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One-pot green synthesis of enamides and 1,3-diynes

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ABSTRACT

A green organic synthetic method combining reductive acylation of ketoximes and oxidative coupling of terminal alkynes was developed. This novel process enables enamides and 1,3-diynes to be synthesized simultaneously in high yields and under mild conditions without the use of terminal reductants/oxidants.

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1. Introduction

Oxidation and reduction are fundamental reactions; however, these reactions produce reduced or oxidized wastes because of their intrinsic properties. In green chemistry, O_2 or H_2O_2 is used in many oxidations [1–5], and H_2 is used in many reductions [6–9]. These reactions, which produce no byproducts or only water as a byproduct, are ideal transformations. However, there are many organic transformations that require stoichiometric or super-stoichiometric terminal oxidants such as $Cr(VI)$, $Cu(II)$, periodate, and *m*-CPBA, or terminal reductants such as nitrites, Zn powder, Fe powder, stannous chloride, and Hantzsch dihydropyridines [10–13]. In accord with the principles of green chemistry [10–16], we hypothesized that if an oxidation was combined with a reduction in one pot, the use of oxidants and reductants could be avoided. This would be an ideal method for minimizing waste generation.

Enamides are versatile building blocks in organic synthesis

[17–24]. However, the preparation of enamides involves reductive acylation of ketoximes in the presence of super-stoichiometric Fe powder, PEt_3 , or $NaHSO_3$ [25–29]. 1,3-Diynes are useful structures in linearly π -conjugated acetylenic oligomers and nonlinear optical materials [30–32]. The conventional method for the synthesis of 1,3-diynes is oxidative homocoupling of terminal alkynes in the presence of Ag_2O , Me_3NO , $Cu(II)$, or O_2 [33–38]. In this paper, we describe a promising example of green organic synthesis, which combines the oxidative coupling of terminal alkynes for 1,3-diyne formation with reductive acylation of ketoximes for enamide preparation in one pot (Scheme 1).

2. Experimental

2.1. General remarks

Unless otherwise stated, all reagents and solvents were

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Scheme 1. [Pd/Cu]-catalyzed synthesis of enamides and 1,3-diynes.

purchased from commercial suppliers and used without further purification. ^1H and ^{13}C NMR spectra were recorded using Varian instruments at 400 and 100 MHz, respectively, with tetramethylsilane as an internal standard. All products were isolated using short chromatography on a silica-gel (200–300 mesh) column, with petroleum ether (60–90 °C) and EtOAc as the eluent, unless otherwise stated. Compounds that had previously been described in the literature were characterized by comparison of their ^1H NMR and ^{13}C NMR spectra with the reported data template.

2.2. General procedure for synthesis of enamide **3a** and 1,3-diyne **4a**

A 25 mL round-bottomed flask charged with ketoxime **1a** (67.5 mg, 0.5 mmol), phenylacetylene **2a** (102.0 mg, 1.0 mmol), acetic anhydride (102.0 mg, 1.0 mmol), pyridine (47.4 mg, 0.6 mmol), CuI (9.5 mg, 10 mol%), and Pd(PPh₃)₂Cl₂ (0.7 mg, 0.2 mol%) in 1,2-dichloroethane (5.0 mL) was stirred at 120 °C for 5 h under Ar. After completion of the reaction (detected using thin-layer chromatography), the reaction mixture was cooled to room temperature, diluted with EtOAc (10 mL), and washed with H₂O (10 mL), brine (10 mL), and CuSO₄ (2 mol/L, 5 mL). The organic layers were dried over anhydrous Na₂SO₄ and evaporated in vacuo. The residue was purified by chromatography on silica gel to afford enamide **3a** (77.3 mg, 96% yield) and 1,3-diyne **4a** (82.8 mg, 82% yield).

2.3. Analytical data for enamides **3** and 1,3-diynes **4**

N-(1-Phenylvinyl)acetamide (**3a**). ^1H NMR (400 MHz, CDCl₃) δ 7.39–7.34 (m, 6H), 5.78 (s, 1H), 5.07 (s, 1H), 2.04 (s, 3H). ^{13}C NMR (100 MHz, CDCl₃) δ 169.4, 140.5, 138.2, 128.5, 126.0, 102.6, 24.3.

N-[1-(*p*-Tolyl)vinyl]acetamide (**3b**). ^1H NMR (400 MHz, CDCl₃) δ 7.30 (d, J = 7.2 Hz, 2H), 7.16 (d, J = 8.0 Hz, 2H), 7.10 (s, 1H), 5.77 (s, 1H), 5.04 (s, 1H), 2.35 (s, 3H), 2.07 (s, 3H). ^{13}C NMR (100 MHz, CDCl₃) δ 169.2, 140.4, 138.5, 135.5, 129.3, 125.9, 101.9, 24.4, 21.1.

N-[1-(4-Methoxyphenyl)vinyl]acetamide (**3c**). ^1H NMR (400 MHz, CDCl₃) δ 7.33 (d, J = 8.0 Hz, 2H), 7.17 (s, 1H), 6.86 (d, J = 8.8 Hz, 2H), 5.69 (s, 1H), 4.99 (s, 1H), 3.79 (s, 3H), 2.06 (s, 3H). ^{13}C NMR (100 MHz, CDCl₃) δ 169.3, 159.8, 140.1, 130.8, 127.3, 113.9, 101.5, 55.3, 24.4.

N-[1-(4-Nitrophenyl)vinyl]acetamide (**3d**). ^1H NMR (400 MHz, CDCl₃) δ 8.19 (d, J = 8.4 Hz, 2H), 7.57 (d, J = 8.0 Hz, 2H), 7.15 (s, 1H), 5.79 (s, 1H), 5.25 (s, 1H), 2.14 (s, 3H). ^{13}C NMR

(100 MHz, CDCl₃) δ 169.2, 147.6, 144.1, 139.2, 126.8, 123.8, 107.1, 24.1.

N-[1-(4-Fluorophenyl)vinyl]acetamide (**3e**). ^1H NMR (400 MHz, CDCl₃) δ 7.36–7.33 (t, J = 7.2 Hz, 2H), 7.28 (s, 1H), 7.02–6.98 (t, J = 8.4 Hz, 2H), 5.67 (s, 1H), 4.99 (s, 1H), 2.02 (s, 3H). ^{13}C NMR (100 MHz, CDCl₃) δ 169.3, 162.8 (J_{CF} = 247.2 Hz), 139.7, 134.3, 127.9 (J_{CF} = 8.2 Hz), 115.4 (J_{CF} = 21.4 Hz), 103.1, 24.2.

N-[1-(4-Chlorophenyl)vinyl]acetamide (**3f**). ^1H NMR (400 MHz, CDCl₃) δ 7.31 (s, 5H), 5.70 (s, 1H), 5.06 (s, 1H), 2.06 (s, 3H). ^{13}C NMR (100 MHz, CDCl₃) δ 169.4, 139.6, 136.5, 134.4, 128.7, 127.4, 103.7, 24.2.

N-[1-(4-Bromophenyl)vinyl]acetamide (**3g**). ^1H NMR (400 MHz, CDCl₃) δ 7.47 (d, J = 8.0 Hz, 2H), 7.27 (d, J = 8.0 Hz, 2H), 7.11 (s, 1H), 5.73 (s, 1H), 5.07 (s, 1H), 2.08 (s, 3H). ^{13}C NMR (100 MHz, CDCl₃) δ 169.2, 139.6, 137.0, 131.7, 127.6, 122.6, 103.7, 24.3.

N-[1-(3,4-Dimethylphenyl)vinyl]acetamide (**3h**). ^1H NMR (400 MHz, CDCl₃) δ 7.18–7.10 (m, 4H), 5.77 (s, 1H), 5.04 (s, 1H), 2.27 (s, 3H), 2.26 (s, 3H), 2.08 (s, 3H). ^{13}C NMR (100 MHz, CDCl₃) δ 169.2, 140.5, 137.2, 136.8, 135.9, 129.8, 127.2, 123.4, 101.6, 24.4, 19.8, 19.5. HRMS Calcd (ESI) m/z for C₁₂H₁₅NNaO: [M + Na]⁺ 212.1046, found: 212.1050.

N-[1-(5,6,7,8-Tetrahydronaphthalen-2-yl)vinyl]acetamide (**3i**). ^1H NMR (400 MHz, CDCl₃) δ 7.14–7.11 (m, 2H), 7.06 (d, J = 8.0 Hz, 1H), 6.87 (s, 1H), 5.82 (s, 1H), 5.03 (s, 1H), 2.77 (s, 4H), 2.12 (s, 3H), 1.80 (s, 4H). ^{13}C NMR (100 MHz, CDCl₃) δ 169.0, 140.5, 137.9, 137.4, 135.6, 129.4, 126.5, 123.1, 101.4, 29.4, 29.1, 24.6, 23.0. HRMS Calcd (ESI) m/z for C₁₄H₁₇NNaO: [M + Na]⁺ 238.1202, found: 238.1207.

N-[1-(2,5-Dimethylphenyl)vinyl]acetamide (**3j**). ^1H NMR (400 MHz, CDCl₃) δ 7.16 (s, 1H), 7.09–7.06 (m, 3H), 5.97 (s, 1H), 4.65 (s, 1H), 2.32 (s, 3H), 2.29 (s, 3H), 1.93 (s, 3H). ^{13}C NMR (100 MHz, CDCl₃) δ 169.0, 140.7, 138.4, 135.3, 132.6, 130.3, 129.8, 129.1, 102.1, 24.2, 20.8, 19.1. HRMS Calcd (ESI) m/z for C₁₂H₁₆NO: [M + H]⁺ 190.1226, found: 190.1227.

N-[1-(3-Methoxyphenyl)vinyl]acetamide (**3k**). ^1H NMR (400 MHz, CDCl₃) δ 7.28–7.24 (m, 2H), 6.98 (d, J = 7.2 Hz, 1H), 6.93 (s, 1H), 6.86 (d, J = 8.0 Hz, 1H), 5.80 (s, 1H), 5.07 (s, 1H), 3.80 (s, 3H), 2.05 (s, 3H). ^{13}C NMR (100 MHz, CDCl₃) δ 169.3, 159.6, 140.4, 139.8, 129.6, 118.4, 113.8, 112.0, 102.6, 55.3, 24.4.

N-[1-(Naphthalen-2-yl)vinyl]acetamide (**3l**). ^1H NMR (400 MHz, CDCl₃) δ 7.84–7.82 (m, 4H), 7.54–7.49 (m, 3H), 7.08 (s, 1H), 5.92 (s, 1H), 5.24 (s, 1H), 2.14 (s, 3H). ^{13}C NMR (100 MHz, CDCl₃) δ 169.2, 140.4, 135.5, 133.2, 133.0, 128.4, 128.1, 127.6, 126.5, 126.4, 124.7, 124.0, 103.4, 24.4.

(*E*)-*N*-(1-Phenylprop-1-en-1-yl)acetamide (**3m**). ^1H NMR (400 MHz, DMSO-*d*₆) δ 9.11 (s, 1H), 7.36–7.22 (m, 5H), 5.89–5.87 (m, 1H), 1.99 (s, 3H), 1.64 (d, J = 6.4 Hz, 3H). ^{13}C NMR (100 MHz, DMSO-*d*₆) δ 167.8, 138.4, 134.7, 128.2, 127.2, 125.1, 119.3, 22.7, 13.8.

N-(2-Methyl-1-phenylprop-1-en-1-yl)acetamide (**3n**). ^1H NMR (400 MHz, DMSO-*d*₆) δ 9.02 (s, 1H), 7.30–7.21 (m, 5H), 1.87 (s, 3H), 1.70 (s, 3H), 1.68 (s, 3H). ^{13}C NMR (100 MHz, DMSO-*d*₆) δ 167.5, 139.1, 128.8, 127.7, 127.3, 126.7, 22.7, 20.7, 20.7.

N-(1-Phenylvinyl)propionamide (**3o**). ^1H NMR (400 MHz,

CDCl_3) δ 7.42–7.32 (m, 5H), 6.96 (s, 1H), 5.87 (s, 1H), 5.07 (s, 1H), 2.36–2.31 (m, 2H), 1.22–1.19 (t, J = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 172.8, 140.4, 138.5, 128.6, 125.9, 102.2, 30.6, 9.5.

N-(3,4-Dihydronaphthalen-1-yl)acetamide (**3p**). ^1H NMR (400 MHz, CDCl_3) δ 7.53 (s, 1H), 7.18–7.12 (m, 4H), 6.26 (s, 1H), 2.72–2.68 (t, J = 8.0 Hz, 2H), 2.32–2.26 (m, 2H), 2.05 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 169.7, 136.5, 131.6, 131.4, 127.5, 127.2, 126.1, 121.0, 119.8, 27.4, 23.7, 22.0.

N-(6-Methoxy-3,4-dihydronaphthalen-1-yl)acetamide (**3q**). ^1H NMR (400 MHz, CDCl_3) δ 7.18 (s, 1H), 7.05 (d, J = 8.0 Hz, 1H), 6.73–6.66 (m, 2H), 6.22–6.19 (t, J = 4.4 Hz, 1H), 3.78 (s, 3H), 2.73–2.69 (t, J = 7.6 Hz, 2H), 2.34–2.29 (m, 2H), 2.11 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 169.4, 158.7, 138.5, 131.3, 124.5, 122.1, 117.2, 113.8, 110.8, 55.1, 28.0, 23.9, 22.1.

N-(1*H*-Inden-3-yl)acetamide (**3r**). ^1H NMR (400 MHz, CDCl_3) δ 7.73 (s, 1H), 7.47 (d, J = 6.8 Hz, 1H), 7.31–7.25 (m, 3H), 6.88 (s, 1H), 3.42 (s, 2H), 2.23 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 168.9, 142.8, 139.7, 135.4, 125.9, 125.4, 124.2, 116.2, 115.7, 36.5, 24.1.

N-(6-Chloro-1*H*-inden-3-yl)acetamide (**3s**). ^1H NMR (400 MHz, $\text{DMSO}-d_6$) δ 9.79 (s, 1H), 7.75 (d, J = 8.4 Hz, 1H), 7.48 (s, 1H), 7.37 (d, J = 8.4 Hz, 1H), 6.75 (s, 1H), 3.39 (s, 2H), 2.10 (s, 3H). ^{13}C NMR (100 MHz, $\text{DMSO}-d_6$) δ 169.0, 144.6, 139.0, 136.1, 130.1, 125.9, 124.1, 119.6, 114.6, 35.9, 23.5.

N-(Cyclohex-1-en-1-yl)acetamide (**3t**). ^1H NMR (400 MHz, CDCl_3) δ 7.19 (s, 1H), 6.05 (s, 1H), 2.19–2.17 (m, 4H), 2.10 (s, 3H), 1.69–1.58 (m, 2H), 1.56–1.55 (m, 2H). ^{13}C NMR (100 MHz, CDCl_3) δ 168.7, 132.8, 113.2, 27.8, 24.2, 23.9, 22.4, 21.9.

N-(Cyclopent-1-en-1-yl)acetamide (**3u**). ^1H NMR (400 MHz, $\text{DMSO}-d_6$) δ 9.38 (s, 1H), 5.72 (s, 1H), 2.35–2.31 (m, 2H), 2.27–2.23 (m, 2H), 1.90 (s, 3H), 1.71–1.68 (m, 2H). ^{13}C NMR (100 MHz, $\text{DMSO}-d_6$) δ 173.0, 142.2, 113.3, 38.0, 35.7, 28.5, 25.8.

1,4-Diphenylbuta-1,3-diyne (**4a**). ^1H NMR (400 MHz, CDCl_3) δ 7.56 (d, J = 7.2 Hz, 4H), 7.39–7.36 (m, 6H). ^{13}C NMR (100 MHz, CDCl_3) δ 132.5, 129.2, 128.4, 121.7, 81.5, 73.9.

1,4-Di-*p*-tolylbuta-1,3-diyne (**4b**). ^1H NMR (400 MHz, CDCl_3) δ 7.43 (d, J = 8.8 Hz, 4H), 7.15 (d, J = 8.0 Hz, 4H), 2.37 (s, 6H). ^{13}C NMR (100 MHz, CDCl_3) δ 139.5, 132.3, 129.2, 118.7, 81.5, 73.4, 21.6.

1,4-Bis(4-methoxyphenyl)buta-1,3-diyne (**4c**). ^1H NMR (400 MHz, CDCl_3) δ 7.46 (d, J = 8.4 Hz, 4H), 6.86 (d, J = 8.8 Hz, 4H), 3.82 (s, 6H). ^{13}C NMR (100 MHz, CDCl_3) δ 160.2, 134.0, 114.1, 113.8, 81.2, 72.9, 55.3.

1,4-Bis(4-fluorophenyl)buta-1,3-diyne (**4d**). ^1H NMR (400 MHz, CDCl_3) δ 7.56–7.52 (m, 4H), 7.09–7.04 (m, 4H). ^{13}C NMR (100 MHz, CDCl_3) δ 163.0 (J_{CF} = 250.5 Hz), 134.5 (J_{CF} = 8.2 Hz), 117.7, 115.9 (J_{CF} = 22.3 Hz), 80.4, 73.5.

1,4-Bis(4-chlorophenyl)buta-1,3-diyne (**4e**). ^1H NMR (400 MHz, CDCl_3) δ 7.46 (d, J = 6.8 Hz, 4H), 7.33 (d, J = 6.4 Hz, 4H).

1,4-Bis(4-bromophenyl)buta-1,3-diyne (**4f**). ^1H NMR (400 MHz, CDCl_3) δ 7.49 (d, J = 8.0 Hz, 4H), 7.38 (d, J = 8.0 Hz, 4H).

Tetradeca-6,8-diyne (**4g**). ^1H NMR (400 MHz, CDCl_3) δ 2.25–2.22 (t, J = 7.2 Hz, 4H), 1.53–1.50 (m, 4H), 1.38–1.29 (m, 8H), 0.91–0.87 (t, J = 7.2 Hz, 6H). ^{13}C NMR (100 MHz, CDCl_3) δ 77.4, 65.2, 30.9, 28.0, 22.1, 19.1, 13.9.

3. Results and discussion

3.1. Optimization of reaction conditions

For the green synthesis of enamides and 1,3-diynes, we tried to perform the reductive acylation of ketoximes and oxidative homocoupling of terminal alkynes in one pot to avoid using terminal reductants and oxidants. After several attempts, enamide **3a** and 1,3-diyne **4a** were obtained in 77% and 59% yields, respectively, in the presence of a $[\text{Pd}(\text{OAc})_2/\text{CuI}]$ catalytic system (Table 1, entry 1). The large difference between the polarities of the enamide and 1,3-diyne makes isolation very easy. This initial result prompted us to optimize the conditions. $[\text{Pd}(\text{PPh}_3)_2\text{Cl}_2/\text{CuI}]$ was the most effective catalytic system (Table 1, entries 2–4). Furthermore, organic bases were screened to improve the efficiency (Table 1, entries 5–8). Pyridine was the most effective, and enamide **3a** and 1,3-diyne **4a** were obtained in 96% and 82% yields, respectively. It should be noted that no reaction occurred when Pd or Cu was used as the sole catalyst, indicating that Pd and Cu catalyzed the reaction synergistically (Table 1, entries 9 and 10).

3.2. Substrate scope

With the optimized conditions in hand, the scope of this protocol was investigated. This transformation displayed high functional group tolerance and proved to be a general protocol for the simultaneous synthesis of enamides **3** and 1,3-diynes **4**. Ketoximes with methyl, methoxy, nitro, and fluoro groups on aryl rings all gave the corresponding enamides **3** and 1,3-diyne **4a** in good to excellent yields (Table 2, entries 2–11). Chloro and bromo substituents on the arenes of ketoximes were tolerated well under the conditions used, and no Sonogashira cross-coupling byproducts were observed (Table 2, entries 6 and 7). The *ortho*-methyl-substituted enamide **3j** was obtained in 97% yield, indicating that the transformation was insensitive to steric hindrance (Table 2, entry 10). 2-Naphthyl ketoxime **1l** also

Table 1

Optimization of combined reaction conditions.

Entry	$[\text{Pd}]/[\text{Cu}]$	Additive	Isolated yield (%)	
			3a	4a
1	$\text{Pd}(\text{OAc})_2/\text{CuI}$	—	77	59
2	$\text{Pd}(\text{PPh}_3)_4/\text{CuI}$	—	72	50
3	$\text{Pd}(\text{PPh}_3)_2\text{Cl}_2/\text{CuBr}$	—	70	48
4	$\text{Pd}(\text{PPh}_3)_2\text{Cl}_2/\text{CuI}$	—	75	70
5	$\text{Pd}(\text{PPh}_3)_2\text{Cl}_2/\text{CuI}$	Et_3N	30	85
6	$\text{Pd}(\text{PPh}_3)_2\text{Cl}_2/\text{CuI}$	Et_2NH	<5	80
7	$\text{Pd}(\text{PPh}_3)_2\text{Cl}_2/\text{CuI}$	Piperidine	<5	62
8	$\text{Pd}(\text{PPh}_3)_2\text{Cl}_2/\text{CuI}$	Pyridine	96	82
9	$\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$	Pyridine	0	0
10	CuI	Pyridine	0	0

Reaction conditions: $[\text{Pd}]$ (0.2 mol%), $[\text{Cu}]$ (10 mol%), ketoxime **1a** (0.5 mmol), phenylacetylene **2a** (1.0 mmol), Ac_2O (1.0 mmol), additive (0.6 mmol), DCE (5 mL), Ar, 120 °C.

Table 2Synthesis of various enamides **3** and 1,3-diyne **4a**.

Entry	Ketoxime 1	Enamide 3	Isolated yield (%)		Entry	Ketoxime 1	Enamide 3	Isolated yield (%)	
			Enamide 3	4a				Enamide 3	4a
1			96	82	12			60	85
2			93	80	13			78	88
3			91	81	14			91	86
4			61	65	15 ^a			70	80
5			75	78	16			96	87
6			92	81	17			93	84
7			90	84	18			75	73
8			81	81	19			70	77
9			93	84	20			52	54
10			97	85	21			64	63
11			96	84					

Reaction conditions: Pd(PPh₃)₂Cl₂ (0.2 mol%), CuI (10 mol%), ketoxime **1** (0.5 mmol), phenylacetylene **2a** (1.0 mmol), Ac₂O (1.0 mmol), pyridine (0.6 mmol), DCE (5 mL), Ar, 120 °C. ^a Propionic anhydride was used.

reacted smoothly to give the corresponding naphthyl enamide **3l** in 60% yield (Table 2, entry 12). The tri- and tetra-substituted enamides **3m** and **3n**, and **3p–3s**, and the

N-propyl enamide **3o** were also obtained in good yields (Table 2, entries 13–19). Aliphatic ketoximes were also tolerated, to give the corresponding enamides **3t** and **3u** in moderate yields

Table 3Synthesis of various symmetrical 1,3-diynes **4** and enamide **3a**.

Entry	Alkyne 2	1,3-diyne 4	Isolated yield (%)
			3a 4
1			89 84
2			88 89
3			91 88
4			90 86
5			85 85
6			85 83

Reaction conditions: Pd(PPh₃)₂Cl₂ (0.2 mol%), CuI (10 mol%), ketoxime **1a** (0.5 mmol), alkyne **2** (1.0 mmol), Ac₂O (1.0 mmol), pyridine (0.6 mmol), DCE (5 mL), Ar, 120 °C, 5 h.

(Table 2, entries 20 and 21).

Next, various terminal alkynes were examined to extend the substrate scope. A series of 1,3-diynes (**4b–4f**) with electron-withdrawing or electron-donating groups such as methyl, methoxy, fluoro, chloro, and bromo on aryl rings, and enamide **3a** were synthesized in high yields (Table 3, entries 1–5). The aliphatic alkyne **2g** also exhibited good reactivity to give 1,3-diyne **4g** in 83% yield (Table 3, entry 6).

3.3. Reaction mechanism

On the basis of the above experiments and previous studies, a tentative mechanism for the transformation is proposed in Scheme 2. In cycle I, the Cu-catalyzed single-electron reduction of ketoxime acetate **A** gives an imino radical intermediate **B** [25,26,39–44]. Further reduction of **B**, followed by acylation

Scheme 2. Tentative mechanism for transformation.

and tautomerization, forms enamide **3** [26,45,46]. In cycle II, deprotonation of terminal alkyne **2** in the presence of CuI and pyridine generates a Cu-acetylide intermediate **E** [33–38]. Double transmetalation of **E** with Pd(II) forms a dialkynylpalladium(II) species **F**. Reductive elimination of **F** affords the 1,3-diyne **4** and Pd(0) [33–38,47–50]. Finally, Pd(0) was oxidized by Cu²⁺ to regenerate the active Pd(II) and Cu(I) catalyst, completing cycles I and II.

4. Conclusions

We have developed a green synthetic protocol for the straightforward synthesis of enamides and 1,3-diynes in one pot in the absence of any terminal oxidants and reductants. The transformation tolerates a range of functional groups and is a novel procedure for the one-pot, high-yielding preparation of valuable enamides and 1,3-diynes. This protocol is a promising method for minimizing reduced or oxidized wastes from both oxidation and reduction reactions. Further study will focus on extending the scope of this green transformation.

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Graphical Abstract

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One-pot green synthesis of enamides and 1,3-diynes

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An oxidation was combined with a reduction in one pot, to give the two corresponding products, i.e., enamides and 1,3-diynes, simultaneously. This new process avoids the use of both terminal oxidants and terminal reductants.

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一锅法绿色合成烯酰胺和1,3-二炔

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摘要: 结合绿色化学概念, 将酮肟还原酰化和末端炔氧化偶联在一锅进行反应, 发展了一种Pd/Cu协同催化一锅绿色合成烯酰胺和1,3-二炔的新方法。该方法无需外加任何氧化剂和还原剂, 可同时得到烯酰胺和1,3-二炔, 产率高, 反应条件温和。

关键词: 绿色合成; 酮肟; 末端炔; 烯酰胺; 1,3-二炔

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