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An expedient synthesis of 1,2-dihydrobenzo[*g*]quinoline-5,10-diones via copper(II) triflate-catalyzed intramolecular cyclization of *N*-propargylaminonaphthoquinones

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ABSTRACT

An expedient synthesis of a series of 1,2-dihydrobenzo[*g*]quinoline-5,10-diones in good yields has been accomplished via three-component one pot sequential reactions of 2-hydroxynaphthalene-1,4-dione, substituted anilines and propargyl as well as 3-ethylpropargyl bromides furnishing *N*-propargylaminonaphthoquinones, and their concomitant copper(II) triflate-catalyzed intramolecular 6-*endo-dig* cyclization.

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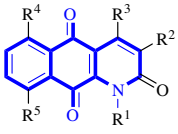
Functionalized heterocyclic building blocks are of great importance in both medicinal and synthetic chemistry and development of new efficient synthetic methodologies for these scaffolds remains a great challenge in modern organic synthesis.[1] 1,2-Dihydrobenzo[*g*]quinoline-5,10-dione framework is an important structural motif prevalent in natural products with interesting biological properties.[2] Interest in 1,2-dihydrobenzo[*g*]quinoline-5,10-dione skeleton is connected to its structural relationship with dielsiquinone and marcanines A–E (Fig. 1). The dielsiquinone is a potent cytotoxic natural product related to anthracyclines that provides the basis for the development of safer anticancer drugs due to its less cardiotoxicity than the clinically used anthracyclines.[2a] Marcanines A–E, isolated from the stem bark of *Goniothalamus marcanii*, exhibit cytotoxic activity against several human tumor cell lines.[2b] Marcanine A displays in vitro antimalarial activity against the drug-resistant K1 strain of *Plasmodium falciparum*.[2c] Previously reported synthesis of 1,2-dihydrobenzo[*g*]-quinoline-5,10-dione skeleton includes that of marcanine,[3] dielsiquinone,[4,2a] 1-aza-2,9,10-anthracenetriones,[5] polyheterocyclic quinones,[6] benzo[*g*]quinoline-2,5,10-trione,[7] and 1,2,5,10-tetrahydrobenzo[*g*]quinoline-5,10-dione.[8]

Alkynes serve as important synthons, besides being the subunits of myriad organic compounds. In particular, recently several reports have appeared on the utility of inter- or intramolecular cyclization of alkyne functionality in the assembly of heterocycles such as oxazolines and oxazoles,[9] acridines and quinolines,[10] isoquinolines and pyridines,[11] *N*-fused imidazoles,[12] 3-acylated indolizines,[13] tetrahydroisoquinolines,[14] aminoindolizines,[15] chromenoquinoxalines,[16] dihydroquinolines and indoles,[17] indolequinone,[18] benzo[*b*]furans,[19] pyrano[4,3-*b*]quinolines,[20] 3-halochalco-genophene[3,2-*c*]chromene,[21] and azaindoles.[22] The azaanthraquinone skeleton has been constructed by the intramolecular cyclization of *N*-propargylaminoquinones.[23] In continuation of our interest in the assembly of functionalized novel heterocycles by tandem, multicomponent, and green transformations,[24] herein we describe the synthesis of *N*-propargylaminonaphthoquinones, from the sequential reaction of readily available starting materials, viz. 2-hydroxynaphthalene-1,4-dione, substituted anilines and propargyl bromide/3-ethylpropargyl bromide, and their subsequent intramolecular cyclization furnishing 1,2-dihydrobenzo[*g*]quinoline-5,10-diones (Scheme 1).



Dielsiquinone, R^1, R^2 = H; R^3 = Me; R^4, R^5 = H
Marcanine A, R^1, R^2 = H; R^3 = Me; R^4, R^5 = H
Marcanine B, R^1 = H; R^2 = OMe; R^3 = Me; R^4, R^5 = H
Marcanine C, R^1 = H; R^2 = OMe; R^3 = CH_2OH; R^4, R^5 = H
Marcanine D, R^1 = H; R^2 = OMe; R^3 = Me; R^4 = OH; R^5 = H
Marcanine E, R^1 = Me; R^2 = OMe; R^3 = Me; R^4 = H; R^5 = OH

Figure 1. Structure of naturally occurring 1,2-dihydrobenzo[*g*]quinoline-5,10-diones.

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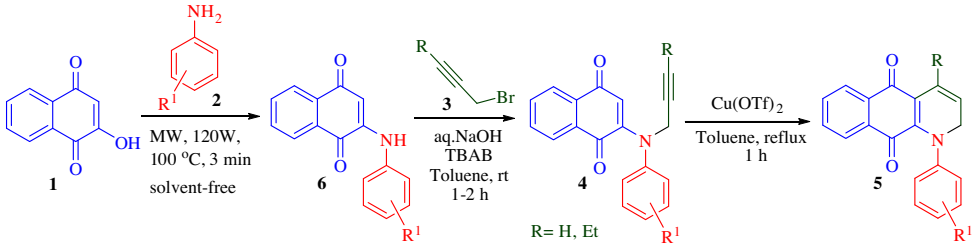


Scheme 1. Synthesis of 1,2-dihydrobenzo[*g*]quinoline-5,10-diones **5**.

Table 1
Solvent- and base-screen for the synthesis of *N*-propargylaminonaphthoquinone **4a**

Entry	Solvent and base	Molar ratio **3**/base/TBAB	Time (h)	Yield of **4a**[a] (%)
1	DMF, K_2CO_3	1:2:0	12	—[b]
2	Acetone, K_2CO_3	1:2:0	10	—[b]
3	DMSO, K_2CO_3	1:2:0	12	—[b]
4	DMF, Cs_2CO_3	1:0.5:0	9	43
5	DMF, Cs_2CO_3	1:1:0	9	43
6	DMSO, Cs_2CO_3	1:0.5:0	9	38
7	Toluene, NaOH	1:0.5:0.2	3	53
8	Toluene, NaOH	1:1:0.2	1	74
9	Dioxane, NaOH	1:2:1	12	—[b]
10	NaH, THF	1:1:0	10	—[b]

[a] Yields after purification by flash column chromatography.
[b] Reaction failed to occur.

Table 2
Synthesis of *N*-propargylaminonaphthoquinones **4**

Entry	Compd	R	R′	Time (h)	Yield of **4a**[a] (%)	mp (°C)
1	**4a**	H	4-Me	1.0	74	99
2	**4b**	H	4-Br	1.0	78	147
3	**4c**	H	4-Cl	1.0	79	131
4	**4d**	H	4-F	1.0	72	104
5	**4e**	H	4-CF_3	1.0	73	165
6	**4f**	H	3-Cl	1.5	76	111
7	**4g**	H	3-OMe	1.0	70	97
8	**4h**	H	2-Me	1.5	72	107
9	**4i**	H	2-Cl	1.0	74	116
10	**4j**	H	2,4-$(Me)_2$	2.0	70	103
11	**4k**	H	2,4-Cl_2	1.5	71	171
12	**4l**	H	2,5-Cl_2	1.0	68	138
13	**4m**	H	H	1.0	71	94
14	**4n**	Et	4-Cl	1.0	70	97

[a] Yields after purification by flash column chromatography.

We first investigated the model three-component reaction of 2-hydroxynaphthalene-1,4-dione **1**, *p*-toluidine **2a,** and propargyl bromide **3** (Scheme 1) in a sequential fashion. In this procedure, initially the model reaction of **1** and **2a** was performed under microwave irradiation at 120 W, 100 °C and 1 bar pressure for 3 min in the absence of any solvent. This reaction of **1** and **2a** led to the exclusive formation of 2-(*p*-tolylamino)naphthalene-1,4-dione **6a** in almost quantitative yield. Then, employing different anilines in the above reaction, a series of 2-arylaminonaphthalene-1,4-diones **6** were obtained. Among the deactivated anilines, viz. *p*-trifluoromethyl- and *p*-nitroanilines used in this reaction, the former afforded a good yield of the product, while the latter did not react. Incidentally, this green protocol for the synthesis of **6** is found to be advantageous than most of the methods reported earlier,[25] which suffer from one or more disadvantages such as long reaction time, use of organic solvents, and moderate yields. It is also pertinent to note that the reaction of 2-hydroxynaphthalene-1,4-dione and aniline when performed in a 1:2 molar ratio, did not afford the product arising from double Michael addition

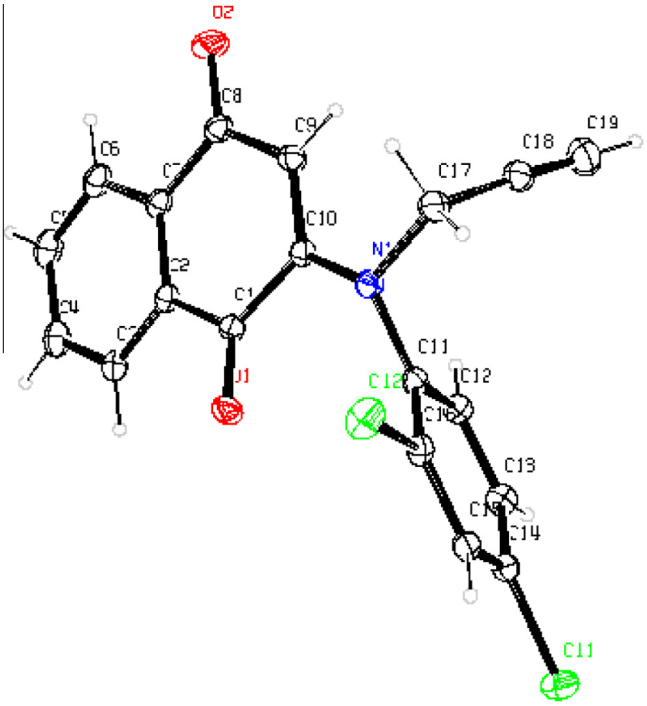
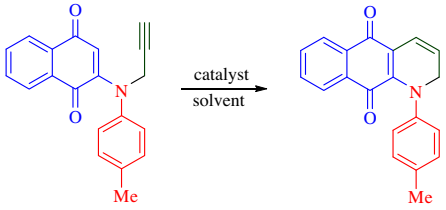


Figure 2. ORTEP diagram of **4k**.

Table 3
Screening of catalysts and solvents for the synthesis of 1,2-dihydrobenzo[*g*]quinoline-5,10-dione **5a**

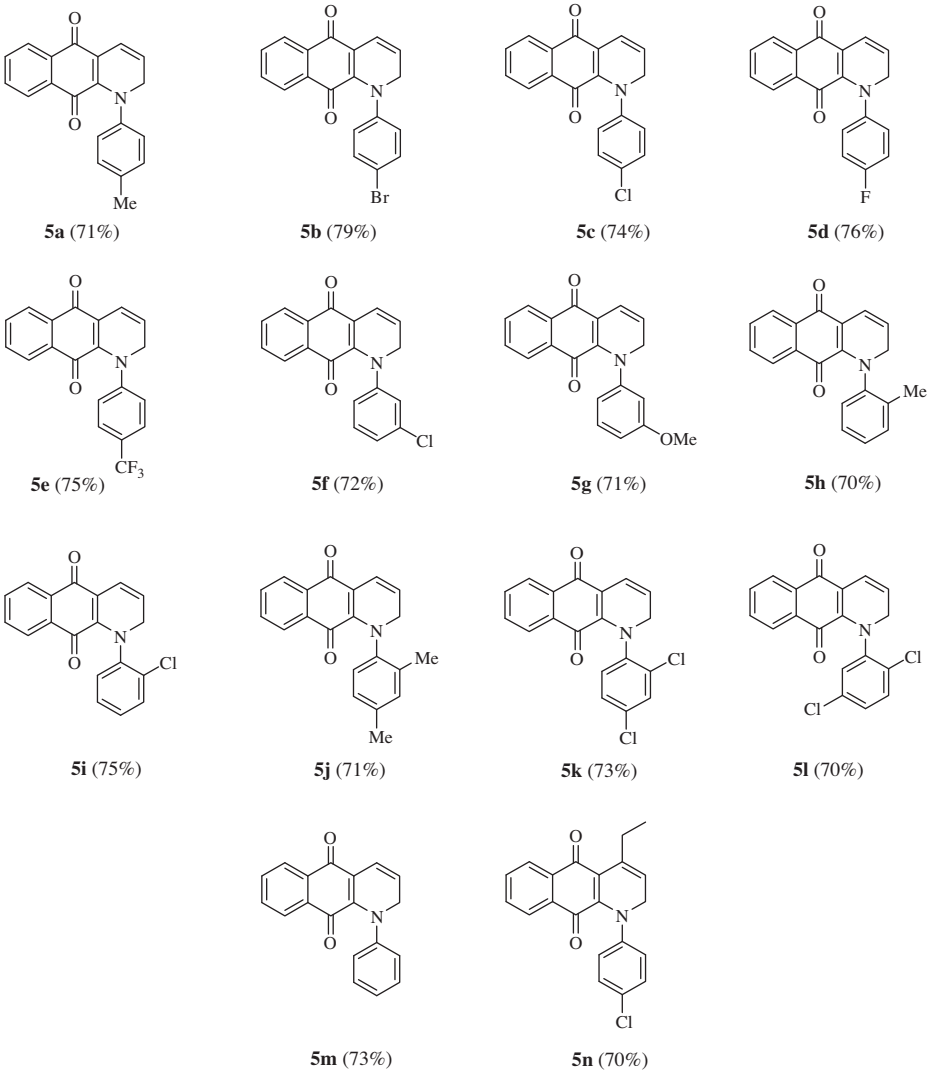


4a **5a**

S. No.	Solvent	Catalyst[a]	Reaction time (h)	Yield[b] (%)
1	Toluene	CuI	8	—[c]
2	Toluene	CuCl	4	20
3	Toluene	$CuCl_2{\cdot}2H_2O$	2	57
4	Toluene	$CuBr_2$	5	19
5	Toluene	$Cu(OAc)_2{\cdot}H_2O$	6	27
6	Toluene	$Cu(NO_3)_2{\cdot}3H_2O$	5	31
7	Toluene	$Cu(OTf)_2$	1	71
8	Toluene	$CuSO_4{\cdot}5H_2O$	6	—[c]
9	CH_3CN	$Cu(OTf)_2$	6	11
10	DMF	$Cu(OTf)_2$	8	21
11	DMSO	$Cu(OTf)_2$	8	—[c]
12	Diaxone	$Cu(OTf)_2$	2	64

[a] All reactions performed with 10 mol % of the catalyst.
[b] Yields after filtration through a pad of silica gel.
[c] Reaction failed to occur.

Table 4
Synthesis of 1,2-dihydrobenzo[*g*]quinoline-5,10-diones **5**[a] via $Cu(OTf)_2$ catalyzed 6-*endo-dig* cyclization



[a] Yield after filtration through a pad of silica gel.

elimination sequence and this reaction also furnished 2-arylaminonaphthalene-1,4-diones exclusively.

The optimization of the reaction conditions for the second step of the reaction, viz. the propargylation of 2-arylaminonaphthalene-1,4-diones **6** was investigated taking 2-(*p*-tolylamino)naphthalene-1,4-dione **6a** as the representative example. Thus, the reaction of 2-(*p*-tolylamino)naphthalene-1,4-dione **6a** with propargyl bromide **3** to obtain **4a** was investigated employing different base-solvent combinations (Table 1). This reaction failed to occur, when DMF/K_2CO_3, acetone/K_2CO_3, DMSO/K_2CO_3, dioxane/NaOH, and THF/NaH were used, while with DMF or DMSO in the presence of Cs_2CO_3, this reaction, even after prolonged reaction time, furnished **4a** in poor yields, 43% and 38%, respectively (Table 1, entries 4 and 6). Interestingly, *N*-propargylaminonaphthoquinone **4a** was obtained in 74% yield in toluene in the presence of NaOH and the phase transfer catalyst, tetrabutylammonium bromide (TBAB). Typically, to a solution of 2-(*p*-tolylamino)naphthalene-1,4-dione **6a**, generated in situ from the reaction of 2-hydroxynaphthalene-1,4-dione and *p*-toluidine (2 mmol each) in toluene (10 ml), propargyl bromide (2.6 mmol), a catalytic amount (20 mol %) of tetrabutylammonium bromide (TBAB), and an aqueous solution of sodium hydroxide (2 mmol in 1 ml of water) were added and the reaction furnishing **4a** was allowed to go to completion at ambient temperature. Then product **4a** was isolated and purified by flash column chromatography. With the above optimized reaction conditions, the scope of this transformation leading to a series of **4** was then investigated using a series of 2-arylaminonaphthoquinones **6** and propargyl/3-ethylpropargyl bromides (Table 2).[26]

The structure of **4** is in accord with elemental analysis and ^1H and ^{13}C NMR spectroscopic data as illustrated with a representative example **4c** (vide Supplementary data). The X-ray crystallo-

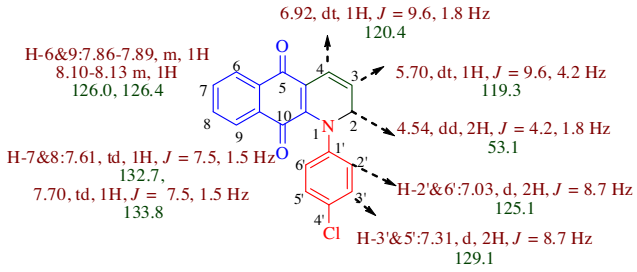
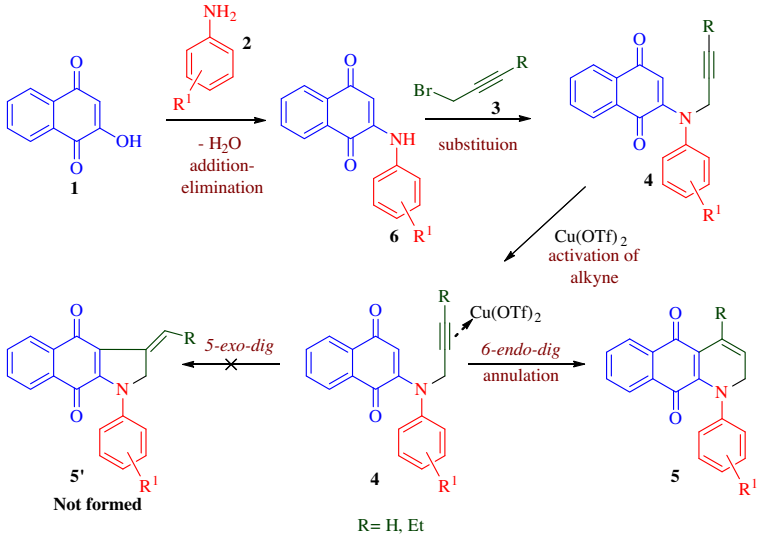


Figure 3. NMR characterization of compound **5c**.



Scheme 2. Plausible mechanism for the synthesis of 1,2-dihydrobenzo[*g*]quinoline-5,10-diones **5**.

graphic study of **4k** (Fig. 2)[27] confirms the structure of **4** deduced from NMR spectroscopic data.

We then explored the intramolecular cyclization of *N*-propargylaminonaphthoquinone **4a** in toluene in the presence of different copper catalysts. When the reaction was performed in the presence of 10 mol % of CuI and $CuSO_4$, the cyclization failed to occur. In the presence of 10 mol % of CuCl, $CuCl_2$, $CuBr_2$, $Cu(OAc)_2$, and $Cu(NO_3)_2$, the cyclized product was obtained in 20%, 57%, 19%, 27%, and 31% yields respectively (Table 3). To our delight, we found that a higher yield of 71% of **5a** could be obtained by performing the reaction in the presence of 10 mol % of $Cu(OTf)_2$ in toluene at 100 °C for 1 h. The reaction in the presence of $Cu(OTf)_2$ in DMSO failed to occur, while in CH_3CN, DMF and dioxane, diminished yield of the product was obtained. Presumably, the heteroatoms present in DMSO, CH_3CN, and DMF quenched the electrophilicity of $Cu(OTf)_2$ by coordination and diminished its catalytic efficacy in this transformation. These results disclose that $Cu(OTf)_2$–toluene pair is the ideal catalyst–solvent pair for this reaction and the scope of the transformation of a series of **4** to obtain **5** was investigated under the optimized reaction conditions (Table 4).[26]

The structure of 1,2-dihydrobenzo[*g*]quinoline-5,10-diones **5** was deduced using one- and two-dimensional NMR spectroscopic data (Fig. 3), mass spectrum, and elemental analysis. As a representative case, the structural assignment of **5c** is described below. The ^{1}H NMR spectrum of **5c** has a doublet of doublets at 4.54 ppm (J = 4.2, 1.8 Hz) for two protons assignable to the methylene hydrogens of the dihydropyridine ring. This signal shows a H,H-COSY correlation with the doublet of triplets at 5.70 ppm (J = 9.6, 4.2 Hz) due to H-3. Further, H-3 shows a H,H-COSY correlation with the doublet of triplets at 6.92 ppm (J = 9.6, 1.8 Hz), which arises from H-4. The very small coupling constant of 1.8 Hz presumably arises from the long range homoallylic coupling between H-2 and H-4. The multiplets occurring at 7.86–7.89 and 8.08–8.11 ppm are assigned to H-6 and H-9. The two triplets of doublets at 7.61 and 7.70 (1H, J = 7.5, 1.5 Hz) are due to H-7 and H-8.

A plausible mechanism for the formation of 1,2-dihydrobenzo[*g*]quinoline-5,10-diones **5** is depicted in Scheme 2. Presumably, the intermediate, 2-(arylamino)naphthalene-1,4-dione **6** was formed from the reaction of 2-hydroxynaphthalene-1,4-dione and substituted anilines by Michael addition-elimination reactions. Then compound **6** upon reaction with propargyl bromide **3** gives the corresponding *N*-propargylaminonaphthoquinone **4**. Ultimately, the intramolecular 6-*endo-dig* annulation of *N*-propargylaminonaphthoquinones furnishing the final product **5** is enabled by the activation of the C–C triple bond by $Cu(OTf)_2$. Presumably, the presence of three sp^2 carbons and the nitrogen, which also could prefer sp^2 hybridization due to conjugation with the quinone ring system, imposes strain to the five-membered ring of **5′**, which could preclude its formation. Relatively, the six-membered ring system in 1,2-dihydrobenzo[*g*]quinoline-5,10-diones could be less strained facilitating the regioselectivity of the annulation process in its favour.

In conclusion, we have developed an efficient synthesis of 1,2-dihydrobenzo[*g*]quinoline-5,10-diones in good yields employing simple starting materials through (i) a facile synthesis of *N*-propargylaminonaphthoquinones and (ii) their copper(II) triflate-catalyzed 6-*endo-dig* cyclization. The synthetic utility of these 1,2-dihydrobenzo[*g*]quinoline-5,10-diones is under further investigation by our research group to obtain more complex heterocycles of biological relevance.

Acknowledgments

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Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.tetlet.2013.04.125.

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26. *General procedure for the synthesis of 1,2-dihydrobenzo[g]quinoline-5,10-diones* **5**
i. Synthesis of N-propargylaminonaphthoquinones **4**
A mixture of 2-hydroxynaphthalene-1,4-dione (**1**) and substituted aniline (**2**) (2 mmol each) was irradiated under microwave irradiation at 120 W, 100 °C and 1 bar pressure for 3 min. The resulting product was dissolved in toluene (10 ml), into which propargyl or 3-ethylpropargyl bromide (**3**) (2.6 mmol) and tetrabutylammonium bromide (TBAB) (20 mol %) were added and the solution was stirred well. Then an aqueous solution of sodium hydroxide (2 mmol; 1 ml) was slowly added and stirring continued at ambient temperature for 1–2 h till the reaction went to completion (TLC). Then, the reaction mixture was washed with water (2 × 20 ml), the organic layer separated and dried over anhydrous sodium sulfate and the solvent was removed under reduced pressure. The resulting crude product was purified by flash column chromatography using petroleum ether–ethyl acetate (19:1 v/v) mixture.
ii. Synthesis of 1,2-dihydrobenzo[g]quinoline-5,10-diones **5**
To a solution of *N*-propargylaminonaphthoquinones (1 mmol) in toluene (10 ml), copper(II) triflate (0. 1 mmol) was added and the flask heated to 100 °C in an oil bath for 1 h. After completion of the reaction (TLC), the solvent was removed under reduced pressure and the resulting crude product was purified by filtration through a pad of silica gel using petroleum ether–ethyl acetate (49:1 v/v) to afford pure **5**
27. Crystallographic data for the derivative **4k** in this manuscript have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication number **CCDC 918355**. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 (0)1223 336033 or e-mail: deposit@ccdc.cam.ac.uk).