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**Intramolecular Acylation of Unactivated Pyridines or Arenes via Multiple C–H  
Functionalizations: Synthesis of all Four Azafluorenones and Fluorenones**

*Joydev K. Laha,\* Krupal P. Jethava, Sagarkumar Patel, and Ketul V. Patel*

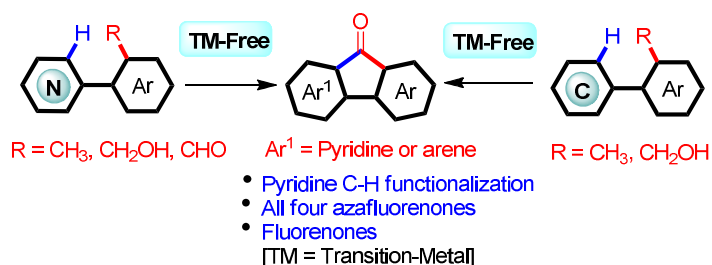
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## ABSTRACT

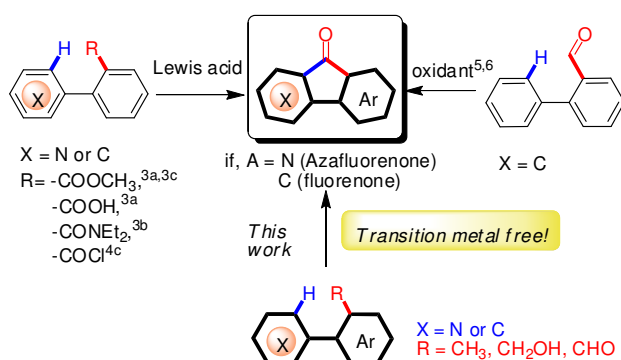


**Abstract:** An unprecedented intramolecular acylation of unactivated pyridines via multiple C(sp<sup>3</sup>/sp<sup>2</sup>)-H functionalizations of a methyl, hydroxymethyl, or aldehyde group has been developed providing a general access to all four azafluorenones. The application of this protocol is further demonstrated to the synthesis of azafluorenone related fused nitrogen heterocycles and fluorenones. In addition, design and synthesis of a novel fluorene based organic emitter for potential use in organic light emitting devices (OLEDs) is also reported.

## INTRODUCTION

Azafluorenones and related heterocycles are privileged fused heterocycles ubiquitously found in natural products and pharmaceuticals showcasing diverse pharmacological and biological activities.<sup>1</sup> In addition, single fluorene molecule based fluorescent organic emissive materials are available as electron-transporting host material capable of being fabricated into the efficient organic light emitting devices (OLED).<sup>2</sup> Despite their diverse applications, the chemistry of azafluorenones has been least investigated. Among the various synthetic approaches reported for the synthesis of azafluorenones<sup>3</sup> and fluorenones,<sup>4</sup> intramolecular acylation reactions have been identified as a major contributor to the synthesis of these heterocycles. The classical Friedel-Crafts acylation approach to the synthesis of azafluorenones (and fluorenones) include intramolecular acylation in 2-arylpyridines or biaryls containing an acyl source appropriately placed in on one of the two rings (Scheme 1).<sup>3a-c,4c</sup> Remarkably, Glorius<sup>5</sup> and Studer<sup>6a</sup> independently reported intramolecular acylation of arenes using an aldehyde group as acylating agent yielding fluorenones in good to excellent yields.

### Scheme 1. Synthetic Approaches to Azafluorenones or Fluorenones from Biaryls

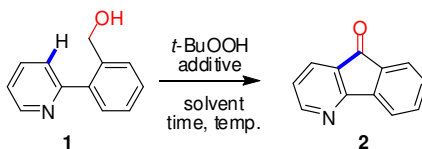


Despite significant advances realized in azafluorenone synthesis largely using classical chemistry, a general strategy which could lead to the synthesis of all four azafluorenones via multiple C–H functionalizations has not been realized. Previously, we reported the synthesis

of 4-azafluorenones via intramolecular acylation of arenes using a methyl or hydroxymethyl group as latent acylating agent present on pyridine ring.<sup>7</sup> However, other azafluorenones were inaccessible by this protocol. Inspired by our recent success, and based on previous experiences on multiple C–H functionalizations in the synthesis of biaryl sultams,<sup>8</sup> heterobiaryl sultams,<sup>9</sup> carbazoles and  $\alpha$ -carboline,<sup>10</sup> we surmised that an intramolecular acylation of unactivated pyridines in arylpyridines containing a latent carbonyl source while an ambitious objective would be a distinct, straightforward gateway to the general synthesis of azafluorenones. Perhaps most importantly, acylation of pyridines using aryl aldehydes or methylarenes as acylating agents is an unsolved problem and remains unexplored, although intermolecular acylation of activated pyridines, such as pyridine-N-oxides via decarboxylative acylations has been achieved.<sup>11</sup> However, they suffer from using additional steps including preparation of pyridine N-oxides and deoxygenation of N-oxides. Therefore, intramolecular acylation of unactivated pyridines, especially under transition-metal-free conditions, to the general synthesis of azafluorenones while attractive would be an elusive problem. Herein, we unveil a first report on intramolecular acylation of unactivated pyridines at 2, 3, or 4-positions via successive C–H functionalizations of a methyl, hydroxymethyl, or aldehyde group present in arylpyridines. The optimized condition in our study is quite resourceful warranting broad applications to the synthesis of all four azafluorenones, fluorenones, and related heterocycles. A key feature of this work includes demonstration, for the first time, of an intramolecular acylation of unactivated pyridines via multiple C(sp<sup>3</sup>/sp<sup>2</sup>)–H bond functionalizations and subsequent preparation of all four azafluorenones that are otherwise accessible by classical acylation with difficulty. Based on a novel synthetic design, a single fluorene molecule coupled with an azafluorenone was also prepared for potential use in OLEDs.

## RESULTS AND DISCUSSION

Our initial investigation was largely focused on finding a condition that could effect intramolecular acylation in 2-arylpyridine via C–H functionalizations of a hydroxymethyl group. We started our optimization study with a model substrate 2-arylpyridine **1** containing a hydroxymethyl group on the phenyl ring. The reaction of **1** in the presence of 8 equiv *t*-BuOOH in DCE at 100 °C for 24 h gave 4-azafluorenone **2** in 42% yield (Table 1, entry 1). Distinct from our previous report,<sup>7</sup> intramolecular acylation of pyridine at the 3-position using a hydroxymethyl group as acyl surrogate via multiple C–H functionalizations yielded 4-azafluorenone **2**. The yield of **2** was improved by lowering the stoichiometric ratios of *t*-BuOOH to 4 equiv, which led to the isolation of **2** in 60% yield (entry 2). In addition to *t*-BuOOH, the presence of a catalytic amount (5 mol%) of TBAI, known to act as an initiator for radical reactions,<sup>12</sup> proved effective providing **2** in 76% isolated yield (entry 3). The higher catalytic loading of TBAI resulted in a reaction of a complex mixture of products (entry 4). Interestingly, a catalytic amount of KI or I<sub>2</sub> completely diminishes the formation of product (entry 5). Further decrease of molar ratios of *t*-BuOOH or temperature did not offer any improvement in the formation of **2** (entries 6–7). The substrate remains unreacted in both protic and aprotic polar solvents (entry 8). The presence of TEMPO could largely suppress the formation of **2** revealing the formation of a radical intermediate in the reaction (entry 9).

**Table 1. Optimization Study of Intramolecular Acylation<sup>a</sup>**

entry	<i>t</i> -BuOOH (equiv)	TBAI (mol %)	temp (°C)	yield of 2 <sup>b</sup> (%)
1	8	-	100	42
2	4	-	100	60
3	4	5	100	76
4	4	10	100	Complex mixture
5 <sup>c</sup>	4	5	100	0
6	2	5	100	38
7	4	5	80	45
8 <sup>d</sup>	4	5	100	0
9 <sup>e</sup>	4	5	100	0

<sup>a</sup>Substrate (0.2 mmol), *t*-BuOOH (2 to 8 equiv), TBAI (5 to 10 mol%), DCE (0.5 mL), 100 °C, 24 h.

<sup>b</sup>isolated yield. <sup>c</sup>KI or I<sub>2</sub> as an additive. <sup>d</sup>MeOH/DMF/DMSO as a solvent. <sup>e</sup>TEMPO (10 equiv) added as a radical quencher.

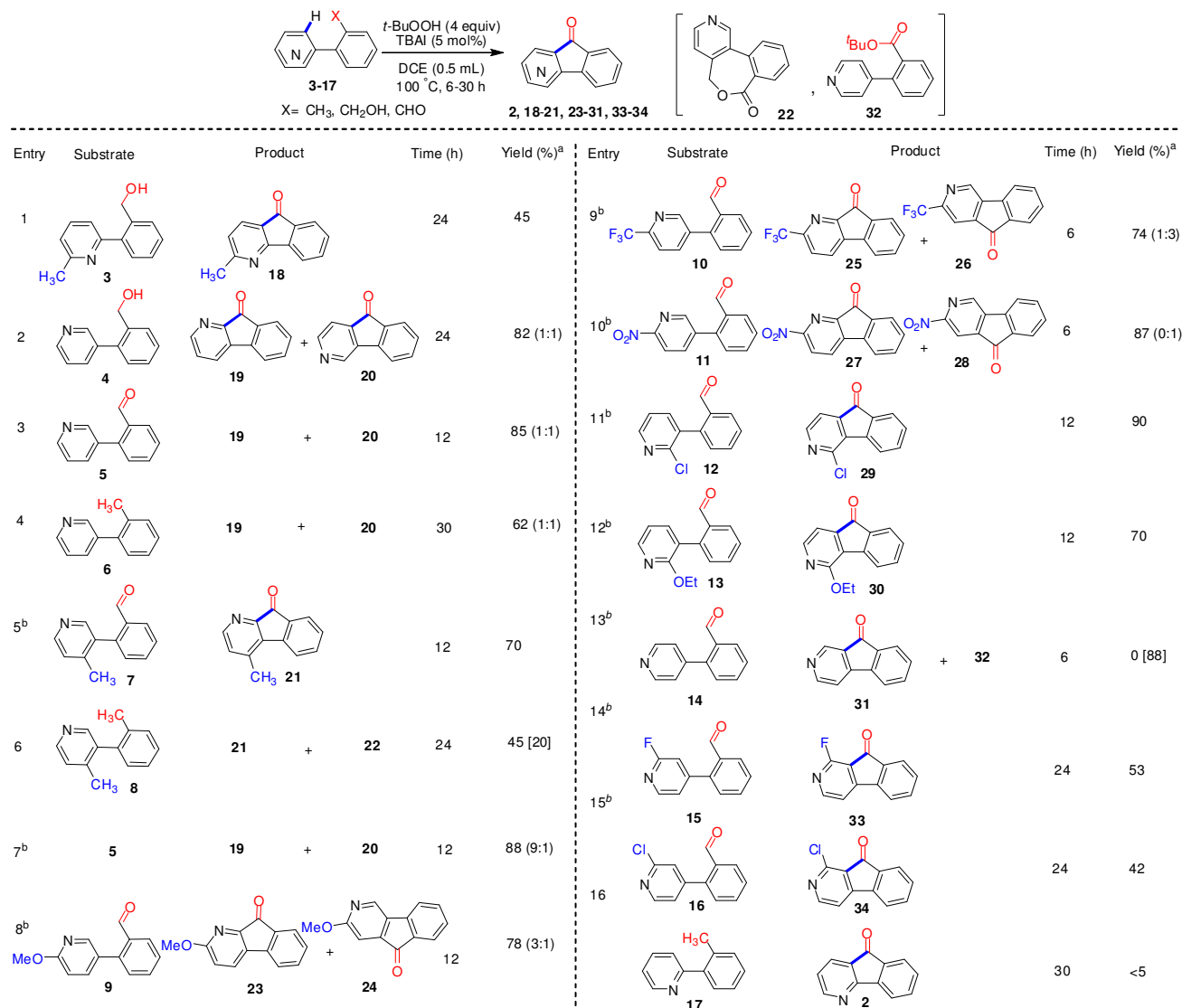
The optimized conditions were utilized to investigate the substrate scope not only for 4-azafluorenones, but also for the synthesis of other azafluorenones (Scheme 2). The preparation of starting arylpyridines **3–17** was achieved from the commercially available materials. When 2-arylpyridine **3** was exposed to the standard conditions, intramolecular acylation occurred at the 3-position yielding 4-azafluorenone **18** in 45% yield (entry 1). The incomplete conversion of **3** to the product **18** could largely account for the observed

moderate yield. Under the optimized conditions, each of 3-arylpyridine **4** and **5** bearing a hydroxymethyl or aldehyde group on arene is intramolecularly acylated at the 2- and 4-positions yielding a 1:1 mixture of 1-azafluorenone (**19**) and 3-azafluorenone (**20**) in comparable combined yields (entries 2-3). More importantly, 3-arylpyridine **6** with a methyl group on arene ring also underwent intramolecular cyclization to give a 1:1 mixture of **19** and **20** in a combined 62% yield (entry 4). The difficulty of C-H functionalizations of a methyl group compared to a hydroxymethyl or aldehyde group could apparently explain the somewhat reduced yield. Evidently, 3-arylpyridine **7** worked eventfully under the optimized conditions, wherein a methyl group remains unaffected (entry 5). When two methyl groups, each on pyridine and phenyl rings are present as in 3-arylpyridine **8**, a competitive C-H functionalization is anticipated between the two methyl groups. However, the methyl group on phenyl ring undergoes C-H functionalizations, and the cyclization occurs regioselectively on the pyridine ring along with a minor product **22** (entry 6). The compound **22** could form by the intramolecular trapping of acyl radical with the hydroxymethyl group, generated in situ from the methyl group. Remarkably, an excellent regiocontrol (1-: 3-azafluorenone = 9:1 ratio) to the formation of 3-azafluorenone **19** was observed when **5** was subjected to the optimized conditions in the absence of TBAI (entry 7). The reasonable explanation for this excellent regioselectivity requires further investigation. However, a moderate regiocontrol (3:1) was observed in the formation of azafluorenones **23** and **24** (entry 8). In addition, reverse regiocontrol (1:3) was observed with trifluoromethyl group at 2-position gave azafluorenones **25** and **26** (entry 9). Nonetheless, strong electron withdrawing group at 2-position in **11** formed only one regioisomer **28** in 87% yield (entry 10). The presence of a chloro substituent at the 2-position of 3-arylpyridine **12** gave 3-azafluorenone **29** in 90% yield under the optimized conditions (entry 11). Similarly, 2-ethoxy-3-arylpyridine **13** also reacted under the optimized conditions resulting in the formation of 3-azafluorenone **30** in



70% yield (entry 12). Attempted preparation of 2-azafluorenone **31** from 4-arylpyridine **14** under the optimized conditions was not successful. However, a *tert*-butyl ester **32** was isolated in this reaction. This suggests that an acyl radical was generated from **14**, which upon subsequent trapping with *t*-butanol gave **32** (entry 13). The poor reactivity at the C-3 position in the 4-arylpyridine ring towards acyl radical was largely circumvented by the presence of an electron-withdrawing group at 2-position. Thus, 4-arylpyridine **15** under the optimized conditions yielded 2-azafluorenone **33** regioselectively in 53% isolated yield (entry 14). This observation indicated that 4-arylpyridine **15** undergoes regioselective cyclization at the more electron-deficient C-3 position. Similarly, 4-arylpyridine **16** undergoes cyclization at 2-position afforded azafluorenone **34** in 42% yield (entry 15). Under the optimized conditions, 2-arylpyridine **17** was less viable for cyclization and gave 4-azafluorenone (**2**) only in trace amount (entry 16). Central to this investigation was an unprecedented intramolecular acylation of unactivated pyridines at 2, 3, and 4-positions occurred under transition-metal-free conditions via multiple C-H functionalizations. The intramolecular acylation of pyridines reported herein is clearly distinct from our previous report and the classical acylation approaches currently available in the literature.

## Scheme 2. Scope of Azafluorenone Synthesis

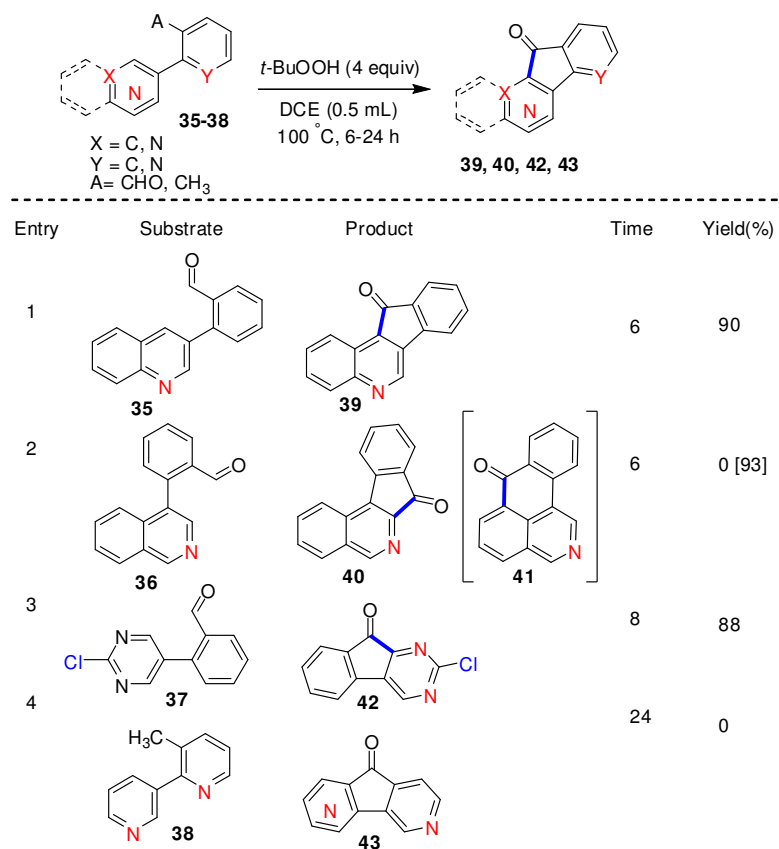


<sup>a</sup>isolated yields of products. <sup>b</sup>reaction without TBAI, DCE (0.2 mL).

The scope of aryl quinoline, aryl isoquinoline, aryl pyrimidine and bipyridine as substrates was also examined (Scheme 3). Under the standard conditions, 3-arylquinoline **35**,

underwent regioselective intramolecular acylation at the 4-position affording **39** in 90% yield. However, aryl isoquinoline **36** failed to undergo intramolecular acylation on the pyridine ring to give compound **40**. Instead, an intramolecular acylation on the arene ring afforded **41** in 93% yield. The aryl pyrimidine **37** was also found useful for cyclization forming **42** in 88% yield. We also prepared a bipyridine compound **38**, which upon attempted cyclization under the standard reaction condition did not give the cyclized product **43**. Nevertheless, our protocol is quite resourceful for the synthesis of azafluorenone related compounds.

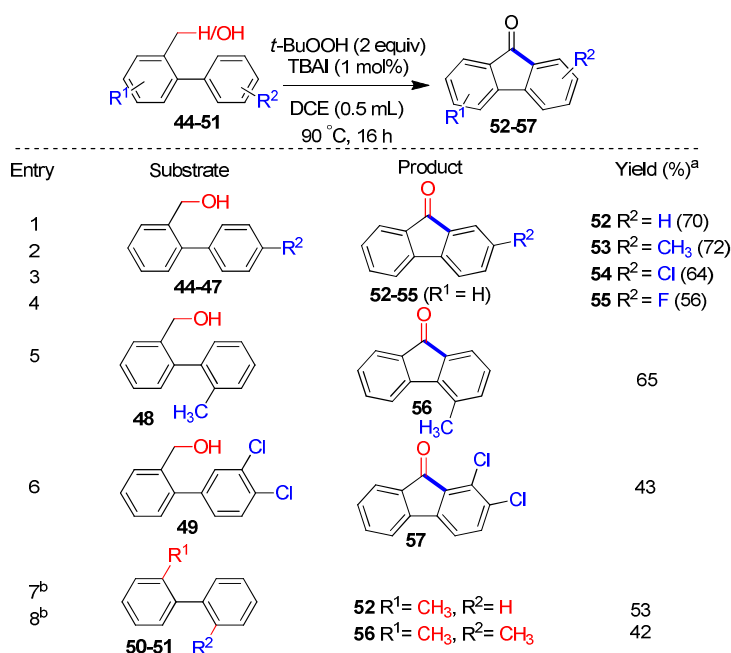
### Scheme 3. Synthesis of Azafluorenone Related Compounds



The application of our protocol was further extended to the synthesis of fluorenones with a methyl or hydroxymethyl group as the acylating agent (Scheme 4). To our delight, intramolecular acylation of 2-phenylbenzylalcohol **44** in the presence of 2 equiv. *t*-BuOOH

and 1 mol% TBAI in DCE at 90 °C gave fluorenone **52** in 70% yield. Various other 2-arylbenzylalcohols **45-49** with an *ortho*, *meta*, or *para*-substituent on the aryl ring reacted eventually affording good to excellent yields (43–72%) of fluorenones **53-57**. Interestingly, a substrate **48** containing both -CH<sub>2</sub>OH and -CH<sub>3</sub> functional groups when exposed to the optimized conditions, the intramolecular acylation occurred involving -CH<sub>2</sub>OH group affording 4-methyl fluorenone (**56**) in 65% yield (entry 5). While an unsymmetrically substituted biaryl could give two different regioisomers, the biaryl **49** regioselectively cyclized at electron-deficient 2-position of aryl rings yielding **57** in 43% yield (entry 6). Furthermore, a substrate **50** with one methyl group cyclized to give fluorenone **52**, while substrate **51** containing two methyl groups, each on a phenyl ring, intramolecular acylation occurred involving one methyl group (entry 7-8).

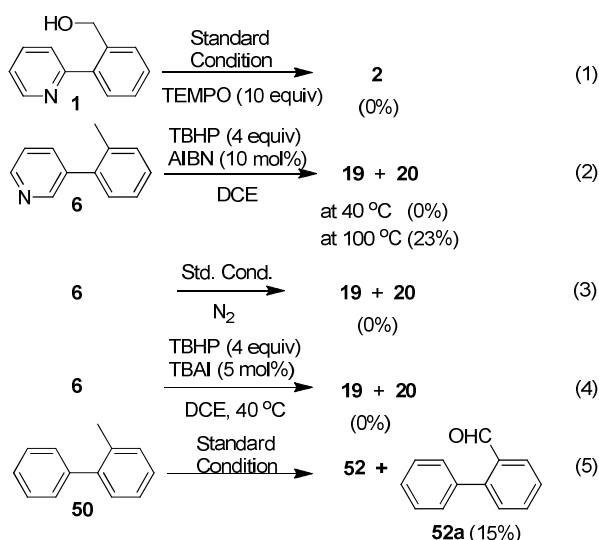
**Scheme 4. Synthesis of Fluorenones from 2-Arylbenzylalcohols and 2-Methylbiaryls**



<sup>a</sup>isolated yields of products. <sup>b</sup>*t*-BuOOH (8 equiv), TBAI (10 mol%), DCE (0.5 mL), 100 °C, 24 h.

To understand the mechanism for intramolecular acylation, we performed some control experiments (Scheme 5). As stated in optimization study, use of a radical quencher TEMPO (10 equiv) largely inhibits the formation of the desired product, suggesting a free radical pathway is involved in this reaction (Eq 1). Reaction of substrate **6** and TBHP (4 equiv) in DCE in the presence of AIBN (10 mol%) at 40 °C did not give any product. However, the corresponding intramolecular cyclization products **19** and **20** were obtained at elevated temperature (100 °C) *albeit* in low yield (23%) (Eq 2). An experiment with compound **6** was performed under the standard condition in an inert atmosphere. Compound **6** did not yield any cyclized product. This observation reveals that oxygen is indeed required as the O source or as an oxidant (Eq 3). Under the standard condition, however, at a lower temperature (at 40 °C), compound **6** did not give any cyclized compound (Eq 4). Interestingly, we also observed that substrate 2-methylbiaryl **50** formed fluorenone **52** along with a minor product **52a** containing an aldehyde group (Eq 5).

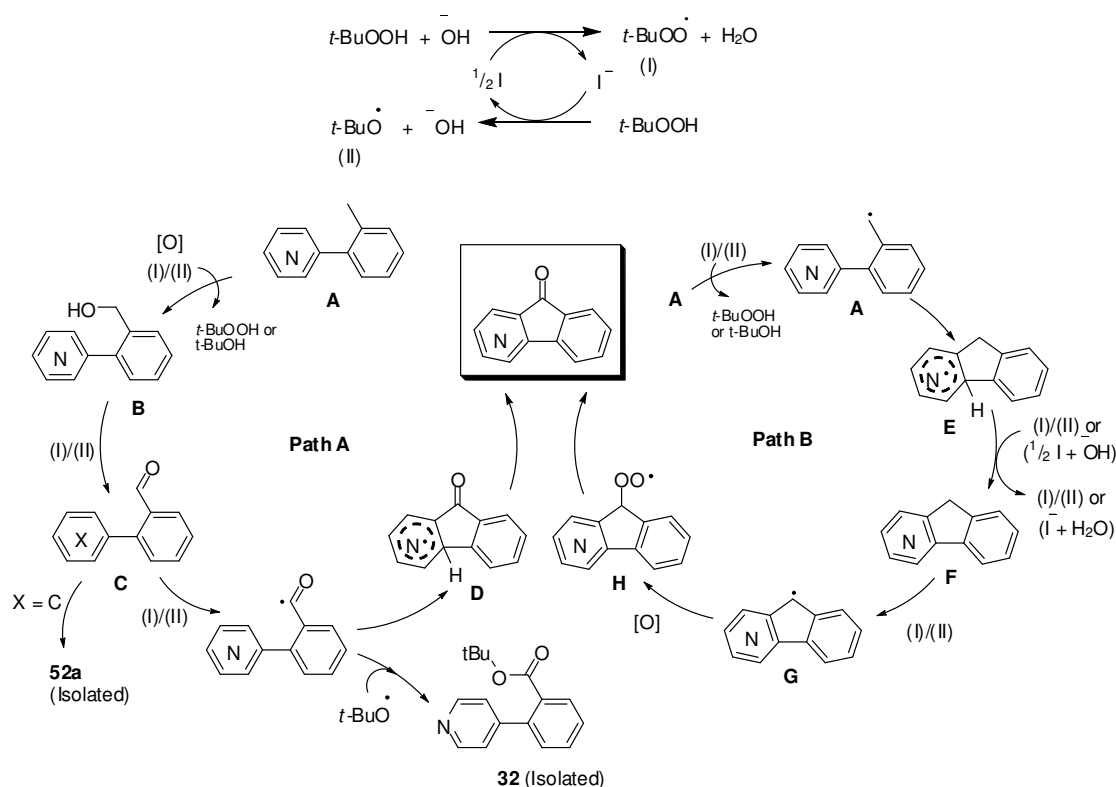
Scheme 5. Control Experiments



Based on these observations and our previous experiences,<sup>7</sup> we propose a plausible mechanism for this intramolecular acylation as depicted in Scheme 6. As the reaction is

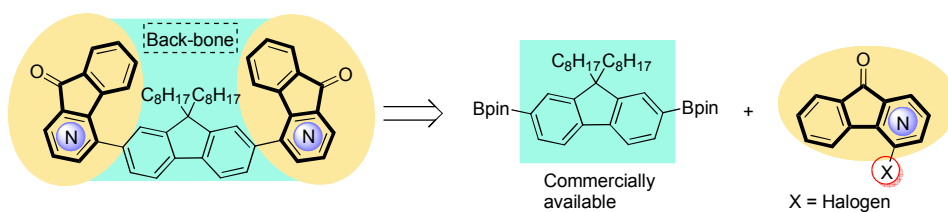
radical in nature, two different pathways could be operative. In Path A, TBAI could promote radical generation<sup>12</sup> from TBHP, which upon H• abstraction from substrate **A** could form benzyl radical. Subsequent oxidation could give a hydroxymethyl containing intermediate **B**. The oxidation of hydroxymethyl could afford intermediate **C** with an aldehyde functionality. Subsequently, a C-centered radical could easily be formed from **C**, which could undergo substitution on the pyridine ring to give heterohexadienyl radical intermediate **D**. The H• abstraction either by TBHP or iodine species would deliver azafluorenone. In Path B, the C-centered radical could undergo direct substitution<sup>13</sup> on the pyridine ring to form intermediate **E**, which upon proton abstraction by excess TBHP or iodine species could deliver azafluorene **F**. Oxidation of **F** could give azafluorenone. Based on our experiments, Path A is more likely in this reaction. However, occurrence of Path B or concurrence of both path ways is not ruled out.

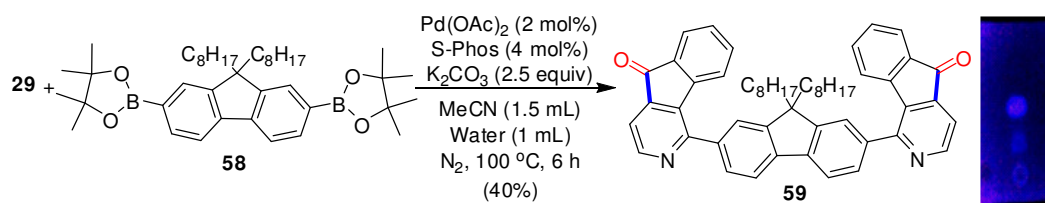
### Scheme 6. Plausible Mechanism



The design of single fluorene molecule based fluorescent organic emissive materials for potential use in organic light emitting devices (OLEDs) is one of the emerging technologies in the field of organic electronics.<sup>14</sup> The currently available single fluorene emitters suffer from many desirable properties, namely, a specific emission, high charge-carrier mobility, good thermal and electrochemical stability, high photoluminescence quantum yield, and facile chemical modification.<sup>15</sup> A chromophoric group incorporated into the fluorene backbone could lead to extensive designing of new OLEDs. A 9,9-dialkylfluorene backbone tethered with azafluorenone has never been explored in OLED preparation despite their potential electron injection properties (Scheme 7). To demonstrate a translational application of our newly developed protocol for the synthesis of azafluorenones, we prepared a fluorene based butterfly shaped molecule **59** tethered with 3-azafluorenone **29**. When 3-azafluorenone **29** was reacted with 9,9-dioctyl-9H-fluorene-2,7-diboronic acid bis(pinacol) ester (**58**) under Suzuki cross-coupling reaction conditions, a novel fluorene-azafluorenone coupled product **59** was obtained. The absorption spectra displayed  $\lambda_{\text{max}}$  at 326 nm while the photoluminescence spectra of **59** displayed  $\lambda_{\text{emission}} = 515$  nm in toluene and 498 nm in cyclohexane, and  $\lambda_{\text{excitation}} = 445$  nm in toluene and 442 nm in cyclohexane (see the Supporting Information). The detailed photophysical properties of **59** will be described elsewhere. This preliminary study could open a new avenue for the preparation of single fluorene based fluorescent organic materials for potential use in OLEDs.

**Scheme 7. Synthesis of Fluorene Based Organic Fluorescent Tethered with 3-Azafluorenone**





In conclusion, we have developed a general strategy to the synthesis of all four azafluorenones. Unlike classical approaches reported for acylations of pyridines, the current study describes intramolecular acylation of unactivated pyridines using a methyl, hydroxymethyl, or aldehyde groups as acylating agent under transition-metal-free conditions. The protocol is extended to the synthesis of fluorenones and related fused heterocycles. Also, we have designed and synthesized a single fluorene molecule based organic materials incorporated with azafluorenone.

## EXPERIMENTAL SECTION

### General Methods

Unless noted otherwise, all reagents and solvents were purchased from commercial sources and used as received. All reactions were performed in a screw-capped vial. The proton (<sup>1</sup>H) and carbon (<sup>13</sup>C) NMR spectra were obtained using a 400 MHz using Me<sub>4</sub>Si as an internal standard and are reported in  $\delta$  units. Coupling constants (*J* values) are reported in Hz. Column chromatography was performed on silica gel (60–120#, 100–200#). High resolution mass spectra (HRMS) were obtained using the electron spray ionization (ESI) technique and as TOF mass analyzer. IR spectra are reported in cm<sup>-1</sup> units. All melting points were taken using a melting point apparatus equipped with a calibrated thermometer and are uncorrected. 2-Bromo-3-methyl pyridine, arylboronic acid derivatives, *t*-butyl hydroperoxide (TBHP, 5.5 M in decane), and *tetra*-butyl ammonium iodide (TBAI), Azobisisobutyronitrile (AIBN) and solvents were purchased and used as received.



General procedure for the Suzuki coupling of bromoheteroarenes with 2-formyl benzeneboronic acid (for compounds **5**, **7**, **9–16**, **35–37**)

Following a literature procedure,<sup>16</sup> a solution of bromoheteroarene (e.g. bromopyridine or 3-bromoquinoline or 4-bromoisoquinoline or 5-bromo 2-chloro pyrimidine) (1 equiv, 0.5 mmol), 2-formyl benzeneboronic acid (1.2 equiv, 0.6 mmol), Pd(PPh<sub>3</sub>)<sub>4</sub> (5 mol %) and sodium carbonate (2 equiv, 1 mmol) in THF:Water (4:1, 3 mL), was heated at 70 °C for 12 h. THF was evaporated *in vacuo*. Water (20 mL) was added, and the reaction mixture was extracted with ethyl acetate (2×10 mL). The organic layers were combined, dried (Na<sub>2</sub>SO<sub>4</sub>), concentrated under reduced pressure, and purified by column chromatography (100–200# silica, ethyl acetate/hexane = 3:7) to give the desired product.

General procedure for the synthesis of compounds **1**, **3** and **4**

Following a literature procedure,<sup>17</sup> a suspension of 2-bromobenzyl alcohol (0.7 mmol), bispinacolato diboron (1.1 equiv, 0.77 mmol), 1,1'-Bis(diphenylphosphino)ferrocene dichloride [Pd(dppf)Cl<sub>2</sub>, 3 mol %], and KOAc (3 equiv, 1.5 mmol) in anhydrous DMF (2 mL) was purged twice with nitrogen balloon and heated at 80 °C for 9 h. After complete consumption of 2-bromobenzylalcohol (monitored by TLC), the reaction mixture was added to the ice cooled water (10 mL) and extracted with ethyl acetate (2×10 mL) and water (2×20 mL), dried (Na<sub>2</sub>SO<sub>4</sub>), and concentrated *in vacuo*. The crude was directly used for the next step without purification. A stirred solution of the crude product, bromopyridine (0.5 mmol), Pd(PPh<sub>3</sub>)<sub>4</sub> (5 mol %) and sodium carbonate (2 equiv, 1 mmol) in THF:Water (4:1, 3 mL) was stirred at 70 °C for 12 h. THF was evaporated *in vacuo*. Water (20 mL) was added, and the reaction mixture was extracted with ethyl acetate (2×10 mL). The organic layers were combined, dried (Na<sub>2</sub>SO<sub>4</sub>), concentrated under reduced pressure, and purified by column chromatography (100–200# silica, ethyl acetate /hexane = 2:8) to give the desired product.

General procedure for the synthesis of (*o*-tolyl)pyridines (compounds **6**, **8**, **17**)

Following a literature procedure,<sup>16</sup> a solution of bromopyridine (1 equiv, 0.5 mmol), 2-methyl benzeneboronic acid (1.2 equiv, 0.6 mmol), Pd(PPh<sub>3</sub>)<sub>4</sub> (5 mol %) and sodium carbonate (2 equiv, 1 mmol) in THF:Water (4:1, 3 mL), was heated at 70 °C for 12 h. THF was evaporated *in vacuo*. Water (20 mL) was added, and the reaction mixture was extracted with ethyl acetate (2×10 mL). The organic layers were combined, dried (Na<sub>2</sub>SO<sub>4</sub>), concentrated under reduced pressure, and purified by column chromatography (100-200# silica, ethyl acetate/hexane = 1:9) to give the desired product.

General procedure for the Suzuki coupling of 2-bromobenzyl alcohols with benzeneboronic acids (compounds **44**, **45**, **47-49**)

Following a literature procedure,<sup>16</sup> a solution of any 2-bromobenzylalcohol (1 equiv, 0.5 mmol), benzene boronic acid (1.2 equiv, 0.6 mmol), Pd(PPh<sub>3</sub>)<sub>4</sub> (5 mol %) and sodium carbonate (2 equiv, 1 mmol) in THF:Water (4:1, 3 mL), was heated at 70 °C for 12 h. THF was evaporated *in vacuo*. Water (20 mL) was added, and the reaction mixture was extracted with ethyl acetate (2×10 mL). The organic layers were combined, dried (Na<sub>2</sub>SO<sub>4</sub>), concentrated under reduced pressure, and purified by column chromatography (100–200# silica, ethyl acetate/hexane = 2:8) to give the desired product.

Procedure for the synthesis of **46**

Following a literature procedure,<sup>17</sup> a suspension of 4-chloro bromobenzene (0.7 mmol), bispinacolato diboron (1.1 equiv, 0.77 mmol), 1,1'-Bis(diphenylphosphino)ferrocene dichloride (Pd(dppf)Cl<sub>2</sub>, 3 mol %), and KOAc (3 equiv, 1.5 mmol) in anhydrous DMF (2 mL) was heated at 80 °C for 5 h under nitrogen atmosphere. After complete consumption of 4-chloro bromobenzene (monitored by TLC), the reaction mixture was added to the ice cooled water (10 mL) and extracted with ethyl acetate (2×10 mL) and water (2×20 mL), dried (Na<sub>2</sub>SO<sub>4</sub>), and concentrated *in vacuo*. The crude was directly used for the next step without purification. A stirred solution of the crude product, 2-bromobenzyl alcohol (0.5 mmol), Pd(PPh<sub>3</sub>)<sub>4</sub> (5 mol %) and sodium carbonate (2 equiv, 1 mmol) in

THF:Water (4:1, 3 mL) was stirred at 70 °C for 12 h. THF was evaporated *in vacuo*. Water (20 mL) was added, and the reaction mixture was extracted with ethyl acetate (2×10 mL). The organic layers were combined, dried (Na<sub>2</sub>SO<sub>4</sub>), concentrated under reduced pressure, and purified by column chromatography (100–200# silica, ethyl acetate /hexane = 1:9) to give the desired product.

General procedure for the synthesis of 2-methyl biaryls (**50**, **51**)

Following a literature procedure,<sup>16</sup> a solution of 2-bromotoluene (1 equiv, 0.5 mmol), benzene boronic acid (1.2 equiv, 0.6 mmol), Pd(PPh<sub>3</sub>)<sub>4</sub> (5 mol %) and sodium carbonate (2 equiv, 1 mmol) in THF:Water (4:1, 3 mL), was heated at 70 °C for 12 h. THF was evaporated *in vacuo*. Water (20 mL) was added, and the reaction mixture was extracted with ethyl acetate (2×10 mL). The organic layers were combined, dried (Na<sub>2</sub>SO<sub>4</sub>), concentrated under reduced pressure, and purified by column chromatography (100–200# silica, ethyl acetate/hexane = 0.1:99.9) to give the desired product.

General procedure for the azafluorenones (**2**, **18**, **19–20**, **21**) [from the substrates containing -CH<sub>2</sub>OH and CH<sub>3</sub>]

In an oven-dried screw capped vial equipped with a magnetic stir bar, a solution of (2-(pyridin-3-yl)phenyl)methanol or 3-(*o*-tolyl)pyridine (0.15 mmol), TBHP (4 equiv), TBAI (5 mol%) and DCE (0.5 mL) was heated at 100 °C for 12–30 h. Silica gel was added to the reaction mixture and the excess solvent was evaporated. The silica gel mixed with the crude product was loaded on the column, which upon chromatography (ethyl acetate /hexane = 1:9 – 3:7) afforded desired product.

General procedure for the azafluorenones (**19–20**, **21**, **23–26**, **28–34**) or azafluorenone related compounds (**39**, **41**, **42**) [from the substrates containing -CHO group]

In an oven-dried screw capped vial equipped with a magnetic stir bar, a solution of 2-(2-pyridin-3-yl)benzaldehyde (0.15 mmol), TBHP (4 equiv) and DCE (0.2 mL) was heated at 100 °C for 6–24 h. Silica gel was added to the reaction mixture and the excess solvent was evaporated. The silica gel mixed

with the crude product was loaded on the column, which upon chromatography (ethyl acetate /hexane = 1:9 – 3:7) afforded desired product.

General procedure for the synthesis of fluorenones (**52–57**) [from the substrates containing –CH<sub>2</sub>OH]

In an oven-dried screw capped vial equipped with a magnetic stir bar, a solution of 2-arylbenzyl alcohol (0.2 mmol), TBHP (2 equiv), TBAI (1 mol%) and DCE (0.5 mL) was heated at 90 °C for 16 h. Silica gel was added to the reaction mixture and the excess solvent was evaporated. The silica gel mixed with the crude product was loaded on the column, which upon chromatography (ethyl acetate /hexane = 0.5:9.5 – 1:9) afforded desired product.

General procedure for the synthesis of fluorenones (**52, 56**) [from the substrates containing –CH<sub>2</sub>OH]

In an oven-dried screw capped vial equipped with a magnetic stir bar, a solution of 2-methylbiaryls (0.2 mmol), TBHP (8 equiv), TBAI (10 mol%) and DCE (0.5 mL) was heated at 100 °C for 24 h. Silica gel was added to the reaction mixture and the excess solvent was evaporated. The silica gel mixed with the crude product was loaded on the column, which upon chromatography (ethyl acetate /hexane = 0.5:9.5 – 1:9) afforded desired product.

#### (2-(Pyridin-2-yl)phenyl)methanol (**1**)

Pale yellow oil; Yield 65% (60 mg); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 8.64 (ddd, *J* = 5.0, 1.8, 1.0 Hz, 1H), 7.89–7.83 (m, 1H), 7.63 (td, *J* = 8.0, 1.0 Hz, 1H), 7.57–7.54 (m, 1H), 7.52–7.48 (m, 1H), 7.45–7.41 (m, 2H), 7.33 (ddd, *J* = 7.5, 5.0, 1.0 Hz, 1H), 4.48 (s, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 159.4, 148.2, 140.4, 140.0, 137.8, 131.3, 130.3, 129.5, 128.4, 124.0, 122.4, 64.8; HRMS: calcd for C<sub>12</sub>H<sub>12</sub>NO [M+H]<sup>+</sup> 186.0919, found 186.0920; IR (neat): 3304, 3062, 2925 cm<sup>-1</sup>.

#### 5*H*-Indeno[1,2-*b*]pyridin-5-one (**2**)<sup>7</sup>

The spectral data were consistent with previous report.<sup>7</sup>

**(2-(6-Methylpyridin-2-yl)phenyl)methanol (3)**

Pale yellow oil; Yield 55% (55 mg);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.73–7.79 (m, 1H), 7.54–7.56 (m, 1H), 7.49–7.51 (m, 1H), 7.41–7.46 (m, 3H), 7.20 (d,  $J$  = 8.0 Hz, 1H), 4.48 (s, 2H), 2.64 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  158.6, 157.0, 140.3, 137.7, 131.1, 130.1, 129.2, 128.1, 121.9, 120.9, 64.7, 24.9; HRMS: calcd for  $\text{C}_{13}\text{H}_{14}\text{NO}$   $[\text{M}+\text{H}]^+$  200.1075, found 200.1079; IR (neat): 3327, 3053, 2974  $\text{cm}^{-1}$ .

**(2-(Pyridin-3-yl)phenyl)methanol (4)**

Pale yellow oil; Yield 70% (65 mg);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.51–8.58 (m, 2H), 7.76 (d,  $J$  = 7.8 Hz, 1H), 7.62 (d,  $J$  = 7.5 Hz, 1H), 7.31–7.48 (m, 3H), 7.25 (d,  $J$  = 7.5 Hz, 1H), 4.57 (s, 2H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  149.5, 148.1, 138.6, 137.4, 136.9, 136.6, 130.1, 129.0, 128.6, 127.8, 123.2, 62.5; HRMS: calcd for  $\text{C}_{12}\text{H}_{12}\text{NO}$   $[\text{M}+\text{H}]^+$  186.0919, found 186.0925; IR (neat): 3310, 3048, 2933  $\text{cm}^{-1}$ .

**2-(Pyridin-3-yl)benzaldehyde (5)**

Off-white solid; Yield 73% (67 mg); mp 65–67  $^{\circ}\text{C}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  9.99 (s, 1H), 8.67–8.71 (m, 2H), 8.06–8.10 (m, 1H), 7.71–7.74 (m, 2H), 7.56–7.59 (m, 1H), 7.42–7.45 (m, 2H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  191.3, 150.1, 149.3, 141.8, 137.2, 133.9, 133.8, 133.7, 131.0, 128.7, 128.5, 123.2; HRMS-ESI  $m/z$  calcd for  $\text{C}_{12}\text{H}_{10}\text{NO}$   $[\text{M}+\text{H}]^+$  184.0762, found 184.0769; IR (KBr): 3067, 2825, 1692  $\text{cm}^{-1}$ .

**3-(*o*-Tolyl)pyridine (6)<sup>18</sup>**

Colorless oil;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.60–8.63 (m, 2H) 7.66–7.70 (m, 1H) 7.38 (ddd,  $J$  = 7.78, 4.89, 0.88 Hz, 1H), 7.28–7.35 (m, 3H), 7.22–7.26 (m, 1H), 2.30 (s, 3H).

**2-(4-Methylpyridin-3-yl)benzaldehyde (7)**

Pale yellow oil; Yield 85% (83 mg);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  9.79 (s, 1H), 8.56 (d,  $J = 5.0$  Hz, 1H), 8.44 (s, 1H), 8.07 (d,  $J = 7.8$  Hz, 1H), 7.70 (t,  $J = 7.5$  Hz, 1H), 7.60 (t,  $J = 7.5$  Hz, 1H), 7.32 (d,  $J = 7.5$  Hz, 1H), 7.27 (d,  $J = 5.0$  Hz, 1H), 2.15 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  191.2, 149.8, 149.3, 145.6, 141.0, 134.2, 134.1, 134.0, 131.1, 128.7, 128.3, 124.9, 19.8; HRMS: calcd for  $\text{C}_{13}\text{H}_{12}\text{NO}$   $[\text{M}+\text{H}]^+$  198.0919, found 198.0910; IR (neat): 3072, 2829, 1695  $\text{cm}^{-1}$ .

#### 4-Methyl-3-(*o*-tolyl)pyridine (8)

Pale yellow oil; Yield 60% (55 mg);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.48 (d,  $J = 5.0$  Hz, 1H), 8.35 (s, 1H), 7.25–7.33 (m, 3H), 7.21 (d,  $J = 5.0$  Hz, 1H), 7.11 (d,  $J = 7.3$  Hz, 1H), 2.1 (s, 3H), 2.0 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  149.7, 148.4, 145.2, 137.5, 137.4, 136.2, 130.1, 129.54, 128.0, 125.8, 124.8, 19.8, 19.3; HRMS: calcd for  $\text{C}_{13}\text{H}_{14}\text{N}$   $[\text{M}+\text{H}]^+$  184.1126, found 184.1121; IR (neat): 3029, 2941  $\text{cm}^{-1}$ .

#### 2-(6-Methoxypyridin-3-yl)benzaldehyde (9)

Light yellow oil; Yield 92% (98 mg);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  10.02 (s, 1H), 8.19 (dd,  $J = 2.6$ , 0.6 Hz, 1H), 8.03–8.07 (m, 1H), 7.67 (td,  $J = 7.5$ , 1.5 Hz, 1H), 7.63 (dd,  $J = 8.5$ , 2.5 Hz, 1H), 7.50–7.56 (m, 1H), 7.40–7.45 (m, 1H), 6.88 (dd,  $J = 8.53$ , 0.75 Hz, 1H), 4.02 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  191.7, 164.1, 147.3, 142.1, 140.0, 133.9, 133.8, 131.0, 128.3, 128.1, 126.6, 110.7, 53.7; HRMS: calcd for  $\text{C}_{13}\text{H}_{12}\text{NO}_2$   $[\text{M}+\text{H}]^+$  214.0868, found 214.0870; IR (neat): 3062, 2947, 1693  $\text{cm}^{-1}$ .

#### 2-(6-(trifluoromethyl)pyridin-3-yl)benzaldehyde (10)

Off-white solid; Yield 82% (102 mg); mp 100–101  $^\circ\text{C}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  10.00 (d,  $J = 0.5$  Hz, 1H), 8.78 (d,  $J = 2.0$  Hz, 1H), 8.10 (dd,  $J = 7.7$ , 1.2 Hz, 1H), 7.92 (ddt,  $J = 8.0$ , 1.4, 0.6 Hz, 1H), 7.83 (dd,  $J = 8.0$ , 0.7 Hz, 1H), 7.73–7.78 (m, 1H), 7.64–7.70 (m, 1H), 7.42–7.48 (m, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  190.8, 150.2, 147.8 ( $J = 34$  Hz), 139.8, 138.4, 137.1, 134.1, 133.8, 131.1, 129.8,

129.5, 122.9 ( $J = 273$  Hz), 120.1 ( $J = 3$  Hz); HRMS: calcd for  $C_{13}H_9F_3NO$   $[M+H]^+$  252.0636, found 252.0643; IR (KBr): 2920, 2077, 1729  $cm^{-1}$ .

### 2-(6-Nitropyridin-3-yl)benzaldehyde (11)

Light yellow solid; Yield 90% (103 mg); mp 122-124 °C;  $^1H$  NMR (400 MHz,  $CDCl_3$ ):  $\delta$  10.01 (s, 1H), 8.66 (dd,  $J = 2.3, 0.8$  Hz, 1H), 8.39 (dd,  $J = 8.3, 0.5$  Hz, 1H), 8.09 (dd,  $J = 7.7, 1.4$  Hz, 1H), 8.06 (dd,  $J = 8.3, 2.3$  Hz, 1H), 7.78 (dt,  $J = 7.5, 1.5$  Hz, 1H), 7.72 (dt,  $J = 7.5, 1.0$  Hz, 1H), 7.45 (dd,  $J = 7.4, 1.1$  Hz, 1H);  $^{13}C$  NMR (100 MHz,  $CDCl_3$ ):  $\delta$  190.6, 156.0, 148.9, 140.6, 140.5, 138.2, 134.2, 133.7, 131.2, 130.0, 117.5; HRMS: calcd for  $C_{12}H_9N_2O_3$   $[M+H]^+$  229.0613, found 229.0609; IR (KBr): 3063, 2887, 1695  $cm^{-1}$ .

### 2-(2-Chloropyridin-3-yl)benzaldehyde (12)

Yellow solid; Yield 83% (90 mg); mp 176-178°C;  $^1H$  NMR (400 MHz,  $CDCl_3$ ):  $\delta$  9.87 (s, 1H), 8.51 (dd,  $J = 4.8, 2.0$  Hz, 1H), 8.06 (dd,  $J = 7.8, 1.0$  Hz, 1H), 7.66–7.76 (m, 2H), 7.58–7.66 (m, 1H), 7.40 (dd,  $J = 7.5, 5.0$  Hz, 1H), 7.35 (dd,  $J = 7.7, 0.9$  Hz, 1H);  $^{13}C$  NMR (100 MHz,  $CDCl_3$ ):  $\delta$  190.7, 150.3, 149.5, 139.9, 139.9, 133.9, 133.7, 131.0, 129.3, 129.0, 122.4; HRMS: calcd for  $C_{12}H_9ClNO$   $[M+H]^+$  218.0372, found 218.0379; IR (KBr): 2924, 2085, 1735, 772  $cm^{-1}$ .

### 2-(2-Ethoxypyridin-3-yl)benzaldehyde (13)

Brown oil; Yield 80% (91 mg);  $^1H$  NMR (400 MHz,  $CDCl_3$ ):  $\delta$  9.93 (d,  $J = 0.7$  Hz, 1H), 7.99 (dd,  $J = 7.9, 1.3$  Hz, 1H), 7.60–7.66 (m, 1H), 7.47–7.53 (m, 1H), 7.41–7.46 (m, 2H), 7.36–7.40 (m, 1H), 6.36 (t,  $J = 6.7$  Hz, 1H), 4.08 (q,  $J = 7.1$  Hz, 2H), 1.41 (t,  $J = 7.2$  Hz, 3H);  $^{13}C$  NMR (100 MHz,  $CDCl_3$ ):  $\delta$  191.6, 161.4, 139.6, 139.5, 137.6, 134.6, 133.6, 131.0, 130.0, 128.3, 127.9, 106.1, 45.7, 14.6; HRMS: calcd for  $C_{14}H_{13}NO_2$   $[M]^+$  227.0946, found 227.0950; IR (neat): 2929, 2081, 1734  $cm^{-1}$ .

### 2-(Pyridin-4-yl)benzaldehyde (14)

Light yellow solid; Yield 81% (74 mg); mp 79-81°C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  9.96 (s, 1H), 8.71 (d,  $J = 5.8$  Hz, 2H), 8.04 (dd,  $J = 7.8, 1.3$  Hz, 1H), 7.63–7.70 (m, 2H), 7.40–7.42 (m, 1H), 7.30–7.32 (m, 2H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  191.2, 149.8, 133.9, 133.5, 132.1, 130.4, 129.1, 128.6, 128.4, 124.8; HRMS: calcd for  $\text{C}_{12}\text{H}_{10}\text{NO}$   $[\text{M}+\text{H}]^+$  184.0762, found 184.0775; IR (KBr): 3080, 2832, 1696  $\text{cm}^{-1}$ .

### 2-(2-Fluoropyridin-4-yl)benzaldehyde (15)

Light yellow solid; Yield 62% (62 mg); mp 104-106 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  9.99 (d,  $J = 0.8$  Hz, 1H), 8.07 (dd,  $J = 4.5$  Hz, 1H), 7.74–7.78 (m, 1H), 7.77–7.64 (m, 2H), 7.40–7.44 (m, 1H), 7.30 (d,  $J = 5.5$  Hz, 2H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  190.8, 164.2, 161.6 ( $J = 261$  Hz), 142.0, 134.0, 133.5, 130.4, 129.4, 129.3, 126.5, 117.7 ( $J = 21$  Hz), 113.6; HRMS: calcd for  $\text{C}_{12}\text{H}_9\text{FNO}$   $[\text{M}+\text{H}]^+$  202.0668, found 202.0670; IR (KBr): 3066, 2933, 1692  $\text{cm}^{-1}$ .

### 2-(2-Chloropyridin-4-yl)benzaldehyde (16)

Off-white solid; Yield 87% (94 mg); mp 100-102 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  10.00 (d,  $J = 0.7$  Hz, 1H), 8.51 (dd,  $J = 5.0, 0.7$  Hz, 1H), 8.05–8.11 (m, 1H), 7.70–7.76 (m, 1H), 7.60–7.67 (m, 1H), 7.38–7.45 (m, 2H), 7.26 (dd,  $J = 5.1, 1.6$  Hz, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  190.6, 151.9, 149.5, 149.2, 141.0, 134.0, 133.4, 130.0, 129.6, 129.0, 124.9, 123.5; HRMS: calcd for  $\text{C}_{12}\text{H}_9\text{ClNO}$   $[\text{M} + \text{H}]^+$  218.0373, found 218.0380; IR (KBr): 3060, 2895, 1698  $\text{cm}^{-1}$ .

### 2-(*o*-Tolyl)pyridine (17)<sup>19</sup>

Colorless oil;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.66–8.72 (m, 1H), 7.74 (td,  $J = 7.7, 1.9$  Hz, 1H), 7.37–7.42 (m, 2H), 7.21–7.31 (m, 4H), 2.36 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  160.0, 149.2, 140.4, 136.2, 135.8, 130.7, 129.6, 128.3, 125.9, 124.1, 121.7, 20.3.

### 2-Methyl-5*H*-indeno[1,2-*b*]pyridin-5-one (18)



Light yellow solid; Yield 45% (13 mg); mp 142–143 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.71(dd,  $J$  = 8.0, 0.6 Hz, 1H), 8.38 (dd,  $J$  = 7.9, 0.8 Hz, 1H), 7.88 (td,  $J$  = 8.0, 1.3 Hz, 1H), 7.68 (td,  $J$  = 8.4, 1.0 Hz, 1H), 7.56 (d,  $J$  = 8.4 Hz, 1H), 7.28–7.30 (m, 1H), 2.68 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  196.4, 160.5, 155.0, 146.0, 135.8, 135.0, 130.3, 130.0, 125.0, 124.7, 123.3, 122.4, 24.22; HRMS: calcd for  $\text{C}_{13}\text{H}_{10}\text{NO}$   $[\text{M}+\text{H}]^+$  196.0762, found 196.0772; IR (KBr): 2924, 1734  $\text{cm}^{-1}$ .

#### **9*H*-Indeno[2,1-*b*]pyridin-9-one (19)<sup>20</sup>**

Yellow solid;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.60 (dd,  $J$  = 4.8, 1.3 Hz, 1H), 7.86 (dd,  $J$  = 7.5, 1.3 Hz, 1H), 7.75 (d,  $J$  = 7.5 Hz, 1H), 7.55–7.57 (m, 2H), 7.31–7.38 (m, 2H).

#### **9*H*-Indeno[2,1-*c*]pyridin-9-one (20)<sup>20</sup>**

Yellow solid;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.92 (s, 1H), 8.22 (dd,  $J$  = 4.5 Hz, 1H), 7.75 (d,  $J$  = 7.4 Hz, 1H), 7.66 (d,  $J$  = 7.4 Hz, 1H), 7.58 (td,  $J$  = 7.5 Hz, 1H), 7.52 (t,  $J$  = 4.6 Hz, 1H), 7.38 (t,  $J$  = 7.4 Hz, 1H).

#### **4-Methyl-9*H*-indeno[2,1-*b*]pyridin-9-one (21)**

Yellow solid; Yield 70% (20 mg); mp 150–152 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.45 (d,  $J$  = 5.0 Hz, 1H), 7.77 (d,  $J$  = 7.4 Hz, 1H), 7.64 (d,  $J$  = 7.5 Hz, 1H), 7.57 (td,  $J$  = 7.5, 1.2 Hz, 1H), 7.39 (td,  $J$  = 7.4, 0.8 Hz, 1H), 7.14 (d,  $J$  = 5.0, 0.6 Hz, 1H), 2.66 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  191.9, 151.8, 148.8, 141.6, 141.2, 137.6, 134.4, 131.2, 128.4, 128.3, 123.8, 122.8, 18.7; HRMS: calcd for  $\text{C}_{13}\text{H}_{10}\text{NO}$   $[\text{M}+\text{H}]^+$  196.0762, found 196.0764; IR (KBr): 3065, 2927, 1730  $\text{cm}^{-1}$ .

#### **Benzo[5,6]oxepino[4,3-*c*]pyridin-7(5*H*)-one (22)**

Pale yellow solid; Yield 20% (8 mg); mp 132–134 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.94 (s, 1H), 8.72 (d,  $J$  = 5.0 Hz, 1H), 8.04–8.09 (m, 1H), 7.72–7.79 (m, 1H), 7.64–7.70 (m, 1H), 7.59–7.64 (m, 1H), 7.42

(d,  $J = 5.0$  Hz, 1H), 5.03 (s, 2H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  169.3, 149.9, 149.0, 142.5, 134.3, 133.8, 133.1, 132.7, 130.8, 129.5, 128.4, 122.4, 67.7; HRMS: calcd for  $\text{C}_{13}\text{H}_{10}\text{NO}_2$   $[\text{M}+\text{H}]^+$  212.0712, found 212.0719; IR (KBr): 3043, 2912, 1745  $\text{cm}^{-1}$ .

### 3-Methoxy-5*H*-indeno[2,1-*b*]pyridin-5-one (23)

Yellow solid; Yield 62% (19 mg); mp 134–136 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.76 (d,  $J = 8.5$  Hz, 1H), 7.65 (dd,  $J = 7.2$ , 0.5 Hz, 1H), 7.48 (td,  $J = 7.5$ , 1.0 Hz, 1H), 7.38 (d,  $J = 7.2$  Hz, 1H), 7.24–7.30 (m, 1H), 6.84 (d,  $J = 8.2$  Hz, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  192.9, 165.9, 150.6, 142.0, 135.3, 134.9, 131.9, 130.6, 128.6, 124.6, 119.8, 115.6, 54.3; HRMS: calcd for  $\text{C}_{13}\text{H}_{10}\text{NO}_2$   $[\text{M} + \text{H}]^+$  212.0712, found 212.0710; IR (KBr): 2922, 2857, 1728  $\text{cm}^{-1}$ .

### 2-Methoxy-9*H*-indeno[1,2-*c*]pyridin-9-one (24)

Light yellow solid; Yield 16% (5 mg); mp 158–160 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.42 (s, 1H), 8.29 (s, 1H), 8.00 (d,  $J = 8.0$  Hz, 1H), 7.84 (td,  $J = 7.6$ , 1.5 Hz, 1H), 7.55–7.61 (m, 1H), 6.84 (d,  $J = 8.5$  Hz, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  194.7, 164.1, 155.4, 135.1, 134.7, 134.3, 130.8, 128.2, 121.2, 120.1, 108.7, 105.9, 54.4; HRMS: calcd for  $\text{C}_{13}\text{H}_{10}\text{NO}_2$   $[\text{M} + \text{H}]^+$  212.0712, found 212.0715; IR (KBr): 2922, 2857, 1728  $\text{cm}^{-1}$ .

### 2-(Trifluoromethyl)-5*H*-indeno[1,2-*b*]pyridin-5-one (25)

Yellow solid; Yield 19% (7 mg); mp 165–166 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.05 (dd,  $J = 8.0$ , 0.5 Hz, 1H), 7.82 (dt,  $J = 7.4$ , 0.9 Hz, 1H), 7.77 (d,  $J = 7.7$  Hz, 1H), 7.62–7.69 (m, 2H), 7.49 (ddd,  $J = 7.4$ , 6.2, 2.3 Hz, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  190.7, 153.4, 148.6 ( $J = 35$  Hz), 142.2, 136.1, 132.8, 131.2, 128.8, 125.3, 124.3 ( $J = 3$  Hz), 124.2, 122.6 ( $J = 274$  Hz), 122.0; HRMS: calcd for  $\text{C}_{13}\text{H}_7\text{F}_3\text{NO}$   $[\text{M}+\text{H}]^+$  250.0480, found 250.0476; IR (KBr): 3052, 2917, 1735  $\text{cm}^{-1}$ .

### 3-(Trifluoromethyl)-5*H*-indeno[1,2-*c*]pyridin-5-one (26)

Yellow solid; Yield 55% (21 mg); mp 153–155 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  9.00 (s, 1H), 7.89 (s, 1H), 7.81 (d,  $J = 7.5$  Hz, 1H), 7.75 (d,  $J = 7.5$  Hz, 1H), 7.66 (t,  $J = 7.4$  Hz, 1H), 7.51–7.46 (m, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  191.2, 150.0, 145.2 ( $J = 36$  Hz), 142.1, 141.7, 140.5, 136.0, 133.6, 131.0, 125.8, 122.5 ( $J = 273$  Hz), 122.0, 114.6; HRMS: calcd for  $\text{C}_{13}\text{H}_7\text{F}_3\text{NO}$   $[\text{M}+\text{H}]^+$  250.0480, found 250.0490; IR (KBr): 3055, 2910, 1735  $\text{cm}^{-1}$ .

### 3-Nitro-5*H*-indeno[1,2-*c*]pyridin-5-one (28)

Yellow solid; Yield 87% (29 mg); mp 208–210 °C:  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.79 (d,  $J = 0.8$  Hz, 1H), 8.35 (d,  $J = 1.0$  Hz, 1H), 7.76–7.81 (m, 1H), 7.74 (d,  $J = 7.5$  Hz, 1H), 7.59–7.66 (m, 1H), 7.43–7.49 (m, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  189.5, 144.3, 143.3, 140.7, 140.5, 136.3, 134.5, 131.7, 126.1, 122.7, 112.7; HRMS: calcd for  $\text{C}_{12}\text{H}_7\text{N}_2\text{O}_3$   $[\text{M} + \text{H}]^+$  227.0457, found 227.0454; IR (KBr): 3043, 2925, 1725  $\text{cm}^{-1}$ .

### 1-Chloro-5*H*-indeno[1,2-*c*]pyridin-5-one (29)

Yellow solid; Yield 90% (29 mg); mp 181–182 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.48 (d,  $J = 4.5$  Hz, 1H), 8.19 (d,  $J = 7.5$  Hz, 1H), 7.78 (d,  $J = 7.2$  Hz, 1H), 7.63 (td,  $J = 7.6, 1.2$  Hz, 1H), 7.51 (d,  $J = 4.5$  Hz, 1H), 7.44–7.45 (m, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  191.6, 151.3, 145.6, 143.5, 142.0, 135.9, 133.2, 130.3, 130.1, 125.3, 124.3, 116.5; HRMS: calcd for  $\text{C}_{12}\text{H}_7\text{ClNO}$   $[\text{M}+\text{H}]^+$  216.0216, found 216.0227; IR (KBr): 3067, 2920, 1726, 1262, 681  $\text{cm}^{-1}$ .

### 1-Ethoxy-5*H*-indeno[1,2-*c*]pyridin-5-one (30)

Yellow solid; Yield 70% (24 mg); mp 148–150 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.01–8.05 (m, 1H), 7.73 (td,  $J = 7.5, 1.2$  Hz, 1H), 7.67 (td,  $J = 7.4, 1.1$  Hz, 1H), 7.27–7.30 (m, 1H), 6.70 (d,  $J = 9.7$  Hz, 1H), 6.52 (d,  $J = 9.7$  Hz, 1H), 3.83–4.02 (m, 2H), 1.17 (t,  $J = 7.1$  Hz, 3H);  $^{13}\text{C}$  NMR (100 MHz,

CDCl<sub>3</sub>):  $\delta$  168.8, 166.9, 162.8, 146.0, 140.1, 135.2, 131.2, 128.0, 125.2, 124.8, 121.1, 35.8, 12.9;

HRMS: calcd for C<sub>14</sub>H<sub>12</sub>NO<sub>2</sub> [M+H]<sup>+</sup> 226.0868, found 226.0880; IR (KBr): 3055, 2933, 1730 cm<sup>-1</sup>.

***tert*-Butyl 2-(pyridin-4-yl)benzoate (32)**

Off-white solid, Yield 88% (34 mg); mp 98–99 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  8.57 (d, *J* = 5.8 Hz, 2H), 7.75 (d, *J* = 7.7 Hz, 1H), 7.54 (t, *J* = 7.5 Hz, 1H), 7.44 (t, *J* = 7.5 Hz, 1H), 7.29 (d, *J* = 7.3 Hz, 1H), 7.22 (d, *J* = 6.0 Hz, 2H) 1.0 (s, 9H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  192.8, 165.7, 149.7, 148.5, 139.5, 132.1, 130.3, 130.2, 128.6, 128.0, 123.4, 83.7, 25.9; HRMS: calcd for C<sub>16</sub>H<sub>18</sub>NO<sub>2</sub> [M+H]<sup>+</sup> 256.1338, found 256.1348; IR (KBr): 3021, 2926, 1755, 1262 cm<sup>-1</sup>.

**1-Fluoro-9*H*-indeno[2,1-*c*]pyridin-9-one (33)**

Light yellow solid; Yield 53% (15 mg); mp 159–161 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  8.54 (d, *J* = 5.8 Hz, 1H), 7.79 (dd, *J* = 7.8, 1.1 Hz, 1H), 7.68 (td, *J* = 7.6, 1.3 Hz, 1H), 7.52 (td, *J* = 7.7, 1.2 Hz, 1H), 7.32 (dd, *J* = 7.7, 0.9 Hz, 1H), 7.13 (dd, *J* = 5.7, 1.0 Hz, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  196.7, 164.0 (*J* = 260 Hz), 161.9, 148.0, 141.1, 133.8, 131.5, 129.0, 127.4, 125.3, 116.8, 113.7, 100.5; HRMS: calcd for C<sub>12</sub>H<sub>7</sub>FNO [M+H]<sup>+</sup> 200.0512, found 200.0518; IR (KBr): 3067, 2930, 1725, 1260 cm<sup>-1</sup>.

**1-Chloro-9*H*-indeno[2,1-*c*]pyridin-9-one (34)**

Light yellow solid; Yield 42% (13 mg); mp 212–214 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  8.52 (dt, *J* = 7.9, 0.6 Hz, 1H), 8.38 (d, *J* = 5.2 Hz, 1H), 8.21 (d, *J* = 8.0 Hz, 1H), 7.94–8.00 (m, 1H), 7.90 (d, *J* = 5.2 Hz, 1H), 7.78–7.84 (m, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  192.8, 158.9, 143.8, 135.5, 131.7, 130.9, 128.8, 128.1, 127.6, 125.6, 122.9, 115.6; HRMS: calcd for C<sub>12</sub>H<sub>7</sub>ClNO [M + H]<sup>+</sup> 216.0216, found 216.0214; IR (KBr): 3053, 2910, 1733 cm<sup>-1</sup>.

**2-(Quinolin-3-yl)benzaldehyde (35)**

Off-white solid; Yield 85% (99 mg); mp 70–72 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  10.06 (s, 1H), 9.00 (d,  $J = 2.2$  Hz, 1H), 8.21 (d,  $J = 9.0$  Hz, 1H), 8.17 (d,  $J = 2.0$  Hz, 1H), 8.13 (dd,  $J = 7.7, 1.0$  Hz, 1H), 7.88–7.94 (m, 1H), 7.82 (ddd,  $J = 8.4, 6.9, 1.5$  Hz, 1H), 7.73–7.79 (m, 1H), 7.60–7.69 (m, 2H), 7.53–7.59 (m, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  191.4, 150.9, 147.5, 141.9, 136.7, 134.1, 134.0, 131.4, 130.9, 130.2, 129.4, 128.7, 128.0, 127.6, 127.3; HRMS: calcd for  $\text{C}_{16}\text{H}_{12}\text{NO}$   $[\text{M} + \text{H}]^+$  234.0919, found 234.0912; IR (KBr): 3066, 2960, 2873, 1723, 1695  $\text{cm}^{-1}$ .

### 2-(Isoquinolin-4-yl)benzaldehyde (36)

Pale yellow oil; Yield 90% (104 mg);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  9.69 (s, 1H), 9.36 (s, 1H), 8.50 (s, 1H), 8.16 (dt,  $J = 7.7, 0.7$  Hz, 1H), 8.08–8.13 (m, 1H), 7.73–7.80 (m, 1H), 7.65–7.70 (m, 3H), 7.50–7.54 (m, 1H), 7.46–7.50 (m, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  191.3, 153.1, 143.5, 140.2, 135.3, 135.0, 134.9, 134.0, 132.0, 131.4, 131.0, 129.0, 128.1, 127.9, 127.7, 124.5; HRMS: calcd for  $\text{C}_{16}\text{H}_{12}\text{NO}$   $[\text{M} + \text{H}]^+$  234.0919, found 234.0910; IR (neat): 2926, 2873, 1725, 1694  $\text{cm}^{-1}$ .

### 2-(2-Chloropyrimidin-5-yl)benzaldehyde (37)

Off-white solid; Yield 88% (96 mg); mp 131–133 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  10.04 (s, 1H), 8.66 (s, 2H), 8.07 (dd,  $J = 7.7, 1.4$  Hz, 1H), 7.77 (dt,  $J = 7.5, 1.6$  Hz, 1H), 7.71 (dt,  $J = 7.5, 1.3$  Hz, 1H), 7.40 (dd,  $J = 7.5, 1.3$  Hz, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  190.6, 160.9, 159.0, 135.4, 134.2, 133.7, 131.9, 131.4, 131.1, 129.9; HRMS: calcd for  $\text{C}_{11}\text{H}_8\text{ClN}_2\text{O}$   $[\text{M} + \text{H}]^+$  219.0325, found 219.0322; IR (KBr): 3068, 2894, 1698  $\text{cm}^{-1}$ .

### 3-Methyl-2,3'-bipyridine (38)

A solution of 2-bromo 3-methylpyridine (1 equiv, 0.5 mmol), 3-pyridylboronic acid (1.2 equiv, 0.6 mmol),  $\text{Pd}_2(\text{dba})_3$  (1 mol %),  $\text{PCy}_3$  (2.4 mol %) and potassium phosphate (1.7 equiv, 0.85 mmol) in dioxane:water (4:1, 3 mL), was heated at 100 °C for 18 h. Then, water (20 mL) was added, and the reaction mixture was extracted with ethyl acetate (2×10 mL). The organic layers were combined, dried

(Na<sub>2</sub>SO<sub>4</sub>), concentrated under reduced pressure, and purified by column chromatography (100-200# silica, ethyl acetate/hexane = 1:1) to give the desired product. Pale yellow oil; Yield 70% (60 mg); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 8.76–8.84 (m, 1H), 8.66 (dd, *J* = 4.7, 1.5 Hz, 1H), 8.57 (d, *J* = 4.5 Hz, 1H), 7.90 (dt, *J* = 7.7, 2.0 Hz, 1H), 7.62–7.66 (m, 1H), 7.42 (ddd, *J* = 7.8, 4.8, 0.8 Hz, 1H), 7.25 (dd, *J* = 7.7, 4.7 Hz, 1H), 2.40 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 155.5, 149.9, 149.0, 147.4, 138.8, 136.5, 136.2, 131.3, 123.2, 122.8, 19.9; HRMS: calcd for C<sub>11</sub>H<sub>10</sub>N<sub>2</sub> [M]<sup>+</sup> 170.0844, found 170.0848; IR (neat): 3044, 2954 cm<sup>-1</sup>.

### 11*H*-Indeno[1,2-*c*]quinolin-11-one (39)

Yellow solid; Yield 90% (31 mg); mp 198–200 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 9.23 (s, 1H), 8.80 (dq, *J* = 8.2, 0.7 Hz, 1H), 8.09 (dt, *J* = 8.7, 0.7 Hz, 1H), 7.69–7.73 (m, 1H), 7.66–7.69 (m, 1H), 7.62–7.66 (m, 2H), 7.53 (td, *J* = 7.4, 1.1 Hz, 1H), 7.35 (td, *J* = 7.4, 1.0 Hz, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 195.1, 150.4, 143.4, 142.7, 137.5, 135.1, 133.4, 133.3, 130.0, 129.8, 129.7, 129.7, 125.1, 124.2, 123.3, 120.8; HRMS: calcd for C<sub>16</sub>H<sub>10</sub>NO [M + H]<sup>+</sup> 232.0762, found 232.0757; IR (KBr): 3047, 2924, 1711 cm<sup>-1</sup>.

### 7*H*-Dibenzo[*de,h*]isoquinolin-7-one (41)

Yellow solid; Yield 93% (32 mg); mp 218–220 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 9.49 (s, 1H), 9.40 (s, 1H), 8.87–8.94 (m, 1H), 8.54 (d, *J* = 8.0 Hz, 1H), 8.39 (d, *J* = 8.0 Hz, 1H), 8.42 (d, *J* = 8.0 Hz, 1H), 7.94 (t, *J* = 7.7 Hz, 1H), 7.78–7.85 (m, 1H), 7.64 (t, *J* = 7.5 Hz, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 193.0, 153.9, 146.1, 142.1, 136.8, 134.9, 132.5, 132.1, 131.0, 130.9, 129.7, 129.5, 129.3, 124.3, 123.9, 123.6; HRMS: calcd for C<sub>16</sub>H<sub>10</sub>NO [M + H]<sup>+</sup> 232.0762, found 232.0754; IR (KBr): 2925, 2853, 1722 cm<sup>-1</sup>.

### 2-Chloro-9*H*-indeno[2,1-*d*]pyrimidin-9-one (42)

Yellow solid; Yield 88% (28 mg); mp 182–184 °C:  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.92 (s, 1H), 7.82 (dt,  $J$  = 7.5, 0.9 Hz, 1H), 7.67–7.70 (m, 2H), 7.48–7.53 (m, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  190.0, 162.9, 162.4, 151.3, 139.1, 136.7, 134.2, 131.6, 131.2, 126.0, 122.2; HRMS: calcd for  $\text{C}_{11}\text{H}_6\text{ClN}_2\text{O}$  [ $\text{M} + \text{H}$ ] $^+$  217.0169, found 217.0173; IR (KBr): 2933, 2859, 1720  $\text{cm}^{-1}$ .

#### [1,1'-Biphenyl]-2-yl-methanol (44)

Pale yellow oil; Yield 73% (67 mg);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.58 (dd,  $J$  = 8.8, 1.9 Hz, 1H), 7.44–7.48 (m, 2H), 7.37–7.43 (m, 5H), 7.32 (dd,  $J$  = 7.1, 1.5 Hz, 1H), 4.63 (s, 2H), 1.9 (s, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  141.3, 140.7, 138.0, 130.1, 129.2, 128.4, 127.7, 127.3, 63.2; HRMS: calcd for  $\text{C}_{13}\text{H}_{13}\text{O}$  [ $\text{M} + \text{H}$ ] $^+$  185.0966, found 185.0969; IR (neat): 3334, 2928  $\text{cm}^{-1}$ .

#### (4'-Methyl-[1,1'-biphenyl]-2-yl)methanol (45)

Pale yellow oil; Yield 76% (75 mg);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.58 (dd,  $J$  = 7.5, 2.0 Hz, 1H), 7.37–7.44 (m, 2H), 7.27–7.33 (m, 5H), 4.66 (s, 2H), 2.46 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  141.3, 138.2, 137.8, 136.9, 130.1, 129.0, 128.4, 127.5, 63.2, 21.2; HRMS: calcd for  $\text{C}_{14}\text{H}_{15}\text{O}$  [ $\text{M} + \text{H}$ ] $^+$  199.1123, found 199.1125; IR (neat): 3327, 2926  $\text{cm}^{-1}$ .

#### (4'-Chloro-[1,1'-biphenyl]-2-yl)methanol (46)

Pale yellow oil; Yield 68% (75 mg);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.56 (dd,  $J$  = 9.0, 1.9 Hz, 1H), 7.37–7.43 (m, 4H), 7.31–7.35 (m, 2H), 7.28 (dd,  $J$  = 9.0, 1.4 Hz, 1H), 4.57 (s, 2H), 2.33 (s, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  140.17, 139.07, 137.94, 133.3, 130.5, 129.9, 128.6, 128.4, 128.0, 127.8, 126.9, 63.0; HRMS: calcd for  $\text{C}_{13}\text{H}_{12}\text{ClO}$  [ $\text{M} + \text{H}$ ] $^+$  219.0577, found 219.0565; IR (neat): 3332, 2926, 727  $\text{cm}^{-1}$ .

#### (4'-Fluoro-[1,1'-biphenyl]-2-yl)methanol (47)

Pale yellow oil; Yield 64% (65 mg);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.57 (dd,  $J$  = 8.8, 1.6 Hz, 1H), 7.35–7.44 (m, 4H), 7.27–7.30 (m, 1H), 7.10–7.17 (m, 2H), 4.61 (d,  $J$  = 5.1 Hz, 2H);  $^{13}\text{C}$  NMR (100

1  
2  
3  
4 MHz, CDCl<sub>3</sub>):  $\delta$  163.5 ( $J$  = 247 Hz), 161.0, 140.4, 138.0, 136.6, 130.8 ( $J$  = 8 Hz), 130.2, 128.6, 127.8,  
5  
6 127.3, 115.3 ( $J$  = 21 Hz), 63.1; HRMS: calcd for C<sub>13</sub>H<sub>12</sub>FO [M+H]<sup>+</sup> 203.0872, found 203.0867; IR  
7  
8 (neat): 3334, 2923, 1253 cm<sup>-1</sup>.  
9  
10

11  
12 **(2'-Methyl-[1,1'-biphenyl]-2-yl)methanol (48)**  
13  
14

15 Pale yellow oil; Yield 60% (60 mg); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.56–7.58 (m, 1H), 7.34–7.44 (m,  
16  
17 3H), 7.24–7.32 (m, 2H), 7.15–7.19 (m, 2H), 4.43 (s, 2H), 2.0 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  
18  
19  $\delta$  140.4, 140.1, 138.4, 135.9, 130.1, 129.6, 129.3, 127.7, 127.4, 125.6, 63.2, 20.0; HRMS: calcd for  
20  
21 C<sub>14</sub>H<sub>15</sub>O [M+H]<sup>+</sup> 199.1123, found 199.1131; IR (neat): 3329, 2922 cm<sup>-1</sup>.  
22  
23  
24

25  
26 **(3',4'-Dichloro-[1,1'-biphenyl]-2-yl)methanol (49)**  
27  
28

29 Brownish yellow oil; Yield 63% (79 mg); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.57 (d,  $J$  = 7.5 Hz, 1H), 7.50  
30  
31 –7.53 (m, 2H), 7.37–7.46 (m, 3H), 7.25–7.28 (m, 1H), 4.59 (s, 2H), 1.83 (s, 1H); <sup>13</sup>C NMR (100 MHz,  
32  
33 CDCl<sub>3</sub>):  $\delta$  140.7, 139.0, 137.8, 132.3, 131.6, 131.1, 130.7, 129.9, 128.9, 128.6, 128.0, 127.0, 62.9;  
34  
35 HRMS: calcd for C<sub>13</sub>H<sub>11</sub>Cl<sub>2</sub>O [M+H]<sup>+</sup> 253.0187, found 253.0199; IR (neat): 3335, 2929, 722 cm<sup>-1</sup>.  
36  
37  
38

39 **2-Methyl-1,1'-biphenyl (50)**<sup>19</sup>  
40  
41

42 Transparent oil; Yield 80% (60 mg); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.49–7.55 (m, 2H), 7.41–7.45 (m,  
43  
44 3H), 7.34–7.36 (m, 4H), 2.23 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  142.0, 135.4, 130.3, 129.3, 129.3,  
45  
46 128.9, 128.1, 127.3, 126.8, 125.9, 20.6; HRMS: calcd for C<sub>13</sub>H<sub>13</sub> [M+H]<sup>+</sup> 169.1017, found 169.1020.  
47  
48  
49

50 **2,2'-Dimethyl-1,1'-biphenyl (51)**<sup>19</sup>  
51  
52

53 Transparent oil; Yield 63% (57 mg); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.31–7.37 (m, 6H), 7.21 (d,  $J$  = 7.2  
54  
55 Hz, 2H), 2.1 (s, 6H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  141.7, 135.9, 129.9, 129.4, 127.2, 125.9, 19.9;  
56  
57 HRMS: calcd for C<sub>14</sub>H<sub>15</sub> [M+H]<sup>+</sup> 183.1174, found 183.1179.  
58  
59  
60



**9H-fluoren-9-one (52)**<sup>21</sup>

Yellow solid; Yield 75% (25 mg); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.68 (d, *J* = 7.4 Hz, 2H), 7.54 (dd, *J* = 6.4, 0.7 Hz, 2H), 7.50 (td, *J* = 7.3, 1.1 Hz, 2H), 7.31 (td, *J* = 7.2, 1.9 Hz, 2H).

**[1,1'-biphenyl]-2-carbaldehyde (52a)**<sup>5</sup>

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 10.01 (s, 1H), 8.06 (dd, *J* = 7.8, 1.2 Hz, 1H), 7.69 (td, *J* = 7.5, 1.4 Hz, 1H), 7.46–7.54 (m, 5H), 7.39–7.42 (m, 2H).

**2-Methyl-9H-fluoren-9-one (53)**<sup>21</sup>

Yellow solid; Yield 70% (27 mg); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.65 (dd, *J* = 3.7, 0.8 Hz, 1H), 7.48–7.50 (m, 3H), 7.42 (d, *J* = 7.5 Hz, 1H), 7.24–7.31 (m, 2H), 2.40 (s, 3H).

**2-Chloro-9H-fluoren-9-one (54)**<sup>21</sup>

Yellow solid; Yield 60% (26 mg); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.68 (d, *J* = 7.4 Hz, 1H), 7.64 (s, 1H), 7.53 (d, *J* = 4 Hz, 2H), 7.47 (d, *J* = 1.0 Hz, 2H), 7.32–7.37 (m, 1H).

**2-Fluoro-9H-fluoren-9-one (55)**<sup>21</sup>

Yellow solid; Yield 55% (22 mg); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.67 (d, *J* = 7.3 Hz, 1H), 7.48–7.53 (m, 3H), 7.36 (d, *J* = 7.0, 2.4 Hz, 1H), 7.29–7.32 (m, 1H), 7.17 (td, *J* = 8.3, 2.5 Hz, 1H).

**4-Methyl-9H-fluoren-9-one (56)**<sup>21</sup>

Yellow solid; Yield 43% (17 mg); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.70 (d, *J* = 7.3 Hz, 1H), 7.64 (d, *J* = 7.6 Hz, 1H), 7.54 (d, *J* = 6.9 Hz, 1H), 7.50 (td, *J* = 7.6, 1.2 Hz, 1H), 7.28–7.32 (m, 2H), 7.20–7.22 (m, 1H), 2.61 (s, 3H).

**1,2-Dichloro-9H-fluoren-9-one (57)**

Yellow solid; Yield 40% (20 mg); mp 129–131 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.70 (d,  $J$  = 7.4 Hz, 1H), 7.57 (d,  $J$  = 7.9 Hz, 1H), 7.52 (d,  $J$  = 3.9 Hz, 2H), 7.39 (d,  $J$  = 6.4 Hz, 1H), 7.34 - 7.38, (m, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  197.7, 144.8, 141.8, 135.4, 135.0, 133.8, 131.1, 129.9, 124.8, 120.5, 119.2; HRMS: calcd for  $\text{C}_{13}\text{H}_7\text{Cl}_2\text{O}$   $[\text{M}+\text{H}]^+$  248.9874, found 248.9869 IR (KBr): 3042, 2923, 1758, 1055  $\text{cm}^{-1}$ .

### 1,1'-(9,9-Dioctyl-9H-fluorene-2,7-diyl)bis(5H-indeno[1,2-c]pyridin-5-one) (59)

**59** was synthesized by following literature protocol for Suzuki coupling of 2-chloropyridine and it is not optimized. In a oven dried screw cap vial, a solution of 9,9-di-n-octylfluorene-2,7-diboronic acid bis(pinacol) ester (1 equiv, 0.5 mmol), 4-methyl-9H-indeno[2,1-*b*]pyridin-9-one (2 equiv, 1 mmol),  $\text{Pd}(\text{OAc})_2$  (2 mol %), S-Phos (4 mol%) and potassium carbonate (2.5 equiv, 1.25 mmol) was purged with nitrogen twice. Then mixture of ACN:Water (1.5 mL: 1.0 mL) was added to the vial and stirred at 100 °C for 6 h under nitrogen atmosphere. After the completion of the reaction, ethyl acetate (2×10 mL) was added and washed with water (2×20 mL). The organic layers were combined, dried ( $\text{Na}_2\text{SO}_4$ ), concentrated under reduced pressure, and purified by column chromatography (100–200# silica, ethyl acetate/hexane = 1:9) to give the desired yellow solid product. Yield 40% (95 mg); mp 190-193°C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.82 (d,  $J$  = 4.5 Hz, 2H), 8.01 (d,  $J$  = 7.7 Hz, 2H), 7.72–7.81 (m, 4H), 7.71 (s, 2H), 7.58 (d,  $J$  = 4.5 Hz, 2H), 7.30–7.35 (m, 2H), 7.24–7.28 (m, 2H), 7.16–7.22 (m, 2H), 2.00–2.11 (m, 4H), 1.02–1.16 (m, 24H), 0.77–0.84 (m, 6H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  193.2, 155.2, 151.4, 151.0, 144.3, 141.7, 138.2, 135.0, 134.9, 133.6, 129.5, 128.0, 125.2, 123.4, 123.2, 120.8, 115.9, 55.8, 40.4, 31.8, 30.6, 29.7, 29.3, 24.3, 22.5, 14.1; HRMS: calcd for  $\text{C}_{53}\text{H}_{53}\text{N}_2\text{O}_2$   $[\text{M} + \text{H}]^+$  749.4107, found 749.4120; IR (KBr): 3422, 2924, 2852, 1721, 1407  $\text{cm}^{-1}$ .

## ASSOCIATED CONTENT

### Supporting Information

Photoluminescence and UV absorption spectra of compound **59**, and copies of  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra for all new compounds. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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## Note

The authors declare no competing financial interest.

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