Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Supporting Information for New Journal of Chemistry

Cu-Doped ZIF-8 metal organic framework as heterogeneous solid catalyst for aerobic oxidation of benzylic hydrocarbons

Nagarathinam Nagarjun and Amarajothi Dhakshinamoorthy*

School of Chemistry, Madurai Kamaraj University, Madurai-625 021, Tamil Nadu, India.

E-mail: admguru@gmail.com

1) Influence of O_2

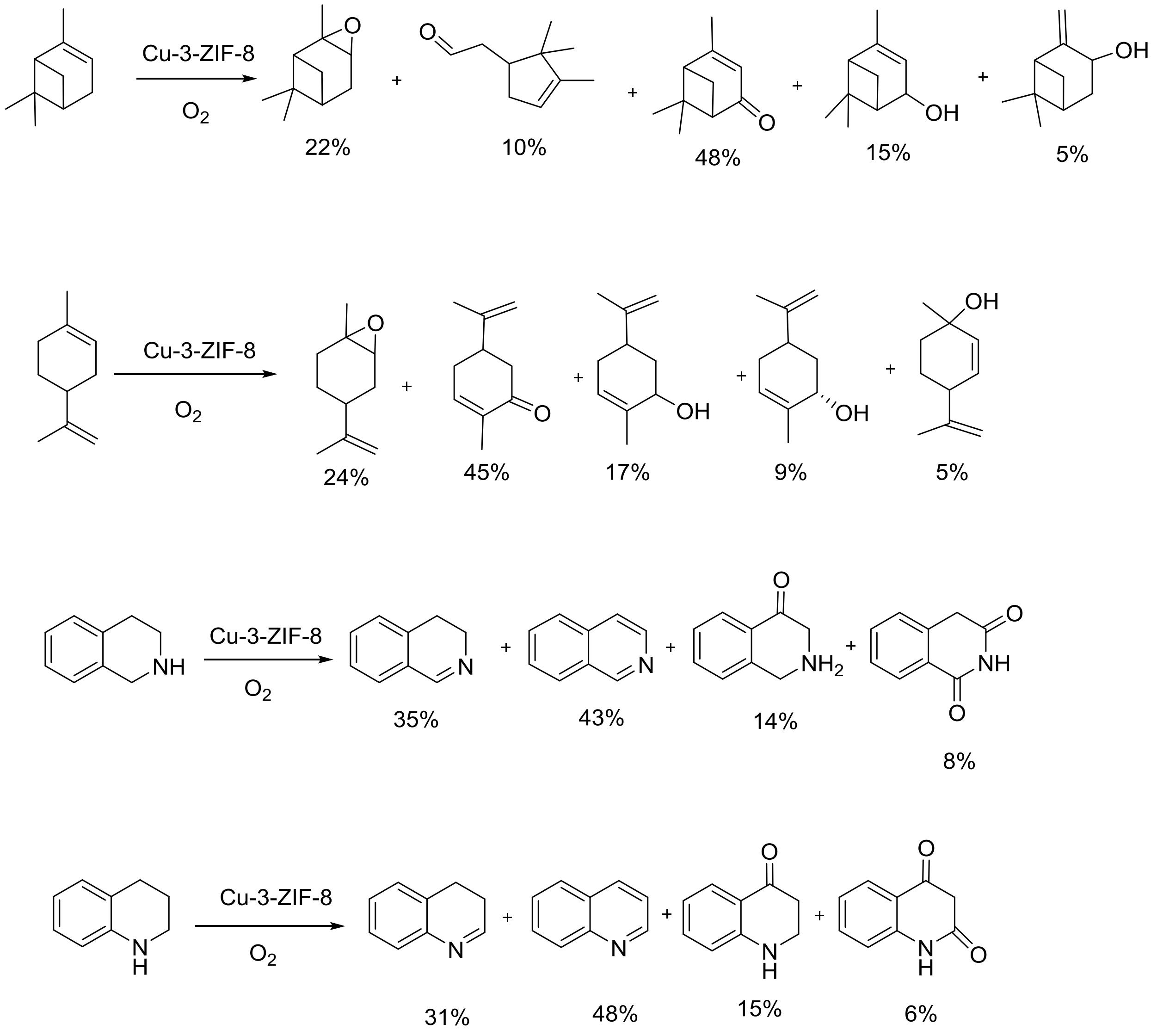
Initially, reaction flask was charged with Cu-doped ZIF-8 (20 mg), cyclooctane (1 mL) and DMF (1 mL). This mixture was connected to N_2 balloon. The system was stirred for 24 h at 120 ^{O}C temperature. After the reaction time, the reaction mixture was extracted with acetonitrile and then the solid catalyst was filtered. The filtrate mixture was analyzed using a GC and observed no cyclooctane conversion. These results indicate the role of molecular oxygen in the oxidation of cyclooctane.

2) Radical trapping experiments

In a reaction flask, 20 mg of Cu-doped ZIF-8, 20 mg of radical scavenger (TEMPO or hydroquinone), cyclooctnae (1 mL) and solvent (1 mL) were added and this mixture was stirred for 24 h at 120 ^{o}C. After 24 h, the reaction mixture was extracted with acetonitrile and then the solid catalyst was filtered. The filtrate mixture was analyzed by GC. It was noticed that the oxidation reaction was apparently suppressed in the presence of radical scavengers, indicating that an organic radical intermediates might be involved in the catalytic cycle. Especially hydroquinone selectively quenches superoxide radical or hydroxyl radicals.

Table S1. Synthesis details for the preparation of Cu-doped samples.

S.No	Zinc nitrate		Copper nitrate		Total mmol	ICP-OES % Cu
	mmol	mg	mmol	mg		
1	1.75	520.55	0.25	60.4	2	0.8
2	1.5	446.19	0.5	120.8	2	1.6
3	1	297.46	1	241.6	2	2.8



Scheme S1. Oxidation of various hydrocarbons to their oxidized products using Cu-3-ZIF-8 as catalyst.

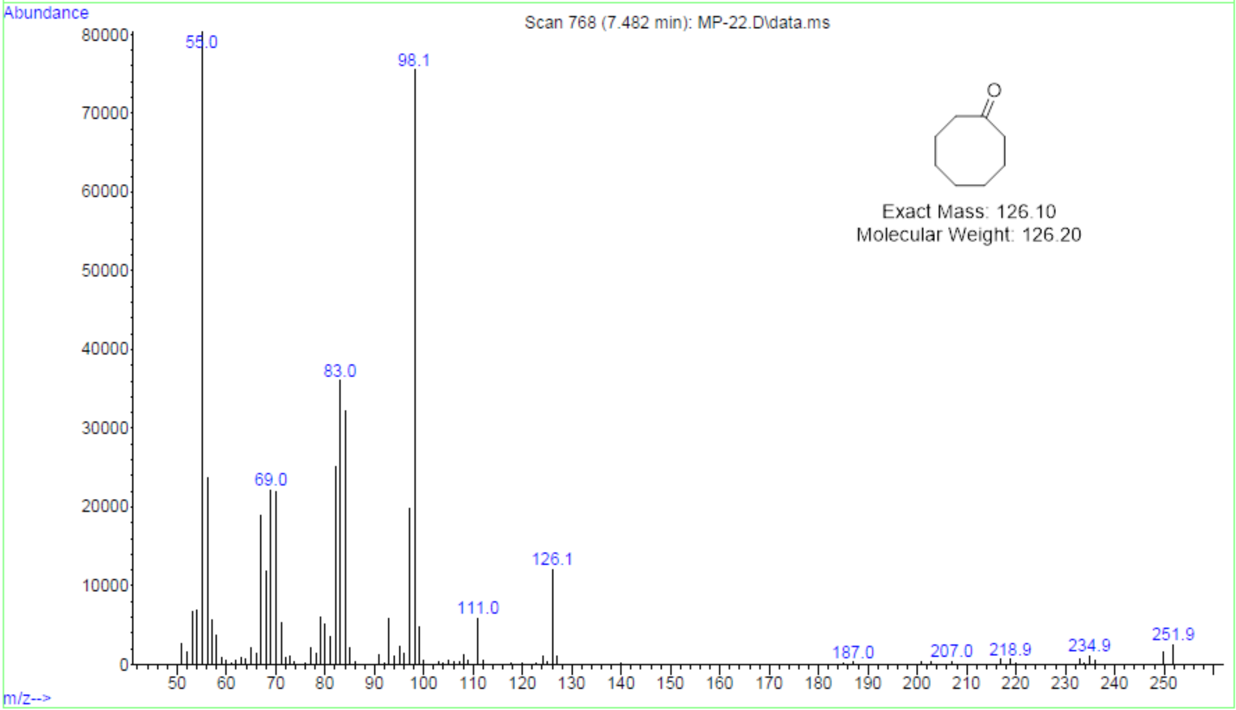


Figure S1. GC-MS traces of cyclooctanone

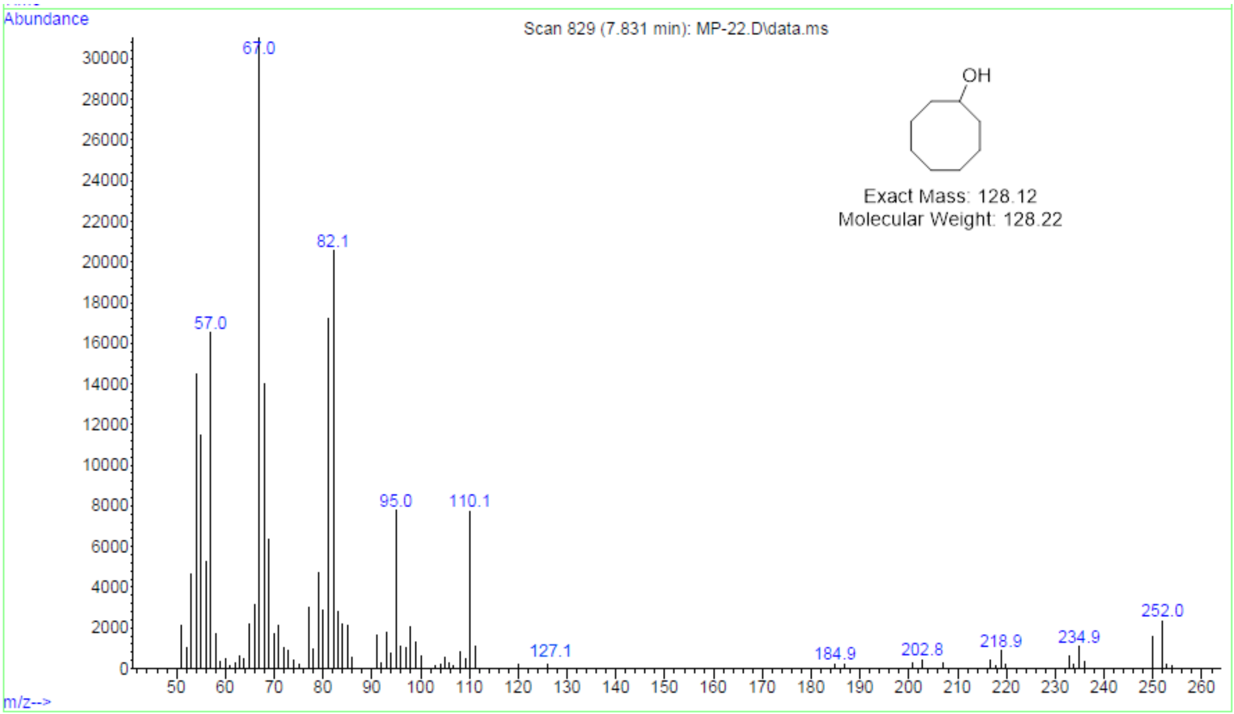


Figure S2. GC-MS traces of cyclooctanol

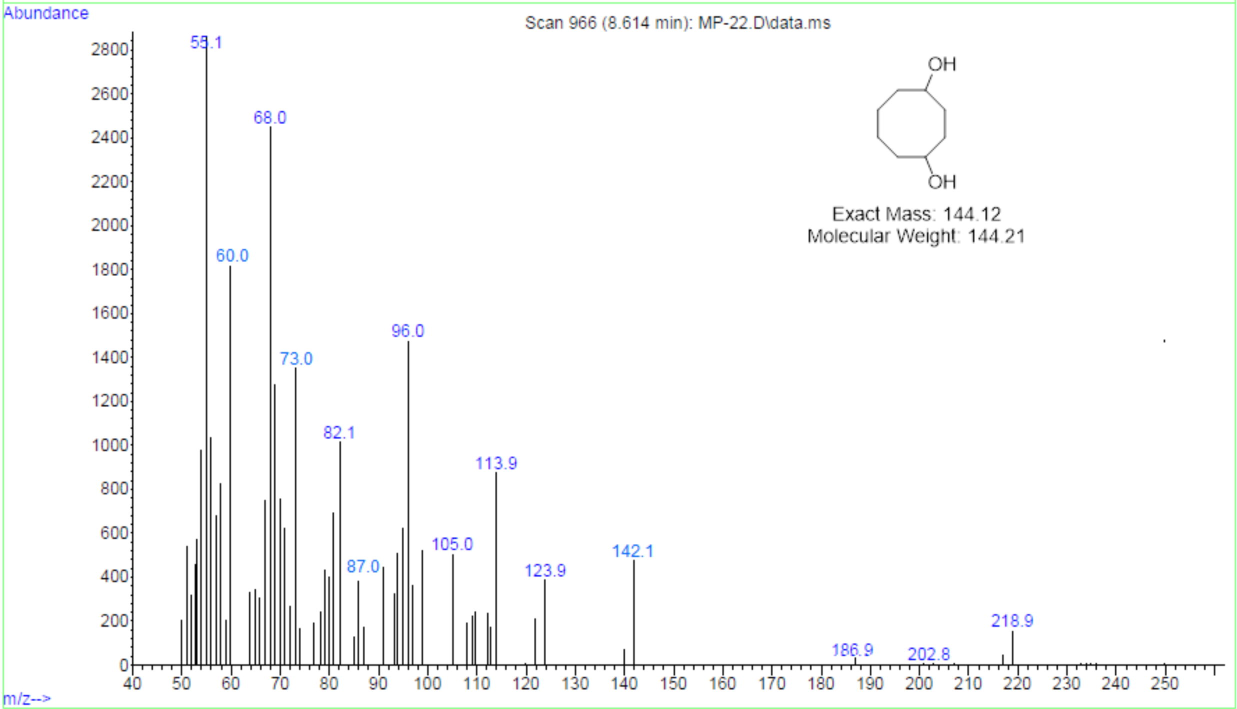


Figure S3. GC-MS trace of cyclooctane-1,4-diol

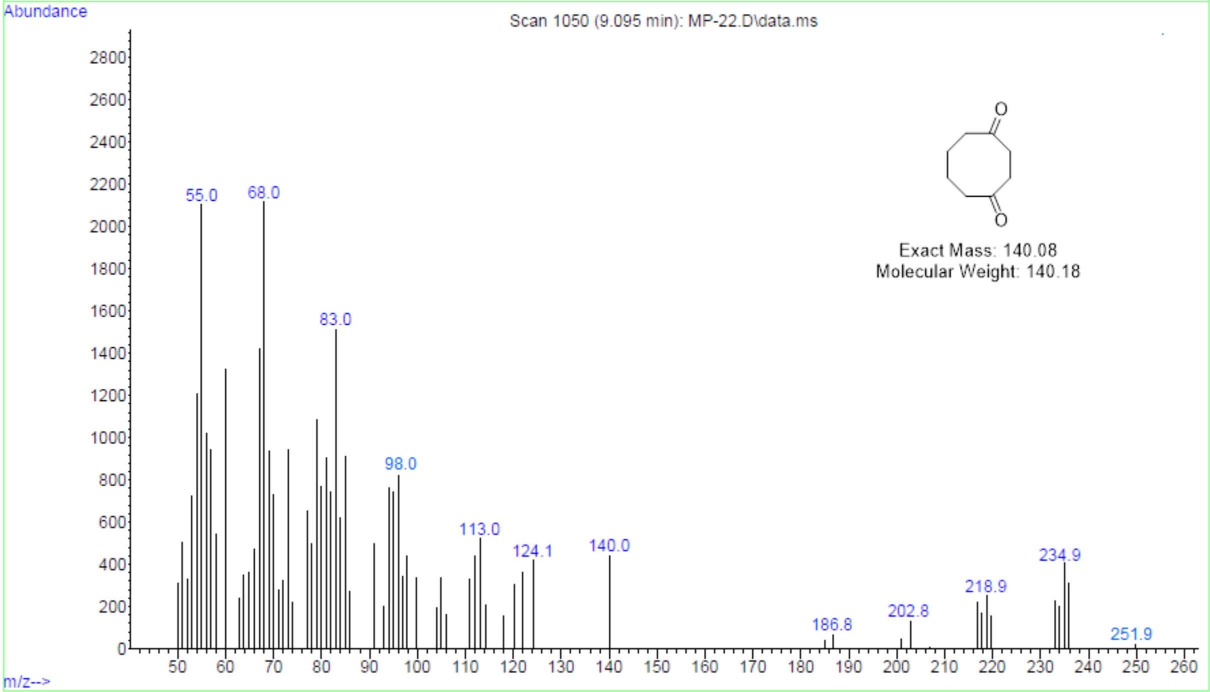


Figure S4. GC-MS traces of cyclooctane-1,4-dione

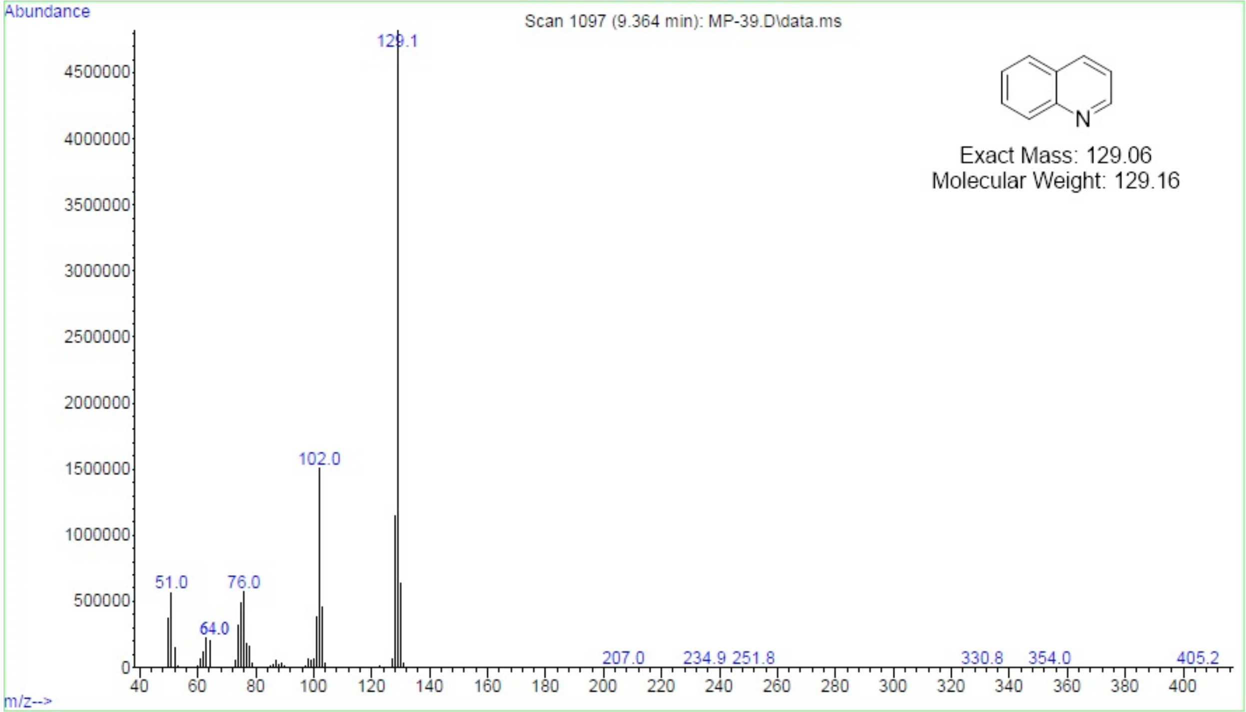


Figure S5. GC-MS traces of quinoline.

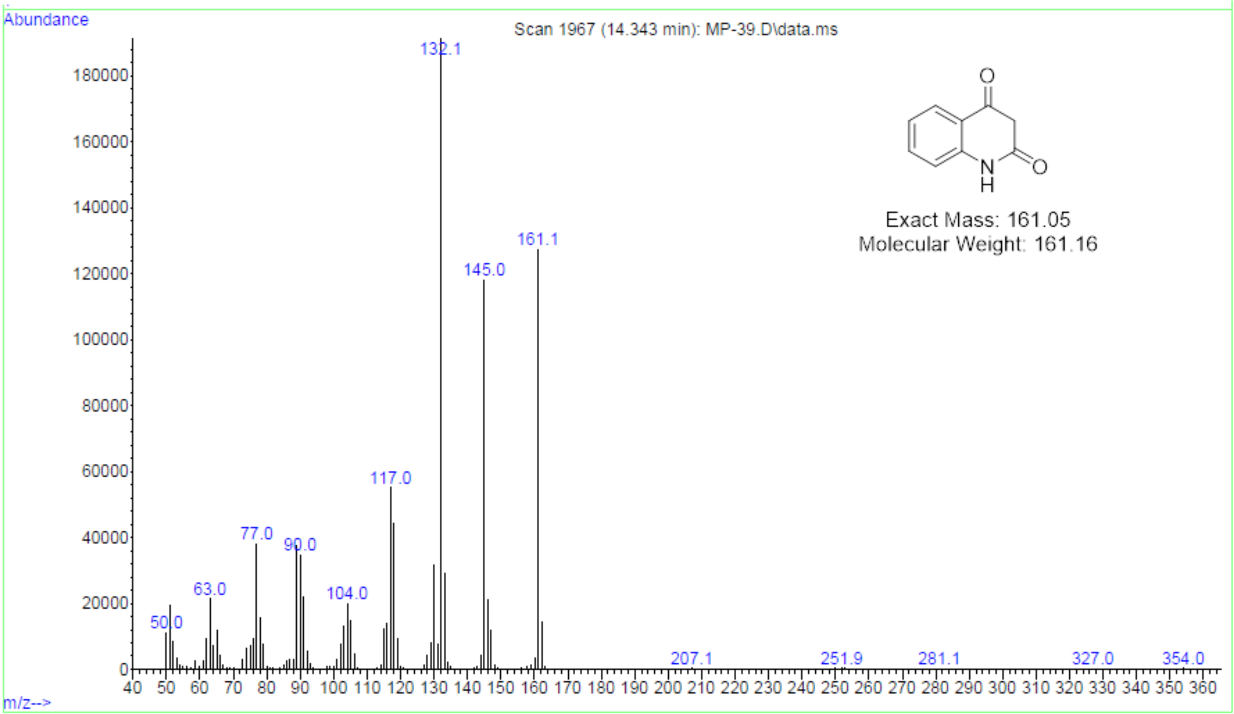


Figure S6. GC-MS traces of quinoline-2,4(*1H*, *3H*)-dione.

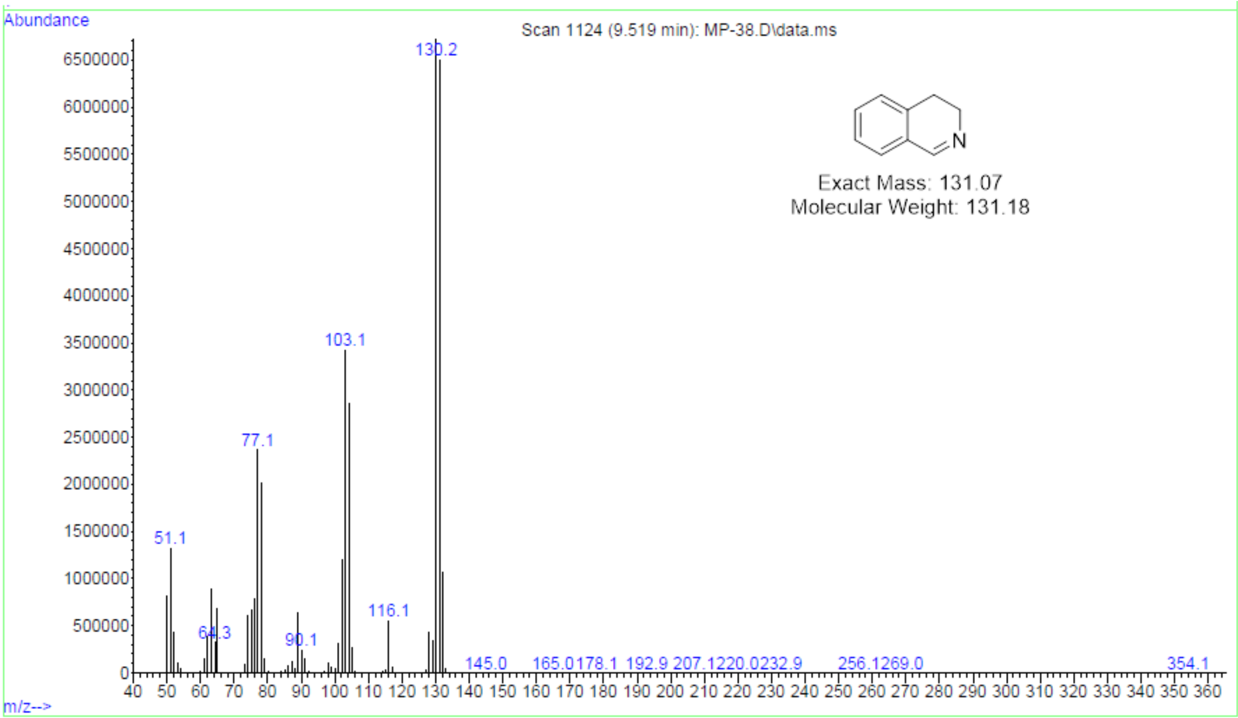


Figure S7. GC-MS traces of 3,4-dihydroisoquinoline.

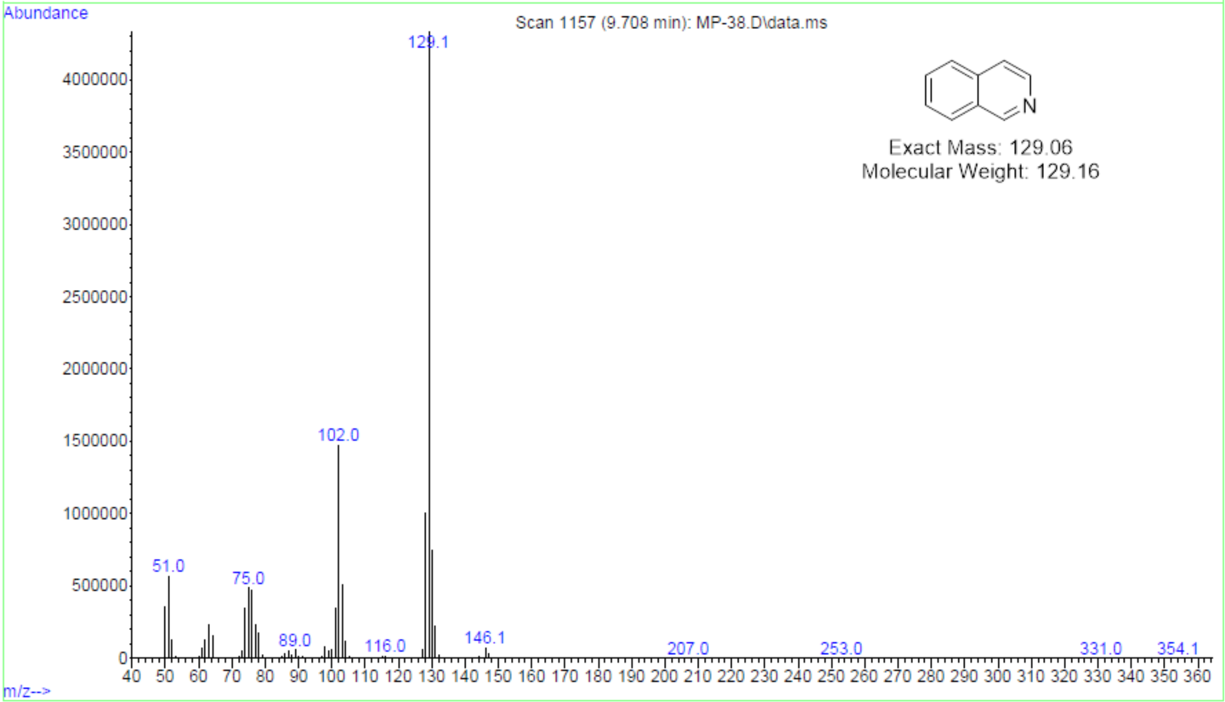


Figure S8. GC-MS traces of isoquinoline.

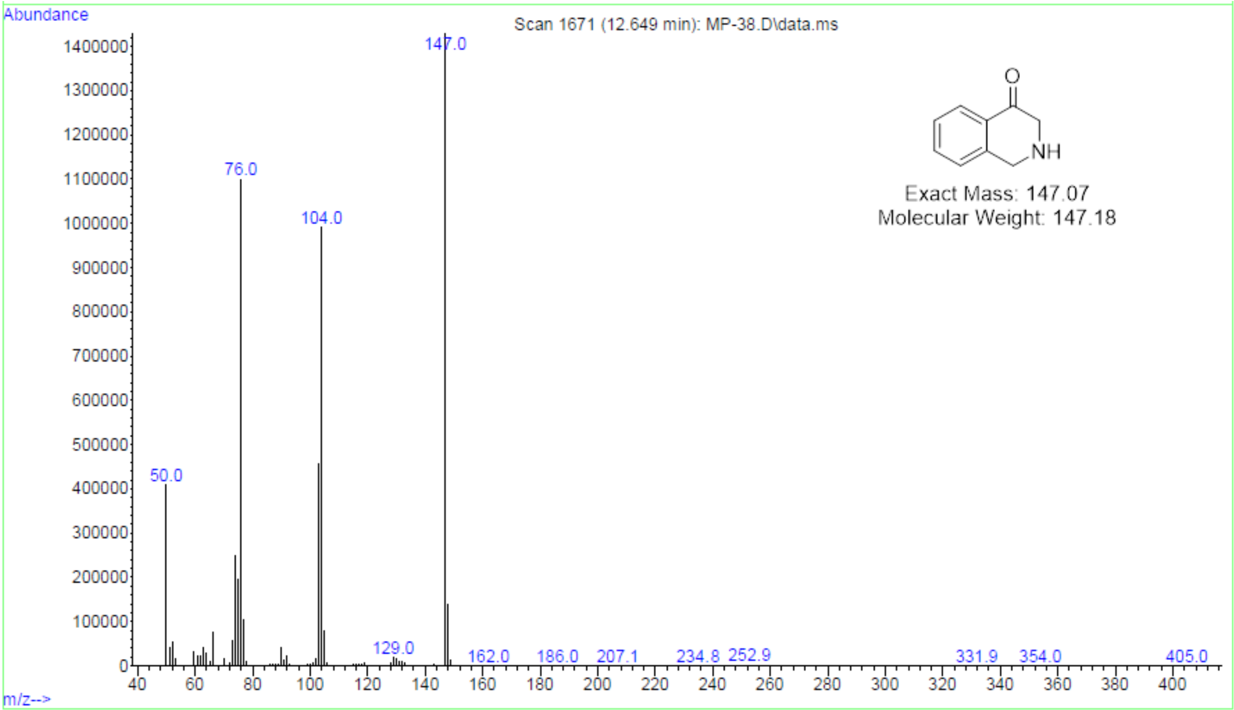


Figure S9. GC-MS traces of 2,3-dihydroisoquinolin-4(1*H*)-one

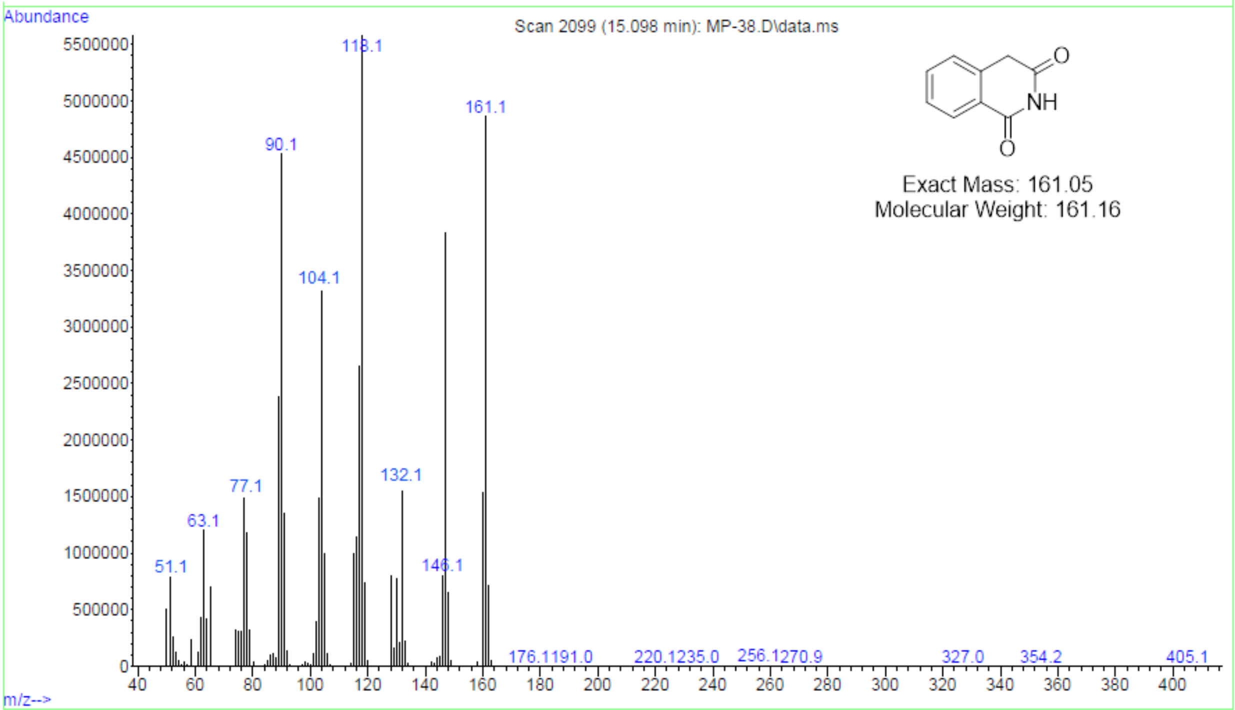


Figure S10. GC-MS traces of isoquinoline-2,4(*1H*, *3H*)-dione

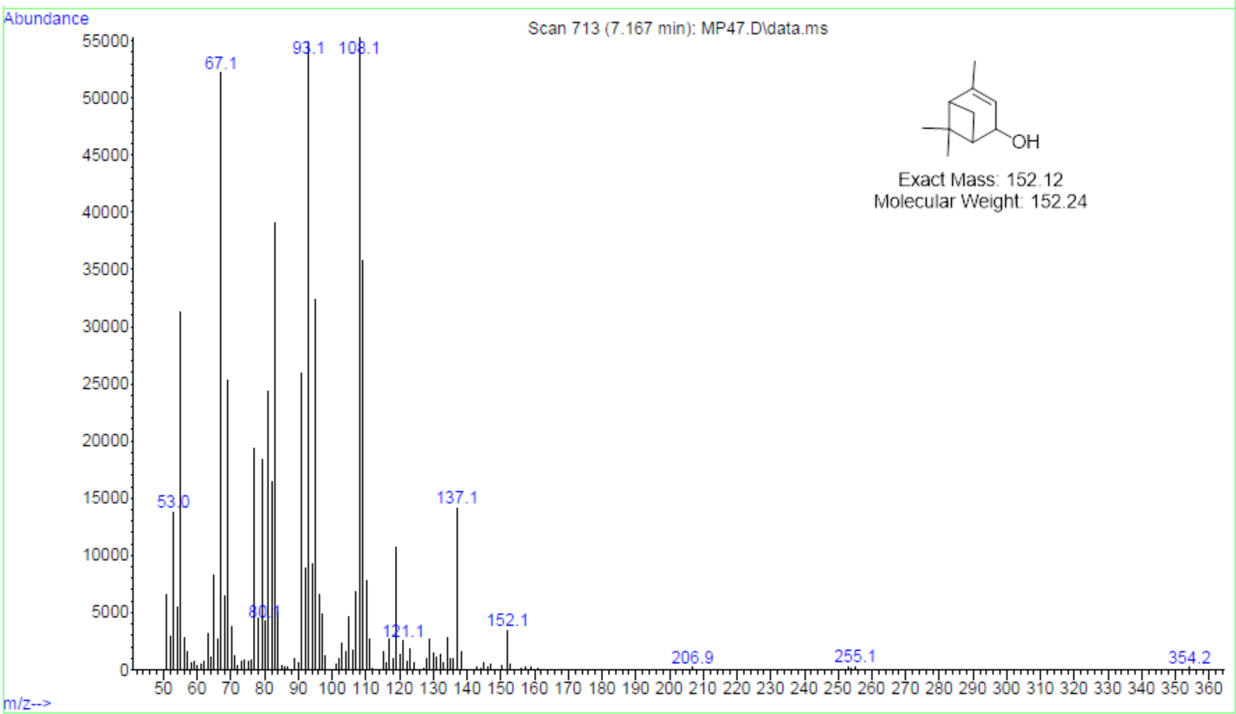


Figure S11. GC-MS traces of verbenol.

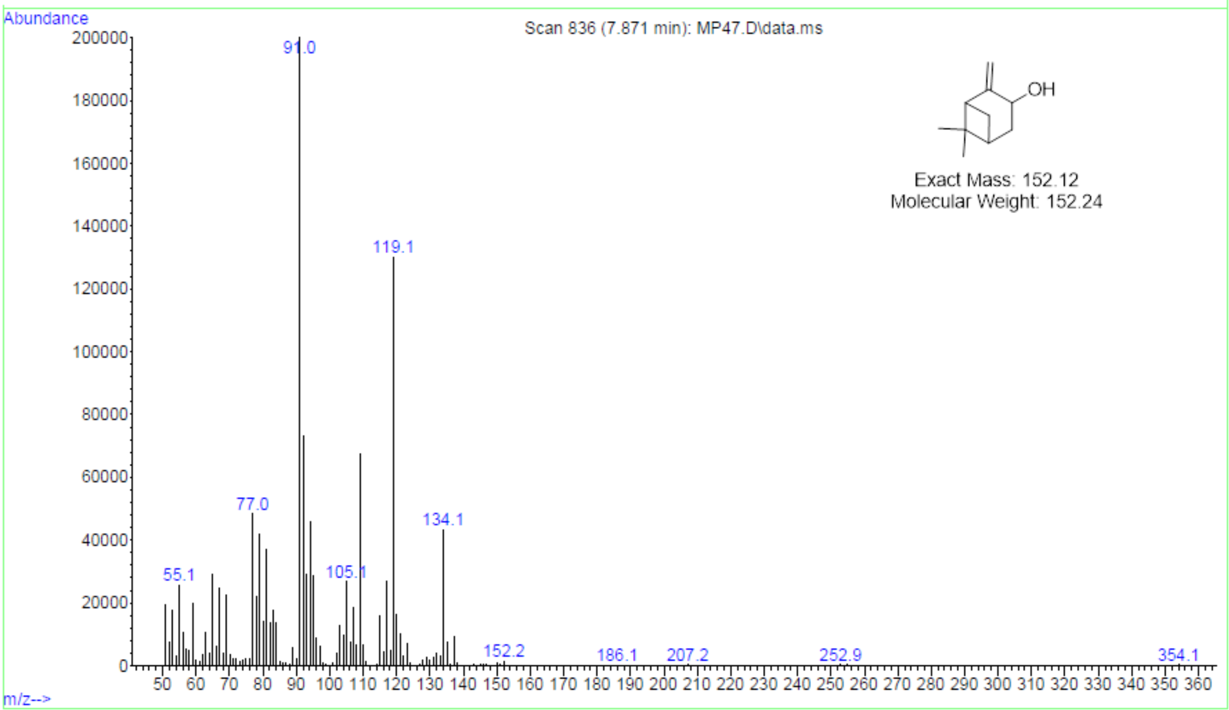


Figure S12. GC-MS traces of pinocarvol.

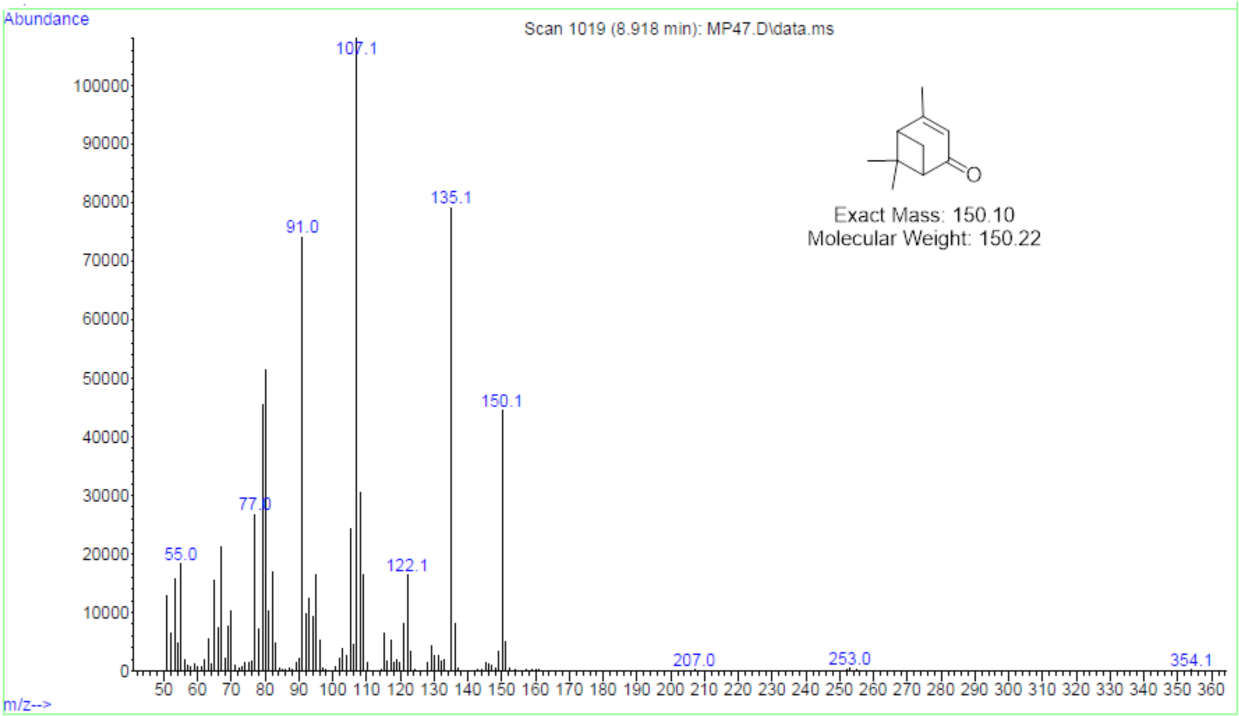


Figure S13. GC-MS traces of verbenone.

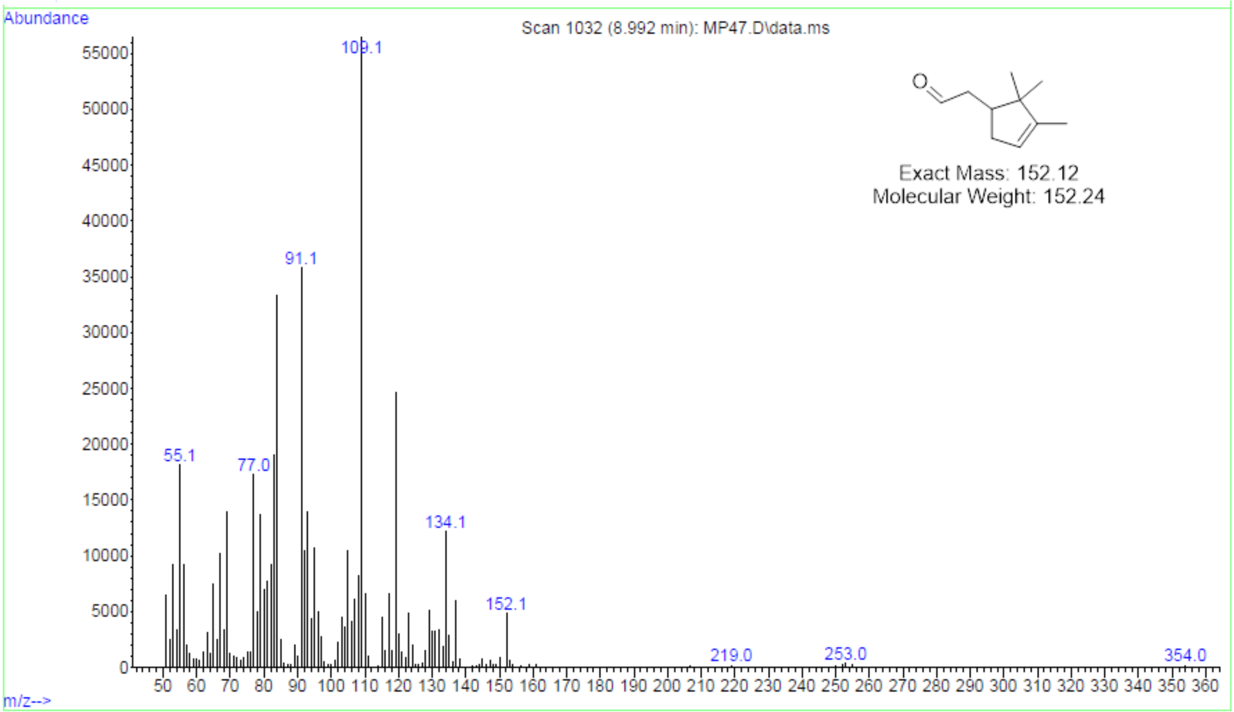


Figure S14. GC-MS traces of campholenic aldehyde.

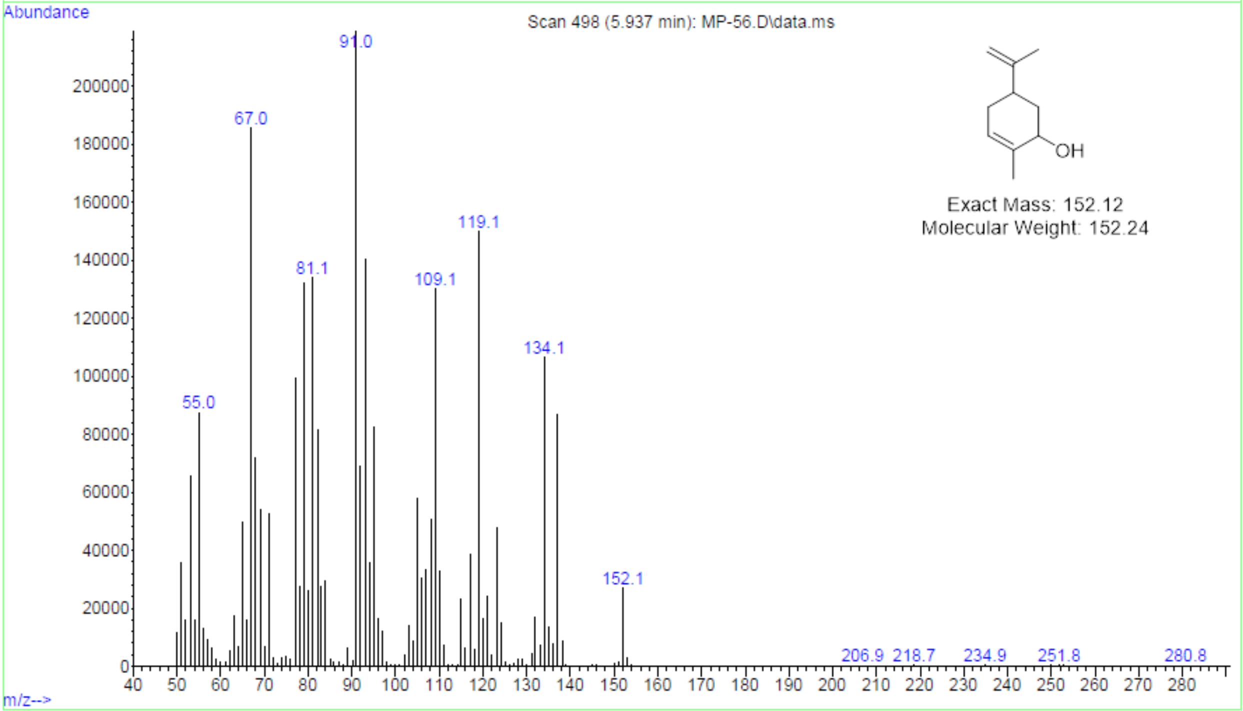


Figure S15. GC-MS traces of carvol.

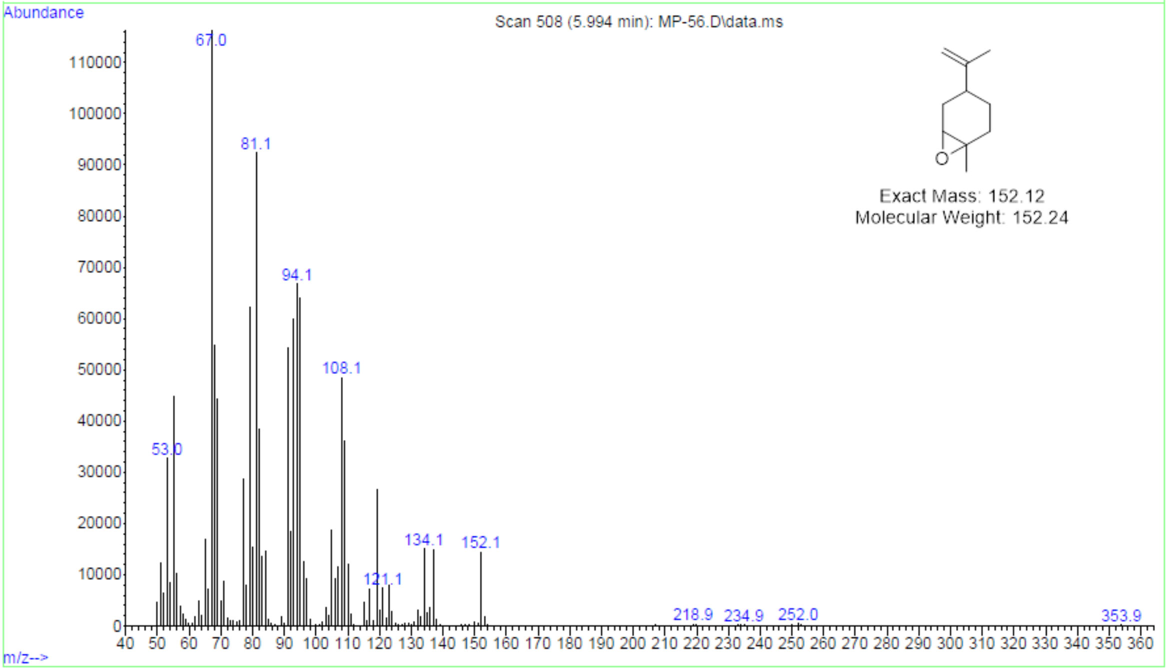


Figure S16. GC-MS traces of limonene oxide

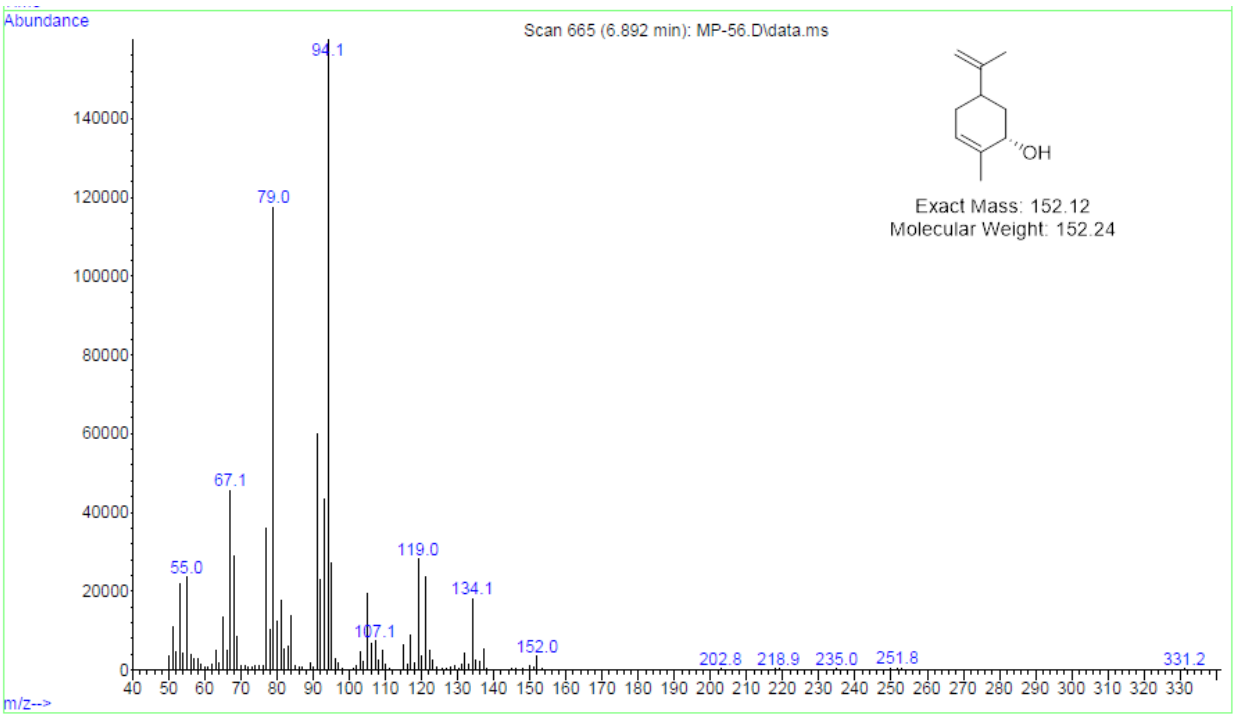


Figure S17. GC-MS traces of carvol (mixture of isomers)

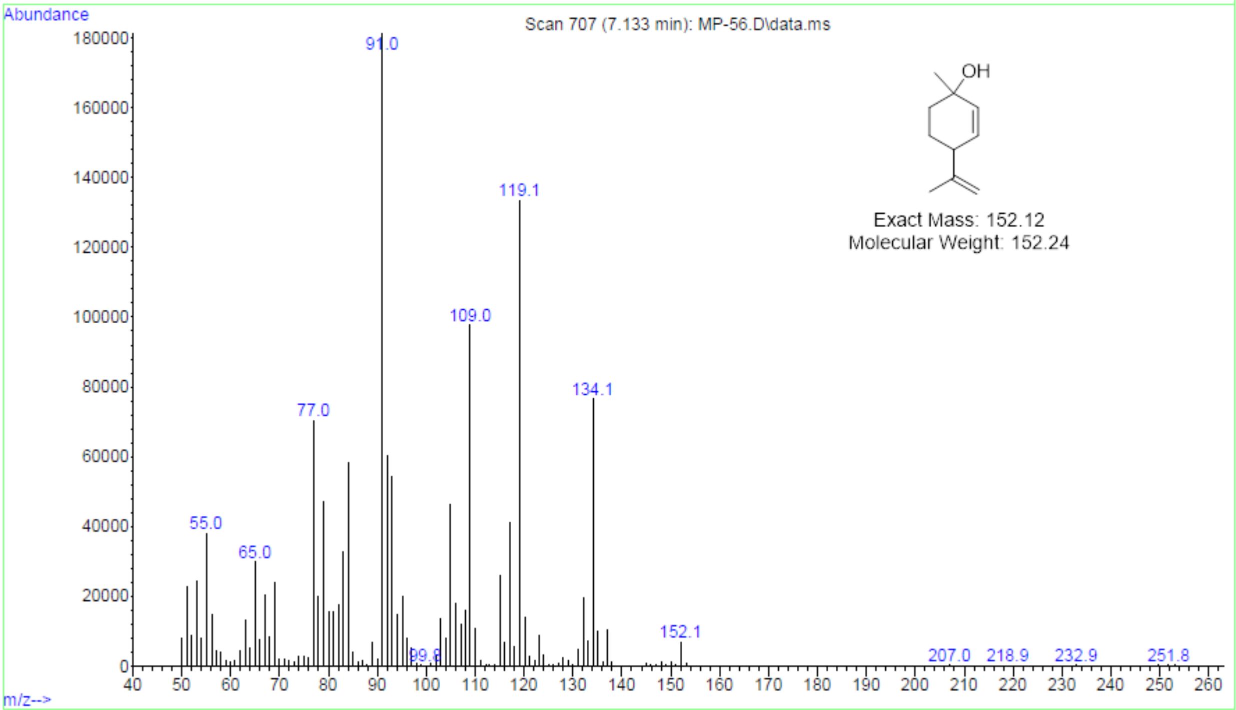


Figure S18. GC-MS traces of 1-methyl-4-(prop-1-en-2yl)cyclohex-2-en-1-ol

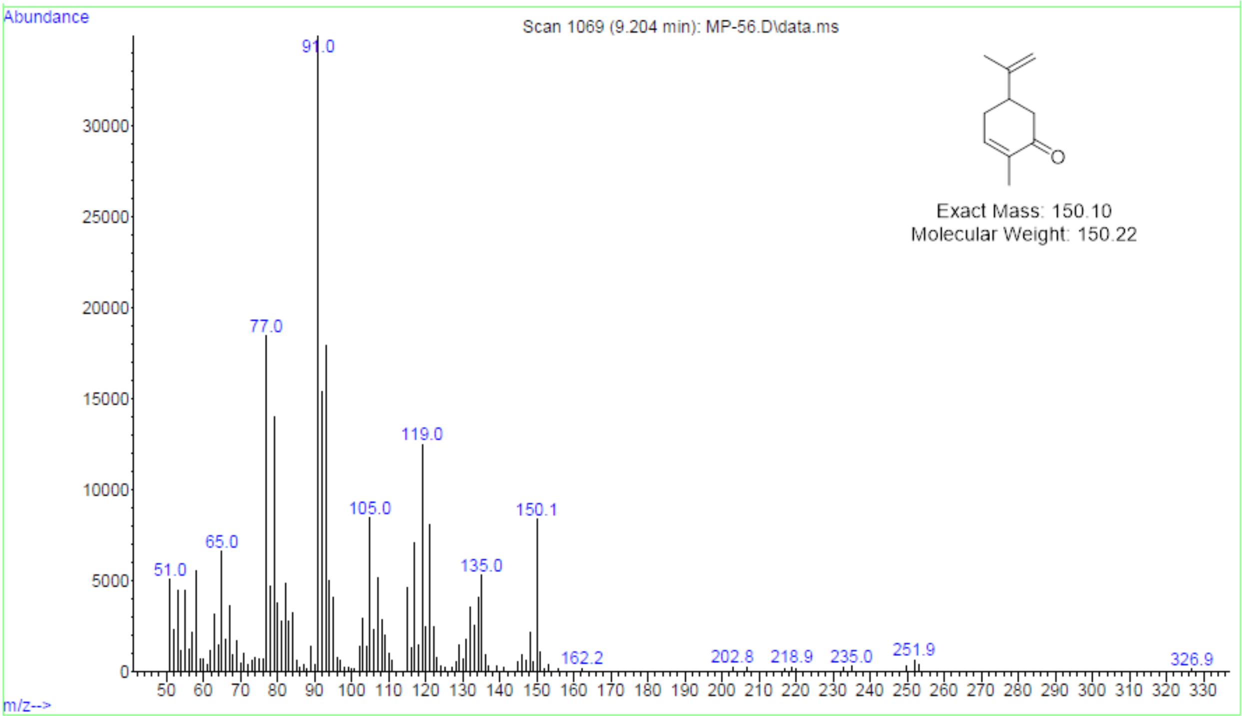


Figure S19. GC-MS traces of carvone.

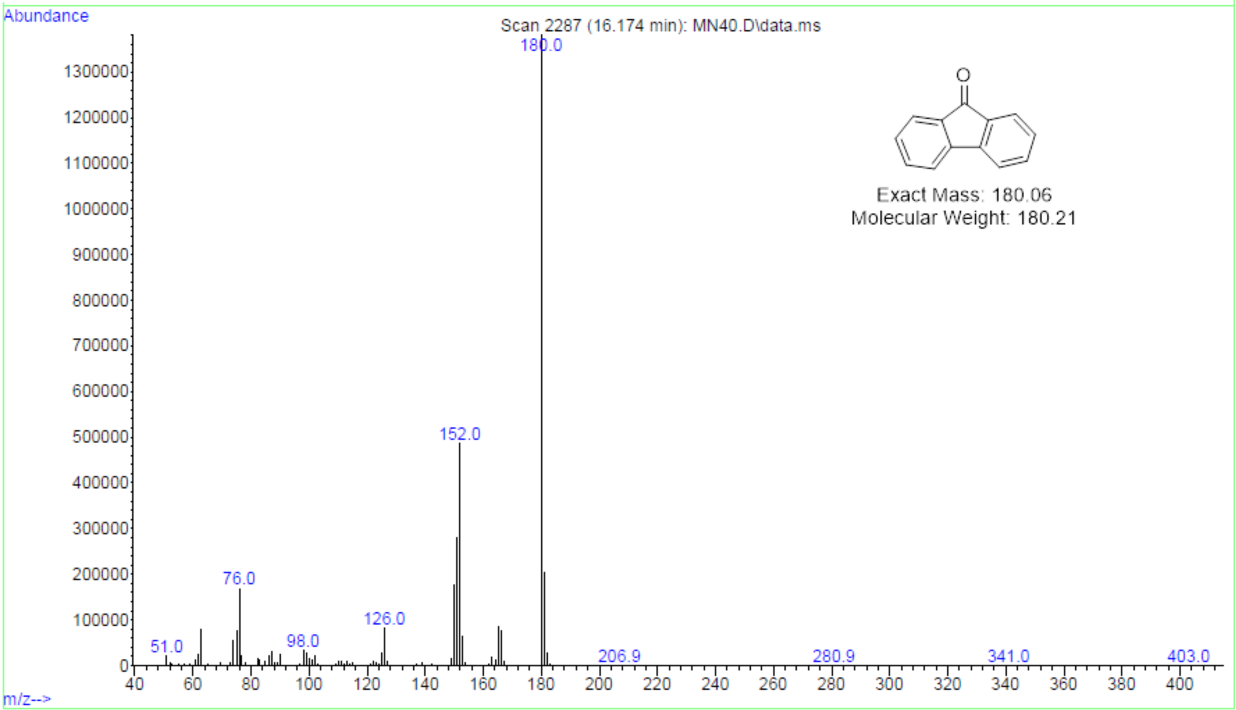


Figure S20. GC-MS traces of fluorenone.

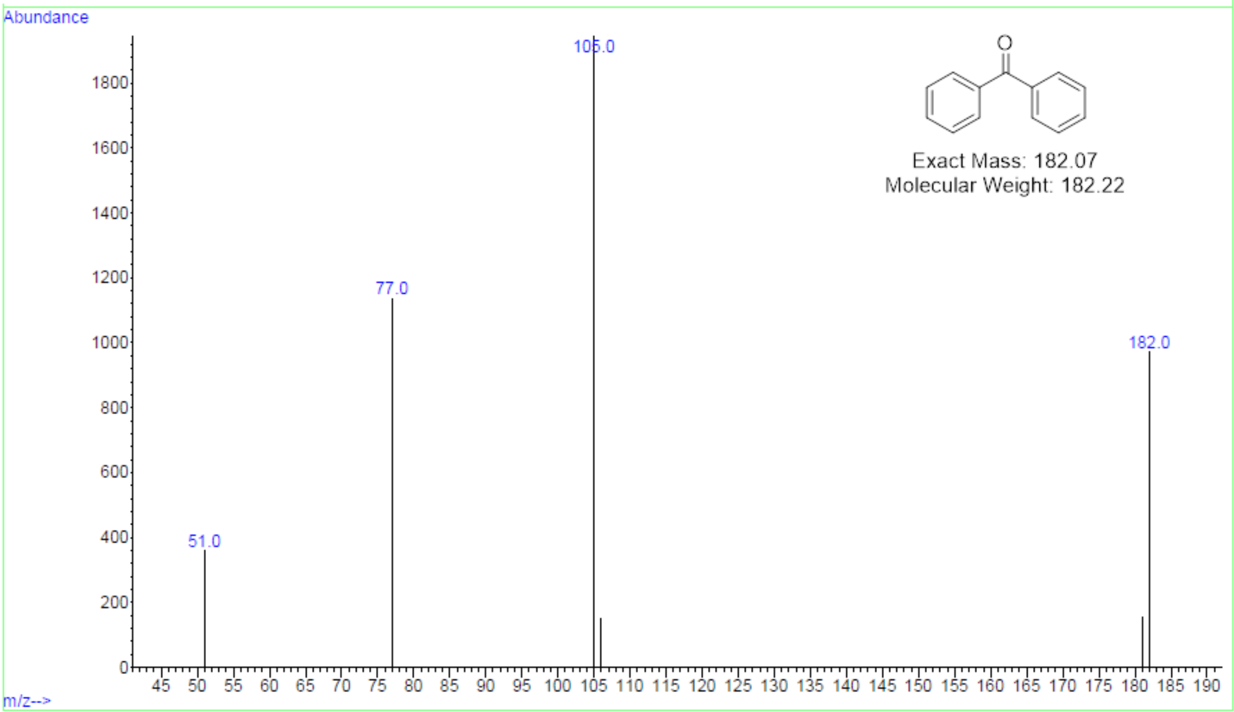


Figure S21. GC-MS traces of benzophenone.

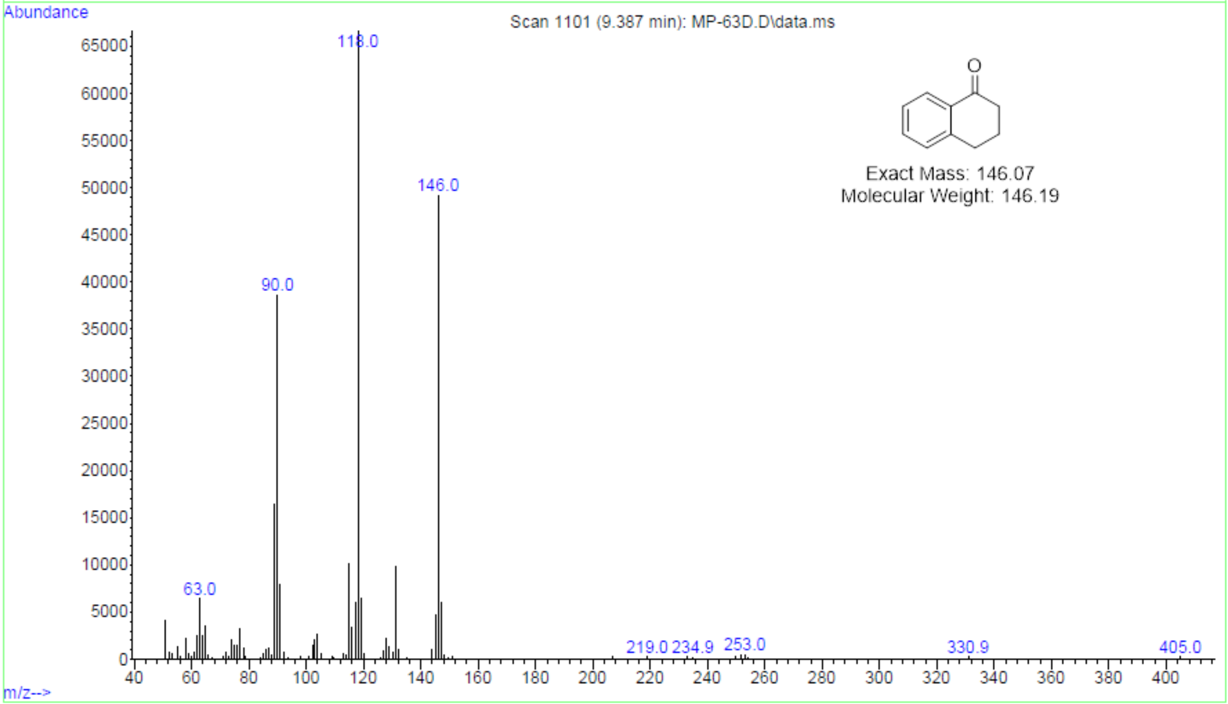


Figure S22. GC-MS traces of tetralone.

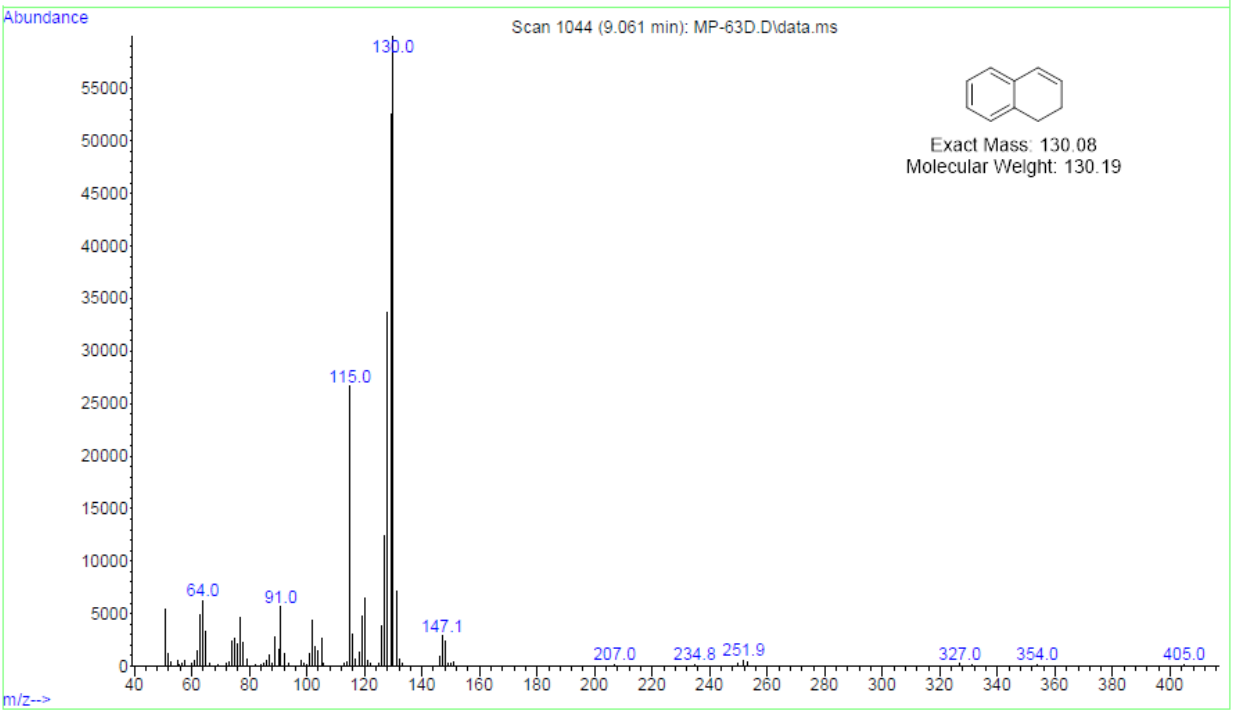


Figure S23. GC-MS traces of 1,2-dihydronaphthalene.

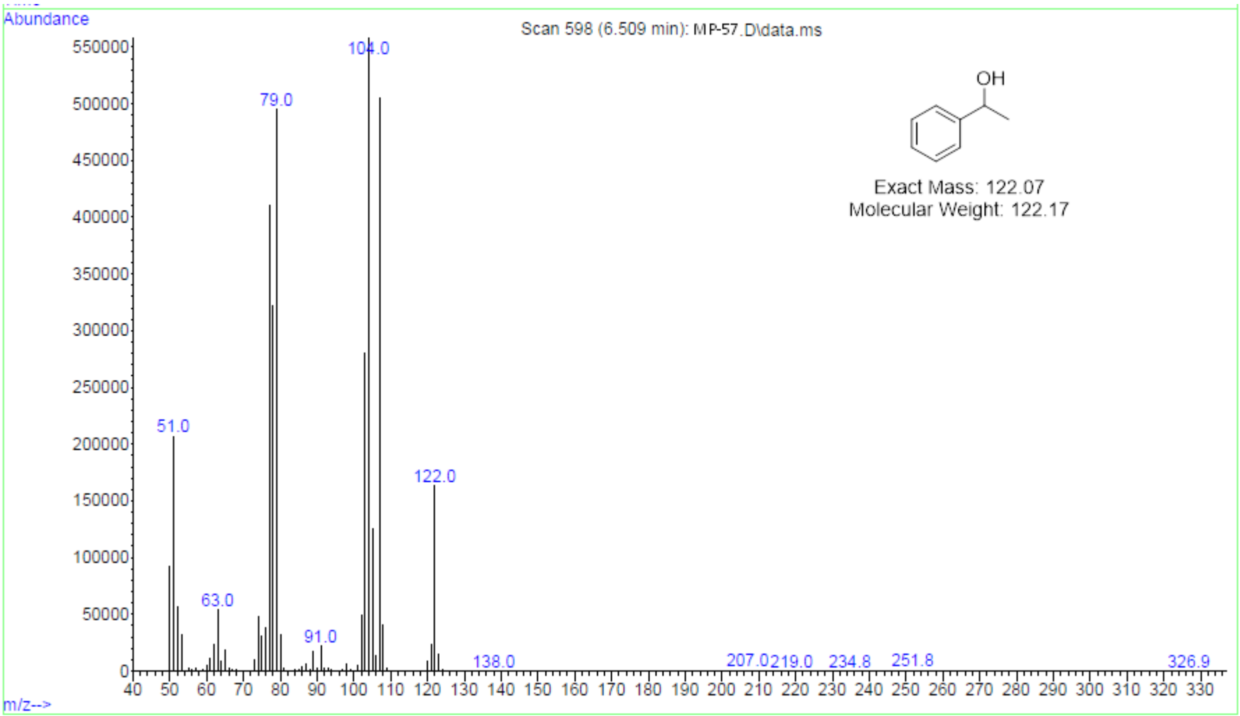


Figure S24. GC-MS traces of 1-phenylethanol.

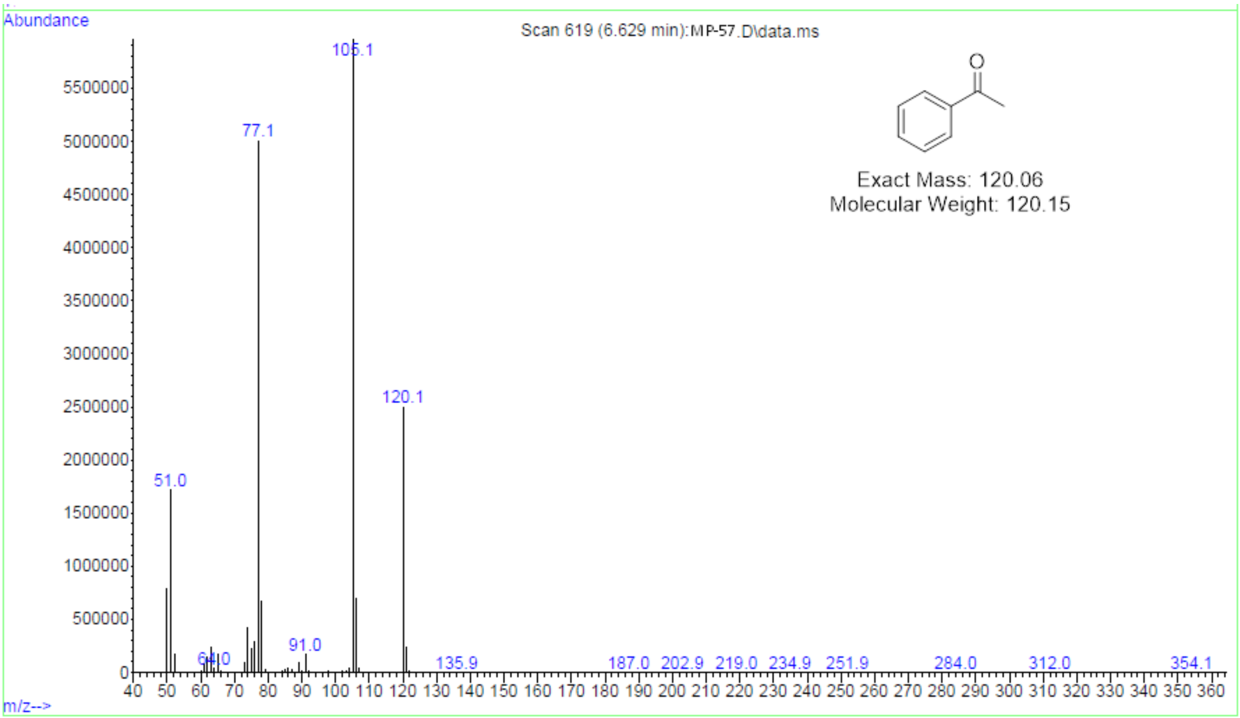


Figure S25 . GC-MS traces of acetophenone.

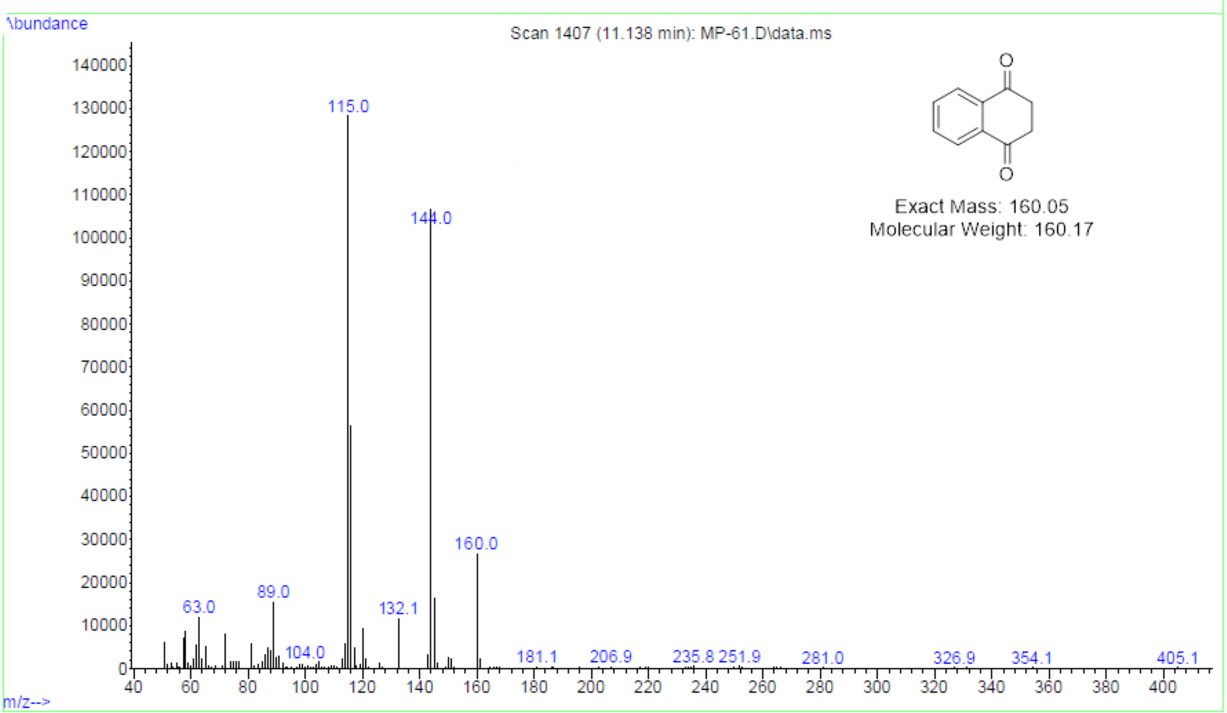


Figure S26 . GC-MS traces of 2,3-dihydronaphthalene-1,4-dione

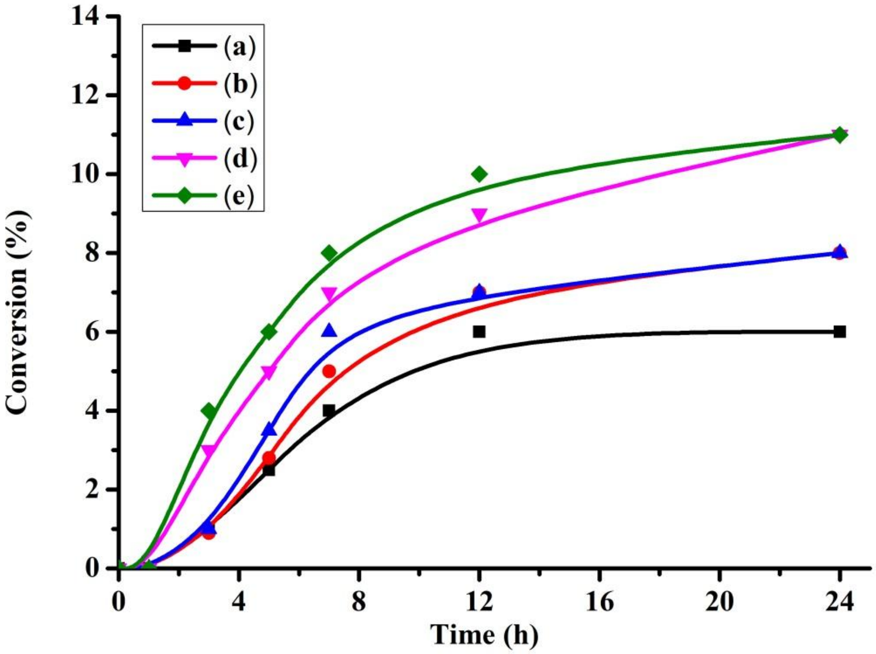


Figure S27. Aerobic oxidation of (a) diphenylmethane, (b) ethylbenzene, (c) tetralin, (d) fluorene and (e) limonene under similar conditions as shown in Table 3.