

## Supporting Information

### Cyclic (amino)(barrelene)carbenes: An original family of CAACs through a Novel Synthetic Pathway

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## Supplementary Methods

### 1. General Considerations

All commercial reagents were used as purchased unless otherwise mentioned. All reactions were performed under an atmosphere of argon using standard Schlenk techniques or in an argon filled glovebox. Acetonitrile, dichloromethane, and *n*-hexanes were distilled over CaH<sub>2</sub>. Diethyl ether and THF were distilled over sodium wire.

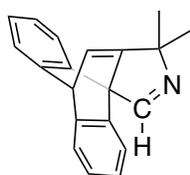
NMR: Multinuclear NMR spectra were recorded on either Bruker Avance 300 MHz, a Varian INOVA 500 MHz (<sup>1</sup>H: 500 MHz, <sup>13</sup>C: 126 MHz) spectrometer, or JOEL 400 MHz (<sup>1</sup>H: 400 MHz, <sup>13</sup>C: 101 MHz) spectrometer with complete proton decoupling for nucleus other than <sup>1</sup>H. Chemical shifts are reported in parts per million with the solvent resonance as the internal standard (CDCl<sub>3</sub>, <sup>1</sup>H: δ 7.26 ppm, <sup>13</sup>C: δ 77.16 ppm). Coupling constants (*J*) are reported in Hertz (Hz). Multiplicities in <sup>1</sup>H NMR are reported using following abbreviations: s = singlet, br s = broad singlet, d = doublet, dd = double doublet, ddd = double double doublet, dt = double triplet, t = triplet, q = quartet, quint = quintet, sept = septet, m = multiplet.

High Resolution Mass Spectrometry (HRMS): HRMS were performed at the UC San Diego Mass Spectrometry Laboratory on an Agilent 6230 Accurate-Mass TOFMS spectrometer using electrospray ionization.

Single crystal X-Ray diffraction data were collected on Bruker Apex II diffractometers using Mo-K<sub>α</sub> radiation (λ = 0.71073 Å) or Cu-K<sub>α</sub> radiation (λ = 1.54178 Å). Crystals were selected under oil, mounted on nylon loops then immediately placed in a cold stream of N<sub>2</sub>. Structures were solved and refined using SHELXTL and Olex2 software.

### 2. Experimental procedures

**1**

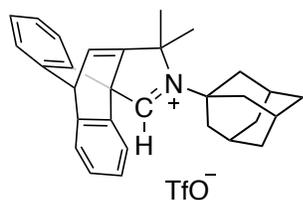


In a Teflon sealed Schlenk, 2-methyl-3-butyn-2-amine (7.7 mL, 73 mmol) was added to a toluene solution of anthracene-9-carboxaldehyde (10.00 g, 48 mmol). The Schlenk was sealed and heated at 120 °C overnight. The mixture was then cooled to room temperature and the volatiles were removed under vacuum. The solid was then crystallized from ethyl acetate (200 mL) and Imine **1** was isolated as a yellow solid (9.30 g, 71%).

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 8.78 (s, 1H), 7.32 (d, *J* = 6.5 Hz, 2H), 7.25 (d, *J* = 6.5 Hz, 2H), 6.97 (m, 4H), 7.58 (d, *J* = 6.0 Hz, 1H), 5.19 (d, *J* = 6.0 Hz, 1H), 1.25 (s, 6H).

<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 160.90, 146.32, 145.57, 124.85, 124, 53, 123.30, 120.27, 72.71, 71.80, 52.09, 29.25.

HRMS: *m/z*. calculated for [C<sub>20</sub>H<sub>17</sub>N+H]<sup>+</sup> [M+H]<sup>+</sup> 272.1434, found 272.1440.

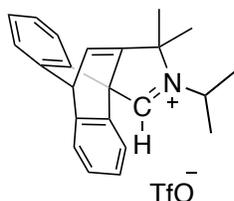
**2a**

In an aluminum foil covered Schlenk, 1-bromoadamantane (1.00 g, 4.648 mmol) and 2,6-di-*tert*-butyl-4-methylpyridine (0.125 g, 0.609 mmol) were dissolved in 15 mL of hexanes. To this solution, silver triflate (1.40 g, 5.438 mmol) was added and the reaction was stirred overnight at room temperature. The mixture was then cannulated into a new Schlenk containing imine **1** with 3 x 15 mL extractions of hexanes. The reaction was stirred for another 24 hours at room temperature to yield a pink suspension. The suspension was dissolved in acetonitrile, filtered, and concentrated. The solid was washed with diethyl ether and then set for crystallization in acetonitrile by slow diffusion of diethyl ether. The resultant white crystals were filtered and washed with diethyl ether (1.81 g, 70%)

**<sup>1</sup>H NMR** (400 MHz, CD<sub>3</sub>CN) δ 10.41 (s, 1H), 7.47 (dd, *J* = 6.9, 1.5 Hz, 2H), 7.36 (dd, *J* = 7.1, 1.5 Hz, 2H), 7.12 (td, *J* = 7.4, 1.5 Hz, 2H), 7.07 (td, *J* = 7.4, 1.5 Hz, 2H), 7.02 (dd, *J* = 6.1, 0.9 Hz, 1H), 5.50 (d, *J* = 6.1 Hz, 1H), 2.51 (d, *J* = 3.0 Hz, 6H), 1.84 (s, 6H), 1.73 (s, 6H).

**<sup>13</sup>C NMR** (101 MHz, CD<sub>3</sub>CN) δ 186.23, 152.30, 144.79, 143.86, 142.80, 134.58, 132.54, 131.43, 127.36, 126.37, 125.60, 121.44, 86.82, 68.37, 52.00, 27.80, 20.92, 19.83.

**HRMS:** *m/z* calculated for [C<sub>30</sub>H<sub>32</sub>N]<sup>+</sup> [M]<sup>+</sup> 406.2529, found 406.2525.

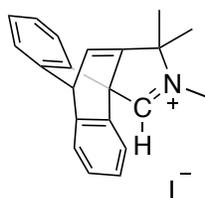
**2b**

In a Teflon sealed Schlenk, 2-bromopropane (1.9 mL, 20 mmol) was added to an acetonitrile solution of Imine **1** (4.10 g, 15 mmol). The Schlenk was sealed and heated at 90 °C overnight. After cooling to room temperature, the volatiles were removed under vacuum and the residue was washed with diethyl ether. The residue was redissolved in dichloromethane (50 mL), and lithium trifluoromethanesulfonate (6.20 g, 40 mmol) was added, and the solution was refluxed at 50 °C for 6 hours. After cooling to room temperature, the solution was filtered, and solvent was concentrated to about 10 mL. Diethyl ether (50 mL) was added to precipitate salt **2b** and the solution was filtered off. Salt **2b** was isolated as an off-white solid off-white solid (6.65 g, 95% yield).

**<sup>1</sup>H NMR** (500 MHz, CD<sub>3</sub>CN) δ 10.51 (s, 1H), 7.47 (d, *J* = 7.3 Hz, 2H), 7.35 (d, *J* = 7.2 Hz, 2H), 7.16 – 6.98 (m, 5H), 5.52 (d, *J* = 6.1 Hz, 1H), 4.54 (sept, *J* = 6.5 Hz, 1H), 1.76 (d, *J* = 6.7 Hz, 6H), 1.53 (s, 6H).

**<sup>13</sup>C NMR** (126 MHz, CD<sub>3</sub>CN) δ 177.54, 152.90, 144.88, 143.72, 132.00, 127.10, 126.03, 125.21, 123.22, 121.53, 120.67, 80.89, 67.72, 55.23, 51.87, 26.77, 24.72.

**HRMS:** *m/z* calculated for [C<sub>23</sub>H<sub>24</sub>N]<sup>+</sup> [M]<sup>+</sup> 314.1903, found 314.1913.

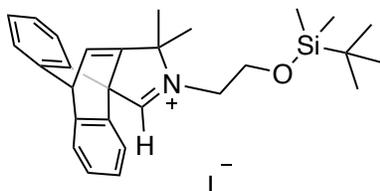
**2c**

In a Teflon sealed Schlenk, iodomethane (1.6 mL, 26 mmol) was added to an acetonitrile solution of Imine **1** (4.10 g, 15 mmol). The Schlenk was sealed and heated at 90 °C overnight. After cooling to room temperature, the volatiles were removed under vacuum and the residue was washed with diethyl ether. Isolated as a yellow solid (5.60 g, 90%).

**<sup>1</sup>H NMR** (500 MHz, CD<sub>3</sub>CN) δ 9.95 (s, 1H), 7.44 (d, *J* = 6.8 Hz, 2H), 7.39 (d, *J* = 6.8 Hz, 2H), 7.02-7.11 (m, 5H), 5.47 (d, *J* = 6.7 Hz, 1H), 3.85 (s, 3H), 1.45 (s, 6H).

**<sup>13</sup>C NMR** (126 MHz, CD<sub>3</sub>CN) δ 178.61, 153.53, 145.03, 143.74, 131.81, 126.99, 125.78, 125.03, 122.44, 78.83, 67.73, 51.92, 39.40, 25.42.

**HRMS**: *m/z* calculated for [C<sub>21</sub>H<sub>20</sub>N]<sup>+</sup> [M]<sup>+</sup> 286.1590, found 286.1589.

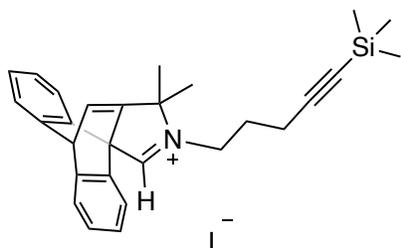
**2d**

In a Teflon sealed Schlenk, *tert*-butyl(2-iodoethoxy)-dimethylsilane (5.70 g, 20 mmol) was added to an acetonitrile solution of Imine **1** (4.10 g, 15 mmol). The Schlenk was sealed and heated at 90 °C overnight. After cooling to room temperature, the volatiles were removed under vacuum and the residue was washed with diethyl ether. Isolated as an off-white solid (7.30 g, 87%).

**<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>) δ 10.96 (s, 1H), 7.65 (d, *J* = 6.3 Hz, 2H), 7.37 (d, *J* = 6.8 Hz, 2H), 6.95-7.05 (m, 5H), 5.36 (d, *J* = 6.6 Hz, 1H), 4.72 (br m, 1H), 4.39 (br m Hz, 1H), 1.48 (s, 6H), 0.92 (s, 9H), 0.18 (m, 6H).

**<sup>13</sup>C NMR** (125 MHz, CDCl<sub>3</sub>) δ 177.11, 152.44, 143.25, 142.38, 130.66, 126.14, 125.46, 124.00, 122.23, 78.63, 67.57, 61.53, 52.89, 51.54, 26.86, 25.88, 18.44, -5.10

**HRMS**: *m/z* calculated for [C<sub>28</sub>H<sub>36</sub>N O Si]<sup>+</sup> [M]<sup>+</sup> 430.2561, found 430.2075.

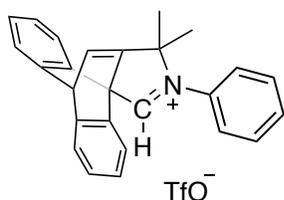
**2e**

In a Teflon sealed Schlenk, *tert*-butyl(2-iodoethoxy)-dimethylsilane (2.4 mL, 20 mmol) was added to an acetonitrile solution of Imine **1** (4.10 g, 15 mmol). The Schlenk was sealed and heated at 90 °C overnight. After cooling to room temperature, the volatiles were removed under vacuum and the residue was washed with diethyl ether. Isolated as an off-white solid (6.50 g, 92%).

**<sup>1</sup>H NMR** (500 MHz, CD<sub>3</sub>CN) δ 10.67 (s, 1H), 7.57 (d, *J* = 6.9 Hz, 2H), 7.47 (d, *J* = 6.9 Hz, 2H), 7.03-7.10 (m, 5H), 5.52 (d, *J* = 6.6 Hz, 1H), 4.28 (t, *J* = 6.5 Hz, 2H), 2.57 (t, *J* = 6.5 Hz, 2H), 2.42 (q, *J* = 6.5 Hz, 2H), 1.52 (s, 6H), 0.17 (m, 9H).

**<sup>13</sup>C NMR** (125 MHz, CD<sub>3</sub>CN) δ 177.72, 153.31, 144.93, 143.71, 131.73, 126.94, 125.80, 125.03, 122.41, 105.35, 87.31, 80.18, 67.85, 51.88, 50.30, 28.36, 26.80, 17.18, -0.04.

**HRMS:** *m/z* calculated for [C<sub>28</sub>H<sub>32</sub>N Si]<sup>+</sup> [M]<sup>+</sup> 410.2299, found 410.2311.

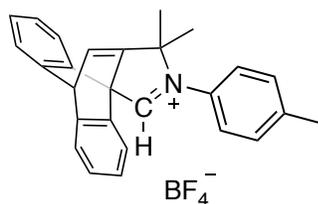
**3a**

In a Schlenk, imine **1** (0.3002 g, 1.106 mmol) was mixed with diphenyliodonium triflate (0.4755 g, 1.105 mmol), and Cu(OAc)<sub>2</sub> (0.011 g, 0.055 mmol) in anhydrous DMF (7 mL) for 24 hours at 100 °C. After removal of solvent, the solid was resuspended in acetonitrile and passed over decolorizing charcoal to yield a clear blue solution that was crystallized by slow diffusion of diethyl ether into acetonitrile. White crystals were washed with diethyl ether and isolated (0.4852 g, 88%). Further purification can be obtained by a recrystallization by slow diffusion of diethyl ether into dichloromethane.

**<sup>1</sup>H NMR** (400 MHz, CD<sub>3</sub>CN) δ 10.32 (s, 1H), 7.87-7.80 (m, 1H), 7.80-7.70 (m, 2H), 7.74-7.67 (m, 2H), 7.56-7.46 (m, 4H), 7.21 (dd, *J* = 6.0, 1.0 Hz, 1H), 7.13 (quintd, *J* = 7.7, 1.5 Hz, 4H), 5.58 (d, *J* = 6.1 Hz, 1H), 1.52 (s, 6H).

**<sup>13</sup>C NMR** (101 MHz, CD<sub>3</sub>CN) δ 182.54, 152.43, 144.86, 143.73, 133.53, 132.60, 131.01, 127.26, 126.96, 126.05, 125.32, 122.18, 83.28, 68.04, 51.96, 27.53.

**HRMS:** *m/z* calculated for [C<sub>26</sub>H<sub>22</sub>N]<sup>+</sup> [M]<sup>+</sup> 348.1747, found 348.1744.

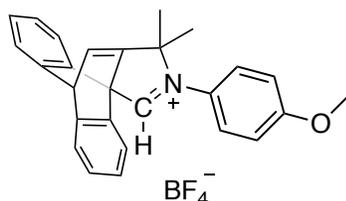
**3b**

In a Schlenk, imine **1** (0.2000 g, 0.737 mmol) was mixed with di(*p*-tolyl)iodonium triflate (0.5067 g, 1.106 mmol), and Cu(OAc)<sub>2</sub> (0.0090 g, 0.050 mmol) in anhydrous DMF (3 mL) at 100 °C for 15 hours. The solvent was then removed under vacuum and the mixture was stirred vigorously in NH<sub>4</sub>OH and extracted 3x with dichloromethane. The combined organic layers were washed 3x with NH<sub>4</sub>OH, followed by brine. The organic layer was dried with MgSO<sub>4</sub> and concentrated to an orange oil. The oil was then resuspended in diethyl ether and HCl Et<sub>2</sub>O (0.45 mL 2M, 1.22 equiv) was added to the solution. The precipitate was filtered, washed with diethyl ether, and resuspended in a warm aqueous solution with spare acetone. A warm aqueous solution of NaBF<sub>4</sub> (0.18 g, 2 equiv) was slowly added and a precipitate evolved. After stirring overnight, a fluffy white precipitate was filtered and washed with diethyl ether (0.20 g, 0.445 mmol, 60%)

<sup>1</sup>H NMR (400 MHz, CD<sub>3</sub>CN) δ 10.24 (s, 1H), 7.56 (s, 4H), 7.52-7.46 (m, 4H), 7.20 (d, *J* = 6.1 Hz, 1H) 7.17-7.06 (m, 4H), 5.56 (d, *J* = 6.1 Hz, 1H) 2.52 (s, 3H), 1.51 (s, 6H).

<sup>13</sup>C NMR (101 MHz, CD<sub>3</sub>CN) δ 182.54, 152.59, 144.91, 144.87, 144.48, 143.77, 132.54, 131.40, 127.25, 126.70, 126.05, 125.29, 122.17, 83.06, 67.92, 51.95, 27.57, 21.27.

HRMS: *m/z* calculated for [C<sub>27</sub> H<sub>24</sub> N]<sup>+</sup> [M]<sup>+</sup> 362.1903, found 362.1904.

**3c**

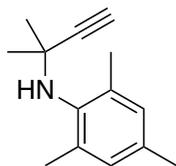
In a Schlenk, imine **1** (0.1001 g, 0.368 mmol) was mixed with (*p*-anisyl)-2,4,6-triisopropylphenyl iodonium tetrafluoroborate (0.1933, 0.368 mmol), and Cu(OAc)<sub>2</sub> (0.0034 g, 0.018 mmol) in anhydrous DMF (6 mL) for 24 hours at 110 °C. After removal of solvent, the solid was resuspended in acetonitrile and passed over decolorizing charcoal to yield a clear lavender solution that was crystallized by slow diffusion of diethyl ether into acetonitrile. Beige crystals were isolated and washed with diethyl ether (0.1118 g, 65%). Compound can be further purified through a recrystallization by slow diffusion of diethyl ether into dichloromethane.

<sup>1</sup>H NMR (500 MHz, CD<sub>3</sub>CN) δ 10.24 (s, 1H), 7.67-7.58 (m, 2H), 7.51 (ddd, *J* = 7.1, 2.9, 1.5 Hz, 4H), 7.28-7.21 (m, 2H), 7.19 (dd, *J* = 6.0, 1.0 Hz, 1H), 7.17-7.06 (m, 4H), 5.56 (d, *J* = 6.1 Hz, 1H), 3.93 (s, 3H), 1.51 (s, 6H).

<sup>13</sup>C NMR (126 MHz, CD<sub>3</sub>CN) δ 181.67, 163.25, 152.50, 144.74, 143.61, 132.48, 132.16, 128.34, 128.21, 127.19, 126.89, 126.02, 125.71, 125.20, 125.01, 122.16, 121.97, 115.87, 115.58, 82.79, 67.61, 56.64, 56.46, 51.82, 51.68, 27.46, 27.30.

HRMS: *m/z* calculated for [C<sub>27</sub> H<sub>24</sub> N O]<sup>+</sup> [M]<sup>+</sup> 378.1852, found 378.1851.

4

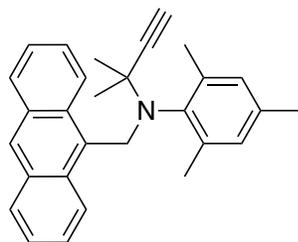


Prepared from a modified procedure of Barmettler and Hansen.<sup>2</sup> A 1,4-dioxane solution of Cu<sup>0</sup> (0.05 g, 2 mol%), CuCl (0.5 g, 14 mol%), 2,4,6-trimethylaniline (5.0 mL, 35.5 mmol) and triethylamine (6.9 mL, 50 mmol) was cooled to 0 °C and stirred vigorously. To this solution 3-chloro-3-methyl-1-butyne<sup>3</sup> (5.5 mL, 53 mmol) was added dropwise. The mixture was warmed to room temperature overnight. The red mixture was then concentrated under reduced pressure and extracted with pentanes. The combined organic layer was concentrated under reduced pressure to yield a red oil, which was then distilled under vacuum at 115 °C to yield an orange oil (3.4 g, 48%). The oil was stored in a -8 °C freezer unless immediately used.

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 6.87 (s, 2H), 2.37 (s, 6H), 2.26 (s, 4H), 1.50 (s, 6H).

<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 139.96, 135.29, 133.59, 129.32, 90.14, 70.27, 52.23, 31.34, 20.86, 20.17.

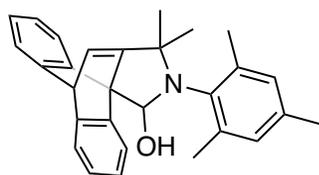
5



In a Schlenk, K<sub>2</sub>CO<sub>3</sub> (4.59 g, 33.19 mmol) was heated under vacuum and allowed to cool to room temperature. Once cooled, 9-(bromomethyl)anthracene<sup>4,5</sup> (1.00 g, 3.69 mmol) and *N*-mesityl dimethyl propargylamine (0.7424 g, 3.69 mmol) were added and dissolved in acetonitrile (30 mL). The mixture was stirred at room temperature for 48 hours. The mixture was then concentrated and an aqueous workup with diethyl ether extractions (3x 50 mL) was performed. The combined organic layer was washed with brine (100 mL) and dried with MgSO<sub>4</sub>. The solution was concentrated under reduced pressure at 25 °C to yield a yellow oil. The crude mixture of **5** and **4** (1.23 g), containing 45% substituted product by NMR, was used in the next step immediately without purification.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.43 (d, *J* = 8.8 Hz, 2H), 8.35 (s, 1H), 7.97-7.91 (m, 2H), 7.45-7.32 (m, 6H), 6.70 (s, 2H), 5.48 (s, 2H), 2.79 (s, 1H), 2.19 (s, 3H), 2.14 (s, 6H), 1.54 (s, 6H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 144.22, 140.38, 135.09, 131.70, 131.62, 131.23, 129.42, 128.87, 127.35, 125.98, 124.88, 124.73, 90.70, 72.47, 55.30, 47.64, 31.29, 20.94, 20.26.

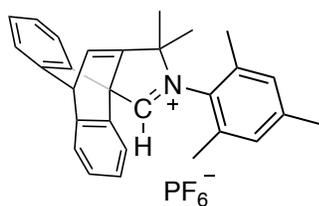
**6d**

To an ethereal solution of the crude substituted anthracene mixture, DDQ (0.84g, 3.69 mmol) was added at room temperature. A maroon precipitate formed and the mixture was stirred overnight. After 12 hours, the mixture was heated at 40 °C for three hours. The mixture was then filtered and the precipitate was washed with diethyl ether (3 x 30 mL). The precipitate was then reacted with excess KOH in DI H<sub>2</sub>O and extracted with diethyl ether (4 x 50 mL). The combined extractions were dried over MgSO<sub>4</sub> and concentrated under vacuum to yield a crude yellow solid (1.43 g, 49%) used in the next step without purification.

Hydroxy pyrrolidine **6d** can be cleanly obtained from the addition of a 1M solution of KOH to iminium **3d** in diethyl ether.

**<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>) δ 8.44 (m, 1H), 7.48 (m, 1H), 7.34 (m, 1H), 7.31 (m, 1H), 7.05 (s, 1H), 6.99 (m, 5H), 6.63 (d, *J* = 4.9 Hz 1H), 6.60 (d, *J* = 6.1 Hz 1H), 5.14 (d, *J* = 6.1 Hz 1H), 2.60 (s, 3H), 2.56 (d, *J* = 5.1 Hz 1H), 2.35 (s, 3H), 2.11 (s, 3H), 1.40 (s, 3H), 1.02 (s, 3H).

**<sup>13</sup>C NMR** (126 MHz, CDCl<sub>3</sub>) δ 164.57, 148.42, 147.51, 146.96, 146.63, 141.75, 140.41, 137.30, 136.29, 130.00, 129.81, 124.98, 124.56, 124.15, 124.08, 124.00, 123.91, 123.02, 122.67, 121.54, 89.77, 63.57, 62.49, 52.14, 33.72, 26.31, 21.25, 20.98, 20.65.

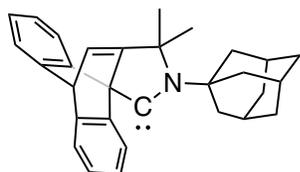
**3d**

The crude mixture of **5** was dissolved in diethyl ether. HCl Et<sub>2</sub>O (1.2 equiv) was added slowly to the solution and a beige precipitate was filtered and washed with diethyl ether. The solid was then dissolved in warm DI H<sub>2</sub>O and a solution of KPF<sub>6</sub> (3.0 equiv) in warm DI H<sub>2</sub>O was slowly added. A beige precipitate formed and after stirring for 5 hours, was filtered and washed with diethyl ether. The solid was then crystallized by slow diffusion of diethyl ether into dichloromethane. White crystals were obtained, filtered, washed with diethyl ether, and then dried under vacuum (0.74 g, 84%).

**<sup>1</sup>H NMR** (400 MHz, CD<sub>3</sub>CN) δ 10.33 (s, 1H), 7.54 (d, *J* = 7.0 Hz, 2H), 7.48 (d, *J* = 7.0 Hz, 2H), 7.27 (s, 2H), 7.16 (m, 5H), 5.60 (d, *J* = 6.1 Hz, 1H), 2.41 (s, 3H), 2.30 (s, 6H), 1.50 (s, 6H).

**<sup>13</sup>C NMR** (101 MHz, CD<sub>3</sub>CN) δ 186.23, 152.30, 144.79, 143.86, 142.80, 134.58, 132.54, 131.43, 127.36, 126.37, 125.60, 121.44, 86.82, 68.37, 52.00, 27.80, 20.92, 19.83.

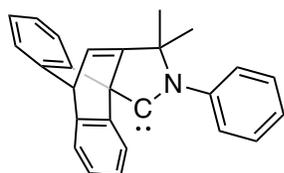
**HRMS:** *m/z* calculated for [C<sub>29</sub>H<sub>28</sub>N]<sup>+</sup> [M]<sup>+</sup> 390.2216, found 390.2215.

**Carb2a**

In a J-Young NMR tube containing iminium salt **2a** (0.052 g, 0.094 mmol) and KHMDS (0.017g, 0.085 mmol), C<sub>6</sub>D<sub>6</sub> (0.5 mL) was added and the tube was inverted to mix the suspension.

**<sup>1</sup>H NMR** (500 MHz, C<sub>6</sub>D<sub>6</sub>) δ 7.95 (m, 2H), 7.22-7.18 (m, 2H), 6.94-6.79 (m, 4H), 6.20 (d, *J* = 5.7 Hz, 1H), 4.94 (d, *J* = 5.7 Hz, 1H), 2.49 (br m 6H), 2.14-2.00 (br s, 3H), 1.74-1.53 (br q, 6H), 1.11 (s, 6H).

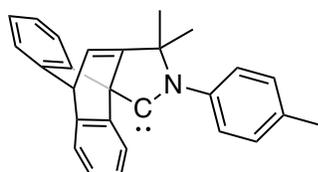
**<sup>13</sup>C NMR** (126 MHz, C<sub>6</sub>D<sub>6</sub>) δ 306.17, 165.12, 149.31, 146.87, 124.86, 124.77, 124.56, 124.51, 124.46, 124.16, 123.22, 122.74, 78.66, 76.27, 65.33, 52.46, 52.01, 45.70, 36.61, 31.48, 30.75.

**Carb3a**

In a J-Young NMR tube containing iminium salt **3a** (0.045 g, 0.104 mmol) and KHMDS (0.020g, 0.101 mmol), C<sub>6</sub>D<sub>6</sub> (0.5 mL) was added and the tube was inverted to mix the suspension.

**<sup>1</sup>H NMR** (500 MHz, C<sub>6</sub>D<sub>6</sub>) δ 8.01 (d, *J* = 8.6 Hz, 2H), 7.20 (t, *J* = 6.5 Hz, 4H), 7.12 (d, *J* = 5.6 Hz, 3H), 6.96 (t, *J* = 7.4 Hz, 2H), 6.88 (t, *J* = 7.4 Hz, 2H), 6.30 (d, *J* = 5.7 Hz, 1H), 4.93 (d, *J* = 5.7 Hz, 1H), 0.87 (s, 6H).

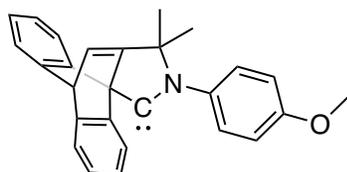
**<sup>13</sup>C NMR** (126 MHz, C<sub>6</sub>D<sub>6</sub>) δ 308.00, 171.33, 160.39, 160.36, 148.69, 146.46, 144.41, 129.43, 128.69, 126.60, 126.27, 125.31, 124.96, 124.55, 124.32, 123.78, 123.55, 122.98, 122.75, 122.66, 78.62, 77.80, 52.54, 51.89, 28.52.

**Carb3b**

In a vial containing iminium salt **3b** (0.060 g, 0.134 mmol) and KHMDS (0.025 g, 0.127 mmol), C<sub>6</sub>D<sub>6</sub> (0.5 mL) was added and the vial was swirled to mix the suspension. The resultant slurry was immediately filtered into a J-Young NMR tube.

**<sup>1</sup>H NMR** (300 MHz, C<sub>6</sub>D<sub>6</sub>) δ 8.02 (d, *J* = 8.3 Hz, 2H), 7.21 (d, *J* = 7.4 Hz, 2H), 6.97 (d, *J* = 7.3 Hz, 5H), 6.88 (t, *J* = 6.8 Hz, 3H), 6.30 (d, *J* = 5.7 Hz, 1H), 4.93 (d, *J* = 6.0 Hz, 1H), 2.13 (s, 3H), 0.91 (s, 6H).

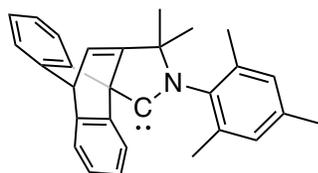
**<sup>13</sup>C NMR** (126 MHz, C<sub>6</sub>D<sub>6</sub>) δ 311.10, 160.81, 149.00, 146.60, 142.37, 137.58, 129.36, 124.81, 124.48, 123.98, 123.29, 122.93, 78.79, 77.60, 52.41, 28.59, 21.01.

**Carb3c**

In a J-Young NMR tube containing iminium salt **3c** (0.072 g, 0.150 mmol) and KHMDS (0.028g, 0.143 mmol), C<sub>6</sub>D<sub>6</sub> (0.5 mL) was added and the tube was inverted to mix the suspension.

<sup>1</sup>H NMR (500 MHz, C<sub>6</sub>D<sub>6</sub>) δ 7.94 (d, *J* = 7.1 Hz, 2H), 7.17 (d, *J* = 7.1 Hz, 2H), 7.10-6.96 (m, 4H), 6.86 (d, *J* = 7.3 Hz, 2H), 6.74 (d, *J* = 3.4 Hz, 2H), 6.27 (d, *J* = 5.9 Hz, 1H), 4.89 (d, *J* = 5.9 Hz, 1H), 3.31 (s, 3H), 0.85 (s, 6H).

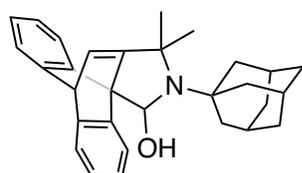
<sup>13</sup>C NMR (126 MHz, C<sub>6</sub>D<sub>6</sub>) δ 303.99, 160.18, 159.75, 148.46, 146.37, 136.93, 128.86, 126.61, 124.99, 124.73, 123.34, 122.57, 114.50, 77.68, 55.03, 52.18, 28.41.

**Carb3d**

In a J-Young NMR tube containing iminium salt **3d** (0.10 g, 0.19 mmol) and KHMDS (0.036 g, 0.18 mmol), C<sub>6</sub>D<sub>6</sub> (0.5 mL) was added and the tube was inverted to mix the sample.

<sup>1</sup>H NMR (500 MHz, C<sub>6</sub>D<sub>6</sub>) δ 8.07 (d, *J* = 7.2 Hz, 2H), 7.23 (d, *J* = 7.1 Hz, 2H), 6.95-6.91 (m, 2H), 6.90-6.86 (m, 2H), 6.80 (s, 2H), 6.30 (d, *J* = 5.7 Hz, 1H), 4.98 (d, *J* = 5.7 Hz, 1H), 2.21 (s, 6H), 2.14 (s, 3H), 0.92 (s, 7H).

<sup>13</sup>C NMR (126 MHz, C<sub>6</sub>D<sub>6</sub>) δ 314.51, 160.36, 149.11, 146.66, 139.75, 136.82, 135.45, 129.91, 125.85, 124.95, 124.56, 123.27, 122.76, 80.94, 52.44, 27.87, 20.88, 19.71.

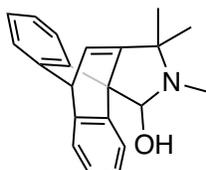
**6a**

Iminium salt **2a** (0.25 g, 0.45 mmol) was dissolved in acetonitrile (15 mL). To this, a solution of KOH (1.50 g) in DI H<sub>2</sub>O (12 mL) was added and the mixture was stirred vigorously for 1 hour. The organic layer was separated and the mixture was extracted 3x with diethyl ether. The combined extractions were concentrated under vacuum and the residue was then extracted with hexanes/diethyl ether (10:1) and dried over MgSO<sub>4</sub>. After filtration, the extracts were dried under vacuum to yield a white solid (0.29 g), a mixture of hydroxy pyrrolidine **6a** (68%) and imine **1** (32%).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.01 (s, 1H), 7.35-7.28 (m, 2H), 7.20 (d, *J* = 6.74 Hz, 1H), 7.00-6.97 (m, 2H), 6.94-6.85 (m, 2H), 6.60 (d, *J* = 6.02 Hz, 1H), 5.21 (d, *J* = 6.05 Hz, 1H), 2.23 (br s, 6H), 2.18 (br s, 3H), 1.75 (br s, 6H), 1.57 (s, 3H), 1.26 (s, 3H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  165.68, 149.04, 147.93, 147.85, 144.81, 125.27, 124.36, 124.11, 123.88, 123.62, 122.62, 122.51, 119.73, 83.80, 63.25, 62.87, 56.21, 51.86, 45.10, 36.70, 34.64, 34.03, 30.34.

### 6c



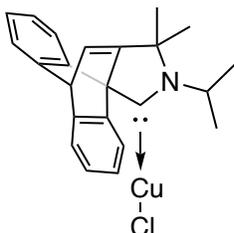
The iminium salt **2c** (0.25 g, 0.61 mmol) was dissolved in acetonitrile (12 mL). To this, a solution of KOH (0.90 g) in DI  $\text{H}_2\text{O}$  (12 mL) was added and the mixture was stirred vigorously for 30 minutes. The organic layer was separated and the mixture was extracted 3x with diethyl ether. The combined extractions were concentrated under vacuum and the residue was then extracted with hexanes/diethyl ether (10:1) and dried over  $\text{MgSO}_4$ . After filtration, the extracts were dried under vacuum to yield **6c** as a pale-yellow solid (0.17 g, 94%).

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.10 (br s, 1H), 7.36, (br s, 1H), 7.29-7.26 (m, 2H), 6.98-6.93 (m, 4H), 6.60 (d,  $J = 6.0$  Hz, 1H) 5.90 (s, 1H), 5.07 (d,  $J = 6.0$  Hz, 1H), 2.58 (s, 3H), 1.20 (br s, 3H), 0.98 (br s, 3H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  162.82, 147.97, 126.14, 124.38, 124.23, 122.85, 90.04, 61.60, 59.76, 51.93, 31.79, 30.18, 14.37.

HRMS:  $m/z$  calculated for  $[\text{C}_{21}\text{H}_{22}\text{NO}]^+$   $[\text{M}+\text{H}]^+$  304.1696, found 304.1693.

### Cu2b

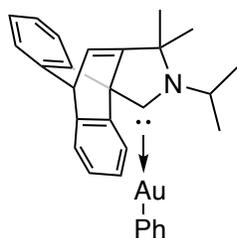


THF was slowly added to a solid mixture of iminium **2b** (230 mg, 0.5 mmol),  $\text{CuCl}$  (99 mg, 1 mmol), and  $\text{KHMDs}$  (100 mg, 0.5 mmol) at  $-78$   $^\circ\text{C}$ . The mixture was stirred in the cold bath and was allowed to slowly warm to room temperature overnight. Solvents and volatiles were evaporated under vacuum and washed with hexanes (2x20 mL). The solid residue was extracted with benzene (2x30 mL). After evaporation under vacuum, complex **Cu2b** was a yellow/off-white solid (97 mg, 47%).

$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.72 (m, 2H), 7.32 (m, 2H), 6.96 (m, 4H), 6.72 (br s, 1H), 5.21 (br s, 1H), 4.15 (br s, 1H), 1.92 (br m, 6H), 1.34 (br m, 6H),

$^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  230.81, 156.10, 145.78, 145.03, 128.27, 125.10, 124.84, 123.46, 121.78, 73.40, 51.62, 51.14, 27.58, 26.29.

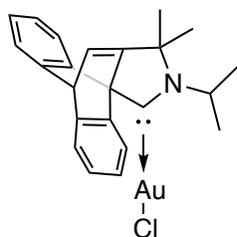
HRMS for  $(\text{C}_{23}\text{H}_{23}\text{ClCuN})$  ( $\text{M}^+$ ): calc.: 411.0815, found: 411.0829.

**Au2b<sub>Ph</sub>**

THF was slowly added to a solid mixture of iminium **2b** (280 mg, 0.6 mmol), Au(PPh<sub>3</sub>)Ph (270 mg, 0.5 mmol), and KHMDS (110 mg, 0.55 mmol) at -78 °C. The mixture was stirred in the cold bath and was allowed to slowly warm to room temperature overnight. Solvents and volatiles were evaporated under vacuum until complete dryness. The solid residue was extracted with benzene (2x30 mL). After evaporation under vacuum, complex **Au2b<sub>Ph</sub>** was an off-white solid (162 mg, 55%).

**<sup>1</sup>H NMR** (500 MHz, C<sub>6</sub>D<sub>6</sub>): δ 8.26 (m, 2H), 7.59 (d, *J* = 7.5 Hz, 2H), 7.29 (d, *J* = 7.5 Hz, 2H), 7.24 (d, *J* = 7.0 Hz, 2H), 7.02 (t, *J* = 7.0 Hz, 1H), 6.97 (m, 4H), 6.74 (d, *J* = 5.7 Hz, 1H), 5.20 (d, *J* = 5.7 Hz, 1H), 4.21 (m, 1H), 2.1 (d, *J* = 7.1 Hz, 6H), 1.34 (s, 6H).

**<sup>13</sup>C NMR** (75 MHz, C<sub>6</sub>D<sub>6</sub>): δ 245.46, 168.90, 156.84, 145.95, 145.04, 141.59, 128.38, 127.27, 125.34, 124.91, 124.76, 123.30, 123.20, 76.49, 75.51, 51.93, 51.20, 27.57, 24.85.

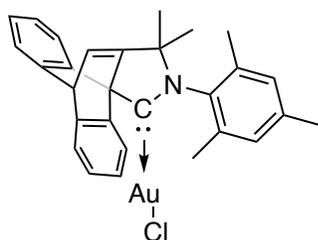
**Au2b**

HCl (300 μL, 2.0M in ether, 0.6 mmol) was added to a solution of complex **Au2b<sub>Ph</sub>** in benzene at room temperature. The solution was stirred for 20 minutes, and volatiles were evaporated under vacuum. The solid residue was washed with hexanes (2x30 mL), and complex **Au2b** was isolated as an off-white solid (146 mg, 98%).

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>): δ 7.80-7.66 (m, 2H), 7.31 (dd, *J* = 4.2, 2.4 Hz, 2H), 6.98 (dd, *J* = 5.9, 2.8 Hz, 4H), 6.73 (s, 1H), 5.21 (d, *J* = 5.9 Hz, 1H), 4.17 (quint, *J* = 6.7 Hz, 1H), 1.94 (d, *J* = 6.6 Hz, 6H), 1.36 (s, 6H).

**<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>): δ 219.45, 155.25, 145.02, 144.64, 129.27, 125.28, 124.91, 123.48, 122.57, 76.71, 73.80, 51.76, 51.65, 27.62, 24.62.

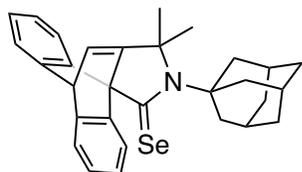
**HRMS** for (C<sub>23</sub>H<sub>23</sub>ClAuN) (M<sup>+</sup>): calc.: 545.1185, found: 545.1209.

**Au3d**

A Schlenk containing iminium salt **3d** (0.50 g, 0.875 mmol), KHMDS (0.17 g, 0.875 mmol), and (tbt)AuCl (0.28 g, 0.875 mmol) was cooled to  $-78\text{ }^{\circ}\text{C}$ . THF (12 mL) was then dripped into the Schlenk and the mixture was allowed to warm to room temperature over 90 minutes. After this time the mixture was concentrated and extracted with dichloromethane. The dichloromethane extractions were then concentrated for a crystallization through slow diffusion of diethyl ether, (0.34 g, 63%).

$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.21-8.18 (m, 2H), 7.35-7.33 (m, 2H), 7.03 (s, 4H), 6.81 (d,  $J=5.94$  Hz, 1H), 5.26 (d,  $J=5.88$  Hz, 1H), 2.35 (s, 3H), 2.28 (s, 6H), 1.31 (s, 6H).

$^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  231.26, 155.53, 144.99, 144.63, 139.34, 136.23, 134.07, 130.47, 129.20, 128.40, 125.36, 125.00, 123.67, 122.44, 80.56, 72.82, 51.75, 28.20, 21.13, 19.78.

**Se2a**

Procedure from iminium **2a**:

In a Schlenk, iminium salt **2a** (0.30 g, 0.524 mmol), KHMDS (0.10 g, 0.501 mmol), and Se powder (0.17 g, 2.15 mmol) were cooled to  $-78\text{ }^{\circ}\text{C}$ . THF (12 mL) was added and the mixture was warmed to room temperature overnight. A thick yellow precipitate formed. The mixture was filtered over celite with copious extractions of THF (100 mL) and DCM (30 mL). The combined filtrate was concentrated and the residue was stirred vigorously in diethyl ether (20 mL) and then filtered. The residue was then stirred vigorously in acetone (20 mL) and filtered. Finally, the residue was stirred vigorously in acetonitrile (10 mL) and filtered to yield a yellow solid (0.11 g, 45%).

Procedure from hydroxy pyrrolidine **6a**:

**Se2a** was also prepared from the hydroxy pyrrolidine **6a** by the following procedure:

A J-Young NMR tube containing hydroxy pyrrolidine **6a** (0.1030 g, 0.243 mmol) and elemental Se (0.0670 g, 0.851 mmol) in THF (0.5 mL) was heated at  $75\text{ }^{\circ}\text{C}$  for 24 hours. After this time the mixture was filtered over celite, extracted with dichloromethane, and then concentrated. The yellow residue was then washed with hexanes and diethyl ether and then dried under vacuum to yield a yellow solid (0.0440 g, 37%).

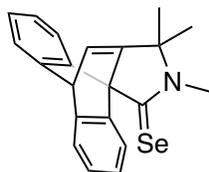
$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.40 (dd,  $J=5.6, 3.3$  Hz, 2H), 7.25 (dd,  $J=5.5, 3.1$  Hz, 2H), 6.96 (dd,  $J=5.5, 3.2$  Hz, 4H), 6.66 (d,  $J=5.9$  Hz, 1H), 5.12 (d,  $J=5.9$  Hz, 1H), 3.16 (s, 6H), 2.25 (s, 3H), 1.88 (d,  $J=12.3$  Hz, 3H), 1.71 (d,  $J=12.3$  Hz, 3H), 1.52 (s, 6H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  195.78, 160.02, 145.44, 145.04, 128.66, 124.60, 124.07, 123.39, 122.60, 76.14, 74.47, 68.12, 51.44, 39.07, 36.23, 32.41, 30.78.

$^{77}\text{Se}$  NMR (57 MHz,  $\text{CD}_2\text{Cl}_2$ )  $\delta$  793.19.

HRMS:  $m/z$  calculated for  $[\text{C}_{30}\text{H}_{32}\text{NSe}]^+ [\text{M}+\text{H}]^+$  486.1696, found 486.1698.

### Se2c



Procedure from iminium **2c**:

THF was slowly added to a solid mixture of iminium **2c** (220 mg, 0.5 mmol), Se powder (160 mg, 2 mmol), and KHMDS (50 mg, 0.5 mmol) at  $-78\text{ }^\circ\text{C}$ . The mixture was stirred in the cold bath and was allowed to slowly warm to room temperature overnight. Solvents and volatiles were evaporated under vacuum until complete dryness. The remaining solid was extracted with hexanes (2x20 mL). The solution was concentrated to about 5 mL. The Schlenk was sealed and stored at  $-20\text{ }^\circ\text{C}$  for 44 hours while compound **Se2c** slowly crystallized out of the hexanes solution. After filtration in air, selenoamide **Se2c** was isolated as yellow crystals (75 mg, 40%).

Procedure from hydroxy pyrrolidine **6c**:

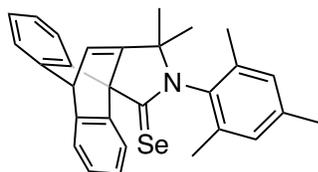
A J-Young NMR tube containing hydroxy pyrrolidine **6c** (0.0600 g, 0.198 mmol) and Se powder (0.0547 g, 0.692 mmol) in THF (0.5 mL) was heated at  $75\text{ }^\circ\text{C}$  for 24 hours. After this time the mixture was filtered over celite, extracted with THF, and then concentrated. The residue was then washed with hexanes (10 mL) and diethyl ether (10 mL) to yield a light pink solid (0.0236 g, 33%).  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  8.35 - 8.19 (m, 2H), 7.34 - 7.28 (m, 2H), 7.03 - 6.93 (m, 4H), 6.83 (d,  $J = 6.0$  Hz, 1H), 5.19 (d,  $J = 6.0$  Hz, 1H), 3.44 (s, 3H), 1.28 (s, 6H).

$^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  196.12, 156.68, 145.03, 144.35, 129.45, 124.82, 124.34, 122.87, 122.57, 72.12, 70.37, 51.42, 34.01, 27.25.

$^{77}\text{Se}$  NMR (57 MHz,  $\text{CDCl}_3$ )  $\delta$  561.68.

HRMS:  $m/z$  calculated for  $[\text{C}_{21}\text{H}_{19}\text{NSe}]^+ [\text{M}+\text{H}]^+$  366.0755, found 366.0772.

### Se3d



In a J-Young NMR tube containing iminium salt **3d** (0.0950 g, 0.177 mmol), KHMDS (0.0340 g, 0.170 mmol) and Se powder (0.042 g, 0.53 mmol), THF (1 mL) was added at room temperature and the mixture was sonicated for one hour. The yellow mixture was then filtered over celite and extracted with dichloromethane (20 mL). The extracts were concentrated and the yellow residue was then vigorously stirred overnight with hexanes (100 mL). After filtration of the hexanes, the

yellow solid was stirred in diethyl ether: acetonitrile (10:1, 10 mL) and filtered. The final yellow solid was dried under vacuum (0.0656 g, 79%).

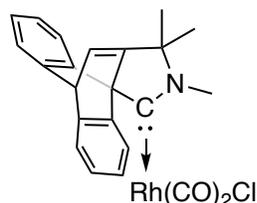
**$^1\text{H NMR}$**  (300 MHz,  $\text{CDCl}_3$ )  $\delta$  8.36 (dd,  $J = 5.5, 3.3$  Hz, 2H), 7.35 (dd,  $J = 5.4, 3.1$  Hz, 2H), 7.12–6.97 (m, 6H), 6.86 (d,  $J = 5.9$  Hz, 1H), 5.25 (d,  $J = 5.9$  Hz, 1H), 2.37 (s, 3H), 2.24 (s, 6H), 1.28 (s, 6H).

**$^{13}\text{C NMR}$**  (126 MHz,  $\text{CDCl}_3$ )  $\delta$  199.73, 157.90, 145.24, 144.59, 138.53, 136.13, 133.86, 130.22, 129.34, 124.94, 124.58, 123.03, 122.54, 75.23, 51.66, 28.30, 21.28, 20.02.

**$^{77}\text{Se NMR}$**  (57 MHz,  $(\text{CD}_3)_2\text{CO}$ )  $\delta$  650.77.

**HRMS:**  $m/z$  calculated for  $[\text{C}_{29}\text{H}_{28}\text{N Se}]^+ [\text{M}+\text{H}]^+$  470.1383, found 470.1383.

### Carb2cRh(CO)<sub>2</sub>Cl



A Schlenk containing iminium salt **2c** (0.070 g, 0.174 mmol), KHMDS (0.0364 g, 0.1827 mmol), and  $[\text{Rh}(\text{COD})\text{Cl}]_2$  (0.0344g, 0.0696 mmol) was cooled to  $-78$  °C. THF was then added to the mixture and the solution was stirred for 20 minutes before being warmed to room temperature. The solution was concentrated and then resuspended in pentanes. A yellow solid was isolated and dissolved in DCM and  $\text{CO}_{(g)}$  was bubbled into the solution for 30 seconds.

**$^1\text{H NMR}$**  (500 MHz,  $\text{CD}_2\text{Cl}_2$ )  $\delta$  8.21 (d,  $J = 7.7$  Hz, 1H), 7.34–7.32 (m, 2H), 7.02–6.97 (m, 4H), 6.76 (d,  $J = 5.8$  Hz, 1H), 5.33 (d,  $J = 6.2$  Hz, 1H), 5.21 (d,  $J = 5.8$  Hz, 1H), 4.05 (s, 3H), 1.33 (s, 6H).

**$^{13}\text{C NMR}$**  (126 MHz,  $\text{CD}_2\text{Cl}_2$ )  $\delta$ , 242.83 (d,  $J_{\text{C-Rh}} = 39.1$  Hz), 186.48 (d,  $J_{\text{C-Rh}} = 54.2$  Hz), 185.12 (d,  $J_{\text{C-Rh}} = 54.2$  Hz), 157.12, 145.58, 145.51, 129.13, 125.37, 124.81, 124.39, 124.00, 123.63, 75.77 (br d,  $J_{\text{C-Rh}} = 1.5$  Hz), 75.66 (br), 52.21, 42.22, 27.34.

**FTIR:** (KBr, DCM solution) 2075.1 (CO), 2001.8 (CO)  $\text{cm}^{-1}$ .

### 3. Spectra

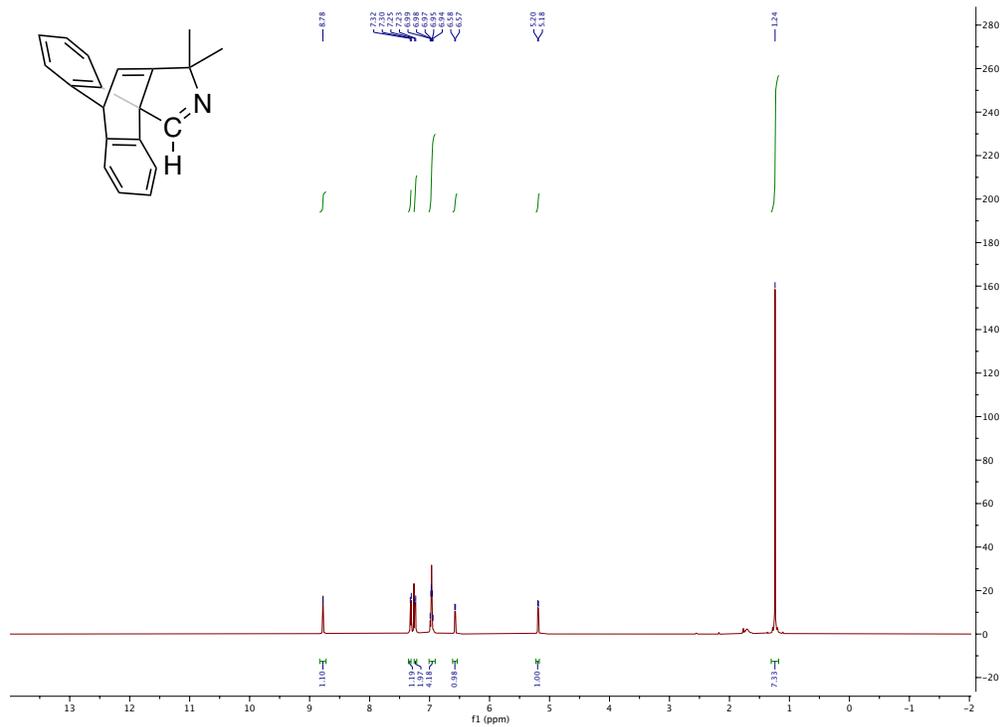


Figure S1: <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) Imine 1

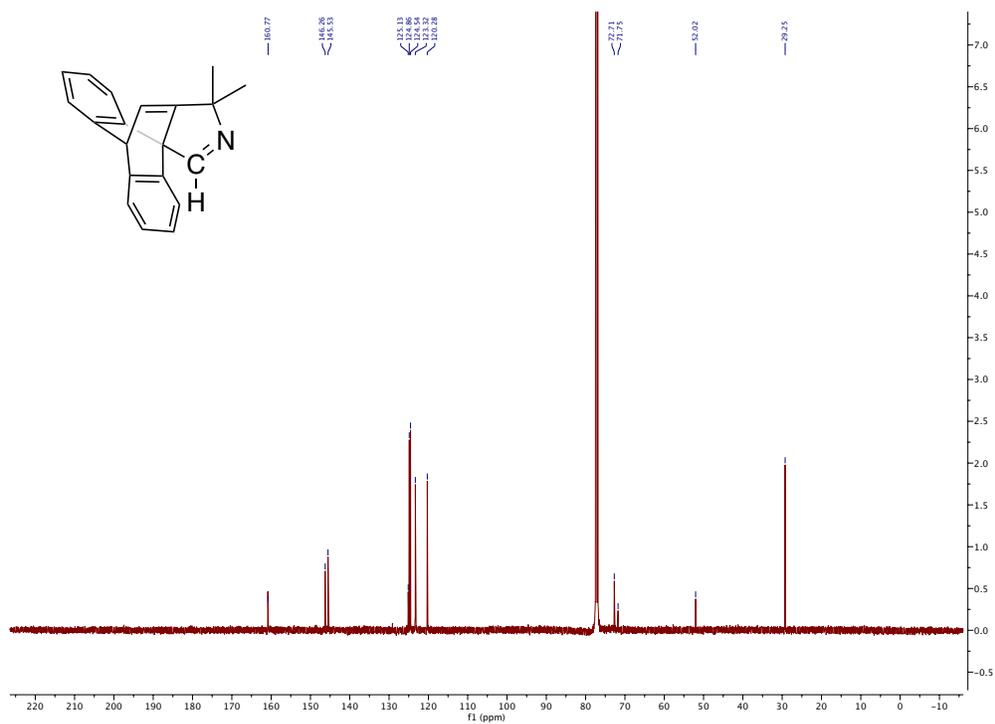
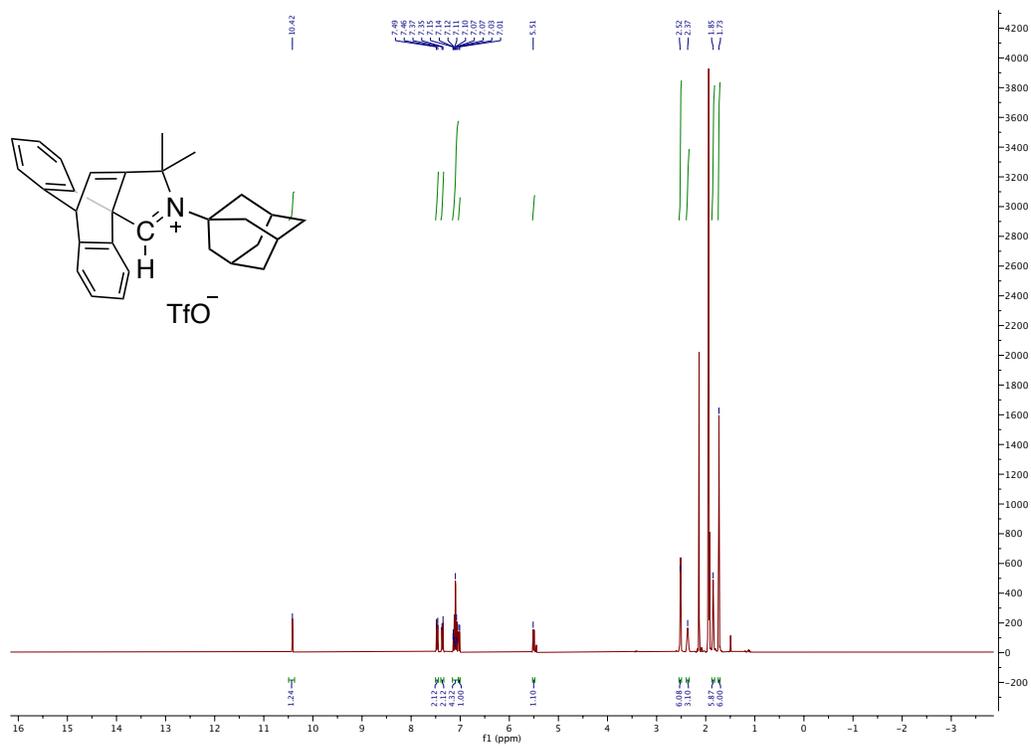
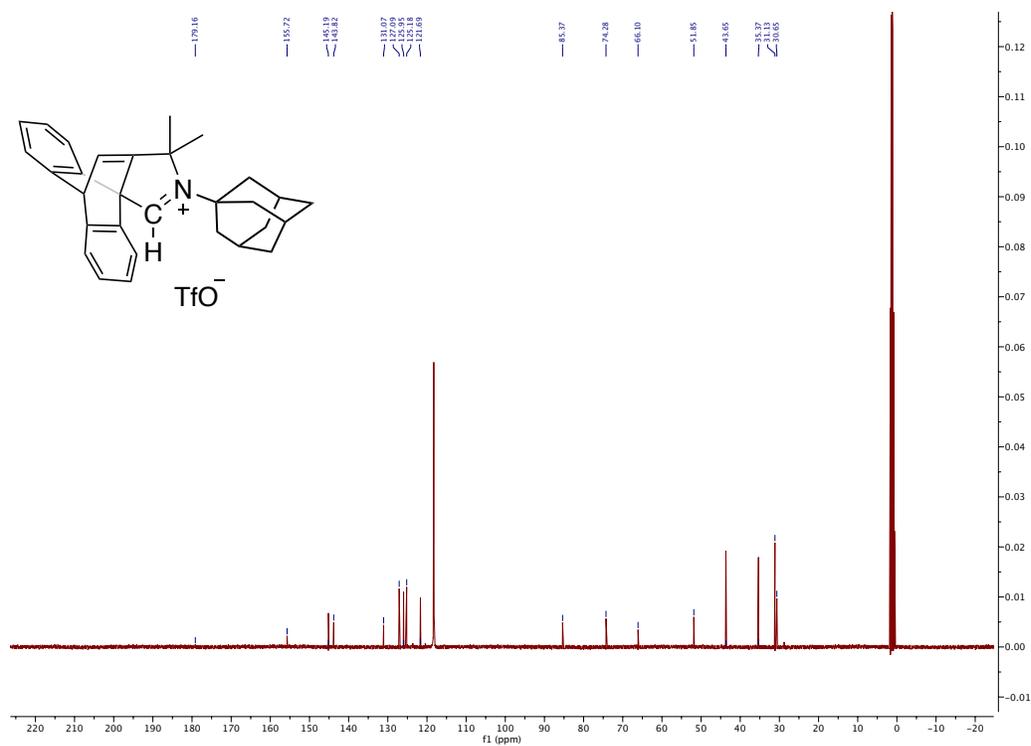


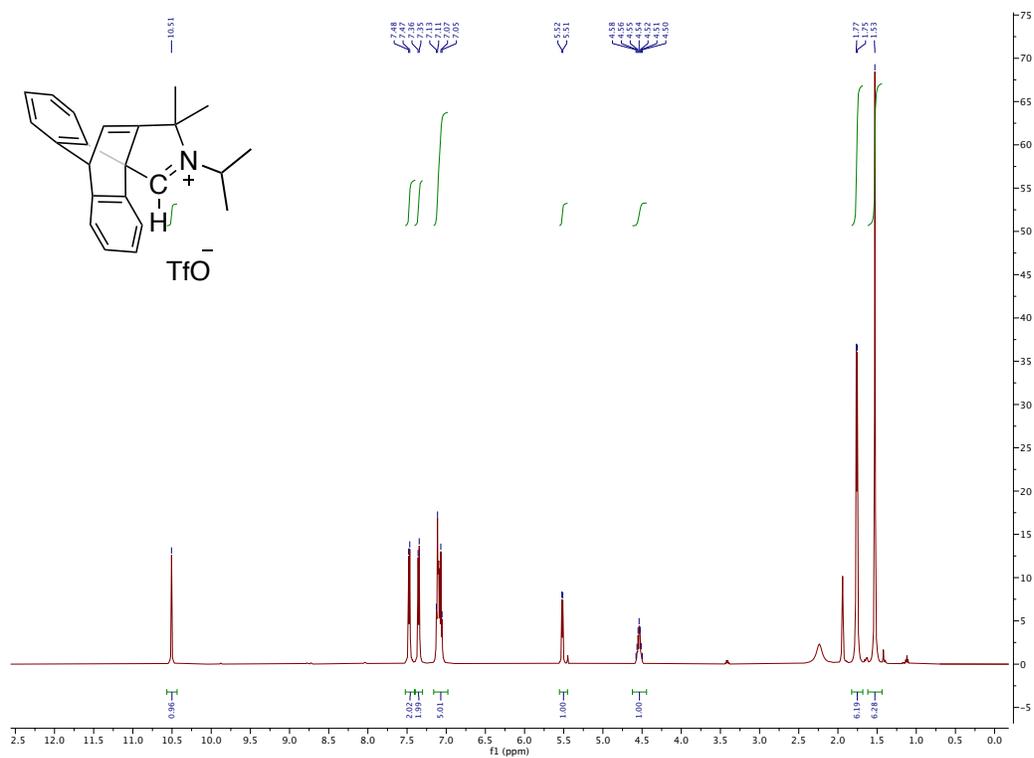
Figure S2: <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) Imine 1



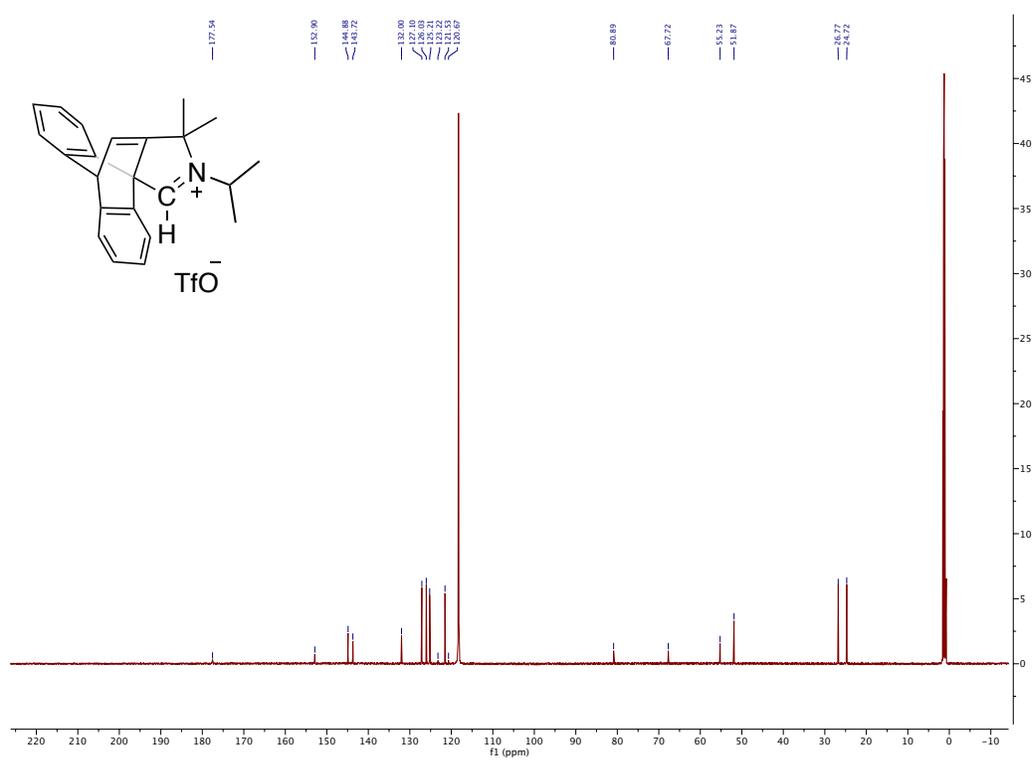
**Figure S3:  $^1\text{H}$  NMR (300 MHz,  $\text{CD}_3\text{CN}$ ) **2a** [ $\text{TfO}$ ] $^-$**



**Figure S4:  $^{13}\text{C}$  NMR (101 MHz,  $\text{CD}_3\text{CN}$ ) **2a** [ $\text{TfO}$ ] $^-$**



**Figure S5:  $^1\text{H}$  NMR (500 MHz,  $\text{CD}_3\text{CN}$ ) **2b** [ $\text{TfO}^-$ ]**



**Figure S6:  $^{13}\text{C}$  NMR (126 MHz,  $\text{CD}_3\text{CN}$ ) **2b** [ $\text{TfO}^-$ ]**

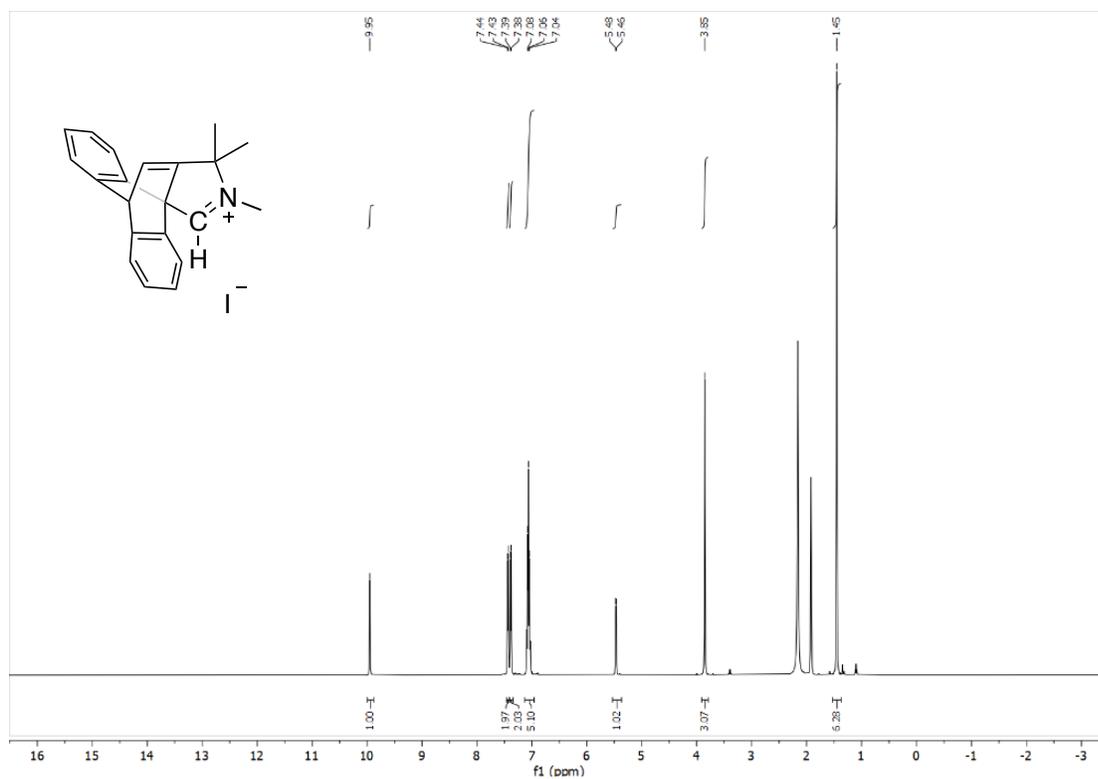


Figure S7:  $^1\text{H}$  NMR (500 MHz,  $\text{CD}_3\text{CN}$ ) 2c [I].

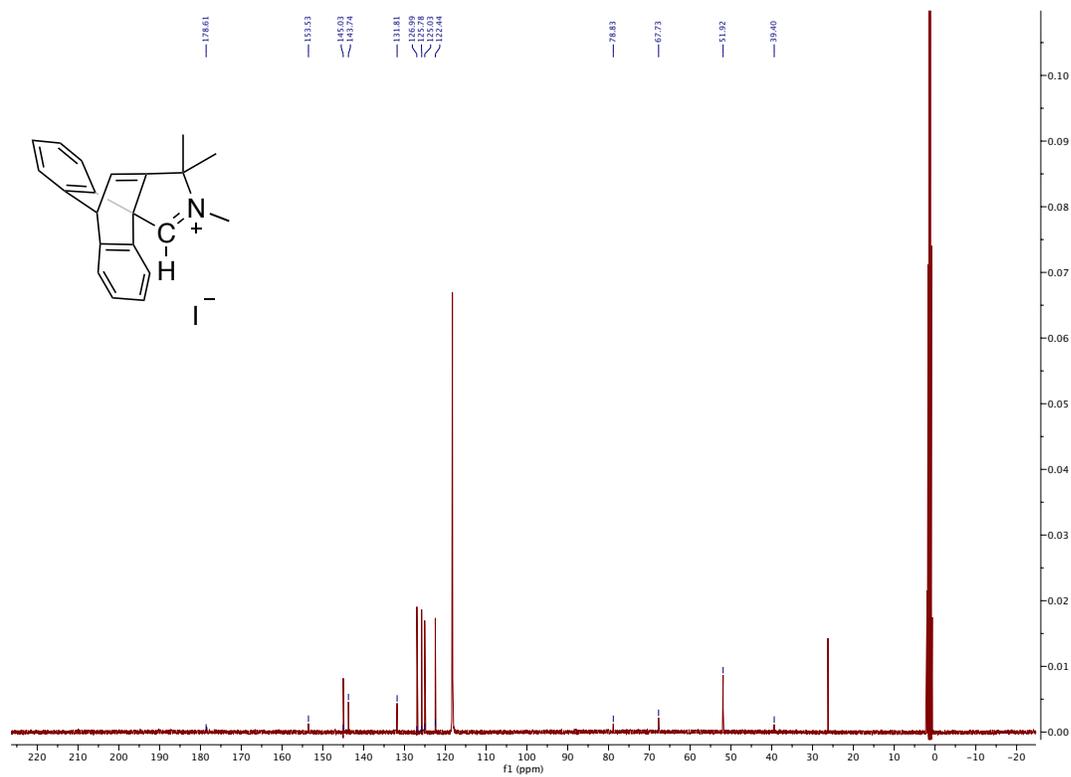
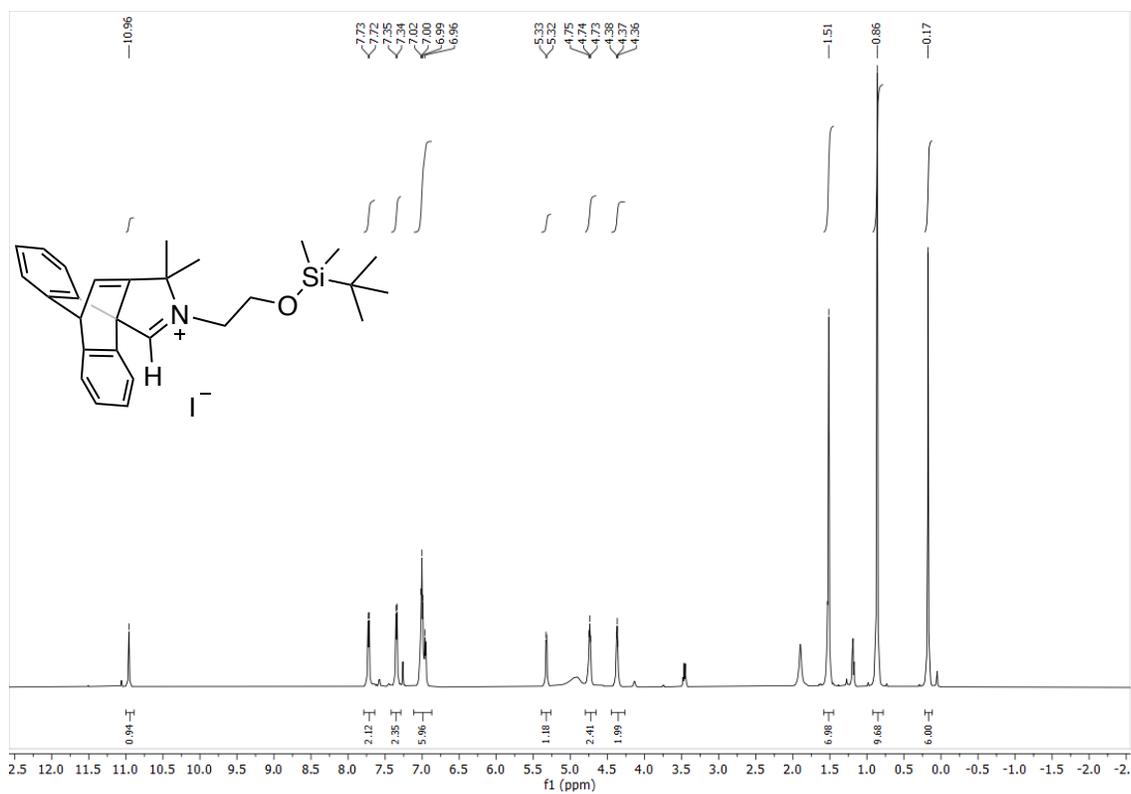
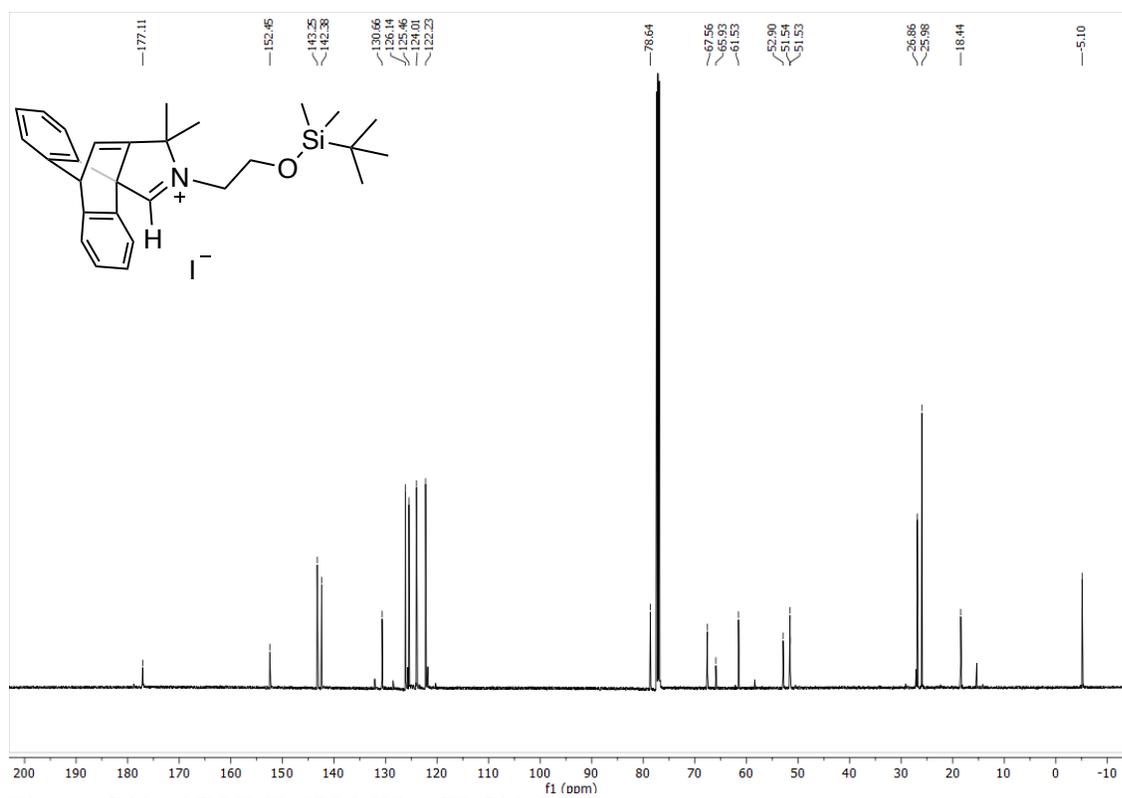


Figure S8:  $^{13}\text{C}$  NMR (101 MHz,  $\text{CD}_3\text{CN}$ ) 2c [I].



**Figure S9:**  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ) **2d [I]<sup>-</sup>**



**Figure S10:**  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ) **2d [I]<sup>-</sup>**



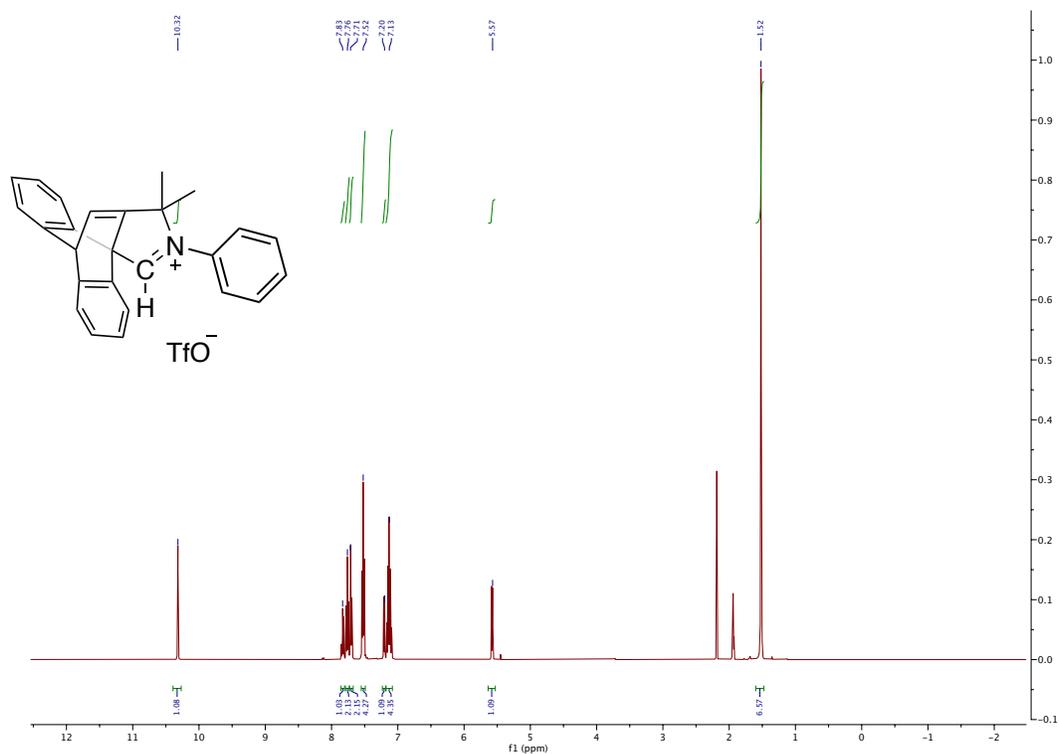


Figure S13: <sup>1</sup>H NMR (400 MHz, CD<sub>3</sub>CN) 3a [TfO]<sup>-</sup>

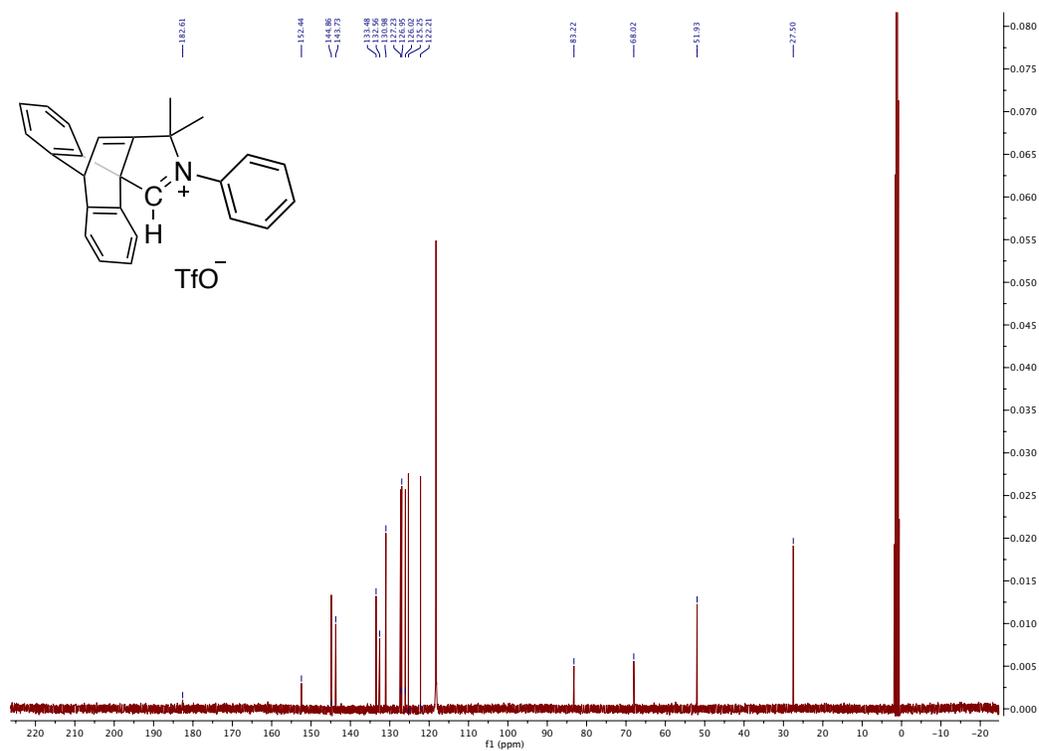


Figure S14: <sup>13</sup>C NMR (101 MHz, CD<sub>3</sub>CN) 3a [TfO]<sup>-</sup>

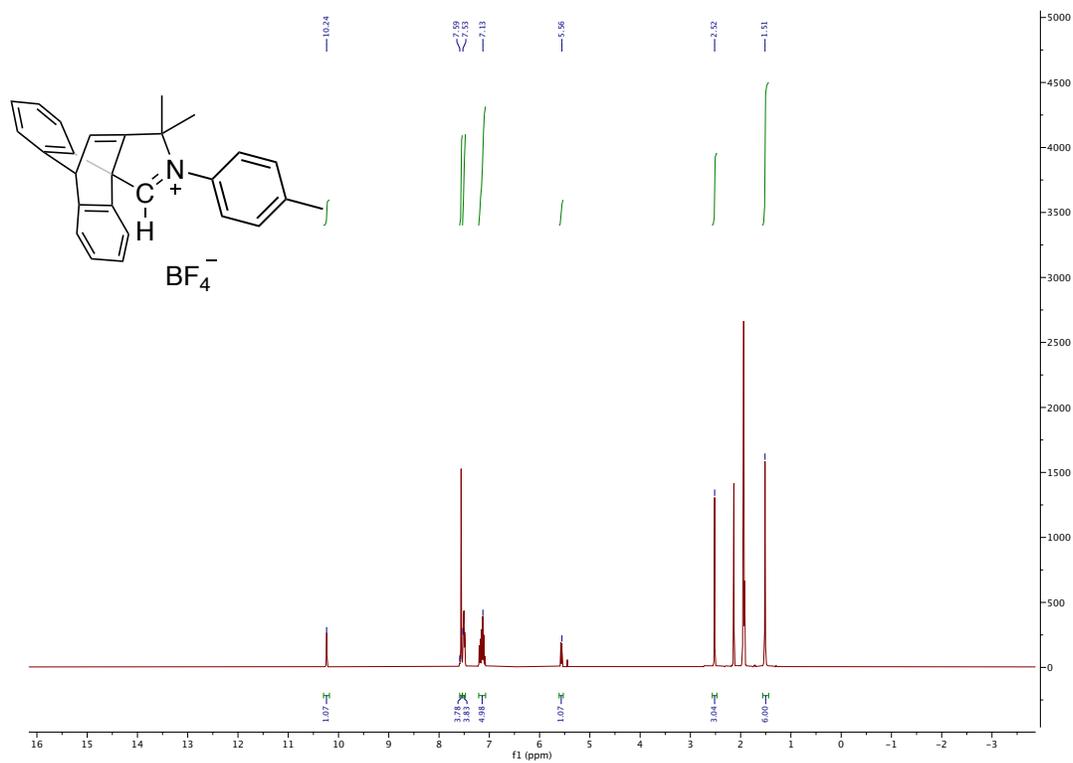


Figure S15: <sup>1</sup>H NMR (300 MHz, CD<sub>3</sub>CN) 3b [BF<sub>4</sub>]<sup>-</sup>

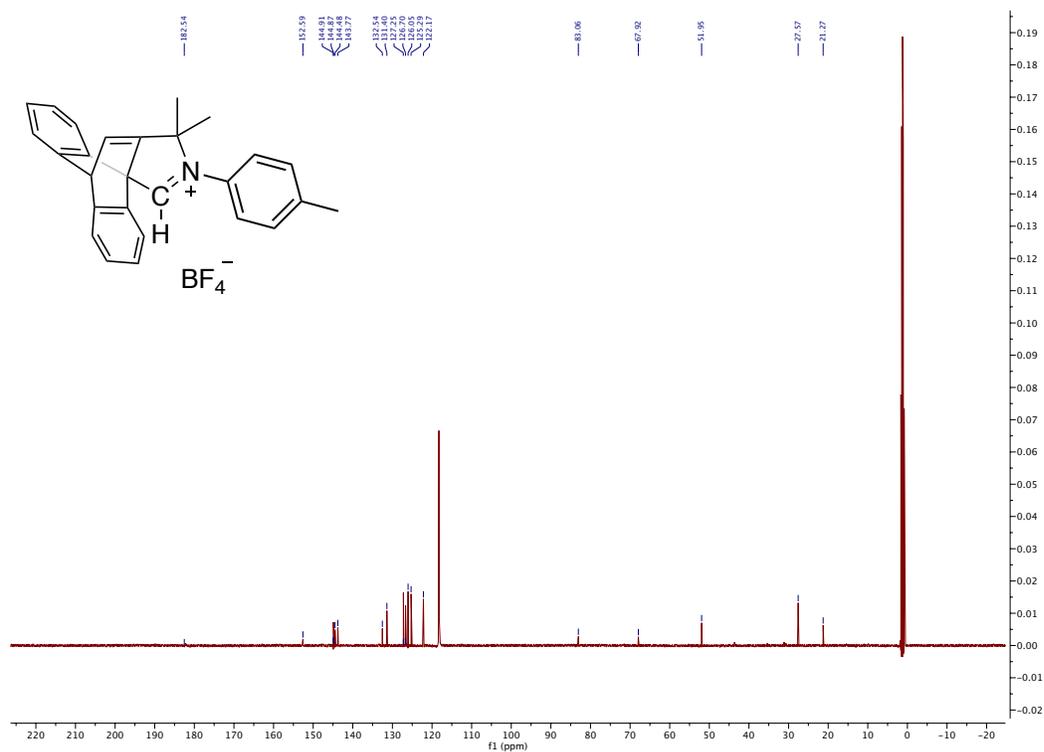
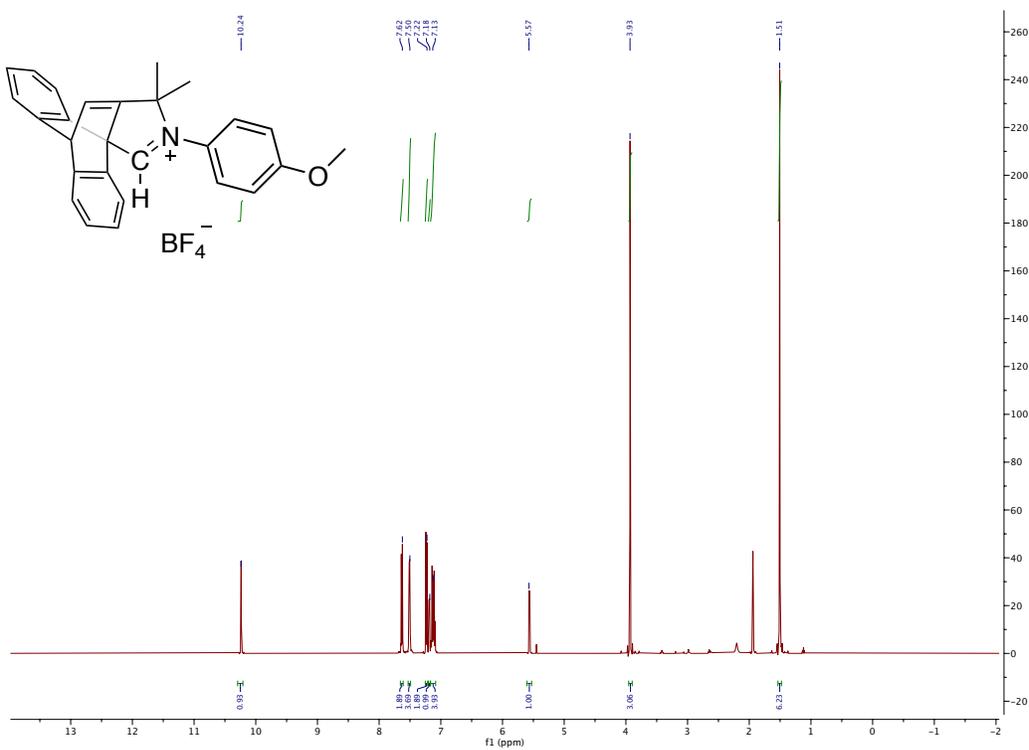
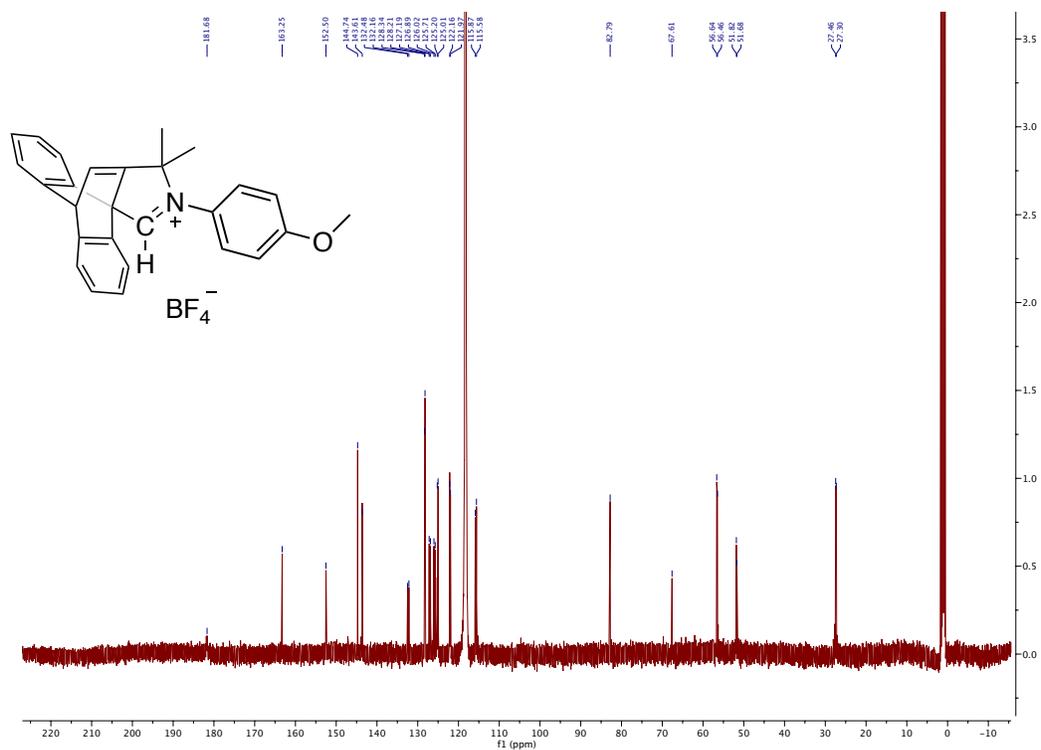


Figure S16: <sup>13</sup>C NMR (101 MHz, CD<sub>3</sub>CN) 3b [BF<sub>4</sub>]<sup>-</sup>



**Figure S17:**  $^1\text{H}$  NMR (500 MHz,  $\text{CD}_3\text{CN}$ )  $3\text{c}[\text{BF}_4]^-$



**Figure S18:**  $^{13}\text{C}$  NMR (126 MHz,  $\text{CD}_3\text{CN}$ )  $3\text{c}[\text{BF}_4]^-$

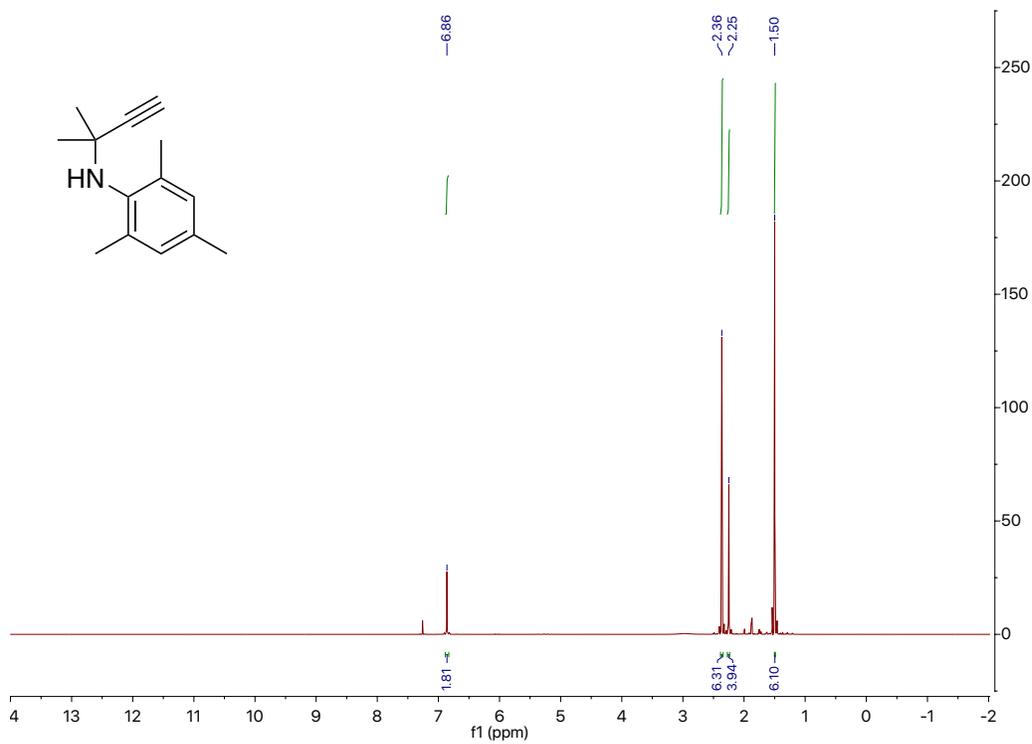


Figure S19:  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ) **4**

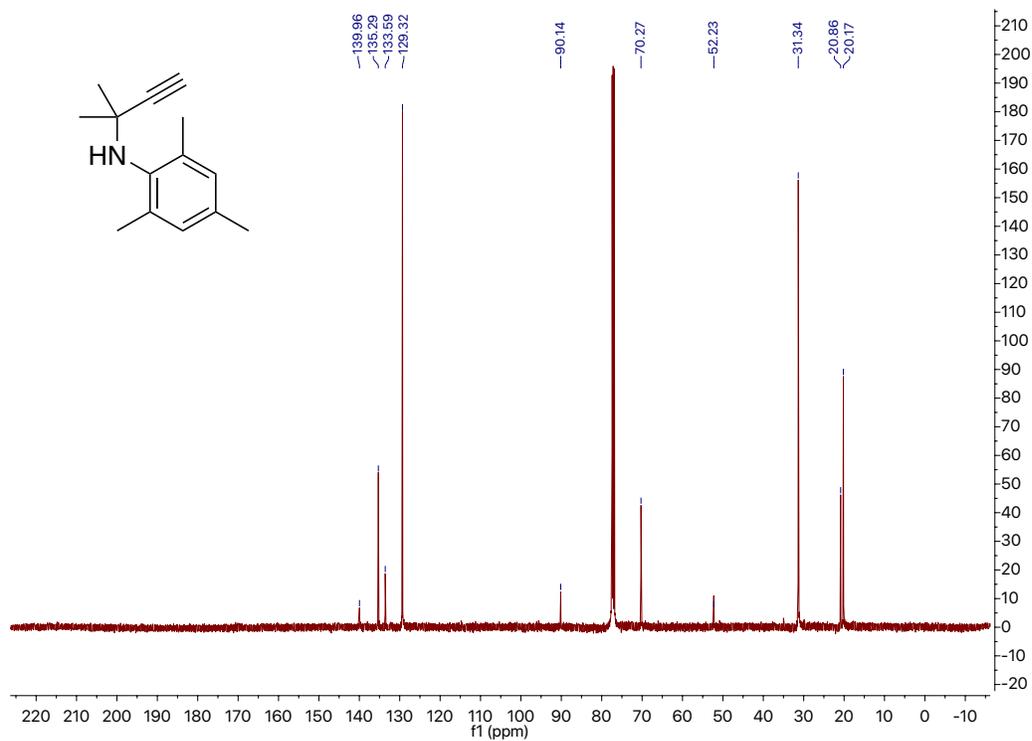
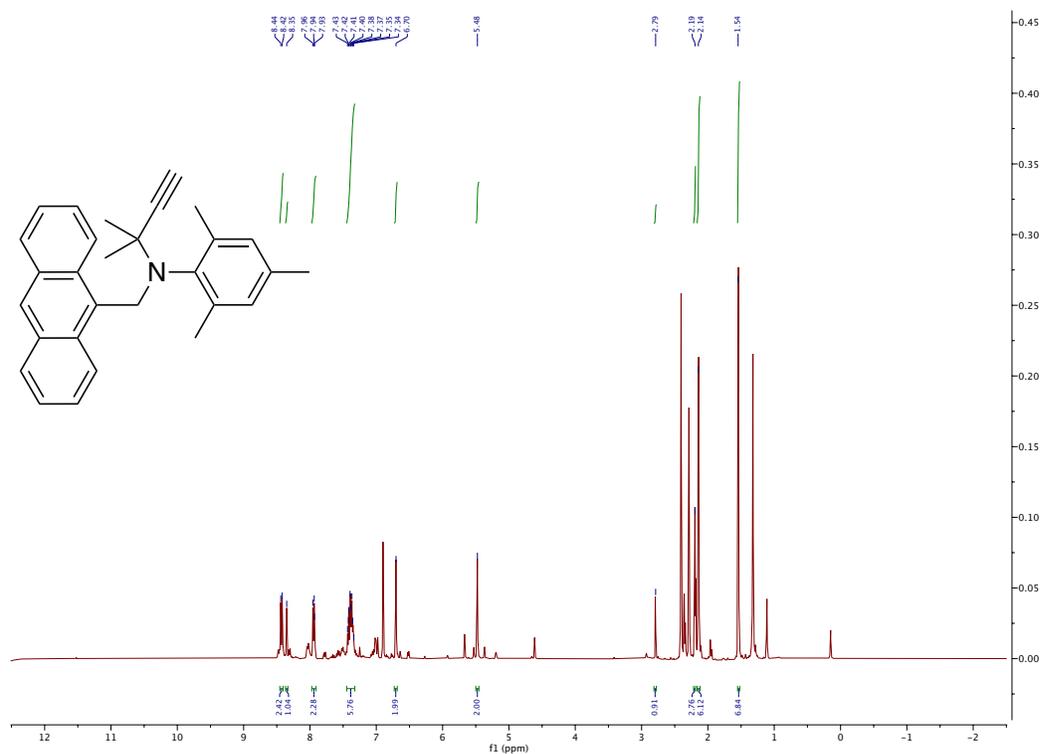
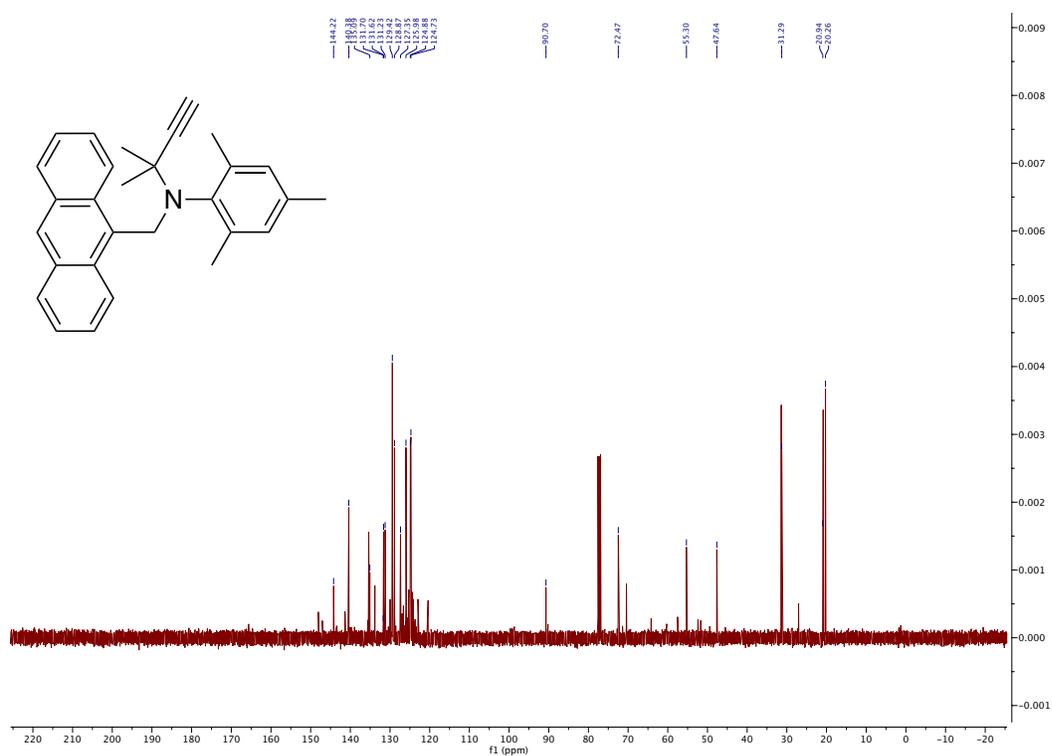


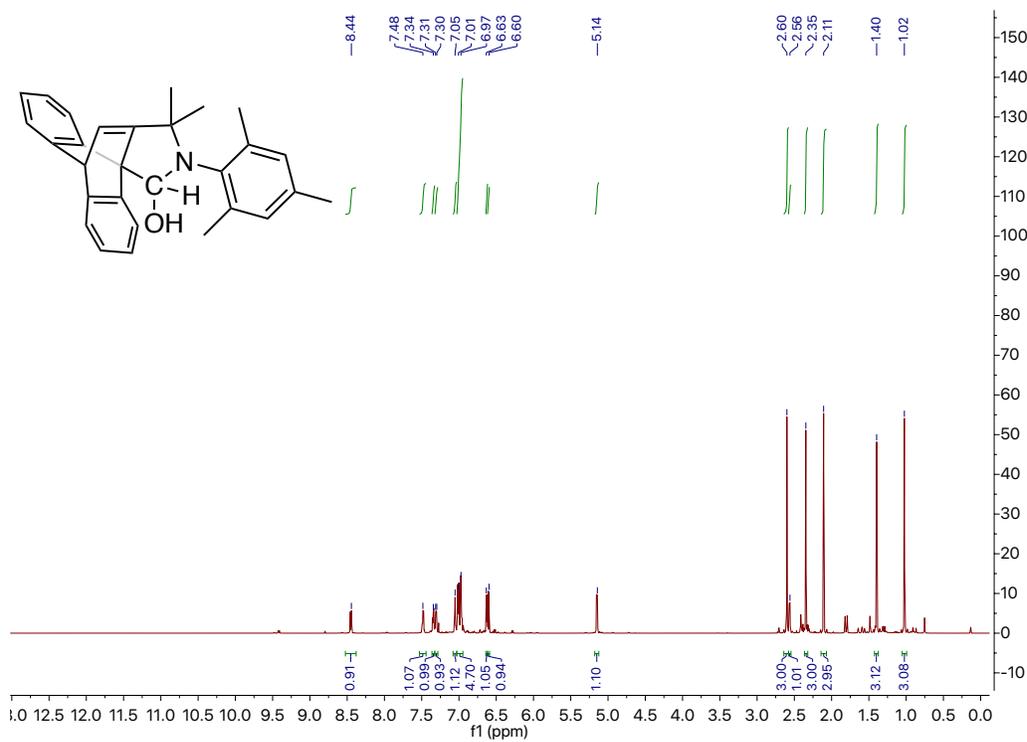
Figure S20:  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ ) **4**



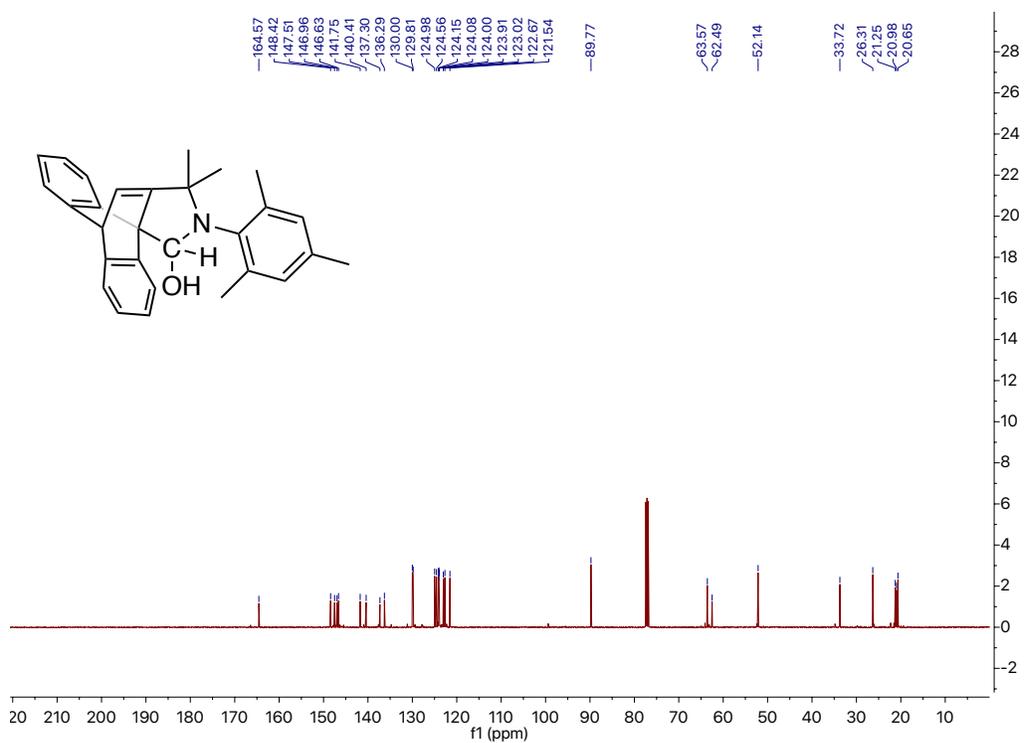
**Figure S21:**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) crude mixture of **5** and **4**



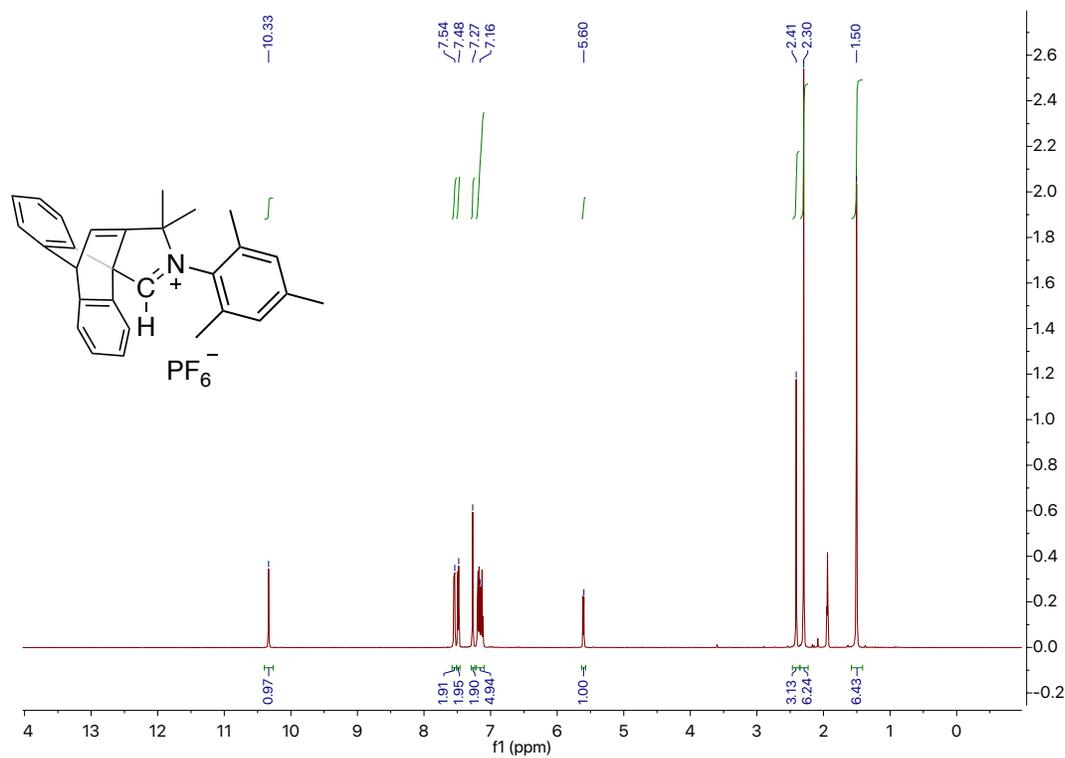
**Figure S22:**  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ ) crude mixture of **5** and **4**



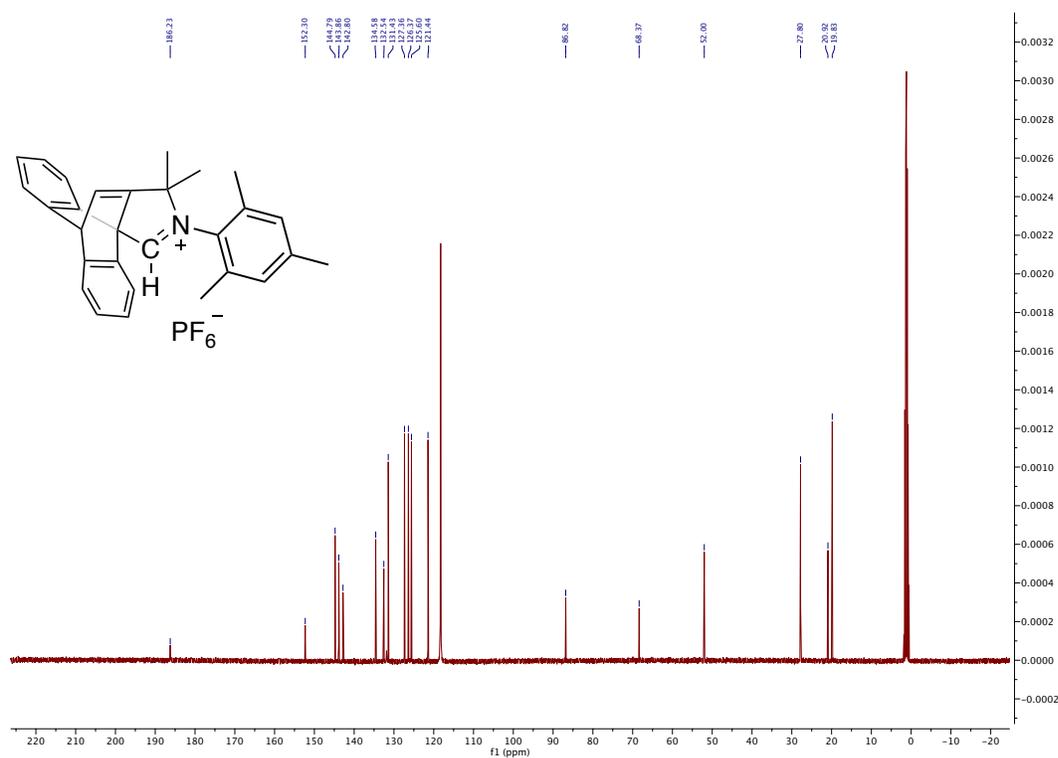
**Figure S23:  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ) 6d**



**Figure S24:  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ ) 6d**



**Figure S25:**  $^1\text{H}$  NMR (400 MHz,  $\text{CD}_3\text{CN}$ ) **3d** [ $\text{PF}_6^-$ ]



**Figure S26:**  $^{13}\text{C}$  NMR (101 MHz,  $\text{CD}_3\text{CN}$ ) **3d** [ $\text{PF}_6^-$ ]

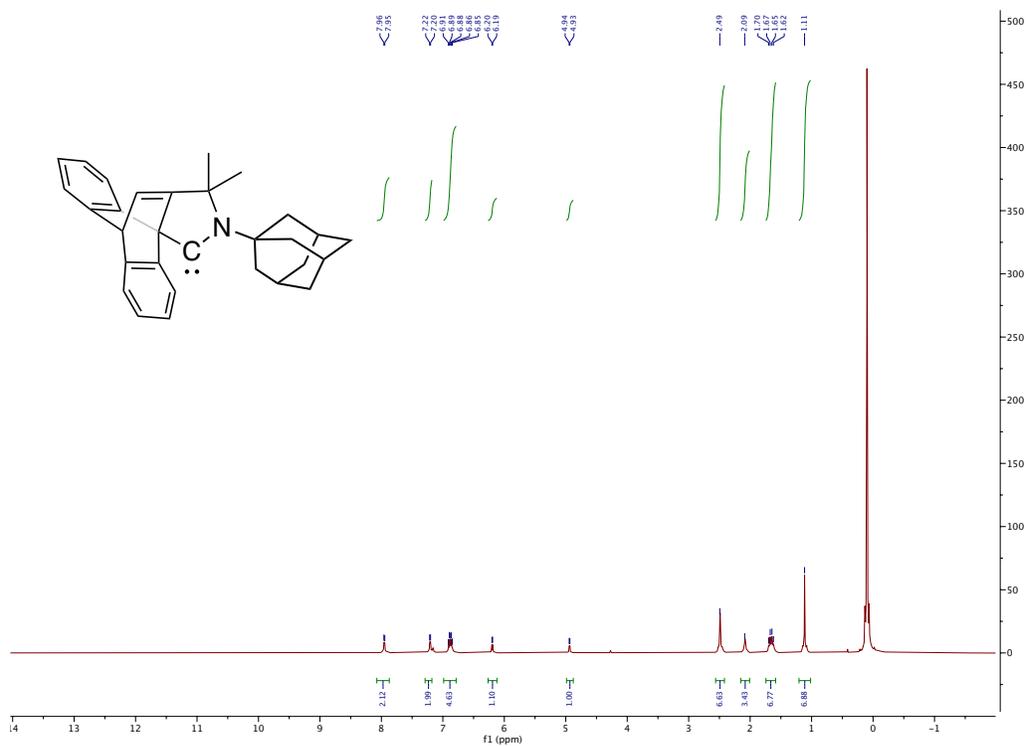


Figure S27:  $^1\text{H}$  NMR (500 MHz,  $\text{C}_6\text{D}_6$ ) Carb2a

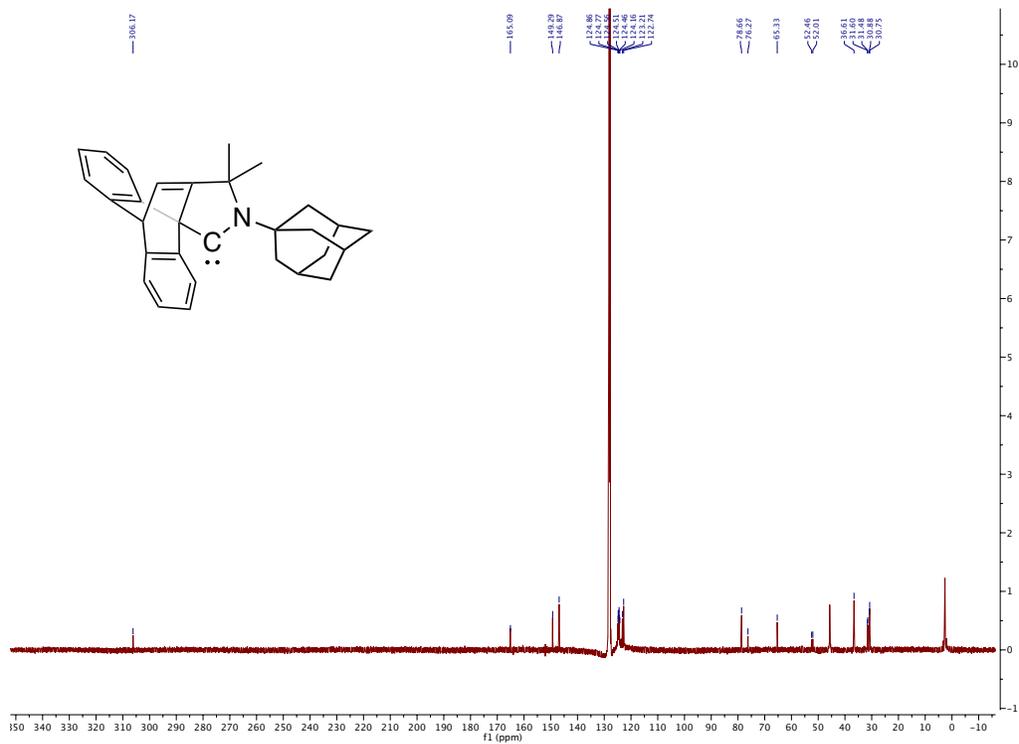


Figure S28:  $^{13}\text{C}$  NMR (126 MHz,  $\text{C}_6\text{D}_6$ ) Carb2a

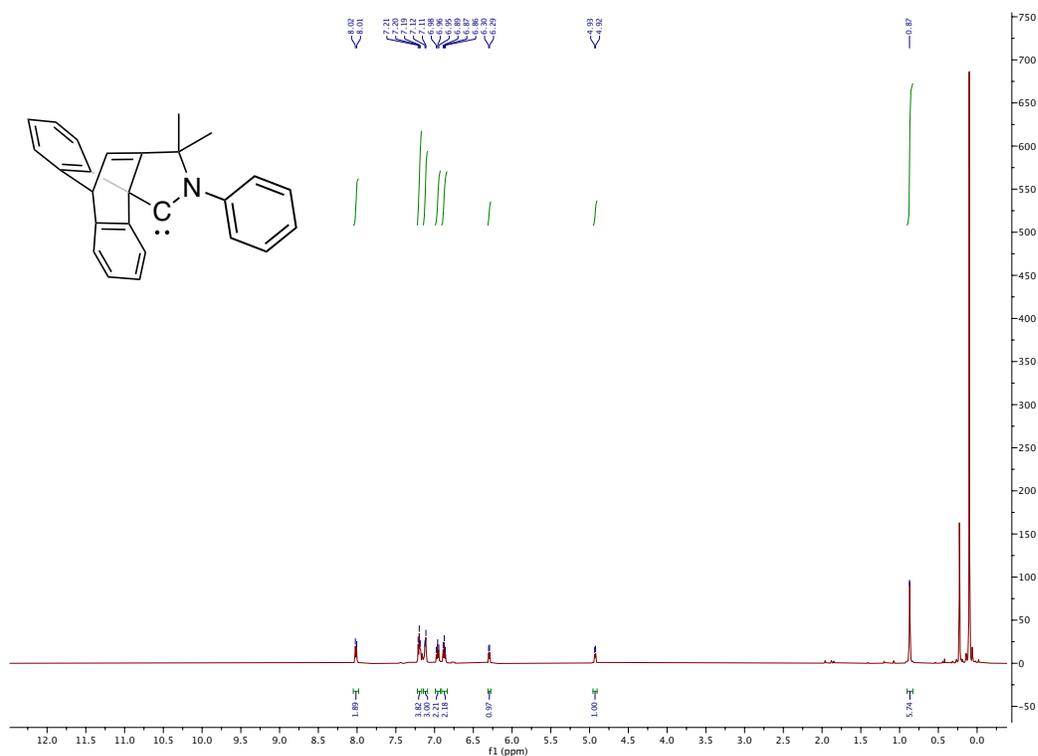


Figure S29:  $^1\text{H}$  NMR (500 MHz,  $\text{C}_6\text{D}_6$ ) Carb3a

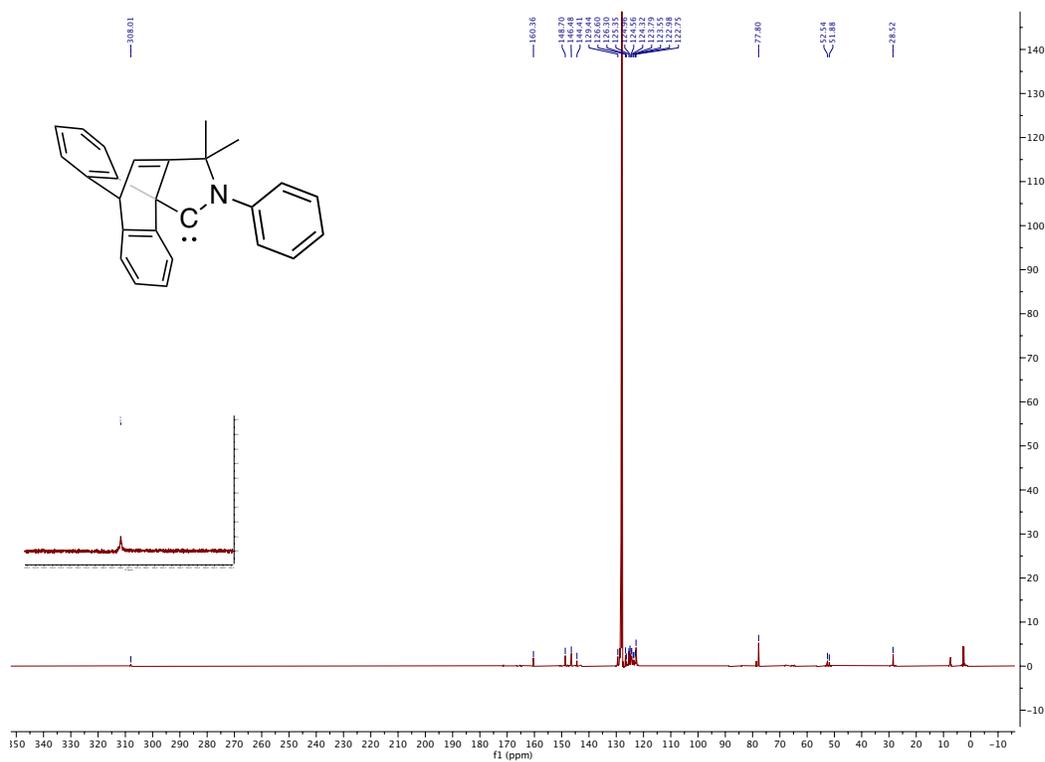


Figure S30:  $^{13}\text{C}$  NMR (126 MHz,  $\text{C}_6\text{D}_6$ ) Carb3a

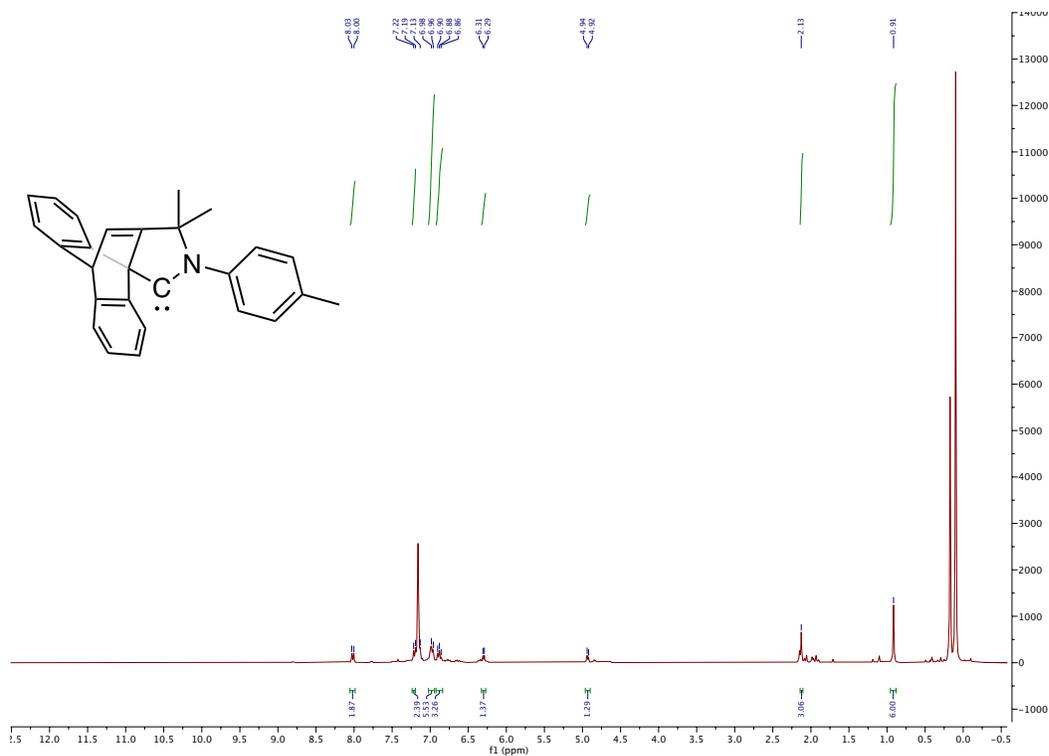


Figure S31: <sup>1</sup>H NMR (500 MHz, C<sub>6</sub>D<sub>6</sub>) Carb3b

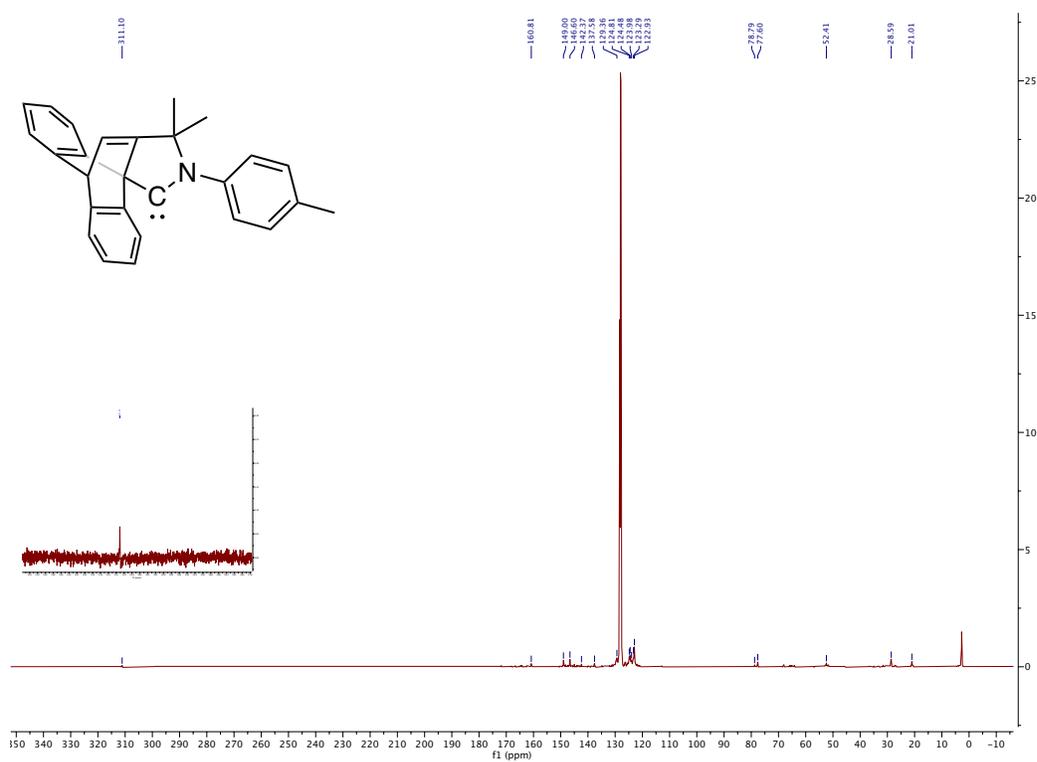


Figure S32: <sup>13</sup>C NMR (126 MHz, C<sub>6</sub>D<sub>6</sub>) Carb3b



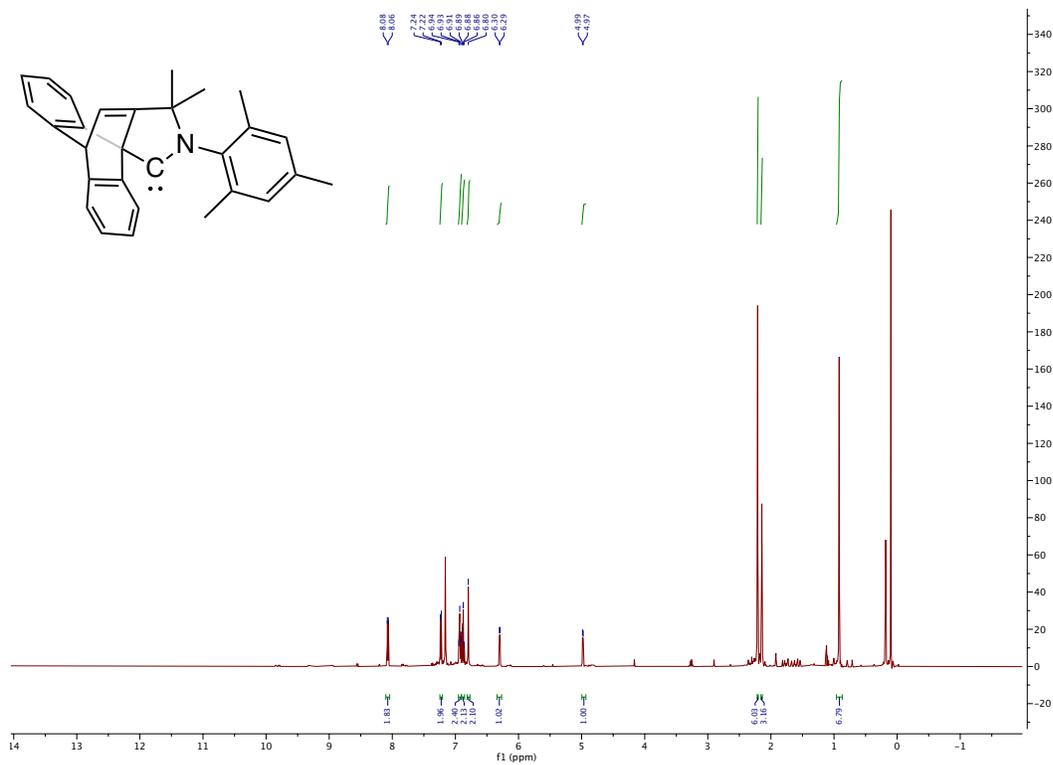


Figure S35: <sup>1</sup>H NMR (500 MHz, C<sub>6</sub>D<sub>6</sub>) Carb3d

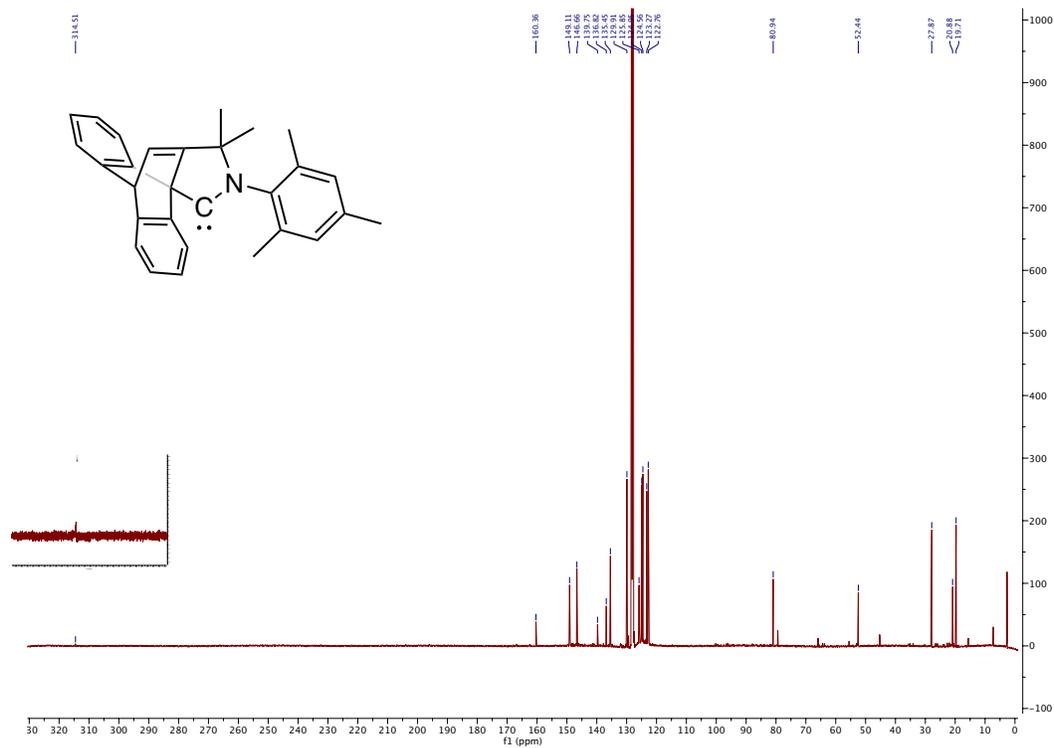


Figure S36: <sup>13</sup>C NMR (126 MHz, C<sub>6</sub>D<sub>6</sub>) Carb3d

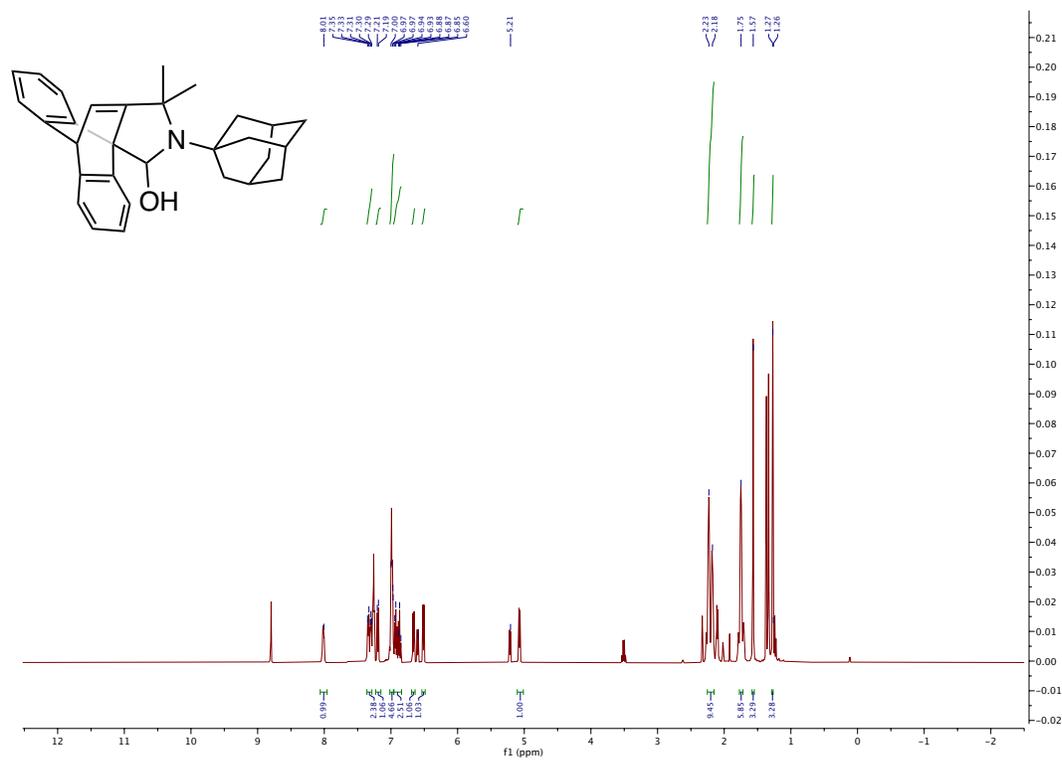


Figure S37:  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) **6a**

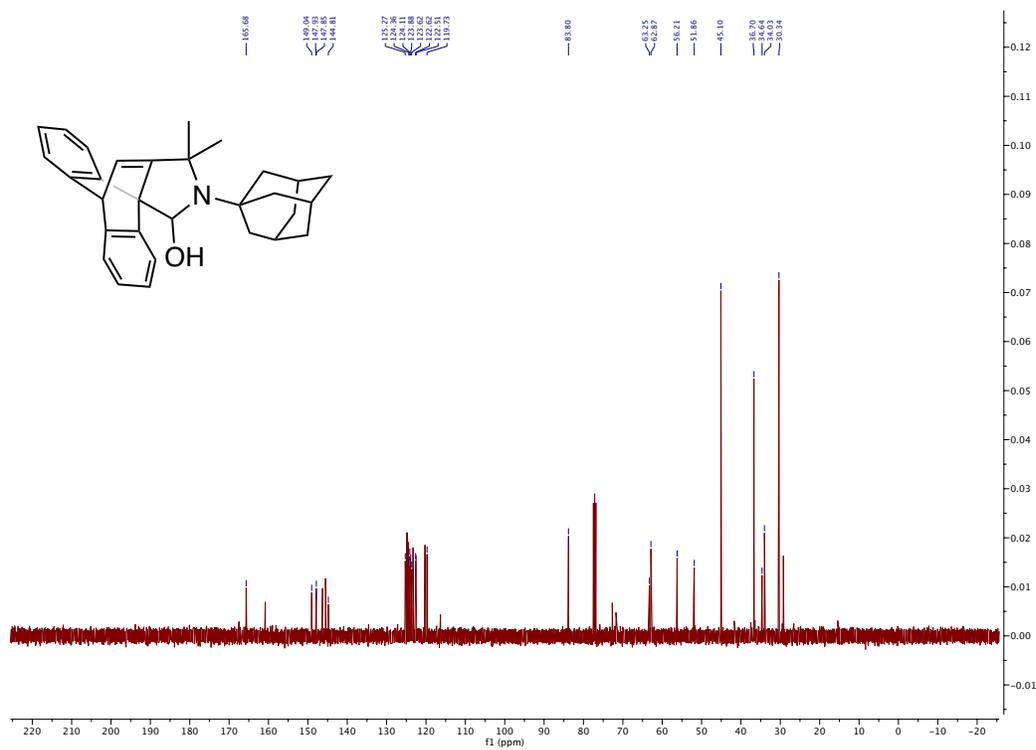
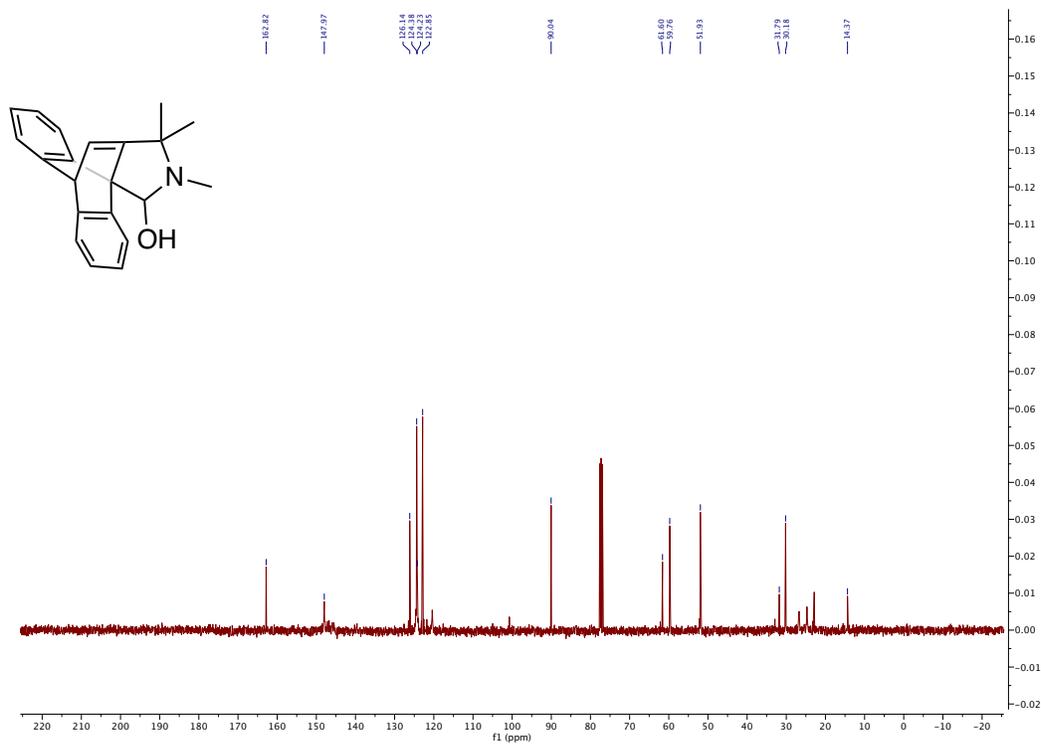
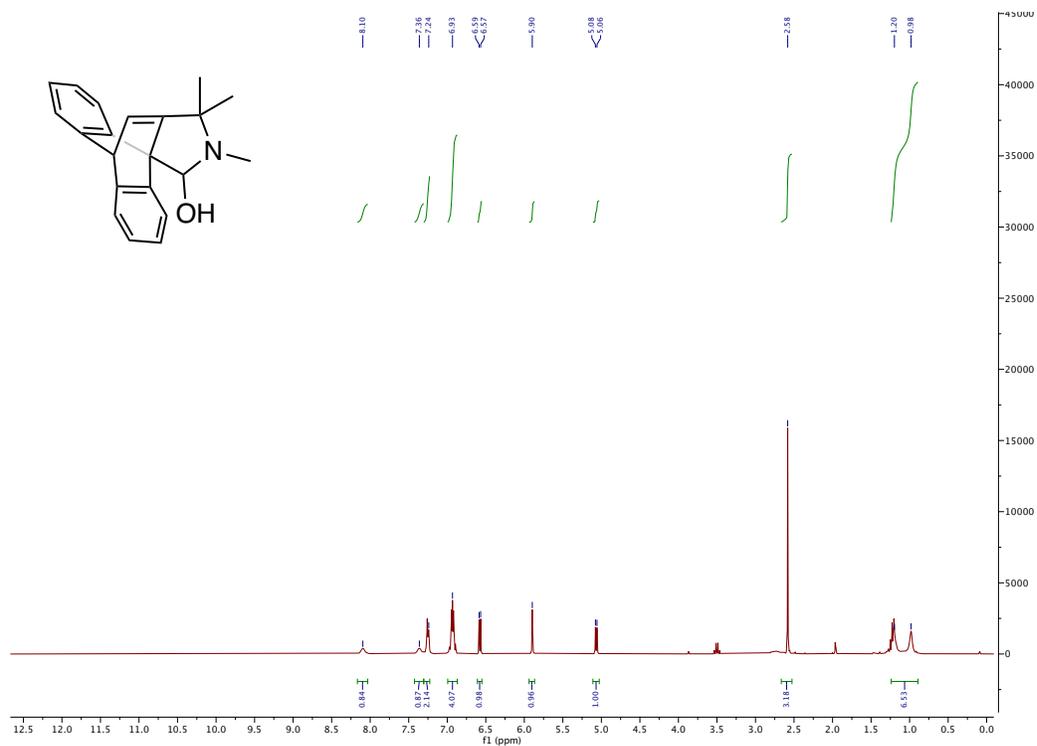
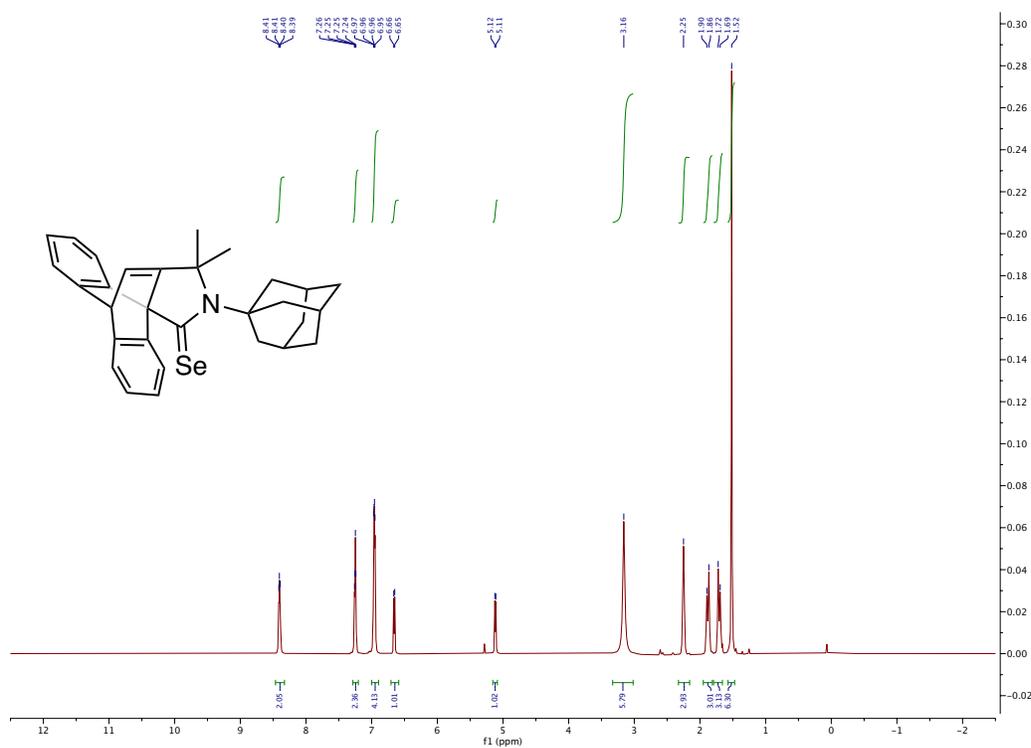
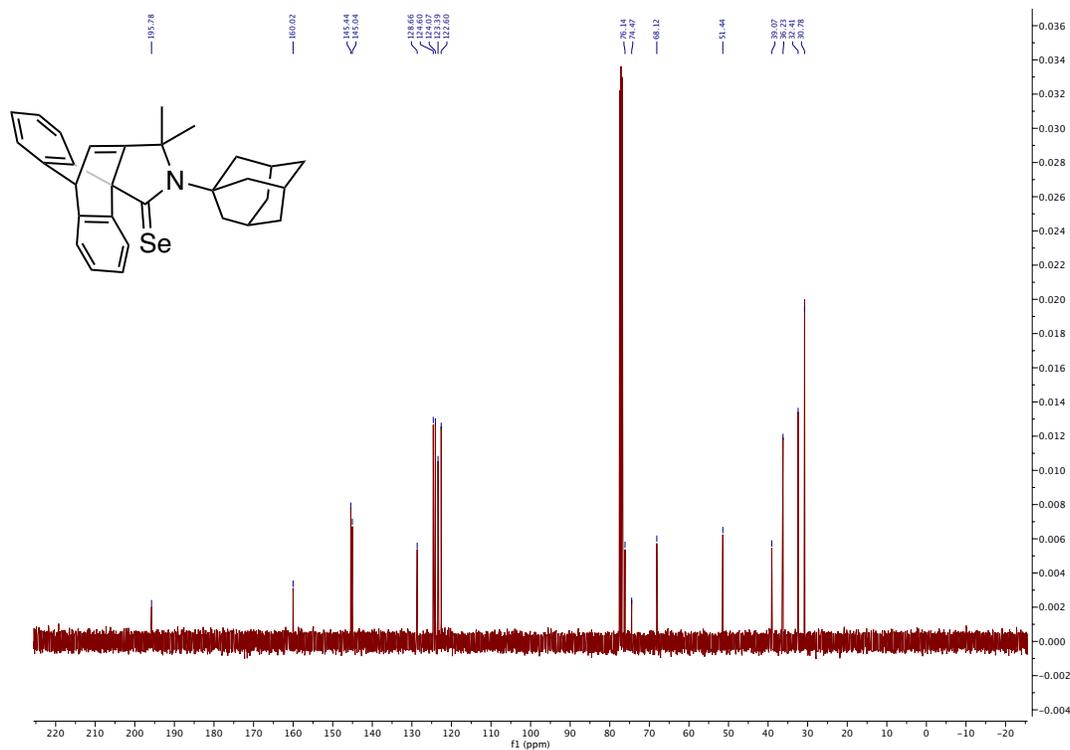


Figure S38:  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ) **6a**

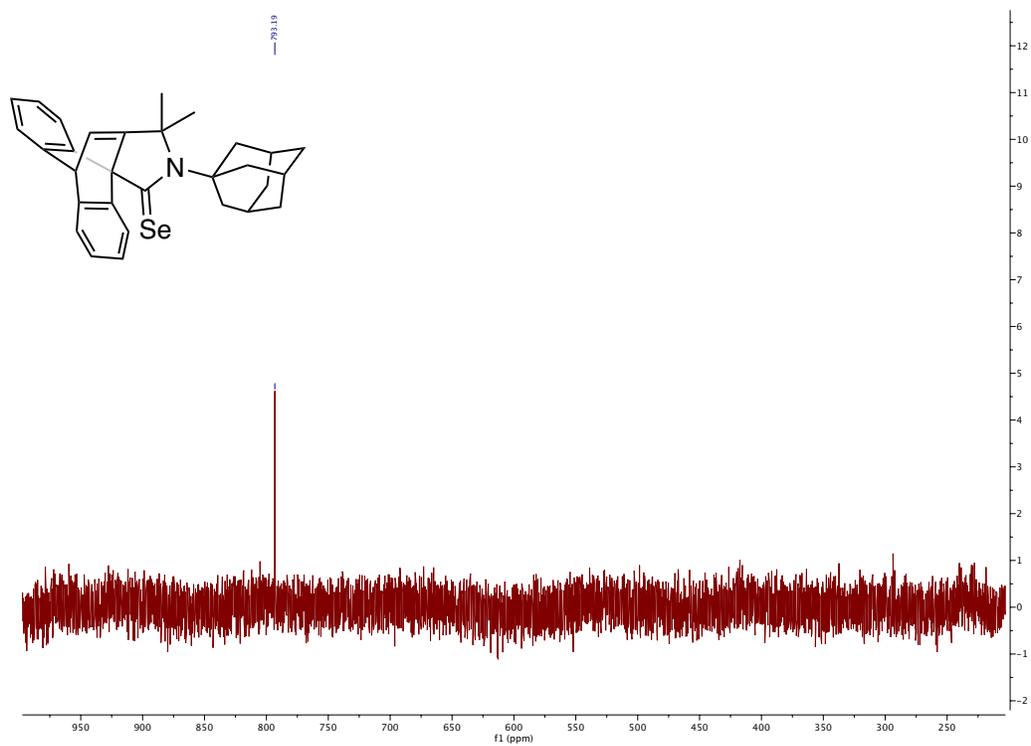




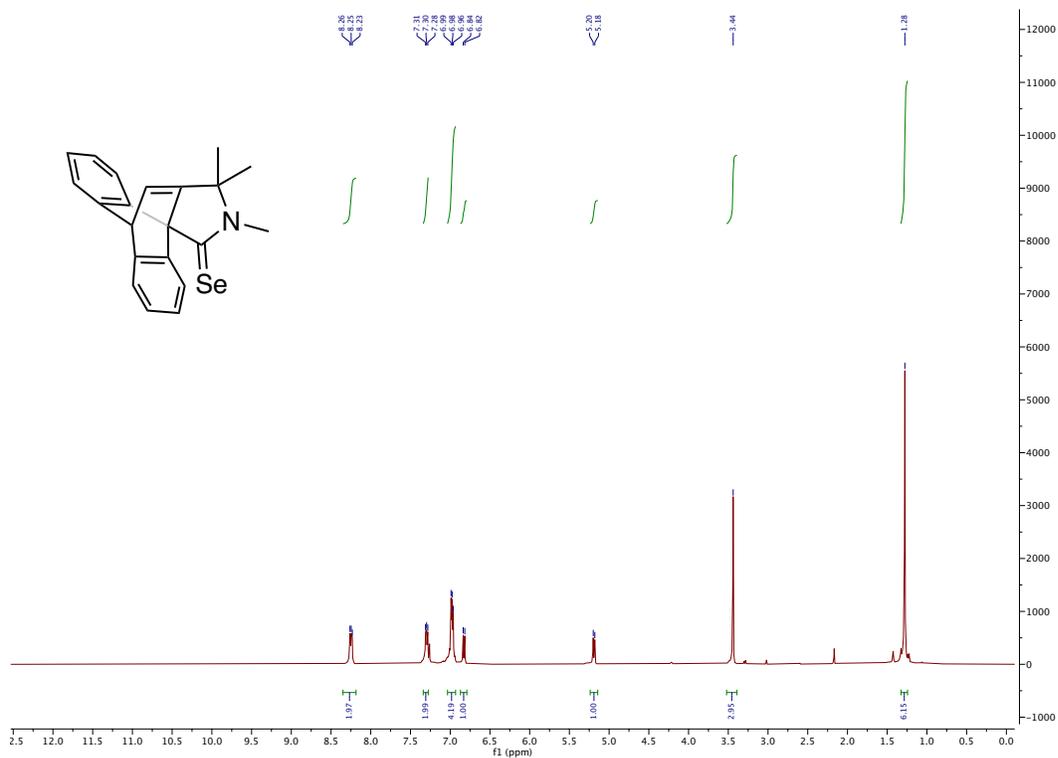
**Figure S41: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) Se2a**



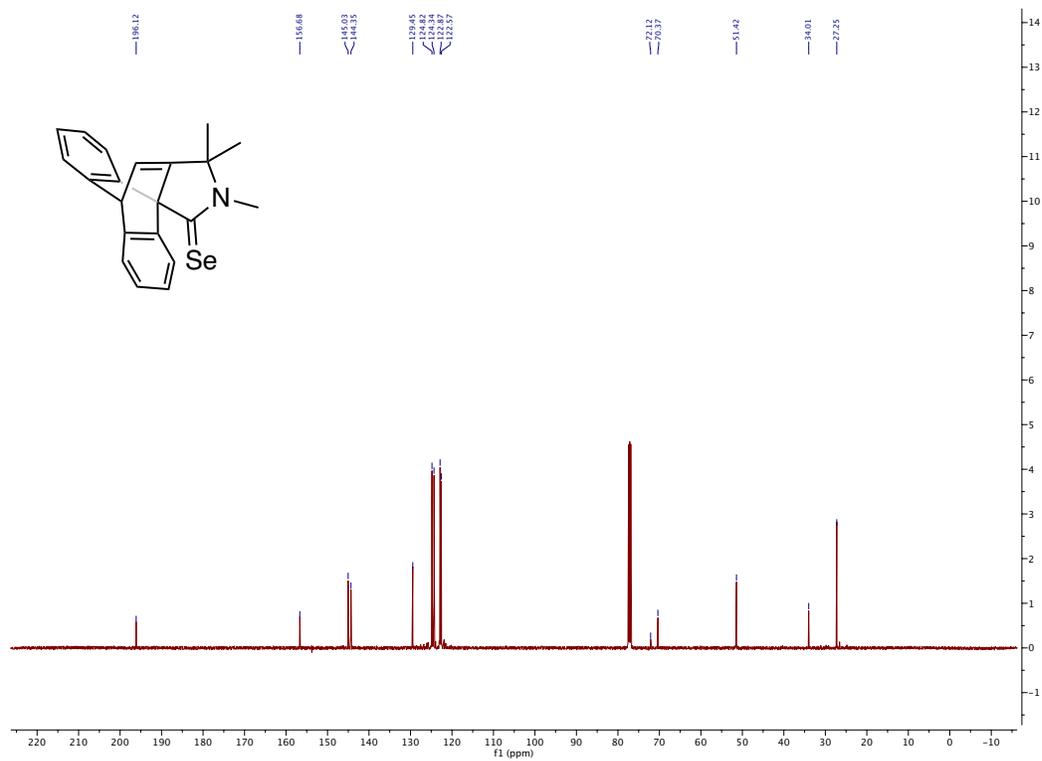
**Figure S42: <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) Se2a**



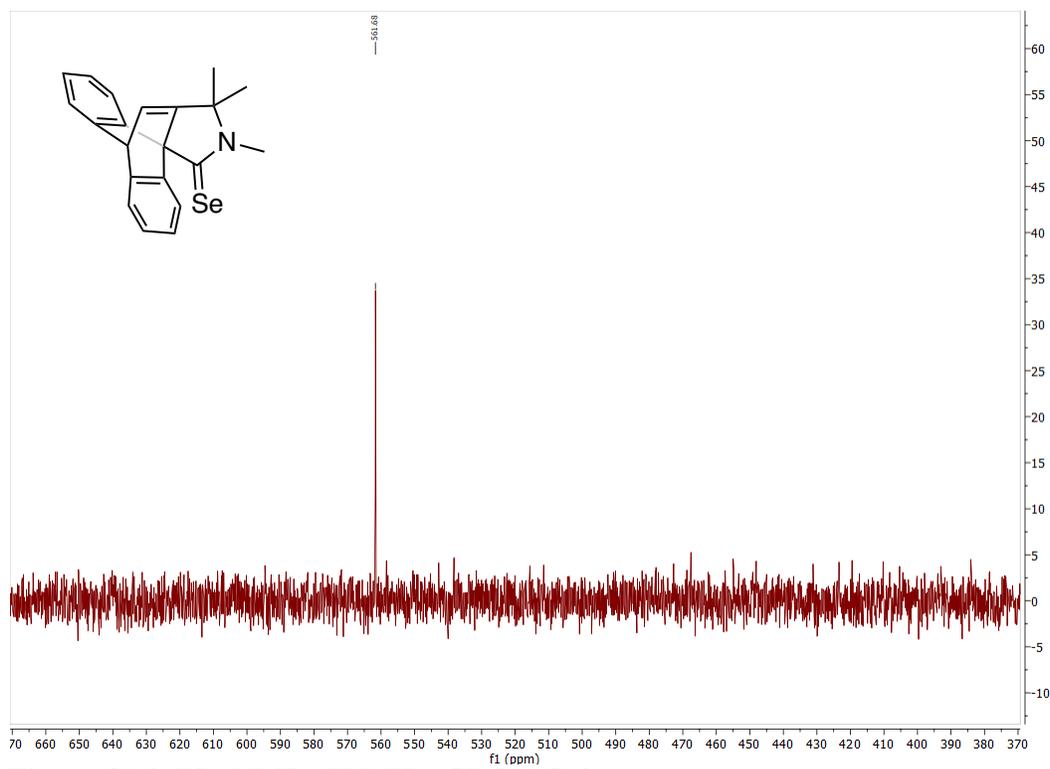
**Figure S43:**  $^{77}\text{Se}$  NMR (57 MHz,  $\text{CD}_2\text{Cl}_2$ ) Se2a



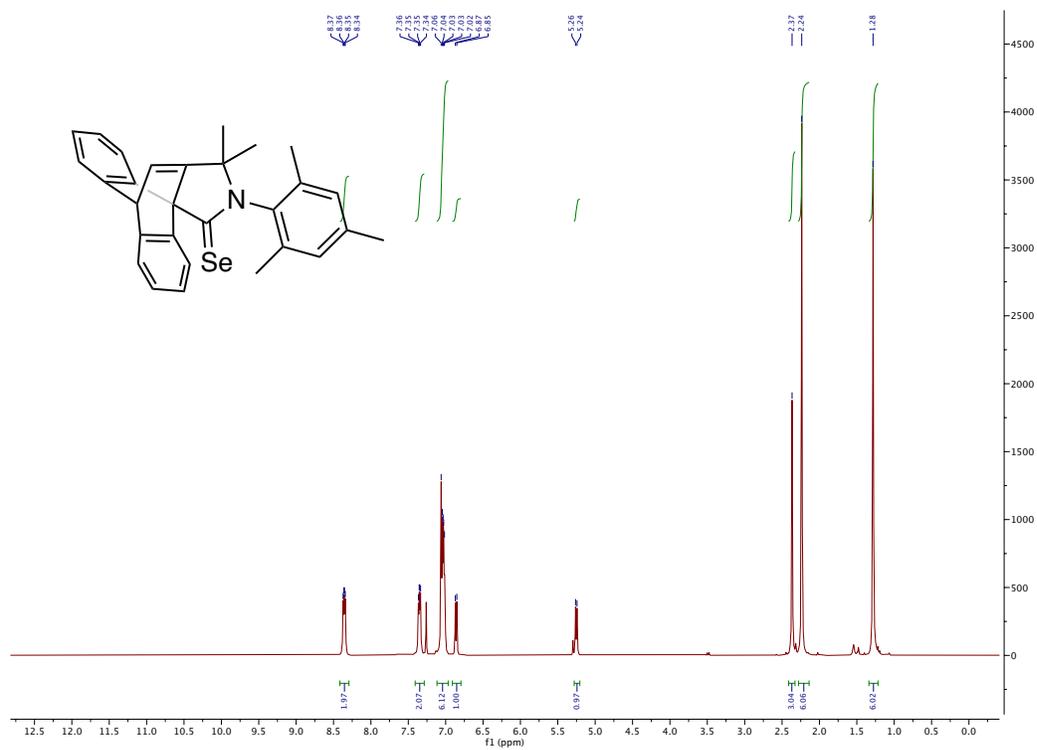
**Figure S44:**  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ) Se2c



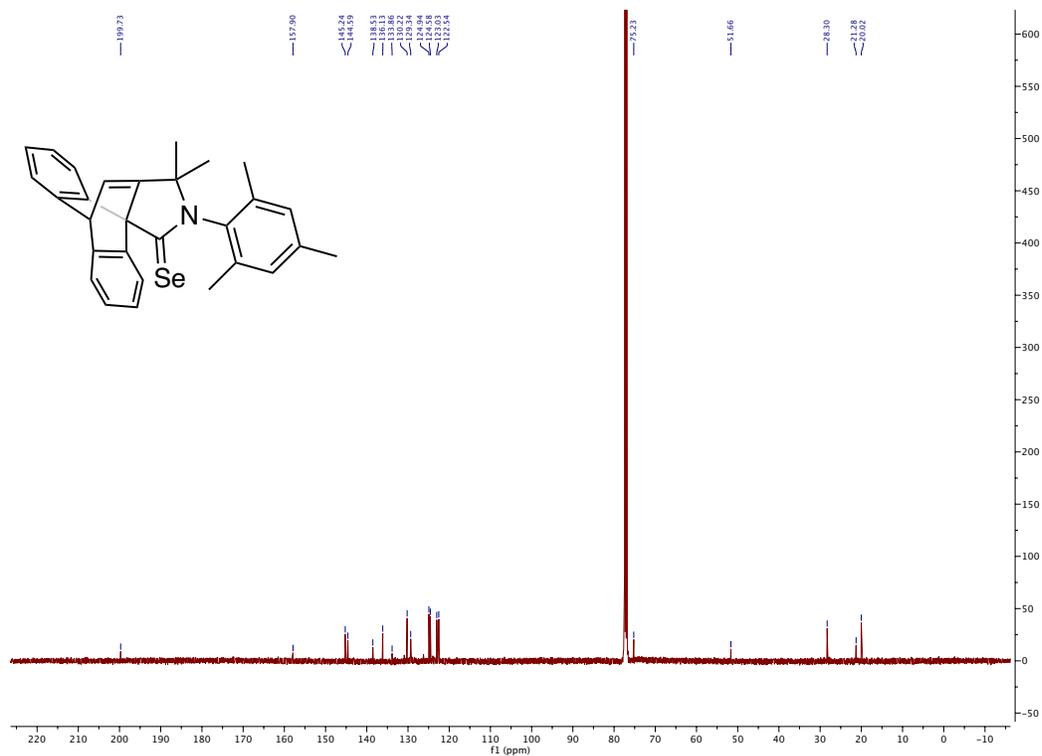
**Figure S45:**  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ ) **Se2c**



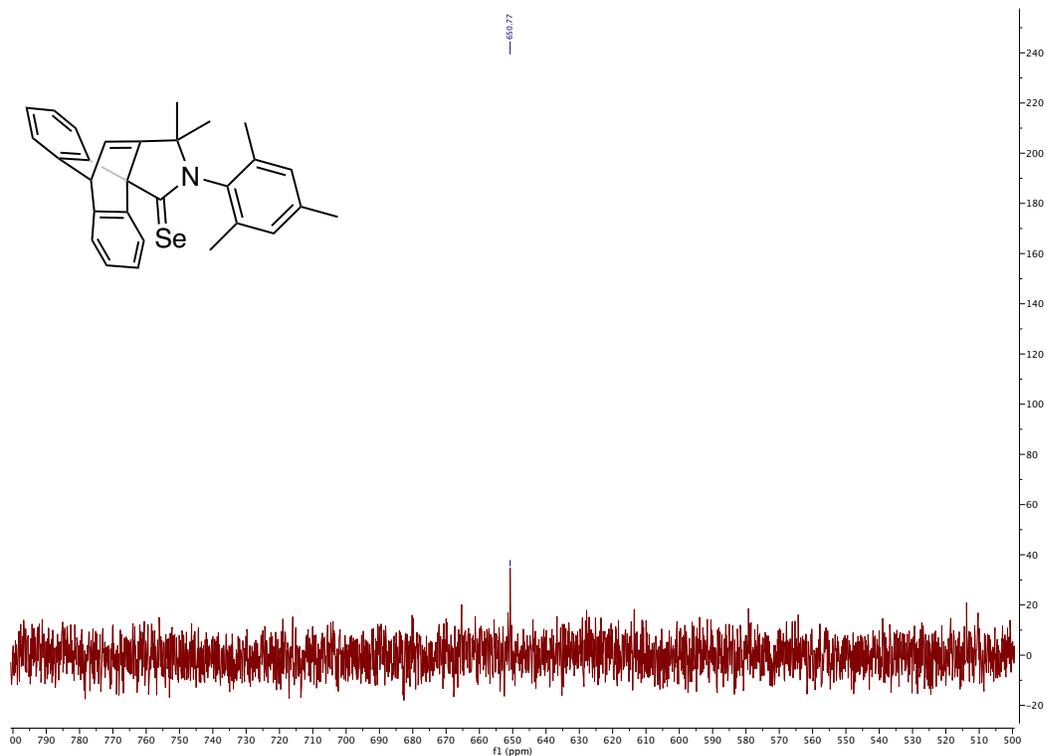
**Figure S46:**  $^{77}\text{Se}$  NMR (57 MHz,  $\text{CDCl}_3$ ) **Se2c**



**Figure S47:**  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ) **Se3d**

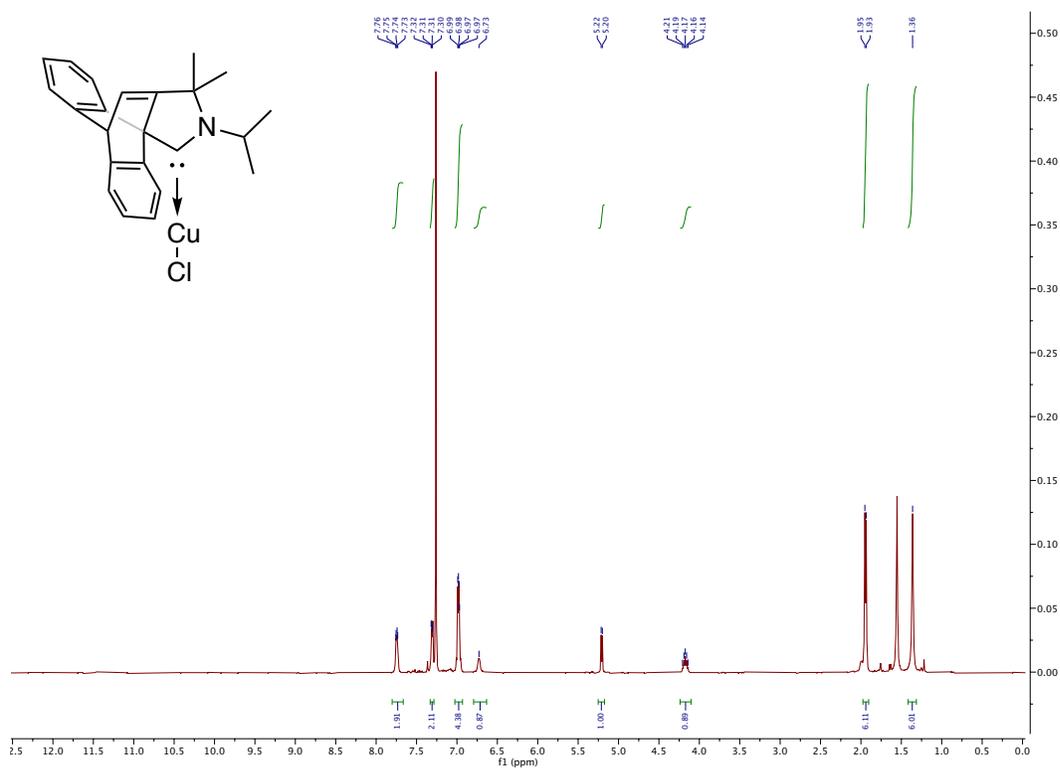


**Figure S48:**  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ ) **Se3d**

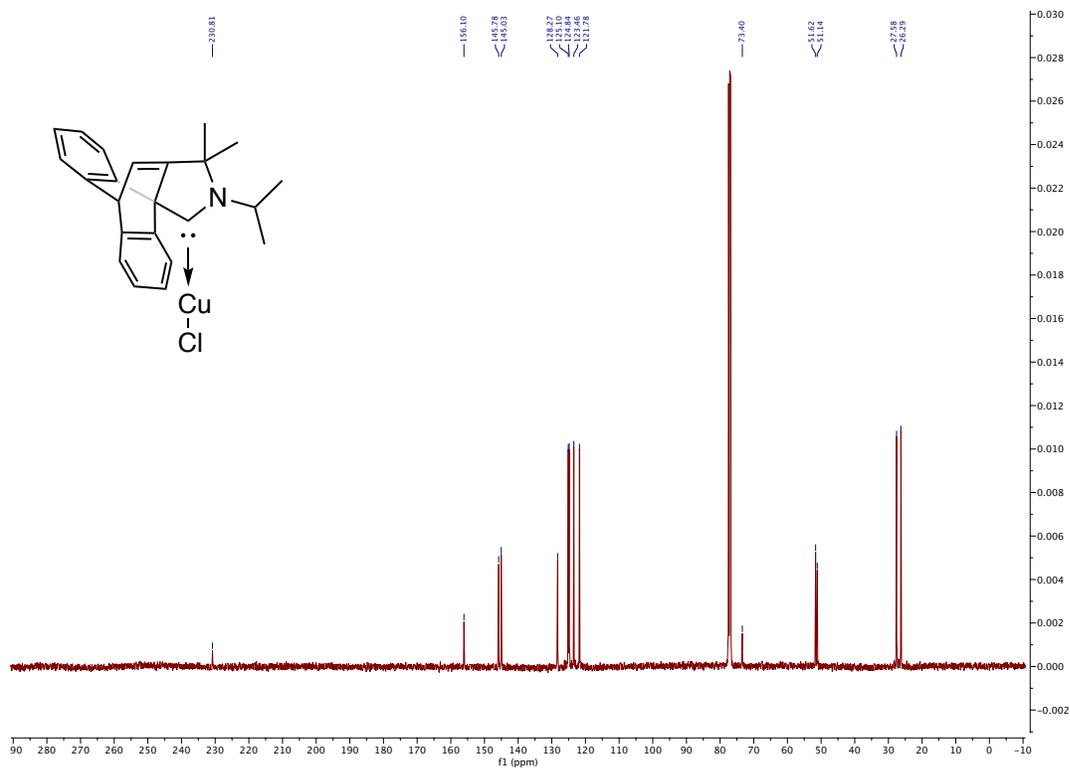


**Figure S49:**  $^{77}\text{Se}$  NMR (126 MHz,  $(\text{CD}_3)_2\text{CO}$ ) Se3d

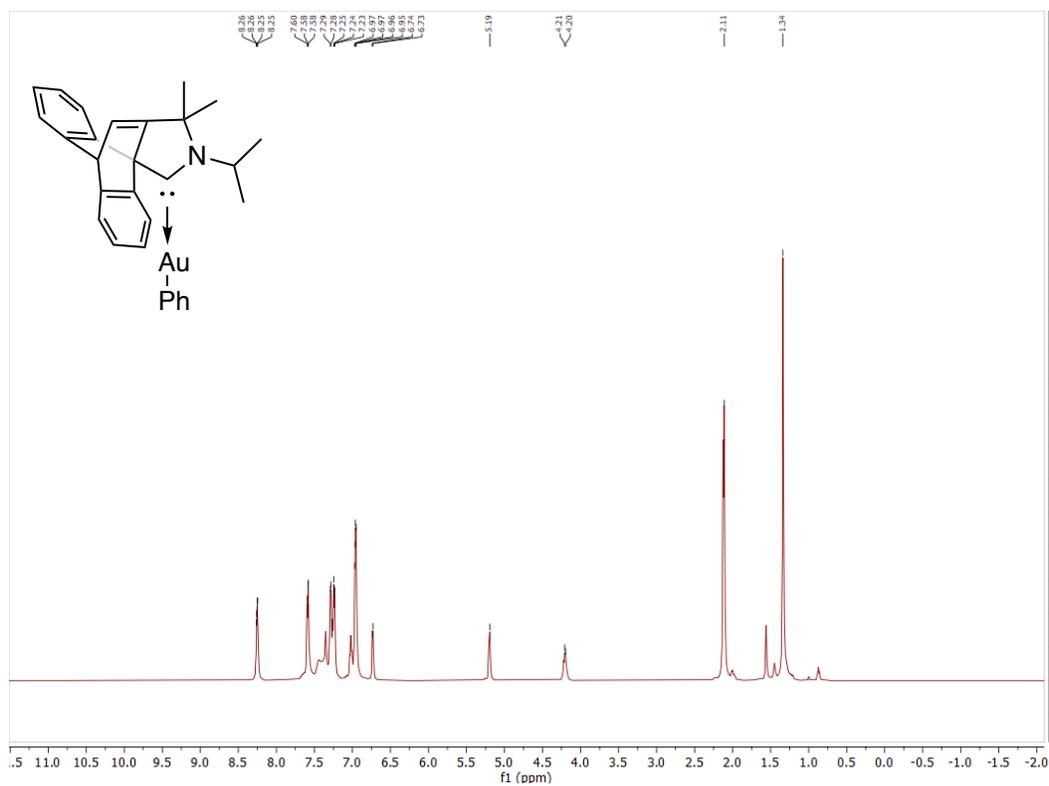
a



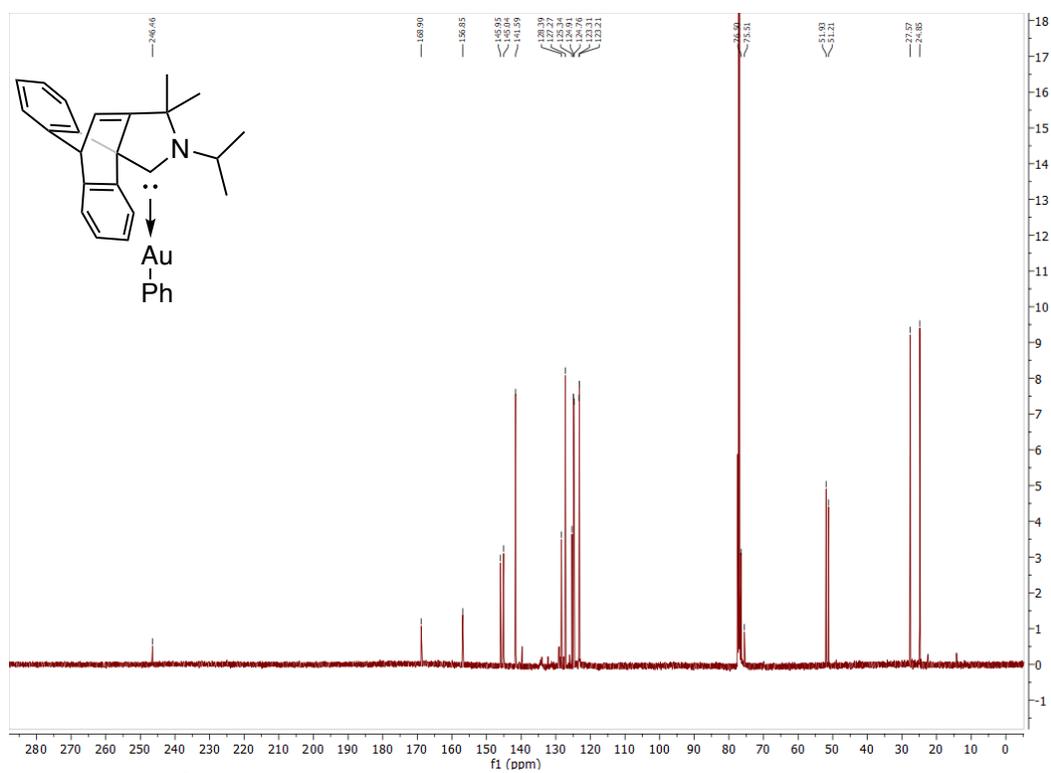
**Figure S50:**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) Cu2b



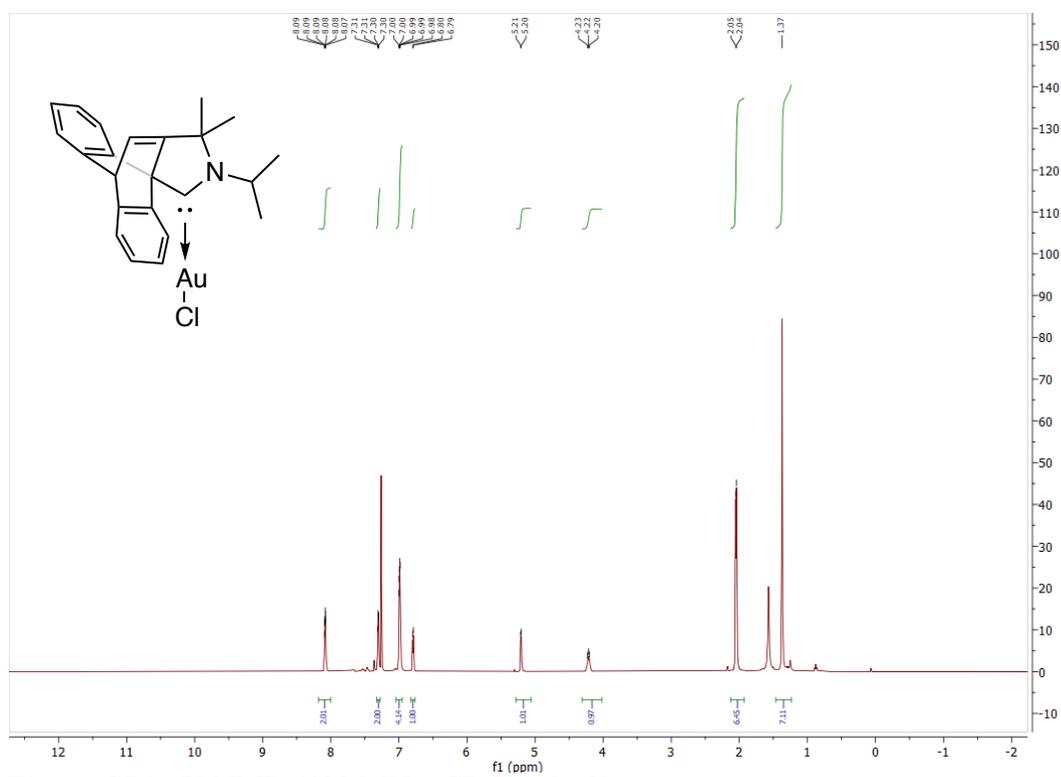
**Figure S51:**  $^{13}\text{C}$  NMR (400 MHz,  $\text{CDCl}_3$ ) **Cu2b**



**Figure S52:**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) **Au2b<sub>Ph</sub>**



**Figure S53:**  $^{13}\text{C}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\text{Au2bPh}$



**Figure S54:**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\text{Au2b}$

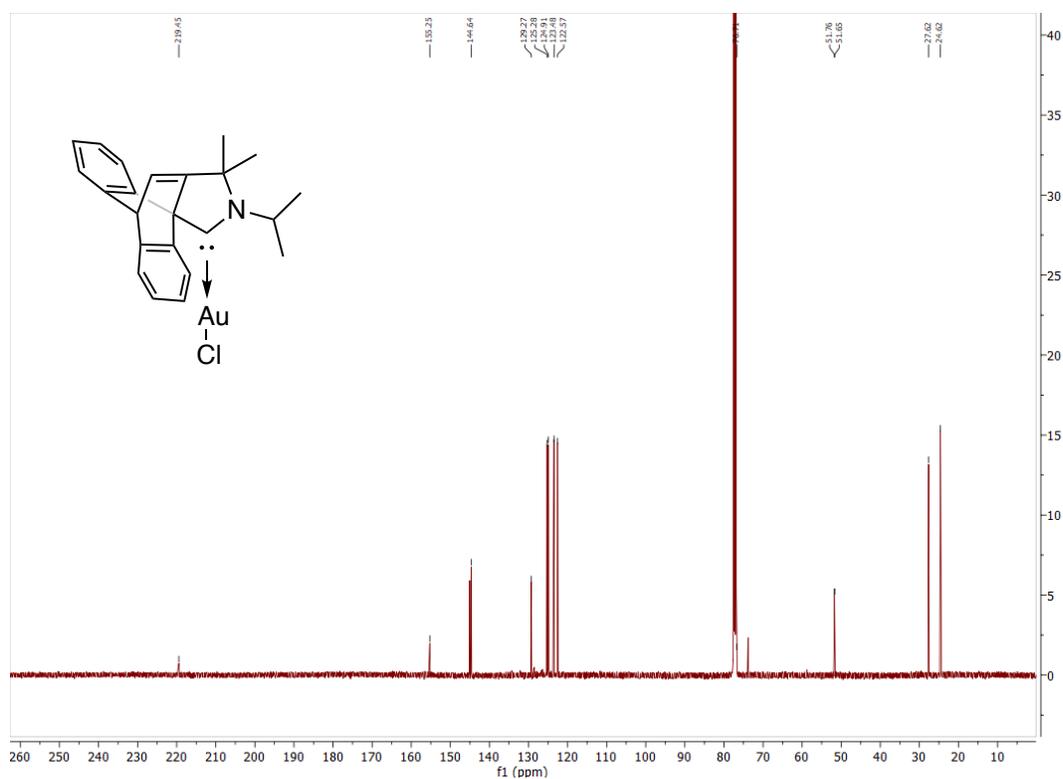


Figure S55:  $^{13}\text{C}$  NMR (400 MHz,  $\text{CDCl}_3$ ) Au2b

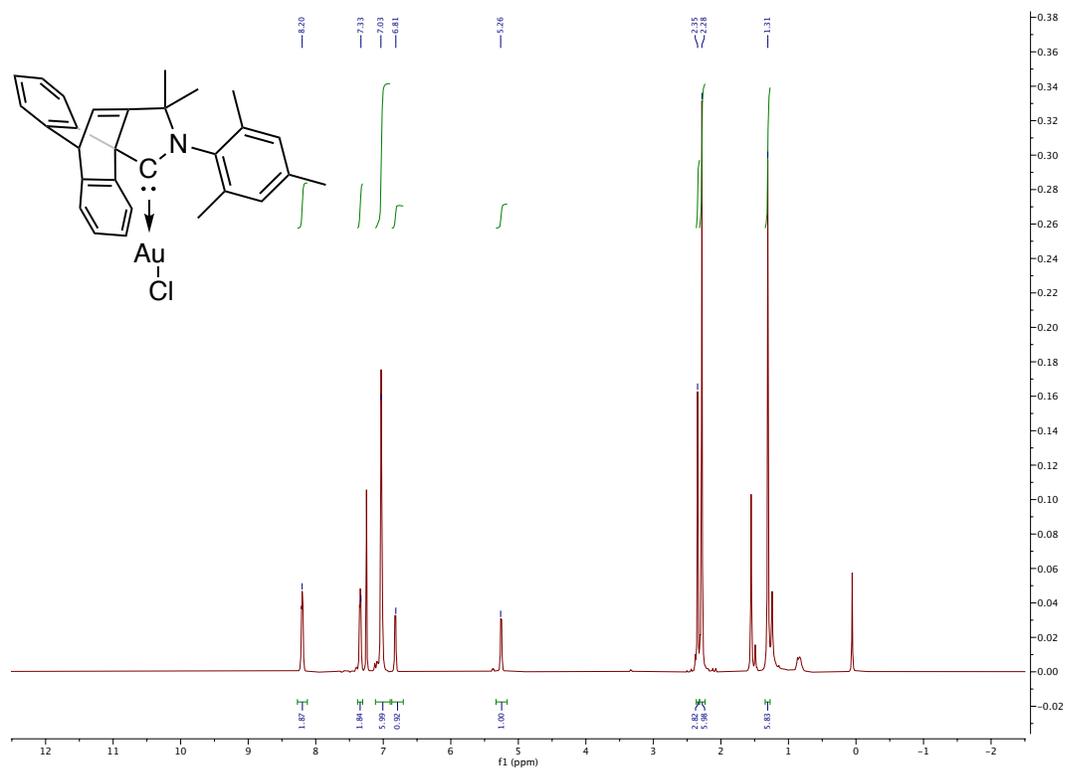
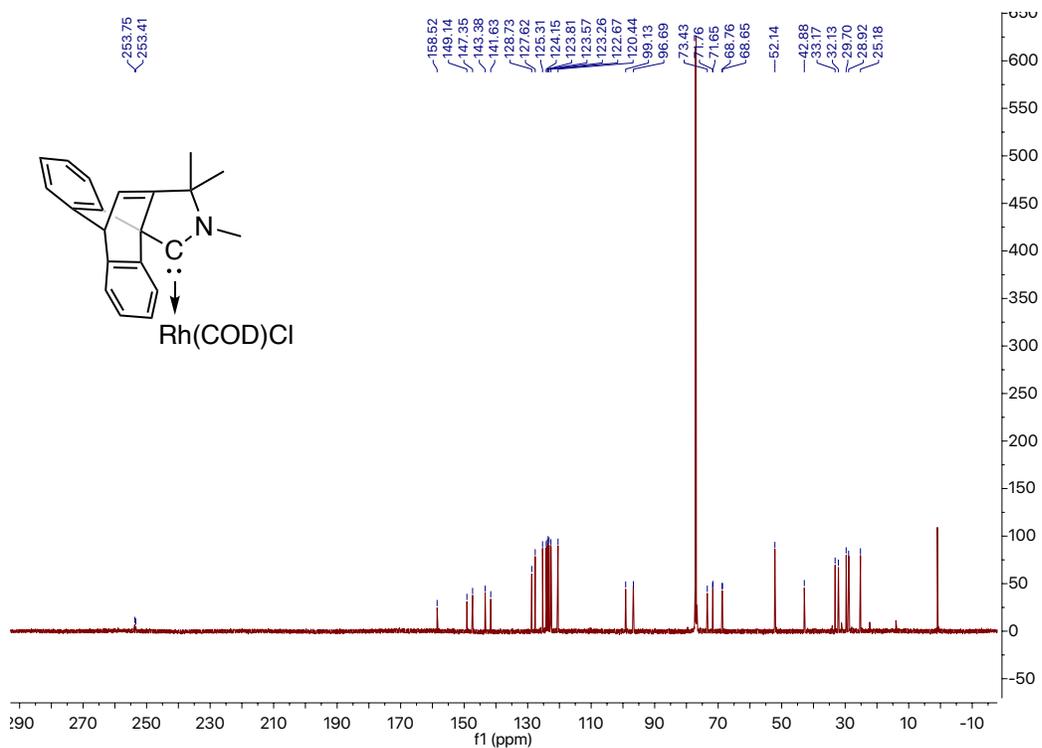
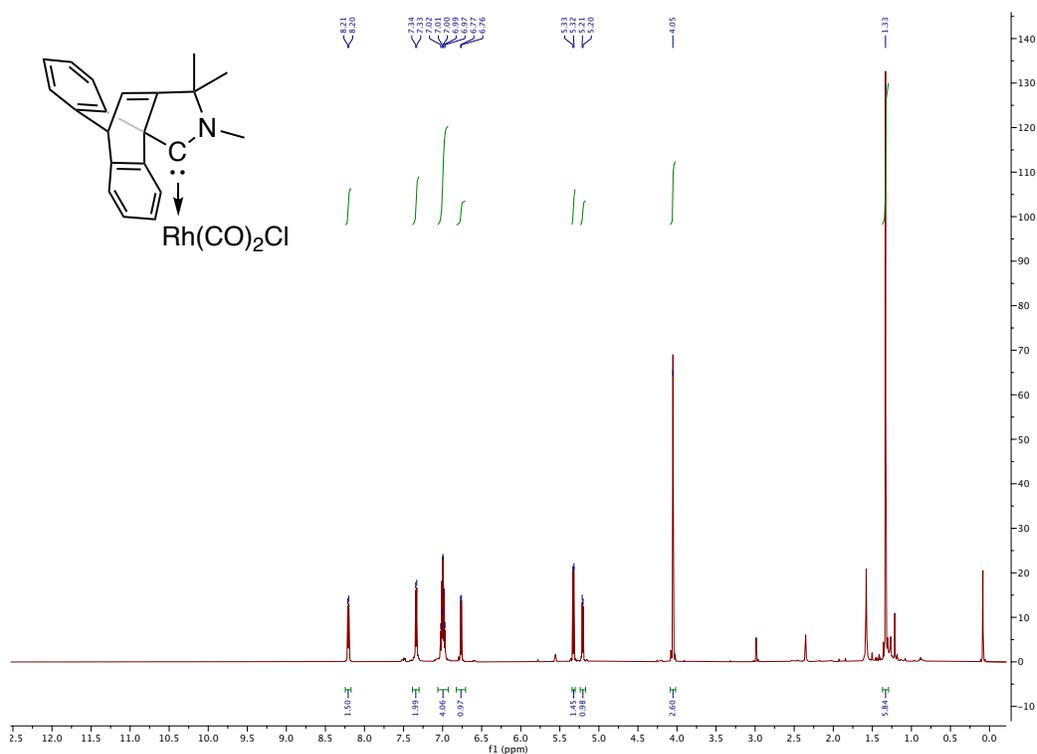


Figure S56:  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) Au3d

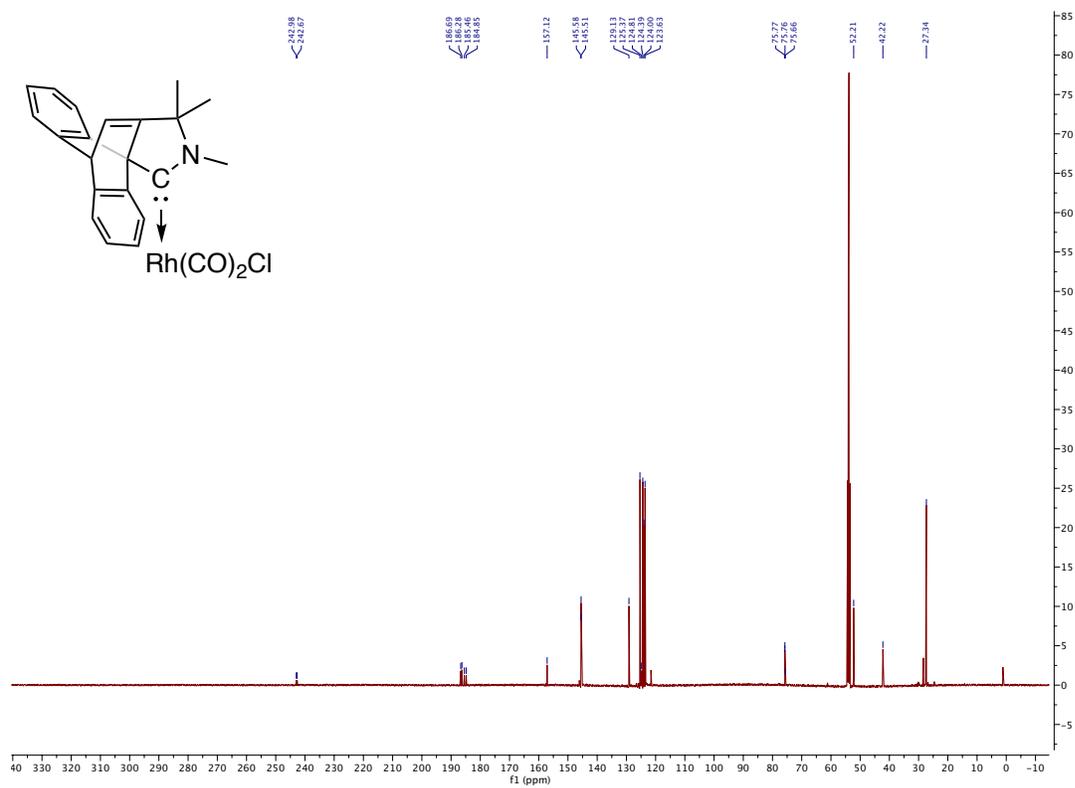




**Figure S59:  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ ) Carb2cRh(COD)Cl**



**Figure S60:  $^1\text{H}$  NMR (500 MHz,  $\text{CD}_2\text{Cl}_2$ ) Carb2cRh(CO) $_2$ Cl**

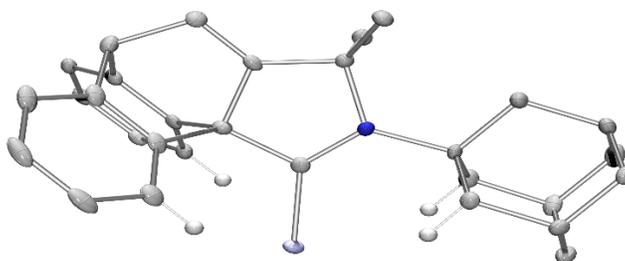


**Figure S61:**  $^{13}\text{C}$  NMR (126 MHz,  $\text{CD}_2\text{Cl}_2$ ) Carb2cRh(CO) $_2$ Cl

#### 4. X-ray Crystallographic Data

Crystallographic data for **Se2a** (CCDC: 2170658), **Se3a** (CCDC: 2170659), **Cu2b** (CCDC: 2170655), **Au2b** (CCDC: 2170657), and **Au3d** (CCDC: 2170656) can be obtained free of charge from [www.ccdc.cam.ac.uk/structures/](http://www.ccdc.cam.ac.uk/structures/)

#### Crystal data and structure refinement for Se2a:

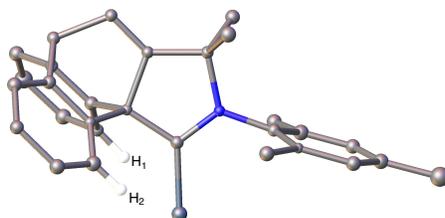


**Table S1:** Crystal data and structure refinement for **Se2a**.

CCDC	<b>2170658</b>	
Empirical formula	C <sub>30</sub> H <sub>31</sub> N Se	
Formula weight	484.52	
Temperature	100.00 K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	P2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub>	
Unit cell dimensions	a = 9.8164(7) Å	α = 90°.
	b = 10.6281(8) Å	β = 90°.
	c = 21.1616(15) Å	γ = 90°.
Volume	2207.8(3) Å <sup>3</sup>	
Z	4	
Density (calculated)	1.458 Mg/m <sup>3</sup>	
Absorption coefficient	1.720 mm <sup>-1</sup>	
F(000)	1008	
Crystal size	0.21 x 0.2 x 0.15 mm <sup>3</sup>	
Theta range for data collection	1.925 to 25.481°.	
Index ranges	-11 ≤ h ≤ 11, -12 ≤ k ≤ 12, -18 ≤ l ≤ 25	
Reflections collected	24772	
Independent reflections	4077 [R(int) = 0.0545]	
Completeness to theta = 25.242°	100.0 %	
Absorption correction	Semi-empirical from equivalents	

Max. and min. transmission	0.6875 and 0.6293
Refinement method	Full-matrix least-squares on F <sup>2</sup>
Data / restraints / parameters	4077 / 0 / 292
Goodness-of-fit on F <sup>2</sup>	1.047
Final R indices [I>2sigma(I)]	R1 = 0.0223, wR2 = 0.0586
R indices (all data)	R1 = 0.0231, wR2 = 0.0589
Absolute structure parameter	0.055(9)
Extinction coefficient	n/a
Largest diff. peak and hole	0.306 and -0.215 e.Å <sup>-3</sup>

Crystal data and structure refinement for Se3d:

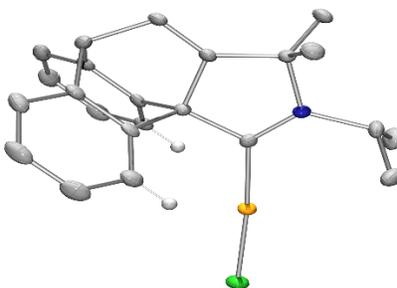


**Table S2:** Crystal data and structure refinement for Se3d.

CCDC	<b>2170659</b>	
Empirical formula	C <sub>29</sub> H <sub>27</sub> N Se	
Formula weight	468.47	
Temperature	100.00 K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	Pnma	
Unit cell dimensions	a = 14.5039(11) Å	α = 90°.
	b = 10.7587(9) Å	β = 90°.
	c = 14.0722(11) Å	γ = 90°.
Volume	2195.9(3) Å <sup>3</sup>	
Z	4	
Density (calculated)	1.417 Mg/m <sup>3</sup>	
Absorption coefficient	1.727 mm <sup>-1</sup>	
F(000)	968	
Crystal size	0.15 x 0.12 x 0.08 mm <sup>3</sup>	
Theta range for data collection	2.016 to 25.435°.	
Index ranges	-17 ≤ h ≤ 17, -12 ≤ k ≤ 12, -13 ≤ l ≤ 16	

Reflections collected	23073
Independent reflections	2143 [R(int) = 0.0683]
Completeness to theta = 25.242°	100.0 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.6257 and 0.4756
Refinement method	Full-matrix least-squares on F <sup>2</sup>
Data / restraints / parameters	2143 / 0 / 160
Goodness-of-fit on F <sup>2</sup>	1.064
Final R indices [I > 2sigma(I)]	R1 = 0.0418, wR2 = 0.1172
R indices (all data)	R1 = 0.0460, wR2 = 0.1211
Extinction coefficient	n/a
Largest diff. peak and hole	0.687 and -1.616 e.Å <sup>-3</sup>

Crystal data and structure refinement for Cu2b:

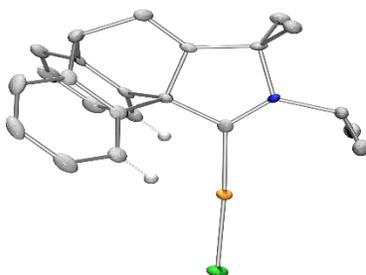


**Table S3:** Crystal data and structure refinement for **Cu2b**.

CCDC	<b>2170655</b>	
Empirical formula	C <sub>24</sub> H <sub>24</sub> Cl <sub>4</sub> Cu N	
Formula weight	531.78	
Temperature	100.0 K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	P2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub>	
Unit cell dimensions	a = 10.6000(11) Å	α = 90°.
	b = 13.4559(14) Å	β = 90°.
	c = 17.580(2) Å	γ = 90°.
Volume	2507.5(5) Å <sup>3</sup>	
Z	4	
Density (calculated)	1.409 Mg/m <sup>3</sup>	
Absorption coefficient	1.308 mm <sup>-1</sup>	

F(000)	1088
Crystal size	0.3 x 0.29 x 0.2 mm <sup>3</sup>
Theta range for data collection	1.906 to 25.384°.
Index ranges	-12<=h<=12, -16<=k<=16, -21<=l<=20
Reflections collected	23506
Independent reflections	4604 [R(int) = 0.0348]
Completeness to theta = 25.242°	100.0 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.2524 and 0.2242
Refinement method	Full-matrix least-squares on F <sup>2</sup>
Data / restraints / parameters	4604 / 0 / 276
Goodness-of-fit on F <sup>2</sup>	1.077
Final R indices [I>2sigma(I)]	R1 = 0.0295, wR2 = 0.0829
R indices (all data)	R1 = 0.0305, wR2 = 0.0836
Absolute structure parameter	0.014(16)
Extinction coefficient	n/a
Largest diff. peak and hole	0.782 and -0.655 e.Å <sup>-3</sup>

Crystal data and structure refinement for **Au2b**:

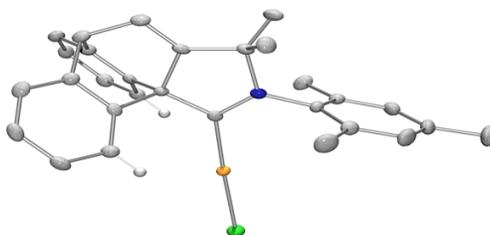


**Table S4:** Crystal data and structure refinement for **Au2b**.

CCDC	<b>2170657</b>	
Empirical formula	C <sub>24</sub> H <sub>24</sub> Au Cl <sub>4</sub> N	
Formula weight	665.21	
Temperature	100.0 K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	P2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub>	
Unit cell dimensions	a = 10.6880(10) Å	α = 90°.
	b = 13.5775(14) Å	β = 90°.

	$c = 17.3369(18) \text{ \AA}$	$\gamma = 90^\circ$ .
Volume	$2515.9(4) \text{ \AA}^3$	
Z	4	
Density (calculated)	$1.756 \text{ Mg/m}^3$	
Absorption coefficient	$6.284 \text{ mm}^{-1}$	
F(000)	1288	
Crystal size	$0.25 \times 0.22 \times 0.09 \text{ mm}^3$	
Theta range for data collection	$2.239$ to $25.430^\circ$ .	
Index ranges	$-12 \leq h \leq 12$ , $-13 \leq k \leq 16$ , $-17 \leq l \leq 20$	
Reflections collected	19666	
Independent reflections	4615 [R(int) = 0.0331]	
Completeness to theta = $25.242^\circ$	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.4901 and 0.4201	
Refinement method	Full-matrix least-squares on $F^2$	
Data / restraints / parameters	4615 / 36 / 303	
Goodness-of-fit on $F^2$	1.055	
Final R indices [ $I > 2\sigma(I)$ ]	$R1 = 0.0194$ , $wR2 = 0.0445$	
R indices (all data)	$R1 = 0.0208$ , $wR2 = 0.0450$	
Absolute structure parameter	$-0.007(4)$	
Extinction coefficient	n/a	
Largest diff. peak and hole	$0.939$ and $-0.475 \text{ e.\AA}^{-3}$	

Crystal data and structure refinement for **Au3d**:



**Table S5:** Crystal data and structure refinement for **Au3d**.

CCDC	<b>2170656</b>
Empirical formula	$\text{C}_{30} \text{H}_{28} \text{Au} \text{Cl}_4 \text{N}$
Formula weight	741.30
Temperature	100.0 K

Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	Pbca	
Unit cell dimensions	a = 16.2539(4) Å	$\alpha = 90^\circ$ .
	b = 12.5480(3) Å	$\beta = 90^\circ$ .
	c = 27.7949(6) Å	$\gamma = 90^\circ$ .
Volume	5668.9(2) Å <sup>3</sup>	
Z	8	
Density (calculated)	1.737 Mg/m <sup>3</sup>	
Absorption coefficient	5.588 mm <sup>-1</sup>	
F(000)	2896	
Crystal size	0.43 x 0.39 x 0.25 mm <sup>3</sup>	
Theta range for data collection	1.465 to 26.440°.	
Index ranges	-17<=h<=20, -13<=k<=15, -33<=l<=34	
Reflections collected	46129	
Independent reflections	5835 [R(int) = 0.0376]	
Completeness to theta = 25.242°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.4908 and 0.4113	
Refinement method	Full-matrix least-squares on F <sup>2</sup>	
Data / restraints / parameters	5835 / 0 / 330	
Goodness-of-fit on F <sup>2</sup>	1.018	
Final R indices [I>2sigma(I)]	R1 = 0.0187, wR2 = 0.0406	
R indices (all data)	R1 = 0.0275, wR2 = 0.0438	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.515 and -0.642 e.Å <sup>-3</sup>	

## 5. Supplementary References

- (1) E. Ciganek, *J. Org. Chem.* 1980, **45**, 1497–1505.
- (2) P. Barmettler and H. J. Hansen, *Helv. Chim. Acta* 1990, **73**, 1515–1573.
- (3) E. Kumarasamy and J. Sivaguru, *Chem. Commun.* 2013, **49**, 4346–4348.
- (4) P. Lan, D. Berta, J. A. Porco, M. S. South and J. J. Parlow, *J. Org. Chem.* 2003, **68**, 9678–9686.
- (5) K. J. Rodriguez, A. M. Hanlon, C. K. Lyon, J. P. Cole, B. T. Tuten, C. A. Tooley, E. B. Berda and S. Pazicni, *Inorg. Chem.* 2016, **55**, 9493–9496.