Synthesis of Polyfunctional Unsaturated Amines by the Addition of Functionalized Organomagnesium Reagents to Unsaturated Imminium Ions

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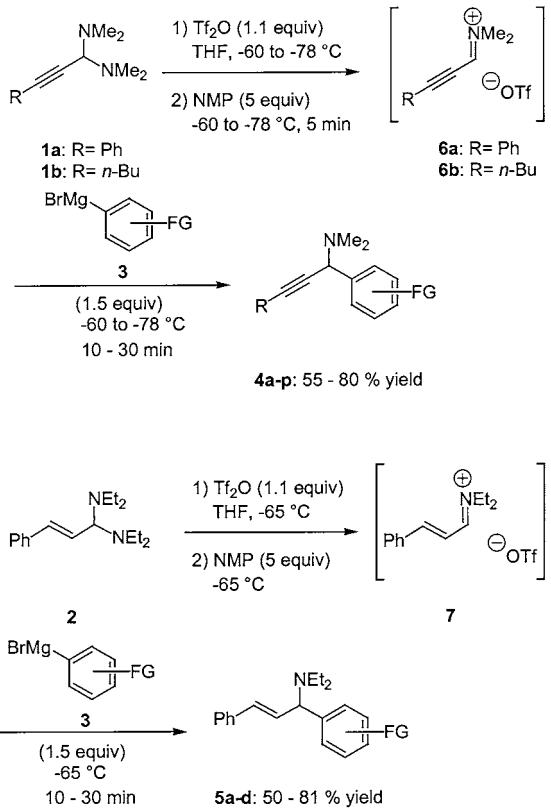
Dedicated to Prof. Dieter Seebach on the occasion of his 65th birthday.

Abstract: The reaction of propargylic and allylic aminals with trifluoromethanesulfonic anhydride at low temperature produces imminium salts, which react in the presence of *N*-methylpyrrolidinone (NMP) with functionalized arylmagnesium compounds, providing polyfunctional propargylic and allylic amines in satisfactory yields.

Key words: functionalized organomagnesium reagents, imminium salts, propargylic amines, allylic amines, aminals

The preparation of polyfunctional organic molecules without the use of protecting groups is an important synthetic task. Polyfunctional organometallics are particularly well suited for achieving this goal.[1] It is well known that functionalized organozinc compounds[2] are compatible with many functional groups, and it has also been shown that polyfunctional organomagnesium reagents can be readily obtained by an iodine- or a bromine-magnesium exchange.[3] The preparation of functionalized unsaturated amines is especially important, since many polyfunctional amino compounds are of interest due to their biological activity.[4] Herein, we wish to report the reaction of the unsaturated aminals **1a**,**b**[5,6] and **2**[7] with functionalized arylmagnesium species of type **3**, leading after treatment with trifluoromethanesulfonic anhydride to amines **4** and **5**. Thus, trifluoromethanesulfonic anhydride reacts with the aminals **1,2**, furnishing the corresponding imminium triflates **6a**,**b** and **7**, which react rapidly with Grignard reagents[8] (see Scheme 1, Tables 1 and 2).



Scheme 1

A range of different functionalized arylmagnesium reagents can be used. Thus, several *para*-substituted arylmagnesium species like **3a**,**b** react well with the alkynyl aminals **1a** and **1b** leading to the corresponding propargyl amine derivatives (**4a**,**b** and **4h**,**i**; entries 1, 2, 8 and 9 of Table 1). Sterically hindered *ortho*-substituted arylmagnesium compounds **3c**–**f** bearing carbethoxy, bromine, nitro or trialkylsilyloxy groups react with **1a**–**b** forming products **4c**–**f** in good yields (55−79%, entries 3−6 of Table 1). The reactions involve treatment of aminals **1a**,**b** with Tf_2O at –65 °C or –78 °C respectively, leading to an intensely yellow solution of the imminium salts **6a**,**b**. A precipitate forms after a few minutes and redissolves after the addition of *N*-methylpyrrolidinone (NMP; 5 equiv). A THF solution of the Grignard reagent of type **3** (1.5 equiv) is added and the addition reaction is complete after 0.5 to 1.0 hours. A heterocyclic magnesium reagent such as 5-carbethoxyfurylmagnesium bromide (**3g**), obtained by a bromine-magnesium exchange,[9] reacts with **1a**,**b** under our standard conditions, furnishing the furans **4g** and **4m** in 65% and 52% yield respectively (entries 7 and 13 of Table 1). Interestingly, alkyl-, alkenyl- or alkynyl magnesium halides, such as octylmagnesium bromide (**3i**), vinylmagnesium chloride (**3j**) and ethynylmagnesium bromide (**3k**) react with **1a**,**b** under typical conditions in satisfactory yields, showing the generality of our procedure.

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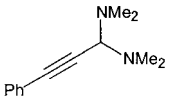
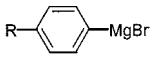
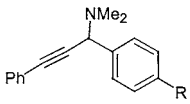
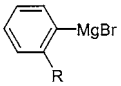
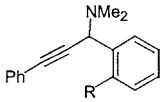
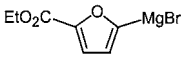
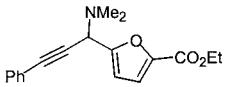
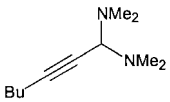
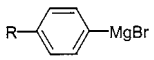
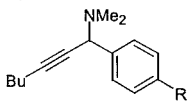
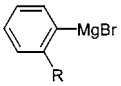
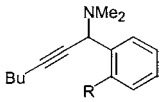
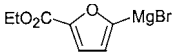
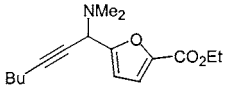
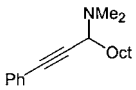
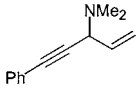
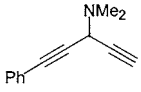
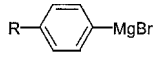
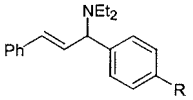
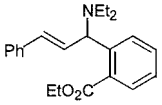
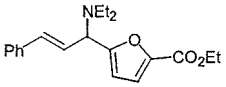
Table 1 Functionalized Propargylic Amines **4a**–**p** Obtained by the Reaction of Funtionalized Arylmagnesium Reagents **3** with Unsaturated Aminals **1a**,**b**

Entry	Aminal	Grignard-Reagent	Product of Type **4**	Yield (%)[a]
				
1	**1a**	**3a** R = OMe	**4a** R = OMe	67
2	**1a**	**3b** R = CO_2Me	**4b** R = CO_2Me	70
				
3	**1a**	**3c** R = CO_2Et	**4c** R = CO_2Et	79
4	**1a**	**3d** R = Br	**4d** R = Br	60
5	**1a**	**3e** R = NO_2	**4e** R = NO_2	68
6	**1a**	**3f** R = OTIPS	**4f** R = OTIPS	55
7	**1a**	 **3g**	 **4g**	65
				
8	**1b**	**3a**	**4h**: R = OMe	76
9	**1b**	**3h** R = CO_2Et	**4i** R = CO_2Et	80
				
10	**1b**	**3c**	**4j** R = CO_2Et	72
11	**1b**	**3d**	**4k** R = Br	69
12	**1b**	**3e**	**4l** R = NO_2	79
13	**1b**	 **3g**	 **4m**	52
14	**1a**	**3i** OctMgBr	 **4n**	80
15	**1a**	**3j** CH_2=CHMgCl	 **4o**	56
16	**1a**	**3k** HC≡C−MgBr	 **4p**	67

[a] Yield of analytically pure product.

As can be seen in Table 2, the unsaturated aminal **2** reacts similarly with arylmagnesium compounds. In this case, the addition of Tf_2O at –65 °C produces an orange precipitate, which redissolves upon addition of NMP (5 equiv). The reactions with the Grignard reagents **3** are complete within 1 hour (Scheme 1 and Table 2). The functionalized allylic amines **5a**–**d** are obtained in 50−81% yield.

Table 2 Functionalized Allylic Amines **5a**–**d** Obtained by the Reaction of Functionalized Arylmagnesium Reagents **3** with the Unsaturated Aminal **2**

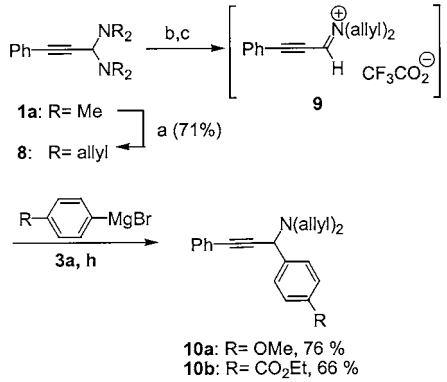
Entry	Grignard-Reagent	Product of Type **5**	Yield (%)[a]
			
1	**3a**	**5a**: R = OMe	81
2	**3h**	**5b**: R = CO_2Et	80
3	**3c**	 **5c**	50
4	**3g**	 **5d**	61

[a] Yield of analytically pure product.

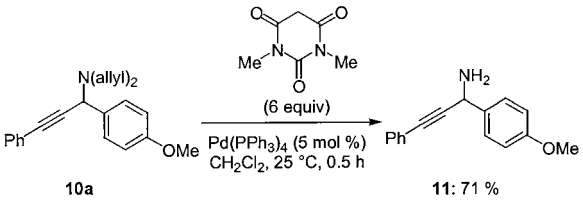
The preparation of primary propargylic amines can be achieved starting from the aminal **1a**. Its treatment with excess diallylamine at 110 °C for 8 h produces the corresponding tetraallylated aminal **8** in 71% yield.[10] The reaction of **8** with Tf_2O leads, after the addition of an organomagnesium reagent, to extensive decomposition. However, the addition of trifluoroacetic anhydride cleanly provides the imminium trifluoroacetate **9** at –60 ºC, which after the addition of NMP (5 equiv) reacts with the arylmagnesium compounds **3a** and **3h**, furnishing the desired proparylic amines **10a**,**b** in 66–76% yield (Scheme 2).

The allyl substituent can be readily removed by using the method of Guibé.[11] Thus, the reaction of **10a** with 1,3-dimethylbarbituric acid (6 equiv) in the presence of $Pd(PPh_3)_4$ (5 mol%) in CH_2Cl_2 at 25 °C leads in 30 minutes to the propargylic amine **11** in 71% yield (Scheme 3).

In conclusion, we have described conditions allowing the addition of a range of functionalized Grignard reagents to alkynyl and alkenyl aminals, leading to functionalized propargylic and allylic amines, respectively.



Scheme 2 Reagents and conditions: (a) diallylamine (excess), 110 °C, 8 h (b) $(CF_3CO)_2O$ (1.1 equiv), –60 °C, 15 min (c) NMP (5 equiv).



Scheme 3.

Commercially available starting materials with a purity >97% were used without further purification. Solvents were dried and distilled before use.

NMR-spectra were recorded in $CDCl_3$ at 300 MHz for ^1H NMR and 75 MHz for ^{13}C NMR (Varian XL 300). Chemical shifts are reported in ppm relative to TMS. IR-spectra were recorded on a Perkin-Elmar FT-IR Spectrum 1000. Low-resolution mass spectra were recorded using a GC/MS-combination of the type HP 6890/MSD 5973 fitted with a HP-5 column (30 m × 0.25 mm × 0.25 μm). High-resolution mass spectra were recorded on a Finnigan-MAT 95Q spectrometer (electron impact, 70 eV). Column chromatographical purifications were carried out using Silicagel 60 (0.063−0.200 mm, purchased from Merck, Darmstadt).

Aminals **1a**−**b** were prepared according to known methods.[5,6] The aminal **2** was obtained by condensation of cinnamaldehyde with diethylamine. The crude product was used without further purification.

Grignard Reagents 3a−h; General procedure[3]

To a stirred soln of the aromatic halide (1.0 equiv, 1.0 to 0.5 mol/L in THF) at –40 → –20 °C, a soln of *i*-PrMgBr (1.05 to 1.1 equiv, 0.5 mol/L in THF) was added dropwise. The halogen-magnesium exchange was followed by GC/MS.

Addition of Grignard Reagents 3 to Aminals 1a−b, 2; General Procedure for 4 and 5

To a stirred soln of the aminal **1a**−**b** or **2** (1.0 mmol) in THF (2 mL) at –60 to –78 °C, Tf_2O (310 mg, 1.1 mmol) was added dropwise. After 10 min, NMP (0.5 mL, 5 mmol) was added. To this soln of the imminium triflate, the soln of the Grignard reagent **3** (1.5 mmol) was added dropwise. After 0.5–1 h, the reaction was complete according to GC/MS-analysis and was quenched with aq NH_4Cl soln (10 mL). The aq layer was extracted with Et_2O (3 × 20 mL), the combined organic layers were washed with brine (30 mL), dried ($MgSO_4$), filtered and evaporated under reduced pressure. Purification by column chromatography with pentane−CH_2Cl_2−MeOH as eluent gave the corresponding products **4** or **5**.

1-(4-Methoxyphenyl)-*N*,*N*-dimethyl-3-phenyl-2-propyn-1-amine (4a)

Column chromatographic purification using CH_2Cl_2–MeOH (100:0→99:1) as eluent yielded **4a** (177 mg, 0.67 mmol, 67%) as a brown oil.

IR (film): 2934 (m), 2858 (w), 2822 (w), 2777 (w), 1610 (m), 1510 (vs), 1490 (m), 1249 (vs), 1173 (s), 1037 (s), 806 (w), 956 (s), 692 (m) cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.54–7.51 (m, 4 H), 7.35–7.32 (m, 3 H), 6.90 (d, *J* = 8.4 Hz, 2 H), 4.78 (s, 1 H), 3.82 (s, 3 H), 2.32 (s, 6 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 159.1, 131.8, 130.9, 129.6, 128.3, 128.1, 123.2, 113.5, 88.1, 85.1, 61.6, 55.3, 41.5.

MS: *m*/*z* (%) = 265 (7) [M^+], 222 (19), 221 (100), 178 (11).

HRMS: *m*/*z* calcd for $C_{18}H_{19}NO$, 265.1467; found, 265.1480.

4-[1-(Dimethylamino)-3-phenyl-2-propynyl]benzoic Acid Methyl Ester (4b)

Column chromatographic purification using CH_2Cl_2–MeOH (100:0→99:1) as eluent yielded **4b** (205 mg, 0.70 mmol, 70%) as a brown oil.

IR (film): 2949 (m), 2861 (w), 2824 (w), 2781 (w), 1723 (vs), 1611 (m), 1435 (s), 1279 (vs), 1112 (s), 1104 (s), 757 (s), 692 (m) cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 8.04 (d, *J* = 8.4 Hz, 2 H), 7.71 (d, *J* = 8.4 Hz, 2 H), 7.69–7.52 (m,
2 H), 7.36–7.33 (m, 3 H), 4.86 (s, 1 H), 3.92 (s, 3 H), 2.33 (s, 6 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 166.9, 143.9, 131.8, 129.5, 128.4, 128.3, 128.2, 122.9, 115.3, 88.9, 83.9, 62.0, 52.1, 41.6.

MS: *m*/*z* (%) = 293 (19) [M^+], 250 (19), 249 (100), 190 (17), 189 (25), 158 (53).

HRMS: *m*/*z* calcd for $C_{19}H_{19}NO_2$, 293.1416; found, 293.1400.

2-[1-(Dimethylamino)-3-phenyl-2-propynyl]benzoic Acid Ethyl Ester (4c)

Column chromatographic purification using CH_2Cl_2–pentane (1:1→1:0) as eluent yielded **4c** (244 mg, 0.79 mmol, 79%) as a brown solid, mp 72 °C.

IR (KBr): 2977 (m), 1723 (vs), 1489 (m), 1443 (m), 1310 (m), 1292 (s), 1262 (s), 1128 (s), 1087 (m), 1045 (m), 1015 (m), 758 (s), 744 (s), 694 (m) cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.79 (dd, *J* = 8.2, 0.8 Hz, 1 H), 7.60 (dd, *J* = 7.5, 1.7 Hz, 1 H), 7.49–7.46 (m, 3 H), 7.38 (td, *J* = 7.5, 1.5 Hz,1 H), 7.29–7.24 (m, 3 H), 5.59 (s, 1 H), 4.30 (qd, *J* = 7.1, 3.4 Hz, 2 H), 2.16 (s, 6 H), 1.32 (t, *J* = 7.1 Hz, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 169.0, 138.8, 132.1, 131.8, 130.3, 129.3, 128.7, 128.3, 128.1, 127.5, 123.2, 89.3, 84.0, 60.9, 58.7, 41.1, 14.2.

MS: *m*/*z* (%) = 307 (17) [M^+], 292 (48), 278 (100), 262 (24), 260 (66), 246 /76), 235 (23), 234 (88), 219 (35), 218 (23), 189 (51), 184 (35), 162 (20), 158 (21), 133 (54).

HRMS: *m*/*z* calcd for $C_{20}H_{21}NO_2$, 307.1572; found, 307.1541.

1-(2-Bromophenyl)-*N*,*N*-dimethyl-3-phenyl-2-propyn-1-amine (4d)

Column chromatographic purification using CH_2Cl_2–pentane (1:1→1:0) as eluent yielded **4d** (188 mg, 0.60 mmol, 60%) as a brown oil.

IR (film): 2943 (m), 2821 (m), 2777 (m), 1490 (s), 1469 (s), 1440 (s), 1028 (s), 753 (vs), 691 (s),
596 (m) cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.76 (dd, *J* = 7.6, 1.8 Hz, 1 H), 7.60 (dd, *J* = 7.9, 1.4 Hz, 1 H), 7.54–7.50 (m, 2 H), 7.35–7.32 (m, 4 H), 7.17 (td, *J* = 7.9, 1.8 Hz, 1 H), 5.13 (s, 1 H), 2.37 (s, 6 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 138.0, 133.2, 131.8, 130.5, 129.7, 128.3, 128.2, 126.9, 125.1, 123.0, 88.5, 84.4, 61.5, 41.5.

MS: *m*/*z* (%) = 315 (13), 314 (11) [M^+], 313 (13), 272 (12), 271 (68), 270 (12), 269 (70), 234 (15),
190 (13), 189 (68), 188 (11), 187 (11), 159 (13), 158 (100), 115 (17).

HRMS: *m*/*z* calcd for $C_{17}H_{16}BrN$, 313.0466; found, 313.0462.

***N*,*N*-Dimethyl-1-(2-nitrophenyl)-3-phenyl-2-propyn-1-amine (4e)**

Column chromatographic purification using CH_2Cl_2–pentane (1:4→1:0) as eluent yielded **4e** (192 mg, 0.68 mmol, 68%) as a brown solid, mp 75 °C.

IR (KBr): 2822 (m), 1540 (vs), 1489 (m), 1359 (s), 1016 (m), 784 (m), 756 (s), 732 (m), 691 (m) cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.96 (d, *J* = 7.5 Hz, 1 H), 7.73 (dd, *J* = 8.0, 1.3 Hz, 1 H), 7.59–7.53 (m, 3 H), 7.40 (td, *J* = 7.6, 1.4 Hz, 1 H), 7.38–7.35 (m, 3 H), 5.66 (s, 1 H), 2.21 (s, 6 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 149.7, 133.3, 131.9, 131.6, 129.9, 128.6, 128.5, 128.4, 124.4, 122.7, 90.2, 82.2, 57.9, 41.4.

MS: *m*/*z* (%) = 280 (2) [M^+], 264 (10), 263 (100), 246 (14), 145 (18), 233 (17), 232 (73), 218 (17), 190 (20), 189 (40), 158 (17), 118 (17), 115 (24), 105 (14), 77 (14).

HRMS: *m*/*z* calcd for $C_{17}H_{16}N_2O_2$, 280.1212; found, 280.1203.

***N*,*N*-Dimethyl-3-phenyl-1-{2-[(trisisopropylsilyl)oxy]-phenyl}-2-propyn-1-amine (4f)**

Column chromatographic purification using CH_2Cl_2–pentane (1:1→1:0) as eluent yielded **4f** (226 mg, 0.55 mmol, 55%) as a brown oil.

IR (film): 2945 (m), 2867 (m), 1490 (s), 1452 (m), 1282 (m), 1266 (m), 920 (m), 756 (s), 690 (m) cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.63 (dd, *J* = 7.9, 2.2 Hz, 1 H), 7.50–7.45 (m, 2 H), 7.32–7.28 (m,
3 H), 7.15 (td, *J* = 8.1, 1.8 Hz, 1 H), 6.95 (td, *J* = 7.5, 1.3 Hz, 1 H), 6.84 (dd, *J* = 8.1, 1.3 Hz, 1 H), 5.16 (s, 1 H), 2.32 (s, 6 H), 1.36 (sept., *J* = 7.2 Hz, 3 H), 1.15 (t, *J* = 7.1 Hz, 18 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 153.8, 131.7, 130.4, 128.8, 128.6, 128.2, 127.8, 123.5, 120.3, 118.5, 86.7, 86.5, 55.8, 41.9, 18.1, 13.1.

MS: *m*/*z* (%) = 407 (32) [M^+], 393 (33), 392 (100), 351 (15), 350 (49), 319 (29), 249 (17), 235 (16),
189 (17), 149 816), 125 (16), 115 (20).

HRMS: *m*/*z* calcd for $C_{26}H_{37}NOSi$, 407.2644; found, 407.2641.

5-[1-(Dimethylamino)-3-phenyl-2-propynyl]-2-furan-carboxylic Acid Ethyl Ester (4g)

Column chromatographic purification using CH_2Cl_2–pentane (1:2)→CH_2Cl_2–MeOH (99:1) as eluent yielded **4g** (192 mg, 0.65 mmol, 65%) as an orange oil.

IR (film): 2979 (m), 2944 (m), 1729 (vs), 1519 (m), 1490 (m), 1298 (vs), 1214 (s), 1136 (vs), 1016 (s), 759 (s), 692 (m) cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.43–7.40 (m, 2 H), 7.27–7.24 (m, 3 H), 7.06 (d, *J* = 3.6 Hz, 1 H), 6.53 (dd, *J* = 3.5, 0.9 Hz, 1 H), 4.84 (s, 1 H), 4.27 (qd, *J* = 7.1, 3.1 Hz, 2 H), 2.27 (s, 6 H), 1.28
(t, *J* = 7.0 Hz, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 158.6, 156.1, 144.8, 131.8, 128.3, 123.1, 122.5, 118.2, 111.1, 87.3, 82.0, 60.9, 56.2, 41.4, 14.3.

MS: *m*/*z* (%) = 297 (9) [M^+], 282 (12), 254 (18), 253 (100), 225 (39).

HRMS: *m*/*z* calcd for $C_{18}H_{19}NO_3$, 297.1365; found, 297.1394.

1-(4-Methoxyphenyl)-*N*,*N*-dimethyl-2-heptyn-1-amine (4h)
Column chromatographic purification using CH_2Cl_2–pentane (1:1)→CH_2Cl_2–MeOH (99:1) as eluent yielded **4h** (189 mg, 0.77 mmol, 77%) as an orange oil.

IR (film): 2957 (s), 2934 (s), 2860 (m), 1611 (m), 1510 (s), 1464 (m), 1248 (vs), 1174 (m), 1038 (m) cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.44 (d, *J* = 8.5 Hz, 2 H), 6.86 (d, *J* = 8.9 Hz, 2 H), 4.51 (s, 1 H), 3.80 (t, *J* = 1.7 Hz, 3 H), 2.32 (td, *J* = 6.7, 1.9 Hz, 2 H), 2.21 (s, 6 H), 1.70–1.40 (m, 4 H), 0.94 (t, *J* = 7.1 Hz, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 158.9, 131.5, 129.5, 113.3, 88.2, 75.2, 61.2, 55.2, 41.3, 31.2, 22.0, 18.4, 13.6.

MS: *m*/*z* (%) = 245 (6) [M^+], 202 (17), 201 (100), 121 (17), 115 (10).

HRMS: *m*/*z* calcd for $C_{16}H_{23}NO$, 245.1780; found, 245.1783.

4-[1-(Dimethylamino)-2-heptynyl]-benzoic Acid Ethyl Ester (4i)
Column chromatographic purification using CH_2Cl_2–pentane (1:2)→CH_2Cl_2–MeOH (99:1) as eluent yielded **4i** (230 mg, 0.80 mmol, 80%) as an orange oil.

IR (film): 2959 (s), 2936 (s), 2863 (m), 1721 (vs), 1275 (vs), 1101 (s), 1018 (m), 753 (m) cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 8.01 (d, *J* = 8.4 Hz, 2 H), 7.61 (d, *J* = 8.0 Hz, 2 H), 4.59 (s, 1 H), 4.37 (q, *J* = 7.1 Hz, 2 H), 2.34 (td, *J* = 7.0, 2.2 Hz, 2 H), 2.21 (s, 6 H), 1.63–1.44 (m, 4 H), 1.39 (t, *J* = 7.1 Hz, 3 H), 0.94 (t, *J* = 7.1 Hz, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 166.5, 144.5, 129.6, 129.3, 128.3, 89.1, 74.2, 61.6, 60.9, 41.5, 31.1, 22.0, 18.4, 14.3, 13.6.

MS: *m*/*z* (%) = 287 (12) [M^+], 243 (12), 242 (10), 155 (10), 139 (12), 138 (100), 129 (11).

HRMS: *m*/*z* calcd for $C_{18}H_{25}NO_2$, 287.2885; found, 287.2838.

2-[1-(Dimethylamino)-2-heptynyl]-benzoic Acid Ethyl Ester (4j)
Column chromatographic purification using CH_2Cl_2–pentane (1:2)→ CH_2Cl_2–MeOH (99:1) as eluent yielded **4j** (208 mg, 0.72 mmol, 72%) as an orange oil.

IR (film): 2958 (s), 2936 (s), 2861 (s), 1723 (vs), 1448 (m), 1261 (vs), 1136 (s), 1077 (s), 1014 (m), 741 (s) cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.78 (d, *J* = 7.4 Hz, 1 H), 7.59 (dd, *J* = 7.1, 1.2 Hz, 1 H), 7.41 (td, *J* = 7.9, 1.6 Hz, 1 H), 7.30 (td, *J* = 7.5, 1.5 Hz, 1 H), 5.36 (t, *J* = 1.8 Hz, 1 H), 4.32 (dq, *J* = 29.1, 7.0 Hz, 2 H), 2.35 (td, *J* = 7.2, 2.2 Hz, 2 H), 2.12 (s, 6 H), 1.64–1.40 (m, 4 H), 1.36 (t, *J* = 7.0 Hz, 3 H), 0.95 (t, *J* = 7.5 Hz, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 169.1, 139.4, 132.2, 130.1, 129.0, 128.6, 127.3, 89.4, 73.9, 60.8, 58.2, 41.0, 31.2, 22.0, 18.5, 14.2, 13.6.

MS: *m*/*z* (%) = 287 (3) [M^+], 272 (42), 259 (26), 258 (95), 245 (76), 242 (27), 226 (24), 214 (31), 197 (15), 184 (67), 173 (19), 172 (100), 170 (18), 143 (15), 128 (17), 115 (18).

HRMS: *m*/*z* calcd for $C_{18}H_{25}NO_2$, 287.1885; found, 287.1869.

1-(4-Bromophenyl)-*N*,*N*-dimethyl-2-heptyn-1-amine (4k)
Column chromatographic purification using CH_2Cl_2–pentane (1:4→1:0) as eluent yielded **4k** (202 mg, 0.69 mmol, 69%) as a brown oil.

IR (film): 2957 (vs), 2934 (vs), 2860 (s), 2821 (m), 2777 (m), 1466 (s), 1440 (s), 1025 (s), 1012 (s), 750 (vs), 683 (m) cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.66 (dd, *J* = 7.4, 1.8 Hz, 1 H), 7.55 (dd, *J* = 7.9, 1.3 Hz, 1 H), 7.29 (td, *J* = 7.9, 1.2 Hz, 1 H), 7.13 (td, *J* = 7.4, 1.8 Hz, 1 H), 4.86 (t, *J* = 2.3 Hz, 1 H), 2.32 (td, *J* = 7.0, 2.3 Hz, 2 H), 2.26 (s, 6 H), 1.62–1.41 (m, 4 H), 0.94 (t, *J* = 7.6 Hz, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 138.6, 133.0, 130.5, 129.0, 126.8, 125.1, 88.7, 74.5, 61.0, 41.4, 31.1, 22.0, 18.4, 13.6.

MS: *m*/*z* (%) = 294 (4) [M^+], 171 (11), 169 (11), 155 (11), 139 (14), 138 (100), 128 (18).

HRMS: *m*/*z* calcd for $C_{15}H_{20}BrN$, 293.0979; found, 293.0973.

***N*,*N*-Dimethyl-1-(2-nitrophenyl)-2-heptyn-1-amine (4l)**
Column chromatographic purification using CH_2Cl_2–pentane (1:4→1:0) as eluent yielded **4l** (205 mg, 0.79 mmol, 79%) as a red oil.

IR (film): 2958 (s), 2937 (s), 2862 (m), 1533 (vs), 1456 (m), 1362 (s), 1015 (m), 730 (m) cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.88 (d, *J* = 7.6 Hz, 1 H), 7.67 (dd, *J* = 8.1, 1.3 Hz, 1 H), 7.52 (td, *J* = 8.0, 1.8 Hz, 1 H), 7.40 (td, *J* = 7.6, 1.2 Hz, 1 H), 5.37 (t, *J* = 2.1 Hz, 1 H), 2.37 (td, *J* = 6.6, 2.1 Hz, 2 H), 2.10 (s, 6 H), 1.65–1.43 (m, 4 H), 0.96 (t, *J* = 7.2 Hz, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 149.7, 134.0, 131.4, 130.0, 128.3, 124.2, 90.5, 72.5, 57.4, 41.2, 31.1, 22.0, 18.4, 13.6.

MS: *m*/*z* (%) = 260 (4) [M^+], 243 (83), 213 (20), 212 (100), 198 (23), 197 (63), 183 (36), 171 (21), 170 (40), 138 (20).

HRMS: *m*/*z* calcd for $C_{15}H_{20}N_2O_2$, 260.1525; found, 260.1504.

5-[1-(Dimethylamino)-2-heptynyl]-2-furancarboxylic Acid Ethyl Ester (4m)
Column chromatographic purification using CH_2Cl_2–pentane (1:4)→CH_2Cl_2–MeOH (99:1) as eluent yielded **4m** (143 mg, 0.52 mmol, 52%) as a brown oil.

IR (film): 2937 (s), 2863 (s), 1732 (vs), 1531 (s), 1519 (s), 1456 (m), 1301 (vs), 1213(s), 1174 (m), 1136 (vs), 1015 (s), 762 (m) cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.10 (d, *J* = 3.2 Hz, 1 H), 6.50 (dd, *J* = 3.2, 1.0 Hz, 1 H), 4.66 (t, *J* = 1.7 Hz, 1 H), 4.33 (qd, *J* = 7.1 Hz, 2.7 Hz, 2 H), 2.29 (td, *J* = 6.5, 1.8 Hz, 2 H), 2.25 (s, 6 H), 1.59–1.39 (m, 4 H), 1.35 (t, *J* = 7.1 Hz, 3 H), 0.93 (t, *J* = 7.1 Hz,. 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 158.7, 157.0, 144.5, 118.2, 110.8, 87.7, 72.4, 60.8, 55.7, 41.3, 30.9, 21.9, 18.3, 14.3, 13.5.

MS: *m*/*z* (%) = 277 (15) [M^+], 234 (17), 233 (100), 204 (37), 159 (12), 153 (12), 138 (15), 131 (20), 125 (31), 91 (11).

HRMS: *m*/*z* calcd for $C_{16}H_{23}NO_3$, 277.1678; found, 277.1632.

***N*,*N*-Dimethyl-1-phenyl-1-undecyn-3-amine (4n)**
Column chromatographic purification using pentane–Et_2O (4:1) as eluent yielded **4n** (235 mg, 0.86 mmol, 86%) as an orange oil.

IR (film): 2927 (vs), 2956 (vs), 2823 (m), 2780 (m), 1490 (m), 1468 (m), 755 (s), 691 (s) cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.44–7.42 (m, 2 H), 7.30–7.24 (m, 3 H), 3.49 (t, *J* = 7.2 Hz, 1 H), 2.31 (s, 6 H), 1.71–1.61 (m, 2 H), 1.54–1.42 (m, 2 H), 1.35–1.26 (m, 10 H), 0.86 (t, *J* = 7.2 Hz, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 131.7, 128.2, 127.8, 123.5, 87.1, 85.9, 58.2, 41.4, 34.0, 31.9, 29.5, 29.4, 29.3, 26.7, 22.7, 14.1.

MS: *m*/*z* (%) = 159 (13), 158 (100), 115 (17).

HRMS: *m*/*z* calcd for $C_{19}H_{27}N$, 270.2222; found, 270.2230.

***N,N*-Dimethyl-1-phenyl-1-penten-4-yn-3-amine (4o)**
Column chromatographic purification using CH_2Cl_2 as eluent yielded **4o** (109 mg, 0.59 mmol, 59%) as a brown oil.

IR (film): 2942 (m), 2860 (m), 2780 (m), 1490 (s), 1031 (s), 993 (m), 928 (m), 756 (vs), 691 (s) cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.49–7.46 (m, 2 H), 7.33–7.29 (m, 3 H), 5.93 (ddd, *J* = 16.9, 10.3, 5.1 Hz, 1 H), 5.59 (dt, *J* = 17.4, 1.8 Hz, 1 H). 5.30 (dt, *J* = 9.9, 1.7 Hz, 1 H), 4.25 (dt, *J* = 4.8, 1.8 Hz, 1 H), 2.34 (s, 6 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 136.0, 131.7, 128.2, 128.1, 123.1, 117.7, 88.2, 83.9, 60.5, 41.5.

MS: *m*/*z* (%) = 185 (14) [M^+], 159 (13), 158 (100), 141 (33), 115 (56).

HRMS: *m*/*z* calcd for $C_{13}H_{15}N$, 185.1204; found, 185.1202.

***N,N*-Dimethyl-1-phenyl-1,4-pentadiyn-3-amine (4p)**
Column chromatographic purification using CH_2Cl_2 as eluent yielded **4p** (122 mg, 0.67 mmol, 67%) as a brown oil.

IR (film): 3293 (m), 2947 (m), 2864 (m), 2827 (m), 2784 (m), 1490 (s), 1285 (m), 1038 (s), 757 (vs), 691 (s), 653 (m) cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.43–7.39 (m, 2 H), 7.27–7.24 (m, 3 H), 4.50 (d, *J* = 2.6 Hz, 1 H), 2.37 (d, *J* = 2.6 Hz, 1 H), 2.36 (s, 6 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 131.8, 128.4, 128.2, 122.4, 84.5, 83.1, 77.9, 72.5, 49.3, 41.2.

MS: *m*/*z* (%) = 183 (34) [M^+], 182 (69), 168 (28), 167 (11), 140 (14), 139 (100).

HRMS: *m*/*z* calcd for $C_{13}H_{13}N$, 183.1048; found, 183.1027.

(2*E*)-*N,N*-Diethyl-1-(4-methoxyphenyl)-3-phenyl-2-propen-1-amine (5a)
Column chromatographic purification using CH_2Cl_2–pentane (1:4)→CH_2Cl_2–MeOH (99:1) as eluent yielded **5a** (239 mg, 0.81 mmol, 81%) as an orange oil.

IR (film): 2968 (s), 2933 (m), 1609 (m), 1509 (vs), 1247 (vs), 1173 (s), 1036 (s), 969 (m), 831 (s), 741 (s), 693 (m) cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.31–7.10 (m, 6 H), 6.79 (d, *J* = 8.9 Hz, 2 H), 6.43 (d, *J* = 15.4 Hz, 2 H), 6.27 (dd, *J* = 15.8, 8.7 Hz, 1 H), 4.18 (d, *J* = 8.5 Hz, 1 H), 3.72 (s, 3 H), 2.54 (qd, *J* = 7.2, 1.4 Hz, 4 H), 0.93 (t, *J* = 7.1 Hz, 6 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 158.5, 137.2, 135.0, 131.8, 130.6, 128.9, 128.5, 127.2, 126.3, 113.7, 68.0, 55.2, 43.0, 11.6.

MS: *m*/*z* (%) = 295 (8) [M^+], 224 (18), 223 (100), 145 (14), 115 (23).

4-[(2*E*)-1-(Diethylamino)]-3-phenyl-2-propenylbenzoic Acid Ethyl Ester (5b)
Column chromatographic purification using CH_2Cl_2–pentane (1:1)→CH_2Cl_2–MeOH (99:1) as eluent yielded **5b** (268 mg, 0.80 mmol, 80%) as an orange oil.

IR (film): 2971 (s), 2817 (m), 1717 (vs), 1609 (s), 1449 (m), 1368 (m), 1275 (vs), 1172 (m), 1104 (s), 1020 (m), 970 (m), 747 (s), 694 (s) cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.96 (d, *J* = 8.3 Hz, 2 H), 7.49 (d, *J* = 8.4 Hz, 2 H), 7.35–7.15 (m, 5 H), 6.52 (d, *J* = 16.0 Hz, 1 H), 6.27 (dd, *J* = 16.0, 8.9 Hz, 1 H), 4.33 (q, *J* = 7.0 Hz, 2 H), 4.31 (d, *J* = 8.8 Hz, 1 H), 2.64–2.51 (m, 4 H), 1.34 (t, *J* = 7.1 Hz, 3 H), 0.97 (t, *J* = 7.1 Hz, 6 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 166.6, 148.5, 136.8, 131.7, 130.5, 129.7, 129.1, 128.5, 127.8, 127.5, 126.4, 68.6, 60.8, 43.1, 14.3, 11.6.

MS: *m*/*z* (%) = 337 (34) [M^+], 336 (38), 265 (69), 246 (39), 192 (34), 191 (41), 189 (26), 188 (69), 115 (100), 91 (28).

HRMS: *m*/*z* calcd for $C_{22}H_{27}NO_2$, 337.2042; found, 337.2005.

2-[(2*E*)-1-(Diethylamino)]-3-phenyl-2-propenylbenzoic Acid Ethyl Ester (5c)
Column chromatographic purification using CH_2Cl_2–pentane (1:1→1:0) as eluent yielded **5c** (169 mg, 0.50 mmol, 50%) as an orange oil.

IR (film): 2972 (s), 2934 (m), 1721 (vs), 1449 (m), 1268 (s), 1253 (s), 1132 (s), 1095 (s), 1074 (s),
146 (s), 695 (s) cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.65 (d, *J* = 7.8 Hz, 1 H), 7.61 (dd, *J* = 7.6, 1.4 Hz, 1 H), 7.43 (dd, *J* = 7.7, 1.3 Hz, 1 H), 7.39–7.36 (m, 3 H), 7.32–7.17 (m, 3 H), 6.62 (d, *J* = 16.0 Hz, 1 H), 6.39 (dd, *J* = 15.9, 9.1 Hz, 1 H), 5.08 (d, *J* = 9.0 Hz, 1 H), 4.37 (qd, *J* = 7.6, 1,7 Hz, 2 H), 2.60 (sept, *J* = 7.5 Hz, 4 H), 1.41 (t, *J* = 7.1 Hz, 3 H), 0.96 (t, *J* = 7.1 Hz, 6 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 169.0, 143.5, 137.2, 131.8, 131.4, 130.8, 130.8, 129.5, 128.5, 128.4, 127.4, 126.5, 126.4, 64.6, 60.9, 43.1, 14.3, 11.3.

MS: *m*/*z* (%) = 337 (6) [M^+], 309 (23), 308 (100), 265 (17), 264 (78), 246 (23), 219 (42), 204 (12), 191 (15), 189 (14), 188 (10), 130 (12), 15 (12), 91 (21).

HRMS: *m*/*z* calcd for $C_{22}H_{25}NO_2$, 336.1965; found, 336.1964.

5-[(2*E*)-1-(Diethylamino)-3-phenyl-2-propenyl]-2-furan-carboxylic Acid Ethyl Ester (5d)
Column chromatographic purification using CH_2Cl_2–pentane (1:1)→CH_2Cl_2–MeOH (99:1) as eluent yielded **5d** (200 mg, 0.61 mmol, 61%) as an orange oil.

IR (film): 2971 (vs), 1725 (s), 1514 (m), 1450 (m), 1300 (s), 1214 (m), 1136 (s), 1017 (m), 762 (m), 699 (m) cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.40–7.20 (m, 5 H), 7.14 (d, *J* = 3.0 Hz, 1 H), 6.57 (d, *J* = 16.0 Hz, 1 H), 6.41–6.33 (m, 2 H), 4.59 (d, *J* = 7.5 Hz, 1 H), 4.34 (q, *J* = 7.0 Hz, 2 H), 2.73–2.51 (m, 4 H), 1.36 (t, *J* = 7.1 Hz, 3 H), 1.05 (t, *J* = 7.1 Hz, 6 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 159.9, 158.8, 143.8, 136.7, 132,9, 128.5, 127.7, 127.5, 126.5, 118.7, 109.5, 61.6, 60.7, 44.0, 14.4, 12.5.

MS: *m*/*z* (%) = 327 (10) [M^+], 256 (21), 255 (100), 227 (54), 209 (26), 181 (18), 153 (27), 152 (16),
115 (12).

HRMS: *m*/*z* calcd for $C_{20}H_{25}NO_3$, 327.1834; found, 327.1831.

***N,N,N′,N′*-Tetraallyl-3-phenyl-2-propin-1,1-diamine (8)**
The aminal **8** was prepared according to a known method[10] using aminal **1a**.

Yield: 1.73 g (5.6 mmol, 71%) orange oil (after distillation at 1.5 × 10^{-1} mbar, bp 93–97 °C).

^1H NMR (300 MHz, C_6D_6): δ = 7.40–7.37 (m, 2 H), 7.00–6.95 (m, 3 H), 5.98–5.85 (m, 4 H), 5.20 (dq, *J* = 17.2, 1.8 Hz, 4 H), 5.09–5.04 (m, 4 H), 4.55 (s, 1 H), 3.65 (ddt, *J* = 14.6, 5.7, 1.4 Hz, 4 H), 3.41 (dd, *J* = 14.1, 7.1 Hz, 4 H).

^{13}C NMR (75 MHz, C_6D_6): δ = 136.5, 132.1, 128.6, 128.4, 123.5, 117.1, 88.1, 85.3, 71.6, 52.5.

Addition of Grignard Reagents 3a−h to Aminal 8: General Procedure for 10
To a stirred soln of the aminal **8** (306 mg, 1.0 mmol) in THF (2 mL) at –60 °C, $(CF_3CO)_2O$ (231 mg, 1.1 mmol) was added dropwise. After 15 min, NMP (0.5 mL, 5 mmol) was added. To this soln, the

Grignard reagent **3** [1.5 mmol, dissolved in THF (3 mL)] was added dropwise. After 0.5 to 1 h, the reaction was complete according to GC/MS-analysis and quenched with sat. aq NH_4Cl soln (10 mL). The aq layer was extracted with Et_2O (3 × 20 mL), the combined organic layers were washed with brine (30 mL), dried ($MgSO_4$), filtered and evaporated under reduced pressure. Purification by column chromatography with pentane–CH_2Cl_2 as eluent gave the corresponding products **10a,b**.

_N,N_-Diallyl-_N_-[1-(4-methoxyphenyl)-3-phenyl-2-propynyl]-amine (10a)

Column chromatographic purification using CH_2Cl_2–pentane (1:4→1:2) as eluent yielded **10a** (242 mg, 0.76 mmol, 76%) as an orange oil.

IR (film): 2931 (w), 2835 (w), 2816 (w), 1610 (m), 1586 (m), 1510 (vs), 1490 (m), 1443 (m), 1249 (vs), 1171 (s), 1036 (m), 920 (m), 757 (s), 691 (m) cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.58 (d, *J* = 8.9 Hz, 2 H), 7.55–7.51 (m, 2 H), 7.35–7.33 (m, 3 H), 6.89 (d, *J* = 8.8 Hz, 2 H), 5.92–5.79 (m, 2 H), 5.30–5.11 (m, 4 H), 5.04 (s, 1 H), 3.82 (s, 3H), 3.27 (ddt, *J* = 14.2, 4.0, 2.2 Hz, 2 H), 3.03 (dd, *J* = 14.2, 7.9 Hz, 2 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 158.9, 136.6, 131.8, 131.4, 129.4, 128.3, 128.1, 123.3, 117.2, 113.4, 87.7, 85.7, 56.0, 55.3, 53.4.

MS: *m*/*z* (%) = 317 (83) [M^+], 222 (20), 221 (100), 178 (10).

HRMS: *m*/*z* calcd for $C_{22}H_{23}NO$, 317.1780; found, 317.1714.

4-[1-(Diallylamino)-3-phenyl-2-propynyl] Benzoic Acid Ethyl Ester (10b)

Column chromatographic purification using CH_2Cl_2–pentane (1:6→1:0) as eluent yielded **10b** (239 mg, 0.66 mmol, 66%) as an orange oil.

IR (film): 2980 (w), 2828 (w), 1719 (vs), 1275 (vs), 1104 (s), 1022 (m), 756 (s), 691 (m) cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 8.03 (d, *J* = 8.4 Hz, 2 H), 7.77 (d, *J* = 8.1 Hz, 2 H), 7.56–7.53 (m, 2 H), 7.38–7.33 (m, 3 H), 5.91–5.78 (m, 2 H), 5.28 (d, *J* = 17.3 Hz, 2 H), 5.14 (d, *J* = 12.4 Hz, 2 H), 5.12 (s, 1 H), 4.38 (q, *J* = 7.1 Hz, 2 H), 3.25 (ddt, *J* = 14.2, 4.5, 2.2 Hz, 2 H), 3.05 (dd, *J* = 14.1, 8.5 Hz, 2 H), 1.40 (t, *J* = 7.1 Hz, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 166.5, 144.7, 136.2, 131.8, 129.7, 129.4, 128.4, 128.3, 128.2, 123.0, 117.6, 88.3, 84.5, 60.9, 56.5, 53.7, 14.3.

MS: *m*/*z* (%) = 359 (11) [M^+], 358 (17), 264 (23), 263 (100), 235 (41), 210 (51), 191 (13), 190 (19), 189 (31).

HRMS: *m*/*z* calcd for $C_{24}H_{24}NO_2$, 358.1807; found, 358.1779.

1-(4-Methoxyphenyl)-3-phenyl-2-propynylamine (11)

To a stirred soln of $Pd(PPh_3)_4$ (16 mg, 0.014 mmol) and *N*,*N*-dimethylbarbituric acid (262 mg, 1.68 mmol) in CH_2Cl_2 (2 mL) was added a soln of **10a** (88 mg, 0.28 mmol) in CH_2Cl_2 (3 mL). After stirring for 30 min at r.t., the reaction was complete according to GC/MS-analysis. The solvent was removed under vacuo and the residue was redispersed in Et_2O (15 mL). The organic layer was washed with sat. Na_2CO_3 soln (2 × 30 mL) and extracted with 2 mol/L HCl (40 mL). The aq phase was washed with Et_2O (2 × 50 mL) and treated with sat. Na_2CO_3 soln in the presence of Et_2O until pH 8 was reached. The aq phase was extracted with CH_2Cl_2 (6 × 25 mL), dried ($MgSO_4$) and filtered. The solvent was removed under reduced pressure to give the primary amine (47 mg, 0.20 mmol, 71%) as a brown oil.

IR (film): 3368 (w), 2959 (m), 2932 (m), 2836 (m), 1608 (s), 1511 (vs), 1490 (s), 1303 (s), 1250 (vs), 1174 (s), 1032 (s), 834 (s), 758 (s), 693 (s) cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.52 (d, *J* = 8.7 Hz, 2 H), 7.47–7.44 (m, 2 H), 7.32–7.29 (m, 3 H), 6.91 (d, *J* = 8.9 Hz, 2 H), 4.97 (s, 1 H), 3.82 (s, 3 H), 1.87 (br s, 2 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 159.1, 134.5, 131.6, 128.2, 128.1, 128.0, 123.1, 113.9, 88.7, 84.1, 55.3, 46.8.

MS: *m*/*z* (%) = 237 (23) [M^+], 236 (100), 222 (29), 221 (19), 206 (17), 193 (13), 178 (10), 129 (21), 128 (15).

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