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One-Pot Synthesis of *O*-Aryl Carbamates

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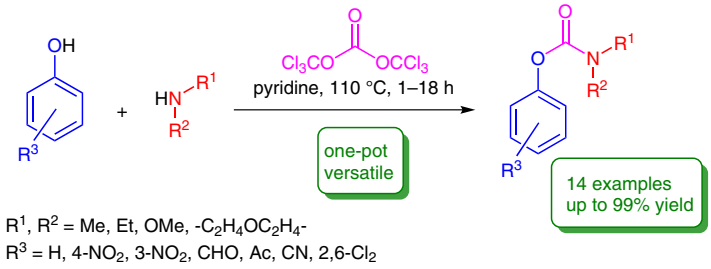

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Abstract A simple, versatile, one-pot procedure for the synthesis of substituted *O*-aryl carbamates has been developed, and a protocol is henceforth described. N-Substituted carbamoyl chloride is formed in situ and subsequently reacted with a substituted phenol, avoiding the direct manipulation of sensitive reactants. This procedure offers an economical and efficient route to many compounds of interest.

Key words *O*-aryl carbamates, phenyl carbamates, one-pot, versatile, safe, high yield

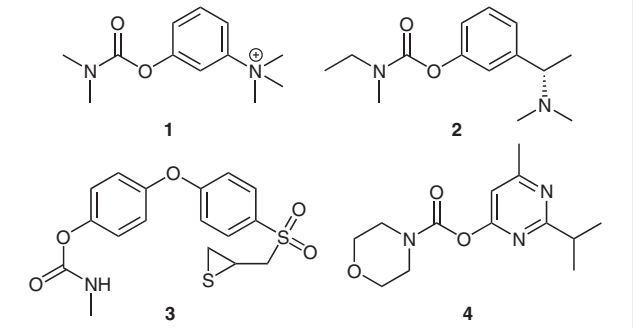


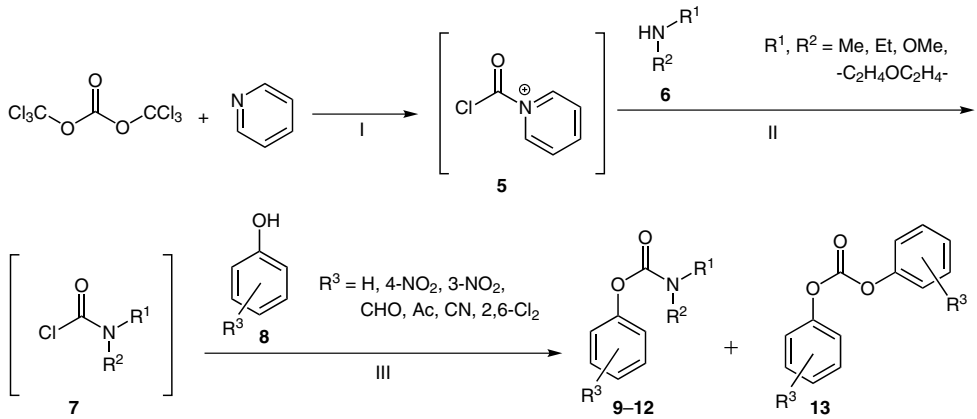
Figure 1 *O*-Aryl carbamate-containing active agents: acetylcholinesterase inhibitors neostigmine (**1**) and rivastigmine (**2**), matrix metalloproteinase-2 inhibitor **3**, and an antifungal agent **4**.

O-Aryl carbamates are an important class of molecules that have a wide range of uses. The pharmaceutical and medical industries have used them as acetylcholinesterase inhibitors for the treatment of debilitating neurodegenerative diseases such as Parkinsonism, myasthenia gravis, and Alzheimer's disease.[1–3] *O*-Aryl carbamates have also been investigated as potential prodrugs for antineoplastic and antifungal drugs (Figure 1).[4,5] Additionally, they have been effectively used as intermediates for the synthesis of a range of antiviral, anti-infective, and antineoplastic drugs in the form of semicarbazides.[6]

The agrochemical industry also has a use for *O*-aryl carbamates in the form of herbicides and insecticides, the difference being the substitution pattern on the *O*-aryl ring.[7] *O*-Aryl carbamates have also been used as synthetic intermediates for a variety of reactions using the carbamate functionality as a directing group (particularly for C–H activation at the *ortho*-position of the phenol) with lithium reagents,[8,9] and more recently rhodium,[10] ruthenium,[11] and palladium catalysts.[12] They have also proven to be effective reagents for nickel-catalyzed α-arylation of esters and amides, which can be further reacted to form α-arylcarboxylic acids and β-arylamines.[13]

An economical means of synthesizing *O*-aryl carbamates directly from the corresponding amine and phenol has not been realized.[6] Current methods include reaction of isolated carbamoyl chlorides with a substituted phenol,[11,12c,14] reaction of isolated aryl chloroformates with an amine,[10,15] or copper catalyzed oxidative cross-couplings of formamides and phenols.[16] These reactions are limited by the availability of aryl chloroformates and carbamoyl chlorides, as well as the highly reactive nature of these compounds. In this work, we communicate a simplified one-pot method for the generation of *O*-aryl carbamates directly from widely commercially available amines and phenols.

In situ formation of the carbamoyl chloride followed by the nucleophilic attack of the aryloxide ion to yield *O*-aryl carbamates in good yields allows for a wide variety of substituents on the *O*-aryl ring and the nitrogen on the amine making the synthesis quite versatile (Scheme 1).



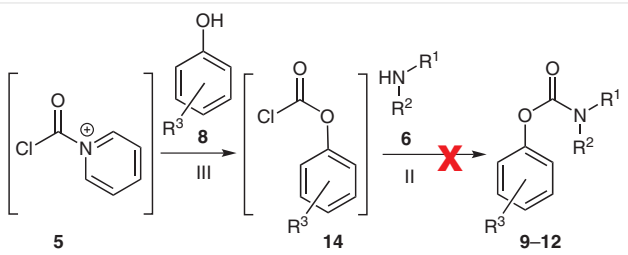
Scheme 1 Reaction route. *Reagents and conditions*: (I) CH_2Cl_2, 0 °C, 20 min; (II) 0 °C to r.t., 1 h; (III) pyridine, r.t. to 110 °C, 1–24 h.

The dropwise addition of pyridine to BTC [bis(trichloromethyl) carbonate, triphosgene] dissolved in dichloromethane, to form pyridiniumchlorocarbonyl chloride (**5**),[17] has to be cooled down to 0 °C in an ice bath as the reaction is highly exothermic and a rise in temperature will release excess amounts of toxic unreacted phosgene. For similar reasons, the selected amine **6** needs to be added in small portions whilst still cooled to 0 °C. After **6** has displaced pyridine to form the corresponding carbamoyl chloride **7**, dichloromethane and excess phosgene has to be removed under reduced pressure or the reaction will not proceed.

However, care must be taken in removing dichloromethane as extended periods under reduced pressure will remove **7**, and hence lower yields significantly.

The selected phenol **8** is dissolved in pyridine and subsequently added to **7** and left to stir for a period of time varying from one hour to one day. Even though the reaction proceeds at ambient temperature for most of the compounds, running the reaction at 110 °C generally gives higher yields and shortens the generalized reaction time to under six hours.[18] After workup, the *O*-aryl carbamates **9**–**12** (Table 1) can be easily purified via column chromatography or recrystallization.

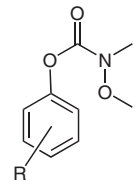
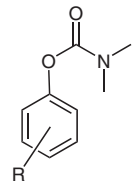
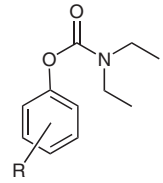
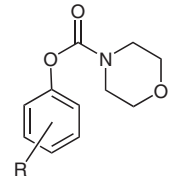
It has been observed that the reaction does not proceed if attempted in 'reverse', that is, the in situ formation of the phenyl chloroformate (**14**) before the addition of **6** (Scheme 2).



Scheme 2 Formation of aryl chloroformate followed by addition of an amine is unsuccessful at forming desired *O*-aryl carbamates

An increase in the acidity of the phenol generally results in higher yields, as noted in comparing **9d** to **9a**, and **11c** to **11b**. This suggests that the rate is dependent on the depro-

Table 1 Reaction Scope

No.	Structure	R	Yield (%)[a]
9		**a**: H **b**: 4-Ac **c**: 3-NO_2 **d**: 4-NO_2 **e**: 2,6-Cl_2	70[b] 87[b] 76[b] 99[b] 88
10		**a**: 4-CHO **b**: 4-Ac **c**: 4-NO_2	96 92 81
11		**a**: 2,6-Cl_2 **b**: 4-Ac **c**: 4-NO_2	99 84 99
12		**a**: 4-CHO **b**: 4-Ac **c**: 4-CN	88 92 98

[a] Isolated yields.
[b] Reactions run at r.t..

tonation of **8** by pyridine to give the more nucleophilic phenoxide ion, which goes on to attack **7**. In an effort to increase yield, the more basic triethylamine was used in place of pyridine; unfortunately this reaction did not proceed even with heating, resulting only in the generation of side-product **13**.

There seems to be no significant correlation between the identity of **6** and the overall yield of **9**–**12**. Recent related work showed similar results,[19] indicating that the *N*,*N*-dialkyl substituents on **7** do not have a significant effect on this reaction.

In summary, we have developed a versatile one-pot synthesis of *O*-aryl carbamates with a large scope of substituents providing high yields. This method is viable for a range of both phenols and disubstituted amines and does not require the isolation or handling of sensitive intermediates.

Chemicals were obtained from Sigma-Aldrich and Fisher Scientific. Column chromatography was performed using silica gel from Macherey-Nagel (60 M, 0.04–0.063 mm). ^{1}H and ^{13}C NMR data were recorded in $CDCl_3$ on either a 300 or 500 MHz Bruker Avance III spectrometer at r.t. Chemical shifts are reported relative to residual $CHCl_3$ (δ = 7.24 for ^{1}H, δ = 77.23 for ^{13}C). IR data were acquired using an ATI Mattson FTIR spectrophotometer on neat samples. MS data were obtained with a Shimadzu GCMS QC2010S spectrometer at 275 °C.

O-Aryl Carbamates; General Procedure

To an oven-dried, argon-flushed 100 mL round-bottom flask was added BTC (1.5 mmol) and CH_2Cl_2 (7.5 mL) at 0 °C, and the mixture was stirred for 5 min. Pyridine (15 mmol) was added dropwise to form a pale yellow precipitate **5**, which redissolved after 20 min of continuous stirring. The selected amine **6** (1.6 mmol) was added in small portions and the mixture resulted in a red solution. This was then left to stir for 1 h at r.t. at which time the solution turned yellow. CH_2Cl_2 was removed under reduced pressure to give a sludge **7**. The selected phenol **8** (1.5 mmol) was dissolved in pyridine (2.5 mL) and added to the sludge. The reaction mixture was then heated at 110 °C and followed by TLC/GC-MS until completion (1–18 h). The reaction was quenched with EtOAc (25 mL) and washed with aq 6 M HCl (2 × 50 mL). The organic layer was dried (Na_2SO_4) and the EtOAc removed under reduced pressure to give a crude product **9**–**12** either as an oil or a solid, which can then be purified by via column chromatography (9:1 hexanes–EtOAc) or recrystallization from hot heptanes.

Phenyl Methoxy(methyl)carbamate (9a)

Yield: 0.420 g (2.31 mmol, 70%); clear oil; R_f = 0.2 (9:1 hexanes–EtOAc).

IR (ATR): 1721, 1592, 1494, 1458, 1409, 1367, 1206, 1181, 1164, 1121, 1027, 962, 909, 838, 747, 689, 633, 600 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.40 (m, 2 H), 7.25 (tt, *J* = 1, 7.5 Hz, 1 H), 7.18 (m, 2 H), 3.84 (s, 3 H), 3.32 (s, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 155.2, 150.9, 129.4, 125.7, 121.6, 61.8, 35.7.

MS (ESI): *m*/*z* = 181 [M]$^+$.

4-Acetylphenyl Methoxy(methyl)carbamate (9b)

Yield: 0.584 g (1.305 mmol, 87%); clear oil; R_f = 0.2 (3:1 hexanes–EtOAc).

IR (ATR): 1725, 1681, 1599, 1408, 1357, 1301, 1264, 1216, 1164, 1120, 1015, 958, 867 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.01 (d, *J* = 9 Hz, 2 H), 7.28 (d, *J* = 9 Hz, 2 H), 3.83 (s, 3 H), 3.32 (s, 3 H), 2.62 (s, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 196.9, 154.6, 154.3, 134.5, 129.9, 121.7, 61.9, 35.6, 26.6.

MS (ESI): *m*/*z* = 223 [M]$^+$.

3-Nitrophenyl Methoxy(methyl)carbamate (9c)

Yield: 0.257 g (1.14 mmol, 76%); clear oil; R_f = 0.1 (3:1 hexanes–EtOAc).

IR (ATR): 1726, 1526, 1472, 1442, 1410, 1347, 1276, 1219, 1182, 1121, 1024, 816, 735 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.14 (dt, *J* = 1.5, 7.5 Hz, 1 H), 8.09 (t, *J* = 1.5 Hz, 1 H), 7.59 (t, *J* = 8 Hz, 1 H), 7.56 (dt, *J* = 1.5, 8.5 Hz, 1 H), 3.85 (s, 3 H), 3.35 (s, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ =154.0, 151.3, 148.8, 129.9, 128.1, 120.6, 117.4, 61.9, 35.6.

MS (ESI): *m*/*z* = 226 [M]$^+$.

4-Nitrophenyl Methoxy(methyl)carbamate (9d)

Yield: 0.681 g (3.0 mmol, 99%); white solid; mp 84–85 °C (heptanes); R_f = 0.1 (3:1 hexanes–EtOAc).

IR (ATR): 1725, 1612, 1594, 1512, 1468, 1438, 1397, 1343, 1237, 1154, 1109, 1018, 964, 862 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.29 (d, *J* = 15 Hz, 2 H), 7.37 (d, *J* = 15 Hz, 2 H), 3.84 (s, 3 H), 3.34 (s, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 155.7, 153.6, 145.1, 125.2, 122.2, 61.9, 35.6.

MS (ESI): *m*/*z* = 226 [M]$^+$.

2,6-Dichlorophenyl Methoxy(methyl)carbamate (9e)

Yield: 0.0330 g (0.132 mmol, 88%); clear oil; R_f = 0.3 (9:1 hexanes–EtOAc).

IR (ATR): 1734, 1575, 1444, 1408, 1373, 1237, 1183, 1117, 1100, 1069, 1039, 1017, 956, 849, 834, 788, 773, 734, 712, 652, 610 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.38 (d, *J* = 8.5 Hz, 2 H), 7.16 (dd, *J* = 7.5, 8.5 Hz, 1 H), 3.88 (s, 3 H), 3.37 (s, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 152.5, 143.9, 129.4, 128.6, 127.1, 61.9, 35.6.

MS (ESI): *m*/*z* (%) = 249 (100), 251 (64, [M]$^+$).

4-Formylphenyl Dimethylcarbamate (10a)

Yield: 0.0278 g (0.144 mmol, 96%); pale yellow oil; R_f = 0.3 (3:1 hexanes–EtOAc).

IR (ATR): 2251, 1719, 1696, 1601, 1486, 1446, 1386, 1300, 1212, 1153, 1065, 1011, 912, 859, 795, 728, 648 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 9.99 (s, 1 H), 7.91 (d, *J* = 8.5 Hz, 2 H), 7.32 (d, *J* = 8.5 Hz, 2 H), 3.13 (s, 3 H), 3.05 (s, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 191.0, 156.4, 153.9, 133.4, 131.1, 122.3, 36.8, 36.5.

MS (ESI): *m*/*z* = 193 [M]$^+$.

4-Acetylphenyl Dimethylcarbamate (10b)

Yield: 0.0286 g (0.138 mmol, 92%); white solid; mp 48–50 °C (heptanes); R_f = 0.2 (3:1 hexanes–EtOAc).

IR (ATR): 1722, 1673, 1597, 1502, 1446, 1410, 1388, 1356, 1267, 1208, 1163, 1116, 1058, 1009, 958, 875, 807, 752, 587 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.99 (d, *J* = 8.5 Hz, 2 H), 7.24 (d, *J* = 8.5 Hz, 2 H), 3.13 (s, 3 H), 3.05 (s, 3 H), 2.61 (s, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 196.9, 155.3, 154.1, 134.1, 129.8, 121.7, 36.8, 36.5, 26.6.

MS (ESI): *m*/*z* = 207 $[M]^+$.

4-Nitrophenyl Dimethylcarbamate (10c)

Yield: 0.255 g (1.22 mmol, 81%); white solid; mp 43–44 °C (heptanes); R_f = 0.1 (3:1 hexanes–EtOAc).

IR (ATR): 1699, 1612, 1593, 1519, 1447, 1394, 1336, 1282, 1217, 1159, 1109, 1059, 1007, 864, 745 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.27 (d, *J* = 9 Hz, 2 H), 7.33 (d, *J* = 9 Hz, 2 H), 3.15 (s, 3 H), 3.07 (s, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 156.4, 153.5, 144.8, 125.6, 125.2, 36.8, 26.6.

MS (ESI): *m*/*z* = 210 $[M]^+$.

2,6-Dichlorophenyl Diethylcarbamate (11a)

Yield: 0.0389 g (0.148 mmol, 99%); clear oil; R_f = 0.4 (9:1 hexanes–EtOAc).

IR (ATR): 1727, 1574, 1444, 1414, 1381, 1314, 1272, 1237, 1218, 1147, 1097, 1069, 1035, 952, 936, 786, 771, 746, 707 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.35 (d, *J* = 8.0 Hz, 2 H), 7.11 (t, *J* = 8.0 Hz, 1 H), 3.53 (q, *J* = 7.0 Hz, 2 H), 3.43 (q, *J* = 7.0 Hz, 2 H), 1.35 (t, *J* = 7.0 Hz, 3 H), 1.24 (t, *J* = 7.0 Hz, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 151.8, 144.7, 129.7, 128.5, 126.5, 42.7, 42.3, 14.2, 13.3.

MS (ESI): *m*/*z* (%) = 261 (100), 263 (64, $[M]^+$).

4-Acetylphenyl Diethylcarbamate (11b)

Yield: 0.0296 g (0.126 mmol, 84%); clear oil; R_f = 0.4 (3:1 hexanes–EtOAc).

IR (ATR): 1716, 1681, 1599, 1506, 1473, 1417, 1359, 1264, 1206, 1149, 1098, 1077, 1039, 1014, 956, 864, 807, 781, 752, 589 cm^{-1}.

^{1}H NMR (500 MHz $CDCl_3$): δ = 7.99 (d, *J* = 8.5 Hz, 2 H), 7.25 (d, *J* = 8.5 Hz, 2 H), 3.47 (q, *J* = 7, 7.5 Hz, 2 H), 3.42 (q, *J* = 7, 7.5 Hz, 2 H), 2.62 (s, 3 H), 1.29 (t, *J* = 7 Hz, 3 H), 1.24 (t, *J* = 7 Hz, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 197.0, 155.4, 153.4, 133.9, 129.8, 121.7, 42.4, 42.0, 26.6, 14.3, 13.3.

MS (ESI): *m*/*z* = 235 $[M]^+$.

4-Nitrophenyl Diethylcarbamate (11c)

Yield: 0.0354 g (0.149 mmol, 99%); clear oil; R_f = 0.3 (3:1 hexanes–EtOAc).

IR (ATR): 2977, 1719, 1613, 1594, 1519, 1473, 1418, 1343, 1272, 1229, 1208, 1146, 1098, 1083, 956, 861, 817, 783, 745, 688, 664 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.27 (d, *J* = 9 Hz, 2 H), 7.33 (d, *J* = 9 Hz, 2 H), 3.47 (q, *J* = 7, 7.5 Hz, 2 H), 3.42 (q, *J* = 7, 7.5 Hz, 2 H), 1.29 (t, *J* = 7 Hz, 3 H), 1.26 (t, *J* = 7 Hz, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 156.5, 152.8, 144.7, 125.0, 122.2, 42.5, 42.1, 14.26, 13.27.

MS (ESI): *m*/*z* = 238 $[M]^+$.

4-Formylphenyl 4-Morpholinecarboxylate (12a)

Yield: 0.0311 g (0.132 mmol, 88%); pale yellow solid; mp 56–58 °C (heptanes); R_f = 0.2 (3:1 hexanes–EtOAc).

IR (ATR): 1713, 1688, 1599, 1459, 1417, 1364, 1304, 1280, 1207, 1157, 1111, 1062, 994, 915, 859, 848, 806, 794, 647, 614, 573 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 10.01 (s, 1 H), 7.94 (d, *J* = 8.5 Hz, 2 H), 7.33 (d, *J* = 8.5 Hz, 2 H), 3.79 (t, *J* = 4.5 Hz, 4 H), 3.72 (br, 2 H), 3.61 (br, 2 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 190.9, 156.0, 152.7, 133.6, 131.2, 122.3, 66.6, 66.5, 44.9, 44.2.

MS (ESI): *m*/*z* = 235 $[M]^+$.

4-Acetylphenyl 4-Morpholinecarboxylate (12b)

Yield: 0.0344 g (0.138 mmol, 92%); pale yellow oil; R_f = 0.1 (3:1 hexanes–EtOAc).

IR (ATR): 1718, 1681, 1599, 1505, 1409, 1359, 1301, 1266, 1203, 1164, 1114, 1057, 1014, 989, 959, 855, 802, 749, 589 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.01 (d, *J* = 9 Hz, 2 H), 7.24 (d, *J* = 9 Hz, 2 H), 3.78 (t, *J* = 5 Hz, 4 H), 3.71 (br, 2 H), 3.61 (br, 2 H), 2.62 (s, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 196.9, 154.9, 152.9, 134.3, 129.9, 121.7, 66.6, 66.5, 44.9, 44.2, 26.6.

MS (ESI): *m*/*z* = 249 $[M]^+$.

4-Cyanophenyl 4-Morpholinecarboxylate (12c)

Yield: 0.0341 g (0.147 mmol, 98%); white solid; mp 132–134 °C (heptanes); R_f = 0.2 (3:1 hexanes–EtOAc).

IR (ATR): 2852, 2229, 1709, 1602, 1501, 1446, 1416, 1279, 1245, 1205, 1164, 1116, 1057, 1015, 990, 881, 855, 803, 749, 554 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.69 (d, *J* = 9 Hz, 2 H), 7.27 (d, *J* = 9 Hz, 2 H), 3.77 (t, *J* = 4.5 Hz, 4 H), 3.68 (br, 2 H), 3.59 (br, 2 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 154.6, 152.4, 133.6, 122.6, 118.3, 109.2, 66.4, 44.9, 44.2.

MS (ESI): *m*/*z* = 232 $[M]^+$.

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