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Palladium-catalyzed coupling of vinyl phosphates with aryl or heteroaryl boronic acids. Application to the synthesis of substituted nitrogen containing heterocycles

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Abstract—Substituted nitrogen-containing heterocycles were prepared in three steps from commercially available derivatives via an extension of the Suzuki reaction involving the palladium-catalyzed coupling of vinyl phosphates with aryl or heteroaryl boronic acids. © 2001 Elsevier Science Ltd. All rights reserved.

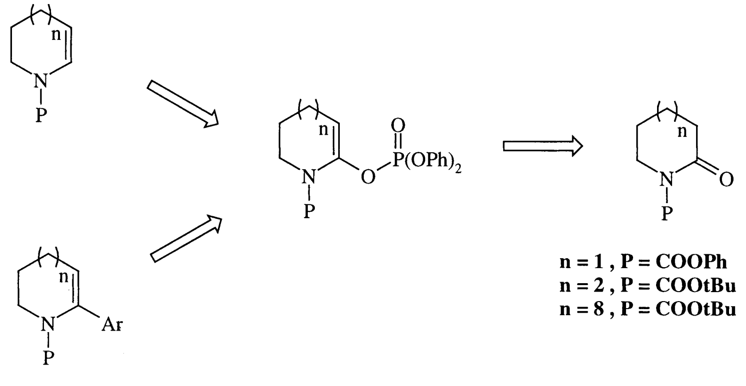
1. Introduction

The synthesis of N-heterocycles of various sizes constitutes a most important theme within organic chemistry owing to their presence in a wide range of natural and synthetic products. Access to substituted N-heterocycles through a process involving the functionalization of lactams via their vinyl triflates was first reported by Isobe a few years ago.[1] Ever since, the triflate-based methodology has been widely used for the elaboration of substituted nitrogen containing heterocycles.[2]

However, in spite of their important potential these vinyl triflates present such drawbacks as a relative lack of stability and the necessity to use expensive triflating agents.

It was reported, first by Nicolaou[3] and next by Jiang,[4] that vinyl phosphates could constitute an interesting alternative to their triflate counterparts. Recently, we also used these reactive intermediates for the synthesis of substituted benzoxazines, pyridoxazines and benzothiazines.[5] These unusual heterocyclic systems were prepared via the first reported extension of the Suzuki[6] reaction involving palladium-catalyzed coupling of vinyl phosphates with aryl or heteroaryl boronic acids. The present paper concerns the application of our methodology to the synthesis of medium-sized and large N-heterocycles. We focused our interest on the preparation of six-, seven- and thirteen-membered rings ene-carbamates substituted or not on position C_2.

The synthesis of vinyl phosphates was realized from the six-membered *N*-COOPh protected lactam and the seven- and thirteen-membered *N*-Boc protected lactams via their corresponding lithium enolates (Scheme 1).



Scheme 1.

Keywords: coupling reactions; palladium and compounds; boronic acids; vinyl phosphates; N-heterocycles.

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2. Results and discussions

2.1. Synthesis, hydrogenolysis and Suzuki coupling of the six-membered ketene aminal diphenyl phosphate 4

The *N*-Boc protected valerolactam was first prepared according to Murai.[2b] Unfortunately, in spite of numerous experiments, we were unable to isolate the corresponding vinyl phosphate in good yield. Consequently we changed the *N*-protecting group and moved to the preparation of N-COOPh protected valerolactam **1** which was obtained in 73% yield according to Comins.[2a] The corresponding lithium enolate obtained at −78°C in dry tetrahydrofuran with LDA (1.2 equiv.) and TMEDA (1.2 equiv.) was then reacted with freshly distilled diphenyl chlorophosphate (1.2 equiv.). Vinyl phosphate **4**, purified by flash chromatography on silica gel was eventually obtained in 82% yield.

The reduction of **4** was first performed by adapting a procedure previously described by Cacchi et al.[7] Treatment of **4** with triethylammonium formate, palladium acetate (0.04 equiv.) and triphenylphosphine (0.08 equiv.) in refluxing tetrahydrofuran led to unsaturated carbamate **7** in 79% yield (Scheme 2).

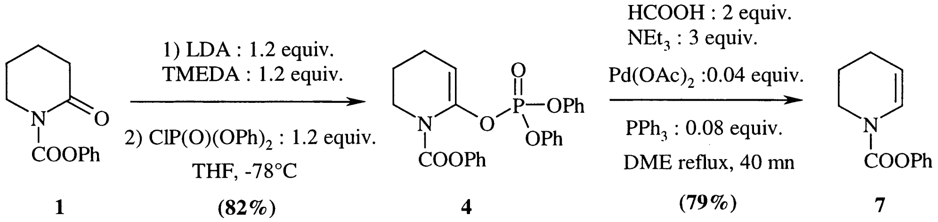
In order to obtain 2-substituted heterocyclic systems, vinyl phosphate **4** was then engaged in palladium-catalyzed coupling reactions involving aryl or heteroaryl boronic acids according to a procedure we previously described[5,8] (Table 1).

Compound **10a** was previously reported by Comins[2a] whereas derivatives **10b–e** were unknown.

2.2. Synthesis, hydrogenolysis and Suzuki coupling of the seven- and thirteen-membered ketene aminal diphenyl phosphates 5 and 6

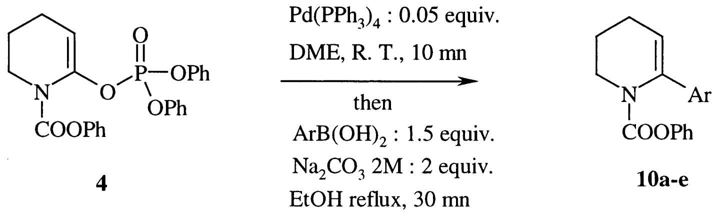
N-Boc lactams **2** and **3** were prepared in 88 and 73% yields, respectively, from the corresponding commercially available lactams by treatment with di-*tert*-butyldicarbonate in tetrahydrofuran, at room temperature in the presence of DMAP. The lithium enolates, obtained from **2** and **3** at −78°C with LDA (1.2 equiv.) in dry tetrahydrofuran in the presence of TMEDA (1.2 equiv.), were quenched with diphenyl chlorophosphate (1.2 equiv.) leading to vinyl phosphates **5** and **6** in good yields (83 and 96%, respectively).

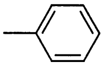
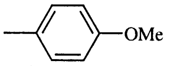
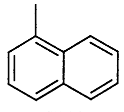
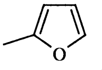
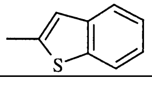
Hydrogenolysis of **5** and **6** according to the procedure previously described led to the corresponding unsaturated



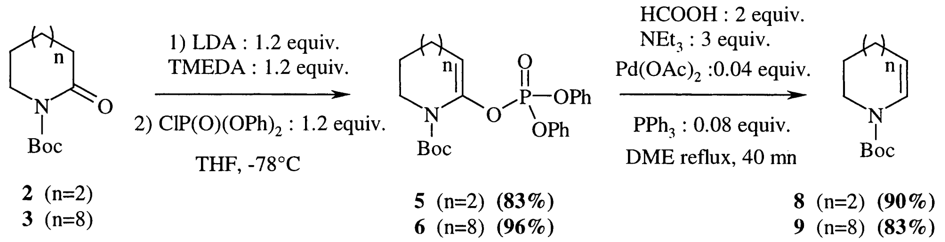
Scheme 2.

Table 1.



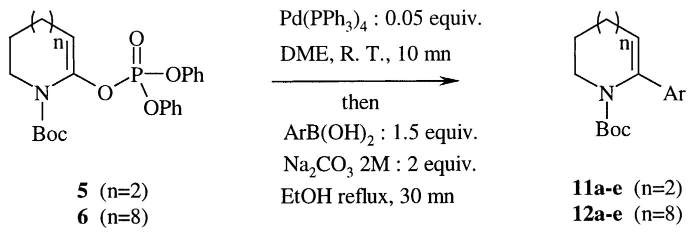
10	Ar	Yield (%)[a]
A		89
B		95
C		90
D		90
E		77

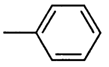
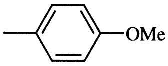
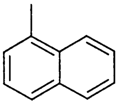
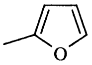
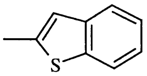
[a] Isolated yields.



Scheme 3.

Table 2.



Ar	*n*	**11**	Yield (%)[a]	*n*	**12**	Yield (%)[a]
	2	a	80	8	a	94
	2	b	79	8	b	83
	2	c	96	8	c	93
	2	d	74	8	d	94
	2	e	91	8	e	90

[a] Isolated yields.

carbamates **8** and **9** in 90 and 83% yields, respectively (Scheme 3).

Vinyl phosphates **5** and **6** were also used in Suzuki type reactions with some typical aryl or heteroaryl boronic acids to obtain medium-sized and large 2-substituted heterocyclic systems **11** and **12**. Table 2 summarizes the results of the palladium-catalyzed coupling reactions.[8]

In conclusion we have shown that an extension of the Suzuki reaction involving the coupling of boronic acids and lactam-derived vinyl phosphates allows, under mild conditions, an easy access to cyclic six-, seven- and thirteen-membered ene-carbamates, substituted on C_2 with aryl or heteroaryl groups. These derivatives constitute ideal precursors for the construction of complex heterocyclic systems likely to be of interest in medicinal chemistry. Studies are currently in progress in this area.

3. Experimental

3.1. General

Melting points were determined with a Büchi SMP-20 melting point apparatus and were uncorrected. IR spectra were recorded on a Perkin–Elmer FT PARAGON 1000 PC. ^{1}H- and ^{13}C NMR were recorded on a Bruker Avance DPX250 spectrometer (250.13 MHz, ^{1}H, 62.89 MHz, ^{13}C), multiplicities were determined by the DEPT 135 sequence. MS were recorded on a Perkin–Elmer SCIEX API 3000 spectrometer. All reactions were carried out in a flame-dried glassware under an argon atmosphere. Thin-layer chromatography (TLC) was carried out on Merck silica gel $60F_{254}$ precoated plates. 'Usual workup' means extraction with EtOAc, drying with $MgSO_4$, filtration and evaporation.

3.1.1. Phenyl 2-oxopiperidine-1-carboxylate (1). To a cold (−78°C) solution of δ-valerolactam (1 g, 10 mmol) in dry THF (50 mL) was added a solution of *n*-BuLi, 1.6 M in hexane (7.5 mL, 12 mmol). The reaction mixture was stirred for 2 h at −78°C and a solution of phenyl chloroformate freshly distilled (2.5 mL, 20 mmol) in dry THF (5 mL) was added dropwise. The mixture was stirred for 2 h at −78°C, allowed to warm to room temperature and treated with water (30 mL). After the usual workup and recrystallization in pentane (60 mL), **1** was obtained as a white solid (1.6 g, 73%). Mp: 117°C. IR (KBr): ν (cm^{-1}) 2944 (C–H); 1777 and 1676 (C=O); 1589, 1485 and 1454

(C=C). ^{1}H NMR (CDCl$_3$): δ (ppm) 1.90–1.93 (m, 4H, H_4 and H_5); 2.62 (t, 2H, H_3, $J_{3,4}$=6.5 Hz); 3.86 (t, 2H, H_6, $J_{5,6}$=6 Hz); 7.16–7.27 (m, 3H); 7.35–7.41 (m, 2H). ^{13}C NMR (CDCl$_3$): δ (ppm) 20.65 and 22.80 (2CH$_2$, C_4 and C_5); 35.15 (CH$_2$, C_3); 47.10 (CH$_2$, C_6); 121.60 (2CH); 126.15 (CH); 129.55 (2CH); 150.80 and 153.15 (2C); 171.40 (C, C_2). MS: *m/z* 220 (M+1).

3.1.2. *tert*-Butyl 2-oxoazepane-1-carboxylate (2). To a solution of ε-caprolactam (5.49 g, 48 mmol) in THF (120 mL) was added 4-dimethylaminopyridine (6.45 g, 52.8 mmol) and di-*tert*-butyldicarbonate (11.52 g, 52.8 mmol). The resulting mixture was stirred at room temperature for 25 h. After concentration and hydrolysis, the reaction mixture was extracted with EtOAc. The combined organic phases were washed with hydrochloric acid solution (5%), brine, dried over MgSO$_4$ and concentrated to give **2** as colorless oil (9.05 g, 88%). IR (NaCl film): ν (cm^{-1}) 2979 and 2933 (C–H); 1768 and 1715 (C=O). ^{1}H NMR (CDCl$_3$): δ (ppm) 1.52 (s, 9H, (CH_3)$_3$C); 1.73 (m, 6H, H_4, H_5 and H_6); 2.65 (m, 2H, H_3); 3.76 (m, 2H, H_7). ^{13}C NMR (CDCl$_3$): δ (ppm) 28.15 (3CH$_3$, (CH$_3$)$_3$C); 23.65, 28.80 and 29.35 (3CH$_2$, C_4, C_5 and C_6); 39.65 (CH$_2$, C_3); 46.25 (CH$_2$, C_7); 82.85 (C, (CH$_3$)$_3$$C$); 153.05 (C, O–C=O); 175.85 (C, C_2). MS: *m/z* 214 (M+1).

3.1.3. *tert*-Butyl 2-oxoazacyclotridecane-1-carboxylate (3). To a solution of 2-azacyclotridecanone (4.03 g, 20 mmol) in THF (40 mL) was added triethylamine (2.8 mL, 20 mmol), 4-dimethylaminopyridine (1.22 g, 20 mmol) and di-*tert*-butyldicarbonate (9 g, 40 mmol). The resulting mixture was stirred at room temperature for 25 h. After concentration and hydrolysis, the reaction mixture was extracted with EtOAc. The combined organic phases were washed with hydrochloric acid solution (5%), brine, dried over MgSO$_4$ and concentrated to give **3** as colorless oil (4.34 g, 73%). IR (NaCl film): ν (cm^{-1}) 2923 and 2861 (C–H); 1733 and 1693 (C=O). ^{1}H NMR (CDCl$_3$): δ (ppm) 1.27 (m, 14H, 7CH$_2$); 1.53 (m, 11H, (CH_3)$_3$C and H_4); 1.69–1.74 (m, 2H, H_{12}); 2.89–2.93 (m, 2H, H_{13}); 3.80–3.84 (m, 2H, H_3). ^{13}C NMR (CDCl$_3$): δ (ppm) 24.30, 25.05, 25.20, 25.35, 25.90, 26.65, 27.10, 27.75 and 28.05 (9CH$_2$); 28.20 (3CH$_3$, (CH$_3$)$_3$$C$); 38.05 (CH$_2$, C_{13}); 44.05 (CH$_2$, C_3); 82.70 (C, (CH$_3$)$_3$$C$); 153.90 (C, O–C=O); 177.10 (C, C_2). MS: *m/z* 298 (M+1).

3.1.4. Phenyl 6-[(diphenoxyphosphoryl)oxo]-3,4-dihydro-1(2*H*)-pyridinecarboxylate (4). To a cold (−78°C) solution of **1** (1 g, 4.56 mmol) in dry THF (40 mL) and *N*,*N*,*N*′,*N*′-tetramethylenediamine (0.85 mL, 5.47 mmol) was added a solution of LDA 2 M in heptane/THF (2.8 mL, 5.47 mmol). The reaction mixture was stirred at −78°C for 2 h and a solution of freshly distilled diphenyl chlorophosphate (1.15 mL, 5.47 mmol) was added dropwise into dry THF (5 mL). The mixture was stirred for 3 h at −78°C, allowed to warm to room temperature and treated with 5% ammonium hydroxide solution (30 mL). After the usual workup and flash chromatography on silica gel with petroleum ether/EtOAc/ triethylamine (80/15/5), **4** was obtained as a pale brown oil (1.68 g, 82%). IR (NaCl film): ν (cm^{-1}) 2936 (C–H); 1736 (C=O); 1591, 1493 and 1457 (C=C); 1380 (P=O). ^{1}H NMR (CDCl$_3$): δ (ppm) 1.82–1.87 (m, 2H, H_5); 2.22–2.26 (m, 2H, H_4); 3.74 (t, 2H, H_6, $J_{5,6}$=6 Hz); 5.24 (td, 1H, H_3, $J_{3,4}$=4 Hz and $J_{\mathrm{H,P}}$=3 Hz); 7.02–7.34 (m, 15H). ^{13}C NMR (CDCl$_3$): δ (ppm) 21.75 (CH$_2$, C_4); 22.75 (CH$_2$, C_5); 46.15 (CH$_2$, C_6); 101.20 (CH, C_3); 120.25, 121.55, 125.60, 129.30 and 129.85 (15CH); 124.95, 139.65, 150.45, 150.95 and 152.55 (5C). MS: *m/z* 452 (M+1).

3.1.5. *tert*-Butyl 7-[(diphenoxyphosphoryl)oxo]-2,3,4,5-tetrahydro-1*h*-azepine-1-carboxylate (5). The reaction was carried out as described above for the synthesis of compound **4** with **2** (0.97 g, 4.56 mmol). Flash chromatography with petroleum ether/EtOAc (80/20) gave **5** as a colorless oil (1.69 g, 83%). IR (NaCl film): ν (cm^{-1}) 2979 and 2930 (C–H); 1713 (C=O); 1690, 1590, 1491 and 1453 (C=C); 1303 (P=O). ^{1}H NMR (CDCl$_3$): δ (ppm) 1.47–1.56 (m, 11H, (CH_3)$_3$C and H_5); 1.67–1.80 (m, 2H, H_6); 2.09–2.14 (m, 2H, H_4); 3.55 (m, 2H, H_7); 5.45 (td, 1H, H_3, $J_{3,4}$=7 Hz and $J_{\mathrm{H,P}}$=3 Hz); 7.19–7.40 (m, 10H). ^{13}C NMR (CDCl$_3$): δ (ppm) 24.05 (CH$_2$, C_5); 24.50 (CH$_2$, C_4); 28.25 (3CH$_3$, (CH$_3$)$_3$$C$); 29.45 (CH$_2$, C_6); 46.70 (CH$_2$, C_7); 81.30 (C, (CH$_3$)$_3$$C$); 109.65 (CH, C_3); 120.15 and 120.25 (4CH); 125.55 (2CH); 129.90 (4CH); 145.25 (C, C_2); 150.60 and 150.70 (2C); 153.15 (C, C=O). MS: *m/z* 446 (M+1).

3.1.6. *tert*-Butyl 2-[(diphenoxyphosphoryl)oxo]aza-2-cyclotridecene-1-carboxylate (6). The reaction was carried out as described above for the synthesis of compound **4** with **3** (1.356 g, 4.56 mmol). Flash chromatography with petroleum ether/EtOAc (80/20) gave **6** as a colorless oil (2.32 g, 96%). IR (NaCl film): ν (cm^{-1}) 2931 and 2859 (C–H); 1715 (C=O); 1592, 1493 and 1457 (C=C); 1318 (P=O). ^{1}H NMR (CDCl$_3$): δ (ppm) 1.26–1.34 (m, 12H, 6CH$_2$); 1.40 (m, 11H, (CH_3)$_3$C and CH$_2$); 1.60–1.65 (m, 2H, H_{12}); 2.13 (m, 2H, H_4); 3.33–3.38 (m, 2H, H_{13}); 5.08 (m, 1H, H_3); 7.18–7.36 (m, 10H). ^{13}C NMR (CDCl$_3$): δ (ppm) 23.70, 24.40, 24.85, 25.10, 25.60, 26.30, 27.35 (9CH$_2$); 28.25 (3CH$_3$, (CH$_3$)$_3$C); 44.95 (CH$_2$, C_{13}); 80.90 (C, (CH$_3$)$_3$$C$); 117.90 (CH, C_3); 120.30 (4CH); 125.50 (2CH); 129.90 (4CH); 139.30 (C, C_2); 150.60 (2C); 154.20 (C, C=O). MS: *m/z* 530 (M+1).

3.1.7. Phenyl 3,4-dihydro-1(2*H*)-pyridinecarboxylate (7). To a solution of **4** (316 mg, 0.7 mmol), triphenylphosphine (15 mg, 0.056 mmol) and palladium(II) acetate (6 mg, 0.028 mmol) in DME (1.4 mL) was added a solution of triethylamine (300 μL, 2.1 mmol) and formic acid (55 μL, 1.4 mmol) in DME (1.4 mL). The reaction mixture was refluxed for 40 min, allowed to cool to room temperature and hydrolyzed with distilled water (20 mL). After the usual workup and flash chromatography on silica gel with petroleum ether/EtOAc (90/10), **7** was obtained as a white solid (112 mg, 79%). Mp: 61°C. IR (KBr): ν (cm^{-1}) 2925 (C–H); 1713 (C=O); 1651, 1596, 1487 and 1456 (C=C). ^{1}H NMR (CDCl$_3$): δ (ppm) 1.86–1.93 (m, 2H, H_5); 2.03–2.10 (m, 2H, H_4); 3.66–3.81 (m, 2H, H_6); 4.96–5.07 (m, 1H, H_3); 6.91–6.97 (m, 1H, H_2); 7.10–7.24 (m, 3H); 7.32–7.38 (m, 2H). ^{13}C NMR (CDCl$_3$): δ (ppm) 21.50 (CH$_2$, C_4); 21.65 (CH$_2$, C_5); 42.55 (CH$_2$, C_6); 107.60 (CH, C_3); 121.75 (2CH); 124.90 (CH, C_2); 125.25 (C); 125.55 (CH); 129.40 (2CH); 151.25 (C, C=O). MS: *m/z* 204 (M+1). Anal. Calcd for C$_{12}$H$_{13}$NO$_2$: C, 70.92; H, 6.45; N, 6.89. Found: C, 70.85; H, 6.47; N, 6.96.

3.1.8. *tert*-Butyl 2,3,4,5-tetrahydro-1*H*-azepine-1-carboxylate (8). The reaction was carried out as described above for the synthesis of compound **7** with **5** (312 mg, 0.7 mmol). Flash chromatography with petroleum ether/EtOAc (80/20) gave **8** as a colorless oil (124 mg, 90%). IR (NaCl film): ν (cm^{-1}) 2982 and 2930 (C–H); 1703 (C=O); 1654 (C=C). ^{1}H NMR (CDCl$_3$): δ (ppm) 1.48 (s, 9H, (CH_3)$_3$C); 1.70–1.80 (m, 4H, H_5 and H_6); 2.14–2.20 (m, 2H, H_4); 3.62–3.66 (m, 2H, H_7); 4.95 (m, 1H, H_3); 6.47 (m, 1H, H_2). ^{13}C NMR (CDCl$_3$): δ (ppm) 25.30 (CH$_2$, C_5); 26.30 (CH$_2$, C_4); 28.45 (3CH$_3$, (CH$_3$)$_3$C); 28.15 (CH$_2$, C_6); 47.00 (CH$_2$, C_7); 80.35 (C, (CH$_3$)$_3$*C*); 114.20 (CH, C_3); 130.70 (CH, C_2); 153.80 (C, C=*O*). MS: *m*/*z* 198 (M+1). Anal. Calcd for $C_{11}H_{19}NO_2$: C, 66.97; H, 9.71; N, 7.10. Found: C, 66.84; H, 9.80; N, 7.18.

3.1.9. *tert*-Butyl aza-2-cyclotridecene-1-carboxylate (9). The reaction was carried out as described above for the synthesis of compound **7** with **6** (371 mg, 0.7 mmol). Flash chromatography with petroleum ether gave **9** as a colorless oil (164 mg, 83%). IR (NaCl film): ν (cm^{-1}) 2928 and 2859 (C–H); 1707 (C=O); 1659 (C=C). ^{1}H NMR (CDCl$_3$): δ (ppm) 1.33–1.48 (m, 23H, (CH_3)$_3$C and 7CH$_2$); 1.58–1.65 (m, 2H, H_{12}); 2.03–2.07 (m, 2H, H_4); 3.45 (m, 2H, H_{13}); 4.94–5.01 (m, 1H, H_3); 6.57–6.81 (m, 1H, H_2). ^{13}C NMR (CDCl$_3$): δ (ppm) 24.05, 24.20, 25.60, 26.20, 26.35, 26.50, 26.75 and 27.40 (8CH$_2$); 28.45 (3CH$_3$, (*C*H$_3$)$_3$C); 30.05 (CH$_2$, C_4); 43.20 (CH$_2$, C_{13}); 80.35 (C, (CH$_3$)$_3$*C*); 111.55 (CH, C_3); 128.30 (CH, C_2); 153.85 (C, *C*=*O*). MS: *m*/*z* 282 (M+1). Anal. Calcd for $C_{17}H_{31}NO_2$: C, 72.55; H, 11.10; N, 4.98. Found: C, 72.70; H, 11.20; N, 4.82.

3.1.10. Phenyl 6-phenyl-3,4-dihydro-1(2*H*)-pyridinecarboxylate (10a). To a suspension of Pd(PPh$_3$)$_4$ (30 mg, 0.025 mmol) in DME (0.5 mL), **4** (226 mg, 0.5 mmol) was added and the mixture was stirred for 10 min at room temperature. Benzeneboronic acid (94 mg, 0.75 mmol) in a minimum of ethanol and aqueous Na$_2$CO$_3$ (2 M solution, 0.5 mL, 1 mmol) were then added. The reaction mixture was refluxed for 0.5 h and allowed to cool to room temperature. After the usual workup and flash chromatography on silica gel with petroleum ether/EtOAc (95/5), **10a** was obtained as a colorless oil (140 mg, 89%). IR (NaCl film): ν (cm^{-1}) 3058 and 2934 (C–H); 1735 (C=O); 1645, 1593, 1494 and 1455 (C=C). ^{1}H NMR (CDCl$_3$): δ (ppm) 1.92–2.03 (m, 2H, H_5); 2.30–2.37 (m, 2H, H_4); 3.83–3.88 (m, 2H, H_6); 5.49 (t, 1H, H_3, $J_{3,4}$=4 Hz); 6.66–6.74 (m, 2H); 7.05–7.41 (m, 8H). ^{13}C NMR (CDCl$_3$): δ (ppm) 23.65 and 23.70 (2CH$_2$, C_4 and C_5); 45.50 (CH$_2$, C_6); 116.90 (CH, C_3); 121.30, 125.25, 125.30, 127.40, 128.30 and 129.10 (10CH); 120.15, 129.50 and 139.70 (3C); 151.00 (C, *C*=*O*). MS: *m*/*z* 280 (M+1). Anal. Calcd for $C_{18}H_{17}NO_2$: C, 77.40; H, 6.13; N, 5.01. Found: C, 77.35; H, 6.16; N, 4.95.

3.1.11. Phenyl 6-(*p*-methoxyphenyl)-3,4-dihydro-1(2*H*)-pyridinecarboxylate (10b). The reaction was carried out as described above for the synthesis of compound **10a** with *p*-methoxybenzeneboronic acid (114 mg, 0.75 mmol). Flash chromatography with petroleum ether/EtOAc (80/20) gave **10b** as a colorless oil (147 mg, 95%). IR (NaCl film): ν (cm^{-1}) 2935 (C–H); 1709 (C=O); 1642, 1609, 1593, 1512 and 1456 (C =C); 1201 (C–O–C). ^{1}H NMR (CDCl$_3$): δ (ppm) 1.92–2.00 (m, 2H, H_5); 2.27–2.34 (m, 2H, H_4); 3.75 (s, 3H, OCH_3); 3.79–3.84 (m, 2H, H_6); 5.39 (t, 1H, H_3, $J_{3,4}$=4 Hz); 6.74–6.85 (m, 4H); 6.81–6.85 (m, 1H); 7.05–7.21 (m, 2H); 7.27–7.30 (m, 2H). ^{13}C NMR (CDCl$_3$): δ (ppm) 23.60 (CH$_2$, C_4); 23.80 (CH$_2$, C_5); 45.60 (CH$_2$, C_6); 55.40 (CH$_3$, OCH$_3$); 113.70 (2CH); 115.60 (CH, C_3); 121.40 (2CH); 125.30 (CH); 126.40 (2CH); 129.15 (2CH); 132.50, 139.35, 151.15, 153.45 and 159.05 (5C). MS: *m*/*z* 310 (M+1). Anal. Calcd for $C_{19}H_{19}NO_3$: C, 73.77; H, 6.19; N, 4.53. Found: C, 73.85; H, 6.13; N, 4.57.

3.1.12. Phenyl 6-(1-naphtyl)-3,4-dihydro-1(2*H*)-pyridinecarboxylate (10c). The reaction was carried out as described above for the synthesis of compound **10a** with 1-naphtylboronic acid (130 mg, 0.75 mmol). Flash chromatography with petroleum ether/EtOAc (95/5) gave **10c** as a white solid (148 mg, 90%) recrystallized in pentane. Mp: 112°C. IR (KBr): ν (cm^{-1}) 3060, 2931 (C–H); 1705 (C=O); 1639, 1591 and 1484 (C=C). ^{1}H NMR (CDCl$_3$): δ (ppm) 2.12 (m, 2H, H_5); 2.43 (m, 2H, H_4); 4.05 (m, 2H, H_6); 5.45 (t, 1H, H_3, $J_{3,4}$=4 Hz); 6.27 (m, 2H); 6.90–7.08 (m, 3H); 7.35–7.45 (m, 4H); 7.71–7.74 (m, 1H); 7.80–7.84 (m, 1H); 7.99–8.03 (m, 1H). ^{13}C NMR (CDCl$_3$): δ (ppm) 23.45 (CH$_2$, C_4); 23.60 (CH$_2$, C_5); 44.90 (CH$_2$, C_6); 117.15 (CH, C_3); 120.95 (2CH); 124.80, 125.00, 125.45, 125.55, 125.65, 126.15, 127.75 and 128.50 (8CH); 128.85 (2CH); 131.15, 133.50, 137.95, 138.05, 150.65 and 152.75 (6C). MS: *m*/*z* 330 (M+1). Anal. Calcd for $C_{22}H_{19}NO_2$: C, 80.22; H, 5.81; N, 4.25. Found: C, 80.32; H, 5.88; N, 4.26.

3.1.13. Phenyl 6-(2-furyl)-3,4-dihydro-1(2*H*)-pyridinecarboxylate (10d). The reaction was carried out as described above for the synthesis of compound **10a** with 2-furylboronic acid (84 mg, 0.75 mmol). Flash chromatography with petroleum ether/EtOAc (95/5) gave **10d** as a colorless oil (121 mg, 90%). IR (NaCl film): ν (cm^{-1}) 2937 (C–H); 1731 (C=O); 1594, 1493 and 1457 (C=C), 1164 (C–O–C). ^{1}H NMR (CDCl$_3$): δ (ppm) 1.89–1.99 (m, 2H, H_5); 2.28–2.35 (m, 2H, H_4); 3.79 (t, 2H, H_6, $J_{5,6}$=5.5 Hz); 5.69 (t, 1H, H_3, $J_{3,4}$=4 Hz); 6.31–6.34 (m, 2H, $H_{3'}$ and $H_{4'}$); 6.96–6.99 (m, 2H); 7.08–7.17 (m, 1H); 7.21–7.32 (m, 3H, 2Harom and $H_{5'}$). ^{13}C NMR (CDCl$_3$): δ (ppm) 23.05 (CH$_2$, C_4); 23.55 (CH$_2$, C_5); 45.05 (CH$_2$, C_6); 105.50 (CH, $C_{4'}$); 111.05 (CH, $C_{3'}$); 115.95 (CH, C_3); 121.35 (2CH); 125.35 (CH); 129.20 (2CH); 130.90 (C); 141.05 (CH, $C_{5'}$); 151.15, 151.80 and 156.30 (3C). MS: *m*/*z* 270 (M+1). Anal. Calcd for $C_{16}H_{15}NO_3$: C, 71.36; H, 5.61; N, 5.20. Found: C, 71.28; H, 5.62; N, 5.26.

3.1.14. Phenyl 6-(2-benzo[*b*]thiophenyl)-3,4-dihydro-1(2*H*)-pyridinecarboxylate (10e). The reaction was carried out as described above for the synthesis of compound **10a** with 2-benzo[*b*]thiophenylboronic acid (136 mg, 0.75 mmol). Flash chromatography with petroleum ether/EtOAc (95/5) gave **10e** as a white solid (129 mg, 77%) recrystallized in pentane. Mp: 129°C. IR (KBr): ν (cm^{-1}) 2935 (C–H); 1727 (C=O); 1641, 1589, 1494 and 1454 (C=C). ^{1}H NMR (CDCl$_3$): δ (ppm) 1.92–2.01 (m, 2H, H_5); 2.33–2.40 (m, 2H, H_4); 3.81–3.86 (m, 2H, H_6); 5.79 (t, 1H, H_3, $J_{3,4}$=4 Hz); 6.87–6.91 (m, 2H); 7.06–7.28 (m, 6H); 7.65–7.75 (m, 2H). ^{13}C NMR (CDCl$_3$): δ (ppm) 23.55 (CH$_2$, C_4); 23.65 (CH$_2$, C_5); 45.65 (CH$_2$, C_6); 119.10 (CH,

C_3); 119.30, 121.45, 122.30, 123.55, 124.30, 124.45 and 125.45 (7CH); 129.20 (2CH); 134.50, 138.80, 139.90, 142.95, 151.10 and 153.65 (6C). MS: *m/z* 336 (M+1). Anal. Calcd for $C_{20}H_{17}NO_2S$: C, 71.62; H, 5.11; N, 4.18. Found: C, 71.58; H, 5.15; N, 4.20.

3.1.15. *tert*-Butyl 7-phenyl-2,3,4,5-tetrahydro-1*H*-azepine-1-carboxylate (11a). The reaction was carried out as described above for the synthesis of compound **10a** with **5** (223 mg, 0.5 mmol). Flash chromatography with petroleum ether/EtOAc (95/5) gave **11a** as a white solid (109 mg, 80%). Mp: 83°C. IR (KBr): ν (cm^{-1}) 2976 and 2934 (C–H); 1697 (C=O); 1636, 1493 and 1447 (C=C). ^1H NMR ($CDCl_3$): δ (ppm) 1.09 (s, 9H, $(CH_3)_3C$); 1.47–1.56 (m, 4H, H_5 and H_6); 1.85 (m, 2H, H_7); 2.30 (m, 2H, H_4); 5.87 (t, 1H, H_3, $J_{3,4}$=6.5 Hz); 7.23–7.30 (m, 5H). ^{13}C NMR ($CDCl_3$): δ (ppm) 24.30 (CH_2, C_5); 27.65 (CH_2, C_4); 28.05 ($3CH_3$, $(CH_3)_3C$); 29.80 (CH_2, C_6); 48.05 (CH_2, C_7); 79.85 (C, $(CH_3)_3C$); 122.55 (CH, C_3); 125.10 (2CH); 127.35 (CH); 128.20 (2CH); 139.85 (C); 144.55 (C, C_2); 154.20 (C, C=O). MS: *m/z* 274 (M+1). Anal. Calcd for $C_{17}H_{23}NO_2$: C, 74.69; H, 8.48; N, 5.12. Found: C, 74.69; H, 8.56; N, 4.99.

3.1.16. *tert*-Butyl 7-(*p*-methoxyphenyl)-2,3,4,5-tetrahydro-1*H*-azepine-1-carboxylate (11b). The reaction was carried out as described above for the synthesis of compound **10a** with **5** (223 mg, 0.5 mmol) and *p*-methoxybenzeneboronic acid (114 mg, 0.75 mmol). Flash chromatography with petroleum ether/EtOAc (95/5) gave **11b** as a white solid (112 mg, 74%). Mp: 79°C. IR (KBr): ν (cm^{-1}) 2969 and 2927 (C–H); 1701 (C=O); 1643, 1608, 1511 and 1444 (C=C); 1249 (C–O–C). ^1H NMR ($CDCl_3$): δ (ppm) 1.09 (s, 9H, $(CH_3)_3C$); 1.44 (m, 4H, H_5 and H_6); 1.81 (m, 2H, H_7); 2.24 (m, 2H, H_4); 3.78 (s, 3H, OCH_3); 5.74 (t, 1H, H_3, $J_{3,4}$=6.5 Hz); 6.80 (d, 2H, $H_{3'}$ and $H_{5'}$, J_{ortho}=9 Hz); 7.21 (d, 2H, $H_{2'}$ and $H_{6'}$, J_{ortho}=9 Hz). ^{13}C NMR ($CDCl_3$): δ (ppm) 24.40 (CH_2, C_5); 27.55 (CH_2, C_4); 28.10 ($3CH_3$, $(CH_3)_3C$); 29.85 (CH_2, C_6); 48.00 (CH_2, C_7); 55.45 (CH_3, OCH_3); 79.70 (C, $(CH_3)_3C$); 113.50 and 114.00 (2CH, $C_{3'}$ and $C_{5'}$); 120.95 (CH, C_3); 126.00 and 126.20 (2CH, $C_{2'}$ and $C_{6'}$); 132.55 (C, $C_{1'}$); 144.20 (C, C_2); 154.25 (C, *C*=*O*); 159.15 (C, $C_{4'}$). MS: *m/z* 304 (M+1). Anal. Calcd for $C_{18}H_{25}NO_3$: C, 71.26; H, 8.31; N, 4.62. Found: C, 71.22; H, 8.40; N, 4.73.

3.1.17. *tert*-Butyl 7-(1-naphtyl)-2,3,4,5-tetrahydro-1*H*-azepine-1-carboxylate (11c). The reaction was carried out as described above for the synthesis of compound **10a** with **5** (223 mg, 0.5 mmol) and 1-naphtylboronic acid (130 mg, 0.75 mmol). Flash chromatography with petroleum ether/EtOAc (95/5) gave **11c** as a white solid (155 mg, 96%). Mp: 116°C. IR (KBr): ν (cm^{-1}) 2930 (C–H); 1690 (C=O); 1643, 1508 and 1441 (C=C). ^1H NMR ($CDCl_3$): δ (ppm) 0.76 (s, 9H, $(CH_3)_3C$); 1.63–1.72 (m, 2H, H_5); 1.87–1.94 (m, 2H, H_6); 2.39–2.46 (m, 2H, H_4); 3.89–3.93 (m, 2H, H_7); 5.66 (t, 1H, H_3, $J_{3,4}$=6 Hz); 7.36–7.44 (m, 4H); 7.51–7.83 (m, 2H); 8.23–8.26 (m, 1H). ^{13}C NMR ($CDCl_3$): δ (ppm) 24.10 (CH_2, C_5); 27.80 ($3CH_3$, $(CH_3)_3C$); 27.95 (CH_2, C_4); 29.25 (CH_2, C_6); 49.30 (CH_2, C_7); 79.90 (C, $(CH_3)_3C$); 125.20 (CH, C_3); 124.45, 125.05, 125.55, 125.75, 125.85, 127.55 and 128.30 (7CH); 131.50, 133.95, 138.80 and 141.75 (4C); 154.25 (C, *C*=*O*). MS: *m/z* 324 (M+1). Anal. Calcd for $C_{21}H_{25}NO_2$: C, 77.99; H, 7.79; N, 4.33. Found: C, 78.13; H, 7.88; N, 4.30.

3.1.18. *tert*-Butyl 7-(2-furyl)-2,3,4,5-tetrahydro-1*H*-azepine-1-carboxylate (11d). The reaction was carried out as described above for the synthesis of compound **10a** with **5** (223 mg, 0.5 mmol) and 2-furylboronic acid (84 mg, 0.75 mmol). Flash chromatography with petroleum ether/EtOAc (95/5) gave **11d** as a pale yellow solid (97 mg, 74%). Mp: 87°C. IR (KBr): ν (cm^{-1}) 2981 and 2933 (C–H); 1697 (C=O); 1648, 1491 and 1449 (C=C); 1158 (C–O–C). ^1H NMR ($CDCl_3$): δ (ppm) 1.27 (s, 9H, $(CH_3)_3C$); 1.45–1.50 (m, 4H, H_5 and H_6); 1.80 (m, 2H, H_7); 2.26 (m, 2H, H_4); 6.04 (t, 1H, H_3, $J_{3,4}$=7 Hz); 6.17 (m, 1H, $H_{4'}$); 6.35 (m, 1H, $H_{3'}$); 7.31 (m, 1H, $H_{5'}$). ^{13}C NMR ($CDCl_3$): δ (ppm) 24.40 (CH_2, C_5); 27.05 (CH_2, C_4); 28.20 ($3CH_3$, $(CH_3)_3C$); 29.90 (CH_2, C_6); 47.45 (CH_2, C_7); 79.95 (C, $(CH_3)_3C$); 105.15 (CH, $C_{4'}$); 111.20 (CH, $C_{3'}$); 121.50 (CH, C_3); 135.95 (C); 141.40 (CH, $C_{5'}$); 153.00 and 154.10 (2C). MS: *m/z* 264 (M+1). Anal. Calcd for $C_{15}H_{21}NO_3$: C, 68.42; H, 8.04; N, 5.32. Found: C, 68.42; H, 7.98; N, 5.21.

3.1.19. *tert*-Butyl 7-(benzo[*b*]thiophenyl)-2,3,4,5-tetrahydro-1*H*-azepine-1-carboxylate (11e). The reaction was carried out as described above for the synthesis of compound **10a** with **5** (223 mg, 0.5 mmol) and 2-benzo[*b*]thiophenylboronic acid (136 mg, 0.75 mmol). Flash chromatography with petroleum ether/EtOAc (95/5) gave **11e** as a white solid (150 mg, 91%). Mp: 153°C. IR (KBr): ν (cm^{-1}) 2972 and 2918 (C–H); 1695 (C=O); 1636, 1519, 1457 and 1439 (C=C). ^1H NMR ($CDCl_3$): δ (ppm) 1.22 (s, 9H, $(CH_3)_3C$); 1.51 (m, 2H, H_5); 1.82–1.87 (m, 2H, H_6); 2.28–2.32 (m, 2H, H_4); 3.43–3.59[†] (m, 2H, H_7); 6.09 (t, 1H, H_3, $J_{3,4}$=6.5 Hz); 7.11 (s, 1H, $H_{2'}$); 7.25–7.30 (m, 2H); 7.63–7.75 (m, 2H). ^{13}C NMR ($CDCl_3$): δ (ppm) 24.25 (CH_2, C_5); 27.55 (CH_2, C_4); 28.15 ($3CH_3$, $(CH_3)_3C$); 29.75 (CH_2, C_6); 47.40 (CH_2, C_7); 80.15 (C, $(CH_3)_3C$); 119.10 (CH, $C_{2'}$); 122.20, 123.40, 124.30 and 124.40 (4CH); 125.25 (CH, C_3); 139.00, 139.50, 140.15 and 143.60 (4C); 154.00 (C, *C*=*O*). MS: *m/z* 330 (M+1). Anal. Calcd for $C_{19}H_{23}NO_2S$: C, 69.27; H, 7.04; N, 4.25. Found: C, 69.30; H, 7.10; N, 4.24.

3.1.20. *tert*-Butyl 2-phenylaza-2-cyclotridecene-1-carboxylate (12a). The reaction was carried out as described above for the synthesis of compound **10a** with **6** (265 mg, 0.5 mmol). Flash chromatography with petroleum ether/EtOAc (95/5) gave **12a** as a colorless oil (169 mg, 94%). IR (NaCl film): ν (cm^{-1}) 2938 and 2859 (C–H); 1698 (C=O); 1638, 1601, 1494 and 1460 (C=C). ^1H NMR ($CDCl_3$): δ (ppm) 1.37–1.42 (m, 23H, $(CH_3)_3C$ and $7CH_2$); 1.76–1.78 (m, 2H, H_{12}); 2.25–2.32 (m, 2H, H_4); 3.57 (m, 2H, H_{13}); 5.55 (m, 1H, H_3); 7.27–7.32 (m, 5H). ^{13}C NMR ($CDCl_3$): δ (ppm) 23.90, 25.05, 26.75 and 28.10 ($9CH_2$); 28.05 ($3CH_3$, $(CH_3)_3C$); 48.35 (CH_2, C_{13}); 79.70 (C, $(CH_3)_3C$); 127.35 (2CH); 127.90 (CH); 128.45 (2CH); 128.80 (CH, C_3); 138.50 and 139.75 (2C); 155.05 (C, *C*=*O*). MS: *m/z* 359 (M+1). Anal. Calcd for $C_{23}H_{35}NO_2$: C, 77.27; H, 9.87; N, 3.92. Found: C, 77.11; H, 9.99; N, 4.10.

[†] Obtained from CH correlation.

3.1.21. *tert*-Butyl 2-(*p*-methoxyphenyl)aza-2-cyclotridecene-1-carboxylate (12b). The reaction was carried out as described above for the synthesis of compound **10a** with **6** (265 mg, 0.5 mmol) and *p*-methoxybenzylboronic acid (114 mg, 0.75 mmol). Flash chromatography with petroleum ether/EtOAc (95/5) gave **12b** as a white solid (167 mg, 86%). IR (KBr): ν (cm^{-1}) 2975 and 2935 (C–H); 1692 (C=O); 1636, 1610, 1513 and 1452 (C=C); 1249 (C–O–C). ^{1}H NMR (CDCl$_3$): δ (ppm) 1.18–1.41 (m, 23H, $(C\mathit{H}_3)_3C$ and 7CH$_2$); 1.76–1.79 (m, 2H, H_{12}); 2.26 (m, 2H, H_4); 3.52 (m, 2H, H_{13}); 3.81 (s, 3H, OCH$_3$): 5.48 (m, 1H, H_3); 6.86 (d, 2H, $H_{3'}$ and $H_{5'}$, J_{ortho}=8.5 Hz); 7.23 (d, 2H, $H_{2'}$ and $H_{6'}$, J_{ortho}=8.5 Hz). ^{13}C NMR (CDCl$_3$): δ (ppm) 23.90, 25.10, 26.75 and 28.05 (9CH$_2$); 28.20 (3CH$_3$, $(\mathit{C}H_3)_3C$); 48.25 (CH$_2$, C_{13}); 55.35 (CH$_3$, OCH$_3$); 79.55 (C, $(CH_3)_3\mathit{C}$); 113.30 (2CH, $C_{3'}$ and $C_{5'}$); 127.80 (CH, C_3); 129.65 (2CH, $C_{2'}$ and $C_{6'}$); 133.55 (C, $C_{1'}$); 139.30 (C, C_2); 155.15 (C, C=O); 158.80 (C, $C_{4'}$). MS: *m/z* 389 (M+1). Anal. Calcd for $C_{24}H_{37}NO_3$: C, 74.38; H, 9.62; N, 3.61. Found: C, 74.32; H, 9.70; N, 3.55.

3.1.22. *tert*-Butyl 2-(1-naphtyl)aza-2-cyclotridecene-1-carboxylate (12c). The reaction was carried out as described above for the synthesis of compound **10a** with **6** (265 mg, 0.5 mmol) and 1-naphtylboronic acid (130 mg, 0.75 mmol). Flash chromatography with petroleum ether/EtOAc (95/5) gave **12c** as a colorless oil (190 mg, 93%). IR (NaCl film): ν (cm^{-1}) 2929 and 2856 (C–H); 1699 (C=O); 1640, 1591 and 1460 (C=C). ^{1}H NMR (CDCl$_3$): δ (ppm) 0.87 (m, 8H, 4CH$_2$); 1.18–1.58 (m, 17H, $(C\mathit{H}_3)_3C$ and 4CH$_2$); 1.91 (m, 2H, H_4); 3.65 (m, 2H, H_{13}); 5.75 (m, 1H, H_3); 7.41–7.48 (m, 4H); 7.76–7.85 (m, 2H); 8.12 (m, 1H). ^{13}C NMR (CDCl$_3$): δ (ppm) 24.00, 24.95, 25.20, 25.85, 25.90, 27.10, 27.85, 28.20 and 28.70 (9CH$_2$); 27.95 (3CH$_3$, $(\mathit{C}H_3)_3C$); 44.05 (CH$_2$, C_{13}); 79.95 (C, $(CH_3)_3\mathit{C}$); 125.20 (2CH); 125.75, 125.85 and 127.05 (3CH); 127.95 (CH, C_3); 128.20 (2CH); 128.40, 132.45, 133.60 and 136.65 (4C); 154.90 (C, C=O). MS: *m/z* 409 (M+1). Anal. Calcd for $C_{27}H_{37}NO_2$: C, 79.56; H, 9.15; N, 3.44. Found: C, 79.32; H, 9.30; N, 3.26.

3.1.23. *tert*-Butyl 2-(2-furyl)aza-2-cyclotridecene-1-carboxylate (12d). The reaction was carried out as described above for the synthesis of compound **10a** with **6** (265 mg, 0.5 mmol) and 2-furylboronic acid (84 mg, 0.75 mmol). Flash chromatography with petroleum ether/EtOAc (95/5) gave **12d** as a colorless oil (164 mg, 94%). IR (NaCl film): ν (cm^{-1}) 2931 and 2858 (C–H); 1701 (C=O); 1464 (C=C); 1156 (C–O–C). ^{1}H NMR (CDCl$_3$): δ (ppm) 1.26–1.62 (m, 23H, $(C\mathit{H}_3)_3C$ and 7CH$_2$); 1.70 (m, 2H, H_{12}); 2.49 (m, 2H, H_4); 3.49 (m, 2H, H_{13}); 5.54 (m, 1H, H_3); 6.24 (m, 1H, $H_{4'}$); 6.40 (m, 1H, $H_{3'}$); 7.39 (m, 1H, $H_{5'}$). ^{13}C NMR (CDCl$_3$): δ (ppm) 23.90, 25.20, 25.55, 25.90, 26.05, 26.15, 27.20 and 28.40 (8CH$_2$); 27.55 (CH$_2$, C_4); 28.20 (3CH$_3$, $(\mathit{C}H_3)_3C$); 48.45 (CH$_2$, C_{13}); 79.60 (C, $(CH_3)_3\mathit{C}$); 108.90 (CH, $C_{4'}$); 110.95 (CH, $C_{3'}$); 129.75 (C); 130.60 (CH, C_3); 131.00 (C); 141.70 (CH, $C_{5'}$); 152.20 and 155.35 (2C). MS: *m/z* 349 (M+1). Anal. Calcd for $C_{21}H_{33}NO_3$: C, 72.58; H, 9.57; N, 4.03. Found: C, 72.31; H, 9.70; N, 4.20.

3.1.24. *tert*-Butyl 2-(benzo[*b*]thiophenyl)aza-2-cyclotridecene-1-carboxylate (12e). The reaction was carried out as described above for the synthesis of compound **10a** with **6** (265 mg, 0.5 mmol) and 2-benzo[*b*]thiophenylboronic acid (136 mg, 0.75 mmol). Flash chromatography with petroleum ether/EtOAc (95/5) gave **12e** as a white solid (187 mg, 90%). Mp: 116°C. IR (KBr): ν (cm^{-1}) 2929 and 2859 (C–H); 1694 (C=O); 1633, 1458 and 1391 (C=C). ^{1}H NMR (CDCl$_3$): δ (ppm) 1.25–1.56 (m, 23H, $(C\mathit{H}_3)_3C$ and 7CH$_2$); 1.77 (m, 2H, H_{12}); 2.53 (m, 2H, H_4); 3.52 (m, 2H, H_{13}); 5.74 (m, 1H, H_3); 7.22–7.32 (m, 3H); 7.71–7.80 (m, 2H). ^{13}C NMR (CDCl$_3$): δ (ppm) 23.90, 24.15, 25.05, 26.35 and 27.55 (8CH$_2$); 28.30 (CH$_2$, C_4); 28.45 (3CH$_3$, $(\mathit{C}H_3)_3C$); 48.10 (CH$_2$, C_{13}); 80.05 (C, $(CH_3)_3\mathit{C}$); 121.65 (C); 122.20, 123.30 and 123.60 (3CH); 124.40 (CH, C_3); 124.45 (2CH); 132.20, 133.75 and 139.60 (3C); 155.00 (C, C=O). MS: *m/z* 415 (M+1). Anal. Calcd for $C_{25}H_{35}NO_2S$: C, 72.60; H, 8.53; N, 3.39. Found: C, 72.56; H, 8.52; N, 3.44.

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