CHEMISTRY

TCI

Aryne / Heteroaryne Precursors

Diels-Alder Reaction

Click Chemistry

Multicomponent Reaction

etc.

Benzyne Precursors

Naphthalyne Precursors

Pyridyne Precursors

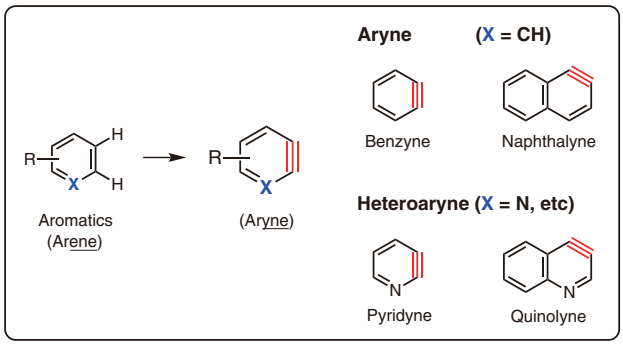
Quinolyne Precursors

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.

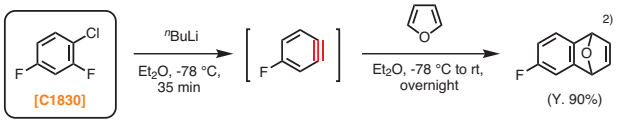
In general, arynes have extremely high reactivity due to their strained structures, thus, they have been widely used in organic synthesis as useful intermediates.[1)]

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 ^{n}BuLi, $NaNH_2$ 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.



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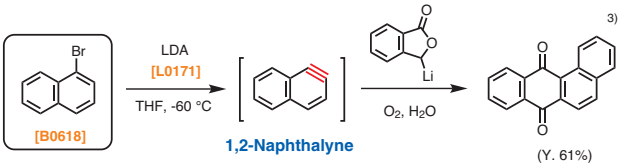

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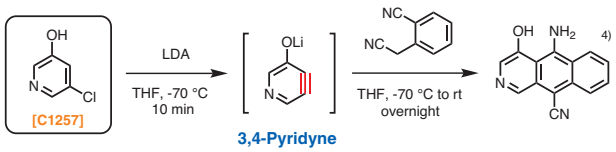
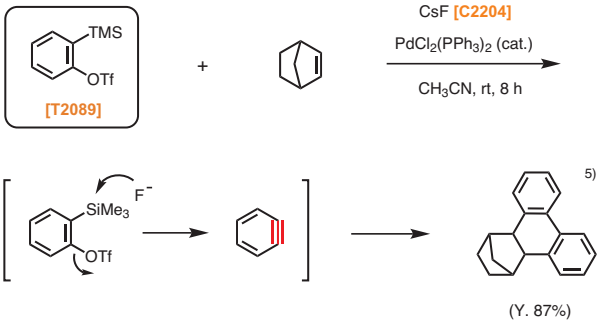


4)

2. The method using 2-TMS-aryl triflates



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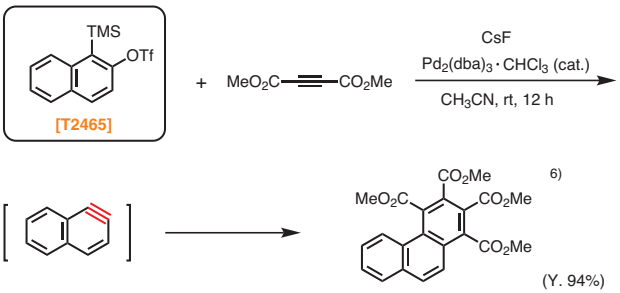
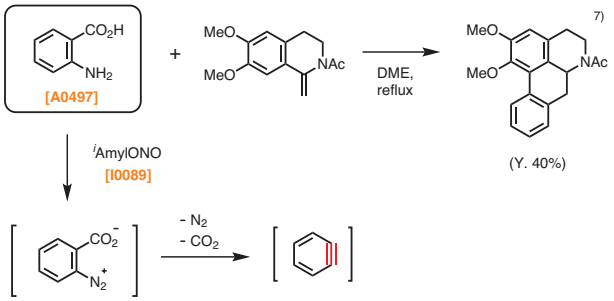


6)

The method using halogenated aryl compounds described in **section 1**. needs strong bases, such as ^{n}BuLi. 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

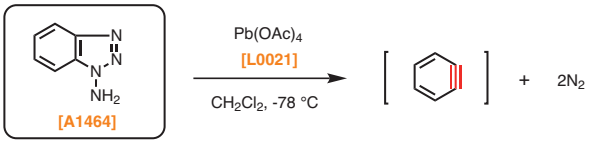
An alternative method using anthranilic acids has been reported. The diazo compounds derived from anthranilic acids are decomposed to generate the corresponding arynes, eliminating nitrogen and carbon dioxide. For the preparation of diazo compounds, nitrite salts are generally well-known. However, in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



4. Other methods for aryne generation

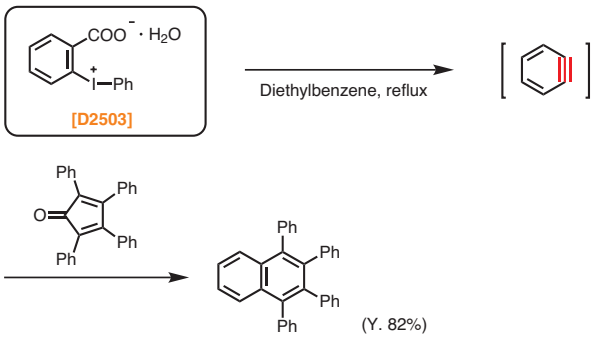
- **Generation of benzyne from 1-aminobenzotriazole**

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)]

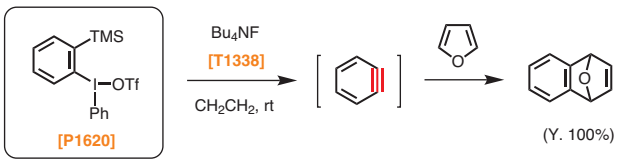


- **The generation of benzyne using hypervalent iodine compounds**

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)]

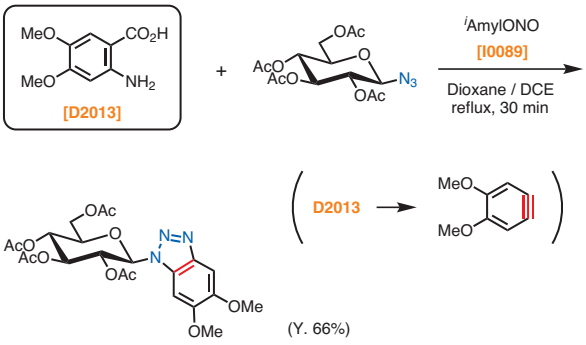


Reaction examples of arynes

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

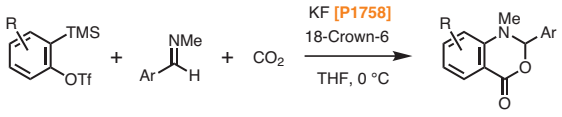
1. Click chemistry

Watt *et al.* have reported the synthesis of glucopyranose derivatives bearing a benzotriazolyl group *via* the Hüisgen reaction (click reaction) of benzynes derived from the corresponding anthranilic acids and sugar azides, and their glycosyl donor abilities.[11)] In the Hüisgen 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

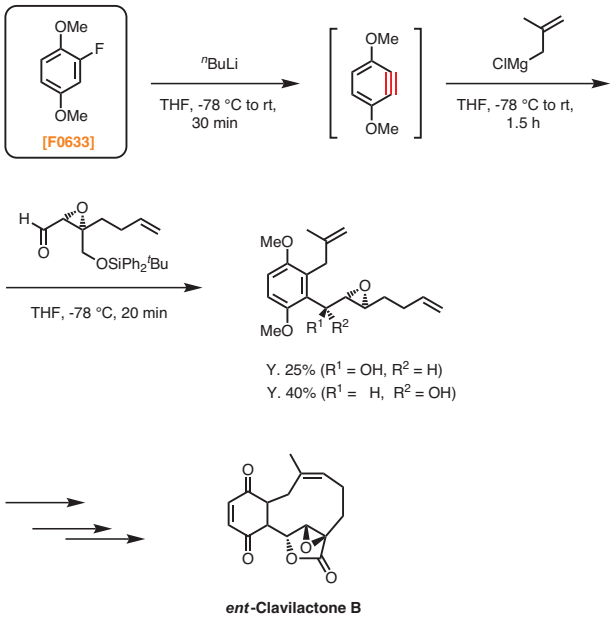
Arynes also have been used for multicomponent reactions (MCR). For example, Yoshida *et al*. have reported the three-component MCR using in situ generated benzynes, imines, and carbon dioxide, affording benzoxadinones.[12)] Recently, much attention has been paid to organic synthesis using carbon dioxide 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
[T2089]	15	(Y. 82%)
[M1884]	46	(Y. 73%)
[T2466]	60	(Y. 44%)

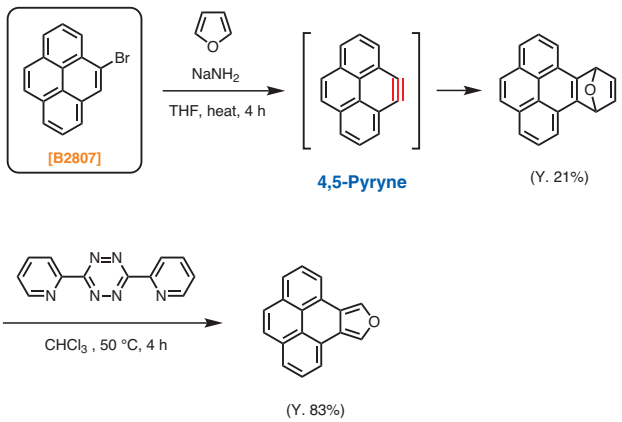
3. Synthesis of key intermediates for total synthesis (*ent*-Clavilactone B)

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)]



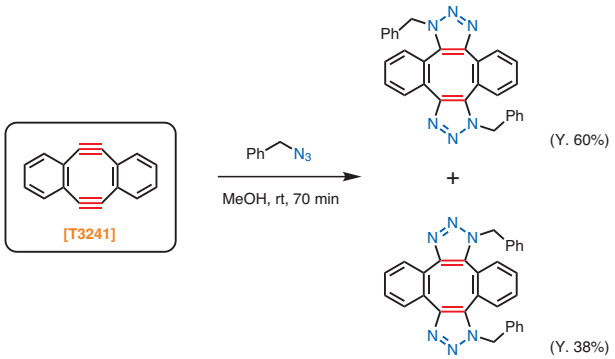
● Other aryne precursors and related compounds

As described above, benzyne, naphthalyne, 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-tetradehydrodibenzo[*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 Rection



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.

References

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Benzyne Precursors

Halogenated Benzenes

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Bromobenzene
CAS RN: 108-86-1

F0034 25g 100g 500g

Fluorobenzene
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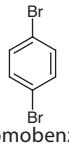
D0170 25g 100g 500g



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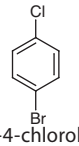

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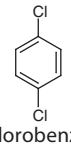

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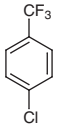

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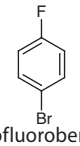

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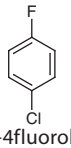

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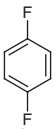

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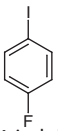

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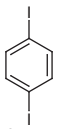

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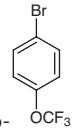

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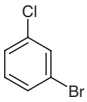

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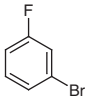

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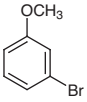

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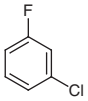

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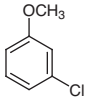

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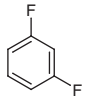

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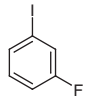

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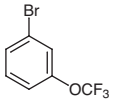

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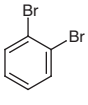

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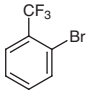

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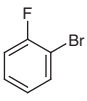

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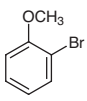

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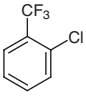
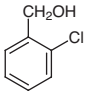
CAS RN: 578-57-4

C0303 25g 500g



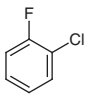
2-Chlorobenzotrifluoride
CAS RN: 88-16-4

C0973 25g



2-Chlorobenzyl Alcohol
CAS RN: 17849-38-6

C0647 10g 25g

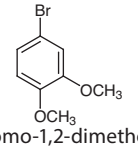


2-Chlorofluorobenzene
CAS RN: 348-51-6

F0253 10g 25g

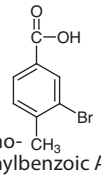
1-Fluoro-2-iodobenzene
CAS RN: 348-52-7

B1021 25g



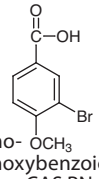
4-Bromo-1,2-dimethoxybenzene
CAS RN: 2859-78-1

B3049 5g 25g



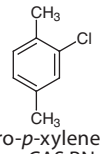
3-Bromo-4-methylbenzoic Acid
CAS RN: 7697-26-9

B3336 5g 25g



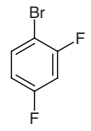
3-Bromo-4-methoxybenzoic Acid
CAS RN: 99-58-1

C0313 25g 500g



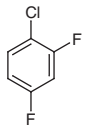
2-Chloro-*p*-xylene
CAS RN: 95-72-7

D1909 25g 500g



1-Bromo-2,4-difluorobenzene
CAS RN: 348-57-2

C1830 25g



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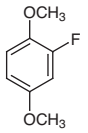
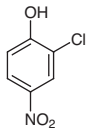
CAS RN: 1435-44-5

F0633 5g



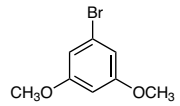
2-Fluoro-1,4-dimethoxybenzene
CAS RN: 82830-49-7

C0227 25g 500g



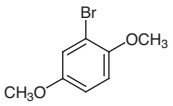
2-Chloro-4-nitrophenol
CAS RN: 619-08-9

B3848 5g 25g



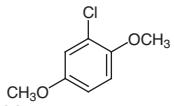
1-Bromo-3,5-dimethoxybenzene
CAS RN: 20469-65-2

B1979 5g 25g



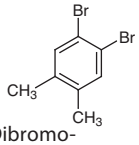
1-Bromo-2,5-dimethoxybenzene
CAS RN: 25245-34-5

C1577 25g 500g



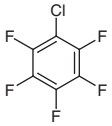
1-Chloro-2,5-dimethoxybenzene
CAS RN: 2100-42-7

D2272 5g 25g



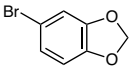
1,2-Dibromo-4,5-dimethylbenzene
CAS RN: 24932-48-7

P0850 25g



Chloropentafluorobenzene
CAS RN: 344-07-0

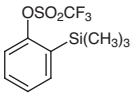
B1230 5g 25g



4-Bromo-1,2-methylenedioxybenzene
CAS RN: 2635-13-4

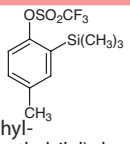
OTf / TMS-Benzenes

T2089 1g 5g 25g



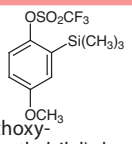
2-(Trimethylsilyl)phenyl Trifluoromethanesulfonate
CAS RN: 88284-48-4

M1882 1g 5g



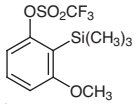
4-Methyl-2-(trimethylsilyl)phenyl Trifluoromethanesulfonate
CAS RN: 262373-15-9

M1885 1g 5g



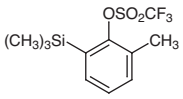
4-Methoxy-2-(trimethylsilyl)phenyl Trifluoromethanesulfonate
CAS RN: 556812-41-0

M1884 1g 5g



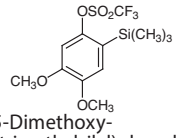
3-Methoxy-2-(trimethylsilyl)phenyl Trifluoromethanesulfonate
CAS RN: 217813-03-1

M1883 1g 5g



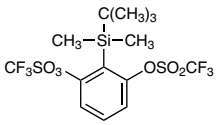
2-Methyl-6-(trimethylsilyl)phenyl Trifluoromethanesulfonate
CAS RN: 556812-44-3

D3883 1g 5g



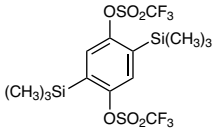
4,5-Dimethoxy-2-(trimethylsilyl)phenyl Trifluoromethanesulfonate
CAS RN: 866252-02-0

B5557 200mg 1g



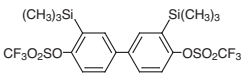
2-(*tert*-Butyldimethylsilyl)-1,3-phenylene Triflate
CAS RN: 1637638-66-4

B5559 1g



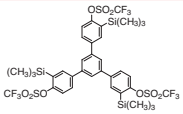
2,5-Bis(trimethylsilyl)-1,4-phenylene Triflate
CAS RN: 613676-07-6

B3047 1g



3,3'-Bis(trimethylsilyl)biphenyl-4,4'-diyl Bis(trifluoromethanesulfonate)
CAS RN: 828282-80-0

T2467 1g



1,3,5-Tris[4-(trifluoromethanesulfonyloxy)-3-(trimethylsilyl)-phenyl]benzene
CAS RN: 847925-63-7

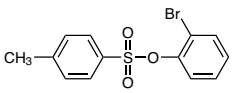
OTf-Benzenes

I0770 5g

2-Iodophenyl Trifluoromethanesulfonate
CAS RN: 129112-26-1

OTs-Benzenes

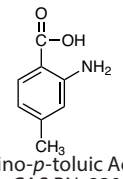
B4528 1g 5g



2-Bromophenyl *p*-Toluenesulfonate
CAS RN: 84672-48-0

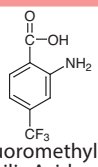
Anthranilic Acid Derivatives

A2538 1g 5g



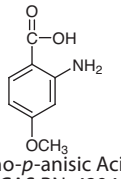
2-Amino-*p*-toluic Acid
CAS RN: 2305-36-4

A2175 5g 25g



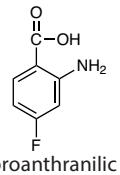
4-(Trifluoromethyl)-anthranilic Acid
CAS RN: 402-13-1

A2319 1g 5g



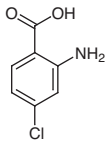
2-Amino-*p*-anisic Acid
CAS RN: 4294-95-5

F0405 1g 5g 25g



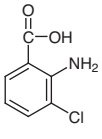
4-Fluoroanthranilic Acid
CAS RN: 446-32-2

A0661 25g



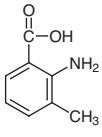
4-Chloroanthranilic Acid
CAS RN: 89-77-0

A0786 5g 25g



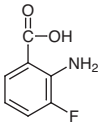
3-Chloroanthranilic Acid
CAS RN: 6388-47-2

A1569 5g 25g



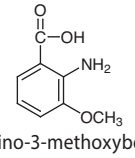
2-Amino-*m*-toluic Acid
CAS RN: 4389-45-1

F0570 1g 5g



3-Fluoroanthranilic Acid
CAS RN: 825-22-9

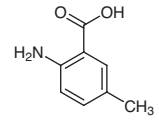
A1378 5g 25g



2-Amino-3-methoxybenzoic Acid
CAS RN: 3177-80-8

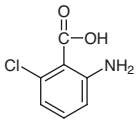
Please inquire for pricing and availability of listed products to our local sales representatives.

A1421 5g 25g



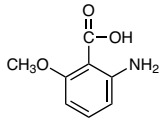
6-Amino-*m*-toluic Acid
CAS RN: 2941-78-8

C2048 5g 25g



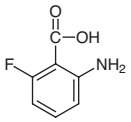
6-Chloroanthranilic Acid
CAS RN: 2148-56-3

A2847 1g 5g



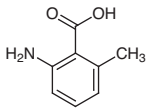
6-Amino-*o*-anisic Acid
CAS RN: 53600-33-2

F0475 1g 5g



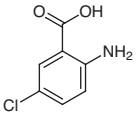
6-Fluoroanthranilic Acid
CAS RN: 434-76-4

A0996 5g 25g



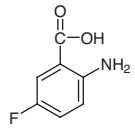
2-Amino-6-methylbenzoic Acid
CAS RN: 4389-50-8

A0665 5g 25g



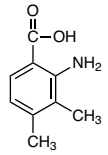
5-Chloroanthranilic Acid
CAS RN: 635-21-2

F0396 1g 5g



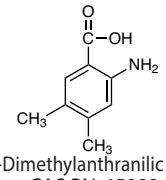
5-Fluoroanthranilic Acid
CAS RN: 446-08-2

D4120 5g 25g



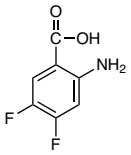
3,4-Dimethylanthranilic Acid
CAS RN: 50419-58-4

A2850 200mg 1g



4,5-Dimethylanthranilic Acid
CAS RN: 15089-51-7

D4063 5g 25g

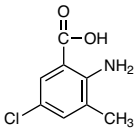


4,5-Difluoroanthranilic Acid
CAS RN: 83506-93-8

D2013 10g

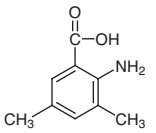
4,5-Dimethoxyanthranilic Acid
CAS RN: 5653-40-7

A2399 5g 25g



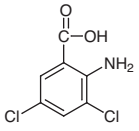
2-Amino-5-chloro-*m*-toluic Acid
CAS RN: 20776-67-4

D2553 1g



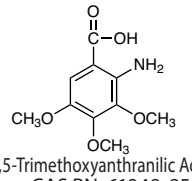
3,5-Dimethylanthranilic Acid
CAS RN: 14438-32-5

D1475 5g 25g



3,5-Dichloroanthranilic Acid
CAS RN: 2789-92-6

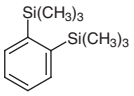
A2770 1g



3,4,5-Trimethoxyanthranilic Acid
CAS RN: 61948-85-4

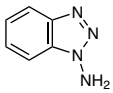
Other Benzyne Precursors

B2299 1g 5g



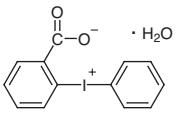
1,2-Bis(trimethylsilyl)benzene
CAS RN: 17151-09-6

A1464 1g 5g



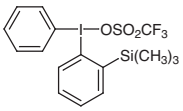
1-Aminobenzotriazole
CAS RN: 1614-12-6

D2503 5g 25g



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

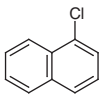
P1620 1g 5g



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

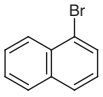
Naphthalyne Precursors

C2310 5g 25g



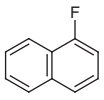
1-Chloronaphthalene
CAS RN: 90-13-1

B0618 25g 100g 500g



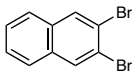
1-Bromonaphthalene
CAS RN: 90-11-9

F0212 5g 25g



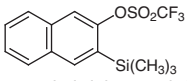
1-Fluoronaphthalene
CAS RN: 321-38-0

D4597 200mg 1g



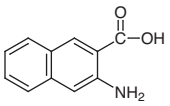
2,3-Dibromonaphthalene
CAS RN: 13214-70-5

T2466 1g 5g



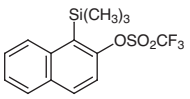
3-(Trimethylsilyl)-2-naphthyl Trifluoromethanesulfonate
CAS RN: 780820-43-1

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

Pyridyne Precursors

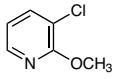
B0651 25g 100g

3-Bromopyridine
CAS RN: 626-55-1

C0280 25g 100g 500g

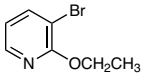
3-Chloropyridine
CAS RN: 626-60-8

C2565 1g 5g



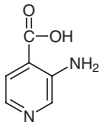
3-Chloro-2-methoxypyridine
CAS RN: 13472-84-9

B4738 1g



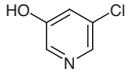
3-Bromo-2-ethoxypyridine
CAS RN: 57883-25-7

A2133 1g 5g



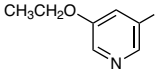
3-Aminoisonicotinic Acid
CAS RN: 7579-20-6

C1257 5g



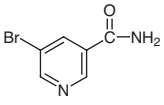
3-Chloro-5-hydroxypyridine
CAS RN: 74115-12-1

B5000 1g 5g



3-Bromo-5-ethoxypyridine
CAS RN: 17117-17-8

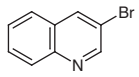
B3536 5g



5-Bromonicotinamide
CAS RN: 28733-43-9

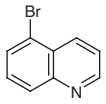
Quinolyne Precursors

B1013 25g



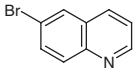
3-Bromoquinoline
CAS RN: 5332-24-1

B3078 1g



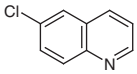
5-Bromoquinoline
CAS RN: 4964-71-0

B2015 1g 5g



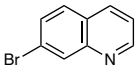
6-Bromoquinoline
CAS RN: 5332-25-2

C0283 1g 5g



6-Chloroquinoline
CAS RN: 612-57-7

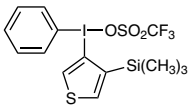
B4155 1g 5g



7-Bromoquinoline
CAS RN: 4965-36-0

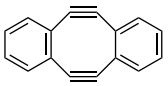
Other Aryne Precursors / Related Compounds

P2097 200mg



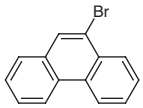
Phenyl[4-(trimethylsilyl)-3-thienyl]iodonium Triflate
CAS RN: 175224-35-8

T3241 100mg 500mg



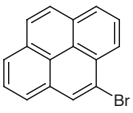
5,6,11,12-Tetradehydrodibenzo-[*a*,*e*]cyclooctene
CAS RN: 53397-65-2

B0838 25g 250g



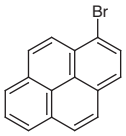
9-Bromophenanthrene
CAS RN: 573-17-1

B2807 1g 5g



4-Bromopyrene
CAS RN: 1732-26-9

B1495 5g 25g



1-Bromopyrene
CAS RN: 1714-29-0

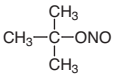
Reagents for the Generation of Arynes

C2204 25g 100g

CsF

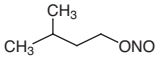
Cesium Fluoride
CAS RN: 13400-13-0

N0357 25mL 250mL



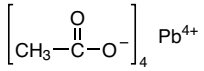
tert-Butyl Nitrite
CAS RN: 540-80-7

I0089 25mL 100mL 500mL



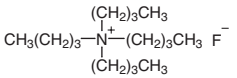
Isoamyl Nitrite
CAS RN: 110-46-3

L0021 25g 500g



Lead Tetraacetate
(contains Acetic Acid)
CAS RN: 546-67-8

T1338 25mL 100mL 500mL



Tetrabutylammonium Fluoride
(*ca.* 1mol/L in Tetrahydrofuran)
CAS RN: 429-41-4

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