

CHEMISTRY & SUSTAINABILITY

CHEM5USCHEM

ENERGY & MATERIALS

Accepted Article

Title: Metal-free Photocatalytic Synthesis of exo-lodomethylene 2-Oxazolidinones: An Alternative Strategy for CO2 Valorization with Solar Energy

Authors: Xing He, Kai-Hong Chen, Xiang-Yang Yao, and Liang-Nian He

This manuscript has been accepted after peer review and appears as an Accepted Article online prior to editing, proofing, and formal publication of the final Version of Record (VoR). This work is currently citable by using the Digital Object Identifier (DOI) given below. The VoR will be published online in Early View as soon as possible and may be different to this Accepted Article as a result of editing. Readers should obtain the VoR from the journal website shown below when it is published to ensure accuracy of information. The authors are responsible for the content of this Accepted Article.

To be cited as: ChemSusChem 10.1002/cssc.201902417

Link to VoR: http://dx.doi.org/10.1002/cssc.201902417



WILEY-VCH

www.chemsuschem.org

Metal-free Photocatalytic Synthesis of exo-Iodomethylene 2-Oxazolidinones: An Alternative Strategy for CO₂ Valorization with Solar Energy

Xing He, Xiang-Yang Yao, Kai-Hong Chen,* and Liang-Nian He*

Dedicated to the 100th birthday anniversary of Professor Ruyu Chen and the 100th anniversary of Nankai University

Abstract: A visible-light-promoted metal-free carboxylative cyclization of propargylic amines with CO_2 is described to offer exo-iodomethylene 2-oxazolidinones. Incorporation of both CO_2 and iodo moiety into the titled compounds is realized efficiently. The mechanism study reveals that this carboxylative cyclization proceeds via a radical path. Notably, the iodine-functionalized 2-oxazolidinone as a platform molecule can be easily converted into wide ranges of value-added chemicals through Buchwald-Hartwig, Suzuki, Sonogashira, photocatalytic ene and photoreduction reaction, respectively. As a result, the plentiful downstream transformations remarkably enlarge the range of chemicals derived from CO_2 and open a potential avenue for CO_2 functionalization to circumvent energy challenge in this field.

Photocatalysis, particularly for visible-light-driven catalysis, has attracted numerous attentions and used as a sustainable and green methodology in organic synthesis, due to the unique advantages of mild conditions, high efficiency and clean energy supply.^[1] Traditionally, organic substrate is activated through three patterns in the photochemical process, i.e., photoredox,^[2] energy transfer,^[3] and photoexcitation.^[4] Different from the first two types, no extra photosensitizer (transition metal complexes or organic dyes) is needed in the third one, some substrates, such as ketones, carboxylic acids, halides and so on, can absorb light, and transforms themselves into reactive intermediates then initiate the photochemical reaction.^[5] Iodine (I₂), a cheap and versatile chemical, is widely used in various synthetic reaction.^[6] The ability to absorb visible light (450-600 nm)^[7] makes I₂ as a photocatalyst in Mallory reaction,^[8] photo-oxidation,^[9] aerobic photo-decarboxylation,^[10] and other photoreactions.^[11] In this regard, I2 has enormous potential in metal-free photocatalysis.

Although known as the major greenhouse gas, CO_2 is an abundant, nontoxic and sustainable C_1 source for the synthesis of various value-added chemicals.^[12] Among the prosperous CO_2 transformations, the carboxylative cyclization of propargylic amines with CO_2 is an appealing and promising approach to offer 2-oxazolidinones. Such a strategy not only is endowed with high atom-economy for CO_2 fixation, but also provides a handily approach to 2-oxazolidinones, which have been found broad applications in organic synthesis and pharmaceutical chemistry.^[13] To date, several catalyst systems have been developed for this reaction,^[14-26] including transition metal catalysts (Cu,^[14] Pd,^[15] Ru,^[16] Au,^[17] Ag^[18] and Zn^[19]) or organocatalysts (such as superbases,^[20] ionic liquids,^[21] *N*-heterocyclic carbene,^[22] *t*-BuOI,^[23] triethanolamine (TEOA)^[24] and NH₄F^[25]). Generally, heating is necessary and serves as energy input for the above

Xing He, Xiang-Yang Yao, Dr. Kai-Hong Chen, Prof. Dr. Liang-Nian He State Key Laboratory of Elemento-Organic Chemistry, College of Chemistry, Nankai University Tianjin, 300071 (P. R. China) E-mail: <u>khchen@nankai.edu.cn</u> (Kai-Hong Chen); <u>heln@nankai.edu.cn</u> (Liang-Nian He) mentioned reactions. From the standpoint of green and sustainable chemistry, developing a renewable and clear energy input mode for CO_2 conversion will show profound significance for CO_2 capture and utilization (CCU).^[12b, c] In this context, we hypothesized whether a reactive intermediate generated from light irradiation, for example, radical ions or radicals, could trigger the carboxylative cyclization of propargylic amines with CO_2 .

To overcome the energy intensive CO_2 conversion, we would like to develop a visible light-induced metal-free protocol for the carboxylative cyclization of propargylic amine with CO_2 by using I₂, resulting in incorporation of CO_2 and iodo moiety into exoiodomethylene 2-oxazolidinone, a potential platform molecule for further downstream transformations (Scheme 1).



Scheme 1. Visible-light-induced formation of exo-iodomethylene 2-oxazolidinones serving as useful derivatization portfolio.

To validate our hypothesis, the carboxylative cyclization of N-benzylprop-2-yn-1-amine (1a) with CO_2 was initially selected as the model reaction under a 300 W xenon lamp (wavelength 400< λ <780 nm) to start our investigation. This reaction in the absence of base failed in forming the target product (E)-3-benzyl-5-iodomethyleneoxazolidin-2-one (2a) (entry 1, Table 1), indicating the base is necessary. Subsequently, the effect of different bases was investigated. The organic base gave better results than inorganic base (entries 7-10 vs. 2-6), being presumably attributed to solubility variation. Specifically, TMG (tetramethylguanidine) and TBD (1,5,7-triazabicyclo[4,4,0]dec-5ene) with stronger basicity than other organic bases in this study, exhibited superior performance (entries 9-10 vs. 7-8). But TMG displayed better reactivity than TBD when the loading was reduced to 0.5 equivalents (entry 11 vs. 12). A sharp decreased yield was obtained upon exclusion of light (entry 13), implying the requirement of visible-light radiation. Further, controlled experiments (Scheme S1, Supporting Information) shown that the reaction underwent a non-radical pathway in the absence of light. Inspired by the available results, a sunlight driven reaction was implemented and a satisfactory yield of 2a was obtained (entry 14). A limited promotion was observed when the reaction time was even prolonged to 24 h (entries 15 and 16). To our delight, 92% yield of **2a** was obtained when the CO_2 pressure was increased to 2.0 MPa (entry 17 vs. 10).

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

Bn⁄N 1a	H I₂ (1 eq + CO₂ hν (400	uiv.), base (1 equiv.), -780 nm), MeCN, 8 h 🔶	
Entry	Base	Time (h)	Yield ^[b] 2a (%)
1	-	8	0
2	tBuOLi	8	5
3	tBuONa	8	4
4	tBuOK	8	4
5	CsF	8	4
6	Cs ₂ CO ₃	8	10
7	TEA	8	9
8	TEOA	8	16
9	TBD	8	63
10	TMG	8	63
11 ^[c]	TBD	8	12
12 ^[c]	TMG	8	21
13 ^[d]	TMG	8	22
14 ^[e]	TMG	8	52
15	TMG	12	75
16	TMG	24	76
17 ^[f]	TMG	8	92
18 ^[f]	TMG	12	95

[a] Reaction conditions: **1a** (36.3 mg, 0.25 mmol), base (0.25 mmol), I₂ (63.4 mg, 0.25 mmol), CH₃CN (1 mL), CO₂ balloon, 300 W xenon lamp (400-780 nm), 8 h. [b] Determined by ¹H NMR, 1,3,5-methoxybenzene was used as internal standard. [c] Base (0.125 mmol). [d] Without light. [e] Conducted under sunlight. [f] 2.0 MPa CO₂.

It is understandable that higher CO_2 pressure is beneficial to the formation of the guanidinium carbamate and thus renders the reaction significantly. Finally, **2a** yield could be increased to 95% with extension of the reaction time to 12 h (entry 18).

With the optimized conditions in hand, the generality of this protocol was further explored with various propargylic amines (Scheme 2). Firstly, methyl substituent at the *para-*, *ortho-* and *meta-*position of benzene ring was tested, demonstrating the steric effect has negligible effect (**2b-d**). Aryl rings with electron-withdrawing were able to offer excellent yields of the corresponding products (**2e-h**). The substrates featuring the electron-donating groups (-OMe, *-t*Bu) also gave moderate yields (**2i, 2j**). Then, a heterocycle substrate with pyridine ring, was capable to provide **2k** with a reasonable yield. Although bearing a *gem*-disubstituent at the propargylic position, **2l** could be obtained

in a 75% yield under the given conditions. In addition, propargylic amines with other substituents except *N*-benzyl group were examined and the corresponding iodine-functionalized 2-oxazolidinones were provided with moderate yield (2m, 2n), showcasing the generality of this protocol.



Scheme 2. Substrate scope. All reactions were run with 1 (0.25 mmol), TMG (28.8 mg, 0.25 mmol) and I_2 (63.4 mg, 0.25 mmol) in MeCN (1 mL) with 2.0 MPa CO₂ under visible-light irradiation (400-780 nm) for 12 h. Yields were provided for isolated yields.

To prove the synthetic utility of this visible-light-driven metal-free protocol for the carboxylative cyclization of propargylic amines with CO₂, we explored diverse transformations of the iodine-functionalized 2-oxazolidinones (Scheme 3, for details see Supporting Information). At the outset, the most desired reaction to be examined is the cross-coupling reaction, being regarded as one of the most useful tools in organic synthesis.^[27] The enamines, obtained from Buchwald-Hartwig reaction, have been known as valuable intermediates in numerous organic synthesis and widespread structural components in many natural products, such as antibiotic or the antitumor Salicylihalamide A, Oximidine.^[28] Thankfully, Buchwald-Hartwig reaction, Suzuki reaction and Sonogashira reaction could be also successfully implemented using 2a as substrate, giving the respective products 3a, 4a and 5a in good to excellent yields. In addition, 6a and 7a could be obtained via the photocatalytic "ene reaction"^[11b, 29] and photoreduction^[30] of 2a, respectively. The product 6a featuring aldehyde group has an ability to be easily transformed into the corresponding alcohols, carboxylic acids, esters or imidazoles.^[31] Similarly, 7a also can be further converted into other fine chemicals due to the exocyclic double bond.^[32] The abundant transformation in this study proves that exo-iodomethylene 2-oxazolidinone, a versatile chemical, can hereby be regarded as a platform compound, which can readily transformed into numerous of useful derivatives. Moreover, this ChemSusChem

methodology also provides an alternative avenue to enlarge domain of value-added products originating from CO_2 .

Gratifyingly, a scale-up reaction (**1a**, 4 mmol) was conveniently implemented to give desired product **2a** in 88% isolated yield (Scheme 4), exhibiting the potential application of this protocol.



Scheme 3. Representative transformations of product 2a.



Scheme 4. The scale-up reaction.

To gain insight into this reaction, a series of control experiments were conducted subsequently. First of all, the role of TMG in the catalytic system was examined. NMR and IR techniques were employed to further investigation. In ¹H NMR (see Fig. S1, SI), the signal of N-H of **1a** at $\delta = 1.54$ ppm disappeared after the addition of TMG, indicating an interaction between 1a and TMG. This interaction was also conformed from ¹³C NMR study (Fig. 1a vs. 1b), in which the chemical shift of 1a changed slightly after mixing with TMG. A new peak appeared at 162.0 ppm after the introduction of CO₂ (Fig. 1c) could be assigned to the carbonyl group of the guanidinium carbamate.^[33] This signal was enhanced when ¹³CO₂ was used (Fig. S2), strongly verified the carbonyl group of the carbamate originating from CO2. In addition, absorption displayed at 1568 cm⁻¹ in IR (Fig. S3) was attributed to the C=O stretching vibration of carbamate intermediate A (Scheme 5), absorption at 1602 cm⁻¹ was related to C=N stretching vibration of intermediate A.^[33] Although in the absence of CO₂, the intermediate I was further converted into 2a with 85% yield (Scheme 5). These results affirm the carbamate is key intermediate in carboxylative cyclization of propargylic amines with CO2, and the main role of TMG is to accelerate the formation of carbamate intermediate I, being consistent with the previous reports.^[20]

 I_2 acts as a reactant and catalyst in this metal-free photocatalytic carboxylative cyclization of propargylic amines with CO₂. Therefore, molecular iodine is crucial to running this reaction smoothly. In general, I_2 may initiate the reaction through two patterns, i.e., iodinium pathway^[23] or iodine radical pathway. When a commercial iodine chloride was chosen as I^+ source for the titled reaction (Scheme 6), no











Contrast experiments



Scheme 6. Contrast experiments and radical-trapping experiments.

Based on the previous reports^[13, 20] and our results, a proposed mechanism for the present visible-light-mediated metal-free carboxylative cyclization of propargylic amines with CO_2 is illustrated (Path A, Scheme 7). Initially, the carbamate (intermediate **A**) is formed

WILEY-VCH

COMMUNICATION

through the reaction between substrate **1a** and CO_2 in the presence of TMG. TMG presumably plays an important role in enhancing nucleophilic of **1a** and accelerating the nucleophilic attack on the C atom of CO_2 . Parallelly, the iodine radical is formed by visible light radiation. Subsequently, the addition of iodine radical to the intermediate **A** results in the formation of carbon radical intermediate **B**. Finally, the intermediate **B** will release the [TMGH]⁺T in the presence of a second iodine radical, the final product **2a** is offered through a intramolecular nucleophilic cyclization. A non-radical pathway (Path B) is also possible for this carboxylative cyclization of propargylic amines with CO_2 in the absence of light. As such, the cyclic iodonium intermediate **C** is formed from intermediate **A** and I₂, and subsequent nucleophilic cyclization to afford the target molecule **2a**.



Scheme 7. Proposed mechanism.

In summary, we have developed a metal-free photocatalysis system for synthesis of iodine-functionalized 2-oxazolidinones through the carboxylative cyclization of propargylic amines with CO₂ initiated by molecular iodine. Control experiments and NMR investigations illuminate the proposed mechanism undergoes a radical path, and I₂ is regarded as radical source. This protocol realizes the incorporation of CO₂ and iodine moiety into exo-iodomethylene oxazolidinone using visible light as energy input. Importantly, the iodine-substituted 2oxazolidinones are able to serve as platform molecules for further downstream transformations including cross coupling reactions, photocatalytic ene reaction and photoreduction reaction. In short, this work represents an alternative example for CO₂ conversion driven by solar energy, and offers a potential tool box for organic synthesis using CO₂ with renewable energy to address energy barrier.

Acknowledgements

This work was financially supported by National Key Research and Development Program (2016YFA0602900), National Natural Science Foundation of China (21672119), China Postdoctoral Science Foundation (2018M641624).

Keywords: carbon dioxide fixation • carboxylative cyclization • iodine • photocatalysis • radicals

- For selected reviews on photocatalysis in organic synthesis, see: a) D. Ravelli,
 S. Protti, M. Fagnoni, *Chem. Rev.* 2016, *116*, 9850-9913; b) C. Michelin, N.
 Hoffmann, *ACS Catal.* 2018, *8*, 12046-12055; c) C. K. Prier, D. A. Rankic, D.
 W. C. MacMillan, *Chem. Rev.* 2013, *113*, 5322-5363.
- [2] For selected reports on photoredox processes, see: a) B. L. Tóth, O. Tischler, Z. Novák, *Tetrahedron Lett.* 2016, *57*, 4505-4513; b) D. Cambié, C. Bottecchia, N. J. W. Straathof, V. Hessel, T. Noël, *Chem. Rev.* 2016, *116*, 10276-10341; c) L. Revathi, L. Ravindar, W. Y. Fang, K. P. Rakesh, H. L. Qin, *Adv. Synth. Catal.* 2018, *360*, 4652-4698; d) R. Li, X. L. Chen, S. K. Wei, K. Sun, L. L. Fan, Y. Liu, L. B. Qu, Y. F. Zhao, B. Yu, *Adv. Synth. Catal.* 2018, *360*, 4807-4813; e) J. R. Chen, X. Q. Hu, L. Q. Lu, W. J. Xiao, *Chem. Soc. Rev.* 2016, *45*, 2044-2056.
- [3] For selected reports on energy transfer processes, see: a) M. N. Alberti, M. Orfanopoulos, *Chem. Eur. J.* 2010, *16*, 9414-9421; b) N. J. Turro, *Pure Appl. Chem.* 1977, *49*, 405-429; c) K. L. Skubi, J. B. Kidd, H. Jung, I. A. Guzei, M. H. Baik, T. P. Yoon, *J. Am. Chem. Soc.* 2017, *139*, 17186-17192; d) R. Alonso, T. Bach, *Angew. Chem. Int. Ed.* 2014, *53*, 4368-4371.
- [4] For selected reports on energy transfer processes, see: a) G. Yilmaz, Y. Yagci, J. Photopolym. Sci. Technol. 2016, 29, 91-98; b) M. Silvi, C. Verrier, Y. P. Rey, L. Buzzetti, P. Melchiorre, Nature Chem. 2017, 9, 868-873; c) L. Marzo, S. K. Pagire, O. Reiser, B. König, Angew. Chem. Int. Ed. 2018, 57, 10034-10072.
- [5] a) J. Schwarz, B. König, *Green Chem.* 2018, 20, 323-361; b) K. Chen, P. He, S. Zhang, P. F. Li, *Chem. Commun.* 2016, 52, 9125-9128; c) J. L. Charlton, M. M. Alauddin, *Tetrahedron* 1987, 43, 2873-2889; d) Y. Masuda, N. Ishida, M. Murakami, *J. Am. Chem. Soc.* 2015, *137*, 14063-14066.
- For selected reviews on iodine-catalyzed reactions, see: a) P. T. Parvatkar, P. S. Parameswaran, S. G. Tilve, *Chem. Eur. J.* 2012, *18*, 5460-5489; b) S. U. Tekale, S. S. Kauthale, S. A. Dake, S. R. Sarda, R. P. Pawar, *Curr. Org. Chem.* 2012, *16*, 1485-1501; c) J. J. Zhao, W. C. Gao, H. H. Chang, X. Li, Q. Liu, W. L. Wei, *Chin. J. Org. Chem.* 2014, *34*, 1941-1957; d) A. N. French, S. Bissmire, T. Wirth, *Chem. Soc. Rev.* 2004, *33*, 354-362.
- [7] A. Saiz-Lopez, R. W. Saunders, D. M. Joseph, S. H. Ashworth, J. M. C. Plane, *Atmos. Chem. Phys.* 2004, *4*, 1443-1450.
- [8] a) F. B. Mallory, C. S. Wood, J. T. Gordon, J. Am. Chem. Soc. 1964, 86, 3094-3102; b) K. B. Jørgensen, *Molecules* 2010, 15, 4334-4358; c) H. Okamoto, H. Takahashi, T. Takane, Y. Nishiyama, K. Kakiuchi, S. Gohda, M. Yamaji, Synthesis 2017, 49, 2949-2957.
- a) T. Nobuta, S. Hirashima, N. Tada, T. Miura, A. Itoh, Org. Lett. 2011, 13, 2576-2579; b) M. X. Liu, Y. M. Li, L. Yu, Q. Xu, X. F. Jiang, Sci. China Chem. 2018, 61, 294-299; c) J. Y. Yang, D. T. Xie, H. Y. Zhou, S. W. Chen, C. D. Huo, Z. Li, Org. Chem. Front. 2018, 5, 1325-1329.
- [10] H. Nakayama, A. Itoh, *Tetrahedron Lett.* **2008**, *49*, 2792-2794.
- [11] a) S. Maejima, E. Yamaguchi, A. Itoh, Adv. Synth. Catal. 2017, 359, 3883-3887; b) Y. L. Liu, B. Wang, X. F. Qiao, C. H. Tung, Y. F. Wang, ACS Catal. 2017, 7, 4093-4099; c) L. Li, W. B. Liu, H. Y. Zeng, X. Y. Mu, G. Cosa, Z. T. Mi, C. J. Li, J. Am. Chem. Soc. 2015, 137, 8328-8331; d) Y. Sudo, E. Yamaguchi, A. Itoh, Org. Lett. 2017, 19, 1610-1613.
- [12] Representative reports on CO2 transformations, see: a) M. Aresta, A. Dibenedetto, E. Quaranta, J. Catal. 2016, 343, 2-45; b) Z. Z. Yang, L. N. He, J. Gao, A. H. Liu, B. Yu, Energy Environ. Sci. 2012, 5, 6602-6639; c) P. Markewitz, W. Kuckshinrichs, W. Leitner, J. Linssen, P. Zapp, R. Bongartz, A. Schreiber, T. E. Müller, Energy Environ. Sci. 2012, 5, 7281-7305; d) Q. W. Song, Z. H. Zhou, L. N. He, Green Chem. 2017, 19, 3707-3728; e) Y. Y. Gui, W. J. Zhou, J. H. Ye, D. G. Yu, ChemSusChem 2017, 10, 1337-1340; f) W. L. Wang, Y. X. Fu, Y. M. Li, R. T. Yao, L. Y. Liu, W. X. Chang, J. Li, Org. Chem. Front. 2018, 5, 3331-3335; g) X. He, Y. Cao, X. D. Lang, N. Wang, L. N. He, ChemSusChem 2018, 11, 3382-3387; h) S. Dabral, T. Schaub, Adv. Synth. Catal. 2019, 361, 223-246; i) S. Wang, C. J. Xi, Chem. Soc. Rev. 2019, 48, 382-404; j) B. Yu, B. Zou, C. W. Hu, J. CO2 Util. 2018, 20, 314-322; j) M. Y. Wang, Y. Cao, X. Liu, N. Wang, L. N. He, S. H. Li, Green Chem. 2017, 19, 1240-1244; k) S. Wang, X. W. Zhang, C. Y. Cao, C. Chen, C. J. Xi, Green Chem. 2017, 19, 4515-4519.
- [13] For recent reviews on carboxylative cyclization of propargylic amines with CO₂, see: a) J. Rintjema, A. W. Kleij, *Synthesis* **2016**, *48*, 3863-3878; b) V. A. Peshkov, O. P. Pereshivko, A. A. Nechaev, A. A. Peshkovc, E. V. V. der

Eycken, *Chem. Soc. Rev.* 2018, *47*, 3861-3898; c) Z. Zhang, J. H. Ye, D. S.
Wu, Y. Q. Zhou, D. G. Yu, *Chem. Asian J.* 2018, *13*, 2292-2306; d) T. Niemi,
T. Repo, *Eur. J. Org. Chem.* 2019, 2019, 1180-1188.

- [14] a) M. Y. Wang, Q. W. Song, R. Ma, J. N. Xie, L. N. He, Green Chem. 2016, 18, 282-287; b) Y. L. Zhao, J. K. Qiu, L. Tian, Z. Y. Li, M. H. Fan, J. J. Wang, ACS Sustainable Chem. Eng. 2016, 4, 5553-5560.
- [15] a) A. Bacchi, G. P. Chiusoli, M. Costa, B. Gabriele, C. Righi, G. Salerno, *Chem. Commun.* **1997**, 1209-1210; b) P. Brunel, J. Monot, C. E. Kefalidis, L. Maron, B. Martin-Vaca, D. Bourissou, *ACS Catal.* **2017**, *7*, 2652-2660.
- [16] T. Mitsudo, Y. Hori, Y. Yamakawa, Y. Watanabe, *Tetrahedron Lett.* 1987, 28, 4417-4418.
- [17] a) S. Hase, Y. Kayaki, T. Ikariya, *Organometallics* 2013, *32*, 5285-5288; b) S.
 Hase, Y. Kayaki, T. Ikariya, *ACS Catal.* 2015, *5*, 5135-5140; c) S. M.
 Sadeghzadeh, *J. Mol. Catal.* A 2016, *423*, 216-223.
- [18] K. Sekine, T. Yamada, Chem. Soc. Rev. 2016, 45, 4524-4532.
- [19] X. Liu, M. Y. Wang, S. Y. Wang, Q. Wang, L. N. He, *ChemSusChem* 2017, 10, 1210-1216.
- [20] a) M. Costa, G. P. Chiusoli, M. Rizzardi, *Chem. Commun.* **1996**, 1699-1700; b)
 M. Costa, G. P. Chiusoli, D. Taffurelli, G. Dalmonego, *J. Chem. Soc. Perkin Trans. 1* **1998**, 1541-1546; c) R. Nicholls, S. Kaufhold, B. N. Nguyen, *Catal. Sci. Technol.* **2014**, *4*, 3458-3462; d) H. Zhou, S. Mu, B. H. Ren, R. Zhang, X. B. Lu, *Green Chem.* **2019**, *21*, 991-994.
- [21] a) J. Y. Hu, J. Ma, Q. G. Zhu, Z. F. Zhang, C. Y. Wu, B. X. Han, Angew. Chem. Int. Ed. 2015, 54, 5399-5403; b) J. Y. Hu, J. Ma, Z. F. Zhang, Q. G. Zhu, H. C. Zhou, W. J. Lu, B. X. Han, Green Chem. 2015, 17, 1219-1225.
- [22] a) K. Fujita, A. Fujii, J. Sato, S. Onozawa, H. Yasuda, *Tetrahedron Lett.* 2016, 57, 1282-1284; b) K. Fujita, J. Sato, A. Fujii, S. Onozawa, H. Yasuda, *Asian J. Org. Chem.* 2016, 5, 828-833.
- [23] Y. Takeda, S. Okumura, S. Tone, I. Sasaki, S. Minakata, Org. Lett. 2012, 14, 4874-4877.
- [24] Y. L. Zhao, J. K. Qiu, Z. Y. Li, H. Y. Wang, M. H. Fan, J. J. Wang, *ChemSusChem* **2017**, *10*, 2001-2007.
- [25] a) A. Fujii, J. C. Choi, K. Fujita, *Tetrahedron Lett.* 2017, *58*, 4483-4486; b) A.
 Fujii, H. Matsuo, J. C. Choi, T. Fujitani, K. Fujita, *Tetrahedron* 2018, *74*, 2914-2920.
- [26] a) Y. Kayaki, M. Yamamoto, T. Suzuki, T. Ikariya, Green Chem. 2006, 8, 1019-1021; b) B. Yu, D. Kim, S. Kim, S. H. Hong, ChemSusChem 2017, 10, 1080-1084.
- [27] For recent reviews on cross coupling reaction involved halohydrocarbon, see:
 a) C. Torborg, M. Beller, Adv. Synth. Catal. 2009, 351, 3027-3043; b) N. J. Race, I. R. Hazelden, A. Faulkner, J. F. Bower, Chem. Sci. 2017, 8, 5248-5260; c) O. M. Kuzmina, A. K. Steib, A. Moyeux, G. Cahiez, P. Knochel, Synthesis 2015, 47, 1696-1705; d) W. J. Zhou, Y. H. Zhang, G. M. Cao, H. D. Liu, D. G. Yu, Chin. J. Org. Chem. 2017, 37, 1322-1337.
- [28] a) J. R. Dehli, J. Legros, C. Bolm, *Chem. Commun.* **2005**, 973-986; b) L. Jiang, G. E. Job, A. Klapars, S. L. Buchwald, *Org. Lett.* **2003**, *5*, 3667-3669.
- [29] M. N. Alberti, M. Orfanopoulos, Chem. Eur. J. 2010, 16, 9414-9421.
- [30] J. D. Nguyen, E. M. D'Amato, J. M. R. Narayanam, C. R. J. Stephenson, *Nat. Chem.* 2012, *4*, 854-859.
- [31] a) A. Stolle, T. Gallert, C. Schmöger, B. Ondruschka, *RSC Adv.* 2013, *3*, 2112-2153; b) S. Tanaka, Y. Kon, Y. Uesaka, R. Morioka, M. Tamura, K. Sato, *Chem. Lett.* 2016, *45*, 188-190; c) C. L. Yi, Y. T. Huang, C. F. Lee, *Green Chem.* 2013, *15*, 2476-2484; d) Y. Li, H. Q. Ma, Y. L. Wang, *Chin. J. Org. Chem.* 2008, *28*, 210-217.
- [32] a) A. Nodzewska, A. Wadolowska, M. Watkinson, *Coord. Chem. Rev.* 2019, 382, 181-216; b) Y. R. Shen, P. P. Jiang, P. T. Wai, Q. Gu, W. J. Zhang, *Catalysts* 2019, 9, 31-57; c) S. W. M. Crossley, C. Obradors, R. M. Martinez, R. A. Shenvi, *Chem. Rev.* 2016, *116*, 8912-9000; d) X. Y. Du, Z. Huang, *ACS Catal.* 2017, 7, 1227-1243.
- [33] a) X. X. Lei, Y. J. Xu, L. L. Zhu, X. H. Wang, *RSC Adv.* 2014, *4*, 7052-7057;
 b) L. Biancalana, G. Bresciani, C. Chiappe, F. Marchetti, G. Pampaloni, *New J. Chem.* 2017, *41*, 1798-1805.

10.1002/cssc.201902417

WILEY-VCH

COMMUNICATION

COMMUNICATION

Enlarged CO₂ transformation: The photocatalytic incorporation of CO₂ and iodine moiety into exo-iodomethylene oxazolidinone performs efficiently, thereby offers a potential tool box for organic synthesis using CO₂ with renewable energy to circumvent energy intensive issue facing great challenge in this field.

Metal-free Photocatalysis High efficiency Plentiful downstream transformations Xing He, Xiang-Yang Yao, Kai-Hong Chen,* Liang-Nian He*

Page No. – Page No.

Metal-free Photocatalytic Synthesis of exo-Iodomethylene 2-Oxazolidinones: An Alternative Strategy for CO₂ Valorization with Solar Energy