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Organocatalyzed arylalkylation of activated alkenes via decarboxylation of $PhI(O_2CR)_2$: efficient synthesis of oxindoles

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ABSTRACT

A novel organocatalyzed arylalkylation of activated alkenes has been developed. This reaction was initiated from the decomposition of $PhI(O_2CR)_2$ to generate alkyl radical, followed by addition to alkenes. Then the formed radical was trapped by aromatic ring to generate the cyclized products. This method presents an efficient road to synthesis of a variety of oxindoles.

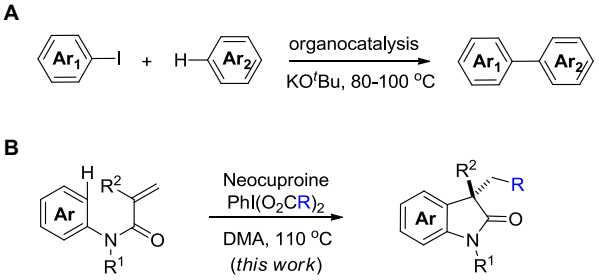
1. Introduction

Difunctionalization of alkenes is an important transformation in organic chemistry, and have been extensively investigated in the last several decades. Among those reactions, transition metal generally exhibits excellent reactivity and selectivity.[1] For instance, palladium-catalyzed oxidative difunctionalization of alkenes presents one of most efficient way to achieve directed transformation of alkenes to a variety of vicinal functionalized compounds,[2] such as aminoalcohol,[3] diamine,[4] diol,[5] and aminohalides.[6] In contrast, oxidative dicarbonation of alkene is less reported.[7]

Recently, Lei,[8] Shi,[9] and Hayashi[10] independently reported a metal-free reaction between aryliodide and aromatic compounds in the present of KO^{t}Bu (Scheme 1A). Notable, organocatalysis plays an important role in those transformations.[11] Herein, we reported a metal free arylalkylation of alkenes. This reaction involves a radical pathway, and the initial alkyl radical generates from decarboxylation of hypervalent dicarboxylate iodide reagent (Scheme 1B).[12,13] It is worth noting that a bisnitrogen ligand plays a significant effect on this transformation.

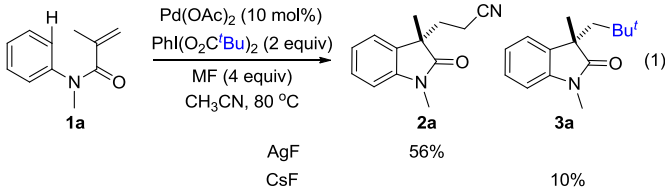
2. Results and discussion

Very recently, our group reported a palladium-catalyzed oxidative arylalkylation of activated alkenes, which involves a dual



Scheme 1. Organocatalyzed reactions.

C–H bond cleavage.[14] During the optimization reaction condition, we found that the reaction afforded 56% yield of **2a** in the presence of AgF. Interestingly, the unexpected product **3a** derived from addition of two carbon nucleophiles cross double bond was obtained in the reaction with CsF as base, albeit in low yield (Eq. 1). And these two carbon nucleophiles were generated from C–H cleavage of aniline and decarboxylation of carboxylic acid, respectively.



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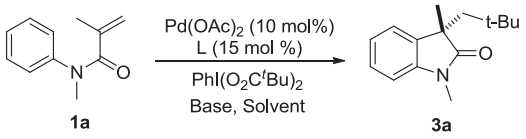
Above observation promoted us to explore this transformation. As shown in Table 1, the screening results of the base indicated that CsOPiv exhibited better reactivity than other bases, such as CsF and NaOPiv (entries 1–3). Further studies exhibited that a bidentate nitrogen-containing ligand is beneficial to the reaction, and the ligand **L3** was shown to give the best yield (entries 4–7, Fig. 1). When $CaCO_3$ was added, the reaction yield was increased to 48% (entry 8). Obvious solvent effect was also observed, and DMA (*N*,*N*-dimethyl acetamide) was proven to be the best for this reaction (entries 8–12). Elevating the reaction temperature, the reaction yielded the highest results at 110 °C (entries 13 and 14). Surprisingly, the controlling experiments showed that Palladium catalyst was not necessary, and a similar yield was given. But the reaction yield was significant reduced in the absence of ligand **L3** (entries 15 and16). In addition, the reaction was inhibited by employing 2,2,6,6-tetramethyl-1-piperidinyloxyl (TEMPO) as a radical scavenger, which suggested that a radical pathway should be involved.[15] Notable, the dinitrogen ligand plays an important role to promote this radical cyclization.

Table 1
Screening results[a]



Entry	Base	Ligand	Solvent	Temp	Yield (**3a**)
1	CsF	—	MeCN	80 °C	5%
2	CsOPiv	—	MeCN	80 °C	18%
3	NaOPiv	—	MeCN	80 °C	0
4	CsOPiv	**L1**	MeCN	80 °C	23%
5	CsOPiv	**L2**	MeCN	80 °C	31%
6	CsOPiv	**L3**	MeCN	80 °C	37%
7	CsOPiv	**L4**	MeCN	80 °C	21%
8[c]	CsOPiv	**L3**	MeCN	80 °C	48%
9[c]	CsOPiv	**L3**	DMA	80 °C	78%
10[c]	CsOPiv	**L3**	Dioxane	80 °C	45%
11[c]	CsOPiv	**L3**	Toluene	80 °C	36%
12[c]	CsOPiv	**L3**	NMP	80 °C	43%
13[c]	CsOPiv	**L3**	DMA	90 °C	80%
14[c]	CsOPiv	**L3**	DMA	110 °C	83% (75%)[b]
15[c,d]	CsOPiv	**L3**	DMA	110 °C	82%
16[c,d]	CsOPiv	—	DMA	110 °C	45%
17[c,e]	CsOPiv	**L3**	DMA	110 °C	0

[a] The reaction was run in 0.1 mmol scale, GC yield with $C_{14}H_{30}$ as internal standard.
[b] Isolated yield.
[c] $CaCO_3$ (3 equiv).
[d] No Pd $(OAc)_2$.
[e] TEMPO (1 equiv).

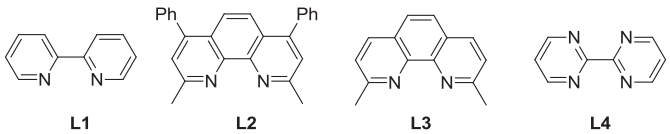
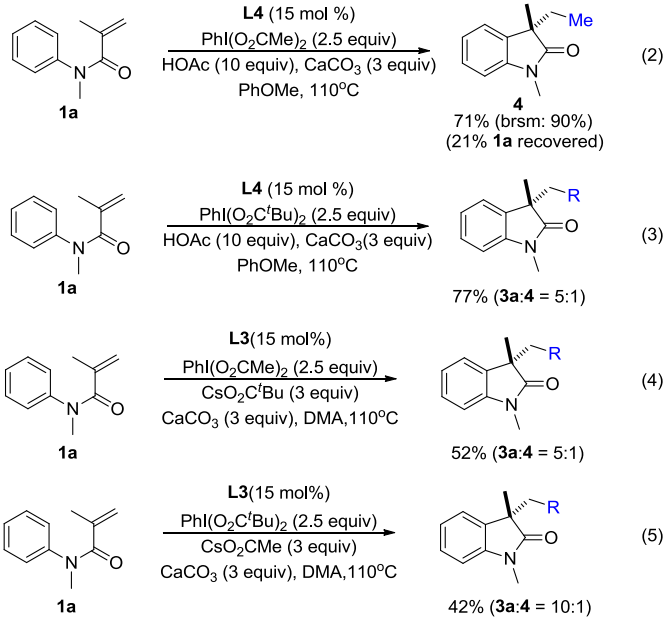


Fig. 1. The structure of ligand **L1**–**L4**.

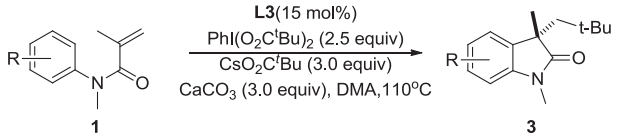
Based on the optimization condition in hand, the scope of substrates was investigated as shown in Table 2. The effect of the protecting group on the nitrogen atom was firstly probed. For the substrate **1a** bearing a methyl group on nitrogen atom, the reaction proceeded smoothly to provide product **2a** in good yield (entry 1). In contrast, the substrates **1b** and **1c** with an electron-withdrawing group on nitrogen did not yield the desired products **3b** and **3c** (entries 2 and 3). For the substrate bearing fluoride (**1d**) or chloride (**1e**) in aromatic ring, the reaction presented similar reactivity to give high yields (entries 4 and 5). However, the active substrate with bromide (**1f**) or iodide (**1g**) gave slightly lower yield (entries 6 and 7). Moreover, when substrate has an electron-withdrawing group, such nitro (**1h**), trifluoromethyl (**1i**), and ester (**1j**) group, the reaction afforded the corresponding oxindole product in low yields (entries 8–10). In contrast, substrate with electron-donating group afforded the desired products **3k**–**s** in good to excellent yields. The position of the substituents on the aryl ring had no significant influence on the efficiency (entries 12 and 14). The substrates having two substituents on the aryl ring were still good for this transformation (**3p**–**r**). Finally, substrate (**1t**), without a substituent at the position of the olefin, did not afford the desired product **3t**.

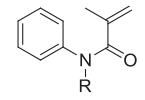
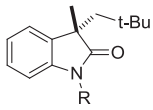
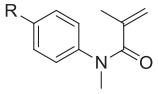
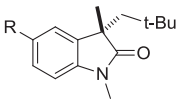
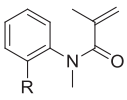
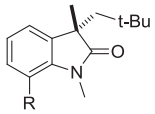
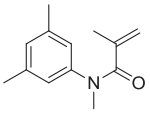
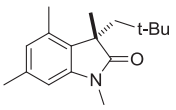
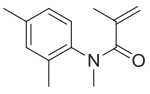
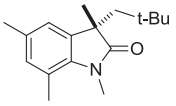
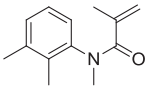
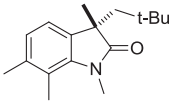
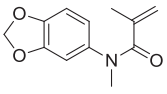
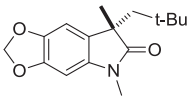
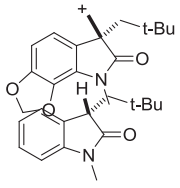
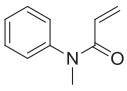
As we mentioned above, this reaction was involved a *tert*-butyl radical, which was generated from the decomposition of PhI(O-Piv)$_2$. In contrast, the methyl radical is less stable than *tert*-butyl radical. Thus, the reaction of PhI$(OAc)_2$ was further studied. It is delighted that the reaction of **1a** with PhI$(OAc)_2$ proceeded smoothly to afford desired decarboxylation product **4** in 71% yield, with recovery of 21% **1a** (Eq. 2).[16] This observation presented an efficient method to introduce a methyl into molecules. When **1a** was treated with the same reaction condition except with PhI(O-Piv)$_2$ instead of PhI$(OAc)_2$, the reaction afforded the mixture of **3a** and **4** with a ratio of 5:1 (Eq. 3). Furthermore, the similar results were obtained in the previous catalytic system (Eqs. 4 and 5). Those observations suggested that an equilibrium was existed between PhI$(OAc)_2$ and PhI$(OPiv)_2$ in the presence of HOAc or HOPiv, and the decarboxylation of PhI$(OPiv)_2$ is much easy than that of PhI$(OAc)_2$.



A possible mechanism was shown in Scheme 2: the reaction was initiated from decomposition of hypervalent iodine to form a *tert*-butyl radical. Then following addition of radical to double bond formed intermediate **I**, which was trapped by a benzenoid π-system. It is worth noting that addition of bidental nitrogen ligand **L3** was significantly helpful in this reaction.[17] It is possible that the radical intermediate stabilized by **L3** had a long life time resulting in full conversion. However, the detailed mechanism for this process is unclear at this moment.

Table 2
Organocatalyzed arylalkylation[a]

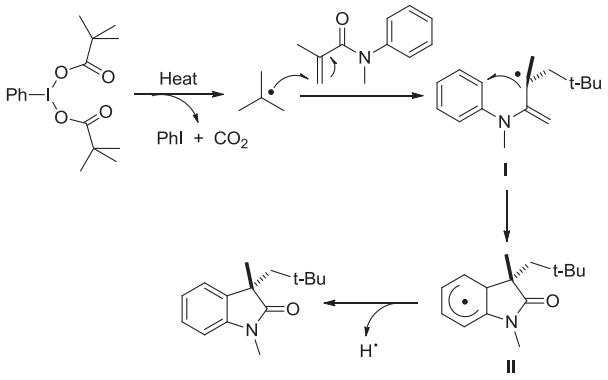


Entry	Substrate		Product		Yield[b]
1		R=Me **1a**		**3a**	75%
2		Ts **1b**		**3b**	0%
3		Ac **1c**		**3c**	0%
4		R=F **1d**		**3d**	71%
5		Cl **1e**		**3e**	76%
6		Br **1f**		**3f**	66%
7		I **1g**		**3g**	59%
8		NO_2 **1h**		**3h**	0%
9		CF_3 **1i**		**3i**	18%
10		CO_2Me **1j**		**3j**	47%
11		OCF_3 **1k**		**3k**	77%
12		Me **1l**		**3l**	86%
13		OMe **1m**		**3m**	67%
14		R=Me **1n**		**3n**	86%
15		Ph **1o**		**3o**	64%
16		**1p**		**3p**	71%
17		**1q**		**3q**	78%
18		**1r**		**3r**	69%
19		**1s**		**3s**	47% (1:1)
				**3s′**	
20		**1t**		**3t**	0

[a] Reaction condition is same with entry 15 in Table 1 in 0.2 mmol scale.
[b] Isolated yield.

3. Conclusion

In conclusion, we have developed a novel organocatalyzed arylalkylation of activated alkenes, which is a decarboxylation of hypervalent dicarboxylate iodide. This reaction represents an efficient way to synthesize a variety of oxindoles from simple aryl acrylamides. The addition of organocatalyst significantly improved the reaction yield. The further studies on the understanding mechanism and application are under progress.



Scheme 2. The proposed mechanism.

4. Experimental section

4.1. General methods

All commercially available compounds were used as received. ^1H, ^{13}C, and ^{19}F spectra were recorded on a Varian Mercury-400 MHz (400 MHz for ^1H; 376 MHz for ^{19}F; 100 MHz for ^{13}C) or a Bucker Avance-300 MHz (300 MHz for ^1H; 282 MHz for ^{19}F; 75 MHz for ^{13}C) spectrometer. $CDCl_3$ was purchased from J&K. The chemical shifts (δ) were given in parts per million relative to internal standard TMS (0 ppm for ^1H), $CDCl_3$ (77.0 ppm for ^{13}C). Flash column chromatography was performed on silica gel 60 (particle size 200–400 mesh ASTM, purchased from Yantai, China) and eluted with petroleum ether/ethyl acetate. Solvents were dried and purified according to the procedure from 'Purification of Laboratory Chemicals book'. Ligands and palladium catalyst were purchased from Aldrich or Alfa Aesar.

4.2. General procedure for aryalkylation of activated alkenes (see Table 2)

In a TFE sealed dry glass tube, CsOPiv (146 mg, 0.6 mmol), $PhI(OOC^tBu)_2$ (204 mg, 0.5 mmol), 2,9-dimethyl-1,10-phenanthroline (6.4 mg, 0.03 mmol), CaCO3 (60 mg), and alkenes **1** (0.2 mmol) were dissolved in dry DMA (1.0 mL). The mixture was stirred at 110 °C for 24 h. Then ethyl acetate was added and the mixture was filtered through a plug of Celite. The solvent was removed under vacuum, and the residue was purified by column chromatography on silica gel with a gradient eluant of petroleum ether (or hexane) and ethyl acetate to afford the products **3**. The results were summarized in Table 2.

4.3. Characterization of products

*4.3.1. 1,3-Dimethyl-3-neopentylindolin-2-one (Table 2, entry 1, **3a**).* Yield 75%. ^1H NMR (400 MHz, $CDCl_3$) δ 7.26 (t, J=8.8 Hz, 1H), 7.20 (d, J=7.6 Hz, 1H), 7.03 (t, J=7.6 Hz, 1H), 6.85 (d, J=8.0 Hz, 1H), 3.22 (s, 3H), 2.15 (d, J=14.4 Hz, 1H), 1.85 (d, J=14.4 Hz, 1H), 1.29 (s, 3H), 0.60 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 181.0, 142.7, 134.0, 127.4, 123.8, 121.9, 107.9, 50.6, 47.3, 31.7, 30.7, 28.2, 26.1. HRMS: m/z (EI) calculated [M+]: 231.1623, measured: 231.1626.

*4.3.2. 5-Fluoro-1,3-dimethyl-3-neopentylindolin-2-one (Table 2, entry 4, **3d**).* Yield 71%. ^1H NMR (400 MHz, $CDCl_3$) δ 7.00–6.93 (m, 2H), 6.77 (dd, J=8.1, 4.2 Hz, 1H), 3.22 (s, 3H), 2.16 (d, J=14.4 Hz,

1H), 1.83 (d, J=14.4 Hz, 1H), 1.29 (s, 3H), 0.63 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 180.6, 159.1 (d, J=238.7 Hz), 137.3 (d, J=275.9 Hz), 135.8, 113.7 (d, J=23.1 Hz), 111.8 (d, J=23.8 Hz), 108.4 (d, J=8.2 Hz), 50.7, 47.8, 31.7, 30.8, 28.2, 26.3. ^{19}F NMR (376 MHz, $CDCl_3$) δ −121.4. HRMS: m/z (EI) calculated [M+]: 249.1529, measured: 249.1530.

4.3.3. 5-Chloro-1,3-dimethyl-3-neopentylindolin-2-one (Table 2, entry 5, ***3e****).* Yield 76%. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.24 (dd, J=8.1, 2.1 Hz, 1H), 7.18 (d, J=2.1 Hz, 1H), 6.79 (d, J=8.4 Hz, 1H), 3.22 (s, 3H), 2.16 (d, J=14.4 Hz, 1H), 1.84 (d, J=14.4 Hz, 1H), 1.29 (s, 3H), 0.62 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 180.3, 141.3, 135.9, 127.3, 124.2, 108.9, 50.6, 47.6, 31.7, 30.8, 28.1, 26.3. HRMS: m/z (EI) calculated [M+]: 265.1233, measured: 265.1234.

4.3.4. 5-Bromo-1,3-dimethyl-3-neopentylindolin-2-one (Table 2, entry 6, ***3f****).* Yield 66%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (d, J=8.4 Hz, 1H), 7.31 (s, 1H), 6.73 (d, J=8.4 Hz, 1H), 3.20 (s, 3H), 2.15 (d, J=14.4 Hz, 1H), 1.83 (d, J=14.4 Hz, 1H), 1.29 (s, 3H), 0.63 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 180.3, 141.9, 136.4, 130.3, 127.0, 114.7, 109.4, 50.7, 47.6, 31.8, 30.8, 28.1, 26.3. HRMS: m/z (EI) calculated [M+]: 309.0728, measured: 309.0725.

4.3.5. 5-Iodo-1,3-dimethyl-3-neopentylindolin-2-one (Table 2, entry 7, ***3g****).* Yield 59%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (d, J=8.0 Hz, 1H), 7.48 (s, 1H), 6.63 (d, J=8.0 Hz, 1H), 3.20 (s, 3H), 2.14 (d, J=14.4 Hz, 1H), 1.82 (d, J=14.4 Hz, 1H), 1.28 (s, 3H), 0.62 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 180.1, 142.5, 136.7, 136.3, 132.6, 110.0, 84.5, 50.7, 47.4, 31.7, 30.8, 28.1, 26.2. HRMS: m/z (EI) calculated [M+]: 357.0590, measured: 357.0591.

4.3.6. 1,3-Dimethyl-3-neopentyl-5-(trifluoromethyl)indolin-2-one (Table 2, entry 9, ***3i****).* Yield 18%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.12 (d, J=8.4 Hz, 1H), 7.09 (s, 1H), 6.83 (d, J=8.4 Hz, 1H), 3.23 (s, 3H), 2.18 (d, J=14.4 Hz, 1H), 1.85 (d, J=14.4 Hz, 1H), 1.31 (s, 3H), 0.61 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 180.7, 141.5, 135.7, 120.8, 117.9, 108.3, 50.8, 47.7, 31.8, 30.8, 30.7, 28.1, 28.0, 26.4. ^{19}F NMR (376 MHz, $CDCl_3$, ppm) δ −58.4. HRMS: m/z (EI) calculated [M+]: 299.1497, measured: 299.1498.

4.3.7. Methyl 1,3-dimethyl-3-neopentyl-2-oxoindoline-5-carboxylate (Table 2, entry 10, ***3j****).* Yield 47%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, J=8.8 Hz, 1H), 7.89 (s, 1H), 6.90 (d, J=8.0 Hz, 1H), 3.92 (s, 3H), 3.27 (s, 3H), 2.17 (d, J=14.4 Hz, 1H), 1.93 (d, J=14.4 Hz, 1H), 1.32 (s, 3H), 0.61 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.6, 162.4, 142.4, 129.6, 125.7, 120.4, 119.3, 102.9, 47.4, 46.1, 42.6, 27.2, 26.2, 23.5, 21.8. HRMS: m/z (EI) calculated [M+]: 289.1678, measured: 289.1674.

4.3.8. 1,3-Dimethyl-3-neopentyl-5-(trifluoromethoxy)indolin-2-one (Table 2, entry 11, ***3k****).* Yield 77%. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.14 (d, J=8.1 Hz, 1H), 7.10 (s, 1H), 6.84 (d, J=8.4 Hz, 1H), 3.23 (s, 3H), 2.18 (d, J=14.4 Hz, 1H), 1.86 (d, J=14.5 Hz, 1H), 1.31 (s, 3H), 0.61 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 180.6, 144.4, 144.3, 141.4, 135.6, 120.7, 117.9, 108.2, 50.7, 47.6, 31.7, 30.7, 28.0, 26.3. ^{19}F NMR (376 MHz, $CDCl_3$) δ −58.8. HRMS: m/z (EI) calculated [M+]: 315.1446, measured: 315.1442.

4.3.9. 1,3,5-Trimethyl-3-neopentylindolin-2-one (Table 2, entry 12, ***3l****).* Yield 86%. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.05 (d, J=10.8 Hz, 1H), 7.02 (s, 1H), 6.74 (d, J=11.2 Hz, 1H), 3.20 (s, 3H), 2.34 (s, 3H), 2.14 (d, J=14.3 Hz, 1H), 1.84 (d, J=14.4 Hz, 1H), 1.28 (s, 3H), 0.61 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 181.0, 134.2, 131.4, 127.7, 124.7, 107.7, 50.7, 47.4, 31.7, 30.8, 28.3, 26.2, 21.2. HRMS: m/z (EI) calculated [M^+]: 245.1780, measured: 245.1781.

4.3.10. 5-Methoxy-1,3-dimethyl-3-neopentylindolin-2-one (Table 2, entry 13, ***3m****).* Yield 67%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.83–6.74 (m, 3H), 3.80 (s, 3H), 3.20 (s, 3H), 2.15 (d, J=14.4 Hz, 1H), 1.83 (d, J=14.4 Hz, 1H), 1.29 (s, 3H), 0.63 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 180.6, 155.6, 136.4, 135.6, 111.6, 111.4, 108.2, 55.8, 50.7, 47.7, 31.7, 30.8, 28.3, 26.2. HRMS: m/z (ESI) calculated [M+H]: 262.1807, measured: 262.1809.

4.3.11. 1,3,7-Trimethyl-3-neopentylindolin-2-one (Table 2, entry 14, ***3n****).* Yield 86%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.02 (d, J=7.2 Hz, 1H), 6.97 (d, J=7.2 Hz, 1H), 6.91 (t, J=7.2 Hz, 1H), 3.50 (s, 3H), 2.60 (s, 3H), 2.14 (d, J=14.3 Hz, 1H), 1.83 (d, J=14.3 Hz, 1H), 1.27 (s, 3H), 0.61 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 181.7, 140.6, 134.7, 131.1, 121.8, 119.5, 50.9, 46.6, 31.7, 30.8, 29.5, 28.6, 19.1. HRMS: m/z (EI) calculated [M+]: 245.1780, measured: 245.1781.

4.3.12. 1,3-Dimethyl-3-neopentyl-7-phenylindolin-2-one (Table 2, entry 15, ***3o****).* Yield 64%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48–7.30 (m, 5H), 7.19 (d, J=6.8 Hz, 1H), 7.09–7.01 (m, 2H), 2.74 (s, 3H), 2.19 (d, J=14.3 Hz, 1H), 1.89 (d, J=14.3 Hz, 1H), 1.34 (s, 3H), 0.67 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 181.9, 139.8, 139.1, 135.0, 130.4, 130.0, 127.7, 127.5, 125.4, 122.7, 121.2, 51.1, 46.6, 31.7, 30.8, 30.2, 28.4. HRMS: m/z (EI) calculated [M+]: 307.1936, measured: 307.1938.

4.3.13. 1,3,4,6-Tetramethyl-3-neopentylindolin-2-one (Table 2, entry 16, ***3p****).* Yield 71%. ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.63 (s, 1H), 6.53 (s, 1H), 3.19 (s, 3H), 2.35 (s, 3H), 2.08 (d, J=3.6 Hz, 2H), 1.34 (s, 3H), 0.64 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 181.3, 143.0, 137.3, 134.4, 128.1, 125.4, 106.7, 49.0, 47.8, 31.6, 29.9, 26.2, 25.3, 21.5, 18.6. HRMS: m/z (EI) calculated [M+]: 259.1936, measured: 259.1932.

4.3.14. 1,3,5,7-Tetramethyl-3-neopentylindolin-2-one (Table 2, entry 17, ***3q****).* Yield 78%. ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.84 (s, 1H), 6.79 (s, 1H), 3.48 (s, 3H), 2.55 (s, 3H), 2.28 (s, 3H), 2.12 (d, J=14.3 Hz, 1H), 1.79 (d, J=14.3 Hz, 1H), 1.26 (s, 3H), 0.62 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 181.7, 138.2, 134.9, 131.6, 131.1, 122.5, 119.2, 50.9, 46.7, 31.7, 30.8, 29.5, 28.7, 20.8, 18.9. HRMS: m/z (EI) calculated [M+]: 259.1936, measured: 259.1935.

4.3.15. 1,3,6,7-Tetramethyl-3-neopentylindolin-2-one (Table 2, entry 18, ***3r****).* Yield 69%. ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.92 (d, J=9.6 Hz, 1H), 6.84 (d, J=9.6 Hz, 1H), 3.52 (s, 3H), 2.49 (s, 3H), 2.31 (s, 3H), 2.13 (d, J=14.3 Hz, 1H), 1.80 (d, J=14.3 Hz, 1H), 1.25 (s, 3H), 0.61 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 182.2, 140.8, 137.0, 132.5, 123.5, 121.0, 118.7, 50.8, 46.3, 31.7, 30.7, 30.4, 28.7, 20.8, 14.1. HRMS: m/z (EI) calculated [M+]: 259.1936, measured: 259.1934.

4.3.16. 5,7-Dimethyl-7-neopentyl-5H-[1,3]dioxolo[4,5-f]indol-6(7H)-one and 6,8-dimethyl-6-neopentyl-6H-[1,3]dioxolo[4,5-g]indol-7(8H)-one (Table 2, entry 19, ***3s*** *and* ***3s′****).* Yield 47% (1:1). Compound **3s** ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.73 (s, 1H), 6.48 (s, 1H), 5.93 (d, J=8.8 Hz, 2H), 3.18 (s, 3H), 2.12 (d, J=14.0 Hz, 1H), 1.77 (d, J=14.0 Hz, 1H), 1.25 (s, 3H), 0.64 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 181.5, 147.2, 144.3, 143.1, 137.2, 115.7, 105.7, 101.2, 92.3, 51.0, 48.0, 32.0, 31.1, 28.6, 26.7. HRMS: m/z (ESI) calculated [M+Na]: 298.1419, measured: 298. 1421. Compound **3s′** ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.71 (d, J=7.6 Hz, 1H), 6.27 (d, J=7.6 Hz, 1H), 5.95 (d, J=8.8 Hz, 2H), 3.18 (s, 3H), 2.09 (d, J=14.4 Hz, 1H), 1.97 (d, J=14.0 Hz, 1H), 1.37 (s, 3H), 0.65 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 180.3, 144.3, 143.1, 137.2, 115.7, 105.7, 101.2, 92.3, 49.6, 46.8, 31.8, 30.3, 27.3, 26.3. HRMS: m/z (ESI) calculated [M+H]: 276.1600, measured: 276.1602.

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Supplementary data

Supplementary data related to this article can be found online at doi:10.1016/j.tet.2012.03.051.

References and notes

1. For the recent reviews, see (a) Bonet, A.; Sole, C.; Gulyas, H.; Fernandez, E. *Curr. Org. Chem.* **2010**, *14*, 2531; (b) Chemler, S. R. *Org. Biomol. Chem.* **2009**, *7*, 3009; (c) Jensen, K. H.; Sigman, M. S. *Org. Biomol. Chem.* **2008**, *6*, 4083; (d) Minatti, A.; Muniz, K. *Chem. Soc. Rev.* **2007**, *36*, 1142.
2. For reviews, see: (a) Kotov, V.; Scarborough, C. C.; Stahl, S. S. *Inorg. Chem.* **2007**, *46*, 1910; (b) Deprez, N. R.; Sanford, M. S. *Inorg. Chem.* **2007**, *46*, 1924.
3. (a) Alexanian, E. J.; Lee, C.; Sorensen, E. J. *J. Am. Chem. Soc.* **2005**, *127*, 7690; (b) Liu, G.; Stahl, S. S. *J. Am. Chem. Soc.* **2006**, *128*, 7179; (c) Desai, L. V.; Sanford, M. S. *Angew. Chem., Int. Ed.* **2007**, *46*, 5737.
4. (a) Streuff, J.; Hövelmann, C. H.; Nieger, M.; Muñiz, K. *J. Am. Chem. Soc.* **2005**, *127*, 14586; (b) Muñiz, K. *J. Am. Chem. Soc.* **2007**, *129*, 14542; (c) Sibbald, P. A.; Michael, F. E. *Org. Lett.* **2009**, *11*, 1147.
5. (a) Li, Y.; Song, D.; Dong, V. M. *J. Am. Chem. Soc.* **2008**, *130*, 2962; (b) Wang, A.; Jiang, H.; Chen, H. *J. Am. Chem. Soc.* **2009**, *131*, 3846.
6. (a) Lei, A.; Lu, X.; Liu, G. *Tetrahedron Lett.* **2004**, *45*, 1785; (b) Manzoni, M. R.; Zabawa, T. P.; Kasi, D.; Chemler, S. R. *Organometallics* **2004**, *23*, 5618; (c) Michael, F. E.; Sibbald, P. A.; Cochran, B. M. *Org. Lett.* **2008**, *10*, 5039; (d) Wu, T.; Liu, G. *J. Am. Chem. Soc.* **2009**, *131*, 16354.
7. For the Pd-catalyzed dicarbonation of alkenes, see: Liao, L.; Jana, R.; Urkalan, K. B.; Sigman, M. S. *J. Am. Chem. Soc.* **2011**, *133*, 5784 and reference therein.
8. Liu, W.; Cao, H.; Zhang, H.; Zhang, H.; Chung, K. H.; He, C.; Wang, H.; Kwong, T. Y.; Lei, A. *J. Am. Chem. Soc.* **2010**, *132*, 16737.
9. Sun, C.-L.; LI, H.; Yu, D.-G.; Yu, M.; Zhou, X.; Lu, X.-Y.; Huang, K.; Zheng, S. F.; Li, B.-J.; Shi, Z.-J. *Nat. Chem.* **2010**, *2*, 1044.
10. Shirakawa, E.; Itoh, K.; Higshino, T.; Hayashi, T. *J. Am. Chem. Soc.* **2010**, *132*, 15537.
11. For more examples, see: (a) Sun, C.-L.; Gu, Y.-F.; Huang, W.-P.; Shi, Z.-J. *Chem. Commun.* **2011**, 9813; (b) Yanagisawa, S.; Ueda, K.; Taniguchi, T.; Itami, K. *Org. Lett.* **2008**, *10*, 4673; (c) Deng, G.; Ueda, K.; Yanagisawa, S.; Itami, K. *Chem.—Eur. J.* **2009**, *15*, 333.
12. For some reactions involving alkyl radical generated from decarboxylation of hypervalent dicaboxylate iodide, see: (a) Sandin, R. B.; McCormack, W. B. *J. Am. Chem. Soc.* **1945**, *67*, 2051; (b) Togo, H.; Aoki, M.; Kuramochi, T.; Yokoyama, M. *J. Chem. Soc., Perkin Trans. 1* **1993**, 2417; (c) Bowry, V. W.; Ingold, K. U. *J. Am. Chem. Soc.* **1992**, *114*, 4992.
13. For some examples for decarboxylative coupling reactions, see: (a) Bi, H.-P.; Zhao, L.; Liang, Y.-M.; Li, C.-J. *Angew. Chem., Int. Ed.* **2009**, *48*, 792; (b) Lalic, G.; Aloise, A. D.; Shair, M. D. *J. Am. Chem. Soc.* **2003**, *125*, 2852; (c) Trost, B. M.; Xu, J. *J. Am. Chem. Soc.* **2005**, *127*, 17180; (d) Mohr, J. T.; Nishimata, T.; Behenna, D. C.; Stoltz, B. M. *J. Am. Chem. Soc.* **2006**, *128*, 11348; (e) Patil, N. T.; Huo, Z.; Yamamoto, Y. *J. Org. Chem.* **2006**, *71*, 6991 For a review, see; (f) Gooβen, L. J.; Rodriguez, N.; Gooβen, K. *Angew. Chem., Int. Ed.* **2008**, *47*, 3100.
14. Wu, T.; Mu, X.; Liu, G. *Angew. Chem., Int. Ed.* **2011**, *50*, 12578.
15. For some examples for the sythesis of oxindole through radical process, see: (a) Fukuyama, T.; Chen, X.; Peng, G. *J. Am. Chem. Soc.* **1994**, *116*, 3127; (b) Tokuyama, H.; Yamashita, T.; Reding, M. T.; Kaburagi, Y.; Fukuyama, T. *J. Am. Chem. Soc.* **1999**, *121*, 3791; (c) Reding, M. T.; Fukuyama, T. *Org. Lett.* **1999**, *1*, 973; (d) Yokoshima, S.; Ueda, T.; Kobayashi, S.; Sato, A.; Kuboyama, T.; Tokuyama, H.; Fukuyama, T. *J. Am. Chem. Soc.* **2002**, *124*, 2137.
16. The reaction gave a very poor yield in the standard reaction of Table 2.
17. A similar reaction was reported to give arylalkylation in low yield in the absence of organocatalyst. For detail, see: Leroi, C.; Bertin, D.; Dufils, P.-E.; Gigmes, D.; Marque, S.; Tordo, P.; Couturier, J.-L.; Guerret, O.; Ciufolini, M. A. *Org. Lett.* **2003**, *5*, 4943.