Synthesis H. Zhang et al. Paper

Direct Synthesis of N-Unsubstituted 4-Aryl-1,2,3-triazoles Mediated by Amberlyst-15

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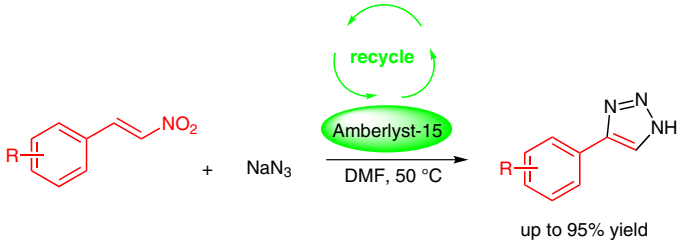


Received: 06.08.2015
Accepted after revision: 14.09.2015
Published online: 28.09.2015
DOI: 10.1055/s-0035-1560488; Art ID: ss-2015-h0467-op

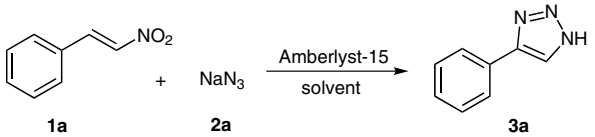
Abstract A highly efficient and effective method for the synthesis of N-unsubstituted 4-aryl-1,2,3-triazoles promoted by Amberlyst-15 is described. The promoter can be recycled and reused up to eight times without any reduction in its catalytic activity.

Key words N-unsubstituted 1,2,3-triazoles, Amberlyst-15, 1,3-dipolar cycloadditions

The synthesis of 1,2,3-trizoles has received significant attention in recent years due to their wide applications in organic synthesis, biology and materials science.[2] At present, N1-substituted 1,2,3-triazoles can be readily obtained via Huisgen azide–alkyne 1,3-dipolar cycloadditions (AACs),[3] transition-metal-catalyzed azide–alkyne cycloadditions,[4] organocatalyzed azide–ketone cycloadditions,[5] etc.[6] However, the preparation of N-unsubstituted 4-aryl-1,2,3-triazoles is still a challenging task. At present, only a few methods can be used to synthesize N-unsubstituted 4-aryl-1,2,3-triazoles: copper(I)-mediated azide–alkyne cycloadditions,[7] reactions between alkenyl bromides and sodium azide,[8] and 1,3-dipolar cycloadditions of nitroolefins and sodium azide.[9] Therefore, the development of more versatile and practical methods for the synthesis of N-unsubstituted 4-aryl-1,2,3-triazoles are still desirable. In continuation of our previous studies on developing improved methodologies for organic reactions, herein, we report an efficient and ecofriendly method for the synthesis of N-unsubstituted 4-aryl-1,2,3-triazoles mediated by Amberlyst-15.

At the beginning of our studies, we attempted to optimize the reaction conditions for the Amberlyst-15-mediated 1,3-dipolar cycloaddition reaction by using nitroolefin **1a** with sodium azide (**2a**) as a model system. In our initial screening experiments, the effects of various solvents and different temperatures on the yields of the model reaction were examined. To our delight, a high yield (95%) of the desired product was obtained when the reaction was conducted in *N*,*N*-dimethylformamide (Table 1, entry 2). The use of dimethyl sulfoxide as the solvent led to a slower reaction and a lower yield (Table 1, entry 1). Poor yields of the desired product were obtained when the reactions were performed in acetonitrile, ethanol and tetrahydrofuran (Table 1, entries 3–5). Only a trace amount of the desired prod-

Table 1 Optimization of the Reaction Conditions[a]



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

Entry	Solvent	Temp (°C)	Yield (%)[b]
1	DMSO	50	79
2	DMF	50	95
3	MeCN	50	11
4	EtOH	50	30
5	THF	50	8
6	toluene	50	trace
7	DMF	30	65
8[c]	DMF	50	96
9[d]	DMF	50	89
10[e]	DMF	50	10

[a] Reaction conditions: **1a** (0.2 mmol), **2a** (0.3 mmol), Amberlyst-15 (30 mg), solvent (2 mL), under air.
[b] Yield of isolated product.
[c] Amberlyst-15 (40 mg) was used.
[d] Amberlyst-15 (20 mg) was used.
[e] No catalyst was used.

uct was isolated when the reaction was carried out in toluene (Table 1, entry 6). The reaction temperature also played an important role in this system. The yield of the reaction decreased significantly when it was carried out at 30 °C (Table 1, entry 7). There was no significant improvement in the yield when the amount of the catalyst was increased (Table 1, entry 8). However, the yield decreased slightly (89%) when the amount of the catalyst was reduced (Table 1, entry 9). Only a 10% yield of the desired product was obtained when no catalyst was employed (Table 1, entry 10).

After optimizing the reaction conditions, a range of nitroolefins was used to investigate the scope of the reaction (Figure 1). Generally speaking, there was no apparent difference in the product yield when using different nitroolefins. All of the examined nitroolefins were excellent substrates regardless of the presence of electron-donating (**3d**,**i**,**n**,**p**) or electron-withdrawing groups (**3c**,**f**–**h**,**j**,**k**,**m**,**q**) on the benzene rings. It is worth mentioning that heterocyclic-substituted nitroolefin **3r** was also a good substrate for this reaction, affording the desired product in 80% yield. Additionally, steric hindrance had little effect on this system. Nitroolefins with substituents at *ortho*-, *meta*- and *para*-positions of the benzene ring all reacted smoothly with sodium azide to afford the corresponding products in good to excellent yields (**3b**,**e**,**l**,**o**). Unfortunately, alkyl-substituted and disubstituted nitroolefins were not suitable substrates for this reaction.

Excellent results were also obtained when this method was performed on gram scale (Scheme 1). This indicates that this reaction may have good synthetic utility in industry.

Finally, the recycling of the Amberlyst-15 catalyst was investigated in the reaction between nitrostyrene **1a** and sodium azide (Table 2). After the reaction was complete, the solution was filtered under vacuum using a sintered glass funnel and the Amberlyst-15 was washed with dichloro-

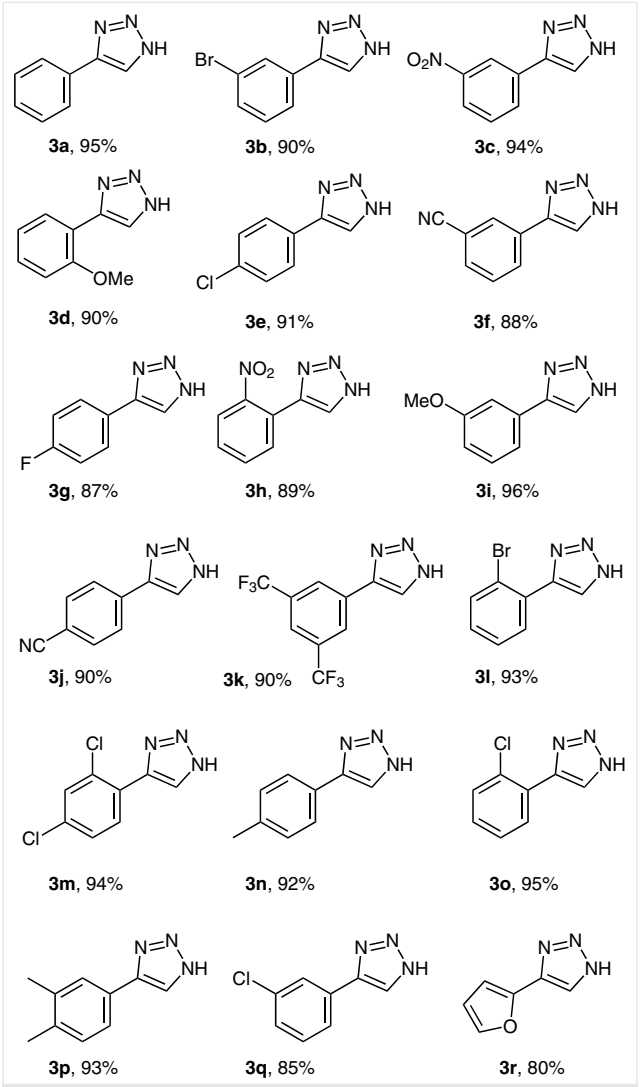
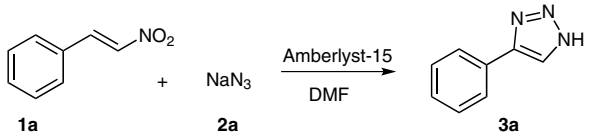


Figure 1 1,3-Dipolar cycloadditions of nitroolefins with NaN_3 for the synthesis of N-unsubstituted 4-aryl-1,2,3-triazoles. *Reaction conditions*: **1** (0.2 mmol), **2** (0.3 mmol), Amberlyst-15 (30 mg), DMF (2 mL), under air.

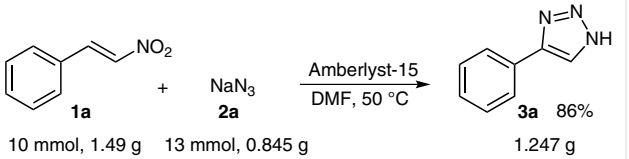
Table 2 Recycling of the Amberlyst-15 Catalyst[a]



Entry	Yield (%)	Entry	Yield (%)
1	95	5	95
2	96	6	92
3	94	7	93
4	93	8	91

[a] Reaction conditions: **1a** (0.2 mmol), **2a** (0.3 mmol), Amberlyst-15 (30 mg), DMF (2 mL), under air.

methane, ethanol, and hexane, respectively. The recovered catalyst was dried and then reused directly without further purification. The catalyst could be recovered and reused up to eight times with no loss of its catalytic activity.



Scheme 1 A gram-scale preparation of 4-phenyl-1*H*-1,2,3-triazole (**3a**)

In summary, a highly efficient method for the synthesis of N-unsubstituted 4-aryl-1,2,3-triazoles has been described. A wide range of functional groups is tolerated using this system, and good to excellent yields of the products were obtained. Furthermore, the catalyst could be recovered by simple filtration and reused up to eight times without any significant decrease in its catalytic activity. Further investigations and mechanistic studies are ongoing in our laboratory in order to identify more effective and economic systems for the synthesis of 1,2,3-triazoles.

All major chemicals and solvents were obtained from commercial sources and were used without further purification. Column chromatography was performed using Shenghai silica gel (200–300 mesh). Petroleum ether (PE) refers to the fraction boiling in the 60–90 °C range. Melting points were determined using an X4/X4A digital display microscopic melting point detector apparatus. IR spectra were recorded on a Nicolet IR200 spectrophotometer. ^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra were recorded using a JOEL JNM-ECA 500 spectrometer. ^{1}H NMR chemical shifts (δ) are given in ppm relative to TMS (δ = 0.0). ^{13}C NMR chemical shifts are reported in parts per million (ppm) relative to TMS with the solvent as the internal standard. ^{1}H NMR data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, dd = doublet of doublets, t = triplet, m = multiplet), coupling constant, integration. LC–MS (ESI) were obtained using an Agilent 1290 Infinity/6460 UHPLC/MS/MS instrument. GC–MS (EI) analysis was performed using an Agilent 5975B/6890N GC/MS instrument. High-resolution mass spectra were recorded on a Thermo exactive mass spectrometer.

N-Unsubstituted 4-Aryl-1,2,3-triazoles; General Procedure

A 25 mL Schlenk tube equipped with a magnetic stir bar was charged with the nitroolefin (0.2 mmol), NaN_3 (0.3 mmol), DMF (2 mL) and Amberlyst-15 (30 mg). The tube was sealed and heated at 50 °C in air for 1–3 h. After completion of the reaction (as indicated by TLC), the resulting solution was extracted with EtOAc (3 × 10 mL). The combined organic layer was dried over anhydrous Na_2SO_4, filtered, and concentrated under vacuum. The residue was chromatographed on a silica gel column (PE–EtOAc) to give the pure product.

The procedure for the large-scale synthesis was the same as that described above. A 250 mL Schlenk tube equipped with a magnetic stir bar was charged with the nitroolefin (10 mmol), NaN_3 (13 mmol), DMF (100 mL) and Amberlyst-15 (1.5 g). The tube was sealed and heated at 50 °C in air. After completion of the reaction (as indicated by TLC), the resulting solution was extracted with EtOAc. The organic layer was dried over anhydrous Na_2SO_4, and concentrated under vacuum. The residue was chromatographed on a silica gel column (PE–EtOAc) to give the pure product.

4-Phenyl-1*H*-1,2,3-triazole (3a)[9]

Yield: 27.5 mg (95%); white solid.

^{1}H NMR (500 MHz, DMSO-d_6): δ = 15.16 (s, 1 H), 8.67–8.06 (m, 1 H), 7.88 (d, *J* = 5.0 Hz, 2 H), 7.47 (s, 2 H), 7.37 (s, 1 H).

^{13}C NMR (126 MHz, DMSO-d_6): δ = 162.79, 130.99, 129.39, 128.59, 127.73, 126.04.

LC–MS (ESI): *m*/*z* = 144.00 [M – H]$^+$.

4-(3-Bromophenyl)-1*H*-1,2,3-triazole (3b)[9]

Yield: 40.3 mg (90%); white solid.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.99 (d, *J* = 10.0 Hz, 2 H), 7.76 (d, *J* = 8.0 Hz, 1 H), 7.51 (d, *J* = 8.0 Hz, 1 H), 7.33 (t, *J* = 8.0 Hz, 1 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 131.99, 131.70, 130.51, 129.14, 124.67, 123.09.

LC–MS (ESI): *m*/*z* = 221.89 [M – H]$^+$.

4-(3-Nitrophenyl)-1*H*-1,2,3-triazole (3c)[9]

Yield: 35.7 mg (94%); white solid.

^{1}H NMR (500 MHz, DMSO-d_6): δ = 8.69–8.66 (m, 1 H), 8.63 (s, 1 H), 8.33 (d, *J* = 8.0 Hz, 1 H), 8.21 (dd, *J* = 8.0, 1.5 Hz, 1 H), 7.77 (t, *J* = 8.0 Hz, 1 H).

^{13}C NMR (126 MHz, DMSO-d_6): δ = 148.86, 144.20, 132.75, 132.20, 131.04, 129.11, 123.03, 120.19.

LC–MS (ESI): *m*/*z* = 189.00 [M – H]$^+$.

4-(2-Methoxyphenyl)-1*H*-1,2,3-triazole (3d)[9]

Yield: 31.5 mg (90%); white solid.

^{1}H NMR (500 MHz, DMSO-d_6): δ = 8.19 (s, 1 H), 7.99 (s, 1 H), 7.35 (t, *J* = 7.5 Hz, 1 H), 7.14 (d, *J* = 8.5 Hz, 1 H), 7.05 (t, *J* = 7.5 Hz, 1 H), 3.91 (s, 3 H).

^{13}C NMR (126 MHz, DMSO-d_6): δ = 156.31, 129.72, 127.87, 121.14, 112.16, 55.93.

LC–MS (ESI): *m*/*z* = 174.00 [M – H]$^+$.

4-(4-Chlorophenyl)-1*H*-1,2,3-triazole (3e)[9]

Yield: 32.6 mg (91%); white solid.

^{1}H NMR (500 MHz, DMSO-d_6): δ = 8.40 (s, 1 H), 8.01–7.82 (m, 2 H), 7.67–7.40 (m, 2 H).

^{13}C NMR (126 MHz, DMSO-d_6): δ = 133.11, 130.48, 129.34, 127.66.

LC–MS (ESI): *m*/*z* = 177.96 [M – H]$^+$.

3-(1*H*-1,2,3-Triazol-4-yl)benzonitrile (3f)[9]

Yield: 30.0 mg (88%); white solid.

^{1}H NMR (500 MHz, DMSO-d_6): δ = 8.50 (d, *J* = 5.0 Hz, 1 H), 8.30 (d, *J* = 7.5 Hz, 1 H), 8.21 (t, *J* = 7.5 Hz, 1 H), 7.89–7.73 (m, 1 H), 7.67 (dd, *J* = 16.5, 8.5 Hz, 1 H).

^{13}C NMR (126 MHz, DMSO-d_6): δ = 144.40, 132.21, 131.99, 130.73, 130.43, 129.30, 119.04, 112.56.

LC–MS (ESI): *m*/*z* = 169.00 [M – H]$^+$.

4-(4-Fluorophenyl)-1*H*-1,2,3-triazole (3g)[9]

Yield: 28.3 mg (87%); white solid.

^{1}H NMR (500 MHz, DMSO-d_6): δ = 8.34 (s, 1 H), 7.91 (dd, *J* = 7.5, 5.5 Hz, 2 H), 7.30 (t, *J* = 8.5 Hz, 2 H).

^{13}C NMR (126 MHz, DMSO-d_6): δ = 163.38, 161.43, 145.06, 128.06 (d, J_{C-F} = 8.2 Hz), 127.86, 116.28 (d, J_{C-F} = 21.7 Hz).

LC–MS (ESI): *m*/*z* = 162.00 [M – H]$^+$.

4-(2-Nitrophenyl)-1*H*-1,2,3-triazole (3h)[9]

Yield: 33.8 mg (89%); white solid.

^{1}H NMR (500 MHz, DMSO-d_6): δ = 8.26 (s, 1 H), 7.92 (d, J = 8.0 Hz, 1 H), 7.84 (dd, J = 7.5, 1.0 Hz, 1 H), 7.76 (dd, J = 14.5, 7.5 Hz, 1 H), 7.63 (t, J = 7.5 Hz, 1 H).

^{13}C NMR (126 MHz, DMSO-d_6): δ = 148.89, 132.95, 131.00, 129.99, 124.34, 124.05.

LC–MS (ESI): m/z = 188.99 [M – H]$^+$.

4-(3-Methoxyphenyl)-1*H*-1,2,3-triazole (3i)[9]

Yield: 33.6 mg (96%); white solid.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.92 (s, 1 H), 7.37–7.23 (m, 3 H), 6.86 (d, J = 8.0 Hz, 1 H), 3.79 (s, 3 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 160.09, 130.09, 118.63, 114.66, 111.41, 55.38.

LC–MS (ESI): m/z = 174.00 [M – H]$^+$.

4-(1*H*-1,2,3-Triazol-4-yl)benzonitrile (3j)[9]

Yield: 30.6 mg (90%); yellow solid.

^{1}H NMR (500 MHz, DMSO-d_6): δ = 8.57 (s, 1 H), 8.16–8.01 (m, 2 H), 7.93 (dd, J = 8.0, 4.0 Hz, 2 H).

^{13}C NMR (126 MHz, DMSO-d_6): δ = 144.79, 135.57, 133.39, 126.56, 119.24, 110.79.

LC–MS (ESI): m/z = 169.00 [M – H]$^+$.

4-[3,5-Bis(trifluoromethyl)phenyl]-1*H*-1,2,3-triazole (3k)[7b]

Yield: 50.6 mg (90%); white solid.

^{1}H NMR (500 MHz, DMSO-d_6): δ = 8.62 (s, 1 H), 8.44 (s, 2 H), 7.91 (s, 1 H).

^{13}C NMR (126 MHz, DMSO-d_6): δ = 143.54, 133.75, 131.85, 131.59, 131.32, 131.06, 126.85, 125.98, 124.68, 122.51, 121.24, 120.35.

LC–MS (ESI): m/z = 279.99 [M – H]$^+$.

4-(2-Bromophenyl)-1*H*-1,2,3-triazole (3l)[9]

Yield: 41.6 mg (93%); white solid.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.30 (s, 1 H), 7.83 (d, J = 7.5 Hz, 1 H), 7.76–7.63 (m, 1 H), 7.42 (dd, J = 14.0, 7.5 Hz, 1 H), 7.27 (dd, J = 11.5, 5.0 Hz, 1 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 133.73, 131.02, 130.77, 129.98, 127.73, 121.93.

LC–MS (ESI): m/z = 221.90 [M – H]$^+$.

4-(2,4-Dichlorophenyl)-1*H*-1,2,3-triazole (3m)[9]

Yield: 40.2 mg (94%); white solid.

^{1}H NMR (500 MHz, DMSO-d_6): δ = 8.42 (s, 1 H), 7.97 (d, J = 8.5 Hz, 1 H), 7.76 (s, 1 H), 7.60–7.41 (m, 1 H).

^{13}C NMR (126 MHz, DMSO-d_6): δ = 141.97, 133.72, 132.17, 131.73, 130.14, 128.80, 128.24.

LC–MS (ESI): m/z = 211.90 [M – H]$^+$.

4-(*p*-Tolyl)-1*H*-1,2,3-triazole (3n)[9]

Yield: 29.2 mg (92%); white solid.

^{1}H NMR (500 MHz, DMSO-d_6): δ = 15.03 (s, 1 H), 8.27 (s, 1 H), 7.75 (d, J = 8.0 Hz, 2 H), 7.27 (d, J = 8.0 Hz, 2 H), 2.33 (s, 3 H).

^{13}C NMR (126 MHz, DMSO-d_6): δ = 146.27, 137.51, 129.50, 127.90, 125.57, 20.85.

LC–MS (ESI): m/z = 158.00 [M – H]$^+$.

4-(2-Chlorophenyl)-1*H*-1,2,3-triazole (3o)[9]

Yield: 34.1 mg (95%); white solid.

^{1}H NMR (500 MHz, DMSO-d_6): δ = 8.35 (s, 1 H), 7.91 (dd, J = 8.0, 1.5 Hz, 1 H), 7.61–7.50 (m, 1 H), 7.49–7.30 (m, 2 H).

^{13}C NMR (126 MHz, DMSO-d_6): δ = 142.73, 131.38, 130.67, 130.14, 129.57, 127.96.

LC–MS (ESI): m/z = 177.97 [M – H]$^+$.

4-(3,4-Dimethylphenyl)-1*H*-1,2,3-triazole (3p)

Yield: 32.1 mg (93%); white solid; mp 167–168 °C.

IR (KBr): 3136, 1615, 1561, 1488, 1451, 1395, 888, 820 cm^{-1}.

^{1}H NMR (500 MHz, DMSO-d_6): δ = 8.24 (s, 1 H), 7.64 (s, 1 H), 7.57 (d, J = 8.0 Hz, 1 H), 7.19 (d, J = 8.0 Hz, 1 H), 2.24 (d, J = 16.0 Hz, 6 H).

^{13}C NMR (126 MHz, DMSO-d_6): δ = 137.21, 136.76, 130.43, 128.15, 127.11, 123.49, 19.82, 19.58.

GC–MS (EI): m/z = 173.0 [M]$^+$.

HRMS (ESI): m/z [M + H]$^+$ calcd for $C_{10}H_{11}N_3$: 174.10257; found: 174.10258.

4-(3-Chlorophenyl)-1*H*-1,2,3-triazole (3q)

Yield: 30.5 mg (85%); white solid; mp 172–173 °C.

IR (KBr): 1602, 1569, 1462, 1447, 799 cm^{-1}.

^{1}H NMR (500 MHz, DMSO-d_6): δ = 8.44 (s, 1 H), 7.93 (t, J = 1.5 Hz, 1 H), 7.84 (d, J = 8.0 Hz, 1 H), 7.47 (t, J = 8.0 Hz, 1 H), 7.39 (dd, J = 7.5, 1.0 Hz, 1 H).

^{13}C NMR (126 MHz, DMSO-d_6): δ = 144.68, 134.26, 132.92, 131.06, 128.19, 125.62, 124.46.

GC–MS (EI): m/z = 178.9 [M]$^+$.

HRMS (ESI): m/z [M + H]$^+$ calcd for $C_8H_6ClN_3$: 180.03230; found: 180.03224.

4-(Furan-2-yl)-1*H*-1,2,3-triazole (3r)[9]

Yield: 21.6 mg (80%); white solid.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.89 (s, 1 H), 7.42 (d, J = 1.0 Hz, 1 H), 6.76 (d, J = 3.5 Hz, 1 H), 6.42 (dd, J = 3.5, 1.5 Hz, 1 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 145.26, 142.80, 139.24, 128.22, 111.61, 107.79.

LC–MS (ESI): m/z = 134.00 [M – H]$^+$.

Acknowledgment

Financial support from the National Natural Science Foundation of China (21402103), the research fund of Qingdao Agricultural University's High-Level Person [631303], and the Scientific Research Foundation of Shandong Province Outstanding Young Scientist Award [BS2013YY024] are gratefully acknowledged. We thank Wen-Hui Zhai, Da-An Song, Qing-Nan Li, Peng-Chao Jiang and Cui-Hua Cao for preparing the Supporting Information and for their helpful discussions.

Supporting Information

Supporting information for this article is available online at http://dx.doi.org/10.1055/s-0035-1560488.

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