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Green and diastereoselective synthesis of *trans*-3-(5-methylisoxazol-3-yl)-3,4-dihydro-2*H*-naphtho[2,3-e][1,3]oxazines

Mehdi Shafiee[a,b], Ahmad Reza Khosropour[b,*], Iraj Mohammadpoor-Baltork [b,*], Majid Moghadam[b], Shahram Tangestaninejad[b], Valiollah Mirkhani[b], Hamid Reza Khavasi[c]

[a] *Chemistry Department, Malek-ashtar University of Technology, Shahin-shahr, 83145-115, Iran.*
[b] *Catalysis Division, Department of Chemistry, University of Isfahan, Isfahan, 81746-7344, Iran.*
[c] *Department of Chemistry, Shahid Beheshti University, Evin, Tehran 1983963113, Iran.*

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ABSTRACT

Reaction between aromatic aldehydes and 3–methyl-1-phenyl-2-pyrazoline-5-one catalyzed by nano-SiO_2/$HClO_4$ in water under reflux provided a simple and efficient route for the synthesis of 4-((5-hydroxy-3-methyl-1-phenyl-1*H*-pyrazol-4-yl)(aryl)methyl)-3-methyl-1-phenyl-1H-pyrazol-5-ol derivatives in high yields.

Keywords: *Betti base, Green chemistry, Aryl aldehydes, Dihydro-2H-naphtho[2,3-e][1,3]oxazines, p-TSA.*

1. Introduction

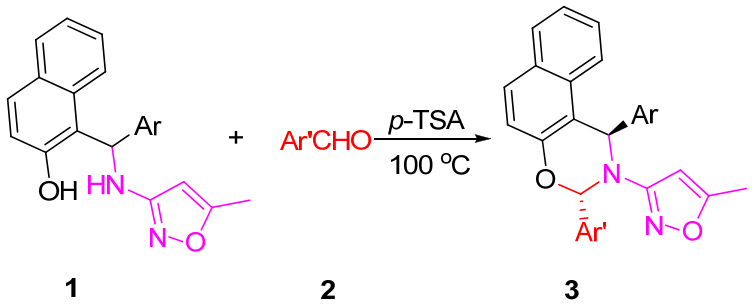
1,3-Oxazines and their derivatives are a prominent class of N,O-heterocyclic compounds due to they constitute a part of many fine chemicals and have been assigned as privileged structures in biologically active pharmaceuticals such as synthetic intermediates for the preparation of heterocycles which have been shown to possess a variety of biological properties [1], as monomers for polymer synthesis [2], as photochromic agents [3], as detecting reagents of cyanide [4], as nonsteroidal progesterone receptor agonist tanaproget [5] and as melatonin receptor [6]. Moreover, it has been found that some of them have plasma lipid altering characteristics [7] act as inhibitors of human leukocyte elastase [8] or as potent non-steroidal progesterone receptor agonists [9]. Among them, 3,4-dihydro-2*H*-naphtho[2,3-e][1,3]oxazines are a useful class of these compounds in the field of medicinal chemistry, including the potent antimicrobial [10] and anti-osteoporotic activities [11]. Moreover, some of these derivatives act as thermally reversible photochromic molecules [12]. Owing to the signify-cance of this structural motif, several syntheses of these compounds have been reported [13].

*Corresponding authors: khosropour@chem.ui.ac.ir, imbaltork@sci.ui.ac.ir
Tel.: +98-311- 668-9732; Fax: +98-311- 668-9732

Albeit the reported approaches are useful tools for the synthesis of 3,4-dihydro-2*H*-naphtho [2,3-e] [1,3] oxazines, most of them suffer from significant limitations such as expensive reagents/catalysts and prolonged reaction times. So, the discovery of more general, efficient, rapid, and viable routes is highly desirable. Furthermore, isoxazole derivatives, especially 5-methylisoxazole represent an interesting class of heterocycles possessing a wide spectrum of biological activities [14]. Thus, new hybrid moieties secured by introducing 5-methylisoxazole on the ring of 1,3-oxazines, promise to offer fascinating scaffolds.

Moreover, Betti bases or amidoalkyl naphthols [15] represent very important bioactive compounds which the bradycardia in human and hypotensive effects of them have been evaluated [16]. Moreover, they are attractive compounds as chiral ligands in enantioselective reactions [17]. They can be used as chiral shift reagents for carboxylic acids or as chiral auxiliaries for the synthesis of α-aminophosphonic acids [18]. In this paper we wish to study other application of these compounds in organic synthesis.

During our ongoing investigations in synthesis of fine chemicals [19] especially developing of methodologies for the preparation of new Betti bases [20], we envisaged to build up diversified 3-(5-methylisoxazol-3-yl)- 3,4- dihydro- 2*H*- naphtho [2,3-e] [1,3] oxazines



1 **2** **3**

Scheme 1. Synthesis of *trans*-3-(5-methylisoxazol-3-yl)-3,4-dihydro-2*H*-naphtho[2,3-e][1,3]oxazines.

via reaction of 1-(aryl (5-methyl-isoxazol-3-ylamino) methyl)naphthalen-2-ols **1** (as procedure that were reported by our group) [20] and arylaldehydes **2** (Scheme 1).

2. Experimental

2.1. General procedure

The Betti base **1** (1.0 mmol), aryl aldehyde (1.0 mmol), and *p*-TSA (0.2 mmol) were added into a 20 mL vial and heated in the 100 °C oil bath with stirring for appropriating times indicated in Table 2 (30-40 minutes). After the reaction was complete (monitored by TLC), the mixture was cooled down to room temperature and diluted with H_2O. The precipitated solid was collected by filtration and washed with cold ethanol to give the desired products.

Selected spectral data:

*4,4'-(2-(5-methylisoxazol-3-yl)-2,3-dihydro-1H-naphtho[1,2-e][1,3]oxazine-1,3-diyl)dibenzonitrile (**3f**)*:
White solid, yield: 95%. m.p.=256-258 °C. ^{1}HNMR (400 MHz, $CDCl_3$): δ = 2.15 (s, 3H, CH_3), 4.97 (s, 1H, C=CH), 6.05 (s, 1H, NCHAr), 6.81 (s, 1H, NCHO), 7.31 (d, J = 9.2 Hz, 1H, ArH), 7.36-4.43 (m, 3H, ArH), 7.63 (d, J = 8.4 Hz, 2H, ArH), 7.70 (d, J = 8.4 Hz, 2H, ArH), 7.73 (s, 4H, HAr), 7.84-7.87 (m, 2H, HAr) ppm. ^{13}CNMR (100 MHz, $CDCl_3$): δ = 12.6, 61.8, 82.5, 96.2, 112.2, 112.7, 112.8, 118.4, 118.5, 118.6, 122.8, 124.5, 126.9, 127.4, 128.8, 129.6, 130.1, 130.4, 131.8, 132.5, 132.6, 141.2, 146.4, 151.8, 164.4, 169.7 ppm. IR (KBr): $\bar{\nu}$ = 2226, 1610, 1490, 1451, 1232, 1002, 812 cm^{-1}. MS: m/z = 468 (M, 32).

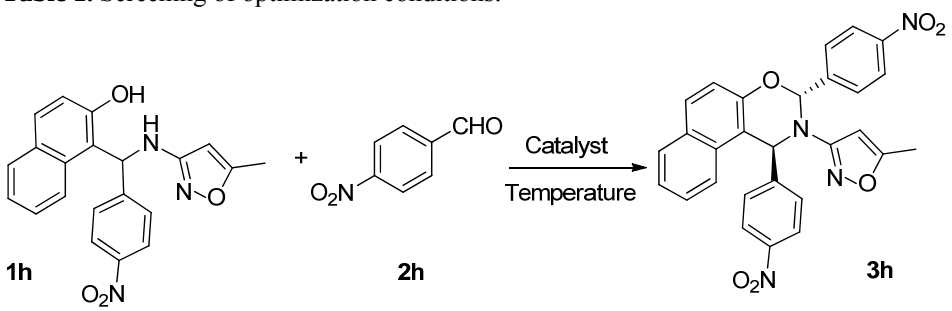
*1-(3-methoxyphenyl)-2-(5-methylisoxazol-3-yl)-3-(4-nitrophenyl)-2,3-dihydro-1H-naphtho[1,2-e][1,3] oxazine (**3w**)*:
White solid, yield: 90%. m.p.= 192-194 °C. ^{1}HNMR (400 MHz, $CDCl_3$): δ = 2.13 (s, 3H, CH_3), 3.80 (s, 3H, OCH_3), 5.07 (s, 1 H, C=CH), 6.26 (s, 1H, NCHAr), 6.73 (s, 1 H, NCHO), 9.90-6.91 (m, 1H, ArH), 7.06-7.07 (m, 2H, ArH), 7.29-7.33 (m, 2H, ArH), 7.36-7.42 (m, 2H, ArH), 7.51-7.53 (m, 1H, ArH), 7.81-7.84 (m, 4H, ArH), 8.26-8.29 (m, 2 H, ArH) ppm. ^{13}CNMR (100 MHz, $CDCl_3$): δ = 12.5, 55.3, 62.3, 82.2, 96.3, 113.1, 113.9, 115.4, 118.5, 121.8, 123.3, 123.7, 124.1, 127.1, 127.2, 128.6, 129.5, 129.7, 129.9, 132.2, 142.8, 143.7, 147.9, 151.6, 159.9, 164.5, 169.3 ppm. IR (KBr): $\bar{\nu}$ = 1599, 1518, 1490, 1342, 1232, 1007, 855 cm^{-1}. MS: m/z = 493 (M, 28).

*1-(4-fluorophenyl)-2-(5-methylisoxazol-3-yl)-3-p-tolyl-2,3-dihydro-1H-naphtho[1,2-e][1,3]oxazine (**3z**)*:
White solid, yield: 70%. m.p. 225-226 °C. ^{1}HNMR (400 MHz, $CDCl_3$): δ = 2.11 (s, 3H, CH_3), 2.41 (s, 3H, CH_3), 4.93 (s, 1H, C=CH), 6.15 (s, 1H, NCHAr), 6.88 (s, 1H, NCHO), 7.03-7.07 (m, 2H, ArH), 7.23 (d, J = 8.4, 2H, ArH), 7.29 (d, J = 8.8 Hz, 1 H, ArH), 7.34-7.41 (m, 2H, ArH), 7.45-7.51 (m, 5H, ArH), 7.79-7.83 (m, 2H, ArH) ppm. ^{13}CNMR (100 MHz, $CDCl_3$): δ= 12.5,21.3, 60.6, 82.9, 96.4, 114.2, 115.3 (d, J = 22 Hz), 118.8, 123.3, 123.9, 125.9, 126.9, 128.5, 129.3, 129.4, 129.6, 131.1 (d, J = 8 Hz), 132.3, 133.5, 137.6 (d, J = 3 Hz), 138.3, 152.3, 162.2 (d, J = 245 Hz), 164.9, 168.6 ppm. IR (KBr): $\bar{\nu}$ = 1602, 1510, 1450, 1233, 997, 812, 765 cm^{-1}. MS: m/z = 450 (M, 33).

3. Results and Discussion

At the outset, the condensation reaction of 1-((5-methylisoxazol-3-ylamino) (4-nitrophenyl) methyl) naphthalen-2-ol (**1h**) and 4-nitrobenzaldehyde (**2h**) in the presence of different catalysts under solvent-free conditions was selected as a template. To our delight, in the presence of *p*-TSA (20 mol%), quantitative conversion (92 %) was registered in 30 min and the adduct **3h** was produced exclusively (Table 1, entry 4). Notably, lower yields were obtained when the same reaction carried out with using of lower amounts of loading of the catalyst (Table 1, entries 1-3). No reaction occurred in the absence of a catalyst (Table 1, entry 5). The results subsequently showed that the temperature appeared to be crucial as the reaction did not take place even after stirring for 5 hours at room temperature (Table 1, entry 6). Running the reaction using a lower temperature (<100 °C), sharply decreased the conversion. The results encouraged us to examine other Brønsted or Lewis acids, such as $CeCl_3.7H_2O$, $InCl_3$, $AlCl_3$, $ZrCl_4$, $ZrOCl_2$, $Zn(OTf)_2$, $NiCl_2.7H_2O$, H_3BO_3, silica sulphuric acid (SSA),

Table 1. Screening of optimization conditions.[a]



Entry	Catalyst /mol%	*T* (ºC)	Yield (%)[b]
1	*p*-TSA/5	100	29
2	*p*-TSA /10	100	52
3	*p*-TSA /15	100	73
4	*p*-TSA /20	100	92
5	-	100	0
6	*p*-TSA /20	25	0
7	*p*-TSA /20	50	45
8	*p*-TSA /20	90	79
9	$BiCl_3$/20	100	59
10	$Bi(NO_3)_3$/20	100	15
11	$CeCl_3$/20	100	5
12	$InCl_3$/20	100	10
13	$AlCl_3$/20	100	12
14	$ZrCl_4$/20	100	77
15	$ZrOCl_2$/20	100	31
16	$Zn(OTf)_2$/20	100	70
17	$NiCl_2$/20	100	0
18	H_3BO_3/20	100	0
19[c]	SSA/20	100	79
20[d]	[Hmim]HSO_4/20	100	20
21[e]	TSIA	100	60

[a]Reaction conditions: **1h** (1.0 mmol), **2h** (1.0 mmol), and catalysts under solvent-free conditions for 30 min.
[b]Isolated yields.
[c]Silica sulfuric acid.
[d]1-Methylimidazolium hydrogen sulfate.
[e]Tungstosilicic acid.

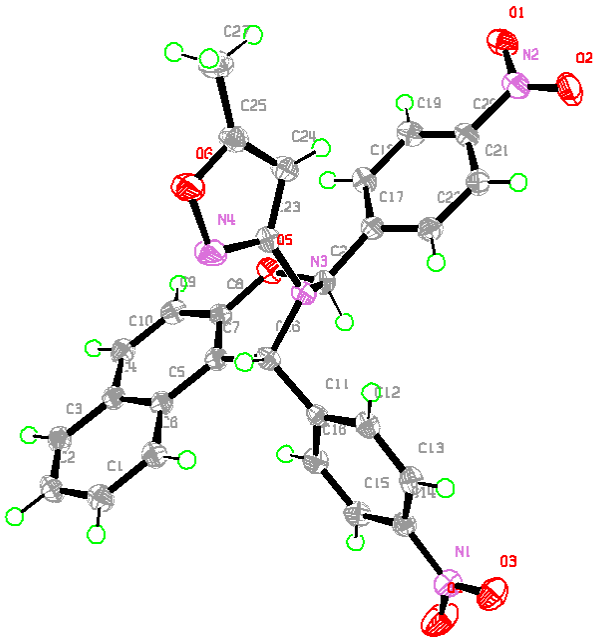


Fig. 1. ORTEP view of compound **3h.**

1-methylimidazolium hydrogensulfate ([Hmim]HSO_4) and tungstosilicic acid (TSIA) (Table 1, entries 9-21), but they led to lower yields of the product. We found that performing the reaction in the presence of 20 mol% of *p*-TSA at 100 ºC under solvent-free conditions provided the best result. The reaction was rapid, and achieved satisfactory conversion without any significant side reactions.

It is worthwhile to note that *trans*-**2i** was unambiguously assigned by X-ray crystallography (CCDC 877995) (Fig. 1) as the major product in racemic form for all the reactions examined in Table 1. Having achieved results from the optimized reaction conditions, the scope of the process was studied. As shown in Table 2, the transformation proceeds very stereoselective and efficient. The stereochemistry of compounds **3a-z** was established by correlation of the spectroscopic data with those obtained for **3h**.

It was observed that both the electron-rich and electron-deficient aryl aldehydes afforded the desired products in excellent yields and extraordinary diastereoselectivity. The structures of all products were established completely on the basis of spectroscopic evidence. The tolerance of functionalities such as fluoro, chloro, bromo, cyano, nitro, methyl and methoxy in this procedure provides the opportunity of their various further chemical manipulations in products. However, it should be noted that this reaction is not applicable to the aliphatic aldehydes because of fewer conversions. Several therapeutically relevant moieties could be incorporated at ease by this method into 3-(5-methylisoxazol-3-yl)-3,4- dihydro-2*H*-naphtho [2,3-e] [1,3] oxazines.

The stereochemical outcome of the reaction of the Betti bases A with aryl aldehydes to naphtho[2,3-e] [1,3]oxazines can be explained by the transition states TS_1 and TS_2 (Fig. 2). Interaction between Ar and Ar' would cause the reaction to take place mainly through TS_1, in which the steric interactions are minimized compared to TS_2, affording the trans-isomer. These results were observed in Table 1.

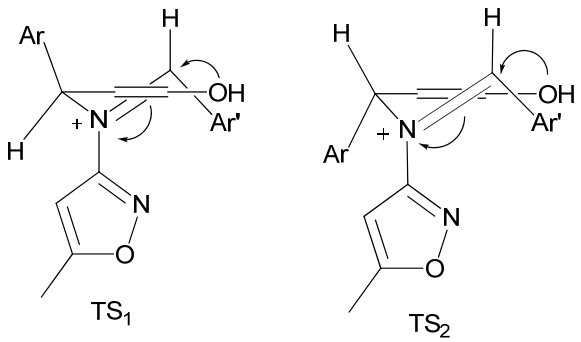


Fig. 2. Proposed transition states to explain the reaction stereochemistry. TS_1 result to trans and TS_2 result to cis.

According to the X-ray crystallographic analysis of **3h**, The Möller-Plesset second order perturbation theory (MP2) calculations using the Dunning's correlation-consistent polarized valence double-zeta (cc-pVDZ) [21] basis set were also employed to investigate the optimized *trans* and *cis* isomers of **3h** without symmetry constraints. The calculations were performed with the TURBOMOLE 6.3 program package, making use of the resolution-of-the-identity (RI) approximation for the evaluation of the electron-repulsion integrals [22]. The computational results show that the energy of the *trans*-**3h** is lower by about 13.9 kJ/mol than that of the *cis*-**3h**, which indicates that *trans* form is the preferable isomer.

As the aforementioned results, a plausible mechanism is illustrated in Scheme 2.

Initially, the Betti base attacks aryl aldehyde in the presence of the catalyst to generate the corresponding imine as the pivotal intermediate (A). Finally, intermediate A undergoes 6-endo-dig to give the corresponding [1,3]oxazine.

4. Conclusions

In conclusion, we have discovered a convenient, efficient green and stereoselective synthesis of *trans*-3-(5-methylisoxazol-3-yl)-3,4- dihydro-2*H*- naphtho[2,3-e] [1,3]oxazine, under solvent-free conditions. To our knowledge, there is no other efficient method for the synthesis of this class of compounds. This reaction includes some important aspects like straightforward operation, easy workup procedure and absence of transition metal catalysts. Further surveys in this field are currently under way and will be reported in due time.

Acknowledgment

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References

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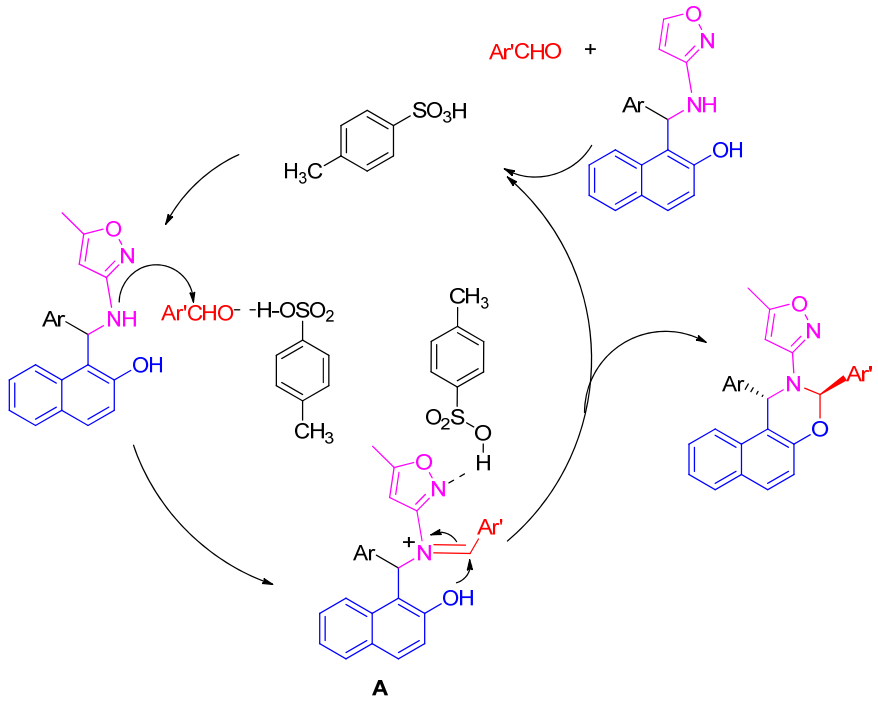


Scheme 2. Plausible mechanism.

Table 2. Stereoselective synthesis of *trans*-3-(5-methylisoxazol-3-yl)-3,4-dihydro-2*H*-naphtho[2,3-e][1,3]oxazine catalyzed by *p*-TSA.

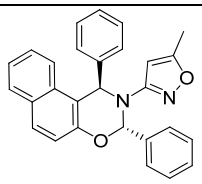
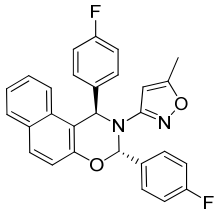
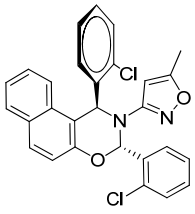
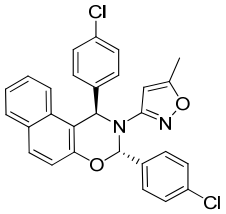
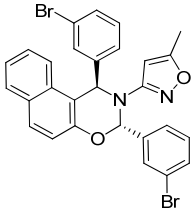
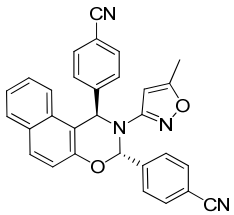
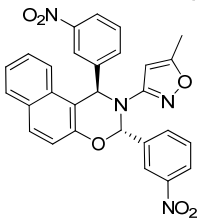
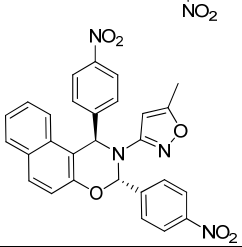
Entry	Ar	Ar'	Product		Time (min)	Yield (%)[a]	d.r.[b]
1	C_6H_5	C_6H_5		**3a**	35	85	91:9
2	4-FC_6H_4	4-FC_6H_4		**3b**	30	98	95:5
3	2-ClC_6H_4	2-ClC_6H_4		**3c**	35	90	94:6
4	4-ClC_6H_4	4-ClC_6H_4		**3d**	35	90	90:10
5	3-BrC_6H_4	3-BrC_6H_4		**3e**	35	90	56:34
6	4-NCC_6H_4	4-NCC_6H_4		**3f**	30	95	67:33
7	3-$O_2NC_6H_4$	3-$O_2NC_6H_4$		**3g**	30	90	60:40
8	4-$O_2NC_6H_4$	4-$O_2NC_6H_4$		**3h**	30	92	91:9

Table 2. *(Continued)*

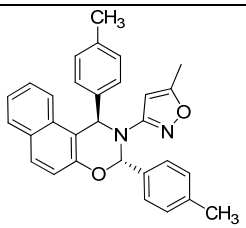
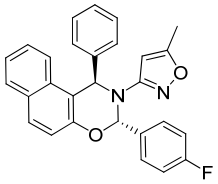
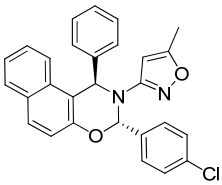
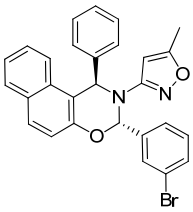
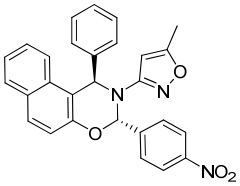
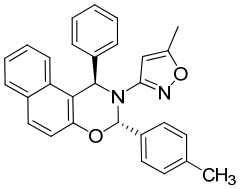
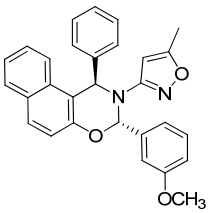
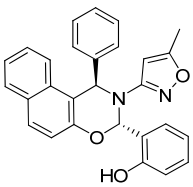
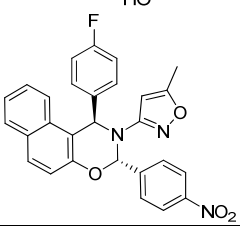
9	4-$H_3CC_6H_4$	4-$H_3CC_6H_4$		**3i**	40	75	95:5
10	C_6H_5	4-FC_6H_4		**3j**	35	90	94:6
11	C_6H_5	4-ClC_6H_4		**3k**	35	90	90:10
12	C_6H_5	3-BrC_6H_4		**3l**	35	85	95:5
13	C_6H_5	4-$O_2NC_6H_4$		**3m**	35	90	56:34
14	C_6H_5	4-$H_3CC_6H_4$		**3n**	35	80	67:33
15	C_6H_5	3-$H_3COC_6H_4$		**3o**	30	90	60:40
16	C_6H_5	2-HOC_6H_4		**3p**	35	90	91:9
17	4-FC_6H_4	4-$O_2NC_6H_4$		**3q**	40	75	95:5

Table 2. *(Continued)*

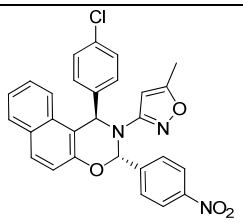
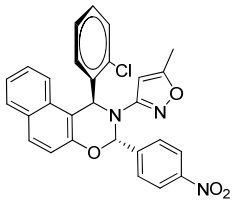
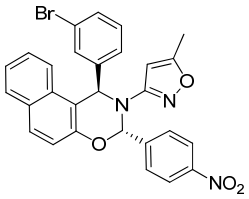
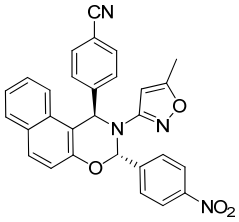
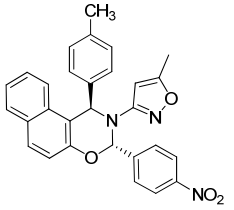
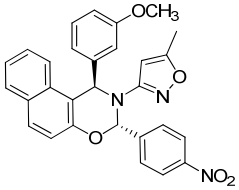
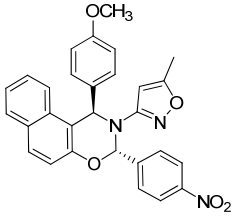
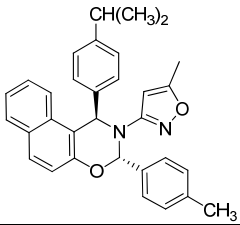
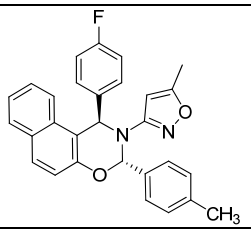
18	4-ClC_6H_4	4-$O_2NC_6H_4$		**3r**	30	95	94:6
19	2-ClC_6H_4	4-$O_2NC_6H_4$		**3s**	30	90	90:10
20	3-BrC_6H_4	4-$O_2NC_6H_4$		**3t**	30	90	92:8
21	4-NCC_6H_4	4-$O_2NC_6H_4$		**3u**	35	85	95:5
22	4-$H_3CC_6H_4$	4-$O_2NC_6H_4$		**3v**	30	90	56:34
23	3-$H_3COC_6H_4$	4-$O_2NC_6H_4$		**3w**	30	90	67:33
24	4-$H_3COC_6H_4$	4-$O_2NC_6H_4$		**3x**	30	85	60:40
25	4-*i*PrC_6H_4	4-$H_3CC_6H_4$		**3y**	40	90	95:5

Table 2. *(Continued)*

26	4-FC_6H_4	4-$H_3CC_6H_4$		**3z**	30	95	94:6

[a]Isolated yield.
[b]Diastereomeric ratio was determined by ^{1}H NMR and ^{13}C NMR spectroscopy of the crude product.

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