Electronic Supplementary Information

A green approach for aerobic oxidation of benzylic alcohols catalysed by Cu^{I}-Y zeolite / TEMPO in ethanol without additional additives

Samuthirarajan Senthilkumar,[a] Wei Zhong,*[a] Mookan Natarajan,[a] Chunxin Lu,[a] Binyu Xu[b] and Xiaoming Liu*[a]

Table S1. EDX analysis results of Cu^{I}-Y zeolite.

Element	Atomic number	Series	normal wt. (%)	normal. at. (%)
Oxygen	8	K-series	42.79	62.41
Aluminium	13	K-series	9.14	7.91
Silicon	14	K-series	25.94	21.55
Copper	29	K-series	22.12	8.13

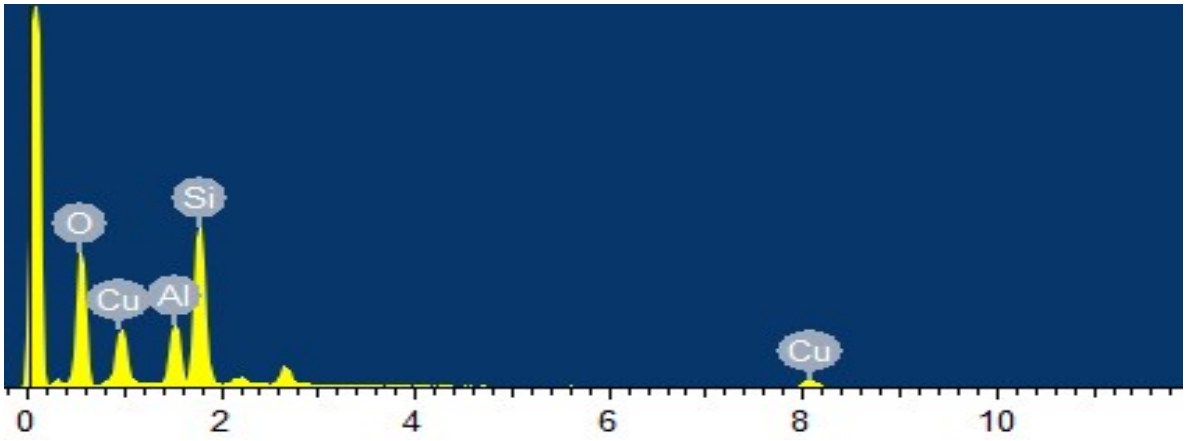


Figure S1. EDX spectrum of Cu^{I}-Y zeolite.

Table S2. The binding energies (eV) of XPS results of Cu, O, Al and Si in fresh and recycled Cu^{I}-Y zeolite.

	Cu^{+} $2p_{1/2}$	**Cu^{2+} $2p_{1/2}$**	**Cu^{2+} Sat.**	**Cu^{+} $2p_{3/2}$**	**Cu^{2+} $2p_{3/2}$**	**Cu^{2+} Sat.**	**O 1s**	**Al 2p**	**Si 2p**
Fresh catalyst	952.13	954.50	943.18	932.25	934.46	962.80	532.50	74.78 77.68	101.98
							531.70		102.58 103.18
							530.80		
Related peak area	24694.50	18721.4	16757.60	28721.70	21078.70	21982.70	36703.70	4186.70	9101.50
							166703.70	2287.50	17688.00
							21703.70		8457.70
5th recycle	952.00	954.98	943.88	932.28	934.88	941.60	532.50	74.60 77.70	101.95
							531.80		102.74
							530.90		103.50
Related peak area	18955.50	21891.30	20443.90	22394.20	19473.50	16268.90	66326.10	4015.30	8938.70
							116703.70	2148.90	17060.00
							15990.00		8429.30

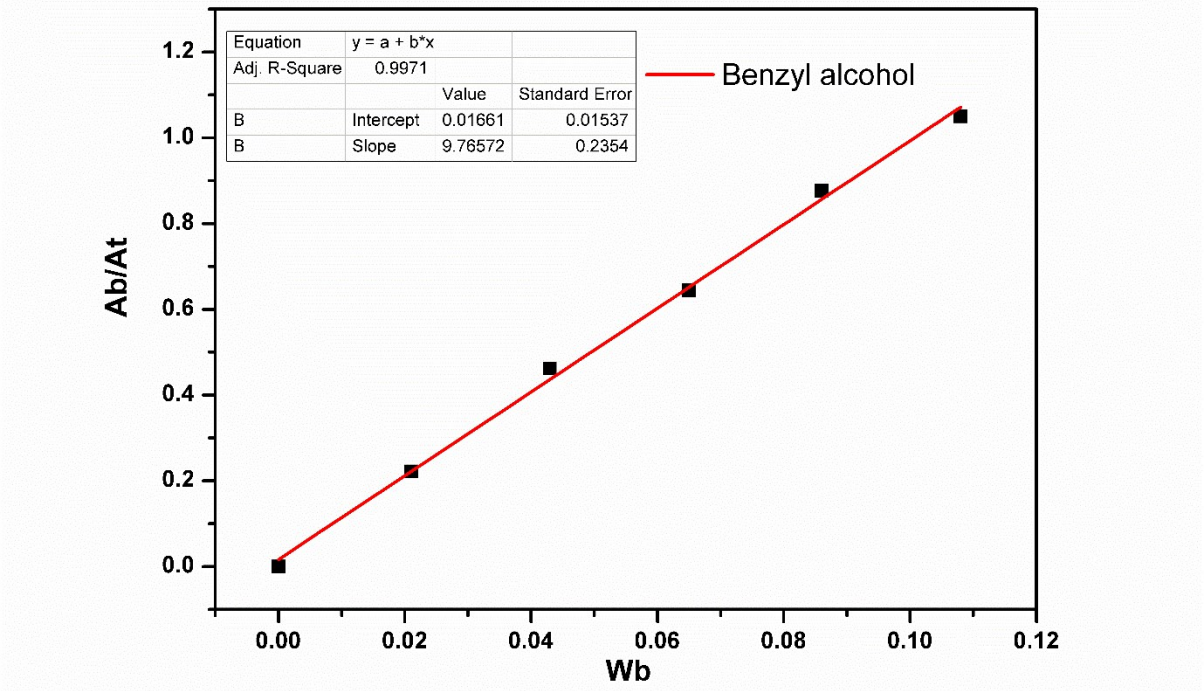


Figure S2. Standard curve for benzyl alcohol using 1,2-dichlorobenzene (1 mmol) as internal standard (Where Ab = area of benzyl alcohol, At = area of 1,2-dichlorobenzene, Wt = Weight percentage of benzyl alcohol).

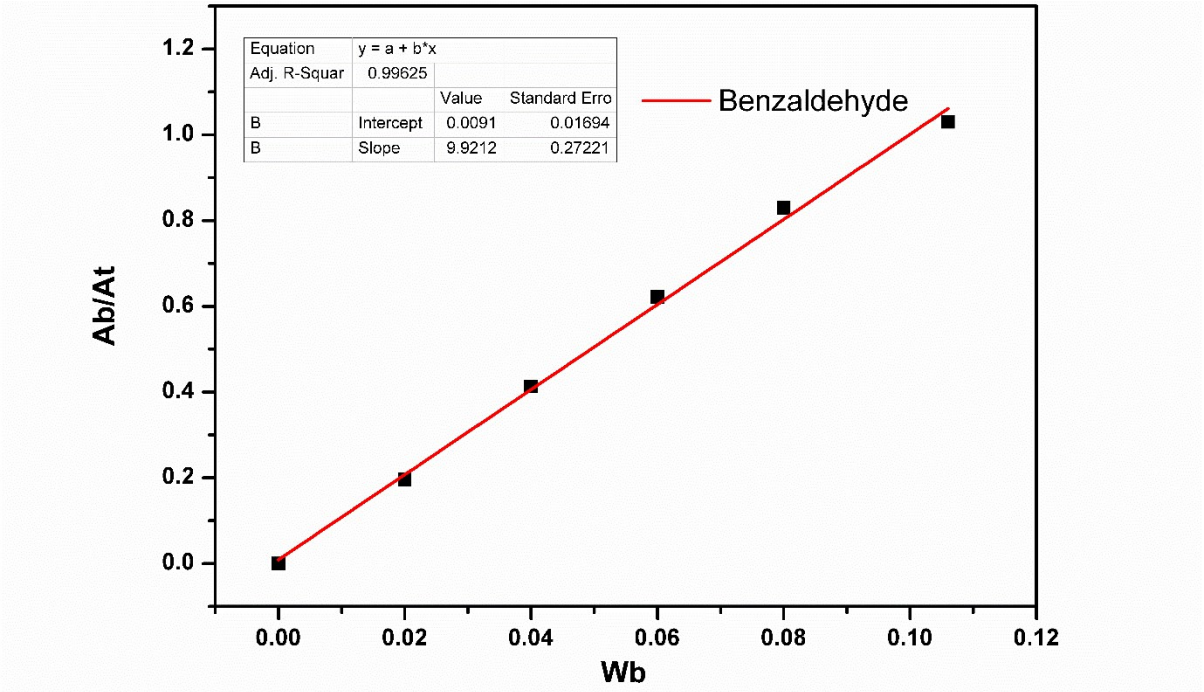


Figure S3. Standard curve for benzaldehyde using 1,2-dichlorobenzene (1 mmol) as internal standard (Where Ab = area of benzaldehyde, At = area of 1,2-dichlorobenzene, Wt = Weight percentage of benzaldehyde).

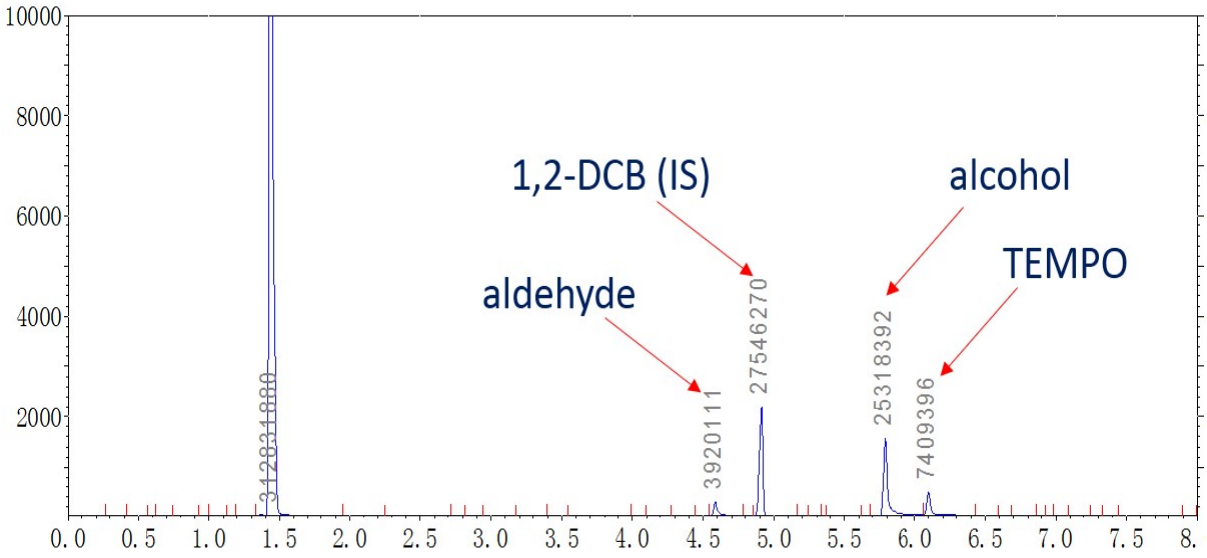


Figure S4. GC Spectrum for oxidation of benzyl alcohol under N_2 atmosphere. (Benzyl alcohol (1 mmol), zeolite catalyst (100 mg), TEMPO (39 mg, 0.25 mmol which 25% based on the substrate), 1,2-dichlorobenzene (1 mmol), solvent (3 mL), 60 °C, 18 hrs.)

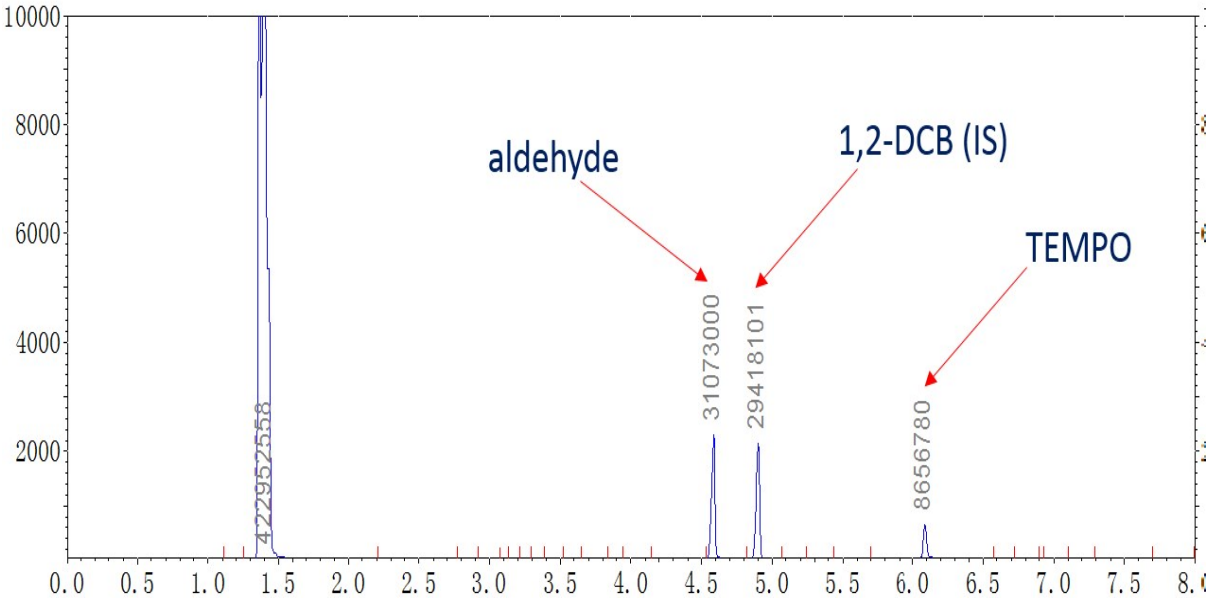
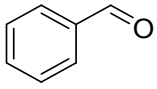


Figure S5. GC Spectrum for aerobic oxidation of benzyl alcohol under atmospheric air. (Benzyl alcohol (1 mmol), zeolite catalyst (100 mg), TEMPO (39 mg, 0.25 mmol which 25% based on the substrate), 1,2-dichlorobenzene (1 mmol), solvent (3 mL), 60 °C, 18 hrs.)

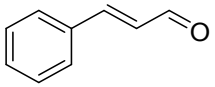
Spectral data of selected compounds:

Benzaldehyde[1]:



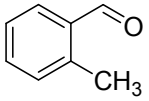
Oily liquid, 105 mg, isolated yield: 99%. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 10.01 (s, 1H), 7.86 (d, *J* = 8, 2H), 7.61 (t, 1H), 7.51 (t, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 192.41, 136.37, 134.45, 129.72, 128.98.

Cinnamaldehyde[1]:



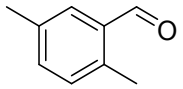
Oily liquid, 113 mg, isolated yield: 85%. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 9.8 (d, *J* = 8, 1H), 7.63 (m, 2H), 7.54 (d, *J* = 8, 4H), 6.82 (dd, *J* = 16, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 193.92, 153.0, 134.09, 131.46, 129.28, 128.75, 128.67.

2-methylbenzaldehyde[2]:



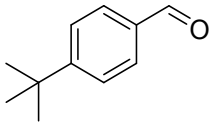
Oily liquid, 107 mg, isolated yield: 89%. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 10.28 (s, 1H), 7.8 (d, *J* = 8, 1H), 7.48 (t, 1H), 7.38 (t, 1H), 7.29 (d, *J* = 4, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 192.84, 133.63, 132.03, 131.76, 126.31, 19.58.

2,5-dimethlbenzaldehyde[3]:



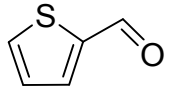
Oily liquid, 85 mg, isolated yield: 63%. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 10.27 (s, 1H), 7.63 (s, 1H), 7.17 (d, *J* = 4, 1H), 7.03 (d, *J* = 4, 1H), 2.40 (s, 3H), 2.31(s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 192.81, 133.63, 132.03, 131.76, 126.31, 19.59.

4-*t*-butylbenzaldehyde[4]:



Oily liquid, 124 mg, isolated yield: 76%. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 9.98 (s, 1H), 7.82 (d, *J* = 4, 1H), 7.55 (d, *J* = 4, 2H), 7.48 (d, *J* = 4, 1H), 1.35 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 192.08, 130.06, 129.68, 125.97, 125.46, 31.05.

2-thiophenecarboxaldehyde[1]:



Brown oily liquid, 56 mg, isolated yield: 50 %. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 9.94 (s, 1H), 7.78 (m, 2H), 7.22 (d, *J* =4, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 182.96, 136.25, 135.1, 128.28.

^{1}H & ^{13}C-NMR spectra of selected compounds：

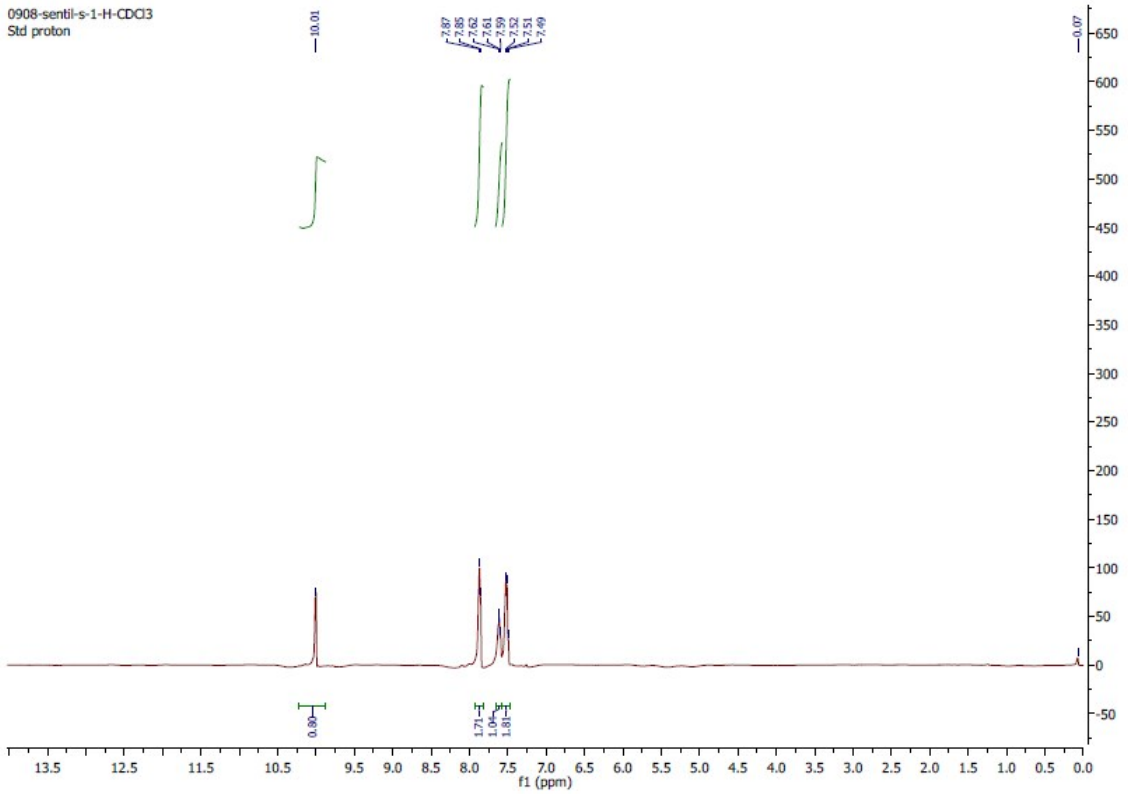


Figure S6. ^{1}H NMR spectrum of benzaldehyde in $CDCl_3$.

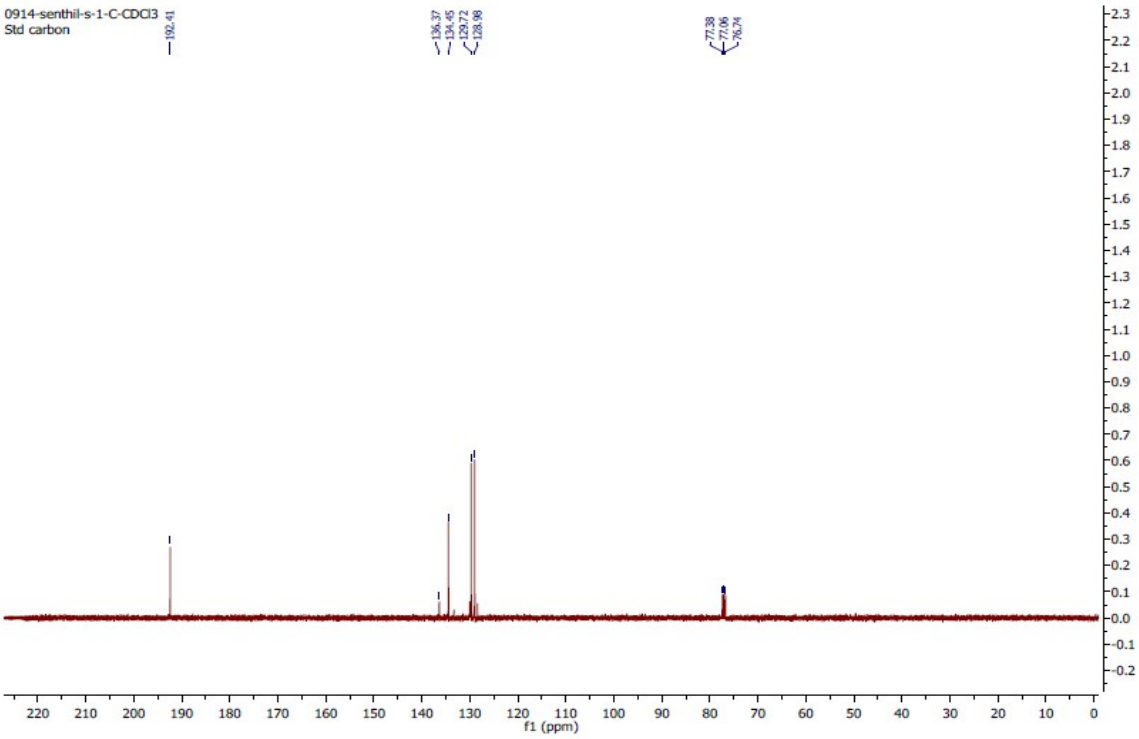


Figure S7. ^{13}C NMR spectrum of benzaldehyde in $CDCl_3$.

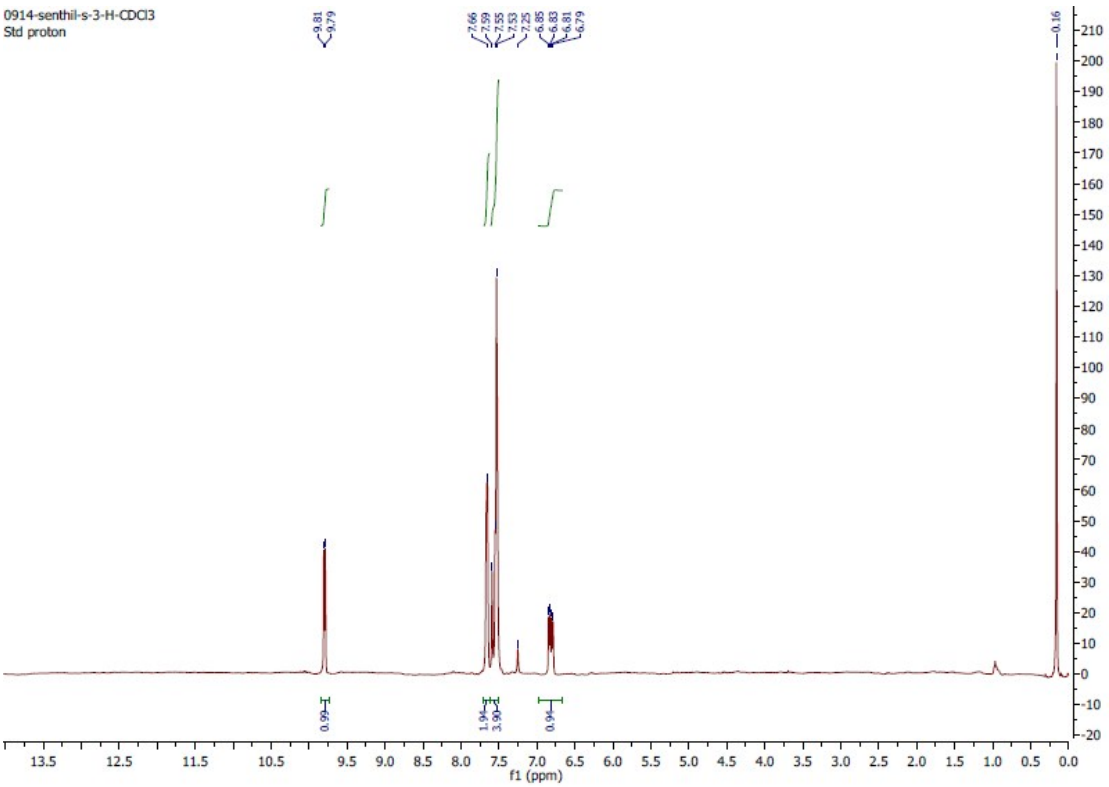


Figure S8. ^{1}H NMR spectrum of cinnamaldehyde in $CDCl_3$.

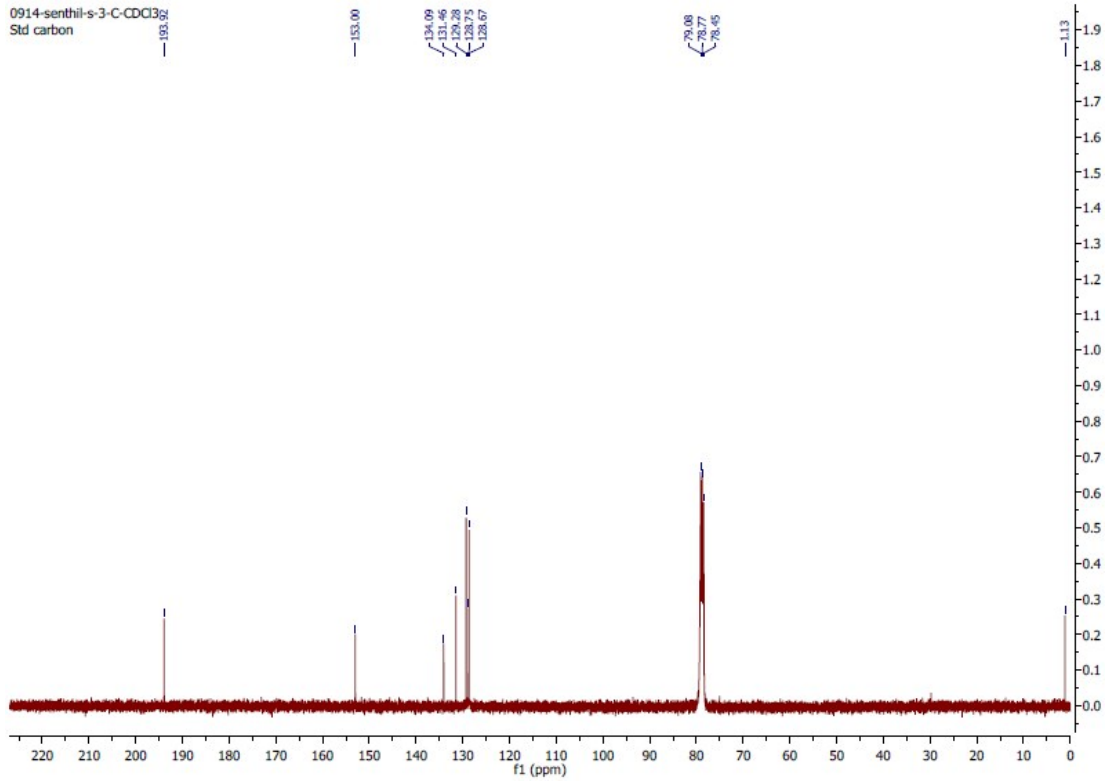


Figure S9. ^{13}C NMR spectrum of cinnamaldehyde in $CDCl_3$.

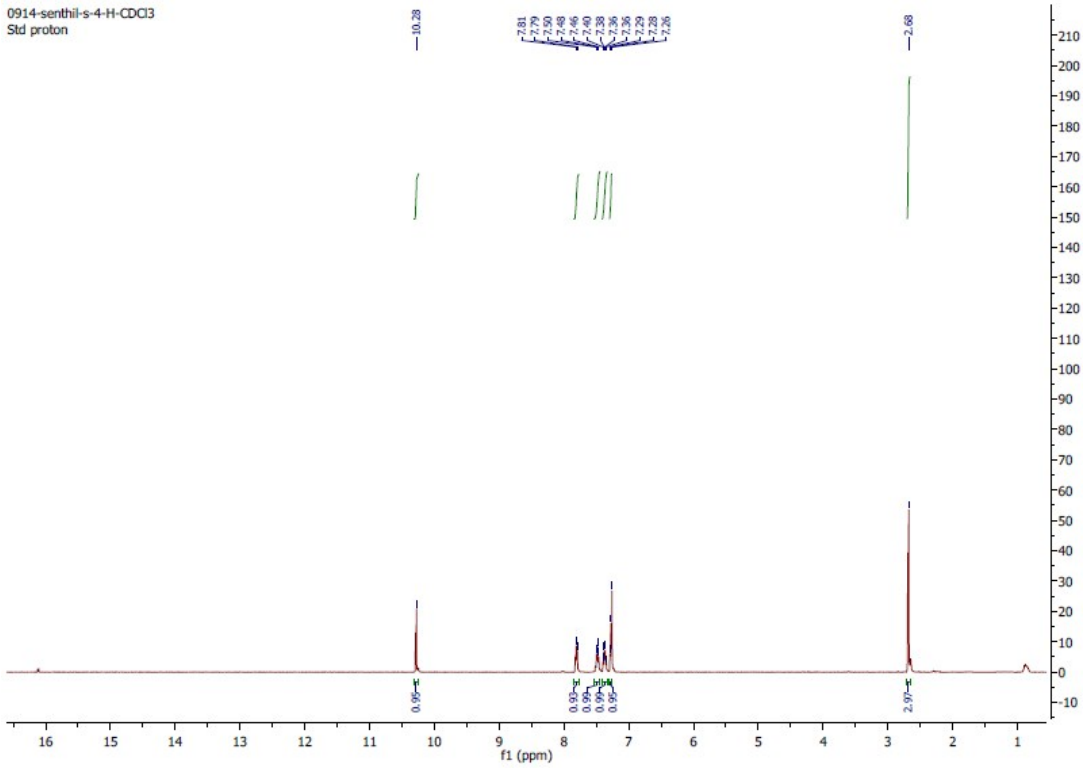


Figure S10. ^{1}H NMR spectrum of 2-methylbenzaldehyde in $CDCl_3$.

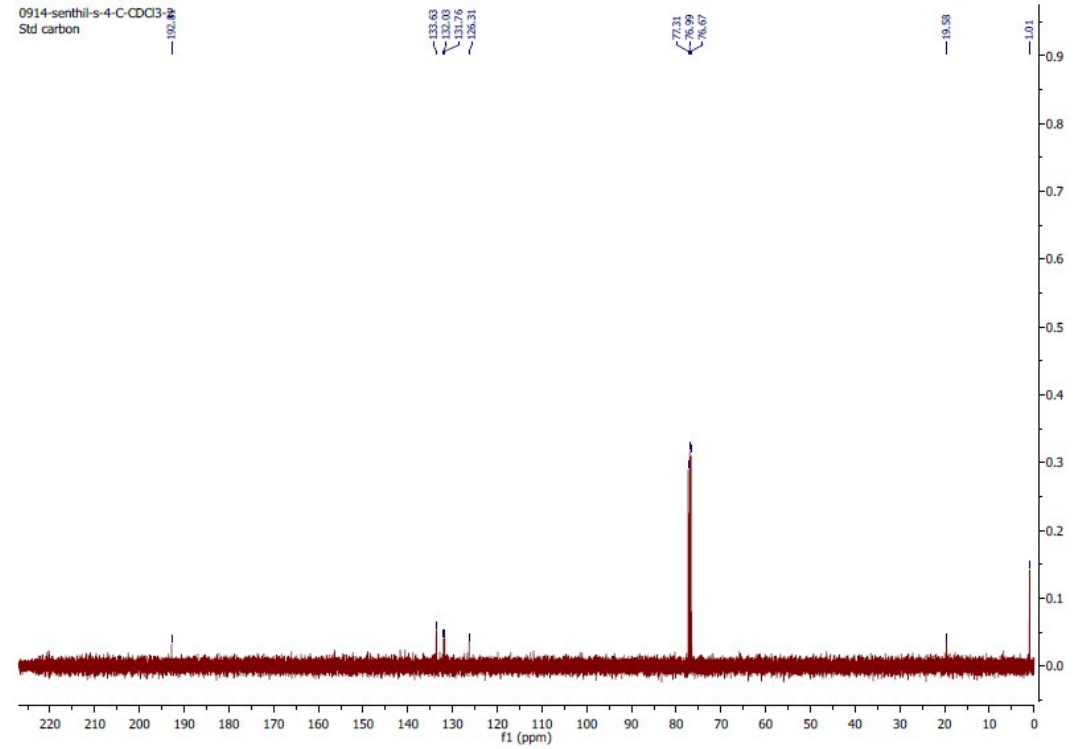


Figure S11. ^{13}C NMR spectrum of 2-methylbenzaldehyde in $CDCl_3$.

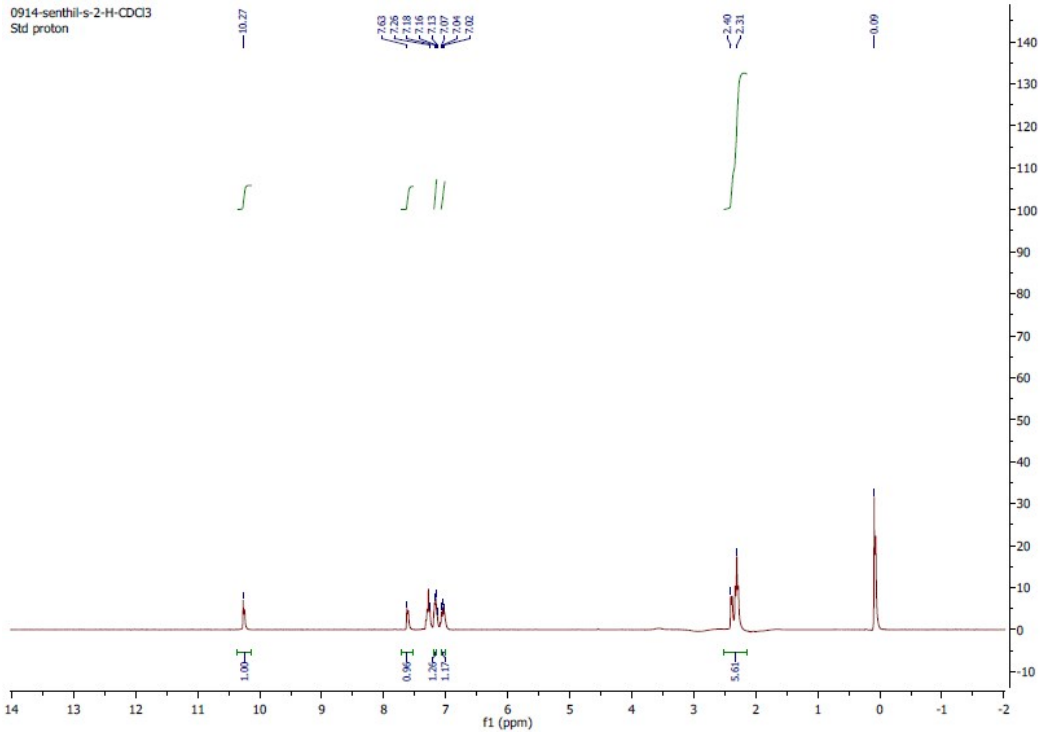


Figure S12. ^{1}H NMR spectrum of 2,5-dimethylbenzaldehyde in $CDCl_3$.

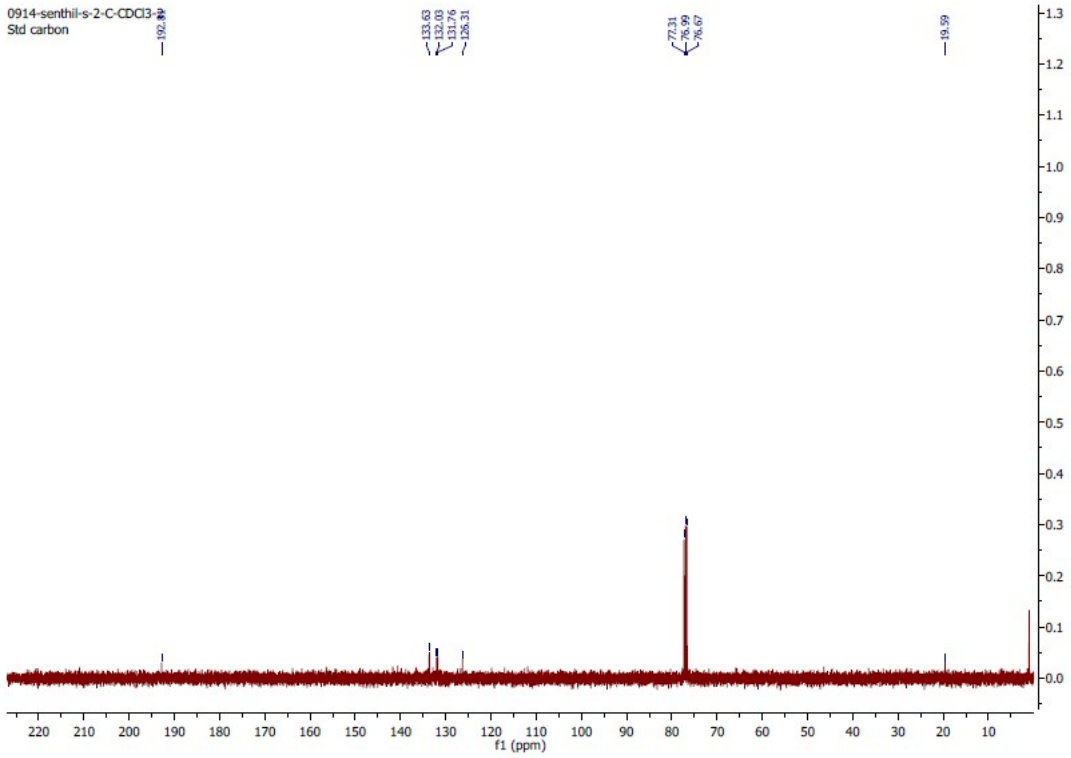


Figure S13. ^{13}C NMR spectrum of 2,5-dimethylbenzaldehyde in $CDCl_3$.

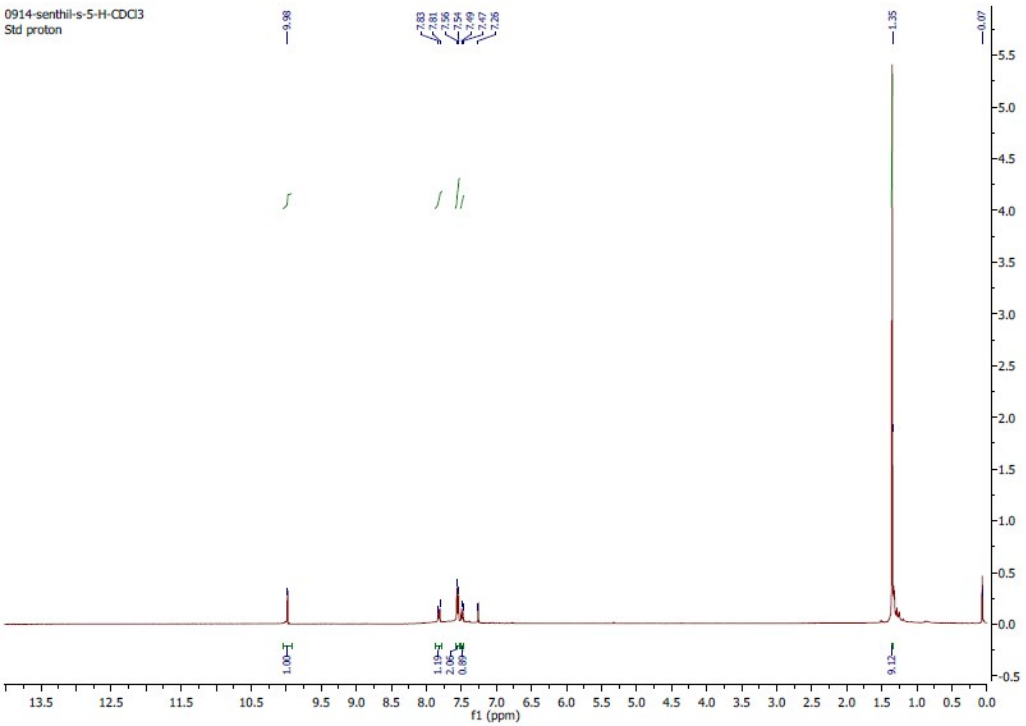


Figure S14. ^{1}H NMR spectrum of 4-*t*-butylbenzaldehyde in $CDCl_3$.

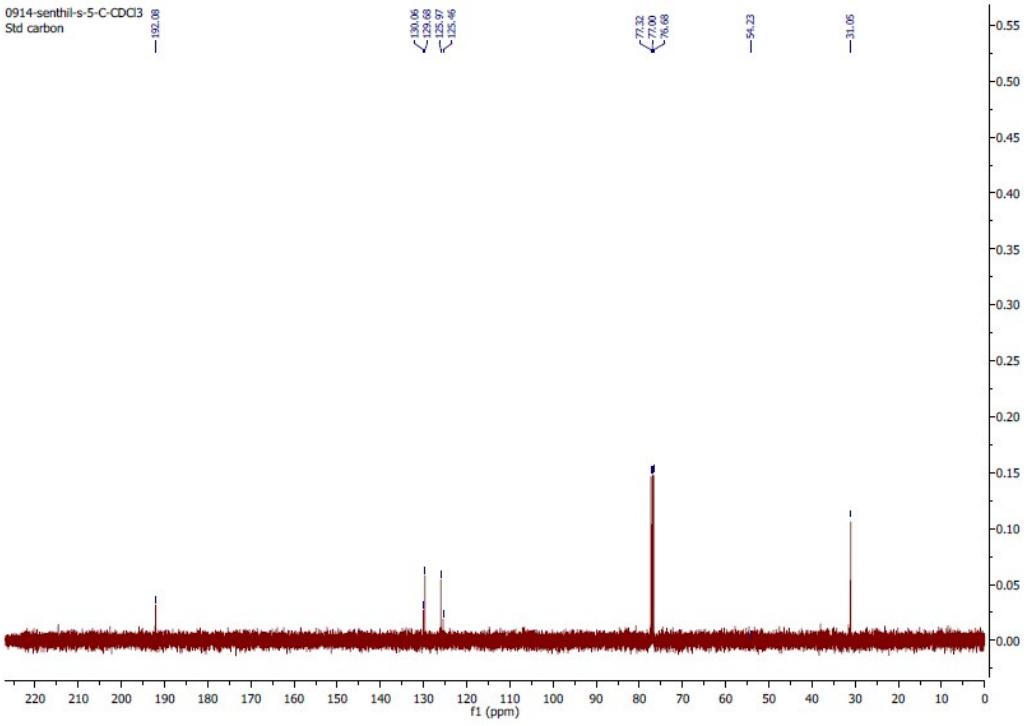


Figure S15. ^{13}C NMR spectrum of 4-*t*-butylbenzaldehyde in $CDCl_3$.

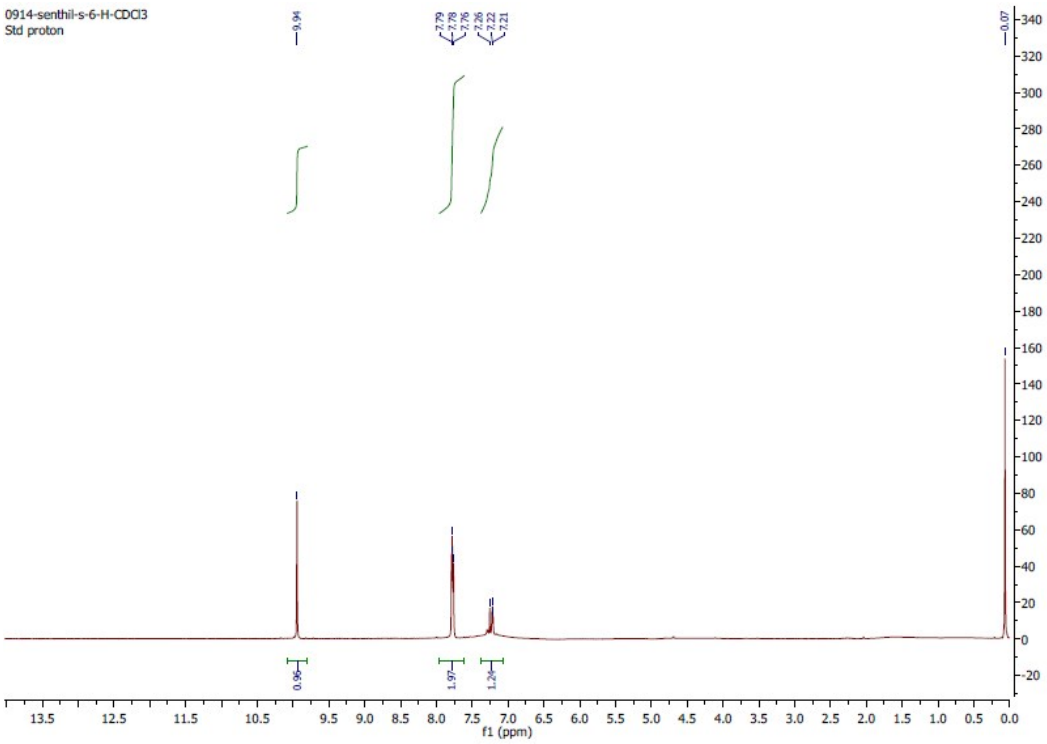


Figure S16. ^{1}H NMR spectrum of 2-thiophenecarboxaldehyde in $CDCl_3$.

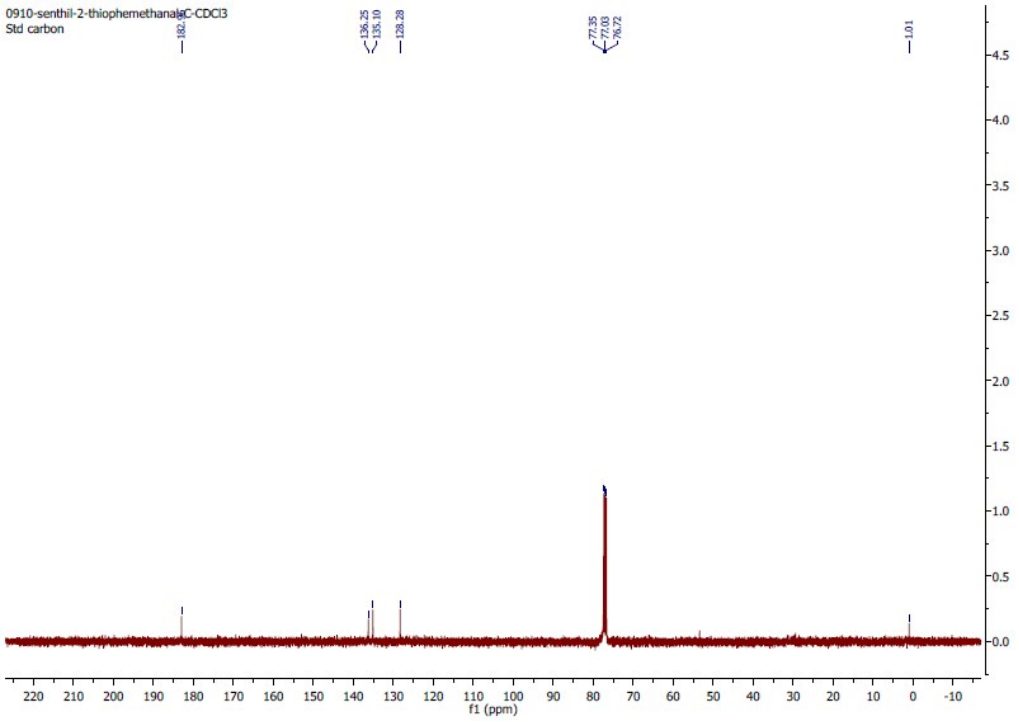


Figure S17. ^{13}C NMR spectrum of 2-thiophenecarboxaldehyde in $CDCl_3$.

GC-MS spectrum of the products as follows：

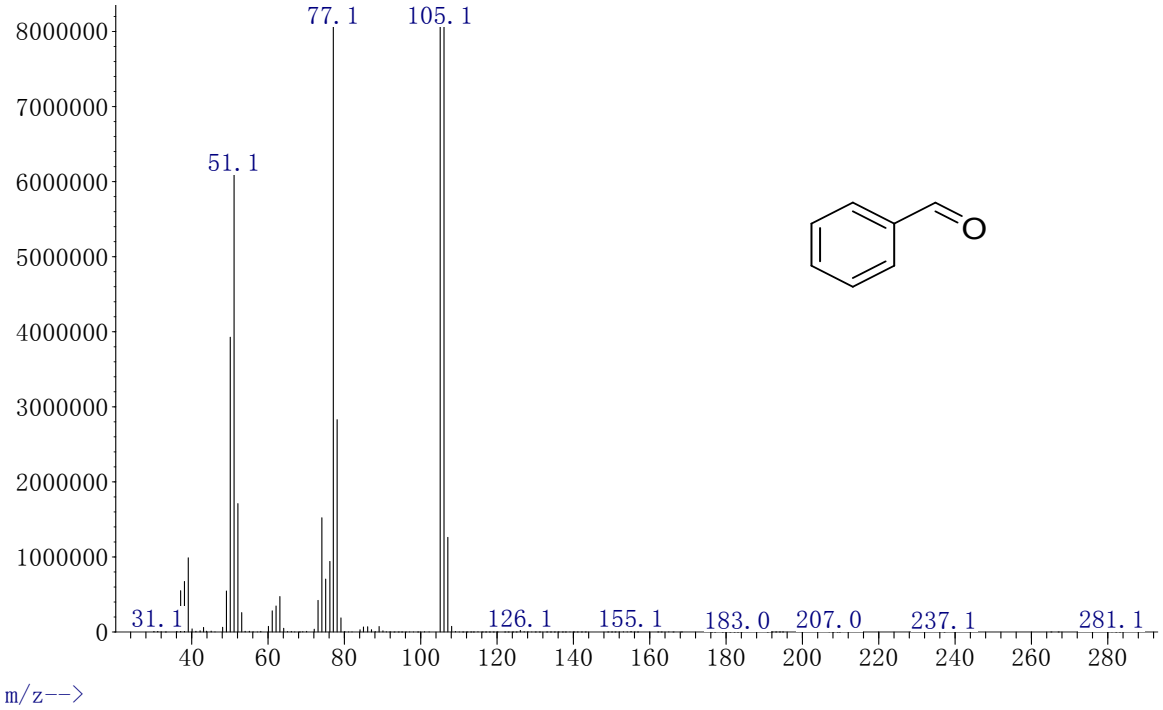


Figure S18. GC-MS spectrum of benzaldehyde.

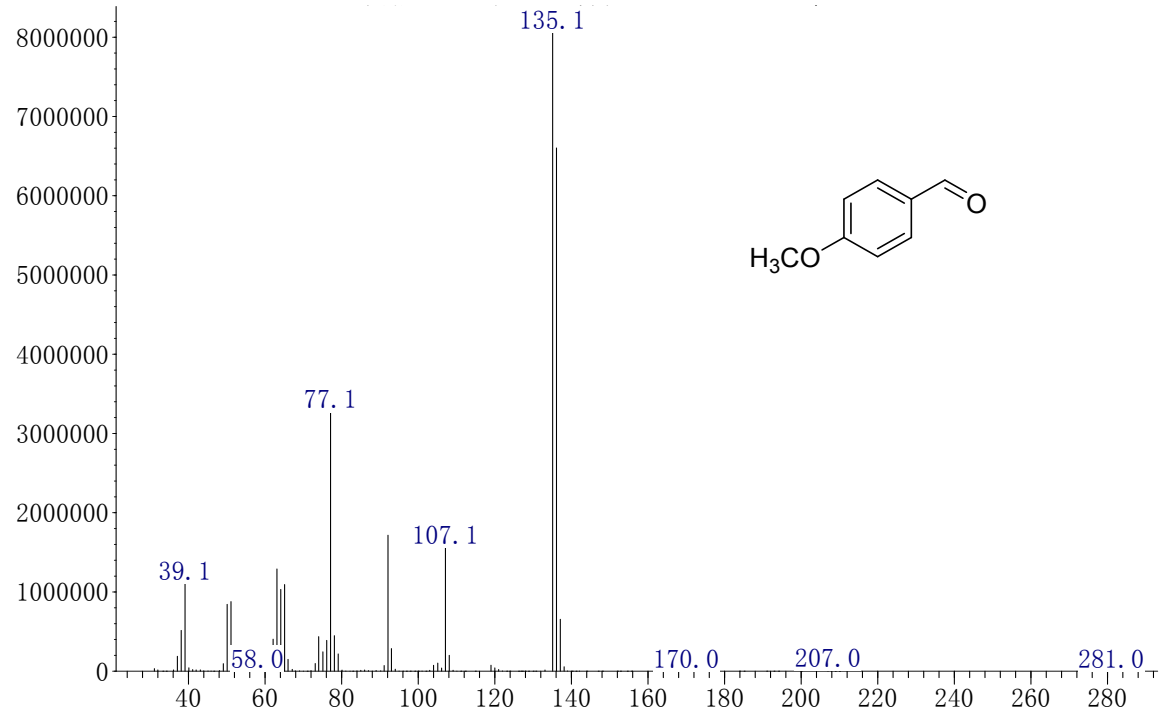


Figure S19. GC-MS spectrum of 4-methoxybenzaldehyde.

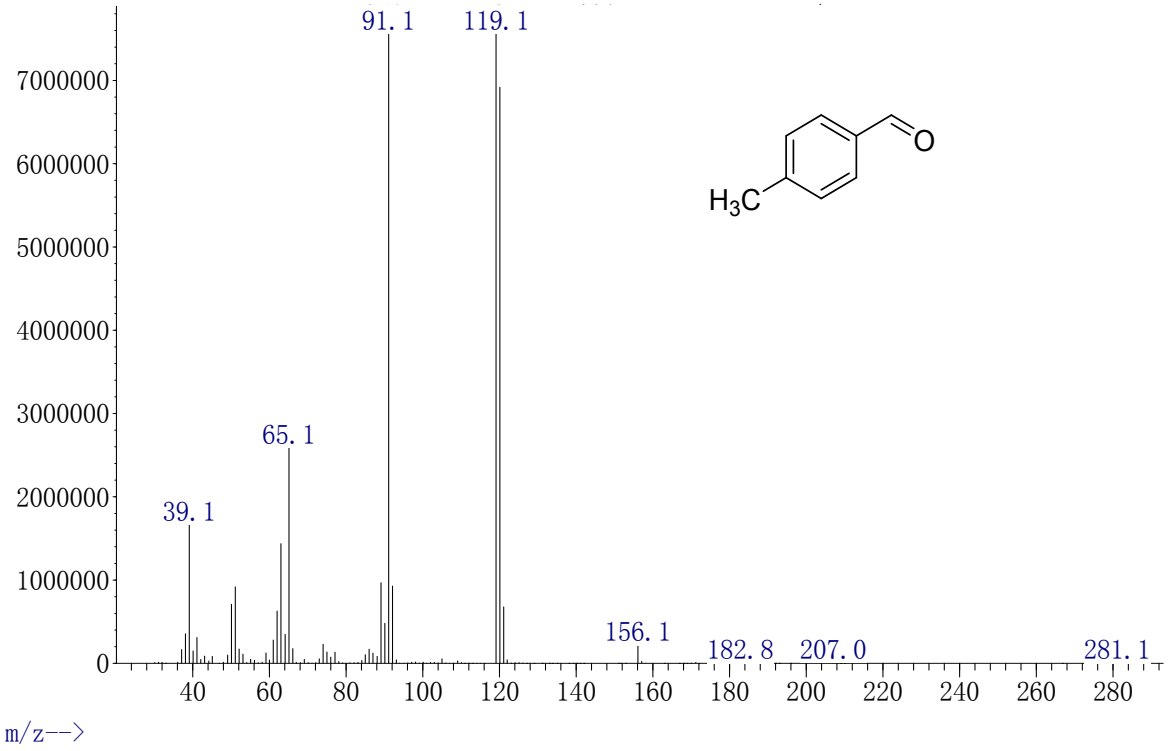


Figure S20. GC-MS spectrum of 4-methylbenzaldehyde.

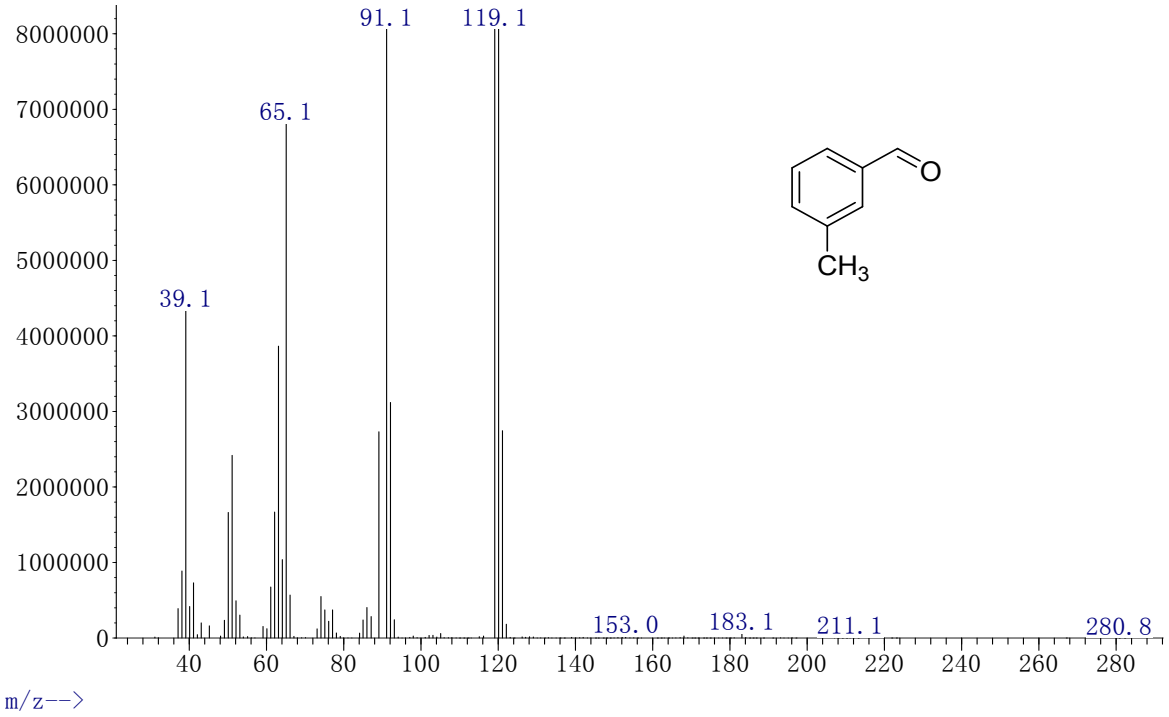


Figure S21. GC-MS spectrum of 3-methylbenzaldehyde.

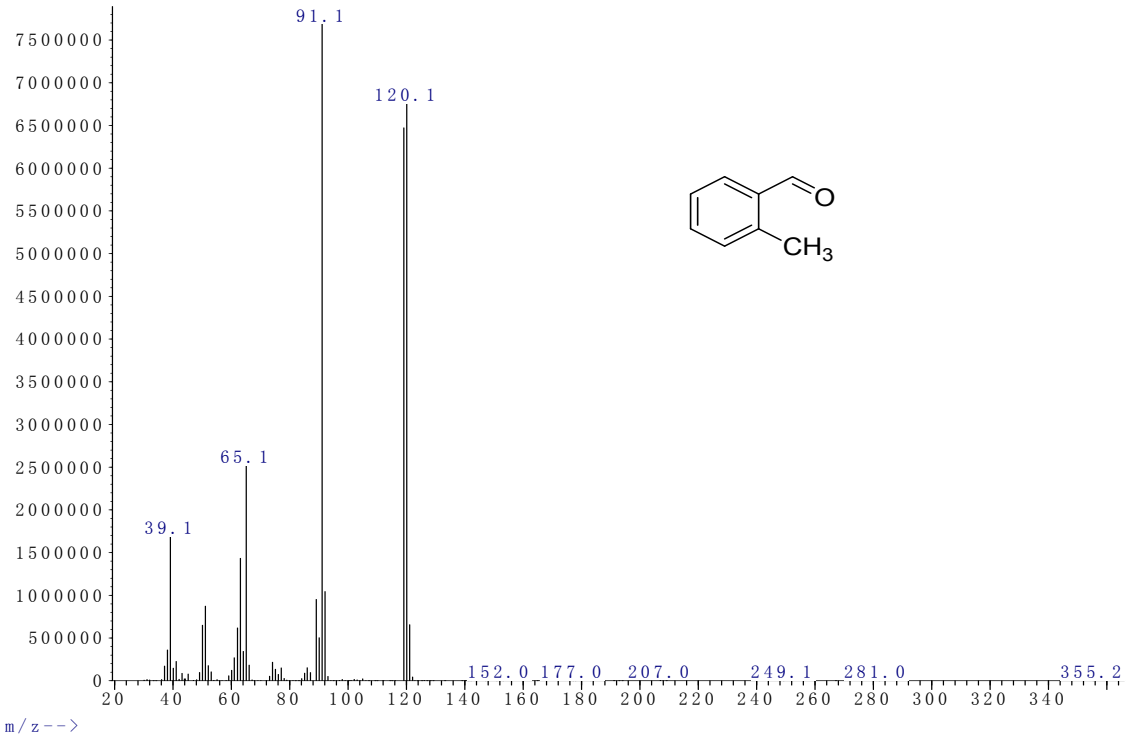


Figure S22. GC-MS spectrum of 2-methylbenzaldehyde.

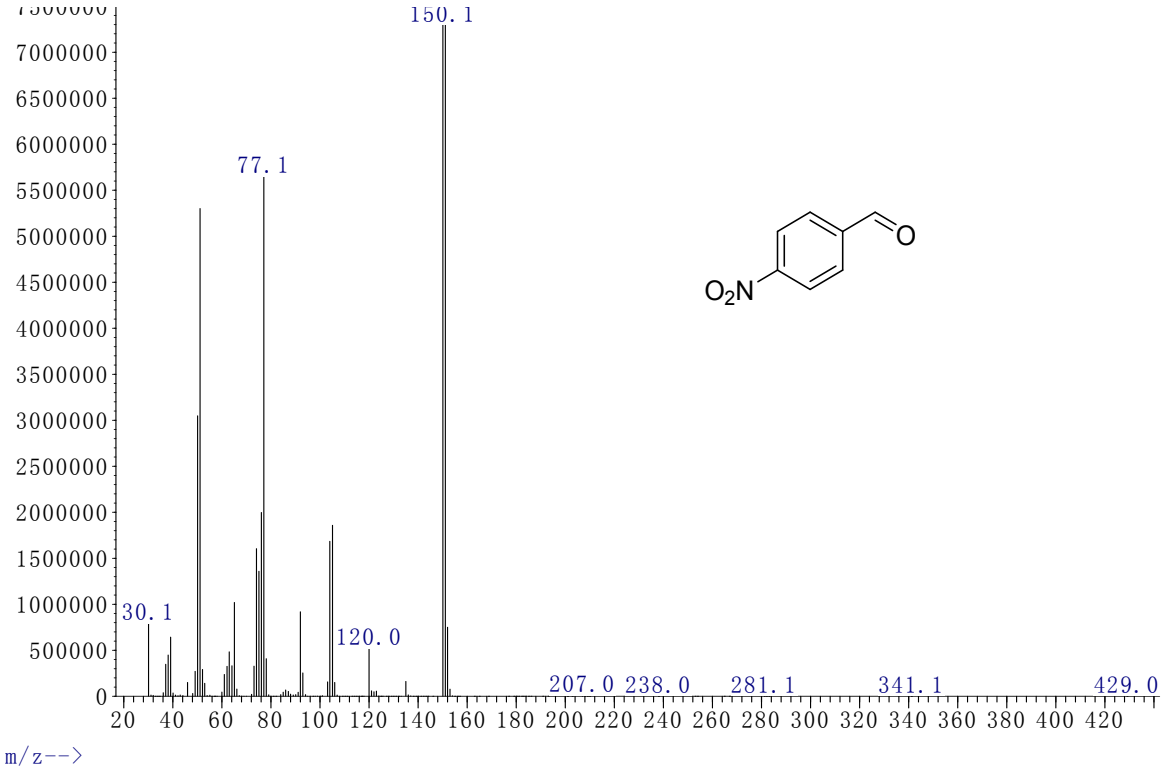


Figure S23. GC-MS spectrum of 4-nitrobenzaldehyde.

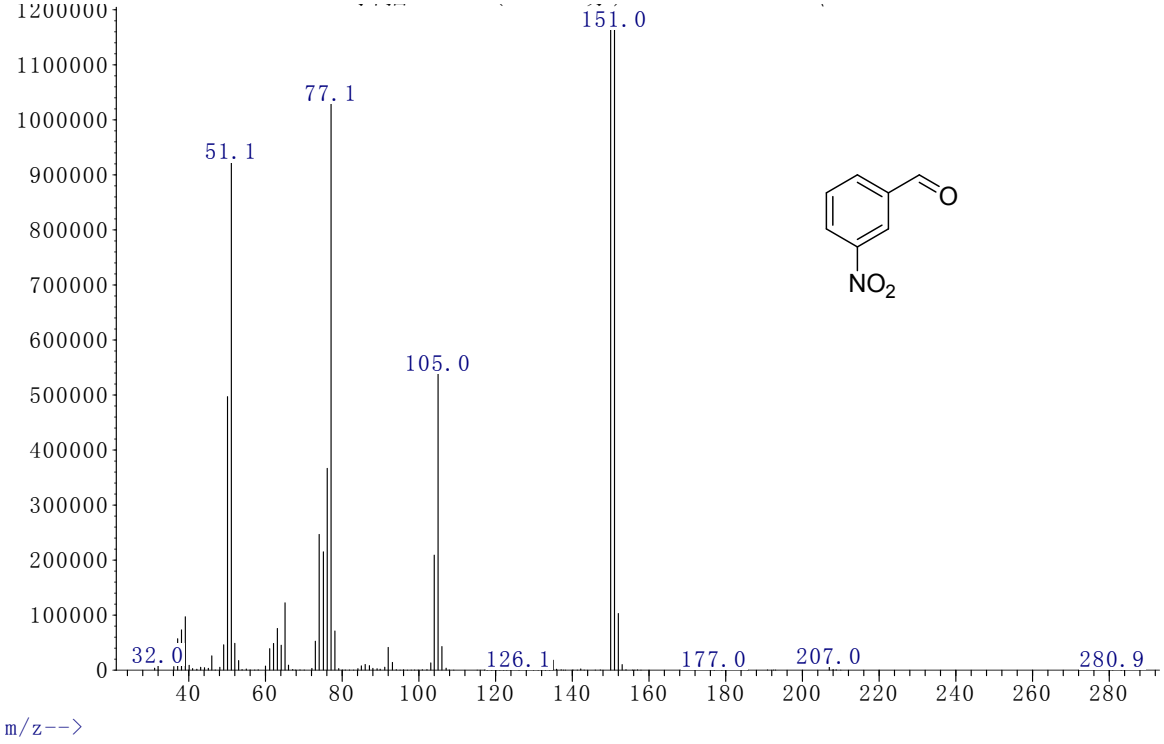


Figure S24. GC-MS spectrum of 3-nitrobenzaldehyde.

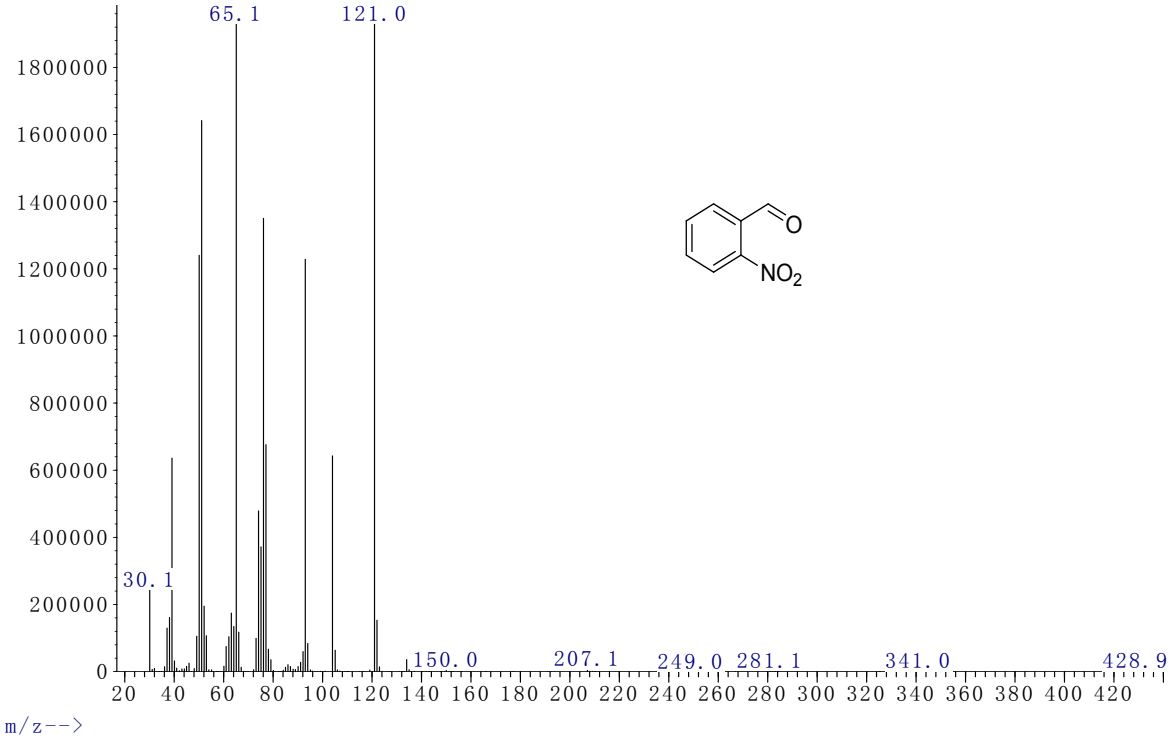


Figure S25. GC-MS spectrum of 2-nitrobenzaldehyde.

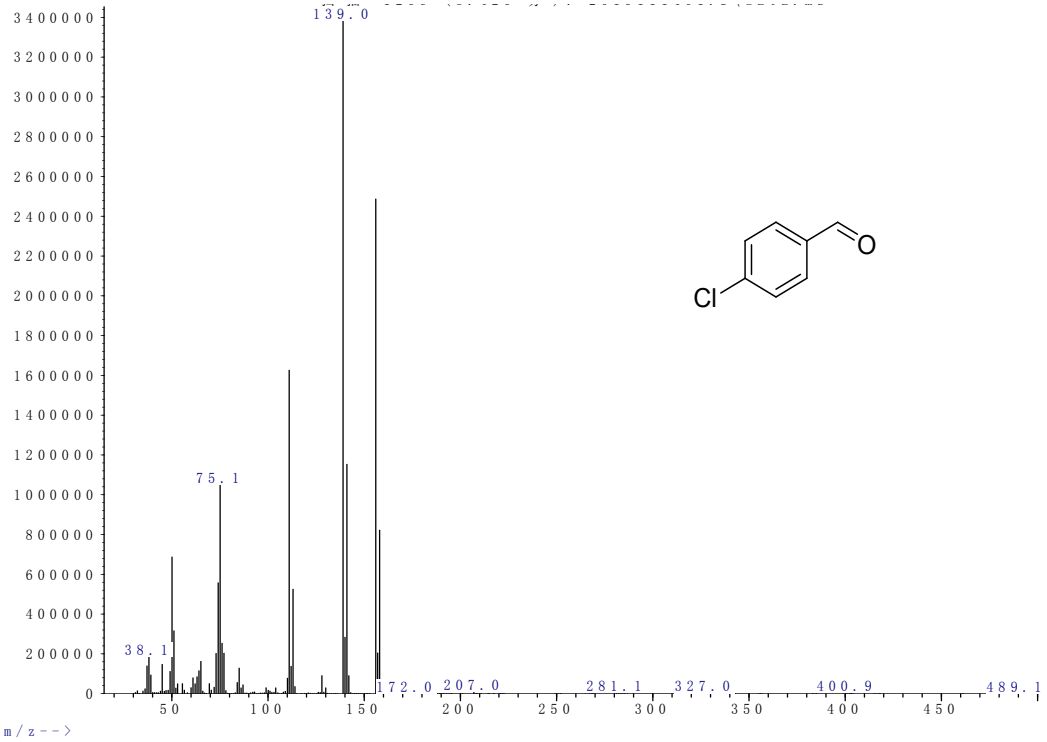


Figure S26. GC-MS spectrum of 4-chlorobenzaldehyde.

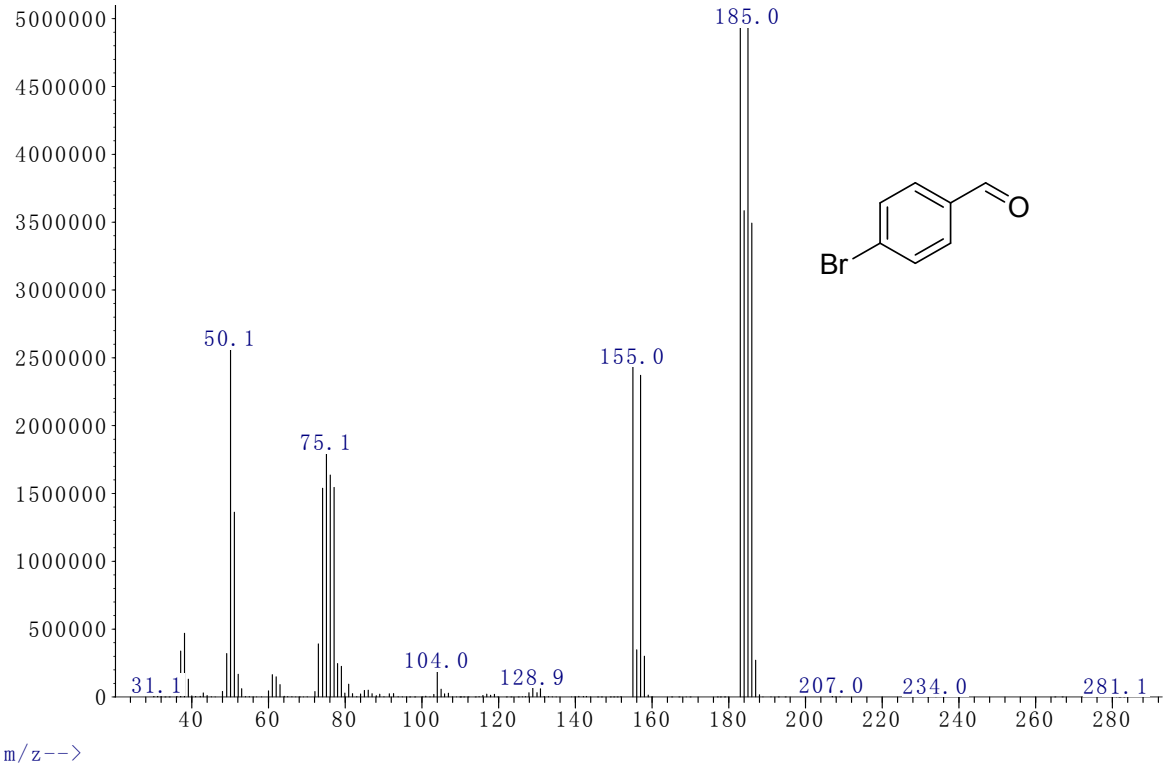


Figure S27. GC-MS spectrum of 4-bromobenzaldehyde.

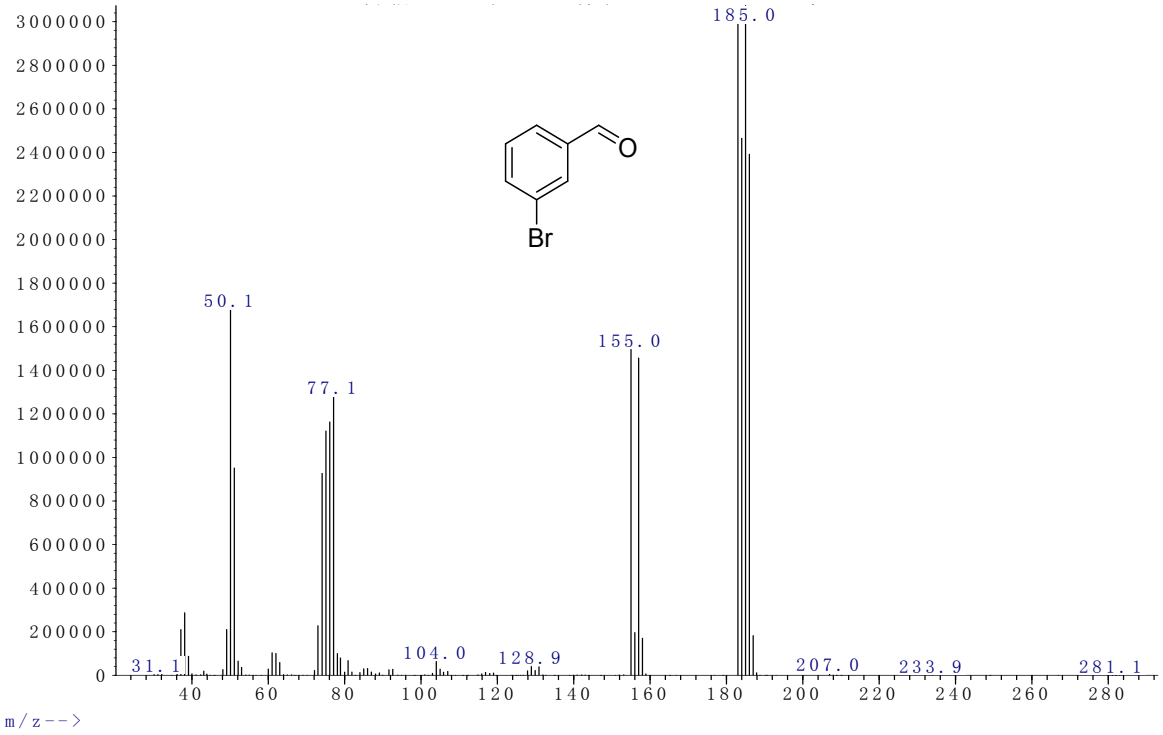


Figure S28. GC-MS spectrum of 3-bromobenzaldehyde.

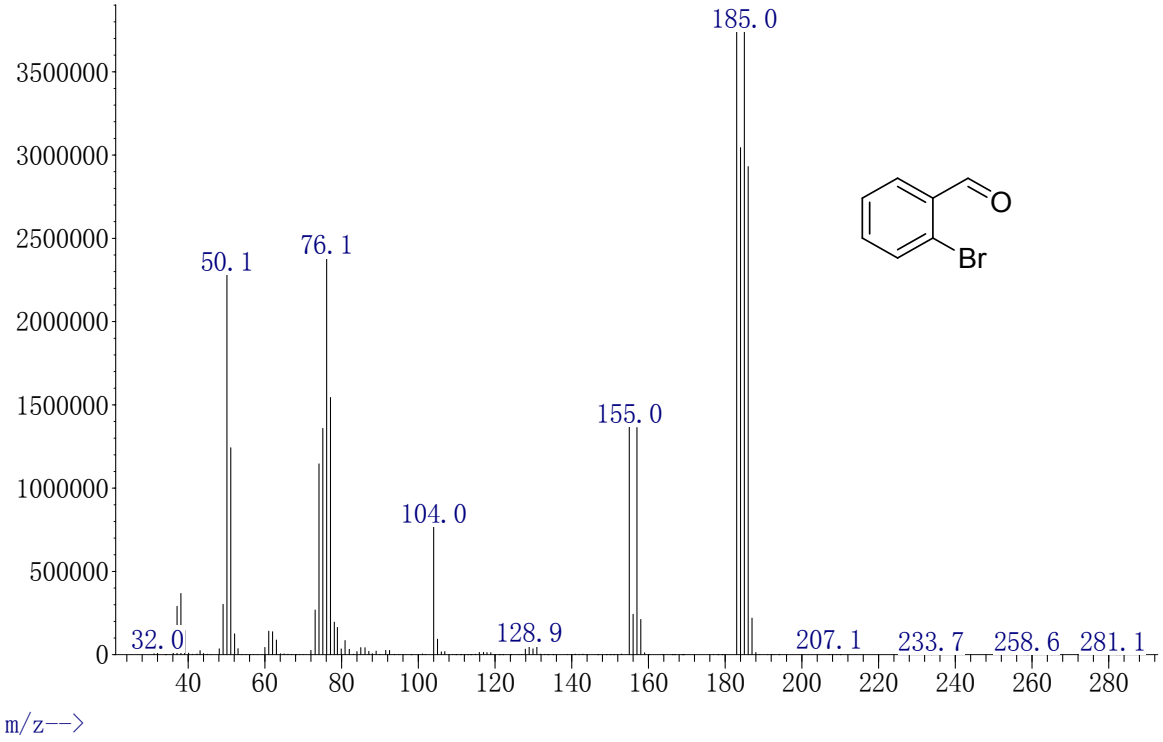


Figure S29. GC-MS spectrum of 2-bromobenzaldehyde.

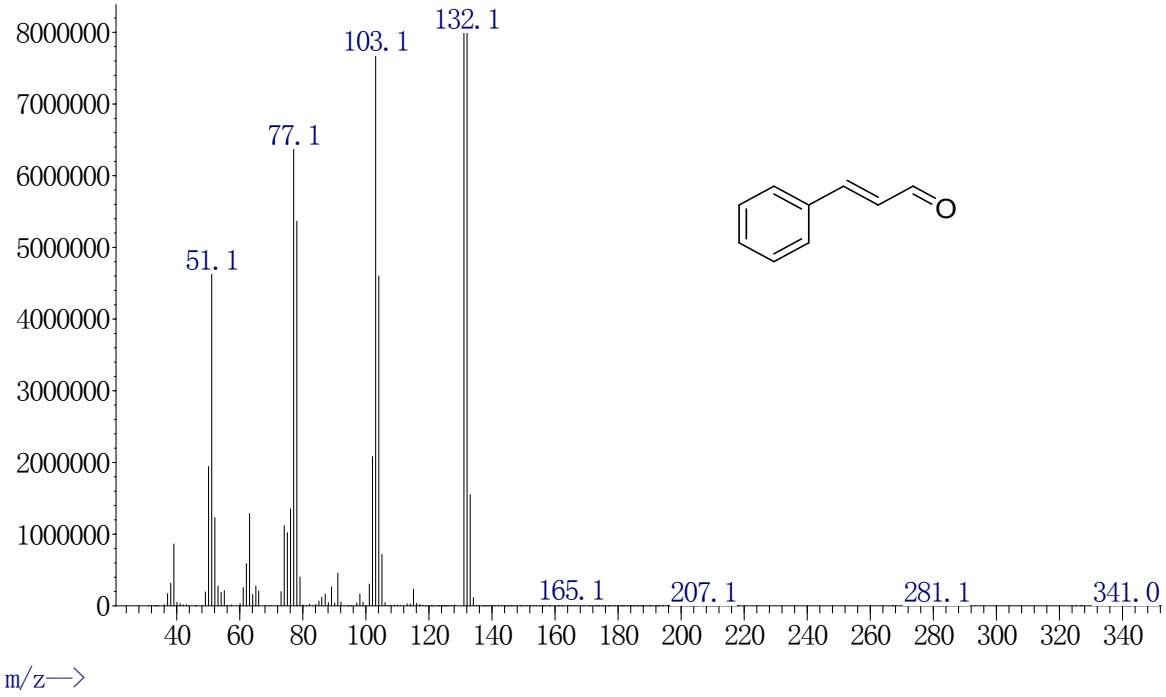


Figure S30. GC-MS spectrum of cinnamaldehyde.

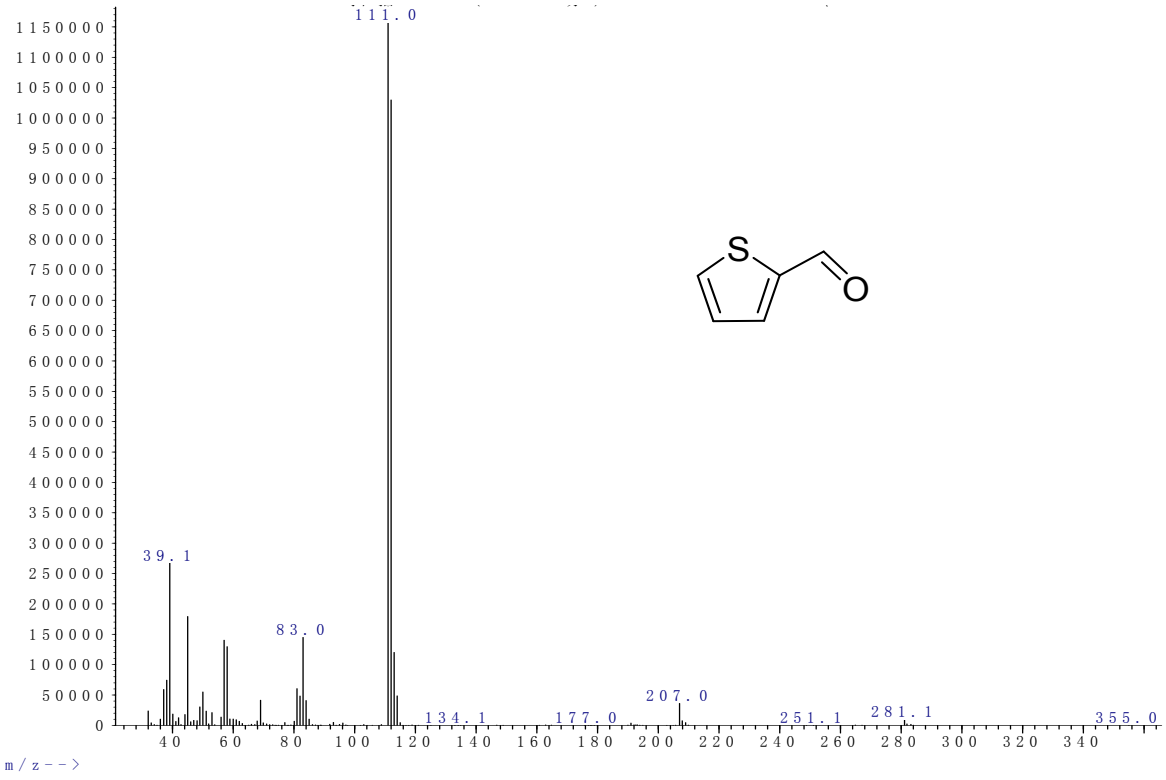


Figure S31. GC-MS spectrum of 2-thiophenecarboxaldehyde.

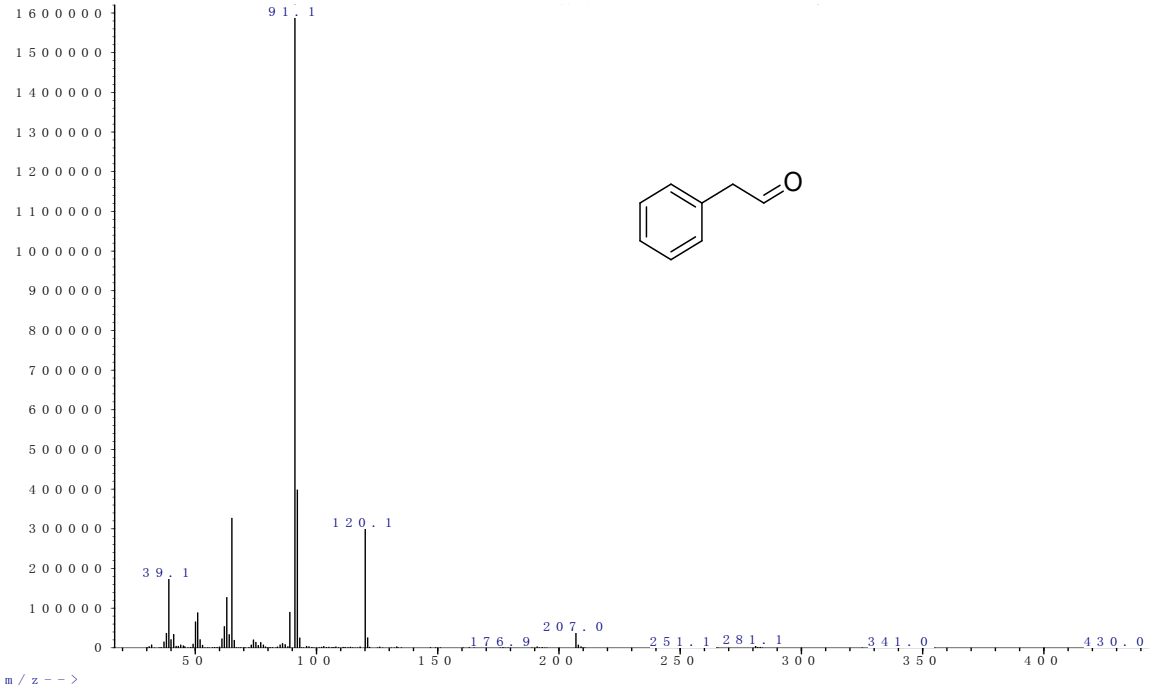


Figure S32. GC-MS spectrum of 2-phenylacetaldehyde.

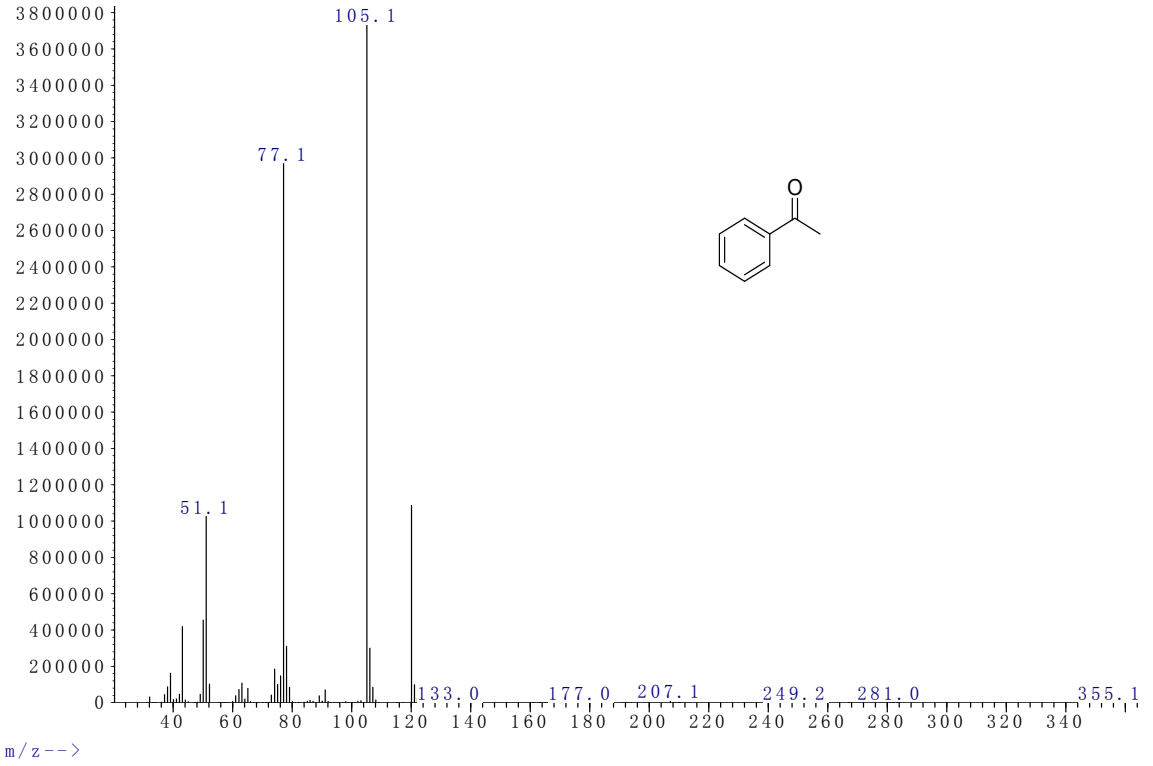


Figure S33. GC-MS spectrum of acetophenone.

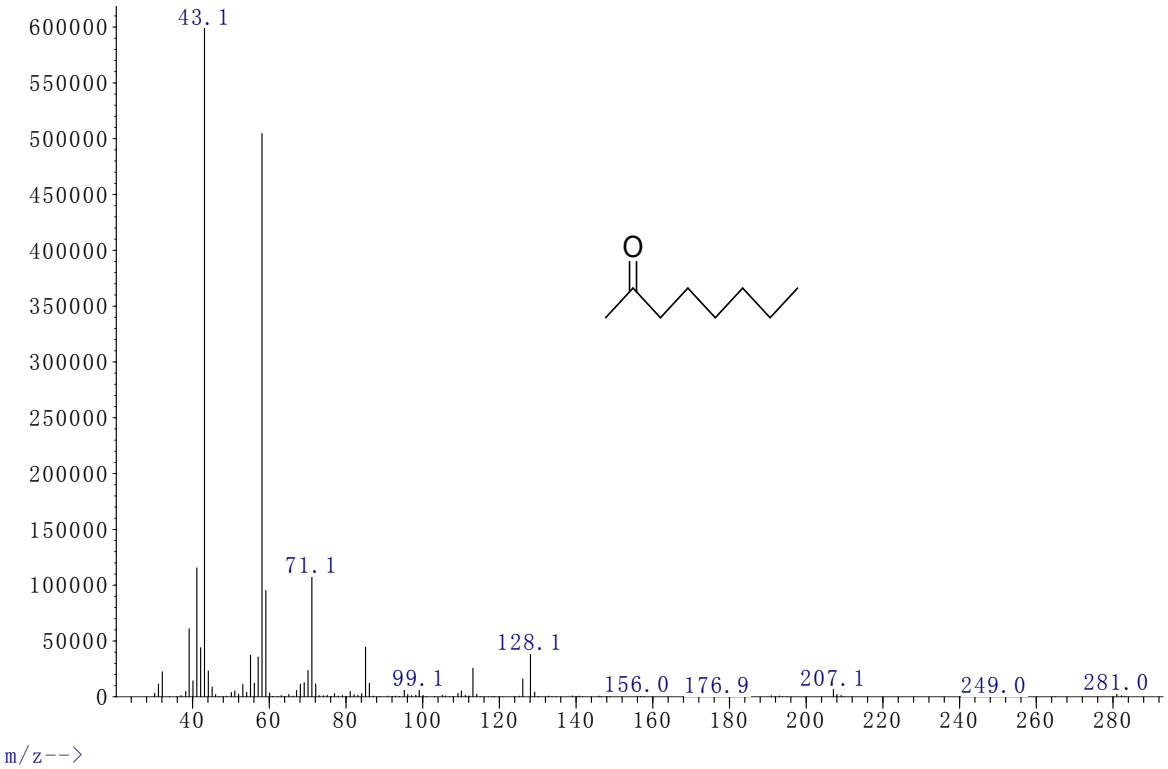


Figure S34. GC-MS spectrum of Octan-2-one

References:

1. J. M. Hoover, S. S. Stahl, J. Am. Chem. Soc. 2011, **133**, 16901-16910.
2. Dadras, M. R. Naimi-Jamal, F. M. Moghaddam and S. E. Ayati, J. Chem. Sci. 2018, **130**, 162-171.
3. J. K. Joseph, S. L. Jain and B. Sain, Eur. J. Org. Chem. 2006, **3**, 590-594.
4. R. Ali, K. Nour, A. Al-warthan and M. R. H. Siddiqui, Arab. J. Chem. 2015, **8**, 512-517.