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# $[RuCl_3(H_2O)_n]$-catalyzed direct arylations

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**Abstract**

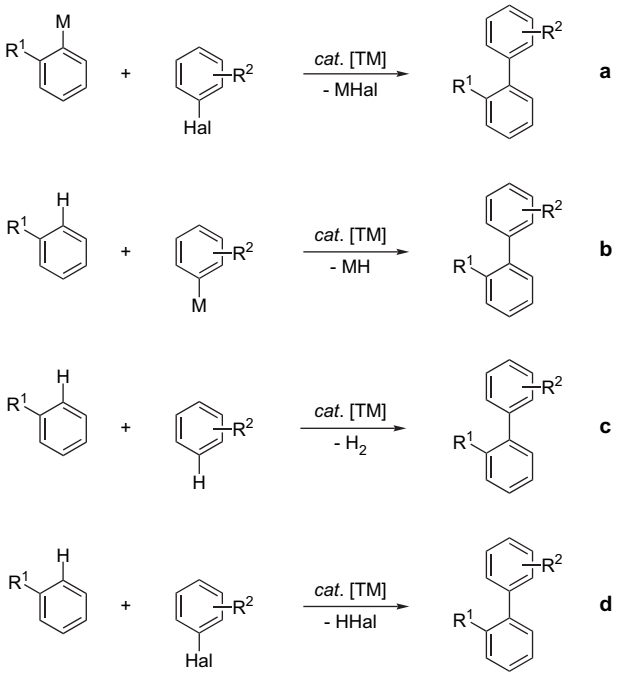
Catalytic amounts of economically attractive $[RuCl_3(H_2O)_n]$ allow for direct arylations via C–H bond functionalization with aryl bromides under phosphine ligand-free reaction conditions. Thereby, a variety of functionalized (hetero)aryl bromides, bearing either electron-withdrawing or electron-releasing substituents, can be employed for direct arylations of pyridine, oxazoline, pyrazole, or ketimine derivatives as pronucleophiles.


## 1. Introduction

Modern methodologies for regioselective $C(sp^2)$–$C(sp^2)$ bond forming reactions employ largely transition metal-catalyzed cross-coupling reactions between organic (pseudo)halides and organometallic reagents.[1,2] The prerequisite organometallic compounds are often commercially unavailable or relatively expensive, and their use gives rise to the formation of undesired side-product. Direct arylation reactions via cross-coupling of C–H bonds with organic electrophiles represent an ecologically benign and economically attractive alternative.[3–6]

In contrast to more traditional cross-coupling reactions with organometallic reagents (Scheme 1, a), pronucleophilic substrates for direct C–H bond arylation reactions do not display a single reactive functional group. Therefore, the regioselective arylation of a specific C–H bond in a given molecule constitutes a major objective for the development of preparatively useful direct arylation methodologies.[7] Intramolecular transformations proceed often with good regioselectivities, and so do direct arylations of various heteroarenes.[8–10] However, the development of regioselective intermolecular direct arylations of (electronically non-activated) arenes represents a notable challenge (Scheme 1, b–d).[7] A solution to this problem is found in the use of (temporarily installed) directing groups, which enable highly regioselective intermolecular arylation reactions.[7]

For these chelation-assisted C–H bond functionalization reactions of arenes either organometallic reagents (Scheme 1, b), arenes (Scheme 1, c), or organic (pseudo)halides (Scheme 1, d)




Scheme 1. Strategies for intermolecular $C(sp^2)$–$C(sp^2)$ bond formation.

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can be employed as arylating reagents. Transformations using stoichiometric amounts of organometallic reagents encounter similar drawbacks as traditional cross-coupling reactions (vide supra, and Scheme 1, a). Oxidative direct arylations of arenes rely on the use of stoichiometric amounts of oxidants, such as oxone, benzoquinone, or copper salts,[11] which give rise to stoichiometric amounts of economically and environmentally undesired side-products. More importantly, regioselectivity is even more difficult to achieve in such intermolecular cross-coupling[12] reactions.[13,14] Hence, a significant amount of research effort has been devoted to the development of direct arylation reactions using organic (pseudo)halides as electrophiles.[5,7]

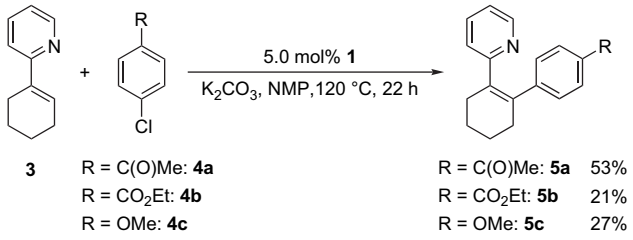
In addition to valuable rhodium- and palladium-catalyzed processes,[15] ruthenium catalysts stabilized by phosphorus-based ligands proved effective and versatile for direct arylation reactions with organic halides.[16–18] In this context, we reported on the use of air-stable secondary phosphine oxides[19] as preligands for ruthenium-catalyzed direct arylation reactions employing readily available, inexpensive chlorides[20] or tosylates[21] as electrophiles. During mechanistic studies on regio- and diastereoselective ruthenium-catalyzed direct arylations of alkenes with aryl chlorides,[22] we noted that simple ruthenium compounds, such as $[RuCl_3(H_2O)_n]$ (**1**) and $[RuCl_2(p\text{-cymene})]_2$ (**2**), could be used as catalysts for direct arylation reactions without the need for an additional phosphorus-based (pre)ligand. While simple palladium salts, such as $Pd(OAc)_2$, had been shown previously to allow for direct arylation reactions with aryl halides,[5,23] effective ruthenium catalysts for regioselective direct arylation reactions relied thus far entirely on the use of phosphorus-based stabilizing (pre)ligands. Hence, we felt attracted by the possibility of employing commercially available and inexpensive ruthenium compounds for direct arylation reactions via C–H bond functionalization. Herein, we wish to provide a full account[24] on the scope and limitations of this economically attractive and simple catalytic system.

## 2. Results and discussion

Among aryl halides, chlorides are arguably the most attractive class of electrophiles for coupling reactions, due to their lower price and higher availability. In traditional cross-coupling reactions of organometallic reagents, the use of stabilizing ligands is necessary in order to funtionalize such electrophiles.[25,26] Generally applicable methods for intermolecular direct arylation reactions employing aryl chlorides were, until recently, not available.[20,27,28] We reported on the use of ruthenium complexes derived from different phosphorus-based (pre)ligands for direct arylation reactions employing aryl chlorides[20] with ample scope. To simplify our approach further we turned our attention to phosphorus-based ligand-free ruthenium catalyst in direct arylations using inexpensive aryl chlorides as electrophiles.

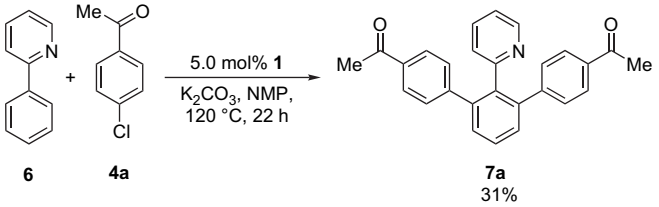
### 2.1. $[RuCl_3(H_2O)_n]$-catalyzed direct arylation with aryl chlorides

First, we probed the catalytic activity of $[RuCl_3(H_2O)_n]$ (**1**) in the regioselective C–H bond functionalization of alkene **3**. While a significant product formation was noted, aryl chlorides **4a–c** were converted only sluggishly (Scheme 2). More generally speaking, it is noteworthy that these ruthenium-catalyzed direct arylations of alkenes[22] are distinct from simple palladium-catalyzed Heck reactions, as substrates not bearing a directing group, such as stilbene, were not converted.




Scheme 2. Direct arylation of alkene **3a** with aryl chlorides **4**.

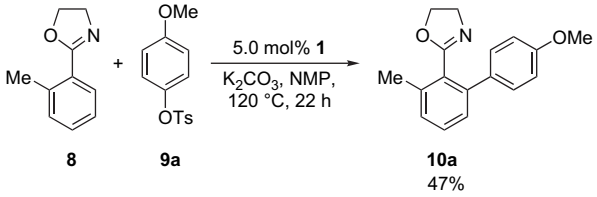
Low isolated yields were also obtained when using an arene as pronucleophile. Thus, arylation of pyridine derivative **6** with aryl chloride **4a** provided the desired product **7a** in only 31% yield (Scheme 3).



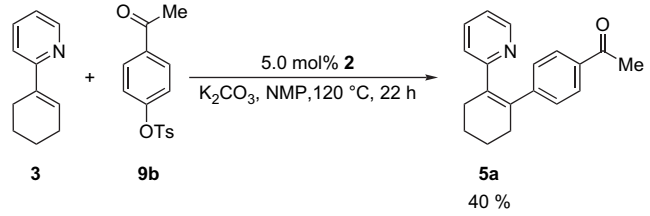

Scheme 3. Direct arylation of pyridine **6**.

### 2.2. $[RuCl_3(H_2O)_n]$-catalyzed direct arylation with aryl tosylates

The possibility of using tosylates as electrophiles in cross-coupling chemistry is attractive, since they can be prepared from readily available phenols or ketones with reagents that are less expensive than those used to prepare the corresponding triflates. Further, tosylates are more convenient to use, being more stable to water than triflates and highly crystalline. However, this greater stability makes tosylates less reactive in transition metal-catalyzed processes. Methods for traditional cross-coupling reactions between aryl tosylates and organometallic reagents are known.[29] In contrast, catalytic, direct arylation reactions through C–H bond activation using tosylates were not reported until recently. Thus, we disclosed the use of a ruthenium catalyst for unprecedented direct arylation reactions with tosylates.[21] Consequently, we explored, within the present study, the use of economically attractive $[RuCl_3(H_2O)_n]$ (**1**) as catalyst for direct arylations using aryl tosylates as electrophiles. Interestingly, significant product formation was noted. Thus, arene **8** was regioselectively arylated in 47% yield (Scheme 4).




Scheme 4. Direct arylation of arene **8** with tosylate **9a**.




Scheme 5. Direct arylation of alkene **3** with tosylate **9b**.

Furthermore, catalytic amounts of complex **2** allowed for a regioselective arylation of alkene **3** (Scheme 5).

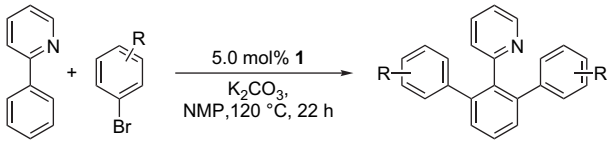
### 2.3. *[RuCl$_3$(H$_2$O)$_n$]-catalyzed direct arylation of pyridine derivatives with aryl bromides*

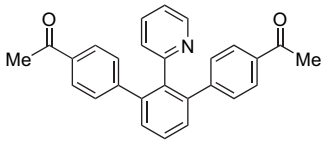
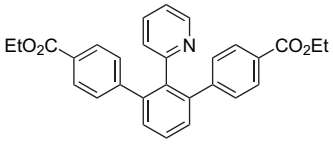
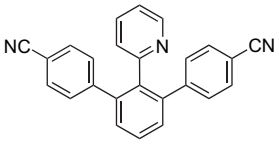
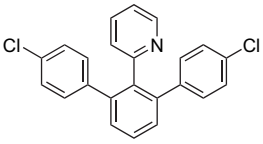
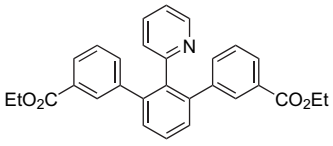
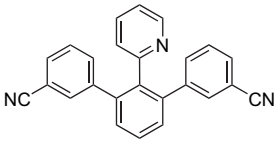
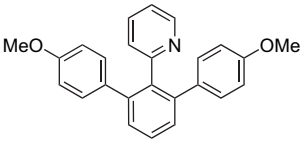
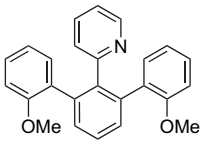
Since [RuCl$_3$(H$_2$O)$_n$]-catalyzed direct arylations with aryl chlorides **4** and tosylates **9** provided generally rather unsatisfactory isolated yields, we turned our attention to the use of aryl bromides **11** as electrophiles (Table 1).

Interestingly, catalytic amounts of commercially available [RuCl$_3$(H$_2$O)$_n$] (**1**) enabled generally applicable direct arylation reactions of pyridine **6** with a variety of bromides **11** (Table 1). Importantly, a high catalytic activity was not only observed when using electron-deficient aryl bromides and iodides, thereby for an oxidative addition electronically activated (entries 1–6), but also for electron-rich aryl bromides (entries 7 and 9) and iodides (entry 8). Further, a number of valuable functional groups were tolerated, including an enolizable ketone (entry 1), ester (entries 2 and 5), nitriles (entry 3 and 6), and a chloride (entry 4). Also a more sterically hindered *ortho*-substituted aryl bromide could be converted with satisfactory isolated yield (entry 9). Additionally, it is noteworthy that catalytic amounts of [RuCl$_3$(H$_2$O)$_n$] (**1**) allowed an efficient direct arylation reaction of 2-phenyl pyridine (**6**) even at the lower reaction temperature of 100 °C (Scheme 6).

Cross-coupling reactions of heteroaromatic (pseudo)halides are of utmost importance, because heterocycles are often indispensable substructures of naturally occurring products and biologically active compounds in pharmaceuticals, as well as agrochemicals. However, only a single heteroaromatic halide was thus far employed in ruthenium-catalyzed direct arylation reactions via C–H bond functionalization.[18] Consequently, we probed the efficacy of our catalytic system in the conversion of furan **12** and thiophene **14**. The functionalized bromide **12** was

Table 1
Direct arylations of pyridine **6** employing [RuCl$_3$(H$_2$O)$_n$] (**1**)[a]

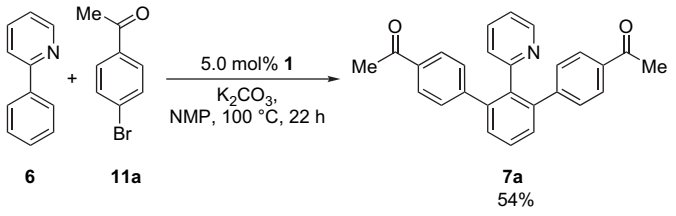



| Entry | R | Product **7** | | Yield (%) |
|---|---|---|---|---|
| 1 | 4-C(O)Me |  | **7a** | 90 |
| 2 | 4-CO$_2$Et |  | **7b** | 94 |
| 3 | 4-CN |  | **7c** | 85 |
| 4 | 4-Cl |  | **7d** | 69 |
| 5 | 3-CO$_2$Et |  | **7e** | 95 |
| 6 | 3-CN |  | **7f** | 51 |
| 7 | 4-OMe |  | **7g** | 61 |
| 8 | 4-OMe[b] | | | 73 |
| 9 | 2-OMe |  | **7h** | 65 |

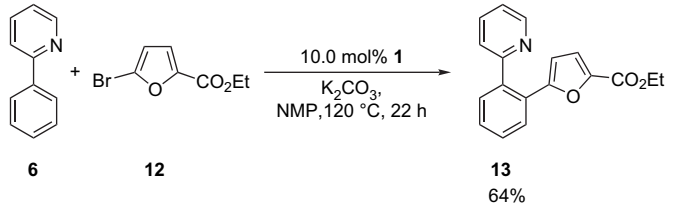
[a] Isolated yields.
[b] Using 4-MeOC$_6$H$_4$I as electrophile.

efficiently converted with catalytic amounts of [RuCl$_3$(H$_2$O)$_n$] (**1**), yielding mono-arylated product **13** in a good isolated yield (Scheme 7).

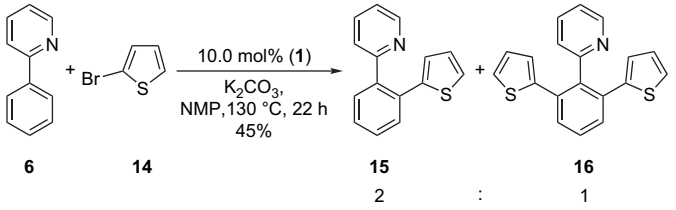
On the contrary, thiophene **14** provided an inseparable mixture of the mono- and di-arylated products **15** and **16** in a combined isolated yield of only 45% (Scheme 8).




Scheme 6. Direct arylation of pyridine **6** at 100 °C.




Scheme 7. Direct arylation with furane **12**.




Scheme 8. Direct arylation with thiophene **14**.

### 2.4. $[RuCl_3(H_2O)_n]$-catalyzed direct arylation of oxazolines with aryl bromides

Since 2-oxazolinyl substituents can be easily converted to valuable functional groups, such as the corresponding carboxylic acids,[30] we studied next the scope of $[RuCl_3(H_2O)_n]$ (**1**) in the catalytic direct arylation of oxazoline **8** (Table 2).

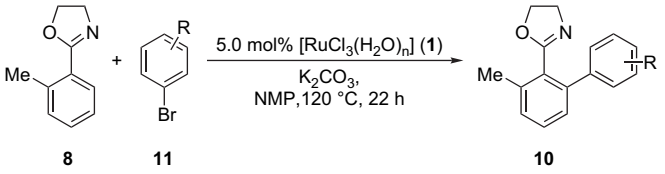
Catalytic amounts of $[RuCl_3(H_2O)_n]$ (**1**) enabled efficient direct arylations with a variety of aryl bromides **11** as electrophiles. Thus, aryl bromides **11** with both electron-withdrawing and electron-releasing substituents proved to be suitable substrates. This allowed for the synthesis of oxazolines **10** with different functional groups, such as an enolizable ketone (entry 1), ester (entries 2 and 4), a nitrile (entry 3), alkyl (entry 5) as well as aryl halides (entry 6), and a terminal alkene (entry 7). On the contrary, an oxazoline, displaying a 2-bromophenyl substituent, gave as pronucleophile an unselective reaction with bromide **11a**.

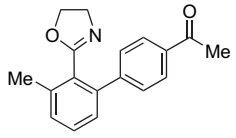
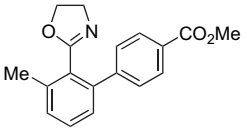
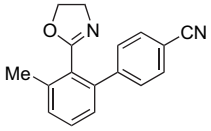
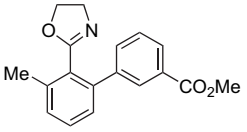
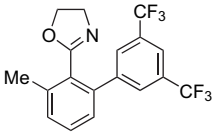
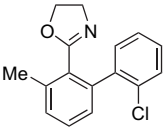
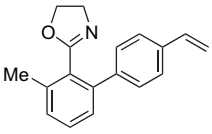
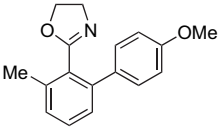
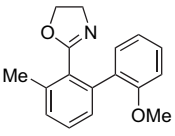
### 2.5. $[RuCl_3(H_2O)_n]$-catalyzed direct arylations of pyrazoles and ketimines with aryl bromides

$[RuCl_3(H_2O)_n]$-catalyzed direct arylations with bromoarenes are not restricted to pyridines or oxazoline derivatives, but can also be applied to the regioselective arylation of other pronucleophiles. Thus, pyrazoles **18a–c** were obtained in good isolated yields (Scheme 9).

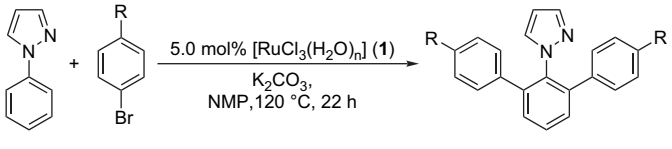
Further, *N*-aryl-substituted ketimine **19** was arylated employing catalytic amounts of $[RuCl_3(H_2O)_n]$ (**1**) (Scheme 10). The corresponding products were conveniently isolated

Table 2
Catalytic direct arylations of oxazoline **8**[a]




| Entry | R | Product **10** | | Yield (%) |
|---|---|---|---|---|
| 1 | 4-C(O)Me |  | **10b** | 68 |
| 2 | 4-$CO_2$Me |  | **10c** | 68 |
| 3 | 4-CN |  | **10d** | 59 |
| 4 | 3-$CO_2$Me |  | **10e** | 77 |
| 5 | 3,5-$(CF_3)_2$ |  | **10f** | 46 |
| 6 | 2-Cl |  | **10g** | 62 |
| 7 | 4-CH=$CH_2$ |  | **10h** | 51 |
| 8 | 4-OMe |  | **10a** | 65 |
| 9 | 2-OMe |  | **10i** | 51 |

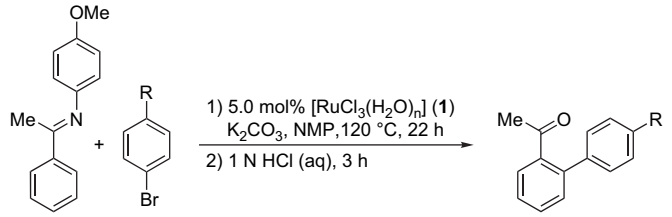
[a] Isolated yields.




| | | | |
|---|---|---|---|
| **17** | R = C(O)Me: **11a** | R = C(O)Me: **18a** | 64% |
| | R = $CO_2$Me: **11b** | R = $CO_2$Me: **18b** | 52% |
| | R = OMe: **11c** | R = OMe: **18c** | 55% |

Scheme 9. Direct arylation of pyrazole **17**.

after hydrolysis as their acetophenone derivatives **20a–c**. Generally, arylation reactions proceeded well with functionalized electron-deficient as well as with electron-rich aryl bromides **11**. Contrary to pyridine, oxazoline or pyrazole derivatives, ketimines **19** yielded selectively the mono-arylated products **20**, as also observed previously for a phosphine-based ruthenium catalyst.[20]




| | | | |
|---|---|---|---|
| **19** | R = C(O)Me: **11a** | R = C(O)Me: **20a** | 68% |
| | R = $CO_2$Et: **11b** | R = $CO_2$Et: **20b** | 65% |
| | R = OMe: **11c** | R = OMe: **20c** | 56% |

Scheme 10. Direct arylation of ketimine **19**.

## 3. Conclusions

In summary, we report herein on the scope and limitations of economically attractive direct arylation reactions catalyzed by $[RuCl_3(H_2O)_n]$ (**1**). While aryl chlorides and tosylates as electrophiles gave rather sluggish product formation, aryl bromides proved suitable substrates. Thus, electron-deficient as well as electron-rich aryl bromides, displaying a variety of valuable functional groups, were converted with high efficacy. Further, heteroaryl bromides could be also employed with our phosphine-free catalyst. The scope of this transformation was not only broad with respect to the electrophile. Hence, various pronucleophiles, such as pyridines, oxazolines, pyrazoles, and ketimines, proved applicable for regioselective direct arylation reactions.

## 4. Experimental

### 4.1. General

All catalytic reactions were carried out under $N_2$ using predried glassware. Chemicals were obtained from commercial sources, and were used without further purification. NMP (extra dry) was obtained from Acros Organics, and was used without further purification. Yields refer to isolated compounds, estimated to be >95% pure as determined by $^1$H NMR and GC, unless otherwise stated. Flash chromatography: Merck silica gel 60 (230–400 mesh). NMR: $^1$H was recorded on a Varian Unity 300, Bruker AC 300, or AMX 600, $^{13}$C was recorded on a Varian Mercury 300, Unity 300, Bruker AC 300, or AMX 600, and $^{19}$F was recorded on a Mercury 300 in the solvent indicated; chemical shifts ($\delta$) are given in parts per million, coupling constants ($J$) in hertz.

#### 4.1.1. Representative procedure for $[RuCl_3(H_2O)_n]$-catalyzed direct arylations: 1-(4-acetyl-2′-pyridin-2-yl-[1,1′:3″,1″]-terphenyl-4″-yl)ethanone (**7a**)[20]

A suspension of **1** (12.6 mg, 0.05 mmol, 5.0 mol %), $K_2CO_3$ (415 mg, 3.00 mmol), **6** (160 mg, 1.03 mmol), and **11a** (438 mg, 2.20 mmol) in dry NMP (2.0 mL) was stirred for 22 h at 120 °C under $N_2$. After the reaction mixture was cooled to ambient temperature, $Et_2O$ (50 mL) and $H_2O$ (40 mL) were added. The separated aqueous phase was extracted with $Et_2O$ (3×50 mL). The combined organic layers were washed with $H_2O$ (50 mL) and brine (50 mL), dried over $Na_2SO_4$, and concentrated in vacuo. The remaining residue was purified by column chromatography on silica gel (*n*-pentane/$Et_2O$, 3:1→2:1→1:1→1:2→1:3) to yield **7a** (361 mg, 90%, mp: 200.5–201.5 °C) as a yellow solid. $^1$H NMR (300 MHz, $CDCl_3$): $\delta$=8.30 (d, $J$=5.0 Hz, 1H), 7.75 (d, $J$=8.1 Hz, 4H), 7.56 (dd, $J$=8.6, 6.4 Hz, 1H), 7.50–7.45 (m, 2H), 7.31 (dt, $J$=7.7, 1.8 Hz, 1H), 7.18 (d, $J$=8.1 Hz, 4H), 6.94 (ddd, $J$=7.5, 4.8, 0.9 Hz, 1H), 6.86 (d, $J$=7.7 Hz, 1H), 2.56 (s, 6H). $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$=197.7 (Cq), 157.9 (Cq), 148.7 (CH), 146.3 (Cq), 140.9 (Cq), 138.3 (Cq), 135.3 (CH), 135.1 (CH), 129.8 (CH), 129.7 (CH), 128.5 (CH), 127.8 (CH), 126.6 (CH), 121.4 (CH), 26.5 ($CH_3$). IR (ATR): 3053, 2919, 1680, 1605, 1268, 958, 809. MS (EI) *m*/*z* (relative intensity): 391 (68) [$M^+$], 390 (100), 348 (13). HRMS (EI) *m*/*z*: calcd for $C_{27}H_{21}NO_2$, 391.1572; found, 391.1550.

#### 4.1.2. 1-[4-(2-Pyridin-2-ylcyclohex-1-enyl)phenyl]ethanone (**5a**)[22]

The representative procedure was followed, using **3** (80.0 mg, 0.502 mmol) and **4a** (93.1 mg, 0.602 mmol). After 22 h, purification by chromatography (*n*-pentane/$Et_2O$, 5:1→3:1→1:1→1:2) yielded **5a** (74 mg, 53%) as a brown solid (mp: 61.1–62.1 °C). $^1$H NMR (600 MHz, $CDCl_3$): $\delta$=8.49 (dq, $J$=4.9, 0.9 Hz, 1H), 7.69 (md, $J$=8.4 Hz, 2H), 7.25 (mt, $J$=7.9 Hz, 1H), 7.06 (dt, $J$=8.4, 1.8 Hz, 2H), 6.95 (ddd, $J$=7.5, 4.8, 1.3 Hz, 1H), 6.66 (md, $J$=7.5 Hz, 1H), 2.61–2.59 (m, 2H), 2.49 (s, 3H), 2.46–2.44 (m, 2H), 1.86–1.83 (m, 4H). $^{13}$C NMR (150 MHz, $CDCl_3$): $\delta$=197.7 (Cq), 161.1 (Cq), 148.9 (CH), 148.6 (Cq), 137.0 (Cq), 136.4 (Cq), 135.4 (CH), 134.9 (Cq), 129.0 (CH), 127.9 (CH), 124.8 (CH), 121.0 (CH), 31.5 ($CH_2$), 30.0 ($CH_2$), 26.4 ($CH_3$), 22.9 ($CH_2$), 22.7 ($CH_2$). IR (ATR): 2930, 2864, 1674, 1599, 1583, 1563, 1460, 1429, 1402, 1358, 1265 cm$^{-1}$. MS (EI) *m*/*z* (relative intensity): 277 (41) [$M^+$], 276 (100), 262 (4), 248 (9), 234 (4), 204 (4), 43 (3). HRMS (EI) *m*/*z*: calcd for $C_{19}H_{19}NO$, 277.1467; found, 277.1432.

#### 4.1.3. 4-(2-Pyridin-2-ylcyclohex-1-enyl)benzoic acid ethyl ester (**5b**)[22]

The representative procedure was followed, using **3** (83.3 mg, 0.523 mmol) and **4b** (108 mg, 0.585 mmol). After 22 h, purification by chromatography (*n*-pentane/$Et_2O$, 5:1→3:1→2:1→1:1) yielded **5b** (34 mg, 21%) as a yellow solid (mp: 88.0–89.0 °C). $^1H$ NMR (600 MHz, $CDCl_3$): $\delta$=8.50 (md, $J$=4.8 Hz, 1H), 7.78 (md, $J$=8.4 Hz, 2H), 7.24 (dt, $J$=7.8, 1.8 Hz, 1H), 7.05 (md, $J$=8.3 Hz, 2H), 6.95 (ddd, $J$=7.5, 4.9, 0.9 Hz, 1H), 6.66 (d, $J$=7.9 Hz, 1H), 4.31 (q, $J$=7.1 Hz, 2H), 2.62–2.59 (m, 2H), 2.47–2.45 (m, 2H), 1.85 (quint, $J$=3.1 Hz, 4H), 1.34 (t, $J$=7.1 Hz, 3H). $^{13}C$ NMR (150 MHz, $CDCl_3$): $\delta$=166.5 (Cq), 161.2 (Cq), 148.9 (CH), 148.3 (Cq), 136.9 (Cq), 136.5 (Cq), 135.4 (CH), 129.1 (CH), 128.8 (CH), 128.1 (Cq), 124.8 (CH), 121.0 (CH), 60.7 ($CH_2$), 31.5 ($CH_2$), 30.0 ($CH_2$), 23.0 ($CH_2$), 22.7 ($CH_2$), 14.3 ($CH_3$). IR (KBr): 2936, 1714, 1604, 1585, 1562, 1427, 1272, 1256, 1181, 1110, 1101, 770, 706 $cm^{-1}$. MS (EI) *m/z* (relative intensity): 307 (33) [$M^+$], 306 (100), 278 (22), 262 (3), 250 (4), 204 (3). HRMS (EI) *m/z*: calcd for $C_{20}H_{21}NO_2$, 307.1572; found, 307.1553.

#### 4.1.4. 2-[2-(4-Methoxyphenyl)cyclohex-1-enyl]pyridine (**5c**)

The representative procedure was followed, using **3** (83.3 mg, 0.523 mmol) and **4c** (86.4 mg, 0.606 mmol). After 22 h, purification by chromatography (*n*-pentane/$Et_2O$, 7:1→5:1→3:1→1:1) yielded **5c** (38 mg, 27%) as a yellow oil. $^1H$ NMR (600 MHz, $CDCl_3$): $\delta$=8.50 (md, $J$=4.9 Hz, 1H), 7.26–7.23 (m, 1H), 6.94–6.92 (m, 1H), 6.90 (md, $J$=8.5 Hz, 2H), 6.68 (md, $J$=7.9 Hz, 1H), 6.65 (md, $J$=8.6 Hz, 2H), 3.71 (s, 3H), 2.60–2.58 (m, 2H), 2.45–2.43 (m, 2H), 1.83 (quint, $J$=3.1 Hz, 4H). $^{13}C$ NMR (150 MHz, $CDCl_3$): $\delta$=162.0 (Cq), 157.9 (Cq), 148.7 (CH), 136.8 (Cq), 135.7 (Cq), 135.1 (CH), 135.0 (Cq), 129.9 (CH), 125.1 (CH), 120.5 (CH), 113.2 (CH), 55.1 ($CH_3$), 32.0 ($CH_2$), 29.9 ($CH_2$), 23.2 ($CH_2$), 22.9 ($CH_2$). IR (ATR): 2929, 2857, 2833, 1606, 1585, 1508, 1463, 1428, 1289, 1243, 1176, 1034 $cm^{-1}$. MS (EI) *m/z* (relative intensity): 265 (32) [$M^+$], 264 (100), 250 (7), 236 (5), 221 (2), 193 (2). HRMS (EI) *m/z*: calcd for $C_{18}H_{19}NO$, 265.1467; found, 265.1451.

#### 4.1.5. 2′-Pyridin-2-yl-[1,1′:3′,1″]-terphenyl-4,4″-dicarboxylic acid diethylester (**7b**)[20]

The representative procedure was followed, using pyridine **6** (155 mg, 1.00 mmol) and 4-bromoethyl benzoate (504 mg, 2.20 mmol). After 22 h, purification by chromatography (*n*-pentane/$Et_2O$, 3:1→1:1) yielded **7b** (424 mg, 94%) as a colorless solid (mp: 160.2–161.1 °C). $^1H$ NMR (300 MHz, $CDCl_3$): $\delta$=8.30 (d, $J$=4.9 Hz, 1H), 7.84 (d, $J$=8.5 Hz, 4H), 7.56 (dd, $J$=8.7, 6.3 Hz, 1H), 7.50–7.45 (m, 2H), 7.31 (dt, $J$=7.7, 1.7 Hz, 1H), 7.16 (d, $J$=8.5 Hz, 4H), 6.94 (ddd, $J$=7.4, 4.8, 1.0 Hz, 1H), 6.86 (d, $J$=7.7 Hz, 1H), 4.33 (q, $J$=7.1 Hz, 4H), 1.36 (t, $J$=7.1 Hz, 6H). $^{13}C$ NMR (75 MHz, $CDCl_3$): $\delta$=166.4 (Cq), 157.9 (Cq), 148.7 (CH), 146.0 (Cq), 141.0 (Cq), 138.3 (Cq), 135.3 (Cq), 129.8 (CH), 129.5 (CH), 128.9 (CH), 128.5 (CH), 128.4 (CH), 126.7 (CH), 121.4 (CH), 60.9 ($CH_2$), 14.3 ($CH_3$). IR (ATR): 3060, 2981, 1714, 1609, 1277, 1101, 1021, 769 $cm^{-1}$. MS (EI) *m/z* (relative intensity): 451 (75) [$M^+$], 450 (100), 422 (11), 394 (17). HRMS (EI) *m/z*: calcd for $C_{29}H_{25}NO_4$, 451.1784; found, 451.1773.

#### 4.1.6. 2′-Pyridin-2-yl-[1,1′;3′,1″]-terphenyl-4,4″-dicarbonitrile (**7c**)

The representative procedure was followed, using pyridine **6** (155 mg, 1.00 mmol) and 4-bromobenzonitrile (400 mg, 2.20 mmol). After 22 h, purification by chromatography (*n*-pentane/$Et_2O$, 3:1→1:1) yielded **7c** (304 mg, 85%) as a colorless solid (mp: 164.5–165.2 °C). $^1H$ NMR (600 MHz, $CDCl_3$): $\delta$=8.33 (d, $J$=4.8 Hz, 1H), 7.59 (t, $J$=7.5 Hz, 1H), 7.48–7.44 (m, 6H), 7.36 (t, $J$=7.7 Hz, 1H), 7.19–7.17 (m, 4H), 7.00 (d, $J$=6.0 Hz, 1H), 6.82 (d, $J$=7.8 Hz, 1H). $^{13}C$ NMR (75 MHz, $CDCl_3$): $\delta$=157.3 (Cq), 149.0 (CH), 145.9 (Cq), 140.3 (Cq), 138.3 (Cq), 135.5 (CH), 131.5 (CH), 130.2 (CH), 130.0 (CH), 128.8 (CH), 126.5 (CH), 121.7 (CH), 118.7 (Cq), 110.4 (Cq). IR (ATR): 3056, 2230, 1675, 1463, 775, 703 $cm^{-1}$. MS (EI) *m/z* (relative intensity): 358 (12), 357 (62) [$M^+$], 356 (100). HRMS (EI) *m/z*: calcd for $C_{25}H_{15}N_3$, 357.1266; found, 357.1267.

#### 4.1.7. 2-(4,4″-Dichloro-[1,1′;3′,1″]-terphenyl-2′-yl) pyridine (**7d**)

The representative procedure was followed, using pyridine **6** (155 mg, 1.00 mmol) and bromo-4-chlorobenzene (421 mg, 2.20 mmol). After 22 h, purification by chromatography (*n*-pentane/$Et_2O$, 3:1→2:1) yielded **7d** (259 mg, 69%) as a colorless oil. $^1H$ NMR (600 MHz, $CDCl_3$): $\delta$=8.35 (d, $J$=4.6 Hz, 1H), 7.52 (t, $J$=7.9 Hz, 1H), 7.42 (d, $J$=7.7 Hz, 2H), 7.35 (t, $J$=7.7 Hz, 1H), 7.13 (d, $J$=8.3 Hz, 4H), 7.02 (d, $J$=8.3 Hz, 4H), 6.97 (t, $J$=6.1 Hz, 1H), 6.85 (d, $J$=7.8 Hz, 1H). $^{13}C$ NMR (150 MHz, $CDCl_3$): $\delta$=158.3 (Cq), 148.8 (CH), 140.7 (Cq), 138.8 (Cq), 138.4 (Cq), 135.2 (CH), 132.5 (Cq), 130.8 (CH), 129.6 (CH), 128.4 (CH), 127.9 (CH), 126.6 (CH), 121.2 (CH). IR (ATR): 3072, 3018, 1603, 1450, 1012, 743 $cm^{-1}$. MS (EI) *m/z* (relative intensity): 376 (78), 375 (64) [$M^+$], 374 (100), 338 (20), 152 (21). HRMS (EI) *m/z*: calcd for $C_{23}H_{15}Cl_2N$, 375.0582; found, 375.0602.

#### 4.1.8. 2′-Pyridin-2-yl-[1,1′;3′,1″]-terphenyl-3,3″-dicarboxylic acid diethylester (**7e**)

The representative procedure was followed, using pyridine **6** (160 mg, 1.03 mmol) and 3-bromoethyl benzoate (504 mg, 2.20 mmol). After 22 h, purification by chromatography (*n*-pentane/$Et_2O$, 3:1→2:1) yielded **7e** (440 mg, 95%) as a yellow oil. $^1H$ NMR (300 MHz, $CDCl_3$): $\delta$=8.31 (d, $J$=4.8 Hz, 1H), 7.84–7.82 (m, 4H), 7.57–7.55 (m, 1H), 7.49 (d, $J$=7.6 Hz, 2H), 7.30 (dt, $J$=7.7, 1.6 Hz, 1H), 7.26–7.24 (m, 2H), 7.20 (t, $J$=7.8 Hz, 2H), 6.91–6.87 (m, 2H), 4.30 (q, $J$=4.3 Hz, 4H), 1.33 (t, $J$=7.1 Hz, 6H). $^{13}C$ NMR (75 MHz, $CDCl_3$): $\delta$=166.4 (Cq), 158.2 (Cq), 148.7 (CH), 141.5 (Cq), 140.9 (Cq), 138.6 (Cq), 135.1 (CH), 133.9 (CH), 130.6 (CH), 130.1 (Cq), 129.7 (CH), 128.5 (CH), 127.7 (CH), 127.6 (CH), 126.8 (CH), 121.1 (CH), 60.8 ($CH_2$), 14.3 ($CH_3$). IR (ATR): 2941, 2223, 1675, 1602, 1485, 1300, 1255, 1213, 1152, 1013, 833 $cm^{-1}$. MS (EI) *m/z* (relative intensity): 452 (24), 451 (100) [$M^+$], 450 (79), 422 (30), 406 (10), 404

(12), 394 (12). HRMS (EI) *m/z*: calcd for $C_{29}H_{25}NO_4$, 451.1784; found, 451.1780.

#### *4.1.9. 2′-Pyridin-2-yl-[1,1′:3′,1″]-terphenyl-3,3″-dicarbonitrile (**7f**)*[20]

The representative procedure was followed, using pyridine **6** (145 mg, 0.93 mmol) and 3-bromobenzonitrile (400 mg, 2.20 mmol). After 22 h, purification by chromatography (*n*-pentane/$Et_2O$, 3:1→1:1) yielded **6a** (169 mg, 51%) as a colorless solid (mp: 144.6–145.1 °C). $^1$H NMR (300 MHz, $CDCl_3$): $\delta$=8.30 (d, *J*=4.9 Hz, 1H), 7.84 (d, *J*=8.5 Hz, 4H), 7.56 (dd, *J*=8.7, 6.3 Hz, 1H), 7.50–7.45 (m, 2H), 7.31 (dt, *J*=7.7, 1.7 Hz, 1H), 7.16 (d, *J*=8.5 Hz, 4H), 6.94 (ddd, *J*=7.4, 4.8, 1.0 Hz, 1H), 6.86 (d, *J*=7.7 Hz, 1H), 4.33 (q, *J*=7.1 Hz, 4H), 1.36 (t, *J*=7.1 Hz, 6H). $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$=166.4 (Cq), 157.9 (Cq), 148.7 (CH), 146.0 (Cq), 141.0 (Cq), 138.3 (Cq), 135.3 (Cq), 129.8 (CH), 129.5 (CH), 128.9 (CH), 128.5 (CH), 128.4 (CH), 126.7 (CH), 121.4 (CH), 60.9 ($CH_2$), 14.3 ($CH_3$). IR (ATR): 3066, 2230, 1583, 1426, 795, 698 cm$^{-1}$. MS (EI) *m/z* (relative intensity): 357 (56) [$M^+$], 356 (100), 354 (6). HRMS (EI) *m/z*: calcd for $C_{25}H_{15}N_3$, 357.1266; found, 357.1233.

#### *4.1.10. 2-(4,4″-Dimethoxy-[1,1′:3′,1″]-terphenyl-2′-yl)-pyridine (**7g**)*[20]

The representative procedure was followed, using pyridine **6** (145 mg, 0.93 mmol) and 4-bromoanisole (411 mg, 2.20 mmol). After 22 h, purification by chromatography (*n*-pentane/$Et_2O$, 5:1→1:1) yielded **7g** (208 mg, 61%) as a colorless solid (mp: 163.1–163.9 °C). $^1$H NMR (300 MHz, $CDCl_3$): $\delta$=8.36 (d, *J*=4.5 Hz, 1H), 7.48 (dd, *J*=8.9, 6.2 Hz, 1H), 7.45–7.35 (m, 2H), 7.33 (dt, *J*=7.8, 1.6 Hz, 1H), 7.01 (d, *J*=8.5 Hz, 4H), 6.92 (dd, *J*=7.6, 5.1 Hz, 1H), 6.88 (d, *J*=7.9 Hz, 1H), 6.70 (d, *J*=8.5 Hz, 4H), 3.74 (s, 6H). $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$=159.2 (Cq), 158.2 (Cq), 148.5 (CH), 141.4 (Cq), 138.4 (Cq), 135.0 (CH), 134.0 (CH), 130.6 (CH), 129.1 (CH), 128.1 (CH), 126.7 (CH), 113.1 (CH), 55.1 ($CH_3$). IR (ATR): 3037, 1609, 1582, 1513, 1233, 1183, 1040, 806 cm$^{-1}$. MS (EI) *m/z* (relative intensity): 367 (95) [$M^+$], 366 (100), 353 (21), 352 (92). HRMS (EI) *m/z*: calcd for $C_{25}H_{21}NO_2$, 367.1572; found, 367.1552.

#### *4.1.11. 2-(2,2″-Dimethoxy-[1,1′;3′,1″]-terphenyl-2′-yl)-pyridine (**7h**)*

The representative procedure was followed, using pyridine **6** (157 mg, 1.01 mmol) and 2-bromoanisole (411 mg, 2.20 mmol). After 22 h, purification by chromatography (*n*-pentane/$Et_2O$, 3:1→2:1) yielded **7h** (241 mg, 65%) as a colorless solid (mp: 186.2–187.3 °C). $^1$H NMR (600 MHz, $CDCl_3$): $\delta$=8.15 (d, *J*=4.2 Hz, 1H), 7.49 (t, *J*=7.5 Hz, 1H), 7.40 (d, *J*=7.7 Hz, 2H), 7.21 (t, *J*=7.8 Hz, 2H), 7.19–7.14 (m, 3H), 6.94–6.85 (m, 3H), 6.78 (t, *J*=7.4 Hz, 1H), 6.65 (br s, 2H), 3.43 (br s, 6H). $^{13}$C NMR (150 MHz, $CDCl_3$): $\delta$=159.5 (Cq), 156.0 (Cq), 147.4 (CH), 140.2 (CH), 137.9 (Cq), 133.5 (CH), 131.9 (CH), 130.8 (CH), 130.0 (CH), 128.1 (CH), 127.5 (Cq), 125.6 (Cq), 120.2 (CH), 120.1 (CH), 110.0 (CH), 54.8 ($CH_3$). IR (ATR): 3042, 2213, 1593, 1467, 1245, 1185, 1178, 823 cm$^{-1}$. MS (EI) *m/z* (relative intensity): 367 (5) [$M^+$], 337 (69), 336 (100), 320 (20). HRMS (EI) *m/z*: calcd for $C_{25}H_{21}NO_2$, 367.1572; found, 367.1571.

#### *4.1.12. 5-(2-Pyridin-2-yl-phenyl)furan-2-carboxylic acid ethyl ester (**13**)*

The representative procedure was followed, using pyridine **6** (155 mg, 1.00 mmol) and **12** (482 mg, 2.20 mmol). After 22 h, purification by chromatography (*n*-pentane/$Et_2O$, 3:1→2:1) yielded **13** (189 mg, 64%) as a brown oil. $^1$H NMR (600 MHz, $CDCl_3$): $\delta$=8.61–8.59 (m, 1H), 7.80–7.77 (m, 1H), 7.63 (dt, *J*=7.8, 1.9 Hz, 1H), 7.45–7.38 (m, 3H), 7.25–7.20 (m, 2H), 6.95 (d, *J*=3.8 Hz, 1H), 5.79 (d, *J*=3.5 Hz, 1H), 4.22 (q, *J*=7.1 Hz, 2H), 1.25 (t, *J*=7.1 Hz, 3H). $^{13}$C NMR (150 MHz, $CDCl_3$): $\delta$=159.0 (Cq), 158.6 (Cq), 156.3 (Cq), 149.1 (Cq), 143.6 (Cq), 138.8 (Cq), 136.5 (CH), 130.4 (CH), 128.9 (CH), 128.7 (CH), 128.3 (CH), 128.1 (CH), 124.4 (CH), 122.3 (CH), 119.2 (CH), 110.6 (CH), 60.7 ($CH_2$), 14.3 ($CH_3$). IR (ATR): 3040, 2872, 2238, 1678, 1120, 904, 814 cm$^{-1}$. MS (EI) *m/z* (relative intensity): 294 (12), 293 (21) [$M^+$], 220 (100), 191 (38), 163 (7). HRMS (EI) *m/z*: calcd for $C_{18}H_{15}NO_3$, 293.1052; found, 293.1024.

#### *4.1.13. 2-(4′-Methoxy-3-methyl-biphenyl-2-yl)-4,5-dihydro-oxazole (**10a**)*[21]

The representative procedure was followed, using oxazoline **8** (161 mg, 1.00 mmol) and 4-bromoanisole (224 mg, 1.20 mmol). After 22 h, purification by chromatography (*n*-pentane/$Et_2O$, 3:1→1:1) yielded **10a** (174 mg, 65%) as a yellow oil. $^1$H NMR (300 MHz, $CDCl_3$): $\delta$=7.37–7.28 (m, 3H), 7.18 (md, *J*=8.1 Hz, 2H), 6.90 (md, *J*=8.8 Hz, 2H), 4.15 (t, *J*=9.3 Hz, 2H), 3.91–3.81 (m, 5H), 2.40 (s, 3H). $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$=164.6 (Cq), 158.8 (Cq), 141.5 (Cq), 137.4 (Cq), 133.6 (Cq), 129.5 (CH), 129.4 (CH), 128.5 (CH), 128.1 (Cq), 127.1 (CH), 113.4 (CH), 67.1 ($CH_2$), 55.2 ($CH_3$), 55.0 ($CH_2$), 19.7 ($CH_3$). IR (ATR): 3062, 2933, 1884, 1666, 1610, 1514, 1461, 1346, 1291, 1248, 1180, 937 cm$^{-1}$. MS (EI) *m/z* (relative intensity): 267 (17) [$M^+$], 266 (100), 222 (4), 152 (2). HRMS (EI) *m/z*: calcd for $C_{17}H_{17}NO_2$, 267.1225; found, 267.1259.

#### *4.1.14. 1-(2′-(4,5-Dihydro-oxazol-2-yl)-3′-methyl-biphenyl-4-yl)ethanone (**10b**)*[21]

The representative procedure was followed, using oxazoline **8** (166 mg, 1.03 mmol) and 4-bromoacetophenone (239 mg, 1.20 mmol). After 22 h, purification by chromatography (*n*-pentane/$Et_2O$, 3:1→1:1) yielded **10b** (197 mg, 68%) as a yellow solid (mp: 88.7–89.1 °C). $^1$H NMR (300 MHz, $CDCl_3$): $\delta$=7.96 (md, *J*=8.6 Hz, 2H), 7.50 (md, *J*=8.6 Hz, 2H), 7.42–7.33 (m, 1H), 7.30–7.18 (m, 2H), 4.15 (t, *J*=8.6 Hz, 2H), 3.85 (t, *J*=8.7 Hz, 2H), 2.62 (s, 3H), 2.42 (s, 3H). $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$=197.8 (Cq), 164.1 (Cq), 146.2 (Cq), 140.8 (Cq), 137.8 (Cq), 135.8 (Cq), 129.7 (CH), 129.6 (CH), 128.6 (CH), 128.1 (CH), 128.0 (Cq), 127.0 (CH), 67.2 ($CH_2$), 55.1 ($CH_2$), 25.6 ($CH_3$), 19.8 ($CH_3$). IR (ATR): 3064, 2878, 1679, 1606, 1402, 1357, 1269, 1253, 1186, 1045, 932, 844 cm$^{-1}$. MS (EI) *m/z* (relative intensity): 279 (17) [$M^+$],

278 (100), 234 (3), 165 (3). HRMS (EI) *m/z*: calcd for $C_{18}H_{17}NO_2$, 279.1259; found, 279.1197.

#### *4.1.15. 2′-(4,5-Dihydro-oxazol-2-yl)-3′-methyl-biphenyl-4-carboxylic acid methyl ester (**10c**)*[21]

The representative procedure was followed, using oxazoline **8** (161 mg, 1.00 mmol) and 4-bromomethyl benzoate (258 mg, 1.20 mmol). After 22 h, purification by chromatography (*n*-pentane/$Et_2O$, 1:1→1:2) yielded **10c** (236 mg, 68%) as a yellow solid (mp: 116.5–117.1 °C). $^1$H NMR (300 MHz, $CDCl_3$): $\delta$=7.96 (md, *J*=8.6 Hz, 2H), 7.50 (md, *J*=8.6 Hz, 2H), 7.41–7.33 (m, 1H), 7.29–7.17 (m, 2H), 4.15 (t, *J*=9.4 Hz, 2H), 3.85 (t, *J*=9.4 Hz, 2H), 2.62 (s, 3H), 2.42 (s, 3H). $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$=167.0 (Cq), 164.1 (Cq), 146.2 (Cq), 140.8 (Cq), 137.8 (Cq), 135.7 (Cq), 129.7 (CH), 129.6 (CH), 129.4 (Cq), 128.6 (CH), 128.1 (CH), 127.0 (CH), 67.2 ($CH_2$), 55.1 ($CH_2$), 29.6 ($CH_3$), 19.8 ($CH_3$). IR (ATR): 3064, 2878, 1726, 1666, 1610, 1460, 1436, 1314, 1280, 1196, 1042, 932, 856 cm$^{-1}$. MS (EI) *m/z* (relative intensity): 295 (17) [M$^+$], 294 (100), 264 (3), 250 (4), 191 (2), 165 (3). HRMS (EI) *m/z*: calcd for $C_{18}H_{17}NO_3$, 295.1208; found, 295.1182.

#### *4.1.16. 2′-(4,5-Dihydro-oxazol-2-yl)-3′-methyl-biphenyl-4-carbonitrile (**10d**)*[21]

The representative procedure was followed, using oxazoline **8** (165 mg, 1.02 mmol) and 4-bromobenzonitrile (218 mg, 1.20 mmol). After 22 h, purification by chromatography (*n*-pentane/$Et_2O$, 3:1→1:3) yielded **10d** (158 mg, 59%) as a brown solid (mp: 102.2–103.4 °C). $^1$H NMR (300 MHz, $CDCl_3$): $\delta$=7.66 (md, *J*=8.6 Hz, 2H), 7.51 (d, *J*=8.6 Hz, 2H), 7.44–7.34 (m, 1H), 7.32–7.25 (m, 1H), 7.21–7.14 (m, 1H), 4.17 (t, *J*=9.5 Hz, 2H), 3.87 (t, *J*=9.4 Hz, 2H), 2.43 (s, 3H). $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$=163.9 (Cq), 146.0 (Cq), 140.1 (Cq), 138.0 (Cq), 131.8 (CH), 130.1 (CH), 129.7 (CH), 129.2 (CH), 128.0 (Cq), 126.9 (CH), 118.9 (Cq), 111.0 (Cq), 67.3 ($CH_2$), 55.1 ($CH_2$), 19.8 ($CH_3$). IR (ATR): 2885, 2231, 1651, 1459, 1346, 1255, 1047, 969, 932, 848, 790, 758 cm$^{-1}$. MS (EI) *m/z* (relative intensity): 262 (18) [M$^+$], 261 (100), 217 (13), 190 (11), 177 (3), 151 (2). HRMS (EI) *m/z*: calcd for $C_{17}H_{14}N_2O$, 262.1106; found, 262.1085.

#### *4.1.17. 2′-(4,5-Dihydro-oxazol-2-yl)-3′-methyl-biphenyl-3-carboxylic acid methyl ester (**10e**)*

The representative procedure was followed, using oxazoline **8** (163 mg, 1.01 mmol) and 3-bromomethyl benzoate (258 mg, 1.20 mmol). After 22 h, purification by chromatography (*n*-pentane/$Et_2O$, 3:1→1:3) yielded **10e** (230 mg, 77%) as a colorless oil. $^1$H NMR (600 MHz, $CDCl_3$): $\delta$=8.06 (s, 1H), 7.95 (d, *J*=7.6 Hz, 1H), 7.52 (d, *J*=7.8 Hz, 1H), 7.52 (d, *J*=7.8 Hz, 1H), 7.39–7.35 (m, 1H), 7.32–7.28 (m, 1H), 7.20–7.15 (m, 1H), 4.09 (t, *J*=9.5 Hz, 2H), 3.84 (s, 3H), 3.78 (t, *J*=9.5 Hz, 2H), 2.35 (s, 3H). $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$=167.0 (Cq), 164.2 (Cq), 141.4 (Cq), 140.8 (Cq), 137.7 (Cq), 132.9 (CH), 130.0 (Cq), 129.6 (CH), 129.4 (CH), 128.3 (CH), 128.2 (Cq), 128.1 (CH), 128.1 (CH), 127.1 (CH), 67.2 ($CH_2$), 55.2 ($CH_2$), 52.1 ($CH_3$), 19.8 ($CH_3$). IR (ATR): 3064, 2952, 1723, 1664, 1581, 1437, 1347, 1313, 1256, 1121, 1044, 972 cm$^{-1}$. MS (EI) *m/z* (relative intensity): 295 (23) [M$^+$], 294 (100), 250 (6), 178 (4), 165 (8). HRMS (EI) *m/z*: calcd for $C_{18}H_{17}NO_3$, 295.1208; found, 295.1174.

#### *4.1.18. 2-(3-Methyl-3′,5′-bis-trifluoromethyl-biphenyl-2-yl)-4,5-dihydro-oxazole (**10f**)*

The representative procedure was followed, using oxazoline **8** (161 mg, 1.00 mmol) and 3,5-bis(trifluoromethyl)bromobenzene (352 mg, 1.20 mmol). After 22 h, purification by chromatography (*n*-pentane/$Et_2O$, 3:1→2:1) yielded **10f** (170 mg, 46%) as a colorless oil. $^1$H NMR (600 MHz, $CDCl_3$): $\delta$=7.91 (s, 2H), 7.84 (s, 1H), 7.43 (t, *J*=7.5 Hz, 1H), 7.33–7.32 (m, 1H), 7.27–7.25 (m, 1H), 4.20 (t, *J*=9.7 Hz, 2H), 3.87 (t, *J*=9.7 Hz, 2H), 2.25 (s, 3H). $^{13}$C NMR (150 MHz, $CDCl_3$): $\delta$=163.9 (Cq), 143.3 (Cq), 138.9 (Cq), 138.6 (Cq), 131.6 (q, *J*=33.2 Hz, Cq), 130.7 (CH), 130.4 (q, *J*=68.7 Hz, CH), 130.2 (CH), 128.9 (CH), 128.6 (Cq), 127.2 (CH), 123.6 (q, *J*=272.7 Hz, Cq), 121.1 (q, *J*=3.8 Hz, CH), 67.5 ($CH_2$), 55.5 ($CH_2$), 20.0 ($CH_3$). $^{19}$F NMR (282 MHz, $CDCl_3$): $\delta$=−63.56 (s). IR (ATR): 2874, 1694, 1453, 1367, 1265, 1148, 1111, 1021, 956, 867 cm$^{-1}$. MS (EI) *m/z* (relative intensity): 373 (100) [M$^+$], 324 (21), 317 (23), 233 (17). HRMS (EI) *m/z*: calcd for $C_{18}H_{13}F_6NO$, 373.0901; found, 373.0917.

#### *4.1.19. 2-(2′-Chloro-3-methyl-biphenyl-2-yl)-4,5-dihydro-oxazole (**10g**)*

The representative procedure was followed, using oxazoline **8** (161 mg, 1.00 mmol) and bromo-2-chlorobenzene (230 mg, 1.20 mmol). After 22 h, purification by chromatography (*n*-pentane/$Et_2O$, 5:1→2:1) yielded **10g** (167 mg, 62%) as a yellow oil. $^1$H NMR (300 MHz, $CDCl_3$): $\delta$=7.31–7.28 (m, 4H), 7.22–7.11 (m, 3H), 4.12 (t, *J*=9.1 Hz, 2H), 3.82 (t, *J*=9.1 Hz, 2H), 2.36 (s, 3H). $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$=164.5 (CH), 141.0 (CH), 139.9 (Cq), 137.9 (Cq), 134.2 (CH), 133.5 (CH), 133.4 (CH), 132.2 (Cq), 131.3 (Cq), 130.0 (CH), 129.8 (Cq), 129.6 (Cq), 128.4 (Cq), 127.3 (Cq), 67.7 ($CH_2$), 55.4 ($CH_2$), 19.8 ($CH_3$). IR (ATR): 3056, 1654, 1489, 1351, 1265, 1003, 943, 856, 767 cm$^{-1}$. MS (EI) *m/z* (relative intensity): 271 (21), [M$^+$], 270 (100), 242 (14), 161 (17), 104 (9). HRMS (EI) *m/z*: calcd for $C_{16}H_{14}ClNO$, 271.0764; found, 271.0765.

#### *4.1.20. 2-(3-Methyl-4′-vinylbiphenyl-2-yl)-4,5-dihydro-oxazole (**10h**)*

The representative procedure was followed, using oxazoline **8** (160 mg, 0.993 mmol) and 4-bromostyrene (226 mg, 1.23 mmol). After 22 h, purification by chromatography (*n*-hexane/EtOAc, 5:1→3:1) yielded **10h** (133 mg, 51%) as a yellow oil. $^1$H NMR (600 MHz, $CDCl_3$): $\delta$=7.43–7.34 (m, 5H), 7.23–7.21 (m, 2H), 6.75 (dd, *J*=17.6, 10.9 Hz, 1H), 5.78 (d, *J*=17.6 Hz, 1H), 5.27 (d, *J*=10.9 Hz, 1H), 4.16 (t, *J*=9.5 Hz, 2H), 3.88 (t, *J*=9.5 Hz, 2H), 2.42 (s, 3H). $^{13}$C NMR (150 MHz, $CDCl_3$): $\delta$=164.4 (Cq), 141.6 (Cq), 140.7 (Cq), 137.5 (Cq), 136.5 (CH), 136.3 (Cq), 129.5 (CH), 129.0 (CH), 128.6 (CH), 128.1 (Cq), 127.1 (CH), 125.9 (CH), 113.8 ($CH_2$), 67.2 ($CH_2$), 55.1 ($CH_2$), 19.8 ($CH_3$). IR (ATR): 1667, 1460, 1342, 1251, 1234, 1041, 933, 895, 849, 794, 762 cm$^{-1}$. MS (EI) *m/z* (relative intensity): 263 (18) [M$^+$], 262 (100),

234 (2), 218 (6), 205 (2), 191 (3), 178 (3), 165 (2). HRMS (EI) *m/z*: calcd for $C_{18}H_{16}NO$, 262.1232; found, 262.1242.

#### 4.1.21. 2-(2′-Methoxy-3-methyl-biphenyl-2-yl)-4,5-dihydro-oxazole (**10i**)[21]

The representative procedure was followed, using oxazoline **8** (161 mg, 1.00 mmol) and 2-bromoanisole (224 mg, 1.20 mmol). After 22 h, purification by chromatography (*n*-pentane/$Et_2O$, 3:1→1:1) yielded **10i** (136 mg, 51%) as a yellow oil. $^1H$ NMR (300 MHz, $CDCl_3$): $\delta$=7.37–7.17 (m, 5H), 6.99–6.89 (m, 2H), 4.05 (t, *J*=9.3 Hz, 2H), 3.84–3.73 (m, 5H), 2.43 (s, 3H). $^{13}C$ NMR (75 MHz, $CDCl_3$): $\delta$=164.5 (Cq), 156.5 (Cq), 138.7 (Cq), 137.2 (Cq), 130.7 (CH), 130.2 (Cq), 129.0 (CH), 128.9 (CH), 128.8 (CH), 128.5 (CH), 128.2 (CH), 120.1 (CH), 110.6 (CH), 66.9 ($CH_2$), 55.5 ($CH_3$), 55.1 ($CH_2$), 20.1 ($CH_3$). IR (ATR): 3063, 2891, 1667, 1496, 1432, 1340, 1234, 1078, 1035, 1020, 935, 894, 761 $cm^{-1}$. MS (EI) *m/z* (relative intensity): 266 (10) [M−$H^+$], 237 (15), 236 (100), 192 (13), 165 (5). HRMS (EI) *m/z*: calcd for $C_{17}H_{17}NO_2$, 267.1259; found, 267.1251.

#### 4.1.22. 1-(4-Acetyl-2′-pyrazol-1-yl-[1,1′;3′,1″]-terphenyl-4″-yl)ethanone (**18a**)

The representative procedure was followed, using **17** (148 mg, 1.03 mmol) and **11a** (438 mg, 2.20 mmol). After 22 h, purification by chromatography (*n*-pentane/$Et_2O$, 3:1→1:1) yielded **18a** (232 mg, 64%) as an off-white solid (mp: 164.2–165.1 °C). $^1H$ NMR (300 MHz, $CDCl_3$): $\delta$=7.83 (dt, *J*=8.4, 1.8 Hz, 4H), 7.65–7.52 (m, 3H), 7.37 (d, *J*=1.8 Hz, 1H), 7.20 (dt, *J*=8.4, 1.8 Hz, 4H), 7.06 (d, *J*=2.3 Hz, 1H), 6.08 (t, *J*=2.2 Hz, 1H), 2.57 (s, 6H). $^{13}C$ NMR (75 MHz, $CDCl_3$): $\delta$=197.6 (Cq), 143.3 (Cq), 139.9 (CH), 139.4 (Cq), 136.4 (Cq), 135.9 (Cq), 132.3 (CH), 130.5 (CH), 129.4 (CH), 128.4 (CH), 128.1 (CH), 106.7 (CH), 26.6 ($CH_3$). IR (ATR): 1675, 1607, 1267, 847, 834, 811, 754, 705, 626, 608, 601, 591 $cm^{-1}$. MS (EI) *m/z* (relative intensity): 380 (48) [$M^+$], 379 (100), 365 (6), 337 (10), 293 (5), 175 (7), 146 (5), 43 (7). HRMS (EI) *m/z*: calcd for $C_{25}H_{20}N_2O_2$, 380.1525; found, 380.1498.

#### 4.1.23. 2′-Pyrazol-1-yl-[1,1′;3′,1″]-terphenyl-4,4″-dicarboxylic acid dimethyl ester (**18b**)

The representative procedure was followed, using **17** (144 mg, 1.00 mmol) and **11b** (473 mg, 2.20 mmol). After 22 h, purification by chromatography (*n*-pentane/$Et_2O$, 3:1→2:1) yielded **18b** (214 mg, 52%) as an off-white solid (mp: 144.2–145.6 °C). $^1H$ NMR (600 MHz, $CDCl_3$): $\delta$=7.92 (d, *J*=8.2 Hz, 4H), 7.60 (t, *J*=8.0 Hz, 1H), 7.55–7.50 (m, 2H), 7.36 (s, 1H), 7.16 (d, *J*=8.1 Hz, 4H), 7.05 (s, 1H), 6.06 (s, 1H), 1.34 (s, 6H). $^{13}C$ NMR (150 MHz, $CDCl_3$): $\delta$=164.0 (Cq), 143.0 (CH), 140.7 (CH), 137.5 (Cq), 137.2 (Cq), 134.1 (Cq), 130.0 (CH), 128.2 (Cq), 127.0 (CH), 125.9 (CH), 106.6 (CH), 104.3 (CH), 120.9 ($CH_3$). IR (ATR): 1719, 1609, 1435, 1401, 1313, 1277, 1188, 1103, 1018, 770, 708 $cm^{-1}$. MS (EI) *m/z* (relative intensity): 412 (43) [$M^+$], 411 (100), 381 (5), 351 (6), 292 (4), 265 (2), 175 (2), 147 (2). HRMS (EI) *m/z*: calcd for $C_{25}H_{20}N_2O_4$, 412.1423; found, 412.1408.

#### 4.1.24. 1-(4,4″-Dimethoxy-[1,1′:3′,1″]-terphenyl-2′-yl)-1H-pyrazole (**18c**)[21]

The representative procedure was followed, using **17** (148 mg, 1.03 mmol) and **11c** (411 mg, 2.20 mmol). After 22 h, purification by chromatography (*n*-pentane/$Et_2O$, 4:1→1:1) yielded **18c** (200 mg, 55%) as a colorless solid (mp: 132.4–133.1 °C). $^1H$ NMR (300 MHz, $CDCl_3$): $\delta$=7.55–7.50 (m, 1H), 7.45–7.42 (m, 3H), 7.09 (d, *J*=2.4, 0.6 Hz, 1H), 7.03 (dt, *J*=9.6, 2.5 Hz, 4H), 6.76 (dt, *J*=9.6, 2.5 Hz, 4H), 6.10–6.09 (m, 1H), 3.77 (s, 6H). $^{13}C$ NMR (75 MHz, $CDCl_3$): $\delta$=158.8 (Cq), 140.1 (Cq), 139.2 (CH), 136.2 (Cq), 132.4 (CH), 131.1 (Cq), 129.6 (CH), 129.3 (CH), 129.0 (CH), 113.5 (CH), 106.0 (CH), 55.1 ($CH_3$). IR (ATR): 1608, 1515, 1462, 1280, 1241, 1183, 1039, 1030, 843, 835, 800, 762 $cm^{-1}$. MS (EI) *m/z* (relative intensity): 355 (100) [M−$H^+$], 341 (6), 311 (4), 297 (2), 269 (2). HRMS (EI) *m/z*: calcd for $C_{23}H_{20}N_2O_2$, 356.1525; found, 356.1537.

#### 4.1.25. 2-(4′-Acetylphenyl)phenylethanone (**20a**)[20]

The representative procedure was followed, using **19** (225 mg, 1.00 mmol) and **11a** (229 mg, 1.20 mmol). After 22 h, purification by chromatography (*n*-pentane/$Et_2O$, 8:1→2:1) yielded **20a** (162 mg, 68%) as a light yellow oil. $^1H$ NMR (300 MHz, $CDCl_3$): $\delta$=7.99 (d, *J*=8.3 Hz, 2H), 7.58 (dd, *J*=7.5, 1.5 Hz, 1H), 7.52 (dt, *J*=7.5, 1.4 Hz, 1H), 7.45 (dd, *J*=7.5, 1.4 Hz, 1H), 7.41 (d, *J*=7.5, 1.3 Hz, 2H), 7.35 (dd, *J*=7.5, 1.3 Hz, 1H), 2.62 (s, 3H), 2.11 (s, 3H). $^{13}C$ NMR (75 MHz, $CDCl_3$): $\delta$=203.5 (Cq), 197.5 (Cq), 145.6 (Cq), 140.3 (Cq), 139.4 (Cq), 136.1 (Cq), 130.9 (CH), 130.2 (CH), 128.9 (CH), 128.5 (CH), 128.1 (CH), 128.0 (CH), 30.2 ($CH_3$), 26.5 ($CH_3$). IR (ATR): 3070, 2945, 1690, 1623, 1476, 1300, 1179, 1035, 771 $cm^{-1}$. MS (EI) *m/z* (relative intensity): 238 (78) [$M^+$], 223 (100), 195 (25), 181 (45), 152 (27). HRMS (EI) *m/z*: calcd for $C_{16}H_{14}O_2$, 238.0994; found, 238.0981.

#### 4.1.26. 4-(2′-Acetylphenyl)benzoic acid ethyl ester (**20b**)[20]

The representative procedure was followed, using **19** (225 mg, 1.00 mmol) and **11b** (275 mg, 1.20 mmol). After 22 h, purification by chromatography (*n*-pentane/$Et_2O$, 4:1→3:1) yielded **20b** (173 mg, 65%) as a yellow oil. $^1H$ NMR (300 MHz, $CDCl_3$): $\delta$=8.10 (d, *J*=8.2 Hz, 2H), 7.59 (dd, *J*=7.5, 1.5 Hz, 1H), 7.51 (dt, *J*=7.4, 1.6 Hz, 1H), 7.45 (dd, *J*=7.4, 1.4 Hz, 1H), 7.40 (d, *J*=8.2 Hz, 2H), 7.38 (d, *J*=1.4 Hz, 1H), 4.30 (q, *J*=7.1 Hz, 2H), 2.08 (s, 3H), 1.41 (t, *J*=7.1 Hz, 3H). $^{13}C$ NMR (75 MHz, $CDCl_3$): $\delta$=203.8 (Cq), 166.2 (Cq), 154.4 (Cq), 140.5 (Cq), 139.5 (Cq), 130.9 (CH), 130.2 (CH), 129.8 (Cq), 129.7 (CH), 128.8 (CH), 128.1 (CH), 128.0 (CH), 61.1 ($CH_2$), 30.4 ($CH_3$), 14.3 ($CH_3$). IR (ATR): 3059, 2988, 1716, 1656, 1244, 1100, 1028, 790 $cm^{-1}$. MS (EI) *m/z* (relative intensity): 268 (60) [$M^+$], 267 (18), 239 (21), 223 (33), 181 (100). HRMS (EI) *m/z*: calcd for $C_{17}H_{16}O_3$, 268.1099; found, 268.1087.

#### 4.1.27. 2-(4′-Methoxyphenyl)phenylethanone (**20c**)[20]

The representative procedure was followed, using **19** (225 mg, 1.00 mmol) and **11c** (224 mg, 1.20 mmol). After 22 h, purification by chromatography (*n*-pentane/$Et_2O$, 4:1→

3:1) yielded **20c** (196 mg, 56%) as a colorless solid (mp: 83.4–84.5 °C). $^1$H NMR (300 MHz, $CDCl_3$): $\delta$=7.45–7.35 (m, 2H), 7.31–7.25 (m, 2H), 7.16 (d, $J$=8.5 Hz, 2H), 6.86 (d, $J$=8.5 Hz, 2H), 3.74 (s, 3H), 1.91 (s, 3H). $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$=205.5 (Cq), 159.5 (Cq), 140.8 (Cq), 140.0 (Cq), 132.9 (CH), 130.6 (CH), 130.0 (CH), 129.9 (CH), 127.7 (CH), 126.9 (CH), 114.0 (CH), 55.2 ($CH_3$), 30.3 ($CH_3$). IR (ATR): 3055, 2981, 1683, 1600, 1267, 1013, 840 cm$^{-1}$. MS (EI) *m/z* (relative intensity): 268 (10) [$M^+$], 253 (65), 211 (100). HRMS (EI) *m/z*: calcd for $C_{15}H_{14}O_2$, 226.0994; found, 226.0987.

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