Application of Metal–Organic Frameworks in Multicomponent Reactions

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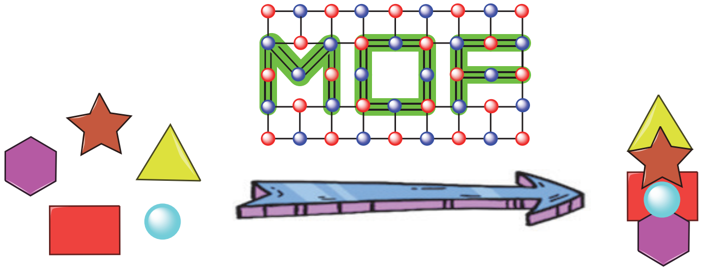

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Abstract Metal-catalyzed multicomponent reactions are versatile synthetic protocols often used to prepare a range of different products. These reactions provide complete molecular diversity and high atom efficiency while saving energy. Recently, metal–organic frameworks have attracted attention as environmentally friendly catalytic systems as they possess an abundance of catalytic sites in ordered crystal skeletons. In this graphical review, we highlight the recent progress made utilizing metal–organic frameworks to facilitate multicomponent reactions.

Key words metal–organic frameworks, multicomponent reactions, heterogeneous catalysis, transition-metal catalysts, organic linkers

Multicomponent reactions (MCRs) are chemical processes where several reactants are combined in one vessel to create a final product that contains most of the atoms from the starting materials. Such processes involve a series of chemical transformations without changing the reaction environment between steps. The result is a diverse range of molecules created more efficiently than traditional step-by-step methods. Compared to multistep synthetic processes, one-pot reactions improve efficiency, reduce waste production, and enable the rapid construction of more complex molecules from simple, readily available starting materials. This efficiency is particularly appealing in the pharmaceutical industry, where quickly creating large libraries of potentially useful compounds is important. Multicomponent reactions have been established incorporating three, four, or more components, and numerous studies have been reported on the development of new MCRs.

MCRs align with the fundamental principles of green chemistry by producing complex final products in a single step through innovative synthetic approaches that are environmentally sustainable. Some notable advantages of utilizing MCRs include generating less waste, conserving resources, and reducing energy requirements. These advantages have captured the attention of researchers aiming to develop cutting-edge green chemistry processes.

In recent years, metal–organic frameworks (MOFs) have become important in chemical research due to their large surface areas, high porosities, low densities, ease of separation, high crystallinities, and abundant catalytic metal centers. These specific properties, combined with the low solubility of MOFs, allow for their wide application as heterogeneous catalysts, facilitating their recovery and reuse. Hence, they are considered to be green and recyclable catalysts. MOFs are made from metal ions or clusters linked by organic molecules and are used in various sustainable technologies. The solvothermal method is commonly used to produce MOFs because it allows precise control over their shape and size. Additionally, microwave-assisted synthesis speeds up the process, resulting in high yields and well-defined properties.

In addition, MOFs are micro/mesoporous crystalline solids. Their lattice is formed by connecting metallic nodes, comprising metal cations or clusters of a few metal ions, with rigid organic linkers possessing two or more coordination positions. The organic linkers are incredibly diverse, mostly based on carboxylates, N-donor groups, or even phosphonates, and have a variety of configurations. MOFs, due to their high abundance, low cost, non-toxicity, and environmentally friendly nature, have attracted significant attention compared to noble-metal-based materials.

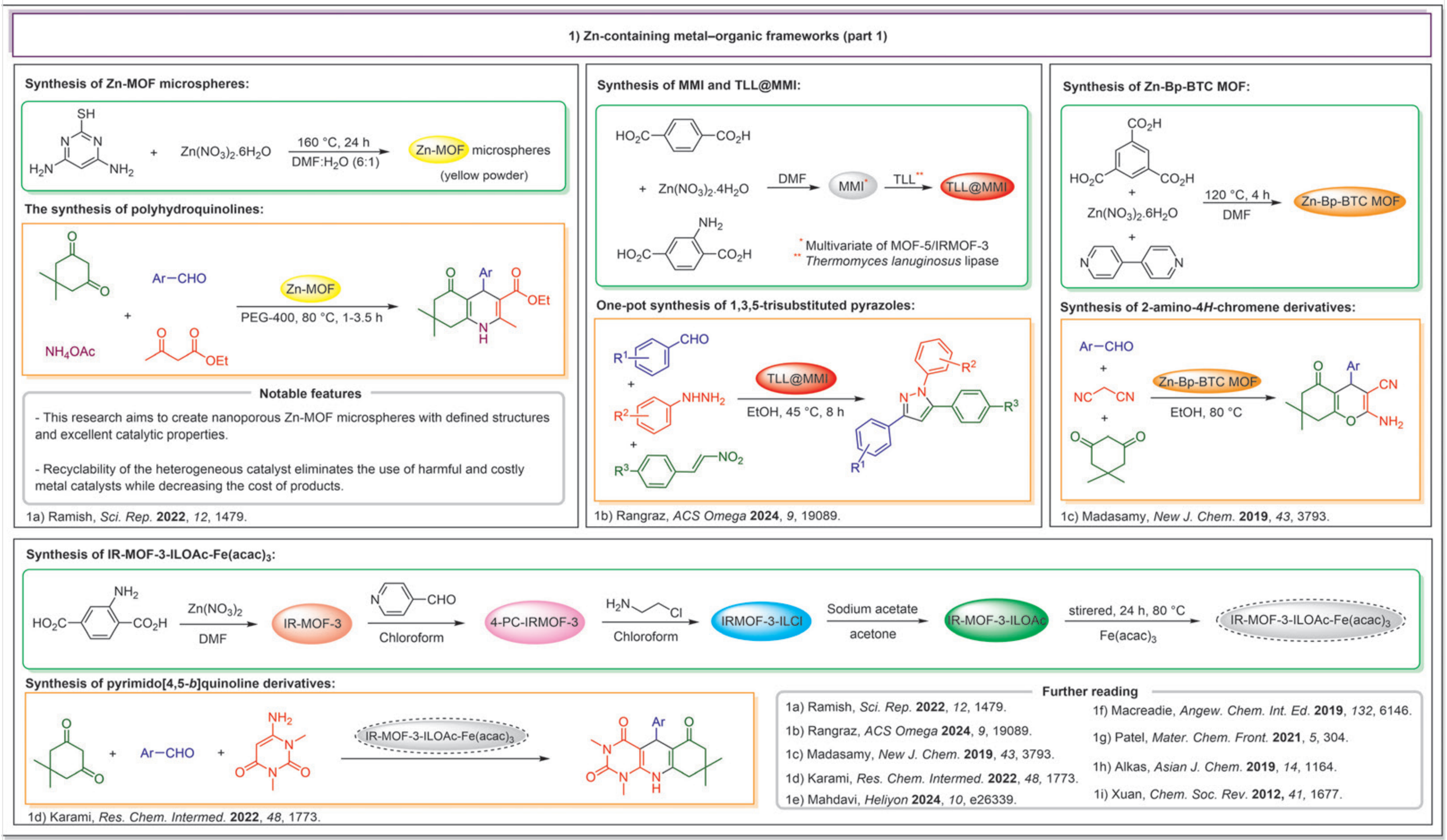
The specific choice of metal ions and organic linkers significantly affects the properties and functionality of MOFs. Metal–organic frameworks exhibit diverse properties based on the types of ligands and surface functional groups they possess. The porosities of MOFs can be adjusted by altering the size of these components. MOFs can also be modified either before or after they are made. Despite their advantages, MOFs face challenges in practical applications, including high production costs, chemical stability issues, and recycling difficulties. However, they show promise as recyclable green catalysts in multicomponent reactions due to their abundant acidic sites. The properties of MOFs bestow them with significant potential for various applications, such as in drug delivery and heterogeneous catalysis, and as heavy metal absorbents, supercapacitors, and sensors. Research in this area is still developing, and this graphical review highlights recent progress in using MOFs to facilitate MCRs.

Biosketches

Younes Latifi was born in Dezful, Iran, in 2001. He earned his Bachelor's degree from Shahid Chamran University in Ahvaz, Iran. In 2023, he joined Prof. Teimouri's research group and is currently a Master's student in organic chemistry at Kharazmi University, Tehran, Iran. His research interests include multicomponent reactions and activities related to the field of green chemistry.

Mahdi Behraveshfar was born in Kermanshah, Iran, in 1999. He received his Bachelor's degree in 2022 from Payame Noor University of Karaj, Iran. In 2023, he joined Prof. Teimouri's research group and is currently a Master's student in organic chemistry at Kharazmi University in Tehran. His research interests include the synthesis of drug compounds using multicomponent reaction methods and suitable catalysts, such as metal–organic frameworks (MOFs).

Mohammad Bagher Teimouri was born in 1975 and studied chemistry at Tabriz University, Iran. He subsequently completed his Ph.D. in 2004 with Prof. Ahmad Shaabani at Shahid Beheshti University. After being an assistant professor at the Iran Polymer and Petrochemical Institute, he moved to Kharazmi University as an associate professor, where he was promoted to full professor in 2022. His research focuses on the development of new multicomponent reactions (MCRs), especially on isocyanide-based and enaminone-based MCRs, MCRs in/on water, stereoselective transformations and the synthesis of novel functional dyes.



- This research aims to create nanoporous Zn-MOF microspheres with defined structures and excellent catalytic properties.

- Recyclability of the heterogeneous catalyst eliminates the use of harmful and costly metal catalysts while decreasing the cost of products.

1a) Ramish, *Sci. Rep.* **2022**, *12*, 1479.

1b) Rangraz, *ACS Omega* **2024**, *9*, 19089.

1c) Madasamy, *New J. Chem.* **2019**, *43*, 3793.

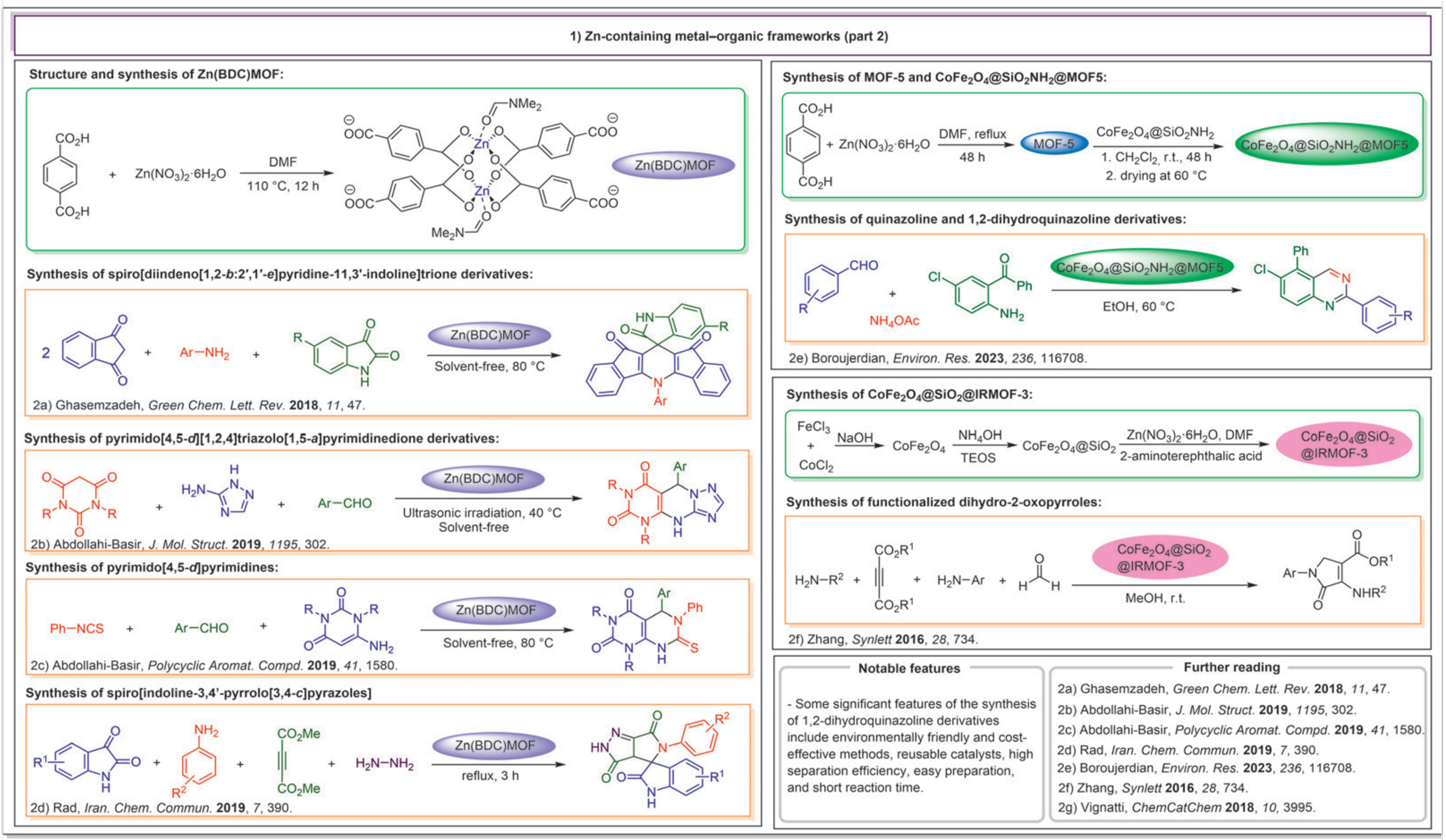
1d) Karami, *Res. Chem. Intermed.* **2022**, *48*, 1773.

Further reading

1a) Ramish, *Sci. Rep.* **2022**, *12*, 1479.
1b) Rangraz, *ACS Omega* **2024**, *9*, 19089.
1c) Madasamy, *New J. Chem.* **2019**, *43*, 3793.
1d) Karami, *Res. Chem. Intermed.* **2022**, *48*, 1773.
1e) Mahdavi, *Heliyon* **2024**, *10*, e26339.
1f) Macreadie, *Angew. Chem. Int. Ed.* **2019**, *132*, 6146.
1g) Patel, *Mater. Chem. Front.* **2021**, *5*, 304.
1h) Alkas, *Asian J. Chem.* **2019**, *14*, 1164.
1i) Xuan, *Chem. Soc. Rev.* **2012**, *41*, 1677.

Figure 1 Zn-containing metal–organic frameworks (part 1)[1a–i]

Georg Thieme Verlag KG, Oswald-Hesse-Straße 50, 70469 Stuttgart, Germany



Notable features

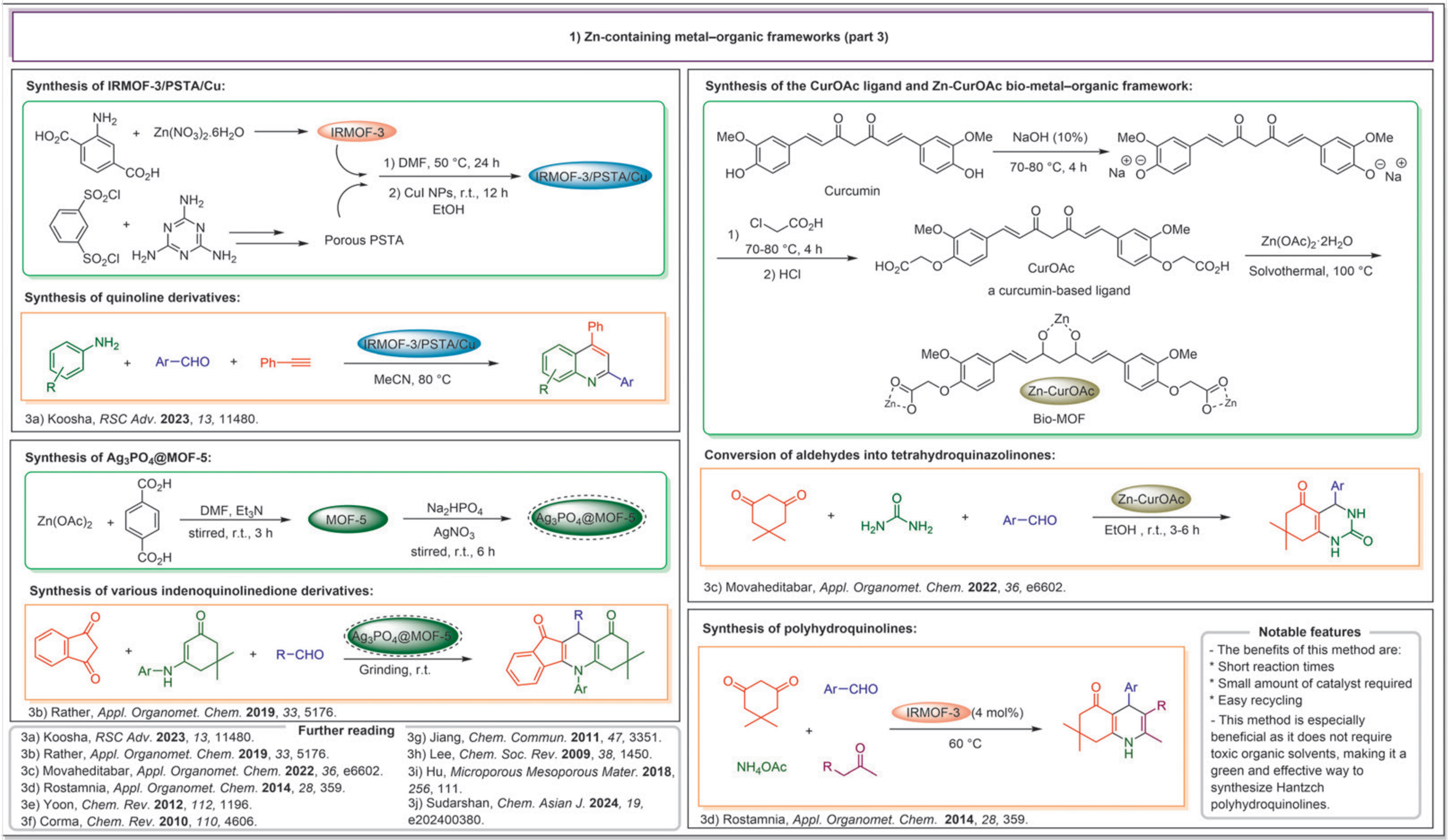
- Some significant features of the synthesis of 1,2-dihydroquinazoline derivatives include environmentally friendly and cost-effective methods, reusable catalysts, high separation efficiency, easy preparation, and short reaction time.

Further reading

2a) Ghasemzadeh, *Green Chem. Lett. Rev.* **2018**, *11*, 47.
2b) Abdollahi-Basir, *J. Mol. Struct.* **2019**, *1195*, 302.
2c) Abdollahi-Basir, *Polycyclic Aromat. Compd.* **2019**, *41*, 1580.
2d) Rad, *Iran. Chem. Commun.* **2019**, *7*, 390.
2e) Boroujerdian, *Environ. Res.* **2023**, *236*, 116708.
2f) Zhang, *Synlett* **2016**, *28*, 734.
2g) Vignatti, *ChemCatChem* **2018**, *10*, 3995.

Figure 2 Zn-containing metal–organic frameworks (part 2)[2a–g]

Georg Thieme Verlag KG, Oswald-Hesse-Straße 50, 70469 Stuttgart, Germany



3a) Koosha, *RSC Adv.* **2023**, *13*, 11480.

3b) Rather, *Appl. Organomet. Chem.* **2019**, *33*, 5176.

3c) Movaheditabar, *Appl. Organomet. Chem.* **2022**, *36*, e6602.

3d) Rostamnia, *Appl. Organomet. Chem.* **2014**, *28*, 359.

Notable features

- The benefits of this method are:
* Short reaction times
* Small amount of catalyst required
* Easy recycling
- This method is especially beneficial as it does not require toxic organic solvents, making it a green and effective way to synthesize Hantzch polyhydroquinolines.

Further reading

3a) Koosha, *RSC Adv.* **2023**, *13*, 11480.
3b) Rather, *Appl. Organomet. Chem.* **2019**, *33*, 5176.
3c) Movaheditabar, *Appl. Organomet. Chem.* **2022**, *36*, e6602.
3d) Rostamnia, *Appl. Organomet. Chem.* **2014**, *28*, 359.
3e) Yoon, *Chem. Rev.* **2012**, *112*, 1196.
3f) Corma, *Chem. Rev.* **2010**, *110*, 4606.
3g) Jiang, *Chem. Commun.* **2011**, *47*, 3351.
3h) Lee, *Chem. Soc. Rev.* **2009**, *38*, 1450.
3i) Hu, *Microporous Mesoporous Mater.* **2018**, *256*, 111.
3j) Sudarshan, *Chem. Asian J.* **2024**, *19*, e202400380.

Figure 3 Zn-containing metal–organic frameworks (part 3)$^{3a–j}$

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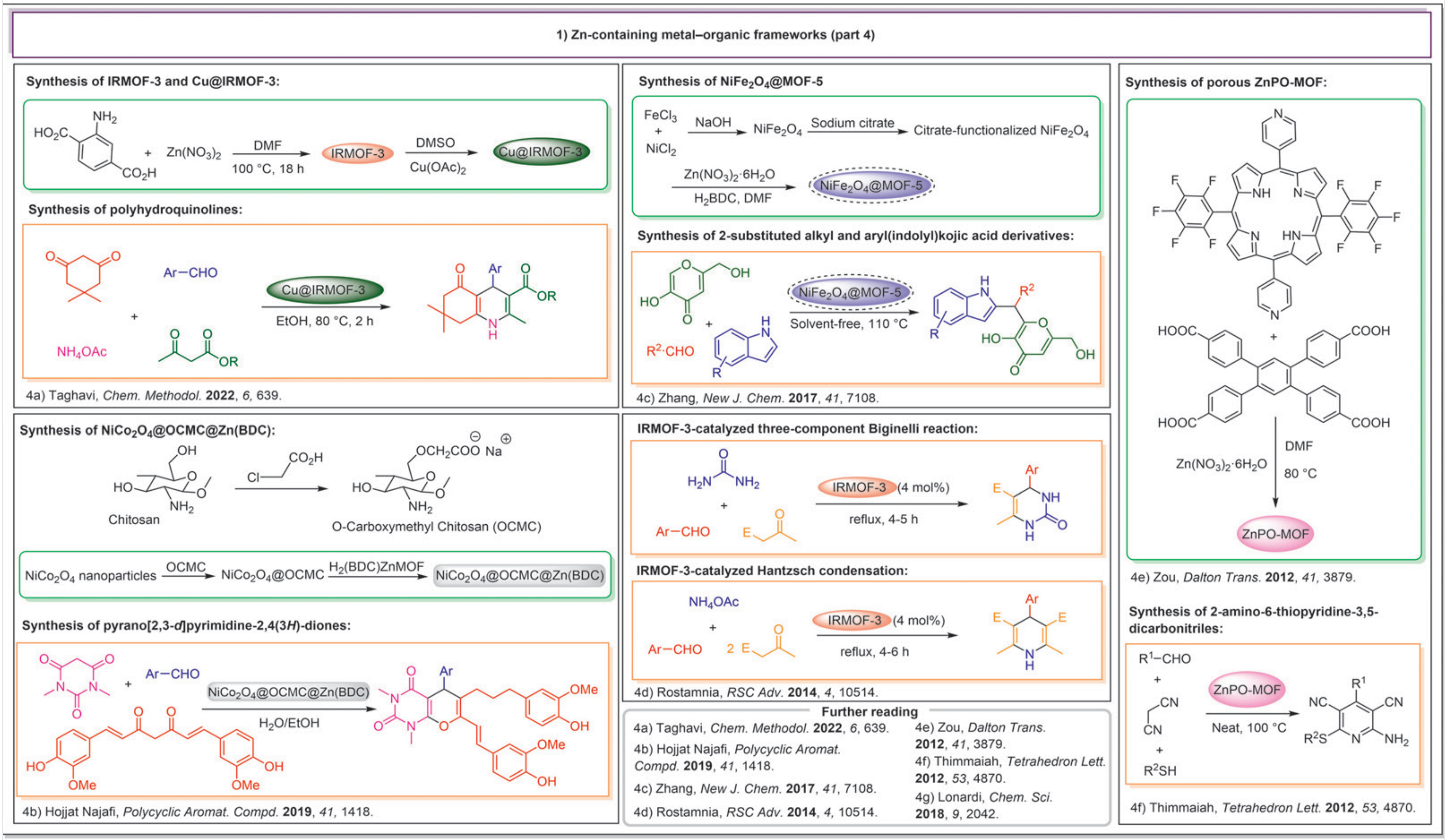


1) Zn-containing metal–organic frameworks (part 4)

Synthesis of IRMOF-3 and Cu@IRMOF-3:

Synthesis of polyhydroquinolines:

4a) Taghavi, *Chem. Methodol.* **2022**, *6*, 639.

Synthesis of $NiFe_2O_4$@MOF-5

Synthesis of 2-substituted alkyl and aryl(indolyl)kojic acid derivatives:

4c) Zhang, *New J. Chem.* **2017**, *41*, 7108.

Synthesis of porous ZnPO-MOF:

4e) Zou, *Dalton Trans.* **2012**, *41*, 3879.

Synthesis of $NiCo_2O_4$@OCMC@Zn(BDC):

Synthesis of pyrano[2,3-*d*]pyrimidine-2,4(3*H*)-diones:

4b) Hojjat Najafi, *Polycyclic Aromat. Compd.* **2019**, *41*, 1418.

IRMOF-3-catalyzed three-component Biginelli reaction:

IRMOF-3-catalyzed Hantzsch condensation:

4d) Rostamnia, *RSC Adv.* **2014**, *4*, 10514.

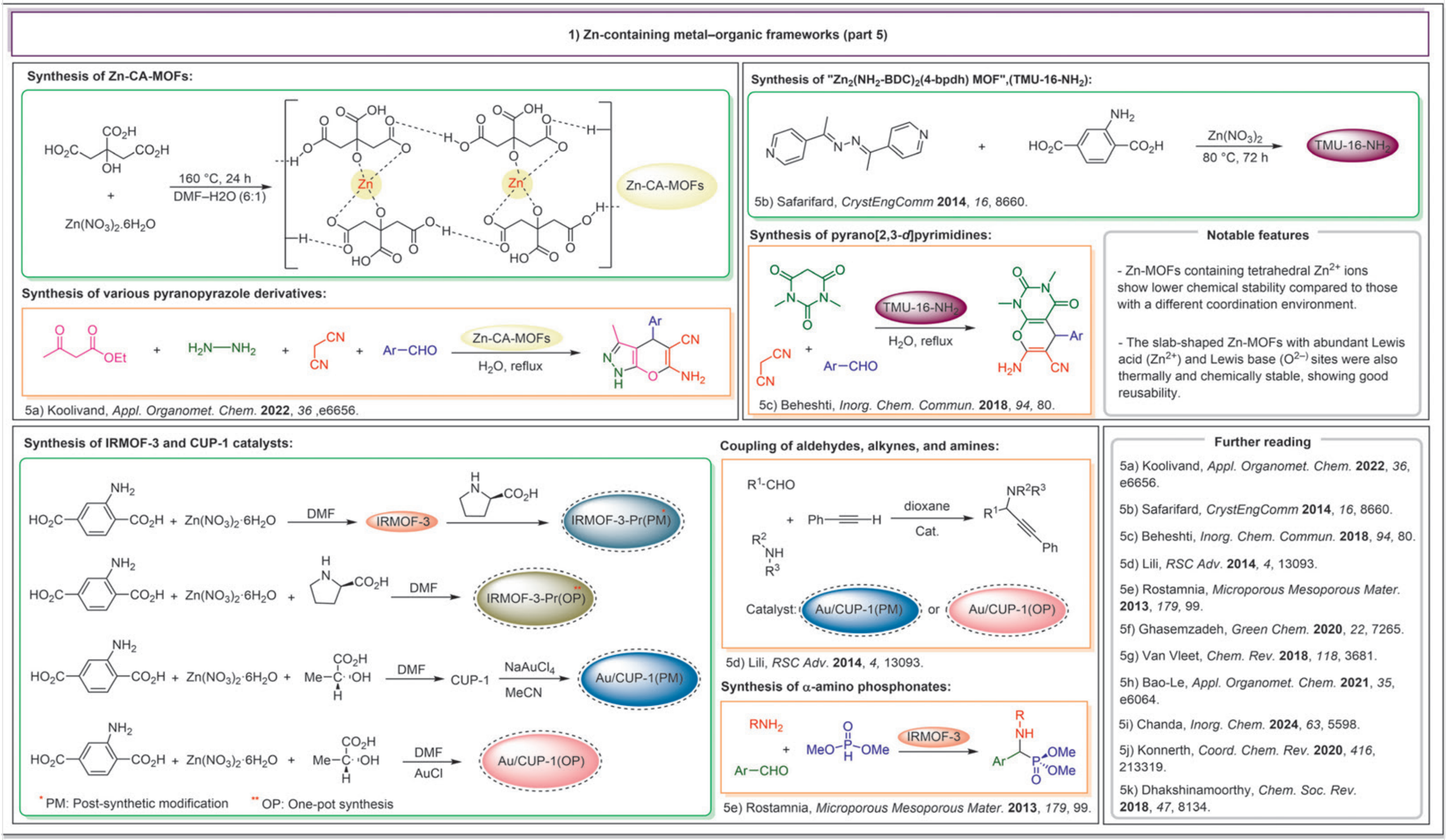
Synthesis of 2-amino-6-thiopyridine-3,5-dicarbonitriles:

4f) Thimmaiah, *Tetrahedron Lett.* **2012**, *53*, 4870.

Further reading

4a) Taghavi, *Chem. Methodol.* **2022**, *6*, 639.
4b) Hojjat Najafi, *Polycyclic Aromat. Compd.* **2019**, *41*, 1418.
4c) Zhang, *New J. Chem.* **2017**, *41*, 7108.
4d) Rostamnia, *RSC Adv.* **2014**, *4*, 10514.
4e) Zou, *Dalton Trans.* **2012**, *41*, 3879.
4f) Thimmaiah, *Tetrahedron Lett.* **2012**, *53*, 4870.
4g) Lonardi, *Chem. Sci.* **2018**, *9*, 2042.

Figure 4 Zn-containing metal–organic frameworks (part 4)[4a–g]



1) Zn-containing metal–organic frameworks (part 5)

Synthesis of Zn-CA-MOFs:

Synthesis of various pyranopyrazole derivatives:

5a) Koolivand, *Appl. Organomet. Chem.* **2022**, *36* ,e6656.

Synthesis of "$Zn_2(NH_2\text{-}BDC)_2(4\text{-}bpdh)$ MOF",($TMU\text{-}16\text{-}NH_2$):

5b) Safarifard, *CrystEngComm* **2014**, *16*, 8660.

Synthesis of pyrano[2,3-*d*]pyrimidines:

5c) Beheshti, *Inorg. Chem. Commun.* **2018**, *94*, 80.

Notable features

- Zn-MOFs containing tetrahedral Zn^{2+} ions show lower chemical stability compared to those with a different coordination environment.

- The slab-shaped Zn-MOFs with abundant Lewis acid (Zn^{2+}) and Lewis base (O^{2-}) sites were also thermally and chemically stable, showing good reusability.

Synthesis of IRMOF-3 and CUP-1 catalysts:

* PM: Post-synthetic modification ** OP: One-pot synthesis

Coupling of aldehydes, alkynes, and amines:

5d) Lili, *RSC Adv.* **2014**, *4*, 13093.

Synthesis of α-amino phosphonates:

5e) Rostamnia, *Microporous Mesoporous Mater.* **2013**, *179*, 99.

Further reading

5a) Koolivand, *Appl. Organomet. Chem.* **2022**, *36*, e6656.

5b) Safarifard, *CrystEngComm* **2014**, *16*, 8660.

5c) Beheshti, *Inorg. Chem. Commun.* **2018**, *94*, 80.

5d) Lili, *RSC Adv.* **2014**, *4*, 13093.

5e) Rostamnia, *Microporous Mesoporous Mater.* **2013**, *179*, 99.

5f) Ghasemzadeh, *Green Chem.* **2020**, *22*, 7265.

5g) Van Vleet, *Chem. Rev.* **2018**, *118*, 3681.

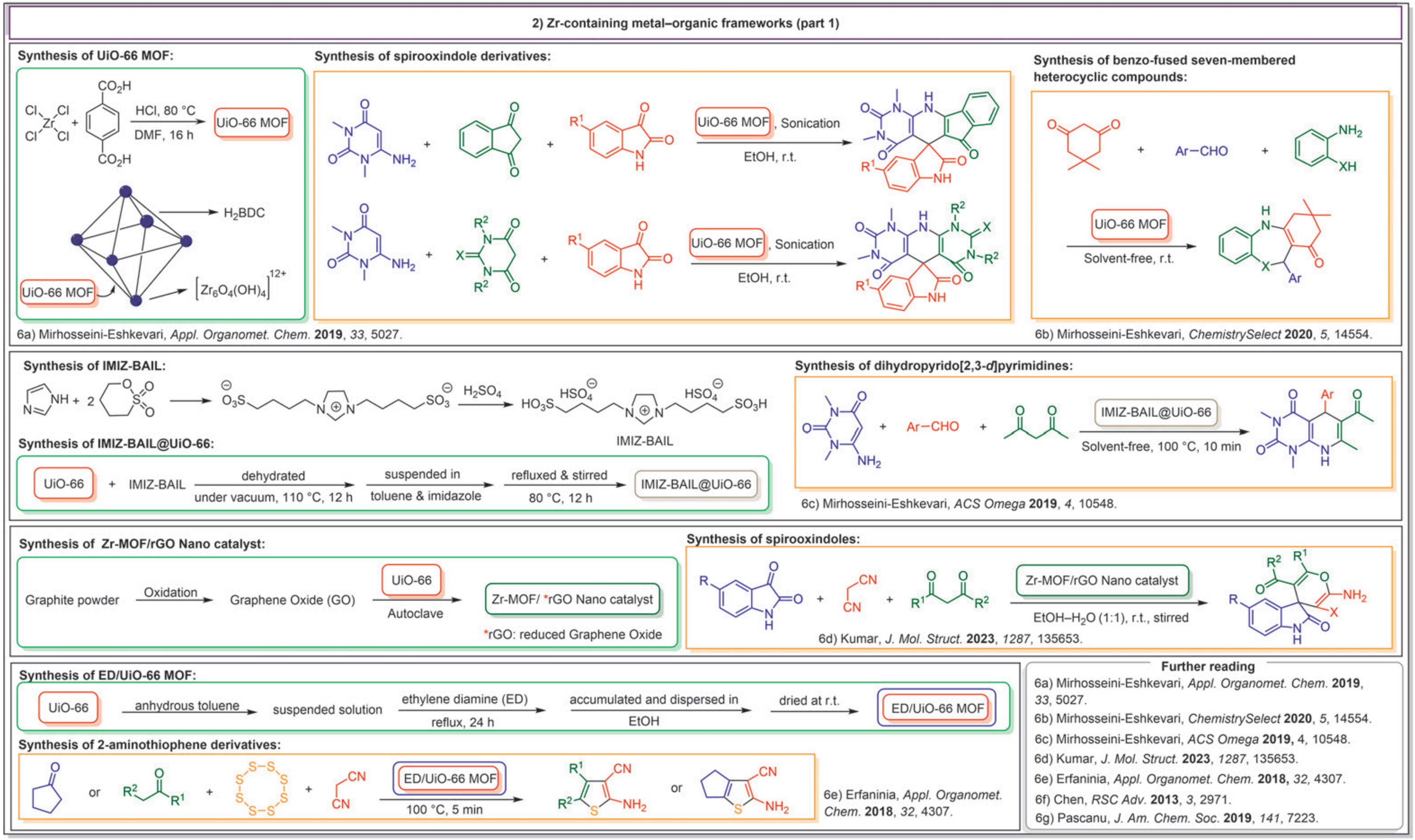
5h) Bao-Le, *Appl. Organomet. Chem.* **2021**, *35*, e6064.

5i) Chanda, *Inorg. Chem.* **2024**, *63*, 5598.

5j) Konnerth, *Coord. Chem. Rev.* **2020**, *416*, 213319.

5k) Dhakshinamoorthy, *Chem. Soc. Rev.* **2018**, *47*, 8134.

Figure 5 Zn-containing metal–organic frameworks (part 5)$^{5a–k}$



2) Zr-containing metal–organic frameworks (part 1)

Synthesis of UiO-66 MOF:

Synthesis of spirooxindole derivatives:

Synthesis of benzo-fused seven-membered heterocyclic compounds:

6a) Mirhosseini-Eshkevari, *Appl. Organomet. Chem.* **2019**, *33*, 5027.

6b) Mirhosseini-Eshkevari, *ChemistrySelect* **2020**, *5*, 14554.

Synthesis of IMIZ-BAIL:

Synthesis of IMIZ-BAIL@UiO-66:

UiO-66 + IMIZ-BAIL $\xrightarrow[\text{under vacuum, 110 °C, 12 h}]{\text{dehydrated}}$ $\xrightarrow[\text{toluene \& imidazole}]{\text{suspended in}}$ $\xrightarrow[\text{80 °C, 12 h}]{\text{refluxed \& stirred}}$ IMIZ-BAIL@UiO-66

Synthesis of dihydropyrido[2,3-*d*]pyrimidines:

6c) Mirhosseini-Eshkevari, *ACS Omega* **2019**, *4*, 10548.

Synthesis of Zr-MOF/rGO Nano catalyst:

Graphite powder $\xrightarrow{\text{Oxidation}}$ Graphene Oxide (GO) $\xrightarrow[\text{Autoclave}]{\text{UiO-66}}$ Zr-MOF/ *rGO Nano catalyst

*rGO: reduced Graphene Oxide

Synthesis of spirooxindoles:

6d) Kumar, *J. Mol. Struct.* **2023**, *1287*, 135653.

Synthesis of ED/UiO-66 MOF:

UiO-66 $\xrightarrow{\text{anhydrous toluene}}$ suspended solution $\xrightarrow[\text{reflux, 24 h}]{\text{ethylene diamine (ED)}}$ $\xrightarrow[\text{EtOH}]{\text{accumulated and dispersed in}}$ $\xrightarrow{\text{dried at r.t.}}$ ED/UiO-66 MOF

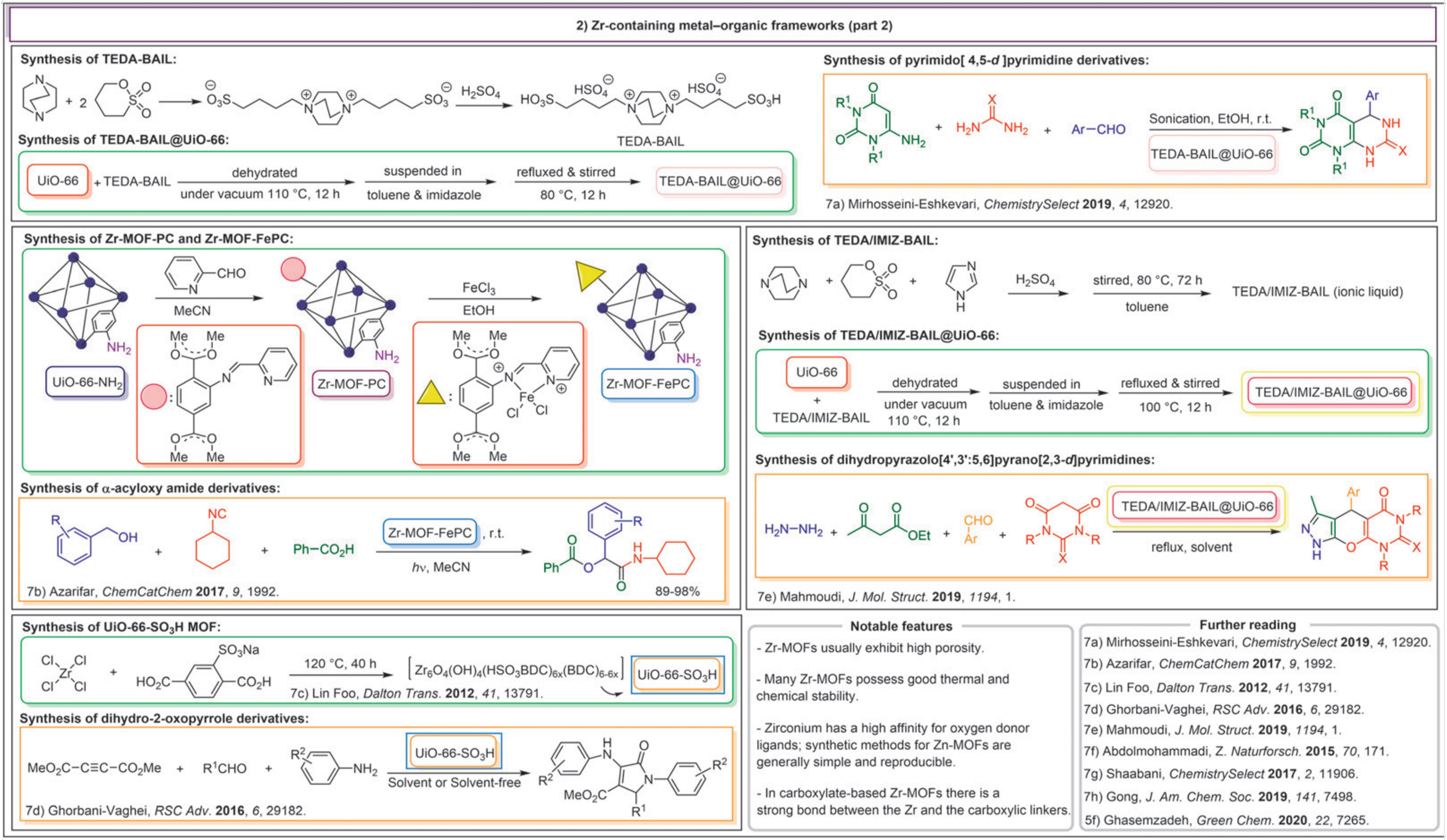
Synthesis of 2-aminothiophene derivatives:

6e) Erfaninia, *Appl. Organomet. Chem.* **2018**, *32*, 4307.

Further reading

6a) Mirhosseini-Eshkevari, *Appl. Organomet. Chem.* **2019**, *33*, 5027.
6b) Mirhosseini-Eshkevari, *ChemistrySelect* **2020**, *5*, 14554.
6c) Mirhosseini-Eshkevari, *ACS Omega* **2019**, 4, 10548.
6d) Kumar, *J. Mol. Struct.* **2023**, *1287*, 135653.
6e) Erfanina, *Appl. Organomet. Chem.* **2018**, *32*, 4307.
6f) Chen, *RSC Adv.* **2013**, *3*, 2971.
6g) Pascanu, *J. Am. Chem. Soc.* **2019**, *141*, 7223.

Figure 6 Zr-containing metal–organic frameworks (part 1)[6a–g]



Notable features

- Zr-MOFs usually exhibit high porosity.
- Many Zr-MOFs possess good thermal and chemical stability.
- Zirconium has a high affinity for oxygen donor ligands; synthetic methods for Zn-MOFs are generally simple and reproducible.
- In carboxylate-based Zr-MOFs there is a strong bond between the Zr and the carboxylic linkers.

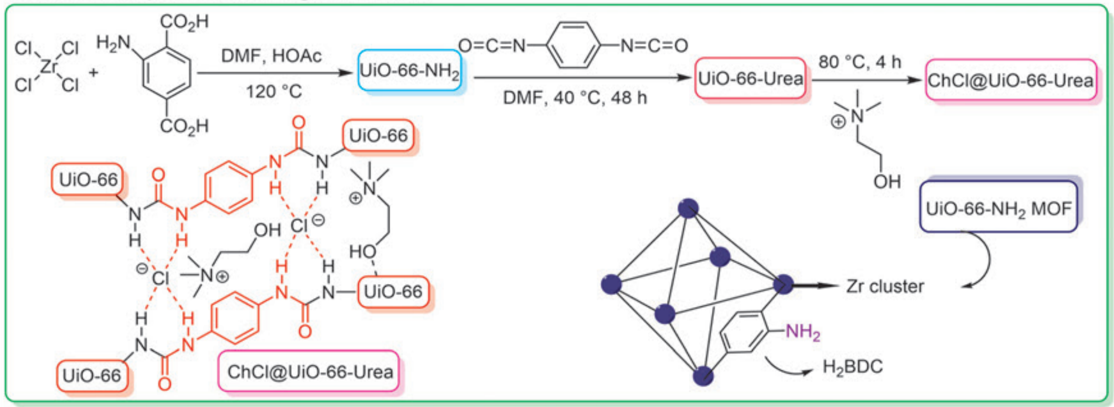
Further reading

7a) Mirhosseini-Eshkevari, *ChemistrySelect* **2019**, *4*, 12920.
7b) Azarifar, *ChemCatChem* **2017**, *9*, 1992.
7c) Lin Foo, *Dalton Trans.* **2012**, *41*, 13791.
7d) Ghorbani-Vaghei, *RSC Adv.* **2016**, *6*, 29182.
7e) Mahmoudi, *J. Mol. Struct.* **2019**, *1194*, 1.
7f) Abdolmohammadi, Z. *Naturforsch.* **2015**, *70*, 171.
7g) Shaabani, *ChemistrySelect* **2017**, *2*, 11906.
7h) Gong, *J. Am. Chem. Soc.* **2019**, *141*, 7498.
5f) Ghasemzadeh, *Green Chem.* **2020**, *22*, 7265.

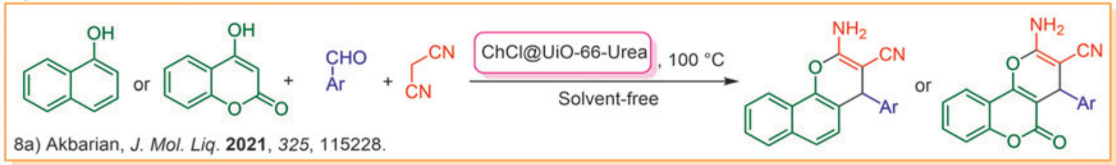
Figure 7 Zr-containing metal–organic frameworks (part 2)[5f,7a–h]

2) Zr-containing metal–organic frameworks (part 3)

Structure and synthesis of ChCl@UiO-66-Urea:

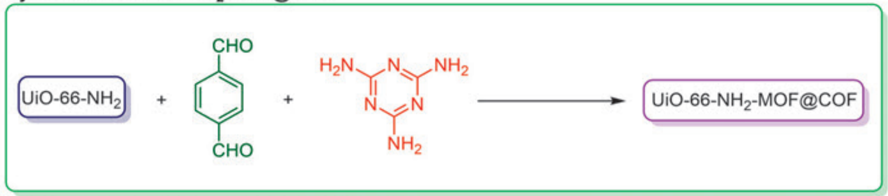


Synthesis of 2-amino-4*H*-chromenes:

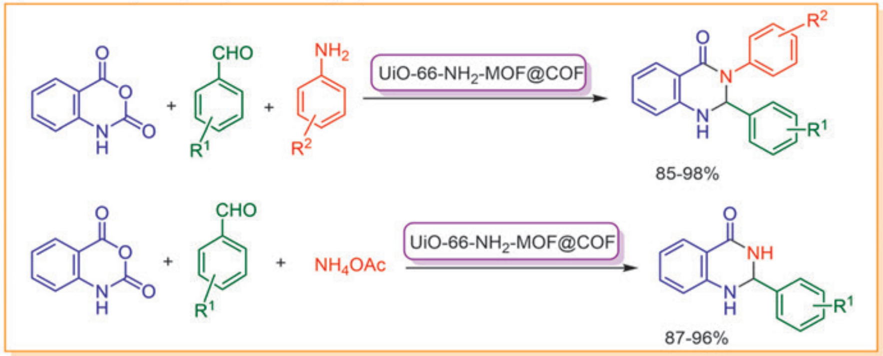


8a) Akbarian, *J. Mol. Liq.* **2021**, *325*, 115228.

Synthesis of UiO-66-NH_2-MOF@COF:

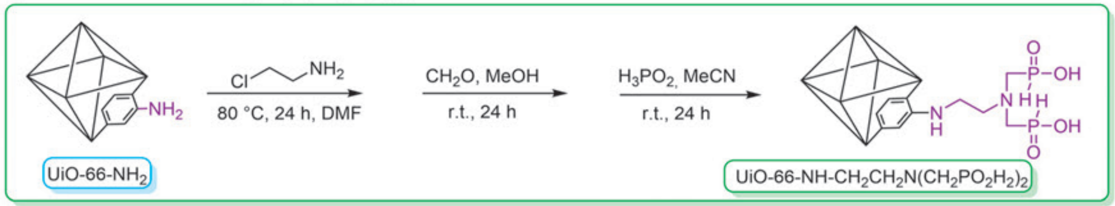


Synthesis of 2,3-dihydroquinazolin-4(1*H*)-ones:

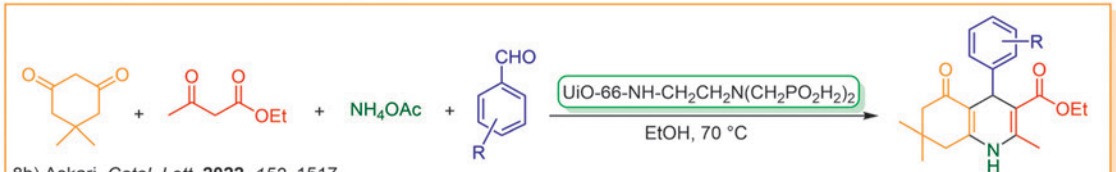


8c) Ghasemzadeh, *Nanoscale Adv.* **2023**, *5*, 7031.

Synthesis of UiO-66-NH-$CH_2CH_2N(CH_2PO_2H_2)_2$:

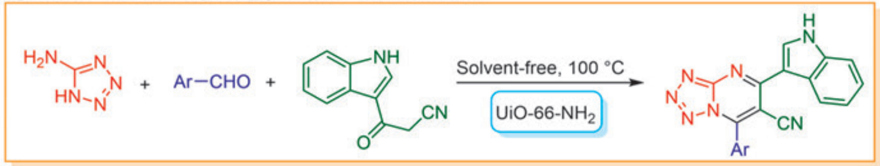


Synthesis of polyhydroquinoline derivatives:



8b) Askari, *Catal. Lett.* **2022**, *152*, 1517.

Synthesis of tetrazolo[1,5-*a*]pyrimidine-6-carbonitriles:



8d) Abdollahi-Basir, *Polycyclic Aromat. Compd.* **2022**, *42*, 5719.

Notable features

- What are COFs?

Covalent Organic Frameworks are a class of crystalline porous materials constructed from organic building blocks linked together by strong covalent bonds into extended two- or three-dimensional frameworks.

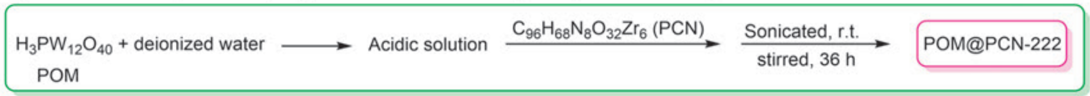
Further reading

8a) Akbarian, *J. Mol. Liq.* **2021**, *325*, 115228.
8b) Askari, *Catal. Lett.* **2022**, *152*, 1517.
8c) Ghasemzadeh, *Nanoscale Adv.* **2023**, *5*, 7031.
8d) Abdollahi-Basir, *Polycyclic Aromat. Compd.* **2022**, *42*, 5719.
8e) Olyaei, *Chem. Heterocycl. Compd.* **2015**, *51*, 899.
8f) Kirchon, *Chem. Soc. Rev.* **2018**, *47*, 8611.
8g) Xu, *Chem. Eur. J.* **2018**, *24*, 15772.

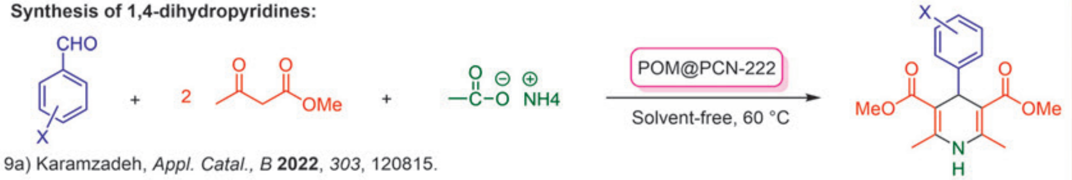
Figure 8 Zr-containing metal–organic frameworks (part 3)[8a–g]

2) Zr-containing metal–organic frameworks (part 4)

Synthesis of POM@PCN-222 (Polyoxometalate-containing mesoporous Zr-MOF):

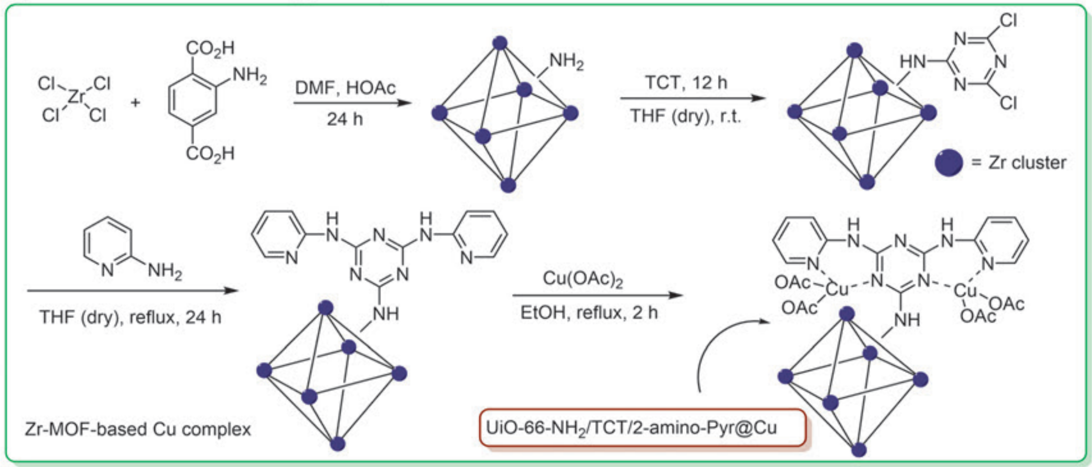


Synthesis of 1,4-dihydropyridines:

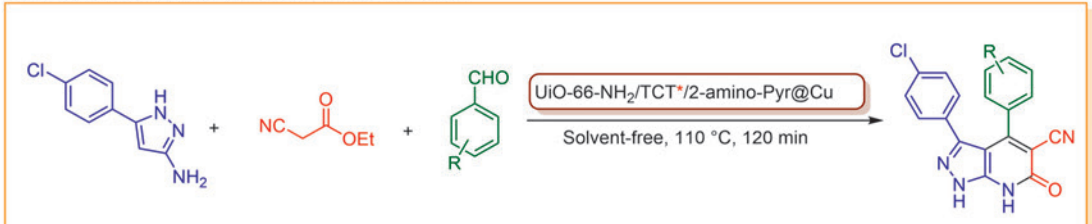


9a) Karamzadeh, *Appl. Catal., B* **2022**, *303*, 120815.

Synthesis of a Zr-MOF-based copper complex:



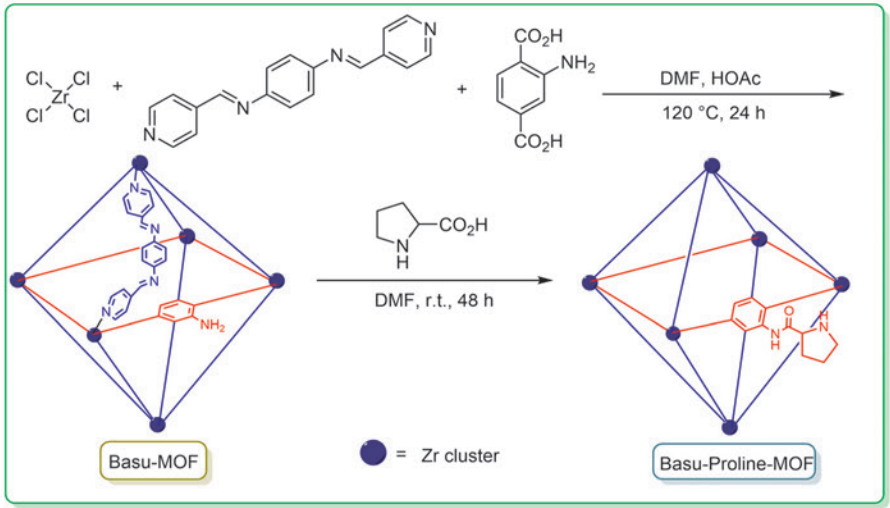
Synthesis of pyrazolo[3,4-*b*]pyridine-5-carbonitriles:



9b) Tavakoli, *Nature* **2023**, *13*, 9388.

* TCT = (2,4,6-trichloro-1,3,5-triazine)

Synthesis of Basu-Proline MOF:



Synthesis of dihydropyrano[3,2-*c*]chromenes:

9c) Benrashid, *Sci. Rep.* **2023**, *13*, 17608.

Further reading

9a) Karamzadeh, *Appl. Catal., B* **2022**, *303*, 120815.
9b) Tavakoli, *Nature* **2023**, *13*, 9388.
9c) Benrashid, *Sci. Rep.* **2023**, *13*, 17608.
9d) Nasr-Esfahani, *J. Mol. Catal. A: Chem.* **2014**, *382*, 99.
9e) Li, *Angew. Chem. Int. Ed.* **2020**, *59*, 9319.
9f) Majewki, *J. Mater. Chem. A*, **2018**, *6*, 7338.
9g) Li, *Sens. Actuators B: Chem.* **2020**, *306*, 127608.
9h) Feng, *Chem. Rev.* **2020**, *120*, 13087.

Notable features

- Pyrazolo[3,4-*b*]pyridine-5-carbonitriles: These compounds may have biological and medicinal applications due to the presence of indole and pyrazole moieties.

- Poly Oxo Metalates (POMs): These metal oxide polyanion compounds are primarily made of early-transition metals linked by oxygen. POMs have been reported for catalytic applications due to their versatile structures.

Figure 9 Zr-containing metal–organic frameworks (part 4)[9a–h]

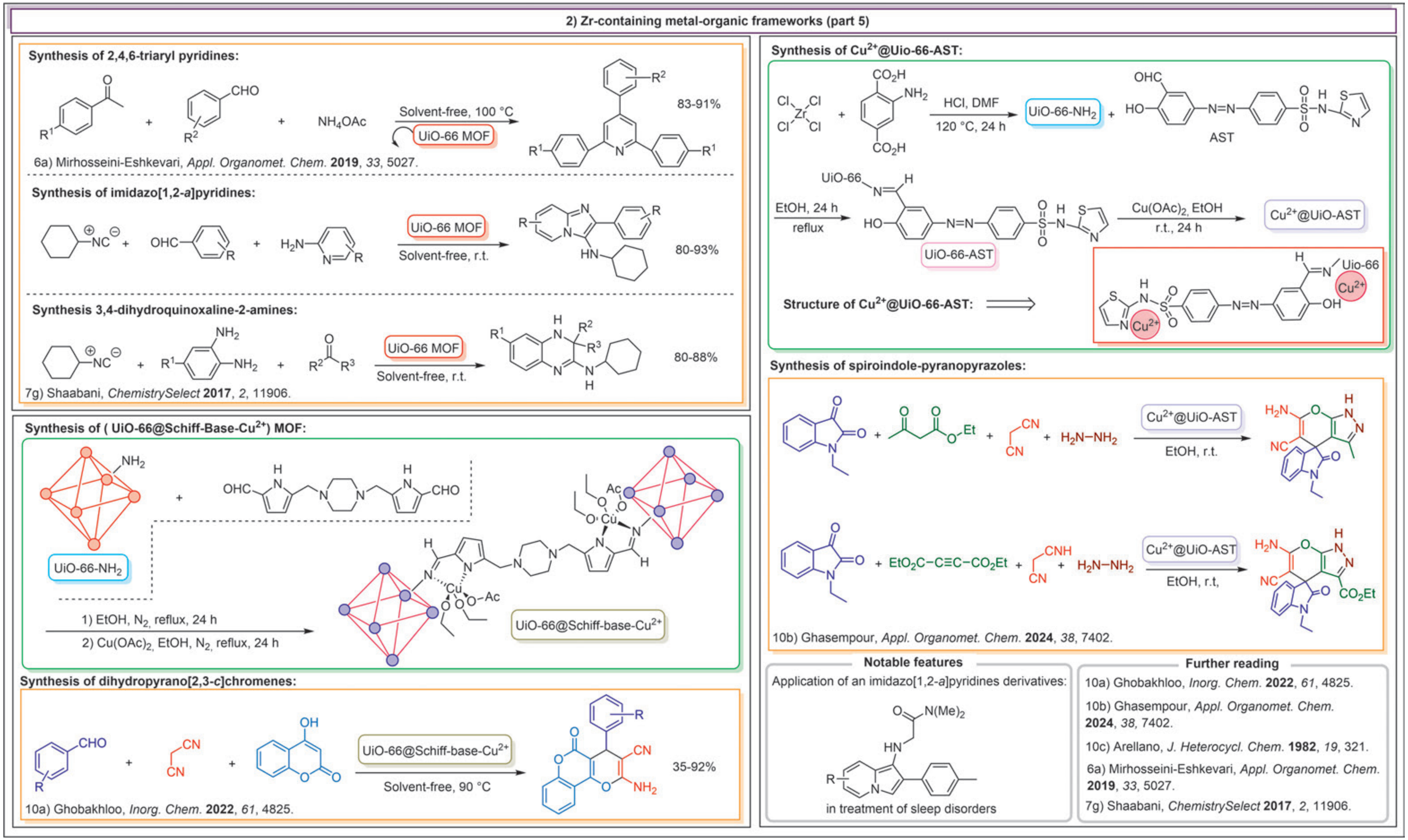
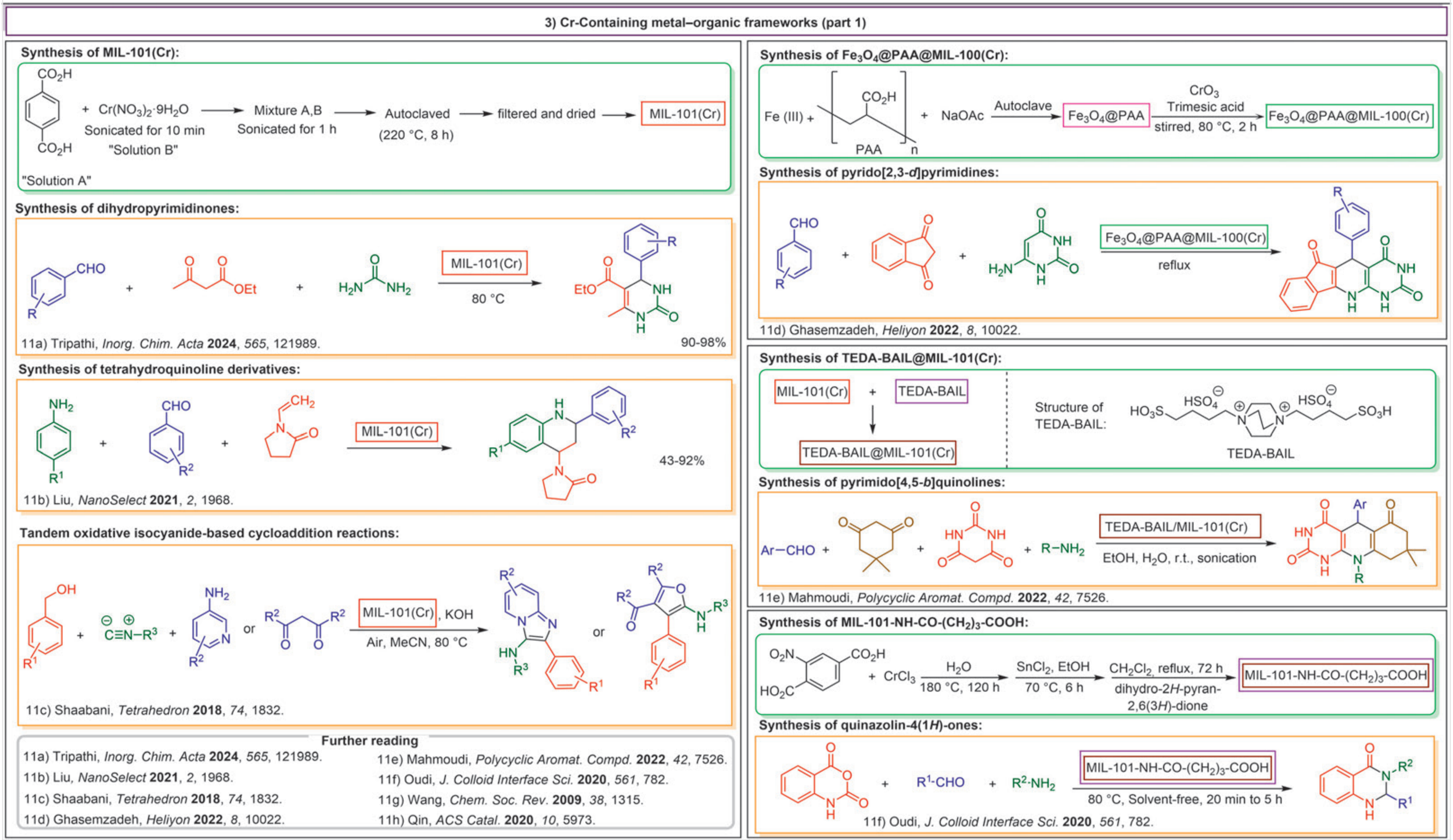


Figure 10 Zr-containing metal–organic frameworks (part 5)[6a,7g,10a–c]



3) Cr-Containing metal–organic frameworks (part 1)

Synthesis of MIL-101(Cr):

Synthesis of dihydropyrimidinones:

11a) Tripathi, *Inorg. Chim. Acta* **2024**, *565*, 121989.

Synthesis of tetrahydroquinoline derivatives:

11b) Liu, *NanoSelect* **2021**, *2*, 1968.

Tandem oxidative isocyanide-based cycloaddition reactions:

11c) Shaabani, *Tetrahedron* **2018**, *74*, 1832.

Further reading

11a) Tripathi, *Inorg. Chim. Acta* **2024**, *565*, 121989.
11b) Liu, *NanoSelect* **2021**, *2*, 1968.
11c) Shaabani, *Tetrahedron* **2018**, *74*, 1832.
11d) Ghasemzadeh, *Heliyon* **2022**, *8*, 10022.
11e) Mahmoudi, *Polycyclic Aromat. Compd.* **2022**, *42*, 7526.
11f) Oudi, *J. Colloid Interface Sci.* **2020**, *561*, 782.
11g) Wang, *Chem. Soc. Rev.* **2009**, *38*, 1315.
11h) Qin, *ACS Catal.* **2020**, *10*, 5973.

Synthesis of Fe_3O_4@PAA@MIL-100(Cr):

Synthesis of pyrido[2,3-*d*]pyrimidines:

11d) Ghasemzadeh, *Heliyon* **2022**, *8*, 10022.

Synthesis of TEDA-BAIL@MIL-101(Cr):

Synthesis of pyrimido[4,5-*b*]quinolines:

11e) Mahmoudi, *Polycyclic Aromat. Compd.* **2022**, *42*, 7526.

Synthesis of MIL-101-NH-CO-$(CH_2)_3$-COOH:

Synthesis of quinazolin-4(1*H*)-ones:

11f) Oudi, *J. Colloid Interface Sci.* **2020**, *561*, 782.

Figure 11 Cr-containing metal–organic frameworks (part 1)[11a–h]

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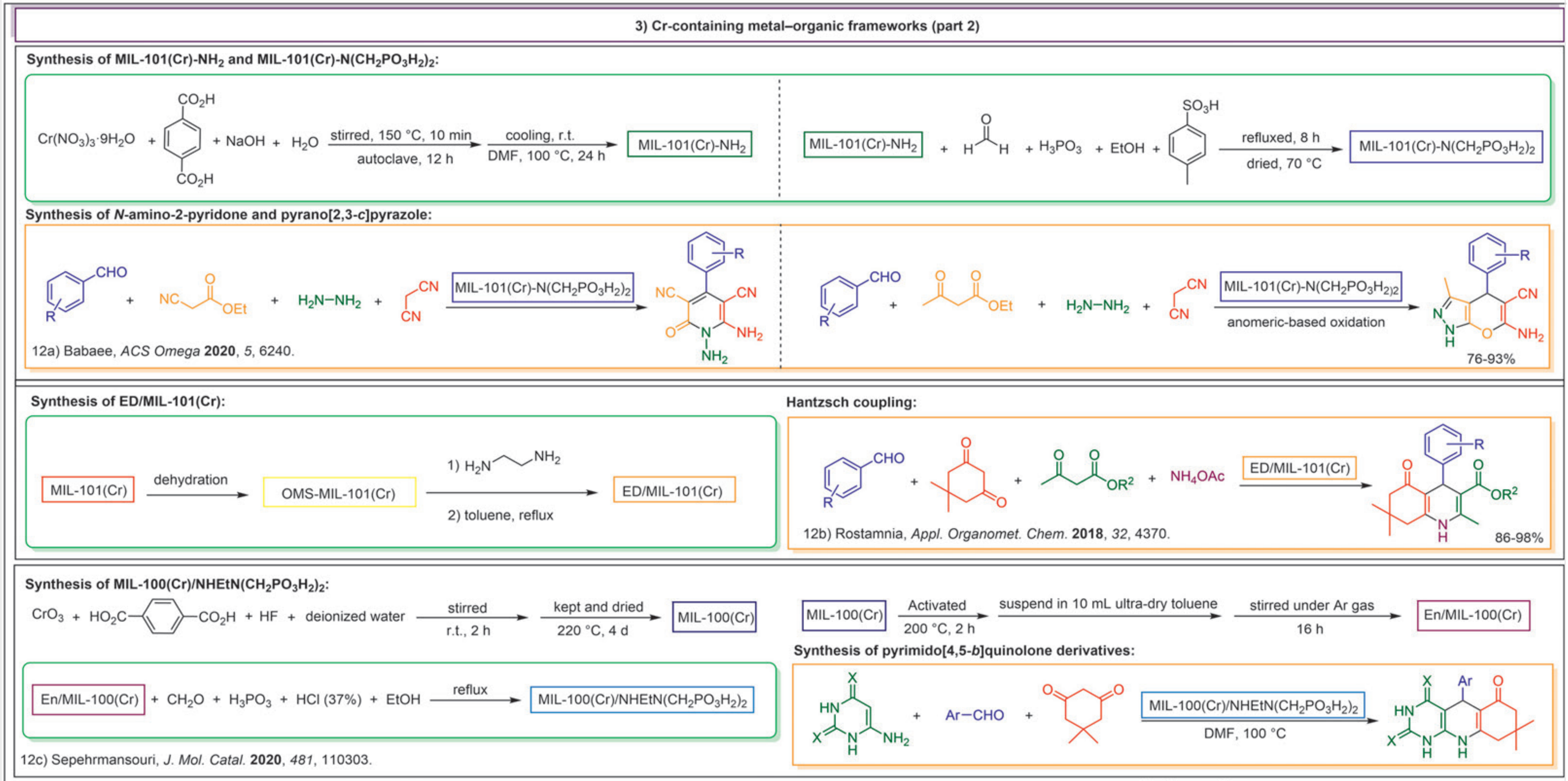

Notable features

- Cr-MOFs exhibit good thermal and chemical stability. This property allows their use under harsh operating conditions.
- The size and shape of the pores in Cr-MOFs can be adjusted by varying the organic ligands used in their construction.

Further reading

12a) Babaee, *ACS Omega* **2020**, *5*, 6240.
12b) Rostamnia, *Appl. Organomet. Chem.* **2018**, *32*, 4370.
12c) Sepehrmansouri, *J. Mol. Catal.* **2020**, *481*, 110303.
12d) Kholdeeva, *Catal. Today.* **2014**, *238*, 54.
12e) Hosseini, *RSC Adv.* **2018**, *8*, 27131.
12f) Safaei-Ghomi, *J. Chem. Res.* **2015**, *39*, 410.
12g) Hu, *Cryst. Eng. Commun.* **2017**, *19*, 4066.
5f) Ghasemzadeh, *Green Chem.* **2020**, *22*, 7265.

Figure 12 Cr-containing metal–organic frameworks (part 2)[5f,12a–g]

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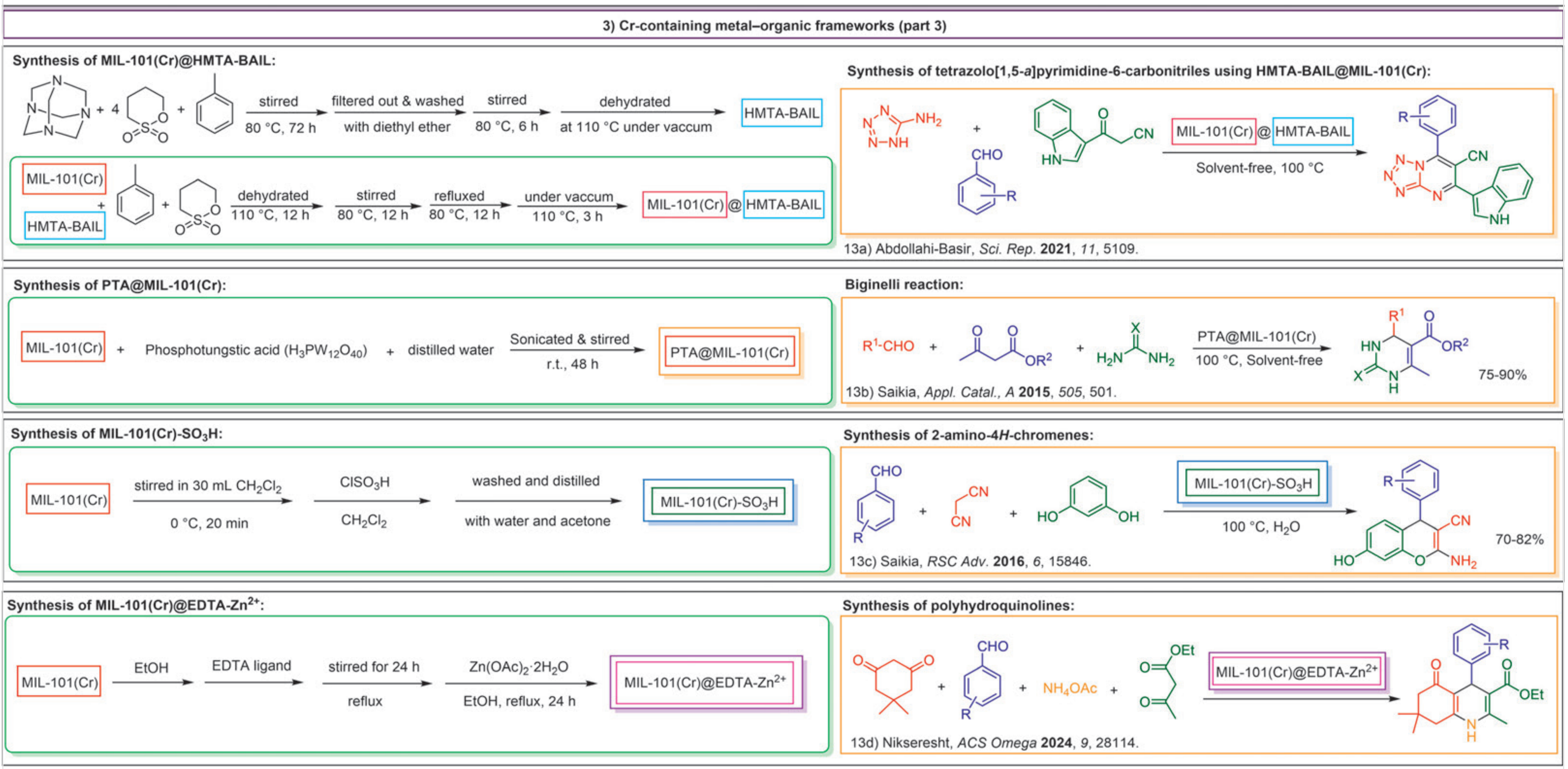


Notable features

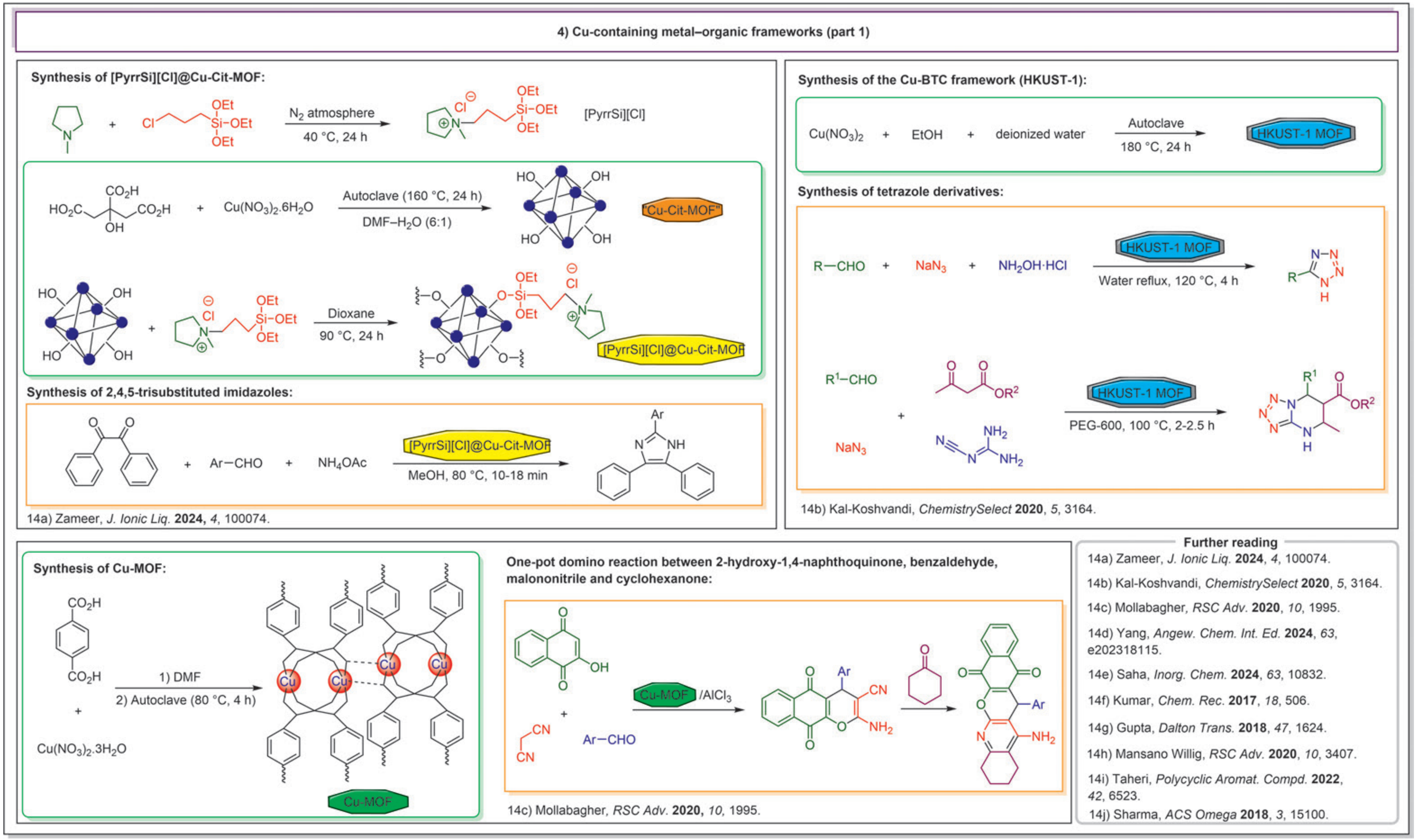
- The presence of high valence Cr^{3+} ions and their strong interactions with the bridging ligands enhances the catalytic activity and adsorption capacity of MOFs.

- Some Cr-MOFs exhibit excellent catalytic properties. This feature enables their use in various chemical reactions.

Further reading

13a) Abdollahi-Basir, *Sci. Rep.* **2021**, *11*, 5109.
13b) Saikia, *Appl. Catal., A* **2015**, *505*, 501.
13c) Saikia, *RSC Adv.* **2016**, *6*, 15846.
13d) Nikseresht, *ACS Omega* **2024**, *9*, 28114.
13e) Zhou, *Green Chem.* **2021**, *23*, 5456.
13f) Karmarker, *Sep. Purif. Technol.* **2019**, *215*, 259.
13g) Liu, *Mater* **2017**, *10*, 99.
11h) Qin, *ACS Catal.* **2020**, *10*, 5973.

Figure 13 Cr-containing metal–organic frameworks (part 3)[11h,13a–g]



14a) Zameer, *J. Ionic Liq.* **2024**, *4*, 100074.

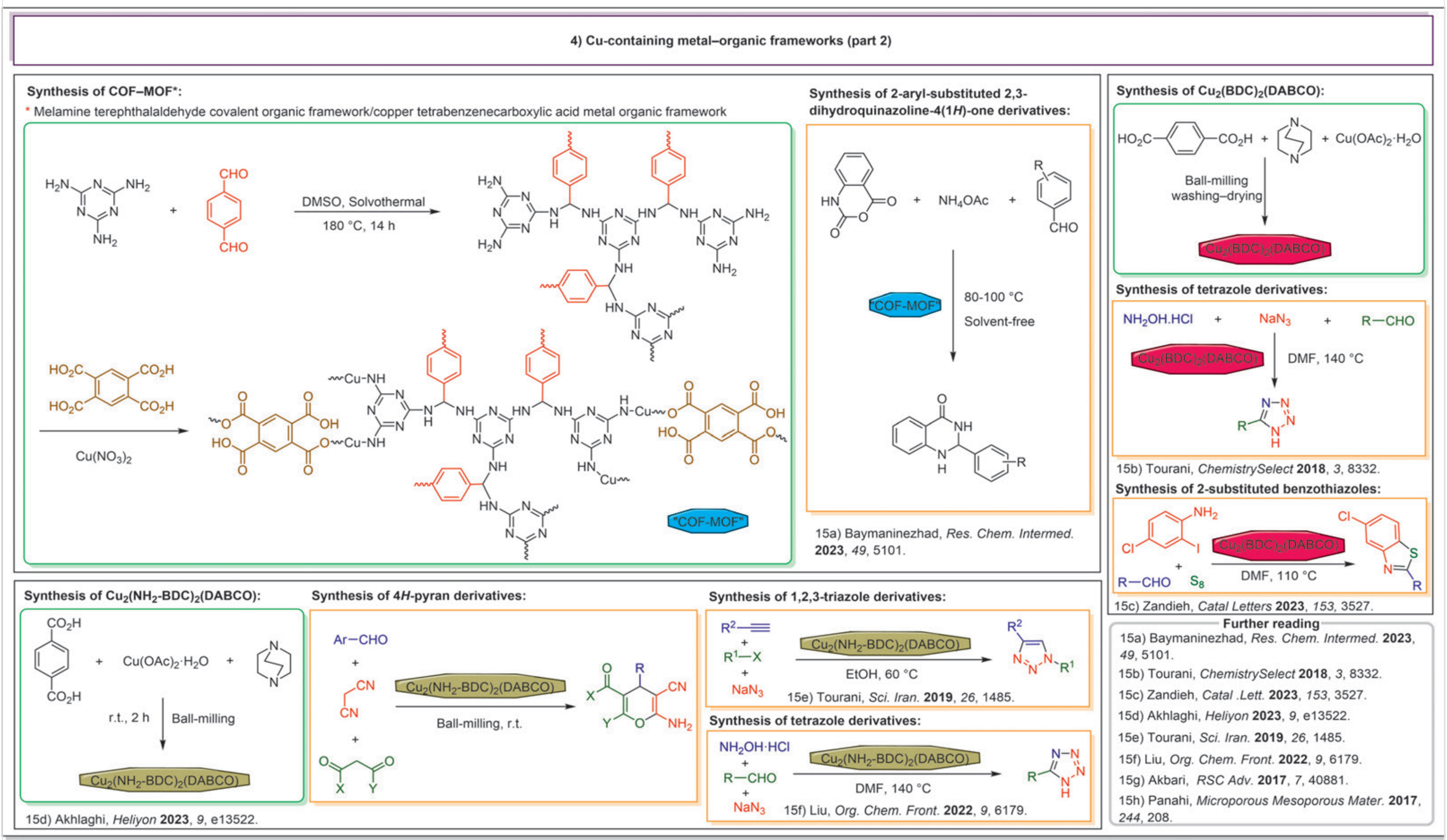
14b) Kal-Koshvandi, *ChemistrySelect* **2020**, *5*, 3164.

14c) Mollabagher, *RSC Adv.* **2020**, *10*, 1995.

Further reading

14a) Zameer, *J. Ionic Liq.* **2024**, *4*, 100074.
14b) Kal-Koshvandi, *ChemistrySelect* **2020**, *5*, 3164.
14c) Mollabagher, *RSC Adv.* **2020**, *10*, 1995.
14d) Yang, *Angew. Chem. Int. Ed.* **2024**, *63*, e202318115.
14e) Saha, *Inorg. Chem.* **2024**, *63*, 10832.
14f) Kumar, *Chem. Rec.* **2017**, *18*, 506.
14g) Gupta, *Dalton Trans.* **2018**, *47*, 1624.
14h) Mansano Willig, *RSC Adv.* **2020**, *10*, 3407.
14i) Taheri, *Polycyclic Aromat. Compd.* **2022**, *42*, 6523.
14j) Sharma, *ACS Omega* **2018**, *3*, 15100.

Figure 14 Cu-containing metal–organic frameworks (part 1)[14a–j]



15a) Baymaninezhad, *Res. Chem. Intermed.* **2023**, *49*, 5101.
15b) Tourani, *ChemistrySelect* **2018**, *3*, 8332.
15c) Zandieh, *Catal .Lett.* **2023**, *153*, 3527.
15d) Akhlaghi, *Heliyon* **2023**, *9*, e13522.
15e) Tourani, *Sci. Iran.* **2019**, *26*, 1485.
15f) Liu, *Org. Chem. Front.* **2022**, *9*, 6179.
15g) Akbari, *RSC Adv.* **2017**, *7*, 40881.
15h) Panahi, *Microporous Mesoporous Mater.* **2017**, *244*, 208.

Figure 15 Cu-containing metal–organic frameworks (part 2)$^{15a–h}$

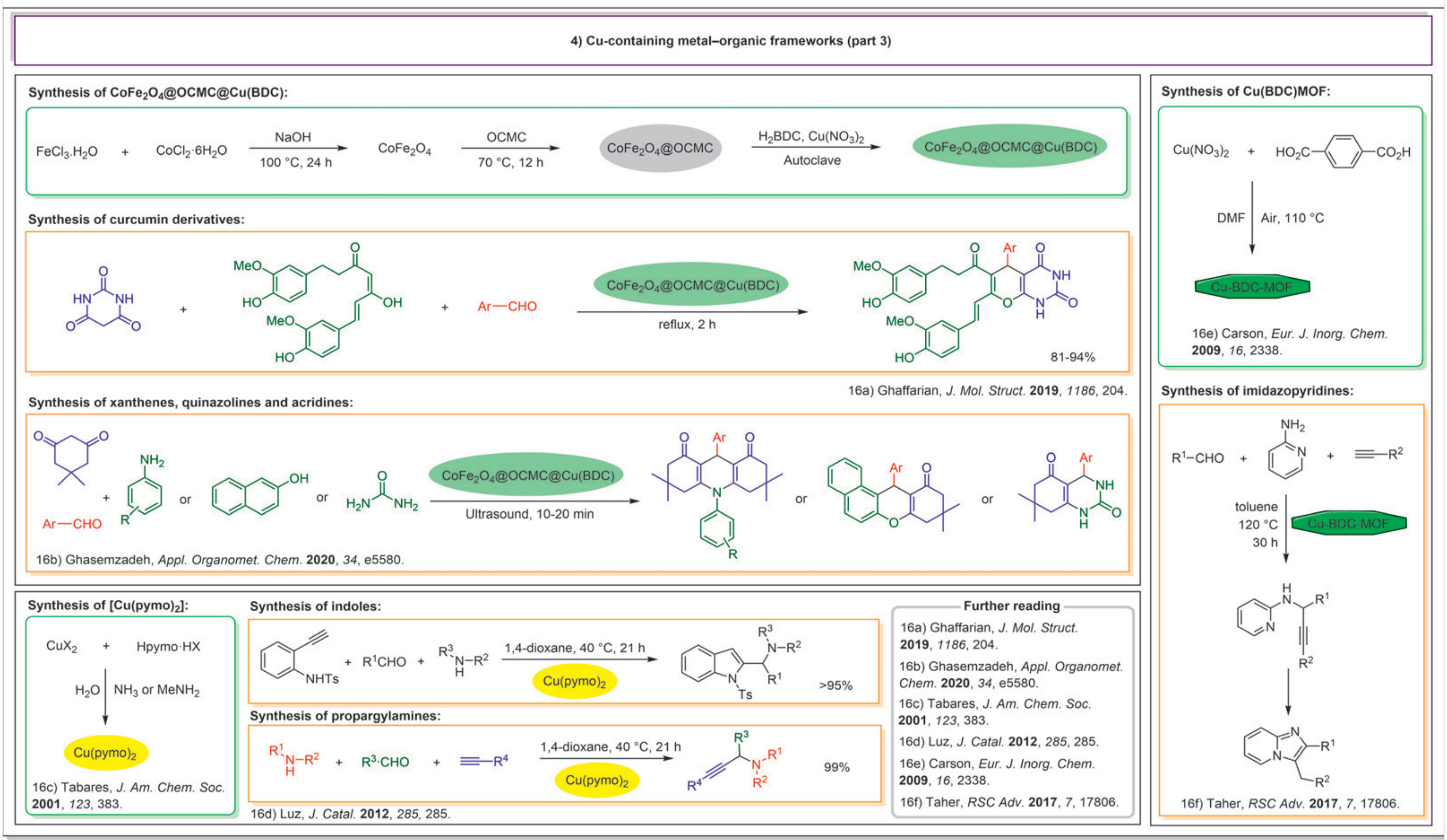


Figure 16 Cu-containing metal–organic frameworks (part 3)$^{16a–f}$

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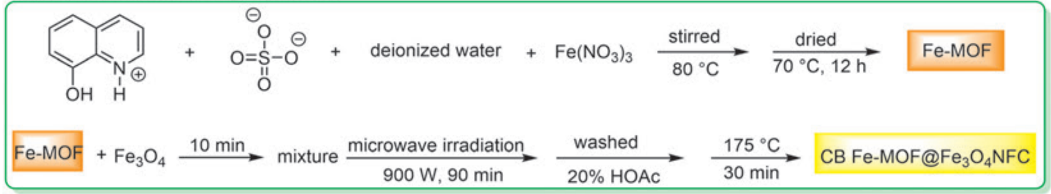
5) Fe-containing metal–organic frameworks (part 1)

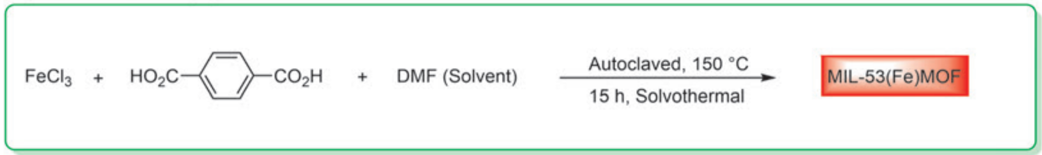
Synthesis of CB Fe-MOF@Fe_3O_4NFC:



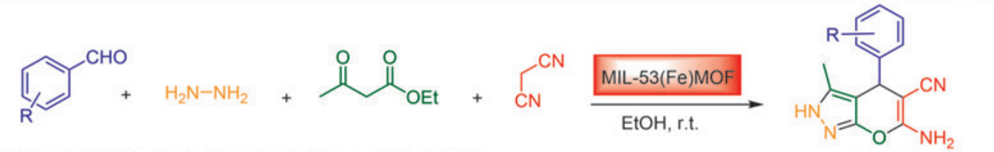
Synthesis of 3,4-dihydropyrano[3,2-c]chromenes:

17a) Sheikhhosseini, *Front. Chem.* **2022**, *10*, 984502.

Synthesis of MIL-53(Fe) MOF:



Synthesis of pyrano[2,3-*c*]-pyrazoles:

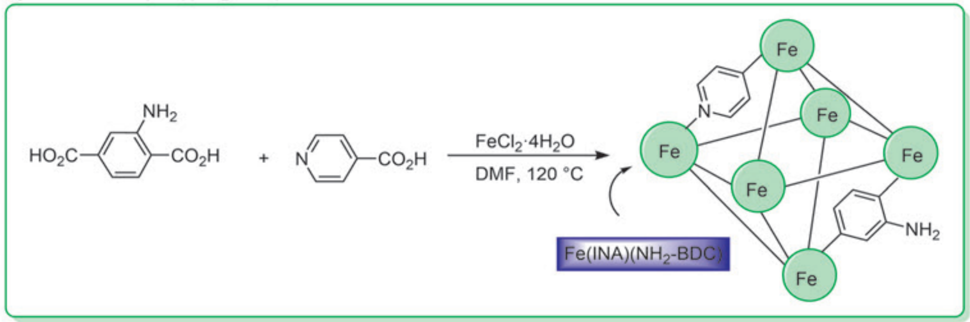


17b) Ghasemzadeh, *Appl. Organomet. Chem.* **2019**, *3*, 4679.

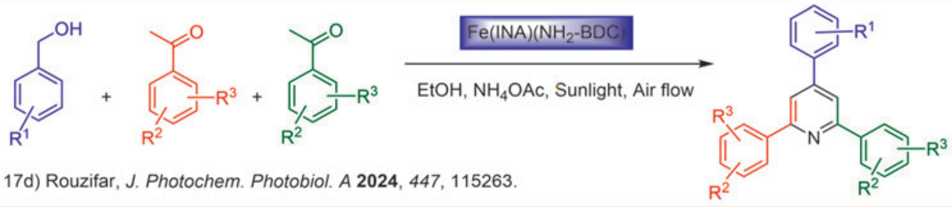
Synthesis of pyrimido[4,5-*d*]pyrimidines:

17c) Abdollahi-Basir, *J. Mol. Struct.* **2019**, *1197*, 318.

Synthesis of Fe(INA)(NH_2-BDC):



Synthesis of TAPs from benzyl alcohols:



17d) Rouzifar, *J. Photochem. Photobiol. A* **2024**, *447*, 115263.

Further reading

17a) Sheikhhosseini, *Front. Chem.* **2022**, *10*, 984502.

17b) Ghasemzadeh, *Appl. Organomet. Chem.* **2019**, *33*, 4679.

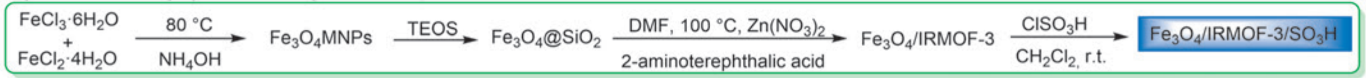
17c) Abdollahi-Basir, *J. Mol. Struct.* **2019**, *1197*, 318.

17d) Rouzifar, *J. Photochem. Photobiol., A* **2024**, *447*, 115263.

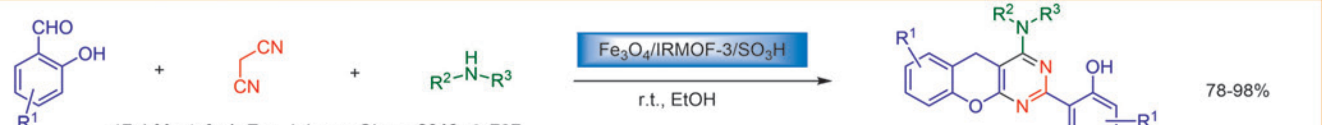
17e) Mostafavi, *Eur. J. Inorg. Chem.* **2019**, *6*, 787.

6g) Pascanu, *J. Am. Chem. Soc.* **2019**, *141*, 7223.

Synthesis of a Fe_3O_4/IRMOF-3/SO_3H nanocomposite:



Synthesis of benzopyranopyrimidines:



17e) Mostafavi, *Eur. J. Inorg. Chem.* **2019**, *6*, 787.

Figure 17 Fe-containing metal–organic frameworks (part 1)[6g,17a–e]

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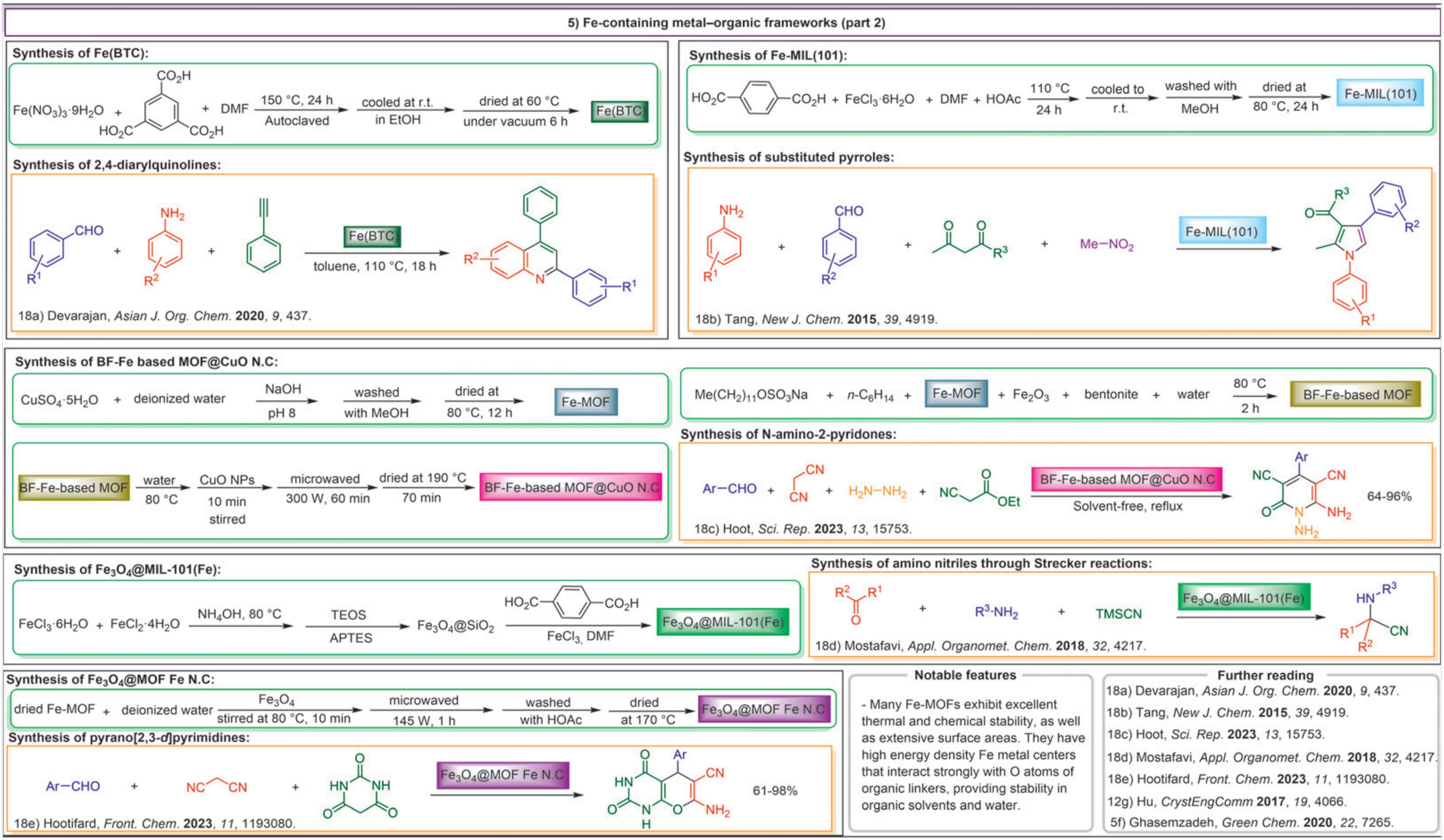


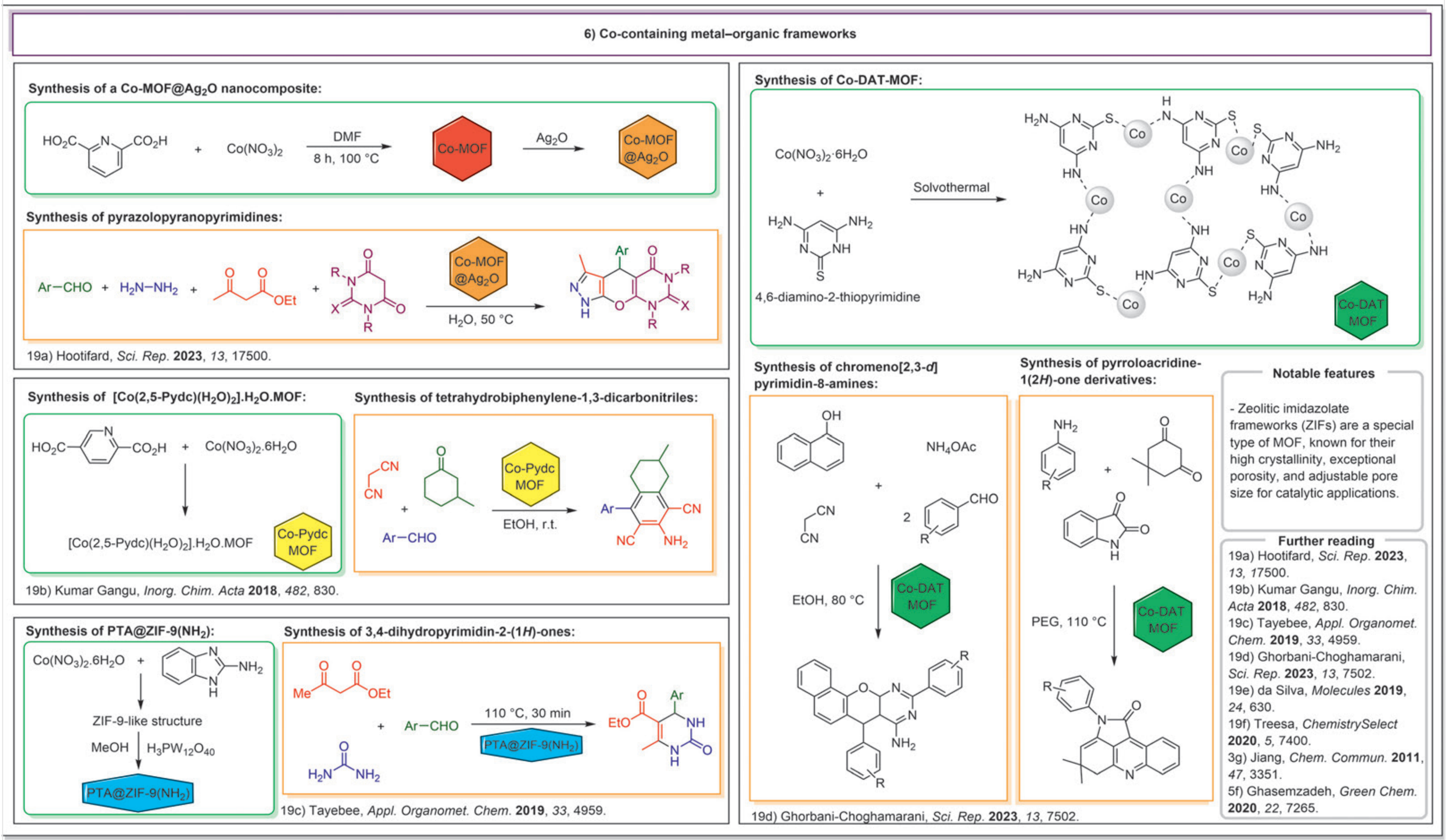
Notable features

- Many Fe-MOFs exhibit excellent thermal and chemical stability, as well as extensive surface areas. They have high energy density Fe metal centers that interact strongly with O atoms of organic linkers, providing stability in organic solvents and water.

Further reading

18a) Devarajan, *Asian J. Org. Chem.* **2020**, *9*, 437.
18b) Tang, *New J. Chem.* **2015**, *39*, 4919.
18c) Hoot, *Sci. Rep.* **2023**, *13*, 15753.
18d) Mostafavi, *Appl. Organomet. Chem.* **2018**, *32*, 4217.
18e) Hootifard, *Front. Chem.* **2023**, *11*, 1193080.
12g) Hu, *CrystEngComm* **2017**, *19*, 4066.
5f) Ghasemzadeh, *Green Chem.* **2020**, *22*, 7265.

Figure 18 Fe-containing metal–organic frameworks (part 2)[5f,12g,18a–e]



6) Co-containing metal–organic frameworks

Synthesis of a Co-MOF@Ag$_2$O nanocomposite:

Synthesis of pyrazolopyranopyrimidines:

19a) Hootifard, *Sci. Rep.* **2023**, *13*, 17500.

Synthesis of [Co(2,5-Pydc)(H$_2$O)$_2$].H$_2$O.MOF:

Synthesis of tetrahydrobiphenylene-1,3-dicarbonitriles:

19b) Kumar Gangu, *Inorg. Chim. Acta* **2018**, *482*, 830.

Synthesis of PTA@ZIF-9(NH$_2$):

Synthesis of 3,4-dihydropyrimidin-2-(1*H*)-ones:

19c) Tayebee, *Appl. Organomet. Chem.* **2019**, *33*, 4959.

Synthesis of Co-DAT-MOF:

Synthesis of chromeno[2,3-*d*] pyrimidin-8-amines:

Synthesis of pyrroloacridine-1(2*H*)-one derivatives:

19d) Ghorbani-Choghamarani, *Sci. Rep.* **2023**, *13*, 7502.

Notable features

- Zeolitic imidazolate frameworks (ZIFs) are a special type of MOF, known for their high crystallinity, exceptional porosity, and adjustable pore size for catalytic applications.

Further reading

19a) Hootifard, *Sci. Rep.* **2023**, *13*, 17500.
19b) Kumar Gangu, *Inorg. Chim. Acta* **2018**, *482*, 830.
19c) Tayebee, *Appl. Organomet. Chem.* **2019**, *33*, 4959.
19d) Ghorbani-Choghamarani, *Sci. Rep.* **2023**, *13*, 7502.
19e) da Silva, *Molecules* **2019**, *24*, 630.
19f) Treesa, *ChemistrySelect* **2020**, *5*, 7400.
3g) Jiang, *Chem. Commun.* **2011**, *47*, 3351.
5f) Ghasemzadeh, *Green Chem.* **2020**, *22*, 7265.

Figure 19 Co-containing metal–organic frameworks[3g,5f,19a–f]

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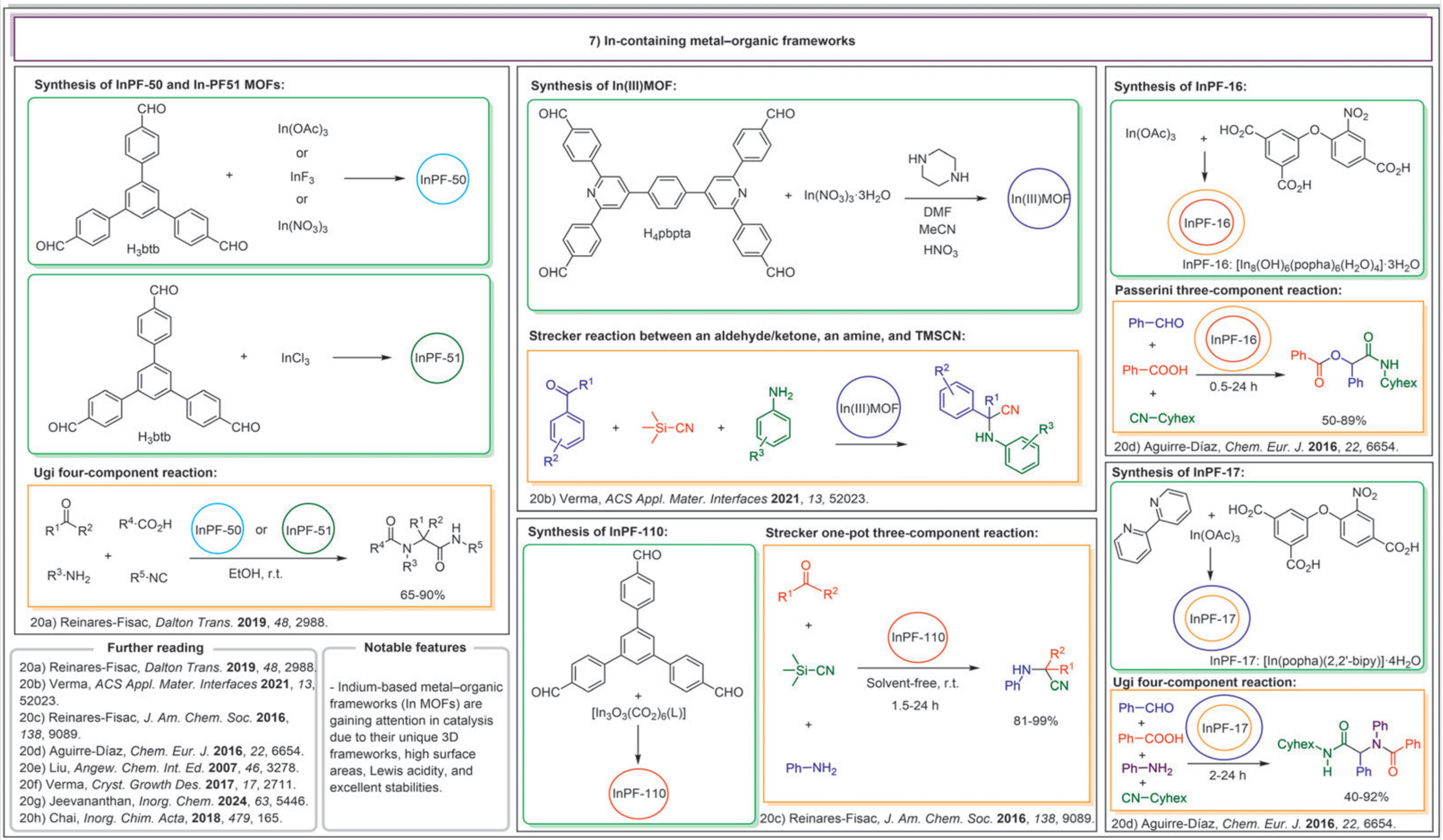


20a) Reinares-Fisac, *Dalton Trans.* **2019**, *48*, 2988.

20b) Verma, *ACS Appl. Mater. Interfaces* **2021**, *13*, 52023.

20c) Reinares-Fisac, *J. Am. Chem. Soc.* **2016**, *138*, 9089.

20d) Aguirre-Díaz, *Chem. Eur. J.* **2016**, *22*, 6654.

20d) Aguirre-Díaz, *Chem. Eur. J.* **2016**, *22*, 6654.

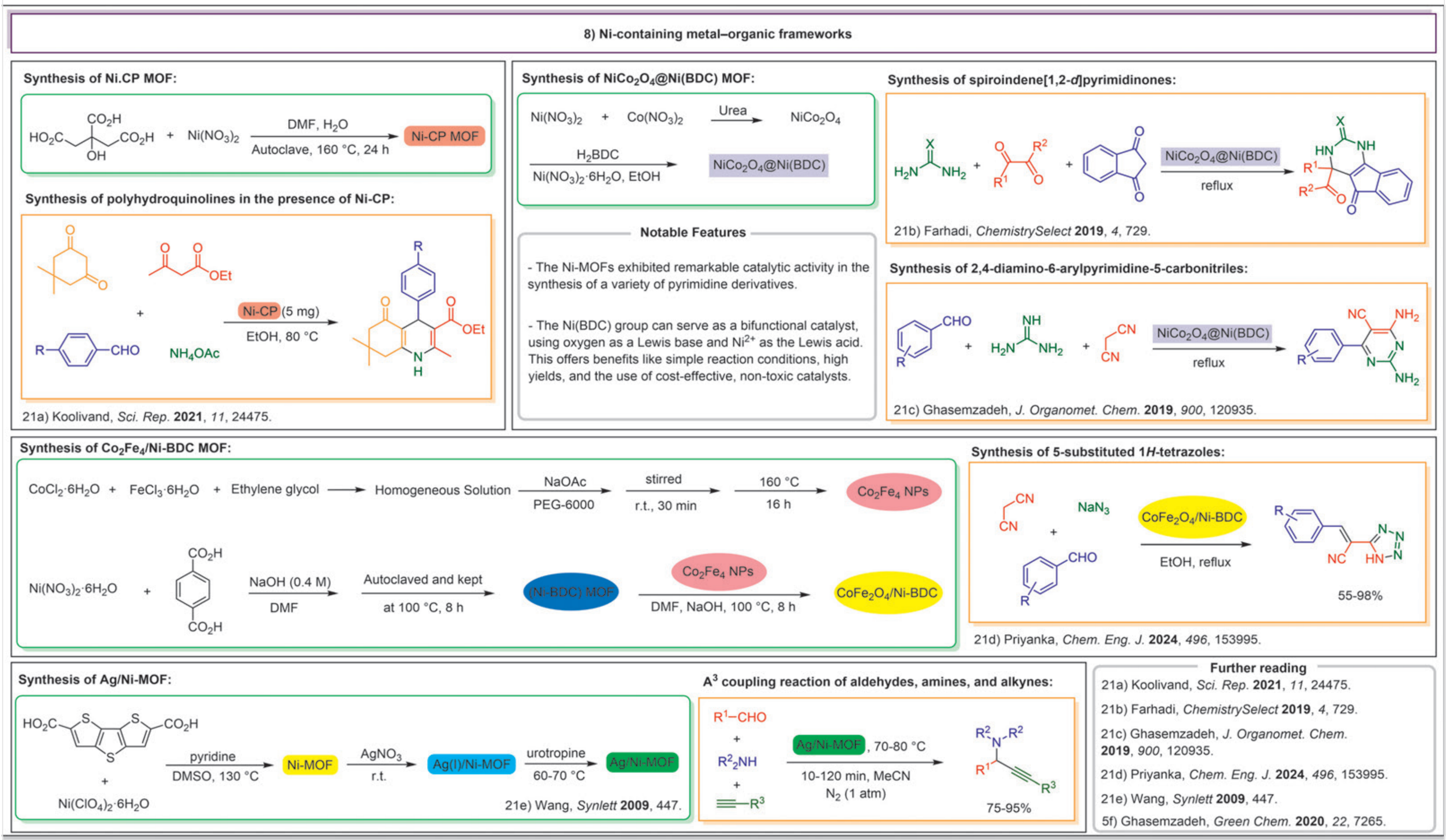
Further reading

20a) Reinares-Fisac, *Dalton Trans.* **2019**, *48*, 2988.
20b) Verma, *ACS Appl. Mater. Interfaces* **2021**, *13*, 52023.
20c) Reinares-Fisac, *J. Am. Chem. Soc.* **2016**, *138*, 9089.
20d) Aguirre-Díaz, *Chem. Eur. J.* **2016**, *22*, 6654.
20e) Liu, *Angew. Chem. Int. Ed.* **2007**, *46*, 3278.
20f) Verma, *Cryst. Growth Des.* **2017**, *17*, 2711.
20g) Jeevananthan, *Inorg. Chem.* **2024**, *63*, 5446.
20h) Chai, *Inorg. Chim. Acta*, **2018**, *479*, 165.

Notable features

- Indium-based metal–organic frameworks (In MOFs) are gaining attention in catalysis due to their unique 3D frameworks, high surface areas, Lewis acidity, and excellent stabilities.

Figure 20 In-containing metal–organic frameworks[20a–h]



21a) Koolivand, *Sci. Rep.* **2021**, *11*, 24475.

21b) Farhadi, *ChemistrySelect* **2019**, *4*, 729.

21c) Ghasemzadeh, *J. Organomet. Chem.* **2019**, *900*, 120935.

21d) Priyanka, *Chem. Eng. J.* **2024**, *496*, 153995.

21e) Wang, *Synlett* **2009**, 447.

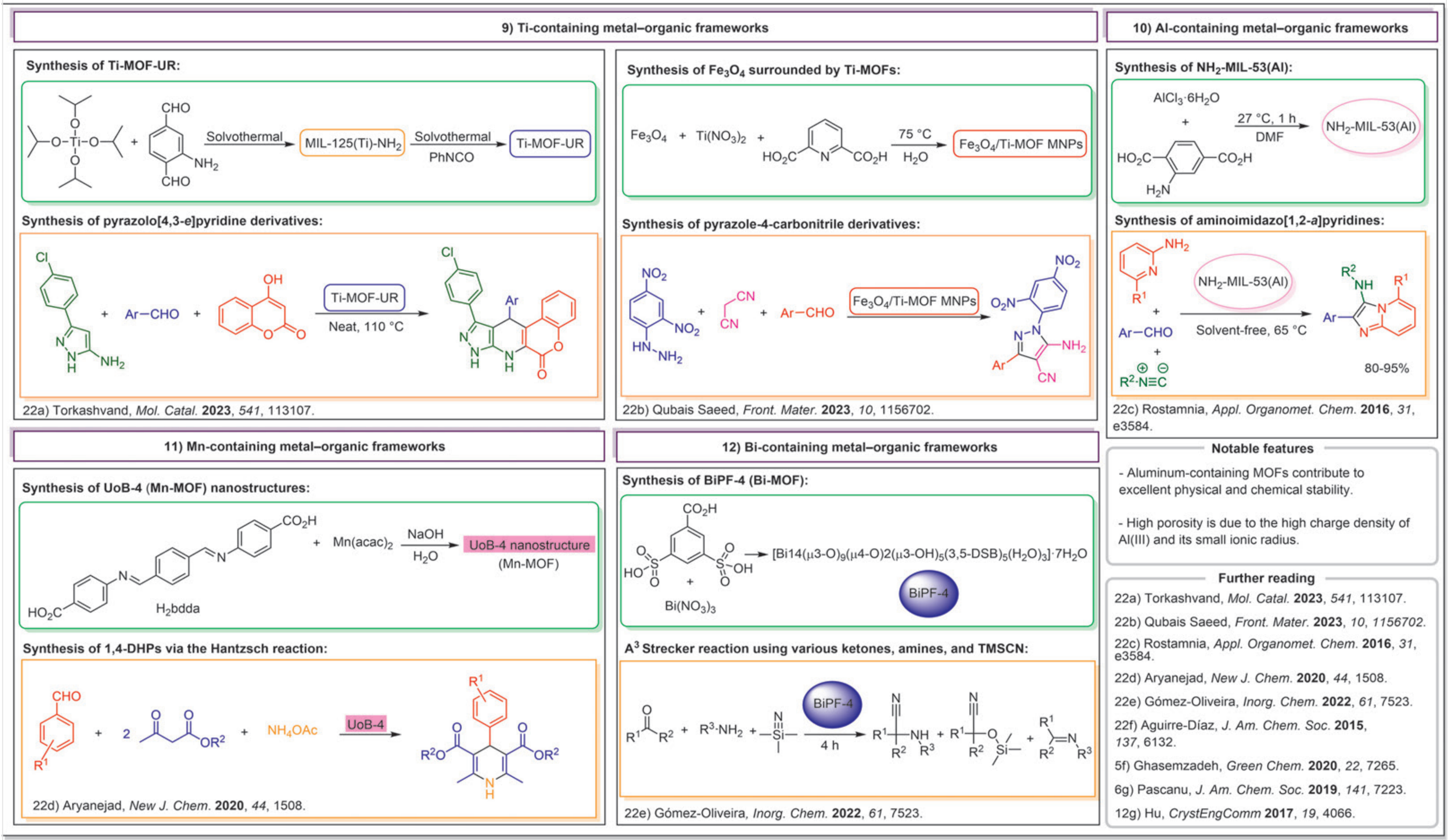
Notable Features

- The Ni-MOFs exhibited remarkable catalytic activity in the synthesis of a variety of pyrimidine derivatives.
- The Ni(BDC) group can serve as a bifunctional catalyst, using oxygen as a Lewis base and Ni^{2+} as the Lewis acid. This offers benefits like simple reaction conditions, high yields, and the use of cost-effective, non-toxic catalysts.

Further reading

21a) Koolivand, *Sci. Rep.* **2021**, *11*, 24475.
21b) Farhadi, *ChemistrySelect* **2019**, *4*, 729.
21c) Ghasemzadeh, *J. Organomet. Chem.* **2019**, *900*, 120935.
21d) Priyanka, *Chem. Eng. J.* **2024**, *496*, 153995.
21e) Wang, *Synlett* **2009**, 447.
5f) Ghasemzadeh, *Green Chem.* **2020**, *22*, 7265.

Figure 21 Ni-containing metal–organic frameworks[5f,21a–e]



22a) Torkashvand, *Mol. Catal.* **2023**, *541*, 113107.

22b) Qubais Saeed, *Front. Mater.* **2023**, *10*, 1156702.

22c) Rostamnia, *Appl. Organomet. Chem.* **2016**, *31*, e3584.

22d) Aryanejad, *New J. Chem.* **2020**, *44*, 1508.

22e) Gómez-Oliveira, *Inorg. Chem.* **2022**, *61*, 7523.

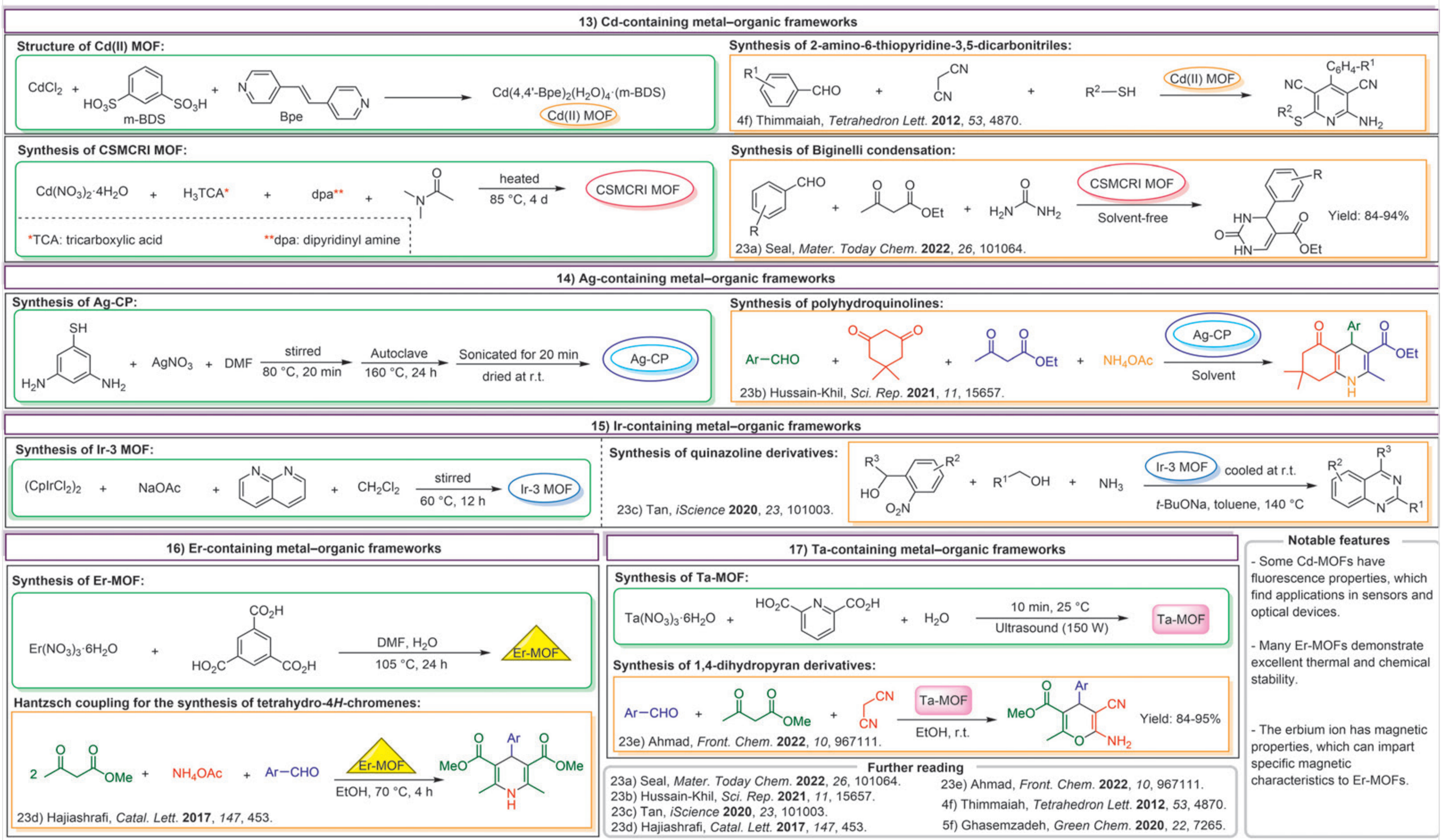
Notable features

- Aluminum-containing MOFs contribute to excellent physical and chemical stability.
- High porosity is due to the high charge density of Al(III) and its small ionic radius.

Further reading

22a) Torkashvand, *Mol. Catal.* **2023**, *541*, 113107.
22b) Qubais Saeed, *Front. Mater.* **2023**, *10*, *1156702*.
22c) Rostamnia, *Appl. Organomet. Chem.* **2016**, *31*, e3584.
22d) Aryanejad, *New J. Chem.* **2020**, *44*, 1508.
22e) Gómez-Oliveira, *Inorg. Chem.* **2022**, *61*, 7523.
22f) Aguirre-Díaz, *J. Am. Chem. Soc.* **2015**, *137*, 6132.
5f) Ghasemzadeh, *Green Chem.* **2020**, *22*, 7265.
6g) Pascanu, *J. Am. Chem. Soc.* **2019**, *141*, 7223.
12g) Hu, *CrystEngComm* **2017**, *19*, 4066.

Figure 22 Ti-, Al-, Mn-, and Bi-containing metal–organic frameworks[5f,6g,12g,22a–f]



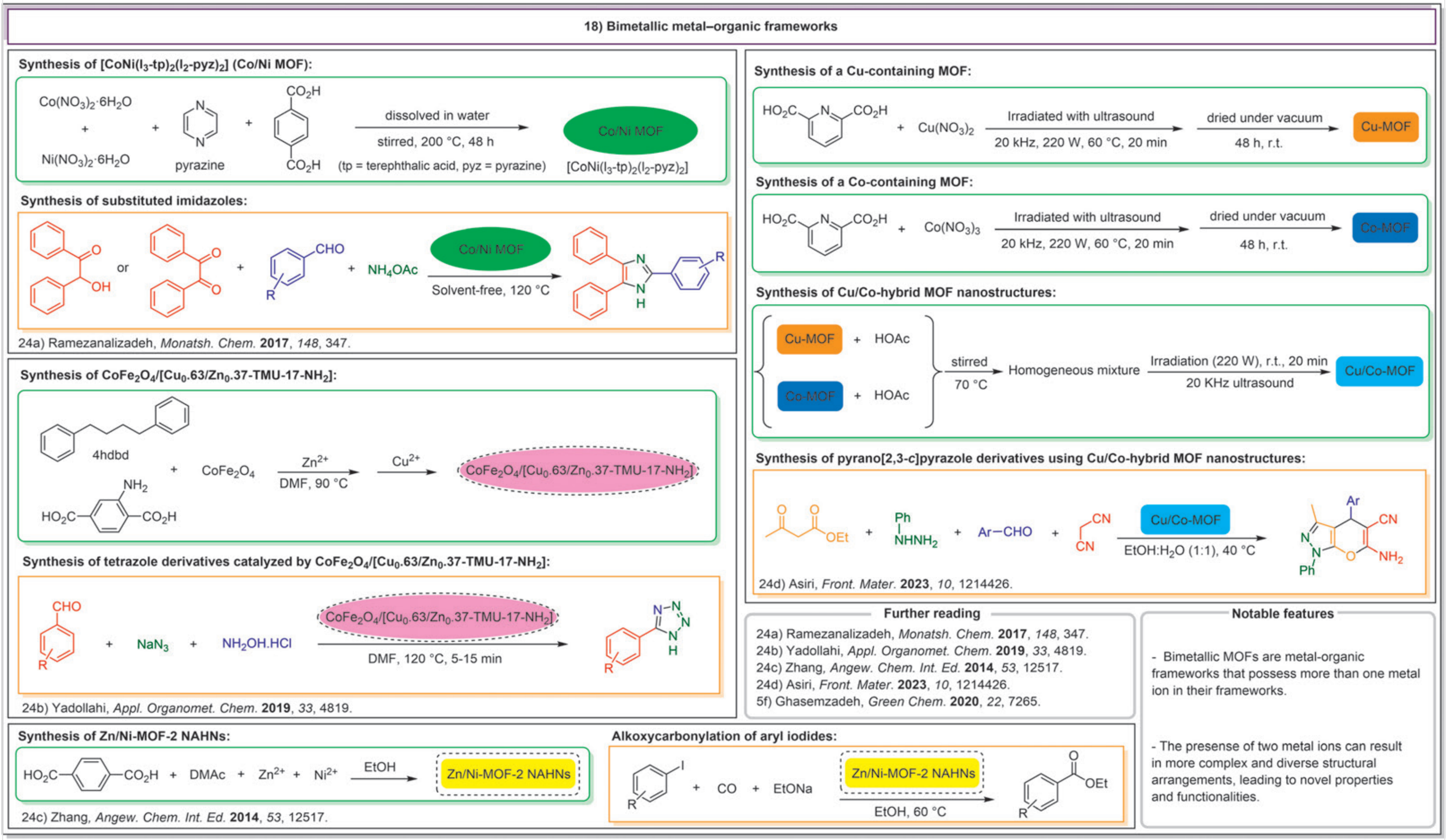
Further reading

23a) Seal, *Mater. Today Chem.* **2022**, *26*, 101064.
23b) Hussain-Khil, *Sci. Rep.* **2021**, *11*, 15657.
23c) Tan, *iScience* **2020**, *23*, 101003.
23d) Hajiashrafi, *Catal. Lett.* **2017**, *147*, 453.
23e) Ahmad, *Front. Chem.* **2022**, *10*, 967111.
4f) Thimmaiah, *Tetrahedron Lett.* **2012**, *53*, 4870.
5f) Ghasemzadeh, *Green Chem.* **2020**, *22*, 7265.

Notable features

- Some Cd-MOFs have fluorescence properties, which find applications in sensors and optical devices.
- Many Er-MOFs demonstrate excellent thermal and chemical stability.
- The erbium ion has magnetic properties, which can impart specific magnetic characteristics to Er-MOFs.

Figure 23 Cd-, Ag-, Ir-, Er-, and Ta-containing metal–organic frameworks[4f,5f,23a–e]



18) Bimetallic metal–organic frameworks

Synthesis of [CoNi(μ_3-tp)$_2$(μ_2-pyz)$_2$] (Co/Ni MOF):

Synthesis of substituted imidazoles:

24a) Ramezanalizadeh, *Monatsh. Chem.* **2017**, *148*, 347.

Synthesis of CoFe$_2$O$_4$/[Cu$_{0}$.63/Zn$_{0}$.37-TMU-17-NH$_2$]:

Synthesis of tetrazole derivatives catalyzed by CoFe$_2$O$_4$/[Cu$_{0}$.63/Zn$_{0}$.37-TMU-17-NH$_2$]:

24b) Yadollahi, *Appl. Organomet. Chem.* **2019**, *33*, 4819.

Synthesis of a Cu-containing MOF:

Synthesis of a Co-containing MOF:

Synthesis of Cu/Co-hybrid MOF nanostructures:

Synthesis of pyrano[2,3-c]pyrazole derivatives using Cu/Co-hybrid MOF nanostructures:

24d) Asiri, *Front. Mater.* **2023**, *10*, 1214426.

Further reading

24a) Ramezanalizadeh, *Monatsh. Chem.* **2017**, *148*, 347.
24b) Yadollahi, *Appl. Organomet. Chem.* **2019**, *33*, 4819.
24c) Zhang, *Angew. Chem. Int. Ed.* **2014**, *53*, 12517.
24d) Asiri, *Front. Mater.* **2023**, *10*, 1214426.
5f) Ghasemzadeh, *Green Chem.* **2020**, *22*, 7265.

Notable features

- Bimetallic MOFs are metal-organic frameworks that possess more than one metal ion in their frameworks.
- The presense of two metal ions can result in more complex and diverse structural arrangements, leading to novel properties and functionalities.

Synthesis of Zn/Ni-MOF-2 NAHNs:

24c) Zhang, *Angew. Chem. Int. Ed.* **2014**, *53*, 12517.

Alkoxycarbonylation of aryl iodides:

Figure 24 Bimetallic metal–organic frameworks[5f,24a–d]

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Conflict of Interest

The authors declare no conflict of interest.

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