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Alkynylation of *N*-tosylimines with aryl acetylenes promoted by $ZnBr_2$ and *N*,*N*-diisopropylethylamine in acetonitrile

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Abstract—We found a suitable condition for the effective alkynylation of *N*-tosylimines with aryl acetylenes. The reaction of *N*-tosylimines and aryl acetylenes in the presence of $ZnBr_2$ and DIEA (*N*,*N*-diisopropylethylamine) in CH_3CN afforded the desired *N*-tosyl propargylamines in moderate to good yields.

The addition reaction of nucleophiles to C=O bond of carbonyl compounds and C=N bond of imines and their derivatives has received much attention to organic chemists. Synthesis of propargylic alcohols and propargylic amines is one of the major topics in recent years due to the usefulness in synthetic organic chemistry as synthetic intermediates and their variety biological activities.[1] For the introduction of triple bond, metal acetylide has been used usually, which was generated in situ from terminal acetylenic compound and *n*-BuLi or EtMgBr.[2a] Recently, acetylide ion was generated and used in the alkynylation of ketones and aldehydes by the use of cesium hydroxide[2b] or nonmetallic benzyltrimethylammonium hydroxide.[2c] However, such processes have some drawbacks. The reaction usually must be carried out under anhydrous conditions with much caution. Due to the strongly basic nature or nucleophilicity of the *n*-BuLi, EtMgBr or quaternary ammonium hydroxide, the reaction may cause some side reactions.

Recently, Carreira and co-workers have reported a mild procedure for the addition reaction of acetylenic compound to nitrones involving the in situ generated zinc acetylide in the presence of a tertiary amine.[3] The concept has been extended further by many chemists.[4–6] Lewis acids such as $ZnCl_2$, $Zn(OTf)_2$, $ZnBr_2$, $InBr_3$, CuBr, GaI_3, $Sn(OTf)_2$ were used with or without the combination of amines depending on the used reagents.[4–6] As the electrophilic components, aldehydes,[4a,b,f,g,6b] imines,[4c,6a] *N*-acyliminium salts,[4e] α,β-unsaturated carbonyls,[4d,5d] and nitrones[3] have been studied. However, to our best knowledge, another reactive electrophile, *N*-tosylimine[7] was not examined. Carreira and co-workers have reported only one example of the reaction of *N*-tosylimine and phenylacetylene in their $Zn(OTf)_2$-mediated synthesis of *N*-hydroxy propargylic amine derivatives.[3]

In some cases, *N*-tosylimine showed higher electrophilicity than the corresponding aldehyde or imine. Thus, we presumed that we could prepare the corresponding *N*-tosyl propargylamine compounds by applying the newly developing concept[3,4] if we successfully find out suitable Lewis acid and amine catalyst combination (Scheme 1). Fortunately, we could find a good condition for the synthesis of *N*-tosyl propargylamines and wish to report herein the results.

Initially, we screened a variety of combinations as shown in Table 1 by using 2-chlorobenzaldehyde *N*-tosylimine (**1a**) and phenylacetylene (**2a**) as the representative examples. The use of indium chloride (entry 1) and zinc chloride (entry 2) was found ineffective. The use of catalytic amounts of zinc bromide (entry 3) gave low yield of product **3a**. The reaction at room temperature with zinc bromide failed completely (entry 4). The use of THF (entry 7) or benzene (entry 8) was found

Keywords: Alkynylation; *N*-Tosylimines; Aryl acetylenes; $ZnBr_2$; DIEA.
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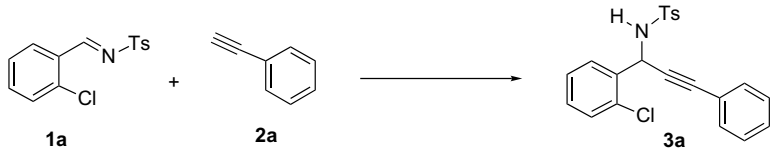


Scheme 1.

Table 1. Optimization of reaction conditions for **3a** from **1a** and **2a**

Entry	Conditions	Yield (%)
1	THF, $InCl_3$ (1.2 equiv) Et_3N (1.2 equiv), 50–60 °C, 60 h	15
2	CH_3CN, $ZnCl_2$ (1.2 equiv) Et_3N (1.2 equiv), 50–60 °C, 20 h	10
3	CH_3CN, $ZnBr_2$ (0.2 equiv) DIEA (1.3 equiv), 50–60 °C, 24 h	22
4	CH_3CN, $ZnBr_2$ (1.2 equiv) Et_3N (1 equiv), rt, 13 h	No reaction
5	CH_3CN, $ZnBr_2$ (1.2 equiv) Et_3N (1.2 equiv), 50–60 °C, 5 h	62
6	CH_3CN, $ZnBr_2$ (1.2 equiv) DIEA (1.2 equiv), 50–60 °C, 6 h	78
7	THF, $ZnBr_2$ (1.2 equiv) Et_3N (1.2 equiv), 50–60 °C, 15 h	31
8	Benzene, $ZnBr_2$ (1.2 equiv) DIEA (1.2 equiv), 50–60 °C, 13 h	48
9	CH_3CN, $ZnBr_2$ (1.2 equiv) DABCO (1.2 equiv), 50–60 °C, 48 h	No reaction

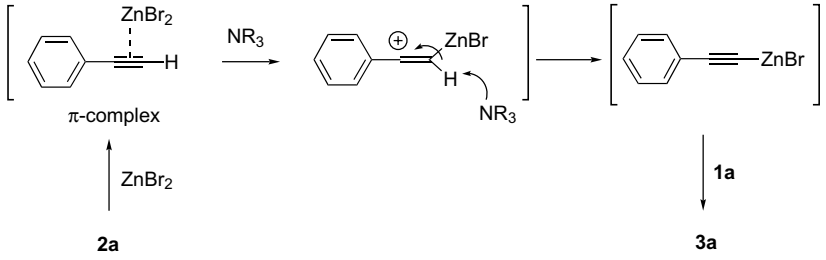
to be less effective than acetonitrile (entry 6). Triethylamine was slightly less effective than DIEA (cf. entries 5 and 6). When we used DABCO as the base catalyst, instant formation of solid materials was observed with no product formation (entry 9). From the preliminary investigation we chose the optimal conditions: $ZnBr_2$ (1.2 equiv), DIEA (1.2 equiv), acetonitrile as solvent, 50–60 °C (entry 6).

The plausible mechanism for formation of the zinc acetylide species from the reaction conditions can be thought as in Scheme 2.[4e,6b] First, formation of weak π-complex between the triple bond and Lewis acid makes the hydrogen of aryl acetylene more acidic. Subsequent deprotonation with amine base generates the zinc acetylide species, which undergo the next addition reaction with *N*-tosylimines.

Table 2 shows the representative examples for the synthesis of *N*-tosyl propargylamines **3**. As shown, versatile combinations of *N*-sulfonylimines (**1a**–**e**) and aryl acetylenes (**2a**–**d**) gave the corresponding products **3a**–**i** in reasonable yields (61–81%). *N*-Methanesulfonylimine of benzaldehyde (**1e**) showed similar reactivity. Unfortunately, phenyl propargyl ether and 1-decyne, as typical aliphatic acetylenes, did not undergo the reaction. This might be due to the low acidity of the acetylenic hydrogen in these substrates.[8]

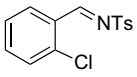
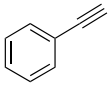
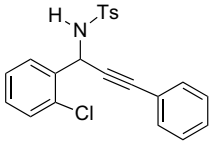
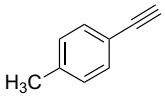
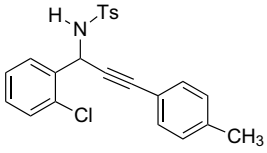
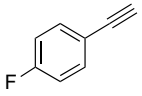
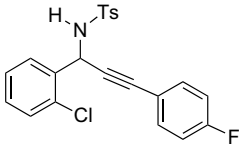
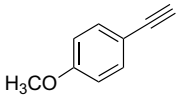
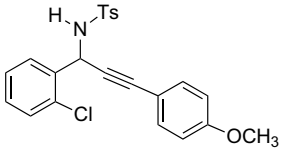
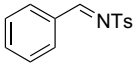
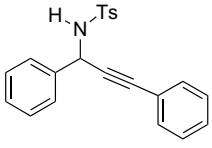
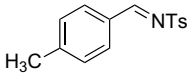
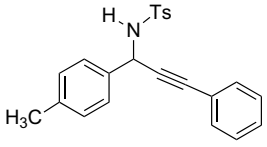
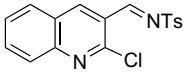
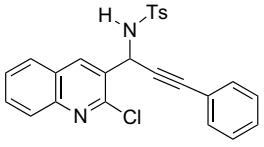
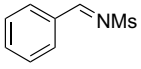
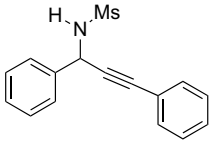
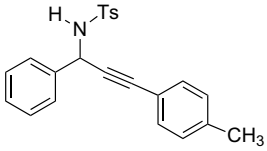
In the reaction of **1a** and ethyl propiolate (**4a**) under the same reaction conditions we could not obtain the corresponding *N*-tosyl propargylamine product. Instead, we isolated 3-(*N*-ethyl-*N*-isopropyl)aminoacrylic acid ethyl ester (**5a**) in 55% yield. The formation of such enaminone ester compound has been reported recently.[5a,9] As shown in Table 3, we examined the reaction of some tertiary amines (DIEA, Et_3N, *N*,*N*-dimethylbenzylamine, DABCO, etc.) and ethyl propiolate (**4a**) and methyl propiolate (**4b**), and ethyl phenylpropiolate (not shown). The use of DABCO (not shown) and *N*,*N*-dimethylbenzylamine did not show good results. In the case of ethyl phenylpropiolate the reaction completely failed. In other cases as shown in Table 3, moderate yields of enaminone esters were obtained. The plausible reaction mechanism is depicted in Scheme 3. Michael-type addition of tertiary amine to the activated propiolate with $ZnBr_2$ would produce zwitterionic species. Dissociation of the zwitterion into product occurred presumably via S_N1-type mechanism, which was evidenced by the selective loss of isopropyl moiety when we used DIEA. This was confirmed once again for the synthesis of **5c** (selective loss of benzyl group in this case).

Synthesized *N*-tosyl propargylamines could be converted easily into *N*-cinnamyl tosylamides by partial reduction of the triple bond with Lindlar catalyst. Derivatives of *N*-cinnamyl tosylamides have been used widely in organic synthesis.[10] Thus we examined the reduction of *N*-tosylpropargyl amine **3a** into **6** with Lindlar catalyst (Scheme 4). In the reaction, small amounts of the fully hydrogenated compound **7** was formed together.



Scheme 2.

Table 2. Synthesis of *N*-tosylpropargylamines **3a–i**[a]

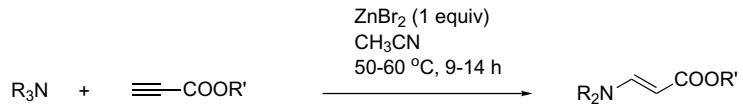
Entry	1	2	Time (h)	Products (%)
1	 **1a**	 **2a**	6	 **3a** (78)
2	**1a**	 **2b**	6	 **3b** (81)
3	**1a**	 **2c**	8	 **3c** (67)
4	**1a**	 **2d**	8	 **3d** (77)
5	 **1b**	**2a**	8	 **3e** (71)[b]
6	 **1c**	**2a**	6	 **3f** (72)
7	 **1d**	**2a**	8	 **3g** (61)
8	 **1e**	**2a**	8	 **3h** (69)
9	**1b**	**2b**	6	 **3i** (74)

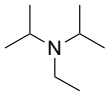
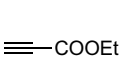
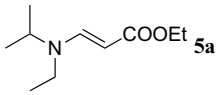
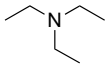
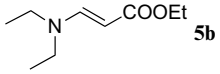
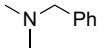
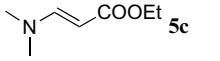
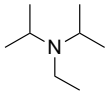
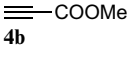
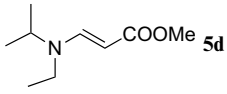
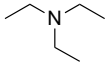
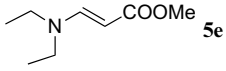
[a] Conditions: sulfonylimine **1** (1.0 equiv), aryl acetylene **2** (1.2 equiv), DIEA (1.2 equiv), $ZnBr_2$ (1.2 equiv), CH_3CN, 50–60 °C, given time.
[b] 43% yield in Ref. 3.

In order to show the general applicability of the reagents system we tried the reaction with in situ generated *N*-benzoylquinolinium chloride (Scheme 5). As expected 2-phenylethynyl-*N*-benzoyl dihydroquinoline **8** was obtained in 74% yield.[14] Typical experimental procedures for the synthesis of **3a**,[11] **5a**,[12] **6**,[13] **8**,[14] and the spectroscopic data of prepared compounds are summarized in the references and notes.

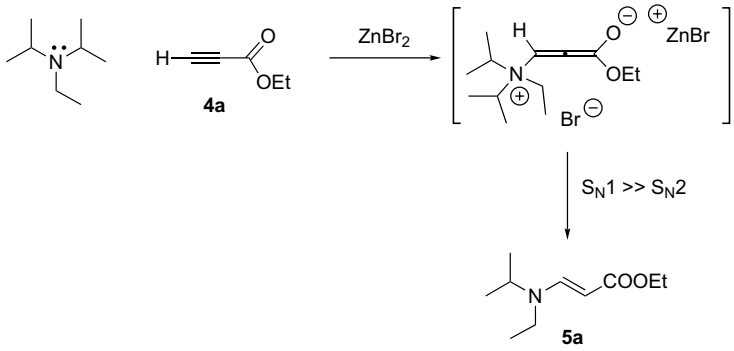
In summary, we disclosed in this paper the synthesis of *N*-tosyl propargylamines from the reaction of *N*-tosylimine and aryl acetylene with the aid of $ZnBr_2$ and

Table 3. Synthesis of enaminone esters **5a**–**e**

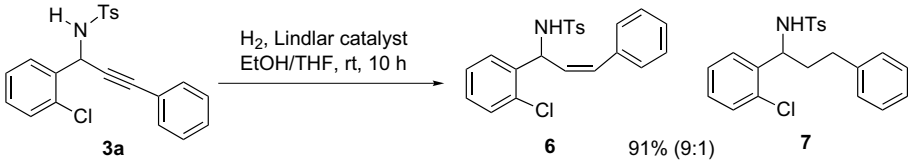


Amine	Propiolate	Time (h)	Product	Yield (%)
	 **4a**	12	 **5a**	55[a]
	**4a**	13	 **5b**	53
	**4a**	14	 **5c**	29
	 **4b**	12	 **5d**	61
	**4b**	9	 **5e**	56

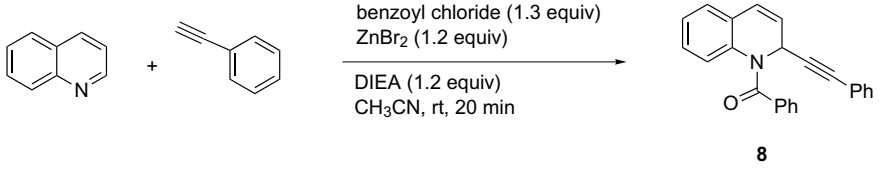
[a] The yield was increased to 61% (toluene, reflux, 20 h).



Scheme 3. Postulated reaction mechanism.



Scheme 4.



Scheme 5.

DIEA in CH_3CN. During the investigation we could widen the scope and understanding of the newly developing concept of acid–base combination for the introduction of acetylenic compounds onto electrophiles.

Acknowledgements

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References and notes

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11. Typical procedure for the synthesis of **3a**: To a stirred solution of **1a** (294 mg, 1.0 mmol) in CH_3CN (3 mL) was added phenylacetylene (**2a**, 123 mg, 1.2 mmol), $ZnBr_2$ (270 mg, 1.2 mmol), and *N*,*N*-diisopropylethylamine (DIEA, 155 mg, 1.2 mmol). The reaction mixture was stirred for 6 h at 50–60 °C. After the usual aqueous workup and column chromatographic purification process (hexanes/ether, 10:1) we obtained **3a** as a white solid, 309 mg (78%). The spectroscopic data of prepared compounds are as follows. **3a**: mp 188–189 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.31 (s, 3H), 5.12 (d, J = 8.4 Hz, 1H), 5.83 (d, J = 8.4 Hz, 1H), 7.14–7.30 (m, 10H), 7.53–7.58 (m, 1H), 7.78 (d, J = 8.4 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.65, 48.24, 85.19, 86.57, 122.13, 127.44, 127.71, 128.33, 128.86, 129.60, 129.70, 130.06, 130.43, 131.84, 133.32, 135.35, 137.48, 143.76; Mass (70 eV) *m/z* (rel. intensity) 91 (100), 105 (64), 139 (41), 240 ($M^+ - SO_2Tol$, 72), 395 (M^+, 0.4). **3b**: mp 127–128 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.30 (s, 3H), 2.31 (s, 3H), 5.36 (d, J = 8.4 Hz, 1H), 5.82 (d, J = 8.4 Hz, 1H), 7.03 (s, 4H), 7.15–7.25 (m, 4H), 7.28–7.33 (m, 1H), 7.54–7.57 (m, 1H), 7.76 (d, J = 8.4 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.59, 21.63, 48.08, 84.53, 86.65, 119.02, 127.38, 127.64, 129.01, 129.56, 129.62, 129.90, 130.24, 131.70, 133.19, 135.49, 137.45, 138.94, 143.61. **3c**: mp 126–127 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ

2.32 (s, 3H), 5.16 (d, J = 9.0 Hz, 1H), 5.53 (d, J = 9.0 Hz, 1H), 6.90–6.96 (m, 2H), 7.07–7.12 (m, 2H), 7.20 (d, J = 8.1 Hz, 2H), 7.29–7.35 (m, 3H), 7.50–7.53 (m, 2H), 7.80 (d, J = 8.4 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.60, 49.90, 85.51 (d, J = 1.4 Hz), 85.74, 115.58 (d, J = 21.8 Hz), 118.27 (d, J = 3.8 Hz), 127.48, 127.72, 128.66, 128.91, 129.70, 133.69 (d, J = 8.3 Hz), 137.57 (d, J = 6.3 Hz), 143.66, 161.10, 164.42. **3d**: mp 122–123 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.29 (s, 3H), 3.75 (s, 3H), 5.30 (d, J = 9.3 Hz, 1H), 5.51 (d, J = 9.3 Hz, 1H), 6.74 (d, J = 8.7 Hz, 2H), 7.03 (d, J = 8.7 Hz, 2H), 7.17 (d, J = 8.1 Hz, 2H), 7.20–7.33 (m, 3H), 7.49–7.53 (m, 2H), 7.76 (d, J = 8.4 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ21.72, 50.11, 55.57, 84.49, 86.89, 114.02, 114.39, 127.63, 127.80, 128.60, 128.92, 129.79, 133.33, 137.74, 138.03, 143.67, 160.01. **3e**: mp 187–188 °C;[1] H NMR (300 MHz, $CDCl_3$) δ 2.31 (s, 3H), 4.96 (d, J = 9.3 Hz, 1H), 5.56 (d, J = 9.3 Hz, 1H), 7.10–7.14 (m, 2H), 7.21–7.38 (m, 8H), 7.53–7.57 (m, 2H), 7.81 (d, J = 8.4 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.40, 49.77, 85.46, 86.68, 121.95, 127.32, 127.52, 128.09, 128.46, 128.57, 128.70, 129.55, 131.55, 137.37, 137.39, 143.55; Mass (70 eV) m/z (rel. intensity) 65 (60), 77 (71), 91 (100), 105 (51), 128 (46), 191 (34), 206 ($M^+ - SO_2Tol$, 90). **3f**: mp 194–195 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.31 (s, 3H), 2.34 (s, 3H), 4.91 (d, J = 9.0 Hz, 1H), 5.52 (d, J = 9.0 Hz, 1H), 7.09–7.29 (m, 9H), 7.42 (d, J = 8.4 Hz, 2H), 7.81 (d, J = 8.4 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.37, 21.68, 49.82, 85.97, 86.75, 122.32, 127.51, 127.81, 128.35, 128.79, 129.64, 129.80, 131.82, 134.76, 137.71, 138.61, 143.77. **3g**: mp 224–225 °C; ^{1}H NMR (300 MHz, $CDCl_3$ + DMSO-d_6) δ 2.21 (s, 3H), 5.83 (s, 1H), 7.15–7.38 (m, 7H), 7.68– 7.74 (m, 3H), 7.86 (t, J = 8.4 Hz, 1H), 7.98 (d, J = 8.7 Hz, 1H), 8.09 (d, J = 7.8 Hz, 1H), 8.59 (s, 1H), 8.91 (br s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$ + DMSO-d_6) δ 19.15, 44.88, 83.35, 84.02, 119.55, 124.98, 125.11, 125.84, 125.89, 126.52, 126.65, 127.18, 127.64, 127.98, 129.52, 129.70, 136.25, 136.37, 141.12, 144.80, 146.61. **3h**: oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.08 (s, 3H), 4.96 (d, J = 8.1 Hz, 1H), 5.64 (d, J = 8.1 Hz, 1H), 7.30–7.49 (m, 8H), 7.60–7.64 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 41.78, 49.80, 86.04, 86.98, 121.78, 127.42, 128.47, 128.73, 128.90, 129.00, 131.67, 137.27. **3i**: mp 145–146 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.33 (s, 6H), 4.94 (d, J = 7.8 Hz, 1H), 5.54 (d, J = 7.8 Hz, 1H), 6.99–7.07 (m, 4H), 7.23 (d, J = 8.7 Hz, 2H), 7.30–7.37 (m, 3H), 7.53–7.57 (m, 2H), 7.81 (d, J = 8.4 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.65, 21.66, 50.03, 85.01, 87.05, 119.10, 127.56, 127.75, 128.63, 128.89, 129.06, 129.76, 131.68, 137.63, 137.77, 138.97, 143.70.

12. Typical procedure for the synthesis of enaminone ester **5a**: To s stirred solution of ethyl propiolate (98 mg, 1.0 mmol) in CH_3CN (3 mL) was added $ZnBr_2$ (225 mg, 1.0 mmol) and *N*,*N*-diisopropylethylamine (130 mg, 1.0 mmol). The reaction mixture was stirred for 12 h at 50–60 °C. After the usual aqueous workup and column chromatographic purification process (hexanes/ether, 5:1) we obtained **5a** as clear oil, 102 mg (55%). The spectroscopic data of prepared compounds are as follows. For **5b** and **5c** we could not obtain the exact ^{13}C NMR spectra due to the line broadening effect of nitrogen atom.
5a: oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.15 (t, J = 7.2 Hz, 3H), 1.21 (d, J = 6.6 Hz, 6H), 1.26 (t, J = 7.2 Hz, 3H) 3.14 (q, J = 7.2 Hz, 2H), 3.52 (septet, J = 6.6 Hz, 1H), 4.13 (q, J = 7.2 Hz, 2H), 4.58 (d, J = 13.2 Hz, 1H), 7.51 (d, J = 13.2 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 12.91, 14.80, 21.70, 41.01, 56.01, 58.84, 83.35, 149.46, 170.17. **5b**: oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.16 (t, J = 7.2 Hz, 6H), 1.26 (t, J = 7.2 Hz, 3H), 3.19 (q, J = 7.2 Hz, 4H), 4.13 (q, J = 7.2 Hz, 2H), 4.57 (d, J = 12.9 Hz, 1H), 7.44 (d, J = 12.9 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.66, 58.79, 83.37, 150.89, 170.00. **5c**: oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.26 (t, J = 7.2 Hz, 3H), 2.88 (s, 6H), 4.13 (q, J = 7.2 Hz, 2H), 4.52 (d, J = 12.9 Hz, 1H), 7.44 (d, J = 12.9 Hz, 1H). **5d**: oil; IR (neat) 3498, 2974, 1689, 1608 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.15 (t, J = 7.2 Hz, 3H), 1.21 (d, J = 6.9 Hz, 6H), 3.14 (q, J = 7.2 Hz, 2H), 3.52 (septet, J = 6.9 Hz, 1H), 3.66 (s, 3H), 4.58 (d, J = 13.2 Hz, 1H), 7.51 (d, J = 13.2 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 12.96, 21.71, 41.09, 50.49, 55.91, 83.00, 149.53, 170.52; Mass (70 eV) m/z (rel. intensity) 41 (100), 56 (97), 70 (72), 140 (56), 156 (49), 171 (M^+, 22). **5e**: oil; IR (neat) 3510, 2978, 1689, 1612 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.16 (t, J = 7.2 Hz, 6H), 3.19 (q, J = 7.2 Hz, 4H), 3.65 (s, 3H), 4.56 (d, J = 12.9 Hz, 1H), 7.44 (d,J = 12.9 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 13.01, 43.31, 50.37, 83.03, 150.98, 170.31; Mass (70 eV) m/z (rel. intensity) 41 (67), 55 (100), 98 (37), 126 (53), 142 (27), 157 (M^+, 26).
13. Spectroscopic data of partial reduction product **6**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.35 (s, 3H), 5.07 (d, J = 5.4 Hz, 1H), 5.61 (dd, J = 9.3 and 5.4 Hz, 1H), 5.87 (dd, J = 11.4 and 9.3 Hz, 1H), 6.57 (d, J = 11.4 Hz, 1H), 7.05–7.33 (m, 11H), 7.49 (d, J = 8.4 Hz, 2H); Mass (70 eV) m/z (rel. intensity) 91 (100), 138 (30), 242 (41), 397 (M^+, 2).
14. To a stirred solution of quinoline (130 mg, 1 mmol) in CH_3CN (2 mL) was added benzoyl chloride (183 mg, 1.3 mmol), phenylacetylene (122 mg, 1.2 mmol), $ZnBr_2$ (270 mg, 1.2 mmol), and *N*,*N*-diisopropylethylamine (155 mg, 1.2 mmol) successively at room temperature. After 20 min the reaction mixture was poured into cold water. After normal workup with ether, removal of solvent, flash column chromatographic purification (hexanes/ether, 40:1) we obtained the desired dihydroquinoline **8**, 248 mg (74%): IR (KBr) 2218, 1651 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.19–6.24 (m, 2H), 6.65–6.70 (m, 2H), 6.90 (t, J = 7.5 Hz, 1H), 7.05 (td, J = 7.5 and 1.2 Hz, 1H), 7.17–7.45 (m, 11H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 44.42, 83.66, 85.07, 122.38, 125.10, 125.61, 125.71, 126.13, 126.53, 126.84, 127.12, 127.98, 128.06, 128.25, 128.98, 130.58, 131.79, 134.94, 135.15, 169.38; Mass (70 eV) m/z (rel. intensity) 77 (52), 105 (100), 129 (18), 230 (14), 306 (13), 335 (M^+, 7).