HETEROCYCLES, Vol. 94, No. 9, 2017, pp. 1775 - 1782. © 2017 The Japan Institute of Heterocyclic Chemistry
Received, 7th June, 2017, Accepted, 30th June, 2017, Published online, 6th July, 2017
DOI: 10.3987/COM-17-13763

SYNTHESIS OF FUSED 1,2,3-TRIAZOLES THROUGH CARBOCATION-MEDIATED INTRAMOLECULAR [3+2] CYCLOADDITION OF AZIDO-PROPARGYL ALCOHOLS

Youlai Zhang,[a] Junru Li,[a] Mengdi Wang,[a] Huan Zhang,[a]* Hiroki Tanimoto,[b] Tsumoru Morimoto,[b] and Kiyomi Kakiuchi[b]

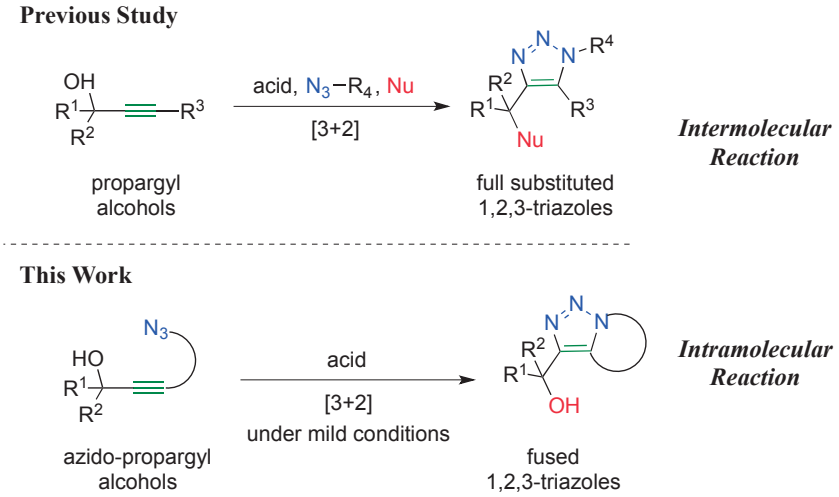
[a]Tianjin Key Laboratory of Organic Solar Cells and Photochemical Conversion, School of Chemistry and Chemical Engineering, Tianjin University of Technology, Tianjin 300384, P.R. China; E-mail: zhanghuan80887@163.com
[b]Graduate School of Materials Science, Nara Institute of Science and Technology (NAIST), 8916-5 Takayama, Ikoma, Nara 630-0192, Japan

Abstract – A practical and efficient intramolecular cyclization reaction with azido-propargyl cations is described. Range of acids and activating reagents were selected to demonstrate the reaction conditions. Organic azides and propargyl cations generated by toluenesulfonic acid gave fused 1,2,3-triazoles undergo metal-free intramolecular azide–alkyne [3+2] cycloaddition reactions. Various fused triazoles were obtained within 30 min in good yields under mild reaction conditions.

Organic azides have been well-utilized in organic synthesis. Especially, azide-alkyne [3+2] cycloadditions which produce triazoles have been the focus in the chemical biology research.[1] The triazole derivatives are found in a large number of compounds possessing antibacterial activity, anti-HIV activity, antihistamine activity and applicable in the designing of new drugs.[2] For preparetion, most of the reported methods require copper catalyzed or typical Huisgen conditions.[3] Most of such copper-catalyzed reactions so far reported are intermolecular versions, although an intramolecular reaction should provide a powerful method for the synthesis of structurally different analogues difficult to obtain by an intermolecular reaction, in particular polycyclic fused triazole derivatives.[4] Thus, the methodologies toward copper-free [3+2] triazole synthesis should be developed.

According to one of our ongoing research projects, we have been developing propargyl cation-mediated intermolecular cycloaddition methodology toward highly substituted 1,2,3-triazole synthesis using propargyl alcohol and organic azides. This method can accept both terminal and internal alkynes under

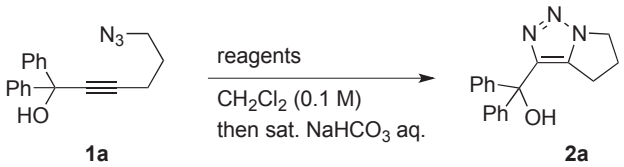
low temperature and multicomponent coupling reactions.[5] Based on the propargyl cation chemistry with this strategy, [3+2] reactions could be achieved with intramolecular cycloadditions.[5a] Herein we report intramolecular metal free [3+2] azide-alkyne cycloadditions to synthesize fused triazoles under mild conditions (Scheme 1).



Scheme 1. Strategy of intramolecular azide-alkyne [3+2] cycloaddition reaction

Using benzyl alcohol **1a** as model substrate, cycloaddition reaction was conducted in the presence of various acids, and the reactions were quenched with a saturated sodium bicarbonate aqueous solution in order to produce triazolylalkanols (Table 1).

Table 1. Optimization of reaction conditions



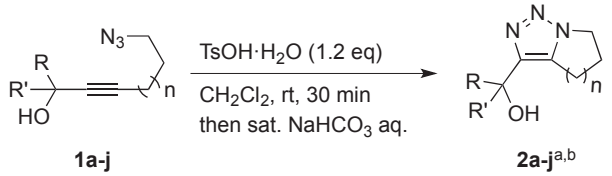
Entry	Equiv	Reagents	Temp (°C)	Time (min)	Yield (%)[a]
1	1.2	TMSOTf	-90	5	91
2	1.2	TMSOTf	0	5	89
3	1.2	$BF_3 \cdot OEt_2$	rt	30	86
4	1.2	$Cu(OTf)_2$	rt	3 h	63
5	1.2	$SnCl_4$	rt	3 h	10
6	1.2	MsOH	rt	30	82
7	1.2	$TsOH \cdot H_2O$	rt	30	99
8	1.05	$TsOH \cdot H_2O$	rt	30	94

9	0.1	$TsOH·H_2O$	rt	3 h	13
10[b]	1.2	$TsOH·H_2O$	rt	30	89
11[c]	1.2	$TsOH·H_2O$	rt	30	90
12	1.2	$TsOH·H_2O$	0	3 h	98

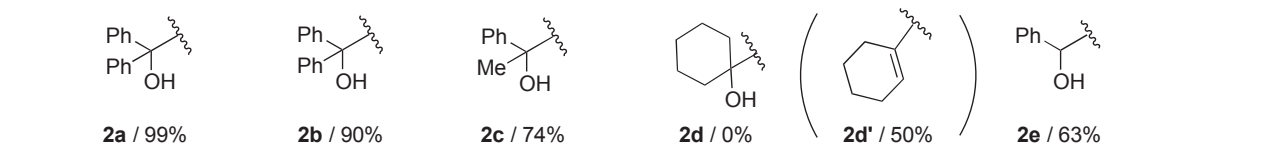
[a] Isolation yield. [b] Performed in acetonitrile. [c] Performed in toluene.

As shown in entry 1, in the presence of 1.2 equiv TMSOTf in CH_2Cl_2 proceeded at -90 °C within 5 min to give desired triazole **2a** in an excellent yield. Further rising temperature conditions were achieved with TMSOTf, also give similar results (entries 2). The boron trifluoride ether complex worked well resulting in a good yield (entry 3). Copper triflate worked to yield **2a** in moderate yield (entry 4) with longer reaction time, and tin tetrachloride ($SnCl_4$) resulted in a much lower yield of **2a** (entry 5). Methanesulfonic acid (MsOH) could produce **2a** in good yield within 30 min (entry 6). The optimal condition was achieved with toluenesulfonic acid (TsOH), and the desired transformation was successfully demonstrated. With 1.2 equiv of TsOH, benzyl alcohol **1a** could be converted to triazolyl alcohol **2a** in almost quantitative yield at ambient temperature (entry 7). Reducing the equivalence of acid reagent could also give similar results (entry 8). Unfortunately, catalytic conditions were ineffective probably due to the basicity of the resulting triazoles (entry 9). Instead of dichloromethane, toluene and acetonitrile could work as efficient solvents (entries 10-11). It should be noted that TsOH could afford **2a** in almost quantitative yield at 0 °C (entry 12).

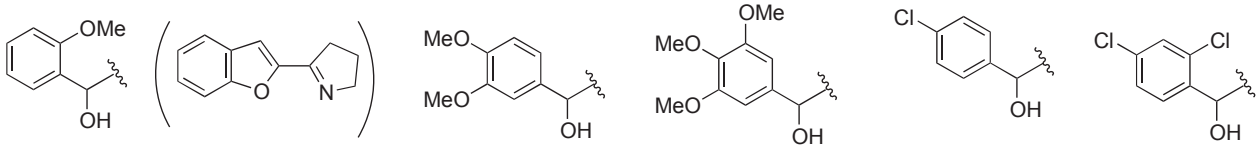
Table 2. Scope of substituents on intramolecular [3+2] reactions



1a-j **2a-j**[a,b]



2a / 99% **2b** / 90% n=2 **2c** / 74% **2d** / 0% **2d'** / 50% **2e** / 63%

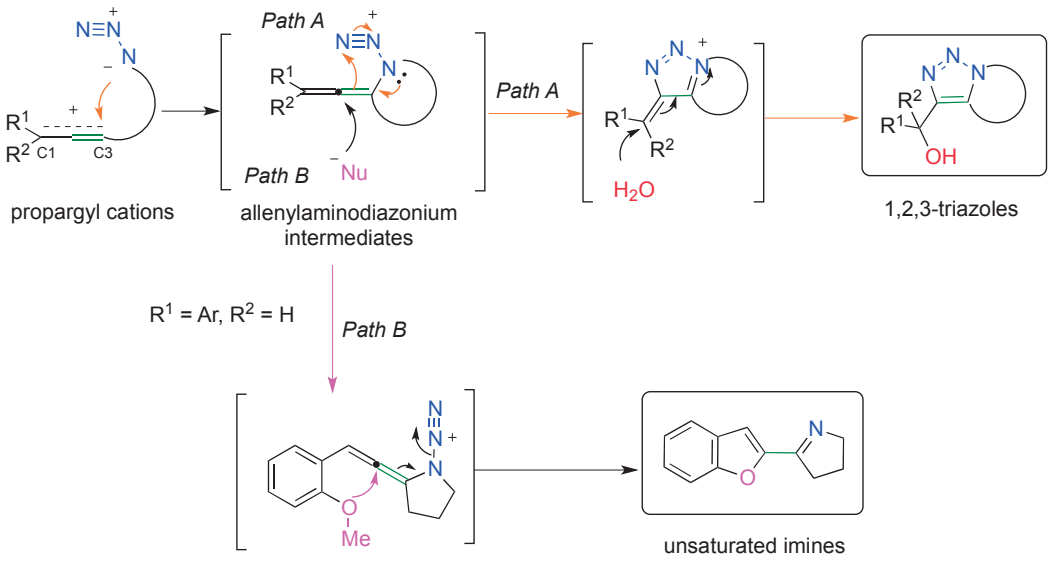


2f / 70% **2f'** / 6% **2g** / 71% **2h** / 84% **2i** / 61% **2j** / 44%

[a] Substrates **1a**, **1c-j**, n=1. [b] Isolated yield.

With optimal conditions determined, our focus was directed toward studying the substrates in the presence of 1.2 equiv TsOH and the reaction temperature was set to rt (Table 2). Under the similar conditions for **2a**, **1b** showed similar reactivity to give the six-member cyclized triazole **2b** in an excellent yield due to the diphenyl group avoided the reaction at C1 by steric and electronic influences.[6] Then, the substituents on alcohols R and R' were investigated to see the substituent effect on the reactivity. Methylphenyl alcohol **1c** gave **2c** in good yield and cyclohexanol derivative **1d** showed lower reactivity to give the dehydrated cyclized product **2d'** in 50% yield. Compared to the substrate **1a**, in the case of benzyl alcohol **1e**, reaction proceeded rather sluggishly to give the cyclized product **2e** in 63% yield due to the lower reactivity of benzylic carbocation compared with diphenyl carbocation. Substitution of phenyl moiety with electron-donating groups **1f-h** could afford the desired triazoles **2f-h** in good yields and electron deficient aryl **1i-j** was found to be uneffective and achieved triazoles in low yields. Benzofuranylpyrroline **2f'** was generated through umpolung cyclization of an allenamine derivative followed by demethylation of the oxonium ion.[5a] Thus, these [3+2] reactions of azido-propargyl alcohols were highly accelerated by the propargylic cation efficiently.

With these results, the reaction mechanism was shown in Scheme 2. The propargyl cations were generated under acid condition. Then azide anions attached to the sp cation, the unstable allenylaminodiazonium intermediates were produced. Capturing diazo moiety, this active allenylaminodiazonium intermediates could be immediately transformed to the desired triazoles (Path A). On the other hand, diazo moiety in diazoallenamines is a good leaving group and the center carbon atom in allene could be a nucleophilic position (Path B). Thus, with *ortho*-substituted phenyl group, benzofuryl imines were produced through intramolecular cyclizations.



Scheme 2. Process of intramolecular [3+2] reaction

In summary, we have developed an efficient intramolecular [3+2] cycloaddition of azido-propargyl alcohols to afford fused 1,2,3-triazoles under metal-free conditions. Via propargyl cations derived from the corresponding alcohols, toluenesulfonic acid was effective in most cases and demonstrated the desired triazoles within 30 min in good yields under mild reaction conditions. This method can provide a new convenient preparation of fused 1,2,3-triazoles and exploration of their uses in synthetic organic chemistry.

EXPERIMENTAL

^{1}H and ^{13}C NMR were recorded on a JEOL JNM-ECP500 spectrometer (500 MHz for ^{1}H NMR, 126 MHz for ^{13}C NMR). Chemical shifts are reported as δ values in ppm and calibrated by residual solvent peak ($CDCl_3$, δ 7.26 for ^{1}H NMR, δ 77.00 for ^{13}C NMR; CD_3OD, δ 3.31 for ^{1}H NMR, δ 49.00 for ^{13}C NMR; CD_2Cl_2, δ 5.32 for ^{1}H NMR, δ 53.8 for ^{13}C NMR) or tetramethylsilane (δ 0 for ^{1}H NMR). Inflared spectra were measured on a JASCO FT/IR-4200 spectrometer. Mass spectra were recorded on a JEOL JMS-700 MStaion [EI (70 eV), CI, FAB and ESI]. Flush column chromatography was performed by MERCK Silica gel 60. The progress of reactions was monitored by silica gel thin layer chromatography plates (MERCKTLC Silicagel 60 F_{254}).

Starting Materials. General experimental procedure of propargyl alcohols (**1a-j)** were prepared using previously reported procedures,[5a] see ESI. All other chemicals in this study were commercially available.

Typical Procedure for the Preparation of Fused 1,2,3-Triazoles (2).

(5,6-Dihydro-4*H*-pyrrolo[1,2-c][1,2,3]triazol-3-yl)diphenylmethanol (2a). To the mixture of propargyl alcohol **1a** (42.0 mg, 0.144 mmol) in CH_2Cl_2 (2 mL) under nitrogen atmosphere, $TsOH\cdot H_2O$ (38.5 mg, 0.173 mmol, 1.2 equiv) was added at ambient temperature. After 30 min, the reaction was quenched with saturated sodium bicarbonate aqueous solution, and was washed with brine. Drying the organic layer over magnesium sulfate followed by concentration in vacuo and silica gel column chromatography afforded triazole (EtOAc/hexane = 1/4 to 1/1) afforded triazole **2a** (41.8 mg, 99%). White crystal; R_f value 0.24 (EtOAc/hexane = 1/1); mp 113–114 °C; IR (NaCl, neat) ν_{max} 3378, 3059, 1491, 1448, 1316, 1168, 1021 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.25–7.34 (m, 10H), 4.24 (t, 2H, J = 7.5 Hz), 4.19 (br-s, 1H, OH), 2.56 (tt, 2H, J = 7.5, 7.5 Hz), 2.07 (t, 2H, J = 7.5 Hz); ^{13}C NMR (126 MHz, $CDCl_3$) δ 145.5, 145.1, 140.2, 127.8, 127.34, 127.29, 76.6, 46.2, 27.9, 20.8; HRMS (ESI) calcd for $C_{18}H_{17}N_3ONa$ $[M+Na]^+$ 314.1269, found 314.1267.

Diphenyl(4,5,6,7-tetrahydro[1,2,3]triazolo[1,5-a]pyridin-3-yl)methanol (2b). Colorless oil; R_f value 0.11 (EtOAc/hexane = 1/3); IR (NaCl, neat) ν_{max} 3376, 2953, 1490, 1447, 1016, 759, 700 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.28–7.31 (m, 10H), 4.34 (t, 2H, J = 6.0 Hz), 4.28 (br, 1H, OH), 2.00 (t, 2H, J = 7.0 Hz), 1.93 (m, 2H), 1.67 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 147.7, 145.2, 131.0, 127.9, 127.7, 127.5,

77.4, 46.6, 22.2, 20.6, 19.9; HRMS (ESI) calcd for $C_{19}H_{19}N_3ONa$ $[M+Na]^+$ 328.1426, found 328.1426.

1-(5,6-Dihydro-4*H*-pyrrolo[1,2-c][1,2,3]triazol-3-yl)-1-phenylethan-1-ol (2c). Colorless oil; R_f value 0.28 (EtOAc/hexane = 1/2); IR (NaCl, neat) ν_{max} 3362, 2980, 1446, 1066, 700 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.48 (d, 2H, *J* = 8.0 Hz), 7.33 (dd, 2H, *J* = 8.0, 7.5 Hz), 7.25 (dd, 1H, *J* = 7.0, 6.5 Hz), 4.25 (t, 2H, *J* = 7.5 Hz), 3.26 (s, 1H, OH), 2.66 (m, 2H), 2.49 (m, 2H), 1.99 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 146.4, 146.2, 138.6, 128.1, 127.0, 125.2, 71.9, 46.2, 30.0, 28.1, 21.2; HRMS (ESI) calcd for $C_{13}H_{15}N_3O$ $[M+Na]^+$ 252.1113, found 252.1118.

3-(Cyclohex-1-en-1-yl)-5,6-dihydro-4*H*-pyrrolo[1,2-c][1,2,3]triazole (2d'). Colorless oil; R_f value 0.13 (EtOAc/hexane = 1/2); IR (NaCl, neat) ν_{max} 2926, 1558 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 6.19 (m, 1H), 4.30 (t, 2H, *J* = 7.5 Hz), 2.96 (t, 2H, *J* = 8.0 Hz), 2.80 (tt, 2H, *J* = 8.0, 7.5 Hz), 2.21-2.18 (m, 2H), 1.78-1.73 (m, 2H), 1.68-1.63 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 141.4, 137.2, 128.6, 124.2, 46.0, 28.3, 26.0, 25.3, 22.5, 22.2, 22.0; HRMS (ESI) calcd for $C_{11}H_{16}N_3$ $[M+H]^+$ 190.1344, found 190.1338.

(5,6-Dihydro-4*H*-pyrrolo[1,2-c][1,2,3]triazol-3-yl)(phenyl)methanol (2e). Colorless oil; R_f value 0.15 (CH_2Cl_2/MeOH = 20/1); IR (NaCl, neat) ν_{max} 3250, 1228, 1487, 1087, 1013, 805 cm^{-1}; cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.43 (d, 2H, *J* = 7.0 Hz), 7.34 (dd, 1H, *J* = 7.0, 7.5 Hz), 7.28 (t, 2H, *J* = 7.5 Hz), 6.01 (sd, 1H, *J* = 2.5 Hz), 4.20 (t, 2H, *J* = 7.0 Hz), 4.12 (sd, 1H, *J* = 3.0 Hz), 2.65-2.55 (m, 2H), 2.48-2.42 (m, 1H), 2.28-2.22 (m, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 143.0, 141.8, 139.4, 128.3, 127.6, 126.1, 68.6, 46.2, 28.0, 20.6; HRMS (ESI) calcd for $C_{12}H_{11}NONa$ $[M+Na]^+$ 238.0956, found 238.0955.

(5,6-Dihydro-4*H*-pyrrolo[1,2-c][1,2,3]triazol-3-yl)(2-methoxyphenyl)methanol (2f). White solid; R_f value 0.43 (CH_2Cl_2/MeOH = 1/10); mp 119.1–119.4 °C; IR (NaCl, neat) ν_{max} 3340, 1490, 1240, 1028 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.47 (dd, 1H, *J* = 7.5, 2.0 Hz), 7.27 (ddd, 1H, *J* = 8.0, 7.5, 2.0 Hz), 6.98 (dd, 1H, *J* = 8.0, 8.0 Hz), 6.87 (d, 1H, *J* = 8.0 Hz), 6.23 (d, 1H, *J* = 5.0 Hz), 4.23 (t, 2H, *J* = 7.0 Hz), 3.80 (s, 3H), 3.69 (d, 1H, OH, *J* = 5.0 Hz), 2.63 (tt, 2H, *J* = 7.5, 7.5 Hz), 2.38 (td, 1H, *J* = 15.0, 7.5 Hz), 2.38 (td, 1H, *J* = 15.0, 7.5 Hz); ^{13}C NMR (126 MHz, $CDCl_3$) δ 156.2, 142.1, 139.2, 129.9, 128.7, 127.2, 120.7, 110.3, 64.7, 55.4, 46.1, 28.0, 20.6; HRMS (ESI) calcd for $C_{13}H_{15}N_3O_2$ $[M+Na]^+$ 268.1062, found 268.1062.

(5,6-Dihydro-4*H*-pyrrolo[1,2-c][1,2,3]triazol-3-yl)(3,4-dimethoxyphenyl)methanol (2g). White solid; R_f value 0.10 (EtOAc/hexane = 1/1); mp 125.4–125.7 °C; IR (NaCl, neat) ν_{max} 3433, 1644, 1514, 1234, 1137 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.01 (d, 1H, *J* = 2.0 Hz), 6.94 (dd, 1H, *J* = 8.0, 2.0 Hz), 6.84 (d, 1H, *J* = 8.0 Hz), 5.95 (s, 1H), 4.24 (t, 2H, *J* = 7.5 Hz), 2.77 (br, 1H, OH), 2.63 (m, 2H), 2.47 (ddd, 1H, *J* = 15.1, 8.5, 6.0 Hz), 2.33 (ddd, 1H, *J* = 15.1, 8.0, 7.5 Hz); ^{13}C NMR (126 MHz, $CDCl_3$) δ 149.0, 148.5, 143.0, 139.2, 134.4, 118.4, 110.8, 109.3, 68.6, 55.9, 46.2, 28.0, 20.7; HRMS (ESI) calcd for $C_{14}H_{17}N_3O_3Na$ $[M+Na]^+$ 298.1168, found 298.1170.

(5,6-Dihydro-4*H*-pyrrolo[1,2-c][1,2,3]triazol-3-yl)(3,4,5-trimethoxyphenyl)methanol (2h). White

crystals; R_f value 0.22 (CH_2Cl_2/MeOH = 20/1); mp 137.8–138.2 °C; IR (NaCl, neat) ν_{max} 3433, 1233, 1124 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 6.66 (s, 2H), 5.91 (s, 1H), 4.17 (t, 2H, *J* = 7.5 Hz), 3.78 (s, 6H), 3.77 (s, 3H), 2.48–2.64 (m, 3H), 2.29 (ddd, 1H, *J* = 16.0, 9.5, 6.0 Hz); ^{13}C NMR (126 MHz, $CDCl_3$) δ 153.0, 143.0, 139.2, 137.7, 137.0, 102.8, 68.3, 60.7, 56.0, 46.1, 27.9, 20.7; HRMS (ESI) calcd for $C_{15}H_{19}N_3O_4Na$ $[M+Na]^+$ 328.1273, found 328.1276.

(4-Chlorophenyl)(5,6-dihydro-4*H*-pyrrolo[1,2-c][1,2,3]triazol-3-yl)methanol (2i). White crystals; R_f value 0.2 (EtOAc/hexane = 1/2); mp 142.8–142.9 °C; IR (NaCl, neat) ν_{max} 3250, 1228, 1487, 1087, 1013, 805 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.38 (d, 2H, *J* = 8.5 Hz), 7.32 (d, 2H, *J* = 8.5 Hz), 6.00 (s, 1H), 4.23 (t, 2H, *J* = 7.5 Hz), 2.64 (m, 2H), 2.47 (ddd, 1H, *J* = 15.0, 8.5, 6.5 Hz), 2.29 (ddd, 1H, *J* = 15.0, 9.0, 6.0 Hz); ^{13}C NMR (126 MHz, $CDCl_3$) δ 142.6, 140.3, 139.3, 133.4, 128.5, 127.6, 68.0, 46.3, 28.0, 20.7; HRMS (ESI) calcd for $C_{12}H_{12}ClN_3ONa$ $[M+Na]^+$ 272.0567, found 272.0570.

(2,4-Dichlorophenyl)(5,6-dihydro-4*H*-pyrrolo[1,2-c][1,2,3]triazol-3-yl)methanol (2j). White crystals; R_f value 0.1 (EtOAc/hexane = 1/2); mp 176.8–170.0 °C; IR (NaCl, neat) ν_{max} 3224, 2879, 1589, 1035, 858 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.76 (d, 1H, *J* = 8.5 Hz), 7.36 (d, 1H, *J* = 1.0 Hz), 7.33 (dd, 1H, *J* = 8.5, 1.0 Hz), 6.30 (s, 1H), 4.43 (br, 1H, OH), 4.25 (t, 2H, *J* = 7.0 Hz), 2.65 (tdd, 2H, *J* = 8.0, 7.5, 7.0 Hz), 2.37 (td, 1H, *J* = 16.0, 7.5 Hz), 2.30 (td, 1H, *J* = 16.0, 8.0 Hz); ^{13}C NMR (126 MHz, $CDCl_3$) δ 141.0, 139.3, 137.9, 133.9, 132.6, 129.0, 128.9, 127.4, 64.9, 46.3, 28.0, 20.5; HRMS (ESI) calcd for $C_{12}H_{11}Cl_2N_3ONa$ $[M+Na]^+$ 306.0177, found 306.0177.

ACKNOWLEDGEMENTS

This work was supported by the National Natural Science Foundation of China (21303120) and the Natural Science Foundation of Tianjin (16JCQNJC13700, 13JCYBJC42100). This research was also supported in part by a Grant-in-Aid for Scientific Research from the Ministry of Education, Culture, Sports, Science and Technology (MEXT) in Japan, for scientific research from Nara Institute of Science and Technology (NAIST) and NAIST Advanced Research Partnership Project, which are gratefully appreciated.

SUPPORTING INFORMATION

Supplementary data (experimental procedures, compound characterization data and copies of NMR spectra for all products) associated with this article can be found, in the online version.

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