

可见光催化的硅烷二氟烯丙基化反应

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摘要 研究了在蓝光照射下,以奎宁环作为氢原子转移试剂,实现了硅烷与 α -三氟甲基烯烃的无金属二氟烯丙基化反应,并且通过使用多种芳香族和杂环 α -三氟甲基烯烃,均能成功得到二氟烯丙基硅烷。本研究为制备二氟烯丙基硅烷提供了一种高效且经济的克级合成方法。

关键词 α -(三氟甲基)苯乙烯;硅烷;光催化;二氟烯丙基硅烷;奎宁环

Difluoroallylation of Silanes under Photoirradiation

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Abstract The synthesis of organosilicon compounds has attracted considerable interest, especially the allyl silanes, which are regarded as ideal building blocks in the synthesis of small molecules and polymers. The traditional synthetic method for allyl silanes relies on the cross-coupling of Grignard reagent and chlorosilane (Silyl-Kumada reaction), transition metal catalyzed silylation of allylic alcohols with disilanes or silylboranes, and regioselective silylation of conjugated alkenes or alkenes. Although some other methods were also developed, the using of transition metal catalysts has resulted in disadvantages such as contamination of desired allyl silanes and high production costs. Therefore, a mild and metal-free practical method is highly desired. We herein describe a metal-free difluoroallylation of silanes with α -trifluoromethyl alkenes in the presence of quinuclidine as hydrogen atom transfer (HAT) reagent under the irradiation of 30 W blue light-emitting diode (LED) (460~470 nm) at room temperature. To an oven dried Schlenk-tube, trifluoromethylpropene (0.1 mmol), silane (0.3 mmol), KHCO_3 (0.1 mmol), 4-CzIPN (1,2,3,5-tetrakis(carbazol-9-yl)-4,6-dicyanobenzene) (0.002 mmol) and MeCN (1 mL) were added under argon atmosphere. The reaction mixture was stirred under the irradiation of 30 W blue LED (460~470 nm) at room temperature. After completion of the reaction, the reaction solution was removed by reduced pressure and the residue was purified by silica gel chromatographic column to obtain gem-difluoroallylation products. A wide range of aromatic and heterocyclic α -trifluoromethyl alkenes were successfully applied in the difluoroallylation of silanes to afford difluoroallylsilanes. And all of the tested silanes, including trimethylsilane, sterically more demanding silanes as well as dimethylphenylsilane all participated in the present transformation readily to afford the corresponding difluoroallylsilanes in excellent yields. The present methodology has provided an efficient and cost-effective gram scale synthetic method for the preparation of difluoroallylsilanes under blue light irradiation in the presence of 4-CzIPN as organic photosensitizer. The scalability in large scale and excellent functional group compatibility of this transformation ensures broad applicability to a variety of difluoroallylsilanes. The proposed reaction mechanism showed that the reaction proceeded through the radical addition of α -trifluoromethyl alkene with silane free radical and subsequent β -fluoride elimination.

Keywords α -(trifluoromethyl)styrenes; silane; photocatalysis; difluoroallylsilane; quinuclidine

1 引言

硅和碳是同一主族的连续元素,因此硅可以替代大量有机化合物中的碳原子,从而形成有机硅化合物,并

表现出不同的化学、物理和生物性能。由于通过基因组学、平行化学和高通量生物学成功实现的药物研究和开发的例子较少,所以药物开发行业一直需要通过寻找新的“类似药物”的候选药物来降低风险和成本。用硅原

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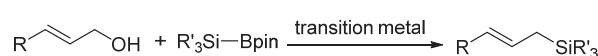
子取代现有药物中的碳原子以寻找新的“类似药物”的候选药物,已成为药物化学研究中一种具有吸引力的策略。例如, Sieburth 团队^[1]制备了硅烷二醇并证明它们可以穿过细胞膜并展示出抗病毒作用。据报道,含硅多肽模拟物是金属蛋白酶血管紧张素转换酶的有效抑制剂^[2]。吡啶美辛的硅衍生物被发现比原来的吡啶美辛表现出更强的抗癌活性^[3]。非天然含硅氨基酸已被证明具有增强的亲脂性、增加的抵抗力和细胞对蛋白水解降解的摄取^[4]。硅取代的氟哌啶醇是多巴胺拮抗剂氟哌啶醇的硅类似物,对 hD₂ 受体的亲和力比氟哌啶醇高五倍^[5]。另一方面,由于其稳定性、溶解性、无毒性以及与有机金属试剂相比易于处理的优点,在适当的碱活化下,有机硅化合物经常作为多功能烯丙基阴离子等价物而广泛应用于多种合成转化中^[6]。

有机硅化合物的合成引起了研究者们相当大的兴趣。特别是烯丙基硅烷,它们被认为是小分子和聚合物合成中的理想砌块^[7]。传统的烯丙基硅烷合成方法有格氏试剂与氯化硅烷的交叉偶联反应(Silyl-Kumada 反应)^[8],过渡金属催化烯丙基醇与二硅烷或硅基硼烷的硅烷化反应^[9],共轭烯烃或烯丙烷的选择性硅烷化反应等^[10]。尽管还发展了一些其他二氟烯丙基硅烷的合成方法^[11],但过渡金属催化剂的使用给这些转化造成了较大局限,比如制备烯丙基硅烷时造成的环境污染和较高的生产成本等。因此,发展一种温和且无金属的实用方法很有必要,在本文的撰写的过程中,光催化烯丙基化曾被报道^[12]。近年来,光催化偶联反应发展迅速^[13],我们组一直对光催化反应感兴趣^[14],本文我们期望报道一种无金属二氟硅烷化反应,该反应在温和的条件下有效地合成了二氟烯丙基硅烷化合物(图 1)。

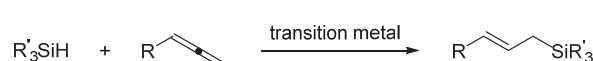
(a) Cross-coupling of Grignard reagent and chloride silane (Silyl-Kumada reaction)



(b) Silylation of allylic alcohols by transition metal catalysis



(c) Silylation of conjugated alkenes or allenes



(d) This work

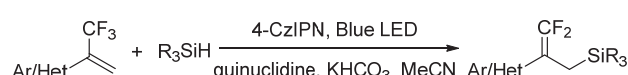


图 1 烯丙基硅烷制备的最新进展

Figure 1 Recent advances of allyl silanes preparations

2 结果与讨论

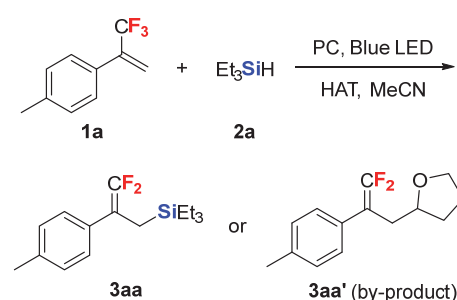
2.1 反应条件优化

研究首先尝试了在 LED (Light-Emitting Diode)照射下,以奎宁环作为 HAT (Hydrogen Atom Transfer)试剂,

使用 α -三氟甲基烯烃 **1a** 与三乙基硅烷 **2a** 进行反应^[15]。对市售光催化剂的初步调查表明, 4-CzIPN 是一种合适的催化剂,并得到了 **3aa'**作为与四氢呋喃(THF)的自由基交叉偶联产物(表 1, Entries 1~8)。令人高兴的是,虽然其他反应溶剂不适宜,但使用乙腈作为溶剂时,以 85%的分离收率得到了预期的二氟烯丙基硅烷产物 **3aa** (表 1, Entries 9~13)。使用其他一些有机碱代替奎宁环反应没有发生(表 1, Entries 14~16)。当添加化学计量的 KHCO₃ (0.1 mmol)能促进当前反应,并以 95%分离收率获得了 **3aa** (表 1, Entry 17)。最后,对照实验确定了所有反应条件的必要性,其中包括 4-CzIPN, 奎宁环和 LED 照射(表 1, Entries 18~20)。

表 1 反应条件优化^a

Table 1 Reaction condition optimizations^a



Entry	Photocatalyst	Additive	Solvent	Yield ^b /%
1	<i>fac</i> -Ir(ppy) ₃	quinuclidine	THF	NR
2	Eosin-Y	quinuclidine	THF	NR
3	DDQ	quinuclidine	THF	NR
4	Riboflavin	quinuclidine	THF	NR
5	Acridine	quinuclidine	THF	NR
6	Orange	quinuclidine	THF	NR
7	Ru(bpy) ₃ Cl ₂	quinuclidine	THF	NR
8	Methyl Orange	quinuclidine	THF	NR
9	4-CzIPN	quinuclidine	THF	80
10	4-CzIPN	quinuclidine	MeCN	(3aa')
11	4-CzIPN	quinuclidine	Toluene	85
12	4-CzIPN	quinuclidine	DMF	ND
13	4-CzIPN	quinuclidine	DCE	23
14	4-CzIPN	quinuclidine	1,4-dioxane	Trace
15	4-CzIPN	DABCO	MeCN	21
16	4-CzIPN	Pyridine	MeCN	NR
17	4-CzIPN	DIPEA	MeCN	NR
18 ^c	4-CzIPN	quinuclidine	MeCN	95
19 ^c	—	quinuclidine	MeCN	NR
20 ^{c,d}	4-CzIPN	—	MeCN	NR

^a Reaction conditions: **1a** (0.1 mmol), **2a** (0.3 mmol), additive (0.02 mmol), and photocatalyst (0.002 mmol) in solvent (1 mL) was allowed to stirred for a certain time under blue LED irradiation. ^b Isolated yields. ^c 0.1 mmol of KHCO₃ was added. ^d Performed in the dark; NR: No reaction; ND: No detected; DMF: *N,N*-dimethylformamide; DCE: dichloroethane; DABCO: triethylenediamine; DIPEA: *N,N*-diisopropylethylamine.

2.2 反应底物普适性的考察

在最优反应条件下,我们研究了各种 α -三氟甲基烯烃作为硅烷二氟烯丙基化反应的底物,制备二氟烯丙基

硅烷衍生物(图 2). 苯环上含有甲基取代的 α -三氟甲基烯烃均能顺利反应并以较高收率得到预期的二氟烯丙基硅烷 **3aa**~**3da**. 含有供电子基团如乙基、异丙基、叔丁基、甲氧基和苄氧基的底物, 也以良好的收率得到了预期产物 **3ea**~**3ja**. 氟和氯取代基团在本反应耐受性较好, 反应产率没有受到显著影响(**3ka**~**3oa**), 但溴和碘取代的底物因大量脱卤而不能得到预期产物. 反应性较活泼的腈基和酯基在转化中耐受性良好(**3pa**~**3qa**). 本反应中, 含有杂环和其它芳香环的 α -三氟甲基烯烃也是合适的底物, 均能转化为预期的二氟烯丙基硅烷(**3ra**~**3va**). 但是, 当使用苄基取代的 α -三氟甲基烯烃, 未观察到目标产物 **3wa**, 提示烷基取代的 α -三氟甲基烯烃不适用于当前反应体系.

接下来, 我们考察了一系列硅烷在最优反应条件下与 α -三氟甲基烯烃 **1a** (图 3) 的反应. 总的来说, 所有被测试的硅烷, 包括三甲基硅烷(**2b**)、空间位阻更大的硅烷(**2c**~**2f**)和二甲基苯基硅烷(**2g**), 都很容易参与到当前的转化中, 并以优良的收率生成了相应的二氟烯丙基

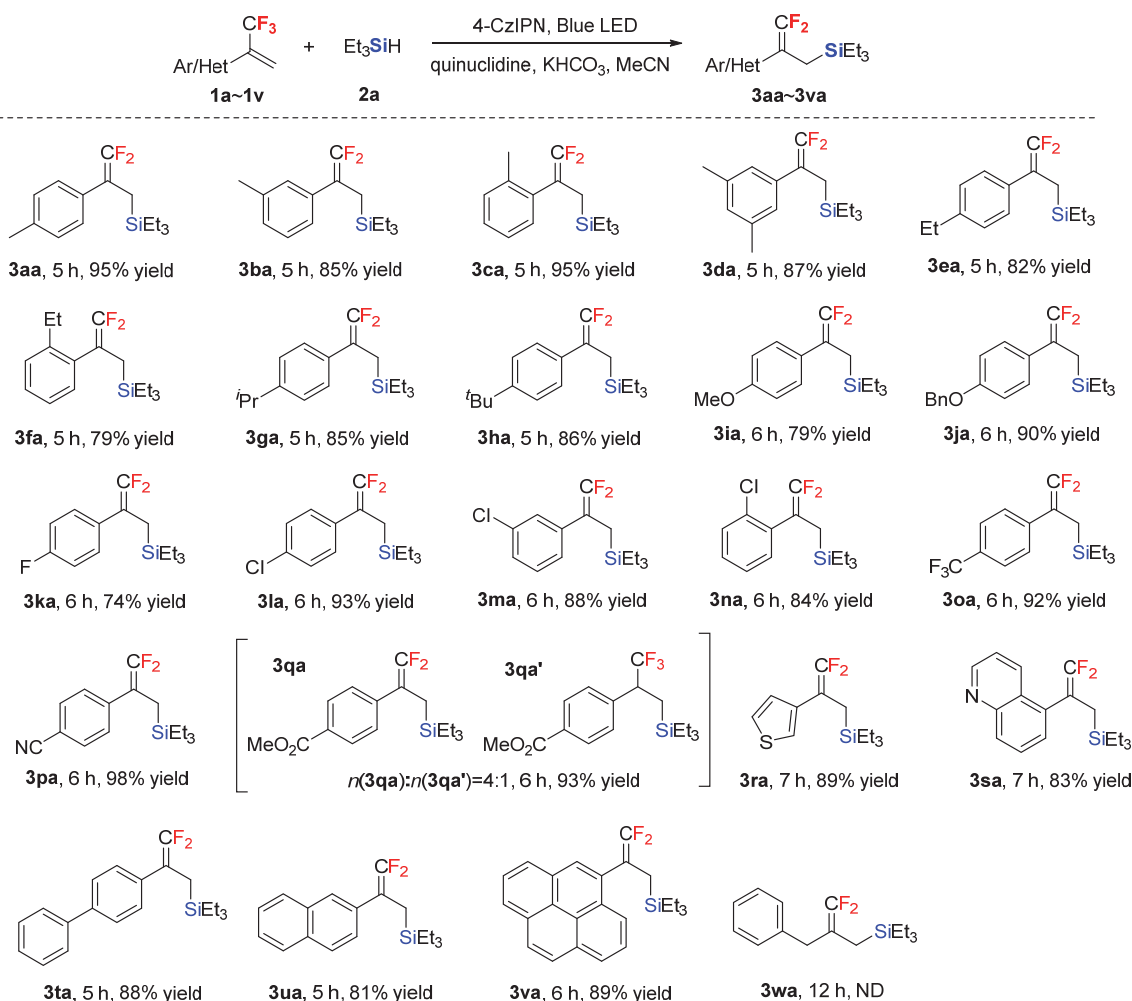
硅烷.

2.3 克级反应

为了探索该二氟烯丙基化反应的实用性和操作简便性, 我们进行了两个更大规模的代表性实例(图 4). 其中, 三乙基硅烷和三甲基硅烷均以优异的收率转化为二氟烯丙基硅烷产品.

2.4 反应机理的推测

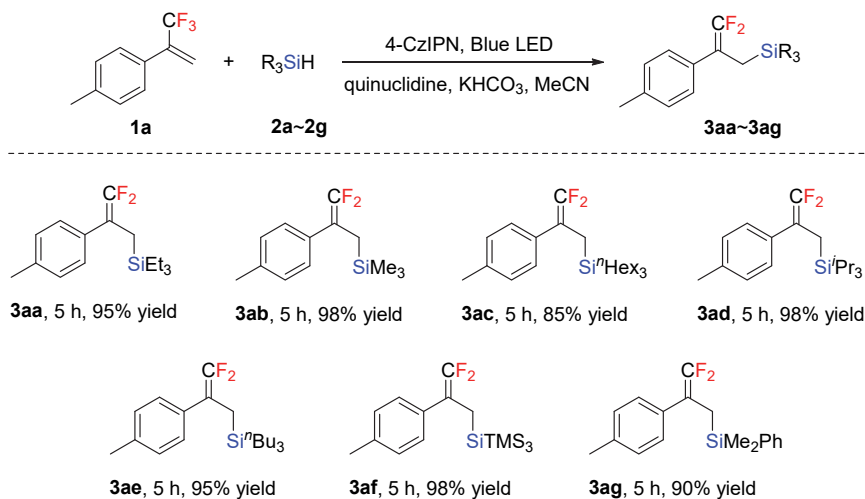
根据荧光发射光谱的结果(见支持信息)和相关文献, 图 5 中提出了反应机理. 最初, 光催化剂(PC)在 LED 蓝光的照射下被激发得到激发态物种 PC^* . 然后, 被激发的 PC^* 被奎宁环 **A** 淬灭, 形成相应的自由基阳离子 **B** 和 $PC^{\cdot-}$. 接下来, 硅烷中与 **B** 发生氢原子转移(HAT), 得到硅烷基自由基 **D** 和质子化的奎宁环阳离子 **C**, 然后质子离去得到奎宁环 **A**. 随后, α -三氟甲基烯烃 **1a** 接受活性硅烷基自由基 **D**, 得到自由基中间体 **E**, 经 $PC^{\cdot-}$ 还原得到阴离子中间体 **F**. 最后, 中间体 **F** 通过 β -氟化物消除得到 **3aa** 的偕二氟烯丙基硅烷化合物.



^a Reaction conditions: **1a** (0.1 mmol), **2a** (0.3 mmol), quinuclidine (0.02 mmol), KHCO_3 (0.1 mmol), and 4-CzIPN (0.002 mmol) in MeCN (1 mL) was allowed to stirred for the time indicated under blue LED irradiation; ^b Isolated yields.

图 2 α -三氟甲基烯烃的底物拓展

Figure 2 Substrate scope for α -trifluoromethyl alkenes



^a Reaction conditions: **1a** (0.1 mmol), **2a** (0.3 mmol), quinuclidine (0.02 mmol), KHCO₃ (0.1 mmol), and 4-CzIPN (0.002 mmol) in MeCN (1 mL) was allowed to stirred for the time indicated under blue LED irradiation; ^b Isolated yields.

图3 硅烷的底物拓展

Figure 3 Substrate scope for silanes

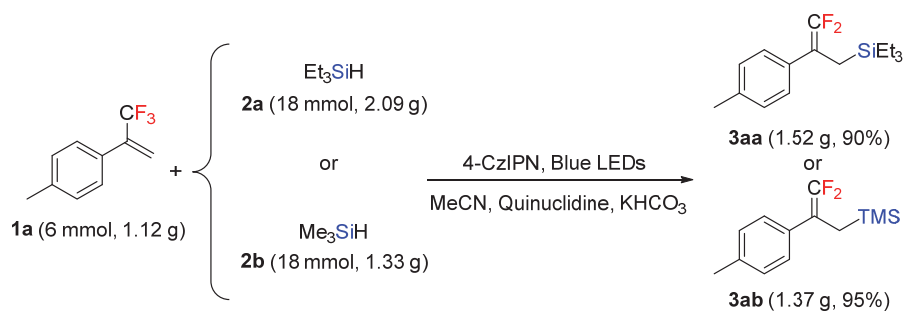


图4 二氟烯丙基硅烷的克级反应

Figure 4 Gram scale synthesis of difluoroallylsilanes

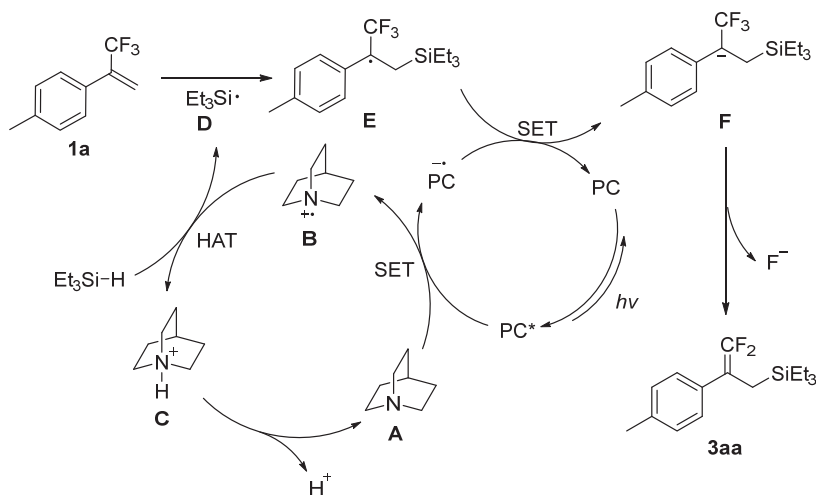


图5 硅烷二氟烯丙基化机理的推测

Figure 5 Proposed mechanism for the difluoroallylation of silanes

3 结论

综上所述, 以 4-CzIPN 作为有机光敏剂, 成功地实现了硅烷与 α -三氟甲基烯烃的二氟烯丙基化反应. 这种

转化优异的反应具有较强的官能团相容性以及在该级反应中的优秀表现, 证明了其用于制备多种二氟烯丙基硅烷的适用性. 反应机理表明, 反应是通过硅烷基自由基与 α -三氟甲基烯烃发生加成, 随后进行 β -氟消除而完

成。

4 实验部分

4.1 蓝光促进 α -三氟甲基烯烃的二氟烯丙基化反应的实验步骤

在氩气保护下, 向 25 mL 干燥的 Schlenk 管中依次加入 KHCO_3 (0.1 mmol)、4-CzIPN (0.002 mmol)、MeCN (1 mL)、 α -三氟甲基烯烃 **1a**~**1v** (0.1 mmol) 和硅烷 **2a** (0.3 mmol)。在 30 W 蓝色 LED (460~470 nm) 的照射下, 使反应液在室温下搅拌。反应结束后, 减压浓缩除去溶剂, 得粗产物。粗产物使用石油醚溶液进行柱层析分离纯化, 减压浓缩, 得到二氟烯丙基化产物 **3aa**~**3va**。

References

- [1] Chen, C.-A.; Sieburth, S. M.; Glekas, A.; Hewitt, G. W.; Trainor, G. L.; Erickson-Viitanen, S.; Garber, S. S.; Cordova, B.; Jeffry, S.; Klabe, R. M. *Chem. Biol.* **2001**, *8*, 1161.
- [2] Mutahi, M. W.; Nittoli, T.; Guo, L.-X.; Sieburth, S. M. *J. Am. Chem. Soc.* **2002**, *124*, 7363.
- [3] Gately, S.; West, R. *Drug Dev. Res.* **2007**, *68*, 156.
- [4] Franz, A. K.; Wilson, S. O. *J. Med. Chem.* **2013**, *56*, 388.
- [5] Tacke, R.; Popp, F.; Müller, B.; Theis, B.; Burschka, C.; Hamacher, A.; Kassack, M. U.; Schepmann, D.; Wünsch, B.; Jurva, U.; Wellner, E. *ChemMedChem* **2008**, *3*, 152.
- [6] For reviews and recent examples, see: (a) Wang, D.; Chen, D.-H. *Acta Chim. Sinica* **1990**, *48*, 516 (in Chinese). (王东, 陈德恒, 化学学报, **1990**, *48*, 516). (b) Fleming, I.; Barbero, A.; Walter, D. *Chem. Rev.* **1997**, *97*, 2063. (c) Hiyama, T. *J. Organomet. Chem.* **2002**, *653*, 58. (d) Chabaud, L.; James, P.; Landais, Y. *Eur. J. Org. Chem.* **2004**, *15*, 3173. (e) Komiyama, T.; Minami, Y.; Hiyama, T. *ACS Catal.* **2017**, *7*, 631.
- [7] For reviews and recent examples, see: (a) Tseng, C.-L.; Zhuo, R.-X.; Liu, J.-W. *Acta Chim. Sinica* **1964**, *30*, 360 (in Chinese). (曾昭抡, 卓仁禧, 刘基万, 化学学报, **1964**, *30*, 360). (b) Chan, T. H.; Wang, D. *Chem. Rev.* **1995**, *95*, 1279. (c) Langkopf, E.; Schinzer, D. *Chem. Rev.* **1995**, *95*, 1375. (d) Barbero, A.; Pulido, F. J. *Acc. Chem. Res.* **2004**, *37*, 817. (e) Nielsen, L.; Skrydstrup, T. *J. Am. Chem. Soc.* **2008**, *130*, 13145. (f) Hu, Y.-Q.; Huang, D.-F.; Wang, K.-H.; Zhao, Z.-X.; Zhao, F.-X.; Xu, W.-G.; Hu, Y.-L. *Chin. J. Org. Chem.* **2020**, *40*, 1689 (in Chinese). (虎永琴, 黄丹凤, 王克虎, 赵转霞, 赵芳霞, 徐炜刚, 胡雨来, 有机化学, **2020**, *40*, 1689).
- [8] For recent examples, see: (a) Murakami, K.; Yorimitsu, H.; Oshima, K. *J. Org. Chem.* **2009**, *74*, 1415. (b) Selander, N.; Paasch, J. R.; Szabó, K. J. *J. Am. Chem. Soc.* **2011**, *133*, 409. (c) Vulovic, B.; Cinderella, A. P.; Watson, D. A. *ACS Catal.* **2017**, *7*, 8113. (d) Larsson, J. M.; Szabó, K. J. *J. Am. Chem. Soc.* **2013**, *135*, 443. (e) Gan, Y.; Xu, W.; Liu, Y.-H. *Org. Lett.* **2019**, *21*, 9652. (f) Yang, B.; Wang, Z.-X. *Org. Lett.* **2019**, *21*, 7965.
- [9] For recent examples, see: (a) Selander, N.; Paasch, J. R.; Szabó, K. J. *J. Am. Chem. Soc.* **2011**, *133*, 409. (b) Larsson, J. M.; Szabó, K. J. *J. Am. Chem. Soc.* **2013**, *135*, 443. (c) Yang, B.; Wang, Z.-X. *Org. Lett.* **2019**, *21*, 7965. (d) Gan, Y.; Xu, W.; Liu, Y.-H. *Org. Lett.* **2019**, *21*, 9652.
- [10] For recent examples, see: (a) Ohmura, T.; Taniguchi, H.; Sugimoto, M. *J. Am. Chem. Soc.* **2006**, *128*, 13682. (b) Miller, Z. D.; Li, W.; Belderrain, T. R.; Montgomery, J. *J. Am. Chem. Soc.* **2013**, *135*, 15282. (c) Miller, Z. D.; Dorel, R.; Montgomery, J. *Angew. Chem. Int. Ed.* **2015**, *54*, 9088. (d) Yeung, K.; Ruscoe, R. E.; Rae, J.; Pulis, A. P.; Procter, D. J. *Angew. Chem. Int. Ed.* **2016**, *55*, 11912. (e) Da, B.-C.; Liang, Q.-J.; Luo, Y.-C.; Ahmad, T.; Xu, Y.-H.; Loh, T.-P. *ACS Catal.* **2018**, *8*, 6239. (f) Da, B.-C.; Liang, Q.-J.; Luo, Y.-C.; Ahmad, T.; Xu, Y.-H.; Loh, T.-P. *ACS Catal.* **2018**, *8*, 6239. (g) Sang, H.-L.; Yu, S.-J.; Ge, S.-Z. *Chem. Sci.* **2018**, *9*, 973. (h) Zeng, J.-H.; Chen, J.-J.; Chen, L.; Zhan, Z.-P. *Org. Chem. Front.* **2020**, *7*, 1132. (i) Xu, J.-L.; Xu, Z.-Y.; Wang, Z.-L.; Ma, W.-W.; Sun, X.-Y.; Fu, Y.; Xu, Y.-H. *J. Am. Chem. Soc.* **2022**, *144*, 5535.
- [11] (a) Takeda, M.; Shintani, R.; Hayashi, T. *J. Org. Chem.* **2013**, *78*, 5007. (b) Xiao, Y.-L.; Pan, Q.; Zhang, X.-G. *Acta Chim. Sinica* **2015**, *73*, 383 (in Chinese). (肖玉兰, 潘强, 张新刚, 化学学报, **2015**, *73*, 383). (c) Mata, S.; López, L. A.; Vicente, R. *Angew. Chem. Int. Ed.* **2017**, *56*, 7930. (d) Hofstra, J. L.; Cherney, A. H.; Ordner, C. M.; Reisman, S. E. *J. Am. Chem. Soc.* **2018**, *140*, 139. (e) Zhao, S.; Li, C.-P.; Xu, B.; Liu, H. *Chin. J. Org. Chem.* **2020**, *40*, 1549 (in Chinese). (赵森, 李淳朴, 许斌, 柳红, 有机化学, **2020**, *40*, 1549).
- [12] (a) Yue, F.-Y.; Liu, J.-H.; Ma, H.-N.; Liu, Y.-X.; Dong, J.-Y.; Wang, Q.-M. *Org. Lett.* **2022**, *24*, 4019. (b) Luo, C.; Zhou, Y.; Chen, H.; Wang, T.; Zhang, Z.-B.; Han, P.; Jing, L.-H. *Org. Lett.* **2022**, *24*, 4286. (c) Xu, W.-G.; Xia, C.-J.; Shao, Q.; Zhang, Q.; Liu, M.-R.; Zhang, H.-W.; Wu, M.-B. *Org. Chem. Front.* **2022**, *9*, 4949.
- [13] (a) Zhou, Q.-Q.; Düsel, S. J. S.; Lu, L.-Q.; König, B.; Xiao, W.-J. *Chem. Commun.* **2019**, *55*, 107. (b) Yu, X.-Y.; Chen, J.-R.; Xiao, W.-J. *Chem. Rev.* **2021**, *121*, 506.
- [14] (a) Li, K.-K.; Zhang, X.-X.; Chen, J.-C.; Gao, Y.; Yang, C.-H.; Zhang, K.-Y.; Zhou, Y.-Y.; Fan, B.-M. *Org. Lett.* **2019**, *21*, 9914. (b) Zhang, X.-X.; Chen, J.-C.; Gao, Y.; Li, K.-K.; Zhou, Y.-Y.; Sun, W.-Q.; Fan, B.-M. *Org. Chem. Front.* **2019**, *6*, 2410. (c) Li, K.-K.; Chen, J.-C.; Yang, C.-H.; Zhang, K.-Y.; Pan, C.-X.; Fan, B.-M. *Org. Lett.* **2020**, *22*, 4261. (d) Lv, H.-P.; Laishram, R. D.; Chen, J.-C.; Khan, R.; Zhu, Y.-B.; Wu, S.-Y.; Zhang, J.-Q.; Liu, X.-Y.; Fan, B.-M. *Chem. Commun.* **2021**, *57*, 3660.
- [15] (a) Zhang, X.-H.; MacMillan, D. W. C. *J. Am. Chem. Soc.* **2017**, *139*, 11353. (b) Le, C.; Liang, Y.-F.; Evans, R. W.; Li, X.-M.; MacMillan, D. W. C. *Nature* **2017**, *547*, 79. (c) Hou, J.; Ee, A.; Cao, H.; Ong, H.-W.; Xu, J.-H.; Wu, J. *Angew. Chem. Int. Ed.* **2018**, *57*, 17220. (d) Lei, G.-Y.; Xu, M.-C.; Chang, R.; Funes-Ardoiz, I.; Ye, J.-T. *J. Am. Chem. Soc.* **2021**, *143*, 11251.

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