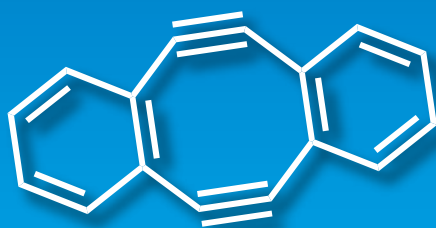
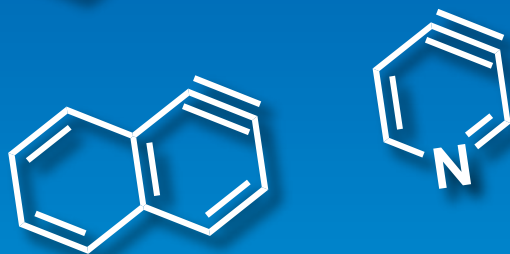


Aryne / Heteroaryne Precursors



Diels-Alder Reaction

Click Chemistry

Multicomponent Reaction

etc.

Benzyne Precursors

Naphthalynes Precursors

Pyridynes Precursors

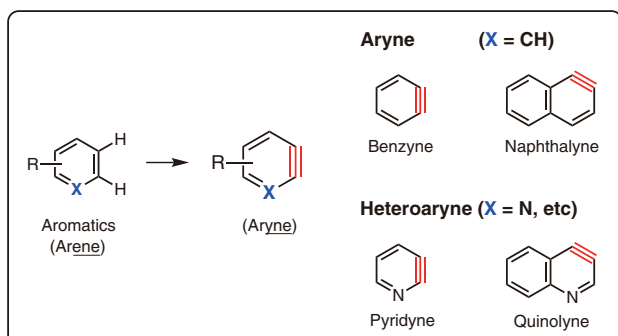
Quinolyne Precursors

Other Aryne Precursors / Related Compounds

Reagents for the Generation of Arynes

Aryne / Heteroaryne Precursors

Arynes are the dehydro hydrocarbons derived from arenes, such as benzene or naphthalene, by abstraction of two hydrogen atoms from adjacent carbon atoms, and they characteristically have triple bonds (-yne) in their aromatic rings.



In addition, arynes which have hetero atoms, such as nitrogen, in their aromatic rings are called "**heteroarynes**". For examples of heteroarynes, pyridynes (derived from the pyridines) or quinolynes (derived from the quinolones) have been known so far.

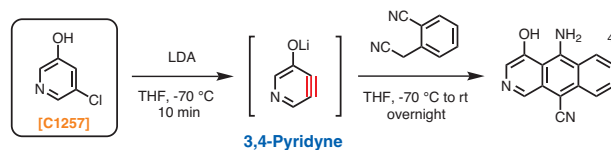
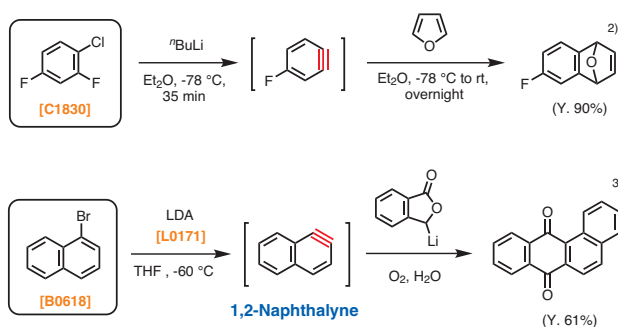
In general, arynes have extremely high reactivity due to their strained structures, thus, they have been widely used in organic synthesis as useful intermediates.¹⁾

● Synthetic methods

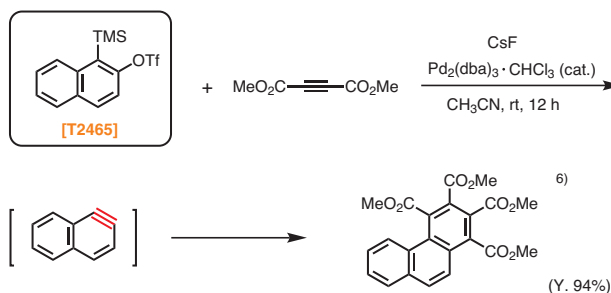
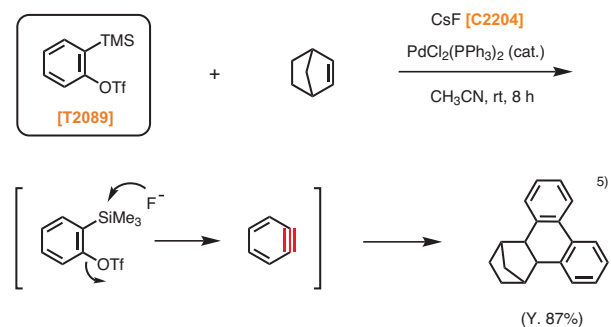
A number of methods for the generation of arynes have been reported so far. Arynes cannot be isolated because of their high reactivity, and they are generally prepared *in situ* in reaction systems. The typical examples are described as below.

1. The method using halogenated aryl compounds

Halogenated aryl compounds are treated with strong bases, such as ^tBuLi, NaNH₂ or Lithium Diisopropylamide (LDA) [L0171], to generate the corresponding arynes. The generation of arynes can be confirmed by trapping reactions with dienes, such as furan, affording the Diels-Alder cycloadducts.



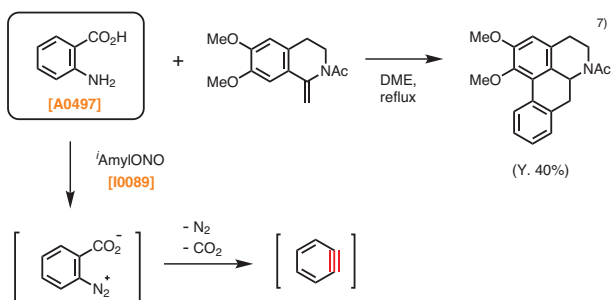
2. The method using 2-TMS-aryl triflates



The method using halogenated aryl compounds described in 1. needs strong bases, such as ^tBuLi. For avoiding that, aryne precursors that can be used in milder conditions also have been developed. 2-TMS-aryl triflates react with fluoride salts, such as cesium fluoride [C2204], to generate the corresponding arynes under mild conditions.

3. The method using anthranilic acids

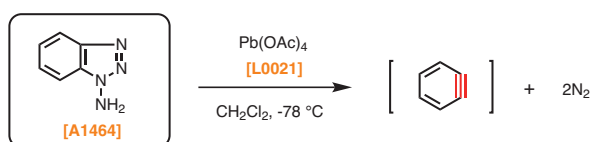
An alternative method using anthranilic acids has been reported. The diazo compounds derived from anthranilic acids are decomposed to generate the corresponding arynes, eliminating nitrogen and carbon dioxide. For the preparation of diazo compounds, nitrite salts are generally well-known. However, in recent years, amyl nitrite [I0089] or *tert*-butyl nitrite [N0357] are frequently used for simple use.



4. Other methods for aryne generation

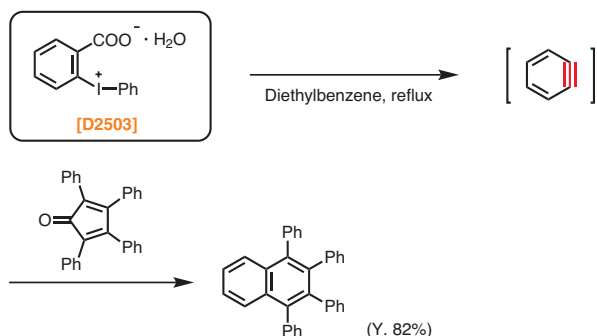
• Generation of benzyne from 1-aminobenzotriazole

Campbell *et al.* have reported the generation reaction of benzyne using 1-aminobenzotriazole [A1464], in which A1464 is oxidatively decomposed by lead acetate [L0021] to generate benzyne, eliminating nitrogen.⁸⁾

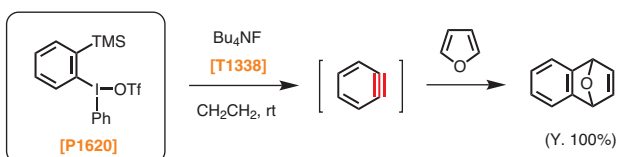


• The generation of benzyne using hypervalent iodine compounds

Diphenyliodonium-2-carboxylate [D2503] has been reported to generate benzyne under reflux conditions in diethylbenzene.⁹⁾



Moreover, phenyl[2-(trimethylsilyl)phenyl]iodonium trifluoromethanesulfonate [P1620], developed by Kitamura *et al.* is a mild benzyne precursor, which is treated with a fluoride salt to efficiently generate benzyne at room temperature.¹⁰⁾

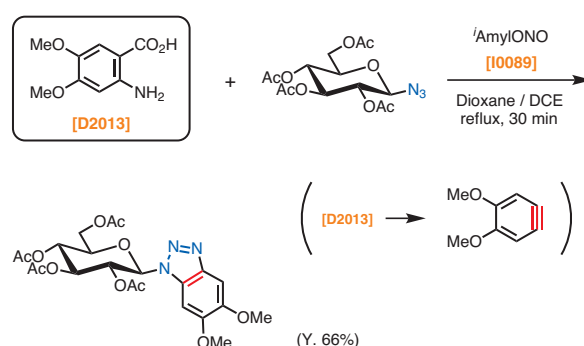


● Reaction examples of arynes

Arynes are widely used as many kinds of synthetic intermediates. The typical application examples are described as below.

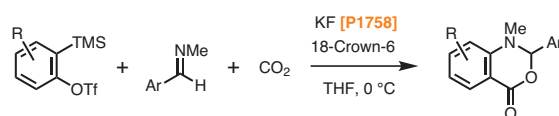
1. Click chemistry

Watt *et al.* have reported the synthesis of glucopyranose derivatives bearing a benzotriazolyl group *via* the Huisgen reaction (click reaction) of benzynes derived from the corresponding anthranilic acids and sugar azides, and their glycosyl donor abilities.¹¹⁾ In the Huisgen reaction, metal catalysts, such as copper sulfate, are generally required for reaction acceleration, however, the strain of the triple bond of the benzyne promotes the reaction without adding metal catalysts.



2. Multicomponent reaction

Arynes also have been used for multicomponent reactions (MCR). For example, Yoshida *et al.* have reported the three-component MCR using in situ generated benzynes, imines, and carbon dioxide, affording benzoxadionones.¹²⁾ Recently, much attention has been paid to organic synthesis using carbon dioxide as a carbon source from the ecological point of view, thus, the reaction above is an extremely useful and eco-friendly reaction.

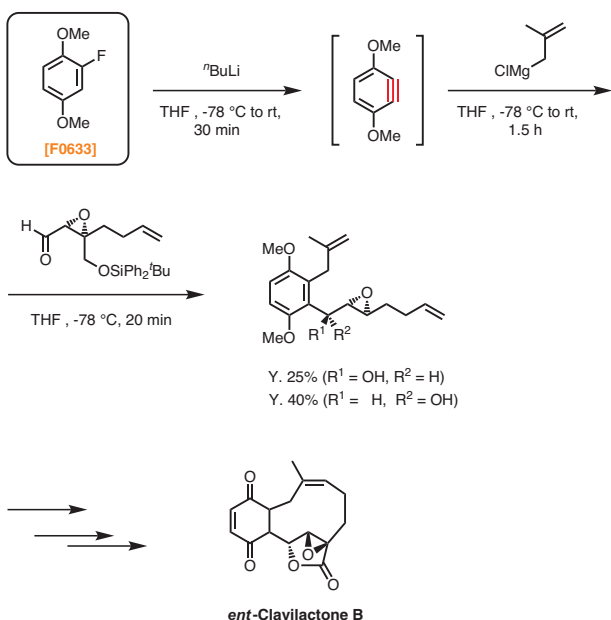


Ar = 2,4,6-trimethylphenyl

Benzyne Precursor	Reaction time (h)	Product
	15	
	46	
	60	

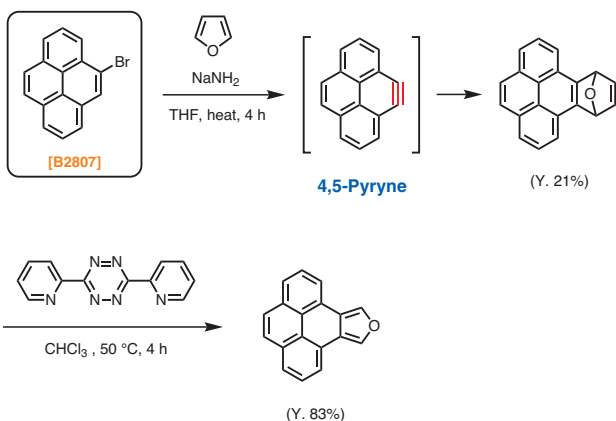
3. Synthesis of key intermediates for total synthesis (*ent*-Clavilactone B)

Arynes are also useful building blocks in total synthesis. For example, Barret *et al.* have reported the total synthesis of a natural product, *ent*-Clavilactone B, which shows tyrosine kinase inhibitory activity, using a benzyne derivative as a key starting material.¹³⁾



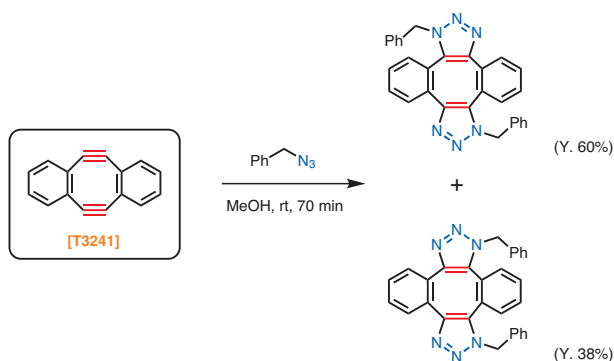
Other aryne precursors and related compounds

As described above, benzyne, naphthalene, or pyridyne are relatively well-known as examples of arynes, however, several arynes derived from other aromatic compounds also have been reported. For example, Moursounidis *et al.* have reported the generation of 4,5-pyryne, derived from 4-bromopyrene [B2807], and the reaction using 4,5-pyryne affording the pyrene-annulated furan derivatives.¹⁴⁾



In general, “cycloalkynes”, such as arynes, have a strained structure, thus, arynes cannot be isolated. On the other hand, 5,6,11,12-tetrahydrodibenzo[*a,e*]cyclooctene [T3241], reported by Sondheimer *et al.*, is relatively more stable than other arynes enough to isolate.¹⁵⁾ The compound also has a strained structure, and has been reported to have high reaction activity. Hosoya *et al.* have reported the “double-click reaction” applying T3241 in click chemistry. The high reactivity of the two alkyne moieties allows the reaction to proceed smoothly without using metal catalysts, such as a copper salt.¹⁶⁾

Metal-Free Double-click Reaction



TCl offers a variety of aryne precursors. All the products in this brochure have been reported to generate the corresponding arynes so far, thus, reaction applications and related information for each product are introduced on our website. In addition, reagents for the generation of arynes are also listed in this brochure.




























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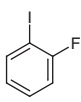
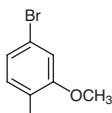
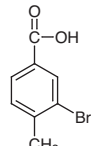
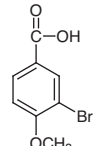
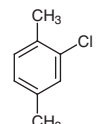
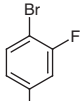
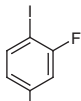
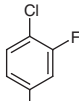
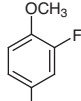
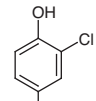
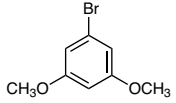
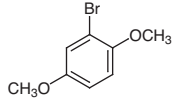
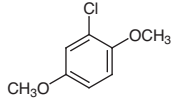
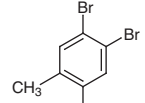
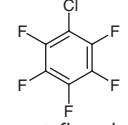
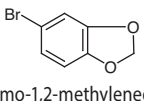
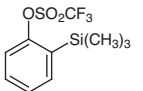
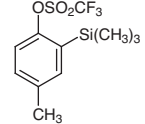
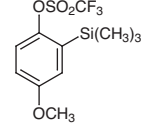
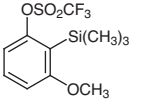
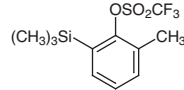
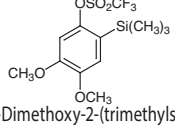
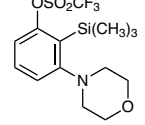
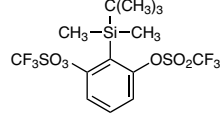
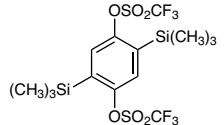
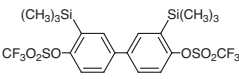
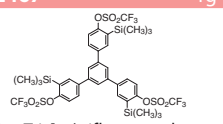
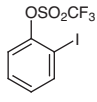
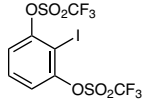
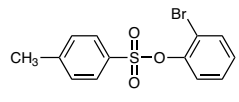
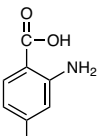
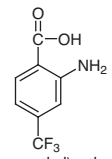
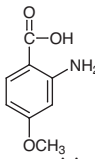
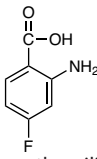
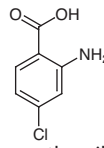
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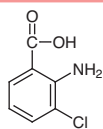
Benzynes Precursors

Halogenated Benzenes

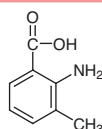
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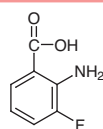
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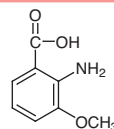
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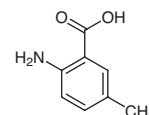
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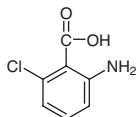
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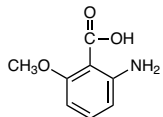
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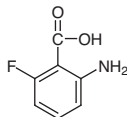
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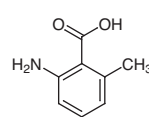
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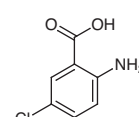
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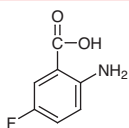
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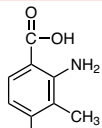
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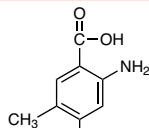
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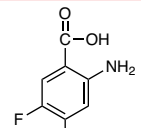
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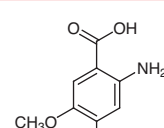
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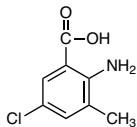
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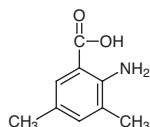
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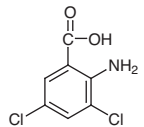
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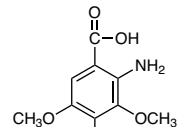
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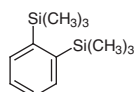
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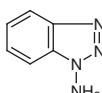
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**Other
Benzene
Precursors**

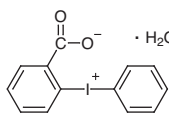
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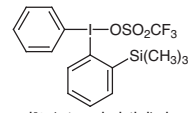
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1-Aminobenzotriazole
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D2503 5g 25g

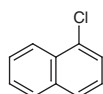
Diphenyliodonium-2-carboxylate
Monohydrate
CAS RN: 96195-89-0

P1620 1g 5g

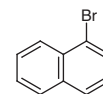
Phenyl[2-(trimethylsilyl)phenyl]-
iodonium Trifluoromethane-
sulfonate
CAS RN: 164594-13-2

Naphthalene Precursors

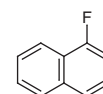
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1-Chloronaphthalene
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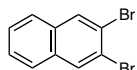
B0618 25g 100g 500g

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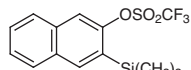
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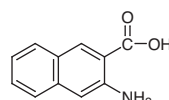
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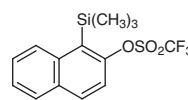
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3-(Trimethylsilyl)-2-naphthyl
Trifluoromethanesulfonate
CAS RN: 780820-43-1

A2258 1g 5g

3-Amino-2-naphthoic Acid
CAS RN: 5959-52-4

T2465 1g 5g

1-(Trimethylsilyl)-2-naphthyl
Trifluoromethanesulfonate
CAS RN: 252054-88-9

Pyridine Precursors

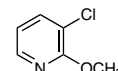
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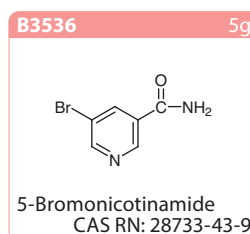
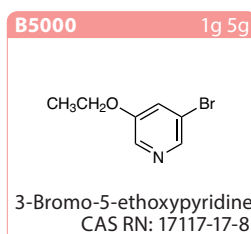
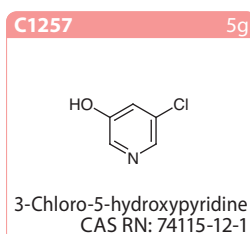
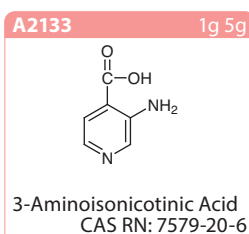
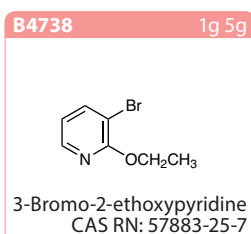
3-Bromopyridine
CAS RN: 626-55-1

C0280 25g 100g 500g

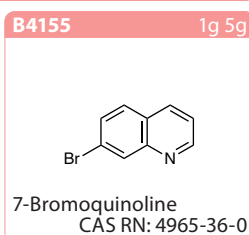
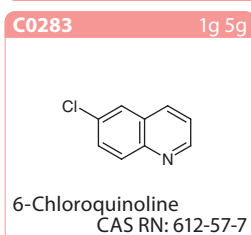
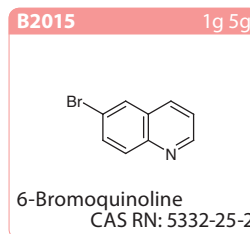
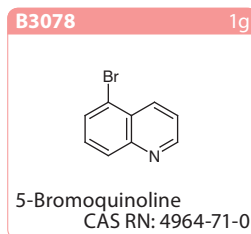
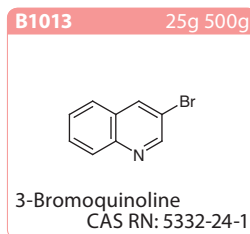
3-Chloropyridine
CAS RN: 626-60-8

C2565 1g 5g

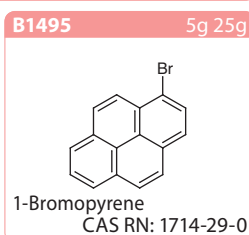
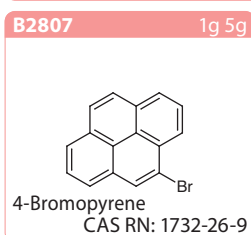
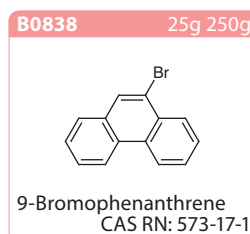
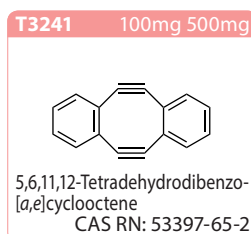
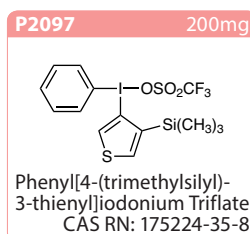
3-Chloro-2-methoxypyridine
CAS RN: 13472-84-9



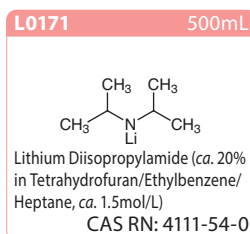
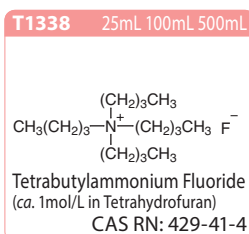
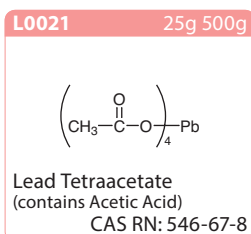
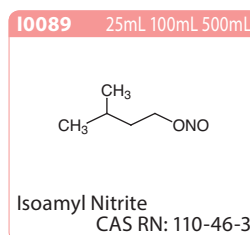
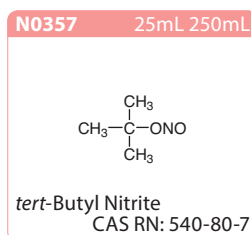
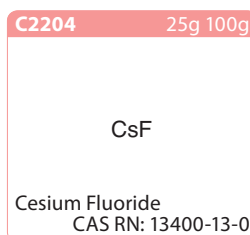
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