Supporting Information

α-Carbamoylsulfides as *N*-Carbamoylimine Precursors in the Visible Light Photoredox-Catalyzed Synthesis of α,α-Disubstituted Amines

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I. General Information:

All reactions were carried out under argon atmosphere in oven dried glassware with magnetic stirring. Reagents were obtained from commercial supplier and used without further purification unless otherwise noted. All solvents used in the reactions were distilled from appropriate drying agents prior to use. Analytical thin layer chromatography (TLC) was purchased from Merck KGaA (silica gel 60 F254). Visualization was accomplished by irradiation with a UV light at 254 nm. Flash column chromatography was carried out using kieselgel 35-70 μ m particle sized silica gel (200-400 mesh). Chromatography was performed using silica gel 60 (0.040-0.063 mm) from Merck.

¹H NMR and ¹³C spectra were recorded with Bruker 500 MHz and 300 MHz instruments. Proton chemical shifts are reported in ppm (δ) relative to tetramethylsilane (TMS) with the solvent resonance employed as the internal standard (CDCl₃, δ 7.26 ppm). Data are reported as follows: chemical shift, multiplicity (s = singlet, br s = broad singlet, d = doublet, t = triplet, q = quartet, qt = quintuplet, h = hexuplet, ht = heptuplet, m = multiplet), coupling constants (Hz) and integration. ¹³C chemical shifts are reported in ppm from tetramethylsilane (TMS) with the solvent resonance as the internal standard (CDCl₃, δ 77.2 ppm).

Infrared spectra were recorded on neat samples, on a Perkin Elmer Spectrum BX FT-IR spectrometer and the characteristic IR absorption frequencies are reported in cm⁻¹.

Melting points were recorded using Reichert melting point apparatus and temperatures were uncorrected.

Optical rotations were performed on a Jasco P-1010 polarimeter (589 nm) using a 700- μ L cell with a path length of 1 dm.

Mass spectra were determined on an AEI MS-9 using electrospray ionization (ESI).

Visible light irradiations were performed with a Flexled INSPIRE LED lamp (3.6 W; λ = 465 nm).

Ru(bpy)₃(PF₆)₂ was purchased from Sigma Aldrich. All other commercially available reagents and solvents were used without further purification. The α -amidosulfides **1** were prepared according to literature procedure.¹

¹ (a) N. George, M. Bekkaye, A. Alix, J. Zhu, G. Masson *Chem. Eur. J.* **2014**, *20*, 3621-3625. (b) N. George, M. Bekkaye, G. Masson, J. Zhu *Eur. J. Org. Chem.* **2011**, 3695-3699. (c) E. Foresti, G. Palmieri, M. Petrini, R. Profeta *Org. Biomol. Chem.* **2003**, *1*, 4275-4281.

II. Reaction Optimization:

	Boc NH Bn SF 1a R = Et 1b R = Ph 1c R = Bn 1d B = + Bi	MeO R + ON 5a	OMe OMe Photocat. 3 (2.5 mol%) Additive (x eq) Solvent Me Blue LEDs 24 h, rt	Boc NH OM Bn MeO 6a	le OMe
	1e R = O ₂ F	'n	3a Ru(bpy) ₃ (PF ₆) ₂ 3b Ir(ppy) ₂ (dtb-bpy)PF ₆		
Entry	1	2	3c Eosin Y	Solvont	Viold $(0/a)$
<u>Enu y</u> 1	12	20	Auunive (x eq)	MoCN	60
2	1a 1a	3a	 HFIP (10.0)	MeCN	77
3	1a	3a	<i>t</i> -BuOH (10.0)	MeCN	87
4	1a	3b	<i>t</i> -BuOH (10.0)	MeCN	70
5	1a	3c	<i>t</i> -BuOH (10.0)	MeCN	63 ^c
6	1a	3a	<i>t</i> -BuOH (10.0)	THF	8
7	1a	3a	<i>t</i> -BuOH (10.0)	CH ₂ Cl ₂	6
8	1a	3a	-	t-BuOH	5
9	1a	3a	<i>t</i> -BuOH (10.0)	MeCN	60 ^d
10	1a	3a	<i>t</i> -BuOH (10.0)	MeCN	90 ^e
11	1a	3a	<i>t</i> -BuOH (5.0)	MeCN	77
12	1a	3a	<i>t</i> -BuOH (20.0)	MeCN	63
13	1a	3a	<i>t</i> -BuOH (10.0)	MeCN	67 ^{<i>f</i>}
14	1a	3a	<i>t</i> -BuOH (10.0)	MeCN	76 ^g
15	1b	3a	<i>t</i> -BuOH (10.0)	MeCN	57
16	1c	3a	<i>t</i> -BuOH (10.0)	MeCN	63
17	1d	3a	<i>t</i> -BuOH (10.0)	MeCN	91
18	1e	3a	<i>t</i> -BuOH (10.0)	MeCN	_h
19	1a	3a	<i>t</i> -BuOH (10.0)	MeCN	_ h, i
20	1a	_	<i>t</i> -BuOH (10.0)	MeCN	_ h

^{*a*}General conditions: **1** (0.10 mmol), 1,3,5-Trimethoxybenzene **5a** (0.15 mmol), **3** (0.025 equiv), Additive (x eq) in MeCN (1.0 mL) irradiated at rt for 24 h. ^{*b*}Yields referred to chromatographically pure product. ^{*c*}Irradiated with Green LEDs. ^{*d*}MeCN (2 mL) was used. ^{*e*}MeCN (0.5 mL) was used. ^{*f*}BrCCl₃ (0.025 mmol) was used as oxidative quencher. ^{*g*} N,N'-dimethyl-4,4'-bipyridinium (0.015 mmol) was used as oxidative quencher. ^{*h*}Starting material was recovered. ^{*f*}Without any irradiation.

III. Mechanistic Studies:



Entry	Control Conditions	Product
1	w/o photocatalyst 3	0%
2	w/o light	0%
3	Standard Conditions, w/all	90%

Fig. S1. Control Experiments.



Entry	Light On and Off Conditions	Product
1	on 1h	8%
2	on 1h, off 23h	30%
3	on 24h	90%

Fig. S2. Light on and off experiments.

1a OMe	AeCN [0.2M] Blue LEDs Me(5 h, rt	OMe

Entry	Degas Procedure	Ratio SM/P ^a
1	Under Ar atmosphere ^b	< 20:1
2	Under Air atmosphere ^b	> 1:20
3	Under O ₂ atmosphere ^b	> 1:20

^a Determined by ¹H NMR.

b. Freeze-pump-thraw degassed solution (3 cycles) of [Ru(bpy)₃(PF₆)₂]in MeCN/*t*-BuOH was used.

Fig. S3. Oxygen Effects.

Control experiment:



Phenyl disulfide was observed in the case of ${\bf 1b}$ was used as α -amidosufide. The NMR data is in accordance with the literature.^2

1,2-diphenyldisulfane





² M. Soleiman-Beigi, I. Yavari, F. Sadeghizadeh RSC Adv. 2015, 5, 87564–87570

IV. Electrochemical studies:

Electrochemical studies were performed using acetonitrile as a solvent, with *N*-tetrabutylammonium hexafluorophosphate (Fluka, puriss.) as the supporting electrolyte. The substrate concentration was ca. 1 mM. A 2 mm platinum electrode was used as the working electrode, along with a Ag⁺/Ag (10⁻² M) reference electrode and a Pt wire counter electrode. The cell was connected to a PAR 273A potentiostat. The reference electrode was checked *vs*. ferrocene as recommended by IUPAC: the oxidation potential of ferrocene was measured at 0.08V. As a consequence, one has to substract 0.08V to the values read on the curves to obtain potentials Vs Fc+/Fc, and to add 0.32V to the values read on the curves to obtain potentials Vs SCE.



Fig S4: Cyclic voltammogram of compound **1a**. Oxidation potential is estimated (irreversible process) at +1.17V Vs SCE which is in agreement with values published for related compounds.³

³ (a) A. J. Perkowski, C. L. Cruz, D. A. Nicewicz *J. Am. Chem. Soc.* **2015**, *137*, 15684–15687; (b) J.-I Yoshida, M. Sugawara, M. Tatsumi, N. Kise *J. Org. Chem.* **1998**, *63*, 5950–5961.



Fig S5: Cyclic voltammograms of compound **1a** (13mM) in presence of increasing amounts of *t*-BuOH. Top: whole cyclic voltamogramms, bottom: zoom on the region of interest.

IV. General Procedure for compounds 6:

A flame-dried test tube, flushed with Argon, was charged with the corresponding α -amidosulfide **1** (0.1 mmol, 1.0 eq) and dissolved in MeCN (0.5 mL) and *t*-BuOH (0.1 mL, 10 eq). Ru(bpy)₃(PF₆)₂ **3a** (2.2 mg, 2.50 mol%) then the corresponding nucleophile **5** (0.15 mmol, 1.50 eq) was then added. The resultant reaction mixture was irradiated with blue LEDs during 24 h. Then, the reaction mixture was directly purified by flash chromatography on silica gel (*n*-Heptane/EtOAc) to afford the corresponding pure compound **6a-6x**.

V. Spectroscopic data for compounds 6:

Data of Compounds **6a**⁴, **6c**⁴, **6e**⁴, **6l**⁴, **6m**⁴, **6n**⁴, **6o**⁵, **6v**⁶, **6w**⁷, **6x**⁴ and **7**⁸ were previously described.

Tert-butyl (3-phenyl-1-(2,4,6-trimethoxyphenyl)propyl)carbamate 6a



According to the general procedure, **6a** was obtained as a colourless oil (36 mg, Isolated yield 90%); ¹**H NMR** (300 MHz, CDCl₃) δ 7.28-7.16 (m, 5H, 5 × CH_{ar}), 6.15 (s, 2H, 2 × CH_{ar}), 5.86 (br. d, *J* = 10.2 Hz, 1H, N*H*), 5.43 (dd, 1H, *J* = 9.9 and 15.3 Hz, C*H*), 3.84 (s, 3H, CH₃), 3.83 (s, 6H, 2 × CH₃), 2.75-2.65 (m, 1H, CH₂), 2.53-2.43 (m, 1H, CH₂), 2.19-1.92 (m, 2H, CH₂), 1.46 (s, 9H, 3 × CH₃) ppm.

Tert-butyl (1-(2,4,6-trimethoxyphenyl)octyl)carbamate **6b**



According to the general procedure, **6b** was obtained as a colourless oil (33.5 mg, Isolated yield 85%); **¹H NMR** (300 MHz, CDCl₃) δ 6.11 (s, 2H, 2 × CH_{ar}), 5.76 (br. d, *J* = 10.2 Hz, 1H, NH), 5.32-5.24 (m, 1H, CH), 3.80 (s, 6H, 2 × CH₃), 3.79 (s, 3H, CH₃), 1.82-1.65 (m, 2H, CH₂), 1.42 (s, 9H, 3 × CH₃), 1.30-1.19 (m, 10H, 5 × CH₂), 0.85 (t, *J* = 6.5 Hz, 3H, CH₃) ppm; ¹³C NMR (75 MHz, CDCl₃) δ 160.0 (*C*_q),

158.7 (C_q), 155.6 (C_q), 111.9 (C_q), 91.5(C_q), 91.1 (3 × CH_{ar}), 78.6 (C_q), 55.9 (2 × CH_3), 55.4 (CH_3), 45.9 (CH), 36.0 (CH_2), 32.0 (CH_2), 29.6 (CH_2), 29.4 (CH_2), 28.7 (3 × CH_3), 26.6 (CH_2), 22.8 (CH_2), 14.2 (CH_3) ppm; **IR**: ν (neat, cm⁻¹) 3458, 2928, 2855, 1710, 1607, 1591, 1493, 1455, 1418, 1364, 1327, 1224, 1204, 1151, 1134, 1061, 1042, 952, 874, 812; **ESI-HRMS (positive)** [M+Na]⁺ Calc. for C₂₂H₃₇NO₅Na 418.2564, found 418.2553.

Tert-butyl (2-methyl-1-(2,4,6-trimethoxyphenyl)propyl)carbamate **6c**



According to the general procedure, **6c** was obtained as a colourless oil (17 mg, Isolated yield 50%); **¹H NMR** (300 MHz, CDCl₃) δ 6.12 (s, 2H, 2 × CH_{ar}), 5.74 (br. d, *J* = 10.6 Hz, 1H, N*H*), 4.98 (t, *J* = 10.3 Hz, 1H, C*H*), 3.80 (s, 3H, CH₃), 3.79 (s, 6H, 2 × CH₃), 2.10-1.95 (m, 1H, C*H*), 1.42 (s, 9H, 3 × CH₃), 1.00 (d, *J* = 6.8 Hz, 3H, CH₃), 0.69 (d, *J* = 6.8 Hz, 3H, CH₃) ppm.

⁴ N. George, M. Bekkaye, A. Alix, J. Zhu, G. Masson *Chem. Eur. J.* **2014**, *20*, 3621–3625.

⁵ J. Jaratjaroonphong, S. Tuengpanya, S. Ruengsangtongkul *J. Org. Chem.* **2015**, *80*, 559–567.

⁶ A. M. Seayad, B. Ramalingam, K. Yoshinaga, T. Nagata, C. L. L. Chai Org. Lett. **2010**, *12*, 264–267.

⁷ S. Lou, P. Dai, S. E. Schaus J. Org. Chem. **2007**, 72, 9998–10008.

⁸ M. P. Muñoz, M. C. de la Torre, M. A. Sierra Chem. Eur. J. 2012, 18, 4499-4504.

Tert-butyl (cyclopropyl(2,4,6-trimethoxyphenyl)methyl)carbamate 6d



According to the general procedure, **6d** was obtained as a colourless oil (18.5 mg, Isolated yield 55%); **¹H NMR** (300 MHz, CDCl₃) δ 6.14 (s, 2H, 2 × C*H*_{ar}), 5.91 (d, *J* = 10.2 Hz, 1H, N*H*), 4.67 (t, *J* = 9.7 Hz, 1H, *CH*), 3.82 (s, 6H, 2 × C*H*₃), 3.80 (s, 3H, C*H*₃), 1.43 (s, 9H, 3 × C*H*₃), 1.36-1.20 (m, 1H, C*H*), 0.56-0.18 (m, 4H, 2 × C*H*₂) ppm; ¹³C NMR (75 MHz, CDCl₃) δ 160.2 (*C*_a), 159.7 (*C*_a), 158.7 (*C*_a), 115.8 (*C*_a), 111.8

 (C_q) , 91.7 (*C*H), 91.2 (*C*H), 78.7 (C_q), 55.9 (2 × *C*H₃), 55.4 (*C*H₃), 50.1 (*C*H), 28.7 (3 × *C*H₃), 17.2 (*C*H), 3.8 (*C*H₂), 3.3 (*C*H₂) ppm; **IR**: ν (neat, cm⁻¹) 3460, 3002, 2975, 2939, 2839, 1709, 1608, 1592, 1493, 1455, 1418, 1390, 1365, 1329, 1223, 1204, 1150, 1111, 1041, 1017, 957, 928, 880, 813; **ESI-HRMS (positive)** [M+Na]⁺ Calc. for C₁₈H₂₇NO₅Na 360.1781, found 360.1784.

Tert-butyl (2-(benzyloxy)-1-(2,4,6-trimethoxyphenyl)ethyl)carbamate 6e



According to the general procedure, **6e** was obtained as a colourless oil (24.0 mg, Isolated yield 58%); ¹**H NMR** (300 MHz, CDCl₃) δ 7.30-7.23 (m, 5H, 5 × CH_{ar}), 6.12 (s, 2H, 2 × CH_{ar}), 5.80-5.72 (m, 2H, CH, NH), 4.64 (br. d, *J* = 11.8 Hz, 1H, CH₂), 4.55 (br. d, *J* = 11.6 Hz, 1H, CH₂), 3.80 (s, 9H, 3 × CH₃), 3.73-3.68 (m, 1H, CH₂), 3.57-3.53 (m, 1H, CH₂), 1.44 (s, 9H, 3 × CH₃) ppm.

Tert-butyl (3-phenyl-1-(2,4,6-trimethoxyphenyl)prop-2-yn-1-yl)carbamate **6f**



According to the general procedure, **6f** was obtained as a colourless oil (26 mg, Isolated yield 65%); **¹H NMR** (300 MHz, CDCl₃) δ 7.40-7.34 (m, 2H, 2 × CH_{ar}), 7.26-7.22 (m, 3H, 3 × CH_{ar}), 6.39 (br. d, *J* = 10.2 Hz, 1H, CH), 6.16 (s, 2H, 2 × CH_{ar}), 5.94 (br. d, *J* = 10.0 Hz, 1H, NH), 3.89 (s, 6H, 2 × CH₃), 3.81 (s, 3H, CH₃), 1.45 (s, 9H, 3 × CH₃) ppm; ¹³C NMR (75 MHz, CDCl₃) δ 161.1 (*C*_q), 158.6 (2 × *C*_q), 155.0

 (C_q) , 131.9 (2 × *C*H), 128.2 (*C*H), 127.9 (2 × *C*H), 123.8 (C_q), 109.5 (C_q), 91.6 (2 × *C*H), 90.0 (C_q), 80.3 (C_q), 79.6 (C_q), 56.3 (2 × *C*H₃), 55.5 (*C*H₃), 37.2 (*C*H), 28.6 (3 × *C*H₃) ppm; **IR**: ν (neat, cm⁻¹) 3454, 2973, 2940, 2841, 1709, 1608, 1594, 1488, 1455, 1419, 1392, 1366, 1322, 1276, 1222, 1205, 1152, 1121, 1042, 1017, 951, 912, 873, 814, 758, 732, 692; **ESI-HRMS (positive)** [M+Na]⁺ Calc. for C₂₃H₂₇NO₅Na 420.1781, found 420.1784.

N-(3-phenyl-1-(2,4,6-trimethoxyphenyl)propyl)benzamide **6g**



According to the general procedure, **6g** was obtained as a colourless oil (30 mg, Isolated yield 74%); **¹H NMR** (300 MHz, CDCl₃) δ 7.77-7.74 (m, 2H, 2 × CH_{ar}), 7.66 (br. d, *J* = 9.7 Hz, 1H, N*H*), 7.50-7.39 (m, 3H, 3 × CH_{ar}), 7.26-7.11 (m, 5H, 5 × CH_{ar}), 6.17 (s, 2H, 2 × CH_{ar}), 6.03-5.94 (m, 1H, C*H*), 3.87 (s, 6H, 2 × CH₃), 3.82 (s, 3H, CH₃), 2.79-2.69 (m, 1H, CH₂), 2.61-2.51 (m, 1H, CH₂), 2.29-2.03 (m, 2H, CH₂) ppm; ¹³C NMR (75 MHz, CDCl₃) δ 166.2 (*C*_q), 160.5 (2 × *C*_q), 158.9 (*C*_q), 142.6 (*C*_q), 135.6 (*C*_q), 131.1 (*C*H_{ar}), 128.6 (2 × CH_{ar}), 128.5 (2 × CH_{ar}),

128.3 (2 × *C*H_{ar}), 127.0 (2 × *C*H_{ar}), 125.7 (*C*H_{ar}), 110.5 (*C*_q), 91.3 (2 × *C*H_{ar}), 56.0 (2 × *C*H₃), 55.5 (*C*H₃), 45.2 (*C*H), 37.3 (*C*H₂), 33.0 (*C*H₂) ppm; **IR**: ν (neat, cm⁻¹) 3444, 2940, 2839, 1652, 1605, 1520, 1488, 1454, 1418, 1361, 1330, 1250, 1224, 1204, 1148, 1118, 1060, 1031, 950, 918, 843, 813, 766, 730, 699; **ESI-HRMS (positive)** [M+Na]⁺ Calc. for C₂₅H₂₇NO₄Na 428.1832, found 428.1841.

4-methoxy-N-(3-phenyl-1-(2,4,6-trimethoxyphenyl)propyl)benzamide 6h



According to the general procedure, **6h** was obtained as a colourless oil (35 mg, Isolated yield 80%); ¹H NMR (300 MHz, CDCl₃) δ 7.74-7.70 (m, 2H, 2 × CH_{ar}), 7.57 (br. d, *J* = 9.7 Hz, 1H, N*H*), 7.26-7.10 (m, 5H, 5 × CH_{ar}), 6.94-6.89 (m, 2H, 2 × CH_{ar}), 6.16 (s, 2H, 2 × CH_{ar}), 6.01-5.93 (m, 1H, C*H*), 3.87 (s, 6H, 2 × CH₃), 3.84 (s, 3H, CH₃), 3.81 (s, 3H, CH₃), 2.84-2.68 (m, 1H, CH₂), 2.60-2.50 (m, 1H, CH₂), 2.28-2.01 (m, 2H, CH₂) ppm; ¹³C NMR (75 MHz, CDCl₃) δ 165.7 (*C*_q), 161.9 (*C*_q), 160.4 (2 × *C*_q), 158.9 (*C*_q), 142.7 (*C*_q), 128.7 (2 × CH_{ar}), 128.4 (2 × CH_{ar}), 128.3 (2 × CH_{ar}), 127.9 (*C*_q), 125.6 (CH_{ar}), 113.7 (2 × CH_{ar}),

110.7 (C_q), 91.3 (2 × CH_{ar}), 56.0 (2 × CH_3), 55.5 (2 × CH_3), 45.0 (CH), 37.4 (CH_2), 33.0 (CH_2) ppm; **IR**: ν (neat, cm⁻¹) 3448, 2938, 2839, 1651, 1605, 1523, 1492, 1454, 1418, 1360, 1330, 1306, 1251, 1224, 1204, 1176, 1148, 1118, 1059, 1031, 950, 910, 844, 813, 766, 731, 699; **ESI-HRMS (positive)** [M+Na]⁺ Calc. for C₂₆H₂₉NO₅Na 458.1938, found 458.1938.

Benzyl (3-phenyl-1-(2,4,6-trimethoxyphenyl)propyl)carbamate 6i



According to the general procedure, **6i** was obtained as a colourless oil (30 mg, Isolated yield 69%); ¹H NMR (300 MHz, CDCl₃) δ 7.39-7.11 (m, 10H, 10 × CH_{ar}), 6.13 (s, 2H, 2 × CH_{ar}), 6.08 (d, J = 10.2 Hz, 1H, NH), 5.53-5.45 (m, 1H, CH), 5.16-5.02 (m, 2H, CH₂), 3.81 (s, 9H, 3 × CH₃), 2.74-2.64 (m, 1H, CH₂), 2.54-2.44 (m, 1H, CH₂), 2.20-1.94 (m, 2H, CH₂) ppm; ¹³C NMR (75 MHz, CDCl₃) δ 160.4 (2 × C_a), 158.7 (C_a), 156.2 (*C*_q), 142.6 (*C*_q), 137.0 (*C*_q), 128.6 (2 × *C*H_{ar}), 128.5 (2 × *C*H_{ar}),

128.3 (2 × CH_{ar}), 128.2 (2 × CH_{ar}), 125.6 (2 × CH_{ar}), 110.7 (C_q), 91.1 (2 × CH_{ar}), 66.6 (CH_2), 55.9 (*C*H₃), 55.5 (2 × *C*H₃), 46.7 (*C*H), 37.4 (*C*H₂), 33.0 (*C*H₂) ppm; **IR**: v (neat, cm⁻¹) 3444, 2939, 2839, 1717, 1607, 1592, 1496, 1454, 1419, 1330, 1204, 1149, 1118, 1038, 950, 814, 740, 698; **ESI-HRMS (positive)** [M+Na]⁺ Calc. for C₂₆H₂₉NO₅Na 458.1938, found 458.1945.

Tert-butyl (((*R*)-2,2-dimethyl-1,3-dioxolan-4-yl)(2,4,6-trimethoxyphenyl)methyl)carbamate 6j



According to the general procedure, **6** was obtained as a colourless oil (20 mg, Isolated yield 50%); dr>95:5; ¹H NMR (300 MHz, CDCl₃) δ 6.13 (s, 1H, CHar), 6.11 (s, 1H, CHar), 5.83-5.77 (m, 1H, NH), 5.46-5.35 (m, 1H, CH), 4.38-4.32 (m, 1H, CH₂), 4.07-3.98 (m, 1H, CH₂), 3.82 (s, 6H, 2 × CH₃), 3.79 (s, 3H, CH₃), 3.75-3.69 (m, 1H, CH₂), 1.43 (s, 9H, 3 × CH₃), 1.60-1.29 (m, 6H, 2 × CH₃) ppm; ¹³C NMR (75 MHz,

CDCl₃) δ 160.8 (*C*_q), 159.7 (*C*_q), 159.1 (*C*_q), 113.2 (*C*_q), 108.7 (*C*_q), 91.2 (2 × *C*H_{ar}), 78.0 (*C*_q), 69.2 (*C*_q), 66.9 (*C*H₂), 56.0 (*C*H₃), 55.8 (*C*H₃), 55.5 (*C*H₃), 49.0 (*C*H) 48.0 (*C*H), 28.6 (3 × *C*H₃), 26.0 (CH₃), 25.8 (CH₃) ppm; **IR**: v (neat, cm⁻¹) 3457, 2980, 2937, 1710, 1607, 1592, 1495, 1455, 1418, 1367, 1220, 1204, 1152, 1131, 1060, 1043, 952, 913, 814, 732; ESI-HRMS (positive) [M+Na]⁺ Calc. for C₂₃H₂₇NO₅Na 420.1993, found 420.1987.

Benzyl (2R)-2-(((tert-butoxycarbonyl)amino)(2,4,6-trimethoxyphenyl)methyl)pyrrolidine-1carboxylate 6k



According to the general procedure, **6k** was obtained as a colourless oil (31 mg, Isolated yield 62%); dr 3:1; ¹H NMR (300 MHz, CDCl₃) (mixture of diastereoisomers and rotamers) δ 7.52-7.14 (m, 7H, CH_{ar}), 6.28-5.78 (m, 2H, CH, NH), 5.19-4.73 (m, 2H, CH₂), 4.34-4.15 (m, 1H, CH), 3.79-3.58 (m, 9H, 3 × CH₃), 3.49-3.11 $(m, 2H, CH_2), 2.11-1.44$ $(m, 4H, 2 \times CH_2), 1.39-1.29$ $(m, 9H, 3 \times CH_3)$ ppm; ¹³C NMR (75 MHz, CDCl₃) (mixture of diastereoisomers and rotamers) δ 160.8-158.5 (2 × C_q), 156.4-155.1 (2 × C_q), 137.6-137.0 (C_q), 129.4-127.5 (5 × CH_{ar}), 109.2-108.5 (C_{q}), 91.1-90.7 (2 × CH_{ar}), 79.1-78.5 (C_{q}), 68.0-65.0 (CH_{2}), 60.9-59.8 (CH),

56.1-54.7 (3 × CH_3), 48.7-47.0 (CH), 46.4-46.0 (CH₂), 28.7-28.6 (3 × CH_3), 28.5-27.9 (CH₂), 23.4-22.3 (CH₂) ppm; IR: v (neat, cm⁻¹) 3501, 2945, 1718, 1596, 1453, 1357, 1216, 1145, 1113, 1002, 945, 801, 737, 673; ESI-HRMS (positive) [M+Na]⁺ Calc. for C₂₇H₃₆N₂O₇Na 523.2420, found 523.2437.

Tert-butyl (phenyl(2,4,6-trimethoxyphenyl)methyl)carbamate **6**



According to the general procedure, **6I** was obtained as a white foam (33 mg, Isolated yield 88%); ¹**H NMR** (300 MHz, CDCl₃) δ 7.26-7.11 (m, 5H, 5 × CH_{ar}), 6.59 (br. d, *J* = 10.1 Hz, 1H, CH), 6.25 (br. d, *J* = 10.2 Hz, 1H, NH), 6.15 (s, 2H, 2 × CH_{ar}), 3.81 (s, 3H, CH₃), 3.77 (s, 6H, 2 × CH₃), 1.47 (s, 9H, CH₃) ppm.

Tert-butyl (furan-2-yl(2,4,6-trimethoxyphenyl)methyl)carbamate 6m



According to the general procedure, **6m** was obtained as a colourless oil (21.5 mg, Isolated yield 59%); **¹H NMR** (300 MHz, CDCl₃) δ 7.27 (s, 1H, CH_{ar}), 6.57 (br. d, *J* = 10.2 Hz, 1H, CH), 6.22 (br. s, 1H, CH_{ar}), 6.15 (s, 2H, 2 × CH_{ar}), 6.10 (br. s, 1H, NH), 5.92 (br. s, 1H, CH_{ar}), 3.81 (s, 3H, CH₃), 3.79 (s, 6H, 2 × CH₃), 1.45 (s, 9H, 3 × CH₃) ppm.

Tert-butyl ((4-(trifluoromethyl)phenyl)(2,4,6-trimethoxyphenyl)methyl)carbamate 6n



According to the general procedure, **6n** was obtained as a white foam (33 mg, Isolated yield 75%); **1H NMR** (300 MHz, CDCl₃) δ 7.48 (d, *J* = 8.4 Hz, 2H, 2 × CH_{ar}), 7.35 (d, *J* = 8.4 Hz, 2H, 2 × CH_{ar}), 6.60 (br. d, *J* = 9.9 Hz, 1H, CH), 6.20 (br. d, *J* = 9.9 Hz, 1H, NH), 6.15 (s, 2H, 2 × CH_{ar}), 3.80 (s, 3H, CH₃), 3.77 (s, 6H, 2 × CH₃), 1.47 (s, 9H, 3 × CH₃) ppm.

Tert-butyl ((4-methoxyphenyl)(2,4,6-trimethoxyphenyl)methyl)carbamate 60



According to the general procedure, **60** was obtained as a white foam (24.5 mg, Isolated yield 60%); ¹**H NMR** (300 MHz, CDCl₃) δ 7.19-7.14 (m, 2H, 2 × CH_{ar}), 6.80-6.75 (m, 2H, 2 × CH_{ar}), 6.52 (br. d, *J* = 10.2 Hz, 1H, CH), 6.23 (br. d, *J* = 10.2 Hz, 1H, NH), 6.15 (s, 2H, 2 × CH_{ar}), 3.80 (s, 3H, CH₃), 3.77 (s, 6H, 2 × CH₃), 3.75 (s, 3H, CH₃), 1.46 (s, 9H, 3 × CH₃) ppm.

Tert-butyl (1-(5-methoxythiophen-2-yl)-3-phenylpropyl)carbamate **6p**



According to the general procedure, **6p** was obtained as a white foam (16.5 mg, Isolated yield 47%); ¹H NMR (300 MHz, CDCl₃) δ 7.22-7.07 (m, 5H, 5 × CH_{ar}), 6.49 (s, 1H, CH_{ar}), 5.95-5.93 (m, 1H, CH_{ar}), 4.74-4.59 (m, 2H, CH, NH), 3.78 (s, 3H, CH₃), 2.65-2.55 (m, 2H, CH₂), 2.05-1.97 (m, 2H, CH₂), 1.37 (s, 9H, 3 × CH₃) ppm; ¹³C NMR (75 MHz, CDCl₃) δ 165.4 (C₀), 155.2 (C₀), 141.5 (C₀), 132.5 (C₀),

128.6 (2 × CH), 128.4 (2 × CH), 126.1 (CH), 121.8 (CH), 103.1 (CH), 80.1 (Cq), 60.4 (CH₃), 50.9 (CH), 38.5 (CH₂), 32.5 (CH₂), 28.5 (3 × CH₃) ppm; **IR**: v (neat, cm⁻¹) 3336, 1762, 1601, 1513, 1473, 1367, 1251, 1140, 1019, 927, 801, 706; ESI-HRMS (positive) [M+Na]+ Calc. for C₁₉H₂₅NO₃SNa 370.1453, found 370.1460.

Tert-butyl ((5-methoxythiophen-2-yl)(phenyl)methyl)carbamate 6q



According to the general procedure, **6q** was obtained as a white foam (16.5 mg, Isolated yield 51%); ¹H NMR (300 MHz, CDCl₃) δ 7.29-7.18 (m, 5H, 5 × CH_{ar}), 6.28 (br. d, I = 3.7 Hz, 1H, CH_{ar}), 5.90 (br. d, J = 3.7 Hz, 1H, CH_{ar}), 5.86 (br. s, 1H, CH), 5.10 (br. s, 1H, NH), 3.75 (s, 3H, CH₃), 1.36 (s, 9H, 3 × CH₃) ppm; ¹³C NMR (75 MHz, CDCl₃) δ 166.3 (*C*_q), 154.9 (*C*_q), 141.5 (*C*_q), 132.1 (*C*_q), 128.7 (2 × *C*H_{ar}), 127.8 (*C*H_{ar}), 127.0 (2 × CH_{ar}), 123.1 (CH_{ar}), 103.2 (CH_{ar}), 80.1 (C_{0}), 60.3 (CH_{3}), 55.0 (CH), 28.5 (3 × CH_{3}) ppm; **IR**: ν (neat, cm⁻¹) 3336, 1795, 1628, 1363, 1147, 1009, 921, 807, 705; ESI-HRMS (positive) [M+Na]⁺ Calc. for C₁₇H₂₁NO₃SNa 319.1242, found 319.1238.

3,3'-(3-phenylpropane-1,1-diyl)bis(1H-indole) 7



According to the general procedure, 7 was obtained as a colourless oil (15 mg, Isolated yield 43%); ¹H NMR (300 MHz, CDCl₃) δ 7.91 (s, 2H, NH), 7.55 (d, J=8.0 Hz, 2H, CH_{ar}), 7.34-6.99 (m, 13H, CH_{ar}), 4.50 (t, J = 7.2 Hz, 1H, CH), 2.75-2.70 (m, 2H, CH₂), 2.59-2.51 (m, 2H, CH₂) ppm.

N-(1-(1*H*-indol-3-yl)-3-phenylpropyl)benzamide **6**r



According to the general procedure with **5** (0.3 mmol, 3.0 eq.), **6r** was obtained as a colourless oil (24 mg, Isolated yield 68%); ¹**H NMR** (300 MHz, CDCl₃) δ 8.21 (br. s, 1H, N*H*), 7.74-7.70 (m, 3H, 3 × *CH*_{ar}), 7.49-7.11 (m, 12H, 12 × *CH*_{ar}), 6.34 (d, *J* = 8.3 Hz, 1H, N*H*), 5.63 (dt, *J* = 8.3 and 7.2 Hz 1H, *CH*), 2.87-2.71 (m, 2H, *CH*₂), 2.45-2.36 (m, 2H, *CH*₂) ppm; ¹³**C NMR** (75 MHz, CDCl₃) δ 166.9 (*C*_q), 142.0 (*C*_q), 136.8 (*C*_q), 131.5 (*C*H_{ar}), 128.7 (2 × *C*H_{ar}), 128.6 (4 × *C*H_{ar}), 127.2 (*C*_q), 127.0 (2 × *C*H_{ar}), 126.0 (2 × *C*H_{ar}), 122.8 (*C*H_{ar}), 121.9 (*C*H_{ar}), 120.2

(*C*_q), 119.6 (*C*H_{ar}), 117.0 (*C*_q), 111.5 (*C*H_{ar}), 47.1 (*C*H), 36.8 (*C*H₂), 33.1 (*C*H₂) ppm; **IR**: ν (neat, cm⁻¹) 3405, 2977, 1697, 1485, 1424, 1375, 1201, 1065, 1001, 700; **ESI-HRMS (positive)** [M+Na]⁺ Calc. for C₂₄H₂₂N₂ONa 377.1630, found 377.1636.

Tert-butyl (1-(3-methyl-1H-indol-2-yl)-3-phenylpropyl)carbamate 6s



According to the general procedure, **6s** was obtained as a colourless oil (25.5 mg, Isolated yield 70%); ¹**H NMR** (300 MHz, CDCl₃) δ 8.46 (s, 1H, NH_{indole}), 7.47 (d, *J* = 7.7 Hz, 1H, CH_{ar}), 7.26–7.01 (m, 8H, CH_{ar}), 4.97 (br. s, 1H, NH) 4.71-4.64 (m, 1H, CH), 2.65-2.48 (m, 2H, CH₂), 2.36-2.12 (m, 2H, CH₂), 2.19 (s, 3H, CH₃), 1.37 (s, 9H, 3 × CH₃) ppm; ¹³**C NMR** (75 MHz, CDCl₃) δ 156.0 (*C*_q), 141.2 (*C*_q), 135.5 (*C*_q),

134.7 (C_q), 129.1 (C_q), 128.6 (2 × CH_{ar}), 128.5 (2 × CH_{ar}), 126.2 (CH_{ar}), 121.9 (CH_{ar}), 119.2 (CH_{ar}), 118.7 (CH_{ar}), 110.9 (CH_{ar}), 107.8 (C_q), 80.2 (C_q), 48.0 (CH), 32.7 (CH_2), 28.5 (3 × CH_3), 28.1 (CH_2), 8.8 (CH_3) ppm; **IR**: ν (neat, cm⁻¹) 3330, 2974, 2922, 1694, 1490, 1467, 1368, 1235, 1160, 1013, 740, 697; **ESI-HRMS (positive)** [M+Na]⁺ Calc. for C₂₃H₂₈N₂O₂Na 387.2048, found 387.2051.

Tert-butyl (1-(1H-indazol-1-yl)-3-phenylpropyl)carbamate 6t



According to the general procedure, **6t** was obtained as a colourless oil (32 mg, Isolated yield 91%); ¹**H NMR** (300 MHz, CDCl₃) δ 8.06 (s, 1H, CH_{ar}), 7.71 (d, *J* = 8.1 Hz, 1H, CH_{ar}), 7.62-7.56 (m, 1H, CH_{ar}), 7.37 (t, *J* = 7.4 Hz, 1H, CH_{ar}), 7.27-7.06 (m, 6H, 6 × CH_{ar}), 6.28-6.17 (m, 1H, CH), 5.58 (br. d, *J* = 8.8 Hz, 1H, NH), 2.64-2.41 (m, 4H, 2 × CH₂), 1.36

(s, 9H, 3 × C*H*₃) ppm; ¹³**C NMR** (75 MHz, CDCl₃) δ 154.9 (*C*_q), 140.5 (*C*_q), 139.8 (*C*_q), 134.5 (*C*H_{ar}), 128.6 (4 x *C*H_{ar}), 126.7 (*C*H_{ar}), 126.3 (*C*H_{ar}), 123.9 (*C*_q), 121.1 (*C*H_{ar}), 120.9 (*C*H_{ar}), 110.0 (*C*H_{ar}), 80.3 (*C*_q), 63.1 (*CH*), 36.6 (*C*H₂), 31.8 (CH₂), 28.4 (3 x *C*H₃) ppm; **IR**: ν (neat, cm⁻¹) 3314, 2969, 1710, 1497, 1337, 1225, 1123, 1037, 1018, 876, 739, 635; **ESI-HRMS (positive)** [M+Na]⁺ Calc. for C₂₆H₂₉NO₅Na 374.1844, found 374.1836.

Tert-butyl (3-phenyl-1-(1*H*-pyrazol-1-yl)propyl)carbamate **6u**



According to the general procedure, **6u** was obtained as a colourless oil (21 mg, Isolated yield 70%); ¹H NMR (300 MHz, CDCl₃) δ 7.55 (br. d, *J* = 1.9 Hz, 1H, CH_{ar}), 7.50 (br. s, 1H, CH_{ar}), 7.27-7.07 (m, 5H, 5 × CH_{ar}), 6.20 (t, *J* = 2.1 Hz, 1H, CH_{ar}), 5.72-5.64 (m, 1H, CH), 5.52 (br. d, *J* = 8.6 Hz, 1H, NH), 2.64-2.43 (m, 4H, 2 × CH₂), 1.36

(s, 9H, $3 \times CH_3$) ppm; ¹³**C NMR** (75 MHz, CDCl₃) δ 154.8 (C_q), 140.3 (CH_{ar}), 130.0 (CH_{ar}), 129.8 (C_q), 128.7 (2 x CH_{ar}), 128.6 (2 x CH_{ar}), 126.4 (CH_{ar}), 105.0 (CH_{ar}), 80.5 (C_q), 66.5 (CH), 36.2 (CH_2), 31.6 (CH_2), 26.4 (3 x CH_3) ppm; **IR**: ν (neat, cm⁻¹) 3303, 2973, 1700, 1504, 1496, 1374, 1329, 1242, 1160, 1090, 1054, 1038, 889, 750, 719, 685, 668, 653; **ESI-HRMS (positive)** [M+Na]⁺ Calc. for C₁₇H₂₃N₃O₂Na 324.1688, found 324.1681.

Tert-butyl (cyano(phenyl)methyl)carbamate 6v



According to the general procedure with KCN (0.3 mmol, 3.0 eq) and a mixture MeCN:H₂O (0.5 mL:0.5 mL), **6v** was obtained as a white foam (21.5 mg, Isolated yield 93%); ¹**H** NMR (300 MHz, CDCl₃) δ 7.50-7.41 (m, 5H, 5 × CH_{ar}), 6.80 (br. d, *J* = 7.7 Hz, 1H, C*H*), 5.13 (br. s, 1H, N*H*), 1.48 (s, 9H, 3 × C*H*₃) ppm.

Tert-butyl (4-acetyl-5-oxo-1-phenylhexan-3-yl)carbamate 6w



According to the general procedure, **6w** was obtained as a white foam (13.5 mg, Isolated yield 40%); ¹**H** NMR (300 MHz, CDCl₃) δ 7.31-7.16 (m, 5H, 5 × CH_{ar}), 5.33 (br. d, *J* = 10.2 Hz, 1H, NH), 4.37-4.27 (m, 1H, CH), 3.87 (d, *J* = 5.1 Hz, 1H, CH), 2.81-2.55 (m, 2H, CH₂), 2.24 (s, 3H, CH₃), 2.10 (s, 3H, CH₃), 1.99-1.86 (m, 1H, CH₂), 1.76-1.63 (m, 1H, CH₂), 1.42 (s, 9H, 3 × CH₃) ppm.

Tert-butyl (2-acetyl-3-oxo-1-phenylbutyl)carbamate **6x**



According to the general procedure, **6x** was obtained as a white foam (15 mg, Isolated yield 49%); ¹**H NMR** (300 MHz, CDCl₃) δ 7.31-7.21 (m, 5H, 5 × CH_{ar}), 5.80 (br. s, 1H, N*H*), 5.46 (br. s, 1H, C*H*), 4.18 (d, *J* = 6.9 Hz, 1H, C*H*), 2.15 (s, 3H, CH₃), 2.08 (s, 3H, CH₃), 1.36 (s, 9H, 3 × CH₃) ppm.

VI. ¹H and ¹³C NMR data for compounds 6:

Tert-butyl (3-phenyl-1-(2,4,6-trimethoxyphenyl)propyl)carbamate **6a**



Tert-butyl (1-(2,4,6-trimethoxyphenyl)octyl)carbamate **6b**



Tert-butyl (2-methyl-1-(2,4,6-trimethoxyphenyl)propyl)carbamate **6c**



Tert-butyl (cyclopropyl(2,4,6-trimethoxyphenyl)methyl)carbamate **6d**





Tert-butyl (2-(benzyloxy)-1-(2,4,6-trimethoxyphenyl)ethyl)carbamate **6e**



Tert-butyl (3-phenyl-1-(2,4,6-trimethoxyphenyl)prop-2-yn-1-yl)carbamate **6f**







4-methoxy-*N*-(3-phenyl-1-(2,4,6-trimethoxyphenyl)propyl)benzamide **6h**





Tert-butyl (((*R*)-2,2-dimethyl-1,3-dioxolan-4-yl)(2,4,6-trimethoxyphenyl)methyl)carbamate **6**j



Benzyl (2*R*)-2-(((*tert*-butoxycarbonyl)amino)(2,4,6-trimethoxyphenyl)methyl)pyrrolidine-1-carboxylate **6**k



Tert-butyl (phenyl(2,4,6-trimethoxyphenyl)methyl)carbamate **6**



Tert-butyl (furan-2-yl(2,4,6-trimethoxyphenyl)methyl)carbamate **6m**









Tert-butyl ((4-methoxyphenyl)(2,4,6-trimethoxyphenyl)methyl)carbamate **60 (14)**



Tert-butyl (1-(5-methoxythiophen-2-yl)-3-phenylpropyl)carbamate **6p**

Tert-butyl ((5-methoxythiophen-2-yl)(phenyl)methyl)carbamate **6q**



3,3'-(3-phenylpropane-1,1-diyl)bis(1*H*-indole) 7





N-(1-(1*H*-indol-3-yl)-3-phenylpropyl)benzamide **6r**



Tert-butyl (1-(3-methyl-1*H*-indol-2-yl)-3-phenylpropyl)carbamate **6s**

Tert-butyl (1-(1*H*-indazol-1-yl)-3-phenylpropyl)carbamate **6t**



Tert-butyl (3-phenyl-1-(1*H*-pyrazol-1-yl)propyl)carbamate **6u**



Tert-butyl (cyano(phenyl)methyl)carbamate **6v**



Tert-butyl (4-acetyl-5-oxo-1-phenylhexan-3-yl)carbamate **6w**



Tert-butyl (2-acetyl-3-oxo-1-phenylbutyl)carbamate **6x**

