Improving the Scratch Resistance of Sol-Gel Coatings Through Use of a Novel Low-Temperature Curing Process Involving Thermogenerated Amines

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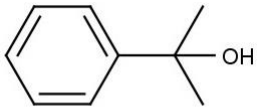
2-Phenyl-2-propanol (**3a**):

3a was synthesised according to F. Galaud, W. D. Lubell, *Biopolymers*, 2005, **80**, 665-674 (Y = 70 %, 2.54 g).



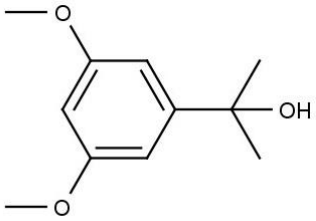
3a

^{1}H-NMR (300 MHz, $CDCl_3$): δ= 7.34 (2H, d, ^{3}J = 7.6 Hz, ortho-CH), 7.19 (2H, t, ^{3}J = 7.6 Hz, meta-CH), 7.09 (1H, d, ^{3}J = 7.6 Hz, para-CH), 2.35 (br s, OH), 1.36 (6H, s, CH_3) ppm.

^{13}C-NMR (75 MHz, $CDCl_3$): δ= 149.3 (ipso-C), 128.3 (meta-CH), 126.7 (ortho-CH), 124.6 (para-CH), 72.6 (C), 31.8 (CH_3) ppm.

2-(3,5-Dimethoxyphenyl)propan-2-ol (**3b**):

3b was synthesised according to N.-Y. Shih, P. Mangiaracina, M. J. Green, A. K. Ganguly, *Tetrahedron Lett.*, 1989, **30**, 5563-5566 (Y = 93 %, 4.87 g).



3b

^{1}H-NMR (300 MHz, $CDCl_3$): δ= 6.60 (2H, d, ^{4}J = 2.2 Hz, ortho-CH), 6.29 (1H, t, ^{4}J = 2.2 Hz, para-CH), 3.77 (6H, s, OCH_3), 1.57 (br s, OH), 1.51 (6H, s, CH_3) ppm.

^{13}C-NMR (75 MHz, $CDCl_3$): δ= 160.6 (meta-C), 151.9 (ipso-C), 102.8 (ortho-CH), 98.2 (para-CH), 72.4 (C), 55.2 (OCH_3), 31.5 (CH_3) ppm.

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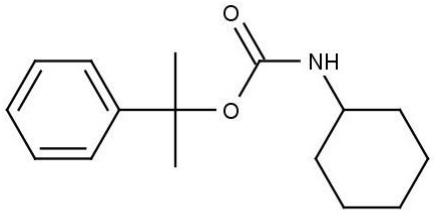
2-Phenylpropan-2-yl N-cyclohexylcarbamate (**5a**):

3a (1.31 g, 9.60 mmol), isocyanatocyclohexane (**4a**, 1.20 g, 9.60 mmol) and dibutyltin dilaureate (**DBTDL**, 0.075 mL, 95 %, 0.1 mmol) were dissolved in 35 mL dry Et_2O and brought to reflux for 24 h. After removing all volatiles under reduced pressure, the crude product was purified *via* flash column chromatography (stationary phase: Merck silica gel 60, eluent: DCM). The pure carbamate **5a** (R_f = 0.49) was obtained in 68 % yield (1.69 g, 6.48 mmol).



5a

^{1}H-NMR (300 MHz, $CDCl_3$): δ□= 7.46-7.20 (5H, m, Ar-H), 4.64 (br s, NH), 3.53-3.33 (1H, m, CH), 2.12-0.99 (10H, m, CH_2), 1.76 (6H, s, CH_3) ppm.

^{13}C-NMR (75 MHz, $CDCl_3$): δ□= 154.6 (C=O), 146.8 (ipso-C), 128.2 (meta-CH), 126.8 (ortho-CH), 124.3 (para-CH), 80.5 (C), 49.6 (CH), 33.6 (CH_2), 29.1 (CH_3), 25.6 (CH_2), 24.9 (CH_2) ppm.

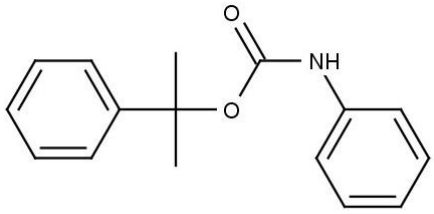
IR: ν_{max} = 3296 (m, N-H), 1676 (s, C=O) cm^{-1}.

MS (EI, 70 eV): 261.3 (M^+), 119.1 m/z.

DSC (40-300 °C, 10 °C · min^{-1}): T_m = 113.3 °C, T_d = 168.3 °C.

2-Phenylpropan-2-yl N-phenylcarbamate (**5b**):

3a (1.06 g, 7.81 mmol), phenylisocyanate (**4b**, 0.93 g, 7.81 mmol) and **DBTDL** (0.05 mL, 95 %, 0.08 mmol) were dissolved in 50 mL dry Et_2O and brought to reflux for 21 h. After removing all volatiles under reduced pressure, the crude product was purified *via* flash column chromatography (stationary phase: Merck silica gel 60, eluent: DCM). The pure carbamate **5b** (R_f = 0.90) was obtained in 32 % yield (0.65 g, 2.53 mmol).



5b

^{1}H-NMR (300 MHz, $CDCl_3$): δ□= 7.36-7.10 (9H, m, Ar-H), 6.91 (1H, t, ^3J = 7.4 Hz, Ar-H), 6.62 (br s, NH), 1.75 (6H, s, CH_3) ppm.

^{13}C-NMR (75 MHz, $CDCl_3$): δ□= 152.1 (C=O), 146.0 (ipso-C), 138.2 (ipso-C), 129.0 (Ar-CH), 128.4 (Ar-CH), 127.1 (Ar-CH), 124.4 (Ar-CH), 123.2 (Ar-CH), 118.6 (Ar-CH), 81.8 (C), 29.0 (CH_3) ppm.

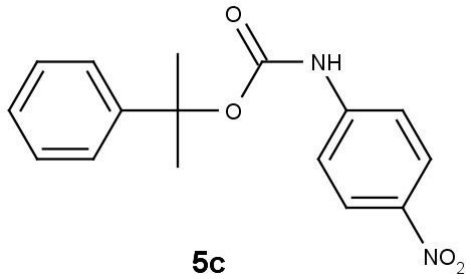
IR: ν_{max} = 3313 (m, N-H), 1699 (s, C=O) cm^{-1}.

MS (EI, 70 eV): 255.2 (M^+), 119.1, 93.0 m/z.

DSC (40-300 °C, 10 °C · min^{-1}): T_m = 106.1 °C, T_d = 161.9 °C.

2-Phenylpropan-2-yl N-(4-nitrophenyl)carbamate (**5c**):

3a (0.95 g, 7.01 mmol), 4-nitrophenylisocyanate (**4c**, 1.15 g, 7.01 mmol) and **DBTDL** (0.075 mL, 95 %, 0.12 mmol) were dissolved in 40 mL dry Et_2O and brought to reflux for 66 h. After removing all volatiles under reduced pressure, the crude product was purified *via* flash column chromatography (stationary phase: Merck silica gel 60, eluent: DCM). The pure carbamate **5c** (R_f = 0.57) was obtained in 86 % yield (1.81 g, 6.02 mmol).



5c

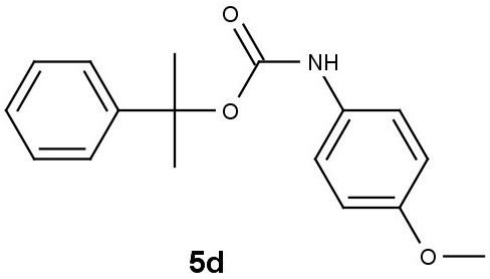
^{1}H-NMR (300 MHz, $CDCl_3$): δ□= 8.06 (2H, m, Ar-H), 7.42-7.17 (7H, m, Ar-H), 7.03 (br s, NH), 1.78 (6H, s, CH_3) ppm.

^{13}C-NMR (75 MHz, $CDCl_3$): δ□= 151.3 (C=O), 145.2 (ipso-C), 144.3 (para-C), 142.8 (ipso-C), 128.5 (meta-CH), 127.5 (ortho-CH), 125.2 (para-CH), 124.3 (meta-CH), 117.6 (ortho-CH), 80.1 (C), 28.9 (CH_3) ppm.

DSC (40-300 °C, 10 °C · min^{-1}): T_m = 147.6 °C, T_d = 155.5 °C.

2-Phenylpropan-2-yl N-(4-methoxyphenyl)carbamate (**5d**):

3a (1.16 g, 8.52 mmol), 4-methoxyphenylisocyanate (**4d**, 1.27 g, 8.52 mmol) and **DBTDL** (0.075 mL, 95 %, 0.12 mmol) were dissolved in 50 mL dry Et_2O and brought to reflux for 66 h. After removing all volatiles under reduced pressure, the crude product was purified *via* flash column chromatography (stationary phase: Merck silica gel 60, eluent: DCM). The pure carbamate **5d** (R_f = 0.54) was obtained in 79 % yield (1.85 g, 6.49 mmol).



5d

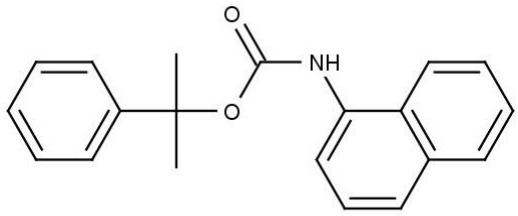
^{1}H-NMR (300 MHz, $CDCl_3$): δ□= 7.48-7.23 (7H, m, Ar-H), 6.84 (2H, d, ^{3}J = 8.8 Hz, Ar-H), 6.56 (br s, NH), 3.79 (3H, s, OCH_3), 1.86 (6H, s, CH_3) ppm.

^{13}C-NMR (75 MHz, $CDCl_3$): δ□= 155.8 (para-C), 152.4 (C=O), 146.1 (ipso-C), 131.4 (ipso-C), 128.4 (meta-CH), 127.1 (ortho-CH), 124.4 (para-CH), 120.4 (ortho-CH), 114.3 (meta-CH), 81.6 (C), 55.6 (OCH_3) 29.1 (CH_3) ppm.

DSC (40-300 °C, 10 °C · min^{-1}): T_m = 101.5 °C, T_d = 178.8 °C.

2-Phenylpropan-2-yl N-(naphthalen-1-yl)carbamate (**5e**):

3a (1.39 g, 10.20 mmol), 2-naphthylisocyanate (**4e**, 1.72 g, 10.20 mmol) and **DBTDL** (0.05 mL, 95 %, 0.08 mmol) were dissolved in 50 mL dry Et_2O and brought to reflux for 21 h. After removing all volatiles under reduced pressure, the crude product was purified *via* flash column chromatography (stationary phase: Merck silica gel 60, eluent: DCM). The pure carbamate **5e** (R_f = 0.96) was obtained in 45 % yield (1.40 g, 4.58 mmol).



5e

^{1}H-NMR (300 MHz, $CDCl_3$): δ□= 7.84-7.69 (3H, m, Naph-H), 7.56-7.12 (9H, m, Naph-H + Ar-H), 6.93 (br s, NH), 1.80 (6H, s, CH_3) ppm.

^{13}C-NMR (75 MHz, $CDCl_3$): δ□= 152.9 (C=O), 146.0 (ipso-Ar-C), 134.1, 132.8 128.8, 128.4, 128.3, 127.1, 126.5, 126.1, 125,9, 125.9, 124.6, 124.4, 120.4, 82.0 (C), 29.1 (CH_3) ppm.

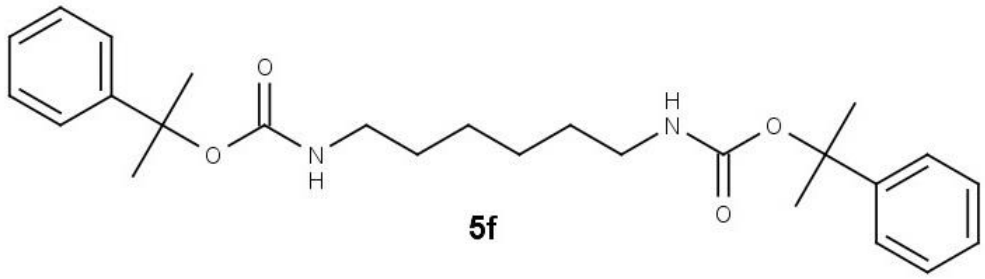
IR: ν_{max} = 3247 (m, N-H), 1689 (s, C=O) cm^{-1}.

MS (EI, 70 eV): 305.3 (M^+), 143.1, 119.1 m/z.

DSC (40-300 °C, 10 °C · min^{-1}): T_m = 135.7 °C, T_d = 174.1 °C.

2-Phenylpropan-2-yl N-[6-({[(2-phenylpropan-2-yl)oxy]carbonyl}amino)hexyl]carbamate (**5f**):

3a (1.64 g, 12.04 mmol), 1,6-diisocyanatohexane (**4f**, 1.01 g, 6.02 mmol) and **DBTDL** (0.1 mL, 95 %, 0.17 mmol) were dissolved in 50 mL dry Et_2O and brought to reflux for 66 h. After removing all volatiles under reduced pressure, the crude product was washed with a few mL *n*-hexane and recrystallised from a DCM/*n*-pentane (1:1) mixture. The dry and pure carbamate **5f** was obtained in 65 % yield (1.72 g, 3.91 mmol).



5f

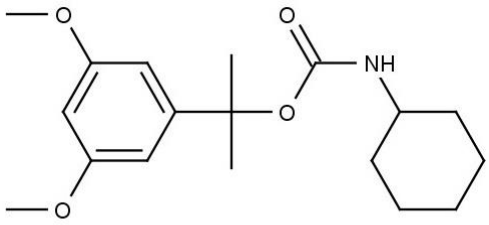
^{1}H-NMR (300 MHz, $CDCl_3$): δ□= 7.33-7.09 (10H, m, Ar-H), 4.70 (2H, br s, NH), 3.04-2.90 (4H, , m, N-CH_2-), 1.69 (12H, s, CH_3), 1.40-1.26 (4H, m, NCH_2-CH_2-), 1.25-1.12 (4H, m, $N(CH_2)_2$-CH_2-) ppm.

^{13}C-NMR (75 MHz, $CDCl_3$): δ□= 155.3 (C=O), 149.3 (ipso-C), 127.5 (meta-CH), 103.1 (ortho-CH), 98.2 (para-CH) , 80.4 (C), 55.3 (N-CH_2-), 29.1 (CH_3), 21.0 (NCH_2-CH_2-), 14.3 ($N(CH_2)_2$-CH_2-) ppm.

DSC (40-300 °C, 10 °C · min^{-1}): T_m = 178.3 °C, T_d = 212.8 °C.

2-(3,5-Dimethoxyphenyl)propan-2-yl N-cyclohexylcarbamate (**6a**):

3b (1.14 g, 5.83 mmol) and 0.02 g fresh Li wire (≈ 50 mol%) were added to 10 mL Et_2O and refluxed for 0.5 h. After the slow addition of **4a** (0.73 g, 5.83 mmol), the resulting mixture was brought to reflux for additional 3 h. After removing all volatiles under reduced pressure, the crude product was purified *via* flash column chromatography (stationary phase: Merck silica gel 60, eluent: *n*-hexane/ethylacetate (85:15)). The pure carbamate **6a** (R_f = 0.45) was obtained in 53 % yield (1.00 g, 3.10 mmol).



6a

^{1}H-NMR (300 MHz, $CDCl_3$): δ□= 6.44 (2H, d, 4J = 2.2 Hz, ortho-CH), 6.27 (1H, t, 4J = 2.2 Hz, para-CH), 4.53 (br s, NH), 3.71 (6H, s, OCH_3), 3.41-3.25 (1H, m, CH), 2.00-0.94 (16H, m, CH_3 + CH_2) ppm.

^{13}C-NMR (75 MHz, $CDCl_3$): δ□= 160.7 (meta-C), 154.4 (C=O), 149.5 (ipso-C), 102.9 (ortho-CH), 98.3 (para-CH), 80.4 (C), 55.3 (OCH_3), 49.6 (CH), 33.6 (CH_2), 29.2 (CH_3), 25.6 (CH_2), 24.9 (CH_2) ppm.

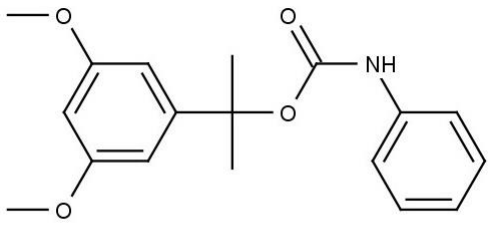
IR: ν_{max} = 3351 (m, N-H), 2854 (m, OCH_3), 1708 (s, C=O) cm^{-1}.

MS (EI, 70 eV): 321.3 (M^+), 196.2, 178.2, 99.1 m/z.

DSC (40-300 °C, 10 °C · min^{-1}): T_m = 89.8 °C, T_d = 212.1 °C.

2-(3,5-Dimethoxyphenyl)propan-2-yl N-phenylcarbamate (**6b**):

3b (0.79 g, 4.03 mmol), **4b (**0.46 g, 3.83 mmol) and **DBTDL** (0.05 mL, 95 %, 0.08 mmol) were dissolved in 10 mL dry Et_2O and brought to reflux for 5 h. After removing all volatiles under reduced pressure, the crude product was purified *via* flash column chromatography (stationary phase: Merck silica gel 60, eluent: DCM). The pure carbamate **6b** (R_f = 0.40) was obtained in 44 % yield (0.56 g, 1.78 mmol).



6b

^{1}H-NMR (300 MHz, $CDCl_3$): δ= 7.27 (2H, d, ^{3}J = 7.5 Hz, ortho-CH), 7.18 (2H, t, ^{3}J = 7.5 Hz), 6.94 (1H, t, ^{3}J = 7.5 Hz, para-CH), 6.58 (br s, NH), 6.49 (2H, d, ^{4}J = 2.2 Hz, ortho-CH), 6.28 (1H, t ^{4}J = 2.2 Hz, para-CH), 3.71 (6H, s, OCH_3), 1.73 (6H, s, CH_3) ppm.

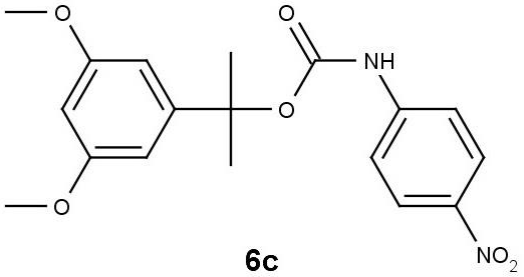
^{13}C-NMR (75 MHz, $CDCl_3$): δ= 160.8 (meta-C), 151.9 (C=O), 148.7 (ipso-C), 138.1 (ipso-C), 129.2 (meta-CH), 123.3 (para-CH), 118.5 (ortho-CH), 103.2 (ortho-CH), 98.3 (meta-CH), 81.7 (C), 55.4 (OCH_3), 29.0 (CH_3) ppm.

MS (EI, 70 eV): 315.2 (M^+), 271.2, 178.1, 93.0 m/z.

DSC (40-300 °C, 10 °C · min^{-1}): T_m = 136.3 °C, T_d = 177.4 °C.

2-(3,5-Dimethoxyphenyl)propan-2-yl N-(4-nitrophenyl)carbamate (**6c**):

3b (0.55 g, 2.80 mmol), **4c** (0.46 g, 2.80 mmol) and **DBTDL** (0.1 mL, 95 %, 0.17 mmol) were dissolved in 40 mL dry Et_2O, brought to reflux for 66 h and, again, stirred for additional 48 h. After removing all volatiles under reduced pressure, the crude product was purified *via* flash column chromatography (stationary phase: Merck silica gel 60, eluent: DCM). The pure carbamate **6c** (R_f = 0.88) was obtained in 88 % yield (0.88 g, 2.45 mmol).



6c

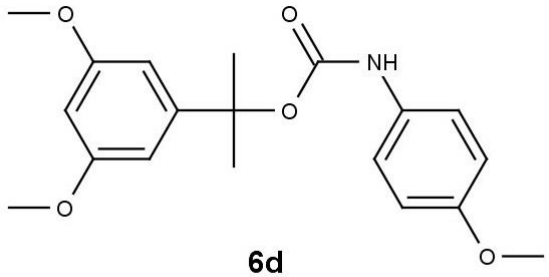
^{1}H-NMR (300 MHz, $CDCl_3$): δ= 8.11-8.05 (2H, m, Ar-H), 7.46-7.39 (2H, m, Ar-H), 6.93 (br s, NH), 6,47 (2H, d, ^{4}J = 2.2 Hz, ortho-CH), 6.31 (1H, t, ^{4}J = 2.2 Hz, para-CH), 3.72 (6H, OCH_3), 1,75 (6H. S, CH3) ppm.

^{13}C-NMR (75 MHz, $CDCl_3$): δ= 160.9 (meta-C), 151.3 (C=O), 148.0 (ipso-C), 144.3 (para-C), 142.9 (ipso-C), 125.3 (meta-CH), 117.7 (ortho-CH), 103.3 (ortho-CH), 98.3 (para-CH), 83.0 (C), 55.3 (OCH_3), 28.9 (CH_3) ppm.

DSC (40-300 °C, 10 °C · min^{-1}): T_m = 116.9 °C, T_d = 143.8 °C.

2-(3,5-Dimethoxyphenyl)propan-2-yl N-(4-methoxyphenyl)carbamate (**6d**):

3b (0.87 g, 4.42 mmol), **4d** (0.66 g, 4.42 mmol) and **DBTDL** (0.075 mL, 95 %, 0.12 mmol) were dissolved in 40 mL dry Et_2O and brought to reflux for 66 h. After removing all volatiles under reduced pressure, the crude product was purified *via* flash column chromatography (stationary phase: Merck silica gel 60, eluent: DCM). The pure carbamate **6d** was obtained in 54 % yield (0.82 g, 2.37 mmol).



6d

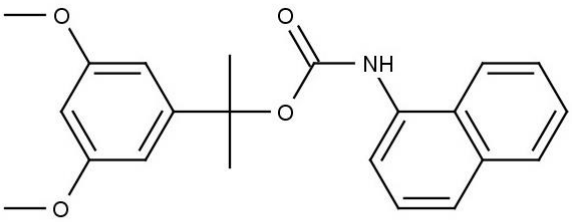
^{1}H-NMR (300 MHz, $CDCl_3$): δ□= 7.24-7.13 (2H, m, ortho-CH), 6.82-6.69 (2H, m, meta-CH), 6.44 (2H, d, ^4J = 2.2 Hz, ortho-CH), 6.27 (1H, t, 4J = 2.2 Hz, para-CH), 4.14 (br s, NH), 3.71 (6H, s, OCH_3), 3.69 (3H, s, OCH_3), 1.72 (6H, s, CH_3) ppm.

^{13}C-NMR (75 MHz, $CDCl_3$): δ□= 160.7 (meta-C), 157.6 (para-C), 155.8 (C=O), 148.8 (ipso-C), 131.2 (ipso-C), 120.5 (ortho-CH), 103.1 (ortho-CH), 98.3 (para-CH), 81.4 (C), 55.5 (OCH_3), 55.3 (OCH_3), 28.9 (CH_3) ppm.

DSC (40-300 °C, 10 °C · min^{-1}): T_m = 102.2 °C, T_d = 185.9 °C.

2-(3,5-Dimethoxyphenyl)propan-2-yl N-(naphthalen-1-yl)carbamate (**6e**):

3b (2.05 g, 10.45 mmol), **4e** (1.77 g, 10.45 mmol) and **DBTDL** (0.075 mL, 95 %, 0.1 mmol) were dissolved in 20 mL dry Et_2O and brought to reflux for 6 h. After removing all volatiles under reduced pressure, the crude product was purified *via* flash column chromatography (stationary phase: Merck silica gel 60, eluent: DCM). The pure carbamate **5e** (R_f = 0.46) was obtained in 37 % yield (1.43 g, 3.91 mmol).



6e

^{1}H-NMR (300 MHz, $CDCl_3$): δ□= 7.86-7.69 (3H, m, Naph-H), 7.58-7.28 (4H, m, Naph-H), 6.92 (br s, NH), 6.51 (2H, d, ^4J = 2.0 Hz, ortho-Ar-CH), 6.29 (1H, t, ^4J = 2.0 Hz, para-Ar-CH), 3.69 (6H, s, OCH_3), 1.77 (6H, s, CH_3) ppm.

^{13}C-NMR (75 MHz, $CDCl_3$): δ□= 160.8 (meta-Ar-C), 154.1 (C=O), 152.8 (ipso-Ar-C), 148.7 (ipso-Naph-C), 134.1, 132.7 128.8, 126.1, 125.9, 125.8, 124.7, 120.4, 109,8, 103.1, 98.4, 82.0 (C), 55.3 (OCH_3), 29.0 (CH_3) ppm.

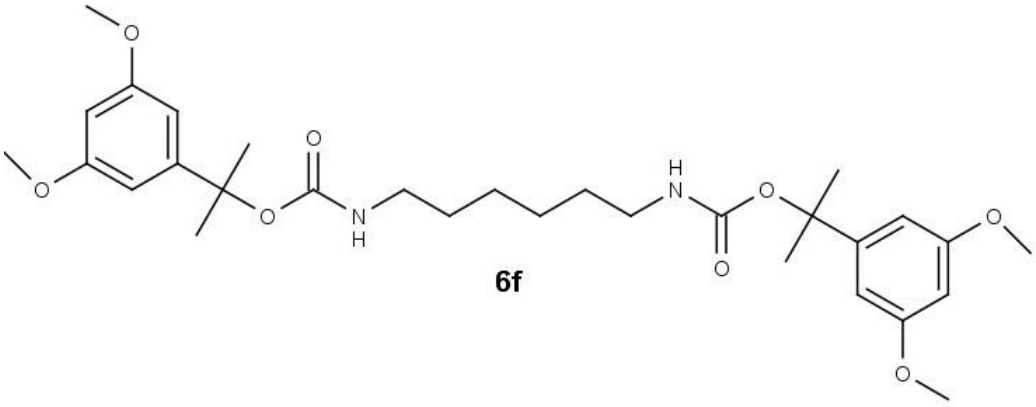
IR: ν_{max} = 3344 (m, N-H), 2838 (m, OCH_3), 1716 (s, C=O) cm^{-1}.

MS (EI, 70 eV): 365.3.3 (M^+), 321.3, 178.2, 143.1 m/z.

DSC (40-300 °C, 10 °C · min^{-1}): T_m = 104.5 °C, T_d = 185.1 °C.

2-(3,5-Dimethoxyphenyl)propan-2-yl N-{6-[({[2-(3,5-dimethoxyphenyl)propan-2-yl]oxy}carbonyl)amino]hexyl}carbamate (**6f**):

3b (2.75 g, 14.02 mmol), **4f** (1.18 g, 7.04 mmol) and **DBTDL** (0.1 mL, 95 %, 0.12 mmol) were dissolved in 60 mL dry Et_2O and brought to reflux for 70 h. After removing all volatiles under reduced pressure, the crude product was washed with a few mL *n*-hexane and recrystallised from a DCM/*n*-pentane (1:1) mixture. The dry and pure carbamate **6f** was obtained in 52 % yield (1.97 g, 3.52 mmol).



6f

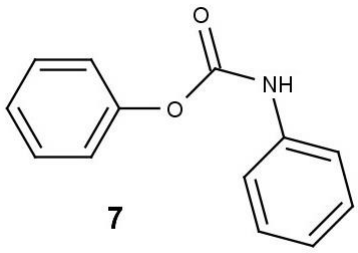
^{1}H-NMR (300 MHz, $CDCl_3$): δ□= 7.33-7.09 (6H, m, Ar-H), 4.70 (2H, br s, NH), 3.71 (12H, s, OCH_3), 3.04-2.90 (4H, , m, N-CH_2-), 1.69 (12H, s, CH_3), 1.40-1.26 (4H, m, NCH_2-CH_2-), 1.25-1.12 (4H, m, $N(CH_2)_2$-CH_2-) ppm.

^{13}C-NMR (75 MHz, $CDCl_3$): δ□= 160.7 (meta-C), 155.3 (C=O), 149.3 (ipso-C), 103.1 (ortho-CH), 98.2 (para-CH) , 80.4 (C), 60.4 (OCH_3), 55.3 (N-CH_2-), 29.1 (CH_3), 21.0 (NCH_2-CH_2-), 14.3 ($N(CH_2)_2$-CH_2-) ppm.

DSC (40-300 °C, 10 °C · min^{-1}): T_m = 185.1 °C, T_d = 227.6 °C.

Phenyl N-phenylcarbamate (**7**):

Phenol (1.11 g, 11.76 mmol), **4b** (1.40 g, 11.76 mmol) and **DBTDL** (0.075 mL, 95 %, 0.12 mmol) were dissolved in 30 mL dry Et_2O, stirred for 12 h at room temperature, brought to reflux for 10 h and, again, stirred for additional 12 h at room temperature. After removing all volatiles under reduced pressure, the crude product was purified *via* flash column chromatography (stationary phase: Merck silica gel 60, eluent: DCM). The pure carbamate **7** was obtained in 90 % yield (2.25 g, 10.57 mmol).



7

^{1}H-NMR (300 MHz, $CDCl_3$): δ□= 7.62-6.99 (11H, m, Ar-H + NH) ppm.

^{13}C-NMR (75 MHz, $CDCl_3$): δ□= 151.9 (C=O), 150.6 (ipso-C), 137.5 (ipso-C), 129.5 (Ar-CH), 129.2 (Ar-CH), 125.8 (Ar-CH), 124.0 (Ar-CH), 121.8 (Ar-CH), 118.9 (Ar-CH) ppm.

DSC (40-300 °C, 10 °C · min^{-1}): T_m = 126.2 °C, T_d = 183.1 °C.