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# Cycloalkenyl nonaflates as electrophilic cross-coupling substrates for palladium catalyzed C–N bond forming reactions with enolizable heterocycles under microwave enhanced conditions†

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Microwave-mediated, palladium catalyzed C–N bond forming reactions with activated cycloalkenyl nonaflates and enolizable heterocycles using cesium carbonate as a base and a catalytic system employing $Pd(OAc)_2$/Xantphos or $Pd(OAc)_2$/dppp were found to be effective in driving the reactions to completion. This method resulted in good to excellent yields of the coupled products (22 examples, 25–90%) in short reaction time (30–60 min). Under optimum conditions, cycloalkenyl nonaflates were found to be an effective alternative to analogous triflates in C–N bond forming processes due to their increased stability under the reaction conditions. The use of tetrabutylammonium bromide ($Bu_4NBr$) as an additive in these transformations proved to be effective and resulted in better yields of the coupled products.

## Introduction

The palladium catalyzed amination of aryl, vinyl, heteroaryl halides and pseudo halides has become a common method in the field of organic synthesis.[1] Recently, the use of arenediazonium salts as electrophilic cross-coupling partners in various palladium mediated cross-couplings has been explored by various researchers.[1b] Also research on palladium(II) catalyzed oxidative amination[1e-j] with olefins is gaining tremendous potential in recent years. Guosheng Liu *et al.* reported a highly efficient protocol for palladium-catalyzed intermolecular aerobic oxidative amination of terminal alkenes for the synthesis of allylamine derivatives. All these protocols have gained much importance in the synthesis and functionalization of heterocyclic analogues. As a part of our research program we were interested in the direct amination reactions of cycloalkenyl nonaflates with enolizable heterocycles.

The use of perfluoroalkene sulfonates as electrophilic cross-coupling substrates in Buchwald–Hartwig cross-coupling reaction has also been explored and studied in detail by various researchers.[2,3] Among these perfluoroalkene sulfonates triflates[4] ($CF_3SO_2O^-$) are the most popular derivatives and have been studied in countless applications. While aryl and alkenyl triflates were found to be suitable cross-coupling substrates in many palladium catalyzed cross-coupling reactions,[5] base promoted nucleophilic cleavage of the triflate moiety can occur with competitive rates lowering the yields of the coupled product. Many improved conditions were explored through the use of weaker bases or by the slow addition of the triflate; however, this protocol is not always successful or practical. An effective alternative to aryl/alkenyl triflates are aryl/alkenyl nonaflates,[6] which can be prepared from the corresponding alcohols or ketones.[7,8] Nonaflates are stable to chromatography[9,10] and can be stored at room temperature.[9] Nonaflates as electrophiles have been shown to have reactivity similar to triflates in metal catalyzed cross-coupling reactions (Suzuki–Miyuara,[11] Negishi[12] and Heck[13]) and are less prone to hydrolysis.[14] Buchwald *et al.* have done extensive optimization studies of palladium-catalyzed amination of aryl nonaflates.[15] Many useful applications of nonaflates (nonafluorobutane sulfonates, $NfO^-$), which are the $C_4$ homologues[16] of triflates have been published emphasizing their tremendous synthetic advantages.[17,18] From a synthetic point of view the transformation of a carbonyl function into an alkenyl sulfonate is of great interest since these intermediates are very

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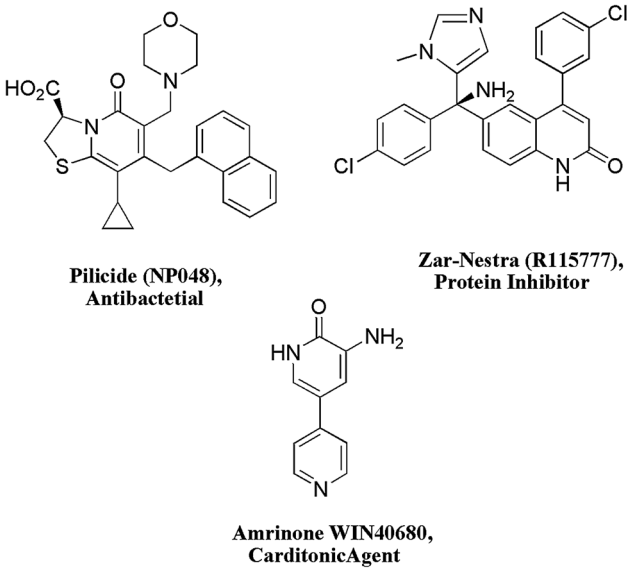



Fig. 1 Pharmacologically relevant pyridones.

frequently employed in metal-catalyzed reactions.[19,20] Although alkenyl bromides[20] and iodides[20b] are commonly used in metal-promoted reactions they are not always easily available. The introduction of halogen substituents can however be tedious and unselective during a complex synthetic process. The conversion of a carbonyl compound into an alkenyl sulfonate, however, can be achieved with fairly simple and highly selective methods.[21–23]

The presence of substituted pyrid-2-ones in biologically relevant analogues (Fig. 1) has attracted synthetic organic chemists and hence an efficient protocol to access these compounds is of high relevance. The presence of these N-alkylated heterocycles in both natural products and pharmacologically relevant molecules renders them as useful synthons in the field of medicinal chemistry. Moreover, enolizable heterocycles,[24] such as 2-hydroxypyridine,[24c] 4-hydroxypyrimidine, 2-hydroxybenzimidazole, 3-hydroxypyridazine *etc.* have provoked great interest in biological and chemical fields as a result of their ability to serve as models for hydrogen bonding[25] tautomerization,[25] and proton shuttling[25] in both chemical and biological processes. These data stimulated our studies on the synthesis of 2,3 substituted cycloalkenes[20a,b,24c] which can be useful synthons in the field of medicinal chemistry during the lead optimization processes. Herein, we report highly efficient protocol for palladium catalysed cross-coupling reactions of cycloalkenyl nonaflates with enolizable heterocycles. Fig. 2 shows the synthetic utility of the central core moiety which allows a diversity oriented synthesis of novel analogues based on this core moiety.

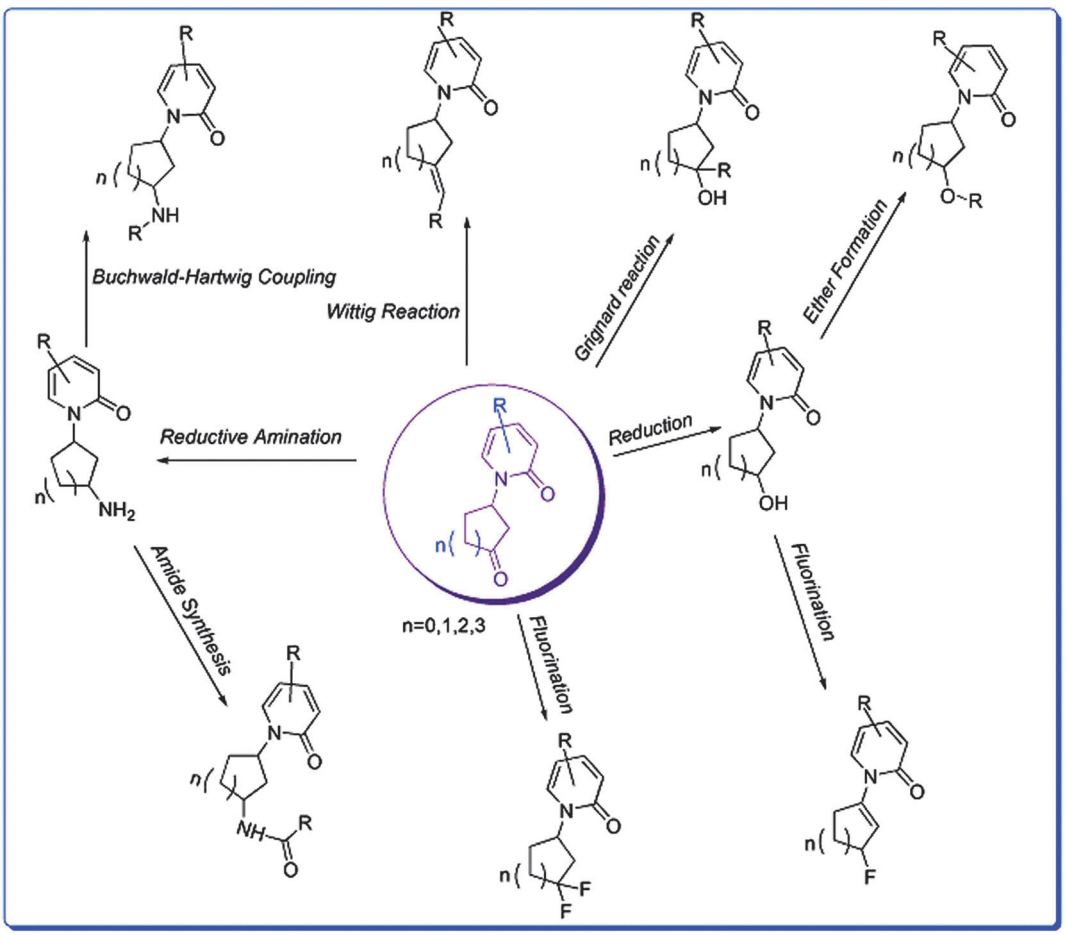



Fig. 2 Synthetic utility of the core moiety.

## Results and discussion

The synthesis of the electrophilic cross-coupling partners (**2a**, **2b**, **3a** and **3b**) employed for the Buchwald–Hartwig coupling reaction were accomplished according to the conditions shown in Fig. 3. Mariano *et al.* reported a general approach for the synthesis of 1-substituted-vinyl-2-pyridones *via* a nucleophilic displacement of cycloalkenyl chlorides with 2-hydroxy pyridine.[24c] Based on these results we were interested in exploring the use of other electrophilic substrates for palladium mediated cross-coupling reactions. Our initial attempts to cross-couple cycloalkenyl triflate **2a** and **2b** with pyridone **4a** using various palladium catalyst and ligand combinations as described in Table 1 under microwave conditions did not yield any product. Different bases ($Cs_2CO_3$, $K_2CO_3$, $Na_2CO_3$, NaO*t*Bu *etc.*) were explored to optimize the reaction condition of **2a** with **4a**. None of the conditions gave any promising results. The cycloalkenyl triflate being an activated triflate was more prone to decomposition under the chosen conditions. The use of soluble organic bases like DBU and DABCO did not lead to any product formation (Table 2). The sluggish reactivity of triflates under these conditions may be due to the enhanced rate of triflate cleavage which competes with the cross-coupling reaction. The use of coordinating solvents such as THF and DMF were also not found to be successful. However, in the presence of $Bu_4NBr$[1j] as additive in these reactions resulted in product formation, though the yields were not promising (Table 1).

Failure of the aforementioned conditions led us to pursue a more robust and stable electrophilic cross-coupling substrate. Our subsequent efforts were to use cycloalkenyl nonaflates as the coupling partner as they are found to be much more stable than the corresponding triflate. To our delight, the coupling of **3a** with **4a** using the catalyst system comprised of $(Pd_2(OAc)_2)$/Xantphos[25,26] and $Cs_2CO_3$ in 1,4-dioxane yielded 50% of product (Table 3) under microwave assisted conditions. From the above results we observed that the use of nonaflates (**3a**, **3b**) resulted in the formation of coupled products in reasonable yields when compared to triflates. Conventional heating conditions were also tried to access these compounds. We found that longer reaction times were required for driving the reactions to completion and the yields were not promising. On the basis of these observations, we speculate that exposing the electrophilic cross-coupling substrate for a onger period of time under heating conditions resulted in its decomposition. Under microwave condition the yields were better which indicates that the rate of this reaction is much faster compared to conventional heating. The development of efficient phosphine ligands[25,29c] (Fig. 5) for Buchwald–Hartwig amination[26,27] reaction provided a

Table 1 Effect of catalyst on cross-coupling of **2a** with **4a**

| Entry | Catalytic system | Yield[a,b] (%) |
|---|---|---|
| 1 | $Pd_2(dba)_3/PPh_3$ | 0 |
| 2 | $Pd_2(OAc)_2$/X-phos | 0 |
| 3 | $Pd_2(dba)_3$/BINAP | Traces |
| 4 | $Pd_2(OAc)_2$/Xantphos | 25 |
| 5 | $Pd_2(OAc)_2$/dppp | 25 |

[a] Method A: Pd catalyst (0.04 equiv.), ligand (0.08 equiv.), $Cs_2CO_3$ (3 equiv.), $Bu_4NBr$ (1.5 equiv.), **2a** (1 equiv.), **4a** (1.2 equiv.), microwave, 120 °C, 30–60 min, 1,4-dioxane (10 vol). [b] Isolated yields.

Table 2 Effect of base on cross-coupling of **2a** with **4a**

| Entry | Base (3 equiv.) | Yield[a,b] (%) |
|---|---|---|
| 1 | $Na_2CO_3$ | 0 |
| 2 | NaO*t*Bu | 0 |
| 3 | $K_2CO_3$ | 0 |
| 4 | CsOAc | 15 |
| 5 | $Cs_2CO_3$ | 25 |
| 6 | DBU | 20 |
| 7 | DABCO | 25 |

[a] Method A: $Pd_2(OAc)_2$ (0.04 equiv.), Xantphos (0.08 equiv.), $Cs_2CO_3$ (3 equiv.), $Bu_4NBr$ (1.5 equiv.), **2a** (1 equiv.), **4a** (1.2 equiv.), microwave, 120 °C, 30–60 min, 1,4-dioxane (10 vol). [b] Isolated yields.

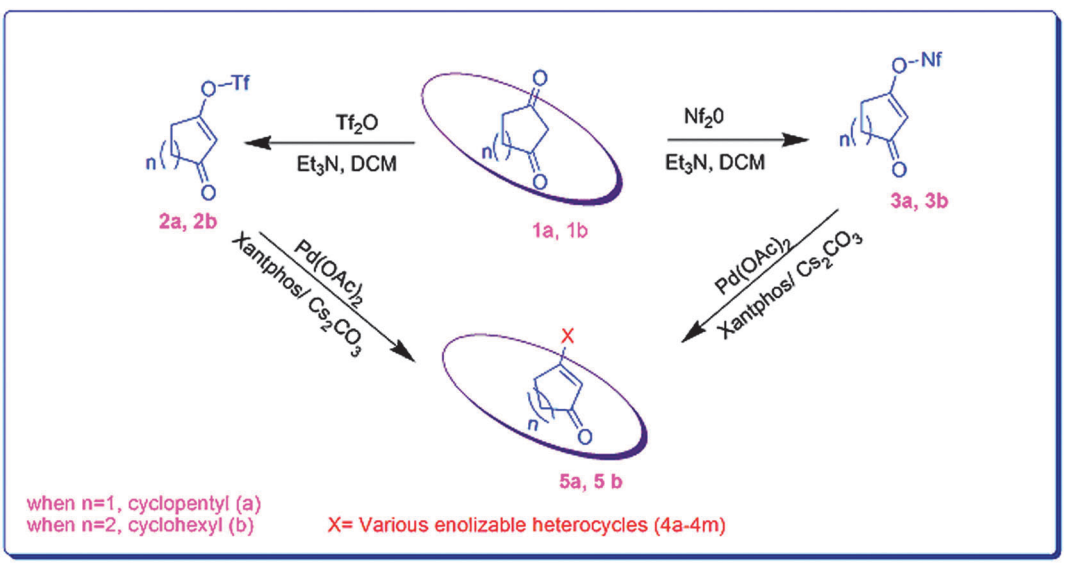



Fig. 3 Synthetic route for N-substituted pyridone.

Table 3 Effect of catalyst on cross-coupling of **3a** with **4a**

| Entry | Catalytic system | Yield[c] (%) |
|---|---|---|
| 1 | $Pd_2(dba)_3/PPh_3$ | 0[b] |
| 2 | $Pd_2(OAc)_2$/X-phos | 15[b] |
| 3 | $Pd_2(dba)_3$/BINAP | 25[b] |
| 4 | $Pd_2(OAc)_2$/Xantphos | 50[b] |
| 5 | $Pd(OAc)_2$/dppp | 55[b] |
| 6 | $Pd_2(OAc)_2$/Xantphos/$Bu_4NBr$ | 80[a] |
| 7 | $Pd(OAc)_2$/dppp/$Bu_4NBr$ | 90[a] |

[a] Method A: catalyst (0.04 equiv.), ligand (0.08 equiv.), $Cs_2CO_3$ (3 equiv.), $Bu_4NBr$ (1.5 equiv.), **3a** (1 equiv.), **4a** (1.2 equiv.), microwave, 120 °C, 30–60 min, 1,4-dioxane (10 vol). [b] Method C: catalyst (0.04 equiv.), ligand (0.08 equiv.), $Cs_2CO_3$ (3 equiv.), **3a** (1 equiv.), **4a** (1.2 equiv.), microwave, 120 °C, 30–60 min, 1,4-dioxane (10 vol). [c] Isolated yields.

reliable extension in using triflates or nonaflates as effective electrophilic cross-coupling substrates. The use of these ligands in these types of reactions typically produces the coupled products at higher rates and better yields than the first generation of catalysts.[15b,28] In this work we also found that the use of chelating diphosphines (dppp and Xantphos) results in better conversions of the coupled products. It is worth emphasizing that the efficiency of the coupling reactions of **2a**, **2b**, **3a** and **3b** with enolizable heterocycles improved drastically by the use of $Bu_4NBr$ as an additive (Table 3).

Various inorganic bases were explored to find an optimum base that would improve the coupling yield of **3a** with **4a**. Cesium acetate and cesium carbonate were found to be very effective for these transformations. The unique effect of cesium salts in palladium catalyzed cross-coupling reactions arise from

Table 4 Effect of bases on cross-coupling of **3a** with **4a**

| Entry | Base | Yield[c] (%) |
|---|---|---|
| 1 | $Na_2CO_3$ | 0 |
| 2 | NaO*t*Bu | 0 |
| 3 | CsOAc | 55 |
| 4 | $K_3PO_4$ | 30 |
| 5 | DBU | 30 |
| 6 | DABCO | 35 |
| 7 | $Cs_2CO_3$ | 55[b] |
| 8 | $Cs_2CO_3$ | 90[a] |

[a] Method A: $Pd_2(OAc)_2$ (0.04 equiv.), Xantphos (0.08 equiv.), $Cs_2CO_3$ (3 equiv.), $Bu_4NBr$ (1.5 equiv.), **3a** (1 equiv.), **4a** (1.2 equiv.), microwave, 120 °C, 30–60 min, 1,4-dioxane (10 vol). [b] Method C: $Pd_2(OAc)_2$ (0.04 equiv.), Xantphos (0.08 equiv.), $Cs_2CO_3$ (3 equiv.), **3a** (1 equiv.), **4a** (1.2 equiv.), microwave, 120 °C, 30–60 min, 1,4-dioxane (10 vol). [c] Isolated yields.

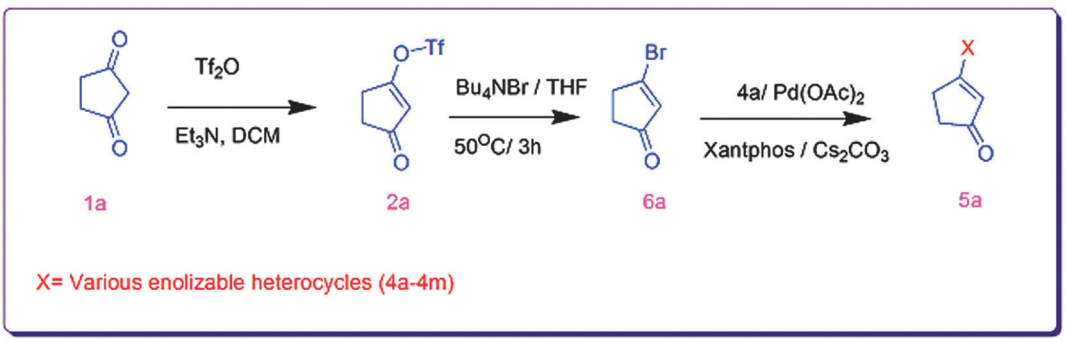



Fig. 4 Synthetic route for N-substituted pyridine using bromo intermediate.

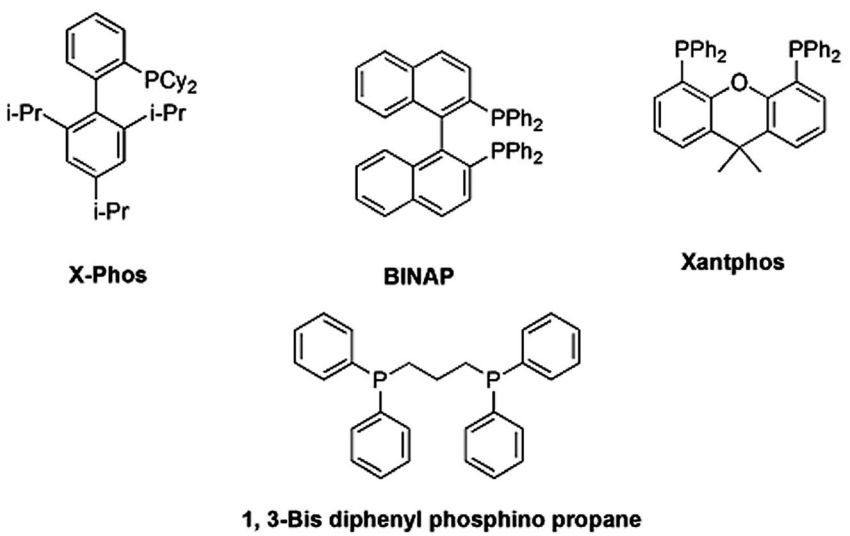



Fig. 5 Ligands used during optimization.

the special properties of cesium cation like very large ionic radius, low charge density and high polarizability. The use of bases like NaO*t*Bu and KO*t*Bu did not lead to any product formation. Organic bases like DBU and DABCO were also explored (Table 4, entry 5 and 6). A series of solvents were also explored to enhance the cross-coupling process as shown in Table 5. Applying these optimized reaction conditions to a series of differentially substituted 2-hydroxypyridines, allowed the rapid synthesis of a variety of N-alkylated pyridones[28,29] in excellent yields (Table 7). For substrates bearing electron-withdrawing groups (**5b**, **5f**, **5g** and **5p**), longer reaction times (1 h compared to 45 min) were required and low yields of the coupled products were obtained. The electron withdrawing groups on pyridone reduces the nucleophilicity of the nitrogen thereby making the reactions very sluggish. To extend the scope of this methodology, we screened a variety of heterocycles containing more than one nitrogen atom (**4h**, **4j**, **4k** and **4m**). Our initial attempts to cross couple 2-hydroxy benzimidazole led to the formation of bis coupled products (**5h** and **5q**). The mono N-alkylated product was obtained in reasonable yields by employing higher equivalents of 2-hydroxy benzimidazole (**5i** and **5r**). The reaction of phthalimide also yielded the coupled product in excellent yields (**5j**). The formation of the products under these optimised conditions was confirmed by $^{1}$H NMR, IR, LCMS and $^{13}$C NMR spectrum analysis. The structural assignment was supported by IR and NMR spectroscopy. The final coupled product shows characteristic IR absorption bands of pyridone at 1670 and 1619 cm$^{-1}$.

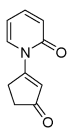
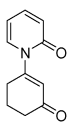
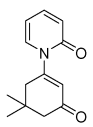
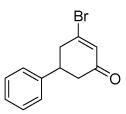
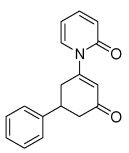
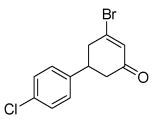
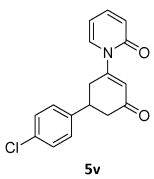
Table 5 Effect of solvents on cross-coupling of **3a** with **4a**

| Entry | Solvent | Yield[a,b] (%) |
|---|---|---|
| 1 | Toluene | 65 |
| 2 | NMP | NR |
| 3 | DMF | Traces |
| 4 | THF | NR |
| 5 | 1,4-Dioxane | 90 |

[a] Method A: $Pd_2(OAc)_2$ (0.04 equiv.), Xantphos (0.08 equiv.), $Cs_2CO_3$ (3 equiv.), $Bu_4NBr$ (1.5 equiv.), **3a** (1 equiv.), **4a** (1.2 equiv.), microwave, 120 °C, 30–60 min, solvents (10 vol). [b] Isolated yields.

During the study we observed that $Bu_4NBr$ is required as an additive for improving the yields of the coupling reaction. Based on the above observation, we tried to figure out the effectiveness of the corresponding cycloalkenyl bromides (**6**), (Fig. 4) for these transformations. Unfortunately, the yields of the coupled products were not promising (Table 6). We speculate that this might be due to the prolonged exposure of

Table 6 Cross-coupling of **6** with **4c**

| Entry | SM1 (6) | SM2 (4) | Catalytic system | Product | Yield[a,b] (%) |
|---|---|---|---|---|---|
| 1 |  **6a** |  **4c** | $Pd_2(OAc)_2$/Xantphos |  **5c** | 30 |
| 2 |  **6b** |  **4c** | $Pd_2(OAc)_2$/Xantphos |  **5m** | 28 |
| 3 |  **6c** |  **4c** | $Pd_2(OAc)_2$/Xantphos |  **5t** | 48 |
| 4 |  **6d** |  **4c** | $Pd_2(OAc)_2$/Xantphos |  **5u** | 30 |
| 5 |  **6e** |  **4c** | $Pd_2(OAc)_2$/Xantphos |  **5v** | 35 |

[a] Method C: catalyst (0.04 equiv.), ligand (0.08 equiv.), $Cs_2CO_3$ (3 equiv.), **6** (1 equiv.), **4a** (1.2 equiv.), microwave, 120 °C, 30–60 min, 1,4-dioxane (10 vol). [b] Isolated yields.

Table 7 Cross-coupling of **3** with pyridones **4a–4m**

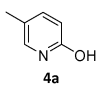
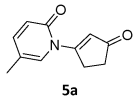
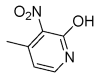
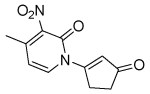
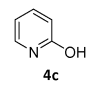
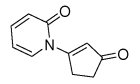
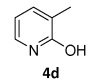
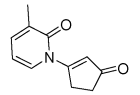
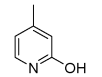
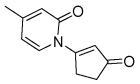
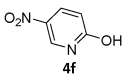
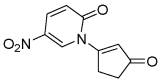
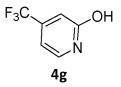
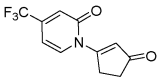
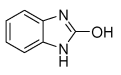
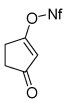
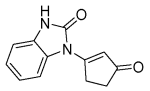
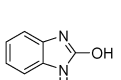
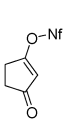
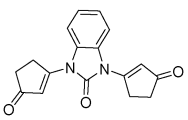
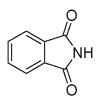
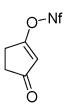
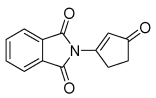
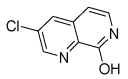
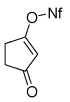
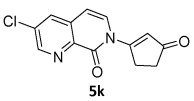
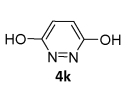
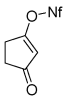
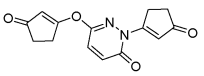
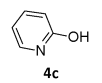
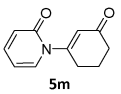
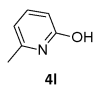
| Entry | SM1 | SM2 (3) | Product | Yield 5[b] (%) |
|---|---|---|---|---|
| 1 |  4a |  |  5a | 90[a] |
| 2 |  4b |  |  5b | 78[c] |
| 3 |  4c |  |  5c | 80[a] |
| 4 |  4d |  |  5d | 82[a] |
| 5 |  4e |  |  5e | 83[a] |
| 6 |  4f |  |  5f | 25[c] |
| 7 |  4g |  |  5g | 34[c] |
| 8 |  4h |  |  5h | 68[a] |
| 9 |  4h |  |  5i | 88[a] |
| 10 |  4i |  |  5j | 72[a] |
| 11 |  4j |  |  5k | 82[c] |
| 12 |  4k |  |  5l | 55[c] |
| 13 |  4c |  |  5m | 85[a] |
| 14 |  4l |  |  5n | 83[a] |

Table 7 (*continued*)

| Entry | SM1 | SM2 (3) | Product | Yield 5[b] (%) |
|---|---|---|---|---|
| 15 |  4a |  |  5o | 78[a] |
| 16 |  4f |  |  5p | 32[c] |
| 17 |  4h |  |  5q | 58[c] |
| 18 |  4h |  |  5r | 78[c] |
| 19 |  4m |  |  5s | 82[c] |
| 20 |  4c |  |  5t | 90[c] |
| 21 |  4c |  |  5u | 88[c] |
| 22 |  4c |  |  5v | 86[c] |

[a] Method A: $Pd_2(OAc)_2$ (0.04 equiv.), Xantphos (0.08 equiv.), $Cs_2CO_3$ (3 equiv.), $Bu_4NBr$ (1.5 equiv.), **3** (1 equiv.), **4** (1.2 equiv.), microwave, 120 °C, 30–60 min, 1,4-dioxane (10 vol). [b] Isolated yields. [c] Method C: $Pd_2(OAc)_2$ (0.04 equiv.), dppp (0.08 equiv.), $Cs_2CO_3$ (3 equiv.), $Bu_4NBr$ (1.5 equiv.), **3** (1 equiv.), **4** (1.2 equiv.), microwave, 120 °C, 30–60 min, 1,4-dioxane (10 vol).

bromo intermediate (**6**) under thermal conditions which resulted in its degradation. Hence our optimal conditions were 1 equiv. of **3**, 1.2 equiv. of **4**, 3 equiv. of $Cs_2CO_3$, 10 vol 1,4-dioxane as solvent, 0.04 equiv. of $Pd_2(OAc)_2$, 0.08 equiv.% of Xantphos, 1.5 equiv. of $Bu_4NBr$, microwave treatment at 120 °C for 30–60 min in a sealed vial. From Table 3 it is very clear that the use of $Pd(OAc)_2$ along with Xantphos gave 55% of the product. 1,3-Bis(diphenylphosphino)propane (dppp) was also found to be an efficient ligand in these transformations as the yields are comparable.

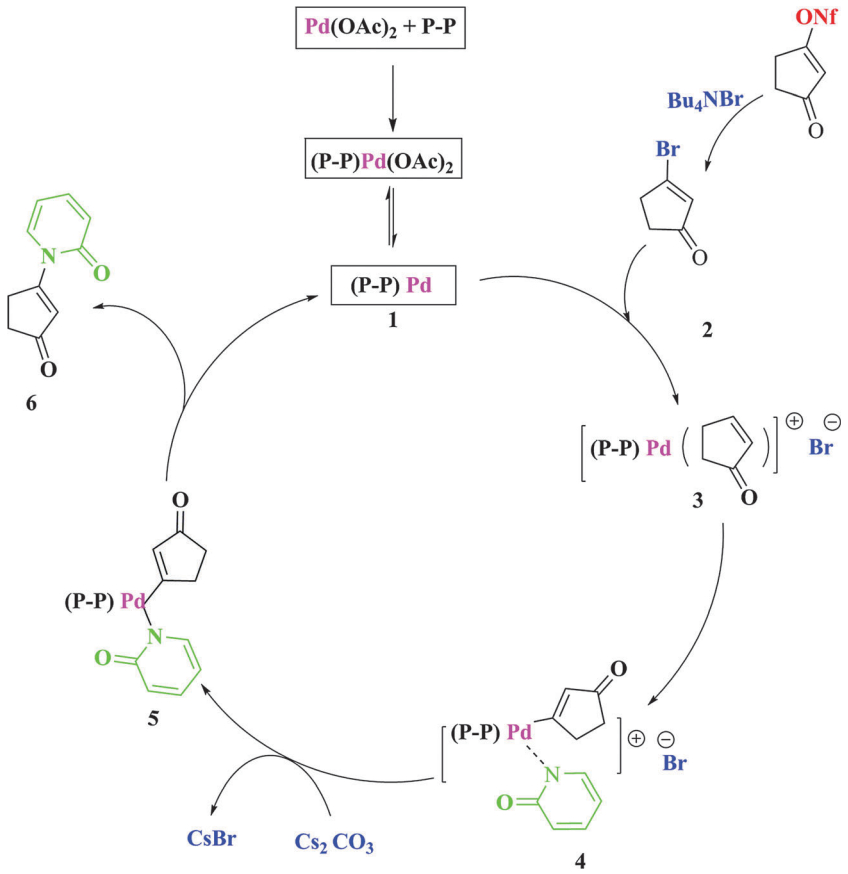



Fig. 6 Mechanism of coupling reaction.

A plausible catalytic cycle[29] for the amination of cycloalkenyl nonaflates is shown in (Fig. 6). The mixture of palladium acetate and bis-(phosphine) (P–P) reacts to form (P–P) $Pd(OAc)_2$ which is then reduced under reaction conditions to a zero valent Pd species [(P–P)Pd], (**1**). Tetrabutylammonium bromide then displaces the nonaflates to give the corresponding bromides, (**2**). Oxidative addition to these species results in the formation of (**3**). Coordination of the enolizable heterocycles follows to give (**4**) which are deprotonated by cesium carbonate to afford complex (**5**). Reductive elimination from (**5**) yields the cross-coupled product (**6**) and regenerates the true palladium(0) catalytic species.

## Conclusion

In summary, we have reported a highly efficient method for the construction of N-alkylated heterocycles using palladium mediated cross-coupling reactions under microwave enhanced conditions from cycloalkenyl nonaflates. The use of ligands Xantphos or 1,3-bis(diphenylphosphino)propane was found to be effective in these transformations, which led to complete conversions to the coupled products in a very short time. The compounds thus synthesized using this methodology can be useful as amine synthons in the field of medicinal chemistry during the lead optimization process.

## Experimental section

All anhydrous solvents and reagents were obtained from commercial suppliers and used without any further purification unless otherwise noted. All the reactions were carried out under an inert atmosphere of argon. A Biotage Initiator 60 instrument was used for all microwave-assisted reactions, using sealed reaction vessels with the temperature measured by an external IR sensor. Analytical TLC was performed on pre-coated aluminum sheets of silica (60 F254 nm) and visualized by short-wave UV light at $\lambda$ 254. Flash column chromatography was carried out on silica gel (230–400 mm) and semi-automated purification was carried out on a Biotage SP1 purification system, using SNAP cartridges, or SINGLE STEP flash column cartridges. Solvent systems are reported by column volume (CV) with the solvent flow rate as stated. Melting points were determined on an EZ-Melt automated melting point apparatus. IR spectra were recorded on a Bruker Alpha P FT-IR spectrometer. Absorption maxima ($\nu_{max}$) are quoted in wave numbers ($cm^{-1}$). $^1H$ NMR spectra were recorded at 400 MHz and 300 MHz using an internal deuterium lock. Chemical shifts were measured in parts per million (ppm) using the following internal references for residual protons in the solvent: $CDCl_3$ ($\delta$ H: 7.26), $CD_3OD$ ($\delta$ H: 3.32) and DMSO-$d_6$ ($\delta$ H: 2.50). Data is presented as follows: chemical shift, multiplicity, coupling constant ($J$) in Hz, and integration. The following abbreviations are used for

the splitting patterns: s for singlet, d for doublet, t for triplet, m for multiplet and br for broad. $^{13}$C NMR spectra were recorded at 100 MHz using an internal deuterium lock. The following internal references were used: $CDCl_3$ ($\delta$ C: 77.0), $CD_3OD$ ($\delta$ C: 49.0) and DMSO-$d_6$ ($\delta$ C: 39.5). $^{19}$F NMR spectra were recorded at 376.5 MHz using an internal deuterium lock. LCMS analyses were performed using ESI/APCI, with an ATLANTIS C18 (50 × 4.6 mm–5 μm), column and a flow rate of 1.2 mL min$^{-1}$. UV detection was at 215 nm.

### General procedure for the preparation of 2

To a solution of 1,3-cyclopentanone (3.0 g, 30.6 mmol) in DCM (30 mL) was added triethylamine (9.3 g, 91.8 mmol) at −10 °C, followed by drop wise addition of triflic anhydride (8.6 g, 30.6 mmol), the reaction mixture was warm up to 0 °C and stirred for about 1 h. The reaction mixture was diluted with DCM (100 mL), bi-phased with water (100 mL), washed with $NaHCO_3$ (100 mL), brine solution (100 mL), the organic layer was dried over $Na_2SO_4$ and concentrated to get the crude material. The crude compound thus obtained was purified by column chromatography packed with 60–120 silica gel, eluted with 10–12% ethyl acetate in petroleum ether to obtain the pure compound (6.5 g, 94%) as a colorless oil.

$^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 6.13–6.12 (t, $J$ = 1.7 Hz, 1H), 2.91–2.88 (m, 2H), 2.65–2.62 (m, 2H).

$^{19}$F NMR (376.5 MHz, $CDCl_3$): $\delta$ = −73.11.

$^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 204.8, 183.5, 118.7, 113.1, 34.2, 28.6 ppm.

### General procedure for the preparation of 3

To a solution of 1,3-cyclopentanone (5.0 g, 51.0 mmol) in DCM (100 mL) triethylamine (15.2 g, 153.0 mmol) was added at −10 °C, followed by the drop wise addition of nonafluorobutane sulfonic anhydride (29.6 g, 51.0 mmol), the reaction mixture was warm up to 0 °C and stirred for about 1 h. The reaction mixture was diluted with DCM (200 mL), bi-phased with water (200 mL), washed with $NaHCO_3$ (250 mL), brine solution (250 mL), the organic layer was dried over $Na_2SO_4$ and concentrated. The crude compound was purified by column chromatography packed with 60–120 silica gel, eluted with 15 to 20% ethyl acetate in petroleum ether to obtain the pure compound (16.5 g, 87%) as a colorless oil.

$^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 5.76–5.75 (t, $J$ = 1.5 Hz, 1H), 2.84–2.81 (m, 2H), 2.59–2.56 (m, 2H).

$^{19}$F NMR (376.5 MHz, $CDCl_3$): $\delta$ = −127.32 to −127.22 (m), −122.78 to −122.68 (m), −115.97 to −115.88 (m), −82.60 to −82.53 (m).

$^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 205.05, 183.45, 140.45, 120.58, 113.05, 110.38, 107.92, 34.27, 28.97 ppm.

### General procedure for the preparation of 5

To a degassed solution of **3** (1.0 equiv.) and **4** (1.2 equiv.) in 1,4-dioxane (10 vol), $Cs_2CO_3$ (3.0 equiv.), $Bu_4NBr$ (1.5 equiv.), $Pd(OAc)_2$ (0.04 equiv.) and Xantphos (0.08 equiv.) were added. The reaction mixture was heated at 120 °C under microwave condition for about 30 min. The reaction mixture was cooled to RT, passed through a celite bed, washed with ethyl acetate (10 mL), bi-phased with saturated $NH_4Cl$ solution (10 mL), washed with water (10 mL), brine solution (10 mL), the organic layer was dried over $Na_2SO_4$ and concentrated. The crude compound was purified by column chromatography packed with 230–400 silica gel, eluted with 25–50% ethyl acetate in petroleum ether which yielded pure compounds (25–90%).

**5-Methyl-1-(3-oxocyclopent-1-enyl)pyridin-2(1H)-one, 5a.** Yielded product as a light brown gummy solid, (90%).

$^1$H NMR (400 MHz, DMSO-$d_6$): $\delta$ = 7.61 (s, 1H), 7.40–7.37 (dd, $J_1$ = 2.3 Hz, $J_2$ = 9.4 Hz, 1H), 6.94–6.93 (d, $J$ = 1.4 Hz, 1H), 6.49–6.47 (d, $J$ = 9.4 Hz, 1H), 3.13–3.11 (m, 2H), 2.43–2.41 (m, 2H), 2.08 (s, 3H).

$^{13}$C NMR (100 MHz, DMSO-$d_6$): $\delta$ = 207.97, 168.87, 161.09, 143.52, 130.95, 121.85, 121.73, 116.10, 33.79, 29.48, 17.11 ppm.

IR (KBr) 3354.4, 2941.7, 2925.3, 2361.4, 2332.8, 1707.9, 1670.8, 1619.8, 1574.4, 1523.7, 1341.1, 1242.7, 1184.2, 1139.8, 988.9, 819.4, 628.4, 467.0, 403.0 cm$^{-1}$.

LCMS: 190.2 (M + H).

Anal. calcd for $C_{22}H_{22}N_2O_4$: C, 69.83; H, 5.86; N, 7.40%, found: C, 69.73; H, 5.99; N, 7.35%.

**4-Methyl-3-nitro-1-(3-oxocyclopent-1-enyl)pyridin-2(1H)-one, 5b.** Yielded product as a brown solid, (78%), Mp (145.6–146.7 °C).

$^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 7.48 (d, $J$ = 7.5 Hz, 1H), 6.93–6.92 (t, $J$ = 1.6 Hz, 1H), 6.28 (d, $J$ = 7.4 Hz, 1H), 3.20–3.17 (m, 2H), 2.65–2.63 (m, 2H), 2.33 (s, 3H).

$^{13}$C NMR (100 MHz, $CD_3OD$): $\delta$ = 207.97, 155.8, 152.4, 151.2, 135.85, 128.73, 112.10, 99.40, 34.79, 30.48, 13.55 ppm.

LCMS: 233.2 (M + H).

IR (KBr) 3784.0, 3096.3, 3064.6, 2920.1, 2361.4, 1978.7, 1672.1, 1582.3, 1523.4, 1432.7, 1404.6, 1370.4, 1272.4, 1241.8 1165.2, 1087.4, 1023.8, 991.7, 898.8, 862.8, 828.2, 798.6, 773.8, 751.2, 623.1, 571.3, 544.9, 513.4, 403.6 cm$^{-1}$.

Anal. calcd for $C_{11}H_{10}N_2O_4$: C, 56.41; H, 4.30; N, 11.96%, found: C, 56.60; H, 4.30; N, 11.86%.

**1-(3-Oxocyclopent-1-enyl)pyridin-2(1H)-one, 5c.** Yielded product as a off-white solid, (80%), Mp (138.6–140.7 °C).

$^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 7.43–7.44 (m, 2H), 6.96–6.95 (t, $J$ = 1.6 Hz, 1H), 6.66–6.64 (d, $J$ = 8.6 Hz, 1H), 6.33–6.29 (m, 1H), 2.62–2.60 (m, 2H).

$^{13}$C NMR (100 MHz, $CD_3OD$): $\delta$ = 206.67, 167.77, 162.02, 142.00, 129.05, 122.75, 122.63, 116.76, 33.75, 29.76 ppm.

LCMS: 176.2 (M + H).

IR (KBr) 3358.4, 3134.4, 2996.9, 2856.1, 2856.1, 2364.4, 2332.4, 1674.4, 1619.8, 1588.9, 1471.2, 1428.4, 1437.4, 1371.2, 1341.1, 1328.4, 1306.4, 1184.2, 1139.8, 1040.2, 988.9, 963.7, 850.6, 846.4, 819.4, 765.2, 628.4, 562.4, 525.0, 497.8, 467.0, 416.9 cm$^{-1}$.

Anal. calcd for $C_{10}H_9NO_2$: C, 68.56; H, 5.18; N, 8.00%, found: C, 68.43; H, 5.25; N, 8.03%.

**3-Methyl-1-(3-oxocyclopent-1-enyl)pyridin-2(1H)-one, 5d.** Yielded product as a off-white solid, (82%), Mp (152.4–153.1 °C).

$^1$H NMR (400 MHz, DMSO-$d_6$): $\delta$ = 8.20–8.19 (dd, $J_1$ = 1.2 Hz, $J_2$ = 4.7 Hz, 1H), 7.87–7.85 (dd, $J_1$ = 0.9 Hz, $J_2$ = 7.4 Hz, 1H), 7.32–7.29 (dd, $J_1$ = 4.8 Hz, $J_2$ = 2.5 Hz, 1H), 5.42 (d, $J$ = 1.08 Hz, 1H), 2.85–2.82 (m, 2H), 2.44–2.41 (m, 2H), 2.25 (s, 3H).

$^{13}$C NMR (100 MHz, $CD_3OD$): $\delta$ = 206.67, 169.99, 162.02, 143.92, 136.99, 134.45, 120.73, 116.16, 33.65, 29.73, 16.16 ppm.

LCMS: 190.2 (M + H).

IR (KBr) 3334.2, 2944.6, 2927.5, 2363.6, 2335.2, 1711.2, 1672.2, 1623.1, 1572.2, 1524.1, 1342.3, 1240.1, 1184.9, 1138.7, 989.9, 818.7, 629.7, 468.9, 406.4 $cm^{-1}$.

LCMS: 190.2 (M + H).

Anal. calcd for $C_{11}H_{11}NO_2$: C, 69.83; H, 5.86; N, 7.40%, found: C, 69.79; H, 5.88; N, 7.38%.

**4-Methyl-1-(3-oxocyclopent-1-enyl)pyridin-2(1H)-one, 5e.** Yielded product as a off-white solid, (83%), Mp (150.1–151.1 °C).

$^1$H NMR (400 MHz, DMSO-$d_6$): $\delta$ = 7.71 (d, $J$ = 7.2 Hz, 1H), 6.97 (s, 1H), 6.39 (d, $J$ = 6.5 Hz, 1H), 6.35–6.31 (t, $J$ = 6.8 Hz, 1H), 3.13–3.11 (m, 2H), 2.45–2.43 (m, 2H), 2.05 (s, 3H).

$^{13}$C NMR (100 MHz, $CD_3OD$): $\delta$ = 205.66, 170.54, 159.91, 148.57, 140.16, 128.01, 114.51, 108.41, 36.45, 25.86, 17.39 ppm.

LCMS: 190.2 (M + H).

IR (KBr) 3058.6, 2948.3, 1657.8, 1615.4, 1588.0, 1464.4, 1427.7, 1368.4, 1327.2, 1250.6, 1212.6, 1158.4, 1128.8, 1046.7, 992.9, 968.2, 908.7, 867.5, 831.3, 788.4, 741.2, 620.3, 589.2, 515.6, 414.2 $cm^{-1}$.

Anal. calcd for $C_{11}H_{11}NO_2$: 69.83; H, 5.86; N, 7.40%, found: 69.95; H, 5.78; N, 7.46%.

**5-Nitro-1-(3-oxocyclopent-1-enyl)pyridin-2(1H)-one, 5f.** Yielded product as a brown solid, (25%), Mp (183.1–184.3 °C).

$^1$H NMR (400 MHz, DMSO-$d_6$): $\delta$ = 8.54 (s, 1H), 7.75–7.69 (dd, $J_1$ = 2.8 Hz, $J_2$ = 10 Hz, 1H), 7.40 (d, $J$ = 6.48 Hz, 1H), 6.35 (d, $J$ = 7.0 Hz, 1H), 3.13–3.12 (m, 2H), 2.45–2.43 (m, 2H).

$^{13}$C NMR (100 MHz, $CD_3OD$): $\delta$ = 205.57, 170.05, 160.59, 150.55, 143.52, 136.59, 122.73, 116.16, 33.69, 29.42 ppm.

LCMS: 221.2 (M + H).

IR (KBr) 3781.3, 3091.3, 3064.6, 2920.1, 2361.3, 2301.3, 1978.7, 1672.1, 1582.3, 1523.4, 1432.7, 1404.6, 1370.4, 1343.2, 1304.6, 1370.4, 1343.2, 1304.3, 1272.4, 1250.6, 1212.6, 1158.4, 1128.8, 991.7, 932.0, 898.8, 862.8, 828.2, 773.8, 751.2, 696.3, 623.1, 571.3, 544.9, 513.4, 403.6 $cm^{-1}$.

Anal. calcd for $C_{10}H_8N_2O_4$: C, 54.55; H, 3.66; N, 12.72%, found: C, 54.45; H, 3.78; N, 12.67%.

**4-(Trifluoromethyl)-1-(3-oxocyclopent-1-enyl)pyridin-2(1H)-one, 5g.** Yielded product as a off-white solid, (34%), Mp (132.7–133.9 °C).

$^1$H NMR (400 MHz, DMSO-$d_6$): $\delta$ = 7.83 (d, $J$ = 3.7 Hz, 1H), 6.87 (s, 1H), 6.58–6.56 (dd, $J_1$ = 1.6 Hz, $J_2$ = 7.4 Hz, 1H), 6.13 (s, 1H), 2.71–2.69 (t, $J$ = 5.6 Hz, 2H), 2.44–2.41 (t, $J$ = 6.6 Hz, 2H).

$^{13}$C NMR (100 MHz, $CD_3OD$): $\delta$ = 207.2, 168.12, 162.71, 158.21, 151.31, 142.76, 138.60, 122.05, 114.32, 32.62, 29.88 ppm.

IR (KBr) 3356.1, 2945.1, 2929.7, 2364.9, 1717.0, 1672.8, 1618.1, 1576.6, 1525.5, 1342.2, 1243.9, 1186.7, 1139.0, 983.6, 819.4, 624.6, 467.9, 404.9 $cm^{-1}$.

LCMS: 244.2 (M + H).

Anal. calcd for $C_{11}H_8F_3NO_2$: C, 54.33; H, 3.32; N, 5.76%, found: C, 54.45; H, 3.26; N, 5.70%.

**1-(3-Oxocyclopent-1-enyl)-1H-benzo[*d*]imidazol-2(3H)-one, 5h.** Yielded product as a white solid, (68%), Mp (167.1–168.4 °C).

$^1$H NMR (400 MHz, DMSO-$d_6$): $\delta$ = 11.29 (s, 1H), 7.21 (d, $J$ = 10.8 Hz, 2H), 7.03 (d, $J$ = 6.8 Hz, 2H), 6.18 (d, $J$ = 9.6 1H), 2.97–2.90 (m, 2H), 2.45–2.39 (m, 2H).

$^{13}$C NMR (100 MHz, $CD_3OD$): 207.7, 158.2, 146.3, 129.5, 127.8, 123.4, 121.8, 112. 2, 32.6, 29.8 ppm.

IR (KBr): 3051.4, 2944.7, 2896.0, 1704.1, 1659.5, 1619.3, 1595.8, 1477.1, 1417.9, 1381.2, 1345.0, 1307.7, 1286.8, 1248.3, 1221.5, 1157.2, 1101.2, 1032.7, 966.9, 931.8, 898.8, 847.3, 808.2, 775.6, 746.1, 727.0, 690.5, 654.3, 604.8, 539.6 $cm^{-1}$.

LCMS: 215.2 (M + H).

Anal. calcd for $C_{11}H_9N_2O_2$: C, 65.66; H, 4.51; N, 13.92%, found: C, 65.75; H, 4.53; N, 13.85%.

**1,3-Bis(3-oxocyclopent-1-enyl)-1H-benzo[*d*]imidazol-2(3H)-one, 5i.** Yielded product as a white solid, (88%), Mp (195.5–196.3 °C).

$^1$H NMR (400 MHz, DMSO-$d_6$): $\delta$ = 7.75–7.73 (dd, $J_1$ = 3.3 Hz, $J_2$ = 6.1 Hz, 2H), 7.33–7.31 (dd, $J_1$ = 3.2 Hz, $J_2$ = 6.1 Hz, 2H), 3.44–3.41 (m, 4H), 2.49–2.47 (m, 4H).

$^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 206.49, 165.66, 149.61, 127.87, 124.71, 119.15, 112.23, 33.94, 29.65 ppm.

LCMS: 295.2 (M + H).

IR (KBr): 3084.4, 1732.6, 1695.6, 1611.8, 1576.5, 1471.7, 1411.8, 1377.5, 1281.2, 1244.7, 1220.9, 1161.7, 1091.8, 995.5, 906.4, 865.7, 842.6, 748.5, 685.9, 626.2, 553.3, 515.0, 488.6, 424.9 $cm^{-1}$.

Anal. calcd for $C_{17}H_{18}N_2O_2$: C, 72.32; H, 6.43; N, 9.92%, found: C, 72.40; H, 6.38; N, 9.95%.

**2-(3-Oxocyclopent-1-enyl)isoindoline-1,3-dione, 5j.** Yielded product as a brown solid, (72%), Mp (172.5–173.1 °C).

$^1$H NMR (400 MHz, DMSO-$d_6$): $\delta$ = 8.0–7.98 (m, 2H), 7.94–7.92 (dd, $J_1$ = 1.0 Hz, $J_2$ = 3.4 Hz, 2H), 6.58–6.57 (t, $J$ = 1.4 Hz, 1H), 3.31–3.29 (m, 2H), 2.36–2.38 (m, 2H).

$^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 207.5, 165.6, 150.6, 133.8, 127.7, 112.2, 33.9, 29.6 ppm.

IR (KBr): 3048.4, 2946.7, 2898.2, 1714.1, 1655.2, 1618.3, 1610.5, 1595.8, 1477.1, 1417.9, 1381.2, 1368.2, 1345.0, 1307.7, 1286.8, 1248.3, 1221.5, 1157.2, 1101.2, 1032.7, 966.9, 931.8, 898.8, 847.3, 808.2, 775.6, 746.1, 727.0, 690.5, 654.3, 614.8, 519.6 $cm^{-1}$.

LCMS: 228.2 (M + H).

Anal. calcd for $C_{13}H_9NO_3$: C, 68.72; H, 3.99; N, 6.16%, found: C, 68.66; H, 3.92; N, 6.23%.

**3-Chloro-7-(3-oxocyclopent-1-enyl)-1,7-naphthyridin-8(7H)-one, 5k.** Yielded product as a light brown solid, (82%), Mp (189.5–191.1 °C).

$^1$H NMR (400 MHz, DMSO-$d_6$): $\delta$ = 8.82 (d, $J$ = 3.0 Hz, 1H), 8.40 (d, $J$ = 3.0 Hz, I H), 7.83 (d, $J$ = 10.4 Hz, 1H), 6.9 (s, 1H), 6.7 (d, $J$ = 10.4 Hz, 1H), 3.17–3.16 (t, $J$ = 3.9 Hz, 2H), 2.49–2.48 (t, $J$ = 4.0 Hz 2H).

$^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 203.43, 163.36, 161.22, 160.05, 143.09, 137.21, 135.60, 134.92, 133.63, 127.31, 121.10, 114.63, 109.74, 37.58, 29.71 ppm.

IR (KBr): 3059.5, 2937.2, 2859.2, 1659.3, 1627.2, 1591.1, 1479.0, 1457.3, 1417.6, 1345.6, 1309.3, 1227.3, 1171.2, 1133.1, 1109.7, 1063.7, 1038.9, 1011.1, 961.4, 895.3, 849.3, 808.2, 782.7, 756.8, 734.0, 691.1, 620.3, 532.1, 502.2, 440.3 $cm^{-1}$.

LCMS: 261.2 (M + H).

Anal. calcd for $C_{13}H_9ClN_2O_2$: C, 59.90; H, 3.48; N, 10.75%, found: C, 59.94; H, 3.55; N, 10.66%.

**6-(3-Oxocyclopent-1-enyloxy)-2-(3-oxocyclopent-1-enyl)pyridazin-3(2H)-one, 5l.** Yielded product as a dark brown solid, (55%), Mp (173.5–174.7 °C).

$^1$H NMR (400 MHz, DMSO-$d_6$): $\delta$ = 7.63–7.61 (dd, $J_1$ = 1.2 Hz, $J_2$ = 10.0 Hz, 1H), 7.3–7.27 (dd, $J_1$ = 1.6 Hz, $J_2$ = 10.0 Hz, 1H), 6.89 (s, 1H), 5.94 (s, 1H), 3.05–3.01 (m, 2H), 2.86–2.84 (m, 2H), 2.40–2.38 (m, 2H), 2.33–2.35 (m, 2H).

LCMS: 273.2 (M + H).

Anal. calcd for $C_{14}H_{12}N_2O_4$: C, 61.76; H, 4.44; N, 10.29%, found: C, 61.80; H, 4.46; N, 10.20%.

**1-(3-Oxocyclohex-1-enyl)pyridin-2(1H)-one, 5m.** Yielded product as a dark brown gummy solid, (85%).

$^1$H NMR (400 MHz, DMSO-$d_6$): $\delta$ = 8.37–8.36 (dd, $J_1$ = 1.8 Hz, $J_2$ = 4.8 Hz, 1H), 7.99–7.95 (m, 1H), 7.36–7.33 (dd, $J_1$ = 5.2 Hz, $J_2$ = 7.2 Hz, 1H), 7.19 (d, $J$ = 8.0 Hz, 1H), 5.16 (s, 1H), 2.63–2.60 (t, $J$ = 6.2 Hz, 2H), 2.30–2.27 (t, $J$ = 6.6 Hz, 2H), 1.94–2.05 (m, 2H).

$^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 199.66, 175.53, 159.92, 148.57, 140.16, 121.53, 114.93, 108.97, 36.62, 25.86, 21.14 ppm.

LCMS: 190.2 (M + H).

IR (KBr) 3058.6, 2948.3, 1657.8, 1615.4, 1588.0, 1464.4, 1427.7, 1368.4, 1250.6, 1212.6, 1158.4, 1128.8, 1046.7, 992.9, 968.2, 908.7, 867.5, 831.3, 788.4, 741.2, 620.3, 589.2, 515.6, 414.2 cm$^{-1}$.

Anal. calcd for $C_{11}H_{11}NO_2$: C, 69.83; H, 5.86; N, 7.40%, found: C, 69.90; H, 5.90; N, 7.48%.

**6-Methyl-1-(3-oxocyclohex-1-enyl)pyridin-2(1H)-one, 5n.** Yielded product as a light brown thick liquid, (83%).

$^1$H NMR (400 MHz, DMSO-$d_6$): $\delta$ = 8.19–8.18 (t, $J$ = 1.6 Hz, 1H), 7.80–7.77 (dd, $J_1$ = 2.4 Hz, $J_2$ = 8.0 Hz, 1H), 7.08 (d, $J$ = 8.0 Hz, 1H), 5.07 (s, 1H), 2.61–2.58 (t, $J$ = 6.0 Hz, 2H), 2.28–2.25 (t, $J$ = 6.8 Hz, 2H), 2.30 (s, 3H), 1.94–1.97 (m, 2H).

$^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 200.5, 176.5, 158.1, 149.7, 141.2, 127.8, 113.3, 109.3, 36.6, 26.6, 21.9, 18.1 ppm.

LCMS: 204.2 (M + H).

IR (KBr) 3353.1, 2946.3, 2368.0, 2340.1, 1715.2, 1675.1, 1625.1, 1569.1, 1533.9, 1348.2, 1266.2, 1189.1, 1145.2, 988.2, 816.8, 620.3, 460.5, 414.1 cm$^{-1}$.

Anal. calcd for $C_{12}H_{13}NO_2$: C, 70.92; H, 6.45; N, 6.89%, found: C, 70.74; H, 6.55; N, 6.93%.

**5-Methyl-1-(3-oxocyclohex-1-enyl)pyridin-2(1H)-one, 5o.** Yielded product as a off-white solid, (78%), Mp (135.6–136.7 °C).

$^1$H NMR (400 MHz, DMSO-$d_6$): $\delta$ = 8.19 (d, $J$ = 1.6 Hz, 1H), 7.80–7.77 (dd, $J_1$ = 2.4 Hz, $J_2$ = 8.0 Hz, 1H), 7.9 (d, $J$ = 8.0 Hz, 1H), 5.07 (s, 1H), 2.61–2.59 (t, $J$ = 6.0 Hz, 2H), 2.30 (s, 3H), 2.29–2.25 (t, $J$ = 6.8 Hz, 2H), 1.98–1.95 (t, $J$ = 6.4, 2H).

$^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 199.66, 175.54, 159.91, 148.57, 140.16, 128.02, 114.54, 108.41, 36.45, 25.86, 21.39, 17.74 ppm.

IR (KBr) 3352.8, 2945.1, 2928.3, 2363.6, 2335.2, 1709.5, 1672.5, 1615.3, 1577.6, 1526.4, 1345.3, 1246.2, 1183.2, 1135.8, 984.9, 815.2, 626.1, 465.2, 404.4 cm$^{-1}$.

Anal. calcd for $C_{12}H_{13}NO_2$: C, 70.92; H, 6.45; N, 6.89%, found: C, 70.76; H, 6.45; N, 6.91%.

**4-(Trifluoromethyl)-1-(3-oxocyclohex-1-enyl)pyridin-2(1H)-one, 5p.** Yielded product as a off-white solid, (32%), Mp (145.6–146.9 °C).

$^1$H NMR (400 MHz, DMSO-$d_6$): $\delta$ = 7.83 (d, $J$ = 7.2 Hz, 1H), 6.87 (s, 1H), 6.58–6.56 (dd, $J_1$ = 1.6 Hz, $J_2$ = 7.4 Hz, 1H), 6.14 (s, 1H), 2.71–2.69 (t, $J$ = 5.6 Hz, 2H), 2.44–2.41 (t, $J$ = 6.6 Hz, 2H), 2.10–2.07 (m, 2H).

$^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 198.66, 175.54, 159.91, 148.57, 140.16, 129.0, 128.02, 114.54, 108.41, 36.45, 26.86, 22.39 ppm.

LCMS: 256.2 (M + H).

Anal. calcd for $C_{12}H_{10}F_3NO_2$: C, 56.04; H, 3.92; N, 5.45%, found: C, 55.94; H, 3.92; N, 5.43%.

**1-(3-Oxocyclohex-1-enyl)-1H-benzo[*d*]imidazol-2(3H)-one, 5q.** Yielded product as a white solid, (58%), Mp (163.1–164.9 °C).

$^1$H NMR (400 MHz, DMSO-$d_6$): $\delta$ = 11.29 (s, 1H), 7.21 (d, $J$ = 10.8 Hz, 2H), 7.11–7.08 (m, 2H), 2.97–2.90 (m, 2H), 6.18 (d, $J$ = 9.6 1H), 2.45–2.39 (t, $J$ = 8.6 Hz, 2H), 2.08–1.97 (m, 2H).

$^{13}$C NMR (100 MHz, $CD_3OD$): 207.7, 158.2, 146.3, 129.5, 127.8, 123.4, 121.8, 112.2, 32.6, 29.8, 22.39 ppm.

LCMS: 229.2 (M + H).

IR (KBr): 3051.4, 2944.7, 2896.0, 1704.1, 1659.5, 1619.3, 1595.8, 1477.1, 1417.9, 1381.2, 1345.0, 1307.7, 1286.8, 1248.3, 1221.5, 1157.2, 1101.2, 1032.7, 966.9, 931.8, 898.8, 847.3, 808.2, 775.6, 746.1, 727.0, 690.5, 654.3, 604.8, 539.6 cm$^{-1}$.

Anal. calcd for $C_{13}H_{12}N_2O_2$: C, 68.41; H, 5.30; N, 12.27%, found: C, 68.58; H, 5.23; N, 12.32%.

**1,3-Bis(3-oxocyclohex-1-enyl)-1H-benzo[*d*]imidazol-2(3H)-one, 5r.** Yielded product as a white solid, (78%), Mp (203.3–204.8 °C).

$^1$H NMR (400 MHz, DMSO-$d_6$): $\delta$ = 7.22–7.17 (m, 2H), 7.11–7.04 (m, 2H), 6.19 (s, 2H), 2.97–2.90 (m, 2H), 2.45–2.39 (m, 4H), 2.08–1.97 (m, 4H).

$^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 207.50, 169.42, 150.82, 127.72, 123.72, 118.25, 114.38, 36.94, 29.65, 23.11 ppm.

LCMS: 323.2 (M + H).

IR (KBr): 3084.4, 1732.6, 1695.6, 1611.8, 1576.5, 1471.7, 1411.8, 1377.5, 1281.2, 1244.7, 1220.9, 1161.7, 1091.8, 995.5, 906.4, 865.7, 842.6, 748.5, 685.9, 626.2, 553.3, 515.0, 488.6, 424.9 cm$^{-1}$.

Anal. calcd for $C_{19}H_{18}N_2O_3$: C, 70.79; H, 5.63; N, 8.69%, found: C, 70.89; H, 5.73; N, 8.54%.

**3-Methoxy-7-(3-oxocyclohex-1-enyl)-1,7-naphthyridin-8(7H)-one, 5s.** Yielded product as a pale brown solid, (82%), Mp (203.9–204.2 °C).

$^1$H NMR (400 MHz, DMSO-$d_6$): $\delta$ = 7.49 (d, $J$ = 2.4 Hz, 1H), 7.2 (d, $J$ = 2.4 Hz, 1H), 7.5 (d, $J$ = 7.6 Hz, 1H), 6.64 (d, $J$ = 7.2 Hz, 1H), 6.1 (s, 1H), 3.94 (s, 3H), 2.81–2.78 (t, $J$ = 6.0 Hz, 2H), 2.45–2.42 (t, $J$ = 6.4 Hz, 2H), 2.07–2.04 (t, $J$ = 6.4 Hz 2H).

$^{13}$C NMR (100 MHz, $CD_3OD$): $\delta$ = 201.46, 164.36, 164.36, 161.22, 160.04, 143.10, 143.10, 137.01, 133.63, 127.30, 127.10, 114.65, 106.78, 56.74, 37.98, 29.75, 23.11 ppm.

LCMS: 271.2 (M + H).

IR (KBr): 3059.5, 2937.2, 1660.3, 1617.2, 1591.1, 1479.0, 1453.3, 1417.6, 1345.6, 1309.3, 1227.3, 1171.2, 1133.1, 1109.7, 1063.7, 1038.9, 1011.1, 961.4, 895.3, 849.3, 808.2, 782.7, 756.8, 734.0, 691.1, 620.3, 532.1, 502.2, 440.3 cm$^{-1}$.

Anal. calcd for $C_{15}H_{14}N_2O_3$: C, 66.63; H, 5.22; N, 10.36%, found: C, 66.66; H, 5.32; N, 10.39%.

**1-(5,5-Dimethyl-3-oxocyclohex-1-enyl)pyridin-2(1H)-one, 5t.** Yielded product as a off-white solid, (90%), Mp (105.3–107.0 °C).

$^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 8.35–8.33 (dd, $J_1$ = 1.8 Hz, $J_2$ = 4.8 Hz, 1H), 7.98–7.95 (m, 1H), 7.23–7.21 (dd, $J_1$ = 5.2 Hz, $J_2$ = 7.2 Hz, 1H), 7.03–7.00 (dd, $J_1$ = 1.8 Hz, $J_2$ = 4.8 Hz, 1H), 5.18 (s, 1H), 2.78 (s, 2H), 2.36 (d, $J$ = 6.6 Hz, 2H), 1.20 (s, 6H).

$^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 201.66, 174.30, 159.92, 146.22, 140.16, 121.53, 114.93, 108.97, 46.62, 37.62, 29.40, 25.86 ppm.

LCMS: 218.2 (M + H).

IR (KBr) 3045.5, 2938.2, 1647.8, 1625.4, 1580.0, 1520.3, 1464.4, 1427.7, 1368.4, 1250.6, 1212.6, 1158.4, 1128.8, 1046.7, 992.9, 968.2, 908.7, 877.5, 831.3, 768.4, 741.2, 620.3, 589.2, 513.6, 410.2 $cm^{-1}$.

Anal. calcd for $C_{13}H_{15}NO_2$: C, 71.87; H, 6.96; N, 6.45%, found: C, 71.86; H, 6.92; N, 6.43%.

**1-(3-Oxo-5-phenylcyclohex-1-enyl)pyridin-2(1H)-one, 5u.** Yielded product as a off-white solid, (88%), Mp (125.6–126.7 °C).

$^1$H NMR (400 MHz, DMSO-$d_6$): $\delta$ = 8.24–8.23 (dd, $J_1$ = 1.8 Hz, $J_2$ = 4.8 Hz, 1H), 7.92–7.88 (m, 1H), 7.28–7.27 (dd, $J_1$ = 5.2 Hz, $J_2$ = 7.2 Hz, 1H), 7.23–7.08 (m, 6H), 5.25 (s, 1H), 3.38–3.12 (m, 2H), 2.90–2.67 (m, 1H), 2.36–2.10 (m, 2H).

$^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 200.11, 174.30, 160.12, 146.22, 141.06, 138.5, 136.20, 135.10, 123.31, 116.3, 109.71, 48.2, 37.60, 30.12 ppm.

LCMS: 266.2 (M + H).

Anal. calcd for $C_{17}H_{15}NO_2$: C, 76.96; H, 5.70; N, 5.28%, found: C, 76.82; H, 5.58; N, 5.08%.

**1-(5-(4-Chlorophenyl)-3-oxocyclohex-1-enyl)pyridin-2(1H)-one, 5v.** Yielded product as a off-white solid, (86%), Mp (137.4–138.7 °C).

$^1$H NMR (400 MHz, DMSO-$d_6$): $\delta$ = 8.14–8.13 (dd, $J_1$ = 1.8 Hz, $J_2$ = 4.8 Hz, 1H), 7.90–7.88 (m, 1H), 7.28–7.27 (dd, $J_1$ = 5.2 Hz, $J_2$ = 7.2 Hz, 1H), 7.23–7.08 (m, 5H), 5.45 (s, 1H), 3.36–3.12 (m, 2H), 2.92–2.77 (m, 1H), 2.42–2.08 (m, 2H).

$^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 201.70, 175.32, 161.22, 146.02, 140.06, 139.15, 138.02, 135.11, 124.13, 118.33, 109.11, 49.34, 36.43, 31.52 ppm.

LCMS: 301.2 (M + H).

Anal. calcd for $C_{17}H_{14}ClNO_2$: C, 68.12; H, 4.71; N, 4.67%, found: C, 68.20; H, 4.54; N, 4.75%.

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