Support Information

Direct synthesis of N-Sulfenylimines through oxidative coupling of amines with disulfides/thiols over copper based metal-organic frameworks

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Additional Figures and Data

Figure S1. Nitrogen sorption isotherms of fresh *pcu*-MOF sample (squares) and used *pcu*-MOF sample (cycles) after five catalysis cycles at 77 K.

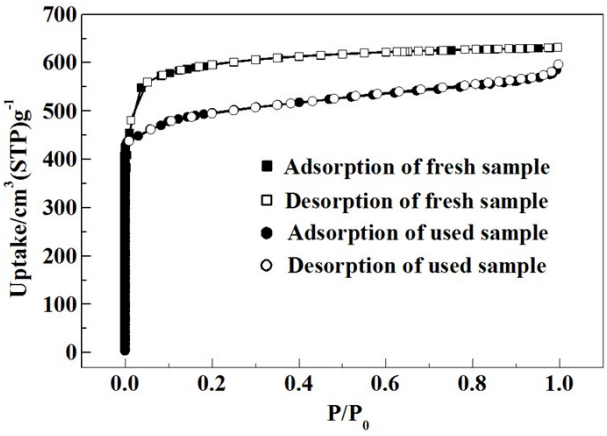


Figure S2. SEM images of fresh (a) and used (b) *pcu*-MOF samples after five catalysis cycles.

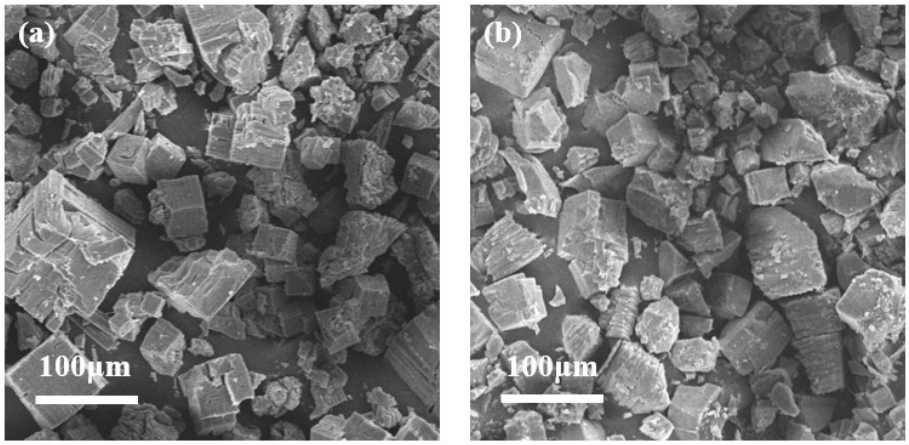


Figure S3. Thermogravimetric curve of the fresh *pcu*-MOF sample under N_2 atmosphere with a heating rate of 10 ^oC/min.

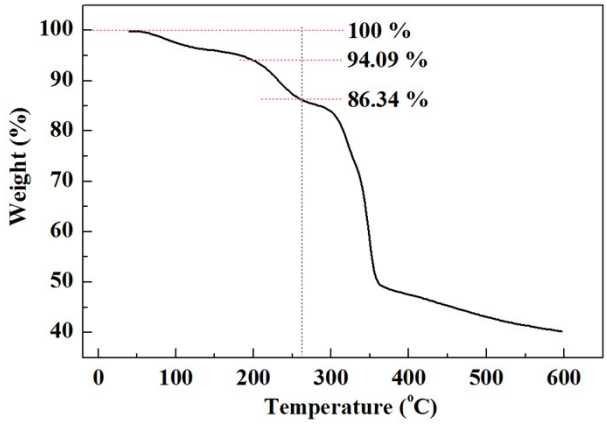


Figure S4. Nitrogen sorption isotherms of fresh CuBTC sample (Its BET surface area of CuBTC sample was 1295 m^2/g).

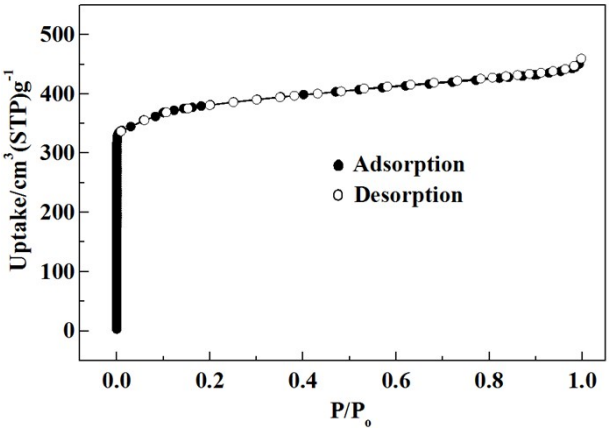


Figure S5. X-ray diffraction patterns of the as-synthesized CuBTC sample.

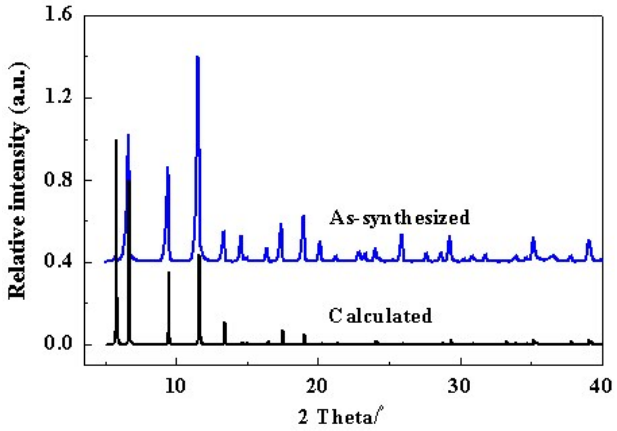


Figure S6. Continuous wave EPR spectra of pure *pcu*-MOF (a), *pcu*-MOF with 4-methoxybenzylamine (b) and *pcu*-MOF with diphenyldisulfide (c) at X-band at 90 °C.

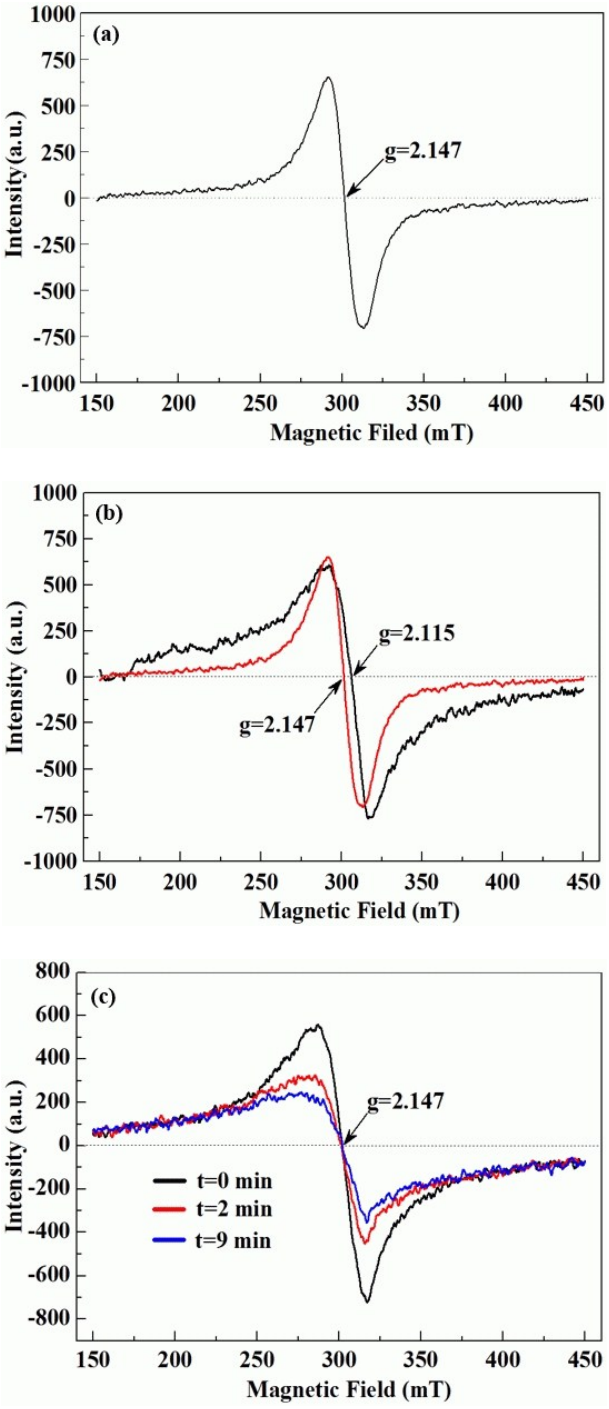
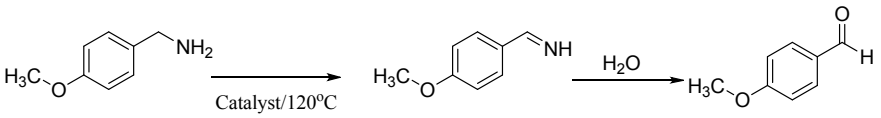


Table S1 Characterization results of fresh and used *pcu*-MOF samples after five catalysis cycles.

	S_{BET}(m^2/g)	V_{total}/cm^3/g	$D_{average}$/nm
Fresh *pcu*-MOF sample	2010	0.979	1.94
Used *pcu*-MOF sample	1743	0.929	2.13

Table S2 Oxidation of 4-methoxylbenzylamine *



Time	***pcu*-MOF + DTBN**§	***pcu*-MOF + TBD**§	***pcu*-MOF**§
4h	29	12	14
8h	53	25	27
12h	67	34	36
24h	95	59	60
36h	96	77	81

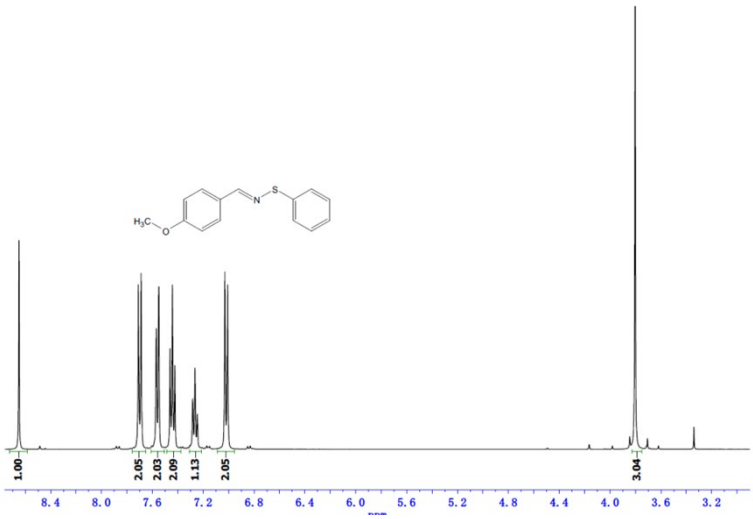
* Reaction condition: 4-methoxylbenzylamine (5 mmol), MOFs (0.125 mmol, based on copper), DTBN (0.5 mmol), or TBD (0.5 mmol), solvent (5 mL), for 18 h under O_2 atmosphere. § Yields of the 4-methoxylbenzylaldehyde.

Table S3 Coupling reaction of diphenylmethylimine and diphenyldisulfide over *pcu*-MOF *

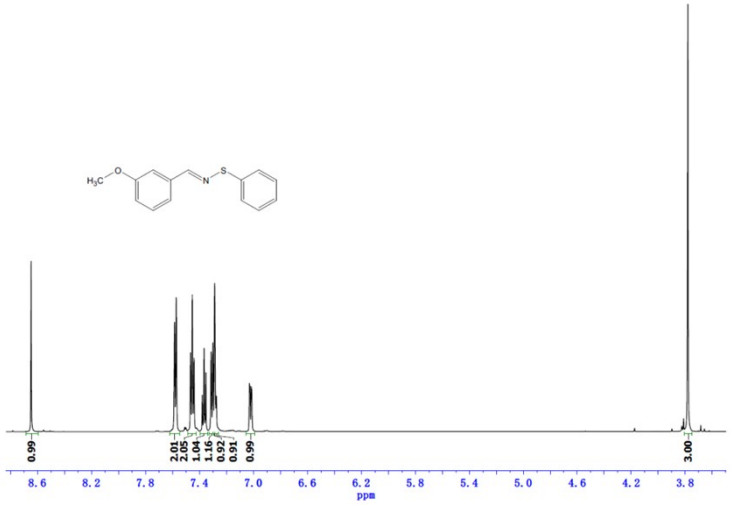
additive	DTBN	TBD	TBD + DTBN	TBD+ DTBN	No additive
Yield	57	59	65[a]	8[b]	5

* Reaction condition: Diphenylmethylimine (5 mmol), diphenyldisulfide (1.25 mmol), *pcu*-MOF (0.125 mmol, based on copper), DTBN (0.5 mmol), or TBD (0.5 mmol), solvent (5 mL), for 18 h under O_2 atmosphere. (a) DTBN (0.25 mmol) and TBD (0.25 mmol) were used; (b) The reaction was carried out under nitrogen atmosphere.

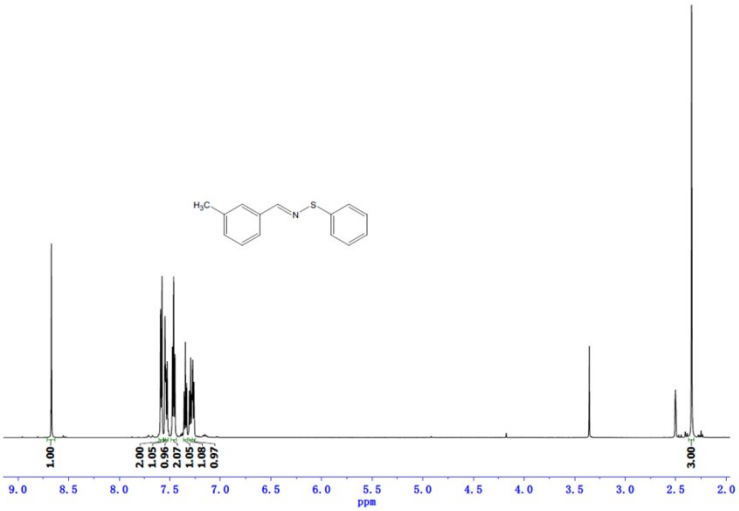
^{1}H-NMR figures of all products



N-(4-methoxybenzylidene)-S-phenylthiohydroxylamine



N-(3-methoxybenzylidene)-S-phenylthiohydroxylamine



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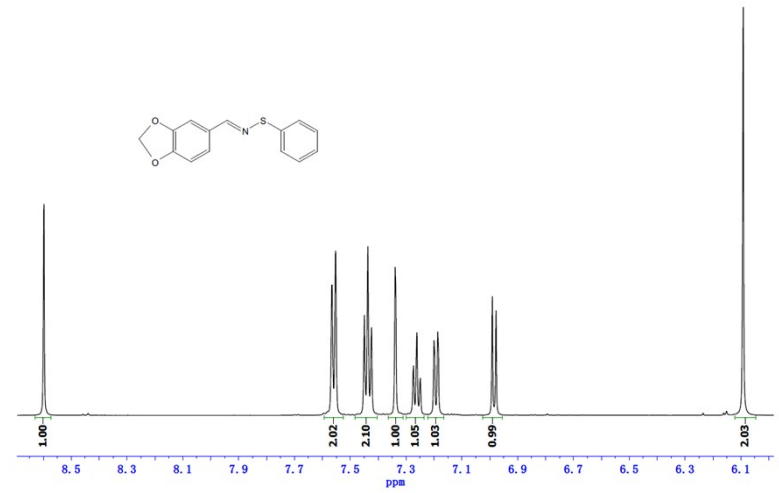
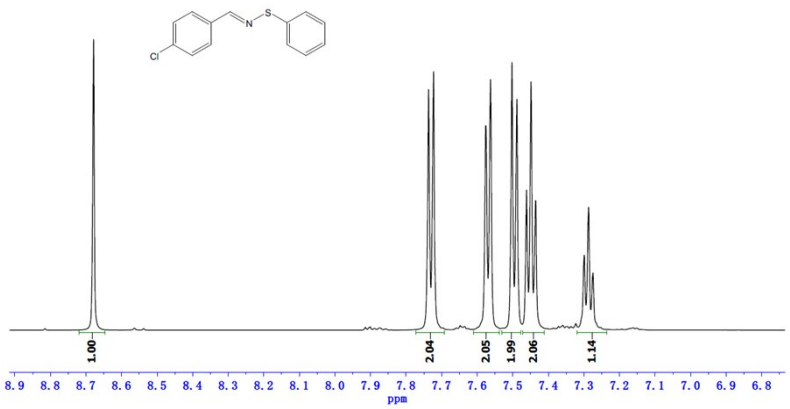
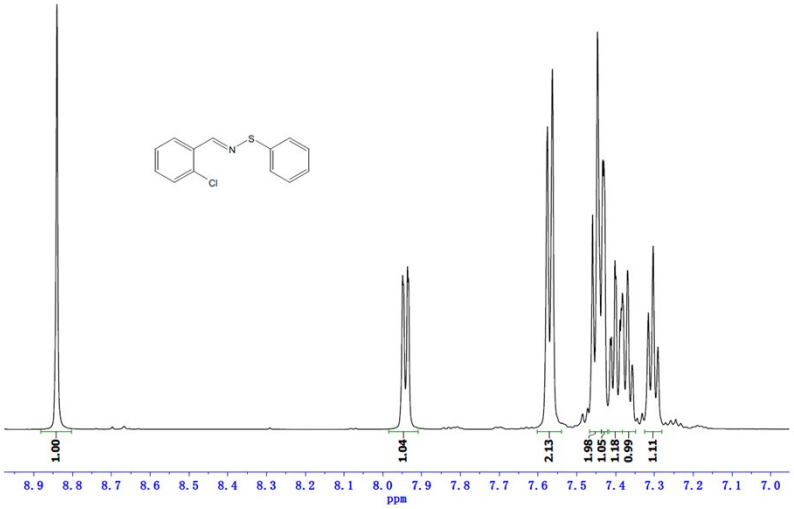


N-(benzo[d][1,3]dioxol-5-ylmethylene)-S-phenylthiohydroxylamine



N-(4-chlorobenzylidene)-S-phenylthiohydroxylamine



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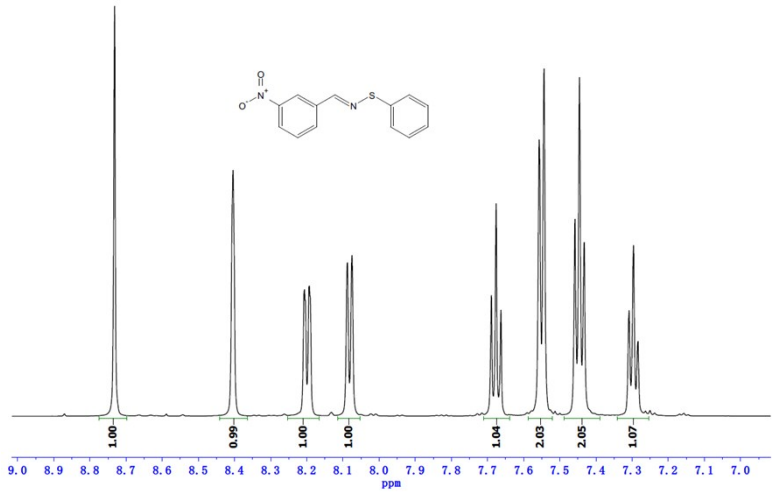

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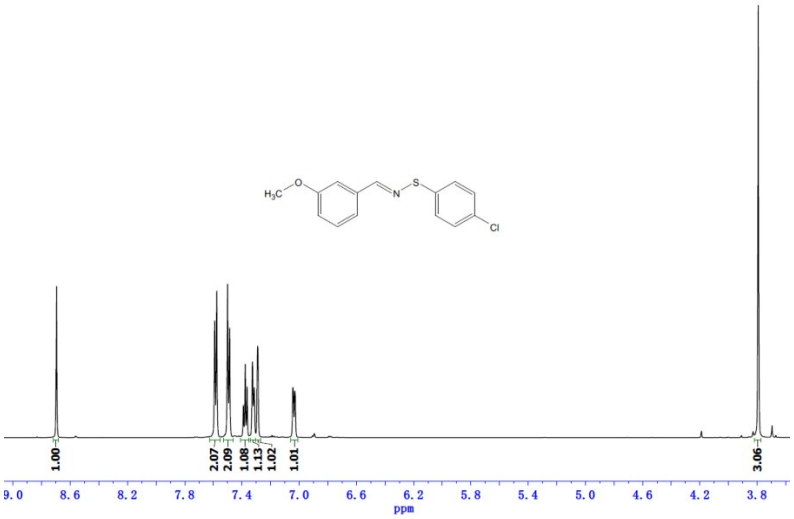

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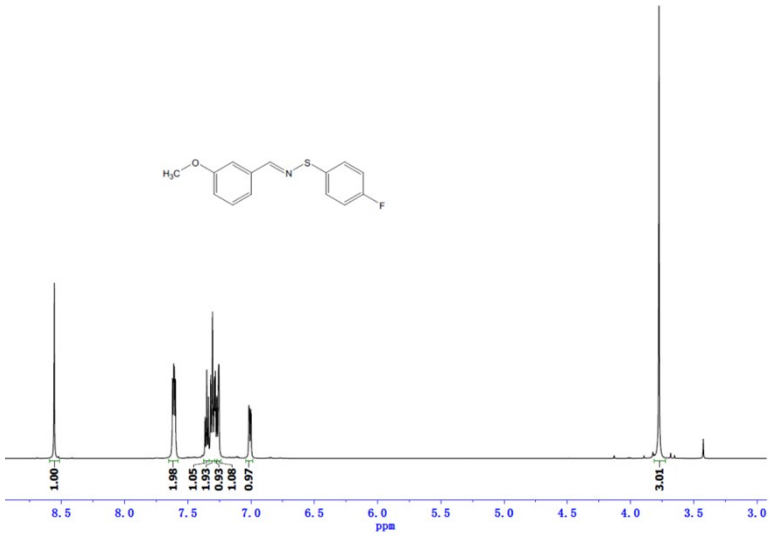

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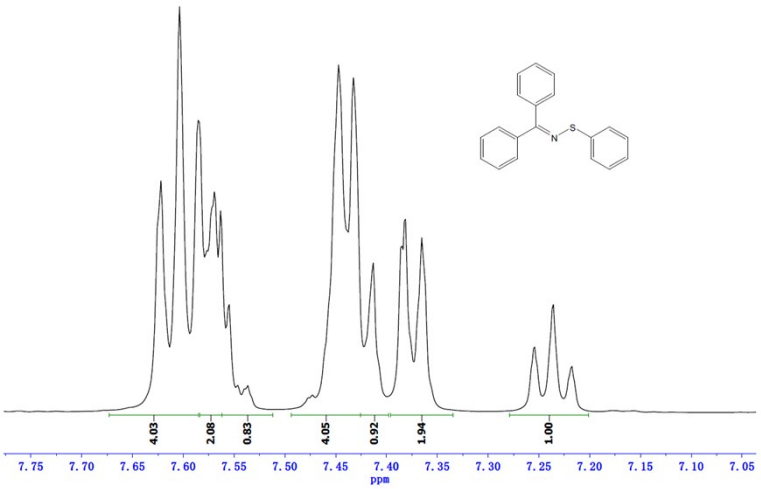
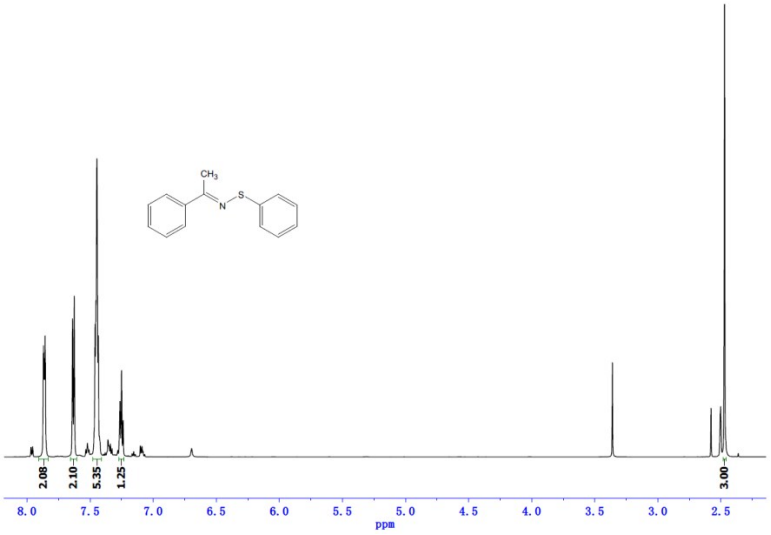
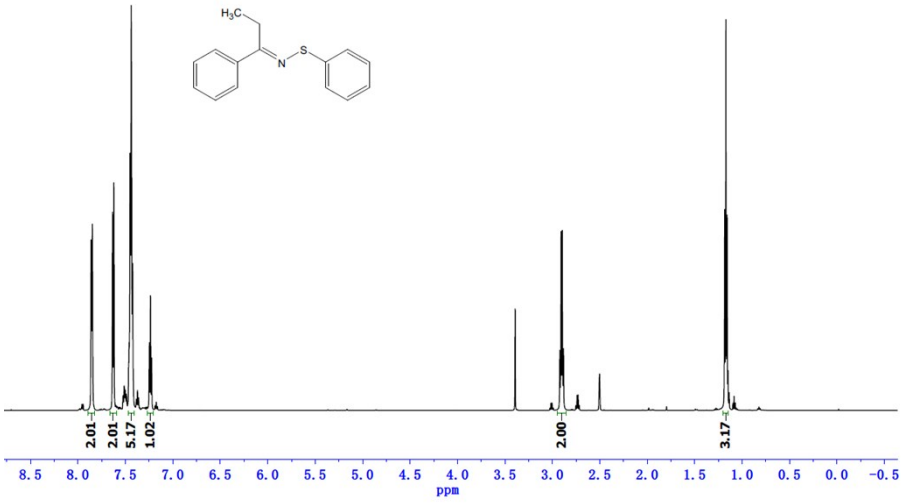


N-(diphenylmethylene)-S-phenylthiohydroxylamine



S-phenyl-N-(1-phenylethylidene)thiohydroxylamine



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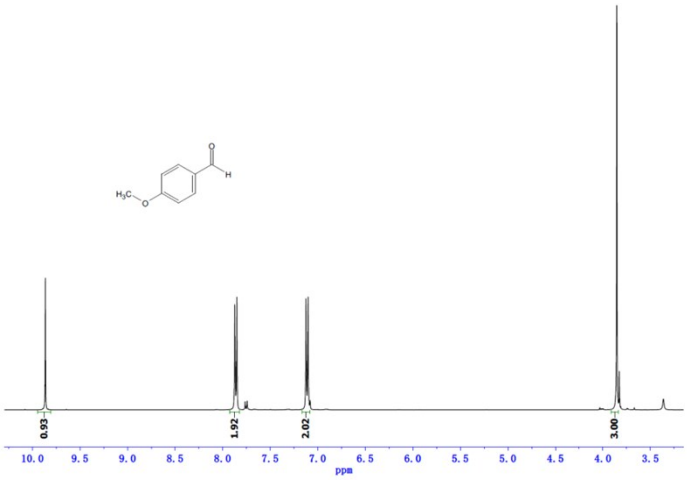
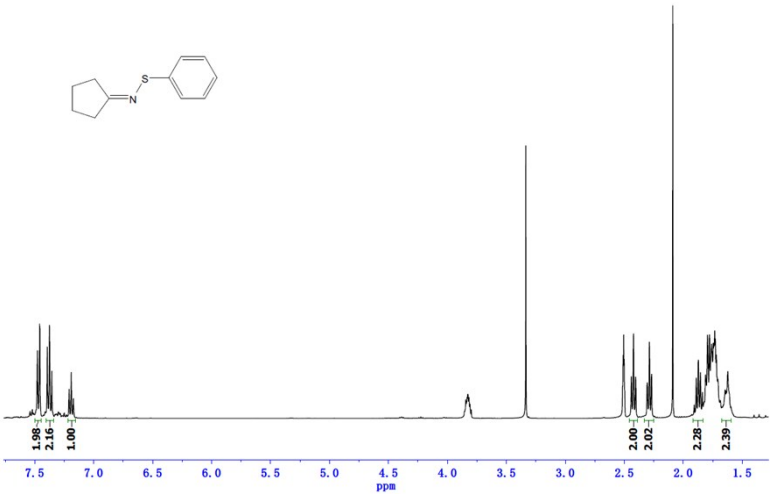
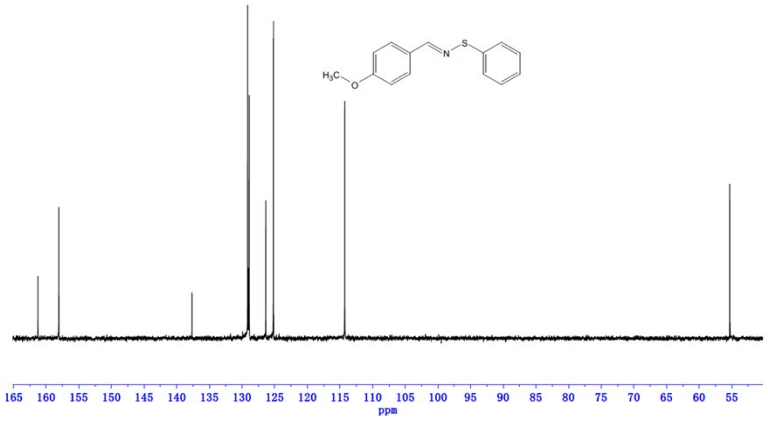


4-methoxybenzaldehyde



N-(cyclohexylidene)-S-phenylthiohydroxylamine

^{13}C-NMR figures of all products



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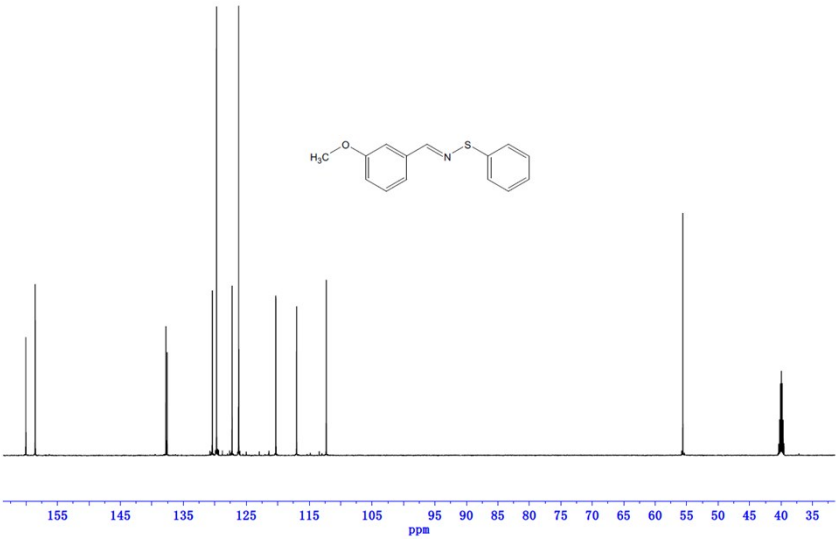
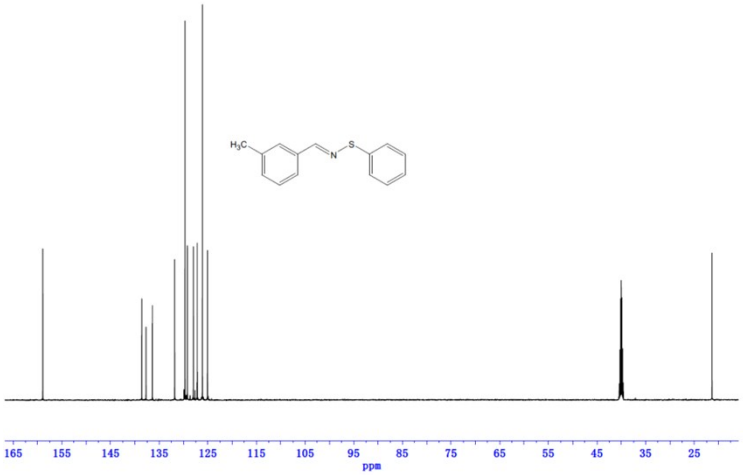


N-(3-methoxybenzylidene)-S-phenylthiohydroxylamine



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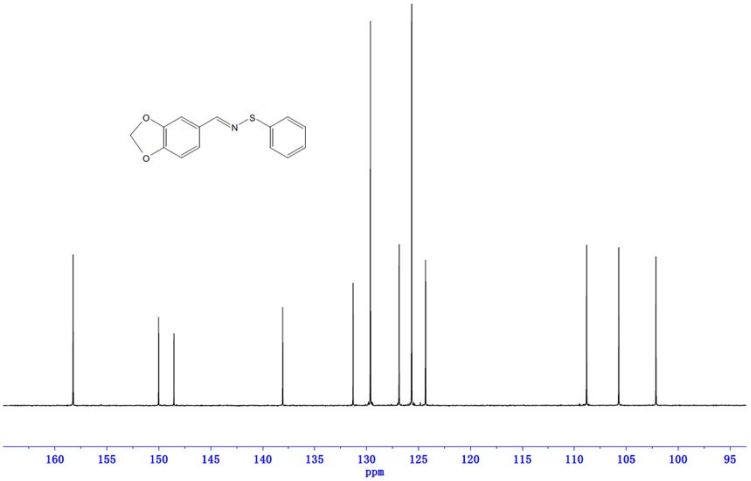
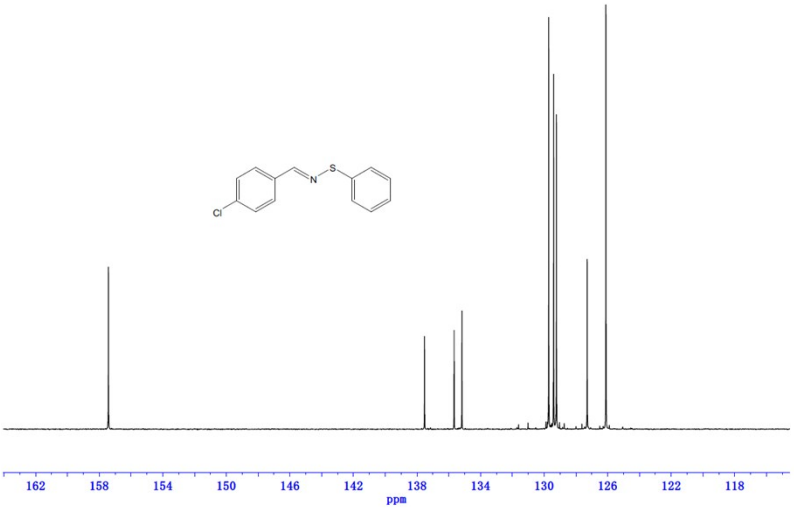


N-(benzo[d][1,3]dioxol-5-ylmethylene)-S-phenylthiohydroxylamine



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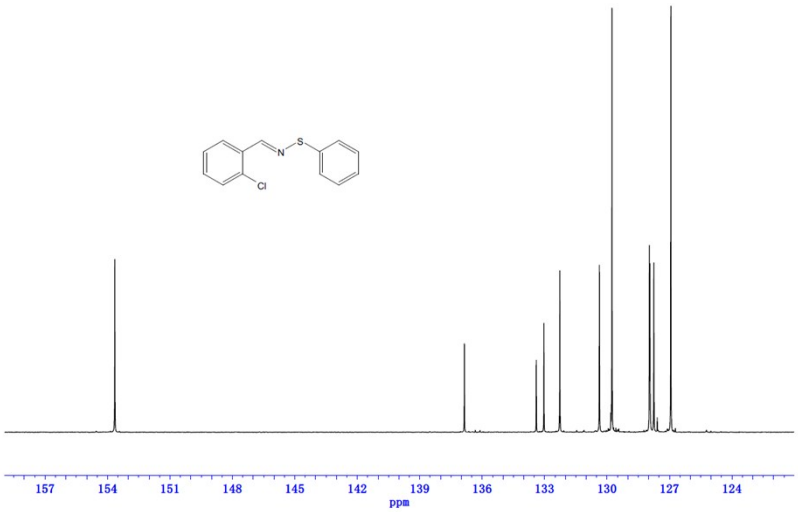

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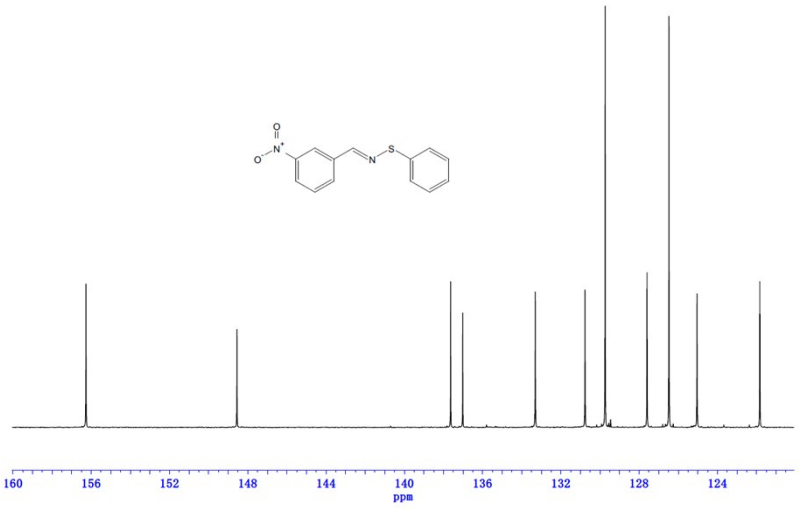

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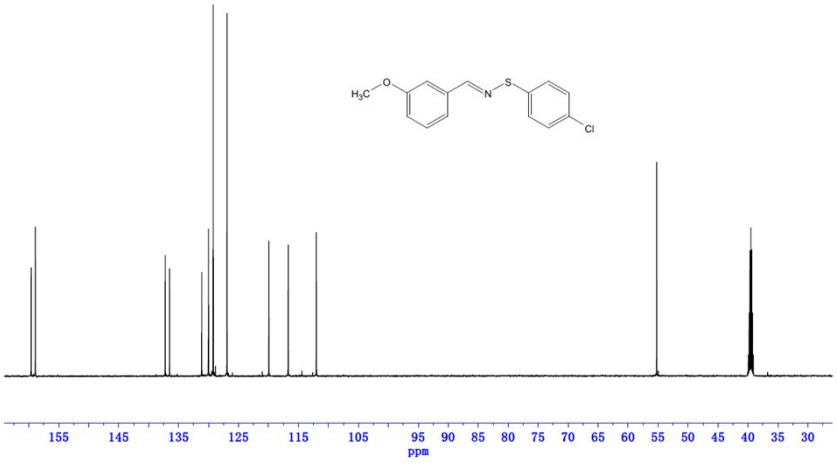

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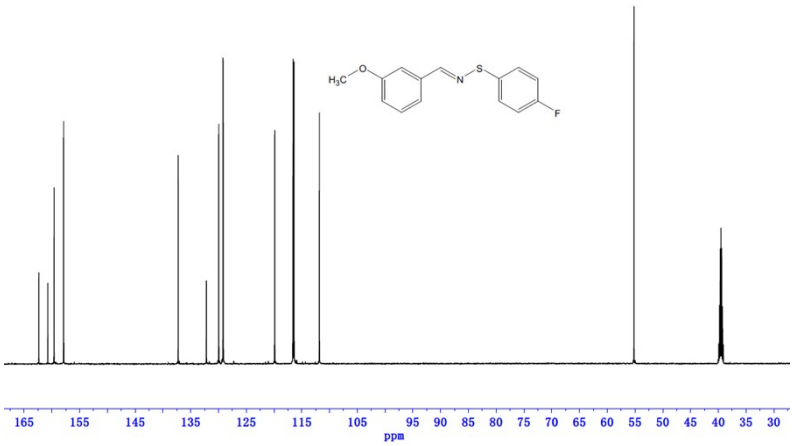

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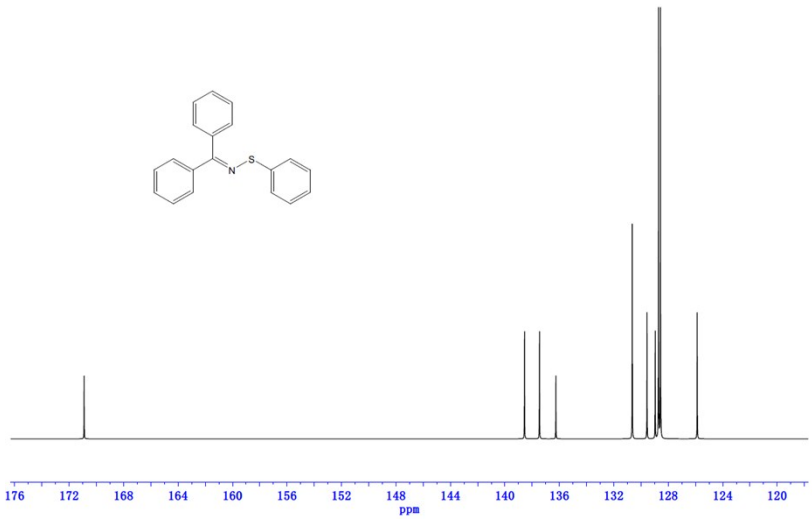
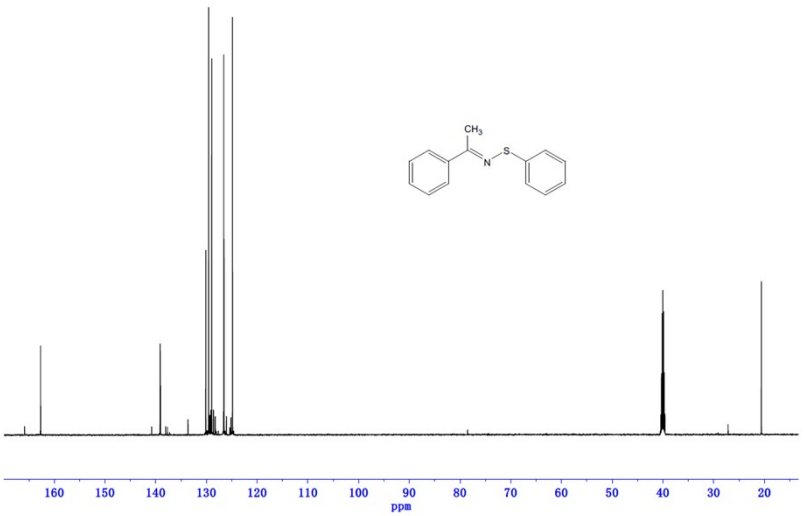
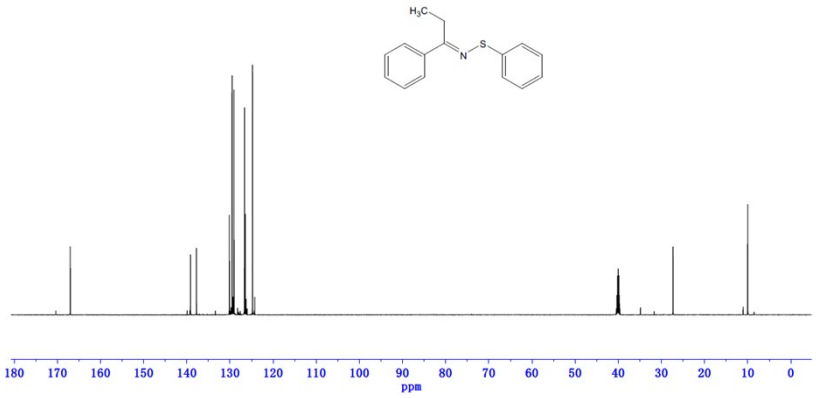


N-(diphenylmethylene)-S-phenylthiohydroxylamine



S-phenyl-N-(1-phenylethylidene)thiohydroxylamine



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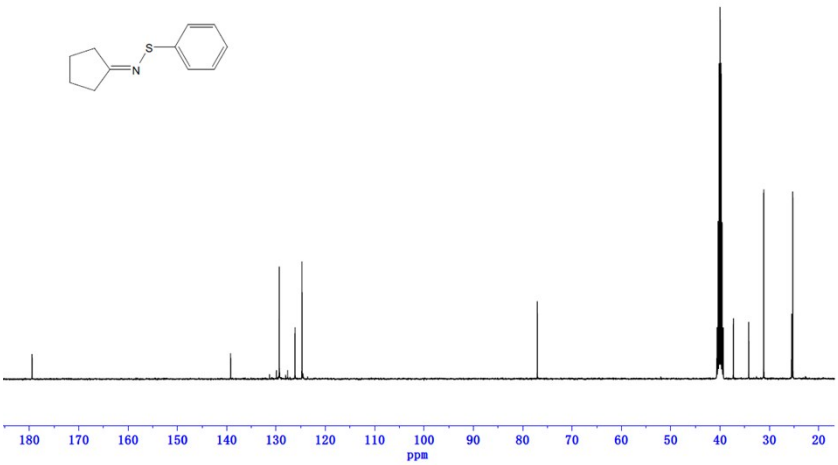

N-(cyclohexylidene)-S-phenylthiohydroxylamine