doi.org/10.1002/adsc.202100852

Advanced Synthesis & Catalysis

Visible-Light-Mediated Nitrogen-Centered Radical Strategy: Preparation of 3-Acylated Spiro[4,5]trienones

Pu Chen,[+a] Jun Xie,[+a] Zan Chen,[a] Bi-Quan Xiong,[a] Yu Liu,[a,*] Chang-An Yang,[a] and Ke-Wen Tang[a]

[a] Department of Chemistry and Chemical Engineering, Hunan Institute of Science and Technology, Yueyang, Hunan 414006, People's Republic of China
]
E-mail: liuyu@hnist.edu.cn

[+] These authors contributed equally to this work

Manuscript received: July 8, 2021; Revised manuscript received: July 21, 2021;
Version of record online: ■■, ■■

Supporting information for this article is available on the WWW under https://doi.org/10.1002/adsc.202100852

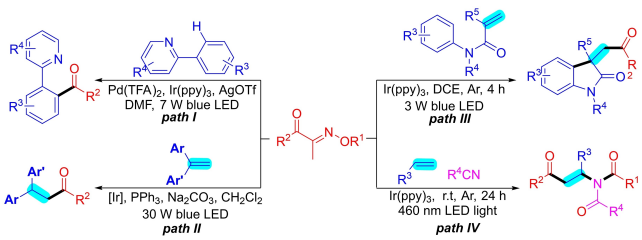
Abstract: A nitrogen-centered radical strategy for the preparation of 3-acylated spiro[4,5]trienones *via* visible-light-mediated acylation/*ipso*-cyclization of alkynes with acyl oxime esters is reported. The alkyl- and aryl-substituted acyl radicals, which generate from the cleavage of carbon-carbon *σ*-bonds in acyl oxime esters *via* nitrogen-centered radical pathway, attack the carbon-carbon triple bonds in propiolamides and then undergo *ipso*-cyclization. This method provides a way for the construction of 3-acyl-substituted spiro[4,5] trienones, which can introduce aryl- or alkyl-substituted acyl into spiro[4,5]trienone skeletons.

Keywords: nitrogen-centered radical; visible-light-mediated; acyl oxime esters; acylation/*ipso*-cyclization; spiro[4,5]trienones

Nitrogen-centered radicals (NCRs), which have the same highly reactive as that of the classical carbon-based radicals, are a common species in organic synthesis.[1] Due to the *N*-substitution and hybridization patterns, NCRs are usually used as nucleophiles or electrophiles to go through various radical reactions.[2–3] Thus, NCR strategies have wide applications in the synthetic chemistry due to their high reactivity and efficiency.[4–5] Compared with CCR (carbon-centered radical) strategies,[6] NCR strategies can be achieved by avoiding usage of strong oxidants and high temperatures.[7–8]

In recent years, NCR strategies have been widely used for the cleavage of carbon-carbon single bonds.[4–5,7–10] For example, Xiao[4] and other chemists[5,7–8] have developed a series of ring-opening of cycloketone oxime derivatives *via* NCR strategies. As shown in Scheme 1, Chen (path I),[11a] Wu (path II),[11b] Yang (path III),[11c] and Wu's groups (path IV)[11d] have developed NCR mediated cleavage of carbon-carbon single bonds in acyl oxime derivatives. In these methods, acyl oxime esters were used as acyl precursors to reat with carbon-carbon double bonds. However, the strategy employing carbon-carbon triple bonds to carpture the acyl radicals, which generate from acyl oxime esters, is lacking.

Spirocyclic compounds, such as spiro[4,5] decatrienones, are important motifs usually encountered in pharmaceutical molecules and natural products.[12] Among them, spiroquinones are common skeletons that can be applied for the construction of diverse important structures.[13–14] Thus, many organic chemists have paied their attention in the development of convenient and efficient strategies for the preparation of spiroquinones,[15–18] especially spiro[4,5] decatrienones.[15c–g,16] The electrophilic *ipso*-cyclization strategies are traditional methods for the construction

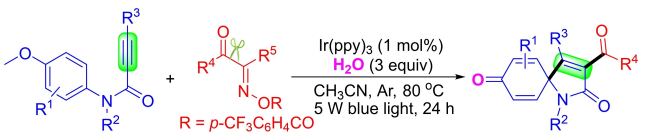


Scheme 1. C–C bond cleavage of acyl oximes *via* NCR strategies.

of substituted spiro[4,5]decatrienones.[17d–k,18f–h] Recently, many chemists, such as Zhang,[15a–d] Zhu,[15e–g] Qiu,[16] Li,[17] Liang,[18a–d] and our group[18e–h] developed many oxidative radical cyclization approaches for the preparation of spiro[4,5]decatrienones. Among these strategies, 3-acylated spiro[4,5]decatrienones could be prepared by several different pathways, which used aldehydes,[17k] ketoacids,[19] acyl chlorides[18f] as acyl precursors. However, most of these methods only provided aryl substituted acyl radicals, the alkyl substituted acyl radicals were quite few.

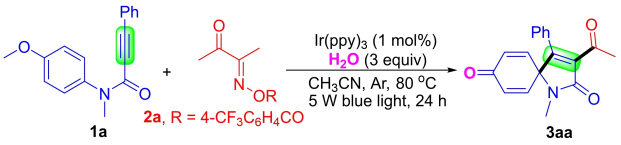
Visible-light-catalysis is a powerful and convenient method, which is usually employed in organic synthesis and drug synthesis.[20] Visible-light-catalysis possesses a series of advantages, such as high efficiency, availability, safety, simple and mild conditions.[20–21] Herein, we develop a nitrogen-centered radical strategy for the preparation of 3-acylated spiro[4,5]trienones *via* visible-light-mediated acylation/*ipso*-cyclization of alkynes with acyl oxime esters, in which a carbon-carbon σ-bond is severed and two new carbon-carbon bonds are constructed (Scheme 2).

To obtain the best reaction conditions, we started to test the reaction between propiolamide **1a** (0.2 mmol) and 3-(4-(trifluoromethyl)benzoyloxyimino)butan-2-one (**2a**, 1.5 equiv.) (Table 1). Conducting the reaction in the presence of $Ir(ppy)_3$ (1 mol%), H_2O (3 equiv.), CH_3CN (2 mL) at 80 °C irradiated by 5 W blue LED light for 24 h could form the target product **3aa** in 84% yield (entry 1). Next, several other *O*-benzoic substrates **2a–1**-**2a–7**, including 4-$NO_2C_6H_4CO$, 4-FC_6H_4CO, 4-MeC_6H_4CO, 4-$OMeC_6H_4CO$, 2-$NO_2C_6H_4CO$, C_6F_5CO and C_6H_5CO, were examined (entries 2–8). The results suggested that different acyl moieties of the oximes affected the reaction yields obviously. *O*–4-CF_3 C_6H_4CO substrate **2a** still afforded the highest yield (entries 2–8 vs entry 1). Additionally, *O*-acetic substrate **2a–8** was also suitable for this transformation, but it could not give higher yield than that of **2a** (entry 9). Conducting the *ipso*-cyclization reaction in the absence of $Ir(ppy)_3$ could not form the target product **3aa** (entry 10). Increasing the dosage of $Ir(ppy)_3$ to 2 mol% afforded the same yield as 1 mol% of $Ir(ppy)_3$ (entry 11). Then, other phtotocatalysts, such as $Ru(bpy)_3Cl_2$, Eosin Y, Na_2-Eosin Y and Mes-Acr^+, were screened (entries 12–15). The reaction yields showed that $Ir(ppy)_3$ was the best choice. The acylation/*ipso*-cyclization transformation could not occur when the reaction was conducted in the absence of additional light irradiation (entry16). These results showed that both photocatalyst and visible-light were indispensable for this NCRs reaction (entries 10 and 16). Next, the test of other different light source indicated that 5 W blue LED light was suitable light



Scheme 2. NCR strategies for tandem acylation/*ipso*-cyclization of alkynes.

Table 1. Screening optimal conditions.[a]



2a-1 R = 4-$NO_2C_6H_4CO$ **2a-5** R = 2-$NO_2C_6H_4CO$
2a-2 R = 4-FC_6H_4CO **2a-6** R = C_6F_5CO
2a-3 R = 4-MeC_6H_4CO **2a-7** R = C_6H_5CO
2a-4 R = 4-$OMeC_6H_4CO$ **2a-8** R = CH_3CO

Entry	Variation from the standard conditions	Isolated yield (%)
1	none	84
2	**2a–1** instead of **2a**	58
3	**2a–2** instead of **2a**	51
4	**2a–3** instead of **2a**	47
5	**2a–4** instead of **2a**	43
6	**2a–5** instead of **2a**	46
7	**2a–6** instead of **2a**	63
8	**2a–7** instead of **2a**	53
9	**2a–8** instead of **2a**	38
10[b]	without $Ir(ppy)_3$	0
11	$Ir(ppy)_3$ (2 mol%)	83
12	$Ru(bpy)_3Cl_2$ (10 mol%) instead of $Ir(ppy)_3$	10
13[b]	Eosin Y (10 mol%) instead of $Ir(ppy)_3$	8
14[b]	Na_2-Eosin Y (10 mol%) instead of $Ir(ppy)_3$	6
15[b]	Mes-Acr^+ (2 mol%) instead of $Ir(ppy)_3$	15
16[b]	without additional light	0
17[c]	36 W compact fluorescent light	44
18[c]	3 W blue LED light	72
19[c]	12 W blue LED light	82
20[b]	DMSO instead of CH_3CN	9
21[b]	DMF instead of CH_3CN	11
22	DCE instead of CH_3CN	80
23	^{n}BuOAc instead of CH_3CN	78
24[b]	toluene instead of CH_3CN	18
25[d]	THF instead of CH_3CN	0
26	H_2O (1 equiv.)	58
27	H_2O (5 equiv.)	66
28[b]	at 100 °C	70
29[b]	at 60 °C	25
30	for 48 h	83
31[e]	none	51

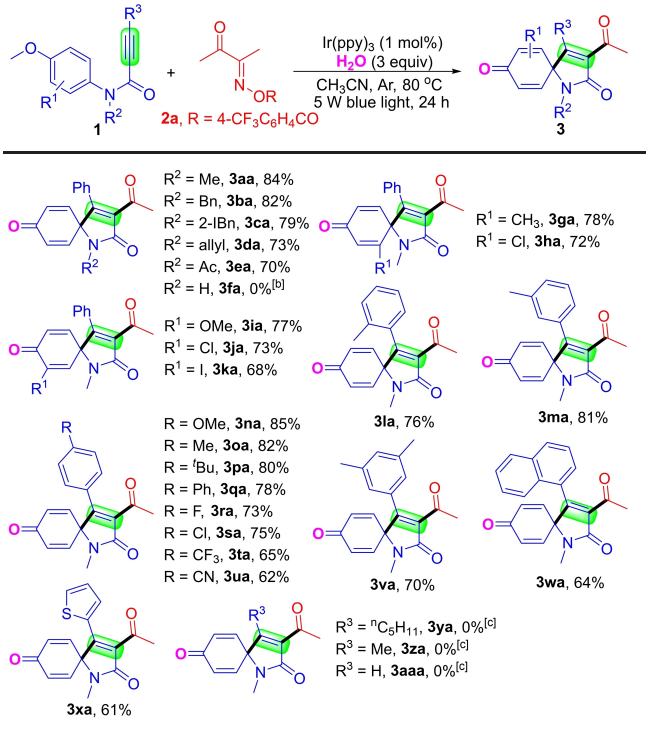
[a] Reaction conditions: **1a** (0.2 mmol), **2a** (0.3 mmol, 1.5 equiv.), H_2O (3 equiv., 10.8 mg), $Ir(ppy)_3$ (1.3 mg, 1 mol%), CH_3CN (2 mL) at 80 °C irradiated by 5 W blue LED light for 24 h.
[b] The rest of substrate **1a** was recovered.
[c] Instead of 5 W blue LED light.
[d] Most of **1a** was decomposed.
[e] **1a** (1.0 g, 3.77 mmol), **2a** (1.5 equiv.), $Ir(ppy)_3$ (1 mol%), H_2O (3 equiv.) and MeCN (40 mL) at 80 °C for 64 h.

source (entry 17). The solvents screening suggested that none of them gave a better result than that of MeCN (entries 20–25). Employing DCE or ^{n}BuOAc as solvents could give thefinal product **3 aa** in 80% and 78% yields, respectively (entries 22–23). Subsequently, the amount of H_2O was investigated. We found that H_2O was important for the reaction and 3 equiv. of H_2O was beneficial to generate the product (entries 26–27 vs entry 1). Changing the reaction temperature to 100 °C or 60 °C could not afford higher yields (entries 28–29). A longer reaction time could also not furnish a higher the reaction yield (entry 30). An amplified experiment could generate the product **3 aa** in moderate yield (entry 31).

Based on the acquired standard conditions, we began to examine the scope of propiolamides **1** in the presence of acyl oxime ester **2 a** (Table 2). First, several kinds of propiolamides **1 a–e** bearing different substituents on N atom were tested. All of them could afford the corresponding products **3 aa–ea** in 70–84% yields. However, the substrate **1 f** bearing a H on the N atom could not undergo this *ipso*-cyclization and most of the starting materials were recovered (product **3 fa**). Next, we investigated the propiolamides **1 g–k** bearing different substituents on the *N*-aryl moiety. This type of substrates could also go through the acylation/*ipso*-cyclization smoothly. Propiolamides **1 l–v** bearing different substituents, including alkyl, phenyl, halo, OMe, CF_3, and CN groups, on the aromatic ring connected with carbon-carbon triple bond were good candidates (products **3 la–va**). The steric effect and electronic effect of the substituents had important effect on the yields of *ipso*-cyclization products. The propiolamides bearing *para*-substituents could afford higher yields than substrates bearing *ortho*- and *meta*-substituents (products **3 la**, **3 ma** and **3 oa**). The propiolamides bearing electron-withdrawing substituents provided lower yields than substrates bearing electron-donating substituents. The propiolamides **1 w** (R^1 = naphthyl) and **1 x** (R^1 = thienyl) could furnish the *ipso*-cyclization products **3 wa** and **3 xa** in moderate yields. However, the alkyl-substituted alkynes **1 y–z** and terminal alkyne **1 aa** could not undergo the acylation/*ipso*-cyclization under the standard conditions with most of the starting materials decomposed (products **3 ya–aaa**).

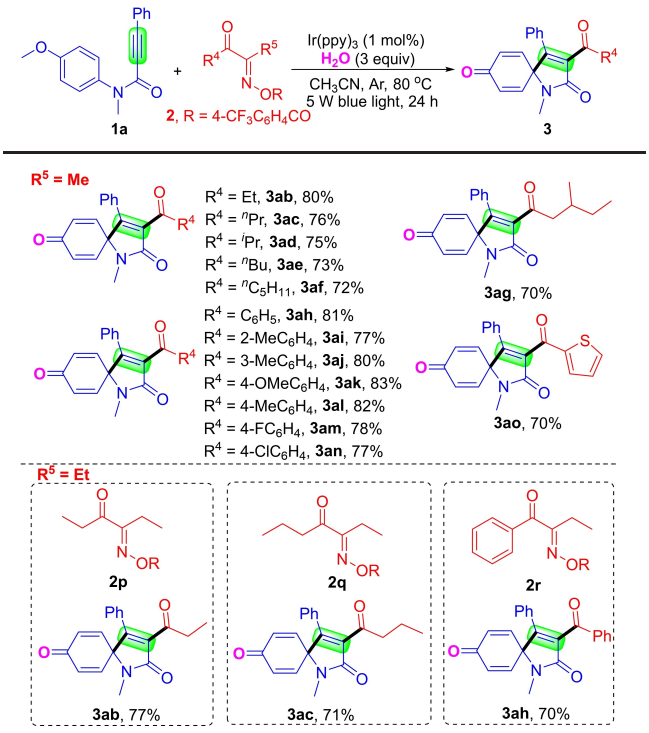
After the investigation of propiolamides, we next examined the scope of acyl oxime esters **2** in the presence of propiolamide **1 a** (Table 3). For R^5=Me, a variety of different acyl oxime esters **2 b–g** bearing alkyl groups on the acyl moieties, including Et, ^{n}Pr, ^{i}Pr, ^{n}Bu, ^{n}C_5H_{11} and 2-methylbutyl, were researched. All of

Table 2. Scope of propiolamides (**1**).[a]



[a] Reaction conditions: **1** (0.2 mmol), **2 a** (1.5 equiv.), H_2O (3 equiv.), $Ir(ppy)_3$ (1 mol%), CH_3CN (2 mL) at 80 °C irradiated by 5 W blue LED light for 24 h.
[b] Most of the substrate **1** was recovered.
[c] Most of the substrate **1** was decomposed.

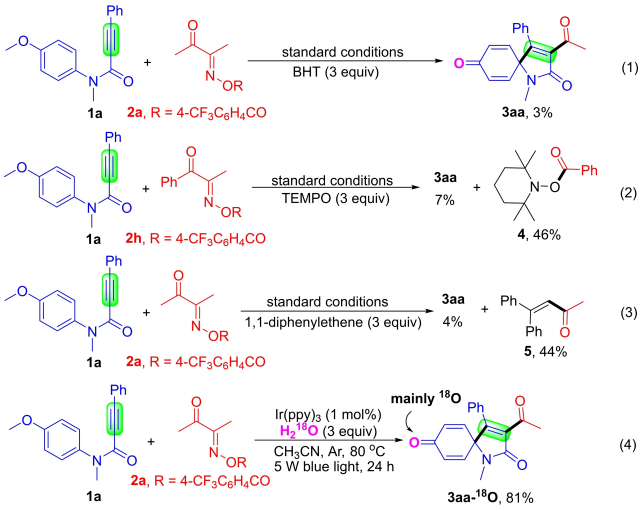
Table 3. Scope of acyl oxime esters (**2**).[a]



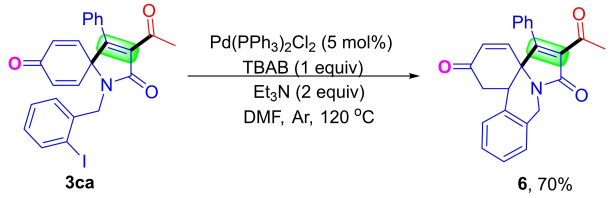
[a] Reaction conditions: **1 a** (0.2 mmol), **2** (1.5 equiv.), H_2O (3 equiv.), $Ir(ppy)_3$ (1 mol%), CH_3CN (2 mL) at 80 °C irradiated by 5 W blue LED light for 24 h.

them could generate the 3-acylated spiro[4,5]trienones **3ab–ag** in 70–80% yields. Aryl-substituted acyl oxime esters **2h–n** were also suitable for this *ipso*-cyclization, affording the target products **3ah–an** in moderate yields. The thienyl-substituted acylation product **3ao** could be furnished from propiolamide **1a** and 1-(thiophen-2-yl)-2-(4-(trifluoromethyl) benzoyloxyimino)propan-1-one **2o**. For R^5=Et, three acyl oxime esters **2p–r** were screened and offered the corresponding products **3ab**, **3ac** and **3ah** in 77%, 71% and 70% yields, respectively.

To obtain a deeper insight of the mechanism of the acylation/*ipso*-cyclization, several control experiments were conducted (Scheme 3). The reactions between propiolamide **1a** and acyl oxime ester **2**, which were carried out under the best conditions in the presence of BHT, TEMPO or 1,1-diphenylethene as radical inhibitors, were suppressed (eqs 1–3, Scheme 3). As employing TEMPO in the reaction, the acyl captured product **4** could be isolated in 46% yield (eq 2, Scheme 3). The acyl-trapping product **5** could be obtained in 44% when 1,1-diphenylethene was used in the reaction (eq 3, Scheme 3). Then, the reaction between **1a** and **2a** was conducted in the presence of $Ir(ppy)_3$ (1 mol%), $H_2{}^{18}O$ (3 equiv.), CH_3CN (2 mL) at 80 °C irradiated by 5 W blue LED light for 24 h (eq 4, Scheme 3). The results indicated that H_2O offered an O atom for building carbonyl group.



Scheme 3. Control Experiments.



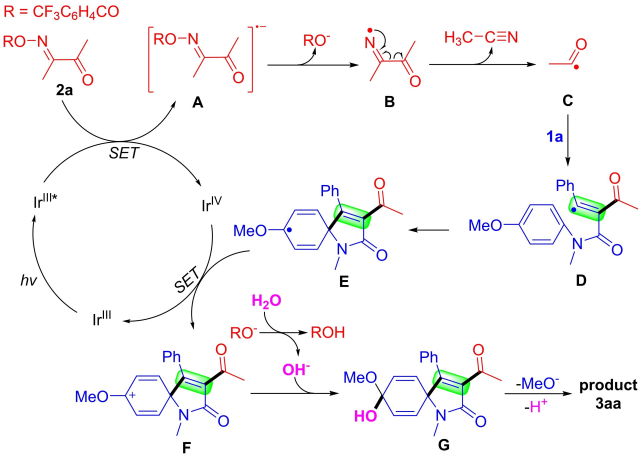
Scheme 4. Applications.

Scheme 4. Applications.

The 2-IBn substituted *ipso*-product **3ca** could undergo intramolecular Heck reaction to afford aza-quaternary tricyclic product **6** in 70% yield (Scheme 4).[17j]

Based on the above results and existing literature,[11,16–18,20–22] we propose a plausible mechanism for the acylation/*ipso*-cyclization of alkynes with acyl oxime esters *via* visible-light-mediated nitrogen-centered radical pathway (Scheme 5). As irradiated by visible-light, Ir^{3+} is tansformed into Ir^{3+*}. The photo-excited Ir^{3+*} gives a single electron to acyl oxime ester **2a**, to form the radical anion **A** and Ir^{4+}. Then, the intermediate **A** decomposes into RO^- and iminyl radical **B**, which deliveres acyl radical **C** and acetonitrile.[11] The substrate **1a** converts into benzyl radical **D** *via* the addition of the intermediate **C** to the carbon-carbon triple bond of **1a**. The intermediate **D** undergoes *ipso*-cyclization to furnish the radical **E**, which goes through *SET* to afford the carbocation **F** under the oxidation of Ir^{4+}, regenerating Ir^{3+}. The hydroxide ion, which comes from H_2O under the action RO^-, attacks the carbocation **F** to assemble the intermediate **G**.[17d–k,18f–h] The intermediate **G** occurrs release of OMe^- and H^+ to provide the target product **3aa**.

In conclusion, we have reported a nitrogen-centered radical strategy for the preparation of 3-acylated spiro [4,5]trienones *via* visible-light-mediated acylation/*ipso*-cyclization of alkynes with acyl oxime esters. The alkyl- or aryl-substituted acyl radicals, which generate from the cleavage of carbon-carbon *σ*-bonds in acyl oxime esters *via* nitrogen-centered radical pathway, attack the carbon-carbon triple bonds in propiolamides and then undergo *ipso*-cyclization. This method provides a way for the construction of 3-acyl-substituted spiro[4,5]trienones, which can introduce aryl- or alkyl-



Scheme 5. Possible Mechanisms.

substituted acyl into spiro[4,5]trienone skeletons. The further study and application of nitrogen-centered radical strategy are currently undergoing in our laboratory.

Experimental Section

Typical Experimental Procedure for the Synthesis of 3-Acylated Spiro[4,5]trienones

To a Schlenk tube were added propiolamides **1** (0.2 mmol, 0.1 M), acyl oxime esters compounds **2** (1.5 equiv.), $Ir(ppy)_3$ (1 mol%), H_2O (3 equiv.) and MeCN (2 mL) at 80 °C under irradiation of 5 W blue light for 24 h. Until complete consumption of the starting material was observed by TLC and/or GC-MS analysis. After the reaction was finished, the reaction mixture removal of the solvent, the crude product was purified by column chromatography (petroleum ether/ethyl acetate, 3:1) to provide the desired products **3**. A scaled-up experiment conducted in the presence of **1a** (1 g, 3.77 mmol), **2a** (1.5 equiv.), $Ir(ppy)_3$ (1 mol%), H_2O (3 equiv.) and MeCN (40 mL) at 80 °C under irradiation of 5 W blue light for 64 h gave the target product **3aa** in 51% yield (563.6 mg).

Acknowledgements

We thank the National Natural Science Foundation of China (No. 22078084 and 51874132), Scientific Research Fund of Hunan Provincial Education Department (No. 20A224 and 18A319), Science and Technology Planning Project of Hunan Province (No. 2020RC3056 and 2018TP1017) and Natural Science Foundation of Hunan Province (No. 2020JJ5221 and 2020JJ5212) for financial support.

References

[1] a) S.-Z. Zard, *Chem. Soc. Rev.* **2008**, *37*, 1603–1618; b) J.-R. Chen, X.-Q. Hu, L.-Q. Lu, W.-J. Xiao, *Chem. Soc. Rev.* **2016**, *45*, 2044–2056; c) T. Xiong, Q. Zhang, *Chem. Soc. Rev.* **2016**, *45*, 3069–3087; d) J. Davies, S. P. Morcillo, J. J. Douglas, D. Leonori, *Chem. Eur. J.* **2018**, *24*, 12154–12163; e) M. D. Kärkäs, *ACS Catal.* **2017**, *7*, 4999–5022; f) Y. Zhao, W. Xia, *Chem. Soc. Rev.* **2018**, *47*, 2591–2608.

[2] a) Z. Hu, L. Fu, P. Chen, W. Cao, G. Liu, *Org. Lett.* **2021**, *23*, 129–134; b) E.-C. Gentry, R.-R. Knowles, *Acc. Chem. Res.* **2016**, *49*, 1546–1556; c) Y. Zhang, S. Zhang, Z. Sun, K. He, Q. Chen, Y. Yuan, X. Jia, *J. Org. Chem.* **2019**, *84*, 14202–14208; d) H. Chen, W. Jin, S. Yu, *Org. Lett.* **2020**, *22*, 5910–5914; e) W. Shang, C. Zhu, F. Peng, Z. Pan, Y. Ding, C. Xia, *Org. Lett.* **2021**, *23*, 1222–1227; f) X.-D. An, Y.-Y. Jiao, H. Zhang, Y. Gao, S. Yu, *Org. Lett.* **2018**, *20*, 401–404.

[3] a) Q.-Q. Zhao, J. Chen, X.-S. Zhou, X.-Y. Yu, J.-R. Chen, W.-J. Xiao, *Chem. Eur. J.* **2019**, *25*, 8024–8029; b) Q.-Q. Zhao, X.-Q. Hu, M.-N. Yang, J.-R. Chen, W.-J. Xiao, *Chem. Commun.* **2016**, *52*, 12749–12752; c) Q.-Q. Zhao, J. Chen, D.-M. Yan, J.-R. Chen, W.-J. Xiao, *Org. Lett.* **2017**, *19*, 3620–3623; d) X.-Q. Hu, J.-R. Chen, Q. Wei, F.-L. Liu, Q.-H. Deng, A.-M. Beauchemin, W.-J. Xiao, *Angew. Chem. Int. Ed.* **2014**, *53*, 12163–12167; *Angew. Chem.* **2014**, *126*, 12359–12363; e) J. Chen, H.-M. Guo, Q.-Q. Zhao, J.-R. Chen, W.-J. Xiao, *Chem. Commun.* **2018**, *54*, 6780–6783; f) H. Kim, T. Kim, D.-G. Lee, S.-W. Roh, C. Lee, *Chem. Commun.* **2014**, *50*, 9273–9276.

[4] a) B. Lu, Y. Cheng, L.-Y. Chen, J.-R. Chen, W.-J. Xiao, *ACS Catal.* **2019**, *9*, 8159–8164; b) X.-Y. Yu, J.-R. Chen, P.-Z. Wang, M.-N. Yang, D. Liang, W.-J. Xiao, *Angew. Chem. Int. Ed.* **2018**, *57*, 738–743; *Angew. Chem.* **2018**, *130*, 746–751; c) X.-S. Zhou, Y. Cheng, J. Chen, X.-Y. Yu, W.-J. Xiao, J.-R. Chen, *Angew. Chem. Int. Ed.* **2019**, *11*, 5300–5305; d) B.-Q. He, X.-Y. Yu, P.-Z. Wang, J.-R. Chen, W.-J. Xiao, *Chem. Commun.* **2018**, *54*, 12262–12265; e) J. Chen, P.-Z. Wang, B. Lu, D. Liang, X.-Y. Yu, W.-J. Xiao, J.-R. Chen, *Org. Lett.* **2019**, *21*, 9763–9768; f) J. Chen, B.-Q. He, P.-Z. Wang, X.-Y. Yu, Q.-Q. Zhao, J.-R. Chen, W.-J. Xiao, *Org. Lett.* **2019**, *21*, 4359–4364.

[5] a) T. Nishimura, T. Yoshinaka, Y. Nishiguchi, Y. Maeda, S. Uemura, *Org. Lett.* **2005**, *7*, 2425–2427; b) T. Nishimura, S. Uemura, *J. Am. Chem. Soc.* **2000**, *122*, 12049–12050; c) H.-B. Yang, N. Selander, *Chem. Eur. J.* **2017**, *23*, 1779–1783; d) H.-B. Yang, S. R. Pathipati, N. Selander, *ACS Catal.* **2017**, *7*, 8441–8455; e) Y.-Q. Tang, J.-C. Yang, L. Wang, M.-J. Fan, L.-N. Guo, *Org. Lett.* **2019**, *21*, 5178–5182; f) J. Wu, J.-Y. Zhang, P. Gao, S.-L. Xu, L.-N. Guo, *J. Org. Chem.* **2018**, *83*, 1046–1055.

[6] a) I.-B. Krylov, O.-O. Segida, A.-S. Budnikov, A.-O. Terent'ev, *Adv. Synth. Catal.* **2021**, *363*, 2502–2528; b) C. Chen, J. Zhao, X. Shi, L. Liu, Y.-P. Zhu, W. Sun, B. Zhu, *Org. Chem. Front.* **2020**, *7*, 1948–1969; c) F. Xiao, Y. Guo, Y.-F. Zeng, *Adv. Synth. Catal.* **2021**, *363*, 120–143; d) T. Xiao, H. Huang, D. Anand, L. Zhou, *Synthesis* **2020**, *52*, 1585–1601; e) X.-Y. Yu, J.-R. Chen, W.-J. Xiao, *Chem. Rev.* **2021**, *121*, 506–561; f) S. Murarka, *Adv. Synth. Catal.* **2018**, *360*, 1735–1753; g) P. Niu, J. Li, Y. Zhang, C. Huo, *Eur. J. Org. Chem.* **2020**, *36*, 5801–5814; h) S.-Q. He, H.-C. Li, X.-L. Chen, I.-B. Krylov, A.-O. Terent'ev, L.-B. Qu, B. Yu, *Chin. J. Org. Chem.* **2021**, *41*. doi: 10.6023/cjoc202105041.

[7] a) J.-J. Zhang, X.-H. Duan, Y. Wu, J.-C. Yang, L.-N. Guo, *Chem. Sci.* **2019**, *10*, 161–166; b) J. Lou, Y. He, Y.-L. Li, Z.-K. Yu, *Adv. Synth. Catal.* **2019**, *361*, 3787–3799; c) Y. He, J. Lou, K.-K. Wu, H.-M. Wang, Z.-K. Yu, *J. Org. Chem.* **2019**, *84*, 2178–2190; d) Z.-P. Yin, J. Rabeah, A. Bruckner, X.-F. Wu, *ACS Catal.* **2018**, *8*, 10926–10930; e) Z.-P. Yin, J. Rabeah, A. Bruckner, X.-F. Wu, *Org. Lett.* **2019**, *21*, 1766–1769.

[8] a) J.-X. Xu, F. Teng, J.-N. Xiang, W. Deng, J.-H. Li, *Org. Lett.* **2019**, *21*, 9434–9437; b) Y. Liu, Q.-L. Wang, Z. Chen, H. Li, B.-Q. Xiong, P.-L. Zhang, K.-W. Tang, *Chem. Commun.* **2020**, *56*, 3011–3014; c) Z. Chen, Q. Zhou, Q.-L. Wang, P. Chen, B.-Q. Xiong, Y. Liang, K.-W. Tang, Y. Liu, *Adv. Synth. Catal.* **2019**, *362*, 3004–3010; d) P. Chen, Z. Chen, B.-Q. Xiong, Y. Liang, K.-W.

Tang, J. Xie, Y. Liu, *Org. Biomol. Chem.* **2021**, *19*, 3181–3190.

[9] a) Q.-Q. Zhao, M. Li, X.-S. Xue, J.-R. Chen, W.-J. Xiao, *Org. Lett.* **2019**, *21*, 3861–3865; b) L.-Q. Nguyen, R.-R. Knowles, *ACS Catal.* **2016**, *6*, 2894–2903; c) M.-D. Abreu, M. Selkti, P. Belmontand, E. Brachet, *Adv. Synth. Catal.* **2020**, *362*, 2216–2222; d) J. Davies, S.-G. Booth, S. Essafi, R.-A.-W. Dryfe, D. Leonori, *Angew. Chem. Int. Ed.* **2015**, *54*, 14017–14021; *Angew. Chem.* **2015**, *127*, 14223–14227; e) J. Hioe, D. Šakić, V. Vrček, H. Zipse, *Org. Biomol. Chem.* **2015**, *13*, 157–169.

[10] a) E. Brachet, L. Marzob, M. Selktic, B. König, P. Belmont, *Chem. Sci.* **2016**, *7*, 5002–5006; b) A.-M. Carestia, D. Ravelli, E.-J. Alexanian, *Chem. Sci.* **2018**, *9*, 5360–5365; c) X.-Q. Hu, J. Chen, J.-R. Chen, D.-M. Yan, W.-J. Xiao, *Chem. Eur. J.* **2016**, *22*, 14141–14146; d) A.-J. Musacchio, L.-Q. Nguyen, G.-H. Beard, R.-R. Knowles, *J. Am. Chem. Soc.* **2014**, *136*, 12217–12220; e) Z. Li, J.-P. Cheng, *J. Org. Chem.* **2003**, *68*, 7350–7360.

[11] a) B.-Q. He, Y. Gao, P.-Z. Wang, H. Wu, H.-B. Zhou, X.-P. Liu, J.-R. Chen, *Synlett.* **2021**, *32*, 373–377; b) X. Fan, T. Lei, B. Chen, C.-H. Tung, L.-Z. Wu, *Org. Lett.* **2019**, *21*, 4153–4158; c) L. Zheng, P.-J. Xia, Q.-L. Zhao, Y.-E. Qian, W.-N. Jiang, H.-Y. Xiang, H. Yang, *J. Org. Chem.* **2020**, *85*, 11989–11996; d) Y.-Y. Cheng, T. Lei, L. Su, X. Fan, B. Chen, C.-H. Tung, L.-Z. Wu, *Org. Lett.* **2019**, *21*, 8789–8794.

[12] a) C.-H. Heathcock, S.-L. Graham, M.-C. Pirrung, F. Plavac, C.-T. White, *The Total Synthesis of Natural Products*, Vol. 5 Apsimon, J., Ed.; Wiley-Interscience: New York **1983**, *1*; b) K. Yoneda, E. Yamagata, T. Nakanishi, T. Nagashima, I. Kawasaki, T. Yoshida, H. Mori, I. Miura, *Phytochemistry* **1984**, *23*, 2068–2069; c) Y.-S. Cai, Y.-W. Guo, K. Krohn, *Nat. Prod. Rep.* **2010**, *27*, 1840–1870; d) W.-T. Wu, L. Zhang, S.-L. You, *Chem. Soc. Rev.* **2016**, *45*, 1570–1580; e) R. Ramon, *Chem. Soc. Rev.* **2012**, *41*, 1060–1074; f) Y.-L. Yang, F.-R. Chang, Y.-C. Wu, *Helv. Chim. Acta.* **2004**, *87*, 1392–1399; g) Z. Jin, *Nat. Prod. Rep.* **2005**, *22*, 111–126; h) V.-A. D'yakonov, O.-A. Trapeznikova, A.-D. Meijere, U.-M. Dzhemilev, *Chem. Rev.* **2014**, *114*, 5775–5814.

[13] a) Z.-Q. Wang, B.-X. Tang, H.-P. Zhang, F. Wang, J.-H. Li, *Synthesis* **2009**, *2009*, 891–902; b) F.-G.-L. Turiso, *Org. Lett.* **2005**, *7*, 151–154; c) W. Wei, H.-H. Cui, D.-S. Yang, H.-L. Yue, C.-L. He, Y.-L. Zhang, H. Wang, *Green Chem.* **2017**, *19*, 5608–5613; d) H.-H. Cui, W. Wei, D.-S. Yang, J.-M. Zhang, Z.-H. Xu, J.-W. Wen, H. Wang, *RSC Adv.* **2015**, *5*, 84657–84661; e) Y. Zhou, X. Zhang, Y. Zhang, L.-X. Ruan, J.-C. Zhang, D. Zhang-Negrerie, Y.-F. Du, *Org. Lett.* **2017**, *19*, 150–153; f) T. Liu, Y. Li, L. Jiang, J. Wang, K. Jin, R. Zhang, C. Duan, *Org. Biomol. Chem.* **2020**, *18*, 1933–1939.

[14] a) S. Manna, P.-K.-S. Ashwathappa, K.-R. Prabhu, *Chem. Commun.* **2020**, *56*, 13165–13168; b) H.-E. Ho, A. Pagano, J.-A. Rossi-Ashton, J.-R. Donald, R.-G. Epton, J.-C. Churchill, M.-J. James, P. O'Brien, R.-J.-K. Taylor, W.-P. Unsworth, *Chem. Sci.* **2020**, *11*, 1353–1360; c) M.-G. Donahue, N.-G. Jentsch, E.-C. Realini, *Tetrahedron Lett.* **2017**, *58*, 3219–3222; d) A. Verma, L.-S. Banjara, R. Meena, S. Kumar, *Asian J. Org. Chem.* **2020**, *9*, 105–110; e) R. Pan, L. Hu, C. Han, A. Lin, H. Yao, *Org. Lett.* **2018**, *20*, 1974–1977; f) W. Dong, L. Qi, J.-Y. Song, J.-M. Chen, J.-X. Guo, S. Shen, L.-J. Li, W. Li, L.-J. Wang, *Org. Lett.* **2020**, *22*, 1830–1835; g) P. Qian, B. Du, R. Song, X. Wu, H. Mei, J. Han, Y. Pan, *J. Org. Chem.* **2016**, *81*, 6546–6553.

[15] a) W. Dong, Y. Yuan, C. Liang, F. Wu, S. Zhang, X. Xie, Z. Zhang, *J. Org. Chem.* **2021**, *86*, 3697–3705; b) W. Dong, Y. Yuan, X. Gao, M. Keranmu, W. Li, X. Xie, Z. Zhang, *J. Org. Chem.* **2019**, *84*, 1461–1467; c) W. Dong, Y. Yuan, X. Gao, M. Keranmu, W. Li, X. Xie, Z. Zhang, *Org. Lett.* **2018**, *20*, 5762–5765; d) W. Dong, Y. Yuan, X. Xie, Z. Zhang, *Org. Lett.* **2020**, *22*, 528–532; e) Z. Gu, H. Zhang, P. Xu, Y. Cheng, C. Zhu, *Adv. Synth. Catal.* **2015**, *357*, 3057–3063; f) H. Zhang, Z. Gu, P. Xu, H. Hu, Y. Cheng, C. Zhu, *Chem. Commun.* **2016**, *52*, 477–480; g) H. Zhang, C. Zhu, *Org. Chem. Front.* **2017**, *4*, 1272–1275.

[16] a) Y. He, G. Qiu, *Org. Biomol. Chem.* **2017**, *15*, 3485–3490; b) G. Qiu, Z.-F. Chen, W. Xie, H. Zhou, *Eur. J. Org. Chem.* **2019**, *2019*, 4327–4333.

[17] a) M. Hu, J.-H. Fan, Y. Liu, X.-H. Ouyang, R.-J. Song, J.-H. Li, *Angew. Chem. Int. Ed.* **2015**, *54*, 9577–9580; *Angew. Chem.* **2015**, *127*, 9713–9716; b) H.-Y. Liu, Y. Lu, Y. Li, J.-H. Li, *Org. Lett.* **2020**, *22*, 8819–8823; c) M. Hu, L.-Y. Guo, Y. Han, F.-L. Tan, R.-J. Song, J.-H. Li, *Chem. Commun.* **2017**, *53*, 6081–6084; d) P.-C. Qian, Y. Liu, R.-J. Song, J.-N. Xiang, J.-H. Li, *Synlett.* **2015**, *26*, 1213–1216; e) W.-T. Wei, R.-J. Song, X.-H. Ouyang, Y. Li, H.-B. Li, J.-H. Li, *Org. Chem. Front.* **2014**, *1*, 484–489; f) X.-H. Ouyang, R.-J. Song, B. Liu, J.-H. Li, *Chem. Commun.* **2016**, *52*, 2573–2576; g) L.-J. Wu, F.-L. Tan, M. Li, R.-J. Song, J.-H. Li, *Org. Chem. Front.* **2017**, *4*, 350–353; h) X.-H. Yang, X.-H. Ouyang, W.-T. Wei, R.-J. Song, J.-H. Li, *Adv. Synth. Catal.* **2015**, *357*, 1161–1166; i) M. Li, R.-J. Song, J.-H. Li, *Chin. J. Chem.* **2017**, *35*, 299–302; j) B.-X. Tang, Y.-H. Zhang, R.-J. Song, D.-J. Tang, G.-B. Deng, Z.-Q. Wang, Y.-X. Xie, Y.-Z. Xia, J.-H. Li, *J. Org. Chem.* **2012**, *77*, 2837–2849; k) X.-H. Ouyang, R.-J. Song, Y. Li, B. Liu, J.-H. Li, *J. Org. Chem.* **2014**, *79*, 4582–4589.

[18] a) D.-P. Jin, P. Gao, D.-Q. Chen, S. Chen, J. Wang, X.-Y. Liu, Y.-M. Liang, *Org. Lett.* **2016**, *18*, 3486–3489; b) L.-J. Wang, A.-Q. Wang, Y. Xia, X.-X. Wu, X.-Y. Liu, Y.-M. Liang, *Chem. Commun.* **2014**, *50*, 13998–14001; c) Z.-Z. Zhou, L. Zheng, X.-B. Yan, D.-P. Jin, Y.-T. He, Y.-M. Liang, *Org. Biomol. Chem.* **2016**, *14*, 4507–4510; d) H.-L. Hua, Y.-T. He, Y.-F. Qiu, Y.-X. Li, B. Song, P. Gao, X.-R. Song, D.-H. Guo, X.-Y. Liu, Y.-M. Liang, *Chem. Eur. J.* **2014**, *21*, 1468–1473; e) Y. Liu, J.-L. Zhang, M.-B. Zhou, R.-J. Song, J.-H. Li, *Chem. Commun.* **2014**, *50*, 14412–14414; f) Y. Liu, Q.-L. Wang, C.-S. Zhou, B. Xiong, P.-L. Zhang, C.-A. Yang, K.-W. Tang, *J. Org. Chem.* **2018**, *83*, 2210–2218; g) Y. Liu, Q.-L. Wang, B.-Q. Xiong, P.-L. Zhang, C.-A. Yang,

Y.-X. Gong, J. Liao, Q. Zhou, *Synlett.* **2018**, *29*, 2396–2403; h) Y. Liu, Q.-L. Wang, Z. Chen, Q. -Zhou, B.-Q. Xiong, P.-L. Zhang, K.-W. Tang, *Chem. Commun.* **2019**, *55*, 12212–12215.

[19] a) C.-R. Reddy, D.-H. Kolgave, M. Subbarao, M. Aila, S.-K. Prajapti, *Org. Lett.* **2020**, *22*, 5342–5346; b) A.-M. Nair, A.-H. Shinde, S. Kumar, C.-M.-R. Volla, *Chem. Commun.* **2020**, *56*, 12367–12370; c) H.-L. Zhu, F.-L. Zeng, X.-L. Chen, K. Sun, H.-C. Li, X.-Y. Yuan, L.-B. Qu, B. Yu, *Org. Lett.* **2021**, *23*, 2976–2980.

[20] a) B.-G. Cai, Z.-L. Chen, G.-Y. Xu, J. Xuan, W.-J. Xiao, *Org. Lett.* **2019**, *21*, 4234–4238; b) H.-H. Zhang, J.-J. Zhao, S.-Y. Yu, *J. Am. Chem. Soc.* **2018**, *140*, 16914–16919; c) J.-J. Zhao, H.-H. Zhang, X. Shen, S.-Y. Yu, *Org. Lett.* **2019**, *21*, 913–916; d) X. Wang, Y.-F. Han, X.-H. Ouyang, R.-J. Song, J.-H. Li, *Chem. Commun.* **2019**, *55*, 14637–14640.

[21] a) Q. L. Wang, W.-Z. Zhang, Q. Zhou, C.-S. Zhou, B.-Q. Xiong, K.-W. Tang, Y. Liu, *Org. Biomol. Chem.* **2019**, *17*, 7918–7926; b) Y. Liu, Z. Chen, Q.-L. Wang, P. Chen, J. Xie, B. Xiong, P.-L. Zhang, K.-W. Tang, *J. Org. Chem.* **2020**, *85*, 2385–2394; c) Y. Liu, Q.-L. Wang, Z. Chen, P. Chen, K.-W. Tang, Q. Zhou, J. Xie, *Org. Biomol. Chem.* **2019**, *17*, 10020–10029; d) Y. Liu, Q.-L. Wang, Z. Chen, Q. Zhou, H. Li, C.-S. Zhou, B.-Q. Xiong, P.-L. Zhang, K.-W. Tang, *J. Org. Chem.* **2019**, *84*, 2829–2839.

[22] a) X.-Y. Yu, Q.-Q. Zhao, J. Chen, W.-J. Xiao, J.-R. Chen, *Acc. Chem. Res.* **2020**, *53*, 1066–1083; b) W. Yin, X. Wang, *New J. Chem.* **2019**, 43, 3254–3264; c) S.-B. Höfling, M.-R. Heinrich, *Synthesis* **2011**, *2*, 173–189; d) W.-C. Yang, M.-M. Zhang, J.-G. Feng, *Adv. Synth. Catal.* **2015**, *362*, 4446–4461.

UPDATES

Visible-Light-Mediated Nitrogen-Centered Radical Strategy: Preparation of 3-Acylated Spiro[4,5]trienones

Adv. Synth. Catal. **2021**, *363*, 1 – 8

P. Chen, J. Xie, Z. Chen, B.-Q. Xiong, Y. Liu*, C.-A. Yang, K.-W. Tang