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$AuCl_3$-catalyzed synthesis of (*E/Z*)–chloroallyl carbazoles via a cascade cyclization process

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Dedicated to Peter Maximus on the occasion of his birthday

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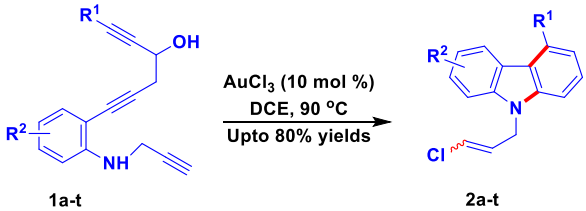
Abstract

An efficient, one pot, high yielding method for the formation of (*E/Z*)–chloroallyl carbazoles has been developed. The strategy involves a gold-catalyzed cascade cyclization and hydroamination reaction sequence, leading to the formation of new C-C, C-N and C-Cl bonds.



Keywords: Carbazoles, cascade reaction, gold catalysis, 5-*exo-dig* cyclization, 6-*endo-dig* cyclization

Introduction

Transition metal-catalyzed formation of C-C, C-N and C-O bonds has received considerable attention in modern organic chemistry.[1-3] Over the last few decades, various C-C and C-N bond formation methods have been developed for the construction of biologically active heterocycles.[4-7] In particular, nitrogen-containing heterocycles are found in many natural products and exhibit a broad spectrum of biological activity.[8-11] Among them, substituted carbazoles such as Murrayamine,[12] and Rimcazole [13] are found in the preparation of life-saving chemicals as shown in Figure 1.[14,15] The recent literature also revealed that substituted carbazoles are useful in the preparation of organic semiconductors, electroluminescent molecules, and organic light-emitting diodes due to their electronic and thermal stability properties.[16,17] Because of their extensive application in medicinal chemistry and material science, the development of new and efficient methods for the synthesis of substituted carbazoles has remained a hot topic in current research.[18-21] Several syntheses have been developed, including using hexen-1,5-diynes through intramolecular cyclization,[22,23] palladium,[24] and iodine[25] promoted reaction of *N,N*-dimethyl ethynylanilines. However, many of these methods require harsh reaction conditions, long reaction times, and multi-step synthesis.

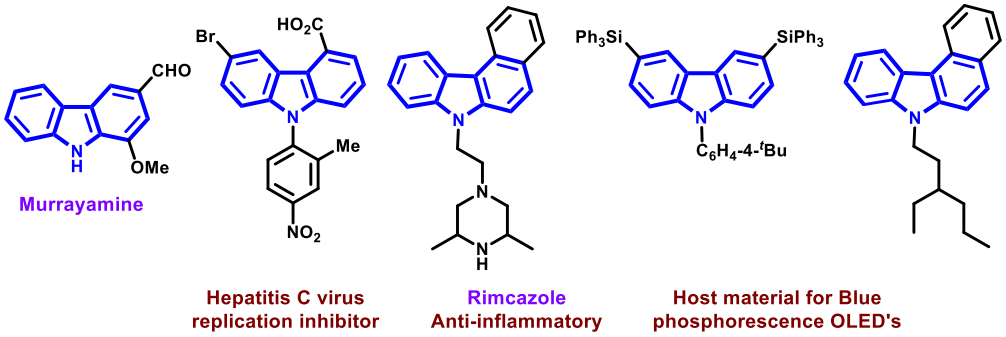
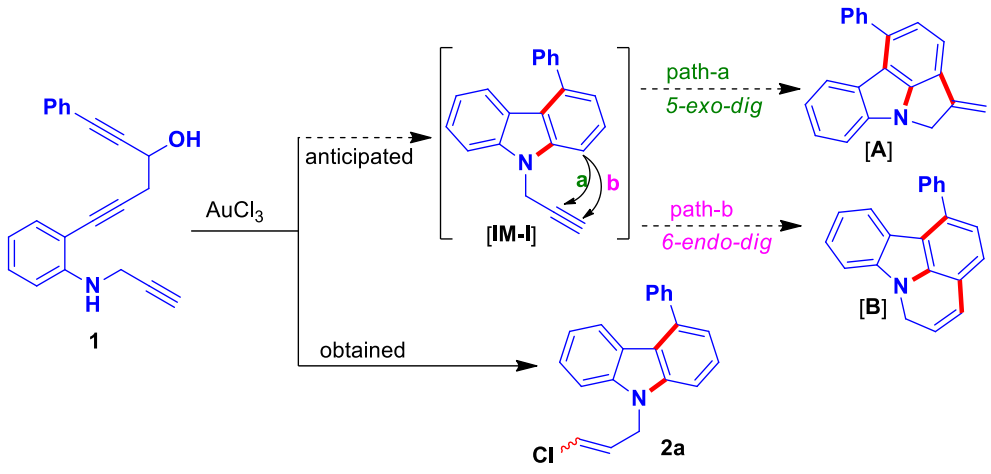


Figure 1. Selected examples bearing carbazole core unit.

In recent years, gold-catalyzed cascade reactions were more explored to generate structurally diverse complex molecules.[26-31] These catalysts have successfully been used for various organic transformations, owing to their ability to conduct reactions in pot manner.[32,33] Moreover, the recent developments in gold catalysts have heightened because of its excellent functional group tolerance.[34,35] In our ongoing investigations on the development of gold-catalyzed cascade reactions of alkynes,[36-41] we anticipated that the use of precursors, which have terminal acetylene **1** could lead to fused carbazoles **A** *via* a 5-*exo-dig* cyclization or **B** *via* a 6-*endo-dig* cyclization in the presence of a gold catalyst (Scheme 1). Instead of the expected substrates **A** or **B**, we observed a 50:50 ratio of (*E/Z*)-chloroallyl-substituted carbazoles **2a** (Scheme 1, bottom).



Scheme 1. Synthesis of (*E/Z*)–chloroallyl carbazoles.

Results and Discussion

The above mechanistic investigation and the scope of the reaction encouraged us to screen this organic transformation by using various catalysts (Table 1). In our initial attempt, the reaction of 1-phenyl-6-[2-(prop-2-yn-1-ylamino)phenyl]hexa-1,5-diyn-3-ol (**1a**) was treated in the presence of $AuClPPh_3$ (10 mol%) in DCE at 90 °C. Interestingly, the unexpected cascade reaction gave a 50:50 mixture of (*E/Z*) allyl-substituted carbazole **2a** in 41% yield (Table 1, entry 1).

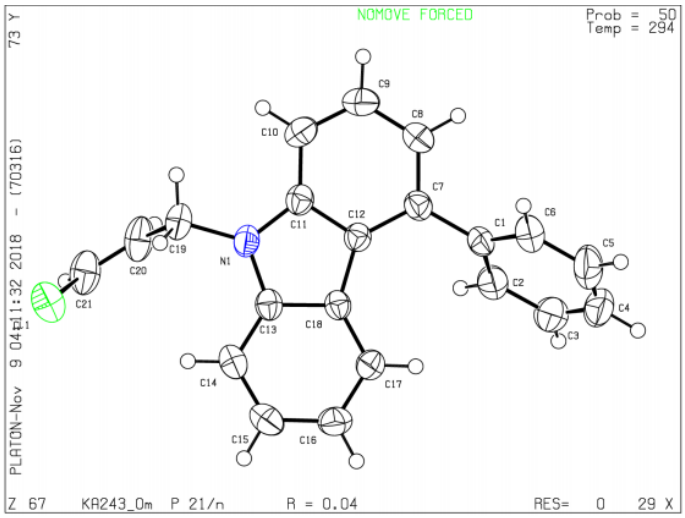
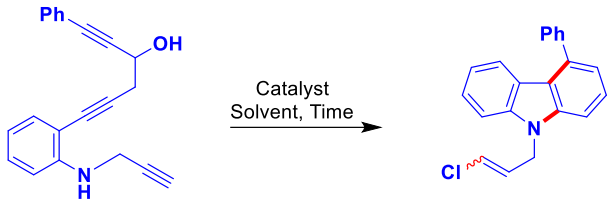


Figure 2. Single-crystal X-ray analysis of compound **2a**, CCDC1877690.[42]

Table 1. Optimization of the reaction conditions[a]



1a **2a**

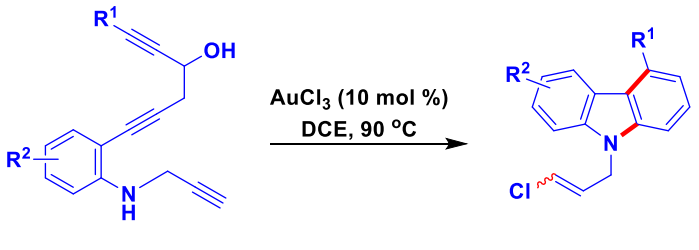
Entry	Catalyst (mol%)	Solvent	Temp (°C)	Time (h)	Yield[b]
1	$AuClPPh_3$ (10)	DCE	90	12	41
2	IPrAuCl (10)	DCE	90	12	15
3	$AuCl_3/AgSbF_6$ (10/15)	DCE	90	12	37
4	$AuCl_3$/AgOTf (10/15)	DCE	90	12	18
5	**$AuCl_3$ (10)**	**DCE**	**90**	**12**	**80**
6	$AuCl_3$ (10)	MeCN	90	18	37
6	$AuCl_3$ (10)	$MeNO_2$	90	24	35
7	$AuCl_3$ (10)	PhMe	90	24	16
8	$AuCl_3$ (10)	MeOH	90	24	21
9	$AuCl_3$ (10)	EtOH	90	16	17
10	$AuCl_3$ (10)	THF	90	24	24
11	$AuCl_3$ (10)	1,4-dioxane	90	20	22
12	$AuCl_3$ (10)	DMF	90	36	nr[c]

[a] Reaction conditions: all of the reactions were performed under a nitrogen atmosphere with **1a** (0.3 mmol) and solvent (3 mL) at 90 °C. [b] Yields of the isolated product. [c] nr = no reaction.

Encouraged by this result, we decided to improve the efficiency of the formation of the product **2a**. Different gold catalysts and catalyst combinations were tried, but most were less efficient (Table 1, entries 2–4). To our delight, when the reaction carried out in the presence of $AuCl_3$ (10 mol%) gave the product **2a** in 80% yield (Table 1, entry 5). We also conducted the experiments to check the effect of the solvent on this organic transformation, none of them gave better yields of product **2a** (Table 1, entries 6–12). Finally, the optimization study indicated that $AuCl_3$ (10 mol%) in DCE at 90 °C was the best conditions for the formation of allyl substituted carbazole **2a** (Table 1, entry 5).

With optimal reaction conditions in hand, we decided to check this organic transformation by using various *N*-propargylic 1,5-diynylanilines **1a-t**. The starting materials **1a–t** were prepared via the literature.[43-46] As shown in Table 2, the substrates **1b** (R^1 = 4-Tol, R^2 = H) and **1c** (R^1 = 4-$MeOC_6H_4$, R^2 = H) which have electron-donating groups at the R^1 positions gave the products **2b** and **2c** in 72 and 76% yields, respectively (Table 2, entries 2 & 3). When the substrate bearing electron-withdrawing group at R^1 position like **1d** (R^1 = 4-FC_6H_4, R^2 = H) gave the product **2d** in 71% yield (Table 2, entry 4). Substrates with aliphatic groups such as **1e** (R^1 = *n*-Pr, R^2 = H), **1f** (R^1 = *n*-C_5H_{11}, R^2 = H), **1g** (R^1 = *n*-C_6H_{13}, R^2 = H) and **1h** (R^1 = *n*-C_8H_{17}, R^2 = H) also provided the corresponding products **2e-h** in good yields (Table 2, entries 5–8).

Table 2. Scope of chloroallyl-substituted carbazole **2**[a]



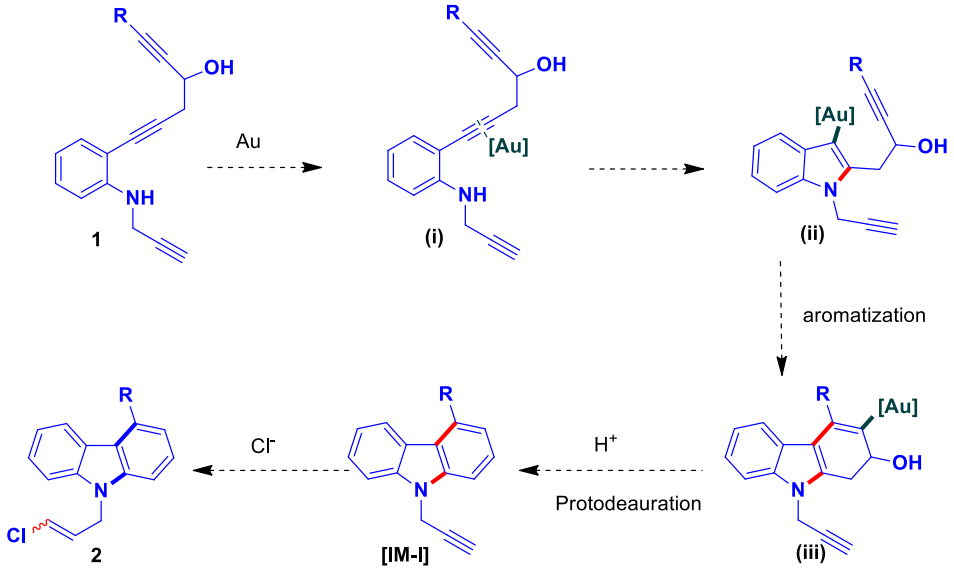
1a-h **2a-h**

Entry	R^1	R^2 [b]	Time (h)	Yield (%)[c]
1	Ph	H	12	**2a** (80)
2	4-Tol	H	14	**2b** (72)
3	4-$MeOC_6H_4$	H	13	**2c** (76)
4	4-FC_6H_4	H	18	**2d** (71)
5	*n*-Pr	H	14	**2e** (75)
6	*n*-C_5H_{11}	H	16	**2f** (76)
7	*n*-C_6H_{13}	H	18	**2g** (74)
8	*n*-C_8H_{17}	H	18	**2h** (78)
9	*n*-C_6H_{13}	3-Me	17	**2i** (72)
10	Ph	3-Cl	14	**2j** (75)
11	4-$MeOC_6H_4$	3-Cl	18	**2k** (66)
12	4-FC_6H_4	3-Cl	16	**2l** (65)
13	*n*-Pr	3-Cl	14	**2m** (77)
14	*n*-C_5H_{11}	3-Cl	16	**2n** (67)
15	*n*-C_6H_{13}	3-Cl	18	**2o** (79)
16	*n*-C_8H_{17}	3-Cl	18	**2p** (75)
17	Ph	2-Cl-3-Me	14	**2q** (73)
18	4-FC_6H_4	2-Cl-3-Me	16	**2r** (68)
19	*n*-C_6H_{13}	2-Cl-3-Me	18	**2s** (75)
20	*n*-C_8H_{17}	2-Cl-3-Me	18	**2t** (80)

[a] Reaction conditions: all reactions were carried out under a nitrogen atmosphere with **1a-t** (0.09 g), $AuCl_3$ (10 mol %) and DCE (3 mL) at 90 °C. [b] Substituent numbering based on the carbazole product. [c] Yields are for isolated products.

Furthermore, a range of substituted *N*-propargylic 1,5-diynylanilines (**1i–t**) were also examined under optimized conditions. The substrate **1i** which bears an electron-donating substitution at R^2 position (R^1 = *n*-C_6H_{13}, R^2 = Me) gave the desired product **2i** in the yield of 72% (Table 2, entry 9). Substitution at R^2 position with an electron-drawing groups like **1j** (R^1 = Ph, R^2 = Cl), **1k** (R^1 = 4-$MeOC_6H_4$, R^2 = Cl), **1l** (R^1 = 4-FC_6H_4, R^2 = Cl) **1m** (R^1 = *n*-Pr, R^2 = Cl), **1n** (R^1 = *n*-C_5H_{11}, R^2 = Cl), **1o** (R^1 = *n*-C_6H_{13}, R^2 = Cl) and **1p** (R^1 = *n*-C_8H_{17}, R^2 = Cl) gave the respective products **2j–p** in good yields (Table 2, entries 10–16). Substrates bearing both electron-donating and electron-withdrawing groups on R^2 position of **1q** (R^1 = Ph, R^2 = 3-Cl, 5-Me), **1r** (R^1 = 4-FC_6H_5, R^2 = 3-Cl, 5-Me), **1s** (R^1 = *n*-C_6H_{13}, R^2 = 3-Cl, 5-Me) and **1t** (R^1 = *n*-C_8H_{17}, R^2 = 3-Cl, 5-Me) were also well tolerated to give the respective products **2q–t** in good yields (Table 2, entries 16–20).

A plausible reaction mechanism can be proposed for the formation of *N*-chloroallyl carbazole **2** from aryl substituted *N*-propargyl 1,5-diynes **1** (Scheme 2). In the presence of gold catalyst substrate **1** can give the intermediate-I (**IM-I**) *via* initial 5-*exo dig* cyclization (i), then 6-*endo-dig* cyclization (ii), followed by aromatization (iii). Subsequently, the addition of chlorine to intermediate (**IM-I**) can be catalyzed by the gold catalyst to finally provide *N*-chloroallyl carbazoles **2**.



Scheme 2. A plausible reaction mechanism

Conclusions

We have developed a new method for the synthesis of 3-chloroallyl carbazoles **2** in very good yields from aryl-substituted *N*-propargyl 1,5-diynes in the presence of a gold catalyst. It is noteworthy that in this reaction 5-*exo dig* and 6-*endo-dig* cyclizations take place sequentially to create new C-C, C-N and C-Cl bonds.

Experimental Section

General. Reactions were carried out in oven dried reaction flasks under nitrogen atmosphere and also solvents and reagents were transferred by oven-dried syringes to ambient temperature. TLC was performed on Merck silica gel aluminium sheets using UV as a visualizing agent. Solvents were removed under reduced pressure. Columns were packed as slurry of silica gel in hexane and ethyl acetate solvent mixture. The elution was assisted by applying pressure with an air pump. ^{13}C NMR spectra were recorded on 75, 100 and 125 MHz spectrometers. ^{1}H NMR spectra were recorded on 300, 400 and 500 MHz spectrometers in appropriate solvents using TMS as internal standard. IR spectra were recorded by using a JASCOFT/IR 5300 spectrometer. The following abbreviations were used to explain multiplicities: s = singlet, d = doublet, dd = double doublet, dt = doublet of triplet, t = triplet, m = multiplet, brs = broad singlet. All reactions were performed under nitrogen atmosphere with freshly distilled and dried solvents. All solvents were distilled using standard procedures. Unless otherwise noted, reagents were obtained from Aldrich, Alfa Aesar, and TCI used without further purification.

Typical procedure for the preparation of (*E/Z*)–chloroallyl carbazoles 2. Synthesis of (*E/Z*) 9-(3-chloroallyl)-4-phenyl-9*H*-carbazole (2a). To a 25 mL, round-bottomed, two-neck flask equipped with magnetic stir bar was added 1-phenyl-6-[2-(prop-2-yn-1-ylamino)phenyl]hexa-1,5-diyn-3-ol (**1a**) (0.09 g, 0.3 mmol), the flask was purged with dry nitrogen, then the compound was dissolved in dry DCE (3 mL). To this reaction flask were added $AuCl_3$ (0.089 g, 0.03 mmol, 10 mol %). The reaction mixture was allowed to stir at 80 °C temperature for 12 h. After completion of the reaction (monitored by TLC), the reaction mixture was filtered through a Celite pad. The organic layer was removed under reduced pressure and extracted with EtOAc (3 × 5 mL). The combined organic layers were washed with saturated brine solution, dried over anhydrous Na_2SO_4 and concentrated under vacuum. The crude residue was purified through a silica gel column chromatography using hexane and EtOAc as eluent (10/0.2) to give mixture of (*E/Z*)-9-(3-chloroallyl)-4-phenyl-*9H*-carbazole (**2a**). A similar experimental procedure, at 0.09 g scale, was adopted for the synthesis of all compounds **2b-t**.

(*E/Z) 9-(3*-Chloroallyl)-4-phenyl-*9H*-carbazole *(2a).* Pale yellow solid (76.3 mg, 80%); mp 107-109 °C (not recrystallised); R_f 0.50 Hexane/EtOAc (20:1); IR (KBr): 3055, 2923, 2852, 1587, 1457, 1325, 754, 565 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): *δ* 7.637.60 (m, 4H), 7.55-7.45 (m, 10H), 7.44-7.37 (m, 6H), 7.13 (dd, *J* 7.3, 1.1 Hz, 2H), 7.03-6.95 (m, 2H), 6.30 (dt, *J* 7.1, 1.8 Hz, 1H), 5.92 (dd, *J* 13.3, 6.2 Hz, 1H), 5.32 (d, *J* 2.0 Hz, 1H), 5.17 (dd, *J* 6.2, 1.8 Hz, 2H), 5.09 (t, *J* 4.0 Hz, 2H), 5.06 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 141.1, 141.0, 140.4, 140.3, 140.2, 137.8, 135.7, 129.1, 128.3, 127.5, 127.4, 126.9, 125.8, 125.7,125.6, 125.5, 122.7, 122.5, 121.4, 121.0, 120.5, 119.3, 118.9, 112.9, 108.4, 108.3, 107.6, 107.5, 48.7, 39.8; MS (ESI, 70 eV) *m*/*z* 318 ($M+H^+$, 100%).

(*E/Z*) 9-(3-Chloroallyl)-4-(*p*-tolyl)-9*H*-carbazole (2b). Pale yellow solid (68.5 mg, 72%); mp 110-112 °C (not recrystallised); R_f 0.45 Hexane/EtOAc (20:1); IR (KBr) 3048, 2930, 2848, 1612, 1432, 1328, 723 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.57-7.46 (m, 8H), 7.40 (dd, *J* 5.1, 2.2 Hz, 4H), 7.38-7.30 (m, 6H), 7.14-7.08 (m, 2H), 7.04-6.97 (m, 2H), 6.27 (dt, *J* 7.1, 1.8 Hz, 1H), 5.89 (dd, *J* 13.3, 6.2 Hz, 1H), 5.30 (d, *J* 1.9 Hz, 1H), 5.15 (dd, *J* 6.2, 1.8 Hz, 2H), 5.03 (s, 2H), 4.93 (dd, *J* 3.6, 1.7 Hz, 1H), 2.49 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 140.5, 140.4, 140.3, 140.2, 138.2, 138.1, 137.9, 137.2, 137.1, 135.7, 129.1, 129.0, 126.9, 125.7, 125.6, 125.5, 122.8, 122.5, 121.5, 121.0, 120.5, 119.2, 118.8, 112.9, 108.4, 108.3, 107.4, 107.3, 48.7, 39.8, 21.3; MS (ESI, 70 eV) *m*/*z* 332 ($M+H^+$, 100%).

***(E/Z)* 9-(3-Chloroallyl)-4-(4-methoxyphenyl)-9*H*-carbazole (2c).** Brown solid (72.1 mg, 76%); mp 118-120 °C (not recrystallised); R_f 0.55 Hexane/EtOAc (20:1); IR (KBr) 3053, 2924, 2853, 1609, 1457, 1325, 723, 572 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): *δ* 7.55 (dd, *J* 8.7, 3.1 Hz, 8H), 7.52-7.45 (m, 2H), 7.39 (dd, *J* 15.1, 6.1 Hz, 8H), 7.12 (d, *J* 6.7 Hz, 2H), 7.09-6.98 (m, 10H), 6.28 (dt, *J* 7.1, 1.7 Hz, 1H), 5.96-5.85 (m, 1H), 5.31 (d, *J* 1.6 Hz, 1H), 5.16 (dd, *J* 6.2, 1.7 Hz, 2H), 5.04 (s, 2H), 4.93 (d, *J* 1.8 Hz, 1H), 3.93 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 159.1, 140.5, 140.3, 137.6, 135.7, 133.4, 130.2, 125.7, 125.8, 122.8, 122.5, 121.5, 121.0, 119.3, 113.7, 112.9, 108.4, 107.34, 55.3, 48.7; MS (ESI, 70 eV) *m*/*z* 348 ($M+H^+$, 100%).

(*E/Z*) 9-(3-Chloroallyl)-4-(4-fluorophenyl)-9*H*-carbazole (2d). Colorless solid (67.5 mg, 71%); mp 116-118 °C (not recrystallised); R_f 0.45 Hexane/EtOAc (20:1); IR (KBr) 3052, 2923, 2853, 1594, 1456, 1323, 722, 561 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): *δ* 7.63-7.54 (m, 4H), 7.53-7.48 (m, 2H), 7.42 (dd, *J* 12.6, 5.0 Hz, 8H), 7.25-7.19 (m, 4H), 7.11 (dd, *J* 7.3, 0.9 Hz, 2H), 7.03 (dd, *J* 8.4, 1.6 Hz, 2H), 6.30 (dt, *J* 7.1, 1.8 Hz, 1H), 5.91 (dd, *J* 13.3, 6.2 Hz, 1H), 5.33-5.30 (m, 1H), 5.17 (dd, *J* 6.2, 1.8 Hz, 2H), 5.06 (t, *J* 1.4 Hz, 2H), 4.94 (dd, *J* 3.7, 1.7 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 166.6 (d, $^1J_{CF}$ 241.3 Hz), 140.3, 136.7, 135.7, 130.8, 130.7, 125.9, 125.7 (d, $^2J_{CF}$ 8.0 Hz), 122.3, 121.4, 119.4, 115.4, 115.2, 112.9, 108.6, 107.8, 48.8; MS (ESI, 70 eV) *m*/*z* 336 ($M+H^+$, 100%).

(*E/Z*) 9-(3-Chloroallyl)-4-propyl-9*H*-carbazole (2e). Viscous orange liquid (72.1 mg, 75%); R_f 0.45 Hexane/EtOAc (20:1); IR (neat) 3045, 2929, 2842, 1623, 1435, 1340, 728 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 8.13 (d, *J* 7.9 Hz, 2H), 7.49-7.43 (m, 2H), 7.39 (dt, *J* 11.0, 3.7 Hz, 4H), 7.31-7.26 (m, 2H), 7.23 (s, 2H), 7.06 (q, *J* 7.8 Hz, 2H), 6.25 (dt, *J* 7.1, 1.8 Hz, 1H), 5.91-5.83 (m, 1H), 5.27 (d, *J* 1.9 Hz, 1H), 5.12 (dd, *J* 6.2, 1.8 Hz, 2H),

5.02-4.97 (m, 2H), 4.87 (dd, *J* 3.5, 1.7 Hz, 1H), 3.25-3.14 (m, 4H), 1.94-1.83 (m, 4H), 1.11-1.07 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$)**:** *δ* 140.5, 140.1, 138.3, 135.7, 127.0, 125.7, 125.5, 125.3, 125.1, 123.1, 122.7, 120.9, 120.8, 120.5, 120.1, 119.7, 119.2, 112.7, 108.5, 108.4, 106.3, 106.2, 48.6, 45.8, 39.7, 36.4, 22.8, 14.2; MS (ESI, 70 eV) *m*/*z* 284 ($M+H^+$, 100%).

(*E/Z*) 9-(3-Chloroallyl)-4-pentyl-9*H*-carbazole (2f). Viscous brown liquid (72.6 mg, 76%); R_f 0.55 Hexane/EtOAc (20:1); IR (neat) 3051, 2926, 2855, 1591, 1460, 1327, 749 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 8.13 (d, *J* 7.9 Hz, 2H), 7.50-7.44 (m, 2H), 7.43-7.35 (m, 2H), 7.31-7.22 (m, 6H), 7.05 (t, *J* 7.0 Hz, 2H), 6.26 (dt, *J* 7.1, 1.8 Hz, 1H), 5.92-5.84 (m, 1H), 5.27 (dd, *J* 3.4, 1.4 Hz, 1H), 5.13 (dd, *J* 6.2, 1.8 Hz, 2H), 5.01 (t, *J* 1.4 Hz, 2H), 4.87 (dd, *J* 3.6, 1.7 Hz, 1H), 3.28-3.15 (m, 4H), 1.90-1.80 (m, 4H), 1.56-1.46 (m, 4H), 1.45-1.37 (m, 4H), 0.93 (t, *J* 7.2 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 140.1, 138.6, 135.7, 127.0, 125.7, 125.3, 122.7, 120.8, 120.4, 119.7, 119.2, 112.8, 108.5, 106.3, 48.6, 39.7, 34.4, 32.0, 22.6, 14.1; MS (ESI, 70 eV) *m*/*z* 312 ($M+H^+$, 100%).

(*E/Z*) 9-(3-Chloroallyl)-4-hexyl-9*H*-carbazole (2g). Viscous yellow liquid (70.5 mg, 74%); R_f 0.45 Hexane/EtOAc (20:1); IR (neat) 3051, 2925, 2854, 1591, 1460, 1327, 722 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 8.13 (d, *J* 7.9 Hz, 2H), 7.50-7.45 (m, 2H), 7.40-7.37 (m, 2H), 7.27-7.30 (m, 4H), 7.04 (t, *J* 7.0 Hz, 2H), 6.26 (dt, *J* 7.1, 1.8 Hz, 1H), 5.88 (dd, *J* 13.3, 6.2 Hz, 1H), 5.27 (d, *J* 1.9 Hz, 1H), 5.13 (dd, *J* 6.2, 1.8 Hz, 2H), 5.01 (s, 2H), 4.87 (dd, *J* 3.5, 1.7 Hz, 1H), 3.28-3.17 (m, 4H), 1.90-1.79 (m, 4H), 1.52 (dd, *J* 14.9, 6.7 Hz, 8H), 1.37-1.33 (m, 4H), 0.90 (t, *J* 7.6 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 140.5, 140.1, 138.6, 135.7, 125.7, 125.2, 122.7, 120.9, 120.4, 119.7, 119.2, 112.2, 108.5, 106.3, 48.6, 39.7, 34.4, 31.7, 29.6, 22.6, 14.0; MS (ESI, 70 eV) *m*/*z* 326 ($M+H^+$, 100%).

(*E/Z*) 9-(3-Chloroallyl)-4-octyl-9*H*-carbazole (2h). Viscous Brown liquid (74.0 mg, 78%); R_f 0.50 Hexane/EtOAc (20:1); IR (neat) 3045, 2930, 2838, 1633, 1450, 1340, 722 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): *δ* 8.13 (d, *J* 7.9 Hz, 2H), 7.46 (dt, *J* 12.9, 5.0 Hz, 4H), 7.38 (dt, *J* 7.5, 3.5 Hz, 2H), 7.31-7.19 (m, 4H), 7.05 (t, *J* 7.7 Hz, 2H), 6.25 (dt, *J* 7.1, 1.8 Hz, 1H), 5.86 (dd, *J* 13.3, 6.2 Hz, 1H), 5.27 (d, *J* 1.6 Hz, 1H), 5.11 (dd, *J* 6.2, 1.8 Hz, 2H), 5.00 (s, 2H), 4.86 (d, *J* 1.8 Hz, 1H), 3.32-2.95 (m, 4H), 1.89-1.77 (m, 4H), 1.58-1.47 (m, 4H), 1.34-1.24 (m, 16H), 0.88 (t, *J* 6.7 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 140.4, 140.0, 138.6, 135.7, 127.0, 125.6, 125.1, 122.7, 120.8, 120.0, 119.2, 112.7, 108.4, 106.2, 48.6, 39.7, 34.4, 31.9, 29.8, 29.5, 29.3, 22.6, 14.1; MS (ESI, 70 eV) *m*/*z* 354 ($M+H^+$, 100%).

(*E/Z*) 9-(3-Chloroallyl)-5-hexyl-3-methyl-9*H*-carbazole (2i). Brown semi solid (68.4 mg, 72%); R_f 0.50 Hexane/EtOAc (20:1); IR (KBr) 3420, 2924, 2854, 1589, 1462, 1377, 1305, 755 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 7.92 (s, 2H), 7.39 (dd, *J* 10.5, 5.0 Hz, 4H), 7.32 (t, *J* 2.3 Hz, 2H), 7.27 (d, *J* 8.0 Hz, 2H), 7.03 (d, *J* 7.3 Hz, 2H), 6.27-6.22 (m, 1H), 5.86 (q, *J* 5.9 Hz, 1H), 5.26 (d, *J* 1.9 Hz, 1H), 5.09 (dd, *J* 6.2, 1.8 Hz, 2H), 4.98 (s, 2H), 4.85 (dd, *J* 3.5, 1.7 Hz, 1H), 3.24-3.17 (m, 4H), 2.56 (s, 6H), 1.90-1.77 (m, 4H), 1.54 (s, 4H), 1.42-1.33 (m, 8H), 0.91 (t, *J* 7.0 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 140.7, 138.6, 135.8, 128.9, 126.5, 125.6, 123.2, 122.8, 120.7, 120.2, 112.6, 108.2, 106.2, 48.7, 34.4, 31.7, 29.6, 29.5, 22.6, 21.6, 14.1; MS (ESI, 70 eV) *m*/*z* 340 ($M+H^+$, 100%).

(*E/Z*) 3-Chloro-9-(3-chloroallyl)-5-phenyl-9*H*-carbazole (2j). Viscous Brown liquid (71.1 mg, 75%); R_f 0.50 Hexane/EtOAc (20:1); IR (neat) 3055, 2926, 2818, 1631, 1430, 1333, 728 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 7.62-7.47 (m, 12H), 7.42 (s, 2H), 7.35 (dd, *J* 11.6, 6.5 Hz, 4H), 7.27 (dd, *J* 15.0, 6.3 Hz, 2H), 7.14 (t, *J* 6.6 Hz, 2H), 6.29 (dt, *J* 7.1, 1.6 Hz, 1H), 5.87 (q, *J* 6.5 Hz, 1H), 5.32 (d, *J* 1.8 Hz, 1H), 5.13 (dd, *J* 6.2, 1.5 Hz, 2H), 5.02 (s, 2H), 4.95-4.91 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 140.9, 140.4, 138.7, 138.1, 135.5, 128.9, 128.5, 127.9, 126.4, 125.8, 122.1, 122.0, 121.7, 119.6, 113.1, 109.4, 107.8, 48.8; MS (ESI, 70 eV) *m*/*z* 352($M+H^+$, 100%).

(*E/Z*) 3-Chloro-9-(3-chloroallyl)-5-(4-methoxyphenyl)-9*H*-carbazole (2k). Brown solid (62.3 mg, 66%); mp 104-106 °C (not recrystallised); R_f 0.45 Hexane/EtOAc (20:1); IR (KBr) 3048, 2949, 2826, 1623, 1450, 1346, 732 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.55-7.49 (m, 4H), 7.48-7.45 (m, 2H), 7.39 (s, 4H), 7.38-7.30 (m, 2H), 7.12-7.04 (m, 6H), 6.30 (dt, *J* 7.2, 1.8 Hz, 1H), 5.92-5.83 (m, 1H), 5.32 (d, *J* 2.1 Hz, 1H), 5.08 (dd, *J* 6.2, 1.8 Hz, 2H), 5.01-4.93 (m, 2H), 4.93 (dd, *J* 3.7, 1.6 Hz, 1H), 3.93 (s, 6H), 2.32 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 159.2,

140.8, 139.4, 137.5, 133.3, 132.0, 130.2, 126.6, 126.1, 125.9, 125.7, 123.8, 121.7, 121.3, 120.0, 113.8, 113.1, 108.8, 108.7, 107.4, 107.3, 55.3, 48.8, 43.5, 39.9, 39.5, 20.3; MS (ESI, 70 eV) 382 ($M+H^+$, 100%).

(*E/Z*) 3-Chloro-9-(3-chloroallyl)-5-(4-fluorophenyl)-9*H*-carbazole (2l). Colorless solid (61.5 mg, 65%); mp 120-122 °C (not recrystallised); R_f 0.50 Hexane/EtOAc (20:1); IR (KBr) 3056, 2924, 2853, 1600, 1456, 1300, 755 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.58-7.49 (m, 6H), 7.43-7.33 (m, 6H), 7.30 (t, *J* 6.9 Hz, 2H), 7.23 (dd, *J* 11.1, 3.0 Hz, 6H), 7.13-7.07 (m, 2H), 6.30 (dt, *J* 7.1, 1.7 Hz, 1H), 5.90-5.84 (m, 1H), 5.34-5.30 (m, 1H), 5.13 (dd, *J* 6.2, 1.8 Hz, 2H), 5.02 (s, 2H), 4.95-4.91 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 163.8, 162.6 (d, $^1J_{CF}$ = 247.2 Hz), 161.3, 140.9, 138.7, 137.0, 135.5, 130.7 (d, $^2J_{CF}$ = 8.0 Hz), 130.6, 126.4, 126.0, 121.9, 121.8, 121.4, 115.6, 115.4, 113.2, 109.6, 108.0, 48.8; MS (ESI, 70 eV) *m*/*z* 370 ($M+H^+$, 100%).

(*E/Z*) 3-Chloro-9-(3-chloroallyl)-5-propyl-9*H*-carbazole (2m). Viscous yellow liquid (73.5 mg, 77%); R_f 0.45 Hexane/EtOAc (20:1); IR (neat) 3045, 2936, 2828, 1632, 1430, 1343, 725 cm^{-1}; ^1H NMR (400 MHz,$CDCl_3$): δ 8.06 (t, *J* 2.2 Hz, 2H), 7.42 (dd, *J* 7.9, 1.7 Hz, 4H), 7.37-7.28 (m, 2H), 7.25-7.21 (m, 2H), 7.07 (dd, *J* 10.3, 3.6 Hz, 2H), 6.27 (dt, *J* 7.2, 1.8 Hz, 1H), 5.89-5.80 (m, 1H), 5.31-5.26 (m, 1H), 5.09 (dd, *J* 6.2, 1.8 Hz, 2H), 5.00-4.96 (m, 2H), 4.87 (dd, *J* 3.7, 1.7 Hz, 1H), 3.22-3.11 (m, 4H), 1.94-1.79 (m, 4H), 1.11 (dt, *J* 7.4, 3.7 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 141.0, 138.5,138.4, 135.5, 126.6, 126.4, 126.3, 125.3, 125.2, 125.1, 124.2, 122.4, 122.3, 121.2, 120.7, 120.4, 120.1, 113.0, 109.4, 109.3, 106.6, 106.5, 48.7, 39.8, 36.1, 22.6, 14.1; MS (ESI, 70 eV) *m*/*z* 318 ($M+H^+$, 100%).

(*E/Z*) 3-Chloro-9-(3-chloroallyl)-5-pentyl-9*H*-carbazole (2n). Viscous Brown liquid (63.6 mg, 67%); R_f 0.50 Hexane/EtOAc (20:1); IR (neat) 3051, 2924, 2854, 1593, 1461, 1327, 722 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 8.13 (d, *J* 7.9 Hz, 2H), 7.50-7.44 (m, 2H), 7.44-7.36 (m, 2H), 7.32-7.22 (m, 4H), 7.05 (t, *J* 7.0 Hz, 2H), 6.26 (dt, *J* 7.2, 1.8 Hz, 1H), 5.88 (dd, *J* 13.3, 6.2 Hz, 1H), 5.27 (d, *J* 1.4 Hz, 1H), 5.13 (dd, *J* 6.2, 1.8 Hz, 2H), 5.01 (s, 2H), 4.87 (dd, *J* 3.6, 1.7 Hz, 1H), 3.28-3.18 (m, 4H), 1.89-1.81 (m, 4H), 1.55-1.45 (m, 4H), 1.46-1.37 (m, 4H), 0.93 (t, *J* 7.2 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 140.1, 138.6, 135.7, 127.0, 125.7, 125.3, 122.7, 120.8, 120.4, 119.7, 119.2, 112.8, 108.5, 106.3, 48.6, 39.7, 34.4, 32.0, 22.6, 14.1; MS (ESI, 70 eV) *m*/*z* 346 ($M+H^+$, 100%).

(*E/Z*) 3-Chloro-9-(3-chloroallyl)-5-hexyl-9*H*-carbazole (2o). Viscous yellow liquid (74.8 mg, 79%); R_f 0.45 Hexane/EtOAc (20:1); IR (neat) 3051, 2926, 2856, 1588, 1460, 1330, 753, 584 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 8.07 (t, *J* 2.0 Hz, 2H), 7.35 (td, *J* 8.0, 2.4 Hz, 4H), 7.35-7.31 (m, 2H), 7.32-7.19 (m, 2H), 7.06 (t, *J* 6.9 Hz, 2H), 6.26 (dt, *J* 7.2, 1.8 Hz, 1H), 5.84 (dd, *J* 13.3, 6.3 Hz, 1H), 5.28 (d, *J* 1.9 Hz, 1H), 5.08 (dd, *J* 6.2, 1.7 Hz, 2H), 4.97 (s, 2H), 4.86 (dd, *J* 3.5, 1.7 Hz, 1H), 3.21-3.13 (m, 4H), 1.82 (dd, *J* 9.3, 3.4 Hz, 4H), 1.56-1.48 (m, 4H), 1.37 (dt, *J* 9.7, 5.6 Hz, 8H), 0.91 (t, *J* 6.9 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 140.9, 138.8, 138.3, 135.5, 126.6, 126.3, 125.1, 122.3, 121.2, 120.6, 120.3, 113.0, 109.3, 106.4, 48.7, 39.8, 34.2, 31.7, 29.4, 22.6, 14.0; MS (ESI, 70 eV) *m*/*z* 360 ($M+H^+$, 100%).

(*E/Z*) 3-Chloro-9-(3-chloroallyl)-5-octyl-9*H*-carbazole (2p). Viscous yellow liquid (70.8 mg, 75%); R_f 0.50 Hexane/EtOAc (20:1); IR (neat) 3050, 2925, 2854, 1594, 1461, 1302, 753, 584 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 8.06 (t, *J* 2.1 Hz, 2H), 7.44-7.36 (m, 4H), 7.34 (d, *J* 7.7 Hz, 2H), 7.32-7.17 (m, 2H), 7.05 (t, *J* 6.9 Hz, 2H), 6.25 (dt, *J* 7.1, 1.8 Hz, 1H), 5.86-5.79 (m, 1H), 5.28 (d, *J* 1.8 Hz, 1H), 5.06 (d, *J* 6.2 Hz, 2H), 4.95 (s, 2H), 4.87-4.84 (m, 1H), 3.16 (t, *J* 7.8 Hz, 4H), 1.86-1.77 (m, 4H), 1.51 (dd, *J* 13.1, 9.9 Hz, 4H), 1.40-1.36 (m, 4H), 1.32-1.26 (m, 12H), 0.88 (t, *J* 6.3 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 140.8, 138.8, 138.3, 135.5, 126.6, 125.2, 124.7, 122.3, 121.2, 120.6, 120.3, 113.0, 109.2, 106.4, 48.7, 39.8, 34.1, 31.8, 29.7, 29.5, 29.2, 22.6, 14.1; MS (ESI, 70 eV) *m*/*z* 388 ($M+H^+$, 100%).

(*E/Z*) 2-Chloro-9-(3-chloroallyl)-3-methyl-5-phenyl-9*H*-carbazole (2q). Viscous Brown liquid (69.1 mg, 73%); R_f 0.50 Hexane/EtOAc (20:1); IR (neat): 3055, 2914, 2834, 1573, 1461, 1327, 725 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.61-7.58 (m, 4H), 7.55-7.47 (m, 8H), 7.36 (s, 2H), 7.34 (s, 2H), 7.29 (s, 2H), 7.14-7.10 (dd, *J* 7.2, 0.7 Hz, 2H), 6.30 (dt, *J* 7.2, 1.7 Hz, 1H), 5.88 (dd, *J* 13.3, 6.3 Hz, 1H), 5.35-5.31 (m, 1H), 5.09 (dd, *J* 6.2, 1.7 Hz, 2H), 4.98 (s,

2H), 4.94 (d, *J* 1.9 Hz, 1H), 2.30 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 140.8, 140.7, 139.5, 137.8, 135.5, 132.2, 129.1, 128.4, 127.7, 127.6, 126.6, 125.9, 123.9, 121.6, 119.9, 113.1, 108.8, 107.7, 48.8, 20.3; MS (ESI, 70 eV) *m*/*z* 366 ($M+H^+$, 100%).

(*E/Z*) 2-Chloro-9-(3-chloroallyl)-5-(4-fluorophenyl)-3-methyl-9*H*-carbazole (2r). Pale Yellow solid (64.2 mg, 68%); mp 130-132 °C (not recrystallised); R_f 0.50 Hexane/EtOAc (20:1); IR (KBr) 3079, 2923, 2853, 1597, 1464, 1300, 755, 588 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 7.56 (dd, *J* 8.8, 2.2 Hz, 4H), 7.51-7.45 (m, 2H), 7.40 (s, 2H), 7.36 (dd, *J* 10.0, 7.3 Hz, 2H), 7.27 (d, *J* 4.9 Hz, 2H), 7.22 (dd, *J* 8.7, 2.3 Hz, 4H), 7.11-7.05 (m, 2H), 6.30 (dt, *J* 7.1, 1.7 Hz, 1H), 5.87 (dd, *J* 13.3, 6.2 Hz, 1H), 5.33 (d, *J* 2.0 Hz, 1H), 5.08 (dd, *J* 6.2, 1.8 Hz, 2H), 4.97 (s, 2H), 4.93 (t, *J* 5.4 Hz, 1H), 2.32 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 163.7, 162.5 (d, $^1J_{CF}$ = 247.9 Hz), 161.3, 140.8, 139.4, 136.6, 136.6, 135.5, 132.2, 131.4 (d, $^2J_{CF}$ = 8.0 Hz), 130.7, 130.6, 126.4, 125.9, 125.7, 123.6, 121.7, 121.4, 121.2, 115.4, 115.2, 113.1, 109.0, 108.8, 107.9, 107.8, 48.8, 39.9, 20.3; MS (ESI, 70 eV) *m*/*z* 384 ($M+H^+$, 100%).

(*E/Z*) 2-Chloro-9-(3-chloroallyl)-5-hexyl-3-methyl-9*H*-carbazole (2s). Viscous yellow liquid (70.9 mg, 75%); R_f 0.45 Hexane/EtOAc (20:1); IR (neat) 3048, 2932, 2845, 1594, 1461, 1312, 753 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 7.86 (s, 2H), 7.42 (s, 2H), 7.40-7.35 (m, 2H), 7.24–7.16 (m, 2H), 7.06-7.00 (dd, *J* 12.0, 5.9 Hz, 2H), 6.21-6.15 (m, 1H), 5.82-5.80 (m, 1H), 5.23-5.15 (m, 1H), 5.02-5.01 (m, 2H), 4.83 (s, 2H), 4.82-4.81 (s, 1H), 3.14-3.04 (m, 4H), 2.48 (s, 6H), 1.80-1.70 (m, 4H), 1.52-1.50 (dt, *J* 14.9, 7.3 Hz, 4H), 1.43-1.35 (m, 8H), 0.84 (t, *J* 7.4 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 140.9, 139.3, 138.5, 135.5, 131.7, 126.9, 125.9, 124.1, 122.0, 121.2, 120.6, 112.9, 108.9, 106.4, 48.7, 39.9, 34.3, 31.7, 29.5, 22.6, 20.5, 14.0; MS (ESI, 70 eV) *m*/*z* 374 ($M+H^+$, 100%).

(*E/Z*) 2-Chloro-9-(3-chloroallyl)-3-methyl-5-octyl-9H-carbazole (2t). Viscous Yellow liquid (75.4 mg, 80%); R_f 0.45 Hexane/EtOAc (20:1); IR (neat) 3049, 2925, 2854, 1596, 1464, 1327, 753 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 7.91 (d, *J* 2.7 Hz, 2H), 7.40-7.32 (m, 4H), 7.23-7.14 (m, 2H), 7.02 (t, *J* 6.9 Hz, 2H), 6.23 (dt, *J* 7.1, 1.8 Hz, 1H), 5.80 (dd, *J* 13.3, 6.2 Hz, 1H), 5.26 (d, *J* 1.9 Hz, 1H), 4.98 (dd, *J* 6.2, 1.6 Hz, 2H), 4.87 (s, 2H), 4.86-4.82 (m, 1H), 3.16 (dd, *J* 10.9, 4.8 Hz, 4H), 2.54 (s, 6H), 1.81 (dd, *J* 8.1, 5.1 Hz, 4H), 1.54-1.47 (m, 4H), 1.38 (dd, *J* 13.2, 6.3 Hz, 4H), 1.31 (d, *J* 13.5 Hz, 12H), 0.88 (t, *J* 6.6 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 140.9, 139.2, 138.5, 135.5, 131.7, 126.8, 125.9, 124.1, 122.0, 121.1, 120.6, 112.9, 108.9, 106.4, 48.7, 39.8, 34.3, 31.8, 29.8, 29.5, 29.2, 22.6, 20.5, 14.1; MS (ESI, 70 eV) *m*/*z* 402 ($M+H^+$, 100%)

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Supplementary Material

^{1}H and ^{13}C NMR Spectra for compounds **2a-t** can be found using the link “Supplementary Material” in the journal issue contents page.

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