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FULL-LENGTH PAPER

Spiro[pyrrolidine-2,3′-oxindole] derivatives synthesized by novel regionselective 1,3-dipolar cycloadditions

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Abstract A series of spiro-oxindole derivatives was synthesized by novel regioselective 1,3-dipolar cycloadditions of isatin, α-amino acids, and (*E*)-β-aryl-nitro-olefins. Regioisomers were produced in each reaction and the major products showed different regioselectivity compared to previously reported spiro-oxindole derivatives.

Keywords 1,3-dipolar cycloaddition · Huisgen reaction · Regioisomers · Spiro compounds · Nitro group

Introduction

1,3-dipolar cycloaddition, also known as the Huisgen reaction [1], provides a direct and straight forward entry for the synthesis of many five-membered heterocyclic compounds, such as pyrrolidines, pyrrolines, and pyrroles. Many spiro derivatives have also been synthesized using cyclic ketones as a reactant. The spiro-oxindole system is the core structure of several natural alkaloids and pharmacological agents, e.g., spirotryprostatin A [2], pteropodine [3], and isopteropodine [4], which have shown important biological activity with potential use in antibacterial, antiprotozoal, and anticancer. Because of their remarkable biological activity, significant efforts have been devoted to the synthesis of natural product-like spiro-oxindole derivatives [2,3,5–7]. Olefins, such as chalcone [4], acrylate, maleimide [2], maleic anhydride 2-arylidene-1-tetralone, and arylidenemalononitrile derivatives [3], have been efficiently used as trapping dipolarophiles in high yield and high regio- and stereoselectivity.

Owing to the interesting bioactivities of spiro-oxindole compounds, many spiro-oxindole derivatives were synthesized according to our previous reports [7]. (*E*)-*β*-Aryl-nitro-olefins were introduced into isatin via a 1,3-dipolar cycloaddition reaction where the easy transformation of the nitro group into amine [8], oxime [9], and hydrogen [10] can provide a wide range of synthetic compounds with potential interesting bioactivities. Here, we report our new findings in the 1,3-dipolar cycloaddition reactions of isatin, *α*-amino acids, and (*E*)-*β*-aryl-nitro-olefins. The synthesis is illustrated in Scheme 1. The final major products were obtained with a different stereochemistry compared to previously reported spiro-oxindole derivatives [2–7].

Results and discussion

In our previous work, several spiro-oxindole derivatives were synthesized with isatin, *L*-proline and several olefins by 1,3-dipolar cycloaddition reactions [8], and most of these reactions provided target products with high yield and regio-selectivity. In this study, it was found that the major products of these reactions showed different regioselectivity

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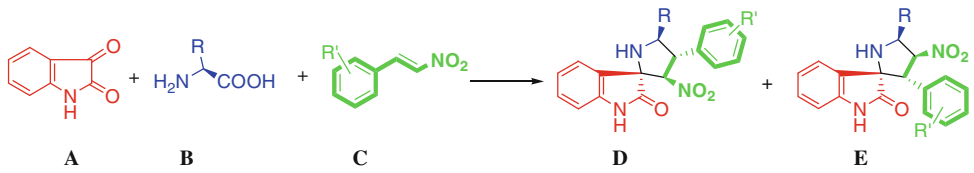


Scheme 1 The synthesis reaction, showing the 1,3-dipolar cycloaddition of isatin (**A**), α-amino acids (**B**), and (*E*)-β-aryl-nitroelfins (**C**), with regioisomers (**D**) and (**E**) as major products

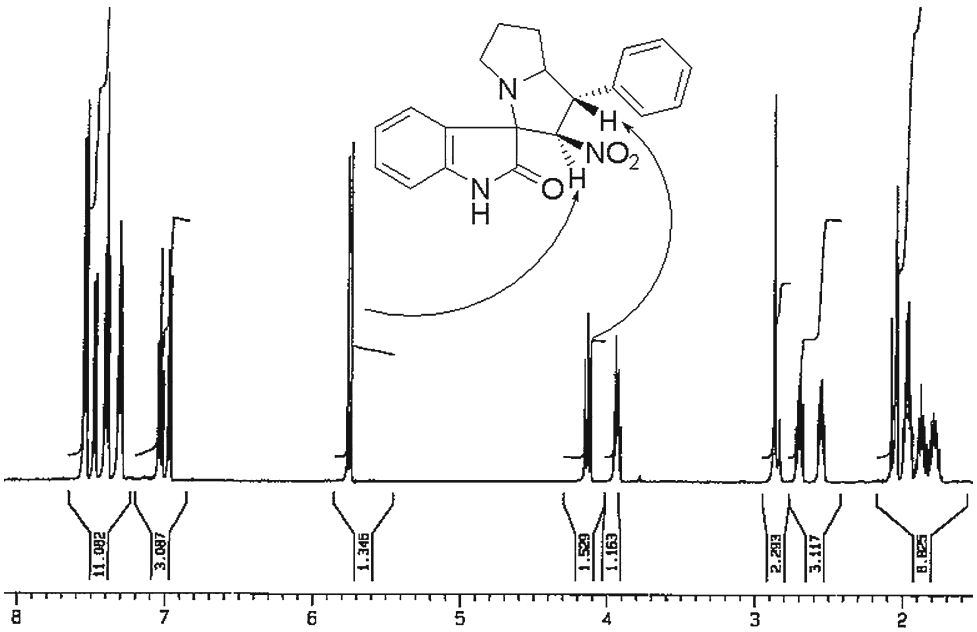


Fig. 1 The 1H NMR spectrum for regioisomer **D1**

from the reported spiro-oxindole derivatives. In the first reaction, the 1H NMR spectrum for regioisomer **D1** (see Fig. 1; Table 1, where **B1** is proline) showed multiplet signals for the protons of the hexahydro-pyrrolizine ring, in the δ range of 1.88–5.75 ppm. The signals in the δ range of 6.97–7.55 ppm were for protons of the aryl groups and the N–H signal was recorded at $\delta = 9.67$ ppm. In the HMBC (Heteronuclear Multiple-Bond Correlation NMR spectroscopy) spectrum, the doublet signal at 5.75 (d, 1H, J=11.5 Hz) indicated the correlation between the nitro group and C-**2** of the newly constructed pyrroline; the multiplet signal at δ 4.41 (m, 1H) showed the correlation between the phenyl group and C-**3** of the newly constructed pyrroline. The 1H NMR spectrum of the other isomer (**E1,** major product) showed a doublet signal at δ 4.57 (d, 1H, $J = 11.0$ Hz) and a multiplet signal at δ 4.75 (m, 1H), which indicate the correlation between the phenyl group with C-**2** and the correlation between the nitro group with C-**3**. All the two dimensional (2D) NMR spectra are consistent with the analysis above. The regioselectivity of this reaction is intriguing. In previously reported experiments, where spiro-oxindole derivatives were synthesized by 1,3-dipolar cycloaddition, only one product was obtained where the electron-withdrawing group (EWG), such as benzoyl group and ester group, usually connects with C-**2** and the phenyl group connects with C-**3** of the newly constructed pyrrolines.

In the following experiment, several (*E*)-β-aryl-nitro-olefins were introduced in this reaction, and similar results were obtained (as shown in Table 1). Furthermore, the stereochemistry of the regioisomers **D2** and **E2** (Fig. 2) was assessed via X-ray crystallography where **D2** was determined to be 2R, 3R, 4S, 5S, and **E2** 2R, 3R, 4S, 5S, both compounds having the same relative configuration as other spiro-oxindole compounds synthesized by this route [2–4].

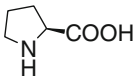
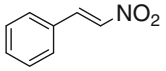
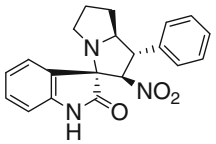
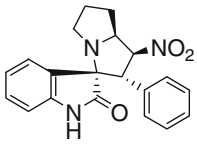
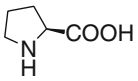
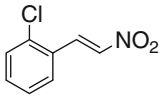
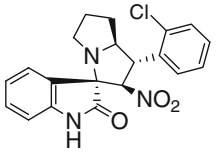
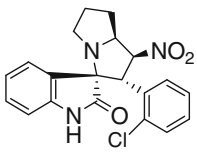
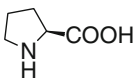
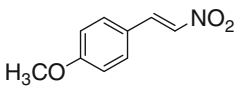
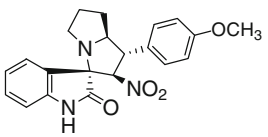
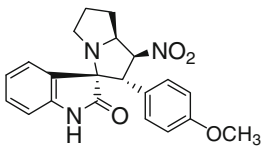
Additional α-amino acids (*L*-Phe, *L*-Leu, and *L*-Ser) were also used, and in each case two regio-isomers were identified (as shown in Table 1). This study provides a way to synthesize various five-membered heterocyclic compounds with different regioselectivity, as well as a way to control the regioselectivity by using different substitutents in the 1,3-dipolar cycloaddition reaction.

Experimental section

General procedure for the 1,3-dipolar cycloadditions of isatin, α-amino acid, and (*E*)-β-aryl-nitro-olefins [2–4]

The required (*E*)-β-aryl-nitro-olefins were prepared by the reacting nitromethane with benzaldehyde in a buffer of AcOH-$AcONH_4$. A solution of isatin (1 mmol), α-amino acid (1 mmol), and (*E*)-β-aryl-nitro-olefins (1.2 mmol) was refluxed in a mixture of methanol and water 9 mL:3 mL. After

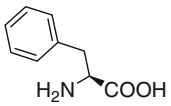
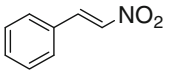
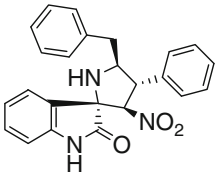
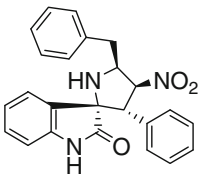
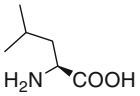
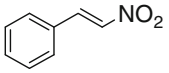
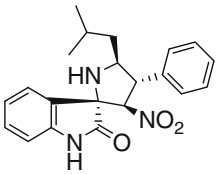
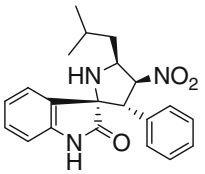
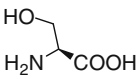
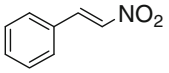
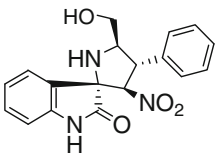
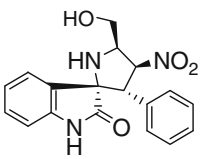
Table 1 Reaction between isatin, α-amino acids and (E)-β-aryl-nitro-olefins

Entry	α-amino acids (**B**)	(E)-β-aryl-nitro-olefins (**C**)	Products (**D** or **E**)	Yield (%)
1	 **B1**	 **C1**	 **D1**	8.5
			 **E1**	67.6
2	 **B1**	 **C2**	 **D2**	12.0
			 **E2**	63.1
3	 **B1**	 **C3**	 **D3**	7.4
				60.8

isatin was complete consumed (monitored by TLC), the solvent was removed under reduced pressure and the residue was subjected to column chromatography (silica gel, petroleum ether: ethyl acetate = 4: 1–1: 1) to give the desired products.

D1: Yield 8.5%; ^{1}H NMR (D_6-Acetone, 500 MHz), δ: 9.67 (1H, s), 7.55 (2H, d, $J = 7.5$ Hz), 7.48 (1H, d, $J = 7.5$ Hz), 7.41 (2H, m), 7.31 (2H, m), 7.04 (1H, m), 6.97 (1H, d, $J = 7.5$ Hz), 5.75 (1H, d, $J = 11.5$ Hz), 4.41 (1H, m), 3.93 (1H,

Table 1 continued

			E3	
4				17.2
	B2	**C1**	**D4**	
				55.3
			E4	
5				7.7
	B3	**C1**	**D5**	
				66.1
			E5	
6				15.3
	B4	**C1**	**D6**	
				52.4
			E6	

m), 2.70 (1H, m), 2.56 (1H, m), 1.88–1.99 (4H, m); ^{13}C NMR (D_6-Acetone, 125 MHz), δ: 178.2, 144.0, 138.3, 131.4, 129.8, 128.6, 128.5, 127.2, 124.0, 122.6, 111.3, 97.4, 73.7, 71.2, 54.0, 48.6, 31.1, 27.6; EI-MS, m/z: 349 (M^+), HRMS (ESI-TOF) calcd for $C_{20}H_{19}N_3O_3Na$, 272.1324; found, 272.1322.

E1: Yield 73.1%; ^{1}H-NMR (D_6-Acetone, 500 MHz), δ: 7.87 (1H, d, $J = 7.5$ Hz), 7.23 (2H, m), 7.14 (3H, m), 7.07 (1H, m), 6.72 (1H, d, $J = 7.5$ Hz), 6.37 (1H, dd, $J = 10.5$, 9.5 Hz), 4.75 (1H, m), 4.57 (1H, d, $J = 11.0$ Hz), 3.37 (1H, m), 2.74 (1H, m), 2.02 (1H, m), 1.97 (1H, m), 1.74 (1H, m),

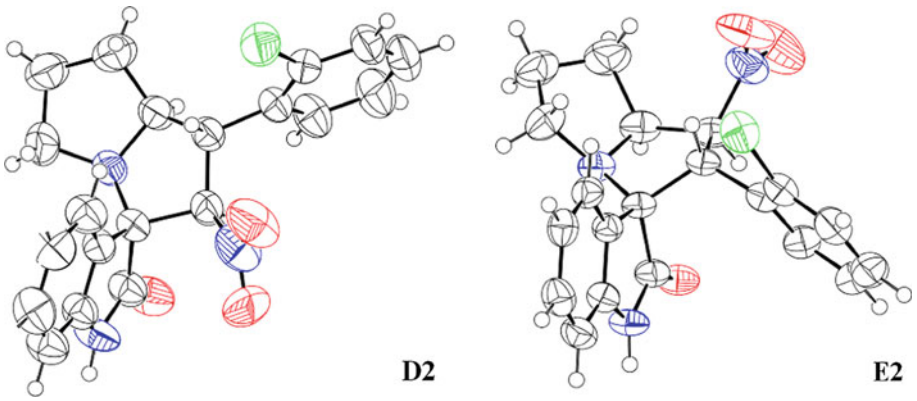


Fig. 2 X-ray crystal structures of **D2** and **E2**

1.44 (1H, m); ^{13}C NMR (D_6-Acetone, 125 MHz), δ: 178.0, 144.0, 134.4, 130.7, 129.4, 129.2, 128.5, 127.6, 126.1, 122.5, 110.6, 92.7, 75.7, 64.3, 52.9, 51.7, 28.6, 26.2; EI-MS, m/z: 349 (M^+), HRMS (ESI-TOF) calcd for $C_{20}H_{19}N_3O_3Na$, 272.1324; found, 272.1321.

D2: Yield 12.0%; ^{1}H NMR ($CDCl_3$-CD_3OD, 500 MHz), δ: 9.45 (1H, b), 7.56 (1H, d, J = 7.5 Hz), 7.40 (1H, d, J = 7.5 Hz), 7.26–7.31 (3H, m), 7.19 (1H, t, J = 7.5 Hz), 7.04 (1H, t, J = 7.5 Hz), 6.90 (1H, d, J = 7.5 Hz), 5.80 (1H, d, J = 11.2 Hz), 4.72 (1H, dd, J = 11.2, 9.6 Hz), 4.03 (1H, m), 2.73 (2H, m), 2.0 (3H, m), 1.69 (1H, m); ^{13}C NMR ($CDCl_3$-CD_3OD, 125 MHz), δ: 178.7, 142.1, 134.7, 134.4, 130.8, 130.0, 128.7, 127.7, 127.5, 125.8, 122.8, 122.7, 111.0, 95.8, 73.5, 70.8, 48.5, 48.1, 30.7, 26.7; EI-MS, m/z: 383 (M^+), HRMS (ESI-TOF) calcd for $C_{20}H_{18}ClN_3O_3Na$, 406.0934; found, 406.0930.

E2: Yield 67.6%; ^{1}H NMR ($CDCl_3$-CD_3OD, 400 MHz), δ: 7.79 (1H, s), 7.70 (1H, d, J = 7.6 Hz), 7.64 (1H, dd, J = 7.6, 1.6 Hz), 7.23 (1H, t, J = 7.6 Hz), 7.18 (1H, dd, J = 8.0, 1.2 Hz), 7.12 (1H, t, J = 7.6 Hz), 7.06 (2H, m), 6.69 (1H, d, J =8.0 Hz), 6.16 (1H, t, J = 10.0 Hz), 5.44 (1H, d, J = 10.8 Hz), 4.89 (1H, dd, J = 17.2, 8.0 Hz), 3.33 (1H, m), 2.88 (1H, t, J = 7.6), 2.17 (1H, m), 2.02 (1H, m), 1.83 (1H, m), 1.52 (1H, m); ^{13}C NMR ($CDCl_3$-CD_3OD, 100 MHz), δ: 178.0, 142.1, 135.1, 130.5, 130.0, 129.7, 128.8, 128.6, 127.4, 127.0, 123.5, 121.6, 109.8, 93.1, 75.2, 63.7, 51.1, 46.6, 27.6, 25.2; EI-MS, m/z: 383 (M^+), HRMS (ESI-TOF) calcd for $C_{20}H_{18}ClN_3O_3Na$, 406.0934; found, 406.0931.

D3: Yield 7.4%; ^{1}H NMR ($CDCl_3$, 400 MHz), δ: 8.71 (1H, s), 7.38 (2H, d, J = 8.8 Hz), 7.30 (2H, m), 7.08 (1H, t, J = 7.6 Hz), 6.97 (1H, d, J = 8.0), 6.92 (2H, d, J = 8.8 Hz), 5.80 (1H, d, J = 11.2 Hz), 4.09 (1H, m), 3.91 (1H, m), 3.80 (3H, s), 2.72 (2H, m), 2.06 (1H, m), 1.93 (2H, m), 1.72 (1H, m);^{13}C NMR ($CDCl_3$, 100 MHz), δ: 178.9, 159.4, 141.8, 130.8, 128.9, 128.6, 126.1, 123.0, 122.6, 114.5, 111.1, 97.0, 73.5, 70.3, 55.3, 52.9, 48.2, 31.2, 27.1; EI-MS, m/z: 379 (M^+), HRMS (ESI-TOF) calcd for $C_{21}H_{21}N_3O_4Na$, 402.1430; found, 402.1432.

E3: Yield 60.8%; ^{1}H NMR (D_6-Acetone, 400 MHz), δ: 9.27 (1H, s), 7.85 (1H, d, J = 7.6 Hz), 7.23 (1H, m), 7.15 (1H, dd, J = 11.6, 3.2 Hz), 7.07–7.10 (2H, m), 6.73 (1H, m), 6.67 (2H, d, J = 8.8 Hz), 6.31 (1H, d, J = 9.6 Hz), 4.74 (1H, dd, J = 16.8, 8.0 Hz), 4.52 (1H, d, J = 11.2 Hz), 3.63 (3H, s), 3.37 (1H, m),, 2.74 (1H, t, J = 7.2 Hz), 2.05 (2H, m), 1.98 (1H, m), 1.74 (1H, m), 1.45 (1H, m); ^{13}C NMR (D_6-Acetone, 100 MHz), δ: 178.2, 160.1, 144.1, 130.6, 130.4, 127.5, 126.3, 126.0, 122.5, 114.5, 110.6, 92.9, 75.6, 64.2, 55.2, 52.4, 51.7, 28.5, 26.2; EI-MS, m/z: 379 (M^+), HRMS (ESI-TOF) calcd for $C_{21}H_{21}N_3O_4Na$, 402.1430; found, 402.1433.

D4: Yield 17.2%; ^{1}H NMR (D_6-DMSO, 400 MHz), δ: 10.65 (1H, s), 7.39–7.46 (3H, m), 7.33 (1H, m), 7.09–7.37 (8H, m), 6.96 (1H, dt, J = 7.6, 1.2 Hz), 6.80 (1H, d,J = 7.2 Hz), 5.39 (1H, d, J = 9.6 Hz), 3.91 (1H, m), 3.88 (1H, m), 3.78 (1H, d, J = 7.6 Hz), 2.74 (2H, m); ^{13}C NMR (D_6-DMSO, 100 MHz), δ: 179.4, 142.4, 138.5, 136.8, 130.1, 129.2, 129.1, 128.2, 128.1, 127.8, 127.4, 126.1, 124.7, 121.9, 109.7, 98.0, 63.9, 54.7, 38.3; EI-MS, m/z: 399 (M^+), HRMS (ESI-TOF) calcd for $C_{24}H_{21}N_3O_3Na$, 422.1481; found, 422.1485.

E4: Yield 55.3%; ^{1}H NMR ($CDCl_3$, 400 MHz), δ: 8.32 (1H, s), 7.63 (1H, d, J = 7.2 Hz), 7.54 (1H, s), 7.08–7.27 (11H, m), 6.96 (1H, d, J = 7.6 Hz), 6.59 (1H, d, J = 7.6 Hz), 6.13 (1H, t, J = 8.8 Hz), 4.84 (1H, m), 4.51 (1H, d, J =9.2 Hz), 2.92 (1H, dd, J = 13.2, 3.6 Hz), 2.71 (1H, m), 2.15 (1H, m);^{13}C NMR ($CDCl_3$, 100 MHz), δ: 179.5, 140.7, 137.3, 132.3, 129.8, 129.3, 128.6, 128.5, 128.4, 128.2, 127.8, 126.7, 124.0, 123.2, 109.9, 90.3, 72.0, 58.5, 57.5, 38.1; EI-MS, m/z: 399 (M^+), HRMS (ESI-TOF) calcd for $C_{24}H_{21}N_3O_3Na$, 422.1481; found, 422.1485.

D5: Yield 7.7%; ^{1}H NMR ($CDCl_3$, 400 MHz), δ: 7.93 (1H, s), 7.26–7.44 (7H, m), 7.07 (1H, t, J = 7.6 Hz), 6.87 (1H, d, J = 7.6 Hz), 5.48 (1H, d, J = 10.0 Hz), 3.99 (1H, m), 3.83 (1H, t, J = 10.0 Hz), 2.38 (1H, b), 1.64 (1H, m), 1.49 (1H, m), 0.98 (1H, m), 0.83 (6H, dd, J = 6.0, 4.8 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz), δ: 172.3, 139.8, 135.0, 130.7, 128.6, 128.2, 127.7,

126.2, 124.2, 121.4, 111.2, 92.0, 70.9, 56.4, 49.8, 25.5, 23.6, 21.5; EI-MS, m/z: 365 (M^+), HRMS (ESI-TOF) calcd for $C_{21}H_{23}N_3O_3Na$, 388.1637; found, 388.1638.

E5: Yield 66.1%; ^{1}H NMR (D_6-DMSO, 400 MHz), δ: 10.09 (1H, s), 7.59 (1H, d, J = 7.2 Hz), 7.17 (4H, m), 7.06 (1H, t, J = 7.6 Hz), 6.99 (2H, m), 6.60 (1H, d, J = 8.0 Hz), 6.12 (1H, t, J = 9.6 Hz), 4.51 (1H, m), 4.31 (1H, d, J = 9.2 Hz), 3.99 (1H, d, J = 7.6 Hz), 1.73 (1H, m), 1.40 (1H, m), 1.10 (1H, m), 0.90 (6H, dd, J = 14, 6.8 Hz);^{13}C NMR (D_6-DMSO, 100 MHz), δ: 178.7, 142.3, 133.4, 129.4, 128.7, 128.3, 127.9, 127.8, 124.1, 121.9, 109.3, 91.7, 72.0, 57.1, 55.3, 24.2, 23.8, 21.1; EI-MS, m/z: 365 (M^+), HRMS (ESI-TOF) calcd for $C_{21}H_{23}N_3O_3Na$, 388.1637; found, 388.1633.

D6: Yield 15.3%; ^{1}H NMR (D_6-Acetone, 400 MHz), δ: 9.70 (1H, s), 7.52 (2H, d, J=7.6 Hz), 7.42 (2H, d, J=7.6 Hz), 7.28–7.35 (3H, m), 7.04 (1H, t, J=7.6 Hz), 6.95 (1H, t, J = 7.6 Hz), 5.59 (1H, d, J = 10.4 Hz), 4.60 (1H, b), 4.38 (1H, t, J = 10.8 Hz), 4.14 (1H, b), 3.88 (1H, m), 3.72 (1H, m), 3.51 (1H, m), 3.34 (1H, b); ^{13}C NMR (D_6-Acetone, 100 MHz), δ: 180.1, 143.4, 138.0, 131.2, 129.8, 129.1, 128.6, 128.4, 125.4, 123.2, 110.8, 99.2, 70.4, 66.0, 60.6, 51.6; EI-MS, m/z: 339 (M^+), HRMS (ESI-TOF) calcd for $C_{18}H_{17}N_3O_4Na$,362.1117; found, 362.1119.

E6: Yield 52.4%; ^{1}H NMR (D_6-Acetone, 400 MHz), δ: 9.05 (1H, s), 7.68 (1H, d, J = 7.6 Hz), 7.10–7.22 (8H, m), 6.27 (1H, dd, J = 10.4, 9.6 Hz), 4.60 (1H, b), 4.43 (1H, d, J = 10.8 Hz), 3.98 (1H, t, J = 5.6 Hz), 3.75 (2H, m), 3.46 (1H, b); ^{13}C NMR (D_6-Acetone, 100 MHz), δ: 179.9, 143.2, 134.0, 130.2, 129.7, 129.1, 128.8, 124.9, 123.0, 110.3, 110.2, 85.6, 72.3, 63.3, 58.9, 57.4; EI-MS, m/z: 339 (M^+), HRMS (ESI-TOF) calcd for $C_{18}H_{17}N_3O_4Na$, 362.1117; found, 362.1118.

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References

1. Huisgen R (1963) Kinetics and Mechanism of 1,3-Dipolar cycloadditions. Angew Chem Int Ed 2:633–645. doi:10.1002/anie.196306331
2. Stanley R, Jan B, Birgitta S (2004) The three-component reaction between isatin, α-amino acids and dipolarophiles. Eur J Org Chem 2:413–418. doi:10.1002/ejoc.200300621
3. Abdel-Aziz S El-Ahl (2002) Three-component 1,3-dipolar cycloaddition reactions in synthesis of spiro [pyrrolidine-2,3′-oxindoline] derivatives. Heteroatom Chem 13:324–329. doi:10.1002/hc.10038
4. Demosthenes F, William JR, David SC, David LC (1998) Solution phase synthesis of a spiro [pyrrolidine-2,3′-oxindole] library via a three component 1,3-dipolar cycloaddition reaction. Tetrahedron Lett 39:2235–2238. doi:10.1016/S0040-4039(98)00234-2
5. Rathna DRSM, Jayadevan JS, Selva K, Raghavachary RR (2006) A novel entry to dispiropyrrolo-bicyclo[2.2.1]heptanes through sequential 1,3-dipolar and Diels-Alder cycloaddition reactions. Tetrahedron Lett 47:829–832. doi:10.1016/j.tetlet.2005.11.089
6. Raj AA, Raghunathan R, Sridevikumari MR, Raman N (2003) Synthesis, antimicrobial and antifungal activity of a new class of spiro pyrrolidines. Bioorgan Med Chem 11:407–419. doi:10.1016/S0968-0896(02)00439-X
7. Chen G, He HP, Ding J, Hao XJ (2009) Synthesis and antitumor activity evaluation of regioselective spiro [pyrrolidine-2,3′-oxindole] compounds. Heterocycl Commun 15:355–360. doi:10.1515/HC.2009.15.5.355
8. Tomotaka O, Yasutaka H, Tomihiro F, Xuenong X, Yoshiji T (2005) Enantio- and diastereoselective Michael reaction of 1,3-dicarbonyl compounds to nitroolefins catalyzed by a bifunctional thiourea. J Am Chem Soc 127:119–125. doi:10.1021/ja044370p
9. Arnaud G, Silvere N, Christophe M, Alain W, Charles M (2004) $NaNO_2$-mediated transformation of aliphatic secondary nitroalkanes into ketones or oximes under neutral, aqueous conditions: How the nitro derivative catalyzes its own transformation. J Org Chem 69:8997–9001. doi:10.1021/jo0489824
10. Ono N, Miyake H, Kamimura A, Hamamoto I, Tamura R, Kaji A (1985) Denitrohydrogenation of aliphatic nitro compounds and a new use of aliphatic nitro compounds as radical precursors. Tetrahedron 41:4013–4023. doi:10.1016/S0040-4020(01)97180-7