Supplementary Material (ESI) for Green Chemistry

Tert-butyl nitrite: a metal-free radical initiator for aerobic cleavage of benzylic C=C bonds in compressed carbon dioxide

Cheng-Xia Miao, Bing Yu and Liang-Nian He*

State Key Laboratory and Institute of Elemento-Organic Chemistry, Nankai University, Tianjin 300071, People's Republic of China
Fax: (+86)-22-2350-4216; Tel: (+86)-22-2350-4216; E-mail: heln@nankai.edu.cn

Contents :

1. General information

Olefins were purchased from J&K Chemical. And tert-butyl nitrite was purchased from Yangzhou Aoxin Chemical Factory. The other organic compounds from the sixth reagent factory of Tianjin were used without further purification except for the solvents, which were distilled by the known method prior to use.

NMR spectra were recorded on a Bruker 300 or 400 spectrometer in $CDCl_3$. ^1H and ^{13}C NMR chemical shifts (δ) are given in ppm relative to TMS. ^1H and ^{13}C positive chemical shifts (δ) in ppm are downfield from tetramethylsilane ($CDCl_3$: $\delta_C = 77.0$ ppm; residual $CHCl_3$ in $CDCl_3$: $\delta_H = 7.26$ ppm). GC-MS were measured on a Finnigan HP G1800 A. GC analyses were performed on a Shimadzu GC-2014 equipped with a capillary column (RTX-5, 30 m×0.25 μm) using a flame ionization detector. Column chromatography was performed by using silica gel 200-300 mesh with ethyl acetate/petroleum as eluent. Oligomer was determined on Agilent 1200 GPC-SEC.

2. Typical procedure for aerobic cleavage of benzylic C=C bond

Styrene was chosen as the model substrate to describe the typical procedure under optimal reaction conditions: A mixture of styrene (0.5 mL, 4.35 mmol) and TBN (11 μL, 2 mol%) was placed in a 25-mL autoclave equipped with an inner glass tube. 2 MPa CO_2 and 1 MPa O_2 were introduced into the autoclave. Then the reactor was heated to the reaction temperature. The final pressure was adjusted to the desired pressure at the reaction temperature by introducing amount of CO_2. The mixture was stirred continuously for the designated reaction time. After cooling, products were then extracted by diethyl ether, and analyzed by gas chromatography (Shimadzu-2014) equipped with a capillary column (RTX-5 30 m × 0.25 mm) using a flame ionization detector. The structure and the purity of the products were further identified using NMR (Bruker-300 MHz, 400 MHz), GC-MS (HP G1800 A), HPLC-MS (LCQ Advantage) and GC, HPLC by comparing retention times and fragmentation patterns with those of authentic samples.

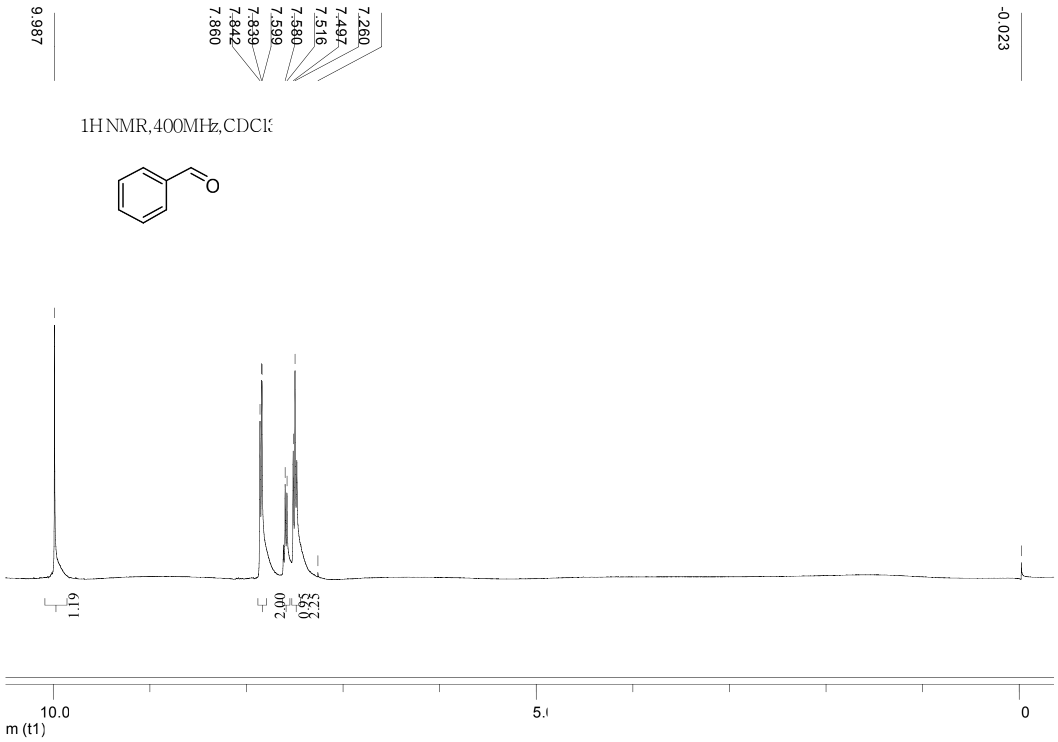
3. **Table S1** TBN-initiated aerobic oxidative cleavage of styrene [a]

Entry	P_{O_2} /MPa	$P_{O_2+CO_2}$ /MPa	Conv. /% [b]	Yield/%[b]	
				Aldehyde	Acid
1	0	0	2	1	0
2[c]	1	1	26	6	0
3	1	1	100	49	21
4	1	4	100	37	9
5	1	7	100	44	7
6	1	10	80	53	6
7	1	13	45	40	0
8	1	16	2	2	0
9[d]	1	13	3	2	0
10[e]	1	13	98	36	18
11[f]	1	13	88	72	5
12[g]	1	13	42	39	0
13[h]	1	13	47	43	0
14[e]	0.5	13	35	32	0
15[e]	2	13	56	48	6
16[i]	1	1	3	0.5	0

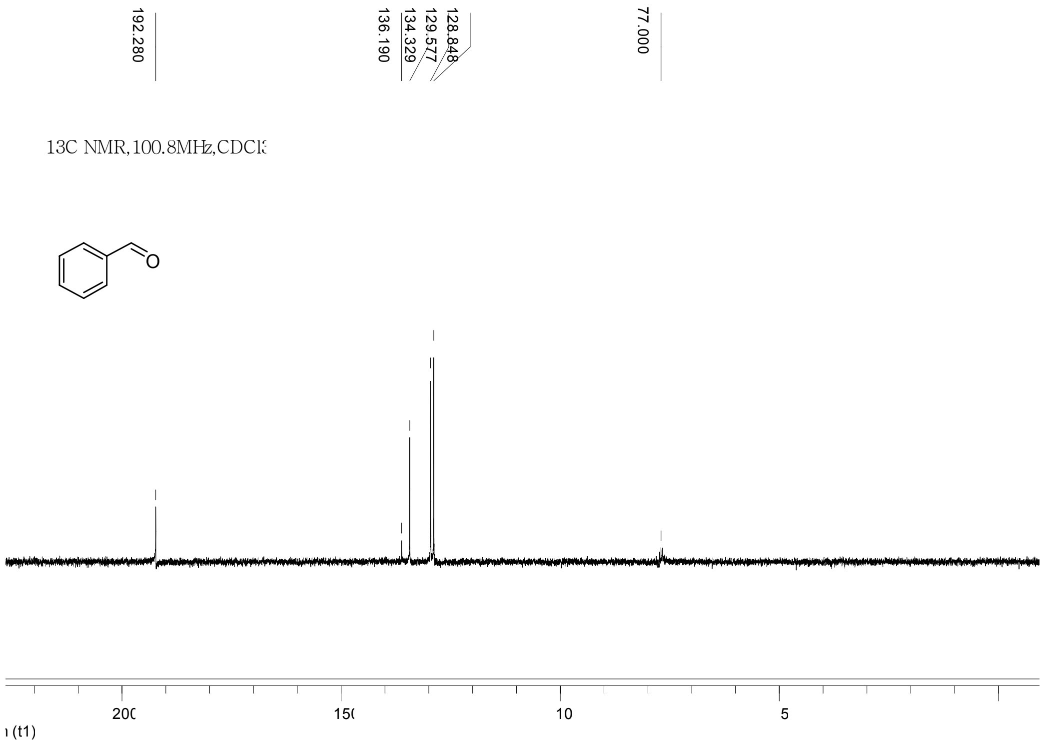
[a] Reaction conditions: styrene (0.5 mL, 4.35 mmol), TBN (11 μL, 2 mmol%), 80 °C, 12 h. [b] Determined by GC using biphenyl as an internal standard. [c] Without TBN. [d] T = 60 °C. [e] T = 120 °C. [f] t = 18 h. [g] TBN (5 μL, 1 mmol%). [h] TBN (27 μL, 5 mmol%). [i] 2 mmol% TEMPO (2, 2, 6, 6-tetramethyl-piperdine-1-oxy) was added.

4. ^{1}H NMR and ^{13}C NMR charts for products identification

Benzyl aldehyde: Light yellow oil liquid

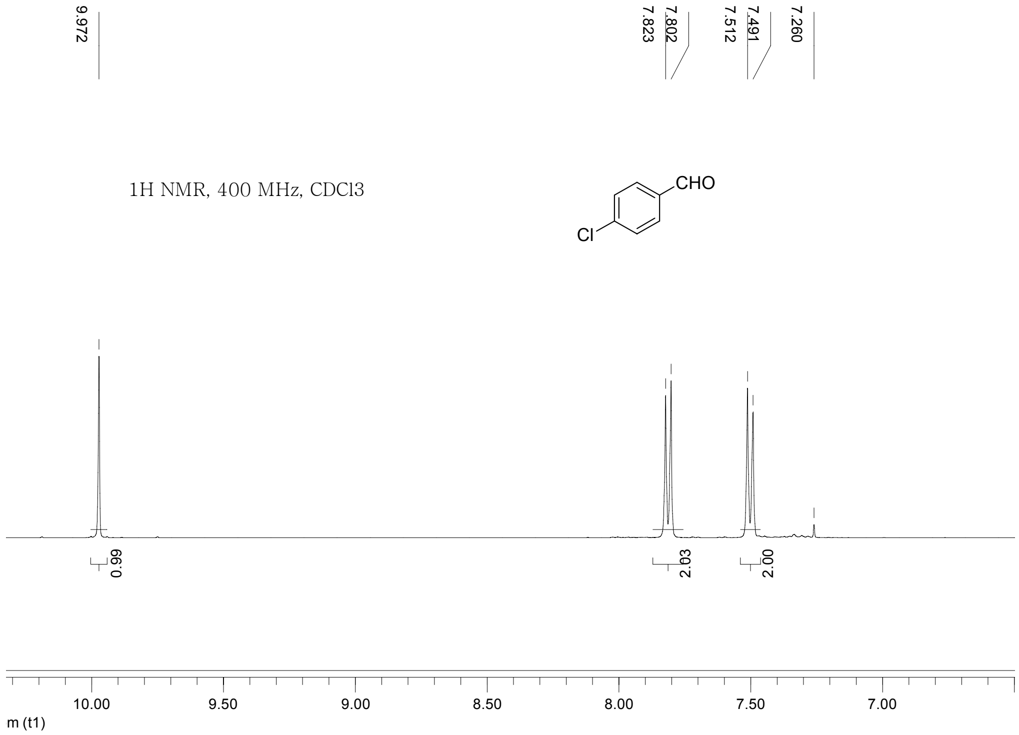


^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.50$ (t, ^3J(H,H) = 7.7 Hz, 2H), 7.60 (t, ^3J(H,H) = 7.4 Hz, 1H), 7.84 (d, ^3J(H,H) = 7.9 Hz, 2H), 9.98 (s, 1H)



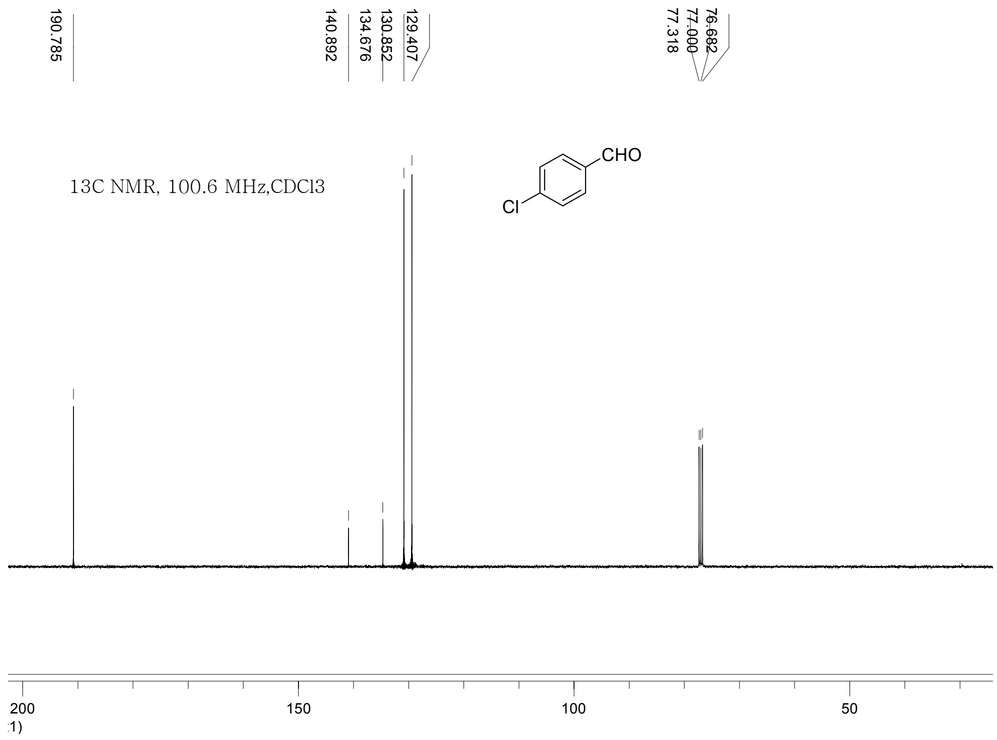
^{13}C {^{1}H} NMR (100.6 MHz, CDCl$_3$): δ = 128.9, 129.6, 134.3, 136.2, 192.3.

4-Cl-benzyl aldehyde：



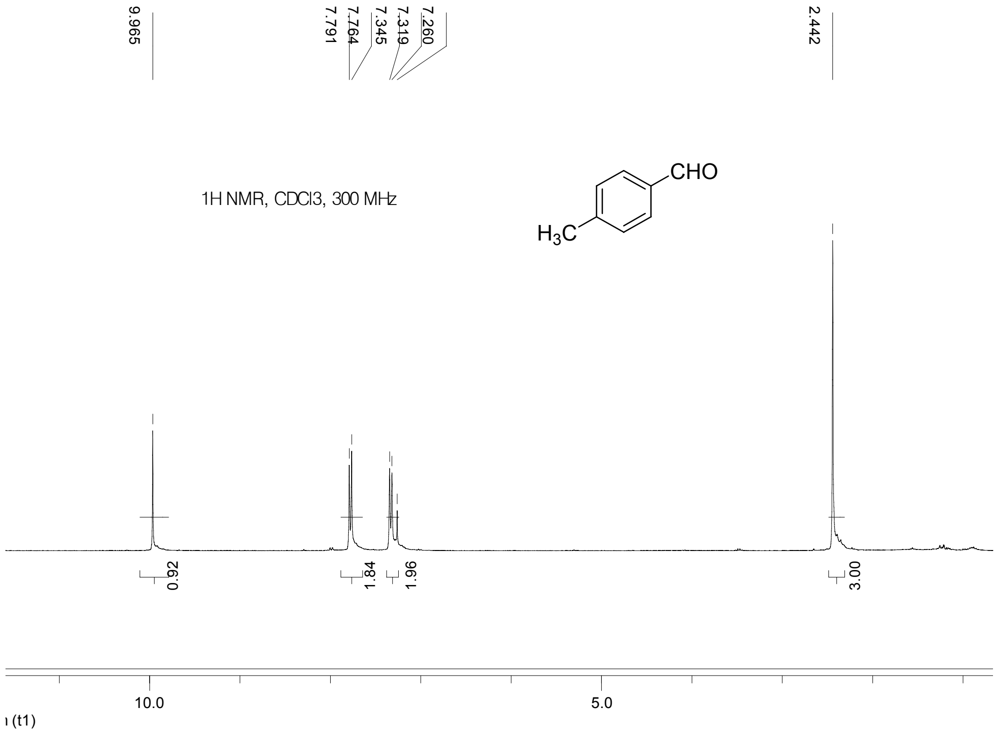
^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.50 (d, ^3J(H,H) = 8.4 Hz, 2H), 7.81 (t, ^3J(H,H) =

8.4 Hz, 2H), 9.97 (s, 1H)



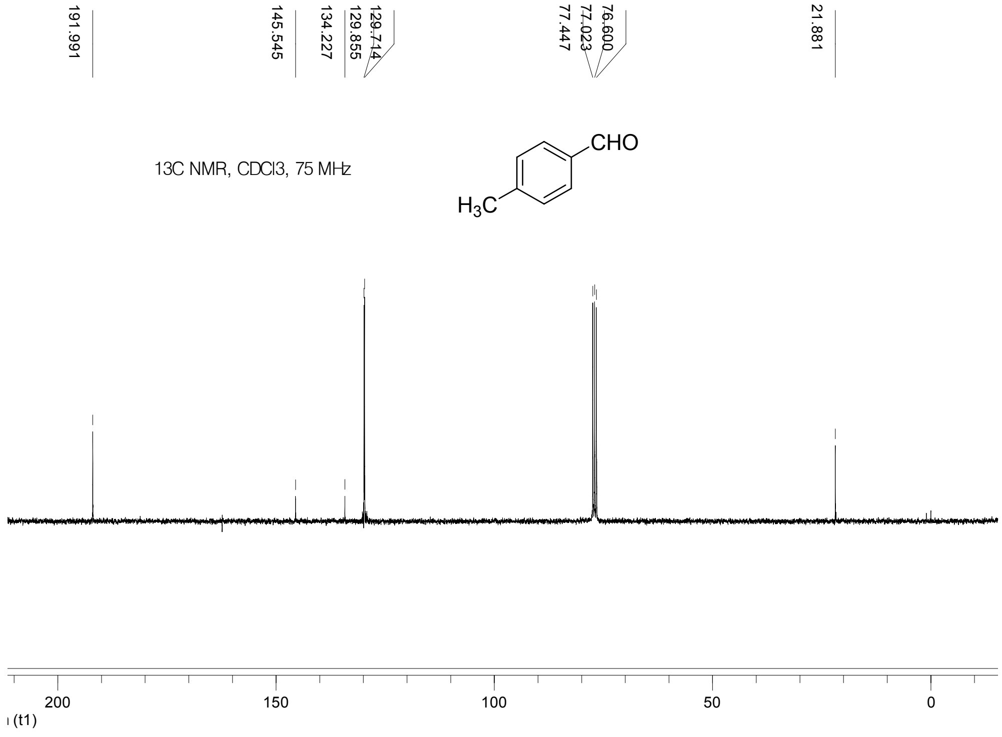
^{13}C {^{1}H} NMR (100.6 MHz, CDCl$_3$): δ = 129.4, 130.9, 134.7, 140.9, 190.8.

4-Methylbenzaldehyde: Colorless liquid



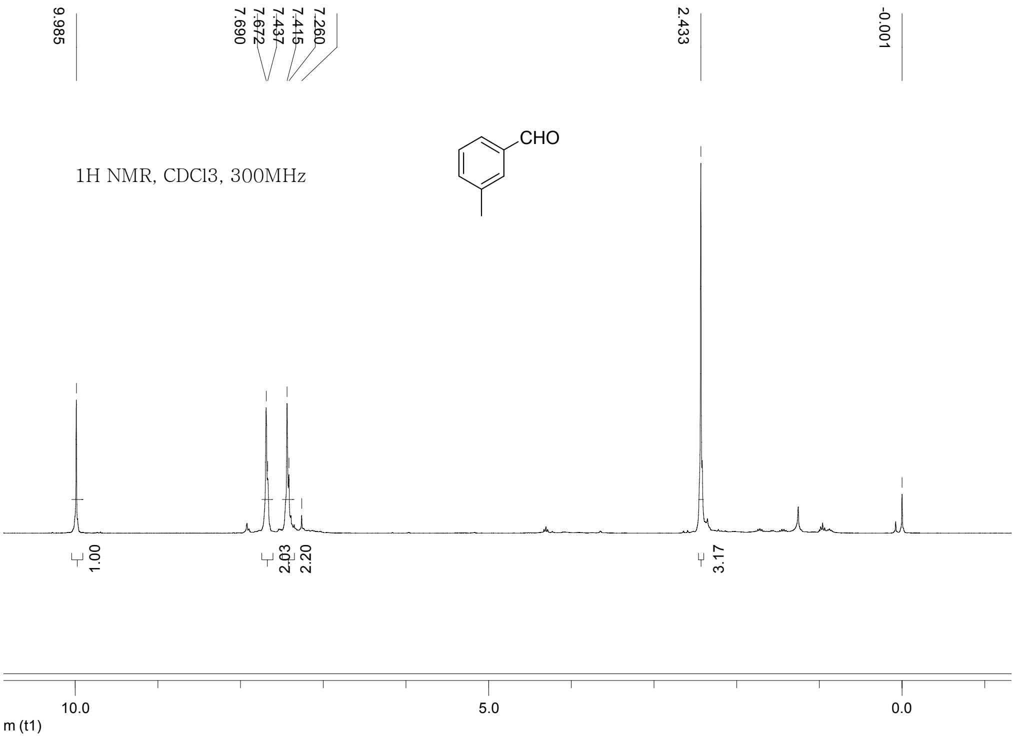
^{1}H NMR (300 MHz, CDCl$_3$): δ = 2.44 (s, 3H), 7.33 (d, ^{3}J(H,H) = 3.9 Hz, 2H), 7.78 (d,

${}^{3}J$(H,H) = 4.1 Hz, 2H), 9.97 (s, 1H)

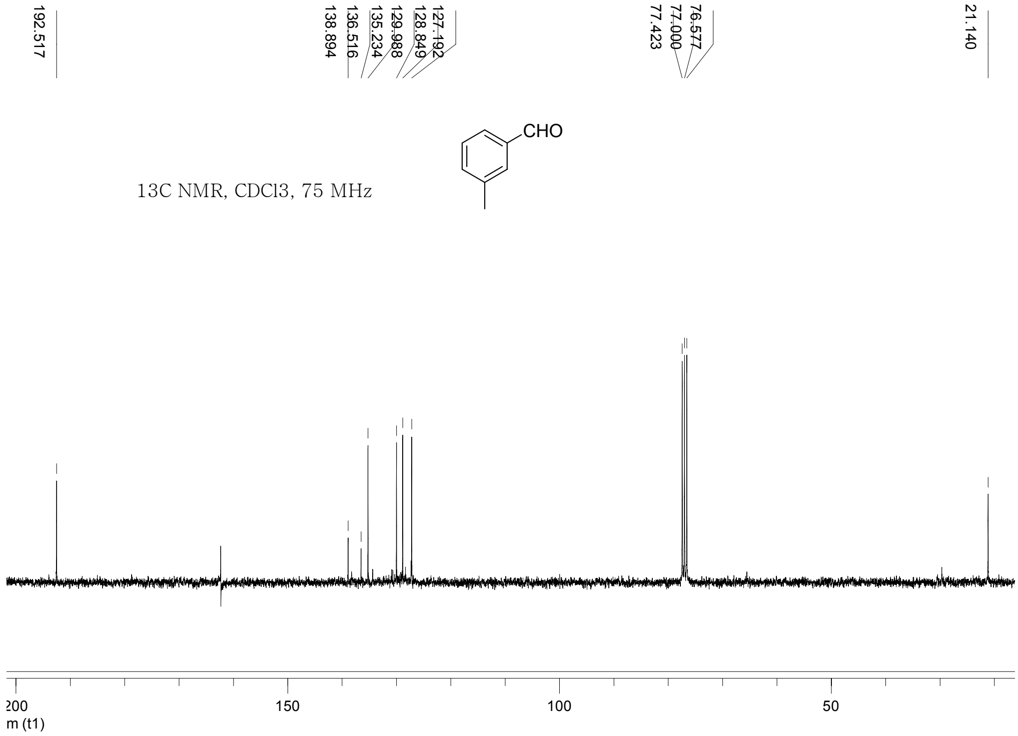


^{13}C {^{1}H} NMR (75 MHz, CDCl$_3$): δ = 21.9, 129.7, 129.9, 134.2, 145.6, 192.0.

3-Methylbenzaldehyde:

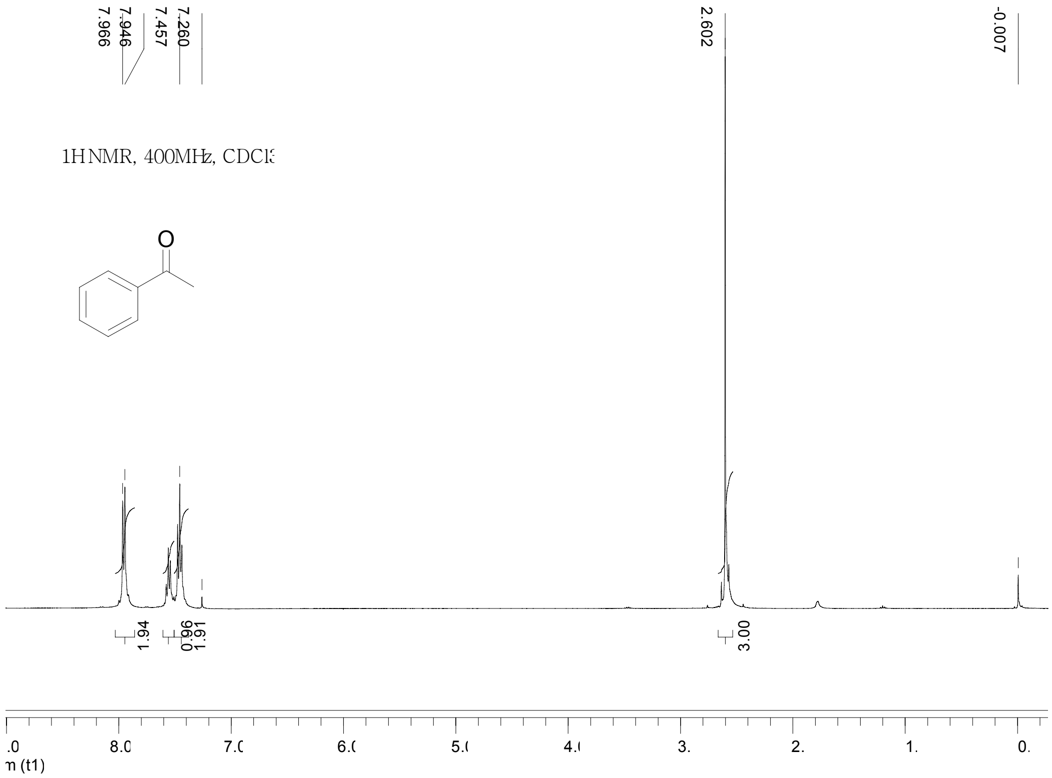


^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.43 (s, 3H), 7.44 (m, 2H), 7.68 (d, ^{3}J(H,H) = 8.0 Hz, 2H), 9.99 (s, 1H)

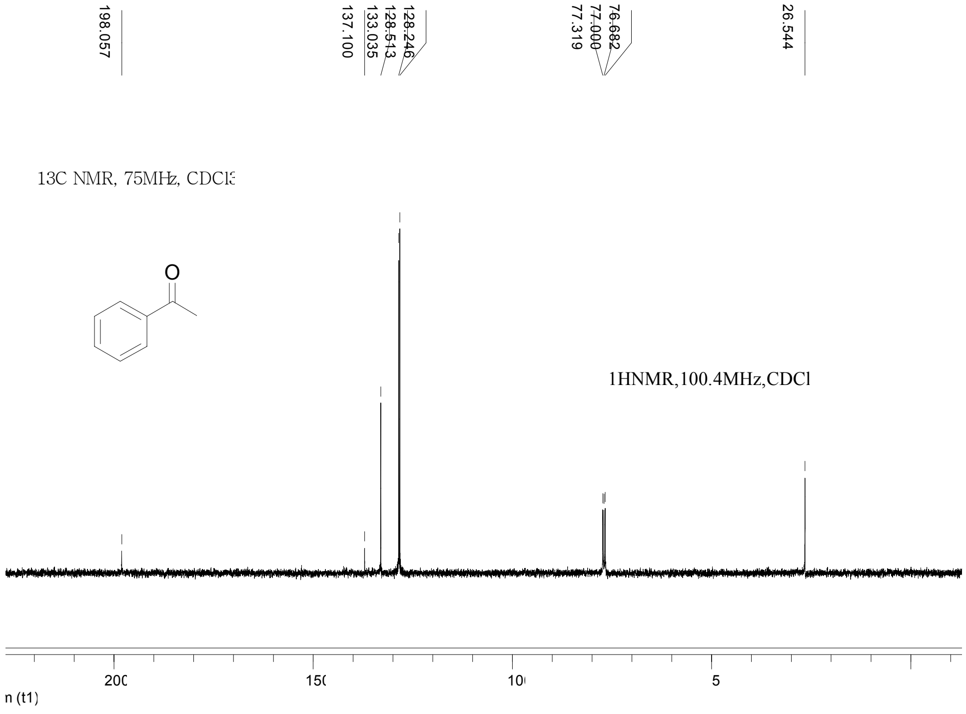


^{13}C {^{1}H} NMR (75 MHz, $CDCl_3$): δ = 21.2, 127.2, 128.8, 130.0, 135.3, 136.4, 138.9, 192.6.

Acetophenone: Light yellow liquid

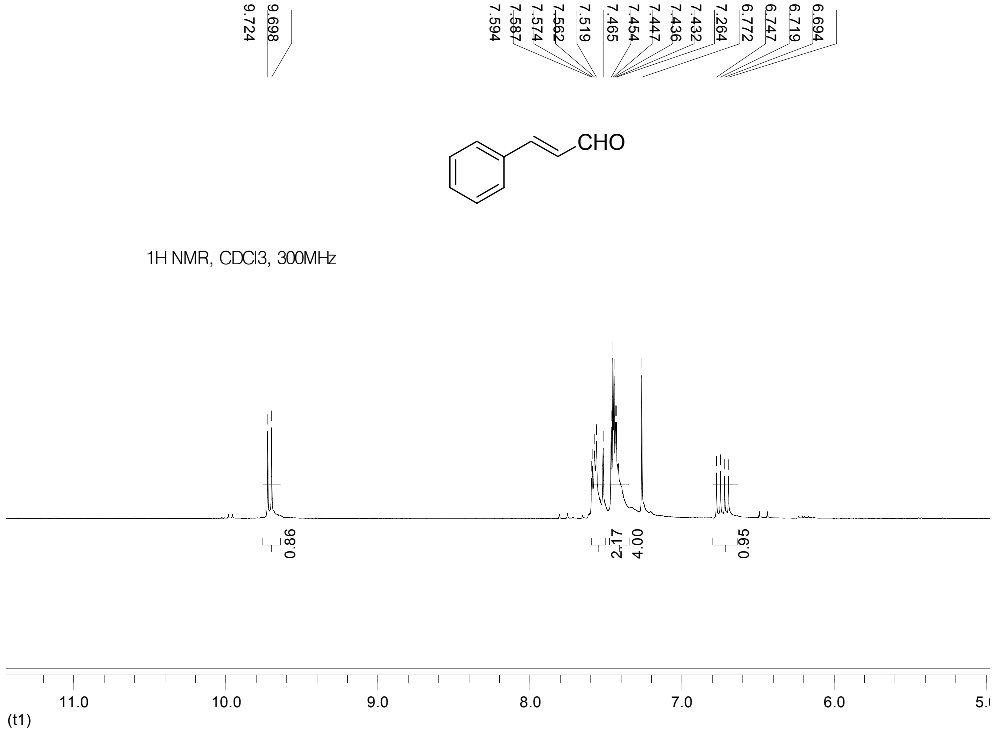


^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 2.60$ (s, 3H), 7.46 (t, $^{3}J(H,H) = 7.7$ Hz, 2H), 7.56 (t, $^{3}J(H,H) = 7.5$ Hz, 1H), 7.96 (d, $^{3}J(H,H) = 7.8$ Hz, 2H)

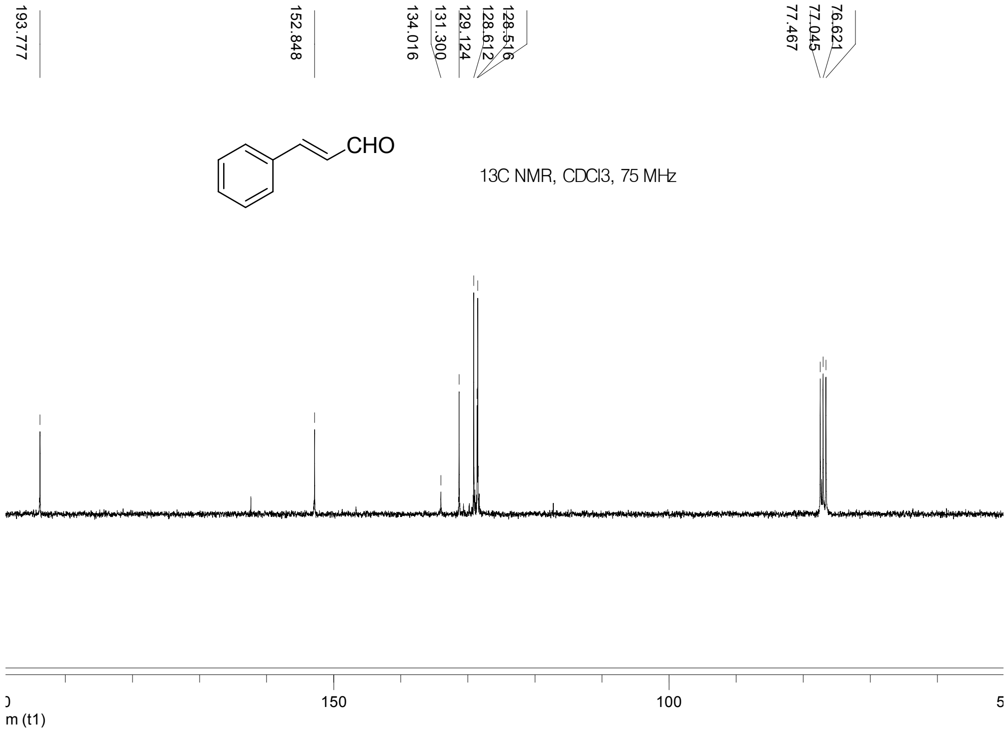


^{13}C {^{1}H} NMR (100.6 MHz, $CDCl_3$): $\delta = 26.5$, 128.2, 128.5, 133.0, 137.1, 198.1.

Cinnamaldehyde: Light yellow liquid

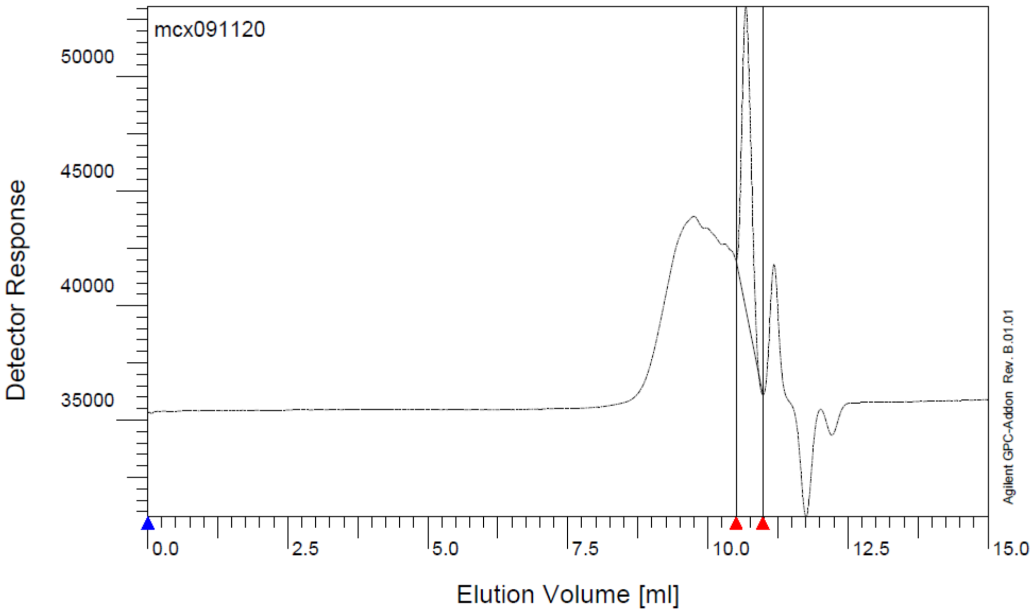


^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.69-6.77 (m, 1H), 7.43-7.47 (m, 4H), 7.52-7.59 (m, 2H), 9.71 (d, ^3J(H,H) = 3.9 Hz, 1H)



^{13}C {^{1}H} NMR (75 MHz, $CDCl_3$): δ = 128.5, 128.6, 129.1, 131.3, 134.0, 152.8, 193.8.

5. GPC investigation of oligomers of styrene



Sample : mcx091120
Injection Date :
Calibration File : lijing 090731.CAL
Calibration Date :
Baseline from : 10.503 min
Integration from: 10.503 min
MHK - A (Cal.): 0.000000E+0
Eluent : THF
Concentration : 1.000 g/l
Column 1 : ....?
Detector 1 : RID A, 09, 11:48:18
Operator : cgh

Baseline to : 10.982 min
Integration to : 10.982 min
MHK - K (Cal.): 1.000000E+0 ml/g
Flowrate : 1.000 ml/min
Inject volume : 20.000 ul
Temperature : 23.000 C
Delay volume : 0.000 ml
Acquisition interval : 0.210 sec

rid1A

Mn :	3.0308e2	g/mol
Mw :	3.0483e2	g/mol
Mz :	3.0657e2	g/mol
Mv :	0.000000	g/mol
D :	1.0058e0	
[n]:	0.000000	ml/g
Vp :	1.0685e1	ml
Mp :	3.0835e2	g/mol
A :	2.5198e3	ml*V
10%	2.7403e2	g/mol
30%	2.9205e2	g/mol
50%	3.0505e2	g/mol
70%	3.1769e2	g/mol
90%	3.3498e2	g/mol