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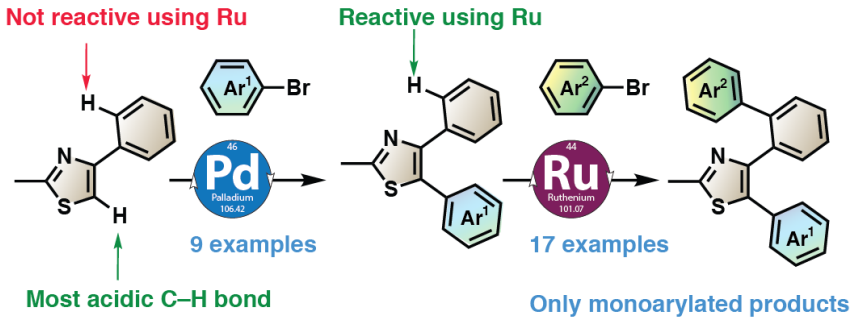
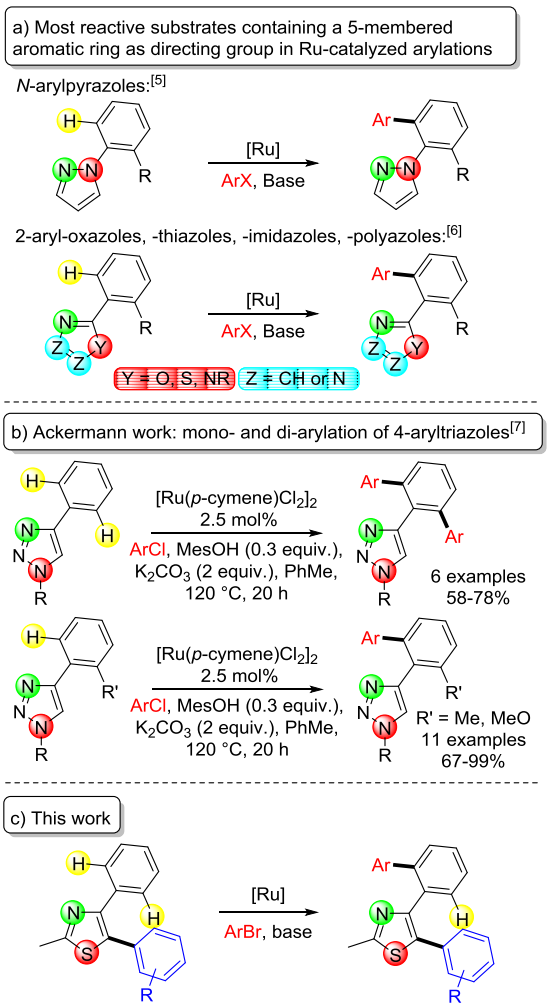


Abstract: The reactivity of the phenyl substituent of 4-phenylthiazoles in Ru-catalyzed direct arylation was studied. 4-Phenylthiazole was found to be unreactive; whereas, the introduction of an aryl unit at C5-position of 4-phenylthiazole enhances its reactivity, allowing the selective mono-arylation of the phenyl unit of 4-phenylthiazoles in moderate to high yields using 5 mol% of $[Ru(p\text{-cymene})Cl_2]_2$ catalyst precursor associated to KOPiv as base. These results reveal that the conformation and electronic properties of 4-phenylthiazoles are crucial to allow the formation of suitable intermediates in the course of the catalytic cycle. The reaction tolerated both electron-rich and electron-poor aryl bromides allowing the straightforward tuning of the electronic properties of the arylated 2-methyl-4-phenyl-5-arylthiazoles.

Introduction

Iridium(III) complexes containing 4-arylthiazole ligands exhibit intriguing photophysical properties.[1a-c] For example, phosphorescent homoleptic thiazole-based Ir(III) emitters were found to exhibit high electroluminescence efficiencies in monochromic PhOLEDs.[1c] They have also been employed as catalysts for enantioselective reactions.[1d-f] Therefore, the

discovery of simple, but general routes to new families of substituted 4-arylthiazole derivatives, used as cyclometallated ligands, will allow to tune easily their steric and electronic properties which have a direct impact on their photophysical and catalytic properties and therefore, this will be useful for organometallic chemists. In recent years, arylations *via* a metal-catalyzed C–H bond activation step, has brought a revolution in the access of polyaromatics.[2] Such C-C couplings are very attractive compared to the more classical Pd-catalyzed reactions such as Negishi, Stille and Suzuki cross-couplings as the synthesis of organometallic derivatives is not requested.[3] The Ru-catalyzed direct arylation of a wide variety of compounds containing a nitrogen atom as directing group such as the use of 2-arylpyridines for access to (hetero)arylated 2-arylpyridines has been largely described.[4] Several examples of Ru-catalyzed arylations *via* a C-H bond activation the aryl substituent of *N*-arylpyrazoles with aryl halides (Scheme 1, a, left)[5] and the arylation or diarylation of the aryl unit of 2-aryl(poly)azoles and 2-arylimidazoles have also been reported (Scheme 1, a, right).[6] In sharp contrast, very few examples of Ru-catalyzed direct arylations of an aryl at C4-position of (poly)azoles have been described, as to our knowledge, only 1,2,3-triazoles have been successfully employed (Scheme 1, b).[7] In 2010, Ackermann et al. reported that the reaction of 4-aryltriazoles with aryl chlorides using [Ru(*p*-cymene)Cl_2)$_2$ delivered the di-arylated 4-aryltriazoles; whereas, the mono-arylated compounds could be obtained with *ortho*- and *meta*-substituted 4-aryltriazoles such as 1-alkyl-4-(*o*-tolyl)-1,2,3-triazoles.[7]
Thiazoles containing a biaryl unit at C4-position are currently prepared *via* Suzuki couplings.[8] To our knowledge, the metal-catalyzed direct arylation of the aryl unit of 4-arylthiazoles has not been described yet. As the discovery of an effective method, for the arylation of the phenyl unit of 4-phenylthiazoles, especially using easily available aryl sources, catalysts and bases is highly desirable, the reactivity 4-phenylthiazoles in direct arylations in the presence of ruthenium catalysts needed to be investigated. Here, we report on the influence of C5-aryl substituents on 4-phenylthiazoles on their reactivity in ruthenium-catalyzed direct arylations, and on the scope of the reaction (Scheme 1, c).

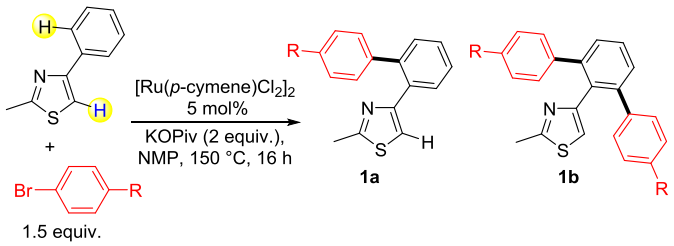


Scheme 1. Ru-catalyzed direct arylations of arenes bearing a 5-membered aromatic ring as directing group.

Results and Discussion

Ethyl 4-bromobenzoate (1.5 equiv.) and 2-methyl-4-phenylthiazole (1 equiv.) were employed as substrates for our initially study (Table 1). We examined the influence of the two solvents NMP (NMP: *N*-Methyl-2-pyrrolidone) and xylene using 5 mol% [Ru(*p*-cymene)Cl_2]$_2$ catalyst and KOPiv as the base as reaction conditions, but in both cases, the desired mono-arylation product **1a** and the di-arylation product **1b** were not detected, and 2-methyl-4-phenylthiazole was recovered unreacted (Table 1, entries 1 and 2). The use of 4-bromoanisole, 4-*tert*-butylbromobenzene and 4-bromobenzonitrile as aryl sources or the addition of 10 mol% $AgSbF_6$ as additive to the reaction mixture also failed to provide any desired coupling product (Table 1, entries 3-6).

Table 1. Influence of the reaction conditions on the Ru-catalyzed arylation of 4-phenylthiazole with aryl bromides.



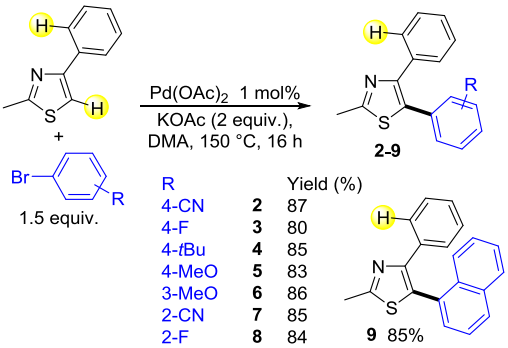
Entry	Solvent	R	Yield in **1a** or **1b** (%)
1	NMP	CO_2Et	0
2	Xylene	CO_2Et	0
3	NMP	CO_2Et	0[a]
4	NMP	OMe	0
5	NMP	CN	0
6	NMP	*t*Bu	0

Conditions: [Ru(*p*-cymene)Cl_2]$_2$ 5 mol%, aryl bromide (1.5 equiv.), 4-phenylthiazole (1 equiv.), KOPiv (2 equiv.), 16 h, 150 °C. [a] With 10 mol% $AgSbF_6$ as additive.

Based on the results of the table 1, we assumed that either the electronic properties and/or the conformation (i.e. position of the phenyl group relative to that of the thiazole ring) of 2-methyl-4-phenylthiazole are not suitable to promote the C-H bond cleavage in the presence of the Ru-catalyst, or a Ru-catalyst poisoning occurred due to the presence of the acidic C-H bond at C5-position on thiazole. Therefore, we introduced a set of aryl substituents at C5-position of 4-phenylthiazole in order to 1) block that position to avoid potential Ru-poisoning, 2) tune the electronic properties of the thiazole ring, 3) more importantly, modify the conformation of 4-arylthiazole *via* the modulation of the steric hindrance of the incorporated aryl groups at C5-position.

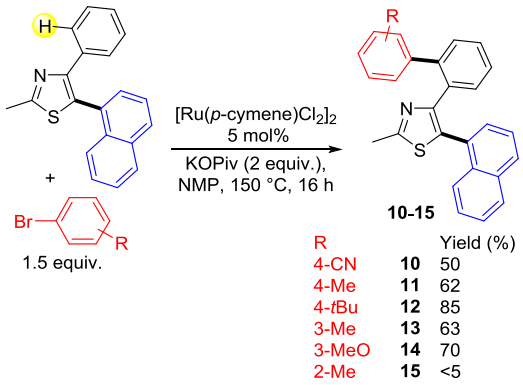
The 2-methyl-4-phenyl-5-arylthiazoles **2-8** were prepared *via* Pd-catalyzed direct arylations of 2-methyl-4-phenylthiazole with a set of aryl bromides using our previously reported optimized reaction conditions,[9] (i.e. 1 mol% of phosphine-free $Pd(OAc)_2$ catalyst, KOAc as the base in DMA) (Scheme 2). Regiospecific C5-arylations and high yields in **2-5** were obtained using aryl bromides bearing cyano, fluoro, *tert*-butyl, or methoxy *para*-substitutents.

A methoxy-substituent at *meta*-position on the aryl bromide was also tolerated giving access to **6** in 86% yield. Reactions with the more hindered substrates, 2-bromobenzonitrile and 1-bromonaphthalene were also successful affording **7** and **9** in 85% yields. The complete regioselectivity in favor of the arylation at C5-position of thiazoles observed with palladium-catalysis is due to the Concerted Metalation Deprotonation CMD mechanism which is operative for these couplings.[10,11]



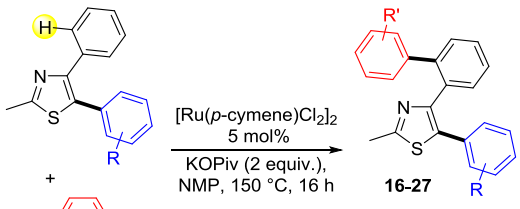
Scheme 2. Scope of the Pd-catalyzed C5-arylation of 2-methyl-4-phenylthiazole.

Then, the reactivity for arylation *via* a Ru-catalyzed C-H bond activation of the phenyl unit of the previously prepared C5-arylated 4-phenylthiazole derivatives **2-9** was evaluated (Schemes 3 and 4). The reaction of 2-methyl-5-(naphthalen-1-yl)-4-phenylthiazole **9** with 4-bromobenzonitrile using 5 mol% [Ru(*p*-cymene)Cl_2]$_2$ catalyst and KOPiv as base in NMP gave **10** in 50% yield (Scheme 3). It should be mentioned that no formation of the 2,6-diarylated phenyl product, which was often obtained in Ru(II)-catalyzed *ortho*-directed C-H bond arylations (see scheme 1, b), was observed. Aryl bromides bearing methyl-, *tert*-butyl- or methoxy-substituents at *para*- or *meta*-positions were also tolerated, and their reaction with **9** afforded the products **11-14** in 62-85% yields. Conversely, the reaction of **9** with 2-bromotoluene was very sluggish affording **15** in <5% yield, revealing that congested aryl bromides are not suitable for such arylations.



Scheme 3. Scope of the Ru-catalyzed arylation of 2-methyl-5-(naphthalen-1-yl)-4-phenylthiazole.

Then, the influence of a set of electron-donating and electron-withdrawing substituents on the aryl group at thiazolyl-C5-position was investigated (Scheme 4). Electron-donating *para*-*tert*-butyl- and *para*-methoxy-substituents were tolerated. From compounds **4** and **5** using 4-bromobenzonitrile as the coupling partner, the target products **16** and **19** were obtained in 73% and 71% yields, respectively. Again, no formation of diarylated products was detected by GC/MS analysis of the crude mixtures. The reaction of 4-bromobenzonitrile with *meta*-methoxy-substituted 5-arylpyrazole **6** afforded the expected product **20** in 70% yield. Conversely, a poor reactivity of the thiazolyl derivative **2** bearing a *para*-cyano-substituent with 4-bromobenzonitrile was observed; whereas, good yields in **22** and **23** were obtained for the reaction of **2** with 4-*tert*-butylbromobenzene or 3-bromotoluene. The position of the cyano-substituent on the aryl unit on thiazole had no significant influence, as from the *ortho*-cyano-substituted compound **7**, the products **24** and **25** were obtained in similar yields than from **2**. The *ortho*- and *para*-fluoro-substituted 5-arylthiazoles **3** and **8** in the presence of 4-*tert*-butylbromobenzene also provided the target products **26** and **27** in good yields.



R	R'		Yield (%)
4-MeO	4-CN	**16**	73
4-MeO	4-CF_3	**17**	61
4-MeO	3-Me	**18**	64
4-*t*Bu	4-CN	**19**	71
3-MeO	4-CN	**20**	70
4-CN	4-CN	**21**	23
4-CN	4-*t*Bu	**22**	73
4-CN	3-Me	**23**	70
2-CN	4-*t*Bu	**24**	76
2-CN	3-Me	**25**	73
4-F	4-*t*Bu	**26**	62
2-F	4-*t*Bu	**27**	67

Scheme 4. Scope of the Ru-catalyzed arylation of 2-methyl-4-phenyl-5-arylthiazole.

In order to gain more insight into the mechanism, we performed DFT calculations and also competition reactions to investigate the impact of the C5-aryl substituent of thiazole for such couplings. The DFT-optimized structures of 2-methyl-4-phenylthiazole, **2** (C_6H_4CN-C5-substituent on thiazole) and **5** (C_6H_4MeO-C5-substituent on thiazole) confirms that 2-methyl-4-phenylthiazole has a low dihedral angle between the thiazole core and the phenyl ring attached at position C4 (9°); whereas this angle is significantly higher for compounds **2** (37°) and **5** (33°) (Figure 1). Moreover, the calculated total charge of the thiazole cycle is -0.30e for 2-methyl-4-phenylthiazole, -0.57e for **2** and -0.77e for **5**, there are therefore significant differences leading to different coordination strengths with Ru.

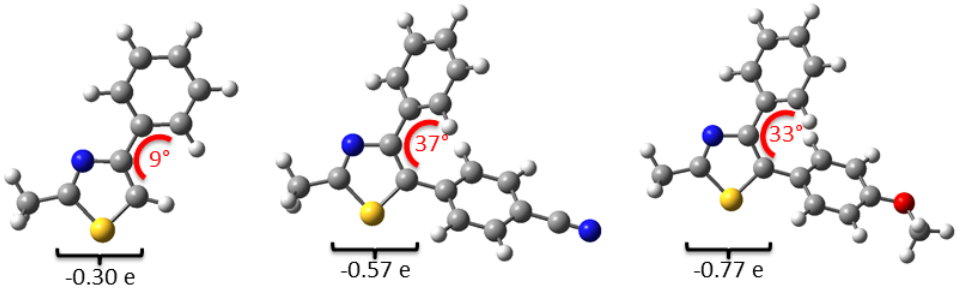
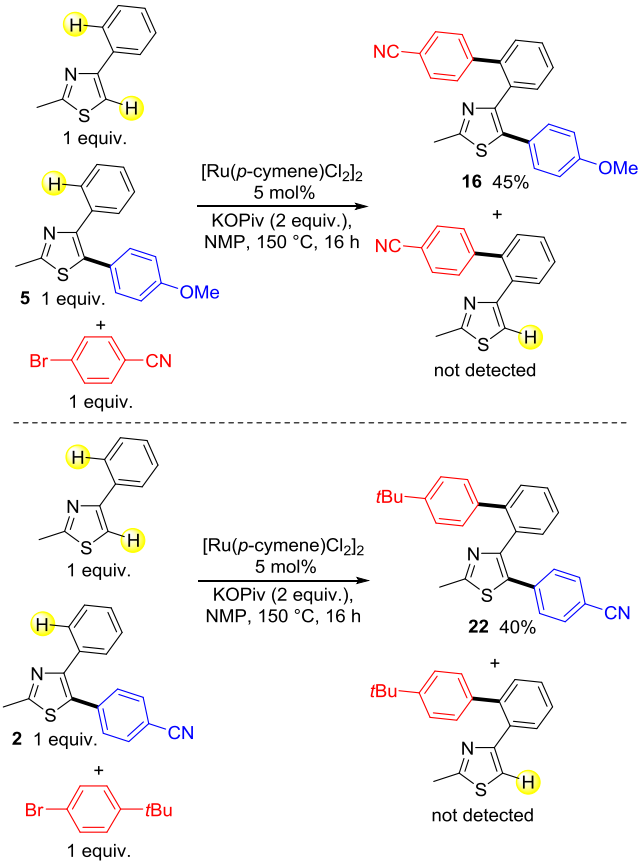


Figure 1. Representation of the DFT-optimized structures of 2-methyl-4-phenylthiazole, **5** and **6**. We provide the dihedral angle between the thiazole core and the phenyl ring attached at position C4 (in degrees) as well as the total charge of the thiazole cycle. See computational part in the experimental section for details.

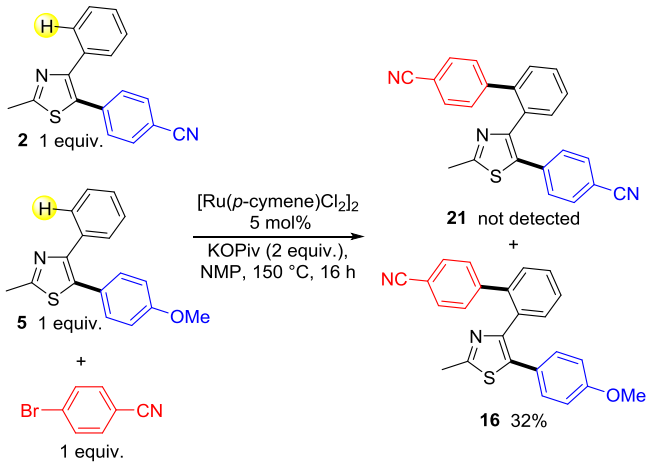
Then three competition reactions were performed (Schemes 5 and 6). From an equimolar mixture of 2-methyl-4-phenylthiazole and 5-(4-methoxyphenyl)-2-methyl-4-phenylthiazole **5**

using 1 equiv. of 4-bromobenzonitrile as the coupling partner, in the presence of 5 mol% [Ru(*p*-cymene)Cl_2]$_2$ catalyst, only the formation the product **16** arising from the arylation of **5** was observed (Scheme 5 top). A similar result was obtained from an equimolar mixture of 2-methyl-4-phenylthiazole and 4-(2-methyl-4-phenylthiazol-5-yl)benzonitrile **2**, as only product **22** was obtained (Scheme 5, bottom). These results confirm that the electronic properties and/or conformation of 2-methyl-4-phenylthiazole are not appropriate for Ru-catalyzed direct arylations, and demonstrate that this substrate is not a poison for the Ru-catalyst.



Scheme 5. Competition reactions for Ru-catalyzed arylations of 2-methyl-4-phenylthiazoles.

The influence of electron-donating and electron-withdrawing substituents on the thiazolyl 5-aryl unit was also examined using an equimolar mixture of 4-(2-methyl-4-phenylthiazol-5-yl)benzonitrile **2** and 5-(4-methoxyphenyl)-2-methyl-4-phenylthiazole **5** (Scheme 6). Only the product **16** arising from the coupling with **5** was observed, confirming a deleterious influence of the presence of a cyano substituent on the thiazolyl C5-aryl unit for couplings with electron-deficient aryl bromides. This indicates that the electronic properties of the C5-aryl group also have an influence on the reactions rates.



Scheme 6. Competition reaction for Ru-catalyzed arylation of 2-methyl-4-phenyl-5-arylthiazoles.

Conclusions

In summary, we demonstrated that 4-phenylthiazole derivatives bearing an aryl group at C5-position are reactive coupling partners in Ru-catalyzed direct arylations affording selectively the mono-arylated compounds. Conversely, under the same conditions, 4-phenylthiazole remained unreacted revealing that appropriate conformation and electronic properties of 4-arylthiazoles are crucial to allow the formation of suitable intermediates in the course of the catalytic cycle. A variety of mono-arylated 2-methyl-4-phenyl-5-arylthiazoles was obtained in moderate to high yields using both electron-rich and electron-poor aryl bromides and 5 mol% of the easily available $[Ru(p\text{-cymene})Cl_2]_2$ catalyst precursor associated to KOPiv as inexpensive base. This strategy allows the straightforward synthesis of arylated 2-methyl-4-phenyl-5-arylthiazole via two successive metal-catalyzed C-H bond functionalization steps from commercially available compounds, allowing to tune easily their steric and electronic properties.

Experimental Section

General procedure for palladium-catalyzed direct arylations: The reaction of the aryl bromide (1.5 mmol), 2-methyl-4-phenylthiazole (1 mmol, 0.175 g), and KOAc (2 mmol, 0.196 g) in the presence of $Pd(OAc)_2$ (0.01 mmol, 2.2 mg), at 150 °C during 16 h in DMA (4 mL) under argon affords the coupling products 2-9 after evaporation of the solvent and

purification on silica gel. Eluent heptane:ethyl acetate 4:1 for compound 7, heptane:ethyl acetate 9:1 for compounds 2, 3, 8; heptane:ethyl acetate 19:1 for compounds 4, 5, 6, 9.

4-(2-Methyl-4-phenylthiazol-5-yl)benzonitrile (2):[12] From 4-bromobenzonitrile (0.182 g, 1 mmol) and 2-methyl-4-phenylthiazole (1 mmol, 0.175 g), product 2 was obtained in 87% yield (0.240 g) as a yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.54 (d, *J* = 8.7 Hz, 2H), 7.47-7.42 (m, 2H), 7.38 (d, *J* = 8.7 Hz, 2H), 7.32-7.26 (m, 3H), 2.75 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 165.3, 151.2, 137.1, 134.3, 132.4, 130.2, 129.9, 129.1, 128.6, 128.4, 118.5, 111.3, 19.3.

5-(4-Fluorophenyl)-2-methyl-4-phenylthiazole (3):[12] From 4-bromofluorobenzene (0.175 g, 1 mmol) and 2-methyl-4-phenylthiazole (1 mmol, 0.175 g), product 3 was obtained in 80% yield (0.215 g) as a yellow solid: mp 85-87 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.51 (d, *J* = 8.5 Hz, 2H), 7.35-7.27 (m, 5H), 7.02 (t, *J* = 8.5 Hz, 2H), 2.77 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 163.8, 162.4 (d, *J* = 248.3 Hz), 149.6, 134.7, 131.3 (d, *J* = 8.1 Hz), 131.2, 129.0, 128.3, 128.2 (d, *J* = 3.5 Hz), 127.8, 115.8 (d, *J* = 21.7 Hz), 19.2.

5-(4-(*tert*-Butyl)phenyl)-2-methyl-4-phenylthiazole (4): From 1-bromo-4-*tert*-butylbenzene (0.213 g, 1 mmol) and 2-methyl-4-phenylthiazole (1 mmol, 0.175 g), product 4 was obtained in 85% yield (0.261 g) as a yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.59 (d, *J* = 8.5 Hz, 2H), 7.39-7.26 (m, 7H), 2.78 (s, 3H), 1.37 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 163.5, 151.0, 149.2, 135.2, 132.6, 129.2, 129.1, 129.0, 128.3, 127.6, 125.6, 34.7, 31.3, 19.3.

Anal. Calcd for $C_{20}H_{21}NS$ (307.46): C, 78.13; H, 6.88; N, 4.56. Found: C, 78.25; H, 7.05; N, 4.30.

5-(4-Methoxyphenyl)-2-methyl-4-phenylthiazole (5):[12] From 4-bromoanisole (0.187 g, 1 mmol) and 2-methyl-4-phenylthiazole (1 mmol, 0.175 g), product 5 was obtained in 83% yield (0.233 g) as a yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.59-7.52 (m, 2H), 7.34-7.24 (m, 5H), 6.86 (d, *J* = 8.7 Hz, 2H), 3.81 (s, 3H), 2.76 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$): δ 163.2, 159.4, 148.9, 135.1, 132.4, 130.8, 129.0, 128.3, 127.5, 124.4, 114.2, 55.3, 19.2.

5-(3-Methoxyphenyl)-2-methyl-4-phenylthiazole (6): From 3-bromoanisole (0.187 g, 1 mmol) and 2-methyl-4-phenylthiazole (1 mmol, 0.175 g), product 6 was obtained in 86% yield (0.241 g) as a yellow oil.
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.56 (d, *J* = 8.3 Hz, 2H), 7.35-7.27 (m, 3H), 7.22 (t, *J* = 7.8 Hz, 1H), 6.95 (d, *J* = 8.2 Hz, 1H), 6.90-6.83 (m, 2H), 3.69 (s, 3H), 2.77 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$): δ 163.8, 159.6, 149.6, 135.0, 133.4, 132.3, 129.7, 129.1, 128.3, 127.7, 122.0, 114.8, 113.9, 55.1, 19.2.
Anal. Calcd for $C_{17}H_{15}NOS$ (281.37): C, 72.57; H, 5.37; N, 4.98. Found: C, 72.76; H, 5.47; N, 5.12.

2-(2-Methyl-4-phenylthiazol-5-yl)benzonitrile (7):[13] From 2-bromobenzonitrile (0.182 g, 1 mmol) and 2-methyl-4-phenylthiazole (1 mmol, 0.175 g), product 7 was obtained in 85% yield (0.235 g) as a white solid: mp 131-133 °C.
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.69 (d, *J* = 8.3 Hz, 1H), 7.55 (td, *J* = 7.8, 1.1 Hz, 1H), 7.47-7.39 (m, 4H), 7.29-7.23 (m, 3H), 2.79 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$): δ 165.8, 152.5, 136.2, 134.2, 133.7, 132.9, 132.1, 128.8, 128.7, 128.4, 128.1, 126.9, 117.4, 113.7, 19.3.

5-(2-Fluorophenyl)-2-methyl-4-phenylthiazole (8): From 2-bromofluorobenzene (0.175 g, 1 mmol) and 2-methyl-4-phenylthiazole (1 mmol, 0.175 g), product 8 was obtained in 84% yield (0.226 g) as a yellow oil.
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.56-7.51 (m, 2H), 7.38-7.26 (m, 5H), 7.16-7.06 (m, 2H), 2.80 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$): δ 165.2, 159.8 (d, *J* = 249.3 Hz), 151.7, 134.9, 132.4 (d, *J* = 2.5 Hz), 130.2 (d, *J* = 8.0 Hz), 128.5, 128.3, 127.8, 124.6, 124.3 (d, *J* = 3.7 Hz), 120.2 (d, *J* = 15.2 Hz), 116.2 (d, *J* = 21.9 Hz), 19.2.
Anal. Calcd for $C_{16}H_{12}FNS$ (269.34): C, 71.35; H, 4.49; N, 5.20. Found: C, 71.19; H, 4.62; N, 5.14.

2-Methyl-5-(naphthalen-1-yl)-4-phenylthiazole (9):[14] From 1-bromonaphthalene (0.207 g, 1 mmol) and 2-methyl-4-phenylthiazole (1 mmol, 0.175 g), product 9 was obtained in 85% yield (0.256 g) as a yellow solid: mp 138-140 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.93 (d, *J* = 8.2 Hz, 2H), 7.85 (d, *J* = 8.4 Hz, 1H), 7.55-7.40 (m, 6H), 7.16-7.08 (m, 3H), 2.86 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 164.8, 151.1, 134.9, 133.9, 132.5, 129.8, 129.7, 129.5, 129.3, 128.5, 128.3, 128.2, 127.6, 126.9, 126.4, 125.8, 125.6, 19.4.

General procedure for ruthenium-catalyzed direct arylations: The reaction of the 2-methyl-4-phenyl-5-arylthiazole derivative (1 mmol), aryl bromide (1.5 mmol), and KOPiv (2 mmol, 0.280 g) in the presence of $[Ru(p\text{-cymene})Cl_2]_2$ (0.05 mmol, 30.5 mg), at 150 °C during 16 h in NMP (4 mL) under argon affords the coupling products 10-27 after evaporation of the solvent and purification on silica gel. Eluent heptane:ethyl acetate 5:1 for compound 10; heptane:ethyl acetate 10:1 for compounds 12, 14, 16, 20, 21; heptane:ethyl acetate 13:1 for compounds 11, 13, 17, 18, 19, heptane:ethyl acetate 20:1 for compounds 22-27.

2'-(2-Methyl-5-(naphthalen-1-yl)thiazol-4-yl)-[1,1'-biphenyl]-4-carbonitrile (10): From 4-bromobenzonitrile (0.273 g, 1.5 mmol) and 2-methyl-5-(naphthalen-1-yl)-4-phenylthiazole 9 (1 mmol, 0.301 g), product 10 was obtained in 50% yield (0.201 g) as a yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.78 (dd, *J* = 7.7, 1.0 Hz, 1H), 7.73 (d, *J* = 8.2 Hz, 1H), 7.68 (d, *J* = 8.2 Hz, 1H), 7.49-7.38 (m, 2H), 7.36 (d, *J* = 8.3 Hz, 1H), 7.30 (td, *J* = 7.6, 1.2 Hz, 1H), 7.23 (td, *J* = 7.6, 1.2 Hz, 1H), 7.12 (dd, *J* = 8.1, 7.3 Hz, 1H), 6.99 (d, *J* = 8.4 Hz, 2H), 6.93 (dd, *J* = 7.7, 0.9 Hz, 1H), 6.68 (dd, *J* = 7.2, 1.0 Hz, 1H), 6.54 (d, *J* = 8.4 Hz, 2H), 2.85 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 165.4, 150.7, 145.9, 139.4, 133.7, 133.4, 131.6, 131.4, 131.2, 131.1, 129.7, 129.0, 128.9, 128.6, 128.5 (*2), 128.4, 127.9, 126.0, 125.0, 124.9, 109.8, 19.4.

Anal. Calcd for $C_{27}H_{18}N_2S$ (402.52): C, 80.57; H, 4.51; N, 6.96. Found: C, 80.82; H, 4.21; N, 7.00.

2-Methyl-4-(4'-methyl-[1,1'-biphenyl]-2-yl)-5-(naphthalen-1-yl)thiazole (11): From 4-bromotoluene (0.256 g, 1.5 mmol) and 2-methyl-5-(naphthalen-1-yl)-4-phenylthiazole 9 (1 mmol, 0.301 g), product 11 was obtained in 62% yield (0.242 g) as a yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.78 (dd, *J* = 7.7, 1.0 Hz, 1H), 7.70 (d, *J* = 8.2 Hz, 1H), 7.66 (d, *J* = 8.2 Hz, 1H), 7.49 (d, *J* = 8.3 Hz, 1H), 7.45 (td, *J* = 7.6, 1.2 Hz, 1H), 7.37-7.30 (m, 3H), 7.17-7.06 (m, 2H), 7.05-6.97 (m, 2H), 6.97 (bs, 1H), 6.88 (d, *J* = 7.6 Hz, 1H), 6.65 (d, *J* = 7.0 Hz, 1H), 2.88 (s, 3H), 2.32 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 164.6, 151.7, 141.5, 138.3, 135.5, 133.7, 133.3, 131.6, 131.2, 130.9, 130.0, 128.9, 128.8, 128.4, 128.3, 128.2, 128.1, 127.7, 127.0, 125.5, 125.4, 125.3, 124.9, 20.9, 19.3.

Anal. Calcd for $C_{27}H_{21}NS$ (391.53): C, 82.83; H, 5.41; N, 3.58. Found: C, 82.60; H, 5.34; N, 3.39.

4-(4'-(*tert*-Butyl)-[1,1'-biphenyl]-2-yl)-2-methyl-5-(naphthalen-1-yl)thiazole (12) From 1-bromo-4-*tert*-butylbenzene (0.320 g, 1.5 mmol) and 2-methyl-5-(naphthalen-1-yl)-4-phenylthiazole 9 (1 mmol, 0.301 g), product 12 was obtained in 85% yield (0.368 g) as a brown oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.72-7.66 (m, 2H), 7.64 (d, *J* = 8.2 Hz, 1H), 7.43 (d, *J* = 8.3 Hz, 1H), 7.35-7.27 (m, 2H), 7.21 (td, *J* = 7.6, 1.3 Hz, 1H), 7.15 (t, *J* = 7.6 Hz, 1H), 7.06 (dd, *J* = 8.1, 7.3 Hz, 1H), 7.02-6.94 (m, 3H), 6.54-6.48 (m, 3H), 2.84 (s, 3H), 1.28 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 164.6, 151.6, 148.7, 141.4, 138.4, 133.8, 133.3, 131.3, 131.1, 131.0, 130.1, 128.8, 128.6, 128.3, 128.1, 127.8, 127.0, 125.7, 125.5, 125.4, 125.0, 124.5, 34.3, 31.4, 19.3.

Anal. Calcd for $C_{30}H_{27}NS$ (433.61): C, 83.10; H, 6.28; N, 3.23. Found: C, 83.02; H, 6.21; N, 3.50.

2-Methyl-4-(3'-methyl-[1,1'-biphenyl]-2-yl)-5-(naphthalen-1-yl)thiazole (13) From 3-bromotoluene (0.256 g, 1.5 mmol) and 2-methyl-5-(naphthalen-1-yl)-4-phenylthiazole 9 (1 mmol, 0.301 g), product 13 was obtained in 63% yield (0.246 g) as a yellow solid: mp 143-145 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.76-7.71 (m, 2H), 7.69 (d, *J* = 8.2 Hz, 1H), 7.44 (d, *J* = 8.4 Hz, 1H), 7.41-7.33 (m, 2H), 7.27 (td, *J* = 7.6, 1.3 Hz, 1H), 7.19 (t, *J* = 7.6 Hz, 1H), 7.13 (dd, *J* = 8.0, 7.3 Hz, 1H), 7.03 (dd, *J* = 7.7, 1.0 Hz, 1H), 6.84 (t, *J* = 7.6 Hz, 1H), 6.72 (d, *J* = 7.6 Hz, 1H), 6.68 (d, *J* = 7.4 Hz, 1H), 6.52 (d, *J* = 7.7 Hz, 1H), 6.27 (s, 1H), 2.87 (s, 3H), 2.01 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 164.5, 151.6, 141.7, 141.2, 137.0, 133.8, 133.3, 131.5, 131.1, 131.0, 130.1, 129.2, 129.0, 128.7, 128.2, 128.1, 127.7, 127.2, 127.1, 126.9, 126.0, 125.6, 125.5, 125.4, 124.9, 21.2, 19.3.

Anal. Calcd for $C_{27}H_{21}NS$ (391.53): C, 82.83; H, 5.41; N, 3.58. Found: C, 82.87; H, 5.62; N, 3.50.

4-(3'-Methoxy-[1,1'-biphenyl]-2-yl)-2-methyl-5-(naphthalen-1-yl)thiazole (14) From 3-bromoanisole (0.280 g, 1.5 mmol) and 2-methyl-5-(naphthalen-1-yl)-4-phenylthiazole 9 (1 mmol, 0.301 g), product 14 was obtained in 70% yield (0.285 g) as a orange oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.76-7.71 (m, 2H), 7.69 (d, *J* = 8.2 Hz, 1H), 7.44 (d, *J* = 8.4 Hz, 1H), 7.41-7.33 (m, 2H), 7.26 (td, *J* = 7.6, 1.3 Hz, 1H), 7.19 (t, *J* = 7.6 Hz, 1H), 7.14 (dd, *J* = 8.0, 7.3 Hz, 1H), 7.04 (dd, *J* = 7.7, 1.0 Hz, 1H), 6.84 (t, *J* = 7.6 Hz, 1H), 6.69 (dd, *J* = 7.4, 0.9 Hz, 1H), 6.49 (dd, *J* = 8.2, 2.0 Hz, 1H), 6.25 (d, *J* = 7.7 Hz, 1H), 6.06 (bs, 1H), 3.53 (s, 3H), 2.86 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 164.6, 158.8, 151.5, 142.6, 141.4, 133.8, 133.3, 131.5, 131.2, 131.1, 129.9, 129.1, 128.6, 128.4, 128.3, 128.2, 127.7, 127.3, 125.7, 125.5, 125.4, 124.9, 121.3, 113.3, 112.6, 54.8, 19.3.

Anal. Calcd for $C_{27}H_{21}NOS$ (407.53): C, 79.58; H, 5.19; N, 3.44. Found: C, 79.47; H, 5.02; N, 3.34.

2'-(5-(4-Methoxyphenyl)-2-methylthiazol-4-yl)-[1,1'-biphenyl]-4-carbonitrile (16) From 4-bromobenzonitrile (0.273 g, 1.5 mmol) and 5-(4-methoxyphenyl)-2-methyl-4-phenylthiazole 5 (1 mmol, 0.281 g), product 16 was obtained in 73% yield (0.279 g) as a white solid: mp 209-211 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.71 (dd, *J* = 7.6, 1.1 Hz, 1H), 7.51 (td, *J* = 7.5, 1.4 Hz, 1H), 7.44 (td, *J* = 7.5, 1.4 Hz, 1H), 7.32 (d, *J* = 8.7 Hz, 2H), 7.21 (dd, *J* = 7.6, 1.0 Hz, 1H), 6.81 (d, *J* = 8.7 Hz, 2H), 6.62-6.54 (m, 4H), 3.77 (s, 3H), 2.74 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 163.8, 159.1, 147.6, 146.0, 139.5, 134.3, 134.0, 131.4, 131.2, 129.7, 129.5, 129.3, 128.8, 128.6, 123.8, 119.1, 113.8, 109.5, 55.3, 19.3.

Anal. Calcd for $C_{24}H_{18}N_2OS$ (382.48): C, 75.37; H, 4.74; N, 7.32. Found: C, 75.50; H, 4.89; N, 7.21.

5-(4-Methoxyphenyl)-2-methyl-4-(4'-(trifluoromethyl)-[1,1'-biphenyl]-2-yl)thiazole (17)

From 4-(trifluoromethyl)bromobenzene (0.338 g, 1.5 mmol) and 5-(4-methoxyphenyl)-2-methyl-4-phenylthiazole 5 (1 mmol, 0.281 g), product 17 was obtained in 61% yield (0.259 g) as a brown oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.72 (dd, *J* = 7.6, 1.1 Hz, 1H), 7.50 (td, *J* = 7.5, 1.4 Hz, 1H), 7.44 (td, *J* = 7.5, 1.4 Hz, 1H), 7.27 (d, *J* = 8.7 Hz, 2H), 7.24 (dd, *J* = 7.6, 1.0 Hz, 1H), 6.82 (d, *J* = 8.7 Hz, 2H), 6.60-6.52 (m, 4H), 3.77 (s, 3H), 2.76 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 163.4, 159.0, 147.6, 144.7, 140.0, 134.2, 133.8, 131.4, 129.8, 129.5, 128.9, 128.6, 128.4, 128.0 (q, *J* = 32.2 Hz), 124.2 (q, *J* = 3.8 Hz), 124.3 (q, *J* = 271.7 Hz), 123.8, 113.7, 55.3, 19.2.

Anal. Calcd for $C_{24}H_{18}F_3NOS$ (425.47): C, 67.75; H, 4.26; N, 3.29. Found: C, 67.49; H, 4.28; N, 3.54.

5-(4-Methoxyphenyl)-2-methyl-4-(3'-methyl-[1,1'-biphenyl]-2-yl)thiazole (18)

From 3-bromotoluene (0.256 g, 1.5 mmol) and 5-(4-methoxyphenyl)-2-methyl-4-phenylthiazole 5 (1 mmol, 0.281 g), product 18 was obtained in 64% yield (0.237 g) as a yellow solid: mp 98-100 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.65 (dd, *J* = 7.6, 1.1 Hz, 1H), 7.46-7.37 (m, 2H), 7.24 (dd, *J* = 7.7, 1.1 Hz, 1H), 6.93 (t, *J* = 7.9 Hz, 1H), 6.88 (d, *J* = 8.0 Hz, 1H), 6.62 (d, *J* = 8.5 Hz, 2H), 6.61-6.56 (m, 3H), 6.51 (bs, 1H), 3.77 (s, 3H), 2.74 (s, 3H), 2.16 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 162.7, 158.8, 148.6, 141.8, 141.0, 137.0, 133.9, 133.8, 131.0, 130.0, 129.7, 129.6, 128.3, 127.4, 127.1, 126.6, 125.8, 124.2, 113.5, 55.2, 21.3, 19.2.

Anal. Calcd for $C_{24}H_{21}NOS$ (371.50): C, 77.60; H, 5.70; N, 3.77. Found: C, 77.69; H, 5.61; N, 3.97.

2'-(5-(4-(*tert*-Butyl)phenyl)-2-methylthiazol-4-yl)-[1,1'-biphenyl]-4-carbonitrile (19)

From 4-bromobenzonitrile (0.273 g, 1.5 mmol) and 5-(4-(*tert*-butyl)phenyl)-2-methyl-4-phenylthiazole 4 (1 mmol, 0.307 g), product 19 was obtained in 71% yield (0.290 g) as a brown oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.74 (dd, *J* = 7.6, 1.1 Hz, 1H), 7.51 (td, *J* = 7.5, 1.4 Hz, 1H), 7.46 (td, *J* = 7.5, 1.4 Hz, 1H), 7.26 (d, *J* = 8.2 Hz, 2H), 7.20 (dd, *J* = 8.6, 1.0 Hz, 1H), 7.07 (d, *J* = 8.2 Hz, 2H), 6.74 (d, *J* = 8.2 Hz, 2H), 6.58 (d, *J* = 8.2 Hz, 2H), 2.76 (s, 3H), 1.30 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 163.7, 150.6, 148.0, 146.0, 139.5, 134.4, 134.0, 131.5, 131.1, 129.7, 129.3, 128.8, 128.7, 128.5, 128.0, 125.2, 125.2, 109.4, 34.5, 31.3, 19.3.
Anal. Calcd for $C_{27}H_{24}N_2S$ (408.56): C, 79.38; H, 5.92; N, 6.86. Found: C, 79.60; H, 6.05; N, 6.67.

2'-(5-(3-Methoxyphenyl)-2-methylthiazol-4-yl)-[1,1'-biphenyl]-4-carbonitrile (20) From 4-bromobenzonitrile (0.273 g, 1.5 mmol) and 5-(3-methoxyphenyl)-2-methyl-4-phenylthiazole 6 (1 mmol, 0.281 g), product 20 was obtained in 70% yield (0.267 g) as a brown solid: mp 197-199 °C.
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.73 (dd, *J* = 7.6, 1.1 Hz, 1H), 7.53 (td, *J* = 7.5, 1.4 Hz, 1H), 7.46 (td, *J* = 7.5, 1.4 Hz, 1H), 7.31 (d, *J* = 8.4 Hz, 2H), 7.23 (dd, *J* = 7.7, 1.1 Hz, 1H), 6.96 (t, *J* = 7.9 Hz, 1H), 6.80 (d, *J* = 8.4 Hz, 2H), 6.69 (ddd, J = 8.3, 2.5, 0.9 Hz, 1H), 6.26 (d, *J* = 7.7 Hz, 1H), 6.14 (t, *J* = 1.8 Hz, 1H), 3.57 (s, 3H), 2.77 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$): δ 164.1, 159.4, 148.4, 145.9, 139.7, 134.3, 133.9, 132.5, 131.3, 131.2, 129.7, 129.4, 129.3, 128.8, 128.7, 120.9, 119.1, 113.8, 113.0, 109.5, 54.9, 19.3.
Anal. Calcd for $C_{24}H_{18}N_2OS$ (382.48): C, 75.37; H, 4.74; N, 7.32. Found: C, 75.37; H, 4.58; N, 7.20.

2'-(5-(4-Cyanophenyl)-2-methylthiazol-4-yl)-[1,1'-biphenyl]-4-carbonitrile (21) From 4-bromobenzonitrile (0.273 g, 1.5 mmol) and and 4-(2-methyl-4-phenylthiazol-5-yl)benzonitrile 2 (1 mmol, 0.276 g), product 21 was obtained in 23% yield (0.087 g) as a brown solid: mp 212-214 °C.
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.73 (d, *J* = 7.6 Hz, 1H), 7.58-7.47 (m, 2H), 7.35 (d, *J* = 8.2 Hz, 2H), 7.32 (d, *J* = 8.2 Hz, 2H), 7.30-7.23 (m, 1H), 6.78 (d, *J* = 8.2 Hz, 2H), 6.76 (d, *J* = 8.2 Hz, 2H), 2.81 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$): δ 165.8, 150.1, 145.5, 139.4, 136.2, 133.0, 132.2, 132.0, 131.4, 131.3, 130.0, 129.5, 129.4, 129.2, 128.7, 118.7, 118.3, 110.8, 110.0, 19.5.
Anal. Calcd for $C_{24}H_{15}N_3S$ (377.47): C, 76.37; H, 4.01; N, 11.13. Found: C, 76.09 H, 3.88; N, 11.09.

4-(4-(4'-(*tert*-Butyl)-[1,1'-biphenyl]-2-yl)-2-methylthiazol-5-yl)benzonitrile (22) From 1-bromo-4-*tert*-butylbenzene (0.320 g, 1.5 mmol) and 4-(2-methyl-4-phenylthiazol-5-

yl)benzonitrile 2 (1 mmol, 0.276 g), product 22 was obtained in 73% yield (0.298 g) as a yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.71 (dd, *J* = 7.6, 1.1 Hz, 1H), 7.51-7.41 (m, 2H), 7.29-7.26 (m, 1H), 7.25 (d, *J* = 8.2 Hz, 2H), 7.03 (d, *J* = 8.2 Hz, 2H), 6.69 (d, *J* = 8.2 Hz, 2H), 6.56 (d, *J* = 8.2 Hz, 2H), 2.82 (s, 3H), 1.30 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 165.0, 151.0, 148.9, 141.2, 137.5, 136.6, 132.9, 131.7, 131.6, 130.9, 130.2, 129.0, 128.7, 128.4, 127.7, 124.5, 118.7, 110.2, 34.3, 31.3, 19.4.

Anal. Calcd for $C_{27}H_{24}N_2S$ (408.56): C, 79.38; H, 5.92; N, 6.86. Found: C, 79.62; H, 5.71; N, 6.98.

4-(2-Methyl-4-(3'-methyl-[1,1'-biphenyl]-2-yl)thiazol-5-yl)benzonitrile (23) From 3-bromotoluene (0.256 g, 1.5 mmol) and 4-(2-methyl-4-phenylthiazol-5-yl)benzonitrile 2 (1 mmol, 0.276 g), product 23 was obtained in 70% yield (0.256 g) as as yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.70 (dd, *J* = 7.6, 1.1 Hz, 1H), 7.50-7.40 (m, 2H), 7.31-7.23 (m, 3H), 6.95-6.85 (m, 2H), 6.74 (d, *J* = 8.3 Hz, 2H), 6.46 (d, *J* = 7.2 Hz, 1H), 6.40 (s, 1H), 2.81 (s, 3H), 2.15 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 165.0, 151.0, 141.5, 140.5, 137.4, 136.5, 132.9, 131.7, 130.9, 130.3, 129.5, 129.0, 128.8, 127.8, 127.4, 126.8, 125.9, 118.7, 110.2, 21.3, 19.4.

Anal. Calcd for $C_{24}H_{18}N_2S$ (366.48): C, 78.66; H, 4.95; N, 7.64. Found: C, 78.42; H, 5.14; N, 7.68.

2-(4-(4'-(*tert*-Butyl)-[1,1'-biphenyl]-2-yl)-2-methylthiazol-5-yl)benzonitrile (24) From 1-bromo-4-*tert*-butylbenzene (0.320 g, 1.5 mmol) and 2-(2-methyl-4-phenylthiazol-5-yl)benzonitrile 7 (1 mmol, 0.276 g), product 24 was obtained in 76% yield (0.310 g) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.77 (dd, *J* = 7.6, 1.1 Hz, 1H), 7.47 (td, *J* = 7.6, 1.4 Hz, 1H), 7.40 (td, *J* = 7.6, 1.3 Hz, 1H), 7.31 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.24-7.11 (m, 3H), 7.10 (d, *J* = 8.2 Hz, 2H), 6.64-6.56 (m, 1H), 6.56 (d, *J* = 8.2 Hz, 2H), 2.85 (s, 3H), 1.35 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 165.7, 152.5, 149.0, 140.9, 137.7, 133.2, 132.5, 131.9, 131.8, 130.8, 130.2, 128.8, 128.2, 128.0, 127.6, 127.3, 125.1, 117.7, 112.1, 34.4, 31.3, 19.4.

Anal. Calcd for $C_{27}H_{24}N_2S$ (408.56): C, 79.38; H, 5.92; N, 6.86. Found: C, 79.47; H, 5.98; N, 6.74.

2-(2-Methyl-4-(3'-methyl-[1,1'-biphenyl]-2-yl)thiazol-5-yl)benzonitrile (25) From 3-bromotoluene (0.256 g, 1.5 mmol) and 2-(2-methyl-4-phenylthiazol-5-yl)benzonitrile 7 (1 mmol, 0.276 g), product 25 was obtained in 73% yield (0.267 g) as as colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.79 (dd, *J* = 7.6, 1.1 Hz, 1H), 7.48 (td, *J* = 7.6, 1.4 Hz, 1H), 7.40 (td, *J* = 7.6, 1.3 Hz, 1H), 7.36 (d, *J* = 8.0 Hz, 1H), 7.25-7.12 (m, 3H), 7.02-6.96 (m, 2H), 6.62 (dd, *J* = 7.5, 1.6 Hz, 1H), 6.49-6.43 (m, 1H), 6.40 (s, 1H), 2.85 (s, 3H), 2.18 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 165.6, 152.5, 141.2, 140.6, 137.6, 135.1, 133.3, 132.6, 131.9, 131.8, 131.0, 130.1, 129.1, 128.8, 128.3, 128.0, 127.7, 127.3, 127.2, 125.8, 112.3, 21.4, 19.4.

Anal. Calcd for $C_{24}H_{18}N_2S$ (366.48): C, 78.66; H, 4.95; N, 7.64. Found: C, 78.48; H, 5.02; N, 7.51.

4-(4'-(*tert*-Butyl)-[1,1'-biphenyl]-2-yl)-5-(4-fluorophenyl)-2-methylthiazole (26) From 1-bromo-4-*tert*-butylbenzene (0.320 g, 1.5 mmol) and 5-(4-fluorophenyl)-2-methyl-4-phenylthiazole 3 (1 mmol, 0.269 g), product 26 was obtained in 62% yield (0.249 g) as a yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.69 (dd, *J* = 7.6, 0.9 Hz, 1H), 7.44 (td, *J* = 7.6, 1.4 Hz, 1H), 7.41 (td, *J* = 7.6, 1.3 Hz, 1H), 7.26 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.05 (d, *J* = 8.4 Hz, 2H), 6.72-6.65 (m, 2H), 6.61 (d, *J* = 8.4 Hz, 2H), 6.58-6.53 (m, 2H), 2.79 (s, 3H), 1.31 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 163.4, 162.0 (d, *J* = 247.1 Hz), 149.4, 148.7, 141.3, 137.9, 133.4, 132.6, 131.0, 130.1, 130.0 (d, *J* = 8.1 Hz), 128.5, 128.3, 127.8 (d, *J* = 3.3 Hz), 127.4, 124.4, 114.9 (d, *J* = 21.6 Hz), 34.3, 31.3, 19.3.

Anal. Calcd for $C_{26}H_{24}FNS$ (401.54): C, 77.77; H, 6.02; N, 3.49. Found: C, 77.89; H, 5.79; N, 3.49.

4-(4'-(*tert*-Butyl)-[1,1'-biphenyl]-2-yl)-5-(2-fluorophenyl)-2-methylthiazole (27) From 1-bromo-4-*tert*-butylbenzene (0.320 g, 1.5 mmol) and 5-(2-fluorophenyl)-2-methyl-4-phenylthiazole 8 (1 mmol, 0.269 g), product 27 was obtained in 67% yield (0.269 g) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.71 (dd, *J* = 7.6, 1.1 Hz, 1H), 7.44 (td, *J* = 7.6, 1.4 Hz, 1H), 7.38 (td, *J* = 7.6, 1.3 Hz, 1H), 7.24 (dd, *J* = 7.8, 1.2 Hz, 1H), 7.13-7.07 (m, 1H), 7.05 (d, *J* = 8.2 Hz, 2H), 6.80-6.70 (m, 2H), 6.62 (d, *J* = 8.2 Hz, 2H), 6.60-6.55 (m, 1H), 2.81 (s, 3H), 1.32 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 164.9, 159.1 (d, *J* = 250.0 Hz), 151.6, 148.8, 141.2, 137.8, 133.6, 131.2 (d, *J* = 2.7 Hz), 131.0, 130.0, 129.0 (d, *J* = 8.1 Hz), 128.4, 128.0, 127.3, 126.1 (d, *J* = 2.3 Hz), 124.5, 123.5 (d, *J* = 3.5 Hz), 119.6 (d, *J* = 14.7 Hz), 115.4 (d, *J* = 22.2 Hz), 34.3, 31.3, 19.2.

Anal. Calcd for $C_{26}H_{24}FNS$ (401.54): C, 77.77; H, 6.02; N, 3.49. Found: C, 77.58; H, 5.89; N, 3.28.

Computational details All DFT calculations were performed using the Gaussian 16.A.03 program,[15] using tightened self-consistent field (10^{-10} a.u.) and geometry optimization (10^{-5} a.u.) convergence thresholds. For all compounds, we optimized the geometries of the ground singlet excited state without imposing symmetry constraints and confirmed their minimal nature through analytical Hessian calculations (no imaginary frequencies). All DFT calculations used the PBE0 hybrid functional,[16] corrected for dispersion effects using the so-called D3-BJ approach,[17] and the 6-311++G(d,p) atomic basis set. The partial atomic charges were obtained using the Natural Population Analysis (NPA) method.[18]

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Keywords: Ruthenium • Palladium • C-H bond activation • C-C bond formation • Arylation

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