Electronic Supplementary Material (ESI) for ChemComm.

N-Alkoxyimidazolylidines (NOHCs): A new class of highly nucleophilic carbenes

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Supplementary information

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1. General information

Unless otherwise noted, chemicals were obtained from commercial suppliers and used without further purification. NMR spectra were recorded at rt using Bruker Avance II 400 MHz, Bruker Avance III 400 MHz, and Bruker Avance III HD 600 MHz spectrometers. Chemical shifts are given in parts per million (ppm). ^{1}H and ^{13}C NMR spectra measured in $CDCl_3$ were referenced to TMS as an internal standard. ^{1}H and ^{13}C NMR spectra measured in THF-d8 were referenced to the residual signal of the solvent. ^{77}Se NMR spectra were referenced to diphenyl diselenide as an external standard and recalculated to dimethyl selenide (δ_{se} + 463 ppm). ^{15}N NMR spectra were referenced to ammonia as an external standard and recalculated to nitromethane (δ_N − 380 ppm). Melting points were measured in closed capillaries on a Krüss KSP1N melting point meter. High-resolution mass spectra were recorded on Bruker Daltonics micrOTOF mass spectrometer using ESI (electrospray ionization). Compounds **7** and **8** were synthesized using previously published procedures.[1, 2]

2. Preparation of N-oxide 3

To a round-bottomed flask hydroxylamine hydrochloride (15 mmol) was added, followed by water (5 mL). The mixture was cooled to 0 °C on an ice bath, then sodium carbonate (25 mmol) added. After 10 min of stirring aqueous solution of glyoxal (40% w/v, 15 mmol) was added dropwise and stirred further 15 min. 1-Adamantylamine (15 mmol) was then dissolved in a small amount of methanol and added dropwise to the reaction mixture over 5 min. After stirring for 1 h, an aqueous solution of formaldehyde (37% w/v, 15 mmol) was added and the reaction mixture was allowed to warm to rt and then stirred for 20 h. The resulting reaction mixture was diluted with water (5 mL) and extracted with ethyl acetate 4×10 mL, the combined organic layers dried over Na_2SO_4 and concentrated to yield a dark brown oil, which was purified via column chromatography (silica gel, ethyl acetate/methanol gradient) to yield an off-white solid. The solid product was dissolved in a small amount of ethyl acetate and precipitated with diethyl ether yielding colorless crystals, which slowly darken on air.

1-(1-adamantanyl)imidazole 3-oxide (3). Colorless crystals in 7% yield. M.p. 210–211 °C (dec.). IR ν_{max}/cm^{-1}: 2909*s*, 2601*s*, 2495*s*, 1475*s*, 1444*m*, 1397*s*, 1171*m*, 1035*s*, 850*w*, 807*m*, 462*m*. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.14–8.09 (*m*, 1H), 7.17–7.10 (*m*, 1H), 6.94–6.88 (*m*, 1H), 2.31–2.24 (*m*, 3H), 2.07–2.01 (*m*, 6H), 1.84–1.69 (*m*, 6H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 124.0

(CH), 121.7 (CH), 112.4 (CH), 57.2 (C), 43.0 (CH_2), 35.5 (CH_2), 29.3 (CH). HRMS (ESI): calcd. for $C_{13}H_{19}N_2O^+$ [M+H$^+$] = 219.1492; found 219.1492.

3. Preparation of imidazolium salts 6 and 9

Imidazolium N-oxide (10 mmol) was dissolved in 25 mL of trifluoroacetic acid followed by addition of 1-adamantyl trifluoroacetate (30 mmol). The resulting solution was refluxed for 16 h and stirred at rt for another 16 h followed by distilling off the trifluoroacetic acid. The resulting light brown oil was separated via column chromatography (silica gel, ethyl acetate/methanol gradient) to yield off-white solid. The solid product was dissolved in a small amount of methanol and precipitated with diethyl ether yielding colorless crystals.

1-(1-adamantanyl)-3-(1-admantyloxy)imidazolium trifluoroacetate (6). Colorless crystals in 42% yield. M.p. 121.8−122.3 °C. IR ν_{max}/cm^{-1}: 2912*m*, 2857*w*, 1690*s*, 1199*s*, 1169*s*, 1127*s*. ^{1}H NMR (600 MHz, $CDCl_3$): δ 10.28–10.25 (*m*, 1H), 7.72–7.67 (*m*, 1H), 7.48–7.42 (*m*, 1H), 2.34–2.26 (*m*, 6H), 2.26–2.19 (*m*, 6H), 1.91–1.84 (*m*, 6H), 1.81–1.73 (*m*, 6H), 1.69–1.56 (*m*, 6H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 160.8 (C, q, $^2J_{CF}$ = 33 Hz), 133.9 (CH), 121.8 (CH), 117.4 (C, q, $^1J_{CF}$ = 297 Hz), 116.3 (CH), 89.6 (C), 61.6 (C), 42.4 (CH_2), 40.2 (CH_2), 35.4 (CH_2), 35.2 (CH_2), 31.1 (CH), 29.5 (CH). HRMS (ESI): calcd. for $C_{27}H_{37}N_2O^+$ [M−CF_3COO^-] = 353.2587; found 353.2588.

1-(1-adamantanyl)-3-(1-admantyloxy)-4,5-dimethylimidazolium trifluoroacetate (9). Colorless to off-white crystals in 45% yield. M.p. 161.0 °C (dec.). IR ν_{max}/cm^{-1}: 2911*m*, 2856*m*, 1685*s*, 1196*s*, 1158*s*, 1105*s*, 1041*m*, 876*m*, 817*m*, 797*m*, 716*m*. ^{1}H NMR (600 MHz, $CDCl_3$): δ 9.75 (*s*, 1H), 2.49 (*s*, 3H), 2.34–2.26 (*m*, 6H), 2.25–2.21 (*m*, 9H), 1.95–1.89 (*m*, 6H), 1.79–1.72 (*m*, 6H), 1.67–1.59 (*m*, 6H). 13C NMR (101 MHz, $CDCl_3$): δ 160.4 (*q*, $^2J_{CF}$ = 32 Hz, C), 133.1 (CH), 127.7 (C), 124.0 (C), 117.6 (q, $^1J_{CF}$ = 298 Hz, C) 90.4 (C), 63.7 (C), 41.5 (CH_2), 40.6 (CH_2), 35.3 (CH_2), 35.3 (CH_2), 31.2 (CH), 29.7 (CH), 12.7 (CH_3), 8.3 (CH_3) ppm. HRMS (ESI+): calcd. for $C_{27}H_{37}N_2O^+$ [M−CF_3COO^-] = 381.2900; found 389.2902.

4. Preparation of free NOHC 4

Imidazolium salt **9** (0.1 g, 0.2 mmol) was placed in the Schlenk tube under N_2 atmosphere. Then dry THF was added and the reaction mixture was cooled to −78 °C with a dry ice acetone bath followed by dropwise addition of LiHMDS (1M in THF, 0.2 mmol). The reaction mixture was allowed to slowly warm to −30 °C over 2 h, then evaporated and the resulting orange solid dissolved in dry pentane and filtered into another dry Schlenk tube flushed with N_2 and kept

at −30 °C. The resulting yellow-orange solution was evaporated to yield an orange solid, which was dissolved in THF-d8 and transferred to a sealed NMR tube under N_2 for analysis. The NMR spectra were recorded at rt. The sample can be stored in a sealed tube under N_2 for at least 3 days at −20 °C without major decomposition.

1-(1-adamantanyl)-3-(1-admantyloxy)-4,5-dimethyl-imidazolylidene (4). ^{1}H NMR (600 MHz, C_4H_8O): δ 2.29–2.23 (*m*, 9H), 2.18–2.10 (*m*, 6H), 2.02–1.99 (*m*, 3H), 1.98–1.94 (*m*, 6H). ^{13}C NMR (151 MHz, C_4H_8O): δ 203.9 (C), 162.3 (C, q, $^{2}J_{CF}$ = 34 Hz), 123.5 (C), 119.9 (C), 117.8 (C, q, $^{1}J_{CF}$ = 293 Hz), 82.4 (C), 58.5 (C), 44.5 (CH_2), 42.3 (CH_2), 37.2 (CH_2), 37.0 (CH_2), 31.9 (CH), 31.1 (CH), 13.3 (CH_3), 8.5 (CH_3).

5. Preparation of gold complex 10

Imidazolium salt **9** (0.2 mmol) was placed together with silver(I) oxide (0.2 mmol) in a Schlenk tube under N_2 atmosphere. Then dry DCM was added and the reaction mixture was stirred in the dark at rt for 4 h. The chloro(dimethyl sulfide)gold(I) complex (0.2 mmol) was then added and the reaction mixture was then stirred in the dark for another 12 h. The reaction mixture was filtered through a short layer of Celite and evaporated at rt yielding yellow-brown solid, which was purified via column chromatography (neutral alumina, DCM + 1% Et_3N). The resulting off-white solid was precipitated with pentane from DCM solution to yield colorless crystals that can be stored in a refrigerator under N_2 for several weeks.

Chloro[1-(1-adamantanyl)-3-(1-admantyloxy)-4,5-dimethyl-imidazolylidene]gold(I) (10). Colorless crystals in 84% yield. M.p. 268.5 (dec.). IR ν_{max}/cm^{-1}: 2904*s*, 2850*m*, 1641*w*, 1446*w*, 1352*m*, 1288*m*, 1045*m*, 888*m*. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.74–2.64 (*m*, 6H), 2.37 (*s*, 3H), 2.29–2.20 (*m*, 6H), 2.16 (*s*, 3H), 2.13–2.04 (*m*, 6H), 1.82–1.67 (*m*, 6H), 1.67–1.58 (*m*, 6H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 165.8 (C), 124.8 (C), 122.9 (C), 88.1 (C), 63.5 (C), 44.3 (CH_2), 42.4 (CH_2), 35.7 (CH_2), 35.7 (CH_2), 31.4 (CH), 30.2 (CH), 15.1 (CH_3), 9.8 (CH_3). HRMS (ESI+): calcd for $C_{25}H_{36}AuClN_2NaO^+$ [M+Na$^+$] = 635.2074; found 635.2076.

6. Preparation of selones 11–13

The respective imidazolium salt (0.2 mmol) was placed together with black selenium (0.6 mmol) in a Schlenk tube under N_2 atmosphere. Dry THF was added and the reaction mixture was cooled to −78 °C with a dry ice acetone bath followed by dropwise addition of LiHMDS (1M in THF, 0.2 mmol). The reaction mixture was allowed to slowly warm to rt over 6 h. The

reaction mixture was filtered through a short layer of Celite and evaporated at rt yielding yellow to red solid, which was purified via column chromatography (neutral alumina, DCM + 1% Et_3N). The resulting off-white to yellow solid was precipitated with pentane from benzene or acetone solution to yield colorless crystals that can be stored in a refrigerator under N_2 for several weeks.

1,3-Bis(1-adamantyloxy)-1,3-dihydro-2-imidazoleselone (11). Colorless to off-white crystals in 88% yield. M.p. 175.3 °C (dec.). IR ν_{max}/cm^{-1}: 2905*s*, 2847*w*, 1590*w*, 1421*w*, 1375*m*, 1354*w*, 1050*m*, 1007*w*, 887*m*. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.83 (*s*, 2H), 2.25–2.16 (*m*, 6H), 2.07–1.98 (*m*, 12H), 1.66–1.54 (*m*, 12H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 155.3 (C), 116.7 (CH), 88.6 (C), 41.6 (CH_2), 35.8 (CH_2), 31.1 (CH). ^{15}N NMR (41 MHz, $CDCl_3$): δ −167. ^{77}Se NMR (114 MHz, $CDCl_3$): δ 70. HRMS (ESI+): calcd for $C_{23}H_{32}N_2NaOSe^+$ [M+Na$^+$] = 471.1521; found 471.1523.

1-(1-Adamantyl)-3-(1-adamantyloxy)-1,3-dihydro-2-imidazoleselone (12). Colorless crystals in 78% yield. M.p. 156.2 °C (dec.). IR ν_{max}/cm^{-1}: 2906*s*, 2849*m*, 1591*w*, 1451*w*, 1355*w*, 1151*w*, 1047*m*, 1010*w*. ^{1}H NMR (600 MHz, $CDCl_3$): δ 6.98 (*d*, *J* = 2.6 Hz, 1H), 6.90 (*d*, *J* = 2.6 Hz, 1H), 2.71–2.63 (*m*, 6H), 2.26–2.19 (*m*, 6H), 2.12–2.04 (*m*, 6H), 1.83–1.75 (*m*, 3H), 1.75–1.67 (*m*, 3H), 1.67–1.58 (*m*, 6H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 151.1 (C), 118.3 (CH), 112.7 (CH), 88.0 (C), 61.7 (C), 41.5 (CH_2), 39.9 (CH_2), 35.9 (CH_2), 35.8 (CH_2), 31.1 (CH), 30.0 (CH). ^{15}N NMR (61 MHz, $CDCl_3$): δ −156 (***N***–OR), −189 (***N***–R). ^{77}Se NMR (114 MHz, $CDCl_3$): δ 129.59. HRMS (ESI+): calcd for $C_{23}H_{32}N_2NaOSe^+$ [M+Na$^+$] = 455.1572; found 455.1574.

1-(1-Adamantyl)-3-(1-adamantyloxy)-4,5-dimethyl-1,3-dihydro-2-imidazoleselone (13): Colorless to light brown crystals in 75% yield. M.p. 159.8 °C (dec.). IR ν_{max}/cm^{-1}: 2904*s*, 2848*m*, 1633*w*, 1443*w*, 1361*w*, 1274*m*, 1251*m*, 1041*m*, 885*w*, 850*w*. ^{1}H NMR (400 MHz, $CDCl_3$/C_6D_6): δ 2.98–2.83 (*m*, 6H), 2.30–2.13 (*m*, 15H), 2.07 (*s*, 3H), 1.95–1.76 (*m*, 3H), 1.69–1.54 (*m*, 9H). ^{13}C NMR (101 MHz, $CDCl_3$/C_6D_6): δ 151.9 (C), 124.8 (C), 121.6 (C), 89.7 (C), 66.6 (C), 42.2 (CH_2), 41.3 (CH_2), 36.1 (CH_2), 36.0 (CH_2), 31.8 (CH), 30.7 (CH), 16.0 (CH_3), 10.5 (CH_3). ^{77}Se NMR (114 MHz, $CDCl_3$): δ 201.2. ^{15}N NMR (41 MHz, $CDCl_3$): δ −154 (***N***–OR), −192 (***N***–R). HRMS (ESI+): calcd for $C_{25}H_{36}N_2NaOSe^+$ [M+Na$^+$] = 483.1885; found 483.1882.

7. NMR Spectra

Figure S1 ^{1}H NMR of 3 (400 MHz, $CDCl_3$)

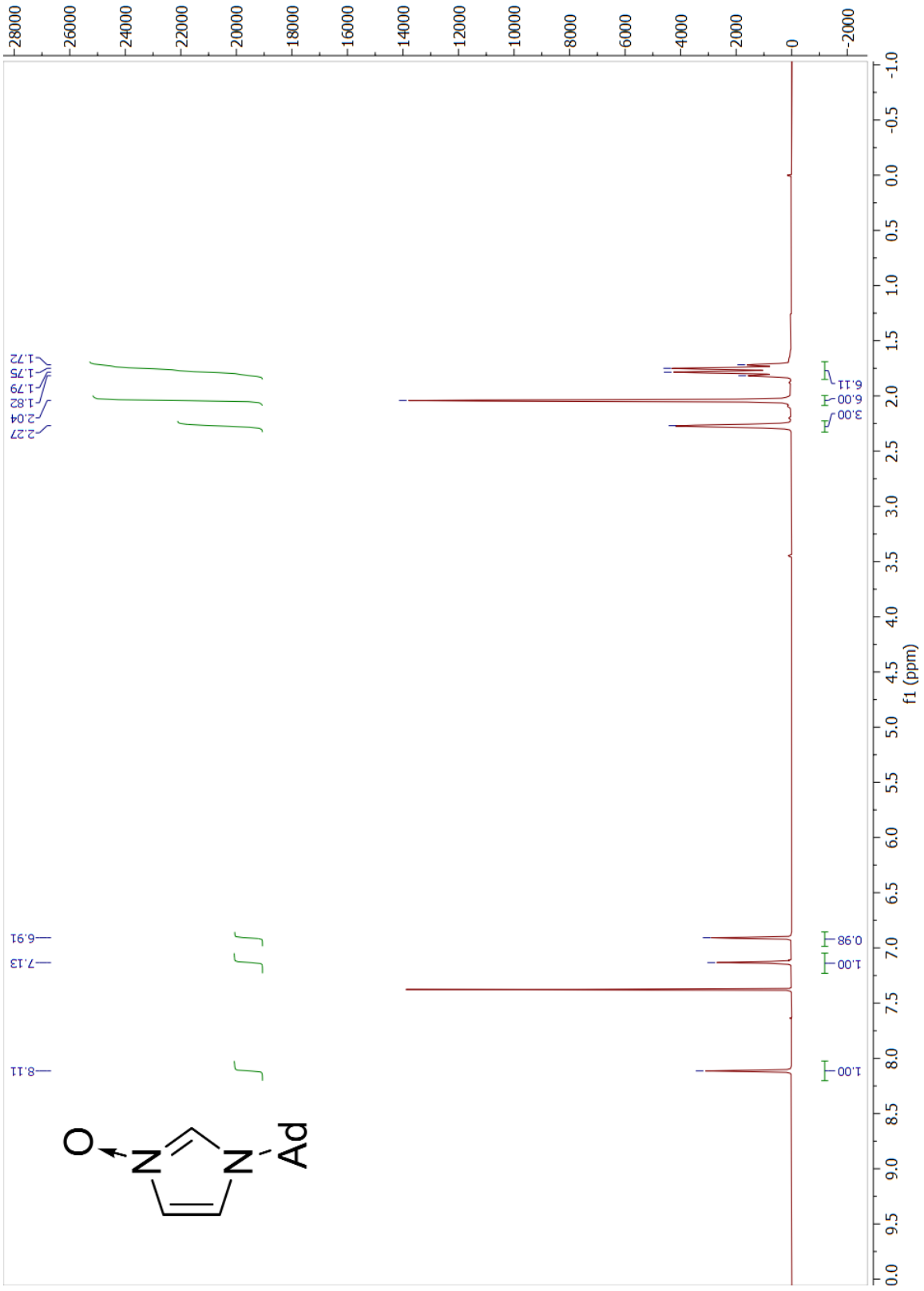


Figure S2 ^{13}C NMR of 3 (101 MHz, $CDCl_3$)

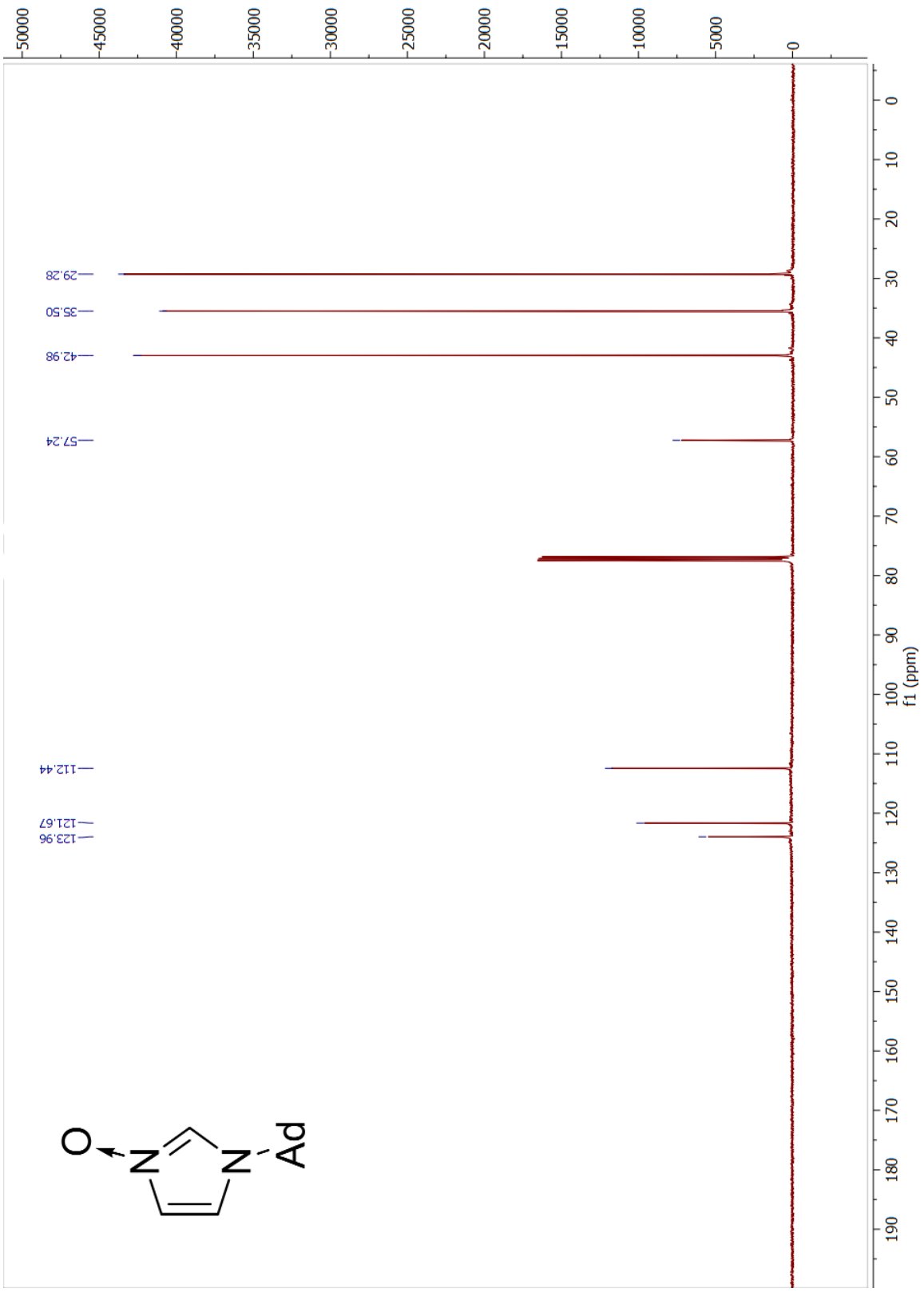


Figure S3 ^{1}H NMR of 6 (400 MHz, $CDCl_3$)

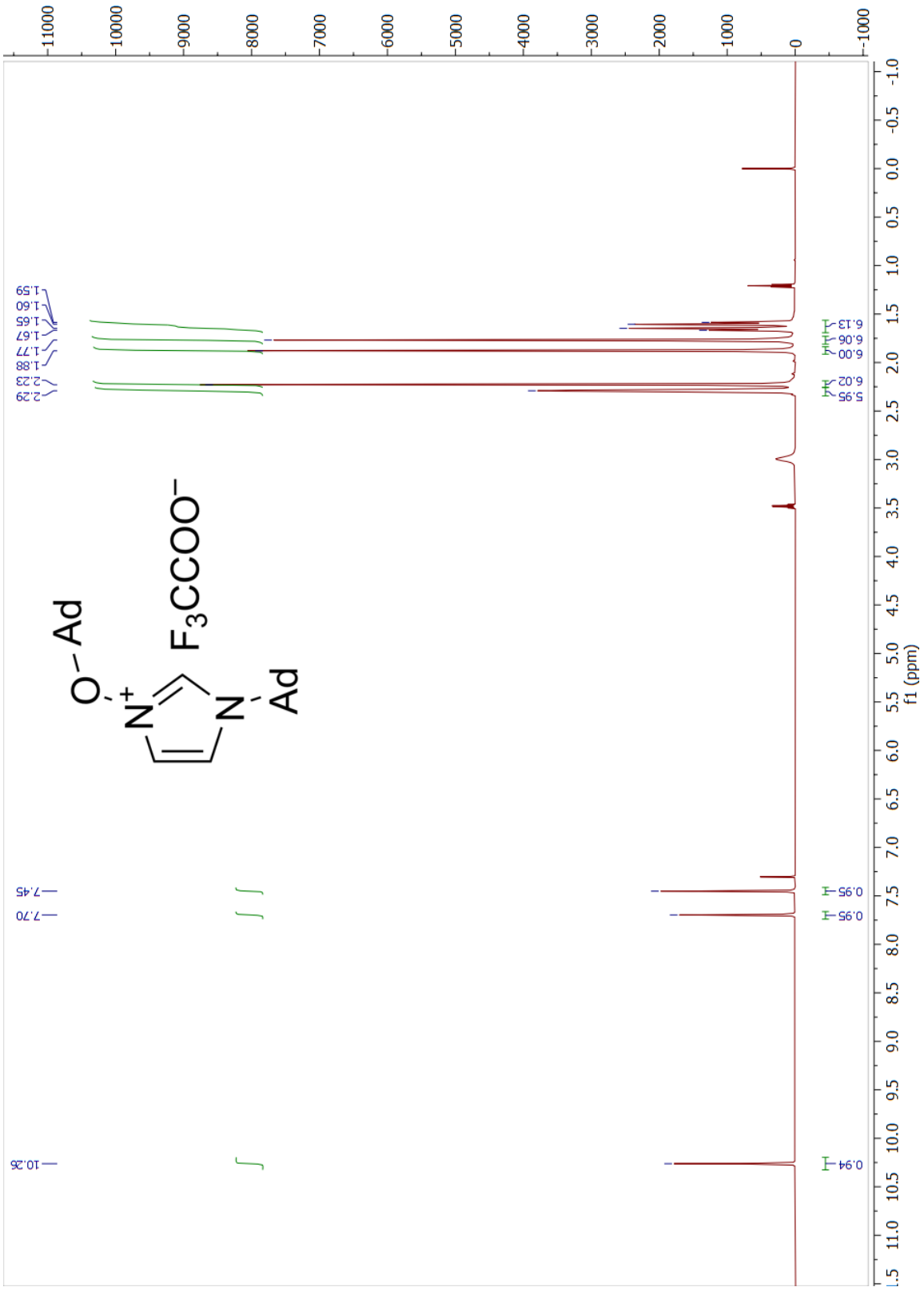


Figure S4 ^{13}C NMR of 6 (101 MHz, $CDCl_3$)

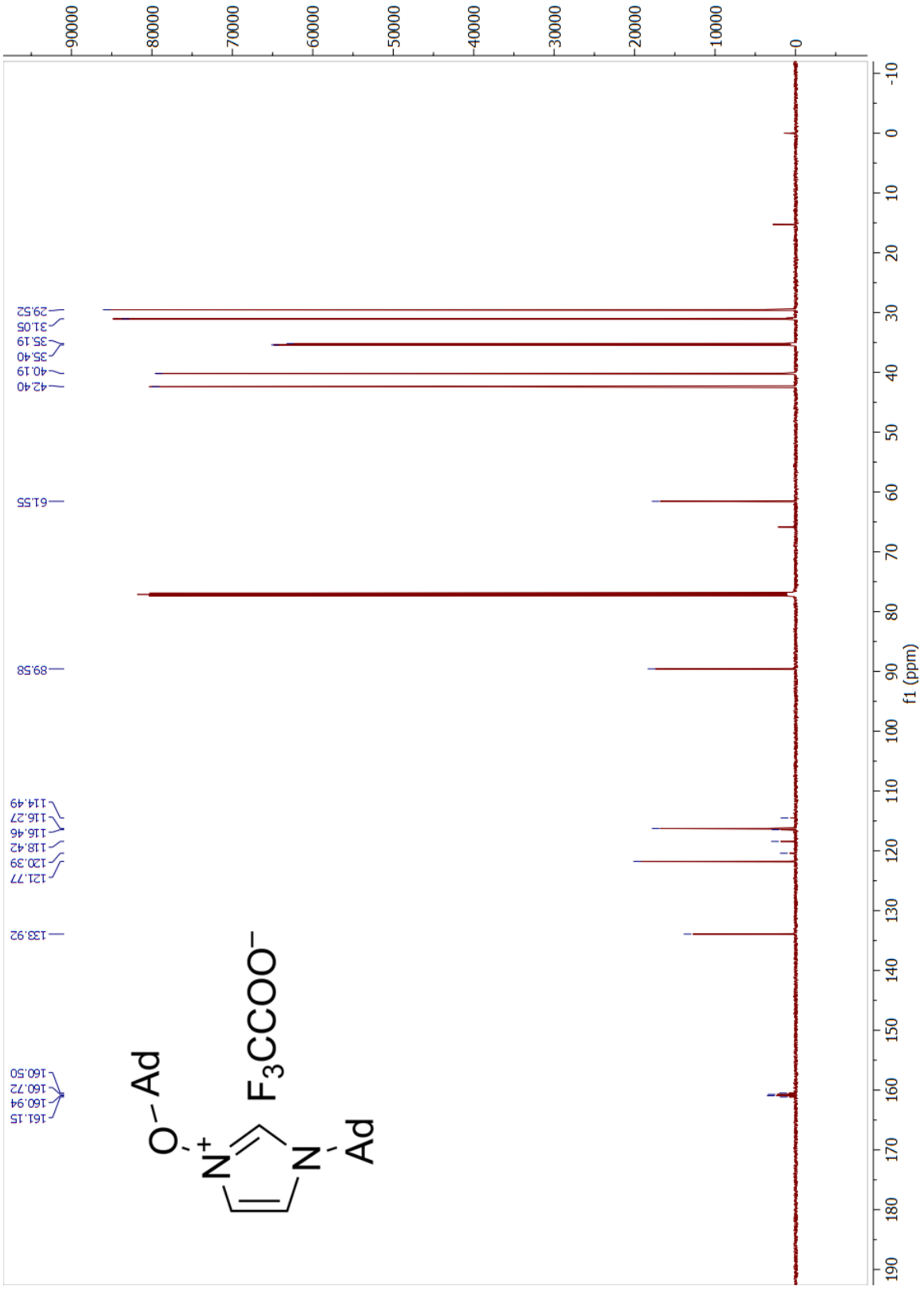


Figure S5 ^{1}H NMR of 9 (600 MHz, $CDCl_3$)

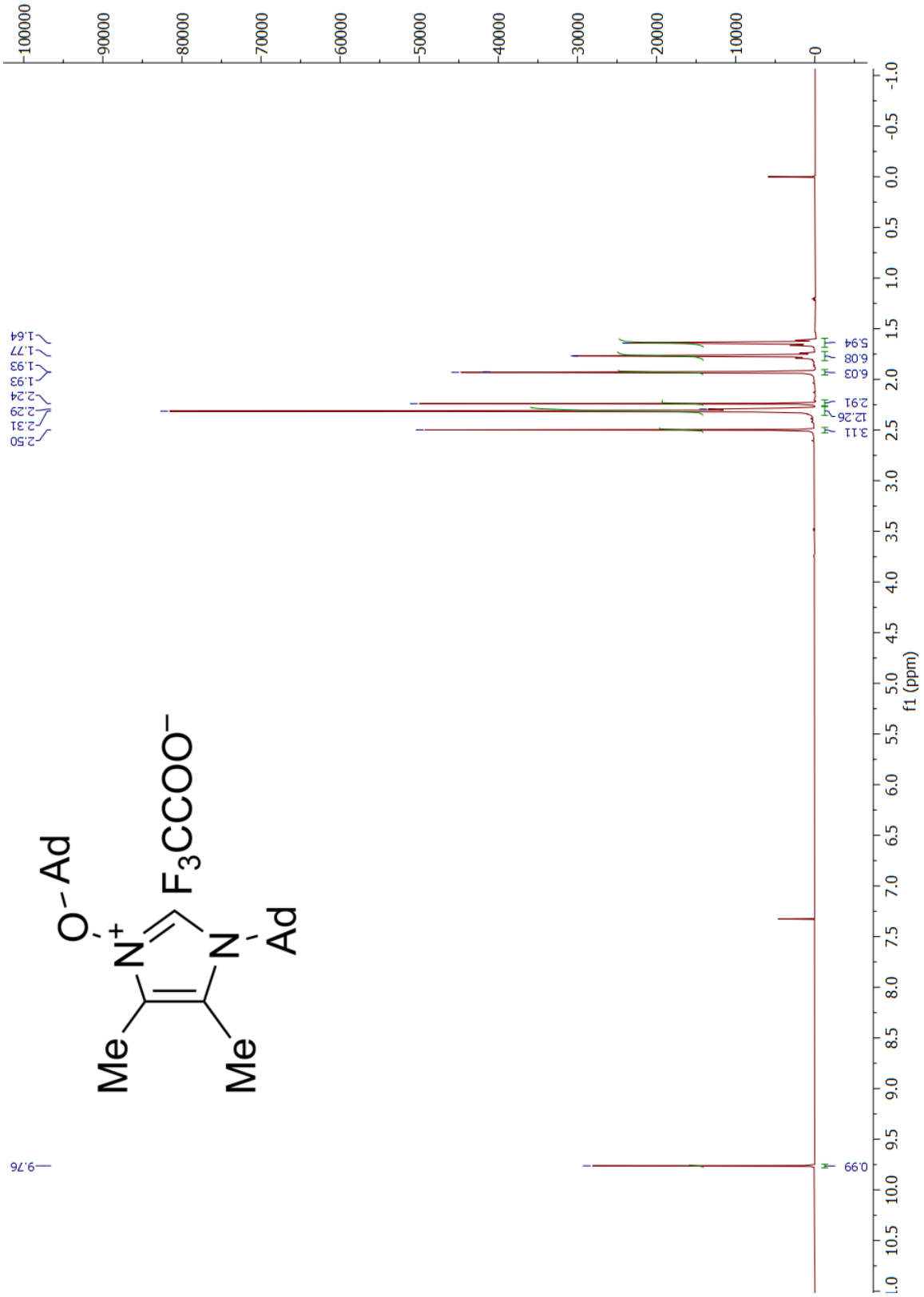


Figure S6 ^{13}C NMR of 9 (101 MHz, $CDCl_3$)

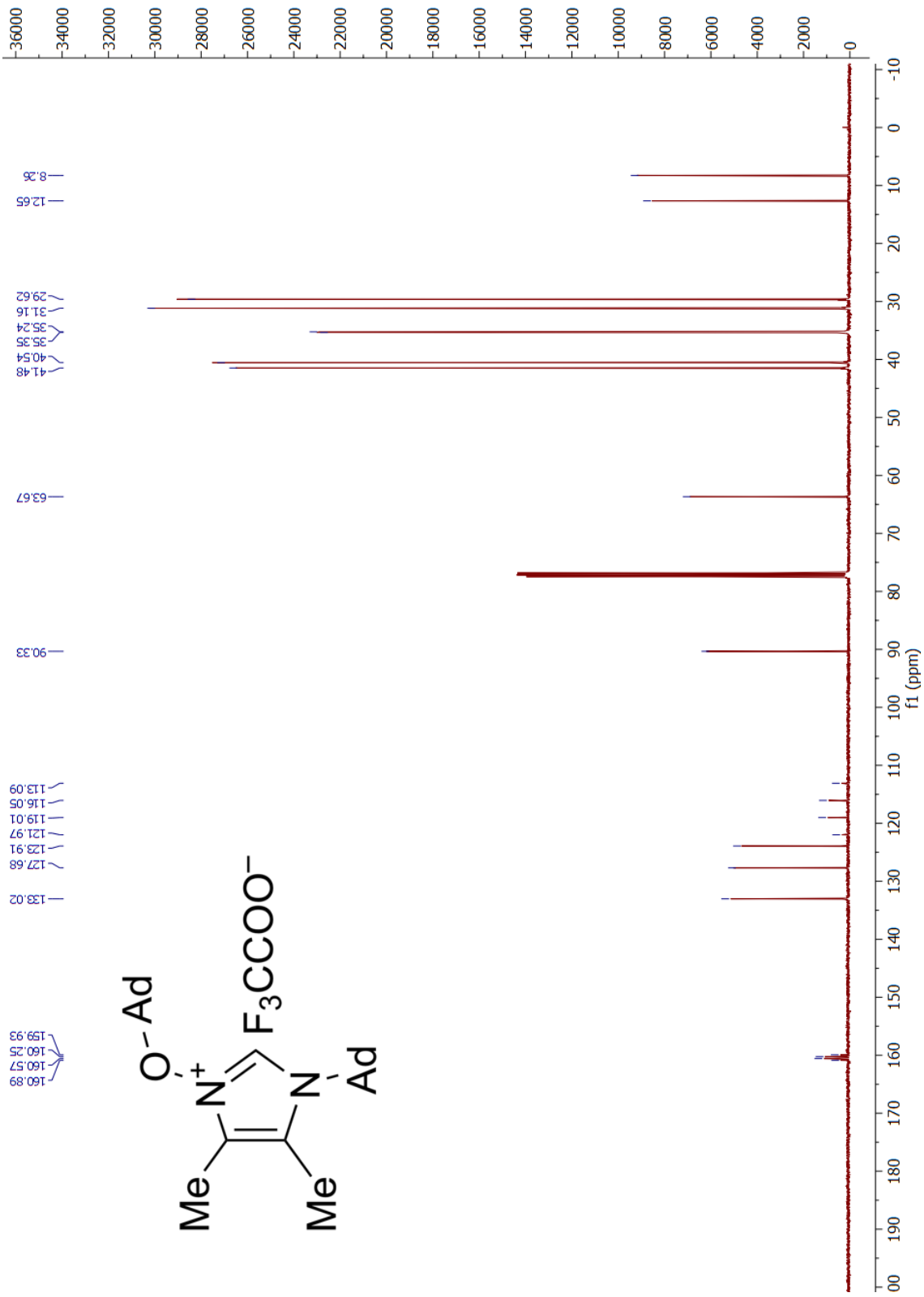


Figure S7 ^{1}H NMR of 4 (600 MHz, C_4H_8O)

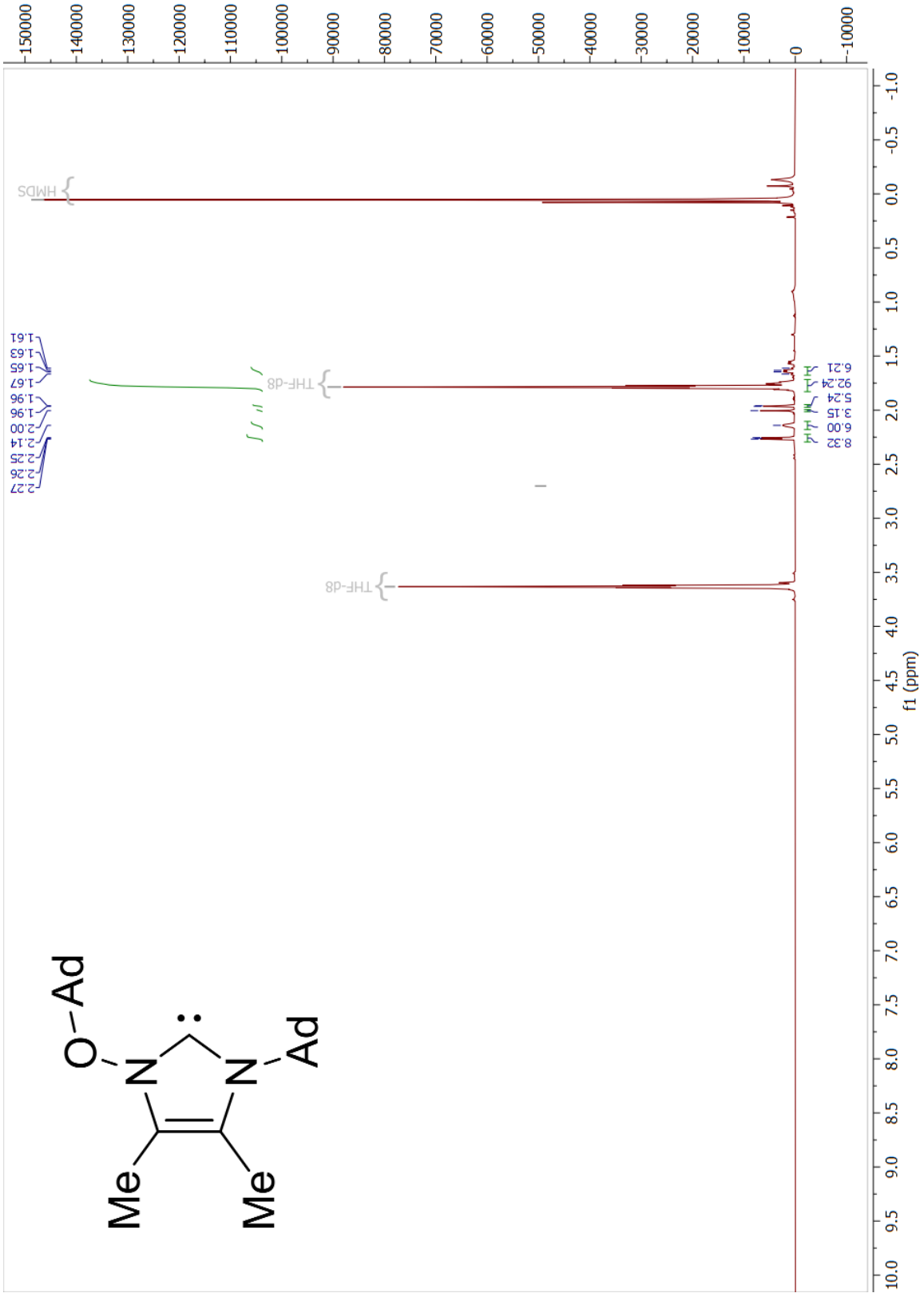


Figure S8 ^{13}C NMR of 4 (151 MHz, C_4H_8O)

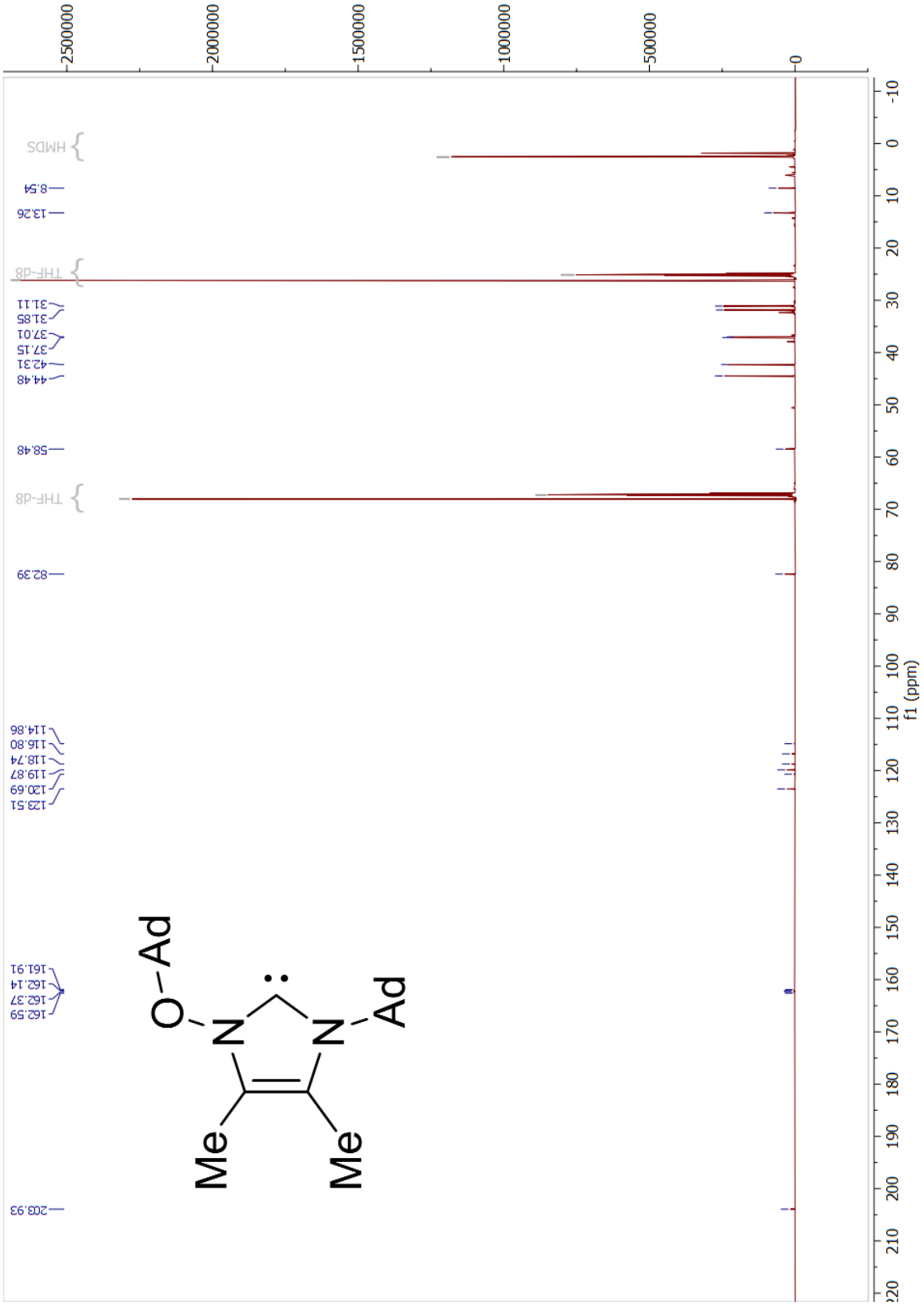


Figure S9 ^{1}H NMR of 10 (400 MHz, $CDCl_3$)

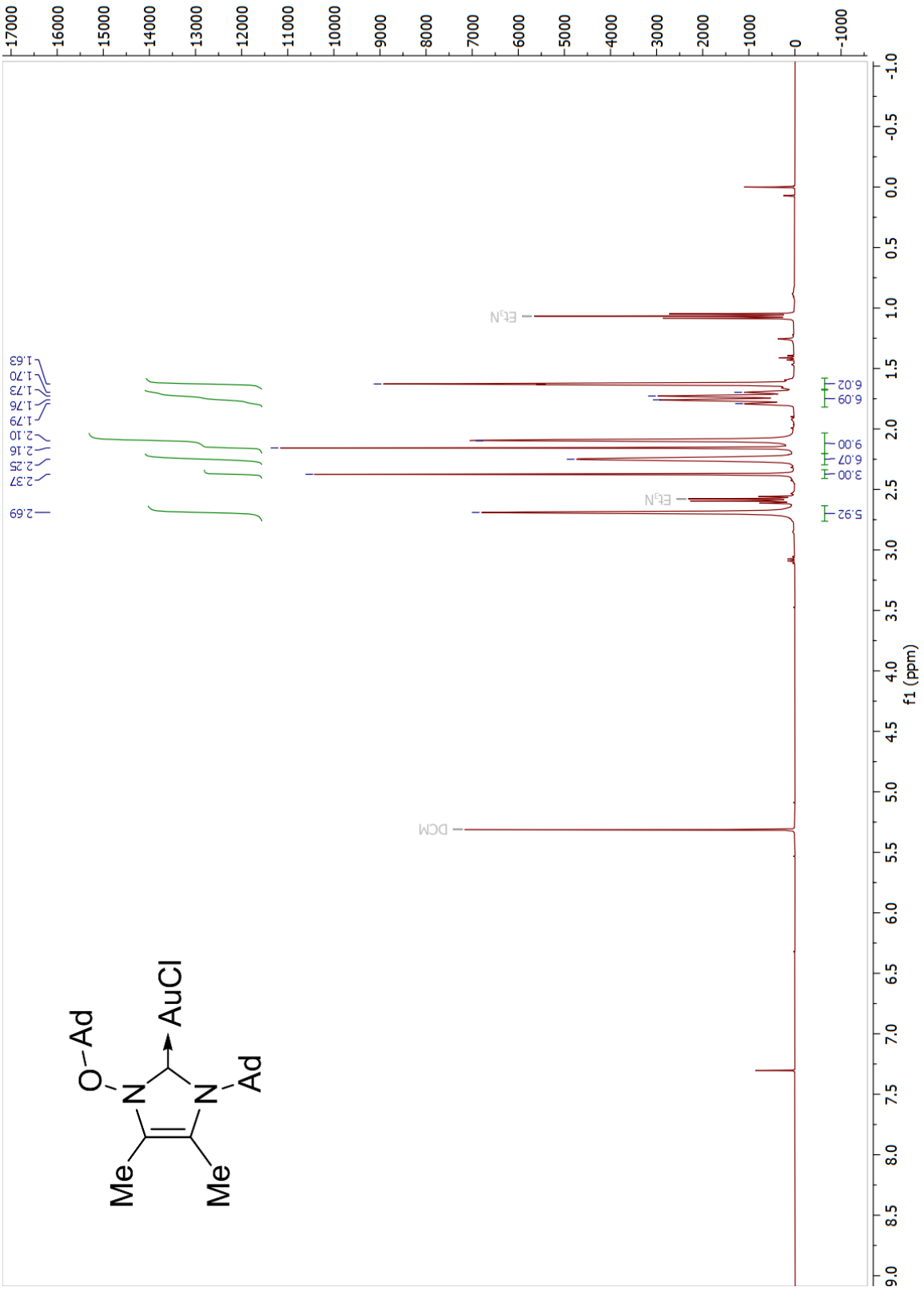


Figure S10 ^{13}C NMR of 10 (101 MHz, $CDCl_3$)

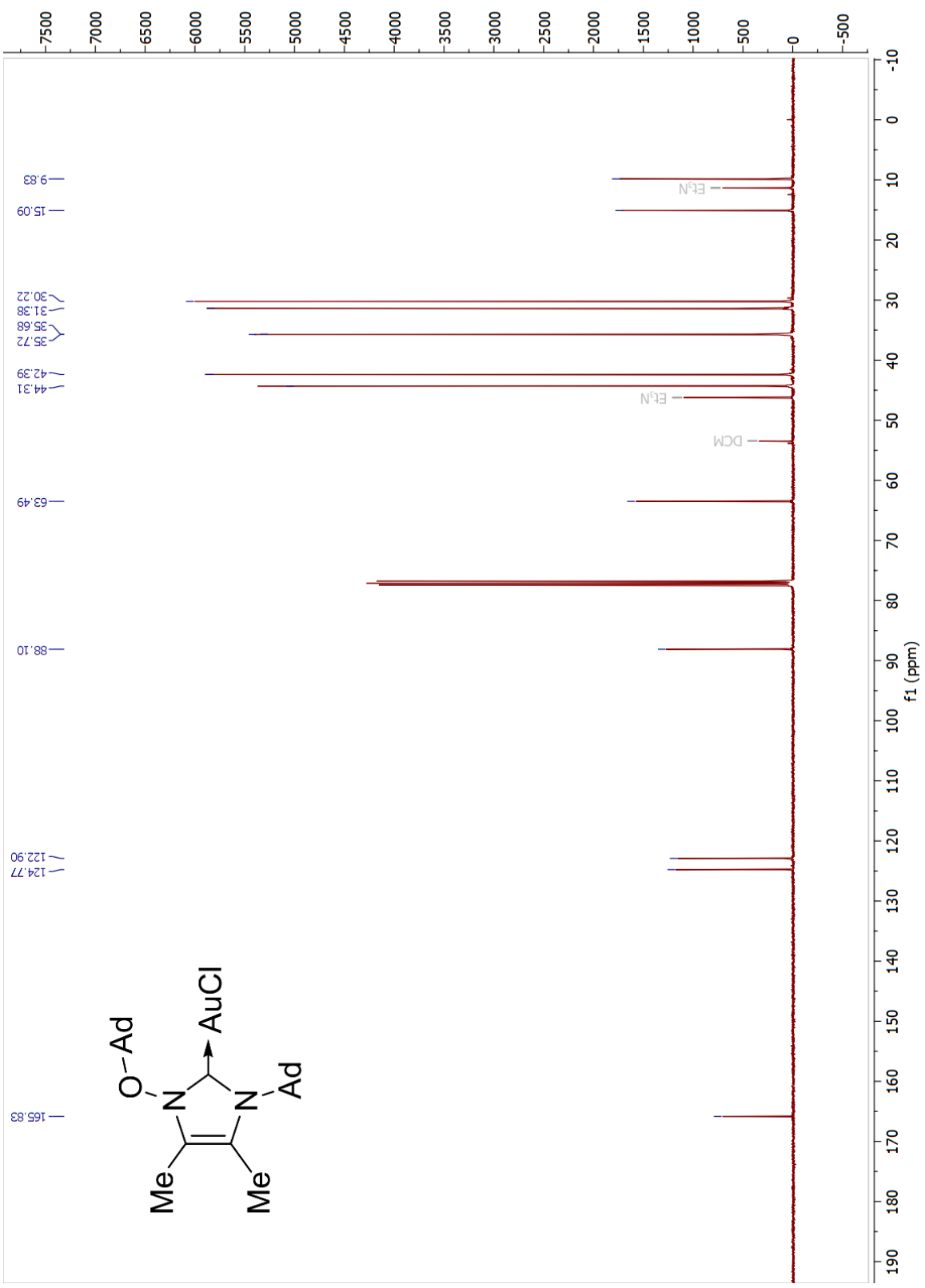


Figure S11 ^{1}H NMR of 11 (400 MHz, $CDCl_3$)

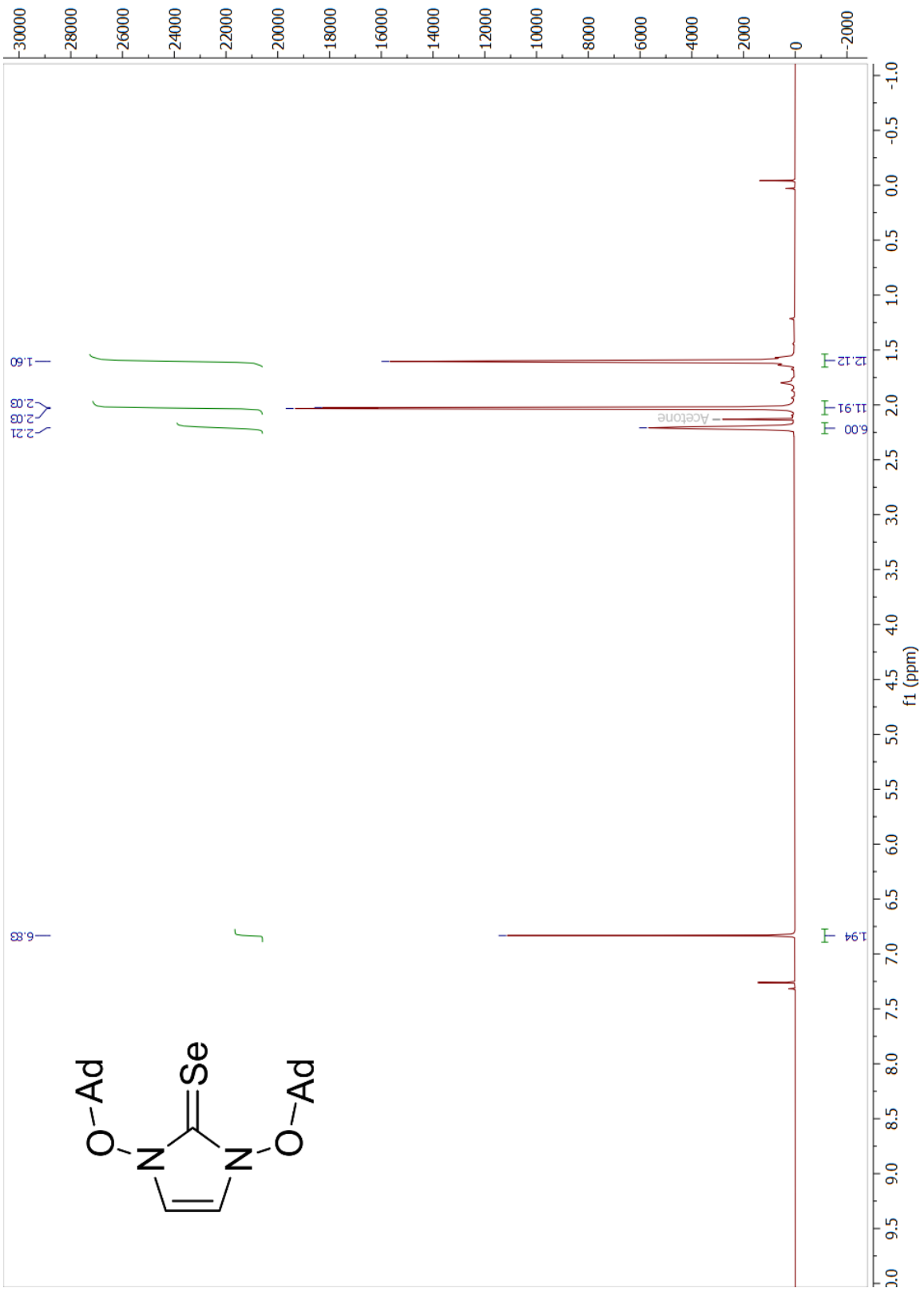


Figure S12 ^{13}C NMR of 11 (101 MHz, $CDCl_3$)

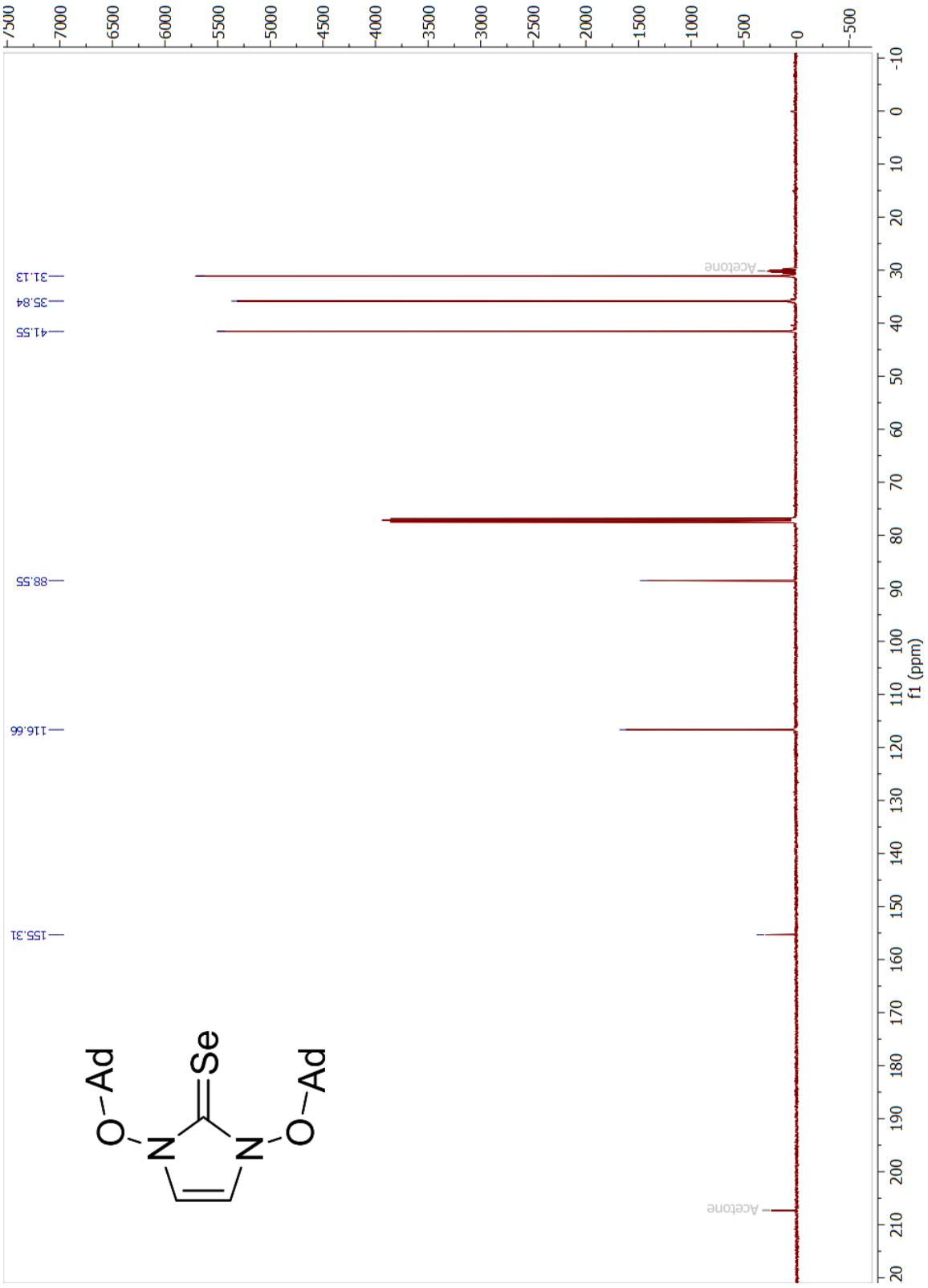


Figure S13 ^{77}Se NMR of 11 (114 MHz, $CDCl_3$)

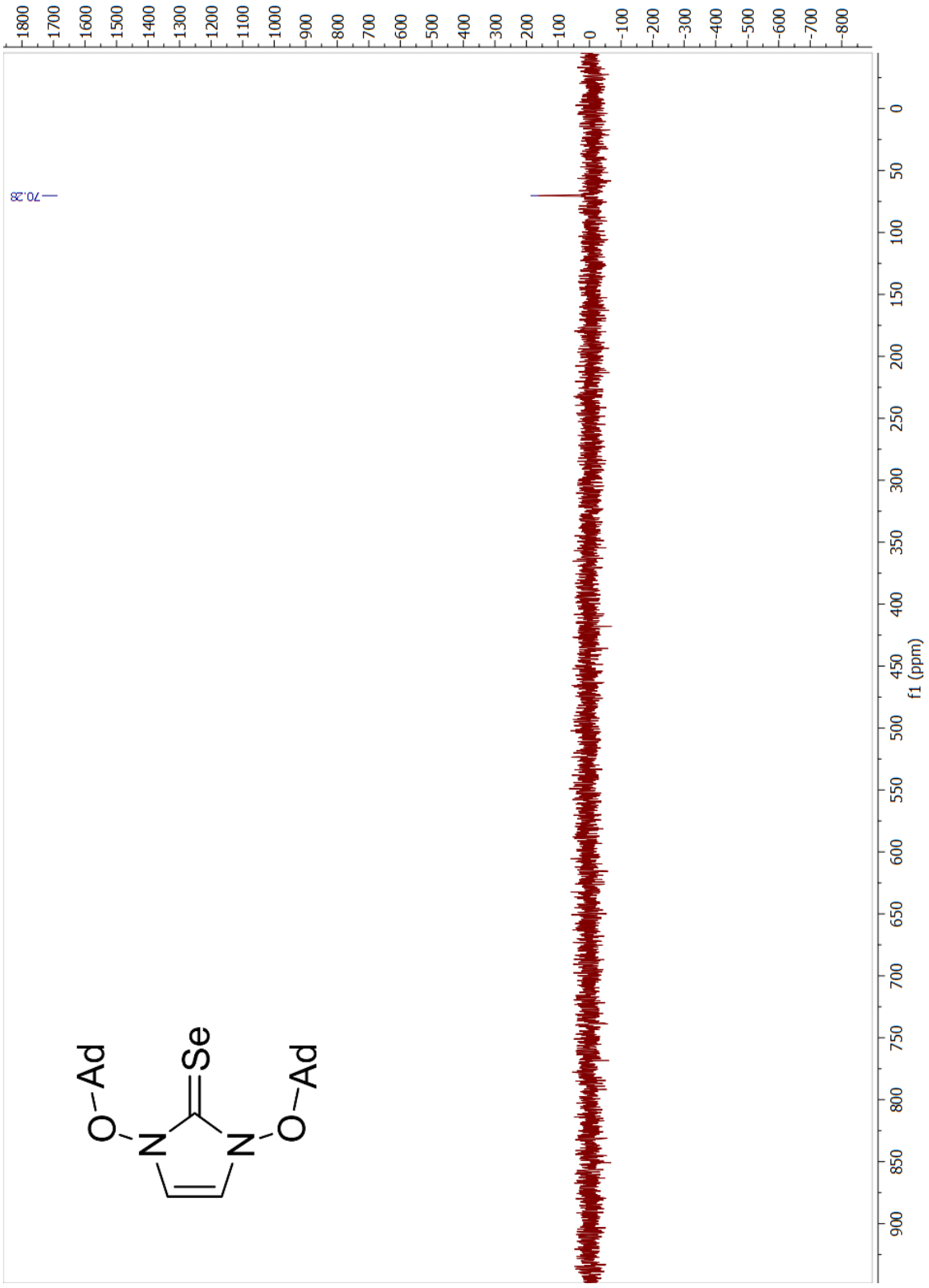


Figure S14 ^{1}H NMR of 12 (600 MHz, $CDCl_3$)

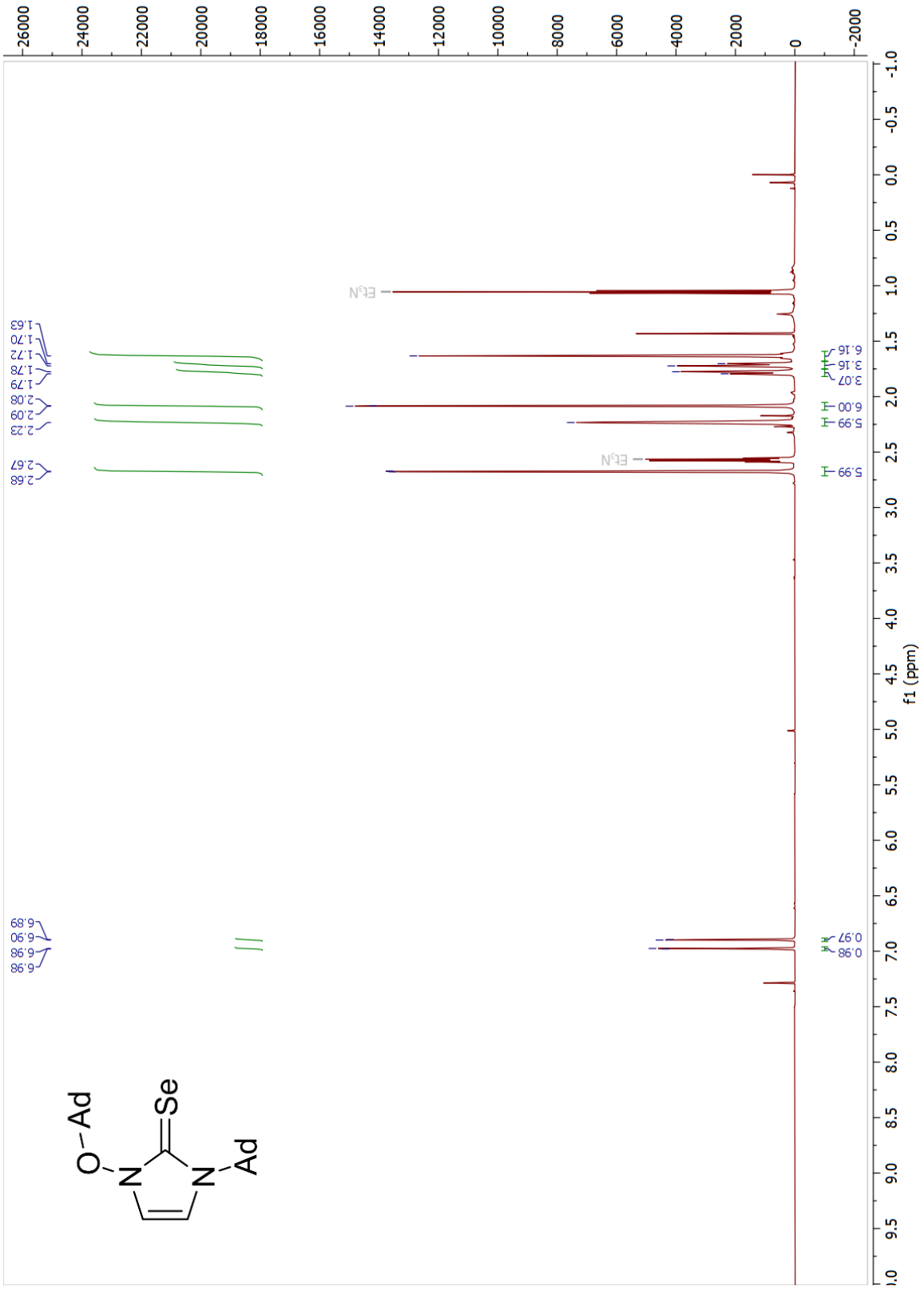


Figure S15 ^{13}C NMR of 12 (151 MHz, $CDCl_3$)

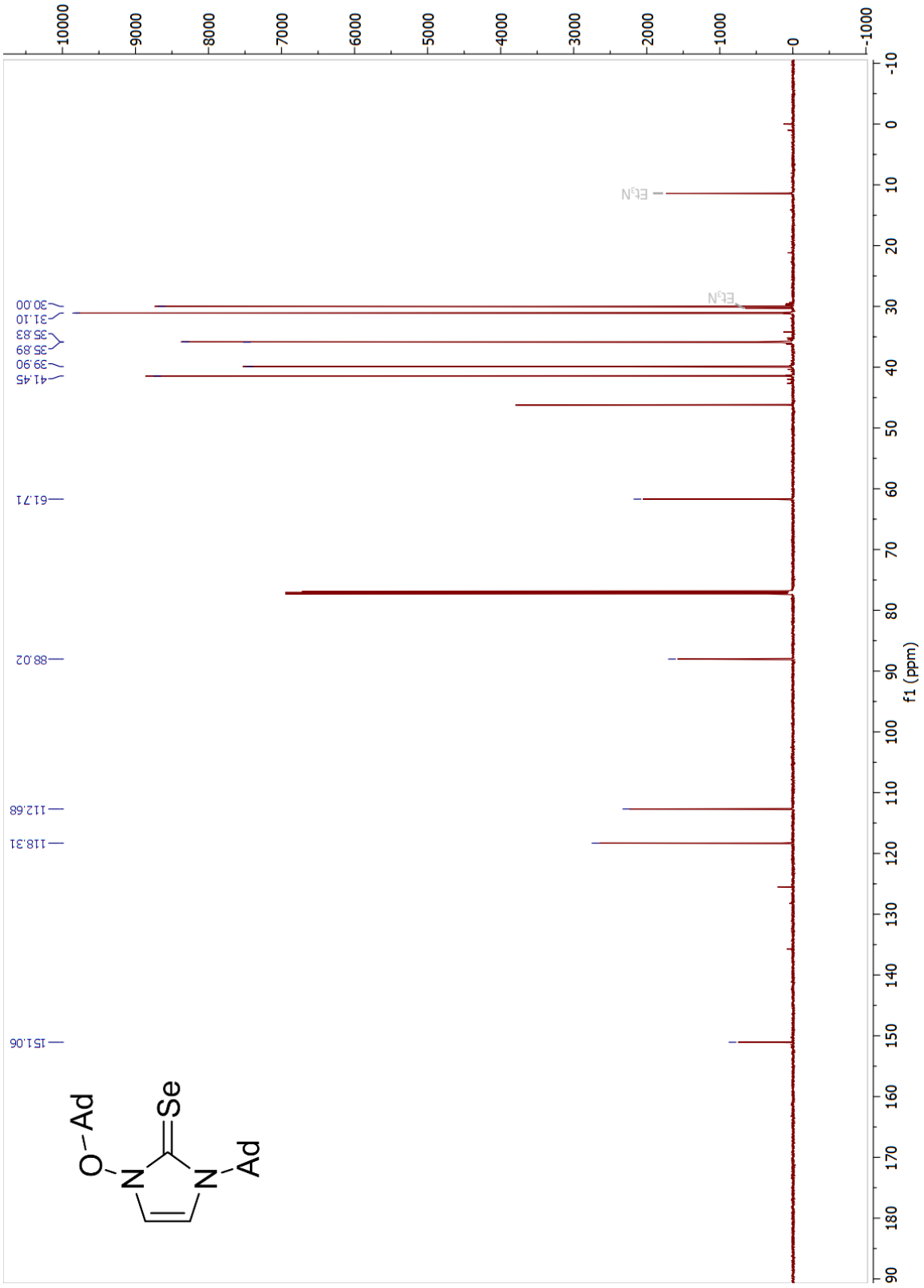


Figure S16 ^{77}Se NMR of 12 (114 MHz, $CDCl_3$)

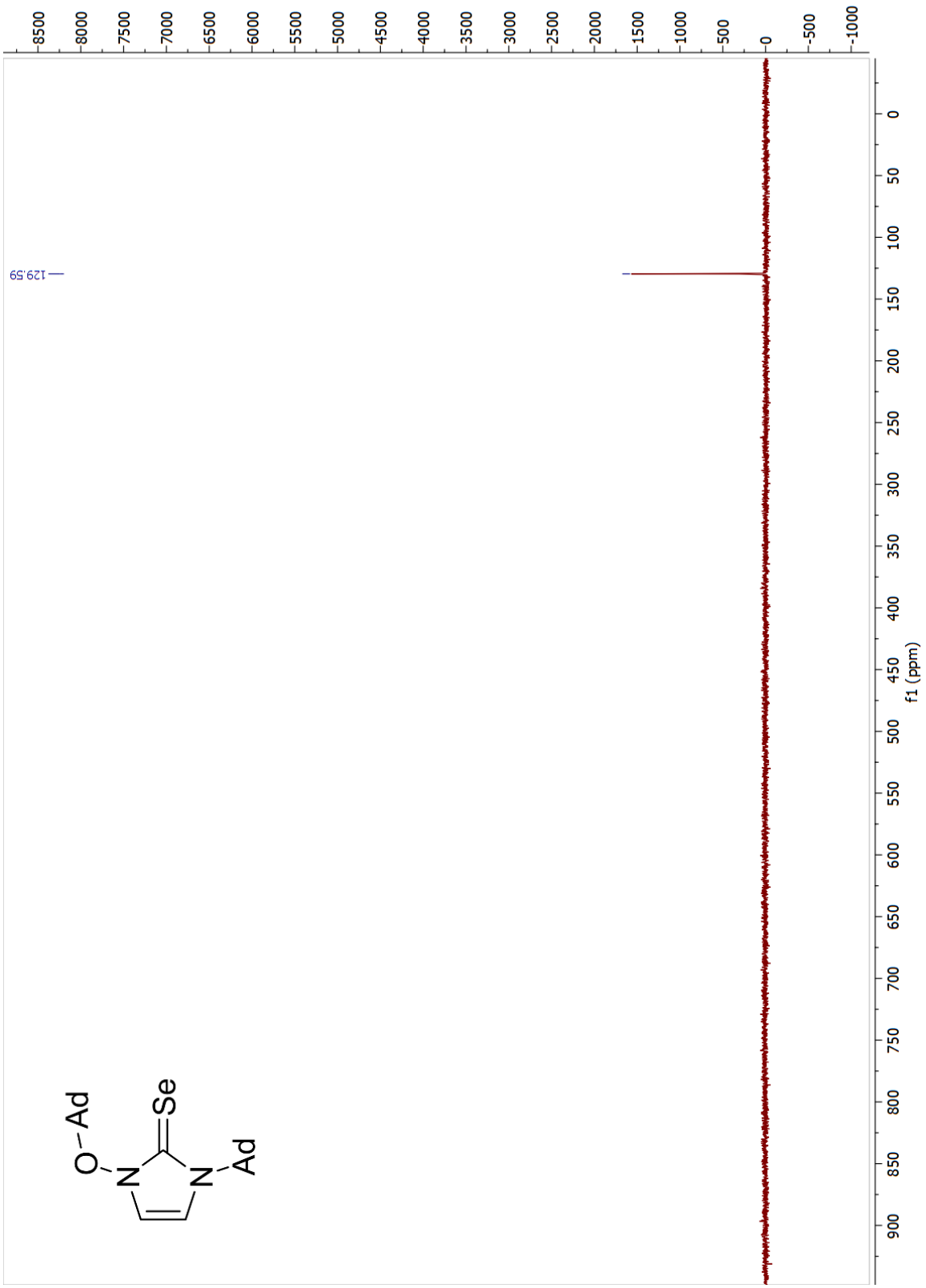


Figure S17 ^{1}H NMR of 13 (400 MHz, $CDCl_3/C_6D_6$)

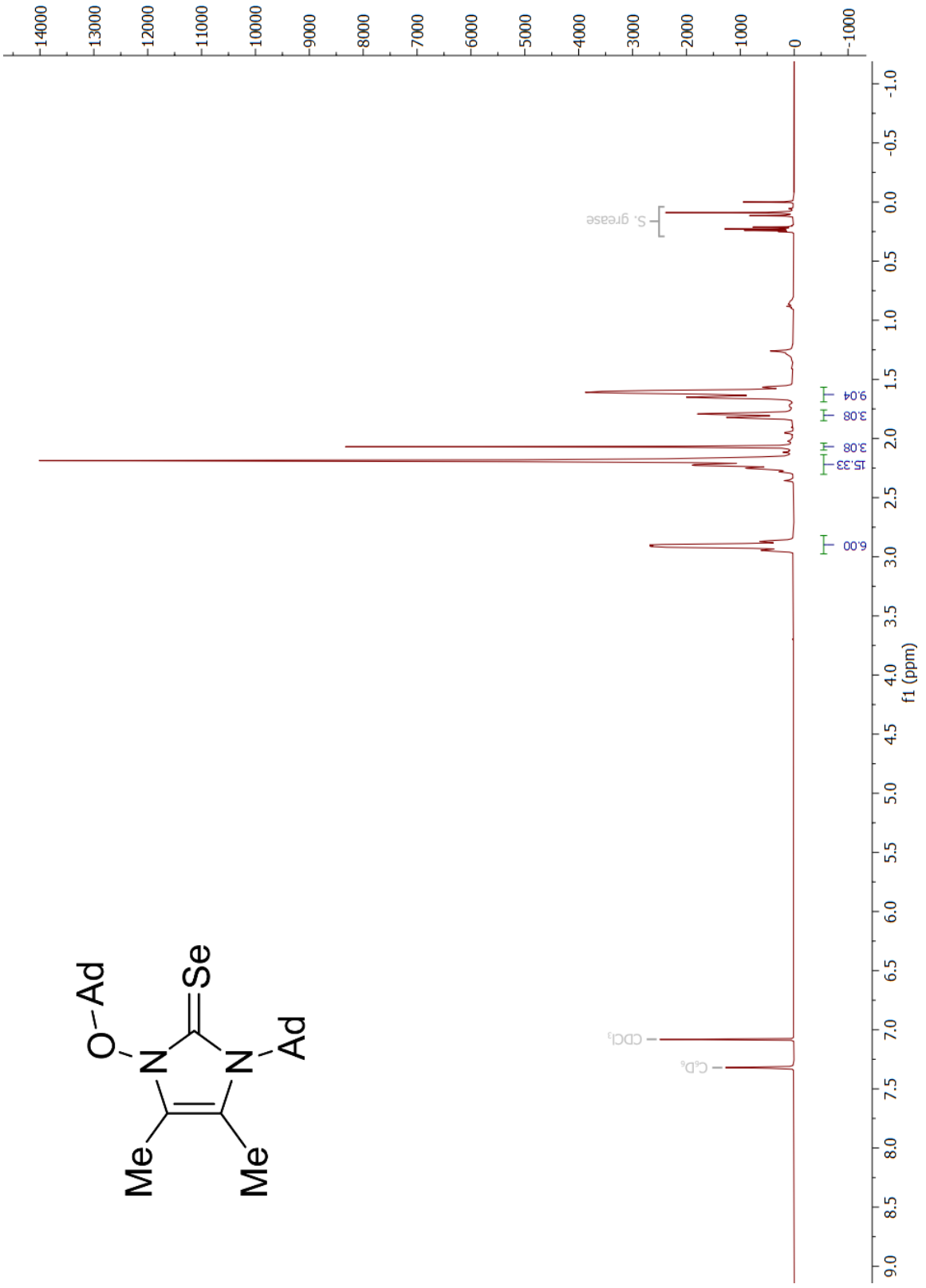


Figure S18 ^{13}C NMR of 13 (101 MHz, $CDCl_3/C_6D_6$)

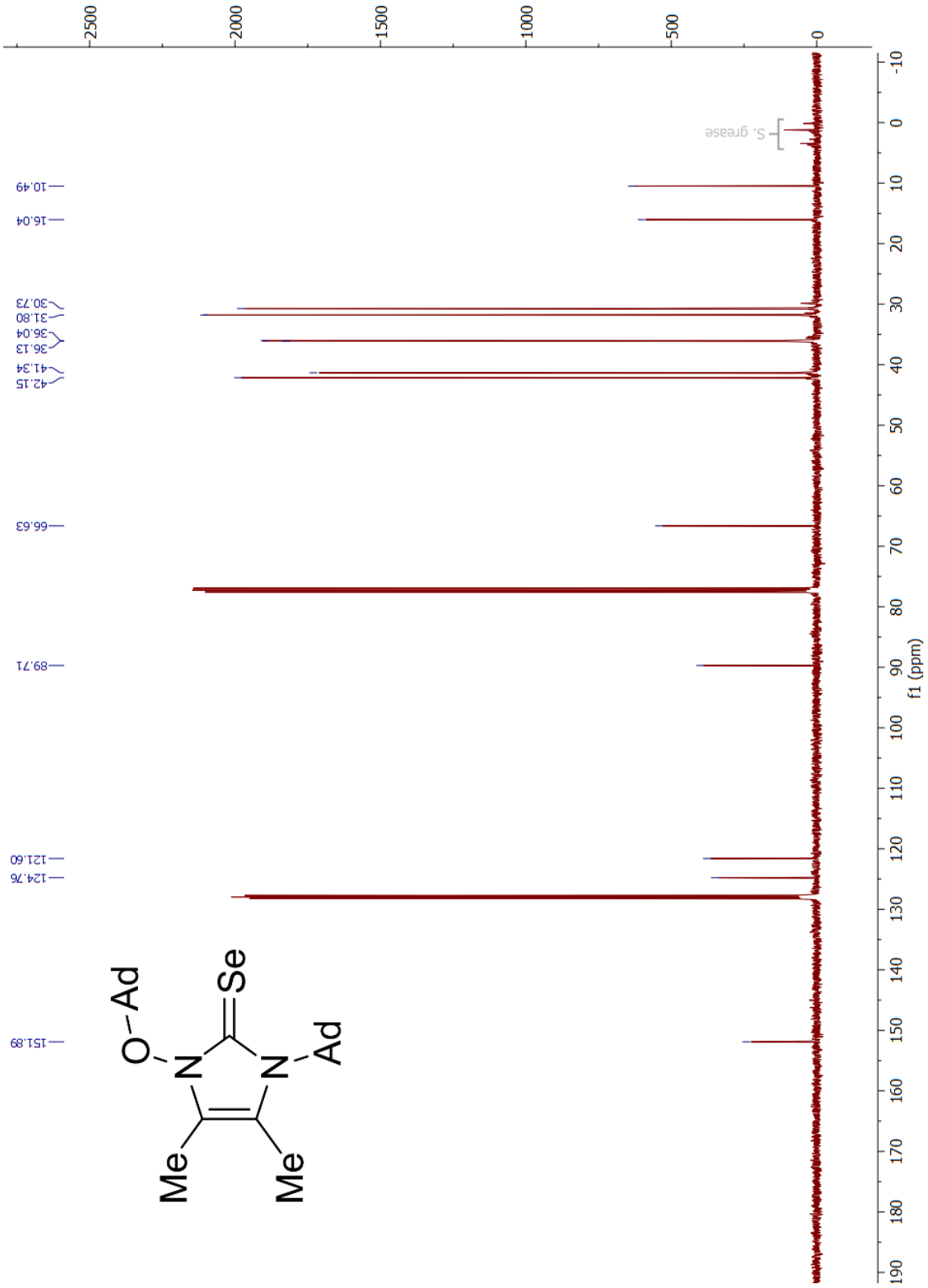
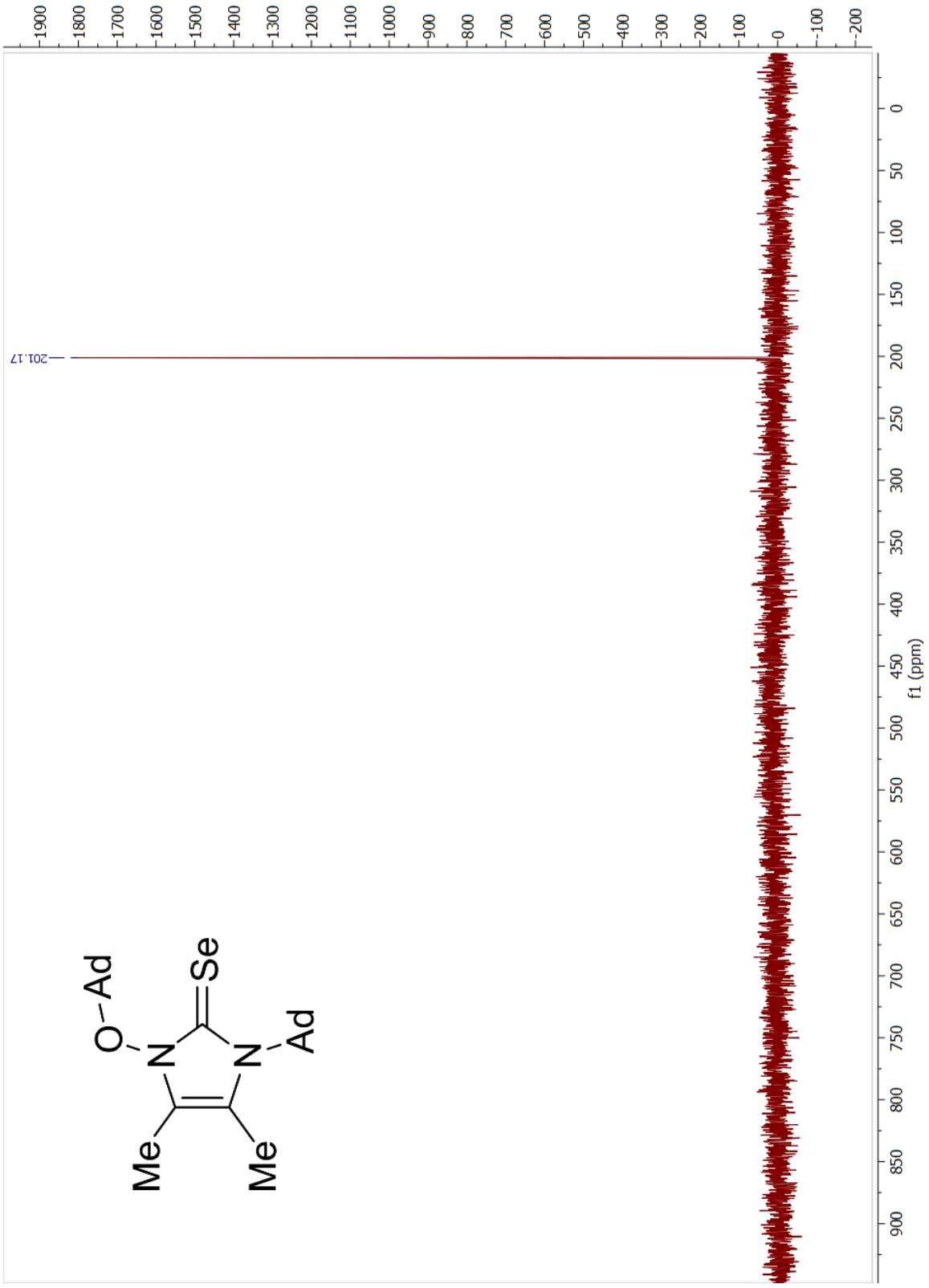


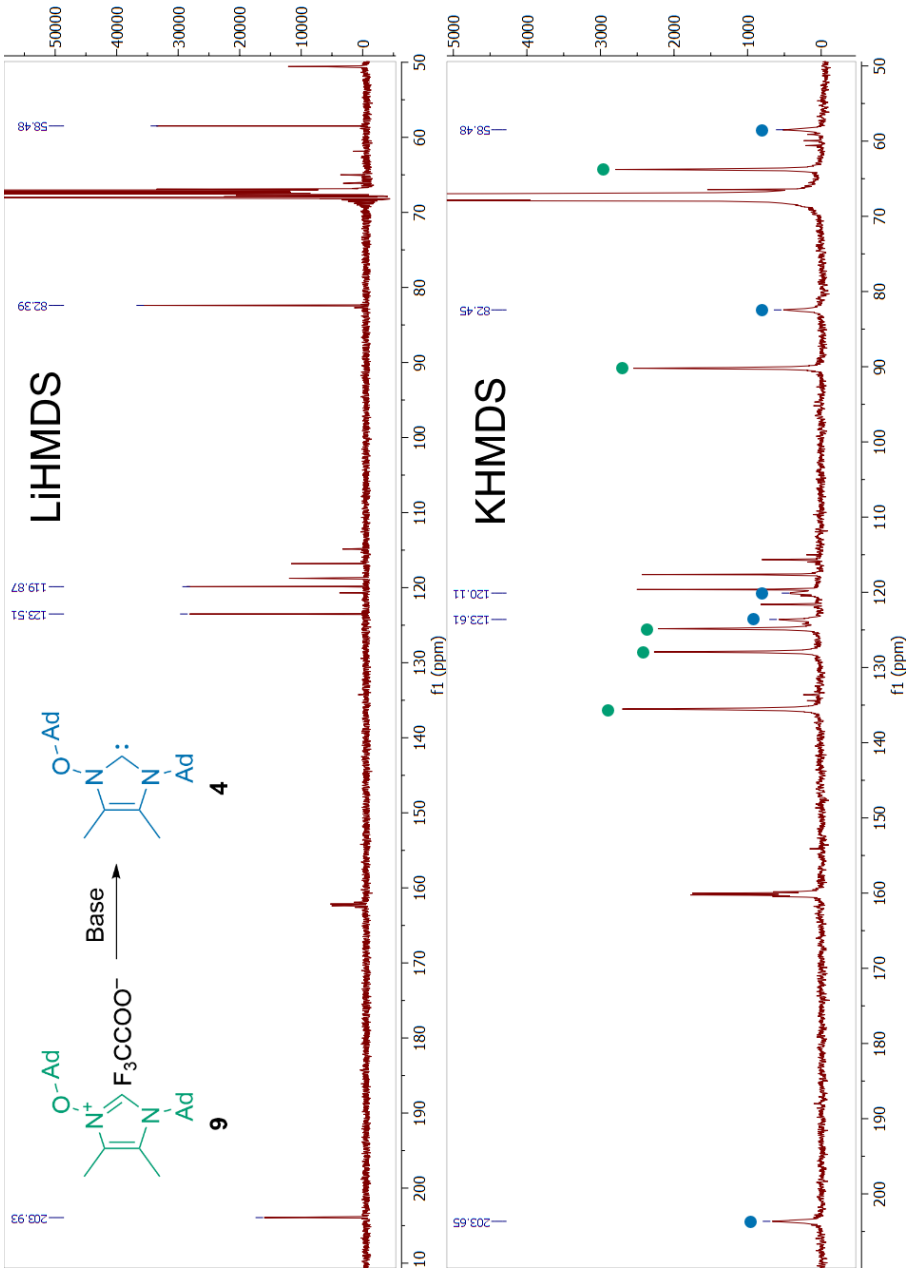
Figure S19 ^{77}Se NMR of 13 (114 MHz, $CDCl_3$)



8. Comparison of bases for the deprotonation of 9 to generate free carbene 4

To further corroborate the formation of free carbene **4**, we reacted imidazolium salt **9** with neat KHMDS (0.95 equiv.) in dry THF-d8 under N_2 at −78 °C and gradually warmed the reaction mixture to −10 °C within 30 min, followed by rapid cooling to −78 °C, filtering, and transferring to a sealed NMR tube. The ^{13}C NMR spectrum was measured at −20 °C and compared to the spectrum obtained by deprotonation with LiHMDS. The shifts are the same considering the line broadening caused by the lower temperature and the low concentration of the analyzed material in case of deprotonation with KHMDS. Upon reaching rt, the reaction mixture containing KHMDS showed almost complete decomposition.

Figure S20 ^{13}C NMR spectra comparison of 4 generated with different bases (114 MHz, THF-d8)



(The spectrum is truncated for clarity)

9. Crystallographic data collection and refinement details

Diffraction data for **10** were collected at low temperatures (100 K) using ϕ- and ω-scans on a BRUKER D8 Venture System equipped with dual IμS microfocus sources, a PHOTON100 detector and an OXFORD CRYOSYSTEMS 700 low temperature system. Mo-Kα radiation with a wavelength of 0.71073 Å and a collimating Quazar multilayer mirror were used. Semi-empirical absorption corrections from equivalents were applied using SADABS.[3] The structure was solved in the monoclinic space group $P2_1/c$ by direct methods using SHELXT[4] and refined as non-merohedral twin against F^2 on all data by full-matrix least squares using SHELXL.[5] The twin ratio was allowed to refine freely and converged to 0.3004(8). All nonhydrogen atoms were refined anisotropically and hydrogen atoms were positioned at geometrically calculated positions and refined using a riding model. The isotropic displacement parameters of all hydrogen atoms were fixed to 1.2x or 1.5x (CH_3 hydrogens) the U_{eq} value of the atoms they are linked to. The asymmetric unit contains one full molecule. All crystallographic data were deposited with the Cambridge Crystallographic Database as 2098148 and can be obtained free of charge.

Table S1. Crystal data and structure refinement for **10**.

CCDC No	2098148	
Empirical formula	C_{25} H_{36} Au Cl N_2 O	
Formula weight	612.97	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions	a = 13.6464(10) Å	α= 90°
	b = 15.4879(12) Å	β= 108.520(2)°
	c = 11.0636(8) Å	γ = 90°
Volume	2217.2(3) Å^3	
Z	4	
Density (calculated)	1.836 Mg/m^3	
Absorption coefficient	6.776 mm^{-1}	
F(000)	1216	
Crystal size	0.177 x 0.172 x 0.053 mm^3	
Theta range for data collection	2.345 to 30.616°.	
Index ranges	-19 ≤ h ≤ 18, 0 ≤ k ≤ 21, 0 ≤ l ≤ 15	
Reflections collected	6746	
Independent reflections	6746 (merged data)	
Completeness to theta = 25.242°	99.9%	
Absorption correction	Semi-empirical from equivalents	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	6746 / 0 / 274	
Goodness-of-fit on F^2	1.046	
Final R indices [I>2σ(I)]	R1 = 0.0418, wR2 = 0.0739	
R indices (all data)	R1 = 0.0730, wR2 = 0.0821	
Largest diff. peak and hole	2.501 and −1.739 e.Å^{-3}	

Table S2. Atomic coordinates *(× 10^4)* and equivalent isotropic displacement parameters *(Å^2 × 10^3)* for **10**. *U(eq)* is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Au(1)	5198(1)	6480(1)	5302(1)	16(1)
Cl(1)	5212(1)	7450(1)	3751(1)	22(1)
O(1)	7025(3)	5308(2)	7111(4)	18(1)
N(1)	6070(4)	5164(3)	7263(5)	17(1)
N(2)	4475(4)	5267(3)	7093(5)	18(1)
C(1)	5209(5)	5613(3)	6653(5)	17(1)
C(2)	5906(5)	4508(4)	8011(6)	20(1)
C(3)	4917(5)	4566(3)	7936(5)	17(1)
C(4)	6695(5)	3840(4)	8626(6)	22(1)
C(5)	4384(5)	3993(4)	8627(6)	26(1)
C(11)	7699(5)	5926(4)	8049(6)	18(1)
C(12)	7497(5)	5968(4)	9323(6)	21(1)
C(13)	8294(5)	6565(4)	10203(6)	21(1)
C(14)	9382(5)	6225(4)	10385(7)	27(2)
C(15)	9580(5)	6185(4)	9105(7)	29(2)
C(16)	8772(5)	5587(4)	8196(6)	25(1)
C(17)	7569(5)	6835(4)	7445(6)	21(1)
C(18)	8389(5)	7430(4)	8349(6)	22(1)
C(19)	8202(5)	7477(4)	9617(6)	24(1)
C(20)	9466(5)	7084(4)	8505(7)	27(1)
C(21)	3357(4)	5529(4)	6720(6)	16(1)
C(22)	2673(5)	4810(4)	5955(6)	18(1)
C(23)	1529(5)	5069(4)	5636(6)	21(1)
C(24)	1286(5)	5240(4)	6877(6)	26(1)
C(25)	1952(5)	5988(4)	7614(6)	23(1)
C(26)	3100(4)	5751(4)	7951(6)	19(1)
C(27)	3150(5)	6354(3)	5897(6)	19(1)
C(28)	2014(5)	6613(4)	5562(6)	21(1)
C(29)	1324(5)	5889(4)	4819(6)	24(1)
C(30)	1736(5)	6805(4)	6780(6)	24(1)

Table S3. Bond lengths *(Å)* and angles *(°)* for **10**.

Au(1)-C(1)	2.005(5)	C(16)-H(16B)	0.9900
Au(1)-Cl(1)	2.2847(13)	C(17)-C(18)	1.546(8)
O(1)-N(1)	1.385(6)	C(17)-H(17A)	0.9900
O(1)-C(11)	1.495(7)	C(17)-H(17B)	0.9900
N(1)-C(1)	1.348(8)	C(18)-C(19)	1.505(8)
N(1)-C(2)	1.373(7)	C(18)-C(20)	1.523(9)
N(2)-C(1)	1.356(8)	C(18)-H(18)	1.0000
N(2)-C(3)	1.434(7)	C(19)-H(19A)	0.9900
N(2)-C(21)	1.504(7)	C(19)-H(19B)	0.9900
C(2)-C(3)	1.329(9)	C(20)-H(20A)	0.9900
C(2)-C(4)	1.493(8)	C(20)-H(20B)	0.9900
C(3)-C(5)	1.501(8)	C(21)-C(22)	1.524(8)
C(4)-H(4A)	0.9800	C(21)-C(27)	1.542(8)
C(4)-H(4B)	0.9800	C(21)-C(26)	1.549(8)
C(4)-H(4C)	0.9800	C(22)-C(23)	1.541(9)
C(5)-H(5A)	0.9800	C(22)-H(22A)	0.9900
C(5)-H(5B)	0.9800	C(22)-H(22B)	0.9900
C(5)-H(5C)	0.9800	C(23)-C(29)	1.532(8)
C(11)-C(16)	1.515(8)	C(23)-C(24)	1.534(9)
C(11)-C(12)	1.521(8)	C(23)-H(23)	1.0000
C(11)-C(17)	1.544(8)	C(24)-C(25)	1.537(8)
C(12)-C(13)	1.522(8)	C(24)-H(24A)	0.9900
C(12)-H(12A)	0.9900	C(24)-H(24B)	0.9900
C(12)-H(12B)	0.9900	C(25)-C(26)	1.535(8)
C(13)-C(14)	1.527(9)	C(25)-C(30)	1.539(9)
C(13)-C(19)	1.543(9)	C(25)-H(25)	1.0000
C(13)-H(13)	1.0000	C(26)-H(26A)	0.9900
C(14)-C(15)	1.525(10)	C(26)-H(26B)	0.9900
C(14)-H(14A)	0.9900	C(27)-C(28)	1.529(9)
C(14)-H(14B)	0.9900	C(27)-H(27A)	0.9900
C(15)-C(20)	1.529(9)	C(27)-H(27B)	0.9900
C(15)-C(16)	1.542(9)	C(28)-C(29)	1.524(8)
C(15)-H(15)	1.0000	C(28)-C(30)	1.540(9)
C(16)-H(16A)	0.9900	C(28)-H(28)	1.0000

C(29)-H(29A)	0.9900	O(1)-C(11)-C(12)	114.7(5)
C(29)-H(29B)	0.9900	C(16)-C(11)-C(12)	111.7(5)
C(30)-H(30A)	0.9900	O(1)-C(11)-C(17)	108.8(5)
C(30)-H(30B)	0.9900	C(16)-C(11)-C(17)	109.7(5)
		C(12)-C(11)-C(17)	109.5(5)
C(1)-Au(1)-Cl(1)	178.76(17)	C(11)-C(12)-C(13)	108.4(5)
N(1)-O(1)-C(11)	114.4(4)	C(11)-C(12)-H(12A)	110.0
C(1)-N(1)-C(2)	113.6(5)	C(13)-C(12)-H(12A)	110.0
C(1)-N(1)-O(1)	124.1(5)	C(11)-C(12)-H(12B)	110.0
C(2)-N(1)-O(1)	122.2(5)	C(13)-C(12)-H(12B)	110.0
C(1)-N(2)-C(3)	109.1(5)	H(12A)-C(12)-H(12B)	108.4
C(1)-N(2)-C(21)	126.5(5)	C(12)-C(13)-C(14)	110.0(5)
C(3)-N(2)-C(21)	124.3(5)	C(12)-C(13)-C(19)	110.0(5)
N(1)-C(1)-N(2)	104.0(4)	C(14)-C(13)-C(19)	108.5(5)
N(1)-C(1)-Au(1)	121.2(4)	C(12)-C(13)-H(13)	109.4
N(2)-C(1)-Au(1)	134.5(5)	C(14)-C(13)-H(13)	109.4
C(3)-C(2)-N(1)	105.6(5)	C(19)-C(13)-H(13)	109.4
C(3)-C(2)-C(4)	130.3(5)	C(15)-C(14)-C(13)	110.1(5)
N(1)-C(2)-C(4)	123.7(6)	C(15)-C(14)-H(14A)	109.6
C(2)-C(3)-N(2)	107.5(5)	C(13)-C(14)-H(14A)	109.6
C(2)-C(3)-C(5)	125.1(5)	C(15)-C(14)-H(14B)	109.6
N(2)-C(3)-C(5)	127.4(6)	C(13)-C(14)-H(14B)	109.6
C(2)-C(4)-H(4A)	109.5	H(14A)-C(14)-H(14B)	108.2
C(2)-C(4)-H(4B)	109.5	C(14)-C(15)-C(20)	110.1(6)
H(4A)-C(4)-H(4B)	109.5	C(14)-C(15)-C(16)	109.2(6)
C(2)-C(4)-H(4C)	109.5	C(20)-C(15)-C(16)	108.1(6)
H(4A)-C(4)-H(4C)	109.5	C(14)-C(15)-H(15)	109.8
H(4B)-C(4)-H(4C)	109.5	C(20)-C(15)-H(15)	109.8
C(3)-C(5)-H(5A)	109.5	C(16)-C(15)-H(15)	109.8
C(3)-C(5)-H(5B)	109.5	C(11)-C(16)-C(15)	109.1(5)
H(5A)-C(5)-H(5B)	109.5	C(11)-C(16)-H(16A)	109.9
C(3)-C(5)-H(5C)	109.5	C(15)-C(16)-H(16A)	109.9
H(5A)-C(5)-H(5C)	109.5	C(11)-C(16)-H(16B)	109.9
H(5B)-C(5)-H(5C)	109.5	C(15)-C(16)-H(16B)	109.9
O(1)-C(11)-C(16)	102.3(4)	H(16A)-C(16)-H(16B)	108.3

C(11)-C(17)-C(18)	107.6(5)	H(22A)-C(22)-H(22B)	108.2
C(11)-C(17)-H(17A)	110.2	C(29)-C(23)-C(24)	109.5(5)
C(18)-C(17)-H(17A)	110.2	C(29)-C(23)-C(22)	109.4(5)
C(11)-C(17)-H(17B)	110.2	C(24)-C(23)-C(22)	109.3(5)
C(18)-C(17)-H(17B)	110.2	C(29)-C(23)-H(23)	109.5
H(17A)-C(17)-H(17B)	108.5	C(24)-C(23)-H(23)	109.5
C(19)-C(18)-C(20)	110.8(5)	C(22)-C(23)-H(23)	109.5
C(19)-C(18)-C(17)	109.3(5)	C(23)-C(24)-C(25)	110.2(5)
C(20)-C(18)-C(17)	109.7(5)	C(23)-C(24)-H(24A)	109.6
C(19)-C(18)-H(18)	109.0	C(25)-C(24)-H(24A)	109.6
C(20)-C(18)-H(18)	109.0	C(23)-C(24)-H(24B)	109.6
C(17)-C(18)-H(18)	109.0	C(25)-C(24)-H(24B)	109.6
C(18)-C(19)-C(13)	109.4(5)	H(24A)-C(24)-H(24B)	108.1
C(18)-C(19)-H(19A)	109.8	C(26)-C(25)-C(24)	109.5(5)
C(13)-C(19)-H(19A)	109.8	C(26)-C(25)-C(30)	109.2(5)
C(18)-C(19)-H(19B)	109.8	C(24)-C(25)-C(30)	109.4(5)
C(13)-C(19)-H(19B)	109.8	C(26)-C(25)-H(25)	109.6
H(19A)-C(19)-H(19B)	108.2	C(24)-C(25)-H(25)	109.6
C(18)-C(20)-C(15)	109.3(5)	C(30)-C(25)-H(25)	109.6
C(18)-C(20)-H(20A)	109.8	C(25)-C(26)-C(21)	109.7(5)
C(15)-C(20)-H(20A)	109.8	C(25)-C(26)-H(26A)	109.7
C(18)-C(20)-H(20B)	109.8	C(21)-C(26)-H(26A)	109.7
C(15)-C(20)-H(20B)	109.8	C(25)-C(26)-H(26B)	109.7
H(20A)-C(20)-H(20B)	108.3	C(21)-C(26)-H(26B)	109.7
N(2)-C(21)-C(22)	110.1(5)	H(26A)-C(26)-H(26B)	108.2
N(2)-C(21)-C(27)	111.4(5)	C(28)-C(27)-C(21)	110.0(5)
C(22)-C(21)-C(27)	108.2(5)	C(28)-C(27)-H(27A)	109.7
N(2)-C(21)-C(26)	108.1(4)	C(21)-C(27)-H(27A)	109.7
C(22)-C(21)-C(26)	112.4(5)	C(28)-C(27)-H(27B)	109.7
C(27)-C(21)-C(26)	106.6(5)	C(21)-C(27)-H(27B)	109.7
C(21)-C(22)-C(23)	109.5(5)	H(27A)-C(27)-H(27B)	108.2
C(21)-C(22)-H(22A)	109.8	C(29)-C(28)-C(27)	110.0(5)
C(23)-C(22)-H(22A)	109.8	C(29)-C(28)-C(30)	109.4(5)
C(21)-C(22)-H(22B)	109.8	C(27)-C(28)-C(30)	110.5(5)
C(23)-C(22)-H(22B)	109.8	C(29)-C(28)-H(28)	108.9

C(27)-C(28)-H(28)	108.9
C(30)-C(28)-H(28)	108.9
C(28)-C(29)-C(23)	109.0(5)
C(28)-C(29)-H(29A)	109.9
C(23)-C(29)-H(29A)	109.9
C(28)-C(29)-H(29B)	109.9
C(23)-C(29)-H(29B)	109.9
H(29A)-C(29)-H(29B)	108.3
C(25)-C(30)-C(28)	108.2(5)
C(25)-C(30)-H(30A)	110.1
C(28)-C(30)-H(30A)	110.1
C(25)-C(30)-H(30B)	110.1
C(28)-C(30)-H(30B)	110.1
H(30A)-C(30)-H(30B)	108.4

Table S4. Anisotropic displacement parameters *($Å^2 \times 10^3$)* for **10**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Au(1)	16(1)	15(1)	17(1)	1(1)	6(1)	-1(1)
Cl(1)	24(1)	20(1)	20(1)	4(1)	5(1)	-3(1)
O(1)	13(2)	21(2)	21(2)	-4(2)	6(2)	-2(2)
N(1)	15(2)	16(2)	20(3)	0(2)	5(2)	-1(2)
N(2)	20(3)	17(2)	21(3)	2(2)	10(2)	3(2)
C(1)	19(3)	17(2)	20(3)	0(2)	11(3)	-1(3)
C(2)	29(4)	14(3)	18(3)	-1(2)	8(3)	-4(3)
C(3)	21(3)	11(2)	20(3)	0(2)	6(3)	-4(2)
C(4)	23(3)	19(3)	23(3)	-1(2)	5(3)	1(3)
C(5)	29(3)	25(3)	26(3)	7(3)	9(3)	-3(3)
C(11)	16(3)	20(3)	17(3)	-3(2)	3(2)	2(2)
C(12)	23(3)	19(3)	25(3)	4(3)	13(3)	-1(3)
C(13)	22(3)	23(3)	17(3)	-3(2)	4(2)	-6(3)
C(14)	17(3)	27(3)	29(4)	-4(3)	-3(3)	-1(3)
C(15)	17(3)	26(3)	41(4)	-12(3)	5(3)	1(3)
C(16)	20(3)	26(3)	30(3)	-6(3)	9(3)	-2(3)
C(17)	21(3)	19(3)	25(3)	2(3)	10(3)	-2(2)
C(18)	31(3)	16(3)	20(3)	3(2)	7(3)	-3(3)
C(19)	29(3)	19(3)	22(3)	-5(2)	3(3)	2(3)
C(20)	24(3)	34(3)	26(3)	-5(3)	12(3)	-13(3)
C(21)	11(3)	17(3)	21(3)	-2(2)	5(2)	1(2)
C(22)	20(3)	15(3)	21(3)	-3(3)	8(3)	-4(2)
C(23)	16(3)	24(3)	22(3)	0(2)	5(3)	-3(2)
C(24)	18(3)	29(3)	29(3)	5(3)	8(3)	-3(3)
C(25)	20(3)	31(3)	20(3)	-3(3)	10(3)	2(3)
C(26)	17(3)	20(3)	17(3)	-1(2)	4(2)	-2(2)
C(27)	13(3)	17(3)	27(3)	0(2)	8(2)	-2(2)
C(28)	19(3)	19(3)	23(3)	1(2)	4(3)	0(2)
C(29)	18(3)	27(3)	23(3)	3(3)	4(3)	3(3)
C(30)	15(3)	23(3)	35(4)	-5(3)	9(3)	6(3)

Table S5. Hydrogen coordinates *(× 10^4)* and isotropic displacement parameters *($Å^2$ × 10^3)* for **10**.

	x	y	z	U(eq)
H(4A)	6744	3782	9525	33
H(4B)	7368	4015	8564	33
H(4C)	6492	3286	8192	33
H(5A)	4682	3412	8705	40
H(5B)	3645	3964	8148	40
H(5C)	4478	4228	9478	40
H(12A)	7552	5383	9702	26
H(12B)	6792	6190	9201	26
H(13)	8176	6597	11049	25
H(14A)	9897	6609	10973	32
H(14B)	9457	5641	10769	32
H(15)	10291	5958	9228	35
H(16A)	8883	5569	7354	30
H(16B)	8847	4993	8545	30
H(17A)	6866	7058	7335	25
H(17B)	7670	6812	6598	25
H(18)	8323	8022	7972	27
H(19A)	7504	7713	9501	29
H(19B)	8716	7866	10196	29
H(20A)	9993	7477	9055	33
H(20B)	9575	7052	7662	33
H(22A)	2804	4269	6457	22
H(22B)	2839	4708	5158	22
H(23)	1080	4591	5155	25
H(24A)	1427	4712	7410	31
H(24B)	546	5386	6678	31
H(25)	1780	6100	8414	27
H(26A)	3256	5248	8535	22
H(26B)	3532	6242	8391	22
H(27A)	3594	6828	6370	22
H(27B)	3323	6249	5105	22
H(28)	1891	7144	5020	25
H(29A)	1475	5782	4014	28
H(29B)	589	6058	4605	28

H(30A)	2158	7292	7249	29
H(30B)	997	6966	6555	29

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