Supplementary Material (ESI) for Organic & Biomolecular Chemistry

# Reusable polystyrene-supported Pd catalyst for Mizoroki-Heck reactions with extremely low amounts of supported Pd

*Carine Diebold, Stéphane Schweizer, Jean-Michel Becht* and Claude Le Drian**

**Université de Haute Alsace**

**Institut de Science des Matériaux de Mulhouse, LRC-CNRS 7228**

**15 rue Jean Starcky, 68057 Mulhouse cedex, France**

***email: jean-michel.becht@uha.fr***

## ***ELECTRONIC SUPPLEMENTARY INFORMATION***

## *Table of contents*

**General Remarks.** The reagents were obtained from commercial sources and were used without further purifications. Catalysts **1a** and **1b** were prepared according to previous reports from our group.[1] The syntheses of compounds **2a-i** were performed in dry glassware under an atmosphere of argon. The reaction mixtures were filtered on a polytetrafluoroethylene Whatman membrane (0.2 µm). $^1$H NMR spectra were recorded using a 400 MHz instrument in $CDCl_3$. Chemical shifts are reported in parts per million (δ) downfield from TMS. Spin multiplicities are indicated by the following symbols: s (singlet), d (doublet), t (triplet) and m (multiplet). The $^1$H NMR spectra of biaryls **2a-i** were in accordance with literature reports (see below).

**(*E*)-Methyl-3-Phenylpropenoate (2a):** Elution with AcOEt / Cyclohexane 1 : 9 afforded 1.60 g (99% yield) of a white solid; mp 37-38 °C (lit. mp 38 °C).[2] $^1$H NMR (400 MHz, $CDCl_3$)[3] δ (ppm): 3.82 (s, 3H), 6.45 (d, $^3J$ = 16.0 Hz, 1H), 7.39 (m, 3H), 7.54 (m, 2H), 7.72 (d, $^3J$ = 16.0 Hz).

**(*E*)-Methyl-3-(4-Methylphenyl)propenoate (2b):** Elution with AcOEt / Cyclohexane 1 : 9 afforded 1.60 g (91% yield) of a white solid; mp 58-59 °C (lit. mp 57-58 °C).[4] $^1$H NMR (400 MHz, $CDCl_3$)[2] δ (ppm): 2.37 (s, 3H), 3.80 (s, 3H), 6.40 (d, $^3J$ = 16.0 Hz, 1H), 7.18 (d, $^3J$ = 8.0 Hz, 2H), 7.41 (d, $^3J$ = 8.0 Hz, 2H), 7.68 (d, $^3J$ = 16.0 Hz, 1H).

**(*E*)-Methyl-3-(3-Methylphenyl)propenoate (2c):** Elution with AcOEt / Cyclohexane 1 : 9 afforded 1.74 g (99% yield) of a colorless oil. $^1$H NMR (400 MHz, $CDCl_3$)[2] δ (ppm): 2.36 (s, 3H), 3.81 (s, 3H), 6.43 (d, $^3J$ = 16.0 Hz, 1H), 7.27 (m, 4H), 7.68 (d, $^3J$ = 16.0 Hz, 1H).

**(*E*)-Methyl-3-(2-Methylphenyl)propenoate (2d):** Elution with AcOEt / Cyclohexane 1 : 9 afforded 1.74 g (99% yield) of a yellow oil. $^1$H NMR (400 MHz, $CDCl_3$)[5] δ (ppm): 2.28 (s, 3H), 3.66 (s, 3H), 6.22 (d, $^3J$ = 15.8 Hz, 1H), 7.08 (m, 3H), 7.38 (d, $^3J$ = 7.8 Hz, 1H), 7.84 (d, $^3J$ = 15.8 Hz, 1H).

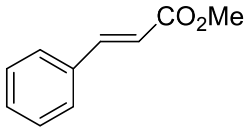
**(*E*)-Methyl-3-(4-Methoxyphenyl)propenoate (2e):** Elution with AcOEt / Cyclohexane 1 : 9 afforded 1.85 g (96% yield) of a yellow solid; mp 87-88 °C (lit. mp 89-90 °C).[6] $^1$H NMR (400 MHz, $CDCl_3$)[2] δ (ppm): 3.68 (s, 3H), 3.71 (s, 3H), 6.20 (d, $^3J$ = 16.1 Hz, 1H), 6.78 (d, $^3J$ = 8.8 Hz, 2H), 7.35 (d $^3J$ = 8.8 Hz, 2H), 7.54 (d, $^3J$ = 16.1 Hz, 1H).

**(*E*)-Methyl-3-(2-Bromophenyl)propenoate (2f):** Elution with AcOEt / Cyclohexane 1 : 9 afforded 2.38 g (99% yield) of a yellow oil. $^1$H NMR (400 MHz, $CDCl_3$)[2] δ (ppm): 3.71 (s, 3H), 6.26 (d, $^3J$ = 16.1 Hz, 1H), 7.13 (m, 2H), 7.46 (m, 2H), 7.93 (d, $^3J$ = 16.1 Hz, 1H).

**(*E*)-Methyl-3-(4-Acetylphenyl)propenoate (2g):** Elution with AcOEt / Cyclohexane 1 : 9 afforded 2.0 g (98% yield) of a yellow solid; mp 112-114 °C (lit. mp 113-115 °C).[7] $^1$H NMR (400 MHz, $CDCl_3$)[8] δ (ppm): 2.46 (s, 3H), 3.67 (s, 3H), 6.35 (d, $^3J$ = 16.1 Hz, 1H), 7.43 (d, $^3J$ = 8.3 Hz, 2H), 7.52 (d, $^3J$ = 16.1 Hz, 1H), 7.80 (d, $^3J$ = 8.3 Hz, 2H).

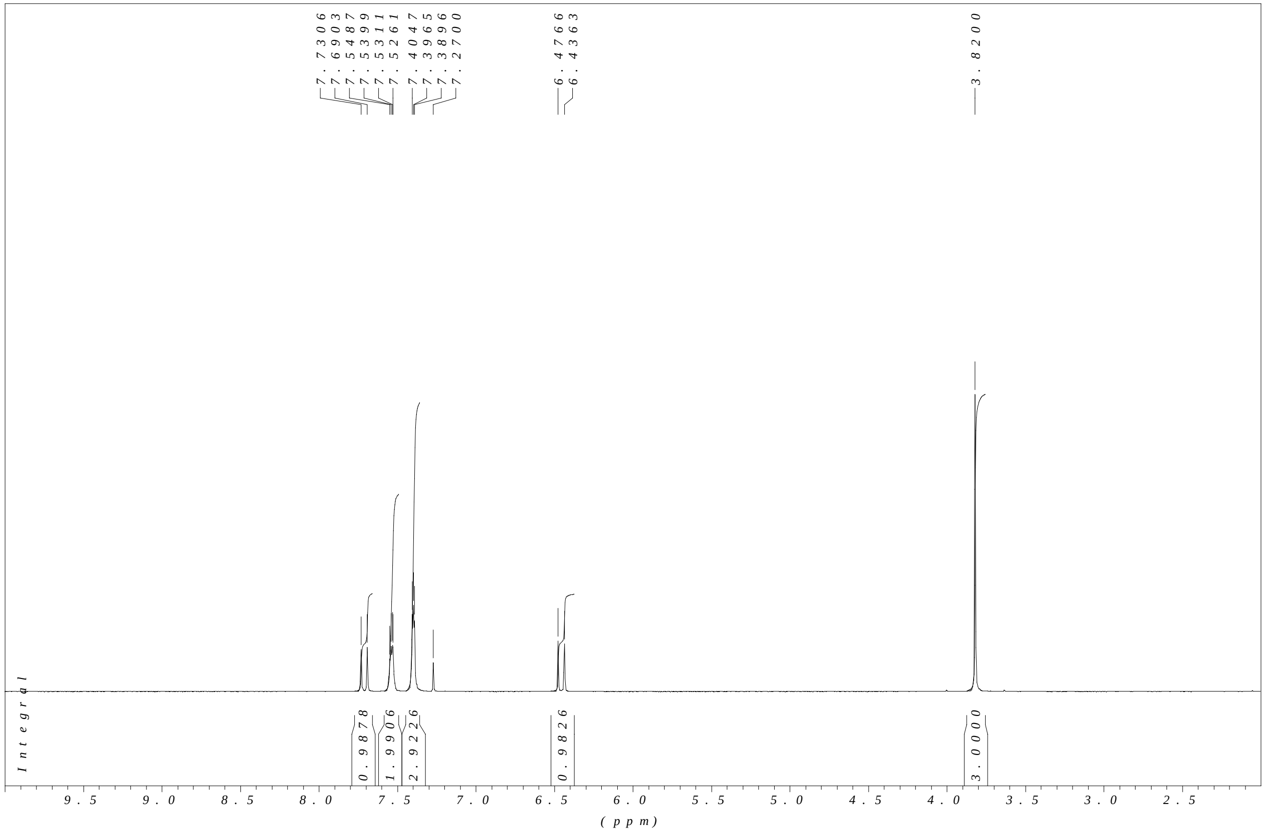
**(*E*)-Methyl-3-(3-Trifluoromethylphenyl)propenoate (2h):** Elution with AcOEt / Cyclohexane 1 : 9 afforded 2.28 g (99% yield) of a yellow solid; mp 112-114 °C (lit. mp 113-115 °C).[4] $^1$H NMR (400 MHz, $CDCl_3$)[9] δ (ppm): 3.82 (s, 3H), 6.50 (d, $^3J$ = 16.1 Hz, 1H), 7.51 (m, 1H), 7.62 (m, 1H), 7.70 (m, 2H), 7.73 (d, $^3J$ = 16.1 Hz, 1H).

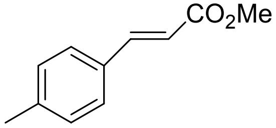
**(*E*)-Methyl-3-[2-Ethoxycarbonyl)phenyl]propenoate (2i):** Elution with AcOEt / Cyclohexane 1 : 9 afforded 2.32 g (99% yield) of a yellow solid; mp 112-114 °C (lit. mp 113-115 °C). $^1$H NMR (400 MHz, $CDCl_3$) δ (ppm): 1.36 (t, $^3J$ = 7.3 Hz, 3H), 3.76 (s, 3H), 4.34 (q, $^3J$ = 7.3 Hz, 2H), 6.25 (d, $^3J$ = 15.9 Hz, 1H), 7.39 (m, 3H), 7.93 (m, 1H), 8.42 (d, $^3J$ = 15.9 Hz, 1H).



**2a**

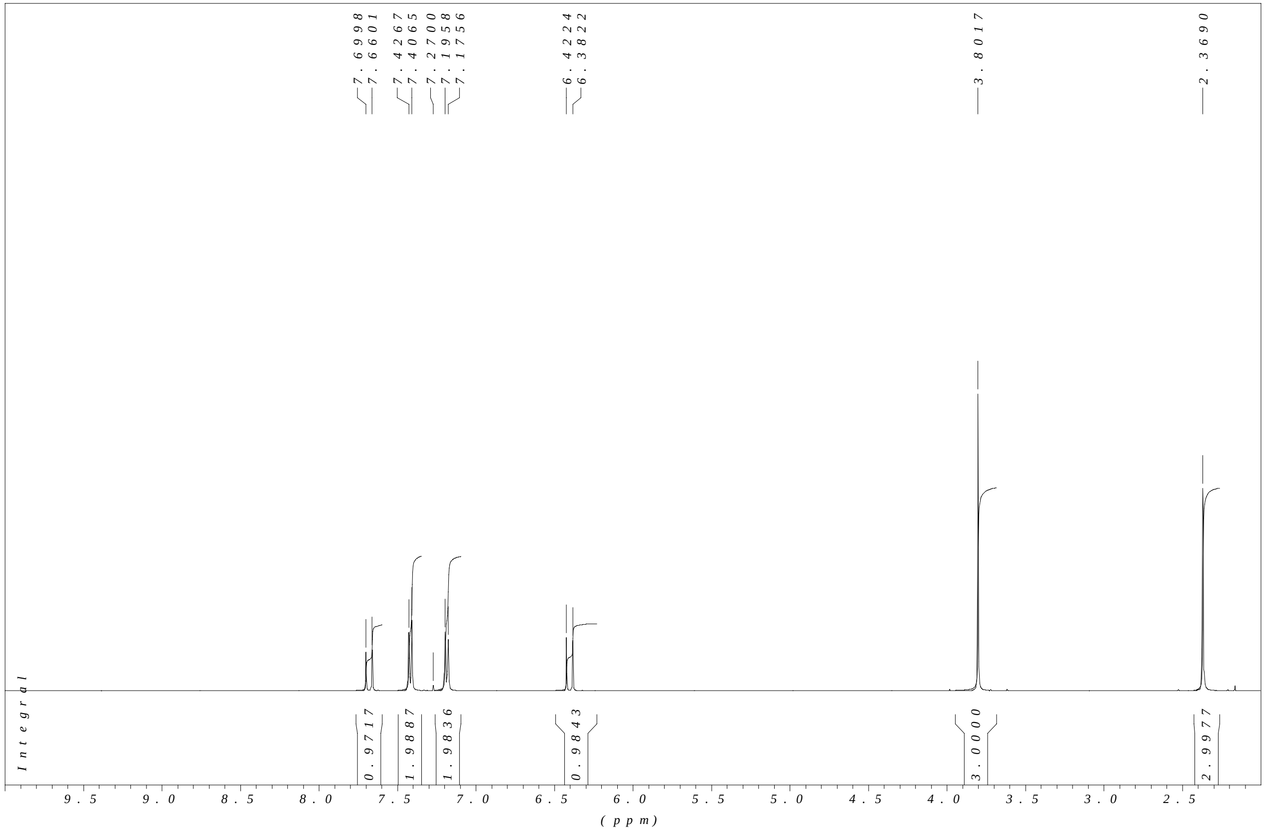
**$^1$H NMR, 400 MHz, $CDCl_3$**

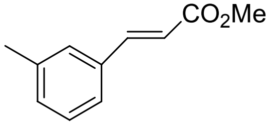




**2b**

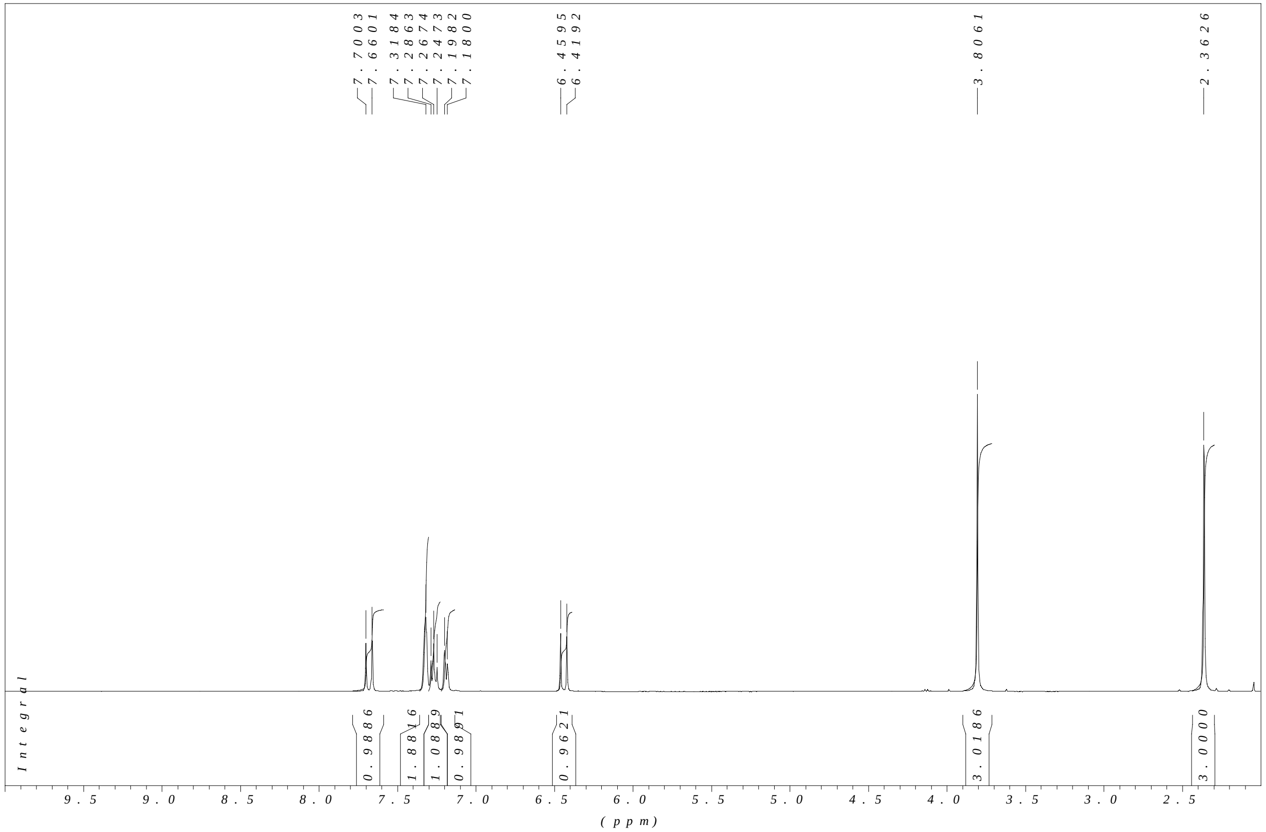
**$^1$H NMR, 400 MHz, CDCl$_3$**

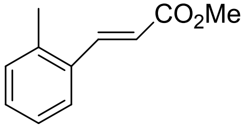




**2c**

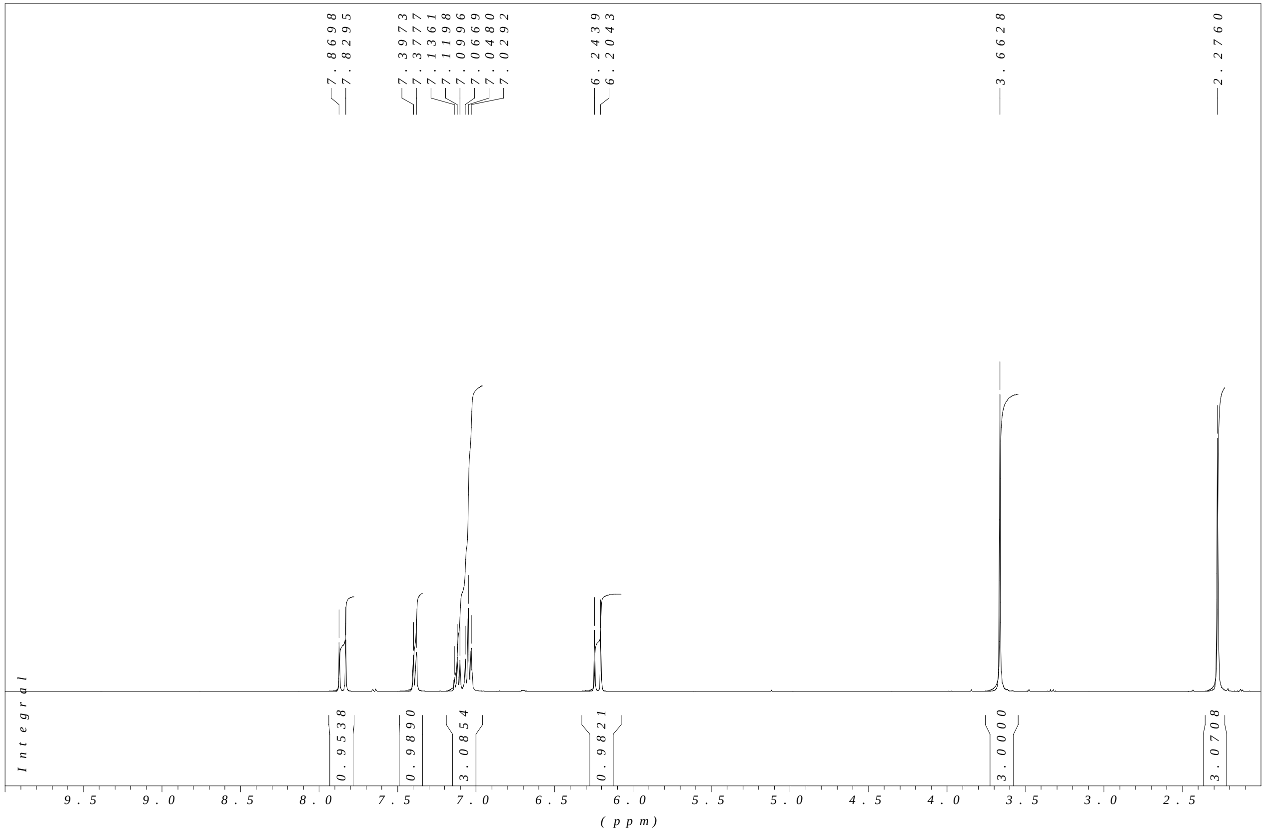
**$^1$H NMR, 400 MHz, $CDCl_3$**

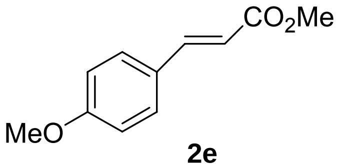




**2d**

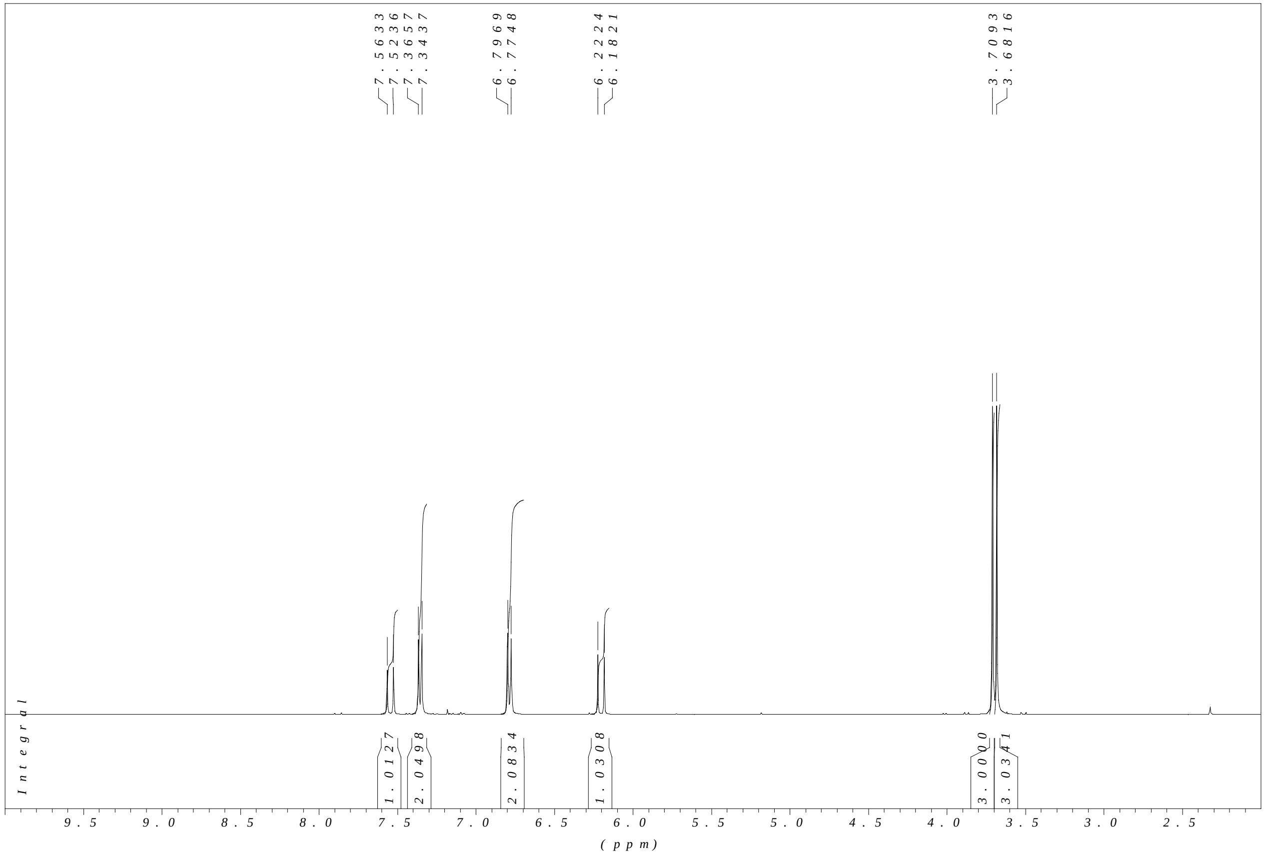
**$^1$H NMR, 400 MHz, $CDCl_3$**

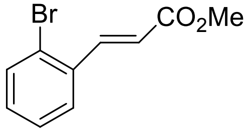




**2e**

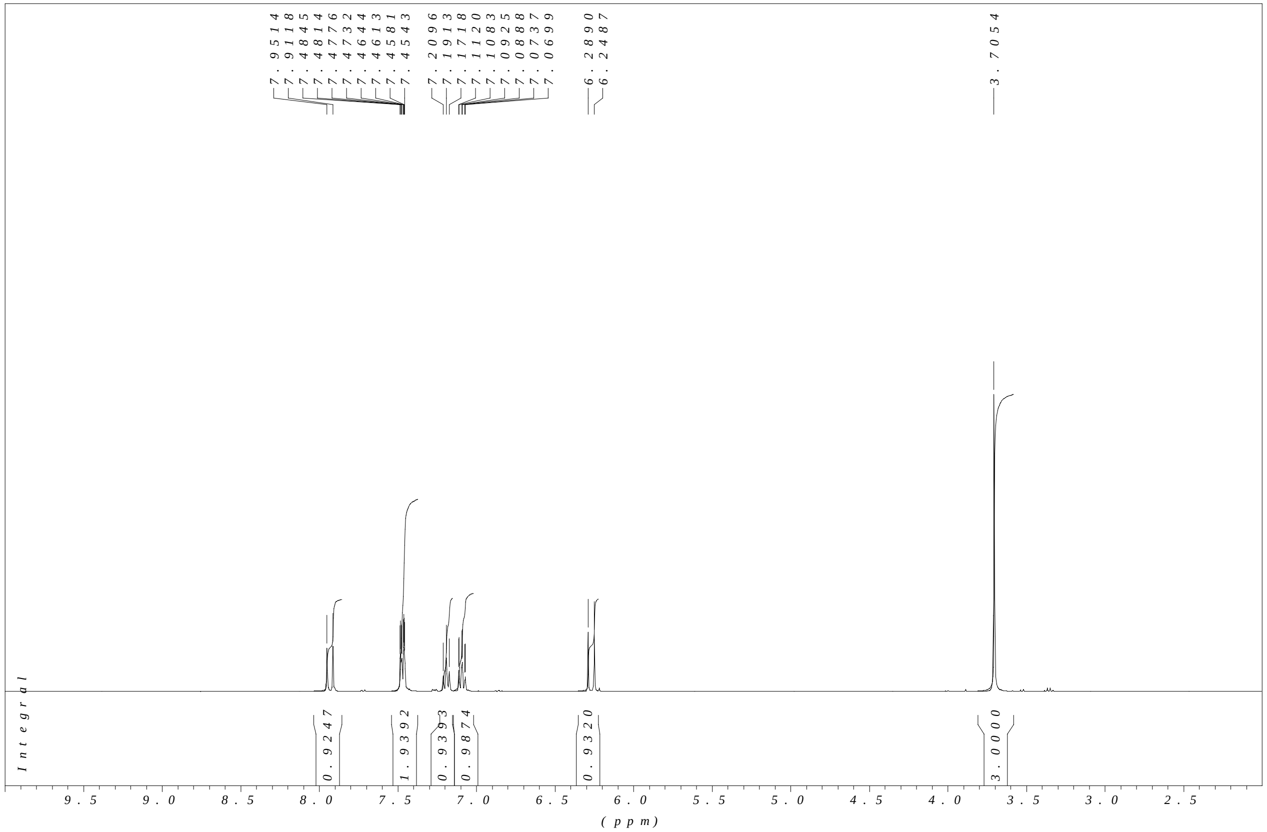
**$^1$H NMR, 400 MHz, CDCl$_3$**

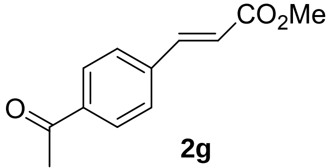




**2f**

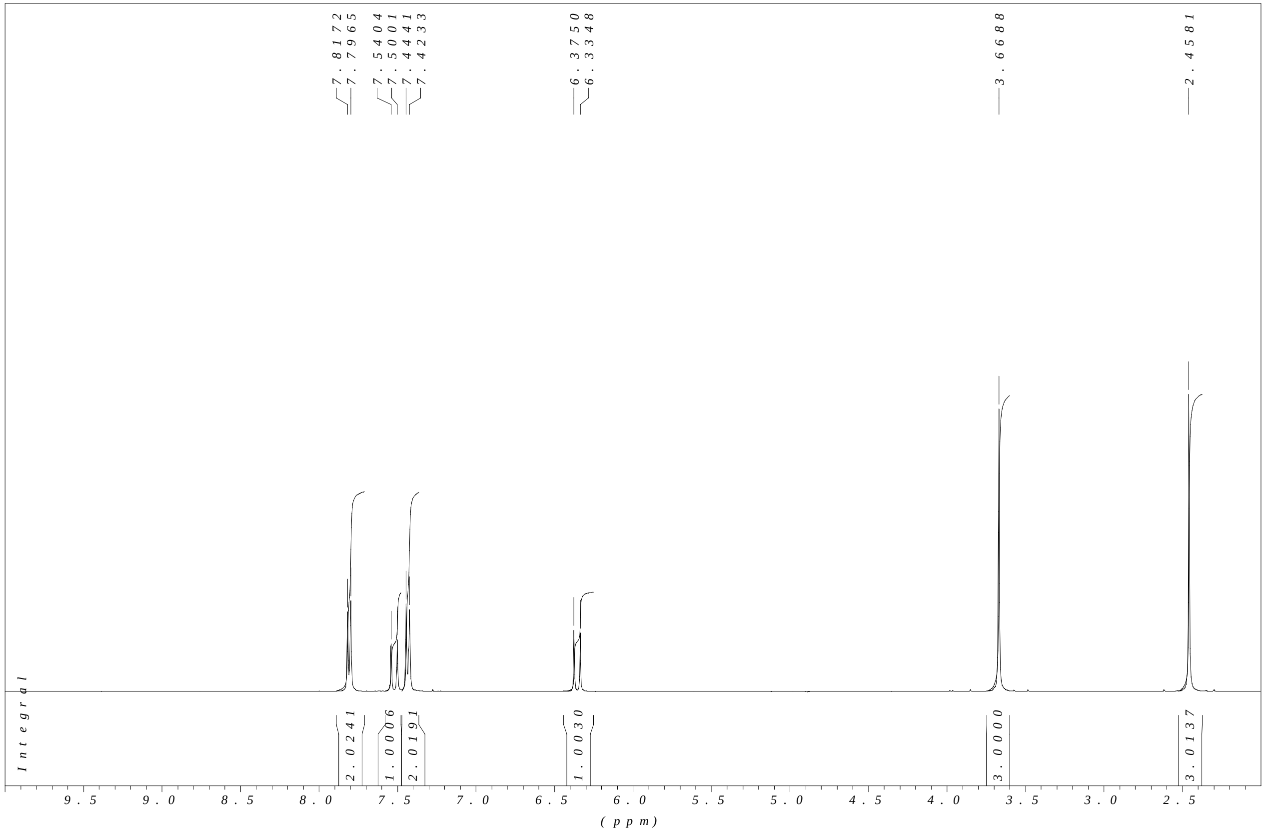
**$^1$H NMR, 400 MHz, $CDCl_3$**

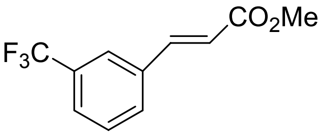




**2g**

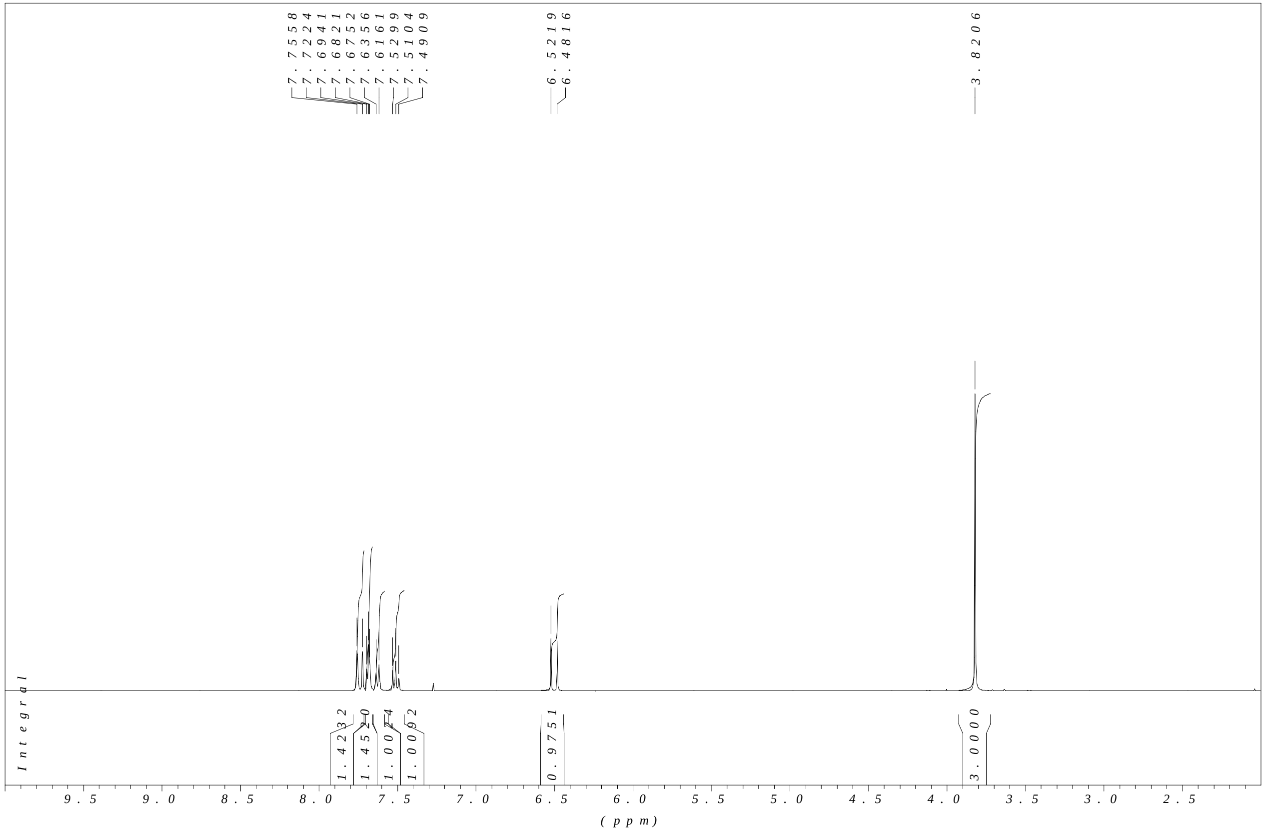
**$^1$H NMR, 400 MHz, $CDCl_3$**

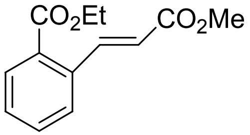




**2h**

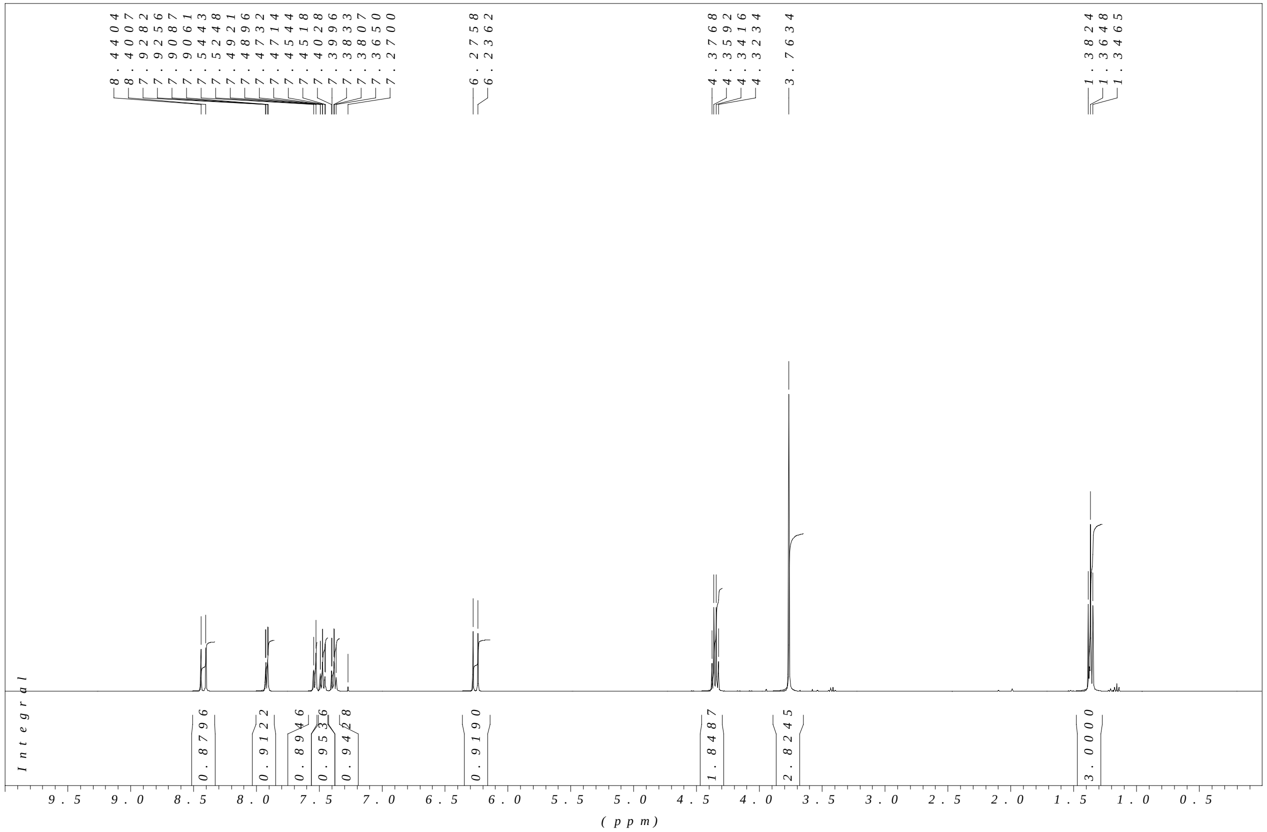
**$^1$H NMR, 400 MHz, $CDCl_3$**





**2i**

**$^1$H NMR, 400 MHz, CDCl$_3$**



## References:

[1] For the preparation of catalyst **1a** see: S. Schweizer, J.-M. Becht, C. Le Drian, *Org. Lett.* 2007, **9**, 3777; For the preparation of catalyst **1b** see: S. Schweizer, J.-M. Becht, C. Le Drian, *Adv. Synth. Catal.* 2007, **349**, 1150.

[2] K. Hamza, R. Abu-Reziq, D. Avnir, J. Blum, *Org. Lett.* **2004**, *6*, 925.

[3] M. Dai, C. Wang, J. Chen, Z. Yang, *Org. Lett.* **2004**, *6*, 221.

[4] G. R. Ramage, *J. Chem. Soc.* **1938**, 397.

[5] J. Ruan, X.Li, O. Saidi, J. Xiao, *J. Am. Chem. Soc.* **2008**, *130*, 2424.

[6] R. F. Heck, *J. Am. Chem. Soc.* **1968**, *311*, 29.

[7] G. Charbonnel-Jobic, J.-P. Guémas, B. Adelaere, J.-L. Parrain, J.-P. Quintard, *Bull. Soc. Chim. Fr.* **1995**, *132*, 624.

[8] B. Karimi, D. Enders, *Org. Lett.* **2006**, *8*, 1237.

[9] R. Bernini, S. Cacchi, G. Fabrizi, G. Forte, S. Niembo, F. Petrucci, R. Pleixats, A. Prastaro, R. M. Sebastiàn, R. Soles, M. Tristany, A. Vallribera, *Org. Lett.* **2008**, *10*, 561.