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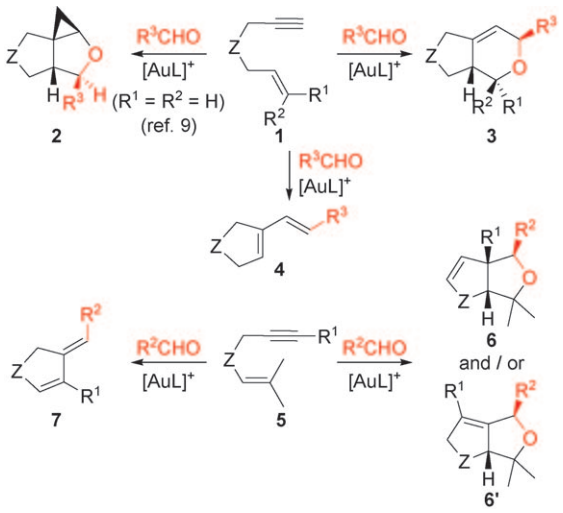
Gold-Catalyzed Reactions of 1,5- and 1,6-Enynes with Carbonyl Compounds: Cycloaddition vs. Metathesis

Ana Escribano-Cuesta,[a] Verónica López-Carrillo,[a] Dominic Janssen,[a] and Antonio M. Echavarren*[a, b]

1,*n*-Enynes ($n=5$–7) undergo skeletal rearrangement in the presence of a variety of electrophilic metals as catalysts,[1] whereas in the presence of hetero- or carbonucleophiles, addition products are formed.[2–7] Carbonyl compounds also act as nucleophiles in intra-[8] and intermolecular reactions of 1,6-enynes.[9] In the latter case, 1,6-enynes **1**, unsubstituted at the terminal alkene ($R^1=R^2=H$), reacted with aldehydes to give tricyclic compounds **2** (Scheme 1).[9] Products **3** of formal [2+2+2] cycloaddition, related to those formed in the intramolecular reaction,[8] were not obtained in this reaction.

In the gold(I)-catalyzed reaction of 1,6-enynes with aldehydes, products **3** of [2+2+2] cycloaddition were indeed formed. However, unexpectedly, 1,3-dienes **4** were the major products in a transformation that corresponds to a formal metathesis between the enyne and the aldehyde. 1,5-Enynes **5** reacted to give cycloadducts **6** and/or **6′** by an initial 5-*endo*-dig cyclization (Scheme 1). For 1,5-enynes with aryl substituents at the alkyne, an unprecedented fragmentation took place to give products of type **7** (Scheme 1).

The reaction between 1,6-enyne **1a** and benzaldehyde in the presence of AuCl (5 mol%) in CH_2Cl_2 gave exclusively the product of skeletal rearrangement,[2a,b] whereas very low conversions ($\leq$7%) were obtained when using $PtCl_2$, $PtCl_4$, $InCl_3$, or $GaCl_3$ as catalysts. Better results were achieved with cationic gold(I) catalysts **8**–**10** (Table 1). Products **3** of



Scheme 1. Different pathways in the gold(I)-catalyzed reactions of 1,5- and 1,6-enynes with aldehydes. $[AuL]^+$ = gold catalyst.

[2+2+2] cycloaddition were isolated from enyne **1a** in 21–85% yield, along with dienes **4a**–**h** (Table 1, entries 1–18). The reaction proceeded readily with electron-rich aldehydes, whereas, in contrast with that shown before for 1,6-enynes **1** without substituents at the alkene,[9] no adduct could be obtained in the reaction of **1a** with *o*-nitrobenzaldehyde (Table 1, entry 17). Interestingly, enynes **1b** and **1c**, with an aryl substituent at the alkene, gave the 1,3-dienes **4** by intermolecular metathesis with the aldehydes (Table 1, entries 19–21). Enynes **1d** and **1e**, which in the absence of nucleophiles reacted by a 6-*endo*-dig pathway,[1a,2] reacted by a 5-*exo*-dig process to give dienes **4i**–**n** (Table 1, entries 22–27).

Reactions were carried out routinely with two equivalents of aldehyde. In the metathesis-like reactions of substrates **1a**, **1d**, and **1e**, acetone was released, but did not efficiently compete with the aldehydes R^3CHO. Therefore, this reaction is applicable to the ready synthesis of C1-substituted 1,3-dienes that would be difficult to prepare by other

[a] A. Escribano-Cuesta, V. López-Carrillo, Dr. D. Janssen, Prof. A. M. Echavarren
Institute of Chemical Research of Catalonia (ICIQ)
Av. Països Catalans 16, 43007 Tarragona (Spain)
Fax: (+34) 977920225
E-mail: aechavarren@iciq.es

[b] Prof. A. M. Echavarren
Departamento de Química Orgánica, Universidad Autónoma de Madrid (UAM)
Cantoblanco, 28049 Madrid (Spain)

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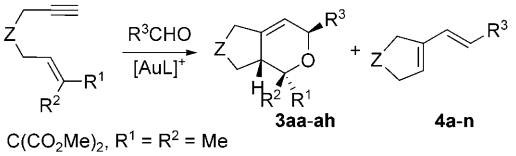
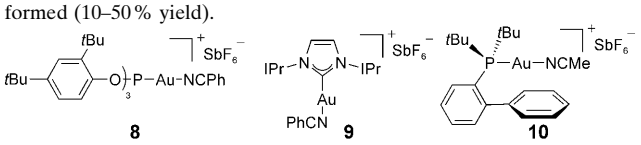
Table 1. Gold-catalyzed reaction of 1,6-enynes with aldehydes.[a]



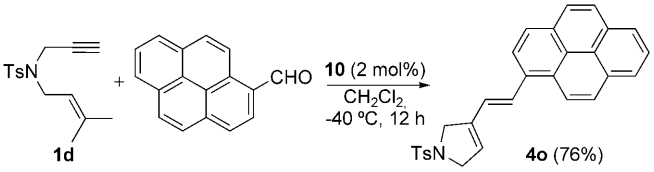
1a Z = $C(CO_2Me)_2$, $R^1 = R^2 = Me$
1b Z = $C(CO_2Me)_2$, R^1 = 3,4-$(MeO)_2C_6H_3$, R^2 = H
1c Z = $C(CO_2Me)_2$, R^1 = 3,4,5-$(MeO)_3C_6H_2$, R^2 = H
1d Z = NTs, $R^1 = R^2 = Me$
1e Z = O, $R^1 = R^2 = Me$

Entry	1	R^3	$[AuL]SbF_6$	3 (Yield [%])	4 (Yield [%])
1	**a**	Ph	**8**	**3aa** (29)[b]	**4a** (61)
2	**a**	Ph	**9**	**3aa** (21)[b]	**4a** (11)[c,d]
3	**a**	Ph	**10**	**3aa** (35)[b]	**4a** (25)[c,d]
4	**a**	4-MeC_6H_4	**8**	**3ab** (22)	**4b** (71)
5	**a**	4-MeC_6H_4	**9**	**3ab** (41)	**4b** (21)[c,d]
6	**a**	2,4-$Me_2C_6H_3$	**8**	**3ac** (41)	**4c** (59)[c]
7	**a**	2,4-$Me_2C_6H_3$	**9**	**3ac** (77)	**4c** (19)
8	**a**	2,4,6-$Me_3C_6H_2$	**8**	**3ad** (53)	**4d** (39)
9	**a**	2,4,6-$Me_3C_6H_2$	**9**	**3ad** (85)	**4d** (9)
10	**a**	4-$MeOC_6H_4$	**8**	**3ae** (30)	**4e** (23)
11	**a**	4-$MeOC_6H_4$	**9**	**3ae** (58)	**4e** (12)
12	**a**	4-$MeOC_6H_4$	**10**	**3ae** (25)	**4e** (27)
13	**a**	3,4-$(MeO)_2C_6H_3$	**8**	**3af** (50)	**4f** (34)[c]
14	**a**	3,4-$(MeO)_2C_6H_3$	**9**	**3af** (63)	**4f** (29)
15	**a**	3,4,5-$(MeO)_3C_6H_2$	**8**	**3ag** (22)	**4g** (76)
16	**a**	3,4,5-$(MeO)_3C_6H_2$	**9**	**3ag** (39)	**4g** (57)
17	**a**	2-$O_2NC_6H_4$	**8**	–	–
18	**a**	*c*-C_3H_5	**8**	**3ah** (24)	**4h** (70)
19	**b**	2,4,6-$Me_3C_6H_2$	**8**	–	**4d** (70)
20	**c**	4-MeC_6H_4	**8**	–	**4b** (41)
21	**c**	2,4,6-$Me_3C_6H_2$	**8**	–	**4d** (81)
22	**d**	Ph	**8**	–	**4i** (65)
23	**d**	4-MeC_6H_4	**8**	–	**4j** (63)
24	**d**	2,4,6-$Me_3C_6H_2$	**10**	–	**4k** (91)
25	**d**	4-BrC_6H_4	**10**	–	**4L** (67)
26	**e**	4-MeC_6H_4	**10**	–	**4m** (34)
27	**e**	2,4,6-$Me_3C_6H_2$	**10**	–	**4n** (60)

[a] Reactions conditions: Aldehyde (2 equivalents) and $[AuL]SbF_6$ (2 mol%) in CH_2Cl_2 at −40°C, 12 h. [b] 9:1–1:1 mixture of **3aa** and its $\Delta^{[4a,5]}$ isomer. [c] Yield determined by ^1H NMR spectroscopy (1,3,5-trimethoxybenzene as standard). [d] Skeletal rearrangement product was also formed (10–50% yield).

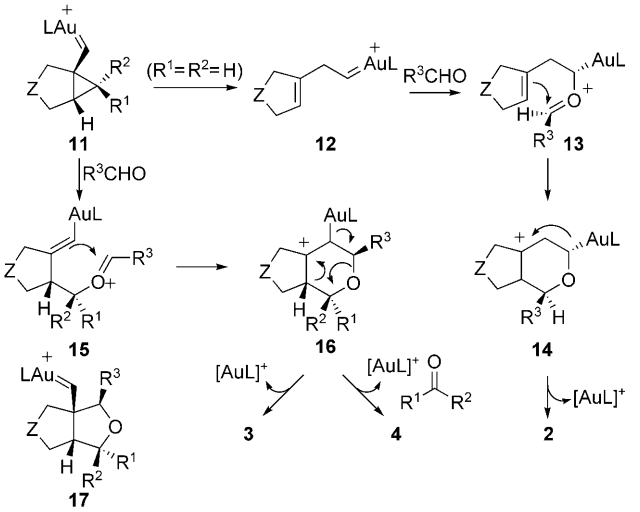


methods. Thus, for example, the reaction of 1,6-enyne **1d** with 1-pyrenecarboxaldehyde in the presence of catalyst **10** (2 mol%) at −40°C gave pyrenyl diene **4o** in 76% yield (Scheme 2).



Scheme 2. Gold-catalyzed reaction of 1,6-enyne **1d** with 1-pyrenecarboxaldehyde.

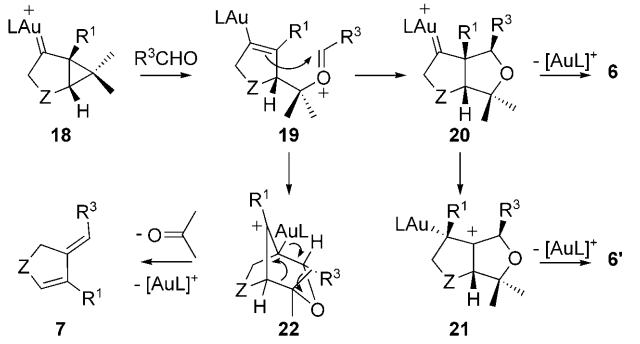
A proposed mechanism for the formation of **2** involved the rearrangement of the cyclopropyl gold carbene **11** to form **12**,[10] which is then trapped by the carbonyl compound to give **13** (Scheme 3).[9] A Prins cyclization would then



Scheme 3. Mechanisms for the intermolecular gold(I)-catalyzed reactions of 1,6-enynes with aldehydes.

form cation **14**, which could evolve by cyclopropane formation to give **2**.[9] In the case of 1,6-enynes substituted at the alkene, direct reaction of the aldehyde with **11** would lead to oxonium cation **15**, which could undergo a Prins cyclization to form tetrahydropyranyl cation **16**.[8,11] Elimination of the metal fragment would then give **3**, whereas a fragmentation reaction would provide **4**. Products derived from intermediate **17**, which would be formed in the intramolecular Prins reaction occurring with the opposite regiochemistry, were not detected.

A similar reaction of 1,5-enynes via gold carbenes **18** would give intermediates **19** (Scheme 4), which undergo a Prins reaction to form **20**. Intermediates **20** would then undergo proton elimination and protodemetalation to give **6** or a 1,2-shift of R^1 to yield **6′** via carbocations **21**. Formation of tetrahydrofurans by the Prins reaction occurs relatively



Scheme 4. Mechanism for the intermolecular gold(I)-catalyzed reactions of 1,5-enynes with aldehydes.

rarely.[12] A Prins reaction of **19** with the alternative regiochemistry would afford **22**,[8,11] which would fragment, releasing acetone, to give rise to dienes **7**.

1,5-Enyne **5a** reacted with aldehydes to give adducts **6aa–ai** as the major products (Table 2, entries 1-13). In some cases, the isomerization products **6′** were obtained in low yield (Table 2, entries 1, 8, and 10). Interestingly, 1,5-enyne **5b** afforded the products of 1,2-alkyl shift, **6′ba**, in 75% yield, along with the expected adduct **6ba** as the minor product (Table 2, entry 15). Reaction of **5a** with ketones also afforded mixtures of the corresponding adducts, **6aj**/**6′aj** and **6ak**/**6′ak** (Table 2, entries 14 and 15).

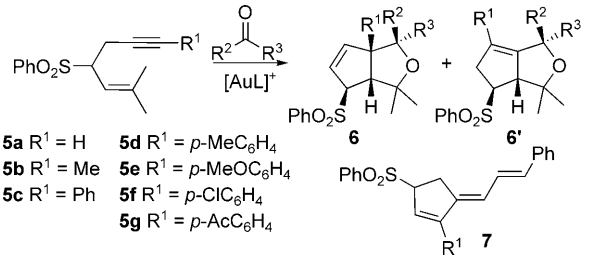
Gold-catalyzed reactions of aryl-substituted 1,5-enynes **5c–g** with carbonyl compounds afforded trienes **7** by a fragmentation process, via intermediate **22** (Scheme 4). The most efficient transformations occurred when *trans*-cinnamaldehyde was used as the carbonyl compound (Table 2, entries 17-23). Compounds **7** were obtained as single *E* stereoisomers, as established by NOESY experiments, which is in accord with a fragmentation occurring via **22** with an equatorial R^3 substituent (Scheme 3).

Enyne **5a** reacted with electron-rich 3,4,5-trimethoxybenzaldehyde in the presence of catalyst **10** to give an unexpected tricyclic product **23** in 47% yield, along with **6ae** (13% yield; Scheme 5). The structure of **23** was confirmed by X-ray diffraction. A plausible mechanism for the formation of **23** involves trapping of the gold carbene in intermediate **24** to give **25** in a Friedel–Crafts process, followed by a proton-promoted cleavage (Scheme 5).

Different types of intramolecular trapping of a gold carbene were found in the reaction of enyne **5h** with aldehydes in the presence of catalyst **10** (Scheme 6). Thus, in the reaction of **5h** with cyclopropanecarbaldehyde, in addition to adduct **6ha** (1.5:1 mixture of epimers, 41% yield), tricyclic compound **26** was isolated in 30% yield. However, reaction of **5h** with mesitaldehyde gave **27** as a single stereoisomer in 43% yield. Tricyclic compounds **26** and **27** were formed by formal insertions of gold carbenes **28a** and **b** into C–H bonds of neighboring groups.[13]

In summary, a clearer picture of the reaction pathways occurring in the gold(I)-catalyzed additions of carbonyl compounds to enynes has emerged from this study, which complements that leading to tricyclic compounds **2**.[9] The reaction of 1,6-enynes with aldehydes gave the expected products of [2+2+2] cycloaddition. However, in most cases, 1,3-dienes **4** were also formed by a metathesis-type reaction of the enyne with the aldehyde. This reaction proceeded by a fragmentation of the tetrahydropyranyl cations formed by an intramolecular Prins reaction. In contrast with the 5-*exo*-dig cyclization of 1,6-enynes, 1,5-enynes reacted with carbonyl compounds to give adducts by an initial 5-*endo*-dig cyclization. Fragmentation of the intermediates also occurred with 1,5-enynes in a few cases. Interestingly, the intermediate cationic gold carbenes can also undergo formal C–H insertion or electrophilic aromatic substitution to form complex carbocyclic skeletons in a stereoselective manner.

Table 2. Gold-catalyzed reaction of 1,5-enynes with carbonyl compounds.[a]



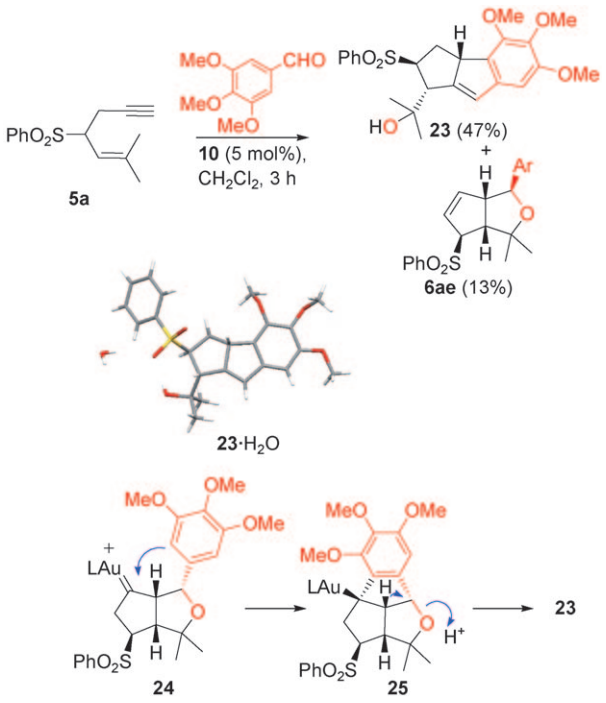
5a R^1 = H **5b** R^1 = Me **5c** R^1 = Ph **5d** R^1 = *p*-MeC_6H_4 **5e** R^1 = *p*-$MeOC_6H_4$ **5f** R^1 = *p*-ClC_6H_4 **5g** R^1 = *p*-AcC_6H_4

Entry	5	R^2, R^3	[AuL]SbF_6	*t* [h]	Product(s) (ratio,[b] yield [%])
1	**a**	2,4-$Me_2C_6H_3$, H	**9**	2.5	**6aa** (7.5:1; 79)+**6′aa** (15)
2	**a**	2,4-$Me_2C_6H_3$, H	**10**	30	**6aa** (7:1; 81)
3	**a**	2,4,6-$Me_3C_6H_2$, H	**8**	4	**6ab** (7:1; 74)
4	**a**	2,4,6-$Me_3C_6H_2$, H	**9**	4	**6ab** (95)
5	**a**	2,4,6-$Me_3C_6H_2$, H	**10**	4	**6ab** (85)
6	**a**	4-BrC_6H_4, H	**9**	2.5	**6ac** (1:1, 78)
7	**a**	3-BrC_6H_4, H	**9**	1	**6ad** (1:1, 62)
8	**a**	2-BrC_6H_4, H	**9**	1	**6ae** (1:1; 59)+**6′ae** (9)
9	**a**	3,4,5-$(MeO)_3C_6H_2$, H	**10**	7	**6af** (2.7:1, 66)
10	**a**	2-Naph, H	**9**	2.5	**6ag** (2.5:1; 51)+**6′ag** (7)
11	**a**	(*E*)-CH=CHPh, H	**9**	0.5	**6ah** (1.5:1, 72)
12	**a**	(*E*)-CH=CHPh, H	**10**	7	**6ah** (2:1, 59)
13	**a**	CH=CMe_2, H	**9**	0.5	**6ai** (3:1, 58)
14[c]	**a**	CD_3, CD_3	**9**	32	**6aj**+**6′aj** (1:1, 55)
15[d]	**a**	$(CH_2)_5$	**9**	20	**6ak**+**6′ak** (1:2, 67)[e]
16	**b**	(*E*)-CH=CHPh, H	**9**	2.5	**6ba** (2:1)+**6′ba** (1:4.7; 75)
17	**c**	(*E*)-CH=CHPh, H	**8**	1	**7c** (75)
18	**c**	(*E*)-CH=CHPh, H	**9**	1	**7c** (50)
19	**c**	(*E*)-CH=CHPh, H	**10**	2	**7c** (75)
20	**d**	(*E*)-CH=CHPh, H	**9**	1	**7d** (80)
21	**e**	(*E*)-CH=CHPh, H	**8**	1	**7e** (79)
22	**f**	(*E*)-CH=CHPh, H	**9**	2	**7f** (67)
23	**g**	(*E*)-CH=CHPh, H	**9**	1	**7g** (78)

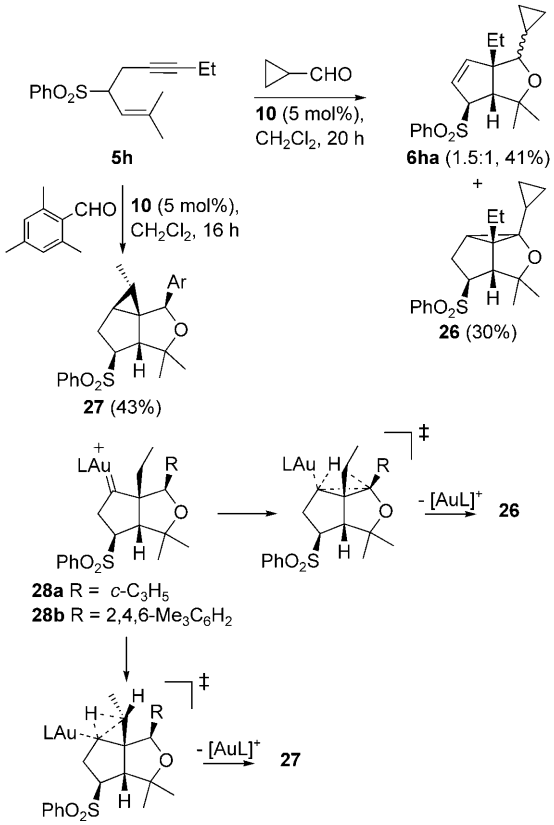
[a] Reaction conditions, unless otherwise stated: Catalysts (5 mol%) with aldehyde (2 equivalents) in CH_2Cl_2 at 23°C. [c] Ratios for **6aa–ba** refer to epimers at C1. [d] Reaction with [D_6]acetone (4 equivalents). [e] Reaction with cyclohexanone (4 equivalents) and catalyst **9** (3 mol%). [f] Cycloisomerization products were also obtained (27%). Naph = naphthyl.

Experimental Section

General procedure for the reaction of 1,6-enynes with aldehydes (Table 1): A solution of 1,6-enyne (80 mg) and the corresponding aldehyde (2 equivalents) in CH_2Cl_2 (ca. 0.1 M) was cooled to −40°C and after 15 min the gold



Scheme 5. Gold-catalyzed reaction of 1,5-enyne **5a** with 3,4,5-trimethoxybenzaldehyde to give tricyclic compound **23**.



Scheme 6. Formal C–H activation reactions in the gold-catalyzed reactions of 1,5-enynes with aldehydes.

complex **8**, **9**, or **10** (2 mol%) was added The solution was kept at −40 °C for 12 h. A 0.1 M solution of Et_3N in hexane (1 mL) was added to deactivate the gold catalyst and the solution was filtered through Celite. After evaporation of the solvent, the residue was purified by flash chromatography on silica gel (hexane/EtOAc eluent).

General procedure for the reaction of 1,5-enynes with carbonyl compounds (Table 2): The starting 1,5-enyne was dried before the reaction by repeated evaporation of a solution of the compound in toluene (1 mL/10 mg of 1,5-enyne) under vacuum. A solution of the 1,5-enyne (30 mg) and the corresponding aldehyde (1.5–2 equivalents) or ketone (4 equivalents) in CH_2Cl_2 (1 mL) was slowly added at room temperature to a solution of the gold complex **9** or **10** in CH_2Cl_2 (0.5 mL). The reaction mixture was stirred for the time stated in Table 2 (monitored by thin-layer chromatography). Work-up was carried out as described above.

See the Supporting Information for details and spectroscopic data on the compounds.

Acknowledgements

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Keywords: aldehydes · cycloaddition · enynes · gold · homogeneous catalysis

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