Efficient Palladium-Catalyzed Suzuki–Miyaura Cross-Coupling of Iodoethynes with Arylboronic Acids under Aerobic Conditions

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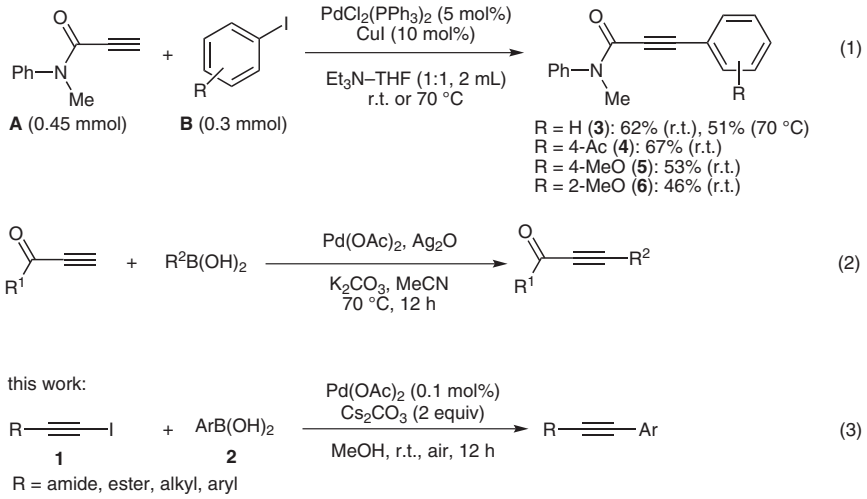
Abstract: Ligand-free palladium-catalyzed Suzuki–Miyaura cross-coupling of iodoethynes with arylboronic acids under aerobic conditions has been developed. In the presence of palladium(II) acetate and cesium carbonate, a variety of iodoethynes underwent the Suzuki–Miyaura cross-coupling reaction with arylboronic acids at room temperature to afford the corresponding internal alkynes in moderate to good yields. It is noteworthy that this protocol proceeds under mild and aerobic conditions without the aid of ligands.

Key words: palladium, iodoethynes, arylboronic acids, Suzuki–Miyaura, cross-coupling , alkynes

Recently, *N*,3-diarylphenylpropiolamides were employed in the synthesis of highly pharmaceutically valuable 2-methyleneindolin-1-ones in our research groups,[1] that of Zhu,[2] and others.[3] Generally, *N*,3-diarylphenylpropiolamides can be prepared through the traditional Sonogashira method using electron-poor alkynes and aryl halides as the reaction partners;[4–6] however, the yields are usually low to moderate depending on the properties of both alkynes and aryl halides (Scheme 1, equation 1).[4c] Therefore, the development of a novel cross-coupling alternative to the synthesis of such alkynes is interesting.[5,6] Very recently, we reported a modified protocol for the synthesis of electron-poor alkynes, such as *N*,3-diarylphenylpropiolamides, by palladium-catalyzed Sonogashira cross-coupling reaction of electron-poor terminal alkynes with arylboronic acids under ligand-free and aerobic conditions (Scheme 1, equation 2).[6d] However, an excess amount of silver salt was required to promote the reaction. As part of our continuing interest in electron-poor internal alkyne synthesis,[6d] we here report another general and efficient palladium-catalyzed Suzuki–Miyaura protocol employing iodoethynes[5g] and arylboronic acids for the synthesis of numerous internal alkynes, including electron-poor internal alkynes (Scheme 1, equation 3).

The reaction between 3-iodo-*N*-methyl-*N*-phenyl propiolamide (**1a**) and phenylboronic acid (**2a**) was chosen as a model reaction to screen the optimal reaction conditions; the results are summarized in Table 1. To our delight, treatment of amide **1a** with **2a** using 1 mol% palladium(II) acetate and two equivalents of cesium carbonate in methanol under air atmosphere afforded the desired product **3** in 82% yield after 12 hours (entry 1). The yield of **3** was increased slightly to 86% at a loading of 0.1 mol% palladium(II) acetate (entry 2). However, only 47% yield was isolated in the presence of 0.01 mol% palladium(II) ace-



Scheme 1 Palladium-catalyzed synthesis of electron-poor internal alkynes

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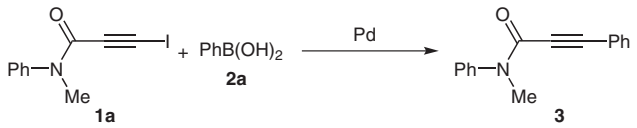
Table 1 Screening Optimal Conditions[a]



Entry	[Pd] (mol%)	Base	Solvent	Isolated yield (%)
1	$Pd(OAc)_2$ (1.0)	Cs_2CO_3	MeOH	82
2	$Pd(OAc)_2$ (0.1)	Cs_2CO_3	MeOH	86
3[b]	$Pd(OAc)_2$ (0.01)	Cs_2CO_3	MeOH	47
4	–	Cs_2CO_3	MeOH	0
5	$Pd(OAc)_2$ (0.1)	K_2CO_3	MeOH	61
6	$Pd(OAc)_2$ (0.1)	Et_3N	MeOH	35
7	$Pd(OAc)_2$ (0.1)	KOAc	MeOH	30
8	$Pd(OAc)_2$ (0.1)	NaOMe	MeOH	57
9	$Pd(OAc)_2$ (0.1)	K_3PO_4	MeOH	31
10	$Pd(OAc)_2$ (0.1)	Cs_2CO_3	EtOH	83
11	$Pd(OAc)_2$ (0.1)	Cs_2CO_3	*i*-PrOH	32
12	$Pd(OAc)_2$ (0.1)	Cs_2CO_3	THF	27
13	$Pd(OAc)_2$ (0.1)	Cs_2CO_3	DMF	25
14	$Pd(OAc)_2$ (0.1)	Cs_2CO_3	MeCN	11
15	$Pd(OAc)_2$ (0.1)	Cs_2CO_3	toluene	trace
16[c]	$Pd(OAc)_2$ (0.1)	Cs_2CO_3	MeOH	56
17[d]	$Pd(OAc)_2$ (0.1)	Cs_2CO_3	MeOH	41
18	$PdCl_2$ (0.1)	Cs_2CO_3	MeOH	75
19	$PdCl_2(PPh_3)_2$ (0.1)	Cs_2CO_3	MeOH	55

[a] Reaction conditions: **1a** (0.3 mmol), **2a** (0.36 mmol), base (2 equiv), solvent (2 mL), 12 h, r.t., air atmosphere.
[b] Reaction performed for 60 h; the conversion of **1a** was 53% (determined by GC analysis).
[c] Ph_3P (0.2 mol%) was added.
[d] DABCO (0.2 mol%) was added.

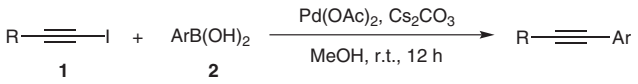
tate, even after prolonging the reaction time to 60 hours (entry 3). It was noted that the reaction did not take place without a palladium catalyst (entry 4).

The effect of the base was then investigated and it was found that the use of other bases, such as potassium carbonate, triethylamine, potassium acetate, sodium methoxide or potassium phosphate, were inferior to cesium carbonate (entries 5–9). Screening revealed that the use of ethanol as solvent gave identical results to those obtained in methanol (entry 10), but other solvents, including isopropanol, tetrahydrofuran, *N*,*N*-dimethylformamide, acetonitrile, and toluene, were less efficient (entries 11–15). Two ligands, triphenylphosphine and 1,4-diazabicyclo[2.2.2]octane (DABCO), were also examined, but the results showed that both reduced the performance of the reaction (entries 16 and 17). Finally, the reaction was carried out using palladium(II) chloride or Bis(triphenylphosphine)palladium(II) chloride $[PdCl_2(PPh_3)_2]$ catalysts, but both were found to be less effective than palladium(II) acetate in terms of yields (entries 18 and 19).

With the optimal reaction conditions in hand, the scope of the reaction was investigated with a range of iodoethynes and arylboronic acids (Table 2). Initially, a variety of arylboronic acids **2b–m** were investigated by their reaction with 3-iodo-*N*-methyl-*N*-phenylpropiolamide (**1a**; entries 1–12). The results demonstrated that the optimal conditions were general for arylboronic acids, and were compatible with several functional groups, including methyl, methoxy, fluoro, chloro, iodo, formyl, acetyl, nitro, and vinyl groups, on the aryl moiety. For example, arylboronic acids **2b–e**, with a methyl or methoxy group, smoothly underwent the reaction with **1a**, 0.1 mol% palladium(II) acetate, and two equivalents of cesium carbonate under air atmosphere in good yields, although the *ortho*-substituents on the aryl ring decreased the substrate activity (entries 1–4). It is pleasing to observe that the optimal conditions were compatible with the use of halo-substituted substrates **2f–h**, which can provide a novel route to compounds **8–10** bearing new functional groups (entries 5–7). Gratifyingly, substrates **2l** and **2m**, with the active formyl or vinyl groups, were tolerated well (entries 11 and 12). Subsequently, the reaction of a number of iodoethynes were examined in the presence of phenylboronic acid (**2a**), palladium(II) acetate, and cesium carbonate (entries 13–24). It was found that N,N-disubstituted iodoamides **1b–i** successfully reacted with phenylboronic acid (**2a**) in moderate to excellent yields (entries 12–20). Although the activity was reduced for the reaction, esters such as phenyl 3-iodopropiolate (**1j**) or (*Z*)-3-phenylallyl 3-iodopropiolate (**1k**), were also suitable substrates, smoothly leading to the desired products **24** and **25**, respectively, in moderate yields (entries 21 and 22). Surprisingly, the reaction of **1j** with **2a** afforded the ester-exchanged product, methyl 3-phenylpropiolate (**24**), in 46% yield (entry 21). To our delight, the optimal conditions could be extended to electron-rich iodoethynes (entries 23 and 24). In the presence of palladium(II) acetate and cesium carbonate, (iodoethynyl)benzene (**1m**) was also suitable for the reaction with phenylboronic acid (**2a**), giving the desired product in 80% yield (entry 23). Using aliphatic iodoalkyne (**1n**), a moderate yield was still achieved under the same conditions (entry 24).

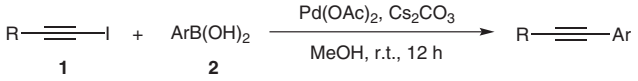
In summary, we have developed a mild, efficient, and general protocol for the synthesis of internal alkynes by palladium-catalyzed Suzuki–Miyaura cross-coupling reaction of iodoalkyne derivatives with arylboronic acids under aerobic and ligand-free conditions. This protocol is highly general for preparing both electron-poor and electron-rich alkynes using a relatively low loading of palladium catalyst. Importantly, this new route allows substrates with halo substituents, even the iodo group, on the aryl ring of the boronic acid to be used, which provides access to alkyne skeletons bearing new functional groups.

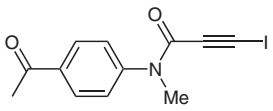
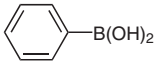
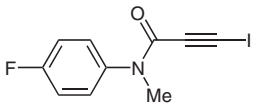
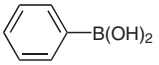
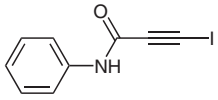
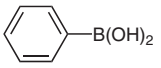
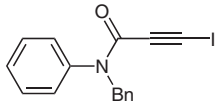
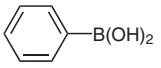
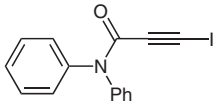
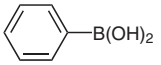
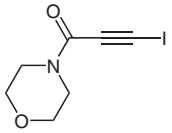
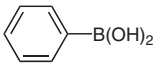
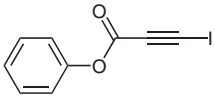
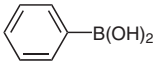
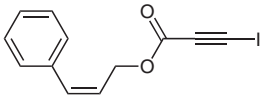
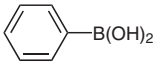
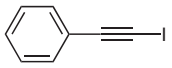
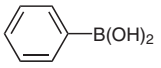
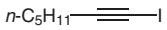
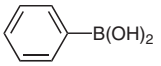
Table 2 Palladium-Catalyzed Suzuki–Miyaura Cross-Coupling Reaction of Iodoalkynes (**1**) with Arylboronic Acid (**2**)[a]



Entry	Iodoalkyne **1**	Arylboronic acid **2**	Product	Yield (%)[b]
1	**1a**	**2b**	**4**	81
2	**1a**	**2c**	**5**	74
3	**1a**	**2d**	**6**	80
4	**1a**	**2e**	**7**	64
5	**1a**	**2f**	**8**	82
6	**1a**	**2g**	**9**	81
7	**1a**	**2h**	**10**	56
8	**1a**	**2i**	**11**	63
9	**1a**	**2j**	**12**	64
10	**1a**	**2k**	**13**	54
11	**1a**	**2l**	**14**	63
12	**1a**	**2m**	**15**	80
13	**1b**	**2a**	**16**	91
14	**1c**	**2a**	**17**	94

Table 2 Palladium-Catalyzed Suzuki–Miyaura Cross-Coupling Reaction of Iodoalkynes (**1**) with Arylboronic Acid (**2**)[a] (continued)



Entry	Iodoalkyne **1**		Arylboronic acid **2**		Product	Yield (%)[b]
15	**1d**		**2a**		**18**	74
16	**1e**		**2a**		**19**	92
17	**1f**		**2a**		**20**	63
18	**1g**		**2a**		**21**	80
19	**1h**		**2a**		**22**	71
20	**1i**		**2a**		**23**	97
21[c]	**1j**		**2a**		**24**	46
22	**1k**		**2a**		**25**	52
23	**1m**		**2a**		**26**	80
24	**1n**		**2a**		**27**	60

[a] Reaction conditions: **1** (0.3 mmol), **2** (0.36 mmol), $Pd(OAc)_2$ (0.1 mol%), Cs_2CO_3 (2 equiv), MeOH (2 mL), r.t., 12 h, air atmosphere.
[b] Isolated yield.
[c] Methyl 3-phenylpropiolate (**24**) was obtained.

NMR spectroscopy was performed with a Bruker-500 spectrometer operating at 500 MHz (^{1}H NMR) and 125 MHz (^{13}C NMR). Tetramethylsilane (TMS) was used an internal standard and $CDCl_3$ was used as the solvent. Mass spectrometric analysis was performed with a GC-MS instrument (SHIMADZU GCMS-QP2010 plus).

Palladium-Catalyzed Suzuki–Miyaura Cross-Coupling Reaction of Iodoalkynes (1) with Arylboronic Acid (2); General Procedure

Iodoalkyne **1** (0.3 mmol), arylboronic acid **2** (0.36 mmol), $Pd(OAc)_2$ (0.1 mol%), Cs_2CO_3 (2 equiv), and MeOH (2 mL) were added in turn to a Schlenk tube. The solution was stirred at r.t. for the indicated time (12 h) until complete consumption of starting material was observed (reaction monitored by TLC and GC-MS analyses). The mixture was washed with brine (3 × 3 mL), extracted with Et_2O (3 × 5 mL), dried over anhydrous Na_2SO_4, and evaporated under vacuum. The residue was purified by flash column chromatography on silica gel (hexane–EtOAc) to afford the desired product.

***N*-Methyl-*N*,3-diphenylpropiolamide (3)[1a]**

White solid; mp 65.2–66.3 °C (uncorrected).

IR (KBr): 2207, 1634 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.45 (t, *J* = 7.5 Hz, 2 H), 7.40–7.38 (m, 1 H), 7.36 (d, *J* = 7.5 Hz, 2 H), 7.34–7.30 (m, 1 H), 7.27–7.22 (m, 2 H), 7.13 (d, *J* = 8.0 Hz, 2 H), 3.39 (s, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 154.3, 143.1, 132.3, 129.9, 129.1, 128.2, 127.9, 127.3, 120.3, 90.8, 82.5, 36.3.

MS (EI, 70 eV): *m*/*z* (%) = 235 (34) [M]$^+$, 129 (100).

N-Methyl-N-phenyl-3-*p*-tolylpropiolamide (4)[7]
Pale-yellow solid; mp 84.0–85.3 °C (uncorrected).

IR (KBr): 2231, 1634, 1589 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.49 (d, *J* = 7.5 Hz, 2 H), 7.45–7.34 (m, 3 H), 7.03 (s, 4 H), 3.39 (s, 3 H), 2.30 (s, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 154.4, 143.2, 140.4, 132.3, 129.0, 129.0, 127.8, 127.3, 117.2, 91.2, 82.1, 36.3, 21.5.

MS (EI, 70 eV): *m*/*z* (%) = 249 (38) [M]$^+$, 143 (100).

N-Methyl-N-phenyl-3-*o*-tolylpropiolamide (5)[1c]
Colorless oil.

IR (KBr): 2218, 1638, 1581 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.43 (t, *J* = 7.5 Hz, 2 H), 7.36 (t, *J* = 8.5 Hz, 3 H), 7.24–7.19 (m, 2 H), 7.06 (t, *J* = 8.0 Hz, 2 H), 3.38 (s, 3 H), 1.92 (s, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 154.4, 143.3, 141.4, 133.1, 129.9, 129.4, 129.3, 128.0, 127.5, 125.5, 120.2, 89.9, 86.2, 36.5, 19.9.

MS (EI, 70 eV): *m*/*z* (%) = 248 (43) [M]$^+$, 143 (100).

3-(4-Methoxyphenyl)-N-methyl-N-phenylpropiolamide (6)[1a]
Pale-yellow solid; mp 93.6–94.9 °C (uncorrected).

IR (KBr): 2210, 1636, 1593 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.45 (t, *J* = 7.5 Hz, 2 H), 7.40–7.35 (m, 3 H), 7.07 (d, *J* = 9.0 Hz, 2 H), 6.75 (d, *J* = 8.5 Hz, 2 H), 3.77 (s, 3 H), 3.39 (s, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 160.8, 154.6, 143.3, 134.2, 129.0, 127.8, 127.4, 113.9, 112.2, 91.4, 81.9, 55.2, 36.2.

MS (EI, 70 eV): *m*/*z* (%) = 256 (33) [M]$^+$, 159 (100).

3-(2-Methoxyphenyl)-N-methyl-N-phenylpropiolamide (7)[1a]
Pale-yellow solid; mp 86.3–87.8 °C (uncorrected).

IR (KBr): 2210, 1638, 1581 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.43 (t, *J* = 7.5 Hz, 2 H), 7.39–7.35 (m, 3 H), 7.29–7.26 (m, 1 H), 7.11–7.09 (m, 1 H), 6.82–6.75 (m, 2 H), 3.69 (s, 3 H), 3.39 (s, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 161.0, 154.4, 143.2, 134.4, 131.5, 129.0, 127.5, 127.3, 120.2, 110.6, 109.7, 87.7, 86.4, 55.4, 36.4.

MS (EI, 70 eV): *m*/*z* (%) = 264 (9) [M]$^+$, 159 (72), 147 (52), 131 (44), 115 (100).

3-(4-Fluorophenyl)-N-methyl-N-phenylpropiolamide (8)[6d]
White solid; mp 50.3–51.6 °C (uncorrected).

IR (KBr): 2231, 1638, 1597 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.46 (t, *J* = 8.0 Hz, 2 H), 7.40 (t, *J* = 7.0 Hz, 1 H), 7.36 (d, *J* = 7.5 Hz, 2 H), 7.13–7.10 (m, 2 H), 6.93 (t, *J* = 8.5 Hz, 2 H), 3.40 (s, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 163.4 (d, *J* = 251.0 Hz), 154.1, 143.1, 134.5, 134.4, 129.1, 127.9, 127.4, 115.7 (d, *J* = 22.3 Hz), 89.7, 82.3, 36.3.

MS (EI, 70 eV): *m*/*z* (%) = 253 (49) [M]$^+$, 147 (100).

3-(4-Chlorophenyl)-N-methyl-N-phenylpropiolamide (9)[1a]
Pale-yellow solid; mp 60.2–61.8 °C (uncorrected).

IR (KBr): 2224, 1640, 1595 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.45 (t, *J* = 7.5 Hz, 2 H), 7.39 (d, *J* = 7.0 Hz, 1 H), 7.36 (t, *J* = 7.5 Hz, 2 H), 7.21 (d, *J* = 8.5 Hz, 2 H), 7.05 (d, *J* = 8.5 Hz, 2 H), 3.39 (s, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 154.0, 143.0, 136.2, 133.5, 129.1, 128.7, 128.0, 127.3, 118.9, 89.5, 83.3, 36.3.

MS (EI, 70 eV): *m*/*z* (%) = 269 (52) [M]$^+$, 163 (100).

3-(4-Iodophenyl)-N-methyl-N-phenylpropiolamide (10)[6d]
White solid; 54.1–55.6 °C (uncorrected).

IR (KBr): 2218, 1646, 1593 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.58 (d, *J* = 8.5 Hz, 2 H), 7.45 (t, *J* = 7.5 Hz, 2 H), 7.39 (d, *J* = 7.5 Hz, 1 H), 7.35 (t, *J* = 7.0 Hz, 2 H), 6.84 (d, *J* = 8.5 Hz, 2 H), 3.39 (s, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 154.0, 143.1, 137.6, 133.6, 129.1, 128.0, 127.4, 119.8, 96.5, 89.7, 83.6, 36.4.

MS (EI, 70 eV): *m*/*z* (%) = 361 (64) [M]$^+$, 255 (100), 128 (46).

3-(4-Acetylphenyl)-N-methyl-N-phenylpropiolamide (11)[1a]
Pale-yellow solid; mp 92.2–93.9 °C (uncorrected).

IR (KBr): 2222, 1681, 1626, 1594 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.82 (d, *J* = 8.5 Hz, 2 H), 7.48–7.45 (m, 2 H), 7.42–7.39 (m, 1 H), 7.37 (t, *J* = 4.5 Hz, 2 H), 7.22 (d, *J* = 8.5 Hz, 2 H), 3.40 (s, 3 H), 2.56 (s, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 197.0, 153.8, 142.9, 137.4, 132.4, 129.2, 128.1, 128.0, 127.3, 125.0, 89.3, 84.8, 36.3, 26.6.

MS (EI, 70 eV): *m*/*z* (%) = 277 (56) [M]$^+$, 171 (100).

3-(4-Nitrophenyl)-N-methyl-N-phenylpropiolamide (12)[7]
Yellow solid; mp 96.1–98.3 °C (uncorrected).

IR (KBr): 2210, 1638, 1585 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.10 (d, *J* = 8.0 Hz, 2 H), 7.47–7.42 (m, 3 H), 7.36 (d, *J* = 6.0 Hz, 2 H), 7.29 (d, *J* = 8.5 Hz, 2 H), 3.41 (s, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 153.4, 148.0, 142.8, 133.0, 129.3, 128.3, 127.4, 127.1, 123.5, 87.8, 86.3, 36.4.

MS (EI, 70 eV): *m*/*z* (%) = 280 (83) [M]$^+$, 174 (100).

N-Methyl-3-(3-nitrophenyl)-N-phenylpropiolamide (13)[6d]
Yellow oil.

IR (KBr): 2210, 1638, 1585 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.18–8.16 (m, 1 H), 7.90 (s, 1 H), 7.51–7.44 (m, 5 H), 7.39–7.37 (m, 2 H), 3.42 (s, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 153.5, 147.9, 142.8, 137.8, 129.6, 129.4, 128.4, 127.4, 127.2, 124.5, 122.2, 87.7, 84.3, 36.4.

MS (EI, 70 eV): *m*/*z* (%) = 280 (99) [M]$^+$, 174 (83), 128 (100).

3-(2-Formylphenyl)-N-methyl-N-phenylpropiolamide (14)[6d]
Yellow solid; mp 63.2–64.5 °C (uncorrected).

IR (KBr): 2214, 1699, 1634, 1593 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 9.36 (s, 1 H), 7.83 (d, *J* = 2.0 Hz, 1 H), 7.82 (d, *J* = 2.0 Hz, 1 H), 7.54–7.45 (m, 5 H), 7.37–7.35 (m, 2 H), 3.41 (s, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 190.5, 153.6, 142.7, 136.8, 134.2, 133.6, 130.3, 129.5, 128.5, 127.4, 126.9, 123.6, 88.4, 85.9, 36.5.

MS (EI, 70 eV): *m*/*z* (%) = 262 (10) [M]$^+$, 234 (100), 101 (67).

N-Methyl-N-phenyl-3-(4-vinylphenyl)propiolamide (15)[6d]
Colorless oil.

IR (KBr): 2216, 1642, 1493 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.45 (t, *J* = 7.5 Hz, 2 H), 7.39 (d, *J* = 7.0 Hz, 1 H), 7.36 (t, *J* = 4.5 Hz, 2 H), 7.26 (t, *J* = 4.0 Hz, 2 H),

7.09 (d, *J* = 8.0 Hz, 2 H), 6.66–6.60 (m, 1 H), 5.74 (d, *J* = 17.5 Hz, 1 H), 5.30 (d, *J* = 6.0 Hz, 1 H), 3.39 (s, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 154.3, 143.2, 139.0, 135.8, 132.6, 129.1, 127.9, 127.3, 126.0, 119.4, 115.8, 90.8, 83.1, 36.3.

MS (EI, 70 eV): *m*/*z* (%) = 253 (49) $[M]^+$, 147 (100).

N-(4-Methylphenyl)-N-methyl-3-phenylpropiolamide (16)[1a]
Yellow oil.

IR (KBr): 1638 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.32 (t, *J* = 7.0 Hz, 1 H), 7.26–7.22 (m, 6 H), 7.16 (d, *J* = 7.5 Hz, 2 H), 3.36 (s, 3 H), 2.41 (s, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 154.4, 140.7, 137.8, 132.3, 129.8, 129.7, 128.2, 127.1, 120.6, 90.7, 82.7, 36.4, 21.1.

MS (EI, 70 eV): *m*/*z* (%) = 249 (55) $[M]^+$, 129 (100).

N-(4-Methoxyphenyl)-N-methyl-3-phenylpropiolamide (17)[7]
Yellow solid; mp 78.4–79.7 °C (uncorrected).

IR (KBr): 2218, 1638, 1507 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.34–7.30 (m, 1 H), 7.28–7.23 (m, 4 H), 7.17 (t, *J* = 4.5 Hz, 2 H), 6.96, 6.95 (dd, *J* = 2.0, 2.0 Hz, 2 H), 3.85 (s, 3 H), 3.35 (s, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 159.0, 154.5, 136.1, 132.4, 129.8, 128.5, 128.3, 120.5, 114.3, 90.9, 82.6, 55.5, 36.5.

MS (EI, 70 eV): *m*/*z* (%) = 265 (51) $[M]^+$, 129 (100).

N-(4-Acetylphenyl)-N-methyl-3-phenylpropiolamide (18)
Yellow solid; mp 109.1–110.7 °C (uncorrected).

IR (KBr): 1681, 1626 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.04 (d, *J* = 8.0 Hz, 2 H), 7.49 (d, *J* = 8.0 Hz, 2 H), 7.36–7.20 (m, 5 H), 3.43 (s, 3 H), 2.64 (s, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 196.9, 153.8, 135.7, 132.3, 130.2, 129.2, 128.4, 127.0, 124.7, 120.1, 103.0, 82.2, 36.4, 26.6.

MS (EI, 70 eV): *m*/*z* (%) = 277 (61) $[M]^+$, 129 (100).

HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_{18}H_{15}NO_2$: 277.1099; found: 277.1095.

N-(4-Fluorophenyl)-N-methyl-3-phenylpropiolamide (19)[1e]
Yellow oil.

IR (KBr): 1638 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.36–7.32 (m, 3 H), 7.27–7.24 (m, 2 H), 7.18–7.10 (m, 4 H), 3.36 (s, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 161.9 (d, *J* = 246.5 Hz), 154.3, 139.3, 132.4, 130.0, 129.3 (d, *J* = 8.5 Hz), 128.4, 120.3, 116.1 (d, *J* = 22.5 Hz), 91.2, 82.3, 36.4.

MS (EI, 70 eV): *m*/*z* (%) = 253 (42) $[M]^+$, 129 (100).

N,3-Diphenylpropiolamide (20)[1a]
White solid; mp 120.3–122.6 °C (uncorrected).

IR (KBr): 2221, 1628 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.17 (s, 1 H), 7.60 (d, *J* = 8.0 Hz, 2 H), 7.50 (d, *J* = 7.5 Hz, 2 H), 7.40 (t, *J* = 7.5 Hz, 1 H), 7.32–7.25 (m, 4 H), 7.12 (t, *J* = 7.5 Hz, 1 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 151.2, 137.4, 132.6, 130.2, 129.0, 128.4, 124.8, 120.0, 119.9, 85.5, 83.4.

MS (EI, 70 eV): *m*/*z* (%) = 261 (14) $[M]^+$, 232 (19), 129 (100).

N-Benzyl-N,3-diphenylpropiolamide (21)[1a]
Pale-yellow solid; mp 84.2–85.7 °C (uncorrected).

IR (KBr): 2216, 1634, 1589 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.36–7.32 (m, 3 H), 7.31–7.28 (m, 6 H), 7.27–7.21 (m, 2 H), 7.19–7.15 (m, 2 H), 7.09 (t, *J* = 4.5 Hz, 2 H), 5.00 (s, 2 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 154.4, 141.6, 136.6, 132.4, 129.9, 128.9, 128.7, 128.6, 128.4, 128.2, 128.1, 127.5, 120.3, 91.4, 82.5, 52.2.

MS (EI, 70 eV): *m*/*z* (%) = 311 (39) $[M]^+$, 129 (100).

N-Phenyl-N,3-diphenylpropiolamide (22)[8]
White solid; mp 125.0–126.7 °C (uncorrected).

IR (KBr): 1638 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.44–7.33 (m, 9 H), 7.27–7.16 (m, 4 H), 7.14 (d, *J* = 1.5 Hz, 2 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 153.7, 132.6, 129.6, 129.0, 128.4, 128.0, 126.5, 125.8, 120.3, 92.2, 83.2.

MS (EI, 70 eV): *m*/*z* (%) = 297 (32) $[M]^+$, 129 (100).

1-Morpholino-3-phenylprop-2-yn-1-one (23)[9]
Colorless oil.

IR (KBr): 2218, 1626 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.55 (d, *J* = 7.0 Hz, 2 H), 7.45–7.42 (m, 1 H), 7.39–7.36 (m, 2 H), 3.85 (t, *J* = 10.0 Hz, 2 H), 3.76 (t, *J* = 10.0 Hz, 2 H), 3.71 (s, 4 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 153.1, 132.3, 130.1, 128.5, 120.1, 91.2, 80.6, 66.8, 66.4, 47.2, 41.9.

MS (EI, 70 eV): *m*/*z* (%) = 215 (29) $[M]^+$, 129 (100).

Methyl 3-Phenylpropiolate (24)[10]
Colorless oil.

IR (KBr): 2210, 1708 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.58 (t, *J* = 7.0 Hz, 2 H), 7.45 (t, *J* = 7.5 Hz, 1 H), 7.39–7.36 (m, 2 H), 3.84 (s, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 154.5, 133.0, 130.7, 128.6, 119.5, 86.5, 80.3, 52.8.

MS (EI, 70 eV): *m*/*z* (%) = 160 (19) $[M]^+$, 129 (100).

Cinnamyl 3-Phenylpropiolate (25)[11]
Colorless oil.

IR (KBr): 1728 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.60–7.58 (m, 2 H), 7.46 (t, *J* = 1.5 Hz, 1 H), 7.45–7.40 (m, 2 H), 7.39–7.32 (m, 4 H), 7.29–7.25 (m, 1 H), 6.73 (d, *J* = 16.0 Hz, 1 H), 6.36–6.30 (m, 1 H), 4.90, 4.88 (dd, *J* = 1.0, 1.0 Hz, 2 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 153.8, 135.9, 135.3, 133.0, 130.7, 128.7, 128.6, 128.3, 126.7, 122.0, 119.5, 86.6, 80.5, 65.5.

MS (EI, 70 eV): *m*/*z* (%) = 262 (100) $[M]^+$, 231 (54), 217 (87), 203 (91), 101 (42).

1,2-Diphenylethyne (26)[12]
White solid; mp 59.4–60.3 °C (uncorrected).

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.54–7.52 (m, 4 H), 7.34 (d, *J* = 6.5 Hz, 6 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 131.6, 128.3, 128.2, 123.3, 89.4.

MS (EI, 70 eV): *m*/*z* (%) = 178 (100) $[M]^+$.

1-(Hept-1-ynyl)-4-methylbenzene (27)[12]
Colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.28 (d, *J* = 8.0 Hz, 2 H), 7.07 (d, *J* = 8.0 Hz, 2 H), 2.38 (t, *J* = 7.5 Hz, 2 H), 2.31 (s, 3 H), 1.60 (t, *J* = 7.5 Hz, 2 H), 1.44–1.41 (m, 4 H), 0.92 (t, *J* = 7.5 Hz, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 137.3, 131.4, 128.9, 121.0, 89.6, 80.5, 31.1, 28.5, 22.2, 21.3, 19.4, 14.0.

MS (EI, 70 eV): *m*/*z* (%) = 186 (33) $[M]^+$, 157 (33), 142 (38), 131 (69), 129 (100).

Supporting Information for this article is available online at http://www.thieme-connect.com/ejournals/toc/synthesis.

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