

# Supporting Information

for

## The role of silver additives in gold-mediated C–H functionalisation

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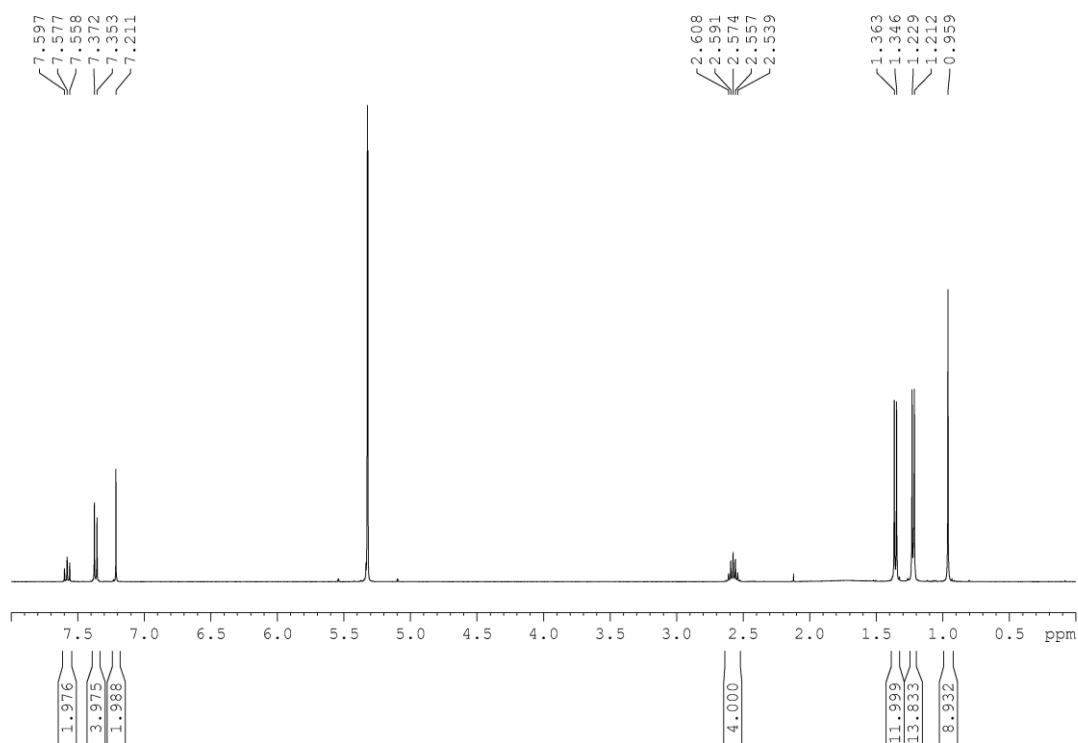
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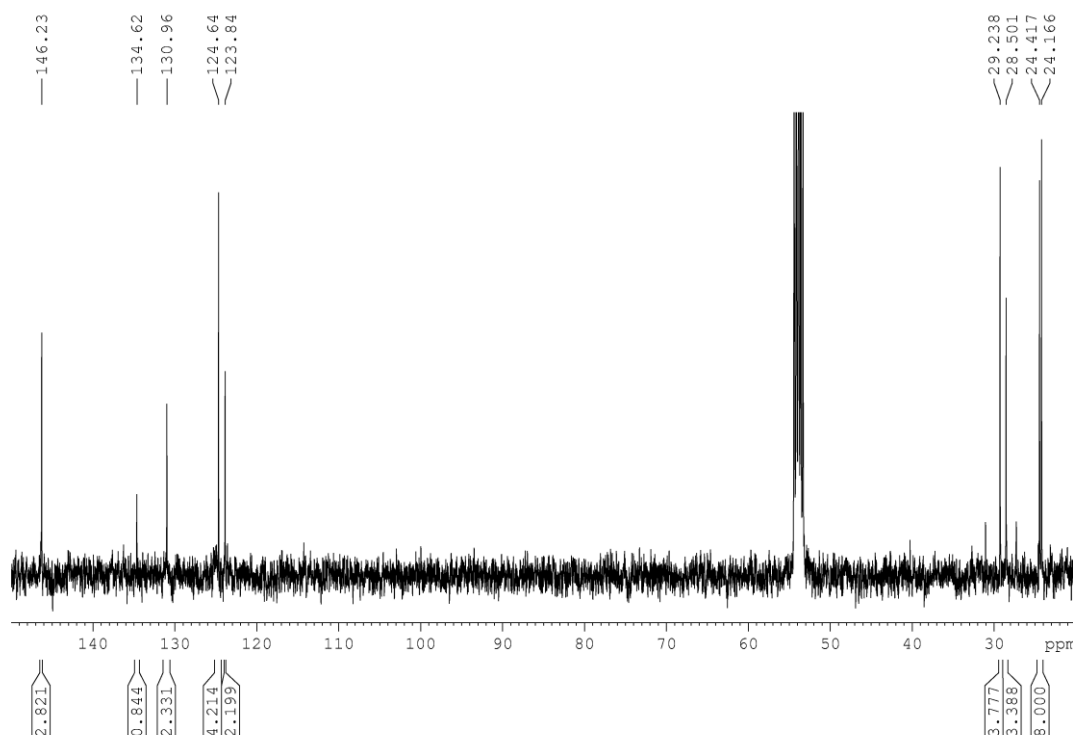
\* Corresponding author

## Detailed experimental procedures for the synthesis of complexes 3–5

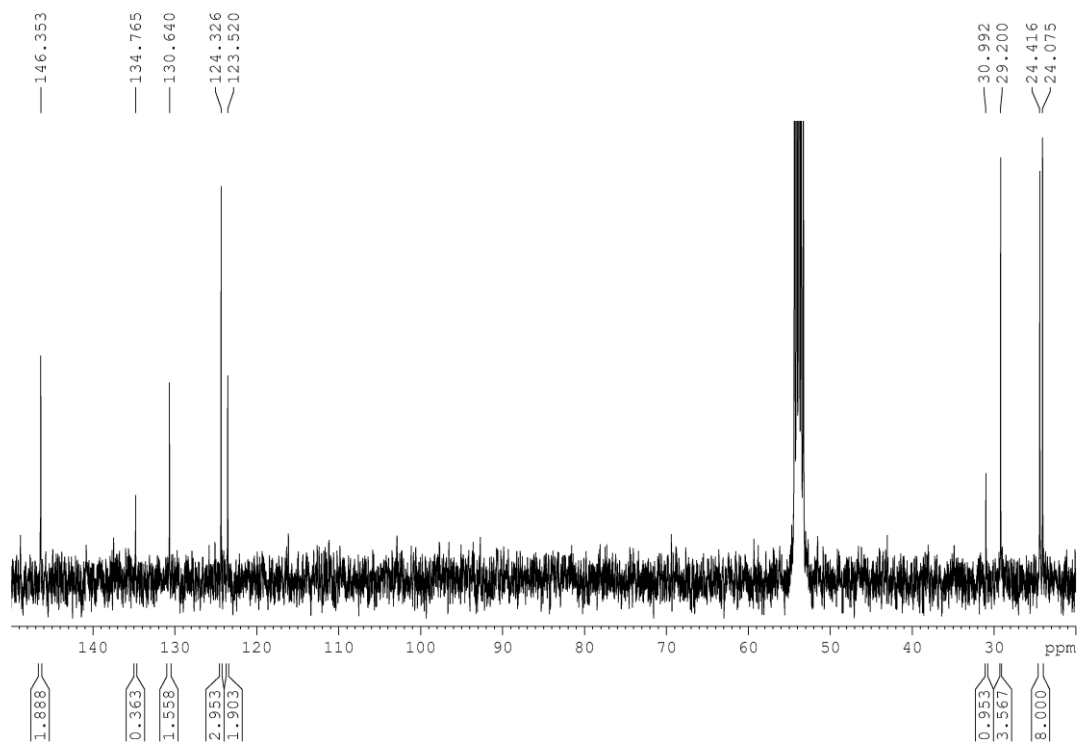
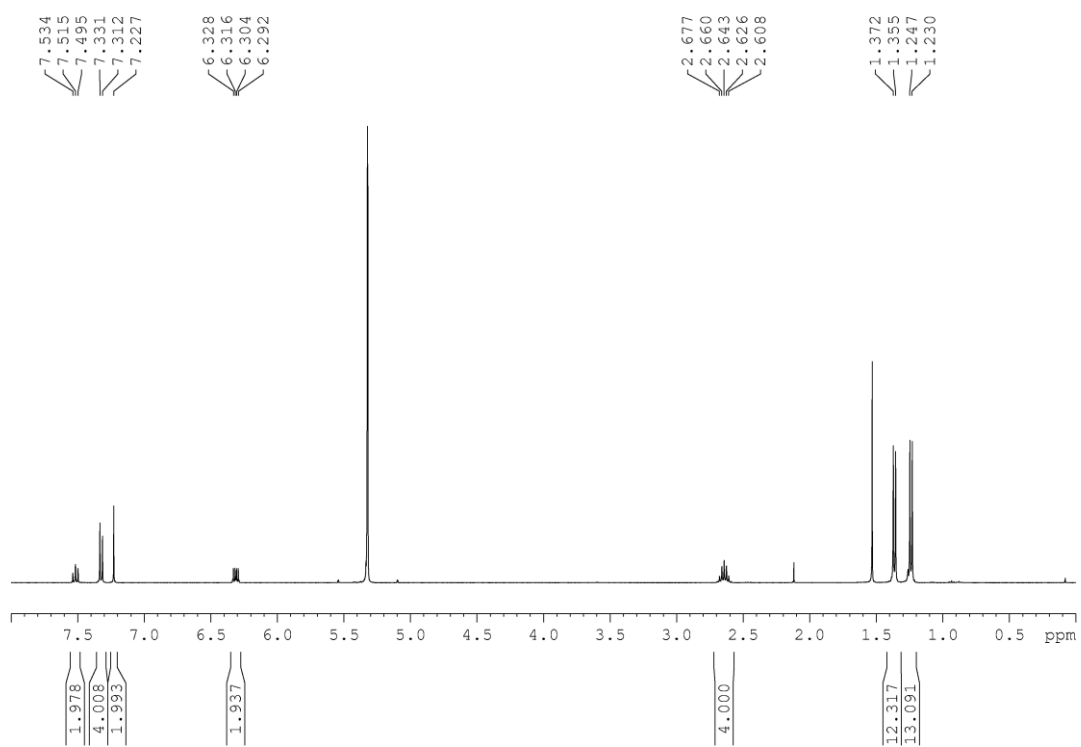
**General considerations:** All reagents were used as received.  $^1\text{H}$ ,  $^{13}\text{C}$  and  $^{19}\text{F}$  NMR spectra were recorded on a Bruker Avance 300 or a Bruker Avance II 400 Ultrashield spectrometer. Elemental analyses were performed by the London Metropolitan University Elemental Analysis Service. Complex **1** has been previously described in the literature [1].

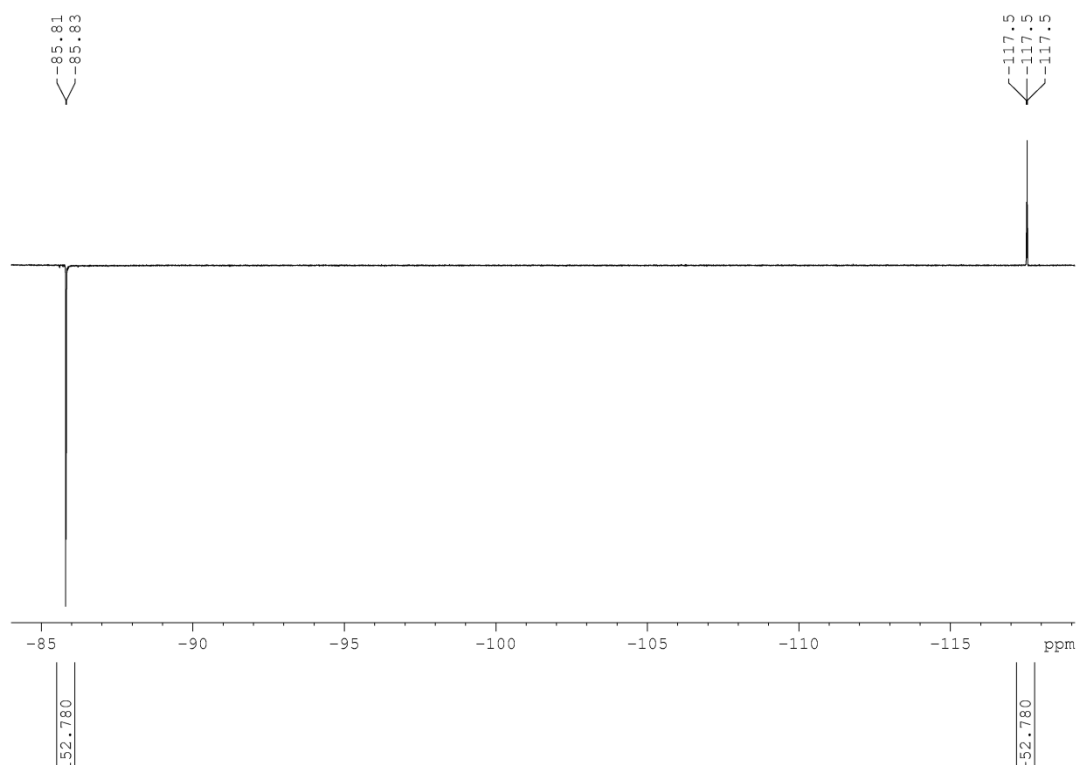
**Synthesis of [Au(OPiv)(IPr)] (3):** A scintillation vial was charged with [Au(OH)(IPr)] (100.0 mg, 0.166 mmol) and pivalic acid (20.3 mg, 0.199 mmol). Toluene (1.5 mL) was then added to the vial and the reaction mixture stirred at room temperature for 21 h. The solvent was evaporated and the residue washed with pentane to give a stoichiometric yield of a white microcrystalline solid.  $^1\text{H}$  NMR (400 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  7.56 (t,  $J = 8.0$  Hz, 2H,  $\text{CH}$  aromatic), 7.36 (d,  $J = 8.0$  Hz, 4H,  $\text{CH}$  aromatic), 7.21 (s, 2H,  $\text{CH}$  imidazole), 2.57 (sept,  $J = 7.0$  Hz, 4H,  $\text{CH}(\text{CH}_3)_2$ ), 1.35 (d,  $J = 6.9$  Hz, 12H,  $\text{CH}_3$ ), 1.22 (d,  $J = 6.9$  Hz, 12H,  $\text{CH}_3$ ), 0.96 (s, 9H,  $(\text{CH}_3)_3$ ) ppm.  $^{13}\text{C}$  NMR (100 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  146.24 (s, 4C), 134.62 (s, 2C), 130.96 (s, 2C), 124.64 (s, 4H), 123.84 (s, 2C), 29.24 (s, 4C), 28.50 (s, 3C), 24.29 (d,  $J = 25.2$  Hz, 8C) ppm. Anal. Calcd. for  $\text{C}_{31}\text{H}_{45}\text{AuN}_2\text{O}$ : C, 56.53; H, 6.89; N, 4.25. Found: C, 55.85; H, 6.95; N, 4.11.



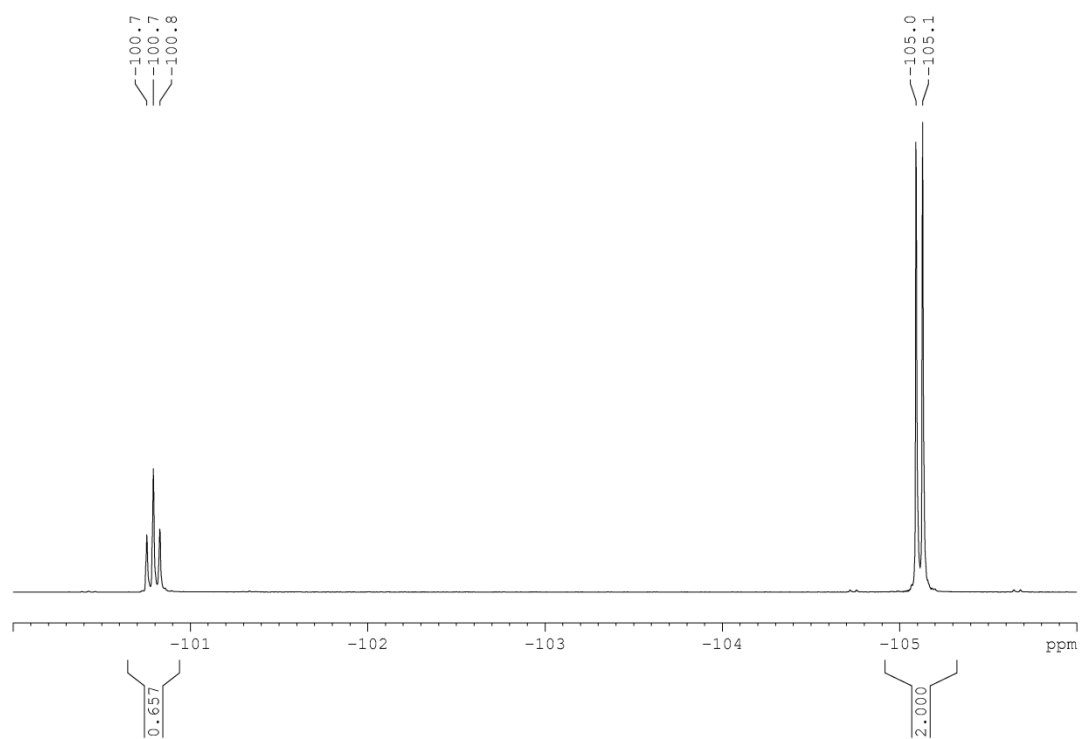
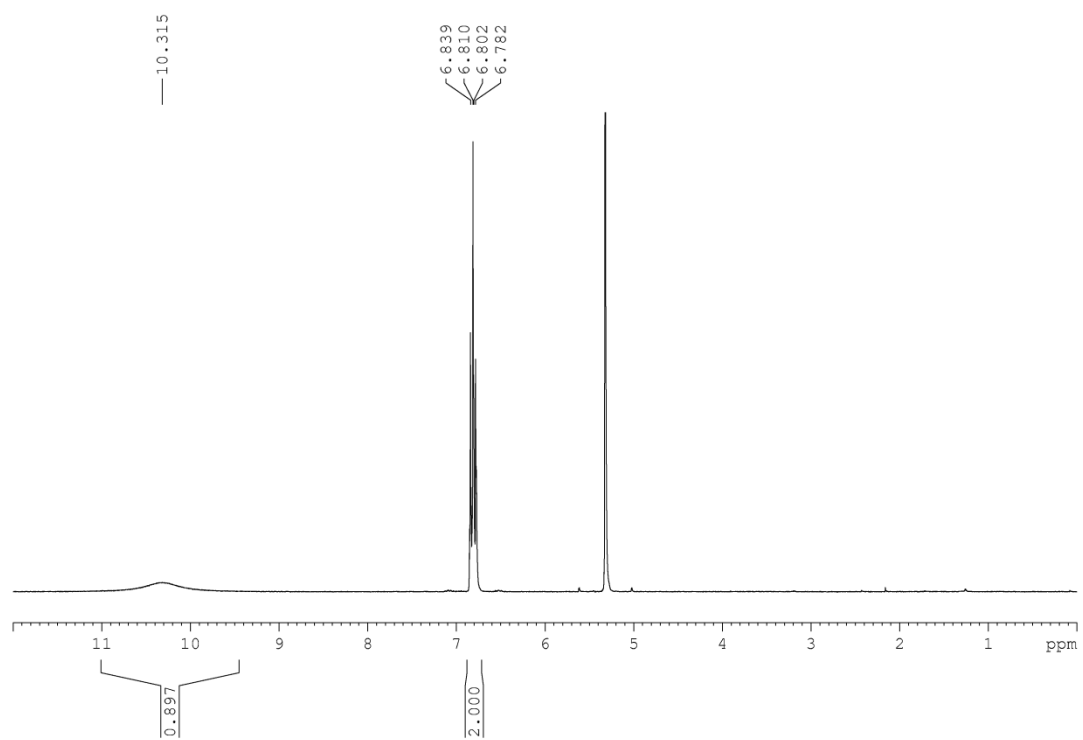


**General procedure for synthesis of  $[\text{Au}(\text{C}_6\text{H}_2\text{F}_3)(\text{IPr})]$  (4):** A scintillation vial was charged with  $[\text{Au}(\text{OH})(\text{IPr})]$  (25.0 mg, 0.041 mmol), silver salt (0.060 mmol) and 1,3,5-trifluorobenzene (24.4 mg, 19.1  $\mu\text{L}$ , 0.185 mmol). DMF (0.8 mL) was then added to the vial and the reaction mixture stirred at 50  $^{\circ}\text{C}$  for 20 h. The resulting mixture was filtered through Celite<sup>®</sup> and the solvent evaporated. The residue was purified via flash chromatography (20% DCM/pentane) to afford a pale yellow microcrystalline solid.  $^1\text{H}$  NMR (400 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  7.50 (t,  $J$  = 7.8 Hz, 2H, CH aromatic), 7.32 (d,  $J$  = 7.6 Hz, 4H, CH aromatic), 7.23 (s, 2H, CH imidazole), 6.31 (q,  $J$  = 4.8 Hz, 2H, CH aromatic), 2.64 (sept,  $J$  = 7.0 Hz, 4H,  $\text{CH}(\text{CH}_3)_2$ ), 1.36 (d,  $J$  = 6.8 Hz, 12H,  $\text{CH}_3$ ), 1.24 (d,  $J$  = 6.8 Hz, 12H,  $\text{CH}_3$ ) ppm.  $^{13}\text{C}$  NMR (100 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  146.35 (s, 2C), 134.76 (s, 1C), 130.64 (s, 2C), 124.32 (s, 4C), 123.52 (s, 2C), 30.99 (s, 1C), 29.20 (s, 4C), 24.25 (d,  $J$  = 34.1 Hz, 8C) ppm.  $^{19}\text{F}$  NMR (376 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  -85.82 (d,  $J$  = 6.4 Hz, 2F), -117.53 (t,  $J$  = 6.4 Hz, 1F) ppm. Anal. Calcd. for  $\text{C}_{33}\text{H}_{38}\text{AuN}_2\text{F}_3$ : C, 55.31; H, 5.34; N, 3.91. Found: C, 55.45; H, 5.41; N, 3.83.





**General procedure for synthesis of 2,4,6-trifluorobenzoic acid (5):** A pressure tube was charged with 1,3,5-trifluorobenzene (0.5 mmol),  $[\text{Au}(\text{OH})(\text{IPr})]$  (3 mol %), silver(I) oxide (3 mol %) and potassium hydroxide (1.5 mmol). THF (1.0 mL) was then added to the vial and the tube was placed under a  $\text{CO}_2$  atmosphere (2 bar). The reaction mixture was stirred at 60 °C for 16 h and the solvent evaporated. The residue was dissolved in water (2 mL) and filtered through cotton. Aqueous HCl (1M, 0.5 mL) was added to the filtrate and the mixture stirred for 30 minutes. The organic product was then extracted with ethyl acetate (3 × 3 mL). The solvent was evaporated to yield a yellow microcrystalline solid.  $^1\text{H}$  NMR (300 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  10.31 (br s, 1H), 6.80 (t,  $J$  = 8.23 Hz, 2H) ppm.  $^{19}\text{F}$  NMR (282 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  -100.79 (t,  $J$  = 10.2 Hz, 1F), -105.11 (d,  $J$  = 10.6 Hz, 2F) ppm.

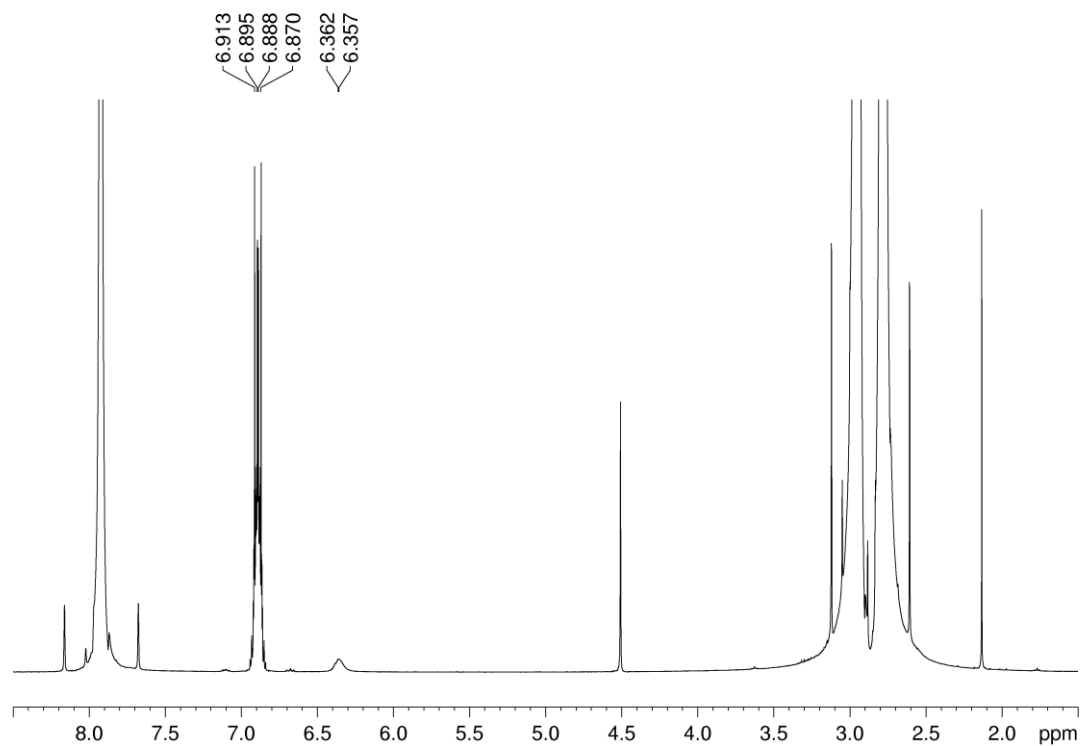


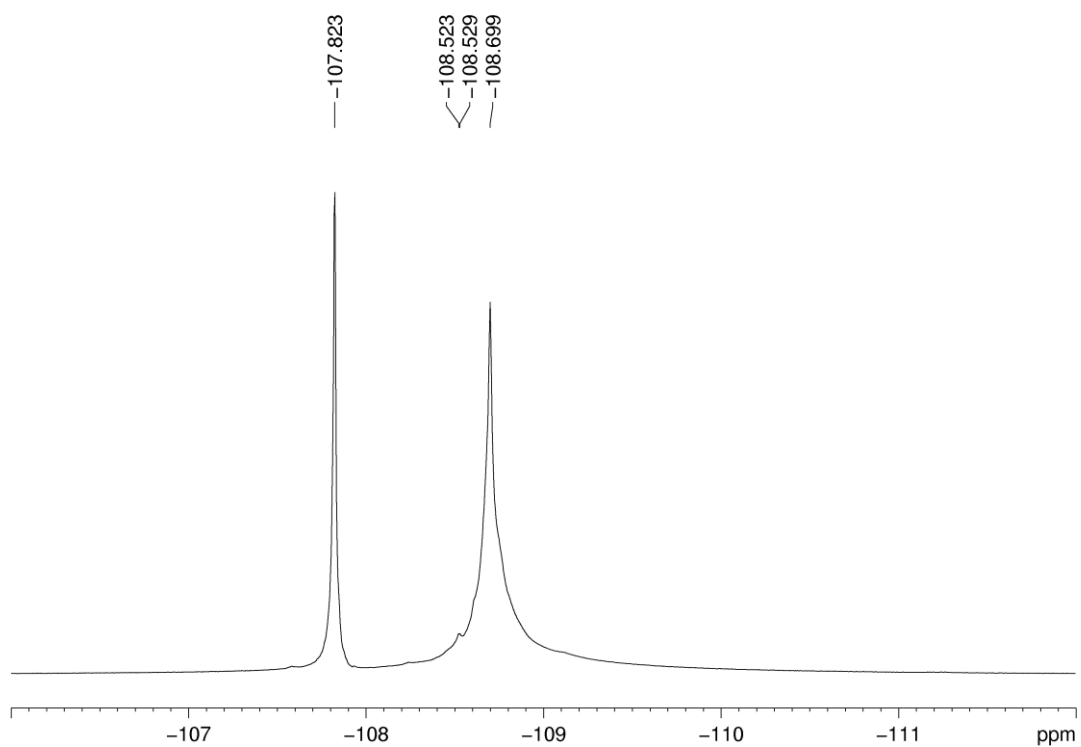
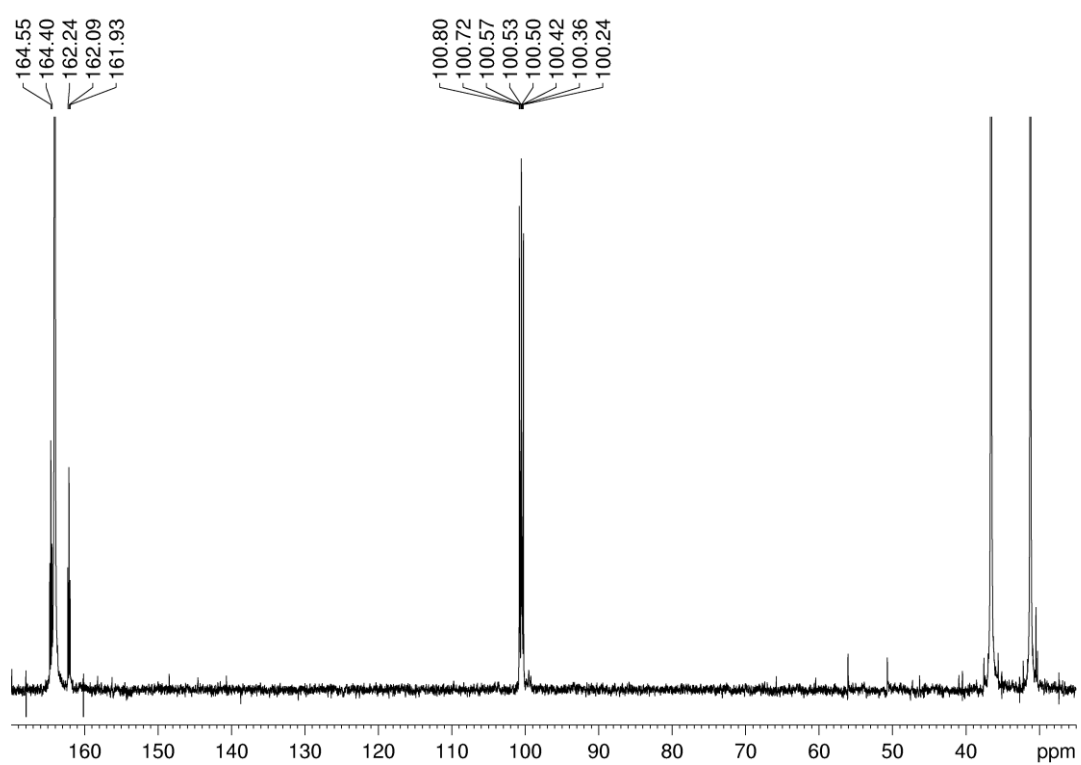
**Conversions using Complex 1<sup>a</sup>:**

Entry	Additive(s)	Solvent	Conversion <sup>b</sup> (%)
1	Ag <sub>2</sub> O	DMF	38
2	Ag <sub>2</sub> O, PivOH	DMF	100
3	PivOH	DMF	0
4 <sup>c</sup>	Ag <sub>2</sub> O	DMF	15
5 <sup>d</sup>	Ag <sub>2</sub> O	DMF	11
6 <sup>e</sup>	Ag <sub>2</sub> O	DMF	0
7	AgF	DMF	100
8	AgOAc	DMF	100
9	AgI	DMF	35
10	AgBF <sub>4</sub>	DMF	30
11	AgO	DMF	30
12	AgCl	DMF	28
13	Ag <sub>2</sub> CO <sub>3</sub>	DMF	20
14	AgOCOCF <sub>3</sub>	DMF	19
15	AgNO <sub>3</sub>	DMF	13
16	AgBr	DMF	7
17	Al <sub>2</sub> O <sub>3</sub>	DMF	0
18	AlCl <sub>3</sub>	THF	0
19	Cu <sub>2</sub> O	DMF	0
20	ZnBr <sub>2</sub>	DMF	0
21	Ag <sub>2</sub> O	THF	59
22	Ag <sub>2</sub> O	Toluene	35
23	Ag <sub>2</sub> O	Dioxane	21
24	Ag <sub>2</sub> O	CPME	3

<sup>a</sup>Unless otherwise noted, all reactions were carried out with [Au(OH)(IPr)] (1 equiv), 1,3,5-trifluorobenzene (4.5 equiv), metal salt (1.5 equiv) and pivalic acid (2.5 equiv) in a 0.2M DMF solution. <sup>b</sup>Conversion to product was determined by <sup>1</sup>H NMR analysis relative to [Au(OH)(IPr)]. <sup>c</sup>Metal salt (0.5 equiv) was used. <sup>d</sup>Metal salt (0.25 equiv) was used. <sup>e</sup>Metal salt (0.1 equiv) was used.

**NMR spectra of reaction between 1,3,5-trifluorobenzene and Ag<sub>2</sub>O:**





1. Gaillard, S.; Slawin, A. M. Z.; Nolan, S. P. *Chem. Commun.* **2010**, 46, 2742–2744.