

Supporting Information

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**Ruthenium-Catalyzed Direct Methylation of Primary and Secondary Aromatic Amines Using Carbon Dioxide and Molecular Hydrogen\*\***

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## Supporting Information

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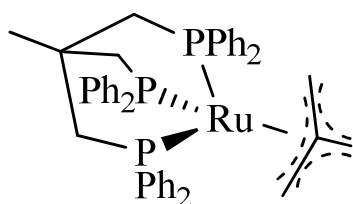
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#### General remarks

For complex synthesis and catalytic experiments moisture and oxygen were excluded by working in a glove box or by using Schlenk techniques. Argon 4.8 (Messer, Germany) was used as inert gas. Glassware was dried under vacuum under heating with a heat gun, evacuated and refilled with argon at least three times. All solvents were purified by distillation prior to use. Tetrahydrofuran, toluene and pentane were degassed by bubbling argon with a frit, dried by passing over activated alumina in steel columns and stored over molecular sieves. All reagents were commercially available and used as received unless stated otherwise. Reaction gases hydrogen (5.0) and carbon dioxide (4.6) were supplied by Linde and PraxAir and used without further purification.

NMR spectra were recorded with spectrometers Bruker AV400 at room temperature in  $\text{CDCl}_3$  solvents. Chemical shifts are given in ppm relative to tetramethylsilane. Gas chromatography was performed on a Trace GC gas chromatograph (Thermo Scientific) equipped with a SSL Inlet (250 °C, Split 60 mL/min), a MN-OPTIMA-5-Amin column (30 m, inner diameter 0.25 mm, film thickness 0.5  $\mu\text{m}$ ) and a flame ionization detector (250 °C) using helium as carrier gas and a temperature program: 5 min isothermal at 50 °C, ramp to 280 °C (8°C/min), 15 min at 280 °C.

### Synthesis of $[\text{Ru}(\text{Triphos})(\text{TMM})]$ :<sup>[1]</sup>



A 35 mL schlenk tube was charged with 159.5 mg (0.5 mmol)  $[\text{Ru}(\text{cod})(\text{methylallyl})_2]$  and 312.0 mg 1,1,1-tris(diphenylphosphino)ethane (Triphos) in 25 mL toluene. After heating for 2 h at 110 °C, the resulting solution was concentrated in vacuo and treated with 10 mL of pentane. The precipitating complex was isolated and washed three times with 10 mL pentane. After drying,  $[\text{Ru}(\text{Triphos})(\text{TMM})]$  was obtained as a bright yellow powder in 75 % yield.

### General procedures for direct methylation of anilines with $\text{CO}_2/\text{H}_2$ .

All high pressure batch experiments were conducted in stainless steel 10 mL autoclaves equipped with a glass inlet and a magnetic stir bar. Prior to use, the autoclave was dried under vacuum for 3 hours and repeatedly filled with argon. Under an argon atmosphere, catalyst  $[\text{Ru}(\text{Triphos})(\text{TMM})]$  (0.019 g, 0.025 mmol) and  $\text{HNTf}_2$  (0.014 g, 0.05 mmol) were weighed in a Schlenk tube. After dissolving in THF (1.0 mL), the mixture was transferred via cannula to the autoclave followed by the addition of the aniline substrate (1.0 mmol) in THF (1.0 mL). The autoclave was then pressurized with  $\text{CO}_2$  to 20 bar and then  $\text{H}_2$  was added up to a total pressure of 80 bar. The reaction mixture was stirred and heated to 150 °C in an oil bath. After 10h, the autoclave was cooled in an ice bath and then carefully vented. The reaction solution

<sup>1</sup> T. vom Stein, T. Weigand, C. Merckens, J. Klankermayer, W. Leitner, *ChemCatChem* **2013**, 5, 439 .

was analyzed by  $^1\text{H-NMR}$  with internal standard mesitylene and the results confirmed by gas chromatography using dodecane as internal standard.

## Further experimental data

### 1) Optimization reactions of the direct methylation of *N*-methylaniline **1**.

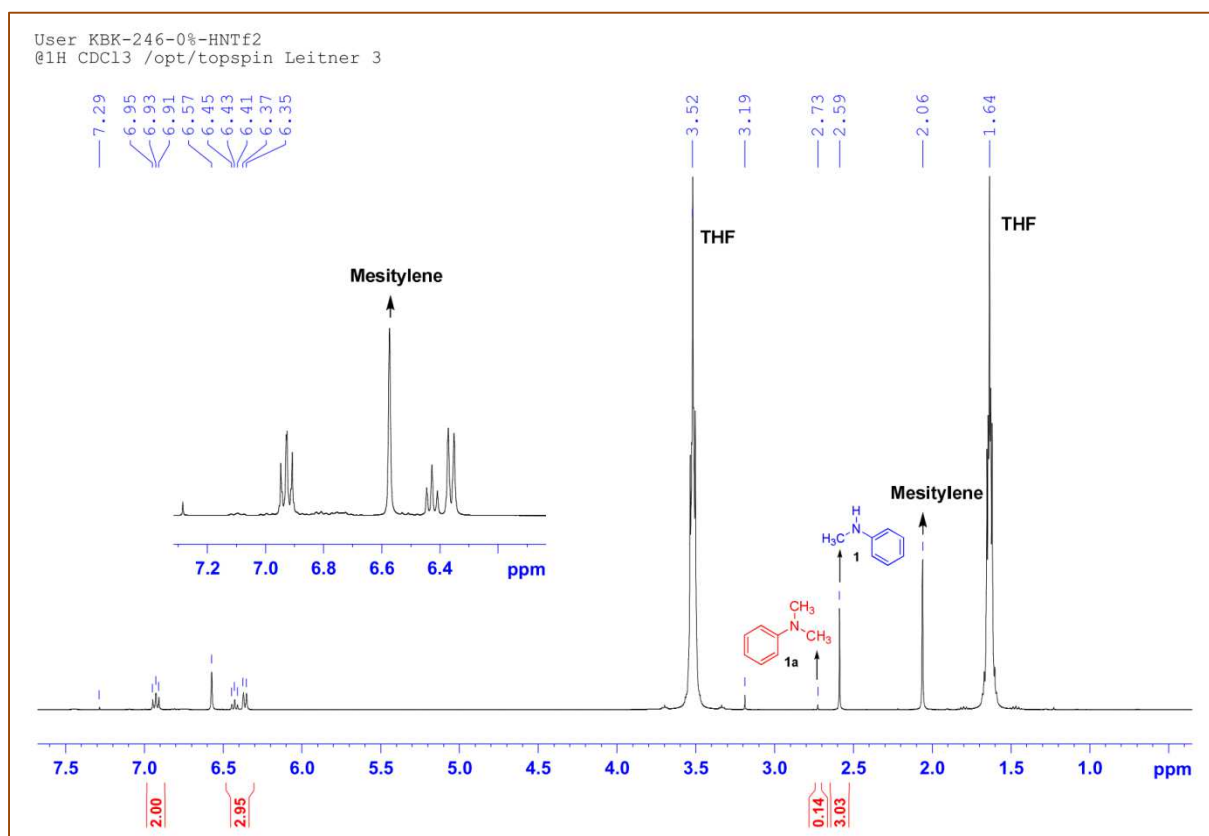
Table S1. Ruthenium catalysed methylation of *N*-methyl aniline **1** with carbon dioxide and molecular hydrogen.<sup>[a]</sup>

Entry	Acid [mol%]	Temp [C <sup>o</sup> ]	Time [h]	Yield [%] <sup>[b]</sup>
1	--	140	10	2
2	HNTf <sub>2</sub> (0.5)	140	22	11
3	HNTf <sub>2</sub> (2.5)	140	22	84
4 <sup>c</sup>	HNTf <sub>2</sub> (5)	140	22	0
5 <sup>d</sup>	HNTf <sub>2</sub> (5)	140	10	50
6	HNTf <sub>2</sub> (5)	140	22	97
7 <sup>e</sup>	HNTf <sub>2</sub> (5)	140	22	25
8	HNTf <sub>2</sub> (5)	120	22	81
9	HNTf <sub>2</sub> (5)	100	22	58
10	HNTf <sub>2</sub> (5)	150	0.5	9
11	HNTf <sub>2</sub> (5)	150	1	20
12	HNTf <sub>2</sub> (5)	150	1.5	29
13	HNTf <sub>2</sub> (5)	150	2	34
14	HNTf <sub>2</sub> (5)	150	3	49
15	HNTf <sub>2</sub> (5)	150	4	69
16	HNTf <sub>2</sub> (5)	150	8	97
17	HNTf <sub>2</sub> (5)	150	10	99
18	MSA (5)	150	10	95
19	<i>p</i> -TsOH (5)	150	10	97

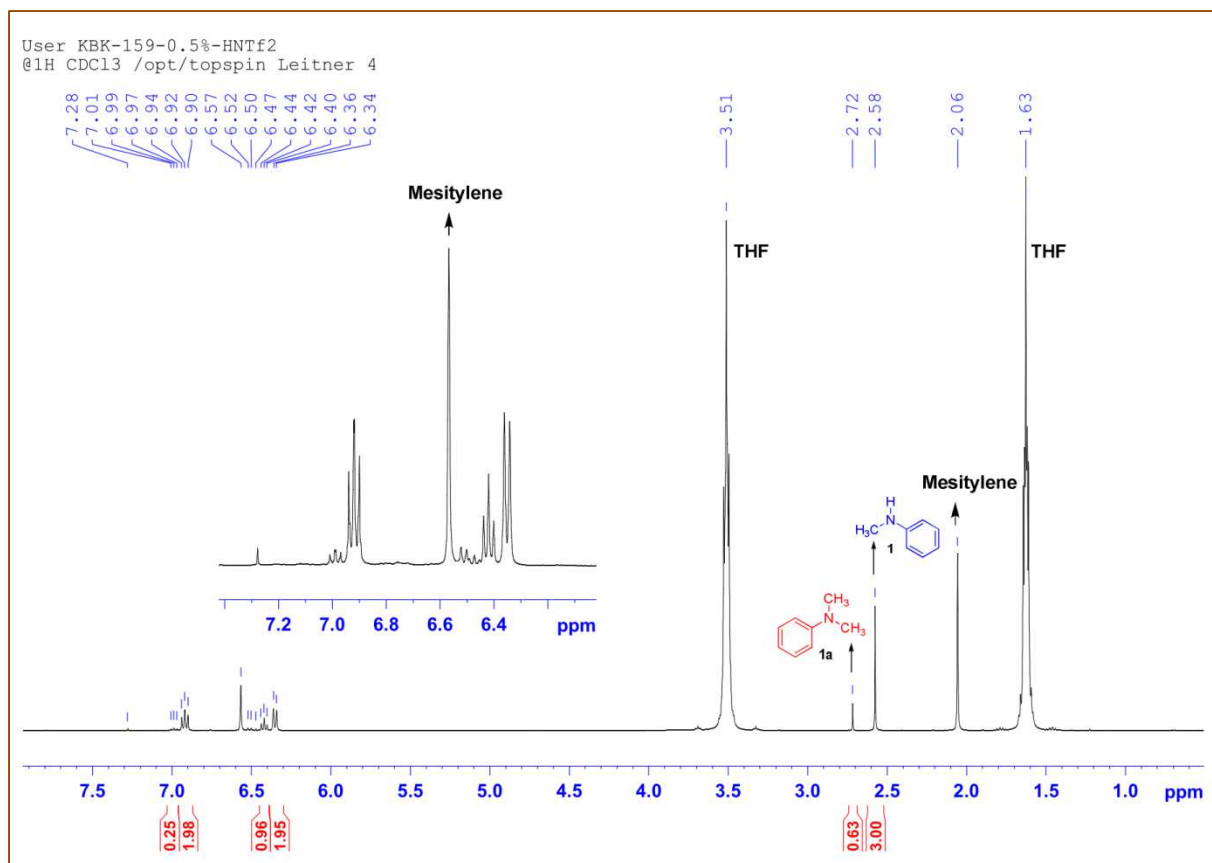
[a] Reaction conditions: *N*-methylaniline **1** (1.0 mmol), [Ru(Triphos)(TMM)] (2.5 mol%), THF (2.0 mL), CO<sub>2</sub>/H<sub>2</sub> (20/60 bar). [b] Yield determined by GC using *n*-dodecane as an internal standard. [c] No catalyst. [d] 1 mol% of [Ru(Triphos)(TMM)] used. [e] CO<sub>2</sub>/H<sub>2</sub>: (10/30 bar).

## $^1\text{H}$ NMR spectra of the direct methylation of *N*-methylaniline **1**

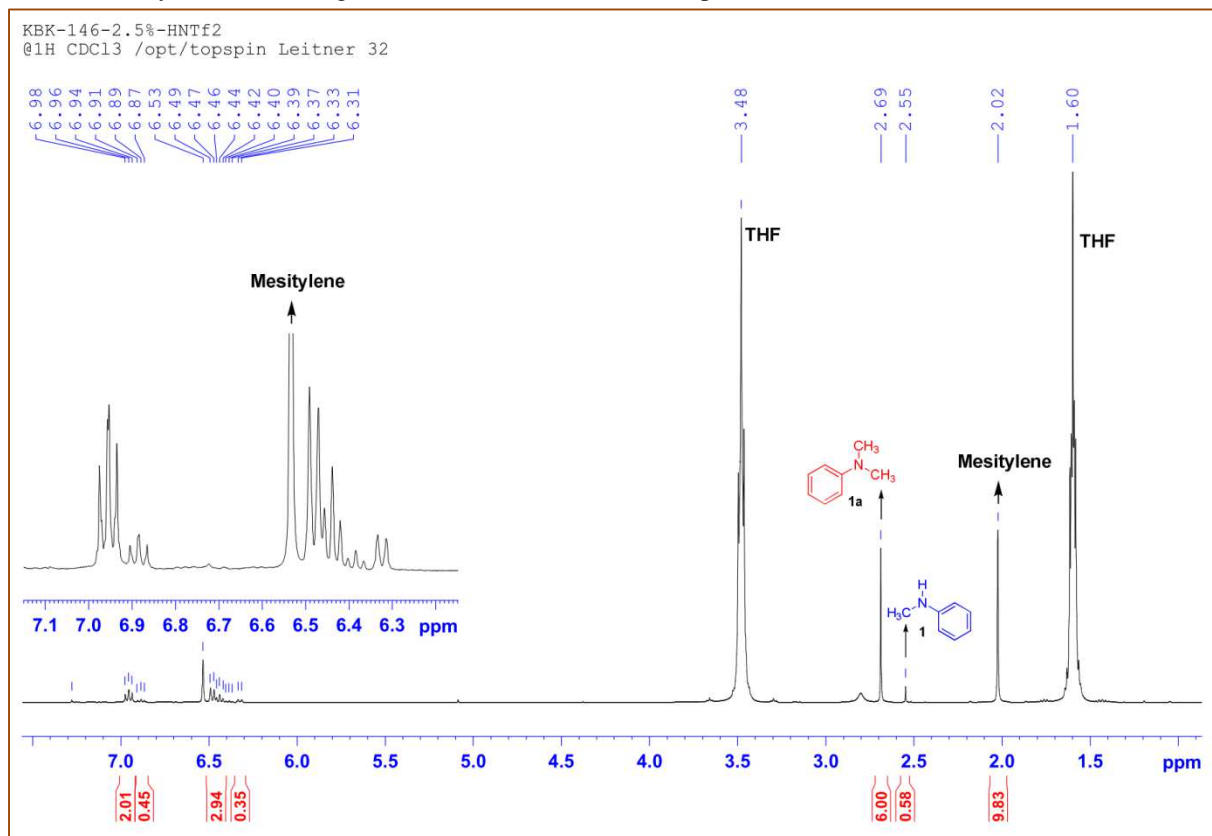
**Figure 1**, **Figure 2**, **Figure 3**, and **Figure 4** show the  $^1\text{H}$  NMR spectra of crude reaction mixtures after applying different acid loadings. In absence of  $\text{HNTf}_2$  or when using 0.5 mol%, 2.5 mol%, or 5 mol% of  $\text{HNTf}_2$ , *N,N*-dimethyl aniline **1a** was afforded in 2%, 11%, 84%, and 97% yield respectively (Figures 1, 2, 3, and 4 respectively). The methyl groups in compounds **1** and **1a** can be easily distinguished via  $^1\text{H}$ -NMR spectroscopy.



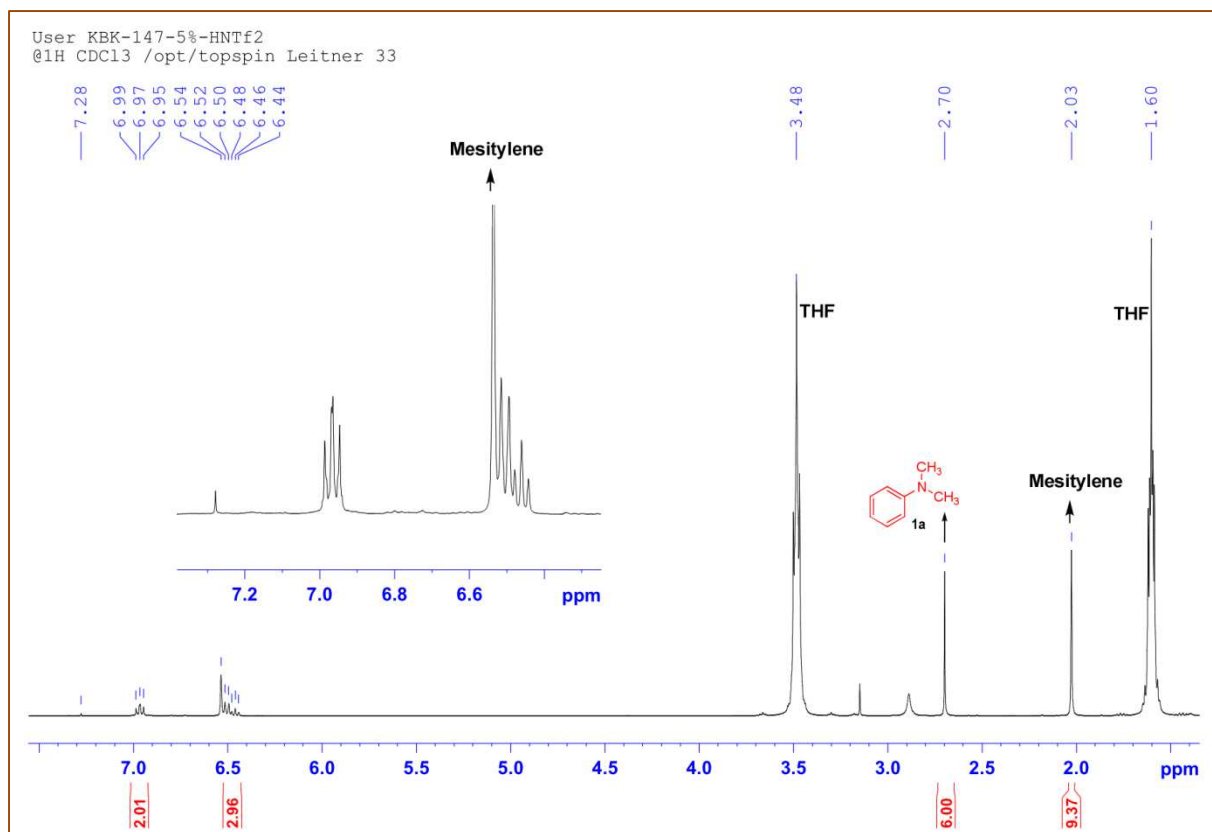
**Figure 1:**  $^1\text{H}$ -NMR spectrum (400 MHz,  $\text{CDCl}_3$ ) of reaction solution from the methylation of *N*-methylaniline **1** to *N,N*-dimethylaniline **1a** in the absence of  $\text{HNTf}_2$  and  $[\text{Ru}(\text{Triphos})(\text{TMM})]$ .



**Figure 2:**  $^1\text{H-NMR}$  spectrum (400 MHz,  $\text{CDCl}_3$ ) of reaction solution from the methylation of *N*-methylaniline **1** to *N,N*-dimethylaniline **1a** using 0.5 mol% of  $\text{HNTf}_2$  and  $[\text{Ru}(\text{Triphos})(\text{TMM})]$ .



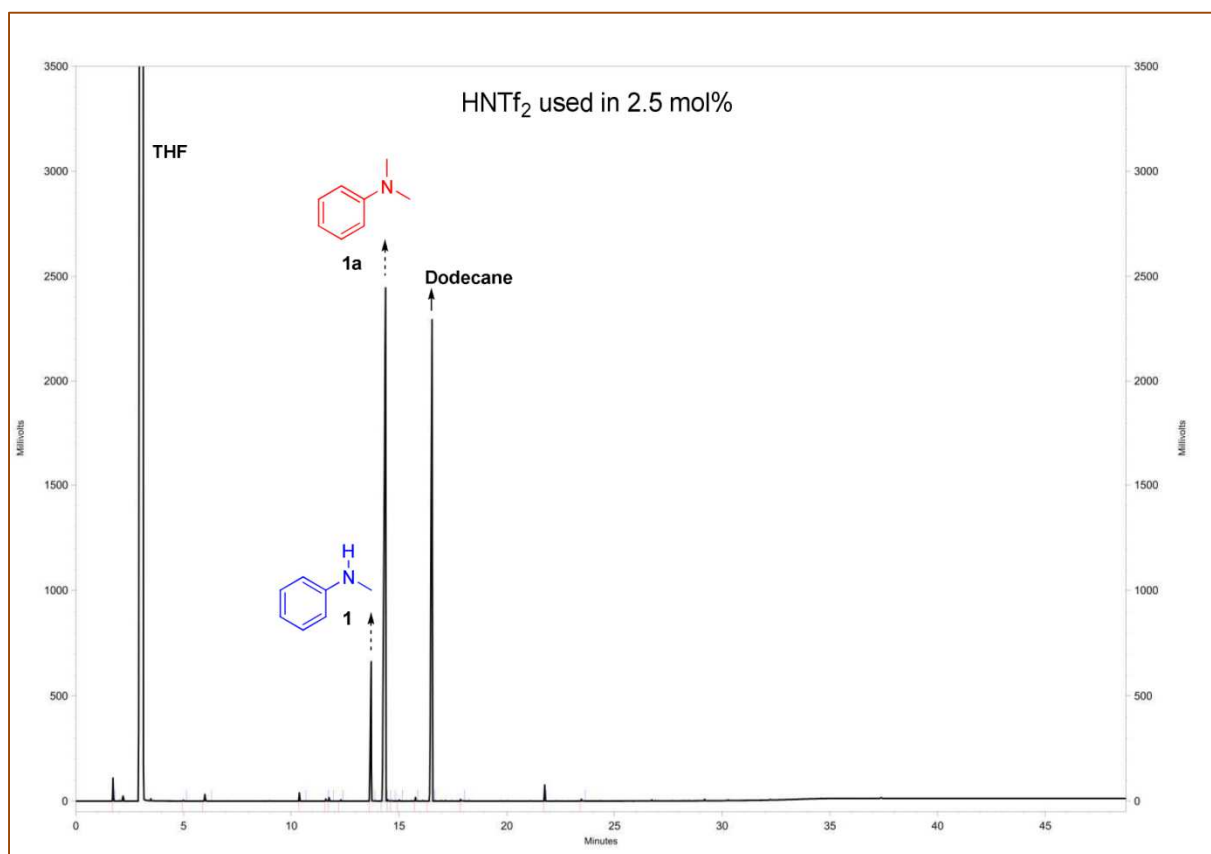
**Figure 3:**  $^1\text{H-NMR}$  spectrum (400 MHz,  $\text{CDCl}_3$ ) of reaction solution from the methylation of *N*-methylaniline **1** to *N,N*-dimethylaniline **1a** using 2.5 mol% of  $\text{HNTf}_2$  and  $[\text{Ru}(\text{Triphos})(\text{TMM})]$ .



**Figure 4:**  $^1\text{H-NMR}$  spectrum (400 MHz,  $\text{CDCl}_3$ ) of reaction solution from the methylation of *N*-methylaniline **1** to *N,N*-dimethylaniline **1a** using 5 mol% of  $\text{HNTf}_2$  and  $[\text{Ru}(\text{Triphos})(\text{TMM})]$ .

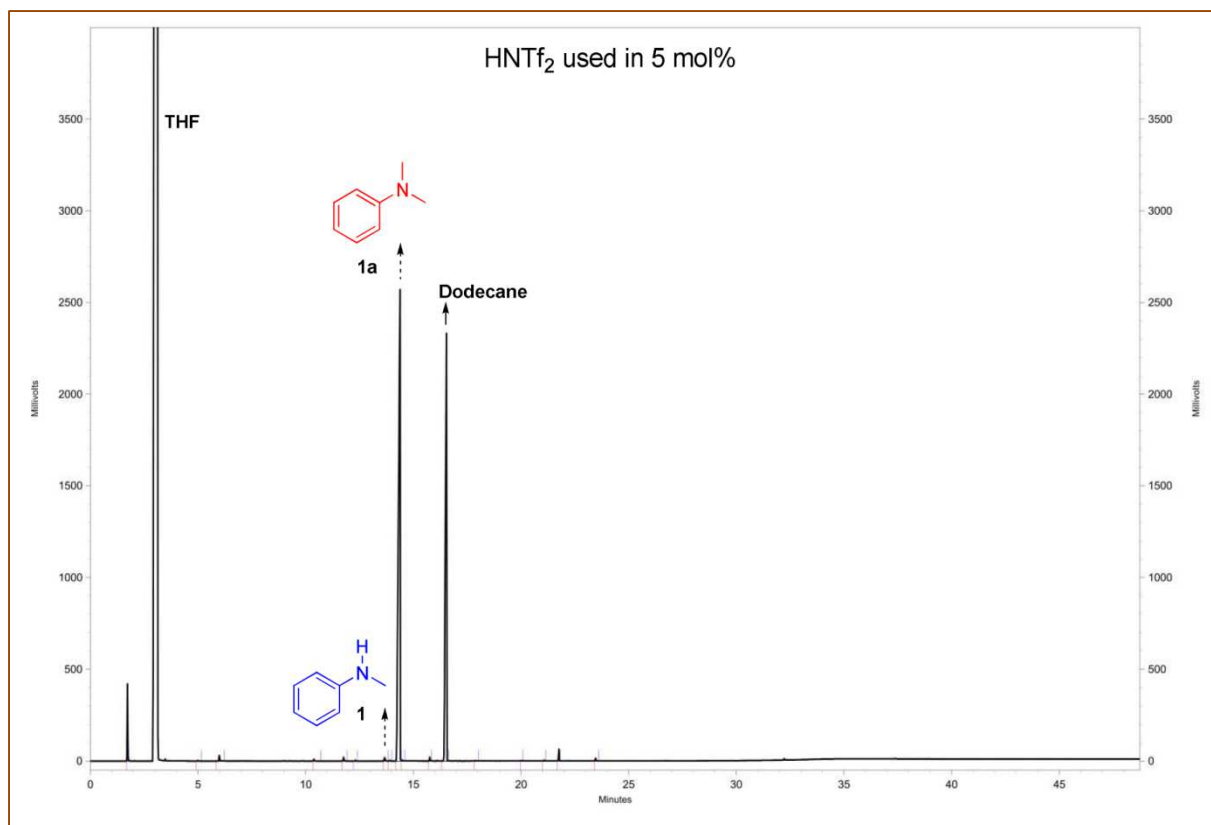
### Gas chromatograms of the direct methylation of *N*-methylaniline **1**

The NMR analysis was further corroborated with gas chromatography analysis. **Figure 5** represents the chromatogram of the reaction mixture, using 2.5 mol% of HNTf<sub>2</sub> whereas **Figure 6** represents the chromatogram of reaction mixture using 5 mol% of HNTf<sub>2</sub>. The chromatogram of reaction performed at 150 °C and with 5 mol% of HNTf<sub>2</sub> is represented in **Figure 7**.

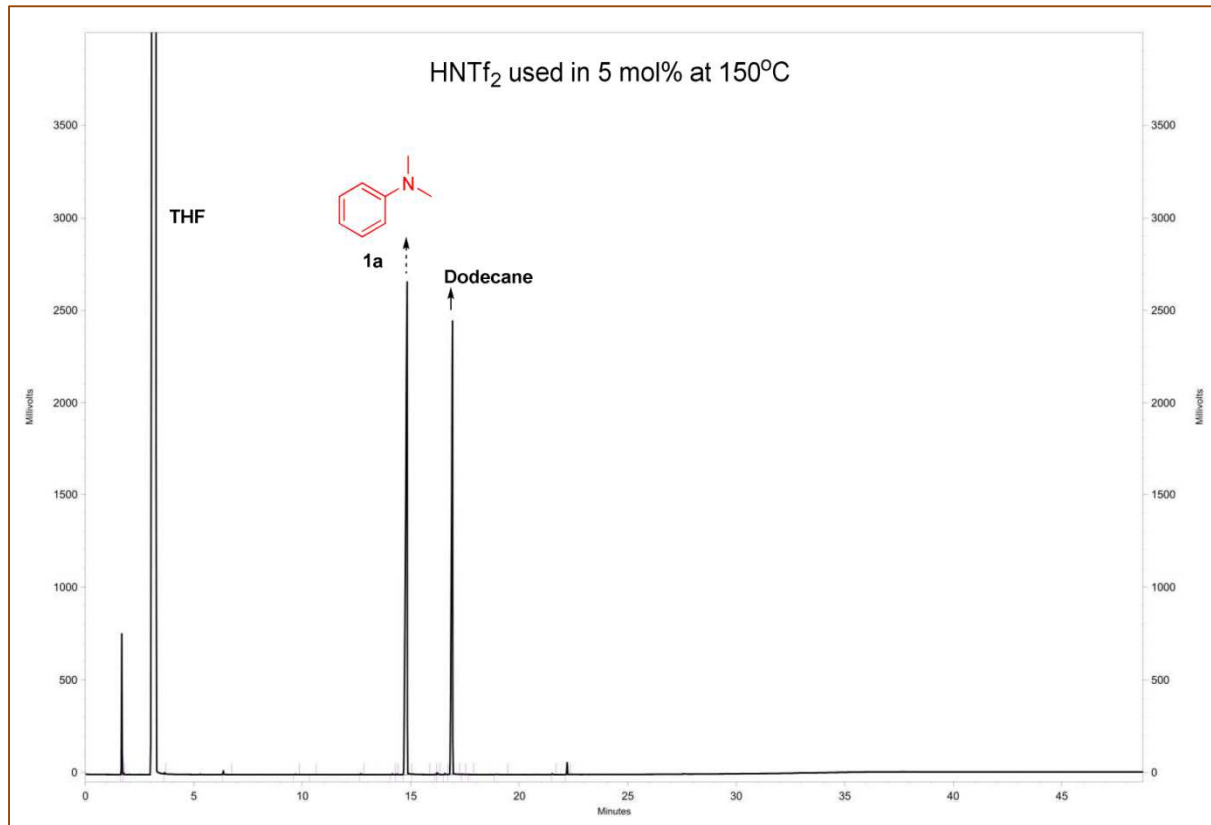


**Figure 5:** Gas chromatogram of reaction solution from the methylation of *N*-methylaniline **1** to *N,N*-dimethylaniline **1a** using 2.5 mol% of HNTf<sub>2</sub> and [Ru(Triphos)(TMM)].





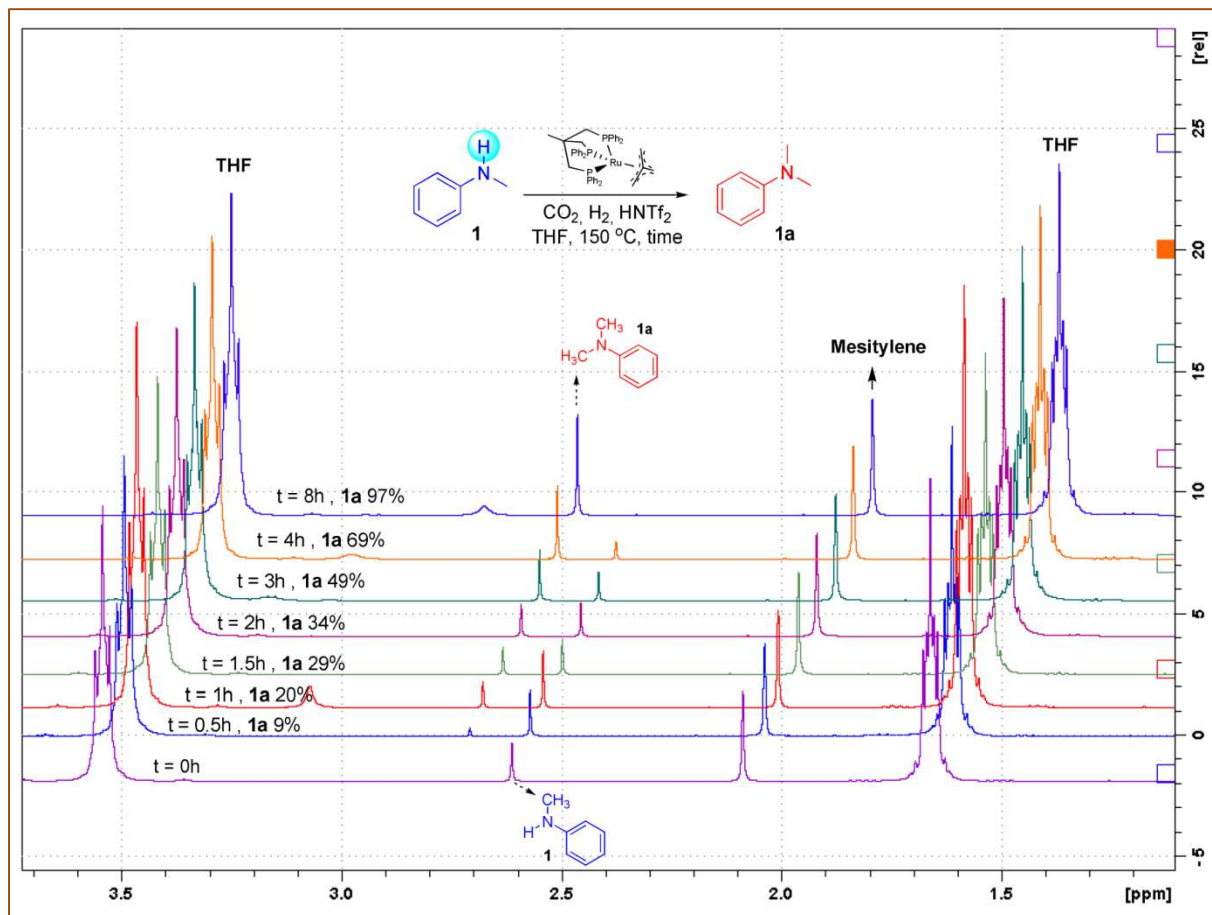
**Figure 6:** Gas chromatogram of reaction solution from the methylation of *N*-methylaniline **1** into *N,N*-dimethylaniline **1a** using 5 mol% of HNTf<sub>2</sub> and [Ru(Triphos)(TMM)].



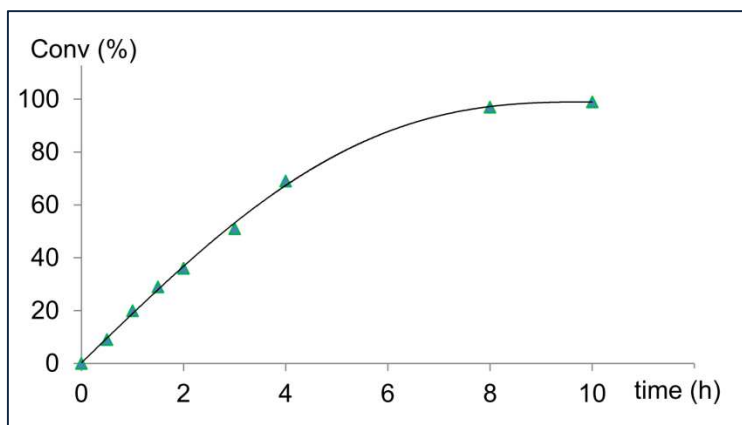
**Figure 7:** Gas chromatogram of reaction solution from the methylation of *N*-methylaniline **1** into *N,N*-dimethylaniline **1a** using 5 mol% of HNTf<sub>2</sub> and [Ru(Triphos)(TMM)] at 150 °C.

Variation of *N,N*-dimethylaniline **1a** yields versus reaction time

**Figure 8** represents the variation of *N,N*-dimethylaniline **1a** yields versus reaction time via  $^1\text{H}$  NMR spectra of the reaction crude mixture at different time intervals. The conversion of *N*-methylaniline **1** to *N,N*-dimethylaniline **1a** was completed after a period of 10 h.



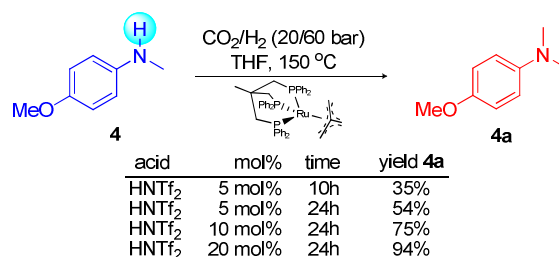
**Figure 8:**  $^1\text{H}$ -NMR spectrum (400 MHz,  $\text{CDCl}_3$ ) of reaction solution from the methylation of *N*-methylaniline **1** to *N,N*-dimethylaniline **1a** after different time intervals.



**Figure 9:** The conversion of *N*-methylaniline **1** versus reaction time.

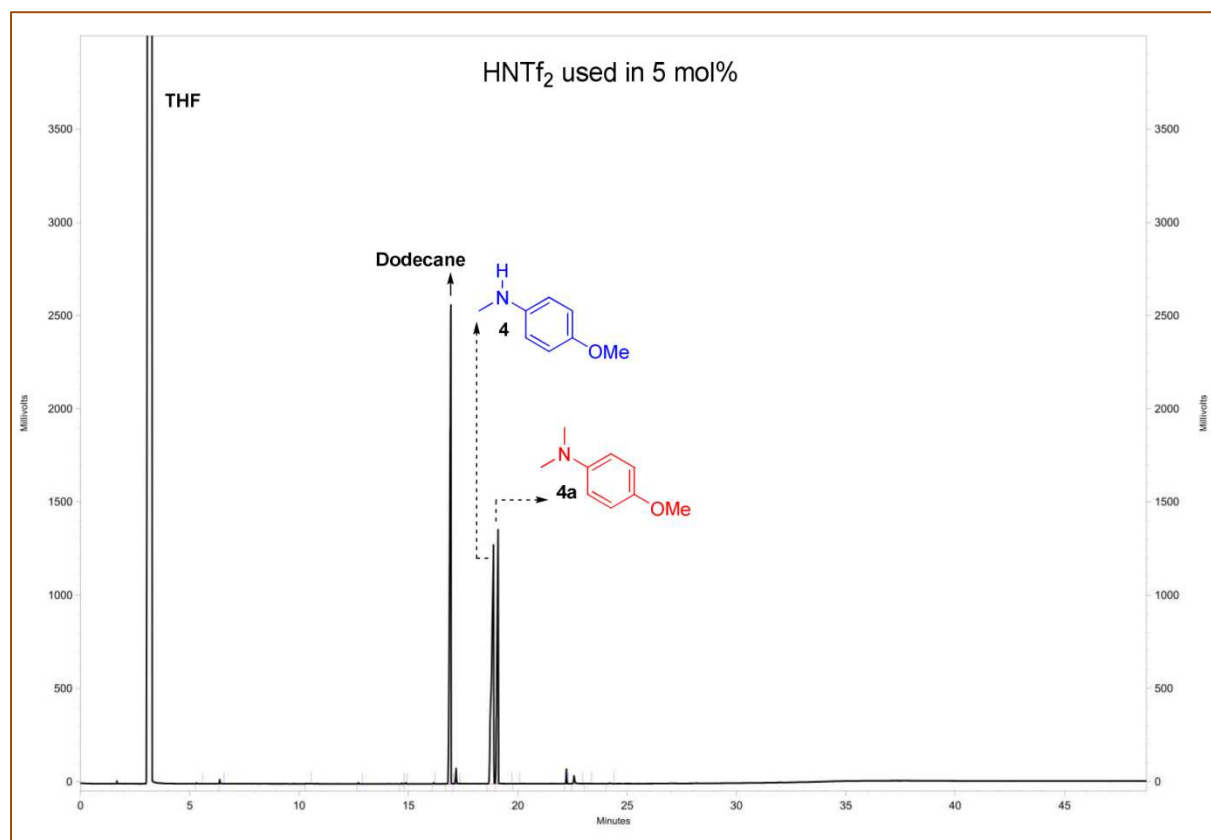
## 2) Optimization reactions of the direct methylation of 4-methoxy-*N*-methylaniline **4**.

Experiments have been performed to study the effect of acid on the conversion of 4-methoxy-*N*-methylaniline **4** to 4-methoxy-*N,N*-dimethylaniline **4a** by introducing variable loadings of HNTf<sub>2</sub>. The acid loading was found to promote the transformation of 4-methoxy-*N*-methylaniline **4**. Upon adding 20 mol% of HNTf<sub>2</sub>, the 4-methoxy-*N,N*-dimethylaniline product **4a** was successfully afforded in 94% yield. These variations of the yield are represented in **Scheme-1** and by the chromatograms of the corresponding reactions mixture shown in **Figure 10**, **Figure 11**, and **Figure 12**.

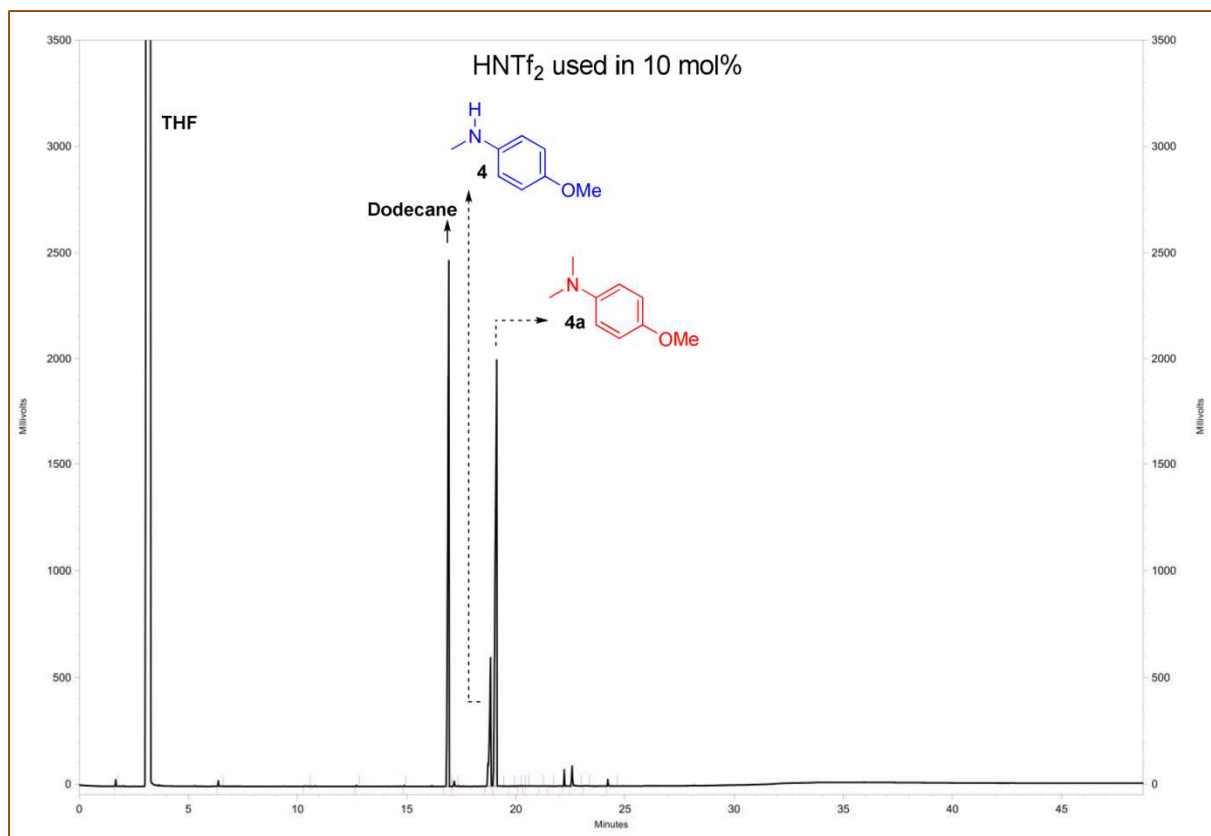


**Scheme 1:** The effect of HNTf<sub>2</sub> acid loadings on the ruthenium-catalysed methylation of 4-methoxy-*N*-methylaniline **4** with carbon dioxide and molecular hydrogen.

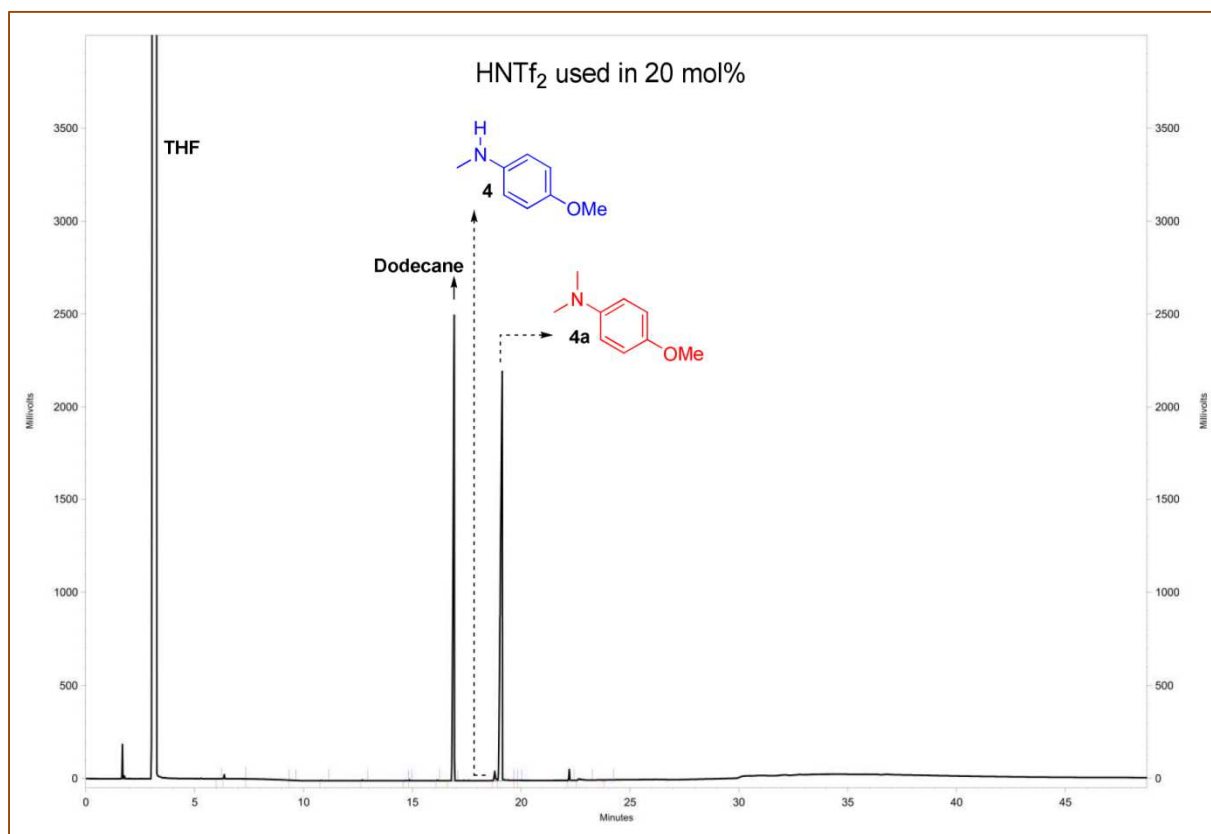
## Gas chromatogram spectra of the direct methylation of 4-methoxy-*N*-methylaniline **4**



**Figure 10:** Gas chromatogram of reaction solution from the methylation of 4-methoxy-*N*-methylaniline **4** to 4-methoxy-*N,N*-dimethylaniline **4a** using 5 mol% of HNTf<sub>2</sub> and [Ru(Triphos)(TMM)].



**Figure 11:** Gas chromatogram of reaction solution from the methylation of 4-methoxy-*N*-methylaniline **4** to 4-methoxy-*N,N*-dimethylaniline **4a** using 10 mol% of HNTf<sub>2</sub> and [Ru(Triphos)(TMM)].



**Figure 12:** Gas chromatogram of reaction solution from the methylation of 4-methoxy-*N*-methylaniline **4** to 4-methoxy-*N,N*-dimethylaniline **4a** using 20 mol% of HNTf<sub>2</sub> and [Ru(Triphos)(TMM)].