

芳炔/杂芳炔前体

Aryne / Heteroaryne Precursors



Diels-Alder Reaction

Click Chemistry

Multicomponent Reaction

etc.

苯炔前体

萘炔前体

吡啶炔前体

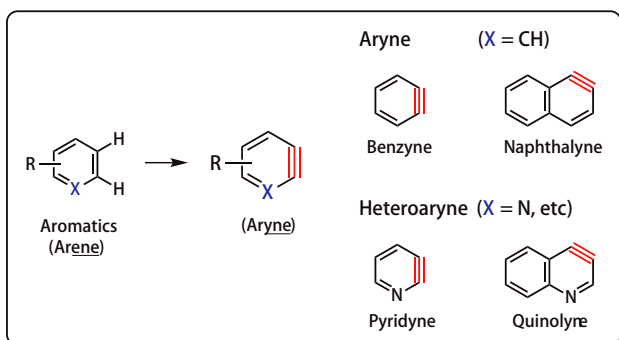
喹啉炔前体

其它芳炔前体/相关化合物

芳炔生成试剂

芳炔/杂芳炔前体

芳炔是芳烃的脱氢产物，比如苯或萘，从相邻的碳原子上脱去两个氢原子后，在各自的芳环中形成标志性的三键（炔）。



此外，芳环中含有氮等杂原子的芳炔称为“杂芳炔(heteroarynes)”。例如，目前已知的吡啶炔（衍生自吡啶）或喹啉炔（衍生自喹啉）等都是杂芳炔。

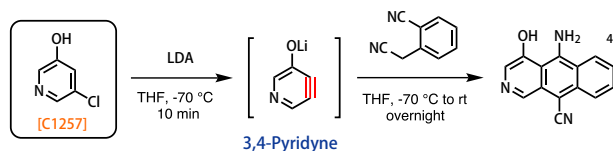
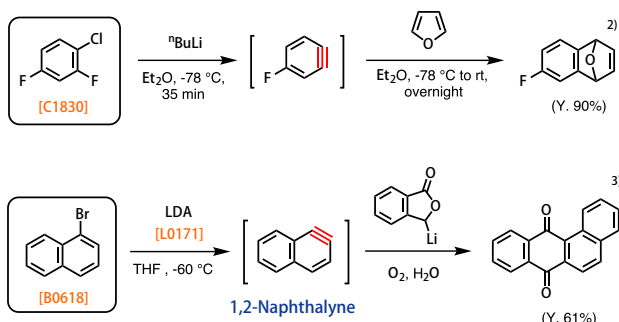
通常，芳炔的应变结构使其具有极高的反应活性，因此作为有用的中间体被广泛应用于有机合成中¹⁾。

● 合成方法

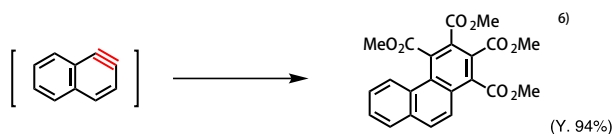
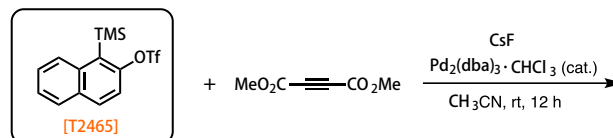
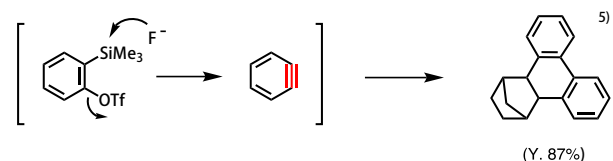
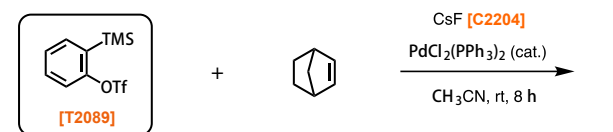
目前，关于芳炔的合成方法已有很多报道。由于具有高反应活性，芳炔并不能被分离出来，一般是在反应体系中原位制备。典型的制备方法有如下几种：

1. 利用卤代芳基化合物

在ⁿBuLi, NaNH₂或二异丙氨基锂(LDA)等强碱的作用下，卤代芳基化合物可以形成相应的芳炔。为了证实芳炔的形成，可使其与呋喃等二烯类化合物进行捕获反应，将其转化为Diels-Alder环加成产物。



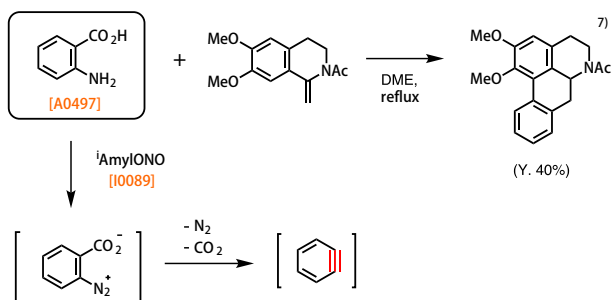
2. 利用2-TMS-芳基三氟甲磺酸酯



1中所述的利用卤代芳基化合物合成芳炔的方法需要ⁿBuLi等强碱的参与。为了避免使用强碱，开发出可以在温和条件下使用的芳炔前体。2-TMS-芳基三氟甲磺酸酯与氟化铯[C2204]等氟化盐反应，即可在温和的条件下生成相应的芳炔。

3. 利用邻氨基苯甲酸

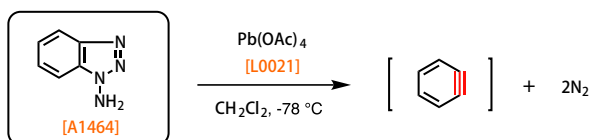
利用邻氨基苯甲酸合成芳炔的替代方法也已有报道。由邻氨基苯甲酸得到的重氮化合物，在脱除氮和二氧化碳后即可形成相应的芳炔。制备重氮化合物时，通常使用亚硝酸盐。不过，近年来常使用亚硝酸戊酯[I0089]或亚硝酸叔丁酯[N0357]作为替代，简单易用。



4. 生成苯炔的其它方法

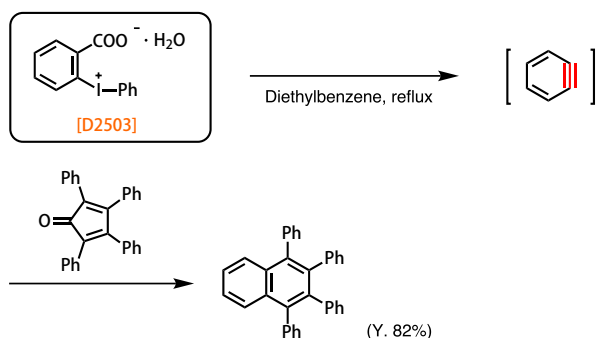
• 利用1-氨基苯并三唑形成苯炔

Campbell等报道了利用1-氨基苯并三唑[A1464]形成苯炔的反应，在此反应中，A1464被醋酸铅[L0021]氧化分解，除去氮，从而形成苯炔⁸⁾。

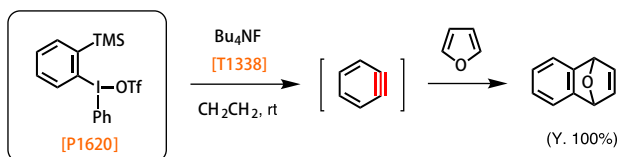


• 利用高价碘化合物形成苯炔

二苯基碘鎓-2-羧酸内盐[D2503]在二乙苯中，回流条件下可以生成苯炔⁹⁾。



另外，Kitamura等开发出一种温和的苯炔前体苯基[2-(三甲基硅基)苯基]三氟甲烷磺酸碘[P1620]，在氟化盐的作用下，室温时即可高效地生成苯炔¹⁰⁾。

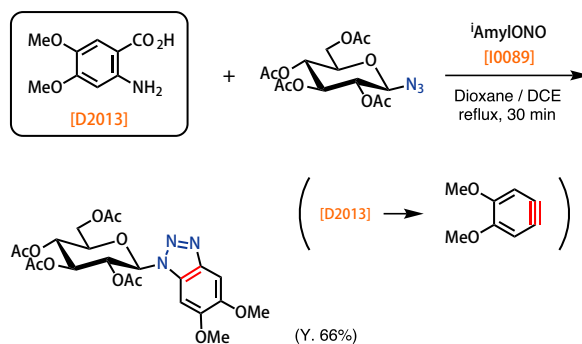


● 芳炔的反应示例

芳炔被广泛用作多种合成中间体，典型的应用示例如下：

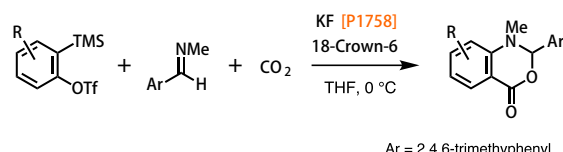
1. 点击化学

Watt等报道了含有一个苯并三唑基团的吡喃葡萄糖衍生物的合成，以及它们作为糖基供体的能力，该反应利用邻氨基苯甲酸衍生出的苯炔和糖叠氮化物，通过Huisgen反应（点击反应）实现¹¹⁾。在Huisgen反应中，通常使用金属催化剂，比如硫酸铜等加速反应。然而，对于此报道中的反应，并不需要金属催化剂，苯炔中三键的张力即可促进反应的进行。



2. 多组分反应

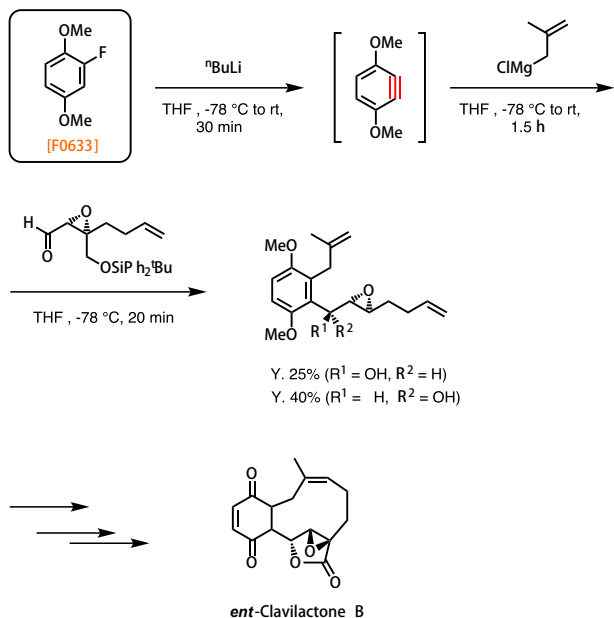
芳炔也可以用于多组分反应(MCR)。比如，Yoshida等报道了使用原位生成的苯炔、亚胺和二氧化碳三者间进行的三组分反应MCR，生成了苯并恶嗪酮¹²⁾。近来，从生态学观点出发，利用二氧化碳作为碳源的有机合成备受关注。因此，上述反应是一类非常有用并且对环境友好的反应。



Benzyne Precursor	Reaction time (h)	Product
	15	
	46	
	60	

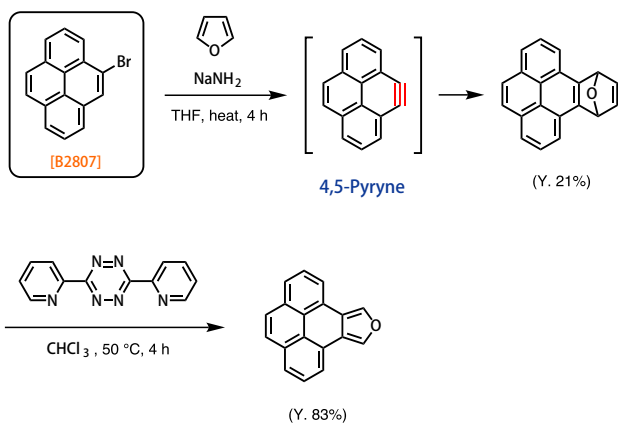
3. 全合成关键中间体的合成(*ent*-Clavilactone B)

芳炔也是全合成中有用的结构砌块。比如, Barret等报道了一种具有酪氨酸激酶抑制活性的天然产物*ent*-Clavilactone B的全合成, 其中苯炔衍生物被用作关键的起始原料¹³⁾。



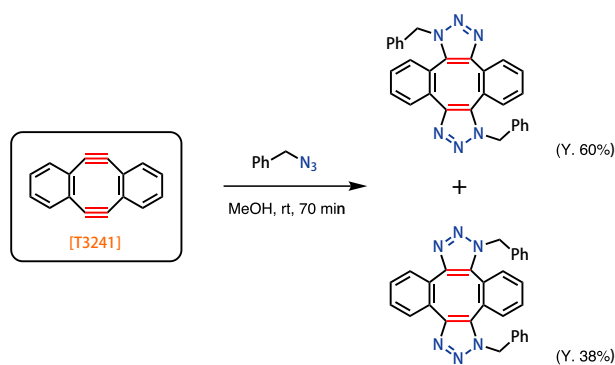
● 其它芳炔前体和相关化合物

以上内容中提到的苯炔, 萘炔或吡啶炔是比较常见的芳炔, 此外, 一些由其它芳香族化合物衍生的芳炔也被报道过。比如, Moursoundis等报道了由4-溴萘[B2807]衍生而来的4,5-萘炔的形成, 利用4,5-萘炔进行反应可以得到萘环吡喃衍生物¹⁴⁾。



通常, 由于“环炔烃”具有应变结构, 如芳炔, 因此不能被分离出来。不过, Sondheimer等发现, 5,6,11,12-四氢二苯并[a,e]环辛烯[T3241]与其它芳炔相比, 更加稳定, 可以实现分离¹⁵⁾。此化合物也具有应变结构和高反应活性。Hosoya等报道了在点击化学中利用T3241实现“双点击反应”。这两种炔烃单元的高反应活性使反应在无金属催化剂(比如铜盐)的条件下也能顺利进行¹⁶⁾。

Metal-Free Double-click Reaction




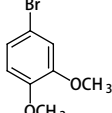
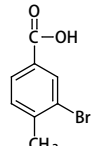
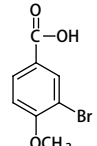
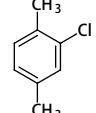
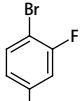
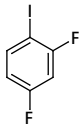
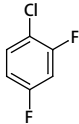
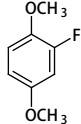
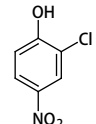
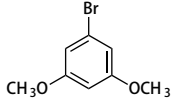
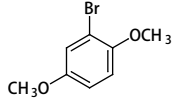
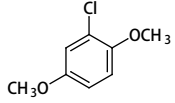
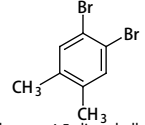
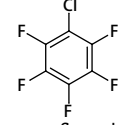
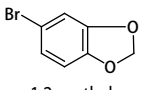
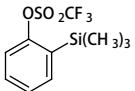
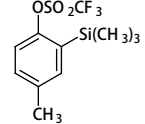
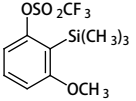
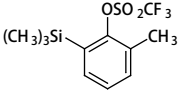
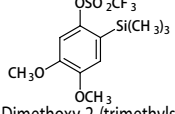
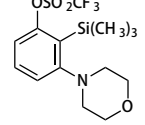
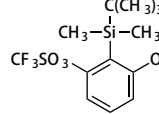
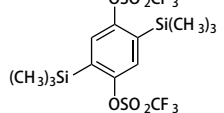
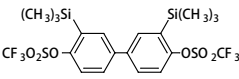
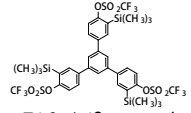

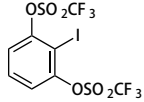
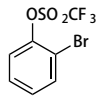
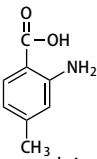
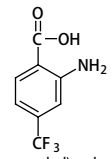
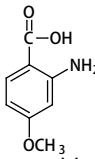
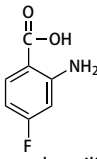
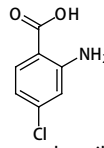
TCI提供多种芳炔前体。本册中列出的所有产品都已有生成芳炔的报道, 产品在反应中的应用及其它相关信息请参考TCI官网。此外, 生成芳炔所用的试剂也在本手册中列出。

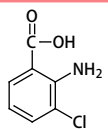
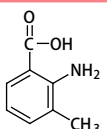
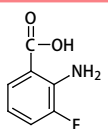
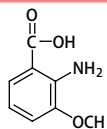
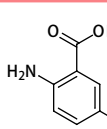
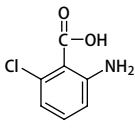
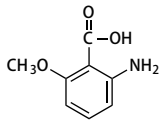
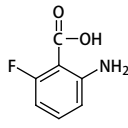
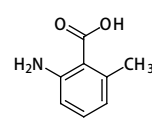
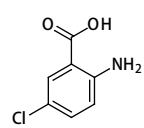
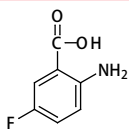
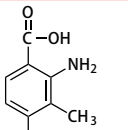
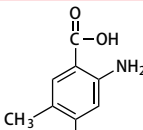
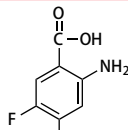
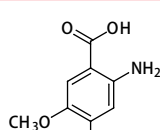
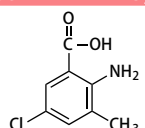
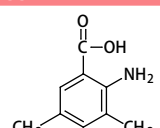
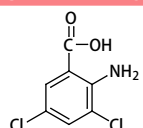
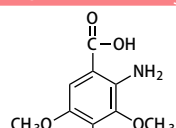
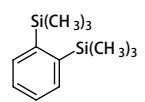
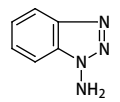
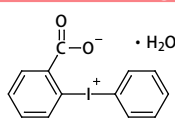
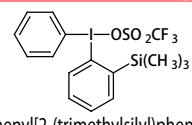
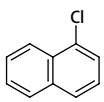
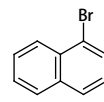
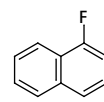
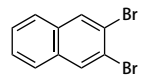
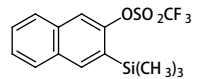
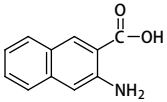
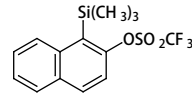


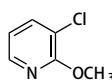
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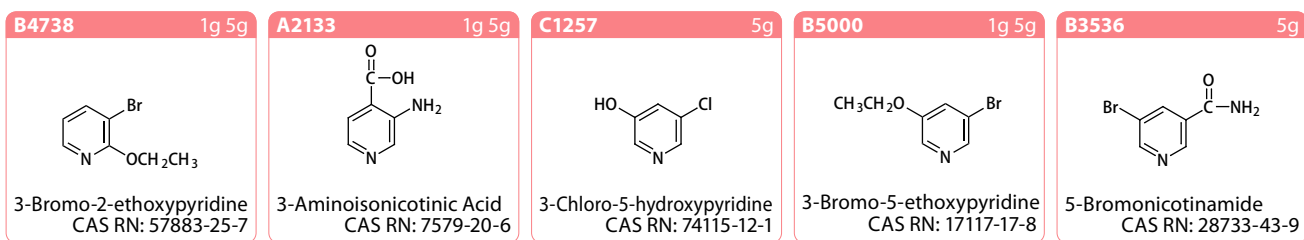
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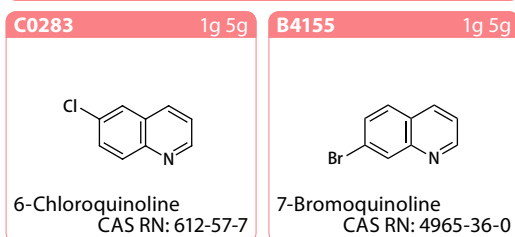
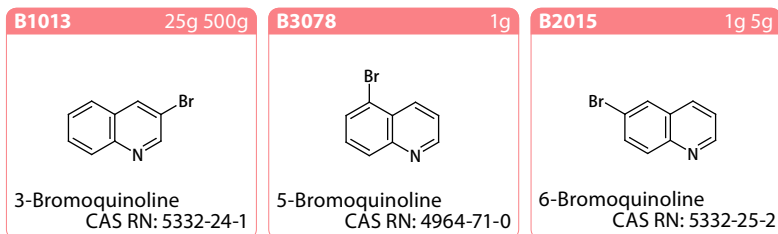
苯炔前体 Benzyne Precursors		卤代苯 Halogenated Benzenes		B0439 25g 500g	F0034 25g 100g 500g
D0170 25g 100g 500g	B0571 25g 100g 500g	D0687 25g 500g	C0305 25g 500g	 Bromobenzene CAS RN: 108-86-1	 Fluorobenzene CAS RN: 462-06-6
 1,4-Dibromobenzene CAS RN: 106-37-6	 1-Bromo-4-chlorobenzene CAS RN: 106-39-8	 1,4-Dichlorobenzene CAS RN: 106-46-7	 4-Chlorobenzotrifluoride CAS RN: 98-56-6	B0884 25g 100g 500g	 4-Bromofluorobenzene CAS RN: 460-00-4
C0659 25g 250g	D1628 5g 25g	F0237 5g 25g	D0608 5g 25g	B1772 5g 25g	 1-Bromo-4-(trifluoromethoxy)benzene CAS RN: 407-14-7
 1-Chloro-4-fluorobenzene CAS RN: 352-33-0	 1,4-Difluorobenzene CAS RN: 540-36-3	 1-Fluoro-4-iodobenzene CAS RN: 352-34-1	 1,4-Diodobenzene CAS RN: 624-38-4	 1-Bromo-3-chlorobenzene CAS RN: 108-37-2	 3-Chloroanisole CAS RN: 2845-89-8
B0570 25g 100g	B0882 25g 100g 250g	B0545 25g 100g 250g	C0648 25g	D1626 25g 100g 500g	F0260 25g
 3-Bromoanisole CAS RN: 2398-37-0	 1-Chloro-3-fluorobenzene CAS RN: 625-98-9	 1,3-Difluorobenzene CAS RN: 372-18-9	 1-Fluoro-3-iodobenzene CAS RN: 1121-86-4	B0659 25g 100g 500g	B0663 25g 250g
 2-Bromofluorobenzene CAS RN: 1072-85-1	 2-Bromoanisole CAS RN: 578-57-4	B2007 5g 25g	C0303 25g 500g	C0973 25g	C0647 10g 25g
 1-Bromo-3-(trifluoromethoxy)benzene CAS RN: 2252-44-0	 2-Chlorobenzotrifluoride CAS RN: 88-16-4	 1,2-Dibromobenzene CAS RN: 583-53-9	 2-Chlorobenzyl Alcohol CAS RN: 17849-38-6	 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- <i>p</i> -xylene CAS RN: 95-72-7
D1909 25g 500g  1-Bromo-2,4-difluorobenzene CAS RN: 348-57-2	D2545 25g  2,4-Difluoro-1-iodobenzene CAS RN: 2265-93-2	C1830 25g  1-Chloro-2,4-difluorobenzene 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-苯 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
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: 866252-52-0	M3222 1g  3-Morpholino-2-(trimethylsilyl)phenyl Triflate CAS RN: 2047348-50-3	B5557 200mg 1g  2-(<i>tert</i> -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-苯 OTf-Benzenes	
I0770 5g  2-Iodophenyl Trifluoromethanesulfonate CAS RN: 129112-26-1	I1102 1g  2-Iodo-1,3-phenylene Bis(trifluoromethanesulfonate) CAS RN: 514826-78-9	OTs-苯 OTs-Benzenes		B4777 1g 5g  2-Bromophenyl Trifluoromethanesulfonate CAS RN: 129112-25-0
A2538 1g 5g  2-Amino- <i>p</i> -toluic Acid CAS RN: 2305-36-4	A2175 5g 25g  4-(Trifluoromethyl)anthranilic Acid CAS RN: 402-13-1	A2319 1g 5g  2-Amino- <i>p</i> -anisic Acid CAS RN: 4294-95-5	F0405 1g 5g 25g  4-Fluoroanthranilic Acid CAS RN: 446-32-2	A0661 25g 500g  4-Chloroanthranilic Acid CAS RN: 89-77-0

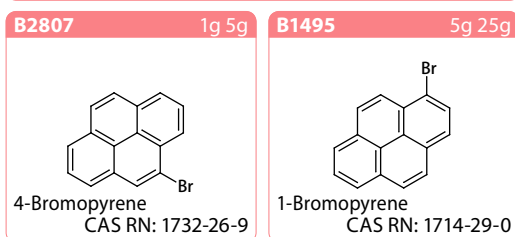
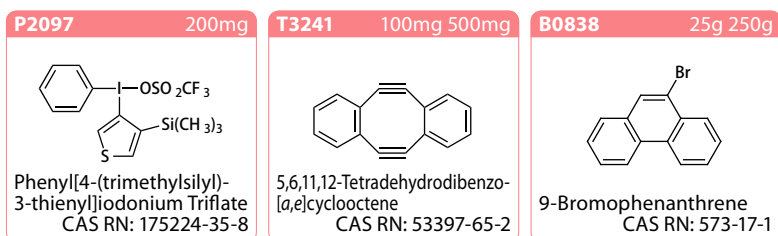
<p>A0786 5g 25g</p>  <p>3-Chloroanthranilic Acid CAS RN: 6388-47-2</p>	<p>A1569 5g 25g</p>  <p>2-Amino-<i>m</i>-toluic Acid CAS RN: 4389-45-1</p>	<p>F0570 1g 5g</p>  <p>3-Fluoroanthranilic Acid CAS RN: 825-22-9</p>	<p>A1378 5g 25g</p>  <p>2-Amino-3-methoxybenzoic Acid CAS RN: 3177-80-8</p>	<p>A1421 5g 25g</p>  <p>6-Amino-<i>m</i>-toluic Acid CAS RN: 2941-78-8</p>
<p>C2048 5g 25g</p>  <p>6-Chloroanthranilic Acid CAS RN: 2148-56-3</p>	<p>A2847 1g 5g</p>  <p>6-Amino-<i>o</i>-anisic Acid CAS RN: 53600-33-2</p>	<p>F0475 1g 5g</p>  <p>6-Fluoroanthranilic Acid CAS RN: 434-76-4</p>	<p>A0996 5g 25g</p>  <p>2-Amino-6-methylbenzoic Acid CAS RN: 4389-50-8</p>	<p>A0665 5g 25g</p>  <p>5-Chloroanthranilic Acid CAS RN: 635-21-2</p>
<p>F0396 1g 5g</p>  <p>5-Fluoroanthranilic Acid CAS RN: 446-08-2</p>	<p>D4120 5g 25g</p>  <p>3,4-Dimethylanthranilic Acid CAS RN: 50419-58-4</p>	<p>A2850 200mg 1g</p>  <p>4,5-Dimethylanthranilic Acid CAS RN: 15089-51-7</p>	<p>D4063 5g 25g</p>  <p>4,5-Difluoroanthranilic Acid CAS RN: 83506-93-8</p>	<p>D2013 10g</p>  <p>4,5-Dimethoxyanthranilic Acid CAS RN: 5653-40-7</p>
<p>A2399 5g 25g</p>  <p>2-Amino-5-chloro-<i>m</i>-toluic Acid CAS RN: 20776-67-4</p>	<p>D2553 1g</p>  <p>3,5-Dimethylanthranilic Acid CAS RN: 14438-32-5</p>	<p>D1475 5g 25g</p>  <p>3,5-Dichloroanthranilic Acid CAS RN: 2789-92-6</p>	<p>A2770 1g 5g</p>  <p>3,4,5-Trimethoxyanthranilic Acid CAS RN: 61948-85-4</p>	<p>其他苯前体 Other Benzyne Precursors</p>
<p>B2299 1g 5g</p>  <p>1,2-Bis(trimethylsilyl)benzene CAS RN: 17151-09-6</p>	<p>A1464 1g 5g</p>  <p>1-Aminobenzotriazole CAS RN: 1614-12-6</p>	<p>D2503 5g 25g</p>  <p>Diphenyliodonium-2-carboxylate Monohydrate CAS RN: 96195-89-0</p>	<p>P1620 1g 5g</p>  <p>Phenyl[2-(trimethylsilyl)phenyl]- iodonium Trifluoromethane- sulfonate CAS RN: 164594-13-2</p>	
<p>萘炔前体 Naphthalene Precursors</p>				
<p>C2310 5g 25g</p>  <p>1-Chloronaphthalene CAS RN: 90-13-1</p>				
<p>B0618 25g 100g 500g</p>  <p>1-Bromonaphthalene CAS RN: 90-11-9</p>				
<p>F0212 5g 25g</p>  <p>1-Fluoronaphthalene CAS RN: 321-38-0</p>				
<p>D4597 200mg 1g</p>  <p>2,3-Dibromonaphthalene CAS RN: 13214-70-5</p>	<p>T2466 1g 5g</p>  <p>3-(Trimethylsilyl)-2-naphthyl Trifluoromethanesulfonate CAS RN: 780820-43-1</p>	<p>A2258 1g 5g</p>  <p>3-Amino-2-naphthoic Acid CAS RN: 5959-52-4</p>	<p>T2465 1g 5g</p>  <p>1-(Trimethylsilyl)-2-naphthyl Trifluoromethanesulfonate CAS RN: 252054-88-9</p>	
<p>吡啶炔前体 Pyridine Precursors</p>				
<p>B0651 25g 100g</p>  <p>3-Bromopyridine CAS RN: 626-55-1</p>				
<p>C0280 25g 100g 500g</p>  <p>3-Chloropyridine CAS RN: 626-60-8</p>				
<p>C2565 1g 5g</p>  <p>3-Chloro-2-methoxypyridine CAS RN: 13472-84-9</p>				



喹啉炔前体 Quinolyne Precursors



其它芳炔前体/ 相关化合物 Other Aryne Precursors / Related Compounds



芳炔生成试剂 Reagents for the Generation of Arynes

