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Iridium-Catalyzed Intermolecular Azide–Alkyne Cycloaddition of Internal Thioalkynes under Mild Conditions**

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Abstract: *An iridium-catalyzed azide–alkyne cycloaddition reaction (IrAAC) of electron-rich internal alkynes is described. It is the first efficient intermolecular AAC of internal thioalkynes. The reaction exhibits remarkable features, such as high efficiency and regioselectivity, mild reaction conditions, easy operation, and excellent compatibility with air and a broad spectrum of organic and aqueous solvents. It complements the well-known CuAAC and RuAAC click reactions.*

Huisgen 1,3-dipolar azide–alkyne cycloaddition (AAC) is the most straightforward and atom-economical synthesis of 1,2,3-triazoles.[1] However, the traditional thermal conditions typically require high temperatures and proceed with limited regioselectivity. In 2002, the groups of Sharpless and Meldal independently reported their pioneering studies on copper-catalyzed AAC, thus providing a mild and efficient synthesis of 1,4-disubstituted 1,2,3-triazoles.[2] Owing to its excellent fidelity and compatibility in a broad context, CuAAC has evolved into a powerful tool with wide applications in organic synthesis, molecular biology, and materials science.[3–6]

In contrast to the widely successful use of terminal alkynes (including metal acetylides) in catalyzed AACs,[3] the corresponding reactions of internal alkynes for the synthesis of fully substituted 1,2,3-triazoles remain a challenge[7] owing to the increased energy barrier and difficulty in regiocontrol, particularly for intermolecular reactions. As a result, most intermolecular AACs of internal alkynes require high temperatures[8] and/or activated substrates, such as electron-deficient alkynes (e.g., haloalkynes)[9,10] or strained alkynes (e.g., cyclooctynes).[11] Mild and regioselective AACs of electron-rich internal alkynes are scarce. While the advent of ruthenium-based catalytic systems (RuAAC) has addressed the challenge to some extent,[12] additional robust catalytic systems complementary to CuAAC and RuAAC remain in high demand. In a continuation of our studies of electron-rich alkynes,[13] we report herein the first iridium-catalyzed AACs of electron-rich internal alkynes. Specifically, a mild intermolecular AAC of internal thioalkynes has been realized for the first time.[14]

Fully substituted 1,2,3-triazoles decorated with a 5-sulfur substituent represent a family of useful molecules. For example, triazoles **I** are potential herbicides with antifungal activity,[15a] and triazole **II** can serve as an excellent chiral ligand in organic synthesis (Figure 1).[15b] However, despite

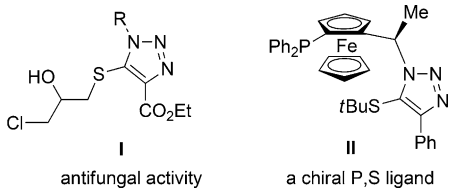

Figure 1. Selected useful 1,2,3-triazoles with a 5-sulfur substituent.

the utility of this core structure, the current strategies for its synthesis are indirect and require multiple steps.[15,16] To date, no mild and direct synthesis by intermolecular AAC between thioalkynes and azides is known.

We started our investigation with thioalkyne **1a** and benzyl azide (**2a**) by using dichloromethane as the solvent. In contrast to the established CuAACs of terminal alkynes, internal alkyne **1a** did not undergo the expected [3+2] cycloaddition in the presence of either CuI or $CuSO_4$ (Table 1, entries 1 and 2). The previous catalysts of choice in RuAAC, $[Cp^*Ru(PPh_3)_2Cl]$ and $[Cp^*Ru(cod)Cl]$,[12] catalyzed the desired reaction with excellent conversion but with mediocre regioselectivity (Table 1, entries 3 and 4). Cationic ruthenium complexes were not effective (Table 1, entries 5 and 6). Further extensive screening of a wide range of metal complexes led us to identify $[\{Ir(cod)Cl\}_2]$ as a superb catalyst for the desired transformation, furnishing adduct **3a** not only in essentially quantitative yield but also with absolute regioselectivity (Table 1, entry 7). Other iridium and rhodium complexes gave inferior results (Table 1, entries 8–16). The reaction catalyzed by $[\{Ir(cod)Cl\}_2]$ works equally well in various polar and nonpolar solvents, including THF, MeCN, $MeNO_2$, toluene, DMF, iPr_2O, and EtOH (Table 1, entry 18). The mild reaction conditions (room temperature) combined with the observed compatibility with a broad spectrum of solvents may lead to the widespread application of this process.

With the standard conditions established, we evaluated the generality of our IrAAC reaction. A wide range of thioalkynes with aryl and alkyl substituents on both termini can participate in the cycloaddition to give the fully substituted 5-thio-1,2,3-triazoles in good to excellent yields

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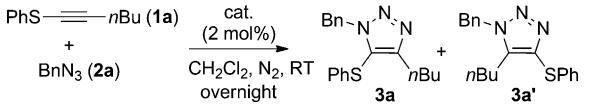
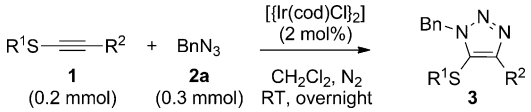
Table 1: Optimization of the reaction conditions.[a]

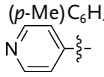


Entry	Cat.	Yield (**3a** + **3a′**) [%][b]	**3a**/**3a′**[c]
1	CuI	0	–
2	$CuSO_4$	< 5	–
3	$[Cp^*Ru(PPh_3)_2Cl]$	90	4.4:1
4	[Cp*Ru(cod)Cl]	> 95	4.5:1
5	$[Cp^*Ru(MeCN)_3]PF_6$	0	–
6	$[CpRu(MeCN)_3]PF_6$	0	–
7	$[\{Ir(cod)Cl\}_2]$	> 95	1:0
8	[(cod)Ir(acac)]	10	1:0
9	$[(CO)_2Ir(acac)]$	< 5	–
10	[(cod)Ir(Me-Cp)]	0	–
11	[(cod)Ir(η^5-indenyl)]	< 5	–
12	[(cod)Ir(acac-F_6)]	30	1:0
13	$[(cod)Ir]BF_4$	75	1:0
14	$[\{(coe)_2IrCl\}_2]$	< 5	–
15	$[\{Cp^*RhCl_2\}_2]$	0	–
16	$[\{Rh(cod)Cl\}_2]$	0	–
17	$[\{(CO)_2RhCl\}_2]$	< 10	–
18	$[\{Ir(cod)Cl\}_2]$ (other solvents)[d]	> 95	1:0

[a] **1a** (0.10 mmol), **2a** (0.15 mmol), cat. (2 mol%), CH_2Cl_2 (1 mL), under N_2 at RT overnight. [b] Yield determined by GC with *n*-decane as the internal standard. For all entries, recovered starting material accounts for the mass balance. [c] Determined by NMR analysis of the crude mixture. [d] Other solvents evaluated (including THF, MeCN, $MeNO_2$, toluene, DMF, iPr_2O, EtOH) all give almost quantitative yield. Cp* = pentamethylcyclopentadiene, cod = cycloocta-1,5-diene, coe = cyclooctene, acac = acetylacetonate, DMF = dimethylformamide.

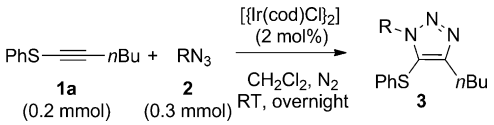
Table 2: Alkyne scope: thioalkynes.

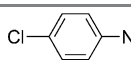
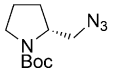
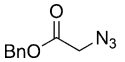
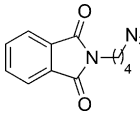
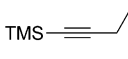


Entry	R^1	R^2	**3**	Yield [%][a]
1	Ph	*n*Bu	**3a**	72
2	Ph	*n*Oct	**3b**	91
3	Ph	cyclopropyl	**3c**	92
4	Ph	C_2H_4OTBS	**3d**	77
5	Ph	C_2H_4OTHP	**3e**	85
6	Ph	C_2H_4OMs	**3f**	82
7	Ph	C_2H_4OAc	**3g**	94
8	Ph	C_2H_4OH	**3h**	60
9	Ph	Ph	**3i**	98
10	(*p*-Me)C_6H_4	*n*Bu	**3j**	99
11	(*p*-OMe)C_6H_4	*n*Bu	**3k**	94
12	(*p*-Cl)C_6H_4	*n*Bu	**3l**	96
13	(*p*-NO_2)C_6H_4	*n*Bu	**3m**	54[b]
14	(*p*-Me)C_6H_4	*t*Bu	**3n**	91
15		*n*Bu	**3o**	61[b]
16	Me	*n*Bu	**3p**	97
17	*n*Bu	*n*Bu	**3q**	82
18	*n*Bu	cyclopropyl	**3r**	86
19	*n*Bu	C_2H_4OTBS	**3s**	86
20	*n*Bu	C_2H_4OTHP	**3t**	89
21	*n*Bu	Ph	**3u**	84
22	*n*Bu	TMS	**3v**	61
23	Bn	*n*Bu	**3w**	89
24	(3-furyl)CH_2	*n*Bu	**3x**	41
25	*i*Pr	*n*Bu	**3y**	93
26	(*p*-OMe)C_6H_4	H	**3z**	22[c]

[a] Yield of isolated product. [b] Incomplete conversion. [c] Approximately 35% conversion by GC analysis. TBS = *tert*-butyldimethylsilyl, THP = tetrahydropyranyl, Ms = methanesulfonyl.

Table 3: Azide scope.



Entry	RN_3	**3**	Yield [%][a]
1	 (**2b**)	**3aa**	87
2	 (**2c**)	**3ab**	89
3	 (**2d**)	**3ac**	86
4	 (**2e**)	**3ad**	92
5	 (**2f**)	**3ae**	56

[a] Yield of isolated product. Boc = *tert*-butoxycarbonyl, TMS = trimethylsilyl.

(Table 2). Increased steric hindrance on the alkyne does not affect the reaction efficiency (**3n** and **3y**). The reaction is also efficient with various alkyl and aryl azides (Table 3). The product structure, in particular with regard to regiochemistry, was confirmed by 2D NMR spectroscopy and X-ray crystallography (see the Supporting Information). The mild reaction conditions mean that the reaction tolerates a diverse set of functional groups, such as silyl- and THP-protected alcohols, ethers, aryl halides, esters, Boc- and phthalimide-protected amines, esters, mesylates, and even free alcohols. Although all the reactions were run overnight (about 10 h) for simplicity, a time-dependence study shows that the reaction of **1a** and **2a** can reach full conversion within one hour. Terminal thioalkyne **1z** gave 1,5-disubstituted triazole **3z**, but with low conversion (Table 2, entry 26).

We also examined other internal alkynes with different electronic properties (Table 4). Most of these electron-rich and normal alkynes show low reactivity, although promising results were observed for aryloxy alkyne **6b** and selenyl alkyne **6c** (low yield but excellent regioselectivity). By contrast, electron-deficient alkynes **6h** and **6i** can participate in the [3+2] cycloaddition with moderate to good efficiency (Table 4, entries 8 and 9). Of note is the opposite regioselectivity of the reaction of sulfonyl alkyne **6h** to form 4-sulfonyl triazole **7h**.[17]

We were interested in knowing the sensitivity of the IrAAC toward moisture and air. To our delight, the reaction of **1a** and **2a** (Table 1, entry 7) exhibited excellent efficiency (> 95% yield as determined by GC) when it was run in an

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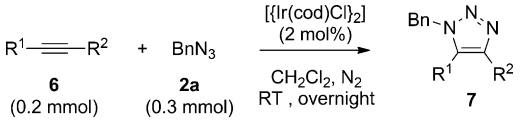
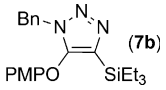
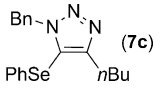
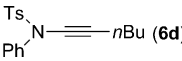
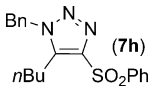
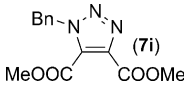
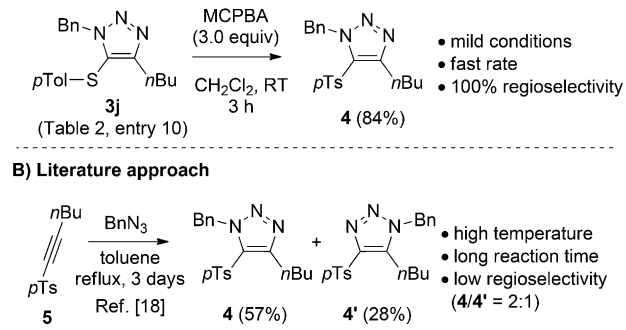
Table 4: Alkyne scope: other alkynes.

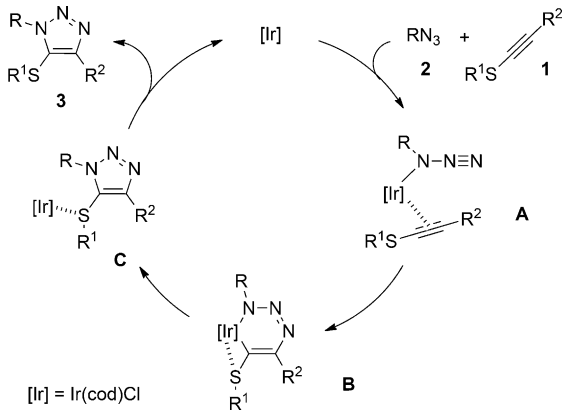


Entry	6	7	Yield [%][a]
1	PMPO—≡—*n*Bu (**6a**)	–	<5[b]
2	PMPO—≡—$SiEt_3$ (**6b**)	 (**7b**)	42
3	PhSe—≡—*n*Bu (**6c**)	 (**7c**)	19[c]
4	 (**6d**)	–	<5[b]
5	Me—≡—Ph (**6e**)	–	<5[b]
6	Ph—≡—Ph (**6f**)	–	<5[b]
7	Et—≡—Et (**6g**)	–	–[c]
8	*n*Bu—≡—SO_2Ph (**6h**)	 (**7h**)	77[e]
9	MeO_2C—≡—CO_2Me (**6i**)	 (**7i**)	56

[a] Yield of isolated product. [b] < 5% conversion as determined by GC analysis. [c] Low conversion, recovered starting alkyne accounts for the mass balance. [d] No desired product, but a complicated reaction mixture was observed. [e] Only one regioisomer. Ts = toluene-4-sulfonyl, PMP = *para*-methoxyphenyl..

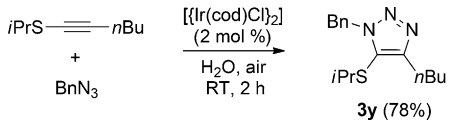


Scheme 1. Synthesis of 5-sulfonyl triazoles.



Scheme 2. Proposed mechanism.

open flask with water additive (10 equiv). Moreover, we carried out a randomly selected reaction (Table 2, entry 25) in water. Notably, although not all the starting materials were fully dissolved, the reaction went smoothly to completion within 2 h without significant loss of efficiency [Eq. (1)]. These results suggest that our IrAAC process is operationally robust.



(1)

To further demonstrate the utility of our process, we have performed derivatization of a triazole product to synthesize 5-sulfonyl triazoles. As shown in Scheme 1 A, triazole **3j** could be easily oxidized with *m*-chloroperbenzoic acid (MCPBA) at room temperature to give 5-sulfonyltriazole **4** as a single isomer in good yield. By contrast, the literature synthesis of this compound starting from alkynyl sulfone **5** requires high temperature and a long reaction time but gives low regioselectivity (Scheme 1 B).[18] These results (combined with those in Table 4, entry 8) clearly demonstrate the exceptional advantages of our approach, which enables the synthesis of both 4- and 5-sulfonyltriazoles efficiently and exclusively.

Scheme 2 depicts a proposed reaction mechanism for the IrAAC of thioalkynes. We propose that the catalytic cycle begins with the complexation of Ir by both substrates to give **A**, in which the azide coordinates through the internal nitrogen atom.[19] Next, oxidative cyclization results in irido heterocycle **B**. The sulfur atom may coordinate to the iridium center to provide additional stabilization.[20] Subsequent reductive elimination of **B** leads to the formation of triazole **3** via **C**. It is unclear whether the coordination of sulfur contributes to the observed regioselectivity. Detailed mechanistic study is required to substantiate the proposed catalytic cycle.[21]

In summary, the first iridium-catalyzed azide–alkyne cycloaddition reaction (IrAAC) of electron-rich internal alkynes is presented. This reaction also represents the first efficient intermolecular AAC of internal thioalkynes. With the proper choice of an iridium catalyst, various internal thioalkynes and azides can participate in this efficient cyclization to furnish a wide range of fully substituted triazoles under mild reaction conditions with complete regioselectivity, thereby complementing the well-known copper- and ruthenium-based catalytic AAC systems. The combination of many remarkable features, such as high efficiency and regioselectivity, mild reaction conditions, and easy operation, as well as excellent compatibility with air and a broad spectrum of organic and aqueous solvents, paves the

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way for subsequent applications in various contexts. Further detailed investigations on IrAAC are underway.

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Keywords: click chemistry · cycloaddition · heterocycles · iridium · triazoles

[1] R. Huisgen in *1,3-Dipolar Cycloaddition Chemistry* (Ed.: A. Padwa), Wiley, New York, **1984**.

[2] a) C. W. Tornøe, C. Christensen, M. Meldal, *J. Org. Chem.* **2002**, *67*, 3057 – 3064; b) V. V. Rostovtsev, L. G. Green, V. V. Fokin, K. B. Sharpless, *Angew. Chem.* **2002**, *114*, 2708 – 2711; *Angew. Chem. Int. Ed.* **2002**, *41*, 2596 – 2599.

[3] Reviews: a) P. Wu, V. V. Fokin, *Aldrichimica Acta* **2007**, *40*, 7 – 17; b) M. Meldal, C. W. Tormøe, *Chem. Rev.* **2008**, *108*, 2952 – 3015; c) J. E. Moses, A. D. Moorhouse, *Chem. Soc. Rev.* **2007**, *36*, 1249 – 1262; d) J. E. Hein, V. V. Fokin, *Chem. Soc. Rev.* **2010**, *39*, 1302 – 1315; e) L. Liang, D. Astruc, *Coord. Chem. Rev.* **2011**, *255*, 2933 – 2945; f) K. C. Majumdar, K. Ray, *Synthesis* **2011**, 3767 – 3783.

[4] Recent examples of using triazoles as useful building blocks or ligands in organic synthesis: a) S. Chuprakov, S. W. Kwok, V. V. Fokin, *J. Am. Chem. Soc.* **2013**, *135*, 4652 – 4655; b) J. E. Spangler, H. M. L. Davies, *J. Am. Chem. Soc.* **2013**, *135*, 6802 – 6805; c) M. Zibinsky, V. V. Fokin, *Angew. Chem.* **2013**, *125*, 1547 – 1550; *Angew. Chem. Int. Ed.* **2013**, *52*, 1507 – 1510; d) K. F. Donnelly, A. Petronilho, M. Albrecht, *Chem. Commun.* **2013**, *49*, 1145 – 1159; e) T. C. Johnson, W. G. Totty, M. Wills, *Org. Lett.* **2012**, *14*, 5230 – 5233; For reviews, see: f) A. V. Gulevich, A. S. Dudnik, N. Chernyak, V. Gevorgyan, *Chem. Rev.* **2013**, *113*, 3084 – 3213; g) B. Chattopadhyay, V. Gevorgyan, *Angew. Chem.* **2012**, *124*, 886 – 896; *Angew. Chem. Int. Ed.* **2012**, *51*, 862 – 872.

[5] Selected reviews on applications in chemical biology: a) P. Thirumurugan, D. Matosiuk, K. Jozwiak, *Chem. Rev.* **2013**, *113*, 4905 – 4979; b) J. C. Jewett, C. R. Bertozzi, *Chem. Soc. Rev.* **2010**, *39*, 1272 – 1279; c) M. F. Debets, S. S. van Berkel, J. Dommerholt, A. J. Dirks, F. P. J. T. Rutjes, F. L. van Delft, *Acc. Chem. Res.* **2011**, *44*, 805 – 815; d) S. G. Agalave, S. R. Maujan, V. S. Pore, *Chem. Asian J.* **2011**, *6*, 2696 – 2718; e) S. K. Mamidyala, M. G. Finn, *Chem. Soc. Rev.* **2010**, *39*, 1252 – 1261.

[6] Selected reviews on applications in materials science: a) P. L. Golas, K. Matyjaszewski, *Chem. Soc. Rev.* **2010**, *39*, 1338 – 1354; b) A. Qin, J. W. Y. Lam, B. Z. Tang, *Chem. Soc. Rev.* **2010**, *39*, 2522 – 2544.

[7] C. Spiteri, J. E. Moses, *Angew. Chem.* **2010**, *122*, 33 – 36; *Angew. Chem. Int. Ed.* **2010**, *49*, 31 – 33.

[8] a) S. Díez-González, A. Correa, L. Cavallo, S. P. Nolan, *Chem. Eur. J.* **2006**, *12*, 7558 – 7564; b) L. Zhang, X. Chen, P. Xue, H. H. Y. Sun, I. D. Williams, K. B. Sharpless, V. V. Fokin, G. Jia, *J. Am. Chem. Soc.* **2005**, *127*, 15998 – 15999; c) M. M. Majireck, S. M. Weinreb, *J. Org. Chem.* **2006**, *71*, 8680 – 8683; d) J. R. Johansson, P. Lincoln, B. Nordén, N. Kann, *J. Org. Chem.* **2011**, *76*, 2355 – 2359; e) M. Lamberti, G. C. Fortman, A. Poater, J. Broggi, A. M. Z. Slawin, L. Cavallo, S. P. Nolan, *Organometallics* **2012**, *31*, 756 – 767; f) S. Oppilliart, G. Mousseau, L. Zhang, G. Jia, P. Thuery, B. Rousseau, J.-C. Cintrat, *Tetrahedron* **2007**, *63*, 8094 – 8098; g) S. Kamijo, T. Jin, Z. Hou, Y. Yamamoto, *Tetrahedron Lett.* **2002**, *43*, 9707 – 9710.

[9] Examples of haloalkynes: a) B. H. M. Kuijpers, G. C. T. Dijkmans, S. Groothuys, P. J. L. M. Quaedflieg, R. H. Blaauw, F. L. van Delft, F. P. J. T. Rutjes, *Synlett* **2005**, 3059 – 3062; b) J. E. Hein, J. C. Tripp, L. B. Krasnova, K. B. Sharpless, V. V. Fokin, *Angew. Chem.* **2009**, *121*, 8162 – 8165; *Angew. Chem. Int. Ed.* **2009**, *48*, 8018 – 8021; c) W. S. Brotherton, R. J. Clark, L. Zhu, *J. Org. Chem.* **2012**, *77*, 6443 – 6455; d) During the preparation of our manuscript, an Ir-catalyzed AAC of bromoalkynes was reported (with mostly moderate efficiency): E. Rasolofonjatovo, S. Theeramunkong, A. Bouriaud, S. Kolodych, M. Chaumontet, F. Taran, *Org. Lett.* **2013**, *15*, 4698 – 4701.

[10] Other internal electron-deficient alkyne substrates or intermediates (sometimes still requiring high temperature): a) propiolamidinium salts: W. Weingärtner, G. Maas, *Eur. J. Org. Chem.* **2012**, 6372 – 6382; b) propiolates: E. Merling, V. Lamm, S. J. Geib, E. Lacôte, D. P. Curran, *Org. Lett.* **2012**, *14*, 2690 – 2693; c) propargylic cation intermediates: H. Zhang, H. Tanimoto, T. Morimoto, Y. Nishiyama, K. Kakiuchi, *Org. Lett.* **2013**, *15*, 5222 – 5225; d) α,β-acetylenic aldehydes: M. Journet, D. Cai, J. J. Kowal, R. D. Larsen, *Tetrahedron Lett.* **2001**, *42*, 9117 – 9118.

[11] Strained alkynes include cyclooctynes and benzynes. Recent examples: a) N. P. Grimster, B. Stump, J. R. Fotsing, T. Weide, T. T. Talley, J. G. Yamauchi, Á. Nemecz, C. Kim, K.-Y. Ho, K. B. Sharpless, P. Taylor, V. V. Fokin, *J. Am. Chem. Soc.* **2012**, *134*, 6732 – 6740; b) G. G. Gordon, J. L. Mackey, J. C. Jewett, E. M. Sletten, K. N. Houk, C. R. Bertozzi, *J. Am. Chem. Soc.* **2012**, *134*, 9199 – 9208; c) T. Ikawa, A. Takagi, M. Goto, Y. Aoyama, Y. Ishikawa, Y. Itoh, S. Fujii, H. Tokiwa, S. Akai, *J. Org. Chem.* **2013**, *78*, 2965 – 2983.

[12] To our knowledge, there is only one report that deals with the reaction of internal electron-rich alkynes under mild conditions: B. C. Boren, S. Narayan, L. K. Rasmussen, L. Zhang, H. Zhao, Z. Lin, G. Jia, V. V. Fokin, *J. Am. Chem. Soc.* **2008**, *130*, 8923 – 8930.

[13] a) W. Zhao, Z. Wang, J. Sun, *Angew. Chem.* **2012**, *124*, 6313 – 6317; *Angew. Chem. Int. Ed.* **2012**, *51*, 6209 – 6213; b) W. Zhao, Z. Li, J. Sun, *J. Am. Chem. Soc.* **2013**, *135*, 4680 – 4683.

[14] Uncatalyzed AACs of internal thioalkynes under thermal conditions: a) L. Garanti, A. Locatelli, G. Zecchi, *J. Heterocycl. Chem.* **1976**, *13*, 657 – 659; b) A. Haas, H.-U. Krächter, *Chem. Ber.* **1988**, *121*, 1833 – 1840.

[15] a) Y. Morzherin, P. E. Prokhorova, D. A. Musikhin, T. V. Glukhareva, Z. Fan, *Pure Appl. Chem.* **2011**, *83*, 715 – 722; b) I. Oura, K. Shimizu, K. Ogata, S.-i. Fukuzawa, *Org. Lett.* **2010**, *12*, 1752 – 1755.

[16] Representative examples: a) N. N. Volkova, E. V. Tarasov, L. V. Meervelt, S. Toppet, W. Dehaen, V. A. Bakulev, *J. Chem. Soc. Perkin Trans. 1* **2002**, 1574 – 2580; b) J. Becher, P. H. Olesen, K. Brøndum, *Heterocycles* **1986**, *24*, 2299 – 2302; c) B. T. Worrell, J. E. Hein, V. V. Fokin, *Angew. Chem.* **2012**, *124*, 11961 – 11964; *Angew. Chem. Int. Ed.* **2012**, *51*, 11791 – 11794.

[17] Without a catalyst, no reaction was observed for **6h**. However, $InCl_3$ (20 mol%) can also promote the desired reaction to selectively afford **7h**, although the conversion is slower than that with the iridium catalyst. It is thus possible that the iridium catalyst serves as a Lewis acid in the reactions of **6h** and **6i**.

[18] D. Gao, H. Zhai, M. Parvez, T. G. Back, *J. Org. Chem.* **2008**, *73*, 8057 – 8068.

[19] An iridium – azide complex in which the azide coordinates through the internal nitrogen is known: G. Albertin, S. Antoniutti, D. Baldan, J. Castro, S. García-Fontán, *Inorg. Chem.* **2008**, *47*, 742 – 748.

[20] For a similar three-membered-ring iridium – sulfur interaction, see: A. F. Dalebrook, L. J. Wright, *Organometallics* **2009**, *28*, 5536 – 5540.

[21] a) P. N. Liu, J. Li, F. H. Su, K. D. Ju, Z. Zhang, C. Shi, H. H. Y. Sung, I. D. Williams, V. V. Fokin, Z. Lin, G. Jia, *Organometallics* **2012**, *31*, 4904 – 4915; b) B. T. Worrell, J. A. Malik, V. V. Fokin, *Science* **2013**, *340*, 457 – 460.

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