Diastereoselective Aerial Oxidative Cyclization of Methylenebisnaphthols Catalyzed by *N*-Hydroxyimides in the Presence of Fe^{3+} and Co^{2+}-Mn^{2+} Catalysts

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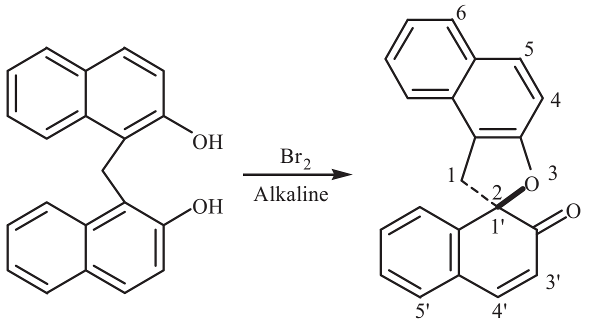
Aerial oxidative cyclization of methylenebisnaphthols to their corresponding spirans has been carried out using catalytic amounts of *N*-hydroxyimides and $FeCl_3 \cdot 6H_2O$ or $Co(OAc)_2 \cdot 4H_2O$-$Mn(OAc)_2 \cdot 4H_2O$. In this article we focus on the use of $FeCl_3 \cdot 6H_2O$ as a highly green and sustainable catalyst.

Key words: Aerial Oxidative Cyclization, Bisnaphthols, Spirodienones, *N*-Hydroxyimides

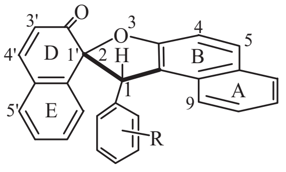
Introduction

Abel was the first to report the alkaline oxidation of methylenebisnaphthols to spirodienones with Br_2 in 1892 though the product of the unsubstituted methylenebisnaphthol **1** was proposed to be a peroxide [1]. However, on the basis of chemical evidence its structure was later determined to be the spirodienone **2** [2, 3]. Spirodienone derivatives of substituted and unsubstituted methylenebisnaphthols have been thoroughly investigated and yet remain one of the most interesting members of the spirodienone family [4 – 18].

As Kasturi has stated in his reports, Abel's ketone derivatives have two sets of diastereomers **3** and **4**, the latter being formed when steric hindrance is the decisive factor [18]. For example, potassium hypobromite, persulfate, trichloroisocyanuric acid (TCCA) [19], chloramine-T and *N*-chlorosuccinimide (NCS) give **3** [12], whereas iodine oxyacids, (diacetoxyiodo)benzene in benzene and aerial oxidation of methylenebisnaphthols catalyzed by Ph_3Bi are specific for **4**. Radical-type oxidants such as hexacyanoferrate(III) in benzene and pyridine, 2,4-di-*tert*-butyl-6-phenylphenoxyl and electrochemical oxidation give mixtures [11 – 13, 19]. In addition, H_2O_2/MoO_3 as an oxidizing system and aerial oxidation in the presence of TEMPO/$FeCl_3$ are two other green procedures for the same purpose [20, 21].



1 **2**



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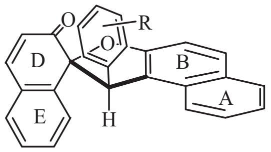

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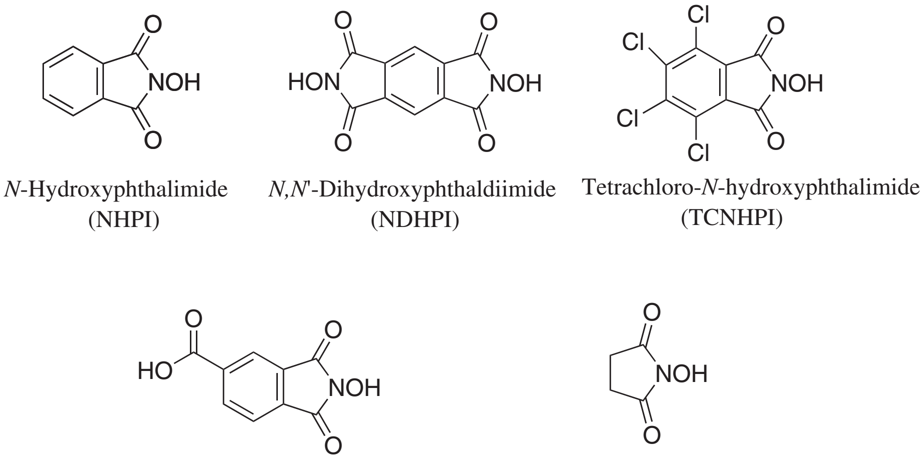
The isomers of series **3** show in their ^{1}H NMR spectra a doublet near $\delta = 6.1$ ppm (vinylic 3-H′), while for isomers of series **4**, this hydrogen appears at about $\delta = 5.4$ ppm, the up-field shift for the latter being due to the shielding effect of the vicinal phenyl ring. Therefore, the chemical shift of the vinylic proton 3′-H is a good evidence to determine which of the two diastereomers is formed.



N-Hydroxyphthalimide (NHPI)

N,N'-Dihydroxyphthaldiimide (NDHPI)

Tetrachloro-*N*-hydroxyphthalimide (TCNHPI)

N-Hydroxyphthalimide-4-carboxylic acid (NHPI-4-COOH)

N-Hydroxysuccinimide (NHSI)

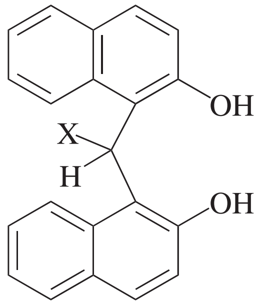
Scheme 1. *N*-Hydroxyimides and their abbreviations.

Most of the above mentioned oxidizing reagents used for the oxidation of methylenebisnaphthols are often hazardous or very toxic, expensive or not readily available. Some reagents often need to be freshly prepared or require drastic conditions, long reaction times and tedious work up [11, 13]. These drawbacks and the need for greener procedures for the preparation of spirodienones on the one hand, and the extensive use of *N*-hydroxyphthalimide (NHPI, Scheme 1) and its analogs in organic synthesis on the other hand, prompted us to conduct oxidative cyclization reactions in the presence of NHPI or its analogs and transition metal cations such as Fe^{3+}. It is therefore necessary to name a few reactions in which *N*-hydroxyimides have been used as organic catalysts.

N-Hydroxyphthalimide is a stable crystalline solid, the preparation of which dates back to 1880 [22]. It is a weak acid ($pK_a = 7$) which forms highly colored salts with metals, ammonia or amines. It is a cheap and non-toxic reagent easily prepared by the reaction of phthalic anhydride and hydroxylamine hydrochloride [23]. It crystallizes in two forms, colorless and yellow, which are substantially identical in all other physical and chemical characteristics [24]. It has been revealed that the phthalimide *N*-oxyl (PINO) radical, generated *in situ* from the NHPI precursor, is an active catalytic species responsible for oxidation reactions [25 – 27]. Notably, by employing NHPI as a radical initiator, a range of organic syntheses have been carried out such as oxygenation of fluorene by organocatalytic reactions [28], oxidation of alkanes [29 – 31], oxidation of alcohols with molecular oxygen in the presence of cobalt cations [32], electrocatalytic oxidation of alcohols [33], selective oxidative deprotection of a variety of structurally diverse trimethylsilyl and *tert*-butyldimethylsilyl ethers using molecular oxygen [34], epoxidation of alkanes by peracids generated *in situ* under mild reaction conditions [35, 36], oxyalkylation of alkenes with alkanes and molecular oxygen [37], nitration of light alkanes and the alkyl side chain of aromatic compounds with NO_2 [38], oxidation of hydroaromatic compounds and diarylalkanes under mild conditions affording the corresponding hydroperoxides with high selectivity [39]. Two reviews published in 2006, the first by Ishi and Sakaguchi and the second by Minisci, describe the aerial oxidation of organic compounds in the presence of *N*-hydroxyderivatives and metal cations [40, 41].

Results and Discussion

With the above background and the emergence of sustainability as one of the key words in discussions in nearly all fields of science, and hence, the need for finding new procedures with the minimum waste – a key challenge in today's environment – we now report the aerial oxidative cyclization of several methylenebisnaphthols (Fig. 1) using catalytic



1, X = H
1a, X = C_6H_5
1b, X = 2-ClC_6H_4
1c, X = 4-$CH_3C_6H_4$
1d, X = 4-ClC_6H_4
1e, X = 2,4-$Cl_2C_6H_3$
1f, X = 4-$CH_3OC_6H_4$
1g, X = 4-FC_6H_4

Fig. 1. Compounds **1** used in this study.

amounts of organic catalysts (*N*-hydroxyimides) and metallic cations (Fe^{3+} or Co^{2+}-Mn^{2+}).

In a control experiment, the oxidation of the phenyl derivative **1a** was run in the presence of NHPI and appropriate amounts of metal cations (0.5 mol-% of Fe^{3+} or up to 5 mol-% of either Co^{2+} or Mn^{2+}) as co-catalysts (Table 1). Through another control test the optimized amount of organic catalysts was determined to be 10 mol-% (5 mol-% for NDHPI, which has two N-OH groups). And finally, the catalytic amount of Co^{2+}-Mn^{2+} co-catalyst was optimized in the oxidative cyclization of **1a** in the presence of NHPI (Table 2).

As shown in Table 1, when Mn^{2+} and Co^{2+} are used separately, we get no satisfactory results (entries 1 and 2). However, when Co^{2+} and Mn^{2+} are taken simultaneously, the product yield is 76 %. Control tests show that for Fe^{3+} its concentration is critical, *i. e.* higher amounts lead to the cleavage of the corresponding bisnaphthol into 2-naphthol and benzaldehyde. This is presumably due to the hydrolysis of bisnaphthols under these reaction conditions (heating and low pH caused by high concentration of Fe^{3+}). Moreover, when the reaction is run in the absence of NHPI with a catalytic amount of Fe^{3+}, no detectable product is obtained though, in the case of Co^{2+}-Mn^{2+}, spirodienones are formed in trace amounts.

The overall results of aerial oxidative reactions in the presence of Fe^{3+} and *N*-hydroxyimides are represented in Scheme 2 and Table 3.

As indicated in Table 3, we have found that aerial oxidation of methylenebisnaphthols in the presence of Fe^{3+} and *N*-hydroxyimides gives a mixture of two sets of diastereomers (integration of ^1H NMR signals shows the predominance of diasteromer **4**). An exception is **1a**, the oxidation product of which is mainly **4a**. In the case of methylenebisnaphthol **2**, trace amounts of the oxidation product are obtained with the reaction

Table 1. Reaction time and yield of oxidation of **1a** in the presence of NHPI.

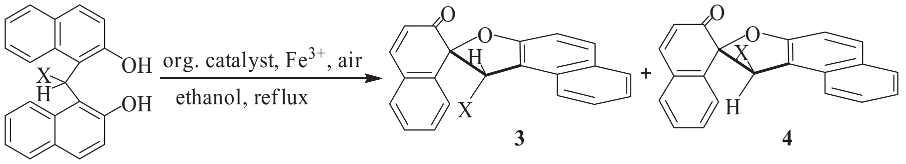
Entry	Metal cation salts	Time (min)	Yield (%)
1	$Mn(OAc)_2{\cdot}4H_2O$ (5 mol-%)		no reaction
2	$Co(OAc)_2{\cdot}4H_2O$ (5 mol-%)	90	18
3	$Co(OAc)_2{\cdot}4H_2O$-$FeCl_3{\cdot}6H_2O$	90	20
4	$Co(OAc)_2{\cdot}4H_2O$-$Mn(OAc)_2{\cdot}4H_2O$	70	76
6	$FeCl_3{\cdot}6H_2O$ (0.5 mol-%)	90	45

Table 2. Yields of the NHPI-catalyzed oxidative cyclization of **1a** in the presence of various amounts of Co^{2+}-Mn^{2+} co-catalyst.

$Co(OAc)_2{\cdot}4H_2O$-$Mn(OAc)_2{\cdot}4H_2O$	0.01 mmol	0.03 mmol	0.05 mmol	0.07 mmol
	33 %	72 %	76 %	76 %

Table 3. Reaction times and product yields for the synthesis of **3** and **4**.

Catalyst	**2**	**4a**		**3b** and **4b**		**3c** and **4c**		**3d** and **4d**		**3e** and **4e**		**3f** and **4f**		**3g** and **4g**	
		Time (min)	Yield (%)	Time (min)	Yield (%)	Time (min)	Yield (%)	Time (min)	Yield (%)	Time (min)	Yield (%)	Time (min)	Yield (%)	Time (min)	Yield (%)
NDHPI	trace	70	47	80	17	100	36	60	16	70	18	120	24	60	19
TCNHPI	trace	70	47	80	28	100	29	60	16	70	10	120	30	60	20
NHSI	trace	90	48	85	51	100	27	90	27	100	40	110	38	80	27
NHPI	trace	90	45	80	40	120	56	80	42	120	57	120	37	90	36
NHPI-4-COOH	trace	40	23	100	54	90	35	110	48	120	54	140	53	40	29



3 **4**

1, X = H
1a, X = C_6H_5
1b, X = 2-ClC_6H_4
1c, X = 4-$CH_3C_6H_4$
1d, X = 4-ClC_6H_4
1e, X = 2,4-$Cl_2C_6H_3$
1f, X = 4-$CH_3OC_6H_4$
1g, X = 4-FC_6H_4

2, X = H
3a, **4a**, X = C_6H_5
3b, **4b**, X = 2-ClC_6H_4
3c, **4c**, X = 4-$CH_3C_6H_4$
3d, **4d**, X = 4-ClC_6H_4
3e, **4e**, X = 2,4-$Cl_2C_6H_3$
3f, **4f**, X = 4-$CH_3OC_6H_4$
3g, **4g**, X = 4-FC_6H_4

Scheme 2. Synthesis of compounds **3** and **4**.

Table 4. Reaction times and yields of oxidation with NHPI and Co^{2+}-Mn^{2+}.

Entry	Product	Time[a]	Total yield (%)	Ratio of **3** to **4**
1	**2**	0–7 h	trace	–
2	**4a**	70	76	[b]
3	**3b**, **4b**	60	64	44 : 56
4	**3c**, **4c**	45	85	38 : 62
5	**3d**, **4d**	40	68	23 : 77
6	**3e**, **4e**	40	84	29 : 71
7	**3f**, **4f**	45	57	9 : 91
8	**3g**, **4g**	40	98	14 : 86

[a] Times are in minutes unless stated otherwise; [b] the sole product is **4**.

time having no significant effect on the product yield. An important point deduced from Table 3 is that NHPI is nearly the best organic catalyst. A similar trend is also seen when reactions are run in the presence of NHPI and Co^{2+}-Mn^{2+} (Table 4).

Generally, oxidation in the presence of *N*-hydroxyimide and Fe^{3+} or Co^{2+}-Mn^{2+} has several advantages such as using oxygen as oxidant, the catalytic amount of *N*-hydroxyimide, the green reaction solvent ethanol, fairly short reaction times and easy product work-up. Using Fe^{3+} as co-catalyst has, however, several other advantages; it is a highly green, sustainable and environment-friendly catalyst, its catalytic amount is as low as 0.5 mol-% (*versus* 5 mol-% for Co^{2+}-Mn^{2+}), and its work-up is very easy with no need for organic solvents. Though for the Co^{2+}-Mn^{2+} system higher yields are obtained at short reaction times, final work-up needs an organic solvent (chloroform). Based on this line of reasoning, therefore, our preferred green catalytic system will be *N*-hydroxyimide/Fe^{3+}.

Table 5. Oxidation of **1d** in the presence of several NHPI and Fe^{3+} and organic catalysts.

Catalyst	Ratio of **3d** to **4d**
NDHPI	6 : 94
TCNHPI	11 : 89
NHSI	15 : 85
NHPI	19 : 81
NHPI-4-COOH	36 : 64

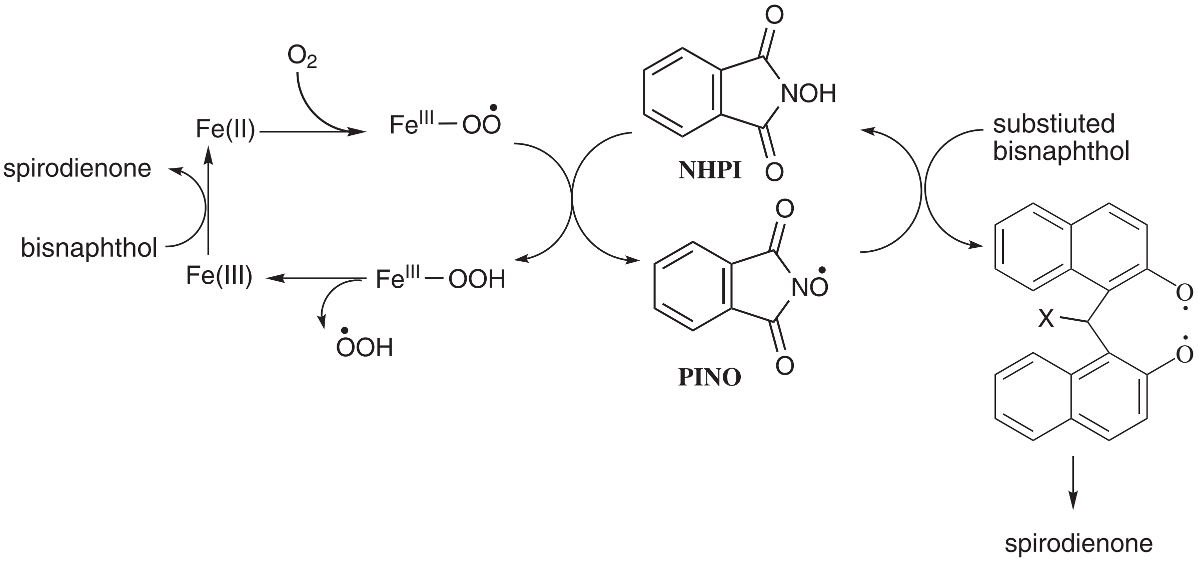
As was mentioned earlier, the distinctive feature of the two diastereomers, **3** and **4**, is the chemical shift of their corresponding proton 3′-H. Therefore, the ratio of these two diastereomers may be obtained from the integral of 3′-H signals. As reported in the literature, the color of **3** is bright yellow while that of **4** is very faintly yellow or cream [11]. The other important point is that diastereomer **4** has a lower solubility in ethanol as compared to **3**, allowing its separation by precipitation from the reaction mixture.

The final point to be noted is that the diastereoselectivity also depends on the *N*-hydroxyimide used; experiments on **1d** as starting material have shown the following trend (Table 5): NDHPI > TCNHPI > NHSI > NHPI > NHPI-4-COOH.

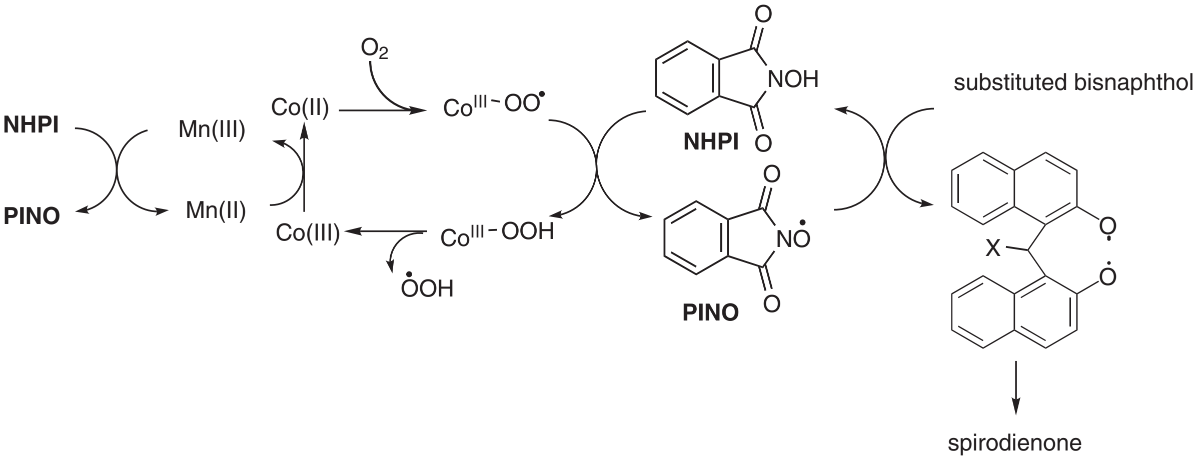
Suggested mechanisms for the reaction catalyzed by Fe^{3+} or Co^{2+}-Mn^{2+} are shown in Schemes 3 and 4, respectively.

As was said earlier, no detectable product was formed with Fe^{3+} in the absence of NHPI. Therefore, it is reasonable to propose that there might be some kind of cooperation between Fe^{3+} and NHPI for the reaction to proceed.

As it is seen in the proposed mechanisms, a diradical is formed in the final step of hydrogen abstraction.



Scheme 3. Mechanism for the reaction catalyzed by Fe^{3+}.



Scheme 4. Mechanism for the reaction catalyzed by Co^{2+}-Mn^{2+}.

It is suggested that the key point for the preferable formation of diastereomer **4** is its lower-energy transition state with respect to that of diastereomer **3**.

Conclusions

In this study, we have succeeded in running diastereoselective aerial oxidative cyclizations of several bisnaphthols using catalytic amounts of several *N*-hydroxyimides and Fe^{3+} or Co^{2+}-Mn^{2+} salts in a green solvent (ethanol). We have also shown the effect of these *N*-hydroxyphthalimides on the diastereoselectivity of the reactions.

Experimental Section

All solvents were used as obtained from Merck. All arylbisnaphthols [11, 42, 43], methylenebisnaphthol [44] and several NHPIs [45–47] were prepared according to known methods. ^{1}H NMR spectra were recorded on a Jeol 90 MHz instrument. The progress of all reactions was monitored by TLC with appropriate mobile phases (acetone-*n*-hexane 2 : 15).

General procedure

(A): Oxidative reaction in the presence of NHPI and Fe^{3+} salt

In a round bottomed flask (50 mL), bisnaphthol (1 mmol), *N*-hydroxyimide (0.1 mmol) and $FeCl_3 \cdot 6H_2O$ (0.005 mmol) were dissolved in 15 – 20 mL ethanol. The solution was refluxed for the appropriate time, with the simultaneous bubbling of air into it. The progress of the reaction was followed by TLC. After the completion of the reaction, an aqueous 2 N solution of NaOH (3 – 5 mL) was added to the flask with stirring. Distilled water (25 mL) was then added to the reaction mixture in order to precipitate the product. The precipitate was filtered, washed several times with distilled water and dried in air.

(B): Oxidative reaction in the presence of NHPI and Co^{2+}-Mn^{2+} salts

The amounts of starting materials were the same as the above, except for the amount of a mixture of $Co(OAc)_2 \cdot 4H_2O$ (0.05 mmol) and $Mn(OAc)_2 \cdot 4H_2O$ (0.05 mmol). After completion of the reaction the organic compounds were extracted with chloroform to remove the inorganic co-catalysts. After evaporation of the solvent, ethanol was added to the dried material. The same procedure as described for $FeCl_3$ was followed to obtain the product.

^{1}H NMR spectral data

*1′-Phenyl-spiro{naphthalene-1(2H),2′(1′H)-naphtho[2,1-b]furan}-2-one (**4a**)* [19]

^{1}H NMR ($CDCl_3$, TMS): $\delta = 5.21$ (s, 1H, 1-H), 5.53 (d, J = 10 Hz, 1H, 3′-H), 6.93 – 7.94 (m, 16H, aryl and 4′-H).

*1′-(2-Chlorophenyl)-spiro{naphthalene-1(2H),2′(1′H)-naphtho[2,1-b]furan}-2-one (**3b** and **4b**)* [19]

^{1}H NMR ($CDCl_3$, TMS): $\delta = 6.01$ and 5.88 (s, 1H, 1-H), 6.25 and 5.54 (d, 1H, both $J = 9.9$ Hz 3′-H), 6.52 – 7.84 and 6.52 – 7.84 (15H, aryl and 4′-H), respectively, for **3b** and **4b**.

*1′-(4-Methylphenyl)-spiro{naphthalene-1(2H),2′(1′H)-naphtho[2,1-b]furan}-2-one (**3c** and **4c**)* [19]

^{1}H NMR ($CDCl_3$, TMS): $\delta = 2.13$ and 2.3 (s, 3H), 5.38 and 5.19 (s, 1H, 1-H), 6.27 and 5.56 (d, J = 9.6 Hz and $J = 9.8$ Hz, H, 3′-H), 6.67 – 7.93 and 6.67 – 7.93 (m,15H, aryl and 4′-H), respectively, for **3c** and **4c**.

*1′-(4-Chlorophenyl)-spiro{naphthalene-1(2H),2′(1′H)-naphtho[2,1-b]furan}-2-one (**3d** and **4d**)* [19]

^{1}H NMR ($CDCl_3$, TMS): $\delta = 5.37$ and 5.18 (s, 1H, 1-H), 6.27 and 5.58 (d, J = 10.2 Hz and J = 10.1 Hz, 1H, 3′-H), 6.86 – 7.94 and 6.86 – 7.94 (m, 15H, aryl and 4′-H), respectively, for **3d** and **4d**.

*1′-(2,4-Dichlorophenyl)-spiro{naphthalene-1(2H),2′(1′H)-naphtho[2,1-b]furan}-2-one (**3e** and **4e**)* [12, 20]

^{1}H NMR ($CDCl_3$, TMS): $\delta = 5.94$ and 5.79 (s, 1H, 1-H), 6.24 and 5.59 (d, 1H, $J = 10.1$ Hz and $J = 9.9$ Hz, 3′-H), 6.80 – 8.00 and 6.80 – 8.00 (m, 14H, aryl and 4′-H), respectively, for **3e** and **4e**.

*1′-(4-Methoxyphenyl)-spiro{naphthalene-1(2H),2′(1′H)-naphtho[2,1-b]furan}-2-one (**3f** and **4f**)* [19]

^{1}H NMR ($CDCl_3$, TMS): $\delta = 3.63$ and 3.74 (3H, s), 5.36 and 5.18 (s, 1H, 1-H), 6.26 and 5.56 (d, 1H, J = 9 Hz and J = 10.3 Hz, 3-H′), 6.41 – 7.93 and 6.41 – 7.93 (m, 15H, aryl and 4′-H), respectively, for **3f** and **4f**.

*1′-(4-Fluorophenyl)-spiro{naphthalene-1(2H),2′ (1′H)-naphtho[2,1-b]furan}-2-one (**3g** and **4g**)* [12, 20]

^{1}H NMR ($CDCl_3$, TMS): $\delta = 5.37$ and 5.20 (s, 1H, 1-H), 6.27 and 5.56 (d, 1H, both J = 10 Hz, due to 3′-H), 6.54 – 7.96 and 6.54 – 7.96 (m, 15H, aryl and 4′-H), respectively, for **3g** and **4g**.

Acknowledgement

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[1] J. Abel, *Chem. Ber.* **1892**, *25*, 3477 – 3484.
[2] R. Pummerer, E. Cherbuliez, *Chem. Ber.* **1914**, *47*, 2957 – 2973.
[3] E. A. Shearing, S. Smiles, *J. Chem. Soc.* **1937**, 1931 – 1936.
[4] T. R. Kasturi, B. Rajasekhar, G. J. Raju, G. M. Reddy, R. Sivaramakrishnan, N. Ramasubbu, K. Venkatesan, *J. Chem. Soc., Perkin Trans. 1* **1984**, 2375 – 2382.
[5] R. S. Ward, *Chem. Brit.* **1973**, *9*, 444 – 449.
[6] T. R. Kasturi, P. V. P. Pragnacharyulu, *Tetrahedron* **1992**, *48*, 4431 – 4438.
[7] T. R. Kasturi, P. V. P. Pragnacharyulu, G. M. Reddy, S. K. Jayaram, S. B. Singh, *Tetrahedron* **1992**, *48*, 5481 – 5496.
[8] O. Dischendorfer, *Chem. Ber.* **1926**, *59*, 774 – 777.

[9] F. M. Dean, H. D. Locksley, *J. Chem. Soc.* **1963**, 393 – 401.

[10] D. J. Bennett, F. M. Dean, A. W. Price, *J. Chem. Soc. C* **1970**, 1557 – 1561.

[11] D. J. Bennett, F. M. Dean, G. A. Herbin, D. A. Martin, A. W. Price, M. L. Robinsin, *J. Chem. Soc., Perkin Trans. 1* **1980**, 1978 – 1985.

[12] A. Khoramabadi-zad, A. Shiri, F. Derakhashan-Panah, Z. Salimi, *Mol. Diversity* **2010**, 829 – 832.

[13] F. M. Dean, G. A. Herbin, D. A. Martin, A. W. Price, M. L. Robinson, *J. Chem. Soc., Perkin Trans. 1* **1980**, 1986 – 1993.

[14] T. R. Kasturi, S. K. Tayaram, P. V. P. Pragnacharyulu, J. A. Sattigeri, G. M. Reddy, K. A. Kumar, *Tetrahedron* **1993**, *49*, 113 – 124.

[15] T. R. Kasturi, K. A. Kumar, P. V. P. Pragnacharyulu, *Tetrahedron* **1993**, *49*, 125 – 134.

[16] T. R. Kasturi, K. A. Kumar, P. V. P. Pragnacharyulu, G. Sridevi, *Tetrahedron* **1993**, *49*, 135 – 140.

[17] T. R. Kasturi, J. A. Sattigeri, P. V. P. Pragnacharyulu, *Tetrahedron* **1995**, *51*, 3051 – 3060.

[18] T. R. Kasturi, B. Rajasekhar, R. Sivaramakrishnan, *Indian J. Chem., Sect. B* **1979**, *18*, 1 – 3.

[19] A. Khoramabadi-zad, I. Yavari, A. Shiri, A. Bani, *J. Heterocycl. Chem.* **2008**, *45*, 1351 – 1357.

[20] A. Alizadeh, M. Khodaei, K. Moradi, *J. Iran. Chem. Soc.* **2010**, *7*, 351 – 358.

[21] A. Khorramabadi-zad, S. Daliran, A. R. Oveisi, *C. R. Chim.* **2013**, *16*, 972 – 976.

[22] L. Cohn, *Ann. Chem.* **1880**, *205*, 295 – 314.

[23] A. Karakurt, S. Dalkara, M. Ozalp, S. Ozbey, E. Kendi, J. P. Stables, *Eur. J. Med. Chem.* **2001**, *36*, 421 – 433.

[24] W. R. Roderich, W. G. Brown, *J. Am. Chem. Soc.* **1957**, *79*, 5196 – 5198.

[25] Y. Ishii, K. Nakayama, M. Takeno, S. Sakaguchi, T. Iwahama, Y. Nishiyama, *J. Org. Chem.* **1995**, *60*, 3934 – 3935.

[26] B. Saha, N. Koshino, J. H. Espenson, *J. Phys. Chem. A* **2004**, *108*, 425 – 431.

[27] C. Annunziatini, M. F. Gerini, O. Lanzalunga, M. Lucarini, *J. Org. Chem.* **2004**, *69*, 3431 – 3438.

[28] G. Yang, Q. Zhang, H. Miao, X. Tong, J. Xu, *Org. Lett.* **2005**, *7*, 263 – 266.

[29] S. Sakaguchi, S. Kato, T. Iwahama, Y. Ishii, *Bull. Chem. Soc. Jpn.* **1998**, *71*, 1237 – 1240.

[30] K. Matsunaka, T. Iwahama, S. Sakaguchi, Y. Ishii, *Tetrahedron Lett.* **1999**, *40*, 2165 – 2168.

[31] T. Iwahama, K. Syojyo, S. Sakaguchi, Y. Ishii, *Org. Process.* **1998**, *2*, 255 – 260.

[32] T. Iwahana, Y. Yoshino, T. Keitoku, S. Sakaguchi, Y. Ishii, *J. Org. Chem.* **2000**, *65*, 6502 – 6507.

[33] K. Gorgya, J. Lepretre, E. Aman, C. Einhorn, J. Einhorn, M. C. J. Pierre, *Electrochim. Acta* **1998**, *44*, 385 – 393.

[34] B. Karimi, F. Rajabi, *Org. Lett.* **2004**, *6*, 2841 – 2844.

[35] F. Minisci, C. Gambarotti, M. Pierini, O. Porta, C. Punta, F. Recupero, M. Lucarinib, V. Mugnainib, *Tetrahedron Lett.* **2006**, *47*, 1421 – 1424.

[36] T. Iwahama, S. Sakaguchi, Y. Ishii, *Chem. Commun.* **1999**, 727 – 728.

[37] T. Hara, T. Iwahama, S. Sakaguchi, Y. Ishii, *J. Org. Chem.* **2001**, *66*, 6425 – 6431.

[38] Y. Nishiwaki, S. Sakaguchi, Y. Ishii, *J. Org. Chem.* **2002**, *67*, 5663 – 5668.

[39] Y. Aoki, S. Sakaguchi, Y. Ishii, *Tetrahedron* **2006**, *62*, 2497 – 2500.

[40] Y. Ishi, S. Sakaguchi, *Catal. Today* **2006**, *117*, 105 – 113.

[41] F. Minisci, C. Punta, F. Recupero, *J. Mol. Catal. A* **2006**, *251*, 129 – 149.

[42] J. T. Hewitt, A. J. Turner, *Ber. Dtsch. Chem. Ges.* **1901**, *34*, 202.

[43] M. S. Kharasch, J. Porsche, *J. Org. Chem.* **1936**, *1*, 265 – 274.

[44] G. S. Mironov, I. V. Budnii, K. A. Chernyakovskaya, M. I. Farberov, *Zh. Org. Khim.* **1972**, *8*, 597 – 600.

[45] N. Sawatari, T. Yokota, S. Sakaguchi, Y. Ishii, *J. Org. Chem.* **2001**, *66*, 7889 – 7891.

[46] C. Einhorn, J. Einhorn, C. Marcadal-Abbadi, *Synth. Commun.* **2001**, *31*, 741 – 748.

[47] E. Fritz-Langhals, U. S. Patent 6316639 B1, **2001**.