Palladium-Catalyzed Cross-Coupling of 1,4-Disubstituted 5-Iodo-1,2,3-triazoles with Organotin Reagents

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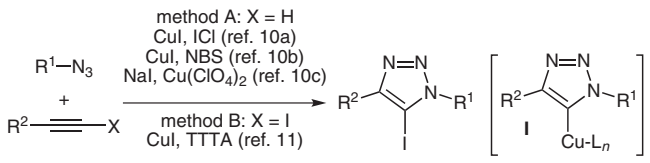
Abstract: In a new synthetic approach for building systems bearing a 1,2,3-triazole moiety, we report here the first Stille cross-coupling reaction of 1,4-disubstituted 5-iodo-1,2,3-triazoles with a range of stannyl derivatives to give the corresponding 5-vinyl-1,2,3-triazoles.

Key words: 1,2,3-triazoles, click chemistry, palladium catalyst, Stille cross-coupling reaction, vinyltin reagents

Although the 1,2,3-triazole core has not been found in natural products to date, this aromatic heterocycle family is very appealing.[1–3] 1,2,3-Triazoles are widely applied in numerous areas of science and they also have industrial uses; they are interesting units for biotechnology. Active 1,2,3-triazoles have been reported in the literature, such as *anti*-HIV[4] or *anti*-microbial agents.[5] Other areas including biological conjugation,[6] catalyst design[7] or materials science and polymer chemistry[2,8] are also impacted.

In this study, we focused on 1,4,5-trisubstituted 1,2,3-triazoles that we planned to access via cross-coupling reactions of 1,4-disubstituted 5-iodo-1,2,3-triazoles. Various strategies have been published for the synthesis of triazoles (Scheme 1). These strategies can be summarized as two general routes based on copper-catalyzed azide–alkyne cycloaddition (CuAAC) reactions.[9] The first route (method A) consists of trapping the copper(I) triazolide intermediate **I** (Scheme 1) with an electrophilic halogenation reagent.[10]



Scheme 1 General methods for the preparation of 5-iodotriazoles

Method B uses a haloalkyne instead of a terminal alkyne. This second route generally allows rapid, and more controlled synthesis of 5-iodotriazoles.[11]

Metal-catalyzed transition sp^2–sp^2 or sp–sp^2 carbon–carbon bond formation has attracted much attention over the last three decades.[12] The palladium–catalyzed cross-coupling reaction (Suzuki–Miyaura, Hiyama, Kharasch, Negishi, Kumada, Liebeskind–Srogl, and Stille) is one of the most efficient methods for the construction of C–C bonds.[13] These reactions are frequently employed in the synthesis of numerous natural products, biologically active molecules, heterocycles, molecular electronics, dendrimers, and conjugated polymers or nanostructures.[14] The reactivity of the halide of 4- or 5-halotriazoles has been widely studied with arylboronic acids, alkenes, and terminal alkynes via Suzuki, Heck, Sonogashira, and even palladium-catalyst-free reactions.[15,16] To the best of our knowledge, Stille-like coupling[17] has been reported on triazol-4-yltin substrates for the synthesis of 1*H*-1,2,4-triazole[18] and triazol-5-yltin[19] substrates to reach 1*H*-1,2,4-triazoles. Other works report the use of the palladium–copper catalyst system with 4- and 5-halotriazole.[20] We report here a convenient two-step route for efficient preparation of 1,4,5-trisubstituted 1,2,3-triazoles from iodotriazole by the Stille cross-coupling reaction.

Azides **1** were generated from organic halides and sodium azide, while the corresponding 5-iodo-1,2,3-triazoles **3a–i** were obtained by method A. Under the optimized click chemistry reaction conditions described by Wu et al.,[10a] azides **1** underwent a copper(I)-catalyzed cycloaddition reaction with various terminal alkynes **2**; the results are reported in Scheme 2. Reaction of ferrocenylacetylene yielded a mixture (70:30) of 5-iodotriazole **3c** and 5*H*-triazole. In the case of ethyl propiolate, a mixture (67:33) of 5-iodo and 4-iodo regioisomers **3g** was obtained. In all other cases, the desired 5-iodo-1,2,3-triazoles were obtained as the exclusive products, in moderate to good yields. Purification of compound **3d′** by silica gel column chromatography led to partial cleavage of the acetal (Scheme 3). Subsequent acidic treatment of the acetal/aldehyde mixture led to 73% overall yield of **3d**. The same treatment with **3a** afforded the triazole **3b**.

To introduce the vinyl group, the reaction was performed with 1.2 equivalents of vinyltin reagent under Stille conditions in the presence of a catalytic amount (6%) of dichlorobis(acetonitrile)palladium(II). Tributyl(vinyl)stannane reagents **4** for use in the Stille cross-coupling of **3** were prepared by transmetalation[21] or by

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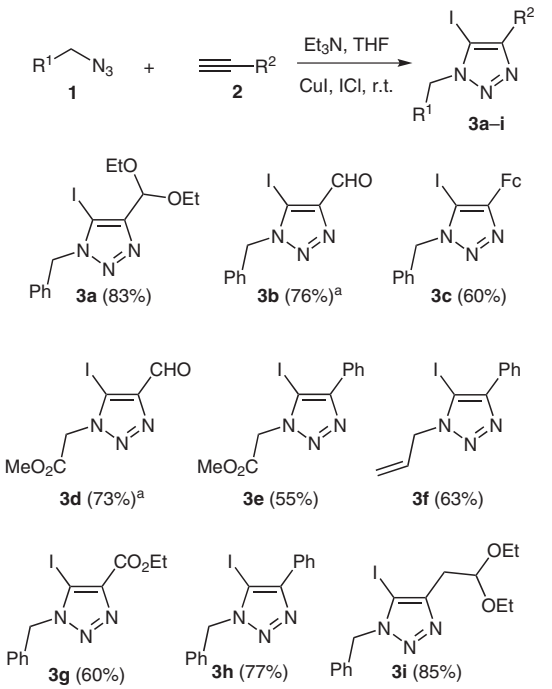
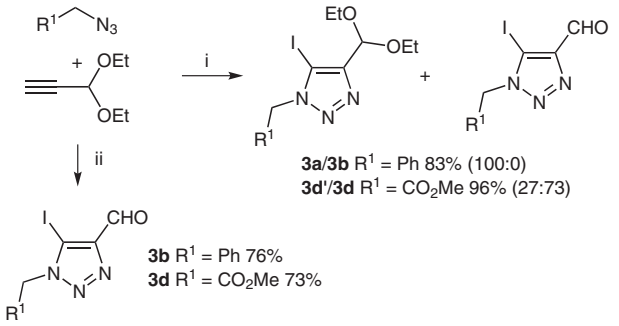


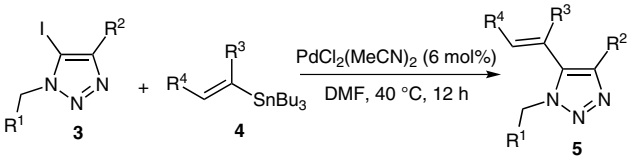
Scheme 2 Synthesis of 5-iodo-1,2,3-triazoles: [a] After treatment with 1 M HCl.



Scheme 3 Reactions with 3,3-diethoxyprop-1-yne. *Reagents and conditions*: (i) CuI (1 equiv), ICl (1 equiv), Et_3N (1.2 equiv), THF, r.t.; (ii) 1. CuI (1 equiv), ICl (1 equiv), Et_3N (1.2 equiv), THF, r.t.; 2. 1 M HCl, THF, 30 min. The proportions of acetal/aldehyde are given in brackets.

hydrostannylation[22] of the corresponding alkynes with tributyltin hydride at 80 °C without any solvent. Compounds **4a** and **4c** were obtained as mixtures of *E*- and *Z*-diastereomers (*E*/*Z* 9:1) and used without separation, because the Stille cross-coupling always yields the thermodynamically more stable *E*-isomers.[23] The results of Stille reaction of 1,4-disubstituted 5-iodo-1,2,3-triazoles **3** are summarized in Table 1. The reaction proceeded with moderate to good yields. In most cases, *E* stereochemistry was observed for the C=C bond in the products (Table 1, entries 1–3, 7; **5a**: $J_{H,H}$ = 19.6 Hz; **5b**: $J_{H,H}$ = 19.4 Hz; **5c**: $J_{H,H}$ = 19.7 Hz; **5g**: $J_{H,H}$ = 19.6 Hz). Purification of the desired compounds was achieved by potassium carbonate–silica column chromatography in order to remove stannic residues.[22]

Table 1 Stille Coupling of 5-Iodo-1,2,3-triazoles



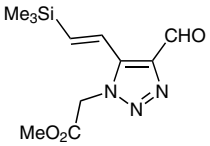
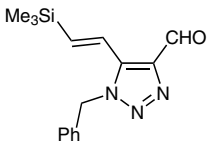
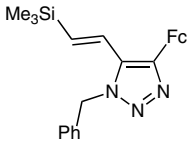
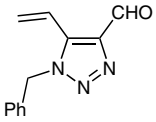
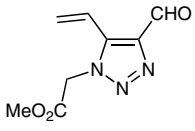
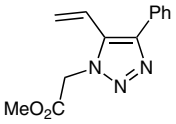
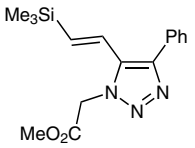
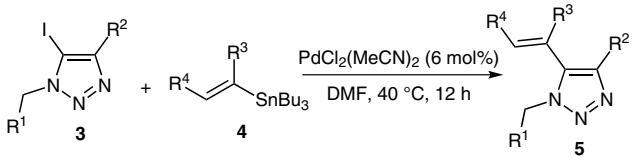
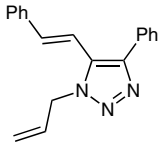
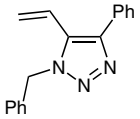
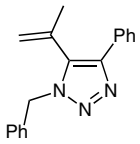
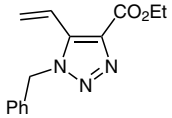
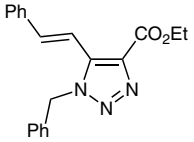
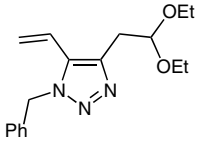
Entry[a]	Vinylstannane	Product **5**	Yield[b] (%)
1	**4a** R^3 = H; R^4 = $SiMe_3$	 **5a**	55
2	**4a**	 **5b**	77
3	**4a**	 **5c**	59
4	**4b** R^3 = R^4 = H	 **5d**	81
5	**4b**	 **5e**	75
6	**4b**	 **5f**	70
7	**4a**	 **5g**	70

Table 1 Stille Coupling of 5-Iodo-1,2,3-triazoles (continued)



Entry[a]	Vinylstannane	Product **5**	Yield[b] (%)
8	**4c** R^3 = H; R^4 = Ph	 **5h**	98
9	**4b**	 **5i**	89
10	**4d** R^3 = Me; R^4 = H	 **5j**	80
11	**4b**	 **5k**	98
12	**4c**	 **5l**	98
13	**4b**	 **5m**	85

[a] Reaction conditions: iodotriazole **3** (1.0 mmol), vinylstannane (1.2 mmol), $PdCl_2(MeCN)_2$ (0.06 mmol), DMF (2 mL), 40 °C, under argon, 12 h.
[b] Isolated yield.

In summary, we have developed an efficient two-step route to 1,4,5-trisubstituted 1,2,3-triazoles using Stille-like methodology. The reaction was easy to implement, as was recovery of the desired compounds. The potential applications of these new compounds are currently under investigation in our laboratory.

Melting points were recorded on a Stuart SMP3 melting point apparatus and are uncorrected. IR spectra were obtained (neat) using a Perkin-Elmer Spectrum-One. NMR spectra were recorded on a Bruker AC 300 MHz spectrometer relative to TMS. HRMS were measured with a Shimadzu QP2010 instrument (ESI mode). Analytical TLC was carried out using pre-coated silica gel 60 F_{254} plates, which were developed using standard visualizing agents: UV light or $KMnO_4$. Purification by flash chromatography was performed using silica gel (230–400 mesh) as the stationary phase and mixtures of pentane and EtOAc as the mobile phase. Alkynes 3,3-diethoxyprop-1-yne and ethynylferrocene were prepared according to literature procedures.[25] Vinyltributyltin was prepared from vinylmagnesium bromide and bis(tributyltin) oxide.[21] Tributyl[2-(trimethylsilyl)vinyl]stannane and tributyl(styryl)stannane were prepared by hydrostannation of (trimethysilyl)acetylene and ethynylbenzene, respectively.[26,23a]

5-Iodo-1,2,3-triazoles; General Procedure
A mixture of azide (10 mmol), terminal alkyne (10 mmol), Et_3N (12 mmol), THF (100 mL), ICl (10 mmol), and CuI (10 mmol) was stirred at r.t. under an argon atmosphere for 60 h. The solvent was removed by distillation under reduced pressure and the crude residue was purified by column chromatography (silica gel, pentane–EtOAc, 100:0 to 80:20).

1-Benzyl-4-(diethoxymethyl)-5-iodo-1*H*-1,2,3-triazole (3a)
Yellowish oil; yield: 3.21 g (83%).

IR (neat): 3065, 3033, 2976, 2929, 2881, 1497, 1456, 1443, 1222, 1121, 1062, 913, 729 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 1.25 (t, *J* = 7.1 Hz, 6 H), 3.62 (dq, *J* = 9.5, 7.1 Hz, 2 H), 3.70 (dq, *J* = 9.5, 7.1 Hz, 2 H), 5.60 (s, 2 H), 5.66 (s, 1 H), 7.24–7.38 (m, 5 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 15.1, 53.9, 61.8, 77.6, 96.5, 127.8, 128.4, 128.8, 134.2, 148.7.

HRMS (ESI): *m/z* $[M + H]^+$ calcd for $C_{14}H_{19}IN_3O_2$: 388.0517; found: 388.0514; *m/z* $[M + Na]^+$ calcd for $C_{14}H_{18}IN_3NaO_2$: 410.0336; found: 410.0334.

1-Benzyl-5-iodo-1*H*-1,2,3-triazole-4-carbaldehyde (3b)
Yellow solid; yield: 2.38 g (76%); mp 122–123 °C.

IR (neat): 2846, 1696, 1494, 1439, 1358, 1240, 1137, 1079, 823, 761, 723 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 5.67 (s, 2 H), 7.27–7.40 (m, 5 H), 10.11 (s, 1 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 54.1, 82.3, 128.0, 128.9, 129.0, 133.3, 147.6, 184.1.

HRMS (ESI): *m/z* $[M + H]^+$ calcd for $C_{10}H_9IN_3O$: 313.9785; found: 313.9782; *m/z* $[M + Na]^+$ calcd for $C_{10}H_8IN_3NaO$: 335.9604; found: 335.9602.

1-Benzyl-4-ferrocenyl-5-iodo-1*H*-1,2,3-triazole (3c)
Orange solid; yield: 2.81 g (60%); mp 160–162 °C (dec.).

IR (neat): 3100, 2924, 1646, 1567, 1495, 1455, 1410, 1221, 1103, 1052, 880, 825, 720 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 4.10 (s, 5 H), 4.33 (t, *J* = 1.8 Hz, 2 H), 5.03 (t, *J* = 1.8 Hz, 2 H), 5.61 (s, 2 H), 7.21–7.38 (m, 5 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 54.0, 67.0, 68.8, 69.5, 70.1, 74.6, 127.5, 128.3, 128.8, 134.5, 150.0.

HRMS (ESI): *m/z* $[M + H]^+$ calcd for $C_{19}H_{17}FeIN_3$: 468.9733; found: 468.9732.

Methyl 2-(4-Formyl-5-iodo-1*H*-1,2,3-triazol-1-yl)acetate (3d)
Yellow solid; yield: 2.15 g (73%); mp 112–113 °C.

IR (neat): 2992, 2956, 2924, 2857, 2781, 1741, 1699, 1504, 1437, 1416, 1372, 1234, 1145, 1087, 972, 835, 750 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.77 (s, 3 H), 5.24 (s, 2 H), 10.04 (s, 1 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 50.8, 53.4, 84.3, 147.6, 165.4, 184.0.

HRMS (ESI): *m/z* [M + H]$^+$ calcd for $C_6H_7IN_3O_3$: 295.9527; found: 295.9526; *m/z* [M + Na]$^+$ calcd for $C_6H_6IN_3NaO_3$: 317.9346; found: 317.9345.

Methyl 2-(5-Iodo-4-phenyl-1*H*-1,2,3-triazol-1-yl)acetate (3e)
White solid; yield: 1.88 g (55%); mp 150–151 °C.

IR (neat): 2961, 1743, 1436, 1422, 1366, 1344, 1238, 1073, 982, 801, 769, 714, 689 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.81 (s, 3 H), 5.27 (s, 2 H), 7.36–7.54 (m, 3 H), 7.96 (d, *J* = 7.2 Hz, 2 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 51.4, 53.1, 77.9, 127.4, 128.6, 128.7, 129.9, 150.1, 166.1.

HRMS (ESI): *m/z* [M + H]$^+$ calcd for $C_{11}H_{11}IN_3O_2$: 343.9891; found: 343.9888; *m/z* [M + Na]$^+$ calcd for $C_{11}H_{10}IN_3NaO_2$: 365.9710; found: 365.9708.

1-Allyl-5-iodo-4-phenyl-1*H*-1,2,3-triazole (3f)
Pale yellow solid; yield: 1.96 g (63%); mp 97–98 °C.

IR (neat): 3079, 3033, 2988, 2931, 1646, 1606, 1578, 1471, 1448, 1345, 1230, 1155, 1066, 986, 915, 763, 692 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.09 (dt, *J* = 5.6, 1.5 Hz, 2 H), 5.22 (br d, *J* = 17.0 Hz, 1 H), 5.35 (br d, *J* = 10.3 Hz, 1 H), 6.01 (ddt, *J* = 17.0, 10.3, 5.6 Hz, 1 H), 7.36–7.51 (m, 3 H), 7.95 (m, 2 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 53.2, 76.5, 119.9, 127.5, 128.6, 128.7, 130.3, 130.8, 150.0.

HRMS (ESI): *m/z* [M + H]$^+$ calcd for $C_{11}H_{11}IN_3$: 311.9992; found: 311.9985.

Ethyl 1-Benzyl-5-iodo-1*H*-1,2,3-triazole-4-carboxylate (3g)[27]
[CAS Reg. No. 1262782-91-1]

Yellow solid; yield: 2.14 g (60%).

1-Benzyl-5-iodo-4-phenyl-1*H*-1,2,3-triazole (3h)[27]
[CAS Reg. No. 860002-66-0]

Yellow solid; yield: 2.78 g (77%).

1-Benzyl-4-(2,2-diethoxyethyl)-5-iodo-1*H*-1,2,3-triazole (3i)
Orange solid; yield: 3.41 g (85%); mp 45–46 °C.

IR (neat): 3086, 3060, 3014, 2975, 2925, 2873, 1604, 1513, 1435, 1352, 1214, 1131, 1025, 898, 803, 727, 706 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.14 (t, *J* = 7.1 Hz, 6 H), 3.01 (d, *J* = 5.9 Hz, 2 H), 3.48 (dq, *J* = 9.3, 7.1 Hz, 2 H), 3.72 (dq, *J* = 9.3, 7.1 Hz, 2 H), 4.88 (t, *J* = 5.9 Hz, 1 H), 5.60 (s, 2 H), 7.22–7.26 (m, 2 H), 7.30–7.38 (m, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 5.3, 31.7, 54.2, 62.4, 80.4, 102.1, 127.6, 128.4, 128.8, 134.5, 148.4.

HRMS (ESI): *m/z* [M + H]$^+$ calcd for $C_{15}H_{21}IN_3O_2$: 402.0678; found: 402.0673.

Stille Reaction; General Method
A mixture of triazole (1.0 mmol), vinylstannane (1.2 mmol), and $PdCl_2(MeCN)_2$ (0.06 mmol) in DMF (2 mL) was stirred overnight at 40 °C under an argon atmosphere for 12 h. The mixture was poured into EtOAc (10 mL), filtered, washed with sat. NH_4Cl (3 × 10 mL) and brine (10 mL), dried ($MgSO_4$), and concentrated under reduced pressure. The crude product was purified by column chromatography (10% w/w anhyd K_2CO_3–silica gel, pentane–EtOAc, 100:0 to 60:40).

Methyl (*E*)-2-{4-Formyl-5-[2-(trimethylsilyl)vinyl]-1*H*-1,2,3-triazol-1-yl}acetate (5a)
Brown oil; yield: 147 mg (55%).

IR (neat): 2957, 2841, 1755, 1694, 1534, 1439, 1367, 1249, 1216, 988, 841, 724 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.16 (s, 9 H), 3.79 (s, 3 H), 5.22 (s, 2 H), 6.83 (d, *J* = 19.6 Hz, 1 H), 7.13 (d, *J* = 19.6 Hz, 1 H), 10.18 (s, 1 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = –1.8, 49.7, 53.3, 124.8, 138.6, 143.5, 146.6, 166.0, 185.3.

HRMS (ESI): *m/z* [M + H]$^+$ calcd for $C_{11}H_{18}N_3O_3Si$: 268.1112; found: 268.1111; *m/z* [M + Na]$^+$ calcd for $C_{11}H_{17}N_3NaO_3Si$: 290.0931; found: 290.0930.

(*E*)-1-Benzyl-5-[2-(trimethylsilyl)vinyl]-1*H*-1,2,3-triazole-4-carbaldehyde (5b)
Colorless oil; yield: 220 mg (77%).

IR (neat): 3034, 2955, 2839, 1694, 1533, 1467, 1430, 1248, 989, 840, 712, 692 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.08 (s, 9 H), 5.61 (s, 2 H), 6.76 (d, *J* = 19.4 Hz, 1 H), 7.15 (m, 2 H), 7.25 (d, *J* = 19.4 Hz, 1 H), 7.28–7.36 (m, 3 H), 10.17 (s, 1 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = –1.9, 52.7, 124.8, 127.2, 128.7, 129.1, 134.1, 138.1, 143.9, 146.4, 185.3.

HRMS (ESI): *m/z* [M + H]$^+$ calcd for $C_{15}H_{20}N_3OSi$: 286.1370; found: 286.1367.

(*E*)-1-Benzyl-4-ferrocenyl-5-[2-(trimethylsilyl)vinyl]-1*H*-1,2,3-triazole (5c)
Red oil; yield: 260 mg (59%).

IR (neat): 3085, 2952, 1655, 1455, 1243, 990, 841, 808, 714, 691 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.12 (s, 9 H), 4.10 (s, 5 H), 4.30 (t, *J* = 1.9 Hz, 2 H), 4.72 (t, *J* = 1.9 Hz, 2 H), 5.56 (s, 2 H), 6.34 (d, *J* = 19.7 Hz, 1 H), 6.75 (d, *J* = 19.7 Hz, 1 H), 7.15 (m, 2 H), 7.27–7.37 (m, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = –1.6, 52.5, 67.4, 68.7, 69.4, 76.0, 127.1, 128.1, 128.2, 128.9, 131.0, 135.4, 139.8, 143.9.

HRMS (ESI): *m/z* [M + H]$^+$ calcd for $C_{24}H_{28}FeN_3Si$: 442.1390; found: 442.1385; *m/z* [M + Na]$^+$ calcd for $C_{24}H_{27}FeN_3NaSi$: 464.1216; found: 464.1218.

1-Benzyl-5-vinyl-1*H*-1,2,3-triazole-4-carbaldehyde (5d)
Yellow solid; yield: 173 mg (81%); mp 50–51 °C.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.65 (s, 2 H), 5.82 (dd, *J* = 11.3, 1.4 Hz, 1 H), 6.59 (dd, *J* = 17.6, 1.4 Hz, 1 H), 6.72 (dd, *J* = 17.6, 11.3 Hz, 1 H), 7.17 (m, 2 H), 7.26–7.37 (m, 3 H), 10.19 (s, 1 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 52.0, 119.0, 126.7, 127.2, 128.4, 128.9, 133.8, 143.7, 185.1.

HRMS (ESI): *m/z* [M + H]$^+$ calcd for $C_{12}H_{12}N_3O$: 214.0975; found: 214.0972; *m/z* [M + Na]$^+$ calcd for $C_{12}H_{11}N_3NaO$: 236.0794; found: 236.0791.

Methyl 2-(4-Formyl-5-vinyl-1*H*-1,2,3-triazol-1-yl)acetate (5e)
Yellowish oil; yield: 146 mg (75%).

IR (neat): 2958, 2921, 2852, 1745, 1691, 1544, 1459, 1364, 1218, 987, 835 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.69 (s, 3 H), 5.17 (s, 2 H), 5.80 (dd, *J* = 11.4, 1.1 Hz, 1 H), 6.43 (dd, *J* = 17.6, 1.1 Hz, 1 H), 6.59 (dd, *J* = 17.6, 11.4 Hz, 1 H), 10.06 (s, 1 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 49.5, 53.3, 119.2, 127.6, 138.1, 143.6, 166.2, 185.3.

HRMS (ESI): *m/z* [M + H]$^+$ calcd for $C_8H_{10}N_3O_3$: 196.0717; found: 196.0717; *m/z* [M + Na]$^+$ calcd for $C_8H_9N_3NaO_3$: 218.0536; found: 218.0534.

Methyl 2-(4-Phenyl-5-vinyl-1*H*-1,2,3-triazol-1-yl)acetate (5f)
Colorless oil; yield: 170 mg (70%).

IR (neat): 2962, 1750, 1438, 1352, 1219, 992, 818, 779, 717, 696 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.75 (s, 3 H), 5.16 (s, 2 H), 5.58 (dd, *J* = 17.9, 0.7 Hz, 1 H), 5.63 (dd, *J* = 11.7, 0.7 Hz, 1 H), 6.60 (dd, *J* = 17.9, 11.7 Hz, 1 H), 7.28–7.43 (m, 3 H), 7.72 (m, 2 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 49.5, 53.0, 122.1, 123.3, 127.6, 128.2, 128.6, 130.9, 131.6, 144.8, 167.0.

HRMS (ESI): *m/z* [M + H]$^+$ calcd for $C_{13}H_{14}N_3O_2$: 244.1081; found: 244.1077; *m/z* [M + Na]$^+$ calcd for $C_{13}H_{13}N_3NaO_2$: 266.0900; found: 266.0897.

Methyl (*E*)-2-{4-Phenyl-5-[2-(trimethylsilyl)vinyl]-1*H*-1,2,3-triazol-1-yl}acetate (5g)
Colorless oil; yield: 220 mg (70%).

IR (neat): 2954, 1754, 1606, 1439, 1354, 1248, 1215, 994, 864, 842, 772, 697 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.15 (s, 9 H), 3.78 (s, 3 H), 5.20 (s, 2 H), 6.36 (d, *J* = 19.7 Hz, 1 H), 6.77 (d, *J* = 19.7 Hz, 1 H), 7.34 (m, 1 H), 7.42 (m, 2 H), 7.74 (m, 2 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = –1.7, 49.7, 52.9, 127.6, 128.0, 128.1, 128.6, 131.1, 132.6, 141.2, 144.6, 166.9.

HRMS (ESI): *m/z* [M + H]$^+$ calcd for $C_{16}H_{22}N_3O_2Si$: 316.1476; found: 316.1474; *m/z* [M + Na]$^+$ calcd for $C_{16}H_{21}N_3NaO_2Si$: 338.1295; found: 338.1292.

(*E*)-1-Allyl-4-phenyl-5-styryl-1*H*-1,2,3-triazole (5h)
Yellow paste; yield: 281 mg (98%).

IR (neat): 3026, 2935, 1644, 1603, 1485, 1440, 1358, 1238, 1072, 975, 915, 771, 756, 718, 702, 691 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.11 (dt, *J* = 5.3, 1.7 Hz, 2 H), 5.21 (br d, *J* = 17.1 Hz, 1 H), 5.38 (br d, *J* = 10.4 Hz, 1 H), 6.12 (ddt, *J* = 17.1, 10.4, 5.3 Hz, 1 H), 6.98 (d, *J* = 16.7 Hz, 1 H), 7.01 (d, *J* = 16.7 Hz, 1 H), 7.31–7.49 (m, 8 H), 7.80 (m, 2 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 51.1, 112.6, 118.8, 126.8, 127.9, 128.2, 128.8, 129.0, 129.1, 131.0, 131.5, 132.0, 135.9, 136.3, 145.2.

HRMS (ESI): *m/z* [M + H]$^+$ calcd for $C_{19}H_{18}N_3$: 276.1495; found: 276.1489.

1-Benzyl-4-phenyl-5-vinyl-1*H*-1,2,3-triazole (5i)
Orange liquid; yield: 232 mg (89%).

IR (neat): 3062, 3032, 1687, 1606, 1496, 1455, 1350, 1239, 1073, 993, 919, 778, 732, 694 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.56 (dd, *J* = 11.6, 0.9 Hz, 1 H), 5.57 (dd, *J* = 18.0, 0.9 Hz, 1 H), 5.62 (s, 2 H), 6.59 (dd, *J* = 18.0, 11.6 Hz, 1 H), 7.20 (m, 2 H), 7.30–7.47 (m, 6 H), 7.76 (m, 2 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 52.3, 122.1, 123.0, 127.0, 127.8, 128.2, 128.3, 128.7, 129.1, 131.0, 131.3, 135.3, 145.3.

HRMS (ESI): *m/z* [M + H]$^+$ calcd for $C_{17}H_{16}N_3$: 262.1339; found: 262.1333.

1-Benzyl-4-phenyl-5-(prop-1-en-2-yl)-1*H*-1,2,3-triazole (5j)
Orange solid; yield: 220 mg (80%); mp 63–64 °C.

IR (neat): 2988, 2957, 2903, 1712, 1641, 1576, 1543, 1446, 1423, 1337, 1248, 1163, 1053, 976, 728, 691 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.72 (dd, *J* = 1.4, 1.0 Hz, 3 H), 5.18 (m, 1 H), 5.54 (s, 2 H), 5.56 (m, 1 H), 7.22 (m, 2 H), 7.28–7.35 (m, 4 H), 7.40 (m, 2 H), 7.84 (m, 2 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 22.4, 51.9, 122.2, 126.5, 127.6, 127.9, 128.2, 128.7, 128.9, 131.2, 133.7, 134.7, 135.7, 143.6.

HRMS (ESI): *m/z* [M + H]$^+$ calcd for $C_{18}H_{18}N_3$: 288.1495; found: 288.1488.

Ethyl 1-Benzyl-5-vinyl-1*H*-1,2,3-triazole-4-carboxylate (5k)
Orange oil; yield: 252 mg (98%).

IR (neat): 2982, 1713, 1540, 1456, 1341, 1240, 1175, 1058, 1026, 944, 849, 731, 695 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.42 (t, *J* = 7.1 Hz, 3 H), 4.43 (q, *J* = 7.1 Hz, 2 H), 5.64 (s, 2 H), 5.74 (dd, *J* = 12.0, 0.8 Hz, 1 H), 5.95 (dd, *J* = 18.0, 0.8 Hz, 1 H), 6.84 (dd, *J* = 18.0, 12.0 Hz, 1 H), 7.12 (m, 2 H), 7.29–7.38 (m, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.4, 52.6, 61.4, 120.7, 125.6, 126.9, 128.6, 129.2, 134.5, 136.8, 138.0, 161.5.

HRMS (ESI): *m/z* [M + H]$^+$ calcd for $C_{14}H_{16}N_3O_2$: 258.1237; found: 258.1232.

Ethyl (*E*)-1-Benzyl-5-styryl-1*H*-1,2,3-triazole-4-carboxylate (5l)
Brown paste; yield: 327 mg (98%).

IR (neat): 2986, 2902, 1711, 1542, 1444, 1248, 1163, 1111, 1052, 976, 753, 727, 691 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.43 (t, *J* = 7.1 Hz, 3 H), 4.44 (q, *J* = 7.1 Hz, 2 H), 5.70 (s, 2 H), 7.13–7.40 (m, 12 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.4, 52.8, 61.3, 111.1, 126.9, 127.2, 128.6, 128.9, 129.3, 129.5, 134.7, 135.6, 136.6, 138.3, 139.4, 161.7.

HRMS (ESI): *m/z* [M + H]$^+$ calcd for $C_{20}H_{20}N_3O_2$: 334.1550; found: 334.1544.

1-Benzyl-4-(2,2-diethoxyethyl)-5-vinyl-1*H*-1,2,3-triazole (5m)
Yellow oil; yield: 256 mg (85%).

IR (neat): 3064, 3033, 2975, 2931, 2879, 1633, 1456, 1373, 1224, 1058, 926, 837, 729, 695 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.14 (t, *J* = 7.0 Hz, 6 H), 3.08 (d, *J* = 5.8 Hz, 2 H), 3.49 (dq, *J* = 9.3, 7.0 Hz, 2 H), 3.73 (dq, *J* = 9.3, 7.0 Hz, 2 H), 4.90 (t, *J* = 5.8 Hz, 1 H), 5.48 (dd, *J* = 11.7, 1.0 Hz, 1 H), 5.55 (s, 2 H), 5.82 (dd, *J* = 17.8, 1.0 Hz, 1 H), 6.46 (dd, *J* = 17.8, 11.7 Hz, 1 H), 7.10–7.16 (m, 2 H), 7.27–7.37 (m, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 15.3, 31.6, 52.2, 62.9, 103.1, 121.2, 121.8, 126.9, 128.2, 128.9, 132.7, 135.2, 141.7.

HRMS (ESI): *m/z* [M + H]$^+$ calcd for $C_{17}H_{24}N_3O_2$: 302.1869; found: 302.1873.

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Supporting Information for this article is available online at http://www.thieme-connect.com/ejournals/toc/synthesis. Included are copies of ^{1}H and ^{13}C NMR spectra of compounds **3** and **5**.

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