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PAPER

Synthesis of functionalized ellipticinium and ellipticine derivatives *via* electrophilic cyclization†

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An efficient methodology for the synthesis of highly functionalized ellipticinium and ellipticine derivatives starting from the corresponding 2-bromocarbazoles *via* an AgOTf or CuI catalyzed electrophilic cyclization of 2-alkynyl-3-carbazolylaldimines is reported.

Introduction

Ellipticine, 5,11-dimethyl-6*H*-pyrido[4,3-*b*]carbazole, was first isolated in 1959 by Goodwin *et al*.[1] The first total synthesis was reported by Woodward and co-workers in the same year.[2] Ellipticine and its derivatives gained considerable attention from 1967 onwards due to their potential antitumour activity.[3] The antitumour properties of ellipticine derivatives are considered to be mainly due to their binding with DNA and/or the inhibition of enzyme topoisomerase II.[4] The synthetic and biological profiles of ellipticines have been extensively reviewed in the literature.[5]

Ellipticine and its derivatives have drawn tremendous attention from synthetic chemists, and many syntheses of ellipticine and its derivatives have been reported.[6] Some of them, such as elliptinium (ellipticinium acetate), datelliptium, retellipticine (BD-84), pazellipticine, *etc.* (Fig. 1), were also tested for clinical use.[7] Elliptinium has been used in the treatment of advanced myeloblastic leukemia.

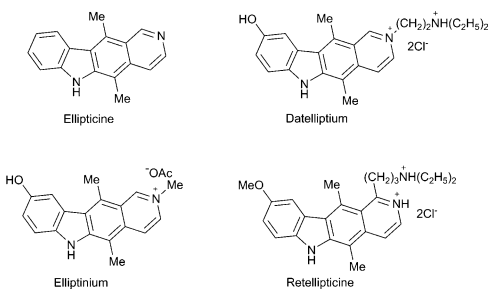

Fig. 1 Ellipticinium derivatives.

In most cases, these compounds were derivatized directly from ellipticine, leaving limited scope to prepare more diverse candidates for clinical trials. Furthermore, there are very few reports available in the literature on the synthesis of these diverse and functionalized ellipticinium and ellipticine derivatives. In this context, the development of a useful methodology for the synthesis of various functionalized ellipticinium and ellipticine derivatives is important. In continuation of our research in the development of efficient methodologies for the synthesis of heteroarylcarbazoles,[8] we started working on the development of a simple and facile methodology for the synthesis of ellipticine derivatives.

Recently, there has been immense synthetic interest in the application of 2-alkynyl arylaldehydes towards the synthesis of isoquinolines, benzofurans, benzopyrans, benzimidazoles and their derivatives by employing various catalysts, including metal salts of Pd, Ag(I) and Cu(I), iodine, *etc.*[9,10] 2-Alkynyl arylaldehydes, on reacting with amines in the presence of various Lewis acidic metal salts, undergo a facile electrophilic cyclization to furnish isoquinolines and their derivatives in excellent yields.[9,10] We envisaged that 2-alkynyl-3-formylcarbazoles would be excellent precursors for the synthesis of ellipticine derivatives. These 2-alkynyl-3-formylcarbazoles, on reacting with various amines, can be successfully converted into their corresponding ellipticine derivatives efficiently. Furthermore, this methodology can be of broad scope in terms of functionalizing the basic ellipticine motif at more positions and so is significant in the synthesis of further derivatives of ellipticines and ellipticiniums.

Results and discussion

As outlined in Scheme 1, these precursor molecules can be prepared from their corresponding 2-bromoformyl carbazoles, which can be further obtained from their corresponding 2-bromocarbazoles.

The syntheses of 2-bromo-9-ethylcarbazoles **8a** and **8b** are depicted in Scheme 2. Arylboronic acids **4a** and **4b**, subjected to Suzuki coupling with 4-bromo-2-nitroiodobenzene **5** in the presence of palladium acetate and PPh_3, provided 4-bromo-2-nitrobiaryls **6a** and **6b** in excellent yields. **6a** and **6b** were subjected to reductive cyclization using triethylphosphite under reflux to give the corresponding bromocarbazoles **7a** and **7b**, which, upon *N*-alkylation using ethyl bromide and potassium hydroxide as base

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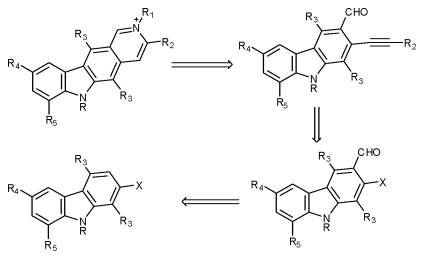
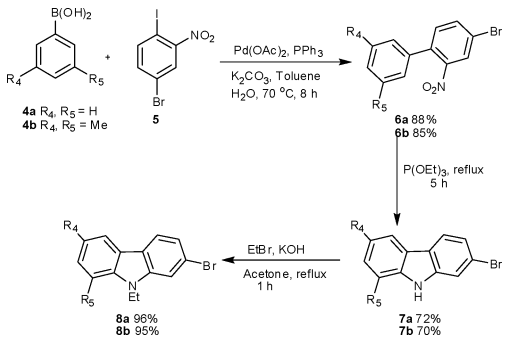
† Electronic supplementary information (ESI) available: ^1H, ^{13}C, LC-MS and elemental analysis spectra of all compounds. CCDC 804670. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c1ob05258f



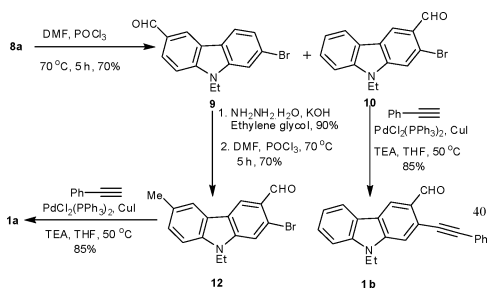
Scheme 1 Outline of the synthetic plan.



Scheme 2 Synthesis of bromocarbazoles.

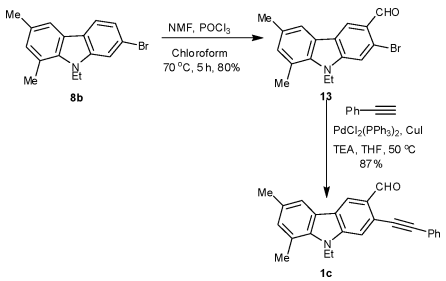
in acetone, provided 2-bromo-9-ethylcarbazoles **8a** and **8b** in 96% and 95% yields, respectively.

As shown in Scheme 3, upon the Vilsmeier–Haack formylation of **8a**, the desired 3-formyl regioisomer, **10**, was obtained in a very low yield, whereas 6-formyl derivative **9** was formed as a major isomer. When we attempted the formylation of **8a** using *N*-methylformanilide as the formylating agent, **9** was obtained exclusively. These observations led us to conclude that it may be due to the bulkiness and deactivating effect of the bromo group that the 6-formyl product is formed as the major isomer. A Wolff–Kishner reduction of 6-formyl derivative **9** provided the 2-bromo-9-ethyl-6-methyl-9*H*-carbazole in excellent yield. A Vilsmeier–Haack formylation of the 6-methyl derivative provided the 2-bromo-3-formyl-6-methyl derivative, **12**, in 70% yield. **12**, upon Sonogashira coupling with phenylacetylene employing bis(triphenylphospine)palladium dichloride, copper(I) iodide and triethylamine as a base, afforded precursor **1a** in 85% yield. By employing similar conditions, precursor **1b** was obtained from **10** in 85% yield.



Scheme 3 Synthesis of precursors **1a** and **1b**.

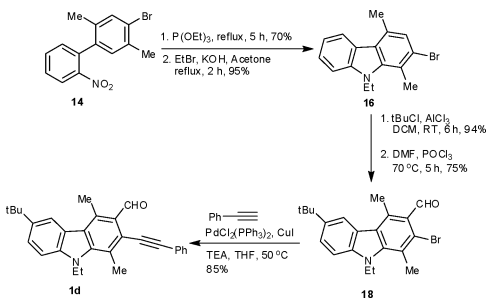
The synthesis of precursor molecule 6,8-dimethyl-3-formyl-2-phenylethynylcarbazole (**1c**) starting from 2-bromo-6,8-dimethyl-9-ethylcarbazole (**8b**) is outlined in Scheme 4. A Vilsmeier–Haack formylation of **8b** using DMF and $POCl_3$ at 70 °C for 5 h provided



Scheme 4 Synthesis of precursor **1c**.

2-bromo-6,8-dimethyl-3-formyl derivative **13** in 40% yield, along with the 7-formyl derivative in 20% yield. As expected, when *N*-methylformanilide was employed as the formylating agent instead of DMF, exclusively **13** was obtained in 80% yield. Because of the bulkiness of the Vilsmeier salt formed from *N*-methylformanilide, the formation of the 7-formyl derivative was hindered. **13**, on coupling with phenylacetylene under Sonogashira conditions, afforded precursor **1c** in 87% yield.

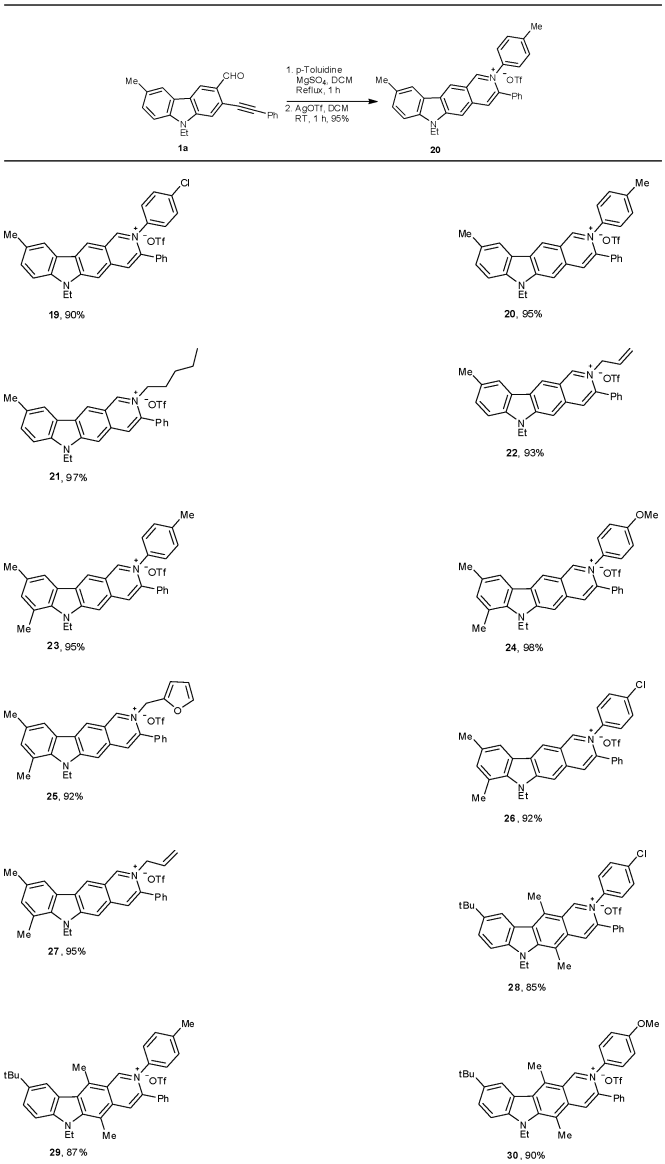
The synthesis of precursor 6-*tert*-butyl-3-formyl-2-phenylethynylcarbazole (**1d**) starting from 4-bromo-2,5-dimethyl-2′-nitrobiphenyl **14** is outlined in Scheme 5. Biphenyl **14** was prepared by the Suzuki coupling of the 4-bromo-2,5-dimethylphenylboronic acid with 2-iodonitrobenzene using $Pd(OAc)_2$ and PPh_3. Reductive cyclization of **14** in triethylphosphite under reflux followed by *N*-alkylation with ethyl bromide using potassium hydroxide as the base afforded 2-bromo-1,4-dimethyl-9-ethylcarbazole (**16**) in 65% overall yield. Upon the Friedel–Crafts alkylation of **16** using *tert*-butyl chloride and aluminium chloride, 2-bromo-6-*tert*-butyl-9-ethyl-1,4-dimethyl-9*H*-carbazole was obtained regioselectively in 94% yield. The formation of the other possible 3-*tert*-butyl regioisomer was not observed, probably due to the bulkier 2-bromo substituent. The 2-bromo-1,4-dimethyl-3-formyl derivative, **18**, was obtained in 75% yield by a Vilsmeier–Haack formylation of the 6-*tert*-butyl derivative. A Sonogashira reaction of **18** with phenylacetylene using $Pd(PPh_3)_2Cl_2$ afforded precursor **1d** in 85% yield.



Scheme 5 Synthesis of precursor **1d**.

Then we attempted the electrophilic cyclization of **1a** with *p*-toluidine by employing AgOTf (Table 1). When the reaction was carried out in one-pot involving both Schiff base formation and cyclization using 4 Å molecular sieves in ethanol, the corresponding ellipticinium triflate was obtained in 70% yield. But, to our delight, when we carried out the cyclization of isolated aldimines by employing AgOTf in dichloromethane, the ellipticinium triflate was obtained in almost quantitative yield. Precursor molecules

Table 1 Synthesis of ellipticinium derivatives



1a–1d were subjected to electrophilic cyclization with various aliphatic and aromatic amines under the optimized conditions to provide highly functionalized ellipticinium derivatives in excellent yields. The results are summarized in Table 1. The structures of compounds **19** and **23** were also determined unambiguously by X-ray crystallography.[11] The ORTEP diagram of **19** is shown in Fig. 2. It is worth noting that various amines with diverse functionalities were employed and that all the ellipticiniums were obtained in excellent yields.

Then we turned our attention towards the synthesis of ellipticine derivatives from the same precursor molecules. By employing the optimized conditions, we successfully prepared ellipticine derivatives in good yields. As described in Scheme 6, **1a**, **1b** and **1c**, on reaction with *tert*-butyl amine followed by a CuI-induced cyclization in DMF, provided the corresponding ellipticines **3a**, **3b** and **3c** in 85–90% yields. Precursor **1d** failed to form an imine with *tert*-butyl amine, probably due to steric hindrance between

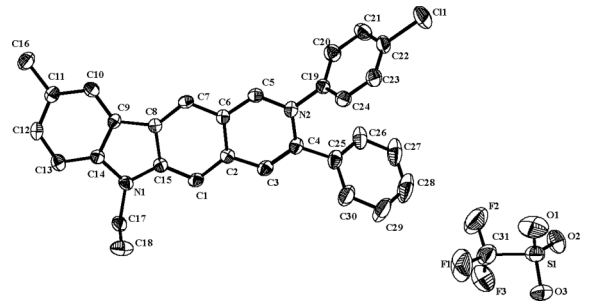
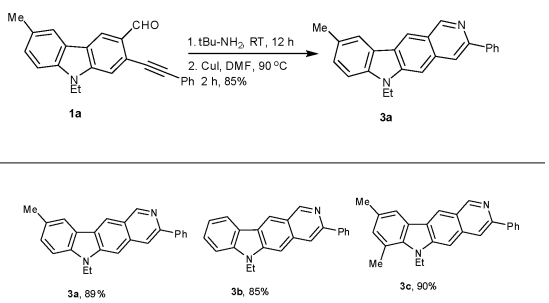


Fig. 2 ORTEP diagram of **19**. Hydrogen atoms are omitted for clarity.



Scheme 6 Synthesis of ellipticine derivatives.

the *tert*-butyl group of the amine and the methyl group of the carbazole.

Conclusion

In conclusion, we have developed a novel and efficient methodology for the synthesis of diverse and highly functionalized ellipticinium and ellipticine derivatives in excellent yields. Many carbazole intermediates of potential synthetic scope were synthesized for the first time. The scope of this synthetic route is general and all the products were obtained in excellent yields. The overall modularity of this process is noteworthy. It is anticipated that this methodology will be extremely valuable for the development of selective anti-cancer agents with a pyrido[4,3-*b*]carbazole skeleton. Studies towards this end will be the focus of future work in our laboratory.

Experimental section

General information

^{1}H and ^{13}C NMR spectra were recorded at 400 and 100 MHz, respectively. Chemical shifts are reported in ppm downfield from TMS (δ = 0) for ^{1}H NMR, and relative to the central $CDCl_3$ resonance (δ = 77.0) and DMSO-d_6 (δ = 39.51) for ^{13}C NMR. The coupling constants, J, are given in Hz. IR spectra were recorded on a FT/IR-5300 instrument. X-Ray diffraction measurements were carried out at 298 K on an automated diffractometer using graphite-monochromated Mo-Kα (λ = 0.71073 Å) radiation with CAD4 software or the X-ray intensity data were measured at 298 K equipped with a graphite monochromator and a Mo-Kα fine-focus sealed tube (λ = 0.71073 Å). Melting points were measured in open capillary tubes and are uncorrected. All reaction

solvents used are of GR grade and used without drying unless mentioned. Triethylphosphite, *N*-methylformanilide, palladium acetate, $Pd(PPh_3)_2Cl_2$, silver triflate (AgOTf) and copper(I) iodide were used directly as purchased. Phenylacetylene, phosphoryl chloride, ethyl bromide, hydrazine hydrate and magnesium sulfate were purchased from local manufacturers. 4-Bromo-2-iodonitrobenzene, 3,5-dimethylphenylboronic acid and 4-bromo-2,5-dimethylphenylboronic acid were prepared according to methods reported in the literature.[12]

2-Bromo-9-ethyl-9*H*-carbazole (8a). An oven-dried 250 mL round-bottomed flask equipped with a Teflon-coated magnetic stirring bar is charged with 10 g (0.04 M) of 2-bromocarbazole and 100 mL of acetone under stirring. 6.8 g (0.12 M) of potassium hydroxide is added and refluxed for 30 min. 5.8 mL (0.08 M) of ethyl bromide is added slowly and reflux continued for 1 h, after which time TLC (90 : 10 hexanes : ethyl acetate) indicated complete conversion. The reaction is allowed to cool to room temperature and acetone is removed under reduced pressure. Residue is dissolved in ethyl acetate, washed with 2% dilute hydrochloric acid, water and brine. The organic layer is dried over anhydrous sodium sulfate and the solvent is removed under reduced pressure to give a white solid. The crude material is used further without purification. Yield: 96% mp: 77–79 °C; ν_{max} (KBr)/cm^{-1}: 3057, 2970, 1591, 1489, 1473, 1448, 1323, 1230, 1153, 1122, 1053, 900, 830, 806, 746, 717, 428; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (d, J = 7.6 Hz, 1H), 7.97 (d, J = 8.0 Hz, 1H), 7.59 (s, 1H), 7.53 (t, J = 6.8 Hz, 1H), 7.43 (d, J = 8.0 Hz, 1H), 7.37 (dd, J = 6.8, 1.6 Hz, 1H), 7.29 (t, J = 8.0 Hz, 1H), 4.28 (q, J = 8.0 Hz, 2H), 1.45 (t, J = 8.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.8, 140.1, 126.1, 122.4, 121.9, 121.9, 121.5, 120.4, 119.4, 119.3, 115.6, 108.7, 37.7, 13.8; m/z = 275, positive mode; anal. calc. for $C_{14}H_{12}BrN$: C, 61.33; H, 4.41; N, 5.11%; found: C, 61.23; H, 4.48; N, 5.15%.

Formylation of 2-bromo-9-ethyl-9*H*-carbazole (9 and 10). An oven-dried 250 mL round-bottomed flask equipped with a Teflon-coated magnetic stirring bar is charged with 10 g (0.036 M) of 2-bromo-9-ethylcarbazole and 80 mL of dimethylformamide under stirring and cooled to 0 °C. 10 mL (0.11 M) of phosphoryl chloride is added dropwise for 15 min. The reaction is allowed to warm to room temperature and heated at 70 °C for 5 h, after which time TLC (90 : 10 hexanes : ethyl acetate) indicated complete conversion. The reaction is allowed to cool to room temperature and quenched with ice. The reaction mass is poured into crushed ice slowly, neutralized with 5% aq. sodium hydroxide and extracted with ethyl acetate. The organic layer is washed with water and brine, dried over anhydrous sodium sulfate and the solvent is removed under reduced pressure. The crude material is purified by column chromatography (eluent: 5–10% ethyl acetate in hexane). The 3-formyl derivative is eluted in 5% eluent as the minor isomer and 6-formyl derivative is eluted in 10% eluent as the major isomer. Yield: 70%.

7-Bromo-9-ethyl-9*H*-carbazole-3-carbaldehyde (9). White solid; mp: 129–131 °C; ν_{max} (KBr)/cm^{-1}: 2974, 2814, 2723, 1582, 1622, 1585, 1485, 1431, 1234, 1170, 1143, 908, 804, 742, 549; ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.12 (s, 1H), 8.52 (s, 1H), 8.02 (d, J = 8.0 Hz, 1H), 7.94 (d, J = 8.0 Hz, 1H), 7.45 (s, 1H), 7.40–7.43 (m, 2H), 4.30 (q, 2H), 1.43 (t, J = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.6, 143.6, 141.4, 129.0, 127.5, 123.5, 122.6, 121.9, 121.9, 120.4, 112.3, 108.9, 38.1, 13.8; m/z = 303, positive mode; anal. calc. for $C_{15}H_{12}BrNO$: C, 59.62; H, 4.00; N, 4.64%; found: C, 59.72; H, 4.08; N, 4.55%

2-Bromo-9-ethyl-9*H*-carbazole-3-carbaldehyde (10). White solid; mp: 125–127 °C; ν_{max} (KBr)/cm^{-1}: 2974, 2852, 1680, 1589, 1469, 1425, 1346, 1317, 1236, 912, 838, 792, 742, 430; ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.42 (s, 1H), 8.63 (s, 1H), 8.08 (d, J = 7.6 Hz, 1H), 7.52–7.57 (m, 2H), 7.40 (d, J = 8.2 Hz, 1H), 7.32 (t, J = 7.6 Hz, 1H), 4.28 (q, J = 7.6 Hz, 2H), 1.45 (t, J = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.7, 143.7, 140.8, 127.2, 124.8, 124.1, 122.8, 122.7, 122.5, 121.0, 120.8, 112.7, 109.3, 37.8, 13.8; m/z = 303, positive mode; anal. calc. for $C_{15}H_{12}BrNO$: C, 59.62; H, 4.00; N, 4.64%; found: C, 59.48; H, 4.12; N, 4.71%.

2-Bromo-9-ethyl-6-methyl-9*H*-carbazole (11). An oven-dried 250 mL round-bottomed flask equipped with a Teflon-coated magnetic stirring bar is charged with 5 g (0.016 M) of 7-bromo-9-ethyl-9*H*-carbazole-3-carbaldehyde and 100 mL of ethylene glycol under stirring. 1.85 g (0.033 M) of potassium hydroxide and 1.65 mL (0.033 M) of hydrazine hydrate are added under stirring. The reaction mixture is refluxed at 200 °C for 3 h, after which time TLC (90 : 10 hexanes : ethyl acetate) indicated complete conversion. The reaction is allowed to cool to room temperature and quenched with ice. The reaction mass is poured into crushed ice slowly, neutralized with 2% dilute hydrochloric acid and extracted with ethyl acetate. The organic layer is washed with water and brine, dried over anhydrous sodium sulfate and the solvent is removed under reduced pressure to give the 2-bromo-9-ethyl-6-methyl-9*H*-carbazole as a pure white solid in almost quantitative yield. Yield: 95%. mp: 78–80 °C; ν_{max} (KBr)/cm^{-1}: 2974, 2922, 1682, 1628, 1593, 1483, 1442, 1228, 1084, 1060, 842, 798, 592, 416; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, J = 8.0 Hz, 1H), 7.87 (s, 1H), 7.54 (s, 1H), 7.31–7.33 (m, 3H), 4.29 (q, J = 8.0 Hz, 2H), 2.56 (s, 3H), 1.42 (t, J = 8.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.0, 138.4, 128.7, 127.4, 122.6, 121.7, 121.6, 121.5, 120.4, 119.1, 111.5, 108.4, 37.7, 21.4, 13.7; m/z = 289, positive mode; anal. calc. for $C_{15}H_{14}BrN$: C, 62.52; H, 4.90; N, 4.86%; found: C, 62.45; H, 4.95; N, 4.81%.

2-Bromo-9-ethyl-6-methyl-9*H*-carbazole-3-carbaldehyde (12). The procedure for the preparation of **9** is followed to give 2-bromo-9-ethyl-6-methyl-9*H*-carbazole-3-carbaldehyde as a white solid after column chromatography. Yield: 70%. mp: 148–150 °C; ν_{max} (KBr)/cm^{-1}: 2916, 2843, 1670, 1595, 1479, 1350, 1302, 1224, 1145, 856, 790, 761, 694, 464, 420; ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.39 (s, 1H), 8.57 (s, 1H), 7.84 (s, 1H), 7.48 (s, 1H), 7.34 (d, J = 8.0 Hz, 1H), 7.27 (d, J = 8.0 Hz, 1H), 4.24 (q, J = 7.6 Hz, 2H), 2.53 (s, 3H), 1.42 (t, J = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.8, 139.6, 130.3, 128.5, 124.5, 123.9, 123.0, 122.5, 122.5, 121.0, 112.5, 108.9, 38.0, 21.4, 13.8; m/z = 317, positive mode; anal. calc. for $C_{16}H_{14}BrNO$: C, 60.78; H, 4.46; N, 4.43%; found: C, 60.58; H, 4.40; N, 4.51%.

9-Ethyl-6-methyl-2-(phenylethynyl)-9*H*-carbazole-3-carbaldehyde (1a). An oven-dried 50 mL Schlenk tube equipped with a Teflon-coated magnetic stirring bar is charged with 1 g (3 mmol) of **12**, 1 g of molecular sieves and 0.42 mL (3.8 mmol) of phenyl acetylene. The tube is evacuated and filled with nitrogen. To it, 10 mL of dry THF and 5 mL of freshly distilled triethylamine are

added under nitrogen, and the reaction is stirred for 10 min at room temperature. 42 mg of $Pd(PPh_3)_2Cl_2$ (2 mol%) and 6 mg of CuI (1 mol%) are added under nitrogen and the Schlenk tube is heated at 60 °C for 4 h, after which time TLC (85 : 15 hexanes : ethyl acetate) indicated complete conversion. The reaction is allowed to cool to room temperature and filtered. The filtrate is poured into crushed ice slowly and extracted with ethyl acetate. The organic layer is washed with water and brine, dried over anhydrous sodium sulfate and the solvent is removed under reduced pressure. The crude material is purified by column chromatography (eluent: 8–15% ethyl acetate in hexane). The product is eluted in 12% eluent as a pale yellow solid. Yield: 85%. mp: 137–139 °C; ν_{max} (KBr)/cm^{-1}: 2916, 2843, 1670, 1595, 1479, 1350, 1302, 1224, 1145, 856, 790, 761, 694, 464, 420; ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.72 (s, 1H), 8.68 (s 1H), 7.91 (s, 1H), 7.63–7.65 (m, 2H), 7.55 (s, 1H), 7.31–7.43 (m, 5H), 4.33 (q, J = 8.0 Hz, 2H), 2.56 (s, 3H), 1.47 (t, J = 8.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.4, 142.8, 139.6, 131.6, 130.1, 128.8, 128.6, 128.5, 127.7, 123.7, 123.3, 123.1, 122.8, 121.1, 120.6, 112.3, 108.8, 95.1, 86.7, 37.9, 21.4, 13.8; m/z = 338, positive mode; anal. calc. for $C_{24}H_{19}NO$: C, 85.43; H, 5.68; N, 4.15%; found: C, 85.21; H, 5.72; N, 4.22%.

9-Ethyl-2-(phenylethynyl)-9*H*-carbazole-3-carbaldehyde (1b). By employing a similar procedure for the synthesis of **1a**, **1b** is obtained as a yellow solid in 85% yield. mp: 110–112 °C; ν_{max} (KBr)/cm^{-1}: 3057, 2970, 2843, 1672, 1620, 1589, 1494, 1469, 1452, 1359, 1329, 1232, 1159, 1126, 1103, 923, 898, 852, 760, 738, 719, 696, 665, 528, 468; ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.74 (s, 1H), 8.74 (s, 1H), 8.14 (d, J = 8.0 Hz, 1H), 7.52–7.65 (m, 4H), 7.41–7.46 (m, 4H), 7.34 (t, J = 7.6 Hz, 1H), 4.38 (q, J = 7.6 Hz, 2H), 1.49 (t, J = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.5, 142.7, 141.3, 131.6, 128.8, 128.5, 127.9, 127.3, 123.9, 123.3, 123.1, 122.7, 121.2, 120.7, 120.6, 112.4, 109.1, 95.2, 86.5, 38.0, 13.8; m/z = 324, positive mode; anal. calc. for $C_{23}H_{17}NO$: C, 85.42; H, 5.30; N, 4.33%; found: C, 85.31; H, 5.41; N, 4.41%.

4-Bromo-3′,5′-dimethyl-2-nitrobiphenyl (6b). By employing a similar procedure for the synthesis of **6a**, **6b** is obtained as a yellow liquid in 85% yield which solidified gradually. mp: 53–55 °C; ν_{max} (KBr)/cm^{-1}: 3086, 2914, 1601, 1523, 1346, 1271, 1205, 1151, 1018, 883, 852, 831, 709, 688, 551, 432; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (s, 1H), 7.73 (d, J = 8.4 Hz, 1H), 7.07 (s, 1H), 6.92 (s, 2H), 2.37 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.6, 138.5, 136.2, 135.5, 135.2, 133.2, 130.3, 126.9, 125.5, 121.0, 21.3; m/z = 308, positive mode; anal. calc. for $C_{14}H_{12}BrNO_2$: C, 54.92; H, 3.95; N, 4.51%; found: C, 54.85; H, 3.92; N, 4.51%.

7-Bromo-1,3-dimethyl-9*H*-carbazole (7b). By employing a similar procedure for the synthesis of **7a**, **7b** is obtained in 70% yield. mp: 123–125 °C; ν_{max} (KBr)/cm^{-1}: 3431, 3074, 2918, 2860, 1882, 1599, 1429, 1331, 1302, 1226, 1051, 1033, 850, 814, 584, 432, 414; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.41 (bs, 1H), 7.87 (d, J = 8.4 Hz, 1H), 7.69 (s, 1H), 7.59 (s, 1H), 7.30–7.33 (m, 1H), 7.10 (s, 1H), 4.15 (q, 2H), 2.52–2.55 (t, 6H), 1.38 (t, J = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.6, 137.3, 129.3, 128.3, 122.6, 122.4, 122.2, 121.4, 119.7, 118.7, 117.6, 113.8, 21.4, 16.2; m/z = 275, positive mode; anal. calc. for $C_{14}H_{12}BrN$: C, 61.33; H, 4.41; N, 5.11%; found: C, 61.24; H, 4.52; N, 5.31%.

7-Bromo-9-ethyl-1,3-dimethyl-9*H*-carbazole (8b). By employing a similar procedure for the synthesis of **8a**, **8b** is obtained in 95% yield. mp: 123–125 °C; ν_{max} (KBr)/cm^{-1}: 3468, 2922, 2864, 1593, 1471, 1439, 1331, 1219, 1055, 889, 842, 804, 582; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, J = 8.0 Hz, 1H), 7.73 (s, 1H), 7.53 (s, 1H), 7.32 (d, J = 8.0 Hz, 1H), 7.07 (s, 1H), 4.49 (q, J = 7.6 Hz, 2H), 2.78 (s, 3H), 2.52 (s, 3H), 1.41 (t, J = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.7, 137.1, 130.9, 128.9, 123.5, 122.1, 121.8, 121.2, 119.9, 119.1, 118.1, 111.6, 39.5, 21.1, 19.8, 15.5; m/z = 303, positive mode; anal. calc. for $C_{16}H_{16}BrN$: C, 63.59; H, 5.34; N, 4.63%; found: C, 63.52; H, 5.41; N, 4.55%.

2-Bromo-9-ethyl-6,8-dimethyl-9*H*-carbazole-3-carbaldehyde (13). An oven-dried 50 mL round-bottomed flask equipped with a Teflon-coated magnetic stirring bar is charged with 2 g (6.6 mmol) of **8b**, 10 mL of chloroform and 3 mL of *N*-methylformanilide. The reaction mixture is cooled in an ice bath at 0–5 °C for 15 min. 2 mL of $POCl_3$ is added to the reaction mixture dropwise under stirring. The reaction mixture is allowed to warm room temperature and refluxed for 6 h, after which time TLC (90 : 10 hexanes : ethyl acetate) indicated complete conversion. The reaction is allowed to cool to room temperature and quenched with ice. The reaction mass is poured into crushed ice slowly, neutralized with an ice cold solution of aq. 5% sodium bicarbonate and extracted with ethyl acetate. The organic layer is washed with water and brine, dried over anhydrous sodium sulfate and the solvent is removed under reduced pressure. The crude material is purified by column chromatography (eluent: 5–10% ethyl acetate in hexane). The product is eluted in 10% eluent as a white solid. Yield: 80%. mp: 139–141 °C; ν_{max} (KBr)/cm^{-1}: 3013, 2878, 2916, 2852, 1668, 1593, 1469, 1442, 1342, 1309, 1222, 1155, 1005, 848, 704, 569, 416; ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.42 (s, 1H), 8.59 (s, 1H), 7.74 (s, 1H), 7.51 (s, 1H), 7.09 (s, 1H), 4.48 (q, J = 7.6 Hz, 2H), 2.76 (s, 3H), 2.42 (s, 3H), 1.45 (t, J = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.7, 144.5, 137.7, 132.0, 130.4, 124.7, 123.9, 123.8, 122.8, 122.2, 120.4, 118.7, 112.7, 39.8, 21.0, 19.6, 15.5; m/z = 331, positive mode; anal. calc. for $C_{17}H_{16}BrNO$: C, 61.83; H, 4.88; N, 4.24%; found: C, 61.75; H, 4.81; N, 4.36%.

9-Ethyl-6,8-dimethyl-2-(phenylethynyl)-9*H*-carbazole-3-carbaldehyde (1c). The general procedure for the synthesis of **1a** and **1b** is employed. **1c** is obtained in 87% yield. mp: 157–159 °C; ν_{max} (KBr)/cm^{-1}: 3009, 2964, 2916, 2843, 1670, 1595, 1496, 1466, 1309, 1217, 842, 763, 690, 578; ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.73 (s, 1H), 8.68 (s, 1H), 7.80 (s, 1H), 7.63–7.65 (m, 2H), 7.57 (s, 1H), 7.41–7.44 (m, 3H), 7.11 (s, 1H), 4.58 (q, J = 7.0 Hz, 2H), 2.86 (s, 3H), 2.79 (s, 3H), 1.45 (t, J = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.4, 143.5, 138.3, 132.1, 131.6, 130.2, 128.7, 128.5, 128.0, 124.3, 123.6, 123.5, 122.8, 120.4, 120.3, 118.9, 112.5, 94.9, 86.7, 39.8, 21.0, 19.7, 15.6; m/z = 352, positive mode; anal. calc. for $C_{25}H_{21}NO$: C, 85.44; H, 6.02; N, 3.99%; found: C, 85.32; H, 6.11; N, 3.89%.

4-Bromo-2,5-dimethyl-2′-nitrobiphenyl (14). The procedure for the synthesis of **6a** and **6b** is employed. Starting from 2-iodonitrobenzene and 4-bromo-2,5-dimethylphenylboronic acid, the biphenyl **14** is obtained in 85% yield. The crude product is used further without purification. mp: 56–58 °C; ν_{max} (KBr)/cm^{-1}: 3088, 2924, 1600, 1527, 1346, 1270, 1204, 1153, 1018, 851, 831, 708; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, J = 8.0 Hz, 1H), 7.66 (t, J = 7.2 Hz, 1H), 7.55 (t, J = 8.1 Hz, 1H), 7.47 (s, 1H), 7.31 (d, J = 7.6 Hz, 1H), 6.98 (s, 1H), 2.38 (s, 3H), 2.06 (s, 3H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 148.9, 136.7, 135.6, 135.1, 135.0, 133.5, 132.7, 132.1, 130.3, 128.5, 124.5, 124.2, 22.3, 19.1; m/z = 306; 279 for the demethylated fragment, positive mode; anal. calc. for $C_{14}H_{12}BrNO_2$: C, 54.92; H, 3.95; N, 4.57%; found: C, 54.85; H, 4.03; N, 4.51%.

2-Bromo-1,4-dimethyl-9*H*-carbazole (15). The general procedure for the synthesis of **7a** is applied. Starting from **14**, the bromocarbazole is obtained in 70% yield. The crude product is used further without purification. mp: 86–88 °C; ν_{max} (KBr)/cm^{-1}: 3412, 3040, 2916, 2856, 1593, 1579, 1454, 1377, 1319, 1288, 1014, 773, 750, 731, 441; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (d, J = 8.0 Hz, 1H), 7.50 (bs, 1H), 7.46–7.48 (m, 2H), 7.28–7.33 (m, 1H), 7.24 (s, 1H), 2.81 (s, 3H), 2.57 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.4, 139.1, 125.4, 124.7, 124.1, 122.5, 121.2, 120.6, 119.9, 116.8, 110.7, 20.1, 16.6; m/z = 275, positive mode; anal. calc. for $C_{14}H_{12}BrN$: C, 61.33; H, 4.41; N, 5.11%; found: C, 61.23; H, 4.46; N, 5.19%.

2-Bromo-9-ethyl-1,4-dimethyl-9*H*-carbazole (16). The general procedure for the synthesis of **8a** is applied. Starting from **15**, the *N*-ethyl-2-bromocarbazole (**16**) is obtained in 95% yield. The crude product is used further without purification. mp: 110–112 °C; ν_{max} (KBr)/cm^{-1}: 2966, 2920, 1608, 1560, 1456, 1346, 1302, 1157, 1113, 1005, 868, 781, 744, 723, 545; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 (d, J = 8.0 Hz, 1H), 7.53 (t, J = 8.0 Hz, 1H), 7.46 (d, J = 8.0 Hz, 1H), 7.28–7.32 (m, 2H), 4.60 (q, J = 7.6 Hz, 2H), 2.93 (s, 3H), 2.83 (s, 3H), 1.48 (t, J = 8.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.2, 139.5, 132.1, 125.3, 125.2, 123.7, 123.4, 122.5, 121.8, 119.5, 117.1, 108.8, 39.9, 20.5, 18.9, 15.5; m/z = 302, positive mode; anal. calc. for $C_{16}H_{16}BrN$: C, 63.59; H, 5.34; N, 4.63%; found: C, 63.48; H, 5.43; N, 4.55%.

2-Bromo-6-*tert*-butyl-9-ethyl-1,4-dimethyl-9*H*-carbazole (17). An oven-dried 100 mL round-bottomed flask equipped with a Teflon-coated magnetic stirring bar is charged with 2 g (6.6 mmol) of **16**, 40 mL of dichloromethane and 0.9 g (6.6 mmol) of anhydrous aluminium chloride under stirring. To it, 2 mL of *tert*-butyl chloride is added slowly and the reaction mixture is stirred at room temperature for 6 h, after which time TLC (98 : 02 hexanes : ethyl acetate) indicated complete conversion. The reaction mass is poured into crushed ice slowly, neutralized with a solution of aq. 5% sodium bicarbonate and extracted with ethyl acetate. The organic layer is washed with water and brine, dried over anhydrous sodium sulfate and the solvent is removed under reduced pressure to give **17** as a white solid in 94% yield. mp: 82–84 °C; ν_{max} (KBr)/cm^{-1}: 2962, 2862, 1566, 1462, 1375, 1309, 1236, 1172, 1120, 1020, 949, 879, 833, 802, 640, 561, 443; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (d, J = 1.6 Hz, 1H), 7.60 (dd, J = 8.8, 2 Hz, 2H), 7.40 (d, J = 8.8 Hz, 1H), 7.28 (s, 1H), 4.60 (q, J = 7.6 Hz, 2H), 2.92 (s, 3H), 2.84 (s, 3H), 1.50 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.3, 139.8, 139.3, 131.8, 125.3, 123.6, 123.3, 123.1, 122.0, 118.6, 117.0, 108.3, 39.0, 34.6, 32.0, 20.6, 19.1, 15.6; m/z = 359, positive mode; anal. calc. for $C_{20}H_{24}BrN$: C, 67.04; H, 6.75; N, 3.91%; found: C, 67.12; H, 6.63; N, 3.85%.

2-Bromo-6-*tert*-butyl-9-ethyl-1,4-dimethyl-9*H*-carbazole-3-carbaldehyde (18). The general procedure for Vilsmeir–Haack formylation is used. Starting from **17**, the formylated product is obtained as a white solid after column purification (eluent: 5–10% ethyl acetate in hexane). The product is eluted in 7% eluent as a white solid. Yield: 75%. mp: 126–128 °C; ν_{max} (KBr)/cm^{-1}: 2964, 2916, 2856, 1672, 1593, 1440, 1340, 1309, 1222, 1155, 898, 846, 704, 569; ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.66 (s, 1H), 8.31 (s, 1H), 7.65 (dd, J = 1.6 Hz, 8.4 Hz, 1H), 7.41 (d, J = 1.2 Hz, 1H), 4.56 (q, J = 7.6 Hz, 2H), 3.10 (s, 3H), 2.90 (s, 3H), 1.50 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.8, 143.5, 141.5, 139.9, 135.7, 128.4, 125.5, 124.2, 123.6, 122.7, 119.7, 118.0, 108.8, 40.3, 34.8, 32.0, 19.0, 17.1, 15.6; m/z = 386, positive mode, 330 and 332 for the fragment without the *t*-butyl group; anal. calc. for $C_{21}H_{24}BrNO$: C, 65.29; H, 6.26; N, 3.63%; found: C, 65.41; H, 6.23; N, 3.56%.

6-*tert*-Butyl-9-ethyl-1,4-dimethyl-2-(phenylethynyl)-9*H*-carbazole-3-carbaldehyde (1d). General Sonogashira reaction conditions are employed as in the cases of **1a–1c**. **1d** is obtained as a light yellow solid in 85% yield. mp: 130–132 °C; ν_{max} (KBr)/cm^{-1}: 2957, 1674, 1556, 1487, 1342, 1307, 1228, 802, 754, 688, 526; ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.06 (s, 1H), 8.37 (s, 1H), 7.62–7.65 (m, 3H), 7.42–7.43 (m, 4H), 4.60 (q, J = 7.6 Hz, 2H), 3.24 (s, 3H), 3.05 (s, 3H), 1.51 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.4, 143.4, 141.1, 140.2, 135.7, 131.4, 128.6, 128.5, 126.6, 125.9, 124.3, 123.9, 123.3, 123.2, 120.2, 119.9, 108.7, 101.0, 86.3, 39.9, 34.8, 32.0, 17.0, 16.99, 15.7; m/z = 408, positive mode; anal. calc. for $C_{29}H_{29}NO$: C, 85.47; H, 7.17; N, 3.44%; found: C, 85.32; H, 7.21; N, 3.51%.

General procedure for the synthesis of ellipticinium triflates. An oven-dried 10 mL round-bottomed flask equipped with a Teflon-coated magnetic stirring bar is charged with 0.3 mmol of 3-formyl-2-phenylethynylcarbazole, 0.3 mmol of amine, 0.5 g of anhydrous magnesium sulfate and 5 mL of dichloromethane. The reaction mixture is refluxed for 1–2 h under stirring. The yellow solution is filtered and the filtrate is concentrated under vacuum. The compound is freshly dissolved in 5 mL of dichloromethane under stirring. To it, 0.3 mmol silver triflate is added and stirred at room temperature for 1 h. The reaction mass is diluted with dichloromethane, filtered and the solvent is removed under reduced pressure. The crude product is recrystallized from ethanol as a dark yellow crystalline solid.

2-(4-Chlorophenyl)-6-ethyl-9-methyl-3-phenyl-6*H*-pyrido[4,3-*b*]carbazol-2-ium triflate (19). mp: 189–191 °C; ν_{max} (KBr)/cm^{-1}: 3488, 2959, 1622, 1454, 1412, 1257, 1035, 837, 765, 632; ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.23 (s, 1H), 9.33 (s, 1H), 8.54 (s, 1H), 8.41 (s, 1H), 8.32 (s, 1H), 7.78 (d, J = 8.4 Hz, 1H), 7.71–7.73 (d, 2H), 7.61–7.64 (m, 3H), 7.43 (s, 6H), 4.63 (d, J = 7.6 Hz, 2H), 2.57 (s, 3H), 2.50 (s, 3H), 1.44 (t, J = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.0, 146.4, 143.1, 141.4, 141.3, 136.1, 135.2, 133.5, 131.6, 131.4, 130.6, 130.1, 129.8, 129.6, 129.1, 128.9, 124.7, 123.9, 122.7, 121.7, 120.2, 112.2, 110.7, 38.5, 21.3, 13.6; m/z = 448, positive mode; anal. calc. for $C_{30}H_{24}ClN_2$: C, 80.43; H, 5.40; N, 6.25%; found: C, 80.25; H, 5.48; N, 6.17%.

6-Ethyl-9-methyl-3-phenyl-2-*p*-tolyl-6*H*-pyrido[4,3-b]carbazol-2-ium triflate (20). mp: 212–214 °C; ν_{max} (KBr)/cm^{-1}: 3028, 2924, 1608, 1564, 1494, 1435, 1259, 1028, 763, 698, 638, 516; ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.13 (s, 1H), 9.27 (s, 1H), 8.49 (s, 1H), 8.43 (s, 1H), 8.38 (s, 1H), 7.64 (d, J = 8.0 Hz, 2H), 7.40–7.57 (m, 5H), 7.34 (s, 1H), 7.03 (d, J = 8.0 Hz, 2H), 4.74 (q, J = 8.0 Hz, 2H), 3.77 (s, 1H), 2.82 (s, 3H), 1.15 (t, J = 8.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.3, 152.0, 147.0, 143.4, 139.7, 136.0, 135.5, 134.8, 133.8, 131.4, 130.5, 129.9, 129.2, 128.9, 128.8, 124.9, 123.2, 122.7,

121.6, 120.4, 120.3, 114.7, 103.3, 56.1, 40.4, 21.0, 19.4, 15.2; *m/z* = 428, positive mode; anal. calc. for $C_{31}H_{27}N_2$: C, 87.06; H, 6.37; N, 6.55%; found: C, 87.15; H, 6.34; N, 6.68%.

6-Ethyl-9-methyl-2-pentyl-3-phenyl-6*H*-pyrido[4,3-*b*]carbazol-2-ium triflate (21). mp: 193–195 °C; ν_{max} (KBr)/cm^{-1}: 3419, 2916, 2862, 2259, 2112, 1653, 1477, 1440, 1019, 1076, 826, 759; ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.15 (s, 1H), 9.31 (s, 1H), 8.52 (s, 1H), 8.38 (s, 1H), 8.27 (s, 1H), 7.75 (d, *J* = 8.0 Hz, 1H), 7.53 (d, *J* = 8.0 Hz, 1H), 7.46–7.39 (m, 7H), 7.32 (d, *J* = 8.0 Hz, 2H), 4.60 (q, *J* = 8.0 Hz, 2H), 2.56 (s, 3H), 1.43 (t, *J* = 8.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.8, 146.3, 143.2, 141.4, 140.3, 136.0, 133.7, 131.5, 131.4, 130.5, 130.2, 129.9, 129.0, 128.8, 127.3, 124.9, 123.8, 122.6, 121.7, 120.2, 110.6, 103.2, 38.0, 21.3, 21.1, 13.6; *m/z* = 408, positive mode; anal. calc. for $C_{29}H_{31}N_2$: C, 85.46; H, 7.67; N, 6.87%; found: C, 85.23; H, 7.76; N, 6.75%.

2-Allyl-6-ethyl-9-methyl-3-phenyl-6*H*-pyrido[4,3-*b*]carbazol-2-ium triflate (22). mp: 185–187 °C; ν_{max} (KBr)/cm^{-1}: 3418, 2872, 2254, 2127, 1651, 1487, 1439, 1028, 1006, 825, 763; ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.08 (s, 1H), 9.10 (s, 1H), 8.21–8.28 (m, 3H), 7.72–7.73 (m, 6H), 7.50 (d, 1H), 4.52 (t, 4H), 2.53 (s, 3H), 1.70 (s, 2H), 1.37 (t, *J* = 7.2 Hz, 3H), 1.08 (s, 4H), 0.71 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.5, 145.9, 142.8, 141.3, 135.2, 133.2, 131.3, 131.0, 130.3, 121.4, 128.8, 125.5, 123.0, 122.6, 122.62, 120.5, 110.3, 103.0, 57.6, 38.3, 30.1, 28.0, 21.6, 21.3, 13.9, 13.6; *m/z* = 376, negative mode; anal. calc. for $C_{27}H_{25}N_2$: C, 85.90; H, 6.68; N, 7.42%; found: C, 85.96; H, 6.61; N, 7.32%.

6-Ethyl-7,9-dimethyl-3-phenyl-2-p-tolyl-6*H*-pyrido[4,3-*b*]carbazol-2-ium triflate (23). mp: 211–213 °C; ν_{max} (KBr)/cm^{-1}: 3418, 2916, 2253, 2125, 166, 1651, 1271, 1224, 1159, 1024, 823, 760; ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.17 (s, 1H), 8.45 (s, 1H), 7.85 (t, *J* = 7.2 Hz, 2H), 7.83 (d, *J* = 8.0 Hz, 2H), 7.40–7.72 (m, 7H), 4.84 (q, *J* = 7.2 Hz, 2H), 3.40 (s, 3H), 3.16 (s, 3H), 1.39 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.0, 145.2, 144.9, 142.4, 141.3, 135.3, 135.1, 135.0, 133.7, 130.9, 129.9, 129.6, 128.8, 128.1, 127.5, 123.1, 122.2, 121.8, 121.2, 120.2, 119.2, 111.3, 110.5, 40.1, 35.1, 32.1, 15.9, 15.7, 13.9; *m/z* = 442, positive mode; anal. calc. for $C_{32}H_{29}N_2$: C, 87.04; H, 6.62; N, 6.34%; found: C, 87.12; H, 6.59; N, 6.45%.

6-Ethyl-2-(4-methoxyphenyl)-7,9-dimethyl-3-phenyl-6*H*-pyrido[4,3-*b*]carbazol-2-ium triflate(24). mp: 204–206 °C; ν_{max} (KBr)/cm^{-1}: 2916, 2856, 1606, 1493, 1439, 1265, 1145, 1028, 634, 516; ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.14 (s, 1H), 9.29 (s, 1H), 8.33 (s, 1H), 8.26 (s, 1H), 8.13 (s, 1H), 7.64–7.68 (m, 6H), 7.29 (s, 1H), 6.42 (q, *J* = 1.2 Hz, 1H), 6.14 (d, *J* = 3.6 Hz, 1H), 5.86 (s, 2H), 4.68 (d, 2H), 2.78 (s, 3H), 2.50 (s, 3H), 1.42 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.2, 147.3, 146.8, 144.8, 142.7, 139.7, 135.6, 134.7, 132.9, 131.2, 130.8, 130.3, 129.4, 129.2, 125.7, 123.0, 122.7, 121.5, 120.6, 120.5, 111.5, 111.4, 103.3, 54.0, 21.0, 19.3, 15.2; *m/z* = 458, positive mode; anal. calc. for $C_{32}H_{29}N_2O$: C, 83.99; H, 6.39; N, 6.12%; found: C, 83.85; H, 6.41; N, 6.32%.

6-Ethyl-2-(furan-2-ylmethyl)-7,9-dimethyl-3-phenyl-6*H*-pyrido[4,3-*b*]carbazol-2-ium triflate (25). mp: 219–221 °C; ν_{max} (KBr)/cm^{-1}: 2947, 2872, 1647, 1518, 1269, 1161, 1028, 825; ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.06 (s, 1H), 9.34 (s, 1H), 8.37 (s, 1H), 8.32 (d, 2H), 7.59–7.76 (m, 7H), 6.0 (m, *J* = 5.2 Hz, 1H), 5.28 (d, *J* = 10.2 Hz, 1H), 5.18 (d, *J* = 5.2 Hz, 1H), 4.95 (d, *J* = 1.7 Hz, 1H), 4.58 (q, *J* = 7.6 Hz, 2H), 2.57 (s, 3H), 1.40 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.8, 146.1, 143.2, 141.4, 135.5, 133.07, 132.6, 131.4, 131.2, 130.8, 130.3, 129.3, 129.0, 125.5, 123.3, 122.7, 121.7, 120.6, 120.3, 110.5, 103.16, 59.6, 38.4, 21.4, 13.6; *m/z* = 432, positive mode; anal. calc. for $C_{30}H_{27}N_2O$: C, 83.50; H, 6.31; N, 6.49%; found: C, 83.39; H, 6.28; N, 6.53%.

2-(4-Chlorophenyl)-6-ethyl-7,9-dimethyl-3-phenyl-6*H*-pyrido[4,3-*b*]carbazol-2-ium triflate (26). mp: 197–199 °C; ν_{max} (KBr)/cm^{-1}: 3485, 2957, 1626, 1458, 1410, 1257, 1032, 833, 763, 638; ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.09 (s, 1H), 8.59 (s, 1H), 8.45 (s, 1H), 7.83 (t, *J* = 6.8 Hz, 2H), 7.58 (d, *J* = 7.6 Hz, 2H), 7.10–7.46 (m, 5H), 7.02 (d, *J* = 8.0 Hz, 2H), 4.82 (s, 2H), 3.96 (s, 3H), 3.69 (s, 3H), 3.15 (s, 3H), 1.46 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.3, 149.1, 145.0, 144.8, 142.8, 142.4, 135.6, 135.2, 134.7, 134.0, 130.8, 129.7, 129.2, 128.7, 128.0, 127.4, 122.0, 121.8, 121.1, 120.2, 114.6, 111.2, 110.5, 56.1, 40.1, 35.1, 32.1, 15.9, 15.7, 14.4; *m/z* = 463, positive mode; anal. calc. for $C_{31}H_{26}ClN_2$: C, 80.59, H, 5.67, N, 6.06%; found: C, 80.45, H, 5.71, N, 6.12%.

2-Allyl-6-ethyl-7,9-dimethyl-3-phenyl-6*H*-pyrido[4,3-*b*]carbazol-2-ium triflate (27). mp: 157–159 °C; ν_{max} (KBr)/cm^{-1}: 3417, 2869, 2248, 2129, 1660, 1488, 1440, 1029, 1011, 825, 762; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.98 (s, 1H), 9.22 (s, 1H), 8.32 (s, 1H), 8.25 (s, 1H), 8.10 (s, 1H), 7.61–7.70 (m, 5H), 7.28 (s, 1H), 6.00 (m, 1H), 5.28 (d, *J* = 10.4 Hz, 1H), 5.17 (d, *J* = 4.4 Hz, 2H), 4.95 (d, *J* = 17.2 Hz, 1H), 4.67 (d, *J* = 8.0 Hz, 2H), 2.78 (s, 3H), 2.48 (s, 3H), 1.41 (t, *J* = 8.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.6, 146.7, 143.0, 139.7, 135.5, 134.7, 133.1, 132.5, 131.2, 130.8, 130.3, 129.9, 129.3, 129.1, 125.5, 122.7, 122.6, 122.0, 121.4, 120.7, 120.4, 103.2, 59.6, 21.0, 19.4, 15.3; *m/z* = 392, positive mode; anal. calc. for $C_{28}H_{27}N_2$: C, 85.89, H, 6.95, N, 7.15%; found: C, 85.76, H, 6.91, N, 7.07%.

9-*tert*-Butyl-2-(4-chlorophenyl)-6-ethyl-5,11-dimethyl-3-phenyl-6*H*-pyrido[4,3-*b*]carbazol-2-ium triflate (28). mp: 193–195 °C; ν_{max} (KBr)/cm^{-1}: 3057, 2957, 1732, 1624, 1587, 1510, 1458, 1410, 1280, 1255, 1141, 1030, 763, 636, 515; ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.10 (d, *J* = 5.6 Hz, 1H), 8.60 (d, *J* = 6.0 Hz, 1H), 8.45 (d, *J* = 6.0 Hz, 1H), 7.83 (d, 2H), 7.27–7.54 (m, 9H), 4.82 (s, 2H), 3.89 (s, 3H), 3.16 (s, 3H), 2.33 (s, 3H), 1.46 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.9, 145.1, 144.8, 142.6, 142.4, 140.3, 140.1, 135.2, 134.8, 134.0, 130.8, 130.0, 129.8, 128.7, 127.6, 127.4, 122.7, 122.3, 121.9, 121.1, 120.2, 111.2, 110.5, 60.2, 35.1, 32.1, 21.2, 15.9, 14.5, 13.9; *m/z* = 518, positive mode; anal. calc. for $C_{35}H_{34}ClN_2$: C, 81.14; H, 6.61; N, 5.41%; found: C, 81.32; H, 6.57; N, 5.45%.

9-*tert*-Butyl-6-ethyl-5,11-dimethyl-3-phenyl-2-p-tolyl-6*H*-pyri-0do[4,3-*b*]carbazol-2-ium triflate (29). mp: 183–185 °C; ν_{max} (KBr)/cm^{-1}: 3057, 2916, 1626, 1601, 1521, 1452, 1275, 1221, 852, 763, 740; ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.17 (s, 1H), 9.28 (s, 1H), 8.51 (s, 1H), 8.39 (s, 1H), 8.13 (s, 1H), 7.69 (d, *J* = 8.4 Hz, 2H), 7.60 (d, *J* = 8.4 Hz, 2H), 7.41 (bs, 5H), 7.35 (s, 1H), 4.75 (q, *J* = 7.2 Hz, 2H), 3.40 (s, 3H), 2.82 (s, 3H), 1.44 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.8, 147.2, 142.9, 141.3, 139.8, 136.1, 135.2, 134.9, 133.4, 131.5, 130.6, 130.1, 129.8, 128.9, 124.9, 123.5, 122.7, 121.7, 120.4, 120.3, 103.4, 40.1, 21.0, 19.4, 15.2; *m/z* = 498, positive mode; anal. calc. for $C_{36}H_{37}N_2$: C, 86.88; H, 7.49; N, 5.63%; found: C, 86.73; H, 7.55; N, 5.71%.

9-*tert*-Butyl-6-ethyl-2-(4-methoxyphenyl)-5,11-dimethyl-3-phenyl-6*H*-pyrido[4,3-*b*]carbazol-2-ium triflate (30). mp: 251–253 °C; ν_{max} (KBr)/cm^{-1}: 3466, 2916, 2852, 1606, 1494, 1435, 1332, 1263, 1032, 763, 698, 516; ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.16 (s, 1H), 9.29 (s, 1H), 8.50 (s, 1H), 8.40 (s, 1H), 8.11 (s, 1H), 7.31–7.51 (m, 10H), 4.76 (s, 2H), 2.83 (s, 3H), 2.33 (s, 3H), 1.45 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.9, 147.0, 143.2, 140.2, 139.8, 136.0, 134.8, 133.8, 131.4, 130.5, 130.2, 129.9, 129.2, 128.8, 127.3, 125.0, 123.3, 122.7, 121.7, 120.4, 103.5, 21.2, 21, 19.4, 15.2; m/z = 514, positive mode; anal. calc. for $C_{36}H_{37}N_2O$: C, 84.17; H, 7.26; N, 5.45%; found: C, 84.07; H, 7.31; N, 5.56%.

General procedure for the synthesis of ellipticines. An oven-dried 10 mL round-bottomed flask equipped with a Teflon-coated magnetic stirring bar is charged with 0.3 mmol of 3-formyl-2-phenylethynylcarbazole and 1 mL of *tert*-butylamine. The reaction mixture is stirred at room temperature for 12 h and excess *tert*-butylamine is removed under vacuum. The residue is dissolved in 3 mL of DMF, CuI (0.03 mmol) is added and heated at 90 °C for 2 h. The reaction is allowed to cool to room temperature, poured into ice and extracted with ethyl acetate. The organic layer is washed with water and brine, dried over anhydrous sodium sulfate and the solvent is removed under reduced pressure. The crude material is purified by column chromatography (eluent: 10% ethyl acetate in hexane). The product is eluted in 10% eluent as a light yellow solid.

6-Ethyl-9-methyl-3-phenyl-6*H*-pyrido[4,3-*b*]carbazole (3a). mp: 176–178 °C; ν_{max} (KBr)/cm^{-1}: 3433, 3057, 2976, 2868, 1876, 1697, 1612, 1412, 1300, 1221, 1016, 935, 696, 464; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.47 (s, 1H), 8.60 (s, 1H), 8.20–8.22 (d, 2H), 8.16 (s, 1H), 8.03 (s, 1H), 7.54–7.58 (m, 3H), 7.40–7.47 (m, 2H), 7.31 (s, 1H), 4.35 (q, J = 7.6 Hz, 2H), 2.60 (s, 3H), 1.48 (t, J = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.0, 149.5, 142.7, 140.8, 140.2, 135.2, 129.0, 129.0, 128.7, 128.1, 127.0, 126.2, 122.8, 122.6, 121.4, 119.0, 115.8, 108.1, 101.4, 37.7, 21.4, 13.2; m/z = 337, positive mode; anal. calc. for $C_{24}H_{20}N_2$: C, 85.68; H, 5.99; N, 8.33%; found: C, 85.51; H, 5.91; N, 8.45%.

6-Ethyl-3-phenyl-6*H*-pyrido[4,3-*b*]carbazole (3b). mp: 170–172 °C; ν_{max} (KBr)/cm^{-1}: 2966, 2924, 1630, 1601, 1466, 1261, 1097, 1018, 800, 690, 468; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.48 (s, 1H), 8.63 (s, 1H), 8.17–8.23 (m, 4H), 7.52–7.67 (m, 4H), 7.39–7.45 (m, 2H), 7.31 (t, J = 7.6 Hz, 1H), 4.37 (q, J = 7.2 Hz, 2H), 1.49 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.0, 149.6, 142.6, 140.1, 135.2, 128.2, 127.8, 127.0, 126.2, 122.7, 122.7, 121.3, 119.6, 115.9, 108.4, 101.5, 37.7, 29.7, 28.3, 13.3; m/z = 323, positive mode; anal. calc. for $C_{23}H_{18}N_2$: C, 85.68; H, 5.63; N, 8.69%; found: C, 85.49; H, 5.71; N, 8.61%.

6-Ethyl-7,9-dimethyl-3-phenyl-6*H*-pyrido[4,3-*b*]carbazole (3c). mp: 183–185 °C; ν_{max} (KBr)/cm^{-1}: 3435, 3052, 2971, 2866, 1873, 1692, 1612, 1409, 1302, 1223, 1016, 690; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.45 (s, 1H), 8.58 (s, 1H), 8.18 (d, J = 1.6 Hz, 2H), 8.15 (s, 1H), 7.88 (s, 1H), 7.57 (s, 1H), 7.55 (t, J = 7.6 Hz, 2H), 7.44 (t, J = 7.2 Hz, 1H), 7.12 (s, 1H), 4.57 (q, J = 7.2 Hz, 2H), 2.78 (s, 3H), 2.53 (s, 3H), 1.45 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.9, 149.4, 143.6, 140.2, 139.4, 135.2, 132.6, 129.2, 128.7, 128.1, 127.0, 126.5, 123.7, 122.7, 119.7, 119.1, 118.6, 115.1, 101.7, 39.7, 29.0, 19.8, 15.0; m/z = 351, positive mode; anal. calc. for $C_{25}H_{22}N_2$: C, 85.68; H, 6.33; N, 7.99%; found: C, 85.51; H, 6.39; N, 7.86%.

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Notes and references

1 S. Goodwin, A. F. Smith and E. C. Horning, *J. Am. Chem. Soc.*, 1959, **81**, 1903.
2 R. B. Woodward, G. A. Iacobucci and F. A. Hochstein, *J. Am. Chem. Soc.*, 1959, **81**, 4434.
3 L. K. Dalton, S. Demerac, B. C. Elmes, J. W. Loder, J. M. Swan and T. Teitei, *Aust. J. Chem.*, 1967, **20**, 2715; G. H. Svoboda, G. A. Poore and M. L. Monfort, *J. Pharm. Sci.*, 1968, **57**, 1720.
4 N. C. Garbett and D. E. Graves, *Curr. Med. Chem.: Anti-Cancer Agents*, 2004, **4**, 149; M. Stiborová, M. S. Rupertova, M. B. Dohalska, M. Weissler and E. Frei, *Chem. Res. Toxicol.*, 2003, **16**, 38; J. F.-A. Stacie, M. W. Patchan, N. Osheroff and R. B. Thompson, *J. Biol. Chem.*, 1995, **270**, 14998.
5 G. W. Gribble and M. G. Saulnier, *Heterocycles*, 1985, **23**, 1277; V. K. Kansal and P. Potier, *Tetrahedron*, 1986, **42**, 2389; G. W. Gribble, *Synlett*, 1991, 289; Ditercalinium Chloride, *Drugs Future*, 1985, **10**, 116; M. Suffness and M. Sainsbury, *Synthesis*, 1977, 437; R. Barone and M. Chanon, *Heterocycles*, 1981, **16**, 1357; H.-J. Knölker, *Chem. Lett.*, 2009, **38**, 8; H.-J. Knölker and K. R. Reddy, *Chem. Rev.*, 2002, **102**, 4303; H.-J. Knölker, in *The Alkaloids*, ed. G. A. Cordell, Academic Press, Amsterdam, 2008, vol. 65, pp. 1–430.
6 Selected publications: T. Konakahara, Y. B. Kiran., Y. Okuno, R. Lkeda and N. Sakai, *Tetrahedron Lett.*, 2010, **51**, 2335; H.-Y. Lee, S. Chen, C. S. Chen and J.-W. Chern, *J. Heterocycl. Chem.*, 2010, **47**, 454; T. Surendiran, S. Balasubramanian and D. Selvaraj, *J. Chem. Environ.*, 2009, **13**, 81; M. Dračínský, J. Sejbal, B. Rygrova and M. Stiborova, *Tetrahedron Lett.*, 2007, **48**, 6893; D. Mal., B. Senapati and P. Pahari, *Synlett*, 2005, 994; N-L. Bennasar, T. Roca and F. Ferrando, *J. Org. Chem.*, 2005, **70**, 9077; J. M. Pedersen, W. R. Bowman, M. R. J. Elsegood, A. J. Fletcher and P. J. J. Lovell, *J. Org. Chem.*, 2005, **70**, 10615; Y. Ergün, S. Patir and G. Okay, *Synth. Commun.*, 2004, **34**, 435; M. Diaz, A. Copas, E. Guitien and L. Castedo, *Eur. J. Org. Chem.*, 2001, 4543; M. G. Saulnier and G. W. Gribble, *J. Org. Chem.*, 1982, **47**, 2810; R. B. Miller and S. Dugar, *Tetrahedron Lett.*, 1989, **30**, 297; R. B. Miller and J. G. Stowell, *J. Org. Chem.*, 1983, **48**, 886; M. Sainsbury and R. F. Schinazati, *J. Chem. Soc., Chem. Commun.*, 1975, 540; T. R. Govindachari, S. Rajappa and V. Sudarsanam, *Ind. J. Chem.*, 1963, **1**, 247; M. G. Ferlin, C. Marzano, V. Gandin, S. Dall'Acqua and L. D. Via, *ChemMedChem*, 2009, **4**, 363.
7 P. Juret, A. Tanguy, A. Girard, J. Y. Le Talaer, J. S. Abbatucci, N. Dat-Xuong, J.-B. Le Pecq and C. Paoletti, *Eur. J. Cancer*, 1978, **14**, 205; C. Paoletti, J.-B. Le Pecq, N. Dat-Xuong, P. Juret, H. Garnier, J.-L. Amiel and J. Rouesse, *Recent Results Cancer Res.*, 1980, **74**, 107; C. Auclair, A. Pierre, E. Voisin, O. Pepin, S. Cros, C. Colas, J.-M. Sauc-ier, B. Verschuere, P. Gros and C. Paoletti, *Cancer Res.*, 1987, **47**, 6254; N. Harada, T. Kawaguchi, I. Inoue, M. Ohashi, K. Oda, T. Hashiyama and K. Tsujihara, *Chem. Pharm. Bull.*, 1997, **45**, 134; G. Atassi, P. Dumont, O. Pepin, O. Gros and P. Gros, *Proc. Annual Meet. Am. Assoc. Cancer Res.*, 1989, **30**, A2458; V. Pierson, A. Pierre, Y. Pommier and P. Gros, *Cancer Res.*, 1988, **48**, 1404.
8 D. K. Sreenivas and R. Nagarajan, *Tetrahedron*, 2010, **66**, 9650; S. Ramesh, V. Gaddam and R. Nagarajan, *Synlett*, 2010, 757; R. Meesala and R. Nagarajan, *Tetrahedron Lett.*, 2010, **51**, 422; T. K. Chaitanya and R. Nagarajan, *Tetrahedron Lett.*, 2007, **48**, 2489; V. Gaddam and R. Nagarajan, *Org. Lett.*, 2008, **10**, 1975.
9 Recent examples: L. Liu, L. Wei and J. Zhang, *Adv. Synth. Catal.*, 2010, **352**, 1920; R. Mancuso, S. Mehta, B. Gabriele, G. Salerno, W. S. Jenks and R. C. Larock, *J. Org. Chem.*, 2010, **75**, 897; N. T. Patil, A. K. Mutyala, P. G. V. V. Lakshmi, P. V. K. Raju and B. Sridhar, *Eur. J. Org. Chem.*, 2010, 1999; R.-Y. Tang and J.-H. Li, *Chem.–Eur. J.*, 2010, **16**, 4733; D. B. Ramachary, R. Mondal and C. Venkaiah, *Eur.*

J. Org. Chem., 2010, **17**, 3205; X. Yu, Q. Ding and J. Wu, *J. Comb. Chem.*, 2010, **12**, 743; M. D. Hill, *Chem.–Eur. J.*, 2010, **16**, 12052; M. Bian, W. Yao, H. Ding and C. Ma, *J. Org. Chem.*, 2010, **75**, 269; A. K. Verma, V. Rustagi, T. Aggarwal and A. P. Singh, *J. Org. Chem.*, 2010, **75**, 7691; F. Yang, T. Jin, M. Bao and Y. Yamamoto, *Tetrahedron Lett.*, 2011, **52**, 936; Z. Chen, G. Huang, H. Jiang, H. Huang and X. Pan, *J. Org. Chem.*, 2011, **76**, 1134; X. Zhang, Y. Zhou, H. Wang, D. Guo, D. Ye, Y. Xu, H. Ziang and H. Liu, *Green Chem.*, 2011, **13**, 397; S. Ye, H. Wang and J. Wu, *Eur. J. Org. Chem.*, 2010, 6436; B. Crone, S. F. Kirch and K.-D. Umland, *Angew. Chem., Int. Ed.*, 2010, **49**, 4661.

10 G. Dai and R. C. Larock, *J. Org. Chem.*, 2003, **68**, 920; G. Dai and R. C. Larock, *J. Org. Chem.*, 2002, **67**, 7042; Q. Huang and R. C. Larock, *J. Org. Chem.*, 2003, **68**, 980; K. R. Roesch and R. C. Larock, *J. Org. Chem.*, 2002, **67**, 86; K. R. Roesch, H. Zhang and R. C. Larock, *J. Org. Chem.*, 2001, **66**, 8042; S. Roy, S. Roy, B. Neunswander, D. Hill and R. C. Larock, *J. Comb. Chem.*, 2009, **11**, 1061; H. Zhang and R. C. Larock, *J. Org. Chem.*, 2002, **67**, 7048; Z. Chen and J. Wu, *Org. Lett.*, 2010, **12**, 4856; H. Waldmann, L. Eberhardt, K. Wittslein and K. Kumar, *Chem. Commun.*, 2010, **46**, 4622; X. Yu and J. Wu, *J. Comb. Chem.*, 2010, **12**, 238; Z. Huo and Y. Yamamoto, *Tetrahedron Lett.*, 2009, **50**, 3651; Y.-N. Niu, Z.-Y. Yan, G.-L. Gao, H.-L. Wang, X.-Z. Shu, K.-G. Ji and Y.-M. Liang, *J. Org. Chem.*, 2009, **74**, 2893; H. Gao and J. Zhang, *Adv. Synth. Catal.*, 2009, **351**, 85; N. Fei, Q. Hou, S. Wang, H. Wang and Z.-J. Yao, *Org. Biomol. Chem.*, 2010, **8**, 4096; Z. Huo and Y. Yamamoto, *Tetrahedron Lett.*, 2009, **50**, 3651; F. Liu, X. Ding, L. Zhang, Y. Zhou, L. Zhao, H. Jiang and H. Liu, *J. Org. Chem.*, 2010, **75**, 5810; Z. Zhang and M. Shi, *Chem.–Eur. J.*, 2010, **16**, 7725; Y. Yamamoto, I. D. Gridnev, N. T. Patil and T. Jin, *Chem. Commun.*, 2009, 5075; S. Mukherjee, G. P. Jana and B. K. Gorai, *J. Organomet. Chem.*, 2009, **694**, 4100; S. Obika, H. Kono, Y. Yasi, R. Yanada and Y. Takemoto, *J. Org. Chem.*, 2007, **72**, 4462; R. P. Korivi and C.-H. Cheng, *Org. Lett.*, 2005, **7**, 5179; B. Wang, B. Lu, Y. Jiang, Y. Zhang and D. Ma, *Org. Lett.*, 2008, **10**, 2761; H.-S. Yeom, S. Kim and S. Shin, *Synlett*, 2008, 924; F. Maassarani, M. Pfeffer and G. Le Borgne, *J. Chem. Soc., Chem. Commun.*, 1987, 565; G. Wu, S. J. Geib, A. L. Rheingold and R. F. Heck, *J. Org. Chem.*, 1988, **53**, 3238; I. R. Girling and D. A. Widdowson, *Tetrahedron Lett.*, 1982, **23**, 4281.

11 The CCDC deposition number of **19** is 804670; molecular formula: $C_{31}H_{24}C_{11}F_3N_2O_3S_1$, unit cell parameters: $a = 8.1010(16)$, $b = 11.081(2)$, $c = 16.926(3)$ Å; space group $P\bar{1}$ The CCDC deposition number of **23** is 805312; molecular formula: $C_{33}H_{29}F_3N_2O_3S_1$, unit cell parameters: $a = 8.1925(3)$, $b = 16.7763(8)$, $c = 21.6041(10)$; space group *Pna*2†.

12 A. K. Flatt, Y. Yao, F. Maya and J. M. Tour, *J. Org. Chem.*, 2004, **69**, 1752; J. M. Lopez-Romero *et al.*, *Tetrahedron Lett.*, 2007, **48**, 6075; D. D. Winkle and K. M. Schaab, *Org. Process Res. Dev.*, 2001, **5**, 450.

