This paper describes objective technical results and analysis. Any subjective views or opinions that might be expressed in the paper do not necessarily represent the views of the U.S. Department of Energy or the United States Government.

SAND2019-10330C

Pd-Catalyzed Oxidative Homocoupling of Pyrazole Boronic Esters to Access Bipyrazoles for Metal–Organic Frameworks

Mercedes Taylor,[†,◊,‡] Martin Juhl,[⊥] Gul Barg Hadaf,[⊥] Dasol Hwang,[⊥] Ever Velasquez,[§] Julia Oktawiec,[◊] Jonathan B. Lefton,[▯] Tomce Runcevski,[▯] Jeffrey R. Long,[§,◊,‡*] Ji-Woong Lee[⊥*]

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[§]Department of Chemical and Biomolecular Engineering, University of California, Berkeley, California 94720, United States
[▯]Department of Chemistry, Southern Methodist University, Texas 75205, United States

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Martin Juhl


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Ever Velazquez


Prof. Tomče Runčevski


Jonathan Lefton


Mercedes Taylor

Center for Gas Separations Relevant to Clean Energy Technologies

CGS

U.S. DEPARTMENT OF ENERGY

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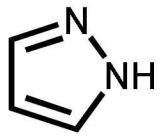
VILLUM FONDEN

novo nordisk fonden

Pyrazole as a coordinating group



1*H*-Pyrazole

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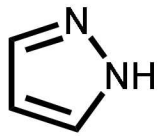

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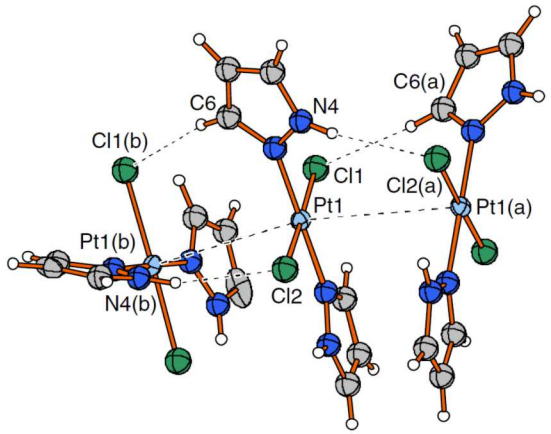

Inorg. Chim. Acta **359** (2006) 320-326.

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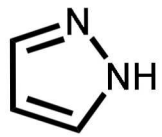

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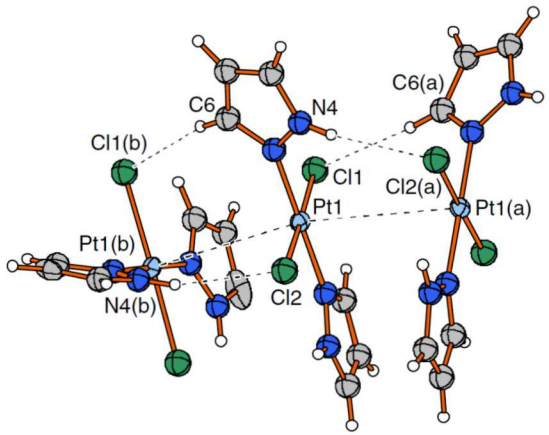

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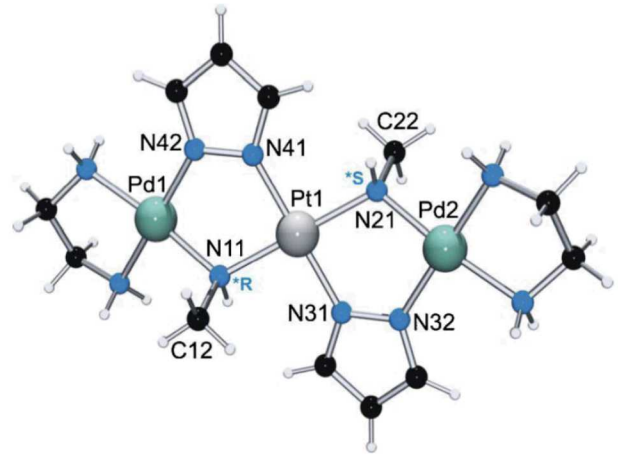

Dalton Trans **40** (2011) 10316-10318.

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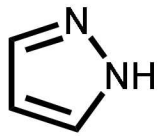

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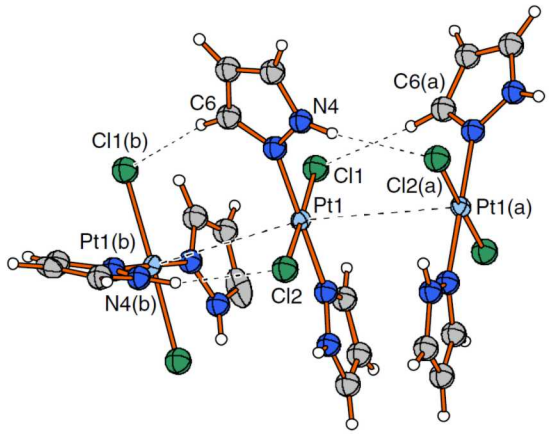

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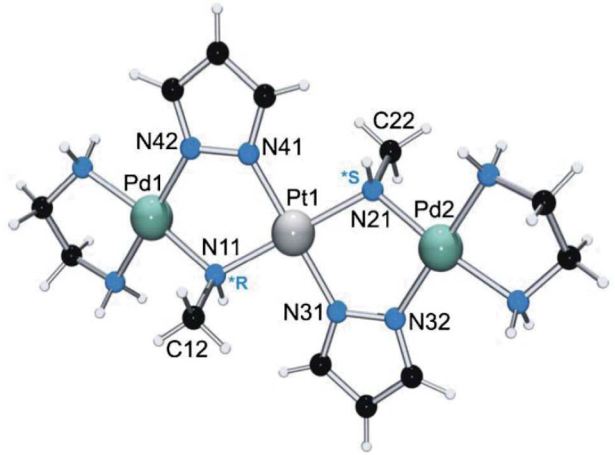

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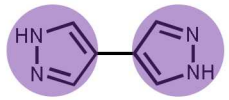
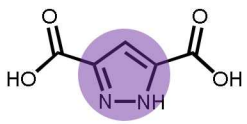
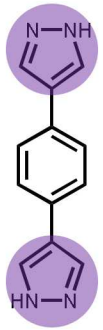


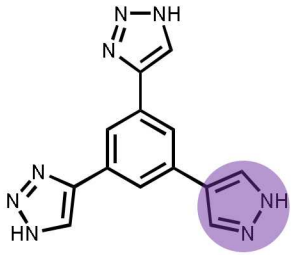
Inorg. Chim. Acta **338** (2002) 69-77



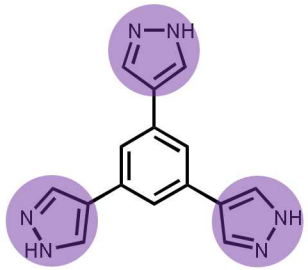
J Inorg. Organomet. Polym. **22** (2012) 1370-1376



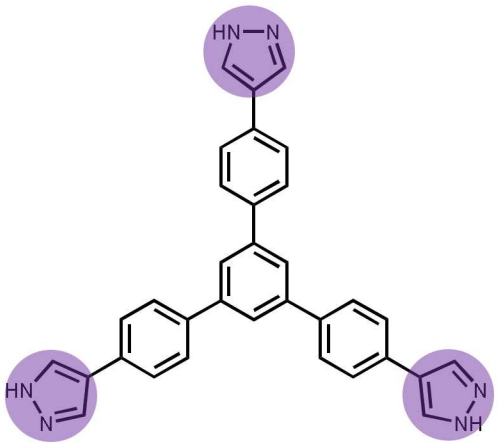
J Am. Chem. Soc. **130** (2008) 7847-7850



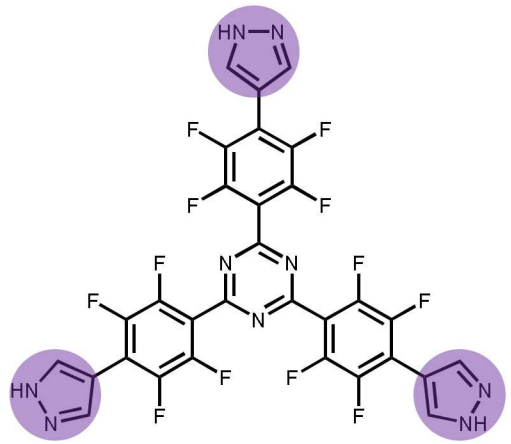
J. Am. Chem. Soc. **138** (2016) 7161−7170



Chem. Sci. **2** (2011) 1311–1319



CrystEngComm **17** (2015) 4992–5001

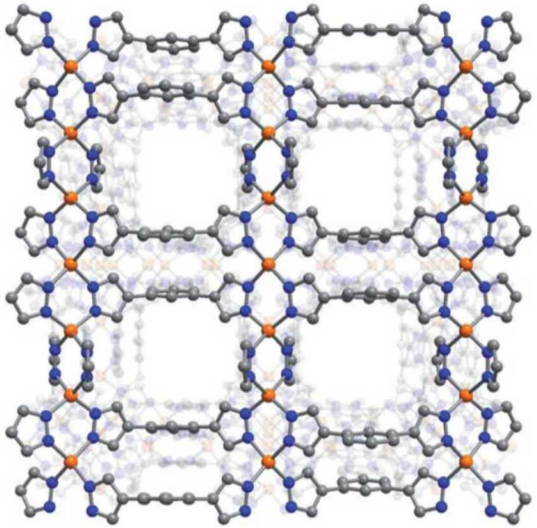


J. Am. Chem. Soc. **140** (2018) 6014−6026

Pyrazolate-based metal–organic frameworks

Metal–organic frameworks:

- 3-dimensional materials
- Metal ions + organic linkers
- Crystalline
- Porous
- Tunable



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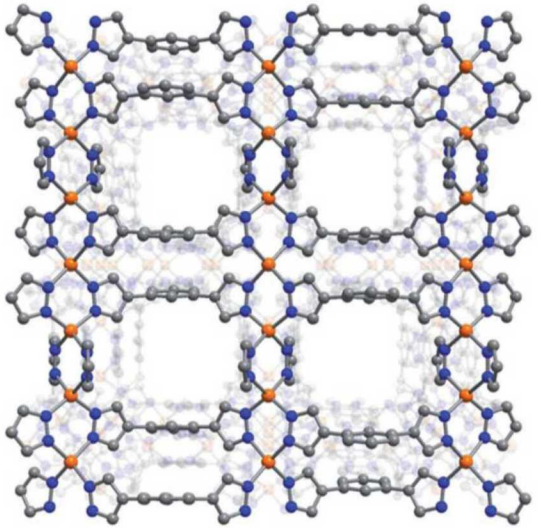

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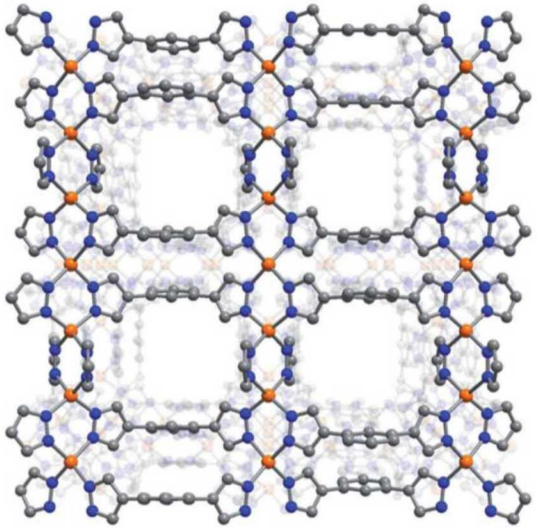

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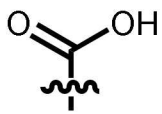
Organic linkers: carboxylate and azolate coordinating groups



pKa: 4.2
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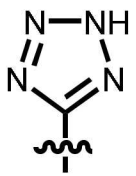

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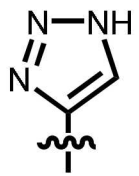

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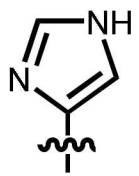

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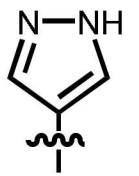

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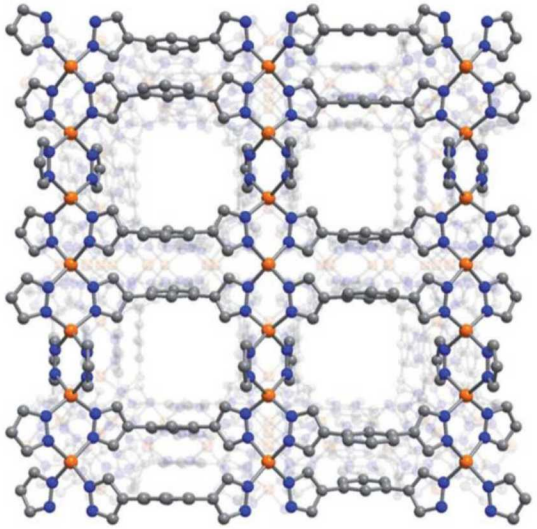

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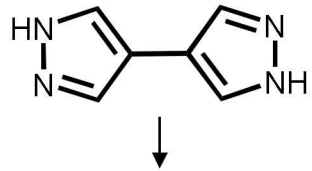
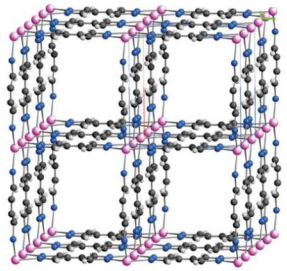
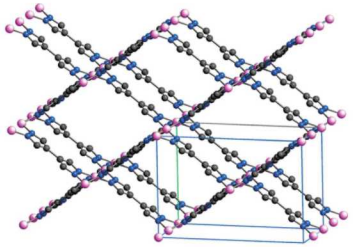




Inorg. Chem. **51** (2012) 5235−5245



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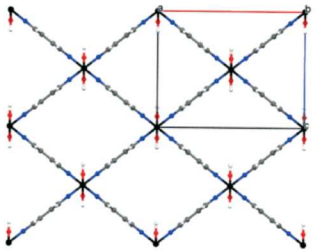

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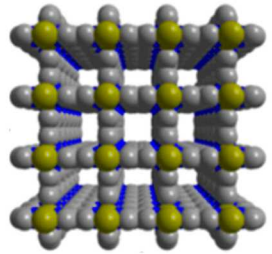

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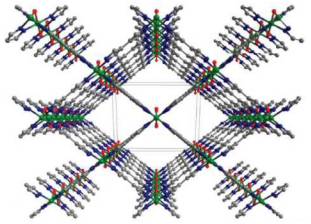
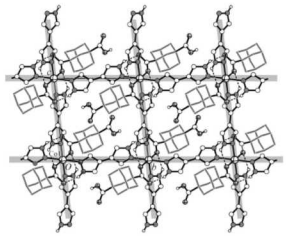


Dalton Trans. **47** (2018) 8779–8786



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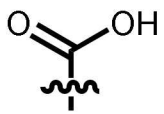

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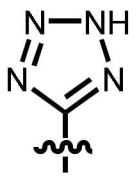

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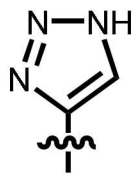

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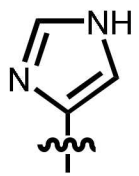

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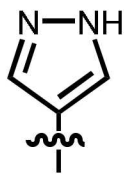

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Traditional route to 4,4’-bipyrazole

- Nine-step synthesis of 4,4’-bipyrazole published in 1964 (*J. Org. Chem.* **1964**, *29*, 3046)

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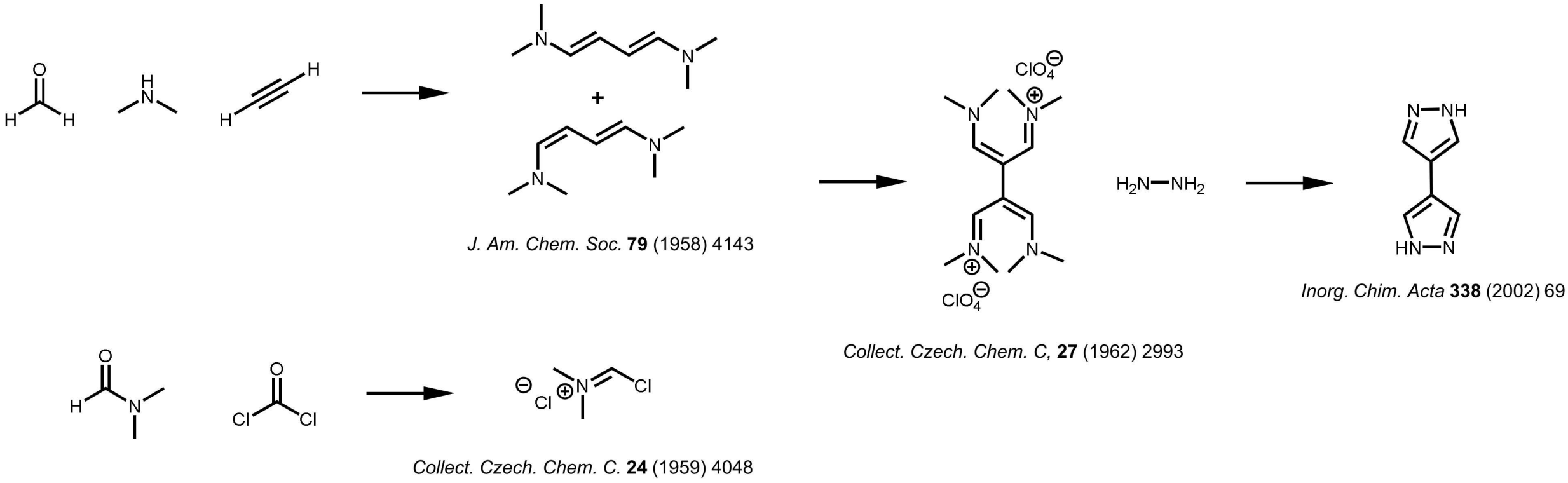
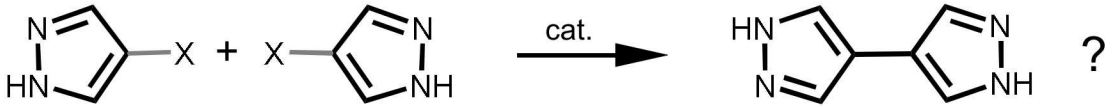


Bipyrazole via homocoupling?

- Symmetrical biaryls should be accessible via transition metal catalyzed C-C bond formation between the two rings



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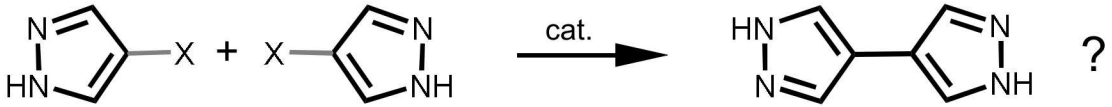

- Protected pyrazole boronic ester found to undergo homocoupling in the presence of $Pd(PPh_3)_4$

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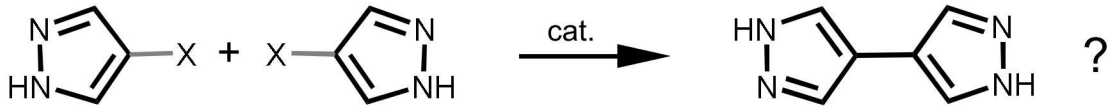

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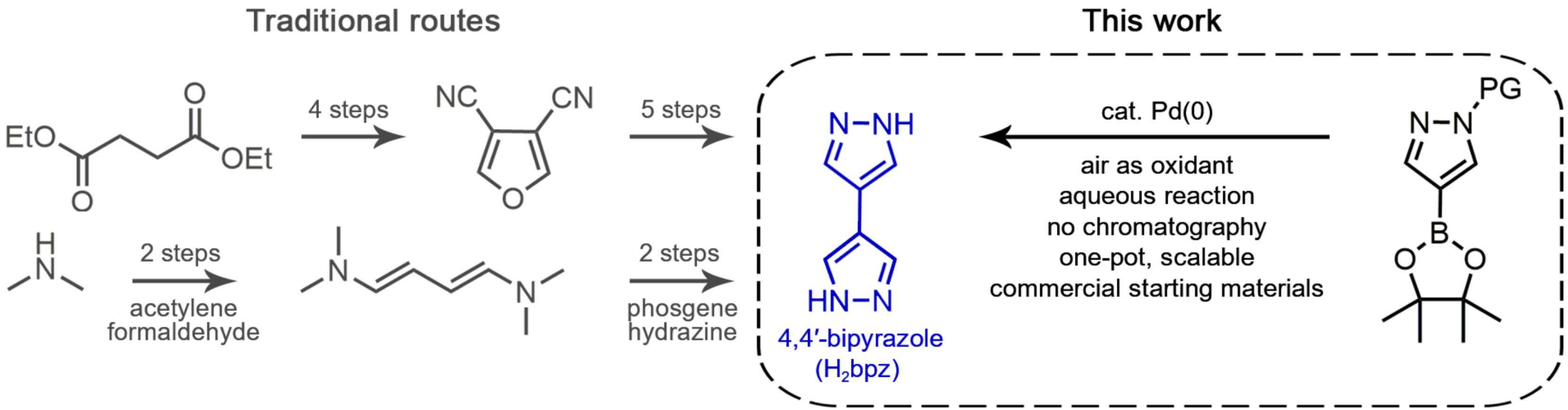

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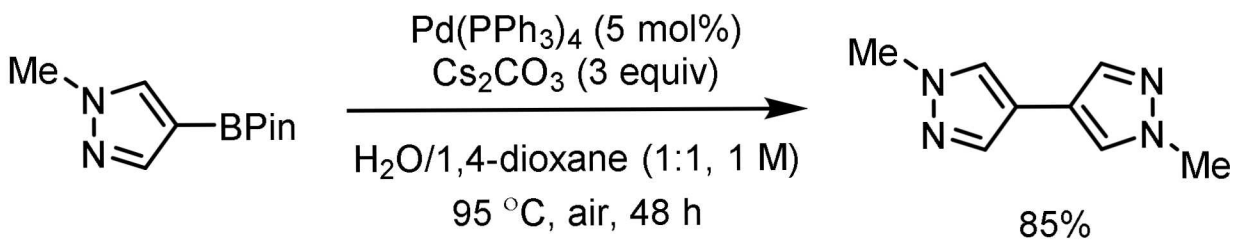
Optimization of Pd-catalyzed homocoupling

- ✓ Catalyst
- ✓ Base
- ✓ Solvent system
- ✓ Atmosphere
- ✓ Temperature
- ✓ Duration
- ✓ Stoichiometry
- ✓ Work-up

Optimized conditions



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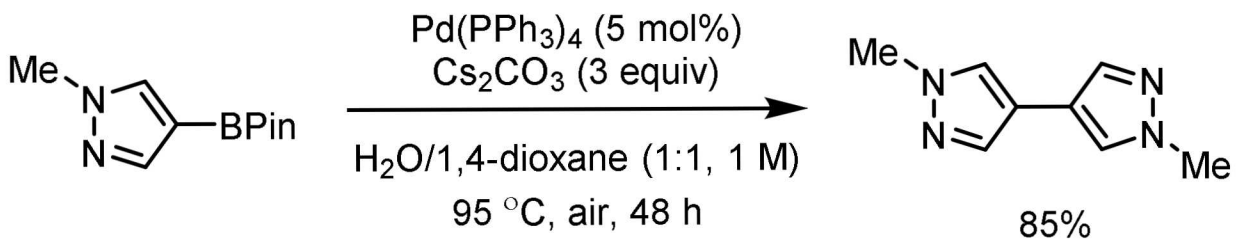
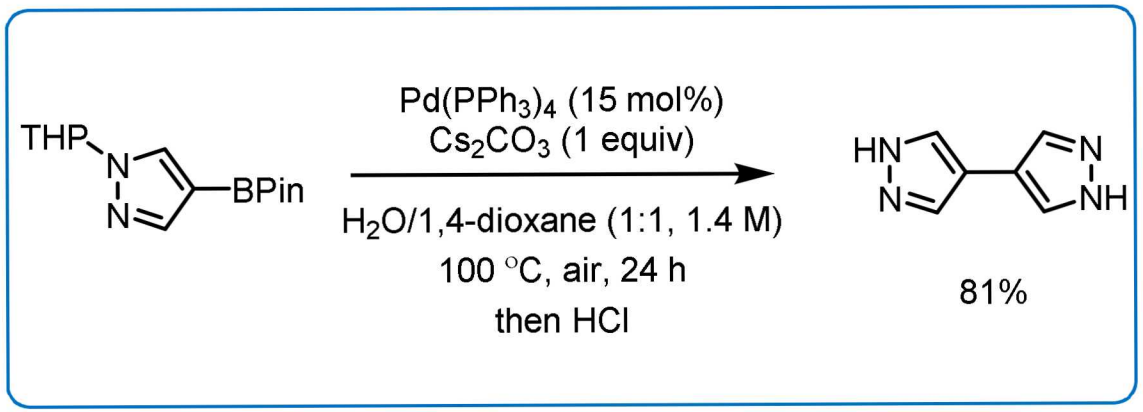


Improved protecting group



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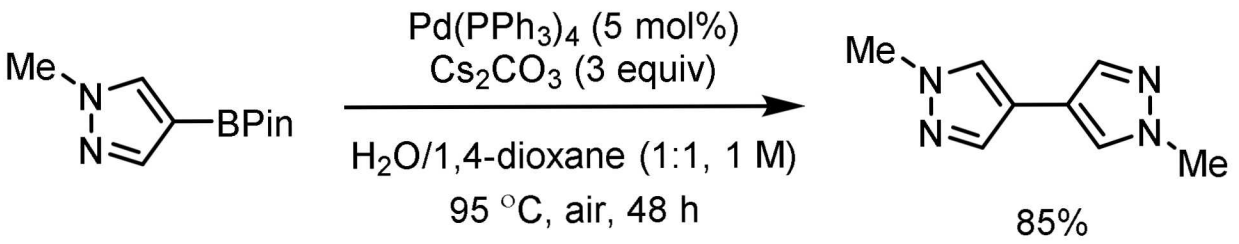
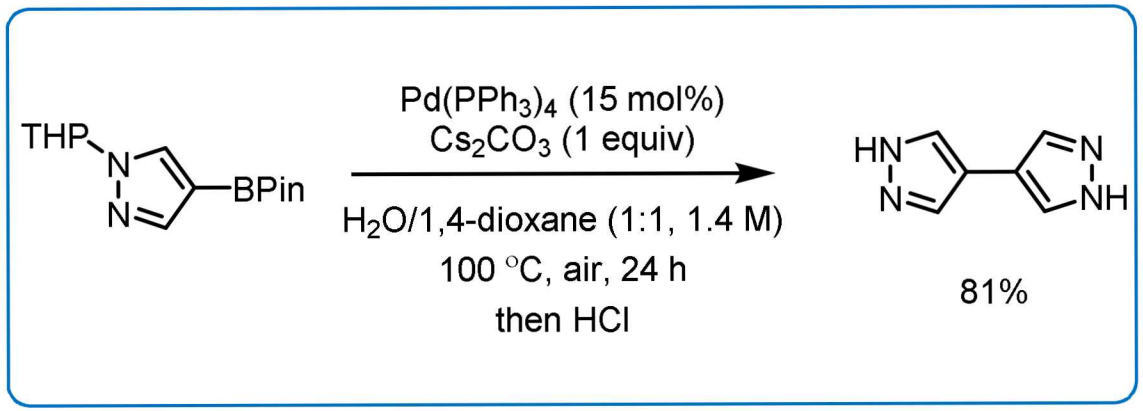
Optimization of Pd-catalyzed homocoupling

- ✓ Catalyst
- ✓ Base
- ✓ Solvent system
- ✓ Atmosphere
- ✓ Temperature
- ✓ Duration
- ✓ Stoichiometry
- ✓ Work-up

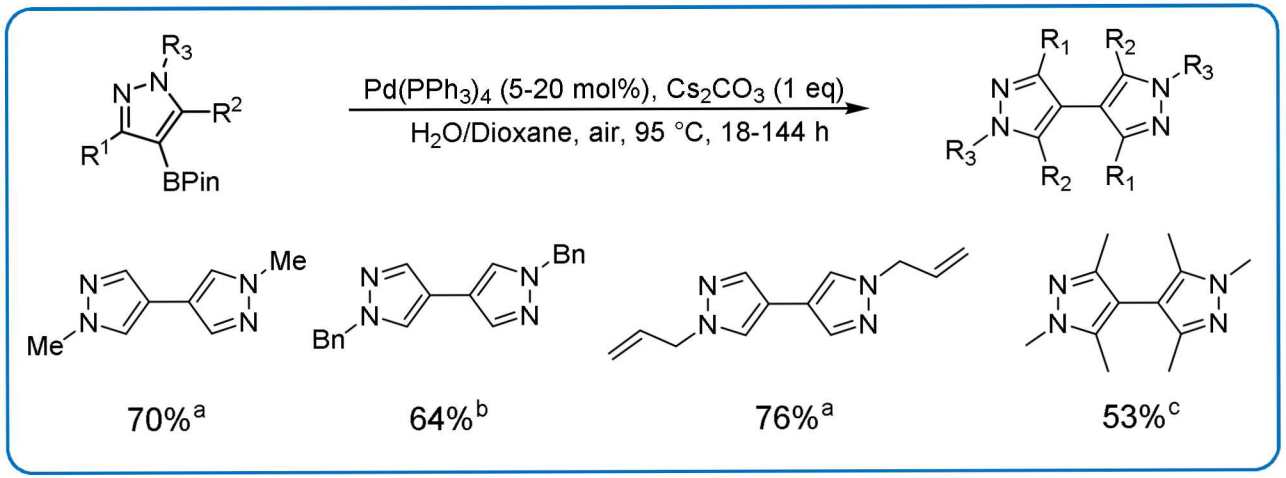
Optimized conditions



Improved protecting group



Substituent variation



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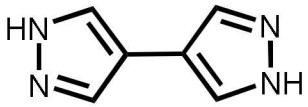
Application to metal–organic framework synthesis

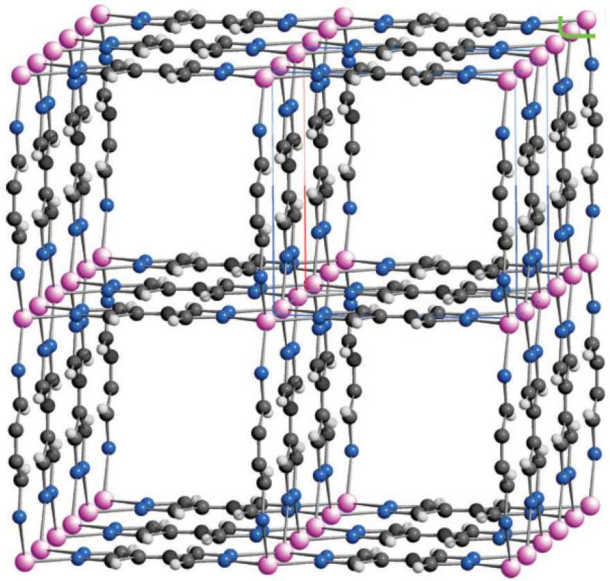


+ $Co(SO_3CF_3)_2$

Co(bpz)

Langmuir surface area

Lit value	1057 m^2/g
This work	1064 m^2/g



Zn(bpz)
Inorg. Chem. **51** (2012) 5235−5245

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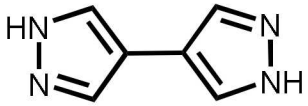

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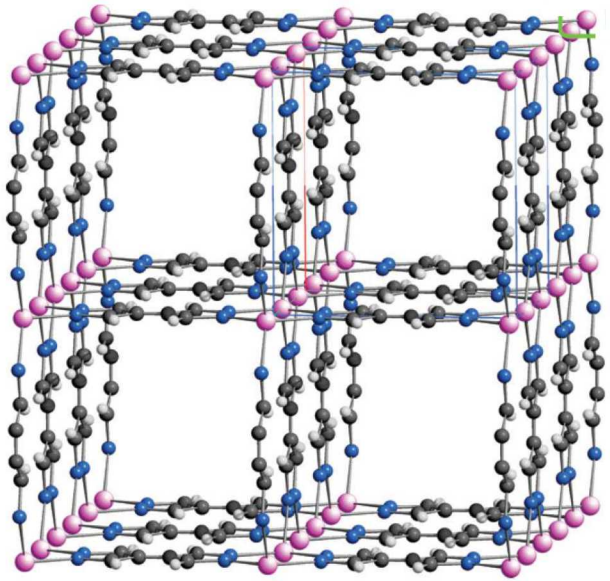

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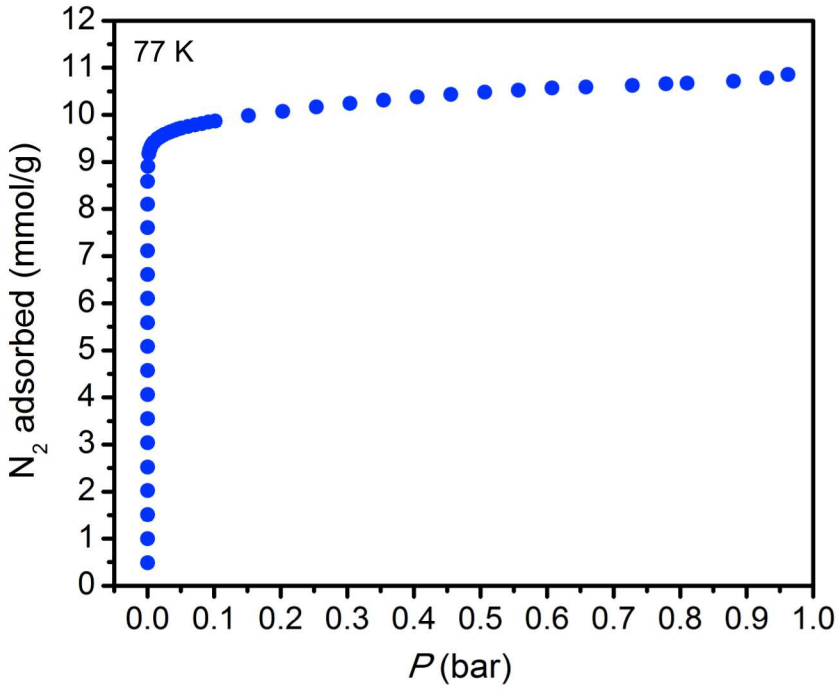

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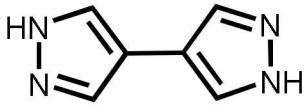

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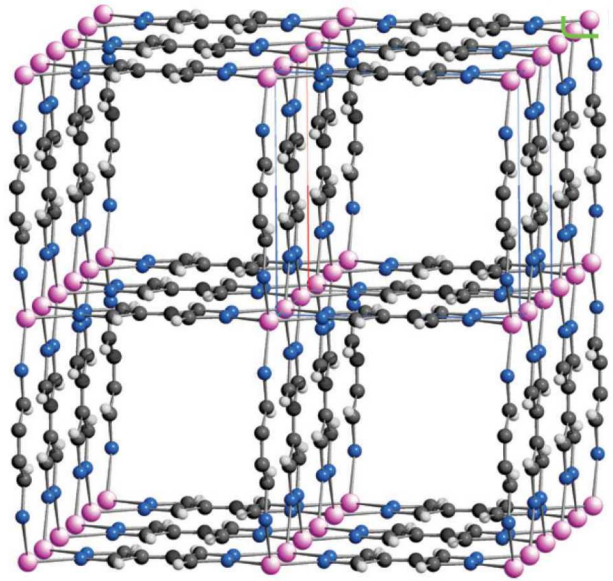

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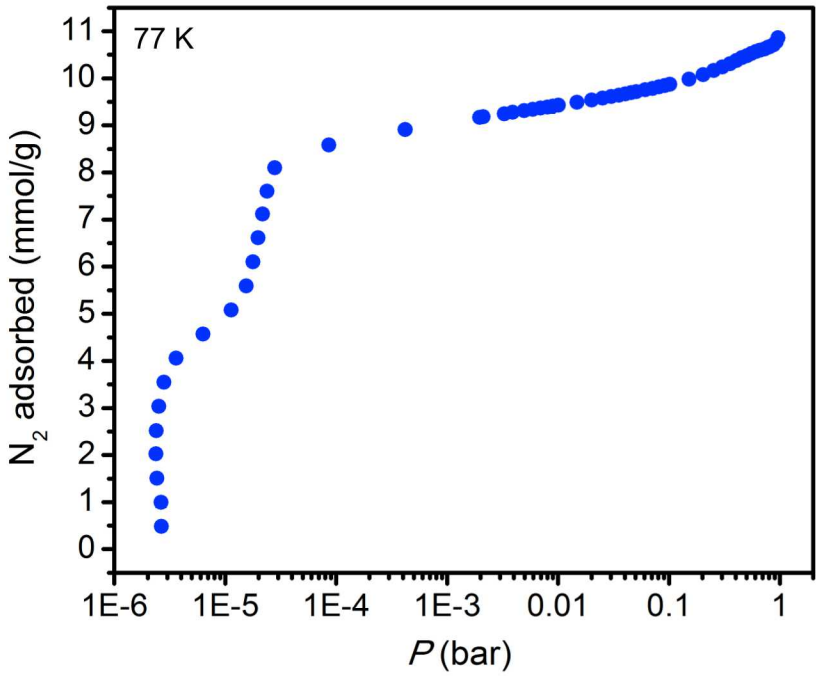

- Co(bpz) reproducibly demonstrates previously unobserved step in N_2 adsorption isotherm

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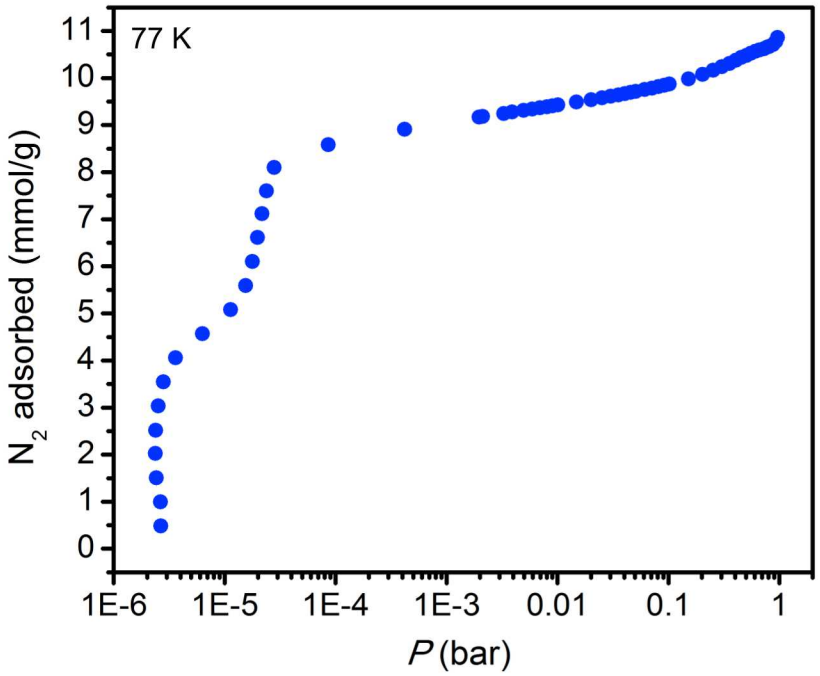
Stepped isotherms in Co(bpz)

N_2 adsorption



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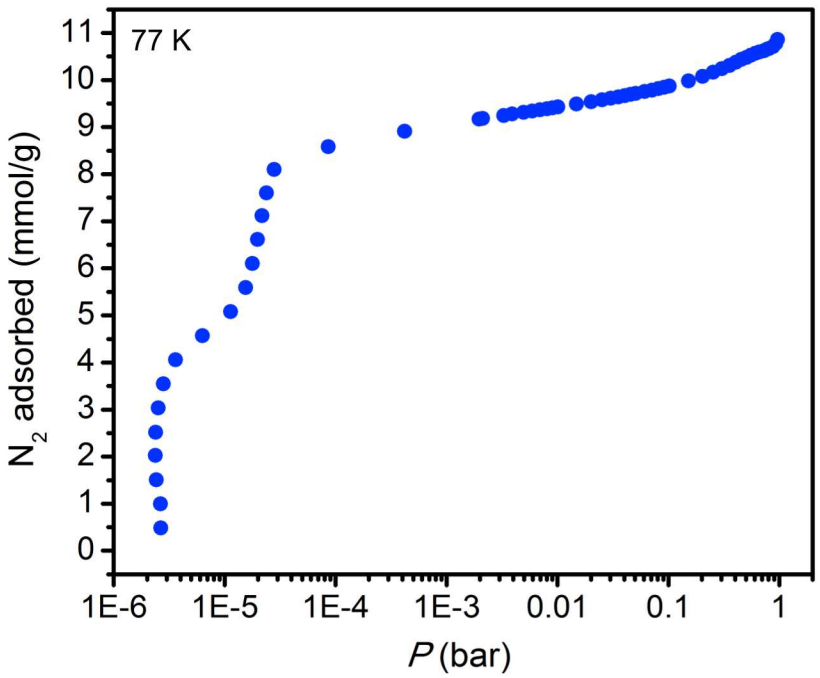
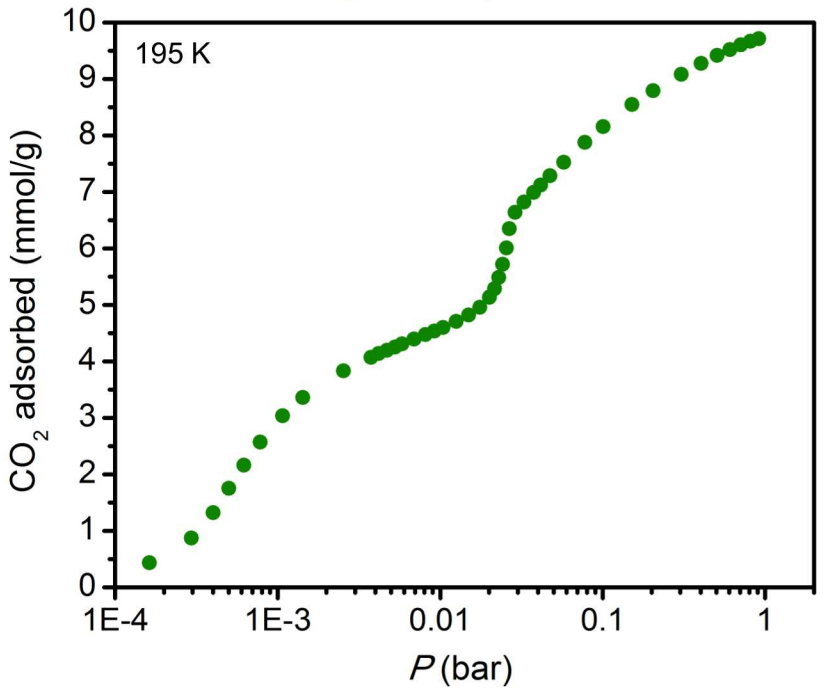
Stepped isotherms in Co(bpz)

N_2 adsorption



CO_2 adsorption



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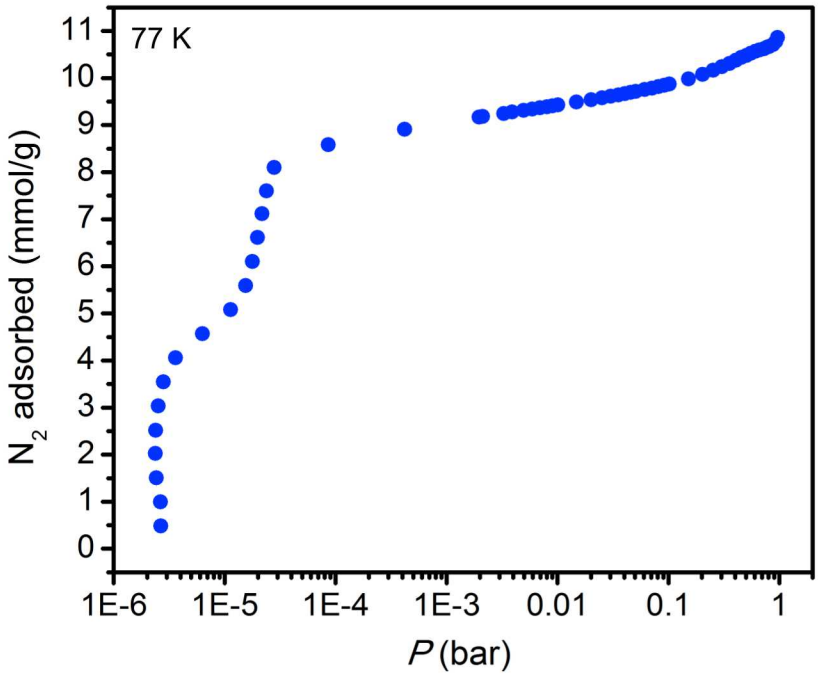
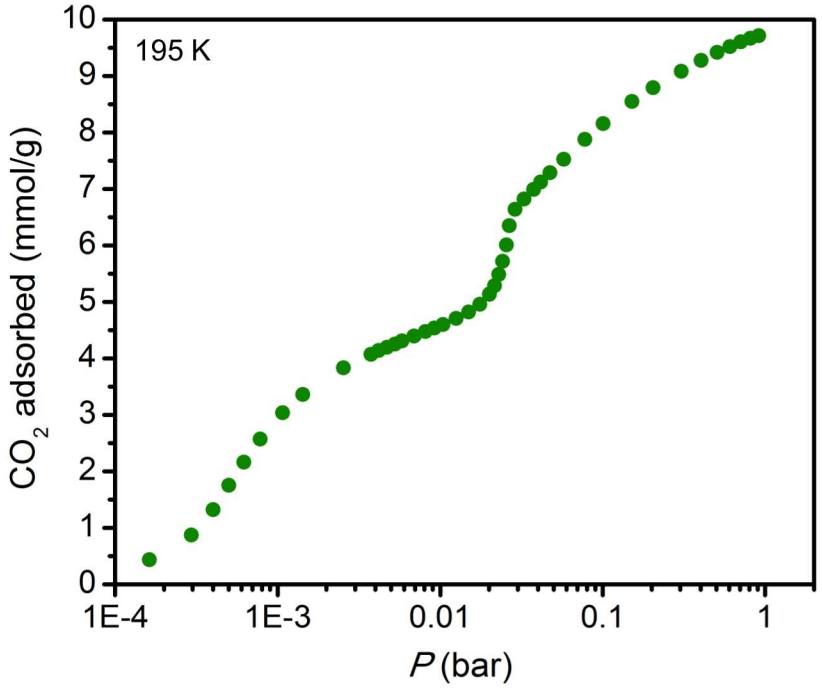
Stepped isotherms in Co(bpz)

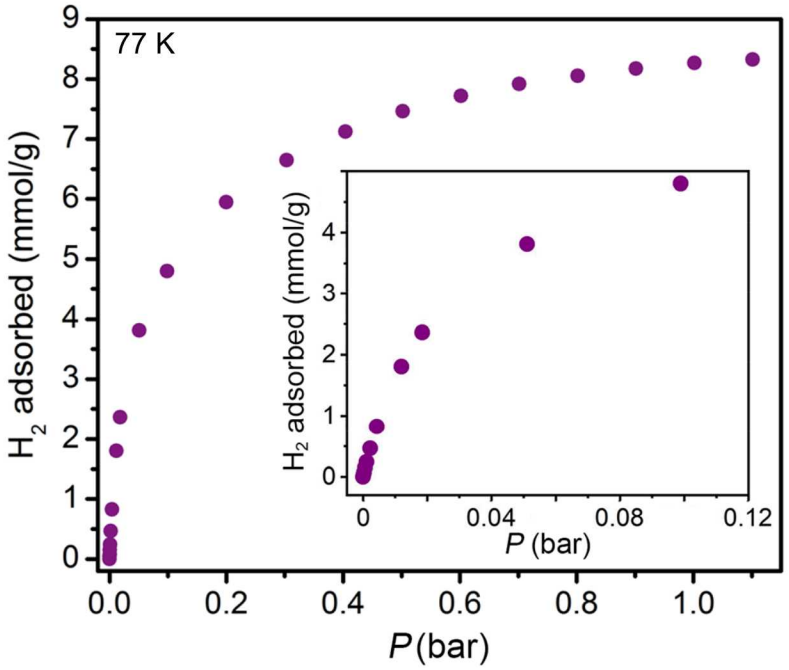
N_2 adsorption



CO_2 adsorption



H_2 adsorption



- N_2 and CO_2 isotherms contain steps while H_2 isotherm does not, under conditions tested

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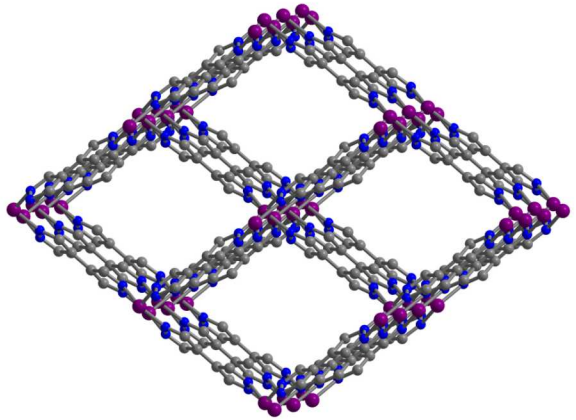
In situ diffraction studies for Co(bpz)

Advanced Photon Source,
Argonne National Lab



Co(bpz), 0 bar

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In situ diffraction studies for Co(bpz)

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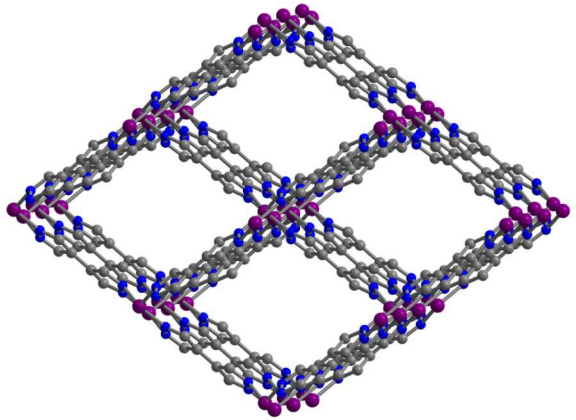
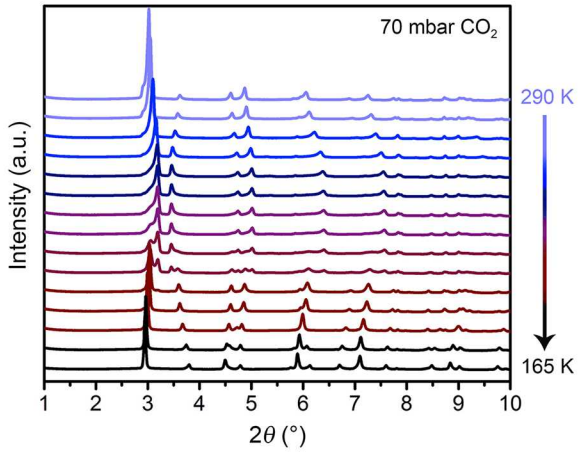


Co(bpz), 0 bar

CO_2 dosing studies



Temperature	225 K	197 K	165 K
Space Group	*C*2/*c*	*C*2/*c*	*C*2/*c*
a (Å)	14.927(4)	14.3231(16)	13.675(5)
b (Å)	9.695(3)	10.6736(14)	11.475(4)
c (Å)	7.0387(17)	7.1453(7)	7.227(2)
Volume (Å^3)	1013.1(5)	1088.0(2)	1128.6(6)

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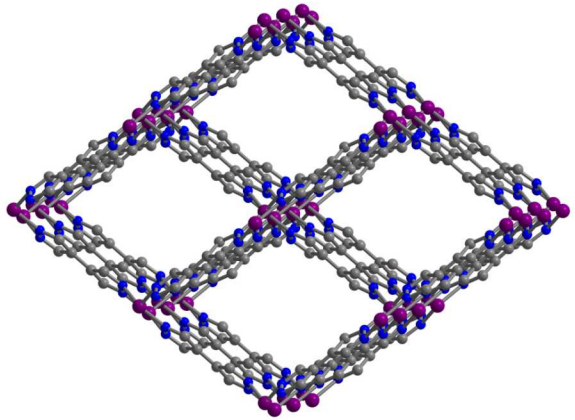
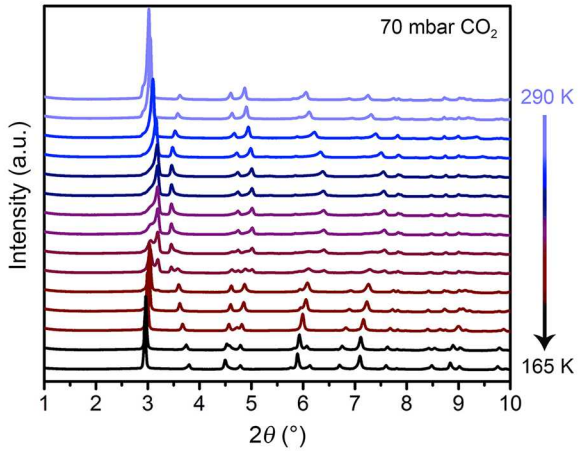


Co(bpz), 0 bar

CO_2 dosing studies



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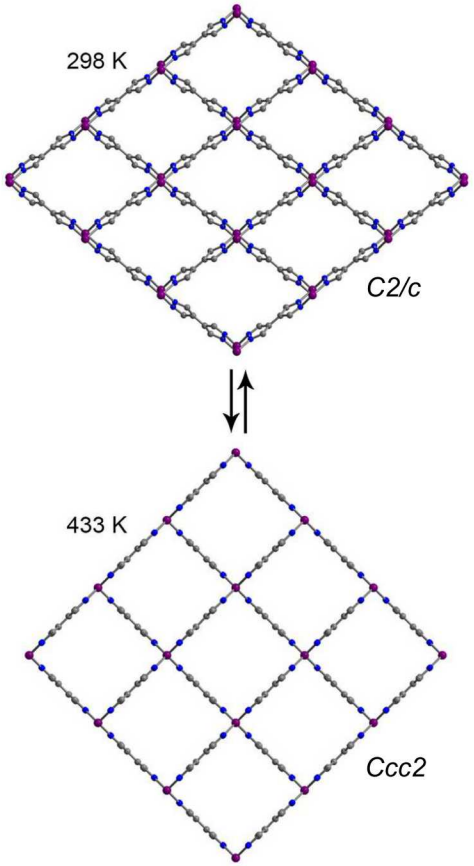
Variable-temperature studies



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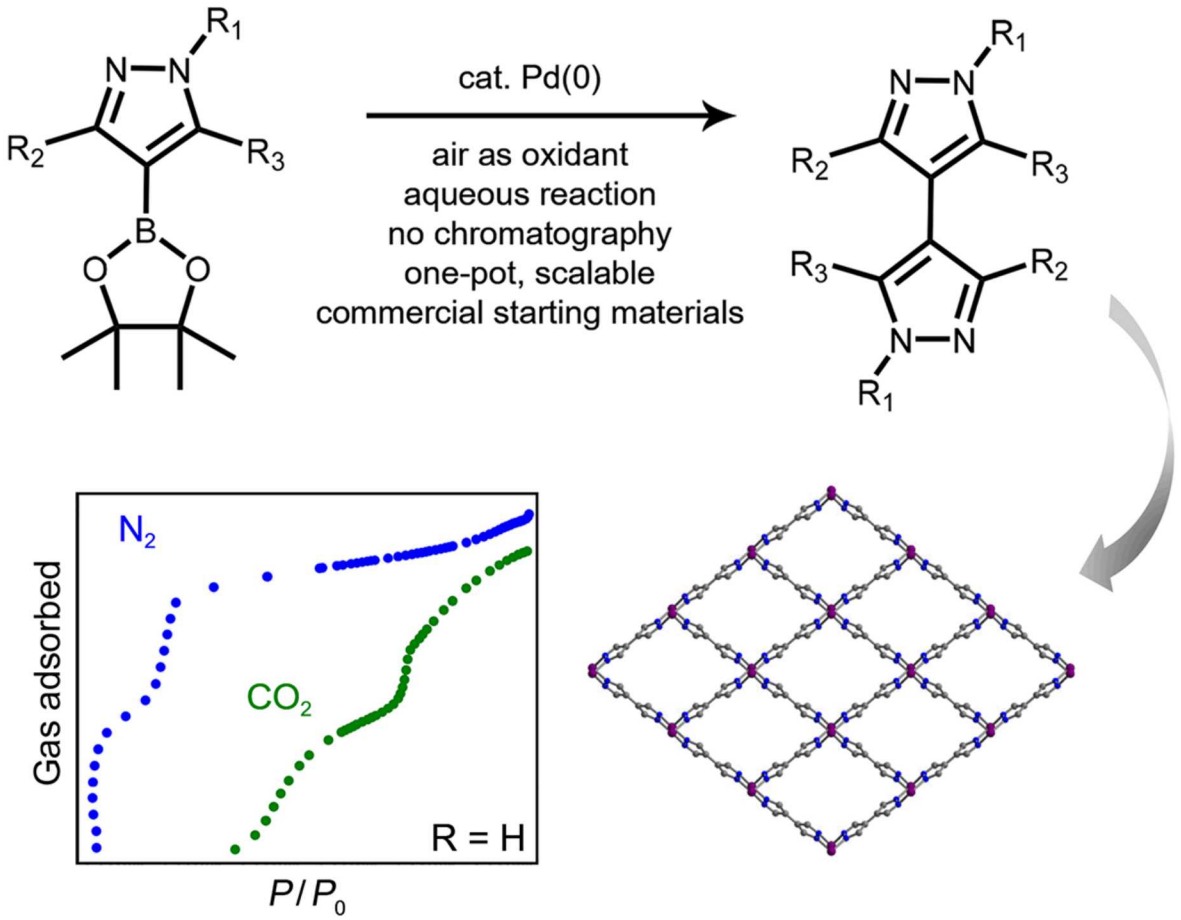
Conclusions and outlook



- First reported homocoupling of pyrazole boronic esters to access symmetrical bipyrazoles
- Optimized reaction conditions improve route to promising ligands for metal-organic frameworks
- Ligand synthesis enabled first crystal structure of Co(bpz)
- Co(bpz) found to possess adsorbate-dependent and temperature-induced structural flexibilty
- Pd-catalyzed homocoupling will allow for more insights into and development of pyrazole-based metal-organic frameworks

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