# SUPPORTING INFORMATION

# Supported $C_{60}$-IL-PdNP as extremely active nanocatalysts for C–C cross coupling reactions

*Francesco Giacalone,[a]* Vincenzo Campisciano,[a] Carla Calabrese,[a,b] Valeria La Parola,[c] Leonarda F. Liotta,[c] Carmela Aprile,[b] Michelangelo Gruttadauria[a]**

[a] Dipartimento Scienze e Tecnologie Biologiche, Chimiche e Farmaceutiche (STEBICEF), Università degli Studi di Palermo, Viale delle Scienze, Ed. 17, 90128 Palermo (Italy).

Email: francesco.giacalone@unipa.it, Tel: +39 09123897530.

michelangelo.gruttadauria@unipa.it. Tel: +39 09123897534.

[b] Laboratory of Applied Material Chemistry (CMA), University of Namur, 61 rue de Bruxelles, 5000 Namur (Belgium).

[c] Istituto per lo Studio dei Materiali Nanostrutturati ISMN-CNR, Via Ugo La Malfa 153, 90146-Palermo (Italy).

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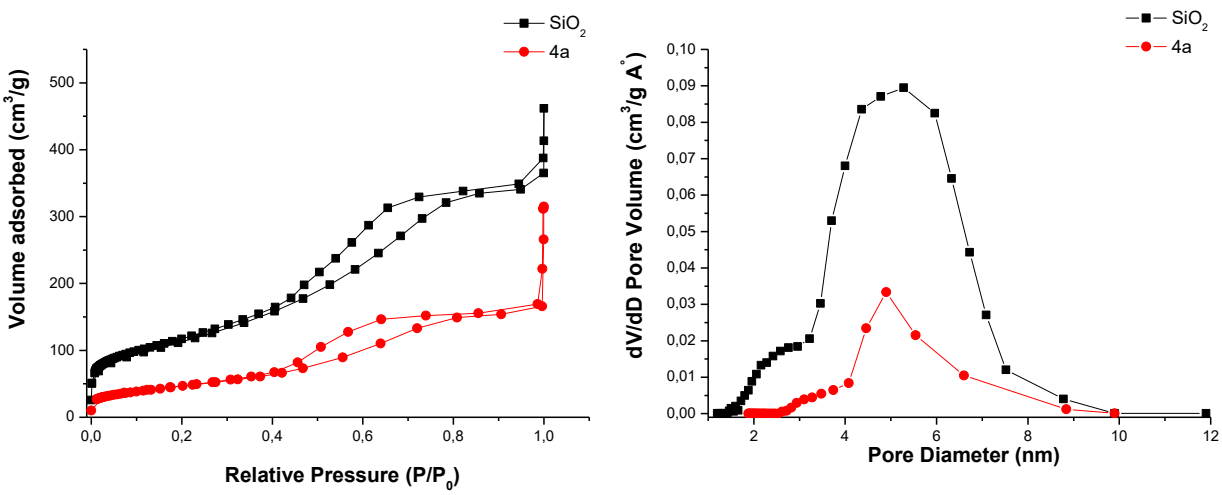



**Figure S1.** $N_2$-adsorption/desorption isotherms and pore size distribution of amorphous silica and **4a**.

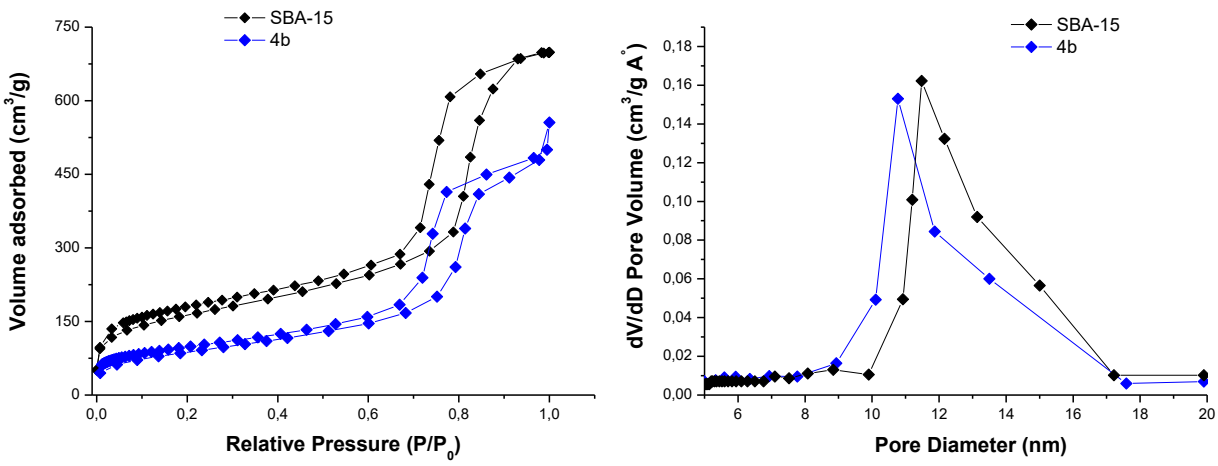



**Figure S2.** $N_2$-adsorption/desorption isotherms and pore size distribution of SBA-15 and **4b**.

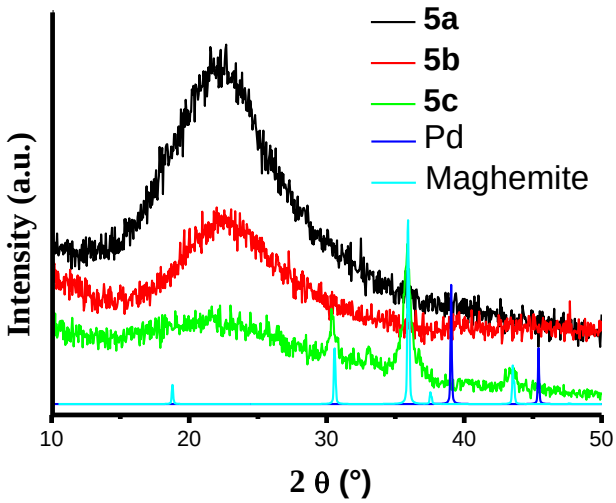



**Figure S3.** Experimental X-ray diffraction pattern of materials **5a-c** and simulated diffraction pattern of palladium and maghemite.

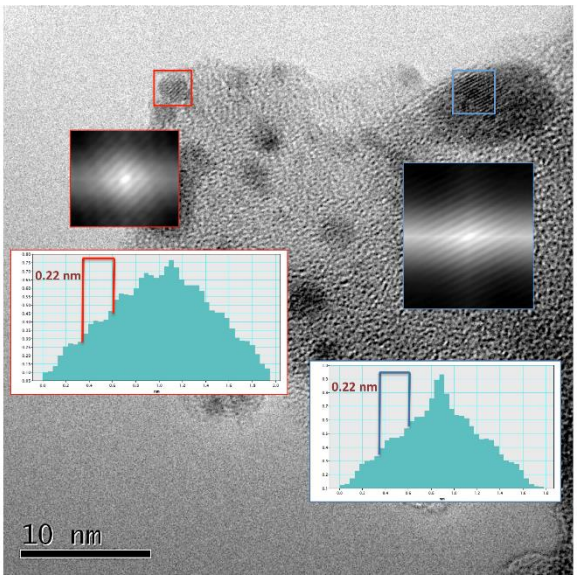



**Figure S4.** HR-TEM of **5a**. Fast Fourier transform (FFT) patterns and autocorrelation profiles are reported in the red and blue squares.

**Table S1.** XPS Pd $3d_{5/2}$ binding energies (eV), Pd/Si, Pd/C, N/Si and N/C surface atomic ratios. The relative percentages are given in parentheses.

| **Material** | **Pd $3d_{5/2}$** | **Pd/Si** | **Pd/C** | **N/Si** | **N/C** |
|---|---|---|---|---|---|
| **5a** | 334.9 (42)<br>336.9 (58) | 0.025 | 0.010 | 0.11 | 0.04 |
| **5b** | 334.9 (46)<br>337 (54) | 0.024 | 0.008 | 0.08 | 0.03 |
| **5c** | 335.3 (37)<br>337.6(63) | 0.094 | 0.005 | 0.52 | 0.03 |

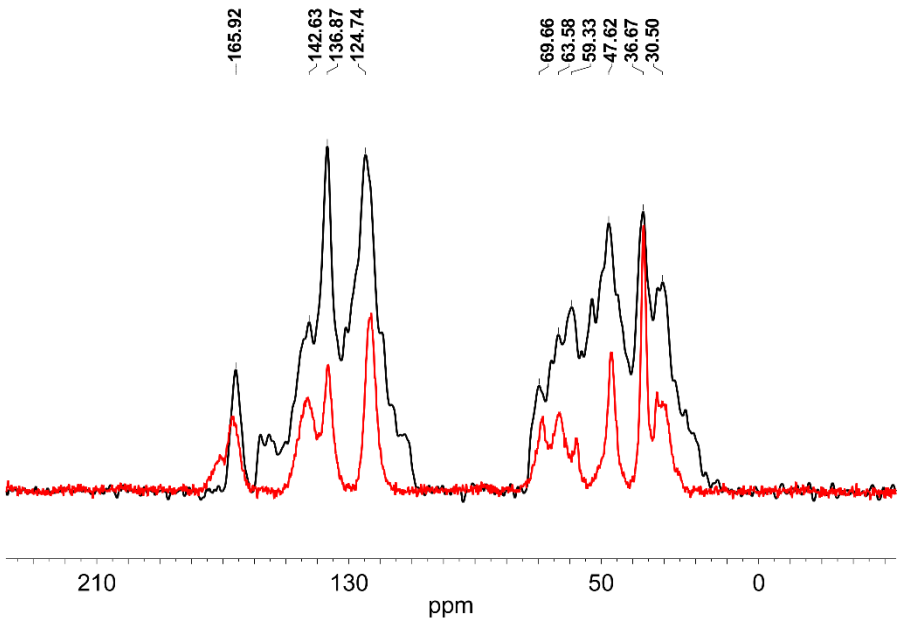
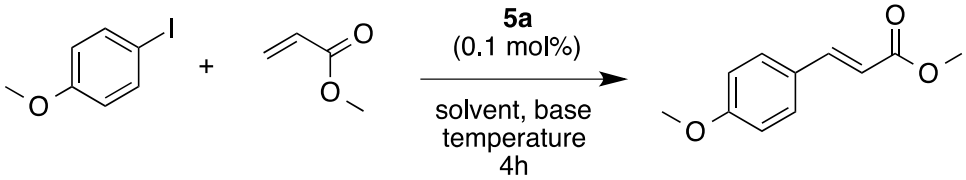



**Figure S5.** Solid-state $^{13}C$ NMR of materials **4a** (red) and **5a** (black).

**Table S2.** Screening of reaction conditions and dependence of reaction yield in function of the temperature in the reaction between 4-iodoanisole and methylacrylate.




| Entry | Solvent | Base | Temperature / °C | Yield[b] % |
|---|---|---|---|---|
| 1 | Toluene | $NEt_3$ | 100 | 22 |
| 2 | Acetonitrile | $NEt_3$ | 100 | 82 |
| 3 | $H_2O$/EtOH (1:3) | $K_2CO_3$ | 100 | 31 |
| 4 | DMF | $NEt_3$ | 120 | >99 |
| 5 | DMF | $NEt_3$ | 90 | 85 |
| 6 | DMF | $NEt_3$ | 60 | 0 |

[a] Reaction conditions: methyl acrylate (0.75 mmol), 4-iodoanisole (0.5 mmol), base (1 mmol), solvent (1 mL), catalyst (0.1 mol%, 2.5 mg). [b] After purification.

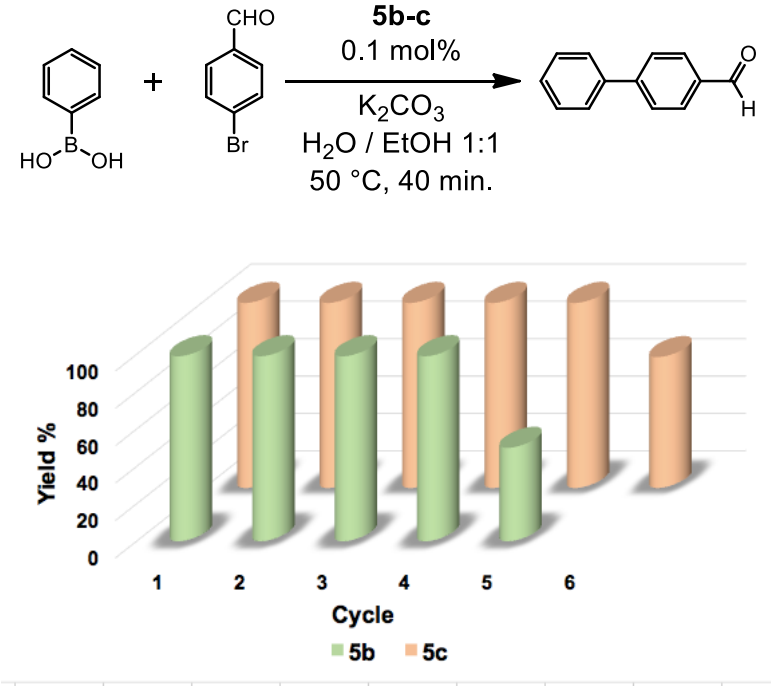



**Figure S6.** Recycling tests of catalysts **5b** and **5c** in the Suzuki reaction.

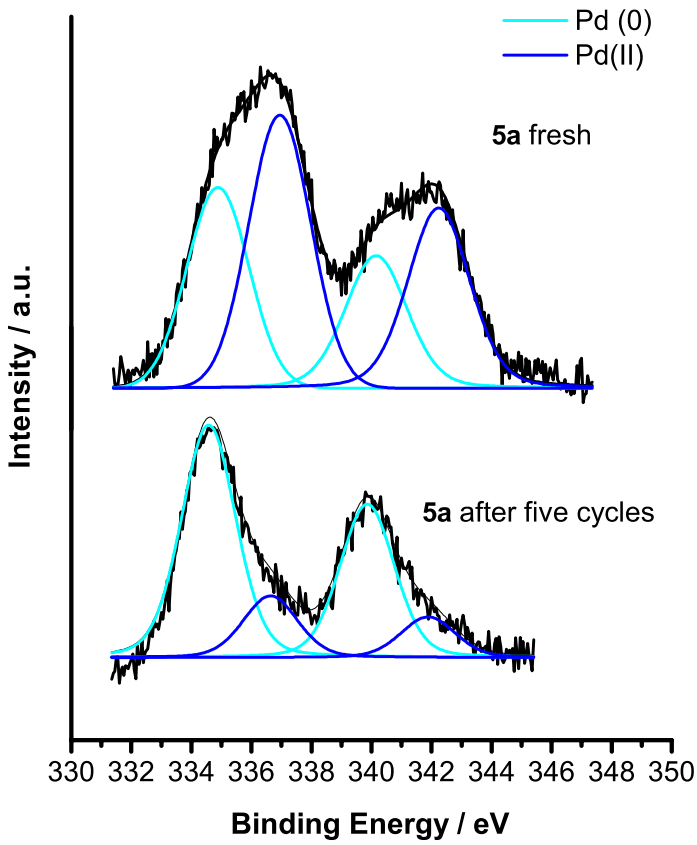
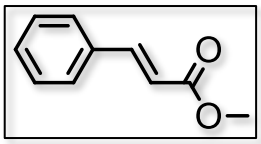
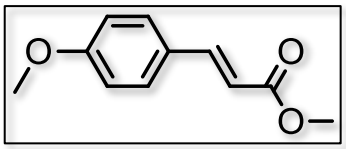



**Figure S7.** High-resolution XPS of Pd3d region of fresh **5a** (up) and reused **5a** for five times (bottom).

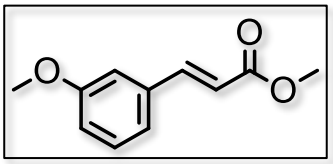
## List of $^1$H NMR spectral data of pure known compounds:



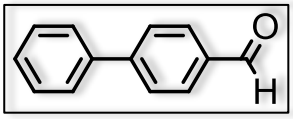
**(E)-Methyl Cinnamate**; **$^1$H NMR** ($CDCl_3$, 300 MHz): δ 7.71 (d, 1H, *J* = 16.0 Hz), 7.55−7.52 (m, 2H), 7.40−7.38 (m, 3H), 6.45 (d, 1H, *J* = 16.0 Hz), 3.82 (s, 3H).



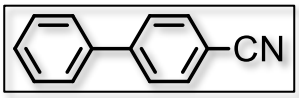
**(E)-Methyl-4-methoxycinnamate**; **$^1$H NMR** ($CDCl_3$, 300 MHz): δ 7.66 (d, 1H, *J* = 16.0 Hz), 7.49 (d, 2H, *J* = 8.7 Hz), 6.91 (d, 2H, *J* = 8.7 Hz), 6.32 (d, 1H, *J* = 16.0 Hz), 3.85 (s, 3H), 3.80 (s, 3H).



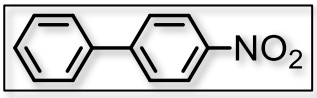
**(E)-Methyl 3-methoxycinnamate**; **$^1$H NMR** ($CDCl_3$, 300 MHz): δ 7.66 (d, 1H, *J* = 16.0 Hz), 7.32-7.27 (m, 1H), 7.12-7.10 (m, 1H), 7.03-7.04 (m, 1H), 6.95-6.92 (m, 1H), 6.43 (d, 1H, *J* = 16.0 Hz), 3.82 (s, 3H) 3.80 (s, 3H).



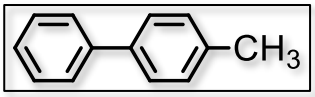
**4-Formylbiphenyl**; **$^1$H NMR** (300 MHz, $CDCl_3$, ppm): δ 10.08 (s, 1H), 7.97 (d, 2H , *J* = 7.7 Hz), 7.77 (d, 2H, *J* = 7.7 Hz), 7.66 (d, 2H, J = 7.5 Hz), 7.52–7.43 (m, 3H).



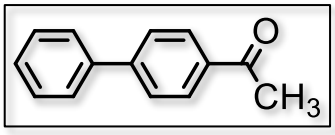
**4-Cyanobiphenyl**; **$^1$H NMR** (300 MHz, $CDCl_3$, ppm): δ 7.76–7.68 (m, 4H), 7.62–7.59 (m, 2H), 7.51–7.42 (m, 3H).



**4-Nitrobiphenyl**; **$^1$H NMR** (300 MHz, $CDCl_3$, ppm): δ 8.32 (d, 2H, *J* = 8.7 Hz), 7.76 (d, 2H, *J* = 8.7 Hz), 7.64 (d, 2H, *J* = 6.7 Hz), 7.54–7.46 (m, 3H).

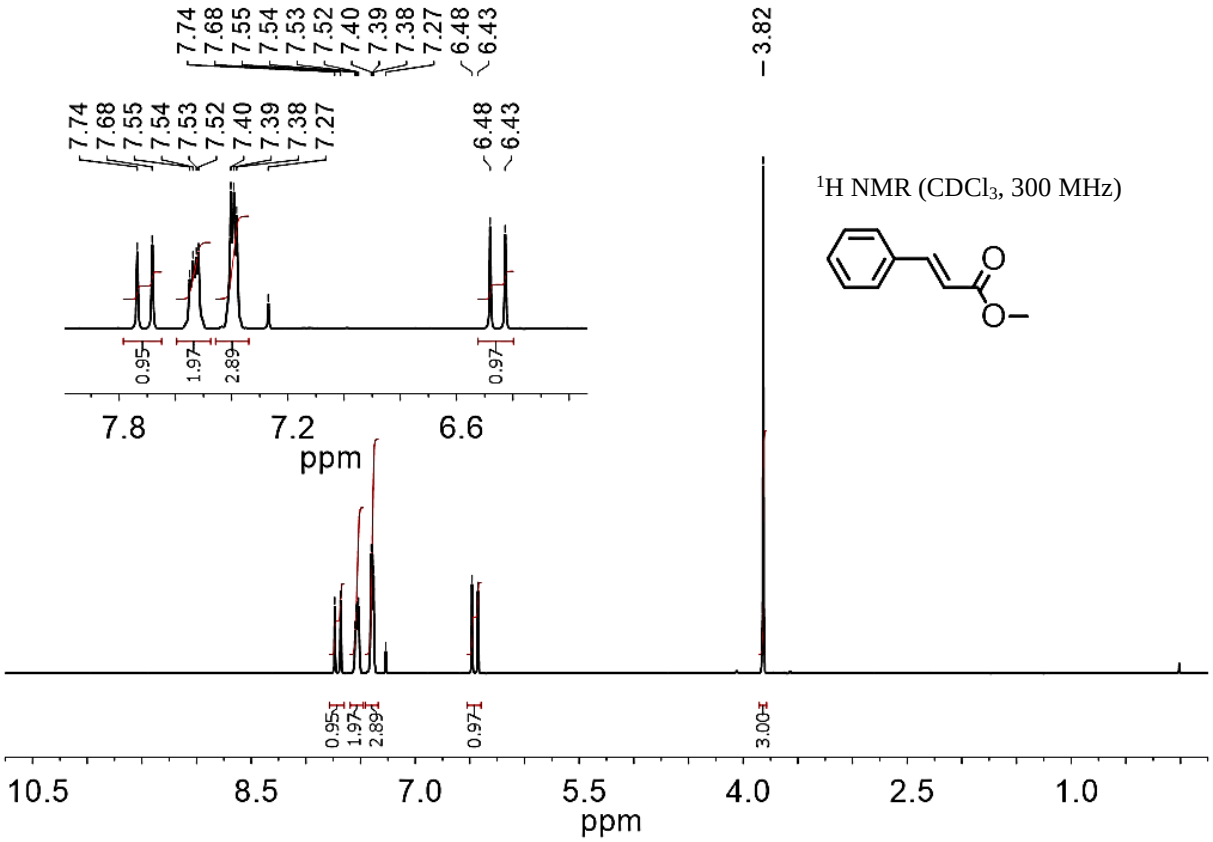


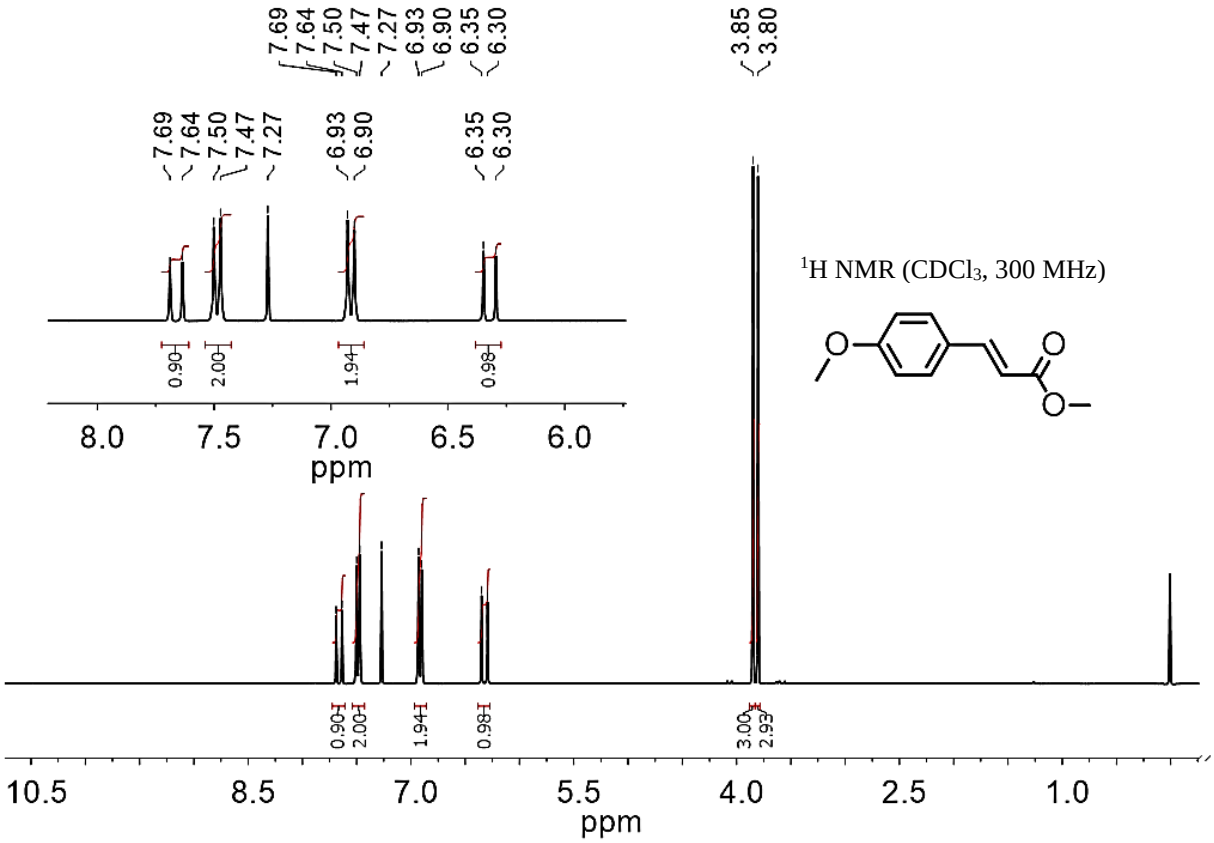

**4-Methylbiphenyl**; **$^1$H NMR** (300 MHz, $CDCl_3$, ppm): δ 7.60 (d, 2H, *J* = 7.3 Hz), 7.54−7.42 (m, 4H), 7.37−7.34 (m, 1H), 7.28 (d, 2H, *J* = 7.9 Hz), 2.42 (s, 3H).

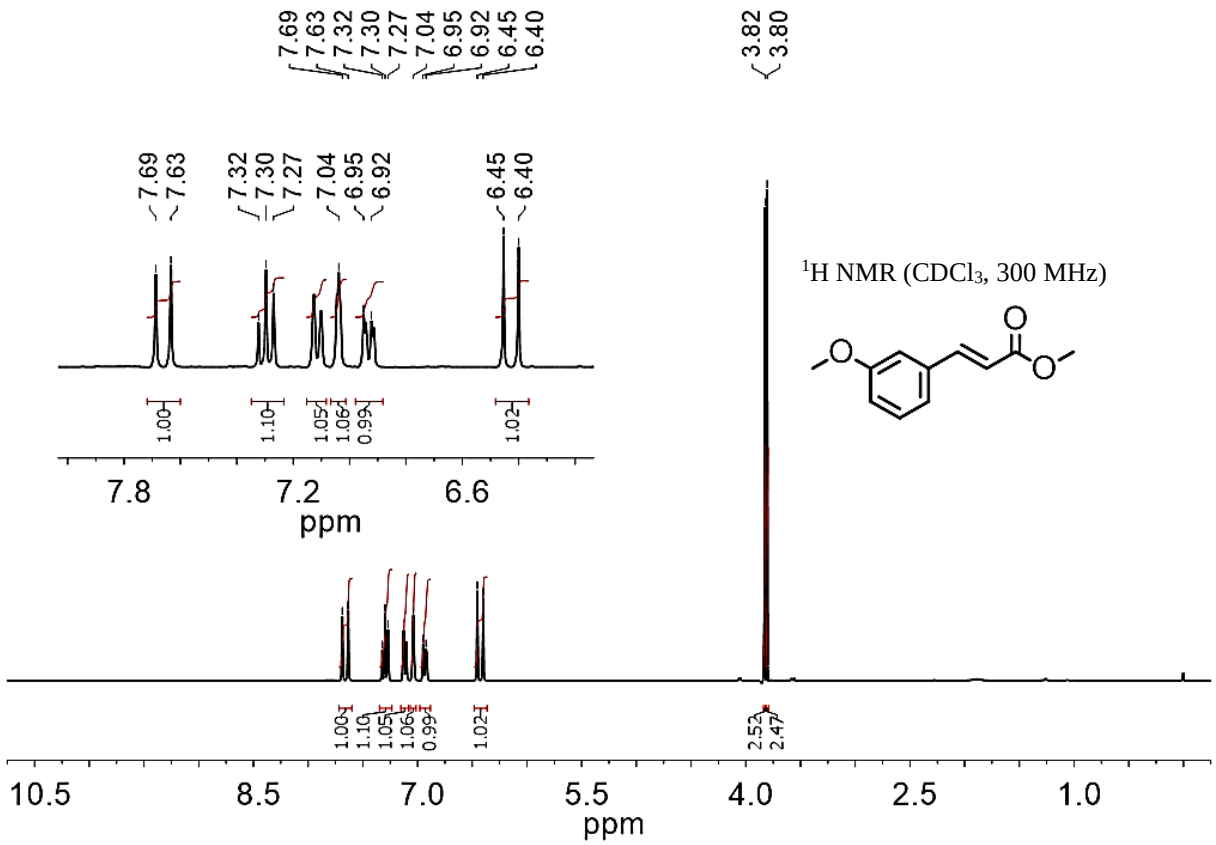



**4-Acetylbiphenyl**; **$^1$H NMR** (300 MHz, $CDCl_3$, ppm): δ 8.05 (d, 2H, *J* = 8.4 Hz), 7.71–7.63 (m, 4H), 7.51–7.40 (m, 3H), 2.65 (s, 3H).

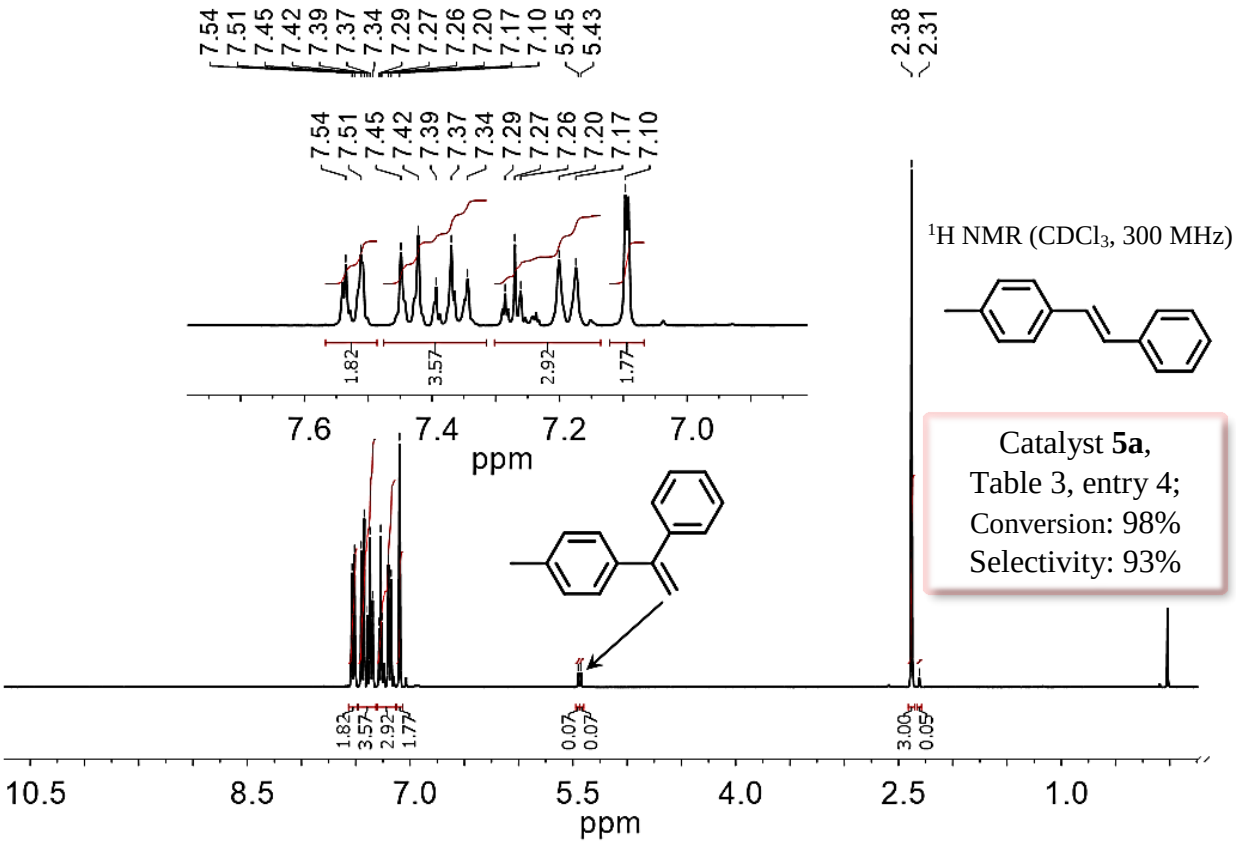
**$^1$H NMR spectra of pure known compounds and those of partially converted mixtures of Heck and Suzuki reactions:**



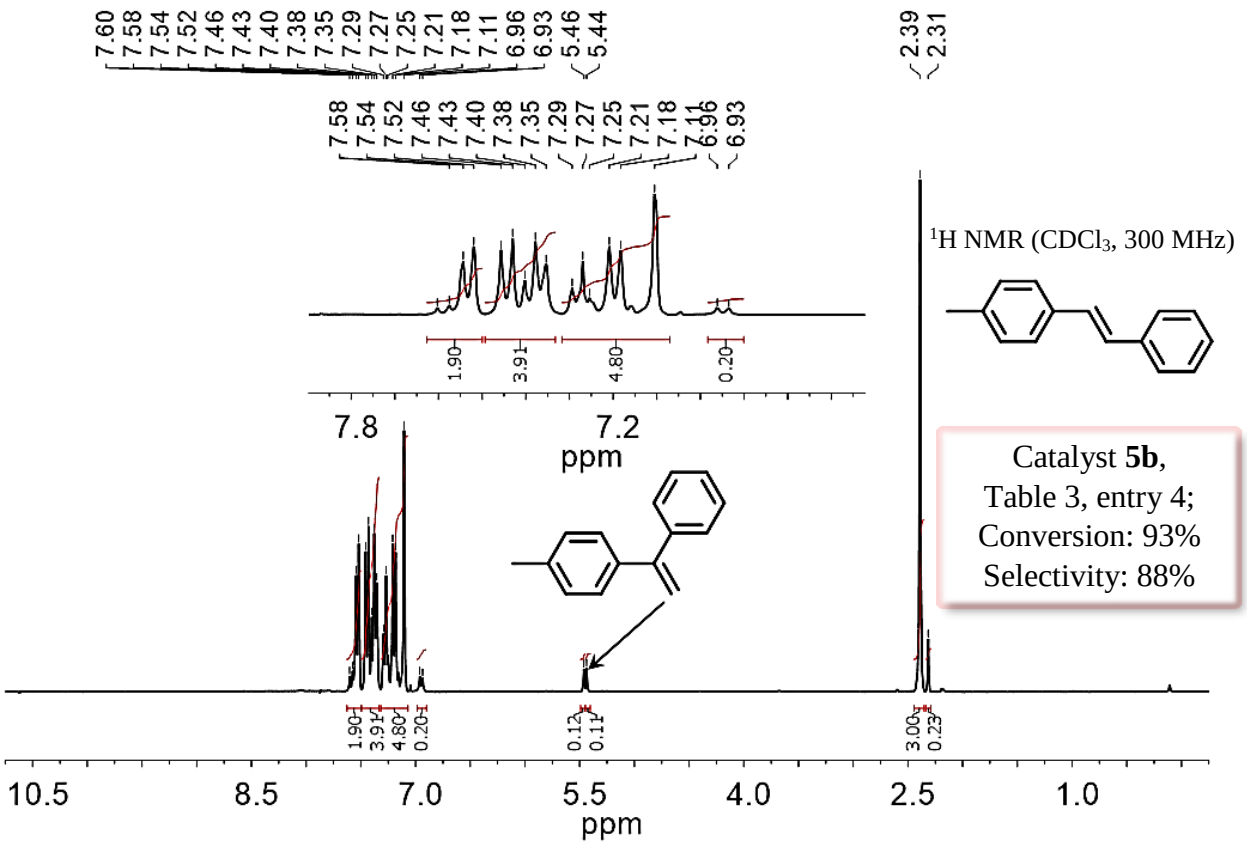


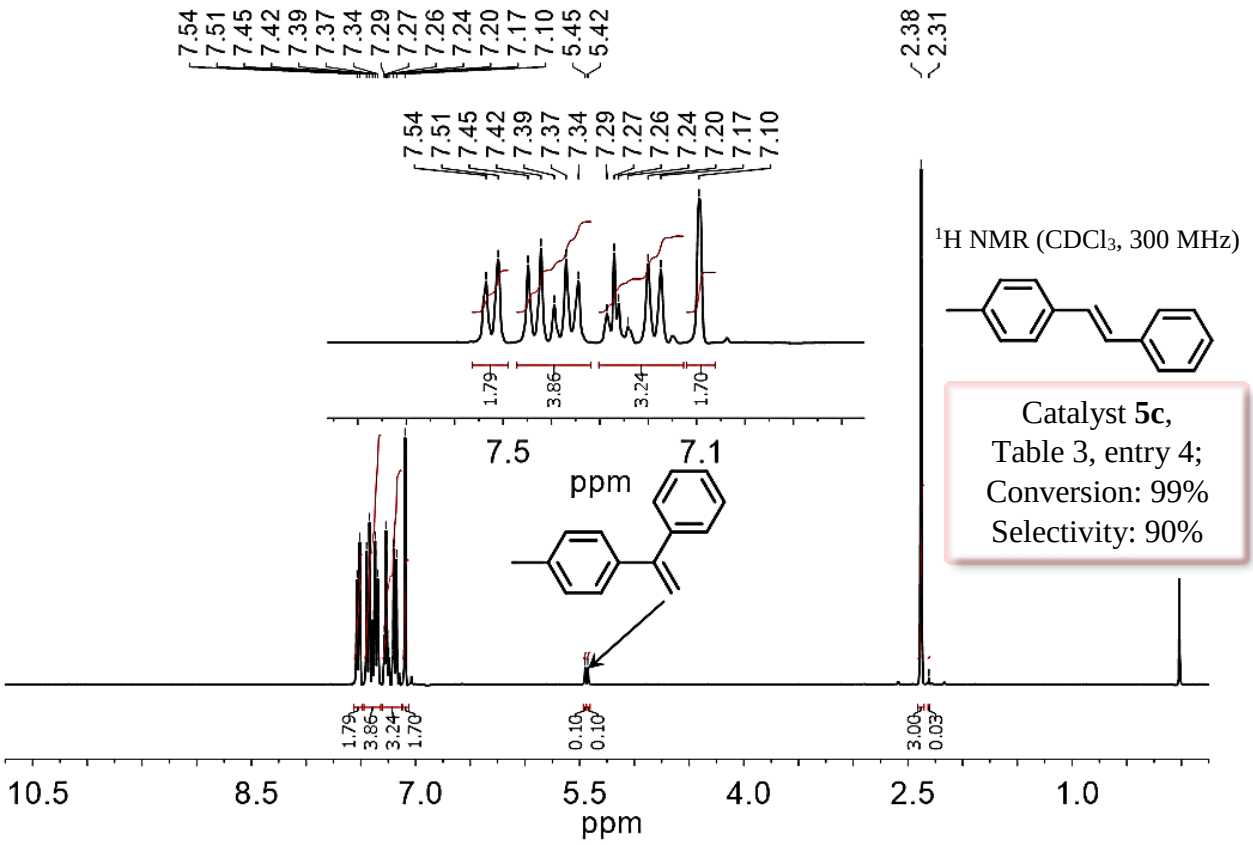

$^1$H NMR ($CDCl_3$, 300 MHz)




$^1$H NMR ($CDCl_3$, 300 MHz)

Catalyst **5a**,
Table 3, entry 4;
Conversion: 98%
Selectivity: 93%


7.60 7.58 7.54 7.52 7.46 7.43 7.40 7.38 7.35 7.29 7.27 7.25 7.21 7.18 7.11 6.96 6.93 5.46 5.44
2.39 2.31
7.58 7.54 7.52 7.46 7.43 7.40 7.38 7.35 7.29 7.27 7.25 7.21 7.18 7.11 6.96 6.93
1.90 3.91 4.80 0.20
7.8
7.2
ppm
$^1$H NMR ($CDCl_3$, 300 MHz)
Catalyst **5b**,
Table 3, entry 4;
Conversion: 93%
Selectivity: 88%
1.90 3.91 4.80 0.20 0.12 0.11 3.00 0.23
10.5 8.5 7.0 5.5 4.0 2.5 1.0
ppm


7.54 7.51 7.45 7.42 7.39 7.37 7.34 7.29 7.27 7.26 7.24 7.20 7.17 7.10 5.45 5.42
2.38 2.31
7.54 7.51 7.45 7.42 7.39 7.37 7.34 7.29 7.27 7.26 7.24 7.20 7.17 7.10
1.79 3.86 3.24 1.70
7.5
7.1
ppm
$^1$H NMR ($CDCl_3$, 300 MHz)
Catalyst **5c**,
Table 3, entry 4;
Conversion: 99%
Selectivity: 90%
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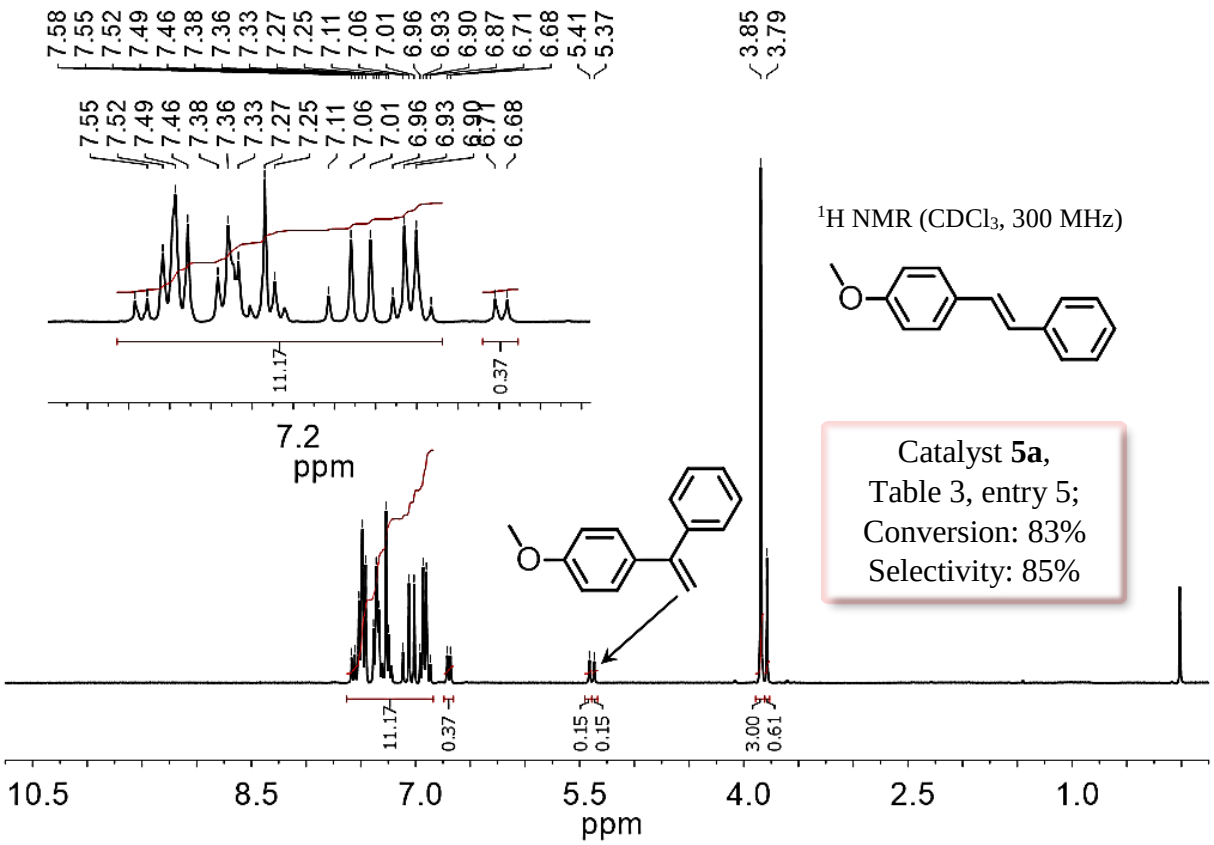
10.5 8.5 7.0 5.5 4.0 2.5 1.0
ppm


7.58 7.55 7.52 7.49 7.46 7.38 7.36 7.33 7.27 7.25 7.11 7.06 7.01 6.96 6.93 6.90 6.87 6.71 6.68 5.41 5.37
3.85 3.79
11.17
0.37
7.2
ppm
0.15 0.15
3.00 0.61
10.5 8.5 7.0 5.5 4.0 2.5 1.0
ppm
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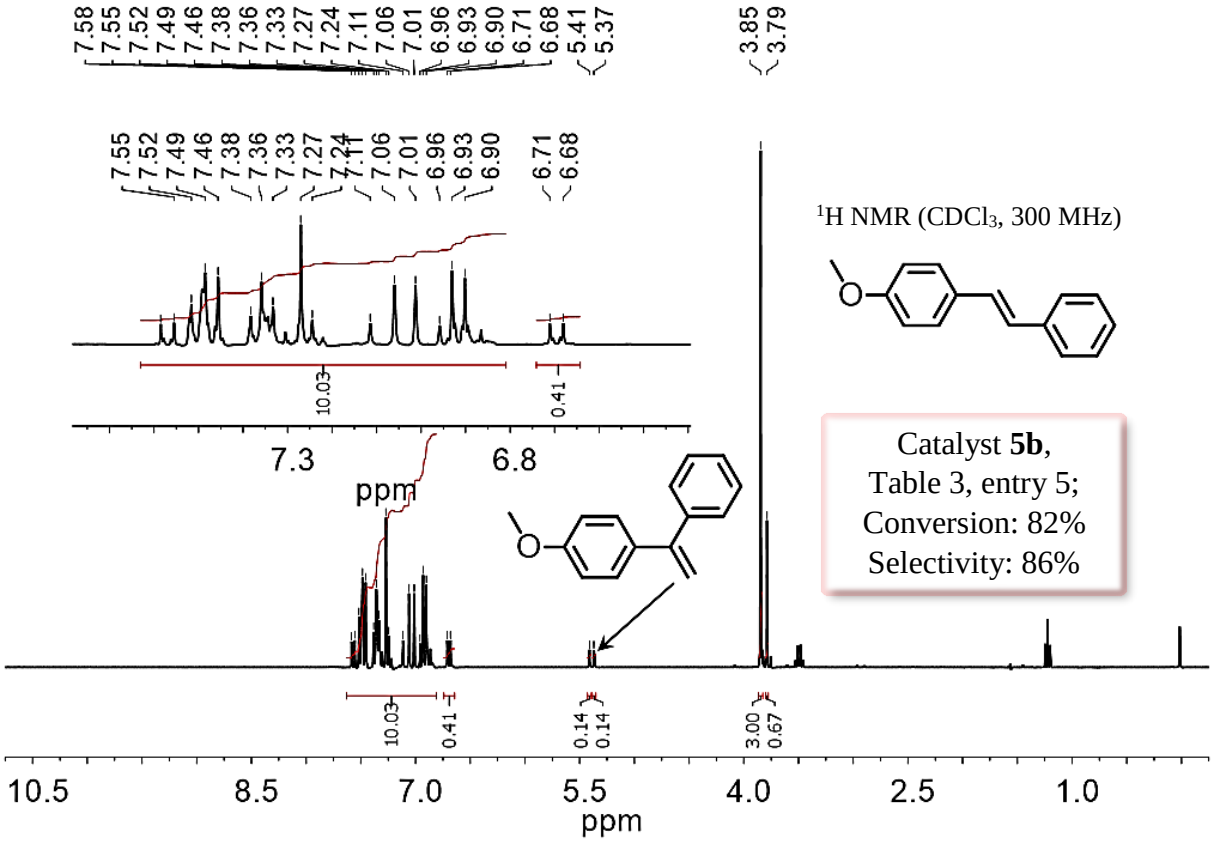
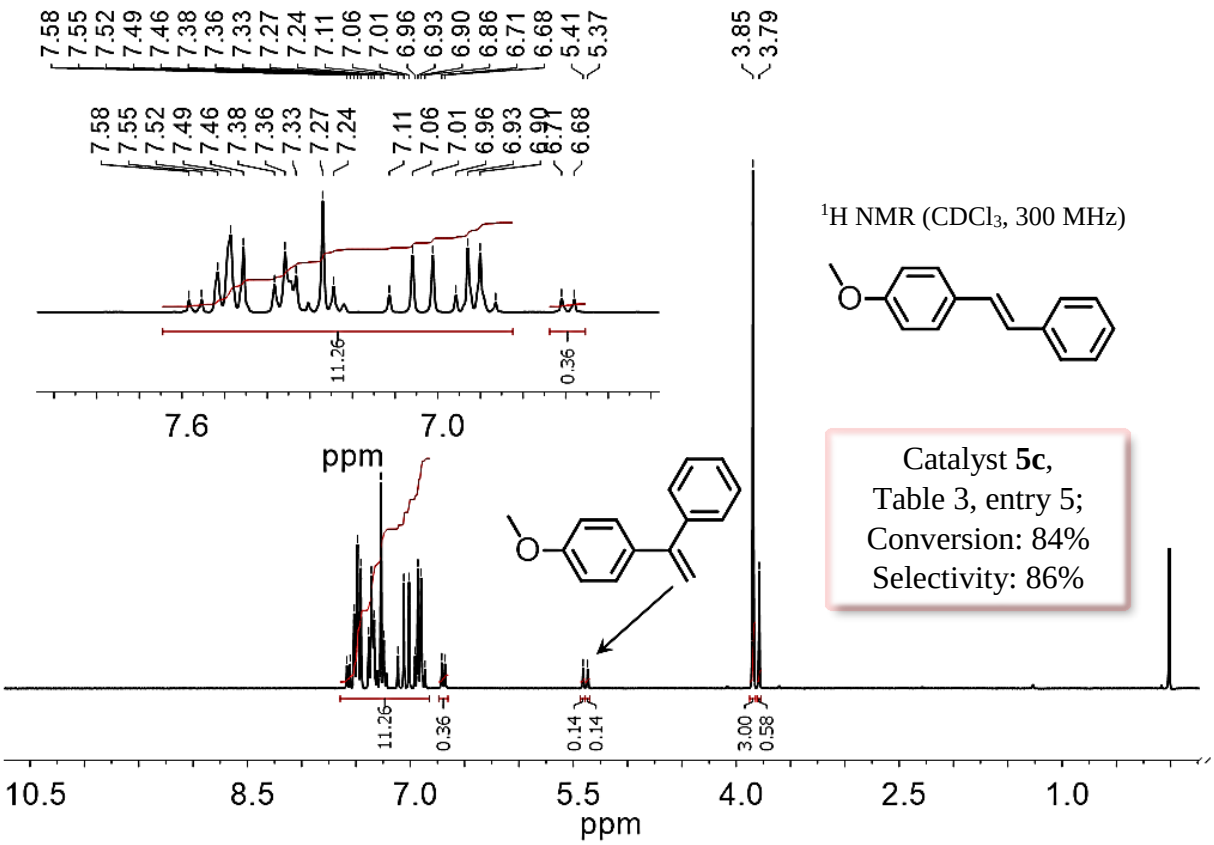
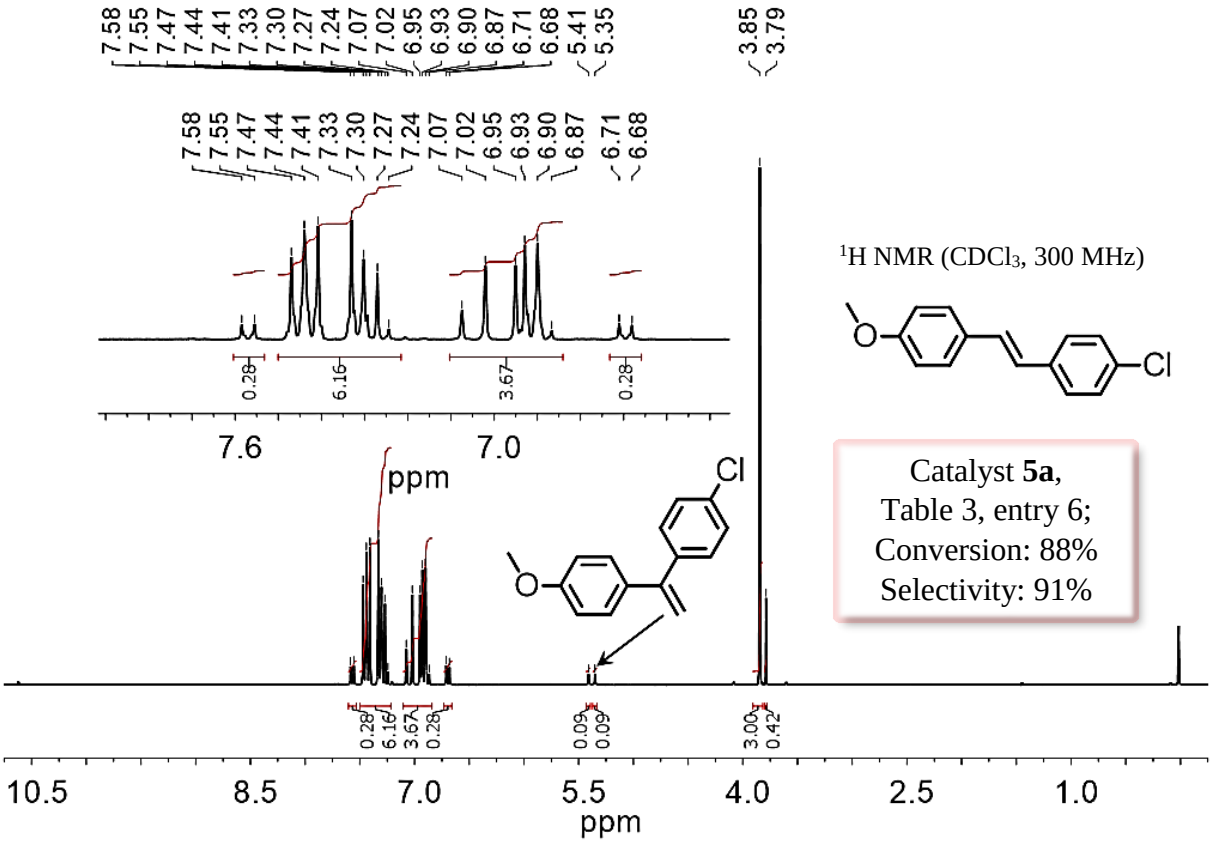
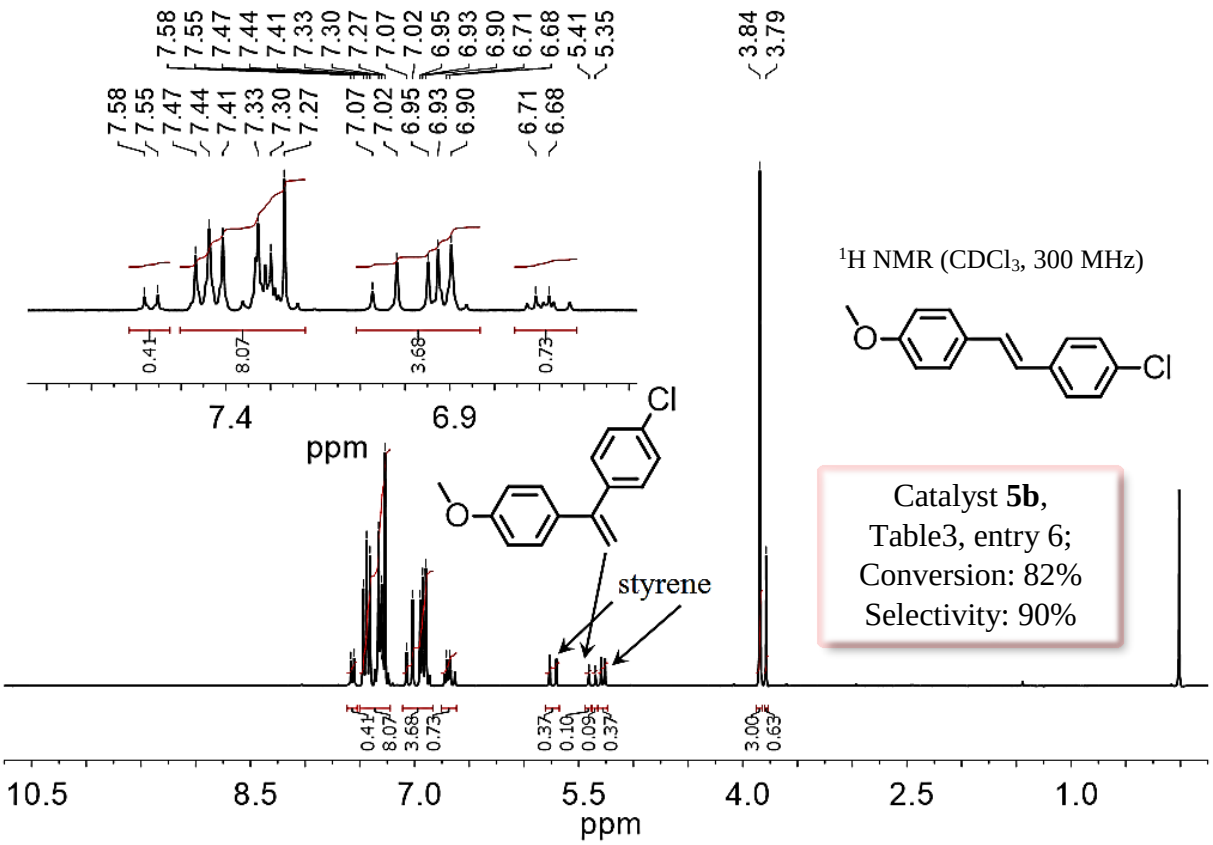
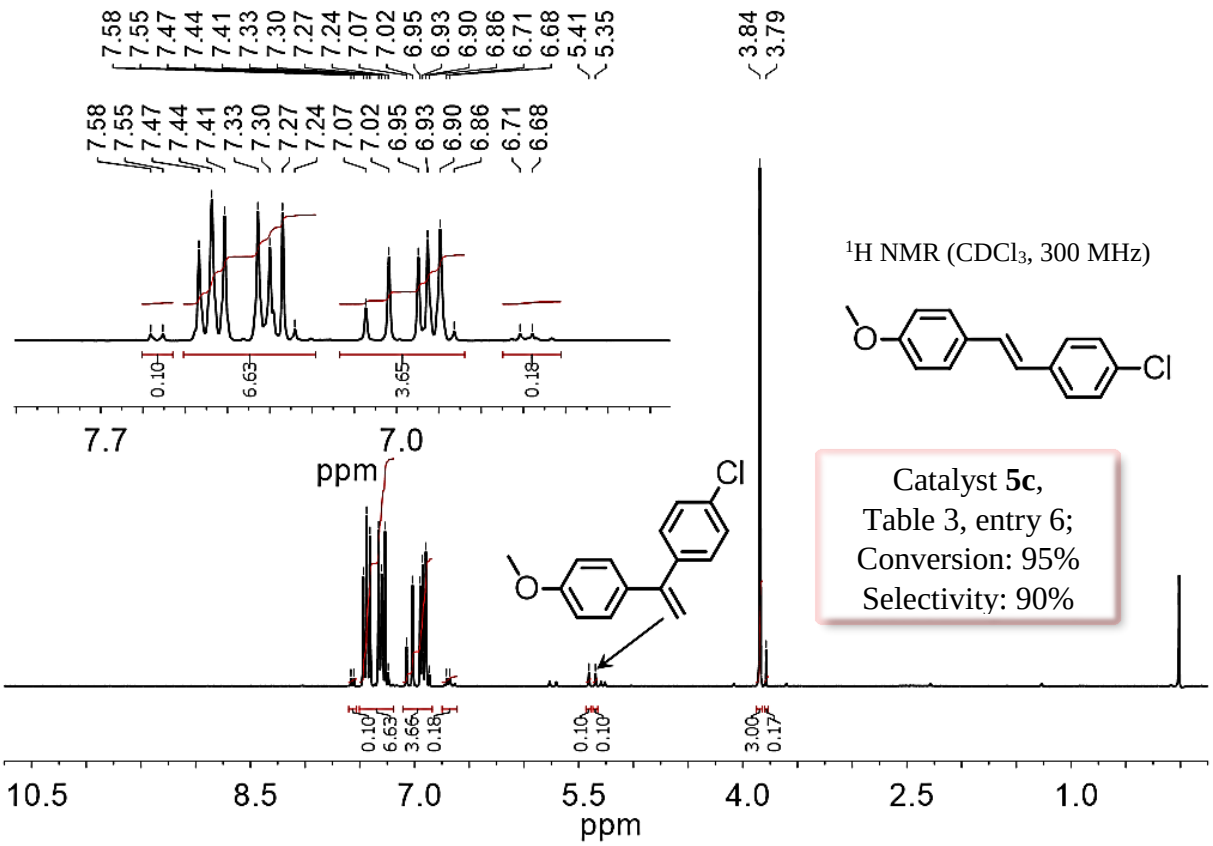
Selectivity: 85%


7.58 7.55 7.52 7.49 7.46 7.38 7.36 7.33 7.27 7.24 7.11 7.06 7.01 6.96 6.93 6.90 6.71 6.68 5.41 5.37
3.85 3.79
10.03
0.41
7.3
6.8
ppm
0.14 0.14
3.00 0.67
10.5 8.5 7.0 5.5 4.0 2.5 1.0
ppm
$^1$H NMR ($CDCl_3$, 300 MHz)
Catalyst **5b**,
Table 3, entry 5;
Conversion: 82%
Selectivity: 86%

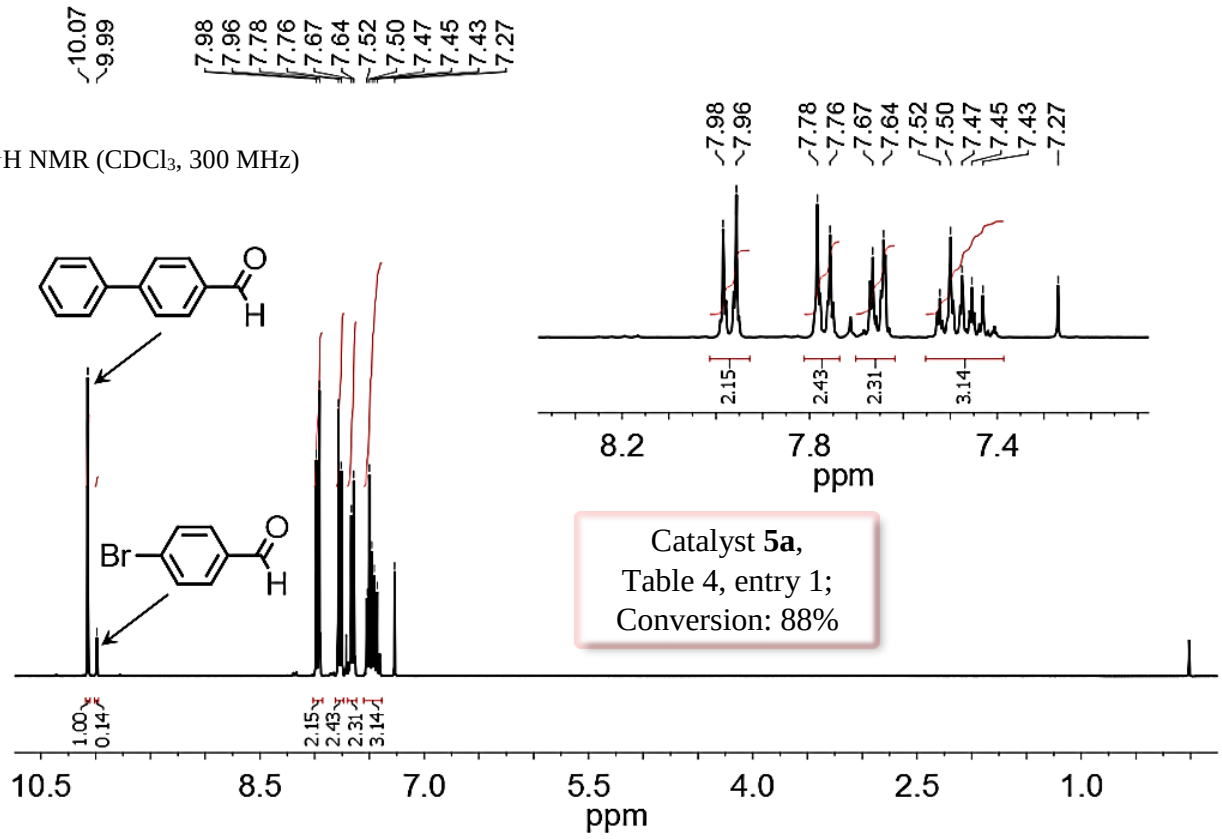

7.58 7.55 7.52 7.49 7.46 7.38 7.36 7.33 7.27 7.24 7.11 7.06 7.01 6.96 6.93 6.90 6.86 6.71 6.68 5.41 5.37
3.85 3.79
11.26
0.36
7.6
7.0
ppm
0.14 0.14
3.00 0.58
10.5 8.5 7.0 5.5 4.0 2.5 1.0
ppm
$^1$H NMR ($CDCl_3$, 300 MHz)
Catalyst **5c**,
Table 3, entry 5;
Conversion: 84%
Selectivity: 86%


7.58 7.55 7.47 7.44 7.41 7.33 7.30 7.27 7.24 7.07 7.02 6.95 6.93 6.90 6.87 6.71 6.68 5.41 5.35
3.85 3.79
0.28
6.16
3.67
0.28
7.6
7.0
ppm
Cl
0.09 0.09
3.00 0.42
10.5 8.5 7.0 5.5 4.0 2.5 1.0
ppm
$^1$H NMR ($CDCl_3$, 300 MHz)
Catalyst **5a**,
Table 3, entry 6;
Conversion: 88%
Selectivity: 91%


7.58 7.55 7.47 7.44 7.41 7.33 7.30 7.27 7.07 7.02 6.95 6.93 6.90 6.71 6.68 5.41 5.35
3.84 3.79
0.41 8.07 3.68 0.73
7.4
6.9
ppm
Cl
styrene
0.37 0.10 0.09 0.37
3.00 0.63
10.5 8.5 7.0 5.5 4.0 2.5 1.0
ppm
$^1$H NMR ($CDCl_3$, 300 MHz)
Cl
Catalyst **5b**,
Table3, entry 6;
Conversion: 82%
Selectivity: 90%


7.58 7.55 7.47 7.44 7.41 7.33 7.30 7.27 7.24 7.07 7.02 6.95 6.93 6.90 6.86 6.71 6.68 5.41 5.35
3.84 3.79
0.10 6.63 3.65 0.18
7.7
7.0
ppm
Cl
0.10 0.10
3.00 0.17
10.5 8.5 7.0 5.5 4.0 2.5 1.0
ppm
$^1$H NMR ($CDCl_3$, 300 MHz)
Cl
Catalyst **5c**,
Table 3, entry 6;
Conversion: 95%
Selectivity: 90%

$^1$H NMR ($CDCl_3$, 300 MHz)




Catalyst **5a**,
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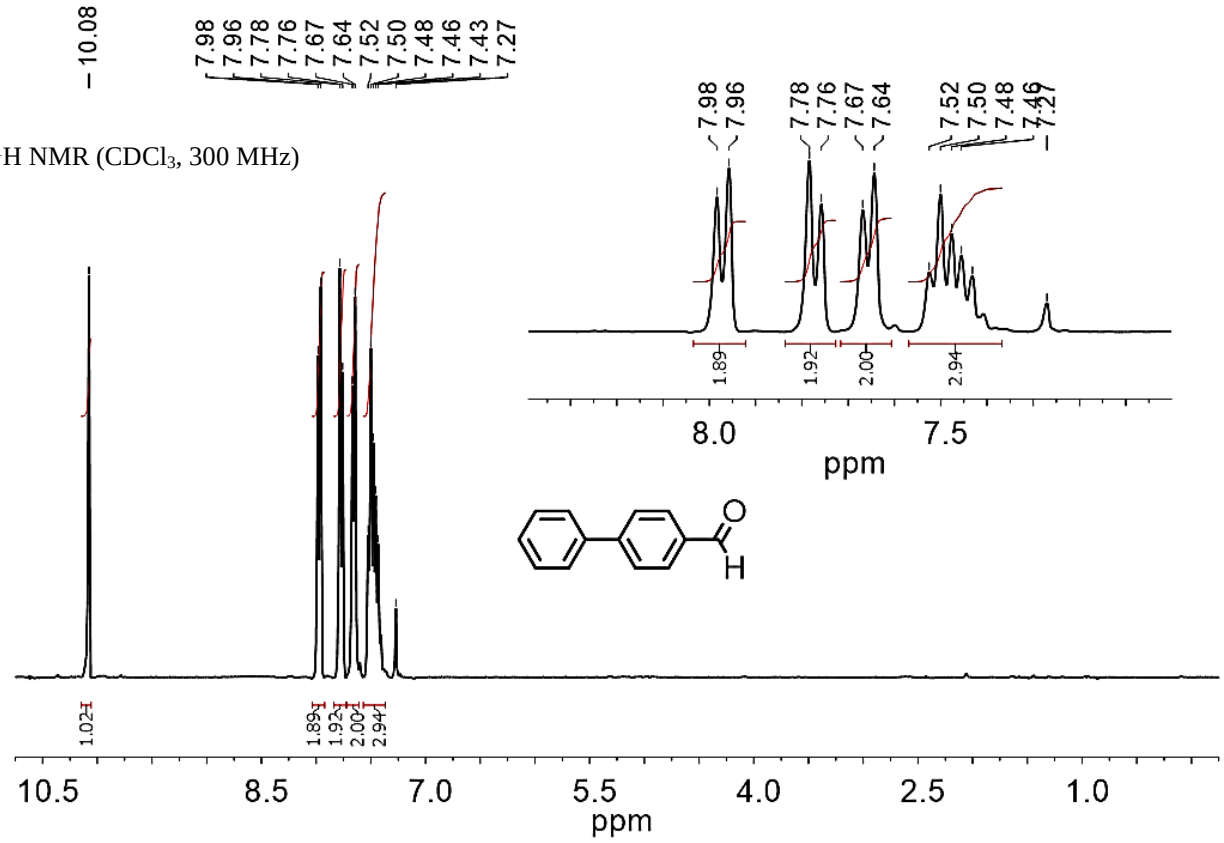
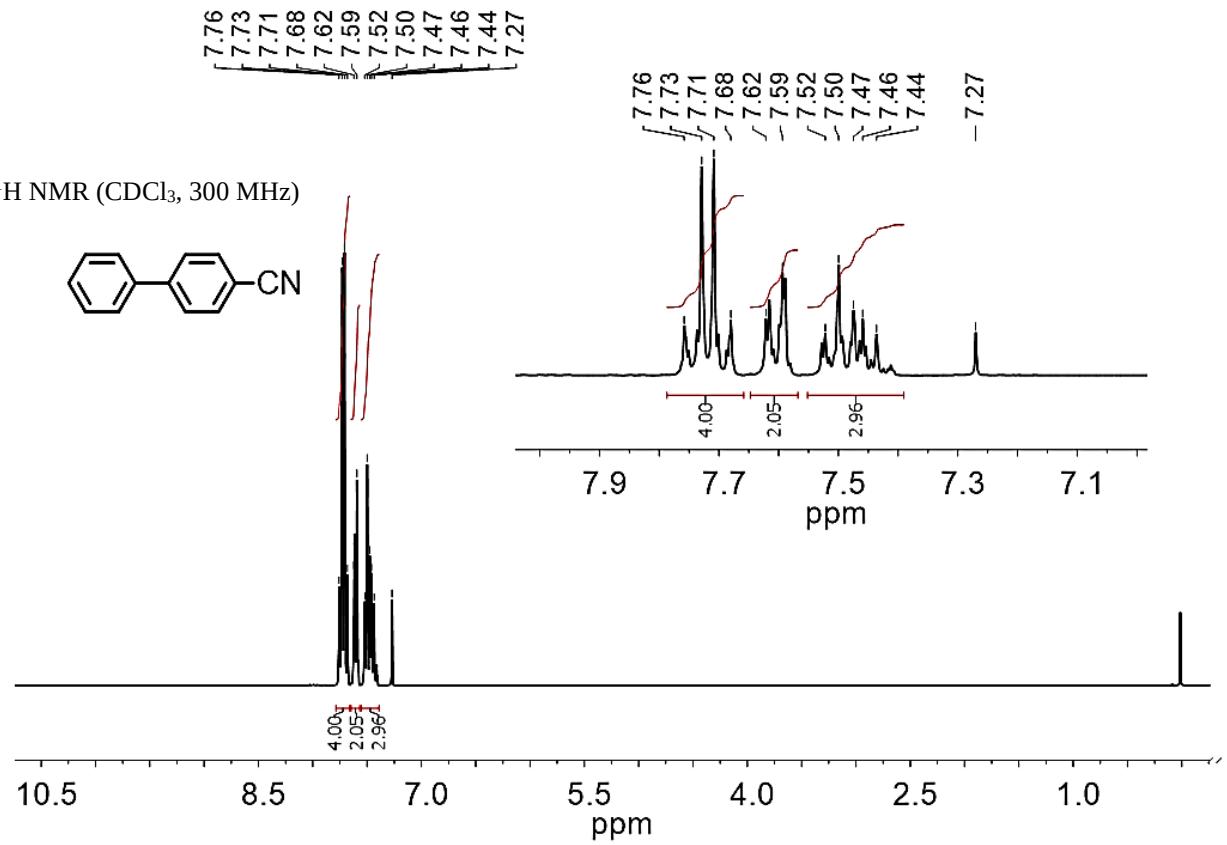
Conversion: 88%

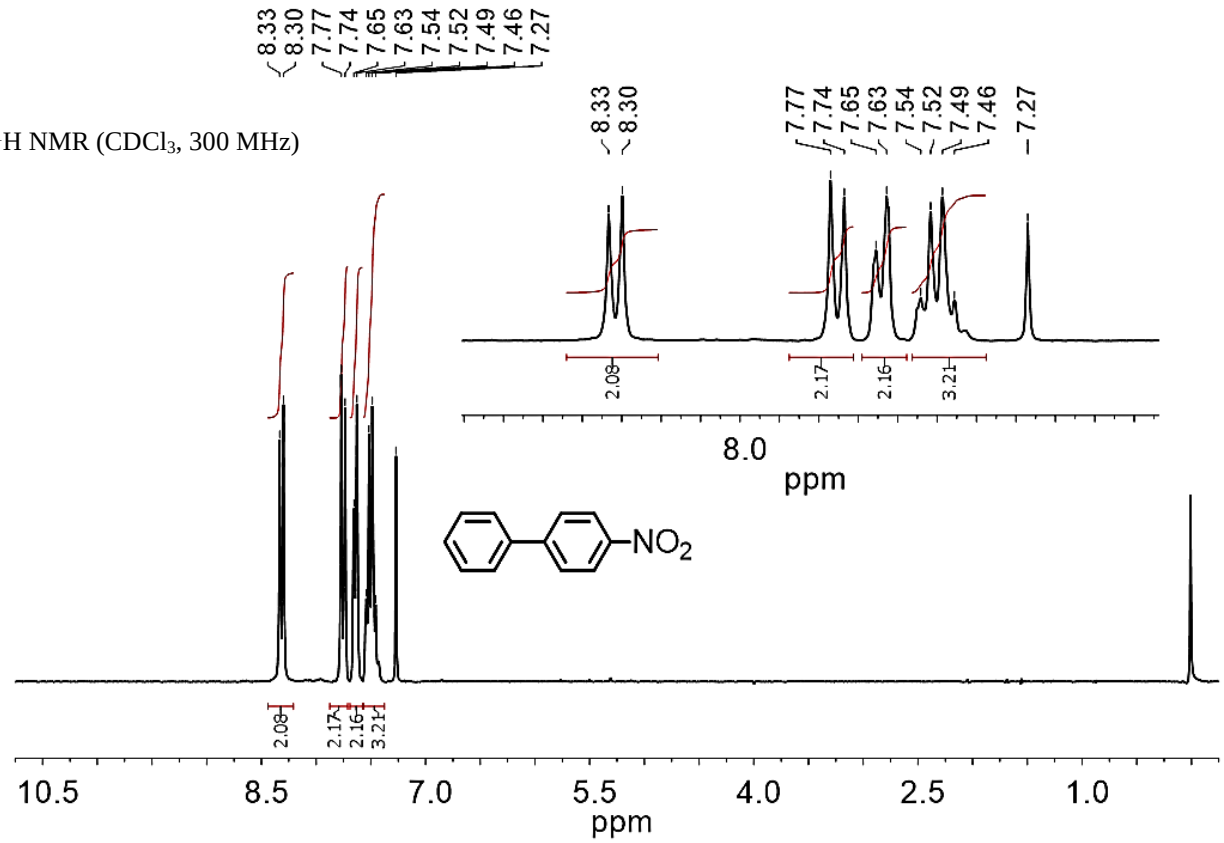
$^1$H NMR ($CDCl_3$, 300 MHz)



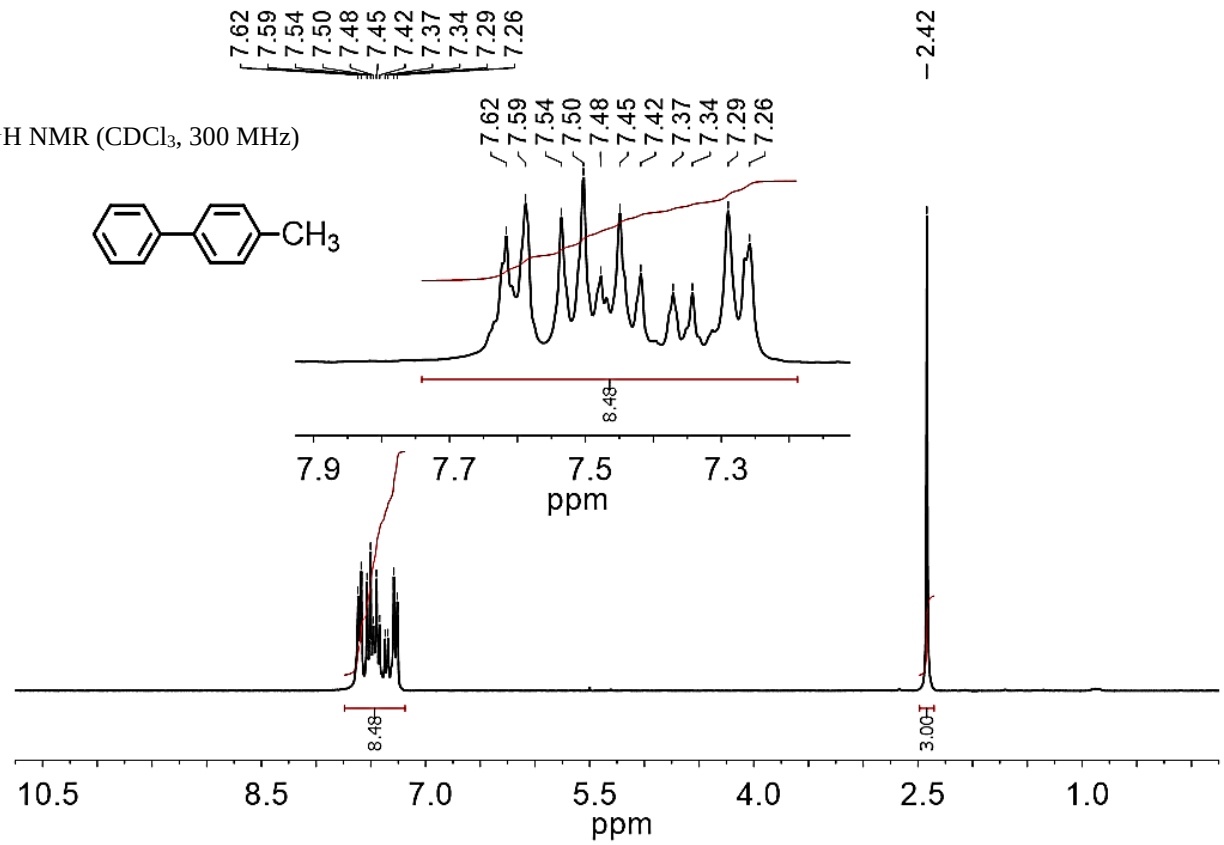
$^1$H NMR ($CDCl_3$, 300 MHz)



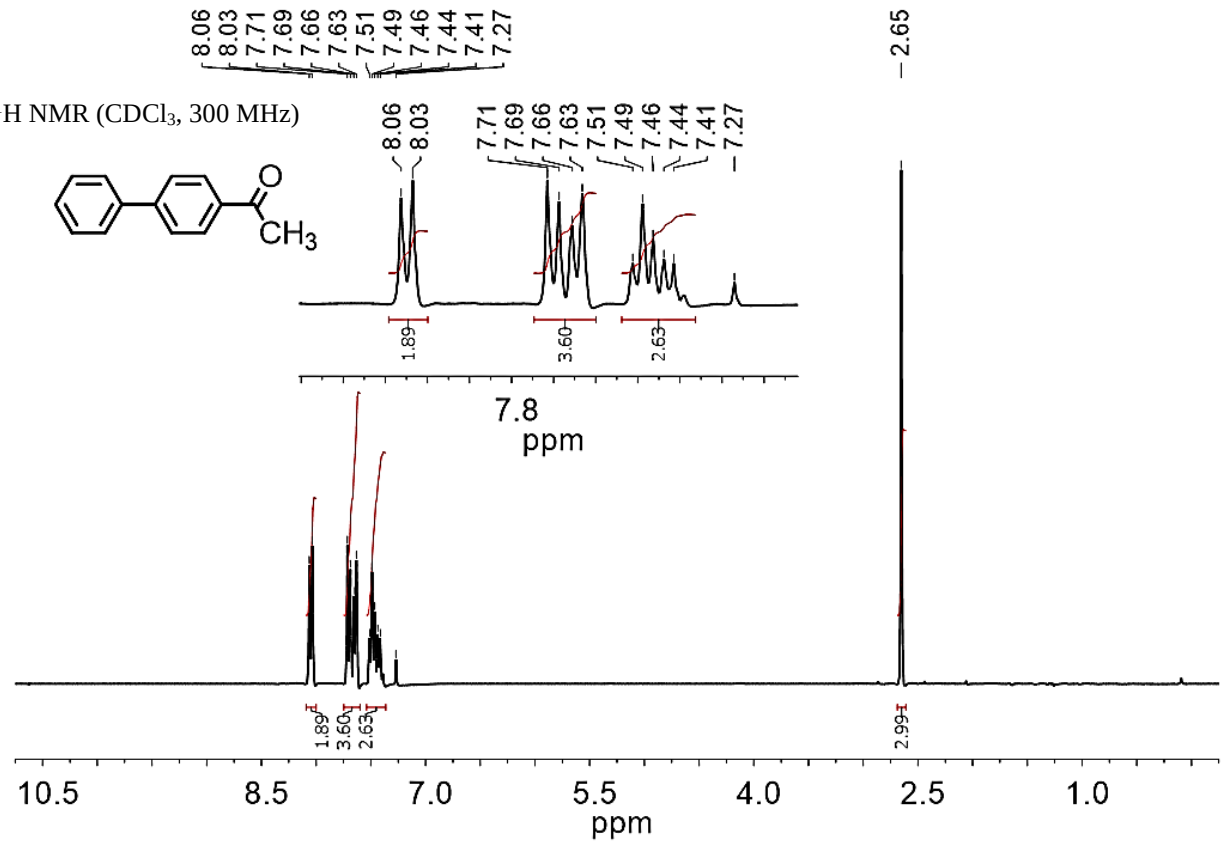

$^1$H NMR ($CDCl_3$, 300 MHz)

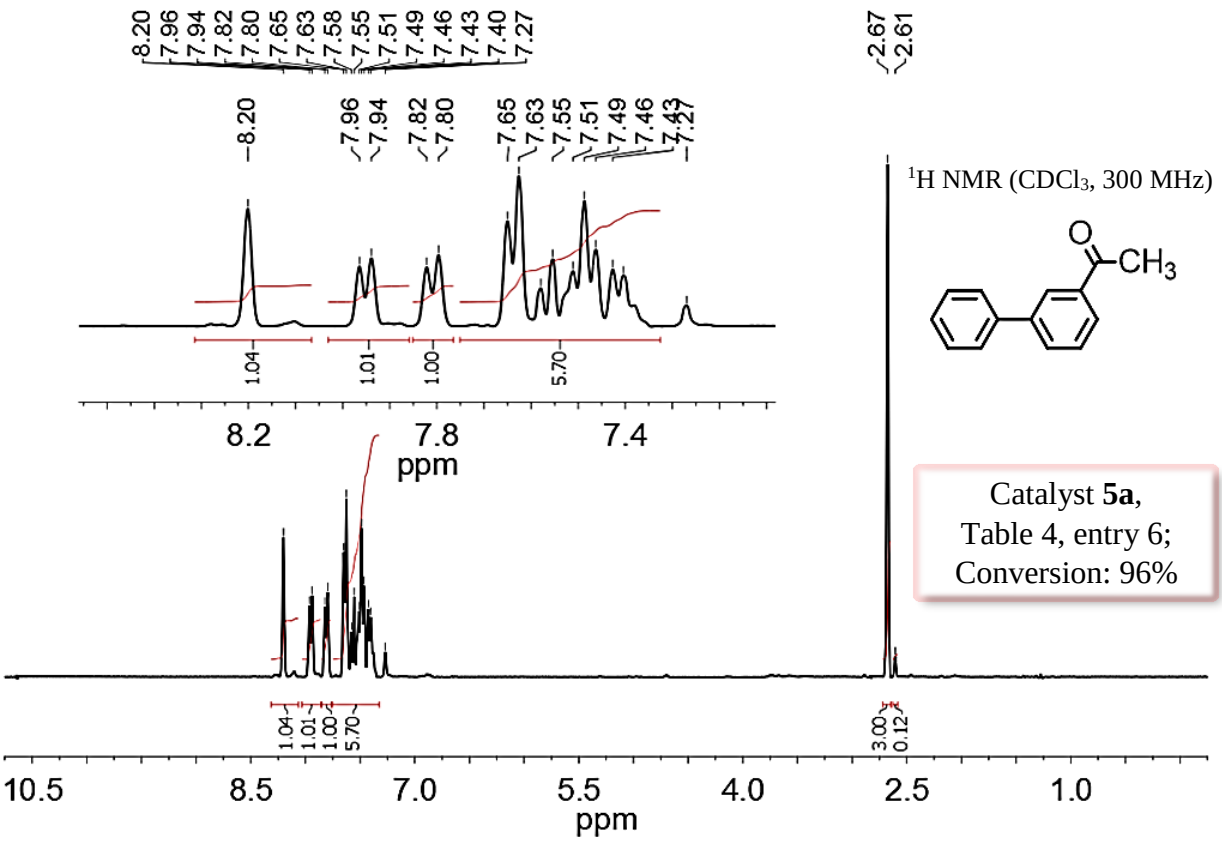


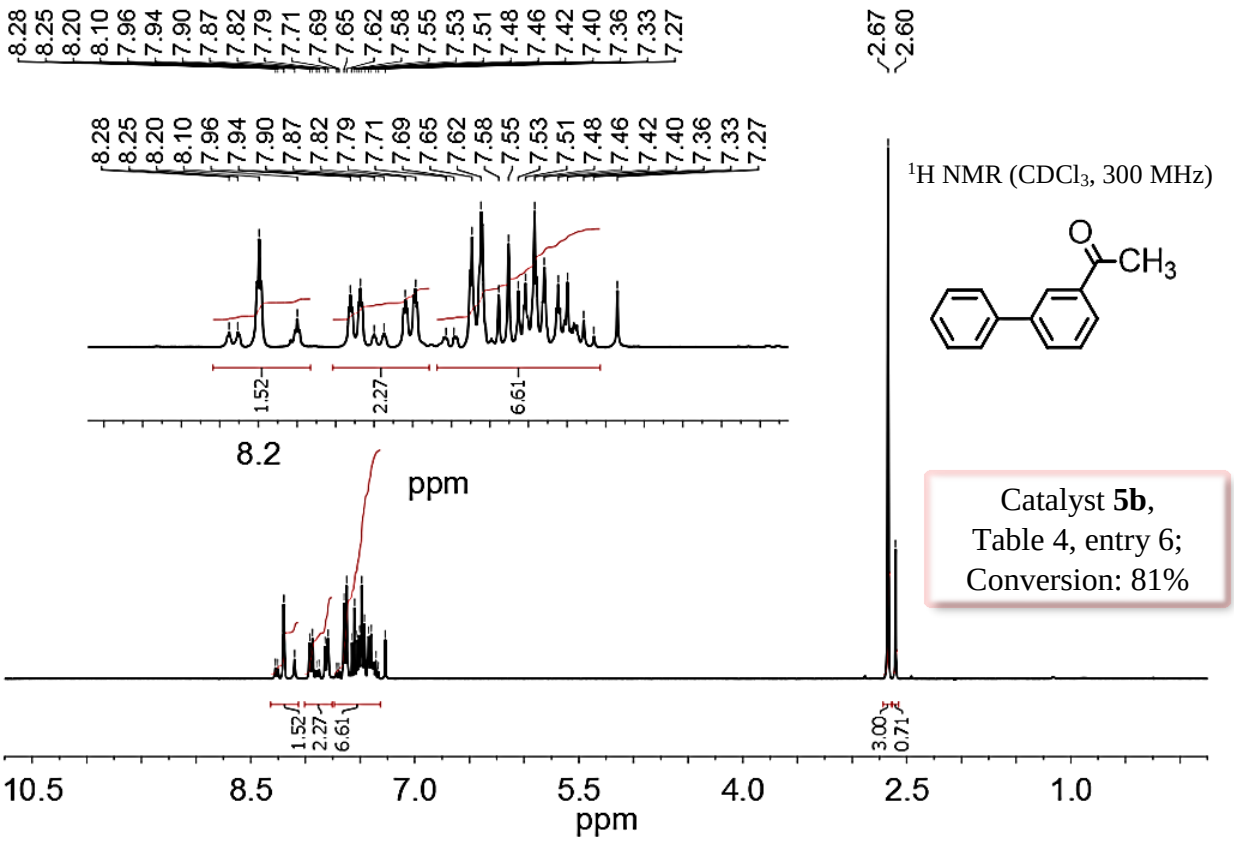
$^1$H NMR ($CDCl_3$, 300 MHz)

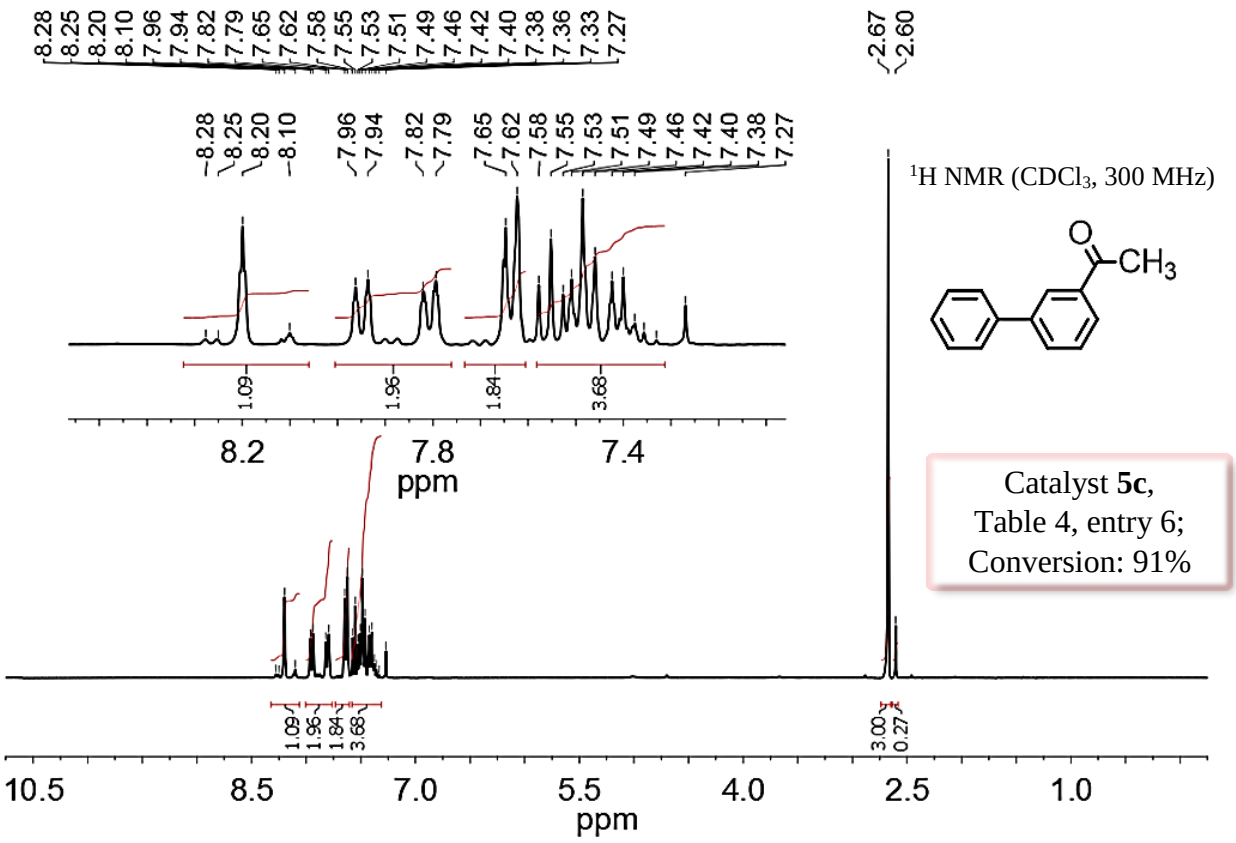



$^1$H NMR ($CDCl_3$, 300 MHz)




$^1$H NMR ($CDCl_3$, 300 MHz)
Catalyst **5a**,
Table 4, entry 6;
Conversion: 96%
ppm


$^1$H NMR ($CDCl_3$, 300 MHz)
Catalyst **5b**,
Table 4, entry 6;
Conversion: 81%
ppm


8.28
8.25
8.20
8.10
7.96
7.94
7.82
7.79
7.65
7.62
7.58
7.55
7.53
7.51
7.49
7.46
7.42
7.40
7.38
7.36
7.33
7.27
2.67
2.60
1.09
1.96
1.84
3.68
8.2
7.8
7.4
ppm
3.00
0.27
10.5
8.5
7.0
5.5
4.0
2.5
1.0
ppm
$^1$H NMR ($CDCl_3$, 300 MHz)
O
$CH_3$
Catalyst **5c**,
Table 4, entry 6;
Conversion: 91%