# SUPPLEMENTARY MATERIAL

## Recyclable Mesoporous Silica-Supported Chiral Ruthenium-(NHC)NN-Pincer Catalysts For Asymmetric Reactions

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SELECTED SPECTRA

FT-IR spectra

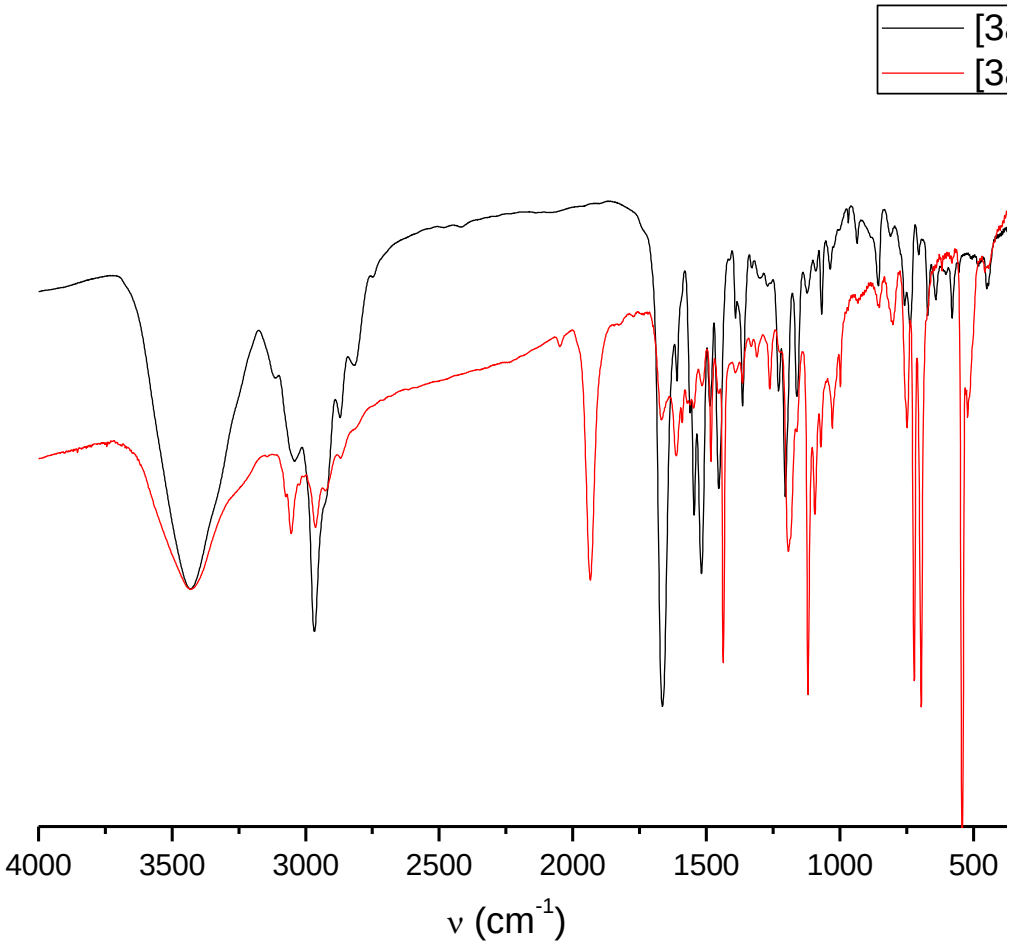


Figure S1

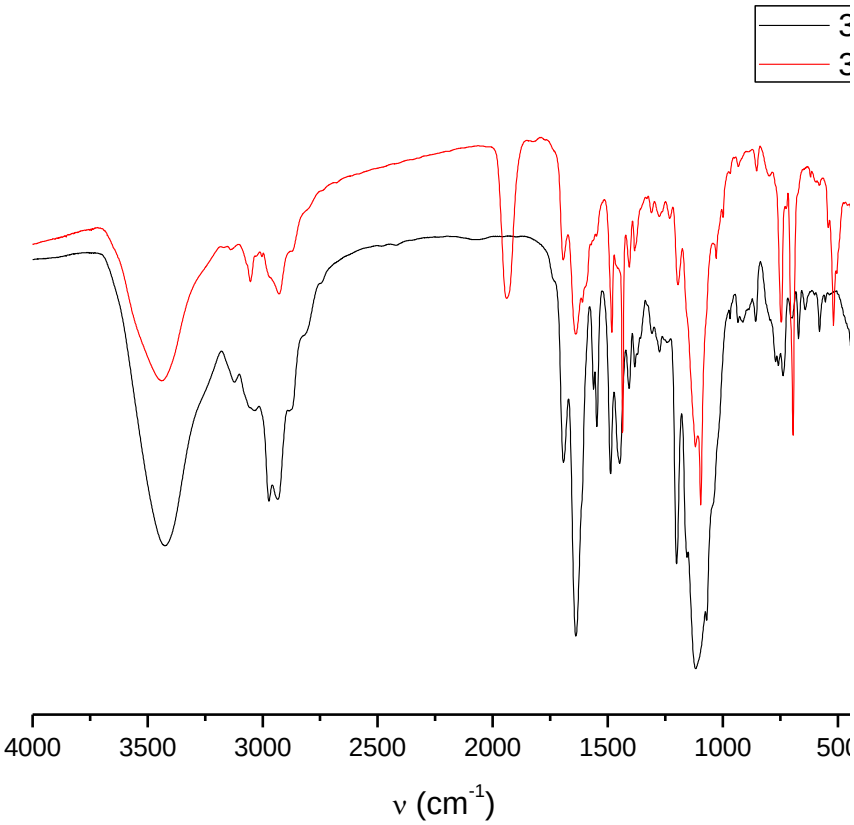


Figure S2

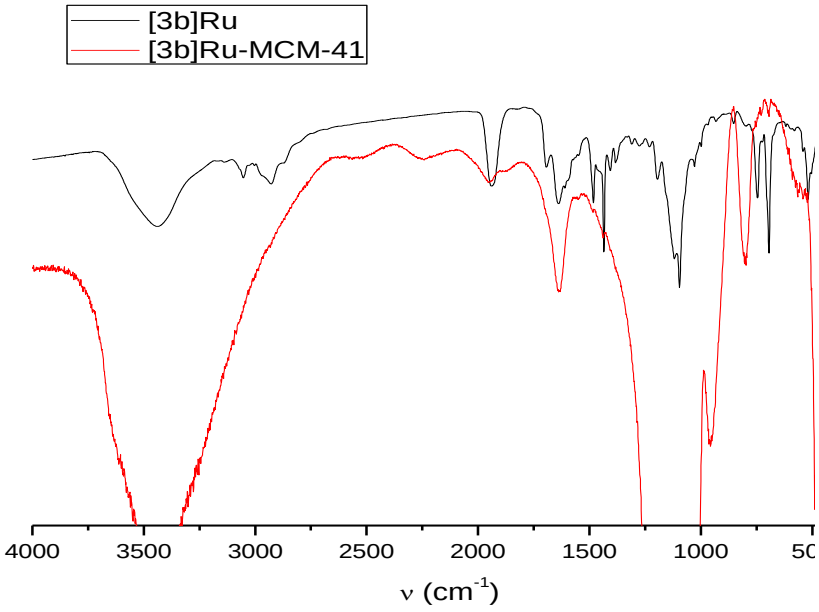


Figure S3

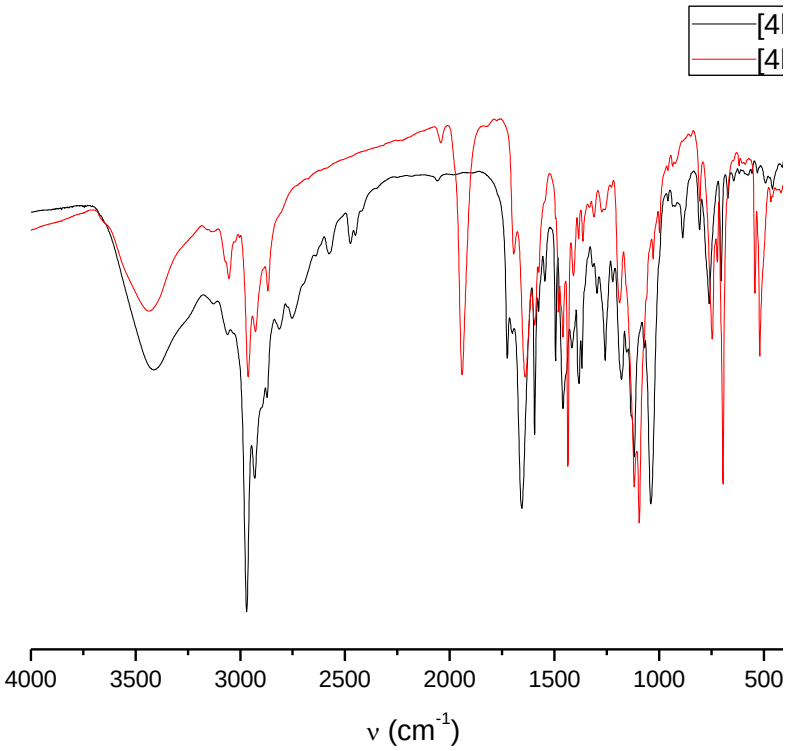


Figure S4

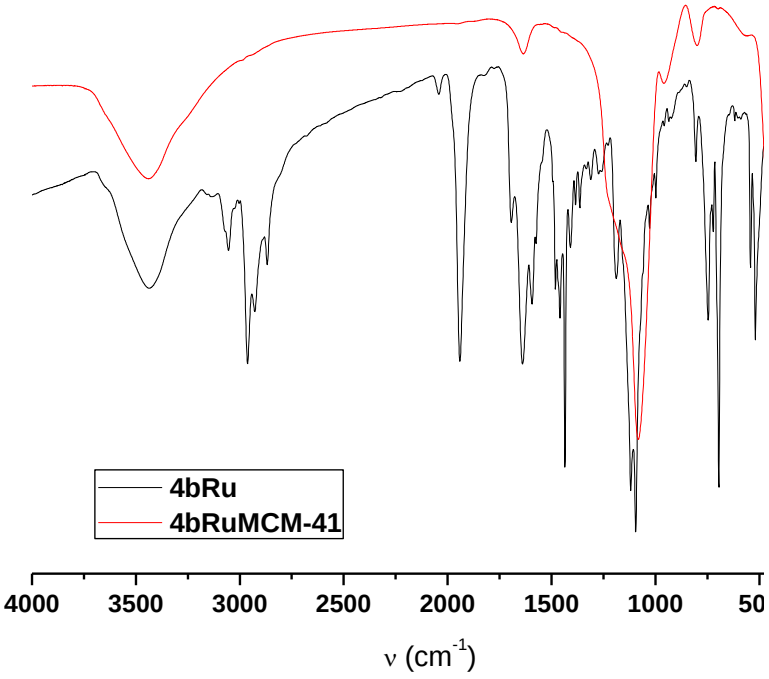


Figure S5A

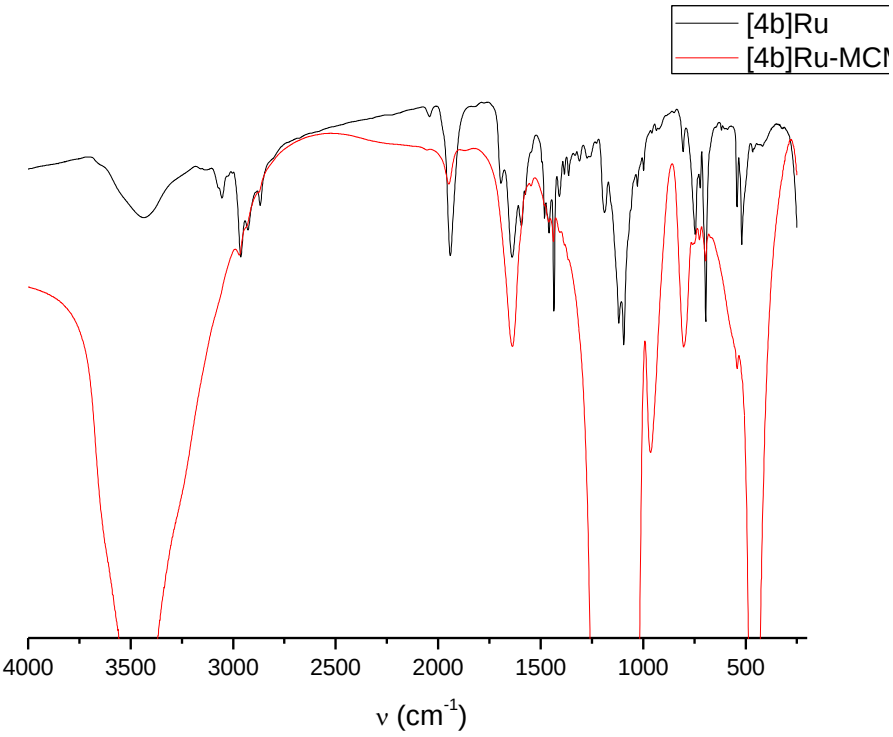


Figure S5B

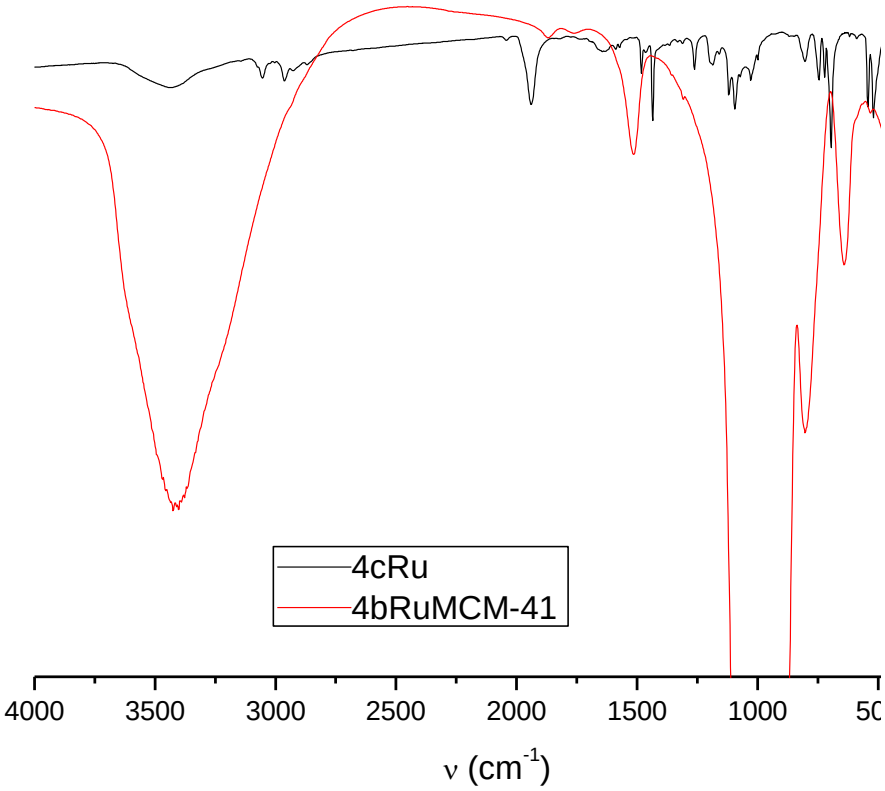


Figure S6

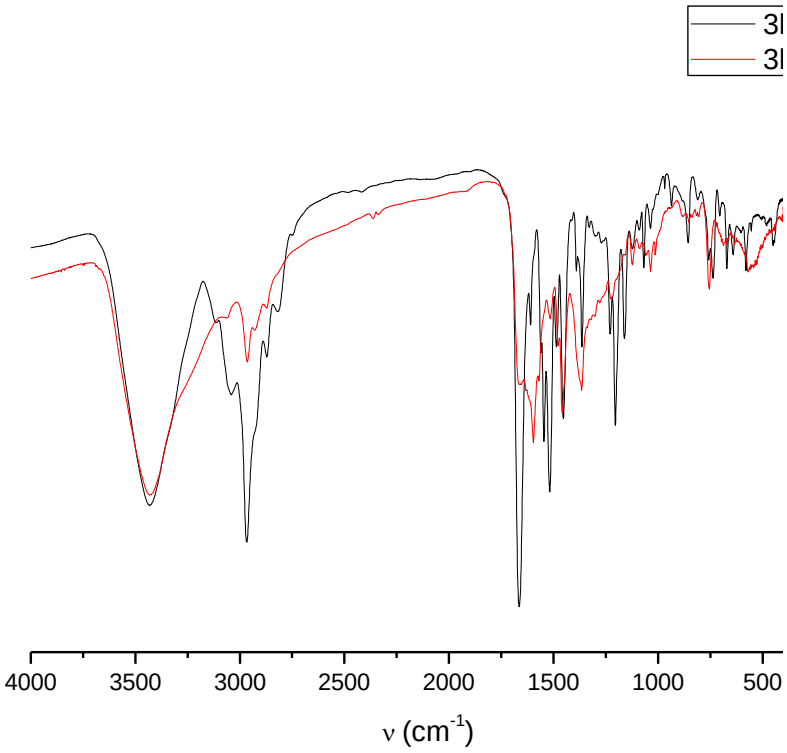


Figure S7

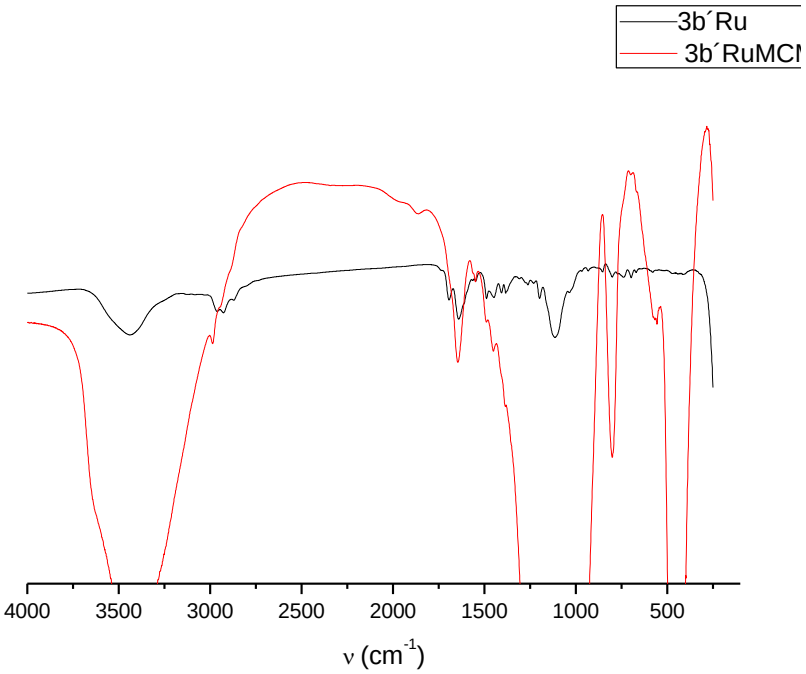


Figure S7

# DRUV

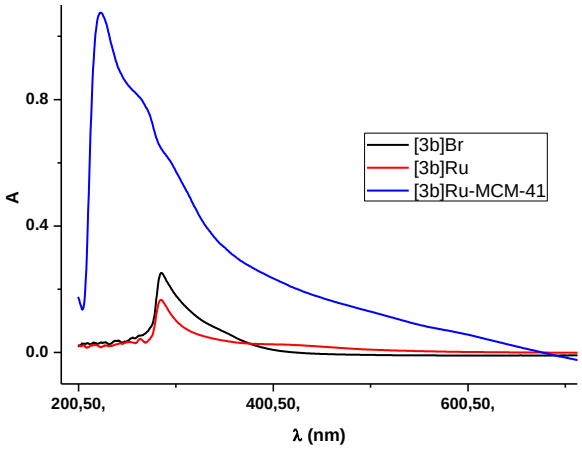


Figure S8

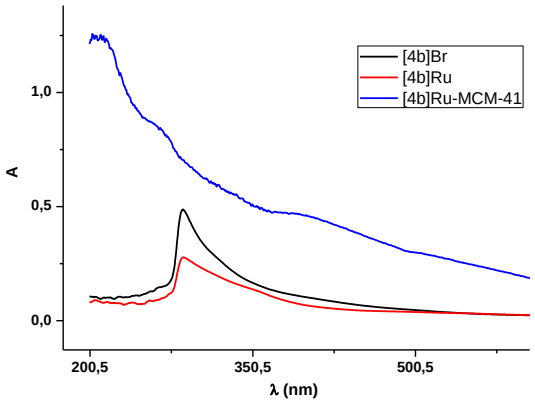


Figure S9

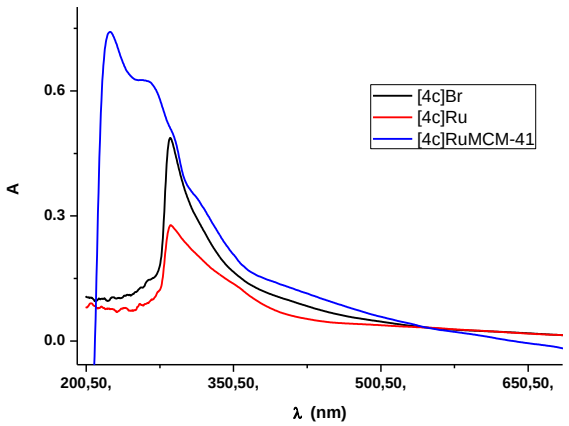


Figure S10

# NMR

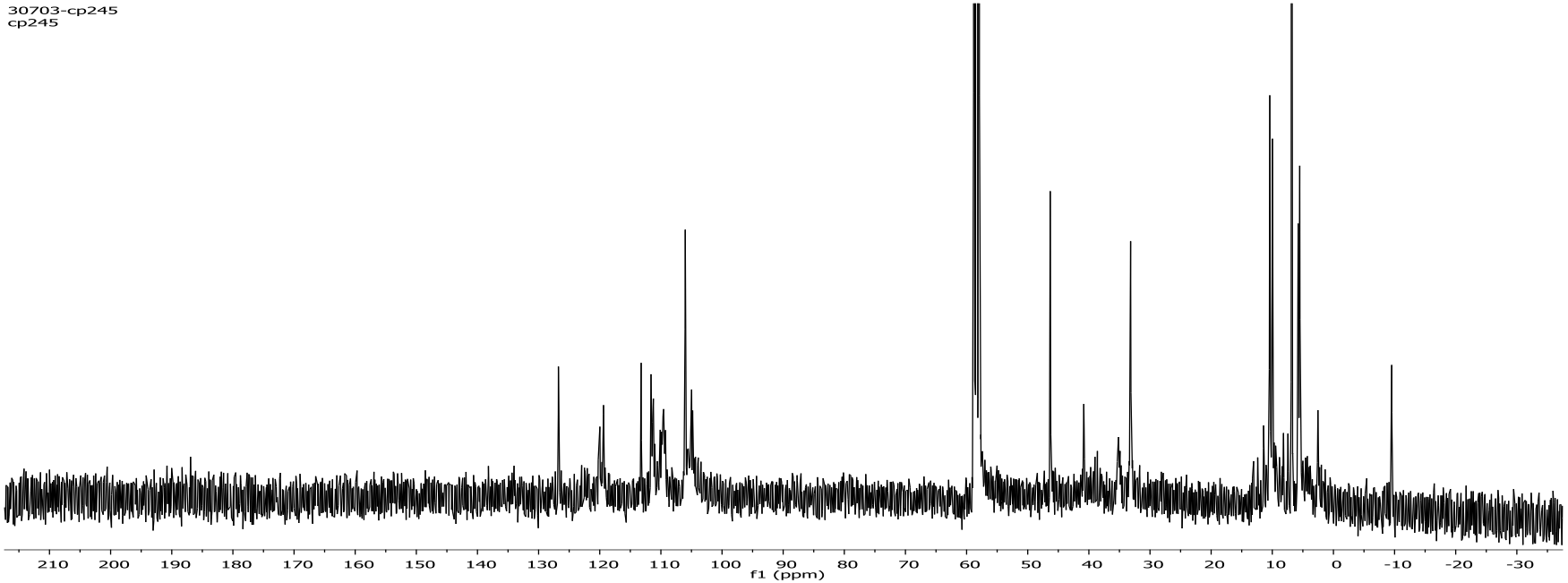


Figure S11. $^{13}$C NMR of **3bBr**

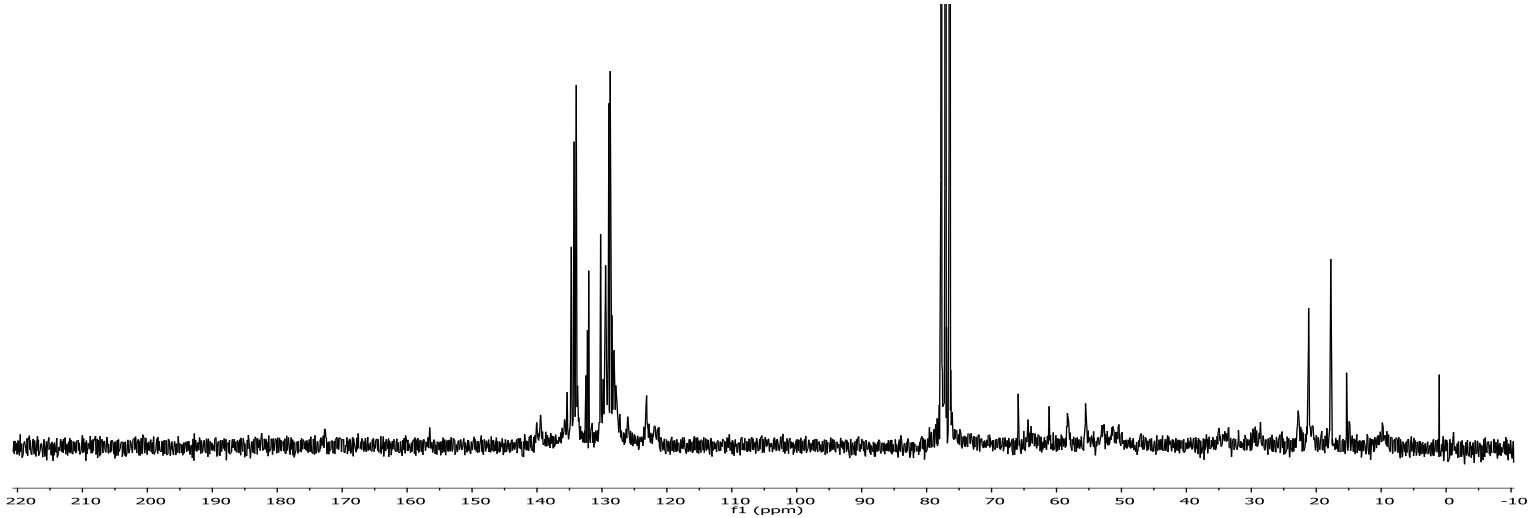


Figure S12. $^{13}$C NMR of **3bRu**

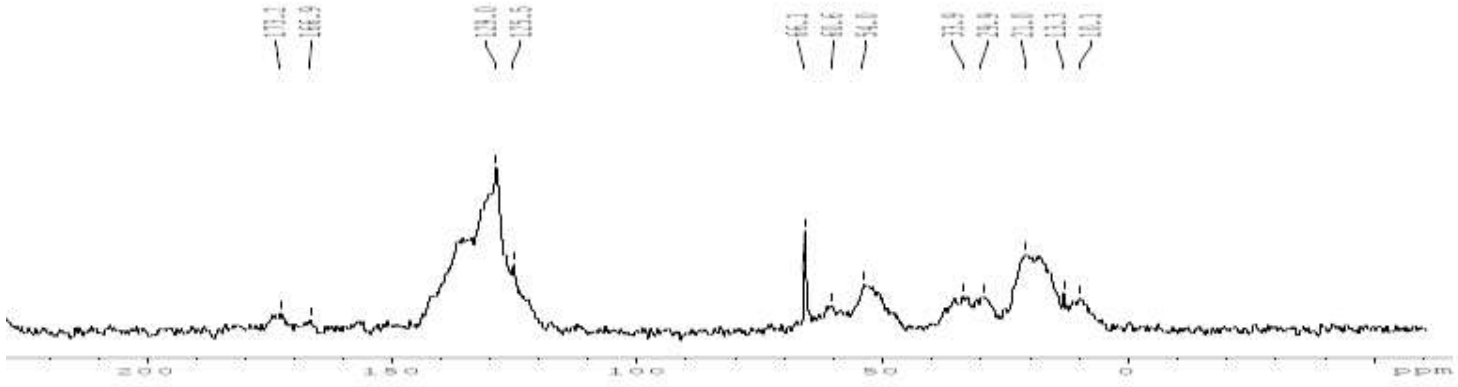


Figure S13. $^{13}$C NMR of **3bRuMCM-41**

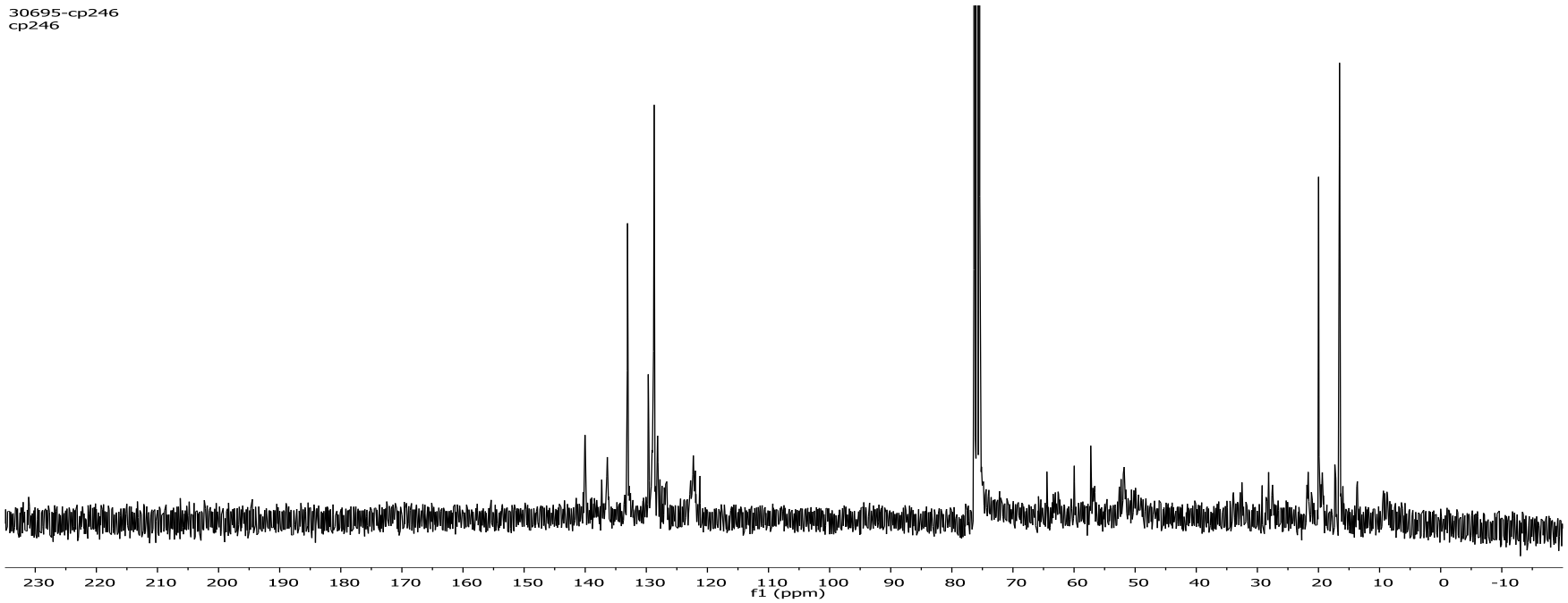


Figure S14. $^{13}$C NMR of **4cBr**

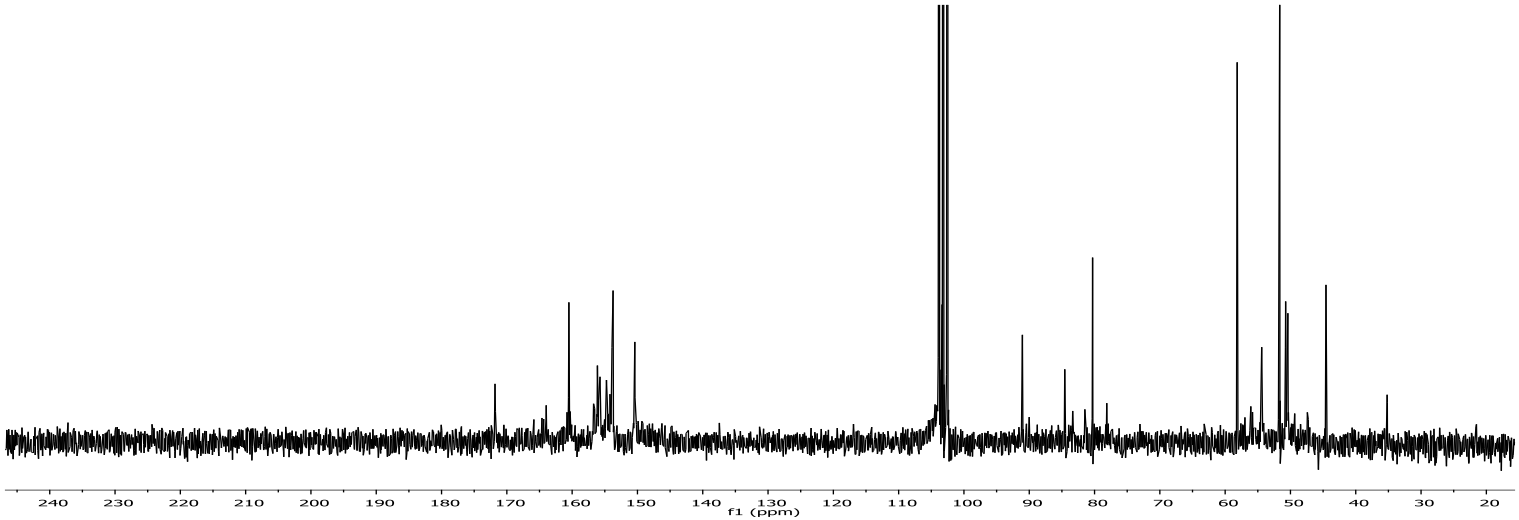


Figure S15. $^{13}$C NMR of **4cRu**

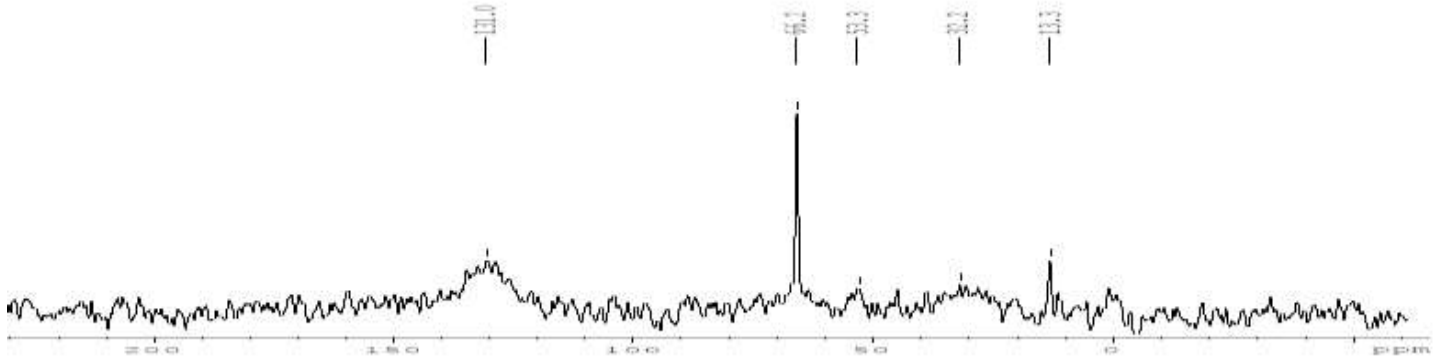


Figure S16. $^{13}$C NMR of **4cRuMCM-41**

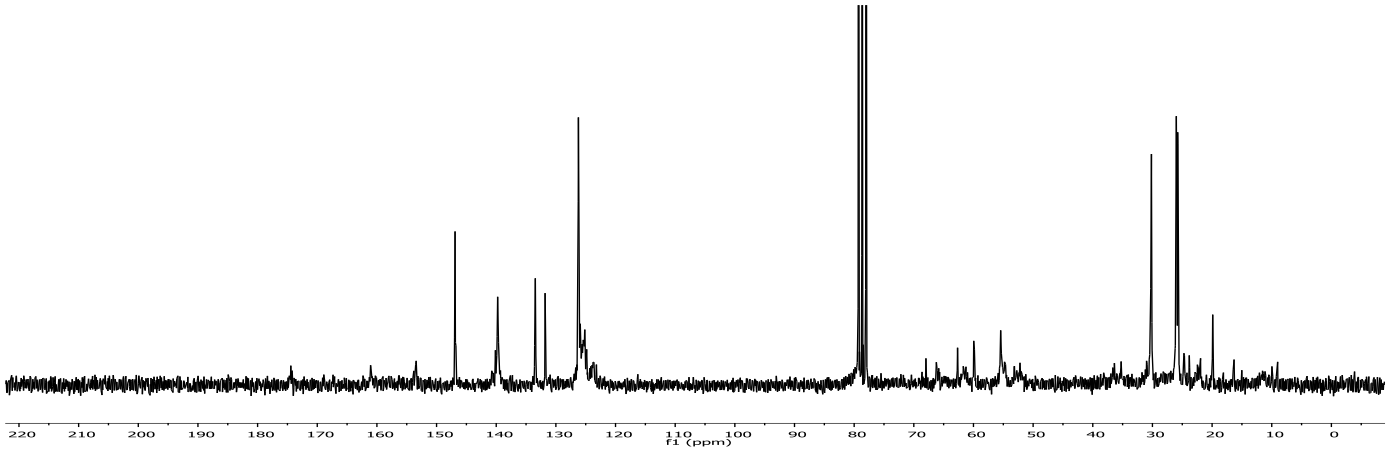


Figure S17. $^{13}$C NMR of **4bRu**

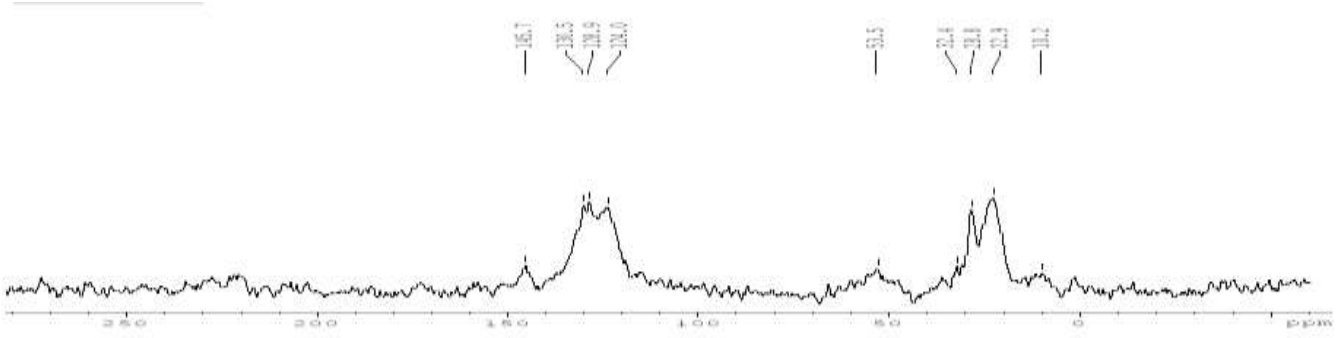


Figure S18. $^{13}$C NMR of **4bRuMCM-41**

# Catalytic Activity

Table 1. Catalytic hydrogenation of diethyl citraconate and (*E*)-diethyl 2-benzylidenesuccinate and with Ru catalysts[a]

| Entry | Catalyst | diethyl citraconate | | (*E*)-diethyl 2-benzylidene succinate | |
|---|---|---|---|---|---|
| | | TOF[b] | ee (%)[c] | TOF[b] | ee (%)[c] |
| 1 | 3aRu[e] | 88 | 5 | 100 | 100(S) |
| 2 | 3bRuMCM[a] | 1200 | 5 | 400 | 98 (S) |
| 3 | 4bRuMCM[a] | 1125 | 5 | 390 | 99(S) |
| 4 | 4cRuMCM[a] | 1321 | 5 | 272 | 98(S) |
| 5 | 3a$_{p\text{-cym}}$ Ru[a] | 90 | 5 | 25 | 98(S) |
| 6 | 3b $_{p\text{-cym}}$ RuMCM[a] | 160 | 5 | 28 | 99(S) |

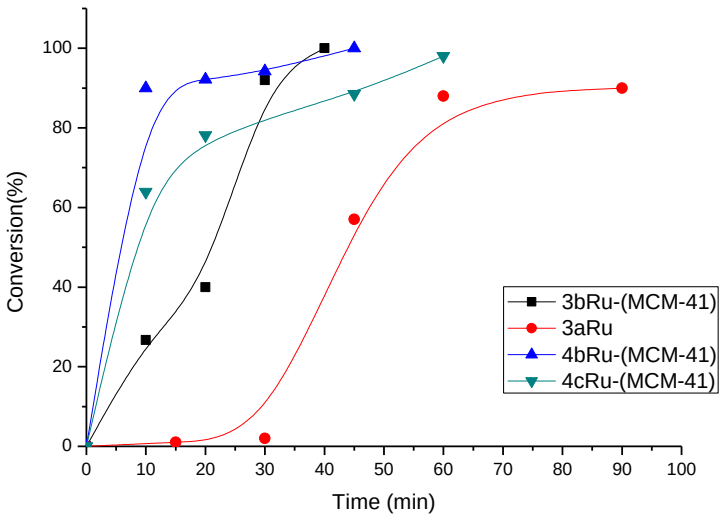


Figure S19. Kinetic profile for hydrogenation of diethyl citraconate with **3aRu, 3bRuMCM-41, 4bRu-MCM-41 and 4cRuMCM-41.**

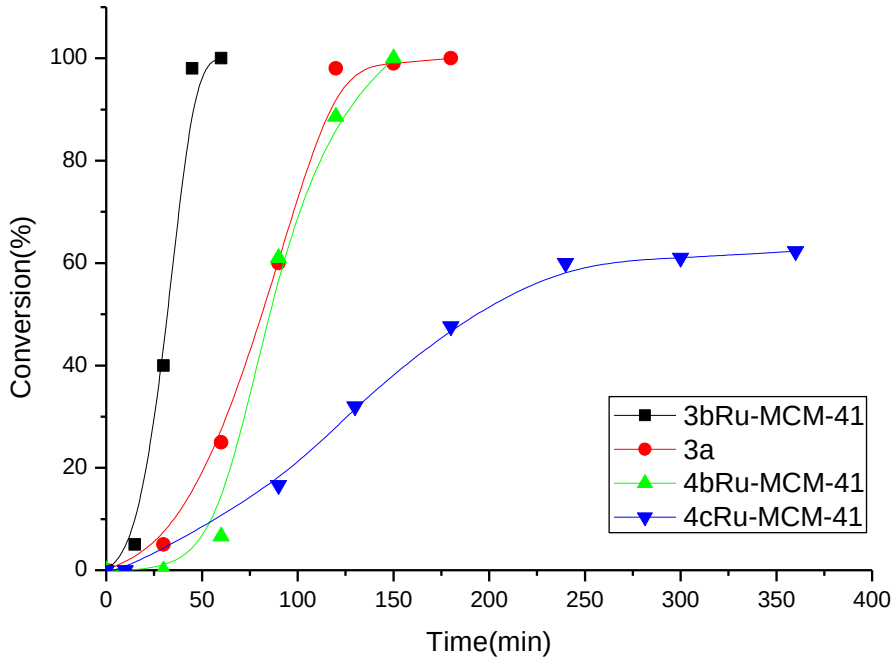


Figure S20. Kinetic profile for hydrogenation of (*E*)-diethyl 2-benzylidene succinate hydride-catalysts**.**

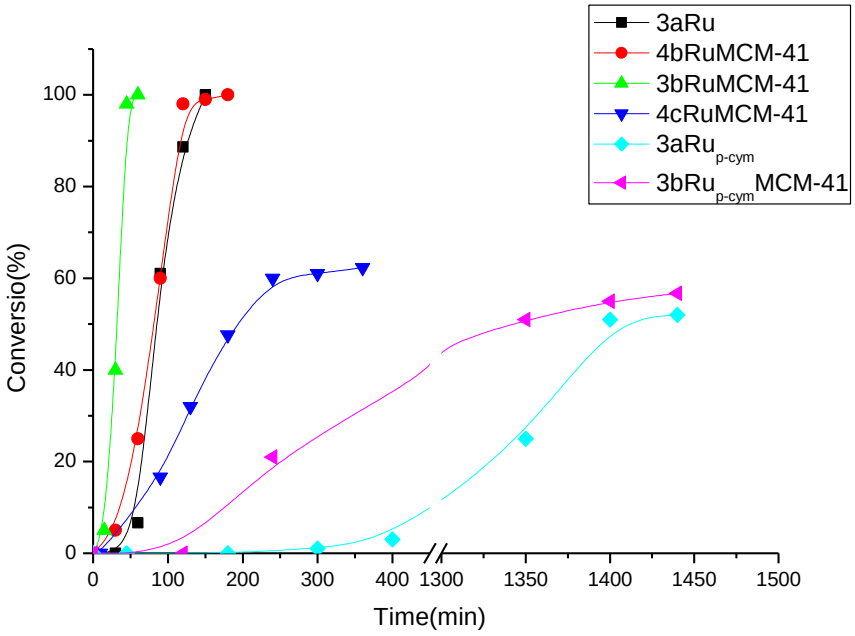


Figure S21. Hydride vs *p*-cymene-catalysts: kinetic profile for hydrogenation of (*E*)-diethyl 2-benzylidene succinate.

Table 2. Asymmetric hydrogenation of different substrates using **3bRuMCM-41** catalyst.

| **Entry** | **Substrate** | **Conv** | **TOF** | ee(%) |
|---|---|---|---|---|
| 1 | (*E*)-diethyl 2-benzylidene succinate | 100 | 1400 | 98 |
| 2 | diethyl citraconate | 100 | 1200 | 5 |
| 3 | (4Z)-4-benzylidene-2-methyl-1,3-oxazol-5(4H)-one | 99 | 535 | - |
| 4 | (1-phenylethylidene)aniline | 70 | 30 | 5 |
| 5 | 5-cyclohexyl-3,4-dihydro-2*H*-pyrrole | 100 | 253 | 15 |

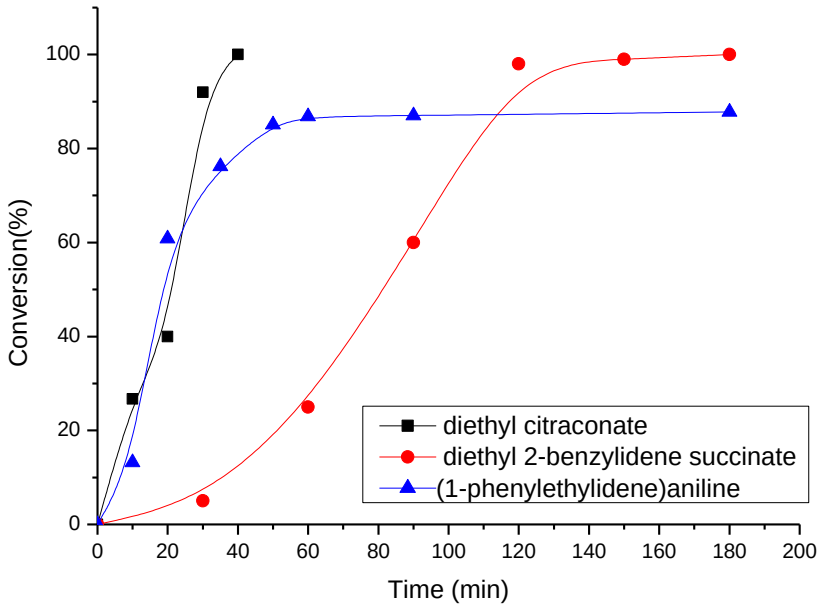


Figure S22. Kinetic profile for hydrogenation of alkenes with **3bRuMCM-41**

**Table 4**. Catalytic results for the cyclopropanation reaction involving styrenes and alkyl diazoacetates.

| Subs. | | 3a'Ru$_{p\text{-cym}}$ | | | | 3b'Ru $_{p\text{-cym}}$MCM-41 | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | Yield [%][b] | *cis*/*trans*[c] | ee [%][d] | | Yield [%] | *cis*/*trans*[c] | ee [%][d] | |
| | | | | *trans* | *cis* | | | *trans* | *cis* |
| | EDA | 45 (48h) | 20/80 | 77 | 5 | 41 (48h) | 40/50 | 65 | 50 |
| | PhEDA | 75 (10h) | 1/100 | 5 | - | 25 (48h) | 1/100 | 56 | <5 |
| | EDA | 10 (48h) | 20/80 | 5 | 5 | Traces (48h) | - | - | - |
| | PhEDA | 100 (10h) | 1/100 | 5 | - | 15 (48h) | 1/100 | <5 | <5 |

[a] Catalyst loading: 5 mol%. [b] Selectivity towards cyclopropanes; the remaining diazo compound was converted into coupling products. [c] Diastereomeric selectivity: (trans_cis)/trans+cis).

## HPLC Traces for hydrogenation reactions

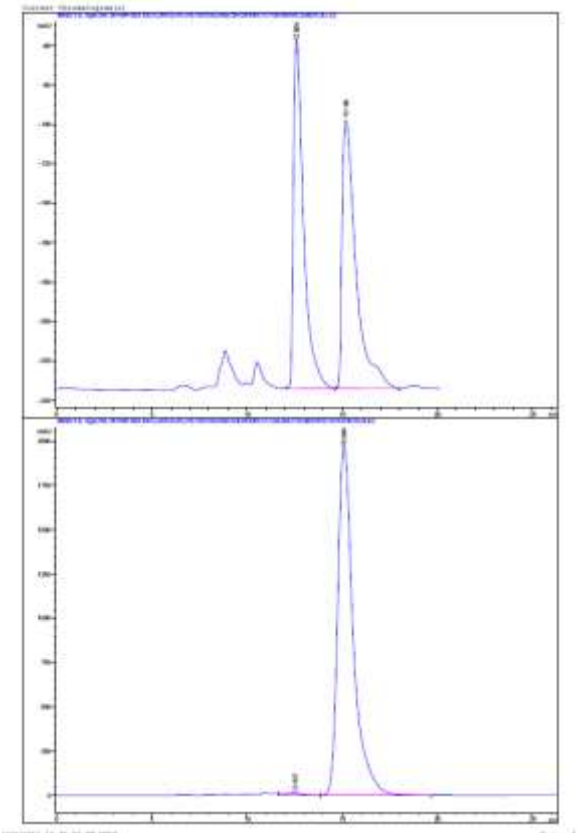

Figure S23. First cycle of Hydrogenation of (*E*)-diethyl 2-benzylidene succinate with **3bRuMCM-41**

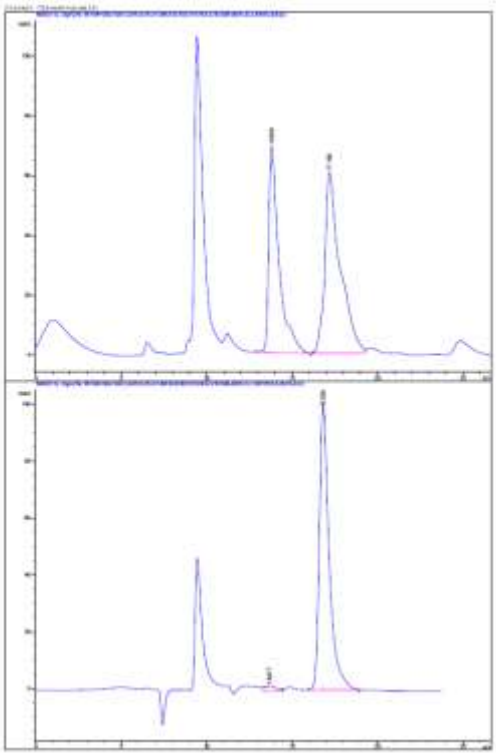

Figure S24. First cycle of hydrogenation of (*E*)-diethyl 2-benzylidene succinate with **4bRuMCM-41**

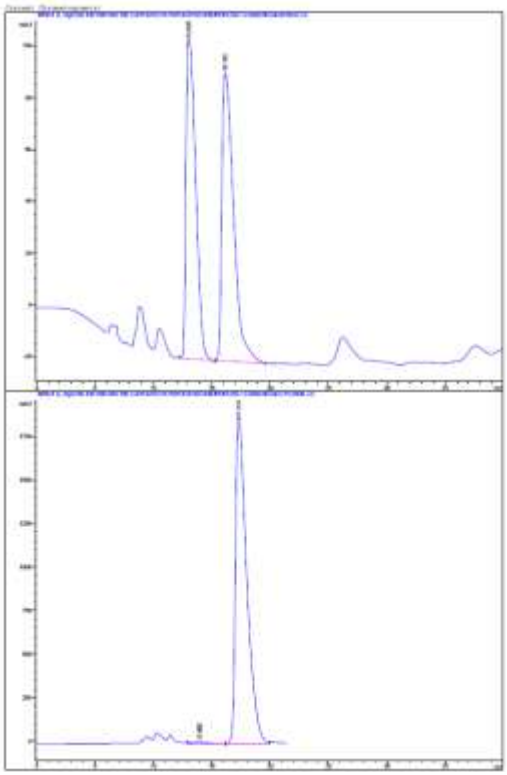

Figure S25. Second cycle of hydrogenation of (*E*)-diethyl 2-benzylidene succinate with **4bRuMCM-41**

## HPLC traces for cyclopropanation of styrene

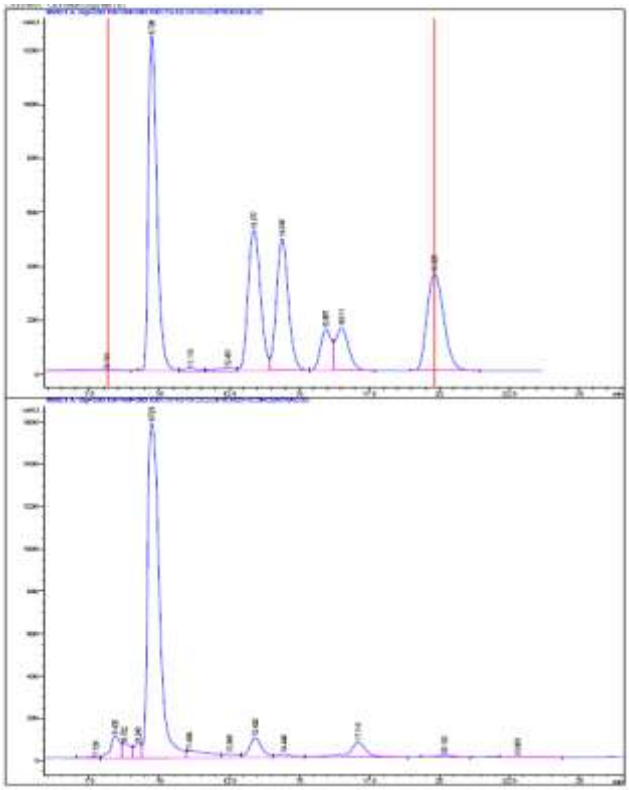

Figure S26. Cyclopropanation of styrene with EDA with **3b´Ru$_{p\text{-cym}}$**

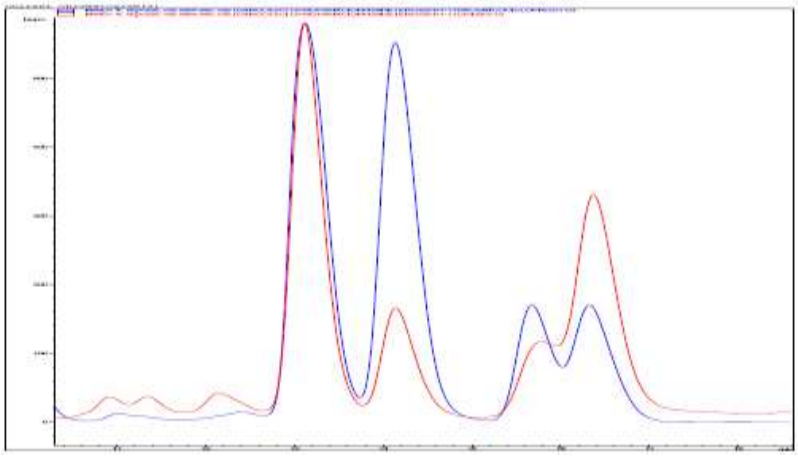

Figure S27. Cyclopropanation of styrene with EDA with **3b´Ru$_{p\text{-cym}}$MCM-41**

**Recycling experiments of hydrogenation reaction**

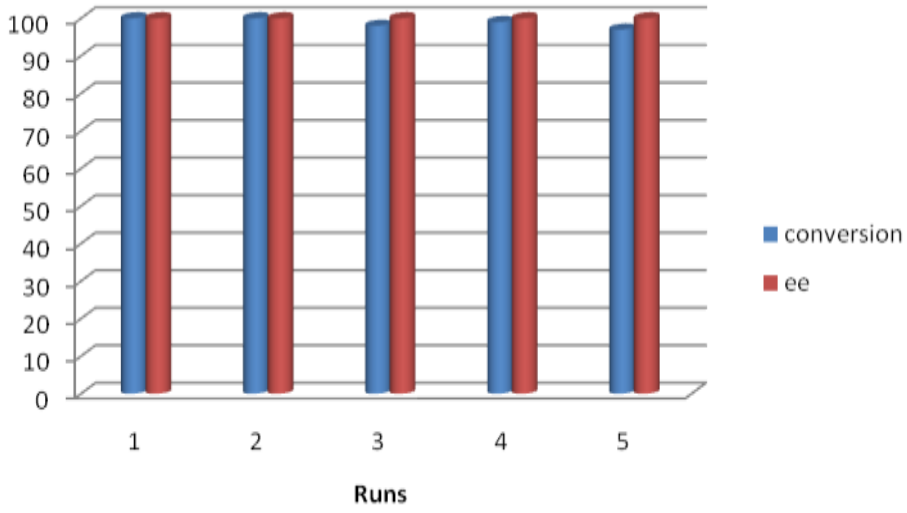


Figure S28

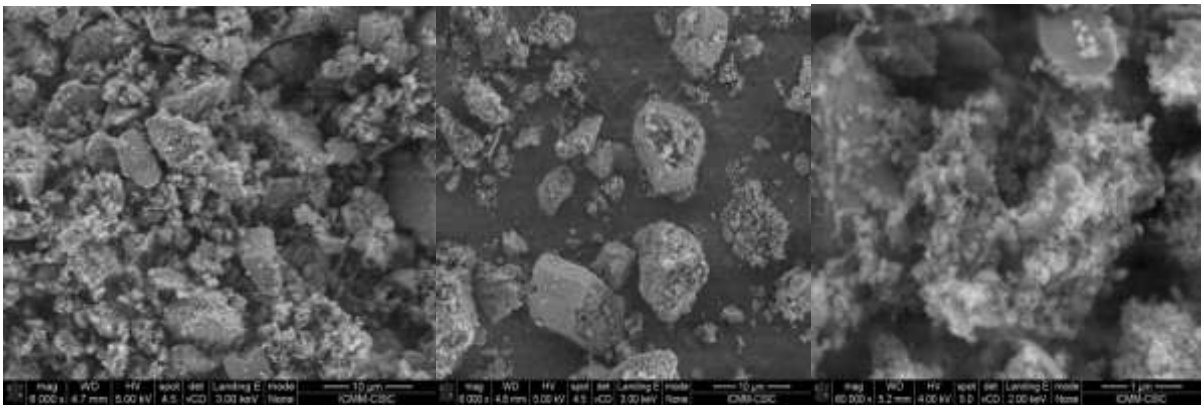

Figure S29. Scanning electron microscopy images (SEM) of **3bRuMCM-41** before reaction.

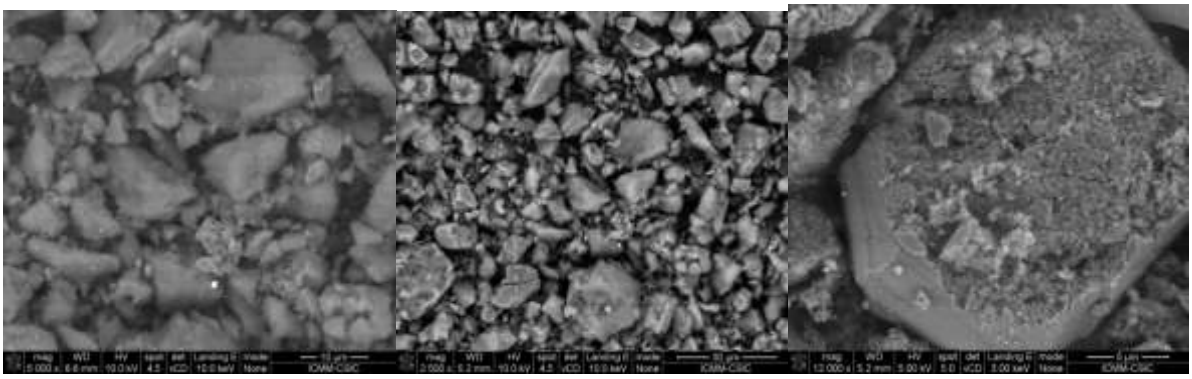

Figure S30. Scanning electron microscopy images (SEM) of **3bRuMCM-41** after reaction.

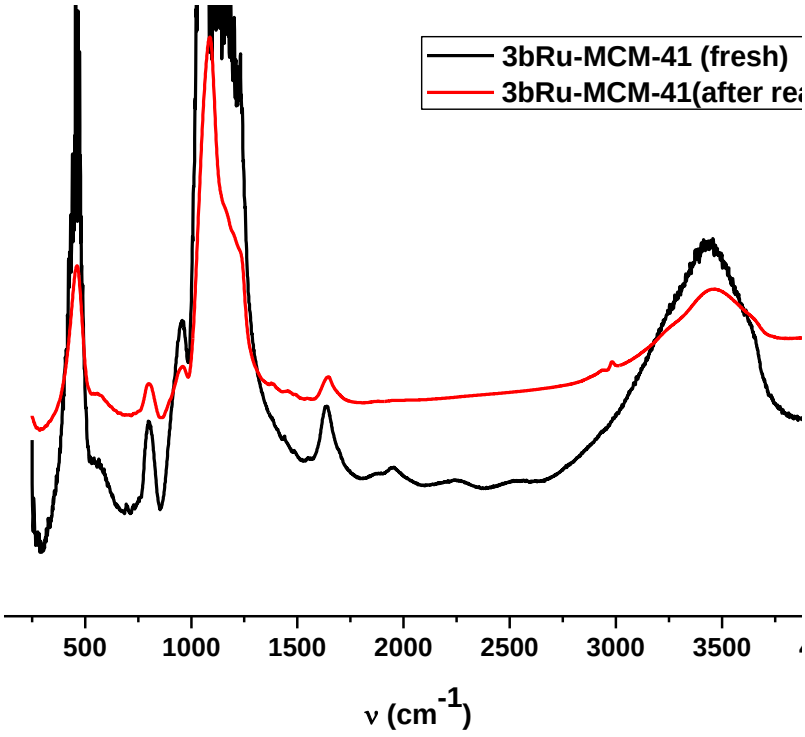


Figure S31

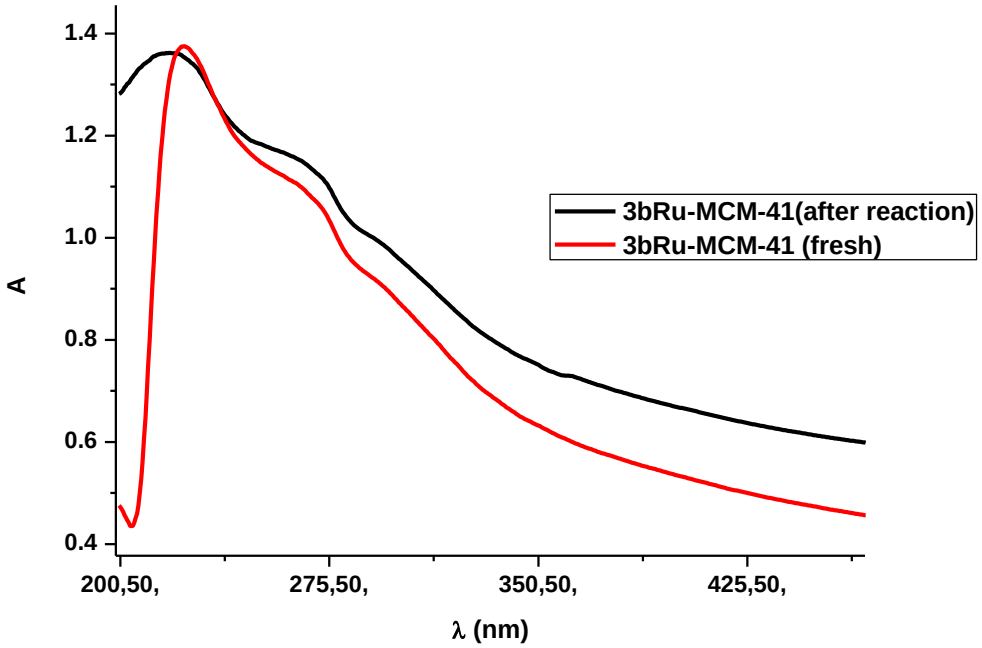


Figure S32

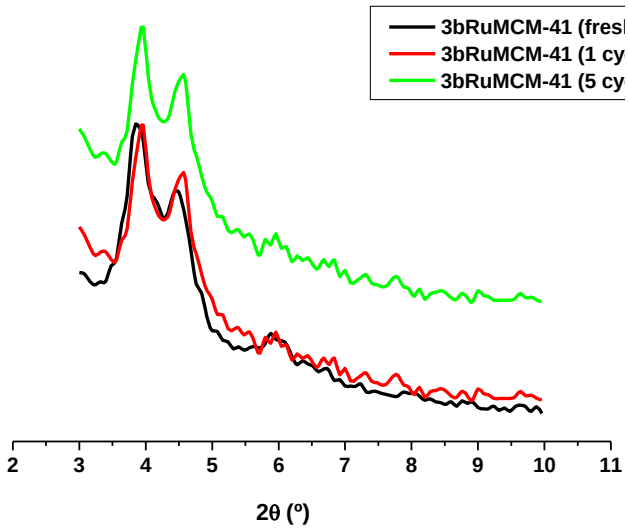


Figure S33. PXRD spectra of fresh **3dRuMCM-41** and this material recovered after fifth runs.

**Table 5.** Recycling experiments in the cyclopropanation of styrene with EDA catalyzed by **3b'Ru$_{p\text{-cym}}$MCM-41** in $CH_2Cl_2$ at room temperature

| Run | Yield[%][a] | *cis/trans* | ee [%][b] | |
|---|---|---|---|---|
| | | | *trans* | *cis* |
| 1 | 41 (48h) | 40/50 | 65 | 50 |
| 2 | 30 (48h) | 50/50 | 65 | 50 |
| 3 | 30 (48h) | 50/50 | 65 | 50 |

[a] Selectivity toward cyclopropanecarboxylates. [b]Determined by chiral HPLC and GC.