Electronic Supplementary Material (ESI) for RSC Advances.

Supporting Information

A supported manganese complex with amine-bis(phenol) ligand for catalytic benzylic C(SP3)-H bond oxidation

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General procedure for monitoring in the C-H bond oxidation

A 5 mL glass flask was charged with catalyst (0.04 g, 2 mol%), ethylbenzene (1 mmol) and TBHP aq. 70% (3 equivalents) as oxidant. The process of reaction was monitored as a function of time at 60 °C up to 10 h in solvent free condition under argon atmosphere. At each hour, a sample of the reaction mixture was isolated using a syringe and after the extraction with ethyl acetate, the reaction progression was monitored by using of gas chromatography (GC).

General procedure for hot filtration test in the C-H bond oxidation

A 5 mL glass flask was charged with catalyst (0.04 g, 2 mol%), ethylbenzene (1 mmol) and TBHP aq. 70% (3 equivalents) as oxidant. The process of reaction was monitored as a function of time at 60 °C up to 10 h in solvent free condition under argon atmosphere. For hot filtration test, at the half of the reaction time (5 h) the catalyst was magnetically separated by placing a permanent magnet in the reactor wall and the catalyst-free solution was allowed to continue for stirring at the same conditions. To analyze the reaction content, every hour a sample was extracted from the reaction mixture and reaction progressing was checked via gas chromatography (GC).

General procedure for recovery of catalyst in the C-H bond oxidation

A 5 mL glass flask was charged with catalyst (0.04 g, 2 mol%), ethylbenzene (1 mmol) and TBHP aq. 70% (3 equivalents) as oxidant. The reaction mixture was continuously stirred at 60 °C for the desired time and the reaction was monitored by TLC, after completion of the reaction, anisole (1 mmol, 1/1 substrate and anisole) as internal standard was added. In continue, the mixture was extracted with ethyl acetate and then the catalyst was magnetically recovered by placing a permanent magnet in the reactor wall. Products were collected with a syringe and analyzed by gas chromatography (GC). The catalyst was washed several times with ethanol and acetone and then dried at 80 °C overnight before being used again for the next reaction. The next reaction was checked at the presence of recovery catalyst.

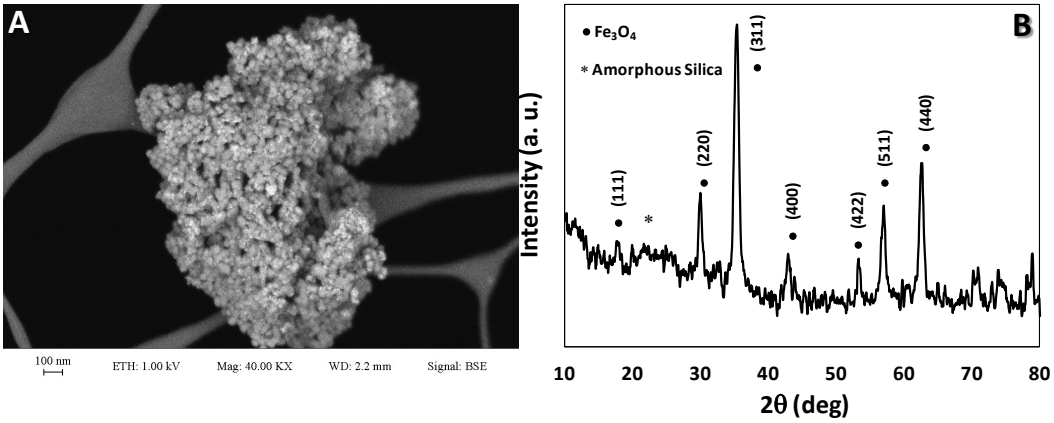


Figure S-1. A) FESEM images B) XRD pattern of recovered catalysts (Fe_3O_4@SiO_2-APTES-MnL^{GDC}).

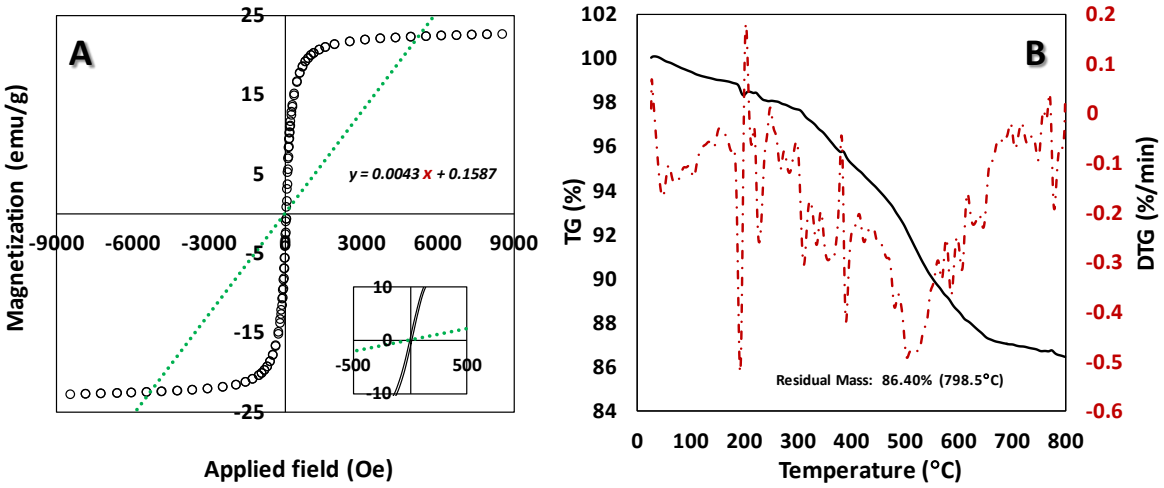


Figure S-2. A) Magnetization curve (Inset: The enlarged image near the coercive field.) B) Thermo-gravimetric analysis (TGA) of recovered catalysts (Fe_3O_4@SiO_2-APTES-MnL^{GDC}).

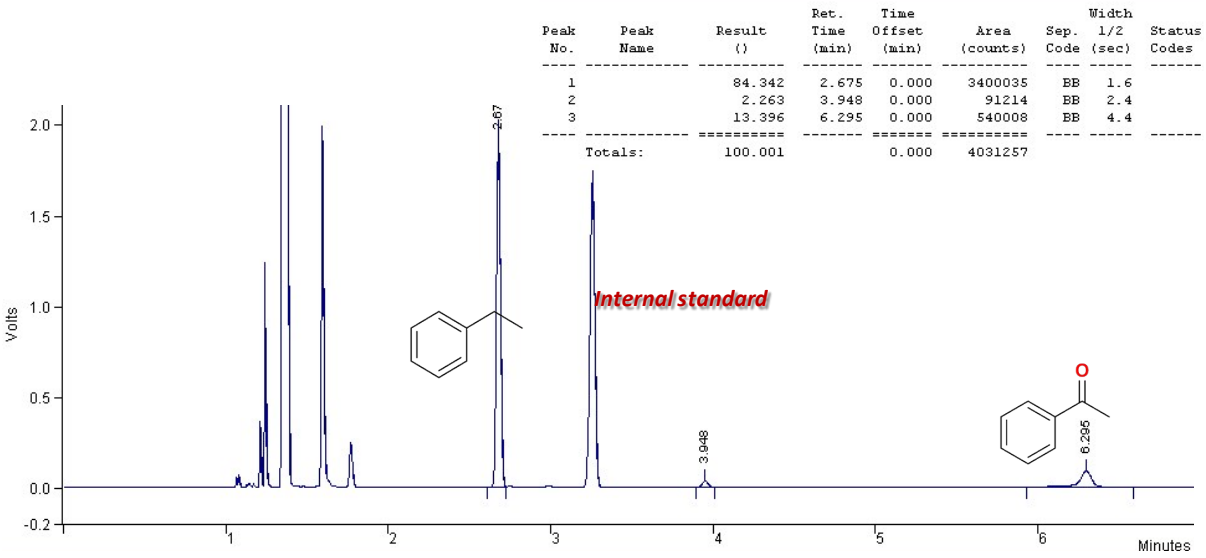


Figure S-3. GC chromatogram for Oxidation of ethylbenzene (Table 1, Entry 1).

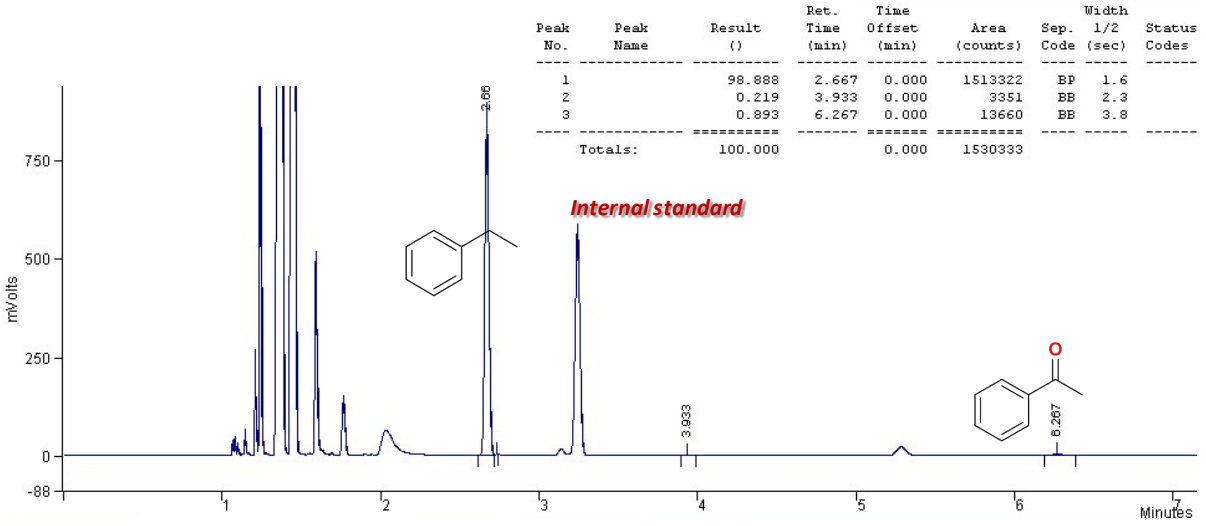


Figure S-4. GC chromatogram for Oxidation of ethylbenzene (Table 1, Entry 2).

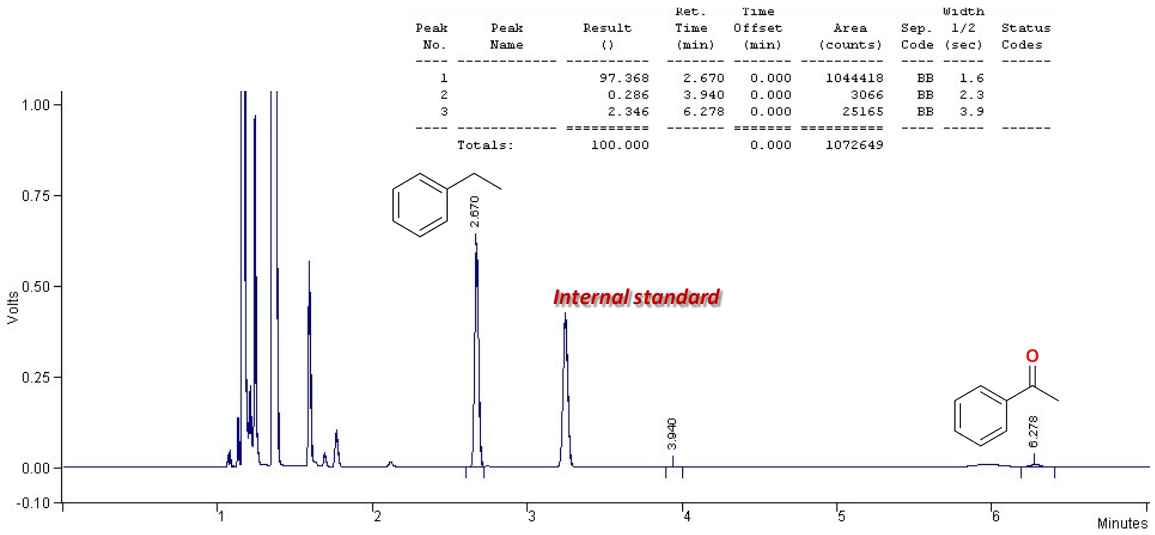


Figure S-5. GC chromatogram for Oxidation of ethylbenzene (Table 1, Entry 3).

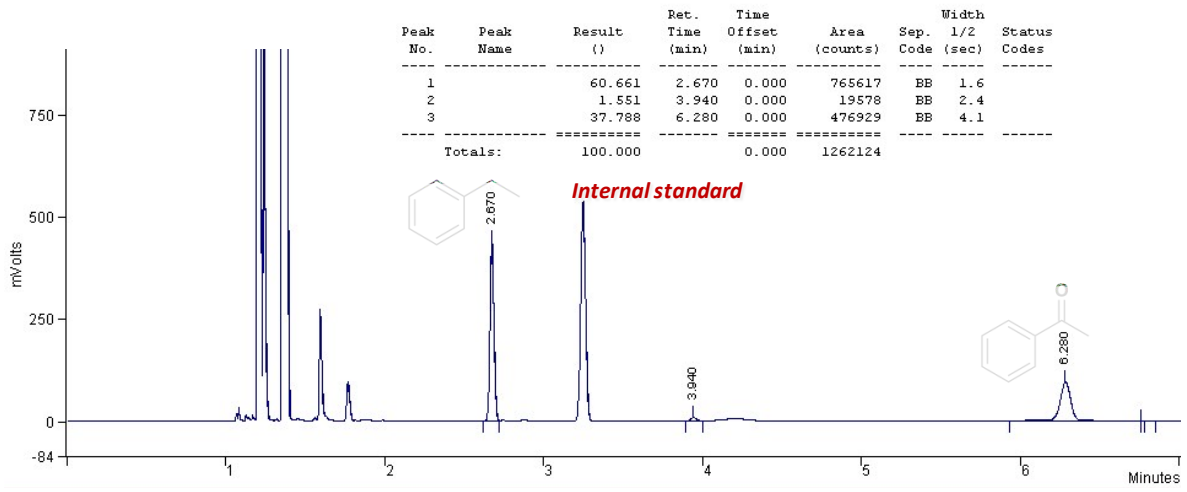


Figure S-6. GC chromatogram for Oxidation of ethylbenzene (Table 1, Entry 4).

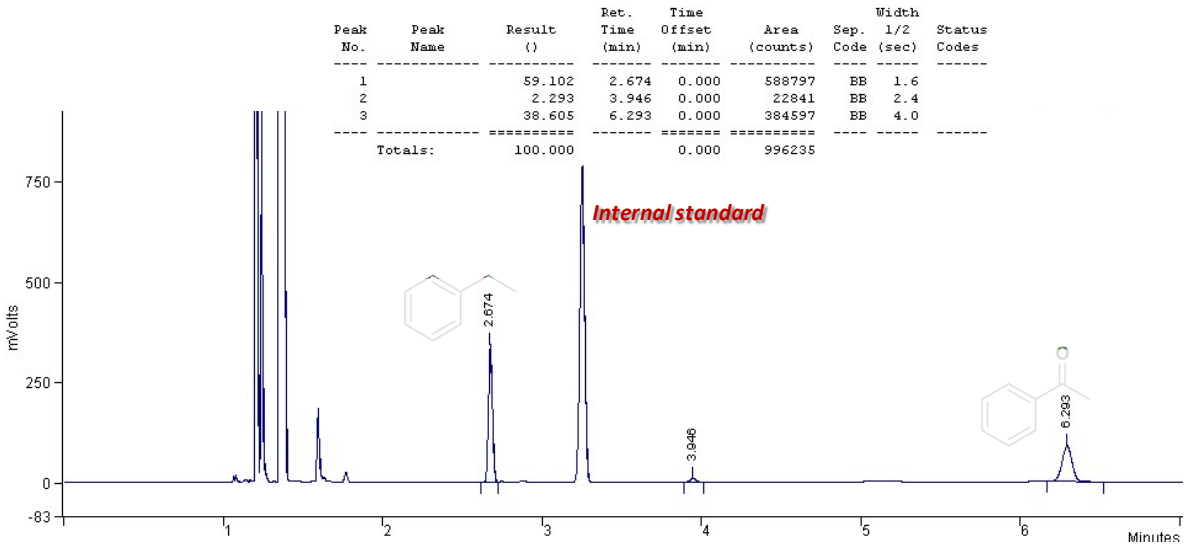


Figure S-7. GC chromatogram for Oxidation of ethylbenzene (Table 1, Entry 5).

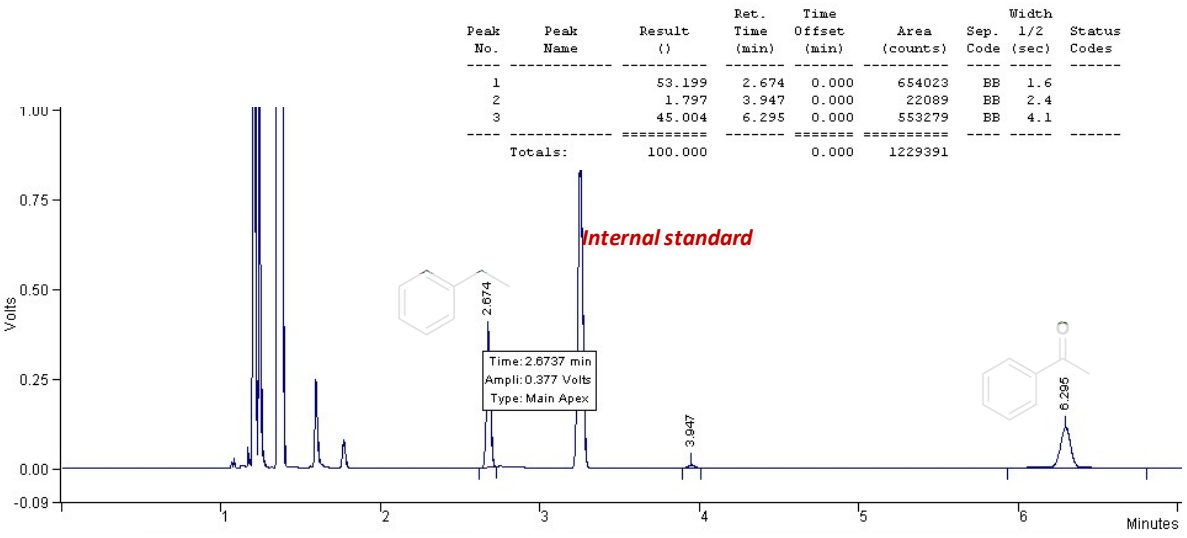


Figure S-8. GC chromatogram for Oxidation of ethylbenzene (Table 1, Entry 6).

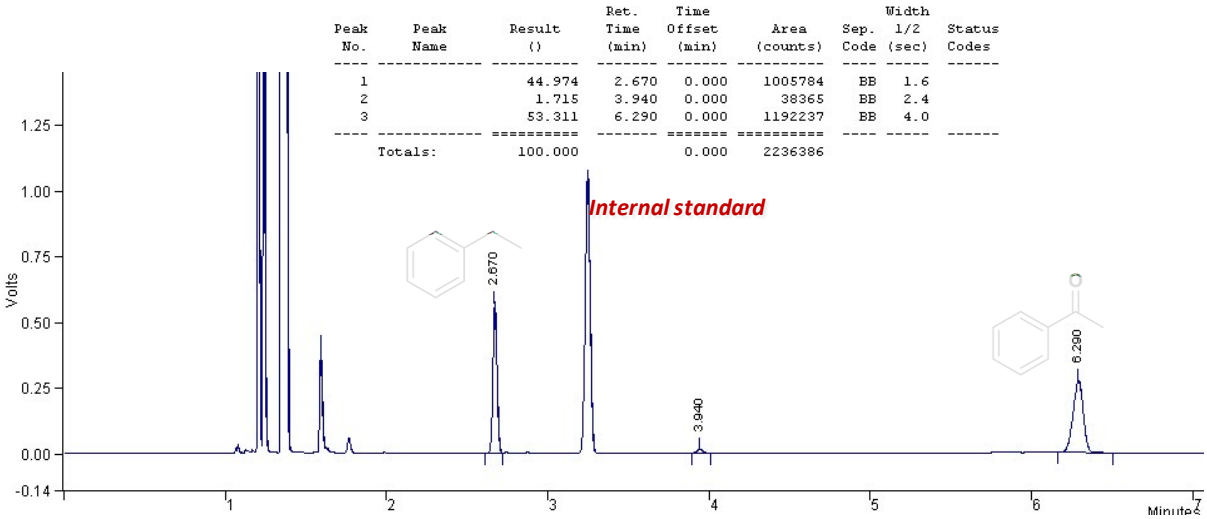


Figure S-9. GC chromatogram for Oxidation of ethylbenzene (Table 1, Entry 7).

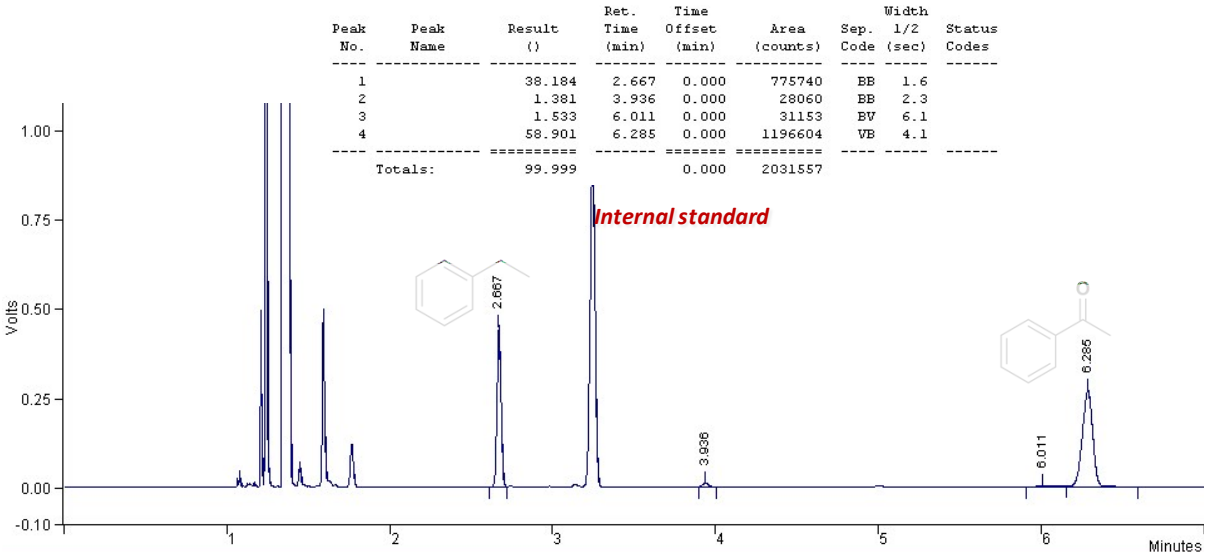


Figure S-10. GC chromatogram for Oxidation of ethylbenzene (Table 1, Entry 8).

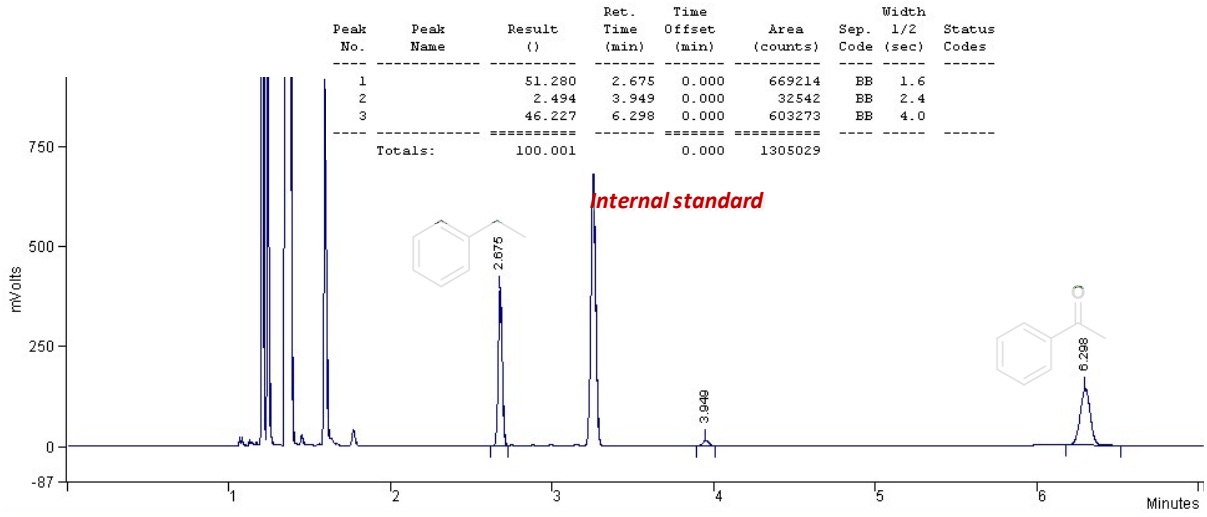


Figure S-11. GC chromatogram for Oxidation of ethylbenzene (Table 1, Entry 9).

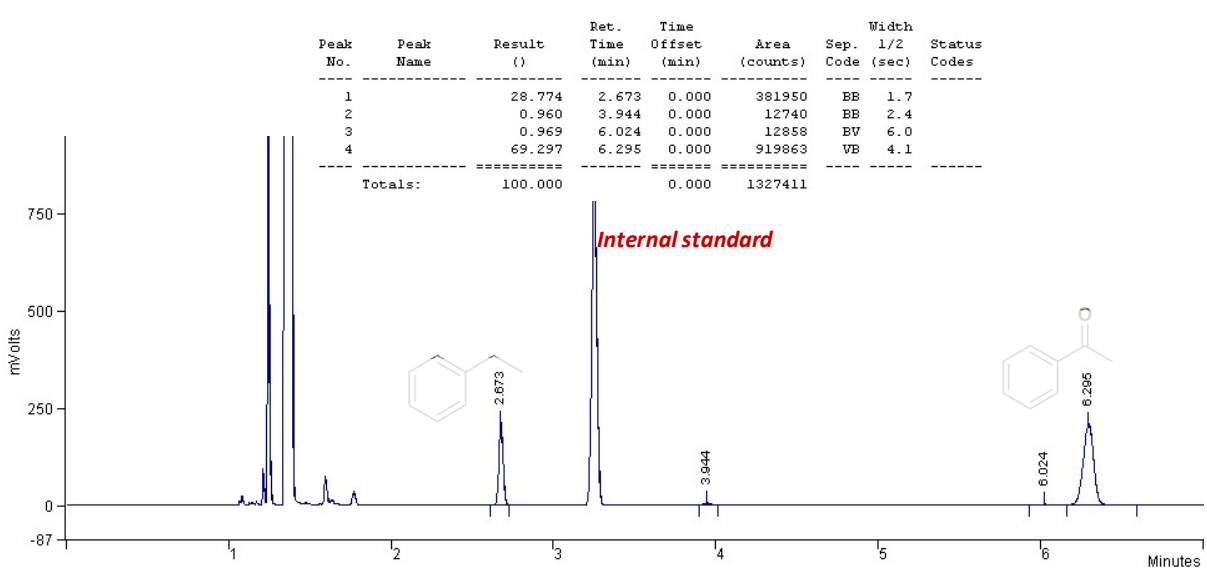


Figure S-12. GC chromatogram for Oxidation of ethylbenzene (Table 1, Entry 10).

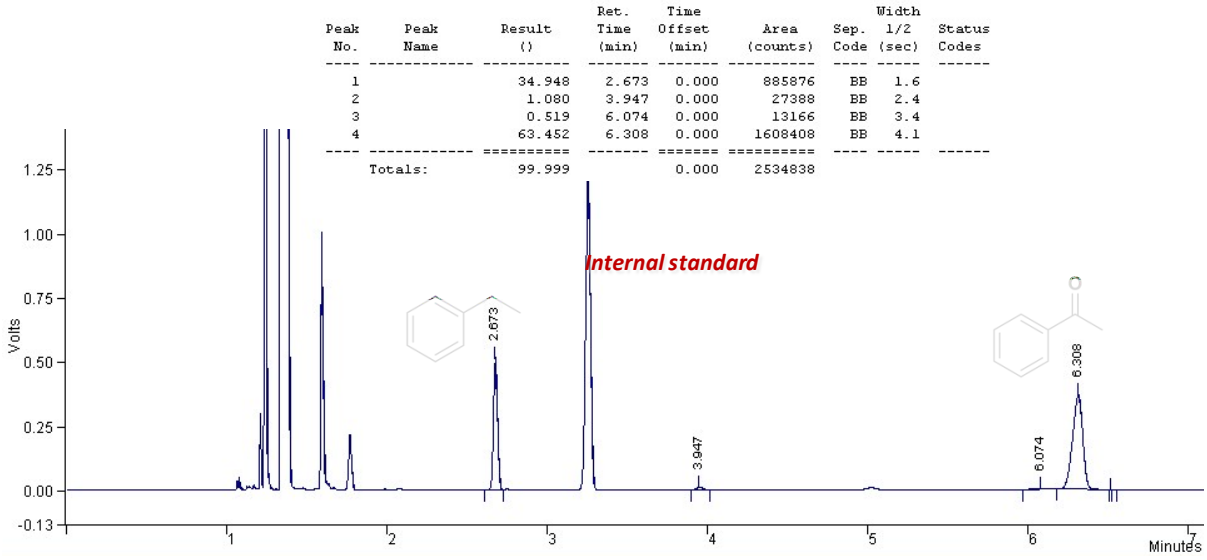


Figure S-13. GC chromatogram for Oxidation of ethylbenzene (Table 1, Entry 11).

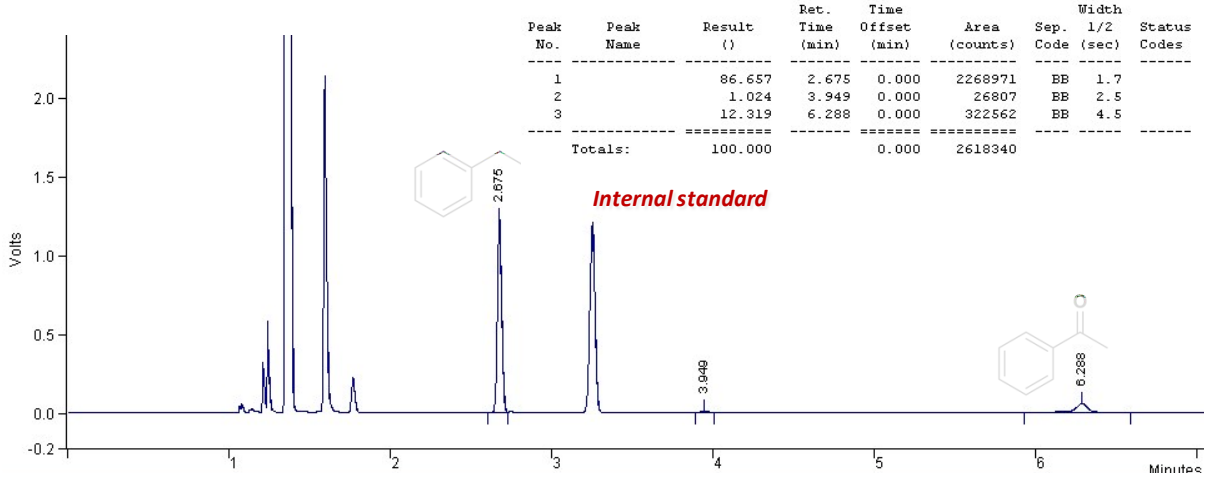


Figure S-14. GC chromatogram for Oxidation of ethylbenzene (Table 1, Entry 12).

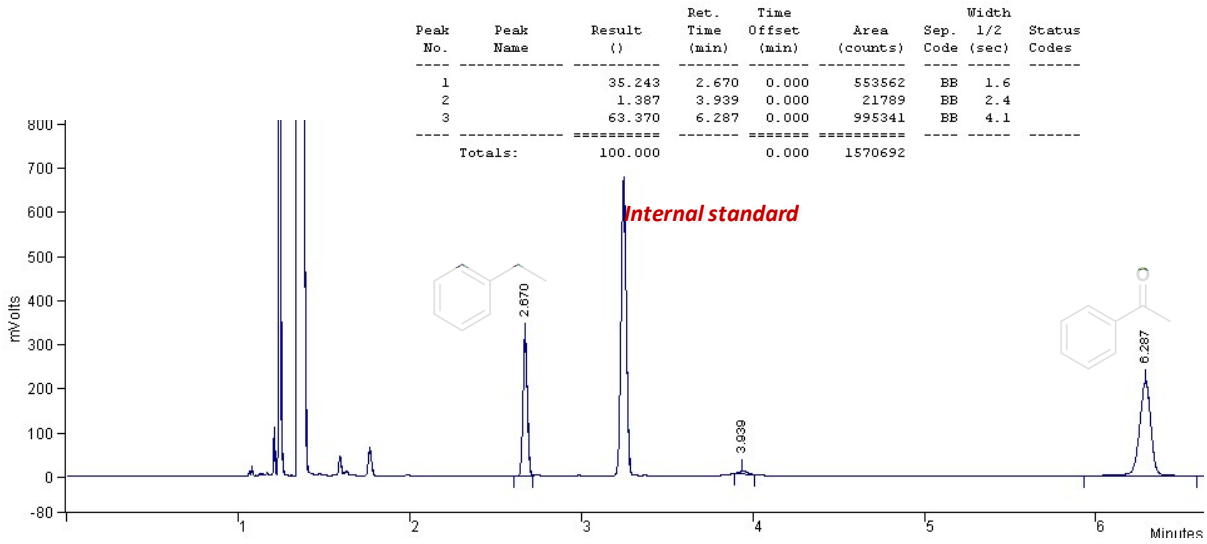


Figure S-15. GC chromatogram for Oxidation of ethylbenzene (Table 1, Entry 13).

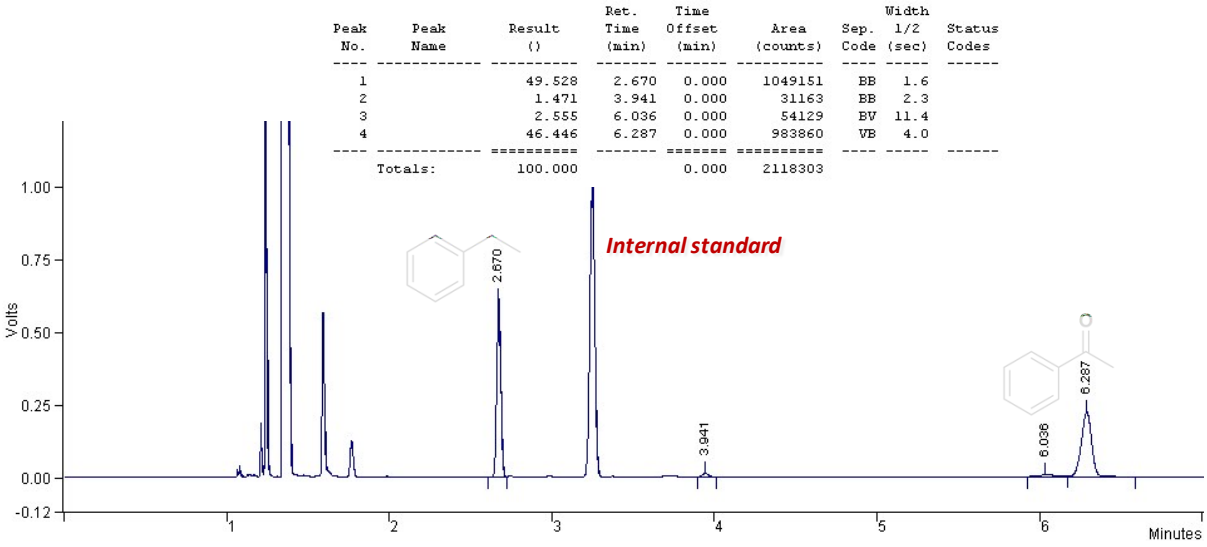


Figure S-16. GC chromatogram for Oxidation of ethylbenzene (Table 1, Entry 14).

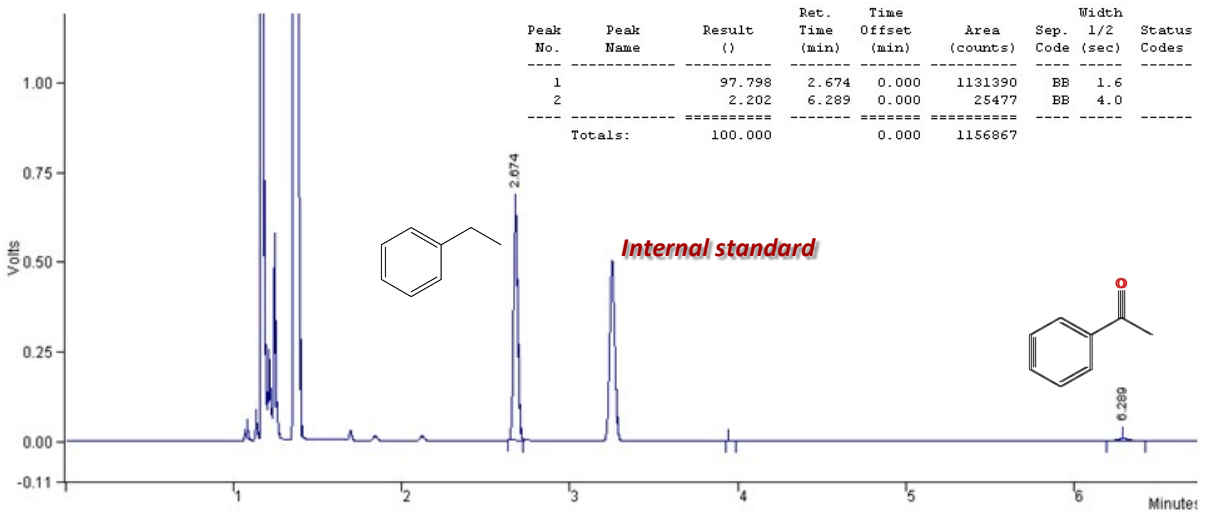


Figure S-17. GC chromatogram for Oxidation of ethylbenzene (Table 1, Entry 15).

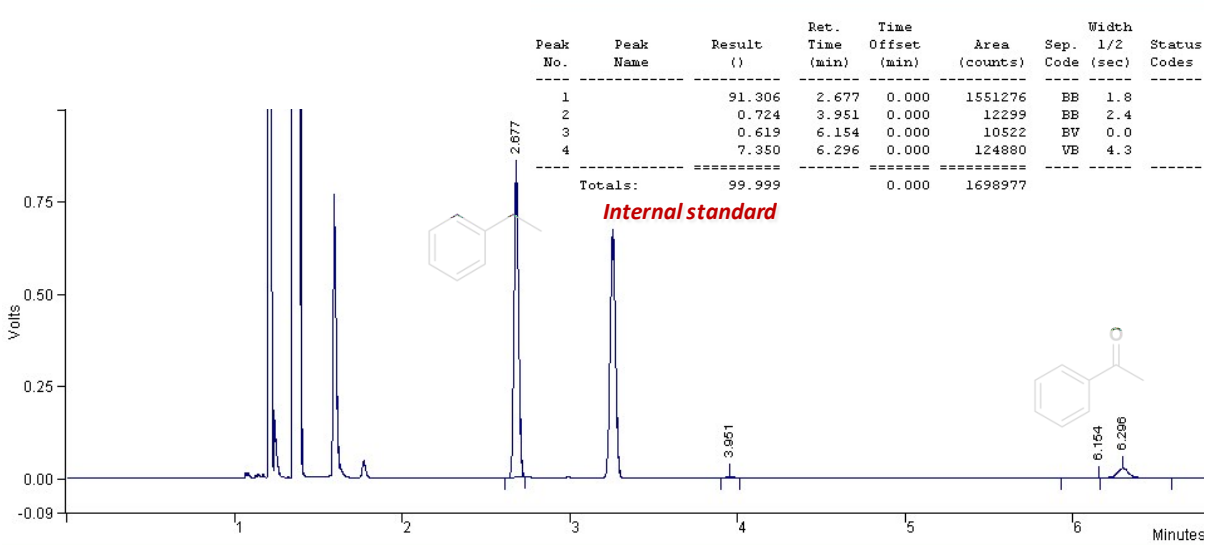


Figure S-18. GC chromatogram for Oxidation of ethylbenzene (Table 1, Entry 16).

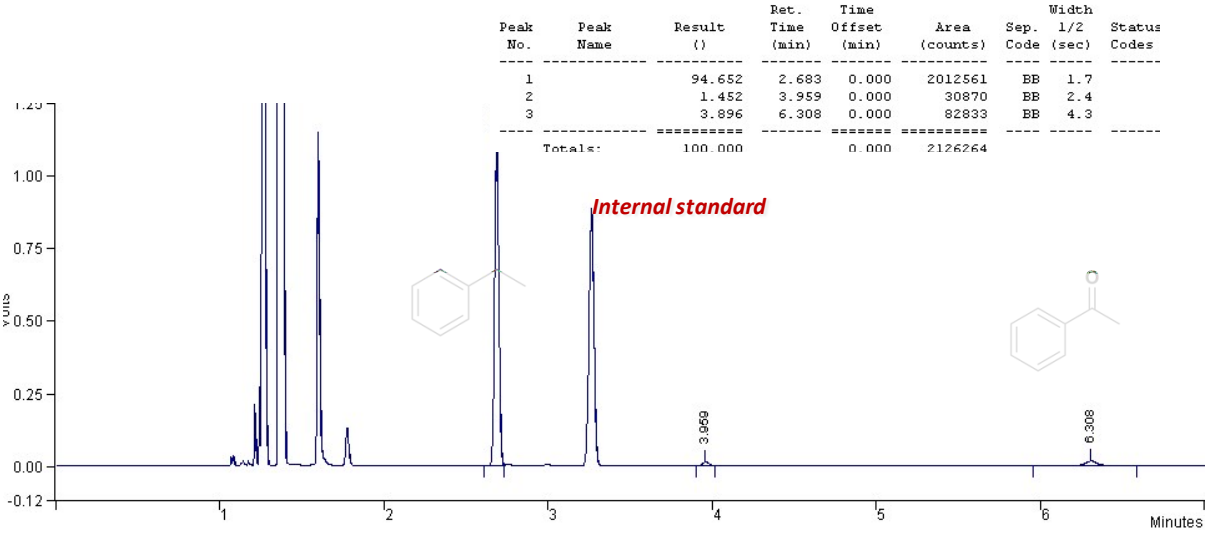


Figure S-19. GC chromatogram for Oxidation of ethylbenzene (Table 1, Entry 17).

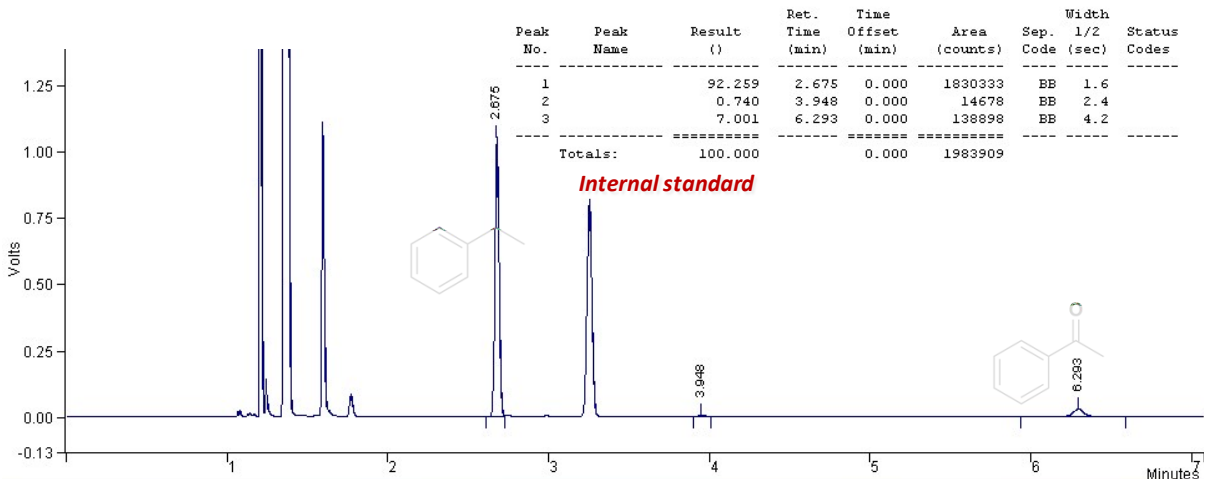


Figure S-20. GC chromatogram for Oxidation of ethylbenzene (Table 1, Entry 18).

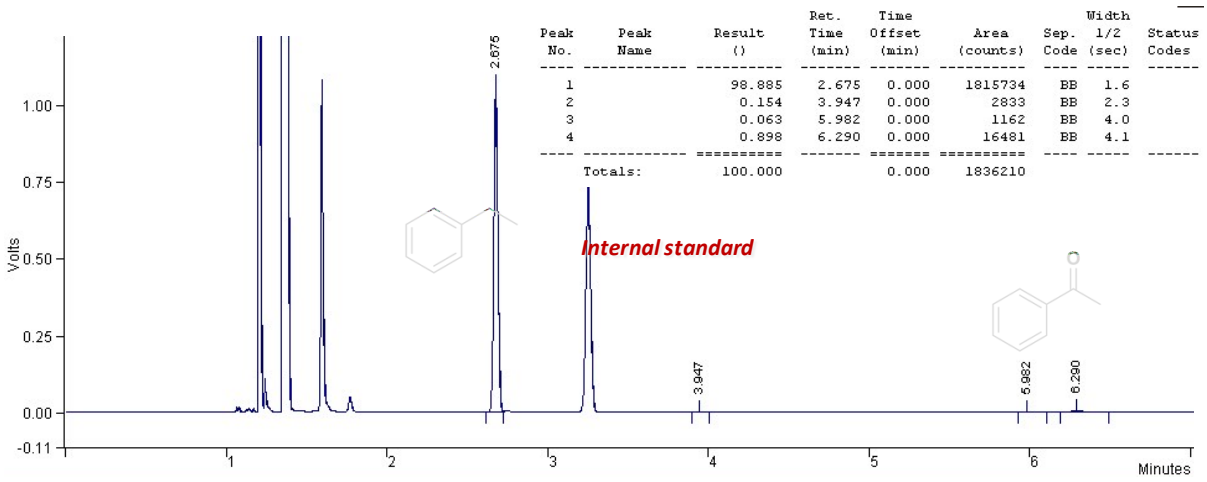


Figure S-21. GC chromatogram for Oxidation of ethylbenzene (Table 1, Entry 19).

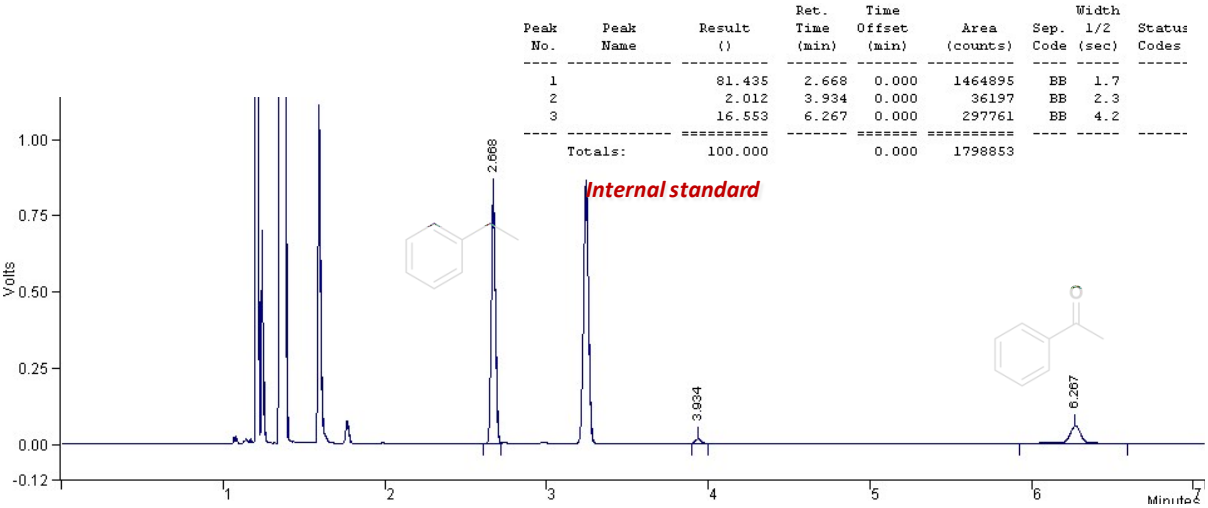


Figure S-22. GC chromatogram for Oxidation of ethylbenzene (Table 1, Entry 20).

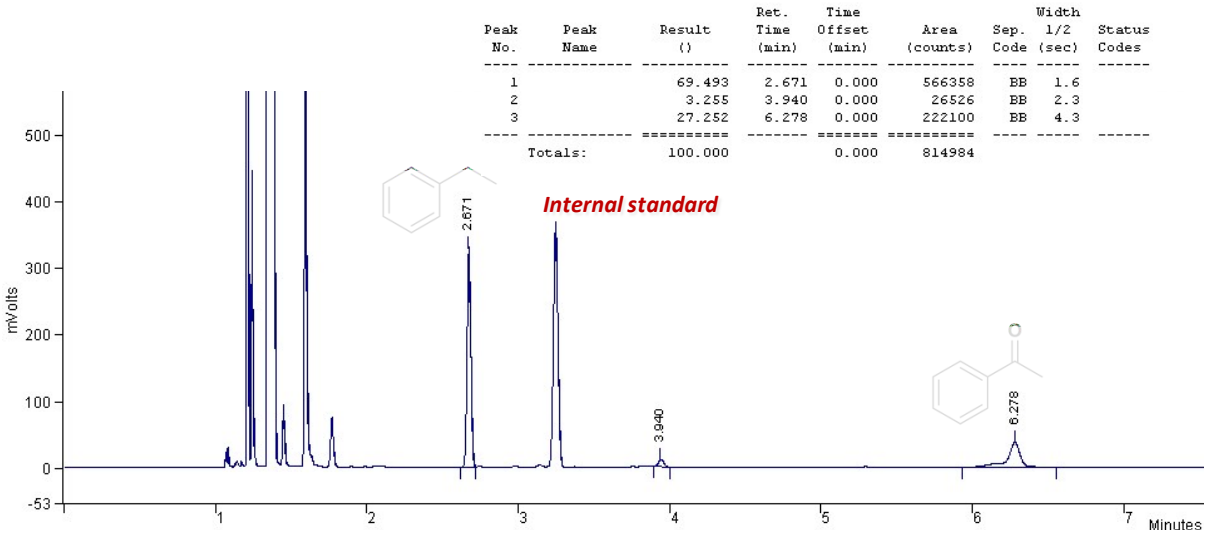


Figure S-23. GC chromatogram for Oxidation of ethylbenzene (Table 1, Entry 21).

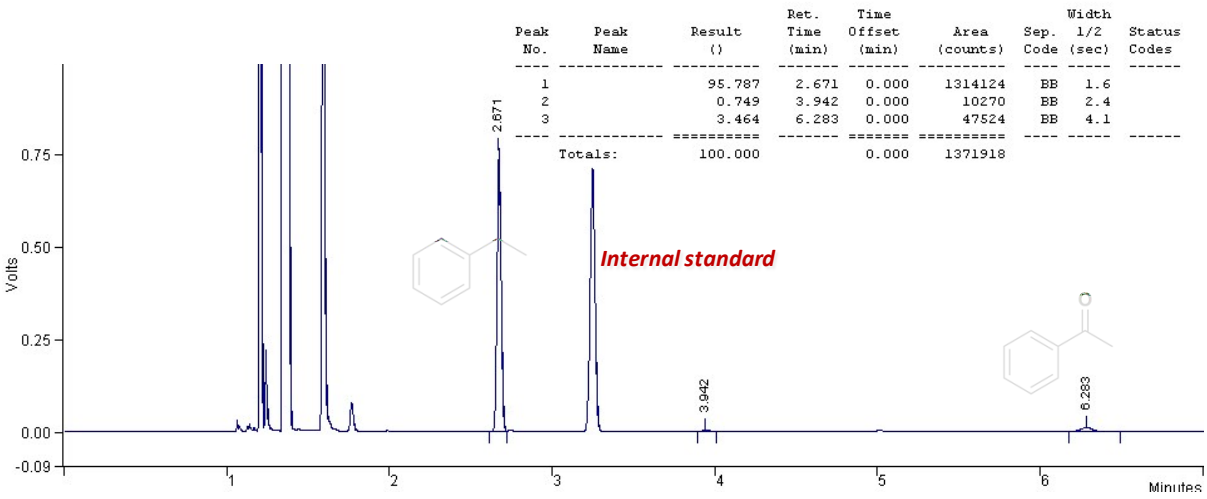


Figure S-24. GC chromatogram for Oxidation of ethylbenzene (Table 1, Entry 22).

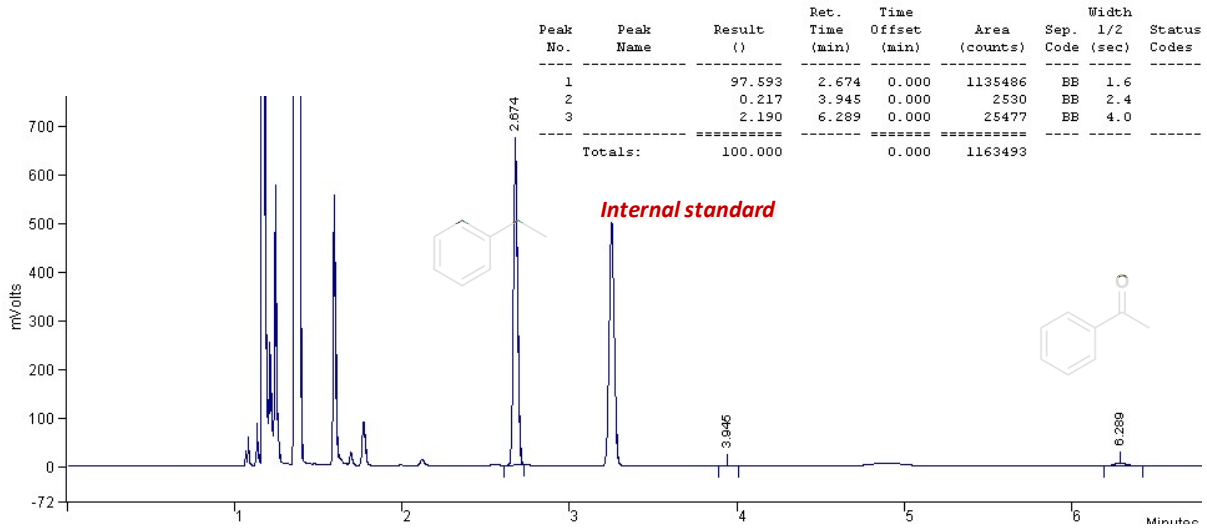


Figure S-25. GC chromatogram for Oxidation of ethylbenzene (Table 1, Entry 23).

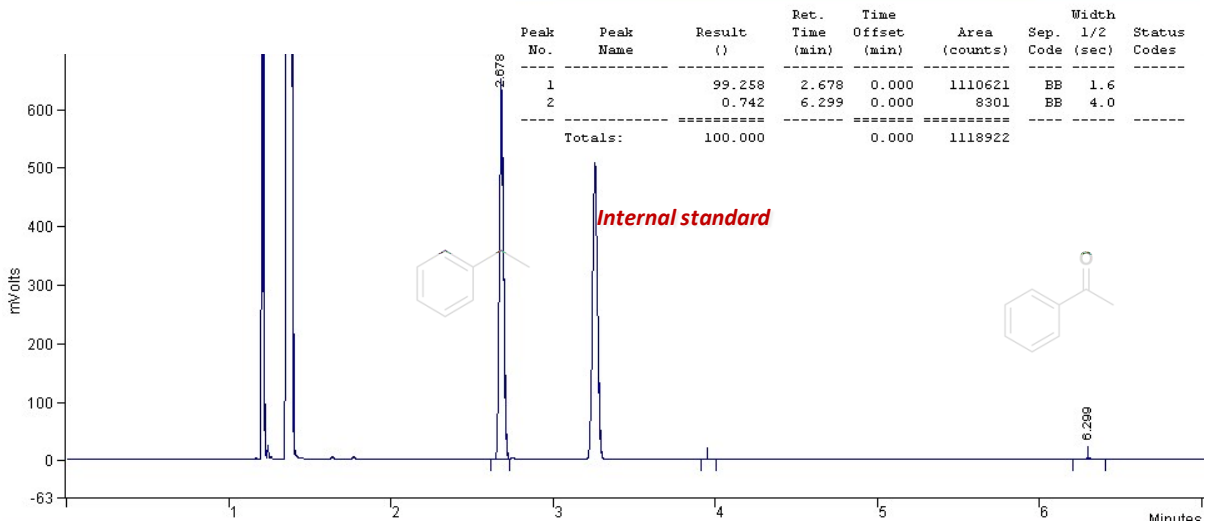


Figure S-26. GC chromatogram for Oxidation of ethylbenzene (Table 1, Entry 24).

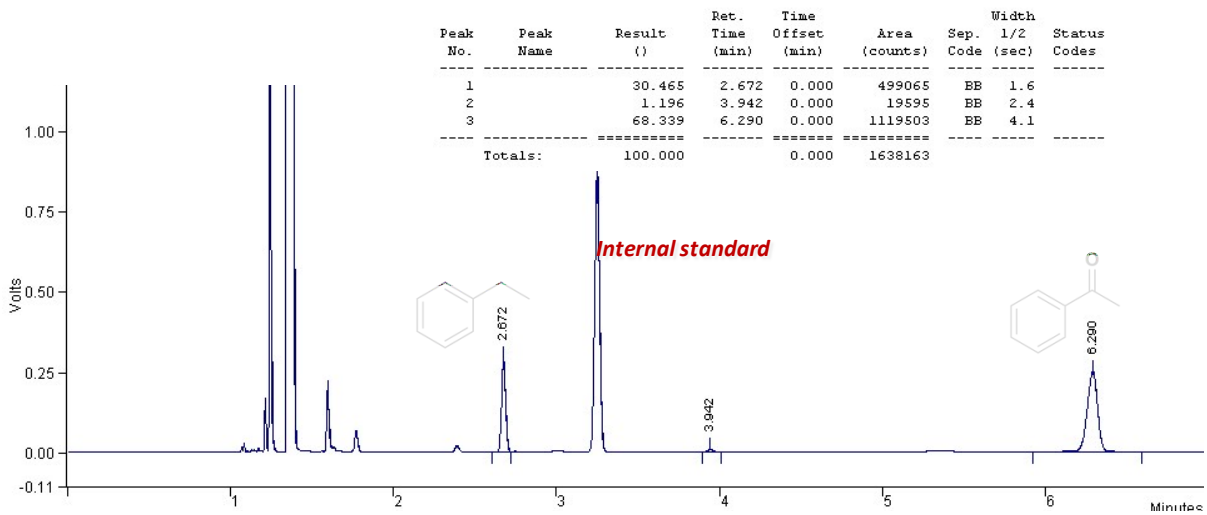


Figure S-27. GC chromatogram for Oxidation of ethylbenzene (Table 1, Entry 25).

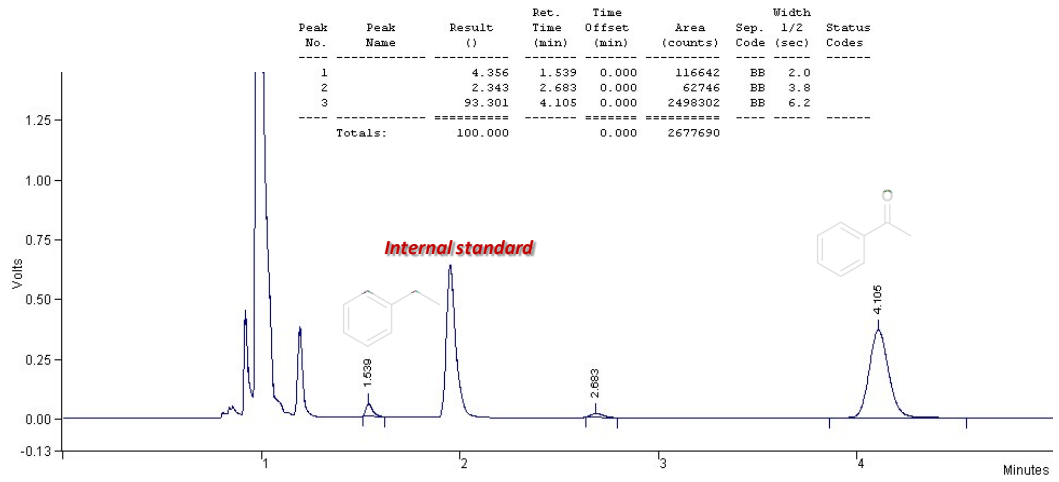


Figure S-28. GC chromatogram for Oxidation of ethylbenzene at the presence of TBHP (Scheme 2-a).

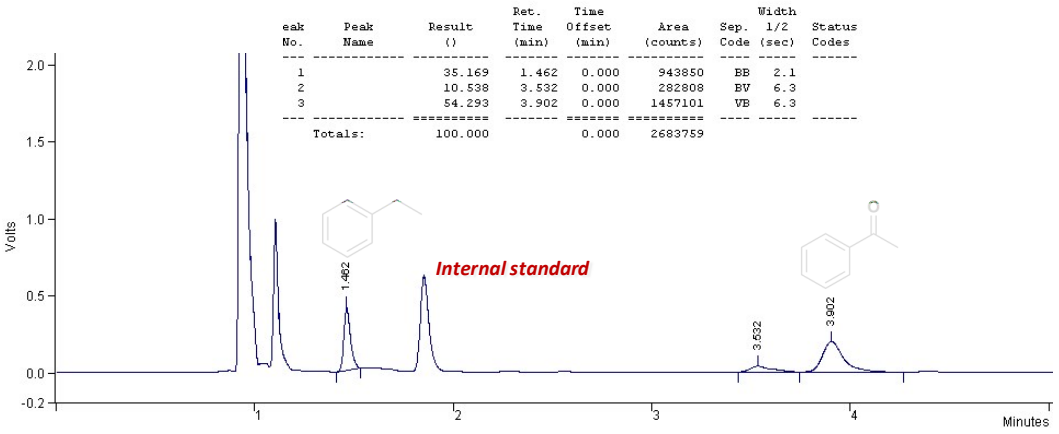


Figure S-29. GC chromatogram for Oxidation of ethylbenzene at the presence of O_2 (Scheme 2-b).

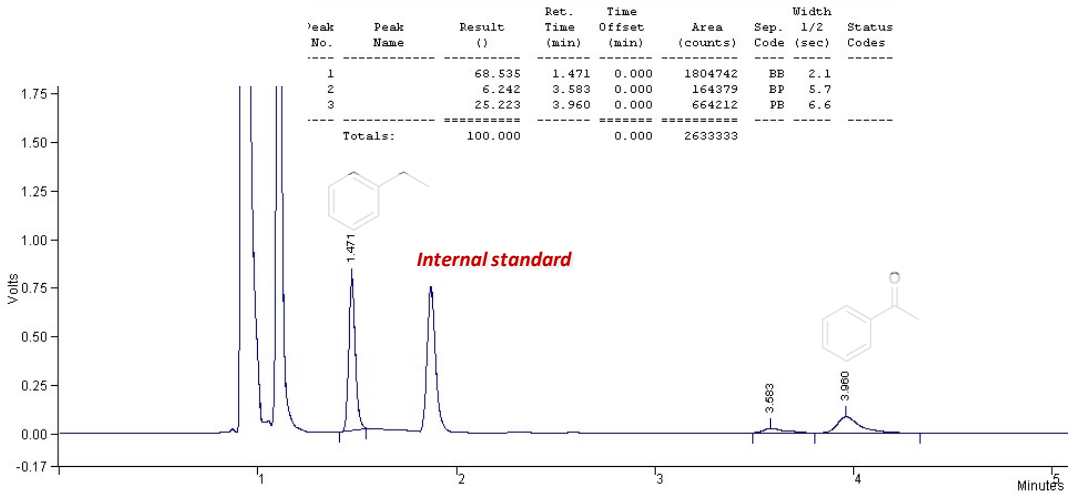


Figure S-30. GC chromatogram for Oxidation of ethylbenzene at the presence of Air (Scheme 2-c).

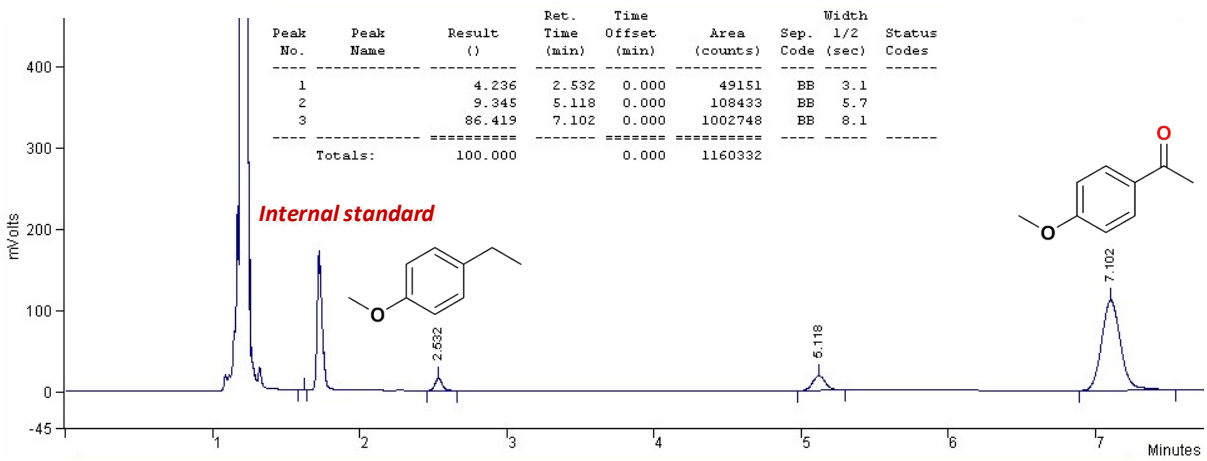


Figure S-31. GC chromatogram for Oxidation of 1-Ethyl-4-methoxybenzene under optimal condition (Table 2, Entry 1).

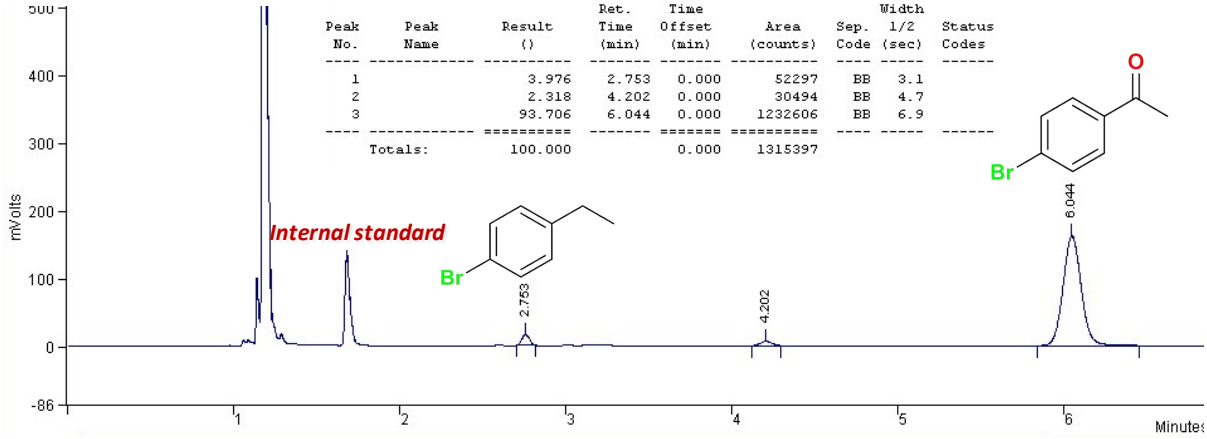


Figure S-32. GC chromatogram for Oxidation of 1-Bromo-4-ethylbenzene under optimal condition (Table 2, Entry 2).

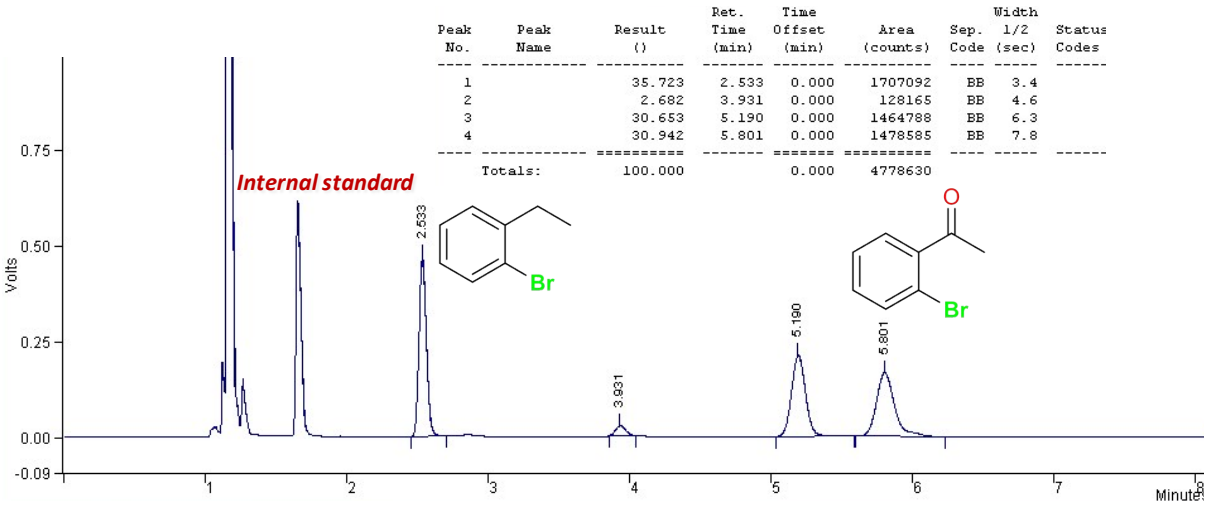


Figure S-33. GC chromatogram for Oxidation of 1-Bromo-2-ethylbenzene under optimal condition (Table 2, Entry 3).

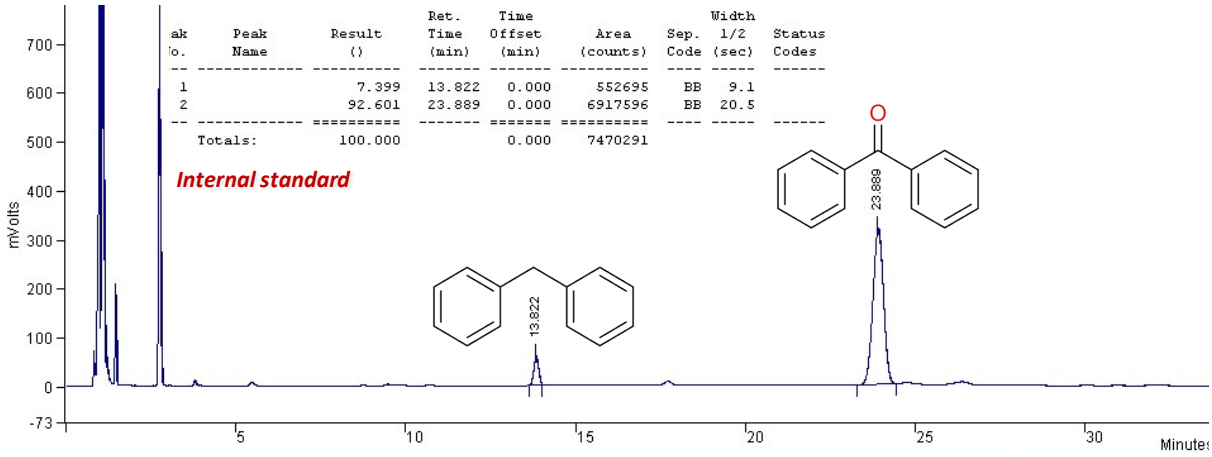


Figure S-34. GC chromatogram for Oxidation of Diphenylmethanol under optimal condition (Table 2, Entry 4).

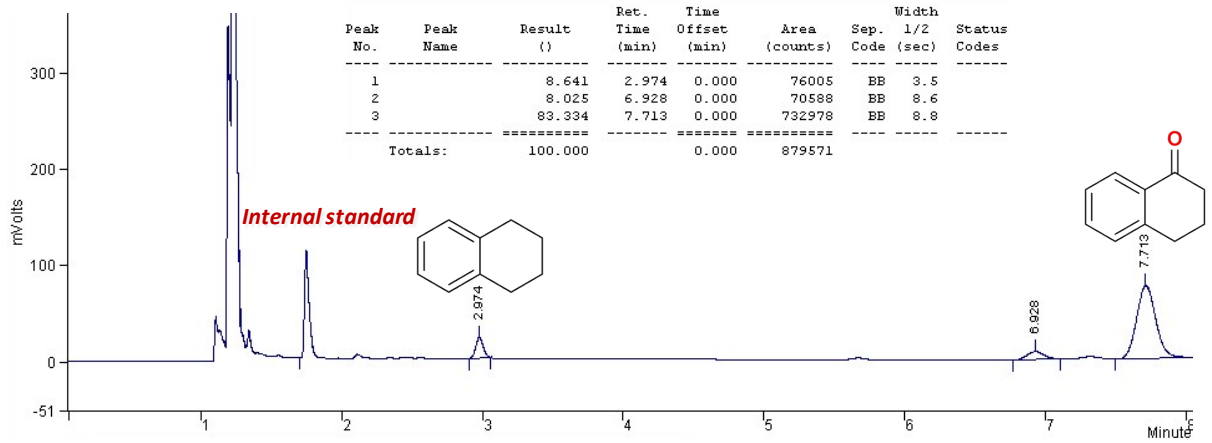


Figure S-35. GC chromatogram for Oxidation of Tetralin under optimal condition (Table 2, Entry 5)**.**

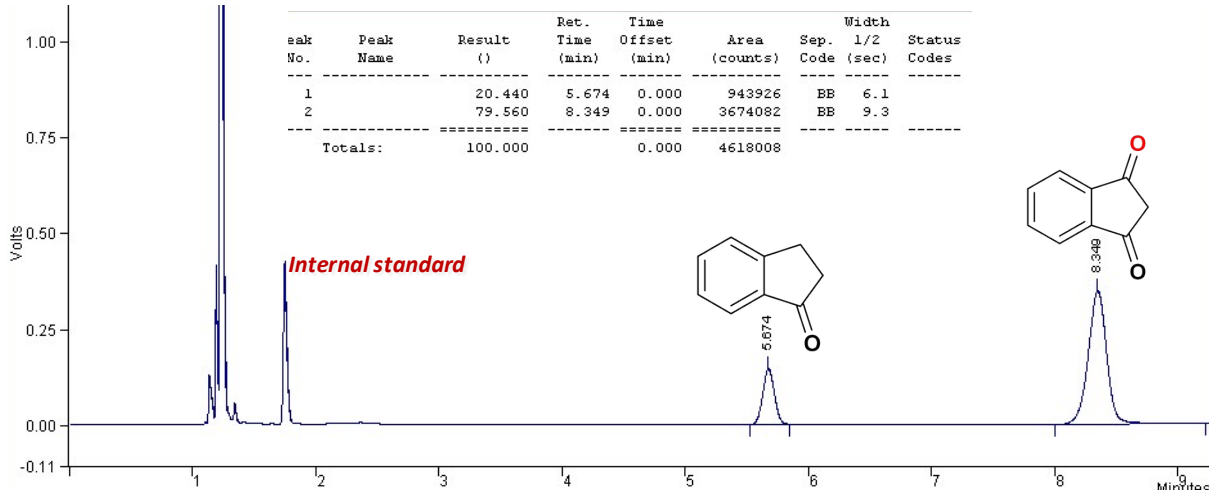


Figure S-36. GC chromatogram for Oxidation of 1-Indanone under optimal condition (Table 2, Entry 6).

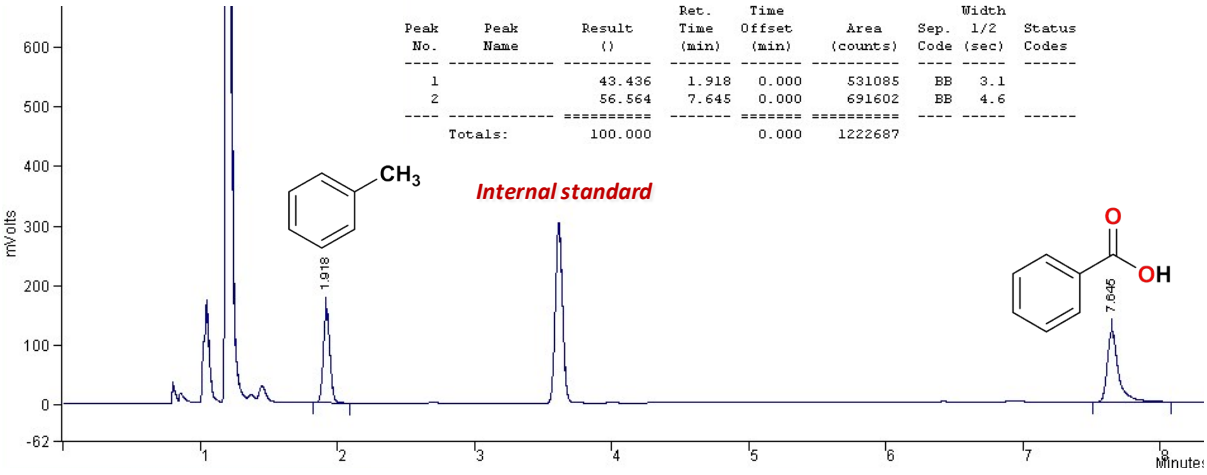


Figure S-37. GC chromatogram for Oxidation of Toluene under optimal condition (Table 2, Entry 7).

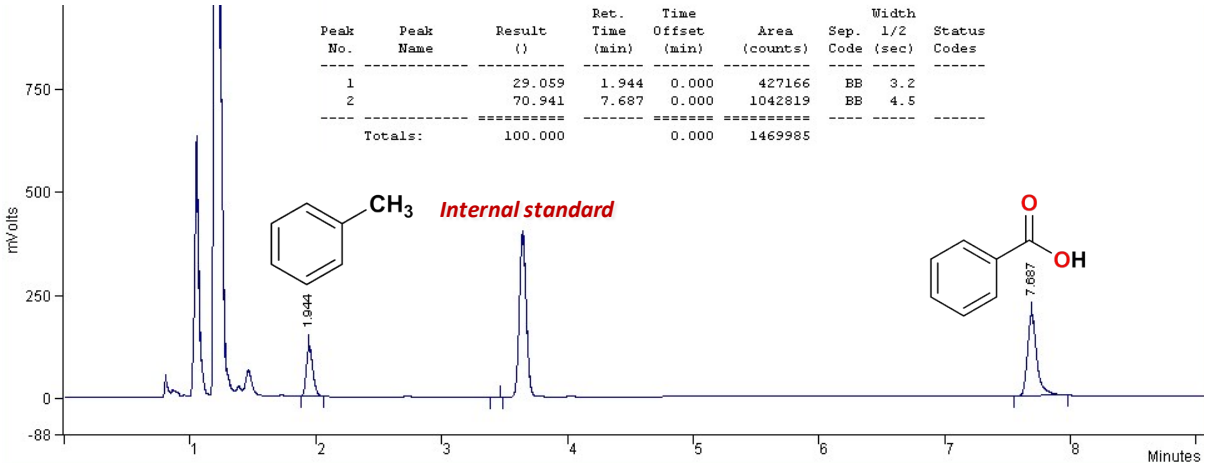


Figure S-38. GC chromatogram for Oxidation of Toluene under optimal condition (Table 2, Entry 8).

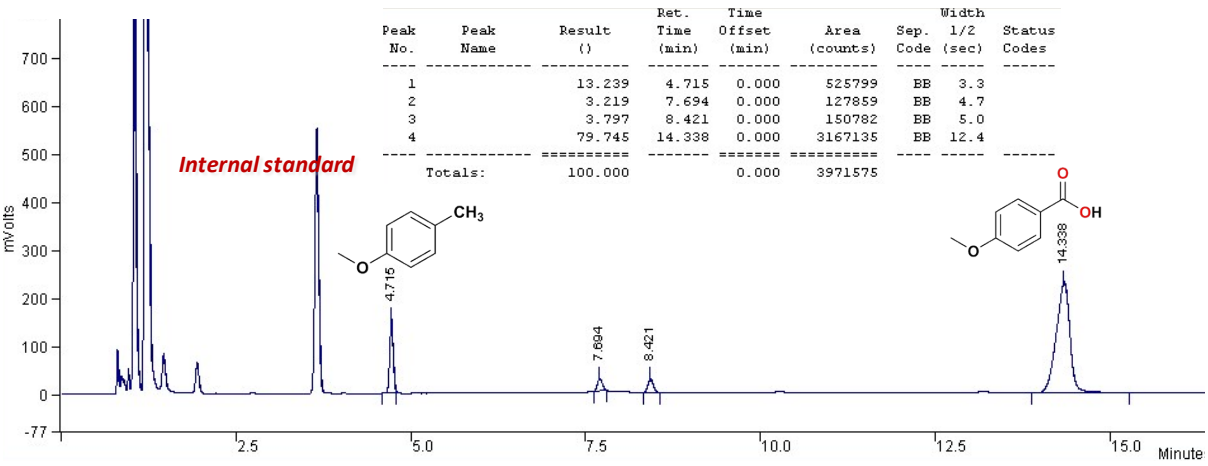
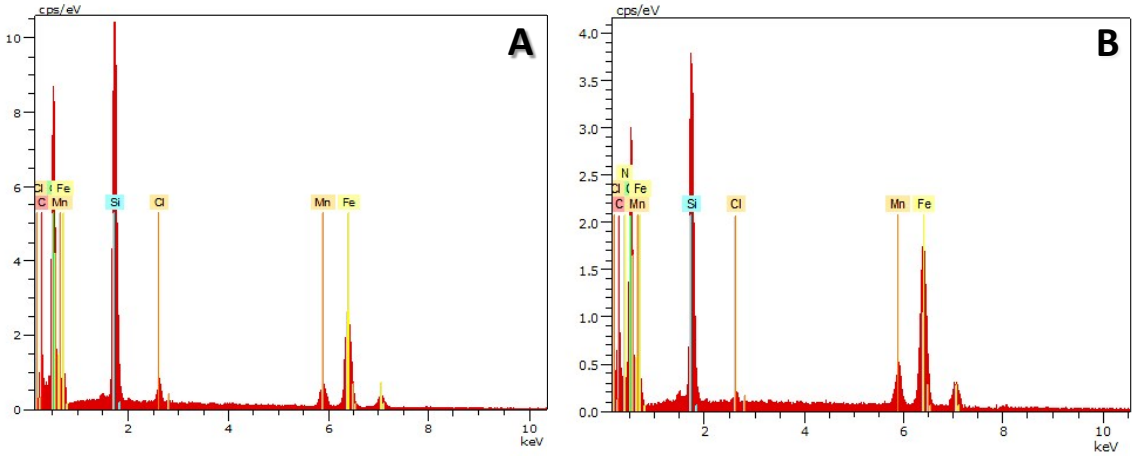


Figure S-39. GC chromatogram for Oxidation of 4-methoxytoluene under optimal condition (Table 2, Entry 9).



El	AN	Series	unn. C [wt.%]	norm. C [wt.%]	Atom. C [at.%]	Error [wt.%]
C	6	K-series	35.01	24.43	39.05	5.1
N	7	K-series	11.75	8.20	11.78	2.6
O	8	K-series	57.43	40.08	48.08	6.9
Si	14	K-series	13.89	9.69	6.62	0.6
Cl	17	K-series	1.40	0.98	0.53	0.1
Mn	25	K-series	3.88	2.70	0.95	0.1
Fe	26	K-series	19.91	13.90	4.78	0.6
Total:			143.27	100.00	100.00	

El	AN	Series	unn. C [wt.%]	norm. C [wt.%]	Atom. C [at.%]	Error [wt.%]
C	6	K-series	32.97	26.16	38.49	5.2
N	7	K-series	11.70	9.28	11.71	2.4
O	8	K-series	41.22	32.70	36.11	5.5
Si	14	K-series	14.18	11.25	7.08	0.6
Cl	17	K-series	0.59	0.47	0.23	0.1
Mn	25	K-series	3.85	3.05	0.98	0.1
Fe	26	K-series	21.53	17.08	5.40	0.6
Total:			126.03	100.00	100.00	

Figure S-40. EDX spectra and elemental composition of the pristine (A) and of recovered catalysts (B).

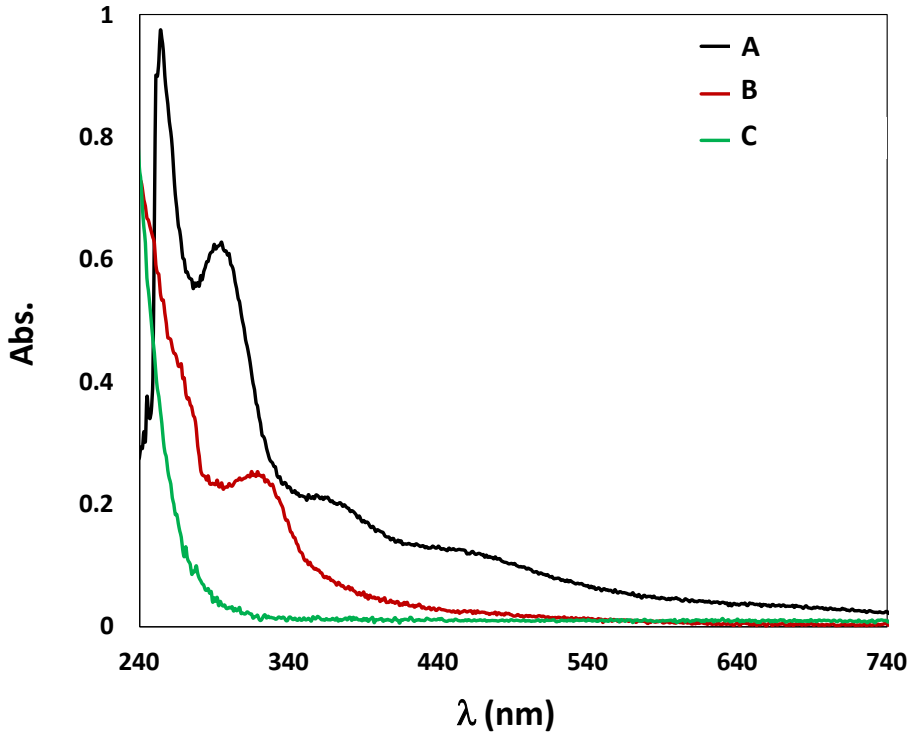


Figure S-41. Electronic absorption spectra of (A) the fresh reaction mixture in the presence of MnL^{GDC} as homogeneous catalyst, (B) an hour after beginning the reaction and (C) $MnCl_2.4H_2O$.

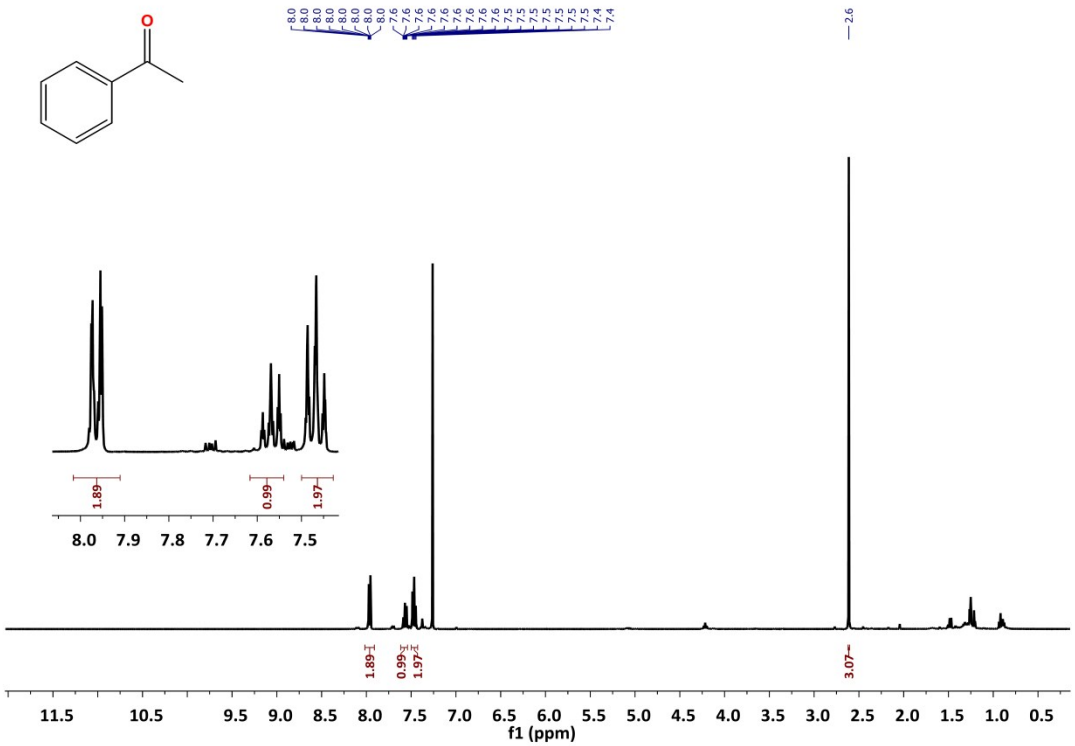


Figure S-42. ^{1}H NMR spectrum ($CDCl_3$) for main product in oxidation reaction of ethylbenzene.

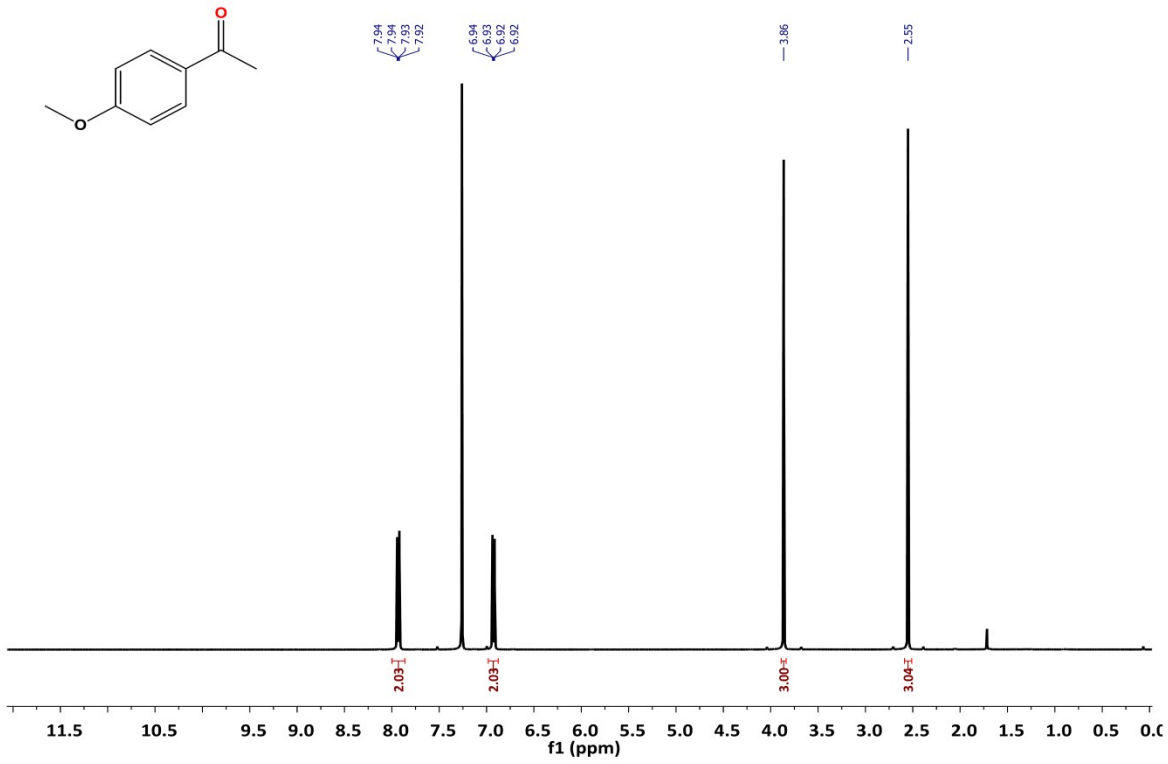


Figure S-43. ^{1}H NMR spectrum ($CDCl_3$) for main product in oxidation reaction of 1-Ethyl-4-methoxybenzene.

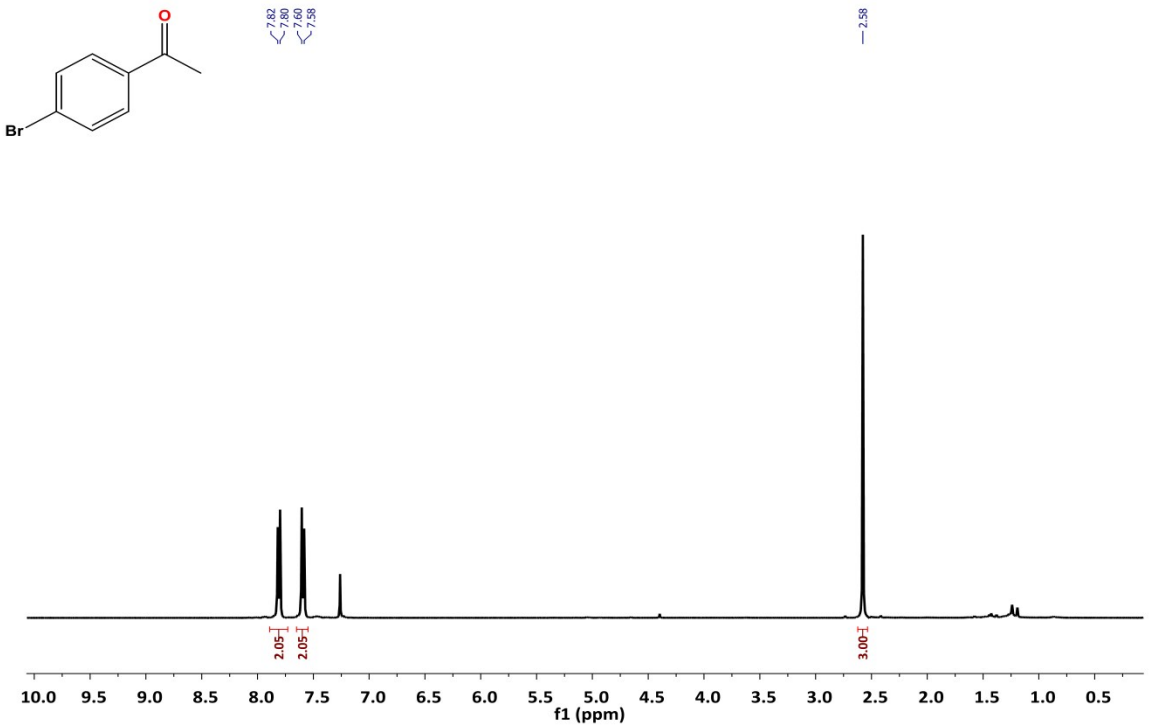


Figure S-44. ^{1}H NMR spectrum ($CDCl_3$) for main product in oxidation reaction of 1-Bromo-4-ethylbenzene.

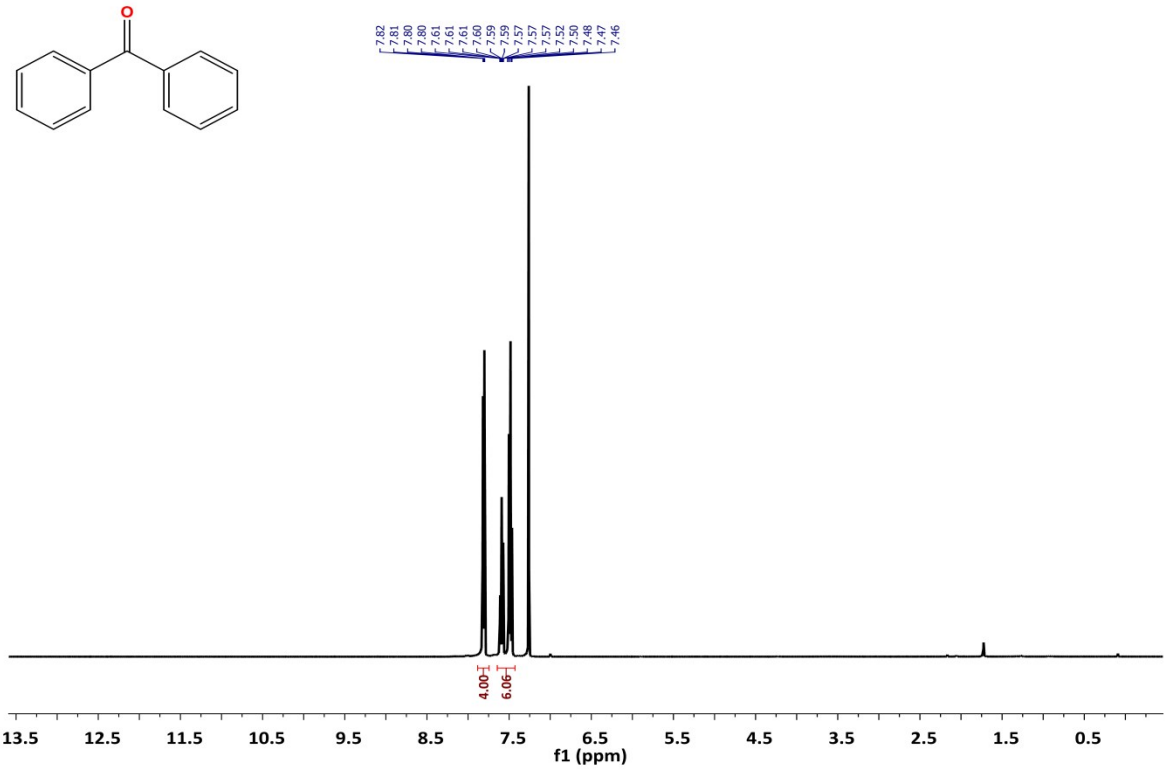


Figure S-45. ^{1}H NMR spectrum ($CDCl_3$) for main product in oxidation reaction of Diphenylmethanol.

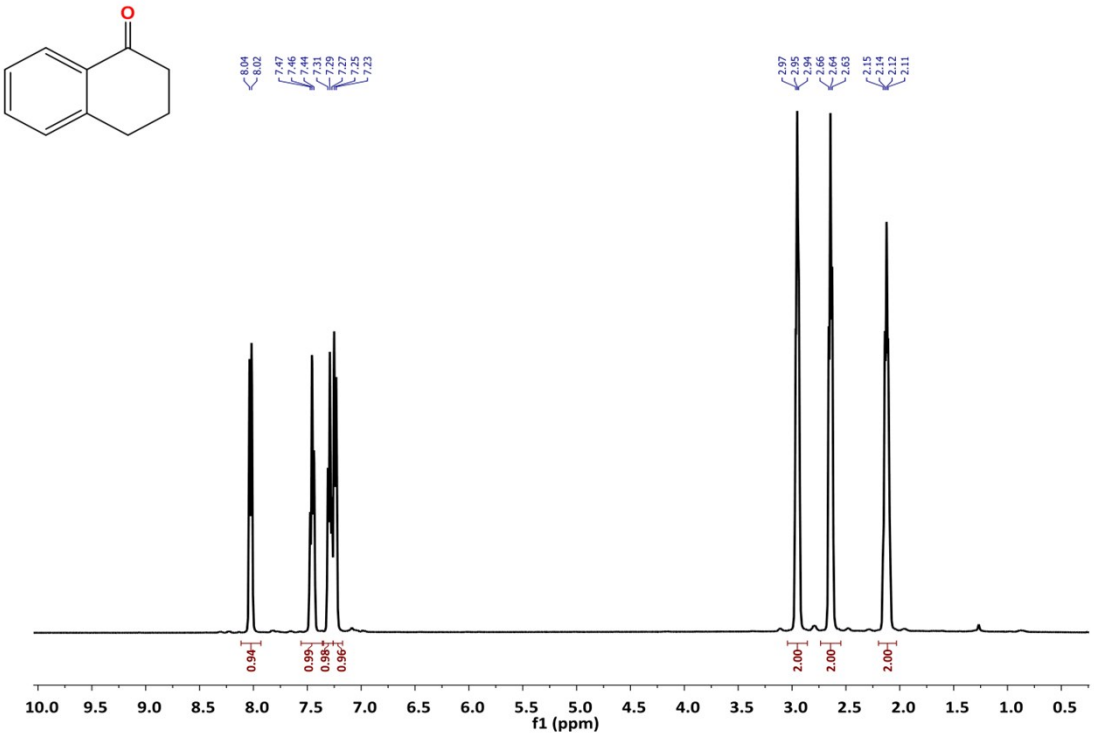


Figure S-46. ^{1}H NMR spectrum ($CDCl_3$) for main product in oxidation reaction of Tetralin.

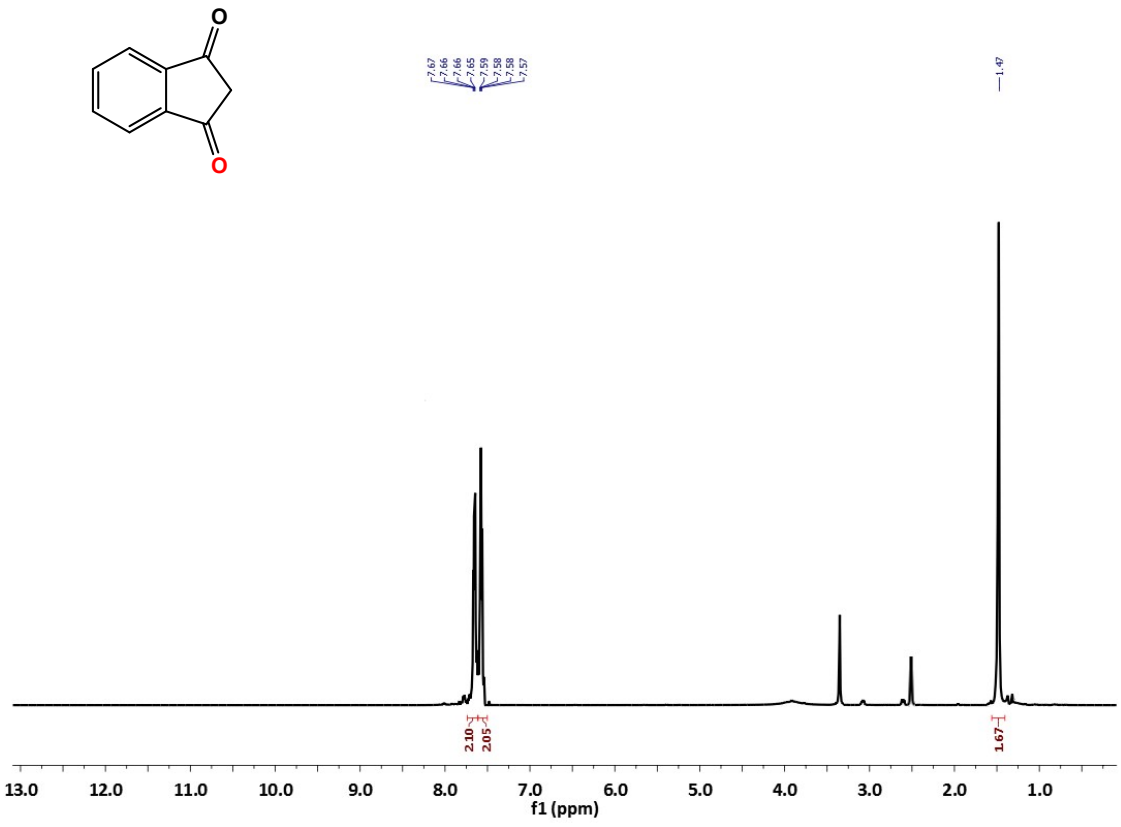


Figure S-47. ^{1}H NMR spectrum (DMSO-d6) for main product in oxidation reaction of 1-Indanone.

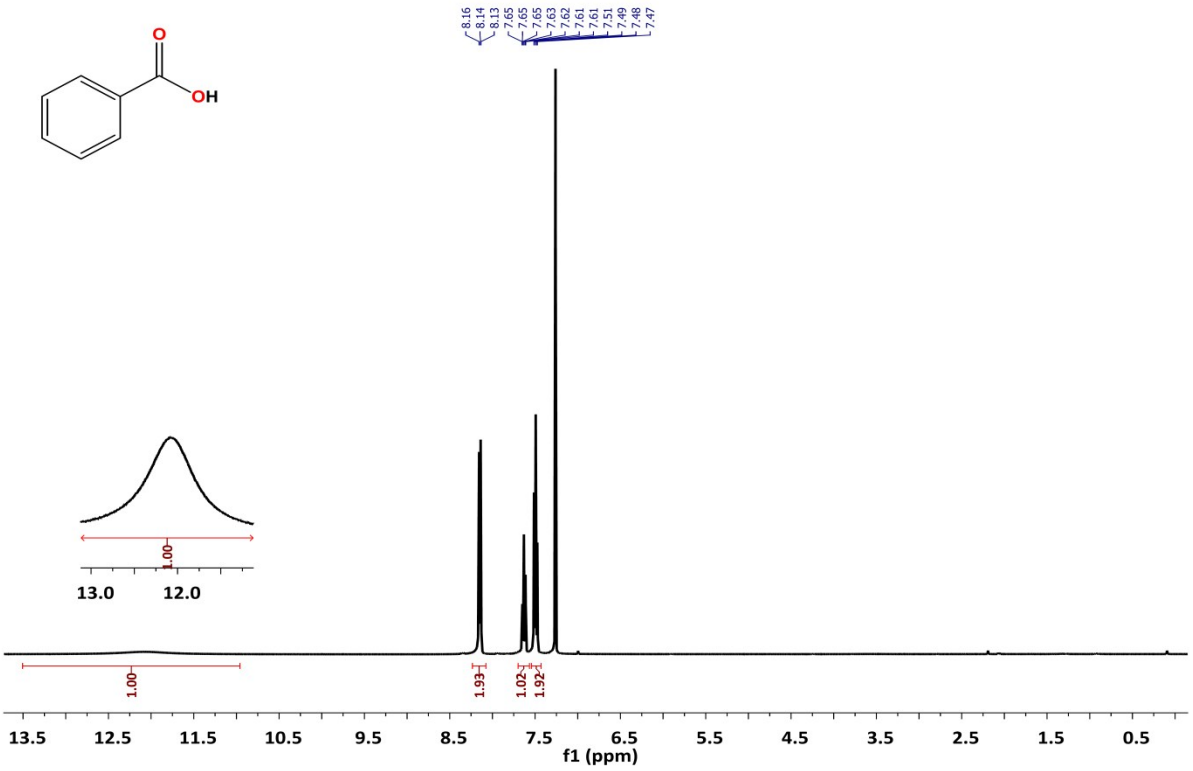


Figure S-48. ^{1}H NMR spectrum ($CDCl_3$) for main product in oxidation reaction of Toluene.

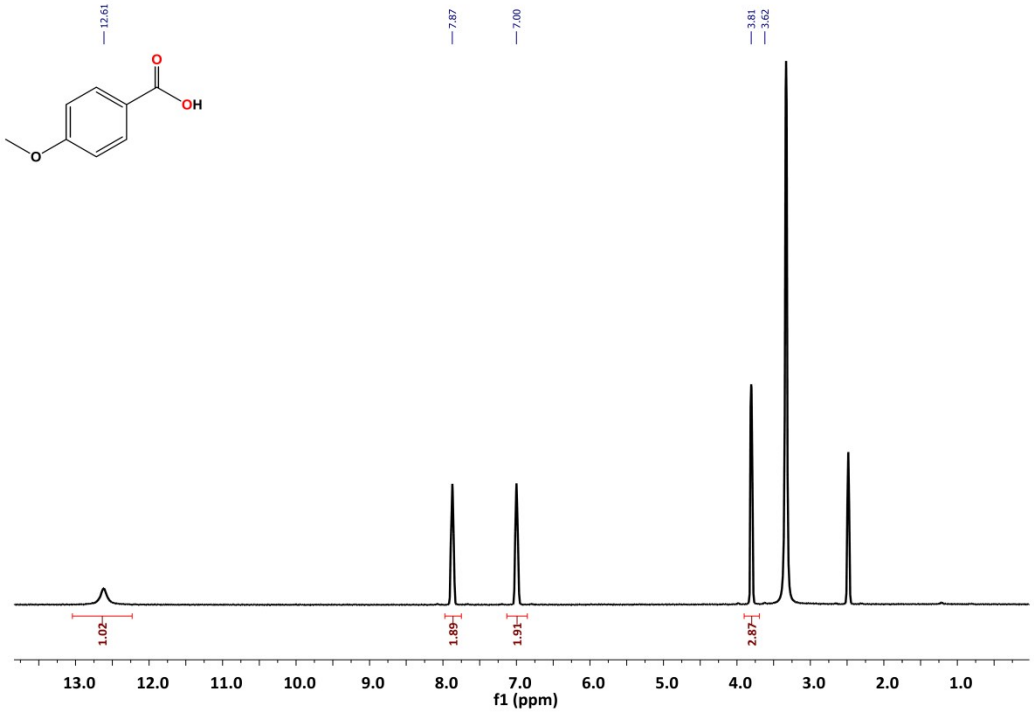


Figure S-49. ^{1}H NMR spectrum (DMSO-d6) for main product in oxidation reaction of 4-methoxytoluene.