

Supporting Information

Keggin-Based Hybrid Solid Emerged as a Promising Candidate for CO₂-Mediated Photocatalytic N-Formylation of Amines

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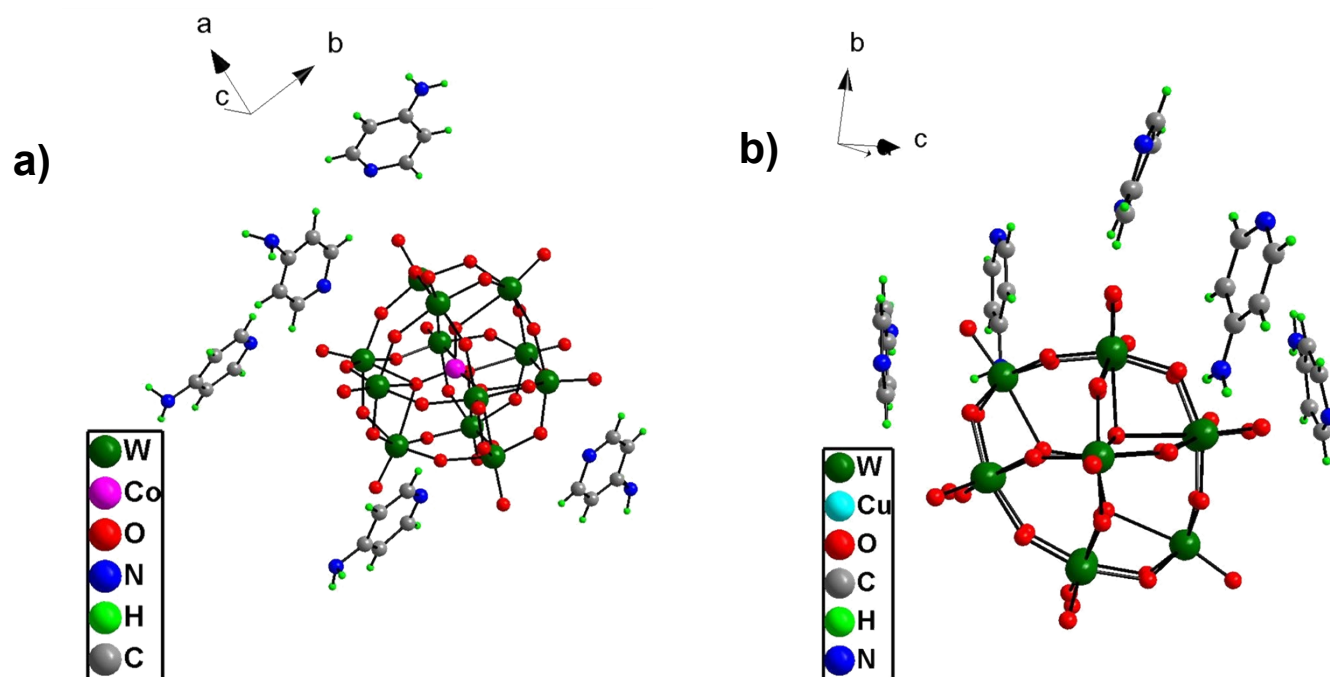
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Table S1. Crystal and structure refinement data for PS-96 and PS-97.

Parameter	(C ₅ H ₇ N ₂) ₅ [CoW ₁₂ O ₄₀] (PS-96)	(C ₅ H ₇ N ₂) ₅ [CuW ₁₂ O ₄₀] (PS-97)
Formula	C ₂₅ H ₃₅ CoW ₁₂ N ₁₀ O ₄₀	C ₂₅ H ₃₅ CuW ₁₂ N ₁₀ O ₄₀
Formula weight, g	3375.60	3380.33
T (K)	150.00(10)	295
Wavelength (Å)	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic
Space Group	C 2/c	C 2/c
a (Å)	14.3244(4)	14.3946(4)
b (Å)	21.9593(4)	22.0069(6)
c (Å)	36.1645(8)	36.3704(10)
α (°)	90	90
β (°)	100.238(2)	99.9820(10)
γ (°)	90	90
V (Å ³)	11194.6(5)	11347.0(5)
Z	8	8
d _{calc} (gcm ⁻³)	4.006	3.957
μ _{MoKα} , (cm ⁻¹)	24.941	24.689
R1(I>2σI)	0.0981	0.0491
WR2(all)	0.2718	0.1398
CCDC/CSD No.	2258691	2271034



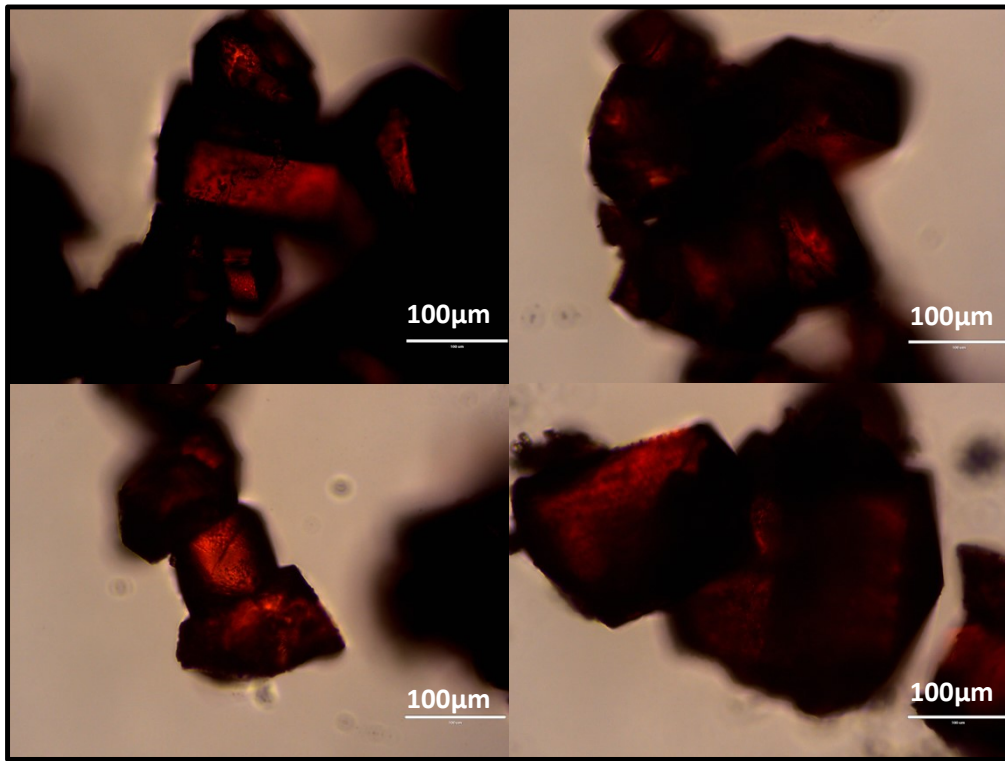


Figure S2. Optical microscopic images of PS-96.

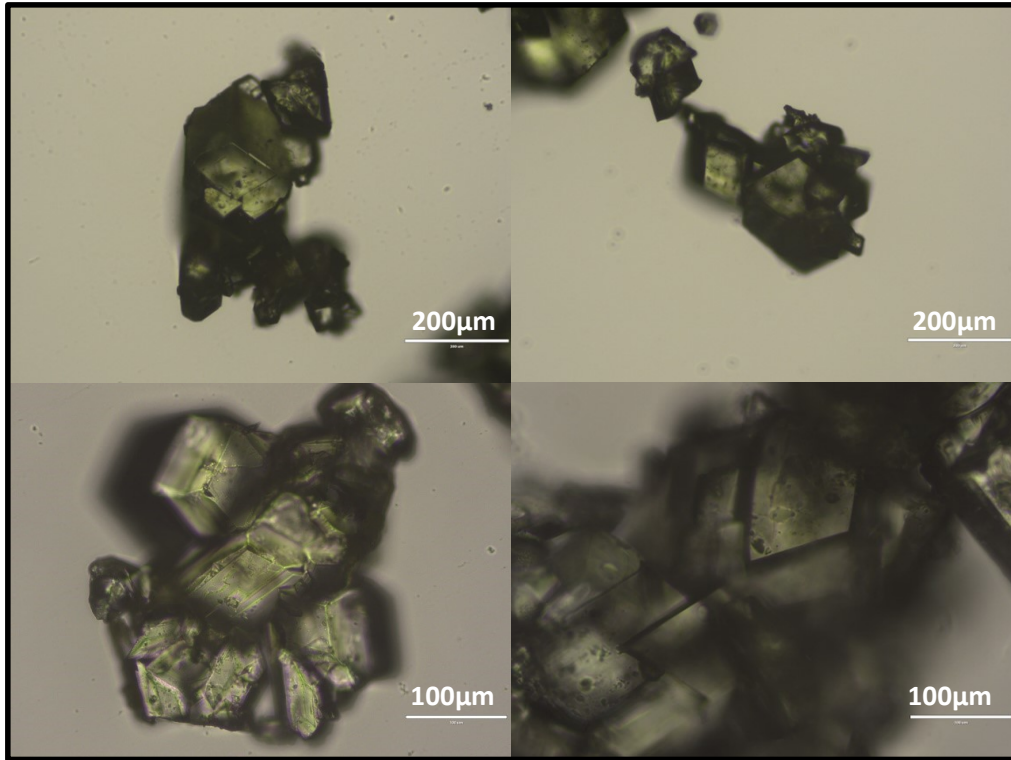


Figure S3. Optical microscopic images of PS-97.

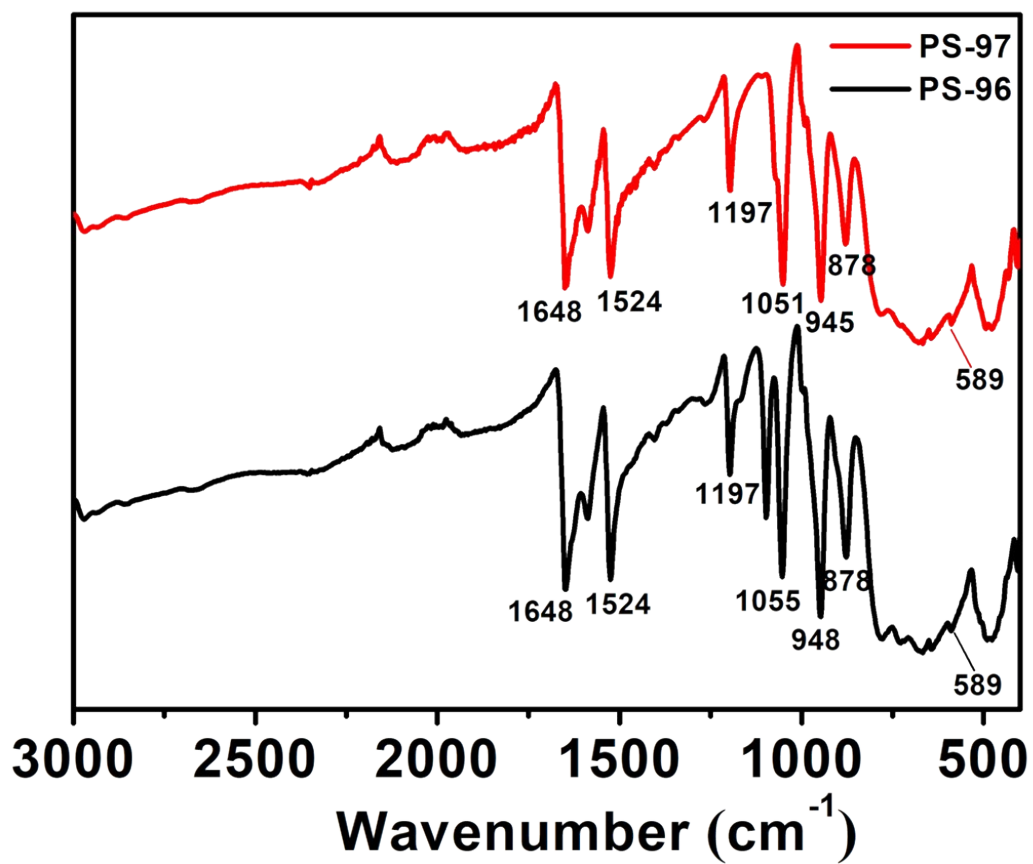


Figure S4. FT-IR spectra of PS-96 and PS-97.

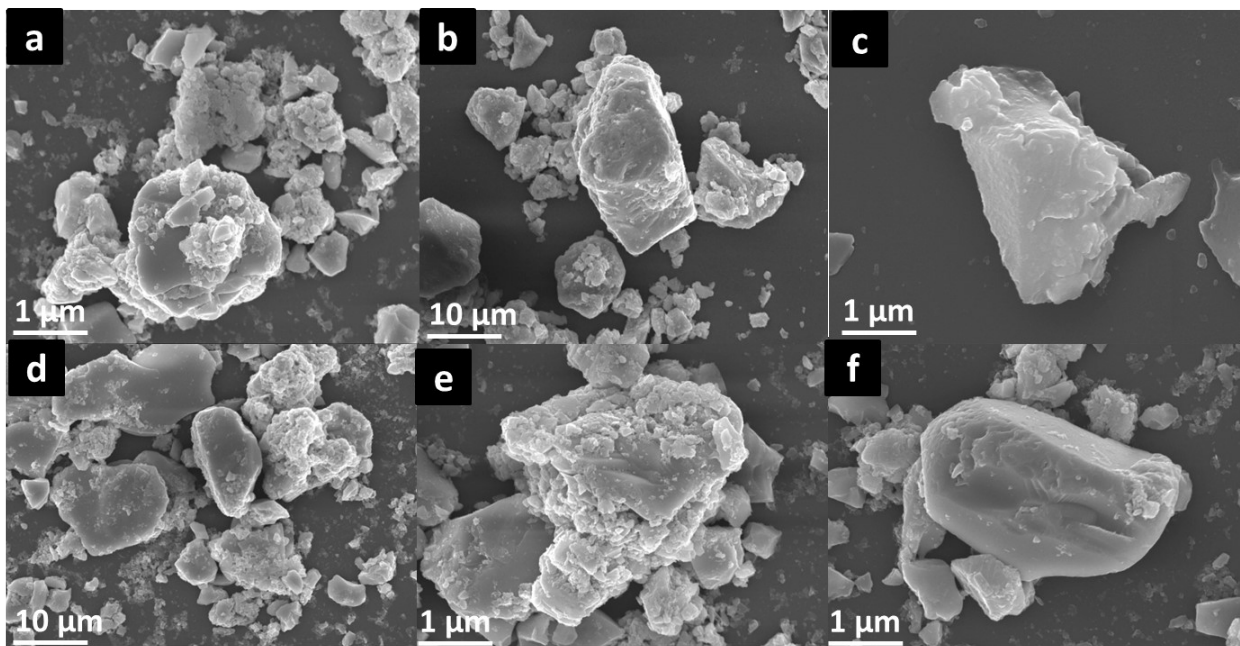


Figure S5. FESEM images of PS-96 (a-c) and PS-97 (d-f).

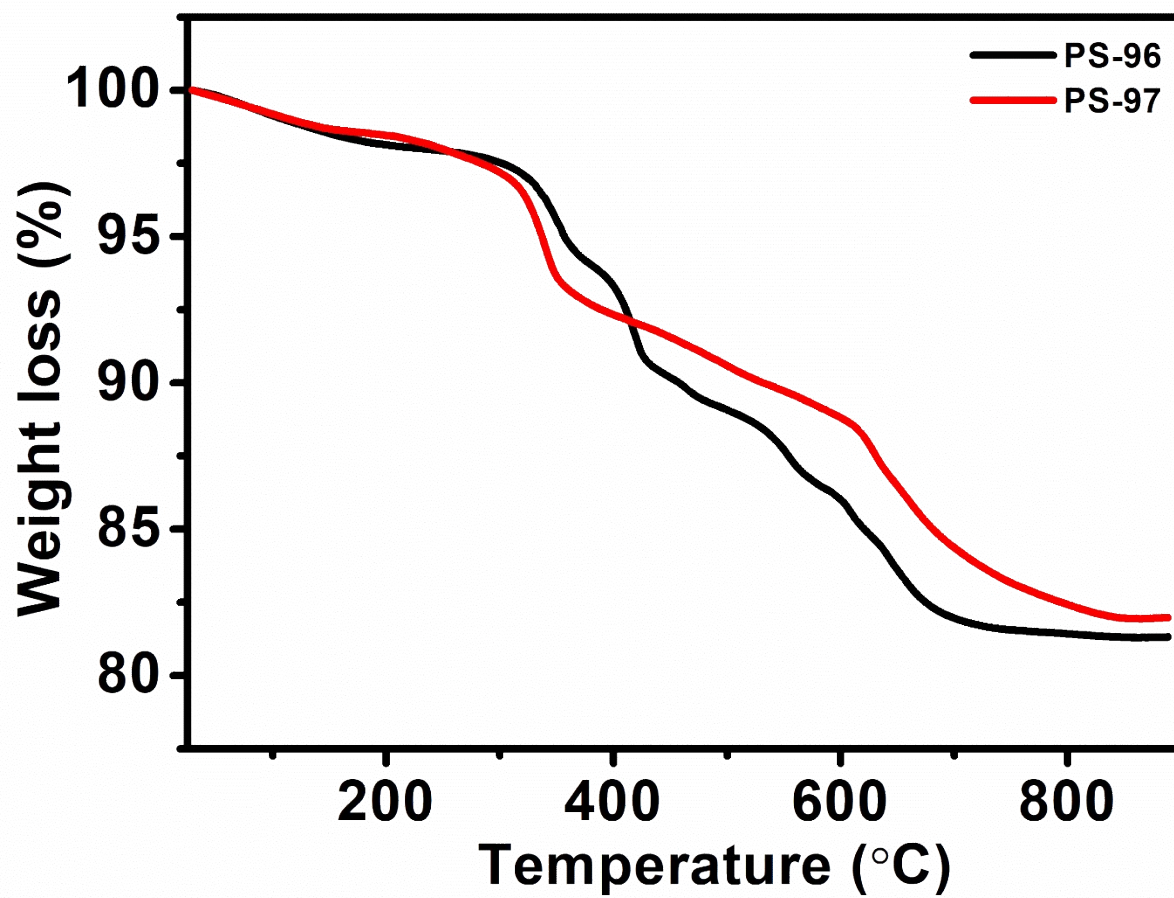


Figure S6. TGA curves of PS-96 and PS-97.

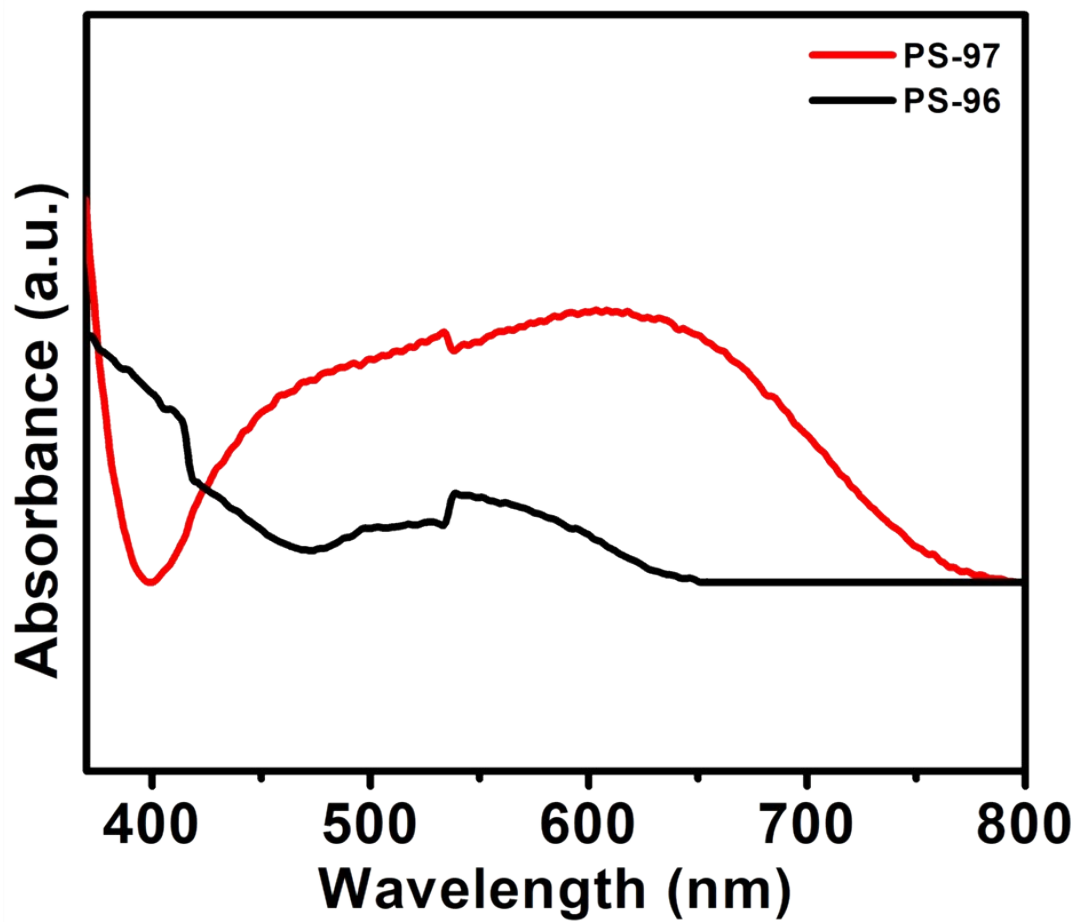


Figure S7. UV-DRS spectra of PS-96 and PS-97.

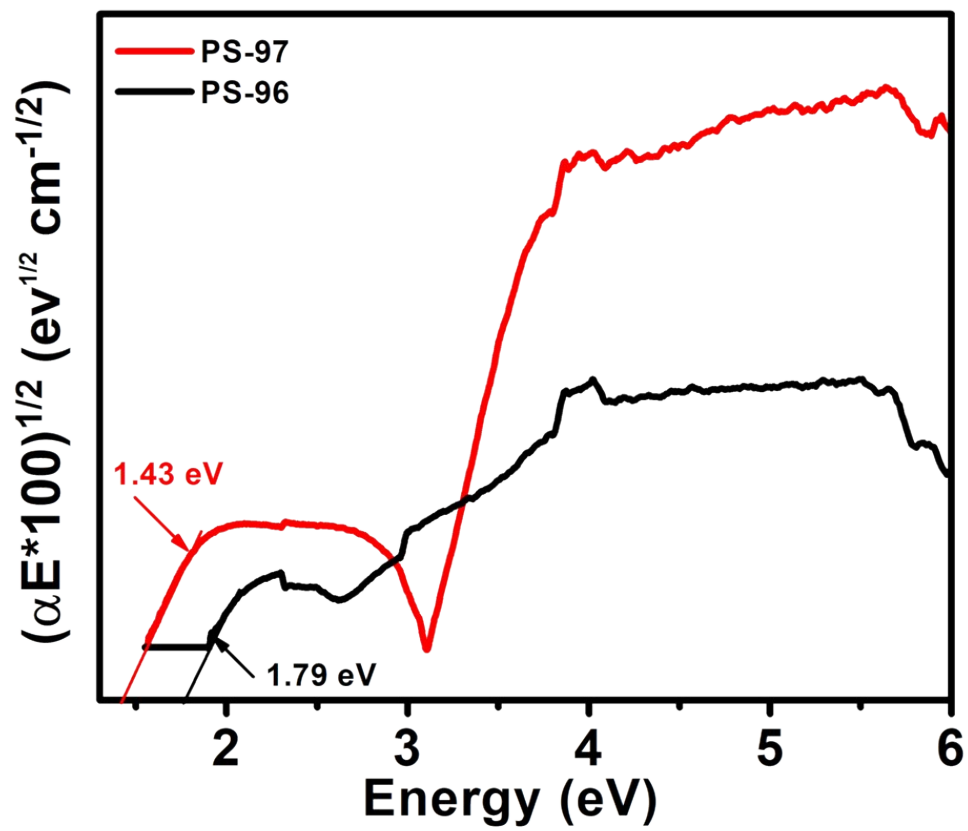


Figure S8. Tauc plots of PS-96 and PS-97.

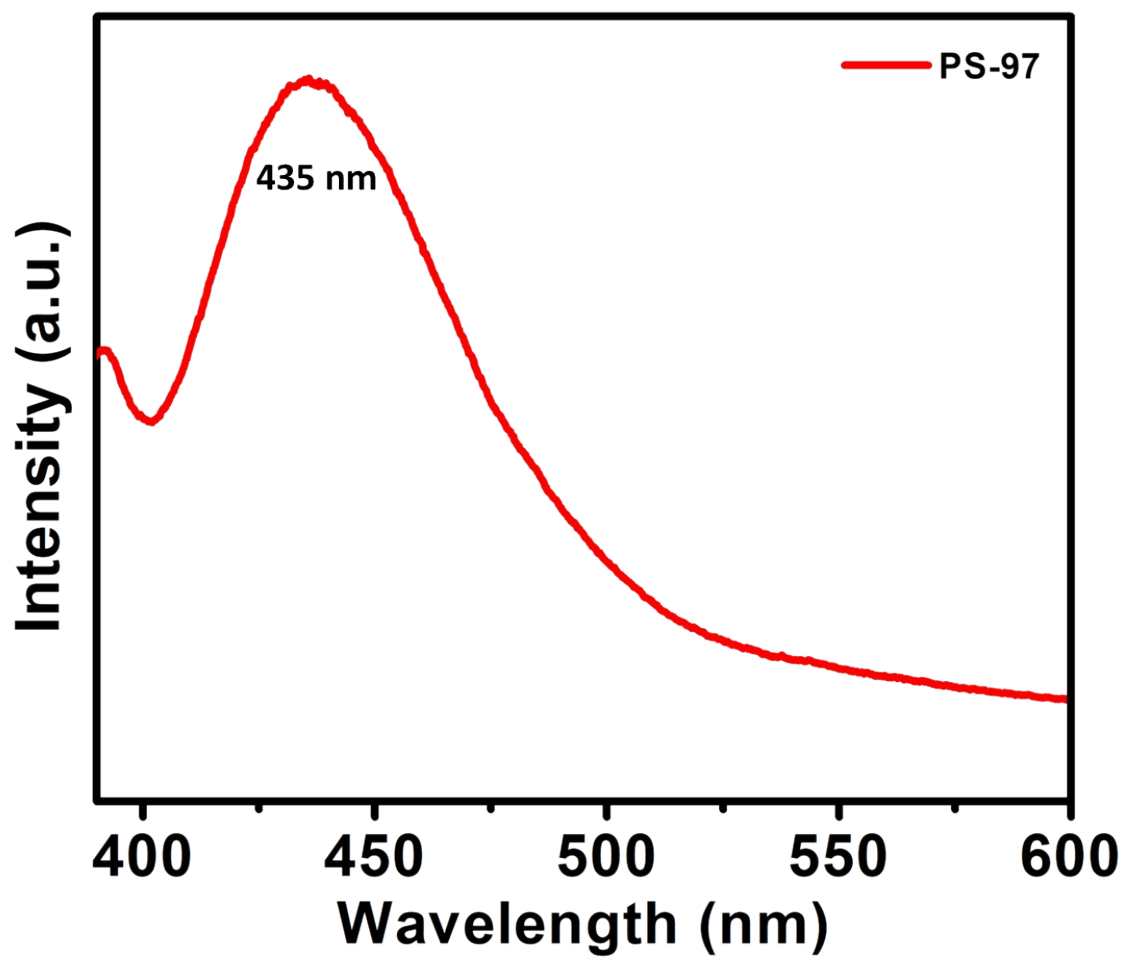


Figure S9. PL spectrum of PS-97.

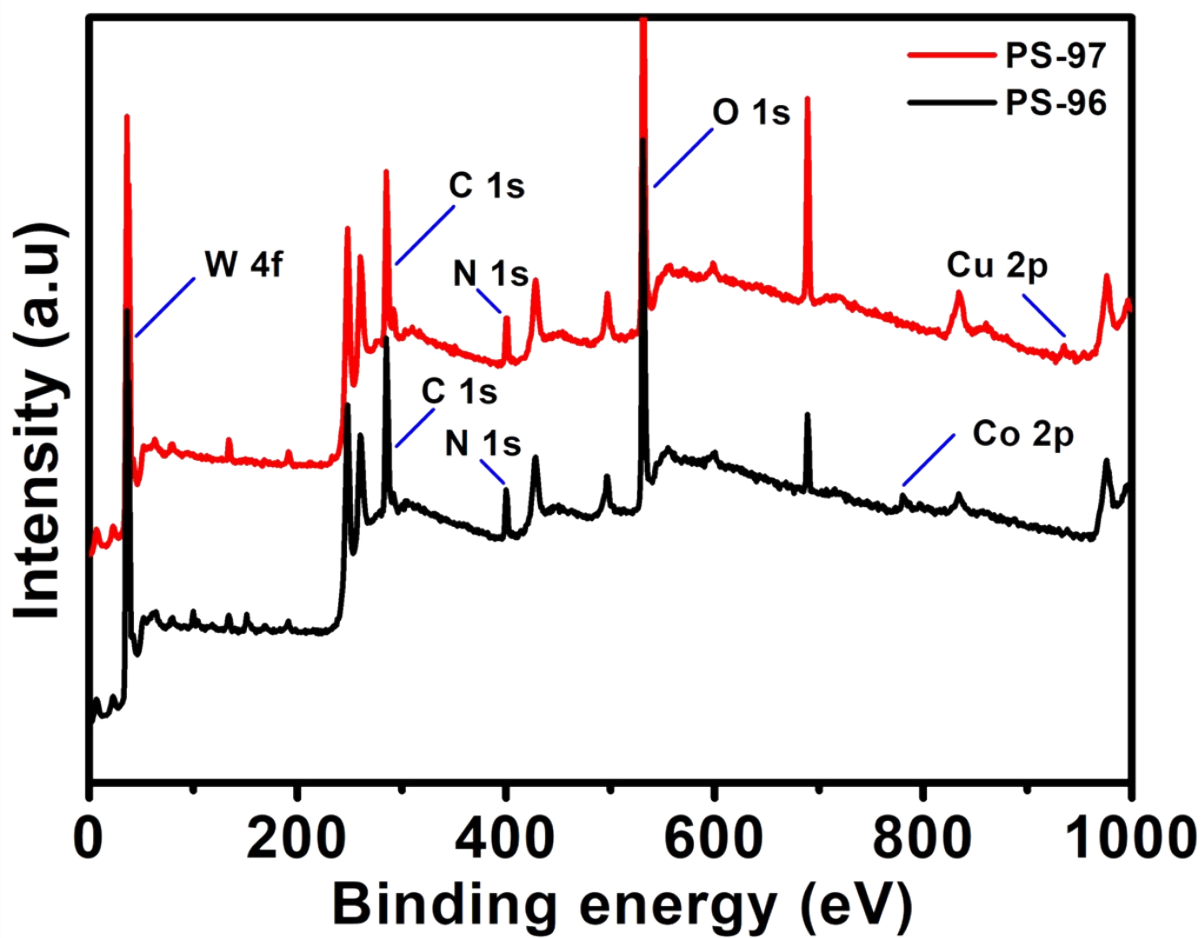


Figure S10. XPS survey spectra of PS-96 and PS-97.

Table S2: The results of the Screening experiments^a

S. No.	Photocatalyst	Irradiation	Solvent	Reducing agent	Reaction Time (h)	Conv ^b (%)	Yield ^{b,c} (%)
1.	Co-Keggin (C ₅ H ₇ N ₂) ₅ [CoW ₁₂ O ₄₀] (PS-96)	yes	DMF	Phenyl silane	22	19	-
2.	Cu-Keggin (C ₅ H ₇ N ₂) ₅ [CuW ₁₂ O ₄₀] (PS-97)	yes	DMF	Phenyl silane	22	81	96
3.	Cu-Keggin	-	DMF	Phenyl silane	22	-	-
4.	-	yes	DMF	Phenyl silane	22	-	-
5.	Cu-Keggin	yes	DMF	Phenyl silane	12	32	67
6.	Cu-Keggin	yes	DMF	Phenyl silane	20	53	78
7.	Cu-Keggin	yes	DMF	Phenyl silane	24	82	96
8.	Cu-Keggin	yes	DMA	Phenyl silane	22	66	74
9.	Cu-Keggin	yes	ACN	Phenyl silane	22	54	76
10.	Cu-Keggin	yes	DMSO	Phenyl silane	22	52	65
11.	Cu-Keggin	yes	CCl ₄	Phenyl silane	22	25	-
12.	Cu-Keggin	yes	Benzene	Phenyl silane	22	-	-
13.	Cu-Keggin	yes	Toluene	Phenyl silane	22	-	-
14 ^d .	Cu-Keggin	yes	DMF	Phenyl silane	22	-	-
15.	Cu-Keggin	yes	DMF	-	22	Trace	Trace
16.	Cu-Keggin	yes	DMF	Dimethyl silane	22	42	68
17.	Cu-Keggin	yes	DMF	Diphenyl silane	22	28	44
18.	Cu-Keggin	yes	DMF	NaBH ₄	22	-	-

Reaction conditions^a: aniline (1mmol), PhSiH₃ (2mmol), Photocatalyst (50 mg), 1 atm CO₂ pressure, 25 °C temperature, and 20W white LED light irradiation, ^{b,c}conversion and product yield was demonstrated by GCMS and identity of the product was confirmed by NMR, ^dreaction without CO₂.

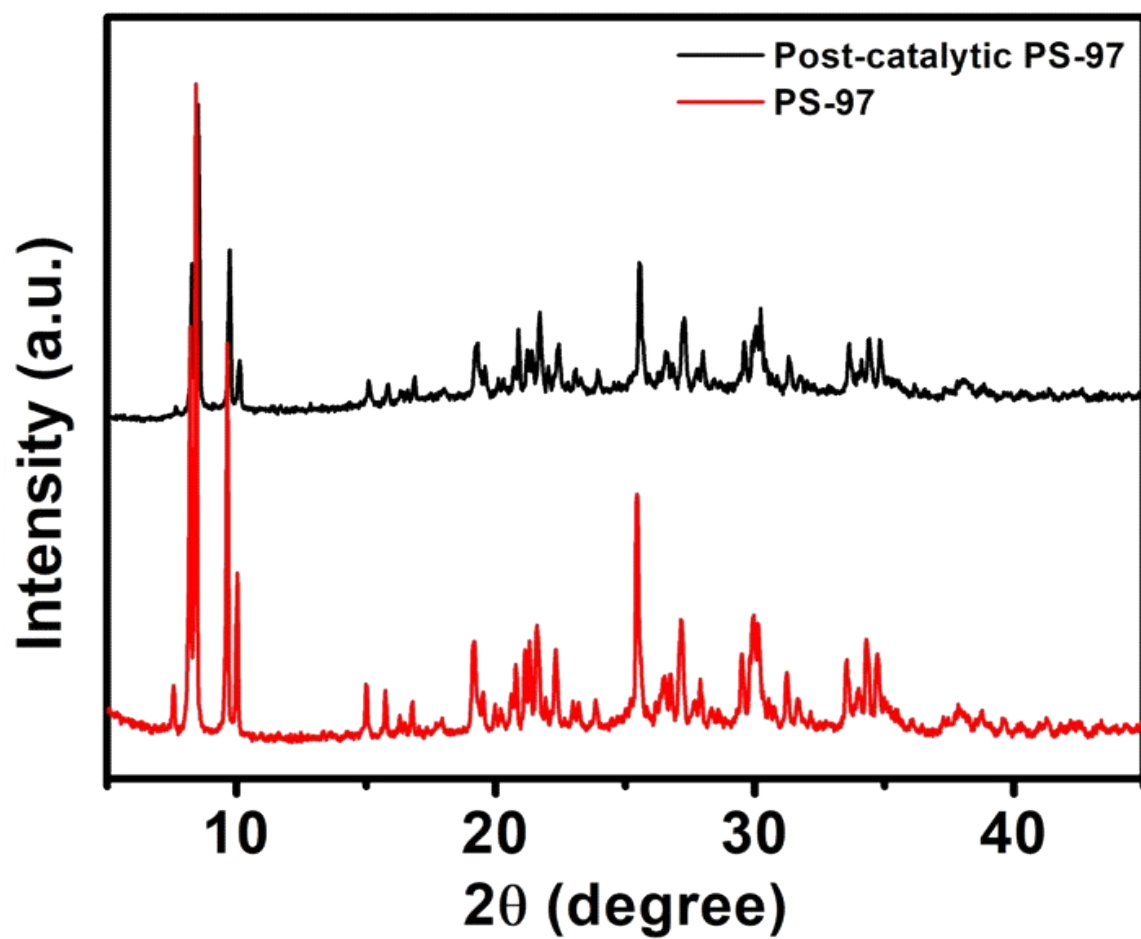


Figure S11. Comparison of pre and post-catalytic PXRD patterns of PS-97.

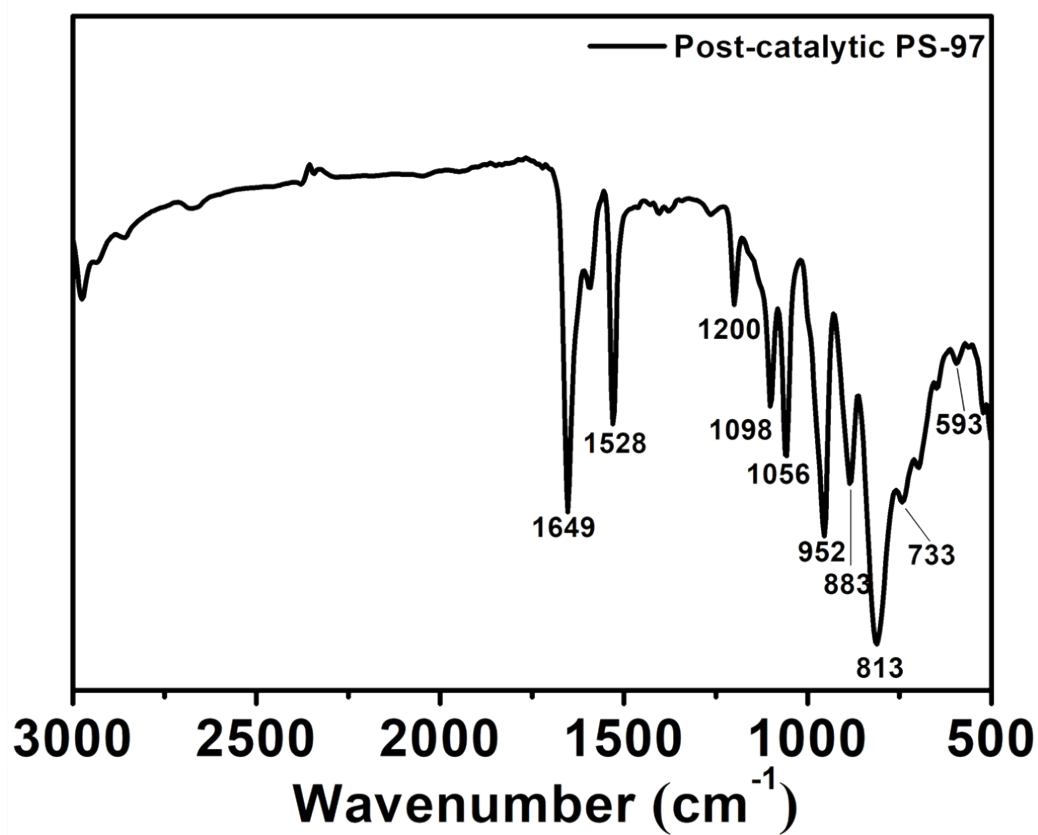


Figure S12. FT-IR spectrum of post-catalytic PS-97.

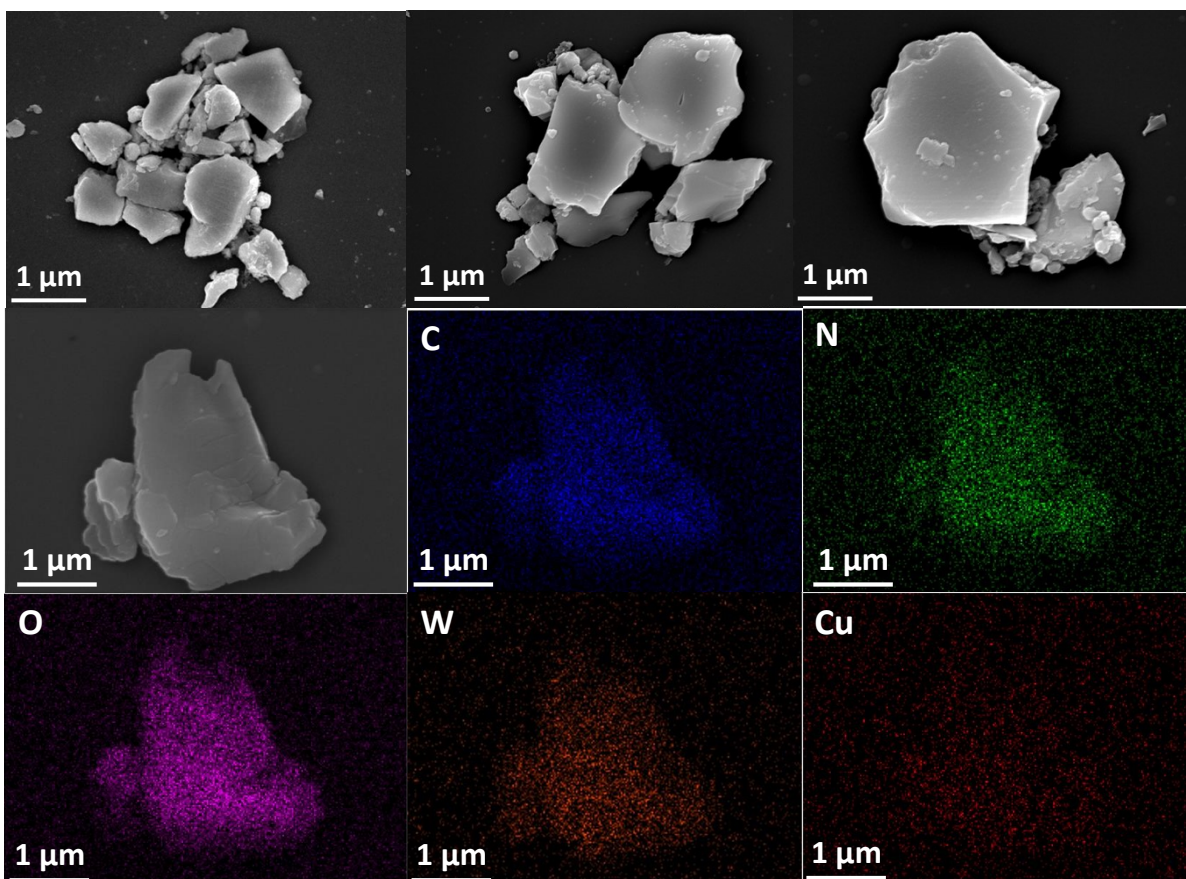


Figure S13. Post-catalytic FESEM images and mapping of PS-97.

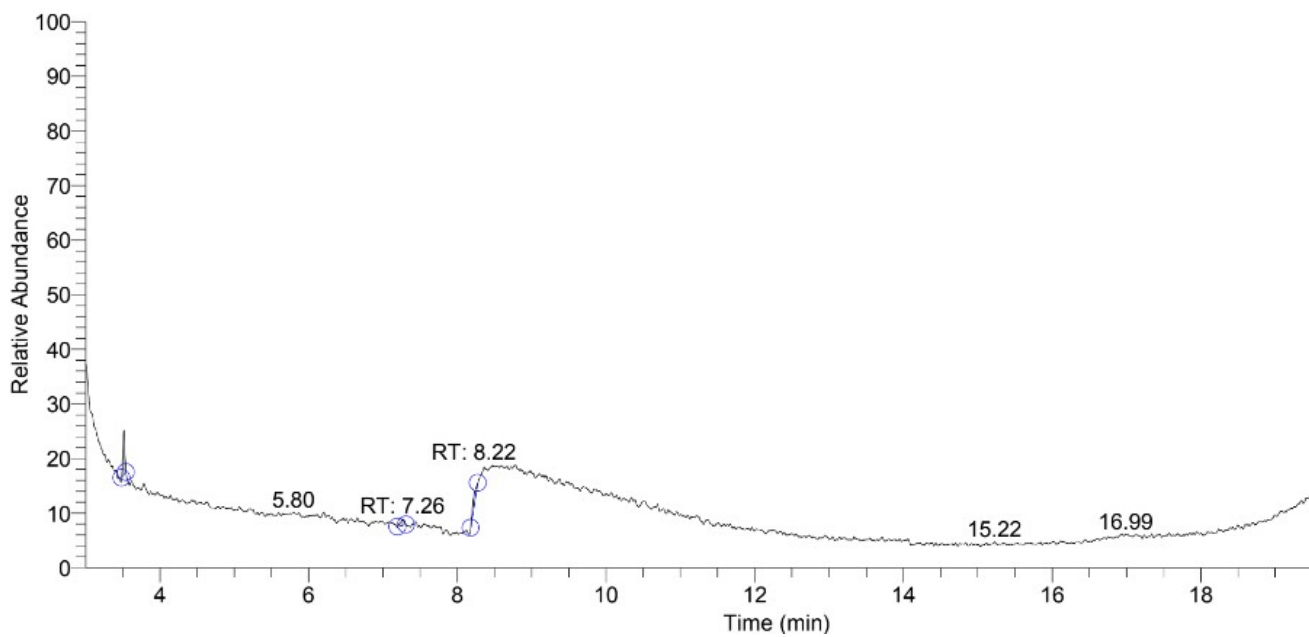


Figure S14. GC spectrum of N-phenylformamide.

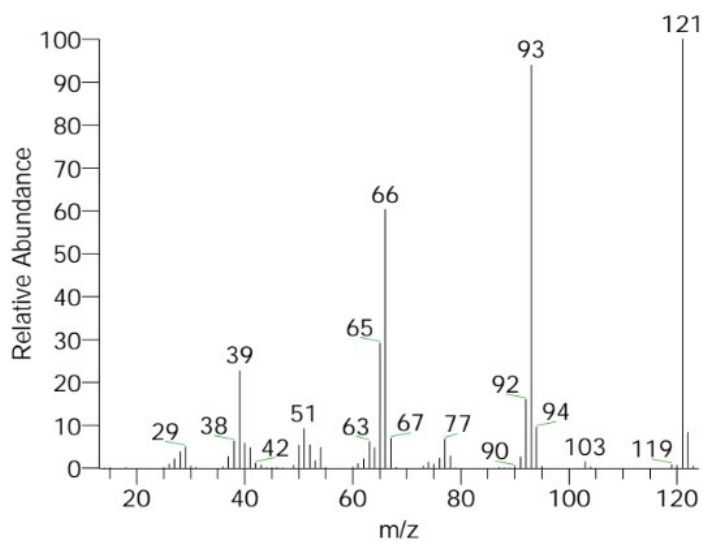


Figure S15. Mass spectrum of N-phenyl formamide.

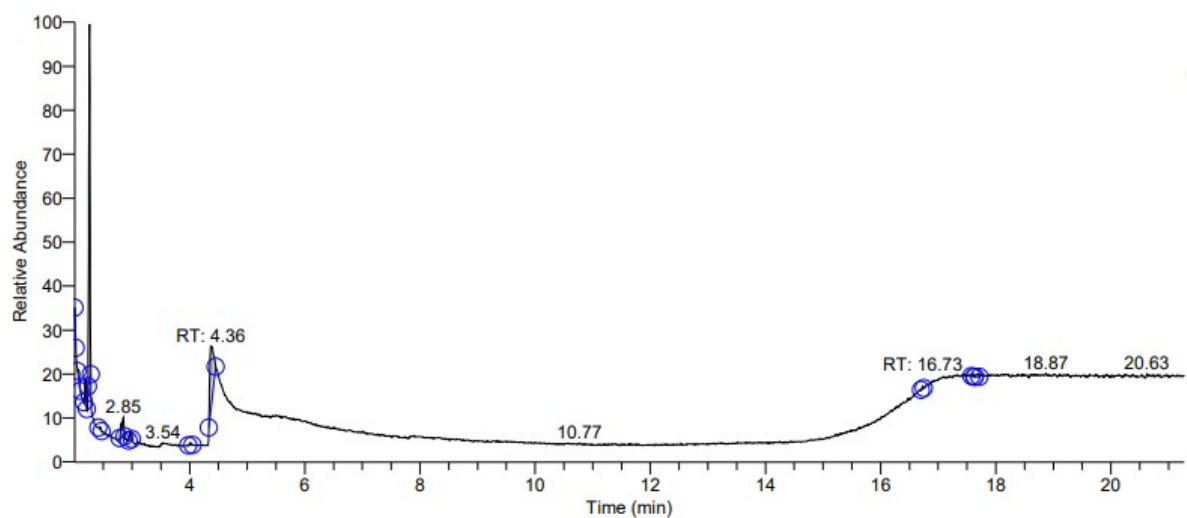


Figure S16. GC spectrum of N-formyl morpholine.

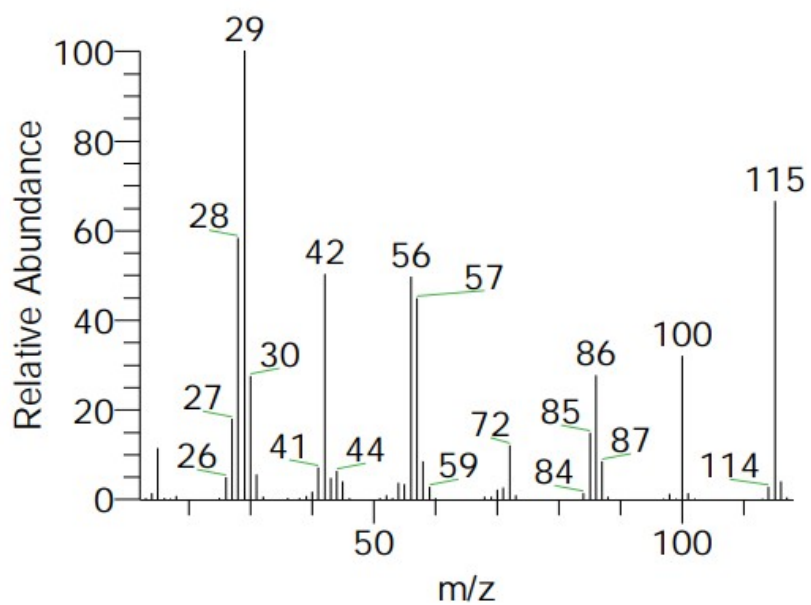


Figure S17. Mass spectrum of N-formyl morpholine.

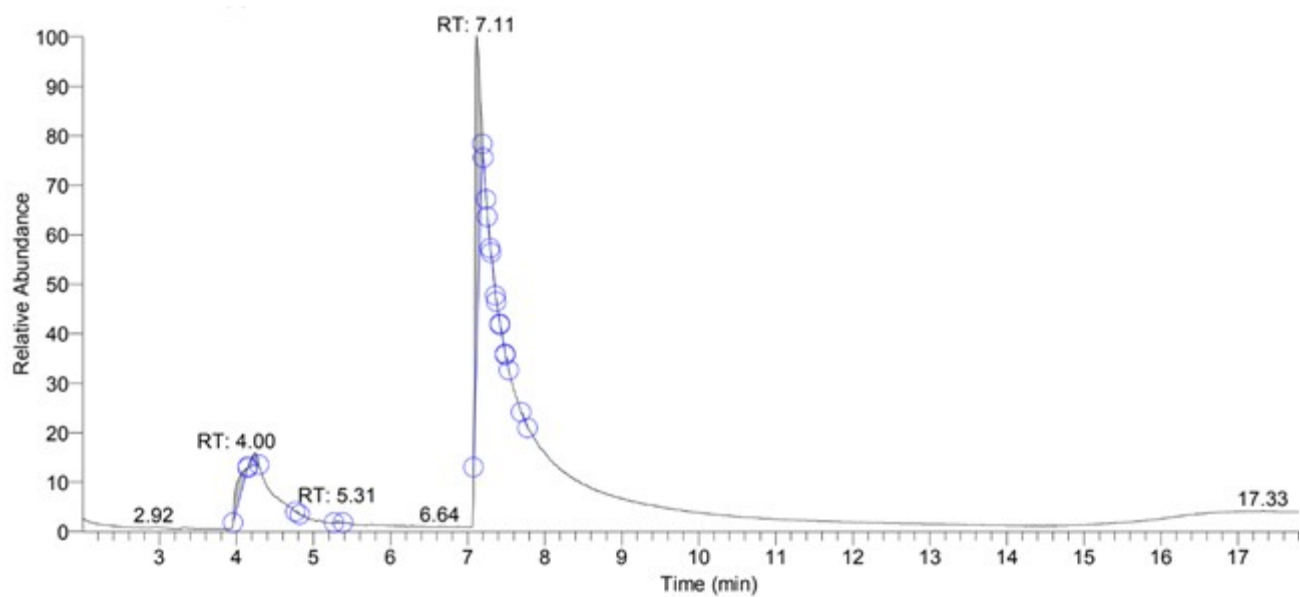


Figure S18. GC spectrum of N-p-tolylformamide.

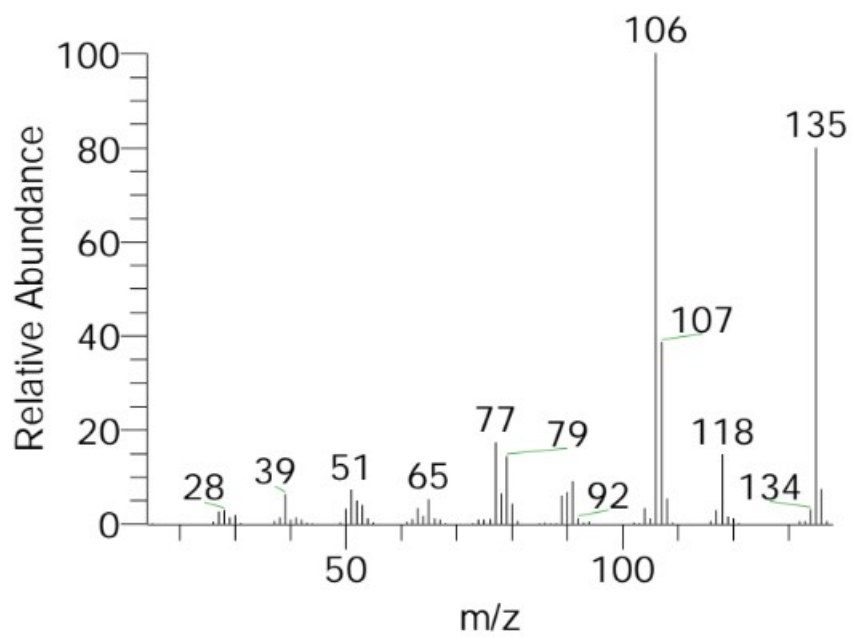


Figure S19. Mass spectra of N-p-tolylformamide.

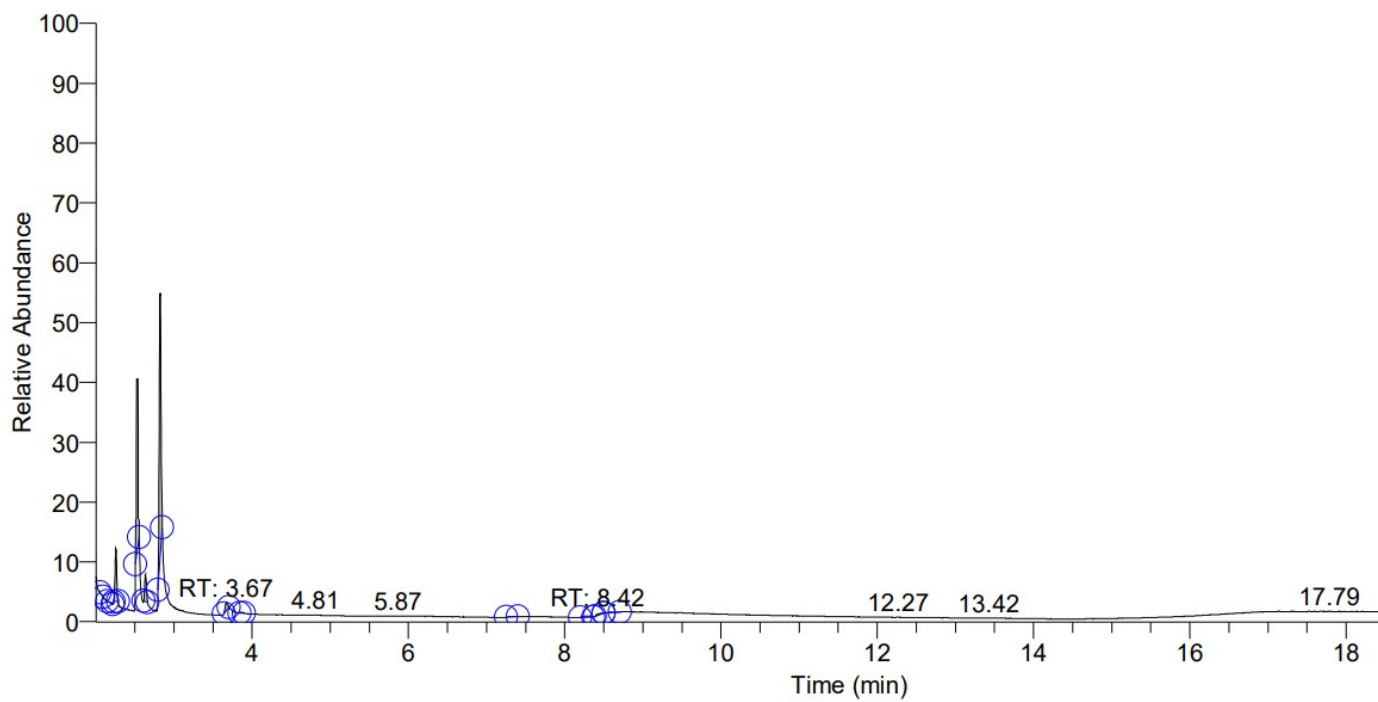


Figure S20. GC spectra of N-methyl-N-phenylformamide

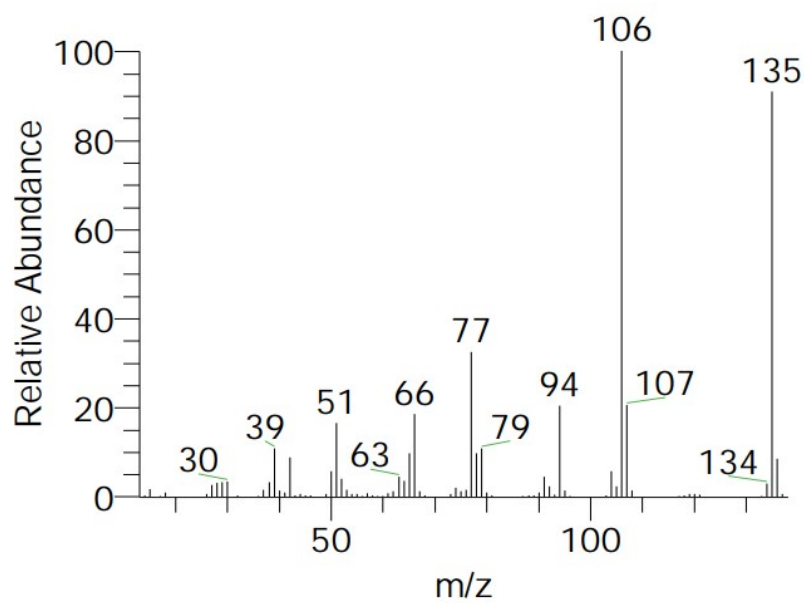


Figure S21. Mass Spectrum of N-methyl-N-phenylformamide

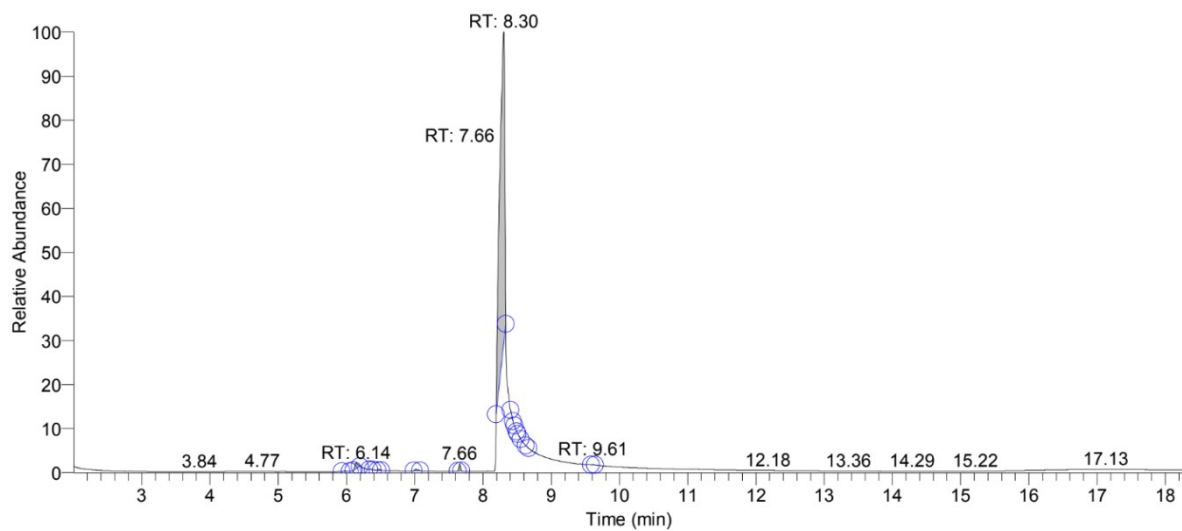


Figure S22. GC spectrum of N-(4-methoxyphenyl)formamide.

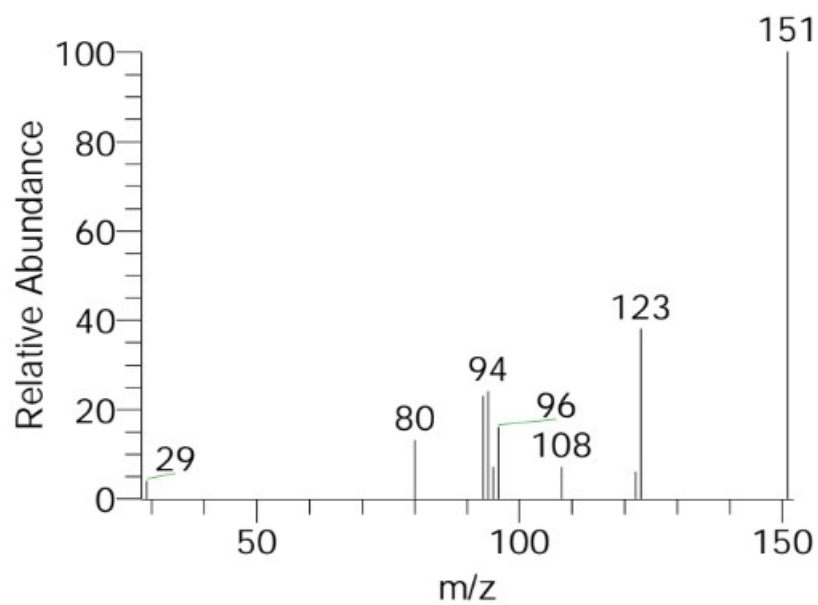


Figure S23. Mass Spectrum of N-(4-methoxyphenyl)formamide.

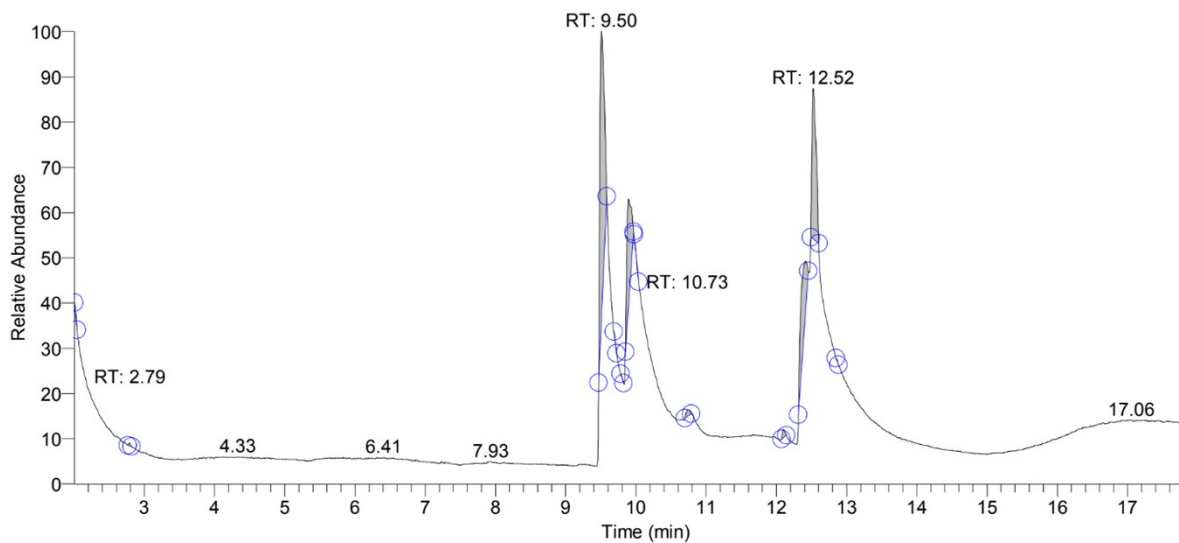


Figure S24. GC spectrum of P-phenoxyformanilide.

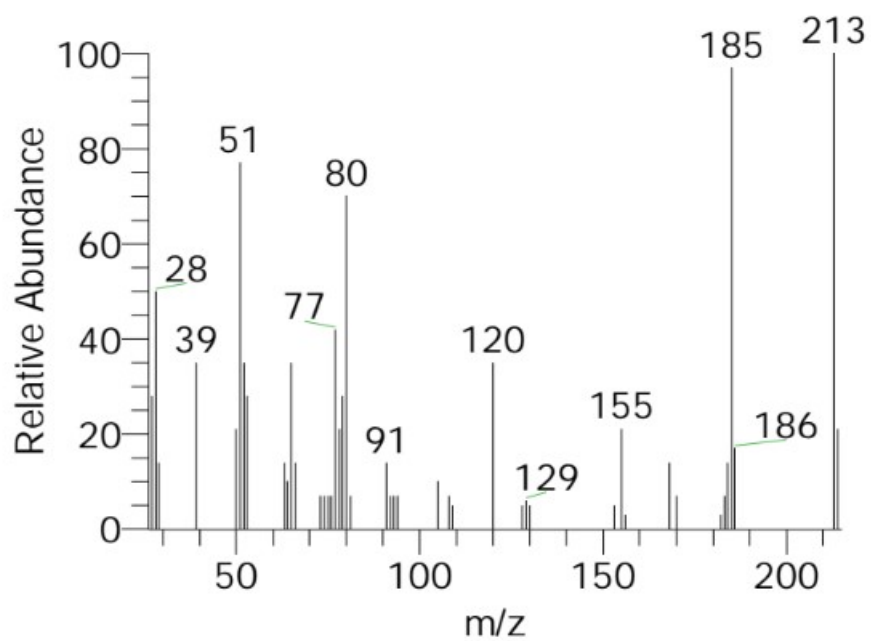


Figure S25. Mass spectrum of P-phenoxyformanilide.

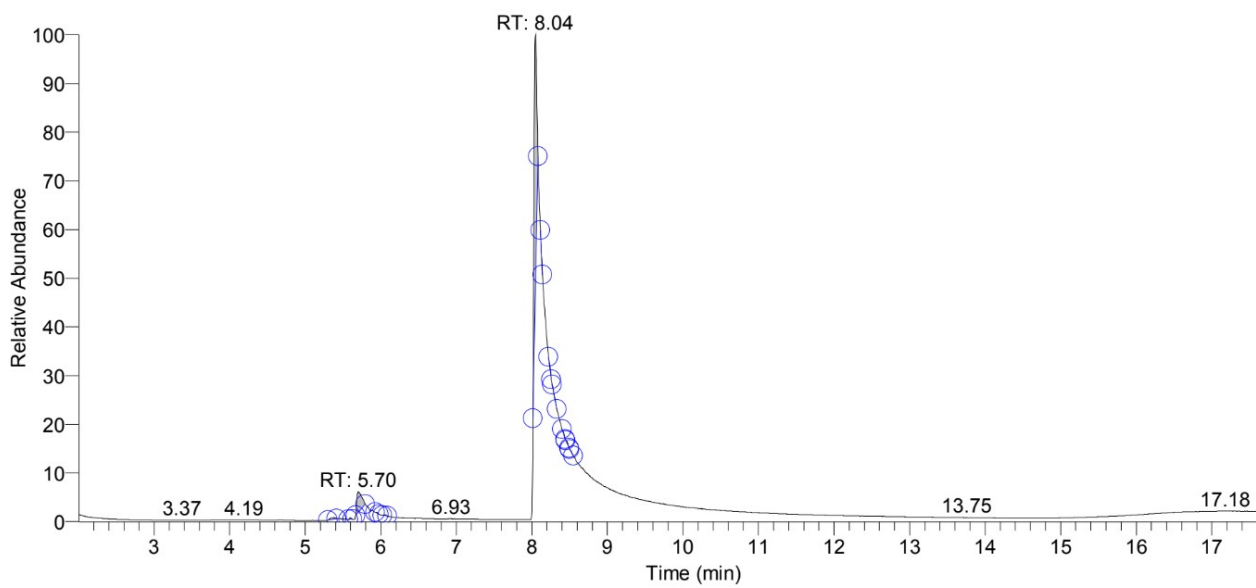


Figure S26. GC spectra of N-(4-chlorophenyl)formamide.

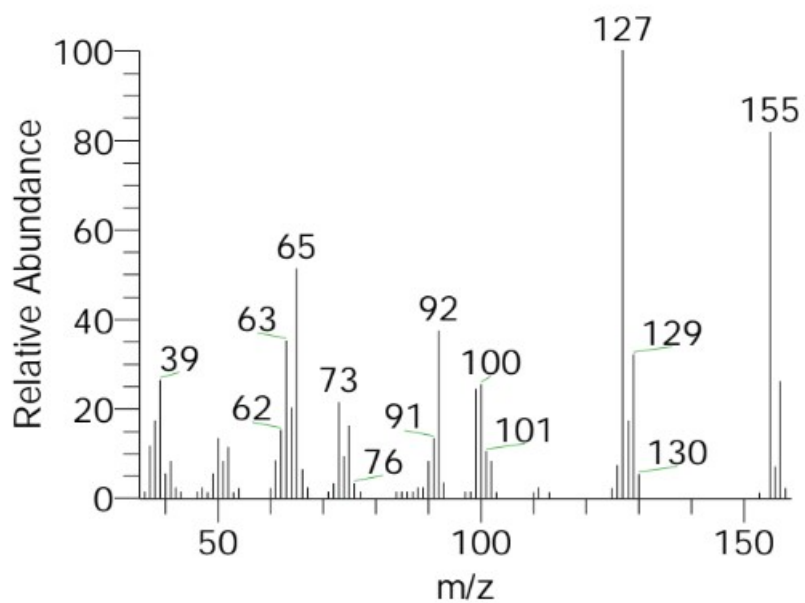


Figure S27. Mass spectra of N-(4-chlorophenyl)formamide.

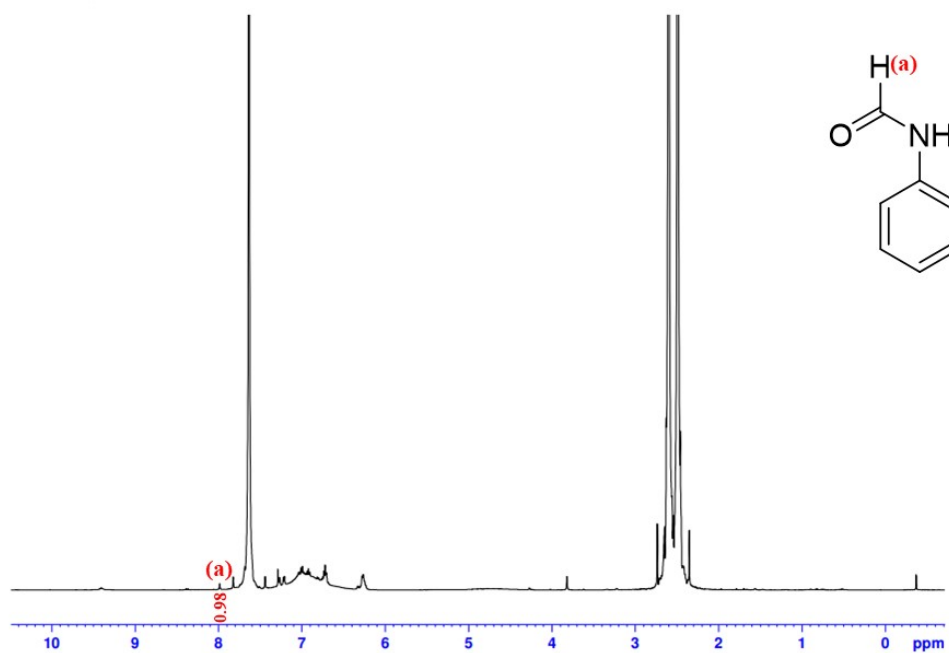


Figure S28. ^1H NMR spectra of N- phenylformamide

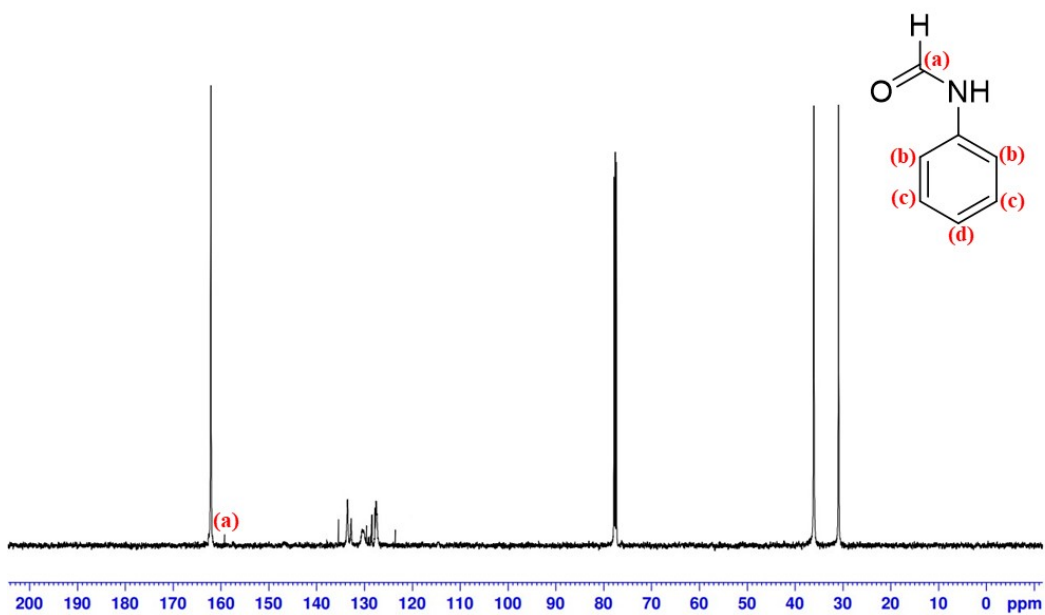


Figure S29. ^{13}C NMR spectra of N- phenylformamide

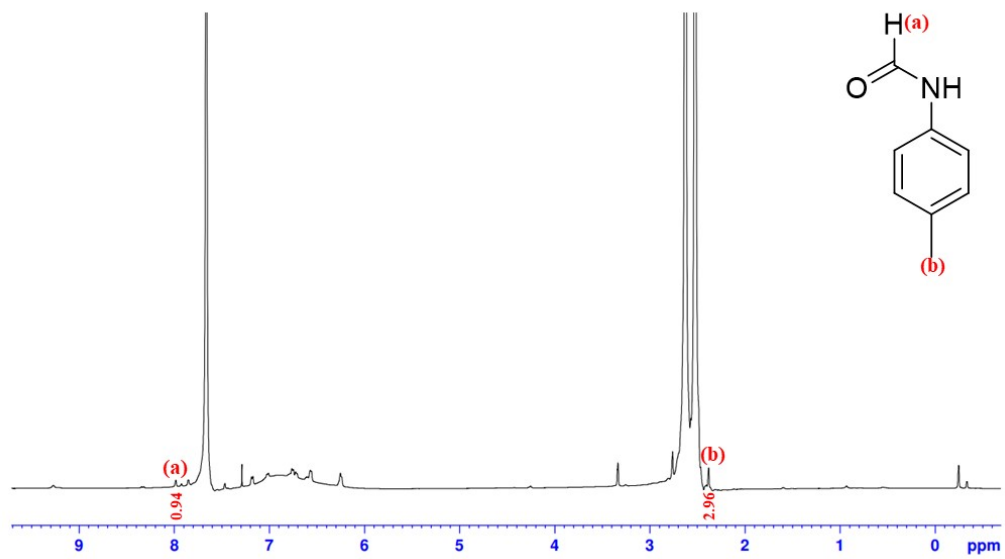


Figure S30. ¹H NMR spectra of N-p-tolylformamide

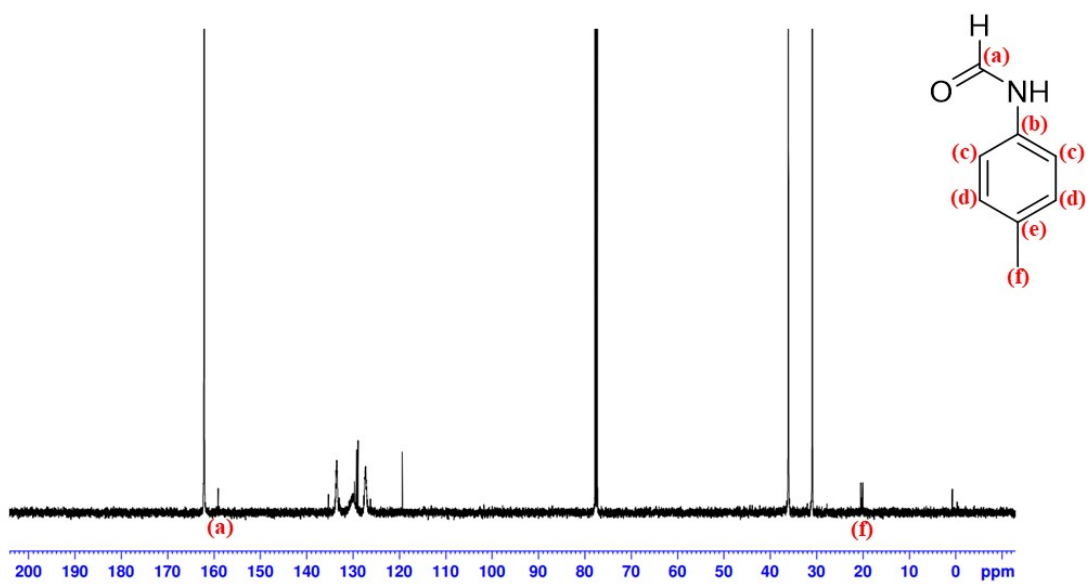
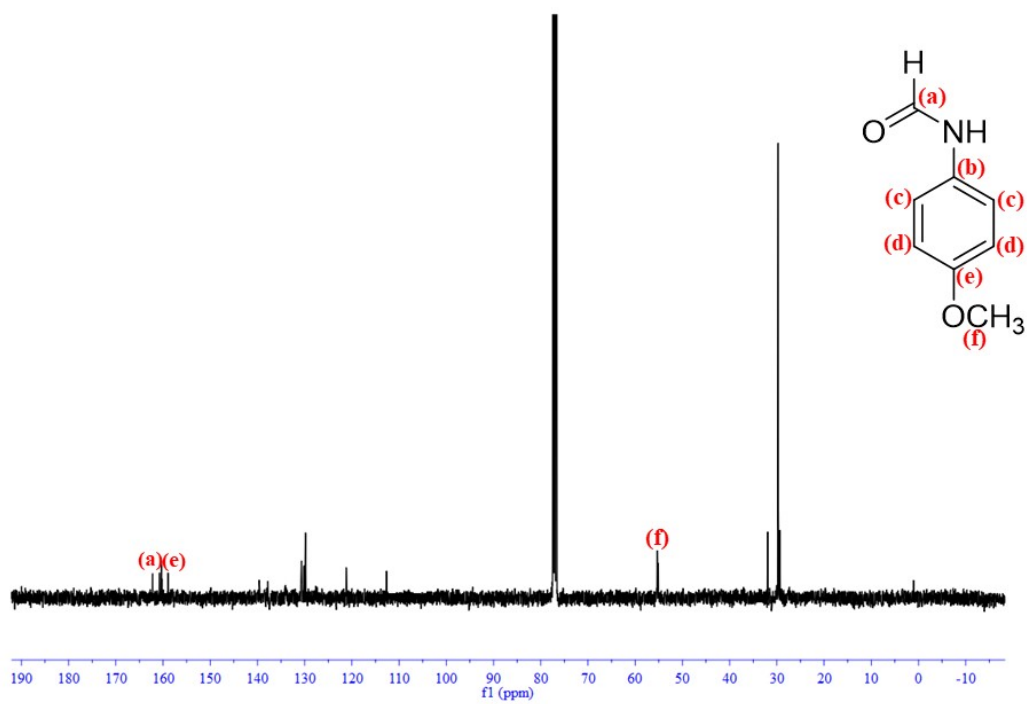
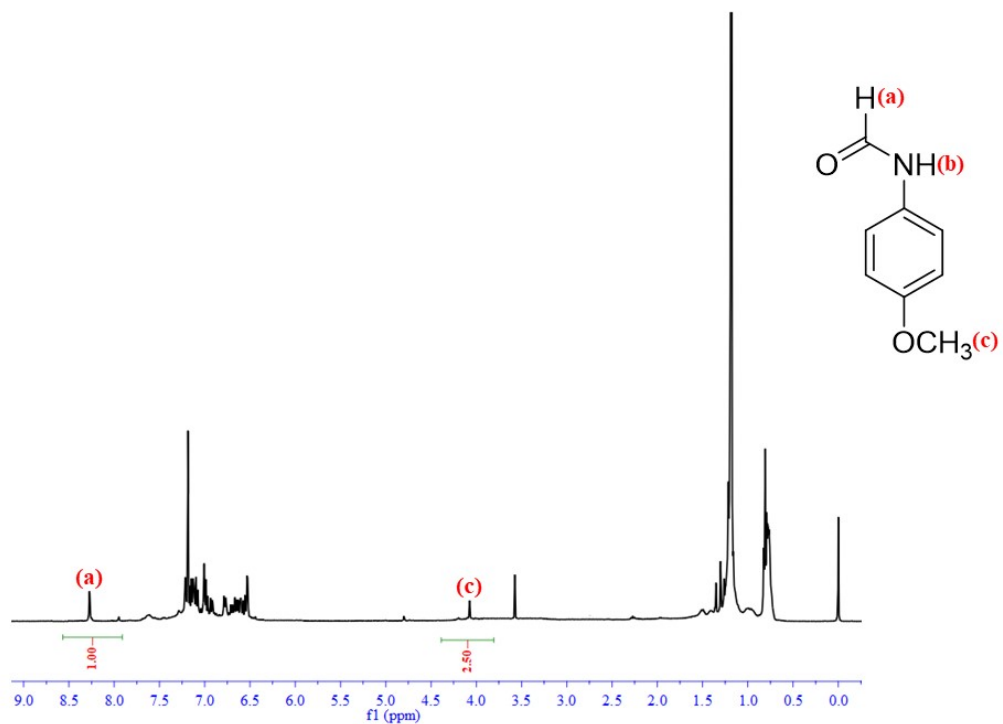


Figure S31. ¹³C NMR spectrum of N-p-tolylformamide.



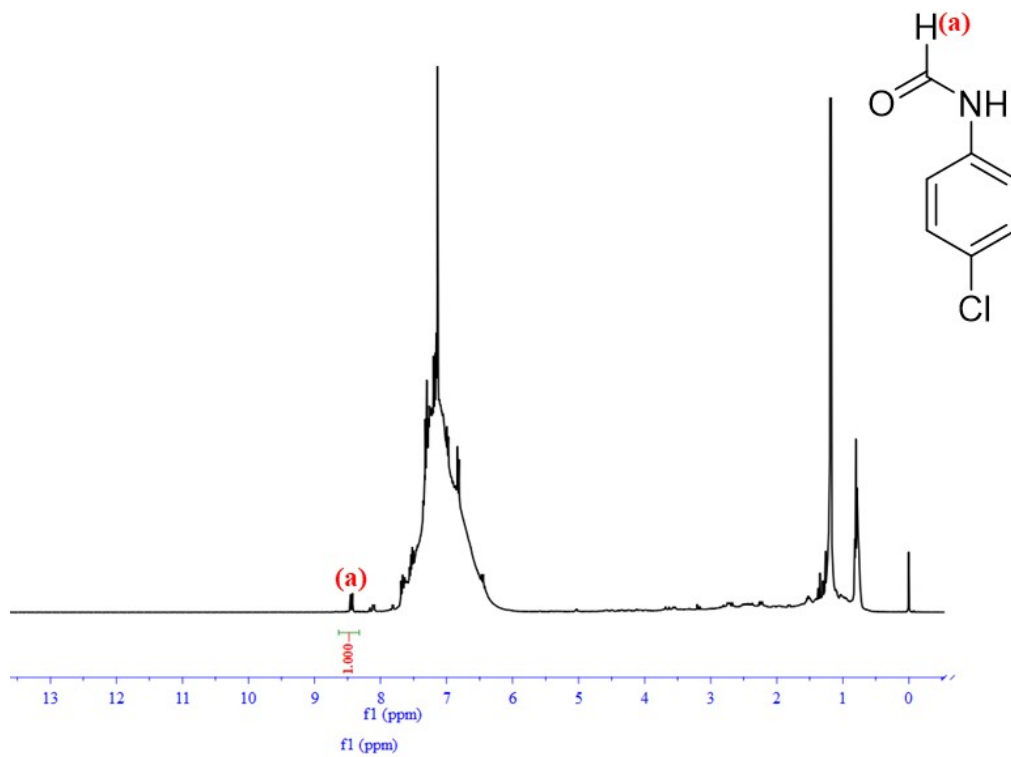


Figure S34. ^1H NMR spectra of N-(4-chlorophenyl)formamide

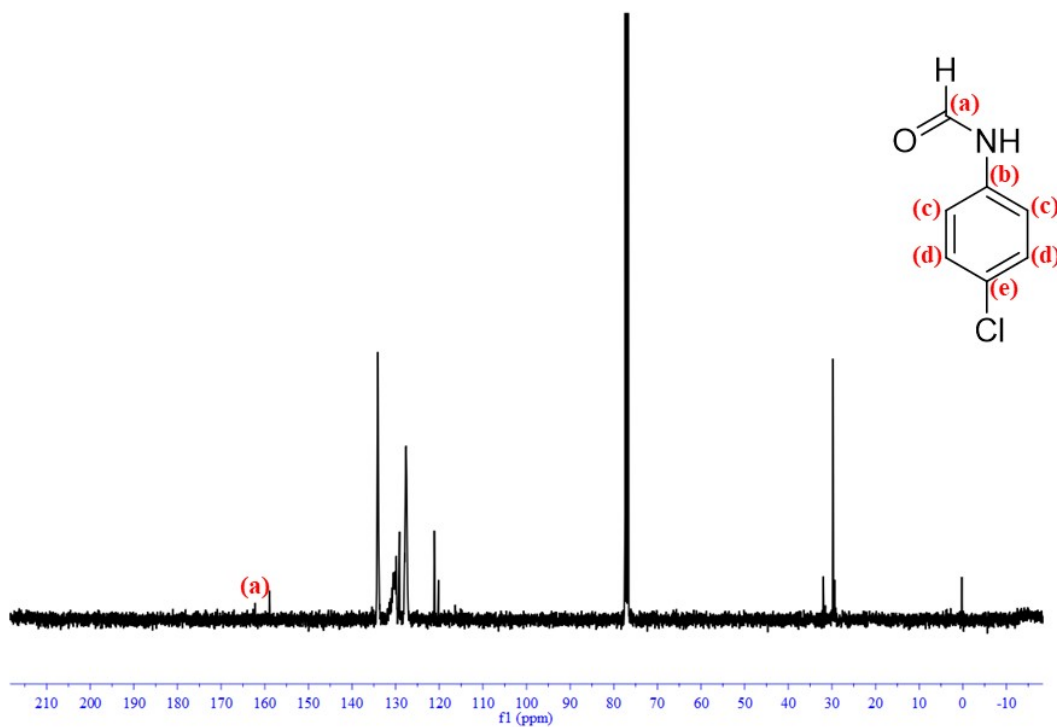
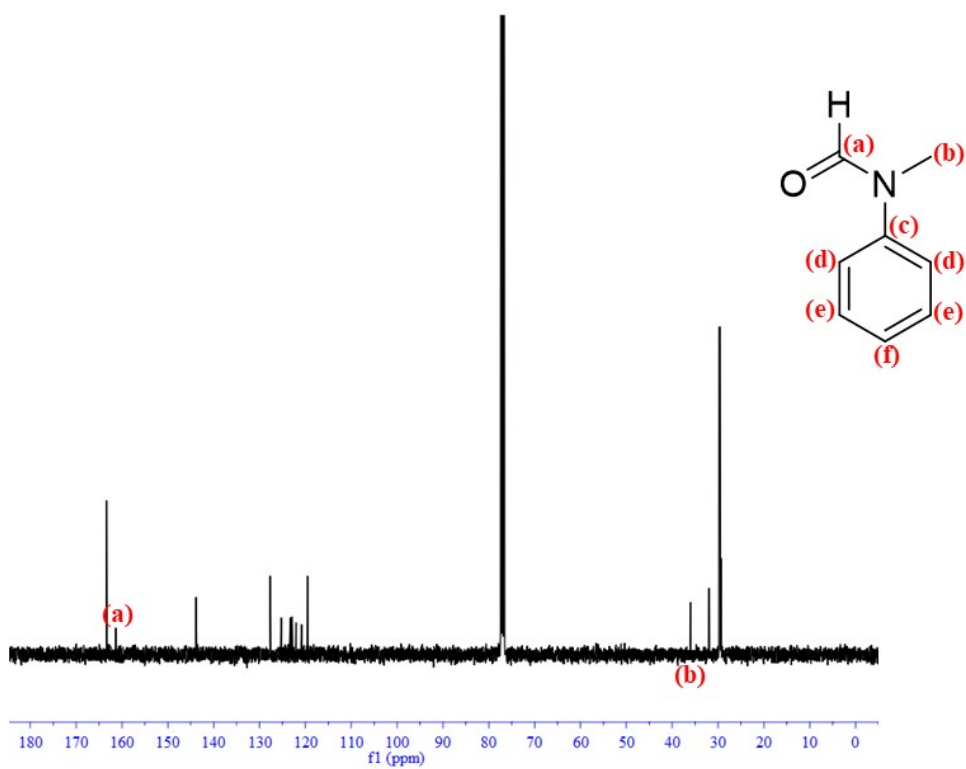
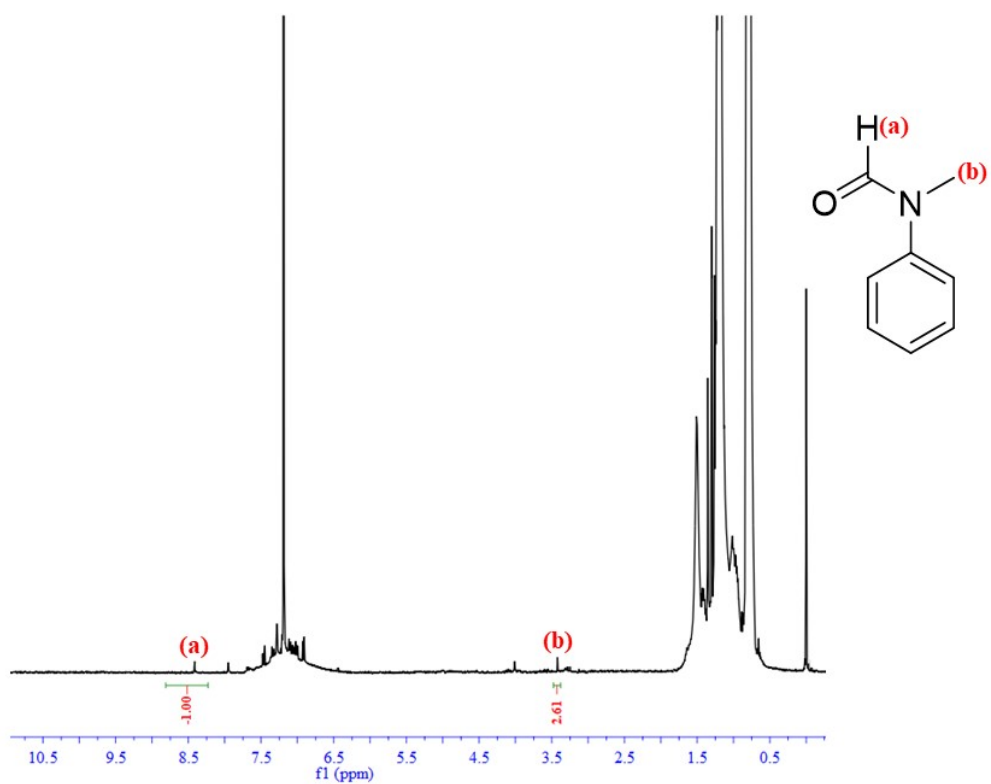


Figure S35. ^{13}C NMR spectra of N-(4-chlorophenyl)formamide



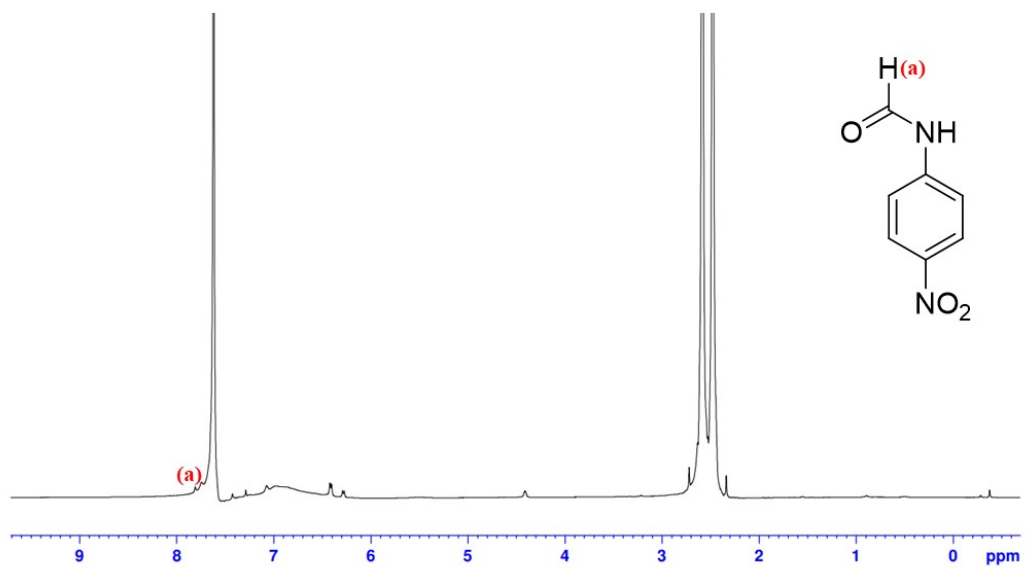


Figure S38. ^1H NMR spectra of N-(4-nitrophenyl)formamide

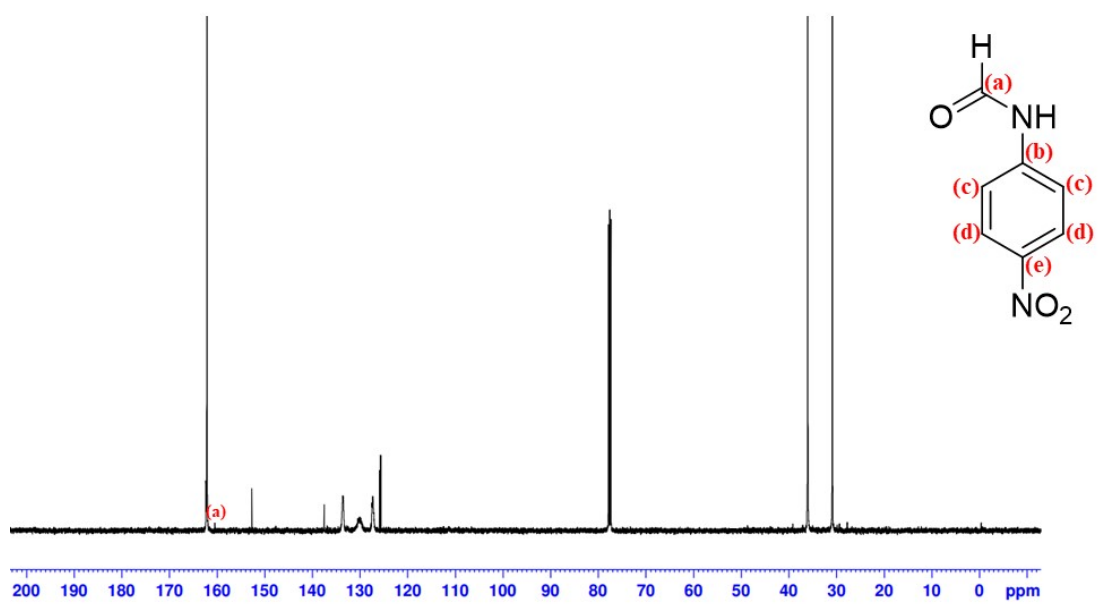


Figure S39. ^{13}C NMR spectra of N-(4-nitrophenyl)formamide

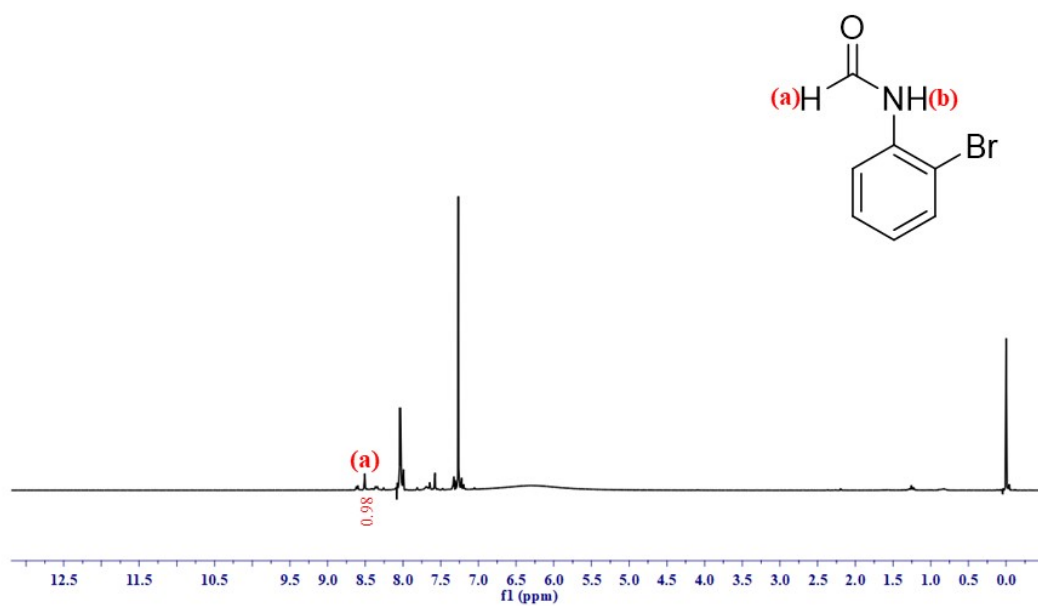


Figure S40. ^1H NMR spectra of N-(2-bromophenyl)formamide

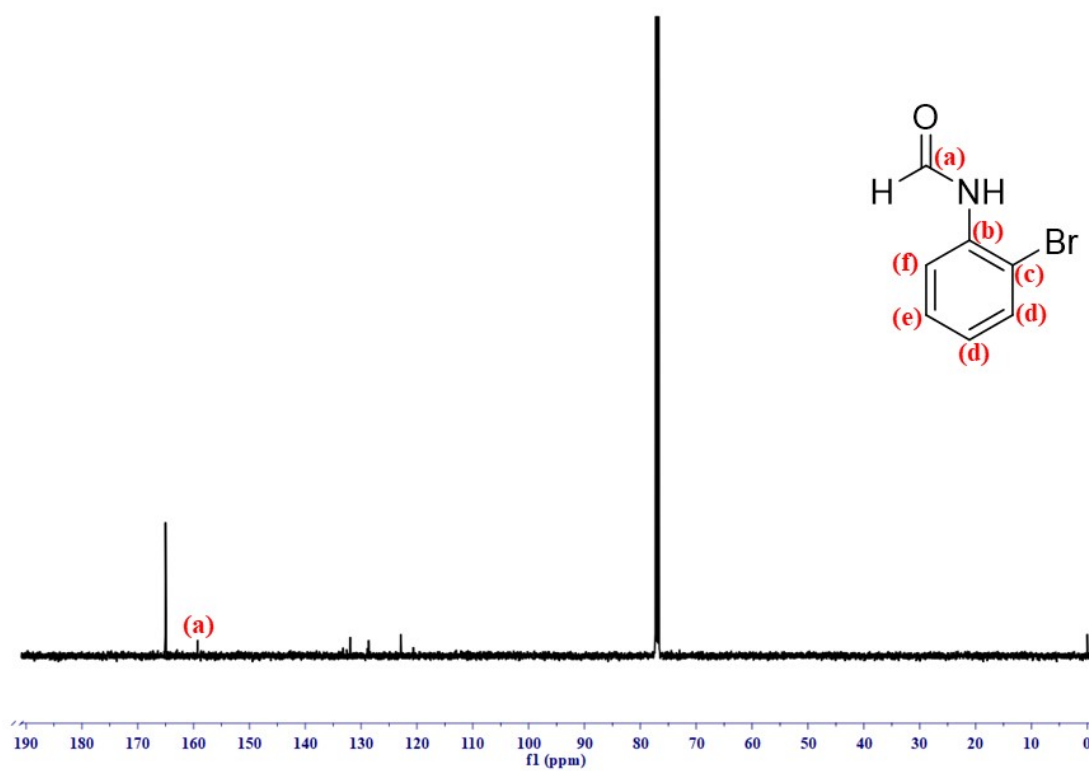


Figure S41. ^{13}C NMR spectra of N-(2-bromophenyl)formamide