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A Tandem Approach to Isoquinolines from 2-Azido-3-arylacrylates and α-Diazocarbonyl Compounds

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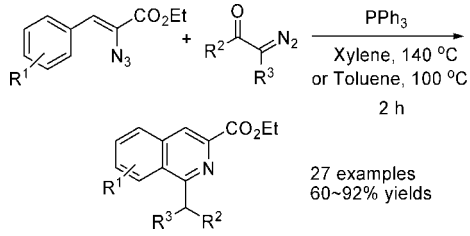

2-Azido-3-arylacrylates react with α-diazocarbonyl compounds and triphenylphosphine to furnish isoquinolines in 60−92% yields. The tandem process involves a Wolff rearrangement, an aza-Wittig reaction, and an electrocyclic ring closure. The procedure is efficient, rapid, and general, and the substrates are readily available.

Isoquinolines constitute an important class of alkaloids commonly found in natural products.[1] They also have been used as building blocks in pharmaceutical compounds,[2] as well as chiral ligands for transition-metal catalysts.[3] Due to their substantial applicability, the synthesis of isoquinolines is an extensively studied topic.[4] The classical methods for the construction of isoquinoline rings include the Bischler−Napieralski, the Pomeranz−Fritsch, and the Pictet−Spengler reactions.[5] Transition-metal-catalyzed synthesis of isoquinolines from the *tert*-butylimine of 2-iodobenzaldehydes and alkynes (or allenes) is a promising method, while it often requires the use of base and long reaction time.[4c,f,6] The intramolecular [4 + 2] cycloaddition reaction of 4-phenyl-2-azabutadienes, followed by dehydrogenation, can also generate isoquinolines.[4e,7] We herein report a new tandem synthesis of substituted isoquinolines.

SCHEME 1. Synthesis of Isoquinoline 3a

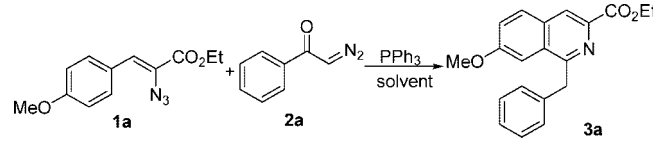

TABLE 1. Optimization of Reaction Conditions[a]

entry	solvent	reaction temperature	reaction time (h)	yield (%)[b]
1	xylene	140 °C	5	82
2	xylene	reflux	5	81
3	xylene	140 °C	2	82
4	xylene	140 °C	1	71
5	THF	reflux	5	0
6	DCE	reflux	5	0
7	toluene	100 °C	5	0
8	toluene	reflux	10	15

[a] Reaction conditions: **1a** (0.5 mmol), **2a** (0.5 mmol), PPh_3 (0.5 mmol), solvent (20 mL), N_2. [b] The yield of the isolated product.

Our initial studies were focused on the reaction of 2-azido-3-(4-methyloxyphenyl)-acrylate (**1a**), 2-diazo-1-phenylethanone (**2a**), and triphenylphosphine (Scheme 1). Thus, heating a solution of 1 equiv each of **1a**, **2a**, and triphenylphosphine in xylene at 140 °C for 5 h gave isoquinoline **3a** in 82% yield (Table 1, entries 1–4). We also examined several other solvents such as THF (Table 1, entry 5), 1,2-dichloroethane (DCE, Table 1, entry 6), and toluene (Table 1, entries 7 and 8). The best yield (82%) was obtained when the reaction was performed in xylene at 140 °C for 2 h (Table 1, entry 3).

Since 2-azido-3-arylacrylates[8] and α-diazocarbonyl compounds[9] are readily available, the tandem approach to isoquinolines is highly appealing. We, therefore, extended the substrate

(1) Bentley, K. W. *The Isoquinoline Alkaloids*; Hardwood Academic: Amsterdam, 1998; Vol. 1.

(2) (a) Kletsas, D.; Li, W.; Han, Z.; Papadopoulos, V. *Biochem. Pharmacol.* **2004**, *67*, 1927–1932. (b) Mach, U. R.; Hackling, A. E.; Perachon, S.; Ferry, S.; Wermuth, C. G.; Schwartz, J.-C.; Sokoloff, P.; Stark, H. *ChemBioChem* **2004**, *5*, 508–518. (c) Muscarella, D. E.; O'Brain, K. A.; Lemley, A. T.; Bloom, S. E. *Toxicol. Sci.* **2003**, *74*, 66–73. (d) Dzierszinski, F.; Coppin, A.; Mortuaire, M.; Dewally, E.; Slomianny, C.; Ameisen, J.-C.; DeBels, F.; Tomavo, S. *Antimicrob. Agents Chemother.* **2002**, *46*, 3197–3207.

(3) (a) Durola, F.; Sauvage, J.-P.; Wenger, O. S. *Chem. Commun.* **2006**, 171–173. (b) Sweetman, B. A.; Müller-Bunz, H.; Guiry, P. J. *Tetrahedron Lett.* **2005**, *46*, 4643–4646. (c) Lim, C. W.; Tissot, O.; Mattison, A.; Hooper, M. W.; Brown, J. M.; Cowley, A. R.; Hulmes, D. I.; Blacker, A. J. *Org. Process Res. Dev.* **2003**, *7*, 379–384. (d) Alcock, N. W.; Brown, J. M.; Hulmes, G. I. *Tetrahedron: Asymmetry* **1993**, *4*, 743–756.

(4) (a) Coffey, D. S.; Kolis, S. P.; May, S. A. In *Progress in Heterocyclic Chemistry*; Gribble, G. W., Gilchrist, T. L., Eds.; Pergamon: Amsterdam, 2002; Vol. 14, Chapter 6.1. (b) Fischer, D.; Tomeba, H.; Pahadi, N. K.; Patil, N. T.; Yamamoto, Y. *Angew. Chem., Int. Ed.* **2007**, *46*, 4764–4766. (c) Konno, T.; Chae, J.; Miyabe, T.; Ishihara, T. *J. Org. Chem.* **2005**, *70*, 10172–10174. (d) Korivi, R. P.; Cheng, C.-H. *Org. Lett.* **2005**, *7*, 5179–5182. (e) Palacios, F.; Alonso, C.; Rodríguez, M.; de Marigorta, E. M.; Rubiales, G. *Eur. J. Org. Chem.* **2005**, 1795–1804. (f) Dai, G. X.; Larock, R. C. *J. Org. Chem.* **2003**, *68*, 920–928. (g) Ichikawa, J.; Wada, Y.; Miyazaki, H.; Mori, T.; Kuroki, H. *Org. Lett.* **2003**, *5*, 1455–1458.

(5) (a) *The Chemistry of Hetrocyclic Compounds: Isoquinolines*; Coppola, G. M., Schuster, H. F., Eds.; John Wiley & Sons: New York, 1981; Vol. 38, Part 3. (b) *Comprehensive Organic Functional Group Ttransformations*, 1st ed.; Katritzky, A. R., Cohn, O. M., Eds.; Pergamon: Chichester U.K., 1991; Vols. 2 and 3, pp 328–419.

(6) (a) Roesch, K. R.; Larock, R. C. *J. Org. Chem.* **2002**, *67*, 86–94. (b) Roesch, K. R.; Zhang, H. M.; Larock, R. C. *J. Org. Chem.* **2001**, *66*, 8042–8051. (c) Dai, G. X.; Larock, R. C. *Org. Lett.* **2001**, *3*, 4035–4038. (d) Huang, Q. H.; Hunter, J. A.; Larock, R. C. *Org. Lett.* **2001**, *3*, 2973–2976. (e) Roesch, K. R.; Larock, R. C. *J. Org. Chem.* **1998**, *63*, 5306–5307.

(7) (a) Palacios, F.; Alonso, C.; Rubiales, G.; Villegas, M. *Tetrahedron* **2005**, *61*, 2779–2794. (b) Palacios, F.; Alonso, C.; Rubiales, G. *J. Org. Chem.* **1997**, *62*, 1146–1154. (c) Rodrigues, J. A. R.; Leiva, G. C.; de Sousa, J. D. F. *Tetrahedron Lett.* **1995**, *36*, 59–62. (d) Palacios, F.; Alonso, C.; Rubiales, G. *Tetrahedron* **1995**, *51*, 3683–3690.

(8) (a) Stokes, B. J.; Dong, H. J.; Leslie, B. E.; Pumphrey, A. L.; Driver, T. G. *J. Am. Chem. Soc.* **2007**, *129*, 7500–7501. (b) Bräse, S.; Gil, C.; Knepper, K.; Zimmermann, V. *Angew. Chem., Int. Ed.* **2005**, *44*, 5188–5240. (c) Moore, A. T.; Rydon, H. N. *Org. Synth.* **1973**, *5*, 586.

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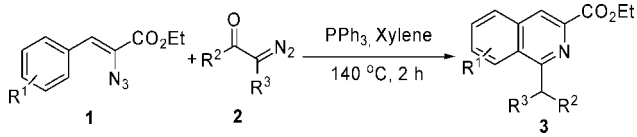
TABLE 2. The Synthesis of Isoquinolines 3[a]



entry	R^1	R^2/R^3	product	yield (%)[b]
1	4-MeO (**1a**)	C_6H_5/H (**2a**)	**3a**	82
2	4-MeO (**1a**)	4-$MeOC_6H_4$/H (**2b**)	**3b**	92
3	4-Br (**1b**)	C_6H_5/H (**2a**)	**3c**	78
4	4-Br (**1b**)	4-$MeOC_6H_4$/H (**2b**)	**3d**	80
5	4-NO_2 (**1c**)	C_6H_5/H (**2a**)	**3e**	70
6	4-NO_2 (**1c**)	4-$MeOC_6H_4$/H (**2b**)	**3f**	73
7	H (**1d**)	4-$MeOC_6H_4$/H (**2b**)	**3g**	85
8	H (**1d**)	C_6H_5/H (**2a**)	**3h**	82
9	4-MeO (**1a**)	Me/CO_2Et (**2c**)	**3i**	80

[a] Reaction conditions: **1** (0.5 mmol), **2** (0.5 mmol), PPh_3 (0.5 mmol), xylene (20 mL), 140 °C, N_2, 2 h. [b] The yield of the isolated product.

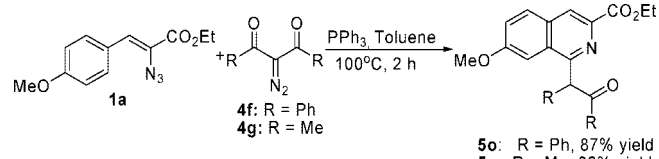
scope to various 2-azido-3-arylacrylates **1** and α-diazoketones **2** using the optimized conditions. As shown in Table 2, a wide range of azides and α-diazoketones resulted in isoquinolines **3** in good yields (70−92%).

Encouraged by these results, we investigated the reaction of 2-diazo-1,3-diones **4** with azides and triphenylphosphine (Table 3). We found that all reactions could take place at lower temperature (100 °C) in toluene, resulting in isoquinolines **5** or a mixture of **5** and their isomers **6**. In most cases, good regioselectivity was obtained (Table 3, entries 1−5 and 7−14), while 2-azido-3-(4-fluorophenyl)acrylate gave equal amounts of **5f** and **6f** (Table 3, entry 6). Moreover, electron-rich azides (Table 3, entries 7−12) gave higher yields than electron-deficient azides (Table 3, entries 1−6).

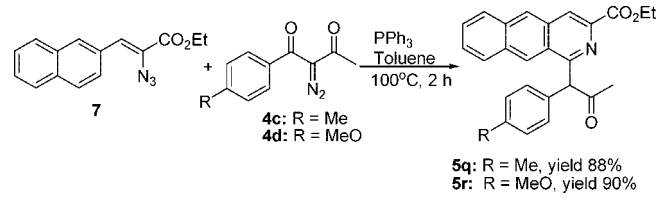
We also examined the symmetrical 2-diazo-1,3-diones **4f** and **4g** using the established procedure and obtained **5o** and **5p** in 87 and 82% yields, respectively (Scheme 2).

Next, our attention was directed toward the construction of the benzoisoquinoline framework using azide **7** as a substrate (Scheme 3). It was found that the reaction afforded the desired benzoisoquinolines **5q** and **5r** in 88 and 90% yields, respectively.

SCHEME 2. The Synthesis of Isoquinolines 5o and 5p



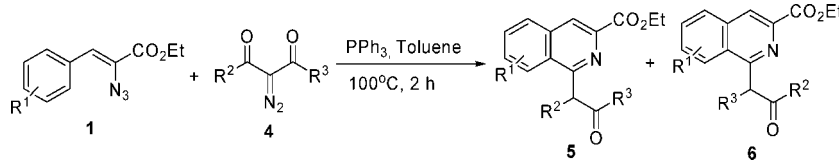
SCHEME 3. The Synthesis of Benzoisoquinolines 5q and 5r



On the basis of these results, we proposed a possible mechanism for our cascade reaction, as shown in Scheme 4. First, azide **1** reacts with triphenylphosphine to form phosphazene **A** via the Staudinger−Meyer reaction,[10] while α-diazoketone **2** transforms to ketene **B** through the Wolff rearrangement reaction.[9b,11] Then the aza-Wittig reaction between phosphazene **A** and ketene **B** affords *N*-vinylic ketenemine **C**.[10b,12] Finally, the electrocyclic ring closure of **C** and a subsequent [1,3]-H immigration led to the formation of isoquinolines **3**. For asymmetrical substrate 2-diazo-1,3-diones **4a**−**e**, the Wolff rearrangement results in two different ketenes, $\mathbf{B_1}$ and $\mathbf{B_2}$, which leads to the formation of two isoquinoline isomers **5** and **6**, respectively (Scheme 5). $\mathbf{B_1}$ should be the major product of the Wolff rearrangement when R^2 is an aryl group and R^3 is an alkyl group, so we obtained **5** as the major product.

In summary, we have developed an efficient synthesis of isoquinolines via a tandem reaction of 2-azido-3-arylacrylates, α-diazocarbonyl compounds, and triphenylphosphine. The procedure is rapid and general, and the substrates are readily available.[8,9,13] Further application of the methodology to synthesize some natural alkaloids and pharmaceutical compounds is in progress in our laboratory.

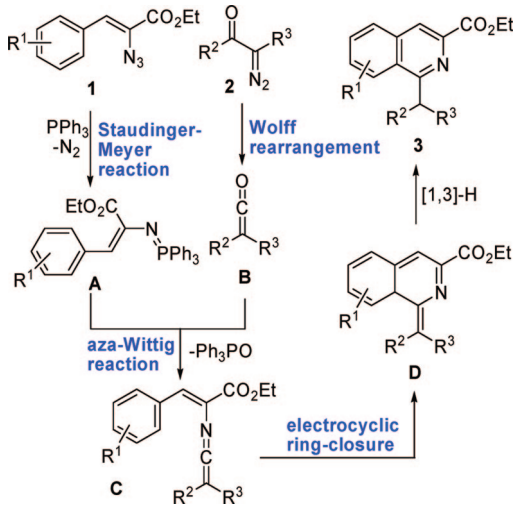
TABLE 3. The Synthesis of Isoquinolines 5 and 6[a]



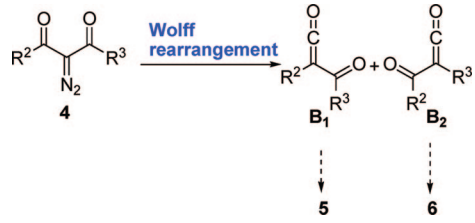
entry	R^1	R^2/R^3	**5/6** (ratio)[b]	yield (%)[c]
1	4-Cl (**1e**)	Ph/Et (**4a**)	**5a/6a** (100:0)	79
2	2-Cl (**1f**)	Ph/Me (**4b**)	**5b/6b** (100:0)	75
3	4-Br (**1b**)	Ph/Me (**4b**)	**5c/6c** (100:0)	68
4	4-Br (**1b**)	Ph/Et (**4a**)	**5d/6d** (100:0)	72
5	4-Br (**1b**)	4-MeC_6H_4/Me (**4c**)	**5e/6e** (>95:5)	71
6	4-F (**1g**)	4-MeC_6H_4/Me (**4c**)	**5f/6f** (50:50)	60
7	4-$PhCH_2O$ (**1h**)	Ph/Me (**4b**)	**5g/6g** (91:9)	86
8	4-$PhCH_2O$ (**1h**)	Ph/Et (**4a**)	**5h/6h** (100:0)	84
9	4-$PhCH_2O$ (**1h**)	4-$MeOC_6H_4$/Me (**4d**)	**5i/6i** (>95:5)	88
10	4-$PhCH_2O$ (**1h**)	4-MeC_6H_4/Me (**4c**)	**5j/6j** (>95:5)	86
11	4-MeO (**1a**)	Ph/Me (**4b**)	**5k/6k** (>95:5)	85
12	4-MeO (**1a**)	Ph/Et (**4a**)	**5l/6l** (100:0)	83
13	4-Ph (**1i**)	2-ClC_6H_4/Et (**4e**)	**5m/6m** (88:12)	78
14	H (**1d**)	4-$MeOC_6H_4$/Me (**4d**)	**5n/6n** (>95:5)	89

[a] Reaction conditions: **1** (0.5 mmol), **2** (0.5 mmol), PPh_3 (0.5 mmol), toluene (20 mL), 100 °C, N_2, 2 h. [b] Determined by ^1H NMR. [c] The yield of the isolated product.

SCHEME 4. A Plausible Mechanism for the Synthesis of Isoquinolines



SCHEME 5. Reaction of Asymmetrical 2-Diazo-1,3-diones



Experiment Section

General Procedure for the Synthesis of Isoquinolines 3. To a solution of PPh_3 (0.131 g, 0.5 mmol) in anhydrous xylene (10 mL) was added dropwise a solution of **1** (0.5 mmol) and **2** (0.5 mmol) in anhydrous xylene (10 mL) at 140 °C under the nitrogen atmosphere over 30 min. The mixture was stirred for 2 h. The solvent was evaporated in vacuum, and the residual oil was purified by silica gel column chromatography using hexane/EtOAc (4:1) as the eluent. The product was recrystallized from hexane/EtOAc (4:1).

Ethyl 1-benzyl-7-methoxyisoquinoline-3-carboxylate (3a): White solid, mp 117–118 °C; IR (KBr) 1724, 1617, 1498, 1408, 1229, 1205, 1028, 845 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 8.42 (s, 1 H), 7.82 (d, J = 8.6 Hz, 1 H), 7.32–7.22 (m, 6 H), 7.17–7.16 (m, 1 H), 4.74 (s, 2 H), 4.53 (q, J = 7.1 Hz, 2 H), 3.78 (s, 3 H), 1.48 (t, J = 7.1 Hz, 3 H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 167.6, 161.3, 160.3, 140.6, 140.5, 132.9, 131.6, 131.4, 130.0, 129.9, 127.7, 124.6, 124.5, 105.9, 63.0, 56.8, 44.5, 15.9 ppm; MS m/z ($[M + H]^+$) 322; RMS m/z calcd for ($C_{20}H_{19}NO_3$ + Na) 344.1257; found 344.1267.

Ethyl 7-methoxy-1-(4-methoxybenzyl)isoquinoline-3-carboxylate (3b): White solid, mp 120–121 °C; IR (KBr) 1728, 1618, 1514, 1500, 1291, 1229, 1207, 1032, 850 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 8.41 (s, 1 H), 7.82 (d, J = 8.8 Hz, 1 H), 7.34–7.27 (m, 2 H), 7.19 (d, J = 8.6 Hz, 2 H), 6.78 (d, J = 8.6 Hz, 2 H), 4.67 (s, 2 H), 4.53 (q, J = 7.1 Hz, 2 H), 3.80 (s, 3 H), 3.73 (s, 3 H), 1.48 (t, J = 7.1 Hz, 3 H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.4, 160.1, 159.4, 158.2, 139.3, 131.7, 131.5, 130.4, 130.2, 129.7, 123.3, 123.2, 114.1, 104.7, 61.8, 55.6, 55.4, 42.3, 14.7 ppm; MS m/z ($[M + H]^+$) 352; HRMS m/z calcd for ($C_{21}H_{21}NO_4$ + Na) 374.1363; found 374.1370.

General Procedure for the Synthesis of Isoquinolines 5. To a solution of PPh_3 (0.5 mmol) in anhydrous toluene (10 mL) was added dropwise a solution of **1** (0.5 mmol) and **4** (0.5 mmol) in anhydrous toluene (10 mL) under the nitrogen atmosphere at 100 °C over 30 min. After the mixture was stirred for 2 h, the solvent was evaporated in vacuum, and residual oil was purified by silica gel column chromatography using hexane/EtOAc (8:1) as the eluent. The product was rescrystallized from hexane/EtOAc (6:1).

Ethyl 7-chloro-1-(2-oxo-1-phenylbutyl)isoquinoline-3-carboxylate (5a): White solid, mp 136–137 °C; IR (KBr) 1716, 1705, 1423, 1241, 1232, 821, 707 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 8.46 (s, 1 H), 7.96 (s, 1 H), 7.90 (d, J = 8.5 Hz, 1 H), 7.63 (d, J = 8.4 Hz, 1 H), 7.33–7.25 (m, 5 H), 5.82 (s, 1 H), 4.50–4.43 (m, 2 H), 2.87–2.83 (m, 1 H), 2.48–2.43 (m, 1 H), 1.45 (t, J = 7.2 Hz, 3 H), 1.15 (t, J = 7.1 Hz, 3 H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 208.7, 165.7, 158.6, 141.1, 137.3, 135.8, 135.0, 132.0, 130.8, 129.5, 129.1, 127.9, 124.8, 123.1, 64.0, 61.9, 35.9, 14.5, 8.4 ppm; MS m/z ($[M + Na]^+$) 404; HRMS m/z calcd for ($C_{22}H_{20}ClNO_3$ + Na) 404.1024; found 404.1021.

Ethyl 5-chloro-1-(2-oxo-1-phenylpropyl)isoquinoline-3-carboxylate (5b): Yellow solid, mp 123–124 °C; IR (KBr) 1709, 1670, 1358, 1240, 1213, 746 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 8.89 (s, 1 H), 7.92 (d, J = 8.5 Hz, 1 H), 7.77 (d, J = 7.5 Hz, 1 H), 7.50 (t, J = 8.1 Hz, 1 H), 7.32–7.23 (m, 5 H), 5.86 (s, 1 H), 4.51–4.48 (m, 2 H), 2.37 (s, 3 H), 1.47 (t, J = 7.1 Hz, 3 H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 206.0, 165.6, 159.4, 141.8, 137.4, 134.8, 133.8, 130.9, 129.6, 129.5, 129.4, 129.1, 127.9, 124.5, 119.8, 65.1, 61.9, 29.8, 14.5 ppm; MS m/z ($[M + Na]^+$) 390; HRMS m/z calcd for ($C_{21}H_{18}ClNO_3$ + Na) 390.0867; found 390.0861.

Ethyl 7-methoxy-1-(3-oxobutan-2-yl)isoquinoline-3-carboxylate (5p): White solid, mp 115–116 °C; IR (KBr) 1713, 1699, 1623, 1313, 1228, 903 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 8.42 (s, 1 H), 7.89 (d, J = 9 Hz, 1 H), 7.40 (dd, J = 9, 2 Hz, 1 H), 7.35 (d, J = 2 Hz, 1 H), 4.61 (q, J = 7 Hz, 1 H), 4.52–4.48 (m, 2 H), 3.95 (s, 3 H), 2.06 (s, 3 H), 1.71 (d, J = 7 Hz, 3 H), 1.47 (t, J = 7 Hz, 3 H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 209.0, 166.1, 160.7, 158.2, 139.6, 131.8, 130.8, 129.8, 123.8, 123.5, 103.3, 61.7, 55.9, 55.5, 28.0, 15.5, 14.6 ppm; MS m/z ($[M + Na]^+$) 324; HRMS m/z calcd for ($C_{17}H_{19}NO_4$ + Na) 324.1206; found 324.1210.

Ethyl 1-(2-oxo-1-*p*-tolylpropyl)benzo[*g*]isoquinoline-3-carboxylate (5q): White solid, mp 129–130 °C; IR (KBr) 1743, 1707, 1257, 1213, 746 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 8.52 (d, J = 8.5 Hz, 1 H), 8.49 (s, 1 H), 7.94–7.90 (m, 2 H), 7.76 (d, J = 8.7 Hz, 1 H), 7.63–7.60 (m, 1 H), 7.54–7.51 (m, 1 H), 7.36 (d, J = 7.7 Hz, 2 H), 7.21 (d, J = 7.7 Hz, 2 H), 6.00 (s, 1 H), 4.51–4.47 (m, 2 H), 2.34 (s, 3 H), 2.22 (s, 3 H), 1.46 (t, J = 7.1 Hz, 3 H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 207.2, 165.7, 157.2, 141.8, 138.8, 137.6, 134.9, 134.4, 132.7, 130.1, 129.6, 129.4, 128.6, 128.1, 127.9, 127.7, 127.6, 126.4, 123.0, 68.0, 61.8, 30.2, 21.4, 14.5 ppm; MS m/z ($[M + Na]^+$) 420; HRMS m/z calcd for ($C_{26}H_{23}NO_3$ + Na) 420.1570; found 420.1569.

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Supporting Information Available: Detailed experimental procedures, characterization data, copies of ^1H and ^{13}C NMR spectra for all products. This material is available free of charge via the Internet at http://pubs.acs.org.

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(9) (a) Danheiser, R. L.; Miller, R. F.; Brisbois, R. G.; Park, S. Z. *J. Org. Chem.* **1990**, *55*, 1959–1964. (b) Ye, T.; Mckervey, M. A. *Chem. Rev.* **1994**, *94*, 1091–1160. (c) Regitz, C. J.; Hocker, J.; Liedhegener, A. *Org. Synth.* **1973**, *5*, 179. (d) Kirmse, W. *Eur. J. Org. Chem.* **2002**, 2193–2256.

(10) (a) Staudinger, H.; Meyer, J. *Helv. Chim. Acta* **1919**, *2*, 635–646. (b) Palacios, F.; Alonso, C.; Aparicio, D.; Rubiales, G.; de los Santos, J. M. *Tetrahedron* **2007**, *63*, 523–575.

(11) Wolff, L. *Liebigs Ann. Chem.* **1912**, *394*, 23.

(12) (a) Palacios, F.; Alonso, C.; Rubiales, G.; Villegas, M. *Tetrahedron* **2005**, *61*, 2779–2794. (b) Cossio, F.; Alonso, C.; Lecea, B.; Ayerbe, M.; Rubiales, G.; Palacios, F. *J. Org. Chem.* **2006**, *71*, 2839–2847.

(13) Many azides have hazardous behavior and some of them are potential energetic materials (See: Badgujar, D. M.; Talawar, M. B.; Asthana, S. N.; Mahulikar, P. P. *J. Hazard. Mater.* **2008**, *151*, 289–305). Although we did not encounter any danger in our experiment, the caution about the potential hazardous behavior of azides should be indicated.