Pergamon

Tetrahedron 56 (2000) 8769–8773

TETRAHEDRON

Microwave-Assisted Preparation of Benzo[b]furans under Solventless Phase-Transfer Catalytic Conditions

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Received 21 February 2000; revised 24 August 2000; accepted 7 September 2000

Abstract—Condensation of salicylaldehyde and its derivatives with various esters of chloroacetic acids in the presence of tetrabutylammonium bromide (TBAB) leads to the synthesis of benzo[b]furans by a solventless phase-transfer catalytic (PTC) reaction under microwave irradiation.

Benzofuran derivatives are nowadays an important class of organic compounds that occur in a great number of natural products,[1] are used in cosmetics[2] and are used as synthetic pharmaceuticals.[3] Moreover, benzo[b]furans are building blocks for optical brighteners and are applied, for example, in combination with benzimidazoles as biphenyl end groups.[4] Many of the natural benzo[b]furans have physiological, pharmacological and toxic properties, and as a result there is continuing interest in their chemical synthesis.[5]

Cyclization reactions of various types have been used to produce substituted benzo[b]furans.[6,7] In the present paper, we report on the modification of one of the most popular routes to substituted benzo[b]furans, i.e. O-alkylation of *o*-hydroxylated aromatic carbonyl compounds with α-halogenated carbonyl compounds, followed by intramolecular cyclization. The reactions are usually catalysed by potassium carbonate in acetone or by potassium hydroxide in ethanol.[8]

Result and Discussion

The use of inorganic solid materials for the support of organic reactants and catalysts has been broadly exemplified and well established as an environmental benign technology.[9] In recent years, it has been shown that microwave irradiation is of particular benefit for such reactions, particularly for these reactions carried out in the absence of solvents.[10] The solventless reactions offer a number of advantages: solvents are often expensive, toxic, and difficult to remove in the case of aprotic solvents with high boiling points. Moreover, the absence of solvent reduces the risk of an explosion when the reaction takes place in a microwave oven, and liquid–liquid extraction can be avoided in the isolation of reaction products. At present, the reactions under solid–liquid phase-transfer catalytic (PTC) conditions which are specially useful for anionic activation processes are numbered among the 'dry' reactions.[11]

Recently, it has been shown that under microwave irradiation in dry media a number of alcohols and phenols could be easily O-alkylated,[12] and aromatic aldehydes could undergo condensation[13] and cyclocondensation reactions.[14] Since, more recently, Varma et al. have reported the preparation of 2-aroylbenzo[b]furans using microwave irradiation to drive the condensation of α-tosyloxyketones with salicylaldehyde derivatives on potassium fluoride doped alumina,[15] we have been prompted to present our results on the synthesis of benzo[b]furans under solid–liquid phase-transfer catalytic (PTC) conditions (Scheme 1).

In a typical experiment, the reactions were carried out by simply mixing a salicylaldehyde derivative with a two fold excess of a chloroacetic acid ester and a catalytic amount of tetrabutylammonium bromide (TBAB). The mixtures were adsorbed on potassium carbonate, then irradiated in an open vessel in a domestic microwave oven for 8–10 min. The results and conditions of the reactions are summarised in Table 1.

We found that the shape and size of the reaction vessel are important factors for microwave heating, the preferred reaction vessel was a conical flask of much larger capacity than the volume of the reaction mixture, bearing a loose cotton cover. Due to difficulties with adjusting temperature in a domestic microwave oven, one of the best solutions is to repeat an experiment a couple of times increasing the power

Keywords: microwave; benzofurans; condensation; phase-transfer catalysis.

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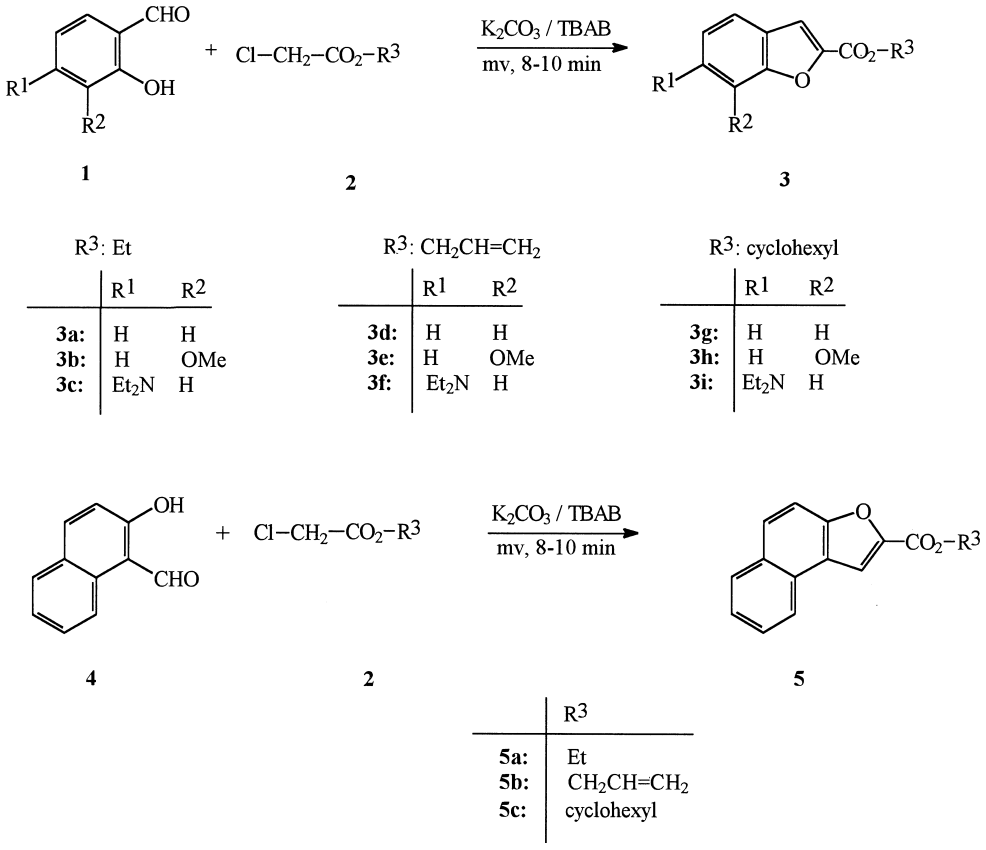
PII: S0040-4020(00)00818-8



Scheme 1.

slowly so that vapours do not escape the flask. Furthermore, at the end of such an experiment, temperature can be measured with a thermocouple.

Conclusion

In conclusion, we have described a highly efficient microwave-induced procedure for the preparation of various benzo[b]furan derivatives, that occurs remarkably fast, under mild conditions, using inexpensive reagents and a household microwave oven as the irradiation source. The advantages of this environmentally benign and safe protocol include a simple reaction set-up, application of commercially available reagents and catalysts, high product yields, short reaction times as well as the elimination of solvents.

Experimental

General methods

Elemental analyses were performed on a Perkin–Elmer 2400 microanalyzer. Melting points, measured on a Boetius-PHMK 05 microscope plates, are uncorrected. The progress of reactions was monitored by a gas chromatography (GC) 5890 Hewlett–Packard coupled with a mass detection (MS) 5971 Hewlett–Packard. ^{1}H NMR spectra were recorded with a TESLA 487 C spectrometer, TMS being used as a internal standard; the chemical shifts are expressed in δ values downfield from TMS. Multiplicities are recorded as s (single), d (doublet), t (triplet), q (quartet), dt (doublet of triplet), and m (multiplet). IR spectra were obtained on a Bio-Rad FT-IR spectrophotometer FTS 165, and the wave numbers were given with a precision of 2 cm^{-1}. Silica gel column chromatography was performed with Fluka Kieselgel 60, using mixtures of cyclohexane and methylene chloride as eluants.

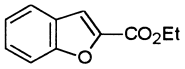
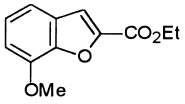
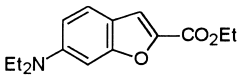
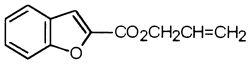
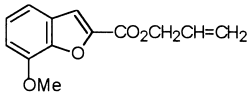
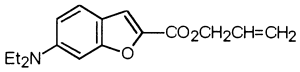
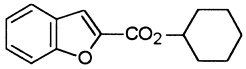
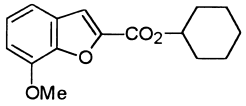
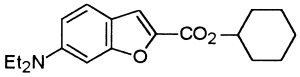
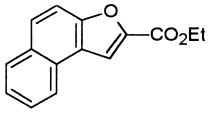
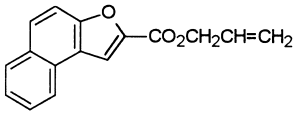
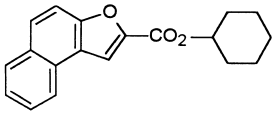
Starting materials

Allyl and cyclohexyl chloroacetates were prepared by the standard esterification method from chloroacetic acid and allyl alcohol and cyclohexanol, respectively. All other reagents were purchased from Aldrich and used as received.

Standard procedure for the preparation of benzo[b]-furan derivatives

Potassium carbonate (2.70 g, 20 mmol), TBAB (0.16 g, 0.50 mmol), and a salicylaldehyde derivative (5.0 mmol) were thoroughly mixed and placed in an open conical, glass flask. Then a chloroacetate ester (10 mmol) was added dropwise, the mixture was thoroughly stirred with a spatula for a few seconds, placed in a domestic microwave oven, and irradiated for 8–10 min (Table 1). The final temperature of the reaction mixture was measured with a thermocouple at the end of the reaction. Upon completion of the reaction, monitored by GC/MS, the mixture was extracted with methylene chloride, and the solvent was then removed. A crude product was purified by column chromatography.

Table 1. Results and conditions of the synthesis of benzo[b]furans derivatives **3a–i** and **5a–c** (in all the reactions under microwave irradiation, full conversions of aromatic aldehydes were achieved; under conventional conditions (oil bath) full conversion of an aldehyde was usually observed after 3 h)

Product	Number	Time (min)	Power[a] (W)	Temp.[b] (°C)	Yield[c] (%)
	**3a**	8	175	175	65
	**3b**	8	250	145	68
	**3c**	8	250	138	82
	**3d**	10	160	120	85
	**3e**	10	160	245	91
	**3f**	10	160	245	72
	**3g**	10	250	175	96
	**3h**	8	300	175	78
	**3i**	10	160	148	88
	**5a**	8	250	191	69
	**5b**	10	160	140	79
	**5c**	8	300	162	94

[a] The reactions were carried out in a Philips household microwave oven with maximum power 900 W which was reduced to the range 160–300 W.
[b] The final temperature of the reaction mixture measured with a thermocouple after the completion.
[c] The final yield after product separation.

Ethyl 2-benzo[b]furancarboxylate (3a). The crude product was purified by column chromatography (cyclohexane/methyl chloride 8:2) yielding **3a** as a colourless oil, $n_D^{20}=-1.5503$; [Found: C, 69.24; H, 5.08 $C_{11}H_{10}O_3$ requires C, 69.46; H, 5.29%]; ν_{max}(liquid film) 2983(m), 1731(s), 1614(w), 1447(m), 1370(m), 1329 (w), 1297(s), 1259(m), 1225(m), 1210(m), 1181(s), 1146(m), 1020(m), 946(w), 888(w), 840(w), 750(s) cm^{-1}; δ_H (80 MHz $CDCl_3$) 7.66–6.91 (5H, m aromatic protons), 4.37 (2H, q, J=7.1 Hz, CH_2–Me), 1.35 (3H, t, J=7.1 Hz, CH_2–*Me*); *m/z* (70 eV) 191 ($(M+1)^+$, 11), 190 (M^+, 82), 162 (83), 145 (100), 118 (27), 89 (34), 63 (14%).

Ethyl 7-methoxy-2-benzo[b]furancarboxylate (3b). The crude product was purified by column chromatography (cyclohexane/methyl chloride 8:3) yielding **3b** as a white solid, mp 73–75°C; [Found: C, 65.31; H, 5.51 $C_{12}H_{12}O_4$ requires C, 65.49; H, 5.49%]; ν_{max}(KBr) 1711(s), 1621(m), 1578(m), 1494(m), 1370(m), 1327(m), 1272(m), 1227(m), 1195(m), 1091(m), 1057(m), 1027(m), 974(s), 942(s), 857(s), 781(s), 761(s), 733(s), 703(m), 624(m), 574(w), 537(s) cm^{-1}; δ_H (80 MHz $CDCl_3$) 7.51–6.91 (4H, m aromatic protons), 4.43 (2H, q, J=7.0 Hz, CH_2–Me), 4.02 (3H, s, OMe) 1.42 (3H, t, J=7.1 Hz, CH_2–*Me*); *m/z* (70 eV)

221 ((M+1)$^+$, 13), 220 (M$^+$, 100), 193 (7.5), 192 (66), 175 (33), 149 (11%).

Ethyl 6-diethylamino-2-benzo[b]furancarboxylate (3c). The crude product was purified by column chromatography (cyclohexane/methyl chloride 8:2) yielding **3c** as a red oil, $n_D^{20}=-1.6163$; [Found: C, 68.69; H, 7.29; N, 5.38 $C_{15}H_{19}NO_3$ requires C, 68.95; H, 7.33; N, 5.36%]; ν_{max}(liquid film) 2973(s), 2931(m), 2899(m), 2872(w), 1716(s), 1626(s), 1578(m), 1556(m), 1509(s), 1398(m), 1372(s), 1357(m), 1303(m), 1270(s),1241(s), 1180(s), 1120(s), 1095(m), 1017(m), 844(w), 795(m), 759(m) cm^{-1}; δ_H (80 MHz $CDCl_3$) 7.49–7.26 (2H, m, aromatic protons), 6.77–6.40 (2H, m aromatic protons), 4.40 (2H, q, *J*=7.0 Hz, C*H*$_2$–*Me*), 3.40 (4H, q, *J*=7.1 Hz, CH$_2$*Me*) 1.40 (3H, t, *J*=7.2 Hz, CH$_2$–*Me*), 1.19 (6H, t, *J*=7.0 Hz, NCH$_2$*Me*); *m/z* (70 eV) 261 (M$^+$, 42), 247 (16), 246 (100), 218 (23), 190 (10), 116 (6.7%).

Allyl 2-benzo[b]furancarboxylate (3d). The crude product was purified by column chromatography (cyclohexane/methyl chloride 8:3) yielding **3d** as a white solid, mp 82–83°C; [Found: C, 71.05; H, 4.92 $C_{12}H_{10}O_3$ requires C, 71.28; H, 4.98%]; ν_{max} (KBr) 3086(w), 2943(w), 1731(s), 1564(m), 1447(m), 1368(m), 1297(s), 1259(w), 1222(m), 1210(w), 1178(s), 1145(m), 1096(m), 977(m), 936(m), 885(w), 835(w), 750(s) cm^{-1}; δ_H (80 MHz $CDCl_3$) 7.74–7.26 (5H, m, aromatic protons), 6.35–5.85 (1H, m, CH$_2$–C*H*=CH$_2$), 5.65–5.26 (2H, m, CH$_2$–CH=C*H*$_2$), 4.88 (2H, dt, *J*=7.0, 1.2 Hz, C*H*$_2$–CH=CH$_2$); *m/z* (70 eV) 203 ((M+1)$^+$, 4.5), 202 (M$^+$, 33), 158 (8.7), 157 (9.4), 146(11), 145 (100), 131 (7.4), 118 (17.8), 89 (32), 63 (16%).

Allyl 7-methoxy-2-benzo[b]furancarboxylate (3e). The crude product was purified by column chromatography (cyclohexane/methyl chloride 8:2) yielding **3e** as a colourless oil, $n_D^{20}=-1.5107$; [Found: C, 67.48; H, 5.29 $C_{13}H_{12}O_4$ requires C, 67.24; H, 5.21%]; ν_{max} (KBr) 2942(w), 1731(s), 1622(w), 1594(m), 1577(m), 1492(s), 1325(w), 1302(m), 1272(m), 1227(w), 1185(s), 1094(s), 974(m), 779(m), 731(m) cm^{-1}; δ_H (80 MHz $CDCl_3$) 7.57–6.97 (4H, m, aromatic protons), 6.40–5.77 (1H, m, CH$_2$–C*H*=CH$_2$), 5.52–5.15(2H, m, CH–CH=C*H*$_2$), 4.88 (2H, dt, *J*=5.4, 1.2 Hz, C*H*$_2$–CH=CH$_2$), 4.02(3H, s, O*Me*); *m/z* (70 eV) 233 ((M+1)$^+$, 12), 232 (M$^+$, 85), 175 (100), 148 (18), 119 (12), 89(11%).

Allyl 6-diethylamino-2-benzo[b]furancarboxylate (3f). The crude product was purified by column chromatography (cyclohexane/methyl chloride 8:2) yielding **3f** as a red oil; $n_D^{20}=-1.6228$; [Found: C, 70.21; H, 7.02; N, 5.14 $C_{16}H_{19}NO_3$ requires C, 70.31; H, 7.01; N, 5.12%]; ν_{max}(KBr) 3086(w), 2973(m), 1719(s), 1626(s), 1577(w), 1554(m), 1510(s), 1356(m), 1304(m), 1270(s), 1240(s), 1175(s), 1121(s), 978(m), 793(m), 758(m) cm^{-1}; δ_H (80 MHz $CDCl_3$) 7.50–7.02 (2H, m, aromatic protons), 6.78–6.69 (2H, m, aromatic protons), 6.40–5.84 (1H, m, CH$_2$–C*H*=CH$_2$), 5.54–5.32 (2H, m, CH=C*H*$_2$), 4.84 (2H, dt, *J*=5.4, 1.3 Hz, C*H*$_2$–CH=CH$_2$), 3.41 (4H, q, *J*=7.0 Hz, C*H*$_2$–CH$_3$), 1.20 (6H, t, *J*=7.0 Hz, CH$_2$–*Me*); *m/z* (70 eV) 274 ((M+1)$^+$, 6.6), 273 (M$^+$, 37), 259 (17), 258 (100), 230 (7.7%).

Cyclohexyl 2-benzo[b]furancarboxylate (3g). The crude product was purified by column chromatography (cyclohexane/methyl chloride 8:3) yielding **3g** as a white solid, mp 70–71°C; [Found: C, 73.72; H, 6.70 $C_{15}H_{16}O_3$ requires C, 73.75; H, 6.60%]; ν_{max}(KBr) cm^{-1}; 2949(m), 2859(m), 1929(s), 1818(s), 1714(s), 1614(m), 1561(s), 1477(m), 1453(s), 1376(s), 1327(s), 1297(s), 1261(s), 1216(s), 1185(s), 1148(m), 1096(s), 1009(s), 954(m), 885(m), 834(m), 760(s) cm^{-1}; δ_H (80 MHz $CDCl_3$) 7.73–7.26 (5H, m, aromatic protons), 5.25–4.84 (1H, m, OC*H*), 2.20–0.95 (10H, m, (C*H*$_2$)$_5$-cyclohexyl); *m/z* (70 eV) 245 [(M+1)$^+$, 1.8%], 244 (M$^+$, 9.7), 163 (19), 162 (100), 89 (14%).

Cyclohexyl 7-methoxy-2-benzo[b]furancarboxylate (3h). The crude product was purified by column chromatography (cyclohexane/methyl chloride 8:2) yielding **3h** as a colourless oil, $n_D^{20}=-1.5551$; [Found: C, 69.68; H, 6.58 $C_{16}H_{18}O_4$ requires C, 70.06; H, 6.61%]; ν_{max}(KBr) 2938(s), 2860(s), 1727(s), 1622(w), 1595(m), 1578(m), 1492(s), 1453(m), 1325(m), 1299(s), 1272(m), 1229(w), 1190(s), 1095(s), 1013(m), 977(w), 956(m), 842(w), 780(m), 731(m) cm^{-1}; δ_H (80 MHz $CDCl_3$) 7.49–6.84 (4H, m, aromatic protons), 5.20–4.45 (1H, m, OC*H*), 4.02 (3H, s, O*Me*), 2.20–0.95 (10H, m, (C*H*$_2$)$_5$-cyclohexyl); *m/z* (70 eV) 275 ((M+1)$^+$, 5.5), 274 (M$^+$, 28), 193 (11), 192 (100), 177 (12), 175 (9.5%).

Cyclohexyl 6-diethylamino-2-benzo[b]furancarboxylate (3i). The crude product was purified by column chromatography (cyclohexane/methyl chloride 8:2) yielding **3i** as a red oil, $n_D^{20}=-1.6022$ [Found: C, 72.12; H, 7.65; N, 4.08 $C_{19}H_{25}NO_3$ requires C, 72.35; H, 7.99; N, 4.44%]; ν_{max}(KBr) 3086(w), 2970(m), 2937(s), 2861(m), 1715(s), 1627(s), 1577(m), 1556(m), 1510(s), 1450(m), 1356(m), 1324(m), 1301(m), 1270(s), 1240(s), 1179(s), 1120(s), 1093(w), 1013(m), 963(m), 842(w), 801(m), 793(m), 759(m) cm^{-1}; δ_H (80 MHz $CDCl_3$) 7.48–7.38 (2H, m aromatic protons), 6.76–6.67 (2H, m aromatic protons), 5.25–4.77 (1H, m, OC*H*), 3.40 (4H, k, *J*=7.0 Hz, 2×N-C*H*$_2$–CH$_3$), 2.15–0.85 (10H, m, (C*H*$_2$)$_5$-cyclohexyl), 1.28–1.19 (6H, t, *J*=7.0 Hz, –CH$_2$–*Me*); *m/z* (70 eV) 316 ((M+1)$^+$, 5.6), 315 (M$^+$, 26), 300 (7.5), 233 (16), 219 (13), 218 (100), 190 (7.7%).

Ethyl naphtho[2,1-b]furan-2-carboxylate (5a). The crude product was purified by column chromatography (cyclohexane/methyl chloride 8:3) yielding **5a** as a white solid, mp 85–88°C; [Found: C, 74.71; H, 5.24 $C_{15}H_{12}O_3$ requires C, 74.99; H, 5.03%;]; ν_{max}(KBr) 3086(w), 3060(w), 2987(m), 1728(s), 1586(m), 1552(s), 1367(m), 1326(s), 1281(m), 1224(m), 1172(s), 1124(m), 1020(s), 823(s), 803(m), 761(s), 743(m) cm^{-1}; δ_H (80 MHz $CDCl_3$) 8.23–7.59 (7H, m, aromatic protons), 4.62–4.35 (2H, q, *J*=7.1 Hz, C*H*$_2$–Me), 1.55–1.37 (3H, t, *J*=7.1 Hz, –CH$_2$–Me); *m/z* (70 eV) 241 ((M+1)$^+$, 16), 240 (M$^+$, 100), 213 (12), 212 (79), 196 (6.6), 195 (27), 168 (24), 139(52).

Allyl naphtho[2,1-b]furan-2-carboxylate (5b). The crude product was purified by column chromatography (cyclohexane/methyl chloride 8:3) yielding **5b** as a white solid, mp 72–74°C; [Found: C, 75.95; H, 4.88 $C_{16}H_{12}O_3$ requires C, 76.18; H, 4.79%;]; ν_{max}(KBr) 3084(w), 3051(w), 2932(w), 1731(s), 1646(w), 1585(m), 1554(w), 14529w),

1378(m), 1331(m), 1283(m), 1224(m), 1175(s), 1123(m), 914(s), 873(m), 830(s), 759(s), 751(s), 562(m) cm^{-1}; δ_H (80 MHz $CDCl_3$) 8.23–7.55 (7H, m, aromatic protons), 6.28–5.88 (1H, m, CH_2–C*H*═CH_2), 5.60–5.29 (2H, m, CH_2–CH═CH_2), 4.97–4.42(2H, m, CH_2–CH═CH_2); *m/z* (70 eV) 253 ($(M+1)^+$, 18), 252 (M^+, 100), 212 (9.8), 208 (8.8), 207 (9.0), 196 (13), 195 (86), 181(8.8), 168 (68), 139 (82%).

Cyclohexyl naphtho[2,1-b]furan-2-carboxylate (5c). The crude product was purified by column chromatography (cyclohexane/methyl chloride 8:3) yielding **5c** as a white solid, mp 134–136°C; [Found: C, 77.50; H, 6.16 $C_{19}H_{18}O_3$ requires C, 77.53; H, 6.16%;]; ν_{max}(KBr) 3106(m), 3050(w), 2933(s), 2857(s), 1713(s), 1627(w), 1589(m), 1562(w), 1450(m), 1354(m), 1307(m), 1320(m), 1283(s), 1237(s), 1170(s), 1116(s), 1014(s), 990(m), 960(m), 930(m), 881(m), 827(w), 807(s), 762(m), 741(m) cm^{-1}; δ_H (80 MHz $CDCl_3$) 8.02–7.54 (7H, m, aromatic protons), 5.25–4.95 (1H, m, OC*H*), 2.15–1.10 (10H, m, $(CH_2)_5$-cyclohexyl); *m/z* (70eV) 295 ($(M+1)^+$, 4.7), 294 (M^+, 21), 212 (100), 213 (15), 195 (9.0), 139 (21%).

Acknowledgements

This work was undertaken as part of the EU sponsored D10 COST Program (Innovative Methods and Techniques for Chemical Transformations).

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