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Nucleophilic Fe-complexes in proton-transfer catalysis: the Fe-catalyzed Dimroth-cyclocondensation

Aslihan Baykal,[a] Dihan Zhang,[a] Jakob Knelles,[a] Isabel T. Alt,[a] and Bernd Plietker*[a]

In memory of Prof. Dr. Dieter Enders.

Abstract: The nucleophilic Fe-complex $Bu_4N[Fe(CO)_3(NO)]$ (TBA[Fe]) is an active catalyst in C-H-amination but also in proton-transfer catalysis. Herein, we describe the successful use of this complex as a proton-transfer catalyst in the cyclocondensation between azides and ketones to the corresponding 1,2,3-triazoles. Cross-experiments indicate that the proton-transfer catalysis is significantly faster than the nitrene-transfer catalysis, which would lead to C-H amination product. A first example for a successful sequential Dimroth triazole-indoline synthesis to the corresponding triazole substituted indolines is presented.

Introduction

Starting from Roustan´s initial seminal reports a range of transformations that are catalyzed by the electron rich ferrate $Bu_4N[Fe(CO)_3(NO)]$ (TBA[Fe]) have been developed by us and others.[1] Apart from the catalytic applications the anionic complex has a rich organometallic chemistry with alkylation using allyl halides and protonation being the most important ones.[2] Whereas the field of TBA[Fe]-catalysis is dominated by allylations[1] catalytic transformations in which a protonation of the ferrate anion takes place are scarce. As a matter of fact, Roustan was able to show that the reported instability of $H[Fe(CO)_3(NO)]$ could be overcome upon addition of triphenylphosphane.[3] The resulting Fe-complex $H[Fe(Ph_3P)_2(CO)(NO)]$ catalyzes both the hydrosilylation of alkynes and ketones/aldehydes and the reduction of phosphine oxides.[4]

More recently, we were able to show that TBA[Fe] catalyzes the conjugate addition of a variety of C-H-acidic pronucleophiles toward polarized olefins (eq. (2), Figure 1).[5] Remarkably, addition of ligands proved to inhibit this reaction. Parallel to this work we realized a TBA[Fe]-catalyzed $C(sp^2)$-[6a] and $C(sp^3)$-H-amination[6b] using azides as N-donors (eq. (1), Figure 1).[6] With regard to these two recent findings we were wondering whether the nucleophilic activation of the azide with release of N_2 might pave the way toward an intermolecular C-H amination at reactive $C(sp^3)$-H-bonds through formation of an intermediate Fe-nitrene species or whether proton-transfer[7] from the $C(sp^3)$-H-bond to the nucleophilic ferrate would set the stage for a Fe-catalyzed version of the Dimroth-triazole synthesis.[8-10] Herein we summarize the results of this study which clearly indicates that proton-transfer catalysis outcompetes the azide activation which led to the development of an Fe-catalyzed triazole synthesis, that shows good substrate scope and functional group tolerance. Moreover, both protocols can be coupled in a consecutive catalysis to obtain highly decorated heterocyclic systems in a one-pot fashion (Figure 1).

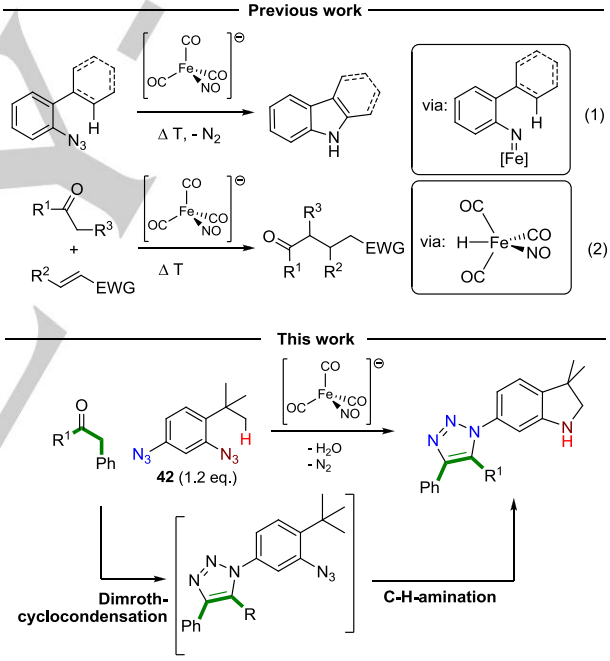

Figure 1. Fe-catalyzed Dimroth-cyclocondensation to triazoles and consecutive catalysis to complex heterocycles.

Results and Discussion

The similar reaction conditions for both the $C(sp^2)$-H amination and the conjugate addition led us to investigate the reaction of *o*-bisarylazide **2** with acetylacetone **1** as acidic pronucleophile in either acetonitrile or 1,2-dichloroethane as solvent under microwave irradiation (Scheme 1). At this early stage of this project we expected a mixture of products but were surprised to find that the product of the Dimroth triazole synthesis was formed exclusively, albeit in only low yields. No C-H-amination products were observed.

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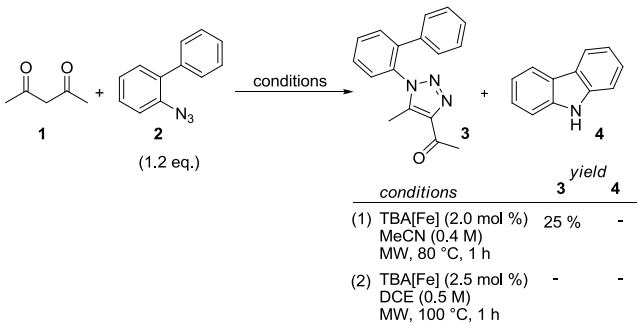
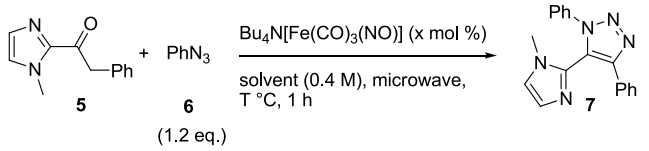


Scheme 1. Fe-catalyzed Dimroth triazole synthesis vs. Fe-catalyzed C-H-amination.

Subsequently, an intense screening of solvent and temperature effects using the more acidic acylimidazole **5** and sterically less congested phenylazide **6** was performed (Table 1).

Table 1. Optimization table.[a]

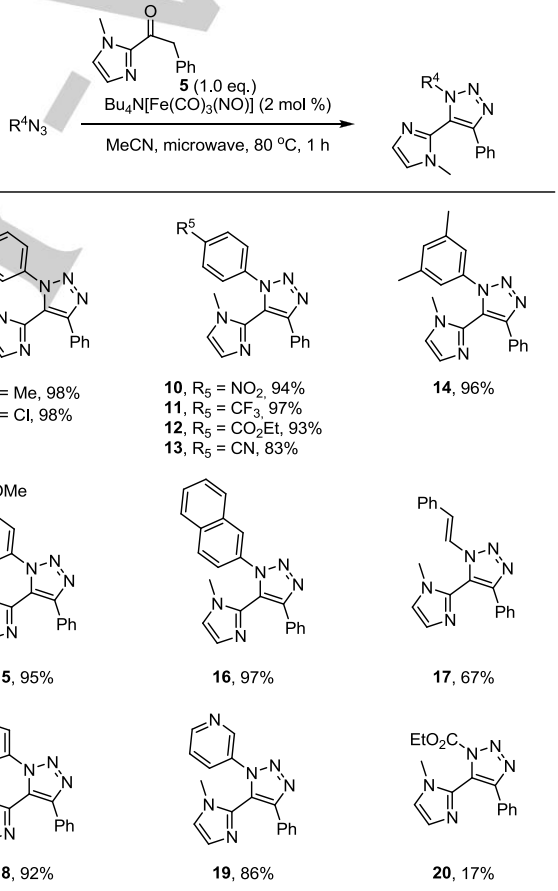


Entry	TBA[Fe] [mol %]	solvent	T [°C]	yield [%][b]
1[c]	5	MeCN	100	76 (67)
2	5	MeCN	80	99 (96)[d]
3	5	MeCN	60	33
4	5	CH_2Cl_2	80	5
5	5	DMF	80	0
6	5	toluene	80	28
7	5	THF	80	74
8	5	1,4-dioxane	80	38
9	5	DMSO	80	76
10	2	MeCN	80	99
11	1	MeCN	80	10

[a] All reactions were performed on a 0.4 mmol scale using ketone **5** (0.4 mmol), azide **6** (0.48 mmol), TBA[Fe] (x mol %) and dry solvent (1 mL) under microwave irradiation (T °C, 1 h) in a closed vessel. [b] Yields were determined by ^{1}H NMR using mesitylene as an internal standard. [c] Reaction was performed under thermal conditions (100 °C, 6 h). [d] Isolated yield.

We were delighted to find that the reaction proceeded in acetonitrile using only 2 mol % of TBA[Fe] in almost quantitative yield after only 1 h reaction time under microwave irradiation (entry 10, Table 1). Lower temperatures than 80 °C resulted in a significant drop of conversion. Importantly, the reaction could also be performed applying conventional heating rather than microwave irradiation, however, reaction times were significantly longer (entry 1, Table 1).

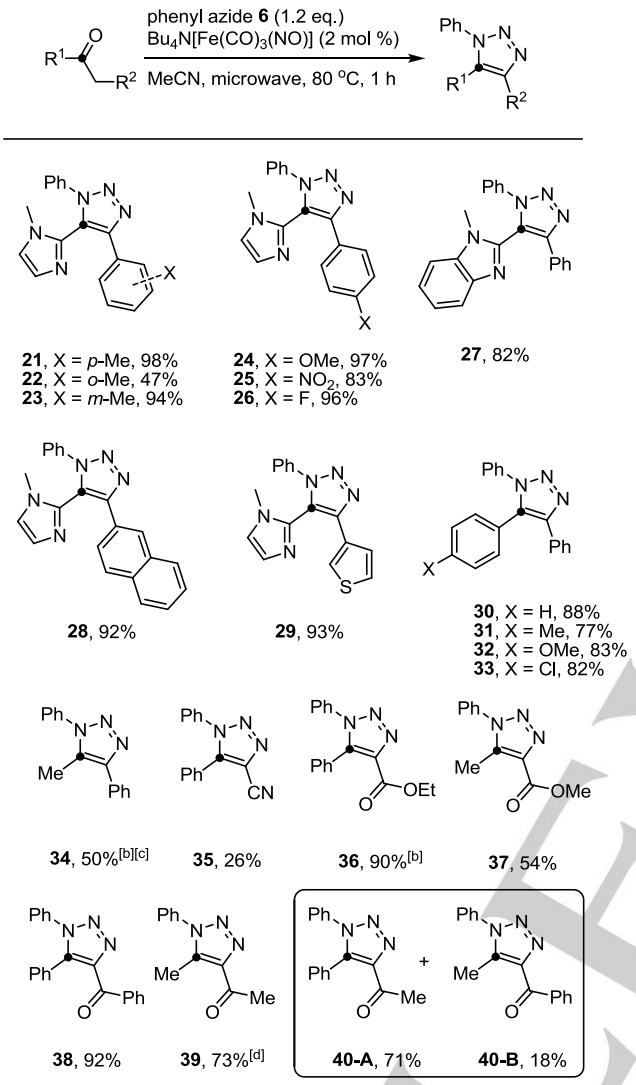
With these optimized conditions in hand we turned our attention to a screening of the azide scope (Scheme 2). A variety of azides, having either electron-donating or -withdrawing groups at *para* or *meta* position of the benzene ring, underwent the reactions smoothly to give the corresponding products **8** - **15** in excellent isolated yields. On the contrary, low yields and product mixtures were obtained upon using *ortho*-substituted azides, these details are found in the supplemental material. As for 2-naphthyl azide, the reaction proceeded smoothly to give the corresponding triazole **16** in 97% yield. With regard to vinyl azide, the corresponding product **17** was obtained in high yield. Heterocyclic substituents were also tolerated leading to products **18** and **19** in 92% and 86% yields, respectively. To our delight, even ethylazidoformate proved to be reactive and allowed the synthesis of ester **20** albeit in only 17% yield.



[a] All reactions were performed on a 0.4 mmol scale using **5** (0.4 mmol), azide (0.48 mmol), TBA[Fe] (2 mol %) and MeCN (1 mL) under microwave irradiation for 1 h at 80 °C. Isolated yields are given.

Scheme 2. Substrate scope of azides.[a]

Subsequently, a variety of ketones were subjected to the reaction conditions (Scheme 3).

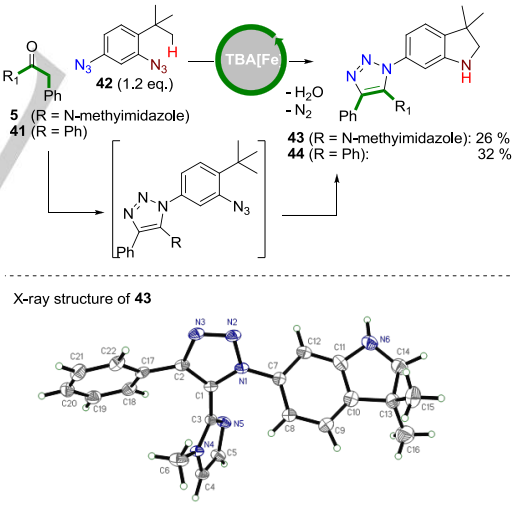


[a] All reactions were performed on a 0.4 mmol scale using ketone (0.4 mmol), azide **6** (0.48 mmol), TBA[Fe] (2 mol %) and MeCN (1 mL) under microwave irradiation for 1 h at 80 °C. Isolated yields are given. [b] In DMSO. [c] 40% of ketone was recovered. [d] Performing the reaction under thermal conditions (80 °C, 6 h) gave the desired product in 58% yield (0.4 mmol scale) and 70% yield (4.0 mmol scale).

Scheme 3. Substrate scope of ketones.[a]

In the case of substrates containing either electron-donating or -withdrawing groups at *para*, *meta*, or *ortho* position of benzene ring of ketone, the reactions proceeded smoothly to furnish the corresponding adducts **21** - **26** in 47 - 98% yields. For benzimidazole, the corresponding product **27** was formed in 82% yield. Also, a naphthyl substituent was well tolerated, which could produce adduct **28** in 92% yield. In addition, the thienyl-substituted ketone reacted successfully to deliver **29** in 93% yield. Using aryl or methyl groups instead of the imidazolyl substituent led to the desired products **30** - **34** efficiently and with exclusive regioselectivity. *Importantly, the use of Ru-catalysts for the 1,3-dipolar cycloaddition of arylazide to the corresponding bis-arylalkynes did not give any conversion to either products* **30** - **33** *underlining that the Dimroth triazole synthesis using TBA[Fe] is a complementary and efficient synthetic approach.*[11] Further examination of substrate having a cyano group revealed that the desired product **35** could be obtained in 26% yield. Remarkably, 1,3-diketones were suitable substrates as well, affording adducts **36** - **39** in good yields. Interestingly, the use of 1-phenyl-1,3-butanedione gave the desired product **40-A** and **40-B** in 71% and 18% yields, respectively.

Knowing that *o*-substituted arylazides are less reactive in Dimroth cyclocondensation reaction (Scheme 1) we wondered whether we could combine both Fe-catalyzed processes, i.e. the cyclocondensation and the C-H-amination, into a one-pot process to give highly substituted N-rich functional building blocks that are not easy to obtain using alternative methods (Scheme 4). Indeed, the combination of both processes into a one-pot procedure was possible as exemplified for the reaction of two different ketones **5** or **41**, and bis-azide **42**. Although the addition of another 2.5 mol % of TBA[Fe] after the Dimroth cyclocondensation turned out to be necessary, the overall process is simple, does not require a change of solvent and forms only water and nitrogen-gas as by-products.[12]



Scheme 4. Fe-catalyzed sequecutive cyclocondensation-C(sp^3)-H amination to functional building blocks.[a]

Our previous experiments and these observations led us to propose that the initial proton-transfer from the ketone to the ferrate is faster than the nucleophilic addition of the ferrate to the azide. Once $H[Fe(CO)_3(NO)]$ is being formed the azide undergoes a fast proton-transfer from the Fe-H-complex. The following C-N-bond forming event gives a triazene which

undergoes a 1,2-addition and condensation to the final product (Figure 2).

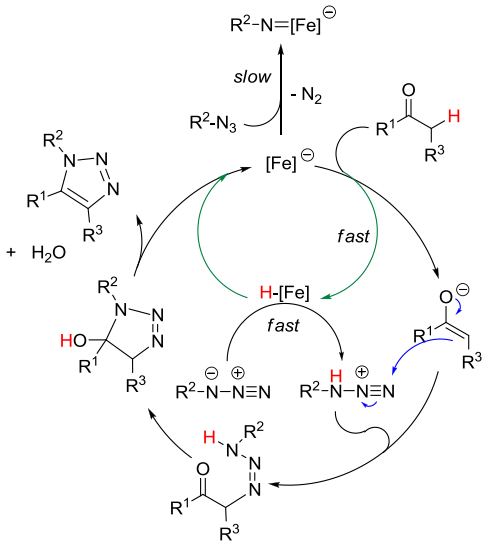


Figure 2. Mechanistic proposal for the TBA[Fe]-catalyzed Dimroth cyclocondensation.

Conclusions

The nucleophilic ferrate $Bu_4N[Fe(CO)_3(NO)]$ (TBA[Fe]) has been used so far in a variety of catalytic transformations. Reactions which rely on the use of this complex in proton-transfer catalysis are scarce. Herein, we report a new catalytic protocol for the Dimroth cyclocondensation between arylazides and ketones to give substituted 1,2,3-triazoles in which the complex ferrate serves as a proton shuttle. The reaction is characterized by low catalyst loading, short reaction times and high yields. Importantly, this study underlines the potential of $H[Fe(CO)_3(NO)]$, which was reported to be thermolabile and to undergo a fast ligand scrambling to give $H_2[Fe(CO)_4]$ and $[Fe(CO)_2(NO)_2]$, to be a catalytic intermediate. This finding opens new perspectives in TBA[Fe]-catalysis.

Experimental Section

General Catalysis Procedure A: A 10 mL microwave tube with a magnetic stirrer was dried under high vacuum using a heat gun for at least 10 minutes. After cooling to room temperature the microwave tube was charged under nitrogen atmosphere with the catalyst TBA[Fe] (2 mol %) and the corresponding ketone (1 eq.). Then MeCN (0.4 M) was added via syringe, followed by the corresponding azide (1.2 eq.). The reaction mixture was stirred at 80 °C for 1 hour under microwave conditions (200 W). Afterwards, purification via column chromatography on silica gel afforded the desired products.

1-(1-([1,1'-Biphenyl]-2-yl)-5-methyl-1*H*-1,2,3-triazol-4-yl)ethanone (3): 28 mg, 25%. Colourless oil. R_f: 0.15 (petroleum ether/ethyl acetate 4:1). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.71 – 7.63 (m, 1*H*), 7.62 – 7.52 (m, 2*H*), 7.48 – 7.41 (m, 1*H*), 7.29 – 7.20 (m, 3*H*), 7.09 – 7.02 (m, 2*H*), 2.69 (s, 3*H*), 1.98 (s, 3*H*). ^{13}C NMR (75 MHz, $CDCl_3$): δ 194.2, 143.0, 139.3, 138.8, 136.8, 132.8, 131.1, 131.0, 128.8, 128.7, 128.3, 128.2, 128.1, 27.7, 9.4. IR (film): ν (cm^{-1}) 3062, 2923, 1679, 1555, 1486, 1416, 1365, 1278, 1081, 951, 764, 737, 684. MS (ESI, m/z): 300.1 $(M+Na)^+$. HRMS (ESI, m/z) calcd. for $C_{17}H_{15}N_3ONa$ $[M+Na]^+$: 300.1107, found: 300.1125.

5-(1-Methyl-1*H*-imidazol-2-yl)-1,4-diphenyl-1*H*-1,2,3-triazole (7): 116 mg, 96%. White solid. R_f: 0.38 (petroleum ether/ethyl acetate 1:1). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.66 (d, *J* = 8.0 Hz, 2*H*), 7.48-7.46 (m, 2*H*), 7.43-7.41 (m, 3*H*), 7.38-7.35 (m, 3*H*), 7.28 (s, 1*H*), 6.99 (s, 1*H*), 3.13 (s, 3*H*). ^{13}C NMR (126 MHz, $CDCl_3$): δ 147.9, 136.4, 134.8, 130.3, 129.8, 129.4, 129.2, 128.8, 128.6, 126.6, 123.6, 123.3, 122.6, 33.0. IR (film): ν (cm^{-1}) 3092, 1497, 689. MS (ESI, m/z): 324.1 $(M+Na)^+$. HRMS (ESI, m/z) calcd. for $C_{18}H_{16}N_5$ $[M+H]^+$: 302.1400, found: 302.1389.

5-(1-Methyl-1*H*-imidazol-2-yl)-4-phenyl-1-(*p*-tolyl)-1*H*-1,2,3-triazole (8): 123 mg, 98%. White solid. R_f: 0.43 (petroleum ether/ethyl acetate 1:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.66 (d, *J* = 8.4 Hz, 2*H*), 7.38-7.32 (m, 5*H*), 7.27 (s, 1*H*), 7.20 (d, *J* = 8.0 Hz, 2*H*), 6.99 (s, 1*H*), 3.12 (s, 3*H*), 2.37 (s, 3*H*). ^{13}C NMR (101 MHz, $CDCl_3$): δ 147.7, 139.4, 135.0, 133.9, 130.3, 129.93, 129.91, 128.7, 128.5, 126.6, 123.4, 123.3, 122.5, 33.0, 21.1. IR (film): ν (cm^{-1}) 3121, 2950, 1512, 695. MS (ESI, m/z): 316.2 $(M+H)^+$. HRMS (ESI, m/z) calcd. for $C_{19}H_{18}N_5$ $[M+H]^+$: 316.1557, found: 316.1562.

1-(4-Chlorophenyl)-5-(1-methyl-1*H*-imidazol-2-yl)-4-phenyl-1*H*-1,2,3-triazole (9): 131 mg, 98%. White solid. R_f: 0.64 (petroleum ether/ethyl acetate 1:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.62 (d, *J* = 8.0 Hz, 2*H*), 7.46-7.33 (m, 7*H*), 7.28 (s, 1*H*), 7.02 (s, 1*H*), 3.15 (s, 3*H*). ^{13}C NMR (101 MHz, $CDCl_3$): δ 147.9, 135.1, 134.8, 134.4, 130.5, 129.6, 129.5, 128.8, 128.7, 126.5, 124.8, 123.2, 122.7, 33.0. IR (film): ν (cm^{-1}) 3092, 2943, 1496, 696. MS (ESI, m/z): 336.1 $(M+H)^+$. HRMS (ESI, m/z) calcd. for $C_{18}H_{15}N_5Cl$ $[M+H]^+$: 336.1010, found: 336.1007.

5-(1-Methyl-1*H*-imidazol-2-yl)-1-(4-nitrophenyl)-4-phenyl-1*H*-1,2,3-triazole (10): 131 mg, 94%. White solid. R_f: 0.54 (petroleum ether/ethyl acetate 1:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.30 (d, *J* = 8.8 Hz, 2*H*), 7.73 (d, *J* = 8.8 Hz, 2*H*), 7.60-7.58 (m, 2*H*), 7.42-7.37 (m, 3*H*), 7.32 (s, 1*H*), 7.08 (s, 1*H*), 3.19 (s, 3*H*). ^{13}C NMR (101 MHz, $CDCl_3$): δ 148.4, 147.5, 141.0, 134.1, 130.8, 129.2, 129.1, 129.0, 126.6, 124.8, 124.0, 123.2, 123.1, 33.1. IR (film): ν (cm^{-1}) 3084, 1524, 1343, 685. MS (ESI, m/z): 369.1 $(M+Na)^+$. HRMS (ESI, m/z) calcd. for $C_{18}H_{15}N_6O_2$ $[M+H]^+$: 347.1251, found: 347.1262.

5-(1-Methyl-1*H*-imidazol-2-yl)-4-phenyl-1-(4-(trifluoromethyl)phenyl)-1*H*-1,2,3-triazole (11): 143 mg, 97%. White solid. R_f: 0.70 (petroleum ether/ethyl acetate 1:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.71-7.60 (m, 6*H*), 7.40-7.35 (m, 3*H*), 7.31 (s, 1*H*), 7.05 (s, 1*H*), 3.17 (s, 3*H*). ^{13}C NMR (101 MHz, $CDCl_3$): δ 148.2, 139.0, 134.3, 131.0 (q, *J* = 32.9 Hz), 130.6, 129.5, 128.90,

128.87, 126.61, 126.56, 123.7, 123.4 (q, *J* = 270.8 Hz), 123.2, 122.9, 33.0. ^{19}F NMR (376 MHz, $CDCl_3$): δ -62.7 (s). IR (film): ν (cm^{-1}) 3127, 3046, 1322, 1128, 695. MS (ESI, m/z): 370.1 $(M+H)^+$. HRMS (ESI, m/z) calcd. for $C_{19}H_{15}F_3N_5$ $[M+H]^+$: 370.1274, found: 370.1267.

Ethyl 4-(5-(1-methyl-1*H*-imidazol-2-yl)-4-phenyl-1*H*-1,2,3-triazol-1-yl)benzoate (12): 139 mg, 93%. White solid. R_f: 0.44 (petroleum ether/ethyl acetate 1:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.10 (d, *J* = 7.6 Hz, 2*H*), 7.65 (d, *J* = 7.6 Hz, 2*H*), 7.55 (d, *J* = 8.0 Hz, 2*H*), 7.37-7.32 (m, 3*H*), 7.30 (s, 1*H*), 7.03 (s, 1*H*), 4.39 (q, *J* = 7.2 Hz, 2*H*), 3.15 (s, 3*H*), 1.39 (t, *J* = 7.2 Hz, 3*H*). ^{13}C NMR (101 MHz, $CDCl_3$): δ 165.3, 148.1, 139.6, 134.5, 130.9, 130.7, 130.6, 129.5, 128.82, 128.77, 126.6, 123.2, 123.1, 122.8, 61.4, 33.0, 14.2. IR (film): ν (cm^{-1}) 3064, 2927, 1715, 1272, 1107, 693. MS (ESI, m/z): 396.1 $(M+Na)^+$. HRMS (ESI, m/z) calcd. for $C_{21}H_{19}NaN_5O_2$ $[M+Na]^+$: 396.1431, found: 396.1429.

4-(5-(1-Methyl-1*H*-imidazol-2-yl)-4-phenyl-1*H*-1,2,3-triazol-1-yl)benzonitrile (13): 108 mg, 83%. Colorless oil. R_f: 0.39 (petroleum ether/ethyl acetate 1:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.73 (d, *J* = 8.4 Hz, 2*H*), 7.66 (d, *J* = 8.4 Hz, 2*H*), 7.60-7.57 (m, 2*H*), 7.41-7.37 (m, 3*H*), 7.31 (s, 1*H*), 7.07 (s, 1*H*), 3.18 (s, 3*H*). ^{13}C NMR (101 MHz, $CDCl_3$): δ 148.3, 139.5, 134.1, 133.3, 130.7, 129.3, 129.0, 128.9, 126.5, 123.9, 123.1, 123.0, 117.6, 112.9, 33.1. IR (film): ν (cm^{-1}) 3065, 2231, 1509, 909, 725. MS (ESI, m/z): 349.1 $(M+Na)^+$. HRMS (ESI, m/z) calcd. for $C_{19}H_{14}NaN_6$ $[M+Na]^+$: 349.1172, found: 349.1178.

1-(3,5-Dimethylphenyl)-5-(1-methyl-1*H*-imidazol-2-yl)-4-phenyl-1*H*-1,2,3-triazole (14): 126 mg, 96%. White solid. R_f: 0.54 (petroleum ether/ethyl acetate 1:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.68 (d, *J* = 8.0 Hz, 2*H*), 7.38-7.31 (m, 3*H*), 7.27 (s, 1*H*), 7.04-7.02 (m, 3*H*), 6.99 (s, 1*H*), 3.12 (s, 3*H*), 2.29 (s, 6*H*). ^{13}C NMR (101 MHz, $CDCl_3$): δ 147.6, 139.2, 136.1, 135.0, 130.8, 130.2, 129.9, 128.7, 128.4, 126.6, 123.3, 122.4, 121.1, 32.9, 21.1. IR (film): ν (cm^{-1}) 2918, 1462, 1280, 682. MS (ESI, m/z): 330.2 $(M+H)^+$. HRMS (ESI, m/z) calcd. for $C_{20}H_{20}N_5$ $[M+H]^+$: 330.1713, found: 330.1704.

1-(3-Methoxyphenyl)-5-(1-methyl-1*H*-imidazol-2-yl)-4-phenyl-1*H*-1,2,3-triazole (15): 126 mg, 95%. White solid. R_f: 0.47 (petroleum ether/ethyl acetate 1:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.68 (d, *J* = 8.0 Hz, 2*H*), 7.38-7.28 (m, 5*H*), 7.06-7.01 (m, 3*H*), 6.94 (dd, *J* = 8.0, 2.4 Hz, 1*H*), 3.75 (s, 3*H*), 3.13 (s, 3*H*). ^{13}C NMR (101 MHz, $CDCl_3$): δ 160.0, 147.8, 137.2, 134.9, 130.3, 130.1, 129.8, 128.7, 128.6, 126.6, 123.2, 122.6, 115.6, 115.3, 108.4, 55.4, 33.0. IR (film): ν (cm^{-1}) 3065, 2945, 1494, 1246, 729. MS (ESI, m/z): 332.2 $(M+H)^+$. HRMS (ESI, m/z) calcd. for $C_{19}H_{18}N_5O$ $[M+H]^+$: 332.1506, found: 332.1513.

5-(1-Methyl-1*H*-imidazol-2-yl)-1-(naphthalen-2-yl)-4-phenyl-1*H*-1,2,3-triazole (16): 136 mg, 97%. Colorless oil. R_f: 0.55 (petroleum ether/ethyl acetate 1:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.96 (d, *J* = 2.0 Hz, 1*H*), 7.88-7.81 (m, 3*H*), 7.72-7.70 (m, 2*H*), 7.57-7.52 (m, 3*H*), 7.40-7.34 (m, 3*H*), 7.30 (s, 1*H*), 6.97 (s, 1*H*), 3.12 (s, 3*H*). ^{13}C NMR (101 MHz, $CDCl_3$): δ 147.9, 134.9, 133.7, 132.9, 130.4, 129.9, 129.4, 128.8, 128.6, 128.5, 127.7, 127.26, 127.16, 126.6, 123.5, 122.6, 122.3, 121.2, 33.0. IR (film): ν (cm^{-1}) 3060, 2948, 1472, 727. MS (ESI, m/z): 352.2 $(M+H)^+$. HRMS (ESI, m/z) calcd. for $C_{22}H_{18}N_5$ $[M+H]^+$: 352.1557, found: 352.1543.

(*E*)-5-(1-Methyl-1*H*-imidazol-2-yl)-4-phenyl-1-styryl-1*H*-1,2,3-triazole (17): 88 mg, 67%. Colorless oil. R_f: 0.58 (petroleum ether/ethyl acetate 1:1). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.66 (d, *J* = 14.4 Hz, 1*H*), 7.56-7.52 (m, 3*H*), 7.46-7.30 (m, 9*H*), 7.10 (d, *J* = 0.9 Hz, 1*H*), 3.21 (s, 3*H*). ^{13}C NMR (75 MHz, $CDCl_3$): δ 146.9, 134.8, 134.0, 130.8, 130.0, 129.0, 128.8, 128.71, 128.68, 127.0, 126.6, 123.8, 123.0, 122.4, 121.0, 33.4. IR (film): ν (cm^{-1}) 3061, 3028, 1281, 691. MS (ESI, m/z): 328.2 $(M+H)^+$. HRMS (ESI, m/z) calcd. for $C_{20}H_{18}N_5$ $[M+H]^+$: 328.1557, found: 328.1540.

5-(1-Methyl-1*H*-imidazol-2-yl)-4-phenyl-1-(3-thienyl)-1*H*-1,2,3-triazole (18): 113 mg, 92%. White solid. R_f: 0.44 (petroleum ether/ethyl acetate 1:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.63 (dd, *J* = 8.0, 2.0 Hz, 2*H*), 7.38-7.32 (m, 5*H*), 7.29-7.24 (m, 2*H*), 7.07 (s, 1*H*), 3.16 (s, 3*H*). ^{13}C NMR (101 MHz, $CDCl_3$): δ 147.5, 134.6, 134.4, 130.4, 129.6, 128.8, 128.6, 126.42, 126.39, 122.8, 122.6, 122.2, 116.7, 33.0. IR (film): ν (cm^{-1}) 3091, 3067, 1412, 775, 689. MS (ESI, m/z): 330.1 $(M+Na)^+$. HRMS (ESI, m/z) calcd. for $C_{16}H_{13}NaN_5S$ $[M+Na]^+$: 330.0784, found: 330.0784.

3-(5-(1-Methyl-1*H*-imidazol-2-yl)-4-phenyl-1*H*-1,2,3-triazol-1-yl)pyridine (19): 104 mg, 86%. White solid. R_f: 0.07 (petroleum ether/ethyl acetate 1:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.72 (d, *J* = 2.4 Hz, 1*H*), 8.67 (dd, *J* = 4.8, 1.2 Hz, 1*H*), 7.97-7.94 (m, 1*H*), 7.60-7.58 (m, 2*H*), 7.43-7.37 (m, 4*H*), 7.28 (s, 1*H*), 7.04 (s, 1*H*), 3.20 (s, 3*H*). ^{13}C NMR (101 MHz, $CDCl_3$): δ 150.2, 148.0, 144.6, 134.2, 133.1, 131.3, 130.7, 129.5, 128.95, 128.90, 126.5, 123.8, 123.5, 122.9, 33.1. IR (film): ν (cm^{-1}) 3133, 3048, 2947, 1429, 698. MS (ESI, m/z): 303.1 $(M+H)^+$. HRMS (ESI, m/z) calcd. for $C_{17}H_{14}NaN_6$ $[M+Na]^+$: 325.1172, found: 325.1179.

Ethyl 5-(1-methyl-1*H*-imidazol-2-yl)-4-phenyl-1*H*-1,2,3-triazole-1-carboxylate (20): 20 mg, 17%. Colorless oil. R_f: 0.21 (petroleum ether/ethyl acetate 2:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.92 (d, *J* = 7.6 Hz, 2*H*), 7.54 (t, *J* = 7.6 Hz, 1*H*), 7.42 (t, *J* = 7.6 Hz, 2*H*), 7.20 (s, 1*H*), 7.13 (s, 1*H*), 4.16-4.10 (m, 5*H*), 1.20 (t, *J* = 7.2 Hz, 3*H*). ^{13}C NMR (101 MHz, $CDCl_3$): δ 161.8, 141.7, 133.2, 133.1, 131.3, 129.9, 129.4, 128.7, 127.6, 63.0, 35.7, 14.0. IR (film): ν (cm^{-1}) 3109, 2981, 1705, 1658, 1398, 1206, 688. MS (ESI, m/z): 298.1 $(M+H)^+$. HRMS (ESI, m/z) calcd. for $C_{15}H_{16}N_5O_2$ $[M+H]^+$: 298.1299, found: 298.1282.

5-(1-Methyl-1*H*-imidazol-2-yl)-1-phenyl-4-(*p*-tolyl)-1*H*-1,2,3-triazole (21): 124 mg, 98%. White solid. R_f: 0.44 (petroleum ether/ethyl acetate 1:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.54 (d, *J* = 8.0 Hz, 2*H*), 7.47-7.40 (m, 5*H*), 7.27 (s, 1*H*), 7.17 (d, *J* = 8.0 Hz, 2*H*), 6.98 (s, 1*H*), 3.13 (s, 3*H*), 2.35 (s, 3*H*). ^{13}C NMR (101 MHz, $CDCl_3$): δ 147.9, 138.5, 136.4, 135.0, 130.3, 129.5, 129.3, 129.1, 127.0, 126.5, 123.5, 123.0, 122.5, 33.0, 21.2. IR (film): ν (cm^{-1}) 3094, 2923, 1496, 763, 691. MS (EI, 70 eV) m/z (%): 315 (7), 287 (100), 169 (45), 77 (12). HRMS (ESI, m/z) calcd. for $C_{19}H_{18}N_5$ $[M+H]^+$: 316.1557, found: 316.1548.

5-(1-Methyl-1*H*-imidazol-2-yl)-1-phenyl-4-(*o*-tolyl)-1*H*-1,2,3-triazole (22): 59 mg, 47%. White solid. R_f: 0.48 (petroleum ether/ethyl acetate 1:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.49-7.42 (m, 5*H*), 7.27-7.26 (m, 3*H*), 7.18-7.15 (m, 2*H*), 6.88 (s, 1*H*), 3.06 (s, 3*H*), 2.34 (s, 3*H*). ^{13}C NMR (101 MHz, $CDCl_3$): δ 148.3, 137.2, 136.6, 134.9, 130.8, 130.3, 130.1, 129.3, 129.2, 128.8, 125.9, 125.0, 123.9, 122.3, 32.9, 20.3. IR (film): ν (cm^{-1}) 3097, 1496, 747. MS (ESI, m/z): 316.2 $(M+H)^+$. HRMS (ESI, m/z) calcd. for $C_{19}H_{18}N_5$ $[M+H]^+$: 316.1557, found: 316.1580.

5-(1-Methyl-1*H*-imidazol-2-yl)-1-phenyl-4-(*m*-tolyl)-1*H*-1,2,3-triazole (23): 119 mg, 94%. White solid. R_f: 0.46 (petroleum ether/ethyl acetate 1:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.59 (s, 1*H*), 7.49-7.41 (m, 5*H*), 7.33 (d, *J* = 7.6 Hz, 1*H*), 7.28 (s, 1*H*), 7.23 (t, *J* = 7.6 Hz, 1*H*), 7.15 (d, *J* = 7.6 Hz, 1*H*), 6.99 (s, 1*H*), 3.13 (s, 3*H*), 2.34 (s, 3*H*). ^{13}C NMR (101 MHz, $CDCl_3$): δ 148.0, 138.4, 136.4, 134.9, 130.4, 129.7, 129.38, 129.36, 129.2, 128.6, 127.4, 123.6, 123.5, 123.3, 122.4, 33.0, 21.4. IR (film): ν (cm^{-1}) 3093, 2920, 1496, 743. MS (ESI, m/z): 316.2 $(M+H)^+$. HRMS (ESI, m/z) calcd. for $C_{19}H_{18}N_5$ $[M+H]^+$: 316.1557, found: 316.1550.

4-(4-Methoxyphenyl)-5-(1-methyl-1*H*-imidazol-2-yl)-1-phenyl-1*H*-1,2,3-triazole (24): 128 mg, 97%. White solid. R_f: 0.33 (petroleum ether/ethyl acetate 1:1). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.60 (d, *J* = 8.7 Hz, 2*H*), 7.48-7.39 (m, 5*H*), 7.26 (s, 1*H*), 6.99 (s, 1*H*), 6.89 (d, *J* = 8.7 Hz, 2*H*), 3.80 (s, 3*H*), 3.12 (s, 3*H*). ^{13}C NMR (75 MHz, $CDCl_3$): δ 159.8, 147.7, 136.4, 135.0, 130.3, 129.3, 129.1, 127.9, 123.4, 122.46, 122.41, 114.2, 55.2, 32.9. IR (film): ν (cm^{-1}) 3096, 3006, 1497, 1258, 1178, 767. MS (ESI, m/z): 332.1 $(M+H)^+$. HRMS (ESI, m/z) calcd. for $C_{19}H_{18}N_5O$ $[M+H]^+$: 332.1506, found: 332.1494.

5-(1-Methyl-1*H*-imidazol-2-yl)-4-(4-nitrophenyl)-1-phenyl-1*H*-1,2,3-triazole (25): 115 mg, 93%. White solid. R_f: 0.49 (petroleum ether/ethyl acetate 1:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.24 (d, *J* = 8.8 Hz, 2*H*), 7.94 (d, *J* = 8.8 Hz, 2*H*), 7.46 (brs, 5*H*), 7.34 (s, 1*H*), 7.04 (s, 1*H*), 3.13 (s, 3*H*). ^{13}C NMR (101 MHz, $CDCl_3$): δ 147.6, 145.7, 136.2, 136.0, 134.0, 130.8, 129.7, 127.2, 124.9, 124.1, 123.4, 123.1, 33.1. IR (film): ν (cm^{-1}) 3110, 2950, 1518, 1497, 1340, 734. MS (EI, 70 eV) m/z (%): 346 (11), 318 (100), 271 (20), 168 (17). HRMS (EI, 70 eV, m/z) calcd. for $C_{18}H_{14}N_6O_2$: 346.1178, found: 346.1168.

4-(4-Fluorophenyl)-5-(1-methyl-1*H*-imidazol-2-yl)-1-phenyl-1*H*-1,2,3-triazole (26): 122 mg, 96%. White solid. R_f: 0.50 (petroleum ether/ethyl acetate 1:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.70-7.67 (m, 2*H*), 7.46-7.40 (m, 5*H*), 7.28 (s, 1*H*), 7.05 (t, *J* = 8.8 Hz, 2*H*), 7.00 (s, 1*H*), 3.12 (s, 3*H*). ^{13}C NMR (101 MHz, $CDCl_3$): δ 162.8 (d, *J* = 247.0 Hz), 146.9, 136.2, 134.5, 130.4, 129.4, 129.2, 128.4 (d, *J* = 8.1 Hz), 126.0 (d, *J* = 3.1 Hz), 123.3, 123.1, 122.6, 115.7 (d, *J* = 21.4 Hz), 32.9. ^{19}F NMR (376 MHz, $CDCl_3$): δ -112.5 ~ -112.6 (m). IR (film): ν (cm^{-1}) 3097, 2945, 1497, 841, 766. MS (ESI, m/z): 320.1 $(M+H)^+$. HRMS (ESI, m/z) calcd. for $C_{18}H_{15}N_5F$ $[M+H]^+$: 320.1306, found: 320.1300.

2-(1,4-Diphenyl-1*H*-1,2,3-triazol-5-yl)-1-methyl-1*H*-benzo[*d*]imidazole (27): 115 mg, 82%. Light yellow solid. R_f: 0.43 (petroleum ether/ethyl acetate 2:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.92-7.85 (m, 1*H*), 7.71-7.65 (m, 2*H*), 7.51-7.44 (m, 2*H*), 7.41-7.29 (m, 9*H*), 3.30 (s, 3*H*). ^{13}C NMR (101 MHz, $CDCl_3$): δ 148.2, 143.2, 141.2, 136.2, 135.3, 129.6, 129.5, 129.4, 128.9, 128.8, 126.8, 124.0, 123.7, 123.2, 123.0, 120.8, 109.9, 30.3. IR (film): ν (cm^{-1}) 3063, 2946, 1459, 907, 726. MS (ESI, m/z): 352.2 $(M+H)^+$. HRMS (ESI, m/z) calcd. for $C_{22}H_{18}N_5$ $[M+H]^+$: 352.1557, found: 352.1550.

5-(1-Methyl-1*H*-imidazol-2-yl)-4-(naphthalen-2-yl)-1-phenyl-1*H*-1,2,3-triazole (28): 129 mg, 92%. White solid. R_f: 0.49 (petroleum ether/ethyl acetate 1:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.17 (s, 1*H*), 7.84-7.78 (m, 3*H*), 7.75-7.72 (m, 1*H*), 7.52-7.42 (m, 7*H*), 7.33 (s, 1*H*), 7.00 (s, 1*H*), 3.12 (s, 3*H*). ^{13}C NMR (101 MHz, $CDCl_3$): δ 147.9, 136.3, 134.9, 133.3, 133.1, 130.5, 129.4, 128.5, 128.4, 127.6, 127.2, 126.4, 126.3, 126.0, 124.1, 123.6, 122.6, 33.0. IR (film): ν (cm^{-1}) 3054, 2949, 1497, 726. MS (ESI, m/z): 352.2 $(M+H)^+$. HRMS (ESI, m/z) calcd. for $C_{22}H_{18}N_5$ $[M+H]^+$: 352.1557, found: 352.1548.

5-(1-Methyl-1*H*-imidazol-2-yl)-1-phenyl-4-(3-thienyl)-1*H*-1,2,3-triazole (29): 114 mg, 93%. White solid. R_f: 0.37 (petroleum ether/ethyl acetate 1:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.56-7.55 (m, 1*H*), 7.47-7.40 (m, 5*H*), 7.35-7.28 (m, 3*H*), 7.02 (s, 1*H*), 3.14 (s, 3*H*). ^{13}C NMR (101 MHz, $CDCl_3$): δ 144.6, 136.3, 134.6, 130.6, 130.4, 129.4, 129.1, 126.1, 126.0, 123.2, 122.8, 122.7, 122.6, 32.9. IR (film): ν (cm^{-1}) 3108, 2948, 1497, 725. MS (ESI, m/z): 308.1 $(M+H)^+$. HRMS (ESI, m/z) calcd. for $C_{16}H_{14}N_5S$ $[M+H]^+$: 308.0964, found: 308.0968.

1,4,5-Triphenyl-1*H*-1,2,3-triazole (30): 105 mg, 88%. White solid. R_f: 0.22 (petroleum ether/ethyl acetate 10:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.60 (dd, *J* = 8.0 Hz, *J* = 2.0 Hz, 2*H*), 7.40-7.30 (m, 11*H*), 7.21 (d, *J* = 6.8 Hz, 2*H*). ^{13}C NMR (101 MHz, $CDCl_3$): δ 144.8, 136.5, 133.6, 130.8, 130.2, 129.4, 129.1, 129.0, 128.9, 128.5, 127.9, 127.7, 127.3, 125.1. MS (ESI, m/z): 298.1 $(M+H)^+$. All spectral data are in agreement with those previously reported.[13]

1,4-Diphenyl-5-(*p*-tolyl)-1*H*-1,2,3-triazole (31): 1 h, 97 mg, 77 %. White solid. R_f: 0.24 (petroleum ether/ethyl acetate 10:1). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.63-7.60 (m, 2*H*), 7.39-7.29 (m, 8*H*), 7.15 (d, *J* = 8.01 Hz, 2*H*), 7.08 (d, *J* = 8.22 Hz, 2*H*), 2.38 (s, 3*H*). ^{13}C NMR (101 MHz, $CDCl_3$): δ 130.0, 129.8, 129.1, 128.9, 128.5, 127.8, 127.4, 125.2, 21.4. IR (film): ν (cm^{-1}) 3050, 2243, 1946, 1594, 1496, 1366, 995, 823, 695. MS (ESI, m/z): 312.15 $(M+H)^+$, 334.13 $(M+Na)^+$. All spectral data are in agreement with those previously reported.[14]

5-(4-Methoxyphenyl)-1,4-diphenyl-1*H*-1,2,3-triazole (32): 1 h, 109 mg 83 %. White solid. R_f: 0.13 (petroleum ether/ethyl acetate 10:1). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.64-7.60 (m, 2*H*), 7.40-7.28 (m, 8*H*), 7.12 (d, *J* = 8.73 Hz, 2*H*), 6.88 (d, *J* = 8.79 Hz, 2*H*), 3.83 (s, 3*H*). ^{13}C NMR (75 MHz, $CDCl_3$): δ 160.3, 144.6, 136.5, 133.6, 131.5, 131.0,129.1, 128.9, 128.5, 127.8, 127.3, 125.2, 119.6, 114.5, 55.3. IR (film): ν (cm^{-1}) 3059, 2940, 2839, 1595, 1497, 1257, 1032, 995, 823, 695. MS (ESI, m/z): 328.14 $(M+H)^+$, 350.13 $(M+Na)^+$. HRMS (ESI, m/z) calcd. for $C_{21}H_{17}N_3NaO$ $[M+Na]^+$: 350.1264, found: 350.1252. All spectral data are in agreement with those previously reported.[15]

5-(4-Chlorophenyl)-1,4-diphenyl-1*H*-1,2,3-triazole (33): 1 h, 108 mg, 82 %, White solid. R_f: 0.21 (petroleum ether/ethyl acetate 10:1). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.60-7.56 (m, 2*H*), 7.43-7.29 (m, 10*H*), 7-15-7.12 (m, 2*H*). ^{13}C NMR (101 MHz, $CDCl_3$): δ 145.0, 136.3, 135.6, 132.5, 131.4, 130.5, 129.5, 129.3, 129.2, 128.6, 128.1, 127.5, 126.2, 125.2. IR (film): ν (cm^{-1}) 3051, 2036, 1594, 1503, 1367, 1093, 995, 831, 695. MS (ESI, m/z): 332.09 $(M+H)^+$. HRMS (ESI, m/z) calcd. for $C_{20}H_{14}ClNaN_3$ $[M+Na]^+$: 354.0768, found: 354.0768. All spectral data are in agreement with those previously reported.[16]

5-Methyl-1,4-diphenyl-1*H*-1,2,3-triazole (34): 47 mg, 50%. White solid. R_f: 0.49 (petroleum ether/ethyl acetate 2:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.79 (d, *J* = 6.8 Hz, 2*H*), 7.60-7.47 (m, 7*H*), 7.39 (t, *J* = 7.2 Hz, 1*H*), 2.50 (s, 3*H*). ^{13}C NMR (101 MHz, $CDCl_3$): δ 144.8, 136.4, 131.4, 129.6, 129.53, 129.48, 128.7,

127.8, 127.2, 125.3, 10.3. MS (ESI, m/z): 236.1 $(M+H)^+$. All spectral data are in agreement with those previously reported.[13]

1,5-Diphenyl-1*H*-1,2,3-triazole-4-carbonitrile (35): 26 mg, 26%. White solid. R_f: 0.34 (petroleum ether/ethyl acetate 4:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.54-7.42 (m, 6*H*), 7.36-7.33 (m, 4*H*). ^{13}C NMR (101 MHz, $CDCl_3$): δ 143.0, 135.3, 131.1, 130.2, 129.7, 129.4, 128.9, 125.1, 123.3, 120.6, 112.1. MS (ESI, m/z): 247.1 $(M+H)^+$. All spectral data are in agreement with those previously reported.[17]

Ethyl 1,5-diphenyl-1*H*-1,2,3-triazole-4-carboxylate (36): 105 mg, 90%. White solid. R_f: 0.51 (petroleum ether/ethyl acetate 2:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.44-7.36 (m, 6*H*), 7.31-7.26 (m, 4*H*), 4.38 (q, *J* = 7.2 Hz, 2*H*), 1.33 (t, *J* = 7.2 Hz, 3*H*). ^{13}C NMR (101 MHz, $CDCl_3$): δ 161.0, 140.8, 136.9, 135.8, 130.2, 129.9, 129.5, 129.3, 128.3, 125.7, 125.2, 61.2, 14.1. MS (ESI, m/z): 316.1 $(M+Na)^+$. All spectral data are in agreement with those previously reported.[17]

Methyl 5-methyl-1-phenyl-1*H*-1,2,3-triazole-4-carboxylate (37): 46 mg, 54%. White solid. R_f: 0.35 (petroleum ether/ethyl acetate 2:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.61-7.56 (m, 3*H*), 7.48-7.45 (m, 2*H*), 4.00 (s, 3*H*), 2.60 (s, 3*H*). ^{13}C NMR (101 MHz, $CDCl_3$): δ 162.1, 138.9, 136.4, 135.3, 130.1, 129.6, 125.3, 52.0, 9.9. MS (ESI, m/z): 240.1 $(M+Na)^+$. All spectral data are in agreement with those previously reported.[18]

(1,5-Diphenyl-1*H*-1,2,3-triazol-4-yl)(phenyl)methanone (38): 120 mg, 92%. White solid. R_f: 0.49 (petroleum ether/ethyl acetate 4:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.29 (d, *J* = 7.2 Hz, 2*H*), 7.60 (t, *J* = 7.2 Hz, 1*H*), 7.50 (t, *J* = 7.6 Hz, 2*H*), 7.43-7.32 (m, 10*H*). ^{13}C NMR (101 MHz, $CDCl_3$): δ 186.7, 143.5, 141.1, 137.1, 135.8, 133.1, 130.7, 130.2, 129.8, 129.5, 129.3, 128.4, 128.2, 126.0, 125.2. MS (ESI, m/z): 348.1 $(M+Na)^+$. All spectral data are in agreement with those previously reported.[17]

1-(5-Methyl-1-phenyl-1*H*-1,2,3-triazol-4-yl)ethanone (39): 59 mg, 73%. White solid. R_f: 0.33 (petroleum ether/ethyl acetate 4:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.62-7.56 (m, 3*H*), 7.47-7.44 (m, 2*H*), 2.77 (s, 3*H*), 2.60 (s, 3*H*). ^{13}C NMR (101 MHz, $CDCl_3$): δ 194.4, 143.7, 137.4, 135.3, 130.1, 129.7, 125.3, 27.9, 10.2. MS (ESI, m/z): 224.1 $(M+Na)^+$. All spectral data are in agreement with those previously reported.[17]

1-(1,5-Diphenyl-1*H*-1,2,3-triazol-4-yl)ethanone (40-A): 75 mg, 71%. White solid. R_f: 0.38 (petroleum ether/ethyl acetate 4:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.42-7.34 (m, 6*H*), 7.29-7.25 (m, 4*H*), 2.77 (s, 3*H*). ^{13}C NMR (101 MHz, $CDCl_3$): δ 192.9, 143.4, 139.0, 135.8, 130.2, 129.9, 129.5, 129.3, 128.4, 125.7, 125.2, 28.4. MS (ESI, m/z): 286.1 $(M+Na)^+$. All spectral data are in agreement with those previously reported.[17]

(5-Methyl-1-phenyl-1*H*-1,2,3-triazol-4-yl)(phenyl)methanone (40-B): 19 mg, 18%. White solid. R_f: 0.47 (petroleum ether/ethyl acetate 4:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.39 (d, *J* = 7.2 Hz, 2*H*), 7.64-7.58 (m, 4*H*), 7.56-7.50 (m, 4*H*), 2.69 (s, 3*H*). ^{13}C NMR (101 MHz, $CDCl_3$): δ 187.6, 143.5, 139.9, 137.4, 135.4, 132.9, 130.6, 130.1, 129.7, 128.3, 125.4, 10.6. IR (film): ν (cm^{-1}) 3061, 2924, 1646, 1500, 1249, 915, 692. MS (ESI, m/z): 286.1 $(M+Na)^+$. HRMS (ESI, m/z) calcd. for $C_{16}H_{13}NaN_3O$ $[M+Na]^+$: 286.0951, found: 286.0949. All spectral data are in agreement with those previously reported.[19]

General Catalysis Procedure B: A 10 mL microwave tube with a magnetic stirrer was dried under high vacuum using a heat gun for at least 10 minutes. After cooling to room temperature the microwave tube was charged under nitrogen atmosphere with the catalyst TBA[Fe] (2 mol %) and the corresponding ketone (1 eq.). Then MeCN (0.4 M) was added via syringe, followed by the corresponding azide (1.2 eq.). The reaction mixture was stirred at 80 °C for 1 hour under microwave conditions (200 W). The reaction mixture was cooled to room temperature, charged with TBA[Fe] (2.5 mol %) and 1,2-DCE (20 mol %) and was stirred at 120 °C for 1 hour. Afterwards, purification via column chromatography on silica gel afforded the desired products.

3,3-Dimethyl-6-(5-(1-methyl-1*H*-imidazol-2-yl)-4-phenyl-1*H*-1,2,3-triazol-1-yl)indoline (43): 38.6 mg, 26%. Light brown solid. **R_f:** 0.16 (petroleum ether/ethyl acetate 1:1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.68-7.62 (m, 2*H*), 7.38-7.30 (m, 3*H*), 7.29 (s, 1*H*), 7.00 (s, 1*H*), 6.97 (d, *J* = 7.9 Hz, 1*H*), 6.76 (s, 1*H*), 6.70 (dd, *J* = 7.8, 1.6 Hz, 1*H*), 3.34 (s, 2*H*), 3.15 (s, 3*H*), 3.10 (bs, 1*H*), 1.30 (s, 6*H*). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 151.3, 147.8, 139.7, 135.9, 135.4, 130.4, 130.3, 128.9, 128.6, 126.8, 123.4, 122.6, 122.4, 113.7, 104.7, 61.9, 41.6, 33.2, 27.7. **IR** (film): ν (cm^{-1}) 3322, 2957, 2864, 1612, 1498, 1464, 1247, 989, 909, 729, 695. **HRMS** (ESI, m/z) calcd. for $C_{22}H_{23}N_6$ $[M+H]^+$: 371.1979, found: 371.1980.

6-(4,5-Diphenyl-1H-1,2,3-triazol-1-yl)-3,3-dimethylindoline (44): 46.3 mg, 32%. Light brown solid. **R_f:** 0.52 (petroleum ether/ethyl acetate 2:1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.64-7.58 (m, 2*H*), 7.42-7.36 (m, 3*H*), 7.34-7.29 (m, 3*H*), 7.27-7.23 (m, 2*H*), 6.94 (d, *J* = 7.8 Hz, 1*H*), 6.62 (d, *J* = 1.7 Hz, 1*H*), 6.55 (dd, *J* = 7.8, 1.9 Hz, 1*H*), 3.82 (bs, 1*H*), 3.36 (s, 2*H*), 1.31 (s, 6*H*). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 151.0, 144.7, 139.4, 136.0, 133.8, 131.2, 130.4, 129.3, 129.0, 128.6, 128.2, 127.9, 127.5, 122.2, 115.7, 106.4, 61.9, 41.6, 27.7. **IR** (film): ν (cm^{-1}) 3337, 2958, 2865, 1613, 1505, 1367, 912, 772, 732, 697. **MS** (GC, m/z): 366 (13), 338 (45), 323 (100), 308 (23), 192 (28), 165 (68), 130 (43). **HRMS** (EI, m/z) calcd. for $C_{24}H_{22}N_4$: 366.1844, found: 366.1832.

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Keywords: Dimroth cyclocondensation • triazoles • cyclocondensation-C-H-amination • homogeneous catalysis • iron

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[12] A coupling of Dimroth-cyclocondensation / Click-chemistry and C-H-amination using either DBU or a Ru-catalyst was not possible. While in the former case amines derived through azide reduction were isolated, in the latter case using internal alkynes no conversion was obtained. See the supporting information for details.

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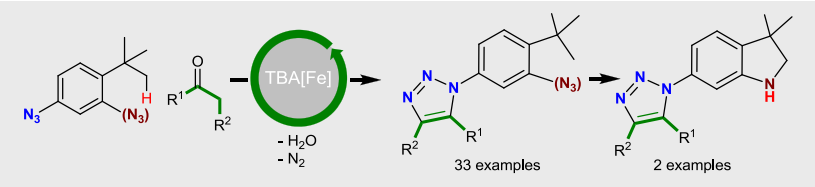

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Nucleophilic Fe-complexes in proton-transfer catalysis: the Fe-catalyzed Dimroth-cyclocondensation

The nucleophilic Fe-complex $Bu_4N[Fe(CO)_3(NO)]$ (TBA[Fe]) catalyzes the Dimroth-cyclocondensation between arylazides and substituted ketones to the corresponding triazols. This process can be coupled to the TBA[Fe]-catalyzed C(sp^3)-H amination and provides a straightforward access to highly decorated *N*-heterocyclic systems.