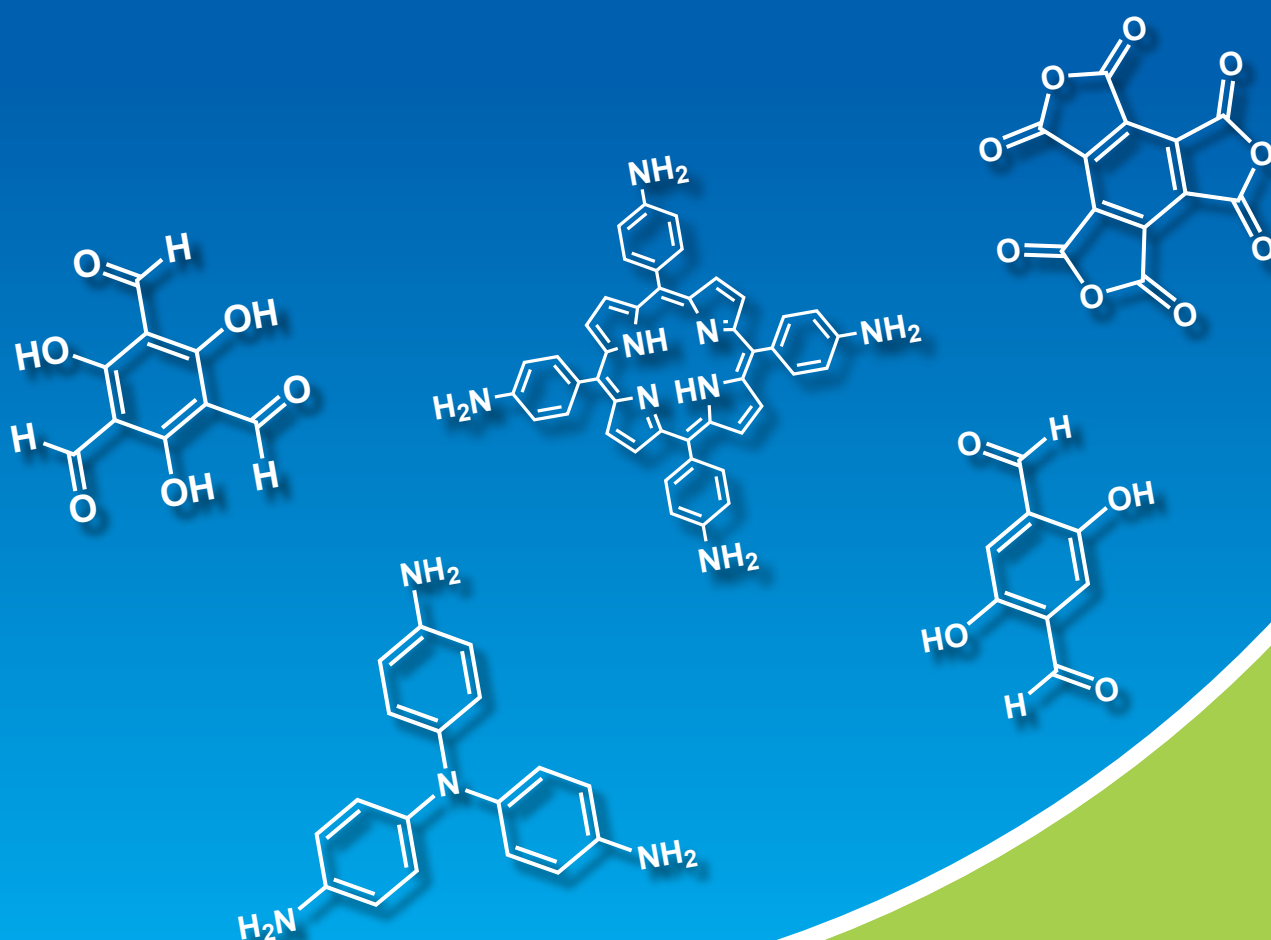


Covalent Organic Framework (COF) Linkers



Amine Linkers

Aldehyde Linkers

Carboxylic Anhydride Linkers

Boronic Acid Linkers

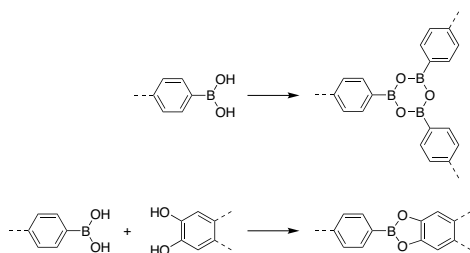
Other Linkers

Covalent Organic Framework (COF) Linkers

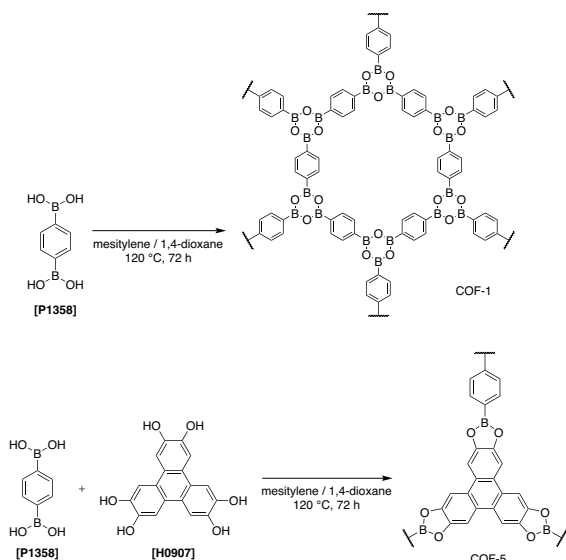
Covalent organic frameworks (COFs) are crystalline organic frameworks consisting of a network structure made of covalent bonds.^{1,2)} COFs are classified as porous crystalline materials similar to metal-organic frameworks (MOFs)/porous coordination polymers (PCPs) and zeolites. They include 2D COFs, which are constructed by stacking layers of 2D covalently bonded sheets, and 3D COFs, which are constructed by 3D connected frameworks. COFs are expected to be used as molecular storage or separation materials, catalysts, electronic materials, energy storage materials, battery materials, and drug delivery materials, due to their porosity, crystallinity, and structural diversity.

COFs are designed and synthesized by combining monomers, also known as linkers, according to intended topology. Some synthetic examples are shown below with synthetic strategies.

● Boroxines and boronic esters

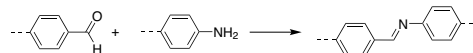


The self-condensation of boronic acids to produce boroxines and the condensation of boronic acids and catechols to produce boronic esters are the first synthetic strategies to synthesize COFs (Scheme 1).¹⁾ The advantages of boroxine-based COFs and boronic ester-based COFs include their tendency to have good crystallinity, large surface area, and high thermal stability.

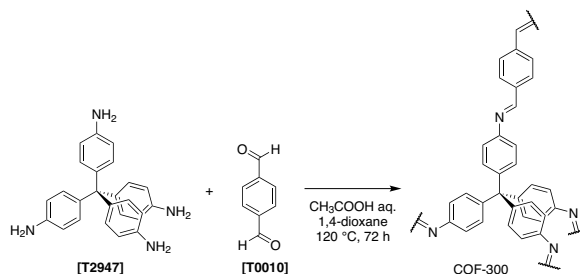


Scheme 1. Synthesis of COF-1 and COF-5¹⁾

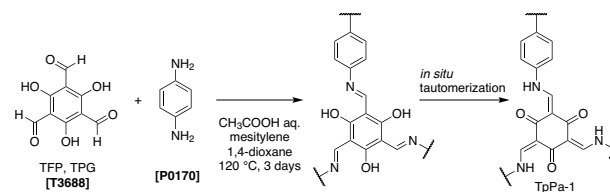
● Imines



Imine-linked covalent organic framework, synthesized by condensation of aldehydes and amines, was first reported in 2009 (Scheme 2),⁴⁾ and imine-based COFs are now the most widely reported COFs. Imine-based COFs have higher chemical stability compared to boroxines and boronic esters. In addition, several researchers have reported post-synthetic modification or functionalization of imine-based COFs, such as the synthesis of COFs for CO₂ capture through the post-synthetic modification and functionalization of imine-based structures.⁵⁾ In 2012, it was reported that β -ketoenamine-type COFs can be synthesized by using 2,4,6-triformylphloroglucinol (TPG, TFP) as an aldehyde linker (Scheme 3).⁶⁾ These compounds have recently received a lot of attention due to their stability towards acids and bases.

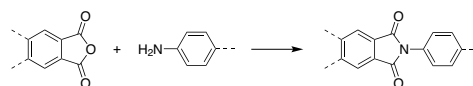


Scheme 2. Synthesis of COF-300⁴⁾



Scheme 3. Synthesis of TpPa-1⁶⁾

● Imides



Imide-linked COFs obtained by condensation of carboxylic anhydrides and amines have also been reported⁷⁾ and are expected to be applied to battery materials⁸⁾ and CO₂ capture materials.⁹⁾

● Other synthetic strategies

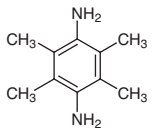
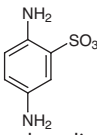
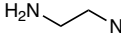
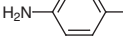
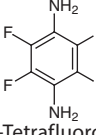
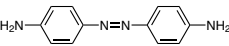
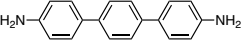
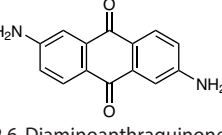
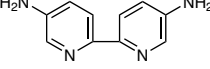
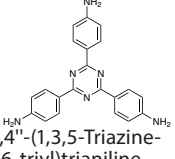
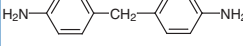
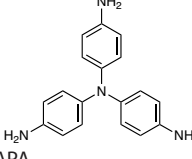
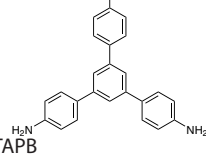
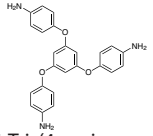
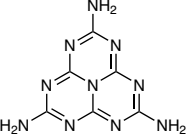
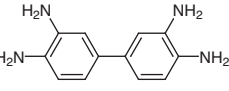
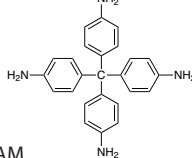
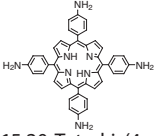
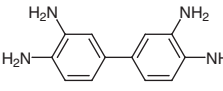
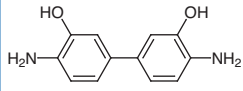
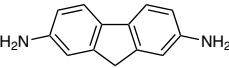
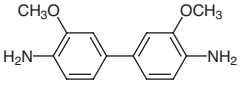
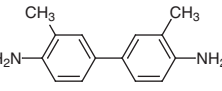
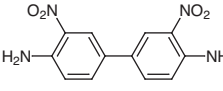
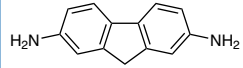
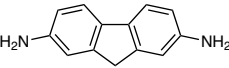
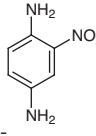
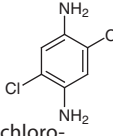
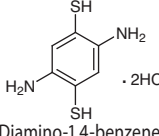
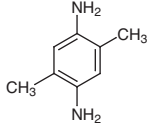
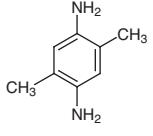
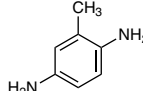
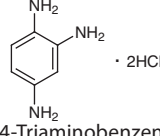
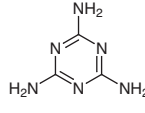
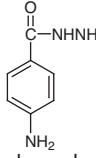
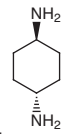
COFs constructed by other linkers besides imines, imides, and boroxines have been realized. Linkers other than amines, aldehydes, carboxylic anhydrides, and boronic acids are used as linkers to prepare these COFs. For example, hydrazone-type

COFs synthesized using hydrazines and aldehydes^{10,11} and ionic COFs synthesized using 1,2,3-triaminoguanidinium chloride¹² were reported.

References

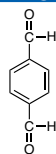
- 1) Porous, Crystalline, Covalent Organic Frameworks
A. P. Côté, A. I. Benin, N. W. Ockwig, A. J. Matzger, M. O’Keeffe, O. M. Yaghi, *Science* **2005**, *310*, 1166.
<https://doi.org/10.1126/science.1120411>
- 2) Covalent Organic Frameworks: Organic Chemistry Extended into Two and Three Dimensions
S. J. Lyle, P. J. Waller, O. M. Yaghi, *Trends in Chemistry* **2019**, *1*, 172.
<https://doi.org/10.1016/j.trechm.2019.03.001>
- 3) Covalent Organic Frameworks: Structures, Synthesis, and Applications
M. S. Lohse, T. Bein, *Adv. Funct. Mater.* **2018**, *28*, 1705553.
<https://doi.org/10.1002/adfm.201705553>
- 4) A Crystalline Imine-Linked 3-D Porous Covalent Organic Framework
F. J. Uribe-Romo, J. R. Hunt, H. Furukawa, C. Klöck, M. O’Keeffe, O. M. Yaghi, *J. Am. Chem. Soc.* **2009**, *131*, 4570.
<https://doi.org/10.1021/ja8096256>
- 5) Covalent Organic Frameworks for Carbon Dioxide Capture from Air
H. Lyu, H. Li, N. Hanikel, K. Wang, O. M. Yaghi, *J. Am. Chem. Soc.* **2022**, *144*, 12989.
<https://doi.org/10.1021/jacs.2c05382>
- 6) Construction of Crystalline 2D Covalent Organic Frameworks with Remarkable Chemical (Acid/Base) Stability via a Combined Reversible and Irreversible Route
S. Kandambeth, A. Mallick, B. Lukose, M. V. Mane, T. Heine, R. Banerjee, *J. Am. Chem. Soc.* **2012**, *134*, 19524.
<https://doi.org/10.1021/ja308278w>
- 7) Designed synthesis of large-pore crystalline polyimide covalent organic frameworks
Q. Fang, Z. Zhuang, S. Gu, R. B. Kaspar, J. Zheng, J. Wang, S. Qiu, Y. Yan, *Nat. Commun.* **2014**, *5*, 4503.
<https://doi.org/10.1038/ncomms5503>
- 8) Covalent Organic Framework with Highly Accessible Carbonyls and π -Cation Effect for Advanced Potassium-Ion Batteries
X.-X. Luo, W.-H. Li, H.-J. Liang, H.-X. Zhang, K.-D. Du, X.-T. Wang, X.-F. Liu, J.-P. Zhang, X.-L. Wu, *Angew. Chem. Int. Ed.* **2022**, *61*, e202117661.
<https://doi.org/10.1002/anie.202117661>
- 9) Synthesis, characterization, and CO₂ uptake of mellitic triimide-based covalent organic frameworks
H. Veldhuizen, A. Vasileiadis, M. Wagemaker, T. Mahon, D. P. Mainali, L. Zong, S. van der Zwaag, A. Nagai, *J. Polym. Sci. Part A: Polym. Chem.* **2019**, *57*, 2373.
<https://doi.org/10.1002/pola.29510>
- 10) Crystalline Covalent Organic Frameworks with Hydrazone Linkages
F. J. Uribe-Romo, C. J. Doonan, H. Furukawa, K. Oisaki, O. M. Yaghi, *J. Am. Chem. Soc.* **2011**, *133*, 11478.
<https://doi.org/10.1021/ja204728y>
- 11) Mechanochemistry of imine, β -ketoenamine, and hydrogen-bonded imine-linked covalent organic frameworks using liquid-assisted grinding
G. Das, D. B. Shinde, S. Kandambeth, B. P. Biswala, R. Banerjee, *Chem. Commun.* **2014**, *50*, 12615.
<https://doi.org/10.1039/C4CC03389B>
- 12) Cationic Covalent Organic Framework Nanosheets for Fast Li-Ion Conduction
H. Chen, H. Tu, C. Hu, Y. Liu, D. Dong, Y. Sun, Y. Dai, S. Wang, H. Qian, Z. Lin, L. Chen, *J. Am. Chem. Soc.* **2018**, *140*, 896.
<https://doi.org/10.1021/jacs.7b12292>

Amine Linkers

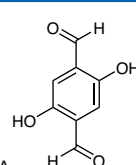
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<p>M0220 25g 500g</p>  <p>4,4'-MDA CAS RN: 101-77-9</p>	<p>T2332 1g 5g</p>  <p>TAPA CAS RN: 5981-09-9</p>	<p>T2728 5g 25g</p>  <p>TAPB CAS RN: 118727-34-7</p>	<p>T3909 200mg 1g</p>  <p>1,3,5-Tris(4-amino-phenoxy)benzene CAS RN: 102852-92-6</p>	<p>M3538 1g</p>  <p>Melem CAS RN: 1502-47-2</p>
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<p>D2183 25g 100g</p>  <p>2,5-Diamino-p-xylene CAS RN: 6393-01-7</p>	<p>D4628 5g 25g</p>  <p>2,5-Diaminotoluene CAS RN: 95-70-5</p>	<p>T0334 1g</p>  <p>1,2,4-Triaminobenzene Dihydrochloride CAS RN: 615-47-4</p>	<p>T0337 5g 25g 500g</p>  <p>Melamine Monomer CAS RN: 108-78-1</p>	<p>A1211 25g</p>  <p>4-Aminobenzohydrazide CAS RN: 5351-17-7</p>
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Aldehyde Linkers

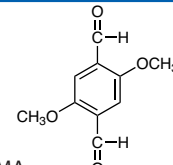
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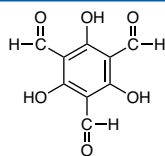
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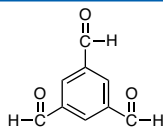
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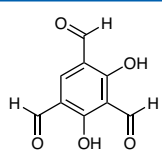
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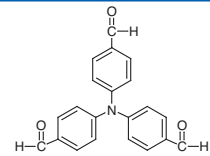
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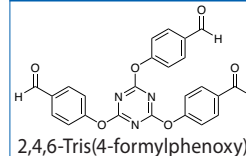
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2,4,6-Triformylresorcinol
CAS RN: 58343-11-6

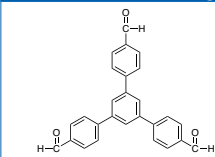
T2310 500mg

Tris(4-formylphenyl)amine
CAS RN: 119001-43-3

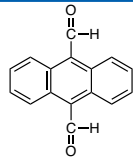
T4077 1g 5g

2,4,6-Tris(4-formylphenoxy)-1,3,5-triazine
CAS RN: 3140-75-8

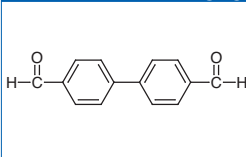
F1252 200mg 1g

TFPB
CAS RN: 118688-53-2

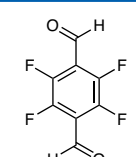
A2664 1g 5g

9,10-Diformylanthracene
CAS RN: 7044-91-9

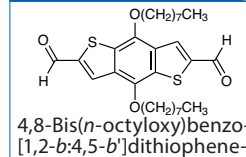
B2854 1g 5g

BPDA
CAS RN: 66-98-8

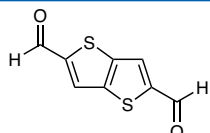
T4088 1g 5g

TFTA
CAS RN: 3217-47-8

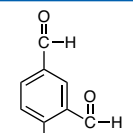
B5484 200mg

4,8-Bis(*n*-octyloxy)benzo[1,2-*b*:4,5-*b'*]dithiophene-2,6-dicarbaldehyde
CAS RN: 1668554-22-0

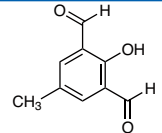
T3212 200mg 1g

Thieno[3,2-*b*]thiophene-2,5-dicarboxaldehyde
CAS RN: 37882-75-0

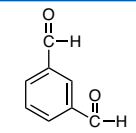
F0310 1g 5g 25g

4-Hydroxyisophthalaldehyde
CAS RN: 3328-70-9

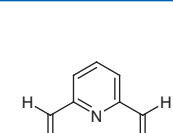
H0683 1g 5g

2-Hydroxy-5-methylisophthalaldehyde
CAS RN: 7310-95-4

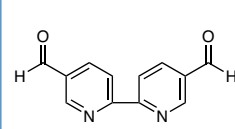
I0153 25g 100g 250g

Isophthalaldehyde
CAS RN: 626-19-7

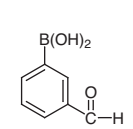
P0949 1g 5g

2,6-Pyridinedicarboxaldehyde
CAS RN: 5431-44-7

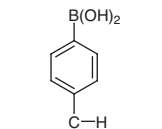
B6576 1g

[2,2'-Bipyridine]-5,5'-dicarbaldehyde
CAS RN: 135822-72-9

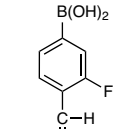
F0445 1g 5g 25g

3-Formylphenylboronic Acid
CAS RN: 87199-16-4

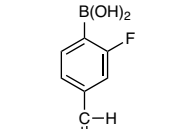
F0446 1g 5g

4-Formylphenylboronic Acid
CAS RN: 87199-17-5

F1051 1g 5g

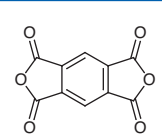
3-Fluoro-4-formylphenylboronic Acid
CAS RN: 248270-25-9

F1079 1g

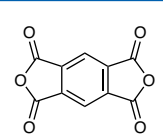
2-Fluoro-4-formylphenylboronic Acid
CAS RN: 871126-22-6

Carboxylic Anhydride Linkers

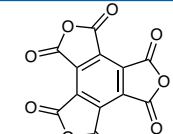
B0040 25g 100g 500g

PMDA
CAS RN: 89-32-7

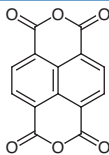
P2103 5g 25g

PMDA (purified by sublimation)
CAS RN: 89-32-7

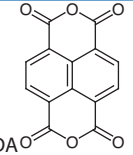
M3617 1g 5g

Mellitic Trianhydride
CAS RN: 4253-24-1

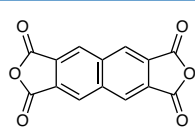
N0369 25g 250g

NTCDA
CAS RN: 81-30-1

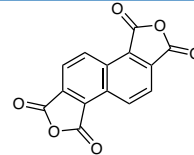
N0755 1g 5g

NTCDA (purified by sublimation)
CAS RN: 81-30-1

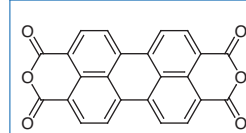
N1128 1g 5g

2,3,6,7-NTCDA
CAS RN: 3711-01-1

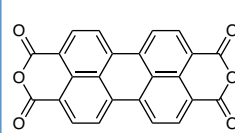
N1247 1g

1,2,5,6-NTCDA
CAS RN: 3711-03-3

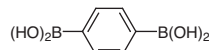
P0972 25g 100g 500g

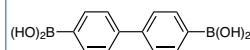
PTCDA
CAS RN: 128-69-8

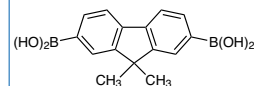
P2102 1g

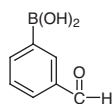
PTCDA (purified by sublimation)
CAS RN: 128-69-8

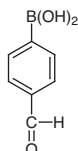
Boronic Acid Linkers

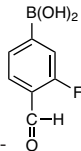
P1358 1g 5g 25g

BDDB
 CAS RN: 4612-26-4

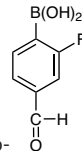
B2490 1g 5g

BPDA
 CAS RN: 4151-80-8

D4701 1g

(9,9-Dimethyl-9H-fluorene-2,7-diyl)diboronic Acid
 CAS RN: 866100-14-3

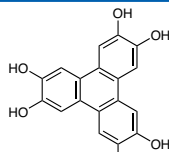
F0445 1g 5g 25g

3-Formylphenylboronic Acid
 CAS RN: 87199-16-4

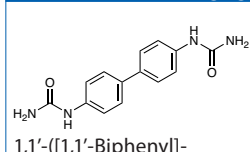
F0446 1g 5g

4-Formylphenylboronic Acid
 CAS RN: 87199-17-5

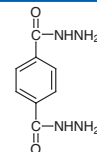
F1051 1g 5g

3-Fluoro-4-formylphenylboronic Acid
 CAS RN: 248270-25-9

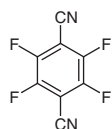
F1079 1g

2-Fluoro-4-formylphenylboronic Acid
 CAS RN: 871126-22-6

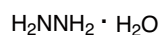
Other Linkers

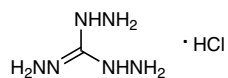
H0907 1g 5g

HHTP
 CAS RN: 4877-80-9

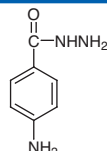
B6577 1g 5g

1,1'-([1,1'-Biphenyl]-4,4'-diyl)diurea
 CAS RN: 13140-82-4

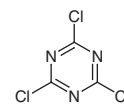
T0758 25g 500g

Terephthalic Dihydrazide
 CAS RN: 136-64-1

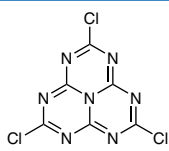
T1050 1g 5g 25g

Tetrafluoroterephthalonitrile
 CAS RN: 1835-49-0

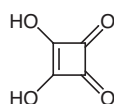
H0172 25mL 500mL

Hydrazine Monohydrate
 CAS RN: 7803-57-8

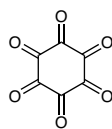
T4080 1g 5g

N,N',N''-Triaminoguanidine Hydrochloride
 CAS RN: 5329-29-3

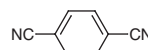
A1211 25g

4-Aminobenzohydrazide
 CAS RN: 5351-17-7

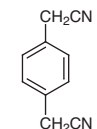
C0460 25g 500g

Cyanuric Chloride
 CAS RN: 108-77-0

T4145 1g

Heptazine Chloride
 CAS RN: 6710-92-5

D1399 5g 25g

Squaric Acid
 CAS RN: 2892-51-5

T0876 1g 5g

Triquinoyl
 CAS RN: 527-31-1

T0016 25g 100g 500g

Terephthalonitrile
 CAS RN: 623-26-7

X0061 5g 25g

1,4-Phenylenediacetonitrile
 CAS RN: 622-75-3

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