Hydration of Alkynes Catalyzed by [AuX(L)(ppy)]X in the Green Solvent γ-Valerolactone under Acid-Free Conditions: the Importance of the Pre-equilibrium Step

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SUPPORTING INFORMATION

SUMMARY:

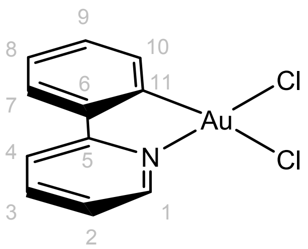
1. GENERAL PROCEDURES AND MATERIALS

$NaAuCl_4 \cdot H_2O$, phenylpyridine, 3-hexyne, γ-valerolactone, silver triflate (AgOTf), tosylate (AgOTs), trifluoroacetate (AgTFA), tetrafluoroborate ($AgBF_4$), and acetate (AgOAc) were purchased from Sigma Aldrich. All the solvents were used as received without any further purification, unless otherwise stated.

2. SYNTHESIS

1,3-bis(diisopropylphenyl)imidazolium chloride (NHC·HCl)[1] and dichlorophenylpyridinegold(III) were synthesized according to the literature.[2] All compounds were characterized in solution by ^{1}H, ^{13}C ^{19}F, and ^{31}P NMR spectroscopies. NMR spectra were recorded on Avance III HD spectrometers. Chemical shifts (ppm) are relative to TMS for both ^{1}H and ^{13}C nuclei, whereas ^{31}P, ^{19}F, and ^{15}N chemical shifts are referenced to 85% H_3PO_4, CCl_3F and CH_3NO_2, respectively. The elemental analyses were carried out with a Carlo Erba 1106 elemental analyzer.

[$AuCl_2$(ppy)]



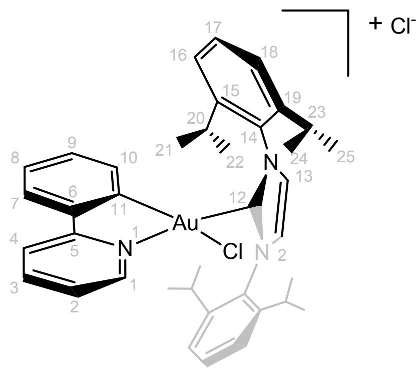
In a Schlenk flask, an acetonitrile solution (1.6 mL) of 2-phenylpyridine (1.0 mmol) was added dropwise, under vigorous stirring, to 1 mmol of $NaAuCl_4 \cdot 2H_2O$ dissolved in 8 mL of water. A bright yellow powder was instantly formed. After 4 hours, the solid was filtered off and dried under vacuum, then it was put in an oven at 165°C for 12 h. The yield of the complex was 76% and it was further used without any purification.

^{1}H NMR (400 MHz, DMSO-d_6, 298 K) δ(ppm) 9.54 (d, 1H, $^3J_{HH}$ = 6.0 Hz, H1), 8.44 – 8.37 (m, 2H, H3,4), 7.97 (dd, 1H, $^3J_{HH}$ = 7.7, $^4J_{HH}$ = 1.7 Hz, H7), 7.83 (dd, 1H, $^3J_{HH}$ = 8.1, $^4J_{HH}$ = 1.1 Hz, H10), 7.78 (td, 1H $^3J_{HH}$ = 5.9, $^4J_{HH}$ = 3.3 Hz, H2), 7.48 (td, 1H, $^3J_{HH}$ = 7.5, $^4J_{HH}$ = 1.2 Hz, H8), 7.39 (td, 1H, $^3J_{HH}$ = 8.9, $^4J_{HH}$ = 7.4, H9).

^{13}C {^{1}H} NMR (101 MHz, DMSO-d_6, 298 K): δ(ppm) 164.46 (C5), 152.76 (C6), 148.53 (C1), 144.45(C4), 143.46 (C11), 132.13 (C9), 130.52 (C10), 129.82 (C8), 127.21 (C7), 125.80 (C2), 122.66 (C3).

Anal. Calc. for $C_{11}H_8AuNCl_2$ (MW: 422.06 g·mol^{-1}) C, 31.30; H, 1.91; Au, 46.67; N, 3.32; Cl, 16.80. Found: C, 31.4; H, 1.9; N 3.2.

[AuCl(NHC)(ppy)]Cl (1)



In a Schlenk flask, 1 equivalent (0.25 mmol) of NHC·HCl, 1.1 equiv. (116.1 mg, 0.275mmol) of [$AuCl_2$(ppy)], and 4 equiv. (100.1 mg, 1 mmol) of $KHCO_3$ were dissolved in 10 mL of acetonitrile and stirred at room temperature overnight. The solvent was then removed under vacuum, the residue was dissolved in dichloromethane (10 mL), and the mixture was filtered through a paddle of Celite. The volume of the solution was reduced to about 2 mL and the complex precipitated by adding *n*-pentane. The white microcrystalline product was collected by filtration, washed with *n*-pentane (2 x 2 mL) and dried under vacuum. Yield was 94%. NMR and elemental analysis data are in accordance with those reported in the literature.

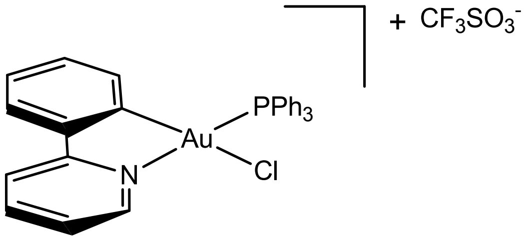
^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ(ppm) 9.28 (dd, 1H, $^{3}J_{HH}$ = 6.1 Hz, $^{4}J_{HH}$ = 1.6 Hz, H1), 8.43 (dd, 1H, $^{3}J_{HH}$ = 8.2, $^{4}J_{HH}$ = 1.4 Hz, H4), 8.34 (td, 1H, $^{3}J_{HH}$ = 7.8 Hz, $^{4}J_{HH}$ = 1.6 Hz, H3), 8.06 – 7.99 (m, 3H, H7,13), 7.57 – 7.44 (m, 4H, H2,8,17), 7.35 (dd, 2H, $^{3}J_{HH}$ = 7.8 Hz, $^{4}J_{HH}$ = 1.6 Hz, H18), 7.32 – 7.26 (m, 1H, H9), 7.24 (dd, 1H, $^{3}J_{HH}$ = 7.8 Hz, $^{3}J_{HH}$ = 1.5 Hz, H16), 6.95 (d, 1H, $^{3}J_{HH}$ = 7.9 Hz, H10), 3.05 (p, 2H, $^{3}J_{HH}$ = 6.7 Hz, H20), 2.89 (p, 2H, $^{3}J_{HH}$ = 6.7 Hz, H23), 1.45 (d, 6H, $^{3}J_{HH}$ = 6.6 Hz, H24), 1.27 (d, 6H, $^{3}J_{HH}$ = 6.7 Hz, H22), 1.13 (d, 6H, $^{3}J_{HH}$ = 6.8 Hz, H25), 0.72 (d, 6H, $^{3}J_{HH}$ = 6.7 Hz, H21).

^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$, 298 K): δ(ppm) 163.80 (1C, C5), 149.20 (1C, C12), 147.26 (1C, C1), 147.20 (1C, C19), 144.93 (2C, C15), 144.43 (1C, C3), 143.40 (1C, C11), 132.62 (1C, C9), 132.58 (1C, C6), 132.50 (2C, C14), 132.21 (1C, C10), 131.98 (2C, C17), 130.02 (1C, C8), 128.67 (2C, C13), 127.59 (1C, C7), 125.16(2C, C16), 124.90 (2C, C18), 124.53 (1C, C2), 122.55 (1C, C4), 29.51 (2C, C23), 29.11 (2C, C20), 26.94 (2C, C25), 26.75 (2C, C22), 22.82 (2C, C21), 22.66 (2C, C24).

^{15}N (41 MHz, acetone-d_6, 298 K): δ(ppm) -147.7 (1N, N1), -189.8 (2N, N2)

Anal. Calc. for $C_{38}H_{44}AuN_3Cl_2$ (MW: 810.66 g·mol^{-1}) C, 56.30; H, 5.47; Au, 24.30; N, 5.18, Cl, 8.75. Found: C, 56.1; H, 5.4; N 5.1.

[AuCl(PPh$_3$)(ppy)]OTf (2)



An acetone solution (9 mL) of [AuCl$_2$(ppy)] (105.5 mg, 0.25 mmol), triphenylphosphine (72.1 mg, 1.1 eq.), and NaCF$_3$SO$_3$ (176 mg, 4 eq.) was stirred overnight in a Schlenk flask. The acetone was then removed under vacuum, dichloromethane (10 mL) was added and the solid was eliminated by filtration through celite. The volume of the solution was reduced to about 2 mL and a white solid precipitated by adding *n*-pentane. (yield 91%).

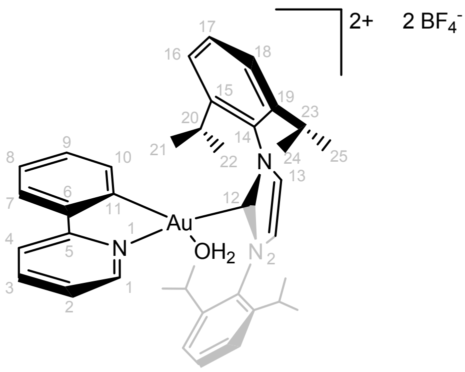
^{1}H NMR (400 MHz, CDCl$_3$, 298 K): δ(ppm) 9.60 (br, 1H), 8.23 (br, 2H), 7.70 (m, 17H), 7.38 (br, 1H), 6.84 (m, 1H), 6.78 (m, 1H)

^{31}P {^{1}H} NMR (162 MHz, CD$_2$Cl$_2$, 298 K): δ(ppm) 43.46 (s).

^{19}F NMR (376 MHz, CD$_2$Cl$_2$, 298 K): δ(ppm) -78.88 (s).

Anal. Calc. for $C_{30}H_{23}AuNO_3F_3PSCl$ (MW: 797.97 g·mol^{-1}) C, 45.16; H, 2.91; Au, 24.68; N, 1.76 O, 6.02; F, 7.14; P, 3.88; S, 4.02; Cl, 4.44. Found: C, 45.1; H, 2.9; N 1.8.

[Au(H$_2$O)(NHC)(ppy)](BF$_4$)$_2$ (3)



The complex [Au(H$_2$O)(NHC)(ppy)](BF$_4$)$_2$ was synthesized in an NMR tube adding an excess of silver tetrafluoroborate to the [AuCl(NHC)(ppy)]Cl complex in deuterated dichloromethane. To the solution was added 10 equivalents of water and the tube was shaken. The complex was characterized by mono and bidimensional ^{1}H, ^{13}C and ^{19}F NMR experiments. The assignment of all ^{1}H, ^{13}C was made with the help of bidimensional experiments such as ^{1}H-^{1}H COSY, ^{1}H-^{13}C HSQC, ^{1}H-^{13}C HMBC and ^{1}H-^{1}H NOESY spectra.

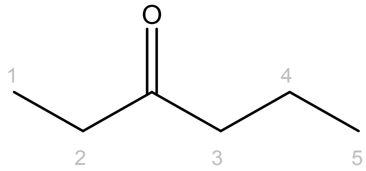
^{1}H NMR(400 MHz, CD$_2$Cl$_2$, 298 K): δ(ppm) = 8.75 (dt, 1H, $^3J_{HH}$ = 5.9, $^4J_{HH}$ = 2.0 Hz, H1), 8.18 (td, 1H, $^3J_{HH}$ = 7.9, $^4J_{HH}$ = 1.6 Hz, H3), 7.93 (dt, 1H, $^3J_{HH}$ = 8.2, $^4J_{HH}$ = 1.1 Hz, H4), 7.71 (s, 2H, H13), 7.66 (dt, 1H, $^3J_{HH}$ = 7.8, $^4J_{HH}$ = 1.8 Hz, H7), 7.61 – 7.52 (m, 3H, H2-17), 7.48 - 7.41 (m, 3H, H8-18), 7.32 (dd, 2H, $^3J_{HH}$ = 7.8, $^4J_{HH}$ = 1.5 Hz, H16), 7.25 (tt, 1H, $^3J_{HH}$ = 7.7, $^4J_{HH}$ = 1.8 Hz, H9), 6.98 (ddd, 1H,

$^{3}J_{HH}$ = 7.9, $^{4}J_{HH}$ = 3.5 Hz, H10), 2.94 (m, 4H, H20-23), 1.46 (d, 6H, $^{3}J_{HH}$ = 6.6 Hz, H24), 1.33 (d, 6H, $^{3}J_{HH}$ = 6.7 Hz, H22), 1.13 (d, 6H, $^{3}J_{HH}$ = 6.8 Hz, H25), 0.94 (d, 6H, $^{3}J_{HH}$ = 6.8 Hz, H21)

^{13}C {^{1}H} NMR (101 MHz, CD_2Cl_2, 298 K) δ(ppm) = 162.20 (1C, C5), 150.56 (1C, C12), 147.36 (1C, C19), 145.61 (d, 1C, C1), 144.91 (1C, C15), 144.16 (1C, C3), 143.05 (1C, C11), 134.70 (1C, C6), 133.32 (d, 1C, C10), 132.73 (1C, C9), 132.12 (2C, C14), 131.83(2C, C17), 129.52 (1C, C8), 127.14 (2C, C13), 126.47 (1C, C7), 124.99-124.96 (4C, C16-18), 124.42 (1C, C2), 120.97 (1C, C4), 29.22-29.17 (4C, C20-23), 26.31 (2C, C22), 26.18 (2C, C25), 22.68 (2C, C21), 22.16-22.10 (d, 2C, C24).

^{19}F NMR (376 MHz, CD_2Cl_2, 298 K): δ(ppm) = -152.74 (d, *J*=20.8 Hz).

3. CATALYSIS



A typical run was performed by mixing 100 μL of 3-hexyne (0.88 mmol), 18 μL of water, 0.088 mmol of catalyst in 400 μL of γ-valerolactone in a 2 mL glass screw top vial. The mixture was stirred in a bath oil at 50 °C. The progress of the reaction was checked by NMR and the sample was prepared as follows: 10 μL of the reaction mixture was taken with a syringe and dissolved in 500 μL of non-anhydrous $CDCl_3$. Conversion was calculated from the integral areas of the corresponding signals (conversion [%] = (n 3-hexanone) / (n 3-hexyne + n 3-hexanone) x 100). Reported yields are an average of three runs. ^1H NMR (400 MHz, $CDCl_3$, 298 K): δ(ppm) 2.36–2.39 (tq, 4H, $^3J_{HH}$ = 7.4 Hz, $^3J_{HH}$ = 7.3 Hz, H2,3), 1.58 (m, 2H, H4), 1.03 (t, 3H, $^3J_{HH}$ = 7.4 Hz, H1), 0.89 (t, 3H, $^3J_{HH}$ = 7.4 Hz, H5).

3.1 Structure effect

3.1.1 Ligand effect

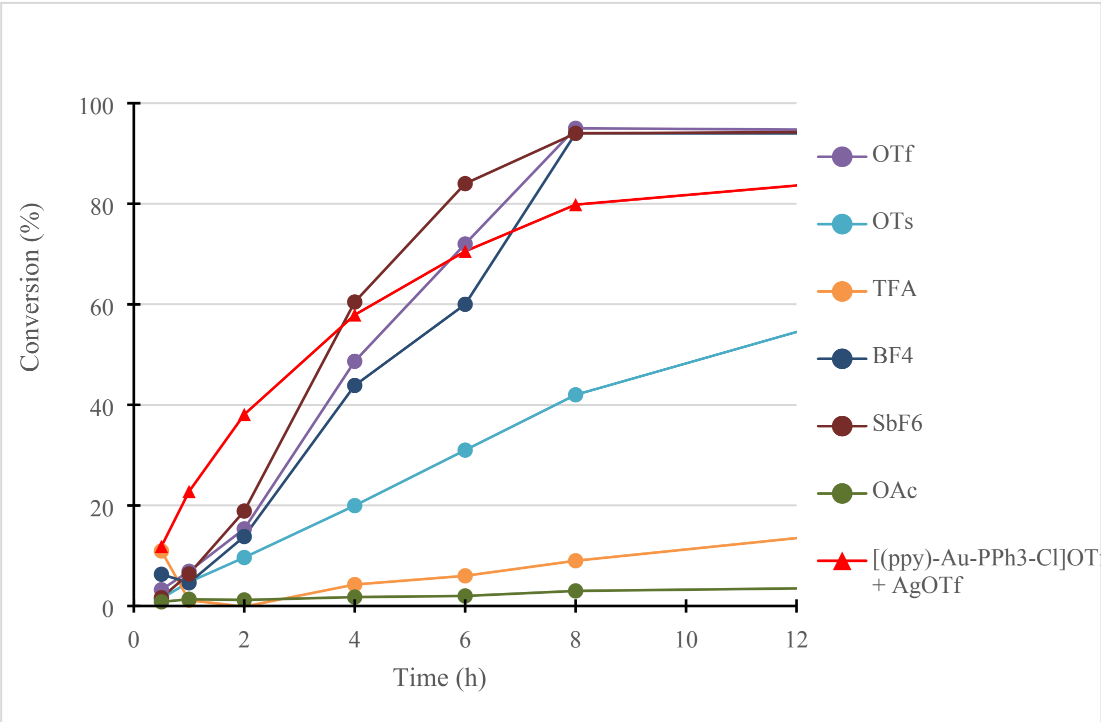
Table 1

Entry	**1**		**2**		**3**		**4**	
Cat.	**[$AuCl_2$(ppy)]**		**[AuCl(NHC)(ppy)]Cl**		**[AuCl(PPh_3)(ppy)]OTf**		**[AuCl(PPh_3)(ppy)]OTf + AgOTf**	
t (h)	Conv (%)	TOF (h^{-1})	Conv (%)	TOF (h^{-1})	Conv (%)	TOF (h^{-1})	Conv (%)	TOF (h^{-1})
0.5	0	0	0	0	0	0	12	23
1	0	0	0	0	0	0	23	23
2	0	0	0	0	0	0	38	19
4	0	0	0	0	0	0	58	14
6	-	-	-	-	-	-	71	12
8	-	-	-	-	-	-	80	10
24	0	0	0	0	0	0	95	4

3.1.2 Anion effect

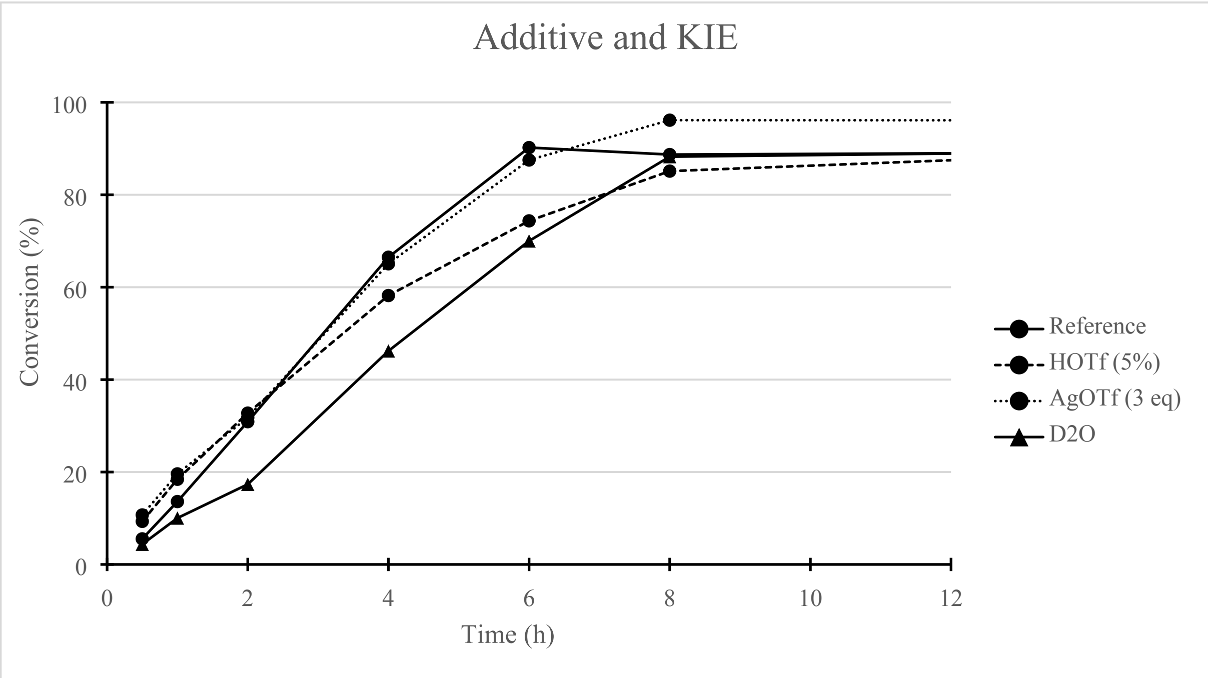
Table 2

In situ: [AuCl(NHC)(ppy)]Cl + 2 AgX												
Entry	**5**		**6**		**7**		**8**		**9**		**10**	
X⁻	**OTf^-**		**TFA^-**		**SbF_6^-**		**OTs^-**		**BF_4^-**		**OAc^-**	
t (h)	Conv (%)	TOF (h^{-1})	Conv (%)	TOF (h^{-1})	Conv (%)	TOF (h^{-1})	Conv (%)	TOF (h^{-1})	Conv (%)	TOF (h^{-1})	Conv (%)	TOF (h^{-1})
0.5	3	7	11	22	2	3	2	3	6	13	1	2
1	7	7	1	1	6	6	5	5	5	5	1	1
2	15	8	0	0	19	9	10	5	14	7	1	1
4	49	12	4	1	60	15	20	5	44	11	2	0
6	72	12	6	1	84	14	31	5	60	15	2	0
8	95	12	9	1	94	12	42	5	94	12	3	0
24	94	4	27	1	95	4	92	3	94	3	5	0



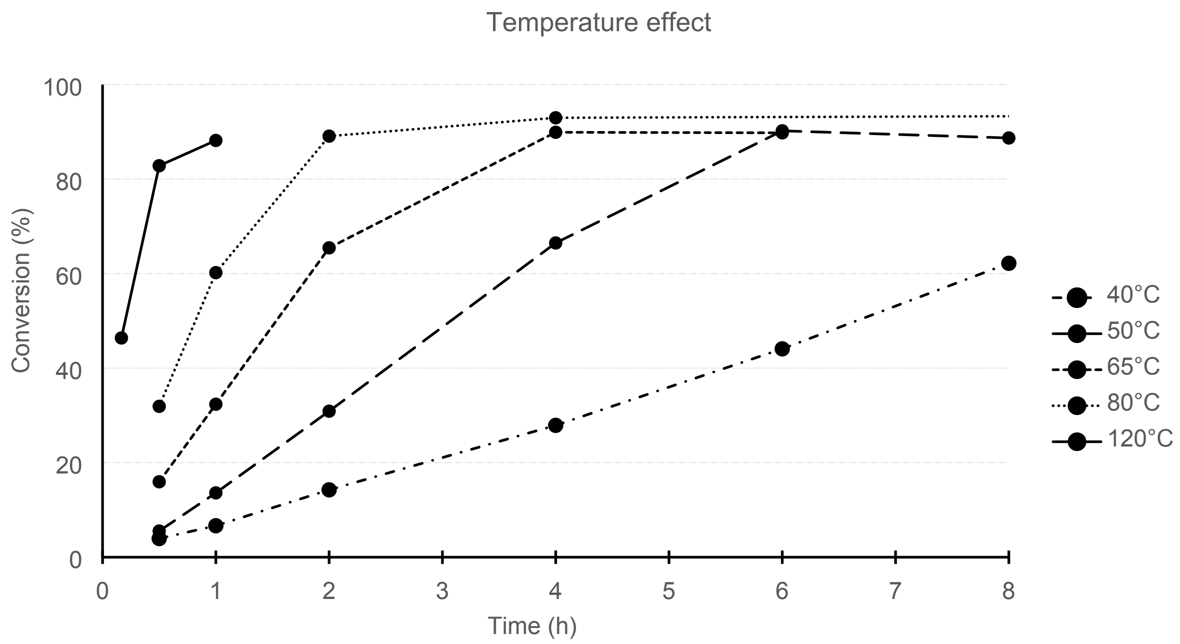
3.2 Role of additive and KIE (Kinetic Isotopic Effect)

	Reference		**HOTf 5%**		**AgOTf 3eq**		**KIE study**		
t (h)	Conv (%)	TOF (h^{-1})	Conv (%)	TOF (h^{-1})	Conv (%)	TOF (h^{-1})	Conv (%)	TOF (h^{-1})	H_2O/D_2O
0.5	6	11	9	19	11	21	4	9	1,27
1	14	14	18	19	20	20	10	10	1,36
2	31	15	33	17	32	17	17	9	1,78
4	66	17	58	15	65	16	46	12	1,44
6	90	15	74	13	88	15	70	12	1,29
8	89	11	85	11	96	12	88	11	1,01
24	90	4	95	4	96	4	91	4	0,99



3.3 Temperature effect

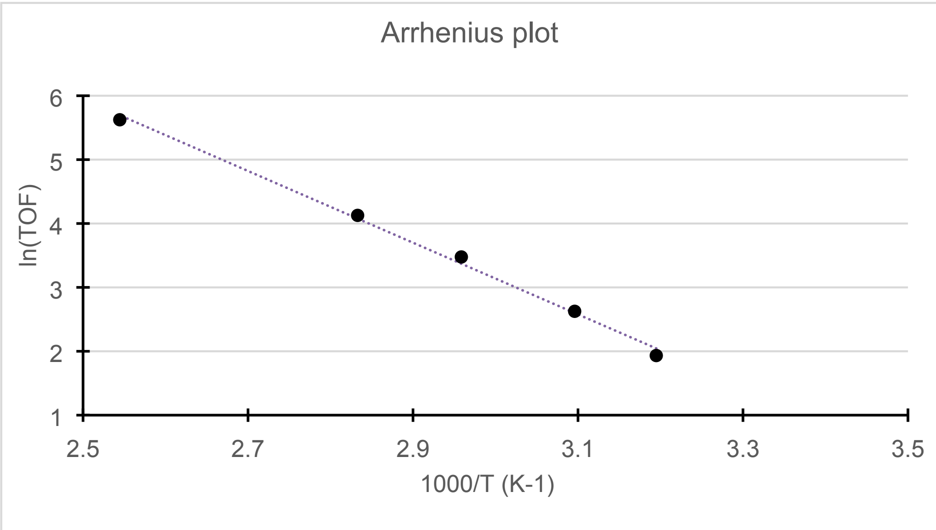
T	40 °C		50 °C		65 °C		80 °C		120 °C	
t (h)	Conv (%)	TOF (h^{-1})	Conv (%)	TOF (h^{-1})	Conv (%)	TOF (h^{-1})	Conv (%)	TOF (h^{-1})	Conv (%)	TOF (h^{-1})
0.17	-	-	-	-	-	-	-	-	46	289
0.5	4	8	6	11	16	32	32	64	83	172
1	7	7	14	14	32	32	60	60	88	92
2	14	7	31	15	65	33	89	45	-	-
4	28	7	66	17	90	22	93	23	-	-
6	44	7	90	15	90	15	-	-	-	-
8	62	8	89	11	-	-	-	-	-	-
24	93	4	90	4	-	-	95	4	-	-



3.3.1 Arrhenius equation

TOF calculated at 50% of conversion

1/T (K^{-1})	**ln(TOF)**
0.0032	1.933
0.0031	2.625
0.0030	3.476
0.0028	4.127
0.0025	5.624



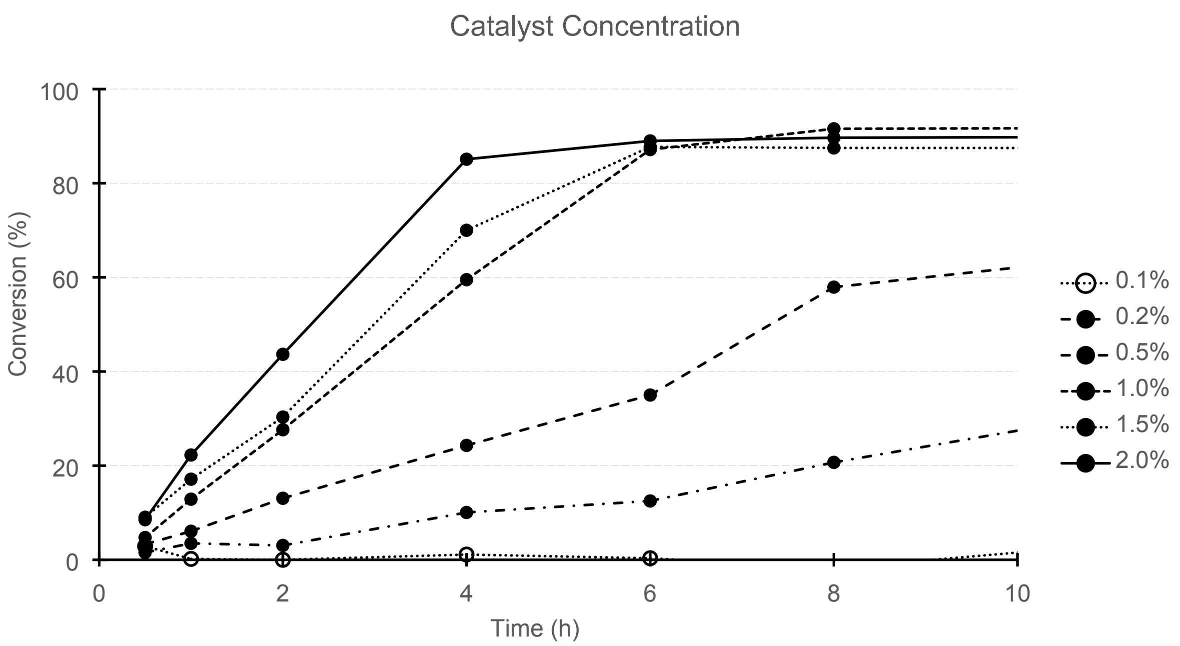
$$k = Ae^{-\frac{E_a}{RT}} \rightarrow \ln(k) = \ln(A) - \frac{E_a}{R} \cdot \frac{1}{T}$$

$$\frac{E_a}{R} = 5.612 \cdot \ 10^3 \rightarrow E_a = 46\ 660\ J = 11\ 150\ cal$$

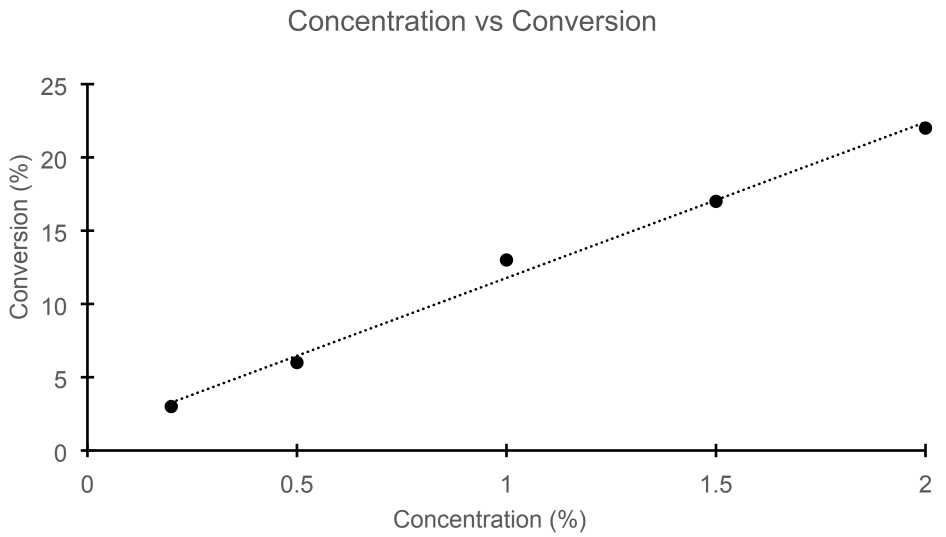
3.4 Concentration

3.4.1 Catalyst concentration

	0.1%		0.2%		0.5%		1.0%		1.5%		2.0%	
t (h)	Conv (%)	TOF (h^{-1})	Conv (%)	TOF (h^{-1})	Conv (%)	TOF (h^{-1})	Conv (%)	TOF (h^{-1})	Conv (%)	TOF (h^{-1})	Conv (%)	TOF (h^{-1})
05	3	58	2	16	3	13	5	10	9	12	9	9
1	0	2	3	17	6	12	13	13	17	11	22	11
2	-	-	3	8	13	13	28	14	30	10	44	11
4	1	3	10	13	24	12	60	15	70	11	85	11
6	0	1	12	10	35	12	87	15	88	10	89	7
8	-2	-2	21	13	58	15	92	12	87	7	90	6
24	25	10	75	16	91	8	92	4	87	2	90	2

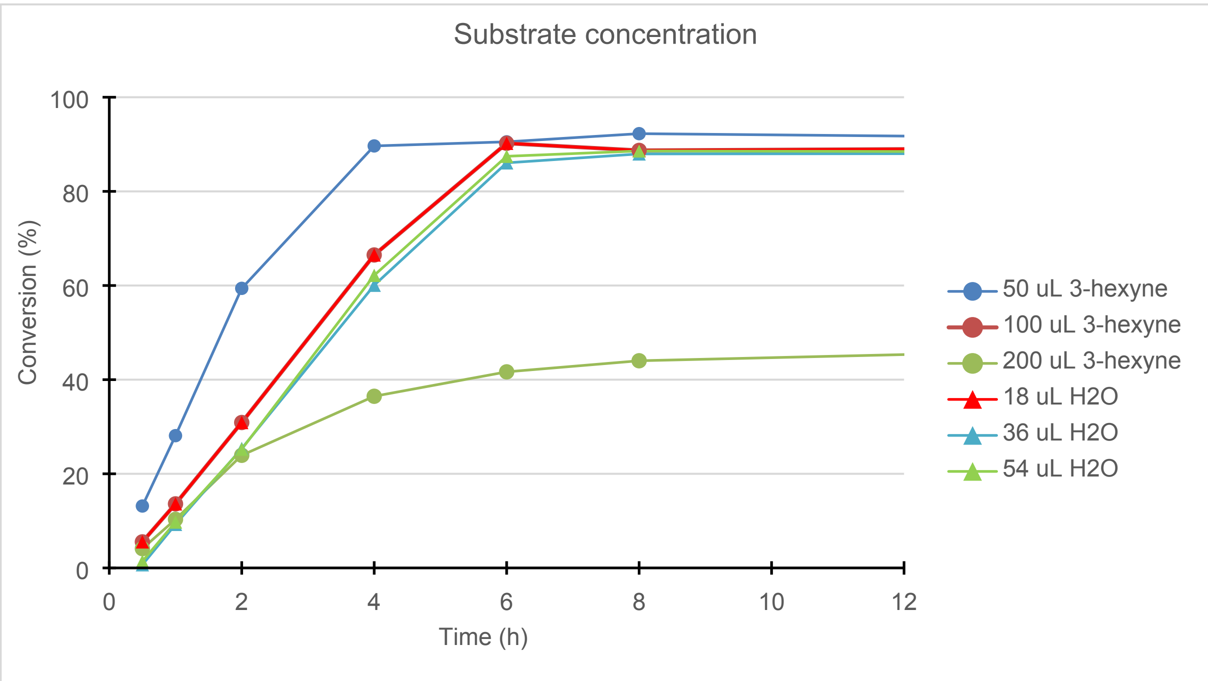


Catalyst conc. (%)	**Conversion after 1h**
0.1	-
0.2	3
0.5	6
1	13
1.5	17
2	22



3.4.2 Substrates concentration

	3-hexyne						H_2O					
Volume	**50 μL**		**100 μL**		**200 μL**		**18 μL**		**36 μL**		**54 μL**	
t (h)	Conv (%)	TOF (h^{-1})	Conv (%)	TOF (h^{-1})	Conv (%)	TOF (h^{-1})	Conv (%)	TOF (h^{-1})	Conv (%)	TOF (h^{-1})	Conv (%)	TOF (h^{-1})
0.5	13	13	6	11	4	16	6	11	1	1	1	3
1	28	14	14	14	10	21	14	14	9	9	10	10
2	59	15	31	15	24	24	31	15	25	12	25	12
4	90	11	66	17	36	18	66	17	60	15	62	15
6	91	8	90	15	42	14	90	15	86	14	87	14
8	92	6	89	11	44	11	89	11	88	11	89	11
24	90	2	90	4	49	4	90	4	88	4	88	4



4. STABILITY STUDIES

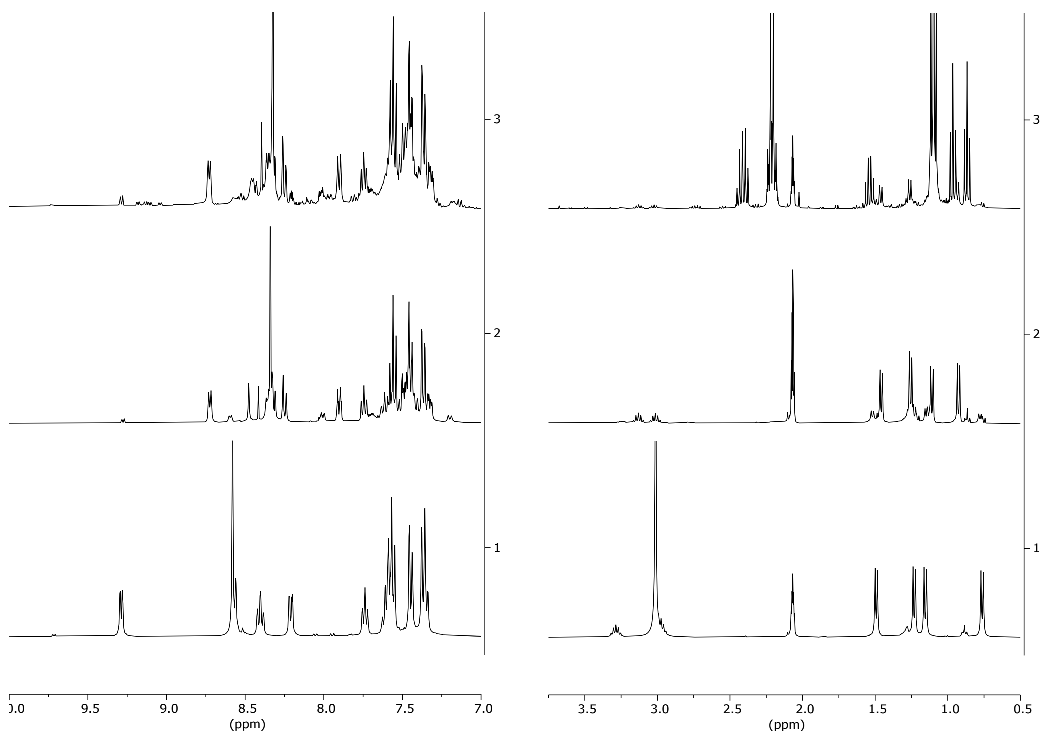
In an NMR tube, the stability of [AuCl(PPh_3)(ppy)]OTf and [AuCl(NHC)(ppy)]Cl has been studied in a catalysis-like system, using acetone-*d*$_6$ as the solvent instead of GVL.

4.1 [AuCl(NHC)(ppy)]Cl (1)

The ^{1}H, ^{13}C DEPT and ^{1}H-^{15}N HMBC spectra were recorded in this order:

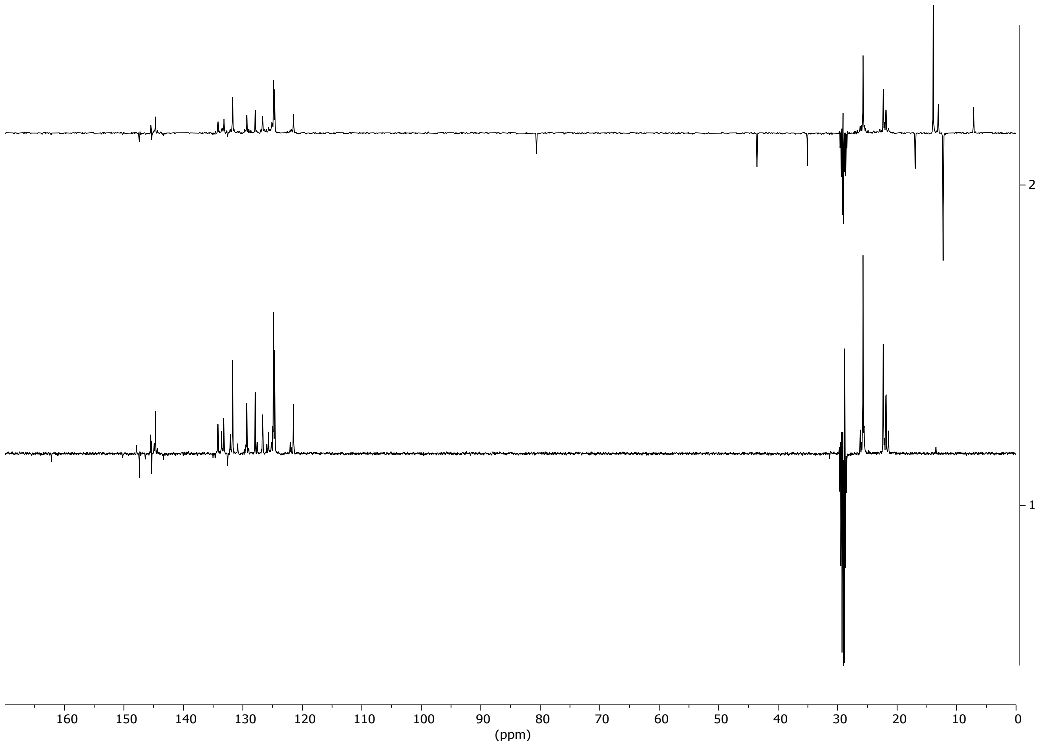
^{1}H NMR in acetone-d$_6$

1. [AuCl(NHC)(ppy)]Cl (20 mg, 0.025 mmol) in 450 µL of acetone-*d*$_6$;
2. Solution A: + $AgBF_4$ (1.5 eq.) + H_2O (4 µL, 0.247 mmol);
3. Solution B: + 3-hexyne (28 µL, 0.25 mmol) at 30% conversion



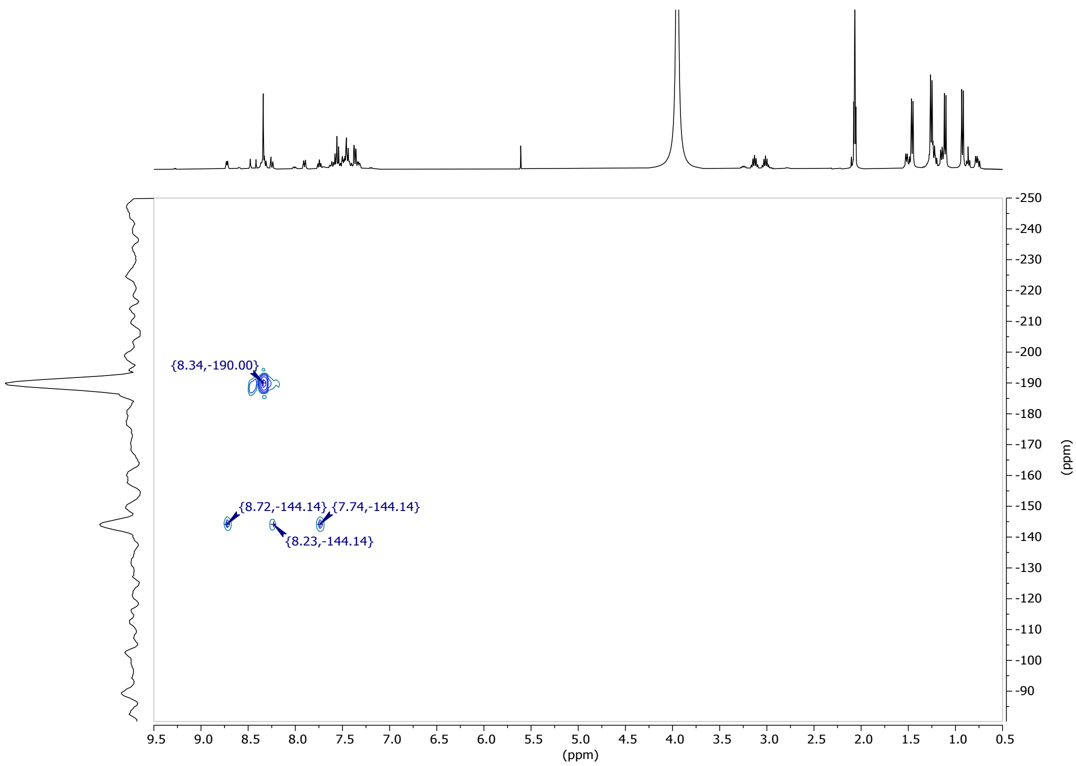
^{13}C NMR in acetone-d_6

1. Solution A
2. Solution B

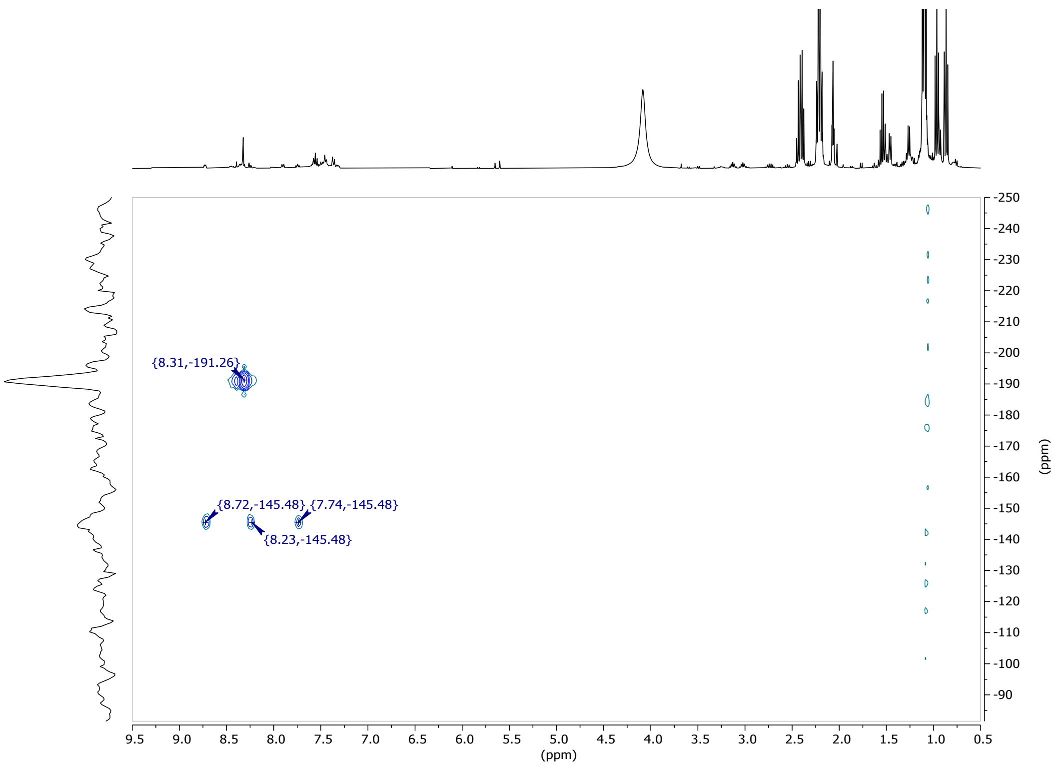


^{1}H-^{15}N HMBC in acetone-d_6

Solution A:



Solution B:

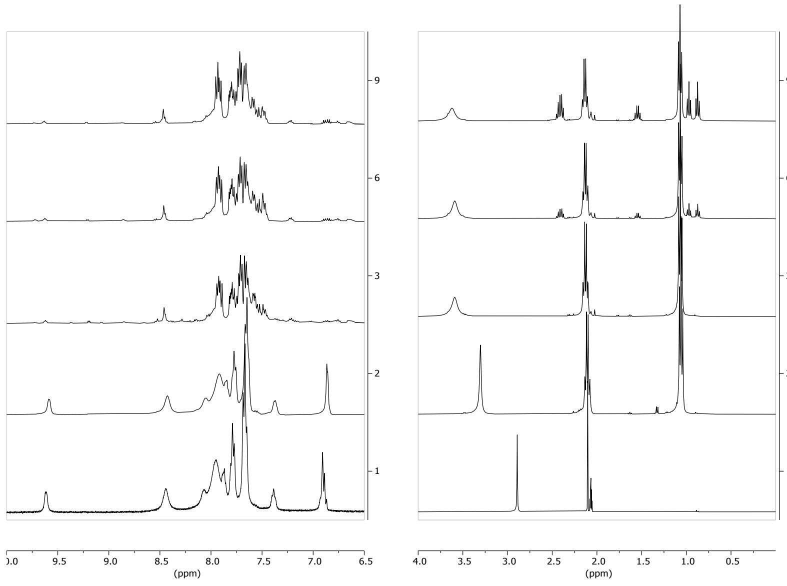


4.2 [AuCl(PPh$_3$)(ppy)]OTf (2)

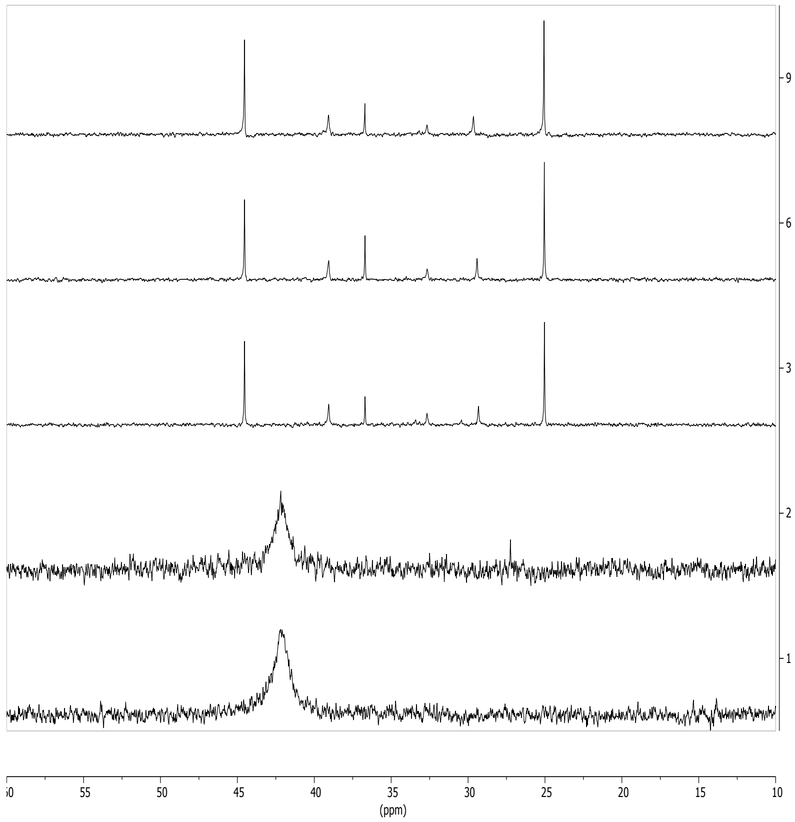
The ^{1}H and ^{31}P spectra were recorded in this order:

1. [AuCl(PPh$_3$)(ppy)]OTf (7 mg, 0.088 mmol) in 400 µL of acetone-*d$_6$*;
2. + 3-hexyne (100 µL, 0.88 mmol) + H_2O (18 µL, 1 mmol);
3. + 1.5 equivalent of AgOTf at 30 °C;
6. After 6h at 30 °C;
9. After 12h at 30 °C;

^{1}H NMR in acetone-d$_6$



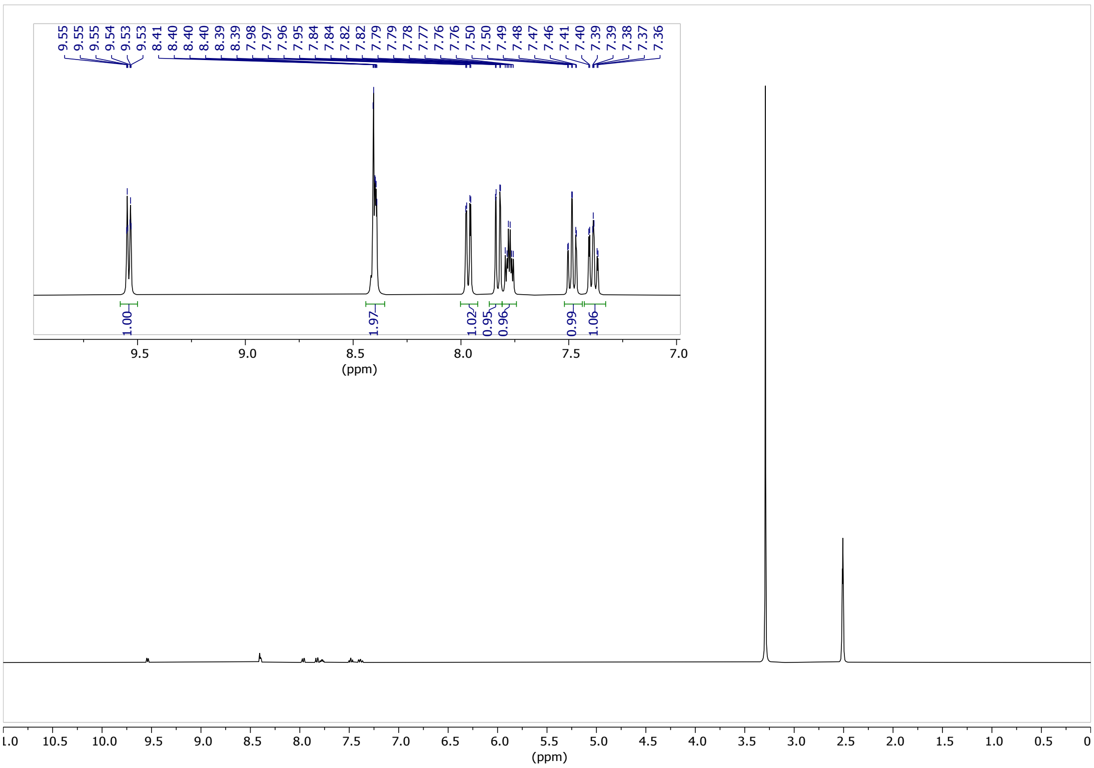
^{31}P NMR in acetone-d_6



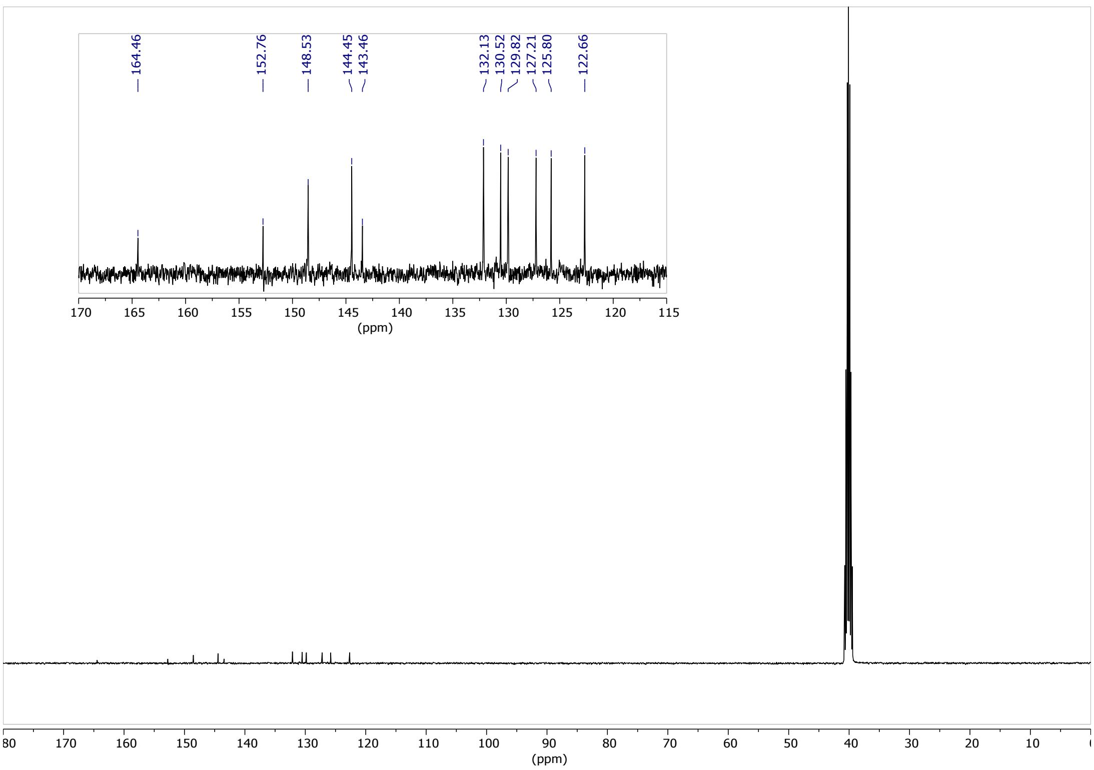
5. NMR SPECTRA

5.1 [AuCl$_2$(ppy)]

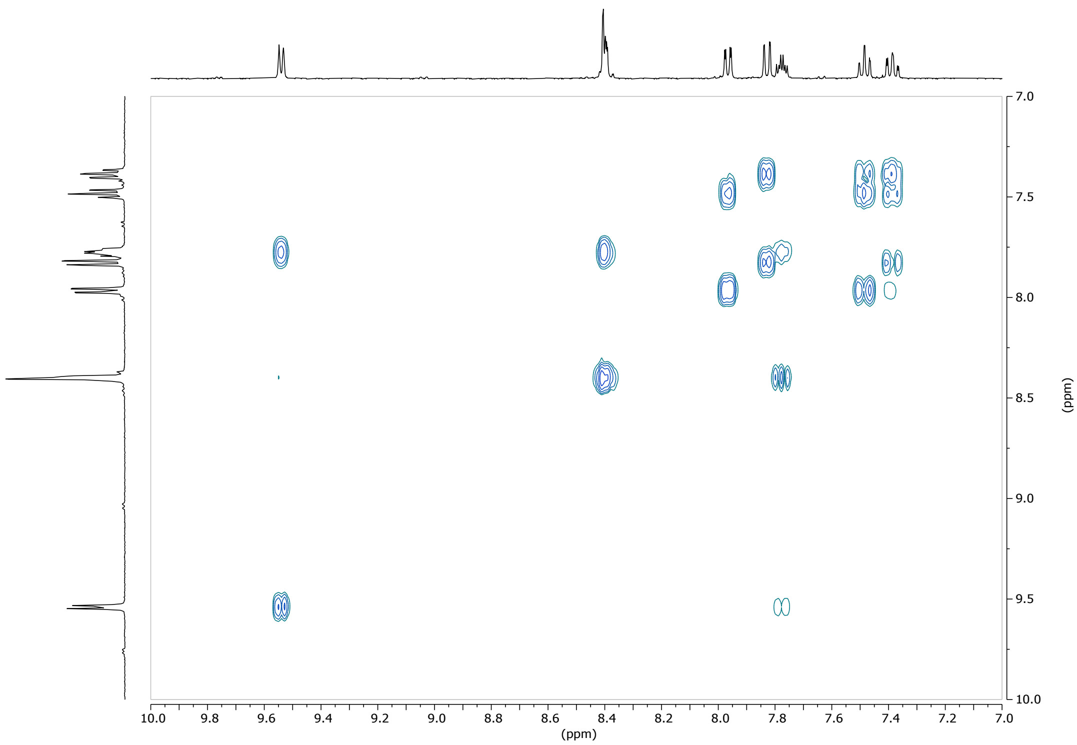
^{1}H NMR in DMSO-d$_6$



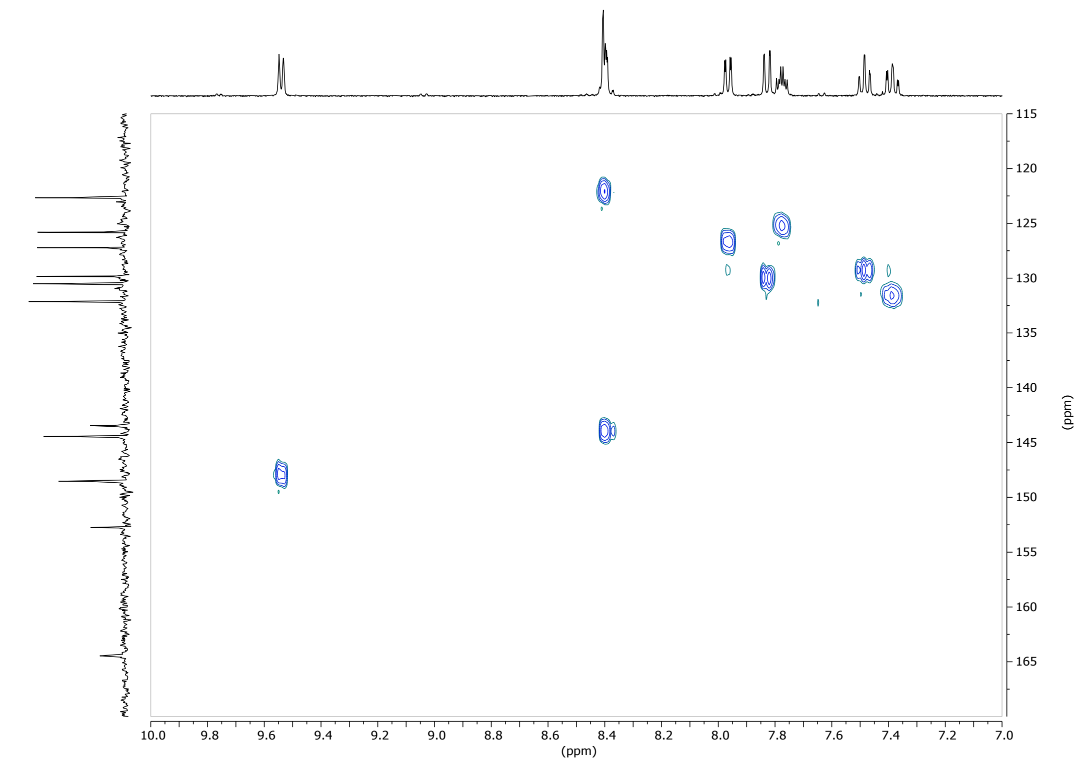
^{13}C {^{1}H} NMR in DMSO-d$_6$



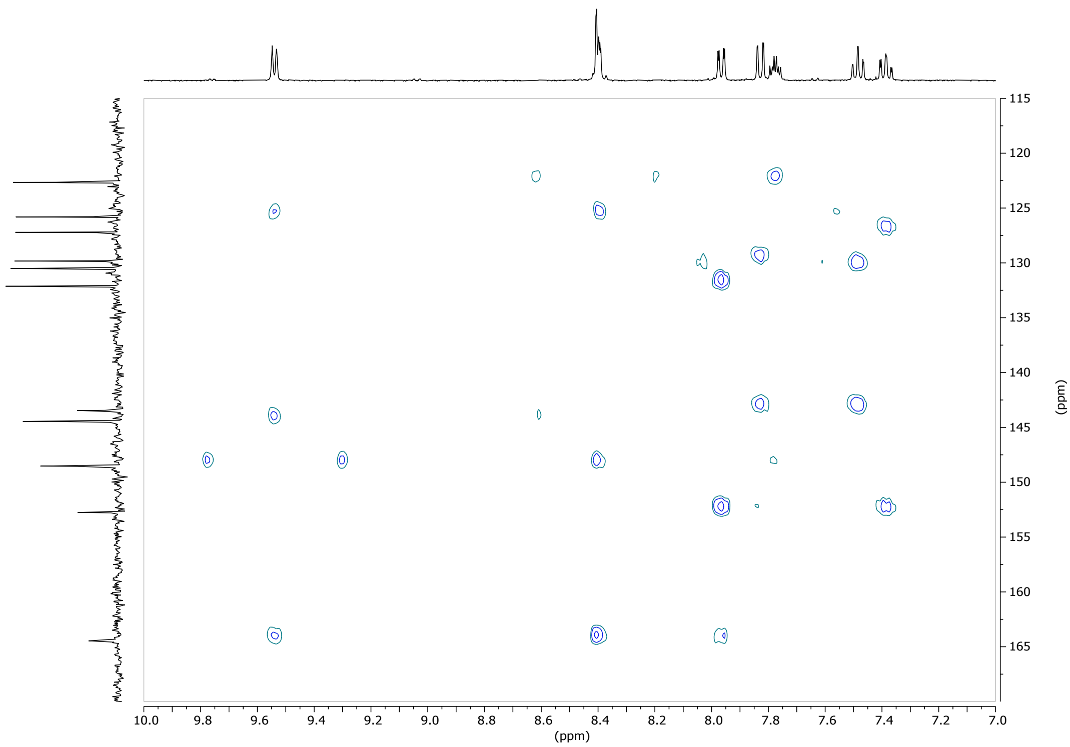
^{1}H-^{1}H COSY in DMSO-d$_6$



^{1}H-^{13}C HSQC in DMSO-d_6

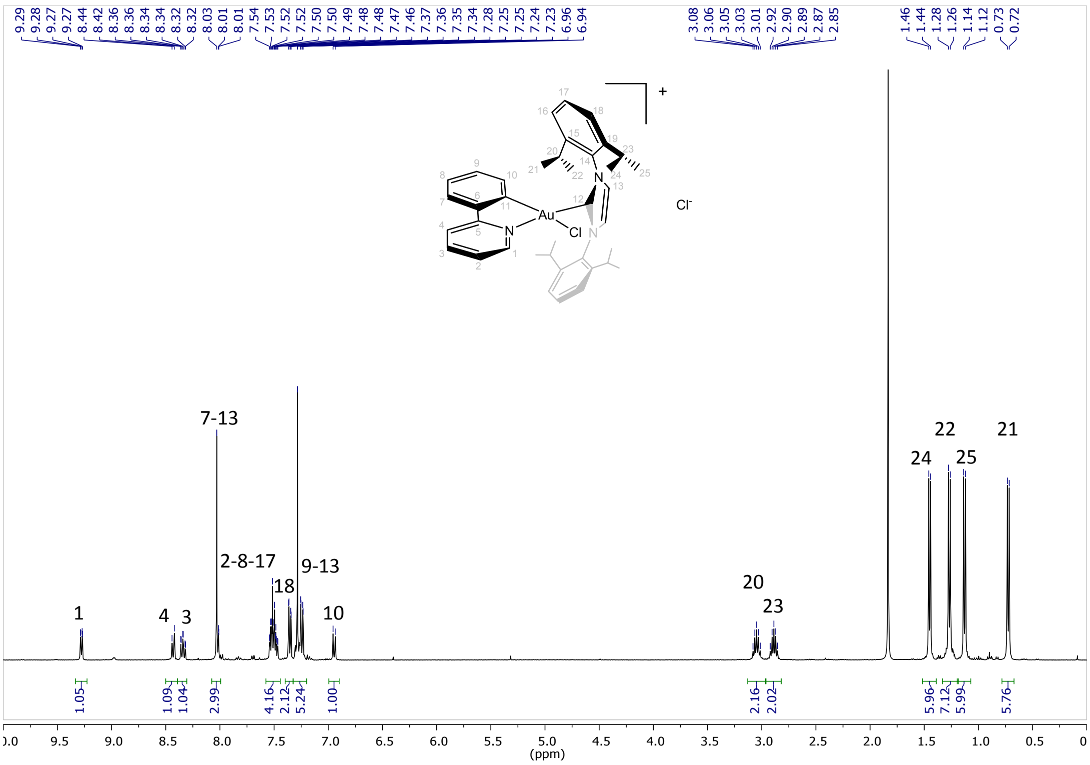


^{1}H-^{13}C HMBC in DMSO-d_6

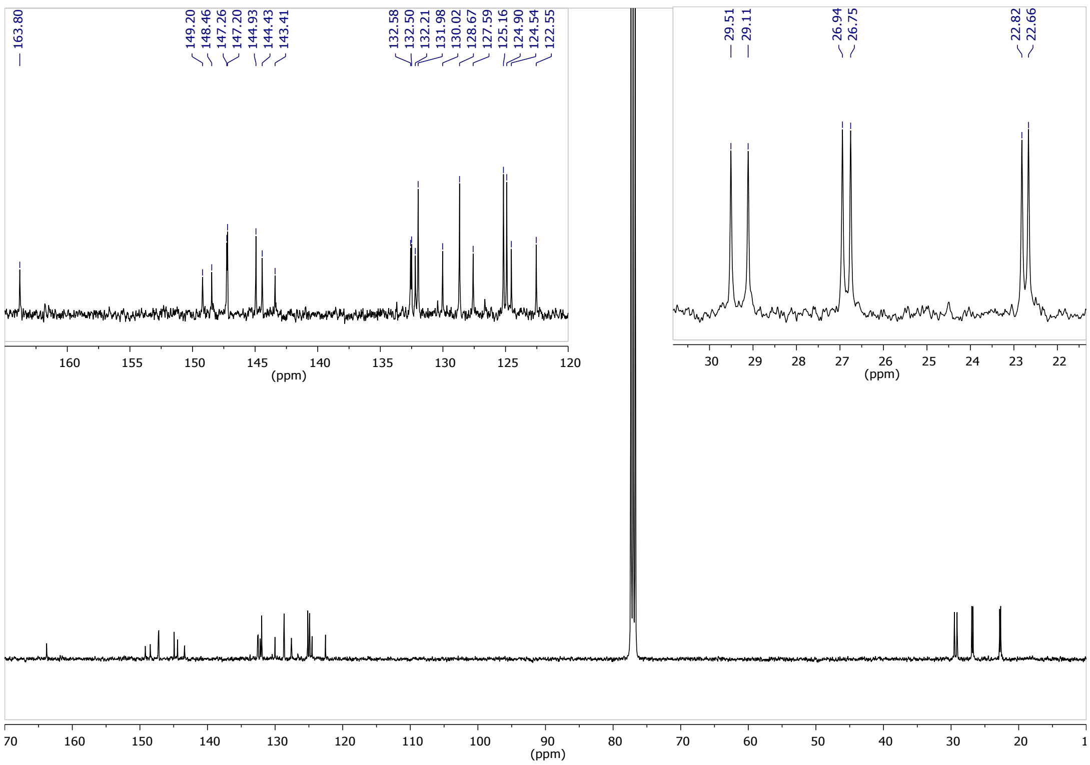


5.2 [AuCl(NHC)(ppy)]Cl (1)

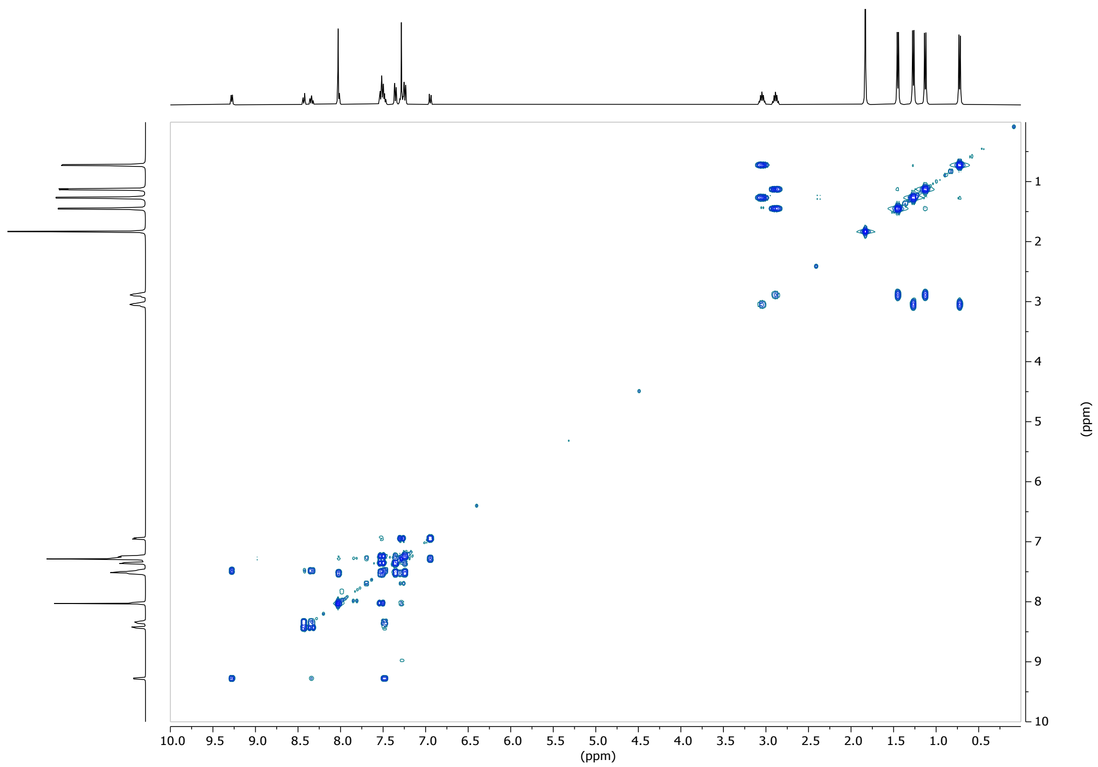
^{1}H NMR in $CDCl_3$



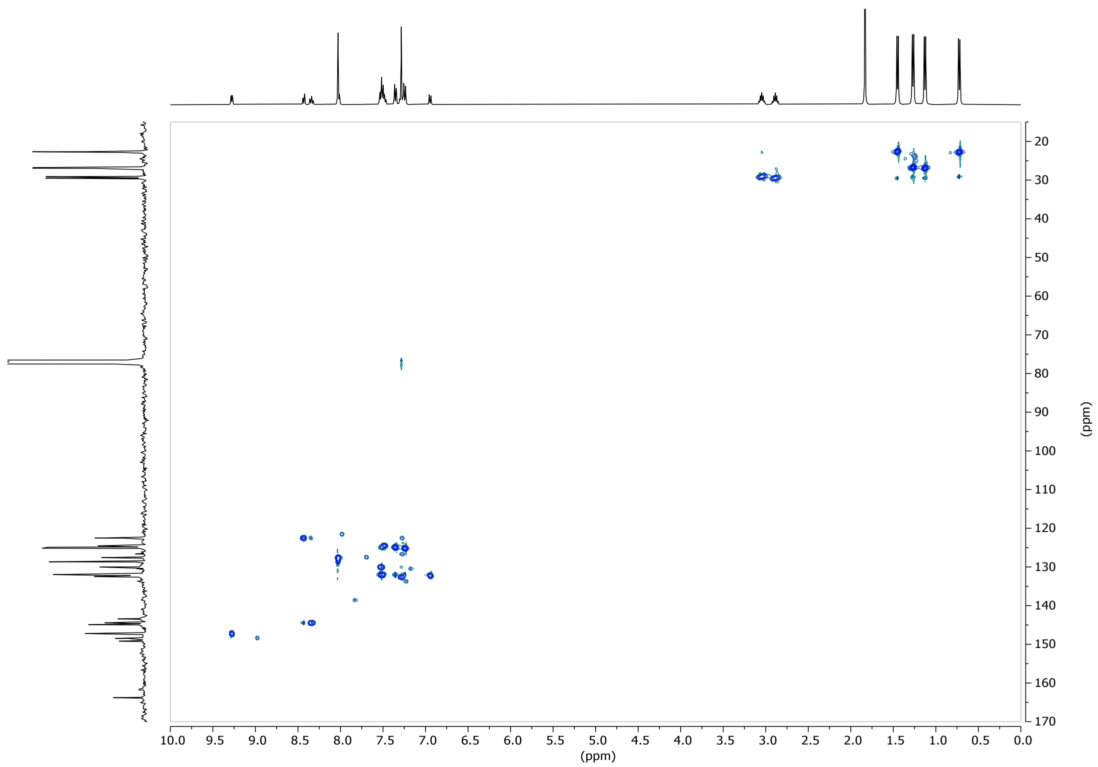
^{13}C {^{1}H} NMR in $CDCl_3$



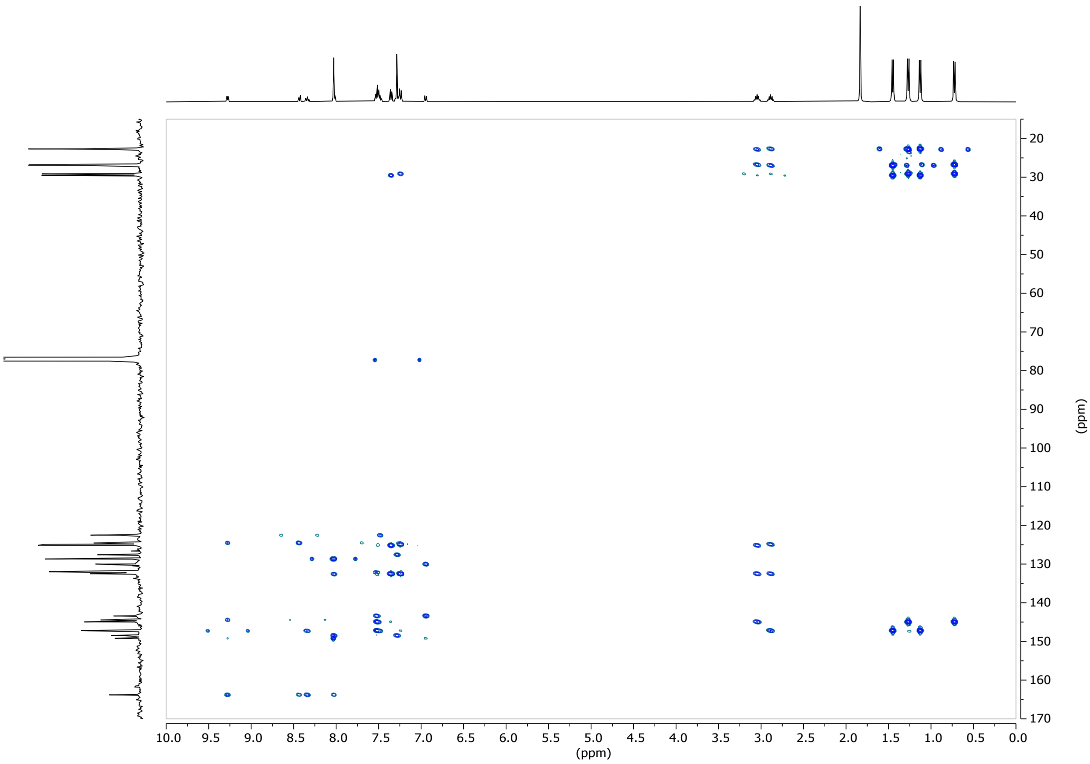
^{1}H-^{1}H COSY in $CDCl_3$



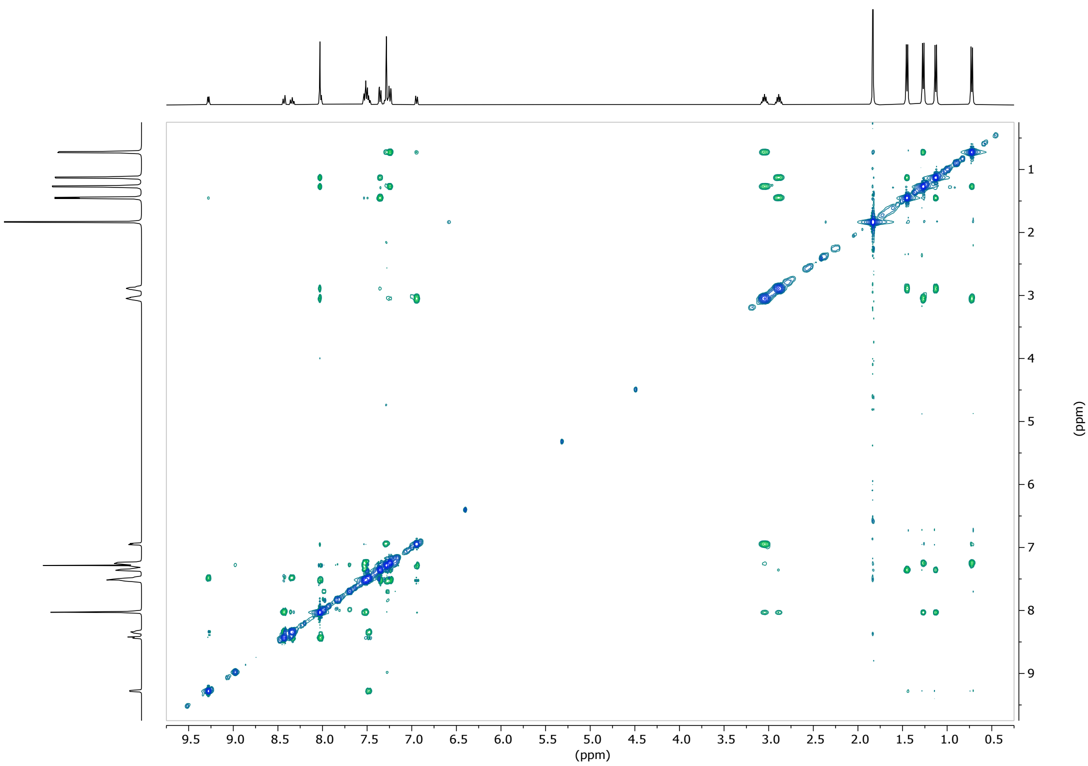
^{1}H-^{13}C HSQC in $CDCl_3$



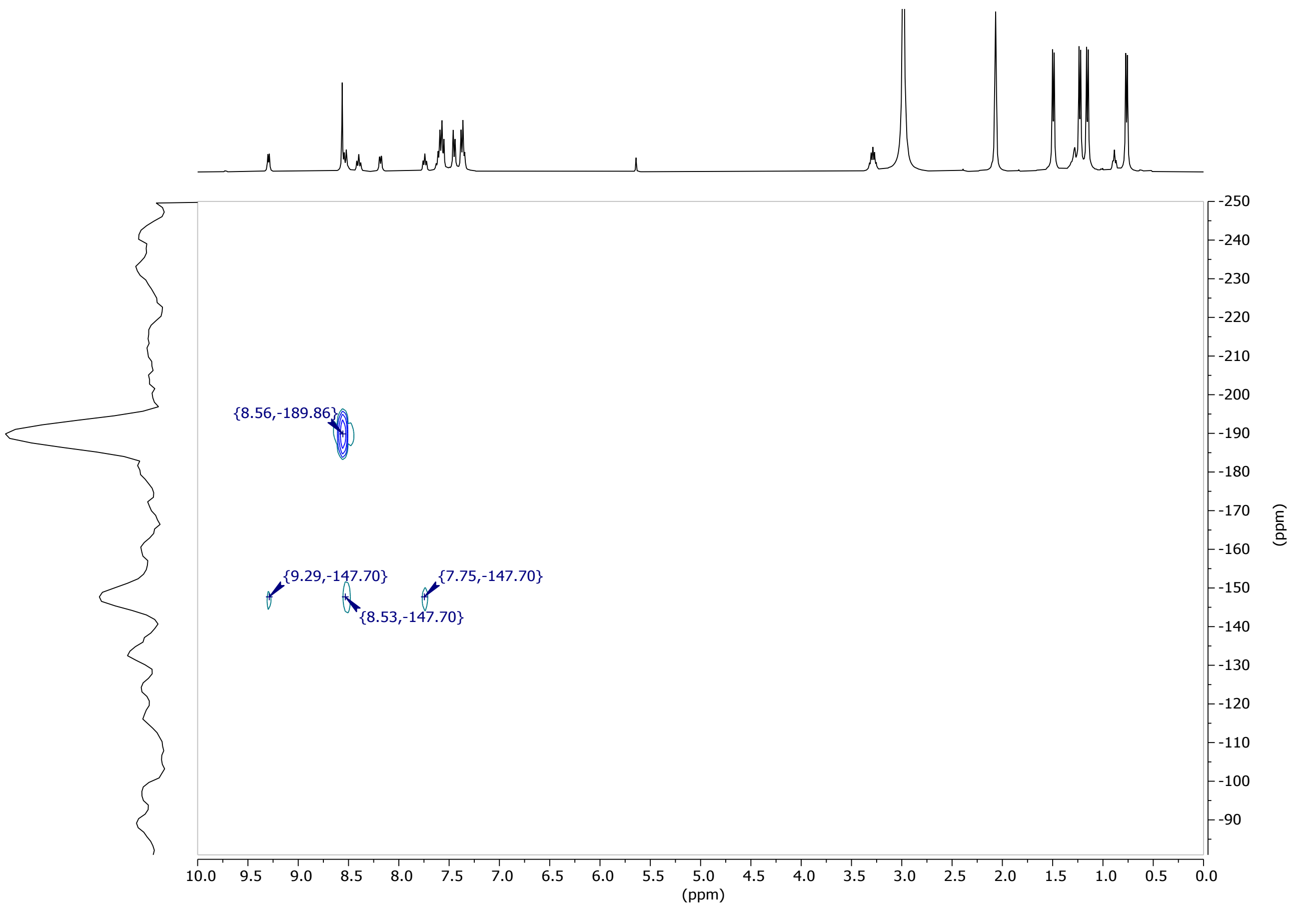
^{1}H-^{13}C HMBC in $CDCl_3$



^1H-^1H NOESY in $CDCl_3$

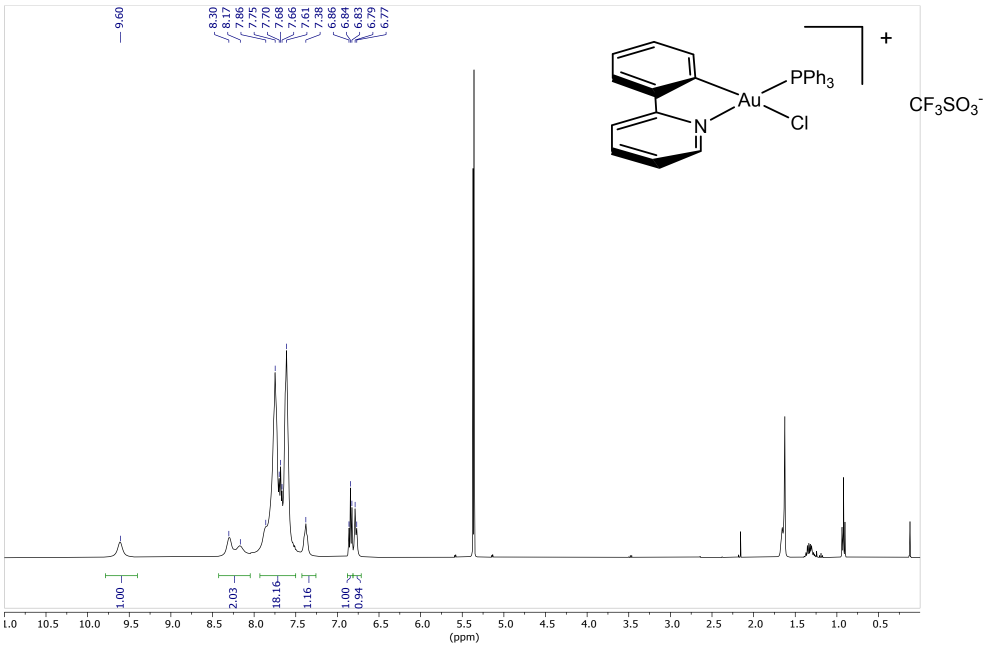


^1H-^{15}N HMBC in acetone-d_6

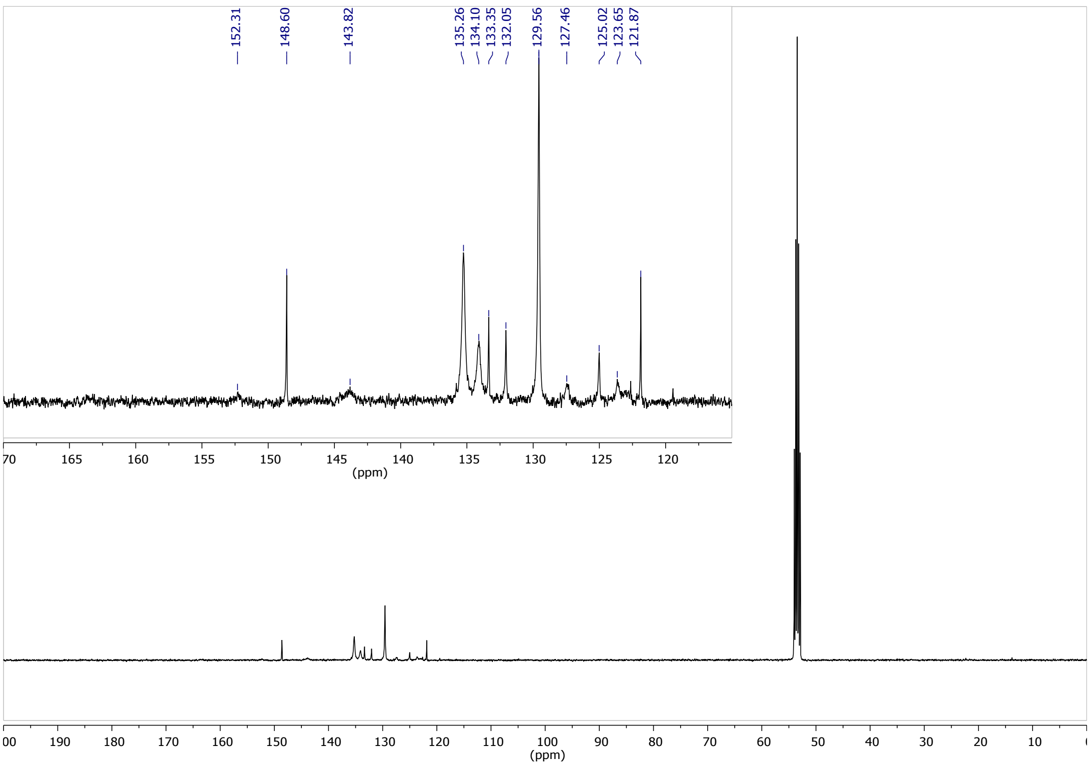


5.3 [AuCl(PPh$_3$(ppy)]OTf (2)

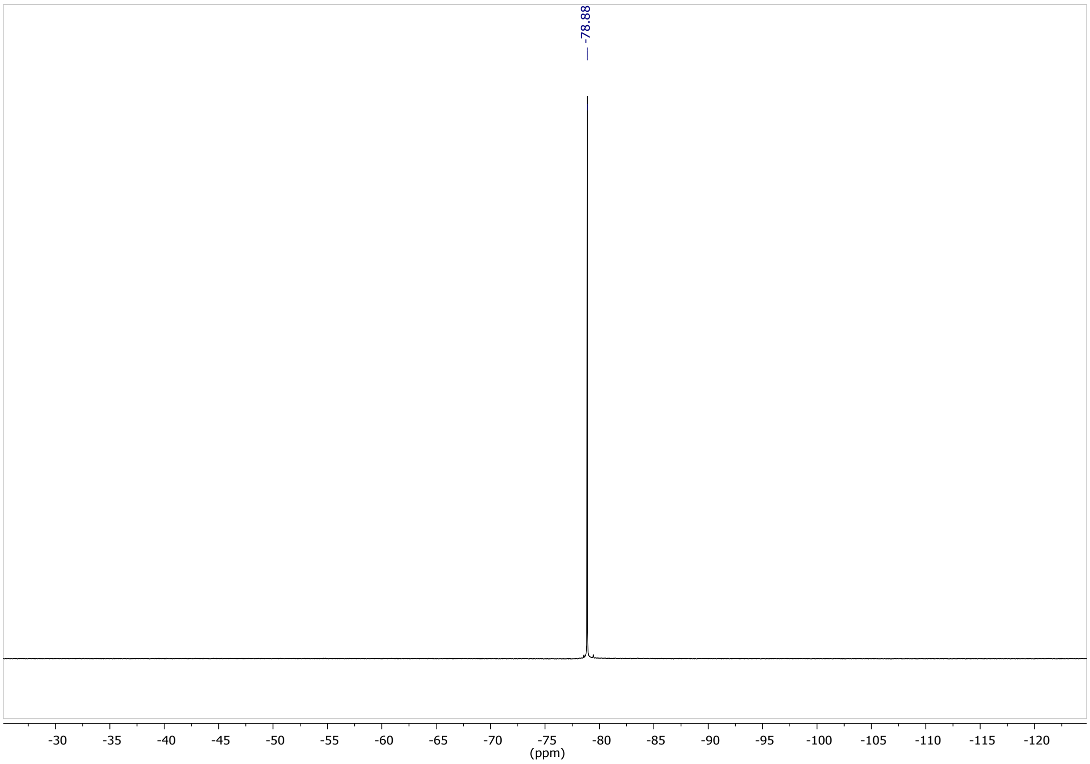
^{1}H NMR in CD_2Cl_2



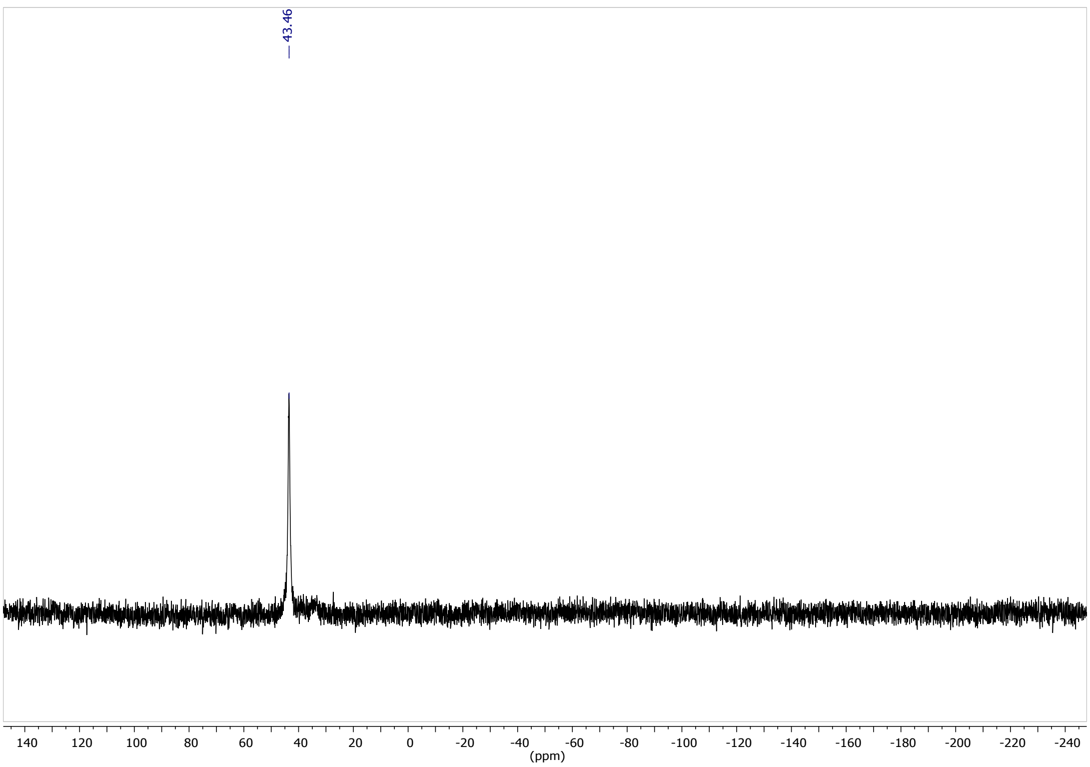
$^{13}C\ \{^{1}H\}$ NMR in CD_2Cl_2



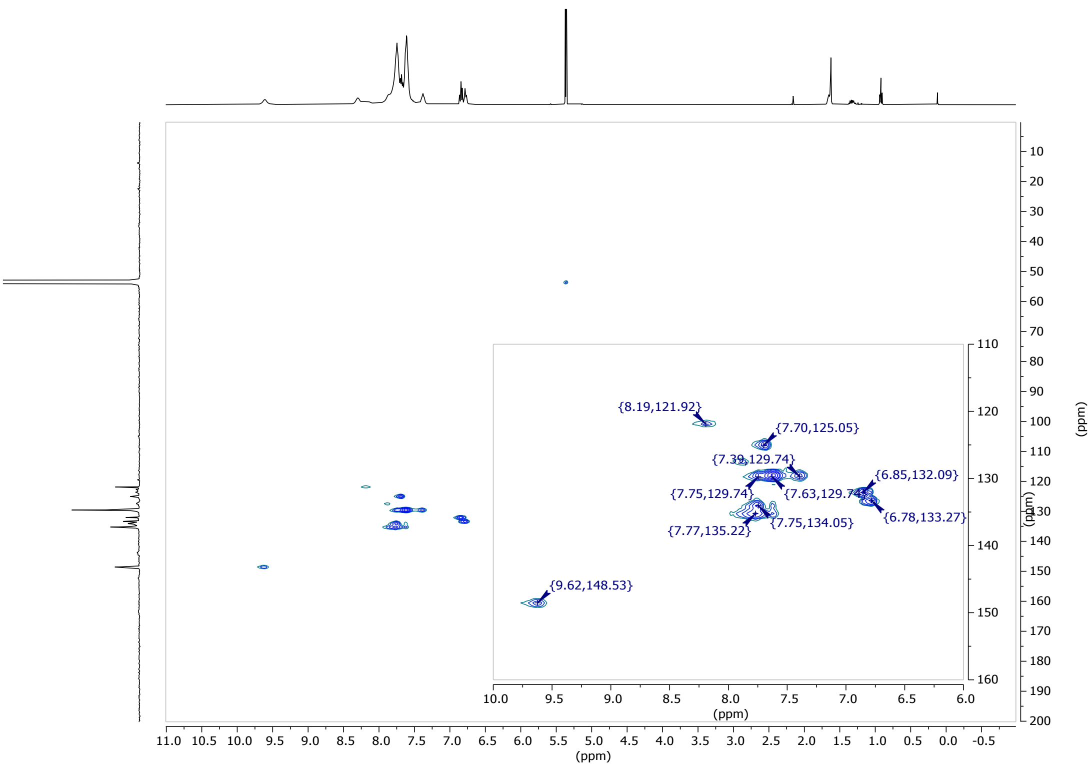
^{19}F NMR in CD_2Cl_2



$^{31}P\ \{^{1}H\}$ NMR in CD_2Cl_2

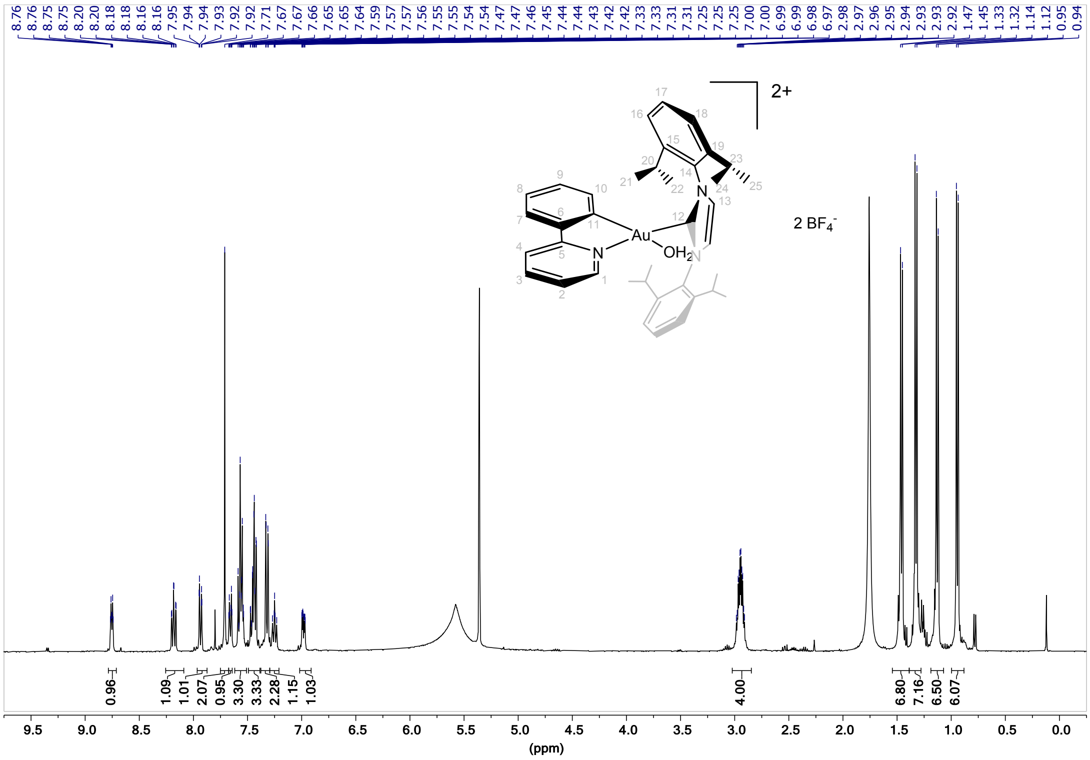


^{1}H-^{13}C HSQC in CD_2Cl_2

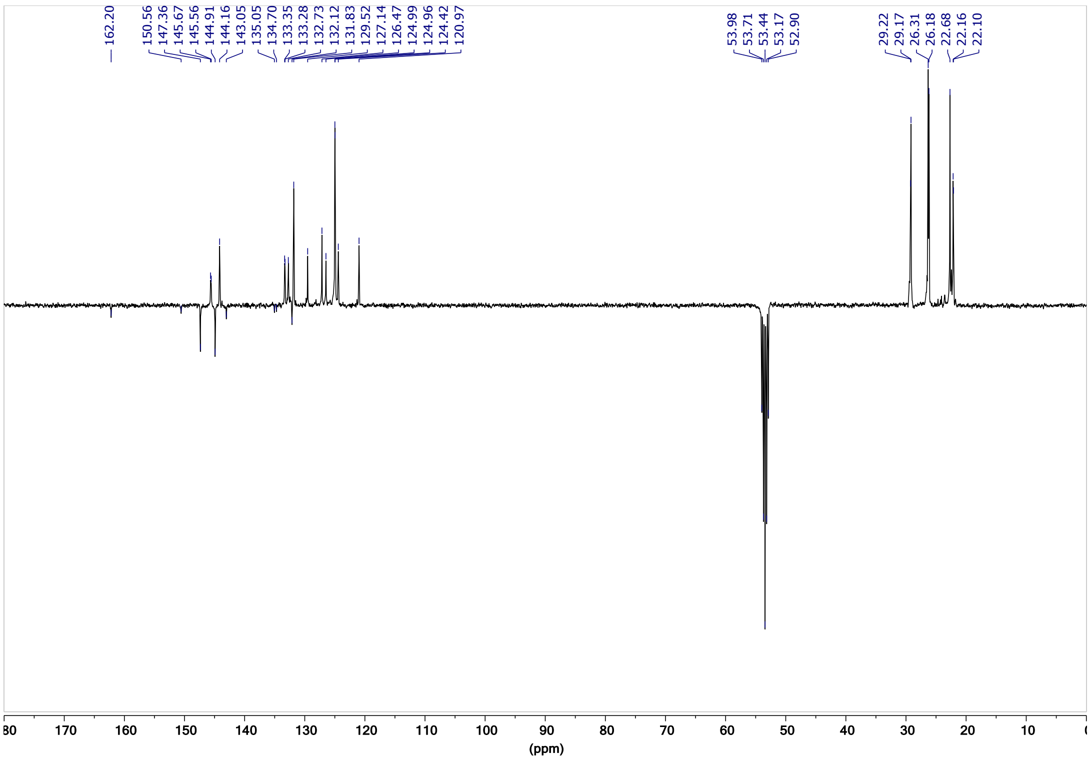


5.4 [Au(H_2O)(NHC)(ppy)](BF_4)$_2$ (3)

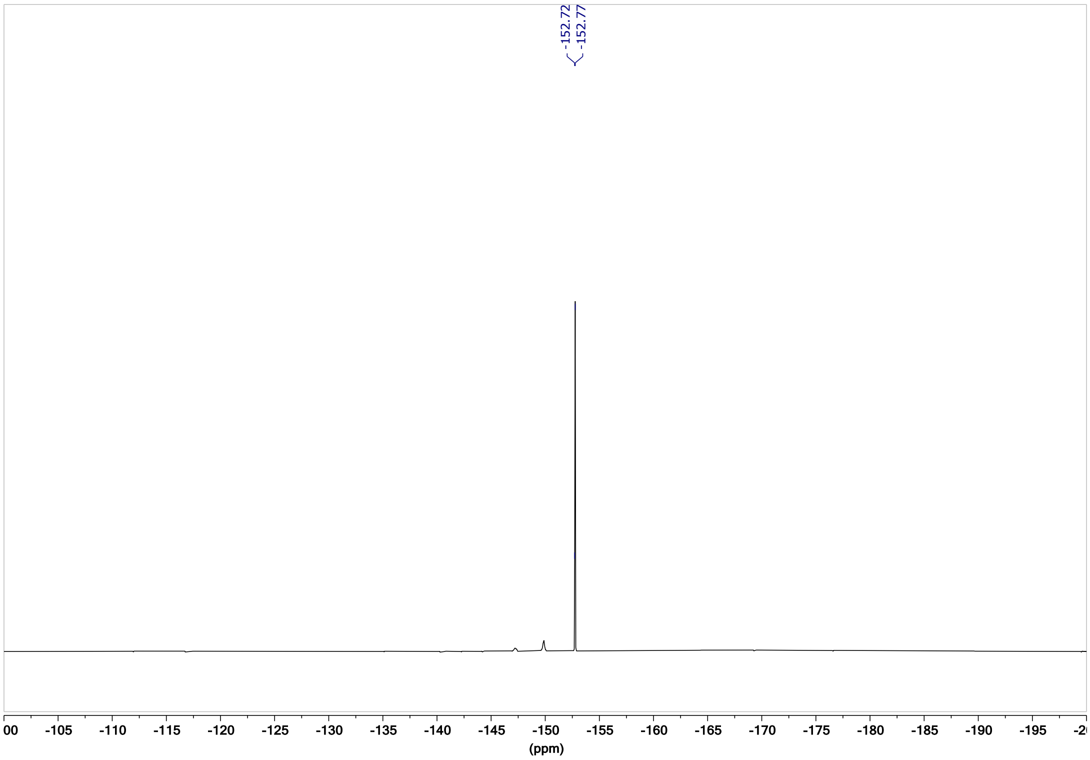
^{1}H NMR in CD_2Cl_2



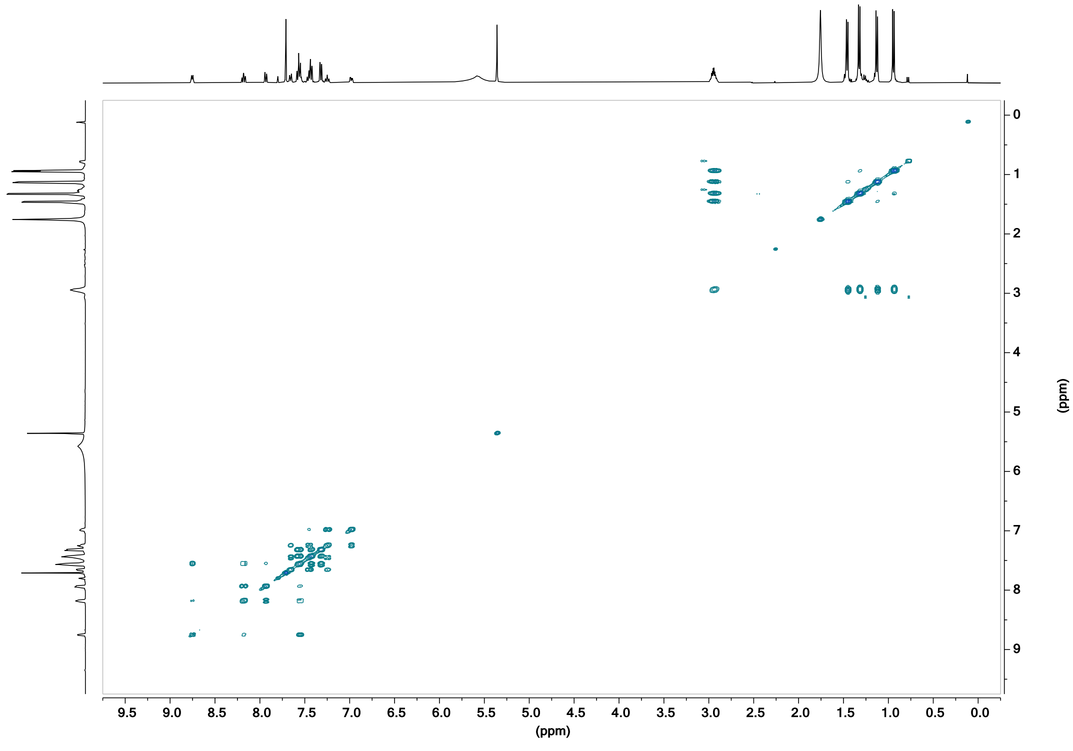
^{13}C {^{1}H} NMR



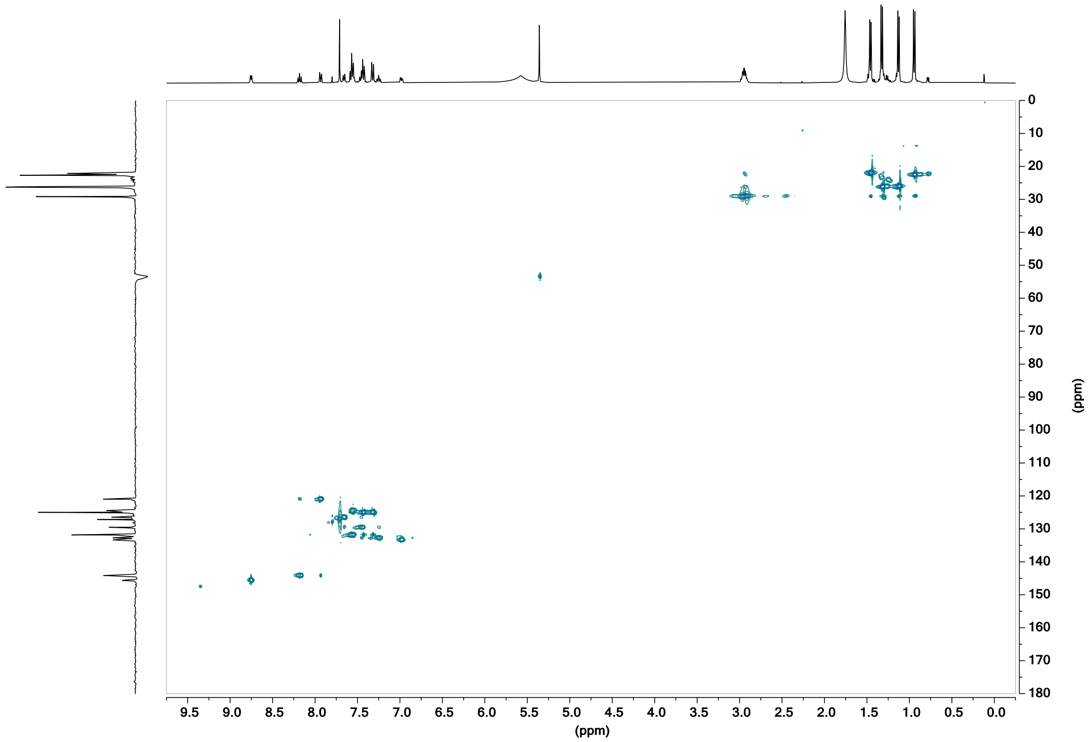
^{19}F NMR in CD_2Cl_2



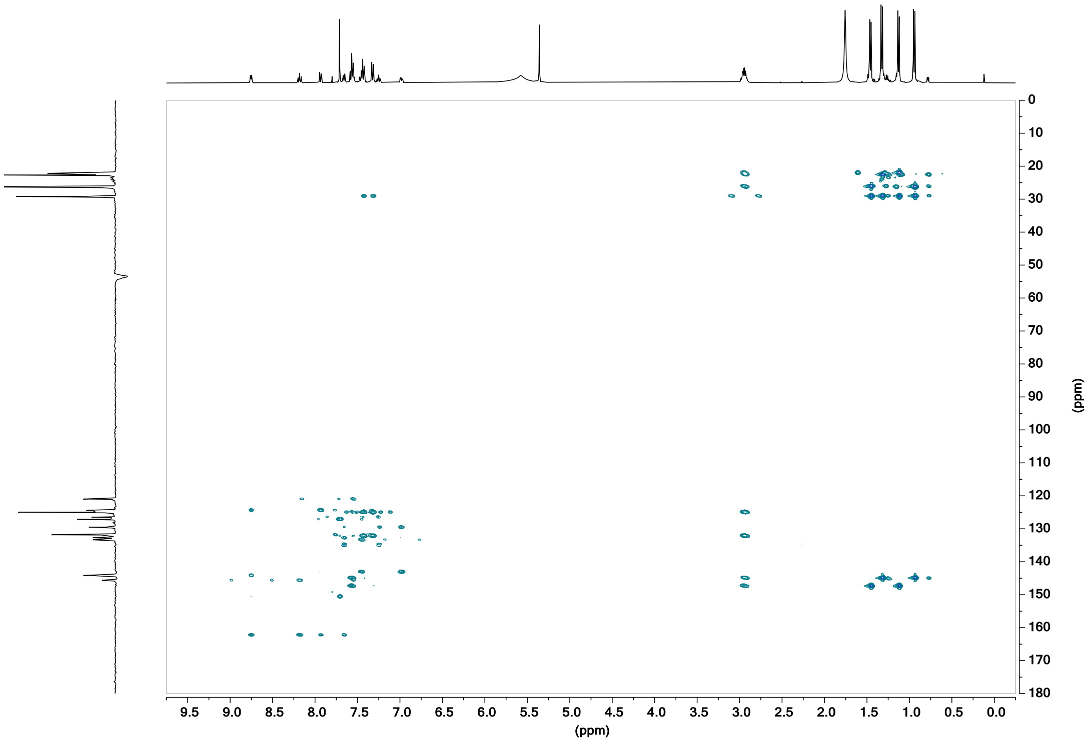
^{1}H-^{1}H COSY in CD_2Cl_2



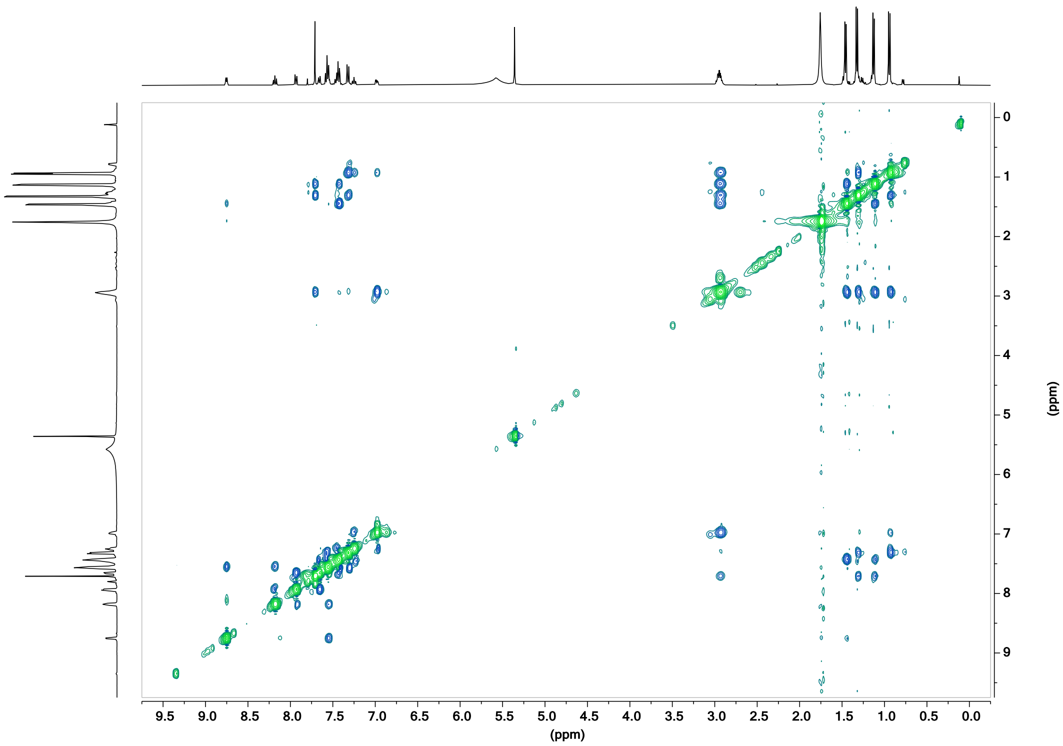
^{1}H-^{13}C HSQC in CD_2Cl_2



^1H-^{13}C HMBC in CD_2Cl_2

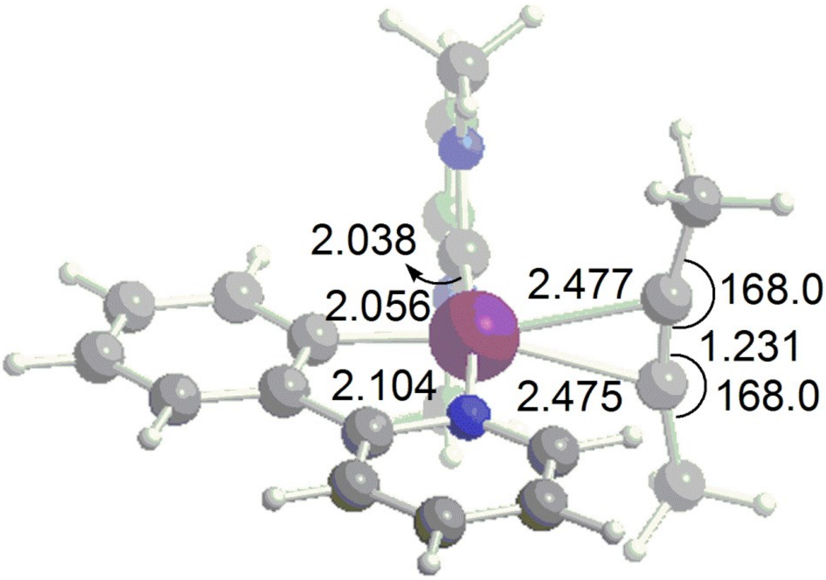


^1H-^1H NOESY in CD_2Cl_2


9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
(ppm)
0 1 2 3 4 5 6 7 8 9
(ppm)

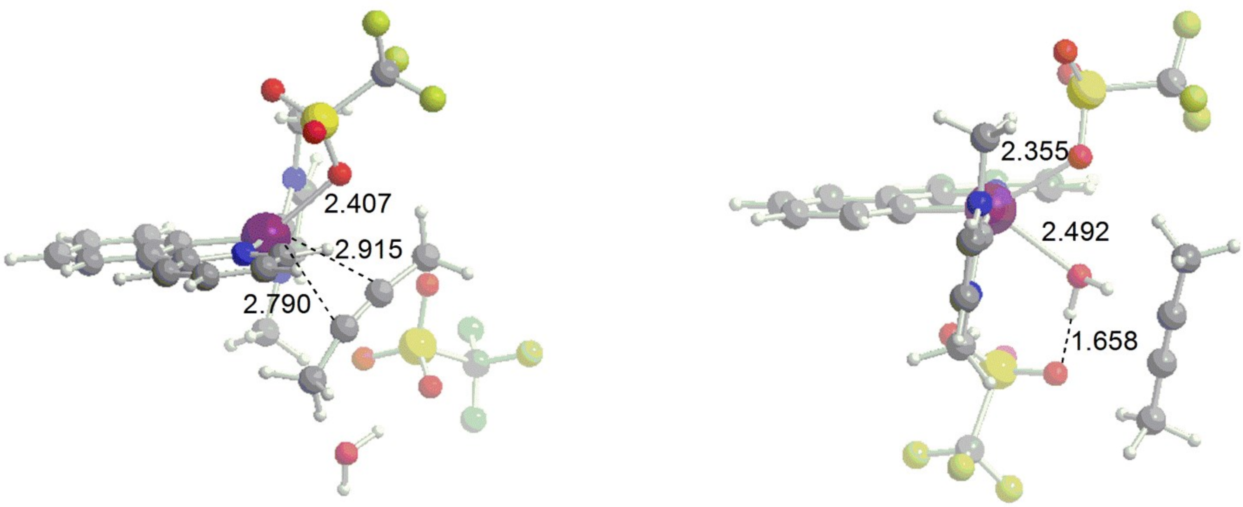
6. COMPUTATIONAL DETAILS

For the DFT study, the ADF2014.05[3,4,5] and the related Quantum-regions Interconnected by Local Descriptions (QUILD)[6] programs were used to identify the structures of reactant complexes, reaction intermediates, transition states and product complexes involved in the mechanism of the [(ppy)Au(NHC)$(OTf)_2$] - catalyzed addition of water to 2-butyne reaction. Geometry optimization calculations were carried out using the GGA functional BP86[7,8] (BP86). All atoms were treated with a Slater-type TZ2P triple-ζ with two polarization functions quality basis set, using the frozen core approximation (core small). Relativistic effects were accounted for with the scalar zero-order regular approximation, ZORA model.[9,10,11] Frequency calculations have been also performed to identify all stationary points as minima (zero imaginary frequencies) or transition states (one imaginary frequency). Final energies have been computed using ORCA program package[12] by single point B2PLYP perturbatively corrected doubly hybrid functional[13] calculations performed on the optimized BP86 gas phase structures in conjunction with a def2-TZVP basis set for all atoms and an ECP pseudopotential for gold to include relativistic effects. This computational set up (referred as BP86/B2PLYP) has been proven to be very accurate in describing catalysis by gold-containing species in benchmark calculations.[14,15,16] Computational mechanistic analysis is presented in enthalpy energies, since both the entropic contribution to the reaction profile has been shown to be small (as reported in the Supporting Information of our previous works[17,18,19,20]) and in order to compare the present results with those previously obtained for gold(I) and gold(III) species.[21] All calculations were carried out for the closed-shell singlet state. Explicit dispersion effect has been evaluated by BP86 including Grimme's D3 dispersion correction[22] (BP86+D) single point calculations on optimized BP86 gas phase structures. Solvation has been taken into account by the Conductor like Screening Model COSMO[23,24,25] using nitromethane as solvent ($\varepsilon_{\text{nitromethane}} \sim \varepsilon_{\text{valerolactone}}$) by single point calculations (BP86+D/COSMO) on optimized BP86 gas phase structures for an estimate of the solvent effect on the activation energy barriers.



$RC_{noanion}$

Figure S1. Optimized geometry of the reactant complex RC in the absence of both OTs^- anions. Distances are in Å.



$TS_{OTf\text{-}2\text{-}butyne}$ $TS_{OTf\text{-}H2O}$

Figure S2. Transition state structures for anion displacement by substrate ($TS_{OTf\text{-}2\text{-}butyne}$) and by water

($TS_{OTf\text{-}H2O}$) steps. Distances are in Å.

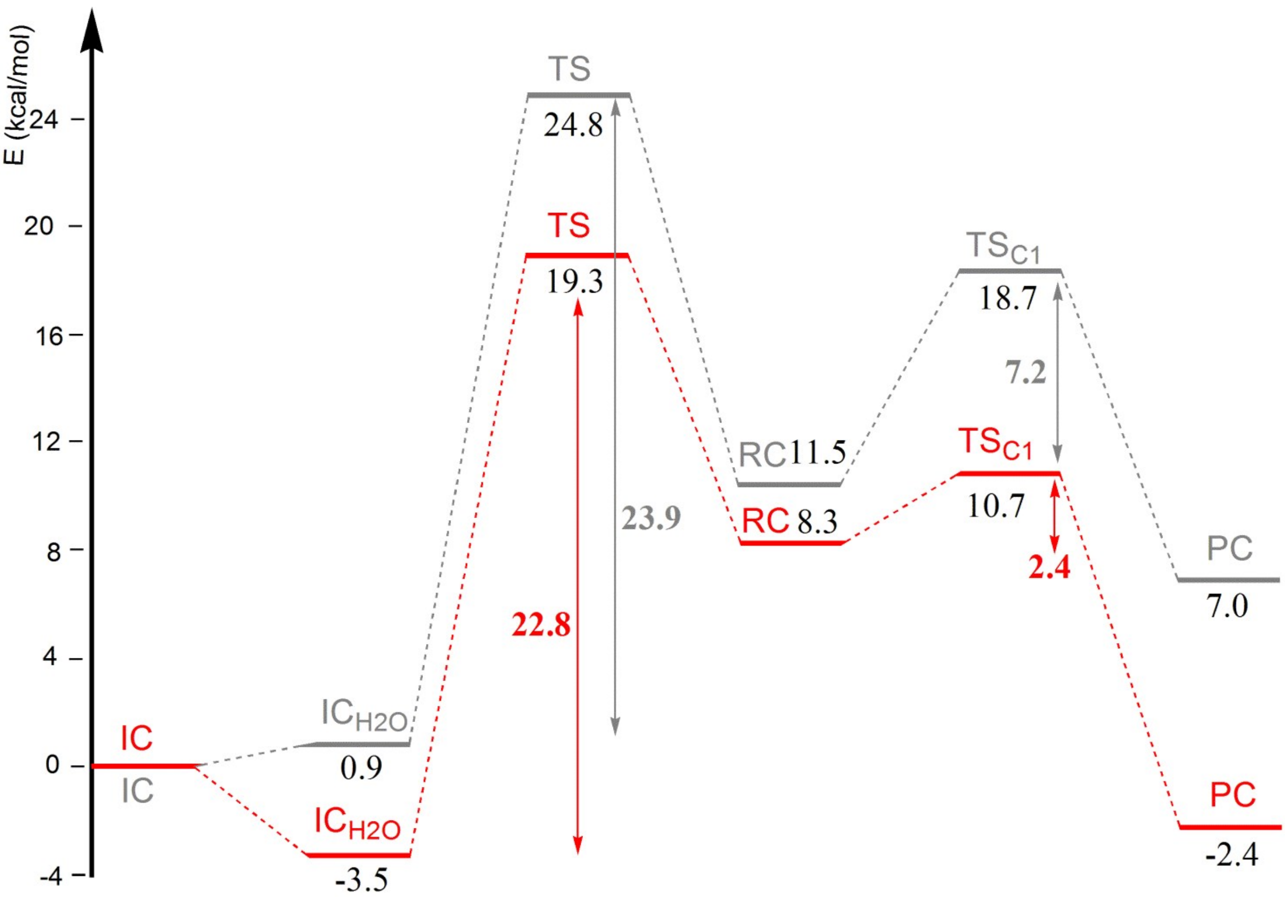


Figure S3. Reaction energy profiles for the pre-equilibrium and nucleophilic attack steps calculated at BP86 level of theory in gas phase: electronic energies E (red line) and Gibbs free energies G (blue line). Energy values refer to the corresponding IC taken as zero.

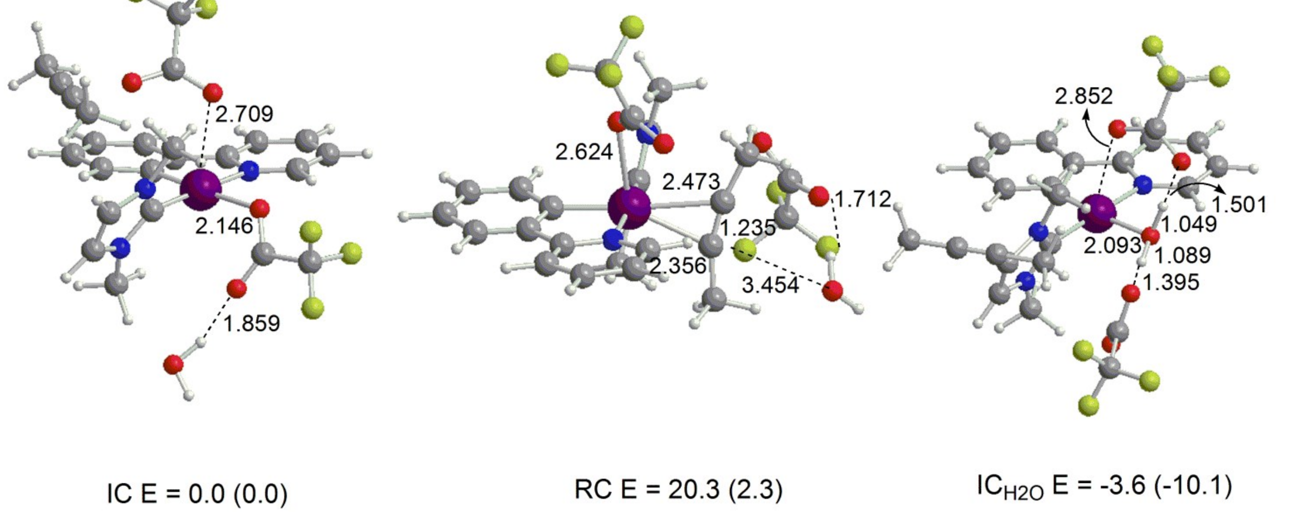


Figure S4. Optimized geometries for the initial complex IC, reactant complex RC and water adduct IC_{H2O} involving two TFA^- counterions in the pre-equilibrium step. Distances are in Å. Energy values (BP86/B2PLYP gas phase) refer to the corresponding IC taken as zero (in kcal/mol). Values in parenthesis are calculated at BP86+D/COSMO level.

Geometries

RC

65

C	3.838283	-3.201952	0.181440
C	2.865770	-2.286503	-0.247816
C	1.695669	-2.122324	0.526995
C	1.514927	-2.850904	1.696768
C	2.498385	-3.757742	2.108983
C	3.655113	-3.933668	1.350712
C	3.018549	-1.453010	-1.439253
N	1.972258	-0.614569	-1.694860
C	2.024809	0.266379	-2.709322
C	3.118168	0.329685	-3.560434
C	4.184640	-0.539092	-3.342846
C	4.133947	-1.429953	-2.278666
AU	0.415270	-0.730394	-0.276059
C	-1.075730	0.236264	-1.818890
C	-0.986078	-1.048621	1.154812
N	-1.142702	-0.388291	2.325458
C	-2.182391	-0.950792	3.040411
C	-2.659821	-1.989237	2.306213
N	-1.902194	-2.046260	1.152002
C	-0.430602	0.813913	2.762871
C	-2.156989	-2.991950	0.068721
O	2.145447	1.108309	0.981850
S	3.155379	1.909382	0.235799
C	3.858753	3.007014	1.593082
F	4.789661	3.849476	1.098969
O	2.565069	2.850990	-0.724881
O	4.306277	1.138807	-0.237504
F	2.877928	3.749023	2.164564
F	4.436140	2.259611	2.562987
H	0.624539	-2.722909	2.308418
H	2.354528	-4.321780	3.030384
H	4.421708	-4.635502	1.676035
H	4.752893	-3.335400	-0.394727
H	4.973595	-2.089084	-2.074240
H	5.063327	-0.506304	-3.985368
H	3.128834	1.065641	-4.360695
H	1.170030	0.929142	-2.818063
H	-3.486101	-2.664160	2.481762

H	-2.509045	-0.541195	3.986294
H	-1.281013	-3.026066	-0.585195
H	-2.326905	-3.986338	0.494772
H	-3.038170	-2.649323	-0.486613
H	0.447389	0.983904	2.130155
H	-1.116238	1.666384	2.702024
H	-0.104923	0.674535	3.799347
C	-0.828822	1.232397	-1.133751
C	-1.628055	-0.650330	-2.839733
C	-0.711879	2.530648	-0.501202
H	-2.445789	-1.247730	-2.416672
H	-2.060029	0.009171	-3.610320
H	-0.871009	-1.304164	-3.290766
H	0.337030	2.808763	-0.326364
H	-1.162598	3.251000	-1.202395
H	-1.298910	2.555227	0.425238
O	-2.900411	2.171659	-3.538055
H	-3.443914	2.724515	-4.121444
H	-3.478529	2.007561	-2.750290
O	-4.407629	1.701587	-1.259067
S	-4.294577	0.684544	-0.198904
C	-6.016378	0.676474	0.559961
O	-4.136060	-0.700485	-0.679658
O	-3.427718	1.054716	0.929493
F	-6.083281	-0.243039	1.560463
F	-6.324655	1.882685	1.083764
F	-6.956379	0.360295	-0.357100

TSC1

65

C	-3.925376	-3.199533	-0.411789
C	-2.948860	-2.325884	0.090312
C	-1.716337	-2.207059	-0.590508
C	-1.479289	-2.951162	-1.741689
C	-2.464342	-3.817990	-2.229600
C	-3.683556	-3.942074	-1.563725
C	-3.152143	-1.491580	1.274691
N	-2.096777	-0.691059	1.608886
C	-2.186087	0.177475	2.631682
C	-3.328549	0.266855	3.412711
C	-4.407147	-0.561887	3.113879
C	-4.317731	-1.440220	2.042021
AU	-0.441994	-0.863365	0.323299
C	0.863764	0.331162	1.652212
C	1.065192	-1.234561	-0.973909
N	1.319536	-0.621001	-2.153087
C	2.410970	-1.211821	-2.762195
C	2.824456	-2.220397	-1.951881
N	1.977000	-2.230269	-0.860125
C	0.638052	0.555777	-2.692927
C	2.144367	-3.125976	0.279731
O	-1.910459	1.321935	-0.975959
S	-3.079449	1.960267	-0.303185
C	-3.660399	3.179481	-1.613212
F	-4.706299	3.905591	-1.165198
O	-2.707008	2.803434	0.837971
O	-4.221940	1.066387	-0.111826

F	-2.662598	4.036675	-1.946256
F	-4.044822	2.531550	-2.737528
H	-0.537773	-2.864952	-2.281335
H	-2.274308	-4.392626	-3.136192
H	-4.451150	-4.612794	-1.947520
H	-4.886940	-3.292990	0.091374
H	-5.162893	-2.069665	1.776371
H	-5.323530	-0.508304	3.700002
H	-3.367040	0.992984	4.221003
H	-1.320090	0.812850	2.799026
H	3.658678	-2.903065	-2.034426
H	2.810565	-0.842479	-3.696535
H	1.240429	-3.088523	0.893987
H	2.290819	-4.148867	-0.083422
H	3.013328	-2.794980	0.859771
H	-0.310678	0.712979	-2.170166
H	1.289082	1.427695	-2.563534
H	0.441779	0.393210	-3.758125
C	0.858218	1.515759	1.215553
C	1.500119	-0.431906	2.763268
C	0.600521	2.668144	0.394056
H	2.422969	-0.902160	2.395029
H	1.772196	0.263684	3.565868
H	0.839093	-1.210283	3.163990
H	-0.201462	2.385116	-0.316324
H	0.190601	3.498741	0.982639
H	1.505272	2.970307	-0.149938
O	2.285437	2.541719	2.721232
H	2.273666	3.496895	2.539639
H	3.125570	2.208028	2.274755
O	4.440599	1.578543	1.513272
S	4.375924	0.669913	0.344564
C	6.134560	0.759463	-0.316685
O	4.209310	-0.750721	0.689735
O	3.551583	1.153431	-0.770324
F	6.268410	-0.054209	-1.395686
F	6.444563	2.016597	-0.700012
F	7.027744	0.367852	0.616245

TSC2

65

C	3.698335	-3.424632	0.214788
C	2.781425	-2.441680	-0.188792
C	1.630657	-2.211238	0.597817
C	1.418073	-2.947104	1.758749
C	2.342764	-3.923655	2.146880
C	3.479589	-4.161629	1.374712
C	2.967619	-1.610659	-1.378163
N	1.961681	-0.720265	-1.628001
C	2.050925	0.149706	-2.650066
C	3.136048	0.150406	-3.513825
C	4.161507	-0.766036	-3.298043
C	4.077047	-1.644506	-2.225773
AU	0.425492	-0.731672	-0.188718
C	-1.288160	0.311006	-2.098952

C	-0.957915	-0.926115	1.274921
N	-1.010634	-0.264962	2.456472
C	-2.071272	-0.738002	3.207639
C	-2.674028	-1.713682	2.479160
N	-1.968193	-1.827860	1.297029
C	-0.117744	0.805776	2.908253
C	-2.350396	-2.720814	0.204076
O	2.312464	1.097612	0.957814
S	3.232002	1.907683	0.114340
C	3.943488	3.119102	1.366929
F	4.816033	3.967312	0.782514
O	2.538072	2.762672	-0.859848
O	4.397736	1.176244	-0.383384
F	2.956227	3.856481	1.935705
F	4.591963	2.459566	2.355314
H	0.541902	-2.773743	2.380853
H	2.170716	-4.494045	3.059669
H	4.201418	-4.917523	1.681001
H	4.595420	-3.610686	-0.374477
H	4.885554	-2.341995	-2.023189
H	5.035523	-0.780145	-3.947590
H	3.176650	0.880216	-4.318635
H	1.233186	0.857262	-2.751552
H	-3.555134	-2.307994	2.678680
H	-2.315042	-0.321149	4.175237
H	-1.463655	-2.937252	-0.399191
H	-2.729667	-3.655044	0.630571
H	-3.126699	-2.229060	-0.398258
H	0.691288	0.954984	2.184114
H	-0.695535	1.730422	3.018374
H	0.313630	0.526591	3.876037
C	-0.778055	0.914970	-1.118422
C	-1.687011	-0.745923	-3.013476
C	-0.733018	2.236723	-0.449794
H	-2.760752	-0.950427	-2.898019
H	-1.480193	-0.466446	-4.052988
H	-1.125966	-1.662626	-2.779383
H	0.302863	2.571757	-0.309359
H	-1.281040	2.969953	-1.054367
H	-1.240331	2.171834	0.520665
O	-2.585798	1.784414	-3.258217
H	-2.190559	2.672885	-3.237064
H	-3.329400	1.818327	-2.572776
O	-4.426289	1.824192	-1.364734
S	-4.472325	0.705753	-0.392581
C	-6.235753	0.811420	0.253717
O	-4.404349	-0.631315	-1.008902
O	-3.648812	0.892725	0.806107
F	-6.441864	-0.149234	1.190753
F	-6.469352	2.011885	0.825441
F	-7.133230	0.629926	-0.736975

PCC1

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N	-1.981167	2.129051	-0.927322

C	-0.917403	1.296255	-1.065130
N	-1.021888	0.764537	-2.308776
C	-2.156235	1.251548	-2.938659
C	-2.758395	2.107039	-2.073474
AU	0.542155	0.958024	0.277644
C	-0.784551	-0.218921	1.445490
C	-1.269161	0.445158	2.715659
C	-0.084868	-0.166577	-2.943453
C	-2.282954	2.952879	0.239736
C	1.901812	2.271705	-0.607107
C	3.127361	2.334319	0.098590
C	4.148540	3.192513	-0.337542
C	3.963014	3.989425	-1.463685
C	2.755582	3.934939	-2.161427
C	1.733807	3.081386	-1.730538
C	3.271837	1.451225	1.259188
N	2.171895	0.697974	1.565759
C	2.212048	-0.213013	2.555245
C	3.343166	-0.390493	3.337400
C	4.466060	0.388766	3.070626
C	4.429459	1.305742	2.028771
C	-1.198702	-1.439074	1.091392
C	-0.805987	-2.310935	-0.049016
O	-2.207027	-2.061340	1.926057
O	-4.362445	-0.749303	1.760556
S	-4.866118	-0.399344	0.321490
O	-4.053644	-1.026563	-0.701858
C	-6.514798	-1.315583	0.328956
F	-7.301133	-0.867493	1.319272
O	-5.196265	1.008953	0.255325
F	-7.125356	-1.109950	-0.851098
F	-6.304926	-2.635033	0.493091
O	2.171687	-1.249509	-1.080341
S	3.098328	-2.096674	-0.286217
O	4.373023	-1.457223	0.043485
C	3.561842	-3.432020	-1.531241
F	4.154200	-2.896693	-2.626002
O	2.444538	-2.842179	0.797376
F	4.415415	-4.331425	-0.992778
F	2.456127	-4.105539	-1.947991
H	0.800588	3.057085	-2.294846
H	2.608009	4.556135	-3.045593
H	4.761958	4.649462	-1.799716
H	5.098279	3.238510	0.194777
H	5.311007	1.892371	1.783754
H	5.377587	0.262259	3.653391
H	3.342008	-1.150555	4.114710
H	1.314529	-0.812390	2.684364
H	-3.673790	2.677065	-2.154858
H	-2.436623	0.933814	-3.933752
H	-1.482152	2.823513	0.971646
H	-2.332874	4.006481	-0.058371
H	-3.241727	2.641235	0.669451
H	0.746614	-0.388503	-2.265984
H	-0.609585	-1.097277	-3.186095
H	0.303589	0.287067	-3.862320
H	-2.134621	1.102468	2.541080
H	-1.581461	-0.294071	3.467117
H	-0.485374	1.069518	3.168135

H	0.063008	-1.902140	-0.575167
H	-0.483806	-3.298746	0.320632
H	-1.646905	-2.457482	-0.744160
H	-2.236717	-3.008667	1.698052
H	-3.499090	-1.357921	1.769350

PCC2

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N	1.757431	1.772767	1.543117
C	0.618118	1.037379	1.478724
N	0.432959	0.526149	2.721649
C	1.459875	0.935284	3.558370
C	2.291375	1.715566	2.819957
AU	-0.552154	0.754484	-0.134334
C	0.760534	-0.827995	-0.682607
C	0.697093	-2.077130	0.154147
C	-0.681560	-0.322278	3.157010
C	2.346369	2.540342	0.448778
C	-1.827718	2.356794	0.266255
C	-2.842897	2.497970	-0.709745
C	-3.775051	3.542814	-0.612051
C	-3.707995	4.446592	0.444671
C	-2.709958	4.311585	1.411161
C	-1.777116	3.272661	1.317317
C	-2.873872	1.500600	-1.782415
N	-1.865070	0.576446	-1.756437
C	-1.825634	-0.427829	-2.651658
C	-2.773164	-0.546322	-3.657077
C	-3.797471	0.394573	-3.721974
C	-3.847388	1.415113	-2.781888
C	1.623667	-0.658162	-1.691495
C	1.759612	0.467538	-2.666610
O	2.612312	-1.657798	-2.013085
O	4.815052	-0.543254	-1.401433
S	5.119012	-0.549401	0.136420
O	4.213505	-1.428925	0.849004
C	6.805257	-1.396374	0.118250
F	7.672175	-0.707053	-0.639191
O	5.361674	0.803005	0.594085
F	7.265045	-1.453719	1.379804
F	6.686287	-2.643961	-0.367475
O	-2.761970	-0.951312	0.936690
S	-3.407589	-1.955705	0.055057
O	-4.495591	-1.432569	-0.771772
C	-4.274344	-3.072490	1.298846
F	-5.174768	-2.376371	2.033220
O	-2.457766	-2.854964	-0.618578
F	-4.927677	-4.081294	0.680757
F	-3.377314	-3.622837	2.159747
H	-1.010134	3.187713	2.088272
H	-2.657905	5.014860	2.243011
H	-4.437051	5.252916	0.516792
H	-4.562673	3.653962	-1.356958
H	-4.659378	2.137486	-2.799188
H	-4.569520	0.319408	-4.486652

H	-2.716689	-1.383181	-4.348736
H	-1.018246	-1.144004	-2.525835
H	3.216909	2.213540	3.075793
H	1.510362	0.624975	4.593464
H	1.781769	2.328055	-0.461701
H	2.284706	3.612080	0.671883
H	3.392522	2.242774	0.317899
H	-1.334484	-0.557647	2.306895
H	-0.281560	-1.251186	3.578593
H	-1.261164	0.207938	3.921315
H	2.756785	0.930751	-2.621264
H	1.624469	0.100911	-3.695390
H	1.004285	1.237027	-2.475876
H	-0.340079	-2.439198	0.213485
H	1.290275	-2.927184	-0.232637
H	1.059923	-1.895446	1.176092
H	2.447691	-2.412985	-1.410811
H	3.936853	-1.082306	-1.636383

IC

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C	1.482972	3.819108	2.145408
C	0.728540	2.958678	1.336090
C	0.581661	1.608324	1.727692
C	1.208746	1.130851	2.871035
C	1.961442	2.006687	3.661919
C	2.089567	3.348125	3.305129
C	0.132047	3.358903	0.065370
N	-0.551297	2.368153	-0.571829
C	-1.103061	2.557240	-1.780161
C	-1.022743	3.786269	-2.419240
C	-0.344831	4.827170	-1.784472
C	0.235611	4.613416	-0.540767
AU	-0.543058	0.537180	0.426143
O	-1.768759	-0.393965	-1.102093
S	-3.163954	-0.930909	-0.797694
C	-3.620622	-1.532140	-2.528563
F	-4.867703	-2.037777	-2.496085
C	-0.544023	-1.163581	1.513436
N	-1.169880	-1.369752	2.698857
C	-0.975617	-2.677430	3.102177
C	-0.209016	-3.277932	2.150300
N	0.049467	-2.331574	1.178912
C	-2.010979	-0.401008	3.407338
C	0.782881	-2.613141	-0.061630
O	-4.123367	0.134698	-0.500698
O	-3.165079	-2.106581	0.058497
F	-3.586937	-0.513156	-3.409609
F	-2.770630	-2.490994	-2.935508
O	-4.932948	0.542448	2.208653
O	1.427052	0.187726	-1.538235
S	2.772771	0.662314	-1.114966
O	3.370922	-0.139176	-0.039521
O	2.884255	2.117026	-0.982966
C	3.832522	0.257677	-2.622070
F	3.388726	0.913234	-3.721059
F	5.119920	0.616955	-2.411856
F	3.808052	-1.071227	-2.891206

C	4.692225	-3.018722	1.357480
C	4.005380	-4.281418	1.122110
C	3.455220	-5.341575	0.912873
C	2.834799	-6.632326	0.642781
H	1.142817	0.083066	3.152928
H	2.457229	1.626472	4.554684
H	2.680330	4.024445	3.921155
H	1.614151	4.860791	1.855659
H	0.789675	5.406976	-0.046034
H	-0.257440	5.800676	-2.265207
H	-1.477117	3.912325	-3.399019
H	-1.603035	1.695288	-2.215912
H	0.186063	-4.282296	2.082286
H	-1.398462	-3.061196	4.020673
H	1.112576	-1.673077	-0.517938
H	1.651885	-3.235063	0.180665
H	0.116212	-3.142970	-0.751538
H	-2.122319	-0.740106	4.441728
H	-1.520997	0.577126	3.402430
H	-3.000999	-0.319276	2.937258
H	-4.757515	0.405430	1.250846
H	-5.808704	0.148696	2.350089
H	5.730560	-3.071143	0.999730
H	4.206703	-2.180341	0.836086
H	4.723215	-2.778317	2.430100
H	2.011930	-6.544188	-0.081887
H	2.427811	-7.086552	1.558260
H	3.564816	-7.339262	0.222504

ICH2O

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C	-1.996181	-3.618418	1.899912
C	-1.353552	-2.683227	1.078122
C	-0.996356	-1.426668	1.619751
C	-1.304425	-1.116066	2.938478
C	-1.952366	-2.062564	3.741736
C	-2.289778	-3.312460	3.225364
C	-1.071612	-2.908323	-0.337139
N	-0.471360	-1.859826	-0.964509
C	-0.189934	-1.889308	-2.274933
C	-0.478319	-3.008109	-3.043972
C	-1.079173	-4.105170	-2.428505
C	-1.379155	-4.054885	-1.072463
AU	-0.077532	-0.231184	0.268206
O	0.900513	0.788594	-1.356216
C	0.343632	1.225233	1.606540
N	1.331338	1.174768	2.537092
C	1.322523	2.332101	3.293632
C	0.312122	3.110445	2.817478
N	-0.282236	2.415135	1.779946
C	2.238484	0.044484	2.762753
C	-1.427959	2.917445	1.012478
O	3.363650	0.332479	-1.668682
S	3.847981	-0.951169	-1.062741
O	2.938756	-1.449864	-0.016900

O	4.367217	-1.916787	-2.013662
C	5.358893	-0.358443	-0.107335
F	5.007559	0.607291	0.790499
F	5.916129	-1.376462	0.579907
F	6.286232	0.161027	-0.933658
O	-2.209989	0.819285	-1.300074
S	-3.545332	0.328227	-0.845593
O	-3.634461	-1.128221	-0.729313
C	-4.626683	0.724832	-2.336031
F	-5.909334	0.370629	-2.110616
O	-4.123383	1.117836	0.243334
F	-4.600545	2.053044	-2.617186
F	-4.193580	0.061268	-3.436278
C	1.372256	3.799295	-1.837701
C	0.253925	3.701775	-2.303437
C	-1.072850	3.606194	-2.898790
C	2.736517	3.942595	-1.342271
H	1.928814	0.613718	-1.432446
H	-1.065956	-0.141273	3.358769
H	-2.198562	-1.810506	4.772982
H	-2.796779	-4.045221	3.851544
H	-2.284585	-4.588151	1.496348
H	-1.862842	-4.896315	-0.582819
H	-1.320110	-4.996587	-3.006256
H	-0.233829	-3.007454	-4.103426
H	0.267092	-0.991581	-2.685097
H	-0.029158	4.093314	3.114371
H	2.037433	2.502643	4.087527
H	-1.667074	2.215850	0.205178
H	-2.301731	2.997466	1.667521
H	-1.170445	3.896490	0.594651
H	2.435965	-0.467109	1.813333
H	3.179360	0.431429	3.164348
H	1.788091	-0.654284	3.477639
H	0.749775	1.761527	-1.482534
H	3.292691	4.664673	-1.956455
H	2.754261	4.303665	-0.304292
H	3.277994	2.986598	-1.380275
H	-0.997998	3.491674	-3.989152
H	-1.658991	4.513367	-2.696116
H	-1.629834	2.743360	-2.504357

TS

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C	0.174719	-2.616833	-2.209500
C	0.051181	-1.750384	-1.114265
C	0.163449	-0.368784	-1.353421
C	0.387843	0.146262	-2.615912
C	0.505182	-0.745717	-3.690161
C	0.398574	-2.118589	-3.486844
C	-0.201051	-2.192698	0.246658
N	-0.296446	-1.188827	1.165048
C	-0.597822	-1.452877	2.448542
C	-0.792311	-2.747675	2.898644
C	-0.669936	-3.795886	1.984326

C	-0.375783	-3.517110	0.659325
AU	-0.006825	0.718854	0.376815
O	-2.129345	1.514859	1.824697
C	0.229420	2.477999	-0.583092
N	-0.766184	3.228921	-1.120769
C	-0.228345	4.351405	-1.722140
C	1.122870	4.283003	-1.561339
N	1.390279	3.121910	-0.860402
C	-2.202439	2.921390	-1.078883
C	2.741936	2.668381	-0.508175
O	-3.923524	-0.289047	1.276002
S	-3.875944	-0.947456	-0.061644
O	-3.195711	-0.136058	-1.083918
O	-3.533448	-2.366001	-0.024768
C	-5.686208	-0.908645	-0.583991
F	-6.141198	0.367437	-0.644682
F	-5.838516	-1.465750	-1.805983
F	-6.458267	-1.588320	0.291498
O	3.016873	-0.405393	0.312998
S	3.872752	-0.934049	-0.787109
O	3.571625	-2.308902	-1.177844
C	5.554985	-1.059483	0.059139
F	6.497563	-1.524728	-0.788507
O	4.100942	0.033572	-1.865735
F	5.965936	0.157930	0.510653
F	5.505866	-1.893126	1.129521
C	0.696039	2.391064	2.565565
C	1.374854	1.403368	2.807543
C	2.285343	0.333774	3.184404
C	0.020821	3.684126	2.495907
H	-2.852323	0.841798	1.568176
H	0.488102	1.211447	-2.800062
H	0.693615	-0.348010	-4.686737
H	0.501678	-2.804917	-4.325313
H	0.101246	-3.691791	-2.055211
H	-0.297568	-4.318649	-0.069706
H	-0.818673	-4.825866	2.304690
H	-1.043304	-2.923573	3.941882
H	-0.681555	-0.592175	3.107097
H	1.912244	4.945897	-1.890206
H	-0.848445	5.089660	-2.213076
H	2.697677	1.653982	-0.093873
H	3.356793	2.626687	-1.412649
H	3.178198	3.361617	0.219830
H	-2.364963	1.836952	-1.119155
H	-2.640770	3.310524	-0.154031
H	-2.675415	3.391389	-1.946173
H	-2.067357	1.436518	2.791095
H	0.072344	4.179803	3.475577
H	0.502626	4.344977	1.761908
H	-1.033951	3.569910	2.218406
H	1.783163	-0.437917	3.782740
H	3.099780	0.756274	3.790465
H	2.727839	-0.135407	2.290202

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C	-3.720044	3.721593	1.023108
C	-3.055885	2.622572	0.455232
C	-1.915202	2.106200	1.114180
C	-1.466493	2.665059	2.304564
C	-2.148582	3.758155	2.851665
C	-3.269392	4.286592	2.211288
C	-3.486452	1.967042	-0.777879
N	-2.717769	0.902150	-1.149256
C	-2.988841	0.192207	-2.257152
C	-4.058888	0.524843	-3.077830
C	-4.862077	1.607200	-2.725062
C	-4.577736	2.330061	-1.571010
AU	-1.117226	0.502466	0.135237
O	-1.518811	-1.823815	-0.335133
S	-2.848558	-2.402784	0.098789
O	-3.216644	-2.032782	1.465251
C	0.450631	0.327670	1.397878
N	0.645136	-0.586453	2.379675
C	1.874620	-0.368207	2.976775
C	2.438735	0.706184	2.363054
N	1.540394	1.135980	1.405708
C	-0.257403	-1.670979	2.767877
C	1.777261	2.299851	0.548146
C	-2.425043	-4.241507	0.180708
F	-1.454116	-4.470798	1.098189
O	-3.881841	-2.311268	-0.926602
F	-3.517039	-4.944737	0.533877

F	-1.990671	-4.687492	-1.015391
C	0.432989	0.576756	-2.182791
C	0.227188	1.863856	-2.844255
C	0.818539	-0.516298	-1.792115
C	1.417197	-1.794989	-1.448269
O	4.907353	1.333930	0.620513
S	4.875960	0.149728	-0.254811
C	6.671887	-0.420189	-0.298854
F	7.474886	0.548281	-0.797803
O	4.583047	0.443603	-1.674081
O	4.155075	-1.009865	0.289717
F	7.106304	-0.723099	0.948395
F	6.812089	-1.522145	-1.070441
O	3.345778	2.759845	-2.489499
H	-0.597612	2.266967	2.822277
H	-1.794716	4.191961	3.786629
H	-3.795526	5.137447	2.641335
H	-4.600994	4.134528	0.532808
H	-5.199212	3.174092	-1.281877
H	-5.713344	1.886359	-3.344749
H	-4.258014	-0.072793	-3.963850
H	-2.331662	-0.649760	-2.457218
H	3.423834	1.150307	2.441959
H	2.253387	-1.019987	3.752137
H	0.871847	2.504288	-0.025537
H	2.015382	3.161431	1.180904
H	2.616616	2.110966	-0.127979
H	-1.259445	-1.495611	2.366927
H	0.119734	-2.622820	2.379328

H	-0.303374	-1.711975	3.861263
H	-0.450139	2.525842	-2.287792
H	1.201928	2.370061	-2.941513
H	-0.199086	1.719369	-3.847088
H	0.692203	-2.456579	-0.960392
H	1.760392	-2.283974	-2.371451
H	2.297948	-1.647079	-0.803411
H	4.043188	3.420547	-2.624998
H	3.840635	1.938942	-2.225603

TSOTf-H2O

65

C	-0.376427551	-3.996451583	-1.007445179
C	-0.434426969	-2.857268563	-0.205186054
N	-0.678801359	-1.647817248	-0.784342021
C	-0.844008665	-1.518879065	-2.109564837
C	-0.788360722	-2.627084999	-2.943875983
C	-0.552096619	-3.879219807	-2.381668490
C	-0.237323751	-2.799222005	1.239420040
C	-0.227896166	-1.521914201	1.843328065
C	-0.061488821	-1.382662216	3.215319564
C	0.110838453	-2.524742602	4.007237804
C	0.113275424	-3.792092229	3.426566655
C	-0.061629414	-3.927065625	2.052648016
AU	-0.531948309	-0.031692991	0.500840497
C	-0.126496933	1.440349868	1.829245061
N	-0.965838553	2.253097735	2.519712186

C	-0.233217589	3.140532394	3.288390027
C	1.081376167	2.866623025	3.071103373
N	1.132400891	1.813728779	2.177330752
C	-2.429375212	2.186592955	2.545224059
C	2.383173765	1.176123688	1.749952317
O	0.739547824	1.040019644	-1.355764910
O	3.102900875	-0.076042502	-1.870285313
S	3.253707982	-1.440984835	-1.293532620
O	3.126937334	-2.537532001	-2.245399376
C	5.072468781	-1.456248491	-0.796464471
F	5.405921509	-2.638761827	-0.233153105
O	2.544485724	-1.600703417	-0.011229284
F	5.875514931	-1.253228528	-1.862595966
F	5.332595968	-0.475968579	0.113250644
O	-1.971835795	1.369380112	-0.728334596
S	-3.414268351	0.975106872	-0.975142048
C	-3.810995694	2.074325805	-2.457848769
F	-3.647577894	3.381475135	-2.149156284
O	-4.317499872	1.432717458	0.078541415
O	-3.578983051	-0.388297952	-1.463768869
F	-3.005339908	1.780828957	-3.501887032
F	-5.089462453	1.883320311	-2.836303674
C	2.206733167	3.888892399	-1.804644523
C	1.076387566	4.290285780	-1.618835878
C	-0.274158895	4.805579298	-1.430293659
C	3.563360210	3.419513430	-2.056631648
H	1.638545320	0.625952352	-1.537280315
H	-0.062201513	-0.403984800	3.689712083
H	0.242137503	-2.412771524	5.083376979
H	0.250278369	-4.677513154	4.045531513

H	-0.062522508	-4.920215234	1.604973342
H	-0.164867716	-4.963167409	-0.557520324
H	-0.488224095	-4.763014314	-3.014666346
H	-0.917376723	-2.495194741	-4.015095834
H	-1.003474836	-0.508962823	-2.475773401
H	-0.710775411	3.889997512	3.905342877
H	1.977734816	3.331183713	3.459899590
H	-2.812989243	1.771150927	1.610099330
H	-2.757430793	1.571507353	3.391708217
H	-2.820063574	3.202561956	2.658316790
H	2.193661786	0.475948282	0.931258372
H	3.082985105	1.949517779	1.419305416
H	2.811152460	0.621190995	2.592477904
H	0.871227325	2.009369434	-1.443286114
H	3.919889065	3.772172207	-3.034713993
H	4.261138347	3.793447741	-1.293647975
H	3.617662595	2.321117584	-2.057107231
H	-0.654818187	5.250439420	-2.360319375
H	-0.296841454	5.584067305	-0.654189615
H	-0.973462571	4.010010957	-1.137588552

ICTFA

63

N	0.961804	2.166948	-0.565557
C	0.084059	1.314884	-1.143923
N	-0.217897	1.838646	-2.357712
C	0.479524	3.019600	-2.542738

C	1.222320	3.221446	-1.420647
AU	-0.637124	-0.372745	-0.306770
O	-1.638272	0.773212	1.206348
C	-2.547143	1.607043	0.827290
C	-1.206449	1.320810	-3.303072
C	1.511717	2.060561	0.790111
C	0.161331	-1.664071	-1.653087
C	-0.246672	-3.002422	-1.435524
C	0.218827	-4.010357	-2.295578
C	1.081952	-3.700354	-3.340366
C	1.505406	-2.382743	-3.523337
C	1.051395	-1.365753	-2.677992
C	-1.086366	-3.264513	-0.270517
N	-1.421491	-2.154000	0.445477
C	-2.123548	-2.238669	1.586307
C	-2.568121	-3.461336	2.069204
C	-2.262992	-4.615497	1.346138
C	-1.518406	-4.518080	0.177458
C	-3.233705	2.292315	2.061484
F	-2.321869	2.891692	2.866540
O	-2.918812	1.889170	-0.308565
F	-4.125474	3.228074	1.678189
F	-3.899882	1.364939	2.804679
O	1.318543	-1.204489	1.372466
C	2.469119	-1.247385	0.846261
C	3.438487	-2.268069	1.560420
F	3.861821	-1.766483	2.760428
O	2.943890	-0.600426	-0.105947
F	2.829797	-3.462431	1.820499
F	4.550958	-2.547415	0.834105

O	-3.321132	3.680047	-2.436916
C	5.308469	1.702366	-0.890936
C	5.046637	3.018147	-0.323139
C	4.851168	4.111851	0.163339
C	4.662398	5.425170	0.766631
H	1.425459	-0.354117	-2.811165
H	2.208073	-2.140715	-4.320508
H	1.442042	-4.488689	-3.999888
H	-0.084425	-5.045128	-2.138731
H	-1.252798	-5.411057	-0.383128
H	-2.594625	-5.590823	1.700378
H	-3.134098	-3.499679	2.996985
H	-2.311213	-1.297142	2.099348
H	1.927853	3.998918	-1.159348
H	0.372041	3.611248	-3.441594
H	1.402437	1.028909	1.138577
H	2.572558	2.328320	0.755950
H	0.967458	2.746494	1.449960
H	-0.734531	1.173038	-4.281139
H	-1.575871	0.364234	-2.926723
H	-2.037278	2.033376	-3.377990
H	-3.330306	3.155029	-1.606597
H	-4.153962	4.177251	-2.424978
H	6.290691	1.330951	-0.565106
H	4.555142	0.959858	-0.583778
H	5.317196	1.741792	-1.990011
H	3.787952	5.445681	1.433681
H	4.518240	6.204418	0.003751
H	5.537935	5.711440	1.367382

RC TFA

63

N	1.905011	2.135657	0.713100
C	1.078180	1.083992	0.953123
N	1.417081	0.608533	2.172304
C	2.473320	1.336804	2.682866
C	2.776870	2.299940	1.775273
AU	-0.399376	0.441109	-0.279521
C	0.900091	-1.585916	-0.842733
C	0.865845	-2.771263	-0.007910
C	0.864398	-0.567162	2.852048
C	1.926017	2.975592	-0.479047
C	-1.655167	1.986689	0.241795
C	-2.839623	2.006577	-0.530098
C	-3.787986	3.015409	-0.297952
C	-3.573591	3.975031	0.685889
C	-2.411740	3.932351	1.456973
C	-1.452054	2.938153	1.235799
C	-3.033780	0.932904	-1.503723
N	-1.999422	0.047233	-1.597310
C	-2.081772	-1.033371	-2.390517
C	-3.194748	-1.264541	-3.188864
C	-4.255485	-0.364283	-3.132441
C	-4.178022	0.733441	-2.282288
C	1.101304	-0.707056	-1.687249
C	1.593718	0.003464	-2.863785
O	-1.865327	-0.978562	1.370146

C	-2.536393	-1.973472	0.954899
C	-3.672253	-2.412091	1.954324
F	-4.306765	-1.348476	2.520886
O	-2.412050	-2.649262	-0.079855
F	-4.624219	-3.172642	1.362307
F	-3.138039	-3.149824	2.973795
O	3.548258	-1.351171	1.336097
C	4.101076	-1.509823	0.227237
O	3.958670	-2.407113	-0.638640
C	5.104049	-0.350529	-0.170945
F	6.038340	-0.715470	-1.081553
F	4.395473	0.699757	-0.746770
F	5.766534	0.182982	0.887898
O	3.731088	-2.231362	-3.327891
H	-0.559305	2.918296	1.857451
H	-2.246691	4.672168	2.240207
H	-4.318972	4.749971	0.859384
H	-4.706227	3.046194	-0.883658
H	-5.009210	1.430017	-2.206535
H	-5.148134	-0.523985	-3.736100
H	-3.225072	-2.150120	-3.818955
H	-1.232461	-1.709857	-2.372270
H	3.550619	3.055307	1.770911
H	2.935155	1.079478	3.625908
H	1.065377	2.721062	-1.102954
H	1.859664	4.029537	-0.186382
H	2.855429	2.802451	-1.032972
H	-0.086175	-0.847156	2.384055
H	1.604244	-1.371790	2.775162
H	0.687928	-0.308360	3.901571

H	2.096434	0.939466	-2.593836
H	2.346670	-0.663105	-3.330818
H	0.789347	0.225277	-3.578060
H	-0.160554	-3.024926	0.282242
H	1.296070	-3.587617	-0.607164
H	1.531314	-2.631342	0.854766
H	4.609581	-2.245179	-3.739109
H	3.917865	-2.302438	-2.346893

ICH2O TFA

63

N	1.735790527	-2.104317821	0.616770701
C	1.001737688	-0.966224036	0.669022622
N	1.755752714	-0.052947163	1.324273359
C	2.977348580	-0.605959773	1.661961347
C	2.964202997	-1.892690912	1.216851118
AU	-0.812926159	-0.685621395	-0.158023557
O	-0.025440267	0.561949301	-1.642965242
C	1.403673129	1.351944542	1.545345801
C	1.374287493	-3.317586367	-0.118299653
N	-2.712285463	-0.556654831	-1.018557107
C	-3.690423761	-1.205834059	-0.324764860
C	-5.007857803	-1.142474251	-0.789593820
C	-5.299538847	-0.426502115	-1.945353616
C	-4.273934871	0.217680839	-2.636847858
C	-2.979648264	0.129919076	-2.140973180
C	-3.221073379	-1.915240532	0.866051217
C	-1.834699998	-1.846820726	1.157522522

C	-1.341852819	-2.486001266	2.292669343
C	-2.203151433	-3.205808723	3.128249299
C	-3.566350539	-3.280542865	2.840861435
C	-4.073126363	-2.634486570	1.717381260
O	2.449614771	0.618851712	-1.831493414
C	2.984577416	-0.480730902	-2.197740529
O	2.469029447	-1.585785381	-2.399719359
C	4.537135512	-0.351428482	-2.410688513
F	5.137399404	-1.554491377	-2.568804679
F	4.822267106	0.393391969	-3.511612821
F	5.143391214	0.255513746	-1.343027655
O	-1.111657063	2.790250254	-1.074638830
C	-1.708000926	2.732232965	0.039204115
O	-1.749282539	1.802769692	0.874198936
C	-2.476719884	4.048555145	0.417004879
F	-3.146645990	4.569184027	-0.644399899
F	-3.381285901	3.856340926	1.408121685
F	-1.594162123	4.995598791	0.849828561
C	5.477615318	1.986104063	2.595591277
C	5.514024139	1.336452324	3.618438152
C	5.591285350	0.583298328	4.863260755
C	5.458603193	2.782957208	1.376444000
H	1.059358587	0.561091019	-1.736347965
H	-0.284694203	-2.428156668	2.545674808
H	-1.802854756	-3.703899034	4.011384399
H	-4.235963425	-3.835836581	3.496261276
H	-5.140807894	-2.688145927	1.506067803
H	-5.798848764	-1.649236741	-0.241931085
H	-6.326229138	-0.370427811	-2.305479117
H	-4.463561414	0.788358376	-3.542940426

H	-2.125093339	0.606171704	-2.619625615
H	3.746056041	-0.029114777	2.168457010
H	3.721125911	-2.664120990	1.255085457
H	0.313870696	1.463537700	1.515397460
H	1.789626377	1.660742270	2.521590207
H	1.856248763	1.960795538	0.754215407
H	1.640673806	-3.172172624	-1.172800052
H	1.926751068	-4.159876214	0.309023552
H	0.299908502	-3.494304802	-0.013469366
H	-0.384451580	1.519256835	-1.406303263
H	4.922104174	3.729933310	1.530074254
H	6.480784644	3.026490250	1.054043856
H	4.971352118	2.249575159	0.548915088
H	5.335288199	1.215411784	5.725660807
H	6.606038694	0.192625642	5.026143111
H	4.902548626	-0.274484531	4.865862126

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