

Supplementary Information

A tropylium annulated N-heterocyclic carbene

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This Supplementary Information file replaces that originally published on 01 July 2020. This new version corrects some inconsistencies between the main article and Supplementary Information which were noticed by a reader. This does not affect the conclusions of the article.

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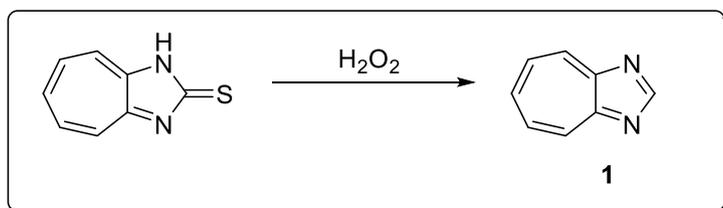
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General Information

All reactions were performed in an oxygen-free dry nitrogen atmosphere using standard Schlenk techniques. Diethyl ether and THF were dried and distilled over sodium/benzophenone, dichloromethane over CaH_2 , and *n*-hexane over sodium. The NMR spectra were recorded on a Bruker Avance III 300, a Bruker Avance DRX 500 and a Bruker Avance III 600. All ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra are referenced to the chemical shifts of residual undeuterated solvent. ^{77}Se NMR spectra were referenced to an external standard KSeCN in D_2O with specific concentration and a chemical shift of $\delta = -316.5$ ppm (4.0 mol/L) or -329.5 ppm (0.25 mol/L). Field stability of the spectrometer was high enough so that reliable spectra could be obtained for samples without an added external standard within 12 hours after calibration of the spectrometer with a standard sample. Mass spectra were recorded on a UHR-QTOF maxis 4G (HR-ESI), a MALDI-TOF Ultraflex, or a triple quadrupole mass spectrometer TSQ 7000 (EI-MS). Elemental analyses were recorded on an Elementar Vario microcube. X-ray crystal structure data were collected on a Bruker Apex Duo. IR spectra were obtained with a Shimadzu IR Affinity-1 spectrometer. Reagents such as KO^tBu and NaHMDS (2 M in THF) were purchased from Acros Organics or Sigma-Aldrich and used as received. Additional reactants such as IBX ,^[1] 1,3- propanediylbis(triphenylphosphonium) dibromide,^[2] $[\text{Rh}(\text{COD})\text{Cl}]_2$,^[3] and tritylium tetrafluoroborate^[4] were synthesized according to literature procedures.

Experimental Procedures and Analytical Data

Synthesis of Compound 1 (1,3-diazaazulene)

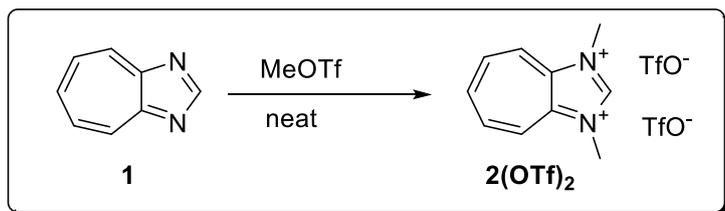


Compound **1** was synthesized according to known literature procedures.^[5-7]

First, a 100 mL Schlenk flask was charged with 2.62 g (16.14 mmol) of cyclohepta[d]imidazole-2(1H)-thione and suspended in 30 mL water. To this was added 13 mL (129 mmol) of a 30 % hydrogen peroxide solution. While heating the reaction mixture to 90 °C for 30 minutes the color changed to dark orange. After cooling to room temperature it was made neutral to slightly basic using NaHCO_3 and then extracted with methylene chloride (3 x 100 mL). The yellow solution was dried over Na_2SO_4 and freed from solvent under reduced pressure to form **1** as a yellow solid (1.27 g, 9.72 mmol, 60 %).

^1H NMR (CDCl_3 , 200 MHz): δ 9.10 (s, 1H, NCHN), 8.87-8.99 (m, 2H, CH), 8.08-8.21 (m, 3H, CH) ppm.

Synthesis of Compound 2(OTf)₂

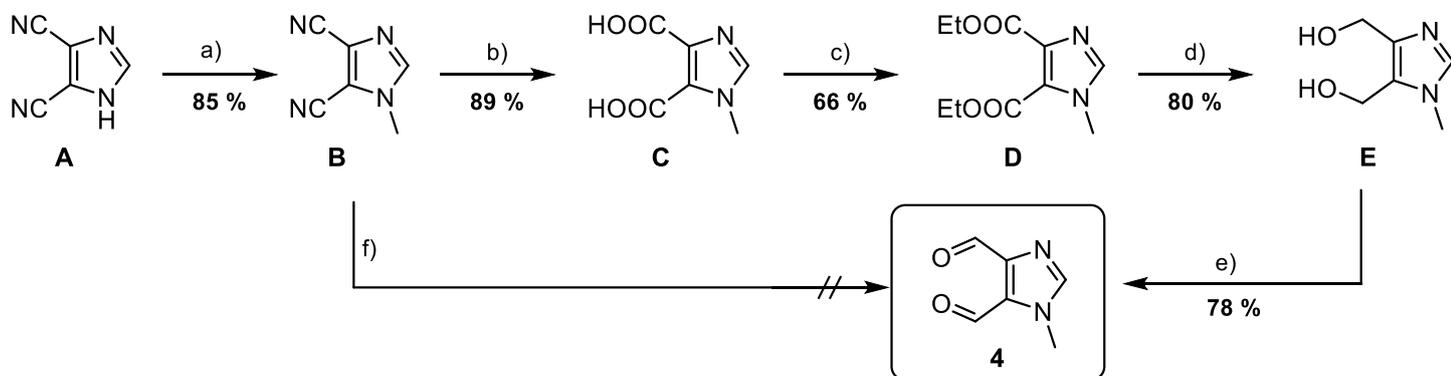


First, 49 mg (0.38 mmol) of **1** was placed in a 10 mL Schlenk flask and cooled down to 0 °C. Then, 420 μ L (3.80 mmol) of MeOTf were added slowly. The suspension was stirred for about 20 minutes at 0 °C. After removing the ice bath, stirring was continued for 120 minutes. Upon adding 7 mL of Et₂O, a grey precipitate was formed which was isolated by decanting the supernatant. The residue was washed twice with 4 mL of Et₂O and dried *in vacuo* to form **1** as a grey solid (135 mg, 0.294 mmol, 78 %).

¹H NMR (CD₃CN, 300 MHz): δ 10.19 (s, 1H, NCHN), 9.72 (dd, $J_{\text{HH}} = 10.4$ Hz, 1.2 Hz, 2H, C4H/C8H), 9.44-9.52 (m, 1H, C6H), 9.33 (td, $J_{\text{HH}} = 10.1$, 1.2 Hz, 2H, C5H/C7H), 4.45 (d, $J_{\text{HH}} = 0.6$ Hz, 6H, N-Me) ppm. ¹³C{¹H} NMR (CD₃CN, 75 MHz): δ 156.3 (s, CH), 154.7 (s, CH, NCHN), 147.8 (s, CH), 147.3 (s, C_{quart.}), 140.9 (s, CH), 121.7 (q, $J_{\text{CF}} = 320.3$ Hz, C_{quart.}, TfO⁻), 36.8 (s, N-Me), ppm. Anal. Calcd for **2(OTf)₂**: C 31.44, H 2.64, N 6.11, S 13.99 Found: C 31.62, H 2.61, N 6.36, S 13.68 %.

Synthesis of 2-methyl-3,4-diformylimidazole **4**

Potential routes toward **4** are depicted below:

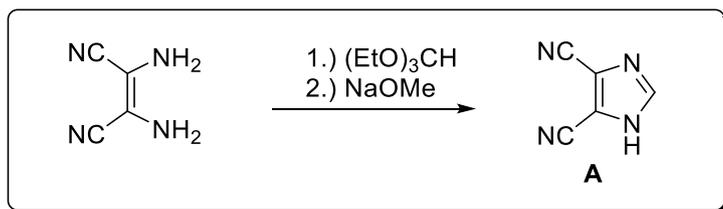


a) 1) (EtO)₃CH, PhOMe, 135 °C, 2 h, 2) NaOMe, 135 °C **b)** 1) 6N NaOH, reflux, 2 h, 2) HCl, pH 2 **c)** SOCl₂, EtOH, cat. DMF, 80 °C, 48 h **d)** 1) LiAlH₄, THF, 0 °C → RT, 2 h, 2) H₂O, NaOH **e)** IBX, DMSO, RT, 12 h **f)** 1) DIBAL-H, PhMe, 4 h, 2) MeOH, H₂O.

The reduction with DIBAL-H, as described by El Borai (route **f**), could not be reproduced in various tests under changing conditions.^[8] At best, the isolated yield using this method, or variations thereof, was a maximum of 4 %. The only difference in the reaction procedure compared to the work of El Borai was the use of DIBAL-H as a two molar solution instead of the use of supposedly pure DIBAL-H as it appears from the publication. However, even when following the instructions precisely using pure DIBAL-H instead of a solution, the yield never exceeded 11 % instead of the reported 56 %.

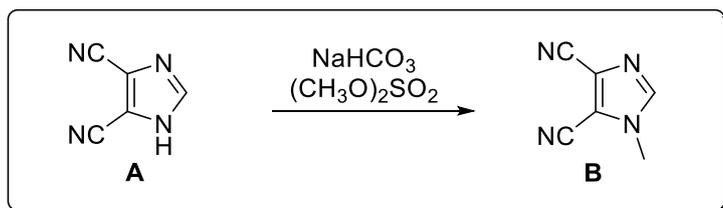
4 was finally prepared starting from dinitrile **A** via the intermediates **B**, **C**, **D** and **E** as described below.

Synthesis of Compound A



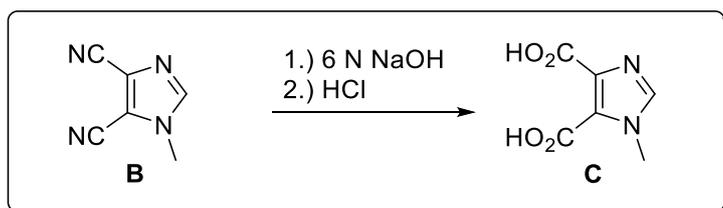
Compound **A** was synthesized according to known literature procedure.^[9]

Synthesis of Compound B



Compound **B** was synthesized according to known literature procedure.^[9]

Synthesis of Compound C



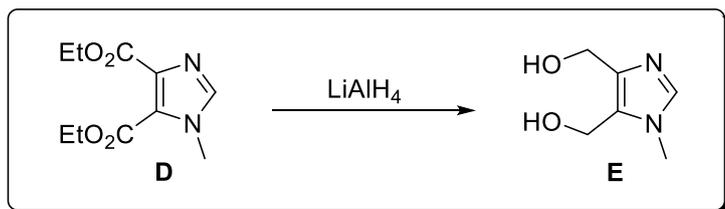
Compound **C** was synthesized according to known literature procedure.^[9]

Synthesis of Compound D



Compound **D** was synthesized according to literature.^[10]

Synthesis of Compound E



Compound **E** was synthesized by a combined method of Hay (synthesis) and Schubert (isolation and purification).^[10,11]

First, a 250 mL Schlenk flask was charged with 2.10 g (55 mmol) LiAlH_4 and suspended in 40 mL of THF. To this was added an inert solution of 5.09 g (22 mmol) of compound **D** dissolved in 10 mL of THF at 0 °C. The reaction mixture was stirred at this temperature for 30 minutes and was then allowed to warm to room temperature and stirring was continued for 5 hours. The reaction was quenched at 0 °C by adding 5 mL water, 2 mL of a 2 M NaOH solution and an additional 5 mL of water. The precipitate was collected by filtration. The residue was extracted with hot ethanol (5 x 100 mL). CO_2 was introduced into the combined ethanolic extracts until saturation. After standing overnight while stirring, the solution was evaporated to dryness *in vacuo*. The residue was extracted again with hot ethanol (3 x 100 mL) and filtered over a plug of Celite. The filtrate was freed from solvent under reduced pressure to yield compound **E** as an off white solid (2.54 g, 18 mmol, 80 %).

Spectroscopic data were consistent with those reported in the literature.^[10]

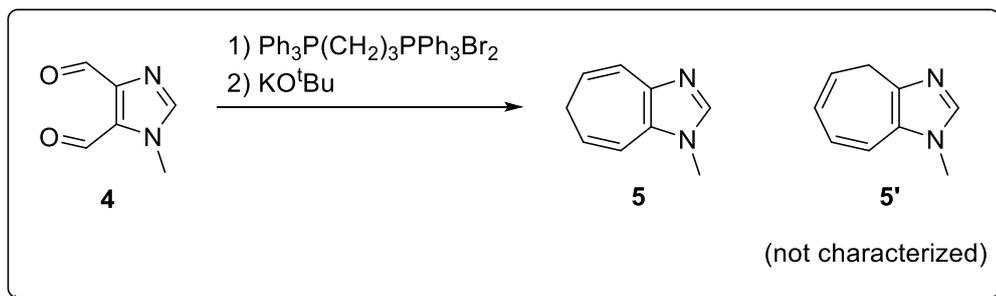
Synthesis of Compound 4



First, 6.05 g (21.6 mmol) of IBX was dissolved in 30 mL of DMSO, and 1.031 g (7.25 mmol) of **E** was added as a solid to the solution.^[12] The reaction mixture was stirred for 22 h at room temperature and 20 mL of water was added to precipitate a white solid. The suspension was filtered and the precipitate washed with dichloromethane (5 x 20 mL). The filtrate was extracted with dichloromethane (10 x 20 mL). The combined organic phases were dried over Na_2SO_4 , filtered off, and all volatile components were removed under vacuum. The crude product was further purified by column chromatography (SiO_2 , $\text{Et}_2\text{O}/\text{THF}$ (1:1), $R_f = 0.37$) to give a white solid (781 mg, 5.66 mmol, 78 %).

^1H NMR (CDCl_3 , 300 MHz): δ 10.37 (d, 1H, $J_{\text{HH}} = 0.7$ Hz, CHO), 10.02 (s, 1H, CHO), 7.64 (s, 1H, NCHN), 3.96 (d, 3H, $J_{\text{HH}} = 0.5$ Hz, Me) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 75 MHz): δ 187.8 (s, CHO), 182.4 (s, CHO), 146.7 (s, $\text{C}_{\text{quart.}}$), 143.1 (s, NCHN), 131.5 (s, $\text{C}_{\text{quart.}}$), 35.1 (s, Me) ppm. MS (EI, 70 eV): m/z 138 $[\text{M}]^+$, 110 $[\text{M}-\text{CHO}]^+$, 82 $[\text{M}-2\cdot\text{CHO}]^+$. Anal. Calcd for **4**: C 52.17, H 4.38, N 20.28 Found: C 51.62, H 4.30, N 19.59 %.

Synthesis of Compound **5** and **5'** via double Wittig reaction

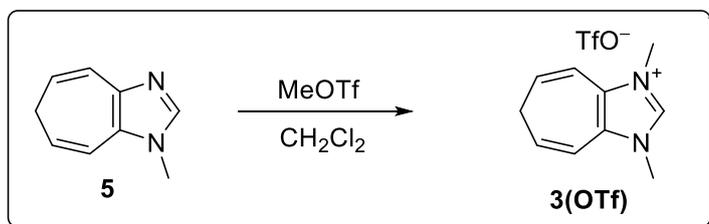


First, 4.039 g (5.56 mmol) of 1,3-Bis-triphenylphosphino-propane-dibromide was suspended in 30 mL of THF, and cooled down to $-78\text{ }^\circ\text{C}$. To this was added a suspension of 1.248 g (11.12 mmol) of KO^tBu in 10 mL THF. The reaction mixture turned yellow, and was stirred for 1 h at $-78\text{ }^\circ\text{C}$. To this mixture was added 768 mg (5.56 mmol) of **4** in 10 mL THF. The mixture was allowed to warm to room temperature and stirred for a total of 3 h, changing color from orange to blue to green. The suspension was filtered, and all volatiles were removed under vacuum. The oily residue was further purified by column chromatography (SiO_2 , EtOAc (100 %), $R_f = 0.2$) to give a yellowish solid (261 mg, 1.78 mmol, 32 %) of **5** and **5'** in a ratio of 91:9 as determined by $^1\text{H-NMR}$ -spectroscopy. Isomerically pure **5** can be obtained by sublimation (1×10^{-3} mbar, $40\text{ }^\circ\text{C}$) as a white crystalline solid (183 mg, 1.25 mmol, 23 %). Single crystals of **5** suitable for X-ray diffraction analysis were obtained by slow sublimation at room temperature (1×10^{-3} mbar).

$^1\text{H NMR}$ (CDCl_3 , 300 MHz): δ 7.48 (s, 1H, NCHN), 6.76 (d, 1H, $J_{\text{HH}} = 9.7$ Hz, H4/8), 6.46 (d, 1H, $J_{\text{HH}} = 9.7$ Hz, H4/8), 5.46 (dt, 1H, $J_{\text{HH}} = 9.7, 6.8$ Hz, H5/7), 5.36 (dt, 1H, $J_{\text{HH}} = 9.7, 6.7$ Hz, H5/7), 3.65 (s, 3H, Me), 2.45 (t, 2H, $J_{\text{HH}} = 6.8$ Hz, CH_2) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 75 MHz): δ 141.9 (s, $\text{C}_{\text{quart.}}$), 137.7 (s, C2), 131.3 (s, $\text{C}_{\text{quart.}}$), 124.6 (s, C5/7), 119.1 (s, C5/7), 117.1 (s, C4/8), 115.9 (s, C4/8), 31.6 (s, Me), 27.2 (s, C6) ppm. HRMS (ESI [+]) m/z 147.0922 (calcd for $\text{C}_9\text{H}_{10}\text{N}_2$ 147.0917, $[\text{M}+\text{H}]^+$). Anal. calcd for **5**: C 73.94, H 6.89, N 19.16 Found: C 74.16, H 6.99, N 19.12 %.

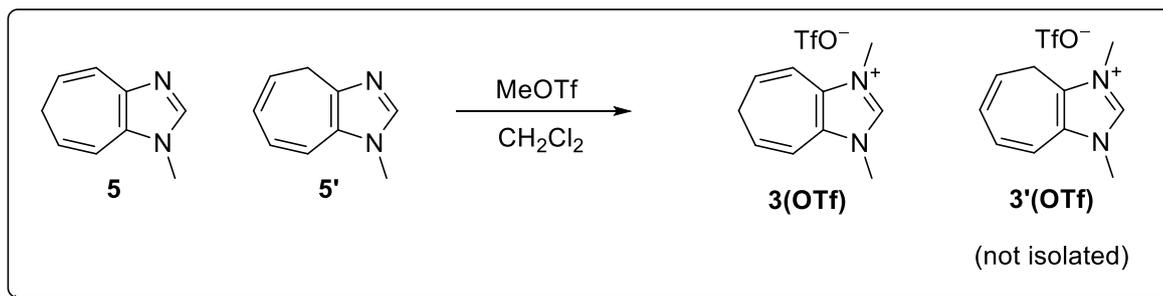
Synthesis of Compound **3(OTf)** and **3'(OTf)**

Procedure A: Starting from Compound **5**



First, 300 mg (2.05 mmol) of **5** was dissolved in 10 mL of dichloromethane, and 225 μL (2.05 mmol) of methyl triflate was added dropwise. The mixture was stirred for 18 h at room temperature, and all volatiles were removed under reduced pressure, giving **3(OTf)** as a white solid in quantitative yield (636 mg, 2.05 mmol, 100 %).

Procedure B: Starting from Compound 5 and 5'

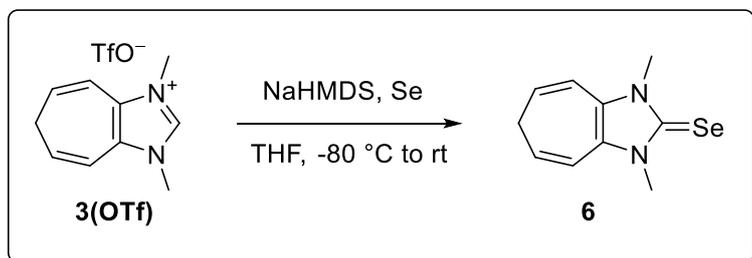


A 25 ml Schlenk flask was charged with 57 mg (0.39 mmol) of a mixture of **5** and **5'** and dissolved in 5 mL of methylene chloride. To this was added 49 μ L (0.43 mmol) of MeOTf and the reaction mixture was stirred overnight at room temperature. All volatiles were removed under reduced pressure. For removal of **3'(OTf)**, the residue was taken up in 1.5 mL acetonitrile and 7 mL Et₂O was added. The precipitate was isolated by centrifugation and decanting the supernatant. Further washing of the precipitate with 5 mL of Et₂O and drying *in vacuo* yielded a white solid (77 mg, 0.25 mmol, 64 %).

¹H NMR (CD₃CN, 300 MHz): δ 8.49 (s, 1H, NCHN), 6.69 (d, 2H, $J_{\text{HH}} = 9.6$ Hz, H_{4/8}), 5.80 (dt, 2H, $J_{\text{HH}} = 9.7, 6.9$ Hz, H_{5/7}), 3.82 (d, 6H, $J_{\text{HH}} = 0.5$ Hz, Me), 2.53 (t, 2H, $J_{\text{HH}} = 6.9$ Hz, CH₂) ppm. ¹³C{¹H} NMR (CD₃CN, 75 MHz): δ 136.5 (s, NCHN), 133.2 (s, C_{quart.}), 126.4 (s, C_{5/7}), 122.1 (q, $J_{\text{CF}} = 321$ Hz, CF₃), 115.7 (s, C_{4/8}), 34.5 (s, Me), 27.5 (s, CH₂) ppm. ¹⁹F{¹H} NMR (CD₃CN, 282 MHz): δ -79.4 (s, CF₃) ppm. HRMS (ESI [+]) m/z 161.1075 (calcd for C₁₁H₁₃F₃N₂O₃S 161.1073, [M]⁺). Anal. calcd for **3(OTf)**: C 42.58, H 4.22, N 9.03, S 10.33 Found: C 42.72, H 4.30, N 8.95, S 10.09 %.

General comment regarding the deprotonation of 3(OTf): deprotonation reactions of **3(OTf)** can be carried out with either KOtBu or NaHMDS as base and representative examples for both procedures are given below.

Synthesis of Compound 6

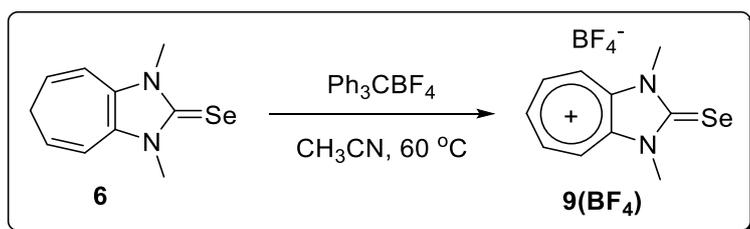


A mixture of 207 mg (667 μ mol) of **3(OTf)** and 57 mg (734 μ mol) of grey selenium powder were cooled down to -78 °C and suspended in 15 mL of THF. Then 367 μ L (734 μ mol) of 2 M NaHMDS in THF was added dropwise, and the reaction mixture was allowed to warm to room temperature over a period of 16 h. All volatile components were removed under reduced pressure and the residue was suspended in dichloromethane and filtered over a plug of Celite. Again, all volatile components were removed in vacuum and the crude product was further purified by column chromatography (SiO₂, Et₂O (100 %), R_f

= 0.8). The Product of **6** was precipitated from a concentrated solution by adding 30 mL of *n*-hexane (125 mg, 523 μ mol, 78 %).

^1H NMR (CDCl_3 , 600 MHz): δ 6.39 (d, 2H, $J_{\text{HH}} = 9.6$ Hz, H4/8), 5.38-5.31 (m, 2H, H5/7), 3.67 (s, 6H, Me), 2.32 (t, 2H, $J_{\text{HH}} = 6.9$ Hz, CH_2) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 150 Hz): δ 157.2 (s, $\text{C}_{\text{Carbene}}$), 130.7 (s, $\text{C}_{\text{quart.}}$), 118.9 (s, C5/7), 115.3 (s; C4/8), 34.0 (s, Me), 27.2 (s, CH_2) ppm. ^{77}Se NMR (CDCl_3 , 114 MHz): δ 20 (s, C=Se) ppm. HRMS (ESI [+]) m/z 240.0238 (calcd for $\text{C}_{10}\text{H}_{12}\text{N}_2\text{Se}$ 240.0166, $[\text{M}]^+$). Anal. calcd for **6**: C 50.22, H 5.06, N 11.71 Found: C 50.19, H 4.92, N 11.42 %.

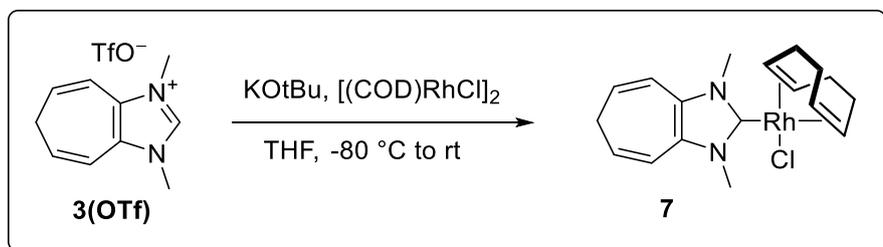
Synthesis of Compound **9**(BF_4)



First, 38 mg (159 μ mol) of **6** was dissolved in 2 mL of acetonitrile, and heated to 60 $^\circ\text{C}$. Then, 1040 μL (159 μ mol) of a solution (50 mg/mL) of tritylium tetrafluoroborate in acetonitrile was added dropwise, turning the solution red. The mixture was stirred for 17 h at 60 $^\circ\text{C}$, and concentrated under vacuum. The product of **9**(BF_4) was precipitated upon addition of 8 mL of diethyl ether. The supernatant was decanted and the product washed with diethyl ether (2×8 mL). All volatiles were removed under reduced pressure giving **9**(BF_4) as a red solid (45 mg, 138 μ mol, 87 %). The product was found to be moisture and air-stable.

^1H NMR (CD_3CN , 600 MHz): δ 8.74 (d, 2H, $J_{\text{HH}} = 10.3$ Hz, H4/8), 8.58 (t, 2H, $J_{\text{HH}} = 10.5$ Hz, C5/7), 8.47 (t, 1H, $J_{\text{HH}} = 9.9$ Hz, C6), 4.10 (s, 6H, Me), $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_3CN , 150 MHz): δ 178.8 (s, $\text{C}_{\text{Carbene}}$), 150.9 (s, $\text{C}_{\text{quart.}}$), 146.2 (s, C5/7), 128.4 (s, C4/8), 35.7 (s, Me) ppm. $^{19}\text{F}\{^1\text{H}\}$ NMR (CD_3CN): δ 151.8 (s, BF_4^-) ppm. ^{77}Se (CD_3CN , 114 MHz): δ 470 (s, C=Se) ppm. HRMS (ESI [+]) m/z 240.0238 (calcd for $\text{C}_{10}\text{H}_{11}\text{N}_2\text{Se}$ 239.0082, $[\text{M}]^+$). Anal. calcd for **9**(BF_4): C 36.96, H 3.41, N 8.62 Found: C 37.19, H 3.44, N 8.22 %.

Synthesis of Compound **7**

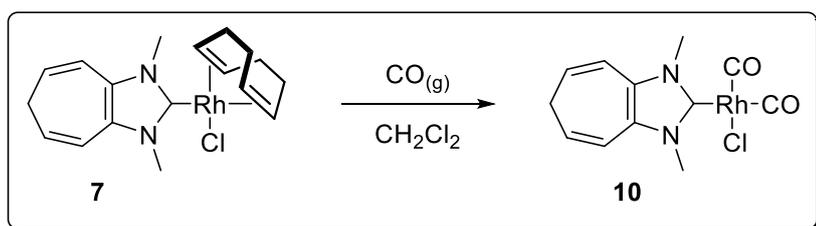


A mixture of 210 mg (677 μ mol) of **3**(OTf), 167 mg (338 μ mol) of $[\text{Rh}(\text{COD})\text{Cl}]_2$, and 84 mg (745 μ mol) of KO^tBu was cooled down to -78 $^\circ\text{C}$, and then 15 mL of THF was added. The reaction mixture was allowed to warm slowly to room temperature and then stirred for another 18 h at that temperature. All volatile components were removed under reduced pressure, and the residue was suspended in

dichloromethane and filtered over a plug of Celite. The solution was concentrated under vacuum and the yellow solid of **7** was precipitated by adding 30 mL of *n*-hexane (255 mg, 627 μ mol, 93 %).

^1H NMR (CD_3Cl , 500 MHz): δ 6.43 (d, 2H, $J_{\text{HH}} = 9.6$ Hz, H4/8), 5.27-5.34 (m, 2H, H5/7), 5.02-5.08 (m, 2H, COD_{ol}), 4.10 (s, 6H, Me), 3.29-3.35 (m, 2H, COD_{ol}), 2.38-2.47 (m, 4H, COD_{al}), 2.36 (t, 2H, $J_{\text{HH}} = 6.9$ Hz, CH_2), 1.92-1.99 (m, 4H, COD_{al}) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_3CN , 125 MHz): δ 185.1 (d, $J_{\text{CRh}} = 51.1$ Hz, $\text{C}_{\text{Carbene}}$), 134.0 (s, C_{quart}), 118.8 (s, C5/7), 116.7 (s, C4/8), 99.0 (d, $J_{\text{CRh}} = 6.9$ Hz, COD_{ol}), 69.2 (d, $J_{\text{CRh}} = 14.3$ Hz, COD_{ol}), 35.9 (s, Me), 33.7 (s, COD_{al}), 29.6 (s, COD_{al}), 28.0 (s, C6) ppm. MS (MALDI, CH_2Cl_2): m/z 371.096 $[\text{M}-\text{Cl}]^+$. Anal. Calcd for **7**: C 53.15, H 5.95, N 6.89 Found: C 53.23, H 5.90, N 6.38 %.

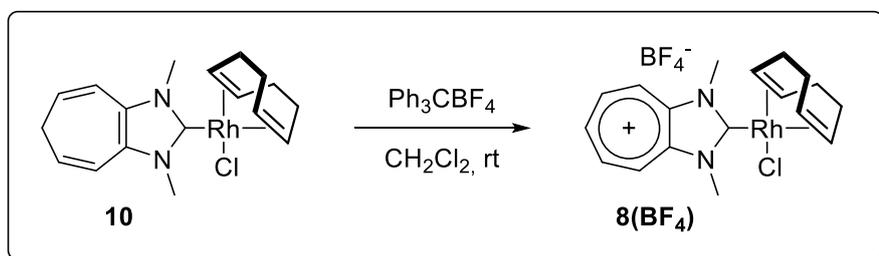
Synthesis of Compound 10



First, 40.0 mg (120 μ mol) of **7** was dissolved in 1 mL of dichloromethane and stirred for several minutes with a continuous flow of carbon monoxide to form **10**. The yield was quantitative according to NMR spectra.

^1H NMR (CDCl_3 , 300 MHz): δ 6.50 (d, 2H, $J_{\text{HH}} = 9.6$ Hz, C4/8), 5.63-5.54 (m, COD_{free}), 5.46 (dt, 2H, $J_{\text{HH}} = 9.6, 6.9$ Hz, C5/7), 3.93 (s, 6H, Me), 2.50-2.40 (m, 2H, CH_2), 2.40-2.32 (m, COD_{free}) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 75 MHz): δ 185.5 (d, $J_{\text{CRh}} = 54$ Hz, CO), 182.7 (d, $J_{\text{CRh}} = 74$ Hz, $\text{C}_{\text{Carbene}}$), 174.9 (d, $J_{\text{CRh}} = 44$ Hz, CO), 133.3 (s, C_{quart}), 128.8 (s, COD_{free}), 120.0 (s, C5/7), 115.6 (s, C4/8), 36.0 (s, Me), 28.1 (s, COD_{free}), 27.2 (s, CH_2) ppm. IR (CH_2Cl_2): $\tilde{\nu}$ 2082 (s, ν_{CO}), 2001 (s, ν_{CO}) $[\text{cm}^{-1}]$. MS (MALDI, CH_3CN): m/z 263 $[\text{M}-2\cdot\text{CO}-\text{Cl}]^+$.

Synthesis of Compound 8(BF₄)

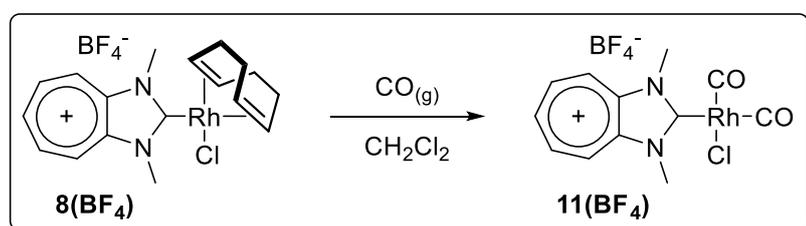


First, 30 mg (79 μ mol) of **7** was dissolved in 1 mL of dichloromethane, then, 480 μ L (74 μ mol) of a solution of tritylium tetrafluoroborate in dichloromethane (50 mg/mL) was added dropwise at room temperature, turning the solution red. The mixture was stirred for 30 min at that temperature. While vigorously stirring, 8 mL of diethyl ether was added at once, precipitating an orange solid. The suspension was transferred into a centrifuge vial for centrifugation. The supernatant was decanted and

the precipitate washed with diethyl ether (2 × 8 mL). All volatiles were removed under reduced pressure giving **8**(BF₄) as a moisture and air-stable orange to red solid (30 mg, 61 μmol, 77 %).

¹H NMR (CD₃CN, 300 MHz): δ 8.98-8.89 (m, 2H, Trop.), 8.86-8.77 (m, 3H, Trop.), 5.34-5.24 (m, 2H, COD_{ol.}), 4.71 (s, 6H, Me), 3.71-3.61 (m, 2H, COD_{ol.}), 2.64-2.45 (m, 4H, COD_{al.}), 2.24-2.12 (m, 4H, COD_{al.}) ppm. ¹³C{¹H} NMR (CD₃CN, 75 MHz): δ 149.4 (s, C_{quart.}), 147.4 (s, Trop.), 145.1 (s, Trop.), 131.1 (s, Trop.), 106.0 (d, J_{CRh} = 5.7 Hz, COD_{ol.}), 73.4 (br m, COD_{ol.} [from HMBC experiment]), 38.0 (s, Me), 33.1 (s, COD_{al.}), 29.3 (s, COD_{al.}) ppm. ¹⁹F{¹H} NMR (CD₃CN, 282 MHz): δ -151.8 (s, BF₄⁻) ppm. MS (MALDI, CH₃CN): *m/z* 370 [M-Cl]⁺, 405 [M]⁺. Anal. Calcd for **8**(BF₄): C 43.89, H 4.71, N 5.69 Found: C 43.28, H 4.87, N 5.57 %.

Synthesis of Compound **11**(BF₄)



First, 40.0 mg (0.12 mmol) of **8**(BF₄) was dissolved in 1 mL of dichloromethane and stirred for several minutes with a continuous flow of carbon monoxide to yield **11**(BF₄). The yield was quantitative according to NMR spectra.

¹H NMR (CD₃CN, 300 MHz): δ 9.29-9.21 (m, 2H, Trop.), 9.10-8.97 (m, 3H, Trop.), 5.59-5.48 (m, COD_{free}), 4.55 (s, 6H, Me), 2.36-2.31 (m, COD_{free}) ppm. IR (CH₂Cl₂) $\tilde{\nu}$: 2100 (s, ν_{CO}), 2025 (s, ν_{CO}) [cm⁻¹].

References

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- [5] T. Nozoe, T. Mukai, I. Murata, *J. Am. Chem. Soc.* **1954**, *76*, 3352–3353.
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- [7] S. Itô, J. Tsunetsugu, T. Kanno, H. Sugiyama, H. Takeshita, *Tetrahedron Lett.* **1965**, *6*, 3659–3663.
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- [9] J. F. O'Connell, P. Jonathan, W. E. Yelle, W. Wang, H. Rapoport, *Synthesis (Stuttg)*. **1988**, *20*, 767–771.
- [10] M. P. Hay, W. R. Wilson, W. A. Denny, *Tetrahedron* **2000**, *56*, 645–657.
- [11] H. Schubert, W. D. Rudolf, *Z. Chem.* **1971**, *11*, 175–176.
- [12] M. Frigerio, M. Santagostino, *Tetrahedron Lett.* **1994**, *35*, 8019–8022.

NMR Spectra

NMR Spectra of Compound 1

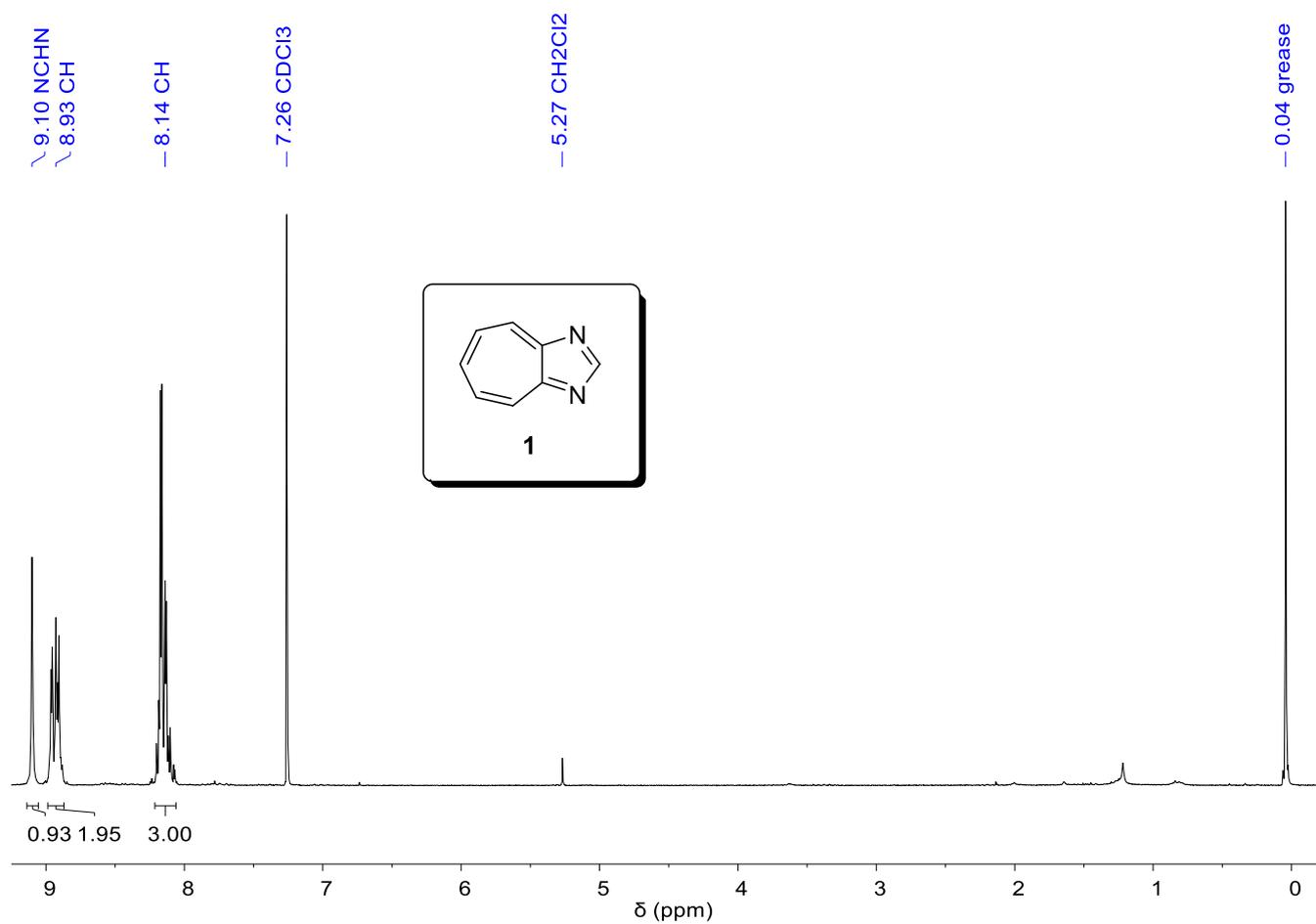


Figure S 1: ¹H NMR (200 MHz) of compound 1 in CDCl₃.

NMR Spectra of Compound 2(OTf)₂

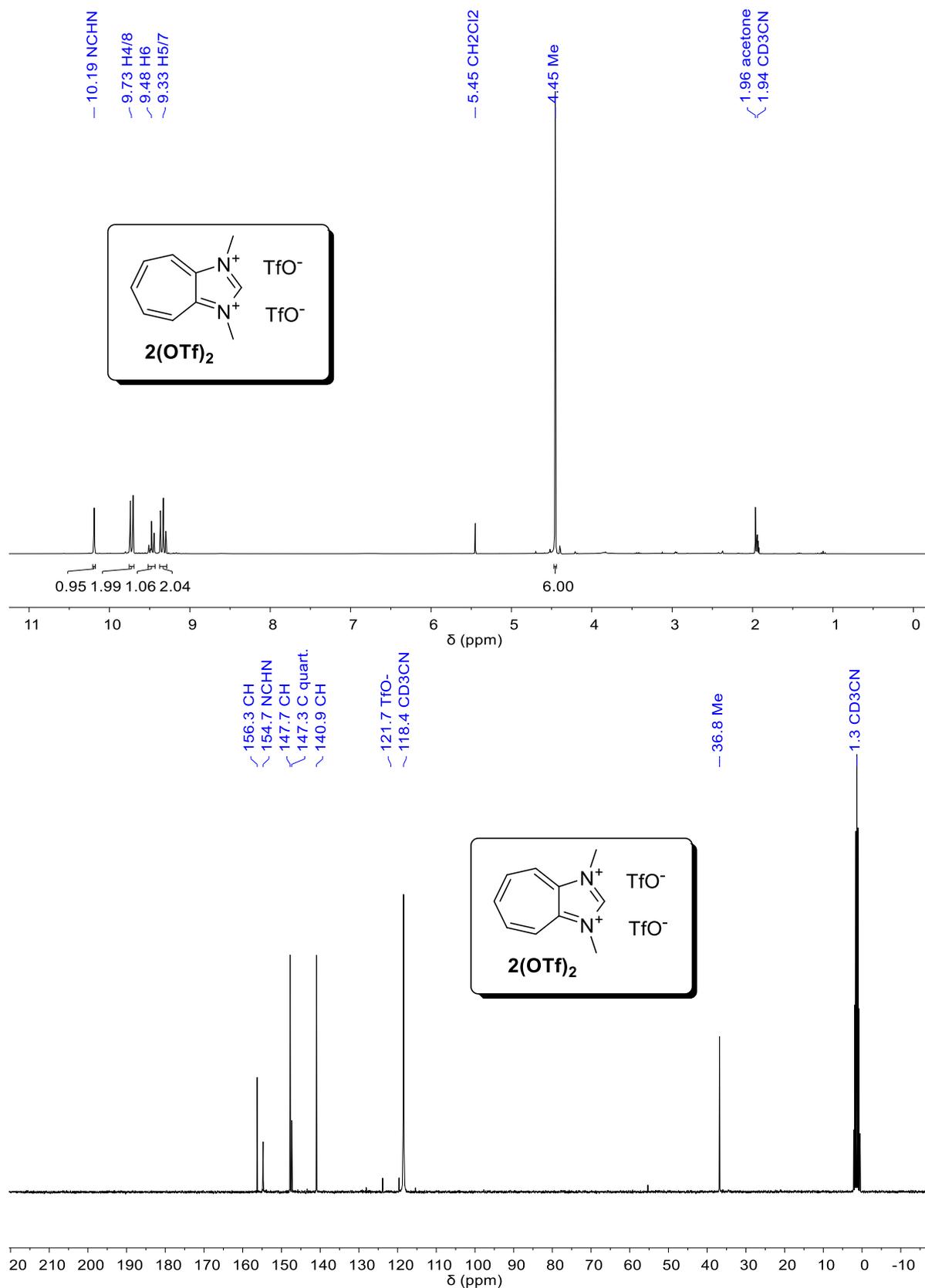


Figure S 2: ¹H NMR (300 MHz, top) and ¹³C{¹H} NMR (75 MHz, bottom) of compound 2(OTf)₂ in CD₃CN.

NMR Spectra of Compound 4

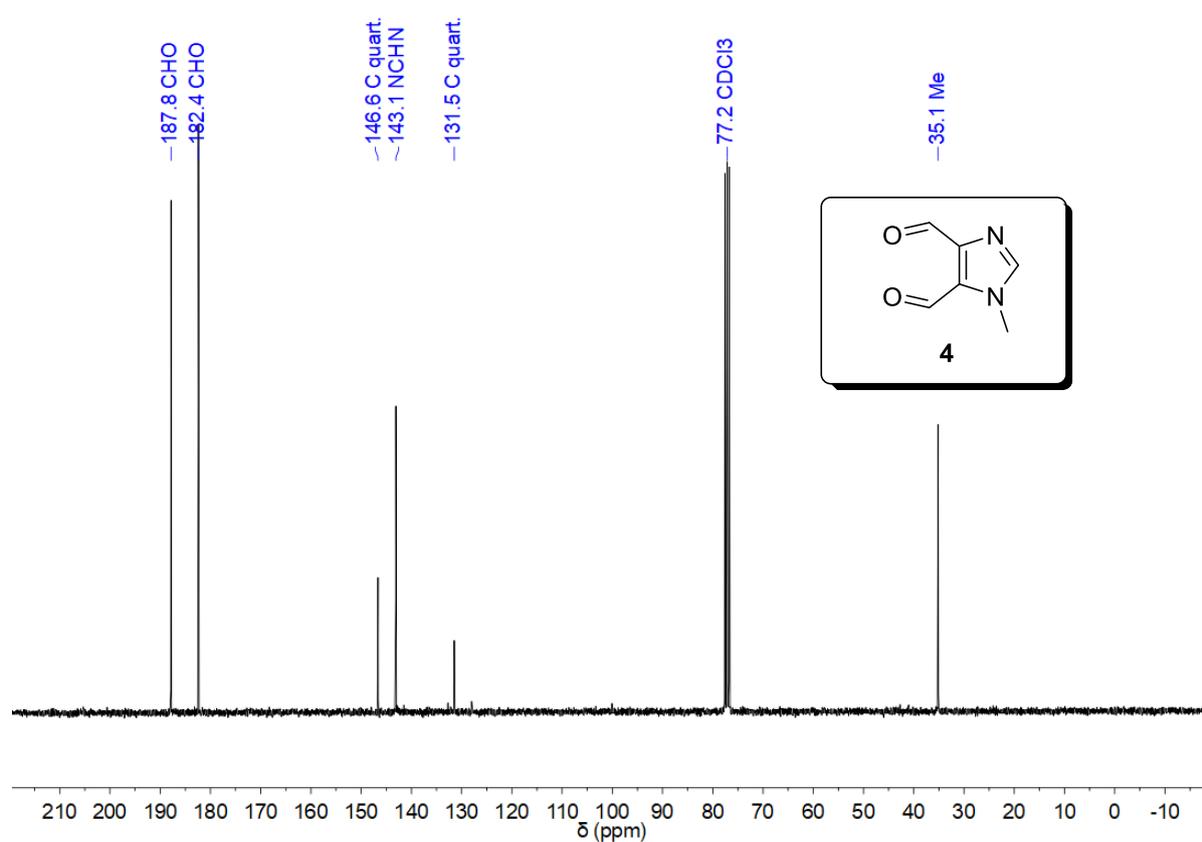
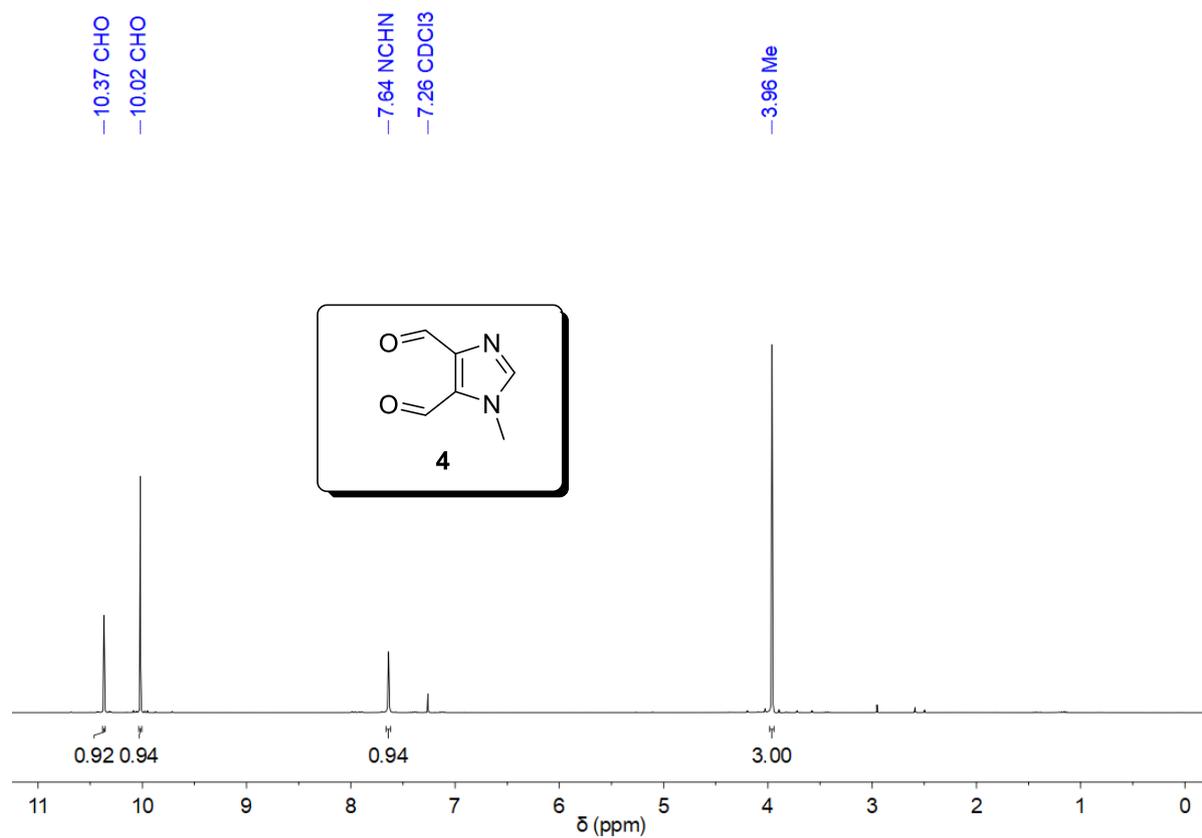


Figure S 3: ¹H NMR (300 MHz, top), ¹³C{¹H} NMR (75 MHz, bottom) of compound 4 in CDCl₃.

NMR Spectra of Compound 5

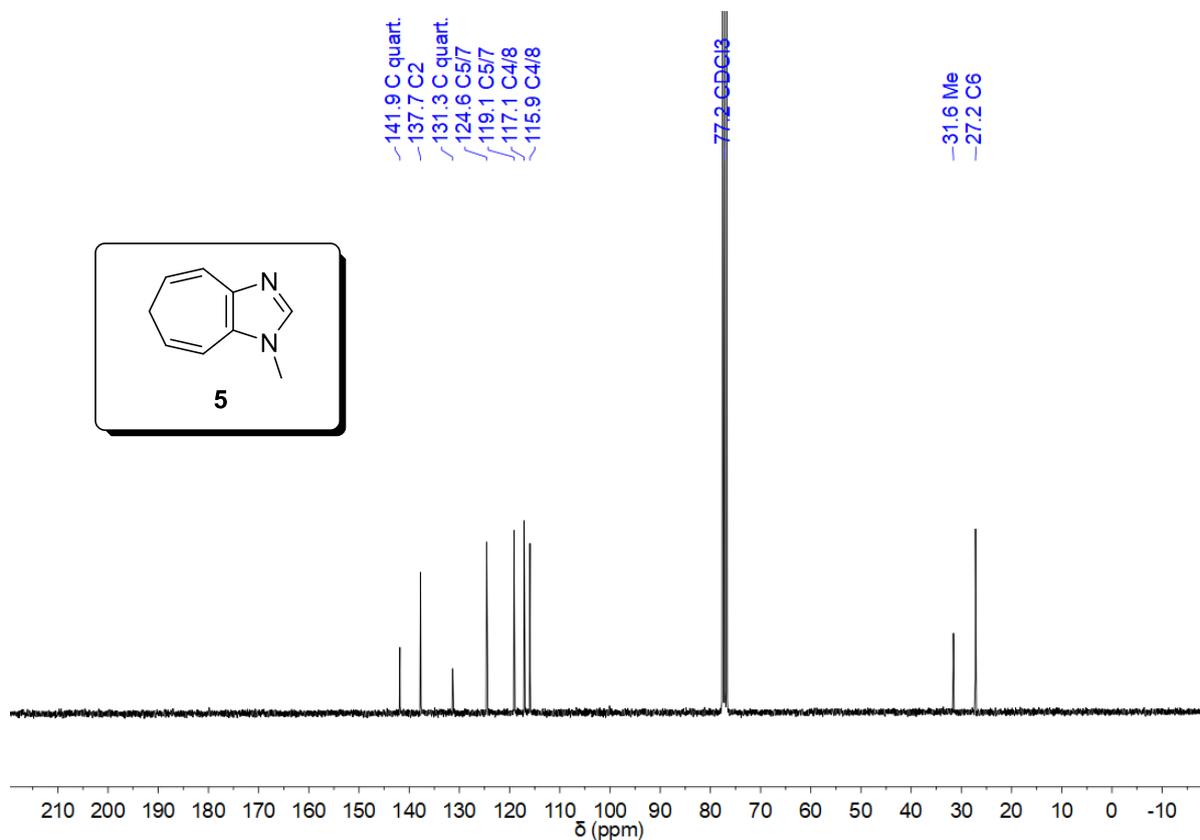
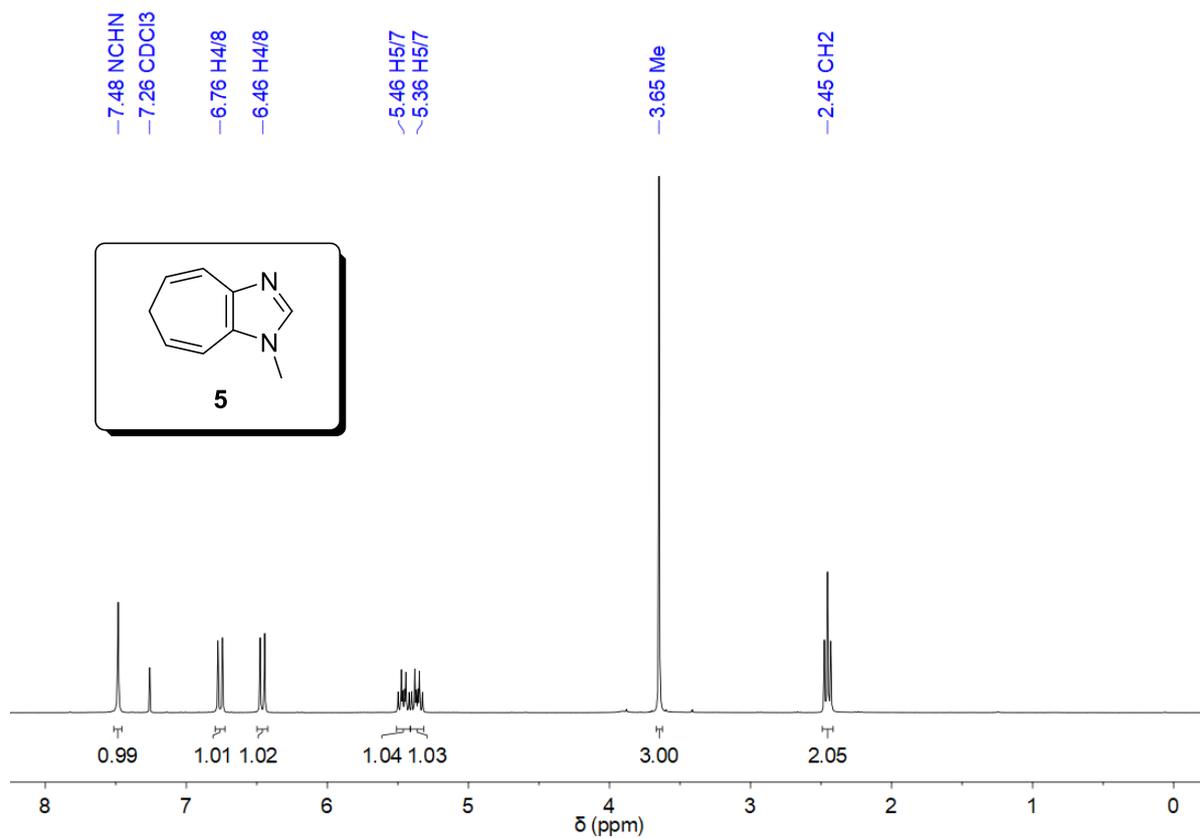


Figure S 4: ¹H NMR (300 MHz, top), ¹³C{¹H} NMR (75 MHz, bottom) of compound isomerically pure 5 in CDCl₃.

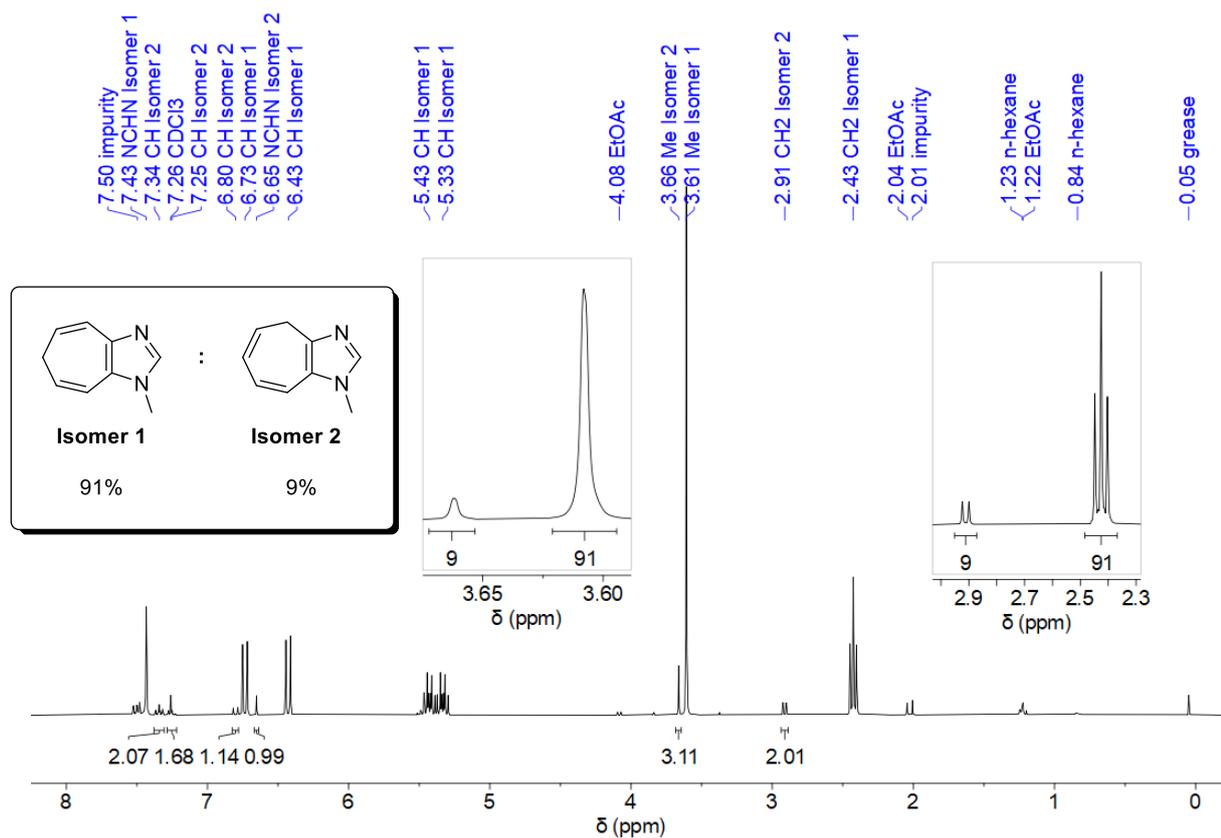


Figure S 5: ¹H NMR (300 MHz, CDCl₃) of the product mixture containing compounds 5 (Isomer 1) and 5' (Isomer 2) in a ratio of 91 : 1.

NMR Spectra of Compound 3(OTf)

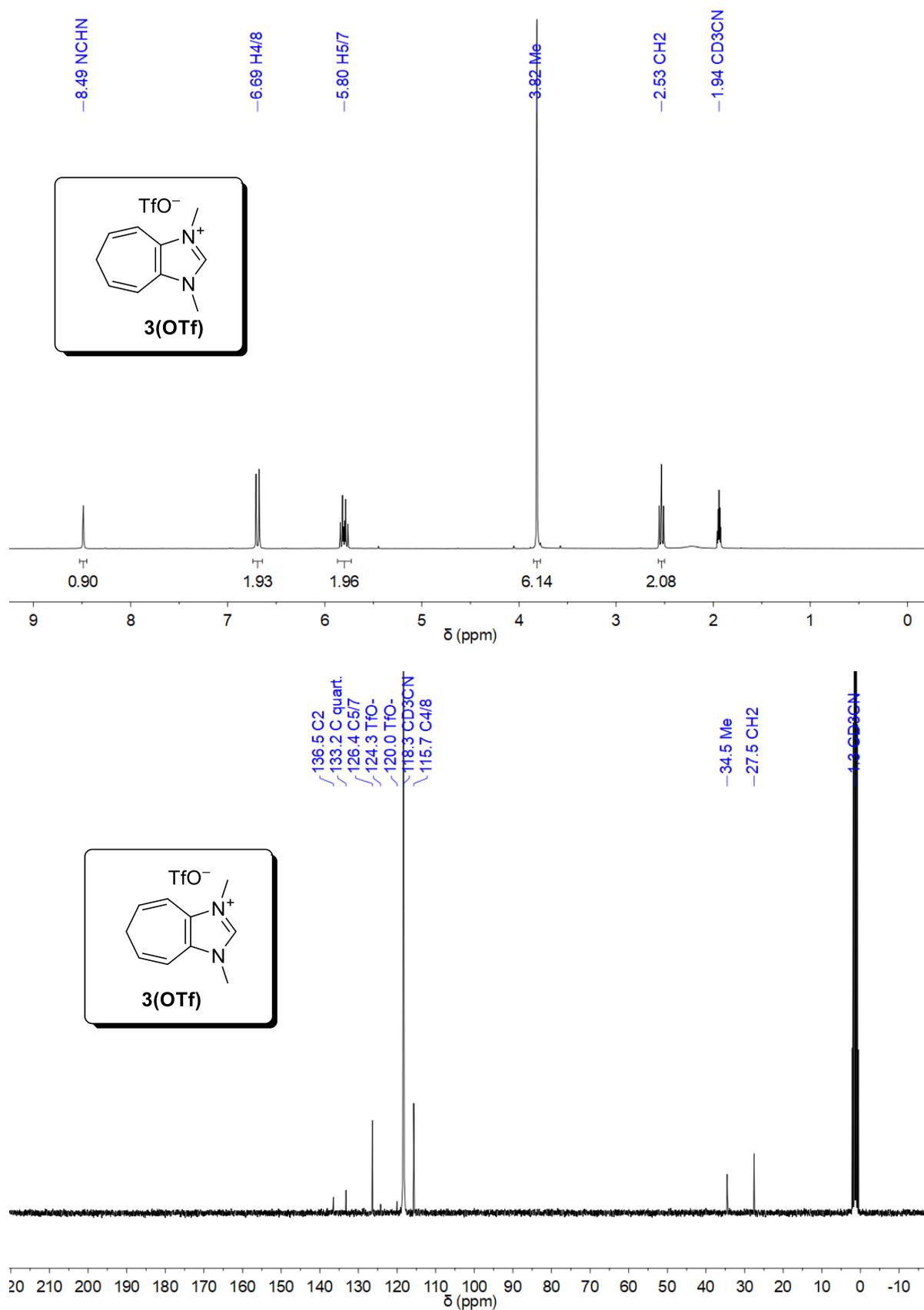


Figure S 6: ¹H NMR (300 MHz, top), ¹³C{¹H} NMR (75 MHz, bottom) of isomerically pure 3(OTf) in CD₃CN.

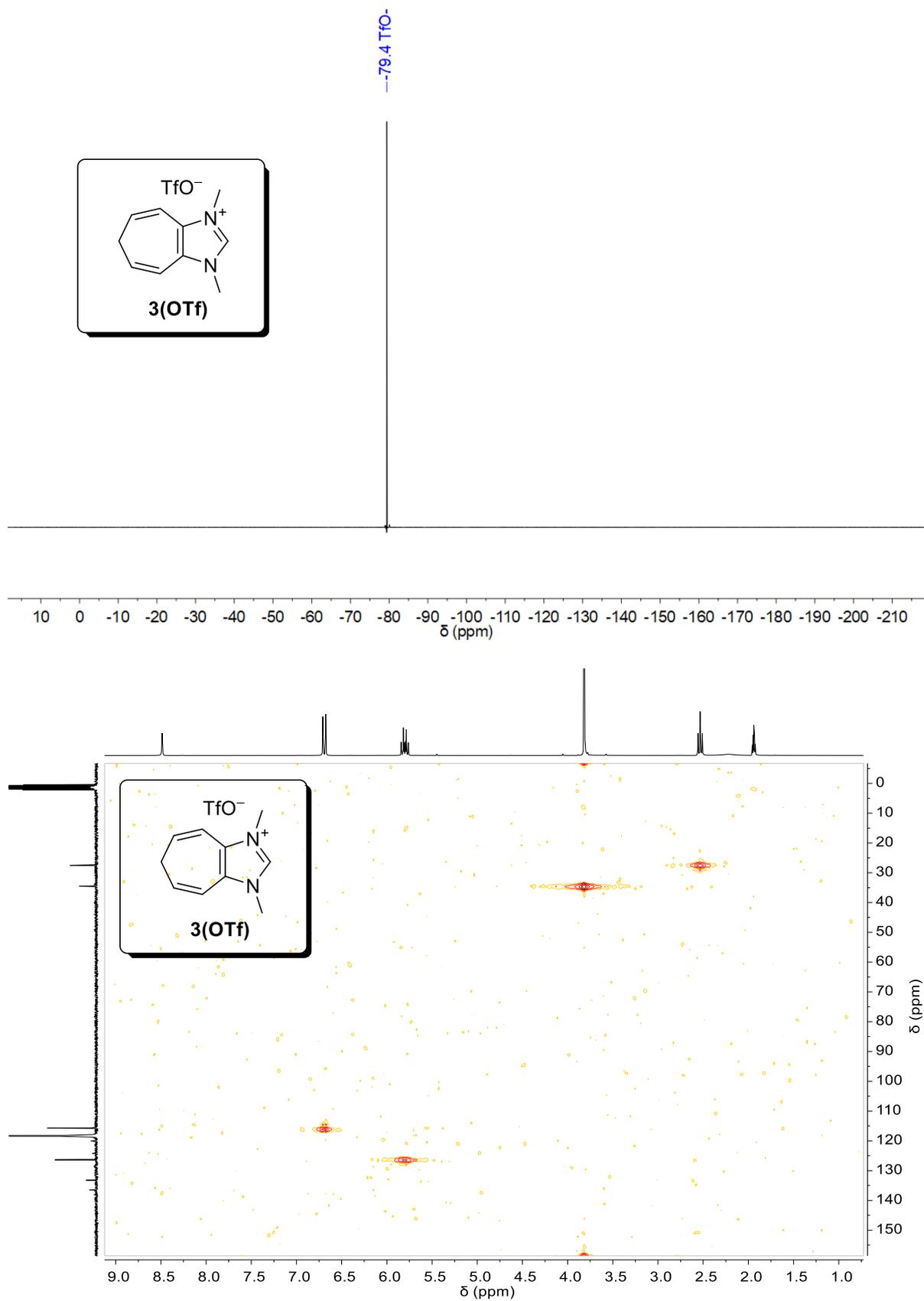


Figure S 7: $^{19}F\{^1H\}$ NMR (300 MHz, top), HSQC NMR (300 MHz, 75 MHz, bottom) of compound **3(OTf)** in CD_3CN .

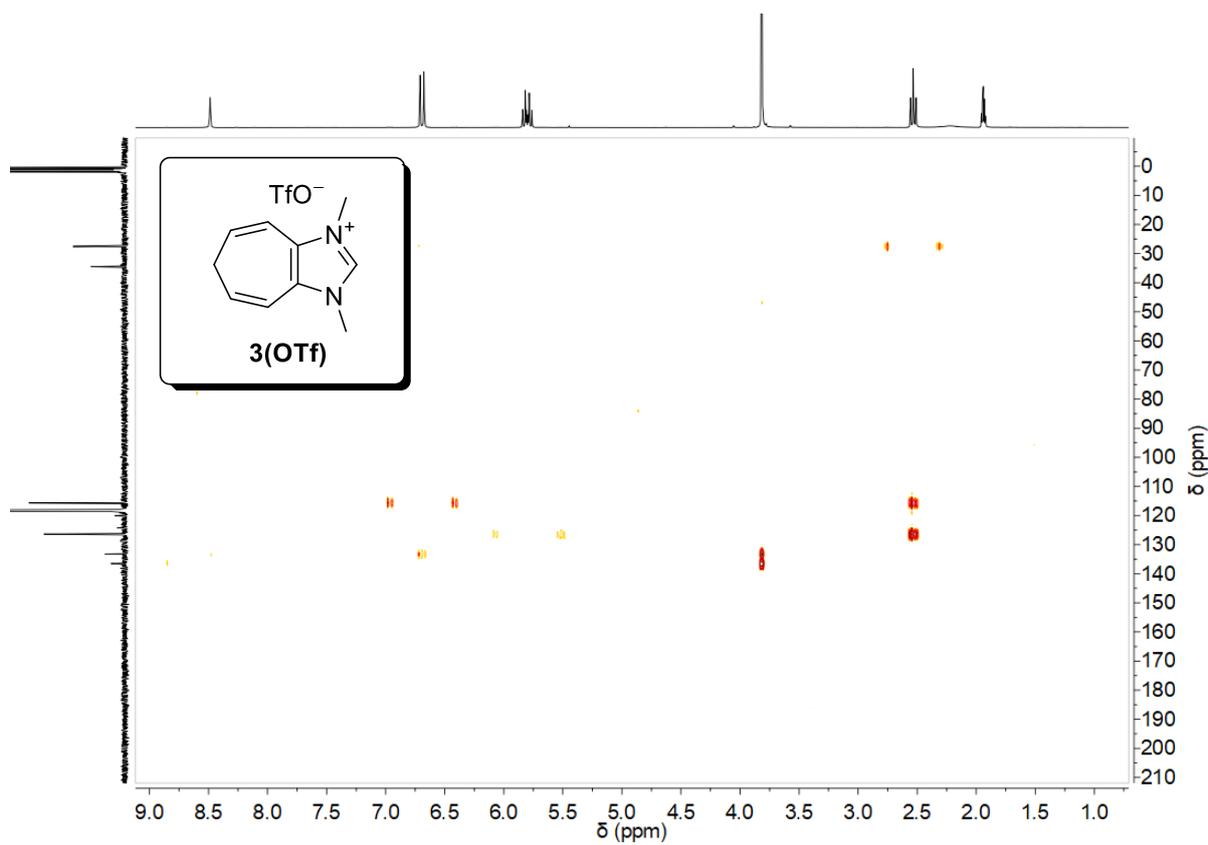


Figure S 8: HMBC NMR (300 MHz, 75 MHz) of compound **3(OTf)** in CD₃CN.

NMR Spectra of Compound 6

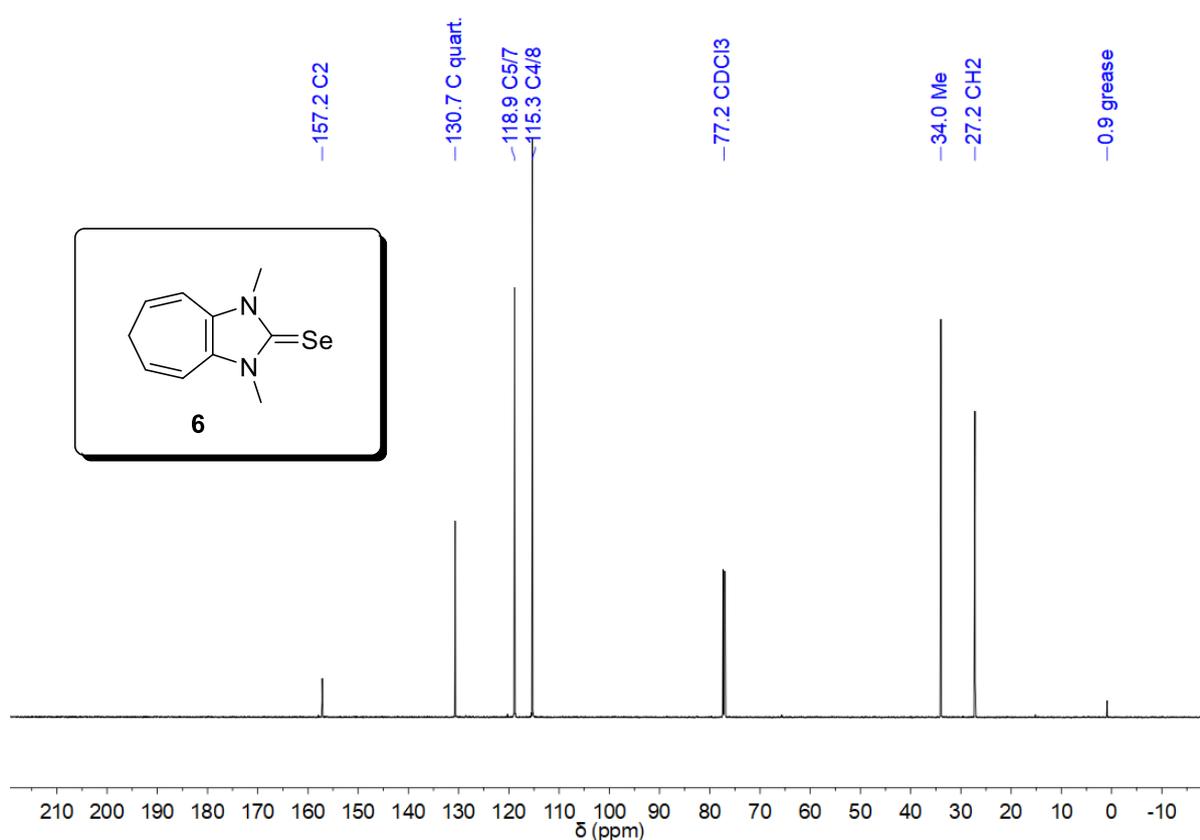
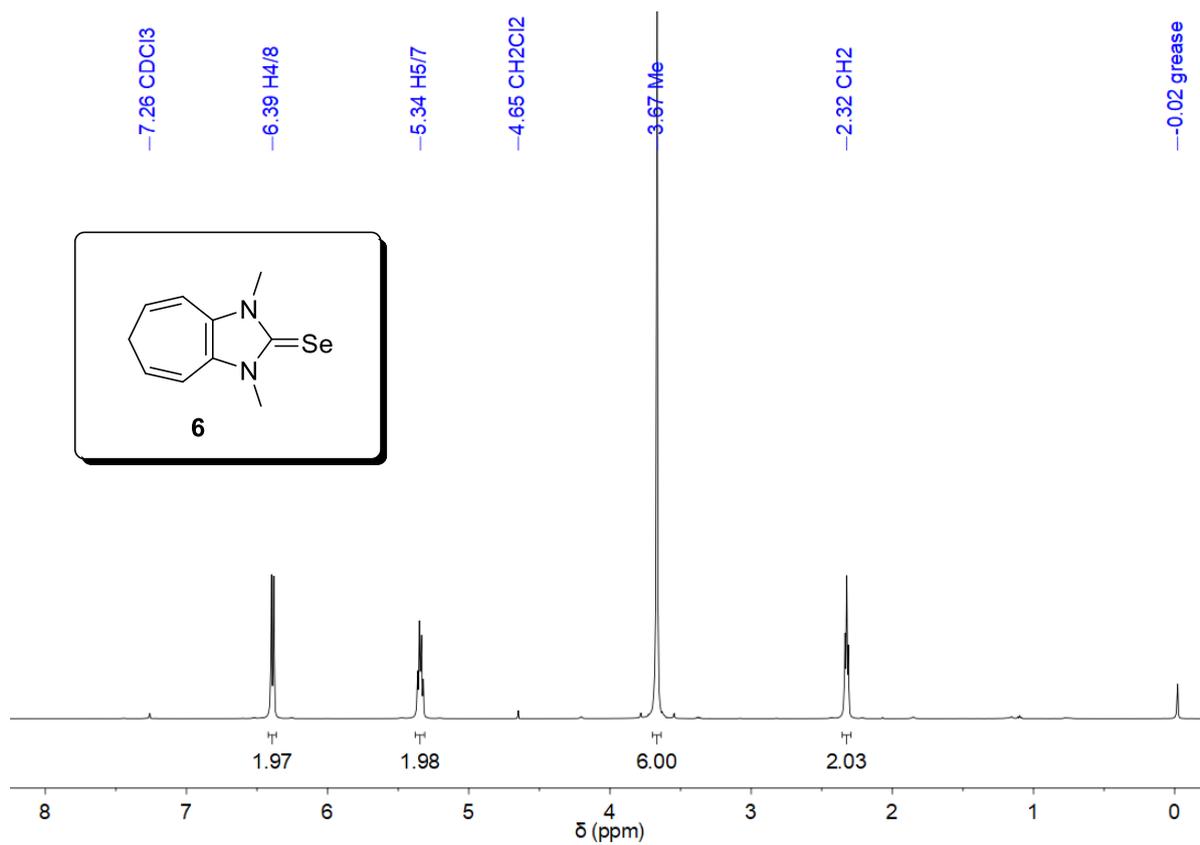


Figure S 9: ¹H NMR (600 MHz top) and ¹³C{¹H} NMR (150 MHz, bottom) of compound 6 in CDCl₃.

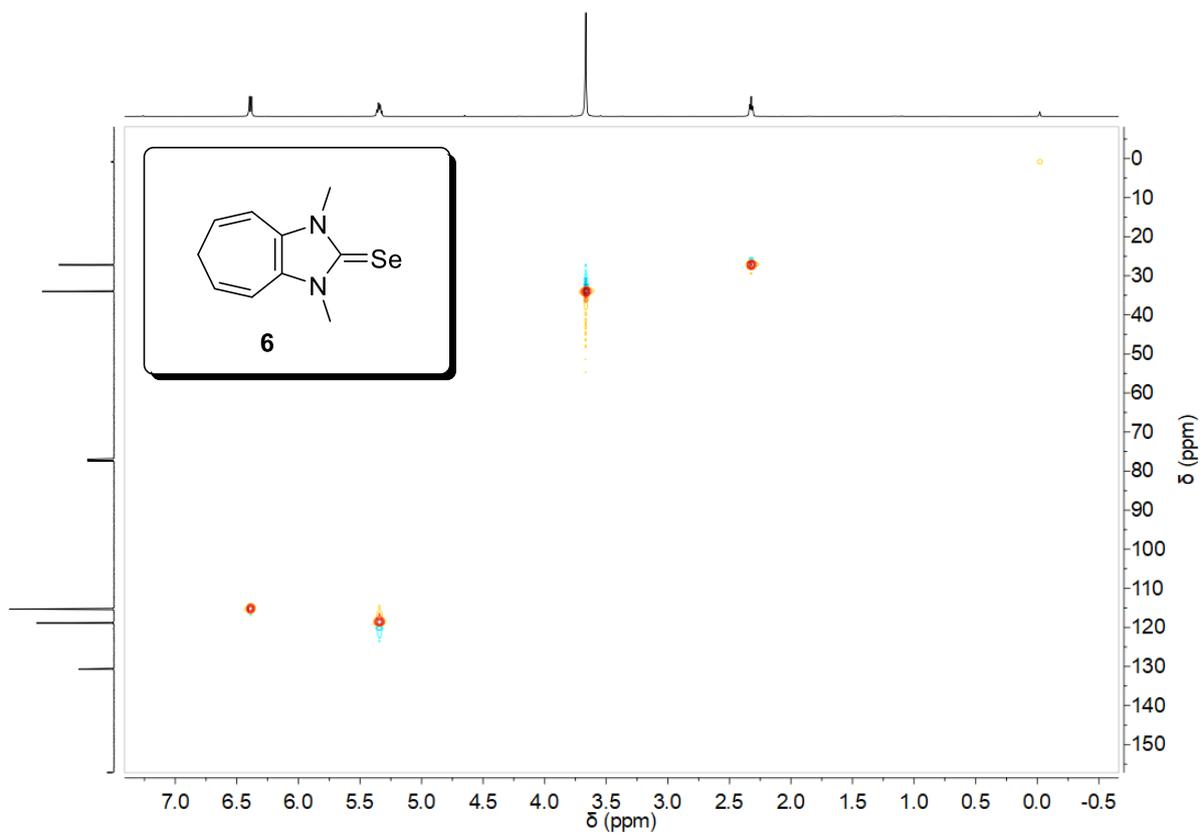
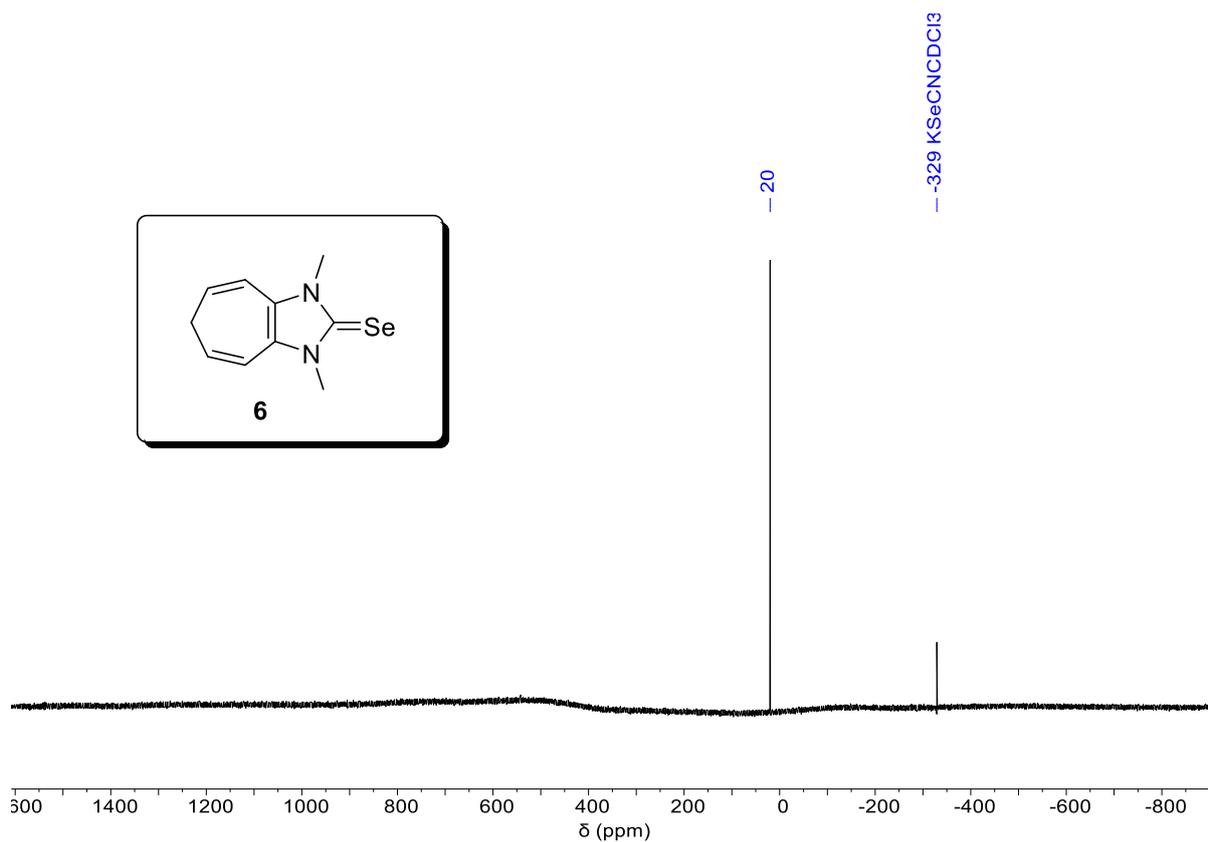


Figure S 10: ^{77}Se NMR (114 MHz top) and HSQC NMR (600 MHz, 150 MHz, bottom) of compound **6** in CDCl_3 .

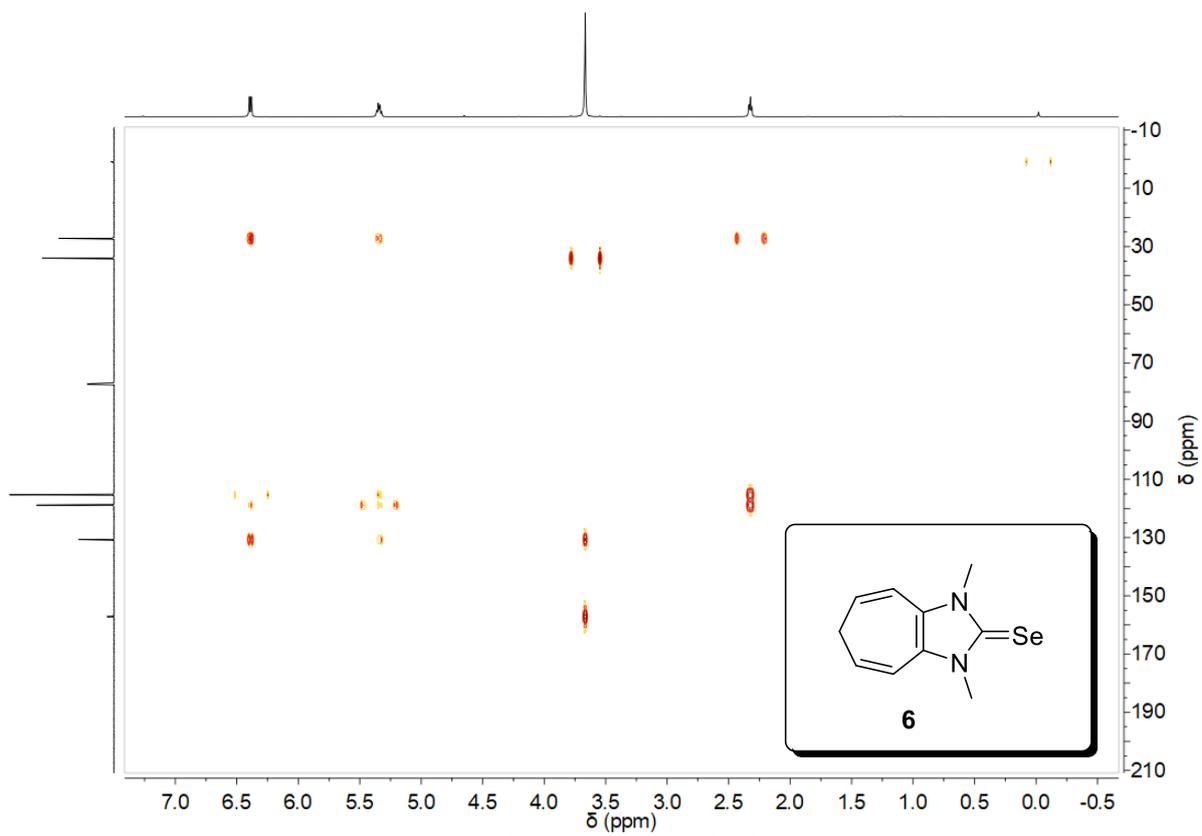


Figure S 11: HMBC NMR (600 MHz, 150 MHz) of compound **6** in CDCl₃.

NMR Spectra of Compound 9(BF₄)

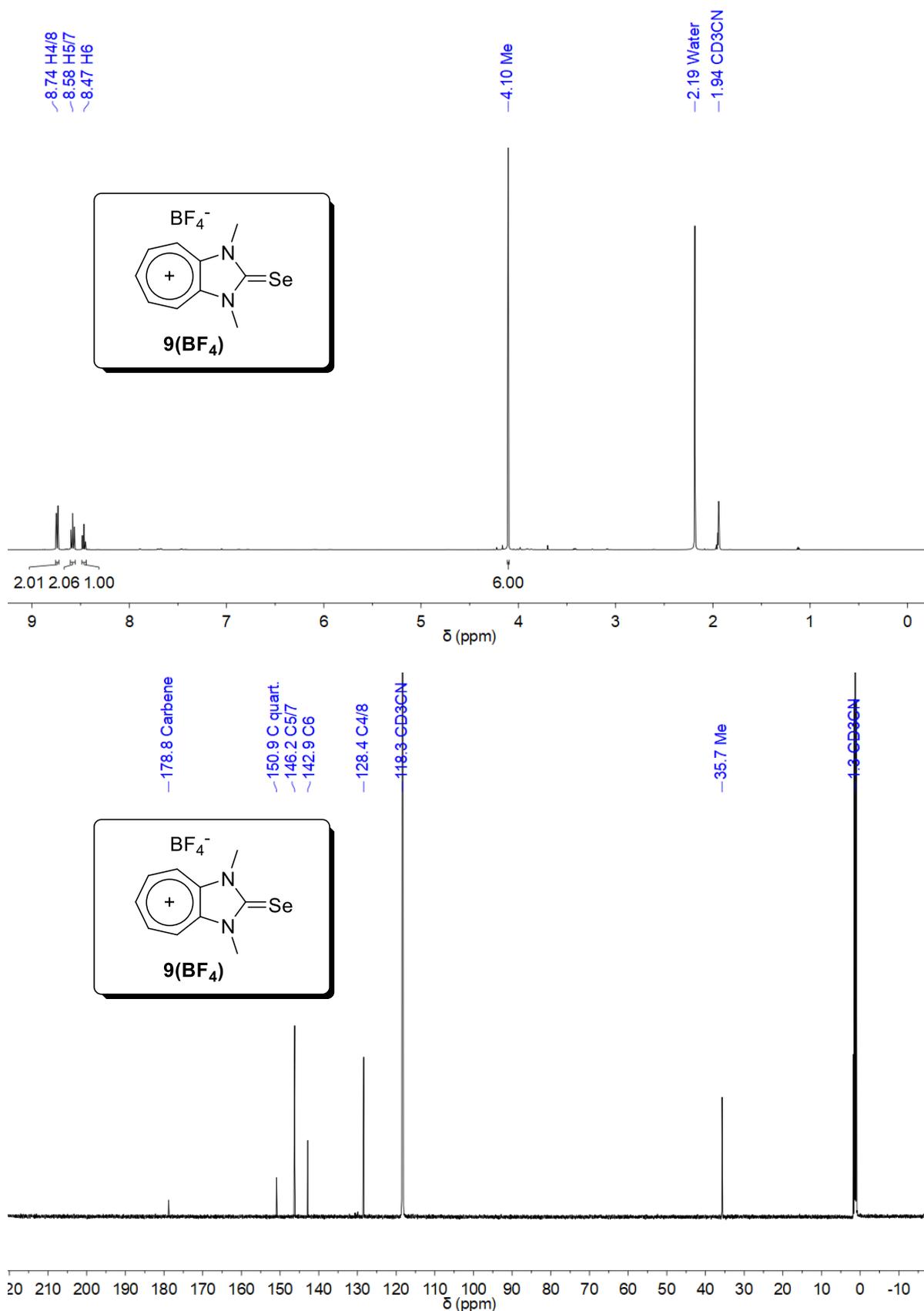


Figure S 12: ¹H NMR (600 MHz, top) and ¹³C{¹H} NMR (150 MHz, bottom) of compound 9(BF₄) in CDCl₃.

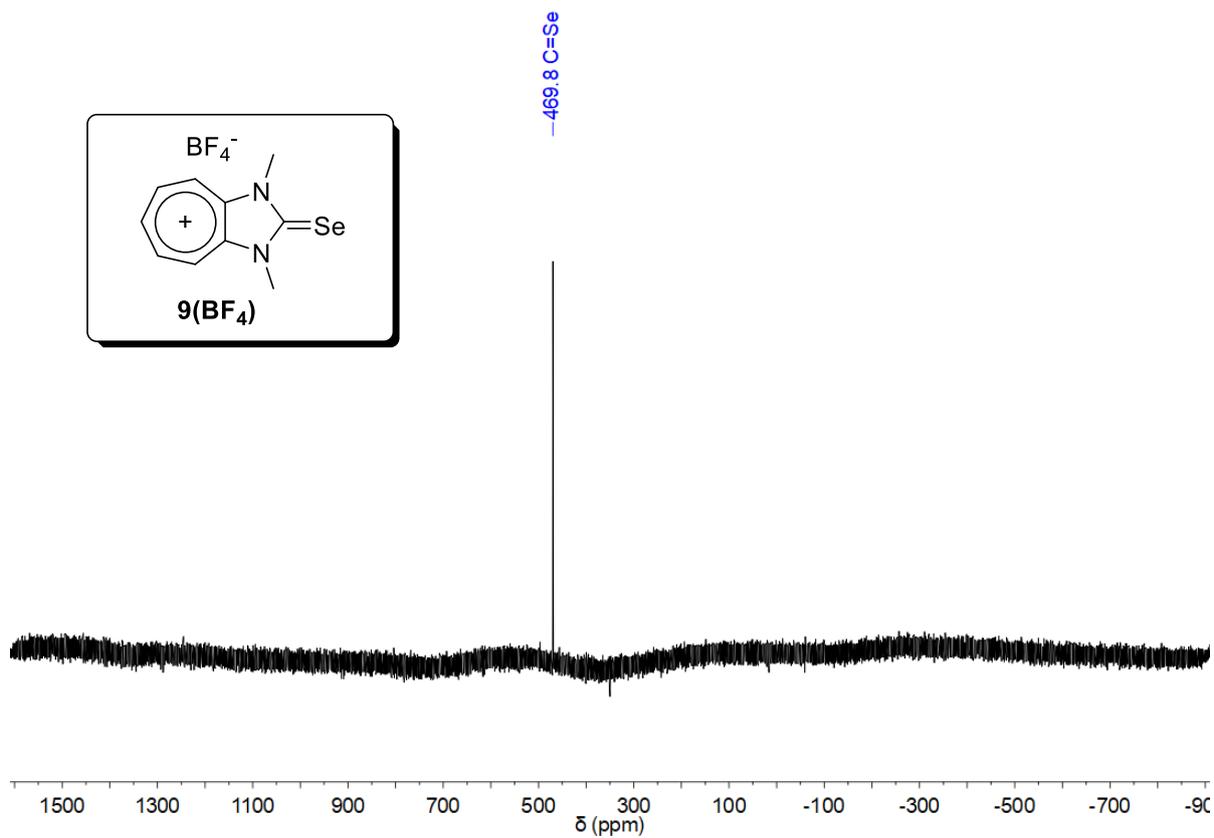
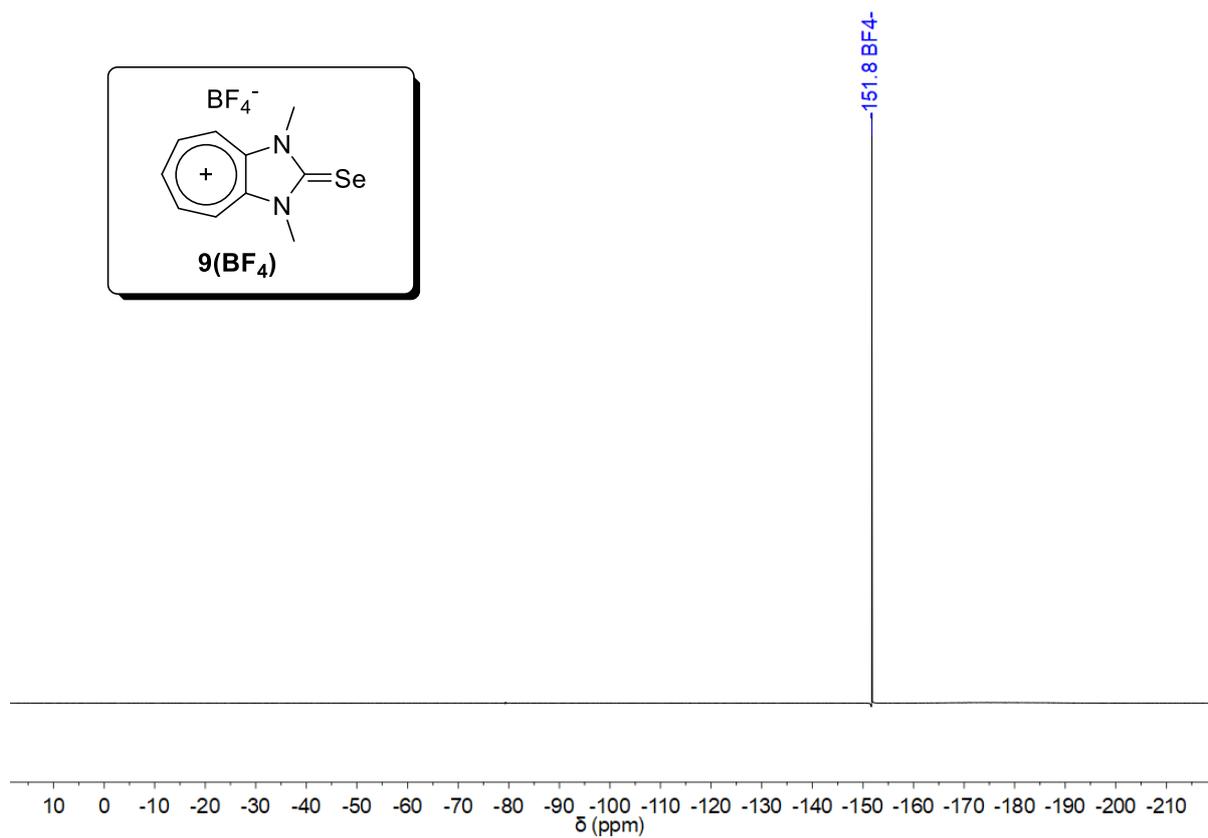


Figure S 13: $^{19}\text{F}\{^1\text{H}\}$ NMR (564 MHz, top) and ^{77}Se NMR (114 MHz, bottom) of compound $9(\text{BF}_4)$ in CD_3CN .

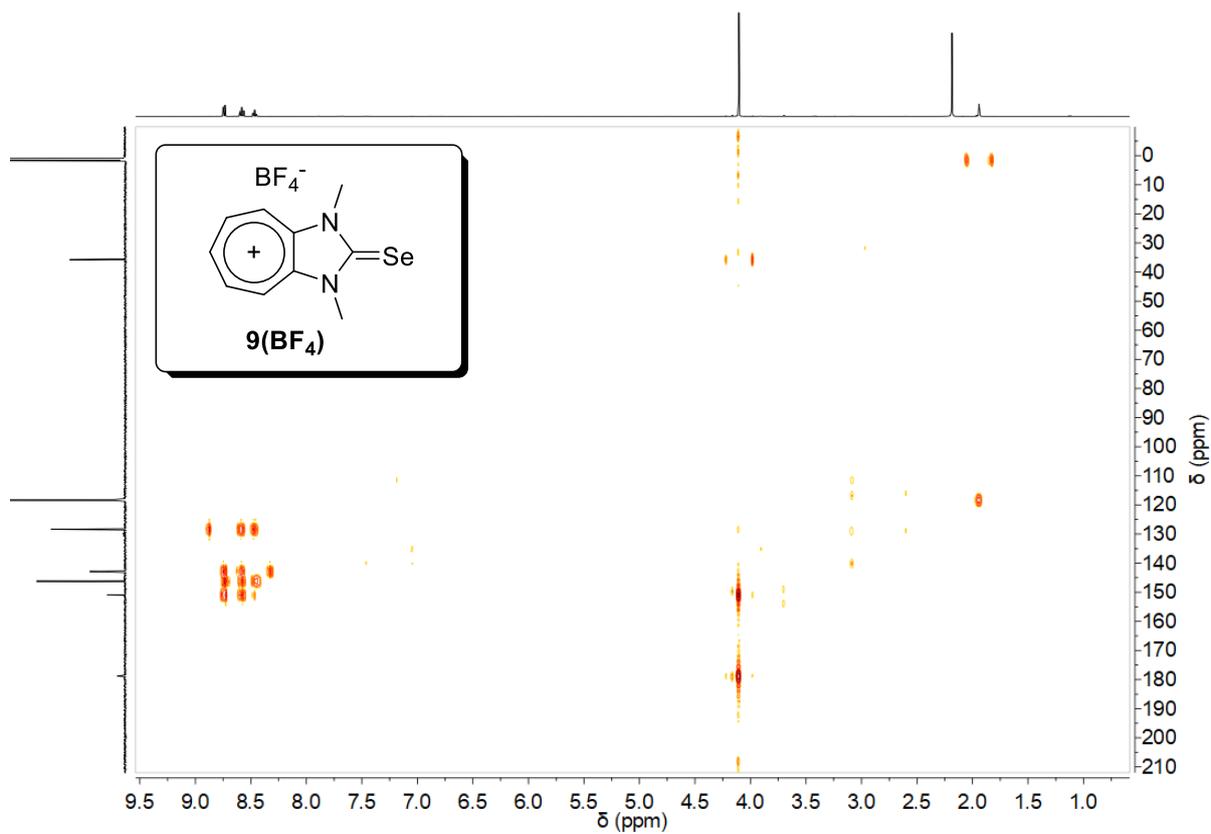
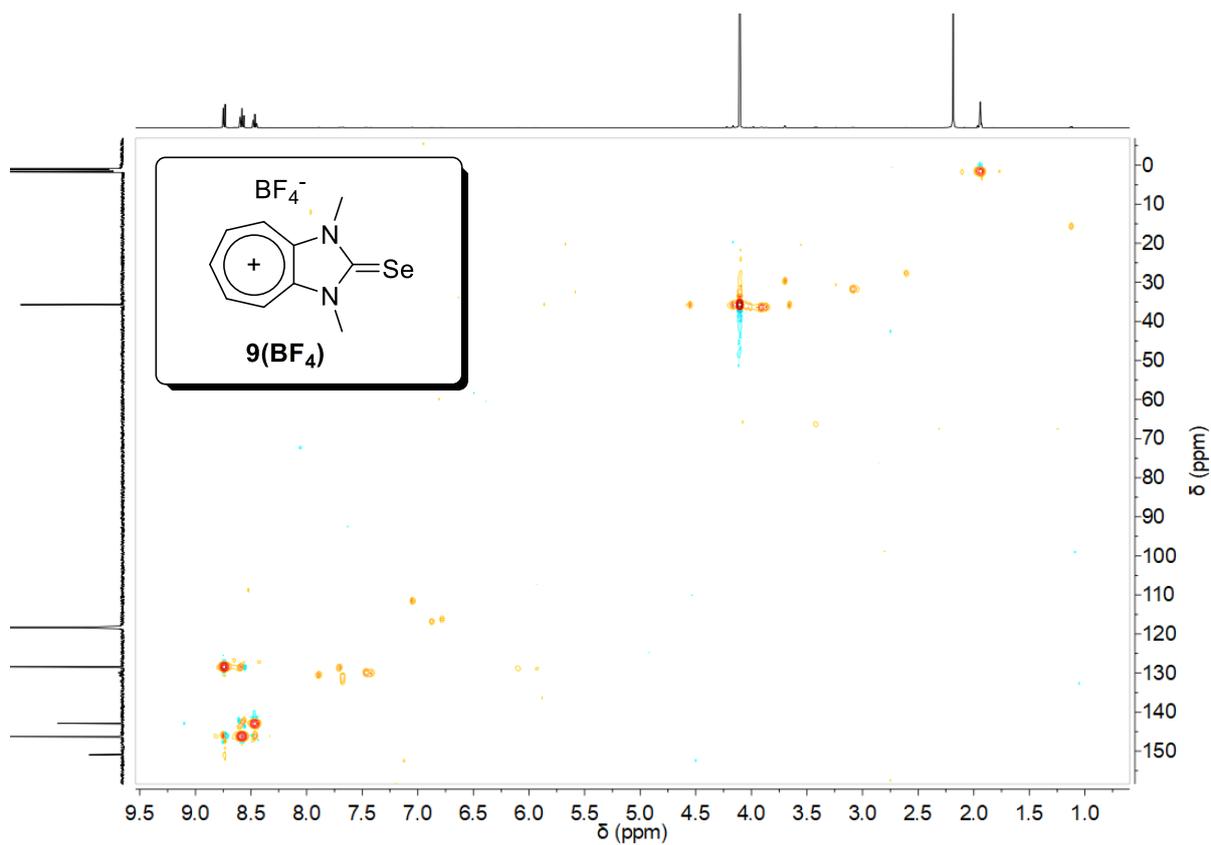


Figure S 14: HSQC NMR (600 MHz, 150 MHz, top) and HMBC NMR (600 MHz, 150 MHz, bottom) of compound **9(BF₄)** in CD₃CN.

NMR Spectra of Compound 7

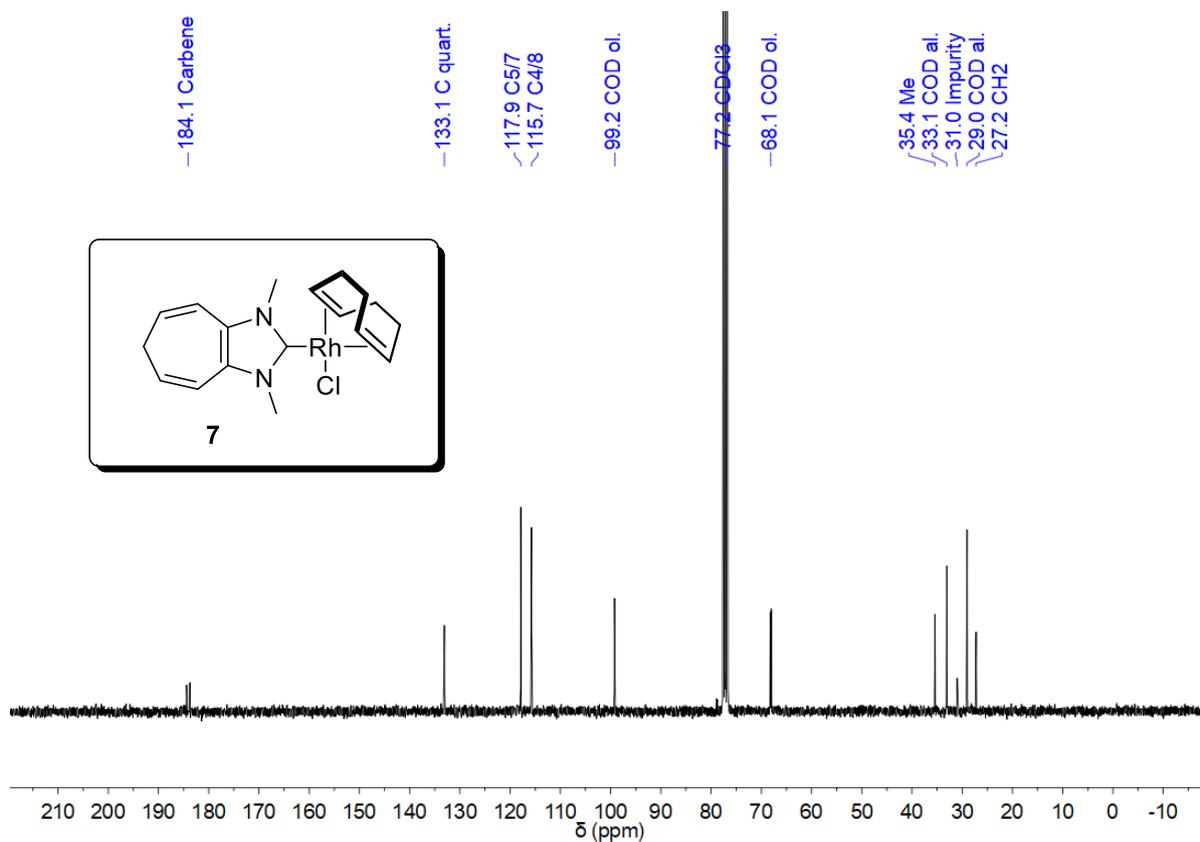
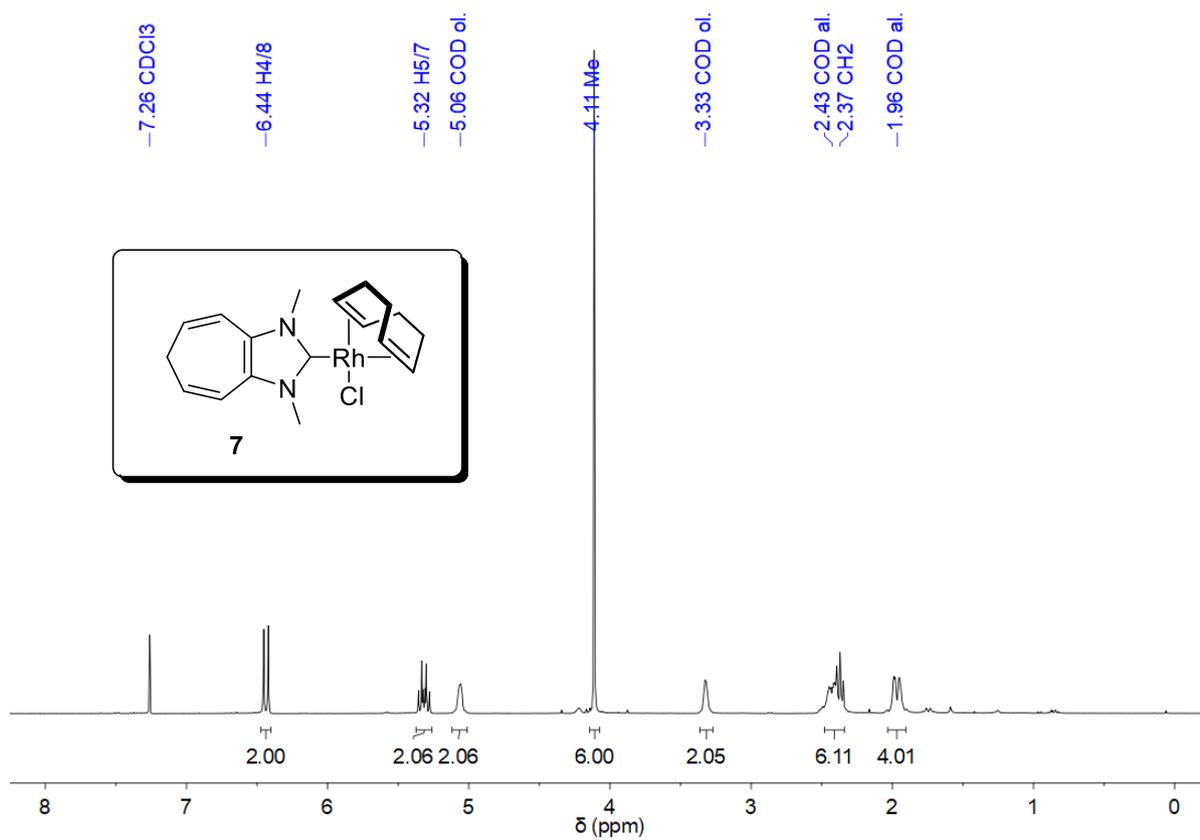


Figure S 15: ¹H NMR (300 MHz, top) and ¹³C{¹H} NMR (75 MHz, bottom) of compound 7 in CDCl₃.

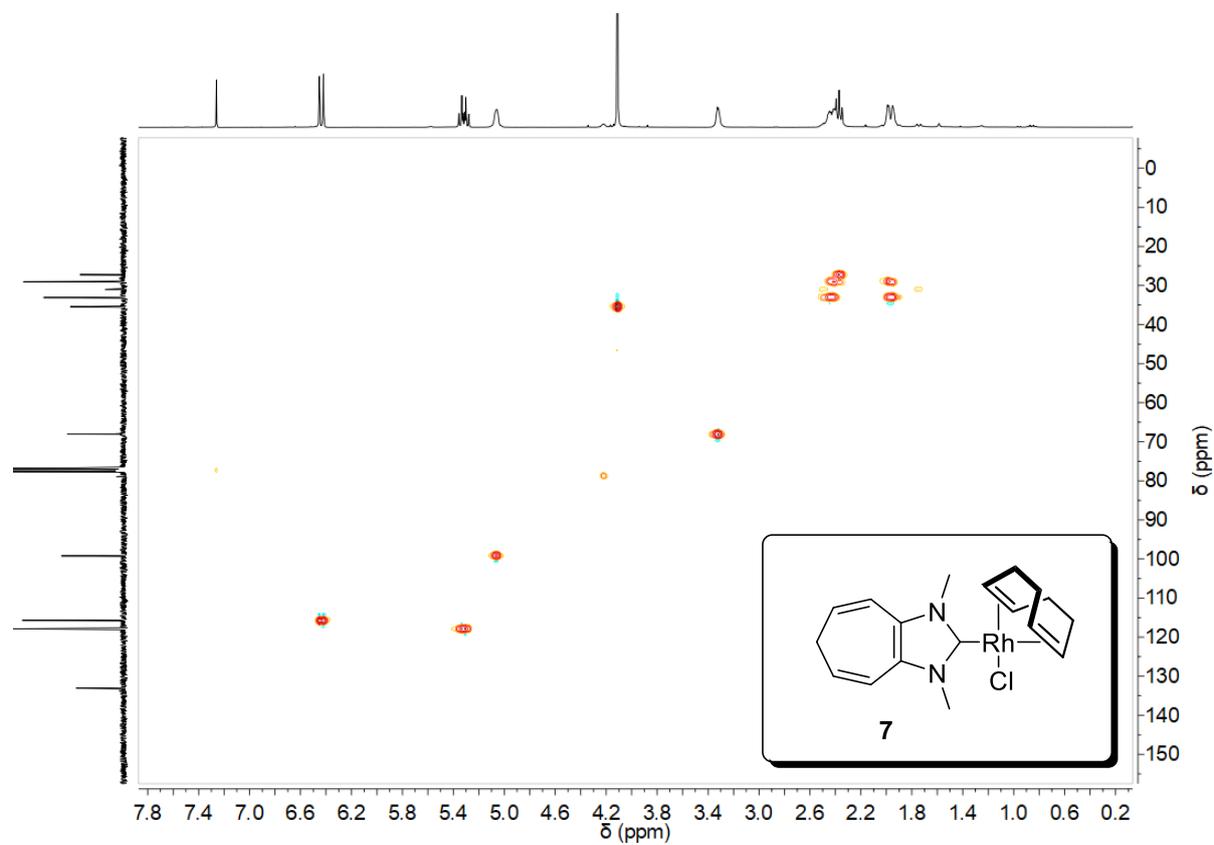
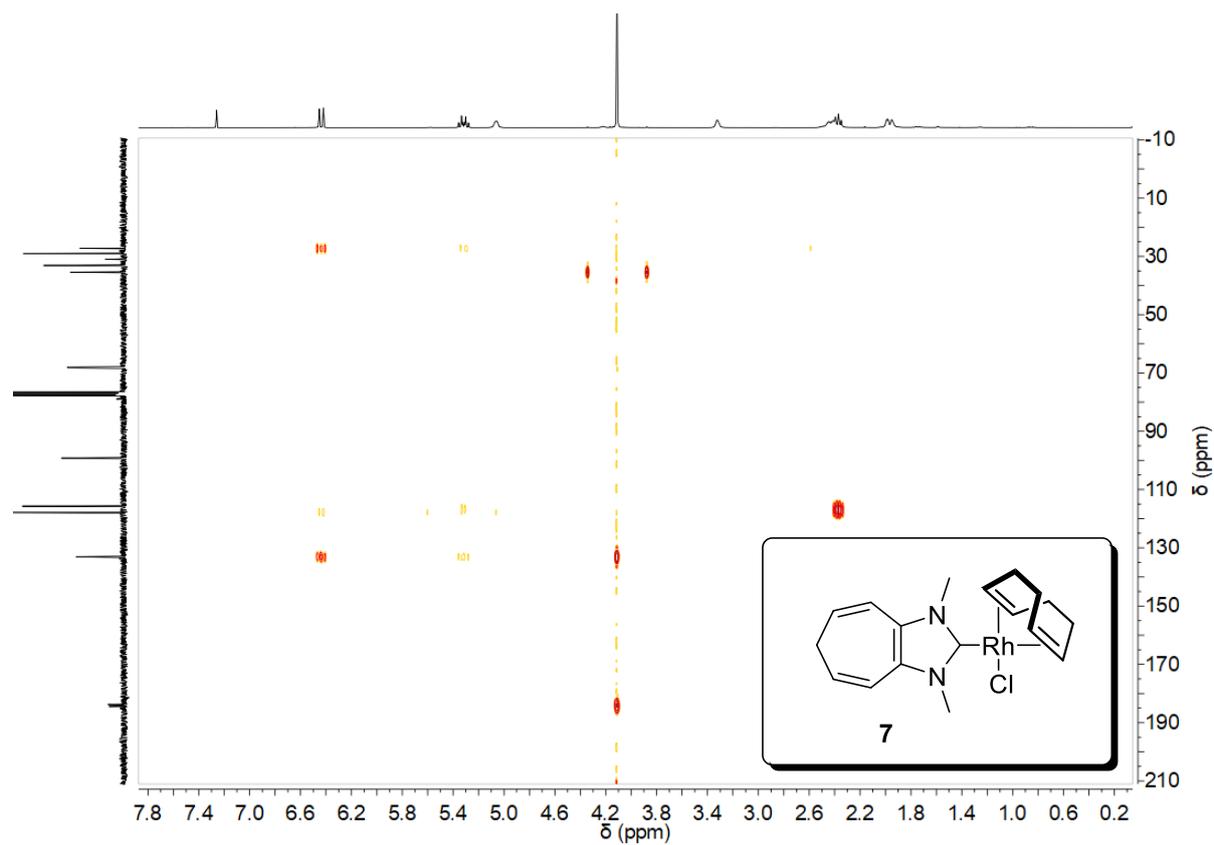


Figure S 16: HSQC NMR (300 MHz, 75 MHz, top) and HMBC NMR (300 MHz, 75 MHz, bottom) of compound **7** in CDCl_3 .

NMR Spectra of Compound 10

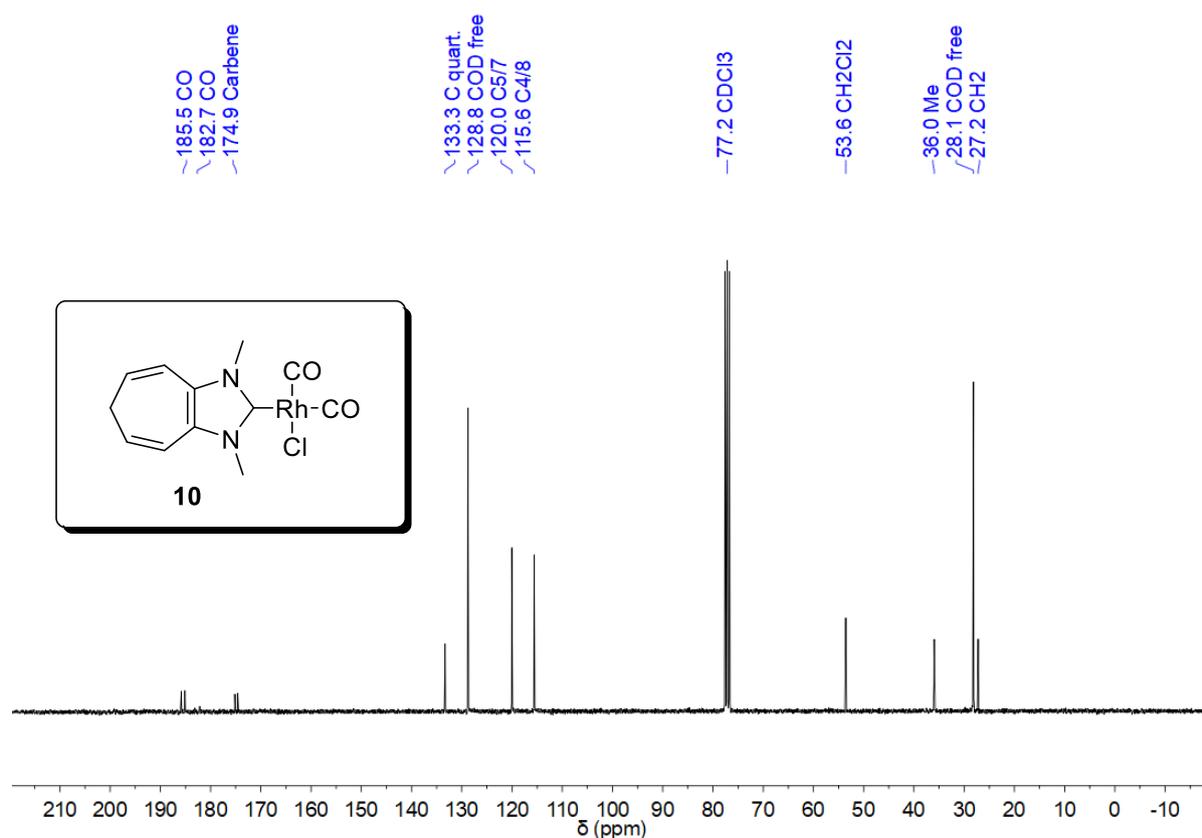
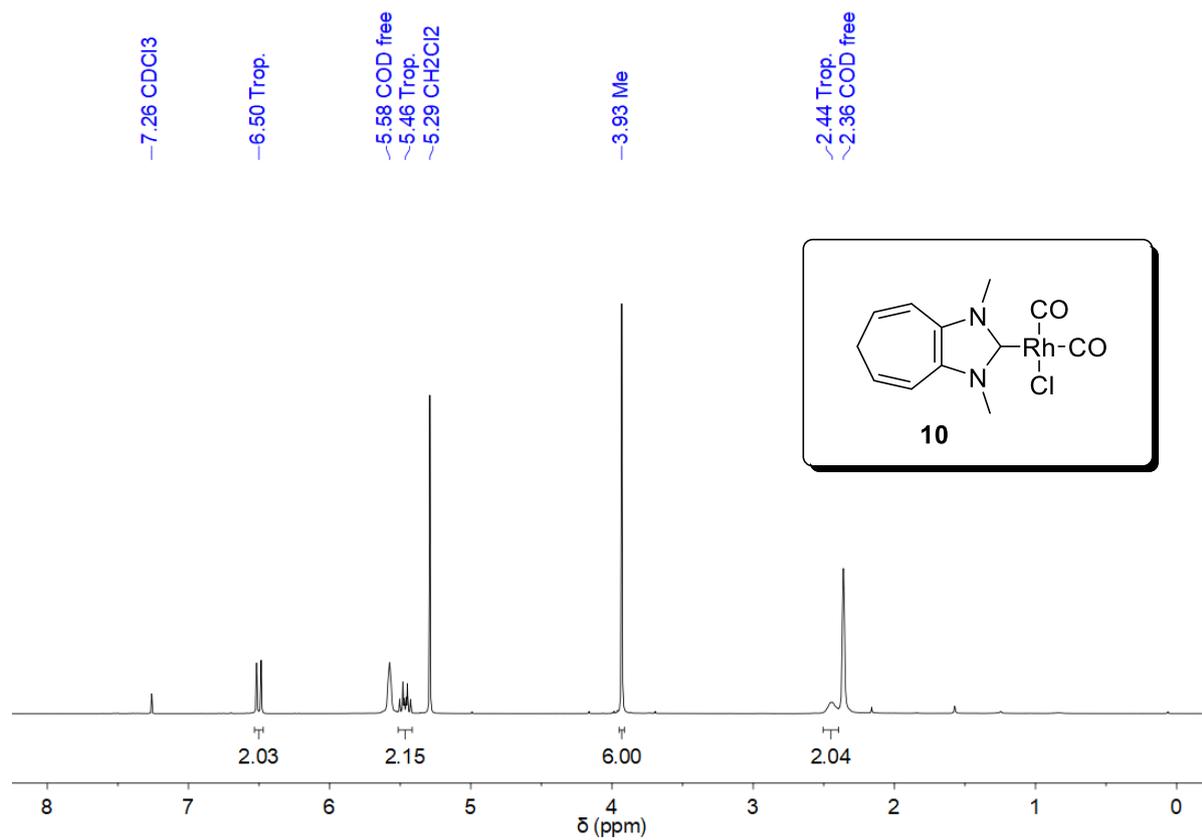


Figure S 17: ¹H NMR (300 MHz, top) and ¹³C{¹H} NMR (75 MHz, bottom) of compound 10 in CDCl₃.

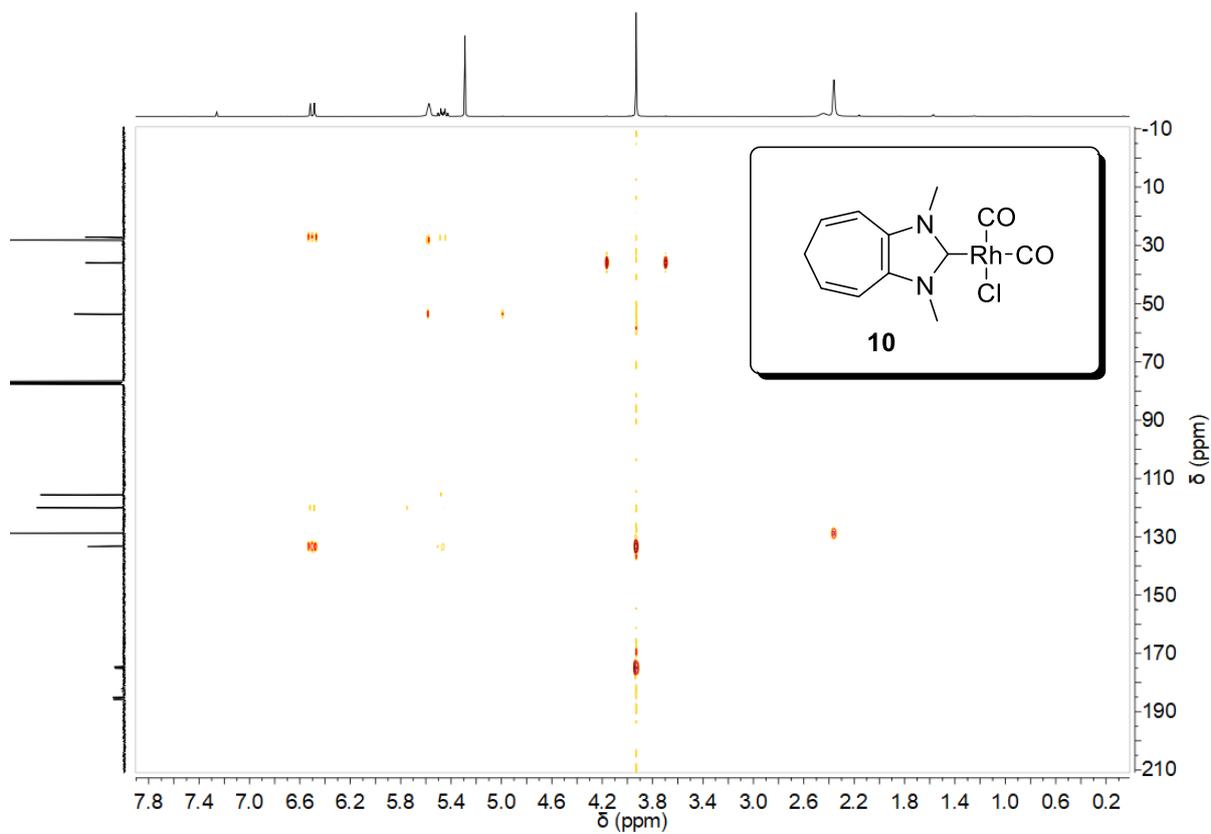
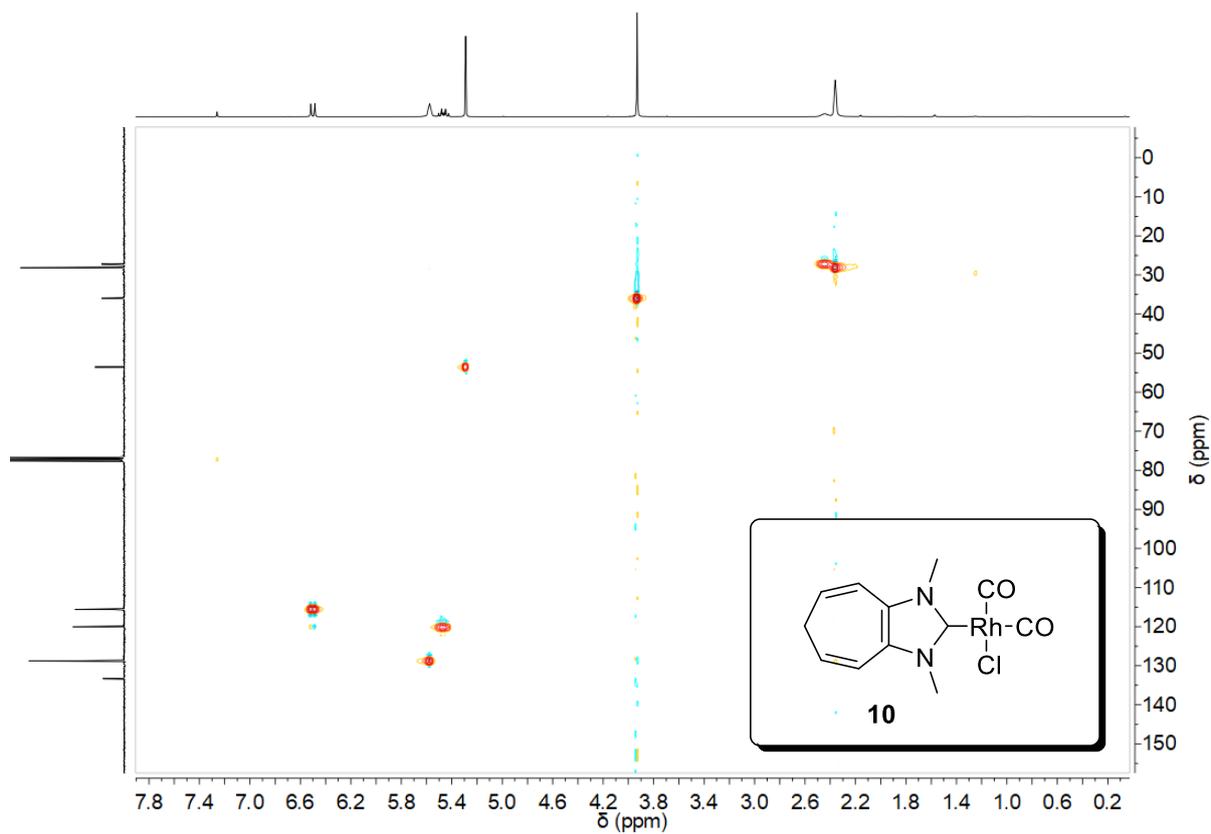


Figure S 18: HSQC NMR (300 MHz, 75 MHz, top) and HMBC NMR (300 MHz, 75 MHz, bottom) of compound **10** in CDCl_3 .

NMR Spectra of Compound 8(BF₄)

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PBP-78

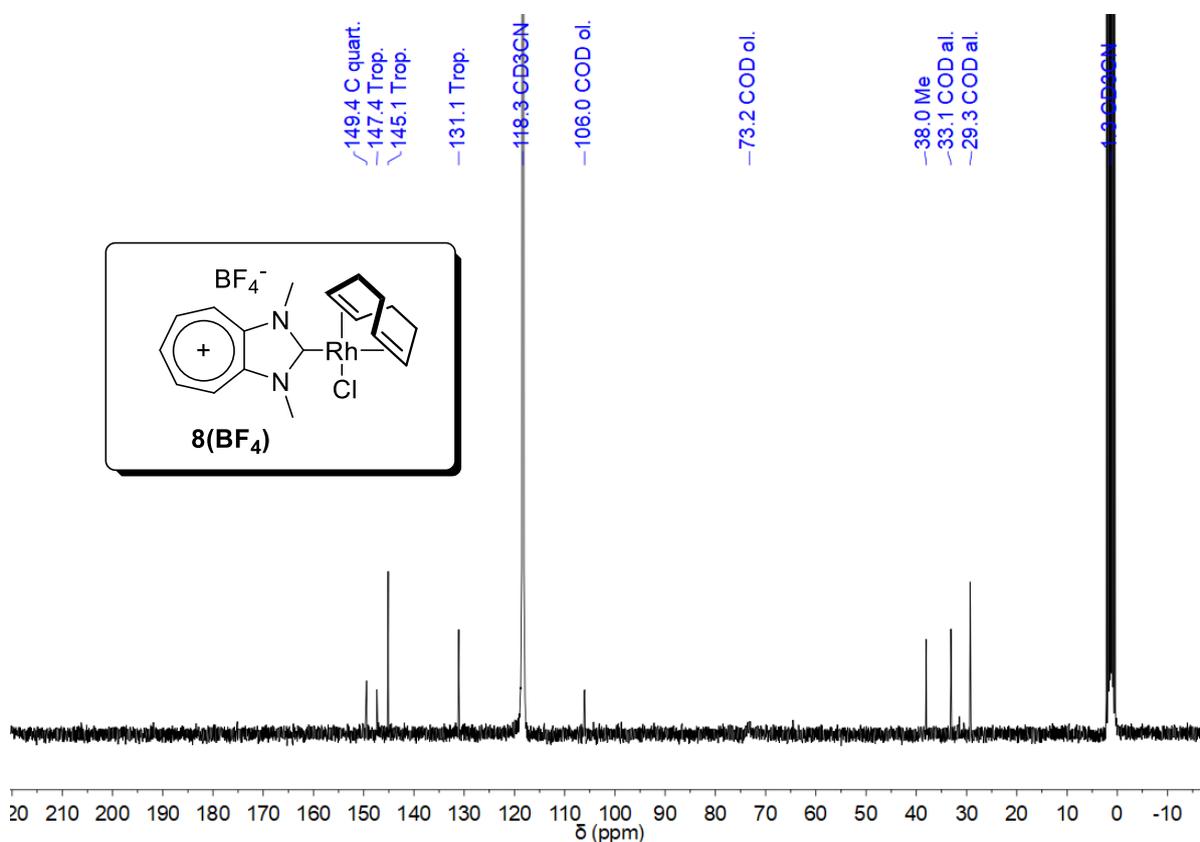
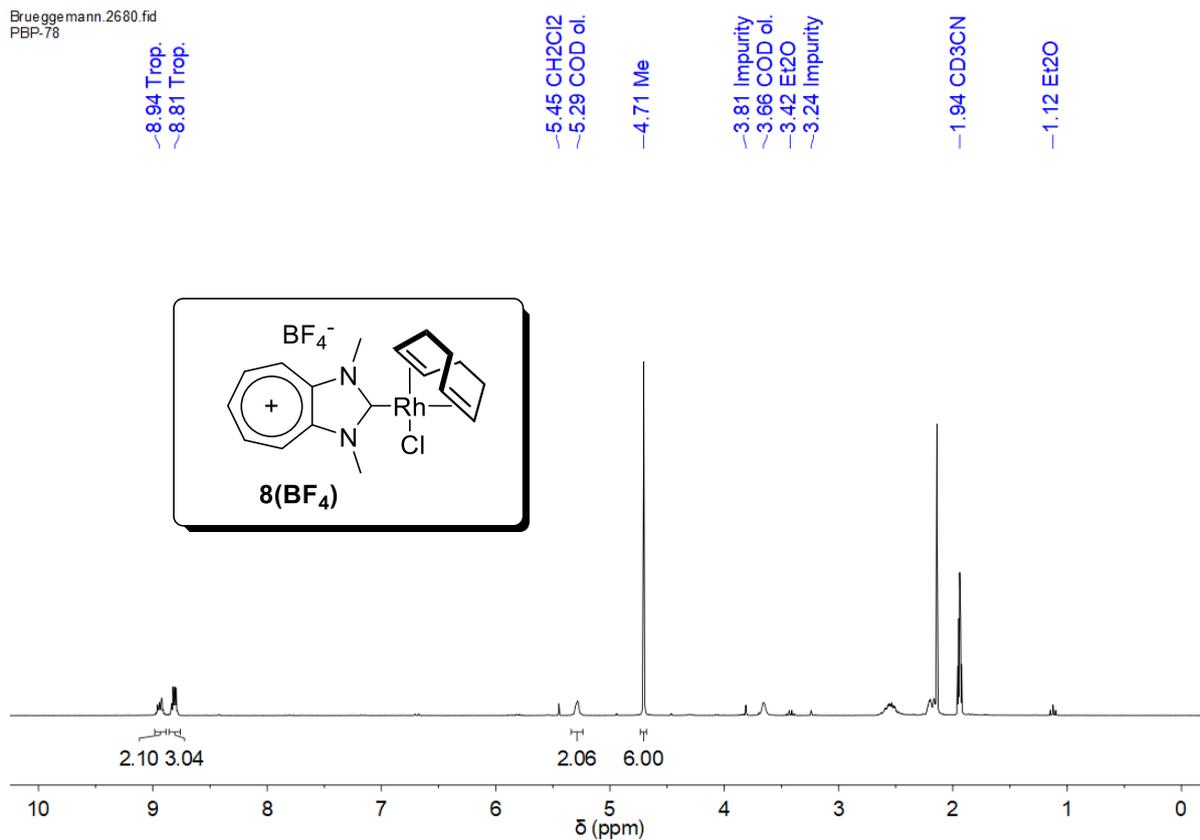


Figure S 19: ¹H NMR (300 MHz, top) and ¹³C{¹H} NMR (75 MHz, bottom) of compound **8(BF₄)** in CD₃CN.

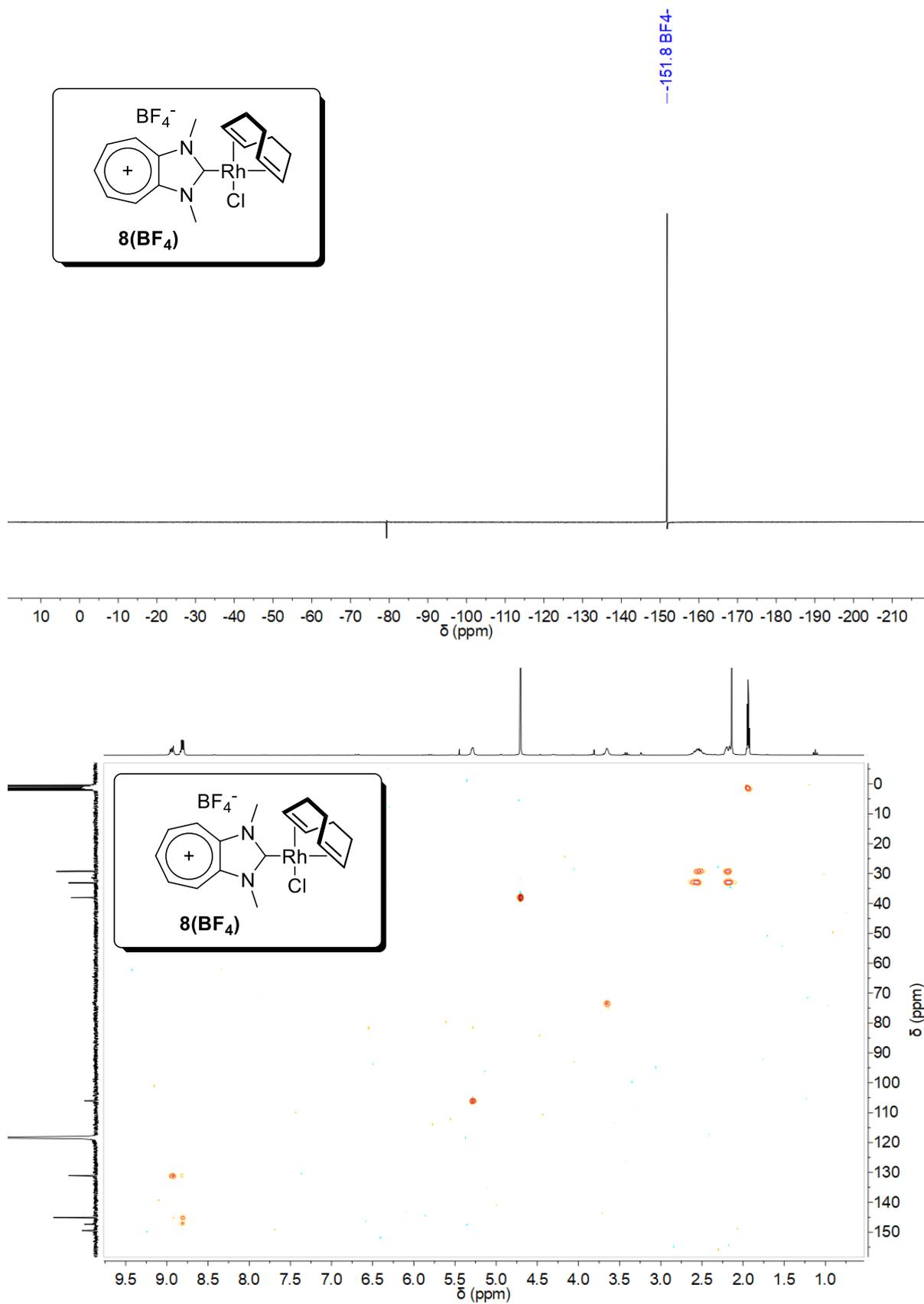


Figure S 20: ¹⁹F{¹H} NMR (282 MHz, top) and HSQC NMR (300 MHz, 75 MHz, bottom) of compound **8(BF₄)** in CD₃CN.

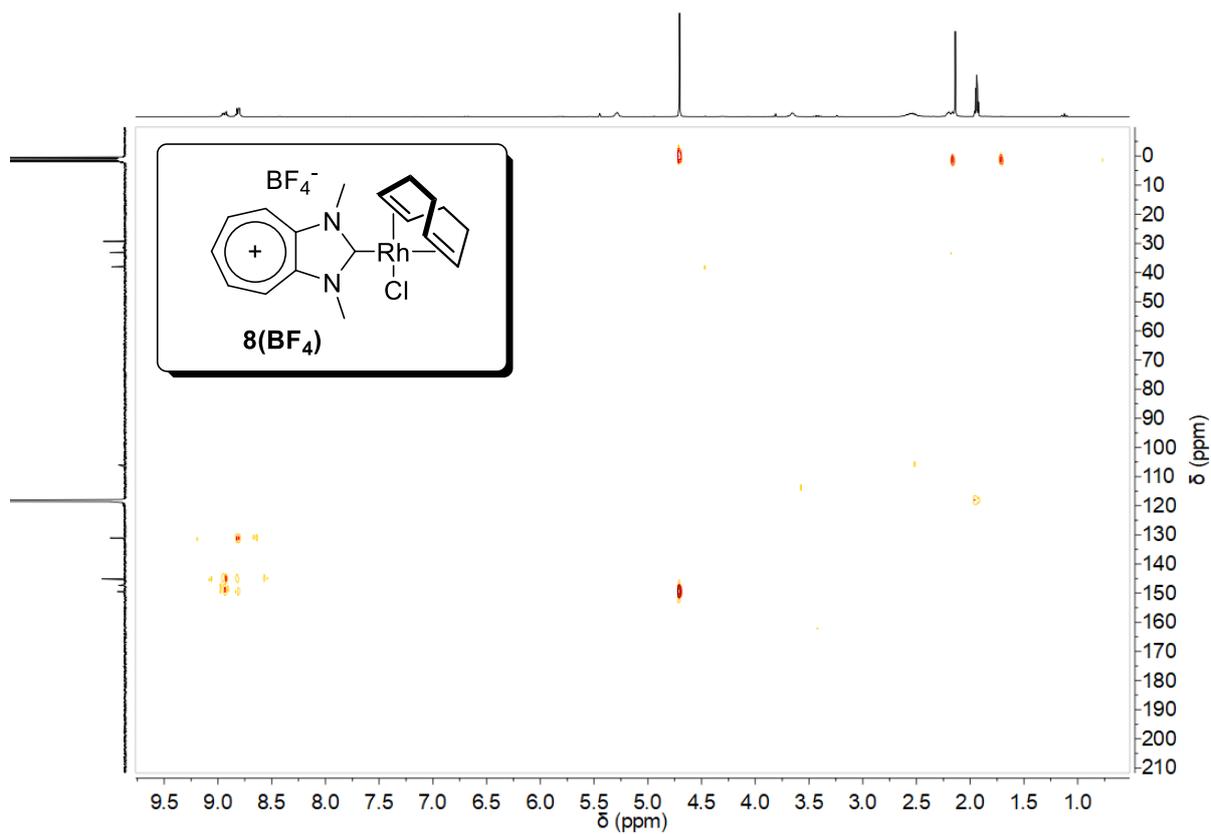


Figure S 21: HMBC NMR (300 MHz, 75 MHz) of compound **8(BF₄)** in CD₃CN.

NMR Spectra of Compound 11(BF₄)

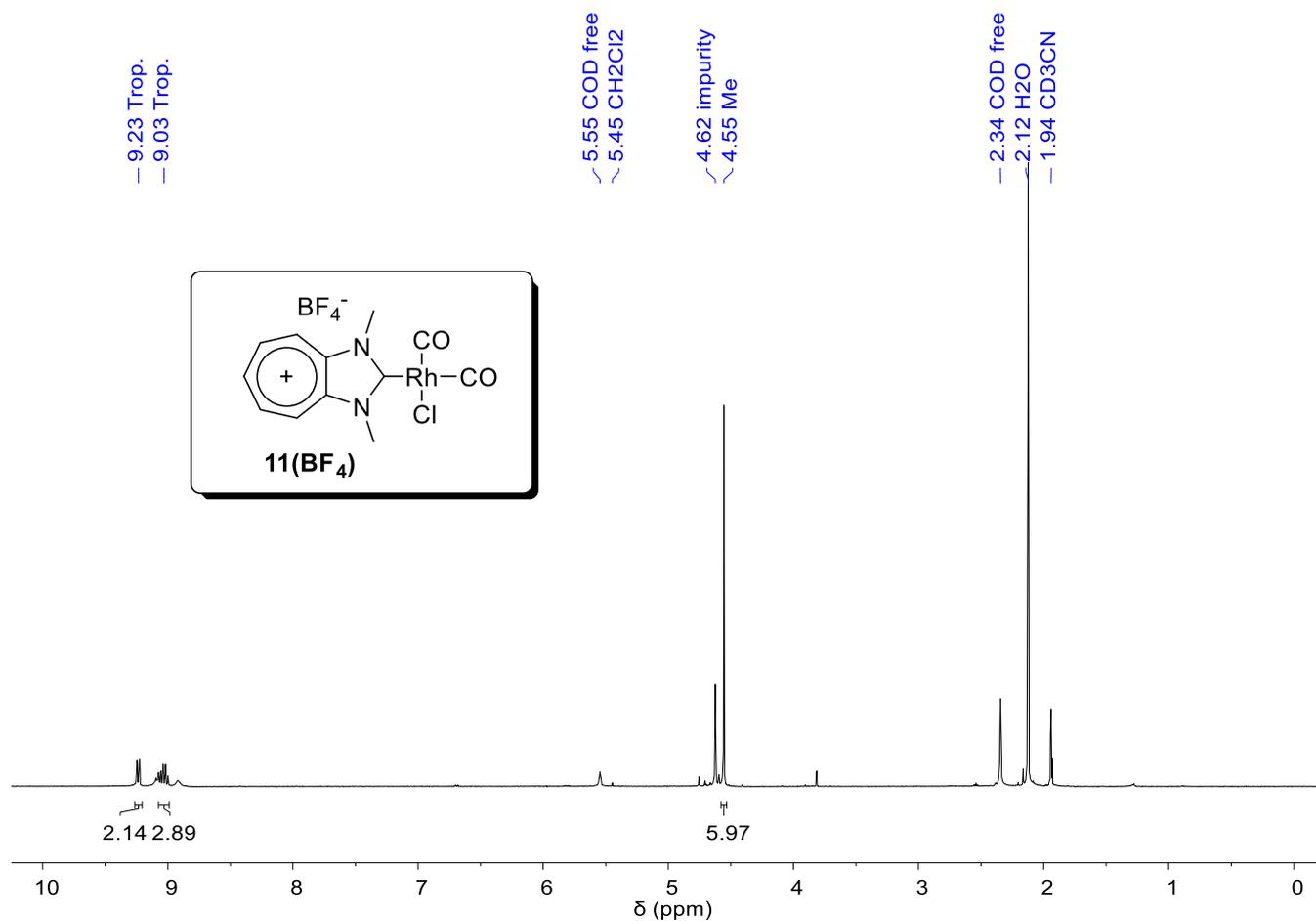


Figure S 19: ¹H NMR (500 MHz) of compound 11(BF₄) in CD₃CN.

Crystal Structure Determinations

Crystals for X-ray diffraction were selected under a polarisation microscope and mounted on a nylon loop. Intensity data were collected on a *Bruker APEX Duo* CCD diffractometer with *multi-layer mirror-monochromated* Mo-K α Strahlung ($\lambda=0.7107$ Å) using the APEX2,^[13] data reduction was done with SAINT (Bruker).^[14] Structures were solved by direct methods (SHELXS-97)^[15] and refined by *Full-matrix least squares on F^2* with SHELX-97. Empirical absorption correction (multi-scan) was carried out with SADABS^[16] (Bruker). Non-H atoms were refined with anisotropic displacement factors. H atoms were positioned geometrically and refined by a *riding-model*. Drawings were prepared using ORTEP3 for Windows, version 2014.1.^[17, 18]

[13] APEX2, *Data Collection Program for the CCD Area-Detector System, Version 2.1-0*, Bruker Analytical X-Ray Systems, Madison (WI), **2006**.

[14] SAINT, *Data Reduction and Frame Integration Program for the CCD Area-Detector System*, Bruker Analytical X-Ray Systems, Madison (WI), **2006**.

[15] G. M. Sheldrick, *Acta Crystallogr., Sect. A: Found. Crystallogr.* **2007**, A64, 112–122.

[16] G. M. Sheldrick, *Program SADABS*, University of Göttingen, Göttingen, **1996**.

[17] L. J. Farrugia, *J. Appl. Crystallogr.* **1997**, 30, 565–565.

[18] M. N. Burnett, C. K. Johnson, *ORTEP-III: Oak Ridge Thermal Ellipsoid Plot Program for Crystal Structure Illustrations*, Oak Ridge National Laboratory Report ORNL-6895, Oak Ridge (TN), **1996**.

Compound	4	2(OTf)₂	6
CCDC No.	1991695	1991696	1991697
Molecular formula	C ₆ H ₆ N ₂ O ₂	C ₁₂ H ₁₂ F ₆ N ₂ O ₆ S ₂	C ₁₀ H ₁₂ N ₂ Se
Molecular weight [g/mol]	138.13	458.36	239.18
Crystal shape and color	colorless block	colorless block	colorless block
Size [mm]	0.40 × 0.30 × 0.10	0.25 × 0.25 × 0.25	0.25 × 0.25 × 0.10
Temperature [K]	296(2)	296(2)	296(2)
Crystal system	orthorhombic	monoclinic	orthorhombic
Space group (no.)	P2 ₁ 2 ₁ 2 ₁ (19)	P2 ₁ /c (14)	P2 ₁ 2 ₁ 2 ₁ (19)
Lattice parameters [Å]	a = 3.87112(16) b = 6.840(3) c = 23.770(9)	a = 6.8205(4) b = 12.3993(7) c = 21.2683(12)	a = 5.8033(8) b = 10.5327(15) c = 16.799(3)
	α = 90 β = 90 γ = 90	α = 90 β = 90.480(3) γ = 90	α = 90 β = 90 γ = 90
Cell volume [Å ³]	629.4(4)	1798.58(18)	1026.8(3)
Z	4	4	4
Calculated density [g/ml]	1.458	1.693	1.547
Absorptioncoefficient [mm ⁻¹]	0.112	3.599	3.612
F (000)	288	928	480
Range Θ [°]	3.099 – 28.195	4.127 – 66.001	2.283 – 24.664
Array bounds	-5 ≤ h ≤ 5	-7 ≤ h ≤ 6	-8 ≤ h ≤ 8
	-9 ≤ k ≤ 8	-12 ≤ k ≤ 13	-14 ≤ k ≤ 14
	-18 ≤ l ≤ 31	-20 ≤ l ≤ 23	-23 ≤ l ≤ 23
Measured reflections	3988	13229	19341
Independent reflections (R _{int})	1563 (0.0255)	2602 (0.0295)	2955 (0.0287)
Final R-value (I > 2σ(I)) ^[a]	R ₁ = 0.0416	R ₁ = 0.0751	R ₁ = 0.0407
	wR ₂ = 0.1037	wR ₂ = 0.2063	wR ₂ = 0.1036
R-value (whole data) ^[a]	R ₁ = 0.0479	R ₁ = 0.0775	R ₁ = 0.0571
	wR ₂ = 0.1071	wR ₂ = 0.2092	wR ₂ = 0.1114
Completeness	99.7%	97.7%	100%
Indep. refl / constr. / parameter	1563 / 0 / 92	2602 / 0 / 290	2955 / 0 / 120
Goodness-of-fit-on F ² ^[b]	1.114	1.039	1.063

[a] $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$; $wR_2 = [\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]]^{1/2}$; $w = 1 / [\sigma^2(F_o^2) + (aP)^2 + bP]$ mit $P = (F_o^2 + 2F_c^2) / 3$

[b] $GooF = S = [(\sum w(F_o^2 - F_c^2)^2) / (m - n)]^{1/2}$. m = Number of reflexes. n = Number of parameter

Compound	9(BF₄)	8(BF₄)	5
CCDC No.	1991698	1991699	1991700
Molecular formula	C ₁₀ H ₁₁ BF ₄ N ₂ Se	C ₁₈ H ₂₃ BClF ₄ N ₂ Rh	C ₉ H ₁₀ N ₂
Molecular weight [g/mol]	324.98	492.55	146.19
Crystal shape and color	colorless block	colorless block	block, colorless
Size [mm]	0.20 × 0.10 × 0.05	0.40 × 0.30 × 0.20	0.20 × 0.20 × 0.10
Temperature [K]	140(2)	140(2)	140(2)
Crystal system	monoclinic	monoclinic	orthorhombic
Space group (no.)	P2 ₁ /n (14)	P2 ₁ /c (14)	P2 ₁ 2 ₁ 2 ₁ (19)
Lattice parameters [Å]	a = 12.1299(18) b = 6.2796(10) c = 16.088(3)	a = 8.0887(4) b = 20.7670(10) c = 11.8752(6)	a = 6.0018(5) b = 8.6564(7) c = 14.5956(13)
	α = 90 β = 94.965(6) γ = 90	α = 90 β = 106.634(2) γ = 90	α = 90 β = 90 γ = 90
Cell volume [Å ³]	1220.8(3)	1911.30(16)	758.30(11)
Z	4	4	4
Calculated density [g/ml]	1.768	1.712	1.281
Absorption coefficient [mm ⁻¹]	3.107	1.076	0.079
F (000)	640	992	312
Range Θ [°]	2.542 – 26.512	3.28 – 41.66	2.791 – 35.564
Array bounds	-12 ≤ h ≤ 15	-14 ≤ h ≤ 12	-9 ≤ h ≤ 9
	-8 ≤ k ≤ 8	-38 ≤ k ≤ 38	-13 ≤ k ≤ 13
	-21 ≤ l ≤ 19	-20 ≤ l ≤ 21	-23 ≤ l ≤ 23
Measured reflections	12836	83649	22988
Independent reflections (R _{int})	2422 (0.0257)	12052 (0.0224)	3301 (0.0272)
Final R-value (I > 2σ(I)) ^[a]	R ₁ = 0.0506	R ₁ = 0.0230	R ₁ = 0.0355
	wR ₂ = 0.1353	wR ₂ = 0.0550	wR ₂ = 0.0951
R-value (whole data) ^[a]	R ₁ = 0.0603	R ₁ = 0.0276	R ₁ = 0.0395
	wR ₂ = 0.1399	wR ₂ = 0.0575	wR ₂ = 0.0981
Completeness	98.3%	99.9%	99.9 %
Indep. refl / constr. / parameter	2422 / 0 / 165	12052 / 0 / 336	3301 / 0 / 101
Goodness-of-fit-on F ² ^[b]	1.113	1.074	1.064

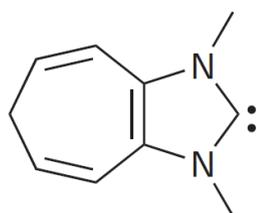
[a] $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$; $wR_2 = [\sum w(F_o^2 - F_c^2)^2 / \sum (wF_o^2)^2]^{1/2}$; $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$ mit $P = (F_o^2 + 2F_c^2)/3$

[b] $\text{GooF} = S = [(\sum w(F_o^2 - F_c^2)^2) / (m - n)]^{1/2}$. m = Number of reflexes. n = Number of parameter

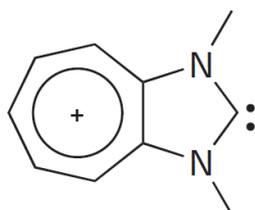
Theoretical Data

Computational Details

The geometries of all molecules were optimized using the B3LYP^[19] functional with *Gaussian09*.^[20] Ahlrichs' def2-TZVP^[21] basis set was used. Harmonic frequency calculations verified the nature of the ground states, having no imaginary frequencies, respectively. Shown energies were calculated as described above. Visualizations of the molecular orbitals were prepared with *Chemcraft*.^[22]



Icht



ITrop⁺

E(RB3LYP) = -497.904674 (**Icht**)

E(RB3LYP) = -497.080896 (**ITrop⁺**)

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Optimised coordinates for Icht

24

C	2.29557	-1.23981	-0.11241
C	2.67744	0.00000	0.65532
C	2.29558	1.23981	-0.11242
C	1.01535	1.56678	-0.36121
C	-0.08937	0.69080	-0.08678
N	-1.42533	1.06368	0.03661
C	-2.27001	0.00000	0.13284
C	-0.08938	-0.69080	-0.08677
N	-1.42533	-1.06367	0.03661
C	-1.89061	-2.43578	0.08560
C	1.01535	-1.56678	-0.36120
H	3.08609	-1.89051	-0.46755
H	3.74551	0.00000	0.86956
H	2.14758	0.00000	1.61684
H	3.08609	1.89051	-0.46756
H	0.79605	2.51292	-0.84390
C	-1.89060	2.43578	0.08561
H	-1.68464	-2.95529	-0.85313
H	-2.96418	-2.40915	0.24870
H	-1.41056	-2.98069	0.90070
H	0.79605	-2.51293	-0.84388
H	-1.68463	2.95529	-0.85313
H	-1.41055	2.98069	0.90070
H	-2.96417	2.40916	0.24871

Optimised coordinates for ITrop⁺

23

C	-2.34381	-1.25908	0.00000
C	-2.93961	0.00000	-0.00001
C	-2.34381	1.25908	-0.00000
C	-0.99481	1.59148	0.00000
C	0.08206	0.71733	0.00000
N	1.40349	1.07589	-0.00000
C	2.25210	0.00000	-0.00000
C	0.08206	-0.71733	0.00000
N	1.40349	-1.07589	-0.00000
C	1.90689	-2.44906	-0.00000
C	-0.99481	-1.59148	0.00001
H	-3.02791	-2.09941	0.00001
H	-4.02326	0.00000	-0.00002
H	-3.02791	2.09941	-0.00001
H	-0.75898	2.64874	0.00001
C	1.90689	2.44906	0.00000
H	1.57215	-2.97772	0.89244
H	2.99032	-2.38935	0.00000
H	1.57216	-2.97771	-0.89246
H	-0.75898	-2.64874	0.00001
H	1.57216	2.97772	0.89245
H	1.57215	2.97772	-0.89244
H	2.99032	2.38935	-0.00000