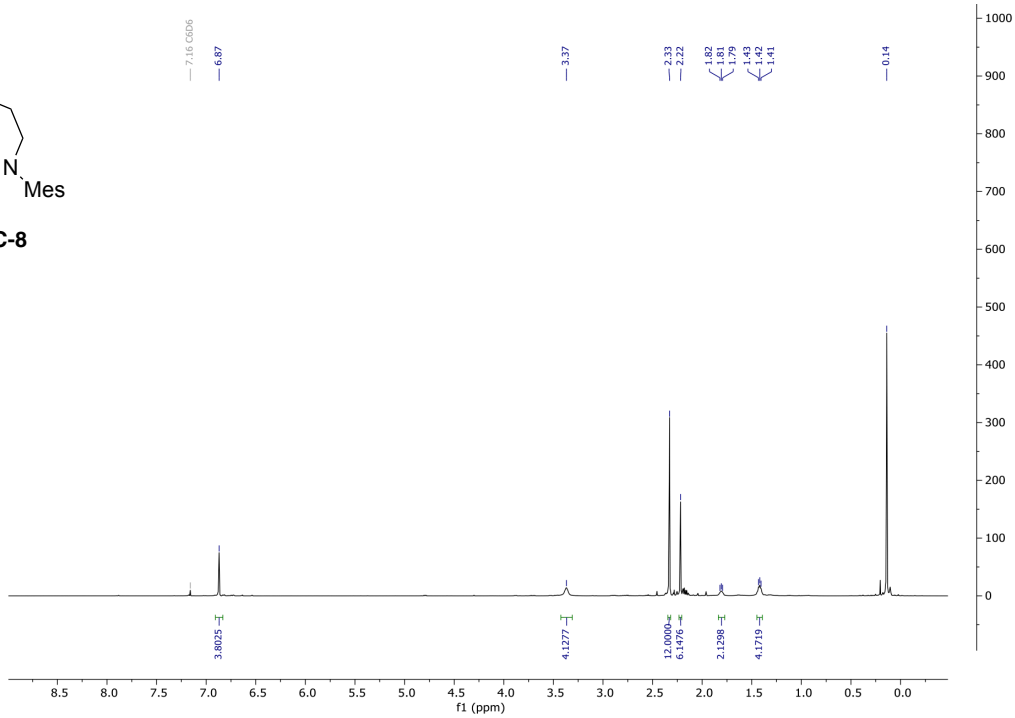


## $^{Mes}$NHC-8

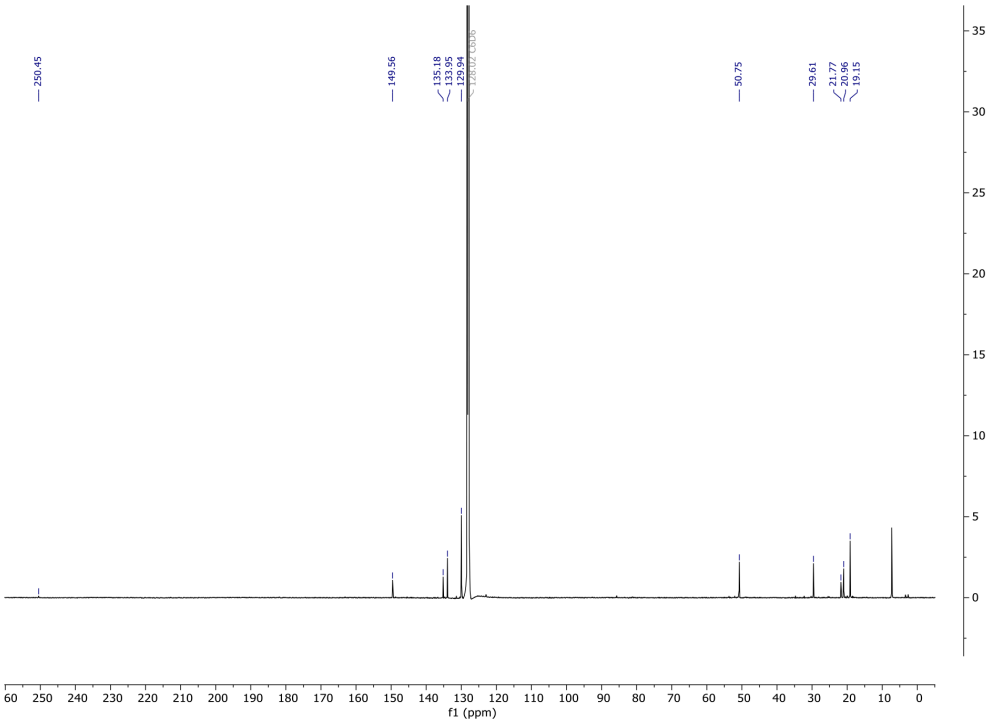
### $^{1}$H




$^{Mes}$NHC-8




### $^{13}$C{$^{1}$H}

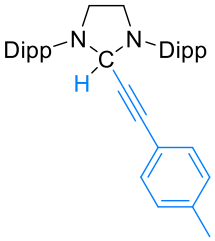


# III. Comparison of Reactivity Between NHC-5,6,7,8

## A. Reactions Between NHC and Alkynes

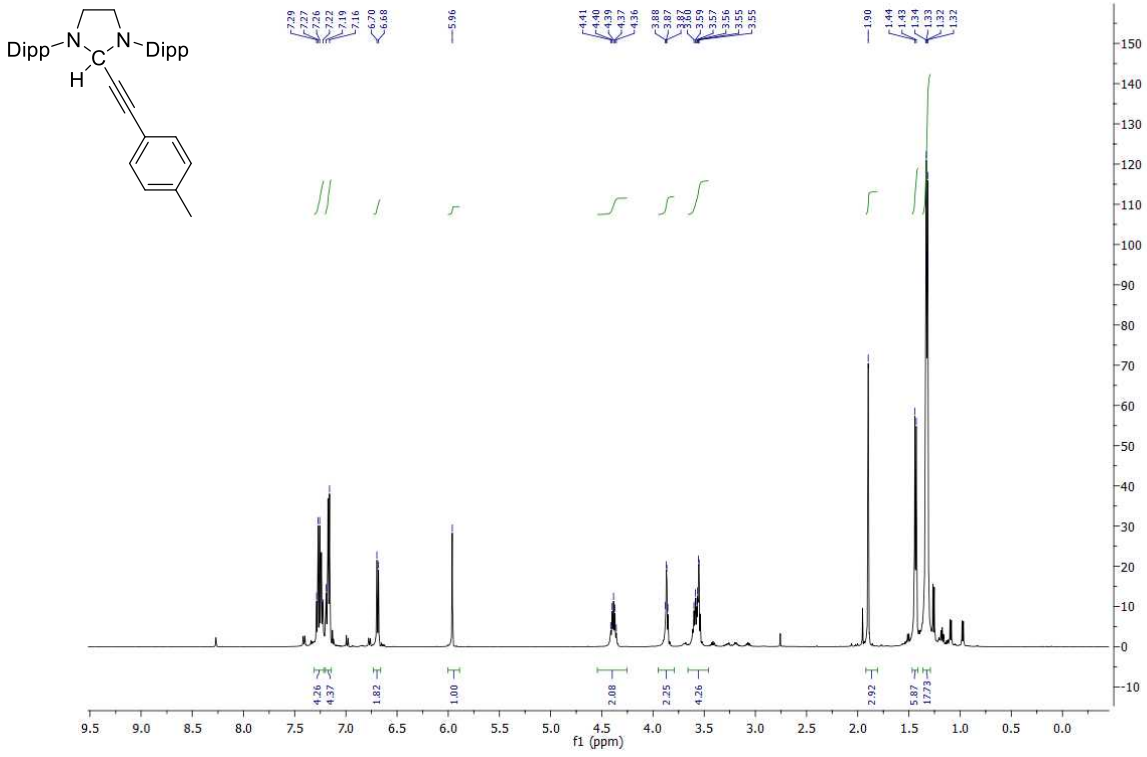
### A.1. NHC-5 with *p*-Tolylacetylene (1e)

$C_6D_6$ (0.7 mL) was added under argon to a J.Young NMR tube containing free carbene NHC-5 (39 mg, 1.0 eq) and 4-ethynyltoluene (13 µL, 1.05 eq). The tube was shaken for 5 minutes at room temperature then heated at 80°C. NMR of the resulting colorless solution showed quantitative formation of the carbene(H)(*p*-tolylacetylene) adduct after 4 hours. *Note: At room temperature no reaction is observed after 1h.*

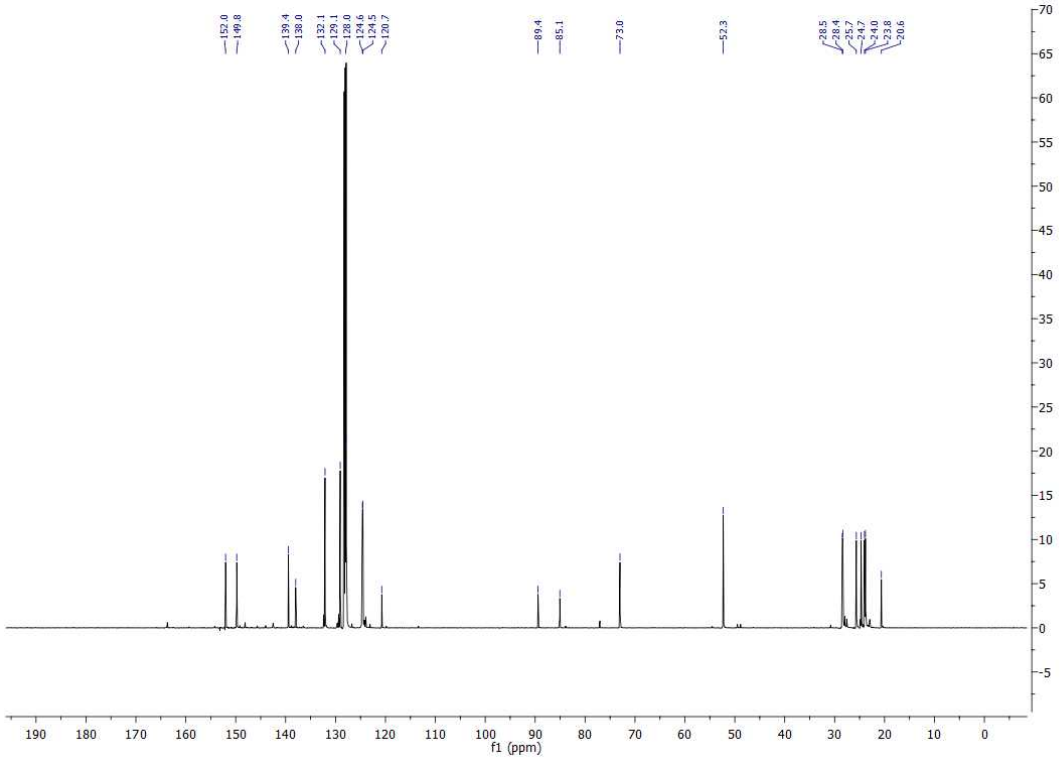



**NHC-5(H)(*p*-tolylacetylene) Adduct:** $^1$H NMR (500 MHz, $C_6D_6$) δ = 7.22-7.29 (m, 4H), 7.16-7.19 (m, 4H), 6.69 (d, 2H, J=8.0Hz), 5.96 (s, 1H), 4.39 (sept, 2H, J=7.0Hz), 3.87 (m, 2H), 3.59 (sept, 2H, J=7.0Hz), 3.56 (m, 2H), 1.90 (s, 3H), 1.43 (d, 6H, J=7.0Hz), 1.33 (d, 6H, J=7.0Hz), 1.32 (d, 6H, J=7.0Hz), 1.32 (d, 6H, J=7.0Hz) $^{13}C\{^1H\}$ NMR (125 MHz, $C_6D_6$) δ = 152.0, 149.8, 139.4, 138.0, 132.1, 129.1, 128.0, 124.6, 124.5, 120.7, 89.4, 85.1, 73.0, 52.3, 28.5, 28.4, 25.7,24.7, 24.0, 23.8, 20.6.

**$^1$H**



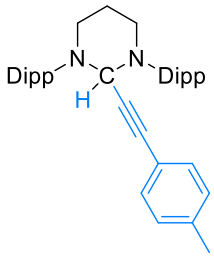
**$^{13}C\{^{1}H\}$**




## A.2. NHC-6 with *p*-Tolylacetylene (1b)

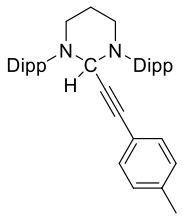
$C_6D_6$ (0.7 mL) was added under argon to a J.Young NMR tube containing free carbene NHC-6 (42 mg, 1.0 eq) and 4-ethynyltoluene (15 µL, 1.05 eq). The tube was shaken for 10 minutes at room temperature. NMR of the resulting colorless solution showed quantitative formation of NHC-6(H)(*p*-tolylacetylene) adduct.

*Note that NHC-6(H)(p-tolylacetylene) adduct did not afford free NHC-6 when heated at 80°C in vacuo and did not demonstrate exchange upon addition of 1-hexyne*.



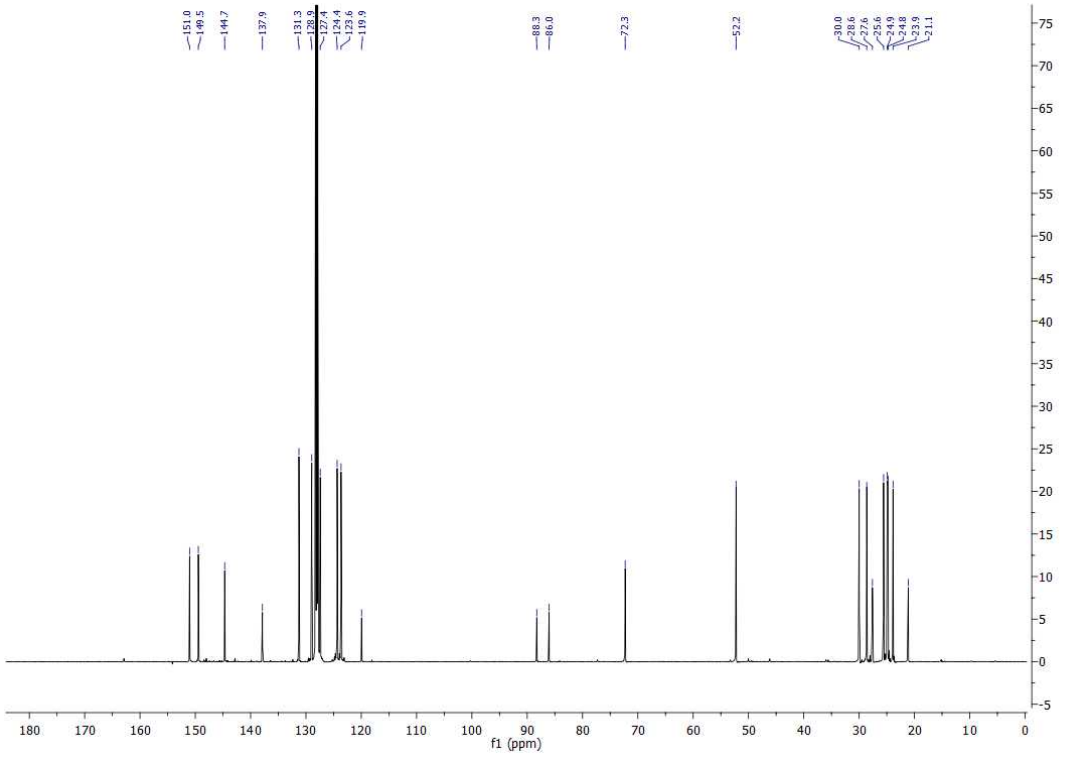

**NHC-6(H)(*p*-tolylacetylene) Adduct:** $^{1}H$ NMR (500 MHz, $C_6D_6$) δ = 7.15-7.19 (m, 4H), 7.03 (dd, 2H, J=6.5Hz), 6.55 (d, 2H, J=8.0Hz), 6.46 (d, 2H, J=8.0Hz), 6.07 (s, 1H), 4.48 (sept, 2H, J=7.0Hz), 3.93 (sept, 2H, J=6.5Hz), 3.38 (m, 4H), 3.13 (m, 2H), 1.69 (s, 3H), 1.36 (d, 6H, J=7.0Hz), 1.36 (d, 6H, J=7.0Hz), 1.29 (d, 6H, J=7.0Hz), 1.24 (d, 6H, J=7.0Hz), 1.23 (m, 2H) $^{13}C\{^{1}H\}$ NMR (125 MHz, $C_6D_6$) δ = 151.0, 149.5, 144.7, 137.9, 131.3, 128.9, 127.4, 124.4, 123.6, 119.9, 88.3, 86.0, 72.3, 52.2, 30.0, 28.6, 27.6, 25.6, 24.9, 24.8, 23.9, 21.1.

**$^{1}H$**


Dipp
N
C
H
N
Dipp

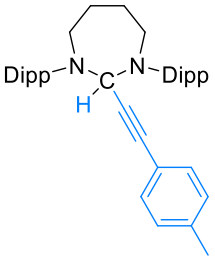

7.19
7.15
7.04
7.03
7.03
7.02
6.55
6.54
6.47
6.45
6.07
4.51
4.49
4.48
4.46
4.45
3.40
3.39
3.38
3.36
3.35
3.14
3.12
1.69
1.37
1.35
1.30
1.29
1.25
1.23
3.80
2.11
1.72
1.67
1.00
2.01
4.24
2.09
2.89
11.96
6.11
7.99
f1 (ppm)

**$^{13}C\{^{1}H\}$**


151.0
149.5
144.7
137.9
131.3
128.9
127.4
124.4
123.6
119.9
88.3
86.0
72.3
52.2
30.0
28.6
27.6
25.6
24.9
24.8
23.9
21.1
f1 (ppm)

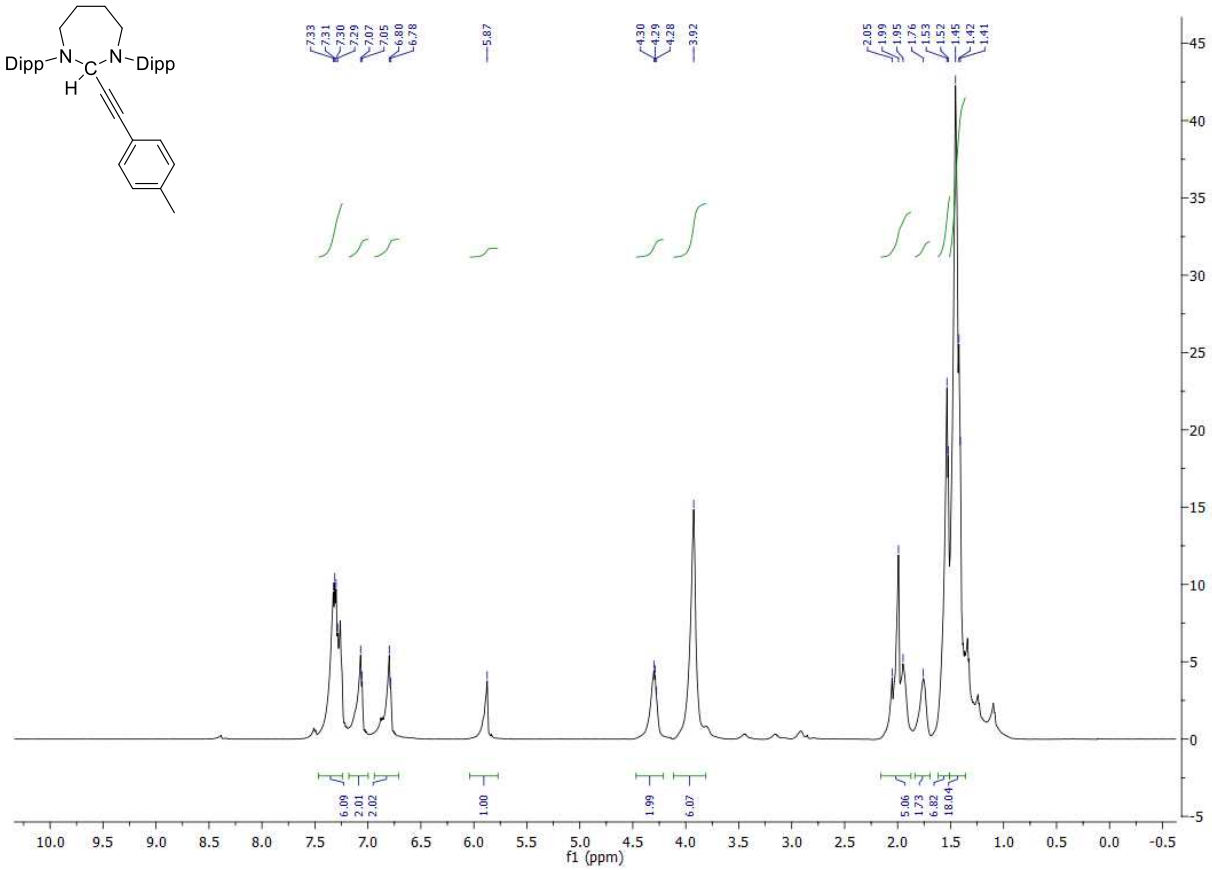
## A.3. NHC-7 with *p*-Tolylacetylene (1c)

$C_6D_6$ (0.7 mL) was added under argon to a J.Young NMR tube containing free carbene NHC-7 (47 mg, 1.0 eq) and 4-ethynyltoluene (14.1 µL, 1.05 eq). The tube was shaken for 10 minutes at room temperature. NMR of the resulting colorless solution showed quantitative formation of NHC-7(H)(*p*-tolylacetylene) adduct. Slow evaporation of $C_6D_6$ under argon gave colorless crystals. Note that the complex $^1$H NMR signals of the aliphatic region of the spectrum can be explained by the presence of conformers. This is supported by the $^{13}$C NMR spectrum which displays only a single species in solution.

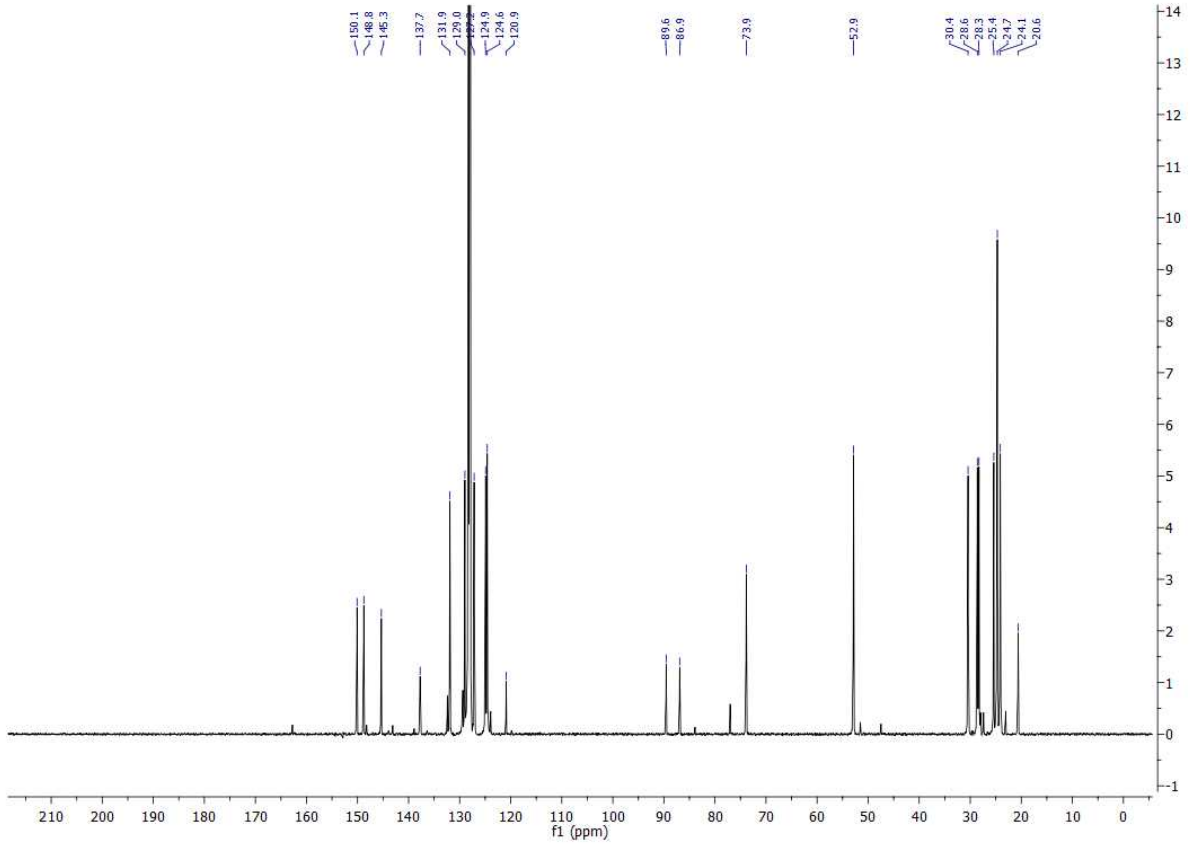



**NHC-7(H)(*p*-tolylacetylene) Adduct:** $^1$H NMR (500 MHz, $C_6D_6$) δ = 7.29-7.33 (m, 6H), 7.06 (d, 2H, J=7.0Hz), 6.79 (d, 2H, J=7.0Hz), 5.87 (s, 1H), 4.30 (sept, 2H, J=6.5Hz), 3.93 (sept, 2H, J=6.5Hz), 3.92 (m, 4H), 1.99 (s, 3H), 1.95-2.05 (m, 2H), 1.72-1.78 (m, 2H), 1.53 (d, 6H, J=6.5Hz), 1.45 (d, 6H, J=6.5Hz), 1.45 (d, 6H, J=6.5Hz), 1.41 (d, 6H, J=6.5Hz) $^{13}$C{$^1$H} NMR (125 MHz, $C_6D_6$) δ = 150.1, 148.8, 145.3, 137.7, 131.9, 129.0, 127.2, 124.9, 124.6, 120.9, 89.6, 86.9, 73.9, 52.9, 30.4, 28.6, 28.3, 25.4, 24.7, 24.7, 24.1, 20.6
HRMS (ESI): m/z calculated for $C_{38}H_{51}N_2$ $[M+H]^+$ 535.4047, found 535.4042.

**$^1$H**



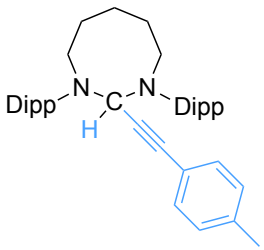
**$^{13}C\{^{1}H\}$**



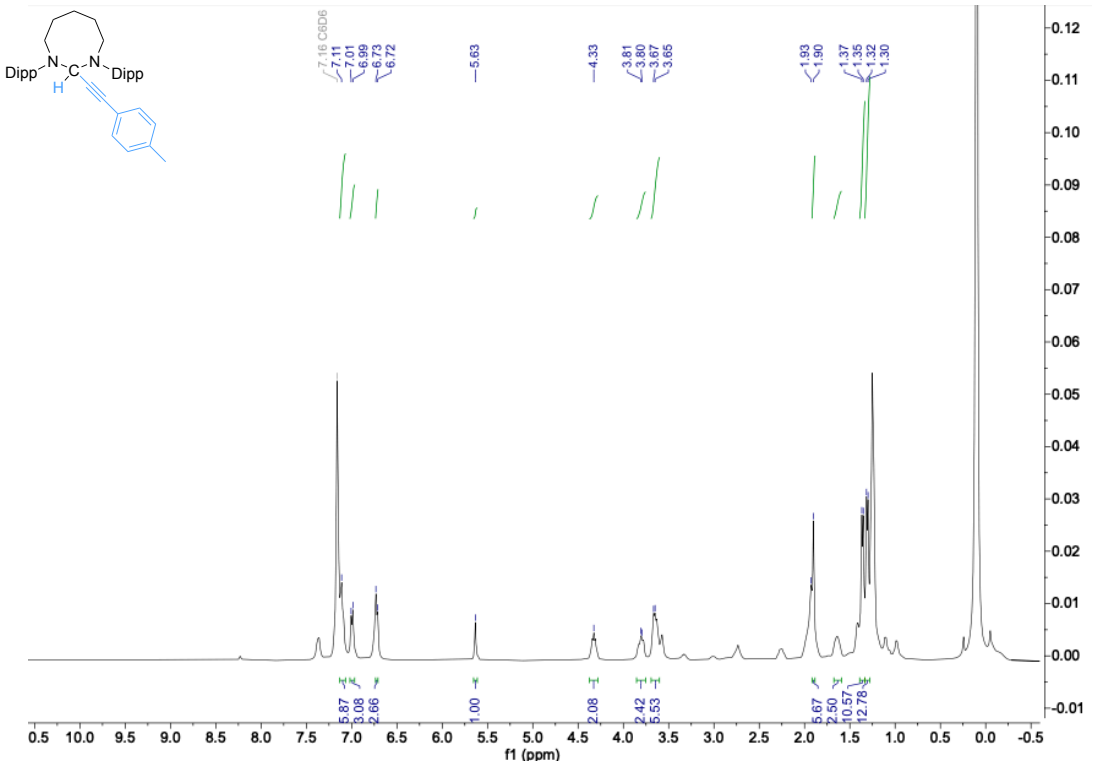

## A.4. NHC-8 with *p*-Tolylacetylene (1d) conformers

$C_6D_6$ (0.7 mL) was added under argon to a J.Young NMR tube containing free carbene NHC-8 (43 mg, 1.0 eq) and 4-ethynyltoluene (13 µL, 1.05 eq). The tube was shaken for 10 minutes at room temperature. NMR of the resulting colorless solution showed quantitative formation of NHC-8(H)(*p*-tolylacetylene) adduct. The NMR contains residual HHMDS that was present with the free NHC-8 carbene. Note that the complex $^{1}H$ NMR signals of the aliphatic region of the spectrum can be explained by the presence of conformers. This is supported by the $^{13}C$ NMR spectrum which only display a single species in solution.

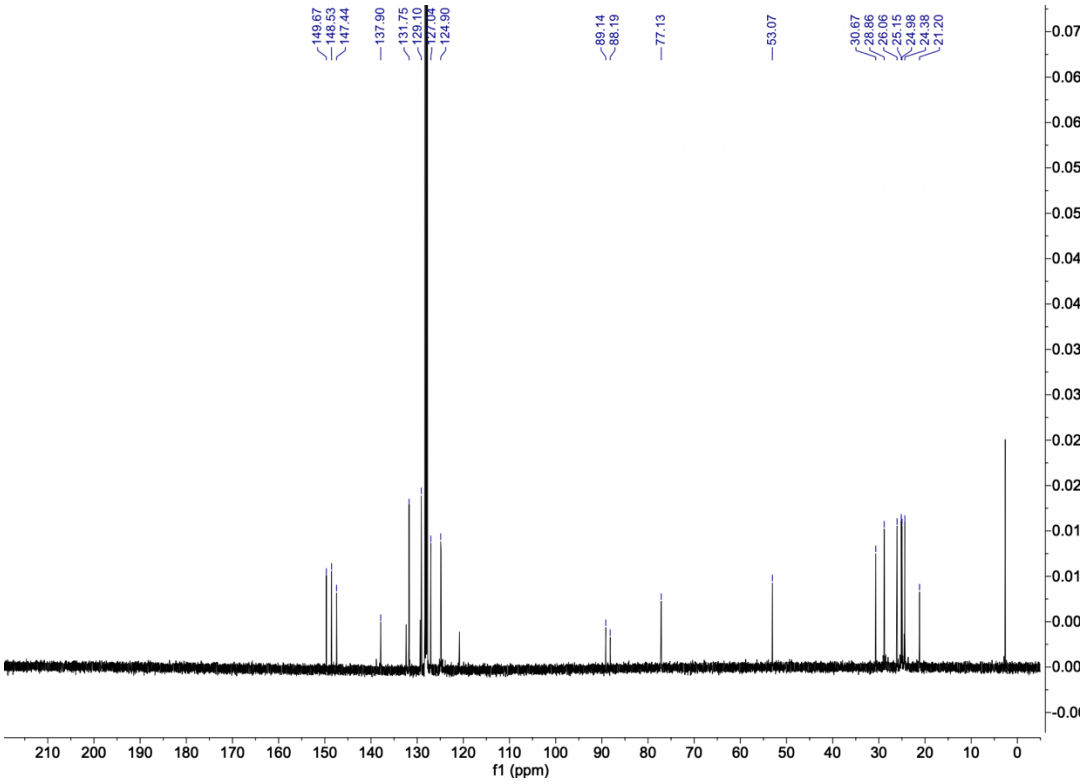
**NHC-8(H)(*p*-tolylacetylene) Adduct:** $^{1}H$ NMR (400 MHz, $C_6D_6$) δ = 7.11-7.16 (m, 6H), 7.00 (d, 2H, J=7.9Hz), 6.73 (d, 2H, J=7.4Hz), 5.63 (s, 1H), 4.33 (m, 2H, J=6.5Hz), 3.81 (m, 2H), 3.66 (m, 4H), 1.93 (s, 3H), 1.90-1.94 (m, 4H), 1.64 (m, 2H), 1.36 (d, 12H, J=6.9Hz), 1.31 (d, 12Hz, J=6.9Hz), $^{13}C\{^{1}H\}$ NMR (100 MHz, $C_6D_6$) δ = 149.7, 148.5, 147.4, 137.9, 131.8, 129.1, 127.0, 124.9, 89.1, 86.2, 77.1, 53.1, 30.7, 28.9, 26.1, 25.2, 25.0, 24.4.



**$^{1}H$**


Dipp
N
C
N
Dipp
H
7.16 C6D6
7.11
7.01
6.99
6.73
6.72
5.63
4.33
3.81
3.80
3.67
3.65
1.93
1.90
1.37
1.35
1.32
1.30
5.87
3.08
2.66
1.00
2.08
2.42
5.53
5.67
2.50
10.57
12.78
f1 (ppm)

**$^{13}C\{^{1}H\}$**

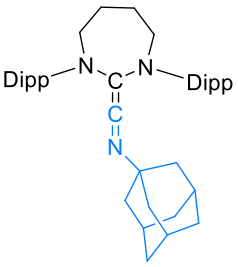

149.67
148.53
147.44
137.90
131.75
129.10
127.04
124.90
89.14
88.19
77.13
53.07
30.67
28.86
26.06
25.15
24.98
24.38
21.20
f1 (ppm)

## B. Reactions Between NHC and Isocyanides

No reaction was observed after 12h by reacting free NHC-5 or NHC-6 with one equivalent of adamantyl isocyanide at room temperature in benzene.

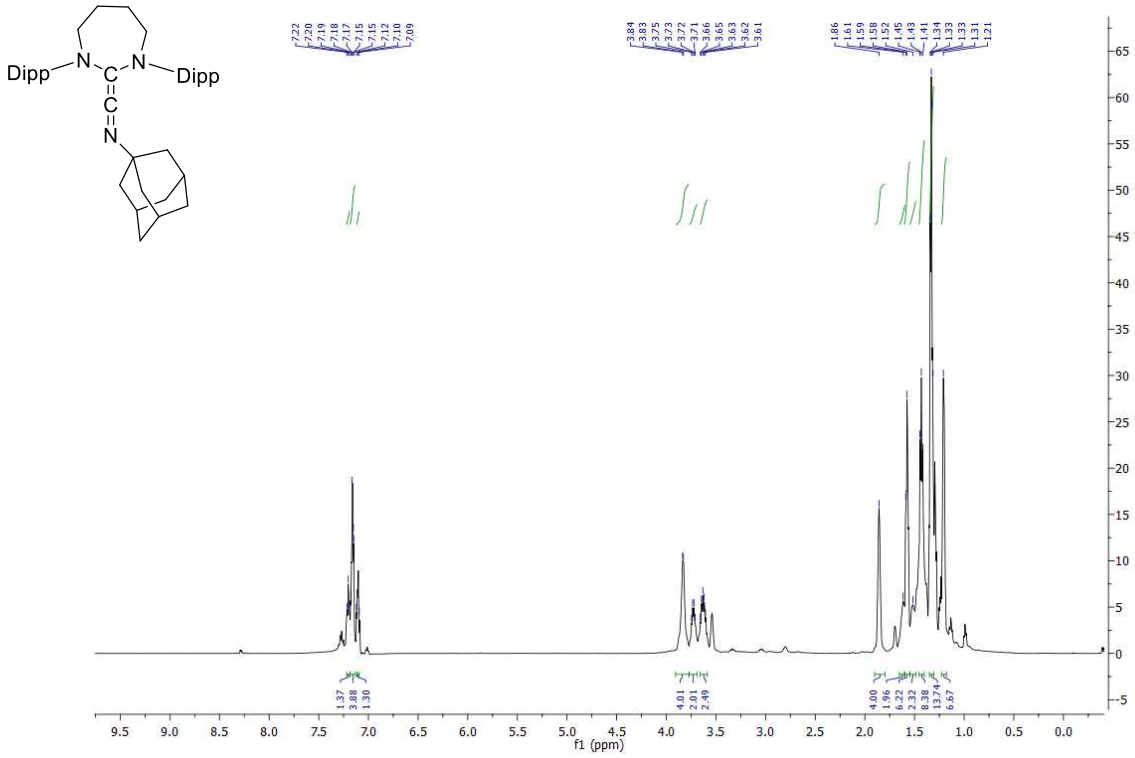
### B.1. NHC-7 with Adamantyl Isocyanide (2b)

$C_6D_6$ (0.7 mL) was added under argon to a J.Young NMR tube containing free carbene NHC-7 (37.1 mg, 1.0 eq) and adamantyl isocyanide (10.9 mg, 1.05 eq). The tube was shaken for 10 minutes at room temperature. NMR of the resulting colorless solution showed quantitative formation of the corresponding ketenimine. Slow evaporation of $C_6D_6$ under argon gave colorless crystals.

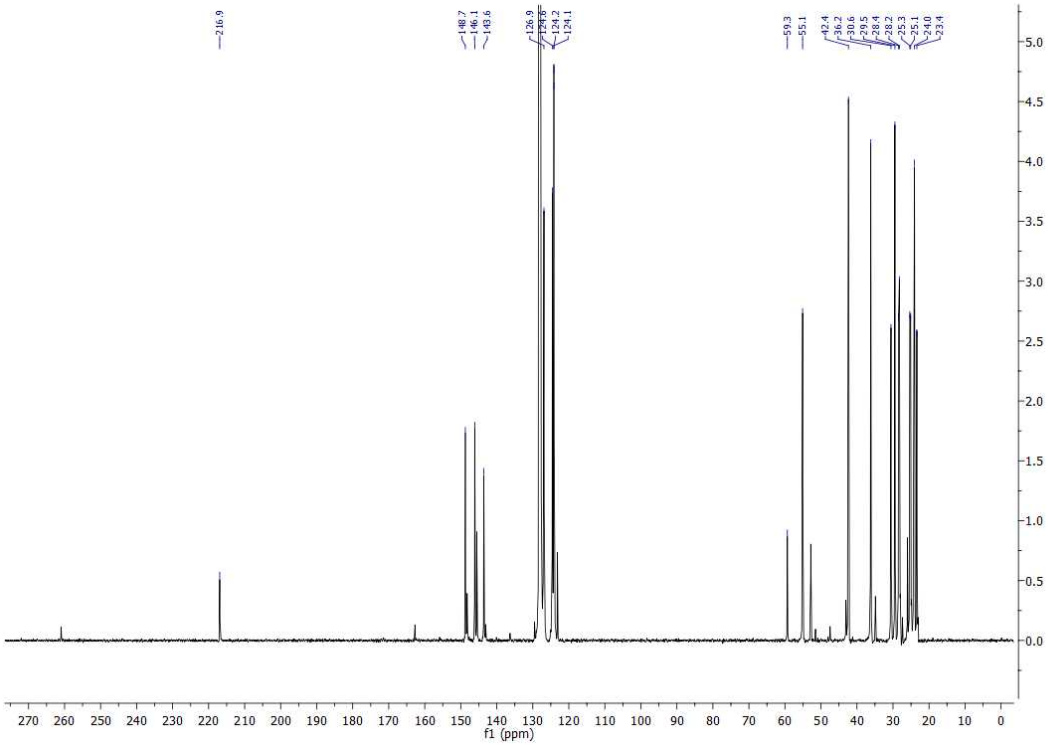



**NHC-7 Adamantyl ketenimine:** $^1$H NMR (500 MHz, $C_6D_6$) δ = 7.20 (t, 1H, J=7.0Hz), 7.17 (dd, 4H, J=7.0Hz), 7.11 (t, 1H, J=7.0Hz), 3.83 (m, 4H), 3.73 (sept, 2H, J=7.0Hz), 3.63 (sept, 2H, J=7.0Hz), 1.86 (m, 4H), 1.61 (m, 2H), 1.58 (d, 6H, J=7.0Hz), 1.52 (m, 2H), 1.43 (t, 8H, J=7.0Hz), 1.38 (m, 1H), 1.33 (d, 6H, J=7.0Hz), 1.32 (d, 6H, J=7.0Hz), 1.21 (d, 6H, J=7.0Hz) $^{13}$C{$^1$H} NMR (125 MHz, $C_6D_6$) δ = 216.9, 148.7, 146.1, 143.6, 126.9, 124.6, 124.2, 124.1, 59.3, 55.1, 42.4, 36.2, 30.6, 29.5, 28.4, 28.2, 25.3, 25.1, 24.0, 23.4 HRMS (ESI): m/z calculated for $C_{40}H_{58}N_3$ $[M+H]^+$ 580.4625, found 580.4620.

**$^1$H**



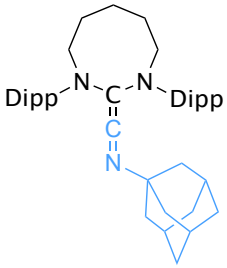
**$^{13}C\{^{1}H\}$**



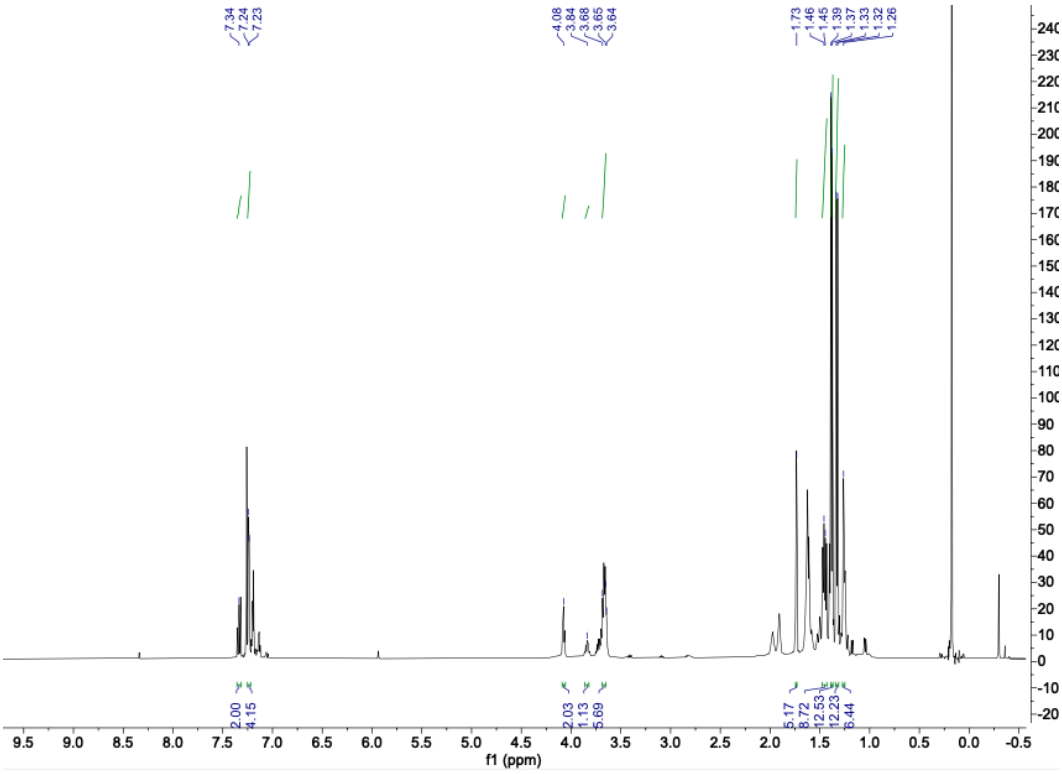

## B.2. NHC-8 with Adamantyl Isocyanide (2c)

$C_6D_6$ (0.7 mL) was added under argon to a J.Young NMR tube containing free carbene NHC-8 (76.2 mg, 1.0 eq) and adamantyl isocyanide (31.2 mg, 1.05 eq). The tube was shaken for 10 minutes and then left to stand for 1 hour at room temperature. NMR of the resulting yellow solution showed quantitative formation of the corresponding ketenimine.

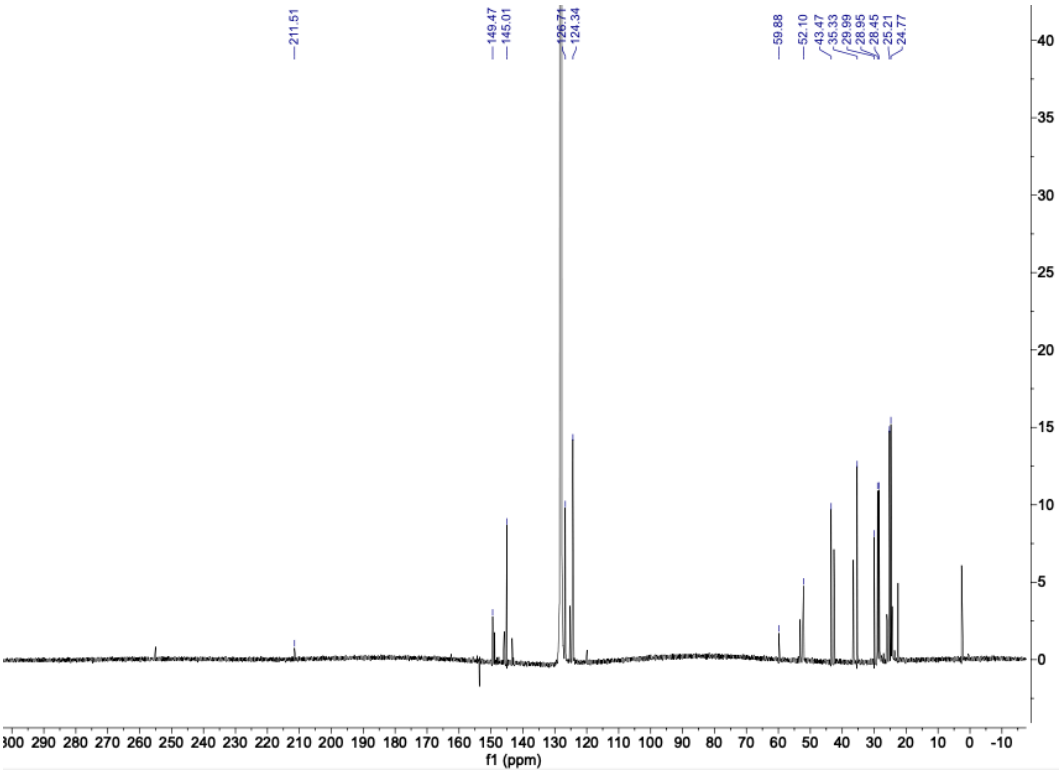
**NHC-8 2,6-Dimethylphenyl ketenimine:** $^{1}H$ NMR (500 MHz, $C_6D_6$) δ = 7.34 (t, 2H, J=7.5Hz), 7.23 (d, 4H, J=7.5Hz), 4.08 (m, 4H), 3.84 (s, 1H, J=6.6Hz), 3.64-3.68 (m, 5H), 1.73 (m, 4H), 1.44-1.47 (m, 4H), 1.38 (d, 12H, J=6.6Hz), 1.33(d, 12H, J=6.6Hz), 1.26 (m, 6H) $^{13}C\{^{1}H\}$ NMR (125 MHz, $C_6D_6$) δ = 211.5149.5, 145.0, 126.7, 124.3, 5939, 52.1, 34.5, 35.3, 29.9, 28.9, 28.5, 25.2, 24.8.




**$^{1}H$**


7.34
7.24
7.23
4.08
3.84
3.68
3.65
3.64
1.73
1.46
1.45
1.39
1.37
1.33
1.32
1.26
2.00
4.15
2.03
1.13
5.69
5.17
8.72
12.53
12.23
8.44
f1 (ppm)

**$^{13}C\{^{1}H\}$**

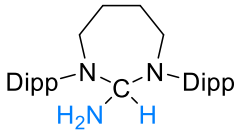

211.51
149.47
145.01
126.71
124.34
59.88
52.10
43.47
35.33
29.99
28.95
28.45
25.21
24.77
f1 (ppm)

## C. Reactions Between NHC and Ammonia

No reaction was observed with free NHC-5, NHC-6, or NHC-8 in the presence of ammonia.

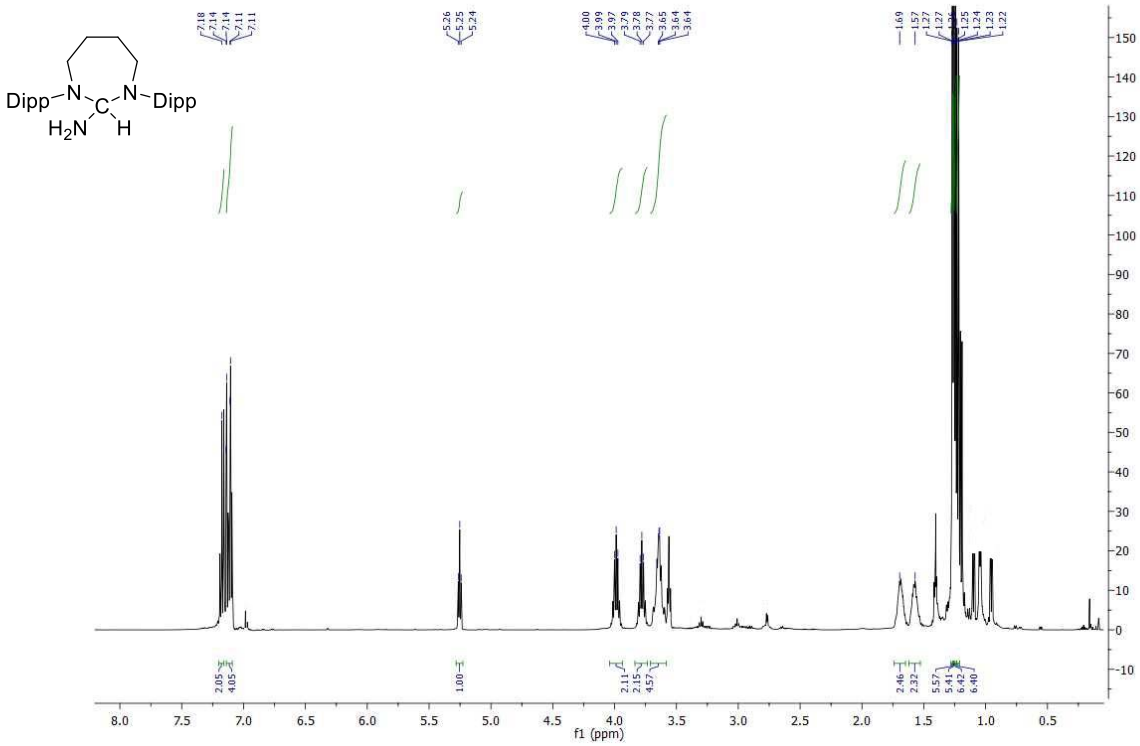
### C.1. NHC-7 with Ammonia (3a)

In a dry pressure Schlenk under argon, free NHC-7 (35 mg) was dissolved in anhydrous THF. The solution was degassed 3 times. $NH_3$ (1 bar) was added at -47°C. Then the solution was stirred overnight from -47°C to room temperature. The solvent was removed under vacuum and NHC-7(H)($NH_2$) adduct was obtained as a yellowish solid – quantitative reaction. Slow diffusion of pentane into a saturated solution of NHC-7(H)($NH_2$) adduct in $C_6D_6$ under argon gave colorless crystals.

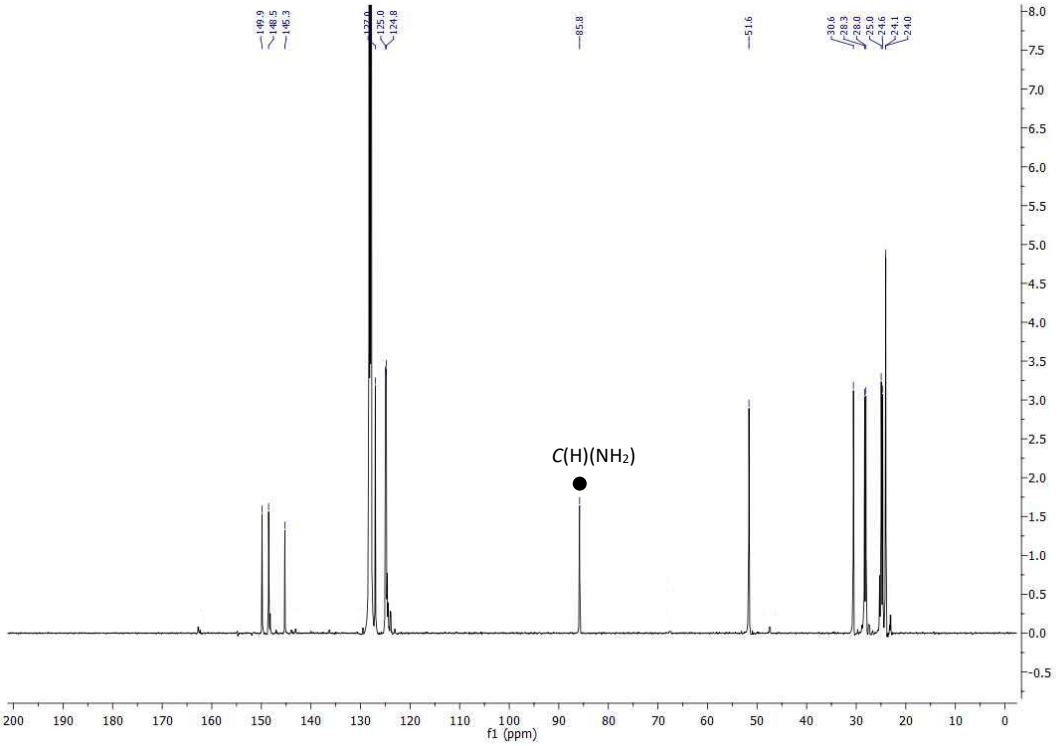



**<u>NHC-7(H)($NH_2$) Adduct:</u>** $^1$H NMR (500 MHz, $C_6D_6$) δ = 7.18 (t, 2H, J=7.5Hz), 7.10-7.12 (m, 4H), 5.25 (t, 1H, J=6.0Hz), 3.99 (sept, 2H, J=6.5Hz), 3.78 (sept, 2H, J=6.5Hz), 3.64 (m, 4H), 1.69 (m, 2H), 1.57 (m, 2H) 1.27 (d, 6H, J=7.5Hz), 1.26 (d, 6H, J=7.5Hz), 1.24 (d, 6H, J=7.5Hz), 1.23 (d, 6H, J=7.5Hz) $^{13}$C{$^1$H} NMR (125 MHz, $C_6D_6$) δ = 149.9 (C), 148.5 (C), 145.3 (C), 127.0 (CH), 125.0 (CH), 124.8 (CH), 85.8 (CH), 51.6 ($CH_2$), 30.6 ($CH_2$), 28.3 (CH), 28.0 (CH), 25.0 ($CH_3$), 24.6 ($CH_3$), 24.1 ($CH_3$), 24.0 ($CH_3$) HRMS (ESI): m/z calculated for C29H43N2 [M-NH3+H]+ 419.3421, found 419.3416.

**$^1$H**



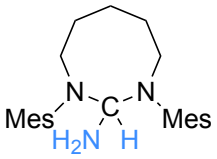
**$^{13}C\{^{1}H\}$**



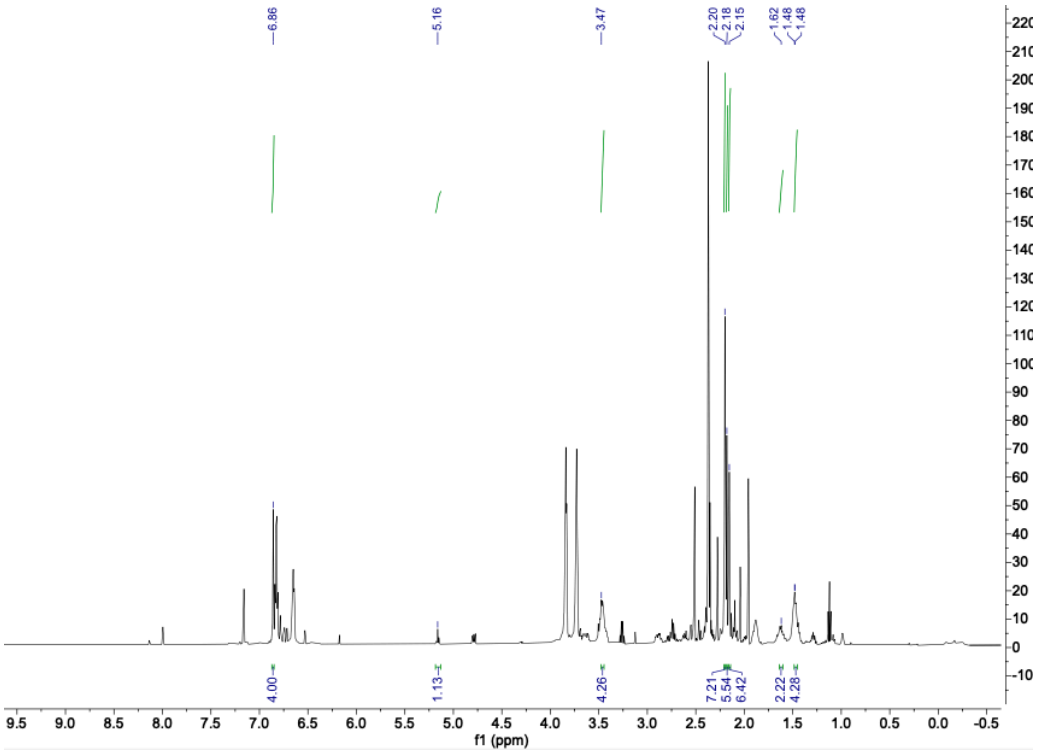

## C.2. $^{Mes}$NHC-8 with Ammonia (3c)

In a dry J Young NMR tube in an Ar-filled glovebox, free $^{Mes}$NHC-8 (35 mg) was dissolved in $C_6D_6$. The NMR tube was brought out of the glovebox and the solution was degassed 3 times (Freeze/Pump/Thaw). $NH_3$ (~2 bar) was added at -78°C. Then the solution was slowly warmed to room temperature and carefully inverted multiple times to mix. Compound **3c** was too reactive to be isolated and was characterized in situ.

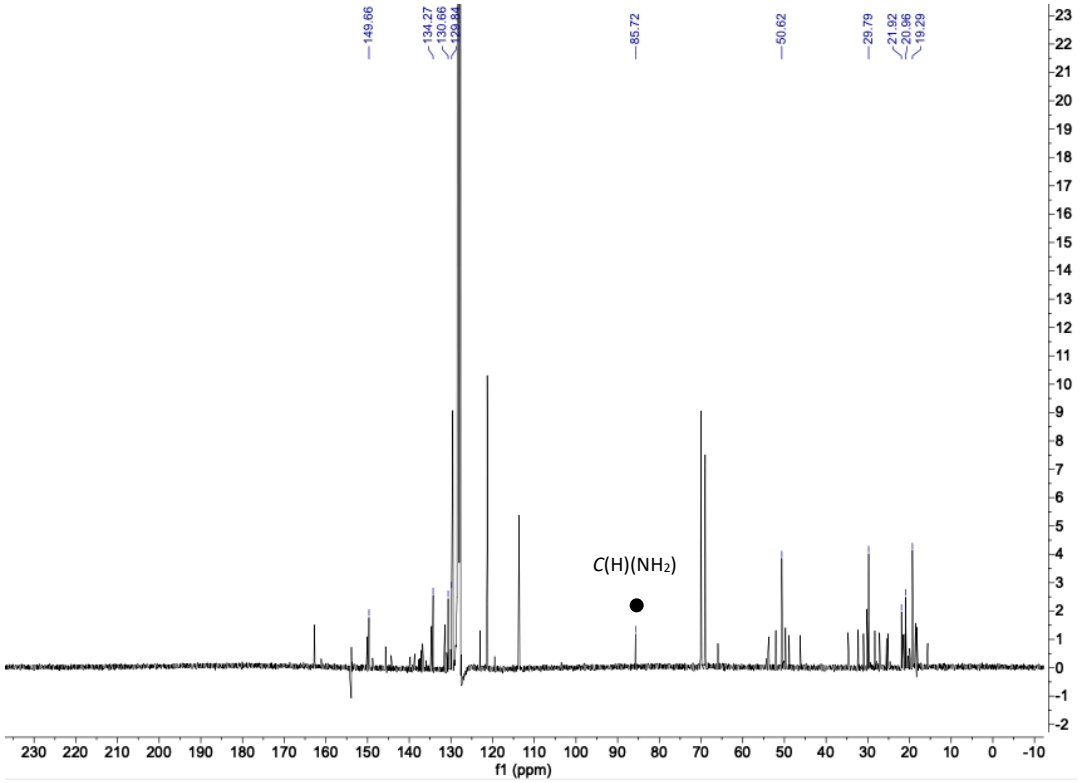
**$^{Mes}$NHC-8(H)($NH_2$) Adduct:** $^{1}$H NMR (500 MHz, $C_6D_6$) δ = 6.86 (s, 4H), 5.16 (t, 1H, J=5.5Hz), 3.47 (m, 4H), 2.20 (s, 6H), 2.18 (s, 6H), 2.15 (s, 6H), 1.62 (m, 2H), 1.48 (m, 4H). $^{13}C\{^{1}H\}$ NMR (125 MHz, $C_6D_6$) δ = 149.7, 134.3, 130.7, 129.8, 85.7, 50.6, 29.8, 21.9, 20.9, 19.3.



**$^{1}H$**


6.86
5.16
3.47
2.20
2.18
2.15
1.62
1.48
1.48
4.00
1.13
4.26
7.21
5.54
6.42
2.22
4.28
f1 (ppm)

**$^{13}C\{^{1}H\}$**

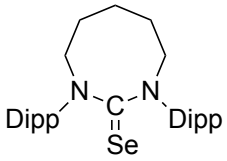

149.66
134.27
130.66
129.84
85.72
50.62
29.79
21.92
20.96
19.29
C(H)(NH2)
f1 (ppm)

## D. Synthesis of NHC-Selenium Adducts

### D.1. NHC-8.HBr with Selenium (4a)

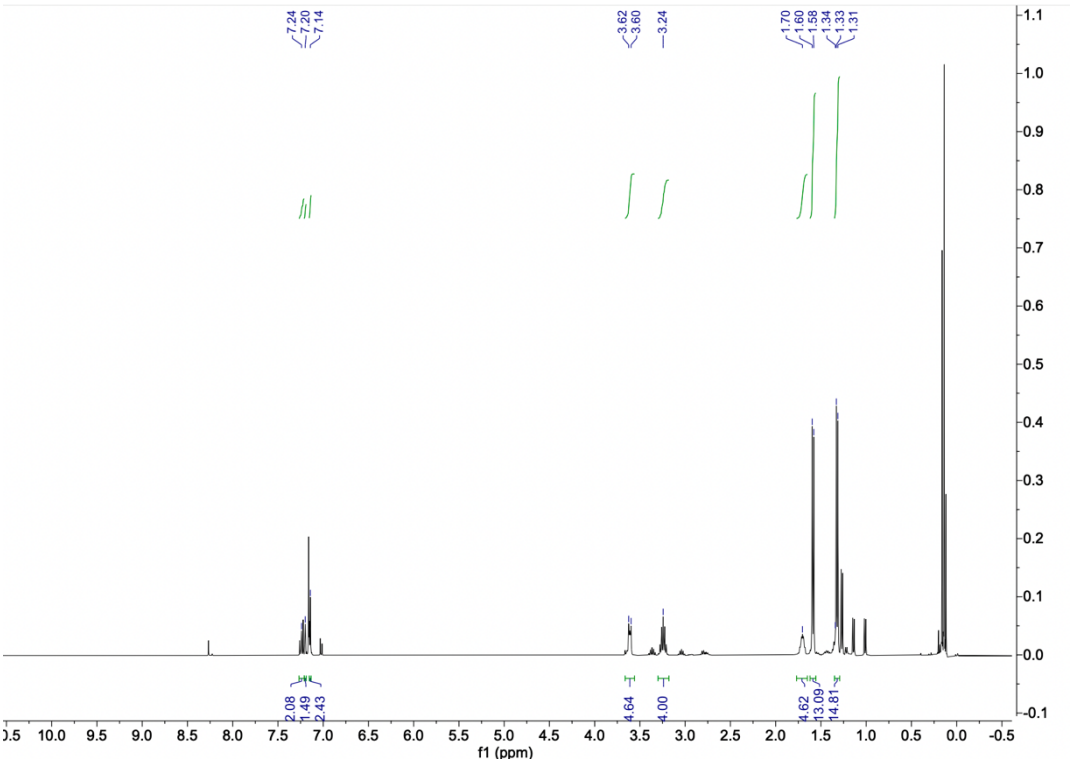
In a 20 mL scintillation vial equipped with mini magnetic stir bar, NHC-8.HBr (51 mg, 1.0 eq), KHMDS (22 mg, 1.1 eq), selenium (15 mg, 2.0 eq), and THF (2.0 mL) were added. The solution was stirred overnight. The solution was filtered and all volatiles removed under vacuum. The resulting solid was redissolved in $C_6D_6$ and the solution allowed to slowly evaporate to give off-white crystals. NMR shows presence of HHMDS and minor amounts of NHC-$8^H$, likely from some hydrolysis.

**NHC-8(Se) Adduct:** $^1$H NMR (500 MHz, $C_6D_6$) δ = 7.24 (t, 2H, J=6.9Hz), 7.20 (m, 2H), 7.14 (d, 2H, J=6.9Hz), 3.61 (m, 4H), 3.24 (sept, 4H, J=7.0Hz), 1.70 (m, 4H), 1.59 (d, 12H, J=7.0Hz), 1.34 (m, 2H) 1.32 (d, 12H, J=7.0Hz). $^{13}$C{$^1$H} NMR (125 MHz, $C_6D_6$) δ = 186.6, 147.5, 144.6, 127.8, 124.9, 55.6, 29.5, 26.1, 24.9, 24.7. $^{77}$Se NMR (76.27 MHz, $C_6D_6$): 571.7.

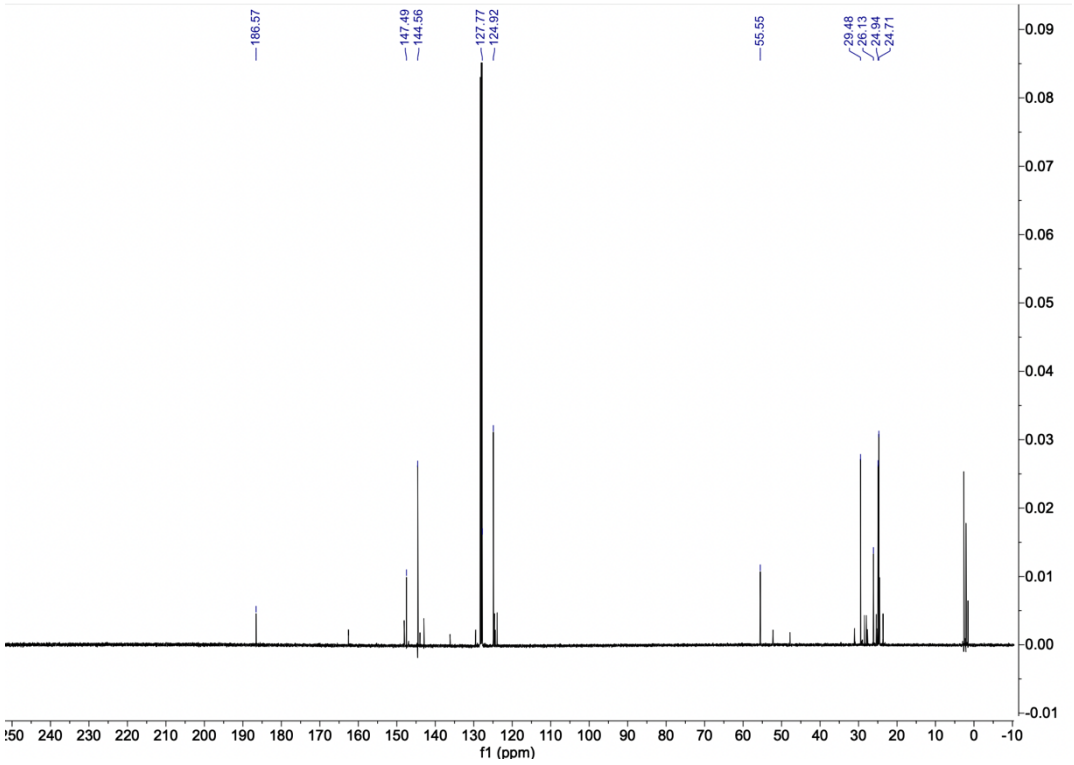



**NHC-8(Se)**

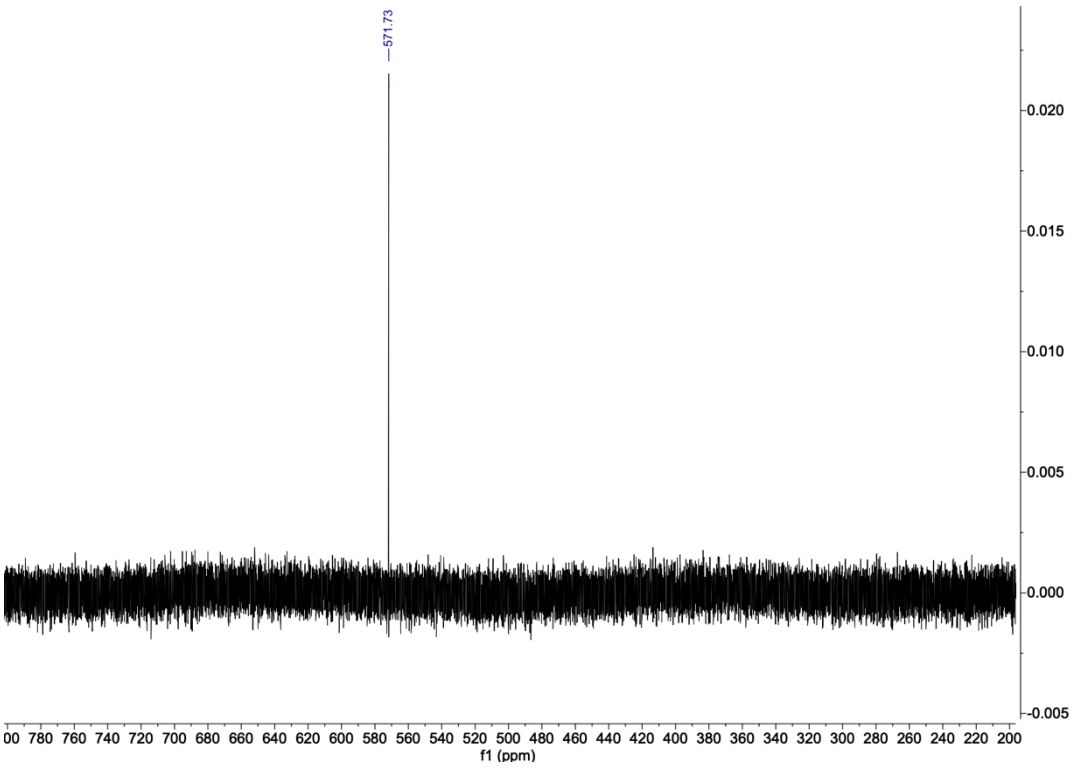
**$^1$H**



**$^{13}C\{^{1}H\}$**


186.57
147.49
144.56
127.77
124.92
55.55
29.48
26.13
24.94
24.71
f1 (ppm)

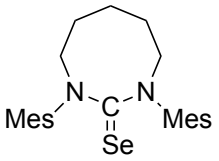
**$^{77}Se$**


571.73
f1 (ppm)

## D.2. $^{Mes}$NHC-8.HBr with Selenium (4b)

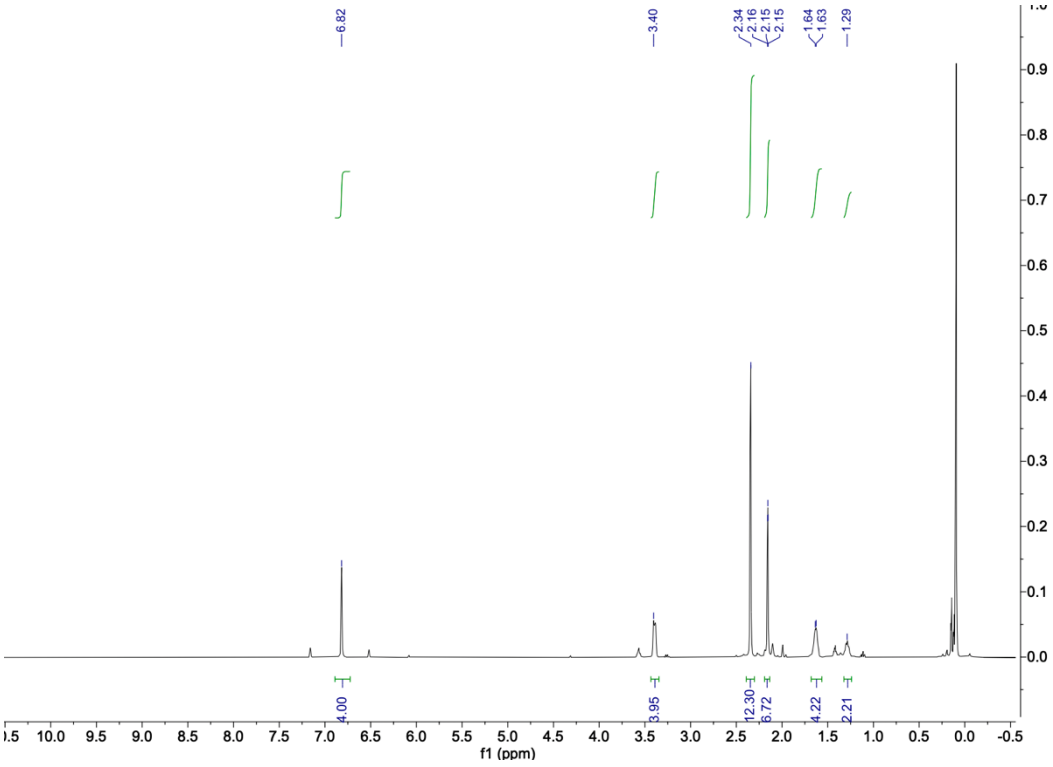
In a 20 mL scintillation vial equipped with mini magnetic stir bar, $^{Mes}$NHC-8.HBr (43 mg, 1.0 eq), KHMDS (22 mg, 1.1 eq), selenium (15 mg, 2.0 eq), and THF (2.0 mL) were added. The solution was stirred overnight. The solution was filtered and all volatiles removed under vacuum. The resulting solid was redissolved in $C_6D_6$ and the solution allowed to slowly evaporate to give off-white crystals.

**$^{Mes}$NHC-8(Se) Adduct:** $^{1}$H NMR (500 MHz, $C_6D_6$) δ = 6.82 (s, 4H), 3.40 (m, 4H), 2.34 (s, 12H), 2.15 (s, 6H), 1.63 (m, 4H), 1.29 (m, 2H). $^{13}C\{^{1}H\}$ NMR (125 MHz, $C_6D_6$) δ = 183.9, 147.2, 136.0, 134.6, 130.2, 54.2, 26.2, 24.1, 21.1, 19.5. $^{77}$Se NMR (76.27 MHz, $C_6D_6$): 437.9.

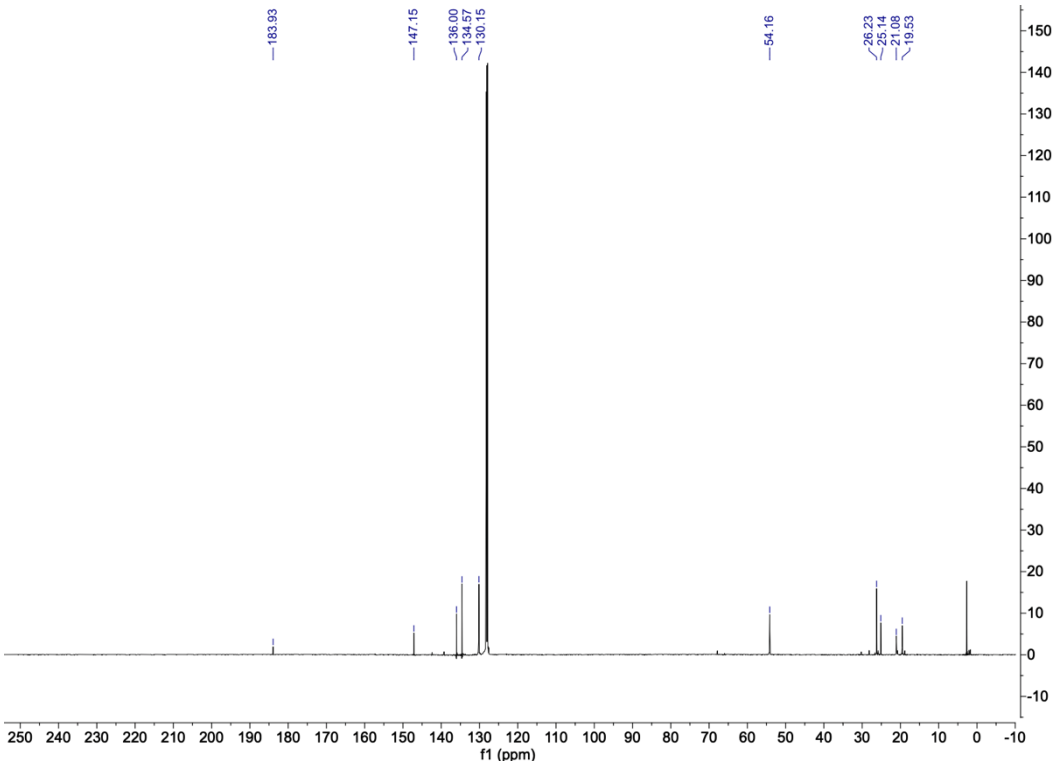



**$^{Mes}$NHC-8(Se)**

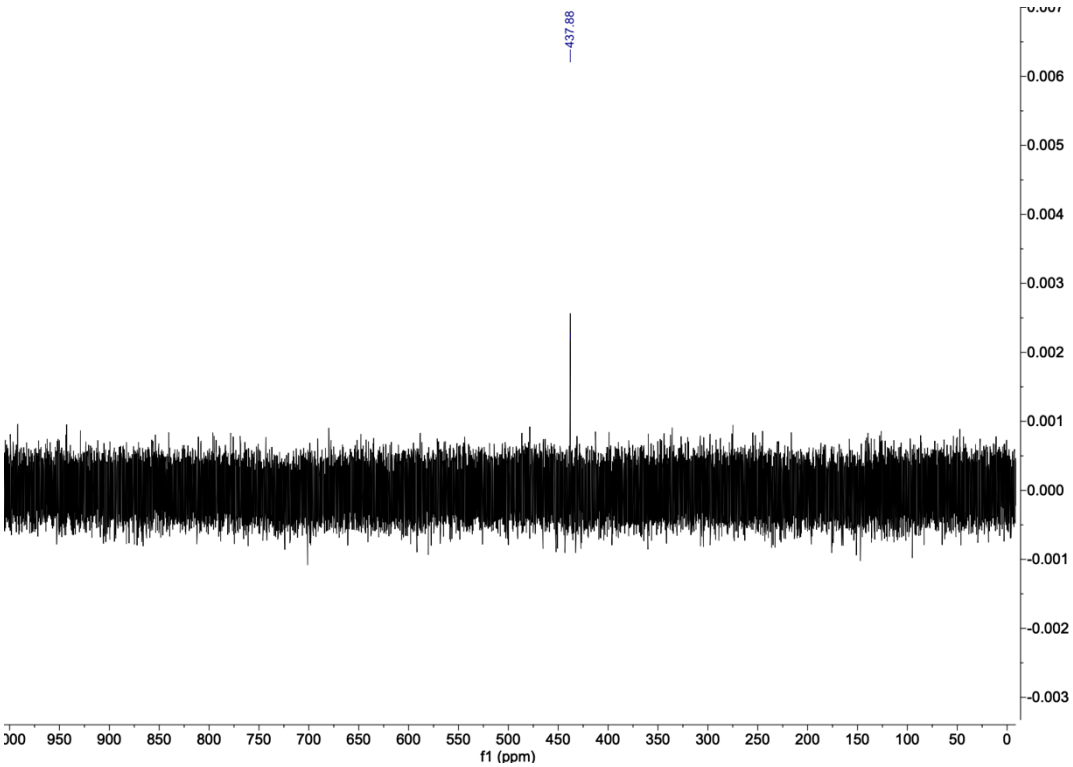
**$^{1}$H**



**$^{13}C\{^{1}H\}$**

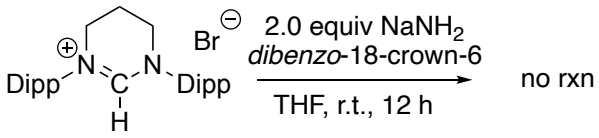

183.93
147.15
136.00
134.57
130.15
54.16
26.23
25.14
21.08
19.53
f1 (ppm)

**$^{77}Se$**


437.88
f1 (ppm)

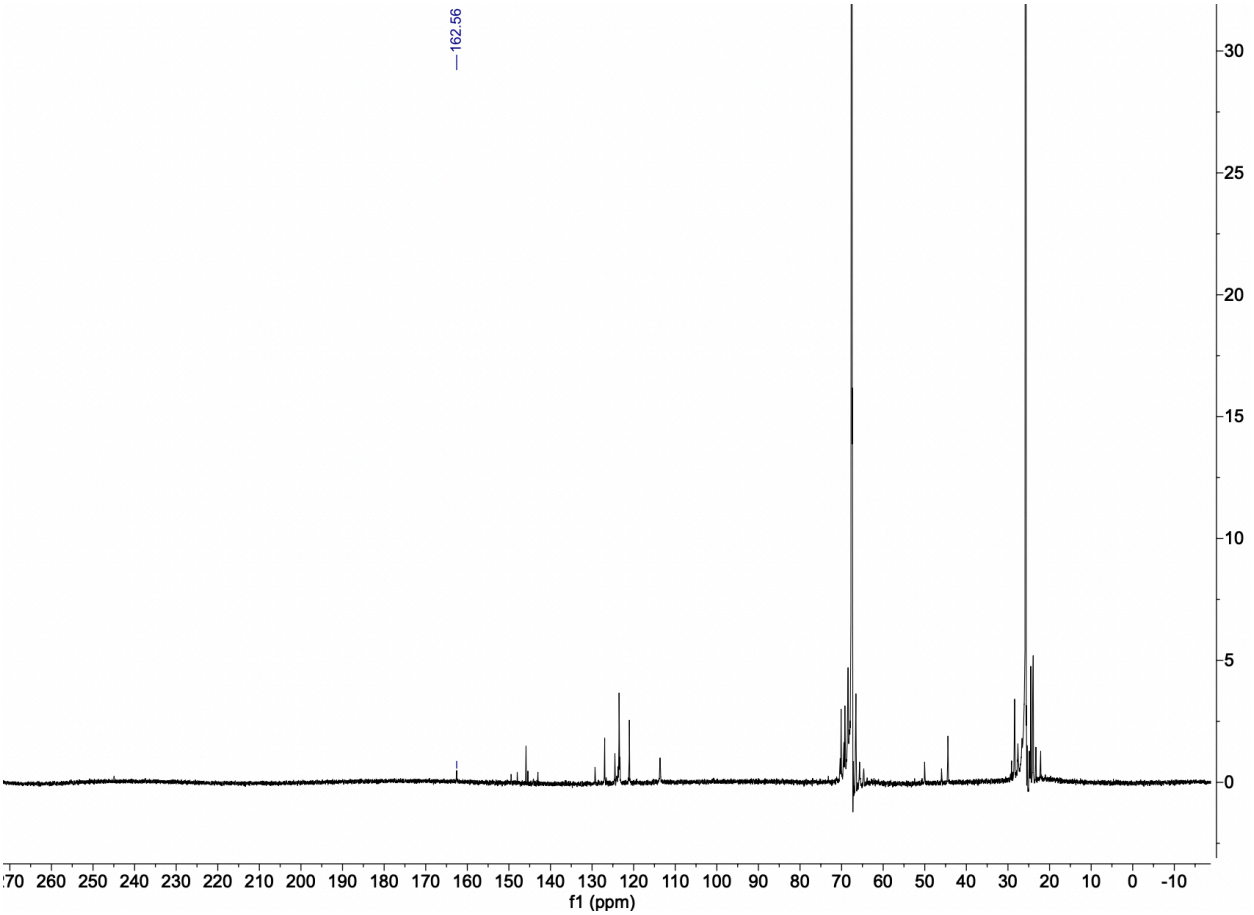
## E. Reactions Between NHC.HBr and $NaNH_2$

### E.1. NHC6.HBr and $NaNH_2$ with *dibenzo*-18-crown-6.

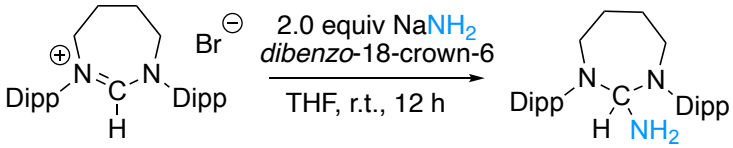



To a 20 mL scintillation vial equipped with a mini magnetic stir bar, NHC6.HBr (48.5 mg, 0.1 mmol), *dibenzo*-18-crown-6 (36.0 mg, 0.1 mmol), $NaNH_2$ (8.0 mg, 0.2 mmol), and THF (2 mL) were added in the glovebox. The vial was capped and the reaction was stirred for 12 hours. The solution was filtered and transferred to an NMR tube and a decoupled $^{13}$C-NMR spectrum was taken to evaluate the disappearance of the amidinium peak and the appearance of a peak around 80-90 ppm. Minor carbene formation was observed.

**$^{13}$C (125 MHz, THF)**

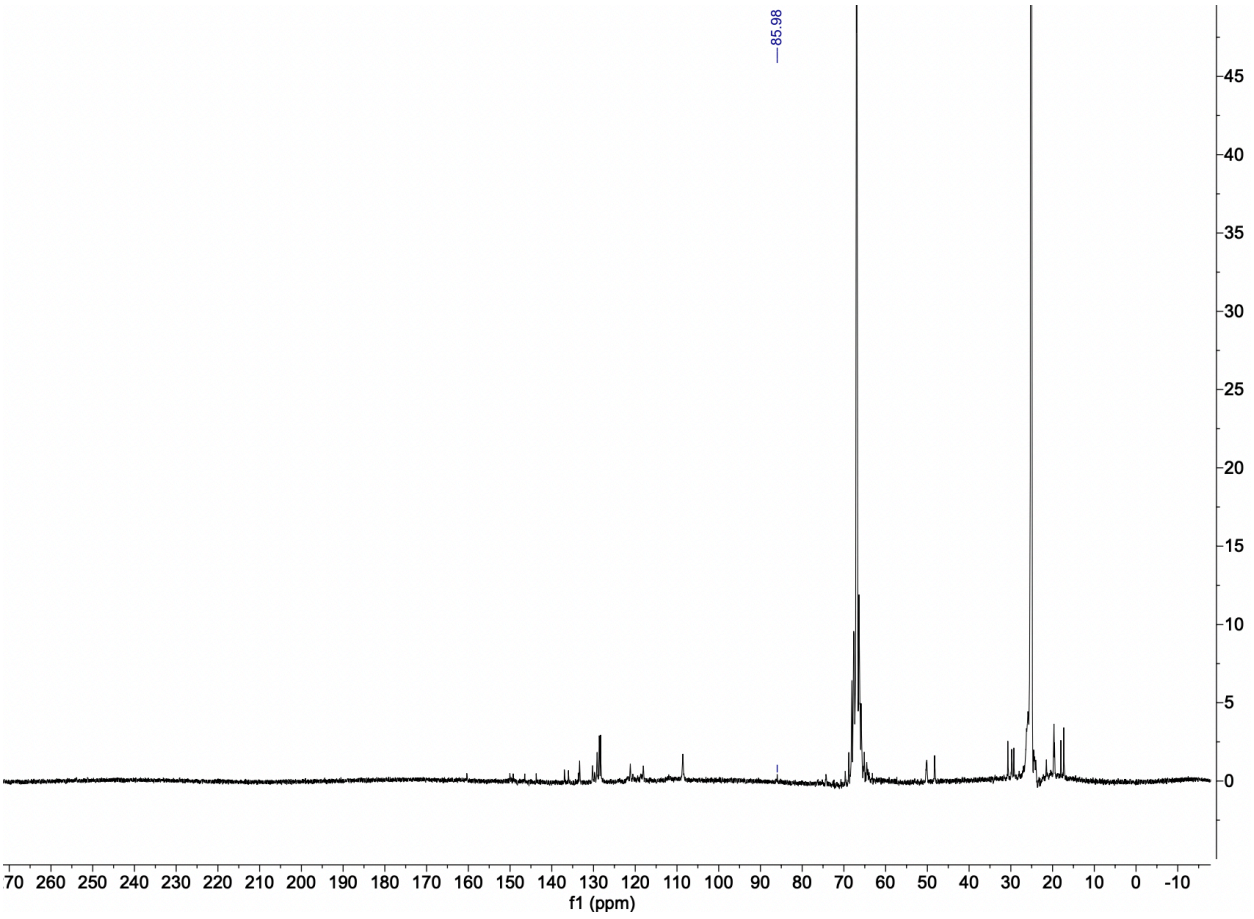


## E.2. NHC6.HBr and $NaNH_2$ with *dibenzo*-18-crown-6.

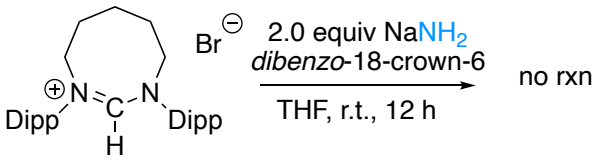



To a 20 mL scintillation vial equipped with a mini magnetic stir bar, NHC7.HBr (50.0 mg, 0.1 mmol), *dibenzo*-18-crown-6 (36.0 mg, 0.1 mmol), $NaNH_2$ (8.0 mg, 0.2 mmol), and THF (2 mL) were added in the glovebox. The vial was capped and the reaction was stirred for 12 hours. The solution was filtered and transferred to an NMR tube and a decoupled $^{13}$C-NMR spectrum was taken to evaluate the disappearance of the amidinium peak and the appearance of a peak around 80-90 ppm.

**$^{13}$C (125 MHz, THF)**

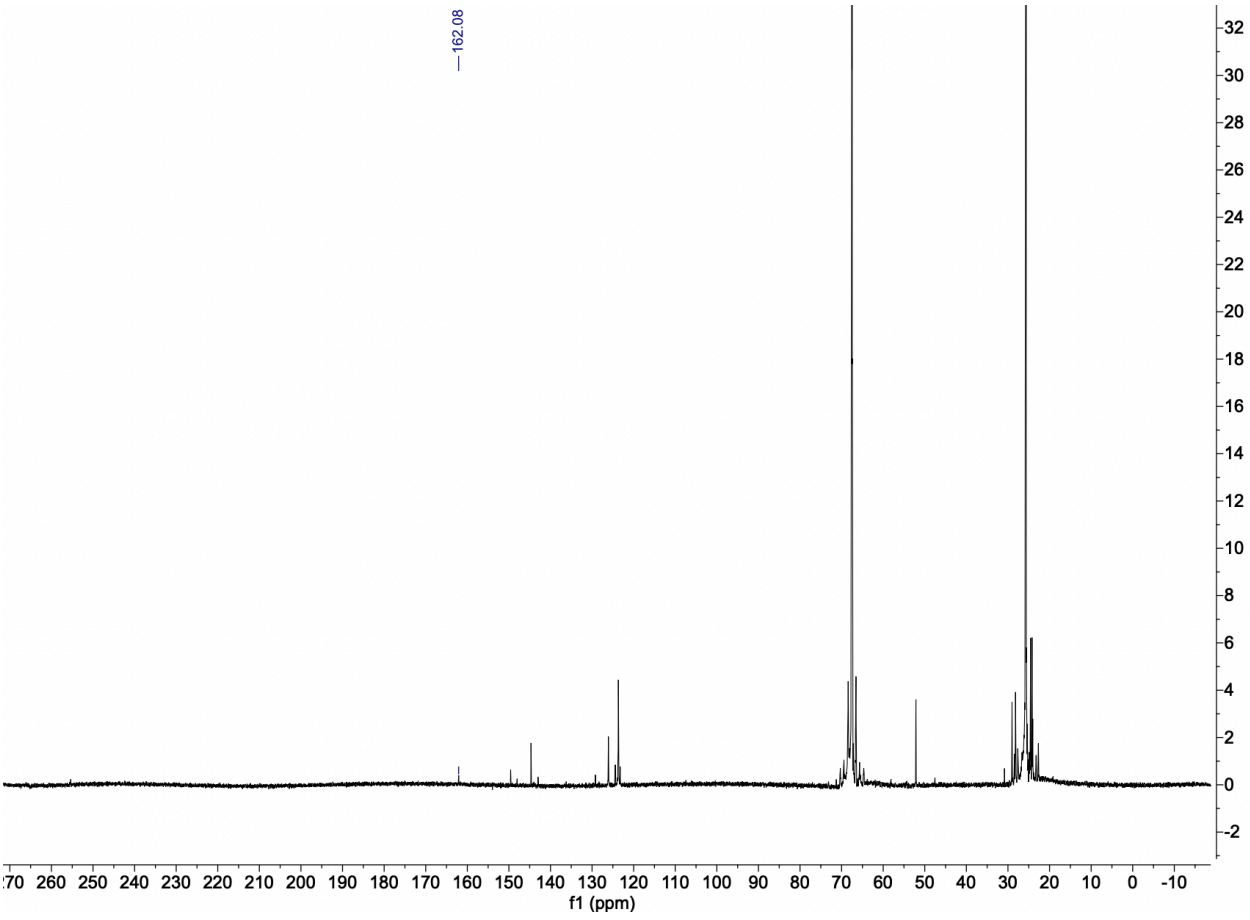


## E.3. NHC8.HBr and $NaNH_2$ with *dibenzo*-18-crown-6.

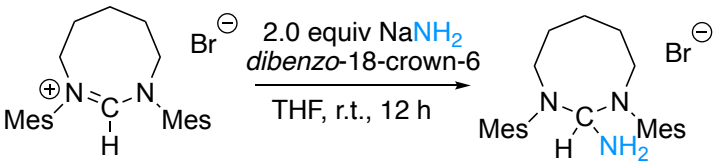



To a 20 mL scintillation vial equipped with a mini magnetic stir bar, NHC8.HBr (51.3 mg, 0.1 mmol), *dibenzo*-18-crown-6 (36.0 mg, 0.1 mmol), $NaNH_2$ (8.0 mg, 0.2 mmol), and THF (2 mL) were added in the glovebox. The vial was capped and the reaction was stirred for 12 hours. The solution was filtered and transferred to an NMR tube and a decoupled $^{13}$C-NMR spectrum was taken to evaluate the disappearance of the amidinium peak and the appearance of a peak around 80-90 ppm. Minor carbene formation was observed.

**$^{13}$C (125 MHz, THF)**

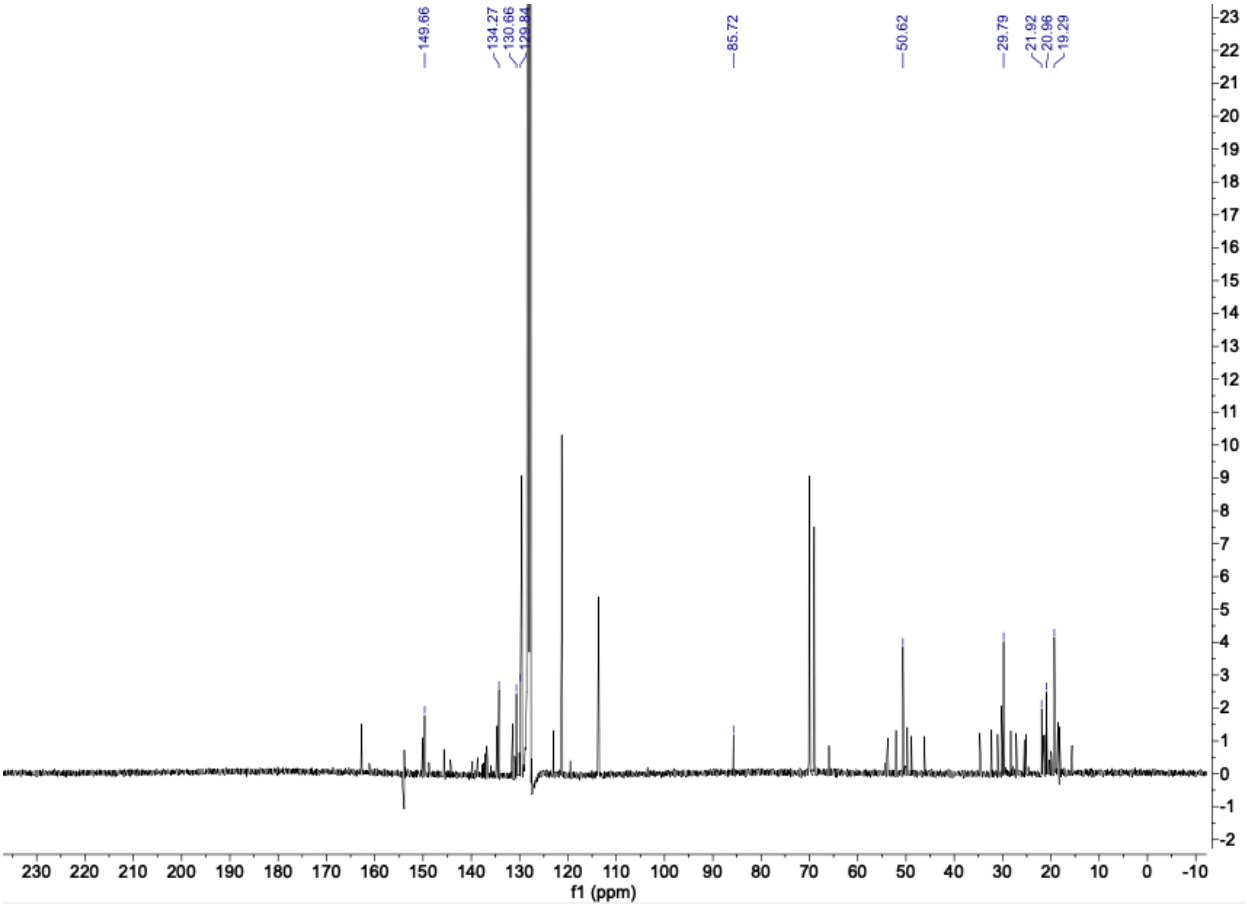


## E.4. NHC8.HBr and $NaNH_2$ with *dibenzo*-18-crown-6.




To a 20 mL scintillation vial equipped with a mini magnetic stir bar, $^{Mes}$NHC8.HBr (43.0 mg, 0.1 mmol), *dibenzo*-18-crown-6 (36.0 mg, 0.1 mmol), $NaNH_2$ (8.0 mg, 0.2 mmol), and $C_6D_6$ (2 mL) were added in the glovebox. The vial was capped and the reaction was stirred for 12 hours. The solution was filtered and transferred to an NMR tube and a decoupled $^{13}$C-NMR spectrum was taken to evaluate the disappearance of the amidinium peak and the appearance of a peak around 80-90 ppm.

**$^{13}$C (125 MHz, $C_6D_6$)**



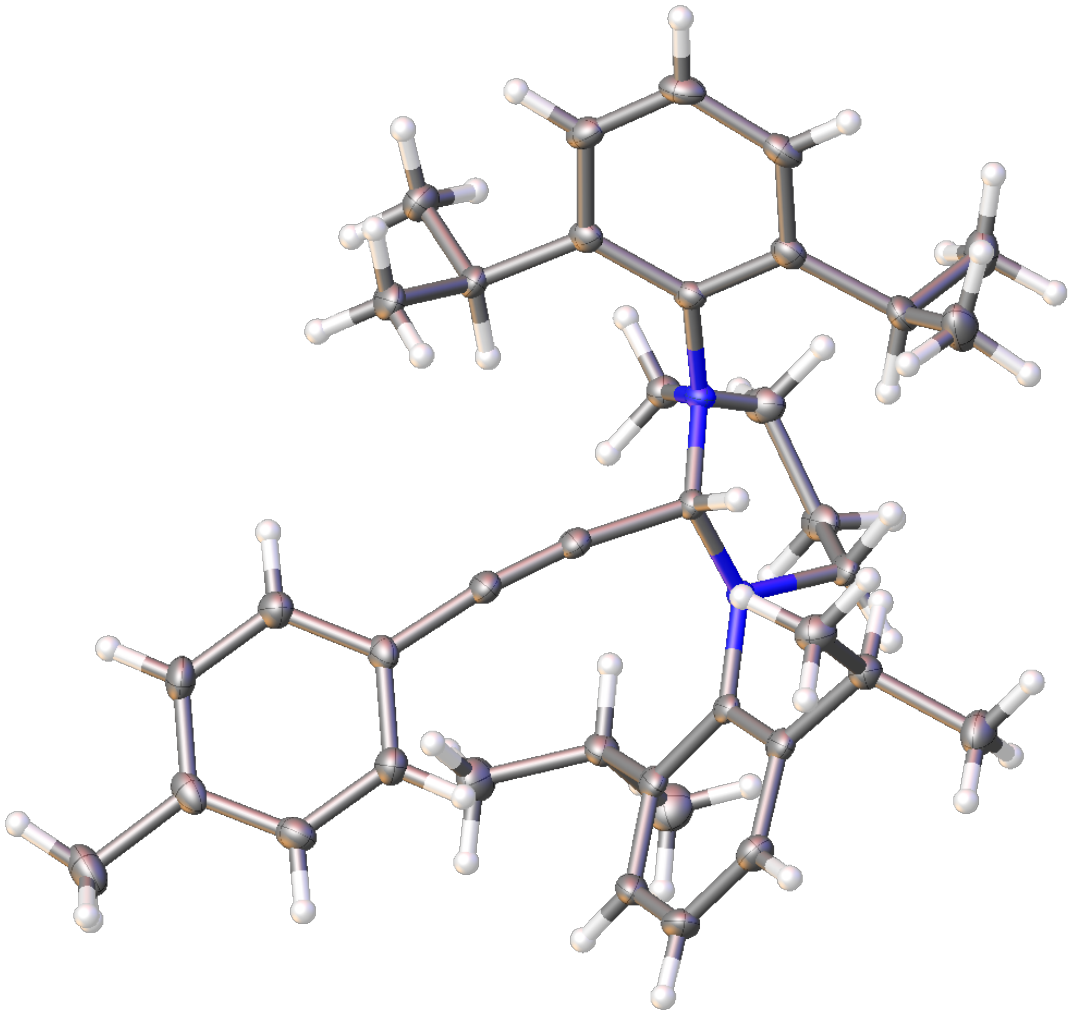
# IV. X-Rays Structures

## IV.1 X-Ray crystal structure determination

Olex2 software[5] was used for the resolution, refinement, and generation of crystallographic information files of every structure. The structures were solved with the ShelXS9[6] structure solution program using Direct Methods and refined with the ShelXL9[6] refinement package using Least Squares minimization. During the final stages of the refinements, all the positional parameters and the anisotropic temperature factors of all the non-H atoms were refined. The H atoms were geometrically located and their coordinates were refined riding on their parent atoms.

## IV.2 X-Ray crystal structure determination for Compound 1c (CCDC 2291449)

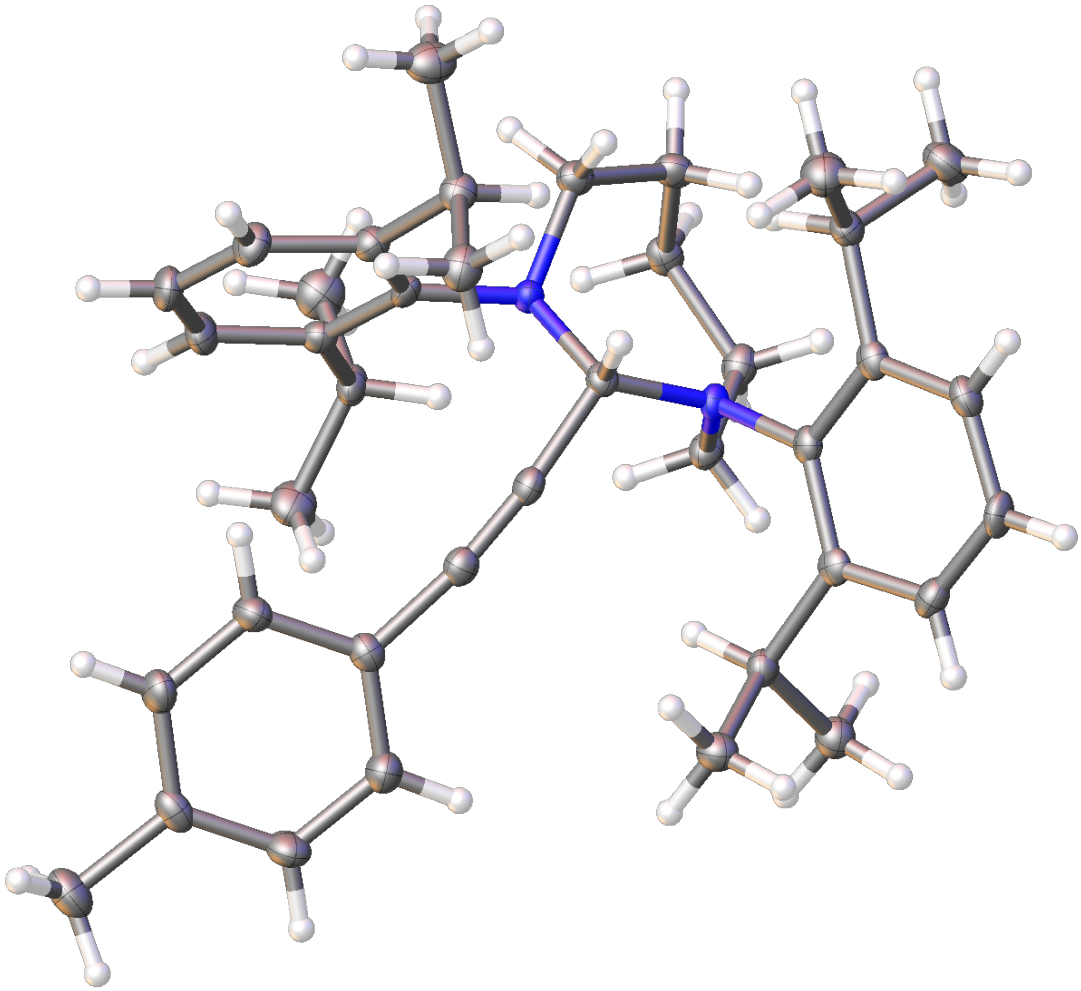
| | |
|---|---|
| Empirical formula | $C_{38}H_{50}N_2$ |
| Formula weight | 534.80 |
| Temperature/K | 100.0 |
| Crystal system | triclinic |
| Space group | P-1 |
| a/Å | 9.9626(2) |
| b/Å | 12.7843(2) |
| c/Å | 13.6552(2) |
| α/° | 69.2430(10) |
| β/° | 75.6740(10) |
| γ/° | 87.5200(10) |
| Volume/Å$^3$ | 1573.84(5) |
| Z | 2 |
| $\rho_{calc}$g/cm$^3$ | 1.129 |
| μ/mm$^{-1}$ | 0.482 |
| F(000) | 584.0 |
| Crystal size/mm$^3$ | 0.05 × 0.05 × 0.04 |
| Radiation | CuKα (λ = 1.54178) |
| 2Θ range for data collection/° | 7.146 to 136.57 |
| Index ranges | -11 ≤ h ≤ 11, -15 ≤ k ≤ 15, -16 ≤ l ≤ 16 |
| Reflections collected | 17967 |
| Independent reflections | 5563 [$R_{int}$ = 0.0422, $R_{sigma}$ = 0.0425] |
| Data/restraints/parameters | 5563/0/370 |
| Goodness-of-fit on $F^2$ | 1.036 |
| Final R indexes [I>=2σ (I)] | $R_1$ = 0.0397, $wR_2$ = 0.0965 |
| Final R indexes [all data] | $R_1$ = 0.0486, $wR_2$ = 0.1023 |
| Largest diff. peak/hole / e Å$^{-3}$ | 0.22/-0.21 |



## IV.3 X-Ray crystal structure determination for Compound 1d (CCDC 2291455)

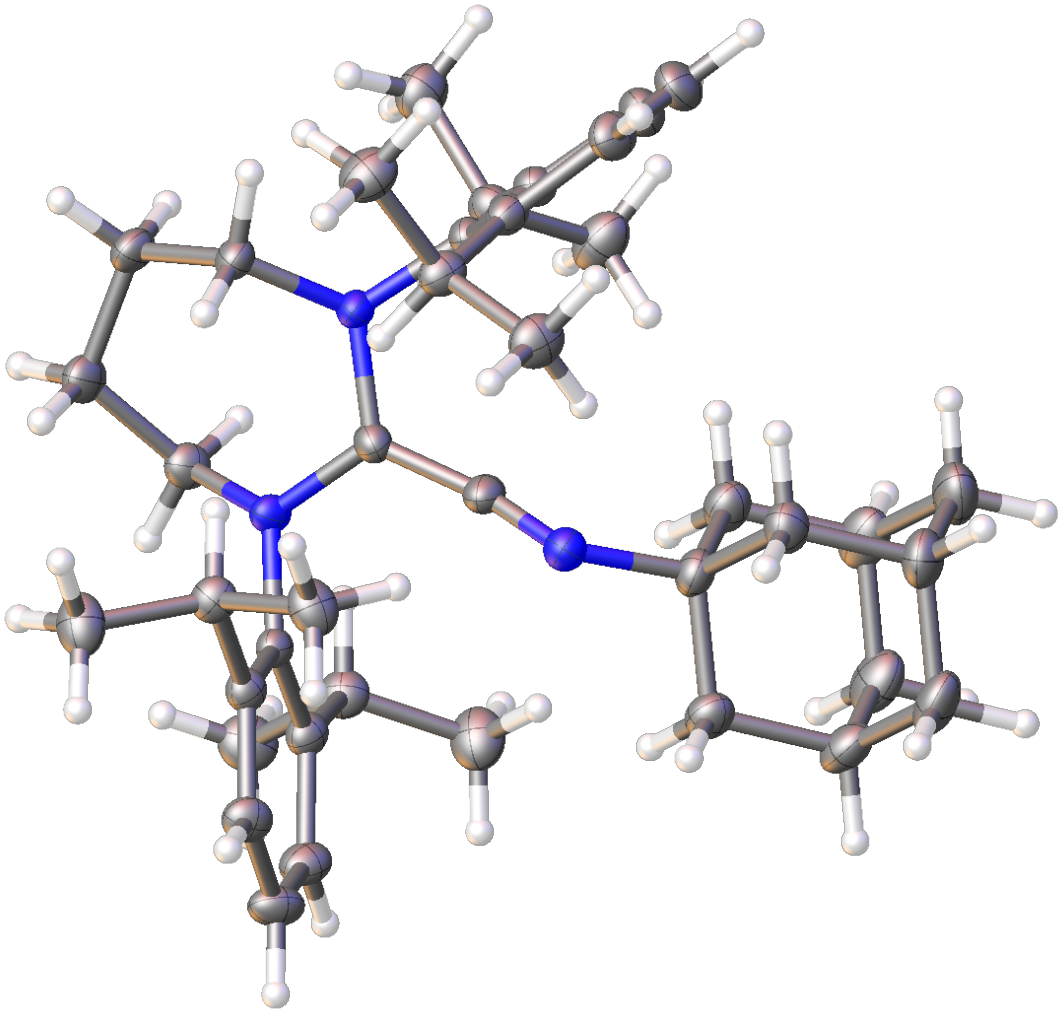
**Table 1 Crystal data and structure refinement for 1d.**

| | |
|---|---|
| Identification code | 1d |
| Empirical formula | $C_{39}H_{52}N_2$ |
| Formula weight | 548.82 |
| Temperature/K | 100 |
| Crystal system | triclinic |
| Space group | P-1 |
| a/Å | 10.2400(3) |
| b/Å | 12.6553(3) |
| c/Å | 13.8707(4) |
| α/° | 68.0400(10) |
| β/° | 75.9920(10) |
| γ/° | 87.3960(10) |
| Volume/Å$^3$ | 1615.48(8) |
| Z | 2 |
| $\rho_{calc}$g/cm$^3$ | 1.128 |
| μ/mm$^{-1}$ | 0.064 |
| F(000) | 600.0 |
| Crystal size/mm$^3$ | 0.025 × 0.012 × 0.01 |
| Radiation | MoKα (λ = 0.71073) |
| 2Θ range for data collection/° | 5.1 to 50.754 |
| Index ranges | -12 ≤ h ≤ 12, -15 ≤ k ≤ 15, -16 ≤ l ≤ 16 |
| Reflections collected | 54670 |
| Independent reflections | 5923 [$R_{int}$ = 0.0694, $R_{sigma}$ = 0.0331] |
| Data/restraints/parameters | 5923/0/379 |
| Goodness-of-fit on $F^2$ | 1.018 |
| Final R indexes [I>=2σ (I)] | $R_1$ = 0.0397, w$R_2$ = 0.0911 |
| Final R indexes [all data] | $R_1$ = 0.0523, w$R_2$ = 0.0978 |
| Largest diff. peak/hole / e Å$^{-3}$ | 0.19/-0.22 |



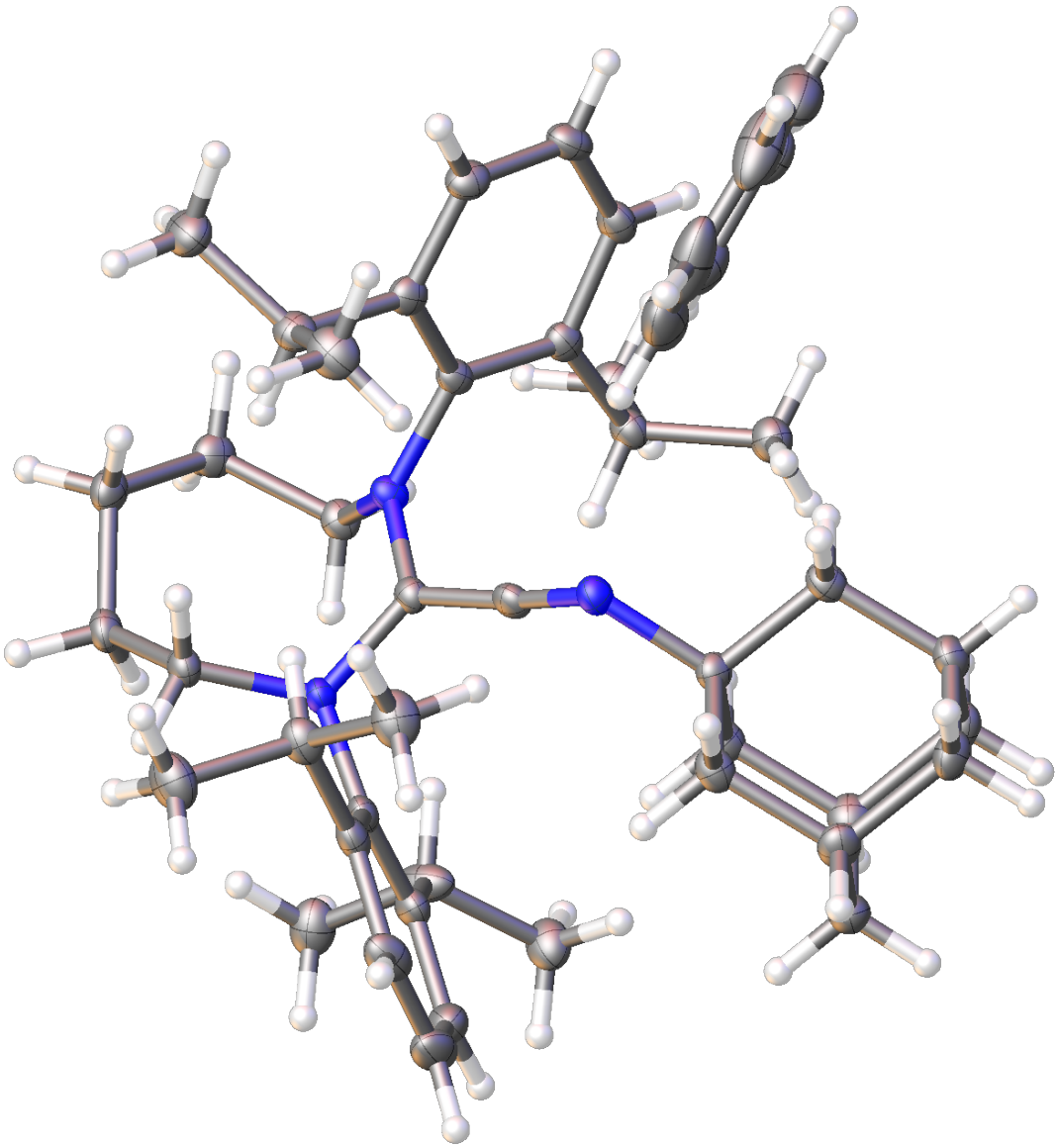
## IV.4 X-Ray crystal structure determination for Compound 2b (CCDC 2291453)

| | |
|---|---|
| Empirical formula | $C_{46}H_{63}N_3$ |
| Formula weight | 657.99 |
| Temperature/K | 100.00 |
| Crystal system | monoclinic |
| Space group | $P2_1/c$ |
| a/Å | 20.277(3) |
| b/Å | 10.5458(12) |
| c/Å | 18.401(2) |
| α/° | 90 |
| β/° | 92.839(6) |
| γ/° | 90 |
| Volume/Å$^3$ | 3930.0(8) |
| Z | 4 |
| $\rho_{calc}$g/cm$^3$ | 1.112 |
| μ/mm$^{-1}$ | 0.478 |
| F(000) | 1440.0 |
| Crystal size/mm$^3$ | 0.23 × 0.15 × 0.01 |
| Radiation | CuKα (λ = 1.54178) |
| 2Θ range for data collection/° | 4.364 to 144.908 |
| Index ranges | $-24 \le h \le 24$, $-12 \le k \le 12$, $-22 \le l \le 22$ |
| Reflections collected | 64029 |
| Independent reflections | 7157 [$R_{int}$ = 0.1170, $R_{sigma}$ = 0.0793] |
| Data/restraints/parameters | 7157/0/450 |
| Goodness-of-fit on $F^2$ | 1.089 |
| Final R indexes [I>=2σ (I)] | $R_1$ = 0.0714, $wR_2$ = 0.1465 |
| Final R indexes [all data] | $R_1$ = 0.0986, $wR_2$ = 0.1601 |
| Largest diff. peak/hole / e Å$^{-3}$ | 0.34/-0.34 |



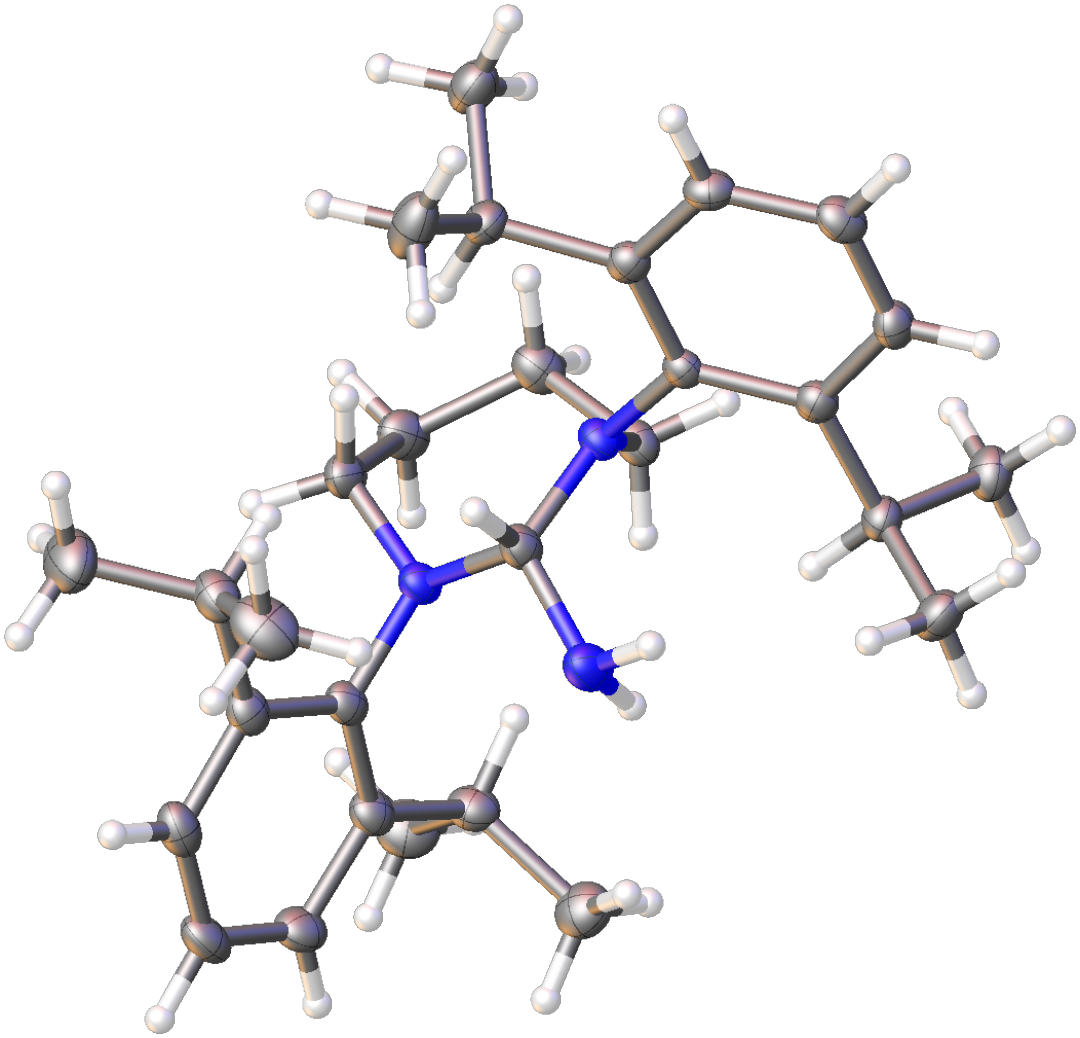
## IV.5 X-Ray crystal structure determination for Compound 2c (CCDC 2291452)

| | |
|---|---|
| Empirical formula | $C_{47}H_{65}N_3$ |
| Formula weight | 672.02 |
| Temperature/K | 273.15 |
| Crystal system | monoclinic |
| Space group | $P2_1/c$ |
| a/Å | 10.1396(4) |
| b/Å | 20.3171(8) |
| c/Å | 19.4251(7) |
| α/° | 90 |
| β/° | 100.0250(10) |
| γ/° | 90 |
| Volume/Å$^3$ | 3940.6(3) |
| Z | 4 |
| $\rho_{calc}$g/cm$^3$ | 1.133 |
| μ/mm$^{-1}$ | 0.065 |
| F(000) | 1472.0 |
| Crystal size/mm$^3$ | 0.024 × 0.023 × 0.01 |
| Radiation | MoKα (λ = 0.71073) |
| 2Θ range for data collection/° | 5.312 to 51.448 |
| Index ranges | -12 ≤ h ≤ 12, -24 ≤ k ≤ 24, -23 ≤ l ≤ 23 |
| Reflections collected | 55840 |
| Independent reflections | 7503 [$R_{int}$ = 0.0799, $R_{sigma}$ = 0.0446] |
| Data/restraints/parameters | 7503/2/480 |
| Goodness-of-fit on $F^2$ | 1.026 |
| Final R indexes [I>=2σ (I)] | $R_1$ = 0.0441, $wR_2$ = 0.0961 |
| Final R indexes [all data] | $R_1$ = 0.0665, $wR_2$ = 0.1063 |
| Largest diff. peak/hole / e Å$^{-3}$ | 0.21/-0.28 |



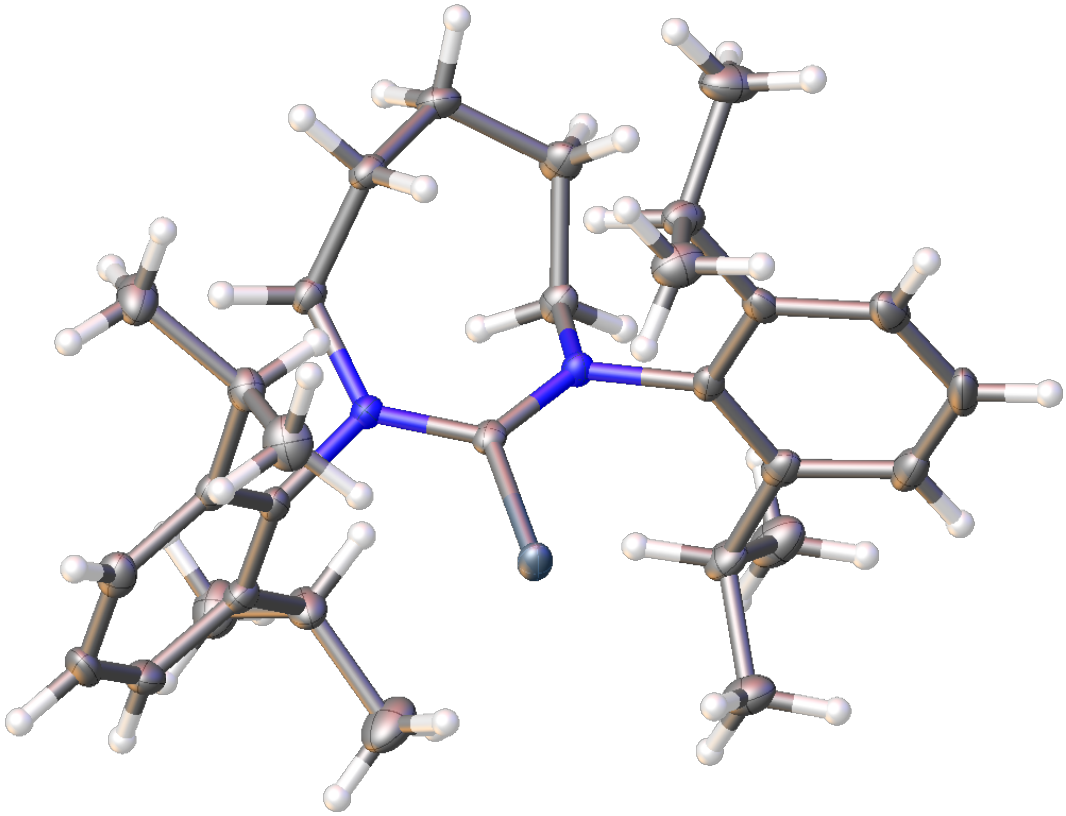
## IV.6 X-Ray crystal structure determination for Compound 3b (CCDC 2291450)

| | |
|---|---|
| Empirical formula | $C_{29}H_{45}N_3$ |
| Formula weight | 435.68 |
| Temperature/K | 100.15 |
| Crystal system | monoclinic |
| Space group | $P2_1/c$ |
| a/Å | 10.4427(9) |
| b/Å | 24.913(2) |
| c/Å | 11.5295(9) |
| α/° | 90 |
| β/° | 116.382(4) |
| γ/° | 90 |
| Volume/Å$^3$ | 2687.2(4) |
| Z | 4 |
| $\rho_{calc}$g/cm$^3$ | 1.077 |
| μ/mm$^{-1}$ | 0.470 |
| F(000) | 960.0 |
| Crystal size/mm$^3$ | 0.04 × 0.021 × 0.01 |
| Radiation | CuKα (λ = 1.54178) |
| 2Θ range for data collection/° | 9.268 to 138.388 |
| Index ranges | $-12 \le h \le 12$, $-29 \le k \le 30$, $-13 \le l \le 13$ |
| Reflections collected | 25294 |
| Independent reflections | 4946 [$R_{int}$ = 0.0628, $R_{sigma}$ = 0.0432] |
| Data/restraints/parameters | 4946/0/305 |
| Goodness-of-fit on $F^2$ | 1.032 |
| Final R indexes [I>=2σ (I)] | $R_1$ = 0.0479, $wR_2$ = 0.1204 |
| Final R indexes [all data] | $R_1$ = 0.0645, $wR_2$ = 0.1317 |
| Largest diff. peak/hole / e Å$^{-3}$ | 0.42/-0.22 |



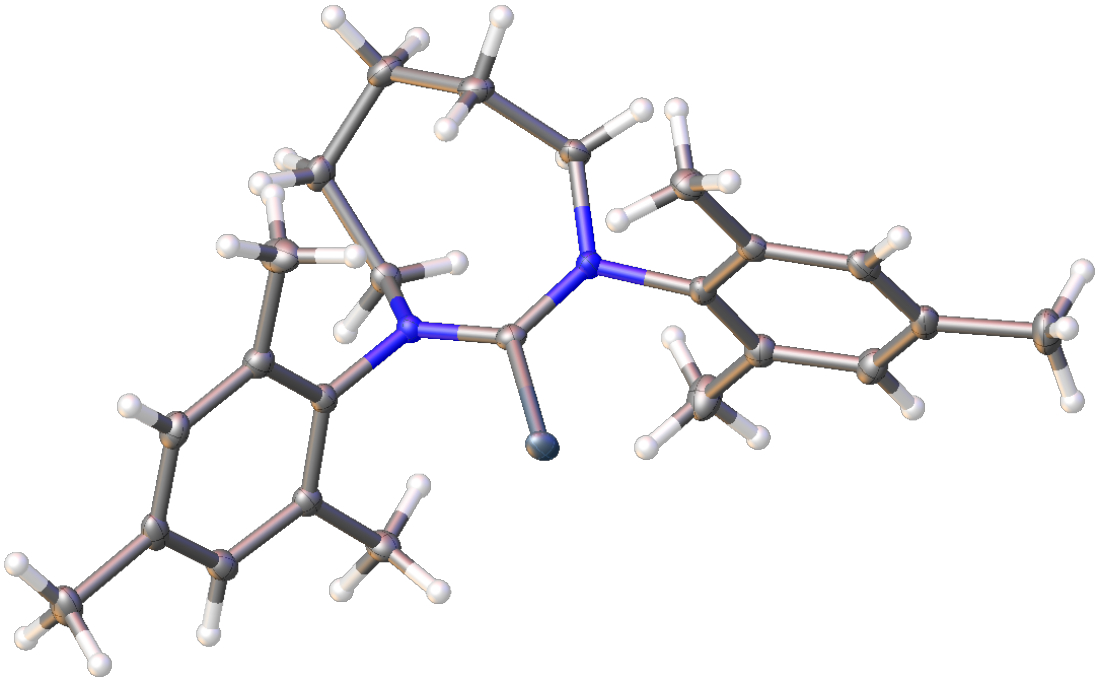
## IV.7 X-Ray crystal structure determination for Compound 4a (CCDC 2291454)

| | |
|---|---|
| Empirical formula | $C_{36}H_{50}N_2Se$ |
| Formula weight | 589.74 |
| Temperature/K | 273.15 |
| Crystal system | monoclinic |
| Space group | $P2_1/c$ |
| a/Å | 15.9260(9) |
| b/Å | 15.8347(8) |
| c/Å | 14.3550(8) |
| α/° | 90 |
| β/° | 116.049(2) |
| γ/° | 90 |
| Volume/Å$^3$ | 3252.4(3) |
| Z | 4 |
| $\rho_{calc}$g/cm$^3$ | 1.204 |
| μ/mm$^{-1}$ | 1.180 |
| F(000) | 1256.0 |
| Crystal size/mm$^3$ | 0.03 × 0.02 × 0.01 |
| Radiation | MoKα (λ = 0.71073) |
| 2Θ range for data collection/° | 5.676 to 50.758 |
| Index ranges | -19 ≤ h ≤ 19, -19 ≤ k ≤ 19, -17 ≤ l ≤ 17 |
| Reflections collected | 70350 |
| Independent reflections | 5970 [$R_{int}$ = 0.0917, $R_{sigma}$ = 0.0401] |
| Data/restraints/parameters | 5970/0/360 |
| Goodness-of-fit on $F^2$ | 1.023 |
| Final R indexes [I>=2σ (I)] | $R_1$ = 0.0320, $wR_2$ = 0.0768 |
| Final R indexes [all data] | $R_1$ = 0.0425, $wR_2$ = 0.0824 |
| Largest diff. peak/hole / e Å$^{-3}$ | 0.42/-0.49 |



## IV.8 X-Ray crystal structure determination for Compound 4b (CCDC 2291451)

| | |
|---|---|
| Empirical formula | $C_{24}H_{32}N_2Se$ |
| Formula weight | 427.494 |
| Temperature/K | 100.00 |
| Crystal system | monoclinic |
| Space group | C2/c |
| a/Å | 19.8071(9) |
| b/Å | 13.3759(7) |
| c/Å | 17.5615(8) |
| α/° | 90 |
| β/° | 110.970(2) |
| γ/° | 90 |
| Volume/Å$^3$ | 4344.5(4) |
| Z | 8 |
| $\rho_{calc}$g/cm$^3$ | 1.307 |
| μ/mm$^{-1}$ | 1.739 |
| F(000) | 1792.7 |
| Crystal size/mm$^3$ | 0.1 × 0.067 × 0.055 |
| Radiation | Mo Kα (λ = 0.71073) |
| 2Θ range for data collection/° | 3.76 to 52.88 |
| Index ranges | -24 ≤ h ≤ 24, -16 ≤ k ≤ 16, -21 ≤ l ≤ 21 |
| Reflections collected | 44841 |
| Independent reflections | 4459 [$R_{int}$ = 0.0474, $R_{sigma}$ = 0.0225] |
| Data/restraints/parameters | 4459/0/250 |
| Goodness-of-fit on $F^2$ | 1.037 |
| Final R indexes [I>=2σ (I)] | $R_1$ = 0.0218, $wR_2$ = 0.0539 |
| Final R indexes [all data] | $R_1$ = 0.0254, $wR_2$ = 0.0555 |
| Largest diff. peak/hole / e Å$^{-3}$ | 0.34/-0.29 |



# X. Computational Data

All calculations were performed with the Gaussian16 program package.[7] The theoretical approach is based on the framework of density functional theory (DFT). All calculations were performed with the B3LYP functional and employing Weigend and Ahlrich's def2-TZVPP basis set.[8] The calculations were benchmarked against the functional-basis set combinations of MO 62x//TZVP and B3LYP//6-31G(d,f). The singlet and triplet states of each carbene were fully optimized without constraints at the aforementioned level of theory. The Gibbs energy corrections from frequency calculations and dispersion corrections were added to the single-point energies to obtain the Gibbs free energies in solution. Gibbs free reaction energies and enthalpies were calculated for standard conditions ($P$ = 1 atm, $T$ = 298 K) and are unscaled and are given in the following Table S1-3. The $\%V_{bur}$ was calculated using the SambVca 2 program and measured at a distance of 0 Å from the carbene carbon.[9] Cartesian coordinates for the optimized structures are given in the following subsection.

**Table S1.** DFT Calculated Geometric and Thermodynamic Data of CAAC-5 and NHCs at the B3LYP//def2-TZVPP level.

| Carbene | $\Delta E_{S\text{-}T}$ (kcal/mol) | Singlet LUMO (eV)<br>Singlet HOMO (eV) | $\Delta E_{H\text{-}L}$ (eV) | Carbene angle (°) |
|---|---|---|---|---|
| CAAC-5 | 45.72 | -0.448<br>-5.290 | 4.842 | 107.3 |
| NHC-5 | 73.08 | -0.359<br>-5.805 | 5.446 | 106.3 |
| NHC-6 | 59.89 | -0.342<br>-5.322 | 4.980 | 116.0 |
| NHC-7 | 50.02 | -0.358<br>-5.103 | 4.745 | 118.7 |
| NHC-8 | 49.29 | -0.384<br>-5.110 | 4.726 | 122.1 |

**Table S2.** DFT Calculated Geometric and Thermodynamic Data of CAAC-5 and NHCs with MO62x//def2-TZVPP level.

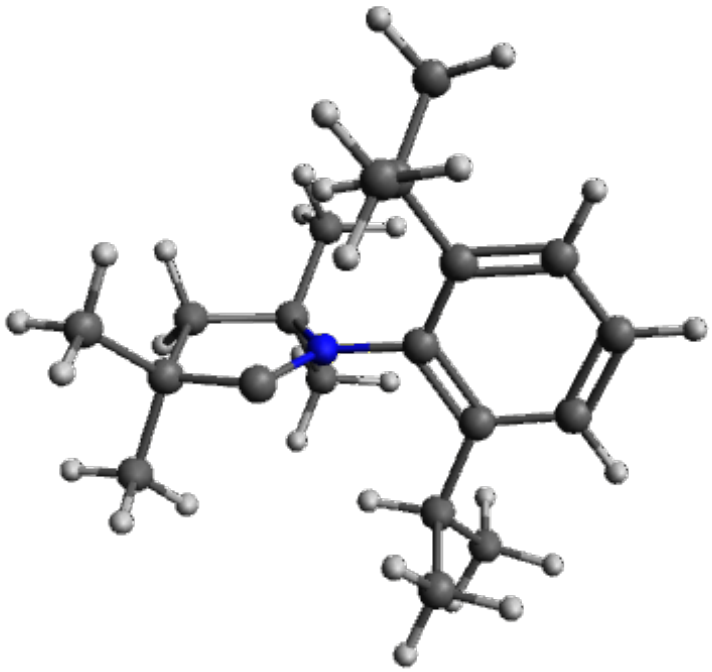
| Carbene | $\Delta E_{S\text{-}T}$ (kcal/mol) | Singlet LUMO (eV)<br>Singlet HOMO (eV) | $\Delta E_{H\text{-}L}$ (eV) | Carbene angle (°) |
|---|---|---|---|---|
| CAAC-5 | 45.72 | -0.448<br>-5.290 | 4.842 | 107.3 |
| NHC-5 | 73.08 | -0.359<br>-5.805 | 5.446 | 106.3 |
| NHC-6 | 59.89 | -0.342<br>-5.322 | 4.980 | 116.0 |
| NHC-7 | 50.02 | -0.358<br>-5.103 | 4.745 | 118.7 |
| NHC-8 | 49.29 | -0.384<br>-5.110 | 4.726 | 122.1 |

**Table S3.** DFT Calculated Geometric and Thermodynamic Data of CAAC-5 and NHCs at the B3LYP//6-31G(d,f) level.

| Carbene | $\Delta E_{S\text{-}T}$ (kcal/mol) | Singlet LUMO (eV)<br>Singlet HOMO (eV) | $\Delta E_{H\text{-}L}$ (eV) | Carbene angle (°) |
|---|---|---|---|---|
| CAAC-5 | 45.72 | -0.448<br>-5.290 | 4.842 | 107.3 |
| NHC-5 | 73.08 | -0.359<br>-5.805 | 5.446 | 106.3 |
| NHC-6 | 59.89 | -0.342<br>-5.322 | 4.980 | 116.0 |
| NHC-7 | 50.02 | -0.358<br>-5.103 | 4.745 | 118.7 |
| NHC-8 | 49.29 | -0.384<br>-5.110 | 4.726 | 122.1 |

## *Optimized x,y,z-coordinates*

**CAAC-5 singlet**

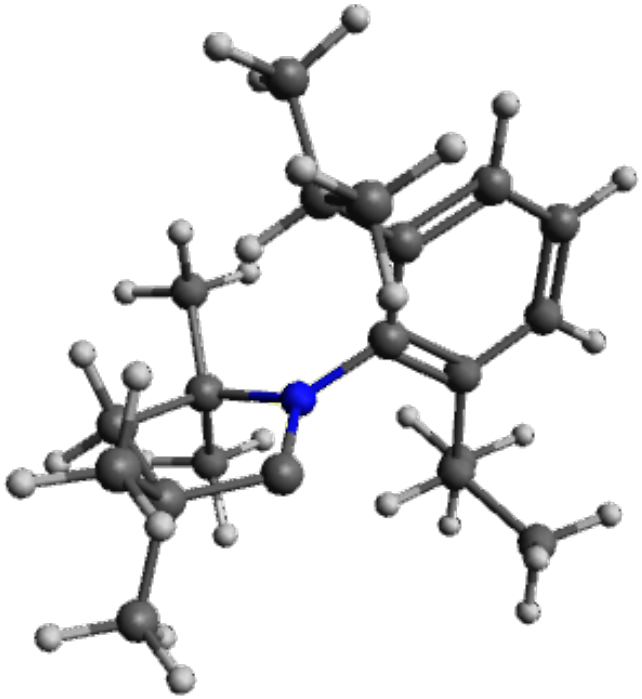


| | |
|---|---|
| **Zero-point correction=** | **0.464716 (Hartree/Particle)** |
| **Thermal correction to Energy=** | **0.487947** |
| **Thermal correction to Enthalpy=** | **0.488891** |
| **Thermal correction to Gibbs Free Energy=** | **0.414529** |
| **Sum of electronic and zero-point Energies=** | **-835.349444** |
| **Sum of electronic and thermal Energies=** | **-835.326213** |
| **Sum of electronic and thermal Enthalpies=** | **-835.325268** |
| **Sum of electronic and thermal Free Energies=** | **-835.399631** |

| | | | | | |
|---|---|---|---|---|---|
| **C** | **-1.33181** | **-0.07661** | **-1.04389** | **C** | **3.60801** | **0.19134** | **-0.01714** |
| **C** | **-2.78932** | **-0.17973** | **-0.62513** | **H** | **4.6885** | **0.2514** | **0.00031** |
| **C** | **-2.77351** | **-0.45341** | **0.90599** | **C** | **2.97987** | **-1.04264** | **-0.04801** |
| **H** | **-3.53022** | **0.12154** | **1.44005** | **H** | **3.58113** | **-1.94079** | **-0.08184** |
| **H** | **-2.97969** | **-1.50788** | **1.09509** | **C** | **1.58935** | **-1.1488** | **-0.06088** |
| **C** | **-1.3577** | **-0.10728** | **1.39875** | **C** | **0.67824** | **2.59354** | **-0.284** |
| **C** | **-3.48192** | **1.14972** | **-0.97893** | **H** | **-0.37121** | **2.39684** | **-0.08838** |
| **H** | **-3.39138** | **1.35431** | **-2.0455** | **C** | **1.11613** | **3.73555** | **0.64232** |
| **H** | **-3.04845** | **1.99363** | **-0.44094** | **H** | **1.06516** | **3.44832** | **1.69318** |
| **H** | **-4.54311** | **1.09923** | **-0.72493** | **H** | **0.46865** | **4.60231** | **0.49835** |
| **C** | **-3.46873** | **-1.31661** | **-1.40045** | **H** | **2.13733** | **4.05902** | **0.43625** |
| **H** | **-4.51296** | **-1.4183** | **-1.09431** | **C** | **0.77564** | **3.01604** | **-1.76094** |
| **H** | **-2.97073** | **-2.27107** | **-1.22188** | **H** | **1.80881** | **3.23099** | **-2.04044** |
| **H** | **-3.43897** | **-1.12106** | **-2.47214** | **H** | **0.18467** | **3.91718** | **-1.93791** |
| **C** | **-1.29707** | **1.24903** | **2.10908** | **H** | **0.40107** | **2.22679** | **-2.41196** |

| | | | | | |
|---|---|---|---|---|---|
| H | -1.83488 | 1.17996 | 3.05576 | C | 0.95793 -2.52043 -0.2612 |
| H | -1.75831 | 2.04109 | 1.52257 | H | -0.10432 -2.43961 -0.04662 |
| H | -0.27015 | 1.53552 | 2.33361 | C | 1.53471 -3.60418 0.65889 |
| C | -0.7825 | -1.16932 | 2.33561 | H | 0.98265 -4.53676 0.52895 |
| H | 0.25811 | -0.96401 | 2.58707 | H | 1.47271 -3.31832 1.70942 |
| H | -0.84755 | -2.16796 | 1.90969 | H | 2.58067 -3.81615 0.43342 |
| H | -1.354 | -1.16886 | 3.2651 | C | 1.07372 -2.9342 -1.73928 |
| C | 0.83265 | 0.03796 | -0.01111 | H | 2.1192 -3.0342 -2.03715 |
| C | 1.45256 | 1.30027 | -0.06818 | H | 0.60329 -2.1931 -2.38484 |
| C | 2.84729 | 1.3474 | -0.05274 | H | 0.58311 -3.89576 -1.90462 |
| H | 3.34537 | 2.30649 | -0.09086 | N | -0.61511 -0.05379 0.04614 |

**CAAC-5 triplet**

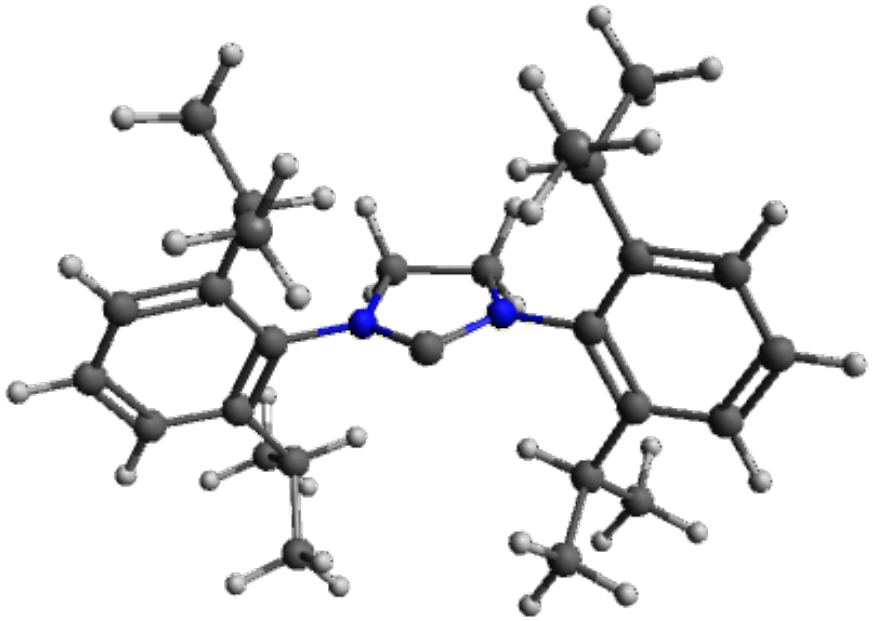


| | |
|---|---|
| Zero-point correction= | 0.462873 (Hartree/Particle) |
| Thermal correction to Energy= | 0.486544 |
| Thermal correction to Enthalpy= | 0.487488 |
| Thermal correction to Gibbs Free Energy= | 0.410338 |
| Sum of electronic and zero-point Energies= | -835.274239 |
| Sum of electronic and thermal Energies= | -835.250568 |
| Sum of electronic and thermal Enthalpies= | -835.249624 |
| Sum of electronic and thermal Free Energies= | -835.326773 |

| | | | | | |
|---|---|---|---|---|---|
| C | -1.28246 | 0.57811 | -1.01322 | C | 3.34246 -1.4734 -0.17851 |
| C | -2.74397 | 0.69528 | -0.69859 | H | 4.31692 -1.9429 -0.21987 |
| C | -2.6613 | 0.58515 | 0.86494 | C | 2.19864 -2.25051 -0.08743 |
| H | -3.32187 | 1.30427 | 1.34988 | H | 2.29275 -3.32823 -0.07212 |

| | | | | | |
|---|---|---|---|---|---|
| H | -2.98401 | -0.41251 | 1.1649 | C | 0.93223 | -1.67166 | -0.02312 |
| C | -1.1796 | 0.7902 | 1.30321 | C | 1.91949 | 2.04146 | -0.37464 |
| C | -3.3384 | 2.03947 | -1.16005 | H | 0.88289 | 2.34083 | -0.25223 |
| H | -3.28477 | 2.12421 | -2.24625 | C | 2.76028 | 2.80556 | 0.65797 |
| H | -2.79864 | 2.88448 | -0.735 | H | 2.48038 | 2.54273 | 1.67894 |
| H | -4.38856 | 2.11945 | -0.86687 | H | 2.62422 | 3.88194 | 0.53707 |
| C | -3.59819 | -0.44324 | -1.28948 | H | 3.82535 | 2.59571 | 0.54542 |
| H | -4.63551 | -0.36749 | -0.95194 | C | 2.32799 | 2.43158 | -1.80531 |
| H | -3.21386 | -1.41962 | -0.99616 | H | 3.36691 | 2.16713 | -2.0112 |
| H | -3.59755 | -0.39476 | -2.37932 | H | 2.22251 | 3.50872 | -1.94984 |
| C | -0.91082 | 2.26395 | 1.64922 | H | 1.70086 | 1.92866 | -2.54164 |
| H | -1.56337 | 2.57892 | 2.46591 | C | -0.28945 | -2.57805 | -0.01069 |
| H | -1.10033 | 2.91327 | 0.79591 | H | -1.1541 | -1.95757 | 0.21337 |
| H | 0.11895 | 2.41143 | 1.972 | C | -0.21652 | -3.6784 | 1.05765 |
| C | -0.81616 | -0.07431 | 2.50815 | H | -1.1546 | -4.23586 | 1.0879 |
| H | 0.24176 | 0.01719 | 2.75605 | H | -0.03589 | -3.26569 | 2.05076 |
| H | -1.0393 | -1.12498 | 2.33703 | H | 0.57898 | -4.39508 | 0.84868 |
| H | -1.39099 | 0.25556 | 3.37502 | C | -0.52097 | -3.1902 | -1.40284 |
| C | 0.8299 | -0.26165 | -0.03277 | H | 0.31386 | -3.83092 | -1.69331 |
| C | 1.98531 | 0.53363 | -0.18726 | H | -0.62839 | -2.41318 | -2.15953 |
| C | 3.23 | -0.09556 | -0.2415 | H | -1.42768 | -3.79882 | -1.40835 |
| H | 4.12407 | 0.5042 | -0.35107 | N | -0.45453 | 0.36062 | 0.06308 |

**NHC-5 singlet**



**Zero-point correction=** **0.590508 (Hartree/Particle)**

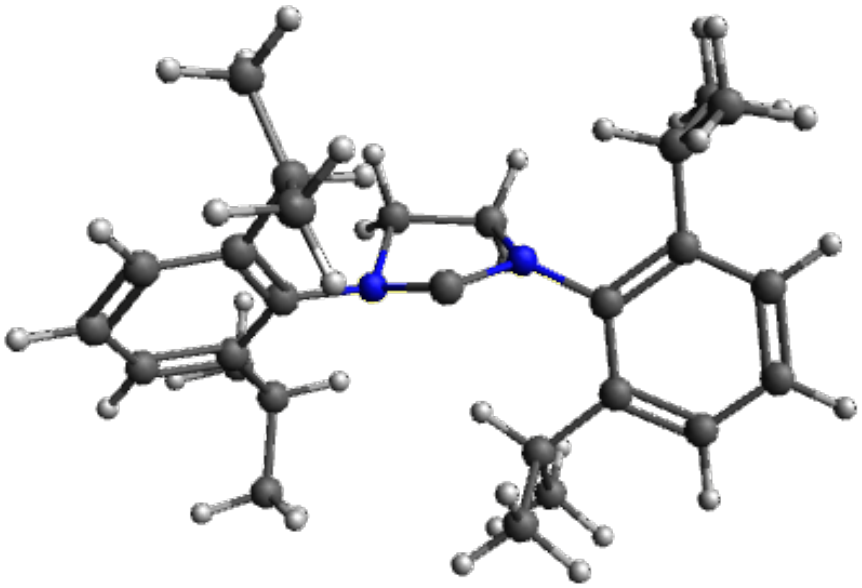
**Thermal correction to Energy=** **0.621778**

**Thermal correction to Enthalpy=** **0.622722**

**Thermal correction to Gibbs Free Energy= 0.525672**
**Sum of electronic and zero-point Energies= -1161.080649**
**Sum of electronic and thermal Energies= -1161.049380**
**Sum of electronic and thermal Enthalpies= -1161.048436**
**Sum of electronic and thermal Free Energies= -1161.145486**

| | | | |
|---|---|---|---|
| N | -1.07505 -0.04006 0.51939 | C | 2.71339 3.838 0.47081 |
| N | 1.07504 0.04001 0.5194 | H | 2.98552 3.55308 1.48827 |
| C | 0. 0. -0.28662 | H | 2.02235 4.68097 0.52857 |
| C | -0.75778 -0.10656 1.96866 | H | 3.61705 4.19256 -0.02721 |
| H | -1.04729 -1.07934 2.37413 | C | -2.42856 -0.15966 0.06904 |
| H | -1.29704 0.66086 2.52391 | C | -3.23884 0.98889 0.02416 |
| C | 0.75775 0.10649 1.96868 | C | -4.56072 0.84965 -0.39756 |
| H | 1.04727 1.07927 2.37417 | H | -5.1997 1.72163 -0.44722 |
| H | 1.297 -0.66095 2.52391 | C | -5.06776 -0.38564 -0.76738 |
| C | 2.42854 0.15964 0.06903 | H | -6.09504 -0.47366 -1.0969 |
| C | 2.92921 1.42229 -0.29752 | C | -4.25572 -1.50766 -0.71969 |
| C | 4.25565 1.50767 -0.71977 | H | -4.65961 -2.46581 -1.01845 |
| H | 4.6595 2.46584 -1.01855 | C | -2.92926 -1.4223 -0.2975 |
| C | 5.06771 0.38567 -0.7675 | C | -2.06151 -2.6714 -0.28531 |
| H | 6.09497 0.4737 -1.09708 | H | -1.13567 -2.42564 0.23261 |
| C | 4.56071 -0.84963 -0.39765 | C | -2.71344 -3.83807 0.47063 |
| H | 5.19971 -1.72159 -0.4473 | H | -2.98551 -3.55332 1.48816 |
| C | 3.23884 -0.98889 0.02412 | H | -2.02243 -4.68109 0.52823 |
| C | 2.70793 -2.36922 0.38028 | H | -3.61713 -4.19252 -0.0274 |
| H | 1.68461 -2.24816 0.73223 | C | -1.67679 -3.08212 -1.71585 |
| C | 3.51271 -3.02994 1.50942 | H | -1.15434 -2.27098 -2.22183 |
| H | 3.54316 -2.40036 2.40004 | H | -2.56219 -3.33724 -2.30168 |
| H | 4.54333 -3.22469 1.20839 | H | -1.02192 -3.95572 -1.70024 |
| H | 3.06507 -3.98644 1.78591 | C | -2.70789 2.36922 0.38025 |
| C | 2.64778 -3.27614 -0.85909 | H | -1.68459 2.24814 0.73227 |
| H | 2.03648 -2.82724 -1.64169 | C | -3.51268 3.03007 1.50931 |
| H | 2.21667 -4.24588 -0.60232 | H | -3.54315 2.40058 2.39999 |
| H | 3.64358 -3.45277 -1.26966 | H | -4.54329 3.22481 1.20824 |
| C | 2.06147 2.6714 -0.28529 | H | -3.06503 3.98659 1.78571 |
| H | 1.13561 2.42563 0.23258 | C | -2.64763 3.27604 -0.85918 |
| C | 1.67683 3.08223 -1.7158 | H | -2.03625 2.8271 -1.64169 |
| H | 1.15442 2.27111 -2.22187 | H | -2.21656 4.24582 -0.60245 |
| H | 2.56226 3.33739 -2.30157 | H | -3.6434 3.45262 -1.26986 |
| H | 1.02195 3.95582 -1.70016 | | |

**NHC-5 triplet**

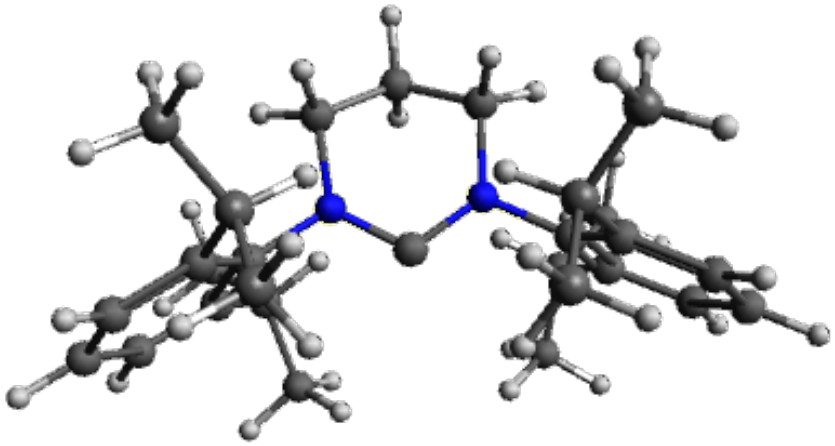


| | |
|---|---|
| **Zero-point correction=** | **0.588413 (Hartree/Particle)** |
| **Thermal correction to Energy=** | **0.619992** |
| **Thermal correction to Enthalpy=** | **0.620936** |
| **Thermal correction to Gibbs Free Energy=** | **0.522394** |
| **Sum of electronic and zero-point Energies=** | **-1160.963004** |
| **Sum of electronic and thermal Energies=** | **-1160.931425** |
| **Sum of electronic and thermal Enthalpies=** | **-1160.930481** |
| **Sum of electronic and thermal Free Energies=** | **-1161.029023** |

| | | | |
|---|---|---|---|
| **N** | **-1.24902 0.32586 0.44966** | **C** | **2.36882 3.96653 0.07441** |
| **N** | **1.0559 0.10195 0.493** | **H** | **2.46168 3.73609 1.13681** |
| **C** | **-0.0714 0.44282 -0.2682** | **H** | **1.65346 4.78433 -0.03281** |
| **C** | **-0.86321 0.23854 1.8744** | **H** | **3.33907 4.32891 -0.27019** |
| **H** | **-1.08768 -0.7643 2.2473** | **C** | **-2.45349 -0.27243 -0.02484** |
| **H** | **-1.39342 0.96384 2.49512** | **C** | **-3.6492 0.46734 0.11705** |
| **C** | **0.65426 0.50473 1.86222** | **C** | **-4.84061 -0.09148 -0.34075** |
| **H** | **0.86135 1.56733 2.03355** | **H** | **-5.76395 0.46302 -0.23329** |
| **H** | **1.18862 -0.08057 2.60868** | **C** | **-4.86298 -1.33386 -0.95369** |
| **C** | **2.40611 0.33443 0.07181** | **H** | **-5.79546 -1.74702 -1.31558** |
| **C** | **2.82241 1.54703 -0.51958** | **C** | **-3.68135 -2.04501 -1.10055** |
| **C** | **4.15633 1.66696 -0.9122** | **H** | **-3.70773 -3.01842 -1.57294** |
| **H** | **4.48833 2.58694 -1.37542** | **C** | **-2.46648 -1.54819 -0.63254** |
| **C** | **5.06965 0.64698 -0.70595** | **C** | **-1.21751 -2.40661 -0.77553** |
| **H** | **6.10091 0.76936 -1.01077** | **H** | **-0.40094 -1.90446 -0.26281** |
| **C** | **4.6544 -0.5295 -0.1039** | **C** | **-1.38655 -3.78244 -0.11122** |
| **H** | **5.37055 -1.32506 0.05571** | **H** | **-1.66719 -3.6846 0.93849** |
| **C** | **3.32916 -0.71354 0.28454** | **H** | **-0.45046 -4.34192 -0.16105** |
| **C** | **2.92135 -2.03779 0.91423** | **H** | **-2.15366 -4.38164 -0.60404** |
| **H** | **1.84857 -1.99018 1.09304** | **C** | **-0.80288 -2.55654 -2.24775** |
| **C** | **3.61496 -2.26561 2.26653** | **H** | **-0.63107 -1.58338 -2.7083** |
| **H** | **3.42408 -1.44351 2.95801** | **H** | **-1.57316 -3.07043 -2.82601** |

| | | | |
|---|---|---|---|
| H | 4.69704 | -2.35195 | 2.15096 |
| H | 3.2571 | -3.18726 | 2.72977 |
| C | 3.17156 | -3.22103 | -0.03306 |
| H | 2.6581 | -3.07895 | -0.98442 |
| H | 2.80891 | -4.14899 | 0.41347 |
| H | 4.23437 | -3.35022 | -0.245 |
| C | 1.89997 | 2.74164 | -0.72617 |
| H | 0.91042 | 2.46668 | -0.36147 |
| C | 1.73511 | 3.08531 | -2.21422 |
| H | 1.35045 | 2.23184 | -2.77331 |
| H | 2.6827 | 3.38281 | -2.66701 |
| H | 1.03391 | 3.91283 | -2.33759 |
| H | 0.11823 | -3.1368 | -2.32973 |
| C | -3.66598 | 1.86093 | 0.72886 |
| H | -2.63266 | 2.13572 | 0.93452 |
| C | -4.43923 | 1.89408 | 2.05664 |
| H | -4.03486 | 1.17769 | 2.77331 |
| H | -5.49277 | 1.64977 | 1.90776 |
| H | -4.38999 | 2.88793 | 2.50619 |
| C | -4.21799 | 2.90856 | -0.25029 |
| H | -3.65391 | 2.90932 | -1.18341 |
| H | -4.15315 | 3.90734 | 0.18613 |
| H | -5.26538 | 2.72214 | -0.49359 |

**NHC-6 singlet**

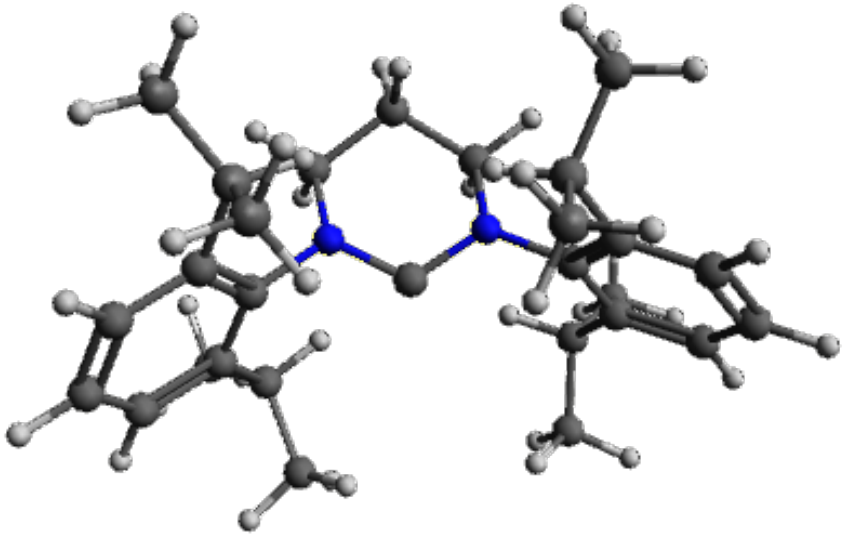


| | |
|---|---|
| Zero-point correction= | 0.619796 (Hartree/Particle) |
| Thermal correction to Energy= | 0.651932 |
| Thermal correction to Enthalpy= | 0.652876 |
| Thermal correction to Gibbs Free Energy= | 0.554296 |
| Sum of electronic and zero-point Energies= | -1200.375792 |
| Sum of electronic and thermal Energies= | -1200.343656 |
| Sum of electronic and thermal Enthalpies= | -1200.342711 |
| Sum of electronic and thermal Free Energies= | -1200.441291 |

| | | | |
|---|---|---|---|
| N | -1.14132 | 0.00275 | 0.69449 |
| N | 1.14075 | -0.06178 | 0.69683 |
| C | 0.00038 | -0.02801 | -0.01769 |
| C | -1.24016 | 0.00432 | 2.16676 |
| H | -2.15705 | -0.51095 | 2.45215 |
| H | -1.32343 | 1.03351 | 2.53337 |
| C | -0.02429 | -0.68041 | 2.76905 |
| C | 3.16388 | -3.58381 | 0.65625 |
| H | 2.6151 | -4.50447 | 0.864 |
| H | 3.46363 | -3.14666 | 1.61003 |
| H | 4.07319 | -3.85859 | 0.11927 |
| C | 1.85463 | -3.25071 | -1.48747 |
| H | 1.31474 | -4.1825 | -1.30759 |
| H | 2.71547 | -3.48066 | -2.11821 |

| | | | | | |
|---|---|---|---|---|---|
| H | -0.0198 | -0.55992 | 3.85273 | H | 1.20092 | -2.57674 | -2.04003 |
| H | -0.06718 | -1.75123 | 2.55991 | C | 1.24287 | -0.09321 | 2.16937 |
| H | 1.41576 | 0.91799 | 2.55307 | C | -2.91372 | 1.34692 | -0.35679 |
| H | 2.11326 | -0.69075 | 2.44118 | C | -4.14993 | 1.40089 | -1.00152 |
| C | -2.39678 | 0.08667 | -0.01096 | H | -4.56261 | 2.36133 | -1.2815 |
| C | -3.10281 | -1.09426 | -0.30226 | C | -2.16922 | 2.64221 | -0.07157 |
| C | -4.33389 | -0.98768 | -0.94837 | H | -1.23696 | 2.38486 | 0.42821 |
| H | -4.88862 | -1.88516 | -1.18937 | C | -2.9608 | 3.56604 | 0.8672 |
| C | -4.85829 | 0.24733 | -1.29464 | H | -2.37888 | 4.45936 | 1.10264 |
| H | -5.81555 | 0.30997 | -1.79595 | H | -3.89708 | 3.89323 | 0.41176 |
| C | -2.55904 | -2.4737 | 0.03789 | H | -3.20775 | 3.0659 | 1.80492 |
| H | -1.61305 | -2.33624 | 0.55857 | C | -1.7947 | 3.36787 | -1.3727 |
| C | -3.49632 | -3.2527 | 0.97352 | H | -1.2109 | 4.2644 | -1.15582 |
| H | -3.04961 | -4.21005 | 1.24905 | H | -1.20181 | 2.72201 | -2.01948 |
| H | -4.45555 | -3.46236 | 0.49734 | H | -2.68326 | 3.67684 | -1.92613 |
| H | -3.69891 | -2.69806 | 1.89108 | C | 3.04523 | 1.16585 | -0.25982 |
| C | -2.25644 | -3.28046 | -1.23431 | C | 4.28273 | 1.14087 | -0.9037 |
| H | -1.81296 | -4.24502 | -0.97914 | H | 4.79447 | 2.07181 | -1.11011 |
| H | -1.56054 | -2.74391 | -1.87823 | C | 2.43761 | 2.50576 | 0.12738 |
| H | -3.16543 | -3.47378 | -1.80684 | H | 1.46616 | 2.31005 | 0.57844 |
| C | 2.39931 | -0.05682 | -0.00847 | C | 3.29513 | 3.24533 | 1.16646 |
| C | 2.97874 | -1.27884 | -0.39394 | H | 2.80986 | 4.17487 | 1.47077 |
| C | 4.21434 | -1.2506 | -1.03979 | H | 3.45437 | 2.63842 | 2.05898 |
| H | 4.67228 | -2.17932 | -1.35427 | H | 4.27653 | 3.50157 | 0.76346 |
| C | 4.86638 | -0.054 | -1.29106 | C | 2.18873 | 3.38737 | -1.10578 |
| H | 5.82592 | -0.05286 | -1.79192 | H | 1.69365 | 4.31635 | -0.81639 |
| C | 2.29275 | -2.61578 | -0.15852 | H | 3.1236 | 3.65234 | -1.60257 |
| H | 1.38791 | -2.42598 | 0.41593 | H | 1.55622 | 2.87492 | -1.82974 |

**NHC-6 triplet**

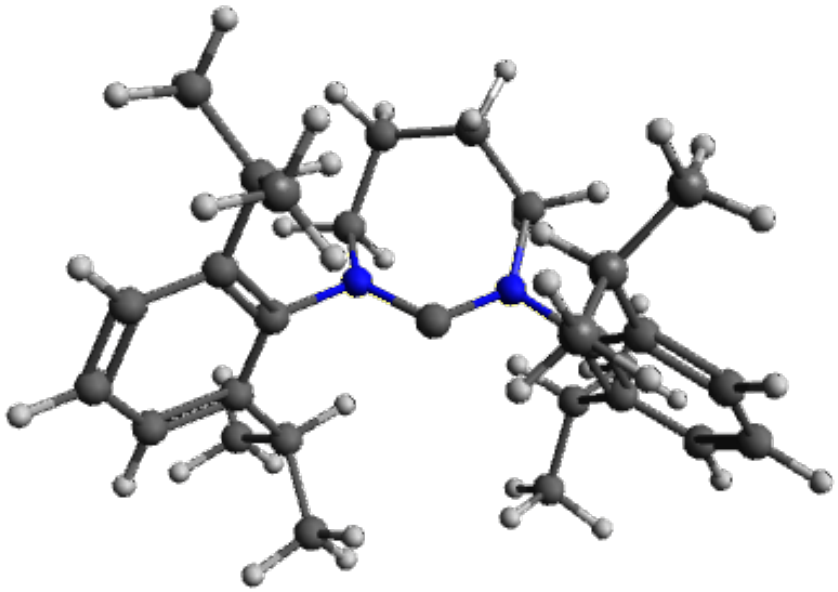


**Zero-point correction=** **0.617580 (Hartree/Particle)**

| | |
|---|---|
| **Thermal correction to Energy=** | **0.650004** |
| **Thermal correction to Enthalpy=** | **0.650948** |
| **Thermal correction to Gibbs Free Energy=** | **0.550312** |
| **Sum of electronic and zero-point Energies=** | **-1200.278577** |
| **Sum of electronic and thermal Energies=** | **-1200.246153** |
| **Sum of electronic and thermal Enthalpies=** | **-1200.245208** |
| **Sum of electronic and thermal Free Energies=** | **-1200.345845** |

| | | | |
|---|---|---|---|
| **N** | **-1.17568 0.04207 0.72877** | **C** | **2.43221 -3.63323 0.86459** |
| **N** | **1.22376 -0.0189 0.7643** | **H** | **1.75068 -4.45338 1.09953** |
| **C** | **0.0504 0.46073 0.21656** | **H** | **2.65482 -3.1031 1.79167** |
| **C** | **-1.24185 0.27259 2.18857** | **H** | **3.36498 -4.06838 0.50038** |
| **H** | **-2.13511 -0.22323 2.56863** | **C** | **1.4374 -3.46691 -1.45516** |
| **H** | **-1.33208 1.34523 2.41051** | **H** | **0.7204 -4.25604 -1.22266** |
| **C** | **0.0135 -0.29284 2.86148** | **H** | **2.30767 -3.94037 -1.91301** |
| **H** | **0.00424 -0.02066 3.91918** | **H** | **0.98604 -2.80879 -2.1981** |
| **H** | **-0.00511 -1.38259 2.79862** | **C** | **1.30395 0.22411 2.21226** |
| **H** | **1.4308 1.29203 2.43679** | **C** | **-2.83143 1.47627 -0.45147** |
| **H** | **2.17217 -0.30824 2.60114** | **C** | **-4.03111 1.55699 -1.16008** |
| **C** | **-2.38926 0.20671 -0.02598** | **H** | **-4.38219 2.52327 -1.49813** |
| **C** | **-3.14787 -0.94984 -0.3036** | **C** | **-2.06748 2.76133 -0.16324** |
| **C** | **-4.34689 -0.81129 -1.00147** | **H** | **-1.16997 2.49805 0.39462** |
| **H** | **-4.94195 -1.68916 -1.21708** | **C** | **-2.88908 3.73345 0.69773** |
| **C** | **-4.78774 0.42947 -1.43163** | **H** | **-2.29501 4.61555 0.94482** |
| **H** | **-5.71852 0.51743 -1.97714** | **H** | **-3.78591 4.07484 0.17764** |
| **C** | **-2.70331 -2.33534 0.13968** | **H** | **-3.20634 3.2675 1.63177** |
| **H** | **-1.7111 -2.22478 0.57456** | **C** | **-1.59306 3.43965 -1.45737** |
| **C** | **-3.62995 -2.90767 1.2243** | **H** | **-1.00409 4.32934 -1.22628** |
| **H** | **-3.26357 -3.87666 1.56937** | **H** | **-0.9702 2.76563 -2.04572** |
| **H** | **-4.64374 -3.05159 0.84544** | **H** | **-2.4335 3.75066 -2.08062** |
| **H** | **-3.69297 -2.24421 2.08798** | **C** | **3.25738 0.87615 -0.31074** |
| **C** | **-2.58566 -3.30825 -1.04264** | **C** | **4.43352 0.62818 -1.01989** |
| **H** | **-2.19409 -4.26972 -0.70478** | **H** | **5.10103 1.44922 -1.24719** |
| **H** | **-1.9141 -2.91984 -1.80835** | **C** | **2.92892 2.30202 0.10824** |
| **H** | **-3.55365 -3.49507 -1.51106** | **H** | **1.94375 2.29249 0.57123** |
| **C** | **2.40977 -0.2108 -0.0195** | **C** | **3.93369 2.84061 1.13902** |
| **C** | **2.7174 -1.51017 -0.47014** | **H** | **3.64994 3.84414 1.4621** |
| **C** | **3.90184 -1.7044 -1.17888** | **H** | **3.98126 2.20209 2.02208** |
| **H** | **4.16109 -2.69706 -1.523** | **H** | **4.93983 2.89947 0.71973** |
| **C** | **4.75929 -0.64833 -1.44711** | **C** | **2.8331 3.24226 -1.10327** |
| **H** | **5.67687 -0.81989 -1.99511** | **H** | **2.52922 4.24081 -0.78323** |
| **C** | **1.80942 -2.69484 -0.18157** | **H** | **3.79047 3.33782 -1.61828** |
| **H** | **0.88938 -2.29507 0.24181** | **H** | **2.09937 2.88033 -1.82357** |

**NHC-7 singlet**

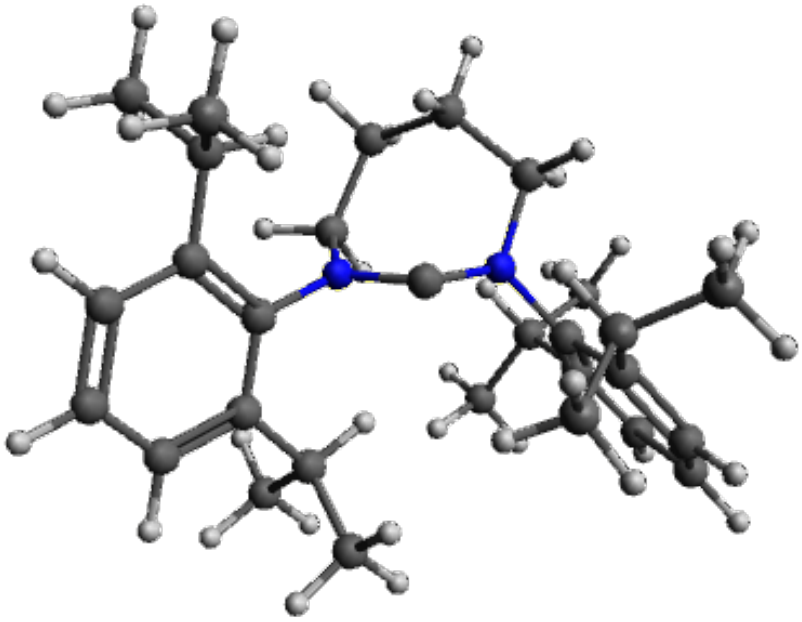


| | |
|---|---|
| **Zero-point correction=** | **0.648623 (Hartree/Particle)** |
| **Thermal correction to Energy=** | **0.681790** |
| **Thermal correction to Enthalpy=** | **0.682734** |
| **Thermal correction to Gibbs Free Energy=** | **0.583904** |
| **Sum of electronic and zero-point Energies=** | **-1239.658797** |
| **Sum of electronic and thermal Energies=** | **-1239.625630** |
| **Sum of electronic and thermal Enthalpies=** | **-1239.624686** |
| **Sum of electronic and thermal Free Energies=** | **-1239.723515** |

| | | | |
|---|---|---|---|
| **C** | **0.01006 -0.02613 0.00511** | **H** | **1.54591 0.41759 2.71241** |
| **N** | **-1.13238 0.18796 0.68423** | **H** | **2.30384 -1.06695 2.19123** |
| **C** | **-1.23938 0.59777 2.10727** | **H** | **5.06687 1.62668 -0.87812** |
| **C** | **-0.99814 -0.5216 3.11344** | **H** | **5.66871 -0.42678 -2.09012** |
| **C** | **0.26075 -1.33145 2.78178** | **H** | **4.16036 -2.36767 -2.04551** |
| **C** | **1.3734 -0.50291 2.14723** | **H** | **0.94527 -2.46283 -0.15265** |
| **N** | **1.15088 -0.20429 0.69751** | **H** | **0.57189 -3.80192 -2.18274** |
| **C** | **2.3644 -0.26308 -0.0914** | **H** | **2.05096 -3.16921 -2.90401** |
| **C** | **3.21313 0.85747 -0.11888** | **H** | **0.69979 -2.0802 -2.56842** |
| **C** | **4.40227 0.7732 -0.84394** | **H** | **1.82554 -4.75745 -0.18444** |
| **C** | **4.74372 -0.38008 -1.53005** | **H** | **3.36337 -4.20442 -0.83989** |
| **C** | **3.89153 -1.47242 -1.5001** | **H** | **2.88404 -3.72961 0.78668** |
| **C** | **2.69652 -1.44292 -0.78201** | **H** | **1.88989 2.041 1.0456** |
| **C** | **1.80056 -2.67182 -0.79083** | **H** | **2.4577 4.24118 0.13127** |
| **C** | **1.24878 -2.94531 -2.19818** | **H** | **3.73498 3.54524 -0.86187** |
| **C** | **2.51244 -3.90968 -0.22345** | **H** | **2.0527 3.12538 -1.17898** |
| **C** | **2.87367 2.1591 0.59395** | **H** | **-5.06915 -1.34412 -1.15263** |
| **C** | **2.77396 3.33511 -0.38968** | **H** | **-5.59145 0.85127 -2.12859** |
| **C** | **-2.33361 0.36139 -0.10605** | **H** | **-4.02903 2.72822 -1.84076** |
| **C** | **-3.21293 -0.72201 -0.27446** | **H** | **-0.82819 2.49813 0.06991** |
| **C** | **-4.38283 -0.51988 -1.0083** | **H** | **-0.40216 4.04173 -1.79709** |
| **C** | **-4.67921 0.71375 -1.56251** | **H** | **-1.90095 3.54853 -2.583** |

| | | | | | |
|---|---|---|---|---|---|
| C | -3.79753 | 1.76963 | -1.39499 | H | -0.59128 | 2.38116 | -2.3764 |
| C | -2.61644 | 1.61941 | -0.66949 | H | -1.98588 | -2.04988 | 0.83109 |
| C | -1.67467 | 2.8074 | -0.53958 | H | -2.4619 | -4.10911 | -0.42596 |
| C | -1.10943 | 3.2175 | -1.90821 | H | -1.93381 | -2.82271 | -1.51846 |
| C | -2.92468 | -2.10697 | 0.28483 | H | -3.63908 | -3.26179 | -1.42767 |
| C | -2.72782 | -3.13444 | -0.84061 | H | 3.57498 | 3.37973 | 2.25294 |
| C | 3.87027 | 2.47299 | 1.721 | H | 4.8757 | 2.63293 | 1.32762 |
| C | -4.00825 | -2.57177 | 1.26945 | H | 3.92621 | 1.65857 | 2.44454 |
| C | -2.34136 | 3.99978 | 0.16386 | H | -3.74258 | -3.53886 | 1.70122 |
| H | -0.52065 | 1.404 | 2.27432 | H | -4.13838 | -1.86021 | 2.0863 |
| H | -2.2277 | 1.02946 | 2.25217 | H | -4.97527 | -2.68614 | 0.77686 |
| H | -0.9022 | -0.06486 | 4.10239 | H | -1.62458 | 4.81283 | 0.29471 |
| H | -1.86345 | -1.18424 | 3.1626 | H | -3.18008 | 4.39049 | -0.4148 |
| H | 0.65124 | -1.79406 | 3.69069 | H | -2.72082 | 3.72228 | 1.1485 |
| H | 0.01403 | -2.15127 | 2.1057 | | | | |

**NHC-7 triplet**

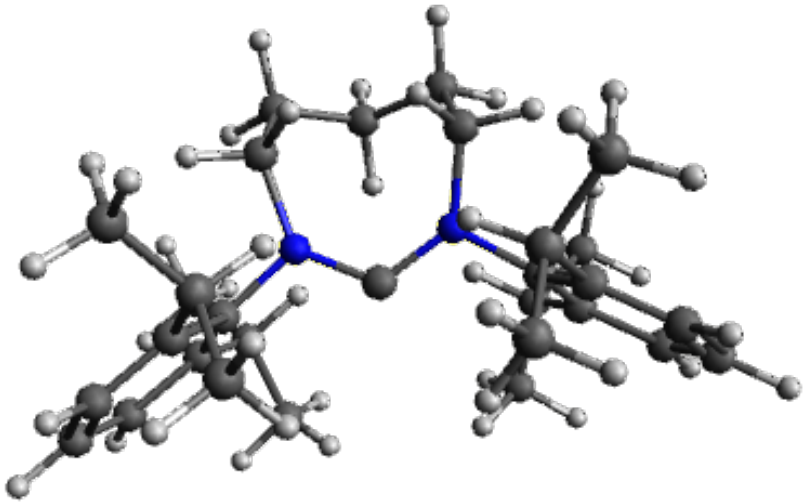


| | |
|---|---|
| Zero-point correction= | 0.646544 (Hartree/Particle) |
| Thermal correction to Energy= | 0.680215 |
| Thermal correction to Enthalpy= | 0.681159 |
| Thermal correction to Gibbs Free Energy= | 0.579326 |
| Sum of electronic and zero-point Energies= | -1239.576580 |
| Sum of electronic and thermal Energies= | -1239.542909 |
| Sum of electronic and thermal Enthalpies= | -1239.541965 |
| Sum of electronic and thermal Free Energies= | -1239.643798 |

| | | | | | |
|---|---|---|---|---|---|
| C | -0.14742 | -0.71702 | 0.00954 | H | 1.99073 | -1.70503 | 2.28107 |

| | | | |
|---|---|---|---|
| N | -1.1798 | -0.03515 | 0.63779 |
| C | -1.05263 | 0.19244 | 2.07553 |
| C | -0.80249 | -1.08157 | 2.93024 |
| C | -0.10532 | -2.27708 | 2.25457 |
| C | 1.22473 | -1.99861 | 1.55892 |
| N | 1.08213 | -0.89816 | 0.58473 |
| C | 2.27983 | -0.42739 | -0.06714 |
| C | 3.09321 | 0.5306 | 0.57128 |
| C | 4.23342 | 0.98388 | -0.09173 |
| C | 4.57489 | 0.50491 | -1.34564 |
| C | 3.78298 | -0.45827 | -1.94947 |
| C | 2.63612 | -0.95158 | -1.32814 |
| C | 1.8347 | -2.04258 | -2.02624 |
| C | 1.19479 | -1.53635 | -3.32757 |
| C | 2.68808 | -3.29444 | -2.28601 |
| C | 2.78102 | 1.07871 | 1.95575 |
| C | 2.56644 | 2.5996 | 1.94176 |
| C | -2.27136 | 0.50156 | -0.11497 |
| C | -3.50177 | -0.18636 | -0.15215 |
| C | -4.55648 | 0.369 | -0.87707 |
| C | -4.4053 | 1.56043 | -1.56676 |
| C | -3.18642 | 2.22033 | -1.53794 |
| C | -2.10591 | 1.71357 | -0.81756 |
| C | -0.80451 | 2.49961 | -0.78188 |
| C | -0.20946 | 2.69648 | -2.18356 |
| C | -3.70891 | -1.51404 | 0.55876 |
| C | -4.07953 | -2.63605 | -0.4233 |
| C | 3.86494 | 0.69431 | 2.9759 |
| C | -4.74821 | -1.4065 | 1.68545 |
| C | -0.98639 | 3.84992 | -0.06984 |
| H | -0.24135 | 0.90563 | 2.25767 |
| H | -1.96941 | 0.677 | 2.40945 |
| H | -0.22959 | -0.77381 | 3.80986 |
| H | -1.75911 | -1.44715 | 3.30901 |
| H | 0.06987 | -3.0453 | 3.0125 |
| H | -0.78323 | -2.719 | 1.52405 |
| H | 1.58087 | -2.91443 | 1.06974 |
| H | 4.86334 | 1.72613 | 0.38133 |
| H | 5.45988 | 0.87472 | -1.84711 |
| H | 4.06441 | -0.84046 | -2.92199 |
| H | 1.01743 | -2.33314 | -1.36882 |
| H | 0.60036 | -2.3262 | -3.79077 |
| H | 1.9505 | -1.2212 | -4.04974 |
| H | 0.53677 | -0.68968 | -3.13426 |
| H | 2.07284 | -4.08706 | -2.71606 |
| H | 3.50161 | -3.09338 | -2.9852 |
| H | 3.13052 | -3.67313 | -1.36348 |
| H | 1.84748 | 0.62543 | 2.28221 |
| H | 2.28633 | 2.95451 | 2.93552 |
| H | 3.47381 | 3.12884 | 1.64631 |
| H | 1.77609 | 2.88225 | 1.24667 |
| H | -5.50818 | -0.14559 | -0.91123 |
| H | -5.23419 | 1.97365 | -2.127 |
| H | -3.07674 | 3.15306 | -2.07602 |
| H | -0.08643 | 1.91756 | -0.20791 |
| H | 0.75404 | 3.20516 | -2.1191 |
| H | -0.8618 | 3.30086 | -2.81656 |
| H | -0.0517 | 1.73972 | -2.68077 |
| H | -2.75814 | -1.78763 | 1.00982 |
| H | -4.15533 | -3.59076 | 0.10128 |
| H | -3.32558 | -2.73668 | -1.20425 |
| H | -5.03986 | -2.44805 | -0.90673 |
| H | 3.58764 | 1.03542 | 3.97533 |
| H | 4.82527 | 1.14838 | 2.7257 |
| H | 4.01289 | -0.38568 | 3.01537 |
| H | -4.83867 | -2.35648 | 2.21625 |
| H | -4.47343 | -0.6388 | 2.41036 |
| H | -5.73477 | -1.15092 | 1.29442 |
| H | -0.03373 | 4.37935 | -0.00429 |
| H | -1.68569 | 4.49309 | -0.60717 |
| H | -1.37022 | 3.71709 | 0.9426 |

**NHC-8 singlet**

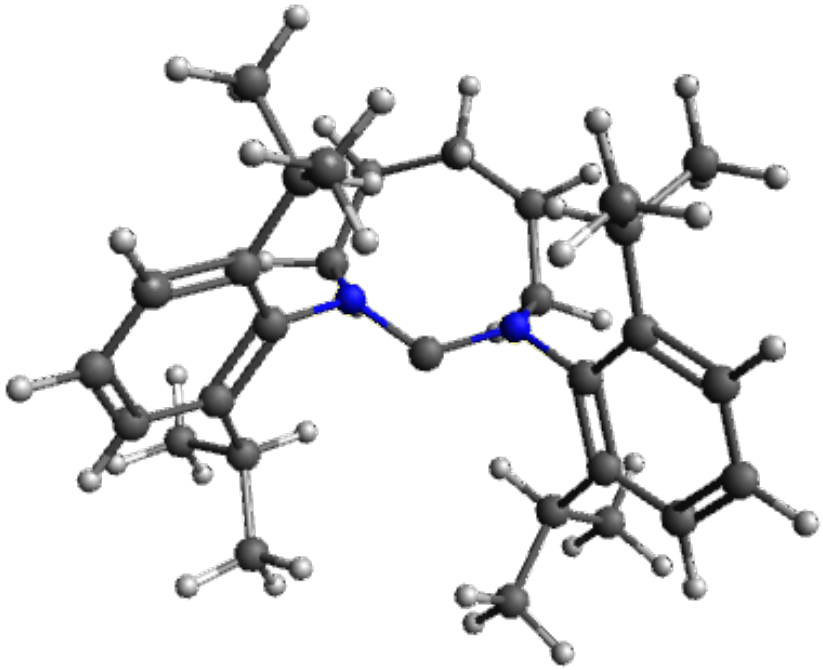


| | |
|---|---|
| **Zero-point correction=** | **0.677907 (Hartree/Particle)** |
| **Thermal correction to Energy=** | **0.712030** |
| **Thermal correction to Enthalpy=** | **0.712974** |
| **Thermal correction to Gibbs Free Energy=** | **0.612343** |
| **Sum of electronic and zero-point Energies=** | **-1278.948681** |
| **Sum of electronic and thermal Energies=** | **-1278.914558** |
| **Sum of electronic and thermal Enthalpies=** | **-1278.913614** |
| **Sum of electronic and thermal Free Energies=** | **-1279.014246** |

| | | | |
|---|---|---|---|
| **C** | **0.00018 0.03429 0.02125** | **C** | **2.09223 4.20491 0.44565** |
| **C** | **-1.5121 -0.25007 2.12847** | **C** | **3.11319 -1.91905 -0.1106** |
| **H** | **-2.5948 -0.14171 2.20112** | **N** | **1.16304 0.19414 0.7017** |
| **H** | **-1.09111 0.59981 2.66468** | **H** | **2.78726 4.71985 -0.22587** |
| **C** | **-1.11856 -1.5687 2.80822** | **H** | **2.64449 3.93783 1.35267** |
| **H** | **-1.34378 -1.45853 3.87838** | **H** | **1.31403 4.92479 0.72197** |
| **H** | **-1.77041 -2.36928 2.43768** | **C** | **-2.18617 -3.97782 -0.63438** |
| **C** | **0.33901 -2.00116 2.62544** | **H** | **-2.70368 -3.95617 0.33065** |
| **H** | **0.51104 -2.90037 3.2297** | **H** | **-1.41653 -4.75619 -0.58901** |
| **H** | **0.48839 -2.30917 1.58554** | **H** | **-2.91406 -4.28548 -1.3926** |
| **C** | **-2.34042 -0.2854 -0.19314** | **C** | **-0.81805 -2.64771 -2.32033** |
| **C** | **-3.27801 0.77302 -0.24479** | **H** | **-0.78972 -2.41805 -0.20264** |
| **C** | **-4.43187 0.60952 -1.02047** | **H** | **-1.521 -2.80753 -3.14566** |
| **H** | **-5.16016 1.41419 -1.06535** | **H** | **-0.08136 -3.45843 -2.34635** |
| **C** | **-4.65621 -0.55544 -1.74532** | **H** | **-0.3016 -1.69799 -2.48348** |
| **H** | **-5.55585 -0.66335 -2.34454** | **C** | **3.00599 -2.81571 -1.35883** |
| **C** | **-3.71345 -1.57585 -1.70589** | **H** | **2.82909 -3.85745 -1.06791** |
| **H** | **-3.88226 -2.47834 -2.2858** | **H** | **3.92675 -2.79096 -1.95166** |
| **C** | **-2.55025 -1.47042 -0.93195** | **H** | **2.18364 -2.49499 -2.00288** |
| **C** | **-3.07119 2.10063 0.48292** | **C** | **4.26203 -2.39403 0.79999** |
| **C** | **-1.54627 -2.61688 -0.96327** | **H** | **2.17891 -2.02549 0.44258** |
| **N** | **-1.17634 -0.15285 0.67133** | **H** | **4.35177 -1.77309 1.69714** |
| **C** | **1.4231 0.34095 2.16809** | **H** | **5.22512 -2.35613 0.27951** |
| **H** | **2.41195 0.79575 2.25926** | **H** | **4.09947 -3.4301 1.11754** |
| **H** | **0.72629 1.0727 2.57973** | **C** | **-4.12475 2.3331 1.58425** |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| C | 1.40963 | -0.96562 | 2.99308 | H | -5.13223 | 2.39663 | 1.15914 |
| H | 1.31393 | -0.68757 | 4.05188 | H | -3.92836 | 3.27272 | 2.11252 |
| H | 2.38759 | -1.44912 | 2.8963 | H | -4.13155 | 1.52646 | 2.32389 |
| C | 2.31058 | 0.53429 | -0.13173 | C | -3.06259 | 3.28553 | -0.5028 |
| C | 2.48327 | 1.87943 | -0.53133 | H | -2.08634 | 2.07364 | 0.95723 |
| C | 3.61106 | 2.21442 | -1.28929 | H | -2.32483 | 3.13522 | -1.29448 |
| H | 3.7482 | 3.24221 | -1.61221 | H | -2.81956 | 4.21659 | 0.02164 |
| C | 4.55688 | 1.25698 | -1.64033 | H | -4.04046 | 3.42153 | -0.97676 |
| H | 5.4284 | 1.53671 | -2.22543 | C | 0.68179 | 3.34354 | -1.49086 |
| C | 4.37335 | -0.06139 | -1.24289 | H | 0.73604 | 2.55502 | 0.49072 |
| H | 5.10743 | -0.81043 | -1.52567 | H | 0.17681 | 2.46141 | -1.8945 |
| C | 3.25735 | -0.4496 | -0.4886 | H | 1.35264 | 3.73851 | -2.26185 |
| C | 1.46073 | 2.9666 | -0.21612 | H | -0.06928 | 4.111 | -1.2745 |

**NHC-8 triplet**

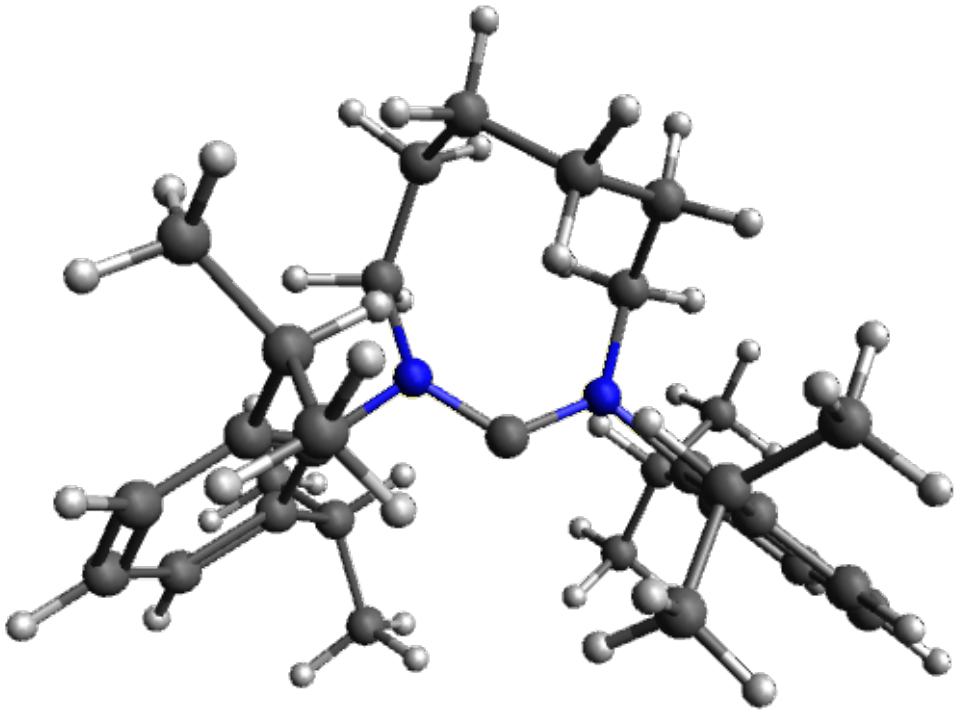


| | |
|---|---|
| Zero-point correction= | 0.675606 (Hartree/Particle) |
| Thermal correction to Energy= | 0.710025 |
| Thermal correction to Enthalpy= | 0.710969 |
| Thermal correction to Gibbs Free Energy= | 0.607825 |
| Sum of electronic and zero-point Energies= | -1278.867915 |
| Sum of electronic and thermal Energies= | -1278.833496 |
| Sum of electronic and thermal Enthalpies= | -1278.832552 |
| Sum of electronic and thermal Free Energies= | -1278.935696 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| C | -0.04524 | 0.51846 | 0.4461 | C | 3.08563 | 3.5668 | 0.90112 |

| | | | |
|---|---|---|---|
| C | -1.67035 0.05794 2.18989 | C | 2.52446 -2.31212 -0.35897 |
| H | -2.75779 0.17586 2.22291 | N | 1.24051 0.06823 0.77104 |
| H | -1.23546 0.98813 2.57794 | H | 3.97288 3.89539 0.34853 |
| C | -1.27332 -1.12699 3.09311 | H | 3.42623 2.93206 1.72513 |
| H | -1.36988 -0.79336 4.13616 | H | 2.61395 4.45666 1.3328 |
| H | -2.01285 -1.92647 2.96197 | C | -2.82131 -3.52847 0.22517 |
| C | 0.10934 -1.75741 2.86451 | H | -3.11495 -3.06709 1.17301 |
| H | 0.17348 -2.63821 3.5159 | H | -2.27611 -4.45192 0.45072 |
| H | 0.1466 -2.13745 1.83958 | H | -3.73928 -3.80335 -0.30659 |
| C | -2.32058 -0.06093 -0.22109 | C | -1.51097 -3.26412 -1.92418 |
| C | -3.01486 1.1445 -0.49031 | H | -1.05702 -2.33795 -0.04489 |
| C | -4.08091 1.11242 -1.39814 | H | -2.36603 -3.60119 -2.52009 |
| H | -4.62654 2.02787 -1.60822 | H | -0.90298 -4.14681 -1.70011 |
| C | -4.45374 -0.06481 -2.03713 | H | -0.91595 -2.5905 -2.54775 |
| H | -5.28582 -0.06793 -2.73563 | C | 2.25265 -3.21378 -1.57645 |
| C | -3.75073 -1.2365 -1.78057 | H | 1.87113 -4.18742 -1.24989 |
| H | -4.04274 -2.15365 -2.28344 | H | 3.16236 -3.40069 -2.1573 |
| C | -2.67752 -1.25921 -0.8809 | H | 1.51398 -2.76742 -2.24733 |
| C | -2.65819 2.47533 0.16936 | C | 3.59243 -2.94972 0.55202 |
| C | -1.9547 -2.57537 -0.62111 | H | 1.59728 -2.23361 0.21369 |
| N | -1.2601 -0.0952 0.76903 | H | 3.78194 -2.3378 1.4392 |
| C | 1.62133 0.29387 2.19171 | H | 4.5447 -3.06379 0.02185 |
| H | 2.68498 0.55079 2.22497 | H | 3.27456 -3.944 0.88562 |
| H | 1.07054 1.16897 2.56057 | C | -3.77001 2.95742 1.1223 |
| C | 1.37305 -0.91802 3.11566 | H | -4.70363 3.14502 0.58056 |
| H | 1.38456 -0.55232 4.15219 | H | -3.47702 3.89244 1.61265 |
| H | 2.22687 -1.60043 3.02783 | H | -3.9841 2.22043 1.90237 |
| C | 2.29173 0.2483 -0.21453 | C | -2.33988 3.55977 -0.87759 |
| C | 2.71516 1.54797 -0.58836 | H | -1.74605 2.3279 0.7533 |
| C | 3.7675 1.67008 -1.50459 | H | -1.5497 3.23052 -1.5575 |
| H | 4.10365 2.66076 -1.79664 | H | -2.00352 4.47811 -0.3838 |
| C | 4.39423 0.55218 -2.04342 | H | -3.21783 3.81416 -1.48111 |
| H | 5.21044 0.67033 -2.75063 | C | 1.58194 3.75573 -1.1297 |
| C | 3.97036 -0.71742 -1.66895 | H | 1.22585 2.53659 0.57848 |
| H | 4.46524 -1.58908 -2.08689 | H | 0.88264 3.23315 -1.78837 |
| C | 2.92072 -0.8959 -0.75869 | H | 2.39813 4.14426 -1.74834 |
| C | 2.09653 2.8226 -0.01782 | H | 1.06202 4.61609 -0.69461 |

**NHC-9 saturated singlet**

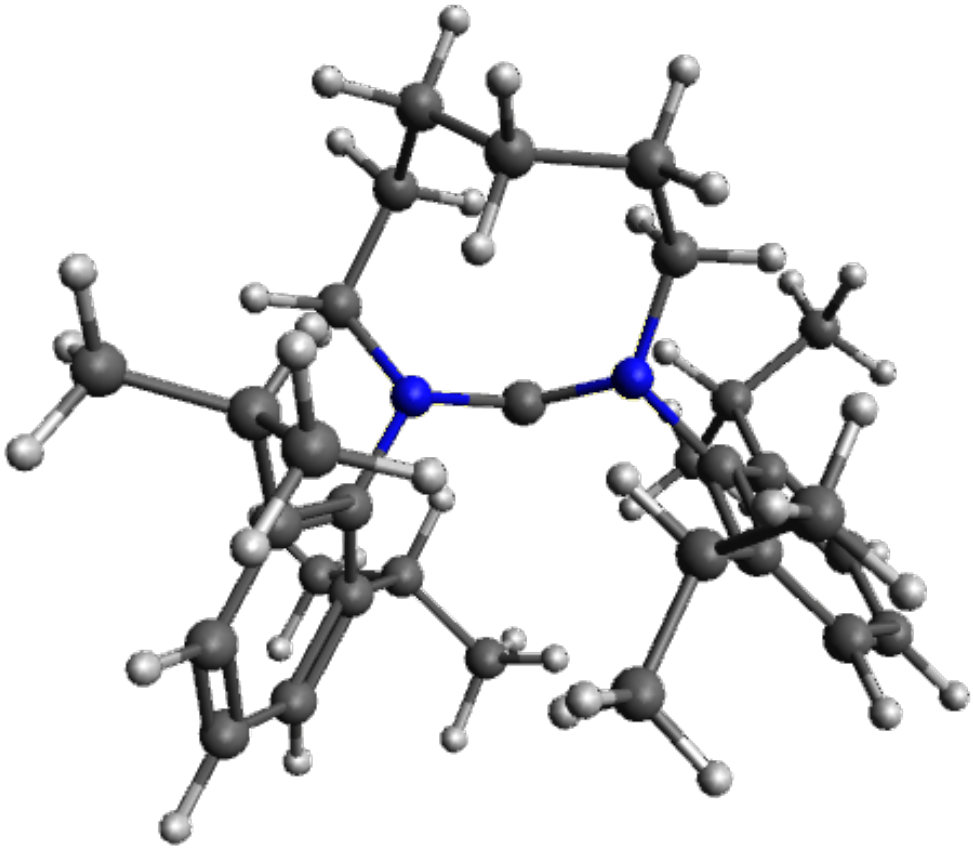


| | |
|---|---|
| **Zero-point correction=** | **0.751461 (Hartree/Particle)** |
| **Thermal correction to Energy=** | **0.791615** |
| **Thermal correction to Enthalpy=** | **0.792559** |
| **Thermal correction to Gibbs Free Energy=** | **0.678053** |
| **Sum of electronic and zero-point Energies=** | **-1623.080476** |
| **Sum of electronic and thermal Energies=** | **-1623.040322** |
| **Sum of electronic and thermal Enthalpies=** | **-1623.039378** |
| **Sum of electronic and thermal Free Energies=** | **-1623.153885** |

| | | | |
|---|---|---|---|
| **N** | **1.17354** | **-0.20428** | **0.59429** |
| **C** | **1.46247** | **-0.48508** | **2.02442** |
| **C** | **1.23499** | **-1.94610** | **2.43796** |
| **H** | **0.89654** | **0.20218** | **2.63922** |
| **H** | **2.50989** | **-0.24923** | **2.19362** |
| **C** | **-0.14487** | **-2.52947** | **2.12533** |
| **H** | **1.44503** | **-2.02371** | **3.51030** |
| **H** | **1.99015** | **-2.55797** | **1.93944** |
| **C** | **-1.31144** | **-2.00719** | **2.97394** |
| **H** | **-0.35518** | **-2.36874** | **1.06978** |
| **H** | **-0.09679** | **-3.61382** | **2.25270** |
| **C** | **-1.35823** | **-0.49967** | **3.24399** |
| **H** | **-1.26972** | **-2.48926** | **3.95549** |
| **H** | **-2.24972** | **-2.33666** | **2.52448** |
| **C** | **-1.50076** | **0.52511** | **2.08447** |
| **H** | **-0.49341** | **-0.24059** | **3.85350** |
| **H** | **-2.21653** | **-0.31493** | **3.89495** |
| **C** | **0.00917** | **0.05898** | **-0.01893** |
| **H** | **-2.25966** | **-1.91471** | **0.33100** |
| **C** | **-1.31458** | **3.03904** | **-0.24821** |
| **C** | **-0.64655** | **3.65480** | **-1.48697** |
| **H** | **-0.17055** | **2.88366** | **-2.09202** |
| **H** | **0.11455** | **4.37810** | **-1.18914** |
| **H** | **-1.37013** | **4.17838** | **-2.11375** |
| **C** | **-1.92963** | **4.13065** | **0.64252** |
| **H** | **-1.16469** | **4.84480** | **0.95421** |
| **H** | **-2.38310** | **3.70762** | **1.54000** |
| **H** | **-2.70494** | **4.68711** | **0.11294** |
| **H** | **-0.52774** | **2.55068** | **0.32288** |
| **C** | **2.54182** | **-1.32231** | **-1.16352** |
| **C** | **3.30187** | **0.77395** | **-0.15373** |
| **C** | **4.46057** | **0.69806** | **-0.92487** |
| **C** | **4.67578** | **-0.35407** | **-1.79888** |
| **C** | **3.71580** | **-1.34334** | **-1.91867** |
| **H** | **5.20072** | **1.48393** | **-0.84973** |
| **H** | **5.58091** | **-0.39642** | **-2.39072** |

| | | | |
|---|---|---|---|
| N | -1.15541 | 0.22616 | 0.64459 |
| H | -0.96721 | 1.43477 | 2.37219 |
| H | -2.54883 | 0.80516 | 2.03475 |
| C | 2.34626 | -0.25794 | -0.26373 |
| C | -2.24371 | 0.63458 | -0.24280 |
| C | -3.20672 | -0.30226 | -0.65669 |
| C | -4.26065 | 0.13415 | -1.46145 |
| C | -4.37278 | 1.45729 | -1.84965 |
| C | -3.41248 | 2.36803 | -1.44113 |
| C | -2.33839 | 1.98288 | -0.64016 |
| H | -5.00444 | -0.57924 | -1.79167 |
| H | -5.19914 | 1.77665 | -2.47135 |
| H | -3.49653 | 3.40050 | -1.75412 |
| C | -3.14169 | -1.77452 | -0.28613 |
| C | -4.36349 | -2.21643 | 0.53438 |
| H | -4.26241 | -3.25961 | 0.84112 |
| H | -5.28475 | -2.13195 | -0.04446 |
| H | -4.48425 | -1.60961 | 1.43301 |
| C | -2.96897 | -2.66252 | -1.52796 |
| H | -3.83608 | -2.60012 | -2.18779 |
| H | -2.85053 | -3.70811 | -1.23575 |
| H | -2.09145 | -2.36588 | -2.10100 |
| H | 3.87870 | -2.15480 | -2.61558 |
| C | 1.52945 | -2.43551 | -1.38296 |
| C | 2.11984 | -3.82574 | -1.10240 |
| H | 1.34771 | -4.59109 | -1.20234 |
| H | 2.53093 | -3.89106 | -0.09390 |
| H | 2.92047 | -4.07512 | -1.80075 |
| C | 0.93583 | -2.36328 | -2.79824 |
| H | 0.70748 | -2.27821 | -0.69183 |
| H | 0.18666 | -3.14525 | -2.93742 |
| H | 0.45988 | -1.39728 | -2.96276 |
| H | 1.70431 | -2.50180 | -3.56108 |
| C | 3.10732 | 1.99648 | 0.73642 |
| C | 3.05800 | 3.28771 | -0.09628 |
| H | 2.29338 | 3.22782 | -0.86921 |
| H | 4.01327 | 3.48273 | -0.58602 |
| H | 2.83339 | 4.14422 | 0.54282 |
| C | 4.18520 | 2.10558 | 1.82703 |
| H | 5.17513 | 2.25038 | 1.39140 |
| H | 4.22925 | 1.21011 | 2.44815 |
| H | 3.98388 | 2.95783 | 2.47907 |
| H | 2.14196 | 1.90440 | 1.23072 |

**NHC-9 saturated triplet**



| | |
|---|---|
| **Zero-point correction=** | **0.751461 (Hartree/Particle)** |
| **Thermal correction to Energy=** | **0.791615** |
| **Thermal correction to Enthalpy=** | **0.792559** |
| **Thermal correction to Gibbs Free Energy=** | **0.678053** |
| **Sum of electronic and zero-point Energies=** | **-1623.080476** |
| **Sum of electronic and thermal Energies=** | **-1623.040322** |
| **Sum of electronic and thermal Enthalpies=** | **-1623.039378** |
| **Sum of electronic and thermal Free Energies=** | **-1623.153885** |

| | | | |
|---|---|---|---|
| **N** | **1.09677** | **-0.95886** | **0.30405** |
| **C** | **1.53078** | **-2.17287** | **1.03902** |
| **C** | **0.64018** | **-3.40709** | **0.87281** |
| **H** | **1.64080** | **-1.93356** | **2.09895** |
| **H** | **2.52521** | **-2.42686** | **0.67347** |
| **C** | **-0.85792** | **-3.25405** | **1.14778** |
| **H** | **1.05699** | **-4.18549** | **1.52231** |
| **H** | **0.75027** | **-3.77488** | **-0.15097** |
| **C** | **-1.30975** | **-2.90601** | **2.57645** |
| **H** | **-1.25617** | **-2.52717** | **0.44545** |
| **H** | **-1.32614** | **-4.20878** | **0.89073** |
| **C** | **-1.04282** | **-1.49743** | **3.13504** |
| **H** | **-0.86219** | **-3.62726** | **3.26858** |
| **H** | **-2.38886** | **-3.08388** | **2.62913** |
| **H** | **-2.86515** | **-1.56769** | **0.30271** |
| **C** | **-0.46432** | **2.88101** | **1.06031** |
| **C** | **0.60495** | **3.57942** | **0.20816** |
| **H** | **1.08317** | **2.87846** | **-0.47569** |
| **H** | **1.37788** | **4.01044** | **0.84705** |
| **H** | **0.18169** | **4.39268** | **-0.38379** |
| **C** | **-1.06708** | **3.85420** | **2.08768** |
| **H** | **-0.28442** | **4.24889** | **2.73874** |
| **H** | **-1.81102** | **3.36060** | **2.71459** |
| **H** | **-1.55395** | **4.70231** | **1.60267** |
| **H** | **0.03905** | **2.08923** | **1.61202** |
| **C** | **1.84606** | **-0.40503** | **-1.96775** |
| **C** | **3.26176** | **0.21341** | **-0.06553** |
| **C** | **4.19572** | **0.72618** | **-0.96531** |

| | | | |
|---|---|---|---|
| C | -1.68026 | -0.31464 | 2.40666 |
| H | 0.02691 | -1.31119 | 3.22966 |
| H | -1.43422 | -1.47217 | 4.15644 |
| C | 0.25605 | -0.05893 | 0.94964 |
| N | -1.12857 | -0.06335 | 1.05507 |
| H | -1.56116 | 0.58219 | 3.02842 |
| H | -2.75390 | -0.47521 | 2.29484 |
| C | 2.08296 | -0.36894 | -0.58016 |
| C | -1.89537 | 0.87423 | 0.25088 |
| C | -3.01891 | 0.40175 | -0.46474 |
| C | -3.72645 | 1.29155 | -1.27160 |
| C | -3.36185 | 2.62270 | -1.37228 |
| C | -2.29288 | 3.08803 | -0.62730 |
| C | -1.55397 | 2.24550 | 0.20481 |
| H | -4.57899 | 0.93216 | -1.83304 |
| H | -3.91703 | 3.29585 | -2.01254 |
| H | -2.03255 | 4.13696 | -0.67811 |
| C | -3.52094 | -1.03245 | -0.37521 |
| C | -4.93973 | -1.09817 | 0.21467 |
| H | -5.24887 | -2.13696 | 0.34670 |
| H | -5.66871 | -0.61714 | -0.43949 |
| H | -4.99341 | -0.60316 | 1.18532 |
| C | -3.46471 | -1.75976 | -1.72637 |
| H | -4.11156 | -1.28371 | -2.46516 |
| H | -3.79463 | -2.79456 | -1.61515 |
| H | -2.45223 | -1.76966 | -2.12842 |
| C | 3.97961 | 0.68413 | -2.33327 |
| C | 2.81112 | 0.12672 | -2.82394 |
| H | 5.10713 | 1.17150 | -0.58813 |
| H | 4.71823 | 1.08829 | -3.01349 |
| H | 2.64581 | 0.09865 | -3.89300 |
| C | 0.58992 | -1.02109 | -2.56313 |
| C | 0.91247 | -2.30559 | -3.34302 |
| H | -0.00365 | -2.76680 | -3.71766 |
| H | 1.42481 | -3.03441 | -2.71334 |
| H | 1.55547 | -2.10006 | -4.20106 |
| C | -0.17839 | -0.02347 | -3.44192 |
| H | -0.05573 | -1.29556 | -1.73116 |
| H | -1.09801 | -0.47618 | -3.81645 |
| H | -0.44995 | 0.87054 | -2.88072 |
| H | 0.40921 | 0.28735 | -4.30761 |
| C | 3.56183 | 0.30308 | 1.42626 |
| C | 3.80112 | 1.75033 | 1.88304 |
| H | 2.95286 | 2.38610 | 1.63472 |
| H | 4.69020 | 2.18045 | 1.41918 |
| H | 3.94585 | 1.78362 | 2.96472 |
| C | 4.75460 | -0.58356 | 1.82180 |
| H | 5.67326 | -0.24676 | 1.33794 |
| H | 4.59684 | -1.62471 | 1.53956 |
| H | 4.91587 | -0.54757 | 2.90107 |
| H | 2.68508 | -0.04843 | 1.96519 |


1 A. J. Arduengo, R. Krafczyk, R. Schmutzler, H. A. Craig, J. R. Goerlich, W. J. Marshall and M. Unverzagt, *Tetrahedron* 1999, **55**, 14523.

2 M. Iglesias, D. J. Beetstra, J. C. Knight, L.-L. Ooi, A. Stasch, S. Coles, L. Male, M. B. Hursthouse, K. J. Cavell, A. Dervisi and I. A. Fallis, *Organometallics*, 2008, **27**, 3279.

3 E. L. Kolychev, I. A. Portnyagin, V. V. Shuntikov, V. N. Khrustalev and M. S. Nechaev, *J. Organomet. Chem.* 2009, **694**, 2454.

4 W. Y. Lu, K. J. Cavell, J. S. Wixey and B. Kariuki, *Organometallics*, 2011, **30**, 5649.

5 O.V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard, H. Puschmann. *J. Appl. Cryst.* 2009, **42**, 339–341.

6 G. M. Sheldrick. *Acta Crystallogr. A.* 2008, **64**, 112–122.

7 Gaussian 16, Revision C.01, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Petersson, G. A.; Nakatsuji, H.; Li, X.; Caricato, M.; Marenich, A. V.; Bloino, J.; Janesko, B. G.; Gomperts, R.; Mennucci, B.; Hratchian, H. P.; Ortiz, J. V.; Izmaylov, A. F.; Sonnenberg, J. L.; Williams-Young, D.; Ding, F.; Lipparini, F.; Egidi, F.; Goings, J.; Peng, B.; Petrone, A.; Henderson, T.; Ranasinghe, D.; Zakrzewski, V. G.; Gao, J.; Rega, N.; Zheng, G.; Liang, W.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Throssell, K.; Montgomery, J. A., Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M. J.; Heyd, J. J.; Brothers, E. N.; Kudin, K. N.; Staroverov, V. N.; Keith, T. A.;

Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell,A. P.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Millam, J. M.; Klene, M.; Adamo, C.; Cammi, R.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Farkas, O.; Foresman, J. B.; Fox, D. J. Gaussian, Inc., Wallingford CT, 2016.

8 F. Weigend and R. Ahlrichs. *Phys. Chem. Chem. Phys.* 2005, **7**, 3297-3305.

9 L. Falivene, Z. Cao, A. Petta, L. Serra, A. Poater, R. Oliva, V. Scarano and L. Cavallo. *Nat. Chem.* 2019, **11**, 872 – 879.