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Supporting information

Platinum Functionalized Multiwall Carbon Nanotube Composites as Recyclable Catalyst for Highly Efficient Asymmetric Hydrogenation of Methyl Pyruvate

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1. TEM and SEM Images of Catalysts

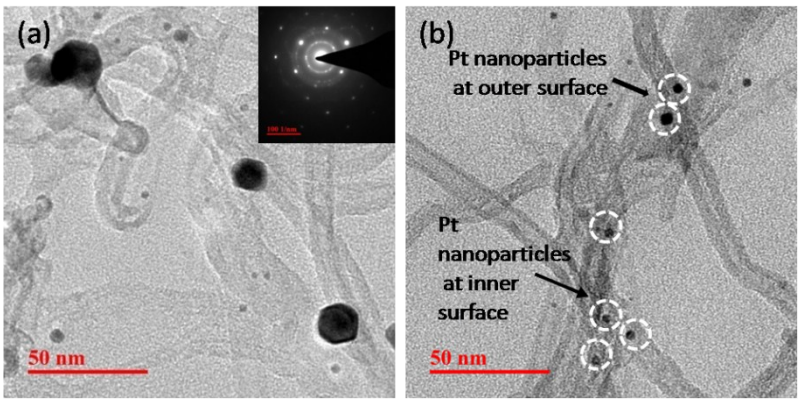

Fig.S1 (a) and (b) TEM images of MWNT(inset shows ED pattern).

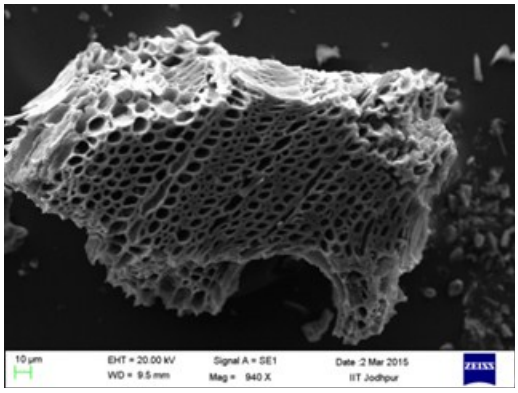

Fig.S2 SEM image of activated carbon.

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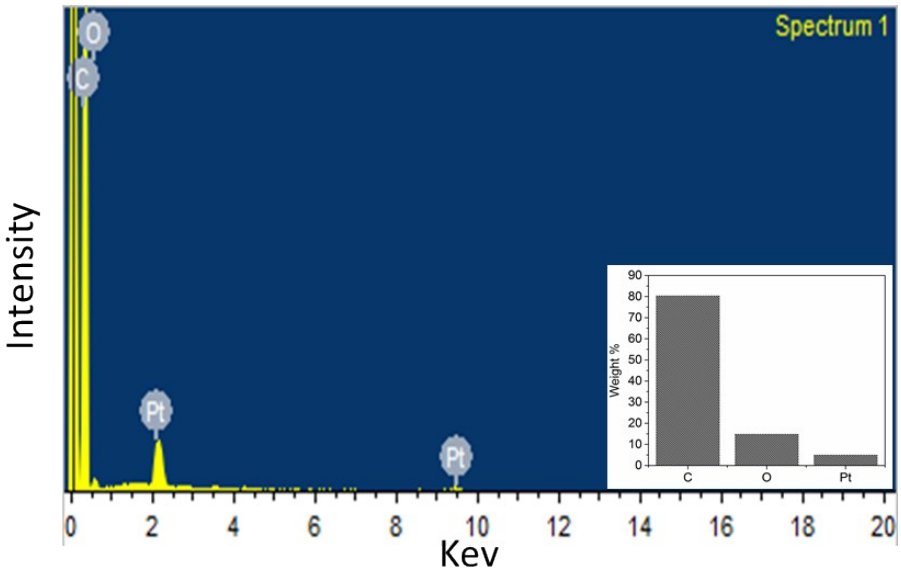

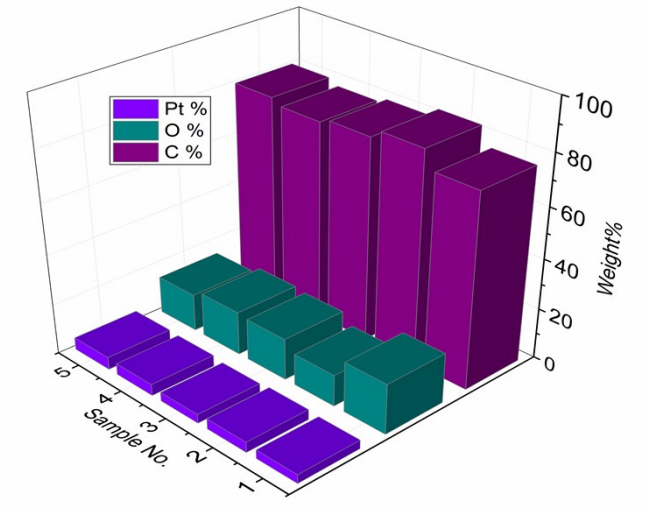

Sample No.	Pt %	O %	C %
1	3.5	20	76.5
2	4.1	12.5	83.4
3	3.5	16.5	80
4	4.5	17.3	78.2
5	4.9	14.8	80.3

Fig.S3 Typical EDX of Pt/MWNT.

Fig.S4 Atomic weight distribution for five different samples of Pt/MWNT.

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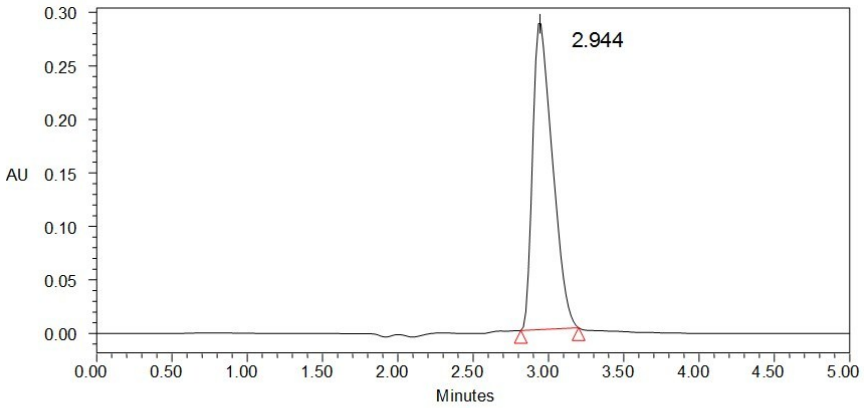
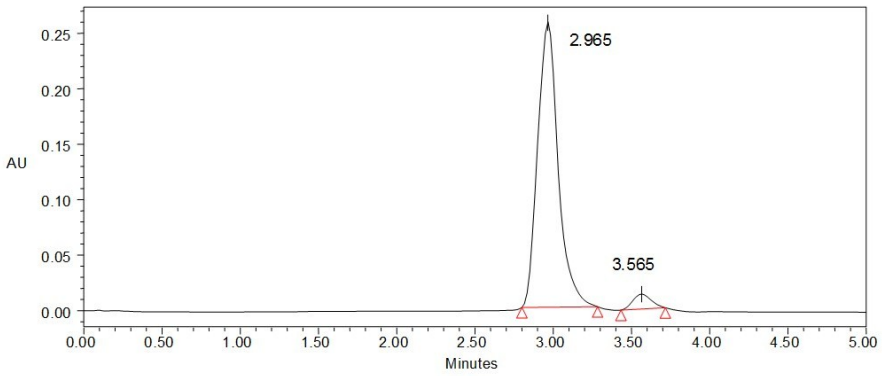
2. HPLC analysis

The enantiomerically excess was determined by HPLC analysis employing a chiral column from waters 2489 (Hexane: i-propanol:: 90:10 with 0.1% $Na_2B_2O_7$ buffer, 1.0 ml/min, λ = 220 nm, t_1= 2.9 min for *R* enantiomer, t_2 = 3.4 min for the *S* enantiomer). It has been established that the R enantiomer elute first by specific rotation. Selective chromatograms are given below for various catalysts.



Name	Retention Time	Area	% Area	Height
(R)-(+)-Methyl lactate	2.944	2609171	100.00	284596

Fig.S5 HPLC chromatogram of asymmetric heterogeneous hydrogenation of methyl pyruvate on Pt/MWNT.



Name	Retention Time	Area	% Area	Height
(R)-(+)-Methyl lactate	2.965	2341750	95.54	256803
(S)-(-)-Methyl lactate	3.565	109322	4.46	13403

Fig.S6 HPLC chromatogram of asymmetric heterogeneous hydrogenation of methyl pyruvate on Pt/Graphene.

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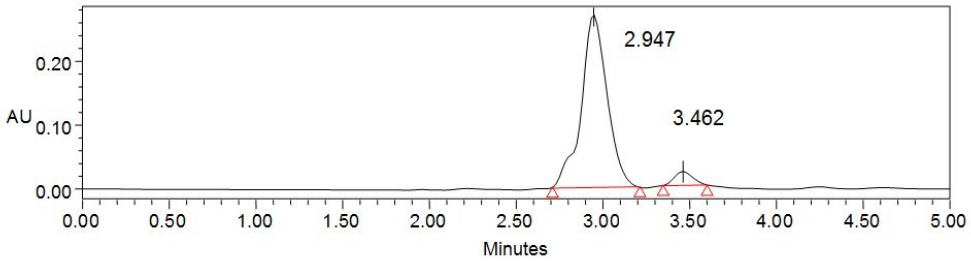
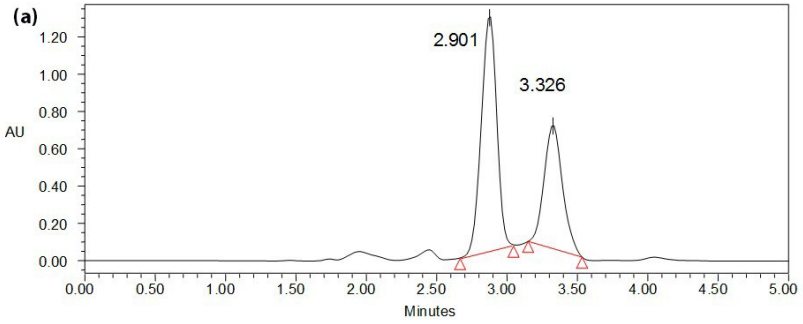
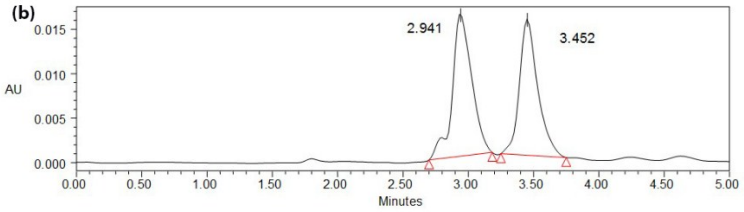


Name	Retention Time	Area	% Area	Height
(R)-(+)-Methyl lactate	2.947	2801796	94.57	269505
(S)-(-)-Methyl lactate	3.462	160877	5.43	21586

Fig. S7 HPLC chromatogram of asymmetric heterogeneous hydrogenation of methyl pyruvate on Pt/Carbon Fiber.



Name	Retention Time	Area	% Area	Height
(R)-(+)-Methyl lactate	2.901	19491979	65.70	2469177
(S)-(-)-Methyl lactate	3.326	13712242	34.30	1489737



Name	Retention Time	Area	% Area	Height
(R)-(+)-Methyl lactate	2.941	165632	52.57	16084
(S)-(-)-Methyl lactate	3.452	149427	47.43	15268

Fig. S8 (a) HPLC chromatogram of asymmetric heterogeneous hydrogenation of methyl pyruvate on commercial Pt/AC. (b) Chromatogram of racemic mixture obtained from reaction without using chiral modifier.

3. FT-IR analysis

Fourier-transform infrared spectra (FT-IR) of the samples were recorded on a Vertex 70 v spectrometer (Bruker) in the range of 400-4000 cm^{-1} with acetic acid as the reference sample. Measurements were performed in the transmission mode with

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spectroscopic grade acetic acid solvent for all liquid samples. Product functional group are observed at 3345.54 cm^{-1} (-OH), 2975.21 cm^{-1} (-C–H), 1000-1266 cm^{-1} (-C-O-), 1379.33 cm^{-1} (-C–H), 1084 cm^{-1} (-CH_3), 1052 cm^{-1} (-O–C), 1710.34 cm^{-1} (-C=O) and 831/827 cm^{-1} (-*C*-*C*-,-*C*-*H*-).

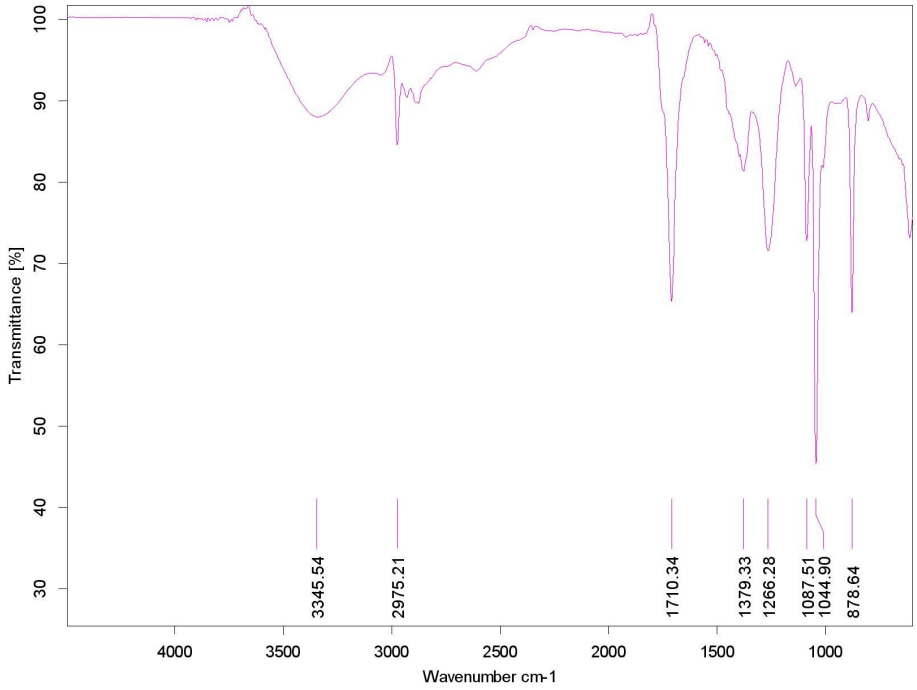

Fig.S9 IR spectrum of methyl lactate.

4. UV visible spectroscopy

UV visible spectroscopy data were carried on Varian Cary 4000 in the range of 200-800 nm.In case of methyl pyruvate two absorption peaks are observed at 210-238 nm and 332.86 nm. Hydrogenation of methyl pyruvate gave methyl lactate by reducing the carbonyl group to hydroxyl group. In that case methyl lactate gave only one peak at 210-250 nm.

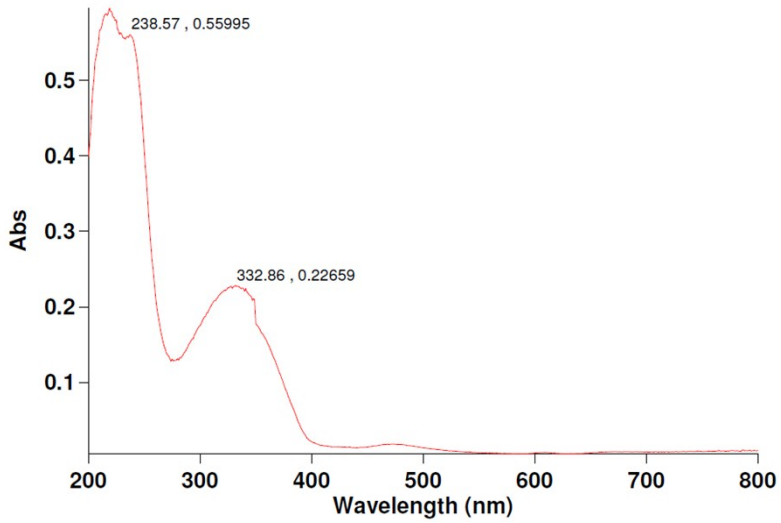

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Fig.S10 UV-vis spectrum of methyl pyruvate.

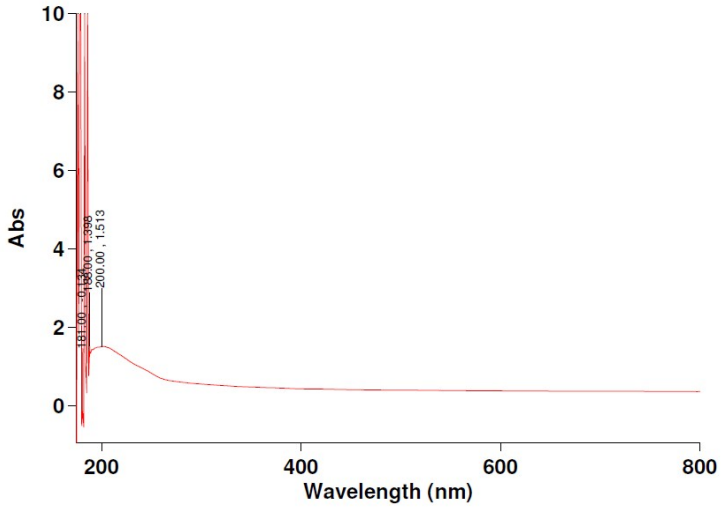

Fig.S11 UV-vis spectrum of methyl lactate.

5. NMR Spectra

Nuclear magnetic resonance spectra (^{1}H NMR) were recorded on a Bruker 500 spectrometer operating at 500 MHz for ^{1}H ($CDCl_3$). Chemical shift for ^{1}H NMR spectra are reported as δ in parts per million (PPM) downfield from $SiMe_4$ (δ 0.0) and relative to the signal of chloroform-d (δ7.26, singlet)

Methyl lactate

^{1}H NMR ($CDCl_3$, 500 MHz) δ: 1.41 (d, 3 H, J = 7.05 Hz, CH_3), 2.93 (d, 1 H, J = 5 Hz OH, D_2O exchangeable), 3.79 (s, 3 H, CH_3), 4.29 (q, 1 H, J = 6.94 Hz, CH).

^{13}C NMR ($CDCl_3$, 125 MHz) δ: 20, 52.2, 66.7, 175.7

$[\alpha]_D^{20^\circ C}$ = +8.9 (C 1.5, 1,4-dioxane)

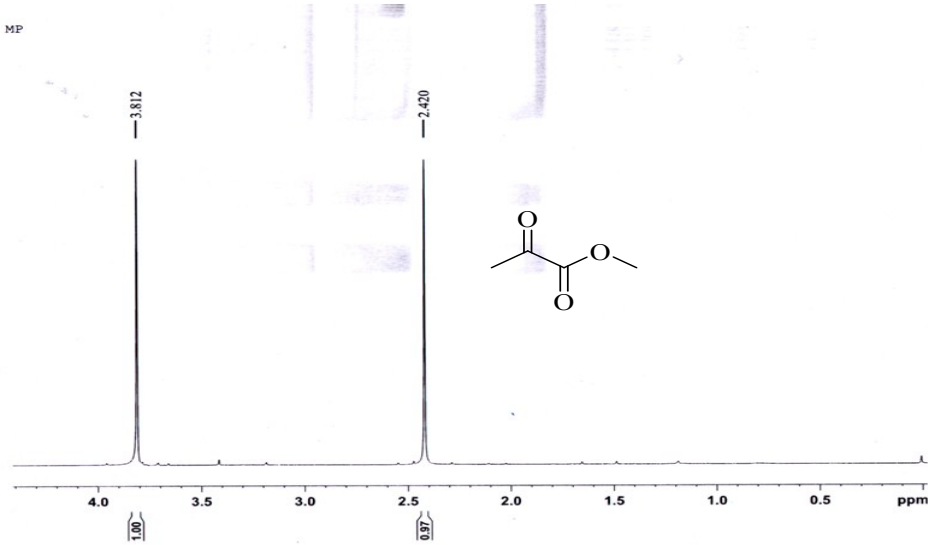

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Fig.S12 [1]H NMR spectrum of methyl pyruvate.

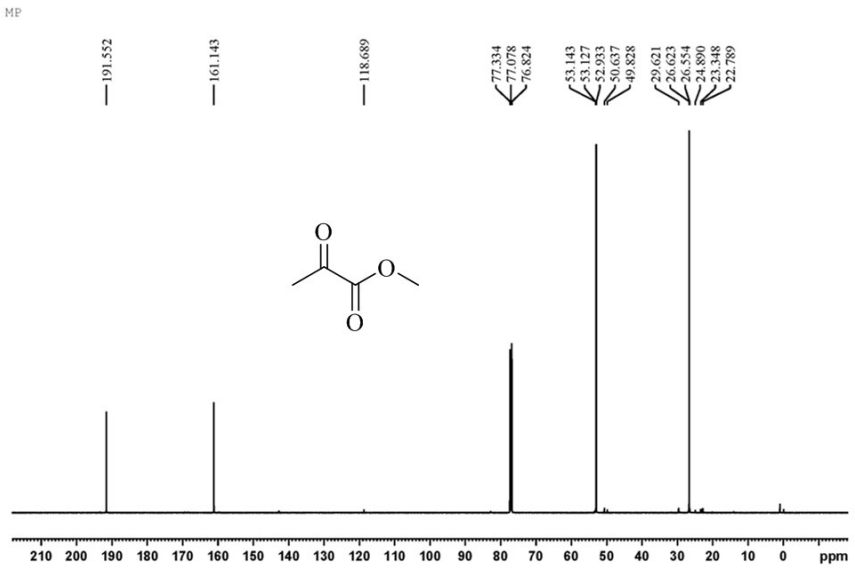

Fig.S13 [13]C NMR spectrum of methyl pyruvate.

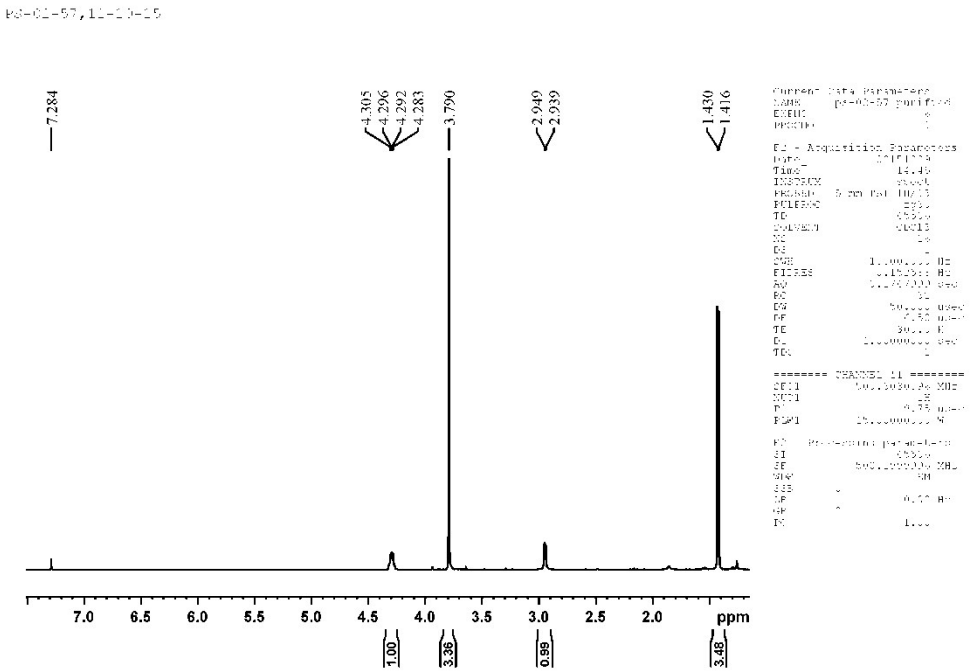

Fig. S14 [1]H NMR spectrum of purified product (Methyl lactate).

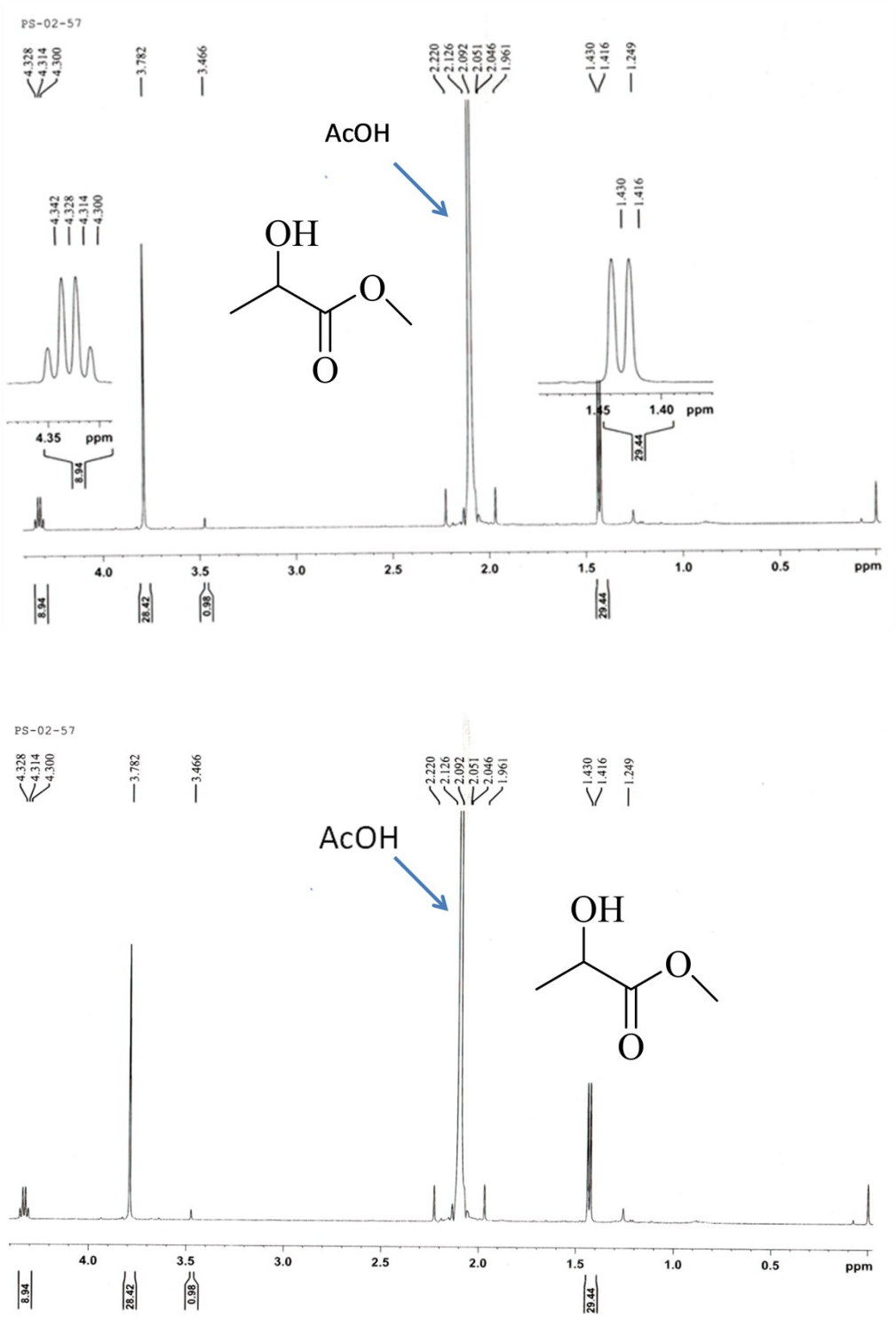

Fig. S15 ^{1}H NMR spectrum of crude product.

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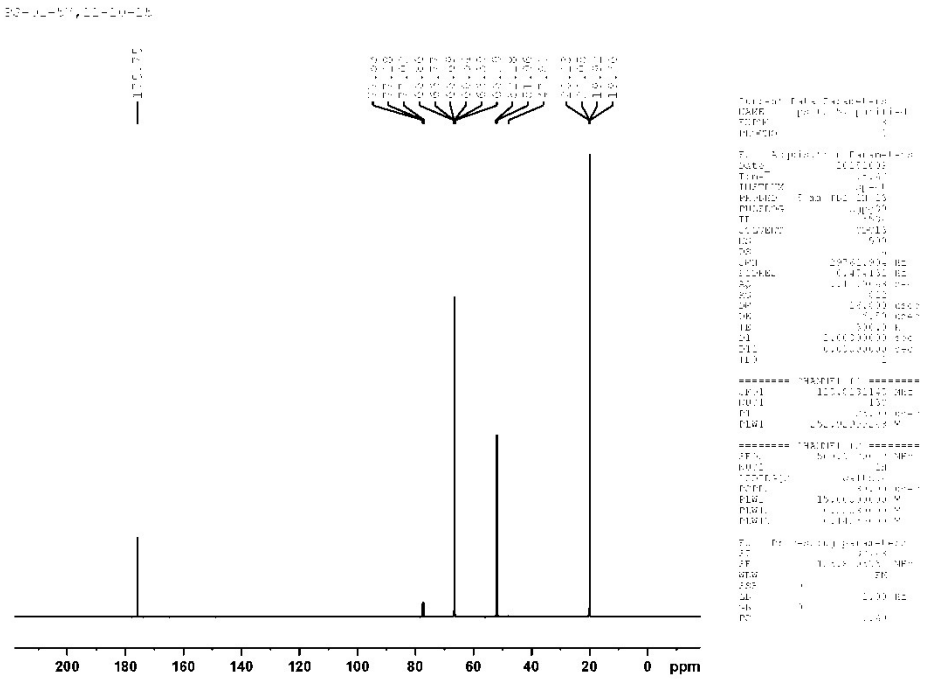
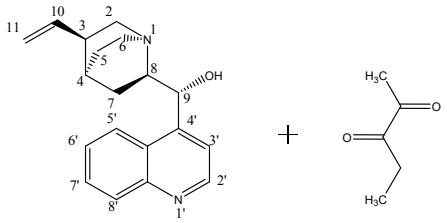
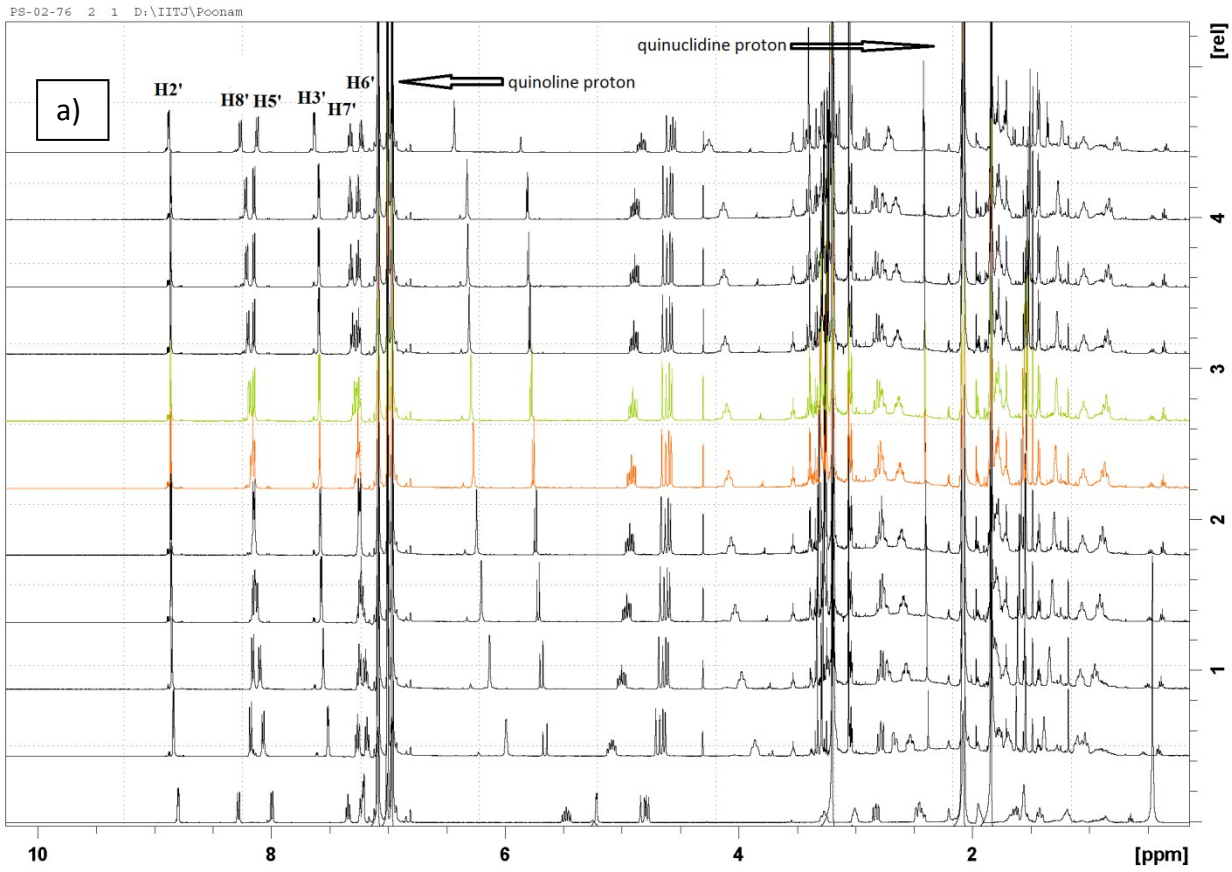


Fig.S16 ^{13}C NMR spectrum of purified product (Methyl Lactate).

6. Time dependent NMR studies for substrate-modifier-catalyst interaction.





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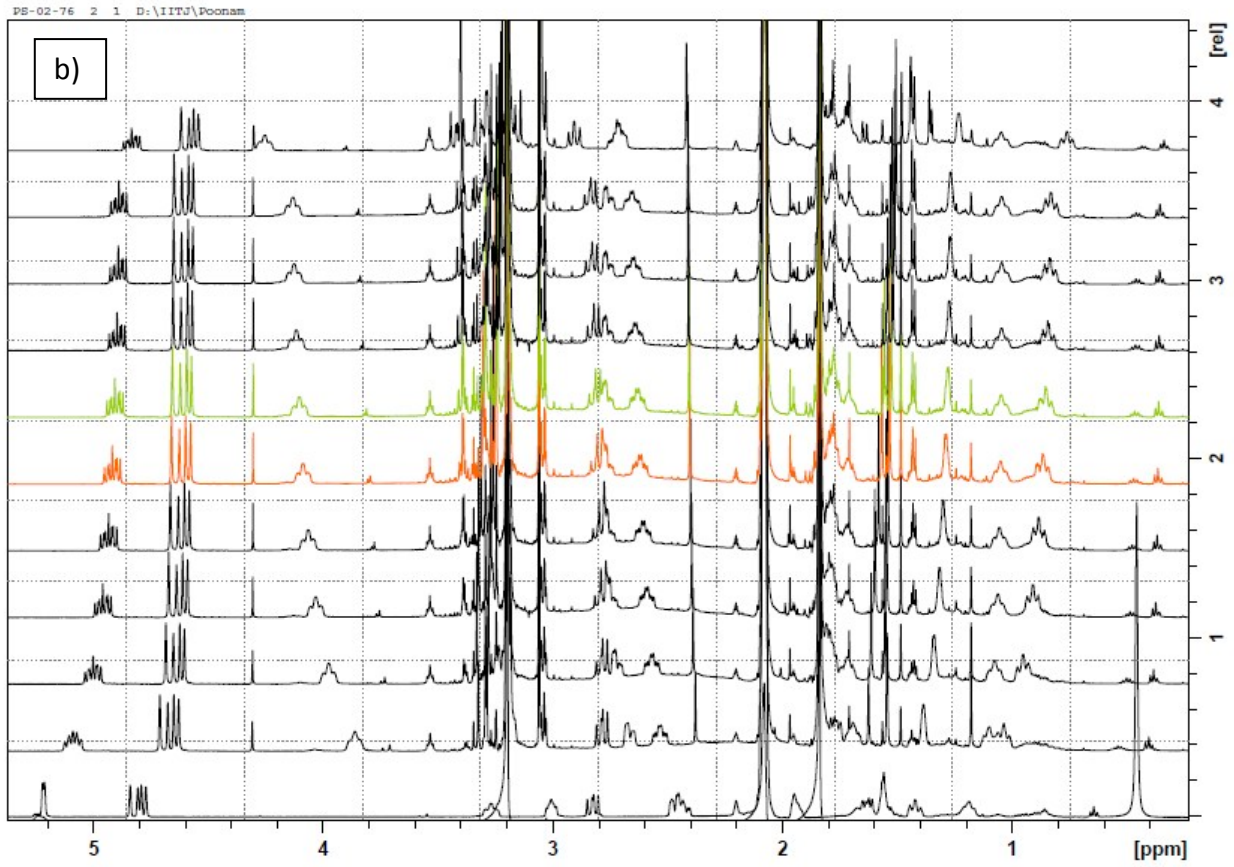
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b)
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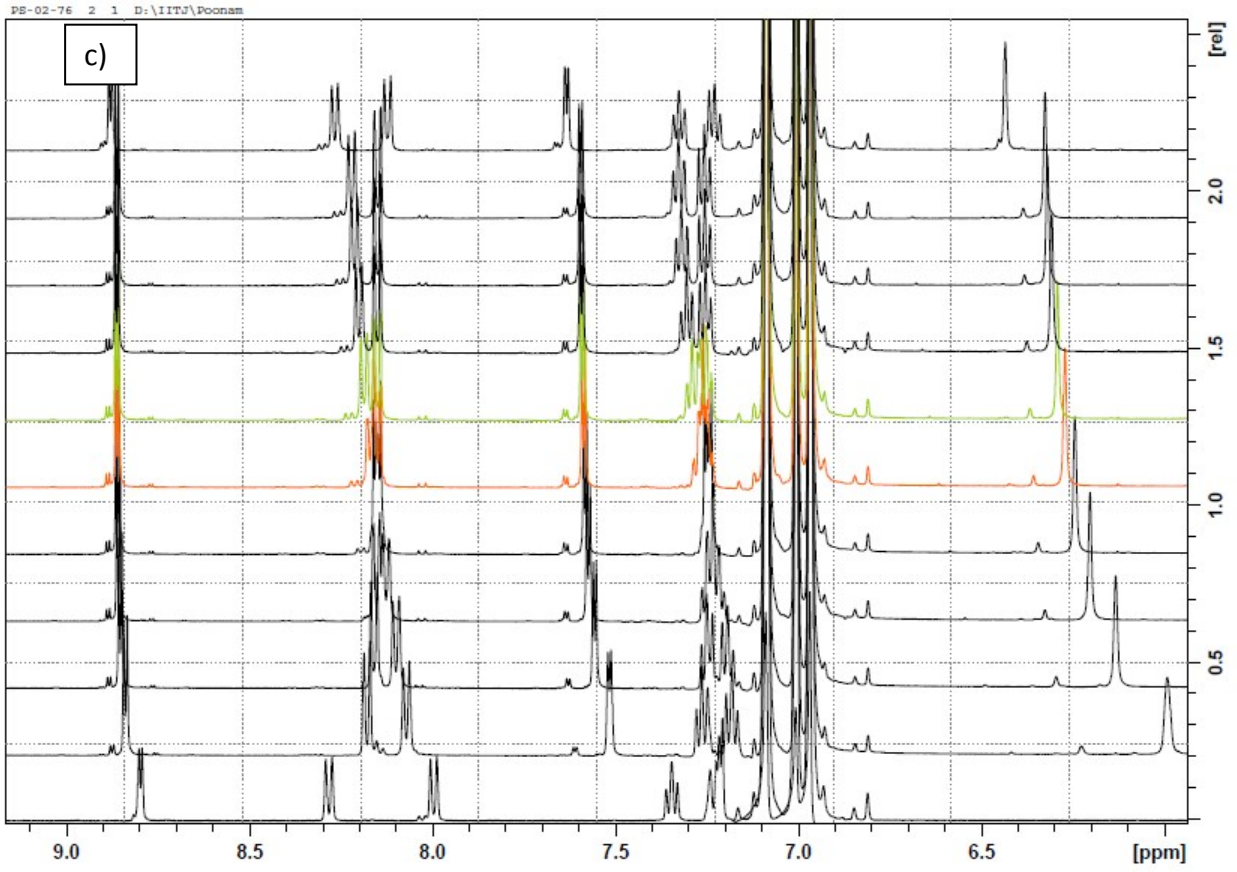
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c)
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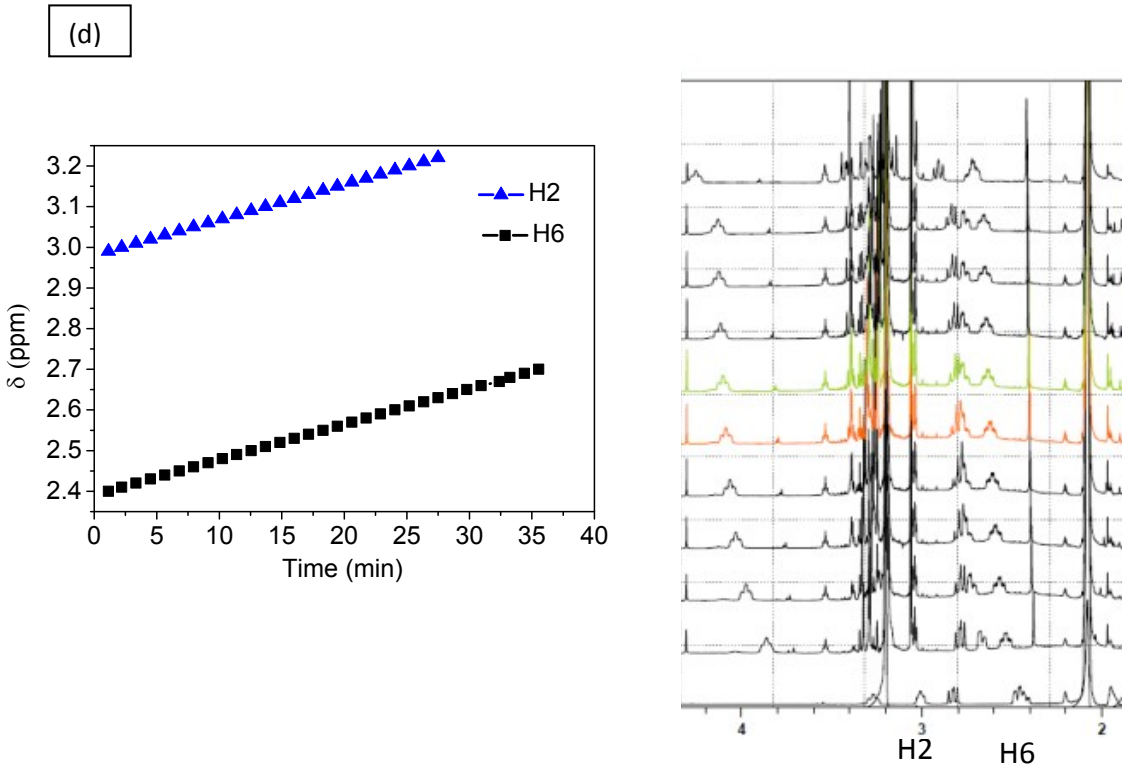

Fig.S17 NMR spectrum of Methyl pyruvate and CD interaction (a, b, c) full spectra (d) chemical shift of H2 and H6 proton.

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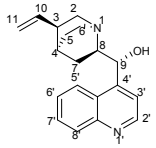
Table S1: Chemical shift during interaction of CD and Methyl pyruvate.



Cinchonidine

Proton	CD	CD + Methyl pyruvate
H2’	8.79	8.87
H3’	7.20	7.62
H5’	8.27	8.11
H6’	7.24	7.31
H7’	7.33	7.24
H8’	7.98	8.25
H6AX	2.40	2.68
H6EQ	2.20	2.20
H5AX	1.61	1.78
H5EQ	1.56	1.42
H4	1.61	1.49
H3	2.11	1.81
H2AX	2.99	3.04
H2EQ	3.24	4.22
H7AX	0.854	0.74
H7EQ	0.633	0.34
H8	2.808	2.88
H9	5.21	5.87

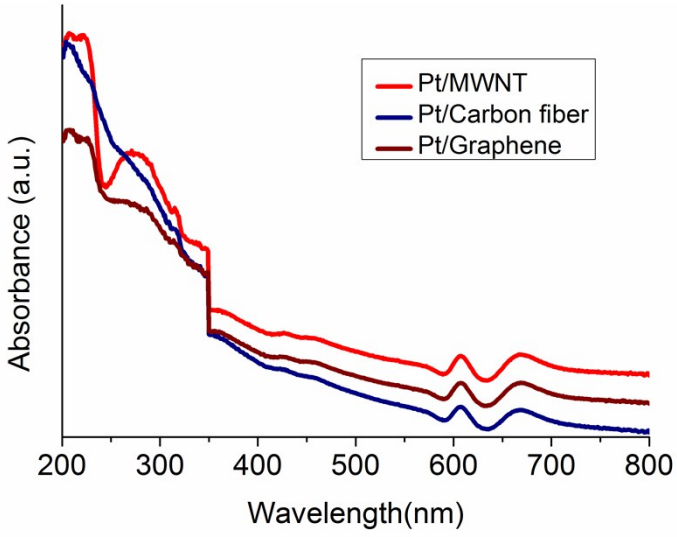


Fig.S18 DRS of Pt/MWNT, Pt/CF and Pt/Graphene.

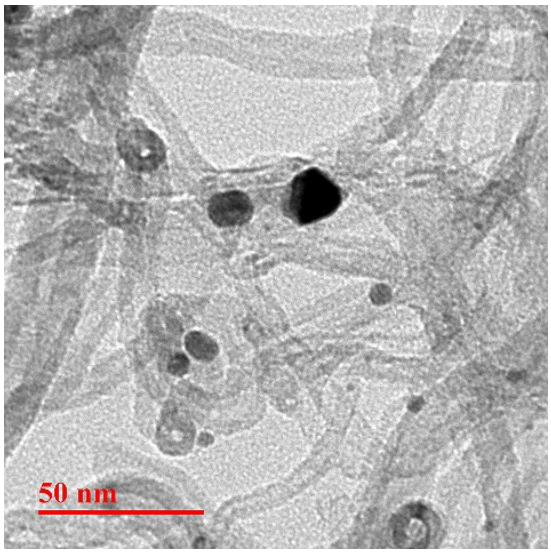


Fig.S19 TEM image of catalyst after 10 cycles with Pt/MWNT.

Table S2: Comparison with other Pt supported catalyst.

S.No.	Catalyst	Substrate	%ee	Reference
1	Pt/SiO_2	Ethyl pyruvate	20	[1] 2015
2	Pt/Al_2O_3	Ethyl pyruvate	70	[2] 2014
3	Pt/Al_2O_3	Methyl pyruvate	70	[3] 2010
4	Pt/Al_2O_3	Ethyl pyruvate	20	[3] 2010
5	Pt/Al_2O_3	Ethyl pyruvate	>80	[4] 2000
6	Pt/Al_2O_3	Ethyl pyruvate	80	[5] 1997
7	Pt/TiO_2	4,4-dimethyldihydrofuran-2,3-dione	79	[6] 1996
8	Pt/Al_2O_3	Ethyl pyruvate	65	[7] 1995
9	Pt/SiO_2	Biacetyl	38	[8] 1993
10	Pt/Al_2O_3	Methyl and Ethyl Pyruvate	>95	[9] 2003
11	Pt/Al_2O_3	Methyl Pyruvate	98	[10] 1999
12	Pt/Al_2O_3	Ethyl Pyruvate	96	[11] 2000
13	Pt/MWNT	Methyl and Ethyl Pyruvate	96	[12] 2011
14	Pt/MWNT	Methyl pyruvate	>99	This work
15	Pt/AC	Methyl pyruvate	31	This work
16	Pt/Graphene	Methyl pyruvate	91	This work
17	Pt/Carbon fiber	Methyl pyruvate	89	This work

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