Ruthenium-Catalyzed C–H Bond Functionalizations of 1,2,3-Triazol-4-yl-Substituted Arenes: Dehydrogenative Couplings Versus Direct Arylations

Lutz Ackermann,* Petr Novák, Rubén Vicente, Valentina Pirovano, Harish K. Potukuchi

Institut für Organische und Biomolekulare Chemie, Georg-August-Universität Göttingen, Tammannstr. 2, 37077 Göttingen, Germany
Fax +49(551)396777; E-mail: Lutz.Ackermann@chemie.uni-goettingen.de

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Abstract: The chemoselectivity of ruthenium-catalyzed C–H bond arylations on triazol-4-yl-substituted arenes was found to depend on the substitution pattern of both substrates. While various aryl chlorides led to products stemming from direct arylations, *ortho*-substituted aryl halides in combination with *ortho*-alkylated arenes preferentially resulted in oxidative homo-couplings.

Key words: arylations, C–H activation, dehydrogenation, ruthenium, triazoles

Huisgen 1,3-dipolar cycloaddition reactions are among the most versatile tools for the synthesis of functionalized heterocycles.[1–4] Particularly, azide–alkyne [3+2] cycloadditions have recently been widely employed for post-synthetic modifications of biologically active compounds or functional materials, since excellent chemoselectivity and site-selectivity could be accomplished with copper[5–7] catalysts.[8] Thus, considering the increasing practical importance of the resulting 1,4-disubstituted 1,2,3-triazole scaffold for synthetic chemistry,[8] we became interested in exploiting this N-heteroaromatic moiety as directing group for a subsequent post-synthetic functionalization, ideally via a modular C–H bond functionalization strategy. As a result, we previously disclosed ruthenium-catalyzed[9,10] direct arylations[11] of arenes displaying triazol-1-yl substituents as directing groups.[12–15] In continuation of our research program on sustainable C–H bond functionalizations,[16,17] we probed the use of 4-aryl-substituted 1,2,3-triazoles **1** as substrates for directed arylations, on which we wish to report herein.[18] A notable feature of this approach is represented by its site-selectivity being complementary to copper or palladium-catalyzed[15] C–H bond functionalizations (Figure 1).

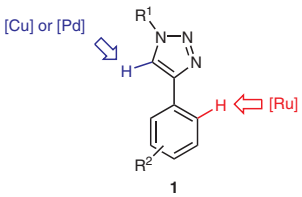

Figure 1 Complementary site-selectivities in post-synthetic C–H bond functionalizations of 1,2,3-triazoles **1**

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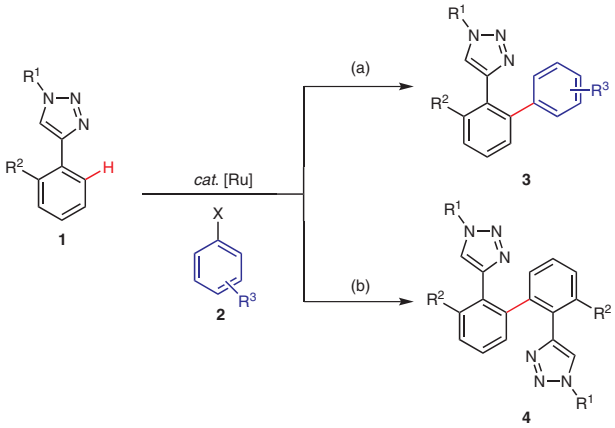
Moreover, these studies resulted in the development of novel reaction conditions for ruthenium-catalyzed[19] dehydrogenative homo-coupling reactions[20] of disubstituted arenes **1**, which involved the use of *ortho*-substituted aryl halides **2** as sacrificial oxidant, and thereby provided access to biaryl derivatives **4** (Scheme 1).



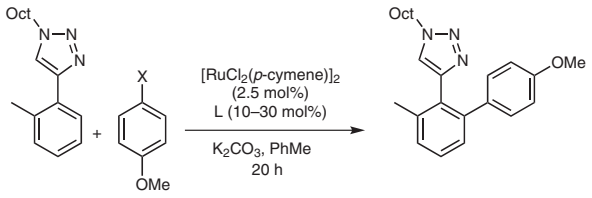
Scheme 1 Chemoselectivity of ruthenium-catalyzed C–H bond functionalization: (a) direct arylation versus (b) oxidative homo-coupling

At the outset of our studies, we tested direct arylations of 4-aryl-1,2,3-triazole **1a** (R^1 = Oct; R^2 = 2-Me) with aryl bromide **2a** in toluene as solvent (Table 1). Notably, no reaction occurred in the absence of additives (entry 1). On the contrary, carboxylic acid $MesCO_2H$ (**5**) was found to generate an active catalyst (entries 2 and 3), which also proved applicable to aryl iodides, and less expensive aryl chlorides (entries 4 and 5). However, ruthenium complexes derived from representative phosphines **6** or N-heterocyclic carbene precursor **7** only provided unsatisfactory results, under otherwise identical reaction conditions (entries 6–8).

Subsequently, we tested the scope of the catalytic system in direct arylations with differently substituted triazol-4-yl-substituted arenes **1** employing economically attractive aryl chlorides **2** (Scheme 2). Here, mono- or *para*-disubstituted arenes **1** as substrates delivered preferentially the diarylated products **3**.

However, monoarylated products **3** were obtained with both *ortho*- (entries 1–10) as well as *meta*-substituted arenes **1** (entry 11, Table 2). In the latter case, the direct

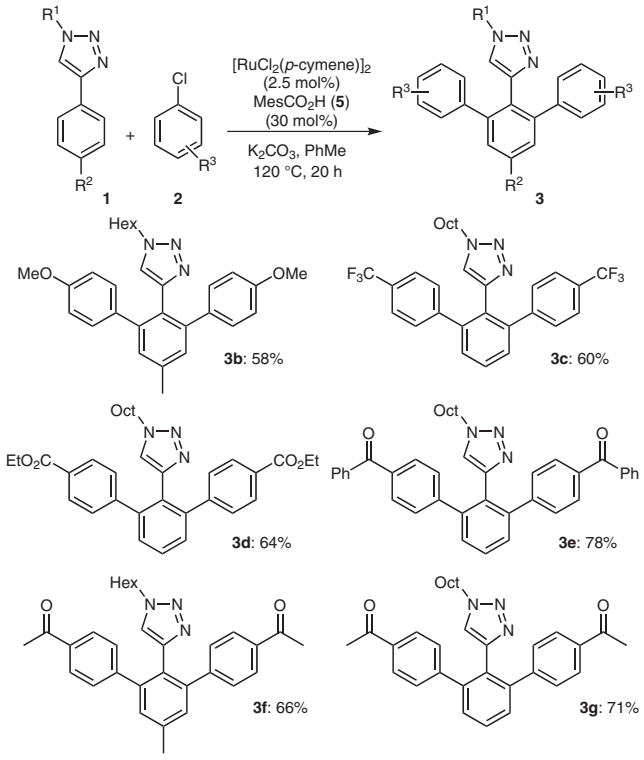
Table 1 Effect of Additives on Direct Arylation of 1,2,3-Triazole **1a**[a]



1a **2** **3a**

Entry	**2**	L	Temp (°C)	Yield (%)
1	Br (**2a**)	–	120	–
2	Br (**2a**)	$MesCO_2H$ (**5**)	120	92
3	Br (**2a**)	$MesCO_2H$ (**5**)	100	67
4	I (**2b**)	$MesCO_2H$ (**5**)	120	79
5	Cl (**2c**)	$MesCO_2H$ (**5**)	120	85
6	Cl (**2c**)	PPh_3 (**6a**)	120	23[c]
7	Cl (**2c**)	PCy_3 (**6b**)	120	27[c]
8	Cl (**2c**)	HIPrCl[b] (**7**)	120	–

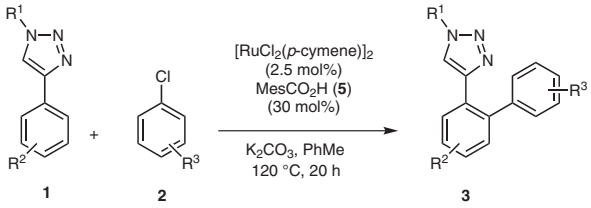
[a] Reaction conditions: **1a** (1.00 mmol), **2** (1.50 mmol), [$RuCl_2$(*p*-cymene)]$_2$ (2.5 mol%), L (10–30 mol%), K_2CO_3 (2.00 mmol), PhMe (4.0 mL), 120 °C, 20 h; yields of isolated products.
[b] HIPr = *N*,*N*′-bis-(2,6-di-isopropylphenyl)imidazolium.
[c] GC conversion.



Scheme 2 Ruthenium-catalyzed direct arylations of 1,2,3-triazoles **1** with an excess of aryl chlorides **2**

functionalization took selectively place at the less sterically hindered C–H bond. Given the remarkably mild reaction conditions, valuable functional groups, such as ester (entries 6 and 7) or ketone substituents (entries 8–11), were well tolerated. On the contrary, the use of an *ortho*-substituted aryl chloride did not allow for a conversion of a *meta*-substituted arene (entry 12).

Table 2 Scope of Direct Arylations of Triazol-4-yl-Substituted Arenes **1**[a]



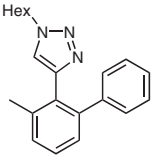
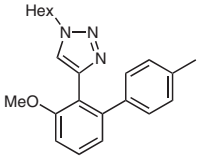
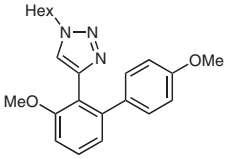
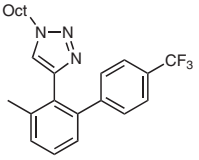
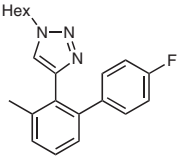
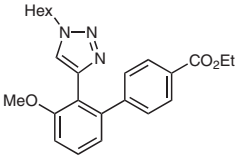
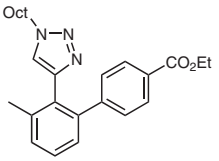
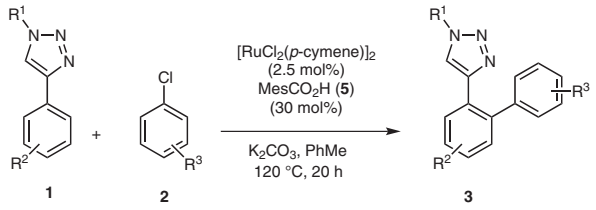
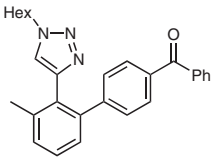
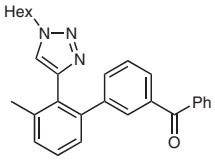
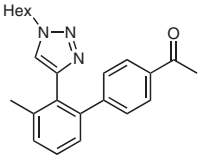
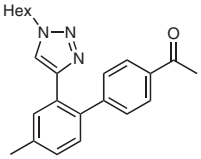
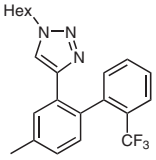
Entry	R^1	R^3	**3**		Yield (%)
1	Hex	H		**3h**	99
2	Hex	4-Me		**3i**	74
3	Hex	4-OMe		**3j**	68
4	Oct	4-CF_3		**3k**	67
5	Hex	4-F		**3l**	89
6	Hex	4-CO_2Et		**3m**	67
7	Oct	4-CO_2Et		**3n**	92

Table 2 Scope of Direct Arylations of Triazol-4-yl-Substituted Arenes **1**[a] (continued)

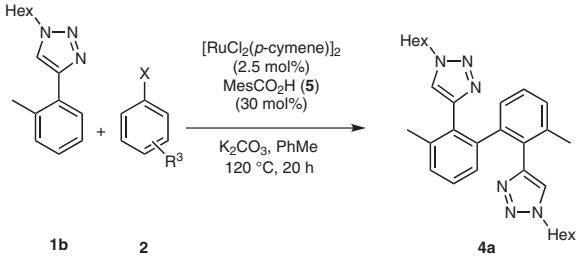


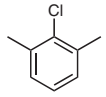
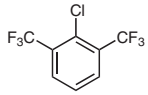
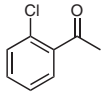
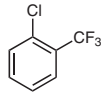
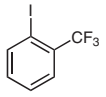
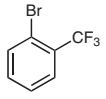
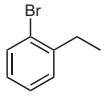
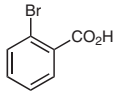
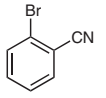
Entry	R^1	R^3	**3**		Yield (%)
8	Hex	4-C(O)Ph		**3o**	95
9	Hex	3-C(O)Ph		**3p**	91
10	Hex	4-C(O)Me		**3q**	88
11	Hex	4-C(O)Me		**3r**	51
12	Hex	4-CF_3		**3s**	–

[a] Reaction conditions: **1** (1.00 mmol), **2** (1.50 mmol), [$RuCl_2$(*p*-cymene]$_2$ (2.5 mol%), **5** (30 mol%), K_2CO_3 (2.00 mmol), PhMe (4.0 mL), 120 °C, 20 h; yields of isolated products.

Moreover, the chemoselectivity of the C–H bond functionalization altered when *ortho*-alkylated arene **1b** served as substrate (Table 3). Hence, 2-chlorotoluene (**2d**) predominantly led to the formation of product **4a** through an oxidative homo-coupling (entry 1). While more sterically congested aryl chlorides **2e** and **2f** turned out to be inferior (entries 2 and 3), mono-*ortho*-substituted aryl chlorides **2g**, and particularly **2h** enabled efficient dehydrogenative arylations (entries 4 and 5). Notably, the oxidative C–H bond functionalization was not restricted to the use of aryl chlorides, but aryl iodide **2i** or aryl bromide **2j** were successfully employed as well (entries 6 and 7). Whereas reactions did not proceed in polar solvent NMP (entry 8), catalysis occurred conveniently under an atmosphere of air (entry 9). Additionally, more electron-rich aryl bromide **2k** proved to be a viable additive, but *ortho*-functionalized bromoarenes **2l** and **2m** gave less satisfactory results (entries 11 and 12).

Table 3 Influence of Aryl Halides **2** on Dehydrogenative Arylations[a]

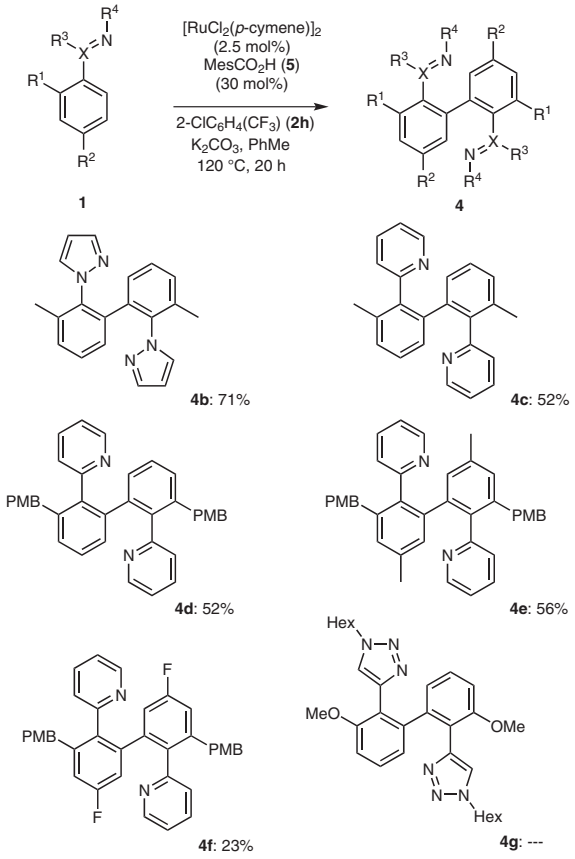


Entry	**2**		Yield (%)
1	**2d**		67
2	**2e**		–
3	**2f**		<10[b]
4	**2g**		49
5	**2h**		81
6	**2i**		53
7	**2j**		73
8			<10[b,c]
9			64[d]
10	**2k**		65
11	**2l**		–
12	**2m**		–

[a] Reaction conditions: **1b** (1.00 mmol), **2** (1.50 mmol), [$RuCl_2$(*p*-cymene]$_2$ (2.5 mol%), **5** (30 mol%), K_2CO_3 (2.00 mmol), PhMe (4.0 mL), 120 °C, 20 h; yields of isolated products.
[b] GC conversion.
[c] In NMP (4.0 mL).
[d] Under an atmosphere of air.

As to the mechanism, acetophenone was isolated as the major by-product in the reaction with 2-chloroacetophenone (**2g**) (entry 4), thus indicating that aryl halides **2** served as formal hydrogen acceptor[21] in the dehydrogenative coupling.

With aryl chloride **2h** as optimal sacrificial oxidant we next explored oxidative homo-couplings of representative arenes **1** bearing various directing groups (Scheme 3). Thus, *ortho*-alkylated pyrazol-1-yl- or pyridin-2-yl-substituted arenes **1** were homo-coupled in a highly regioselective fashion to yield biaryl derivatives **4b–e**. However, a more electron-deficient arene provided product **4f** in significantly diminished yield, while *ortho*-alkoxy-substituted derivatives were not functionalized. Thus, dehydrogenative homo-coupling reactions with aryl chlorides **2** are restricted to electron-rich *ortho*-alkyl-substituted arenes, which in turn defines the scope of ruthenium-catalyzed direct arylations.



Scheme 3 Scope of ruthenium-catalyzed oxidative homo-coupling

In summary, we have reported on the chemoselectivity of ruthenium-catalyzed C–H bond functionalizations of triazol-4-yl-substituted arenes with aryl halides. A catalytic system derived from $MesCO_2H$ (**5**) enabled broadly applicable direct arylations. Contrarily, oxidative homo-couplings of electron-rich *ortho*-alkylated arenes preferentially occurred when *ortho*-substituted aryl halides were employed.

All catalytic reactions were carried out under N_2 in dry glassware, unless otherwise noted. Toluene was freshly distilled over Na/benzophenone. Yields refer to isolated compounds, estimated to be >95% pure as judged by ^{1}H NMR and GC analyses. Flash chromatography was conducted on Macherey-Nagel silica gel 60 (70–230 mesh). NMR spectra were recorded on a Varian VXR 300, or a Varian 600 MHz NMR instrument in the solvent indicated; chemical shifts (δ) are given in ppm.

Ruthenium-Catalyzed Direct Monoarylation of Triazoles 1; 3′-Methyl-2′-(1-*n*-octyl-1*H*-1,2,3-triazol-4-yl)biphenyl-4-carboxylic Acid Ethyl Ester (3n); Representative Procedure A (Table 2, Entry 7)

A suspension of $[RuCl_2(p\text{-cymene})]_2$ (15.4 mg, 0.025 mmol, 2.5 mol%), **5** (49.2 mg, 0.30 mmol, 30 mol%), K_2CO_3 (276 mg, 2.00 mmol), 1-*n*-octyl-4-*o*-tolyl-1,2,3-triazole (271 mg, 1.00 mmol) and 4-chlorobenzoic acid ethyl ester (276 mg, 1.50 mmol) in PhMe (4.0 mL) was stirred at 120 °C for 20 h. EtOAc (50 mL) and H_2O (50 mL) were added to the cold reaction mixture. The separated aqueous phase was extracted with EtOAc (2 × 50 mL). The combined organic layers were washed with H_2O (50 mL) and brine (50 mL), dried (Na_2SO_4), and concentrated under vacuum. The remaining residue was purified by column chromatography on silica gel (*n*-hexane–EtOAc, 5:1) to yield **3n** as a colorless oil; yield: 385 mg (92%).

IR (NaCl): 2926, 2858, 1716, 1642, 1274 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.85 (m, 2 H), 7.40–7.29 (m, 2 H), 7.24–7.11 (m, 3 H), 6.82 (s, 1 H), 4.32 (q, *J* = 7.1 Hz, 2 H), 4.18 (t, *J* = 7.0 Hz, 2 H), 2.28 (s, 3 H), 1.71–1.61 (m, 2 H), 1.34 (t, *J* = 7.1 Hz, 3 H), 1.20 (m, 8 H), 1.06 (m, 2 H), 0.84 (t, *J* = 6.9 Hz, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 166.4 (C_q), 146.5 (C_q), 145.2 (C_q), 141.8 (C_q), 138.9 (C_q), 129.9 (CH), 129.5 (CH), 129.0 (C_q), 128.9 (CH), 128.5 (C_q), 128.4 (CH), 127.1 (CH), 122.8 (CH), 60.8 (CH_2), 50.0 (CH_2), 31.6 (CH_2), 30.1 (CH_2), 28.9 (CH_2), 28.7 (CH_2), 26.0 (CH_2), 22.5 (CH_2), 20.9 (CH_3), 14.3 (CH_3), 14.0 (CH_3).

MS (EI): *m*/*z* (%) = 419 (92, [M$^+$]), 391 (100), 219 (23).

HRMS (ESI): *m*/*z* calcd for $C_{26}H_{33}N_3O_2$ + H$^+$: 420.2649; found: 420.2646.

1-(4′-Methoxy-3-methylbiphenyl-2-yl)-4-*n*-octyl-1*H*-1,2,3-triazole (3a)

Representative procedure A was followed, using 1-*n*-octyl-4-*o*-tolyl-1,2,3-triazole (136 mg, 0.50 mmol) and 4-chloroanisole (108 mg, 0.75 mmol) at 120 °C. After 20 h, purification by chromatography (*n*-hexane–EtOAc, 8:1) yielded **3a** (160 mg, 85%) as a colorless oil.

IR (NaCl): 2928, 2855, 1609, 1513, 1463, 1289, 1214, 1178, 1036, 833, 789, 758 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.34–7.18 (m, 3 H), 7.00 (d, *J* = 8.7 Hz, 2 H), 6.82 (s, 1 H), 6.71 (d, *J* = 8.7 Hz, 2 H), 4.21 (t, *J* = 7.0 Hz, 2 H), 3.73 (s, 3 H), 2.28 (s, 3 H), 1.70 (q, *J* = 7.0 Hz, 2 H), 1.30–1.21 (m, 8 H), 1.15–1.08 (m, 2 H), 0.85 (t, *J* = 6.6 Hz, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 158.3 (C_q), 145.8 (C_q), 142.4 (C_q), 138.7 (C_q), 134.1 (C_q), 130.6 (CH), 129.1 (CH), 129.0 (C_q), 128.4 (CH), 127.4 (CH), 122.8 (CH), 113.1 (CH), 55.1 (CH_3), 50.0 (CH_2), 31.7 (CH_2), 30.2 (CH_2), 29.0 (CH_2), 28.9 (CH_2), 26.2 (CH_2), 22.6 (CH_2), 21.0 (CH_3), 14.1 (CH_3).

MS (EI): *m*/*z* (%) = 377 (88, [M$^+$]), 348 (100), 249 (30), 233 (21), 221 (10), 209 (65), 195 (16), 178 (14), 165 (12), 152 (7), 140 (4), 71 (25), 57 (37), 43 (42).

HRMS (ESI): *m*/*z* calcd for $C_{24}H_{31}N_3O$ + H^+: 378.2540; found: 378.2539.

1-*n*-Hexyl-4-(3-methylbiphenyl-2-yl)-1*H*-1,2,3-triazole (3h)

Representative procedure A was followed, using 1-*n*-hexyl-4-*o*-tolyl-1,2,3-triazole (243 mg, 1.00 mmol) and chlorobenzene (169 mg, 1.50 mmol) at 120 °C. After 20 h, purification by chromatography (*n*-hexane–EtOAc, 5:1) yielded **3h** (316 mg, 99%) as a colorless oil.

IR (NaCl): 2928, 1711, 1642, 1456, 1222 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.41–7.25 (m, 2 H), 7.25–7.13 (m, 4 H), 7.07 (m, 2 H), 6.78 (s, 1 H), 4.18 (t, *J* = 6.9 Hz, 2 H), 2.31 (s, 3 H), 1.73–1.57 (m, 2 H), 1.31–1.16 (m, 4 H), 1.15–1.03 (m, 2 H), 0.86 (t, *J* = 6.7 Hz, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 145.7 (C_q), 142.8 (C_q), 141.8 (C_q), 138.7 (C_q), 129.5 (CH), 129.4 (CH), 129.1 (C_q), 128.3 (CH), 127.7 (CH), 127.3 (CH), 126.4 (CH), 122.8 (CH), 50.0 (CH_2), 31.1 (CH_2), 30.2 (CH_2), 25.8 (CH_2), 22.4 (CH_2), 21.1 (CH_3), 14.0 (CH_3).

MS (EI): *m*/*z* (%) = 319 (100, [M^+]), 291 (71), 220 (78), 204 (42).

HRMS (ESI): *m*/*z* calcd for $C_{21}H_{25}N_3$ + H^+: 320.2122; found: 320.2121.

1-*n*-Hexyl-4-(3-methoxy-4′-methylbiphenyl-2-yl)-1*H*-1,2,3-triazole (3i)

Representative procedure A was followed, using 4-*o*-anisyl-1-*n*-hexyl-1,2,3-triazole (259 mg, 1.00 mmol) and 1-chloro-4-methylbenzene (190 mg, 1.50 mmol) at 120 °C. After 20 h, purification by chromatography (*n*-hexane–EtOAc, 5:1) yielded **3i** (259 mg, 74%) as a colorless oil.

IR (NaCl): 2923, 2855, 1699, 1642, 1459, 1366 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.45–7.32 (m, 1 H), 7.07–6.90 (m, 7 H), 4.22 (t, *J* = 7.0 Hz, 2 H), 3.80 (s, 3 H), 2.27 (s, 3 H), 1.69 (m, 2 H), 1.31–1.07 (m, 6 H), 0.86 (t, *J* = 6.9 Hz, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 158.0 (C_q), 144.0 (C_q), 142.7 (C_q), 138.2 (C_q), 136.1 (C_q), 129.4 (CH), 129.3 (CH), 128.4 (CH), 123.3 (CH), 122.4 (CH), 118.8 (C_q), 109.8 (CH), 56.0 (CH_3), 50.0 (CH_2), 31.1 (CH_2), 30.1 (CH_2), 25.9 (CH_2), 22.4 (CH_2), 21.0 (CH_3), 14.0 (CH_3).

MS (EI): *m*/*z* (%) = 349 (100, [M^+]), 321 (45), 250 (86).

HRMS (ESI): *m*/*z* calcd for $C_{22}H_{27}N_3O$ + H^+: 350.2222; found: 350.2225.

4-(3,4′-Dimethoxybiphenyl-2-yl)-1-*n*-hexyl-1*H*-1,2,3-triazole (3j)

Representative procedure A was followed, using 4-*o*-anisyl-1-*n*-hexyl-1,2,3-triazole (259 mg, 1.00 mmol) and 1-chloro-4-methoxybenzene (214 mg, 1.50 mmol) at 120 °C. After 20 h, purification by chromatography (*n*-hexane–EtOAc, 5:1) yielded **3j** (249 mg, 68%) as a colorless oil.

IR (NaCl): 2933, 1641, 1461, 1248, 1030 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.44–7.31 (m, 1 H), 7.08–6.88 (m, 5 H), 6.80–6.65 (m, 2 H), 4.22 (t, *J* = 7.1 Hz, 2 H), 3.79 (s, 3 H), 3.73 (s, 3 H), 1.84–1.65 (m, 2 H), 1.23 (s, 6 H), 0.86 (t, *J* = 6.7 Hz, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 158.3 (C_q), 158.0 (C_q), 143.7 (C_q), 142.7 (C_q), 133.5 (C_q), 130.5 (CH), 129.4 (CH), 123.3 (CH), 122.3 (CH), 118.7 (C_q), 113.1 (CH), 109.6 (CH), 55.9 (CH_3), 55.0 (CH_3), 49.9 (CH_2), 31.1 (CH_2), 30.1 (CH_2), 25.9 (CH_2), 22.3 (CH_2), 13.9 (CH_3).

MS (EI): *m*/*z* (%) = 365 (100, [M^+]), 337 (63), 266 (69), 226 (71).

HRMS (ESI): *m*/*z* calcd for $C_{22}H_{27}N_3O_2$ + H^+: 366.2176; found: 366.2175.

4-(3-Methyl-4′-(trifluoromethyl)biphenyl-2-yl)-1-*n*-octyl-1*H*-1,2,3-triazole (3k)

Representative procedure A was followed, using 1-*n*-octyl-4-*o*-tolyl-1,2,3-triazole (271 mg, 1.00 mmol) and 1-chloro-4-(trifluoromethyl)benzene (271 mg, 1.50 mmol) at 120 °C. After 20 h, purification by chromatography (*n*-hexane–EtOAc, 5:1) yielded **3k** (278 mg, 67%) as a colorless oil.

IR (NaCl): 2926, 2857, 2226, 1362, 1221 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.52–7.42 (m, 2 H), 7.39–7.29 (m, 2 H), 7.26–7.14 (m, 3 H), 6.89 (s, 1 H), 4.22 (t, *J* = 7.0 Hz, 2 H), 2.26 (s, 3 H), 1.71 (m, 2 H), 1.22 (m, 8 H), 1.09 (s, 2 H), 0.86 (t, *J* = 6.8 Hz, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 146.6 (C_q), 144.9 (C_q), 140.9 (C_q), 139.1 (C_q), 131.4 (CH), 130.3 (CH), 130.3 (CH), 128.9 (C_q), 128.7 (CH), 127.0 (CH), 122.6 (CH), 118.7 (C_q), 110.3 (C_q), 50.1 (CH_2), 31.6 (CH_2), 30.1 (CH_2), 29.0 (CH_2), 28.8 (CH_2), 26.1 (CH_2), 22.5 (CH_2), 20.8 (CH_3), 14.0 (CH_3).

MS (EI): *m*/*z* (%) = 372 (64), 344 (56), 245 (71), 44 (100).

4-(4′-Fluoro-3-methylbiphenyl-2-yl)-1-*n*-hexyl-1*H*-1,2,3-triazole (3l)

Representative procedure A was followed, using 1-*n*-hexyl-4-*o*-tolyl-1,2,3-triazole (243 mg, 1.00 mmol) and 1-chloro-4-fluorobenzene (196 mg, 1.50 mmol) at 120 °C. After 20 h, purification by chromatography (*n*-hexane–EtOAc, 5:1) yielded **3l** (300 mg, 89%) as a colorless oil.

IR (NaCl): 2930, 1641, 1550, 1223 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.35–7.21 (m, 2 H), 7.21–7.12 (m, 1 H), 7.08–6.95 (m, 2 H), 6.92–6.73 (m, 3 H), 4.20 (t, *J* = 6.9 Hz, 2 H), 2.25 (s, 3 H), 1.77–1.57 (m, 2 H), 1.32–1.14 (m, 4 H), 1.08 (m, 2 H), 0.84 (t, *J* = 6.8 Hz, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 161.5 ($^1J_{C,F}$ = 246 Hz, C_q), 145.4 (C_q), 141.6 (C_q), 138.6 (C_q), 137.6 ($^4J_{C,F}$ = 3 Hz, C_q), 131.0 ($^3J_{C,F}$ = 8 Hz, CH), 129.4 (CH), 129.1 (CH), 128.3 (CH), 127.1 (CH), 122.6 (CH), 114.4 ($^2J_{C,F}$ = 21 Hz, CH), 49.9 (CH_2), 30.9 (CH_2), 30.1 (CH_2), 25.7 (CH_2), 22.2 (CH_2), 20.8 (CH_3), 13.8 (CH_3).

MS (EI): *m*/*z* (%) = 337 (100, [M^+]), 309 (44), 238 (89).

HRMS (ESI): *m*/*z* calcd for $C_{21}H_{24}FN_3$ + H^+: 338.2022; found: 338.2025.

2′-(1-*n*-Hexyl-1*H*-1,2,3-triazol-4-yl)-3′-methoxybiphenyl-4-carboxylic Acid Ethyl Ester (3m)

Representative procedure A was followed, using 4-*o*-anisyl-1-*n*-hexyl-1,2,3-triazole (259 mg, 1.00 mmol) and 4-chlorobenzoic acid ethyl ester (277 mg, 1.50 mmol) at 120 °C. After 20 h, purification by chromatography (*n*-hexane–EtOAc, 5:1) yielded **3m** (273 mg, 67%) as a colorless oil.

IR (NaCl): 2926, 1711, 1641, 1363, 1270 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.92–7.80 (m, 2 H), 7.40 (t, *J* = 8.0 Hz, 1 H), 7.23–7.13 (m, 2 H), 7.09 (s, 1 H), 6.99 (d, *J* = 8.0 Hz, 2 H), 4.32 (q, *J* = 7.1 Hz, 2 H), 4.22 (t, *J* = 7.0 Hz, 2 H), 3.80 (s, 3 H), 1.81–1.64 (m, 2 H), 1.34 (t, *J* = 7.1 Hz, 3 H), 1.29–1.02 (m, 6 H), 0.84 (t, *J* = 6.9 Hz, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 166.7 (C_q), 158.2 (C_q), 146.3 (C_q), 143.2 (C_q), 142.3 (C_q), 129.9 (CH), 129.7 (CH), 129.2 (CH), 128.9 (C_q), 123.7 (CH), 122.5 (CH), 119.0 (C_q), 110.7 (CH), 61.1 (CH_2), 56.2 (CH_3), 50.3 (CH_2), 31.3 (CH_2), 30.3 (CH_2), 26.1 (CH_2), 22.6 (CH_2), 14.5 (CH_3), 14.2 (CH_3).

MS (EI): *m*/*z* (%) = 407 (95, [M^+]), 379 (100), 308 (61).

HRMS (ESI): *m*/*z* calcd for $C_{24}H_{29}N_3O_3$ + H^+: 408.2282; found: 408.2281.

{2′-(1-*n*-Hexyl-1*H*-1,2,3-triazol-4-yl)-3′-methylbiphenyl-4-yl}(phenyl)methanone (3o)

Representative procedure A was followed, using 1-*n*-hexyl-4-*o*-tolyl-1,2,3-triazole (243 mg, 1.00 mmol) and (4-chlorophenyl)(phenyl)methanone (325 mg, 1.50 mmol) at 120 °C. After 20 h, purification by chromatography (*n*-hexane–EtOAc, 5:1) yielded **3o** (402 mg, 95%) as a colorless oil.

IR (NaCl): 2929, 2090, 1650, 1455, 1278, 928 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.73 (dd, *J* = 5.2, 3.3 Hz, 2 H), 7.69–7.61 (m, 2 H), 7.55 (ddd, *J* = 6.6, 3.9, 1.4 Hz, 1 H), 7.50–7.28 (m, 4 H), 7.27–7.17 (m, 3 H), 6.89 (s, 1 H), 4.21 (t, *J* = 7.1 Hz, 2 H), 2.29 (s, 3 H), 1.78–1.61 (m, 2 H), 1.23–1.01 (m, 6 H), 0.78 (t, *J* = 6.9 Hz, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 196.2 (C_q), 146.2 (C_q), 145.2 (C_q), 141.7 (C_q), 138.9 (C_q), 137.5 (C_q), 135.4 (C_q), 132.3 (CH), 130.0 (CH), 129.8 (CH), 129.6 (CH), 129.5 (CH), 129.0 (C_q), 128.5 (CH), 128.2 (CH), 127.2 (CH), 122.8 (CH), 50.0 (CH_2), 30.9 (CH_2), 30.2 (CH_2), 25.8 (CH_2), 22.3 (CH_2), 20.9 (CH_3), 13.9 (CH_3).

MS (EI): *m*/*z* (%) = 423 (56, [M^+]), 395 (45), 284 (7), 218 (8), 105 (100).

HRMS (ESI): *m*/*z* calcd for $C_{28}H_{29}N_3O$ + H^+: 424.2383; found: 424.2383.

{2′-(1-*n*-Hexyl-1*H*-1,2,3-triazol-4-yl)-3′-methylbiphenyl-3-yl}(phenyl)methanone (3p)

Representative procedure A was followed, using 1-*n*-hexyl-4-*o*-tolyl-1,2,3-triazole (243 mg, 1.00 mmol) and (3-chlorophenyl)(phenyl)methanone (325 mg, 1.50 mmol) at 120 °C. After 20 h, purification by chromatography (*n*-hexane–EtOAc, 5:1) yielded **3p** (385 mg, 91%) as a colorless oil.

IR (NaCl): 3137, 2928, 1710, 1656, 1452, 717 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.74–7.61 (m, 3 H), 7.55 (m, 2 H), 7.45 (m, 2 H), 7.40–7.16 (m, 5 H), 6.92 (s, 1 H), 4.21 (t, *J* = 7.1 Hz, 2 H), 2.27 (s, 3 H), 1.80–1.60 (m, 2 H), 1.31–1.00 (m, 6 H), 0.81 (t, *J* = 6.8 Hz, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 196.2 (C_q), 145.2 (C_q), 141.8 (C_q), 141.7 (C_q), 138.8 (C_q), 137.1 (C_q), 137.0 (C_q), 133.6 (CH), 132.4 (CH), 131.0 (CH), 129.8 (CH), 129.7 (CH), 129.1 (C_q), 128.4 (CH), 128.3 (CH), 128.1 (CH), 127.6 (CH), 127.2 (CH), 122.8 (CH), 50.0 (CH_2), 30.9 (CH_2), 30.1 (CH_2), 25.8 (CH_2), 22.3 (CH_2), 20.9 (CH_3), 13.9 (CH_3).

MS (EI): *m*/*z* (%) = 423 (95, [M^+]), 378 (37), 318 (52), 105 (100).

HRMS (ESI): *m*/*z* calcd for $C_{28}H_{29}N_3O$ + H^+: 424.2383; found: 424.2383.

1-{2′-(1-*n*-Hexyl-1*H*-1,2,3-triazol-4-yl)-3′-methylbiphenyl-4-yl}ethanone (3q)

Representative procedure A was followed, using 1-*n*-hexyl-4-*o*-tolyl-1,2,3-triazole (243 mg, 1.00 mmol) and 1-(4-chlorophenyl)ethanone (232 mg, 1.50 mmol) at 120 °C. After 20 h, purification by chromatography (*n*-hexane–EtOAc, 5:1) yielded **3q** (318 mg, 88%) as a colorless oil.

IR (NaCl): 2926, 1641, 1361, 1264 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.83–7.71 (m, 2 H), 7.32 (m, 2 H), 7.25–7.14 (m, 3 H), 6.86 (s, 1 H), 4.20 (t, *J* = 7.0 Hz, 2 H), 2.53 (s, 3 H), 2.28 (s, 3 H), 1.68 (m, 2 H), 1.19 (m, 4 H), 1.08 (m, 2 H), 0.83 (t, *J* = 6.7 Hz, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 197.6 (C_q), 146.8 (C_q), 145.2 (C_q), 141.6 (C_q), 138.9 (C_q), 135.1 (C_q), 130.0 (CH), 129.8 (CH), 128.9 (C_q), 128.5 (CH), 127.7 (CH), 127.1 (CH), 122.7 (CH), 50.0 (CH_2), 30.9 (CH_2), 30.1 (CH_2), 26.5 (CH_3), 25.8 (CH_2), 22.3 (CH_2), 20.9 (CH_3), 13.9 (CH_3).

MS (EI): *m*/*z* (%) = 361 (100, [M^+]), 333 (58), 220 (63), 179 (56).

HRMS (ESI): *m*/*z* calcd for $C_{23}H_{27}N_3O$ + H^+: 362.2227; found: 362.2227.

1-{2′-(1-*n*-Hexyl-1*H*-1,2,3-triazol-4-yl)-4′-methylbiphenyl-3-yl}ethanone (3r)

Representative procedure A was followed, using 1-*n*-hexyl-4-*m*-tolyl-1,2,3-triazole (243 mg, 1.0 mmol) and 1-(4-chlorophenyl)ethanone (232 mg, 1.5 mmol) at 120 °C. After 20 h, purification by chromatography (*n*-hexane–EtOAc, 5:1) yielded **3r** (184 mg, 51%) as a colorless oil.

IR (NaCl): 2927, 2861, 1642, 1361, 1264, 1224 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.98–7.82 (m, 3 H), 7.38–7.27 (m, 2 H), 7.20 (m, 2 H), 6.53 (s, 1 H), 4.15 (t, *J* = 7.1 Hz, 2 H), 2.60 (s, 3 H), 2.43 (s, 3 H), 1.76–1.61 (m, 2 H), 1.32–1.05 (m, 6 H), 0.84 (t, *J* = 6.8 Hz, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 197.5 (C_q), 146.6 (C_q), 146.0 (C_q), 138.3 (C_q), 136.2 (C_q), 135.7 (C_q), 129.8 (CH), 129.8 (CH), 129.7 (CH), 128.9 (CH), 128.8 (C_q), 128.2 (CH), 121.9 (CH), 50.2 (CH_2), 31.1 (CH_2), 30.2 (CH_2), 26.7 (CH_2), 26.0 (CH_3), 22.5 (CH_3), 21.2 (CH_2), 14.0 (CH_3).

MS (EI): *m*/*z* (%) = 361 (100, [M^+]), 333 (48), 220 (98), 179 (79).

HRMS (ESI): *m*/*z* calcd for $C_{23}H_{27}N_3O$ + H^+: 362.2233; found: 362.2231.

Ruthenium-Catalyzed Direct Diarylation of Triazoles 1; 4-{2′,6′-Di-(4″-Ethoxycarbonylphenyl)phenyl}-1-*n*-octyl-1*H*-1,2,3-triazole (3d); Representative Procedure B (Scheme 2)

A suspension of $[RuCl_2(p\text{-cymene})]_2$ (15.4 mg, 0.025 mmol, 2.5 mol%), **5** (49.2 mg, 0.300 mmol, 30 mol%), K_2CO_3 (276 mg, 2.00 mmol), 1-*n*-octyl-4-phenyl-1,2,3-triazole (257 mg, 1.00 mmol) and 4-chlorobenzoic acid ethyl ester (552 mg, 3.00 mmol) in PhMe (4.0 mL) was stirred at 120 °C for 20 h. EtOAc (50 mL) and H_2O (50 mL) were added to the cold reaction mixture. The separated aqueous phase was extracted with EtOAc (2 × 50 mL). The combined organic layers were washed with H_2O (50 mL) and brine (50 mL), dried (Na_2SO_4), and concentrated under vacuum. The residue was purified by column chromatography on silica gel (*n*-hexane–EtOAc, 5:1) to yield **3d** (354 mg, 64%) as a white solid; mp 133.5–135.8 °C.

IR (NaCl): 2925, 2855, 1706, 1642, 1270, 1108 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.87 (m, 4 H), 7.53 (dd, *J* = 8.6, 6.7 Hz, 1 H), 7.48–7.38 (m, 2 H), 7.28–7.17 (m, 4 H), 6.75 (s, 1 H), 4.32 (q, *J* = 7.1 Hz, 4 H), 4.07 (t, *J* = 6.9 Hz, 2 H), 1.63–1.45 (m, 2 H), 1.35 (t, *J* = 7.1 Hz, 6 H), 1.28–1.09 (m, 8 H), 0.95 (m, 2 H), 0.85 (t, *J* = 6.9 Hz, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 166.4 (C_q), 145.9 (C_q), 144.4 (C_q), 142.5 (C_q), 129.5 (CH), 129.0 (CH), 129.0 (CH), 128.8 (C_q), 128.7 (CH), 128.1 (C_q), 123.2 (CH), 60.9 (CH_2), 49.9 (CH_2), 31.7 (CH_2), 30.1 (CH_2), 28.9 (CH_2), 28.6 (CH_2), 25.9 (CH_2), 22.5 (CH_2), 14.3 (CH_3), 14.0 (CH_3).

MS (EI): *m*/*z* (%) = 553 (13, [M^+]), 525 (19), 43 (100).

HRMS (ESI): *m*/*z* calcd for $C_{34}H_{39}N_3O_4$ + H^+: 554.3013; found: 554.3010.

4-{2′,6′-Di-(4″-methoxyphenyl)-4′-methylphenyl}-1-*n*-octyl-1*H*-1,2,3-triazole (3b)

Representative procedure B was followed, using 1-*n*-hexyl-4-*p*-tolyl-1,2,3-triazole (229 mg, 1.00 mmol) and 1-chloro-4-methoxybenzene (428 mg, 3.00 mmol) at 120 °C. After 20 h, purification by chromatography (*n*-hexane–EtOAc, 5:1) yielded **3b** (264 mg, 58%) as a white solid; mp 78.4–80.8 °C.

IR (NaCl): 2934, 2860, 1709, 1610, 1510, 1245, 1035 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.18 (s, 2 H), 7.14–7.03 (m, 4 H), 6.79–6.64 (m, 5 H), 4.10 (t, *J* = 6.9 Hz, 2 H), 3.73 (s, 6 H), 2.42 (s, 3 H), 1.67–1.51 (m, 2 H), 1.28–1.11 (m, 4 H), 1.00 (m, 2 H), 0.84 (t, *J* = 6.7 Hz, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 158.1 (C_q), 145.3 (C_q), 142.8 (C_q), 138.0 (C_q), 134.0 (C_q), 130.5 (CH), 129.6 (CH), 125.4 (C_q), 123.0 (CH), 112.9 (CH), 55.1 (CH_3), 49.8 (CH_2), 31.1 (CH_2), 30.2 (CH_2), 25.7 (CH_2), 22.4 (CH_2), 21.3 (CH_3), 14.0 (CH_3).

MS (EI): *m*/*z* (%) = 455 (66, [M$^+$]), 427 (100), 356 (19), 316 (45).

HRMS (ESI): *m*/*z* calcd. for $C_{29}H_{33}N_3O_2$ + H$^+$: 456.2646; found: 456.2645.

4-{2′,6′-Di-(4″-trifluoromethyl)phenyl}-1-*n*-octyl-1*H*-1,2,3-triazole (3c)

Representative procedure A was followed, using 1-*n*-octyl-4-phenyl-1,2,3-triazole (259 mg, 1.00 mmol) and 1-chloro-4-(trifluoromethyl)benzene (542 mg, 3.00 mmol) at 120 °C. After 20 h, purification by chromatography (*n*-hexane–EtOAc, 5:1) yielded **3c** (327 mg, 60%) as a white solid; mp 132.5–134.2 °C.

IR (NaCl): 2928, 2860, 1643, 1323, 1117 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.55 (dd, *J* = 8.5, 6.8 Hz, 1 H), 7.45 (ddd, *J* = 9.4, 8.5, 0.8 Hz, 6 H), 7.29 (dd, *J* = 8.7, 0.8 Hz, 4 H), 6.75 (s, 1 H), 4.10 (t, *J* = 7.0 Hz, 2 H), 1.56 (m, 2 H), 1.31–1.08 (m, 8 H), 0.98 (m, 2 H), 0.86 (t, *J* = 6.9 Hz, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 144.7 (C_q), 144.2 (C_q), 142.1 (C_q), 129.4 (CH), 129.1 (CH), 128.4 ($^2J_{C,F}$ = 33 Hz, C_q), 128.3 (CH), 127.7 (C_q), 124.7 ($^1J_{C,F}$ = 272 Hz, C_q), 124.6 ($^3J_{C,F}$ = 4 Hz, CH), 122.6 (CH), 49.9 (CH_2), 31.8 (CH_2), 30.2 (CH_2), 29.0 (CH_2), 28.7 (CH_2), 26.0 (CH_2), 22.6 (CH_2), 14.1 (CH_3).

MS (EI): *m*/*z* (%) = 545 (31, [M$^+$]), 517 (25), 418 (22), 43 (100).

HRMS (ESI): *m*/*z* calcd for $C_{30}H_{29}F_6N_3$ + H$^+$: 546.2338; found: 546.2337.

4-{2′,6′-Di-(4″-phenylcarbonylphenyl)phenyl}-1-*n*-octyl-1*H*-1,2,3-triazole (3e)

Representative procedure A was followed, using 1-*n*-octyl-4-phenyl-1,2,3-triazole (259 mg, 1.00 mmol) and (4-chlorophenyl)(phenyl)methanone (650 mg, 3.00 mmol) at 120 °C. After 20 h, purification by chromatography (*n*-hexane–EtOAc, 5:1) yielded **3e** (482 mg, 78%) as a white solid; mp 135.8–137.6 °C.

IR (NaCl): 2926, 1649, 1277, 927 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.75 (dd, *J* = 8.0, 1.0 Hz, 4 H), 7.72–7.63 (m, 4 H), 7.63–7.52 (m, 3 H), 7.52–7.40 (m, 6 H), 7.29 (d, *J* = 8.1 Hz, 4 H), 6.83 (s, 1 H), 4.11 (t, *J* = 7.0 Hz, 2 H), 1.60 (m, 2 H), 1.21–1.06 (m, 8 H), 1.01 (m, 2 H), 0.79 (t, *J* = 6.8 Hz, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 196.2 (C_q), 145.6 (C_q), 144.4 (C_q), 142.5 (C_q), 137.6 (C_q), 135.7 (C_q), 132.3 (CH), 129.9 (CH), 129.6 (CH), 129.5 (2 × CH), 128.8 (C_q), 128.2 (CH), 128.1 (CH), 123.3 (CH), 49.9 (CH_2), 31.6 (CH_2), 30.2 (CH_2), 28.9 (CH_2), 28.7 (CH_2), 26.0 (CH_2), 22.5 (CH_2), 14.0 (CH_3).

MS (EI): *m*/*z* (%) = 617 (5, [M$^+$]), 589 (7), 105 (100).

HRMS (ESI): *m*/*z* calcd for $C_{42}H_{39}N_3O_2$ + H$^+$: 618.3115; found: 618.3112.

4-{2′,6′-Di-(4″-methylcarbonylphenyl)-4′-methylphenyl}-1-*n*-octyl-1*H*-1,2,3-triazole (3f)

Representative procedure A was followed, using 1-*n*-hexyl-4-*p*-tolyl-1,2,3-triazole (229 mg, 1.00 mmol) and 1-(4-chlorophenyl)ethanone (464 mg, 3.00 mmol) at 120 °C. After 20 h, purification by chromatography (*n*-hexane–EtOAc, 5:1) yielded **3f** (317 mg, 66%) as a white solid; mp 163.1–165.4 °C.

IR (NaCl): 2926, 1678, 1361, 1264, 837 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.76 (d, *J* = 8.3 Hz, 4 H), 7.32–7.14 (m, 6 H), 6.78 (s, 1 H), 4.06 (t, *J* = 6.8 Hz, 2 H), 2.50 (s, 6 H), 2.43 (s, 3 H), 1.63–1.46 (m, 2 H), 1.21–1.07 (m, 4 H), 0.93 (m, 2 H), 0.79 (t, *J* = 6.7 Hz, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 197.2 (C_q), 146.0 (C_q), 144.1 (C_q), 142.0 (C_q), 138.4 (C_q), 135.0 (C_q), 130.0 (CH), 129.5 (CH), 127.5 (CH), 124.9 (C_q), 123.1 (CH), 49.7 (CH_2), 30.8 (CH_2), 29.9 (CH_2), 26.4 (CH_3), 25.4 (CH_2), 22.2 (CH_2), 21.1 (CH_3), 13.8 (CH_3).

HRMS (ESI): *m*/*z* calcd for $C_{31}H_{33}N_3O_2$ + H$^+$: 480.2646; found: 480.2645.

4-{2′,6′-Di-(4″-methylcarbonylphenyl)phenyl}-1-*n*-octyl-1*H*-1,2,3-triazole (3g)

Representative procedure A was followed, using 1-*n*-octyl-4-phenyl-1,2,3-triazole (259 mg, 1.00 mmol) and 1-(4-chlorophenyl)ethanone (464 mg, 3.00 mmol) at 120 °C. After 20 h, purification by chromatography (*n*-hexane–EtOAc, 5:1) yielded **3g** (350 mg, 71%) as a white solid; mp 170.4–172.2 °C.

IR (NaCl): 2924, 2090, 1642, 1364, 1254 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.87–7.73 (m, 4 H), 7.54 (dd, *J* = 8.5, 6.7 Hz, 1 H), 7.43 (dd, *J* = 7.6, 0.8 Hz, 2 H), 7.31–7.19 (m, 4 H), 6.77 (s, 1 H), 4.08 (t, *J* = 7.0 Hz, 2 H), 2.56 (s, 6 H), 1.64–1.48 (m, 2 H), 1.30–1.10 (m, 8 H), 0.96 (m, 2 H), 0.85 (t, *J* = 6.9 Hz, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 197.6 (C_q), 146.1 (C_q), 144.4 (C_q), 142.4 (C_q), 135.4 (C_q), 129.8 (CH), 129.6 (CH), 128.8 (CH), 128.0 (C_q), 127.8 (CH), 123.2 (CH), 49.9 (CH_2), 31.7 (CH_2), 30.1 (CH_2), 29.0 (CH_2), 28.7 (CH_2), 26.5 (CH_3), 25.9 (CH_2), 22.5 (CH_2), 14.0 (CH_3).

MS (EI): *m*/*z* (%) = 493 (100, [M$^+$]), 279 (44), 239 (76).

HRMS (ESI): *m*/*z* calcd for $C_{32}H_{35}N_3O_2$ + H$^+$: 494.2794; found: 494.2802.

Ruthenium-Catalyzed Oxidative Homo-Coupling; 3,3′-Dimethyl-2,2′-di(1*H*-pyrazol-1-yl)biphenyl (4b); Representative Procedure C (Scheme 3)

A suspension of $[RuCl_2(p\text{-cymene})]_2$ (7.7 mg, 0.012 mmol, 2.5 mol%), **5** (24.6 mg, 0.15 mmol, 30 mol%), K_2CO_3 (138 mg, 1.00 mmol), 1-*o*-tolyl-1*H*-pyrazole (79.1 g, 0.50 mmol), and **2h** (135 mg, 0.75 mmol) in PhMe (2 mL) was stirred at 120 °C for 20 h. MTBE (25 mL) and H_2O (25 mL) were added to the cold reaction mixture. The separate aqueous phase was extracted with MTBE (2 × 25 mL). The combined organic layers were washed with H_2O (25 mL) and brine (25 mL), dried (Na_2SO_4), and concentrated under vacuum. The remaining residue was purified by column chromatography on silica gel (*n*-hexane–EtOAc, 10:1 → 5:1) to yield **4b** (56 mg, 71%) as a white solid; mp 146.9–147.4 °C.

IR (NaCl): 3445, 1713, 1362, 1222, 761 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.63–7.46 (m, 4 H), 7.14 (d, *J* = 7.5 Hz, 2 H), 7.06 (t, *J* = 7.5 Hz, 2 H), 6.82 (d, *J* = 7.5 Hz, 2 H), 6.18 (t, *J* = 2.0 Hz, 2 H), 2.05 (s, 6 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 139.6 (CH), 138.3 (C_q), 136.6 (C_q), 136.0 (C_q), 131.9 (CH), 129.9 (CH), 127.8 (CH), 127.4 (CH), 105.6 (CH), 17.7 (CH_3).

MS (EI): *m*/*z* (%) = 314 (64, [M$^+$]), 233 (100), 191 (3).

HRMS (ESI): *m*/*z* calcd for $C_{20}H_{18}N_4$ + H$^+$: 315.1604; found: 315.1606.

2,2′-Bis(1-*n*-hexyl-1*H*-1,2,3-triazol-4-yl)-3,3′-dimethylbiphenyl (4a)

Representative procedure C was followed using 1-*n*-hexyl-4-*o*-tolyl-1,2,3-triazole (243 mg, 1.00 mmol) and **2h** (338 mg, 1.50

mmol) at 120 °C. After 20 h, purification by chromatography (*n*-hexane–EtOAc, 3:1) yielded **4a** (192 mg, 81%) as a colorless oil.

IR (NaCl): 3448, 3131, 2928, 2861, 1710, 1456, 1049, 731 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.23 (s, 2 H), 7.14–7.01 (m, 4 H), 6.90 (dd, *J* = 7.2, 1.7 Hz, 2 H), 4.20 (t, *J* = 6.9 Hz, 4 H), 2.20 (s, 6 H), 1.76–1.59 (m, 4 H), 1.22 (m, 8 H), 1.05 (m, 4 H), 0.86 (t, *J* = 6.8 Hz, 6 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 145.1 (C_q), 142.2 (C_q), 137.8 (C_q), 129.9 (C_q), 129.0 (CH), 127.6 (CH), 127.2 (CH), 123.4 (CH), 50.0 (CH_2), 31.1 (CH_2), 30.1 (CH_2), 25.7 (CH_2), 22.4 (CH_2), 21.0 (CH_3), 14.0 (CH_3).

MS (EI): *m*/*z* (%) = 484 (64, [M^+]), 399 (14), 385 (100), 345 (21).

HRMS (ESI): *m*/*z* calcd for $C_{30}H_{40}N_6$ + H^+: 485.3387; found: 485.3387.

3,3′-Dimethyl-2,2′-di(pyridin-2-yl)biphenyl (4c)

Representative procedure C was followed, using 2-*o*-tolylpyridine (84.6 mg, 0.50 mmol) and **2h** (135 mg, 0.75 mmol) at 120 °C. After 20 h, purification by chromatography (*n*-hexane–EtOAc, 5:1 → 1:1) yielded **4c** (44 mg, 52%) as a green solid; mp 154.1–154.9 °C.

IR (NaCl): 3445, 3053, 1710, 1584, 1462, 1029, 789, 752 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 8.51 (d, *J* = 4.4 Hz, 2 H), 7.48 (td, *J* = 7.6, 1.7 Hz, 2 H), 7.25 (d, *J* = 7.6 Hz, 2 H), 7.01 (ddd, *J* = 8.5, 4.9, 2.4 Hz, 4 H), 6.88 (t, *J* = 7.6 Hz, 2 H), 6.72 (d, *J* = 7.3 Hz, 2 H), 2.04 (s, 6 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 159.4 (C_q), 148.7 (CH), 140.2 (C_q), 139.7 (C_q), 135.9 (C_q), 135.4 (CH), 128.8 (CH), 128.5 (CH), 126.6 (CH), 125.6 (CH), 121.1 (CH), 20.5 (CH_3).

MS (EI): *m*/*z* (%) = 336 (77, [M^+]), 335 (100), 258 (23), 168 (17).

HRMS (ESI): *m*/*z* calcd for $C_{24}H_{20}N_2$ + H^+: 337.1699; found: 337.1699.

3,3′-Di(4-methoxybenzyl)-2,2′-di(pyridin-2-yl)biphenyl (4d)

Representative procedure C was followed, using 2-[2-(4-methoxybenzyl)phenyl]pyridine (138 mg, 0.50 mmol) and **2h** (135 mg, 0.75 mmol) at 120 °C. After 20 h, purification by chromatography (*n*-hexane–EtOAc, 5:1 → 1:1) yielded **4d** (72 mg, 52%) as a green solid; mp 123.3–124.2 °C.

IR (NaCl): 3051, 3003, 2958, 2910, 2837, 1610, 1587, 1470, 1446, 1421, 1298, 1177, 1151, 1034, 906, 807, 792 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 8.52 (s, 2 H), 7.45–7.33 (m, 2 H), 7.23–6.88 (m, 9 H), 6.84–6.62 (m, 9 H), 3.90–3.63 (m, 10 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 158.9 (C_q), 157.6 (C_q), 148.4 (CH), 140.6 (C_q), 139.9 (C_q), 139.2 (C_q), 135.0 (CH), 133.5 (C_q), 129.6 (CH), 128.9 (CH), 128.6 (CH), 126.8 (CH), 126.1 (CH), 121.2 (CH), 113.4 (CH), 55.2 (CH_3), 38.4 (CH_2).

MS (ESI): *m*/*z* = 549 (100%, [M^+]).

HRMS (ESI): *m*/*z* calcd for $C_{38}H_{32}N_2O_2$ + H^+: 549.2537; found: 549.2538.

5,5′-Dimethyl-3,3′-di(4-methoxybenzyl)-2,2′-di(pyridin-2-yl)biphenyl (4e)

Representative procedure C was followed, using 2-[2-(4-methoxybenzyl)-4-methylphenyl]pyridine (145 mg, 0.50 mmol) and **2h** (135 mg, 0.75 mmol) at 120 °C. After 20 h, purification by chromatography (*n*-hexane–EtOAc, 5:1 → 1:1) yielded **4e** (81 mg, 56%) as a brown oil.

IR (NaCl): 3042, 3001, 2952, 2915, 2836, 1607, 1590, 1510, 1456, 1427, 1297, 1244, 1177, 1034, 909, 866, 819, 802, 733 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 8.52 (d, *J* = 4.3 Hz, 2 H), 7.38 (t, *J* = 7.0 Hz, 2 H), 7.17–6.94 (m, 4 H), 6.85–6.58 (m, 12 H), 3.87–3.63 (m, 10 H), 2.07 (s, 6 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 159.1 (C_q), 157.5 (C_q), 148.2 (CH), 140.6 (C_q), 138.9 (C_q), 137.1 (C_q), 136.2 (C_q), 134.8 (CH), 133.7 (C_q), 129.8 (CH), 129.6 (CH), 129.2 (CH), 126.2 (CH), 121.0 (CH), 113.3 (CH), 55.1 (CH_3), 38.2 (CH_2), 20.8 (CH_3).

MS (ESI): *m*/*z* = 577 (100%, [M^+]).

HRMS (ESI): *m*/*z* calcd for $C_{40}H_{36}N_2O_2$ + H^+: 577.2850; found: 577.2850.

5,5′-Difluoro-3,3′-di(4-methoxybenzyl)-2,2′-di(pyridin-2-yl)biphenyl (4f)

Representative procedure C was followed, using 2-[4-fluoro-2-(4-methoxybenzyl)phenyl]pyridine (147 mg, 0.50 mmol) and **2h** (135 mg, 0.75 mmol) at 120 °C. After 20 h, purification by chromatography (*n*-hexane–EtOAc, 5:1 → 1:1) yielded **4f** (34 mg, 23%) as a green oil.

IR (NaCl): 3048, 3002, 2956, 2931, 2836, 1734, 1566, 1510, 1456, 1427, 1298, 1034, 909, 870, 819, 733, 646, 624 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 8.55 (s, 2 H), 7.52–7.39 (m, 2 H), 7.24–7.03 (m, 4 H), 6.84–6.64 (m, 10 H), 6.52 (dd, *J* = 9.2, 2.6 Hz, 2 H), 3.75 (m, 10 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 160.9 (C_q, $^1J_{C,F}$ = 247 Hz), 157.7 (C_q), 157.5 (C_q), 148.6 (CH), 142.1 (C_q, $^3J_{C,F}$ = 9 Hz), 141.5 (C_q, $^3J_{C,F}$ = 9 Hz), 135.9 (C_q), 135.3 (CH), 132.2 (C_q), 129.6 (CH), 126.1 (CH), 121.6 (CH), 115.6 (CH, $^2J_{C,F}$ = 23 Hz), 115.2 (CH, $^2J_{C,F}$ = 23 Hz), 113.6 (CH), 55.23 (CH_3), 38.43 (CH_2).

^{19}F NMR (285 MHz, $CDCl_3$): δ = –115.2 (s).

MS (ESI): *m*/*z* = 585 (100%, [M^+]).

HRMS (ESI): *m*/*z* calcd for $C_{38}H_{30}F_2N_2O_2$ + H^+: 585.2348; found: 585.2351.

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