

Electronic Supplementary Information for:

## Conversion of haloform to carbonate by iridium *N*-heterocycle stabilized carbene complexes and silver(I) oxide

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## Experimental details

### Materials

Complexes **1a**,<sup>1</sup> **1b**<sup>1</sup> and **1c**<sup>2</sup> were prepared as previously described. Silver(I) oxide (Aldrich), chloroform (Aldrich), bromoform (BDH) and iodoform (BDH) were used as supplied.

### NMR tube reactions between silver(I) oxide and **1a**, **1b** and **1c**

Silver(I) oxide (*ca.* 0.025 g, 0.1 mmol) was added to a solution of **1a**, **1b** or **1c** (*ca.* 20 mg, 0.03 mmol) in deuteriochloroform (*ca.* 1 cm<sup>3</sup>) in an NMR tube. The solution was monitored regularly over 7 to 10 days and by <sup>1</sup>H and <sup>19</sup>F NMR spectroscopy. Once the reaction had reached completion, the solution was diluted with CHCl<sub>3</sub> and filtered through Celite. The product was obtained as a brown-beige or yellow solid on slow evaporation of the solvent, or on precipitation by addition of petroleum ether (b.p. 60-80°C).

### *η*<sup>5</sup>-Pentamethylcyclopentadienyliridium(1-(2-chloro-6-fluorophenylmethyl)-3-methylimidazolin-2-ylidene) carbonate (**2a**)

Calculated for C<sub>22</sub>H<sub>25</sub>ClFIrN<sub>2</sub>O<sub>3</sub>: C, 43.2; H, 4.1; N, 4.6. Found: C, 43.8; H, 5.3; N, 4.9%. Repeated recrystallization failed to give satisfactory analyses. Mass spectrometric analysis of **2a** did not produce a recognisable anion or cation.

<sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 7.36 (1H, d. t. *J*<sub>HF</sub> 5.8, *J*<sub>HH</sub> 8.1, C<sub>6</sub>H<sub>3</sub>ClF), 7.31 (1H, m, C<sub>6</sub>H<sub>3</sub>ClF), 7.07 (1H, m, C<sub>6</sub>H<sub>3</sub>ClF), 6.85 (1H, d, <sup>3</sup>*J*<sub>HH</sub> 2.0, HCCH), 6.37 (1H, d, <sup>3</sup>*J*<sub>HH</sub> 2.0, HCCH), 5.69 (1H, dd, <sup>2</sup>*J*<sub>HH</sub> 14.5, <sup>4</sup>*J*<sub>HF</sub> 1.7, NCHH), 5.34 (1H, dd, <sup>2</sup>*J*<sub>HH</sub> 14.5, <sup>4</sup>*J*<sub>HF</sub> 1.6, NCHH), 3.79 (3H, s, NCH<sub>3</sub>), 1.78 (15H, s, C<sub>5</sub>(CH<sub>3</sub>)<sub>5</sub>).

<sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>): δ 168.1 (CO<sub>3</sub>), 163.8 (IrC<sub>carbene</sub>), 162.3 (d, <sup>1</sup>*J*<sub>CF</sub> 252, CF), 137.1 (d, *J*<sub>CF</sub> 5, C<sub>6</sub>H<sub>3</sub>ClF), 131.3 (d, *J*<sub>CF</sub> 10, C<sub>6</sub>H<sub>3</sub>ClF), 126.1 (d, *J*<sub>CF</sub> 3, C<sub>6</sub>H<sub>3</sub>ClF), 121.9 (NCH), 120.9 (d., *J*<sub>CF</sub> 17, C<sub>6</sub>H<sub>3</sub>ClF), 119.4 (NCH), 114.8 (d, *J*<sub>CF</sub> 22, Ph), 86.2 (C<sub>5</sub>(CH<sub>3</sub>)<sub>5</sub>), 45.2 (d, <sup>3</sup>*J*<sub>CF</sub> 3, NCH<sub>2</sub>), 37.8 (NCH<sub>3</sub>), 9.8 (C<sub>5</sub>(CH<sub>3</sub>)<sub>5</sub>).

<sup>19</sup>F NMR (CDCl<sub>3</sub>): δ -110.29 (1F, m).

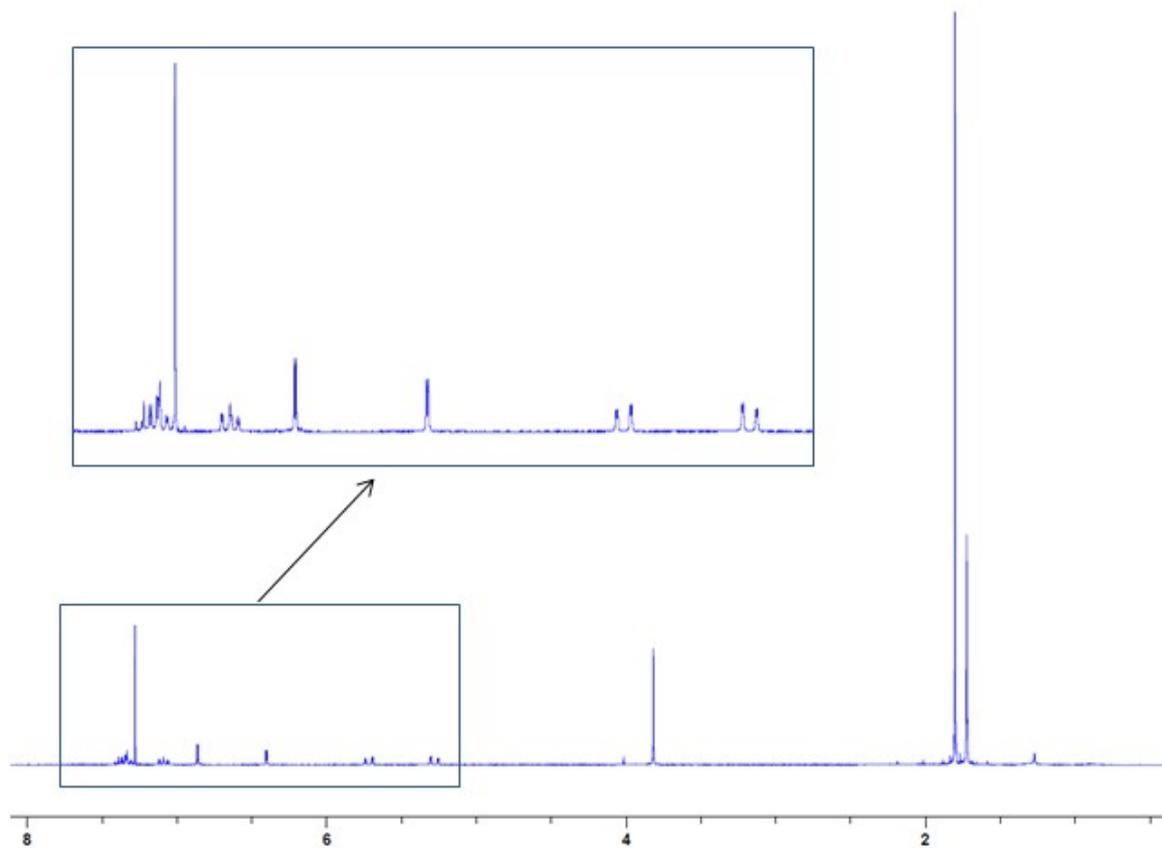
Shifts for the carbonate complex obtained in the NMR tube reaction between **1a**, Ag<sub>2</sub>O and a drop of chloroform in deuterio-dimethylsulphoxide:

<sup>1</sup>H NMR ((CD<sub>3</sub>)<sub>2</sub>SO): δ 7.56 (1H, d. t. *J*<sub>HF</sub> 6.1, *J*<sub>HH</sub> 8.2, C<sub>6</sub>H<sub>3</sub>ClF), 7.48 (1H, m, C<sub>6</sub>H<sub>3</sub>ClF), 7.35\* (1H, m, C<sub>6</sub>H<sub>3</sub>ClF), 7.35\* (1H, d, <sup>3</sup>*J*<sub>HH</sub> 2.0, HCCH), 6.62 (1H, d, <sup>3</sup>*J*<sub>HH</sub> 2.0, HCCH), 5.48 (1H, d. d, <sup>2</sup>*J*<sub>HH</sub> 14.9, <sup>4</sup>*J*<sub>HF</sub> 1.2, NCHH), 5.18 (1H, d. d, <sup>2</sup>*J*<sub>HH</sub> 14.9, <sup>4</sup>*J*<sub>HF</sub> 1.2, NCHH), 3.70 (3H, s, NCH<sub>3</sub>), 1.70 (15H, s, C<sub>5</sub>(CH<sub>3</sub>)<sub>5</sub>).

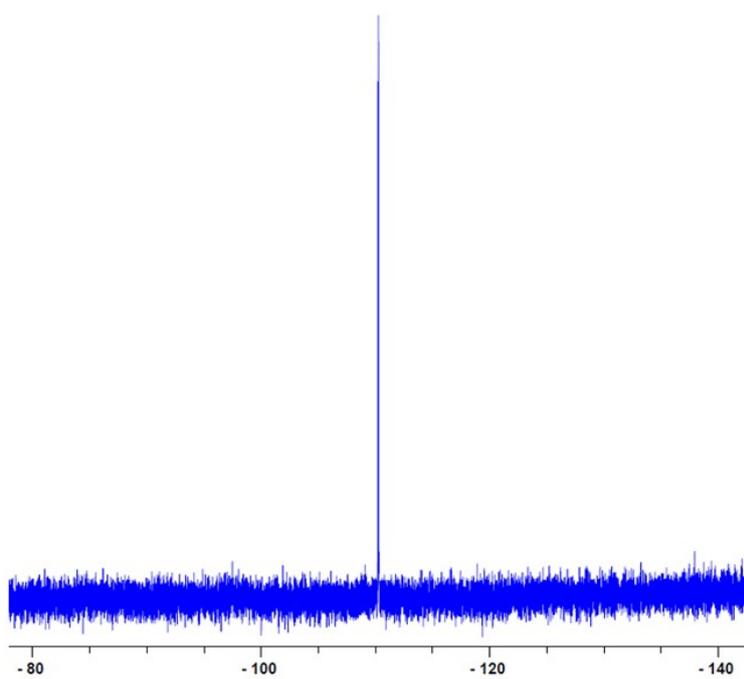
\*These resonances are coincident.

<sup>19</sup>F NMR ((CD<sub>3</sub>)<sub>2</sub>SO): δ -111.77 (1F, m).

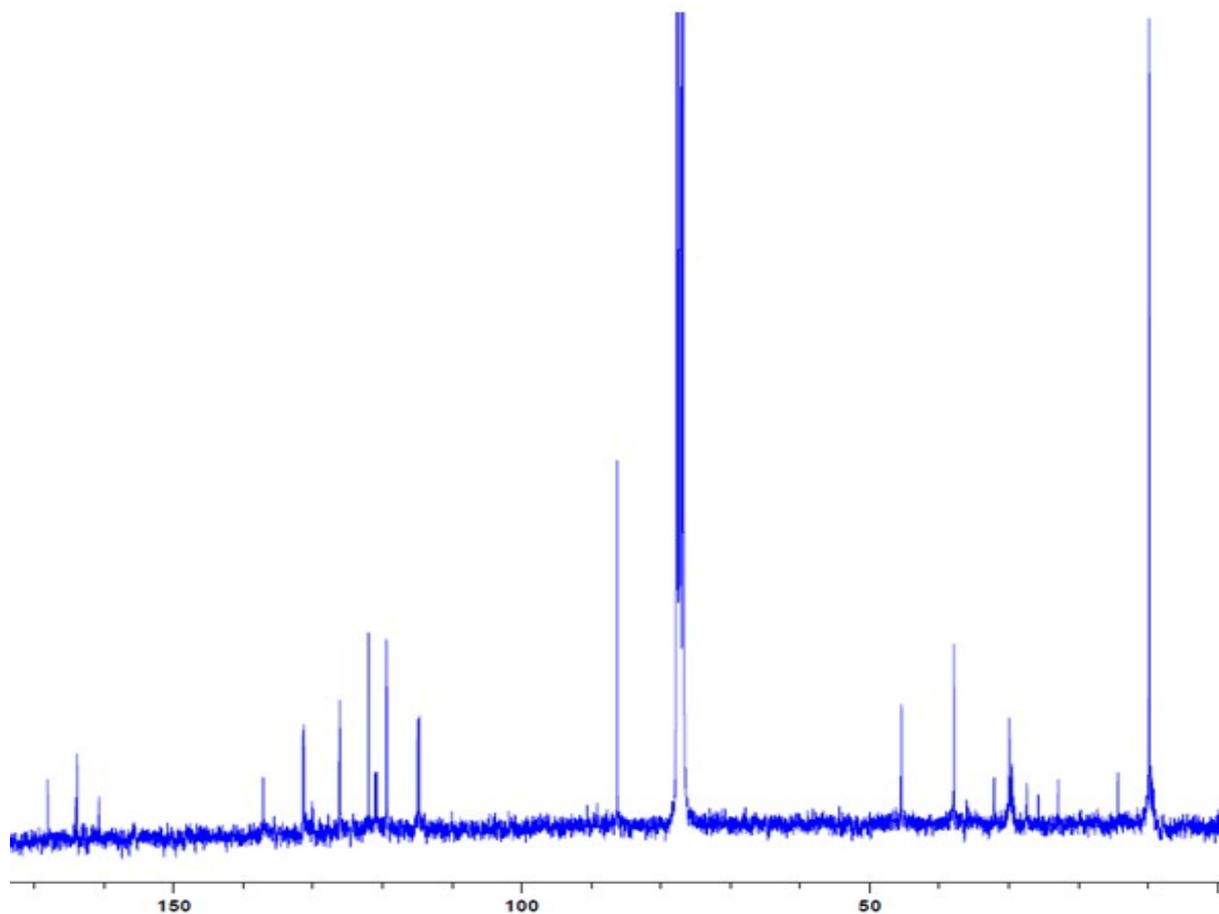
**Figure S1.**  $^1\text{H}$  NMR spectrum of **2a** in  $\text{CDCl}_3$



**Figure S2.**  $^{19}\text{F}$  NMR spectrum of **2a** in  $\text{CDCl}_3$



**Figure S3.**  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of **2a** in  $\text{CDCl}_3$



*$\eta^5$ -Pentamethylcyclopentadienyliridium(1-(2,6-difluorophenylmethyl)-3-methylimidazolin-2-ylidene) carbonate (**2b**)*

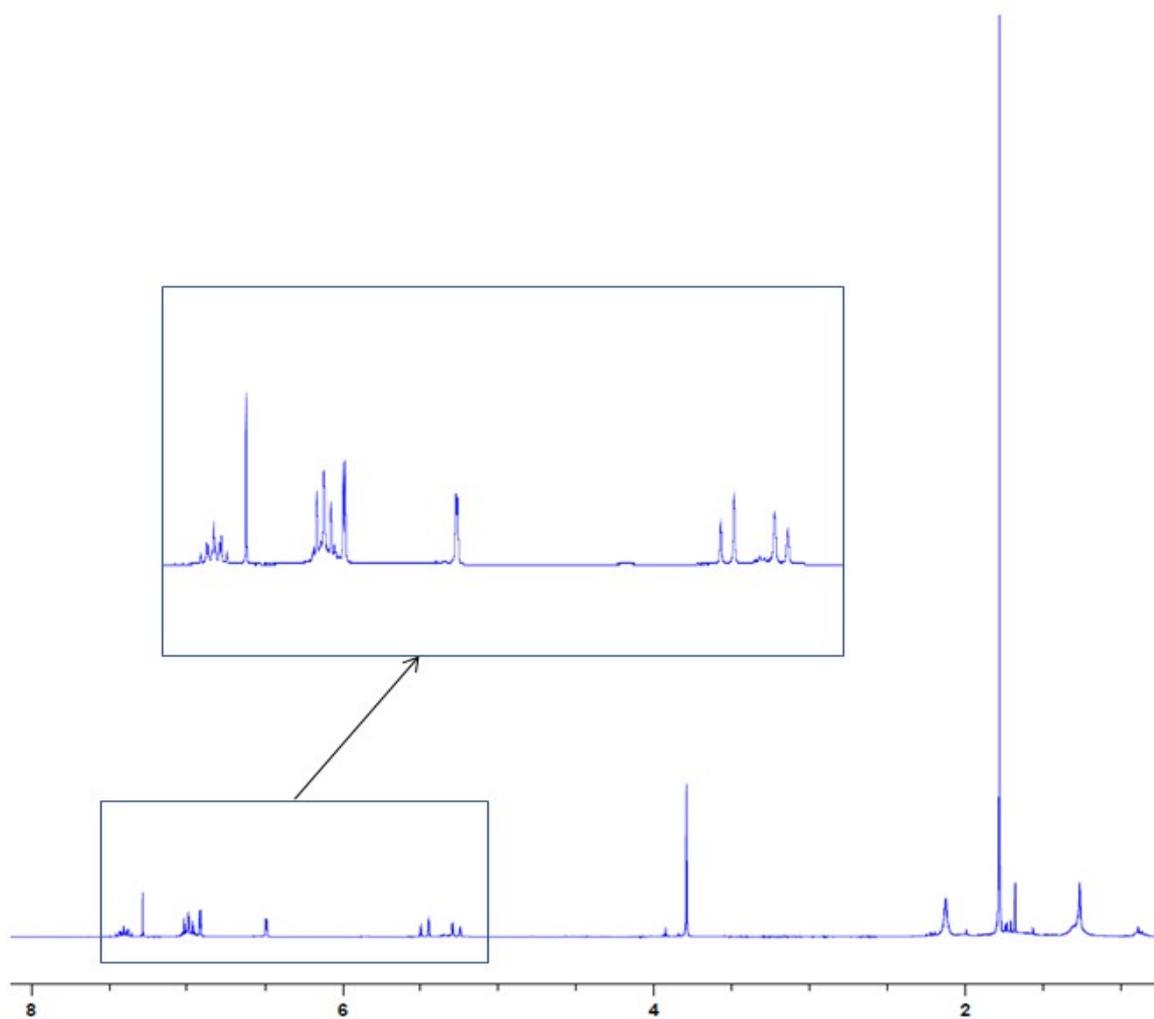
Calculated for  $\text{C}_{22}\text{H}_{25}\text{F}_2\text{IrN}_2\text{O}_3$ : C, 44.4; H, 4.2; N, 4.7. Found: C, 44.0; H, 5.2; N, 5.0%. Repeated recrystallization failed to give satisfactory analyses. Mass spectrometric analysis of **2b** did not produce an recognisable anion or cation.

$^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  7.38 (1H, m,  $\text{H}_{para}$ ), 6.97 (2H, m,  $\text{H}_{meta}$ ), 6.89 (1H, d,  $^3J_{\text{HH}}$  2.1, HCCH), 6.47 (1H, d,  $^3J_{\text{HH}}$  2.0, HCCH), 5.46 (1H, d,  $^2J_{\text{HH}}$  15.2, NCHH), 5.26 (1H, d,  $^2J_{\text{HH}}$  15.2, NCHH), 4.78 (3H, s,  $\text{NCH}_3$ ), 1.77 (15H, s,  $\text{C}_5(\text{CH}_3)_5$ ).

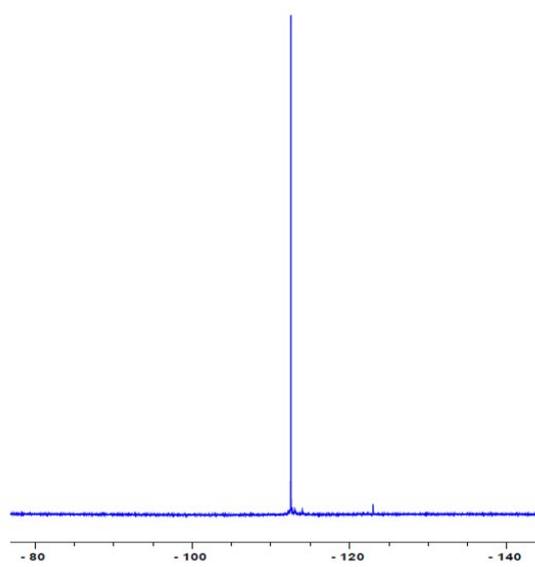
$^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  168.1 ( $\text{CO}_3$ ), 164.3 ( $\text{IrC}_{\text{carbene}}$ ), 162.1 (dd,  $^1J_{\text{CF}}$  251,  $^3J_{\text{CF}}$  8, CF), 131.3 (t,  $J_{\text{CF}}$  10,  $\text{C}_6\text{H}_3\text{F}_2$ ), 122.2 (NCH), 119.5 (NCH), 112.0 (dm,  $J_{\text{CF}}$  25,  $\text{C}_6\text{H}_3\text{F}_2$ ), 111.2 (t,  $J_{\text{CF}}$  25,  $\text{C}_6\text{H}_3\text{F}_2$ ), 86.3 ( $\text{C}_5(\text{CH}_3)_5$ ), 42.1 ( $\text{NCH}_2$ ), 37.8 ( $\text{NCH}_3$ ), 9.7 ( $\text{C}_5(\text{CH}_3)_5$ ).

$^{19}\text{F}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  -112.46 (2F, br t,  $J$  6.7, F).

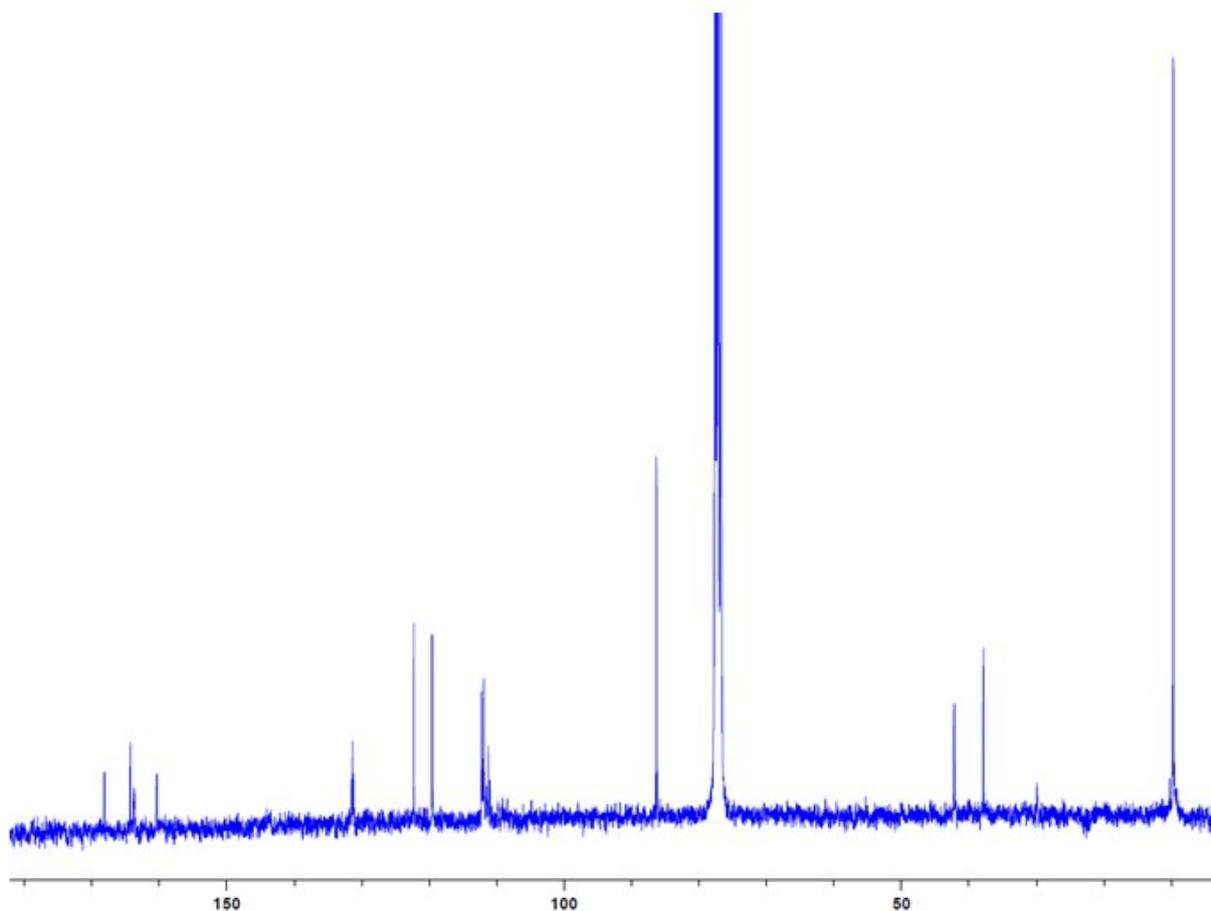
**Figure S4.**  $^1\text{H}$  NMR spectrum of **2b** in  $\text{CDCl}_3$



**Figure S5.**  $^{19}\text{F}$  NMR spectrum of **2b** in  $\text{CDCl}_3$



**Figure S6.**  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of **2b** in  $\text{CDCl}_3$



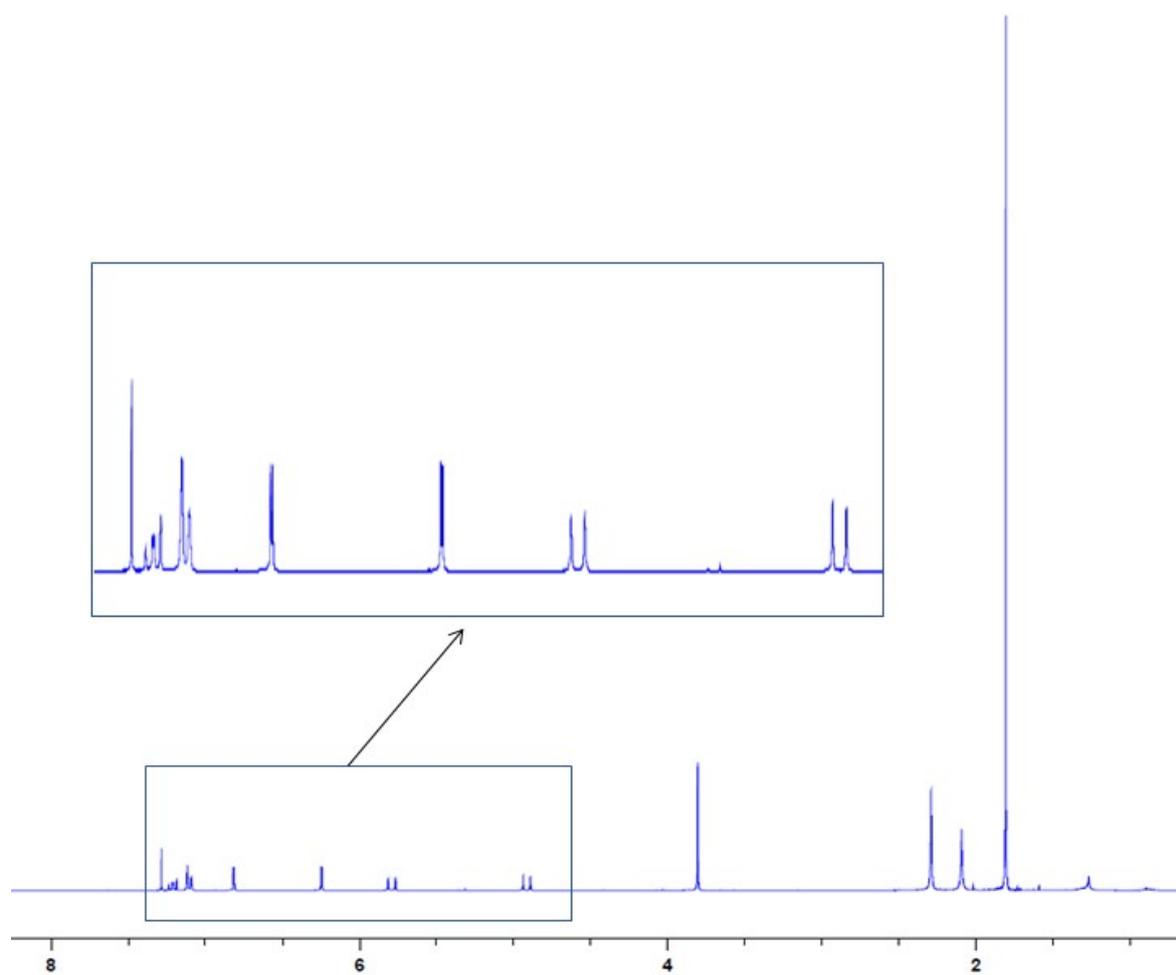
*$\eta^5$ -Pentamethylcyclopentadienyliridium(1-(2,6-dimethylphenylmethyl)-3-methylimidazolin-2-ylidene) carbonate (2c)*

Calculated for  $\text{C}_{24}\text{H}_{31}\text{IrN}_2\text{O}_3$ : C, 49.05; H, 5.3; N, 4.8. Found: C, 48.8; H, 6.2; N, 3.9%. Repeated recrystallization failed to give satisfactory analyses. Mass spectrometric analysis of **2c** did not produce a recognisable anion or cation.

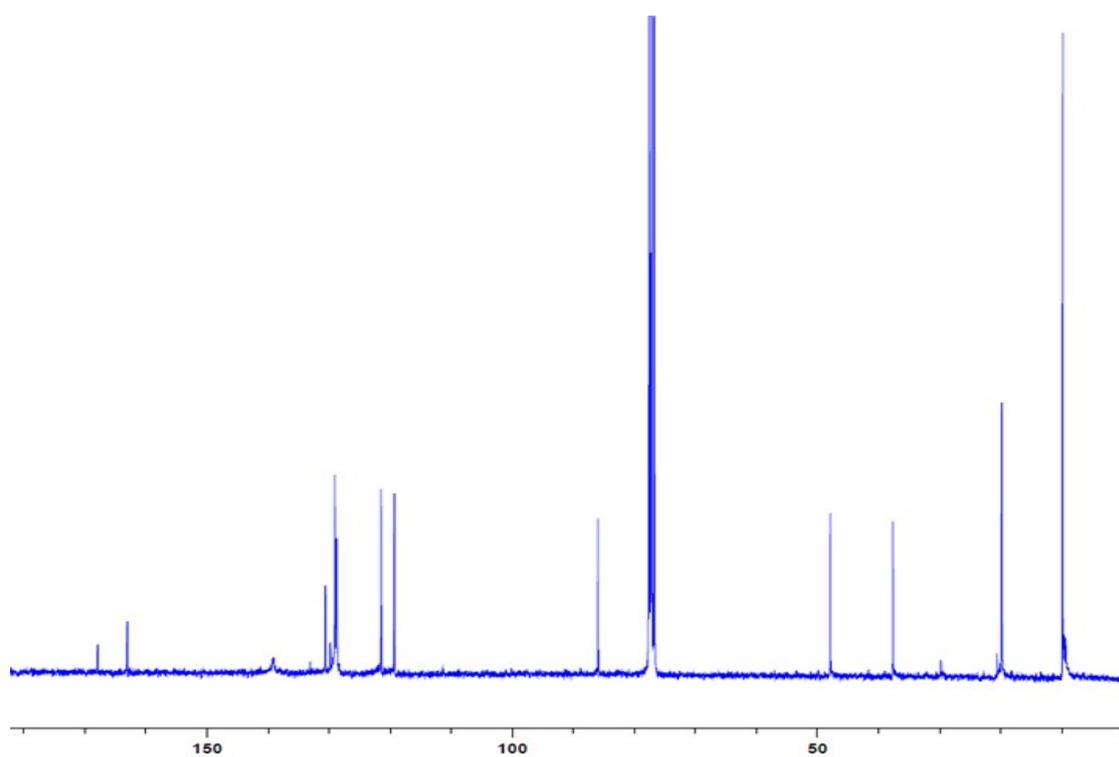
$^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  7.19 (1H, m,  $\text{H}_{para}$ ), 7.08 (2H, m,  $\text{H}_{meta}$ ), 6.79 (1H, d,  $J_{\text{HH}}$  2.0, HCCH), 6.22 (1H, d,  $J_{\text{HH}}$  2.0, HCCH), 5.78 (1H, d,  $^2J_{\text{HH}}$  14.0, NCHH), 4.89 (1H, d,  $^2J_{\text{HH}}$  14.0, NCHH), 3.78 (3H, s,  $\text{NCH}_3$ ), 2.27 (6H, s,  $\text{C}_6\text{CH}_3$ ), 1.78 (15H, s,  $\text{C}_5(\text{CH}_3)_5$ ).

$^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  167.9 ( $\text{CO}_3$ ), 163.1 ( $\text{Ir}_{\text{carbene}}$ ), 130.6 ( $\text{C}_6\text{H}_3\text{Me}_2$ ), 129.8 ( $\text{C}_6\text{H}_3\text{Me}_2$ ), 129.1 ( $\text{C}_6\text{H}_3\text{Me}_2$ ), 128.8 ( $\text{C}_6\text{H}_3\text{Me}_2$ ), 121.5 (NCH), 119.3 (NCH), 86.0 ( $\text{C}_5(\text{CH}_3)_5$ ), 47.9 ( $\text{NCH}_2$ ), 37.6 ( $\text{NCH}_3$ ), 19.8 ( $\text{C}_6(\text{CH}_3)_2$ ), 9.9 ( $\text{C}_5(\text{CH}_3)_5$ ).

**Figure S7.**  $^1\text{H}$  NMR spectrum of **2c** in  $\text{CDCl}_3$



**Figure S8.**  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of **2c** in  $\text{CDCl}_3$



### **Synthesis of 2a, 2b and 2c using silver(I) carbonate**

Complexes **2a**, **2b** and **2c** were generated in NMR tubes by the reaction of **1a**, **1b** and **1c** with silver(I) carbonate in deuterio-chloroform. The NMR data are identical to those obtained by the reaction of **1a**, **1b** and **1c** with silver(I) carbonate in deuterio-chloroform.

### **Synthesis of $\eta^5$ -pentamethylcyclopentadienylrhodium(1-(2,6-difluorophenylmethyl)-3-methylimidazolin-2-ylidene) carbonate**

The rhodium analogue of complex **2a** was generated in an NMR tube by the reaction of **1a** with silver(I) carbonate in deuterio-chloroform.

$^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  7.36 (1H, d, t.  $J_{\text{HF}}$  5.8,  $J_{\text{HH}}$  8.1,  $\text{C}_6\text{H}_3\text{ClF}$ ), 7.28 (1H, m,  $\text{C}_6\text{H}_3\text{ClF}$ ), 7.05 (1H, m,  $\text{C}_6\text{H}_3\text{ClF}$ ), 6.91 (1H, d,  $^3J_{\text{HH}}$  2.0, *HCCH*), 6.38 (1H, d,  $^3J_{\text{HH}}$  2.0, *HCCH*), 5.67 (1H, dd,  $^2J_{\text{HH}}$  14.5,  $^4J_{\text{HF}}$  1.7, *NCHH*), 5.34 (1H, dd,  $^2J_{\text{HH}}$  14.5,  $^4J_{\text{HF}}$  1.4, *NCHH*), 3.80 (3H, s,  $\text{NCH}_3$ ), 1.75 (15H, s,  $\text{C}_5(\text{CH}_3)_5$ ).

$^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  174.8 (d,  $^1J_{\text{RhC}}$  60,  $\text{RhC}_{\text{carbene}}$ ), 166.4 ( $\text{CO}_3$ ), 162.3 (d,  $^1J_{\text{CF}}$  253, CF), 137.0 (d,  $J_{\text{CF}}$  5,  $\text{C}_6\text{H}_3\text{ClF}$ ), 131.3 (d,  $J_{\text{CF}}$  10,  $\text{C}_6\text{H}_3\text{ClF}$ ), 126.1 (s,  $\text{C}_6\text{H}_3\text{ClF}$ ), 122.7 (*NCH*), 120.8 (d.,  $J_{\text{CF}}$  17,  $\text{C}_6\text{H}_3\text{ClF}$ ), 120.0 (*NCH*), 114.8 (d,  $J_{\text{CF}}$  22, Ph), 93.7 ( $\text{C}_5(\text{CH}_3)_5$ ), 45.5 (d,  $^3J_{\text{CF}}$  3,  $\text{NCH}_2$ ), 37.9 ( $\text{NCH}_3$ ), 9.6 ( $\text{C}_5(\text{CH}_3)_5$ ).

$^{19}\text{F}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  -110.17 (1F, m).

### **Reaction between 1a and haloform in deuterio-dimethylsulphoxide**

Silver(I) oxide (ca. 0.025 g, 0.1 mmol) was added to a solution of **1a** (ca. 20 mg, 0.03 mmol) in deuterio-dimethylsulphoxide (ca. 1  $\text{cm}^3$ ) in an NMR tube. A drop of chloroform or bromoform or a few crystals of iodoform (ca. 25 mg, 0.06 mmol) was added. Integration of appropriate NMR resonances was used to determine the ratio of **1a** to haloform, and the amount of haloform adjusted to achieve a ratio close to 1:1. The reaction was monitored regularly over several days by  $^1\text{H}$  and  $^{19}\text{F}$  NMR spectroscopy.

Shifts for the carbonate complex obtained in the NMR tube reaction between **1a**,  $\text{Ag}_2\text{O}$  and a drop of chloroform in deuterio-dimethylsulphoxide:

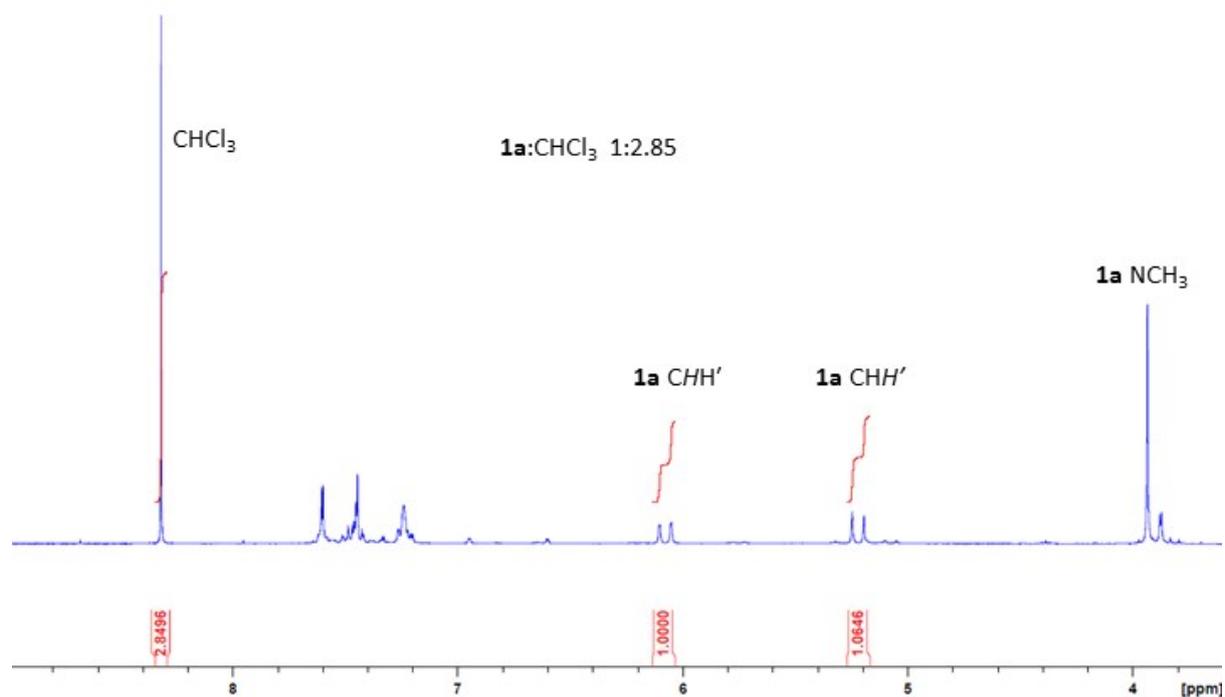
$^1\text{H}$  NMR ( $(\text{CD}_3)_2\text{SO}$ ):  $\delta$  7.56 (1H, d, t.  $J_{\text{HF}}$  6.1,  $J_{\text{HH}}$  8.2,  $\text{C}_6\text{H}_3\text{ClF}$ ), 7.48 (1H, m,  $\text{C}_6\text{H}_3\text{ClF}$ ), 7.35\* (1H, m,  $\text{C}_6\text{H}_3\text{ClF}$ ), 7.35\* (1H, d,  $^3J_{\text{HH}}$  2.0, *HCCH*), 6.62 (1H, d,  $^3J_{\text{HH}}$  2.0, *HCCH*), 5.48 (1H, d, d,  $^2J_{\text{HH}}$  14.9,  $^4J_{\text{HF}}$  1.2, *NCHH*), 5.18 (1H, d, d,  $^2J_{\text{HH}}$  14.9,  $^4J_{\text{HF}}$  1.2, *NCHH*), 3.70 (3H, s,  $\text{NCH}_3$ ), 1.70 (15H, s,  $\text{C}_5(\text{CH}_3)_5$ ).

\*These resonances are coincident.

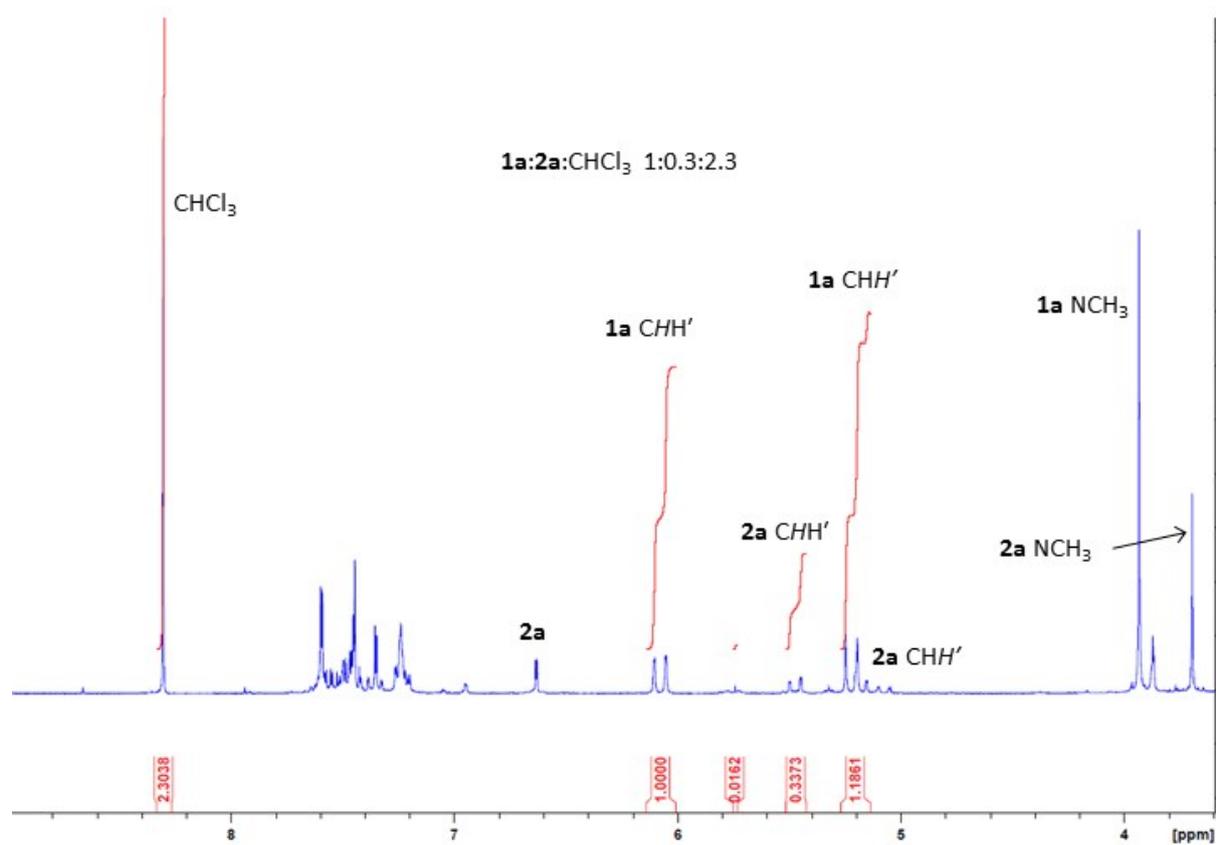
$^{19}\text{F}$  NMR ( $(\text{CD}_3)_2\text{SO}$ ):  $\delta$  -111.77 (1F, m).

**Figure S9.**  $^1\text{H}$  NMR spectra of the reaction between **1a**, silver oxide and  $\text{CHCl}_3$  in  $(\text{CD}_3)_2\text{SO}$ .

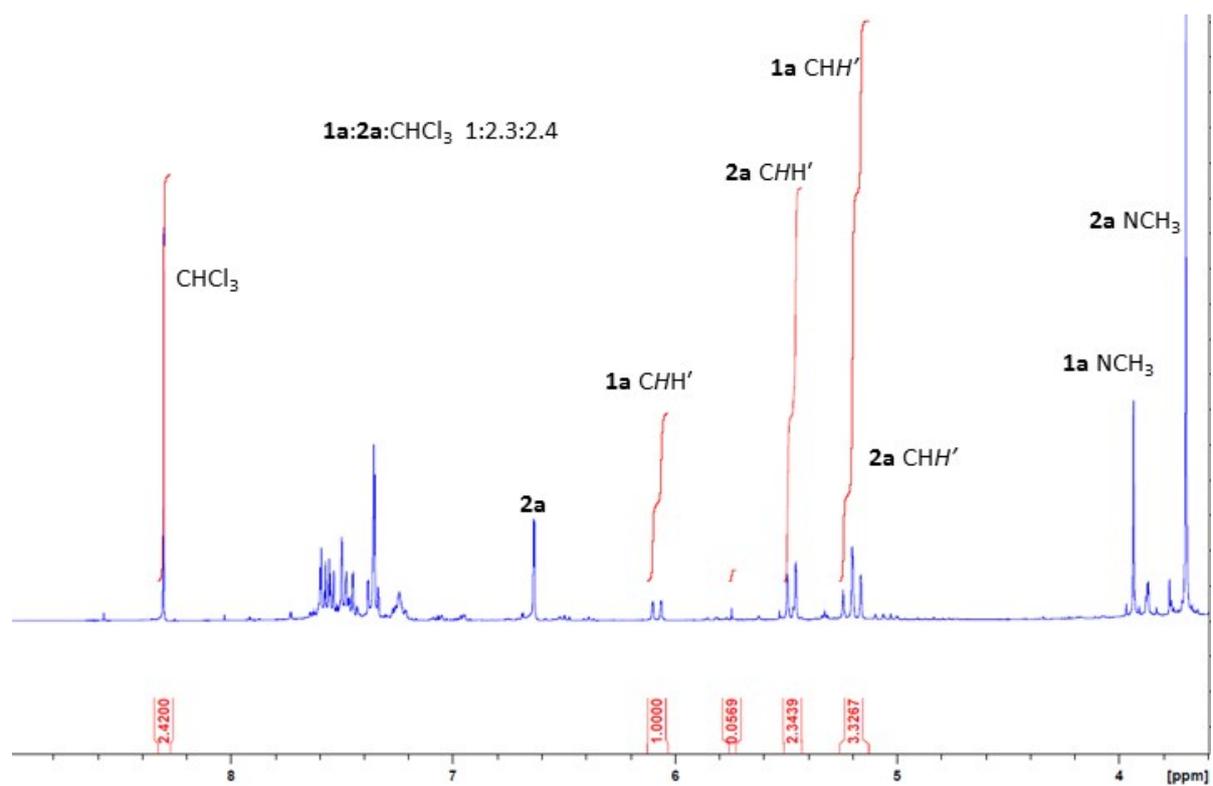
**a) 0 hours**



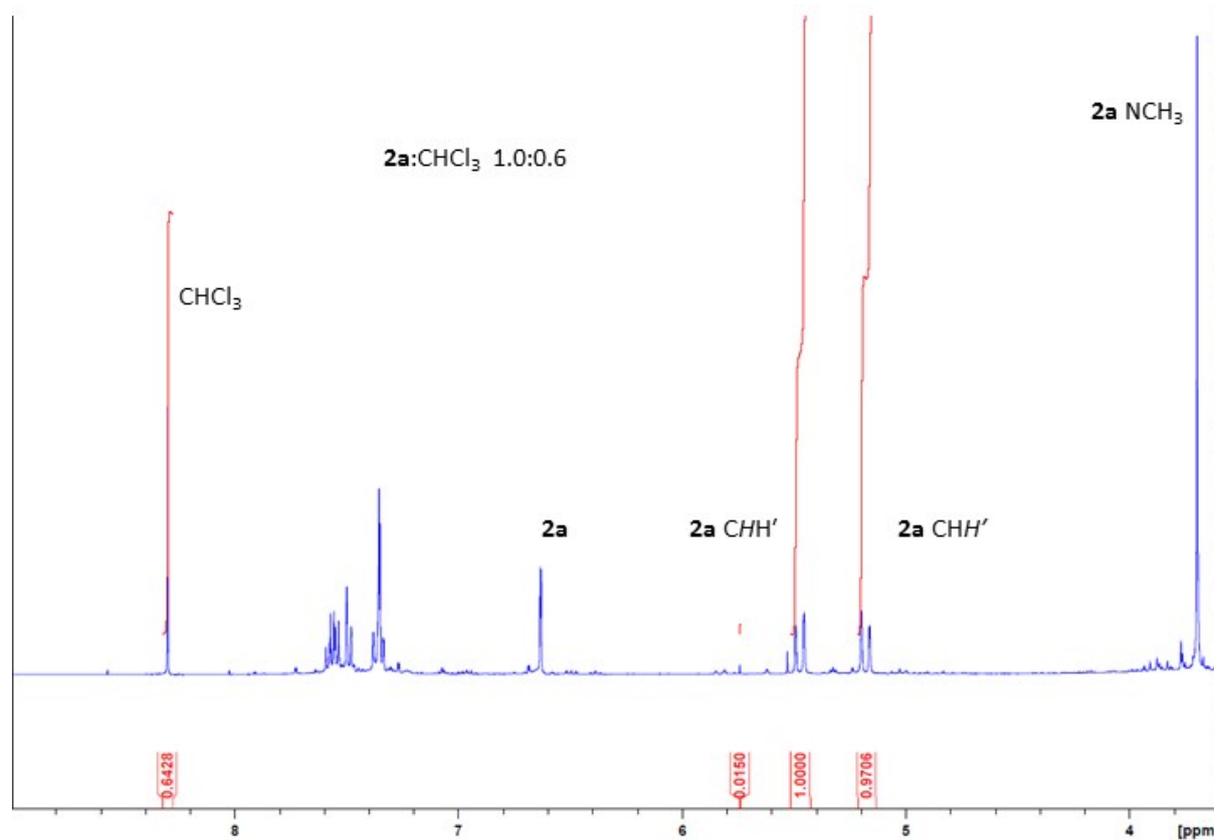
**b) 3 days**



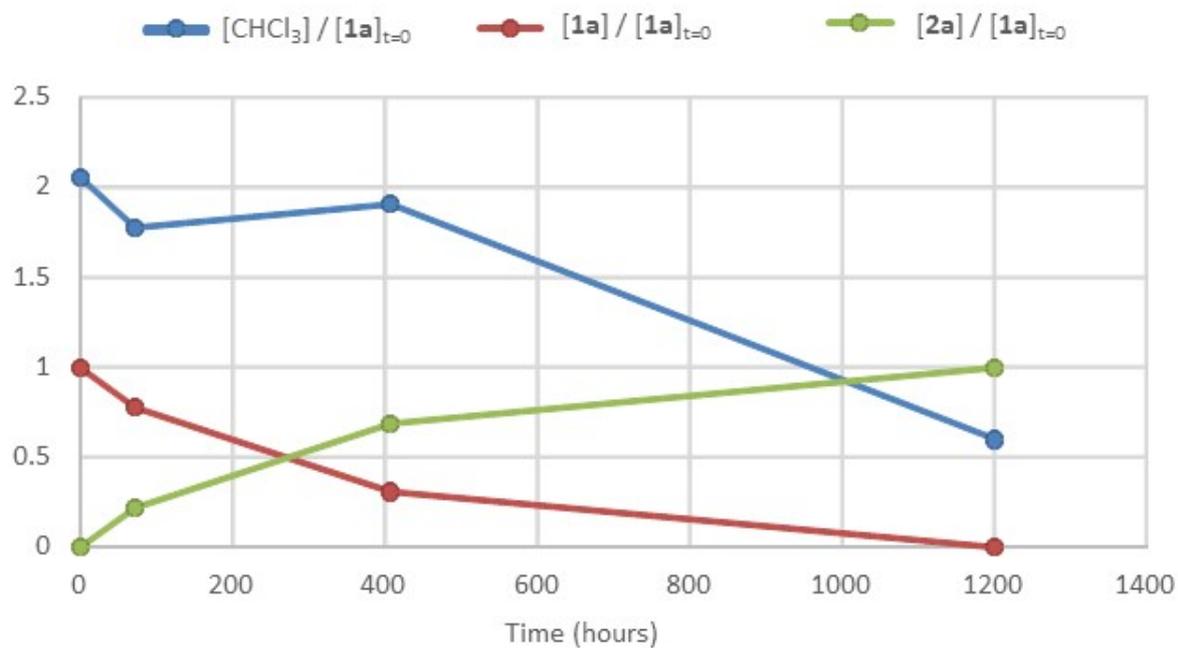
c) 17 days



d) 50 days

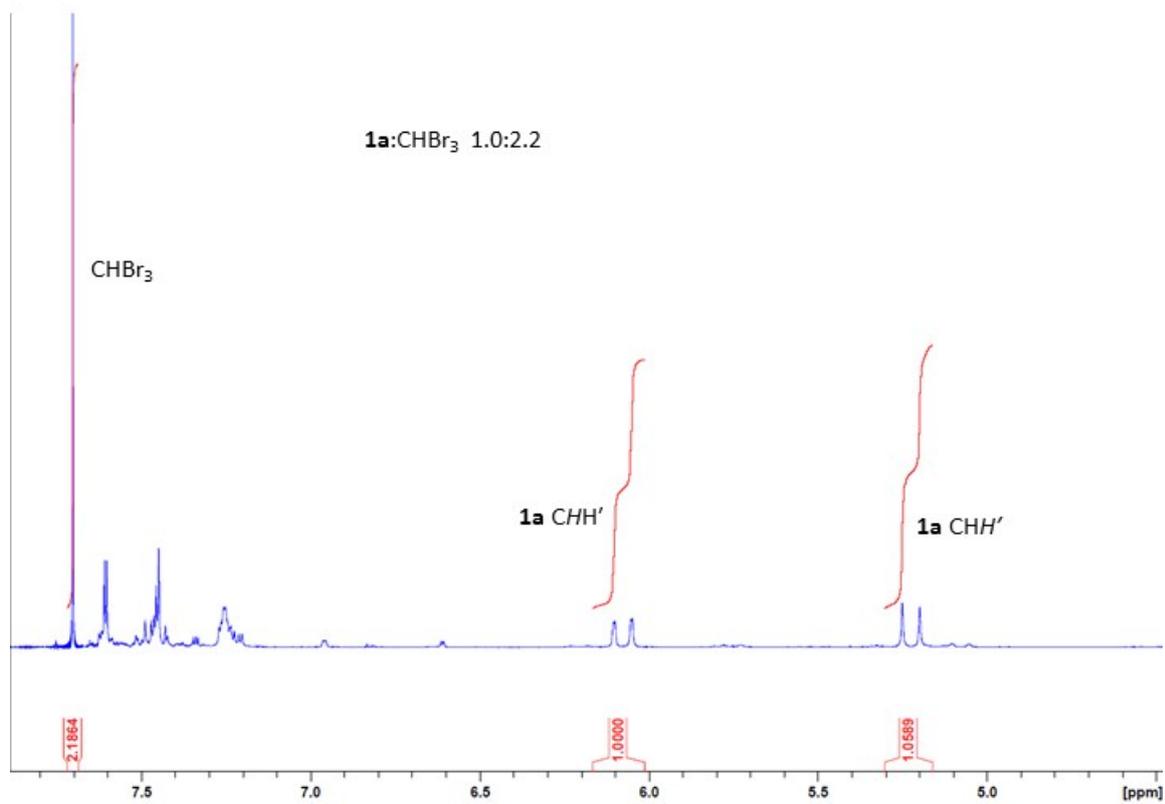


**Figure S10.** Variation of the concentrations of **1a**, **2b** and  $\text{CHCl}_3$  (relative to the initial concentration of **1a**) with time the reaction between **1a**, silver oxide and  $\text{CHCl}_3$  in  $(\text{CD}_3)_2\text{SO}$ .

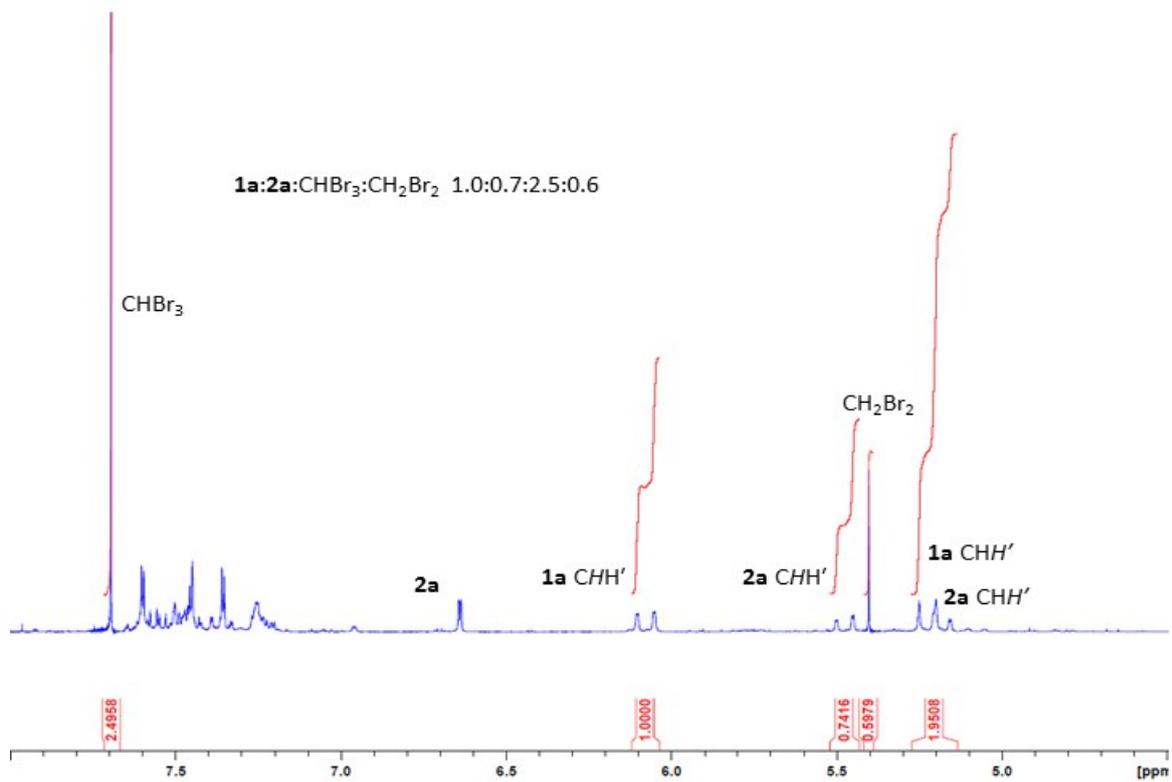


**Figure S11.**  $^1\text{H}$  NMR spectra of the reaction between **1a**, silver oxide and  $\text{CHBr}_3$  in  $(\text{CD}_3)_2\text{SO}$ .

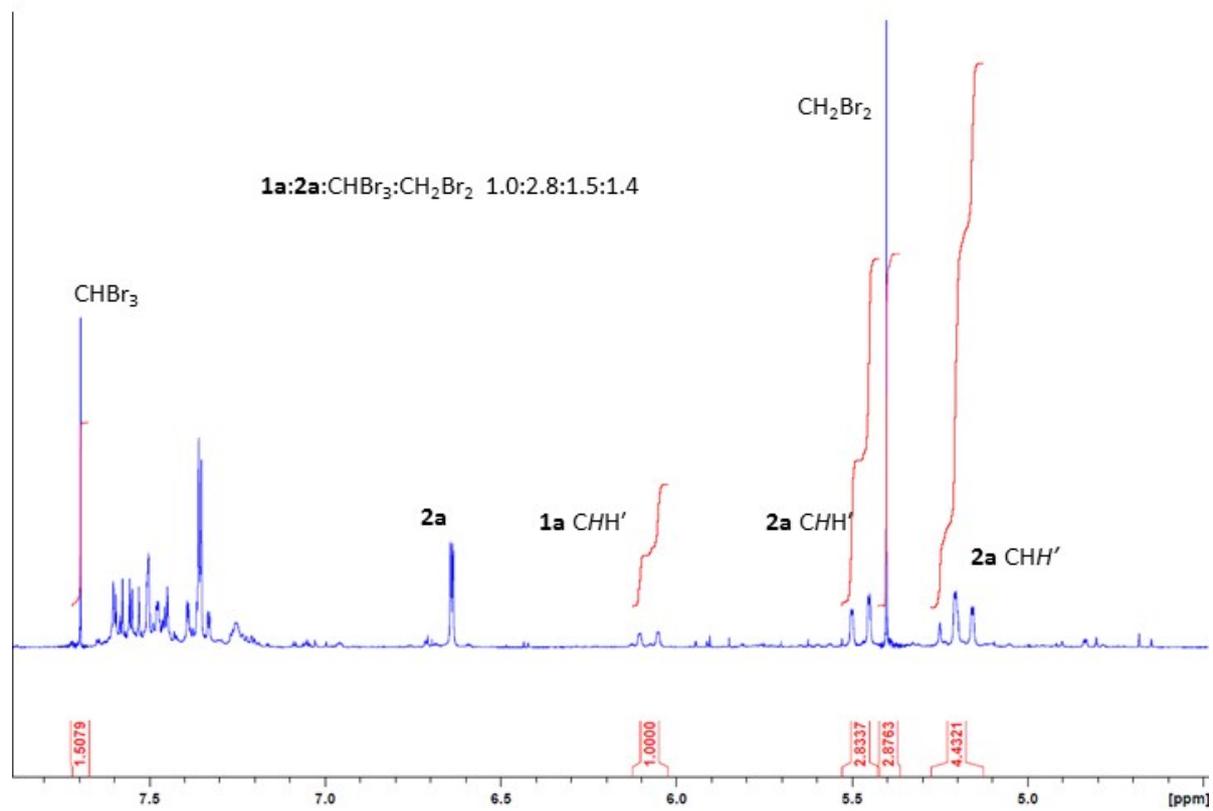
**a) 0 hours**



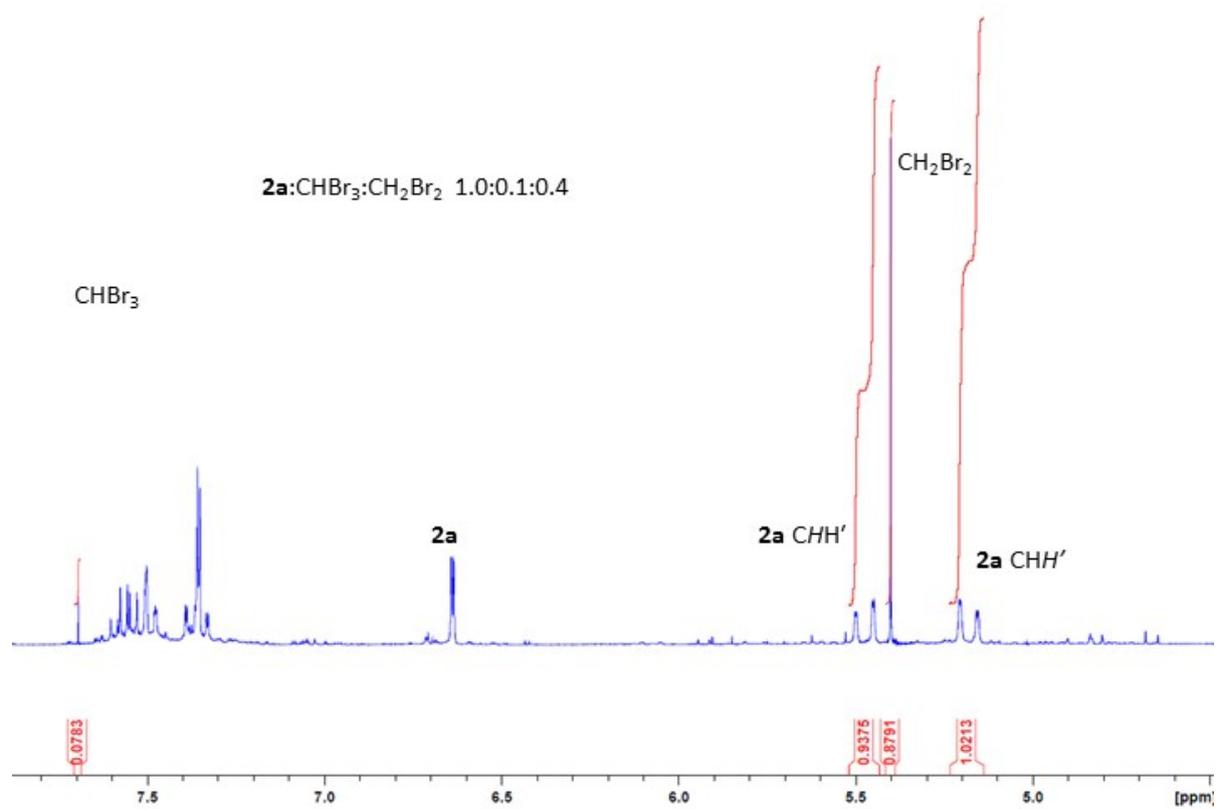
**b) 7 days**



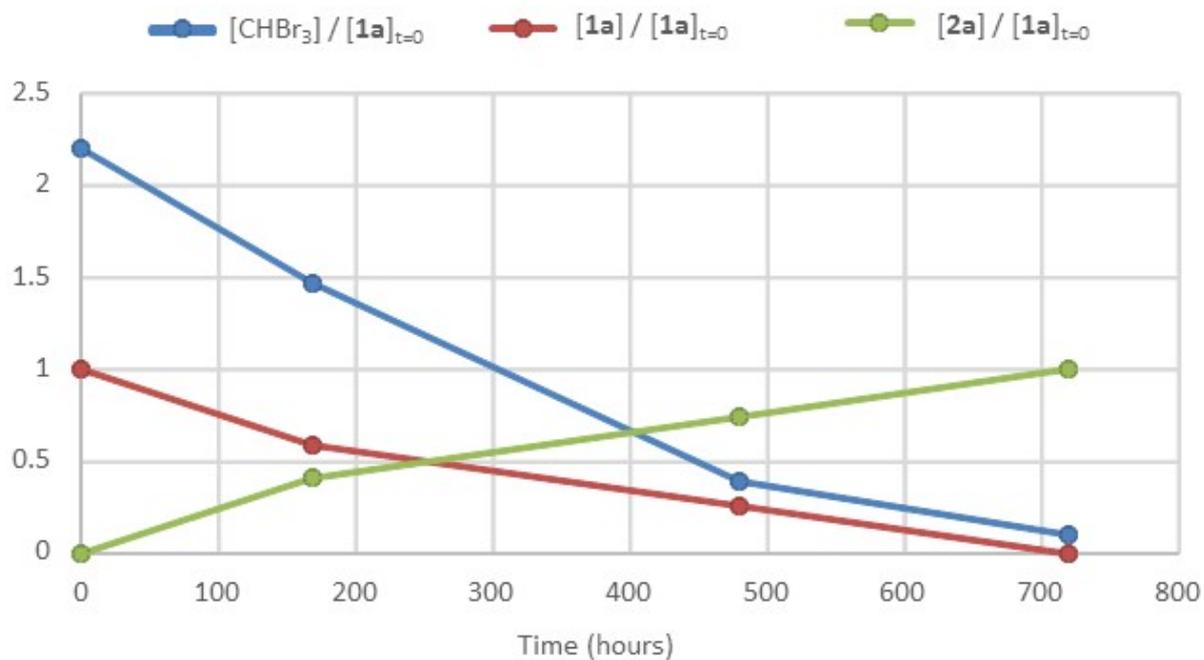
c) 20 days



d) 30 days

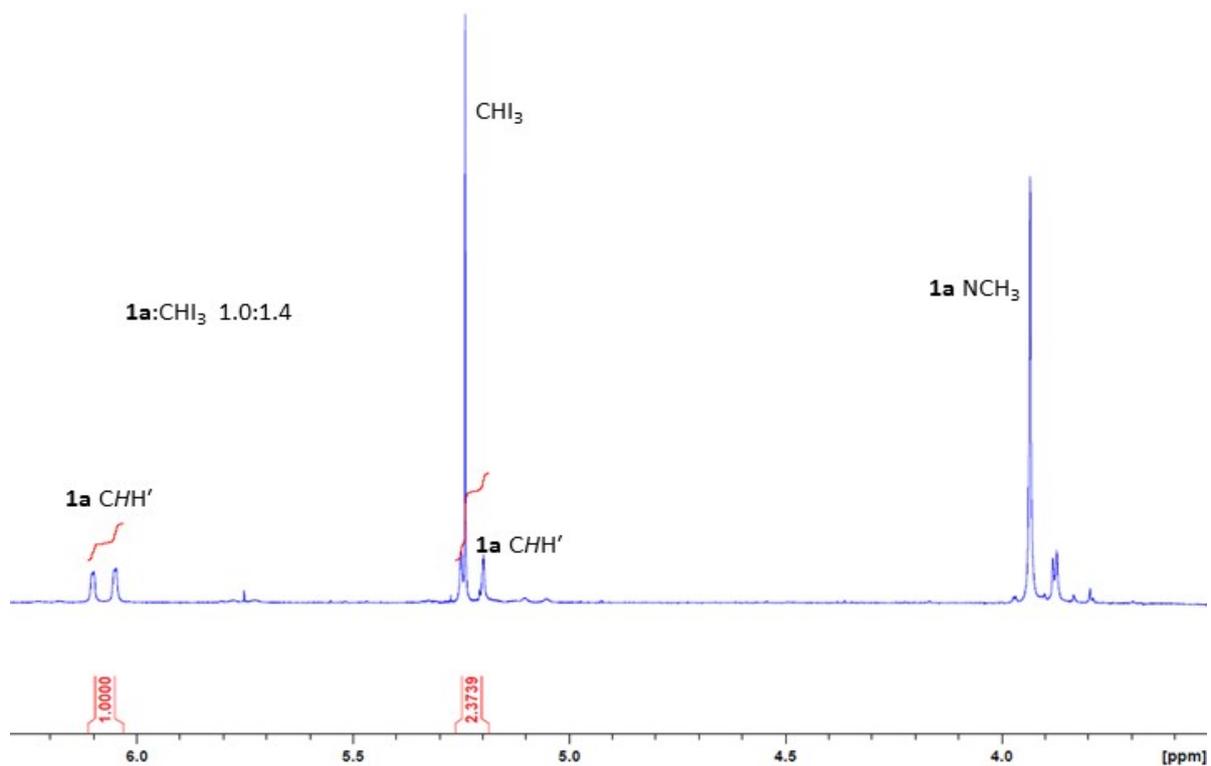


**Figure S12.** Variation of the concentrations of **1a**, **2b** and  $\text{CHBr}_3$  (relative to the initial concentration of **1a**) with time the reaction between **1a**, silver oxide and  $\text{CHBr}_3$  in  $(\text{CD}_3)_2\text{SO}$ .

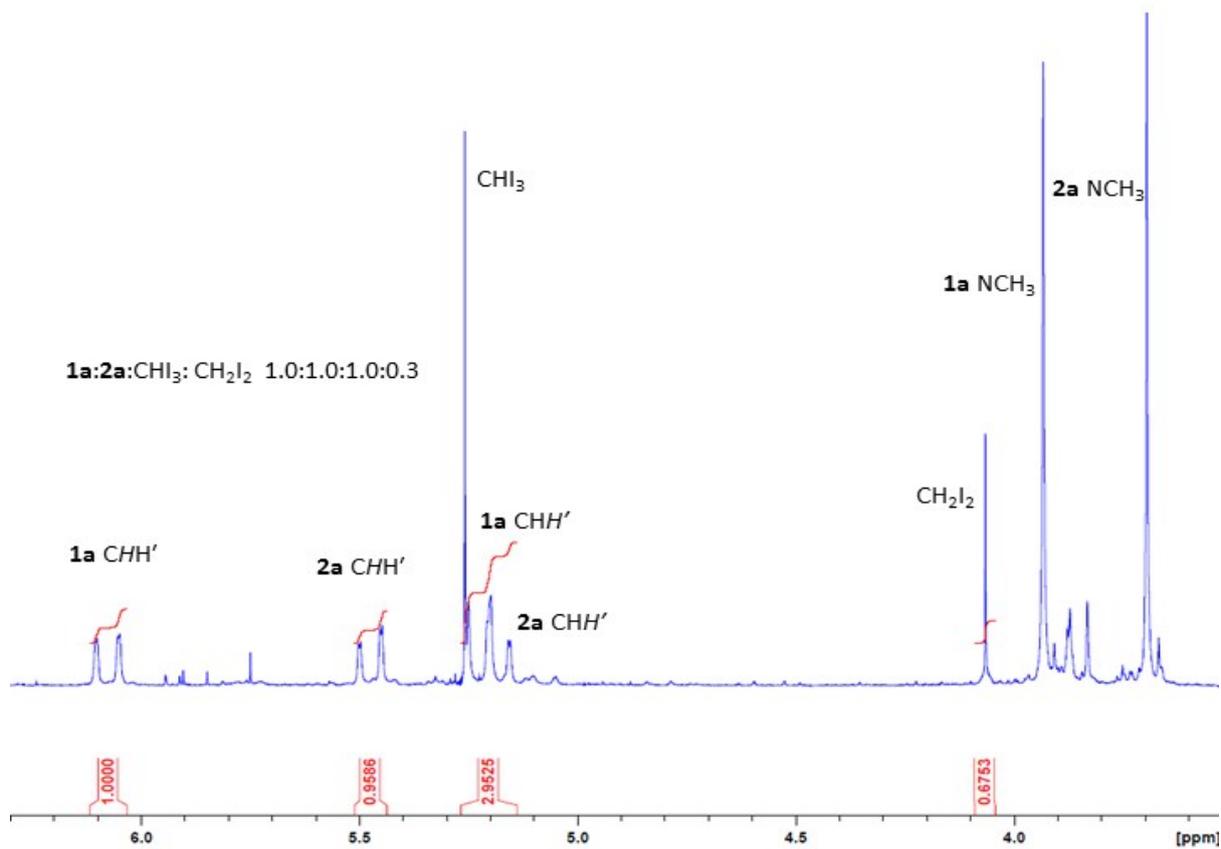


**Figure S13.**  $^1\text{H}$  NMR spectra of the reaction between **1a**, silver oxide and  $\text{CHI}_3$  in  $(\text{CD}_3)_2\text{SO}$ .

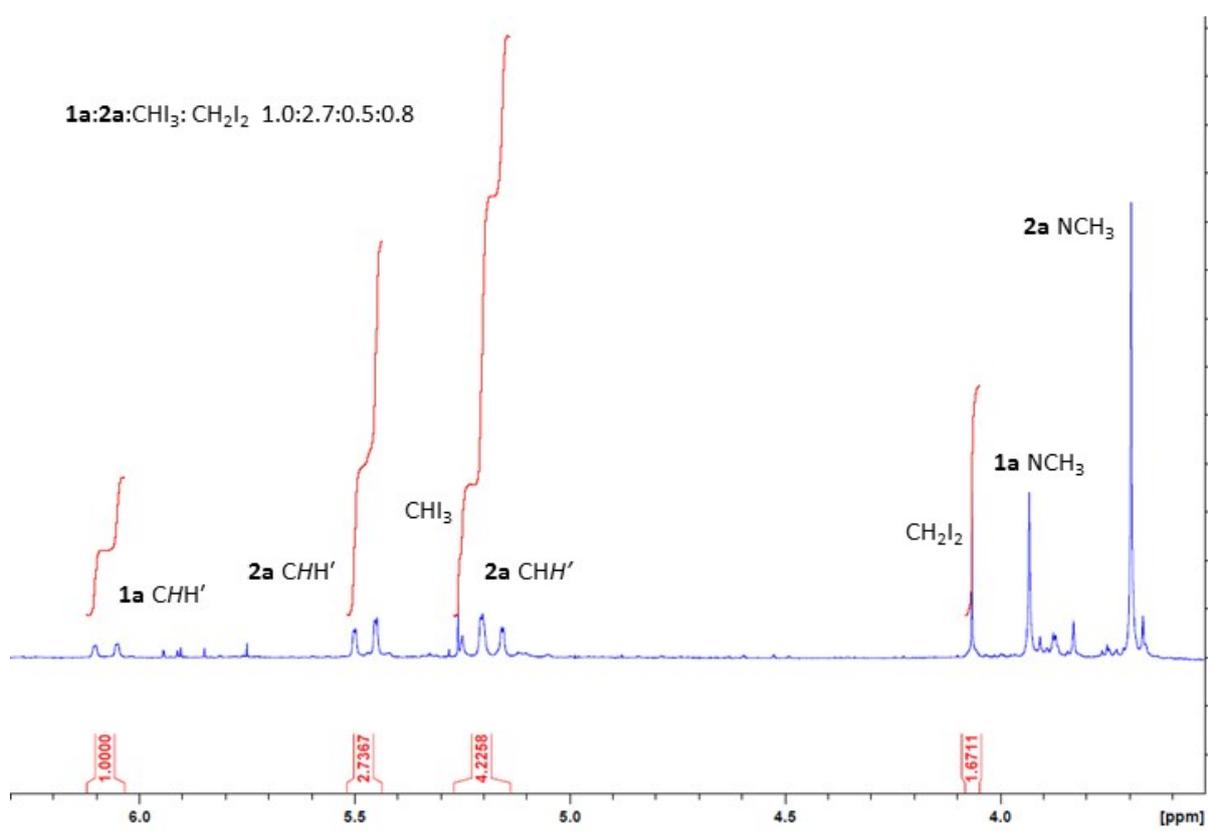
**a) 0 hours**



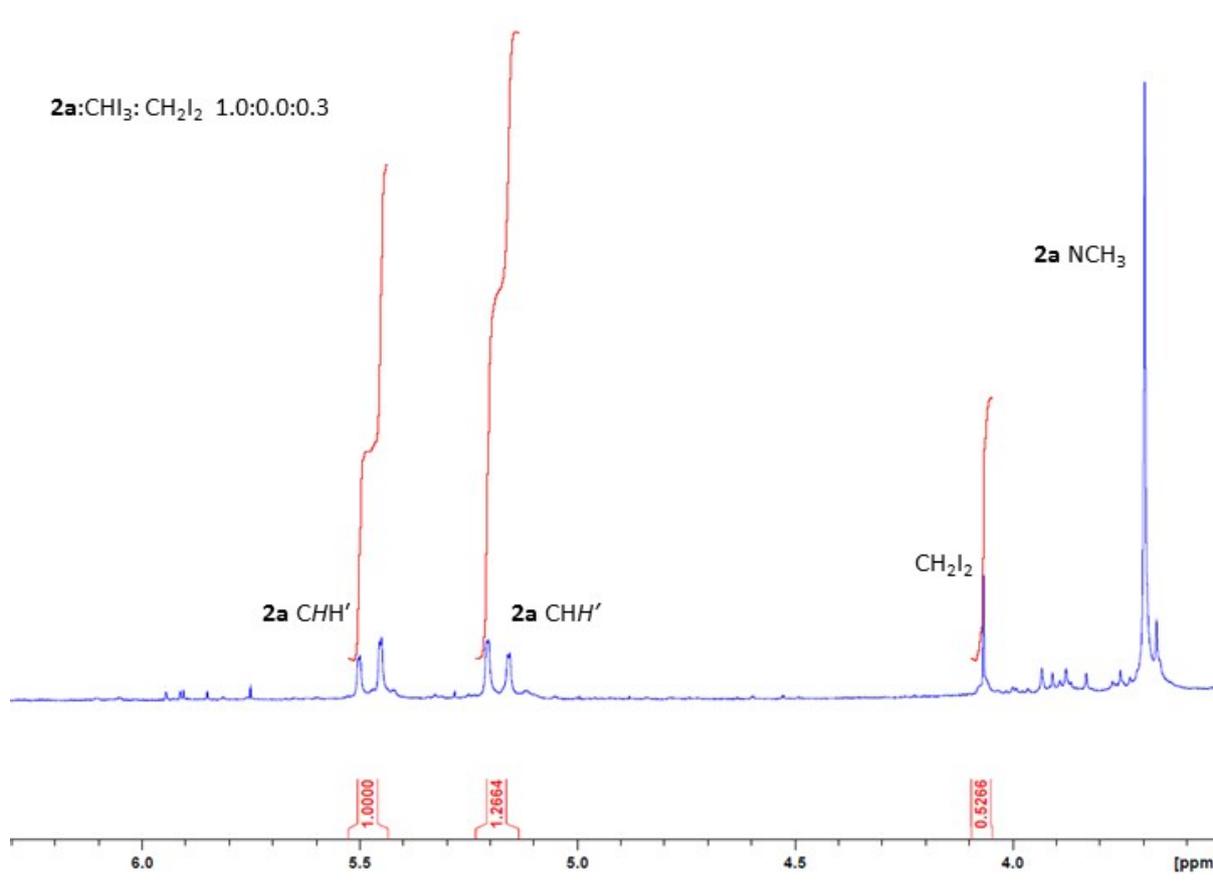
**b) 3 days**



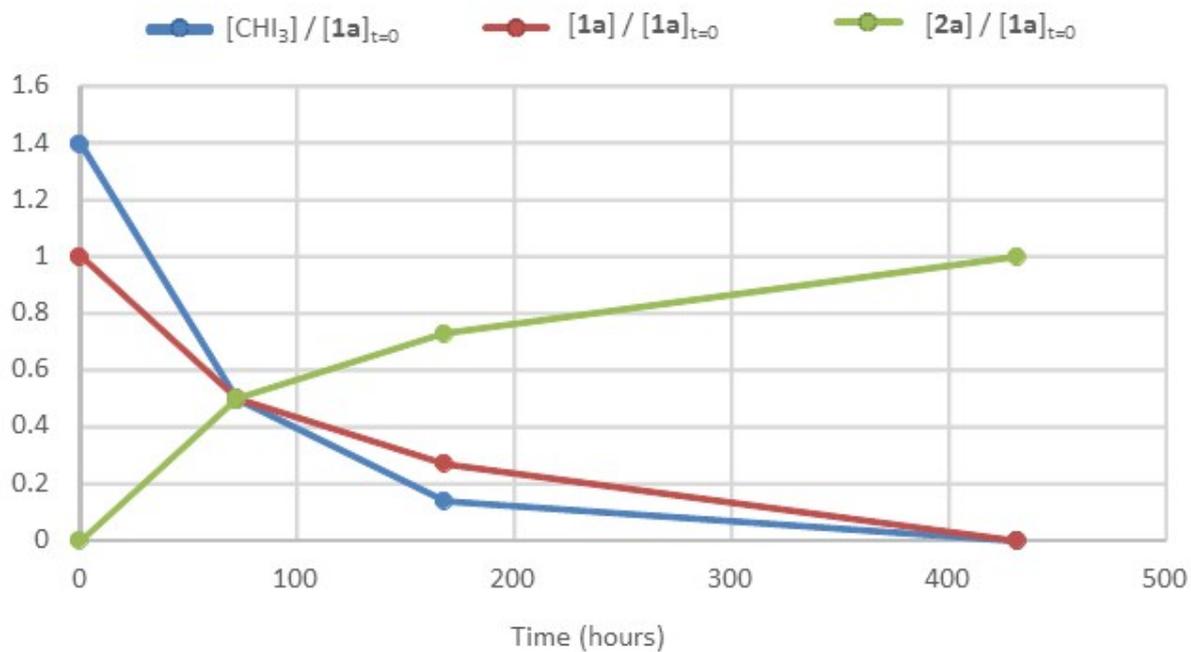
c) 7 days



d) 18 days



**Figure S14.** Variation of the concentrations of **1a**, **2b** and  $\text{CHI}_3$  (relative to the initial concentration of **1a**) with time the reaction between **1a**, silver oxide and  $\text{CHI}_3$  in  $(\text{CD}_3)_2\text{SO}$ .



### ***Identification of silver and silver chloride in the residue of the reaction between 1a and chloroform***

The black solid residue (Fig. S15a) remaining after the reaction between **1a**, chloroform and silver oxide in deuterio-dimethylsulphoxide was treated with dilute (2M) aqueous ammonia, in which both silver chloride and silver oxide are soluble. Most of the material dissolved to produce a colourless solution leaving a small amount of black solid (Fig. S15b). Nitric acid added was added to the decanted solution resulting in a white precipitate (Fig. S15c).<sup>3</sup> The observations are consistent with the presence of silver chloride. The black solid was found to dissolve in nitric acid (Fig. S15d), which is consistent with elemental silver. **[CARE:** While no adverse incidents occurred during these experiments, dissolution of silver(I) oxide in aqueous ammonia can lead to the formation of explosive and shock sensitive silver nitride (fulminating silver). Dilute (2 M) aqueous ammonia was used, and the samples were treated with acid immediately after each experiment had been completed to prevent the formation of the nitride.]

**Figure S15.** Analysis of the residue from the reaction between **1a**, silver oxide and  $\text{CHCl}_3$  in  $(\text{CD}_3)_2\text{SO}$ .

**a** Black residue



**b** Addition of  $\text{NH}_3(\text{aq})$



**c** Addition of  $\text{HNO}_3$  to ammoniacal solution



**d** Addition of  $\text{HNO}_3$  to insoluble solid



### X-ray crystallographic study

Crystals of **2a** were obtained by vapour diffusion of pentane into a chloroform solution. Crystal data are listed in Table S1. Diffraction data were collected on an Agilent SuperNova, single source at offset, Atlas diffractometer with graphite-monochromated Cu—K $\alpha$  radiation. The structure was solved using Olex2<sup>5</sup> and refined with the olex2.refine<sup>6</sup> refinement package using Gauss-Newton minimization. The non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atom positions were added in idealized positions and a riding model with fixed thermal parameters ( $U_{ij} = 1.2U_{eq}$  for the atom to which they are bonded (1.5 for CH<sub>3</sub>)) was used for subsequent refinements. The function minimized was  $\Sigma[w(|F_o|^2 - |F_c|^2)^2]$  with reflection weights  $w^{-1} = [\sigma^2 |F_o|^2 + (g1P)^2 + (g2P)^2]$  where  $P = [\max |F_o|^2 + 2|F_c|^2]/3$ .

CCDC 1864957 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

Figure S16. Molecular structure of **2a**

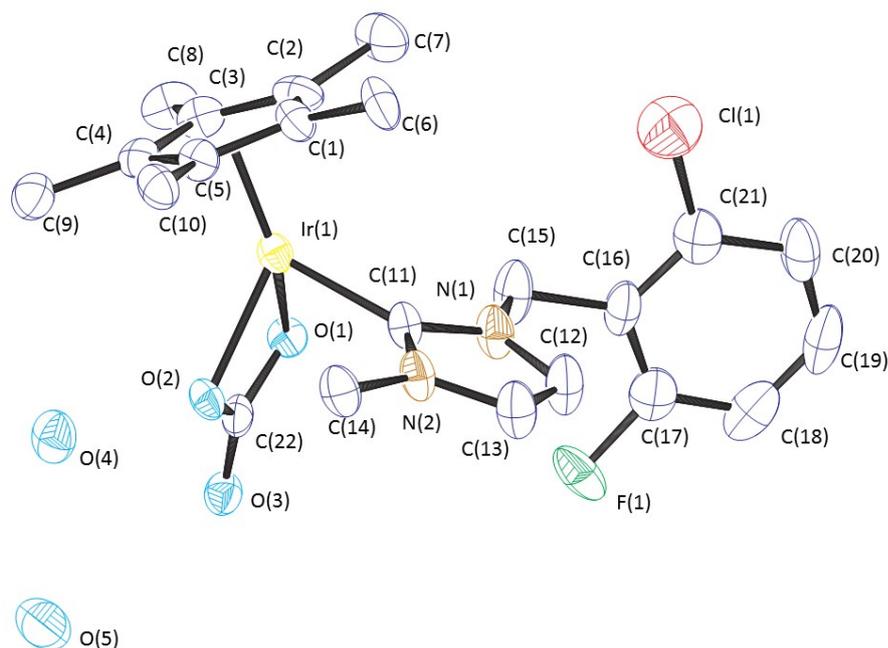


Table S1. Crystallographic data for  $[(\eta^5\text{-C}_5\text{Me}_5)\text{Ir}(\kappa^2\text{O-CO}_3)(\kappa\text{C-MeNC}_3\text{H}_2\text{NCH}_2\text{C}_6\text{H}_3\text{F-2-Cl-6})].2\text{H}_2\text{O}$  (**2a**. $2\text{H}_2\text{O}$ ).

Formula	$\text{C}_{22}\text{H}_{25}\text{ClFIrN}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$
Formula weight	648.15
Crystal system	orthorhombic
Space group	<i>Pbcn</i>
<i>a</i> , Å	24.4133(4)
<i>b</i> , Å	15.2016(2)
<i>c</i> , Å	12.9342(2)
<i>V</i> , Å <sup>3</sup>	4800.18(13)
<i>Z</i>	8
<i>D<sub>c</sub></i> (g cm <sup>-3</sup> )	1.7936
Crystal size (mm <sup>3</sup> )	0.097 × 0.051 × 0.023
$\mu$ (mm <sup>-1</sup> )	12.166
$\theta$ range (°)	3.42 - 73.99
Total reflections	18,286
Unique reflections ( <i>R<sub>int</sub></i> )	4,708 (0.0504)
Observed reflections [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]	3,682
Parameters	301
Final <i>R</i> indices [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]	<i>R</i> <sub>1</sub> = 0.0409, <i>wR</i> <sub>2</sub> = 0.1101
<i>R</i> indices (all data)	<i>R</i> <sub>1</sub> = 0.0545, <i>wR</i> <sub>2</sub> = 0.12.59
Weighting scheme	$w = 1/[\sigma^2(F_o)^2 + \{0.0720 (F_o^2 + 2F_c^2)/3\}^2 + 9.8380 (F_o^2 + 2F_c^2)/3]$
Max., min. $\Delta\rho$ (eÅ <sup>-3</sup> )	2.303, -1.466
Goodness of fit on <i>F</i> <sup>2</sup>	1.0599

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