Highly Efficient Cadmium-Catalyzed Three-Component Coupling of an Aldehyde, Alkyne, and Amine via C–H Activation under Microwave Conditions

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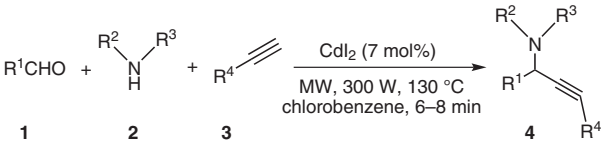
Abstract: The first use of Cd^{2+} as catalyst for a facile three-component coupling of an aldehyde, alkyne, and amine has been demonstrated to synthesize propargylamines under microwave irradiation in chlorobenzene without the use of a co-catalyst or activator in the absence of inert atmosphere. This method has been proved to be applicable to a wide range of substrates.

Key words: transition-metal catalyst, multicomponent reaction, aldehydes, A^3 coupling, propargylamines

Transition-metal-catalyzed multicomponent reactions are of utmost importance in organic synthesis, comprising a plethora of versatile carbon–carbon and carbon–heteroatom bond-forming processes and asymmetric transformations.[1] Such processes are endowed with high yields and impressive regio- and stereoselectivities; thus becoming a part of an ever-growing armory of useful synthetic tools available to organic chemists today. Improved syntheses of propargylamines via the activation of a terminal alkyne C–H bond using metal-catalyzed multicomponent strategies remain of continued interest to organic chemists in terms of operational simplicity and cost effectiveness. Being important building blocks and versatile synthons, propargylamines are highly featured in organic syntheses of many biologically active nitrogen-containing compounds[2] such as conformationally restricted peptide isosteres, oxotremorine analogues, allylamines, oxazoles, pyrroles, and β-lactams.[3] Classical methods for the preparation of propargylamines have usually exploited the relatively high acidity of a terminal acetylenic C–H bond to form alkynyl-metal reagents by the reaction with strong bases such as butyllithium,[4a] organomagnesium compounds,[4b] or LDA.[5] These reagents are, however, highly moisture sensitive and are required in stoichiometric quantities under strictly controlled reaction conditions. In recent years, enormous progress has been made in expanding the scope of the direct addition of alkynes to carbon–nitrogen double bonds either preformed (imines) or in one-pot (from aldehyde and amine) by employing various complexes and salts of transition metals, such as iron,[6] zinc,[7] copper,[8] ruthenium–copper,[9] silver,[10] indium,[11] iridium,[12] gold,[13] mercury,[14] and nickel.[15] Microwave,[8a,16a] and ultrasonic irradiation[16b] have also been used in the presence of Cu(I) salts.

Despite the availability of a number of methods for the synthesis of propargylamines, the improved and alternative approach to propargylamines employing new transition-metal-catalyzed multicomponent strategies remains of current interest to organic chemists in terms of efficiency, yield, cost, and simplicity of operations involved. The long reaction time, which is frequently required for full conversions, has limited the exploitation of catalyses in high-throughput synthesis. Rapid and reliable applications are therefore desired not only for high-speed production of new chemical entities,[17] but also for catalysis in general. As a part of our ongoing program on multicomponent reactions,[18] we found that a combination of CdI_2 catalysis and microwave irradiation leads to very strong acceleration of the process (the reaction time shortens from hours to minutes) and considerable increase in product yields (Scheme 1).



Scheme 1 CdI_2-catalyzed A^3 coupling

This is the first example of a truly catalytic synthesis of propargylamines using cadmium salts, motivated by its use as catalyst.[19] In order to develop a viable approach, a variety of catalysts was first investigated for the typical multicomponent reaction of benzaldehyde (**1a**), morpholine, and phenylacetylene under conventional as well as microwave irradiation conditions. The outcome is given in Table 1. The data reveal that CdI_2 under conventional conditions brings about the reaction to afford the product **4a** in 87% yield (Table 1, entry 26). Application of monomode MW irradiation at the same temperature, however, brought about a notable increase in the yield as well as a dramatic reduction in the reaction time, the best result being obtained using 300 W at 130 °C in just 7 minutes using 7 mol% CdI_2 (cf. entry 26). It is noticed that, in the absence of CdI_2, no conversion to the product was obtained even after 20 minutes of MW heating or 10 hours of reflux.

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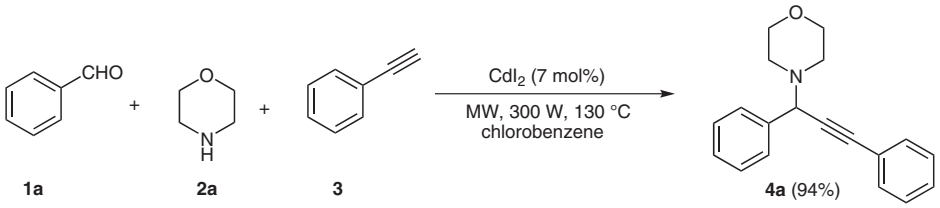
The use of catalysts such as $Cd(OAc)_2·2H_2O$, $Cd(NO_3)_2·2H_2O$, $CdCl_2·H_2O$, $SnCl_2$, and $SnCl_2·2H_2O$ also promoted the reaction to a reasonable extent (Table 1, entries 2–6), but other catalysts such as Cd^{2+}-K10, $SnCl_4$, $MnCl_2·6H_2O$, and $Sc(OTf)_3$ did not work well (Table 1, entries 1, 7–9).

Table 1 Screening of Reaction Parameters for the Synthesis[a] of **4a**



Entry	Catalyst (mol%)	Solvent	Conventional			Microwave			
			Temp (°C)	Time (h)	Yield (%)[b]	Power (W)	Temp (°C)	Time (min)	Yield (%)[b]
1	Cd^{2+}-K10	chlorobenzene	130	8	45	300	130	20	58
2	$Cd(OAc)_2×2H_2O$ (10)	chlorobenzene	130	10	65	300	130	20	78
3	$Cd(NO_3)_2×2H_2O$ (10)	chlorobenzene	130	8	50	300	130	20	62
4	$CdCl_2×H_2O$ (10)	chlorobenzene	130	8	78	300	130	20	85
5	$SnCl_2$(10)	chlorobenzene	130	8	55	300	130	20	68
6	$SnCl_2×2H_2O$(10)	chlorobenzene	130	10	50	300	130	20	60
7	$SnCl_4$ (10)	chlorobenzene	130	10	45	300	130	20	54
8	$MnCl_2×6H_2O$ (10)	chlorobenzene	130	10	30	300	130	20	42
9	$Sc(OTf)_3$ (10)	chlorobenzene	130	10	25	300	130	20	30
10	CdI_2 (10)	chlorobenzene	130	8	88	300	130	10	94
11	CdI_2 (10)	EtOH	78	8	25	300	78	20	35
12	CdI_2 (10)	MeOH	68	8	30	300	68	20	40
13	CdI_2 (10)	THF	65	8	trace	300	65	20	trace
14	CdI_2 (10)	ethylene glycol	130	10	38	300	130	20	46
15	CdI_2 (10)	DCE	83	8	trace	300	83	20	trace
16	CdI_2 (10)	H_2O	100	8	20	300	100	20	35
17	CdI_2 (10)	Bimim[BF_4]	130	8	35	300	130	20	47
18	CdI_2 (10)	MeCN	81	10	60	300	81	20	75
19	CdI_2 (10)	toluene	111	10	81	300	110	20	55
20	CdI_2 (10)	dichlorobenzene	130	10	60	300	130	20	68
21	CdI_2 (10)	nitrobenzene	130	10	65	300	130	20	70
22	CdI_2 (10)	nitromethane	100	10	trace	300	100	20	trace
23	CdI_2 (10)	NMP	130	10	trace	300	130	20	20
24	CdI_2 (10)	no solvent	130	10	n.r.[c]	300	130	20	n.r.[c]
25	CdI_2 (7)	chlorobenzene	100	10	68	300	100	15	75
26	CdI_2 (7)	chlorobenzene	130	5	87	300	130	7	94
27	CdI_2 (5)	chlorobenzene	130	8	74	300	130	15	85

[a] Used benzaldehyde–morpholine–phenylacetylene (1:1.1:1.2).
[b] Isolated yield based on benzaldehyde.
[c] n.r. = no reaction.

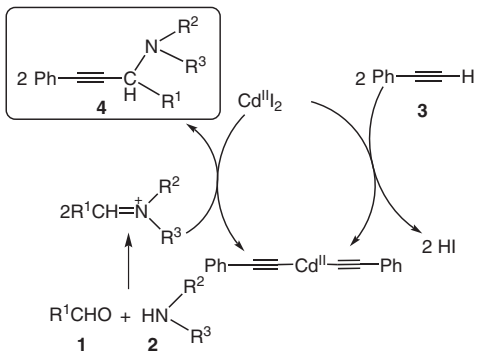
In order to screen the solvent effect, the model reaction was carried out in different solvents using 10 mol% of CdI_2 under conventional and MW conditions (cf. Table 1). In all the solvents tried, the optimum conversion was observed at reflux temperature. An advantage of chlorobenzene (at 130 °C) was conspicuous as compared to toluene (at 110 °C; Table 1, entries 10, 19). With other solvents, the yield of the product was either very low (Table 1, entries 11–17, 22, and 23), or medium (Table 1, entries 18, 20, and 21). In terms of the catalyst concentration, 7 mol% of cadmium iodide was sufficient and necessary for completion of the A^3-coupling reaction (entry 26), albeit the reaction remained incomplete when 5 mol% of the catalyst was used (Table 1, entry 27). When the test reaction was conducted under inert atmosphere using argon or nitrogen, the yields were comparable to those obtained under aerobic conditions.

Intrigued by these observations, the reaction was carried out under controlled microwave irradiation by varying different parameters such as MW power (200 W, 250 W, and 300 W), temperature, time, and solvents. The 300 W power output and reflux temperature of the solvent was required to accomplish the maximum conversion and therefore the same was applied to test the efficacy of other catalysts for 20 minutes (Table 1). As evident from Table 1, the best result is obtained using 300 W at 130 °C in 7 minutes in the presence of 7 mol% CdI_2 in chlorobenzene (cf. entry 26); further increase in temperature of the sealed reaction vessel and time did not enhance the product yield. Other solvents did not work well under microwave irradiation. Under the optimized set of MW reaction conditions (300 W, 130 °C), benzaldehyde (**1a**) underwent multicomponent reaction with morpholine and phenyl acetylene in a molar ratio of 1:1.1:1.2 with CdI_2 (7 mol%) in chlorobenzene to afford propargylamine **4a** in 94% yield in 7 minutes (Table 1). Under the optimized set of reaction conditions, a number of aldehydes and amines was subsequently reacted with phenylacetylene to afford various propargylamines in excellent yields (Table 2).[20] Interestingly, aldehydes such as benzaldehyde, *p*-methoxybenzaldehyde, *p*-methylbenzaldehyde, *p*-chlorobenzaldehyde, *m*-chlorobenzaldehyde, and *p*-bromo-benzaldehyde reacted effectively with morpholine/piperidine and phenyl acetylene to produce the corresponding propargylic amines in exellent yields (Table 2, entries 1–6 and 17–21); but *p*-nitrobenzaldehyde did not react (Table 2, entry 7). Similarly, heteroaromatic aldehydes such as thiophene-2-carboxaldehyde and furan-2-carboxaldehyde also participated well in these reactions (Table 2, entries 8, 9, and 22). In addition to aromatic aldehydes, the aliphatic aldehydes formaldehyde and pentanal also underwent efficient conversion (Table 2, entries 10 and 11). As regards the reactivity of various amines, piperizine, benzylamine, aniline, and piperidine, (Table 2, entries 12 and 14–16) gave rise to smooth coupling, whereas methylamine did not react (Table 2, entry 13). The analytical data of all the products are in full agreement with the assigned structures.

Table 2 One-Pot Synthesis of Propargylamines[a] Using CdI_2 as Catalyst

Entry	R^1	Amine	R^3	Product	Time (min)	Yield (%)[b]
1	Ph	morpholine	Ph	**4a**	7	94
2	4-$MeOC_6H_4$	morpholine	Ph	**4b**	7	92
3	4-MeC_6H_4	morpholine	Ph	**4c**	8	90
4	4-BrC_6H_4	morpholine	Ph	**4d**	7	92
5	4-ClC_6H_4	morpholine	Ph	**4e**	8	89
6	3-ClC_6H_4	morpholine	Ph	**4f**	7	88
7	4-$O_2NC_6H_4$	morpholine	Ph	**4g**	8	n.r.[c]
8	2-furan	morpholine	Ph	**4h**	7	93
9	2-thiophene	morpholine	Ph	**4i**	7	92
10	H	morpholine	Ph	**4j**	8	90
11	Bu	morpholine	Ph	**4k**	8	82
12	Ph	piperazine	Ph	**4l**	8	90
13	Ph	methylamine	Ph	**4m**	8	n.r.[c]
14	Ph	benzylamine	Ph	**4n**	8	72
15	Ph	aniline	Ph	**4o**	7	80
16	Ph	piperidine	Ph	**4p**	6	96
17	4-$MeOC_6H_4$	piperidine	Ph	**4q**	7	94
18	4-MeC_6H_4	piperidine	Ph	**4r**	7	92
19	4-BrC_6H_4	piperidine	Ph	**4s**	7	92
20	4-ClC_6H_4	piperidine	Ph	**4t**	8	90
21	3-ClC_6H_4	piperidine	Ph	**4u**	8	89
22	2-furan	piperidine	Ph	**4v**	7	94

[a] Reaction conditions: aldehyde (1 mmol), amine (1.1 mmol), phenylacetylene (1.2 mmol), CdI_2 (7 mol%), chlorobenzene (2 mL), MW, 300 W, 130 °C.
[b] Isolated yield based on aldehyde.
[c] n.r. = no reaction.



Scheme 2 Plausible mechanism for the cadmium-catalyzed synthesis of propargylamines

A plausible mechanism for the investigated reaction is outlined in Scheme 2. The formation of dialkynyl cadmium species is well established,[21] and the presence of an excess of phenylacetylene is expected to give a dialkynyl cadmium species to initiate reaction.

In conclusion, we have successfully developed an efficient microwave protocol using CdI_2 as catalyst for one-pot multicomponent synthesis of diverse propargylamines in excellent yields. Notable features of the protocol include clean and simple reaction conditions, use of a readily available and inexpensive catalyst, tolerance of various functional groups, and aerobic conditions. We believe that this protocol will be a valuable addition to modern synthetic methodologies for one-pot synthesis of propargylamines.

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References and Notes

(1) (a) D'Souza, D. M.; Muller, T. J. J. *Chem. Soc. Rev.* **2007**, *36*, 1095. (b) *Multicomponent Reactions*; Zhu, J.; Bienayme, H., Eds.; Wiley: Weinheim, **2005**.

(2) (a) Dyker, G. *Angew. Chem. Int. Ed.* **1999**, *38*, 1698. (b) Naota, T.; Takaya, H.; Murahashi, S. I. *Chem. Rev.* **1998**, *98*, 2599. (c) Konishi, M.; Ohkuma, H.; Tsuno, T.; Oki, T.; VanDuyne, G. D.; Clardy, J. *J. Am. Chem. Soc.* **1990**, *112*, 3715. (d) Naoi, M.; Maruyama, W.; Youdim, M. B. H.; Yu, P.; Boulton, A. A. *Inflammopharmacology* **2003**, *11*, 175.

(3) (a) Zani, L.; Bolm, C. *Chem. Commun.* **2006**, 4263. (b) Wei, C.; Li, Z.; Li, C.-J. *Synlett* **2004**, 1472.

(4) (a) Wakefield, B. J. In *Organolithium Methods in Organic Synthesis*; Academic Press: London, **1988**, Chap. 3, 32. (b) Wakefield, B. J. *Organomagnesium Methods in Organic Synthesis*; Academic Press: London, **1995**, Chap. 3, 46.

(5) (a) Harada, T.; Fujiwara, T.; Iwazaki, K.; Oku, A. *Org. Lett.* **2000**, *2*, 1855. (b) Rosas, N.; Sharma, P.; Alvarez, C.; Gomez, E.; Gutierrez, Y.; Mendez, M.; Toscano, R. A.; Maldonado, L. A. *Tetrahedron Lett.* **2003**, *44*, 8019. (c) Ding, C.-H.; Chen, D.-D.; Luo, Z.-B.; Dai, L.-X.; Hou, X.-L. *Synlett* **2006**, 1272.

(6) (a) Chen, W.-W.; Nauyen, R. V.; Li, C.-J. *Tetrahedron Lett.* **2009**, *50*, 2895. (b) Sreedhar, B.; Suresh Kumar, A.; Reddy, P. S. *Tetrahedron Lett.* **2010**, *51*, 1891.

(7) (a) Lee, K. Y.; Lee, C. G.; Na, J. E.; Kim, J. N. *Tetrahedron Lett.* **2005**, *46*, 69. (b) Zani, L.; Alesi, S.; Cozzi, P. G.; Bolm, C. *J. Org. Chem.* **2006**, *71*, 1558. (c) Ramu, E.; Varala, R.; Sreelatha, N.; Adapa, S. R. *Tetrahedron Lett.* **2007**, *48*, 7184. (d) Kantam, M. L.; Balasubrahmanyam, V.; Kumar, K. B. S.; Venkanna, G. T. *Tetrahedron Lett.* **2007**, *48*, 7332.

(8) (a) Shi, L.; Tu, Y.-Q.; Wang, M.; Zhang, F.-M.; Fan, C.-A. *Org. Lett.* **2004**, *6*, 1001. (b) Huma, H. Z. S.; Halder, R.; Karla, S. S.; Das, J.; Iqbal, J. *Tetrahedron Lett.* **2002**, *43*, 6485. (c) Kabalka, G. W.; Wang, L.; Pagni, R. M. *Synlett* **2001**, 676. (d) Wei, C.; Li, C.-J. *J. Am. Chem. Soc.* **2002**, *124*, 5638. (e) Wei, C.; Mague, J. T.; Li, C. J. *Proc. Natl. Acad. Sci. U.S.A.* **2004**, *101*, 5749. (f) Gommarman, N.; Koradin, C.; Polborn, K.; Knochel, P. *Angew. Chem. Int. Ed.* **2003**, *42*, 5763. (g) Colombo, F.; Benaglia, M.; Orlandi, S.; Usuelli, F. *J. Mol. Catal. A: Chem.* **2006**, *260*, 128. (h) Gommermann, N.; Knochel, P. *Chem. Eur. J.* **2006**, *12*, 4380. (i) Bisai, A.; Singh, V. K. *Org. Lett.* **2006**, *8*, 2405. (j) Li, P.; Wang, L. *Tetrahedron* **2007**, *63*, 5455. (k) Park, S. B.; Alper, H. *Chem. Commun.* **2005**, 1315. (l) Choudary, B. M.; Sridhar, C.; Kantam, M. L.; Sreedhar, B. *Tetrahedron Lett.* **2004**, *45*, 7319. (m) Wang, M.; Li, P.; Wang, L. *Eur. J. Org. Chem.* **2008**, 2255. (n) Sreedhar, B.; Reddy, P. S.; Krishna, C. S. V.; Babu, P. V. *Tetrahedron Lett.* **2007**, *48*, 7882. (o) Likhar, P. R.; Roy, S.; Roy, M.; Subhas, M. S.; Kantam, M. L.; De R, L. *Synlett* **2007**, 2301. (p) Kantam, M. L.; Yadav, J.; Laha, S.; Jha, S. *Synlett* **2009**, 1791. (q) Kantam, M. L.; Laha, S.; Yadav, J.; Bhargava, S. *Tetrahedron Lett.* **2008**, *49*, 3083. (r) Kidwai, M.; Bansal, V.; Mishra, N. K.; Kumar, A.; Mozumdar, S. *Synlett* **2007**, 1581. (s) Aliaga, M. J.; Ramon, D. J.; Yus, M. *Org. Biomol. Chem.* **2010**, *8*, 43. (t) Patil, M. K.; Keller, M.; Reddy, B. M.; Pale, P.; Sommer, J. *Eur. J. Org. Chem.* **2008**, 4440.

(9) Li, C. J.; Wei, C. *Chem. Commun.* **2002**, 268.

(10) (a) Wei, C.; Li, Z.; Li, C.-J. *Org. Lett.* **2003**, *5*, 4473. (b) Li, Z.; Wei, C.; Chen, L.; Varma, R. S.; Li, C.-J. *Tetrahedron Lett.* **2004**, *45*, 2443. (c) Reddy, K. M.; Babu, N. S.; Prasad, P. S. S.; Lingaiah, N. *Tetrahedron Lett.* **2006**, *47*, 7563. (d) Zhang, X.; Corma, A. *Angew. Chem. Int. Ed.* **2008**, *47*, 4358. (e) Li, P.; Wang, L.; Zhang, Y.; Wang, M. *Tetrahedron Lett.* **2008**, *49*, 6650. (f) Yan, W.; Wang, R.; Xu, Z.; Xu, J.; Lin, L.; Shen, Z.; Zhou, Y. *J. Mol. Catal. A: Chem.* **2006**, *255*, 81. (g) Wang, S.; He, X.; Song, L.; Wang, Z. *Synlett* **2009**, 447.

(11) (a) Zhang, Y.; Li, P.; Wang, M.; Wang, L. *J. Org. Chem.* **2009**, *74*, 4364. (b) Jadav, J. S.; Reddy, B. V. S.; Gopal, A. V. H.; Patil, K. S. *Tetrahedron Lett.* **2009**, *50*, 3993.

(12) (a) Fischer, C.; Carreira, E. M. *Org. Lett.* **2001**, *3*, 4319. (b) Sakaguchi, S.; Kubo, T.; Ishii, Y. *Angew. Chem. Int. Ed.* **2001**, *40*, 2534. (c) Sakaguchi, S.; Mizuta, T.; Furuwan, M.; Kubo, T.; Ishii, Y. *Chem. Commun.* **2004**, 1638.

(13) (a) Wei, C.; Li, C.-J. *J. Am. Chem. Soc.* **2003**, *125*, 9584. (b) Lo, V. K.-Y.; Liu, Y.; Wong, M.-K.; Che, C.-M. *Org. Lett.* **2006**, *8*, 1529. (c) Kantam, M. L.; Prakash, B. V.; Reddy, C. R. V.; Sreedhar, B. *Synlett* **2005**, 2329.

(14) Hua, L. P.; Lei, W. *Chin. J. Chem.* **2005**, *23*, 1076.

(15) Namitharan, K.; Pitchumani, K. *Eur. J. Org. Chem.* **2010**, 411.

(16) (a) Leadbeater, N. E.; Torenius, H. M.; Tye, H. *Mol. Diversity* **2003**, *7*, 135. (b) Sreedhar, B.; Reddy, P. S.; Prakash, B. V.; Ravindra, A. *Tetrahedron Lett.* **2005**, *46*, 7019.

(17) (a) Loupy, A. In *Microwaves in Organic Synthesis*, 2nd ed.; Wiley-VCH: Weinheim, **2006**. (b) Caddick, S.; Fitzmaurice, R. *Tetrahedron* **2009**, *65*, 3325. (c) Dallinger, D.; Kappe, C. O. *Chem. Rev.* **2007**, *107*, 2563. (d) Kappe, C. O. *Angew. Chem. Int. Ed.* **2004**, *43*, 6250. (e) Kappe, C. O.; Stadler, A. In *Microwaves in Organic and Medicinal Chemistry*; Wiley-VCH: Weinheim, **2005**, 182. (f) Shore, G.; Morin, S.; Organ, M. G. *Angew. Chem. Int. Ed.* **2006**, *45*, 276. (g) Comer, E.; Organ, M. G. *J. Am. Chem. Soc.* **2005**, *127*, 8160.

(18) (a) Raghuvanshi, D. S.; Singh, K. N. *ARKIVOC* **2010**, *(x)*, 305. (b) Singh, K. N.; Singh, S. K. *ARKIVOC* **2009**, *(xiii)*, 153. (c) Singh, S. K.; Singh, K. N. *J. Heterocycl. Chem.* **2010**, *47*, 194. (d) Raghuvanshi, D. S.; Singh, K. N. *J. Heterocycl. Chem* **2010**, *47*, 1323.

(19) (a) Narsaiah, A. V.; Basak, A. K.; Nagaiah, K. *Synthesis* **2004**, 1253. (b) Saito, M.; Nakajima, M.; Hashimoto, S. *Chem. Commun.* **2000**, 1851.

(20) **General Procedure for the Synthesis of Propargylamines**
Aldehyde (1 mmol), amine (1.1 mmol), alkyne (1.2 mmol), CdI_2 (7 mol%), and chlorobenzene (2 mL) were placed in a sealed pressure-regulation 10 mL pressurized vial with 'snap-on' cap, and the mixture was irradiated in a single-mode microwave synthesis system at 300 W and 130 °C for 7–8 min. After completion of the reaction (as monitored by TLC), the solvent was evaporated under vacuum. Water (20 mL) was added to the reaction mixture, and the product was extracted with EtOAc (3 × 10 mL). The combined organic phases were dried over anhyd $MgSO_4$, filtered, and the solvent was evaporated under vacuum. The residue was purified by column chromatography on silica gel (EtOAc–hexane, 1:9) to afford the pure propargylamines.

Representative Data
4-(1,3-Diphenylprop-2-ynyl)morpholine (4a)
FT-IR (KBr): 2935, 2756, 1590, 1490, 1451, 1319, 1152, 757, 694 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.61 (d, *J* = 7.2 Hz, 2 H), 7.49 (m, 2 H), 7.39–7.25 (m, 6 H), 4.78 (s, 1 H), 3.76–3.72 (m, 4 H), 2.64–2.61 (m, 4 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 137.7, 131.7, 128.5, 128.2, 128.3, 128.0, 127.7, 122.9, 88.4, 84.9, 67.1, 62.0, 49.8. Anal. Calcd for $C_{19}H_{19}NO$: C, 82.28; H, 6.90; N, 5.05. Found: C, 82.32; H, 6.82; N, 5.12.

(21) Barr, D.; Edwards, A. J.; Raithby, P. R.; Rennie, M.-A.; Verhorevoort, K.; Wright, D. S. *Chem. Commun.* **1994**, 1627.