Supplementary Information

Enantioselective aerobic oxidation of olefins by magnetite nanoparticles at room temperature: a chiral carboxylic acid strategy

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Content

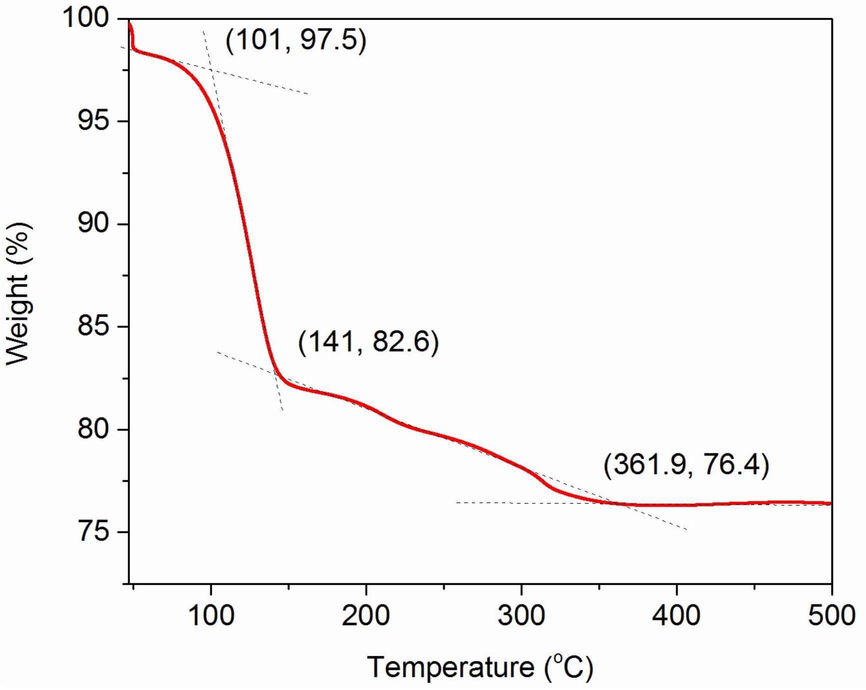


Fig. S1 Thermal gravimetric analysis of Fe_3O_4/tar-NPs

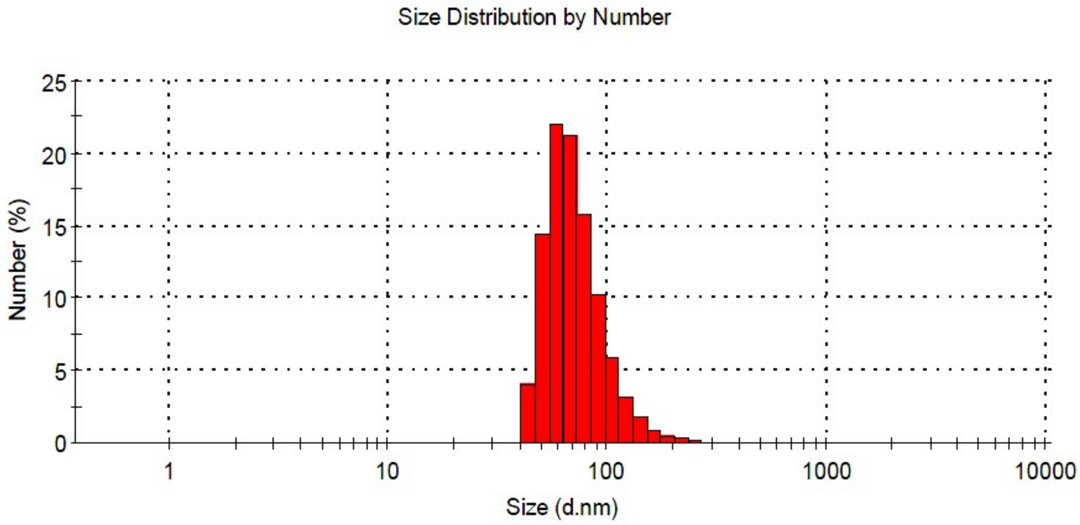


Fig. S2 Example of a histogram of the number-size-distribution for Fe_3O_4/tart-NPs from dynamic light scattering (DLS) with medium diameter (hydrodynamic diameter) of 74 nm.

The magnetic properties of the synthesized Fe_3O_4/tart-NPs were analyzed by vibrating sample magnetometry (VSM). The field-dependent magnetization curve shown in Fig. 5 indicates the magnetization as a function of applied magnetic field, measured at room temperature. The magnetization value of Fe_3O_4/tart-NPs is approximately the same with the value of Fe_3O_4-NPs and higher than the magnetization of core-shell Fe_3O_4/SiO_2-NPs.[1] This finding shows the negligible effect of diamagnetic tartaric acid coating over the Fe_3O_4-NPs and a favorable property for magnetic separation by a conventional magnet. The hysteresis loops of the powdered material showed no magnetic hysteresis, with both the magnetization and demagnetization curves passing through the origin, which clearly indicates the superparamagnetic nature of the material. Moreover, the synthesized heterogeneous nanocatalysts possess strong magnetic responsivity due to a high saturation magnetization value (55 emu g^{-1}).

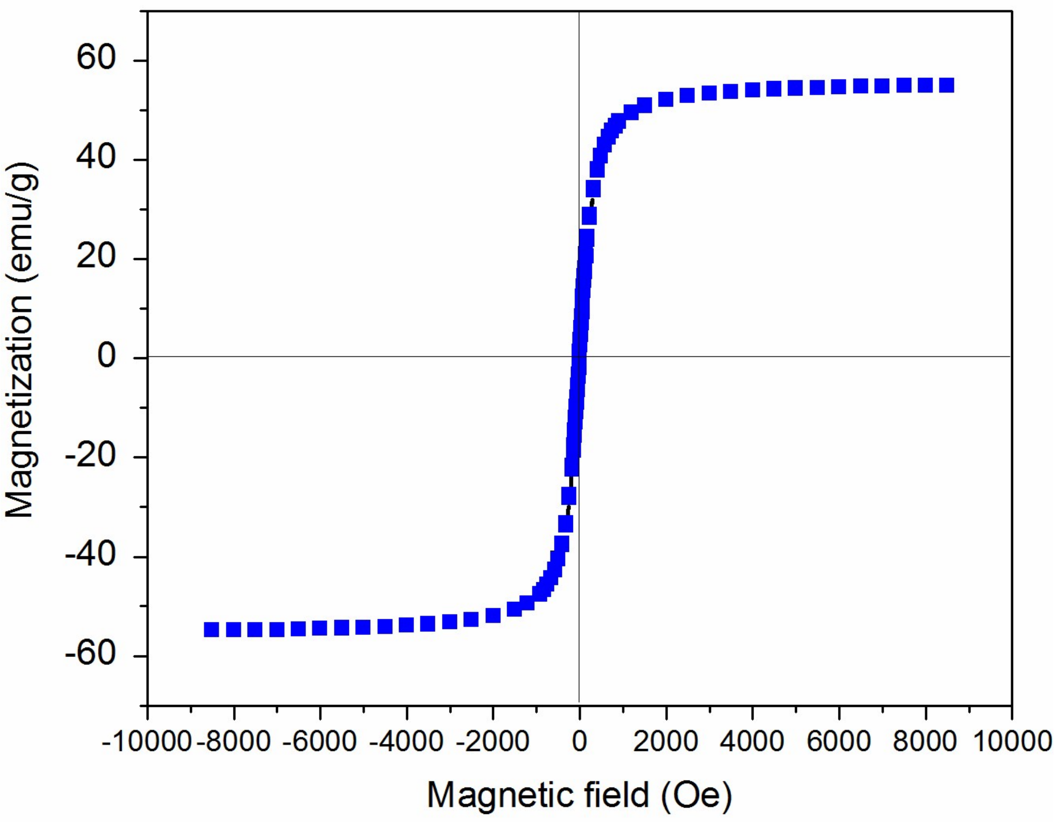


Fig. S3 Magnetization curve of Fe_3O_4/tart-NPs.

Ménage *et al.* used chiral bipyridine to construct a catalytically-active diiron complex which was effective in the epoxidation of a range of olefins in up to 63% ee (for *trans*-b-methylcinnamate; 35% yield) using 0.2 mol% of catalyst with peracetic acid as the oxidant.[2] The majority of olefins were oxidised in rather low ee (max 28%) however. The results of the oxidation of *cis*- and *trans*-stilbene by dioxygen in the presence of some homogeneous and heterogeneous iron catalysts are compared with catalyst Fe_3O_4/tart-NPs in Table S1. In addition to epoxide selectivity and conversion percent, the reaction conditions of room temperature, O_2 pressure 2 bar and reaction time of 7 h for our new catalyst Fe_3O_4/tart-NPs are greatly remarkable.

Table S1 Comparison of the olefin oxidation by different catalysts [a]

Entry	Catalyst	Substrate	Conditions (sol, T, t, atm, additives or co-catalyst)	Conversion (%)	Epoxide Selectivity (%)	Ref
1	$FeCl_3·6H_2O$	*trans*-stilbene *cis*-stilbene	CH_3CN, rt, 20 h, O_2 1 atm, imidazole/β-keto ester	91 28	26 35	3
3	Fe^{2+}-NaY	*trans*-stilbene α-methylstyrene	DMF, 100 °C, 24 h, O_2 40 atm, no additive	34 82	60 12	4
4	$[NMe_4]_3[Fe(opba)(CO_3)]·5H_2O$ (opba = *ortho*-phenylenebis(oxamato))	*trans*-stilbene *cis*-stilbene	Fluorobenzene, rt, 3 h, O_2 1 atm, pivaldehyde	95 20	95 15	5
5	Fe_3O_4/tart-NPs	*trans*-stilbene *cis*-stilbene	CH_3CN, 25 °C, 7 h, O_2 atm, isobutyraldehyde	100 100	56 92	This work

[a] S = substrate; sol = solvent; T = temperature; t = time; atm = gas atmosphere.

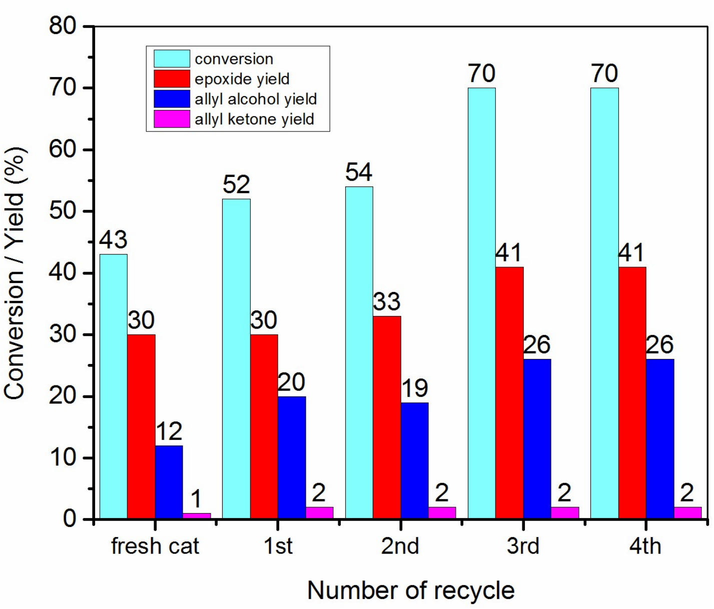


Fig. S4 Reuse of the catalyst in the aerobic oxidation of cyclohexene**.**

Conditions: catalyst Fe_3O_4/tart-NPs 1.0 mg, isobutyraldehyde 5 mmol, substrate 2 mmol, CH_3CN 3 ml, chlorobanzene 0.1 g, oxygen 2 bar, time 7 h at 25 °C.

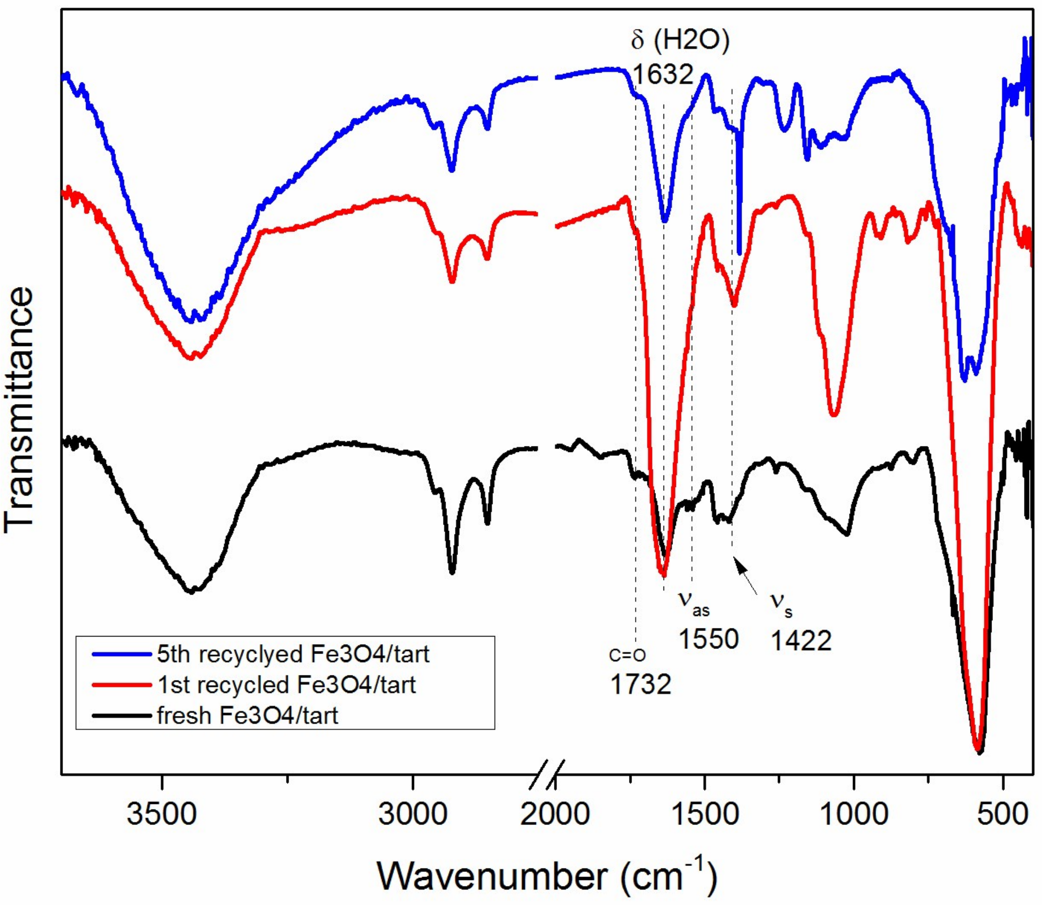


Fig. S5. Comparison of the FT-IR spectra of the fresh and used Fe_3O_4/tart-NPs

The textural properties of fresh Fe_3O_4/tart-NPs and used Fe_3O_4/tart-NPs were monitored by N_2 adsorption–desorption analysis and the structural parameters for these materials are presented in Table S2. The used catalyst shows an increase in its specific surface area and pore volume (Fig. S6). The surface area of the used catalyst Fe_3O_4/tart-NPs increased from 85.454 $m^2\ g^{-1}$ to 107.580 $m^2\ g^{-1}$ after two times recycle.

Table S2 Textural properties of fresh Fe_3O_4/tart-NPs and used Fe_3O_4/tart-NPs.

Catalyst	Surface area ($m^2\ g^{-1}$)	Pore volume ($cm^3\ g^{-1}$)	Pore diameter (nm)
Fresh Fe_3O_4/tart-NPs	85	0.19	8.77
Used Fe_3O_4/tart-NPs	108	0.1 9	7.06

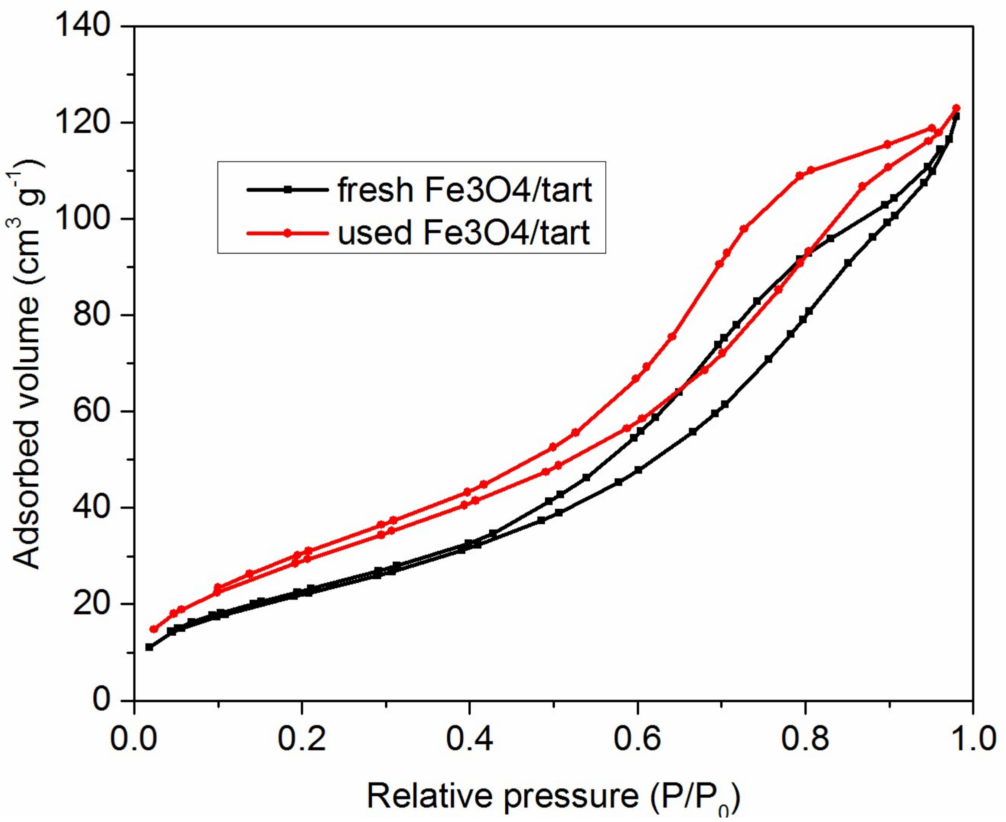
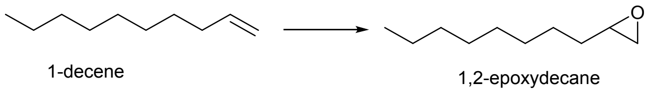


Fig. S6 Nitrogen adsorption-desorption isotherm of the fresh Fe_3O_4/tart-NPs and used Fe_3O_4/tart-NPs after catalysis



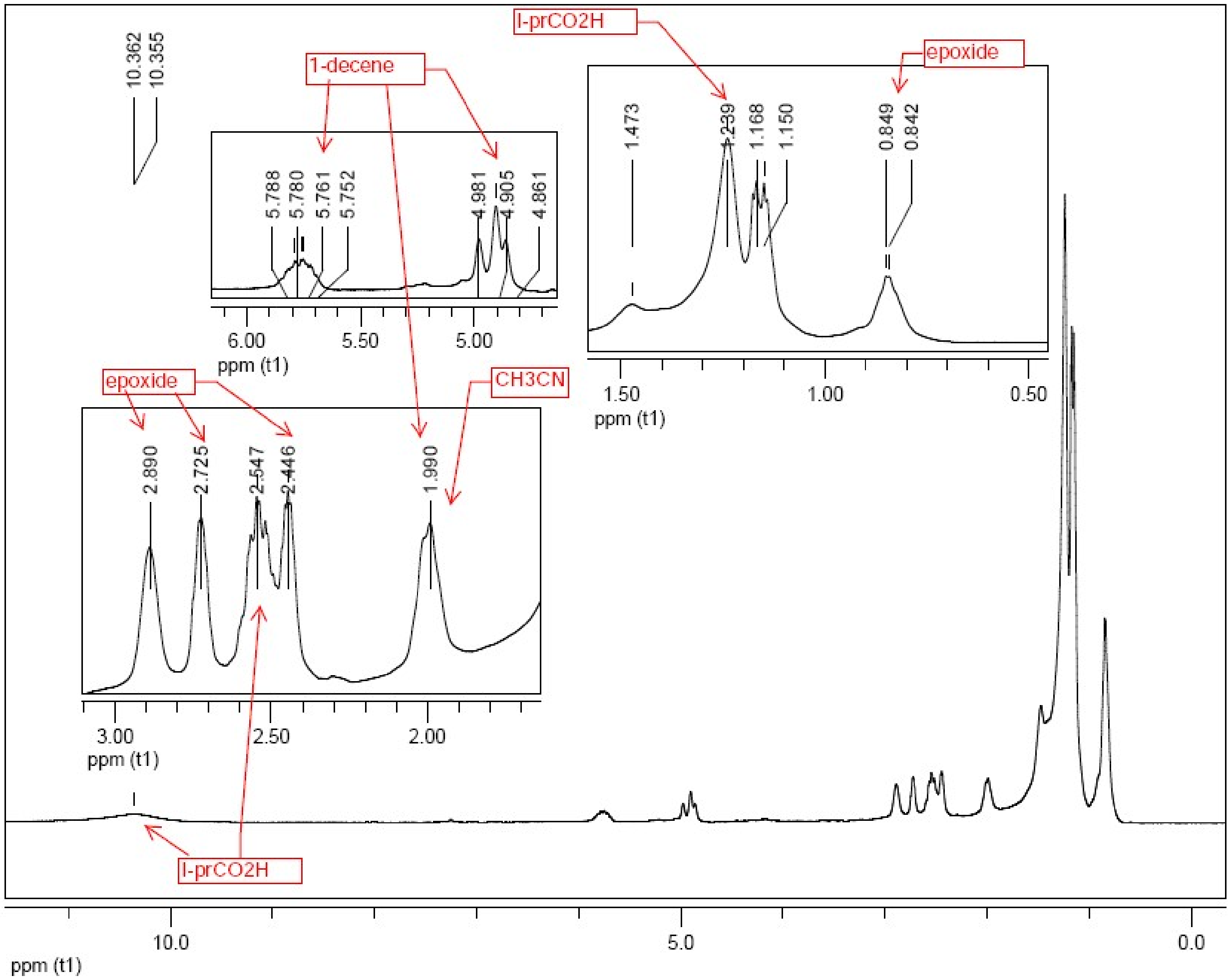


Fig. S7 ^{1}H NMR spectrum in $CDCl_3$ of the crude product obtained upon oxidation of 1-decene provided 77% conversion with 1,2-epoxydecane 77%.

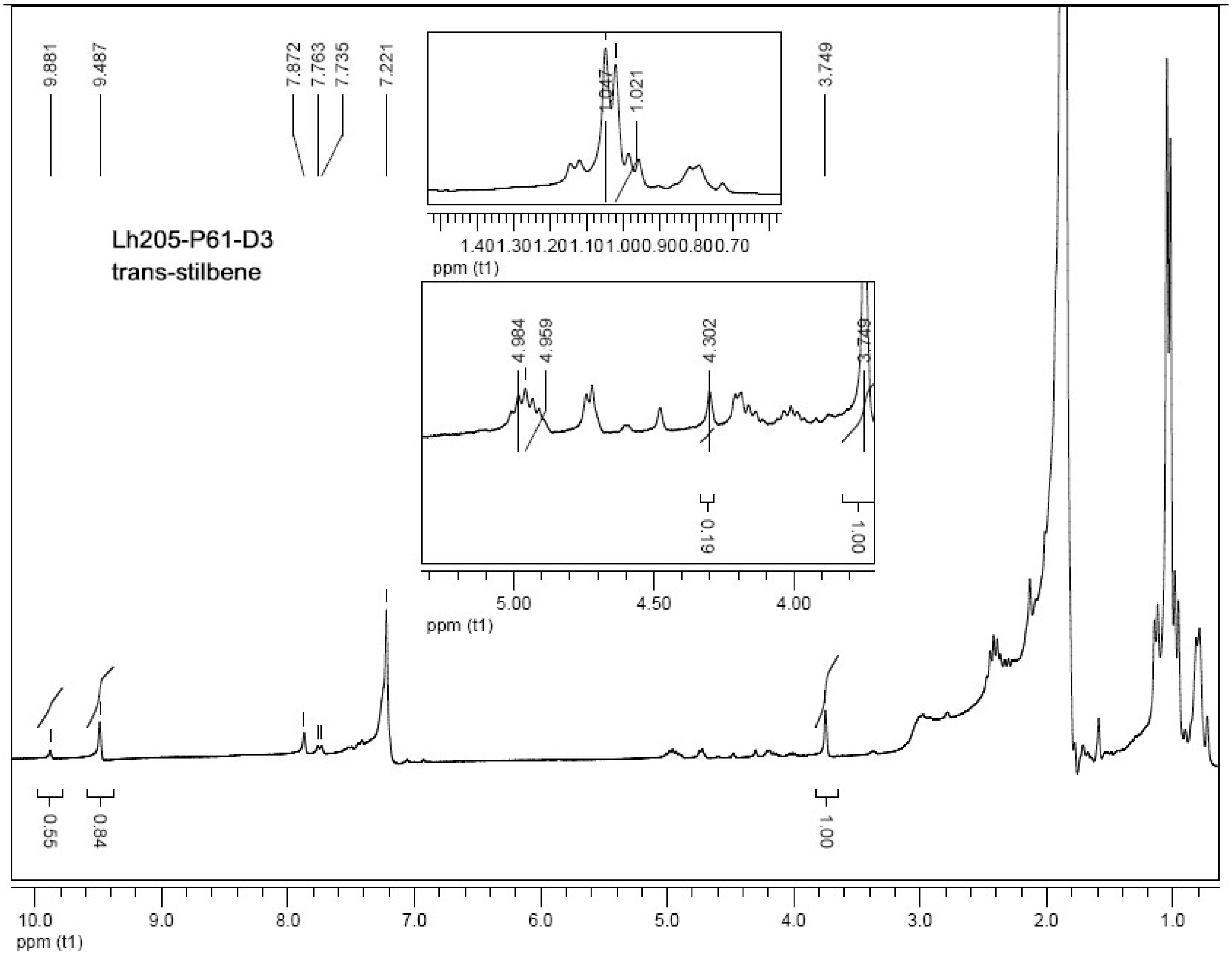


Fig. S8 ^{1}H NMR spectrum in $CDCl_3$ of the crude product obtained upon oxidation of trans-stilbene provided 100% conversion with trans-stilbene oxide 48%, cis-stilbene oxide 8% and benzaldehyde 44%.

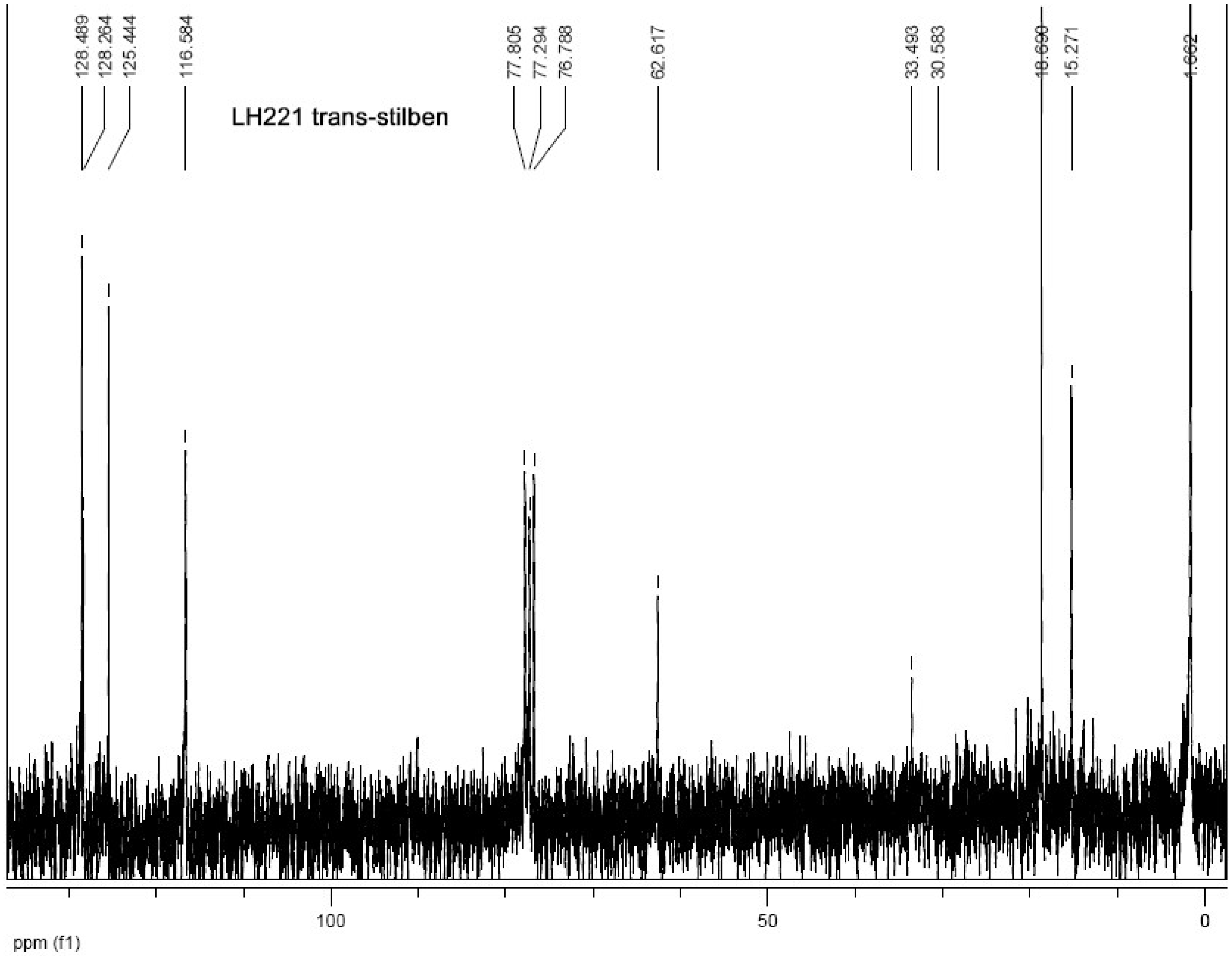


Fig. S9 ^{13}C NMR spectrum in $CDCl_3$ of the crude product obtained upon oxidation of *trans*-stilbene

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