Tetrahedron 67 (2011) 6833–6837

Contents lists available at ScienceDirect

Tetrahedron

journal homepage: www.elsevier.com/locate/tet

$InCl_3$-assisted one-pot synthesis of 1-aminocarbazoles

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ARTICLE INFO

Article history:
Received 6 May 2011
Received in revised form 8 June 2011
Accepted 24 June 2011
Available online 30 June 2011

Keywords:
1-Amminocarbazoles
Indium chloride
One-pot reactions
Domino reactions
Lewis acids

ABSTRACT

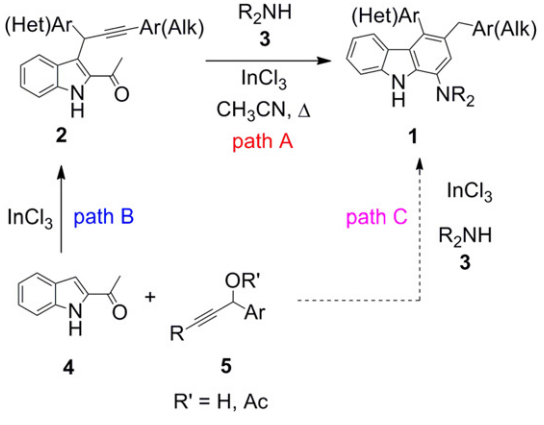
A novel $InCl_3$-mediated one-pot reaction leading to 1-aminocarbazoles is reported. Starting from easily available 2-acetyl-1*H*-indole, the reaction involves the alkylation of C-3 with a prop-2-yn-1-ol followed by a domino aminobenzannulation reaction in the presence of a secondary amine. The indium salt is most likely involved as catalyst in all three steps of the one-pot reaction. Starting from 2-acetyl-1*H*-indole and a series of prop-2-yn-1-ols and secondary amines a small library of products has been obtained.

1. Introduction

Carbazole derivatives are widely utilized in medicinal,[1] organic,[2] and material chemistry.[3] In particular, 1-aminocarbazoles have been identified as Bcl-2 protein inhibitors,[4] NPY5 antagonists,[5] and anion receptors.[6] Due to their relevance, in the last decades many synthetic approaches have been developed in order to obtain carbazoles bearing different functionalities. However, only a few reports on the synthesis of 1-aminocarbazoles have appeared in the literature. The reported methods involve sequential electrophilic nitration/hydrogenation reactions on the carbazole nucleus,[7] intramolecular Pd(II)-mediated oxidative coupling of diphenylamine derivatives,[8] and [3+3]carbocyclisation reactions of *C*-heteroarylimines with α,β-unsaturated Fischer carbene complexes.[9]

Our research group has been interested in the development of domino and multicomponent reactions for the construction of heterocyclic rings from simple starting materials. Following these strategies, during the last five years we achieved the synthesis of pyrazino[1,2-*a*]indoles,[10] 4-aminoquinolines, and 4-amino[1,8]naphthyridines,[11] [1,4]oxazino[4,3-*a*]indoles,[12] 2,2′-biindolyls,[13] pyrrolo[1,2-*a*]indol-2-carbaldehydes,[14] quinolines,[15] 4-substituted-2-phenylimidazoles,[16] isoxazolino[4,5-*c*]quinolines,[17] pyrrolo[1,2-*a*]pyrazines,[18] pyrimido[1,6-*a*]indolones,[19] dihydroisobenzofurans,[20] and isoquinolines.[21,18] All reported syntheses proceed under Lewis acid and/or transition metals catalysis and involve a nucleophilic attack of a hetero- or carbon-based nucleophile over a carbon–carbon triple bond.[22] Moreover, in a recent work[23] we reported an indium(III)-promoted domino aminobenzannulation reaction giving rise to 1-aminocarbazoles **1** starting from 2-acyl-3-propargyl-1*H*-indoles **2** and pyrrolidine **3a**, Scheme 1, path A.

Also the high-yielding synthesis of 2-acyl-3-propargyl-1*H*-indoles **2** was achieved by $InCl_3$-catalyzed propargylation of 2-acyl-1*H*-indole **4** with prop-2-yn-1-ols, or the corresponding acetates, **5**,[24] Scheme 1, path B.



Scheme 1.

With these results in hand, in this work we have explored an indium(III)-promoted multicomponent reaction (MCR) for the synthesis of 1-aminocarbazoles **1** starting directly from 2-acyl-1*H*-

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doi:10.1016/j.tet.2011.06.091

indole **4**, propynyl alcohols or propynyl acetates **5** and a secondary amine **3**, Scheme 1, Path C.

MCRs allow the coupling of three or more simple and flexible building blocks in a one-pot operation, giving rise to complex structures by simultaneous formation of two or more bonds, according to the domino principle. Multicomponent reactions fulfill the requirements of an environmentally friendly process by reducing the number of synthetic steps, the energy consumption, and the waste production. Moreover, over the past 10 years industrial and academic researchers have transformed this powerful technology into one of the most efficient and economic tools for combinatorial and parallel synthesis, as demonstrated by the increase in the literature devoted to this research field.[25]

It is worth to note that indium catalysis has been applied in MCRs for the synthesis of heterocyclic systems, such as imidazoles,[26] piperidines,[27] pirazolines,[28] tetrahydoquinolines,[29] dihydropyrimidines,[30] and heterocycle-annulated pyrimidines.[31]

2. Results and discussion

2-Acylindole **4** was easily prepared in multigram scale starting from indole-2-carboxylic acid and methyllithium.[32] Propynyl alcohols **5** could be easily obtained by reaction between the appropriate aldehyde and terminal alkyne in the presence of butyllithium, alcohols were converted into the corresponding acetates with acetic anhydride in pyridine.[33]

The optimal MCR conditions were investigated using the 2-acetyl-1*H*-indole **4**, 3-phenyl-1-*p*-tolylprop-2-ynyl acetate **5a**, and pyrrolidine **3a** as model system, Table 1. All reactions were run overnight in a screwed-cap tube at 75 °C in dry acetonitrile using the following molar ratios: **4**, **5a**, **3a**, $InCl_3$=1:1:1.2:0.1.

In a first run (entry 1, method A, multicomponent approach) the catalyst was added to a solution containing **4**, **5a**, and **3a**, and the obtained mixture was then heated at reflux. However, under these conditions, 2-acetyl-1*H*-indole **4** was recovered unreacted even after a prolonged reaction time. On the contrary, good yield of the desired 1-aminocarbazole **1a** could be obtained adding up the reactants as follows: **4** and **5a** were dissolved together with the catalyst in dry acetonitrile and the reaction mixture was stirred for 10 min, then the amine **3a** was added and the solution warmed overnight, (entry 2, method B, one-pot approach). The deferred addition of the secondary amine to the reaction mixture is probably required to avoid a Lewis acid–Lewis base interaction between $InCl_3$ and pyrrolidine 3 with consequent catalyst deactivation.

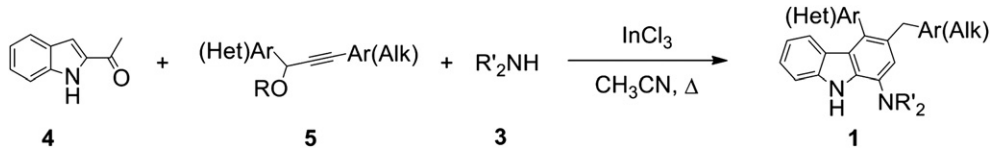
Starting from these results a small library of 1-aminocarbazoles **1a**–**h** has been prepared starting from 2-acetyl-1*H*-indole **4**, a series of propynyl alcohols or propynyl acetates **5a**–**g** and secondary amines **3a**, **b** under $InCl_3$ catalysis, Table 1.

Compounds **1** have been obtained in moderate to good yields after flash chromatographic purification over silica gel.

It is worth to note that propynyl alcohols work better than the corresponding propynyl acetates (cf. entry 2 and 3), so we moved up our attention to alcohols, which were synthesized avoiding the tedious acylation steps.

In order to evaluate the generality of our protocol, different substituted propynyl alcohols were tested. The synthetic strategy proved to be effective with both electron withdrawing and electron donating aryl substituent as well as with aliphatic and heterocyclic substituent.

Table 1
1-Aminocarbazoles **1a**–**h**



4 **5** **3** **1**

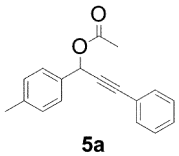
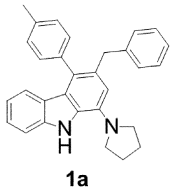
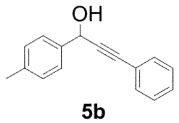
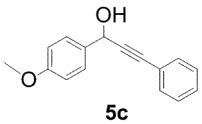
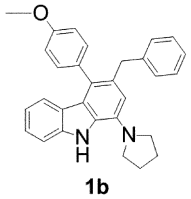
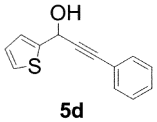
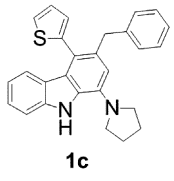
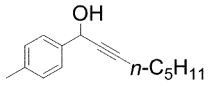
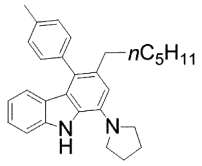
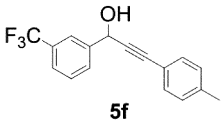
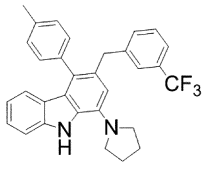
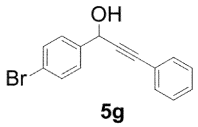
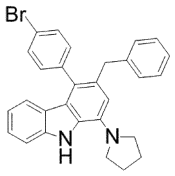
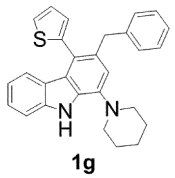
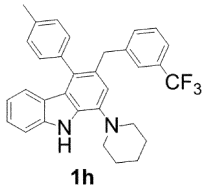
Entry	Propynyl alcohol or acetate **5**	Secondary amine **3**	Method	Product **1**	Yield[a] (%)
1	 **5a**	 **3a**	A	 **1a**	—
2	**5a**	**3a**	B	**1a**	63
3	 **5b**	**3a**	B	**1a**	78
4	 **5c**	**3a**	B	 **1b**	68
5	 **5d**	**3a**	B	 **1c**	65

Table 1 (*continued*)

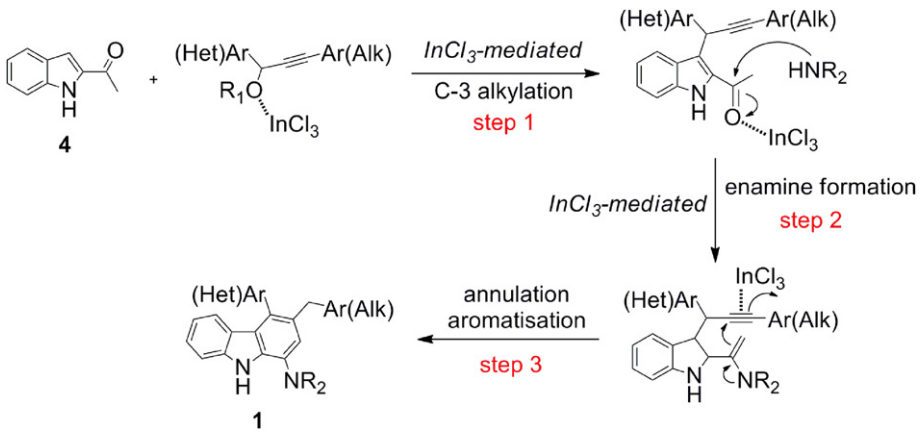
Entry	Propynyl alcohol or acetate **5**	Secondary amine **3**	Method	Product **1**	Yield[a] (%)
6	 **5e**	**3a**	B	 **1d**	61
7	 **5f**	**3a**	B	 **1e**	71
8	 **5g**	**3a**	B	 **1f**	89
9	**5d**	 **3b**	B	 **1g**	58
10	**5f**	**3b**	B	 **1h**	67

[a] Yields are referred to pure isolated compounds after chromatographic purification.

The three-steps reaction pathway giving rise to 1-aminocarbazoles **1**, Scheme 2, involves the In(III)-catalyzed C-3 alkylation of **4** (step 1) followed by the In(III)-catalyzed enamine formation (step 2) and by the final 6-*exo*-*dig* cyclisation/aromatisation step (step 3).

The exact mechanism of the In(III)-mediated hydroxyl activation (step 1) is not totally clear. Carbocationic species (free[34] or incipient[35]) as well as allenyl cations[36] has been proposed by several authors as possible intermediates. Several mechanistic aspects connected to steps 2 and 3 and to the dual role exerted by $InCl_3$, for these and related reactions, have been discussed elsewhere.[23]

As already stated, the deferred addition of the secondary amine to the reaction mixture is probably required to avoid catalyst



Scheme 2.

deactivation. This hypothesis is supported by the analysis of several ^{1}H NMR experiments performed in CD_3CN. The ^{1}H NMR spectrum of pure **5b** shows the resonance of the benzylic hydrogen at 6.61 ppm. In the presence of 0.1 mol of $InCl_3$ the resonance at 6.61 decreases progressively and two new peaks appear at 5.88 and 5.56 ppm, Fig. 1. In our opinion these two new resonances could be attributed to intermediate(s) involving interaction of both oxygen and triple bond with $InCl_3$. Moreover, when 1 mol of pyrrolidine is added to the same solution, no change in the spectrum is observed.

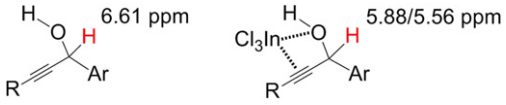


Fig. 1. Resonances of benzylic hydrogen of **5b**.

On the contrary, when **5b**, $InCl_3$, and pyrrolidine are added to CD_3CN at the same time the benzylic hydrogen at 6.61 ppm remains unchanged. This supports the existence of an interaction between $InCl_3$ and pyrrolidine, which inhibits the coordination between $InCl_3$ and **5b**.

3. Conclusion

In conclusion, this approach leads to an effective synthesis of a small library of 1-aminocarbazoles with a wide-range of substituent, in moderate to good yields. The mild conditions and the high-substrate tolerance represent the main outcomes of this useful protocol. The reaction is catalyzed by a water-tolerant Lewis acid as $InCl_3$, and this allows operating under mild conditions, because no anhydrous or inert conditions are strictly required.

Unfortunately, as already described by other research groups,[37] indium(III) salts are able to enhance the electrophilic character in the carbon atom, and thus to promote the indole alkylation step, only in aryl substituted secondary (benzylic) propynyl alcohols (or acetates). Thus, primary or alkyl substituted secondary propynyl derivatives cannot be used as substrates in these reactions. Further work is in progress to overcome this drawback and also to extend the methodology to other heterocyclic systems.

4. Experimental

4.1. General

All chemicals and solvents are commercially available and were used after distillation or treatment with drying agents. Silica gel F_{254} thin-layer plates were employed for thin-layer chromatography (TLC). Silica gel 40–63 micron/60 Å was employed for all flash column chromatography. Melting points were measured with a Perkin–Elmer DSC 6 calorimeter at a heating rate of 5 °C min^{-1} and are uncorrected. Infrared spectra were recorded with a Perkin–Elmer FTIR 16 PC spectrometer by using KBr tablets. ^{1}H and ^{13}C NMR spectra were determined with a Varian-Gemini 200 or a Bruker 500 Advance spectrometer at room temperature in $CDCl_3$, CD_3CN, or C_6D_6 with residual solvent peaks as the internal reference. The APT sequence was used to distinguish the methyne and methyl carbon signals from those arising from methylene and quaternary carbon atoms. Low resolution MS spectra were recorded with a Thermo-Finnigan LCQ advantage AP electrospray/ion trap equipped instrument by using a syringe pump device to directly inject sample solutions.

4.2. General procedure for the synthesis of 1-aminocarbazoles 1a–h

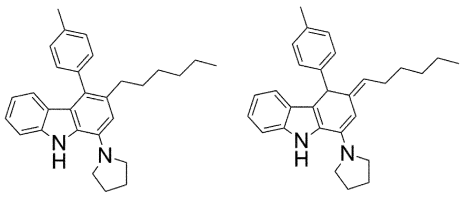
A well stirred solution of 2-acetyl-1*H*-indole **4** (250 mg, 1.57 mmol), the appropriate propynyl alcohol or acetate **5** (1.57 mmol), and $InCl_3$ (35 mg, 0.16 mmol) in dry acetonitrile (5 ml) was heated at 75 °C in a screwed-cap tube for 15 min. Then, the secondary amine **3** (1.88 mmol) was added and the resulting mixture stirred overnight at 75 °C. The reaction was then allowed to cool at room temperature and the solvent removed under reduced pressure. The resulting crude product was purified by flash chromatography over silica gel to yield the desired 1-aminocarbazole **1**.

*4.2.1. 3-Benzyl-4-(4-methylphenyl)-1-(pyrrolidin-1-yl)-9H-carbazole (**1a**).* Eluent for chromatography: *n*-hexane/EtOAc, 90:10; yield (from **5a**) 412 mg, 63%. Yield (from **5b**) 510 mg, 78%; yellow oil; ν_{max} 2920, 2244, 1899, 1493; δ_H (200 MHz, $CDCl_3$) 2.05 (4H, m, $2CH_2$ pyrrolidine), 2.48 (3H, s, CH_3), 3.48 (4H, m, 2N–CH_2), 3.93 (2H, s, Ar–CH_2), 6.69–7.59 (14H, m, arom.), 8.18 (1H, s, NH); δ_C (50.3 MHz, C_6D_6) 21.2 (CH_3), 39.1 (Ar–CH_2), 24.9, 50.3 (CH_2 pyrrolidine), 110.7, 113.4, 119.4, 122.9, 125.1, 125.7, 128.3, 129.1, 129.5, 130.4 (C_{sp2}–H), 124.8, 129.0, 130.6, 130.8, 135.4, 136.5, 138.0, 140.0, 143.4 (quat. C_{sp2}); *m*/*z* (ESI$^+$) 417 (100, MH$^+$); $C_{30}H_{28}N_2$ (416.56): calcd C 86.50, H 6.78, N 6.72; found C 86.37, H 6.53, N 6.89.

*4.2.2. 3-Benzyl-4-(4-methoxyphenyl)-1-(pyrrolidin-1-yl)-9H-carbazole (**1b**).* Eluent for chromatography: *n*-hexane/EtOAc, 90:10; yield 462 mg, 68%; yellow oil; ν_{max} 2924, 1608, 1507, 1240; δ_H (200 MHz, $CDCl_3$) 2.06 (4H, m, $2CH_2$ pyrrolidine), 3.50 (4H, m, 2N–CH_2), 3.92 (3H, s, OCH_3), 3.96 (2H, s, Ar–CH_2), 6.72 (1H, s, arom.), 6.76–7.42 (13H, m, arom.), 8.18 (1H, s, NH); δ_C (50.3 MHz, $CDCl_3$) 25.3, 50.8 (CH_2 pyrrolidine), 39.0 (Ar–CH_2), 55.6 (OCH_3), 110.7, 113.0, 114.2, 119.1, 122.5, 125.2, 125.7, 128.3, 129.0, 131.5 (C_{sp2}–H), 123.8, 124.3, 126.9, 130.2, 130.9, 132.8, 135.1, 139.8, 143.1, 158.9 (quat. C_{sp2}); *m*/*z* (ESI$^+$) 433.2 (100, MH$^+$); $C_{30}H_{28}N_2O$ (432.56): calcd C 83.30, H 6.52, N 6.48; found C 82.96, H 6.45, N 6.62.

*4.2.3. 3-Benzyl-1-(pyrrolidin-1-yl)-4-thien-2-yl-9H-carbazole (**1c**).* Eluent for chromatography: *n*-hexane/EtOAc, 90:10; yield: 417 mg, 65%; yellow oil; ν_{max} 2921, 1641, 1592, 1385; δ_H (200 MHz, $CDCl_3$) 2.05 (m, 4H, $2CH_2$ pyrrolidine), 3.53 (m, 4H, 2N–CH_2), 4.08 (s, 2H, Ar–CH_2), 6.68 (s, 1H, arom.), 6.83–7.03 (m, 3H, arom.), 7.14–7.46 (m, 9H, arom.), 8.27 (s, 1H, NH); δ_C (50.3 MHz, $CDCl_3$) 39.1 (Ar–CH_2), 39.1, 50.6 (CH_2 pyrrolidine), 110.8, 112.4, 119.4, 122.5, 125.5, 125.8, 126.1, 127.5, 127.8, 128.4, 129.1 (C_{sp2}–H), 119.0, 123.8, 124.8, 129.5, 133.3, 136.3, 139.8, 141.3, 142.9 (quat. C_{sp2}); *m*/*z* (ESI$^+$) 409 (100, MH$^+$); $C_{27}H_{24}N_2S$ (408.56): calcd C 79.37, H 5.92, N 6.86; found C 79.18, H 5.76, N 6.97.

*4.2.4. 3-Hexyl-4-(4-methylphenyl)-1-(pyrrolidin-1-yl)-9H-carbazole (**1d**).* Eluent for chromatography: *n*-hexane/EtOAc, 90:10; yield: 200 mg, 61%; yellow oil; ν_{max} 2865, 1548, 1321; the ^{1}H and ^{13}C NMR analysis of the purified compound show the presence of two isomers **1d** and **1d′** in a 1:3 ratio.



δ_H (500 MHz, C_6D_6) 0.91–0.97 (m, 3H, aliph.), 1.33–1.35 (m, 4H, aliph.), 1.41–1.47 (m, 2H, aliph.), 1.76 (m, 4H, $2CH_2$ pyrrolidine), 1.84–1.90 (m, 2H, aliph.), 2.35 (s, 3H, CH_3), 2.93 (t, J=7.8 Hz, 2H, Ar–CH_2), 3.27 (m, 4H, 2N–CH_2), 6.78 (s, 1H, arom.), 7.06–7.68 (m, 8H, arom.), 8.23 (s, 1H, NH); the presence of isomer **1d′** with an exocyclic bond is detectable by the following characteristic signals: δ_H (500 MHz, C_6D_6) 2.24 (s, CH_3), 2.25 (s, C_{sp3}–H), 4.55 (t, ^3J=1.5 Hz, C_{sp2}–H); δ_C (125.8 MHz, C_6D_6) 13.4, 20.4 (CH_3), 22.0, 28.8, 31.2, 32.2, 32.7 (CH_2), 24.1, 49.8 (CH_2 pyrrolidine). The signal splitting in the aromatic region evidences the presence of the two isomers: δ_C (125.8 MHz, C_6D_6) 109.2, 109.3, 110.0, 111.9, 112.0, 118.4, 120.1, 122.0, 122.3, 124.3, 125.3, 125.4, 128.3, 128.7, 129.7 (C_{sp2}–H), 124.0, 123.1, 127.1, 127.9, 130.0, 131.9, 134.3, 134.8, 135.6, 135.8, 137.1, 139.4, 142.1 (quat. C_{sp2}); isomer **1d′** shows the characteristic signals: δ_C (125.8 MHz, C_6D_6) 13.3, 24.6 (CH_3), 22.1, 27.4, 28.8 (CH_2), 73.5 (C_{sp3}–H); m/z (ESI^+) 411 (100, MH^+); $C_{29}H_{34}N_2$ (410.59): calcd C 84.83, H 8.35, N 6.82; found C 84.65, H 8.11, N 6.93.

*4.2.5. 4-(4-Methylphenyl)-1-(pyrrolidin-1-yl)-3-[3-(trifluoromethyl) benzyl]-9H-carbazole (**1e**).* Eluent for chromatography: *n*-hexane/EtOAc, 99:1; yield: 388 mg, 71%; yellow oil; ν_{max} 2963, 1593, 1450, 1330; δ_H (500 MHz, $CDCl_3$) 2.07 (4H, m, $2CH_2$ pyrrolidine), 2.47 (3H, s, CH_3), 3.51 (4H, m, 2N–CH_2), 3.97 (2H, s, Ar–CH2), 6.67 (1H, s, arom.), 6.71–6.69 (2H, m, arom.), 7.13–7.41 (10H, m, arom.), 8.20 (1H, s, NH); δ_C (125.8 MHz, $CDCl_3$) 21.4 (CH_3), 25.1, 50.6 (CH_2 pyrrolidine), 38.9 (Ar–CH_2), 110.5, 112.5, 119.0, 122.4, 125.1, 128.4, 129.4, 130.0, 132.2 (C_{sp2}–H), 122.3 (q, $^3J_{C,F}$=3.8 Hz, C_{sp2}–H), 125.5 (q, $^3J_{C,F}$=3.8 Hz, C_{sp2}–H), 123.4, 123.9128.3, 129.6, 130.1, 135.0, 136.8, 136.9, 139.6, 143.7 (quat. C_{sp2}), 124.4 (q, $^1J_{C,F}$=272.4 Hz, CF_3), 130.2 (q, $^2J_{C,F}$=31.8 Hz, quat. C_{sp2}); m/z (ESI^+): (%)=485 (100, M^+); $C_{31}H_{27}F_3N_2$ (484.55): calcd C 76.84, H 5.62, N 5.78; found C 76.73, H 5.52, N 5.86.

*4.2.6. 3-Benzyl-4-(4-bromophenyl)-1-(pyrrolidin-1-yl)-9H-carbazole (**1f**).* Eluent for chromatography: *n*-hexane/EtOAc, 90:10, yield: 673 mg, 89%; yellow oil; ν_{max} 2963, 1596, 1451, 1332; δ_H (200 MHz, $CDCl_3$) 2.07 (4H, m, $2CH_2$ pyrrolidine), 3.52 (4H, m, 2N–CH_2), 3.89 (2H, s, Ar–CH_2), 6.73 (2H, d, J=8.2 Hz, arom.), 6.99–7.03 (1H, m, arom.), 7.12–7.39 (9H, m, arom.), 7.57 (2H, d, J=8.3 Hz, arom.), 8.29 (1H, s, NH); (50.3 MHz, $CDCl_3$) 39.0 (Ar–CH_2), 25.3, 50.8 (CH_2 pyrrolidine), 110.4, 112.5, 121.2, 122.3, 123.3, 125.8, 126.7, 128.4, 129.0, 131.9 (C_{sp2}–H), 121.4, 123.8, 127.8, 130.2, 130.5, 135.4, 135.7, 137.8, 139.9, 142.7 (quat. C_{sp2}); m/z (ESI^+) 481 (100, MH^+); $C_{29}H_{25}BrN_2$ (481.43): calcd C 72.35, H 5.23, N 5.82; found C 72.28, H 5.21, N 5.92.

*4.2.7. 3-Benzyl-1-(piperidin-1-yl)-4-(thiophen-2-yl)-9H-carbazole (**1g**).* Eluent for chromatography: *n*-hexane/EtOAc, 95:5; yield: 385 mg, 58%; yellow oil; ν_{max} 2930, 1599, 1318, 695; δ_H (200 MHz, $CDCl_3$) 1.68 (2H, m, CH_2 piperidine), 1.86 (4H, m, CH_2 piperidine), 3.12 (4H, m, 2N–CH_2), 4.09 (2H, s, Ar–CH_2), 6.85–7.52 (13H, m, arom.), 8.20 (1H, s, NH); (50.3 MHz, $CDCl_3$) 24.7, 26.9, 39.0, 53.1 (CH_2), 110.9, 116.9, 119.5, 122.4, 125.6, 125.8, 126.2, 127.5, 127.6, 128.4, 129.0 (C_{sp2}–H), 123.0, 124.2, 124.3, 132.8, 132.9, 139.3, 139.9, 140.8, 142.8 (quat. C_{sp2}); m/z (ESI^+) 423 (100, MH^+); $C_{28}H_{26}N_2S$ (422.58): calcd C 79.58, H 6.20, N 6.63; found C 79.42, H 6.16, N 6.77.

*4.2.8. 1-(Piperidin-1-yl)-4-p-tolyl-3-(3-(trifluoromethyl)benzyl)-9H-carbazole (**1h**).* Eluent for chromatography: *n*-hexane/EtOAc, 95:5; yield: 524 mg, 67%; yellow oil; ν_{max} 3300, 1642, 1522, 739; δ_H (200 MHz, $CDCl_3$) 1.66–1.71 (2H, m, CH_2 piperidine), 1.79–1.84 (4H, m, $2CH_2$ piperidine), 2.47 (3H, s, CH_3), 3.09–3.14 (4H, m, 2N–CH_2), 3.99 (2H, s, Ar–CH_2), 6.73–7.70 (13H, m, arom.), 8.22 (1H, s, NH); δ_C (50.3 MHz, $CDCl_3$) 24.9, 27.0, 39.2, 53.5 (CH_2), 26.3 (CH_3), 110.4, 112.7, 119.4, 121.3, 123.5, 125.6, 128.7, 129.7, 130.0 (C_{sp2}–H), 122.7 (q, $^3J_{C,F}$=3.8 Hz, C_{sp2}–H), 125.8 (q, $^3J_{C,F}$=3.8 Hz, C_{sp2}–H), 124.6, 128.0, 129.7, 133.4, 135.8, 137.0, 137.3, 137.9, 140.1, 144.0 (quat. C_{sp2}), 121.1 (q, $^1J_{C,F}$=272.4 Hz, CF_3), 129.7 (q, $^2J_{C,F}$=31.8 Hz, quat. C_{sp2}); m/z (ESI^+) 499 (100, MH^+); $C_{32}H_{29}F_3N_2$ (498.58): calcd C 77.09, H 5.86, N 5.62; found C 76.95, H 5.82, N 5.66.

Supplementary data

Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.tet.2011.06.091. These data include MOL files and InChIKeys of the most important compounds described in this article.

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