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PII: S0040-4039(15)30082-4
DOI: http://dx.doi.org/10.1016/j.tetlet.2015.09.040
Reference: TETL 46712

To appear in: *Tetrahedron Letters*

Received Date: 29 June 2015
Revised Date: 11 September 2015
Accepted Date: 14 September 2015

Please cite this article as: Misra, A.K., Bokor, É., Kun, S., Bolyog-Nagy, E., Kathó, Á., Joó, F., Somsák, L., Chemoselective hydration of glycosyl cyanides to *C*-glycosyl formamides using ruthenium complexes in aqueous media, *Tetrahedron Letters* (2015), doi: http://dx.doi.org/10.1016/j.tetlet.2015.09.040

Graphical Abstract

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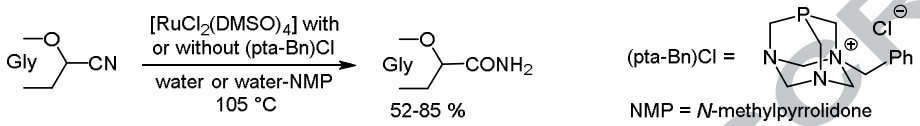

OAc, OBz, OBn protective groups, anomeric Br and N_3 substituents, and double bonds are all compatible with the reaction conditions

Tetrahedron Letters
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Chemoselective hydration of glycosyl cyanides to *C*-glycosyl formamides using ruthenium complexes in aqueous media

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ARTICLE INFO

Article history:
Received
Received in revised form
Accepted
Available online

Keywords:
C-glycoside
amide
nitrile
ruthenium complex
water

ABSTRACT

$[RuCl_2(DMSO)_4]$ in the presence of *N*-benzylated 1,3,5-triaza-7-phosphaadamantane efficiently catalyzed the hydration of glycosyl cyanides to the corresponding formamide derivatives in water or water–*N*-methylpyrrolidone solvent mixtures at 105 ºC. *O*-Acetyl, *O*-benzoyl, and *O*-benzyl protecting groups, anomeric bromide and azide substituents as well as double bonds were shown to be compatible with these reaction conditions.

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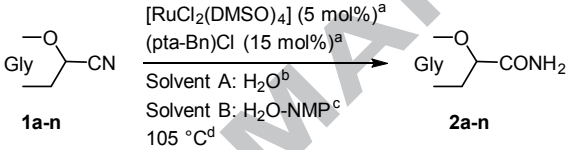
C-Glycosyl formamide (anhydro-aldonamide) derivatives are an important class of molecules used in the synthesis of several *C*-glycosylated and glycosylidene-spiro-heterocyclic compounds which possess promising pharmaceutical applications.[1,2] The most straightforward and atom economical approach for the preparation of these compounds is the hydration of glycosyl cyanides (anhydro-aldononitriles). This transformation is conventionally performed using harsh acidic reaction conditions (e.g. HBr-AcOH[3] or $TiCl_4$[4]), involving the requirement of several additional precautionary measures. Therefore, it is quite pertinent to develop a mild, neutral and user friendly reaction to obtain these versatile intermediates.

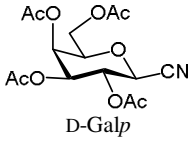
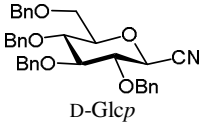
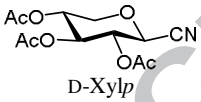
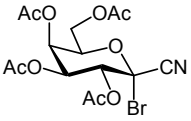
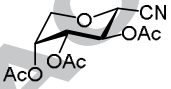
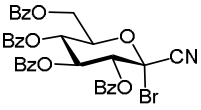
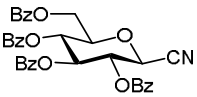
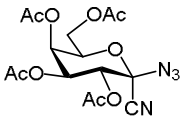
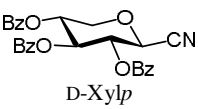
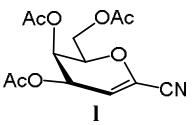
A large number of reports have appeared regarding chemoselective hydration of the nitrile group using a variety of reaction conditions.[5] Among several approaches, metal catalyzed reactions have attracted special attention due to the fact that metal ions are able to activate the nitrile group and water as the nucleophile by forming a coordination transition state complex. Efforts have been made to develop transition metal catalyzed homogeneous[6] and heterogeneous[7] reaction conditions. Besides these, chitosan supported ruthenium catalyst,[8] potassium *tert*-butoxide mediated hydration,[9] and microwave assisted hydration of nitriles[10] were also studied. Several reports have also appeared on the use of biocatalysis for this transformation.[11] Recently, the hydration of aromatic and aliphatic nitriles under aqueous reaction conditions has been reported from one of our laboratories using a combination of a water soluble catalyst, $[RuCl_2(DMSO)_4]$, and *N*-benzylated 1,3,5-triaza-7-phosphaadamantane (pta-Bn)Cl, as a ligand (catalyst:ligand ratio; 1:3).[12]

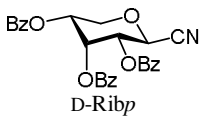
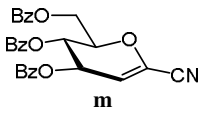
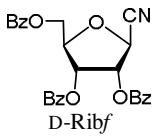
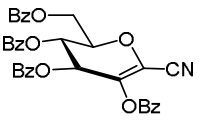
Expanding on this earlier report, herein, we disclose the application of this catalyst system for the preparation of *C*-glycosyl formamide derivatives from glycosyl cyanides (Table 1). Initially a combination of $[RuCl_2(DMSO)_4]$ (10 mol%) and (pta-Bn)Cl (30 mol%) were added to a suspension of *O*-peracetylated β-D-galactopyranosyl cyanide (**1a**; 100 mg) in water (5 mL) and the reaction mixture stirred vigorously at 105 °C. A clear solution was observed after 10 min, and the *C*-galactosyl formamide derivative **2a** was formed cleanly in 85% yield after 2 h. After optimizing the reaction conditions, it was established that a combination of 5 mol% catalyst and 15 mol% ligand in water (4 mL/100 mg of substrate) was sufficient to obtain compound **2a** in 85% yield. Application of the optimized conditions to other *O*-acetyl protected glycosyl cyanides (**1b,c**) furnished the corresponding products **2b,c** with excellent yields (Table 1).[13]

Table 1. Chemoselective hydration of glycosyl cyanides.

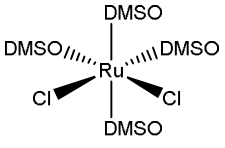


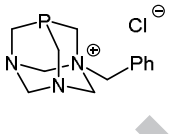
1a-n **2a-n**

Gly-CN	Solvent	Time (h)	**2** yield[e] (%)	Ref.	Gly-CN	Solvent	Time (h)	**2** yield[e] (%)	Ref.
 D-Gal*p* **a**	A	2	85 (84)[f]	4	 D-Glc*p* **h**	A[g] B	55 30	50 74	16
 D-Xyl*p* **b**	A	3	82	13	 **i**	A[g] B	4 3	-[h] -[h]	-
 D-Ara*p* **c**	A	3	87	-	 **j**	A[g] B	60 48	- 52[i]	3b
 D-Glc*p* **d**	A[g] B	60 20	65 82	3b	 **k**	A[g] B	72 8	-[h] 72[j]	17
 D-Xyl*p* **e**	A[g] B	50 5	68 80	14	 **l**	A	2	84	2h

 D-Rib*p* **f**	B	4	80	-	 **m**	A	6	80	-
 D-Rib*f* **g**	B	3	84	[15]	 **n**	A[g] B	48 48	-[h] -[h]	-

[a] See structures below for $[RuCl_2(DMSO)_4]$ and (pta-Bn)Cl (*N*-benzylated 1,3,5-triaza-7-phosphaadamantane); [b] 4 mL/100 mg; [c] *N*-Methyl-2-pyrrolidone (2:1 *v/v*; 3 mL/100 mg); [d] Oil bath temp.; [e] Isolated yield; [f] Yield obtained using 2 g of the substrate; [g] Sodium dodecyl sulphate (SDS, 5 mol%) was added; [h] Starting material consumed to produce a complex reaction mixture; [i] Starting material not fully consumed and was recovered (20%); [j] Reaction carried out using $[RuCl_2(DMSO)_4]$ (15 mol%) in the absence of (pta-Bn)Cl.


$[RuCl_2(DMSO)_4]$


(pta-Bn)Cl

When *O*-perbenzoylated β-D-glucopyranosyl cyanide **1d** was treated with the catalyst combination in water at 105 °C the reaction mixture did not become homogeneous and the compound remained suspended even after 48 h, with TLC indicating no transformation. It was reasoned that the failure of the reaction could be due to the significantly lower solubility of the *O*-benzoyl derivatives in comparison to that of the *O*-acetylated compounds. Therefore, sodium dodecyl sulphate (SDS, 5 mol%) was added to the reaction mixture as a surfactant resulting in the formation of the corresponding formamide derivative **2d** in 65% yield after 60 h. Addition of SDS was also beneficial in the cases of **1e** and the *O*-perbenzylated **1h**, which gave the corresponding formamide derivatives **2e** and **2h** in good yields (Table 1).

An additional method to improve the solubility of the substrates by adding a co-solvent was also tried. Thus, compounds **1d-h** were treated with the catalyst combination in a mixed solvent [water-NMP (*N*-Methyl-2-pyrrolidone) = 2:1 v/v] at 105 °C. In these cases the reaction mixtures became clear after 5 min and smooth formation of the corresponding formamide derivatives **2d-h** was achieved in very good yields and significantly shorter times (Table 1).

Next, more complex substrates with bromo (**1i,j**) and azido (**1k**) substituents as well as double bonds (**1l-n**) were studied under the optimized conditions. Using water as the solvent and SDS (5 mol%) as the additive, the reactions of compounds **1i-k** produced complex mixtures from which the expected products could not be detected by TLC. In the mixed water-NMP solvent, *O*-acetylated **1i** also gave a complex mixture, however, the analogous *O*-benzoylated **1j** produced the corresponding formamide **2j** in 52% yield together with unreacted starting material. Since these substrates contained bromo and azido groups, which might have cross reactivity with the (pta-Bn)Cl ligand, the reactions were then carried out in the absence of (pta-Bn)Cl. However, bromo-cyanide **1i** produced a complex mixture upon treatment with $[RuCl_2(DMSO)_4]$ (15 mol%) both in water and the mixed solvent. Although the reaction in water resulted in formation of a complex mixture, gratifyingly azido-cyanide **1k** furnished the corresponding formamide derivative **2k** in 72% yield after 8 h upon treatment with $[RuCl_2(DMSO)_4]$ (15 mol%) in the mixed solvent. It is presumed that the adjacent azido and cyano groups could form a coordination complex with the Ru atom, which could support the hydration of this nitrile. Unsaturated compounds **1l** and **1m** furnished the respective formamides **2l** (84%) and **2m** (80%) in water without the requirement of the surfactant additive (SDS). The enol-ester type **1n** did not furnish any of the expected product under the examined reaction conditions.

In order to check the role of the ligand in the reaction, compound **1a** was treated with $[RuCl_2(DMSO)_4]$ (varied quantities from 5 to 15 mol%) in water as well as mixed solvent in the absence of the (pta-Bn)Cl ligand. Under these conditions only decomposition of **1a** was observed even after a prolonged reaction time of 2 days, while formation of the expected product **2a** could not be detected by TLC.

It is worth mentioning that no trace of the corresponding carboxylic acid resulting from over-hydrolyzed product was observed under the reaction conditions. The *C*-glycosyl formamide derivatives were identified by NMR and mass spectral analysis.[18] The reaction was successfully applied in a scaled up preparation of *C*-glycosyl formamide **2a** (84 % yield in a 2 g batch). In the cases of compounds **1a-c,l,m** the catalyst combination present in the aqueous phase after reaction work-up was recycled up to three times without any significant loss of the catalytic potential.

Typical procedure using water as solvent: To a solution of compound **1a** (100 mg, 0.28 mmol) in water (4 mL) were added $[RuCl_2(DMSO)_4]$ (7 mg, 0.014 mmol) and (pta-Bn)Cl (12 mg, 0.042 mmol) and the reaction mixture was stirred at 105 °C (bath temperature) for 2 h. The mixture was cooled to room temperature and extracted with EtOAc (20 mL). The organic layer was dried (Na_2SO_4) and concentrated under reduced pressure. The crude product was crystallized from EtOH to give pure **2a** (90 mg, 85%). The aqueous layer was reused for another batch of reaction by adding **1a** (100 mg, 0.28 mmol) and stirring at 105 °C for 2 h to give **2a** (90 mg, 85%). Similar recycling of the catalyst system was applied for the preparation of **2b,c,l,m** to furnish the products as mentioned in Table 1.

Typical procedure using water-NMP as solvent: To a solution of compound **1d** (100 mg, 0.16 mmol) in water-NMP (3 mL; 2:1 v/v) were added $[RuCl_2(DMSO)_4]$ (4 mg, 0.008 mmol)

and (pta-Bn)Cl (7 mg, 0.024 mmol) and the reaction mixture was stirred at 105 °C (bath temperature) for 20 h. The mixture was cooled to room temperature, diluted with H_2O (30 mL) and extracted with EtOAc (20 mL). The organic layer was dried (Na_2SO_4) and concentrated under reduced pressure. The crude product was crystallized from EtOH to give pure **2d** (85 mg, 82%). Similar reaction conditions were applied for the preparation of **2e-h,j,k**.

In summary, efficient chemoselective reaction conditions have been developed for the hydration of glycosyl cyanides to *C*-glycosyl formamide derivatives using a water soluble ruthenium complex in aqueous media. These conditions can be considered as practical alternatives to the existing protocols for this transformation due to their environmental compatibility, mild conditions, operational simplicity, high yields with excellent chemoselectivity, and applicability in the presence of the acid and base sensitive functional groups used in carbohydrate derivatization.

Acknowledgments

A.K.M. thanks the Indian National Science Academy (INSA), the Hungarian Academy of Science (HAS), and Bose Institute, Kolkata, India for financing his stay at the University of Debrecen. The work was supported by the Hungarian Scientific Research Fund (OTKA PD105808) as well as the BAROSS REG_EA_09-1-2009-0028 (LCMS_TAN) project. Dr. A. Kiss-Szikszai is thanked for recording the mass spectra and elemental analyses.

References and notes

1. a) Somsák, L.; Czifrák, K.; Tóth, M.; Bokor, É.; Chrysina, E. D.; Alexacou, K.-M.; Hayes, J. M.; Tiraidis, C.; Lazoura, E.; Leonidas, D. D.; Zographos S. E.; Oikonomakos, N. G. *Curr. Med. Chem.* **2008**, *15*, 2933-2983; (b) Somsák, L.; Nagy, V.; Hadady, Z.; Docsa, T.; Gergely, P. *Curr. Pharm. Design*, **2003**, *9*, 1177-1189; (c) Somsák, L. *Comptes Rendus Chimie* **2011**, *14*, 211-223.
2. (a) Páhi, A.; Czifrák, K.; Kövér, K. E.; Somsák, L. *Carbohydr. Res.* **2015**, *403*, 192-201; (b) Bokor, É.; Szilágyi, E.; Docsa,T.; Gergely, P.; Somsák, L.*Carbohydr. Res.* **2013**, *381*, 179-186; (c) Somsák, L.; Kovács, L.; Tóth, M.; Ősz, E.; Szilágyi, L.;Györgydeák, Z.; Dinya, Z.; Docsa, T.; Tóth, B.; Gergely, P. *J. Med. Chem.* **2001**, *44*, 2843-2848; (d) Bokor, É.; Docsa, T.; Gergely, P.; Somsák, L. *ACS Med. Chem. Lett*. **2013**, *4*, 612-615; (e) Felföldi, N.; Tóth, M.; Chrysina, E. D.; Charavgi, M.-D.; Alexacou, K.-M.; Somsák, L. *Carbohydr. Res*. **2010**, *345*, 208-213; (f) McMillan, K. G.; Tackett, M. N.; Dawson, A.; Fordyce, E.; Paton, R. M. *Carbohydr. Res*. **2006**, *341*, 41-48; (g) Lichtenthaler, F. W.; Nakamura, K.; Klotz, J. *Angew. Chem. Int. Ed. Engl*. **2003**, *42*, 5838-5843; (h) Kiss, L.; Somsák, L. *Carbohydr. Res*. **1996**, *291*, 43-52; (i) Poonian, M. S.; Nowoswiat, E. F. *J. Org. Chem.* **1980**, *45*, 203-208.
3. (a) Myers, R. W.; Lee, Y. C. *Carbohydr. Res*. **1986**, *152*, 143-158; (b) Somsák, L.; Nagy, V. *Tetrahedron: Asymmetry* **2000**, *11*, 1719-1727.
4. BeMiller, J. N.; Yadav, M. P.; Kalabokis, V. N.; Myers, R. W. *Carbohydr. Res*. **1990**, *200*, 111-126.
5. (a) Schaefer, F. C. In The Chemistry of the Cyano Group: Nitrile Reactivity; Rappoport, Z., Ed.; Interscience: New York, **1970**; pp 239-305; (b) Bailey, P. D.; Mills, T. J.; Pettecrew, R. A. in Comprehensive Organic Functional Group Transformations II; Katritzky, A. R.; Taylor, R. J. K. Eds., Vol 5, Elsevier, Oxford, **2005**, pp 201-294.
6. (a) Kukushkin, V. Y.; Pombeiro, A. J. L. *Chem. Rev*. **2002**, *102*, 1771-1802; (b) Pombeiro, A. J. L.; Kukushkin, V. Y. *Comprehensive Coordination Chemistry* II, **2004**, *1*, 639-660; (c) Yamaguchi, K.; Matsushita, M.; Mizuno, N. *Angew. Chem. Int. Ed. Engl*. **2004**, *43*, 1576-1580; (d) Ahmed, T. J.; Knapp, S. M. M.; Tyler, D. R. *Coord. Chem. Rev*. **2011**, *255*, 949-974; (e) Garcia-Alvarez, R.; Francos, J.; Tomas-Mendivil, E.; Crochet, P.; Cadierno, V. *J. Organometallic Chem.* **2014**, *771*, 93-104.
7. (a) Tamura, M.; Wakasugi, H.; Shimizu, K. -I.; Satsuma, A. *Chem. Eur. J.* **2011**, *17*, 11428-11431; (b) Liu, Y. -M.; He, L.; Wang, M.-M.; Cao, Y.; He, H.-Y.; Fan, K.-N.; *ChemSusChem* **2012**, *5*, 1392-1396; (c) Hirano, T.; Uehara, K.; Kamata, K.; Mozuno, N. *J. Am. Chem. Soc.* **2012**, *134*, 6425-6433; (d) Battilocchio, C.; Hawkins, J. M.; Ley, S. V. *Org. Lett*. **2014**, *16*, 1060-1063.
8. Matsuoka, A.; Isogawa, T.; Morioka, Y.; Knappett, B. R.; Wheatley, A. E. H.; Saito, S.; Naka, H. *RSC Adv.* **2015**, *5*, 12152-12160.
9. Midya, G. C.; Kapat, A.; Maiti, S.; Dash, J. *J. Org. Chem.* **2015**, *80*, 4148-4151.
10. Tu, T.; Wang, Z.; Liu, Z.; Feng, X.; Wang, Q. *Green Chem.* **2012**, *14*, 921-924.
11. (a) Kovacs, J. A. *Chem. Rev*. **2004**, *104*, 825-848; (b) Kobayashi, M.; Shimizu, S. *Curr. Opin. Chem. Biol*. **2000**, *4*, 95-102.
12. Bolyog-Nagy, E.; Udvardy, A.; Joó, F.; Kathó, Á. *Tetrahedron Lett*. **2014**, *55*, 3615-3617.
13. McMillan, K. G.; Tackett, M. N.; Dawson, A.; Fordyce, E.; Michael Paton, R. *Carbohydr. Res*. **2006**, *341*, 41-48.
14. Somsák, L.; Bokor, É.; Czibere, B.; Czifrák, K.; Koppány, C.; Kulcsár, L.; Kun, S.; Szilágyi, E.; Tóth, M.; Docsa, T.; Gergely, P. *Carbohydr. Res*. **2014**, *399*, 38-48.
15. Buffel, D. K.; Simons, B. P.; Deceuninck, J. A.; Hoornaert, G. J. *J. Org. Chem.* **1984**, *49*, 2165-2168.
16. DeShong, P.; Soli, E. D.; Slough, G. A.; Sidler, D. R.; Elango, V.; Rybczynski, P. J.; Vosejpka, L. J. S.; Lessen, T. A.; Le, T. X.; Anderson, G. B.; von Philipsborn, W.; Vöhler, M.; Rentsch, D.; Zerbe, O. *J. Organometallic Chem.* **2000**, *593-594*, 49-62.
17. Somsák, L.; Sós, E.; Györgydeák, Z.; Praly, J.-P.; Descotes, G. *Tetrahedron* **1996**, *52*, 9121-9136.
18. Analytical data for the compounds which have not been reported earlier:
Compound 2c: R_f = 0.2 (hexane-EtOAc; 2:3); $[\alpha]_D^{25}$ –53.1 (*c* 1.0, $CHCl_3$); ^{1}H NMR (360 MHz, $CDCl_3$): δ 6.46 (br s, 1 H, N*H*), 6.12 (br s, 1 H, N*H*), 5.40 (pseudo t, *J* = 8.0 Hz, 1 H, H-3), 5.32 (br s, 1 H, H-5), 5.13 (dd, *J* = 11.0, 3.5 Hz, 1 H, H-4), 4.09 (dd, *J* = 12.5, 4.0 Hz, 1 H, H-6_a), 3.84 (d, *J* = 8.0 Hz, 1 H, H-2), 3.77 (dd, *J* = 12.5, 2.5 Hz, 1 H, H-6_b), 2.16, 2.08, 2.02 (3 s, 9 H, 3 COCH_3); ^{13}C NMR (90 MHz, $CDCl_3$): δ 170.1, 169.9 ($CONH_2$, $COCH_3$), 76.7 (C-2), 70.7 (C-4), 67.9 (C-5), 67.3 (C-6), 66.8 (C-3), 20.8, 20.7, 20.5 (COCH_3); ESI-MS: 326.0 [M+Na]$^+$; Anal. Calcd for $C_{12}H_{17}NO_8$: C, 47.53; H, 5.65; N, 4.62. Found: C, 47.68; H, 5.77; N, 4.69.
Compound 2f: R_f = 0.2 (hexane-EtOAc; 3:2); $[\alpha]_D^{25}$ –41.4 (*c* 1.0, $CHCl_3$); ^{1}H NMR (360 MHz, $CDCl_3$): δ 8.10-7.29 (m, 15 H, Ar-H), 6.47 (br s, 1 H, N*H*), 6.15-6.13 (m, 1 H, H-4), 5.82 (br s, 1 H, N*H*), 5.62 (dd, *J* = 7.8, 2.4 Hz, 1 H, H-3), 5.50-5.45 (m, 1 H, H-5), 4.53 (d, *J* = 7.8 Hz, 1 H, H-2), 4.27 (dd, *J* = 9.3, 4.5 Hz, 1 H, H-6_a), 4.04 (t, *J* = 9.3 Hz each, 1 H, H-6_b); ^{13}C NMR (90 MHz, $CDCl_3$): δ 170.2, 165.2, 165.1 (*C*ONH_2, Ph*C*O), 133.5, 133.4, 133.2, 129.9, 129.8, 129.7, 129.5, 129.2, 129.0, 128.6, 128.4, 128.3 (Ar-C), 73.9 (C-2), 68.7 (C-3), 68.4 (C-4), 67.1 (C-5), 63.8 (C-6); ESI-MS: 512.1 [M+Na]$^+$; Anal. Calcd for $C_{27}H_{23}NO_8$: C, 66.25; H, 4.74; N, 2.86. Found: C, 66.32; H, 4.80; N, 2.80.
Compound 2m: R_f = 0.18 (hexane-EtOAc; 7:3); $[\alpha]_D^{25}$ –21.8 (*c* 0.5, $CHCl_3$); ^{1}H NMR (360 MHz, $CDCl_3$): δ 8.05-7.38 (m, 15 H, Ar-H), 6.51 (br s, 1 H, N*H*), 6.30 (d, *J* = 2.7 Hz, 1 H, H-3), 6.12 (br s, 1 H, N*H*), 5.90 (strongly coupled m, 1 H, H-4), 5.81 (dd, *J* = 6.7, 5.3 Hz, 1 H, H-5), 4.85-4.81 (m, 1 H, H-6), 4.78-4.67 (m, 2 H, H-7_{ab}); ^{13}C NMR (90 MHz, $CDCl_3$): δ 166.1, 165.4, 165.0 (Ph*C*O), 162.7 (*C*ONH_2), 146.5 (C-2), 133.7, 133.4 (2), 129.9, 129.8, 129.7, 129.3, 129.2, 128.8, 128.5 (2), 128.4 (Ar-C), 103.6 (C-3), 75.3 (C-4), 67.3 (C-5), 67.2 (C-6), 61.5 (C-7); ESI-MS: 524.1 [M+Na]$^+$; Anal. Calcd for $C_{28}H_{23}NO_8$: C, 67.06; H, 4.62; N, 2.79. Found: C, 67.30; H, 4.75; N, 2.76.