SUPPORTING INFORMATION

Synthesis of 4-Aryl-1,2,3-1*H*-triazoles through TBAF-Catalyzed [3+2] Cycloaddition of 2-Aryl-1-Nitroethenes with $TMSN_3$ under Solvent-Free Condition

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CONTENTS

Experimental Section

CAUTION: *Azides can be very explosive compounds and should be handled with great care. During our study we encountered no problems.*[1] All chemicals were purchased and used without any further purification. GC-MS analyses were carried out with 70 eV electron energy. All ^{1}H NMR and ^{13}C NMR spectra were recorded at 200 MHz or 400 MHz, and at 50.3 or 100.6 MHz respectively, using a convenient deuterated solvent (reported in the characterization charts) and the residual peak as internal standard, or TMS in the case of $CDCl_3$. C-4 and C-5 signals of triazoles **2** were often too broad to be detected and in such cases ^{13}C NMR analysis was in performed in CD_3OD by adding trifluoroacetic acid. All melting points are uncorrected. Thin Layer Cromatography analyses were performed on silica gel on aluminum plates and UV and/or $KMnO_4$ were used as revealing agents. Column chromatography were performed by using silica gel 230-400 mesh and eluting as reported in the following characterization charts. Nitroethenes **1** were prepared according to reported procedure.[2] Triazole **2h** is a known compound,[3] triazoles **2a**-**d**,[4] **2f**-**g**,[4] **2j**,[5] have been already prepared but spectroscopic data have not been reported, triazoles **2e**, **2i**, **2k-p** are new compounds. Characterizion charts (^{1}H NMR, ^{13}C NMR, IR, R_f) for all triazoles with exception of **2h** are reported below.

1 For a discussion on the hazards associated with azides, see: Prudent Practice for Handling Hazardous Chemicals in Laboratories; National Academic Press: Washington, DC, **1983**, 87-88; for human toxicity, see: *The Merck Index, 12th ed.*; Merck & Co.: Rahway, NJ, **1996**; pp 4818 and 8726

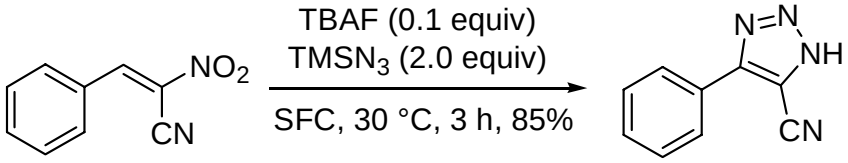
2 (a) Lehnert, W. *Tetrahedron* **1972**, *28*, 663-666. (b) Amantini, D.; Fringuelli, F.; Piermatti, O.; Pizzo, F.; Vaccaro, L. *Green Chem.* **2001**, *3*, 229-232.

3 Haryu, K.; Vahermo, M.; Mutikainen, I.; Yli-Kauhauloma, J. *J. Comb. Chem.* **2003**, *5*, 826-833.

4 Beck, G.; Günther, D. *Che. Ber.* **1973**, *106*, 2758-2766.

5 Tanaka, Y.; Miller, S. I. *J. Org. Chem.* **1972**, *37*, 3370-3372.

Chem. Name	4-phenyl-1*H*-1,2,3-triazole-5-carbonitrile (2a)



1a **2a**

Method: In a screw capped vial equipped with a magnetic stirrer, TBAF·$3H_2O$ (0.064 g, 0.2 mmol), (*E*)-1-cyano-2-phenyl-1-nitroethene (**1a**) (0. 348 g, 2.0 mmol) and $TMSN_3$ (0.460 g, 4.0 mmol) were consecutively added and the resulting mixture was left under vigorous stirring at 30 °C for 3 h. The crude reaction mixture was charged on a silica gel column chromatography (Etp/AcOEt 8/2, gradient; silica/sample: 15:1). Pure 4-phenyl-1*H*-1,2,3-triazole-5-carbonitrile (**2a**) was isolated as a white solid in 85% yield (0.289 g).

Mol Formula	$C_9H_6N_4$	m.p.	185/186 (AcOEt)
Tlc - R_f (eluent)	0.20 (Etp/AcOEt/AcOH), 10:17:3)		

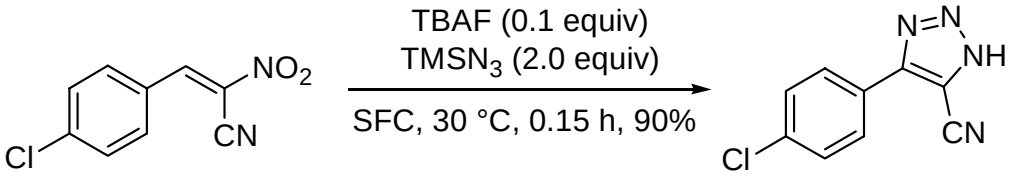
FT-IR (KBr, cm^{-1}): 687 (s), 775 (s), 1273 (s), 1497 (m), 2241 (m), 2809 (m), 2845 (m), 2906 (m), 3076 (m), 3104 (m)

Elemental Analysis: C, 63.52; H, 3.55; N, 32.92. Found: C, 63.38; H. 3.11; N, 32.80

^{1}H NMR 200 MHz CD_3OD	δ value	No. H	Mult.	j value/Hz
	7.40-7.70	2	*m*	
	7.90-7.96	3	*m*	

^{13}C NMR (50.3 MHz, CD_3OD) δ : 114.0, 117.9, 127.0, 127.7, 130.3, 132.2, 148.4

Chem. Name	4-(4'-chlorophenyl)-1*H*-1,2,3-triazole-5-carbonitrile (2b)



1b **2b**

Method: In a screw capped vial equipped with a magnetic stirrer, TBAF·$3H_2O$ (0.064 g, 0.2 mmol), (*E*)-1-cyano-2-(4'-chlorophenyl)-1-nitroethene (**1b**) (0.416 g, 2.0 mmol) and $TMSN_3$ (0.460 g, 4.0 mmol) were consecutively added and the resulting mixture was left under vigorous stirring at 30 °C for 0.15 h. The crude reaction mixture was charged on a silica gel column chromatography (Etp/AcOEt 8/2, gradient; silica/sample: 15:1). Pure 4-(4'-chlorophenyl)-1*H*-1,2,3-triazole-5-carbonitrile (**2b**) was isolated as a white solid in 90% yield (0.367 g).

Mol Formula	$C_9H_5ClN_4$	m.p.	180/182 (AcOEt)
Tlc - R_f (eluent)	0.15 (Etp/AcOEt/AcOH), 10:17:3)		

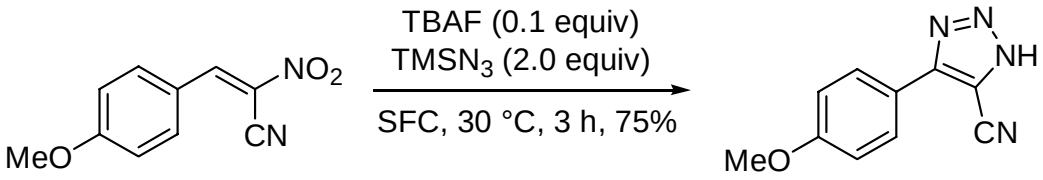
FT-IR (KBr, cm^{-1}): 831 (s), 991 (s), 1094 (s), 1155 (s), 1460 (m), 2256 (m), 3218 (s)

Elemental Analysis: C, 52.83; H, 2.46; N, 27.38. Found: C, 52.88; H. 2.41; N, 27.22

^{1}H NMR 200 MHz DMSO-d6	δ value	No. H	Mult.	j value/Hz
	7.68	2	*d*	*J* = 7.6 Hz
	7.89	2	*d*	*J* = 7.6 Hz

^{13}C NMR (50.3 MHz, DMSO-d6) δ : 113.2, 116.4, 125.0, 128.5, 129.6, 135.2, 145.9

Chem. Name	**4-(4'-methoxyphenyl)-1*H*-1,2,3-triazole-5-carbonitrile (2c)**



1c **2c**

Method: In a screw capped vial equipped with a magnetic stirrer, TBAF·$3H_2O$ (0.064 g, 0.2 mmol), (*E*)-1-cyano-2-(4'-methoxyphenyl)-1-nitroethene (**1c**) (0.408 g, 2.0 mmol) and $TMSN_3$ (0.460 g, 4.0 mmol) were consecutively added and the resulting mixture was left under vigorous stirring at 30 °C for 3 h. The crude reaction mixture was charged on a silica gel column chromatography (Etp/AcOEt 8/2, gradient; silica/sample: 15:1). Pure 4-(4'-methoxyphenyl)-1*H*-1,2,3-triazole-5-carbonitrile (**2c**) was isolated as a white solid in 75% yield (0.300 g).

Mol Formula	$C_{10}H_8N_4O$	**m.p.**	197/199 (AcOEt)
Tlc - R_f (eluent)	0.14 (Etp/AcOEt/AcOH), 10:17:3)		

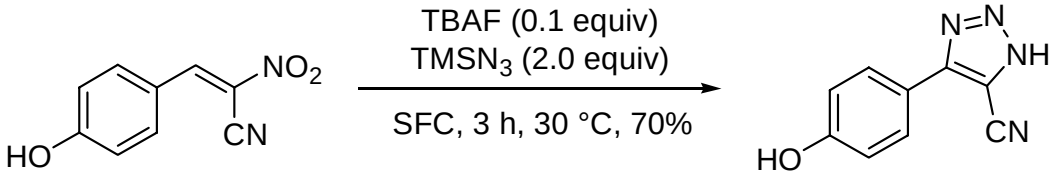
FT-IR (KBr, cm^{-1}): 800 (m), 840 (s), 1264 (s), 1513 (m), 1614 (s), 2237 (m), 2848 (s), 2919 (s)

Elemental Analysis: C, 59.99; H, 4.03; N, 27.99. Found: C, 59.90; H. 4.11; N, 27.85

^{1}H NMR 400 MHz CD_3OD	**δ value**	**No. H**	**Mult.**		**δ value**	**No. H**	**Mult.**	***j value/Hz***
	3.84	3	*s*		7.08	2	*d*	*J* = 8.9 Hz
	4.99	1	*bs (NH)*		7.83	2	*d*	*J* = 8.9 Hz

^{13}C NMR (100.6 MHz, CD_3OD) δ : 55.9, 111.8, 114.2, 115.8, 177.2, 129.4, 160.1, 163.0

Chem. Name	**4-(4'-hydroxyphenyl)-1*H*-1,2,3-triazole-5-carbonitrile (2d)**



1d **2d**

Method: In a screw capped vial equipped with a magnetic stirrer, TBAF·$3H_2O$ (0.064 g, 0.2 mmol), (*E*)-1-cyano-2-(4'-hydroxyphenyl)-1-nitroethene (**1d**) (0.380 g, 2.0 mmol) and $TMSN_3$ (0.460 g, 4.0 mmol) were consequtively added and the resulting mixture was left under vigorous stirring at 30 °C for 3 h. The crude reaction mixture was charged on a silica gel column chromatography (Etp/AcOEt 8/2, gradient; silica/sample: 15:1). Pure 5-(4'-hydroxyphenyl)-1*H*-1,2,3-triazole-5-carbonitrile (**2d**) was isolated as a white solid in 70% yield (0.260 g).

Mol Formula	$C_9H_6N_4O$	**m.p.**	191/194 (AcOEt)

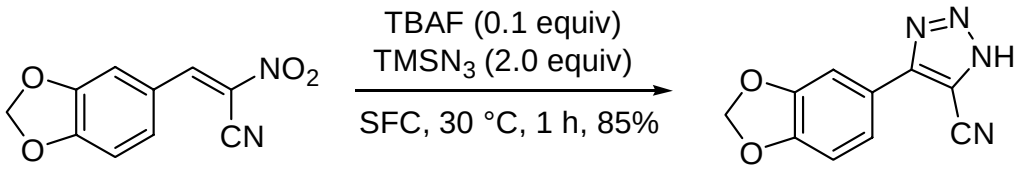
FT-IR (Nujol, cm^{-1}): 723 (w), 835 (w), 1160 (w), 1280 (w), 1377 (s), 1477 (s), 1847 (s), 2958 (s)

Elemental Analysis: C, 58.06; H, 3.25; N, 30.09. Found: C, 52.88; H. 3.21; N, 30.11

^{1}H NMR 400 MHz CD_3OD	**δ value**	**No. H**	**Mult.**	**j value/Hz**
	5.21	2	*bs*	
	6.91	2	*d*	*J* = 8.8 Hz
	7.71	2	*d*	*J* = 8.8 Hz

^{13}C NMR (100.6 MHz, CD_3OD) δ : 114.3, 116.9, 117.2, 117.9, 129.5, 158.8, 161.1

Chem. Name	**4-(1',3'-benzodioxol-5-yl)-1*H*-1,2,3-triazole-5-carbonitrile (2e)**



1e **2e**

Method: In a screw capped vial equipped with a magnetic stirrer, TBAF·$3H_2O$ (0.064 g, 0.2 mmol), (*E*)-1-cyano-2-(1',3'-benzodioxol-5'-yl)-1-nitroethene (**1e**) (0.436 g, 2.0 mmol) and $TMSN_3$ (0.460 g, 4.0 mmol) were consecutively added and the resulting mixture was left under vigorous stirring at 30 °C for 1 h. The crude reaction mixture was charged on a silica gel column chromatography (Etp/AcOEt 8/2, gradient; silica/sample: 15:1). Pure 4-(1',3'-benzodioxol-5'-yl)-1*H*-1,2,3-triazole-5-carbonitrile (**2c**) was isolated as a white solid in 85% yield (0.357 g).

Mol Formula	$C_{10}H_6N_4O_2$	**m.p.**	189/190 (Etp/AcOEt 1/1)
Tlc - R_f (eluent)	0.26 (Etp/AcOEt/MeOH AcOH), 10:17:2:1)		

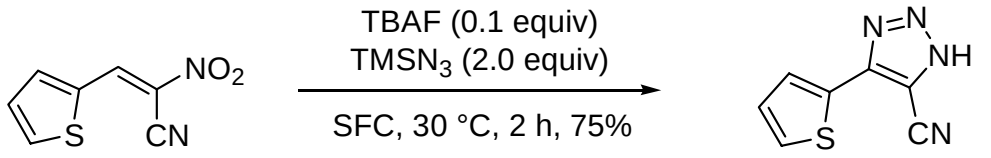
FT-IR ($CHCl_3$, cm^{-1}): 817 (m), 888 (m), 394 (s), 985 (m), 1111 (w), 2245 (m), 2902 (s)

Elemental Analysis: C, 56.08; H, 2.82; N, 26.16. Found: C, 56.00; H. 2.91; N, 26.03.

^{1}H NMR 400 MHz CD_3OD	**δ value**	**No. H**	**Mult.**		**δ value**	**No. H**	**Mult.**	***j value/Hz***
	4.93	1	*bs (NH)*		6.92	1	*d*	*J* = 8.2 Hz
	6.02	2	*s*		7.29	1	*d*	*J* = 1.7 Hz
					7.40	1	*dd*	*J* = 1.7, 8.2 Hz

^{13}C NMR (100.6 MHz, CD_3OD) δ: 103.3, 107.7, 109.9, 111.8, 114.1, 114.6, 117.4, 122.4, 150.0, 150.9

Chem. Name	**4-(thien-2'-yl)-1*H*-1,2,3-triazole-1-carbonitrile (2f)**



1f **2f**

Method: In a screw capped vial equipped with a magnetic stirrer, TBAF·$3H_2O$ (0.064 g, 0.2 mmol), (*E*)-1-cyano-2-(thien-2'-yl)-nitroethene (**1f**) (0.360 g, 2.0 mmol) and $TMSN_3$ (0.460 g, 4.0 mmol) were consequtively added and the resulting mixture was left under vigorous stirring at 30 °C for 2 h. The crude reaction mixture was charged on a silica gel column chromatography (Etp/AcOEt 8/2, gradient; silica/sample: 15:1). Pure 4-(thien-2'-yl)-1*H*-1,2,3-triazole-5-carbonitrile (**2f**) was isolated as a white solid in 75% yield (0.264 g).

Mol Formula	$C_7H_4N_4S$	**m.p.**	182/183 (AcOEt)

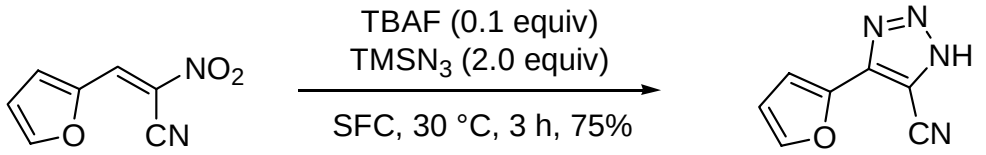
FT-IR ($CHCl_3$, cm^{-1}): 853 (w), 960 (m), 963 (m), 1110 (w), 1157 (w), 1602 (m), 2246 (m), 2928 (s)

Elemental Analysis: C, 58.06; H, 3.25; N, 31.80. Found: C, 58.08; H. 3.41; N, 31.73

^{1}H NMR 200 MHz CD_3OD	**δ value**	**No. H**	**Mult.**	**j value/Hz**
	4.96	1	*bs*	
	7.21	1	*dd*	*J* = 3.6, 5.0 Hz
	7.64	1	*dd*	*J* = 1.1, 5.0 Hz
	7.75	1	*dd*	*J* = 1.1, 3.6 Hz

^{13}C NMR (100.6 MHz, CD_3OD) δ : 112.9, 115.4,127.5, 127.9, 128.6, 129.5, 142.8

Chem. Name	**4-(furan-2'-yl)-1*H*-1,2,3-triazole-1-carbonitrile (2g)**



1g **2g**

Method: In a screw capped vial equipped with a magnetic stirrer, TBAF·$3H_2O$ (0.064 g, 0.2 mmol), (*E*)-1-cyano-2-(furan-2'-yl)-1-nitroethene (**1g**) (0.328 g, 2.0 mmol) and $TMSN_3$ (0.460 g, 4.0 mmol) were consecutively added and the resulting mixture was left under vigorous stirring at 30 °C for 3 h. The crude reaction mixture was charged on a silica gel column chromatography (Etp/AcOEt 8/2, gradient; silica/sample: 15:1). Pure 4-(furan-2'-yl)-1*H*-1,2,3-triazole-5-carbonitrile (**2g**) was isolated as a white solid in 75% yield (0.240 g).

Mol Formula	$C_7H_4N_4O$	**m.p.**	184/186 (AcOEt)

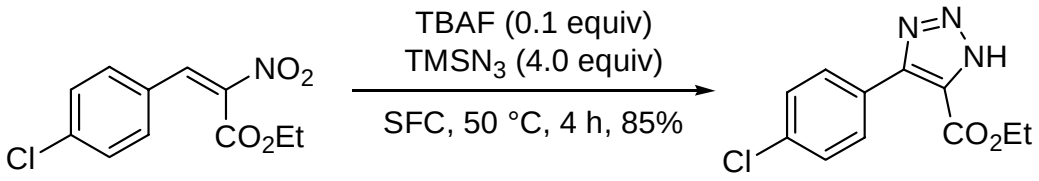
FT-IR ($CHCl_3$, cm^{-1}): 851 (w), 908 (s), 983 (m), 1013 (w), 1157 (w), 1602 (m), 2247 (m), 2857 (s), 3136 (s)

Elemental Analysis: C, 52.50; H, 2.52; N, 34.99. Found: C, 52.58; H. 2.41; N, 34.87.

^{1}H NMR 200 MHz CD_3OD	**δ value**	**No. H**	**Mult.**	**j value/Hz**
	4.95	1	*bs*	
	6.67	1	*dd*	*J* = 1.8, 3.5 Hz
	7.08	1	*d*	*J* = 3.5 Hz
	7.76	1	*d*	*J* = 1.1 Hz

^{13}C NMR (50.3 MHz, CD_3OD) δ : 112.2, 113.0, 113.1, 116.6, 140.3, 142.9, 146.0

Chem. Name	**Ethyl 4-(4'-chlorophenyl)-1*H*-1,2,3-triazole-5-carboxylate (2i)**



1i **2i**

Method: In a screw capped vial equipped with a magnetic stirrer, TBAF·$3H_2O$ (0.064 g, 0.2 mmol), (*E*)-1-carboethoxy-2-(4'-chlorophenyl)-1-nitroethene (**1i**) (0.510 g, 2.0 mmol) and $TMSN_3$ (0.920 g, 8.0 mmol) were consecutively added and the resulting mixture was warmed to 50 °C and left under vigorous stirring for 4 h. The crude reaction mixture was charged on a silica gel column chromatography (Etp/AcOEt 8/2, gradient; silica/sample: 15:1). Pure ethyl 4-(4'-chlorophenyl)-1*H*-1,2,3-triazole-5-carboxylate(**2i**) was isolated as a white solid in 85% yield (0.427 g).

Mol Formula	$C_{11}H_{10}ClN_3O_2$	**m.p.**	129/131 (AcOEt)
Tlc - R_f (eluent)	0.33 (Etp/AcOEt/AcOH), 60:37:3)		

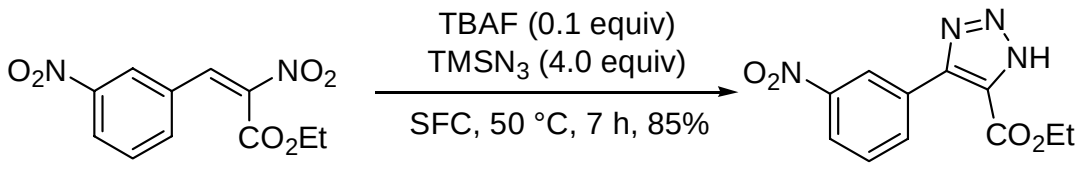
FT-IR (KBr, cm^{-1}): 835 (w), 990 (m), 1095 (m), 1137 (m), 1190 (m), 1472 (m), 1725 (s), 3134 (m)

Elemental Analysis: C, 52.50; H, 4.01; N, 16.70. Found: C, 52.58; H. 4.11; N, 16.54.

^{1}H NMR 200 MHz acetone-d6	**δ value**	**No. H**	**Mult.**	**j value/Hz**
	1.31	3	*t*	*J* = 7.1 Hz
	4.34	2	*q*	*J* = 7.1 Hz
	7.51	2	*d*	*J* = 8.3 Hz
	7.94	2	*d*	*J* = 8.3 Hz

^{13}C NMR (100.6 MHz, DMSO-d6) δ : 13.9, 60.9, 128.3, 130.9, 131.6, 133.3, 134.0, 160.6 (one carbon missing)

Chem. Name	Ethyl 4-(3'-nitrophenyl)-1*H*-1,2,3-triazole-5-carboxylate (2j)



1j **2j**

Method: In a screw capped vial equipped with a magnetic stirrer, TBAF·$3H_2O$ (0.064 g, 0.2 mmol), (*E*)-1-carboethoxy-2-(3'-nitrophenyl)-1-nitroethene (**1j**) (0.532 g, 2.0 mmol) and $TMSN_3$ (0.920 g, 8.0 mmol) were consecutively added and the resulting mixture was warmed at 50 °C and left under vigorous stirring for 7 h. The crude reaction mixture was charged on a silica gel column chromatography (Etp/AcOEt 8/2, gradient; silica/sample: 15:1). Pure ethyl 4-(3'-nitrophenyl)-1*H*-1,2,3-triazole-5-carboxylate(**2j**) was isolated as a white solid in 85% yield (0.445 g).

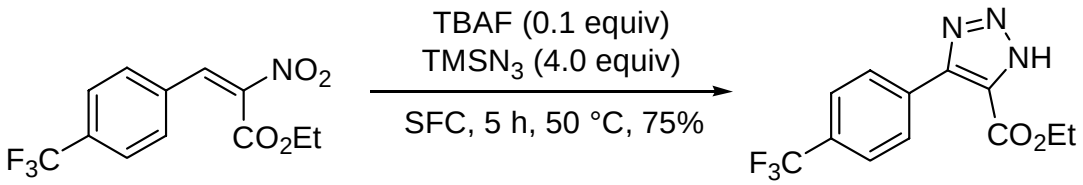
Mol Formula	$C_{11}H_{10}N_4O_4$	m.p.	103/104 (AcOEt)

Elemental Analysis: C, 50.38; H, 3.84; N, 21.37. Found: C, 50.58; H. 3.81; N, 21.31.

^{1}H NMR 400 MHz CD_3OD	δ value	No. H	Mult.	j value/Hz
	1.33	3	*t*	*J* = 7.1 Hz
	4.38	2	*q*	*J* = 7.1 Hz
	7.68	1	*t*	*J* = 8.0 Hz
	8.22	1	*d*	*J* = 8.0 Hz
	8.29	1	*d*	*J* = 8.0 Hz
	8.75	1	*s*	

^{13}C NMR (100.6 MHz, CD_3OD) δ: 14.3, 62.8, 124.9, 125.2, 130.6, 134.5, 136.3, 146.0, 149.4, 160.5, 161.9

Chem. Name	**Ethyl 4-(4'-trifluoromethylphenyl)-1*H*-1,2,3-triazole-5-carboxylate (2k)**



1k **2k**

Method: In a screw capped vial equipped with a magnetic stirrer, TBAF·$3H_2O$ (0.064 g, 0.2 mmol), (*E*)-1-carboethoxy-2-(4'-trifluoromethylphenyl)-1-nitroethene (**1k**) (0.578 g, 2.0 mmol) and $TMSN_3$ (0.920 g, 8.0 mmol) were consequtively added and the resulting mixture was warmed to 50 °C and left under vigorous stirring at 50 °C for 5 h. The crude reaction mixture was charged on a silica gel column chromatography (Etp/AcOEt 8/2, gradient; silica/sample: 15:1). Pure ethyl 4-(4'-trifluoromethylphenyl)-1*H*-1,2,3-triazole-5-carboxylate (**2k**) was isolated as a white solid in 75% yield (0.428 g).

Mol Formula	$C_{12}H_{10}F_3N_3O_2$	**m.p.**	149/151 (AcOEt)

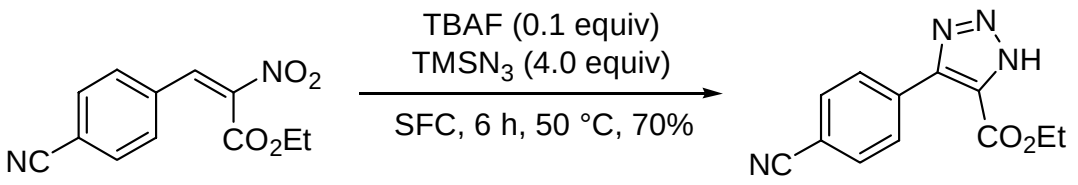
FT-IR (KBr, cm^{-1}): 850 (w), 1070 (m), 1135 (w), 1170 (m), 1326 (m), 1727 (m), 2997 (m)

Elemental Analysis: C, 50.53; H, 3.53; N, 14,73. Found: C, 50.51; H. 3.41; N, 14.65.

^{1}H NMR 400 MHz CD_3OD	**δ value**	**No. H**	**Mult.**	**j value/Hz**
	1.33	3	*t*	*J* = 7.1 Hz
	4.35	2	*q*	*J* = 7.1 Hz
	7.74	2	*d*	*J* = 8.2 Hz
	8.01	2	*d*	*J* = 8.2 Hz

^{13}C NMR (100.6 MHz, C_3OD) δ: 14.3, 64.0, 121.5, 125.5 (*q*), 126.1, 131.0, 132.1 (*q*), 146.0, 134.0, 162.0

Chem. Name	**Ethyl 4-(4'-cyanophenyl)-1*H*-1,2,3-triazole-5-carboxylate (2l)**



1l **2l**

Method: In a screw capped vial equipped with a magnetic stirrer, TBAF·$3H_2O$ (0.064 g, 0.2 mmol), (*E*)-1-carboethoxy-2-(4'-cyanophenyl)-1-nitroethene (**1l**) (0.492 g, 2.0 mmol) and $TMSN_3$ (0.920 g, 8.0 mmol) were consecutively added and the resulting mixture was warmed to 50 °C and left under vigorous stirring for 6 h. The crude reaction mixture was charged on a silica gel column chromatography (Etp/AcOEt 8/2, gradient; silica/sample: 15:1). Pure ethyl 4-(4'-cyanophenyl)-1*H*-1,2,3-triazole-5-carboxylate (**2l**) was isolated as a white solid in 70% yield (0.363 g).

Mol Formula	$C_{12}H_{10}N_4O_2$	**m.p.**	117/120 (AcOEt)

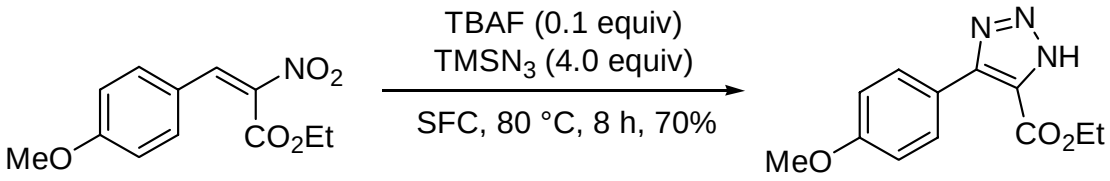
FT-IR (KBr, cm^{-1}): 849 (w), 1018 (m), 1138 (w), 1482 (m), 1727 (s), 2232 (m), 3142 (m)

Elemental Analysis: C, 59.50; H, 4.16; N, 23.13. Found: C, 59.51; H. 4.19; N, 23.04

^{1}H NMR 400 MHz CD_3OD	**δ value**	**No. H**	**Mult.**	**j value/Hz**
	1.32	3	*t*	*J* = 7.1 Hz
	4.35	2	*q*	*J* = 7.1 Hz
	7.74	2	*d*	*J* = 8.7 Hz
	8.01	2	*d*	*J* = 8.7 Hz

^{13}C NMR (100.6 MHz, C_3OD) δ : 14.4, 62.7, 113.8, 119.0, 119.4, 131.2, 133.1, 135.0, 146.4, 161.9

Chem. Name	**Ethyl 4-(4'-methoxyphenyl)-1*H*-1,2,3-triazole-5-carboxylate (2m)**



1m **2m**

Method: In a screw capped vial equipped with a magnetic stirrer, TBAF·$3H_2O$ (0.064 g, 0.2 mmol), (*E*)-1-carboethoxy-2-(4'-methoxyphenyl)-1-nitroethene (**1m**) (0.502 g, 2.0 mmol) and $TMSN_3$ (0.920 g, 8.0 mmol) were consecutively added and the resulting mixture was warmed to 80 °C and left under vigorous stirring for 8 h. The crude reaction mixture was charged on a silica gel column chromatography (Etp/AcOEt 8/2, gradient; silica/sample: 15:1). Pure ethyl 4-(4'-methoxyphenyl)-1*H*-1,2,3-triazole-5-carboxylate (**2m**) was isolated as a white solid in 70% yield (0.346 g).

Mol Formula	$C_{12}H_{13}N_3O_3$	**m.p.**	123-125 (AcOEt)

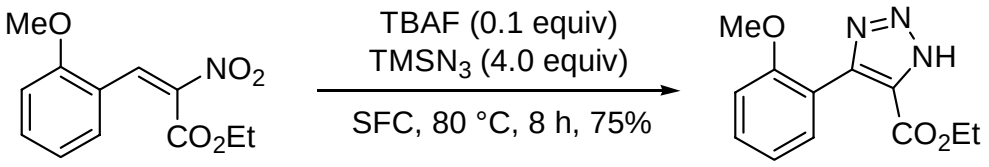
FT-IR (KBr, cm^{-1}): 837 (w), 1027 (m), 1145 (s), 1483 (m), 1724 (s), 3135 (m)

Elemental Analysis: C, 58.29; H, 5.30; N, 16.99. Found: C, 58.31; H. 5.29; N, 16.88

^{1}H NMR 400 MHz CD_3OD	**δ value**	**No. H**	**Mult.**	**j value/Hz**
	1.31	3	*t*	*J* = 7.1 Hz
	3.82	3	*s*	
	4.34	2	*q*	*J* = 7.1 Hz
	7.70	2	*d*	*J* = 8.2 Hz
		2	*d*	*J* = 8.2 Hz

^{13}C NMR (100.6 MHz, C_3OD) δ: 14.4, 55.8, 62.4, 114.8, 120.2, 131.8, 134.0, 145.3, 162.3, 162.5

Chem. Name	**Ethyl 4-(2'-methoxyphenyl)-1*H*-1,2,3-triazole-5-carboxylate (2n)**



1n **2n**

Method: In a screw capped vial equipped with a magnetic stirrer, TBAF·$3H_2O$ (0.064 g, 0.2 mmol), (*E*)-1-carboethoxy-2-(2'-methoxyphenyl)-1-nitroethene (**1n**) (0.502 g, 2.0 mmol) and $TMSN_3$ (0.920 g, 8.0 mmol) were consecutively added and the resulting mixture was warmed to 80 °C and left under vigorous stirring for 8 h. The crude reaction mixture was charged on a silica gel column chromatography (Etp/AcOEt 8/2, gradient; silica/sample: 15:1). Pure ethyl 5-(2'-methoxyphenyl)-1*H*-1,2,3-triazole-5-carboxylate (**2n**) was isolated as a white solid in 75% yield (0.370 g).

Mol Formula	$C_{12}H_{13}N_3O_3$	**m.p.**	125-127 (AcOEt)

FT-IR (KBr, cm^{-1}): 845 (w), 1025 (m), 1148 (s), 1471 (m), 1725 (s), 3145 (m)

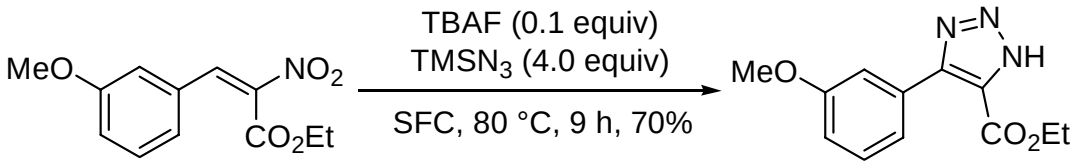
Elemental Analysis: C, 58.29; H, 5.30; N, 16.99. Found: C, 58.35; H. 5.23; N, 16.82

^{1}H NMR 400 MHz CD_3OD

δ **value**	**No. H**	**Mult.**	**j value/Hz**
1.23	3	*t*	*J* = 7.1 Hz
3.80	3	*s*	
4.26	2	*q*	*J* = 7.1 Hz
7.05	1	*t*	*J* = 7.5 Hz
7.11	1	*d*	*J* = 8.0 Hz
7.43	1	*d*	*J* = 8.0 Hz
7.47	1	*d*	*J* = 7.5 Hz

^{13}C NMR (100.6 MHz, C_3OD) δ : 14.3, 56.0, 62.1, 111.8, 121.4, 132.1, 132.6, 145.5, 160.2, 162.5

Chem. Name	**Ethyl 4-(3'-methoxyphenyl)-1*H*-1,2,3-triazole-5-carboxylate (2o)**



1o **2o**

Method: In a screw capped vial equipped with a magnetic stirrer, TBAF·$3H_2O$ (0.064 g, 0.2 mmol), (*E*)-1-carboethoxy-2-(3'-methoxyphenyl)-1-nitroethene (**1o**) (0.502 g, 2.0 mmol) and $TMSN_3$ (0.920 g, 8.0 mmol) were consecutively added and the resulting mixture was warmed to 80 °C and left under vigorous stirring for 9 h. The crude reaction mixture was charged on a silica gel column chromatography (Etp/AcOEt 8/2, gradient; silica/sample: 15:1). Pure ethyl 4-(3'-methoxyphenyl)-1*H*-1,2,3-triazole-5-carboxylate (**2o**) was isolated as a white solid in 70% yield (0.346 g).

Mol Formula	$C_{12}H_{13}N_3O_3$	**m.p.**	131-133 (AcOEt)

FT-IR (KBr, cm^{-1}): 860 (w), 1034 (m), 1178 (s), 1467 (m), 1725 (s), 3415 (m)

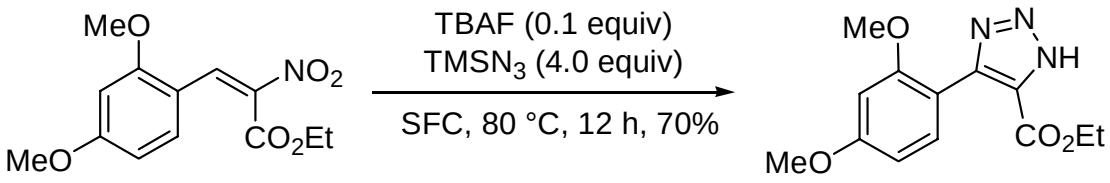
Elemental Analysis: C, 58.29; H, 5.30; N, 16.99. Found: C, 58.25; H. 5.24; N, 16.87

^{1}H NMR 400 MHz CD_3OD

δ value	**No. H**	**Mult.**	**j value/Hz**
1.26	3	*t*	*J* = 7.1 Hz
3.76	3	*s*	
4.30	2	*q*	*J* = 7.1 Hz
6.96	1	*d*	*J* = 7.2 Hz
7.25-7.35	3	*m*	

^{13}C NMR (100.6 MHz, $CDCl_3$) δ : 14.3, 55.8, 62.4, 115.8, 116.4, 122.5, 129.9, 130.4, 134.4, 145.7, 160.8, 162.3

Chem. Name	**Ethyl 4-(2',4'-dimethoxyphenyl)-1*H*-1,2,3-triazole-5-carboxylate (2o)**



1p **2p**

Method: In a screw capped vial equipped with a magnetic stirrer, TBAF·$3H_2O$ (0.064 g, 0.2 mmol), (*E*)-1-carboethoxy-2-(2',4'-dimethoxyphenyl)-1-nitroethene (**1p**) (0.562 g, 2.0 mmol) and $TMSN_3$ (0.920 g, 8.0 mmol) were consecutively added and the resulting mixture was warmed to 80 °C and left under vigorous stirring for 12 h. The crude reaction mixture was charged on a silica gel column chromatography (Etp/AcOEt 8/2, gradient; silica/sample: 15:1). Pure ethyl 5-(2',4'-dimethoxyphenyl)-1*H*-1,2,3-triazole-5-carboxylate (**2p**) was isolated as a white solid in 70% yield (0.388 g).

Mol Formula	$C_{13}H_{15}N_3O_4$	**m.p.**	150-152 (AcOEt)

FT-IR (KBr, cm^{-1}): 840 (w), 1031 (m), 1163 (s), 1467 (m), 1720 (s), 3007 (m)

Elemental Analysis: C, 56.31; H, 5.45; N, 15.15. Found: C, 56.35; H. 5.48; N, 15.15

^{1}H NMR 400 MHz CD_3OD	**δ value**	**No. H**	**Mult.**	**j value/Hz**
	1.24	3	*t*	*J* = 7.1 Hz
	3.78	3	*s*	
	3.84	3	*s*	
	4.28	2	*q*	*J* = 7.1 Hz
	6.58-6.67	2	*m*	
	7.39	1	*d*	*J* = 8.3 Hz

^{13}C NMR (100.6 MHz, $CDCl_3$) δ : 14.4, 56.0, 56.1, 62.1, 98.4, 106.0, 109.2, 133.5, 136.4, 140.6, 159.3, 162.9, 164.3