Electronic Supplementary Information

An iron catalyzed regioselective oxidation of terminal alkenes to aldehydes

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1. General information

All the reactions were performed using standard Schlenk techniques in oven-dried glassware under an atmosphere of argon and air, unless otherwise specified. Solvents were dried by standard procedures under argon and used immediately.[S1] Molecular sieves (3Å) were crushed and activated by putting it under vacuum in a flask and heated with a Bunsen burner prior to use. Solvents were purchased from Merck, India and all other reagents and chemicals were obtained from Aldrich, USA. Only styrene substrates were purified by passing through a plug of activated alumina before use and other reagents were used as received. PhIO was prepared from $PhI(OAc)_2$ according to literature reported procedure.[S2] Column chromatography was performed by using a silica gel column (60-120 mesh, Merck India). TLC experiments were carried out on Merck silica gel 60 F_{254} pre-coated sheets and visualized by UV (254 nm) lamp.

NMR spectra were recorded by 400 MHz Bruker spectrometer in $CDCl_3$. Chemical shift data are quoted as δ in ppm, coupling constants (J) are reported in Hertz (Hz) and s, d, dd, t, q, m and br represent singlet, doublet, doublet of doublet, triplet, quartet, multiplet and broad respectively. HRMS spectra were recorded using micromass Q-TOF mass spectrometer. GC analysis was done by Shimadzu GC-2014 gas chromatograph with a FID detector using a capillary column (112-2562 CYCLODEXB, from J & W Scientific, length 60 m, inner diameter 0.25 mm, film 0.25 μm) and GC-MS analysis was performed on an Agilent Technologies 7890A GC system coupled with 5975C inert XL EI/CI Mass Selective Detector (GCMSD) with its triple axis detector.

The yields of the *non-isolated products* were determined either by ^{1}H NMR or by GC. Response factors for the alkenes and aldehydes were determined with respect to the internal standard, dodecane (1 mmol) for the GC-yield analysis. 1.0 μL aliquot was subjected for the analysis by GC-FID in each case. ^{1}H NMR yield was evaluated using 1 mmol of CH_2Cl_2 as an internal standard which was added after the synthetic work-up i.e. just prior to the NMR analysis.

2. General method for formation of aldehydes (3a-n) from aromatic alkenes (2a-n)

In a 25 mL Schlenk tube, $Fe(BF_4)_2.6H_2O$ (6.75 mg, 0.02 mmol), pyridine-2,6-dicarboxylic acid (3.5 mg, 0.02 mmol) and 200 mg of crushed molecular sieves (3Å) were taken in 3 mL chloroform and stirred for 5 min. 1.5 equivalent of PhIO in 1 mL chloroform was then added after evacuating the air inside the flask and backfilling the flask three times with zero-air. The resulting heterogeneous reaction mixture was then stirred at room temperature for additional 1 min. The corresponding styrene (1 mmol) was then added in additional 1 mL chloroform and then stirred at room temperature for 20 h. The solution turned yellowish during the reaction. The solvent was then removed in *vacuo* and the resultant material was passed through a short silica gel column using hexane:ethyl acetate (20:1→10:1, v/v) as eluent to afford the desired product. The formation of product was confirmed by GC against authentic samples and/or GCMSD. The yield was then determined by either GC with respect to the internal standard, n-dodecane or ^{1}H NMR.

To ensure the general synthetic utility of our catalytic system, products were isolated in most cases and characterized by NMR (in $CDCl_3$ with TMS as an internal standard) and HRMS (Tables 1-2).[S3] Most of the aldehydes reported in this work are previously reported in the literature.[S2,S4-S15] All the reactions were performed thrice to establish the reproducibility and reliability.

3. General method for formation of aldehydes (3o-s) from aliphatic alkenes (2o-s)

In a 25 mL Schlenk tube, $Fe(BF_4)_2.6H_2O$ (6.75 mg, 0.02 mmol), pyridine-2,6-dicarboxylic acid (3.5 mg, 0.02 mmol) and 200 mg of crushed molecular sieves (3Å) were taken in 3 mL chloroform and stirred for 5 min. 1.5 equivalent of PhIO in 1 mL chloroform was then added after evacuating the air inside the flask and backfilling the flask three times with zero-air. The resulting heterogeneous reaction mixture was then stirred at room temperature for additional 1 min. The corresponding alkene (1 mmol) was then added in additional 1 mL chloroform and then stirred at 333K for 48 h. The solution turned yellowish during the reaction. The solvent was then removed in *vacuo* and the resultant material was passed through a short silica gel column using hexane:ethyl acetate

(20:1→10:1, v/v) as eluent to afford the desired product. The product was confirmed by GC against authentic samples and/or GCMSD. The products were either isolated or yield was determined by ^{1}H NMR. The products were then further characterized by NMR (in $CDCl_3$ with TMS as an internal standard) and HRMS (Table 2). Most of the aldehydes reported in this work are previously reported in the literature.[S2,S4-S15] All the reactions were performed thrice to establish the reproducibility and reliability.

4. General method for phenylacetaldehydes formation (3a) from styreneoxide

In a 25 mL Schlenk tube, $Fe(BF_4)_2.6H_2O$ (6.75 mg, 0.02 mmol), pyridine-2,6-dicarboxylic acid (3.5 mg, 0.02 mmol) and 200 mg of crushed molecular sieves (3Å) were taken and stirred for 5 min in 3 mL chloroform. Styrene oxide (1 mmol) was then added in additional 1 mL chloroform and then stirred at room temperature for 6 h. The solution turned yellowish during the reaction. The solvent was then removed in *vacuo* and the resultant material was then passed through a short silica gel column using hexane:ethyl acetate (10:1, v/v) as eluent to isolate the desired product. The product was confirmed by NMR (in $CDCl_3$ with TMS as an internal standard) and HRMS.

5. General method for control reaction in presence of formic acid

In a 25 mL Schlenk tube, $Fe(BF_4)_2.6H_2O$ (6.75 mg, 0.02 mmol), pyridine-2,6-dicarboxylic acid (3.5 mg, 0.02 mmol) and 200 mg of crushed molecular sieves (3Å) were taken in 3 mL chloroform and stirred for 5 min. 1.5 equivalent of PhIO in 1 mL chloroform was then added after evacuating the air inside the flask and backfilling the flask three times with zero-air. The resulting heterogeneous reaction mixture was then stirred at room temperature for additional 1 min. The corresponding styrene (1 mmol) and formic acid (1 mmol) each was then added in additional 1 mL chloroform and then stirred at room temperature for 20 h. The solution turned yellowish during the reaction. The solvent was then removed in *vacuo* and potassium carbonate (0.5 mmol) in 6mL methanol was then added and stirred for 6h at room temperature. Again solvent was removed in *vacuo* and passed through a short silica gel column using petether:ethyl acetate (3:2, v/v) as eluent to afford the desired products. The products were confirmed

by GC against authenticated samples and characterized by NMR (in $CDCl_3$ with TMS as an internal standard) and HRMS.

6. Optimized large scale synthesis of 2-phenylacetaldehyde (3a) from styrene (2a)

$Fe(BF_4)_2.6H_2O$ (94.5 mg, 0.28 mmol), pyridine-2,6-dicarboxylic acid (49 mg, 0.28 mmol) and 1.8 g of crushed molecular sieves (3Å) were taken in 25 mL chloroform in a 100 mL round-bottom flask and stirred for 10 min. 1.5 equivalent of PhIO in 1 mL chloroform was then added after evacuating the air inside the flask and backfilling the flask three times with zero-air. The reaction flask was sealed with a rubber-septum and a needle was placed on it as an outlet. The resulting heterogeneous reaction mixture was then stirred at room temperature for additional 3 min. The styrene (1.5 g, 14 mmol) in 10 mL chloroform was then added into the above mixture drop wise over a period of 5 min through a syringe under vigorous stirring (≥1250 rpm) condition. The stirring was further continued for 20 h under room temperature. The solution turned yellowish during the course of the reaction. The progress of the reaction was monitored periodically by TLC as well as by GC against authentic samples. The solvent was then removed under reduced pressure and the desired product was purified by using a silica gel column with hexane:ethyl acetate (10:1, v/v) as eluent (isolated yield: 1.37 g, 82%).[S16]

Details of product characterization

2-phenylacetaldehyde (3a)[S4]

^{1}H NMR (400 MHz, $CDCl_3$): δ 9.73 (t, J = 2.5 Hz, 1H), 7.38-7.18 (m, 5H), 3.68 (d, J = 2.4 Hz, 2H); ^{13}C NMR (400 MHz, $CDCl_3$): δ 199.6, 131.9, 129.7, 129.1, 127.5, 50.7; HRMS(ESI+): m/z 143.0472 (Calcd. for [M+Na$^+$]: 143.0473).

2-*m*-tolylacetaldehyde (3b)[S4]

^{1}H NMR (400 MHz, $CDCl_3$): δ 9.72 (t, J = 2.3 Hz, 1H), 7.30-7.04 (m, 4H), 3.66 (d, J = 2.2 Hz, 2H), 2.33 (S, 3H); ^{13}C NMR (400 MHz, $CDCl_3$): δ 199.9, 138.9, 135.5, 131.3, 129.2, 127.1, 126.4, 50.8, 21.4; HRMS(ESI+): m/z 157.0629 (Calcd. for [M+Na$^+$]: 157.0629).

2-*p*-tolylacetaldehyde (3c)[S4]

^{1}H NMR (400 MHz, $CDCl_3$): δ 9.70 (t, J = 2.0 Hz, 1H), 7.18 (d, J=7.8, 2H), 7.11 (d, J=7.8, 2H), 3.65 (d, J=2.1 Hz, 2H), 2.19 (s, 3H); ^{13}C NMR (400 MHz, $CDCl_3$): δ 199.6, 137.6, 130.4, 129.2, 127.6, 50.6, 21.2; HRMS(ESI+): m/z 157.0630 (Calcd. for [M+Na$^+$]: 157.0629).

2-phenylpropanal (3d)[S5]

^{1}H NMR (400 MHz, $CDCl_3$): δ 9.62 (d, J = 2.0 Hz, 1H), 7.31-7.06 (m, 5H), 3.49 (q, J = 7.2 Hz, 1H), 1.37 (d, J = 7.2 Hz, 3H); ^{13}C NMR (400 MHz, $CDCl_3$): δ 206.3, 137.4, 129.5, 129.1, 127.4, 50.9, 15.1; HRMS(ESI+): m/z 157.0629 (Calcd. for [M+Na$^+$]: 157.0629).

Propiophenone (3e, 3f)[S6]

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.0-7.95 (m, 2H), 7.68-7.28 (m, 3H), 3.0 (q, J = 3.5 Hz, 1H), 1.22 (t, J = 5.1 Hz, 3H); ^{13}C NMR (400 MHz, $CDCl_3$): δ 201.2, 137.0, 132.5, 128.8, 127.9, 31.7, 8.2; HRMS(ESI+): m/z 135.0809 (Calcd. for [M+H$^+$]: 135.0809).

2-(4-chlorophenyl)acetaldehyde (3g)[S7]

^{1}H NMR (400 MHz, $CDCl_3$): δ 9.71 (t, *J*= 2.1, 1H), 7.82 (d, *J*=8.6, 2H), 7.30 (d, *J*= 8.6, 2H), 3.88 (d, *J*= 2.0, 2H); ^{13}C NMR (400 MHz, $CDCl_3$): δ 199.9, 134.2, 130.80, 129.0, 128.6, 50.0; HRMS(ESI+): m/z 177.0084 (Calcd. for [M+Na$^+$]: 177.0083).

2-(4-fluorophenyl)acetaldehyde (3h)[S8]

^{1}H NMR (400 MHz, $CDCl_3$): δ 9.75 (t, *J*= 1.7, 1H), 7.29 (d, *J*=8.4, 2H), 7.18 (d, *J*= 8.4, 2H), 3.69 (d, *J*= 1.8, 2H); ^{13}C NMR (400 MHz, $CDCl_3$): δ 199.9, 160.5, 132.7, 130.9, 115.2, 51.1; HRMS(ESI+): m/z 161.0378 (Calcd. for [M+Na$^+$]: 161.0378).

2-(naphthalen-2-yl)acetaldehyde (3i)[S9-S10]

^{1}H NMR (400 MHz, $CDCl_3$): δ 9.73 (t, *J* = 2.1 Hz, 1H), 7.80-7.65 (m, 4H), 7.48-7.08 (m, 3H), 3.82 (d, *J* = 2.1 Hz, 2H); ^{13}C NMR (400 MHz, $CDCl_3$): δ 200.1, 137.1, 133.6, 132.3, 128.3, 128.2, 127.8, 127.5, 126.9, 126.1, 50.5; HRMS(ESI+): m/z 193.0630 (Calcd. for [M+Na$^+$]: 193.0629).

2-(2-methoxyphenyl)acetaldehyde (3j)[S9]

^{1}H NMR (400 MHz, $CDCl_3$): δ 9.68 (t, *J* = 2.2 Hz, 1H), 7.26-6.93 (m, 4H), 3.82 (s, 3H), 3.65 (d, *J*=2.1 Hz, 2H); ^{13}C NMR (400 MHz, $CDCl_3$): δ 200.1, 157.4, 131.9, 128.2, 126.0, 120.7, 112.6, 56.3, 49.4; HRMS(ESI+): m/z 135.0808 (Calcd. for [M+H$^+$]: 135.0809).

2-(4-methoxyphenyl)acetaldehyde (3k)[S11]

^{1}H NMR (400 MHz, $CDCl_3$): δ 9.71 (t, *J* = 2.4 Hz, 1H), 7.10-6.93 (m, 4H), 3.80 (s, 3H), 3.63 (d, *J* = 2.1 Hz, 2H); ^{13}C NMR (400 MHz, $CDCl_3$): δ 199.9, 158.9, 130.4, 124.5, 114.5, 113.8, 55.3, 49.7; HRMS(ESI+): m/z 157.0629 (Calcd. for [M+Na$^+$]: 157.0629).

1-phenylcyclopentanecarbaldehyde (3l)[S12]

^{1}H NMR (400 MHz, $CDCl_3$): δ 9.38 (s, 1H), 7.28-7.24 (m, 2H), 7.19-7.15 (m, 3H), 2.54-2.48 (m, 2H), 1.90-1.84 (m, 2H), 1.75-1.71 (m, 2H), 1.67-1.61 (m, 2H); ^{13}C NMR (400 MHz, $CDCl_3$): δ 200.8, 140.3, 128.7, 127.6, 127.1, 63.6, 32.3, 24.2; HRMS(ESI+): m/z 197.0942 (Calcd. for [M+Na^+]: 197.0942).

2-(4-(chloromethyl)phenyl)acetaldehyde (3m)

^{1}H NMR (400 MHz, $CDCl_3$): δ 9.83 (t, J = 2.4 Hz, 1H), 7.30-7.10 (m, 4H), 4.61 (s, 2H), 3.66 (d, J = 2.1 Hz, 2H); ^{13}C NMR (400 MHz, $CDCl_3$): δ 199.9, 138.8, 131.4, 128.9, 128.3, 50.5, 42.3; HRMS(ESI+): m/z 191.0239 (Calcd. for [M+Na^+]: 191.0239).

2,2'-(biphenyl-4,4'-diyl)diacetaldehyde (3n)

^{1}H NMR (400 MHz, $CDCl_3$): δ 9.72 (t, J = 2.4 Hz, 2H), 7.35-7.26 (m, 8H), 3.66 (d, J= 2.4, 4H); ^{13}C NMR (400 MHz, $CDCl_3$): δ 199.9, 139.2, 130.6, 129.8, 128.6, 50.5; HRMS(ESI+): m/z 239.1072 (Calcd. for [M+Na^+]: 239.1072).

3-phenylpropanal (3o)[S13]

^{1}H NMR (400 MHz, $CDCl_3$): δ 9.79 (t, J = 2.8 Hz, 1H), 7.33-7.19 (m, 5H), 2.96 (t, J = 7.5 Hz, 2H), 2.79 (t, J = 7.5 Hz, 2H); ^{13}C NMR (400 MHz, $CDCl_3$): δ 201.8, 140.4, 128.6, 128.4, 125.9, 45.4, 28.2; HRMS(ESI+): m/z 157.0628 (Calcd. for [M+Na^+]: 157.0629).

3-(4-methoxyphenyl)propanal (3p)

^{1}H NMR (400 MHz, $CDCl_3$): δ 9.85 (t, J = 2.4 Hz, 1H), 7.20-6.95 (m, 4H), 3.86 (s,3H), 2.85-2.74 (m, 4H); ^{13}C NMR (400 MHz, $CDCl_3$): δ 202.2, 158.0, 132.0, 129.6, 114.2, 56.2, 44.3, 27.6; HRMS(ESI+): m/z 187.0735 (Calcd. for [M+Na^+]: 187.0735).

2-cyclohexylacetaldehyde (3q)[S14]

^{1}H NMR (400 MHz, $CDCl_3$): δ 9.76 (t, J = 2.33, 1H), 2.30 (dd, J = 7.1, 2H), 1.86-0.98

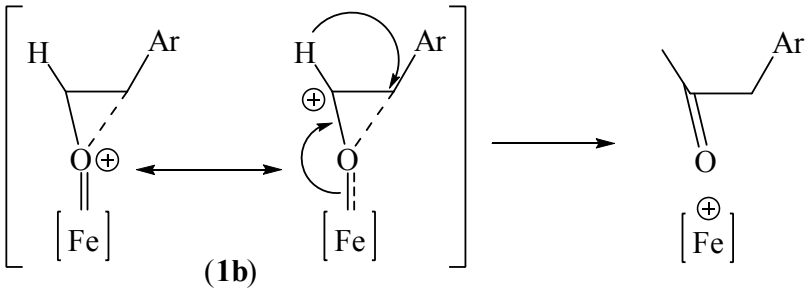
(m, br, 11H); ^{13}C NMR (400 MHz, $CDCl_3$): δ 203.0, 51.4, 33.2, 32.7, 26.1, 26.0; HRMS(ESI+): m/z 149.0943 (Calcd. for [M+Na^+]: 149.0942).

Do-decanal (3r)[S15]

^{1}H NMR (400 MHz, $CDCl_3$): δ 9.74 (s, 1H,), 2.60-2.40(m, 2H), 1.80-1.62 (m, 2H), 1.28-1.33 (m, 16H), 0.93(t, J = 6.1 Hz, 3H); ^{13}C NMR (400 MHz, $CDCl_3$): δ 203.8, 47.2, 32.6, 30.8, 29.7, 29.3, 23.7, 22.3, 14.2; HRMS(ESI+): m/z 185.1906 (Calcd. for [M+Na^+]: 185.1905).

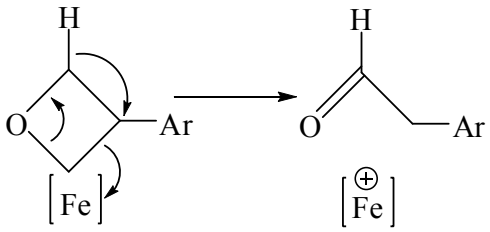
Decanal (3s)[S15]

^{1}H NMR (400 MHz, $CDCl_3$): δ 9.75 (s, 1H,), 2.55-2.40(m, 2H), 1.75-1.58 (m, 2H), 1.29-1.31 (m, 12H), 0.90(t, J = 5.9 Hz, 3H); ^{13}C NMR (400 MHz, $CDCl_3$): δ 202.9, 44.8, 31.9, 29.7, 29.6, 29.3, 28.2, 22.8, 14.8. HRMS(ESI+): m/z 157.1592 (Calcd. for [M+Na^+]: 157.1592).

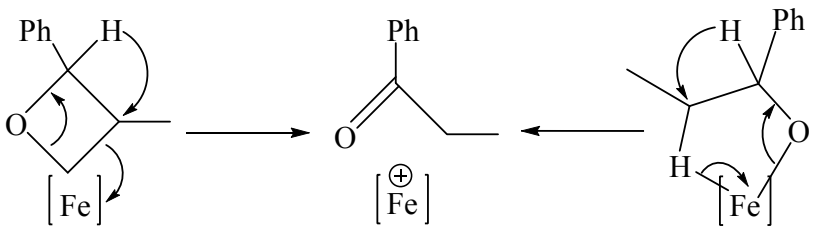


(**1b**)

Scheme S1. Pinacol like rearrangement to 2-phenylacetaldehyde involving cationic intermediate (**1b**) as postulated by Groves[S17] and Collman et al.[S18]

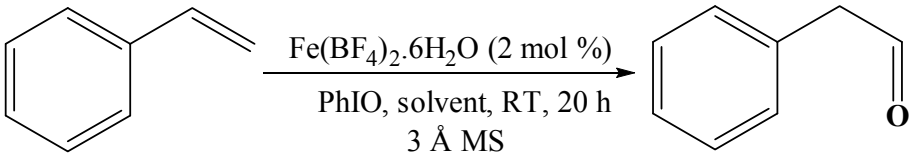


Scheme S2. Alternate possible hydrogen migration pathway for the decomposition of metallaoxetane like intermediate to 2-phenylacetaldehyde. Here two β-hydrogens are stereochemically distinct. This may proceed stepwise as well.[S18]



Scheme S3. The proposed mechanistic pathway for the reversal of regioselectivity for cis- and trans-β-methyl styrenes (**2e** and **2f**) as substrates.

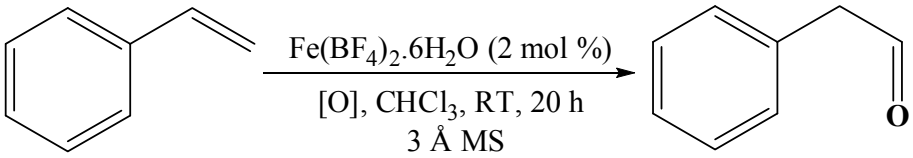
Table S1 Influence of solvent[a]



Entry	Solvent	Conversion (%)	Yield (%)[b]
1	$CHCl_3$	100	92[c]
2	CH_2Cl_2	55	52
3	$ClCH_2CH_2Cl$	61	57
4	THF	<1	0
5	Toluene	0	0
6	CH_3CN	11	<1
7	Dioxane	11	5
8	EtOAc	52	<1

[a] Reaction conditions: 2 mol % $Fe(BF_4)_2.6H_2O$, 2 mol % dipic, styrene, 1.5 equiv. PhIO in 4 mL solvent, RT, 20 h. See the experimental section for the details. [b] Determined by GC using n-dodecane as an internal standard.[c] Isolated yield.

Table S2 Influence of oxidants[a]



Entry	Oxidant	Conversion (%)	Yield (%)[b]
1	PhIO	100	92[c]
2	H_2O_2(30% aq.)	31	10
3	^{t}Butylhydroperoxide	11	5
4	m-Chloroperbenzoic acid	<1	0
5	NaOCl	0	0
6	O_2 (1 atm)	0	0
7	Oxone	0	0
8	Urea peroxide	0	0

[a] Reaction conditions: 2 mol % $Fe(BF_4)_2.6H_2O$, 2 mol % dipic, styrene, 1.5 equiv. oxidant in 4 mL $CHCl_3$, RT, 20 h. See the experimental section for the details. [b] Determined by GC using n-dodecane as an internal standard. [c] Isolated yield.

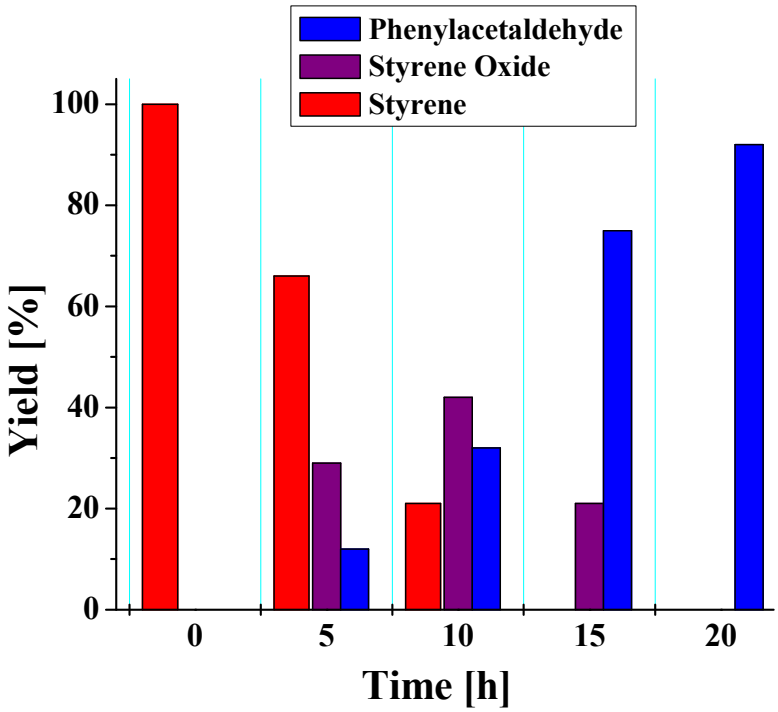


Fig. S1 Yield *versus* time diagram for the oxidation of styrene to phenylacetaldehyde. Substrate styrene has been consumed during the course of reaction at ~15h and then styrene oxide is isomerized to phenylacetaldehyde indicating the existence of tandem epoxidation-isomerzation pathway as well as pinacol rearrangement.

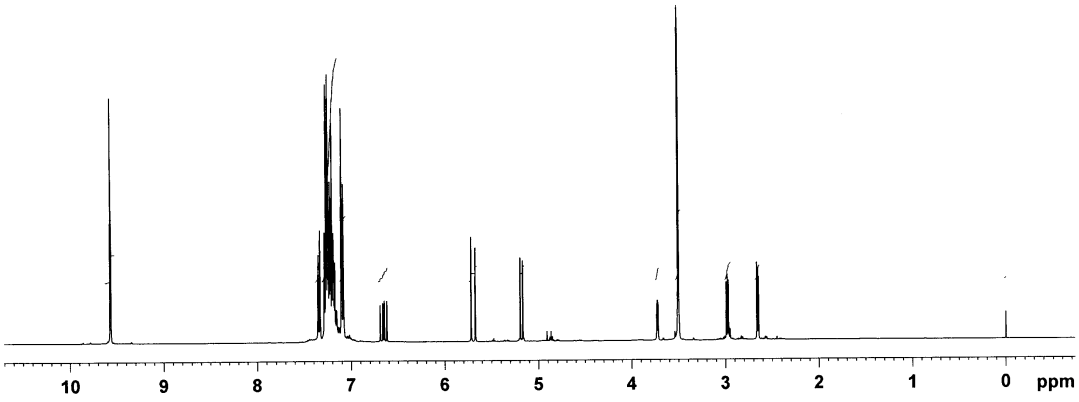


Fig. S2 The ^{1}H NMR spectrum of the control reaction with styrene (**2a**) as a substrate, indicating the existence of unreacted styrene (**2a**), styrene oxide and 2-phenylacetaldehyde (**3a**).

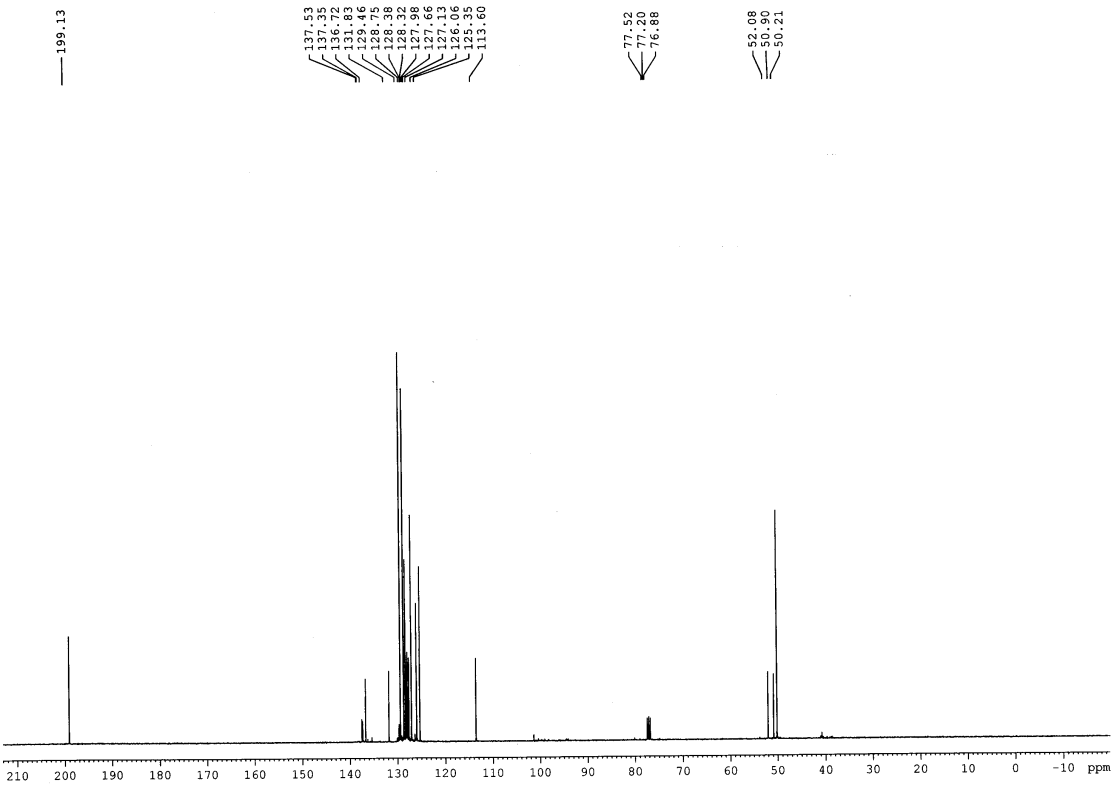


Fig. S3 The ^{13}C NMR spectrum of the control reaction with styrene (**2a**) as a substrate, indicating the existence of unreacted styrene (**2a**), styrene oxide and 2-phenylacetaldehyde (**3a**).

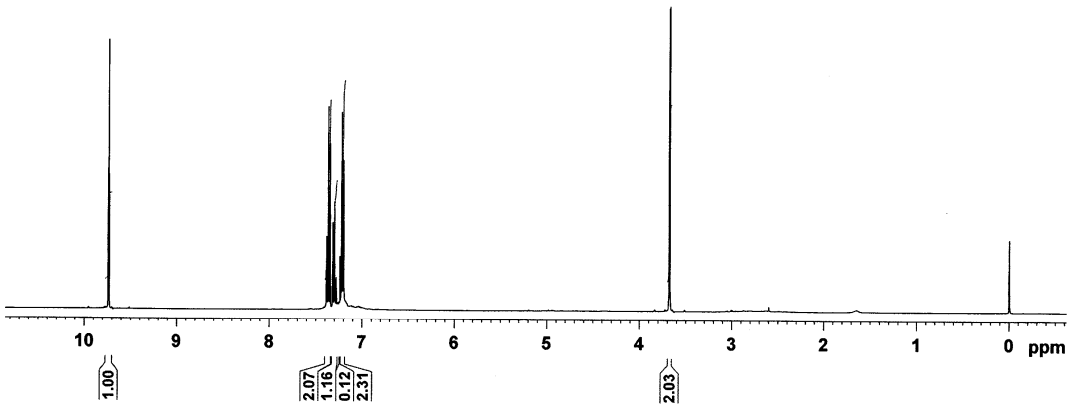


Fig. S4 The ^{1}H NMR spectrum of the 2-phenylacetaldehyde (**3a**).

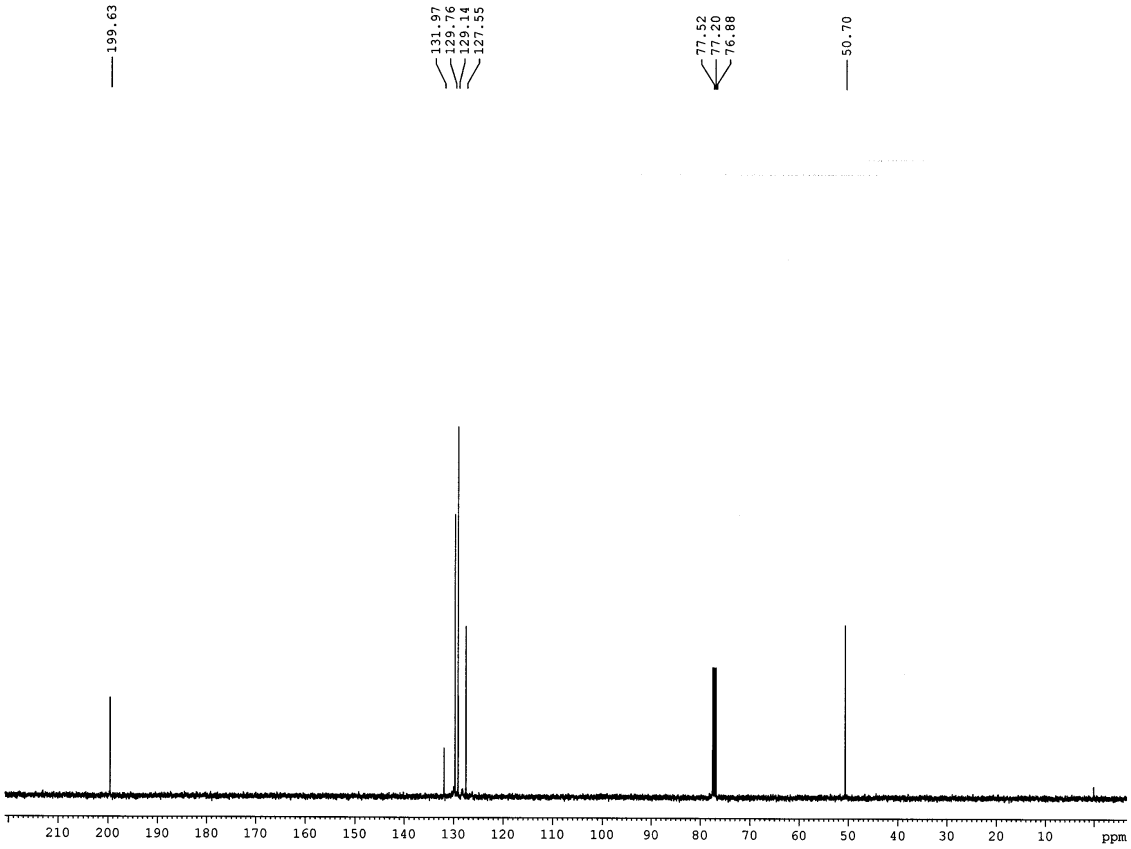


Fig. S5 The ^{13}C NMR spectrum of the 2-phenylacetaldehyde (**3a**).

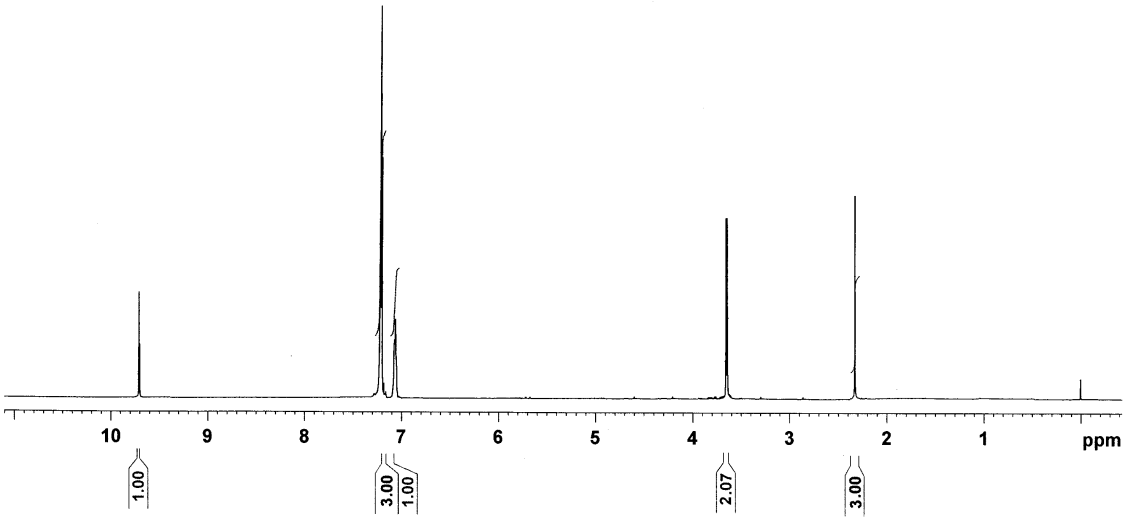


Fig. S6 The ^{1}H NMR spectrum of 2-*m*-tolylacetaldehyde (**3b**).

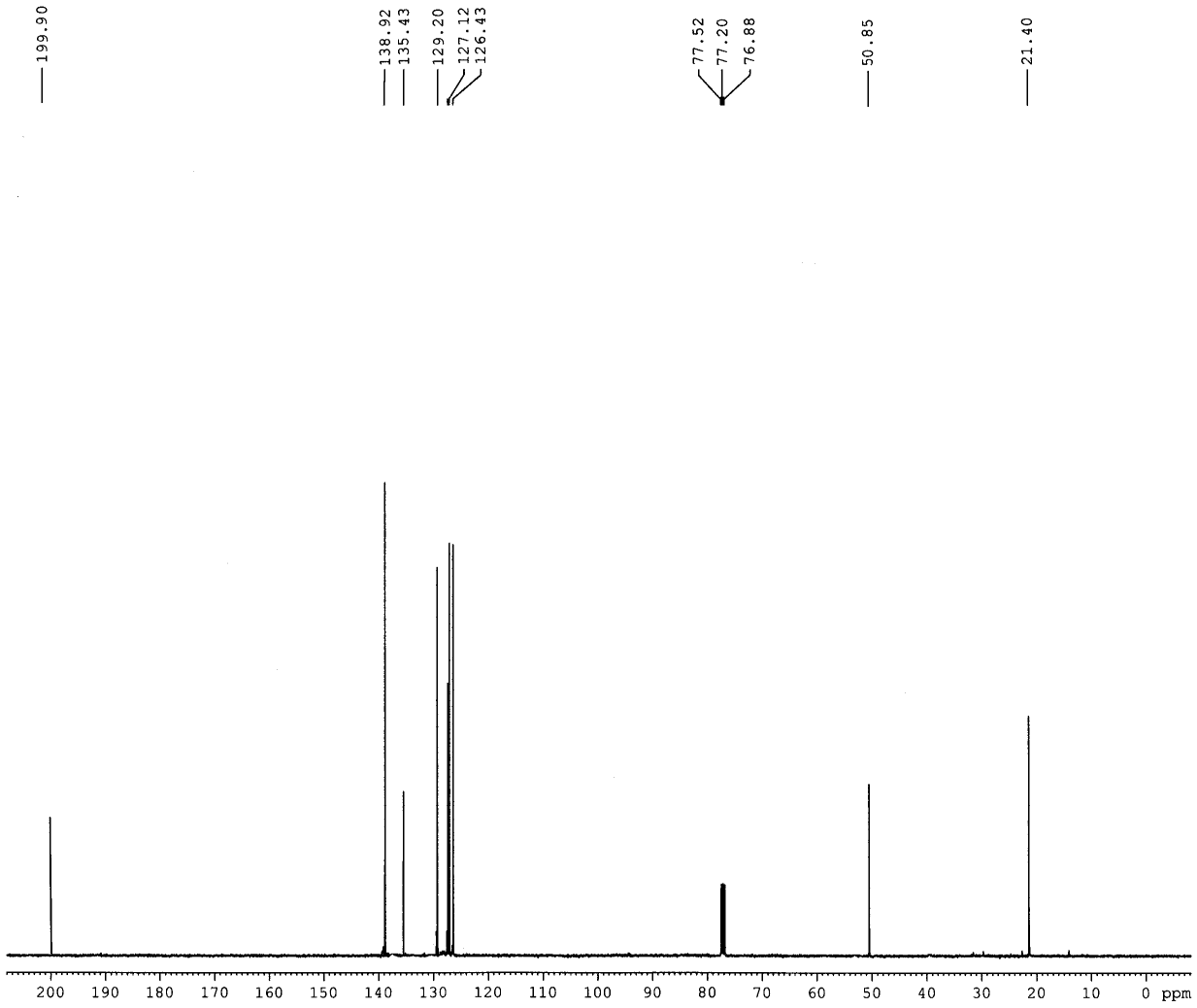


Fig. S7 The ^{13}C NMR spectrum of 2-*m*-tolylacetaldehyde (**3b**).

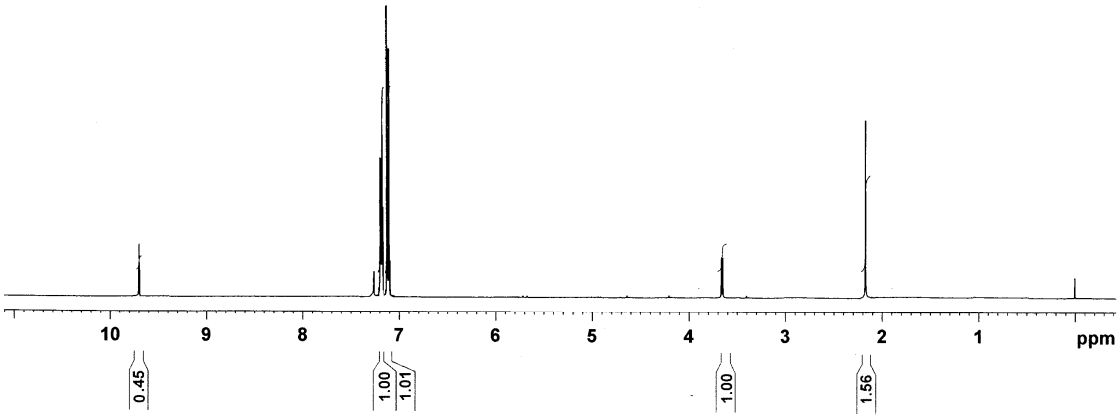


Fig. S8 The ^{1}H NMR spectrum of 2-*p*-tolylacetaldehyde (**3c**).

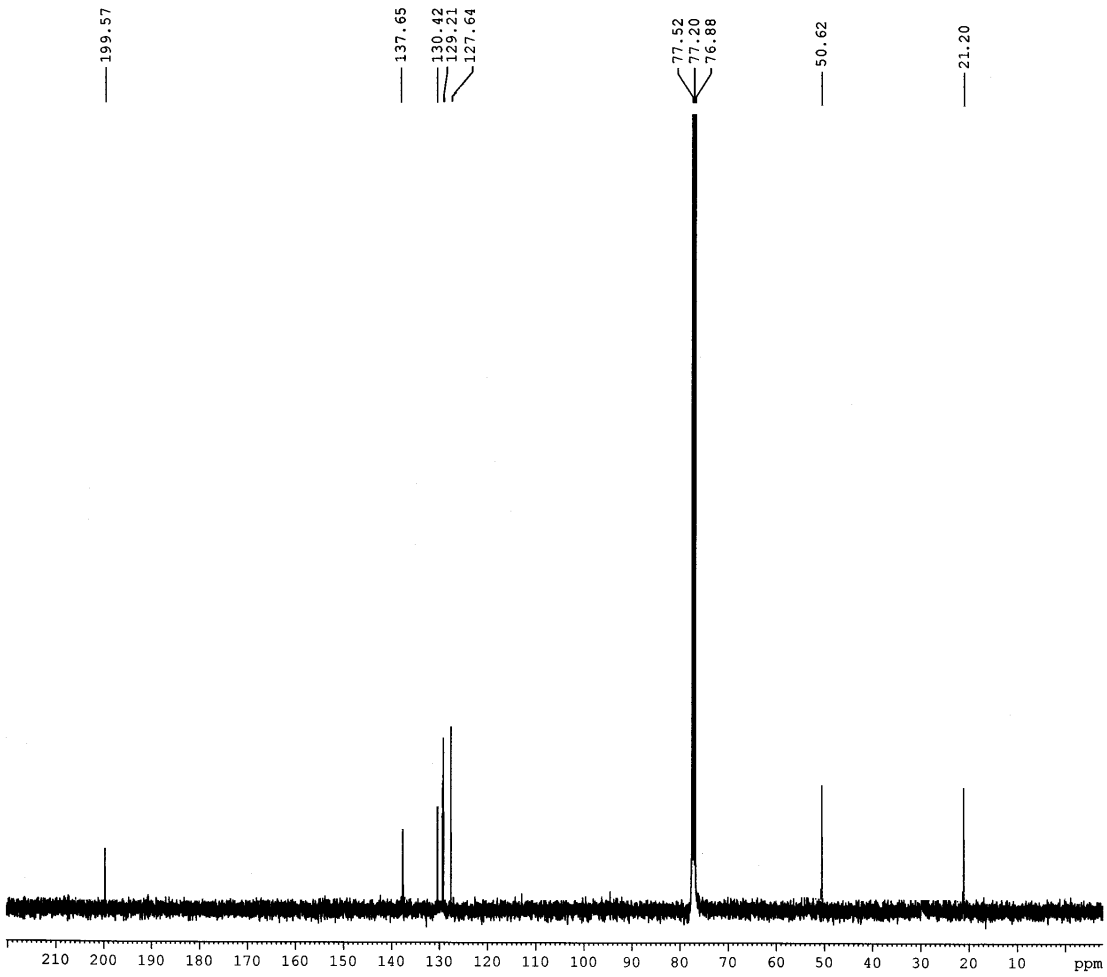


Fig. S9 The ^{13}C NMR spectrum of 2-*p*-tolylacetaldehyde (**3c**).

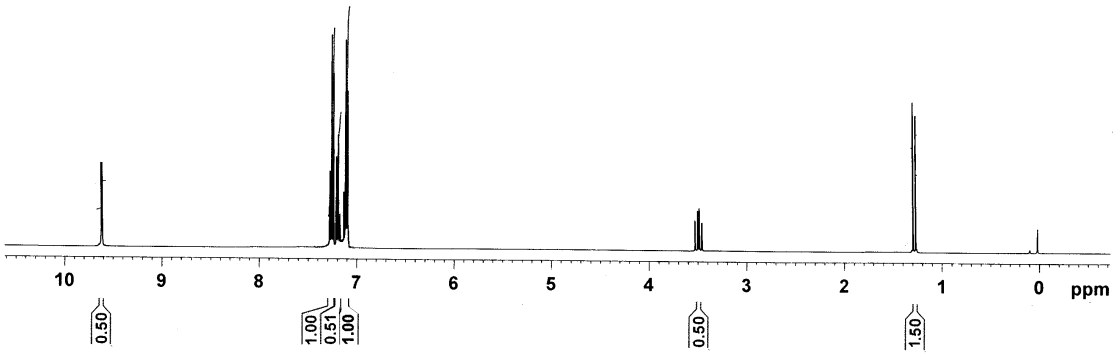


Fig. S10 The ^{1}H NMR spectrum of 2-phenylpropanal (**3d**).

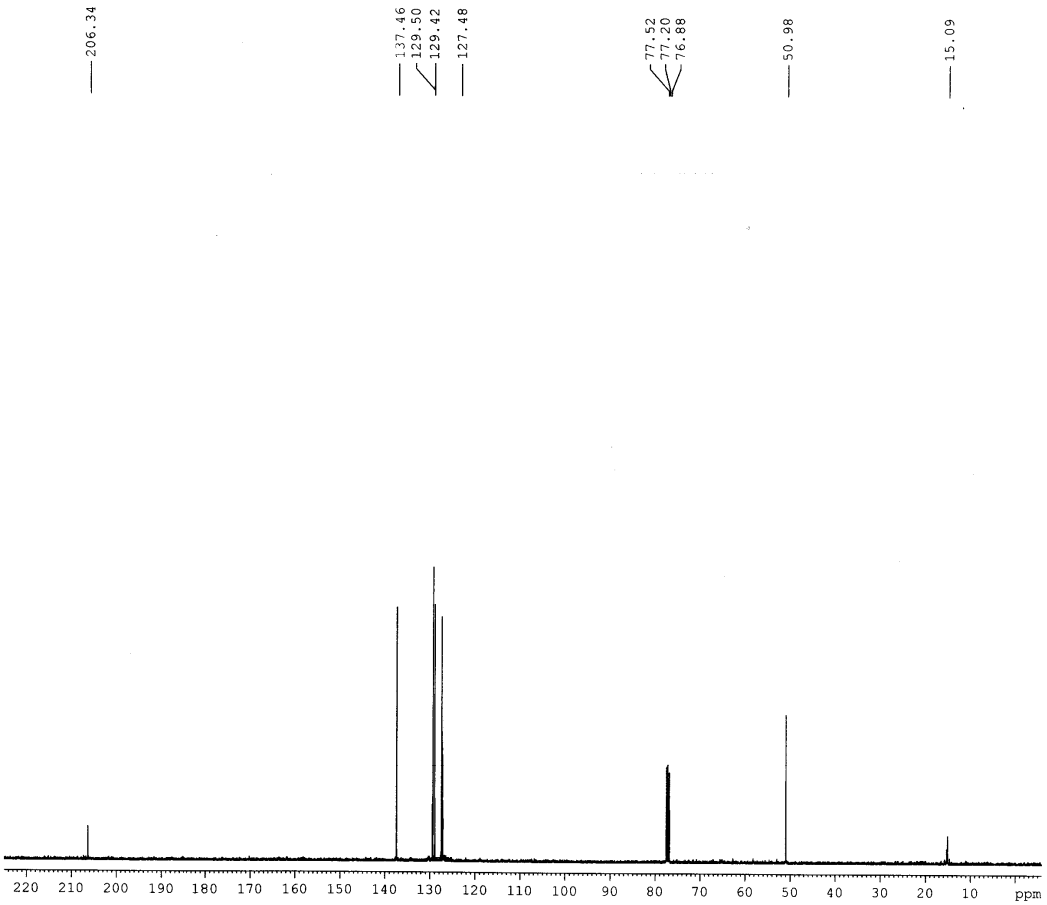


Fig. S11 The ^{13}C NMR spectrum of 2-phenylpropanal (**3d**).

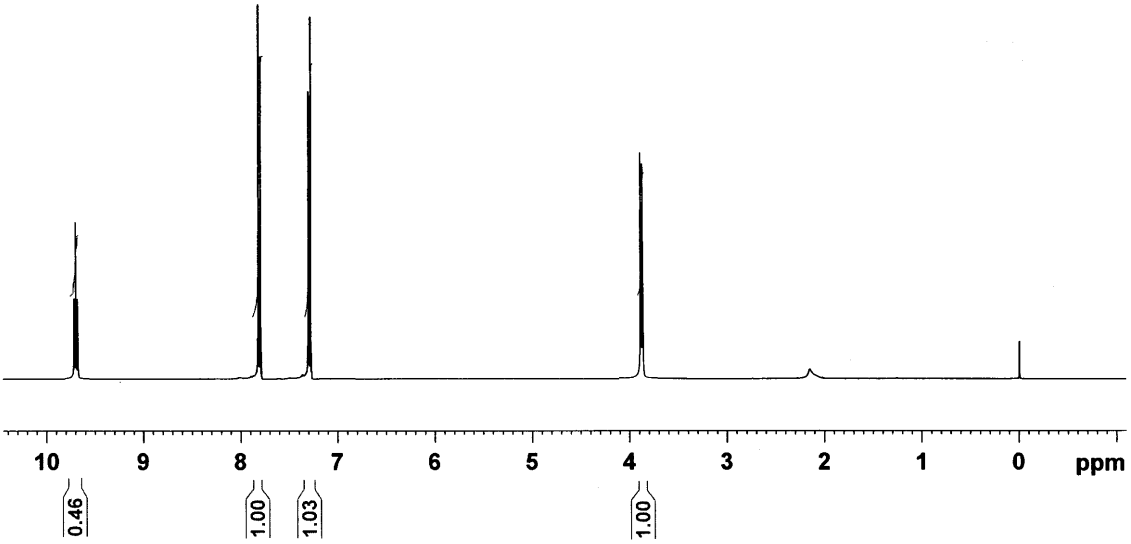


Fig. S12 The ^{1}H NMR spectrum of 2-(4-chlorophenyl)acetaldehyde (**3g**).

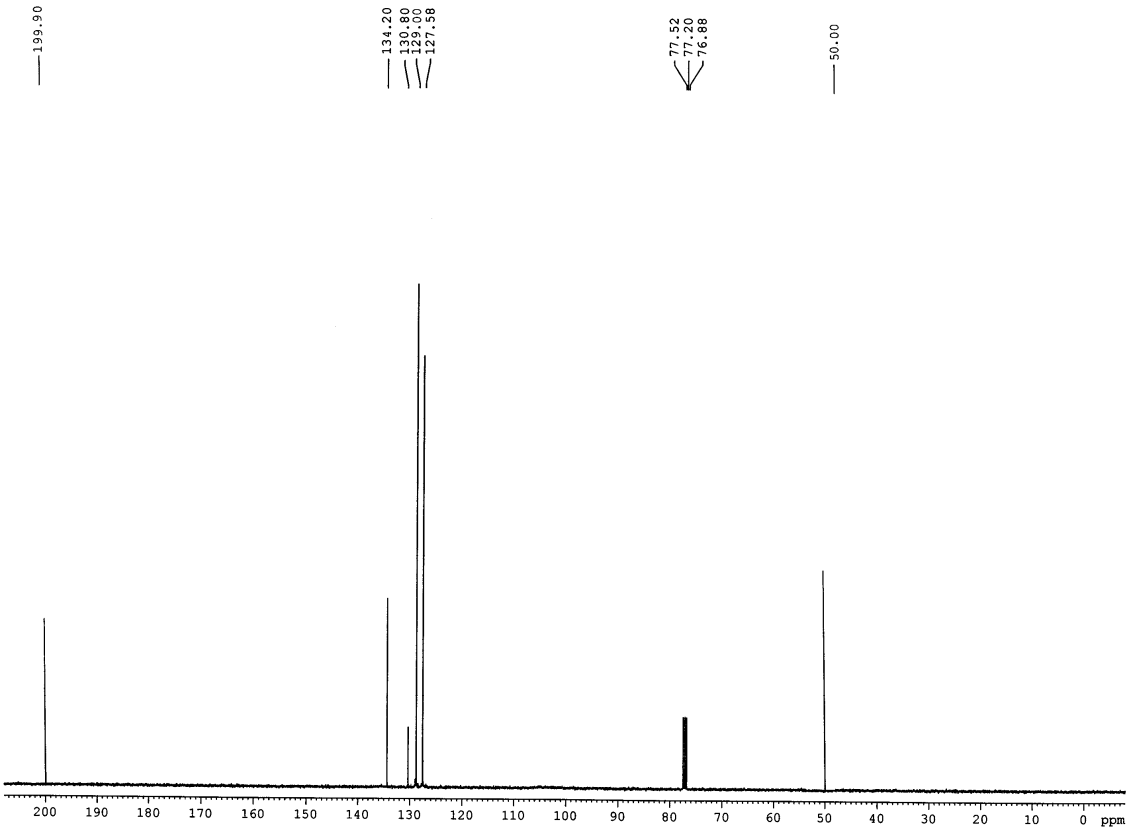


Fig. S13 The ^{13}C NMR spectrum of 2-(4-chlorophenyl)acetaldehyde (**3g**).

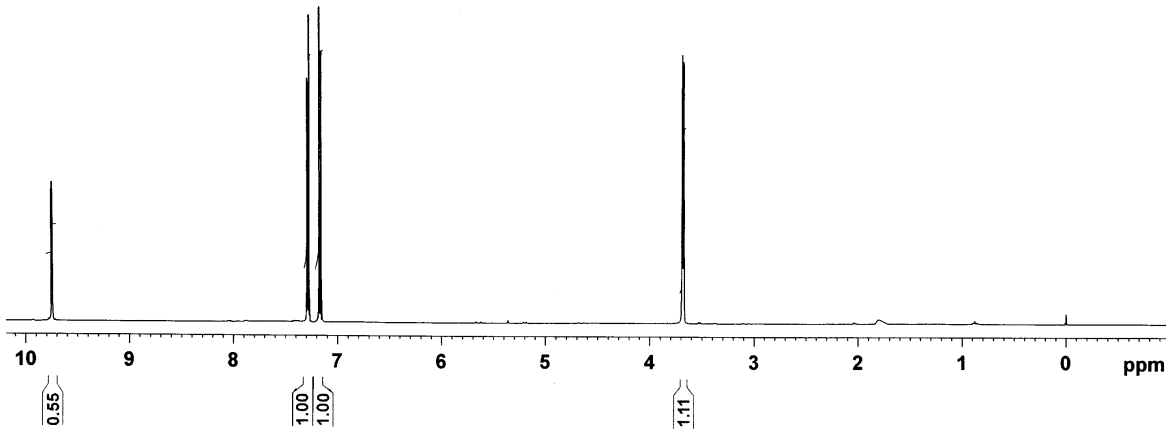


Fig. S14 The ^{13}C NMR spectrum of 2-(4-fluorophenyl)acetaldehyde (**3h**).

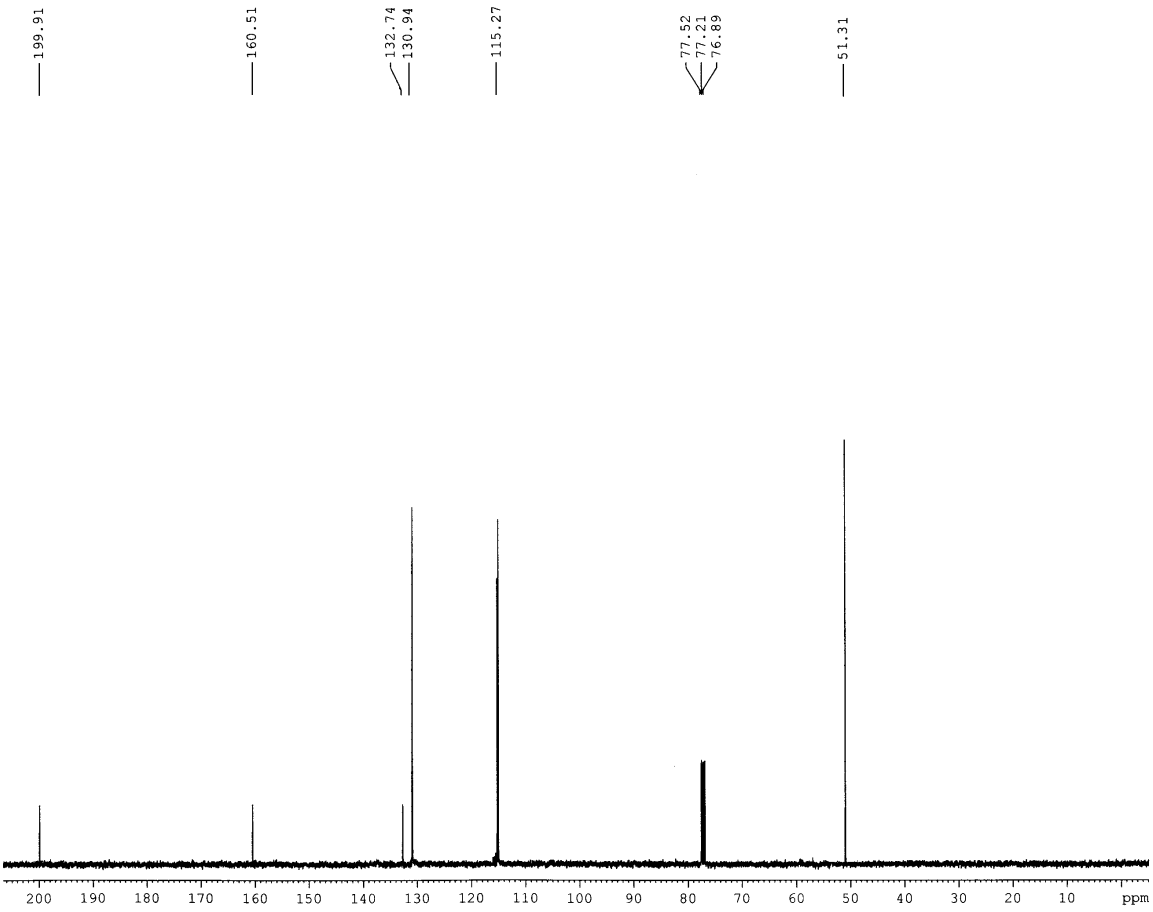


Fig. S15 The ^{13}C NMR spectrum of 2-(4-fluorophenyl)acetaldehyde (**3h**).

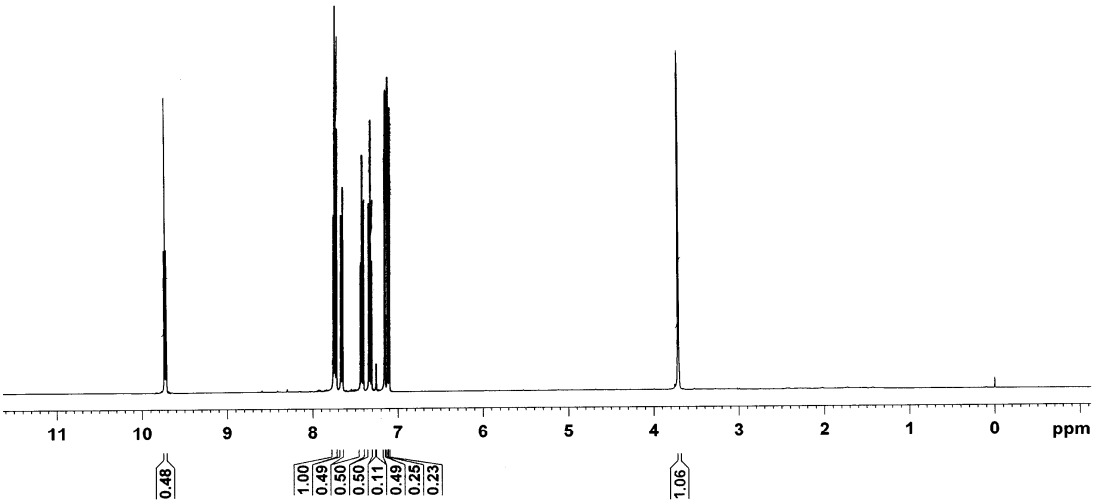


Fig. S16 The ^{1}H NMR spectrum of 2-(naphthalen-2-yl)acetaldehyde (**3i**).

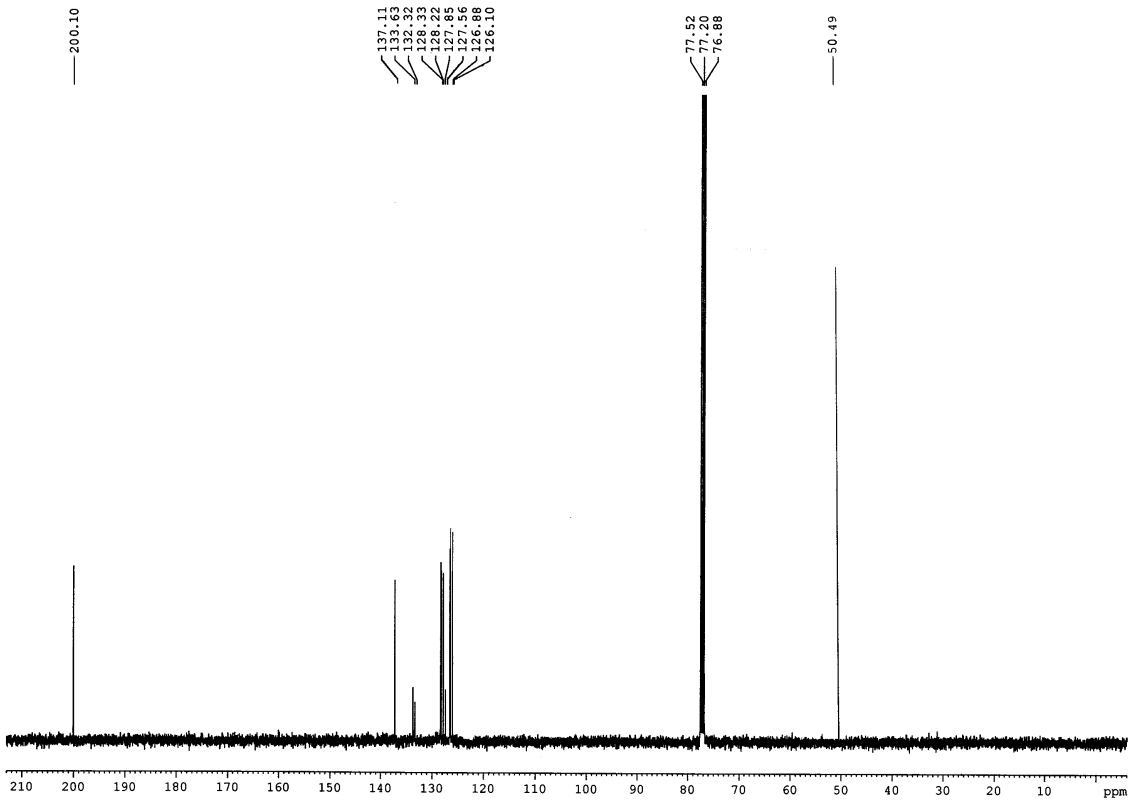


Fig. S17 The ^{13}C NMR spectrum of 2-(naphthalen-2-yl)acetaldehyde (**3i**).

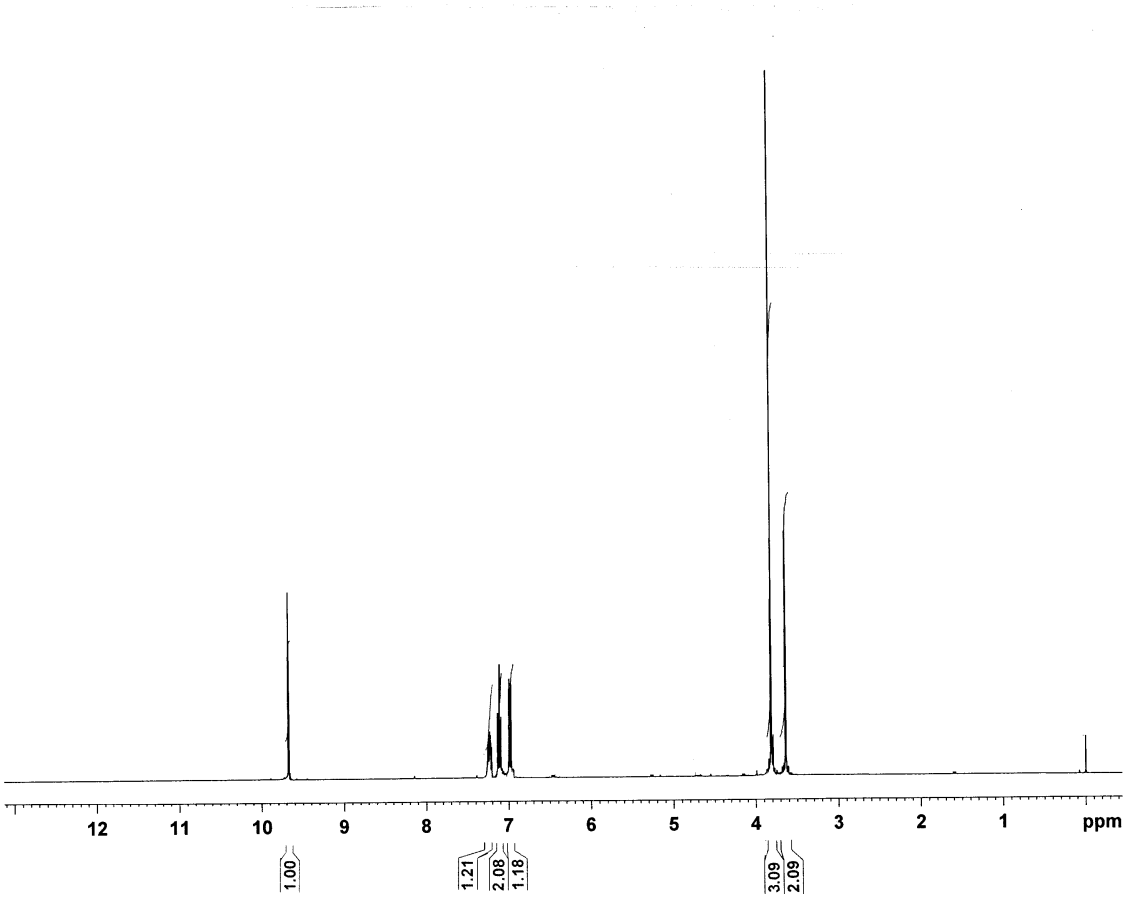


Fig. S18 The ^{1}H NMR spectrum of 2-(2-methoxyphenyl)acetaldehyde (**3j**).

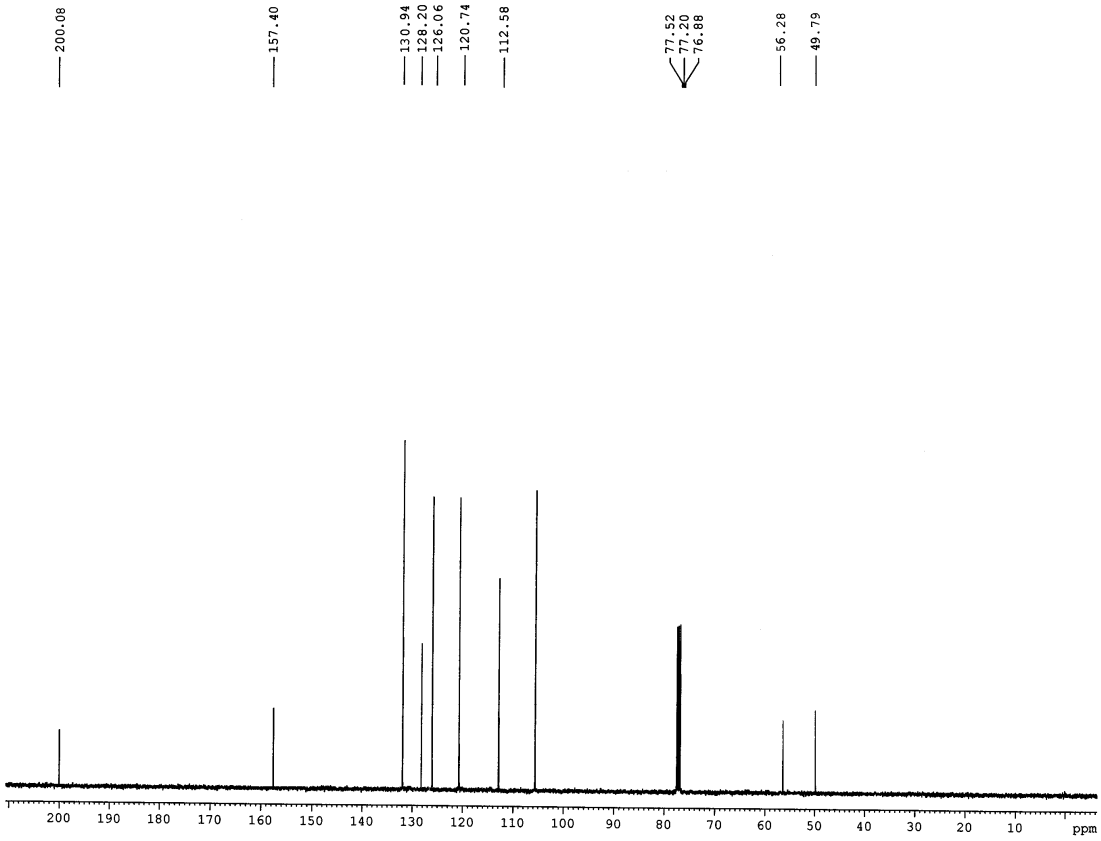


Fig. S19 The ^{13}C NMR spectrum of 2-(2-methoxyphenyl)acetaldehyde (**3j**).

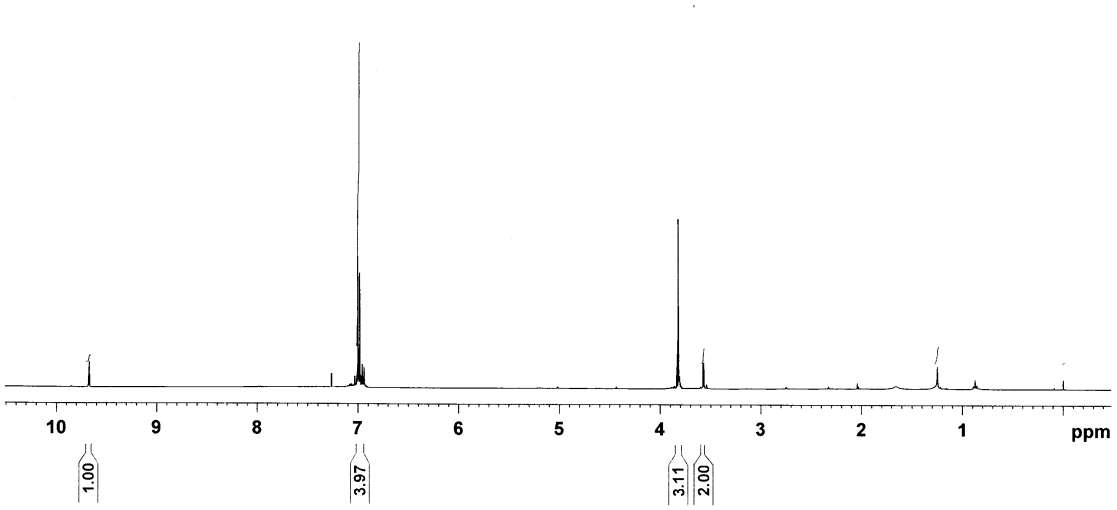


Fig. S20 The ^{1}H NMR spectrum of 2-(4-methoxyphenyl)acetaldehyde (**3k**).

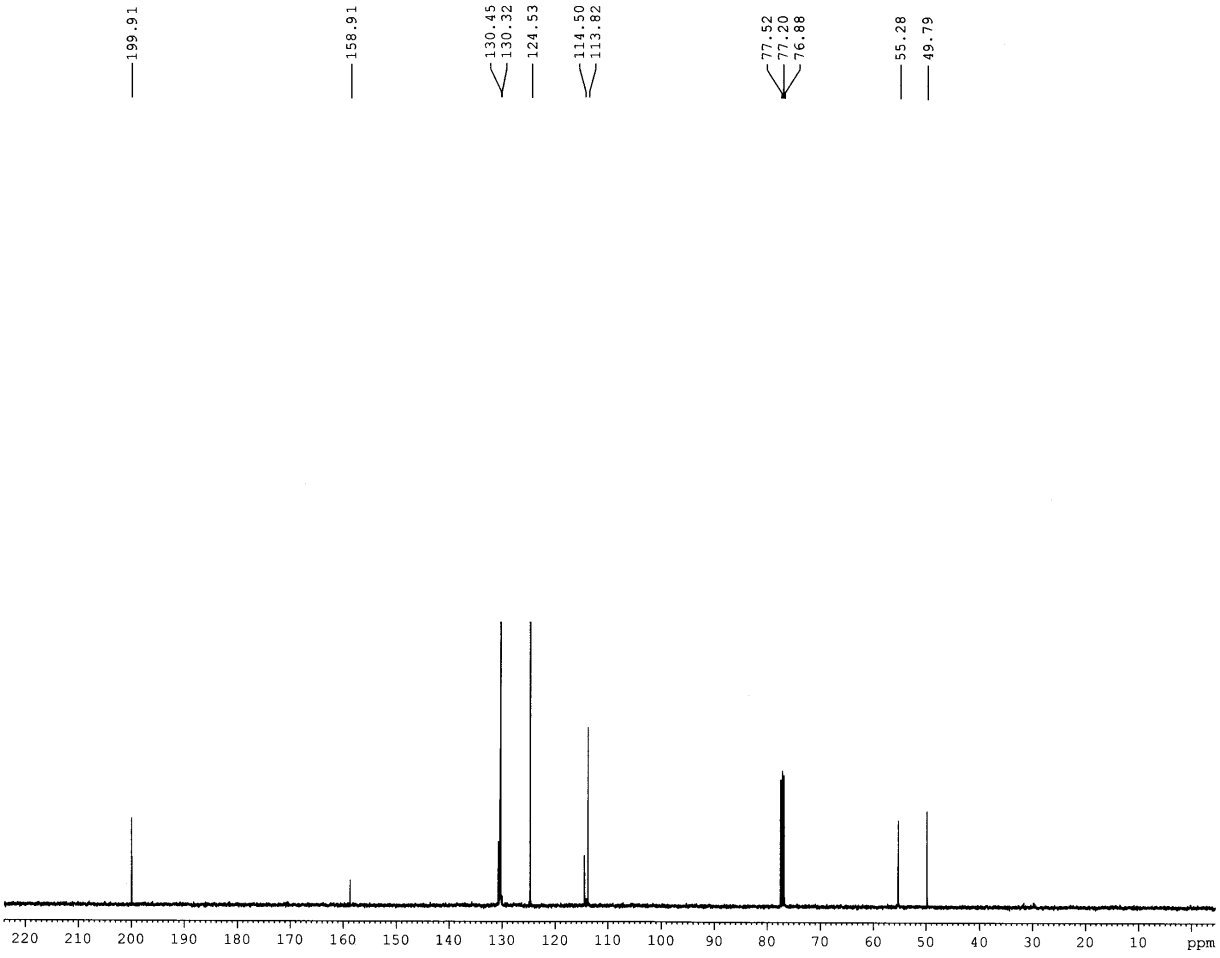


Fig. S21 The ^{13}C NMR spectrum of 2-(4-methoxyphenyl)acetaldehyde (**3k**).

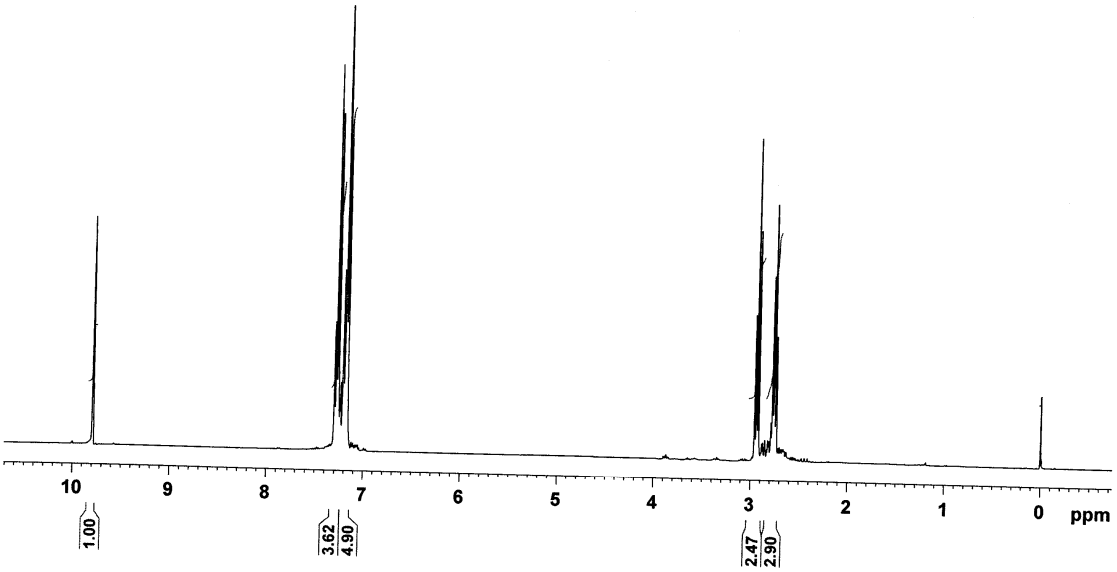


Fig. S22 The ^{1}H NMR spectrum of 3-phenylpropanal (**3o**).

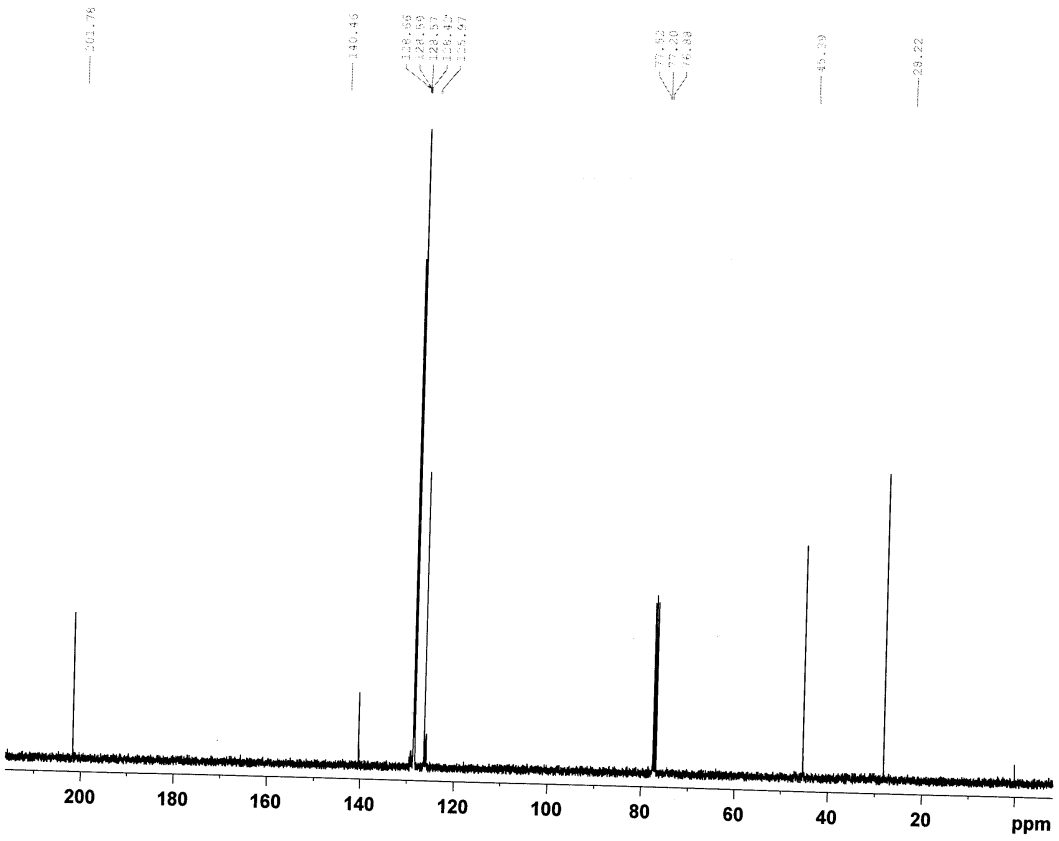


Fig. S23 The ^{13}C NMR spectrum of 3-phenylpropanal (**3o**).

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