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Synthesis of 2-ynamides by direct palladium-catalyzed oxidative aminocarbonylation of alk-1-ynes

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Abstract

A novel synthesis of 2-ynamides (**3**) by palladium-catalyzed oxidative aminocarbonylation of alk-1-ynes (**1**) is reported. Reactions are catalyzed by PdI_2/KI and are carried out at 100°C in dioxane as the solvent in the presence of dialkylamines (**2**) as nucleophiles (amine/alk-1-yne molar ratio = 1/1) using a 4/1 CO/air mixture (20 atm total pressure at 25°C). © 2001 Elsevier Science B.V. All rights reserved.

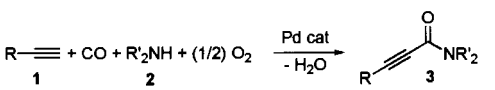
Keywords: Alk-1-ynes; Amides; Aminocarbonylation; Carbonylation; Palladium; 2-Ynamides

1. Introduction

2-Ynamides (**3**) are useful intermediates for the synthesis of some biologically active molecules [1] and heterocyclic derivatives [2]. They are generally prepared by Pd/Cu-catalyzed reaction between alk-1-ynes and carbamoyl chlorides [1,3]. The possibility to obtain **3** by direct aminocarbonylation of alk-1-ynes **1** appears therefore synthetically attractive. However, although the catalytic oxidative monocarbonylation of **1** with alcohols as nucleophiles to obtain alkynyl esters has been known for many years [4], to our knowledge no analogous catalytic aminocarbonylation [5] has been described to date. The only example reported in the literature of formation of **3** from **1**, **2** and CO involves a non-catalytic reaction promoted by a Ni(II) complex [6].

The application of the Pd-catalyzed oxidative monocarbonylation methodology [4] to the synthesis of 2-ynamides using amines as nucleophiles rather than alcohols proved to be ineffective, as shown by the following experiments. The reaction between phenylacetylene and diethylamine carried out using the system $PdCl_2/CuCl_2$/AcONa under the conditions described in Ref. [4a] using diethylamine as the solvent in place of methanol gave only a 5% yield of the diethylamide of 3-phenylpropynoic acid **3c**, the main reaction product being 1,4-diphenyl-1,3-butadiyne (34%) at total substrate conversion. Practically the same results were obtained with dioxane as the solvent using a 1/1 molar ratio phenylacetylene/diethylamine (6% of **3c**, 41% of 1,4-diphenyl-1,3-butadiyne at total substrate conversion).

We now wish to report the Pd-catalyzed aminocarbonylation of **1**, which occurs under relatively mild conditions and affords **3** in satisfactory yields (Eq. 1).



a R = Bu, R' = Et
b R = *t*-Bu, R' = Et
c R = Ph, R' = Et
d R = *p*-$MeOC_6H_4$, R' = Et
e R = *p*-BrC_6H_4, R' = Et
f R = *p*-NCC_6H_4, R' = Et
g R = *p*-$O_2NC_6H_4$, R' = Et
h R = Ph, R' = Bu
i R = Ph, R'_2 = $-(CH_2)_2O(CH_2)_2-$ (1)

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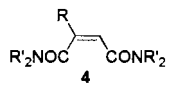
2. Results and discussion

This new method consists of the reaction of alk-1-ynes (**1**) and dialkylamines (**2**) (1/1 molar ratio) at 100°C with carbon monoxide and oxygen (CO/air = 4/1, 20 atm total at 25°C) in dioxane as the solvent in the presence of PdI_2 (0.2 mol%) and KI (2 mol%) [7]. Representative results are collected in Table 1.

Both alky- and arylacetylenes could be used successfully, the latter being consistently more reactive (compare entries 1–2 with entries 3–9). Moreover, alkylacetylenes also gave small amounts of products resulting from oxidative diaminocarbonylation of the triple bond, i.e. bis-diethylamides of alkylmaleic acid **4** (4–9%, entries 1–2). Thus, the reaction between hex-1-yne or *t*-butylacetylene with CO, oxygen and diethylamine afforded after 24 h, **3a** (58%) or **3b** (42%) together with **4a** (9%) or **4b** (4%) at 71% or 50% substrate conversion, respectively (entries 1, 2). Practically the same results were obtained when the reaction time was prolonged to 48 h or when a molar ratio **1**/PdI_2 of 200 (with KI/PdI_2 = 10) was used instead of 500.



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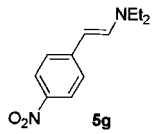
a R = Bu, R' = Et
b R = *t*-Bu, R' = Et

Arylacetylenes could bear π-donor as well as π-acceptor substituents (entries 4–7). Indeed, reaction kinetics and product yields were quite insensitive to the nature of the substituent on the ring (compare entries 3–6), with the exception of *p*-nitrophenylacetylene, whose conversion rate was higher with respect to the other arylacetylenes tested. With this substrate, however, a side-reaction resulting from amine addition to the triple bond with formation of a 21% yield of (*E*)-diethyl-[2-(4-nitrophenyl)vinyl]amine **5g** took place, which lowered the yield of the desired product **3g** to 32% (entry 7).



5g

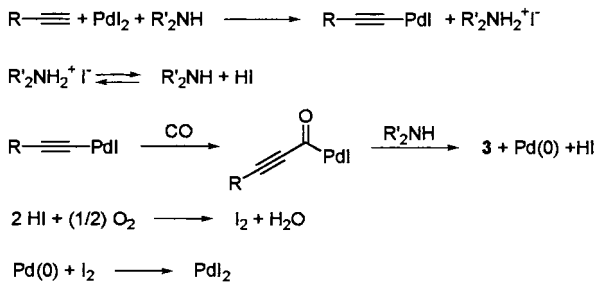
A nucleophilic secondary amine such as diethylamine (entries 1–7), dibutylamine (entry 8) or morpholine (entry 9) was required for the reaction to occur, hindered amines (such as diisopropylamine) or amines of low basicity (like *N*-methylaniline) being unreactive. On the other hand, the use of primary amines led to complex reaction mixtures, in which the 2–alkynamides were present in only limited amounts. The main reaction products in this case resulted from oxidative carbonylation of the amino group, with formation of ureas, as indicated by GLC-MS analysis.

According to what previously proposed for the formation of alkynyl esters by $PdCl_2$-catalyzed oxidative monoalkoxycarbonylation of alk-1-ynes [4], the catalytic process leading to **3** should occur via formation of an alkynylpalladium species as the key intermediate. This species, which is apparently stabilized by iodide ligands, results from the reaction between the alk-1-yne, PdI_2 and the amine (Scheme 1; anionic iodide ligands are omitted for simplicity). Subsequent carbon monoxide insertion into the carbon-palladium bond followed by nucleophilic displacement by the amine affords product **3** and Pd(0), whose reoxidation according to the usual mechanism [7] regenerates the catalytically active species PdI_2. Attack by the amine on the

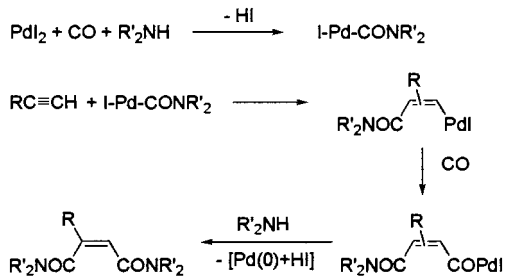
Table 1
Synthesis of 2-alkynylamides **3** by PdI_2/KI-catalyzed oxidative aminocarbonylation of alk-1-ynes **1** [a]

Run	R	**2**	Conversion of **1** (%) [b]	Yield of **3** (%) [c]	
1	Bu	Et_2NH	71	**3a**	58 (54) [d]
2	*t*-Bu	Et_2NH	50	**3b**	42 (36) [e]
3	Ph	Et_2NH	90	**3c**	81 (73)
4	*p*-$MeOC_6H_4$	Et_2NH	83	**3d**	80 (73)
5	*p*-BrC_6H_4	Et_2NH	82	**3e**	74 (68)
6	*p*-NCC_6H_4	Et_2NH	95	**3f**	70 (66)
7 [f]	*p*-$O_2NC_6H_4$	Et_2NH	100	**3g**	32 (28) [g]
8	Ph	Bu_2NH	90	**3h**	70 (62)
9	Ph	Morpholine	93	**3i**	70 (64)

[a] Unless otherwise noted, all reactions were carried out in dioxane (0.5 mmol of **1**/ml of dioxane, 10 mmol scale based on **1**) using a 1/1 molar ratio **1**/**2** at 100°C for 24 h under 20 atm of a 4/1 mixture of CO/air in the presence of PdI_2 (0.2%) and KI (2%).
[b] Determined by GLC.
[c] GLC yield (isolated yield) based on starting **1**.
[d] Bis-diethylamide of butylmaleic acid **4a** (9% GLC yield, 6% isolated) was also present in the reaction mixture.
[e] Bis-diethylamide of *t*-butylmaleic acid **4b** (4% GLC yield, 2% isolated) was also present in the reaction mixture.
[f] The reaction time was 15 h.
[g] (*E*)-Diethyl-[2-(4-nitrophenyl)vinyl]amine **5g** was also formed in 21% GLC yield.



Scheme 1.



Scheme 2.

alkynoylpalladium complex apparently requires a sufficiently nucleophilic amine, since as mentioned before, no aminocarbonylation was observed with hindered amines. It is worth noting that the possibility to obtain a 2-ynamide by a sequence of steps strictly analogous to that proposed starting from a Ni(II) complex has been demonstrated [6]. The following sequence of reactions has been carried out: (a) reaction between acetylene, $Ni(PPh_3)_2Br_2$ and triethylamine to give an ethynylnickel complex; (b) reaction of this complex with CO to obtain the corresponding propynoylnickel complex; (c) reaction of the latter with diethylamine to form the diethylamide of propynoic acid and Ni(0).

Side-products **4a–b**, i.e. maleic bis-amides, correspond to oxidative dicarbonylation of the triple bond, and are formed through a competitive reaction pathway, involving *syn* addition of a carbamoylpalladium species to the triple bond followed by carbon monoxide insertion and nucleophilic displacement by the amine (Scheme 2). It is important to note that, as previously reported [7a], oxidative carbonylation of alkyl- and arylacetylenes catalyzed by the PdI_2/KI catalytic system with alcohols as nucleophiles instead of amines resulted in *exclusive* formation of maleic derivatives through an analogous reaction pattern. Clearly, the shift towards the oxidative monocarbonylation observed in the case of amines is due to the basicity of the latter, which promotes the first step showed in Scheme 1, i.e. formation of the alkynylpalladium species.

In conclusion, we have developed the first example of catalytic synthesis of 2-ynamides **3** via oxidative monoaminocarbonylation of alk-1-ynes **1**. The reaction is quite selective and the synthetic procedure is simple. Moreover, catalytic efficiencies as high as 400 mol of **3** per mol of catalyst used have been achieved.

3. Experimental

3.1. General

Melting points were determined on a Reichert Thermovar melting point apparatus and are uncorrected. Elemental analyses were carried out with a Carlo Erba Elemental Analyzer Mod. 1106. ^{1}H-NMR and ^{13}C-NMR spectra were taken on a Bruker AC300 spectrometer and run on $CDCl_3$ solutions with Me_4Si as internal standard and recorded at 300 and 75 MHz, respectively. Chemical shifts and coupling constants (J) are given in ppm (δ) and in Hz, respectively. IR spectra were taken on a Perkin-Elmer Paragon 1000 PC FT-IR spectrometer. Mass spectra were obtained using an HP 5972A GC-MS apparatus at 70 eV ionization voltage. All reactions were analyzed by TLC on silica gel 60 F_{254} or by GLC using a Shimadzu GC-14A gas chromatograph and capillary columns with polymethylsilicone + 5% phenylsilicone as the stationary phase (HP-5). Column chromatography was performed on silica gel 60 (Merck, 70-230 mesh). Dioxane was distilled over sodium before use. Starting hex-1-yne, *t*–butylacetylene, phenylacetylene, diethylamine, dibutylamine, and morpholine were commercially available and were used without further purification. *p*-Methoxyphenylacetylene [8], *p*-bromophenylacetylene [9], *p*-cyanophenylacetylene [10] and *p*-nitrophenylacetylene [8] were prepared according to literature procedures.

3.2. Typical procedure for oxidative aminocarbonylation of alk-1-ynes

In a typical experiment, a 300 ml stainless steel autoclave with magnetic stirring was charged in the presence of air with PdI_2 (7.0 mg, 0.019 mmol), KI (32 mg, 0.19 mmol) and a solution of **1** (9.6 mmol) and **2** (9.6 mmol) in dioxane (19 ml). The autoclave was pressurized with stirring at room temperature with CO (16 atm) and air (up to 20 atm of total pressure), and then heated at 100°C with stirring for 24 h. The autoclave was then cooled and degassed and products separated as described below.

3.3. Separation of products

Products **3a–f** and **3h–i** were easily isolated by column chromatography on silica gel after removal of the solvent under reduced pressure: **3a** (0.94 g, 54%) and **4a** (0.16 g, 6%) were eluted in this order using hexane/AcOEt from 6:4 to 2:8; **3b** (0.63 g, 36%) and **4b**

(54 mg, 2%) were eluted in this order using hexane/AcOEt from 6:4 to 2:8; **3c** (6:4 hexane/AcOEt, 1.41 g, 73%); **3d** (6:4 hexane/AcOEt, 1.62 g, 73%); **3e** (7:3 hexane/AcOEt, 1.82 g, 68%); **3f** (hexane/AcOEt from 7:3 to 6:4, 1.44 g, 66%); **3h** (7:3 hexane/AcOEt, 1.54 g, 62%); **3i** (hexane/AcOEt from 7:3 to 6:4, 1.33 g, 64%). Products **3g** and **5g** were consistently obtained in a mixture by column chromatography of the crude deriving from carbonylation of *p*-nitrophenylacetylene and diethylamine. In order to obtain pure **3g** the reaction crude was extracted with diethyl ether and washed with a solution of NH_4Cl. The aqueous phase was extracted with diethyl ether and the combined organic layers dried over Na_2SO_4. After filtration and removal of the solvent by distillation under reduced pressure, column chromatography (hexane/AcOEt = 7:3) afforded **3g** (0.66 g, 28%). Pure product **5g** was obtained by the reaction between *p*-nitrophenylacetylene (170 mg, 1.16 mmol), diethylamine (85 mg, 1.16 mmol) in dioxane (2.3 ml) in the presence of PdI_2 (1.0 mg, $2.78 \cdot 10^{-3}$ mmol) and KI (4.6 mg, 0.028 mmol) under nitrogen at 100°C for 15 h. The solvent was removed by distillation under reduced pressure, and column chromatography (hexane/AcOEt = 8:2) afforded **5g** (60 mg, 24% yield).

3.4. Characterization of products

Known products **3a** [6b,11], **3c** [6a], and **4a** [6b] were characterized by comparison with literature data. As explained above, product **5g** could not be isolated from the crude reaction deriving from carbonylation of *p*-nitrophenylacetylene and diethylamine, and was characterized by GC-MS comparison with the pure product obtained by PdI_2/KI–catalyzed addition of diethylamine to *p*-nitrophenylacetylene.

3.4.1. Diethylamide of 4,4-dimethylpent-2-ynoic acid (3b)

Yellow oil. IR (neat) 2972 (s), 2935 (m), 2228 (m), 1628 (s), 1459 (m), 1426 (s), 1282 (m), 1155 (w), 738 (w) cm^{-1}; ^{1}H-NMR δ 3.55 (q, $J = 7.1$, 2 H, CH_2CH_3), 3.41 (q, $J = 7.1$, 2 H, CH_2CH_3), 1.29 (s, 9 H, *t*-Bu), 1.21 (t, $J = 7.1$, 3 H, CH_2CH_3), 1.13 (t, $J = 7.1$, 3 H, CH_2CH_3); ^{13}C-NMR δ 154.33, 98.78, 73.19, 43.61, 39.32, 30.26, 27.74, 14.25, 12.91; MS *m*/*e* 181 (13, M^+), 180 (8), 166 (29), 138 (16), 125 (19), 124 (8), 110 (13), 109 (100), 81 (41), 79 (25), 67 (9), 65 (8), 53 (15). Anal. Calc. for $C_{11}H_{19}NO$: C, 72.88; H, 10.56; N, 7.73. Found: C, 72.55; H, 10.60; N, 7.77%.

3.4.2. Diethylamide of 3-(4-methoxyphenyl)propynoic acid (3d)

Yellow solid, m.p. 59–60°C. IR (KBr) 2979 (w), 2935 (w), 2200 (m), 1628 (s), 1601 (m), 1508 (m), 1431 (m), 1250 (m), 1136 (m), 1028 (m), 839 (m) cm^{-1}; ^{1}H-NMR δ 7.51–7.46 (m, 2 H on phenyl ring), 6.91–6.85 (m, 2 H on phenyl ring), 3.83 (s, 3 H, OMe), 3.66 (q, $J = 7.1$, 2 H, CH_2CH_3), 3.47 (q, $J = 7.2$, 2 H, CH_2CH_3), 1.28 (t, $J = 7.1$, 3 H, CH_2CH_3), 1.17 (t, $J = 7.2$, 3 H, CH_2CH_3); ^{13}C-NMR δ 161.02, 154.33, 134.11, 114.31, 112.89, 89.50, 81.39, 55.40, 43.61, 39.34, 14.44, 12.94; MS *m*/*e* 231 (10, M^+), 230 (9), 216 (16), 160 (12), 159 (100), 144 (15), 132 (34), 116 (17), 88 (15), 72 (12), 62 (10). Anal. Calc. for $C_{14}H_{17}NO_2$: C, 72.70; H, 7.41; N, 6.06. Found: C, 72.95; H, 7.36; N, 6.12%.

3.4.3. Diethylamide of 3-(4-bromophenyl)propynoic acid (3e)

Yellow solid, m.p. 98–100°C. IR (KBr) 2980 (w), 2936 (w), 2209 (m), 1613 (s), 1480 (s), 1432 (s), 1292 (m), 1062 (m), 1008 (m), 838 (m), 733 (m) cm^{-1}; ^{1}H-NMR δ 7.54–7.48 (m, 2 H on phenyl ring), 7.42–7.37 (m, 2 H on phenyl ring), 3.65 (q, $J = 7.2$, 2 H, CH_2CH_3), 3.48 (q, $J = 7.1$, 2 H, CH_2CH_3), 1.28 (t, $J = 7.2$, 3 H, CH_2CH_3), 1.18 (t, $J = 7.1$, 3 H, CH_2CH_3); ^{13}C-NMR δ 153.74, 133.69, 131.92, 124.50, 119.86, 87.81, 83.11, 43.62, 39.43, 14.44, 12.86; MS *m*/*e* 281 (7, $M^+ + 2$), 280 (15, $M^+ + 1$), 279 (8, M^+), 278 (16), 266 (8), 264 (8), 209 (97), 207 (100), 128 (30), 101 (7), 100 (20), 99 (9), 75 (7), 74 (21), 72 (7), 56 (12). Anal. Calc. for $C_{13}H_{14}BrNO$: C, 55.73; H, 5.04; Br, 28.52; N, 5.00. Found: C, 55.66; H, 5.09; Br, 28.91; N, 4.97%.

3.4.4. Diethylamide of 3-(4-cyanophenyl)propynoic acid (3f)

Yellow solid, m.p. 94–95°C. IR (KBr) 2977 (w), 2940 (w), 2225 (m), 1618 (s), 1437 (w), 1250 (m), 832 (m), 731 (m) cm^{-1}; ^{1}H-NMR δ 7.72–7.62 (m, 4 H on phenyl ring), 3.67 (q, $J = 7.2$, 2 H, CH_2CH_3), 3.50 (q, $J = 7.2$, 2 H, CH_2CH_3), 1.30 (t, $J = 7.2$, 3 H, CH_2CH_3), 1.20 (t, $J = 7.2$, 3 H, CH_2CH_3); ^{13}C-NMR δ 153.14, 132.76, 132.21, 125.61, 117.98, 113.32, 86.55, 85.40, 43.67, 39.50, 14.48, 12.81; MS *m*/*e* 226 (18, M^+), 225 (37), 211 (12), 155 (15), 154 (100). Anal. Calc. for $C_{14}H_{14}N_2O$: C, 74.31; H, 6.24; N, 12.38. Found: C, 74.13; H, 6.27; N, 12.26%.

3.4.5. Diethylamide of 3-(4-nitrophenyl)propynoic acid (3g)

Yellow solid, m.p. 113–115°C. IR (KBr) 2984 (w), 2937 (w), 2224 (w), 1615 (s), 1519 (s), 1434 (m), 1345 (s), 1100 (m), 859 (m) cm^{-1}; ^{1}H-NMR δ 8.27–8.21 (m, 2 H on phenyl ring), 7.74–7.68 (m, 2 H on phenyl ring), 3.69 (q, $J = 7.1$, 2 H, CH_2CH_3), 3.51 (q, $J = 7.1$, 2 H, CH_2CH_3), 1.31 (t, $J = 7.1$, 3 H, CH_2CH_3), 1.21 (t, $J = 7.1$, 3 H, CH_2CH_3); ^{13}C-NMR δ 153.11, 148.18, 133.14, 127.52, 123.74, 86.31, 86.02, 43.74, 39.56, 14.49, 12.81; MS *m*/*e* 246 (14, M^+), 245 (32), 231 (14), 175 (11), 174 (100), 144 (6), 128 (33), 116 (7), 100 (11), 74 (10). Anal. Calc. for $C_{13}H_{14}N_2O_3$: C, 63.40; H, 5.73; N, 11.38. Found: C, 63.62; H, 5.77; N, 11.28%.

*3.4.6. Dibutylamide of 3-phenylpropynoic acid (**3h**)*

Yellow oil. IR (neat) 2959 (s), 2932 (s), 2873 (m), 2214 (m), 1627 (s), 1425 (m), 1298 (m), 1209 (m), 1140 (m), 758 (m), 691 (m) cm^{-1}; ^{1}H-NMR δ 7.55–7.50 (m, 2 H on phenyl ring), 7.42–7.32 (m, 3 H on phenyl ring), 3.64–3.57 (m, 2 H, NCH_2CH_2), 3.44–3.37 (m, 2 H, NCH_2CH_2), 1.72–1.25 (m, 8 H, 2 $CH_2CH_2CH_3$), 0.97 (t, 3 H, $J = 7.3$, CH_2CH_3), 0.94 (t, 3 H, $J = 7.3$, CH_2CH_3); ^{13}C-NMR δ 154.49, 132.33, 129.84, 128.54, 121.02, 89.27, 82.36, 48.99, 44.71, 31.12, 29.70, 20.27, 20.06, 13.83; MS *m/e* 257 (2, M^+), 215 (7), 214 (15), 130 (11), 129 (100), 75 (6). Anal. Calc. for $C_{17}H_{23}NO$: C, 79.33; H, 9.01; N, 5.44. Found: C, 79.72; H, 9.09; N, 5.39%.

*3.4.7. 1-Morpholino-4-yl-3-phenylpropynone (**3i**)*

Yellow solid, m.p. 53–54°C. IR (KBr) 2974 (w), 2862 (w), 2215 (m), 1626 (s), 1431 (s), 1280 (m), 1212 (m), 1112 (m), 851 (m), 760 (m), 728 (m), 690 (m) cm^{-1}; ^{1}H-NMR δ 7.57–7.52 (m, 2 H on phenyl ring), 7.44–7.33 (m, 3 H on phenyl ring), 3.87–3.82 (m, 4 H, CH_2OCH_2), 3.78–3.73 (m, 4 H, CH_2NCH_2); ^{13}C-NMR δ 153.26, 132.41, 130.18, 128.59, 120.46, 91.15, 80.94, 66.95, 66.54, 47.39, 42.09; MS *m/e* 215 (21, M^+), 186 (9), 185 (6), 156 (6), 130 (12), 129 (100), 116 (8), 102 (7), 101 (10), 86 (22), 75 (21), 74 (8), 56 (28). Anal. Calc. for $C_{13}H_{13}NO_2$: C, 72.54; H, 6.09; N, 6.51. Found: C, 72.71; H, 6.03; N, 6.60%.

*3.4.8. Bis-diethylamide of (Z)-2-t-butylbut-2-enedioic acid (**4b**)*

Yellow oil. IR (neat) 2969 (s), 2874 (w), 1631 (s), 1461 (s), 1430 (s), 1258 (m), 1142 (m), 1081 (w) cm^{-1}; ^{1}H-NMR δ 6.04 (s, 1 H, =CH), 3.69–3.21 (m, 8 H, 4 CH_2CH_3), 1.22 (s, 9 H, *t*-Bu), 1.22–1.06 (m, 12 H, 4 CH_2CH_3); ^{13}C-NMR δ 169.05, 165.96, 155.07, 117.08, 42.94, 42.77, 40.02, 37.53, 30.11, 14.52, 13.20, 12.48; MS *m/e* 282 (M^+, absent), 225 (12), 211 (26), 210 (100), 182 (15), 126 (35), 100 (9), 72 (86), 67 (7). Anal. Calc. for $C_{16}H_{30}N_2O_2$: C, 68.04; H, 10.71; N, 9.92. Found: C, 68.21; H, 10.64; N, 9.98%.

*3.4.9. (E)-Diethyl-[2-(4-nitrophenyl)vinyl]amine (**5g**)*

Brown oil. IR (neat) 2974 (w), 2933 (w), 1631 (m), 1574 (s), 1518 (m), 1345 (s), 1293 (s), 1103 (m), 852 (m) cm^{-1}; ^{1}H-NMR δ 8.01–7.94 (m, 2 H on phenyl ring), 7.13–7.06 (m, 2 H on phenyl ring), 7.04 (d, $J = 13.7$, 1 H, HC=C*H*N), 5.16 (d, $J = 13.7$, 1 H, *H*C=CHN), 3.26 (q, $J = 7.1$, 4 H, 2 CH_2CH_3), 1.20 (t, $J = 7.1$, 6 H, 2 CH_2CH_3); ^{13}C-NMR δ 148.57, 141.90, 124.56, 123.75, 121.99, 94.49, 45.95, 13.34; MS *m/e* 220 (100, M^+), 205 (80), 191 (17), 175 (17), 159 (29), 158 (66), 130 (27), 56 (40). Anal. Calc. for $C_{12}H_{16}N_2O_2$: C, 65.43; H, 7.32; N, 12.72. Found: C, 65.28; H, 7.39; N, 12.61%.

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