Carbocatalytic Synthesis of Azines by Oxidized Multiwalled Carbon Nanotubes

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Outline

Introduction and goal

Results

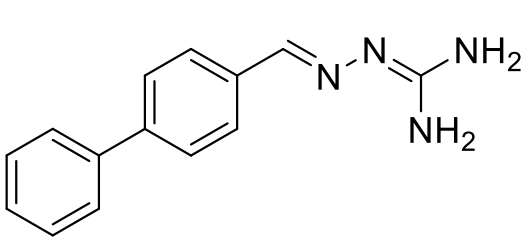
- Catalyst preparation
- Mechanistic Insights
- Scope and recycling

Conclusions

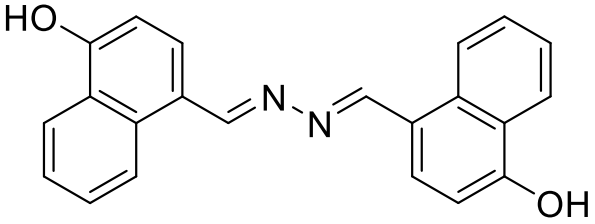
Acknowledgments

Introduction

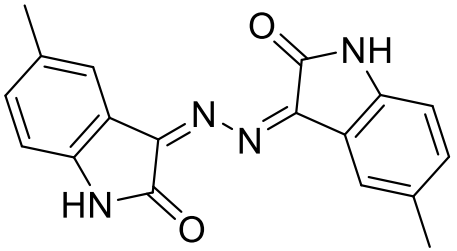
Azines (*N*-*N*-linked diimines) are very important organic molecules that find application in different fields:



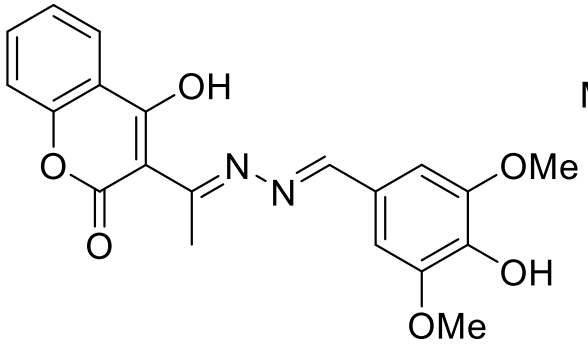
Antibacterial



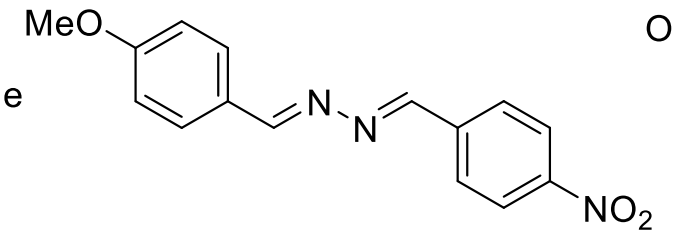
Antifungal



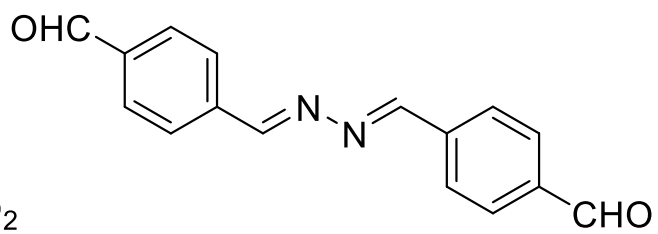
Anticancer



Antimicrobial



Nonlinear optics



Materials Building blocks

Org. Biomol. Chem., **2019**, *17*, 8486-8521.

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87 Fr Francium [223] | 8 O Oxygen 15.9994 | 7 N Nitrogen 14.0067 | 6 C Carbon 12.0107 | 85 At Astatine [210]

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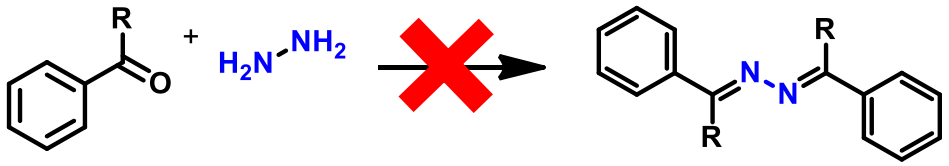
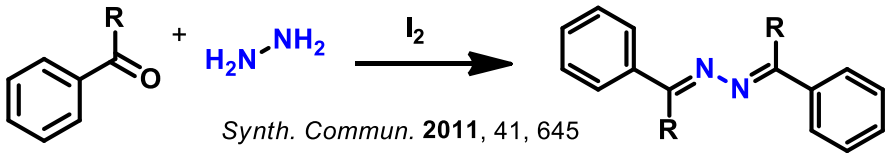
Introduction

Azines should be prepared by direct condensation between a carbonyl and hydrazine



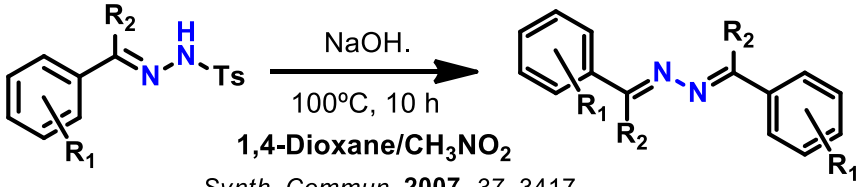
Instead of easy synthesis, harsh conditions are required for azine synthesis:

Iodine mediated



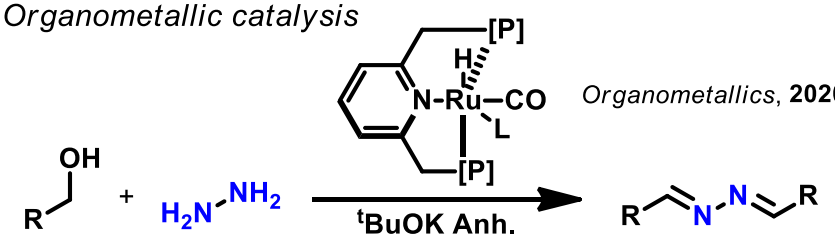
Synth. Commun. **2011**, 41, 645

Base mediated



Synth. Commun. **2007,** *37*, 3417

Organometallic catalysis



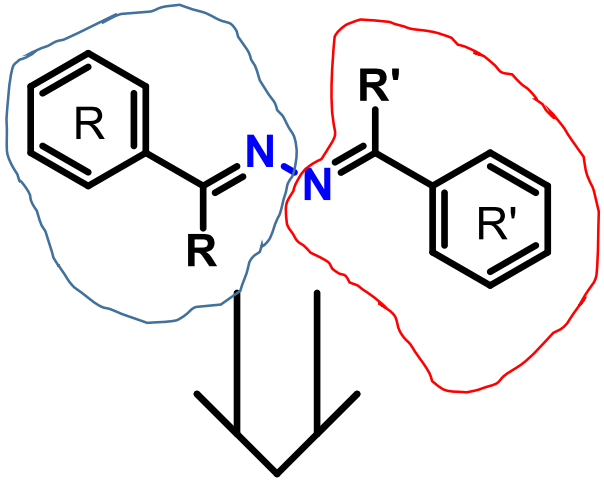
Organometallics, **2020**, *39*, 3194.

(or Ni-pincer complex) *Catal. Commun.*, **2019**, 124, 19

- Toxic byproducts
- Harsh conditions
- Lack of general methods

Introduction

Each azine requires specific synthetic conditions:



R = R' → One specific set of conditions

R ≠ R' → Different set of conditions

Org. Biomol. Chem., **2019**, *17*, 8486-8521.

Would be desiderable to develop a general method

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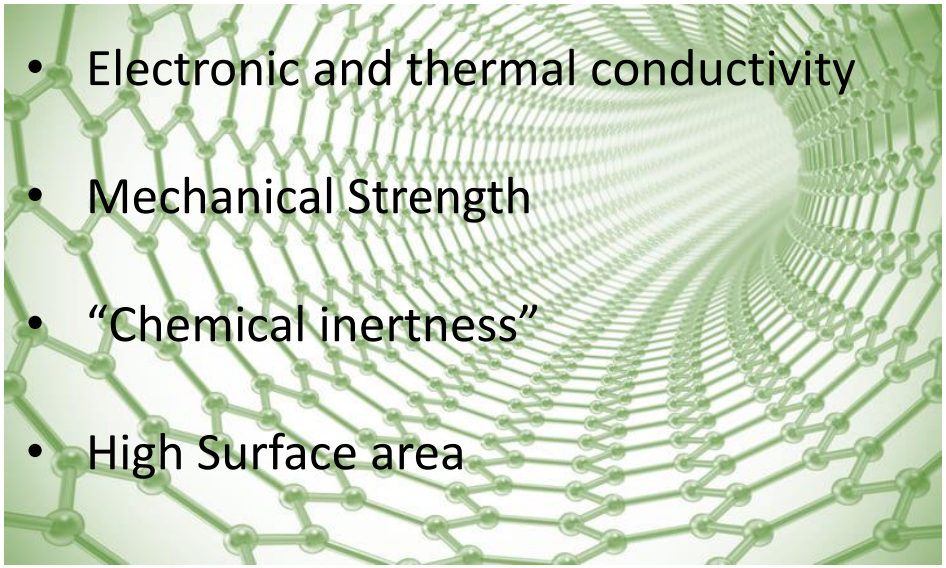
Introduction

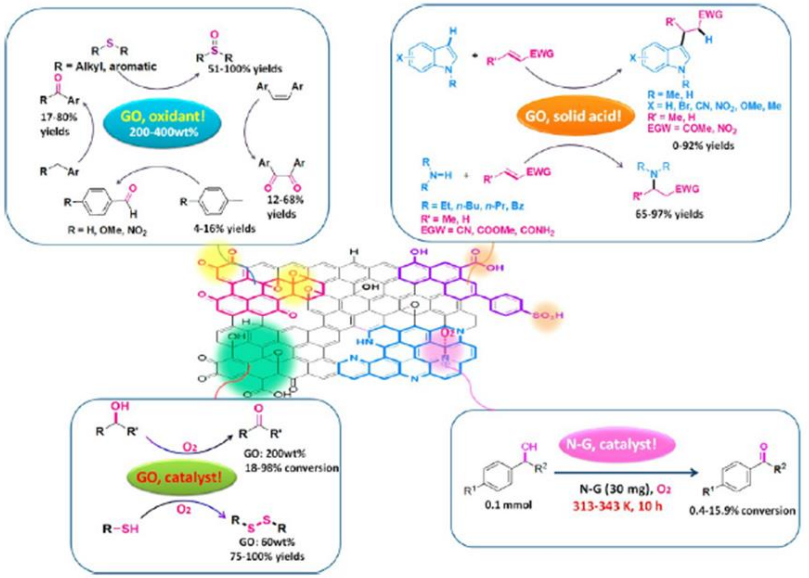
Carbon nanomaterials



- Electronic and thermal conductivity
- Mechanical Strength
- "Chemical inertness"
- High Surface area

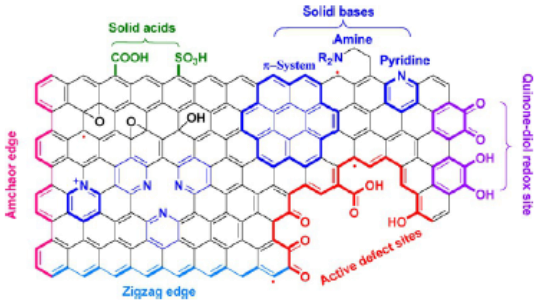
Materials Science and Engineering: R: Reports **2004**, *43*, 61-102

Carbon nanomaterials as carbocatalysts



Acc. Chem. Res. **2013**, *46*, 2275

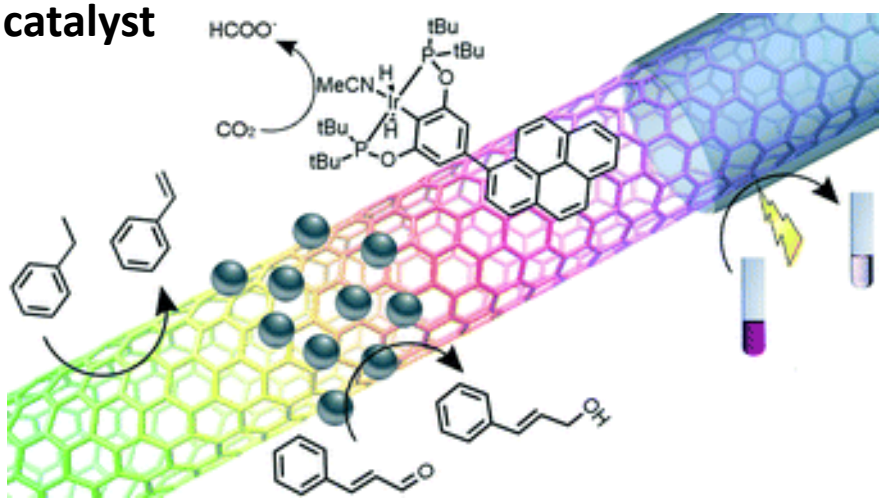
Main catalyst: **Graphene oxide**



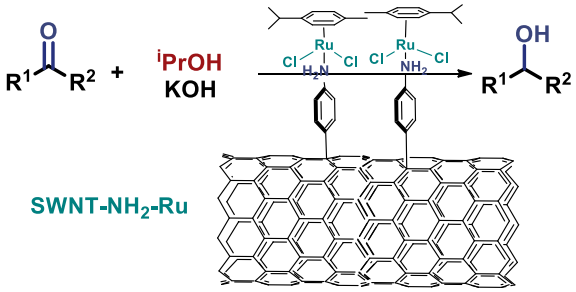
ECSOC 26

Introduction

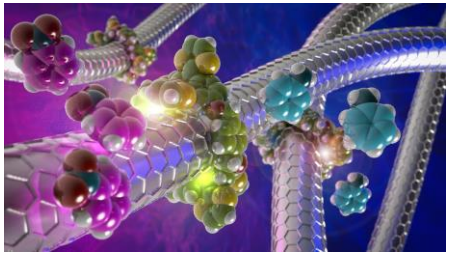
Carbon nanotubes as catalyst



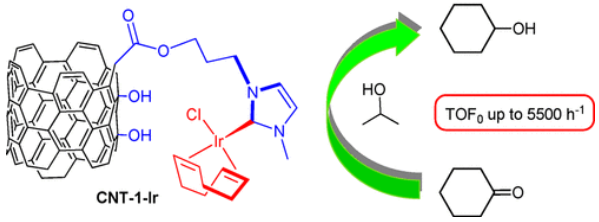
Catal. Sci. Technol., **2015**, *5*, 3859



ChemCatChem **2021,** *13,* 5156-5165



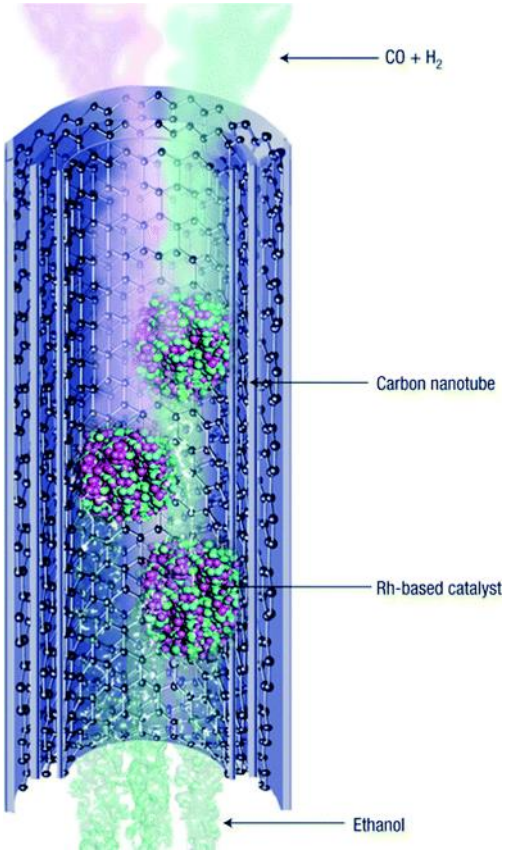
Nat Commun **2018**, *9,* 2671



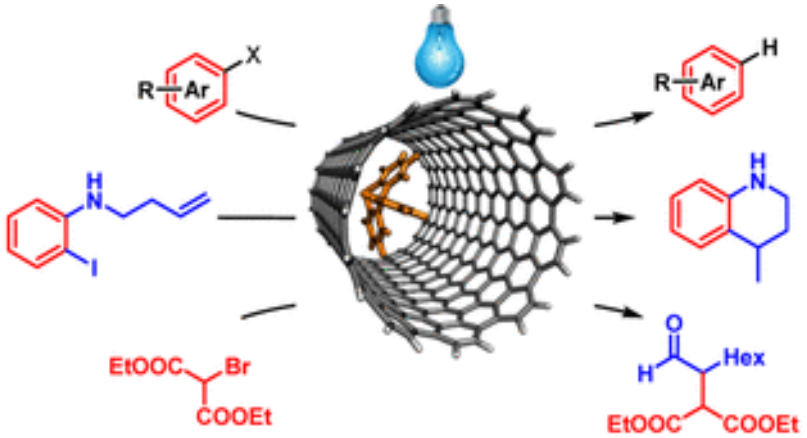
ACS Catal. **2013**, *3*, 1307

Introduction

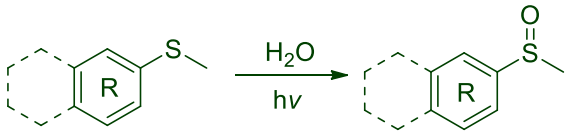
Carbon nanotubes as catalyst

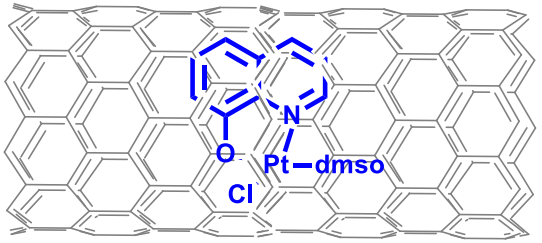


Catal. Sci. Technol., **2015**, 5, 3859



ACS Appl. Mater. Interfaces **2021**, *13*, 24877

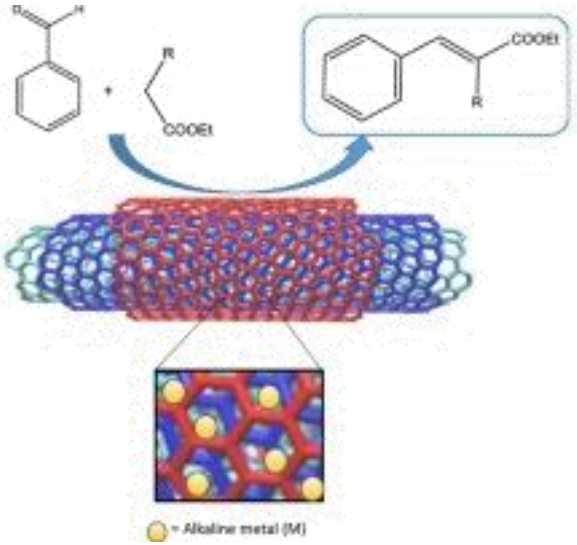




J. Catal. **2022**, *413*, 274

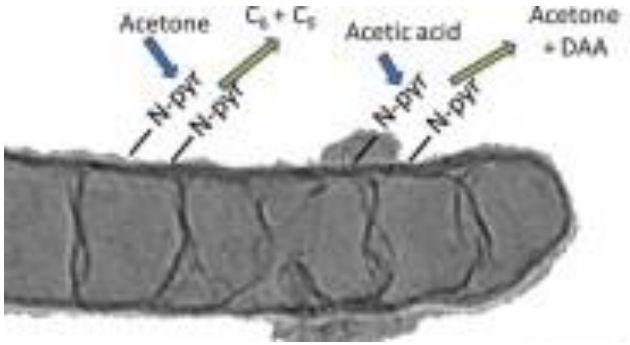
Introduction

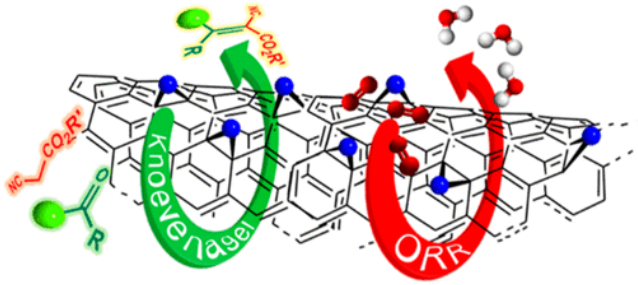
Carbon nanotubes as carbocatalyst



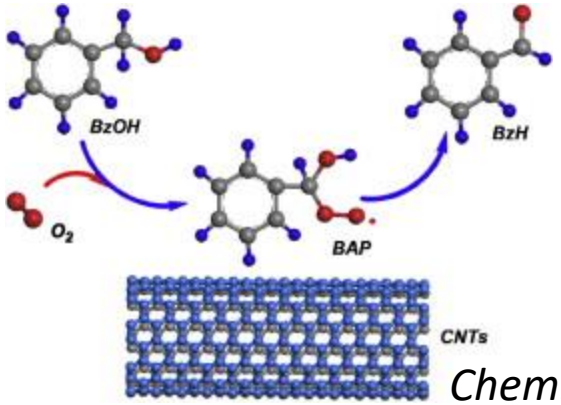
Molecular Catal. **2017,** *443*, 101

Appl. Catal. A. **2013**, *458*, 155





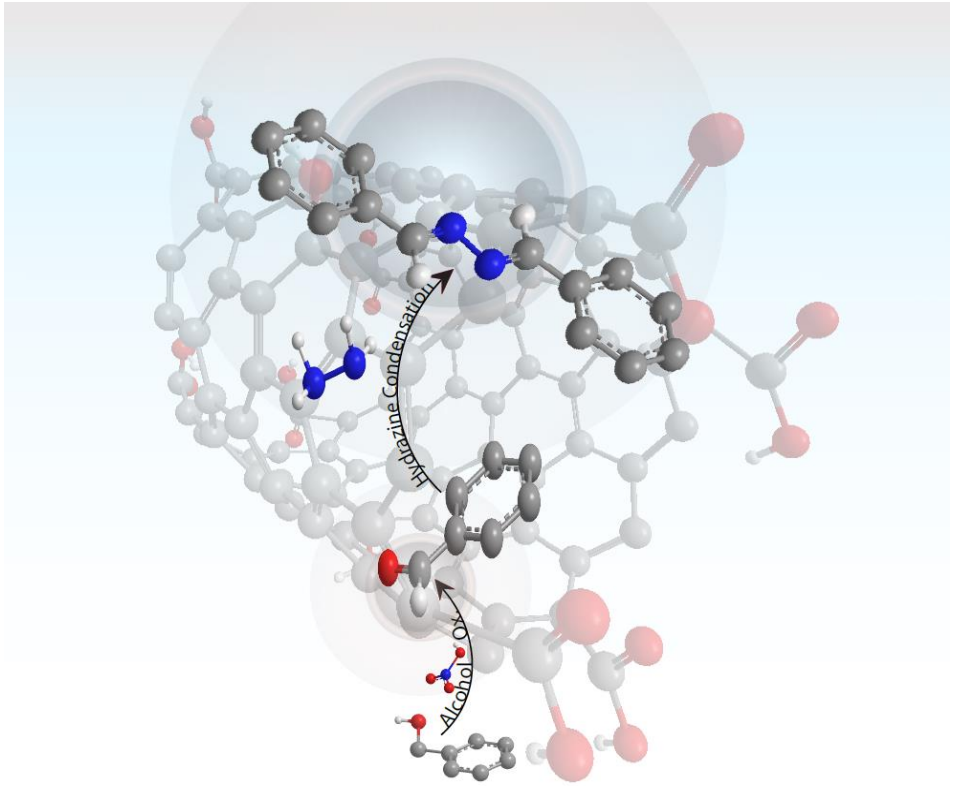
ACS Appl. Mater. Interfaces **2016**, *8*, 30099



Chem. Eng. J. **2014**, *240*, 434

Goal

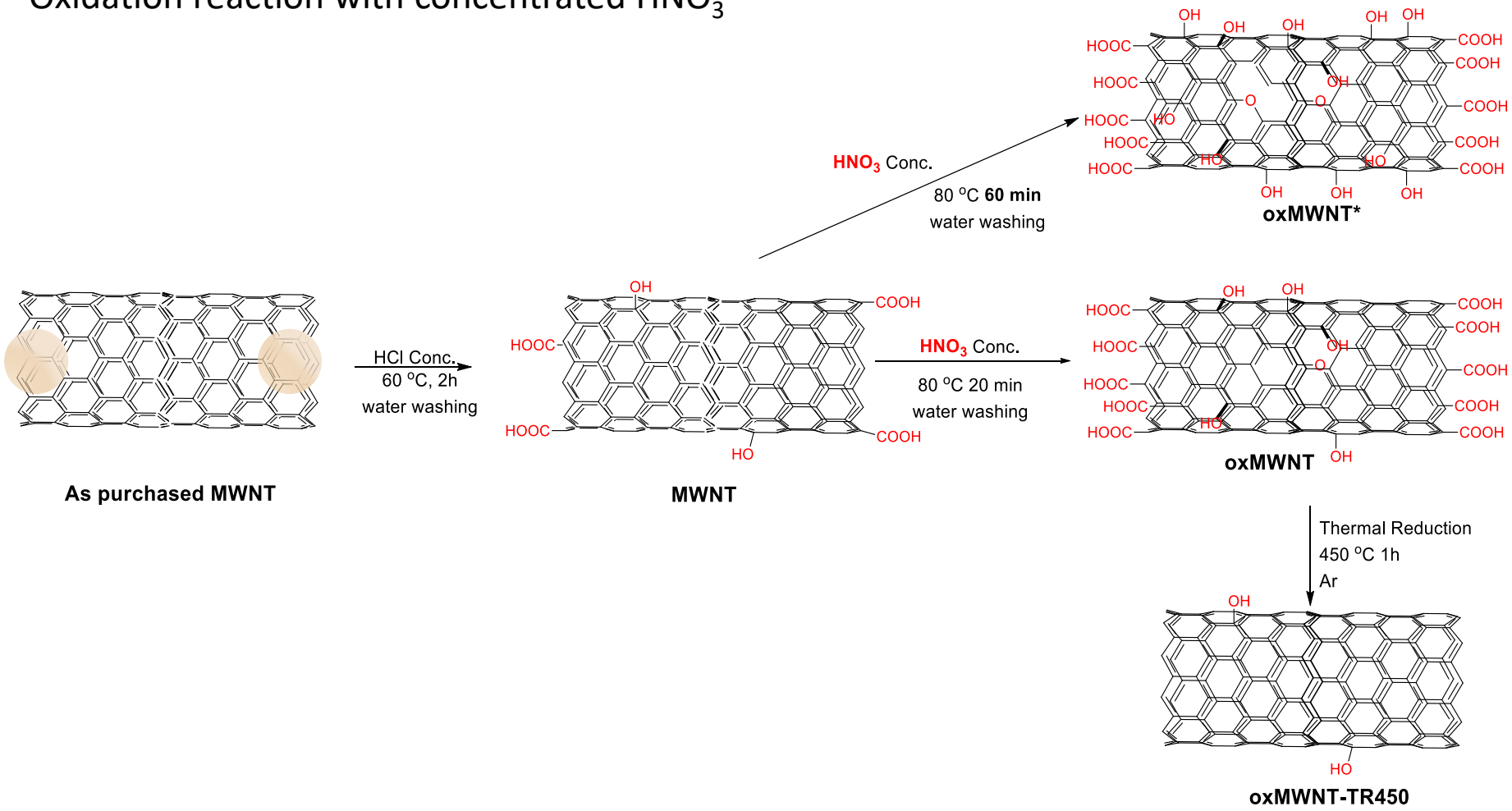
Develop a nanotube-based catalyst able to carry out condensation reactions to yield azines in a milder and more efficient fashion.



J. Catal. **2022**, *406*, 174

Results: Catalyst preparation

Oxidation reaction with concentrated HNO_3



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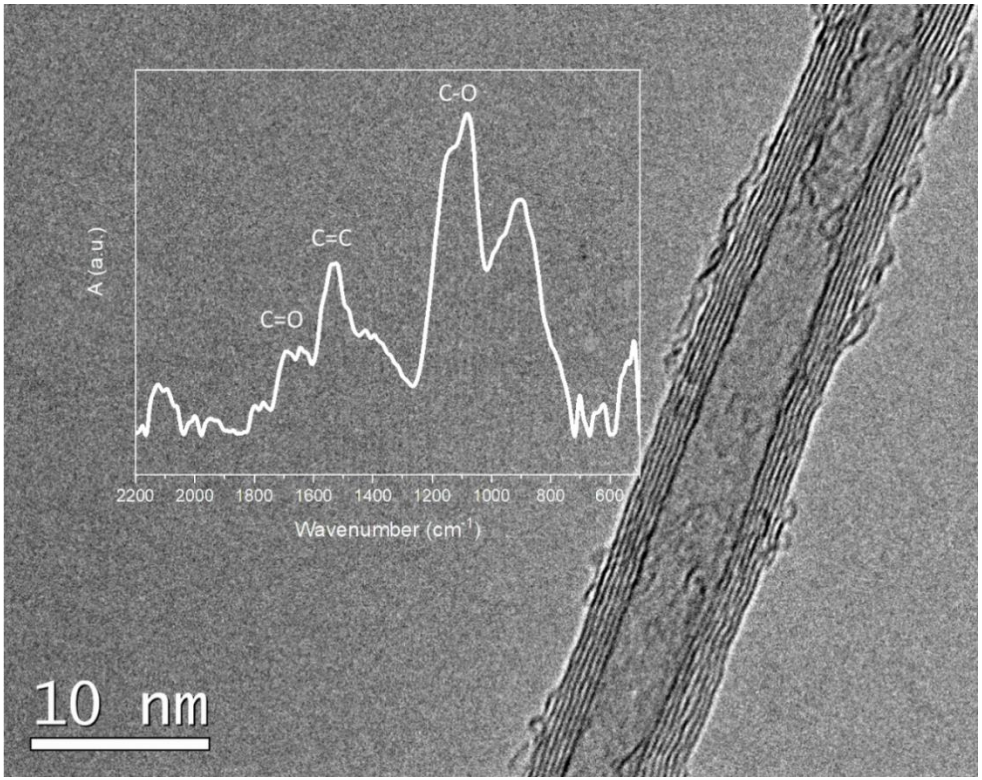
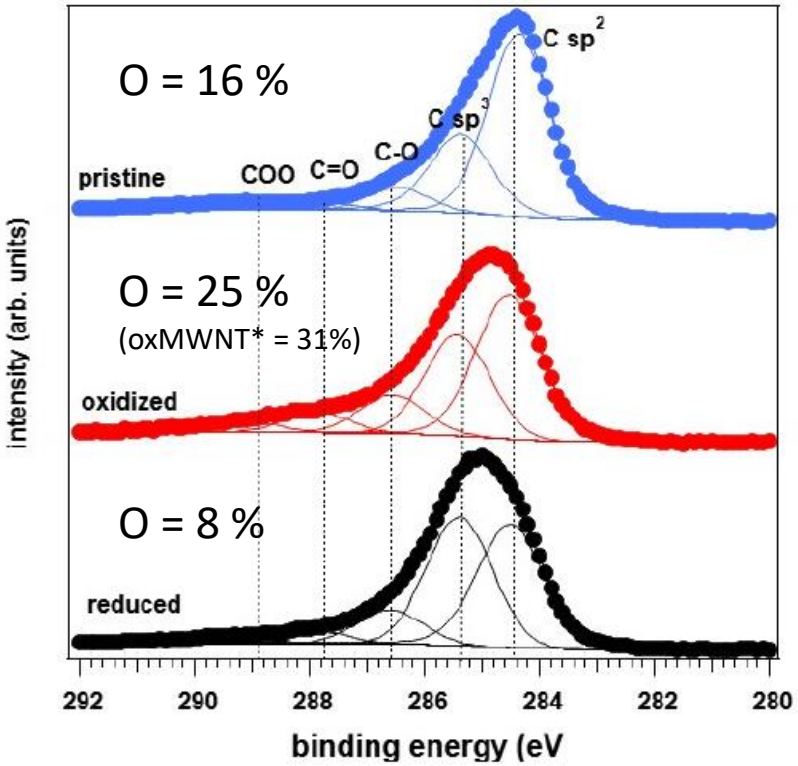
Results: Catalyst preparation

Characterization





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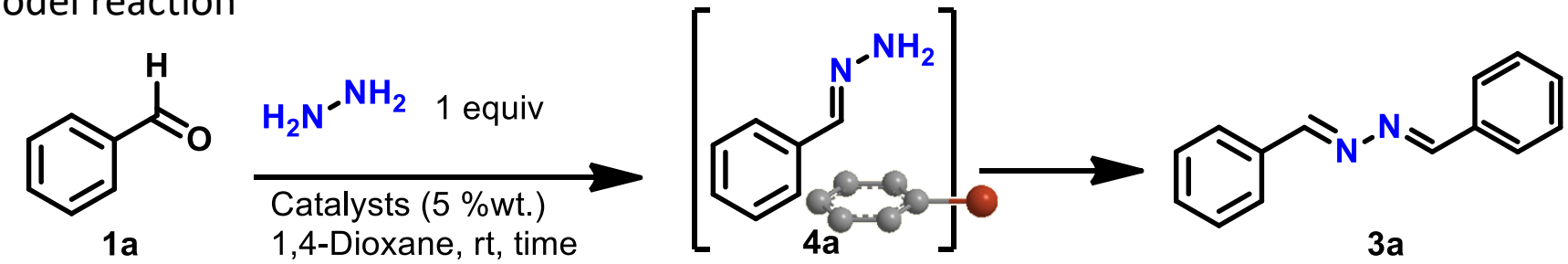
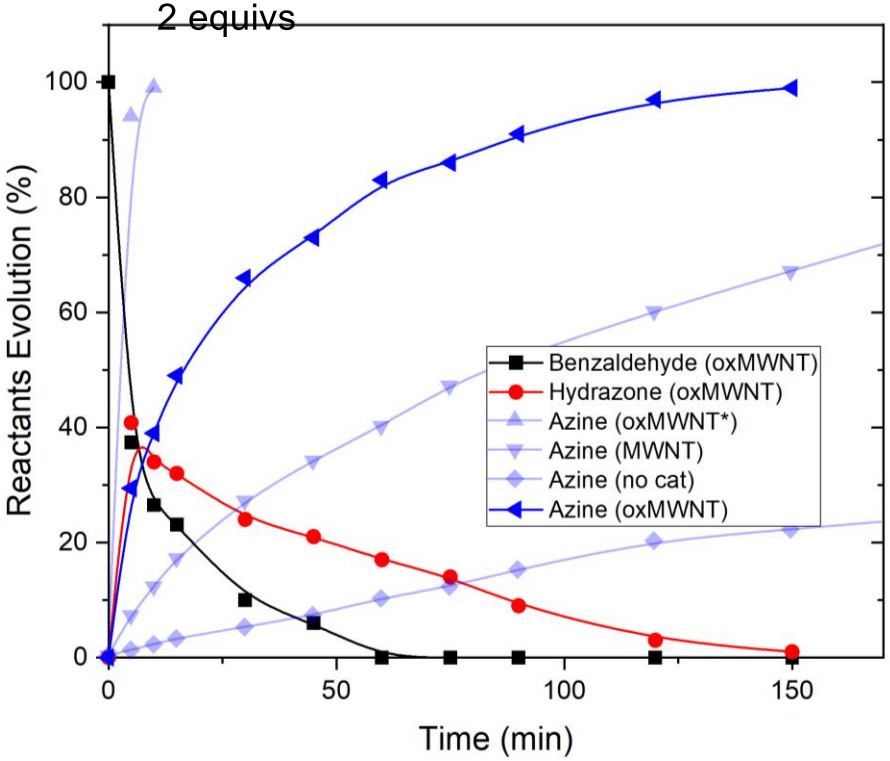
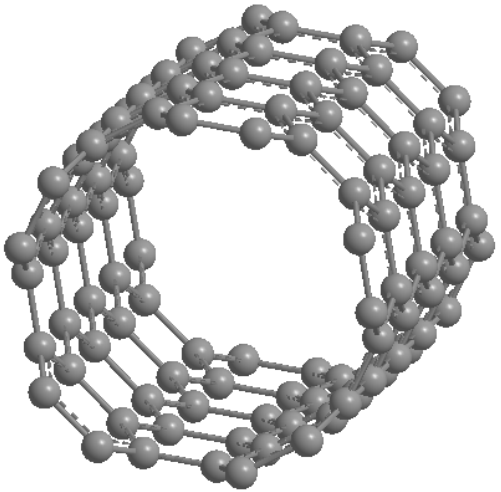
Results: Mechanistic Insights

Model reaction



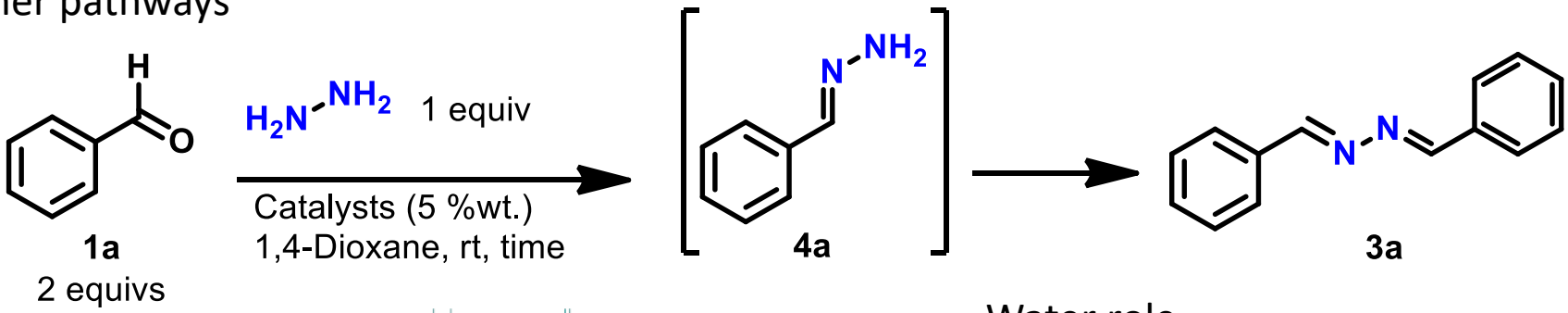


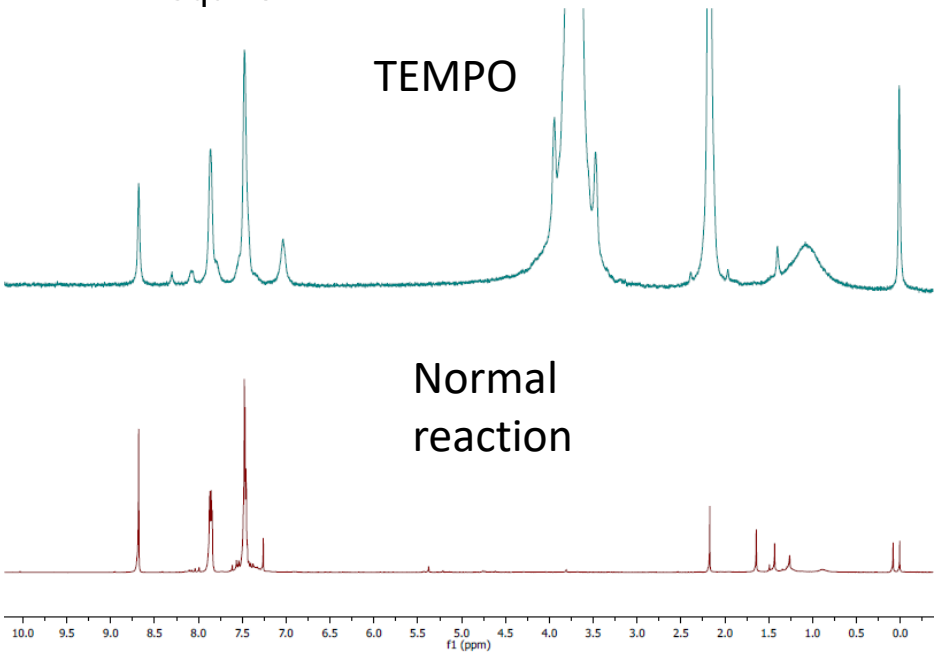


Surface version of classic condensation

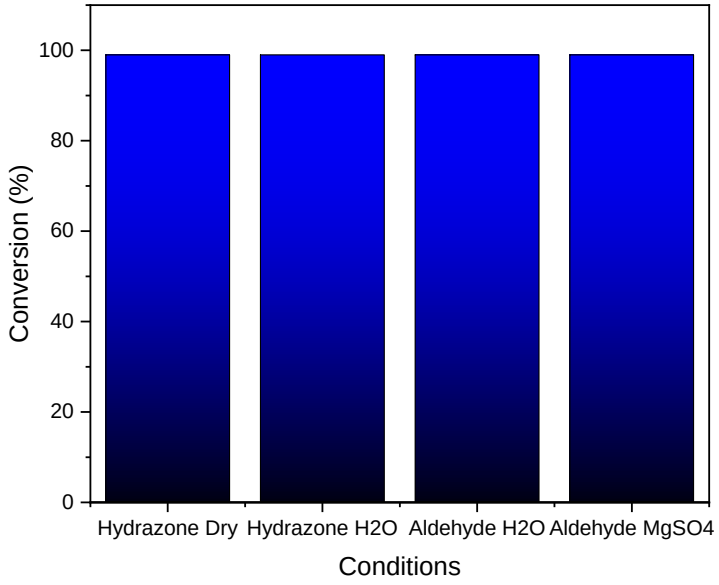
Results: Mechanistic Insights

Other pathways

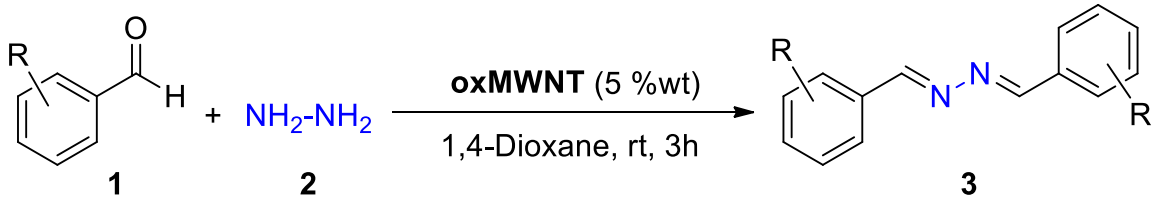




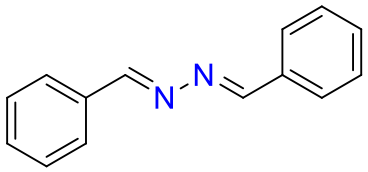
Water role



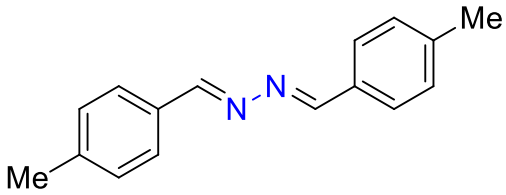
Results: Scope (symmetric azines)



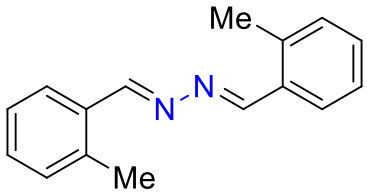
1 2 3



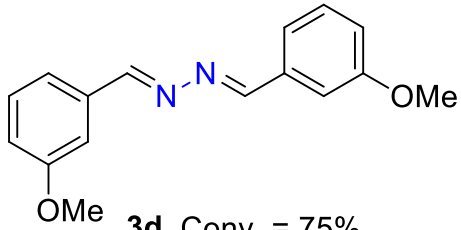
3a, Conv. > 99%
Yield = 93%
Yield* = 85%



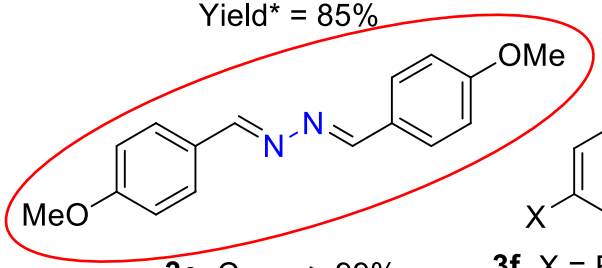
3b, Conv. > 99%
Yield = 89%



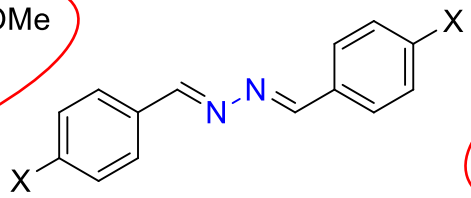
3c, Conv. = 93%
Yield = 89%



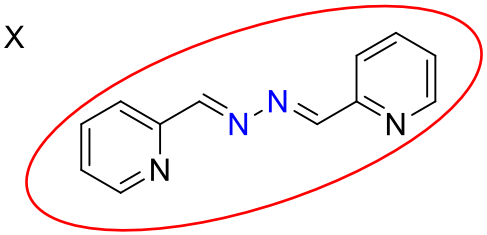
3d, Conv. = 75%
Yield = 61%



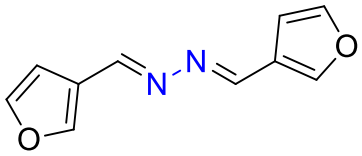
3e, Conv. > 99%
Yield = 92%
Yield* = 84%



3f, X = F (Conv.>99%,Yield = 94%),
3g, X =Cl (Conv.>99%,Yield = 95%),
3h, X = Br (Conv.>99%,Yield = 91%)

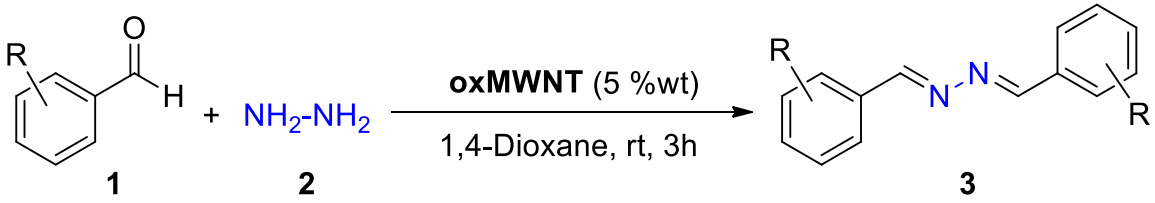


3i, Conv. > 99%
Yield = 92%
Yield* = 87%

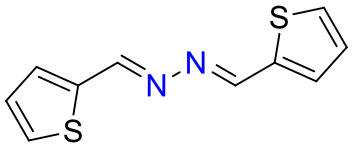


3j, Conv. > 99%
Yield = 87%

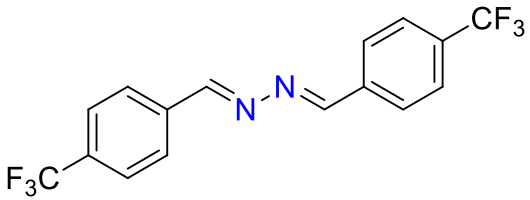
Results: Scope (symmetric azines)



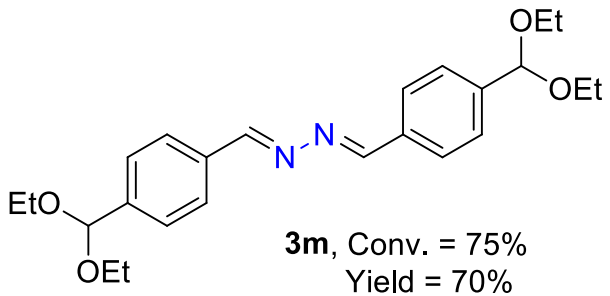
1 2 3



3k, Conv. > 99%
Yield = 96%

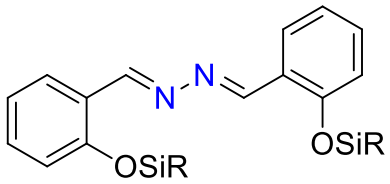


3l, Conv. = 21%

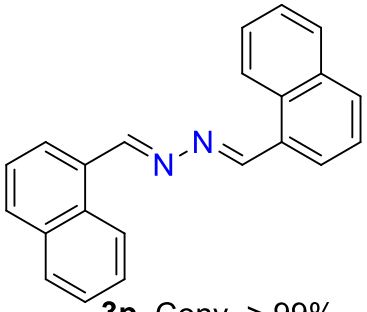


3m, Conv. = 75%
Yield = 70%

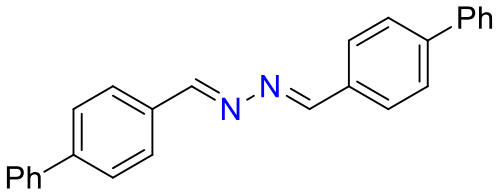
Protected Building block target for materials crafting



3n, R = TIP (Conv.>99%,Y=94%),
3o, R = TBDP (Conv.>99%,Y=89%)



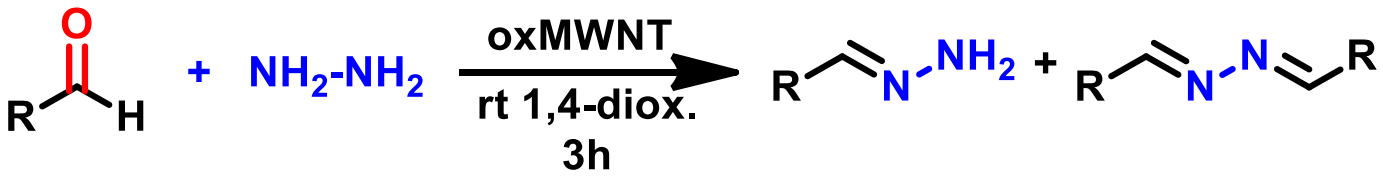
3p, Conv. > 99%
Yield = 84%



3q, Conv > 99%
Yield = 93%

Results: Scope (symmetric azines)

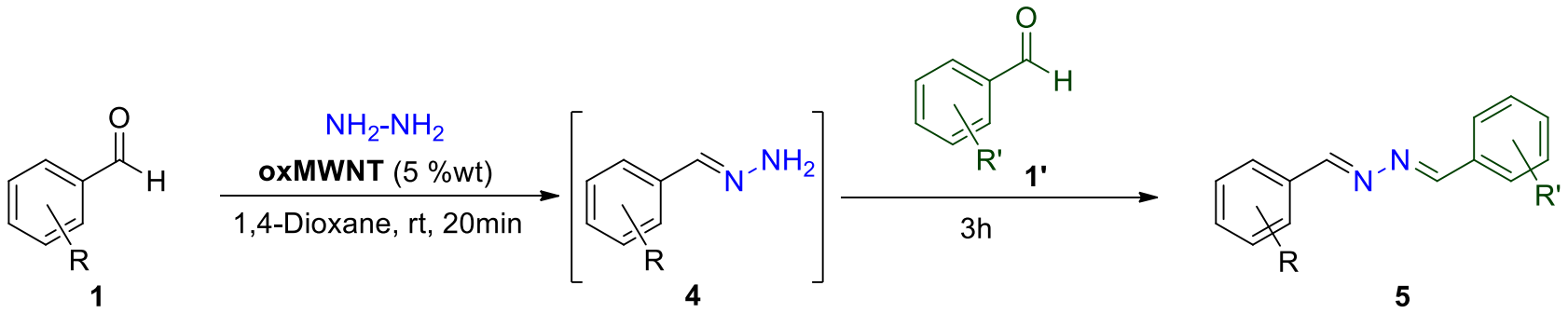
Aliphatic substrates

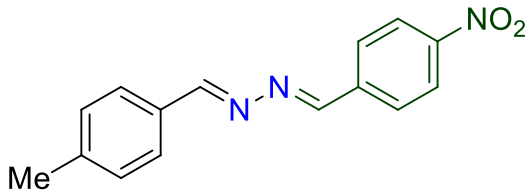


R	% Hydrazone[b]	% Azine[b]
Propyl	>99	<1
Butyl	98	2
Pentyl	>99	<1
Tert-butyl	>99	<1

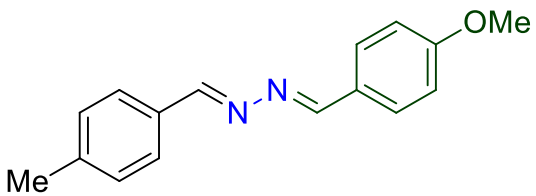
Low affinity by π-interactions with the nanotube: **Bulk reaction**

Results: Scope (asymmetric azines)

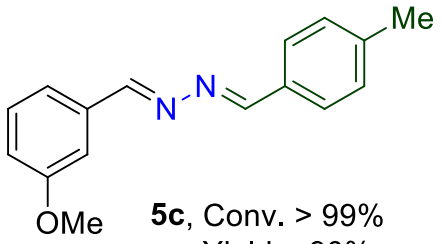




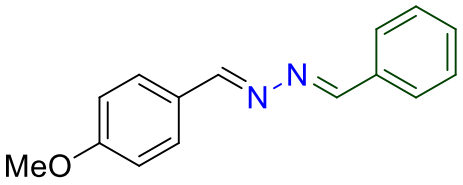
5a, Conv. > 99%
Yield = 88%



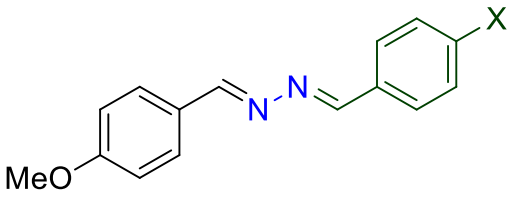
5b, Conv. > 99%
Yield = 91%



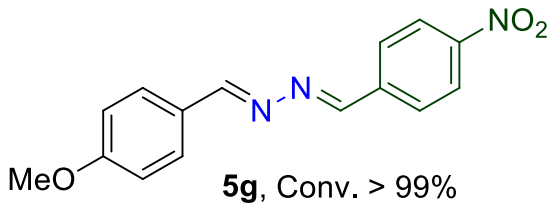
5c, Conv. > 99%
Yield = 90%



5d, Conv. > 99%
Yield = 40%



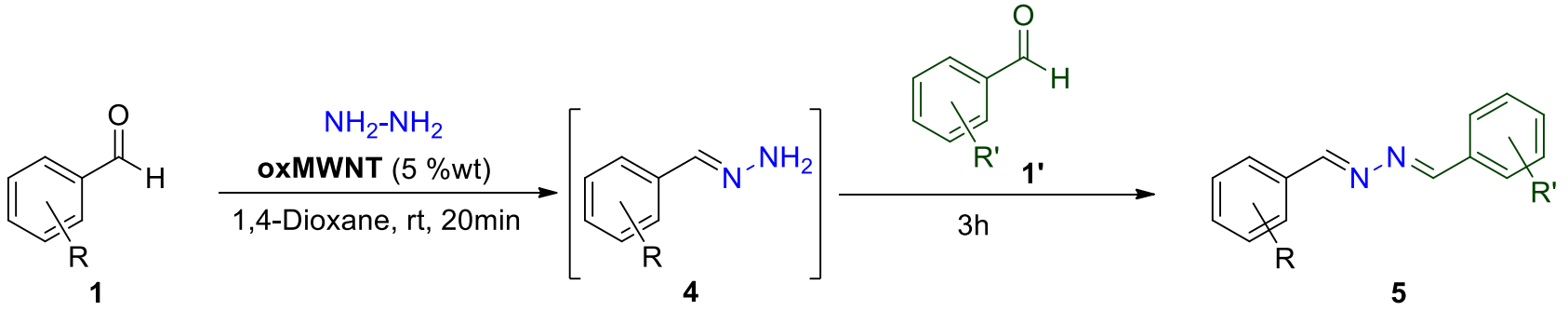
5e, X = F (Conv. > 99%, Yield = 88%)
5f, X = Br (Conv. > 99%, Yield = 94%)

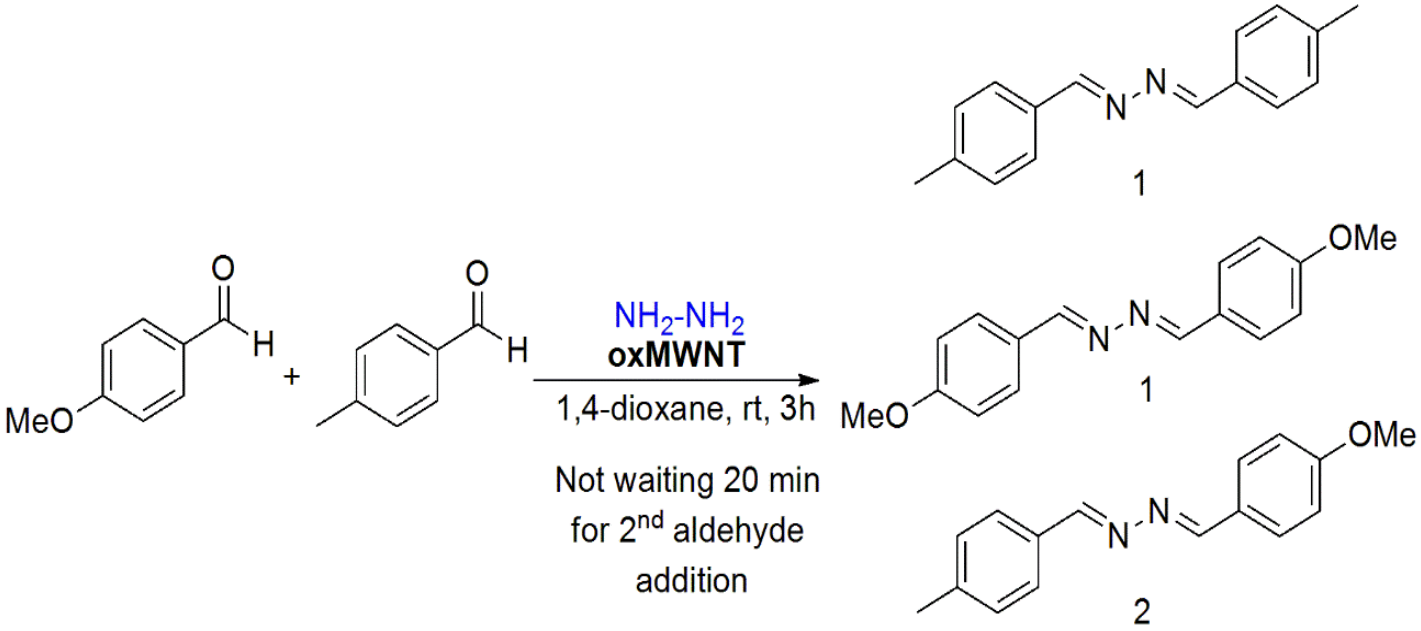


5g, Conv. > 99%
Yield = 92%

Non-linear optics target molecule

Results: Scope (asymmetric azines)

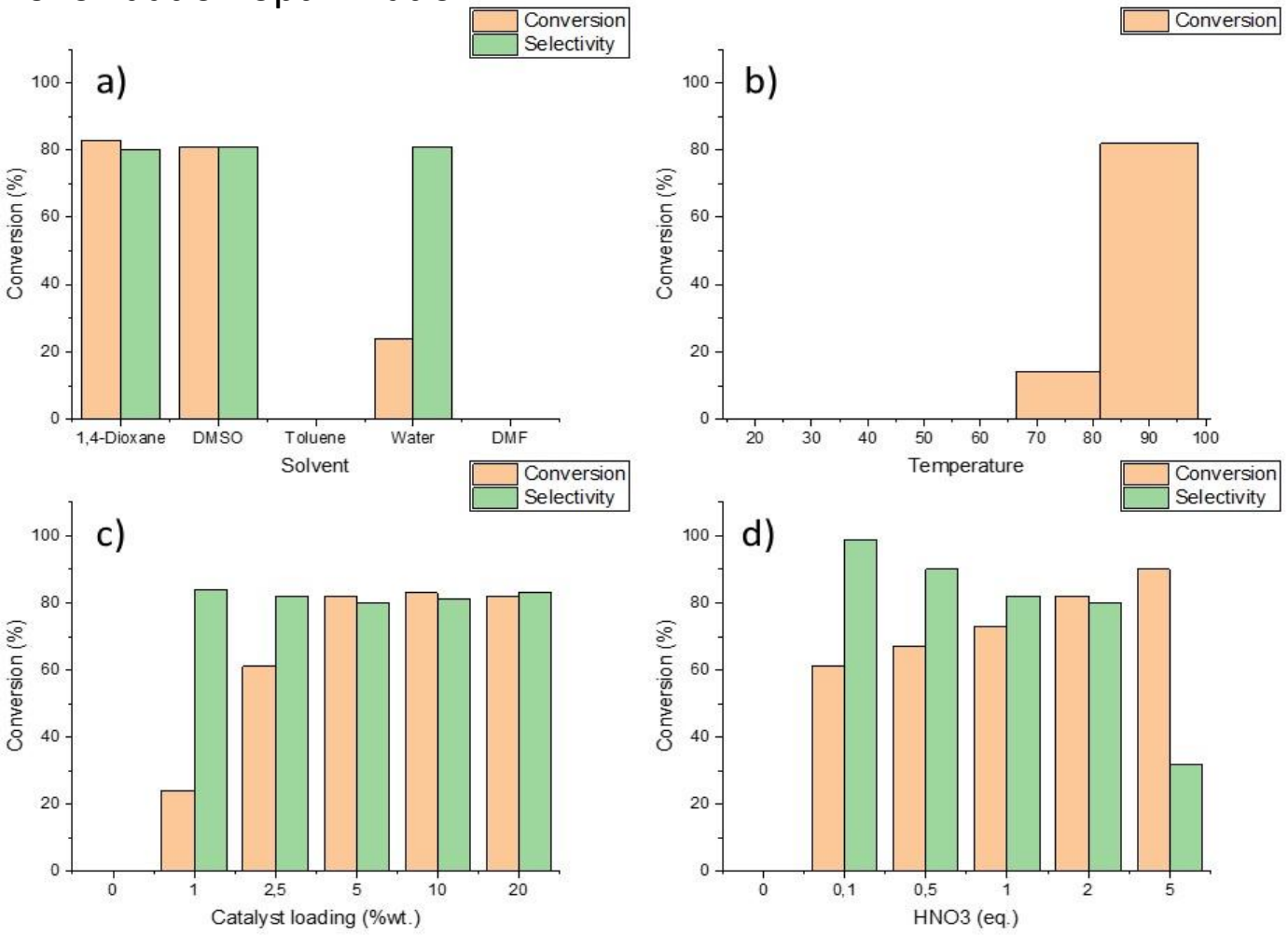




Statistic mixture

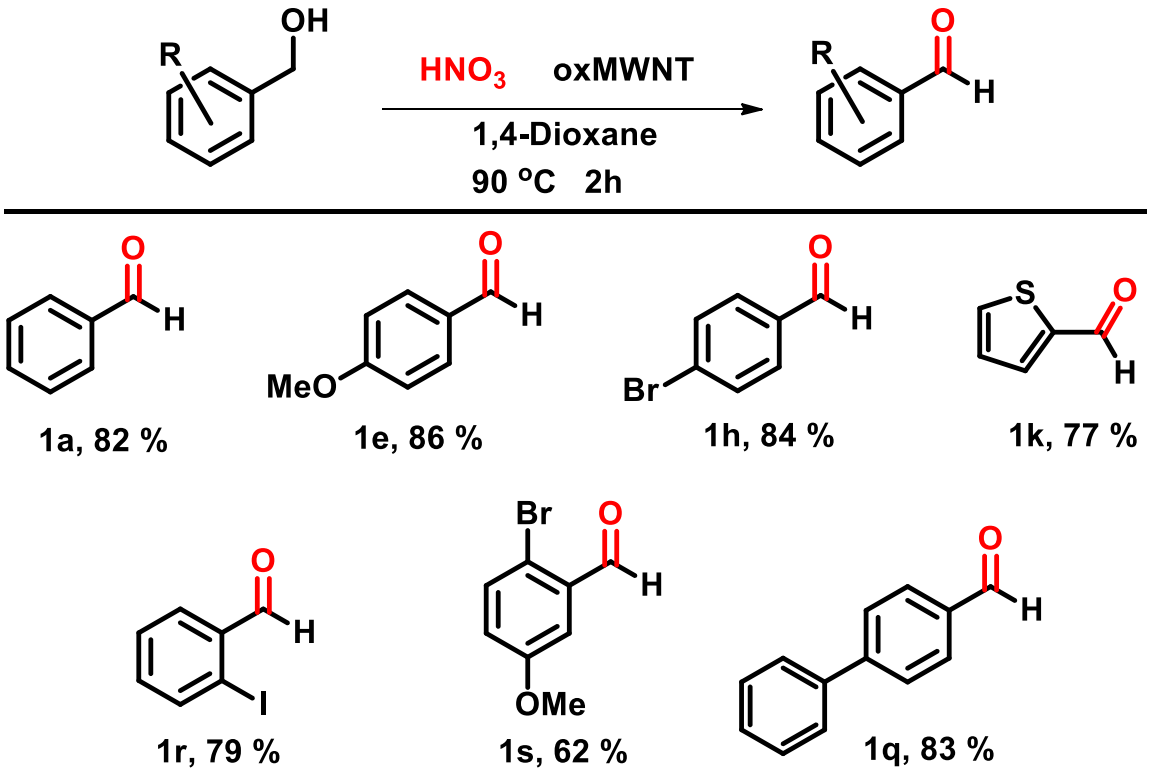
Results: Scope (one pot synthesis)

Benzyl alcohol oxidation optimization



Results: Scope (one pot synthesis)

Benzyl alcohol oxidation optimization



Reaction conditions: 0.25 mmol of alcohol, 0.5 mmol of HNO_3, 0.5 M 1,4-dioxane, 5 %wt. oxMWNT, for 2h at 90 °C. Values stand for conversion (determined by ^{1}H-NMR)

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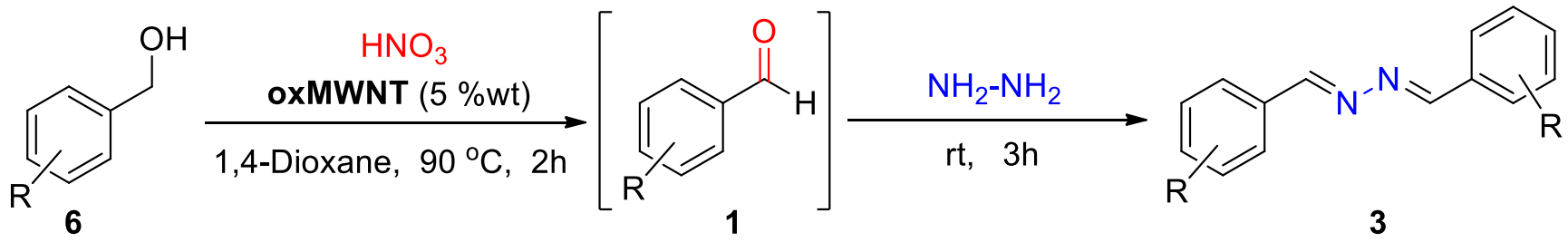
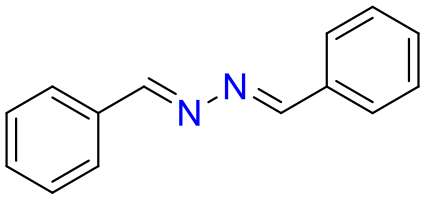
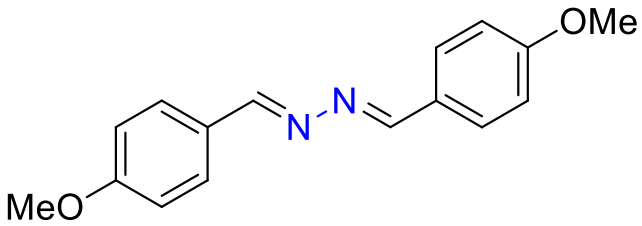
Results: Scope (one pot synthesis)

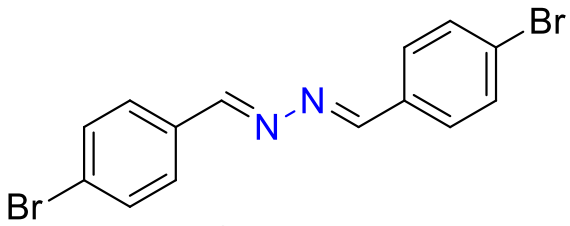




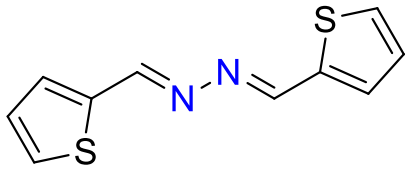
3a, 79%



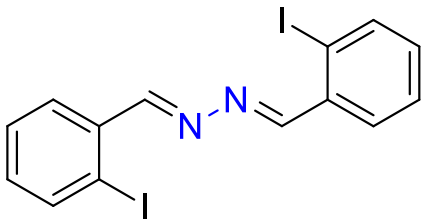
3e, 70%



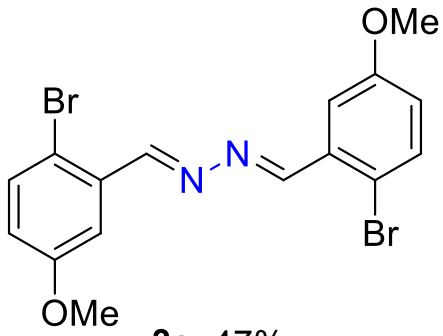
3h, 72%



3k, 66%



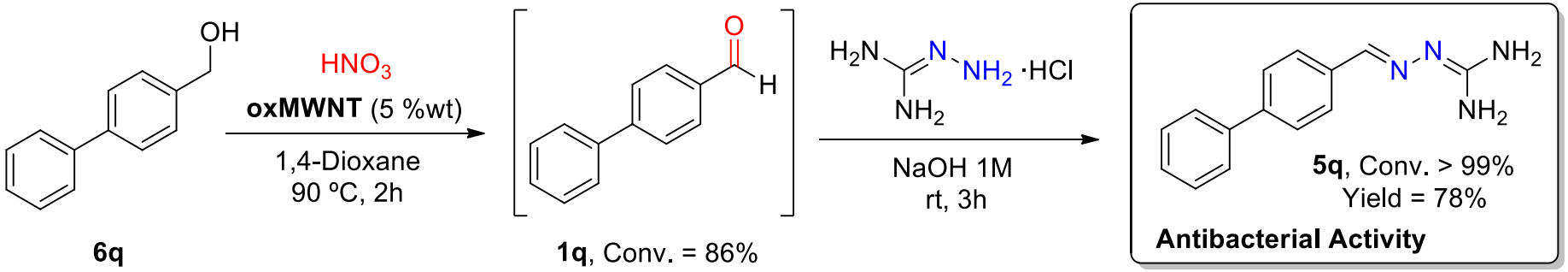
3r, 76%



3s, 47%

Results: Scope (bioactive azines)

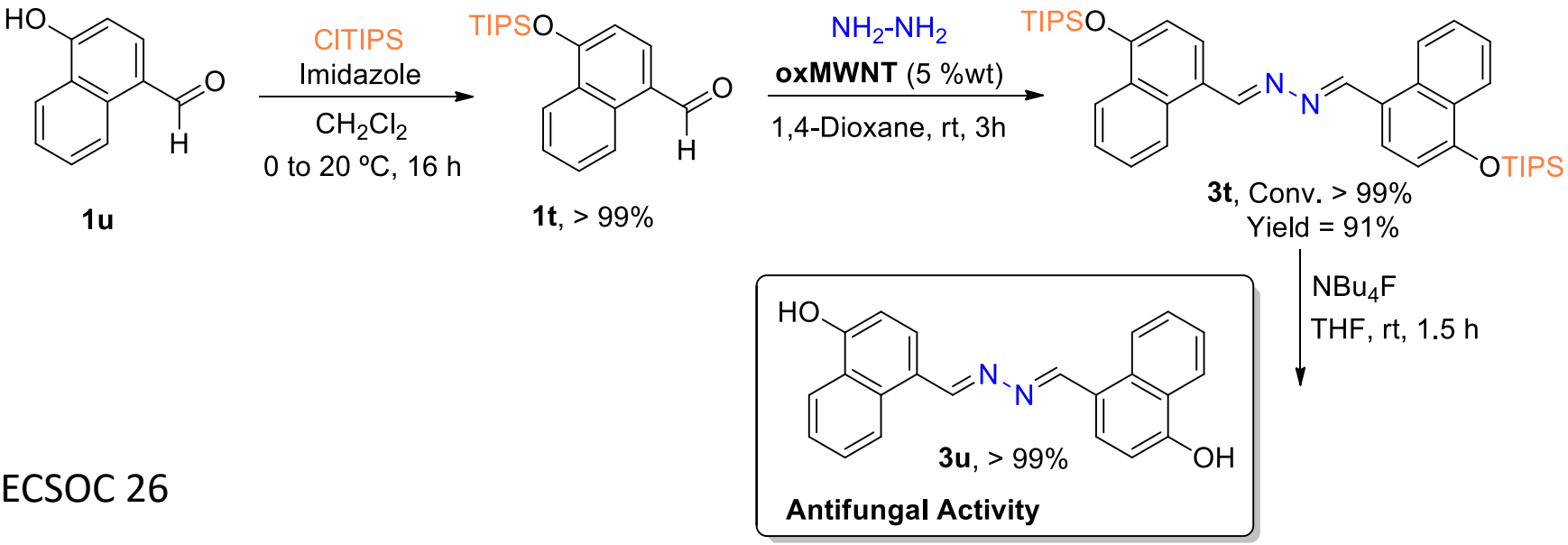
a) Synthesis of (E)-4-([1,1'-biphenyl]-4-yl)-1,1-diamino-2,3-diazabuta-1,3-diene



6q

1q, Conv. = 86%

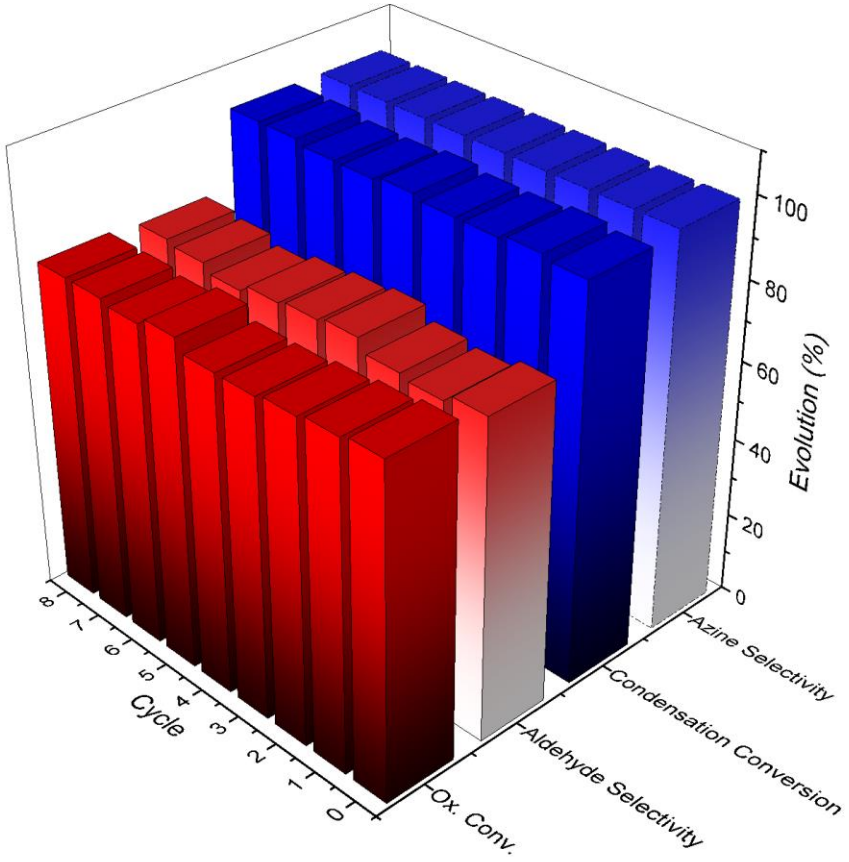
b) Synthesis of 4,4'-((1E,1'E)-hydrazine-1,2-diylidenebis(methanylylidene))bis(naphthalen-1-ol)

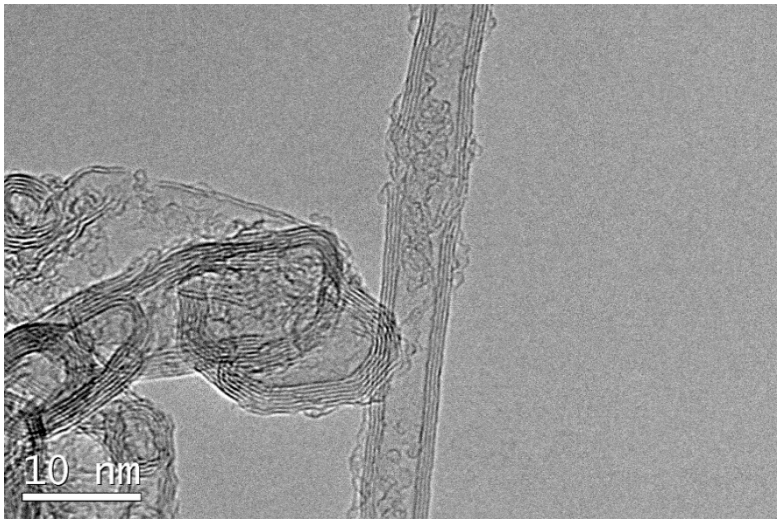


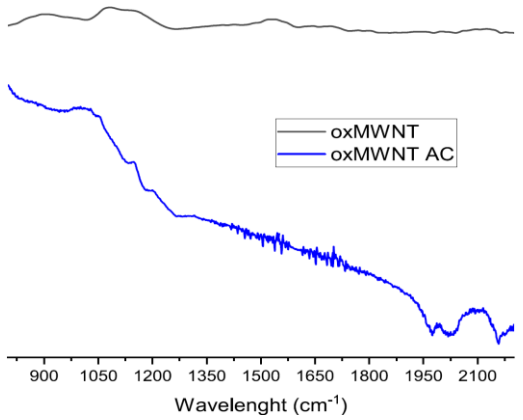
1u

1t, > 99%

Results: Catalyst Recovery

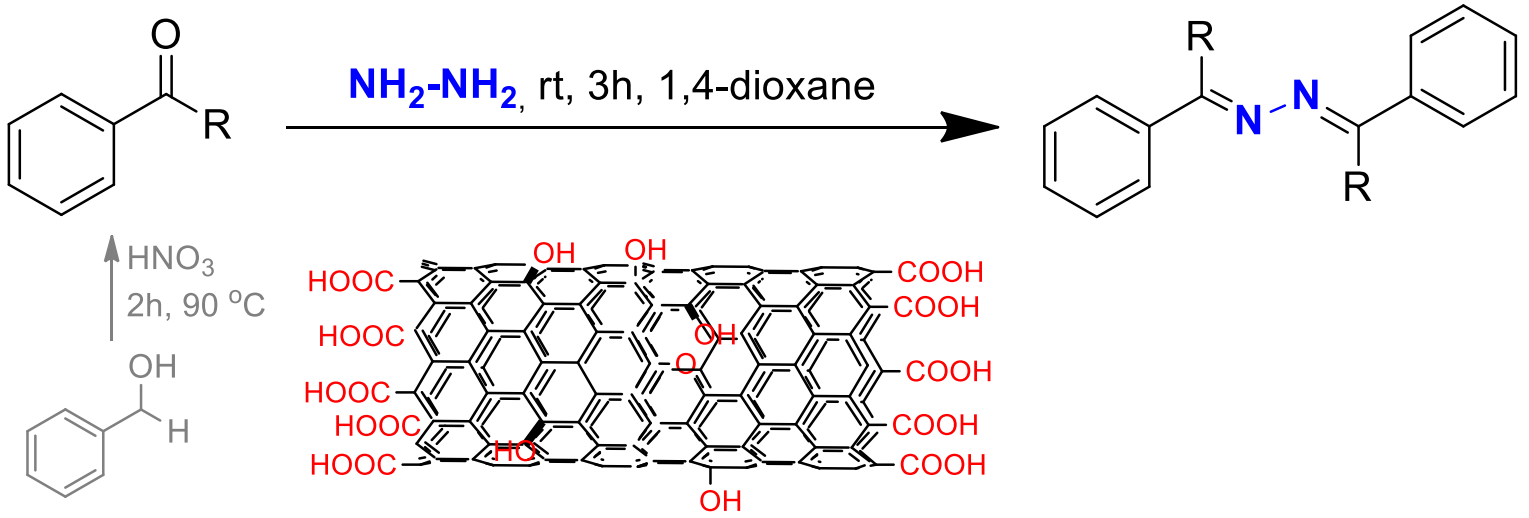






Conclusions

Carbocatalytic metal-free synthesis of azines using oxidized Carbon Nanotubes



- Reaction can be scaled up to the gram scale
- Yielding of symmetric and asymmetric azines
- One pot synthesis using alcohols
- Selectivity for aromatic aldehydes due to π-interactions with the nanotube
- Surface version of classic condensation due to solid acid caracter by oxygen chem.

Acknowledgments

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87 Fr Francium [223] | 8 O Oxygen 15.9994 | 7 N Nitrogen 14.0067 | 6 C Carbon 12.0107 | 85 At Astatine [210]

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Carbocatalytic synthesis of azines by oxidized multiwalled carbon nanotubes

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Thank you