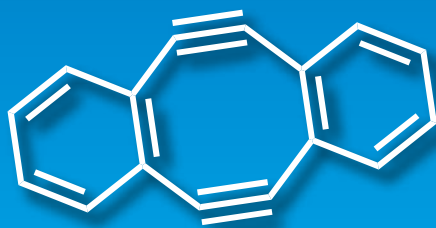


Aryne / Heteroaryne Precursors



Diels-Alder Reaction

Click Chemistry

Multicomponent Reaction

etc.

Benzyne Precursors

- Halogenated Benzenes
- OTf / TMS-Benzenes
- OTf-Benzenes
- OTs-Benzenes
- Anthranilic Acid Derivatives
- Other Benzyne Precursors

Naphthalynes Precursors

Pyridyne Precursors

Quinolyne Precursors

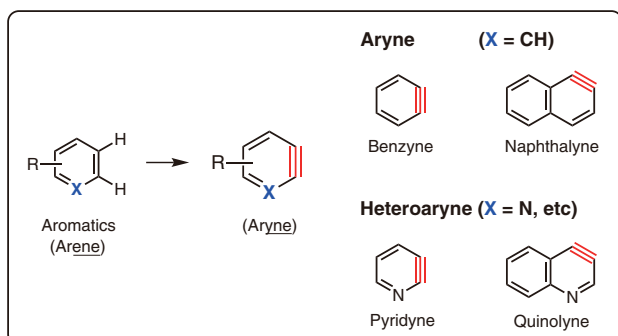
Other Aryne Precursors / Related Compounds

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.

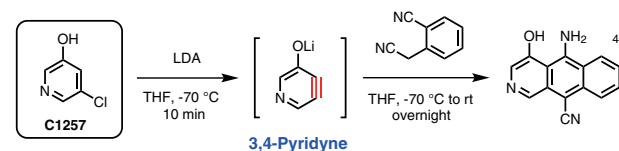
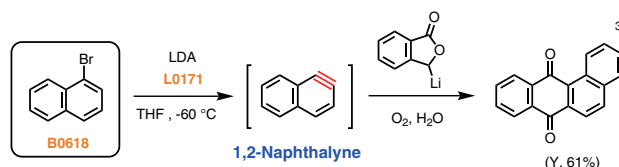
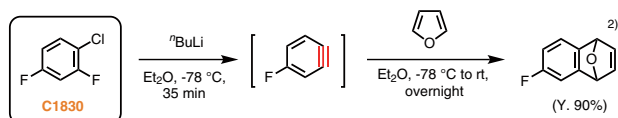
In general, arynes have extremely high reactivity due to their strained structures, thus, they have been widely used in organic synthesis as useful intermediates.¹⁾

● Synthetic methods

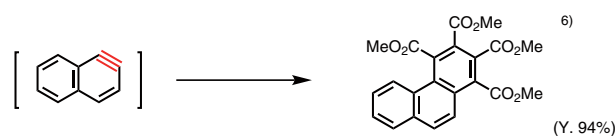
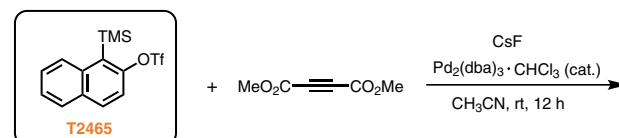
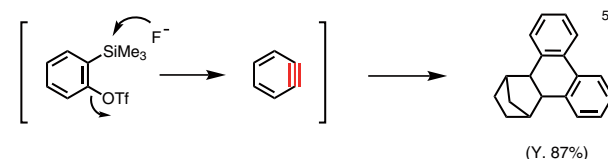
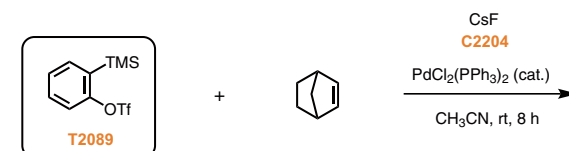
A number of methods for the generation of arynes have been reported so far. Arynes cannot be isolated because of their high reactivity, and they are generally prepared *in situ* in reaction systems. The typical examples are described as below.

1. The method using halogenated aryl compounds

Halogenated aryl compounds are treated with strong bases, such as ⁿBuLi, 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 cyclo-adducts.



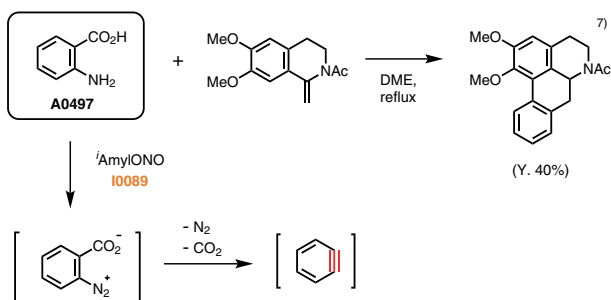
2. The method using 2-TMS-aryl triflates



The method using halogenated aryl compounds described in 1. needs strong bases, such as ⁿBuLi. 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

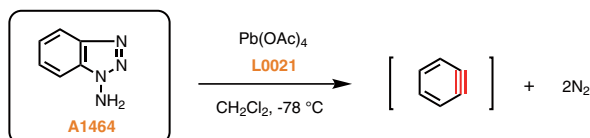
An alternative method using anthranilic acids has been reported. The diazo compounds derived from anthranilic acids are decomposed to generate the corresponding arynes, eliminating nitrogen and carbon dioxide. For the preparation of diazo compounds, nitrite salts are generally well-known. However, in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



4. Other methods for arylene generation

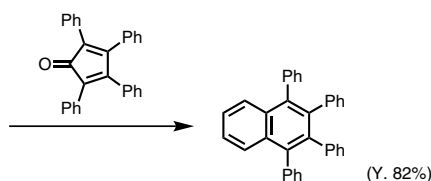
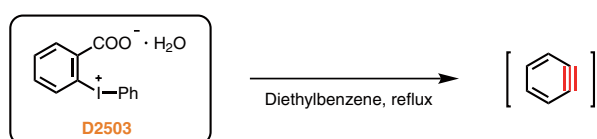
• Generation of benzyne from 1-aminobenzotriazole

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⁾

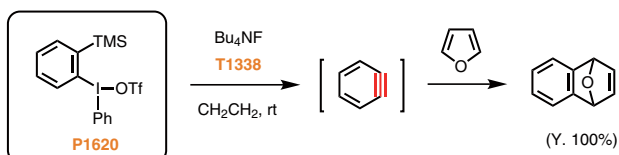


• The generation of benzyne using hypervalent iodine compounds

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⁾

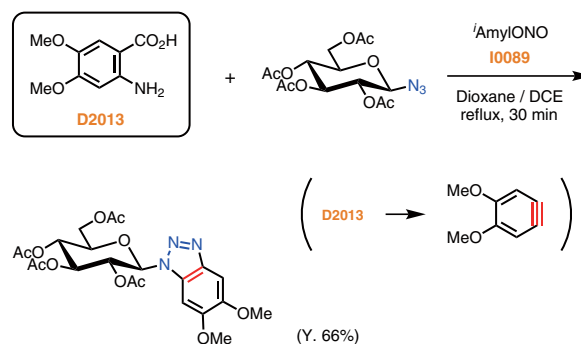


● Reaction examples of arynes

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

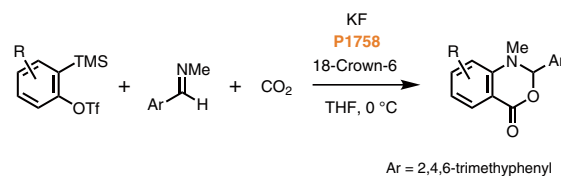
1. Click chemistry

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.



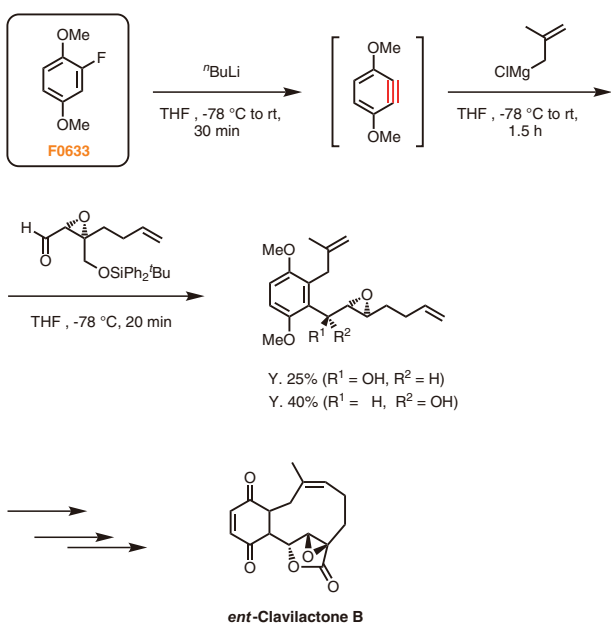
Benzyne Precursor	Reaction time (h)	Product
	15	 (Y. 82%)
	46	 (Y. 73%)

Ar = 2,4,6-trimethylphenyl



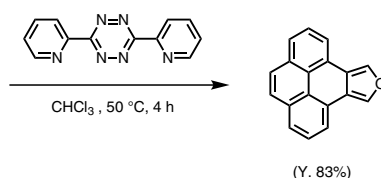
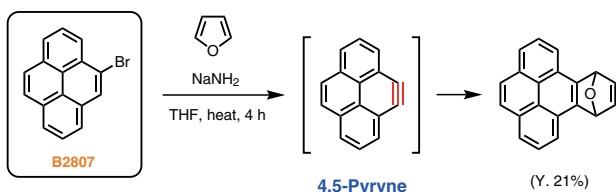
3. Synthesis of key intermediates for total synthesis (*ent*-Clavilactone B)

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⁾



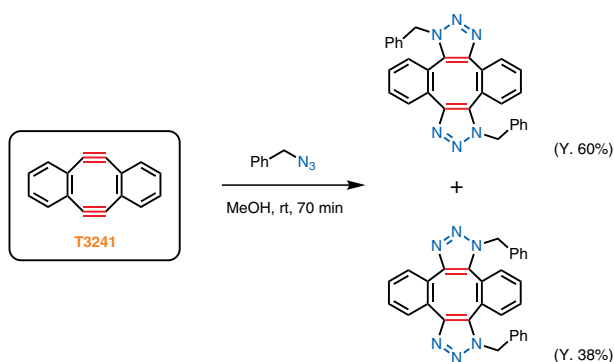
Other aryne precursors and related compounds

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



TCI 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.





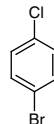



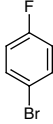
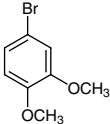
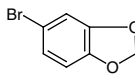
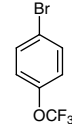
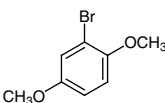
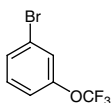
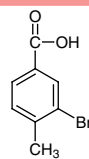
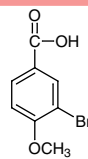
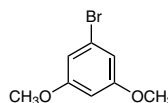
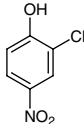

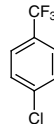
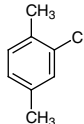


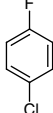


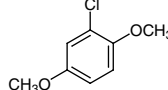
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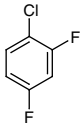

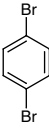
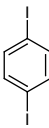
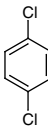
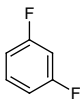
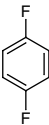
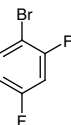
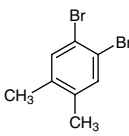
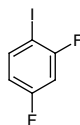

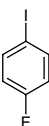


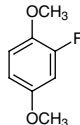
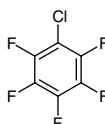
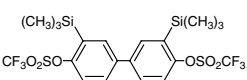
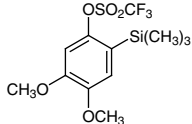
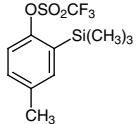
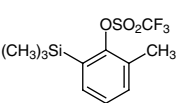
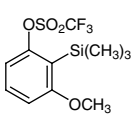
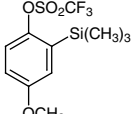
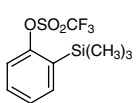
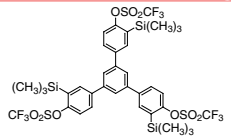


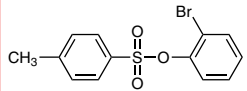
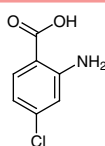
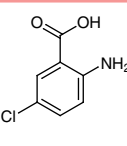
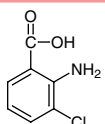
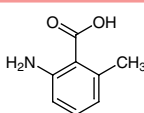
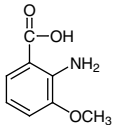
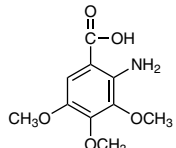
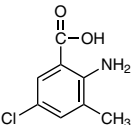
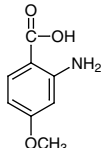
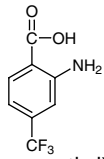
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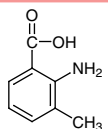
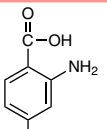
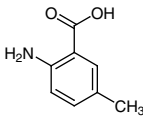
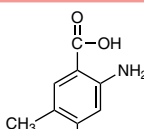
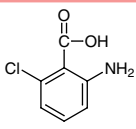
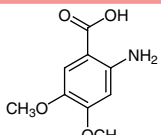
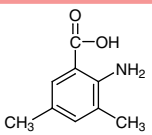
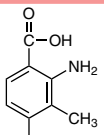
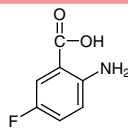
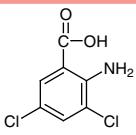
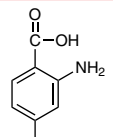
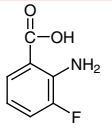
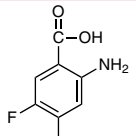
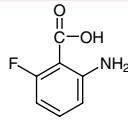
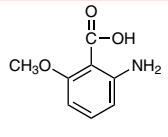
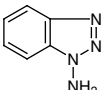
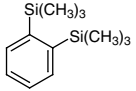
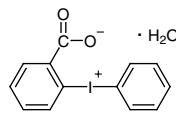
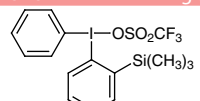
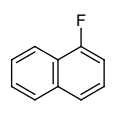
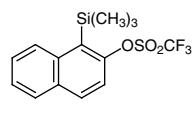
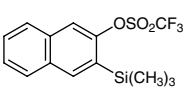
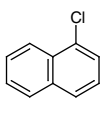
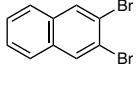
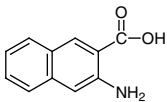
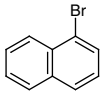
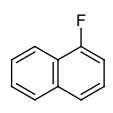
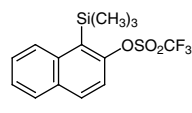
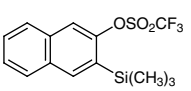
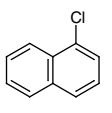
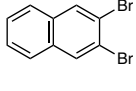
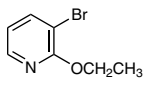
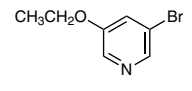

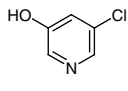
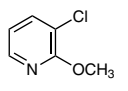
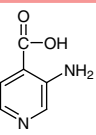

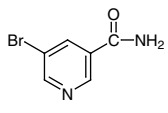
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Benzene Precursors

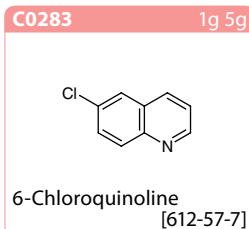
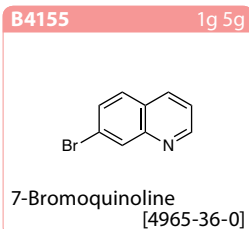
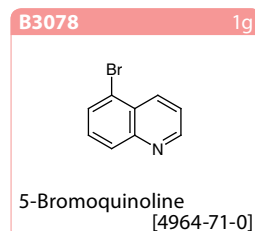
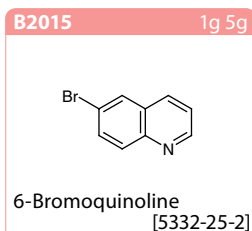
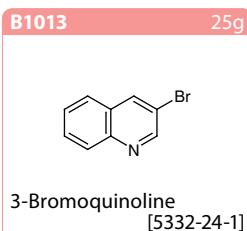
Halogenated Benzenes

				B0439 25g 500g  Bromobenzene [108-86-1]	B0545 25g 250g  3-Bromoanisole [2398-37-0]
B0546 25g 100g 500g  2-Bromoanisole [578-57-4]	B0570 25g 100g  1-Bromo-3-chlorobenzene [108-37-2]	B0571 25g 100g 500g  1-Bromo-4-chlorobenzene [106-39-8]	B0663 25g 250g  2-Bromobenzotrifluoride [392-83-6]	B0882 25g 250g  3-Bromofluorobenzene [1073-06-9]	
B0883 25g 100g 500g  2-Bromofluorobenzene [1072-85-1]	B0884 25g 100g 500g  4-Bromofluorobenzene [460-00-4]	B1021 25g  4-Bromo-1,2-dimethoxybenzene [2859-78-1]	B1230 5g 25g  4-Bromo-1,2-methylenedioxybenzene [2635-13-4]	B1772 5g 25g  1-Bromo-4-(trifluoromethoxy)benzene [407-14-7]	
B1979 5g 25g  1-Bromo-2,5-dimethoxybenzene [25245-34-5]	B2007 5g 25g  1-Bromo-3-(trifluoromethoxy)benzene [2252-44-0]	B3049 5g 25g  3-Bromo-4-methylbenzoic Acid [7697-26-9]	B3336 5g 25g  3-Bromo-4-methoxybenzoic Acid [99-58-1]	B3848 5g 25g  1-Bromo-3,5-dimethoxybenzene [20469-65-2]	
C0227 25g 500g  2-Chloro-4-nitrophenol [619-08-9]	C0303 25g 500g  2-Chlorobenzotrifluoride [88-16-4]	C0305 25g 500g  4-Chlorobenzotrifluoride [98-56-6]	C0313 25g 500g  2-Chloro-p-xylene [95-72-7]	C0647 10g 25g  2-Chlorofluorobenzene [348-51-6]	
C0648 25g  1-Chloro-3-fluorobenzene [625-98-9]	C0659 25g  1-Chloro-4-fluorobenzene [352-33-0]	C0973 25g  2-Chlorobenzyl Alcohol [17849-38-6]	C1148 25g  3-Chloroanisole [2845-89-8]	C1577 25g 500g  1-Chloro-2,5-dimethoxybenzene [2100-42-7]	

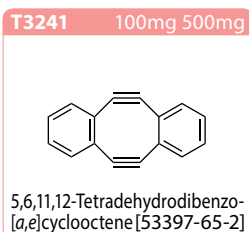
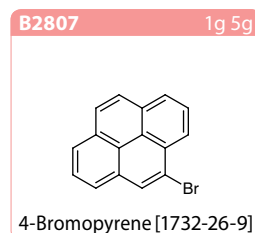
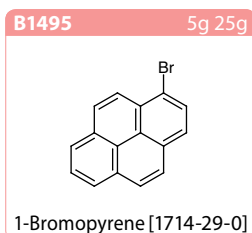
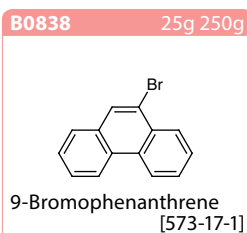
<p>C1830 25g</p>  <p>1-Chloro-2,4-difluorobenzene [1435-44-5]</p>	<p>D0168 25g 100g</p>  <p>1,2-Dibromobenzene [583-53-9]</p>	<p>D0170 25g 100g 500g</p>  <p>1,4-Dibromobenzene [106-37-6]</p>	<p>D0608 5g 25g</p>  <p>1,4-Diiodobenzene [624-38-4]</p>	<p>D0687 25g 500g</p>  <p>1,4-Dichlorobenzene [106-46-7]</p>	
<p>D1626 25g 500g</p>  <p>1,3-Difluorobenzene [372-18-9]</p>	<p>D1628 5g 25g</p>  <p>1,4-Difluorobenzene [540-36-3]</p>	<p>D1909 25g 500g</p>  <p>1-Bromo-2,4-difluorobenzene [348-57-2]</p>	<p>D2272 5g 25g</p>  <p>1,2-Dibromo-4,5-dimethylbenzene [24932-48-7]</p>	<p>D2545 25g</p>  <p>2,4-Difluoro-1-iodobenzene [2265-93-2]</p>	
<p>F0034 25g 100g 500g</p>  <p>Fluorobenzene [462-06-6]</p>	<p>F0237 5g 25g</p>  <p>1-Fluoro-4-iodobenzene (stabilized with Copper chip) [352-34-1]</p>	<p>F0253 10g 25g</p>  <p>1-Fluoro-2-iodobenzene [348-52-7]</p>	<p>F0260 25g</p>  <p>1-Fluoro-3-iodobenzene (stabilized with Copper chip) [1121-86-4]</p>	<p>F0633 5g</p>  <p>2-Fluoro-1,4-dimethoxybenzene [82830-49-7]</p>	
<p>P0850 25g</p>  <p>Chloropentafluorobenzene [344-07-0]</p>	<p>OTf / TMS-Benzenes</p>		<p>B3047 1g</p>  <p>3,3'-bis(trimethylsilyl)biphenyl-4,4'-diyl bis(trifluoromethanesulfonate) [828282-80-0]</p>	<p>D3883 1g 5g</p>  <p>4,5-Dimethoxy-2-(trimethylsilyl)phenyl trifluoromethanesulfonate [866252-52-0]</p>	<p>M1882 1g 5g</p>  <p>4-Methyl-2-(trimethylsilyl)phenyl trifluoromethanesulfonate [262373-15-9]</p>
<p>M1883 1g 5g</p>  <p>2-Methyl-6-(trimethylsilyl)phenyl trifluoromethanesulfonate [556812-44-3]</p>	<p>M1884 1g 5g</p>  <p>3-Methoxy-2-(trimethylsilyl)phenyl trifluoromethanesulfonate [217813-03-1]</p>	<p>M1885 1g 5g</p>  <p>4-Methoxy-2-(trimethylsilyl)phenyl trifluoromethanesulfonate [556812-41-0]</p>	<p>T2089 1g 5g 25g</p>  <p>2-(Trimethylsilyl)phenyl trifluoromethanesulfonate [88284-48-4]</p>	<p>T2467 1g</p>  <p>1,3,5-Tris[4-(trifluoromethanesulfonyloxy)-3-(trimethylsilyl)phenyl]benzene [847925-63-7]</p>	
<p>OTf-Benzenes</p>		<p>B4777 1g 5g</p>  <p>2-Bromophenyl trifluoromethanesulfonate [129112-25-0]</p>	<p>I0770 5g</p>  <p>2-Iodophenyl trifluoromethanesulfonate [129112-26-1]</p>	<p>OTs-Benzenes</p>	
<p>OTs-Benzenes</p>		<p>B4528 1g 5g</p>  <p>2-Bromophenyl p-Toluenesulfonate [84672-48-0]</p>			
<p>Anthranilic Acid Derivatives</p>		<p>A0661 25g</p>  <p>4-Chloroanthranilic Acid [89-77-0]</p>	<p>A0665 5g 25g</p>  <p>5-Chloroanthranilic Acid [635-21-2]</p>	<p>A0786 5g 25g</p>  <p>3-Chloroanthranilic Acid [6388-47-2]</p>	<p>A0996 5g 25g</p>  <p>2-Amino-6-methylbenzoic Acid [4389-50-8]</p>
<p>A1378 5g 25g</p>  <p>2-Amino-3-methoxybenzoic Acid [3177-80-8]</p>	<p>A2770 1g 5g</p>  <p>3,4,5-Trimethoxyanthranilic Acid [61948-85-4]</p>	<p>A2399 5g 25g</p>  <p>2-Amino-5-chloro-m-toluic Acid [20776-67-4]</p>	<p>A2319 1g 5g</p>  <p>2-Amino-p-anisic Acid [4294-95-5]</p>	<p>A2175 5g 25g</p>  <p>4-(Trifluoromethyl)anthranilic Acid [402-13-1]</p>	

<p>A1569 5g 25g</p>  <p>2-Amino-<i>m</i>-toluic Acid [4389-45-1]</p>	<p>A2538 1g 5g</p>  <p>2-Amino-<i>p</i>-toluic Acid [2305-36-4]</p>	<p>A1421 5g 25g</p>  <p>6-Amino-<i>m</i>-toluic Acid [2941-78-8]</p>	<p>A2850 200mg 1g</p>  <p>4,5-Dimethylanthranilic Acid [15089-51-7]</p>	<p>C2048 5g 25g</p>  <p>6-Chloroanthranilic Acid [2148-56-3]</p>
<p>D2013 10g</p>  <p>4,5-Dimethoxyanthranilic Acid [5653-40-7]</p>	<p>D2553 1g</p>  <p>3,5-Dimethylanthranilic Acid [14438-32-5]</p>	<p>D4120 5g 25g</p>  <p>3,4-Dimethylanthranilic Acid [50419-58-4]</p>	<p>F0396 1g 5g</p>  <p>5-Fluoroanthranilic Acid [446-08-2]</p>	<p>D1475 5g 25g</p>  <p>3,5-Dichloroanthranilic Acid [2789-92-6]</p>
<p>F0405 1g 5g 25g</p>  <p>4-Fluoroanthranilic Acid [446-32-2]</p>	<p>F0570 1g 5g</p>  <p>3-Fluoroanthranilic Acid [825-22-9]</p>	<p>D4063 5g 25g</p>  <p>4,5-Difluoroanthranilic Acid [83506-93-8]</p>	<p>F0475 1g 5g</p>  <p>6-Fluoroanthranilic Acid [434-76-4]</p>	<p>A2847 1g 5g</p>  <p>6-Amino-<i>o</i>-anisic Acid [53600-33-2]</p>
<p>Other Benzyne Precursors</p>	<p>A1464 1g 5g</p>  <p>1-Aminobenzotriazole [1614-12-6]</p>	<p>B2299 1g 5g</p>  <p>1,2-Bis(trimethylsilyl)-benzene [17151-09-6]</p>	<p>D2503 5g 25g</p>  <p>Diphenyliodonium-2-carboxylate Monohydrate [96195-89-0]</p>	<p>P1620 1g 5g</p>  <p>Phenyl[2-(trimethylsilyl)-phenyl]iodonium Trifluoromethanesulfonate [164594-13-2]</p>
<p>Naphthalene Precursors</p>				
<p>F0212 5g 25g</p>  <p>1-Fluoronaphthalene [321-38-0]</p>	<p>T2465 1g 5g</p>  <p>1-(Trimethylsilyl)-2-naphthyl Trifluoromethanesulfonate [252054-88-9]</p>	<p>T2466 1g 5g</p>  <p>3-(Trimethylsilyl)-2-naphthyl Trifluoromethanesulfonate [780820-43-1]</p>	<p>C2310 5g 25g</p>  <p>1-Chloronaphthalene [90-13-1]</p>	<p>D4597 200mg 1g</p>  <p>2,3-Dibromonaphthalene [13214-70-5]</p>
<p>A2258 1g 5g</p>  <p>3-Amino-2-naphthoic Acid [5959-52-4]</p>	<p>B0618 25g 100g 500g</p>  <p>1-Bromonaphthalene [90-11-9]</p>			
<p>Pyridine Precursors</p>				
<p>F0212 5g 25g</p>  <p>1-Fluoronaphthalene [321-38-0]</p>	<p>T2465 1g 5g</p>  <p>1-(Trimethylsilyl)-2-naphthyl Trifluoromethanesulfonate [252054-88-9]</p>	<p>T2466 1g 5g</p>  <p>3-(Trimethylsilyl)-2-naphthyl Trifluoromethanesulfonate [780820-43-1]</p>	<p>C2310 5g 25g</p>  <p>1-Chloronaphthalene [90-13-1]</p>	<p>D4597 200mg 1g</p>  <p>2,3-Dibromonaphthalene [13214-70-5]</p>
<p>B4738 1g 5g</p>  <p>3-Bromo-2-ethoxypyridine [57883-25-7]</p>	<p>B5000 1g 5g</p>  <p>3-Bromo-5-ethoxypyridine [17117-17-8]</p>	<p>C0280 25g 100g 500g</p>  <p>3-Chloropyridine [626-60-8]</p>	<p>C1257 5g</p>  <p>3-Chloro-5-hydroxypyridine [74115-12-1]</p>	<p>C2565 1g 5g</p>  <p>3-Chloro-2-methoxypyridine [13472-84-9]</p>
<p>A2133 1g 5g</p>  <p>3-Aminoisonicotinic Acid [7579-20-6]</p>	<p>B0651 25g 100g</p>  <p>3-Bromopyridine (stabilized with Copper chip) [626-55-1]</p>	<p>B3536 5g</p>  <p>5-Bromonicotinamide [28733-43-9]</p>		

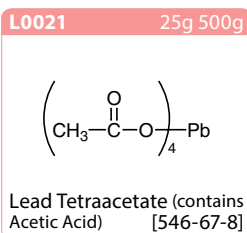
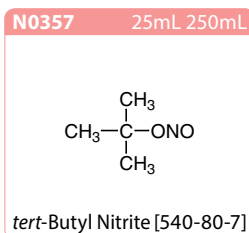
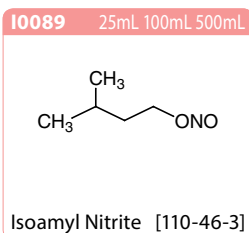
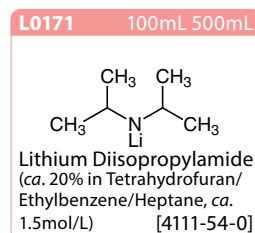
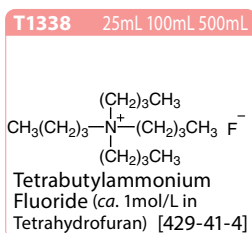
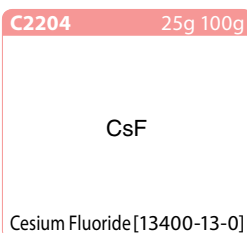
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