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Nickel catalyzed intramolecular oxidative coupling: synthesis of 3-aryl benzofurans†

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Recent research has been focused on the transition metal-catalyzed reactions. Herein we have developed nickel-catalyzed synthesis of 3-aryl benzofurans from *ortho*-alkenyl phenols *via* intramolecular dehydrogenative coupling. Notably, simple O_2 gas served as an oxidant, without using any sacrificial hydrogen acceptor. The strategy enabled the synthesis of 3-aryl benzofurans in good to excellent yields.

Introduction

Benzofuran is a heterocyclic compound made up of benzene ring fused with a furan ring and a prominent structural motif that constitutes naturally occurring compounds, pharmaceuticals, photosensitizers and molecules of biological relevance.[1–3] Some of the biologically active compounds containing benzofuran skeleton are fused tricyclic compound (R7000) **I**, furomollugin **II**, amiodarone **III**, Iantheran A **IV**, viniferifuran **V** and pterolinus A **VI** (Fig. 1).[3]

Due to their wide occurrence and interesting biological properties, numerous reports have disclosed the synthesis of benzofurans.[4–22] In this context, most of the reports mainly centered on the synthesis of 2,3-diaryl benzofurans, either *via* intermolecular annulation of *ortho*-halophenols with olefins or *via* intramolecular annulation of *ortho*-vinyl phenols promoted by Lewis acids/oxidants/some strong acids/bases.[5–9] All of them

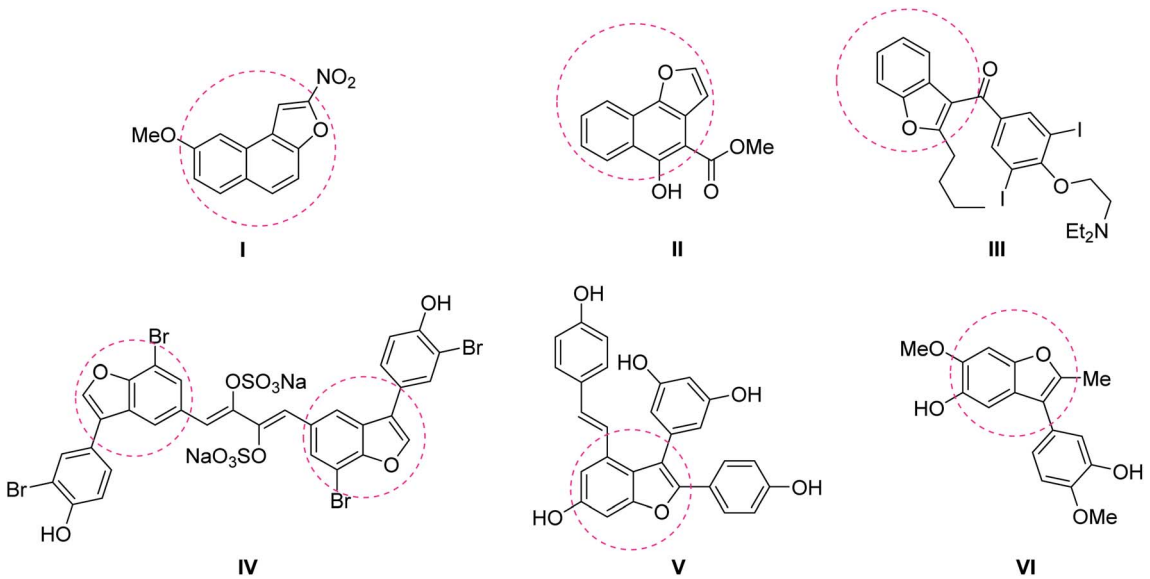

Fig. 1 Representative examples of benzofurans of biological relevance.

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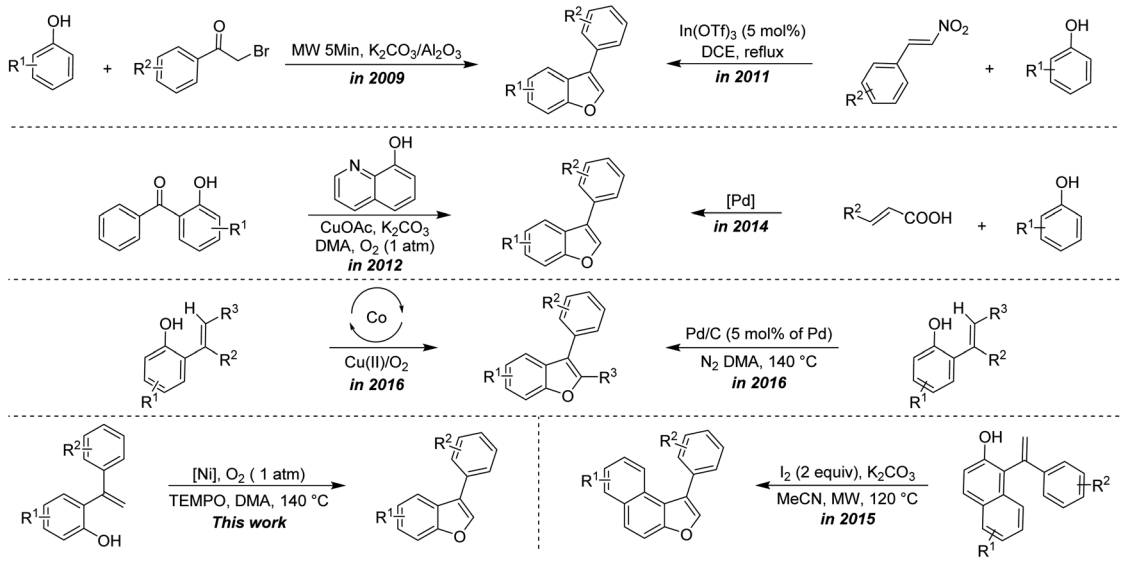


Scheme 1 Representative approaches for the synthesis of 3-aryl benzofurans.[12,14,20a,20b,22a,22b,22d]

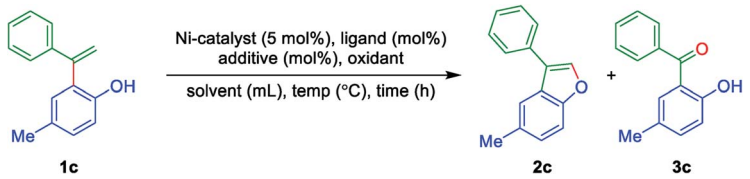
require stoichiometric amounts of acid/oxidant/base. Arcadi *et al.* described a first palladium-catalyzed synthesis of 2,3-diaryl benzofuran *via* intramolecular cyclization of *ortho*-alkynes substituted phenols.[6a] Subsequently, a reasonable number of reports have appeared on the synthesis of 2,3-diarylbenzofurans using transition metal catalysts like Au, Ir, Rh, Cu, Pd and Fe *etc.*[10] The best synthetic route to accomplish benzofuran could be the intramolecular cyclization from *ortho*-alkenyl phenol, unfortunately, this protocol requires a stoichiometric amount of sacrificial hydrogen acceptor-like DDQ.[8b] Notably, recently, the oxidative C–H functionalization of *ortho*-alkenyl phenols to generate benzofurans has been accomplished using some transition metals without the need of any sacrificing hydrogen acceptor.[9,22b,22d] Most of the earlier reports are devoted to the formation of 2,3-diaryl benzofurans/2-aryl benzofurans, whereas the synthesis of 3-aryl benzofurans from *ortho*-alkenyl phenols was scarcely explored.[20,22] Some of the representative examples of the previous study *versus* the present protocol is described in Scheme 1.

We have been interested in the ambitious catalytic nature of late transition metals.[23] Recently, we have developed a synthesis of 2,3-diaryl benzofuran by using phenols and internal alkynes[11a] and also reported a synthesis of 2*H*/4*H*-chromenes from phenols with terminal alkynes (aryl/alkyl) using Lewis acidic conditions.[11b] With this background of phenols and the alkyne chemistry. We intended to develop nickel catalyzed oxidative cross coupling reactions. Herein, we describe an efficient method to cyclize *ortho*-alkenyl phenols to give benzofurans facilitated by $Ni(acac)_2$ and O_2 as an oxidant.

Results and discussion

To begin with, it was contemplated that 3-aryl benzofuran can be achieved from *ortho*-vinyl phenols using intramolecular oxidative coupling feasible by means of a suitable metal catalyst and an oxidant. The required *ortho*-vinyl phenols have prepared from the reaction of phenols and terminal arylacetylenes using Friedel–Crafts alkenylation induced by a suitable Lewis acid. With the available *ortho*-alkenyl phenols, it is set for the optimization study to achieve 3-aryl benzofurans. Thus, initially, *ortho*-alkenyl phenol **1c** was chosen as the model compound for the preparation of 3-aryl benzofuran **2c**. Various screening conditions (*i.e.*, by varying ligand, additive, oxidant, reaction time and solvent *etc.*) have explored to find the best-optimized conditions and the outcomes are summarised in Table 1. To begin with, the reaction was performed with $Ni(acac)_2$ (5 mol%), 1,10-phenanthroline (10 mol%) and DMF as solvent under inert conditions (nitrogen atmosphere) at 140 °C for 48 h. The expected 3-aryl benzofuran **2c** was obtained albeit in moderate yield along with a minor side product (2-hydroxy-5-methylphenyl)(phenyl)methanone **3c** (Table 1, entry 1). Even switching to PPh_3 as the ligand, furnished the product **2c** in more or less same yield (Table 1, entry 2). Interestingly, under the same reaction conditions (*i.e.* Table 1, entry 2), but with molecular O_2 as the oxidant, there was a drastic change in the yield of **2c** along with the minimal amount of ketone **3c** (Table 1, entry 3). However, with additive TEMPO and with PPh_3 under open air at 140 °C for 48 h, improved the yield of **2c** to 80% (Table 1, entry 4). Performing the reaction with TEMPO/PPh_3 and under an oxygen atmosphere, gave the product **2c** in the same yield but with a reduced amount of time 36 h (Table 1, entry 5). On the other hand, the other additives (DDQ, Oxone, $K_2S_2O_8$ and TBHP/H_2O, under oxygen atmosphere) in the same solvent DMF were not active improve the yields of **2c** (Table 1, entries 6 to 9). The reaction was inferior in solvents, such as H_2O and *ortho*-xylene, under oxygen atmosphere (Table 1, entries 10 & 11), while in DMSO under an oxygen atmosphere, gave **2c** in 70% yield (Table 1, entry 12). To our delight, the reaction in solvent DMA under oxygen atmosphere afforded the product **2c** in 81% yield (Table 1, entry 13). When the reaction

Table 1 Screening conditions for the formation of 3-aryl benzofurans **2c** from **1c**[a,e]



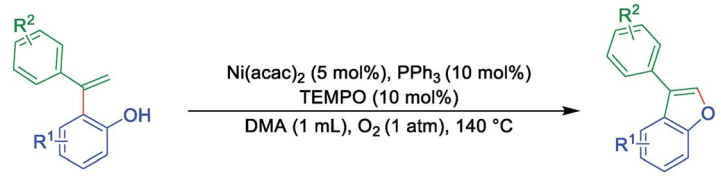
Entry	Catalyst (mol%)	Ligand (10 mol%)	Additives (mol%)	Oxidant	Solvent (mL)	Time (h)	Temp. (°C)	Yield **2c** (%)
1	$Ni(acac)_2$ (5)	1,10-Phen	—	—[b]	DMF (1.5)	48	140	40[c,d]
2	$Ni(acac)_2$ (5)	PPh_3	—	—[b]	DMF (1.5)	36	140	42
3	$Ni(acac)_2$ (5)	PPh_3	—	O_2	DMF (1.5)	36	140	70[d]
4	$Ni(acac)_2$ (5)	PPh_3	TEMPO (10)	Open air	DMF (2)	48	140	80[d]
5	$Ni(acac)_2$ (5)	PPh_3	TEMPO (10)	O_2	DMF (2)	36	140	80[d]
6	$Ni(acac)_2$ (5)	PPh_3	DDQ (10)	O_2	DMF (1.5)	36	140	—[c]
7	$Ni(acac)_2$ (5)	PPh_3	OXONE (10)	O_2	DMF (1.5)	36	140	30[c,d]
8	$Ni(acac)_2$ (5)	PPh_3	$K_2S_2O_8$ (10)	O_2	DMF (1.5)	48	140	34[c,d]
9	$Ni(acac)_2$ (5)	PPh_3	TBHP in H_2O (10)	O_2	DMF (1.5)	48	140	48[c,d]
10	$Ni(acac)_2$ (5)	PPh_3	TEMPO (10)	O_2	H_2O (1)	48	140	—[c]
11	$Ni(acac)_2$ (5)	PPh_3	TEMPO (10)	O_2	*o*-Xylene (1)	36	140	—[c]
12	$Ni(acac)_2$ (5)	PPh_3	TEMPO (10)	O_2	DMSO (1.5)	36	140	70[c]
13	**$Ni(acac)_2$ (5)**	**PPh_3**	**TEMPO (10)**	**O_2**	**DMA (1)**	**36**	**140**	**81[d]**
14	$Ni(acac)_2$ (2)	PPh_3	TEMPO (10)	O_2	DMA (1)	36	140	70[d]
15	$Ni(acac)_2$ (5)	1,10-Phen	TEMPO (10)	Open air	DMA (1)	36	140	64[d]
16	$Ni(acac)_2$ (5)	1,10-Phen	TEMPO (10)	O_2	DMA (1)	40	140	60[d]
17	$Ni(acac)_2$ (5)	—	—	O_2	DMA (1)	40	140	45
18	$Ni(acac)_2$ (5)	—	TEMPO (5)	Open air	CH_3CN (2)	72	140	60[d]
19	$Ni(acac)_2$ (5)	—	DDQ (5)	Open air	CH_3CN (2)	72	140	50[d]
20	$Ni(acac)_2$ (5)	PPh_3	K_2CO_3 (2 equiv.)	Open air	DMA (1)	72	140	—[c]
21	$Ni(acac)_2$ (5)	PPh_3	K_2CO_3 (2 equiv.)	O_2	DMA (1)	72	140	—[c]
22	$NiCl_2$ (5)	PPh_3	TEMPO (10)	O_2	DMA (1)	48	140	50[d,e]
23	$Ni(acac)_2$ (5)	PPh_3	TEMPO (10)	O_2	DMA (1)	36	120	30[c]
24	$Ni(acac)_2$ (5)	PPh_3	TEMPO (10)	O_2	DMA (1)	36	80	—[c]
18	$Ni(acac)_2$ (5)	—	TEMPO (5)	Open air	CH_3CN (2)	72	140	60[d]
19	$Ni(acac)_2$ (5)	—	DDQ (5)	Open air	CH_3CN (2)	72	140	50[d]

[a] All reactions were carried out using *ortho*-alkenyl phenol **1c** (83 mg, 0.4 mmol), $Ni(acac)_2$ [0.008 mmol (2 mol%) to 0.02 mmol (5 mol%)], ligand (0.04 mmol, 10 mol%). [b] Reaction was conducted under nitrogen atmosphere. [c] Very less conversion was observed. [d] The by-product **3c** was formed (up-to 5–20% yields). [e] Some other volatile by-products also formed along with **2c**, which were not isolable.

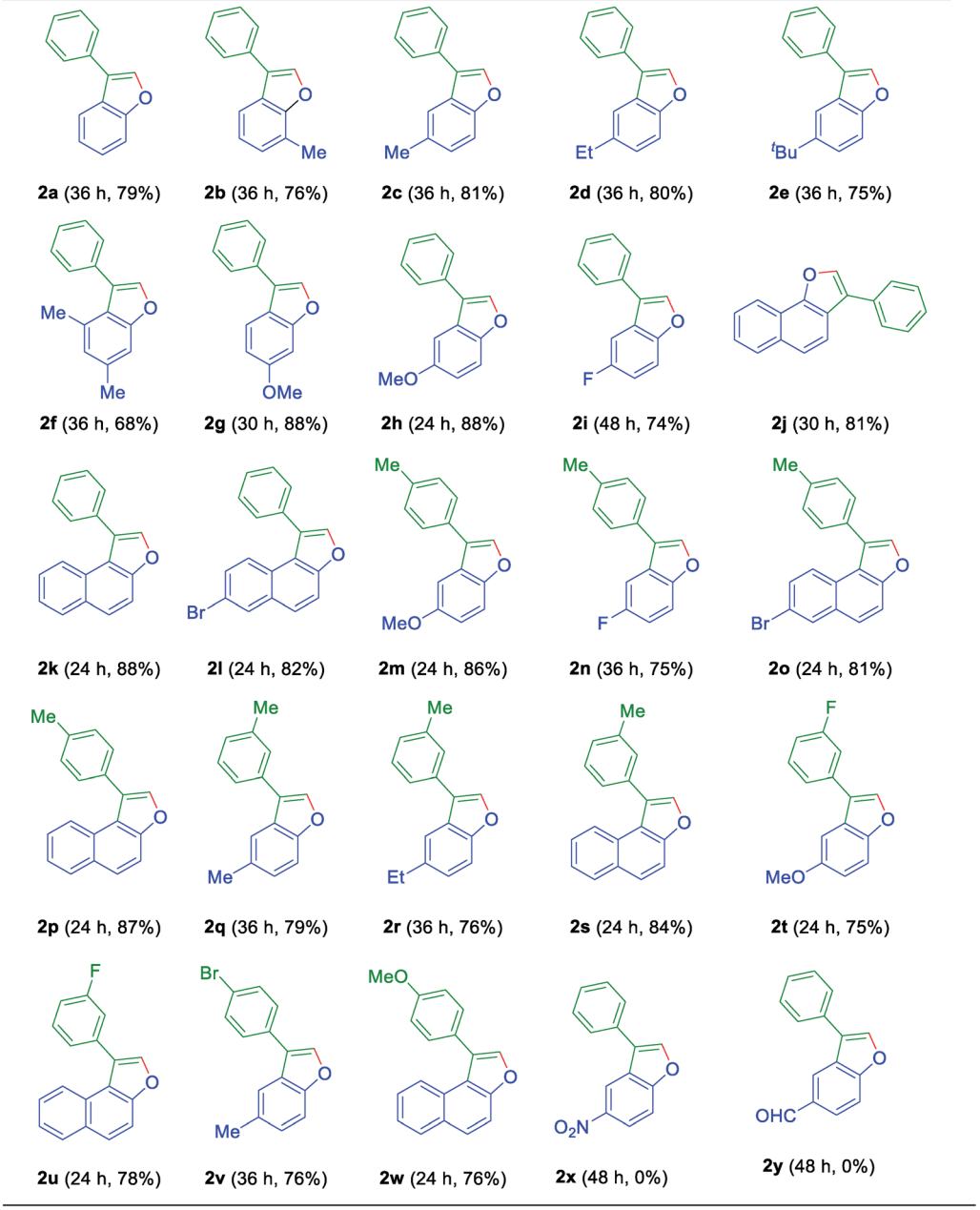
conducted using 2 mol% of the catalyst $Ni(acac)_2$, under an oxygen atmosphere, afforded the product **2c** but with slightly decreased yield (Table 1, entry 14). Replacing the ligand PPh_3 with 1,10-phenanthroline in the open air and an oxygen atmosphere, gave the product **2c** in 64% and 60% yields, respectively (Table 1, entries 15 & 16). The reaction without ligand and additive, under oxygen atmosphere, afforded **2c** in 45% moderate yield (Table 1, entry 17). On the other hand, treatment of **1c** either with TEMPO or DDQ as additive without ligand and in the open air in CH_3CN as a solvent found to be slightly inferior (Table 1, entries 18 & 19). While using K_2CO_3 as the base instead of additive TEMPO, in the open air and in the presence of oxygen atmosphere showed no progress indicating the importance of TEMPO to initiate the reaction (Table 1, entries 20 & 21). On the other hand, by employing $NiCl_2$ as a catalyst, only a 50% yield of the product **2c** was obtained (Table 1, entry 22). Further, the reaction at reduced temperatures 120 °C and 80 °C, showed little conversion and no conversion, respectively (Table 1, entries 23 & 24).

Now to test the scope and applicability of the strategy, best-optimized conditions (Table 1, entry 15) applied to different *ortho*-alkenyl phenols **1a–w**. This protocol was found to be quite successful and afforded the corresponding 3-aryl benzofurans **2a–w**, good to very good yields (Table 2). For example, the reaction was amenable with electron-donating groups like Me, Et, OMe substituents on phenol moiety of *ortho*-alkenyl phenols (Table 2). The reaction also found smooth with the α-naphthol, β-naphthol, and 6-bromo-2-naphthol derived alkenols (Table 2). Moreover, the reaction was obedient with the electron donating (Me and OMe) and the partial electron withdrawing substituents (F and Br) on the ring of terminal alkynes of *ortho*-alkenyl phenols (Table 2). All synthesized 3-aryl benzofurans **2a–w**, are characterized by spectrometric data (^{1}H-NMR and ^{13}C-NMR and Mass Spectrometry) and also with the earlier literature. However, it is essential to note that even alkenylation reaction did not proceed when electron withdrawing groups such as CHO and NO_2 flanked to the phenol moiety. And it can be justified based on the fact that electron withdrawing functional

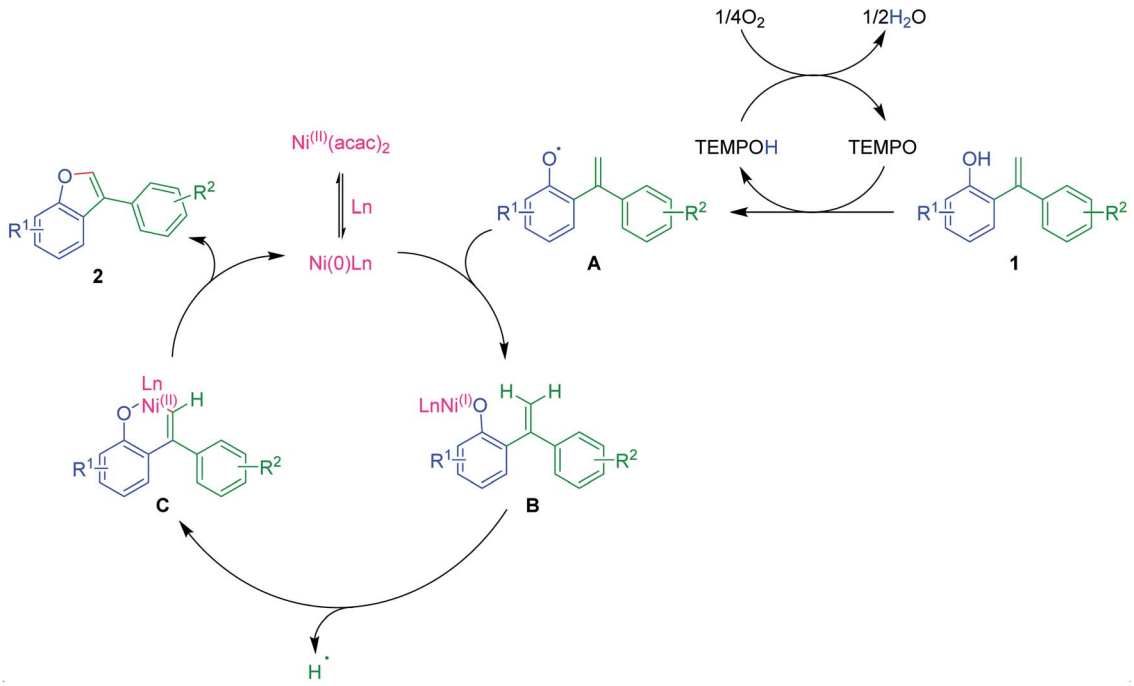
Table 2 Scope for the formation of 3-aryl benzofurans **2a–w**[a,b]



1a-w **2a-w**



[a] Reactions were carried out using *ortho*-alkenyl phenols **1a–w** (79.0–110.0 mg, 0.4 mmol), $Ni(acac)_2$ (5.2 mg, 0.02 mmol, 5 mol%), PPh_3 (10.5 mg, 0.04 mmol, 10 mol%), TEMPO (6.5 mg, 0.04 mmol) at 140 °C under oxygen atmosphere. [b] Yields in the parenthesis are isolated yields of products.



Scheme 2 Plausible mechanism for the formation of 3-aryl benzofurans **2** from **1**.

groups retard the Friedel–Crafts alkylation/alkenylation reactions. Similarly, the attempt made to synthesis *ortho*-alkenyl phenols were not successful with *meta*-amino functionality on the aromatic ring of the alkyne. This could be due to the more reactive nature of the amino group under Lewis acid conditions. Moreover, aliphatic alkynes could not make compatible to give *ortho*-alkenylation products as well.

Plausible mechanism

Though the exact mechanism is not very certain at this stage, based on the present observations and literature reports,[12,20,23] we have attempted to propose a plausible reaction mechanism as depicted in Scheme 2. Initially, Ni(II) could combine with phosphine ligand PPh_3 converted into its reduced Ni(0)-catalyst, which may act as an active catalyst. On the other hand, in an independent path, *ortho*-alkenyl phenol **1** would be transformed into its oxy-radical **A** under probable catalytic oxidative conditions of TEMPO/O_2 system. Now coupling of oxy-radical **A** with Ni(0)-catalyst would lead to the formation of intermediate **B**. Subsequently, intramolecular π-complexation with olefinic double bond followed by olefinic C–H activation could generate a six-membered oxa-nickelacycle **C** *via* the removal of H-radical. Finally, reductive elimination of catalyst from **C** gives 3-aryl benzofuran **2** and regenerates the Ni(0)-catalyst. Thus, completes the catalytic cycle.

Conclusion

In summary, we have established a nickel-catalyzed synthesis of 3-aryl benzofurans *via* intramolecular oxidative cyclization of *ortho*-alkenyl phenols. Notably, simple oxygen served as the sole oxidant and precludes the use of sacrificial hydrogen acceptor. This methodology found viable for accomplishing several different 3-arylbenzofuran derivatives in good to very good yields.

Experimental section

IR spectra recorded on a Bruker Tensor 37 (FT-IR) spectrophotometer. ^{1}H-NMR spectra recorded on Bruker Avance 400 (400 MHz) spectrometer at 295 K in $CDCl_3$; chemical shifts (δ in ppm) and coupling constants (J in Hz) reported in standard fashion with reference to either internal standard tetramethylsilane (TMS) (δ_H = 0.00 ppm) or $CHCl_3$ (δ_H = 7.25 ppm). ^{13}C-NMR spectra recorded on Bruker Avance 400 (100 MHz) spectrometer at RT in $CDCl_3$; chemical shifts (δ in ppm) are reported relative to $CDCl_3$ [δ_C = 77.00 ppm (central line of the triplet)]. In the ^{13}C-NMR, the nature of carbons (C, CH, CH_2 and CH_3) was determined by recording the DEPT-135 spectra, and is given in parentheses and noted as s = singlet (for C), d = doublet (for CH), t = triplet (for CH_2) and q = quartet (for CH_3). In the ^{1}H-NMR, the following abbreviations were used throughout: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet. The assignment of signals confirmed by ^{1}H, ^{13}C CPD and DEPT spectra. High-resolution mass spectra (HR-MS) were recorded on an Agilent 6538 UHD Q-TOF using multi-mode source. Reactions were monitored by TLC on silica gel coated on alumina plate or glass plate using a mixture of petroleum ether and ethyl acetate as eluents. Reactions carried out under oxygen atmosphere.

Materials

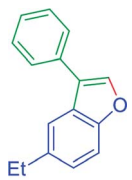
All solvents distilled before using; petroleum ether with a boiling range of 60 to 80 °C, dichloromethane (DCM), ethyl acetate, dry DMA (boiling range 160 to 170 °C; with purity 99%)

were purchased from Sigma Aldrich & locally available commercial sources used. Acme's silica gel (100–200 mesh) used for column chromatography.

GP (general procedure for the synthesis of 3-aryl benzofurans)

To an oven dry Schlenk tube was equipped with a magnetic stir bar, were added $Ni(acac)_2$ (5.2 mg, 0.02 mmol), PPh_3 (10.5 mg, 0.04 mmol), TEMPO (6.3 mg, 0.04 mmol), *ortho*-alkenyl phenols **1a–w** (79–110.0 mg, 0.4 mmol), and DMA (1 mL). Then a balloon filled with O_2 was attached to the Schlenk tube. The reaction mixture stirred at 140 °C for 24 to 36 h. TLC monitored the progress of the reaction. The reaction mixture was then cooled to room temperature and extracted by using ethyl acetate (3 × 20 mL). The organic layers were washed with saturated NH_4Cl solution, dried by Na_2SO_4 and then filtered. Evaporation of the solvent(s) under reduced pressure and refinement of the crude mixture by silica gel column chromatography (petroleum ether/ethyl acetate), gave the 3-aryl benzofurans (68–88%) as semi-solid or liquid.

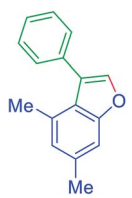
5-Ethyl-3-phenylbenzofuran (2d).



2d

GP was carried out with **1d** (89 mg, 0.4 mmol) using $Ni(acac)_2$ (5.2 mg, 0.02 mmol), PPh_3 (10.5 mg, 0.04 mmol), TEMPO (6.3 mg, 0.04 mmol) and allowed the reaction mixture to stirred at 140 °C for 36 h for the product **2d** formation. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate, 100 to 99 : 01), furnished the product **2d** (71 mg, 80%) as pale yellow viscous liquid. [TLC control (petroleum ether/ethyl acetate 99 : 01), R_f(**1d**) = 0.10, R_f(**2d**) = 0.60, UV detection]. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.77 (s, 1H, Ar–O–CH), 7.70–7.57 (m, 3H, Ar–H), 7.56–7.44 (m, 3H, Ar–H), 7.43–7.28 (m, 1H, Ar–H), 7.27–7.13 (m, 1H, Ar–H), 2.79 (q, 2H, J = 7.6 Hz, Ar–CH_2CH$_3$), 1.31 (t, 3H, J = 7.6 Hz, Ar–CH$_2$$CH_3$) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 154.3 (s, Ar–C), 141.5 (d, Ar–O–CH), 139.2 (s, Ar–C), 132.3 (s, Ar–C), 128.9 (d, 2C, 2 × Ar–CH), 127.5 (d, 2C, 2 × Ar–CH), 127.3 (d, Ar–CH), 126.5 (s, Ar–C), 124.8 (d, Ar–CH), 122.1 (s, Ar–C), 119.0 (d, Ar–CH), 111.4 (d, Ar–CH), 29.01 (t, Ar–CH_2), 16.44 (q, Ar–CH_2–CH_3) ppm. HR-MS (ESI$^+$) m/z calculated for $[C_{16}H_{14}OK]^+ = [M + K]^+$: 261.0676; found 261.0859.

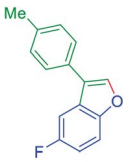
4,6-Dimethyl-3-phenylbenzofuran (2f).



2f

GP was carried out with **1f** (89 mg, 0.4 mmol) using $Ni(acac)_2$ (5.2 mg, 0.02 mmol), PPh_3 (10.5 mg, 0.04 mmol), TEMPO (6.3 mg, 0.04 mmol) and allowed the reaction mixture to stirred at 140 °C for 36 h for the product **2f** formation. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate, 100 to 99 : 01), furnished the product **2f** (60 mg, 68%) as pale yellow viscous liquid. [TLC control (petroleum ether/ethyl acetate 99 : 01), R_f(**1f**) = 0.10, R_f(**2f**) = 0.60, UV detection]. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.47 (s, 1H, Ar–O–CH), 7.46–7.30 (m, 5H, Ar–H), 7.19 (s, 1H, Ar–H), 6.84 (s, 1H, Ar–H), 2.44 (s, 3H, CH_3), 2.21 (s, 3H, CH_3) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 155.9 (s, Ar–C), 141.4 (d, Ar–O–CH), 134.6 (s, Ar–C), 133.1 (s, Ar–C), 131.4 (s, Ar–C), 130.1 (d, 2C, 2 × Ar–CH), 128.0 (s, 2C, Ar–CH), 127.4 (d, Ar–CH), 125.9 (d, Ar–CH), 123.5 (s, Ar–C), 123.2 (s, 1Ar–C), 109.4 (d, Ar–CH), 21.4 (q, CH_3) 19.7 (q, CH_3) ppm. HR-MS (ESI$^+$) m/z calculated for $[C_{16}H_{18}OFN]^+ = [M + NH_4]^+$: 240.1383; found 240.2062.

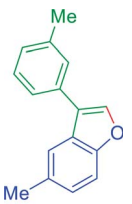
5-Fluoro-3-(*p*-tolyl)benzofuran (2n).



2n

GP was carried out with **1n** (90 mg, 0.4 mmol) using $Ni(acac)_2$ (5.2 mg, 0.02 mmol), PPh_3 (10.5 mg, 0.04 mmol), TEMPO (6.3 mg, 0.04 mmol) and allowed the reaction mixture to stirred at 140 °C for 36 h for the product **2n** formation. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate, 100 to 99 : 01), furnished the product **2n** (68 mg, 75%) as pale yellow viscous liquid. [TLC control (petroleum ether/ethyl acetate 99 : 01), R_f(**1n**) = 0.10, R_f(**2n**) = 0.60, UV detection]. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.78 (s, 1H, Ar–O–CH), 7.54–7.41 (m, 4H, Ar–H), 7.28 (d, 2H, J = 7.8 Hz, Ar–H), 7.05 (td, 1H, J = 9.1, 2.45 Hz, Ar–H), 2.41 (s, 3H, Ar–CH_3) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 160.6 (s, Ar–C), 158.3 (s, Ar–C), 152.0 (s, Ar–C), 142.7 (d, Ar–O–CH), 137.5 (s, Ar–C), 129.8 (d, 2C, 2 × Ar–CH), 128.5 (s, Ar–C), 127.5 (s, Ar–C), 127.4 (s, Ar–C) 127.2 (d, 2C, 2 × Ar–CH), 122.5 (s, Ar–C), 122.4 (s, Ar–C), 112.4 (d, Ar–CH), 112.3 (d, Ar–CH), 112.1 (d, Ar–CH), 106.2 (d, Ar–CH), 105.9 (d, Ar–CH), 21.23 (q, Ar–CH_3) ppm. HR-MS (ESI$^+$) m/z calculated for $[C_{15}H_{10}F]^+ = [(M + H) + (-H_2O)]^+$: 209.0761; found 209.0765.

5-Methyl-3-(*m*-tolyl)benzofuran (2q).

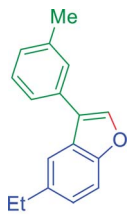


2q

GP was carried out with **1q** (89 mg, 0.4 mmol) using $Ni(acac)_2$ (5.2 mg, 0.02 mmol), PPh_3 (10.5 mg, 0.04 mmol), TEMPO (6.3 mg, 0.04 mmol) and allowed the reaction mixture to stirred at 140 °C for 36 h for the product **2q** formation. Purification of

the crude material by silica gel column chromatography (petroleum ether/ethyl acetate, 100 to 99 : 01), furnished the product **2q** (70 mg, 79%) as pale yellow viscous liquid. [TLC control (petroleum ether/ethyl acetate 99 : 01), R_f(**1q**) = 0.10, R_f(**2q**) = 0.60, UV detection]. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.73 (s, 1H Ar–O–CH), 7.61 (s, 1H, Ar–H), 7.47–7.33 (m, 4H, Ar–H), 7.23–7.08 (m, 2H, Ar–H), 2.47 (s, 3H, Ar–CH_3), 2.44 (s, 3H, Ar–CH_3) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 154.2 (s, Ar–C), 141.4 (d, Ar–O–CH), 138.6 (s, Ar–C), 132.4 (s, Ar–C), 132.1 (s, Ar–C), 128.8 (d, Ar–CH), 128.2 (d, Ar–CH), 128.1 (d, Ar–CH), 126.6 (s, Ar–C), 125.7 (d, Ar–CH), 124.6 (d, Ar–CH), 122.0 (s, Ar–C), 120.2 (d, Ar–CH), 111.2 (d, Ar–CH), 21.5 (q, Ar–CH_3), 21.5 (q, Ar–CH_3) ppm. HR-MS (ESI$^+$) *m*/*z* calculated for $[C_{16}H_{18}NO]^+ = [M + NH_4]^+$: 240.1383; found 240.1373.

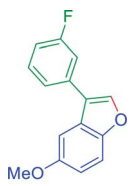
5-Ethyl-3-(*m*-tolyl)benzofuran (2r).



2r

GP was carried out with **1r** (94 mg, 0.4 mmol) using Ni(acac)$_2$ (5.2 mg, 0.02 mmol), PPh_3 (10.5 mg, 0.04 mmol), TEMPO (6.3 mg, 0.04 mmol) and allowed the reaction mixture to stirred at 140 °C for 36 h for the product **2r** formation. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate, 100 to 99 : 01), furnished the product **2r** (71 mg, 76%) as pale yellow viscous liquid. [TLC control (petroleum ether/ethyl acetate 99 : 01), R_f(**1r**) = 0.10, R_f(**2r**) = 0.60, UV detection]. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.74 (s, 1H, Ar–O–CH), 7.62 (d, 1H, J = 0.1 Hz, Ar–H), 7.51–7.41 (m, 3H, Ar–H), 7.39–7.33 (m, 1H, Ar–H), 7.21–7.15 (m, 2H, Ar–H), 2.77 (q, 2H, J = 7.3 Hz, Ar–CH_2CH$_3$), 2.44 (s, 3H, CH_3), 1.28 (t, 3H, J = 7.6 Hz, Ar–CH$_2$$CH_3$) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 154.3 (s, Ar–C), 141.5 (d, Ar–O–CH), 139.1 (s, Ar–C), 138.6 (s, Ar–C), 132.2 (s, Ar–C), 128.8 (d, Ar–CH), 128.2 (d, Ar–CH), 128.2 (d, Ar–CH), 126.6 (s, Ar–C), 124.7 (d, Ar–CH), 124.6 (d, Ar–CH), 122.2 (s, Ar–C), 119.0 (d, Ar–C), 111.3 (d, Ar–C), 29.0 (t, CH_2), 21.5 (q, CH_3), 16.5 (q, CH_3) ppm. HR-MS (ESI$^+$) *m*/*z* calculated for $[C_{17}H_{19}NO]^+ = [M + NH_4]^+$: 253.1461; found: 254.2219.

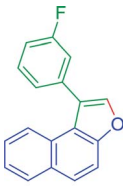
3-(3-Fluorophenyl)-5-methoxybenzofuran (2t).



2t

GP was carried out with **1t** (98 mg, 0.4 mmol) using Ni(acac)$_2$ (5.2 mg, 0.02 mmol), PPh_3 (10.5 mg, 0.04 mmol), TEMPO (6.3 mg, 0.04 mmol) and allowed the reaction mixture to stirred at 140 °C for 24 h for the product **2t** formation. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate, 100 to 99 : 01), furnished the product **2t** (74 mg, 75%) as pale yellow viscous liquid. [TLC control (petroleum ether/ethyl acetate 99 : 01), R_f(**1t**) = 0.10, R_f(**2t**) = 0.60, UV detection]. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.77 (s, 1H, Ar–O–CH), 7.49–7.43 (m, 2H, Ar–H), 7.41 (dd, J = 3.4, 1.9 Hz, 1H, Ar–H), 7.32 (ddd, J = 9.8, 2.4, 1.6 Hz, 1H, Ar–H), 7.24 (d, J = 2.6 Hz, 1H, Ar–H), 7.11–7.03 (m, 1H, Ar–H), 6.98 (dd, J = 8.9, 2.6 Hz, 1H, Ar–H), 3.88 (s, 3H, OCH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ = 163.2 (d, J_{c-f} = 294 Hz, Ar–CF), 156.38 (s, Ar–C), 150.76 (s, Ar–C), 142.57 (d, Ar–CH), 134.3 (d, J_{c-f} = 8 Hz, Ar–C), 130.5 (d, J_{c-f} = 9 Hz, Ar–CH), 126.57 (s, Ar–C), 123.02 (d, J_{c-f} = 2 Hz, Ar–CH), 121.4 (s, Ar–C), 114.2 (d, J_{c-f} = 21 Hz, Ar–CH), 114.2 (d, J_{c-f} = 21 Hz, Ar–CH), 113.50 (d, Ar–CH), 112.31 (d, Ar–CH), 102.65 (d, Ar–CH), 56.03 (q, OCH_3) ppm. HR-MS (ESI$^+$) *m*/*z* calculated for $[C_{15}H_{13}FKO_3]^+ = [(M + K) + (-H_2O)]^+$: 263.0269; found 263.0273.

1-(3-Fluorophenyl)naphtho[2,1-*b*]furan (2u).



2u

GP was carried out with **1u** (105 mg, 0.4 mmol) using Ni(acac)$_2$ (5.2 mg, 0.02 mmol), PPh_3 (10.5 mg, 0.04 mmol), TEMPO (6.3 mg, 0.04 mmol) and allowed the reaction mixture to stirred at 140 °C for 24 h for the product **2u** formation. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate, 100 to 99 : 01), furnished the product **2u** (82 mg, 88%) as pale yellow viscous liquid. [TLC control (petroleum ether/ethyl acetate 99 : 01), R_f(**1u**) = 0.10, R_f(**2u**) = 0.60, UV detection]. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.86 (d, J = 8.2 Hz, 1H, Ar–H), 7.80 (d, J = 8.0 Hz, 1H, Ar–H), 7.63 (d, J = 9.0 Hz, 1H, Ar–H), 7.55 (d, J = 9.8 Hz, 2H, Ar–H), 7.37–7.29 (m, 2H, Ar–H), 7.25 (t, J = 7.5 Hz, 2H, Ar–H), 7.18 (d, J = 9.6 Hz, 1H, Ar–H), 7.09–6.98 (m, 1H, Ar–H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ = 162.8 (d, J_{c-f} = 245 Hz, Ar–C), 153.2 (s, Ar–C), 141.8 (d, Ar–CH), 135.3 (d, J_{c-f} = 8 Hz, Ar–C), 130.8 (s, Ar–C), 130.0 (d, J_{c-f} = 9 Hz, Ar–CH), 129.0 (d, Ar–CH), 128.1 (s, Ar–C), 126.1 (d, J_{c-f} = 5 Hz, Ar–CH), 125.6 (d, J_{c-f} = 3 Hz, Ar–CH), 124.5 (d, Ar–CH), 123.3 (d, J_{c-f} = 2 Hz, Ar–C), 123.2 (d, Ar–CH), 120.3 (s, Ar–C), 116.8 (d, J_{c-f} = 22 Hz, Ar–CH), 114.8 (d, J_{c-f} = 21 Hz, Ar–CH), 112.6 (d, Ar–CH) ppm. HR-MS (ESI$^+$) *m*/*z* calculated for $[C_{18}H_{12}FO]^+ = [M + H]^+$: 263.0867; found 263.0862.

Conflicts of interest

There are no conflicts of interest to declare.

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