

A cost-effective shortcut to prepare organoselenium catalysts via decarboxylative coupling of phenylacetic acid with elemental selenium

Hongen Cao^{1,2} | Mingxuan Liu¹ | Rongrong Qian³ | Xu Zhang¹ | Lei Yu^{1,2}

¹Guangling College, School of Chemistry and Chemical Engineering, and Institute of Pesticide of School of Horticulture and Plant Protection, Yangzhou University, Yangzhou, Jiangsu 225002, China

² Jiangsu Key Laboratory of Zoonosis, Yangzhou University, Yangzhou 225009, China

³Jiangsu College of Tourism, Yangzhou 225009, China

Correspondence

Xu Zhang and Lei Yu, Guangling College, School of Chemistry and Chemical Engineering, Institute of Pesticide of School of Horticulture and Plant Protection, Yangzhou University, Yangzhou, Jiangsu 225002, China. Email: zhangxu@yzu.edu.cn; yulei@yzu. edu.cn

Funding information

NNSFC, Grant/Award Number: 21202141; Priority Academic Program Development of Jiangsu Higher Education Institutions (PAPD), Grant/Award Number: 21202141; the Nature Science Foundation of Guangling College, Grant/Award Numbers: ZKZD17005 and ZKZZ18001; the Open Project Program of Jiangsu Key Laboratory of Zoonosis, Grant/Award Numbers: R1509 and R1609; Top-notch Academic Programs Project of Jiangsu Higher Education Institutions (TAPP)

1 | INTRODUCTION

Organoselenium compounds have been widely employed in biochemistry, medicinal chemistry, organic synthesis and materials science for their unique bioactivities and chemical activities.^[1] Recently, much attention has been paid to the eco-friendly aspects of organoselenium chemistry^[2] and among reported works, organoselenium catalysis is one of the most important research directions for its clean procedures, transition-metal-free reaction conditions and the metabolizable catalytic Se element that affords a potential alternative to transition metal catalysts.^[3] Researchers have reported a series of organoselenium-catalyzed reactions and this field has seen rapid progress in recent years.^[4,5] However, up to the present, the frequently used method for introducing

An interesting decarboxylative coupling reaction of phenylacetic acid with elemental selenium was discovered and employed for the preparation efficient organoselenium catalysts for Baeyer–Villiger reaction and oxidative deoximation reaction. Compared with the traditionally used Grignard reagent method, the decarboxylative coupling reaction with selenium powders provides a shortcut for the preparation of organoselenium catalysts free of carcinogenic organohalide starting materials, toxic and odorous selenol intermediates and magnesium salt solid wastes. This may be helpful for reducing the cost of selenium catalysts to facilitate the application of organoselenium-catalyzed green reactions in large-scale production.

KEYWORDS

Selenium, organoselenium catalysis, green chemistry, diselenide, decarboxylative coupling

Se into molecules to synthesize Se catalysts is via the Grignard reagent reaction, which is very tedious to operate and suffers from the use of carcinogenic organohalide starting materials that are hazardous to the environment (Scheme 1). The method inevitably generates toxic and odorous selenol intermediates and magnesium salts as solid wastes (Scheme 1). Therefore, developing a more direct and environment-friendly method for the synthesis of Se catalysts is an inescapable step before any application of the organoselenium catalysis techniques in largescale production.

Decarboxylative coupling reactions^[6] are promising because of the solid-waste-free procedures and the easily accessible and halogen-free starting materials. Releasing harmless CO₂ gas provides strong driving forces for these transformations. The decarboxylative coupling reactions may proceed via free radical mechanisms.^[7] During our continuing investigations of green synthesis,^[5,8,9] it was found that heating elemental Se could lead to Se₈ bi-radicals, which were efficient selenylation reagents for the preparation of cyclic diselenides.^[9] Thus, we considered that catalytically active Se compounds might also be synthesized through the direct decarboxylative coupling reactions of carboxylic acids with Se powders via thermoinitiated free radical mechanisms. Efforts were made to achieve this objective and it was found that benzyl Se catalysts for Baeyer-Villiger reactions and oxidative deoximation reactions could be easily synthesized via an interesting transition-metal-free decarboxylative coupling reaction of phenylacetic acid with elemental Se. Herein we report the details of this work.

2 | RESULTS AND DISCUSSION

Phenylacetic acid (1) was initially heated with Se powders in dimethylformamide (DMF) at 150 $^{\circ}\mathrm{C}$ under N_2

RSeH $\xrightarrow{O_2}$ (RSe)₂

$$(RSe)_2 \xrightarrow{Cl_2} RSeCl \xrightarrow{PhCH_2MgCl} R_2Se$$

SCHEME 1 Introduction of Se into molecules through the Grignard reagent method

protection, but, unfortunately, no desired product was observed after 20 h of reaction (Table 1, entry 1). Tertiary amines, such as tri-n-butylamine, tri-n-octylamine, N,Ndiisopropylethylamine (DIEA) and 1-methylpiperidine, were comprehensively introduced as additives to improve the reaction and it was found that DIEA was the most favorable base, affording dibenzyl diselenide in 26% vield, while dibenzyl selenide was also obtained in 37% yield as the co-product. The Se content index (n) of mixture 2 was calculated to be 1.41 according to ¹H NMR analysis (Table 1, entry 2).^[10] Secondary amines, such as diethylamine, di-n-butylamine (DNBA), pyridine, piperidine, pyrrolidine, 1-methylpiperazine and morpholine, were examined, and DNBA was found to be the favorable base, affording 2 in 59% yield, while n was also calculated to be 1.41 (Table 1, entry 3).^[10] Other bases, including aniline derivatives or inorganic bases such as NaOH, KOH, Na₂CO₃ and K₂CO₃, were all unfavorable additives for the reaction (Table 1, entries 4 and 5).^[10] A series of parallel experiments were then performed to determine the preferable amount of base for the reaction. Using 100 mol% of DIEA (versus substrate 1) as the base additive, the reaction led to 2 in 29% yield, with n = 1.34(Table 1, entry 6) and it was contrarily restrained with further increase of DIEA amount over 200 mol% (Table 2, entries 7 and 8 versus 2). Similar trends were also observed in the reactions with DNBA as the base, and using 200 mol% of DNBA was also found to be the preferable amount (Table 1, entry 3).^[10] Effects of the amount of Se on the reaction were then examined. The reaction of 1 with 50 mol% of Se afforded 2 in 29% vield, with n = 1.30 (Table 1, entry 9). With 100 mol% of Se, the reaction afforded 2 in 34% yield (Table 1, entry 10). The product yield could be further enhanced by using an increased amount of Se powders, and 400 mol% of Se was found to be the better amount (Table 1, entries 2 versus 9–13). Interestingly, the values of n for products 2 were almost invariable, regardless of the amount of Se used (Table 1, entries 2, 10-13).

We then tried to improve the reaction conditions by screening the reaction solvent and temperature. No product was obtained under solvent-free reaction conditions or in a low-polarity solvent such as CHCl₃ or CH₂Cl₂ (Table 2, entries 1 and 2). In MeCN, the product **2** (n = 1.45) was obtained in 22% yield (Table 2, entry 3). The reactions in EtOH or EtOH-H₂O both led to poor product yields (Table 2, entries 4 and 5). It was then found that the high-polarity solvents dimethylsulfoxide (DMSO) and DMF were favorable for the reaction, affording **2** in 53–63% yields (n = 1.41-1.42; Table 2, entries 6 and 7). A series of reactions at various temperatures were conducted. The results demonstrated that 140–160°C was the favorable reaction temperature range,

NILEY Organometallic 3 of 8 Chemistry

TABLE 1 Screening of bases and amount of Se for decarboxylative coupling of phenylacetic acid with Se^a

Ph CO ₂ H + 1	Se (x mol %) base (y m DMF, 15 20 h,	$rac{Nol \%}{S0 °C} Ph Se_n Se_n$ N ₂ 2	Ph	
Entry	Base (amount, %) ^b	Se amount (%) ^b	n ^c	Yield (%) ^d
1	_	400	_	0
2	DIEA (200)	400	1.41	63
3	DNBA (200)	400	1.41	59
4	Anilines (200)	400	—	0–24
5	Inorganic bases (200)	400	—	0
6	DIEA (100)	400	1.34	29
7	DIEA (300)	400	1.33	30
8	DIEA (400)	400	—	0
9	DIEA (200)	50	1.30	29
10	DIEA (200)	100	1.44	34
11	DIEA (200)	200	1.41	59
12	DIEA (200)	600	1.43	44
13	DIEA (200)	800	1.40	25

^a1 mmol of **1**, 4 mmol of Se and 1 ml of DMF solvent were employed.

^bMolar ratio versus substrate 1.

 $^{\circ}$ Values of Se content index (*n*) were calculated from the molar ratios of diselenide versus selenide determined by 1 H NMR analysis (for details, see supporting information).

^dIsolated yields.

TABLE 2 Optimization of reaction conditionsa^a

Ph CO ₂ H + Se 1	DIEA (200 mol %) solvent, T, 20 h, N ₂ ► P	°h Sen Ph 2		
Entry	Solvent	<i>T</i> (°C)	n	Yield (%) ^b
1	No solvent	150	_	0
2	CHCl ₃ or CH ₂ Cl ₂	150 ^c	_	0
3	MeCN	150 ^c	1.45	22
4	EtOH	150 ^c	1.43	23
5	EtOH-H ₂ O (1/1)	150 ^c	1.40	10
6	DMSO	150	1.42	53
7	DMF	150	1.41	63
8	DMF	120	—	0
9	DMF	130	1.33	33
10	DMF	140	1.41	59
11	DMF	160 ^c	1.42	55
12	DMF	170 ^c	1.33	27
13	DMF	180 ^c		0

 $^{\mathrm{a}}\mathrm{1}$ mmol of 1, 4 mmol of Se, 2 mmol of DIEA and 1 ml of solvent were employed.

^bIsolated yields.

^cReaction performed in a sealed tube.

4 of 8 WILEY Organometalli

affording **2** in 55–63% yields (Table 2, entries 7, 10, 11 versus 8, 9, 12, 13). No desired product was obtained at a temperature lower than 120°C or exceeding 180°C (Table 2, entries 8 and 13). In the former reaction, much unconverted **1** was observed using TLC (Table 2, entry 8), while in the latter one, a series of complex by-products were generated (Table 2, entry 13). The values of *n* were generally invariable in the reactions at the preferable reaction temperatures (Table 2, entries 7, 10 and 11).

Mechanisms of this interesting reaction were our next concern, and metal catalysts were introduced into the reaction to investigate their catalytic activities. The standard reaction (Table 1, entry 2) with 10 mol% of CuI, CuBr, Cu(OAc)₂, FeCl₃ or FeCl₂ generated no desired diselenide or selenide product, while much unconverted 1 was observed using TLC, indicating that the metal salts actually restrained the reactions. Reactions with 10 mol% of ZnI₂ or ZnCl₂ as catalyst produced 2 in 26 and 17% yields with n = 1.42 and 1.35, respectively. These results demonstrated that, different from previous report.^[7] this decarboxylative coupling reaction proceeded through a non-metal-catalyzed mechanism. In order to gain essential information for the mechanism study, a control reaction with 1 eq. of hydroquinone as a free radical scavenger was performed. It was found that the reaction was completely prohibited (Scheme 2), indicating that this decarboxylative coupling reaction with Se occurs via a free radical mechanism as in previous reports.^[6,7] Moreover, since it was found that a white precipitate was produced on mixing the reaction liquid with lime water,

it was corroborated that carbon dioxide was generated during the processes.

Thus, based on these experimental results as well as literature reports,^[7,9] a plausible mechanism of this interesting transition-metal-free decarboxylative coupling reaction is proposed. As shown in Scheme 3, Se powders (Se_8) might first generate the Se bi-radical 3 under thermal conditions.^[9] Capturing a hydrogen from substrate 1, 3 is transformed into intermediate 4 and the carboxyl radical 5 is generated. Decarboxylation of 5 produces the benzyl free radical $6^{[7]}$ which is thermodynamically stabilized by the p- π conjugation of the adjacent phenyl ring. The reaction of 6 with Se₈ leads to intermediate 7, which might produce 8 via a deselenization reaction.^[9] Dimerization of 8 leads to dibenzyl diselenide (n = 2), while the possible reaction of 8 with benzyl radical 6 produces dibenzyl selenide (n = 1). Although this mechanism remains to be fully clarified and alternative processes might also occur due to the complexity of the free radical reactions, Scheme 3 should be the most likely mechanism on the basis of the experimental results and literature reports.^[7,9]

Because of the complex free radical mechanism, it was difficult to control the reaction selectivities between diselenide and selenide. Worse yet, due to the similar polarities of the diselenide and selenide, it was also difficult to separate them via regular chromatography methods such as the flash column chromatography or preparative TLC. Therefore, this decarboxylative coupling method is of less utility for the purposes of



SCHEME 2 Control reaction with hydroquinone as free radical scavenger



synthesizing pure dibenzyl diselenide or dibenzyl selenide. Fortunately, since the literature demonstrates that both diselenides and selenides are efficient catalysts in oxidation reactions,^[4,5] their mixtures may also be effective catalysts in related reactions. For this reason, we investigated the catalytic activities of mixtures **2** in the useful Baeyer–Villiger oxidation reaction of (*E*)-4phenylbut-3-en-2-one (**9**) with H_2O_2 to produce vinyl ester **10** (Scheme 4).^[11]

As shown in Figure 1, the oxidation reaction of 9 catalyzed by pure dibenzyl diselenide (n = 2) led to 10 in 82% yield; whereas, the same reaction with pure dibenzyl selenide (n = 1) as the catalyst resulted in a decreased yield of 42%. Using mixture **2** with n = 1.69 as the catalyst (prepared by the reaction of Table S1, entry 15), the Baeyer-Villiger reaction of 9 afforded 10 in 73% yield, while the reaction in the presence of catalytic mixture 2 with n = 1.41 (prepared by the reaction of Table 1, entry 2) could still produce 10 in an acceptable yield of 60%. The same oxidation reactions of 9 catalyzed by electronenriched Se catalysts (4-MeOC₆H₄Se)₂/(4-MeOC₆H₄)₂Se or electron-deficient Se catalysts (4-FC₆H₄Se)₂/(4-FC₆H₄)₂Se were also examined and they all led to decreased yields of 10 (Figure 1). Thus, considering the catalyst cost and catalytic performances, the mixtures of dibenzyl diselenide and dibenzyl selenide, prepared via the decarboxylative coupling reaction of phenylacetic



SCHEME 4 Baeyer–Villiger reaction of **9** catalyzed by **2**

acid with elemental Se reported in this work, should be preferable catalysts.

pplied rganometallic

5 of 8

Oxidative deoximation reactions are also very important in synthetic organic chemistry^[12] because oximes are easily prepared and stable compounds that allow the utilization of oximation–deoximation strategies in protection and purification of carbonyl compounds in total synthesis.^[13] They are also widely employed in the preparation of ketones from non-carbonyl starting materials, such as in the production of the spice carvone from limonene.^[14] Therefore, we then evaluated the catalytic performances of mixtures **2** in oxidative deoximation reaction, with the reaction of diphenylmethanone oxime (**11**) being chosen as the model reaction (Scheme 5).

As shown in Figure 2, catalyzed by pure dibenzyl diselenide (n = 2), the reaction of **11** afforded diphenylmethanone (**12**) in 89% yield, while the pure dibenzyl selenide (n = 1)-catalyzed reaction led to a moderate product yield of 63%. Using mixtures **2** with n = 1.69 and 1.41 as the catalysts (prepared by the reaction of Table S1, entry 15 and Table 1 entry 2), the reactions afforded **12** in 88 and 84% yields, respectively, which showed that mixtures **2** were almost as active as pure diselenide (n = 2) in a much broader range of n in this deoximation reaction than that in the previously investigated Baeyer–Villiger reaction (light blue symbols in Figure 2 versus Figure 1). The catalytic



SCHEME 5 Oxidative deoximation reaction of 11 catalyzed by 2



FIGURE 1 Baeyer–Villiger oxidation reactions of 9 catalyzed by diselenide/ selenide mixtures



FIGURE 2 Oxidative deoximation reactions of 11 catalyzed by diselenide/ selenide mixtures

performances of electron-enriched and electron-deficient diselenides/selenides were also evaluated in the deoximation reaction (red and black diamonds in Figure 2), and they were found to be less reactive than mixtures **2** (blue diamonds in Figure 2), which were even cheaper for being prepared using unsubstituted **1** as the more accessible and inexpensive starting material.

Moreover, a series of organoselenium compounds were synthesized through the decarboxylative coupling method and their catalytic activities were investigated in the oxidative deoximation reactions of **11** (Figure 3). Introducing an electron-donating group into the substrate did not affect the reaction (Figure 3, black bars, entries 2 versus 1), while electron-deficient substrates were preferable, affording elevated product yields (Figure 3, black bars, entries 3–5 versus 1 and 2). The method was also applicable for the preparation of branched or cyclic aliphatic organoselenium compounds (Figure 3, black



FIGURE 3 Synthesis and evaluation of diselenide/selenide mixtures

bars, entries 6–8). Chained aliphatic organoselenium compounds were also accessible (Figure 3, black bars, entries 9 and 10) and showed higher catalytic activities in the oxidative deoximation reactions (Figure 3, blue bars, entries 9 and 10 versus 6–8). Electron-enriched or electron-deficient diselenide/selenide mixtures were less catalytically active than the dibenzyl diselenide/selenide mixture (Figure 3, blue bars, entries 2–10 versus 1), albeit their higher *n* values (Figure 3, red bars, entries 2–10 versus 1). The decarboxylative coupling reaction of benzoic acid could not occur, possibly due to the good stability of the substrate as well as the instability of the phenyl free radical intermediate (Figure 3, black bar, entry 11).

3 | CONCLUSIONS

We have found an interesting transition-metal-free decarboxylative coupling reaction of phenylacetic acid with elemental Se. Compared with traditional methods to introduce Se into molecules, this reaction employs cheap Se powders as the Se source and the generation of toxic and odorous selenol intermediates and solid wastes such as magnesium salts can be avoided, affording a more direct and relatively green access to dibenzyl diselenide/selenide mixtures, which are found to be good catalysts in Baeyer–Villiger reactions and oxidative deoximation reactions. The idea of using easily accessible organoselenium compound mixtures as catalysts is novel and will be helpful for reducing catalyst costs, so that the application of organoselenium catalysis in large-scale production may be realized in not far distant future.

4 | EXPERIMENTAL PROCEDURES

4.1 | General methods

Chemicals were purchased from a commercial source with purities of more than 98%. Solvents were analytically pure (AR) and were directly used without any special treatment. NMR spectra were recorded with a Bruker Avance 400 instrument (400 MHz for ¹H NMR, 100 MHz for ¹³C NMR). Chemical shifts for ¹H NMR were referred to internal Me₄Si (0 ppm).

4.2 | Typical procedure for decarboxylative coupling of phenylacetic acid with elemental Se

To a reaction tube, 1 mmol of **1**, 4 mmol of Se powders, 2 mmol of DIEA and 1 ml of DMF were added. The tube was then charged with N_2 and was heated at 150°C for

20 h. After cooling to room temperature, the produced mixtures **2** containing dibenzyl diselenide and dibenzyl selenide could be isolated by flash column chromatography (eluent: petroleum ether). They were subjected to ¹H NMR analysis to calculate the Se content indexes *n* (for details, see the supporting information). The molar ratio of diselenide versus selenide could be calculated by the equation: diselenide/selenide = (n - 1)/(2 - n).

4.3 | Details of Baeyer–Villiger oxidation of (*E*)-4-phenylbut-3-en-2-one with H_2O_2

To a reaction tube, 1 mmol of (*E*)-4-phenylbut-3-en-2one, 0.05 mmol of **2**, 4 mmol of H_2O_2 and 2 ml of MeCN were added. The mixture was then stirred at room temperature for 24 h. An amount of 5 ml of water was added and the liquid was extracted with EtOAc (5 ml × 3). The combined organic layers were dried with anhydrous Na₂SO₄ and the organic solvent was evaporated using a rotary evaporator. The residue was separated by flash column chromatography (eluent: petroleum ether– EtOAc = 8/1) to afford the vinyl ester product **10**.

4.4 | Details of oxidative deoximation of diphenylmethanone oxime

To a reaction tube, 1 mmol of diphenylmethanone oxime, 0.05 mmol of **2**, 0.3 mmol of H_2O_2 and 2 ml of MeCN were added. The mixture was then stirred in open air at 60°C for 24 h. An amount of 5 ml of water was added and the liquid was extracted with EtOAc (5 ml × 3). The combined organic layers were dried with anhydrous Na₂SO₄ and the organic solvent was evaporated using a rotary evaporator. The residue was separated by flash column chromatography (eluent: petroleum ether–EtOAc = 10/1) to afford the diphenylmethanone product **12**.

ACKNOWLEDGMENTS

We thank NNSFC (21202141), Priority Academic Program Development of Jiangsu Higher Education Institutions (PAPD), Top-notch Academic Programs Project of Jiangsu Higher Education Institutions (TAPP), the Nature Science Foundation of Guangling College (ZKZD17005, ZKZZ18001) and the Open Project Program of Jiangsu Key Laboratory of Zoonosis (R1509, R1609) for financial support.

ORCID

Lei Yu bhttps://orcid.org/0000-0001-5659-7289

8 of 8 WILEY Organometallic Chemistry

REFERENCES

- a) A. M. S. Recchi, D. F. Back, G. Zeni, J. Org. Chem. 2017, 82, 2713. b) S. Kodama, T. Saeki, K. Mihara, S. Higashimae, S. Kawaguchi, M. Sonoda, A. Nomoto, A. Ogawa, J. Org. Chem. 2017, 82, 12477. c) H.-X. Luan, H.-J. Sun, B.-J. Xue, X.-Y. Li, Chin. J. Org. Chem. 2017, 37, 1392. d) M. Wang, Q.-L. Fan, X.-F. Jiang, Org. Lett. 2016, 18, 5756. e) L. Sancineto, A. Mariotti, L. Bagnoli, F. Marini, J. Desantis, N. Iraci, C. Santi, C. Pannecouque, O. Tabarrini, J. Med. Chem. 2015, 58, 9601.
- [2] For reviews, see:aD. M. Freudendahl, S. Santoro, S. A. Shahzad, C. Santi, T. Wirth, *Angew. Chem.* 2009, 121, 8559. b) *Angew. Chem. Int. Ed.* 2009, 48, 8409. c) C. Santi, S. Santoro, B. Battistelli, *Curr. Org. Chem.* 2010, 14, 2442. d) S. Santoro, J. B. Azeredo, V. Nascimento, L. Sancineto, A. L. Braga, C. Santi, *RSC Adv.* 2014, 4, 31521. e) J. Młochowski, H. Wójtowicz-Młochowska, *Molecules* 2015, 20, 10205. f) A. Breder, S. Ortgies, *Tetrahedron Lett.* 2015, 56, 2843. g) R.-Z. Guo, L.-H. Liao, X.-D. Zhao, *Molecules* 2017, 22, 835.
- [3] M. P. Rayman, Lancet 2012, 379, 1256.
- [4] For selected articles, please see:a)X. Liu, Y.-Y. Liang, J.-Y. Ji, J. Luo, X.-D. Zhao, J. Am. Chem. Soc. 2018, 140, 4782. b) J. Luo, Q. Cao, X. Cao, X. Zhao, Nat. Commun. 2018, 9, 527. c) R.-Z. Guo, J.-C. Huang, X.-D. Zhao, ACS Catal. 2018, 8, 926. d) Z.-C. Zhu, J. Luo, X.-D. Zhao, Org. Lett. 2017, 19, 4940. e) L. Sancineto, F. Mangiavacchi, C. Tidei, L. Bagnoli, F. Marini, A. Gioiello, J. Scianowski, C. Santi, Org. Chem. 2017, 6, 988. f) S. Ortgies, C. Depken, A. Breder, Org. Lett. 2016, 18, 2856. g) R.-Z. Guo, J.-C. Huang, H.-Y. Huang, X.-D. Zhao, Org. Lett. 2016, 18, 504. h) A. J. Cresswell, S. T.-C. Eey, S. E. Denmark, Nat. Chem. 2015, 7, 146. i) S. Ortgies, A. Breder, Org. Lett. 2015, 17, 2748. j) L. Sancineto, C. Tidei, L. Bagnoli, F. Marini, E. J. Lenardao, C. Santi, Molecules 2015, 20, 10496. k) F. Chen, C. K. Tan, Y.-Y. Yeung, J. Am. Chem. Soc. 2013, 135, 1232; I)J. Trenner, C. Depken, T. Weber, A. Breder, Angew. Chem. 2013, 125, 9121. m) Angew. Chem. Int. Ed. 2013, 52, 8952. n) D. W. Tay, I. T. Tsoi, J. C. Er, G. Y. C. Leung, Y.-Y. Yeung, Org. Lett. 2013, 15, 1310. o) S. Santoro, C. Santi, M. Sabatini, L. Testaferri, M. Tiecco, Adv. Synth. Catal. 2008, 350, 2881.
- [5] For selected recent articles of our group on organoselenium catalysis, see:a)T.-T. Wang, X.-B. Jing, C. Chen, L. Yu, J. Org. Chem. 2017, 82, 9342. b) X.-B. Jing, T.-T. Wang, Y.-H. Ding, L. Yu, Appl. Catal. A 2017, 541, 107. c) X.-B. Jing, D.-D. Yuan, L. Yu, Adv. Synth. Catal. 2017, 359, 1194. d) F. Wang, L. Xu, C. Sun, Q. Xu, J.-J. Huang, L. Yu, Chin. J. Org. Chem. 2017, 37, 2115. e) Y.-G. Wang, L.-H. Yu, B.-C. Zhu, L. Yu, J. Mater. Chem. A 2016, 4, 10828. f) L. Yu, F.-L. Chen, Y.-H. Ding, ChemCatChem 2016, 8, 1033. g) L. Yu, Z.-B. Bai, X. Zhang, X.-H. Zhang, Y.-H. Ding, Q. Xu, Catal. Sci. Technol. 2016, 6, 1804. h) X. Zhang, J.-Q. Ye, L. Yu, X.-K. Shi, M. Zhang, Q. Xu, M. Lautens, Adv. Synth. Catal. 2015, 357, 955.
- [6] a) Z.-F. Cheng, T.-T. Tao, Y.-S. Feng, W.-K. Tang, J. Xu, J.-J. Dai, H.-J. Xu, J. Org. Chem. 2018, 83, 499. b) W.-K. Tang, Y.-S. Feng, Z.-W. Xu, Z.-F. Cheng, J. Xu, J.-J. Dai, H.-J. Xu,

Org. Lett. 2017, 19, 5501. c) G. J. P. Perry, I. Larrosa, Eur. J.
Org. Chem. 2017, 3517. d) Y.-H. Jin, H. Fu, Asian J. Org. Chem.
2017, 6, 368. e) Y.-G. Wang, R.-R. Liu, J.-R. Gao, Y.-X. Jia,
Chin. J. Org. Chem. 2017, 37, 691. f) Z. Zhang, S.-H. Lu, B.
Xu, X.-C. Wang, Chin. Chem. Lett. 2017, 28, 1074. g) Z.-J. Fu,
Z.-J. Li, Q.-H. Xiong, H. Cai, Chin. J. Org. Chem. 2015, 35,
984. h) Q.-L. Song, Q. Feng, K. Yang, Org. Lett. 2014, 16, 624.
i) P.-F. Wang, X.-Q. Wang, J.-J. Dai, Y.-S. Feng, H.-J. Xu,
Org. Lett. 2014, 16, 4586. j) Q.-L. Song, Q. Feng, M.-X. Zhou,
Org. Lett. 2013, 15, 5990. k) J.-J. Dai, G.-Z. Wang, X.-L. Xu,
H.-J. Xu, Chin. J. Org. Chem. 2013, 33, 2460. and references therein

- [7] a) H.-X. Zou, Y. Li, Y. Yang, J.-H. Li, J.-N. Xiang, Adv. Synth. Catal. 2018, 360, 1439. b) H. Li, C. P. Breen, H. Seo, T. F. Jamison, Y.-Q. Fang, M. W. Bio, Org. Lett. 2018, 20, 1338. c) X.-S. Liu, Z.-T. Wang, X.-M. Cheng, C.-Z. Li, J. Am. Chem. Soc. 2012, 134, 14330.
- [8] a) D.-L. Zhang, Z. Wei, L. Yu, *Sci. Bull.* 2017, *62*, 1325. b) H.-L.
 Zhou, J.-J. Gong, B.-L. Xu, L. Yu, Y.-N. Fan, *Appl. Catal. A* 2016, *527*, 30. c) L. Yu, Z. Han, *Mater. Lett.* 2016, *184*, 312.
- [9] L. Yu, Y.-L. Wu, T. Chen, Y. Pan, Q. Xu, Org. Lett. 2013, 15, 144.
- [10] For details, see supporting information.
- [11] a) X.-Z. Cui, J.-L. Shi, *Sci. China Mater.* 2016, *59*, 675. b) C. Jimenez-Sanchidrian, J. R. Ruiz, *Tetrahedron* 2008, *64*, 2011.
 c) G. J. ten Brink, I. W. C. E. Arends, R. A. Sheldon, *Chem. Rev.* 2004, *104*, 4105.
- [12] G. Zhang, X. Wen, Y. Wang, W. Mo, C. Ding, Prog. Chem. 2012, 24, 361. and references therein
- [13] E. J. Corey, P. B. Hopkins, S. Kim, S. E. Yoo, K. P. Nambiar, J. R. Falck, J. Am. Chem. Soc. 1979, 101, 7131.
- [14] a) C. Isart, D. Bastida, J. Burés, J. Vilarrasa, Angew. Chem. **2011**, 123, 3333. b) Angew. Chem. Int. Ed. **2011**, 50, 3275. c) A. Grirrane, A. Corma, H. Garcia, J. Catal. **2009**, 268, 350. d) R. Reitsema, J. Org. Chem. **1958**, 23, 2038. e) E. E. Royals, S. E. Horne Jr., J. Am. Chem. Soc. **1951**, 73, 5856.

SUPPORTING INFORMATION

Additional supporting information may be found online in the Supporting Information section at the end of the article.

How to cite this article: Cao H, Liu M, Qian R, Zhang X, Yu L. A cost-effective shortcut to prepare organoselenium catalysts via decarboxylative coupling of phenylacetic acid with elemental selenium. *Appl Organometal Chem*. 2018;e4599. https://doi.org/10.1002/aoc.4599