Electronic Supplementary Material (ESI)

for

Functionalization of graphene oxide with a hybrid P, N ligand for immobilizing and stabilizing economical and non−toxic nanosized CuO: An efficient, robust and reusable catalyst for C−O coupling reaction in O-arylation of phenol

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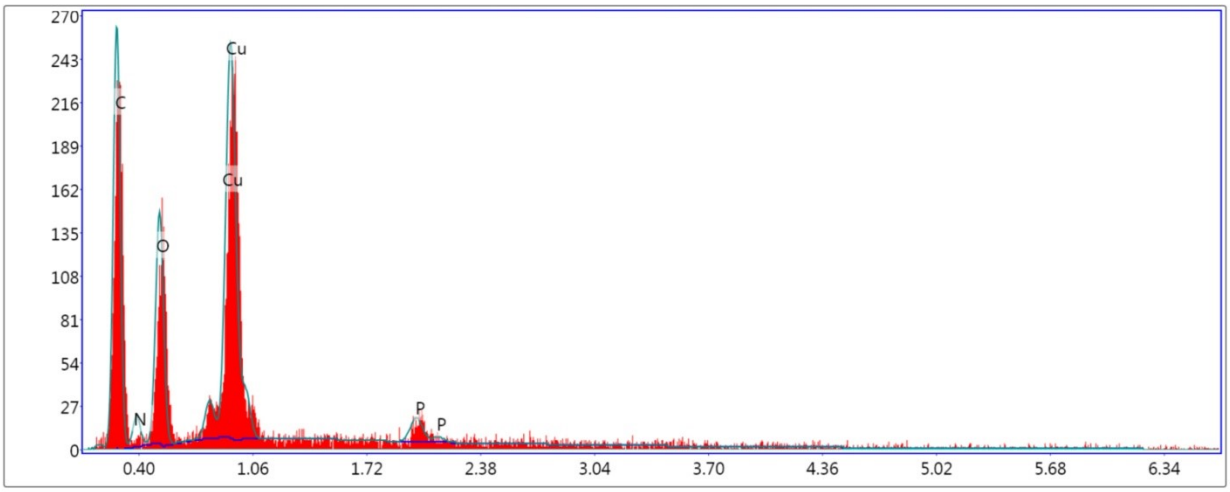
S1. SEM-EDS DATA



Element	Weight %	Atomic %	Error %	Kratio
C K	40.33	58.89	9.61	0.20
N K	7.63	9.56	22.80	0.02
O K	20.36	22.32	11.67	0.07
CuL	29.98	8.28	5.44	0.19
P K	1.69	0.96	26.83	0.01

Fig. S1. EDS spectrum of GO-PN-CuO

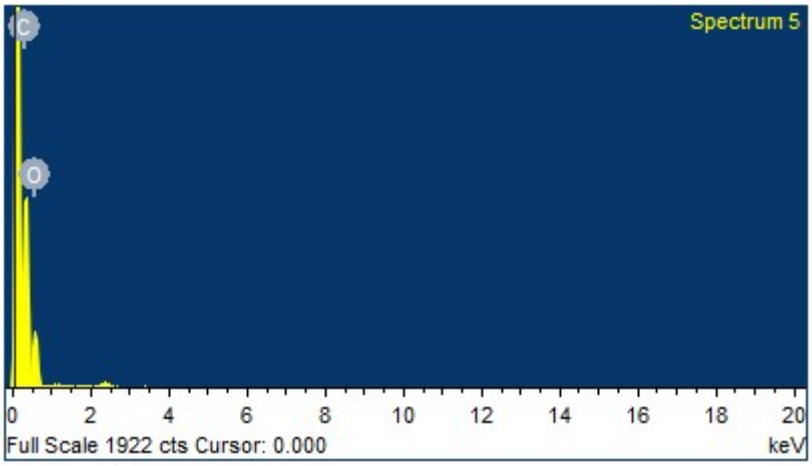


Fig. S2. EDS spectrum of GO

Element	Atomic %	Weight %
C	72.88	66.86
O	27.12	33.14

Fig. S3. EDS analysis of GO

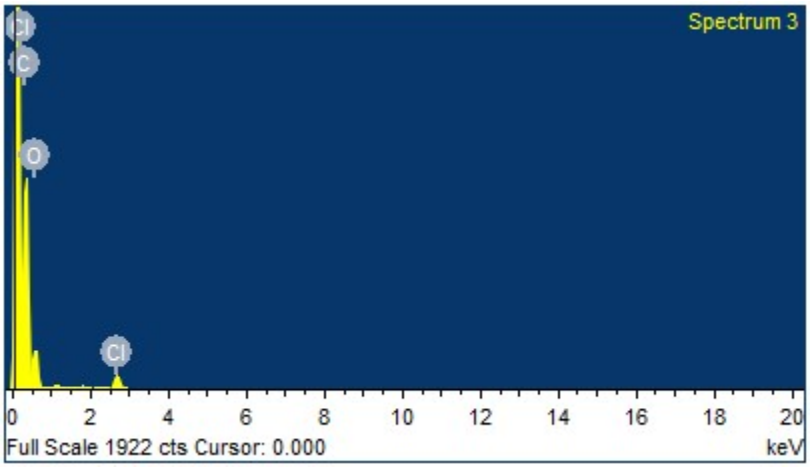


Fig. S4. EDS spectrum of GO-COCl

Element	Atomic %	Weight %
C	79.61	73.68
O	19.61	24.18
Cl	0.78	2.14

Fig. S5. EDS analysis of GO-COCl

S2. FTIR DATA

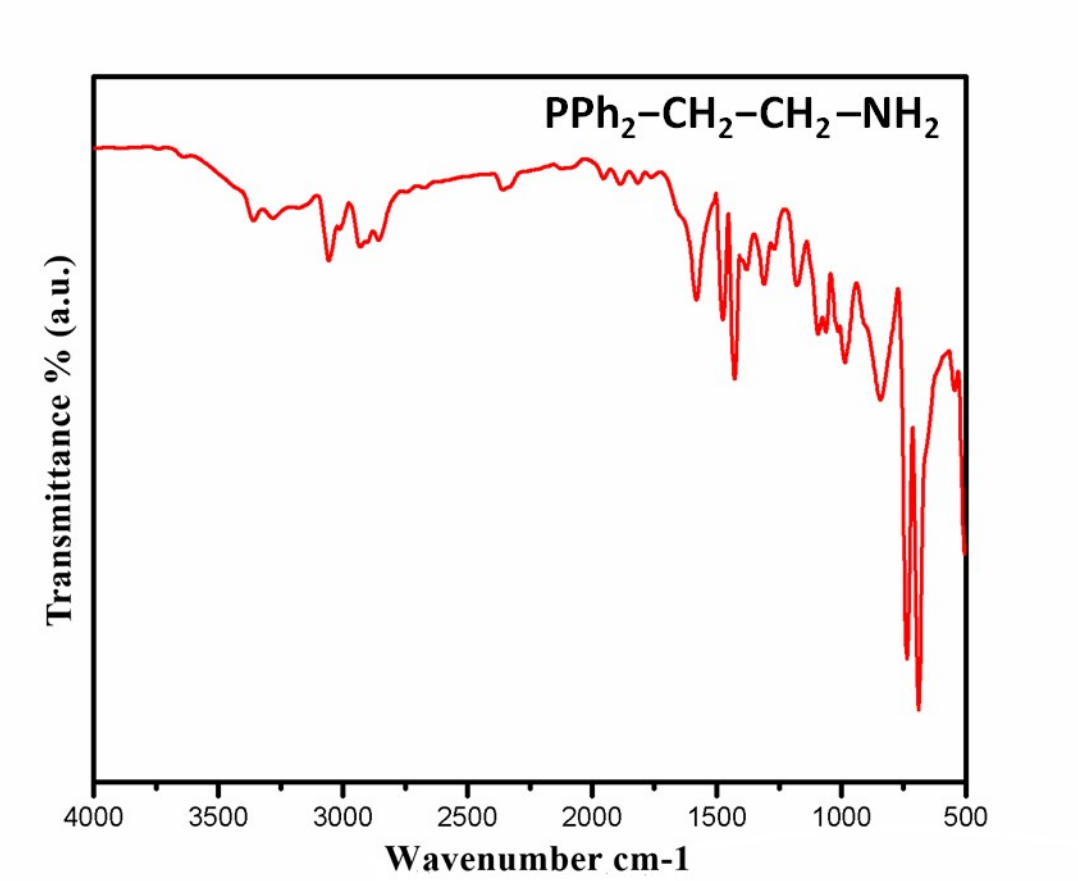


Fig. S6. FTIR spectrum of hybrid P,N ligand

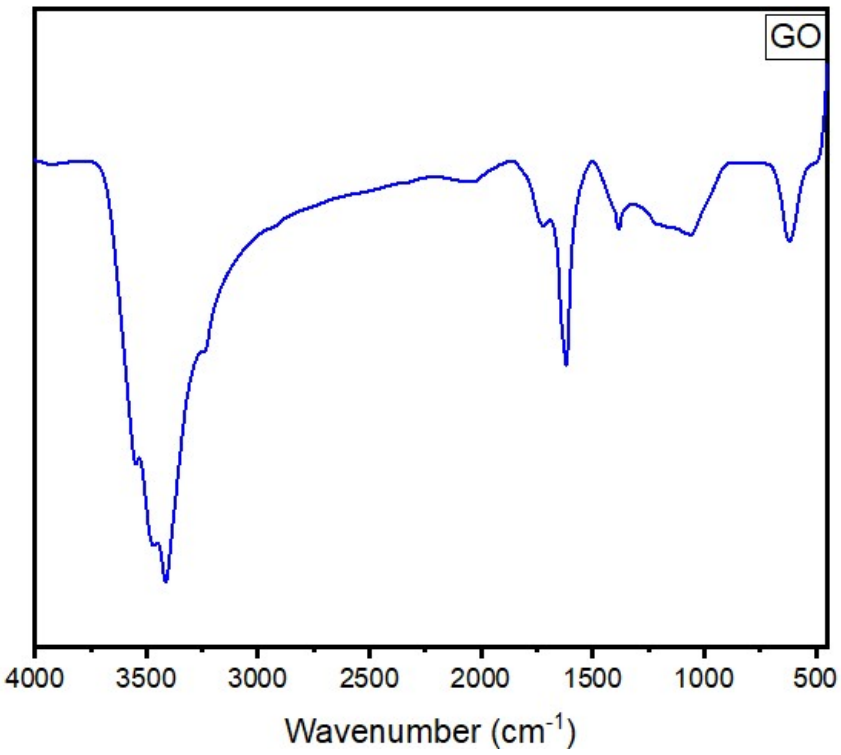


Fig. S7. FTIR spectra of GO

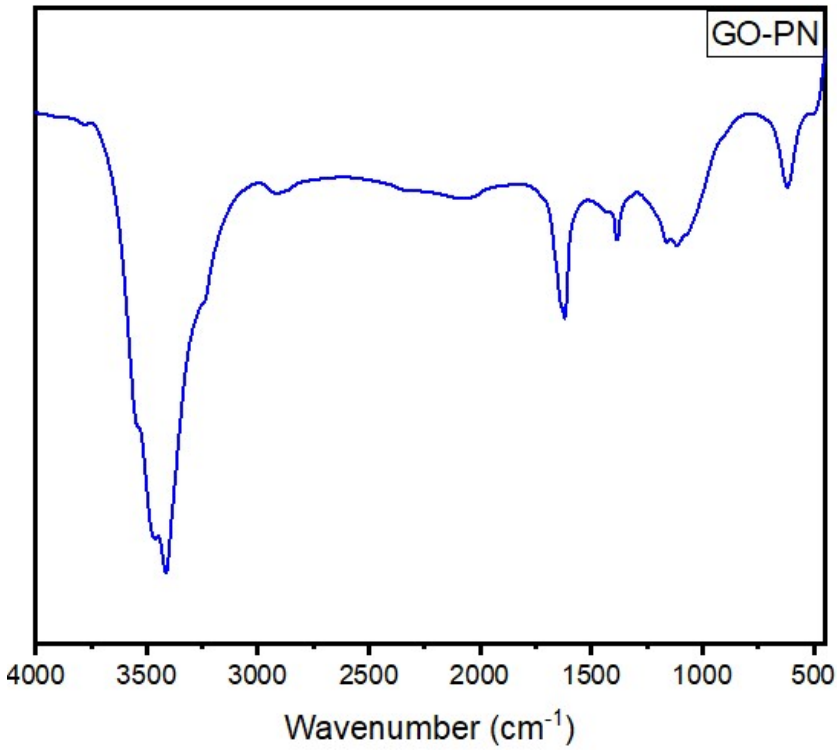


Fig. S8. FTIR spectra of GO-PN

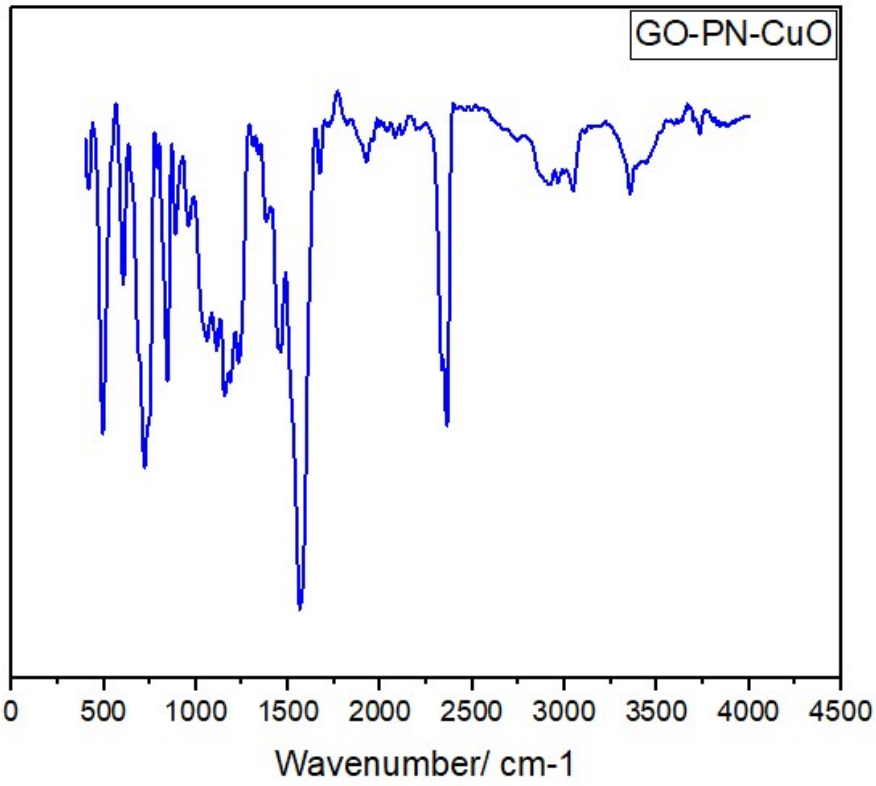


Fig. S9. FTIR spectra of GO-PN-CuO

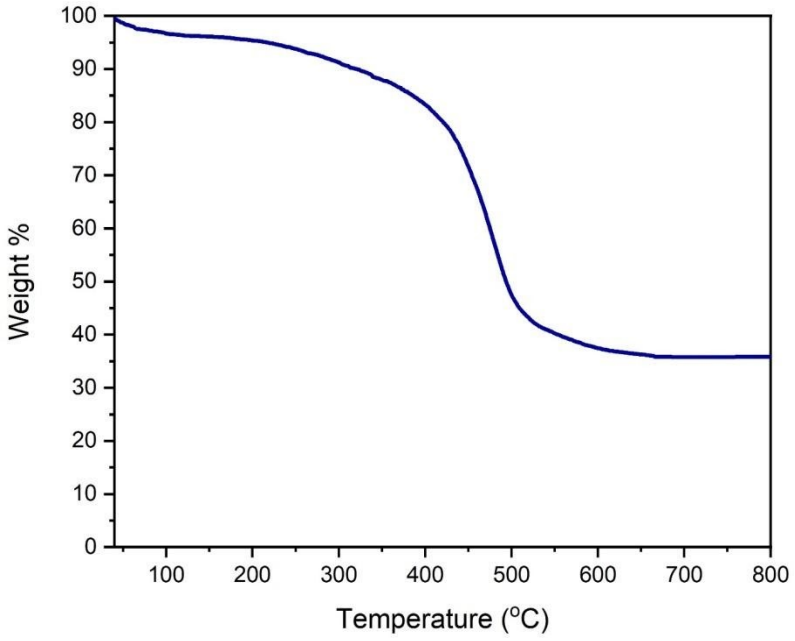


Fig. S10. TGA curve for GO−PN−CuO catalyst

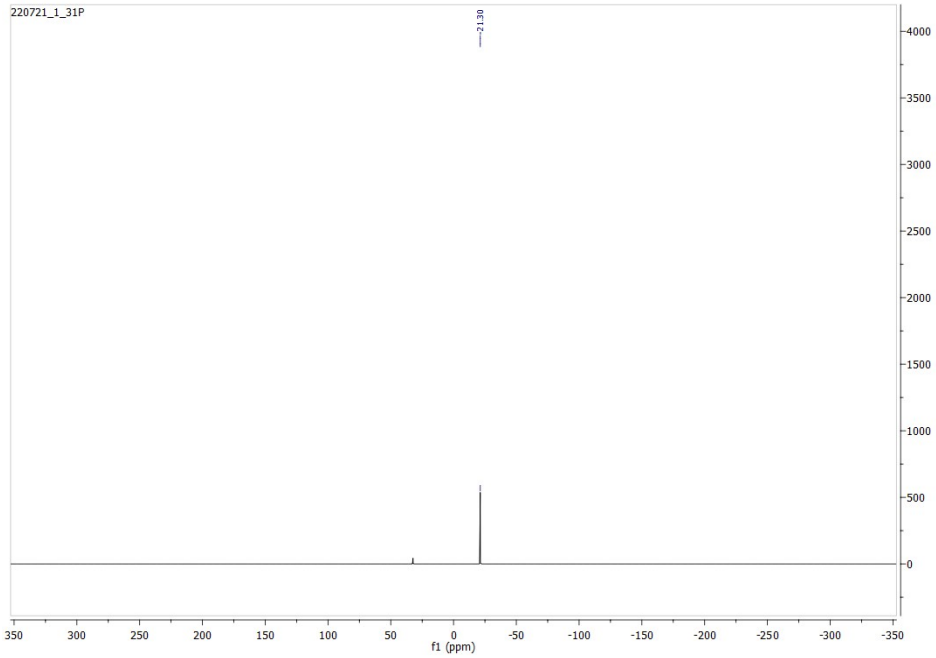


Fig. S11. $^{31}P\{^{1}H\}$ NMR spectrum of hybrid P, N ligand (Ph_2P-CH_2-CH_2-NH_2) having signal at −21.30 ppm.

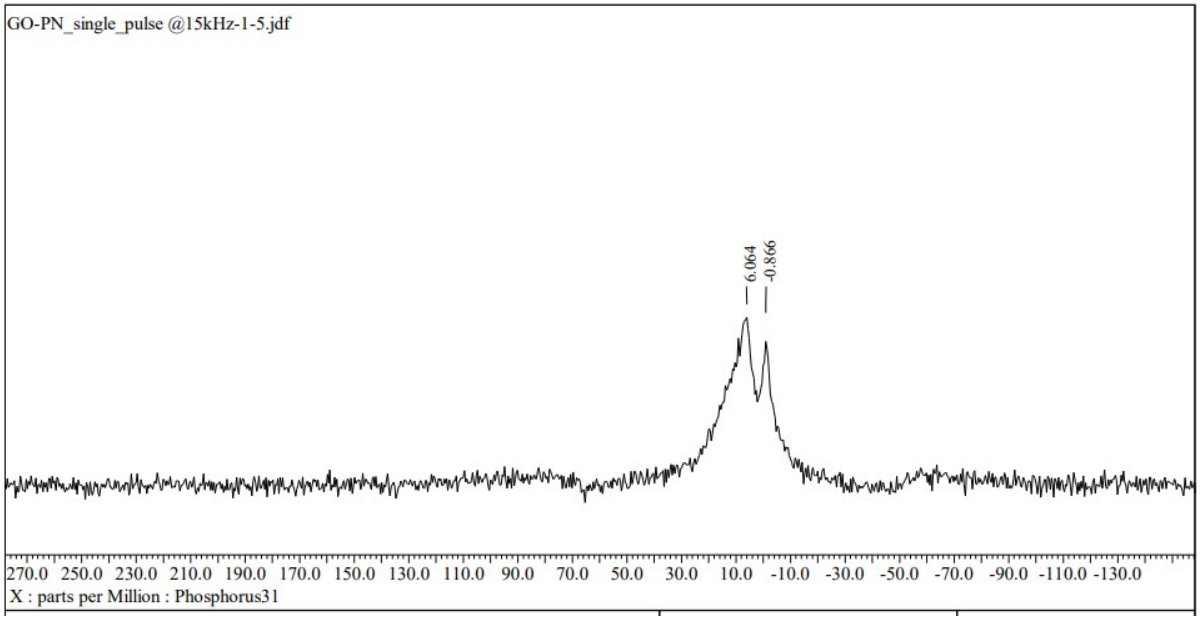


Fig. S12. Solid state ^{31}P NMR spectrum of GO-PN having Ph_2P-CH_2-CH_2-NH_2 on the surface of Graphene Oxide.

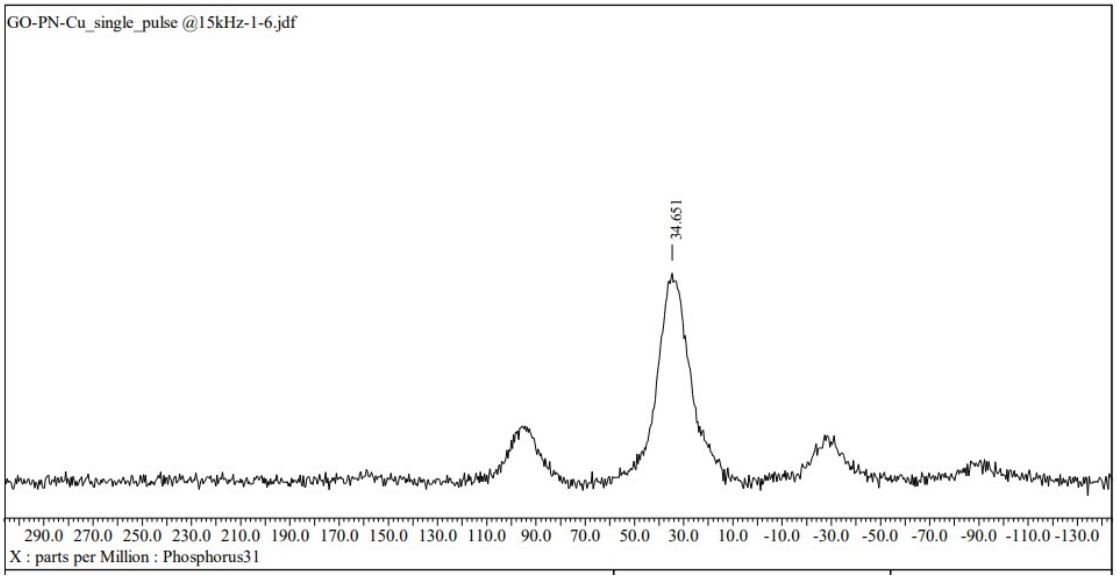


Fig. S13. Solid state ^{31}P NMR spectrum of GO-PN-CuO having immobilized nanoparticles of copper(II) oxide on functionalized Graphene Oxide with Ph_2P-CH_2-CH_2-NH_2

S4. Comparative study of GO-PN-CuO catalyst with reported/known catalytic systems.

The efficacy of GO−PN−CuO nanocatalytic system for C−O coupling reaction of bromobenzene with phenol has been compared with some earlier reported catalysts as demonstrated in Table S1. As can be seen, GO−PN−CuO performs the reaction at 100 °C in 12 h of reaction time at a low

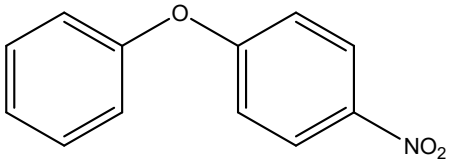
catalyst loading of 2.25 mol% and exhibits high catalytic efficiency upto 99% conversion for this reaction.

Table S1. Comparison of present catalyst (GO-PN-CuO) with previously reported Cu-catalytic system for O−arylation reaction

Entry	Catalyst	Solvent	Catalyst Amount	Time	Temperature	Yield	Reference
1.	$Cu_{1.8}S$ nanoflowers*	DMSO	1.25 mol%	8h	120°C	61%	1
2.	GO-$Cu_{1.8}S$ nanocomposite*	DMSO	1.25 mol%	8h	120°C	74%	1
3.	NF/GNRS/Cu	ACN	10 mol%	7h	80°C	90%	2
4.	Fe3O4@SiO2-BT-Cu	DES	2 mol%	10h	100°C	93%	3
5.	Cu_2O NPs	DMAc	3 mol%	24h	27°C	79%	4
6.	CuNPs@Q-POP	DMF	7.3 mol%	24h	110°C	80%	5
7.	$CuFe_2O_4$/Ligand	NMP	5 mol%	24h	135°C	34%	6
8.	This work	DMSO	2.25 mol%	12h	110°C	99%	

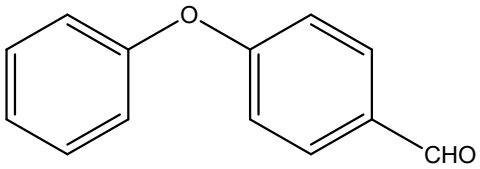
S5. NMR data of cross-coupled products of C−O coupling reactions of aryl halides and phenol or derivatives of phenol

S5.1. 1-Nitro-4-phenoxy benzene:



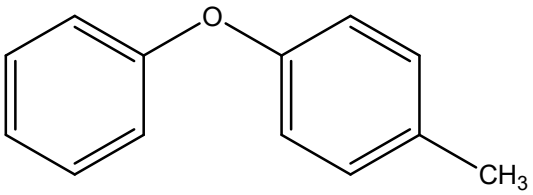
Yellow solid, m.p. 52-55 ˚C (Lit. 56-57 ˚C)[7]. ^{1}H NMR (500 MHz, $CDCl_3$, 25°C vs TMS), δ(ppm): 8.11-8.14 (d, 2H), 7.34-7.40 (t, 2H), 7.16-7.21 (t, 1H), 7.01-7.03 (d, 2H), 6.92-6.95 (d, 2H).

S5.2. 4-Phenoxybenzaldehyde:



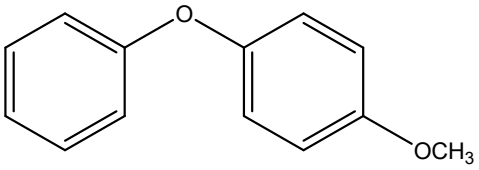
Yellow liquid, m.p. 24-26 ˚C. ^{1}H NMR (500 MHz, $CDCl_3$, 25°C vs TMS), δ(ppm): 9.92 (s, 1H), 7.84-7.86 (d, 2H), 7.40-7.45 (t, 2H), 7.20-7.26 (m, 1H), 7.05-7.11 (t, 4h).

S5.3. 1-Methyl-4-phenoxybenzene:



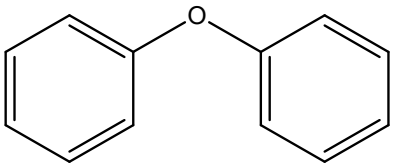
Colorless solid, m.p. 100-104 ˚C . ^{1}H NMR (500 MHz, $CDCl_3$, 25°C vs TMS), δ(ppm): 7.46-7.48 (m, 2H), 7.23-7.26 (t, 2H), 7.06-7.07 (m, 1H), 6.98-7.04 (m, 2H), 6.89-6.91 (m, 2H), 2.26 (s, 3H).

S5.4. 1-Methoxy-4-phenoxybenzene:



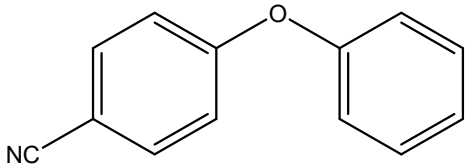
Colorless liquid, m.p. 10-14 ˚C . ^{1}H NMR (500 MHz, $CDCl_3$, 25°C vs TMS), δ(ppm): 7.25-7.32 (m, 2H), 7.01-7.06 (t, 1H), 6.93-7.01 (m, 4H), 6.86-6.90 (m, 2H), 3.81 (s, 3H).

S5.5. Diphenyl ether:



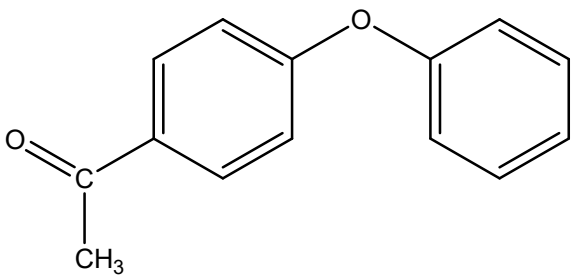
Colorless liquid, m.p. 25-29 ˚C (Lit. 26-27 ˚C)[8]. ^{1}H NMR (500 MHz, $CDCl_3$), δ(ppm): 7.25 (t, 4H), 6.93 (t, 2H), 7.37 (d, 4H).

S5.6. 4-Phenoxybenzonitrile:



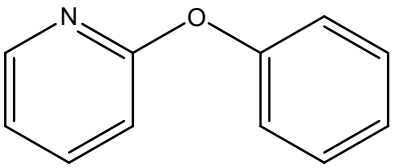
Colourless solid, m.p. 41-44 ˚C (Lit. 45-46 ˚C)[9]. ^{1}H NMR (500 MHz, $CDCl_3$), δ(ppm): 7.55 (d, 2H), 7.43 (t, 2H), 7.20 (t, 1H), 7.00 (d, 2H), 6.95 (d, 2H).

S5.7. 1-(4-Phenoxyphenyl)ethanone:



Colourless solid, m.p. 50-52 ˚C. ^{1}H NMR (500 MHz, $CDCl_3$), δ(ppm): 7.93 (m, 2H), 7.37-7.41 (m, 2H), 7.18-7.21 (t, 1H), 7.08-7.06 (m, 2H), 6.98-7.00 (m, 2H), 2.57 (s, 3H).

S5.8. 2-Phenoxy pyridine:



Colourless oil, m.p. 46-48 ˚C. ^{1}H NMR (500 MHz, $CDCl_3$), δ(ppm): 7.689-7.65 (M, 1H), 7.48-7.46 (m, 1H), 7.12 (t, 2H), 6.89-6.84 (m, 5H).

S6. NMR spectra of cross-coupled products of C-O coupling reactions:

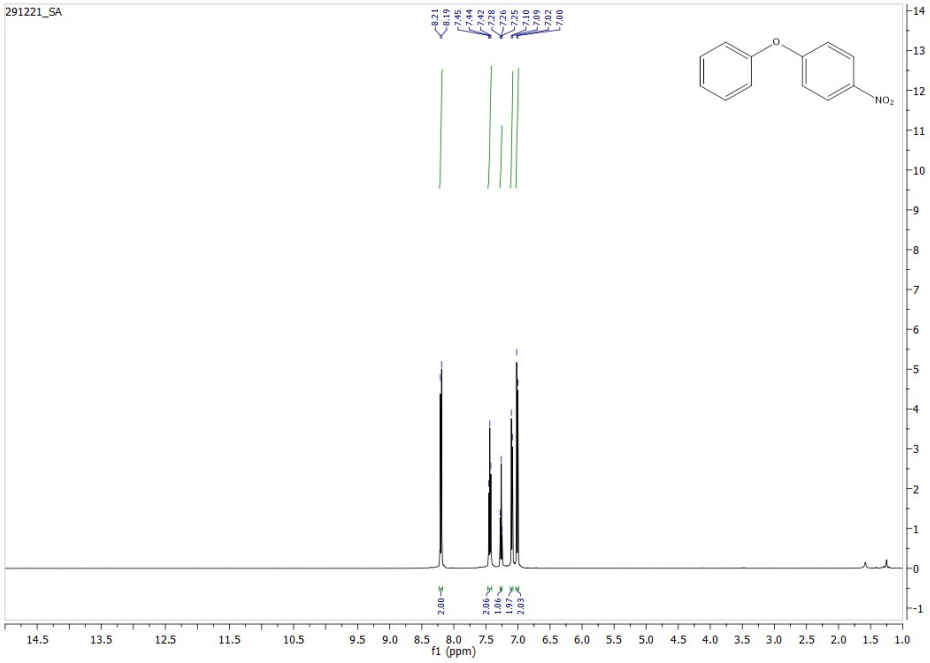


Fig. S14. ^{1}H NMR spectrum (scale: 1.0 to 15.0 ppm) of 4-nitrodiphenylether

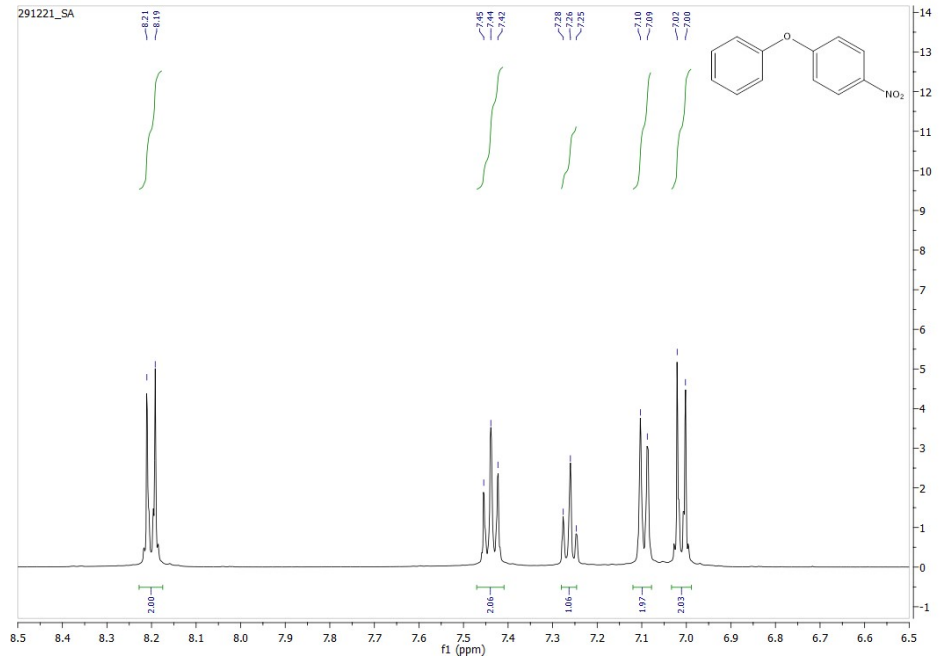


Fig. S15. ^{1}H NMR spectrum (scale: 6.5 to 8.5 ppm) of 4-nitrodiphenylether

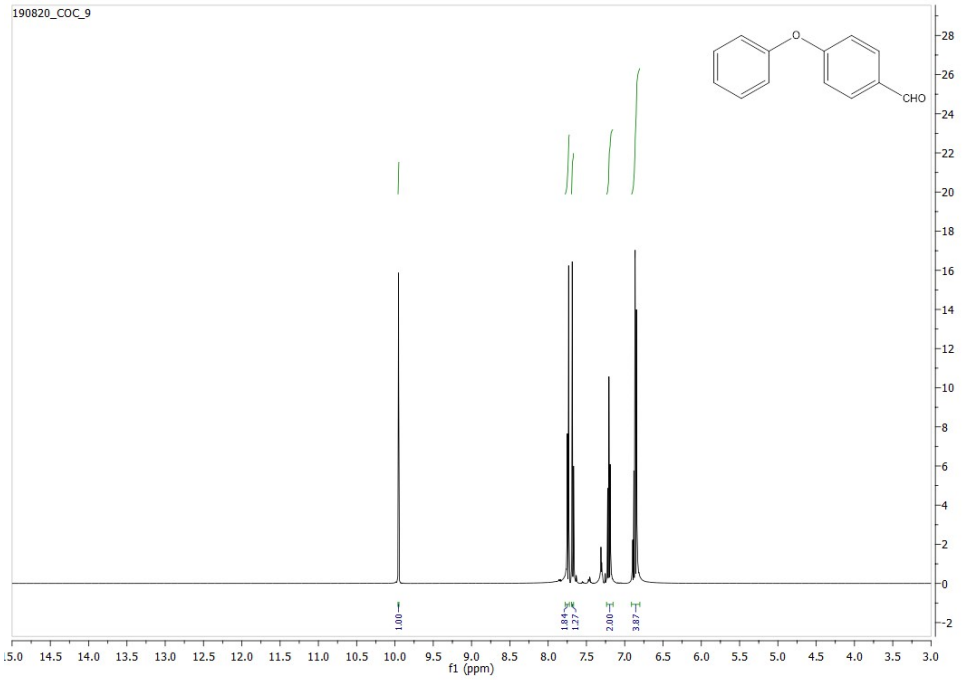


Fig. S16. ^{1}H NMR spectrum (scale: 3.0 to 15.0 ppm) of 4-phenoxy benzaldehyde

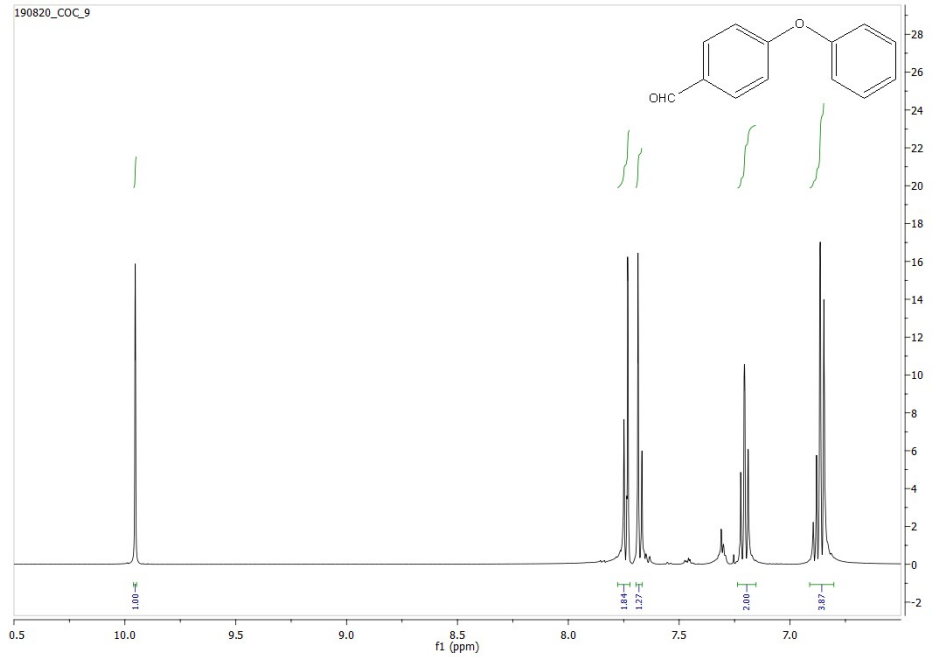


Fig. S17. ^{1}H NMR spectrum (scale: 6.5 to 10.5 ppm) of 4-phenoxy benzaldehyde

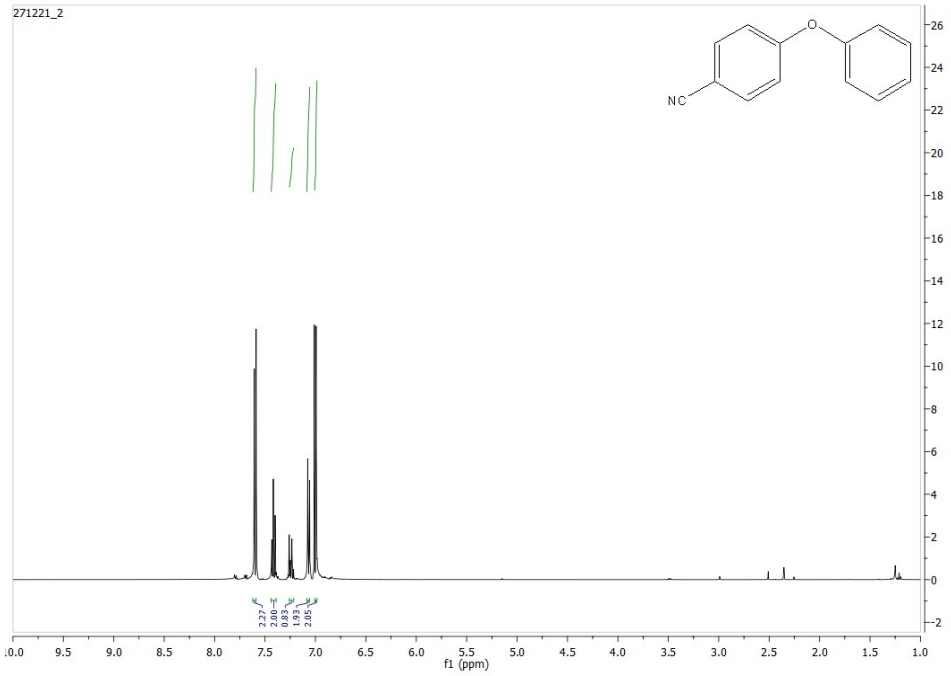


Fig. S18. ^{1}H NMR spectrum (scale: 10.0 to 1.0 ppm) of 4-phenoxy benzonitrile

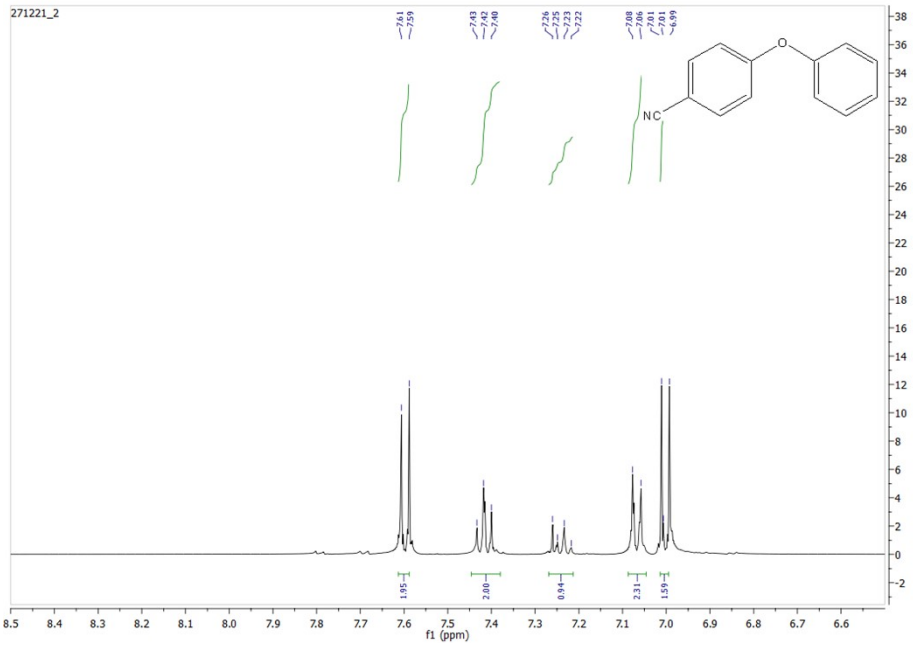


Fig. S19. ^{1}H NMR spectrum (scale: 6.5 to 8.5 ppm) of 4-phenoxy benzonitrile

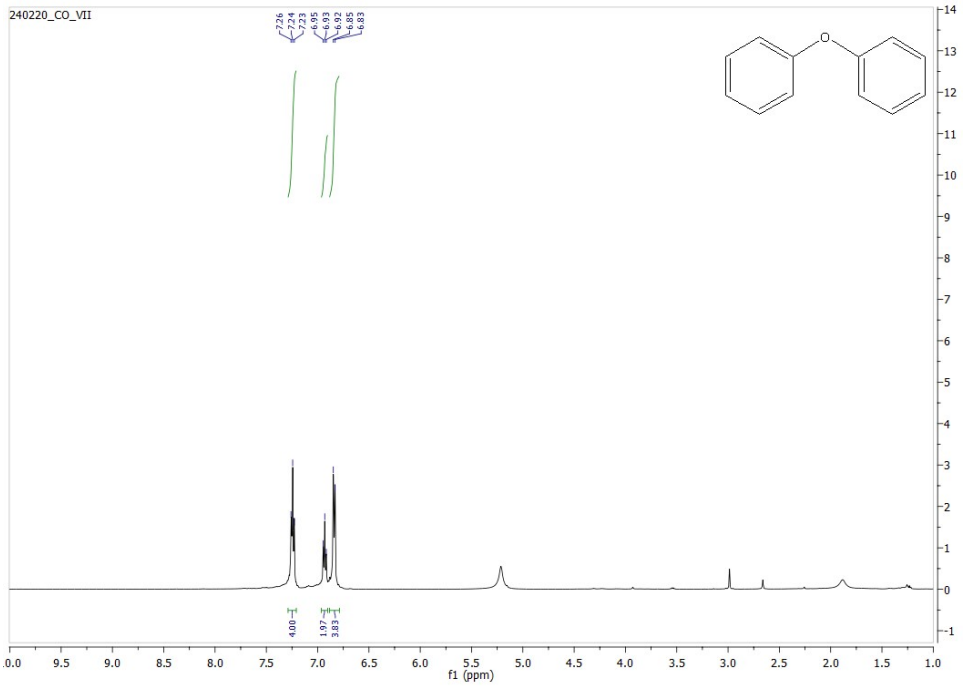


Fig. S20. ^{1}H NMR spectrum (scale: 1.0 to 10.0 ppm) of diphenylether

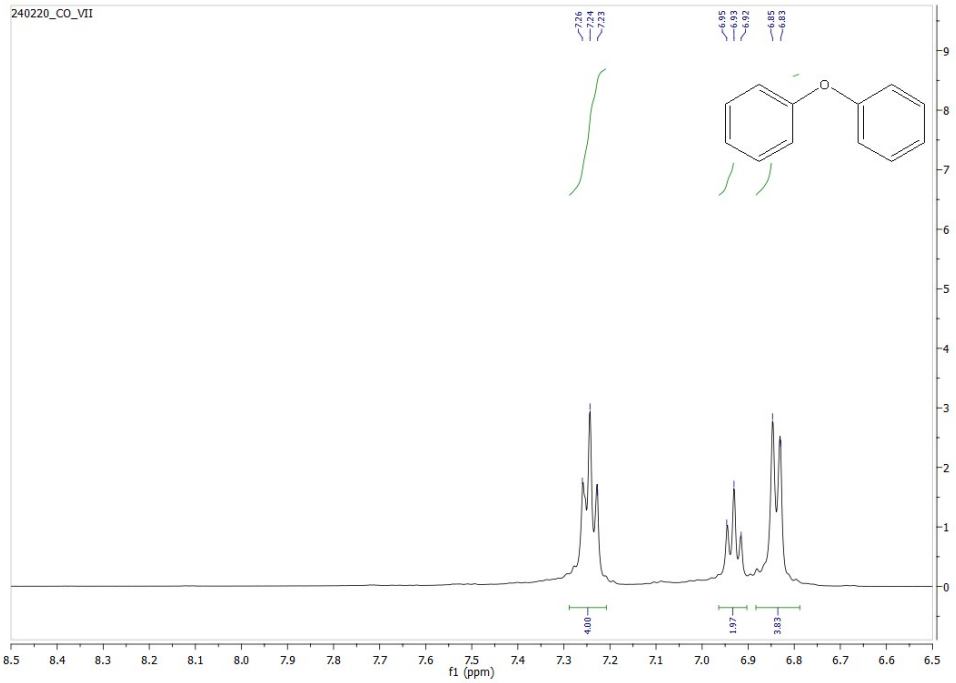


Fig. S21. ^{1}H NMR spectrum (scale: 6.5 to 8.5 ppm) of diphenylether

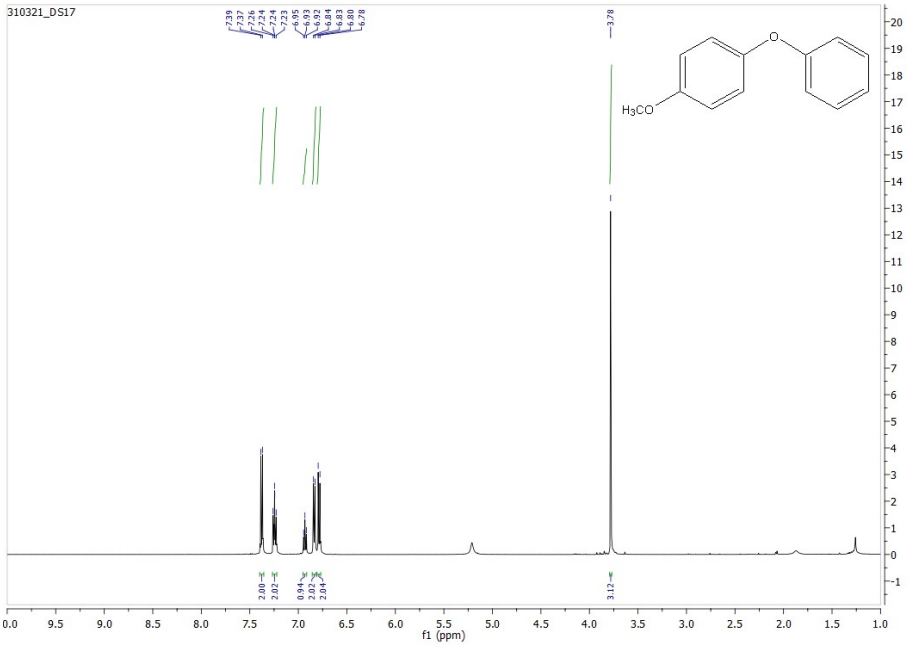


Fig. S22. ^{1}H NMR spectrum (scale: 1.0 to 10.0 ppm) of 4-methoxy diphenylether

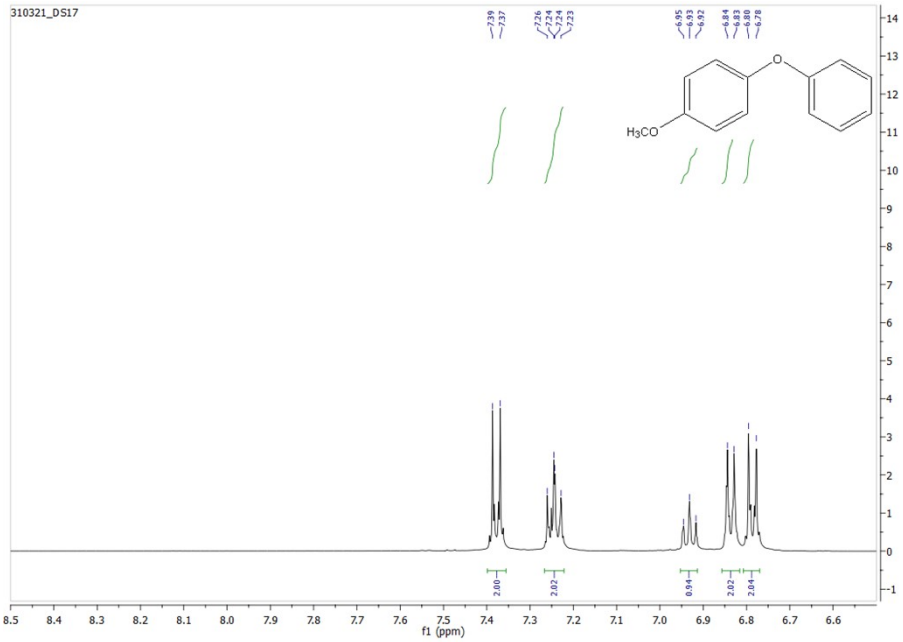


Fig. S23. ^{1}H NMR spectrum (scale: 6.5 to 8.5 ppm) of 4-methoxy diphenylether

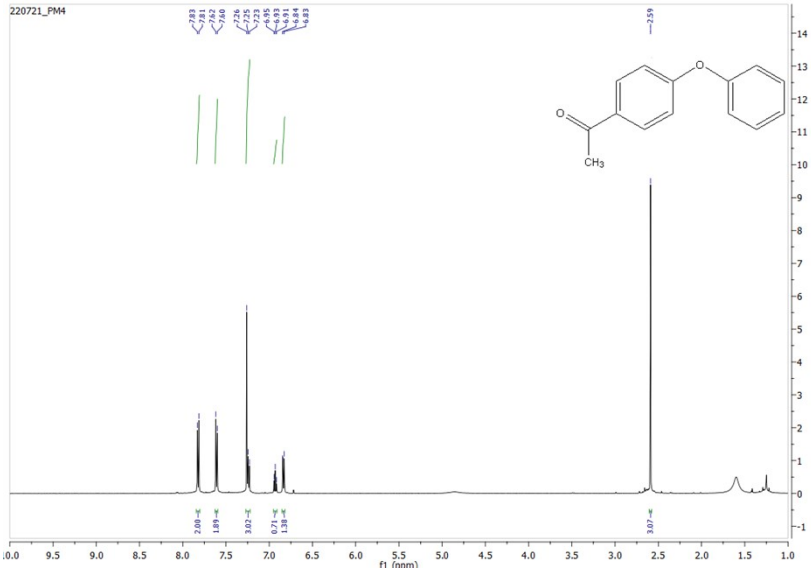


Fig. S24. ^{1}H NMR spectrum (scale: 6.5 to 8.5 ppm) of 4-acetyl diphenylether

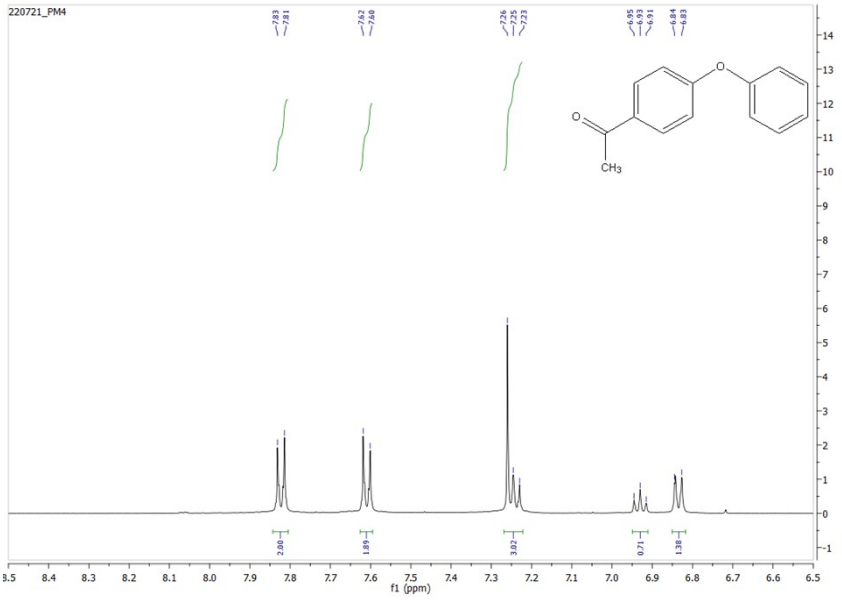


Fig. S25. ^{1}H NMR spectrum (scale: 6.5 to 8.5 ppm) of 4-acetyl diphenylether

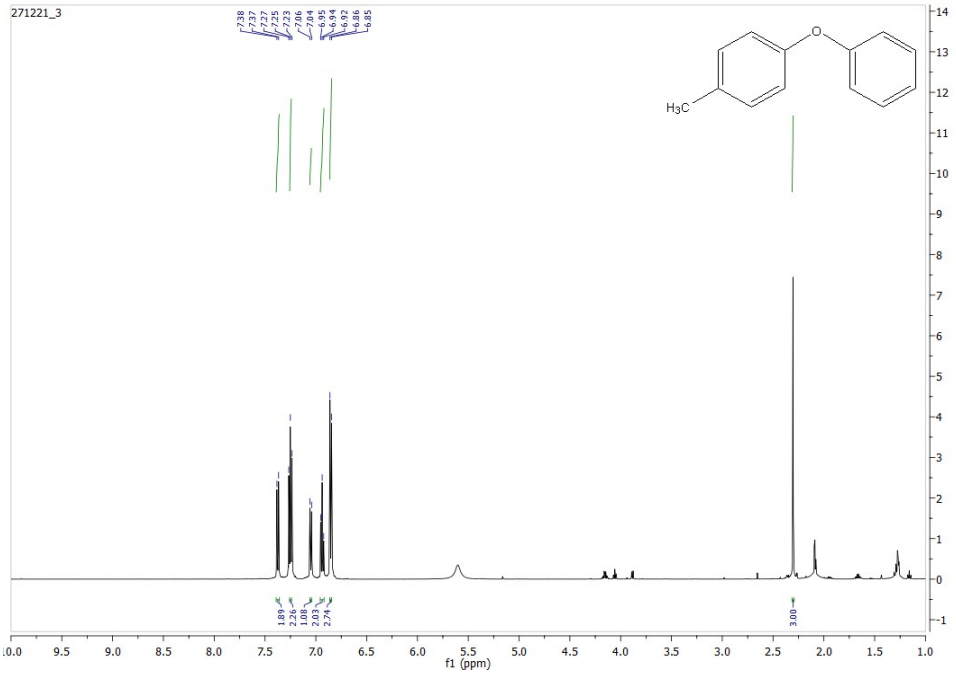


Fig. S26. ^{1}H NMR spectrum (scale: 1.0 to 10.0 ppm) of 4-methyl diphenylether

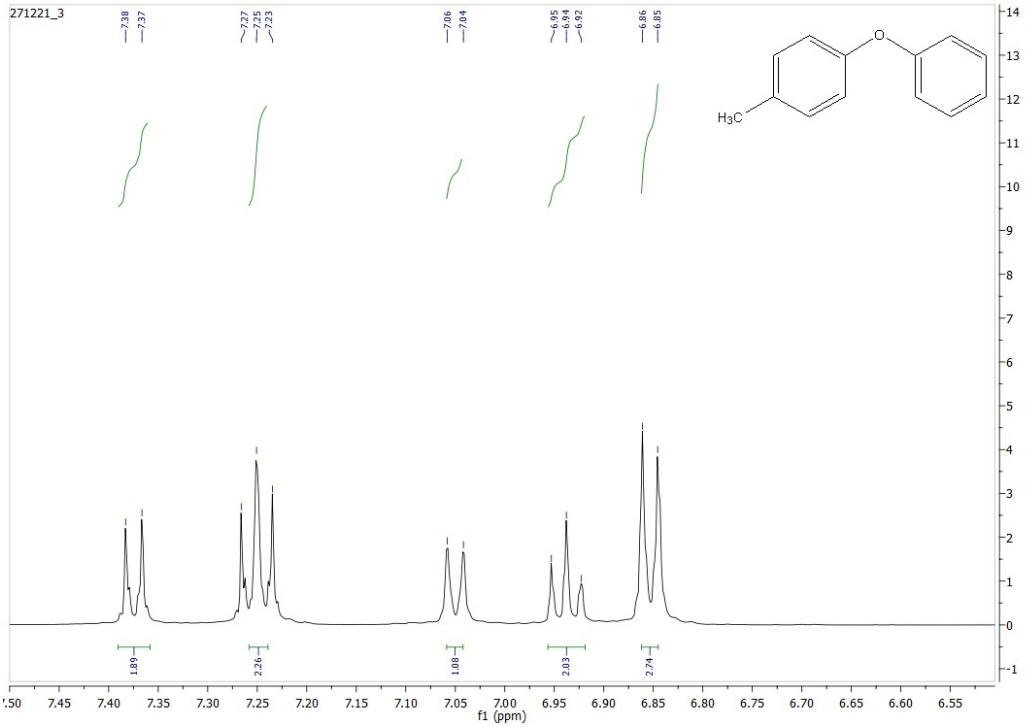


Fig. S27. ^{1}H NMR spectrum (scale: 6.5 to 7.5 ppm) of 4-methyl diphenylether

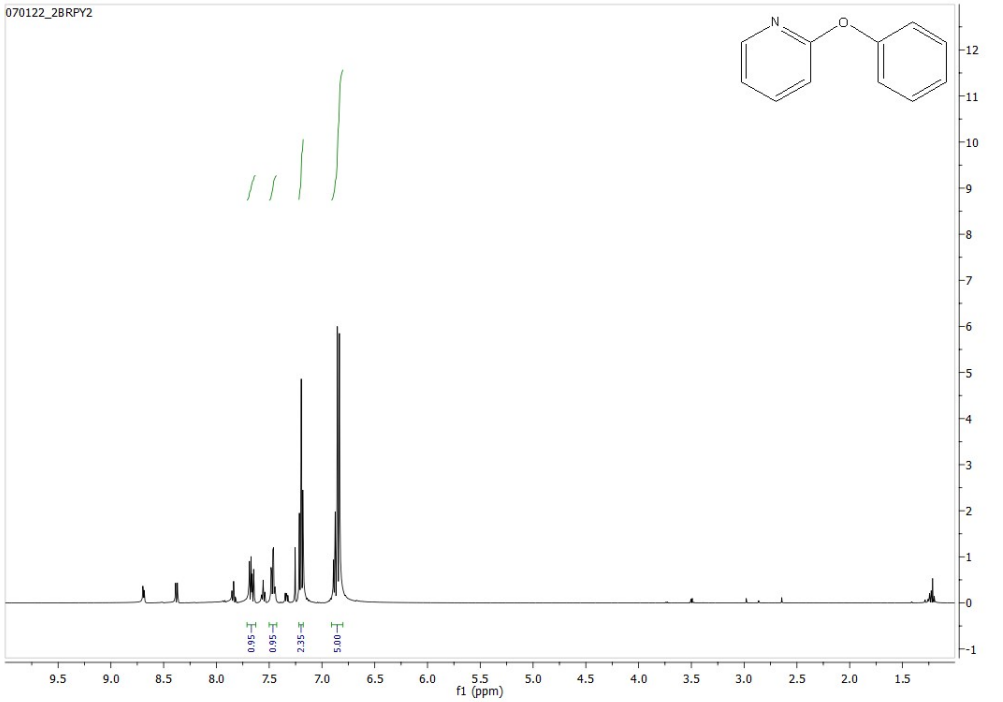


Fig. S28. ^{1}H NMR spectrum (scale: 1.0 to 10.0 ppm) of 2-pyridine phenylether

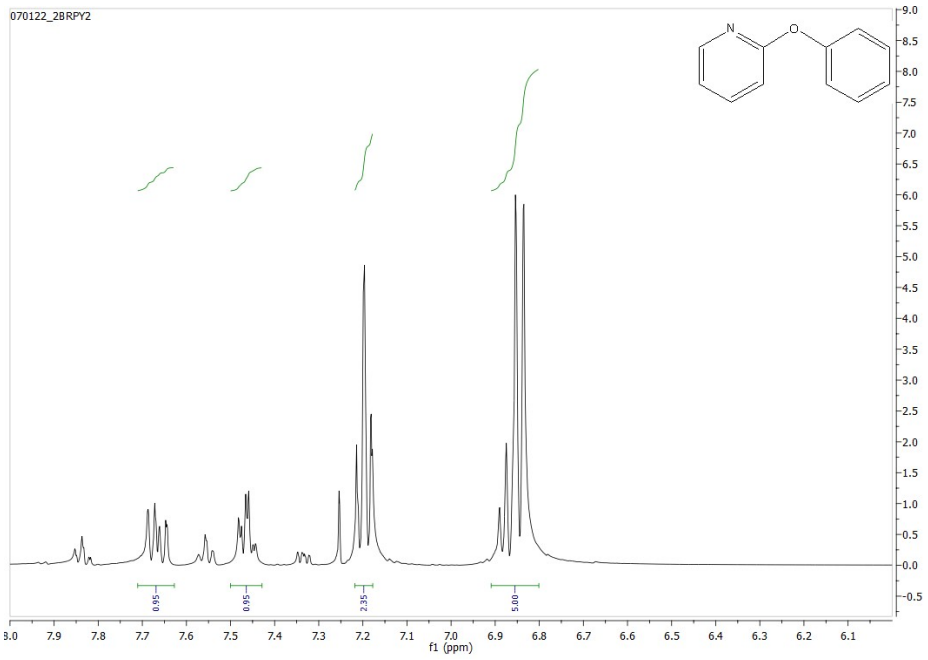


Fig. S29. ^{1}H NMR spectrum (scale: 6.0 to 8.0 ppm) of 2-pyridine phenylether

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