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Facile Synthesis for Benzo-1,4-Oxazepine Derivatives by Tandem Transformation of C-N Coupling/C-H Carbonylation

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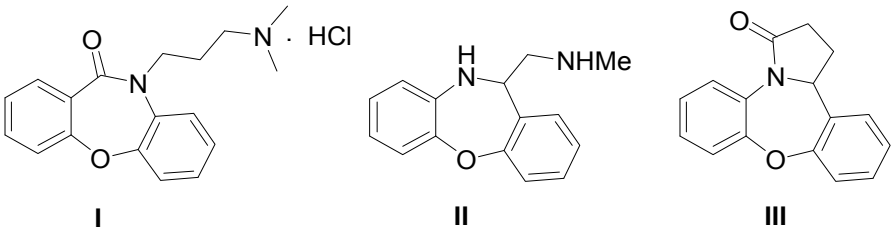
Academic Editor: Derek J. McPhee
Received: 21 November 2016; Accepted: 28 December 2016; Published: 30 December 2016

Abstract: A tandem transformation of C-N coupling/C-H carbonylation has been developed for the synthesis of benzo-1,4-oxazepine pharmaceutically derivatives. Notably, this reaction was accomplished by various phenylamine with ally halides under carbon dioxide atmosphere employing 2-(2-dimethylamino-vinyl)-1*H*-inden-1-olcatalyzed. Furthermore, under the optimized conditions, various benzo-1,4-oxazepine derivatives were obtained in good yields. Finally, a plausible Cu^{I}/Cu^{III} mechanism of C-N coupling/C-H carbonylation transformation was proposed.

Keywords: benzo-1,4-oxazepine; copper catalyst; tandem transformation; C-N coupling; C-H carbonylation

1. Introduction

The heterocycle benzoxazepines are privileged scaffolds in natural biologically products [1–4], pharmaceutical chemistry [5,6] and functionalized materials [7–10]. As such, Sintamilv (**I**) is an efficient antidepressant [11]; H1 receptor antagonist (**II**) is a selective antihistaminic agent [12]; and Sintamil (**III**) is a benzoxazepine analogue (Scheme 1) [13]. Furthermore, the therapeutic applications of benzoxazepines are for the central nervous system, along with anti-breast cancer activity and inhibitors of HIV [14,15].



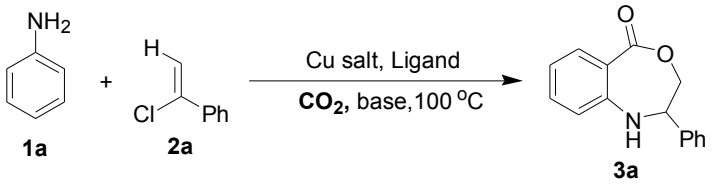
Scheme 1. The important benzo-1,4-oxazepine derivatives.

Currently, the challenge in organic synthesis is developing an efficient and eco-friendly protocol, especially in the area of drug discovery and natural products. Benzoxazepines are generally synthesized by condensation of 2-aryloxyethylamines with 2-formylbenzoic acid [16]. Others have also been synthesized from amides [17] and amino acids [18,19]. However, most of these methodologies are associated with several drawbacks, such as low synthetic efficiency and sensitivity. Thus, a remarkable gap remains in the search of economical synthesis methods. Tandem transformation is one of the most

effective ways to achieve this goal. Considering the above points, herein we report the tandem reaction green protocol for the synthesis of benzo-1,4-oxazepine pharmaceutical derivatives.

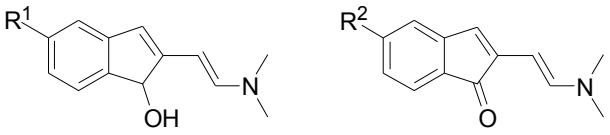
The reaction conditions were screened based on a model reaction of phenylamine **1a** and (1-chloro-vinyl)-benzene **2a** (Table 1). The ligands were mainly based on the derivatives of 2-(2-dimethylamino-vinyl)-1*H*-inden-1-ol. It was discovered that ligand **L1** was the ideal choice for this transformation (Entries 5–10). CuI exhibited superior catalytic efficiency over all other examined Cu^I catalysts (Entries 1–5), and Cs_2CO_3 turned out to be the proper base additive (Entries 11–12). Meanwhile, the reaction temperature was 100 °C (Entries 15–16).

Table 1. Optimization of the reaction conditions [a].



1a **2a** **3a**

Entry	Ligand	Cu Salt	Base	Yield (%) [b]
1	**L1**	$Cu(OAc)_2$	Cs_2CO_3	8
2	**L1**	$CuSO_4$	Cs_2CO_3	0
3	**L1**	CuBr	Cs_2CO_3	23
4	**L1**	$CuBr_2$	Cs_2CO_3	19
5	**L1**	CuI	Cs_2CO_3	81
6	**L2**	CuI	Cs_2CO_3	29
7	**L3**	CuI	Cs_2CO_3	36
8	**L4**	CuI	Cs_2CO_3	47
9	**L5**	CuI	Cs_2CO_3	16
10	**L6**	CuI	Cs_2CO_3	38
11	**L1**	CuI	K_2CO_3	42
12	**L1**	CuI	K_3PO_4	0
13	**L1**	CuI	Cs_2CO_3	61 [c]
14	**L1**	CuI	Cs_2CO_3	69 [d]



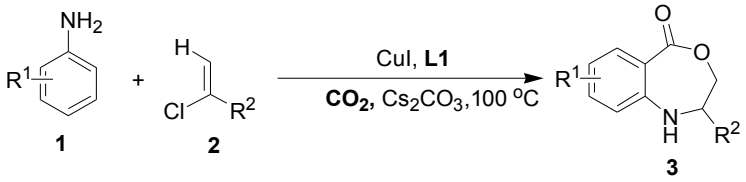
L1: R^1 = H
L2: R^1 = Cl
L3: R^1 = CH_3

L4: R^2 = H
L5: R^2 = Cl
L6: R^2 = CH_3

[a] Unless otherwise noted, reactions conditions were **1a** (0.5 mmol), **2a** (0.6 mmol), Cu salt (10 mol %), ligand (10 mol %), base (2 eq.), DMSO (4 mL) reacted in CO_2 at 100 °C for 12 h; [b] isolated yield; [c] reaction under 90 °C; [d] reaction under 110 °C.

With the optimal conditions established, the reaction scope was further investigated. A wide array of phenylamine **1** and ally halide **2** was subjected to this reaction in moderate to good yields (Table 2). Phenylamine derivatives bearing either an electron-withdrawing or electron-donating group reacted smoothly with **2**. This transformation is applicable for *para*-substituted phenylamines. Chloroethylene bearing an electron-donating group showed better reactivity than those with an electron-withdrawing group (All the product spectrums, please see Supplementary Materials).

Table 2. Synthesis of benzo-1,4-oxazepin-5-one **3** [a].



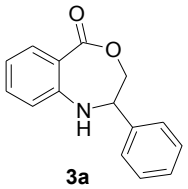
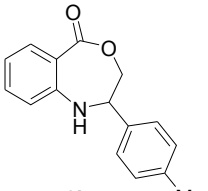
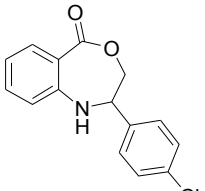
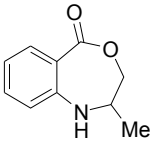
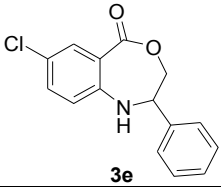
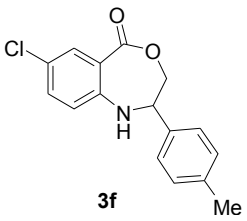
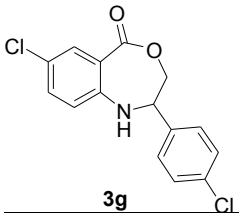
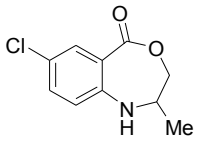
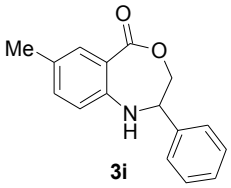
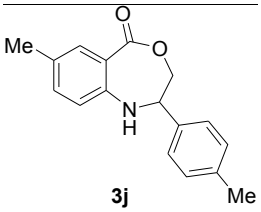
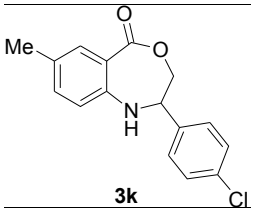
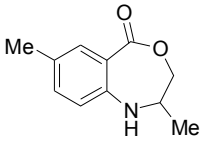
Entry	R^1	R^2	Product 3	Yield (%) [b]
1	H	Ph	 **3a**	81
2	H	4-$CH_3C_6H_4$	 **3b**	78
3	H	4-ClC_6H_4	 **3c**	85
4	H	CH_3	 **3d**	74
5	4-Cl	Ph	 **3e**	79
6	4-Cl	4-$CH_3C_6H_4$	 **3f**	76

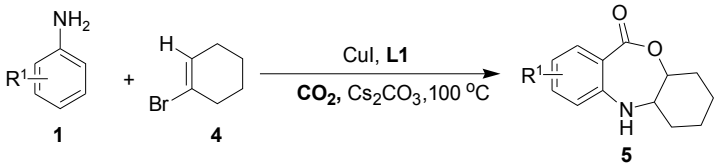
Table 2. *Cont.*

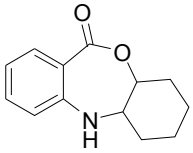
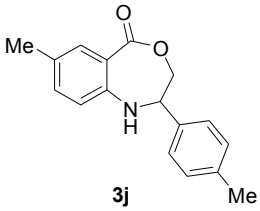
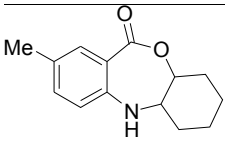
Entry	R^1	R^2	Product 3	Yield (%) [b]
7	4-Cl	4-ClC_6H_4	 **3g**	86
8	4-Cl	CH_3	 **3h**	84
9	4-CH_3	Ph	 **3i**	76
10	4-CH_3	4-$CH_3C_6H_4$	 **3j**	75
11	4-CH_3	4-ClC_6H_4	 **3k**	82
12	4-CH_3	CH_3	 **3l**	72

[a] Reactions conditions were **1** (0.5 mmol), **2** (0.6 mmol), CuI (10 mol %), **L1** (10 mol %), Cs_2CO_3 (2 equiv.), DMSO (4 mL) at 100 °C reacted in CO_2 for 10 h; [b] isolated yield.

Interestingly, we found that 1-bromo-cyclohexene **4** has also been rapidly synthesized in good yields, and the results are summarized in Table 3. In addition, the reaction works well for both bearing electron-donating and electron-withdrawing groups.

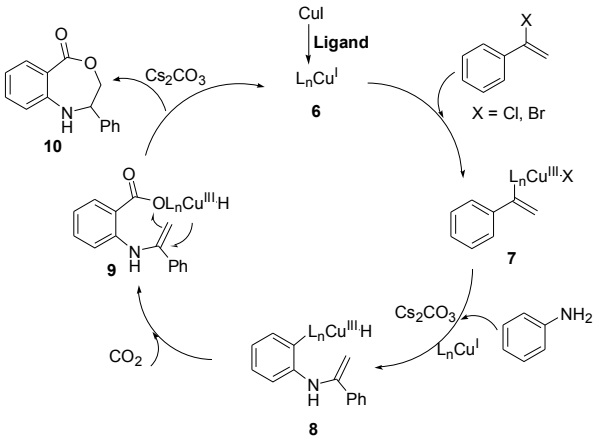
Table 3. Synthesis of benzo-1,4-oxazepin-5-one **5** [a].



Entry	R^1	Product 5	Yield (%) [b]
1	H	 **5a**	78
2	4-Cl	 **3j**	84
3	4-CH_3	 **5c**	75

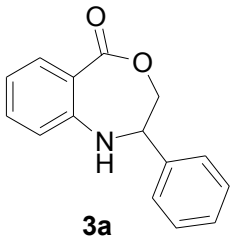
[a] Reactions conditions were **1** (0.5 mmol), **2** (0.6 mmol), CuI (10 mol %), **L1** (10 mol %), Cs_2CO_3 (2 equiv.), DMSO (4 mL) at 100 °C reacted in CO_2 for 10 h; [b] isolated yield.

On the basis of the above experimental results, we tentatively proposed a reaction mechanism as shown in Scheme 2. At the beginning, Cu^I activate **6** was been formed through copper iodide coordinating with ligand. Next, complex **6** reacted with vinyl halides by oxidative addition produced a Cu^{III} complex **7**. The complex **7** reacted with aniline obtained the key intermediate complex **8** [20,21]. Selective *ortho*-carbonylation of the phenylamine was determined by Complex **9**. Through the reductive elimination of Complex **9**, Complex **10** was obtained, which regenerates Complex **6** for the next catalytic cycle [22,23]. However, how the ligand promotes this transformation is a part of ongoing study.



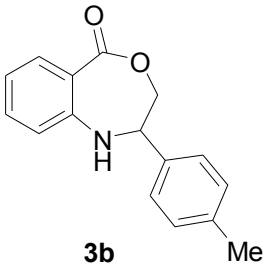
Scheme 2. A plausible mechanism of the catalytic cycle.

2. Results and Discussion



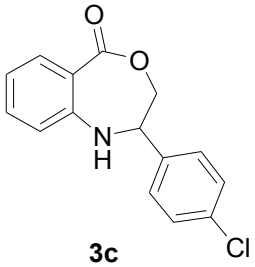
3a

2-Phenyl-2,3-dihydro-1H-benzo[e][1,4]oxazepin-5-one (**3a**): A mixture of phenylamine **1a** (0.5 mmol, 46.5 mg), (1-chloro-vinyl)-benzene **2a** (0.6 mmol, 83.4 mg), CuI (10 mol %, 9.5 mg), **L1** (10 mol %, 20.1 mg) and Cs_2CO_3 (2 equiv., 325.8 mg) in DMSO (4 mL) was stirred in CO_2 at 100 °C for 10 h. After completion of the reaction, the mixture was quenched with saturated salt water (10 mL); the solution was extracted with ethyl acetate (3 × 10 mL). The organic layers were combined and dried over sodium sulfate. The pure product was obtained by flash column chromatography on silica gel to afford **3a** 96.8 mg in 81% yield. The spectroscopic data of all of the products are presented below. Yellowish oil. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.63 (m, 1H), 7.43 (br, 1H), 7.08–7.43 (m, 8H), 5.07 (dd, *J* = 8.0, 5.7 Hz, 1H), 4.08 (dd, *J* = 12.3, 8.0 Hz, 1H), 3.96 (dd, *J* = 12.3, 5.6 Hz, 1H); ^{13}C-NMR (100 MHz, $CDCl_3$): 168.3, 147.7, 139.1, 132.9, 130.3, 128.6, 127.5, 126.6, 117.8, 116.4, 109.1, 77.6, 60.2; EIMS (*m*/*z*): 239 [M^+]; Anal. Calcd. for $C_{15}H_{13}NO_2$: C, 75.30; H, 5.48; N, 5.85; Found: C, 75.62; H, 5.13; N, 5.68.



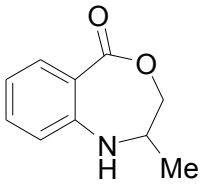
3b

2-p-Tolyl-2,3-dihydro-1H-benzo[e][1,4] xazepine-5-one (**3b**): Yellowish oil. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.61 (m, 1H), 7.44 (br, 1H), 7.04–7.31 (m, 7H), 5.07 (dd, *J* = 8.0, 5.7 Hz, 1H), 4.07 (dd, *J* = 12.3, 8.0 Hz, 1H), 3.95 (dd, *J* = 12.3, 5.7 Hz, 1H), 2.39 (s, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$): 168.6, 147.8, 138.3, 135.3, 132.3, 130.5, 128.1, 127.6, 118.2, 115.9, 109.5, 77.5, 60.3, 25.2; EIMS (*m*/*z*): 253 [M^+]; Anal. Calcd. for $C_{16}H_{15}NO_2$: C, 75.87; H, 5.97; N, 5.53; Found: C, 75.50; H, 6.20; N, 5.88.



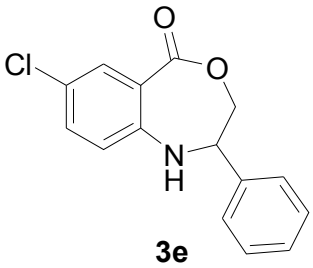
3c

2-(4-Chloro-phenyl)-2,3-dihydro-1H-benzo[e][1,4] xazepine-5-one (**3c**): Yellowish oil. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.64 (m, 1H), 7.47 (br, 1H), 7.07–7.48 (m, 7H), 5.08 (dd, *J* = 8.1, 5.6 Hz, 1H), 4.09 (dd, *J* = 12.3, 8.1 Hz, 1H), 3.95 (dd, *J* = 12.3, 5.6 Hz, 1H); ^{13}C-NMR (100 MHz, $CDCl_3$): 168.3, 147.7, 139.3, 133.3, 132.4, 130.5, 128.6, 127.8, 118.4, 116.3, 110.1, 77.3, 60.9;EIMS (*m*/*z*): 273 [M^+]; Anal. Calcd. for $C_{15}H_{12}ClNO_2$: C, 65.82; H, 4.42; N, 5.12; Found: C, 65.51; H, 4.61; N, 5.33.



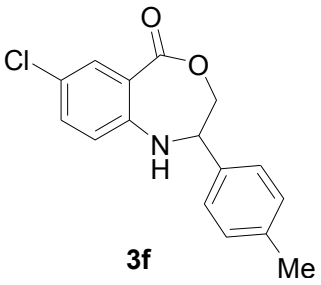
3d

2-Methyl-2,3-dihydro-1H-benzo[e][1,4]oxazepin-5-one (**3d**): Yellowish oil. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.62 (m, 1H), 7.42 (br, 1H), 7.05–7.21 (m, 3H), 4.58 (dd, *J* = 12.3, 8.0 Hz, 1H), 3.96 (dd, *J* = 12.2, 5.6 Hz, 1H), 3.12–3.71 (m, 1H), 1.35 (d, *J* = 7.1 Hz, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$): 168.2, 147.3, 132.8, 130.4, 118.7, 116.6, 109.7, 77.1, 53.1, 18.2; EIMS (*m*/*z*): 177.08 [M^+]; Anal. Calcd. for $C_{10}H_{11}NO_2$: C, 67.78; H, 6.26; N, 7.90; Found: C, 68.14; H, 6.55; N, 7.53.



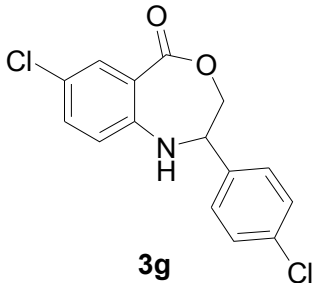
3e

7-Chloro-2-phenyl-2,3-dihydro-1H-benzo[e][1,4]oxazepin-5-one (**3e**): Yellowish oil. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.63 (m, 1H), 7.43 (br, 1H), 7.10–7.46 (m, 7H), 5.08 (dd, *J* = 8.1, 5.6 Hz, 1H), 4.10 (dd, *J* = 12.4, 8.1 Hz, 1H), 3.97 (dd, *J* = 12.4, 5.6 Hz, 1H); ^{13}C-NMR (100 MHz, $CDCl_3$): 168.3, 147.4, 139.5, 133.2, 130.2, 128.7, 127.5, 126.8, 123.8, 115.4, 109.2, 77.5, 60.2; EIMS (*m*/*z*): 273 [M^+]; Anal. Calcd. for $C_{15}H_{12}ClNO_2$: C, 65.82; H, 4.42; N, 5.12; Found: C, 65.70; H, 4.61; N, 5.44.



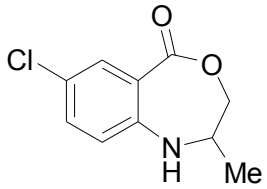
3f

7-Chloro-2-p-tolyl-2,3-dihydro-1H-benzo[e][1,4]oxazepin-5-one (**3f**): Yellowish oil. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.64 (m, 1H), 7.43 (br, 1H), 7.07–7.38 (m, 6H), 5.08 (dd, *J* = 8.1, 5.9 Hz, 1H), 4.10 (dd, *J* = 12.4, 8.1 Hz, 1H), 3.96 (dd, *J* = 12.4, 5.9 Hz, 1H), 2.40 (s, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$): 168.2, 147.1, 139.2, 135.8, 133.4, 130.5, 128.7, 126.9, 123.5, 115.5, 109.3, 77.2, 60.4, 25.7; EIMS (*m*/*z*): 287.07 [M^+]; Anal. Calcd. for $C_{16}H_{14}ClNO_2$: C, 66.79; H, 4.90; N, 4.87; Found: C, 66.95; H, 4.63; N, 5.23.



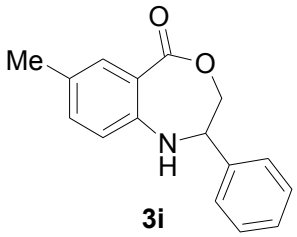
3g

7-Chloro-2-(4-chloro-phenyl)-2,3-dihydro-1H-benzo[e][1,4]oxazepin-5-one (**3g**): Yellowish oil. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.66 (m, 1H), 7.46 (br, 1H), 7.09–7.50 (m, 6H), 5.10 (dd, *J* = 8.2, 5.6 Hz, 1H), 4.11 (dd, *J* = 12.4, 8.2 Hz, 1H), 3.96 (dd, *J* = 12.4, 5.6 Hz, 1H); ^{13}C-NMR (100 MHz, $CDCl_3$): 168.2, 147.4, 139.6, 133.2, 131.8, 130.2, 128.9, 126.7, 123.8, 115.2, 109.6, 77.5, 60.3; EIMS (*m*/*z*): 307 [M^+]; Anal. Calcd. for $C_{15}H_{11}Cl_2NO_2$: C, 58.46; H, 3.60; N, 4.55; Found: C, 58.23; H, 3.92; N, 4.67.



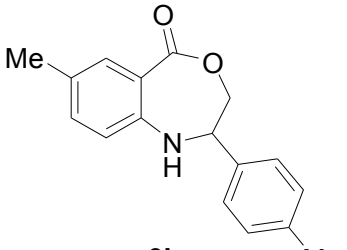
3h

7-Chloro-2-methyl-2,3-dihydro-1H-benzo[e][1,4]oxazepin-5-one (**3h**): Yellowish oil. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.64 (m, 1H), 7.45 (br, 1H), 7.06–7.23 (m, 2H), 4.6 (dd, *J* = 12.2, 8.1 Hz, 1H), 3.98 (dd, *J* = 12.2, 5.6 Hz, 1H), 3.12–3.71 (m, 1H), 1.36 (d, *J* = 7.2 Hz, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$): 168.5, 147.3, 133.1, 130.2, 123.1, 116.8, 109.3, 77.5, 53.4, 18.3; EIMS (*m*/*z*): 211 [M^+]; Anal. Calcd. for $C_{10}H_{10}ClNO_2$: C, 56.75; H, 4.76; N, 6.62; Found: C, 56.89; H, 5.18; N, 6.34.



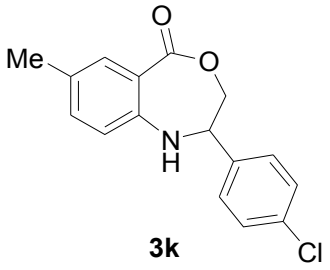
3i

7-Methyl-2-phenyl-2,3-dihydro-1H-benzo[e][1,4]oxazepin-5-one (**3i**): Yellowish oil. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.58 (m, 1H), 7.41 (br, 1H), 7.06–7.40 (m, 7H), 5.00 (dd, *J* = 8.0, 5.6 Hz, 1H), 4.06 (dd, *J* = 12.2, 8.0 Hz, 1H), 3.92 (dd, *J* = 12.2, 5.6 Hz, 1H), 2.40 (s, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): 168.5, 147.2, 139.4, 133.3, 130.8, 128.9, 127.7, 126.9, 126.2, 116.7, 109.3, 77.8, 60.3, 25.3; EIMS (*m*/*z*): 253 [M^+]; Anal. Calcd. for $C_{16}H_{15}NO_2$: C, 75.87; H, 5.97; N, 5.53; Found: C, 75.65; H, 6.28; N, 5.33.



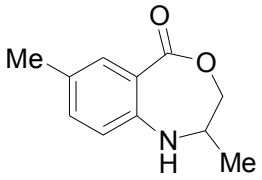
3j

7-Methyl-2-p-tolyl-2,3-dihydro-1H-benzo[e][1,4]oxazepin-5-one (**3j**): Yellowish oil. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.56 (m, 1H), 7.44 (br, 1H), 7.06–7.36 (m, 6H), 4.98 (dd, *J* = 7.9, 5.6 Hz, 1H), 4.02 (dd, *J* = 12.2, 7.9 Hz, 1H), 3.90 (dd, *J* = 12.2, 5.6 Hz, 1H), 2.39 (s, 6H); ^{13}C-NMR (100 MHz, $CDCl_3$): 168.2, 147.5, 138.3, 135.1, 132.4, 130.8, 128.8, 127.5, 126.2, 116.2, 109.1, 77.2, 60.5, 25.8, 25.3; EIMS (*m*/*z*): 267 [M^+]; Anal. Calcd. for $C_{17}H_{17}NO_2$: C, 76.38; H, 6.41; N, 5.24; Found: C, 76.69; H, 6.24; N, 5.53.



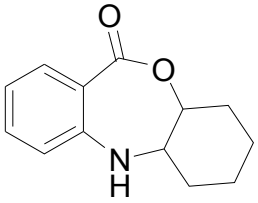
3k

2-(4-Chloro-phenyl)-7-methyl-2,3-dihydro-1H-benzo[e][1,4]oxazepin-5-one (**3k**): Yellowish oil. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.60 (m, 1H), 7.47 (br, 1H), 7.06-7.44 (m, 6H), 5.08 (dd, *J* = 8.0, 5.7 Hz, 1H), 4.10 (dd, *J* = 12.2, 8.0 Hz, 1H), 3.98 (dd, *J* = 12.2, 5.7 Hz, 1H), 2.42 (s, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$): 168.1, 147.5, 139.6, 133.5, 132.2, 131.1, 128.3, 127.5, 126.4, 115.7, 109.7, 77.4, 60.7, 25.4; EIMS (*m*/*z*): 287 [M^+]; Anal. Calcd. for $C_{16}H_{14}ClNO_2$: C, 66.79; H, 4.90; N, 4.87; Found: C, 67.09; H, 4.99; N, 4.54.



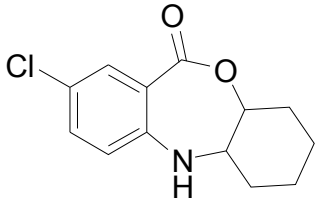
3l

2,7-Dimethyl-2,3-dihydro-1H-benzo[e][1,4] xazepine-5-one (**3l**): Yellowish oil. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.62 (m, 1H), 7.43 (br, 1H), 7.04–7.20 (m, 2H), 4.56 (dd, *J* = 12.2, 8.0 Hz, 1H), 3.93 (dd, *J* = 12.2, 5.4 Hz, 1H), 3.10–3.70 (m, 1H), 2.41 (s, 3H), 1.34 (d, *J* = 7.0 Hz, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$): 168.3, 147.1, 133.5, 130.9, 126.8, 115.8, 109.2, 77.5, 53.4, 25.3, 18.3; EIMS (*m*/*z*): 191 [M^+]; Anal. Calcd. for $C_{11}H_{13}NO_2$: C, 69.09; H, 6.85; N, 7.32; Found: C, 69.41; H, 6.55; N, 7.16.



5a

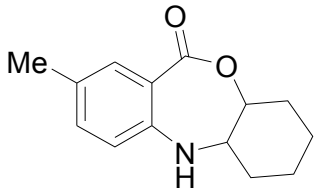
5a,6,7,8,9,9a-Hexahydro-5H-10-oxa-5-aza-dibenzo[a,d]cyclohepten-11-one (**5a**): Yellowish oil. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.60 (m, 1H), 7.48 (br, 1H), 7.02–7.39 (m, 3H), 4.22 (dd, *J* = 11.3, 3.4 Hz, 1H), 3.11 (dd, *J* = 11.3, 3.5 Hz, 1H), 1.61–1.93 (m, 4H), 1.43–1.52 (m, 4H); ^{13}C-NMR (100 MHz, $CDCl_3$): 168.2, 147.6, 132.6, 130.1, 118.2, 115.9, 108.8, 85.8, 56.1, 28.5, 27.6, 22.9, 21.7; EIMS (*m*/*z*): 217 [M^+]; Anal. Calcd. for $C_{13}H_{15}NO_2$: C, 71.87; H, 6.96; N, 6.45; Found: C, 71.72; H, 6.66; N, 6.73.



5b

2-Chloro-5a,6,7,8,9,9a-hexahydro-5H-10-oxa-5-aza-dibenzo[a,d]cyclohepten-11-one (**5b**): Yellowish oil. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.62 (m, 1H), 7.49 (br, 1H), 7.05–7.43 (m, 2H), 4.26 (dd, *J* = 11.3, 3.5 Hz,

1H), 3.11 (dd, *J* = 11.3, 3.7 Hz, 1H), 1.62–1.95 (m, 4H), 1.43–1.54 (m, 4H); ^{13}C-NMR (100 MHz, $CDCl_3$): 168.3, 147.1, 133.1, 130.4, 122.5, 116.1, 108.2, 85.6, 56.5, 28.8, 27.2, 22.7, 21.5; EIMS (*m*/*z*): 251 [M^+]; Anal. Calcd. for $C_{13}H_{14}ClNO_2$: C, 62.03; H, 5.61; N, 5.56; Found: C, 62.19; H, 5.31; N, 5.34.



5c

2-Methyl-5a,6,7,8,9,9a-hexahydro-5H-10-oxa-5-aza-dibenzo[a,d]cyclohepten-11-one (**5c**): Yellowish oil. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.58 (m, 1H), 7.46 (1H, br), 7.00–7.35 (m, 2H), 4.20 (dd, *J* = 11.2, 3.2 Hz, 1H), 3.09 (dd, *J* = 11.2, 3.4 Hz, 1H), 2.40 (s, 3H), 1.60–1.91 (m, 4H), 1.42–1.50 (m, 4H); ^{13}C-NMR (100 MHz, $CDCl_3$): 168.4, 147.3, 133.4, 130.8, 126.1, 116.1, 108.5, 85.4, 56.3, 28.7, 27.8, 22.8, 21.5; EIMS (*m*/*z*): 231 [M^+]; Anal. Calcd. for $C_{14}H_{17}NO_2$: C, 72.70; H, 7.41; N, 6.06; Found: C, 72.99; H, 7.28; N, 6.48.

3. Experimental Section

3.1. General Procedure for Preparation of **L1**–**L6**

Dimethylformamide dimethyl acetal (DMF-DMA) (10 mmol, 1.19 g) and 1-(1-hydroxy-1*H*-inden-2-yl)-ethanone (10 mmol, 1.74 g) were dissolved in *p*-xylene (5 mL). Additionally, the mixture was refluxed during a period of 5–12 h, during which time a yellow precipitate formed. The precipitate was filtered out and washed with petroleum ether three times. The solid was vacuum-dried, and 1.89 g (yield 94%) of a yellow solid were obtained, **L1** 2-(2-dimethylamino-vinyl)-1*H*-inden-1-ol. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.23 (m, 2H), 7.17–7.07 (t, *J* = 8.0 Hz, 2H), 7.01–6.90 (t, *J* = 7.8 Hz, 1H), 6.60 (s, 1H), 6.07–6.05 (d, *J* = 12 Hz, 1H), 2.47 (s, 3H), 2.42 (s, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ 146.1, 141.2, 133.8, 130.2, 127.9, 126.9, 123.2,121.2, 120.6, 104.1, 75.4, 46.1, 38.6.

3.2. 2-Phenyl-2,3-dihydro-1H-benzo[e][1,4]oxazepin-5-one (**3a**)

A mixture of phenylamine **1a** (0.5 mmol, 46.5 mg), (1-chloro-vinyl)-benzene **2a** (0.6 mmol, 83.4 mg), CuI (10 mol %, 9.5 mg), **L1** (10 mol %, 20.1 mg) and Cs_2CO_3 (2 equiv., 325.8 mg) in DMSO (4 mL) was stirred in CO_2 at 100 °C for 10 h. After completion of the reaction, the mixture was quenched with saturated salt water (10 mL); the solution was extracted with ethyl acetate (3 × 10 mL). The organic layers were combined and dried over sodium sulfate. The pure product was obtained by flash column chromatography on silica gel to afford **3a** 96.8 mg in 81% yield. The spectroscopic data of all of the products are represented below. Yellowish oil. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.63 (m, 1H), 7.43 (br, 1H), 7.08–7.43 (m, 8H), 5.07 (dd, *J* = 8.0, 5.7 Hz, 1H), 4.08 (dd, *J* = 12.3, 8.0 Hz, 1H), 3.96 (dd, *J* = 12.3, 5.6 Hz, 1H); ^{13}C-NMR (100 MHz, $CDCl_3$): 168.3, 147.7, 139.1, 132.9, 130.3, 128.6, 127.5, 126.6, 117.8, 116.4, 109.1, 77.6, 60.2; EIMS (*m*/*z*): 239 [M^+]; Anal. Calcd. for $C_{15}H_{13}NO_2$: C, 75.30; H, 5.48; N, 5.85; Found: C, 75.62; H, 5.13; N, 5.68.

4. Conclusions

In conclusion, we have found a green protocol for the synthesis of benzo-1,4-oxazepine derivatives involving tandem transformation of C-N coupling/C-H carbonylation. The method was economically viable and relevant to green chemistry.

Supplementary Materials: Supplementary materials can be accessed at: http://www.mdpi.com/1420-3049/21/1/53/s1.

Acknowledgments: This work was supported by the Natural Science Foundation of Zhejiang Province (No. LQ15B020004), Natural Science Foundation ZA & FU (No. 04251700011).

Author Contributions: R.S.X. designed the experiments; J.Z. and Z.Z. analyzed the data and wrote the paper; X.J.Z. performed the experiments.

Conflicts of Interest: The authors declare no conflict of interest.

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Sample Availability: Samples of the compounds are available from the authors.