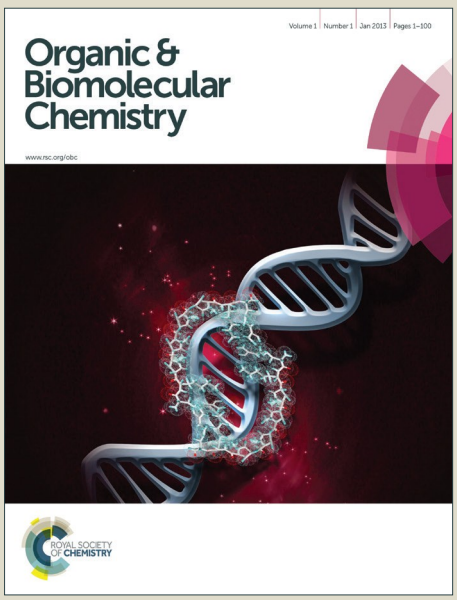
Organic & Biomolecular Chemistry

Accepted Manuscript

This article can be cited before page numbers have been issued, to do this please use: V. D. Mane, J. Pandey, N. Ayyagari, C. Dey, R. Kale and I. N. Namboothiri, *Org. Biomol. Chem.*, 2016, DOI: 10.1039/C5OB02656C.



ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/obc

View Article Online
DOI: 10.1039/C5OB02656C

Journal Name

ARTICLE

Synthesis of hydrazinoheterocycles from Morita-Baylis-Hillman adducts of nitroalkenes with azodicarboxylates

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

Vaijinath Mane, Jyoti Pandey, Narasihmam Ayyagari, Chandan Dey, Raju Kale and Irishi N. N. Namboothiri*

Conjugated nitroalkenes and nitrodienes undergo smooth α-hydrazination with azodicarboxylates through an imidazole catalyzed carbon-heteroatom bond formation under Morita-Baylis-Hillman conditions. The resulting hydrazinonitroalkenes take part in 1,3-dipolar cycloaddition with azide under mild conditions to give hydrazinotriazoles. A [3+2] annulation with phenols and naphthols involving Michael addition and cyclization as the key steps lead to arenodihydrofurans bearing a key hydrazinodicarboxylate moiety. Both regioisomers of naphthodihydrofurans could be synthesized by our methodology by employing the appropriate naphthol.

Introduction

Functionalization of electron deficient alkenes at the α-position, normally under amine or phosphine catalysed conditions, popularly known as the Morita-Baylis-Hillman (MBH) reaction, is an efficient methodology for the synthesis of multi-functional molecules.[1] Although various electron deficient alkenes such as α,β-unsaturated carbonyl compounds, nitriles, sulfones and phosphonates have been employed as substrates in the MBH reaction[1] and its vinylogous version, the Rauhut-Currier (RC) reaction,[2] for over four decades, α,β-unsaturated nitro compounds emerged as potential substrates only in the last decade.[3-5] In recent years, the applications of MBH and RC adducts of nitroalkenes have been extensively investigated in the synthesis of complex molecules,[6-9] including several carbocycles[7] and heterocycles.[8-9] However, there are only handful of examples for the synthesis of MBH adducts via carbon-heteroatom bond formation.[4-5,10] To our knowledge, such MBH adducts have not been exploited for the synthesis of complex molecules, especially heterocycles.

From another perspective, 1,2,3-triazoles are versatile heterocycles, easily synthesized by azide-alkyne cycloaddition (Huisgen 1,3-dipolar cycloaddition/click reaction)[11] or via other miscellaneous methods including condensation of azide with an active methylene compound (Dimroth triazole synthesis).[12] 1,2,3-Triazoles are extensively employed as biological agents[13] and co-ordinating ligands.[14] However, synthesis of 1,2,3-triazoles bearing a hydrazine moiety did not receive sufficient attention,[15] and, to our knowledge, 1,2,3-triazoles bearing a hydrazinodicarboxylate moiety remains unreported in the literature.

Arenodihydrofurans belong to an important class of heterocycles that has been extensively investigated from both synthetic[16-17] and biological[18] perspective. Natural products Bicunningines,[19] Conocarpan[20] and Megapodiol[21] as well as synthetic compounds possessing an arenodihydrofuran skeleton exhibit potent biological properties (Figure 1).[22] In spite of the above, there is no general and convenient approach for the synthesis of arenodihydrofurans and, to our knowledge, such skeletons bearing a key hydrazinodicarboxylate moiety remains unreported hitherto.

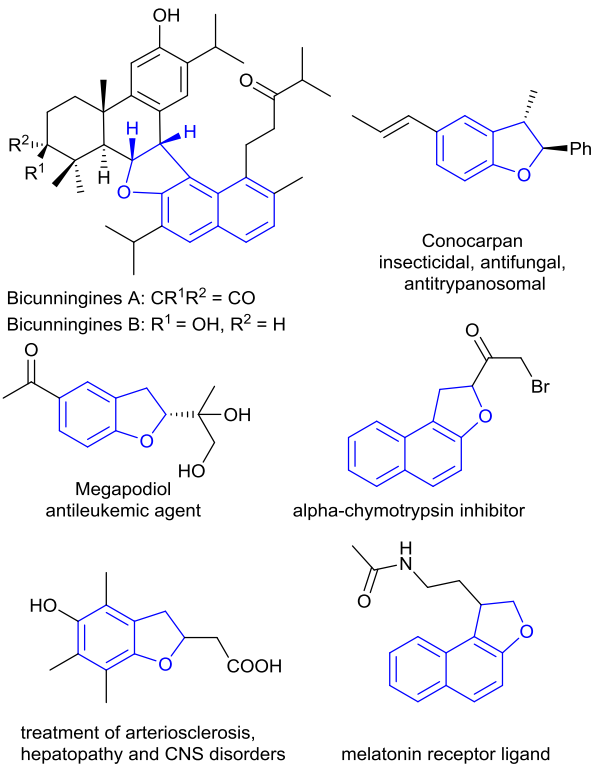


Figure 1

Department of Chemistry, Indian Institute of Technology Bombay, Mumbai 400076, India

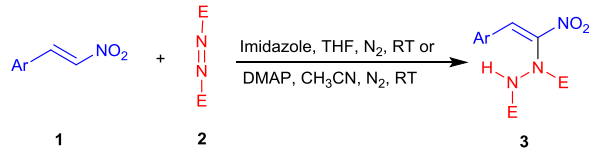
Electronic Supplementary Information (ESI) available: X-ray data tables and copies of NMR spectra. CCDC reference numbers CCDC 1444163-1444164. For ESI and crystallographic data in CIF or other electronic format See DOI: 10.1039/x0xx00000x

View Article Online
DOI: 10.1039/C5OB02656C

Earlier, we reported our preliminary results on the synthesis of α-hydrazinonitroalkenes via MBH reaction of nitroalkenes with azodicarboxylates in the presence of stoichiometric amounts imidazole or DMAP.[4] Later on, this reaction has been carried out under the co-catalytic influence of DMAP and a thiazolium derived NHC.[5] This is a full version of our preliminary communication which describes not only further scope of the reaction but applications of the hydrazinonitroalkenes in the synthesis of heterocycles such as triazoles and arenodihydrofurans bearing a key hydrazinodicarboxylate moiety.

Results and discussion

For the first time, we reported the MBH reaction of nitroalkenes **1** with heteroatom centered electrophiles such as azodicarboxylates **2** which afforded α-hydrazinonitroalkenes **3** (Scheme 1).[4] The reaction was carried out under two different conditions, namely, in the presence of imidazole in THF and DMAP in CH_3CN at room temperature under N_2. The imidazole catalyzed reactions were superior to the DMAP catalyzed reactions in terms of product yield although the reaction times were comparable.



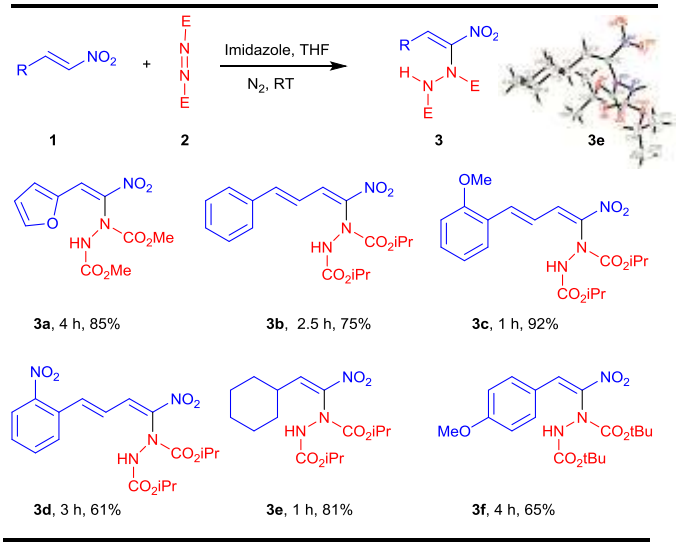
Ar = aryl, heteroaryl; E = CO_2iPr, CO_2Et; 15 examples
Method A: Imidazole, THF, 30 min-6 h, 84-100% yield
Method B: DMAP, CH_3CN, 15 min-8 h, 43-87% yield

Scheme 1 Our previous report on the MBH reaction of nitroalkenes **1** with azodicarboxylates **2**[4]

Since the ^{1}H NMR and, to some extent, the ^{13}C NMR spectra of the MBH adducts **3** recorded at room temperature consisted of broad signals, we recorded the ^{1}H NMR spectra of a selected compound at different temperatures (233-328 K).[4] This led to sharp multiple signals at low temperatures and relatively sharp averaged signals at high temperatures. This phenomenon was attributed to the anisotropy of the carbonyl group which in turn was a result of the restricted rotation about the C-N bond of the hydrazinodicarboxylate moiety due to its partial double bond character. However, the spectral pattern was quite complex due to the two isopropyl groups. Therefore, in order to further simplify the observed spectral pattern, a selected MBH adduct **3a** has been prepared using dimethyl azodicarboxylate **2** (E = CO_2Me) as the electrophile under imidazole catalyzed conditions (Table 1).

The ^{1}H NMR spectrum of **3a** recorded at room temperature showed single but broad signals for the olefinic proton and the aromatic protons. However, two separate signals, one almost at the base line, were observed for the methyl protons. Subsequently, variable temperature ^{1}H NMR spectra of **3a** were recorded in the range -50 to +50 $^{\circ}$C (223-323 K) with a gap of 10 $^{\circ}$C (Figure 2). As the temperature was lowered (10 to -50 $^{\circ}$C), gradual broadening of the signals followed by their multiplication was observed indicating slower rotation about the C-N bond resulting in several rotamers. On the other hand, upon increasing the temperature, relatively sharp averaged signals were observed for all the protons due to faster rotation about the C-N bond.

Table 1 MBH reaction of nitroalkenes and nitrodienes **1** with various azodicarboxylates **2**[a]



[a]Yields after purification by silica gel column chromatography.

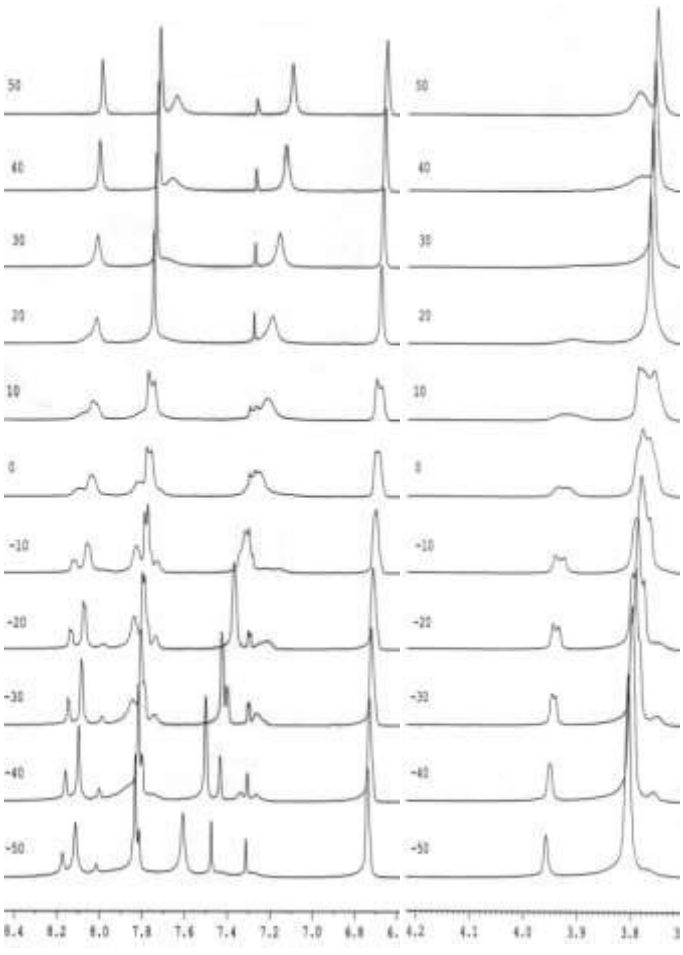


Figure 2 Variable temperature ^{1}H NMR spectra of **3a** recorded at different temperatures in the range -50 to +50 $^{\circ}$C (223-323 K)

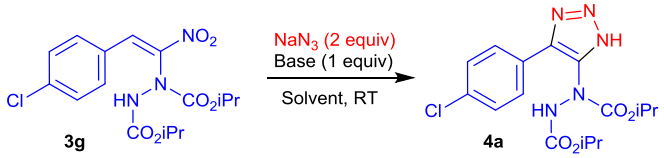
The scope of nitroalkenes was successfully extended by synthesizing diisopropyl hydrazinodicarboxylates of nitrodienes **3b-**

3d, aliphatic nitroalkenes **3e** and those with other dialkyl hydrazinodicarboxylates **3f** in good to excellent yields (Table 1). For instance, while a nitrodiene bearing an electron donating *ortho*-substituted aryl group afforded the product **3c** in excellent yield (92%), the yield was 75% with the phenyl derivative **3b** and was much lower (61%) with an electron withdrawing ortho-substituted aryl group **3d**. The product **3e** was isolated in high yield (81%) when a representative β-alkyl nitroalkene **1e** was subjected to α-hydrazination. The structure, including double bond geometry of **3e**, was unambiguously established by single crystal X-ray analysis. Further, the reaction of 4-methoxynitrostyrene **1f** with di-*tert*-butyl azodicarboxylate **2** (E = CO_2tBu) led to the product **3f** in 65% yield, much lower compared to the yields obtained with DIAD.[4]

Subsequently, we decided to investigate the possible applications of hydrazinonitroalkenes **3** as potential substrates for the synthesis of heterocycles possessing a key hydrazinodicarboxylate moiety. This is based on the presumption that elimination of nitro group would be more facile when compared to hydrazinodicarboxylate moiety.

At the outset, the MBH adduct **3g** was selected as the model substrate for the 1,3-dipolar cycloaddition with sodium azide for the synthesis of hydrazinotriazoles (Table 2). When inorganic bases such as K_2CO_3 and Cs_2CO_3 were employed for the reaction in DMF at room temperature, the product **4a** was isolated in 50% yield in 4-5 h (entries 1-2). However, a mild amine base such as imidazole and a quaternary ammonium salt such as tetrabutylammonium hydrogen sulfate (TBAHS) turned out to be better mediators for this reaction. While the product **4a** was isolated in 60% yield in the presence of imidazole (entry 3), the yield was much higher (72%) in the presence of TBAHS (entry 4). However, the TBAHS mediated reaction in other solvents such as THF and dioxane gave only complex mixtures (entries 5-6). Other quaternary ammonium salts such as tetrabutylammonium bromide (TBAB) and tetrabutylammonium iodide (TBAI) were unsuitable for our reaction (entries 7-8).

Table 2 Optimization of the reaction conditions for the 1,3-dipolar cycloaddition of sodium azide with MBH adducts **3**



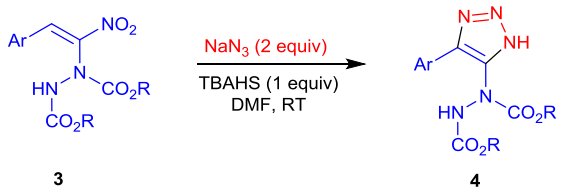
3g 4a

Entry	Base	Solvent	Time (h)	% Yield [a]
1	K_2CO_3	DMF	5	50
2	Cs_2CO_3	DMF	4	50
3	Imidazole	DMF	4	60
4	**TBAHS**	**DMF**	**3**	**72**
5	TBAHS	THF	3	- [b]
6	TBAHS	1,4-dioxane	3	- [b]
7	TBAB	DMF	4	40
8	TBAI	DMF	4	- [b]

[a]After purification by silica gel column chromatography. [b]Complex mixture

The above optimized conditions were employed for the cycloaddition of other selected MBH adducts **3f** and **3h** with sodium azide (Table 3). It is discernible from Table 3 that there is no appreciable substituent effect in this reaction as substrates bearing both electron withdrawing and electron donating aryl groups afford the

Table 3 Substrate scope for the synthesis of triazoles **4**



3 4

Entry	**3,** Ar, R	**4**	Time (h)	% Yield [a]
1	**3g,** 4-ClC_6H_4, *i*Pr	**4a**	3	72
2	**3h**, 4-FC_6H_4, *i*Pr	**4b**	3.5	68
3	**3i,** 2-$NO_2C_6H_4$, *i*Pr	**4c**	2.5	64
4	**3j,** 4-OMeC_6H_4, *i*Pr	**4d**	20	65
5	**3k**, (3,4-OMe)$_2C_6H_3$, *i*Pr	**4e**	22	62
6	**3l,** 2-Thienyl, *i*Pr	**4f**	18	60
7	**3f,** 4-OMeC_6H_4, *t*Bu	**4g**	22	70

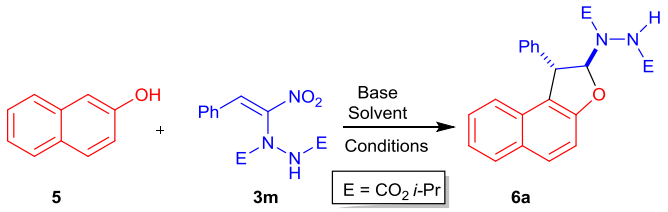
[a]After purification by silica gel column chromatography

products in 60-72% yield (entries 1-7). While increase in deactivation of the aryl group from Cl **(3g)** to F (**3h**) to NO_2 **(3i)** appears to lower the yield marginally (72%, 68% and 64%, respectively, for **4a**, **4b** and **4c**, entries 1-3), no such trend is observed in the case of substrates bearing electron rich aryl groups (entries 4-7). Thus the MBH adducts bearing aryl groups with single and multiple electron donating substituents **3j** and **3k** and the one bearing a heteroaryl group **3l** furnish the corresponding products **4d**, **4e** and **4f**, respectively, in comparable yields (60-65%, entries 4-6). Finally, the effect of R group in the hydrazinodicarboxylate moiety was investigated by replacing *iso*-propyl with *tert*-butyl (**3f**) which led to the formation of product **4g** in 70% yield (entry 7).

Having demonstrated the application of MBH adducts **3** in the synthesis of hydrazinotriazoles **4**, we pursued other targets, namely, hydrazinodihydrofurans **6**, **8** and **10** which appeared accessible from MBH adducts **3** and various arenols **5**, **7** and **9** via a cascade intermolecular Friedel-Crafts reaction-intramolecular cyclization. At the outset, β-naphthol **5** and MBH adduct **3m** were chosen as model substrates for the synthesis of hydrazinonaphthofuran **6a** (Table 4). Initially, when inorganic bases such as K_2CO_3 and Cs_2CO_3 were screened for this reaction in THF at room temperature, the product **6a** was isolated in 68% and 89% yields, respectively (entries 1-2). While Et_3N was ineffective for this reaction (entry 3), other amine bases such as DMAP, DBU and DABCO afforded the product **6a** only in low to moderate yield (31-54%, entries 4-6). In view of the modest performance of amine bases in our reaction, we turned back to Cs_2CO_3 and also subjected the reaction mixture to microwave irradiation at 100 °C. We were pleased to observe the completion of the reaction in 10 min to afford the product **6a** in 91% yield (entry 7). Further screening of solvents such as CH_3CN, 1,4-dioxan and $CHCl_3$ (entries 8-10) confirmed that the best solvent was CH_3CN (93% yield, entry 8).

View Article Online
DOI: 10.1039/C5OB02656C

Table 4 Optimization of the reaction conditions for the [3+2] annulation of β-naphthol **5** with hydrazinonitroalkene **3m**[a]



5 3m 6a

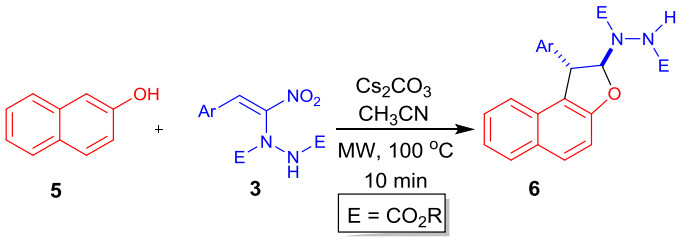
Entry	Base	Solvent	Time	% Yield[a]
1	K_2CO_3	THF	24 h	68
2	Cs_2CO_3	THF	18 h	89
3	Et_3N	THF	24 h	-[b]
4	DMAP	THF	48 h	45
5	DBU	THF	48 h	54
6	DABCO	THF	32 h	31
7	Cs_2CO_3	THF	10 min	91[c]
8	**Cs_2CO_3**	**CH_3CN**	**10 min**	**93**[c]
9	Cs_2CO_3	1,4-dioxan	12 min	83[d]
10	Cs_2CO_3	$CHCl_3$	10 min	77[d]

[a]After silica gel column chromatography; [b]No reaction; [c]The reaction was carried out under microwave at 100 °C.

The above optimized conditions were subsequently employed to investigate the scope of the MBH adduct **3** in the synthesis of hydrazinodihydrofurans **6** (Table 5). Thus MBH adducts **3** bearing various aromatic groups at the β-position were employed for reaction with β-naphthol **5** under the optimized conditions. While the MBH adduct **3m**, bearing parent phenyl, furnished the product **6a** in excellent yield (93%, entry 1), the yields of hydrazinodihydrofurans **6b-d**, derived from other MBH adducts **3n**, **3j** and **3k**, bearing electron rich aryl groups, were also good (71-76%). However, in the case of **3h**, bearing an electron deficient aryl group, lower yield of the product **6e** (53%) was encountered (entry 5). Hydrazinonitroalkenes possessing other groups β to nitro group such as a fused aromatic ring (**3o**) and heteroaryl groups, thienyl and furyl (**3l** and **3p**), were also excellent substrates which provided the products **6f-h** in 77-92% yield (entries 6-8). A nitrodiene derived MBH adduct **3b** also delivered the desired product **6i** in satisfactory yield (63%, entry 9). Besides diisopropylhydrazinodicarboxylates of nitroalkenes **3b-p** (entries 1-9), diethyl- **3q-s** and di-*t*-butyl **3t** derivatives were also amenable for our reaction affording the products **6j-m** in good to excellent yield (71-88%, entries 10-13).

After successful execution of our methodology for the synthesis of hydrazinonaphtho[2,1-b]furans **6** from β-naphthol **5**, we shifted our focus to the synthesis of regioisomers of **6**, viz. hydrazinonaphtho[1,2-b]furans **8** (Table 6). This required only the replacement of β-naphthol **5** with α-naphthol **7**. Selected MBH adducts **3** were treated with α-naphthol **7** under the optimized conditions. It may be noted that though the reactions were complete in 10 min, the yields of naphthofurans **8** were considerably lower (34-52%) due to decomposition. Attempts to improve the yield by microwave irradiation at lower temperature were either not successful (entry 1) or met with only marginal success (entry 4). But, nevertheless, we were pleased to note that hydrazinonaphthofurans **8a-f** were easily accessible via cascade reaction of various aryl and heteroaryl MBH adducts **3** with α-naphthol **7**.

Table 5 Synthesis of dihydronaphthofurans **6** via cascade reaction of β-naphthol **5** with hydrazinonitroalkenes **3**

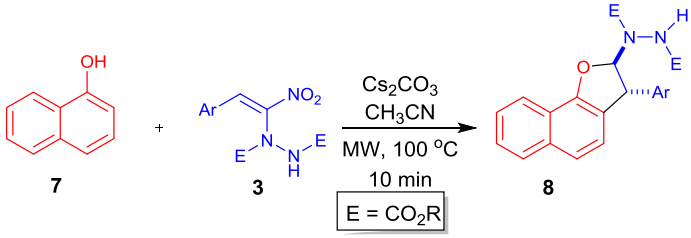


5 3 6

Entry	**3**, Ar	R	**6**	% Yield[a]
1	**3m**, C_6H_5	*i*-Pr	**6a**	93
2	**3n**, 4-MeC_6H_4	*i*-Pr	**6b**	76
3	**3j**, 4-OMeC_6H_4	*i*-Pr	**6c**	73
4	**3k**, 3,4-$(OMe)_2C_6H_3$	*i*-Pr	**6d**	71
5	**3h**, 4-FC_6H_4	*i*-Pr	**6e**	53
6	**3o**, 1-naphthyl	*i*-Pr	**6f**	86
7	**3l**, 2-Thienyl	*i*-Pr	**6g**	92
8	**3p**, 2-furyl	*i*-Pr	**6h**	77
9	**3b**, C_6H_5CH=CH	*i*-Pr	**6i**	63
10	**3q**, 4-OMeC_6H_4	Et	**6j**	81
11	**3r**, 4-ClC_6H_4	Et	**6k**	71
12	**3s**, 2-Thienyl	Et	**6l**	88
13	**3t**, 4-OMeC_6H_4	*t*-Bu	**6m**	79

[a]After silica gel column chromatography.

Table 6 Synthesis of dihydronaphthofurans **8** by cascade reaction of α-naphthol **7** with hydrazinonitroalkenes **3**



7 3 8

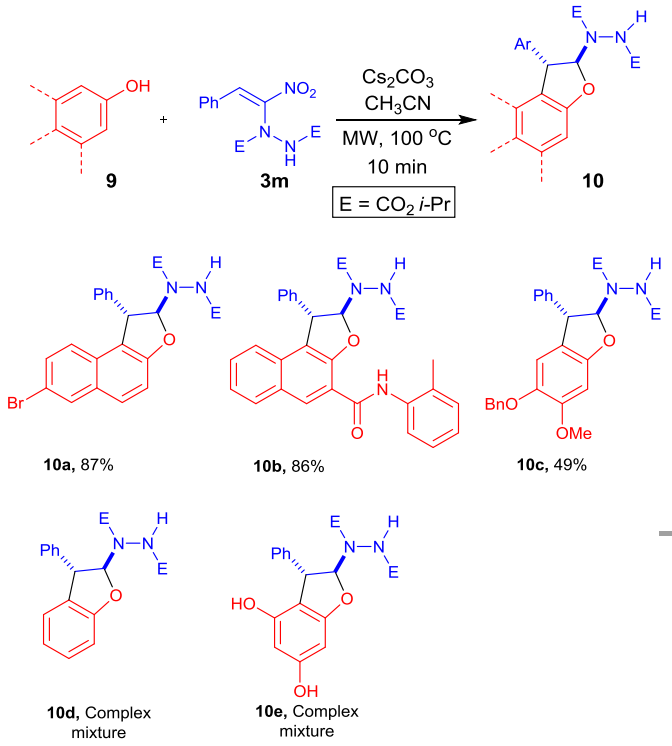
Entry	**3**, Ar	R	**8**	% Yield[a]
1	**3m**, C_6H_5	*i*-Pr	**8a**	52[b]
2	**3j**, 4-OMeC_6H_4	*i*-Pr	**8b**	34
3	**3k**, 3,4-$(OMe)_2C_6H_3$	*i*-Pr	**8c**	36
4	**3l**, 2-Thienyl	*i*-Pr	**8d**	50[c]
5	**3p**, 2-furyl	*i*-Pr	**8e**	40
6	**3q**, 4-OMeC_6H_4	Et	**8f**	46

[a]After silica column chromatography; [b]The yields were 52% and 50% when the reactions were carried out at 70 °C and 40 °C, respectively; [c]The reaction was carried out at 40 °C; the yield was 41% when the reaction was carried out at 100 °C.

Further scope of our methodology was investigated using substituted β-naphthols and phenols **9** (Table 7). For instance, 6-bromo-2-naphthol **9a** reacted well with MBH adduct **3m** and afforded dihydronaphthofuran **10a** in excellent yield (87%). 3-

Amido-2-naphthol **9b** also took part in the cascade Friedel-Crafts reaction-cyclization with MBH adduct **3m**, despite the decreased nucleophilicity of naphthol due to the presence of the amido group, and delivered the desired product **10b** in 86% yield. While substituted phenol **9c** performed reasonably well by providing dihydrobenzofuran **10c** in 49% yield, parent phenol **9d** and phloroglucinol **9e** provided only complex mixtures under our experimental conditions.

Table 7 Scope of naphthols and phenols **9** for the synthesis of dihydrofurans **10**[a]



[a]Yields after silica gel column chromatography.

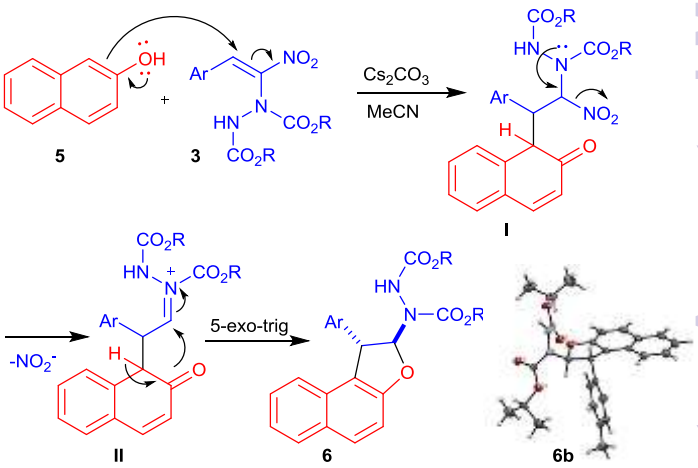
The relative stereochemistry of the aryl group and the hydrazinodicarboxylate moiety was assigned to be *trans* from ^{1}H-^{1}H-NOESY experiment with a representative compound **6c**. This is based on the absence of any NOE interaction between the aromatic protons of 4-methoxyphenyl and the isopropyl protons of hydrazinodicarboxylate. Later single crystal analysis of a representative compound **6b** confirmed this assignment (>90° dihedral angle for ArC-C-C-N).

The proposed mechanism, taking β-naphthol **5** as the representative arenol, envisages Cs_2CO_3 mediated addition of **5** to MBH adduct **3** in a Michael fashion leading to the formation of intermediate **I** which forms an acyliminium type intermediate **II** with the loss of nitro group. Enolization of **II** and intramolecular 5-*exo-trig* cyclization gives rise to product **6**.

Conclusions

α-Hydrazination of a variety of nitroalkenes and nitrodienes using azodicarboxylates proceeds in the presence of a mild nucleophilic amine catalyst such as imidazole to afford hydrazinodicarboxylates of nitroalkenes which exhibit dynamic phenomenon on NMR time scale. These compounds have been utilized for the first time for the synthesis of various heterocycles such as triazoles and arenofurans possessing a key hydrazinodicarboxylate moiety by taking advantage of the relative ease of elimination of nitro group when compared to the hydrazinodicarboxylate moiety.

Scheme 2 Proposed mechanism for the formation of dihydroarenofurans



Experimental Section

General. The melting points recorded are uncorrected. NMR spectra (^{1}H, ^{1}H decoupled ^{13}C, ^{19}F, ^{13}C-APT, ^{1}H-^{1}H COSY and ^{1}H-^{1}H NOESY) were recorded with TMS as the internal standard. The coupling constants (*J* values) are given in Hz. High resolution mass spectra were recorded under ESI Q-TOF conditions. X-ray data were collected on a diffractometer equipped with graphite monochromated Mo Kα radiation. The structure was solved by direct methods SHELXS-97 and refined by full-matrix least squares against F^2 using SHELXL-97 software. Complete characterization data including NMR spectra for compounds **3g-l** were reported earlier.[4]

General procedure for the synthesis of MBH Adducts 3. To a stirred solution of nitroalkene **1** (1 mmol) in THF (2 ml), under N_2 and protected from light, was added imidazole (68 mg, 1 mmol) followed by diazo compound **2** (1.5 mmol) and the reaction mixture was stirred at room temperature. After the completion of the reaction (monitored by TLC), THF was removed *in vacuo*, the residue was treated with water (10 ml) and acidified with 5N HCl (10 ml). The aqueous layer was extracted with ethyl acetate (3 × 10 ml), the combined organic layers were washed with brine (20 ml), dried over anhydrous Na_2SO_4 and concentrated *in vacuo*. The crude residue was purified by silica gel column chromatography (10-20% EtOAc/pet ether, gradient elution).

(*E*)-Dimethyl 1-(2-(furan-2-yl)-1-nitrovinyl)hydrazine-1,2-dicarboxylate (3a). Yellow solid; Yield 242 mg, 85%; mp 145 °C; IR (KBr, cm^{-1}) 3451 (m), 3299 (s), 1748 (vs), 1657 (s), 1522 (s), 1464 (s),

1303 (vs); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.75 (s, 6H), 6.66 (unresolved m, 1H), 7.14 (br s, 1H), 7.73 (unresolved m, 2H), 8.00 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 53.1, 54.7, 114.0, 120.5, 122.2, 139.3, 145.6, 148.2, 154.7, 156.0; m/z (QTOF ES$^+$, Ar) 308 (MNa^+, 100); HRMS (QTOF ES$^+$, Ar) calcd for $C_{10}H_{11}N_3O_7Na$ (MNa^+) 308.0489, found 308.0495.

Diisopropyl 1-((1*E*,3*E*)-1-nitro-4-phenylbuta-1,3-dienyl)hydrazine-1,2-dicarboxylate (3b). Yellow crystalline solid; Yield 283 mg, 75%; mp 88-90 ^{o}C; IR (KBr, cm^{-1}) 3460 (m), 3276 (m), 1750 (s), 1716 (s), 1634 (m), 1526 (m), 1375 (m), 1320 (s); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.18-1.31 (br unresolved, 12H), 5.03 (septet, *J* = 5.8 Hz, 2H), 6.95-7.00 (br unresolved, 1H), 7.19-7.23 (br unresolved, 1H), 7.39-7.40 (m, 3H), 7.60 (br unresolved, 3H), 7.81 (d, *J* = 11.0 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 21.6, 21.8, 70.3, 72.5, 121.2, 128.2, 128.9, 130.4, 134.5, 135.4, 142.9, 146.8, 153.9, 155.6; m/z (QTOF ES$^+$, Ar) 400 (MNa^+, 100), 203 (8), 142 (8), 115 (8); HRMS (QTOF ES$^+$, Ar) calcd for $C_{18}H_{23}N_3O_6Na$ (MNa^+) 400.1485, found 400.1473.

Diisopropyl 1-((1*E*,3*E*)-4-(2-methoxyphenyl)-1-nitrobuta-1,3-dienyl)hydrazine-1,2-dicarboxylate (3c). Yellow crystalline solid; Yield 374 mg, 92%; mp 128-130 ^{o}C; IR (KBr, cm^{-1}) 3484 (m), 3267 (m), 1770 (s), 1751 (s), 1716 (s), 1525 (m), 1376 (m); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.17 (d, *J* = 5.8 Hz, 6H), 1.25-1.30 (br unresolved, 6H), 3.91 (s, 3H), 5.02 (septet, *J* = 6.2 Hz, 2H), 6.90-7.01 (m, 3H), 7.34-7.38 (unresolved m, 1H), 7.63-7.69 (unresolved m, 2H), 7.84 (d, *J* = 10.9 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 21.8, 22.0, 55.6, 70.4, 72.5, 111.2, 121.0, 121.4, 124.6, 128.3, 132.0, 135.9, 142.2, 142.4, 154.2, 155.7, 158.2; m/z (QTOF ES$^+$, Ar) 430 (MNa^+, 100), 362 (6), 173 (2); HRMS (QTOF ES$^+$, Ar) calcd for $C_{19}H_{25}N_3O_7Na$ (MNa^+) 430.1590, found 430.1593.

Diisopropyl 1-((1*E*,3*E*)-1-nitro-4-(2-nitrophenyl)buta-1,3-dienyl)hydrazine-1,2-dicarboxylate (3d). Pale yellow crystalline solid; Yield 257 mg, 61%; mp 157-159 ^{o}C; IR (KBr, cm^{-1}) 3467 (m), 3289 (m), 1745 (s), 1715 (vs), 1538 (m), 1518 (m), 1495 (m), 1310 (m); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.28-1.32 (br unresolved, 12H), 5.03 (septet, *J* = 5.9 Hz, 2H), 6.95-7.05 (br unresolved, 1H), 7.51-7.55 (unresolved, 1H), 7.66-7.70 (m, 3H), 7.82-7.89 (br unresolved m, 2H), 8.02 (d, *J* = 7.6 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 21.7, 21.9, 70.6, 72.8, 124.9, 125.7, 129.0, 130.2, 130.9, 133.2, 133.6, 140.1, 144.4, 148.2, 153.8, 155.7; m/z (QTOF ES$^+$, Ar) 445 (MNa^+, 100), 399 (13), 313 (45), 248 (22), 227 (59), 121 (19), 77 (25); HRMS (QTOF ES$^+$, Ar) calcd for $C_{18}H_{22}N_4O_8Na$ (MNa^+) 445.1335, found 445.1314.

(*E*)-Diisopropyl (2-cyclohexyl-1-nitrovinyl)hydrazine-1,2-dicarboxylate (3e).[5] Pale yellow solid; Yield 289 mg, 81%; mp 81-83 ^{o}C (lit[5] 92-94 ^{o}C); IR (KBr, cm^{-1}) 3286 (s), 1754 (s), 1721 (vs), 1540 (s), 1504 (m), 1376 (m); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.20-1.29 (m, 17H), 1.66-1.77 (m, 6H), 2.90-3.00 (unresolved m, 1H), 5.00 (septet, *J* = 8.2 Hz, 2H), 6.83 (br s, 1H), 7.08 (d, *J* = 11.0 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 21.7, 22.0, 24.8, 25.7, 30.7, 31.4, 36.9, 70.3, 72.5, 142.4, 144.1, 154.2, 155.4; m/z (QTOF ES$^+$, Ar) 380 (MNa^+, 100), 358 (34), 311 (34), 225 (19), 183 (48); HRMS (QTOF ES$^+$, Ar) calcd for $C_{16}H_{27}N_3O_6Na$ (MNa^+) 380.1798, found 380.1791; Selected X-Ray data: $C_{16}H_{27}N_3O_6$, M = 357.41, Triclinic, space group *P* -1, *a* = 9.777 (5) Å, *b* = 10.159 (5) Å, *c* = 10.306 (5) Å, α = 102.265(7)°, β = 100.480 (6)°, *γ* = 90.508 (8)°, V = 982.4 (8) Å^3, Dc = 1.208 Mg/m^3, *Z* = 2, *F*(000) = 384, *λ* = 0.71070 Å, *μ* = 0.093 mm^{-1}, total/unique reflections = 17915/5352 [R(int) = 0.0759], *T* = 293(2) K, *ϑ* range = 3.03 to 29.30°, Final *R* [*I>2 σ (I)*]: R1 = 0.0497, wR2 = 0.1054; R (all data): R1 = 0.0876, wR2 = 0.1212.

Di-*tert*-butyl (*E*)-1-(2-(4-methoxyphenyl)-1-nitrovinyl)hydrazine-1,2-dicarboxylate (3f). Yellow solid; Yield 380 mg, 93%; mp 140-142^{o}C; IR (KBr, cm^{-1}) 3366 (s), 1744 (vs), 1648 (m), 1605 (s), 1488 (vs), 1394 (m), 1369 (m); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.28, 1.47, 1.48, 1.51 (s, 18H), 3.87 (s, 3H), 6.80 (br s, 1H), 6.99 (d, *J* = 8.0 Hz, 2H), 7.92 (s, 1H), 8.12 (br unresolved d, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 27.8, 28.0, 28.2, 28.3, 55.6, 81.9, 84.2, 114.7, 122.3, 131.6, 135.0, 142.2, 153.2, 154.9, 163.1; HRMS (ES$^+$) calcd for $C_{19}H_{27}N_3O_7Na$ (MNa^+) 432.1741, found 432.1746.

General procedure for the synthesis of triazoles 4 from MBH adducts 3 and sodium azide. To a stirred solution of MBH adduct **3** (1.0 mmol) in dry DMF (2 mL) was added NaN_3 (130 mg, 2.0 mmol) followed by tetrabutylammonium hydrogen sulfate (TBAHS, 339 mg, 1.0 mmol) and the reaction mixture was stirred at room temperature. After completion of the reaction (monitored by TLC), saturated aqueous $NaHCO_3$ was added and the reaction mixture was extracted with diethyl ether (3 × 10 mL). The organic layer was washed with brine (10 mL), dried over Na_2SO_4 and concentrated in *vacuo*. The crude product was purified by silica gel column chromatography using 35% EtOAc: pet ether (gradient elution).

Diisopropyl 1-(4-(4-chlorophenyl)-1*H*-1,2,3-triazol-5-yl)hydrazine-1,2-dicarboxylate (4a). White foam; Yield 275 mg, 72%; IR (KBr, cm^{-1}) 3246 (br vs), 1739 (br vs), 1406 (m); ^{1}H NMR ($CDCl_3$, 300 MHz, 50 ^{o}C) δ 0.99 (6H, broad unresolved d), 1.23 (d, *J* = 6.2 Hz, 6H), 4.87 (septet, *J* = 6.2 Hz, 1H), 5.00 (septet, *J* 6.2 Hz, 1H), 7.39 (d, *J* = 8.4 Hz, 2H), 7.87 (br s, 1H), 7.94 (d, *J* = 8.4 Hz, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz, 50 ^{o}C) δ 21.6, 22.0, 70.7, 72.2, 128.0, 128.8, 129.0, 135.0, 154.1, 156.0; MS (ES$^+$, Ar) m/z (rel intensity) 384 (35, $[MH+2]^+$), 382 (100, MH^+), 340 (12), 296 (10); HRMS cal for $C_{16}H_{21}N_5O_4Cl$ (MH^+) 382.1282, found 382.1278.

Diisopropyl 1-(4-(4-fluorophenyl)-1H-1,2,3-triazol-5-yl)hydrazine-1,2-dicarboxylate (4b). White solid; Yield 248 mg, 68%; mp 121-123 ^{o}C; IR (KBr, cm^{-1}) 3281 (br m), 1724 (vs); ^{1}H NMR ($CDCl_3$, 500 MHz, 55 ^{o}C) δ 1.01 (partially resolved d, *J* = 4.0 Hz, 6H), 1.25 (d, *J* = 6.2 Hz, 6H), 4.88 (septet, *J* = 6.2 Hz, 1H), 5.03 (d, *J* = 6.2 Hz, 1H), 7.14 (t, *J* = 8.8 Hz, 2H), 7.90 (s, 1H), 8.01 (dd, *J* = 8.8, 5.5 Hz, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz, 55 ^{o}C) δ 21.6, 22.0, 70.6, 72.2, 115.8 (d, $J_{C\text{-}F}$ = 22.5 Hz), 125.6, 129.5 (d, $J_{C\text{-}F}$ = 8.0 Hz), 139.3, 142.7, 154.2, 156.0, 163.3 (d, $J_{C\text{-}F}$ = 247.4 Hz); ^{19}F -112.2; MS (ES$^+$, Ar) m/z (rel intensity) 405 ([M+1]K$^+$, 98), 389 (]M+1]Na$^+$, 65), 388 (MNa^+, 100), 367 ([M+2]$^+$, 97); HRMS (ES$^+$) calcd for $C_{16}H_{20}N_5O_4FNa$ (MNa^+) 388.1392, found 388.1390.

Diisopropyl 1-(4-(2-nitrophenyl)-1H-1,2,3-triazol-5-yl)hydrazine-1,2-dicarboxylate (4c). Brown foam; Yield 64%; IR (KBr, cm^{-1}) 3349 (br vs), 1734 (m), 1717 (m), 1533 (s), 1377 (m); ^{1}H NMR (CD_3OD, 300 MHz, 50 ^{o}C) δ 0.97-1.07 (br unresolved, 6H), 1.21 (d, *J* = 6.2 Hz, 6H), 4.80 (septet, *J* = 6.2 Hz, 1H), 4.86 (septet, *J* = 6.2 Hz, 1H), 7.64 (td, *J* =7.5, 1.3 Hz, 1H), 7.72 (td, *J* = 7.5, 1.3 Hz, 1H), 7.82-7.93 (br unresolved, 1H), 8.01 (br d, *J* = 7.5 Hz, 1H); ^{13}C NMR (CD_3OD, 75 MHz, 50 ^{o}C) δ 21.9, 22.3, 71.1, 72.9, 125.6, 131.2, 133.3, 133.9, 150.3, 155.3, 157.9; MS (ES$^+$, Ar) m/z (rel intensity) 415 (MNa^+, 100); HRMS cal for $C_{16}H_{20}N_6O_6Na$ 415.1337, found 415.1337.

Diisopropyl 1-(4-(4-methoxyphenyl)-1*H*-1,2,3-triazol-5-yl)hydrazine-1,2-dicarboxylate (4d). White foam; Yield 245 mg, 65%; IR (KBr, cm^{-1}) 3263 (br vs), 1739 (m), 1716 (m), 1516 (m), 1386 (m); ^{1}H NMR ($CDCl_3$, 300 MHz, 50 ^{o}C) δ 0.95-1.05 (broad unresolved d, 6H), 1.22 (d, *J* = 6.2 Hz, 6H), 3.81 (s, 3H), 4.82-4.90 (br unresolved septet, 1H), 4.99 (septet, *J* = 6.3 Hz, 1H), 6.95 (d, *J* 8.7 Hz, 2H), 7.95 (d, *J* = 8.7 Hz, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz, 50 ^{o}C) δ 21.7, 22.1, 55.5, 70.5, 72.0, 114.4, 121.8, 128.9, 139.2, 142.3, 154.4, 156.1,

160.4; MS (ES^+, Ar) m/z (rel intensity) 378 (100, MH^+), 336 (8), 292 (7); HRMS cald for $C_{17}H_{24}N_5O_5$ (MH^+) 378.1777, found 378.1780.

Diisopropyl 1-(4-(3,4-dimethoxyphenyl)-1H-1,2,3-triazol-5-yl)hydrazine-1,2-dicarboxylate (4e). White solid; Yield 255 mg, 62%; mp 107-109 °C; IR (KBr, cm^{-1}) 3276 (w), 1732 (s); ^1H NMR ($CDCl_3$, 400 MHz, 55 °C) δ 0.97 (partially resolved d, *J* = 3.3 Hz, 6H), 1.21 (d, *J* = 6.2 Hz, 6H), 3.88 (s, 3H), 3.93 (s, 3H), 4.85 (septet, *J* = 6.2 Hz, 1H), 4.98 (septet, *J* = 6.2 Hz, 1H), 6.91 (d, *J* = 8.4 Hz, 1H), 7.53 (dd, *J* = 8.1, 1.5 Hz, 1H), 7.75 (br s, 1H), 8.08 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz, 55 °C) δ 21.5, 21.9, 56.0, 56.3, 70.2, 71.8, 110.6, 111.3, 111.7, 120.1, 121.9, 142.1, 149.5, 149.8, 154.3, 155.8; MS (ES^+, Ar) m/z (rel intensity) 430 (MNa^+, 100), 408 MH^+, 62); HRMS (ES^+) calcd for $C_{18}H_{25}N_5NaO_6$ (MNa^+) 430.1697, found 430.1702.

Diisopropyl 1-(4-(thiophen-2-yl)-1H-1,2,3-triazol-5-yl)hydrazine-1,2-dicarboxylate (4f). Brown foam; Yield 212 mg, 60%; IR (KBr, cm^{-1}) 3518 (br m), 3230 (br m), 1720 (vs), 1377 (s); ^1H NMR (CD_3OD, 300 MHz, 50 °C) δ 1.02-1.18 (br unresolved d, 6H), 1.23 (d, *J* = 6.2 Hz, 6H), 4.80-4.90 (unresolved septet, 1H), 4.94 (septet, *J* 6.2 Hz, 1H), 7.11 (dd, *J* = 4.5, 3.6 Hz, 1H), 7.46 (d, 4.5 Hz, 1H), 7.55-7.65 (br unresolved, 1H); ^{13}C NMR (CD_3OD, 75 MHz, 50 °C) δ 22.0, 22.3, 71.1, 72.9, 127.5, 128.1, 128.7, 131.6, 143.0, 155.8, 158.0; MS (ES^+, Ar) m/z (rel intensity) 354 (100, MH^+), 312 (15), 268 (12); HRMS cal for $C_{14}H_{20}N_5O_4S$ (M^+) 354.1236, found 354.1231.

Di-*tert*-butyl 1-(1-(4-methoxyphenyl)-1,2-dihydronaphtho[2,1-b]furan-2-yl)hydrazine-1,2-dicarboxylate (4g). White solid; Yield 282 mg, 70 %; mp 193-195 °C; IR (KBr, cm^{-1}) 3284 (br w), 1728 (s); ^1H NMR ($CDCl_3$, 500 MHz, 55 °C) δ 1.26 (s, 9H), 1.49 (s, 9H), 3.49 (br s, 1H), 3.85 (s, 3H), 6.97 (d, *J* = 7.6 Hz, 2H), 7.11 (s, 1H), 7.88 (d, 7.6 Hz, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz, 55 °C) δ 27.9, 28.4, 55.4, 82.0, 83.3, 114.4, 122.2, 128.8, 153.2, 155.2, 160.3; MS (ES^+, Ar) m/z (rel intensity) 444 (MK^+, 50), 428 (MNa^+, 100), 406 (MH^+, 12), 372 (10); HRMS (ES^+) calcd for $C_{19}H_{27}N_5O_5Na$ (MNa^+) 428.1904, found 428.1902.

General procedure for the tandem Michael/Friedel-Crafts reaction of arenols 5, 7 and 9 with hydrazinonitroalkenes 3. A solution of arenol **5**, **7** or **9** (0.4 mmol), hydrazinonitroalkene **3** (0.48 mmol, 1.2 equiv) and Cs_2CO_3 (156 mg, 0.48 mmol, 1.2 equiv) in CH_3CN (2 ml) was irradiated with microwave radiation at 100 °C for ~10 min (monitored by TLC). The reaction mixture was concentrated *in vacuo* and the crude residue was purified by silica gel column chromatography by eluting with ethyl acetate/pet ether (10-15%, gradient elution).

Diisopropyl 1-*trans*-(1-phenyl-1,2-dihydronaphtho[2,1-b]furan-2-yl)hydrazine-1,2-dicarboxylate (6a). White solid; Yield 178 mg, 93%; mp 81-83 °C; IR (KBr, cm^{-1}) 3310 (br m), 1726 (s); ^1H NMR ($CDCl_3$, 500 MHz) δ 1.15-1.38 (br poorly resolved d, 12H), 4.98-5.05 (m, 2H), 5.05-5.15 (br unresolved d, 1H), 6.35-6.40 (br unresolved d, 1H), 6.65 (br s, 1H), 7.21 (d, *J* = 8.8 Hz, 1H), 7.27-7.33 (m, 8H), 7.80 (d, *J* = 8.8 Hz, 1H), 7.83-7.85 (m, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 21.8, 22.0, 50.5, 70.4, 71.6, 97.6, 111.6, 119.7, 123.3, 126.9, 127.4, 128.3, 128.9, 129.1, 130.0, 130.3, 130.4, 141.3, 154.6, 156.7; HRMS (ES^+) calcd for $C_{26}H_{28}N_2O_5Na$ (MNa^+) 471.1890, found 471.1890.

Diisopropyl 1-*trans*-(1-(p-tolyl)-1,2-dihydronaphtho[2,1-b]furan-2-yl)hydrazine-1,2-dicarboxylate (6b). White solid; Yield 140 mg, 76%; mp 141-143 °C; IR (KBr, cm^{-1}) 3307 (br m), 1728 (vs); ^1H NMR ($CDCl_3$, 500 MHz) δ 1.15-1.46 (br poorly resolved d, 12H), 2.34 (s, 3H), 4.97-5.04 (m, 2H), 5.10-5.15 (br unresolved d, 1H), 6.35-6.40 (br unresolved d, 1H), 6.65 (br s, 1H), 7.11-7.23 (m, 5H), 7.28-7.34 (m, 3H), 7.79 (d, *J* = 8.8 Hz, 1H), 7.82-7.85 (m, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 21.3, 21.8, 22.0, 50.0, 50.4, 70.4, 71.5, 97.7, 111.7, 119.9, 123.3, 123.4, 126.9, 128.1, 128.9, 129.8, 130.0, 130.2, 130.5, 137.0, 138.2, 154.7, 156.7; HRMS (ES^+) calcd for $C_{27}H_{30}O_5N_2Na$ (MNa^+) 485.2047, found 485.2051; Selected X-ray data: $C_{27}H_{30}N_2O_5$, M = 462.53, Triclinic, space group P -1, a = 11.116(3)Å, b = 11.260(3)Å, c = 11.711(3)Å, α = 63.523(15)°, β = 71.584(17)°, γ = 69.128(17)°, V = 1204.2(6) Å^3, Dc = 1.276 Mg/m^3, Z = 2, $F(000)$ = 492, λ = 0.71075 Å, μ = 0.088 mm^{-1}, total/unique reflections = 12275/4222 [$R_{(int)}$ = 0.0404], T = 150 K, θ range = 3.064 to 25.000°, Final R [$I>2\,\sigma\,(I)$]: R1 = 0.0421, wR2 = 0.0969; R (all data): R1 = 0.0527, wR2 = 0.1031.

Diisopropyl 1-*trans*-(1-(4-methoxyphenyl)-1,2-dihydronaphtho[2,1-b]furan-2-yl)hydazine-1,2-dicarboxylate (6c). White solid; Yield 131 mg, 73%; mp 81-82 °C; IR (KBr, cm^{-1}) 3306 (br s), 1728 (vs); ^1H NMR ($CDCl_3$, 400 MHz) δ 1.10-1.29 (br poorly resolved d, 12H), 3.74 (s, 3H), 4.91-5.03 (m, 2H), 5.08 (br unresolved d, 1H), 6.45-6.50 (br unresolved d, 1H), 6.56 (br s, 1H), 6.80 (d, *J* = 8.7 Hz, 2H), 7.15 (d, *J* = 9.2 Hz, 1H), 7.19 (d, *J* = 8.7 Hz, 2H), 7.22-7.30 (m, 3H), 7.73 (d, *J* = 9.2 Hz, 1H), 7.76-7.80 (m, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 21.7, 21.9, 49.6, 55.3, 70.3, 71.5, 97.7, 111.6, 114.4, 119.9, 123.2, 123.3, 126.8, 128.9, 129.0, 129.3, 129.9, 130.1, 130.4, 133.3, 154.7, 156.6, 158.9; HRMS (ES^+) calcd for $C_{27}H_{30}O_6N_2K$ (MK^+) 517.1735, found 517.1738.

Diisopropyl 1-*trans*-(1-(3,4-dimethoxyphenyl)-1,2-dihydronaphtho[2,1-b]furan-2-yl)hydrazine-1,2-dicarboxylate (6d). White solid; Yield 145 mg, 71%; mp 91-92 °C; IR (KBr, cm^{-1}) 3312 (br, m), 1728 (s); ^1H NMR ($CDCl_3$, 400 MHz) δ 1.11-1.27 (br poorly resolved d, 12H), 3.74 (s, 3H), 3.81 (s, 3H), 4.95-5.00 (m, 2H), 5.05-5.15 (br unresolved d, 1H), 6.45-6.50 (br unresolved d, 1H), 6.67 (br s, 1H), 6.76, 6.80 (ABq, *J* = 10.0 Hz, 2H), 6.87 (s, 1H), 7.14 (d, *J* = 8.3 Hz, 1H), 7.24-7.30 (m, 2H), 7.31-7.35 (m, 1H), 7.73 (d, *J* = 8.3 Hz, 1H), 7.78 (d, *J* = 7.4 Hz, 1H), Confirmed by ^1H-^1H COSY experiment; ^{13}C NMR ($CDCl_3$, 125 MHz) δ 21.6, 21.9, 50.0, 55.8, 55.8, 69.9, 70.1, 71.4, 97.5, 111.2, 111.5, 111.5, 119.6, 120.2, 123.2, 123.2, 126.7, 128.8, 129.8, 130.1, 130.4, 133.6, 148.2, 149.3, 154.6, 156.5; HRMS (ES^+) calcd for $C_{28}H_{32}N_2O_7Na$ (MNa^+, 100) 531.2102, found 531.2100.

Diisopropyl 1-*trans*-(1-(4-fluorophenyl)-1,2-dihydronaphtho[2,1-b]furan-2-yl)hydrazine-1,2-dicarboxylate (6e). White solid; Yield 99 mg, 53%; mp 80-83 °C; IR (KBr, cm^{-1}) 3302 (br s), 1732 (vs); ^1H NMR ($CDCl_3$, 500 MHz) δ 1.13-1.26 (br poorly resolved d, 12H), 4.95-5.01 (m, 2H), 5.10-5.15 (br unresolved d, 1H), 6.40-6.45 (br unresolved d, 1H), 6.60 (br s, 1H), 6.99 (t, *J* = 8.3 Hz, 2H), 7.17 (d, *J* = 8.8 Hz, 1H), 7.22-7.30 (m, 5H), 7.78 (d, *J* = 8.8 Hz, 1H), 7.80-7.83 (m, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 21.8, 22.0, 22.1, 49.8, 70.5, 71.7, 97.5, 111.7, 115.9 (d, $J_{C\text{-}F}$ = 21.3 Hz), 119.4, 123.2, 123.4, 127.0, 129.0, 129.9 (d, $J_{C\text{-}F}$ = 7.5 Hz), 130.0, 130.3, 130.5, 136.9, 154.6, 156.7, 162.3 (d, $J_{C\text{-}F}$ = 243.8 Hz); ^{19}F NMR ($CDCl_3$, 470 MHz) -115.4 (major), -115.1 (minor); HRMS (ES^+) calcd for $C_{26}H_{27}O_5N_2FNa$ (MNa^+, 100) 489.1796, found 489.1797.

Diisopropyl 1-*trans*-(1-(naphthalen-1-yl)-1,2-dihydronaphtho[2,1-b]furan-2-yl)hydrazine-1,2-dicarboxylate (6f). White solid; Yield 171 mg, 86%; mp 162-163 °C; IR (KBr, cm^{-1}) 3304 (br s), 1728 (vs); ^1H NMR ($CDCl_3$, 400 MHz) δ 1.00-1.50 (br poorly resolved d, 12H), 4.98-5.17 (m, 2H), 5.75-6.00 (br unresolved d, 1H), 6.20-6.51 (br unresolved d, 1H), 6.74 (br s, 1H), 7.19-7.31 (m, 6H), 7.59-7.96 (m, 6H), 8.60-8.90 (br unresolved m, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 21.6, 22.0, 46.7, 70.3, 71.7, 97.6, 111.6, 119.4, 123.4, 123.7, 124.6, 125.2, 125.5, 125.7, 126.0, 126.5, 127.0, 128.0, 128.9, 130.0, 130.3, 130.6, 132.1, 134.4, 136.8, 154.3, 157.3; HRMS (ES^+) calcd for $C_{30}H_{30}O_5N_2Na$ (MNa^+, 100) 521.2047, found 521.2046.

DOI: 10.1039/C5OB02656C

Diisopropyl 1-*trans*-(1-(thiophen-2-yl)-1,2-dihydronaphtho[2,1-b]furan-2-yl)hydrazine-1,2-dicarboxylate (6g). White solid; Yield 167 mg, 92%; mp 105-107 ^{o}C; IR (KBr, cm^{-1}) 3304 (br s), 1729 (vs); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.03-1.40 (br unresolved d, 12H), 4.85-5.05 (m, 2H), 5.35-5.45 (br poorly resolved d, 1H), 6.20-6.40 (br unresolved d, 1H), 6.39 (br s, 1H), 6.92 (dd, *J* = 5.0, 3.5 Hz, 1H), 6.96-7.03 (unresolved m, 1H), 7.14 (d, *J* = 8.8 Hz, 1H), 7.16-7.20 (br unresolved m, 2H), 7.25-7.33 (m, 3H), 7.43 (d, *J* = 7.9 Hz, 1H), 7.75 (d, *J* = 8.8 Hz, 1H), 7.79 (d, *J* = 7.9 Hz, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 21.7, 21.9, 22.0, 22.0, 45.8, 70.4, 71.6, 73.1, 97.4, 111.7, 119.4, 123.1, 123.4, 125.2, 126.1, 127.1, 127.2, 128.5, 128.9, 130.0, 130.4, 130.7, 144.4, 154.6, 156.4; HRMS (ES$^+$) calcd for $C_{24}H_{26}N_2O_5SNa$ (MNa^+, 100) 477.1455, found 477.1453.

Diisopropyl 1-*trans*-(1-(furan-2-yl)-1,2-dihydronaphtho[2,1-b]furan-2-yl)hydrazine-1,2-dicarboxylate (6h). White solid; Yield 135 mg, 77%; mp 66-67 ^{o}C; IR (KBr, cm^{-1}) 3306 (br m), 1732 (s); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.09-1.36 (br poorly resolved d, 12H), 4.90-4.98 (br unresolved m, 1H), 5.02 (septet, *J* = 6.2 Hz, 1H), 5.19-5.25 (br m, 1H), 6.10-6.20 (br unresolved d, 1H), 6.25-6.35 (br unresolved m, 2H), 6.60-6.90 (br unresolved m, 1H), 7.15 (d, *J* = 8.8 Hz, 1H), 7.27-7.31 (m, 1H), 7.34-7.39 (m, 2H), 7.49 (d, *J* = 8.0 Hz, 1H), 7.76 (d, *J* = 8.8 Hz, 1H), 7.80 (d, *J* = 8.0 Hz, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 21.7, 22.0, 44.9, 70.4, 71.6, 94.4, 108.0, 110.6, 111.7, 117.5, 122.7, 123.4, 127.1, 128.9, 129.9, 130.4, 130.5, 142.6, 153.0, 154.5, 156.3; HRMS (ES$^+$) calcd for $C_{24}H_{26}N_2O_6Na$ (MNa^+, 100) 461.1683, found 461.1679.

(*E*)-Diisopropyl 1-*trans*-(1-styryl-1,2-dihydronaphtho[2,1-b]furan-2-yl)hydrazine-1,2-dicarboxylate (6i). White solid; Yield 120 mg, 63%; mp 71-74 ^{o}C; IR (KBr, cm^{-1}) 3306 (br s), 1725 (vs); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.09-1.28 (br poorly resolved d, 12H), 4.75 (br unresolved m, 1H), 4.91 (br unresolved m, 1H), 5.02 (septet, *J* = 6.1 Hz, 1H), 6.42 (dd, *J* = 15.8, 8.6 Hz, 2H), 6.75 (d, *J* = 15.8 Hz, 1H), 7.12 (d, *J* = 8.8 Hz, 1H), 7.18-7.24 (m, 1H), 7.25-7.33 (m, 3H), 7.34-7.41 (m, 3H), 7.66-7.76 (m, 1H), 7.72 (d, *J* = 8.8 Hz, 1H), 7.78 (d, *J* = 8.2 Hz, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 21.7, 22.0, 22.0, 48.3, 70.2, 71.6, 95.7, 111.6, 119.2, 122.9, 123.3, 123.5, 126.6, 127.0, 127.7, 128.6, 128.9, 129.8, 130.1, 130.7, 133.2, 136.8, 154.7, 156.1, 156.3; HRMS (ES$^+$) calcd for $C_{28}H_{30}N_2O_5Na$ (MNa^+) 497.2047, found 497.2060.

Diethyl 1-*trans*-(1-(4-methoxyphenyl)-1,2-dihydronaphtho[2,1-b]furan-2-yl)hydrazine-1,2-dicarboxylate (6j). White solid; Yield 146 mg, 81%; mp 83-84 ^{o}C; IR (KBr, cm^{-1}) 3307 (br m), 1732 (vs); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.19-1.32 (br poorly resolved t, 6H), 3.80 (s, 3H), 4.10-4.18 (unresolved m, 1H), 4.26 (q, *J* = 6.7 Hz, 3H), 5.07-5.13 (br unresolved d, 1H), 6.52-6.57 (br unresolved d, 1H), 6.86 (d, *J* = 8.5 Hz, 2H), 7.19 (d, *J* = 8.8 Hz, 1H), 7.22 (br d, *J* = 8.5 Hz, 2H), 7.27-7.30 (m, 3H), 7.78 (d, *J* = 8.8 Hz, 1H), 7.81-7.85 (m, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 14.5, 49.8, 55.4, 62.5, 63.6, 98.7, 111.6, 114.5, 119.9, 123.4, 126.9, 128.9, 129.3, 130.0, 130.3, 130.4, 133.3, 155.2, 156.5, 159.0; HRMS (ES$^+$) calcd for $C_{25}H_2O_6N_2Na$ (MNa^+) 473.1683, found 473.1680.

Diethyl 1-*trans*-(1-(4-chlorophenyl)-1,2-dihydronaphtho[2,1-b]furan-2-yl)hydrazine-1,2-dicarboxylate (6k). White solid; Yield 130 mg, 71%; mp 82-84 ^{o}C; IR (KBr, cm^{-1}) 3305 (br m), 1732 (vs); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.17 (t, *J* = 6.9 Hz, 3H), 1.24 (t, *J* = 6.5 Hz, 3H), 4.08-4.28 (m, 4H), 5.11 (d, *J* = 4.1 Hz, 1H), 6.50 (bs, 1H), 6.55-6.60 (br unresolved d, 1H), 7.15 (d, *J* = 8.8 Hz, 1H), 7.19-7.30 (m, 7H), 7.76 (d, *J* = 8.8 Hz, 1H), 7.79-7.81 (m, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 14.4, 14.4, 50.0, 62.6, 63.7, 97.8, 111.6, 119.0, 123.2, 123.5, 127.1, 129.0, 129.3, 129.7, 130.0, 130.2, 130.6, 133.4, 139.6, 155.1, 156.7; HRMS (ES+) calcd for $C_{24}H_{23}ClO_5N_2Na$ (MNa^+, 100) 477.1188, found 477.1188.

Diethyl 1-*trans*-(1-(thiophen-2-yl)-1,2-dihydronaphtho[2,1-b]furan-2-yl)hydrazine-1,2-dicarboxylate (6l). White solid; Yield 150 mg, 88%; mp 76-78 ^{o}C; IR (KBr, cm^{-1}) 3303 (br m), 1731 (vs); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.17-1.32 (br m, 6H), 4.21-4.28 (br m, 4H), 5.48 (br unresolved d, 1H), 6.60 (br s, 1H), 6.65-6.75 (br unresolved d, 1H), 6.98-7.05 (br unresolved m, 2H), 7.19 (d, *J* = 8.7 Hz, 1H), 7.22-7.26 (br unresolved m, 1H), 7.30-7.38 (m, 2H), 7.46-7.52 (br unresolved m, 1H), 7.80 (d, *J* = 8.7 Hz, 1H), 7.84 (d, *J* = 7.9 Hz, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 14.4 (× 2), 45.9, 62.5, 63.6, 97.6, 111.6, 119.3, 123.1, 123.4, 125.3, 126.1, 127.1, 127.2, 128.9, 130.0, 130.3, 130.7, 144.3, 155.1, 156.3, 156.7; HRMS (ES$^+$) calcd for $C_{22}H_{22}O_5N_2SNa$ (MNa^+) 449.1142, found 449.1141.

Di-*tert*-butyl 1-*trans*-(1-(4-methoxyphenyl)-1,2-dihydronaphtho[2,1-b]furan-2-yl)hydrazine-1,2-dicarboxylate (6m). White solid; Yield 160 mg, 79%; mp 97-99^{o}C; IR (KBr, cm^{-1}) 3323 (br w), 1726 (vs); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.41, 1.49 (s, 18H), 3.77 (s, 3H), 5.05-5.60 (br unresolved d, 1H), 6.33 (br unresolved d, 1H), 6.62 (br s, 1H), 6.83 (d, *J* = 8.6Hz, 2H), 7.15-7.25 (m, 3H), 7.27-7.32 (m, 3H), 7.76 (d, *J* = 8.6 Hz, 1H), 7.78-7.82 (m, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 28.2, 28.2, 49.6, 55.3, 81.6, 82.9, 97.4, 111.7, 114.4, 120.0, 123.2, 123.3, 126.8, 128.9, 129.3, 129.9, 130.1, 130.5, 133.5, 153.9, 155.6, 156.7, 158.8; HRMS (ES$^+$) calcd for $C_{29}H_{34}N_2O_6K$ (MK^+) 545.2048, found 545.2042.

Diisopropyl 1-*trans*-(3-phenyl-2,3-dihydronaphtho[1,2-b]furan-2-yl)hydrazine-1,2-dicarboxylate (8a). White solid; Yield 93 mg, 52%; mp 174-175 ^{o}C; IR (KBr, cm^{-1}) 1725 (vs); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.20-1.50 (br poorly resolved d, 12H), 4.90-5.10 (partially resolved m, 3H), 6.43-6.49 (br unresolved d, 1H), 6.80 (br s, 1H), 7.19 (d, *J* = 8.2 Hz, 1H), 7.28-7.36 (m, 5H), 7.44 (d, *J* = 8.2 Hz, 1H), 7.48-7.52 (m, 2H), 7.84-7.86 (m, 1H), 8.00-8.05 (m, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 21.9, 22.0, 51.4, 70.3, 71.6, 97.4, 120.2, 121.2, 121.7, 122.1, 122.8, 125.7, 126.2, 127.5, 128.1, 128.4, 129.0, 134.4, 141.5, 154.2, 154.7, 156.4; HRMS (ES$^+$) calcd for $C_{26}H_{28}N_2O_5Na$ (MNa^+) 471.1890, found 471.1890.

Diisopropyl 1-*trans*-(3-(4-methoxyphenyl)-2,3-dihydronaphtho[1,2-b]furan-2-yl)hydrazine-1,2-dicarboxylate (8b). White solid; Yield 65 mg, 34%; mp 142-143 ^{o}C; IR (KBr, cm^{-1}) 3301 (br m), 1728 (vs); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.15-1.35 (br unresolved d, 12H), 3.79 (s, 3H), 4.89-4.90 (br poorly resolved d, 1H), 4.95-5.05 (m, 2H), 6.39-6.40 (br unresolved d, 1H), 6.65 (br s, 1H), 6.85 (d, *J* = 8.6 Hz, 2H), 7.15 (d, *J* = 8.3 Hz, 1H), 7.20-7.26 (m, 2H), 7.42 (d, *J* = 8.3 MHz, 1H), 7.45-7.50 (m, 2H), 7.82-7.84 (m, 1H), 7.98-8.00 (m, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 21.9, 22.1, 50.6, 55.4, 70.3, 71.6, 97.9, 114.4, 120.2, 121.2, 121.7, 122.4, 122.8, 125.7, 126.2, 128.1, 129.5, 133.6, 134.4, 154.1, 154.8, 156.5, 159.0; HRMS (ES$^+$) calcd for $C_{27}H_{30}N_2O_6Na$ (MNa^+) 501.1996, found 501.1992.

Diisopropyl 1-*trans*-(3-(3,4-dimethoxyphenyl)-2,3-dihydronaphtho[1,2-b]furan-2-yl)hydrazine-1,2-dicarboxylate (8c). White solid; Yield 73 mg, 36%; mp 131-132 ^{o}C; IR (KBr, cm^{-1}) 3308 (br m), 1728 (vs); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.22-1.31 (br poorly resolved d, 12H), 3.83 (s, 3H), 3.89 (s, 3H), 4.90-4.95 (br unresolved d, 1H), 4.96-5.06 (m, 2H), 6.43-6.73 (br unresolved, 2H), 6.78-6.88 (m, 3H), 7.17 (d, *J* = 8.1 Hz, 1H), 7.41 (d, *J* = 8.2 Hz, 1H), 7.44-7.48 (m, 2H), 7.79-7.84 (m, 1H), 7.95-8.01 (m, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 21.8, 21.9, 22.0, 50.9, 56.0, 70.1, 71.5, 97.5, 111.5, 120.1, 120.4, 121.2, 121.7, 122.0, 122.8, 125.6, 126.2, 128.1, 133.8, 134.3,

148.4, 149.4, 154.0, 154.8, 156.6; HRMS (ES^+) calcd for $C_{28}H_{32}N_2O_7Na$ (MNa^+) 531.2102, found 531.2107.

Diisopropyl 1-*trans*-(3-(thiophen-2-yl)-2,3-dihydronaphtho[1,2-b]furan-2-yl)hydrazine-1,2-dicarboxylate (8d). White solid; Yield 89 mg, 50%; mp 137-139 ^oC; IR (KBr, cm^{-1}) 3303 (br m), 1732 (vs); ^1H NMR ($CDCl_3$, 400 MHz) δ 1.18-1.29 (br poorly resolved d, 12H), 4.93-5.10 (br unresolved m, 2H), 5.21-5.27 (br unresolved d, 1H), 6.35-6.45 (br unresolved, 1H), 6.97-6.99 (dd, *J* = 4.8, 3.6 Hz, 1H), 7.04-7.08 (br unresolved m, 1H), 7.22-7.24 (br unresolved m, 1H), 7.30 (d, *J* = 8.3 Hz, 1H), 7.45 (d, *J* = 8.3 Hz, 1H), 7.47-7.49 (m, 2H), 7.80-7.85 (m, 2H), 7.97-8.00 (m, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 21.9, 22.1, 46.7, 70.4, 71.8, 97.2, 120.2, 121.3, 121.6, 121.8, 122.6, 125.1, 125.8, 126.2, 126.4, 127.3, 128.2, 134.6, 144.4, 153.8, 154.7, 156.4; HRMS (ES^+) calcd for $C_{24}H_{26}N_2O_5SNa$ (MNa^+) 477.1455, found 477.1453.

Diisopropyl 1-*trans*-(3-(furan-2-yl)-2,3-dihydronaphtho[1,2-b]furan-2-yl)hydrazine-1,2-dicarboxylate (8e). White solid; Yield 72 mg, 40%; mp 119-120 ^oC; IR (KBr, cm^{-1}) 3386 (br w), 1728 (s); ^1H NMR ($CDCl_3$, 400 MHz) δ 1.15-1.29 (br poorly resolved d, 12H), 4.88-4.98 (br unresolved d, 1H), 5.00-5.08 (br unresolved m, 2H), 6.10-6.23 (br unresolved, 1H), 6.30-6.34 (br unresolved, 1H), 6.40-6.46 (br unresolved, 1H), 6.70-7.00 (br unresolved, 1H), 7.27 (d, *J* = 8.3 Hz, 1H), 7.37-7.38 (unresolved m, 1H), 7.39 (d, *J* = 8.3 Hz, 1H), 7.42-7.47 (m, 2H), 7.79-7.7.83 (m, 1H), 7.96-7.80 (br poorly resolved m, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 21.8, 22.0, 45.5, 70.3, 71.6, 94.3, 107.3, 110.5, 119.7, 120.2, 121.2, 121.7, 122.3, 125.7, 126.3, 128.1, 134.5, 142.7, 153.4, 153.9, 154.6, 156.3; HRMS (ES^+) calcd for $C_{24}H_{26}N_2O_6Na$ (MNa^+) 461.1683, found 461.1684.

Diethyl 1-*trans*-(3-(4-methoxyphenyl)-2,3-dihydronaphtho[1,2-b]furan-2-yl)hydrazine-1,2-dicarboxylate (8f). White solid; Yield 83 mg, 46%; mp 95-97 ^oC; IR (KBr, cm^{-1}) 3301 (br m), 1732 (vs); ^1H NMR ($CDCl_3$, 400 MHz) δ 1.22-1.28 (br poorly resolved q, 6H), 3.79 (s, 3H), 4.15-4.28 (m, 4H), 4.88-4.93 (br unresolved d, 1H), 6.53-6.58 (br unresolved d, 1H), 6.70 (br s, 1H), 6.86 (d, *J* = 8.6 MHz, 2H), 7.15 (d, *J* = 8.2 Hz, 1H), 7.21 (br d, *J* = 8.6 Hz, 2H), 7.43 (d, *J* = 8.2 Hz, 1H), 7.46-7.50 (m, 2H), 7.82-7.84 (m, 1H), 7.98-8.02 (m, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 14.5 (× 2), 50.7, 55.4, 62.5, 63.6, 98.0, 114.4, 120.1, 121.3, 121.7, 122.3, 122.8, 125.8, 126.2, 128.1, 129.5, 133.5, 134.4, 154.0, 155.3, 156.8, 159.1; HRMS (ES^+) calcd for $C_{25}H_{26}N_2O_6Na$ (MNa^+) 473.1683, found 473.1681.

Diisopropyl 1-*trans*-(7-bromo-1-phenyl-1,2-dihydronaphtho[2,1-b]furan-2-yl)hydrazine-1,2-dicarboxylate (10a). White solid; Yield 183 mg, 87%; mp 218-219 ^oC; IR (KBr, cm^{-1}) 3358 (br s), 1741 (s), 1736 (s); ^1H NMR ($CDCl_3$, 500 MHz) δ 1.09-1.30 (br poorly resolved d, 12H), 4.70-5.20 (br unresolved, 3H), 6.50-6.80 (br unresolved, 1H), 7.16-7.50 (m, 7H), 7.50-7.90 (br unresolved, 3H), 8.40-8.60 (br m, 1H), 9.60-9.77 (br m, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 21.9, 22.1, 49.5, 70.5, 71.9, 99.0, 121.2, 122.8, 124.3, 127.9, 128.0, 128.8, 129.3, 129.6, 130.1, 131.6, 132.9, 140.3, 152.5, 154.9, 157.0, 162.5; HRMS (ES^+) calcd for $C_{26}H_{27}BrO_5N_2Na$ (MNa^+) 549.0996, found 549.0998.

Diisopropyl 1-*trans*-(1-phenyl-4-(o-tolylcarbamoyl)-1,2-dihydronaphtho [2,1-b]furan-2-yl)hydrazine-1,2-dicarboxylate (10b). White solid; Yield 200 mg, 86%; mp 217-218 ^oC; IR (KBr, cm^{-1}) 3376 (br s), 3230 (br m), 1728 (vs), 1669 (s); **^1H NMR ($CDCl_3$, 500 MHz, 294K)** δ 1.15-1.50 (br poorly resolved d, 12H), 2.27 (br s, 3H), 4.50-4.70 (br unresolved, 1H), 5.00-5.15 (br unresolved septet, 2H), 5.15-5.20 (br unresolved d, 1H), 6.70-7.40 (br unresolved, 13H), 8.10-8.90 (br unresolved, 2H), 9.50-9.65 (br unresolved, 1H); **^{13}C NMR ($CDCl_3$, 125 MHz, 297K)** δ 18.2, 22.1 (× 2), 49.3, 70.1, 71.4, 98.3, 116.9, 120.1, 120.8, 122.6, 123.9, 124.1, 126.0, 127.0, 127.7, 128.1, 128.7, 129.2, 129.5, 129.7, 130.3, 131.4, 132.4, 136.7, 140.4, 152.6, 155.0, 157.2, 162.2; **^1H NMR ($CDCl_3$, 500 MHz, 323K)** δ 1.15-1.31 (br poorly resolved d, 12H), 2.27 (s, 3H), 4.85-5.00 (br unresolved, 1H), 5.04 (heptet, *J* = 6.3 Hz, 1H), 5.15-5.20 (br unresolved d, 1H), 6.77-6.84 (br unresolved, 1H), 6.93-6.99 (br, unresolved 1H), 7.00-7.03 (br unresolved, 1H), 7.13-7.20 (br m, 2H), 7.21-7.32 (m, 8H), 7.50-7.80 (br unresolved, 1H), 8.35 (d, *J* = 8.0 Hz, 1H), 8.45-8.55 (br unresolved, 1H), 9.48-9.56 (br unresolved, 1H); **^1H NMR (DMSO-d_6, 500 MHz, 333K)** δ 1.00-1.25 (br unresolved, 6H), 1.23 (d, *J* = 6.3 Hz, 6H), 2.36 (s, 3H), 4.50-4.53 (br unresolved, 1H), 4.90 (heptet, *J* = 6.3 Hz, 2H), 5.10-5.20 (br unresolved, 1H), 6.65-6.75 (br unresolved, 1H), 7.09 (t, *J* = 7.4 Hz, 1H), 7.23-7.34 (m, 6H), 7.37 (t, *J* = 7.3 Hz, 3H), 7.42-7.47 (br unresolved, 1H), 8.10 (d, *J* = 8.2 Hz, 1H), 8.24 (br d, *J* = 6.1 Hz, 1H), 8.60 (s, 1H), 9.45-9.60 (br unresolved, 1H); **^{13}C NMR (DMSO-d_6, 125 MHz, 333K)** δ 17.2, 21.3, 49.0, 68.5, 70.5, 97.9, 118.0, 121.4, 122.0, 123.9, 124.0, 126.0, 127.3, 128.5, 128.8, 128.9, 129.9, 130.1, 130.6, 131.6, 136.6, 140.3, 152.3, 161.2; HRMS (ES^+) calcd for $C_{34}H_{35}N_3O_6Na$ (MNa^+) 604.2418, found 604.2425.

Diisopropyl 1-*trans*-(5-(benzyloxy)-6-methoxy-3-phenyl-2,3-dihydrobenzofuran-2-yl) hydrazine-1,2-dicarboxylate (10c). White solid; Yield 104 mg, 49%; mp 122-123 ^oC; IR (KBr, cm^{-1}) 3307 (br m), 1727 (vs); ^1H NMR ($CDCl_3$, 500 MHz) δ 1.20-1.40 (br poorly resolved d, 12H), 3.89 (s, 3H), 4.65-4.75 (br unresolved, 1H), 4.95-5.05 (br unresolved, 2H), 5.01 (s, 2H), 6.20-6.50 (br unresolved, 2H), 6.53 (s, 1H), 6.64 (s, 1H), 7.16-7.27 (br poorly resolved multiplet, 2H), 7.28-7.36 (m, 6H), 7.38-7.41 (m, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 22.0, 22.1, 22.1, 50.6, 56.3, 70.3, 71.6, 72.6, 95.0, 113.3, 118.7, 127.4, 127.8, 127.9, 128.2, 128.5, 128.9, 137.4, 141.2, 142.9, 151.2, 153.7, 154.7, 156.4; HRMS (ES^+) calcd for $C_{30}H_{34}N_2O_7Na$ (MNa^+) 557.2258, found 557.2258.

Acknowledgements

INNN thanks SERB, DST India for financial assistance. VM and NA thank CSIR India and UGC India, respectively, for a senior research fellowship. JP thanks DST India and RK thanks IIT Bombay for a postdoctoral research associateship. The authors thank Dr. Mamta Dadwal for performing preliminary studies in this project.

Notes and references

1 (*a*) K. Morita, Z. Suzuki and H. Hirose, *Bull. Chem. Soc. Jpn.,* 1968, **41**, 2815; (*b*) A. B. Baylis and M. E. D. Hillman, *Ger. Offen.* 2155113, 1972; *Chem. Abstr.,* 1972, **77**, 34174q; M. E. D. Hillman, A. B. Baylis, *U. S. Patent* 1973, US3743669; Selected recent reviews: (*c*) Y. Wei and M. Shi, *Chem. Rev.*, 2013, **113**, 6659; (*d*) D. Basavaiah and B. C. Sahu, *Chimia*, 2013, **67**, 8; (*e*) Guillena, D. J. Ramon and M. Yus, *Catalysis*, 2012, **24**, 223; (*f*) D. Basavaiah and G. Veeraraghavaiah, *Chem. Soc. Rev.*, 2012, **41**, 68; (*g*) V. Singh and S. Batra, *Tetrahedron*, 2008, **64**, 4511; (h) V. Declerck, J. Martinez and F. Lamaty, *Chem. Rev.* 2009, **109**, 1.

2 (*a*) M. M. Rauhut and H. Currier, *U. S. Patent* 1963, 3074999; *Chem. Abstr*. 1963, **58,** 11224a. Review: (*b*) C. E. Aroyan, A. Dermenci and S. J. Miller, *Tetrahedron,* 2009, **65**, 4069.

3 Review: (*a*) K. Kaur and I. N. N. Namboothiri, *Chimia,* 2012, **66,** 913; Articles: (*b*) N. Rastogi, I. N. N. Namboothiri and M. Cojocaru, *Tetrahedron. Lett.,* 2004, **45,** 4745; (*c*) R. Mohan, N. Rastogi, I. N. N. Namboothiri, S. M. Mobin and D. Panda,

Bioorg. Med. Chem., 2006, **14**, 8073; (*d*) I. Deb, M. Dadwal, S. M. Mobin and I. N. N. Namboothiri, *Org. Lett*., 2006, **8**, 1201; (*e*) M. Dadwal, R. Mohan, D. Panda, S. M. Mobin and I. N. N. Namboothiri, *Chem. Commun.,* 2006, 338; (*f*) N. Rastogi, R. Mohan, D. Panda, S. M. Mobin and I. N. N. Namboothiri, *Org. Biomol. Chem.,* 2006, **4**, 3211; (*g*) I. Deb, P. Shanbhag, S. M. Mobin and I. N. N. Namboothiri, *Eur. J. Org. Chem.,* 2009, 4091; (*h*) H.-H. Kuan, R. J. Reddy and K. Chen, *Tetrahedron,* 2010, **66,** 9875; (*i*) K. Rajesh, P. Shanbhag, M. Raghavendra, P. Bhardwaj and I. N. N. Namboothiri, *Tetrahedron Lett.,* 2010, **51,** 846; (*j*) S. Takizawa, A. Horii and H. Sasai, *Tetrahedron: Asymmetry,* 2010, **21,** 891; (k) P. Shanbhag, P. R. Nareddy, M. Dadwal, S. M. Mobin and I. N. N. Namboothiri, *Org. Biomol. Chem.,* 2010, **8,** 4867; (*l*) R. Kumar, T. Kumar, S. M. Mobin and I. N. N. Namboothiri, *J. Org. Chem*., 2013, **78**, 5073; For closely related work: (*m*) X. Wang, Y.-F. Chen, L.-F. Niu and P.-F. Xu, *Org. Lett.,* 2009, **11,** 3310; (*n*) R. Ballini, L. Barboni, G. Bosica, D. Fiorini, E. Mignini and A. Palmieri, *Tetrahedron,* 2004, **60,** 4995.

4 M. Dadwal, S. M. Mobin and I. N. N. Namboothiri, *Org. Biomol. Chem.,* 2006, **4,** 2525.

5 X.-Y. Chen, F. Xia and S. Ye, *Org. Biomol. Chem.* 2013, **11**, 5722.

6 Selected articles: (*a*) V. Barbier, F. Couty and O. R. P. David, *Eur. J. Org. Chem.,* 2015, 3679; (*b*) B. Han, X. Xie, W. Huang, X. Li, L. Yang and C. Peng, *Adv. Synth. Catal.,* 2014, **356**, 3676; (*c*) J.-Q. Zhang, J.-J. Liu, C.-L. Gu, D. Wang and L. Liu, *Eur. J. Org. Chem.,* 2014, 5885; (*d*) N. Lu, H. Wang and Y. Wang, *Bull. Kor. Chem. Soc.,* 2013, **34**, 3591; (*e*) X.-Y. Chen, F. Xia and S. Ye, *Org. Biomol. Chem.,* 2013, **11**, 5722; (*f*) N. Lu, L. Meng, D. Chen and G. Zhang, *RSC Adv.,* 2011, **1**, 1113; (*g*) X. Wang, Y.-F. Chen, L.-F. Niu and P.-F. Xu, *Org. Lett.,* 2009, **11**, 3310; (*h*) S. Chandrasekhar, K. Mallikarjun, G. Pavankumarreddy, K. V. Rao and B. Jagadeesh, *Chem. Commun*., 2009, 4985; (*i*) S. Fioravanti, L. Pellacani and P. A. Tardella, *Tetrahedron,* 2009, **65**, 5747; (*j*) Y. Wu, A. Lu, Y. Liu, X. Yu, Y. Wang, G. Wu, H. Song, Z. Zhou and C. Tang, *Tetrahedron: Asymmetry,* 2010, **21**, 2988; (*k*) Y. Wang, S. Zhu and D. Ma, *Org. Lett.,* 2011, **13**, 1602; (*l*) A. Rai and L. D. S. Yadav, *Tetrahedron,* 2012, **68**, 2459; (*m*) Z.-W. Guo, J.-W. Xie, C. Chen and W.-D. Zhu, *Org. Biomol. Chem.,* 2012, **10**, 8471; (*n*) G. Talavera, E. M. Reyes, J. L. Vicario and L. Carrillo, *Angew. Chem. Int. Ed.,* 2012, **51**, 4104; (*o*) B.-C. Hong, D.-J. Lan, N. S. Dange, G.-H. Lee and J.-H. Liao, *Eur. J. Org. Chem.,* 2013, 2472; (*p*) J. An, L.-Q. Lu, Q.-Q. Yang, T. Wang and W.-J. Xiao, *Org. Lett.,* 2013, **15**, 542; (*q*) M. Yaqub, C. Y. Yu, Y. M. Jia and Z. T. Huang, *Synlett,* 2008, **9**, 1357; (*r*) N. Lu, L. Meng, D. Chen and G. Zhang, *RSC Adv.,* 2011, **1**, 1113; (*s*) M. Bakthadoss, N. Sivakumar, A. Devaraj and D. S. Sharada, *Synthesis,* 2011, **13**, 2196.

7 (*a*) Terphenyls: E. Gopi and I. N. N. Namboothiri, *J. Org. Chem*., 2014, **79**, 7468; (*b*) Cyclopentenes: L. F. Yeh, S. Anwar and K. Chen, *Tetrahedron,* 2012, **68**, 7317; Bicyclic skeletons: (*c*) C.-L. Cao, Y.-Y. Zhou, J. Zhou, X.-L. Sun, Y. Tang, Y.-X. Li, G.-Y. Li and J. Sun, *Chem. Eur. J.,* 2009, **15**, 11384; (d) P. Shanbhag, V. Mane, C. Hazra and I. N. N. Namboothiri, *J. Ind. Chem. Soc.* 2013, **90**, 1713.

8 (*a*) Imidazopyridines: D. K. Nair, S. M. Mobin and I. N. N. Namboothiri, *Org. Lett.,* 2012, **14**, 4580; (*b*) Pyranonaphthaquinones: D. K. Nair, R. F. S. Menna-Barreto, E. N. da Silva Júnior, S. M. Mobin and I. N. N. Namboothiri, *Chem. Commun*., 2014, **50**, 6973; (*d*) Pyrroles: D. R. Magar, Y.-J. Ke and K. Chen, *Asian J. Org. Chem.,* 2013, **2**, 330; (*e*) T. Chen, N. Shao, H. Zhu, B. Zhang and H. Zou, *Tetrahedron,* 2013, **69**, 10558; (*f*) Oxa- and aza-triquinanes: J. An, L.-Q. Lu, Q.-Q. Yang, T. Wang and W.-J. Xiao, *Org. Lett.,* 2013, **15**, 542; (*g*) Tetrahydropyridines: M. Yaqub, C.-Y. Yu, Y.-M. Jia and Z.-T. Huang, *Synlett,* 2008, 1357; Imidazoles: (*h*) T. Kumar, D. Verma, R. F. S. Menna-Barreto, W. O. Valenca, E. N. da Silva Júnior and I. N. N. Namboothiri, *Org. Biomol. Chem.,* 2015, **13**, 1996; (*i*) E. Gopi, T. Kumar, R. F. S. Menna-Barreto, W. O. Valenca, E. N. da Silva Junior and I. N. N. Namboothiri, *Org. Biomol. Chem.* 2015, **13**, 9862; (*j*) Different heterocyclic scaffolds: H. Zhu, N. Shao, T. Chen and H. Zou, *Chem. Commun.,* 2013, **49**, 7738.

9 Furans from 1, 3-dicarbonyl compounds: (*a*) D. K. Nair, S. M. Mobin and I. N. N. Namboothiri, *Tetrahedron Lett.,* 2012, **53**, 3349; (*b*) W.-Y. Huang, Y.-C. Chen and K. Chen, *Chem. Asian J.,* 2012, **7**, 688; (c) V. Mane, T. Kumar, S. Pradhan, S. Katiyar and I. N. N. Namboothiri, *RSC Advances* 2015, **5**, 69990; Arenofurans from arenols: (*d*) T. Kumar, S. M. Mobin and I. N. N. Namboothiri, *Tetrahedron,* 2013, **69**, 4964; (*e*) S. Anwar, W.-Y. Huang, C.-H. Chen, Y.-S. Cheng and K. Chen, *Chem. Eur. J.,* 2013, **19**, 4344.

10 For DABCO catalyzed reactions of azodicarboxylates with (*a*) vinyl ketones: A. Kamimura, Y. Gunjigake, H. Mitsudera and S. Yokoyama, *Tetrahedron Lett.,* 1998, **39**, 7323; (*b*) acrylates and acrylonitrile: M. Shi and G.-L. Zhao, *Tetrahedron*, 2004, **60**, 2083.

11 Selected Reviews: (*a*) K. C. Majumdar and K. Ray, *Synthesis,* 2011, **23,** 3767; (*b*) A. Lauria, R. Delisi, F. Mingoia, A. Terenzi, A. Martorana, G. Barone and A. M. Almerico, *Eur. J. Org. Chem.,* 2014, 3289; (*c*) S. Mohapatra, C. Bhanja, S. Jena, S. Chakroborty and S. Nayak, *Synth. Commun.,* 2013, **43,** 1993.

12 Selected Reviews: (*a*) J.-P. Wan, D. Hu, Y, Liu and S. Sheng, *ChemCatChem,* 2015, **7,** 901; (*b*) Y. Jiang and C. Kuang, *Mini-Rev. Med. Chem.,* 2013, **13,** 713; (*c*) M. D. Hill, *Name Reactions in Heterocyclic Chemistry* II, J. J. Li (Ed.) 2011, 269.

13 Selected Reviews: (*a*) Antitubercular: R. S.Keri, S. A. Patil, S. Budagumpi and B. M. Nagaraja, *Chem. Biol. Drug Des.,* 2015, **86,** 410; (*b*) Anticancer: M. A. Dar, S. Shrivastava and P. F. Iqbal, *World J. Pharm. Res.,* 2015, **4,** 1949; (*c*) Peptidomimetic: I. E. Valverde and T. L. Mindt, *Chimia,* 2013, **67,** 262.

14 Selected Reviews: (*a*) P. I. P. Elliott, *Organomet. Chem.,* 2014, **39,** 1; (*b*) D. Huang and A. Zhao, *Coord. Chem. Rev.,* 2014, **272,** 145.

15 G. L'Abbe, A. Vandendriessche, E. G. Van and S. Toppet, *Soc. Chim. Belg,* 1988, **97,** 543.

16 D. M. X. Donnelly and M. J. Meegan, *Compreh. Heterocycl. Chem.,* A. R. Katrizky and C. W. Rees, Pergamon, Oxford, UK, 1984, vol. 4.

17 Synthesis of dihydroarenofurans, selected articles: (*a*) I. C. Chipoline, V. F. Ferreira and F. de. C. da Silva, *Curr. Org. Synth.,* 2015, **12,** 565; (*b*) M. Sadeghpour, A. Olyaei, J. Lotfiyan and F. Rajabi, *Synth. Commun.,* 2015, **45,** 1311; (*c*) P. K. Basu and A. Ghosh, *J. Ind. Chem. Soc.,* 2014, **91,** 575; (*d*) M. Kitamura, K. Araki, H. Matsuzaki and T. Okauchi, *Eur. J. Org. Chem,* 2013, 5045; (*e*) L. Xia and Y. R. Lee, *Org. Biomol. Chem.,* 2013, **11,** 6097; (*f*) V. A. Osyanin, D. V. Osipov and Y. N. Klimochkin, *J. Org. Chem.,* 2013, **78,** 5505; (*g*) A. Jha, T.-Y. Chou and D. Vaughan, *Molecular Diversity,* 2013, **17,** 261; (*h*) C. Jarava-Barrera, F. Esteban, C. Navarro-Ranninger, A. Parra and J. Aleman, *Chem. Commun.,* 2013, **49,** 2001; (*i*) C. Huo, X. Xu, J. An, X, Jia, X. Wang and C. Wang, *J. Org. Chem.,* 2012, **77,** 8310; (*j*) A. V. Butin, S. E. V. Fin'ko and F. A. Tsiunchik, *Chem. Heterocycl. Compd.,* 2011, **47,** 644; (*k*) R. Okamoto, E. Okazaki, K. Noguchi and K. Tanaka, *Org.*

View Article Online
DOI: 10.1039/C5OB02656C

Lett., 2011, **13,** 4894; (*l*) E. N. da Silva Jr., C. A. De Simone, M. O. F. Goulart, C. K. Z. Andrade, R. S. F. Silva and A. V. Pinto, *Acta Crystallogr. Sect. E: Struct. Rep. Online,* 2008, **64,** o2348; (*m*) M. Dixit, R. Raghunandan, B. Kumar, P. R. Maulik and A. Goel, *Tetrahedron,* 2007, **63,** 1610; (*n*) I. Yavari, M. Anary-Abbasinejad, and Z. Hossaini, *Pol. J. Chem.,* 2004, **78,** 361; (*o*) S. E. Vaillard, A. Postigo and R. A. Rossi, *J. Org. Chem.,* 2002, **67,** 8500; (*p*) S. Chackalamannil, D. Doller, M. Clasby, Y. Xia, K. Eagen, Y. Lin, H.-A. Tsai and A. T. McPhail, *Tetrahedron Lett.,* 2000, **41,** 4043; (*q*) T. D. Haselgrove, M. Jevric, D. K. Taylor and E. R. T. Tiekink, *Tetrahedron*, 1999, **55,** 14739; (*r*) S. A. Snyder, A. Gollner and M. I. Chiriac, *Nature,* 2011, **474,** 461; (s) A. Lu, K. Hu, Y. Wang, H. Song, Z. Zhou, J. Fang and C. Tang, *J. Org. Chem.,* 2012, **77,** 6208; (*t*) F. Bertolini, P. Crotti, V. D. Bussolo, F. Macchia and M. Pineschi, *J. Org. Chem.,* 2007, **72,** 7761; (u) G. Liu and X. Lu, *Tetrahedron,* 2008, **64,** 7324.

18 Biological properties of dihydroarenofurans, selected articles: (*a*) Antioxidant and antibacterial: L. Xia, A. Idhayadhulla, Y. R. Lee, S. H. Kim and Y.-J. Wee, *Med. Chem. Res.*, 2014, **23,** 3528; (*b*) Antiinflammatory and breast cancer migration inhibitory: (*c*) S. El, A. Khalid, A. I. Foudah, A. M. S. Mayer, A. M. Crider and D. Song, *Med. Chem. Commun.,* 2013, **4,** 1231; (*d*) Antimicrobial: S. S. Gaikwad, V. S. Suryawanshi, D. R. Kulkarni, D. V. Jadhav and N. D. Shinde, *Org. Chem. Ind. J.,* 2012, **8,** 241; (*e*) PTP1B inhibitory activity: M. Dixit, U. Saeed, A. Kumar, M. I. Siddiqi, A. K. Tamrakar, A. K. Srivastava and A. Goel, *Med. Chem.,* 2008, **4,** 18; (*f*) Trypanocidal activity: R. A. Tapia, C. Salas, A. Morello, J. D. Maya and A. Toro-Labbe, *Bioorg. Med. Chem.,* 2004, **12,** 2451.

19 (*a*) X.-F. Hou, S. You, A. Ma´ndi, T. Kurta´in, C.-P. Tang, C.-Q. Ke, X.-Q. Li and Y. Ye, *Org. Lett*., 2012, **14,** 460; (*b*) M. U. S. Sultanbawa, S. Surendrakumar, M. I. M. Wazeer and P. Bladon, *J. Chem. Soc*. *Chem. Commun*., 1981, 1204; (*c*) H.-Q. Yin, B.-W. Lee, Y.-C. Kim, D.-H. Shon and B.-H. Lee, *Arch. Pharmacal Res*. 2004, **27**, 919; (*d*) M. A. Calter and N. Li, *Org. Lett*., 2011, **13,** 3686.

20 (*a*) T. Hayashi and R. H. Thomson, *Phytochemistry,* 1975, **14,** 1085; (*b*) D. C. Chauret, C. B. Bernard, J. T. Arnason and T. Durst, *J. Nat. Prod*., 1996, **59,** 152; (*c*) M. P. De Campos, V. C. Filho, R. Z. Da Silva, R. A. Yunes, S. Zacchino, S. Juarez, R. C. Bella Cruz and A. Bella Cruz, *Biol. Pharm. Bull*., 2005, **28,** 1527; (*d*) P. S. Luize, T. Ueda-Nakamura, B. P. D. Filho, D. A. G. Cortez and C. V. Nakamura, *Biol. Pharm. Bull*., 2006, **29,** 2126; (*e*) P. J. C. Benevides, P. Sartorelli and M. J. Kato, *Phytochemistry,* 1999, **52,** 339.

21 C.-H. Chen, C.-Y. Shaw, C.-C. Chen and Y.-C. Tsai, *J. Nat. Prod*., 2002, **65,** 740.

22 (*a*) S. Ohkawa, K. Fukatsu, S. Miki, T. Hashimoto, J. Sakamoto, T. Dio, Y. Nagai and T. Aono, *J. Med. Chem*., 1997, **40,** 559; (*b*) V. A. Osyanin, D. V. Osipov and Y. N. Klimochkin, *J. Org. Chem*., 2013, **78,** 5505.

23 For the synthesis of arenofurans from nitroalkenes derivatives and phenols/naphthols: (a) D. Kundu, M. Samim, A. Majee and A. Hajra, *Chem. Asian J.* 2011, **6**, 406; (b) Ref 9d.