Tetrahedron 67 (2011) 5304–5318

Contents lists available at ScienceDirect

Tetrahedron

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

Synthesis of carbazoles and 1,2-dihydrocarbazoles by domino 'twofold Heck/6π-electrocyclization' reactions of di-, tri- and tetrabromoindoles

Munawar Hussain [a], Serge-Mithérand Tengho Toguem [a], Rasheed Ahmad [a,b], Đặng Thanh Tùng [a], Ingo Knepper [a], Alexander Villinger [a], Peter Langer [a,c,*]

[a] Institut für Chemie, Universität Rostock, Albert-Einstein-Str. 3a, 18059 Rostock, Germany
[b] Department of Petroleum Technology, University of Karachi, University Road, Karachi 75270, Pakistan
[c] Leibniz-Institut für Katalyse e. V. an der Universität Rostock, Albert-Einstein-Str. 29a, 18059 Rostock, Germany

ARTICLE INFO

Article history:
Received 18 March 2011
Received in revised form 3 May 2011
Accepted 5 May 2011
Available online 14 May 2011

Keywords:
Carbazoles
Catalysis
Cyclizations
Indoles
Heck reaction
Palladium

ABSTRACT

Di-, tri- and tetra-alkenylindoles were prepared by palladium(0)-catalyzed Heck cross-coupling reactions of di-, tri- and tetrabromo-*N*-methylindoles. The reactions were carried out at 90 °C using a novel biaryl monophosphine ligand developed by Buchwald and co-workers. 1,2-Dihydrocarbazoles were formed by a domino 'twofold Heck/6π-electrocyclization' when the reaction was carried out at higher temperature. The regioselectivity of the Heck reaction of 2,3,6-tribromo-*N*-methylindoles was in favour of carbon atoms C-2 and C-3. The 1,2-dihydrocarbazoles were transformed, by Pd/C-catalyzed dehydrogenation, into the corresponding carbazoles in high yield.

1. Introduction

Carbazole is a natural product isolated for the first time from coal tar in 1872 by Graebe and Glaser. Carbazole derivatives are of significant pharmacological relevance because of their antifungal, antibiotic and antitumour activities. Simple carbazole alkaloids were isolated in the 1960s as natural products from plant sources. Murrayafoline A and murrayaquinone B are examples of naturally occurring carbazoles and carbazolequinones isolated from the root bark of *Murraya euchrestifolia Hayata* (Fig. 1).[1,2]

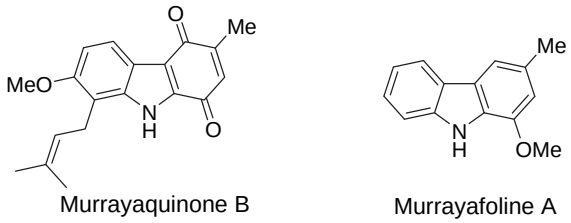


Fig. 1. Carbazoles isolated from the root bark of *Murraya euchrestifolia Hayata.*

A number of synthetic approaches to carbazoles have been reported. In recent years, transition metal catalyzed reactions have been extensively used for the synthesis of carbazoles. For example, a general approach to carbazoles relies on iron-mediated cyclization reactions (stoichiometric use of iron complexes).[1d] Later, a catalytic approach to carbazoles has been developed, which is based on Buchwald–Hartwig reactions of aryl halides with anilines and subsequent oxidative cyclizations.[3] Carbazoles have been also prepared by palladium-catalyzed cyclization of anilines with 1,2-dihaloalkenes, a domino reactions recently developed by Ackermann and Althammer.[4] Classic syntheses of carbazoles include, for example, Diels–Alder reactions of 2- or 3-vinylindoles with various dienophiles.[5] Carbazoles have also been prepared by thermal 6π-electrocyclization reactions of 2,3-di(alkenyl)indoles.[6,7] The scope of this method was severely limited by the fact that the synthesis of the precursors, 2,3-di(alkenyl)indoles, was complicated and required many steps. Acceptor-substituted 2,3-di(alkenyl)indoles were prepared by Pd(II)-catalyzed reactions of carbon atom C-3 of 2-formylindoles with alkenes to form 2-formyl-3-vinylindoles. The aldehyde group was subsequently transformed into an alkenyl group by means of a Wittig reaction. Attempts to prepare 2,3-di(alkenyl)indoles by double Wittig reaction of 2,3-diformyl-*N*-methylindole proved to be unsuccessful, due to the unstable nature of the bis-aldehyde and low yields.

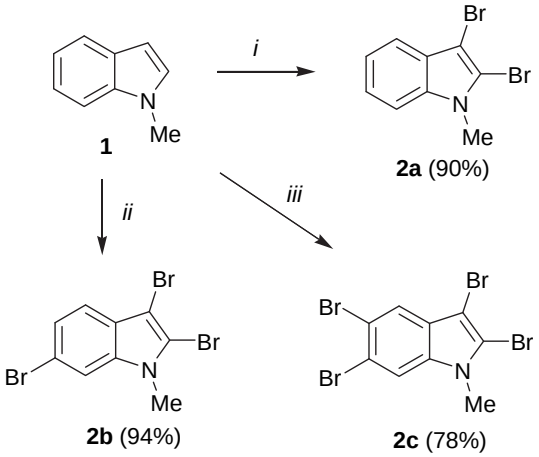
* Corresponding author. Fax: +49 381 4986412; e-mail address: peter.langer@uni-rostock.de (P. Langer).

0040-4020/$ – see front matter © 2011 Elsevier Ltd. All rights reserved.
doi:10.1016/j.tet.2011.05.014

De Meijere and co-workers described an efficient annulations process based on twofold Heck reactions of 1,2-dibromocycloalk-1-enes and subsequent 6π-electrocyclizations.[8] In recent years, we have applied this approach to a variety of heterocyclic substrates.[9] Recently, we have reported preliminary results related to the synthesis of carbazoles by domino twofold Heck/electrocyclization/dehydrogenation reactions.[9a] Herein, we wish to report full details and a significant extension of the preparative scope. With regard to our preliminary communication, we also report, for the first time, Heck reactions of 2,3,5,6-tetrabromo-*N*-methylindole. Bis-Sonogashira reactions proved to be not general, due to the highly unstable nature of the 2,3-bis(alkynyl)indoles. The chemistry reported herein is of considerable synthetic usefulness because positions 2 and 3 of the carbazole system cannot be directly accessed by functionalization reactions of carbazole derivatives. In fact, the substituted carbazole derivatives reported herein are not readily available by other methods.

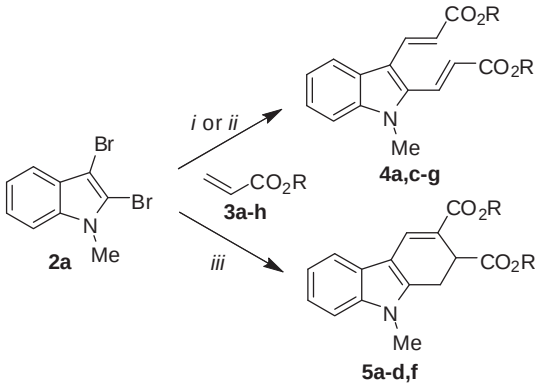
2. Results and discussion

Our starting point was the synthesis of various brominated indole derivatives. The reaction of *N*-methylindole (**1**) with copper(II) bromide has been reported to afford 2,3-dibromo-*N*-methylindole (**2a**) in 64% yield.[10] We were able to increase the yield of **2a** to 90% by reaction of *N*-methylindole (**1**) with NBS (2.1 equiv) in THF (−78 °C, 4 h) (Scheme 1). During the optimization, it proved to be important to add NBS portionwise. Dibromide **2a** and 2,3,6-tribromo-*N*-methylindole (**2b**) are natural products[11–14] and **2a** has been previously converted into **2b** by bromination (Br_2, $CHCl_3$) in 70–80% yield.[14] Our goal was to develop a direct synthesis of **2b**. After some experimentation, we have found that **2b** can be prepared in 94% yield by reaction of **1** with NBS (3.1 equiv) in THF (−78 °C, 4 h). During the optimization, it proved to be mandatory to carry out the reaction at low temperature and to add NBS in small portions. A complex mixture was obtained when NBS was added at room temperature. The reaction of **1** with NBS (5.0 equiv) in THF (−78 °C, 1 h, then reflux for 4 h) afforded 2,3,5,6-tetrabromo-*N*-methylindole (**2c**) in 78% yield.



Scheme 1. Bromination of *N*-methylindole (**1**); conditions: *i*, NBS (2.1 equiv), THF, −78 °C, 4 h; *ii*, NBS (3.1 equiv), THF, −78 °C, 4 h, then 20 °C, 14 h; *iii*, NBS (5.0 equiv), THF, −78 °C, 1 h, then reflux, 4 h.

The Heck reaction of **2a** with acrylates **3a**,**c**–**g** afforded the 2,3-di(alkenyl)indoles **4a**,**c**–**g** in good yields (Scheme 2, Tables 1 and 2). The best yields were obtained when the reactions were carried out using $Pd(OAc)_2$ (5 mol %) and SPhos (10 mol %) developed by Buchwald and Billingsley (Fig. 2).[15] Lower catalyst loading resulted in complex mixtures (Table 1). The reactions were carried out in DMF at 90 °C for 36 h. Recently, Li and Wang reported[16] that triethanolamine represents an efficient and reusable combined base, ligand, and solvent for palladium(0)-catalyzed Heck reactions. The application of these conditions to the reaction of **2a** with acrylate **3g** proved to be successful and resulted in the formation of **4g** in 63% yield.



Scheme 2. Synthesis of **4b**–**e** and **5a**–**d**,**f**. Conditions: *i*, for **4b**–**e**: $Pd(OAc)_2$ (5 mol %), SPhos (10 mol %), NEt_3, DMF, 90 °C, 36 h; *ii*, for **4e**: $Pd(OAc)_2$ (5 mol %), $N(CH_2CH_2OH)_3$ (3 mL), 90 °C, 36 h; *iii*, $Pd(OAc)_2$ (5 mol %), SPhos (10 mol %), NEt_3 (8.0 equiv), DMF, 120 °C, 48 h.

Table 1
Optimization of the reaction conditions for the synthesis of **4c**,**f**

Entry	Catalyst	Temp (°C)	% (**4c**)[a]	% (**4f**)[a]
1	$Pd(PPh_3)_4$ (5 mol %)	90	Complex mixture	Complex mixture
2	$Pd(OAc)_2$ (5 mol %), XPhos (10 mol %)	90	65	71
3	$Pd(OAc)_2$ (5 mol %), SPhos (10 mol %)	90	72	78
4	$Pd(OAc)_2$ (5 mol %), SPhos (10 mol %)	100	—[b]	—[b]
5	$Pd(OAc)_2$ (3 mol %), SPhos (6 mol %)	90	Complex mixture	Complex mixture
6	$Pd(OAc)_2$ (2 mol %), SPhos (4 mol %)	100	—[c]	—[c]
7	$Pd(OAc)_2$ (2 mol %), SPhos (4 mol %)	120	**5c** (77%)	**5f** (85%)

[a] Yields of isolated products; all reactions were carried out in DMF using NEt_3 as base (36 h).
[b] Mixture of **4c**,**f** and **5c**,**f**, respectively (TLC).
[c] Approx. 50% conversion (estimated by TLC).

Table 2
Synthesis of **4a**,**c**–**g** and **5a**–**c**,**e**,**f**,**h**

4,**5**	**3**	R	% (**4**)[a]	%(**5**)[a]
a	**a**	Me	77	69
b	**b**	Et	—[b]	93
c	**c**	^{n}Bu	72	77
d	**d**	^{i}Bu	—[b]	66
e	**e**	^{n}Hex	77	81
f	**f**	^{t}Bu	78	85
g	**g**	^{i}Oct	76	—[b]
h	**h**	$(CH_2)_2NMe_2$	—[b]	79

[a] Yields of isolated products based on **2a**.
[b] Experiment was not carried out.

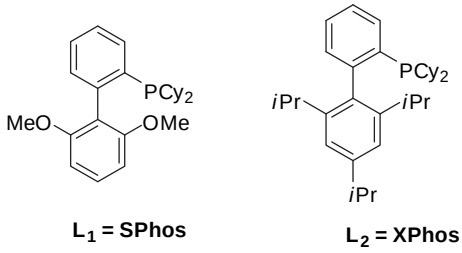


Fig. 2. Structures of ligands (**L**) SPhos and XPhos.

When the reaction of **2a** with acrylates **3a**–**c**,**e**,**f**,**h** was carried out at 120 °C instead of 90 °C, the 1,2-dihydrocarbazoles **5a**–**c**,**e**,**f**,**h** were formed by a domino 'twofold Heck/6π-electrocyclization' cyclization. The initially formed 2,3-dihydrocarbazoles undergo a sigmatropic rearrangement into the more stable 1,2-dihydro carbazoles. The structure of **5b** was independently confirmed by an X-ray crystal structure analysis (Fig. 3).[17]

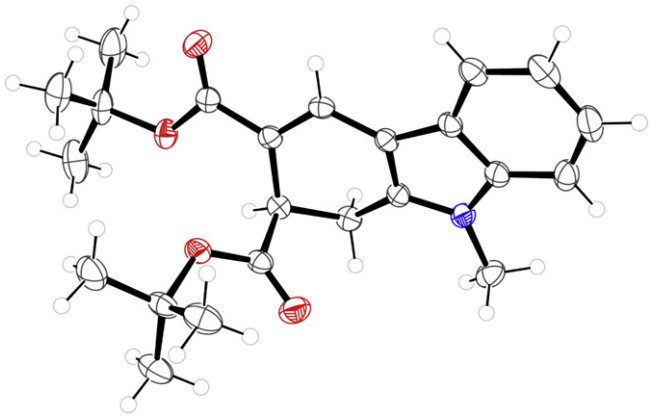
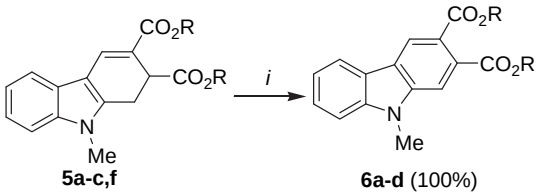


Fig. 3. Ortep plot of **5f**.

The dehydrogenation of 1,2-dihydrocarbazoles to carbazoles was next studied. Pindur reported the synthesis of 2,3-di(methoxycarbonyl)-*N*-phenylsulfonylcarbazole by reaction of the corresponding 1,2-dihydrocarbazole with DDQ, albeit, in only 18% yield.[5] We have obtained equally disappointing results. The reaction of 1,2-dihydrocarbazole **5b** with DDQ afforded carbazole **6b** in only 20% yield. After some optimization of the conditions, we have achieved a dramatic increase of the yield (100%) using Pd/C (10 mol %) as the catalyst (xylene, reflux) (Scheme 3, Table 3). The structure of carbazole **6a** was independently confirmed by X-ray crystal structure analysis (Fig. 4).



Scheme 3. Synthesis of carbazole **6a**–**d**; conditions: *i*, Pd/C (10 mol %), xylene, reflux, 48 h.

Table 3
Synthesis of **6a**–**d**

5	6	R	% (**6**)[a]
b	**a**	Et	100
c	**b**	^{n}Bu	100
e	**c**	^{n}Hex	100
f	**d**	^{t}Bu	100

[a] Yields of isolated products based on **5a**–**d**.

The $Pd(OAc)_2$/SPhos-catalyzed reaction of **2a** with acrylonitrile (120 °C, 48 h) afforded the unexpected carbazole **7** in 49% yield (Scheme 4). The formation of **7** can be explained by twofold Heck reaction of **2a** to give intermediate **A**, electrocyclization

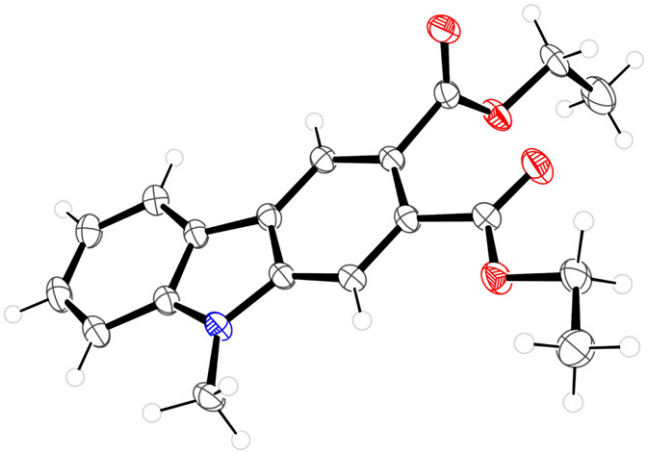
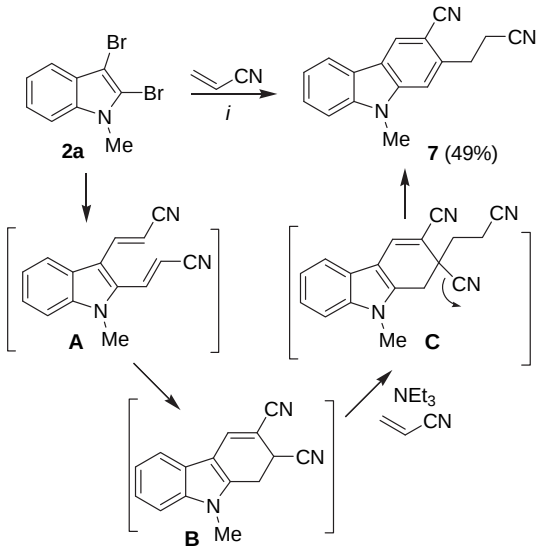


Fig. 4. Crystal structure of **6a**.

(intermediate **B**), base-mediated conjugate addition to give intermediate **C**, and subsequent aromatization by elimination of HCN. The structure of **7** was independently confirmed by X-ray crystal structure analysis (Fig. 5).



Scheme 4. Possible mechanism of the formation of **7**. Conditions: *i*, $Pd(OAc)_2$ (5 mol %), SPhos (10 mol %), NEt_3, DMF, 120 °C, 48 h.

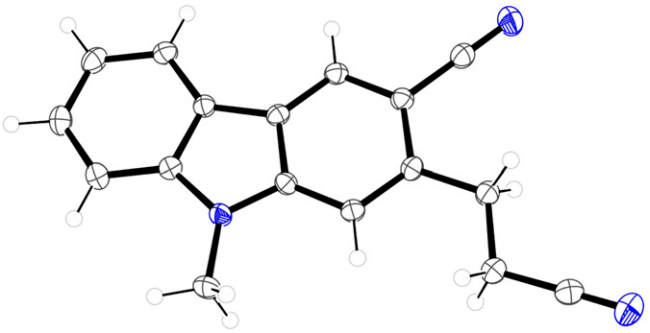
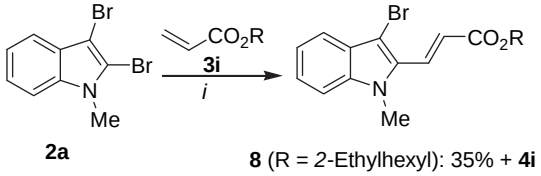


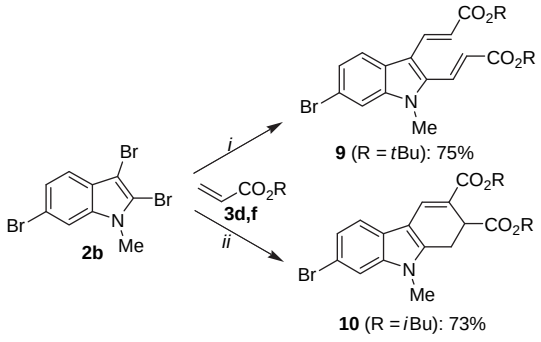
Fig. 5. Crystal structure of **7**.

The reaction of 2,3,6-tribromo-*N*-methylindole (**2b**) with acrylate **3f** (90 °C, 36 h) afforded the di(alkenyl)indole **9** in 75% yield (Scheme 5). The structure was confirmed by 2D NMR experiments (NOESY, HMBC). The formation of **9** can be explained by Heck reaction of **2b** at carbon C-2, which is most electron-deficient. Due to

the electron-withdrawing effect of the 2-(alkoxycarbonyl)alkenyl substituent, carbon C-3 becomes more electron-deficient and, as a consequence, more reactive than C-6. It was earlier noted[18] that Suzuki reactions of *N*-TBDS-protected 3,6-dibromoindole proceeded by first attack on position C-6. This might also explain the observation that the reaction of 2,3-dibromoindole **2a** with only 1 equiv of acrylate mainly results in the formation of 2,3-di[2-(alkoxycarbonyl)ethenyl]indole **4** and starting material, except for the case of acrylate **3i** where **8** was isolated in 35% yield along with **4i**. Product **8** was an unstable compound and at room temperature it underwent decomposition within 24 h providing a dark brown coloured material, probably due to the loss of Br (Scheme 5). Therefore, pure compounds of type **8** could not be isolated. The $Pd(OAc)_2$/**L**-catalyzed reaction of **2b** with acrylate **3f**, carried out at 120 rather than 90 °C, afforded the 1,2-dihydrocarbazole **10** in 73% yield (Scheme 6).

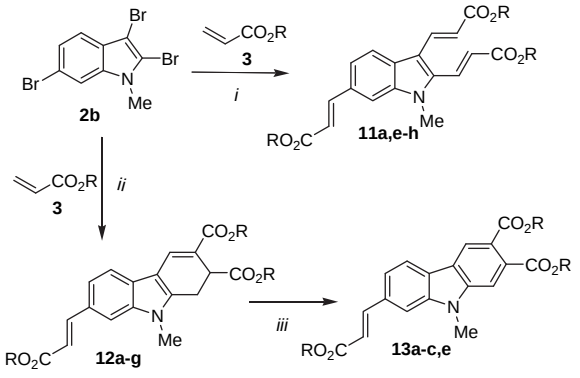


Scheme 5. Synthesis of **8**. Conditions: *i*, $Pd(OAc)_2$ (5 mol %), SPhos (10 mol %), NEt_3, DMF, 90 °C, 24 h.



Scheme 6. Synthesis of **9** and **10**. Conditions: *i*, $Pd(OAc)_2$ (5 mol %), SPhos (10 mol %), NEt_3, DMF, 90 °C, 24 h; *ii*, $Pd(OAc)_2$ (5 mol %), SPhos (10 mol %), NEt_3, DMF, 120 °C, 48 h .

The Heck reaction of **2b** with an excess of acrylates **3** (90 °C, 36 h) afforded the 2,3,6-tris(alkenyl)indoles **11a**,**e**–**h** in good yields (Scheme 7, Table 4). 7-Alkenyl-1,2-dihydrocarbazoles **12a**–**g** were isolated when the cross-coupling reactions of **2b** with **3** were carried out at 120 instead of 90 °C. The structure of **12c** was independently confirmed by X-ray crystal structure analysis (Fig. 6). The dehydrogenation of **12a**–**c**,**e**, carried out using Pd/C (10 mol %) in refluxing xylene, afforded the carbazoles **13a**–**c**,**e**.



Scheme 7. Synthesis of **11a**,**e**–**h**, **12a**–**g** and **13a**–**c**,**e**. Conditions: *i*, $Pd(OAc)_2$ (5 mol %), SPhos (10 mol %), NEt_3, DMF, 90 °C, 36 h; *ii*, $Pd(OAc)_2$ (5 mol %), SPhos (10 mol %), NEt_3, DMF, 120 °C, 48 h; *iii*, Pd/C (10 mol %), xylene, reflux, 48 h.

Table 4
Synthesis of **11a**,**e**–**h**, **12a**–**g** and **13a**–**c**,**e**

11,12,3	R	% (**11**)[a]	% (**12**)[a]	% (**13**)[a]
a	Me	69	79	100
b	Et	—[b]	67+10[c]	100
c	^{n}Bu	—[b]	95	100
d	^{i}Bu	—[b]	72	—[b]
e	^{n}Hex	74	74	100
f	^{t}Bu	76	79	—[b]
g	^{i}Oct	73	74	—[b]
h	^{n}Octadec	64	—[b]	—[b]

[a] Yields of isolated products based on **2b**.
[b] Experiment was not carried out.
[c] Compound **14** was isolated as a by-product in 10%.

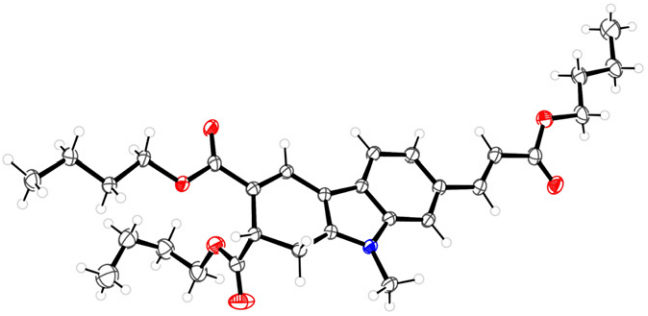


Fig. 6. Crystal structure of **12c**.

Along with **12b**, a side product **14** was also isolated, which was formed by reduction of carbon atom C-2 or C-3 (Fig. 7). The structure of the product could not be unambigiously confirmed.

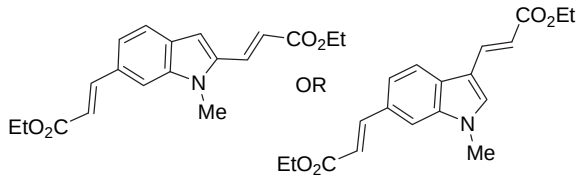
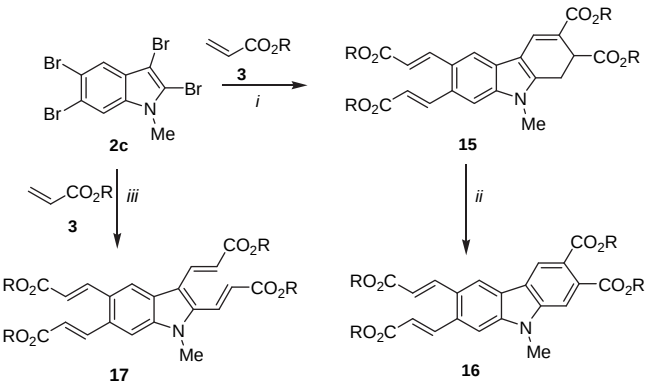


Fig. 7. Possible structures of side product **14** derived from **12b**.

The $Pd(OAc)_2$/SPhos-catalyzed reaction of 2,3,5,6-tetrabromoindole **2c** with an excess of acrylates **3** (120 °C, 48 h) afforded the 6,7-di(alkenyl)-1,2-dihydrocarbazoles **15a**–**h** in good yields (Scheme 8, Table 5). The Pd/C-catalyzed dehydrogenation of



Scheme 8. Synthesis of **15a**–**h**, **16a**–**d**,**g** and **17b**,**c**,**e**,**g**. Conditions: *i*, $Pd(OAc)_2$ (5 mol %), SPhos (10 mol %), NEt_3, DMF, 120 °C, 48 h; *ii*, Pd/C (10 mol %), xylene, reflux, 2 d, *iii*, $Pd(OAc)_2$ (5 mol %), SPhos (10 mol %), NEt_3, DMF, 90 °C, 36 h.

Table 5
Synthesis of **15a**–**h**, **16a**–**d** and **1b**,**c**,**e**,**g**

15,16,17	R	% (15) [a]	% (16) [a]	% (17)[a]
a	Me	68	100	—[b]
b	Et	86	—[b]	76
c	^{n}Bu	71	100	71
d	^{i}Bu	72	—[b]	—[b]
e	^{t}Bu	72	—[b]	88
f	^{n}Hex	80	—[b]	—[b]
g	2-Ethylhexyl	71	100	75
h	^{i}Oct	74	—[b]	—[b]

[a] Yields of isolated products.
[b] Experiment was not carried out.

12a–**d**,**g** afforded the carbazoles **13a**–**d**,**g** in quantitative yield. An electrocyclization involving the alkenyl groups attached to carbon atoms C-5 and C-6 was not observed. This can be explained by the aromaticity of the benzene ring, which would be interrupted by the electrocyclization. Tetra-alkenylated indoles **17b**,**c**,**e**,**g** could be successfully prepared when the reaction was performed at 90 instead of 120 °C. Side-product **18** was isolated in 7% yield along with **17b**, due to reduction of carbon atoms C-2 and C-3 (Fig. 8).

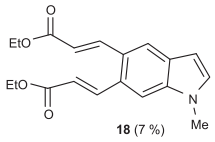
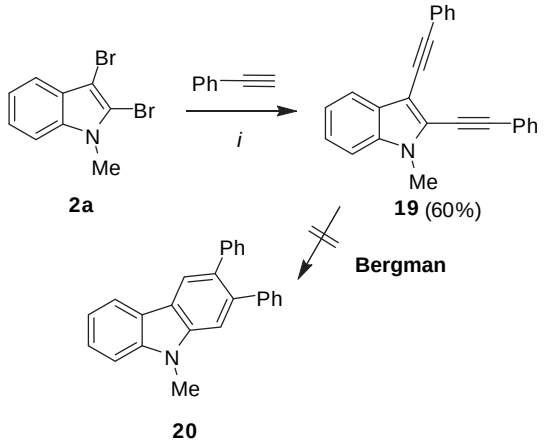


Fig. 8. Structure of side product **18** derived from **17b**.

An alternative synthetic approach to carbazoles based on twofold Sonogashira reactions of 2,3-dibromoindole **2a** with acetylenes and subsequent Bergman cyclization was next studied. The Sonogashira reaction of **2a** with phenylacetylene, in the presence of $Pd(OAc)_2$ (5 mol %) and XPhos (10 mol %), provided the unstable bis-alkynylated indole **19c** in 60% yield (Scheme 9). The product proved to be very unstable and rapidly decomposed. It was not possible to prepare other derivatives because they decomposed under the conditions of their preparation. All attempts to induce a thermal Bergman cyclization of **19** by heating in the presence of dihydrobenzene to prepare carbazole **20** failed (decomposition). All efforts to achieve a regioselective alkynylation of **2a** using 1.0 equiv of acetylene also failed.



Scheme 9. Bis-alkynylation of **2a**. *i*, $Pd(OAc)_2$ (5 mol %), XPhos (10 mol %), phenylacetylene (2.5 equiv), CuI (10 mol %), $(^{i}Pr)_2NH$, 120 °C, 36 h.

In conclusion, we have reported the synthesis of di-, tri- and tetra-alkenylindoles by palladium(0)-catalyzed Heck cross-coupling reactions of di-, tri- and tetrabromo-*N*-methylindoles. The reactions were carried out at 90 °C using a novel biaryl monophosphine ligand developed by Buchwald and co-workers. 1,2-Dihydrocarbazoles were formed by a domino 'twofold Heck/6π-electrocyclization' when the reaction was carried out at 120 rather than 90 °C. The regioselectivity of the Heck reaction of 2,3,6-tribromo-*N*-methylindoles was in favour of carbon atoms C-2 and C-3. Some of the 1,2-dihydrocarbazoles prepared were transformed, by Pd/C-catalyzed dehydrogenation, into the corresponding carbazoles in high yield.

3. Experimental section

3.1. Synthesis of 2,3-dibromo-*N*-methylindole (2a)

To a THF solution (20 mL) of *N*-methylindole **1** (1.0 mL, 8.0 mmol) was portionwise added NBS (3.30 g, 18.4 mmol) at −78 °C and the solution was stirred at this temperature for 4 h. To the solution was added water (25 mL). The organic and the aqueous layer were separated and the latter was extracted with CH_2Cl_2 (3×25 mL). The combined organic layers were washed with a saturated aqueous solution of $NaHCO_3$, dried (Na_2SO_4), filtered and concentrated in vacuo. The residue was purified by flash silica column chromatography (pure heptanes) to yield **2a** as a colourless solid (1.83 g, 90%).

3.2. Synthesis of 2,3,6-tribromo-*N*-methylindole (2b)

To a THF solution (50 mL) of *N*-methylindole (**1**) (2.0 mL, 16.0 mmol) was portionwise added NBS (9.40 g, 52.8 mmol) at −78 °C and the solution was stirred at this temperature for 4 h and then at 20 °C for 14 h. To the solution was added water (25 mL). The organic and the aqueous layer were separated and the latter was extracted with CH_2Cl_2 (3×30 mL). The combined organic layers were washed with a saturated aqueous solution of $NaHCO_3$, dried (Na_2SO_4), filtered and concentrated in vacuo. The residue was purified by flash silica column chromatography (pure heptanes) to yield **2b** as a colourless solid (5.50 g, 94%).

3.3. Synthesis of 2,3,5,6-tetrabromo-*N*-methylindole (2c)

To a THF solution (100 mL) of *N*-methylindole (**1**) (4.9 mL, 38.0 mmol) was portionwise added NBS (33.80 g, 190.0 mmol) at −78 °C and the solution was stirred at this temperature for 1 h and then under reflux for 4 h. To the solution was added water (50 mL). The organic and the aqueous layer were separated and the latter was extracted with CH_2Cl_2 (3×50 mL). The combined organic layers were washed with a saturated aqueous solution of $NaHCO_3$, dried (Na_2SO_4), filtered and concentrated in vacuo. The residue was purified by flash silica column chromatography (pure heptanes) to yield **2c** as a colourless solid (13.20 g, 78%). ^{1}H NMR (250 MHz, $CDCl_3$): δ=3.70 (s, 3H, NCH_3), 7.60 (s, 1H, ArH), 7.70 (s, 1H, ArH). ^{13}C NMR (62 MHz, $CDCl_3$): δ=32.7 (NCH_3), 91.9 (C), 114.4 (CH), 116.4, 117.2, 118.4 (C), 123.1 (CH), 127.4, 135.7 (C).

3.4. General procedure A for Heck cross-coupling reactions

In a pressure tube (glass bomb) a suspension of $Pd(OAc)_2$ (12 mg, 0.05 mmol, 5 mol %) and SPhos (**L_1**) (41 mg, 0.10 mmol) in DMF (5 mL) was purged with argon and stirred at 20 °C to get a yellowish or brownish transparent solution. To the stirred solution were added the brominated indole **2a**–**c** (1.0 mmol), NEt_3 and the acrylate. The reaction mixture was stirred at 90 °C for 36 h. The solution was cooled to 20 °C, poured into H_2O and CH_2Cl_2 (25 mL each), and the organic and the aqueous layer were separated. The

latter was extracted with CH_2Cl_2 (3×25 mL). The combined organic layers were washed with H_2O (3×20 mL), dried (Na_2SO_4), and concentrated in vacuo. The residue was purified by chromatography (flash silica gel, heptanes/EtOAc).

3.5. Synthesis of 2,3-bis(alkenyl)-*N*-methylindoles 4

*3.5.1. Dimethyl 3,3′-(1-methyl-1H-indole-2,3-diyl)diacrylate (**4a**).* Starting with $Pd(OAc)_2$ (12 mg, 5 mol %) and SPhos (**L_1**) (41 mg, 10 mol %), brominated indole **2a** (288 mg, 1.0 mmol) **4a** was isolated as yellow oil (231 mg, 77%). ^{1}H NMR (250 MHz, $CDCl_3$): δ=3.53 (s, 3H, CH_3O), 3.75 (s, 3H, CH_3O), 3.78 (s, 3H, CH_3N), 6.25 (d, 1H, J=15.9 Hz), 6.49 (d, 1H, J=15.8 Hz), 6.8–7.3(m, 3H, ArH), 7.70 (d, 1H, ArH), 7.82 (d, 1H, J=16.6 Hz), 7.93 (d, 1H, J=16.6 Hz). ^{13}C NMR (62 MHz, $CDCl_3$): δ=31.2 (CH_3CN), 51.3, 51.5 (CH_3O), 109.7 (C), 110.0, 116.1, 120.2, 120.8 (CH), 124.2 (C), 131.3, 135.6 (CH), 136.3, 137.1 (C), 143.2 (CH), 166.4, 168.2 (CO). IR (KBr): ν=2948, 2841 (w), 1702, 1618, 1433 (s), 1410, 1372, 1341 (m), 1269, 1190, 1165, 1132 (s), 1035, 1013, 967 (m), 739 (s), 648, 560 (w) cm^{-1}. GC–MS (EI, 70 eV): m/z (%)= 299 (M^+, 60), 240 (67), 209 (64), 181 (100), 120 (32), 77 (19), 41 (19). HRMS (ESI-TOF): m/z calcd for $C_{17}H_{18}NO_4$ $[M+H]^+$: 300.12303; found: 383.12291.

*3.5.2. Dibutyl 3,3′-(1-methyl-1H-indole-2,3-diyl)diacrylate (**4c**).* Product **4c** was prepared starting with **2a** (289 mg, 1.0 mmol), butyl acrylate (**3c**) (0.36 mL, 2.5 mmol), $Pd(OAc)_2$ (11 mg, 5 mol %), SPhos (10 mol %), NEt_3 (1.10 mL, 8.0 mmol), DMF (5 mL) at 90 °C for 24 h following general procedure A, as a brownish oil (276 mg, 72%). ^{1}H NMR (250 MHz, $CDCl_3$): δ=0.90 (t, 6H, J=7.1 Hz, $2CH_3$), 1.30–1.40 (m, 4H, $2CH_2$), 1.60–1.70 (m, 4H, $2CH_2$), 3.70 (s, 3H, NCH_3), 4.10 (t, 2H, J=6.3 Hz, CH_2O), 4.20 (t, 2H, J=6.3, $2CH_2O$), 6.30 (d, 1H, J=16.1 Hz, CH), 6.50 (d, 1H,, J=15.8 Hz, CH), 7.20–7.40 (m, 3H, ArH), 7.80 (d, 1H, J=16.1 Hz, CH), 7.80 (br d, 1H, J=8.0 Hz, ArH), 7.90 (d, 1H, J=15.8 Hz, CH). ^{13}C NMR (62 MHz, $CDCl_3$): δ=13.7, 13.8 (CH_3), 19.2, 19.3 (CH_2), 30.8, 30.9 (CH_2), 31.2 (NCH_3), 64.2, 64.9 (CH_2O), 110.0 (CH), 114.1 (C), 116.6, 121.1, 122.0, 124.7, 124.8 (CH), 125.5 (C), 131.1, 136.5 (CH), 136.8, 139.0 (C), 166.2, 168.0 (CO). IR (KBr): ν=2957, 2932, 2872 (m), 1706, 1616, 1466 (s), 1364, 1326 (w), 1274, 1235, 1165 (s), 1132, 1115, 1061, 1046, 1027, 968, 844, 8215 (m), 739 (s), 561 (w) cm^{-1}. MS (EI, 70 eV): m/z (%)=383 (M^+, 3), 381 (62), 325 (13), 308 (06), 269 (09), 252 (100), 225 (08). HRMS (EI, 70 eV): calcd for $C_{23}H_{29}NO_4$ $[M]^+$: 383.20911; found: 383.208695.

*3.5.3. Dihexyl 3,3′-(1-methyl-1H-indole-2,3-diyl)diacrylate (**4e**).* Product **4e** was prepared starting with **2a** (289 mg, 1.0 mmol), hexyl acrylate (**3e**) (0.44 mL, 2.5 mmol), $Pd(OAc)_2$ (11 mg, 5 mol %), SPhos (10 mol %), NEt_3 (1.10 mL, 8.0 mmol), DMF (5 mL) at 90 °C for 36 h following general procedure A, as a deep yellow highly viscous oil (337 mg, 77%). ^{1}H NMR (250 MHz, $CDCl_3$): δ=0.80 (t, 6H, J=7.8 Hz, $2CH_3$), 1.20–1.40 (m, 16H, $8CH_2$), 3.70 (s, 3H, NCH_3), 4.20 (t, 4H, J=6.8 Hz, $2CH_2O$), 6.20 (d, 1H, J=16.0 Hz, ArH), 6.50 (d, 1H, J=15.9 Hz, ArH), 7.10–7.30 (m, 3H, ArH), 7.70 (d, 1H, J=15.8 Hz, ArH), 7.80 (d, 2H, J=8.1 Hz, ArH), 7.90 (d, 1H, J=16.0 Hz, ArH). ^{13}C NMR (62 MHz, $CDCl_3$): δ=13.0 ($2CH_3$), 21.4, 21.5, 24.4, 24.8, 27.3, 27.7 (CH_2), 29.9 (NCH_3), 30.3, 30.5 (CH_2), 63.5, 64.2 (CH_2O), 109.7 (CH), 113.0 (C), 120.0, 120.2, 121.0, 123.2, 1236 (CH), 124.5 (C), 130.1, 134.2 (CH), 135.5, 138.0 (C), 165.2, 166.9 (CO). IR (KBr): ν=2955, 2929, 2857 (m), 1712 (s), 1625, 1529, 1467, 1360, 1283, 1238 (w), 1170 (s), 1133, 1049, 972, 916 (w), 735 (s) cm^{-1}. GC–MS (EI, 70 eV): m/z (%)=439 ($[M]^+$, 44), 338 (06), 310 (28), 252 (11), 226 (100), 208 (68), 182 (84). HRMS (EI, 70 eV): calcd for $C_{27}H_{37}NO_4$ $[M]^+$: 439.27171; found: 439.270972.

*3.5.4. Di(tert-butyl) 3,3′-(1-methyl-1H-indole-2,3-diyl)diacrylate (**4f**).* Product **4f** was synthesized starting with **2a** (289 mg, 1.0 mmol), *tert*-butyl acrylate (**3f**) (0.37 mL, 2.5 mmol), $Pd(OAc)_2$ (11 mg, 5 mol %), SPhos (10 mol %), NEt_3 (1.10 mL, 8.0 mmol), DMF (5 mL) at 90 °C for 36 h following general procedure A, as a yellowish highly viscous oil (299 mg, 78%, E/Z=7:3). ^{1}H NMR (250 MHz, $CDCl_3$): δ=1.50 (s, 18H, $6CH_3$), 3.70 (s, 3H, NCH_3), 6.20 (d, 1H, J=16.0 Hz, ArH), 6.40 (d, 1H, J=16.0 Hz, ArH), 7.20–7.30 (m, 3H, ArH), 7.60 (d, 1H, J=15.8 Hz, ArH), 7.70 (d, 1H, J=16.0 Hz, ArH), 8.00 (d, 1H, J=7.9 Hz, ArH). ^{13}C NMR (75 MHz, $CDCl_3$): δ=27.2, 27.3 ($3CH_3$), 30.1 (NCH_3), 79.0, 80.2 (C–O), 108.6 (CH), 112.8 (C), 117.2, 120.2, 120.6, 123.8 (CH), 124.5 (C), 125.4, 129.2, 134.7 (CH), 135.9, 137.2 (C), 164.4, 166.3 (C=O). IR (KBr): ν=2964, 2930 (w), 1722, 1710, 1693, 1680, 1613, 1469, 1453, 1391, 1366 (m), 1281, 1258, 1144, 1090, 1017 (s), 845 (m), 797, 741 (s), 663, 563 (w) cm^{-1}. GC–MS (EI, 70 eV): m/z (%)=383 (M^+, 39), 271 (13), 227 (84), 226 (100), 225 (52), 208 (31), 182 (69), 167 (54), 152 (21), 57 (79), 41 (42). HRMS (EI, 70 eV): calcd for $C_{23}H_{29}NO_4$ $[M]^+$: 383.20911; found: 383.20905.

*3.5.5. Bis(6-methylheptyl) 3,3′-(1-methyl-1H-indole-2,3-diyl)diacrylate (**4g**).* Product **4g** was prepared starting with **2a** (289 mg, 1.0 mmol), isooctyl acrylate (**3g**) (0.52 mL, 2.5 mmol), $Pd(OAc)_2$ (11 mg, 5 mol %), SPhos (10 mol %), NEt_3 (1.10 mL, 8.0 mmol), DMF (5 mL) at 90 °C for 36 h following general procedure A, as a yellow oil (377 mg, 76%). ^{1}H NMR (250 MHz, $CDCl_3$): δ=0.60–0.90 (m, 12H, $4CH_3$), 1.00–1.40 (m, 12H, $6CH_2$), 1.50–1.60 (m, 6H, aliphatic), 3.80 (s, 3H, NCH_3), 4.10 (t, 2H, J=6.7 Hz, CH_2O), 4.20 (t, 2H, J=6.8 Hz, CH_2O), 6.40 (d, 1H, J=16.1 Hz, ArH), 6.50 (d, 1H, J=16.0 Hz, ArH), 7.10–7.20 (m, 3H, ArH), 7.80 (d, 1H, J=15.7 Hz, ArH), 7.80 (br d, 1H, J=7.6 Hz, ArH), 7.90 (d, 1H, J=15.7 Hz, ArH). ^{13}C NMR (62 MHz, $CDCl_3$): δ=13.0, 14.6 (CH_3), 21.5, 24.5, 27.5 (CH_2) 29.5 (NCH_3), 45.5 (CH_2), 63.7, 63.8 (CH_2O), 108.1 (C), 108.7 (CH), 115.7, 120.0, 120.4, 123.2 (CH), 124.5, 125.0 (C), 127.6, 130.1, 134.3 (CH), 137.3 (C), 165.3, 167.0 (CO). IR (KBr): ν=2955, 2927, 2871 (m), 1709, 1620, 1465 (s), 1367, 1280, 1235 (m), 1164 (s), 1132, 1048, 969, 849, 818 (w), 740 (s), 662, 561 (w) cm^{-1}. GC–MS (EI, 70 eV): m/z (%)=495 ($[M]^+$, 32), 337 (16), 281 (14), 253 (10), 252 (22), 226 (100), 208 (75), 182 (45). HRMS (EI, 70 eV): calcd for $C_{31}H_{45}NO_4$ $[M]^+$: 495.33431; found: 495.33390.

3.6. Synthesis of bis(2-ethylhexyl) 3,3′-(1-methyl-1*H*-indole-2,3-diyl)diacrylate (4i)

Product **4i** was prepared starting with **2a** (289 mg, 1.0 mmol), 2-ethylhexyl acrylate (0.27 mL, 1.25 mmol) (0.52 mL, 2.5 mmol), $Pd(OAc)_2$ (11 mg, 5 mol %), SPhos (10 mol %), NEt_3 (1.10 mL, 8.0 mmol), DMF (5 mL) at 90 °C for 24 h following general procedure A, as a yellow oil (50 mg, 10%+35% **8**). ^{1}H NMR (250 MHz, $CDCl_3$): δ=0.90 (t, 12H, J=7.5 Hz, $4CH_3$), 1.20–1.40 (m, 16, $8CH_2$), 1.20–1.60 (m, 2H, CH), 3.80 (s, 3H, NCH_3), 4.00–4.10 (m, 4H, CH_2O), 6.30 (d, 1H, J=16.0 Hz, ArH), 6.50 (d, 1H, J=16.0 Hz, ArH), 7.20–7.30 (m, 3H, ArH), 7.80 (d, 1H, J=16.0 Hz, ArH), 7.90 (d, 1H, J=8.1 Hz, ArH), 8.00 (d, 1H, J=15.9 Hz, ArH). ^{13}C NMR (75 MHz, $CDCl_3$): δ=11.0, 11.1, 14.0 (CH_3), 22.9, 23.0, 23.8, 24.0, 28.9, 29.0, 30.4, 30.5 (CH_2), 31.2 (CH_3CN), 38.8, 38.9 (CH-aliphatic), 66.8, 67.6 (CH_2O), 109.0 (CH), 113 (C), 115.7, 121.2, 122.0, 123.5, 123.6 (CH), 124.5 (C), 131.1, 135.5 (CH), 135.8, 138.0 (C), 165.3, 167.0 (CO). IR (KBr): ν=3052 (w), 2957, 2927, 2872, 2858 (m), 1706, 1620 (s), 1464 (m), 1411, 1378, 1352, 1339 (w), 1280, 1250, 1235 (m), 1165 (s), 1132, 1031, 1016, 1016, 968 (m), 850, 818, 766 (w), 740 (s), 655, 561 (w) cm^{-1}. GC–MS (EI, 70 eV): m/z (%)=595 ($[M]^+$, 60), 367 (9), 337 (15), 269 (10), 253 (15), 226 (72), 208 (100), 151 (13). HRMS (EI, 70 eV): calcd for $C_{31}H_{45}NO_4$ $[M]^+$: 495.33431; found: 495.33712.

*3.6.1. (E)-2-Ethylhexyl 3-(3-bromo-1-methyl-1H-indol-2-yl)acrylate (**8**).* Product **8** (138 mg, 35%) was isolated along with **4i** (50 mg, 10%) as a light brown oil (138 mg, 35%+10% of **4i**). ^{1}H NMR (250 MHz, $CDCl_3$): δ=0.87 (t, J=7.3, 6H, $2CH_3$), 1.18–1.45 (m, 8H), 1.53–1.66 (m, 1H), 3.75 (s, 3H, CH_3N), 4.08 (dd, J=0.8, 6.0 Hz, 2H, CH_2O), 6.80 (d, 1H, J=16.2 Hz, CH), 7.08–7.15 (m, 1H, ArH), 7.22–7.25 (m, 2H, ArH), 7.48–7.52 (m, 1H, ArH), 7.774 (d, 1H,

J=16.3 Hz, CH). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ=9.8, 13.1 (CH_3), 22.0, 22.9, 27.8, 29.5 (CH_2), 30.2 (CH), 37.9 (NCH_3), 66.2 (CH_2O), 95.0 (C), 108.8, 119.1, 119.4, 120.0, 124.0 (CH), 126.2, 129.8 (C), 130.0 (CH), 137.0 (C), 166.2 (CO). IR (KBr): ν=2956, 2926, 2871, 2858 (m), 1706 (s), 1625, 1462, 1372, 1325, 1260, 1233, 1207 (m), 1167 (s), 1014, 930, 767 (w), 738 (m) cm^{-1}. HRMS (ESI$^+$): calcd for $C_{20}H_{26}BrNO_2$ (M^+, [^{79}Br]): 391.11469; found: 391.11433, calcd for $C_{20}H_{26}BrNO_2$ (M^+, [^{81}Br]): 393.11263; found: 393.11453.

3.7. General procedure B for Heck cross-coupling reactions

In a pressure tube (glass bomb) a suspension of $Pd(OAc)_2$ (12 mg, 0.05 mmol) and SPhos (L_1) (41 mg, 0.10 mmol) in DMF (5 mL) was purged with argon and stirred at 20 °C to get a yellowish or brownish transparent solution. To the stirred solution were added the brominated indole **2a**–**c** (1.0 mmol), NEt_3 (1.1 mL, 8.0 mmol) and the acrylate (1.25 equiv per Br). The reaction mixture was stirred at 120 °C for 48 h. The solution was cooled to 20 °C, poured into H_2O and CH_2Cl_2 (25 mL each), and the organic and the aqueous layer were separated. The latter was extracted with CH_2Cl_2 (3×25 mL). The combined organic layers were washed with H_2O (3×20 mL), dried (Na_2SO_4), and concentrated in vacuo. The residue was purified by chromatography (flash silica gel, heptanes/EtOAc).

3.8. Synthesis of 2,3-dihydrocarbazoles 5

*3.8.1. Dimethyl 9-methyl-2,9-dihydro-1H-carbazole-2,3-dic arboxylate (**5a**).* Starting with $Pd(OAc)_2$ (12 mg, 5 mol %), SPhos (41 mg, 10 mol %), methyl acrylate (0.26 mL, 2.5 mmol), brominated indole **2a** (288 mg, 1.0 mmol) **5a** was isolated as yellow oil (206 mg, 69%). ^{1}H NMR (300 MHz, $CDCl_3$): δ=2.99 (dd, 1H, J=8.6, 17.0 Hz, C(1)); 3.50 (dd, 1H, J=2.6, 17.2 Hz, H-1), 3.52 (s, 3H, CH_3N), 3.63 (s, 3H, CH_3O); 3.76 (s, 3H, CH_3O), 4.01 (dd, 1H, J=2.4, 8.7 Hz, C(2)), 7.08–7.22 (m, 4H, ArH), 7.92 (s, 1H, C(4)). ^{13}C NMR (62 MHz, $CDCl_3$): δ=23.9 (CH_2), 29.8 (C(4)H), 38.8 (CH_3N). 51.6 (CH_3O), 52.5 (CH_3O), 109.3, 109.6 (CH), 115.7, 117.9 (CH), 117.3, 121.0, 121.9 (CH), 125.1 (C), 132.7 (CH), 138.0, 139.8 (C), 167.7, 173.8 (CO). IR (KBr): ν=2949, 2845 (w), 1720, 1692 (s), 1605, 1524, 1467, 1434, 1270 (m), 1234, 1241, 1191 (s), 1048, 750 (m) cm^{-1}. GC–MS (EI, 70 eV): m/z (%)=299 (M^+, 58), 268 (6), 240 (73), 208 (92), 181 (100), 152 (31), 104 (5), 76 (22). HRMS: m/z calcd for $C_{17}H_{18}NO_4$ $[M+H]^+$ 300.12303; found: 300.122761.

*3.8.2. Diethyl 9-methyl-2,9-dihydro-1H-carbazole-2,3-dicarboxylate (**5b**).* Product **5b** was prepared starting with **2a** (289 mg, 1.0 mmol), ethyl acrylate (0.27 mL, 2.5 mmol), $Pd(OAc)_2$ (11 mg, 5 mol %), SPhos (10 mol %), NEt_3 (1.10 mL, 8.0 mmol), DMF (mL) at 120 °C for 48 h according to general procedure B, as a yellow solid (303 mg, 93%), mp 100–103 °C. ^{1}H NMR (250 MHz, $CDCl_3$): δ=1.10 (s, 3H, CH_3), 1.30 (s, 3H, CH_3), 2.90 (dd, 1H$_\alpha$, J=8.8, 17.1 Hz, H-1), 3.50 (dd, 1H$_\beta$, J=2.6, 17.2 Hz, H-1), 3.60 (s, 3H, NCH_3), 3.90–4.10 (m, 3H, H_α and CH_2O), 4.20 (q, J=7.1, 13.5 Hz, 2H, CH_2O), 7.10–7.20 (m, 3H, ArH), 7.50–7.60 (m, 1H, ArH), 7.90 (s, 1H, H-4). ^{13}C NMR (75 MHz, $CDCl_3$): δ=13.0 (CH_3), 13.5 (CH_3), 22.8 (CH_2), 28.7 (CH, C-4), 37.7 (NCH_3), 59.3 (CH_2O), 60.1 (CH_2O), 108.3 (C), 108.6 (CH), 115.4 (C), 116.9, 120.0, 120.8 (CH), 124.1(C), 131.2 (CH), 137.0, 138.6 (C), 166.3, 172.3 (CO). IR (KBr): ν=2981, 2928, 2854 (w), 1725(s), 1629, 1599 (w), 1470, 1454 (m), 1372, 1261, 1238 (s), 1109, 1079, 147 (m), 787, 747, 723, 608, 561 (w) cm^{-1}. GC–MS (EI, 70 eV): m/z (%)=325 ($[M-2]^+$ (carbazole), 89), 280 (13), 252 (100), 208 (07), 179 (13). HRMS (ESI$^+$): calcd for $C_{19}H_{19}NO_4$ $[M-2]^+$ (carbazole): 325.13141; found: 325.13161.

*3.8.3. Dibutyl 9-methyl-2,9-dihydro-1H-carbazole-2,3-dicarboxylate (**5c**).* Product **5c** was prepared starting with **2a** (289 mg, 1.0 mmol), butyl acrylate (0.36 mL, 2.5 mmol), $Pd(OAc)_2$ (11 mg, 5 mol %), SPhos (10 mol %), NEt_3 (1.10 mL, 8.0 mmol), DMF (mL) at 120 °C for 48 h according to general procedure B, as a yellow highly viscous oil (294 mg, 77%). ^{1}H NMR (250 MHz, $CDCl_3$): δ=0.80 (t, 3H, J=7.3 Hz, CH_3), 0.90 (t, 3H, J=7.4 Hz, CH_3), 1.10–1.30 (m, 2H, CH_2), 1.30–1.50 (m, 4H, $2CH_2$), 1.60–1.70 (m, 2H, CH_2), 3.00 (dd, 1H$_\alpha$, J=8.6, 17.0 Hz, H-1), 3.60 (dd, 1H$_\beta$, J=2.3, 17.0 Hz, H-1), 3.70 (s, 3H, NCH_3), 3.80–4.00 (m, 2H, CH_2O), 4.00 (dd, 1H$_\alpha$, J=2.3, 8.3 Hz, H-2), 4.20 (t, 2H, J=6.6 Hz, CH_2O), 7.00–7.20 (m, 3H, ArH), 7.50–7.60 (m, 1H, ArH), 7.90 (s, 1H, H-4). ^{13}C NMR (62 MHz, $CDCl_3$): δ=13.6 (CH_3), 13.8 (CH_3), 19.0, 19.3, 23.8 (CH_2), 29.8 (CH_3N), 30.5, 31.0 (CH_2), 39.0 (CH, C-2), 64.2, 65.0 (CH_2O), 109.4 (C), 109.6 (CH), 116.5 (C), 118.0, 121.0, 121.8 (CH), 125.2 (C), 132.1 (CH), 138.0, 139.7 (C), 167.4, 173.4 (CO). IR (KBr): ν=2956, 2932, 2872 (m), 1709 (s), 1629, 1599, 1559, 1562 (w), 1500, 1464, 1387, 1362, 1340, 1325 (m), 1257, 1222 (s), 1131, 1106, 1077, 1045, 1015 (m), 950, 902, 843, 830, 783, 765 (w), 742, 720 (m), 632, 608, 561 (w) cm^{-1}. GC–MS (EI, 70 eV): m/z (%)= 383 ($[M]^+$, 46), 310 (06), 282 (34), 226 (87), 208 (67), 182 (100), 152 (13). HRMS (EI, 70 eV): m/z calcd for $C_{23}H_{29}NO_4$ $[M]^+$: 383.20911; found: 383.20824.

*3.8.4. Diisobutyl 9-methyl-2,9-dihydro-1H-carbazole-2,3-dic arboxylate (**5d**).* Starting with Pd(OAc)2 (12 mg, 0.05 mmol) and SPhos (41 mg, 0.10 mmol), isobutyl acrylate (0.36 mL, 2.5 mmol), brominated indole **2a** (288 mg, 1.0 mmol) **5d** was following general procedure B, and was isolated as yellow oil (252 mg, 66%). ^{1}H NMR (250 MHz, $CDCl_3$): δ=0.73 (d, 6H, J=7.6 Hz, $2CH_3$), 0.76 (d, 6H, J=7.6 Hz, $2CH_3$), 0.88–0.92 (m, 2H, CH), 3.01 (dd, 1H, J=8.5, 17.3 Hz, C(1)), 3.03 (dd, 1H, J=2.7, 17.2 Hz, C(1)), 3.68 (d, 2H, J=7.6 Hz, CH_2O), 3.72 (d, 2H, J=7.7 Hz, CH_2O), 3.96 (s, 3H, CH_3N), 4.05 (dd, 1H, J=2.4, 8.8 Hz C (2)), 7.09–7.21 (m, 4H, ArH), 7.92 (s, 1H, C(4)). ^{13}C NMR (250 MHz, $CDCl_3$): δ=18.1, 18.3 ($2CH_3$), 23.2 (CH_2), 29.7 (C(2)H), 38.7 (CH_3N), 51.6 (CH_2O), 51.8 (CH_2O), 109.1 (C), 109.3, 118.0 (CH), 118.6 (C), 120.3, 121.5 (CH), 125.0 (C), 130.3 (CH), 137.8, 139.5 (C), 166.8, 172.6 (CO). IR (KBr): ν=2958, 2927, 2872 (w), 1727, 1464, 1263, 1194, 1158 (m), 1029, 1010 (m), 737 (s), 711, 660, 573 (w) cm^{-1}. GC–MS (EI, 70 eV): m/z (%)=383 (M^+, 60), 309 (21), 282 (54), 226 (100), 208 (80), 182 (77), 167 (22). HRMS: m/z calcd for $C_{23}H_{29}NO_4$ $[M]^+$: 383.2098; found: 383.20933.

*3.8.5. Dihexyl 9-methyl-2,9-dihydro-1H-carbazole-2,3-dicarboxylate (**5e**).* Compound **5e** was synthesized starting with **2a** (289 mg, 1.0 mmol), hexyl acrylate (0.44 mL, 2.5 mmol), $Pd(OAc)_2$ (11 mg, 5 mol %), SPhos (10 mol %), NEt_3 (1.10 mL, 8.0 mmol), DMF (mL) at 120 °C for 48 h following general procedure B, as a yellowish solid (357 mg, 81%), mp 107–109 °C. ^{1}H NMR (250 MHz, $CDCl_3$): δ=0.70 (t, 3H, J=7.0 Hz, CH_3), 0.80 (t, 3H, J=7.0 Hz, CH_3), 1.10–1.20 (m, 6H, $3CH_2$), 1.20–1.50 (m, 8H, $4CH_2$), 1.60–1.70 (m, 2H, CH_2), 3.00 (dd, 1H$_\alpha$, J=8.8, 17.1 Hz, H-1), 3.50 (dd, 1H$_\beta$, J=2.3, 17.1 Hz, H-1), 3.60 (s, 3H, NCH_3), 3.80–4.00 (m, 2H, CH_2O), 4.00 (dd, 1H$_\alpha$, J=2.4, 8.8 Hz, H-2), 4.10 (t, 2H, J=6.8 Hz, CH_2O), 7.00–7.20 (m, 3H, ArH), 7.50–7.60 (m, 1H, ArH), 7.90 (s, 1H, H-4). ^{13}C NMR (75 MHz, $CDCl_3$): δ=12.9, 13.0 (CH_3), 21.5, 21.6, 22.8, 24.4, 24.8, 27.4, 27.9 (CH_2), 28.7 (NCH_3), 30.3, 30.5 (CH_2), 38.0 (CH, C-4), 63.5, 64.2 (CH_2O), 108.3(C), 108.5 (CH), 115.5 (C), 116.9, 120.0, 121,0 (CH), 124.1 (C), 131.0 (CH), 137.0, 138.7 (C), 166.4, 172.3 (CO). IR (KBr): ν=2953, 2928, 2857 (m), 1724, 1691 (s), 1615, 1605, 1526, 1465, 1392, 1311, 1307, 1268 (m), 1223, 1180 (s), 1086, 1046 (m), 915, 835, 767 (w), 738 (s), 653, 626, 546 (w) cm^{-1}. GC–MS (EI, 70 eV): m/z (%)=439 ($[M]^+$, 41), 310 (30), 226 (100), 208 (68), 182 (84), 152(08). HRMS (EI, 70 eV): calcd for $C_{27}H_{37}NO_4$ $[M]^+$: 439.27171; found: 439.27110.

*3.8.6. Di-tert-butyl 9-methyl-2,9-dihydro-1H-carbazole-2,3-dic arboxylate (**5f**).* Compound **5f** was prepared starting with **2a** (367 mg, 1.0 mmol), *tert*-butyl acrylate (0.37 mL, 2.5 mmol), $Pd(OAc)_2$ (11 mg, 5 mol %), SPhos (10 mol %), NEt_3 (1.1° mL,

8.0 mmol), DMF (mL) at 120 °C for 48 h according to general procedure B, as a light brown solid (325 mg, 85%), mp 105–107 °C. ^{1}H NMR (250 MHz, $CDCl_3$): δ=1.30 (s, 9H, $3CH_3$), 1.50 (s, 9H, $3CH_3$), 2.90 (dd, $1H_\alpha$, J=8.9, 17.1 Hz, H-1), 3.50 (dd, $1H_\beta$, J=2.5, 17.1 Hz, H-1), 3.60 (s, 3H, NCH_3), 3.90 (dd, $1H_\alpha$, J=2.1, 8.9 Hz, H-2), 7.00–7.10 (m, 2H, ArH), 7.10–7.20 (m, 1H, ArH), 7.50–7.60 (m, 1H, ArH), 7.80 (s, 1H, H-4). ^{13}C NMR (75 MHz, $CDCl_3$): δ=23.6 (CH_2), 27.9 ($3CH_3$), 28.4 ($3CH_3$), 29.7 (CH, C-4), 39.7 (CH_3N), 79.7 (C–O), 81.0 (C–O), 109.2 (C), 109.5 (CH), 118.0 (CH), 118.7 (C), 120.7, 121.5 (CH), 125.2 (C), 130.6 (CH), 137.9, 139.6 (C), 166.8, 172.5 (CO). IR (KBr): ν=3049, 2973, 2930 (w), 1712 (s), 1614, 1598, 1470, 1455, 1390 (m), 1365, 1272, 1242, 1152, 1128, 1110 (s), 1046, 1014 (w), 872, 846, 836 (m), 747, 739 (s), 666, 597, 550 (w) cm^{-1}. GC–MS (EI, 70 eV): m/z (%)= 383 ([M]$^+$, 7), 325 (54), 269 (100), 252 (86), 225 (80), 207 (44), 179 (82). HRMS (EI, 70 eV): calcd for $C_{23}H_{29}NO_4$ [M]$^+$: 383.20966; found: 383.20855.

*3.8.7. Bis[2-(dimethylamino)ethyl] 9-methyl-2,9-dihydro-1H-carbazole-2,3-dicarboxylate (**5h**).* Compound **5h** was synthesized starting with **2a** (289 mg, 1.0 mmol), 2-(diethylamino)ethyl acrylate (0.38 mL, 2.5 mmol), $Pd(OAc)_2$ (11 mg, 5 mol %), SPhos (10 mol %), NEt_3 (1.10 mL, 8.0 mmol), DMF (mL) at 120 °C for 48 h following general procedure B, as a yellow highly viscous oil (326 mg, 79%). ^{1}H NMR (250 MHz, $CDCl_3$): δ=2.10 (s, 6H, $2CH_3$), 2.30 (s, 6H, $2CH_3$), 3.00 (dd, $1H_\alpha$, J=8.8, 17.1 Hz), 3.50–3.60 (m, 4H, NCH_3 and H_β-1), 4.00–4.10 (m, 5H, $2NCH_2$ and H_α-2), 3.30 (t, 4H, J=6.3 Hz, $2CH_2O$), 7.10–7.20 (m, 3H, ArH), 7.50 (dd, 1H, J=2.3, 8.5 Hz, ArH), 7.90 (s, 1H, H-4). ^{13}C NMR (62 MHz, $CDCl_3$): δ=23.8 (CH_2, C-1), 29.8 (NCH_3), 38.9 (CH, C-2), 45.5, 45.8 ($2CH_3$), 57.3, 57.9 (NCH_2), 62.3, 63.2 (CH_2O), 109.3 (C), 109.6 (CH), 115.7 (C), 117.9, 121.1, 122.0 (CH), 125.1 (C), 132.8 (CH), 138.0, 139.8 (C), 167.2, 173.1 (CO). IR (KBr): ν=2943, 2857, 2820, 2769 (w), 1691, 1614, 1525, 1455 (s), 1394, 1370, 1332, 1286 (m), 1225, 1166 (s), 1130, 1097 (m), 1031 (s), 954, 919, 835 (w), 739 (s), 627 (w) cm^{-1}. GC–MS (EI, 70 eV): m/z (%)=413 ([M]$^+$, 13), 297 (98), 252 (06), 227 (04), 225 (13), 208 (56), 180 (17), 58 (100). HRMS (EI, 70 eV): calcd for $C_{23}H_{31}N_3O_4$ [M]$^+$: 413.23091; found: 413.230881.

3.9. General procedure C for the transformation of 1,2-dihydrocarbazoles to carbazoles

To solution of xylene (5 mL) were added the 1,2-dihydrocarbazole (100 mg) and Pd/C (10 mg, 10 mol %). The solution was stirred under reflux for 48 h under argon atmosphere. The reaction mixture was filtered and the filtrate was concentrated in vacuo.

3.10. Synthesis of 3,4-di-substituted carbazoles 6

*3.10.1. Diethyl 9-methyl-9H-carbazole-2,3-dicarboxylate (**6a**).* Starting with **5b** (100 mg) following general procedure C, **6a** was prepared as a light yellow oil (99 mg, 100%). ^{1}H NMR (300 MHz, $CDCl_3$): δ=1.31 (t, 3H, J=7.1 Hz, CH_3), 1.33 (t, 3H, J=7.1 Hz, CH_3), 3.81 (s, 3H, CH_3N), 4.32 (q, 2H, J=7.2 Hz, CH_2O), 4.43 (q, 2H, J=7.2 Hz, CH_2O), 7.21–7.31 (m, 1H, ArH), 7.32–7.41 (m, 1H, ArH), 7.40–7.51 (m, 1H, ArH), 7.60 (s,1H, ArH), 8.00–8.11 (m, 1H, ArH), 8.51 (s, 1H, ArH). ^{13}C NMR (62 MHz, $CDCl_3$): δ=13.2, 13.3 (CH_3), 28.4 (CH_3N), 60.3 (CH_2O), 60.7 (CH_2O), 108.0, 108.1, 119.2, 120.0 (CH) 120.6, 121.2 (C), 121.4 (CH), 122.7, (C), 126.1 (CH), 130.1, 140.5, 141.2 (C), 166.8, 168.2 (CO). IR (KBr): ν=2916 (w), 1713, 1702, 1628, 1599, 1559, 1499, 1475, 1447, 1427 (m), 1392, 1372, 1339, 1328 (s), 1254, 1240, 1227 (w), 1124, 1106, 1080, 1047, 1030, 953, 913, 868, 835, 794, 781, 765, 748, 725, 664, 656, 626, 590, 556 (s) cm^{-1}. GC–MS (EI, 70 eV): m/z (%)=325 (M$^+$, 95), 280 (12), 253 (21), 252 (100), 251 (5), 208 (7), 179 (12), 152 (9). HRMS: m/z calcd for $C_{19}H_{19}NO_4$ [M]$^+$: 325.13141; found: 325.131001.

*3.10.2. Dibutyl 9-methyl-9H-carbazole-2,3-dicarboxylate (**6b**).* Product **6b** was prepared starting with **5c** (100 mg, 0.26 mmol), following general procedure C, as a light yellow solid (99 mg, 100%). ^{1}H NMR (250 MHz, $CDCl_3$): δ=0.90 (t, 3H, J=7.4 Hz, CH_3), 0.90 (t, 3H, J=7.3 Hz, CH_3), 1.30–1.50 (m, 4H, $2CH_2$), 1.60–1.80 (m, 4H, $2CH_2$), 3.80 (s, 3H, NCH_3), 4.30 (t, 2H, J=6.8 Hz, CH_2O), 4.30 (t, 2H, J=6.7 Hz, CH_2O), 7.20–7.30 (m, 1H, ArH), 7.30–7.40 (m, 1H, ArH), 7.40–7.50 (m, 1H, ArH), 7.60 (s, 1H, H-1), 8.00–8.10 (m, 1H, ArH), 8.40 (s, 1H, H-4). ^{13}C NMR (62 MHz, $CDCl_3$): δ=13.7, 13.8 (CH_3), 19.2, 19.3 (CH_2), 29.4 (NCH_3), 30.6, 30.8 (CH_2), 65.3, 65.7 (CH_2O), 109.0, 109.1, 120.2, 121.0 (CH), 121.7, 122.2 (C), 122.4 (CH), 123.6 (C), 127.1 (CH), 131.1, 141.5, 142.1 (C), 167.9, 169.4 (CO). IR (KBr): ν=2956, 2931, 2871 (w), 1709 (s), 1464, 1387, 1362, 1340, 1325 (m) 1255, 1221 (s), 1131, 1106, 1077, 1045 (m), 950, 902, 843, 829 (w), 784, 743, 721 (m), 632, 608, 561 (w) cm^{-1}. GC–MS (EI, 70 eV): m/z (%)=381(M$^+$, 56), 308 (15), 280 (100), 224 (87), 212 (27), 206 (77), 180 (10), 152 (11). HRMS (EI, 70 eV): calcd for $C_{23}H_{27}NO_4$ [M]$^+$: 381.19401; found: 381.19422.

*3.10.3. Dihexyl 9-methyl-9H-carbazole-2,3-dicarboxylate (**6c**).* Starting with **5e** (100 mg) following general procedure C, as a yellow oil (99 mg, 100%). ^{1}H NMR (300 MHz, $CDCl_3$): δ=0.82 (t, 3H, J=7.1 Hz, CH_3), 0.83 (t, 3H, J=7.0 Hz, CH_3), 1.24–1.30 (m, 8H, $4CH_2$), 1.33–1.40 (m, 4H, $2CH_2$), 1.66–1.73 (m, 4H, $2CH_2$), 3.75 (s, 3H, CH_3N), 4.26 (t, 2H, J=6.7 Hz, CH_2O), 4.28 (t, 2H, J=6.7 Hz, CH_2O), 7.17–7.23 (m, 1H, ArH), 7.32 (d, 1H, J=8.2 Hz, ArH), 7.42–7.47 (m, 1H, ArH), 7.53 (s, 1H, ArH), 8.01 (d, 1H, J=7.8 Hz, ArH), 8.42 (s, 1H, ArH). ^{13}C NMR (62.9 MHz, $CDCl_3$): δ=14.0 ($2CH_3$), 22.6 ($2CH_2$), 25.7, 25.7, 28.6, 28.7 (CH_2), 28.7 (CH_3N), 31.5, 30.6 (CH_2) 65.6, 66.0 (CH_2O), 109.0, 109.1, 120.1, 120.9 (CH), 121.7, 122.2 (C), 122.3 (CH), 123.6 (C), 127.1 (CH), 131.1, 141.4, 142.1 (C), 167.8, 169.3 (CO). IR (KBr): ν=3054, 2953, 2928, 2856 (w), 1712 (s), 1629, 1599, 1561, 1501 (w), 1466 (m), 1387 (w), 1363, 1340, 1325 (m), 1257, 1222 (s), 1132 (m), 1108 (s) 1079, 1046, 1015, 981, 907 (m), 867, 883 (w), 785, 766 (m), 729, 722 (s), 646 (m), 633, 609, 561 (w) cm^{-1}. GC–MS (EI, 70 eV): m/z (%)= 437 (M$^+$, 41), 353 (10), 252 (100), 225 (10), 182 (84), 152(08). HRMS: m/z calcd for $C_{27}H_{35}NO_4$ [M]$^+$: 437.25661; found: 437.25410.

*3.10.4. Di-tert-butyl 9-methyl-9H-carbazole-2,3-dicarboxylate (**6d**).* Starting with **5f** (100 mg) following general procedure C, as a light yellow oil (99 mg, 100%). ^{1}H NMR (300 MHz, $CDCl_3$): δ=1.57 (s, 9H, $3CH_3$), 1.58 (s, 9H, $3CH_3$), 3.78 (s, 3H, CH_3N); 7.17–7.23 (m, 1H, ArH), 7.33 (d, 1H, J=8.2 Hz, ArH), 7.42–7.47 (m, 1H, ArH), 7.50 (s,1H, ArH), 8.03 (d, 1H, J=7.8 Hz, ArH), 8.33 (s,1H, ArH). ^{13}C NMR (75 MHz, $CDCl_3$): δ=28.1 ($3CH_3$), 28.3 ($3CH_3$), 29.4 (CH_3N). 81.2 (C–O), 81.8 (C–O), 109.0, 109.1, 119.0, 120.9, 122.0 (CH), 122.4, 123.2, 123.8 (C), 126.8 (CH), 132.8, 141.3, 142.2 (C), 167.0, 168.4 (CO). IR (KBr): ν=2975, 2929, 2849 (w), 1713 (s), 1702, 1628, 1596, 1562, 1530, 1503, 1475, 1455, 1390 (w), 1365, 1337, 1324, 1269, 1251, 1228, 1165, 1129, 1108 (s), 1079, 1046, 1014, 955, 895, 876, 863, 834, 800, 787, 777, 763, 756, 738, 718 (m), 666, 634, 598, 565, 555 (w) cm^{-1}. EI$^+$ (70 eV): m/z (%)=381 ([M]$^+$, 27), 325 (5), 270 (13), 269 (100), 251 (48), 252 (33), 225 (8), 207 (10), 179 (35). HRMS: m/z calcd for $C_{23}H_{28}NO_4$ [M+H]$^+$: 382.20128; found: 382.20055.

3.11. Synthesis of 2-(2-cyanoethyl)-9-methyl-9*H*-carbazole-3-carbonitrile (7)

Product **7** was prepared, starting with **2a** (289 mg, 1.0 mmol), $Pd(OAc)_2$ (11 mg, 5 mol %), acrylonitrile (0.17 mL, 2.5 mmol), SPhos (10 mol %), NEt_3 (1.10 mL, 8.0 mmol), DMF (5 mL) at 120 °C for 48 h according to general procedure B, as a light yellow crystals (127 mg, 49%), mp 185–187 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ=2.80 (t, 2H,

J=7.1 Hz, CH_2), 3.30 (t, 2H, J=7.1 Hz, CH_2), 3.80 (s, 3H, NCH_3), 7.20–7.30 (m, 1H, ArH), 7.30 (s, 1H, H-1), 7.40 (d, 1H, J=8.2 Hz, ArH), 7.40–7.50 (m, 1H, ArH), 8.00 (d, 1H, J=7.9 Hz, ArH), 8.30 (s, 1H, H-4). ^{13}C NMR (75 MHz, $CDCl_3$): δ=18.0 (CH_2), 28.4 (NCH_3), 30.0 (CH_2), 100.4 (C), 108.2, 108.9 (CH), 117.6, 118.1 (CN), 119.6, 119.7 (CH), 120.6, 121.2 (C), 125.1, 126.3 (CH), 137.1, 140.8, 141.9 (C). IR (KBr): ν=2914, 2852 (w), 2206 (s), 1631, 1597, 1557, 1504, 1464, 1432, 1366, 1330, 1320, 1264, 1253 (m), 1112, 1153, 1014, 966, 898 (w), 844, 800, 767, 754 (s), 725, 666, 652, 550, 530 (w) cm^{-1}. GC–MS (EI, 70 eV): m/z (%)=259 ([M]$^+$, 53), 243 (23), 198 (100), 152 (68), 112 (38). HRMS (EI, 70 eV): calcd for $C_{17}H_{13}N_3$ [M]$^+$: 259.11095; found: 259.11041.

3.12. Synthesis of 6-bromo-2,3-bis(alkenyl)-*N*-methylindole 9

*3.12.1. Di(tert-butyl) 3,3′-(6-bromo-1-methyl-1H-indole-2,3-diyl)diacrylate (**9**).* Product **9** was prepared starting with **2b** (368 mg, 1.0 mmol) and *tert*-butyl acrylate (0.37 mL, 2.5 mmol), $Pd(OAc)_2$ (11 mg, 5 mol %), SPhos (10 mol %), NEt_3 (1.10 mL, 8.0 mmol), DMF (5 mL) at 90 °C for 24 h following general procedure A, as a yellow solid (276 mg, 75%), mp 148–152 °C. The structure was confirmed by 2D NMR analysis (NOESY, HMBC). ^{1}H NMR (250 MHz, $CDCl_3$): δ=1.50 (s, 18H, $6CH_3$), 3.70 (s, 3H, NCH_3), 6.20 (d, 1H, J=16.1 Hz, ArH), 6.30 (d, 1H, J=16.1 Hz, ArH), 7.20 (d, 1H, J=8.4 Hz, ArH), 7.20 (dd, 1H, J=1.7, 8.6 Hz, ArH), 7.20 (d, J=1.5 Hz, 1H, ArH), 7.80 (d, 1H, J=16.1 Hz), 7.70 (d, 1H, J=15.9 Hz, ArH). ^{13}C NMR (75 MHz, $CDCl_3$): δ=28.0 ($2CH_3$), 28.2 ($2CH_3$), 28.3 ($2CH_3$), 31.3 (NCH_3), 81.0, 81.3 (C–O), 113.0 (CH), 113.8, 118.0 (C), 118.9, 122.3 (CH), 124.3 (C), 124.9, 127.0, 129.8, 135.2 (CH), 137.0, 139.0 (C), 165.2, 167.0 (C=O). IR (KBr): ν=3090, 2978, 2929 (w), 1709, 1674, 1633, 1615 (s), 1470, 1454 (m), 1365, 1278, 1252, 1147 (s), 1064, 1038 (w), 970, 948 (m), 843, 829, 805 (s), 772, 757, 737, 640, 589 (w) cm^{-1}. MS (EI, 70 eV): m/z (%)=461 ([M$^+$, ^{79}Br] 13), 349 (16), 331 (17), 305 (46), 259 (35), 225 (100), 181 (97), 57 (38). HRMS (EI, 70 eV): calcd for $C_{23}H_{28}BrNO_4$ [M, ^{79}Br]$^+$: 461.11962; found: 461.11828.

*3.12.2. Di(isobutyl) 7-bromo-9-methyl-2,9-dihydro-1H-carbazole-2,3-dicarboxylate (**10**).* Product **10** was synthesized starting with **2b** (367 mg, 1.0 mmol), *iso*-butyl acrylate (0.36 mL, 2.5 mmol), $Pd(OAc)_2$ (11 mg, 5 mol %), SPhos (10 mol %), NEt_3 (1.10 mL, 8.0 mmol), DMF (5 mL) at 120 °C for 48 h according to general procedure A, as a yellowish highly viscous oil (335 mg, 73%). ^{1}H NMR (250 MHz, $CDCl_3$): δ=0.70 (d, 6H, J=6.7 Hz, $2CH_3$), 0.80 (d, 6H, J=6.7 Hz, $2CH_3$), 1.60–1.80 (m, 1H, CH), 1.90–2.00 (m, 1H, CH), 3.50 (dd, $1H_\alpha$, J=2.1, 17.2 Hz, H-1), 3.60 (s, 3H, NCH_3), 3.70 (dd, 2H, J=3.6, 6.6 Hz, CH_2O), 3.90 (dd, 2H, J=0.7, 6.5 Hz, CH_2O), 3.90 (dd, $1H_\beta$, J=0.7, 6.5 Hz, H-1), 4.00 (dd, $1H_\alpha$, J=2.0, 8.6 Hz, H-2), 7.20 (dd, 1H, J=1.6, 8.4 Hz, ArH), 7.30 (d, 1H, J=1.4 Hz, ArH), 7.40 (d, 1H, J=8.4 Hz, ArH), 7.80 (s, 1H, H-4). ^{13}C NMR (75 MHz, $CDCl_3$): δ=18.8, 18.9 (CH_3), 19.3 ($2CH_3$), 23.7 (CH_2), 27.6, 28.0 (CH), 29.9 (NCH_3), 38.8 (CH, C-2), 70.6, 71.2 (CH_2O), 109.4 (C), 112.7 (CH), 115.2, 117.5 (C), 119.1 (CH), 123.9 (C), 124.1, 131.3 (CH), 138.8, 140.2 (C), 167.2, 173.1 (CO). IR (KBr): ν=3052, 2948, 2867 (w), 1728, 1703, 1664, 1588, 1573, 1473, 1435 (s), 1392, 1379, 1325 (m), 1269, 1244, 1189, 1140, 1079, 1040 (s), 998, 975, 934, 904, 872, 853, 813 (w), 776, 736, 691 (s), 660, 646, 608, 576, 562 (m) cm^{-1}. GC–MS (EI, 70 eV): m/z (%)=461 ([M, ^{79}Br]$^+$, 5), 436 (54), 389(10), 299 (100), 267 (70), 225 (12), 178 (17). HRMS (EI, 70 eV): calcd for $C_{23}H_{28}BrNO_4$ [M, ^{79}Br]$^+$: 461.12017; found: 461.12020.

3.13. Synthesis of 2,3,6-tris(alkenyl)-*N*-methylindoles 11

*3.13.1. Trimethyl 3,3′,3″-(1-methyl-1H-indole-2,3,6-triyl)triacrylate (**11a**).* Product **11a** was prepared starting with **2b** (368 mg, 1.0 mmol), methyl acrylate (0.34 mL, 3.75 mmol), $Pd(OAc)_2$ (11 mg, 5 mol %), SPhos (10 mol %), DMF (5 mL), NEt_3 (1.10 mL, 8.0 mmol) and *tert*-butyl acrylate (0.3 mL, 3.3 mmol), at 90 °C for 36 h following general procedure D, as a yellowish highly viscous oil (264 mg, 69%). ^{1}H NMR (250 MHz, $CDCl_3$): δ=3.60 (s, 3H, CH_3O), 3.70 (s, 3H, OCH_3), 3.70 (s, 3H, NCH_3), 3.80 (s, 3H, OCH_3), 6.20 (d, 1H, J=16.1 Hz, ArH), 6.40 (d, 1H, J=15.9 Hz, ArH), 6.40 (d, 1H, J=15.9 Hz, ArH), 7.20–7.40 (m, 2H, ArH), 7.70 (d, 1H, J=15.9 Hz, ArH), 7.80 (d, 1H, J=16.2 Hz, ArH), 7.80 (dd, 1H, J=1.3, 7.5 Hz, ArH), 7.90 (d, 1H, J=15.9 Hz, ArH). ^{13}C NMR (75 MHz, $CDCl_3$): δ=29.4 (CH_3CN), 51.0, 52.1, 52.2 (OCH_3), 108.7 (C), 110.6, 115.0, 115.3, 119.3, 119.4, 123.0 (CH), 125 (C), 128.9 (CH), 129.0 (C), 134.2 (CH), 136.3, 137.1 (C), 143.2 (CH), 164.4, 165.6, 166.1 (CO). IR (KBr): ν=3028, 2950, 2848 (w), 1710, 1615, 1606 (s), 1298, 1283 (m), 1163, 1138 (s), 1037, 973 (m), 842, 781, 767, 746, 628, 606, 585 (w) cm^{-1}. GC–MS (EI, 70 eV): m/z (%)=383 (M$^+$, 60), 352 (07), 324 (64), 292 (100), 265 (32), 234 (19), 204 (19). HRMS (EI, 70 eV): calcd for $C_{21}H_{21}NO_6$ [M]$^+$: 383.13634; found: 383.136074.

*3.13.2. Trihexyl 3,3′,3″-(1-methyl-1H-indole-2,3,6-triyl)triacrylate (**11d**).* Product **11d** was prepared starting with **2b** (367 mg, 1.0 mmol), *n*-hexyl acrylate (0.66 mL, 3.75 mmol), $Pd(OAc)_2$ (11 mg, 5 mol %), SPhos (10 mol %), NEt_3 (1.10 mL, 8.0 mmol), DMF (5 mL) at 90 °C for 36 h following general procedure A, as a yellow highly viscous oil (437 mg, 74%). ^{1}H NMR (250 MHz, $CDCl_3$): δ=0.80 (t, 9H, J=6.6 Hz, $3CH_3$), 1.10–1.30 (m, 16H, $8CH_2$), 1.60–1.70 (m, 8H, $4CH_2$), 3.80 (s, 3H, NCH_3), 3.90 (t, J=6.7 Hz, 2H, CH_2), 4.10–4.30 (m, 4H, $2CH_2$), 6.20 (d, 1H, J=16.0 Hz, ArH), 6.40 (d, 1H, J=15.9 Hz, ArH), 6.50 (d, 1H, J=16.0 Hz, ArH), 7.20–7.40 (m, 2H, ArH), 7.70 (d, 1H, J=15.9 Hz, ArH), 7.70 (d, 1H, J=16.1 Hz, ArH), 7.80 (d, 1H, J=8.9 Hz, ArH), 7.90 (d, 1H, J=16.0 Hz, ArH). ^{13}C NMR (62 MHz, $CDCl_3$): δ=14.0 ($3CH_3$), 22.6, 25.7, 28.7 ($3CH_2$), 31.3 (CH_3N), 31.5 ($3CH_2$), 64.0, 64.7, 65.3 (CH_2O), 109.5 (C), 110.5, 117.3, 117.6 (CH), 117.6(C), 120.3, 120.4, 125.3 (CH), 126.9, 129.6 (C), 130.6, 136.0 (CH), 137.3, 138.0 (C) 143.9 (CH), 165.0, 166.1, 167.7 (CO). IR (KBr): ν=2953, 2927, 2857 (m), 1703, 1610 (s), 1560, 1530 (w), 1465, 1269, 1241, 1204 (m), 1160 (s), 1037, 979, 906, 845, 808, 764, 724, 609, 583 (w) cm^{-1}. MS (EI, 70 eV): m/z (%)=593 (M$^+$, 90), 492 (12), 463 (69), 406 (29), 380 (100), 362 (74), 336 (14), 278 (25), 234 (69). HRMS (EI, 70 eV): calcd for $C_{36}H_{51}NO_6$ [M]$^+$: 593.37109; found: 593.36965.

*3.13.3. Tris(tert-butyl) 3,3′,3″-(1-methyl-1H-indole-2,3,6-triyl)triacrylate (**11f**).* Product **11f** was synthesized starting with **2b** (367 mg, 1.0 mmol), *tert*-butyl acrylate (0.55 mL, 3.75 mmol), $Pd(OAc)_2$ (11 mg, 5 mol %), SPhos (10 mol %), NEt_3 (1.10 mL, 8.0 mmol), DMF (5 mL) at 90 °C for 36 h following general procedure A, as a yellow oil (387 mg, 76%). ^{1}H NMR (250 MHz, $CDCl_3$): δ=1.50 (s, 9H, $3CH_3$), 1.50 (s, 18H, $6CH_3$), 3.80 (s, 3H, NCH_3), 6.20 (d, 1H, J=16.1 Hz, ArH), 6.40 (d, 1H, J=15.8 Hz, ArH), 6.40 (d, 1H, J=16.1 Hz, ArH), 7.30 (dd, 1H, J=1.0, 8.4 Hz, ArH), 7.40 (s, 1H, ArH), 7.70 (d, 1H, J=16.1 Hz, ArH), 7.80 (d, 1H, J=16.1 Hz, ArH), 7.80 (d, 1H, J=16.1 Hz, ArH), 7.90 (d, 1H, J=8.5 Hz, ArH). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ=28.1 ($3CH_3$), 28.2 ($3CH_3$), 28.3 ($3CH_3$), 31.2 (NCH_3), 80.1, 80.4, 81.4 (C–O), 110.6 (CH), 114.0 (C), 118.9, 119.5, 121.2, 121.4 (CH), 127.0 (C), 127.2, 129.9 (CH), 130.9 (C), 135.3 (CH), 138.3, 139.0 (C), 144.0 (CH), 165.2, 166.4, 167.0 (CO). IR (KBr): ν=2976, 2931 (w), 1699, 1621, 1614 (s), 1455, 1391, 1366 (m), 1306, 1280, 1252, 1140 (s), 1038, 975, 844, 809, 763, 729, 609 (m), 584 (w) cm^{-1}. MS (EI, 70 eV): m/z (%)=509 (M$^+$, 10), 453 (04), 395 (06), 352 (13), 339 (100), 321 (53), 311 (06), 295 (38), 265 (32), 234 (29), 204 (12). HRMS (EI, 70 eV): calcd for $C_{30}H_{39}NO_6$ [M]$^+$: 509.27719; found: 509.27692.

*3.13.4. Tris(6-methylheptyl) 3,3′,3″-(1-methyl-1H-indole-2,3,6-triyl) triacrylate (**11g**).* Product **11g** was synthesized starting with **2b** (367 mg, 1.0 mmol), $Pd(OAc)_2$ (11 mg, 5 mol %), isooctyl acrylate (0.79 mL, 3.75 mmol), SPhos (10 mol %), NEt_3 (1.10 mL, 8.0 mmol), DMF (5 mL) at 90 °C for 36 h following general procedure A, as a yellow oil (493 mg, 73%). ^{1}H NMR (250 MHz, $CDCl_3$): δ=0.60–1.80 (m, 45H, aliphatic protons), 3.80 (s, 3H, NCH_3), 4.00–4.30 (m, 6H,

3CH_2O), 6.30 (d, 1H, J=15.7 Hz, ArH), 6.40 (d, 1H, J=16.4 Hz, ArH), 6.50 (d, 1H, J=16.1 Hz, ArH), 7.30–7.40 (m, 2H, ArH), 7.70 (d, 1H, J=16.1 Hz, ArH), 7.80 (br d, 1H, J=8.7 Hz, ArH), 7.80 (d, 1H, J=16.8 Hz, ArH), 7.80 (d, 1H, J=15.9 Hz, ArH). ^{13}C NMR (62.9 MHz, $CDCl_3$): δ=13.0, 14.6, 15.2 (CH_3), 20.1, 22.9, 24.5, 25.9, 26.7, 27.5 (CH_2), 31.2 (NCH_3), 45.6 (CH_2), 63.0, 63.8, 65.6 (CH_2O), 110.6 (CH), 114 (C), 117.0, 117.9, 121.3, 121.4, 125.3 (CH), 126.9, 130.7 (C), 130.9, 136.0 (CH), 138.3, 139.0 (C), 145 (CH), 165.9, 167.3, 167.7 (CO). IR (KBr): ν=2955, 2927, 2870 (m), 1705, 1623 (s), 1561, 1533 (w), 1463 (s), 1380 (w), 1267, 1234, 1161 (s), 1036, 977, 845, 808, 768, 740, 609 (w) cm^{-1}. MS (EI, 70 eV): m/z (%)=677 (M^+, 90), 563 (16), 519 (60), 436 (38), 408 (69), 390 (59), 295 (30), 278 (34), 252 (22), 226 (06), 208 (10), 194 (11). HRMS (EI, 70 eV): calcd for $C_{42}H_{63}NO_6$ $[M]^+$: 677.46499; found: 677.463279.

*3.13.5. (2E,2′E,2″E)-trioctadecyl 3,3′,3″-(1-methyl-1H-indole-2,3,6-triyl)triacrylate (**11h**).* Starting with $Pd(OAc)_2$ (12 g, 5 mol %) and SPhos (41 mg, 0.10 mmol), brominated indole **2b** (367 mg, 1.0 mmol), **11h** was isolated as a yellow oil (702 mg, 64%). ^{1}H NMR (300 MHz, $CDCl_3$): δ=0.80 (t, 9H, J=7.6 Hz, 3CH_3), 0.91–1.21 (m, 96H, 48CH_2), 3.62–3.75 (m, 4H, 2CH_2O), 3.79 (s, 3H, CH_3N), 3.82 (t, 2H, J=6.9 CH_2O), 6.24 (d, 1H, J=16.1 Hz, CH), 6.43 (d, 1H, J=15.9 Hz, CH), 6.42 (d, 1H, J=15.9 Hz, CH), 7.23–7.43 (m, 2H, ArH), 7.72 (d, 1H, J=15.9 Hz, CH), 7.83 (d, 1H, J=16.2 Hz, CH), 7.88 (dd, 1H, J=1.3, 7.5 Hz, ArH), 7.95 (d, 1H, J=15.9 Hz, CH). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ=14.1 (CH_3), 22.6 (CH_2), 28.4–29.6 (CH_2), 32.8 (CH_3CN), 63.9, 64.6, 65.2 (CH_2O), 108.7 (C), 110.5, 114.2, 115.3, 117.3, 121.3, 123.0 (CH), 125.4 (C), 128.9 (CH), 129.0 (C), 134.2 (CH), 138.3, 139.0 (C), 144.8 (CH), 166.0, 167.1, 167.7 (CO). GC–MS (EI, 70 eV): m/z (%)=1097 (M^+,9), 801 (2), 575 (7), 228 (4), 189 (5), 97 (21), 69 (27), 44 (100). HRMS (ESI^-): m/z calcd for $C_{72}H_{123}NO_6$ $[M]^+$: 1097.93504; found: 1097.935219.

3.14. Synthesis of 6-alkenyl-2,3-dihydrocarbazoles 12

*3.14.1. Dimethyl 7-(3-methoxy-3-oxoprop-1-enyl)-9-methyl-2,9-dihydro-1H-carbazole-2,3-dicarboxylate (**12a**).* Compound **12a** was prepared starting with **2b** (367 mg, 1.0 mmol), methyl acrylate (0.34 mL, 3.75 mmol), $Pd(OAc)_2$ (11 mg, 5 mol %), SPhos (10 mol %), NEt_3 (1.10 mL, 8.0 mmol), DMF (5 mL) at 120 °C for 48 h according to general procedure B, as a brownish highly viscous oil (302 mg, 79%). ^{1}H NMR (250 MHz, $CDCl_3$): δ=3.00 (dd, 1H$_\alpha$, J=8.5, 17.3 Hz, H-1), 3.50 (s, 3H, NCH_3), 3.60 (dd, 1H$_\beta$, J=2.4, 17.3 Hz, H-1), 3.60 (s, 3H, OCH_3), 3.70 (s, 3H, OCH_3), 3.80 (s, 3H, OCH_3), 4.00 (dd, 1H$_\alpha$, J=2.4, 8.8 Hz, H-2), 6.40 (d, 1H, J=15.9 Hz, ArH), 7.30–7.40 (m, 2H, ArH), 7.50 (d, 1H, J=8.6 Hz, ArH), 7.70 (d, 1H, J=15.9 Hz, ArH), 7.90 (s, 1H, H-4). ^{13}C NMR (75 MHz, $CDCl_3$): δ=23.0 (CH_2), 29.7 (CH, C-4), 38.7 (NCH_3), 51.6 (OCH_3), 51.8 (OCH_3), 52.6 (OCH_3), 108.7, 110.4 (CH), 114.6, 115.9 (CH), 117.3, 120.0 (CH), 125.8, 127.4, 131.0 (CH), 137.2, 141.0, 145.0 (CH), 166.5, 166.8, 172.5 (C). IR (KBr): ν=2999, 2950, 2846 (w), 1709 (s), 1628, 1605, 1270, 1231, 1188, 1166, 1110, 1040, 1060 (m), 973, 803 (s), 778 (s), 727 (m) cm^{-1}. GC–MS (EI, 70 eV): m/z (%)=383 $[M]^+$, 353 (69), 323 (61), 293 (40), 284 (51), 189 (31), 102 (100), 77 (22). HRMS (EI, 70 eV): calcd for $C_{21}H_{21}NO_6$ $[M]^+$: 383.13689; found: 383.13632.

*3.14.2. Diethyl 7-(3-ethoxy-3-oxoprop-1-enyl)-9-methyl-2,9-dihydro-1H-carbazole-2,3-dicarboxylate (**12b**).* Product **12b** was synthesized starting with **2b** (367 mg, 1.0 mmol), ethyl acrylate (0.41 mL, 3.75 mmol), $Pd(OAc)_2$ (11 mg, 5 mol %), SPhos (10 mol %), NEt_3 (1.1° mL, 8.0 mmol), DMF (5 mL) at 120 °C for 48 h following general procedure B, as yellowish highly viscous oil (285 mg, 67%). ^{1}H NMR (250 MHz, $CDCl_3$): δ=1.10 (t, 3H, J=7.3 Hz, CH_3), 1.20 (t, 3H, J=7.1 Hz, CH_3), 1.30 (t, 3H, J=7.0 Hz, CH_3), 3.00 (dd, 1H$_\alpha$, J=8.8, 17.2 Hz, H-1), 3.50 (dd, 1H$_\beta$, J=2.4, 17.2 Hz, H-1), 3.60 (s, 3H, NCH_3), 3.80–4.10 (m, 3H and 1H$_\alpha$, H-2 and CH_2O), 4.10–4.30 (m, 4H, 2CH_2O), 6.40 (d, 1H, J=15.9 Hz), 7.30 (m, 2H, ArH), 7.50 (d, 1H, J=8.5 Hz, ArH), 7.70 (d, 1H, J=15.8 Hz), 7.80 (s, 1H, H-4). ^{13}C NMR (62 MHz, $CDCl_3$): δ=14.0 (CH_3), 14.4 (CH_3), 14.5 (CH_3), 23.8 (CH_2), 29.8 (NCH_3), 38.8 (CH, C-2), 60.3 (CH_2O), 60.4 (CH_2O), 61.2 (CH_2O), 109.6 (C), 110.2, 115.9 (CH), 117.4 (C), 118.2, 120.8 (CH), 126.7, 128.3 (C), 131.5 (CH), 138.1, 141.8 (C), 145.7 (CH), 167.1, 167.3, 173.0 (CO). IR (KBr): ν=2979, 2931 (m), 1731, 1697, 1606 (s), 1475, 1274 (m), 1227, 1168 (s), 1034, 982, 962, 852, 811, 771, 710 (s), 605, 582 (w) cm^{-1}. MS (EI, 70 eV): m/z (%)=425 (M^+, 76), 380 (12), 352 (100), 324 (23), 306 (98), 279 (77), 262 (30), 251 (16), 234 (92), 206 (22). HRMS (EI, 70 eV): calcd for $C_{24}H_{27}NO_6$ $[M]^+$: 425.18329; found: 425.18236.

*3.14.3. Dibutyl 7-(3-butoxy-3-oxoprop-1-enyl)-9-methyl-2,9-dihydro-1H-carbazole-2,3-dicarboxylate (**12c**).* Product **12c** was prepared, following general procedure B, starting with **2b** (367 mg, 1.0 mmol), $Pd(OAc)_2$ (11 mg, 5 mol %), *n*-butyl acrylate (0.53 mL, 3.75 mmol), SPhos (10 mol %), NEt_3 (1.10 mL, 8.0 mmol), DMF (5 mL) at 120 °C for 48 h as a yellow solid (483 mg, 95%), mp 112–114 °C. ^{1}H NMR (250 MHz, $CDCl_3$): δ=0.80 (t, 3H, J=7.3 Hz, CH_3), 0.90 (t, 3H, J=7.3 Hz, CH_3), 0.90 (t, 3H, J=7.3 Hz, CH_3), 1.10–1.30 (m, 2H, CH_2), 1.30–1.50 (m, 6H, 3CH_2), 1.60–1.70 (m, 4H, 2CH_2), 3.00 (dd, 1H$_\alpha$, J=8.6, 17.2 Hz, H-1), 3.60 (dd, 1H$_\beta$, J=2.2, 17.2 Hz, H-1), 3.70 (s, 3H, NCH_3), 3.80–4.00 (m, 2H, CH_2O), 4.00 (dd, 1H$_\alpha$, J=1.9, 8.6 Hz, H-2), 4.10–4.20 (m, 4H, 2CH_2O), 6.40 (d, 1H, J=15.8 Hz, CH), 7.20–7.30 (m, 2H, ArH), 7.50 (d, 1H, J=8.3 Hz, ArH), 7.70 (d, 1H, J=16.1 Hz, ArH), 7.80 (s, 1H, H-4). ^{13}C NMR (75 MHz, $CDCl_3$): δ=13.6 (CH_3), 13.7 (CH_3), 13.8 (CH_3), 19.0 (CH_2), 19.2 (CH_2), 19.3 (CH_2), 24.0 (CH_2), 29.9 (CH_3), 30.4 (CH_2), 30.8 (CH_2), 31.0 (CH_2), 38.8 (NCH_3), 64.3 (CH_2O), 64.4 (CH_2O), 65.1 (CH_2O), 109.7 (C), 110.2, 116.0 (CH), 117.6 (C), 118.2, 120.8 (CH), 126.7, 128.4 (C), 131.4 (CH), 138.2, 141.8 (C), 145 (CH), 167.2, 167.5, 173.1 (CO). IR (KBr): ν=2954, 2931 (m), 1721, 1703, 1676 (s), 1469, 1277 (m), 1219, 1167 (s), 1042, 998, 960, 854 (w), 821, 770, 735 (m), 605, 582, 553 (w) cm^{-1}. MS (EI, 70 eV): m/z (%)=509 ($[M]^+$, 78), 436 (14), 408 (72), 378 (20), 352 (100), 334 (94), 308 (18), 278 (31), 234 (94). HRMS (EI, 70 eV): calcd for $C_{30}H_{39}NO_6$ $[M]^+$: 509.27719; found: 509.276955.

*3.14.4. Di(isobutyl) 7-(3-isobutoxy-3-oxoprop-1-enyl)-9-methyl-2,9-dihydro-1H-carbazole-2,3-dicarboxylate (**12d**).* Product **12d** was prepared starting with **2b** (367 mg, 1.0 mmol), *iso*-butyl acrylate (0.54 mL, 3.75 mmol), $Pd(OAc)_2$ (11 mg, 5 mol %), SPhos (10 mol %), NEt_3 (1.10 mL, 8.0 mmol), DMF (5 mL) at 120 °C for 48 h following general procedure B, as a yellow solid (363 mg, 72%). ^{1}H NMR (250 MHz, $CDCl_3$): δ=0.70 (d, 6H, J=6.7 Hz, 2CH_3), 0.90 (dd, 12H, J=3.4, 6.7 Hz, 4CH_3), 1.70–1.80 (m, 1H, CH), 1.90–2.00 (m, 2H, CH), 3.00 (dd, 1H$_\alpha$, J=8.7, 17.2 Hz, H-1), 3.60 (dd, 1H$_\beta$, J=2.0, 17.2 Hz, H-1), 3.60–3.70 (m, 5H, NCH_3 and CH_2O), 3.90–4.00 (m, 4H, 2CH_2O), 4.10 (dd, 1H$_\alpha$, J=2.0, 8.5 Hz, H-2), 6.20 (d, 1H, J=15.8 Hz, ArH), 7.30 (d, 1H, J=8.4 Hz, ArH), 7.40 (s, 1H, ArH), 7.60 (d, 1H, J=8.2 Hz, ArH), 7.80 (d, 1H, J=15.9 Hz, ArH), 7.90 (s, 1H, H-4). ^{13}C NMR (75 MHz, $CDCl_3$): δ=18.8 (CH_3), 18.9 (CH_3), 19.2 (2CH_3), 19.3 (2CH_3), 23.9 (CH_2), 27.6, 27.9, 28.0 (CH), 29.9 (NCH_3), 38.8 (CH, C-2), 70.5, 70.6, 71.2 (CH_2O), 109.7 (C), 110.3, 116.3 (CH), 117.6 (C), 118.2, 120.9 (CH), 126.7, 128.4 (C), 131.3 (CH), 138.2, 141.9 (C), 145.7(CH), 167.1, 167.5, 173.0 (CO). IR (KBr): ν=2956, 2872 (w), 1715, 1693 (s), 1633, 1608, 1529, 1494, 1468, 1454, 1392, 1375, 1355, 1309, 1278 (m), 1228, 1205, 1166 (s), 1110, 1086, 1038, 1017, 989 (m), 942, 930, 852, 832, 799, 779, 756, 731, 705, 650, 615, 600, 550 (w) cm^{-1}. GC–MS (EI, 70 eV): m/z (%)=507 ($[M-2]^+$ (carbazole), 100), 451 (36), 407 (22), 378 (78), 352 (29), 278 (18), 251 (11), 234 (25), 204 (12). HRMS (EI, 70 eV): calcd for $C_{30}H_{37}NO_6$ $[M-2]^+$ (carbazole): 507.26154; found: 507.26138.

*3.14.5. Dihexyl 7-(3-(hexyloxy)-3-oxoprop-1-enyl)-9-methyl-2,9-dihydro-1H-carbazole-2,3-dicarboxylate (**12e**).* Product **12e** was

prepared, starting with **2b** (367 mg, 1.0 mmol), *n*-hexyl acrylate (0.66 mL, 3.75 mmol), $Pd(OAc)_2$ (11 mg, 5 mol %), SPhos (10 mol %), NEt_3 (1.10 mL, 8.0 mmol), DMF (5 mL) at 120 °C for 48 h following general procedure B, as a yellowish highly viscous oil (435 mg, 74%). ^{1}H NMR (300 MHz, $CDCl_3$): δ=0.70 (t, 3H, J=6.9 Hz, CH_3), 0.80 (t, 3H, J=6.3 Hz, CH_3), 0.80 (t, 3H, J=6.9 Hz, CH_3), 1.00–1.20 (m, 6H, $3CH_2$), 1.20–1.40 (m, 14H, $7CH_2$), 1.60–1.70 (m, 4H, $2CH_2$), 3.00 (dd, $1H_\alpha$, J=8.6, 17.1 Hz, H-1), 3.60 (dd, $1H_\beta$, J=2.1, 17.1 Hz, H-1), 3.70 (s, 3H, NCH_3), 3.80–4.00 (m, 2H, CH_2O), 4.00 (dd, $1H_\alpha$, J=2.1, 8.7 Hz, H-2), 4.10 (t, 2H, J=6.8 Hz, CH_2O), 4.20 (t, 2H, J=6.8 Hz, CH_2O), 6.40 (d, 1H, J=15.8 Hz, ArH), 7.30 (d, 1H, J=8.4 Hz, ArH), 7.30 (s, 1H, ArH), 7.50 (d, 1H, J=8.1 Hz, ArH), 7.70 (d, 1H, J=16.0 Hz, CH), 7.80 (s, 1H, H-4). ^{13}C NMR (62 MHz, $CDCl_3$): δ=13.9 (CH_3), 14.0 ($2CH_3$), 22.4 (CH_2), 22.5 ($2CH_2$), 23.9, 25.4, 25.6, 25.7, 28.4, 28.7, 28.8 (CH_2), 29.9 (NCH_3), 31.3, 31.4, 31.5 (CH_2), 38.8, (C(2)H), 64.5, 64.7, 65.3 (CH_2O), 109.7 (C), 110.2, 116.0 (CH), 117.6 (C), 118.2, 120.8 (CH), 126.7, 128.4 (C), 131.4 (CH), 138.1, 141.8 (C), 145,7 (CH), 167.1, 167.4, 173.1 (CO). IR (KBr): ν=2954, 2928, 2857 (m), 1715, 1695, 1629, 1605 (s), 1558, 1527, 1488 (w), 1471 (w), 1395, 1303, 1278 (m), 1245, 1228 (w), 1162 (s), 974, 908, 848, 821, 754, 730, 700, 607, 592 (w) cm^{-1}. MS (EI, 70 eV): m/z (%)=593 ([M]$^+$, 62), 492 (09), 464 (41), 406 (07), 380 (100), 362 (72), 336 (08), 278 (20), 251 (9), 234 (53). HRMS (EI, 70 eV): calcd for $C_{36}H_{51}NO_6$ [M]$^+$: 593.37109; found: 593.37046.

*3.14.6. Di(tert-butyl) 7-(3-tert-butoxy-3-oxoprop-1-enyl)-9-methyl-2,9-dihydro-1H-carbazole-2,3-dicarboxylate (**12f**).* Product **12f** was synthesized starting with **2b** (367 mg, 1.0 mmol), $Pd(OAc)_2$ (11 mg, 5 mol %), *tert*-butyl acrylate (0.55 mL, 3.75 mmol), SPhos (10 mol %), NEt_3 (1.10 mL, 8.0 mmol), DMF (5 mL) at 120 °C for 48 h following general procedure B, as a yellow oil (401 mg, 79%). ^{1}H NMR (250 MHz, $CDCl_3$): δ=1.30 (s, 9H, $3CH_3$), 1.40 (s, 9H, $3CH_3$), 1.50 (s, 9H, $3CH_3$), 3.00 (dd, $1H_\alpha$, J=8.7, 17.1 Hz, H-1), 3.60 (dd, $1H_\beta$, J=2.2, 17.1 Hz, H-1), 3.70 (s, 3H, NCH_3), 3.90 (dd, $1H_\alpha$, J=2.2, 8.7 Hz, H-2), 6.30 (d, 1H, J=16.0 Hz, ArH), 7.30 (dd, 1H, J=1.2, 8.2 Hz, ArH), 7.30 (s, 1H, ArH), 7.50 (d, 1H, J=8.2 Hz, ArH), 7.60 (d, 1H, J=15.9 Hz, ArH), 7.70 (s, 1H, H-4). ^{13}C NMR (75 MHz, $CDCl_3$): δ=23.6 (CH_2), 27.9, 28.2, 28.3 ($3CH_3$), 29.8 (NCH_3), 39.6 (CH, C-2), 78.9, 79.2, 80.1 (C–O), 108.5 (C), 109.9, 116.7, 117.2 (CH), 118.6, (C), 119.6 (CH), 125.6, 127.3 (C), 130 (CH), 137.1, 140.7 (C), 143.8 (CH), 165.5, 165.7, 171.2 (C=O). IR (KBr): ν=2976, 2931 (w), 1705 (s), 1631, 1612, 1469, 1461, 1454, 1391 (w), 1366, 1277, 1255 (m), 1147 (s), 1113, 1080, 1041, 980, 846, 812, 791, 765, 608 (w) cm^{-1}. MS (EI, 70 eV): m/z (%)=509 ([M]$^+$, 02), 507 (33), 451 (51), 395 (39), 378 (15), 339 (95), 321 (100), 295 (17), 277 (34), 249 (80), 204 (12), 176 (5). HRMS (EI, 70 eV): calcd for $C_{30}H_{37}NO_6$ ([M−2H]$^+$ carbazole): 507.26154; found: 507.26178.

*3.14.7. Bis(6-methylheptyl) 9-methyl-7-(3-(6-methylheptyloxy)-3-oxoprop-1-enyl)-2,9-dihydro-1H-carbazole-2,3-dicarboxylate (**12g**).* Compound **12g** was synthesized starting with **2b** (367 mg, 1.0 mmol), isooctyl acrylate (0.79 mL, 3.75 mmol), $Pd(OAc)_2$ (11 mg, 5 mol %), SPhos (10 mol %), NEt_3 (1.10 mL, 8.0 mmol), DMF (5 mL) at 120 °C for 48 h following general procedure B, as a yellow oil (501 mg, 74%). ^{1}H NMR (250 MHz, $CDCl_3$): δ=0.60–1.80 (m, 45H, aliphatic), 3.00 (dd, $1H_\alpha$, J=8.9, 17.2 Hz, H-1), 3.60–3.70 (m, 4H, 1× H_β-1 and NCH_3), 3.90–4.30 (m, 7H, $3CH_2O$ and H_α-2), 6.40 (d, 1H, J=15.9 Hz, ArH), 7.30–7.40 (m, 2H, ArH), 7.50 (d, 1H, J=8.8 Hz, ArH), 7.80 (d, 1H, J=16.4 Hz), 7.90 (s, 1H, H-4). ^{13}C NMR (75 MHz, $CDCl_3$): δ=12.2 ($2CH_3$), 14.1 ($2CH_3$), 14.4 ($2CH_3$), 19.6, 23.4, 29.1 (CH_2), 25.0, 27.0 (CH), 29.9 (CH_3N), 31.9 (CH), 38.8 (CH, C-2), 46.5, 46.6, 46.7 (CH_2), 64.9, 65.0, 65.3 (CH_2O), 108.7 (C), 109.2, 115.0 (CH), 116.6 (C), 117.2, 119.9 (CH), 125.7, 127.6 (C), 130.4 (CH), 137.2, 140.9 (C), 145.7 (CH), 166.1, 166.5, 172.1 (CO). IR (KBr): ν=2955, 2927 (w), 1704, 1631, 1608 (s), 1562, 1527 (w), 1462, 1382, 1366, 1305 (m), 1267, 1228, 1206, 1161 (s), 1112, 1084, 1039, 847, 809, 780 (m), 609, 581 (w) cm^{-1}. MS (EI, 70 eV): m/z (%)=677 ([M]$^+$, 100), 563 (21), 548 (14), 519 (44), 434 (60), 408 (99), 390 (81), 234 (44). HRMS (EI, 70 eV): calcd for $C_{42}H_{63}NO_6$ [M]$^+$: 677.46499; found: 677.46337.

3.15. Synthesis of 6-alkenylcarbazoles 13

*3.15.1. (E)-Dimethyl 7-(3-methoxy-3-oxoprop-1-enyl)-9-methyl-9H-carbazole-2,3-dicarboxylate (**13a**).* Starting with **12a** (100 mg) following general procedure C, **13a** was isolated as a yellow oil (98 mg, 100%). ^{1}H NMR (300 MHz, $CDCl_3$): δ=3.77 (s, 3H, CH_3N), 3.83 (s, 3H, CH_3O), 3.89 (s, 3H, CH_3O), 3.91 (s, 3H, CH_3O), 6.51 (d, 1H J=16.0 Hz), 7.44 (d, 1H, J=8.2 Hz, ArH), 7.49 (s, 1H, ArH), 7.59 (s, 1H, ArH), 7.82 (d, 1H, J=16.0 Hz, ArH), 8.03 (d, 1H, J=8.1 Hz, ArH), 8.48 (s, 1H, ArH). ^{13}C NMR (62.9 MHz, $CDCl_3$): δ=29.5 (CH_3N), 51.8, 52.5, 52.8 (CH_3O), 109.2, 109.3, 118.0, 120.1, 121.3 (CH) 121.7 (C), 122.9 (CH), 123.3, 123.9, 131.4, 133.5, 142.3, 142.4 (C), 145.3 (CH), 167.4, 168.0, 169.4 (CO). IR (KBr): ν=3047, 3004, 2917, 2848 (w), 1708 (s), 1627 (m), 1563, 1498 (w), 1431 (m), 1376 (w), 1351, 1314 (m), 1272, 1259, 1245, 1232, 1173, 1110 (s), 1080, 1039, 974, 964 (m), 930, 900, 881 (w), 839, 826,803, 777, 760 (m), 747, 729 (w), 711, 653, 603, 584 (m), 551(w) cm^{-1}. GC–MS (EI, 70 eV): m/z (%)=381 ([M]$^+$, 100), 351 (16), 350 (80), 204 (11), 159 (42), 145 (22). HRMS: m/z calcd for $C_{21}H_{19}NO_6$ [M]$^+$: 381.12069; found: 381.120947.

*3.15.2. (E)-Diethyl 7-(3-ethoxy-3-oxoprop-1-enyl)-9-methyl-9H-carbazole-2,3-dicarboxylate (**13b**).* Starting with **12b** (100 mg) following general procedure C, **13b** was prepared as a yellow oil (98 mg, 100%). ^{1}H NMR (300 MHz, $CDCl_3$): δ=1.23 (t, 3H, J=7.1 Hz, CH_3), 1.31 (t, 3H, J=7.1 Hz, CH_3), 1.32 (t, 3H, J=7.1 Hz, CH_3), 3.81 (s, 3H, CH_3N), 4.20 (q, 2H, J=7.0 Hz, CH_2O), 4.31 (q, 2H, J=7.0 Hz, CH_2O), 4.31 (q, 2H, J=7.0 Hz, CH_2O), 6.51 (d, 1H, J=15.7 Hz), 7.40 (d, 1H, J=7.9 Hz, ArH), 7.41 (s, 1H, ArH), 7.51 (s, 1H, ArH), 7.80 (d, 1H, J=15.7 Hz), 8.02 (d, 1H, J=7.9 Hz, ArH), 8.41 (s, 1H, ArH). ^{13}C NMR (62 MHz, $CDCl_3$): δ=14.1 (CH_3), 14.3 (CH_3), 14.4 (CH_3), 29.4 (CH_3N), 60.5, 61.4, 61.8 (CH_2O), 109.0, 109.2, 118.4, 120.0, 121.3 (CH), 122.1 (C), 122.7 (CH), 123.1, 123.8, 131.7, 133.4, 142.2, 142.3 (C), 145.0 (CH), 167.0, 167.5, 169.0 (CO). IR (KBr): ν=2979, 2849 (m), 1703 (s), 1628, 1604, 1560, 1498, 1473, 1391, 1373, 1343, 130 (m), 1258, 1240, 1227 (s), 1173, 1108, 1078, 1039, 975 (m), 908, 874, 842, 804 (w), 779, 730, 664, 606, 585 (s) cm^{-1}. GC–MS (EI, 70 eV): m/z (%)=423 ([M]$^+$, 99), 378 (6), 349 (41), 322 (6), 162 (7), 153 (100), 139 (58). HRMS: m/z calcd for $C_{24}H_{25}NO_6$ [M]$^+$: 423.16764; found: 423.16659.

*3.15.3. (E)-Dibutyl 7-(3-butoxy-3-oxoprop-1-enyl)-9-methyl-9H-carbazole-2,3-dicarboxylate (**13c**).* Starting with **12c** (100 mg) following general procedure C, **13c** was prepared as a yellow oil (99 mg, 100%). ^{1}H NMR (300 MHz, $CDCl_3$): δ=0.81 (t, 3H, J=7.4 Hz, CH_3), 0.91 (t, 3H, J=7.4 Hz, CH_3), 0.93 (t, 3H, J=7.4 Hz, CH_3), 1.10–1.31 (m, 2H, CH_2), 1.31–1.52 (m, 6H, $3CH_2$), 1.57–1.71 (m, 4H, $2CH_2$), 3.71 (s, 3H, CH_3N), 4.22 (t, 2H, J=6.9 Hz, CH_2O), 4.31 (t, 2H, J=6.6 Hz, CH_2O), 4.34 (t, 2H, J=6.6 Hz, CH_2O), 6.52 (d, 1H, J=16.1 Hz, CH), 7.42 (d, 1H, J=8.5 Hz, ArH), 7.51 (s, 1H, ArH), 7.62 (s, 1H, ArH), 7.80 (d, 1H, J=15.3 Hz, CH), 8.01 (d, 1H, J=7.6 Hz, ArH), 8.51 (s, 1H, ArH). ^{13}C NMR (62.9 MHz, $CDCl_3$): δ=13.8 ($3CH_3$), 19.3 ($3CH_2$), 29.5 (CH_3N), 30.6, 30.7, 30.8 (CH_2), 64.5, 65.4, 65.8 (CH_2O), 109.1, 109.2, 118.4, 120.1, 121.3 (CH), 122.3 (C), 122.7 (CH), 123.2, 123.9, 131.8, 133.5, 142.3, 142.4 (C), 145.0 (CH), 167.1, 167.6, 169.1 (CO). IR (KBr): ν=2931 (w), 1706, 1627, 1602, 1563, 1500, 1455, 1387, 1343 (w), 1258 (m), 1223, 1163, 1106, 1077, 1038, 977, 901, 843, 810, 779, 738, 715, 663, 609, 583 (s) cm^{-1}. MS (EI, 70 eV): m/z (%)=507 ([M]$^+$, 100), 434 (6), 378 (33), 332 (7), 278 (4). HRMS: m/z calcd for $C_{30}H_{37}NO_6$ [M]$^+$: 507.26154; found: 507.26156.

*3.15.4. (E)-Dihexyl 7-(3-(hexyloxy)-3-oxoprop-1-enyl)-9-methyl-9H-carbazole-2,3-dicarboxylate (**13e**).* Starting with **12e** (100 mg) following general procedure C, **13e** was isolated as yellow oil (98 mg, 100%). ^{1}H NMR (300 MHz, $CDCl_3$): δ=0.81 (t, 3H, J=6.9 Hz, CH_3),

0.82 (t, 6H, J=7.0 Hz, $2CH_3$), 1.21–1.33 (m, 12H, $6CH_2$), 1.30–1.41 (m, 6H, $3CH_2$), 1.61–1.70 (m, 6H, $3CH_2$), 3.81 (s, 3H, CH_3N), 4.10 (t, 2H, J=6.7 Hz, CH_2O), 4.21 (t, 2H, J=7.0 Hz, CH_2O), 4.32 (t, 2H, J=7.0 Hz, CH_2O), 6.52 (d, 1H, J=16.2 Hz), 7.41 (d, 1H, J=8.1 Hz, ArH), 7.51 (s, 1H, ArH), 7.63 (s, 1H, ArH), 7.81 (d, 1H, J=16.2 Hz), 8.01 (d, 1H, J=8.1 Hz, ArH), 8.41 (s, 1H, ArH). ^{13}C NMR (75 MHz, $CDCl_3$): δ=13.0 ($3CH_3$), 22.6 ($4CH_2$), 24.5 ($3CH_2$), 27.5, 27.6, 27.7 (CH_2), 28.4 (CH_3N), 30.5 ($2CH_2$), 63.8, 64.7, 65.1 (CH_2O), 108.0, 108.2, 117.4, 119.0, 120.3 (CH), 121.2 (C), 121.7 (CH), 122.1, 122.9, 130.8, 132.4, 141.2, 141.3 (C), 144.0 (CH), 166.1, 166.6, 168.1 (CO). IR (KBr): ν=2927 (w), 1708 (s), 1627, 1602, 1563, 1500, 1455, 1388, 1369, 1343, 1305 (m), 1259, 1224, 1163, 1108 (s), 1078, 1038, 979, 905, 845, 810, 781, 725, 663, 642, 609, 583,543 (w) cm^{-1}. (EI$^+$, 70 eV): m/z (%)=591 ([M]$^+$, 100), 406 (26), 322 (05), 43 (08). HRMS: m/z calcd for $C_{36}H_{49}NO_6$ [M]$^+$: 591.35544; found: 591.35593.

*3.15.5. (2E,2′E)-Diethyl 3,3′-(1-methyl-1H-indole-2,6-diyl)diacrylate or (2E,2′E)-diethyl 3,3′-(1-methyl-1H-indole-3,6-diyl)diacrylate (**14**).* Pro duct **14** was isolated as a side product of **12b** as a light brown oil. ^{1}H NMR (250 MHz, $CDCl_3$): δ=1.19–1.31 (m, 6H, $2CH_3$), 3.78 (s, 3H, NCH_3), 4.16–4.26 (m, 4H, $2CH_2O$), 6.41 (d, 1H, J=15.9 Hz, CH), 6.44 (d, 1H, J=15.7 Hz, CH), 6.87 (s, 1H, ArH), 7.27 (dd, J=1.2, 8.5, ArH), 7.3 (s, 1H, ArH), 7.50 (d, 1H, J=8.5 Hz, ArH), 7.70 (d, 1H, J=15.4 Hz, ArH), 7.73 (d, 1H, J=15.4 Hz, ArH). ^{13}C NMR (62.9 MHz, $CDCl_3$): δ=14.4, 30.1 (NCH_3), 60.4, 60.7 (CH_2O), 102.7, 110.5, 116.6, 119.4, 119.9, 121.6 (CH), 128.1, 128.9 (C), 131.0 (CH), 136.0, 138.0 (C), 144.7 (CH), 165.8, 166.3 (CO). IR (KBr): ν=2978, 2929, 2852 (w), 1705, 1699, 1628, 1604 (s), 1464, 1362, 1302, 1284, 1261, 1242 (m), 1157, 1137, 1090, 1032, 975, 964 (s), 867 (m), 805 (s), 744, 700, 646, 600, 582 cm^{-1}. MS (EI, 70 eV): m/z (%)=327 (M$^+$, 100), 282 (15), 255 (04), 180 (05). HRMS (EI, 70 eV): calcd for $C_{23}H_{29}NO_4$ [M]$^+$: 327.14706; found: 327.14715.

*3.15.6. Dimethyl 6,7-bis((E)-3-methoxy-3-oxoprop-1-enyl)-9-methyl-2,9-dihydro-1H-carbazole-2,3-dicarboxylate (**15a**).* Product **15a** was prepared starting with **2c** (446 mg, 1.0 mmol), 2-ethylhexyl acrylate (0.5 mL, 5.0 mmol), $Pd(OAc)_2$ (11 mg, 5 mol %), SPhos (10 mol %), NEt_3 (1.10 mL, 8.0 mmol), DMF (5 mL) at 120 °C for 48 h following general procedure B, as a yellow highly viscous oil (316 mg, 68%). ^{1}H NMR (300 MHz, $CDCl_3$): δ=3.01–3.61 (m, $2H_{\alpha/\beta}$, C-1), 3.52 (s, 3H, CH_3N), 3.62 (s, 3H, CH_3O), 3.71 (s, 6H, $2CH_3O$), 3.81 (s, 3H, CH_3O), 4.01 (br d, 1H, J=7.2 Hz C-2), 6.42 (d, 1H, J=15.6 Hz, CH), 6.43 (d, 1H, J=15.6 Hz, CH), 7.32 (s, 1H, ArH), 7.71 (s, 1H, ArH), 7.82 (s, 1H, CH), 8.02 (d, 1H, J=15.8 Hz, CH), 8.03 (d, 1H, J=15.7 Hz, CH). ^{13}C NMR (62.9 MHz, $CDCl_3$): δ=23.9 (CH_2), 30.0 (CH_3N), 38.6 (C(4)H), 51.6, 51.7, 51.8, 52.6 (CH_3O), 108.5 (CH), 109.7 (C), 117.1 (CH), 117.3 (C), 119.1, 119.2 (CH), 126.4, 127.8, 128.3 (C), 131.4 (CH), 138.8 (C), 142.6, 142.7 (CH), 142.9 (C), 167.0, 167.1, 167.3, 173.4 (CO). IR (KBr): ν=2950, 2921, 2851 (w), 1693, 1625, 1602, 1525, 1433, 1365 (s), 1310, 1271, 1228, 1189, 1162, 1088 (m), 1035, 972, 912, 919, 853, 802, 775, 725 (s) cm^{-1}. GC–MS (EI, 70 eV): m/z (%)=467 (M$^+$, 75), 434 (38), 405 (100), 374 (59), 347 (26), 316 (15). HRMS: m/z calcd for $C_{25}H_{25}N\,NaO_8$ [M+Na]$^+$: 490.14724; found: 490.14693.

*3.15.7. Diethyl 6,7-bis((E)-3-ethoxy-3-oxoprop-1-enyl)-9-methyl-2,9-dihydro-1H-carbazole-2,3-dicarboxylate (**15b**).* Compound **15b** was synthesized starting with **2c** (446 mg, 1.0 mmol), following general procedure B, as a yellow highly viscous oil (450 mg, 86%). ^{1}H NMR (250 MHz, $CDCl_3$): δ=1.10 (t, 3H, J=7.0 Hz, CH_3), 1.30 (t, 6H, J=7.1 Hz, $2CH_3$), 1.30 (t, 3H, J=7.0 Hz, CH_3), 3.00 (dd, $1H_\alpha$, J=8.8, 17.1 Hz, H-1), 3.60 (dd, $1H_\beta$, J=2.3, 17.1 Hz, H-1), 3.70 (s, 3H, NCH_3), 3.90–4.00 (m, 2H, CH_2O), 4.10 (dd, $1H_\alpha$, J=2.6, 9.0 Hz, H-2), 4.20–4.30 (m, 6H, $3CH_2O$), 6.20 (d, 1H, J=15.7 Hz, ArH), 6.30 (d, 1H, J=15.7 Hz, ArH), 7.40 (s, 1H, ArH), 7.70 (s, 1H, ArH), 7.80 (s, 1H, H-4), 8.00 (d, 1H, J=15.8 Hz, ArH), 8.10 (d, 1H, J=15.8 Hz, ArH). ^{13}C NMR (62 MHz, $CDCl_3$): δ=14.0 (CH_3), 14.3 ($2CH_3$), 14.5 (CH_3), 23.8 (CH_2), 30.0 (NCH_3), 38.8 (CH, C-2), 60.4, 60.5, 60.5, 61.3 (CH_2O), 108.6 (CH), 109.8 (C), 117.3 (CH), 118.0 (C), 119.6, 119.8 (CH), 126.4, 127.9, 128.8 (C), 130.8 (CH), 138.8 (C), 142.5, 142.6 (CH), 142.7 (C), 166.6, 166.7, 166.9, 172.9 (CO). IR (KBr): ν=2989, 2934, 2903 (w), 1694, 1625, 1604 9 (s), 1528, 1477, 1464, 1446, 1392, 1367 (m), 1274, 1220, 1158 (s), 1111, 1092, 1034, 973, 914, 855 (m), 777 (w), 727 (m), 660, 646, 612, 558 (w) cm^{-1}. GC–MS (EI, 70 eV): m/z (%)=523 (M$^+$, 100), 478 (18), 450 (88), 404 (84), 375 (23), 332 (22), 303 (34), 275 (25), 231 (51), 217 (9). HRMS (EI, 70 eV): calcd for $C_{29}H_{33}NO_8$ (M$^+$): 523.22062; found: 523.22073.

*3.15.8. Dibutyl 6,7-bis((E)-3-butoxy-3-oxoprop-1-enyl)-9-methyl-2,9-dihydro-1H-carbazole-2,3-dicarboxylate (**15c**).* Product **15c** was prepared starting with **2c** (446 mg, 1.0 mmol), *n*-butyl acrylate (0.70 mL, 5.0 mmol), $Pd(OAc)_2$ (11 mg, 5 mol %), SPhos (10 mol %), NEt_3 (1.10 mL, 8.0 mmol), DMF (5 mL) at 120 °C for 48 h following general procedure B, as a yellow highly viscous oil (450 mg, 71%). ^{1}H NMR (300 MHz, $CDCl_3$): δ=0.9 (t, 3H, J=7.2 Hz, CH_3), 0.9 (t, 3H, J=7.4 Hz, CH_3), 0.9 (t, 6H, J=7.3 Hz, $2CH_3$), 1.3–1.4 (m, 8H, $4CH_2$), 1.6–1.7 (m, 8H, $4CH_2$), 3.0 (dd, $1H_\alpha$, J=8.5, 17.3, Hz, C-1), 3.6 (dd, $1H_\beta$, J=2.0, 17.2 Hz, C-1),3.7 (s, 3H, CH_3N), 4.0 (dd, 1H, J=2.0, 8.8 Hz, C-2), 4.1 (t, 4H, J=6.7 Hz, $2CH_2O$), 4.2 (t, 4H, J=6.7 Hz, $2CH_2O$), 6.2 (d, 1H, J=15.5 Hz, CH), 6.3 (d, 1H, J=16.4 Hz, CH), 7.4 (s, 1H, ArH), 7.8 (s, 1H, ArH), 7.8 (s, 1H, C-4), 8.0 (d, 1H, J=16.4 Hz, H), 8.0 (d, 1H, J=15.5 Hz, CH). ^{13}C NMR (62.9 MHz, $CDCl_3$): δ=13.6 (CH_3), 13.7 ($2CH_3$), 13.8 (CH_3), 18.9 (CH_2), 19.2 ($2CH_2$), 19.3 (CH_2), 23.8 (CH_2), 30.0 (CH_3N), 30.4 (CH_2), 30.8 ($2CH_2$), 30.9 (CH_2), 38.8 (CH, C-2), 64.4 (CH_2O), 64.5 ($2CH_2O$), 65.2 (CH_2O), 108.6 (CH), 109.9 (C), 117.4 (CH), 118.2 (C), 119.7, 119.9 (CH), 126.4, 128.0, 128.5 (C), 130.7 (CH), 138.8 (C), 142.6, 142.7 (CH) 142.8 (C), 166.7, 166.8, 167.0, 172.9 (CO). IR (KBr): ν=2932 (w), 1698, 1624, 1604, 1528 (s), 1464 (m), 1700, 1622 (s), 1548, 1380, 1287, 1274, 1243, 1213 (m), 1168 (s), 1062, 1025, 965, 864 (m), 780, 738, 721, 549 (w) cm^{-1}. (EI, 70 eV): m/z (%)=635 ([M]$^+$, 12), 591 (2), 531 (7), 380 (24), 379 (100), 304 (5), 215 (20), 67 (12). HRMS: m/z calcd for $C_{37}H_{49}NO_8$ (M)$^+$: 635.34527; found: 635.34556.

*3.15.9. Di(isobutyl) 6,7-bis((E)-3-isobutoxy-3-oxoprop-1-enyl)-9-methyl-2,9-dihydro-1H-carbazole-2,3-dicarboxylate (**15d**).* Compound **15d** was synthesized starting with **2c** (455 mg, 1.0 mmol) and, isobutyl acrylate (0.72 mL, 5.0 mmol) following general procedure B, as a yellow highly viscous oil (455 mg, 72%). ^{1}H NMR (250 MHz, $CDCl_3$): δ=0.70 (d, 6H, J=6.9 Hz, $2CH_3$), 0.90–1.00 (m, 18H, $6CH_3$), 1.70–1.80 (m, 3H, CH), 1.90–2.00 (m, 1H, CH), 3.00 (dd, $1H_\alpha$, J=8.6, 17.2 Hz, H-1), 3.60 (dd, $1H_\beta$, J=1.8, 17.3 Hz, H-1), 3.60–3.70 (m, 5H, NCH_3 and CH_2O), 3.90–4.00 (m, 6H, $3CH_2O$), 4.00–4.10 (dd, $1H_\alpha$, J=1.6, 8.4 Hz, H-2), 6.20 (d, 1H, J=15.6 Hz, ArH), 6.30 (d, 1H, J=15.6 Hz, ArH), 7.40 (s, 1H, ArH), 7.70 (s, 1H, ArH), 7.80 (s, 1H, H-4), 8.10 (d, 2H, J=15.6 Hz, ArH). ^{13}C NMR (75 MHz, $CDCl_3$): δ=18.7 (CH_3), 18.8 (CH_3), 19.2 ($4CH_3$), 19.3 ($2CH_3$), 23.7 (CH_2), 27.6 (CH), 27.8 (2CH), 27.9 (CH), 30.0 (NCH_3), 38.7 (CH, C-2), 70.5, 70.6, 70.7, 71.2 (CH_2O), 108.6 (CH), 109.8 (C), 117.3 (CH), 118.2 (C), 119.6, 119.8 (CH), 126.4, 127.9, 128.3 (C), 130.5 (CH), 138.8 (C), 142.5, 142.6 (CH), 142.9 (C), 166.6, 166.7, 166.9, 172.8 (CO). IR (KBr): ν=2958, 2932, 2873 (w), 1702, 1692 (s), 1623, 1605, 1528, 1483, 1468, 1393, 1375, 1342, 1287, 1271 (m), 1219, 1163 (s), 1084, 1035, 980 (m), 945, 908, 884, 863, 778, 729, 645, 613, 572 (w) cm^{-1}. GC–MS (EI, 70 eV): m/z (%)=635 (M$^+$, 100), 578 (27), 498 (55), 409 (43), 375 (32), 333 (51), 288 (16), 275 (33), 196 (22), 173(77). HRMS (EI, 70 eV): calcd for $C_{37}H_{49}NO_8$ (M$^+$): 635.34582; found: 635.34571.

*3.15.10. Di(tert-butyl) 6,7-bis((E)-3-tert-butoxy-3-oxoprop-1-enyl)-9-methyl-2,9-dihydro-1H-carbazole-2,3-dicarboxylate (**15e**).* Compound **15e** was synthesized starting with **2c** (446 mg, 1.0 mmol), following general procedure B, as a yellow highly viscous oil (463 mg, 72%). ^{1}H NMR (250 MHz, $CDCl_3$): δ=1.30 (s, 9H, $3CH_3$), 1.50 (s, 18H, $6CH_3$), 1.50 (s, 9H, $3CH_3$), 3.00 (dd, $1H_\alpha$, J=8.9, 17.2 Hz, H-1), 3.50 (dd, $1H_\beta$, J=2.2, 17.2 Hz, H-1), 3.70 (s, 3H, NCH_3), 3.90 (dd, $1H_\alpha$, J=2.2, 8.6 Hz, H-2), 6.20 (d, 1H, J=15.5 Hz, ArH), 6.30 (d, 1H, J=15.5 Hz, ArH), 7.40 (s, 1H,

ArH), 7.70 (s, 1H, ArH), 7.80 (s, 1H, H-4), 7.90 (d, 1H, J=15.7 Hz, ArH), 8.00 (d, 1H, J=15.7 Hz, ArH). ^{13}C NMR (75 MHz, $CDCl_3$): δ=23.6 (CH_2), 27.9 ($3CH_3$), 28.1 (CH_3), 28.3 ($6CH_3$), 28.4 ($2CH_3$), 30.0 (CH_3CN), 39.5 (C(2)H), 80.1, 80.4, 80.5, 81.3 (C), 108.4 (CH), 109.7 (C), 117.2 (CH), 120.3 (C), 121.3, 121.6 (CH), 126.4, 127.9, 128.4 (C), 129.3(CH), 138.7 (C), 141.8, 141.9(CH), 142.6 (C), 166.0, 166.1, 166.4, 172.1 (CO). IR (KBr): ν=2977, 2929 (w), 1713 (s), 1611, 1530, 1478, 1455, 1392, 1367, 1285, 1256, 1221 (m), 1152 (s), 1089, 979, 847, 794, 530 (w) cm^{-1}. MS (EI, 70 eV): m/z (%)=635 (M^+, 15), 634 (10), 577 (46), 562 (100), 259 (25), 225 (50), 181 (97), 63 (37). HRMS (EI, 70 eV): calcd for $C_{37}H_{49}NO_8$ (M^+): 635.34582; found: 635.34535.

*3.15.11. Dihexyl 6,7-bis((E)-3-(hexyloxy)-3-oxoprop-1-enyl)-9-methyl-2,9-dihydro-1H-carbazole-2,3-dicarboxylate (**15f**).* Product **15f** was prepared starting with **2c** (446 mg, 1.0 mmol), *n*-hexyl acrylate (0.9 mL, 5.0 mmol), $Pd(OAc)_2$ (11 mg, 5 mol %), SPhos (10 mol %), NEt_3 (1.10 mL, 8.0 mmol), DMF (5 mL) at 120 °C for 48 h following general procedure B, as a yellow highly viscous oil (598 mg, 80%). ^{1}H NMR (300 MHz, $CDCl_3$): δ=0.81–0.93 (m, 12H, CH_3), 1.32–1.41 (m, 16H, $8CH_2$), 1.61–1.72 (m, 16H, $8CH_2$), 3.00 (dd, $1H_\alpha$, J=8.5, 17.1 Hz, C-1); 3.61 (dd, $1H_\beta$, J=2.1, 17.1 Hz, C-1), 3.82 (s, 3H, CH_3N), 3.91 (dd, $1H_\alpha$, J=1.7, 6.7 Hz, C-2), 4.12–4.22 (m, 8H, $4CH_2O$), 6.31 (d, 2H, J=16.0 Hz, CH), 7.30 (s, 1H, ArH), 7.49 (s, 1H, ArH), 8.01 (s, 1H, C-4), 8.02 (d, 2H, J=16.0 Hz, CH). ^{13}C NMR (62.9 MHz, $CDCl_3$): δ=14.0 (CH_3), 22.5 (CH_2), 25.7 (CH_2), 28.4 (CH_2), 28.7 (CH_2), 28.8, 29.7 (CH_2), 30.1 (CH_3N), 31.2 (CH_2), 31.5 (CH_2), 31.6 (CH_2), 33.3 (CH), 64.5, 64.8, 64.8, 65.4 (CH_2O), 108.9 (CH), 109.6, 112.8 (C), 120.0, 120.4, 120.5 (CH), 127.4, 128.1, 129.6 (C), 136.6 (CH), 138.6, 138.7 (C), 142.5, 142.6 (CH), 166.6, 166.8, 168.0, 172.8 (CO). IR (KBr): ν=2953, 2926, 2856 (w), 1701, 1622, 1605 (s), 1551, 1527, 1465, 1455, 1378, 1337 (w), 1242 (m), 1159 (s), 973, 908, 849, 728, 674, 648, 605 (w) cm^{-1}. (EI$^+$, 70 eV): m/z (%)=747 (M^+, 10), 596 (11), 595 (31), 594 (37), 595 (100), 492 (20), 465 (16), 464 (33), 463 (68), 407 (07), 380 (30), 362 (35), 336 (13), 355 (18), 278 (13), 251 (13), 234 (23). HRMS: m/z calcd for $C_{45}H_{65}NO_8$ (M^+): 747.47047; found: 747.46850.

*3.15.12. Bis(2-ethylhexyl) 6,7-bis((E)-3-(2-ethylhexyloxy)-3-oxoprop-1-enyl)-9-methyl-2,9-dihydro-1H-carbazole-2,3-dicarboxylate (**15g**).* Product **15g** was prepared starting with **2c** (446 mg, 1.0 mmol), 2-ethylhexyl acrylate (1.10 mL, 5.0 mmol), $Pd(OAc)_2$ (11 mg, 5 mol %), SPhos (10 mol %), NEt_3 (1.10 mL, 8.0 mmol), DMF (5 mL) at 120 °C for 48 h following general procedure B, as a yellow highly viscous oil (618 mg, 72%). ^{1}H NMR (300 MHz, $CDCl_3$): δ=0.82–0.93 (m, 24H, $8CH_3$), 1.21–1.43 (m, 32H, Aliphatic), 1.51–1.62 (m, 4H, CH-aliphatic), 3.02–3.61 (dd, $2H_{\alpha/\beta}$, C-1), 3.71 (s, 3H, CH_3N), 3.82 (dd, $1H_\alpha$, J=3.2, 5.3 Hz, C-2), 4.12 (dd, 8H, J=2.4, 5.8 Hz, $4CH_2O$), 6.32 (d, 1H, J=15.7 Hz), 6.33 (d, 1H, J=15.7 Hz), 7.41 (s, 1H, ArH), 7.72 (s, 1H, ArH), 7.83 (s, 1H, C(4)), 8.01 (d, 1H, J=15.7 Hz), 8.12 (d, 1H, J=15.7 Hz). ^{13}C NMR (62 MHz, $CDCl_3$): δ=10.9 (CH_3), 11.0 (CH_3), 14.1 (CH_3), 23.0 (CH_2), 23.9 (CH_2), 29.0 (CH_2), 29.7 (CH_2), 30.1 (CH_3N), 30.5 (CH_2), 31.2, 38.6, 38.7 (CH), 38.9 (CH-2), 38.9 (CH), 67.0, 67.1, 67.3, 67.5 (CH_2O), 108.6 (CH), 110.0 (C), 117.3 (CH), 118.0 (C), 119.7, 120.0 (CH), 126.4, 128.0, 128.5 (C), 130.5 (CH), 138.8 (C), 142.5, 142.6 (CH), 142.8 (C), 166.8, 166.9, 167.0, 173.0 (CO). IR (KBr): ν=2928, 2925, 2858 (w), 1703 (s), 1631, 1605, 1528, 1460, 1380, 1265, 1220 (m), 1161 (s), 1113, 1085, 1031, 974 (m), 852, 773, 730, 695, 645, 609 (w) cm^{-1}, (EI, 70 eV): m/z (%)=859 (M^+, 12), 699 (10), 590 (11), 588 (11), 572 (11), 460 (5), 83 (20), 71 (22), 70 (11), 69 (16), 57 (100), 44 (93). HRMS: m/z calcd for $C_{53}H_{81}NO_8$ (M^++1): 859.596901; found: 859.59567.

*3.15.13. Bis(6-methylheptyl) 9-methyl-6,7-bis((E)-3-(6-methylheptyloxy)-3-oxoprop-1-enyl)-2,9-dihydro-1H-carbazole-2,3-dicarboxylate (**15h**).* Product **15h** was prepared starting with **2c** (446 mg, 1.0 mmol), 6-methylheptyl acrylate (1.0 mL, 5.0 mmol), $Pd(OAc)_2$ (11 mg, 5 mol %), SPhos (10 mol %), NEt_3 (1.10 mL, 8.0 mmol), DMF (5 mL) at 120 °C for 48 h following general procedure B, as a yellow highly viscous oil (636 mg, 74%). ^{1}H NMR (300 MHz, $CDCl_3$): δ=0.8–0.9 (m, 24H, aliphatic), 0.9–1.2 (m, 12H, $6CH_2$), 1.2–1.3 (m, 12H, $6CH_2$), 0.8–0.9 (m, 8H, $2CH_2$), 3.0 (dd, $1H_\alpha$, J=8.6, 17.2 Hz, C-1), 3.6 (m, $1H_\beta$, C-1), 3.7 (s, 3H, CH_3N), 3.9–4.1 (m, 3H, $1H_\alpha$, C-2/CH_2O), 4.1–4.2 (m, 6H, $3CH_2O$), 6.3 (d, 1H, J=15.6 Hz, CH), 6.3 (d, 1H, J=15.7 Hz, CH), 7.4 (s, 1H, ArH), 7.7 (s, 1H, ArH), 7.8 (s, 1H, C-4, CH), 8.1 (d, 2H, J=15.6 Hz, CH). ^{13}C NMR (62.9 MHz, $CDCl_3$): δ=11.4, 12.1, 14.0, 14.3, 15.3, 15.3, 17.9, 19.5, 19.7 (CH_3), 17.0, 19.2 (CH), 19.9 (CH_2), 19.3 (CH), 22.6, 23.7, 23.8, 26.1, 26.2, 26.3, 26.4, 26.7, 26.8 (CH_2), 28.7 (CH_3N), 30.3, 30.5, 30.1, 33.0 (CH_2), 38.0 (CH), 63.1, 63.7, 64.8, 65.1 (CH_2O), 108.5 (CH), 109.9 (C), 117.3 (CH), 118.2 (C), 119.7, 119.9 (CH), 126.4, 128.0, 128.5 (C), 130.7 (CH), 138.8, 142.6 (C), 142.6 (CH), 166.7, 166.8, 166.9, 173.0 (CO). IR (KBr): ν=2953, 2926, 2870 (w), 1701, 1626 (m), 1605, 1551, 1527, 1465, 1455, 1378 (w), 1272 (s), 1220 (m), 1160 (s), 1034, 974, 855, 777, 735, 700, 661, 642 (w) cm^{-1}. (EI$^+$, 70 eV): m/z (%)=859 (M^+, 32), 857 (11), 734 (09), 678 (11), 677 (26), 676 (25), 572 (10), 519 (12), 434 (12), 390 (12), 84 (39), 83 (24), 71 (22), 70 (34), 69 (65), 57 (64), 56 (59), 55 (62), 44 (87), 43 (100). HRMS [ESI$^+$] (Carbazole): m/z calcd for $C_{53}H_{80}NO_8$ (M+H): 858.58698; found: 658.58698.

*3.15.14. Dimethyl 6,7-bis((E)-3-methoxy-3-oxoprop-1-enyl)-9-methyl-9H-carbazole-2,3-dicarboxylate (**16a**).* Compound **16a** was synthesized starting with **15a** (100 mg, 0.22 mmol), following general procedure C, as a yellow highly viscous oil (99 mg, 100%). ^{1}H NMR (300 MHz, $CDCl_3$): δ=3.54 (s, 3H, CH_3), 3.64 (s, 3H, CH_3), 3.74 (s, 6H, $2CH_3$), 3.77 (s, 3H, CH_3), 6.3 (d, 1H, J=15.6 Hz, CH), 6.4 (d, 1H J=16.3 Hz, CH), 7.4 (s, 1H, ArH), 7.5 (s, 1H, ArH), 8.0 (d, 1H, J=15.6 Hz, CH), 8.1 (d, 1H, J=15.6 Hz, CH), 8.5 (s, 2H, ArH). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ=29.6 (CH_3N), 52.5, 52.6, 52.8, 52.9 (CH_3O), 107.9, 109.4, 119.6, 120.2, 122.7, 122.9 (CH), 123.1, 123.8, 124.5, 125.5, 126.0, 126.9, 128.9, 133.7 (C), 142.0, 142.4 (CH), 166.7, 167.1, 167.8, 169.4 (CO). IR (KBr): ν=3089 (w), 1652 (s), 1455, 1277 (m), 1097, 1060 (s), 912 (w), 845, 798, 699 (s) cm^{-1}. GC–MS (EI, 70 eV): m/z (%)=465 (M^+, 53), 434 (31), 405 (100), 374 (83). HRMS: m/z calcd for $C_{25}H_{23}NO_8$ (M^+): 465.14181; found: 465.141506.

*3.15.15. Dibutyl 6,7-bis((E)-3-butoxy-3-oxoprop-1-enyl)-9-methyl-9H-carbazole-2,3-dicarboxylate (**16c**).* Compound **16c** was synthesized starting with **15c** (100 mg, 0.16 mmol), following general procedure C, as a yellow highly viscous oil (98 mg, 100%). ^{1}H NMR (300 MHz, $CDCl_3$): δ=0.9 (t, 3H, J=7.3 Hz, CH_3), 0.9 (t, 3H, J=7.3 Hz, CH_3), 0.9 (t, 3H, J=7.5 Hz, CH_3), 0.9 (t, 3H, J=7.3 Hz, CH_3), 1.3–1.4 (m, 8H, $4CH_2$), 1.6–1.7 (m, 8H, $4CH_2$), 3.7 (s, 3H, CH_3N), 4.1 (t, 4H, J=6.7 Hz, $2CH_2O$), 4.2 (t, 2H, J=7.1 Hz, CH_2O), 4.3 (t, 2H, J=6.9 Hz, CH_2O), 6.3 (d, 1H, J=15.9 Hz), 6.4 (d, 1H, J=15.9 Hz), 7.4 (s, 1H, ArH), 7.4 (s, 1H, ArH), 8.0 (d, 1H, J=15.2 Hz), 8.1 (d, 1H, J=15.8 Hz), 8.1 (s, 1H, ArH), 8.3 (s, 1H, ArH). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ=13.7, 13.7 (CH_3), 19.2 (CH_2), 19.2 (CH_2), 19.3 (CH_2), 29.5 (CH_3N), 30.6 (CH_2), 30.7 ($2CH_2$), 30.8 (CH_2), 64.5, 64.6, 65.4, 65.8 (CH_2O), 107.7, 109.2, 119.8, 120.0, 121.8, 122.5 (CH), 122.5, 122.9, 123.6, 126.8, 132.4, 133.6 (C), 141.6, 142.0 (CH), 142.7 (C), 166.3, 166.7, 167.2, 168.9 (CO). IR (KBr): ν=2957, 2932, 2872 (w), 1705 (s), 1623, 1596, 1561, 1463 (m), 1387, 1341 (w), 1262, 1226, 1162, 1107 (s), 1080, 1063, 1021, 967 (m), 906, 856, 774, 737, 713, 659, 618, 594 (w) cm^{-1}. (EI$^+$, 70 eV): m/z (%)=633 (M^+, 24), 560 (09), 531 (69), 507 (100), 458 (29), 378 (41), 302 (28). HRMS (ESI$^+$): m/z calcd for $C_{37}H_{48}NO_8$ [M+H]$^+$: 634.33744; found: 634.33799.

*3.15.16. Bis(2-ethylhexyl) 6,7-bis((E)-3-(2-ethylhexyloxy)-3-oxoprop-1-enyl)-9-methyl-9H-carbazole-2,3-dicarboxylate (**16g**).* Compound **16g** was synthesized starting with **15g** (100 mg, 0.12 mmol), following general procedure C, as a yellow highly viscous oil (99 mg, 100%). ^{1}H NMR (300 MHz, $CDCl_3$): δ=0.8–0.9 (m, 24H, $8CH_3$), 1.2–1.4 (m, 32H, CH-aliphatic), 1.6–1.7 (m, 4H, aliphatic), 3.9 (s, 3H, CH_3N),

4.1 (dd, 4H, J=2.6, 5.7 Hz, $2CH_2O$), 4.2 (dd, 4H, J=2.6, 5.7 Hz, $2CH_2O$), 6.4 (d, 1H, J=15.7 Hz, CH), 6.4 (d, 1H, J=15.7 Hz, CH), 7.5 (s, 1H, ArH), 7.6 (s, 1H, ArH), 8.1 (d, 1H, J=15.7 Hz, CH), 8.2 (d, 1H, J=15.8 Hz, CH), 8.3 (s, 1H, ArH), 8.5 (s, 1H, ArH). ^{13}C NMR (62.9 MHz, $CDCl_3$): δ=10.9 ($3CH_3$), 11.0 (CH_3), 14.1 ($4CH_3$), 23.0 ($2CH_2$), 23.7 ($2CH_2$), 23.8 ($2CH_2$), 23.9 ($2CH_2$), 28.9 ($2CH_2$), 29.0 ($2CH_2$), 29.6 (CH_3N), 30.4 ($2CH_2$), 30.5 ($2CH_2$), 30.9, 38.5, 38.7, 38.8, (CH), 67.1, 67.3, 68.1, 68.5 (CH_2O), 107.8, 109.4, 120.1, 120.3, 122.0, 122.7 (CH), 122.9, 123.1, 123.8, 127.0, 132.7, 133.8 (C), 141.8, 142.2 (CH), 142.8, 142.9 (C), 166.5, 166.8, 167.4, 169.1 (CO). IR (KBr): ν=2927(w), 1712, 1624, 1601, 1562, 1459, 1379, 1260, 1229, 1165, 1108, 1081, 1015, 975, 858, 774, 726, 615 (s) cm^{-1}. GC–MS (EI$^+$, 70 eV): m/z (%)=857 (M^+, 23), 699 (23), 588 (27), 346 (18), 302 (29). HRMS: m/z calcd for $C_{53}H_{79}NO_8$ (M^+): 857.5806; found: 857.5803.

*3.15.17. (2E,2′E,2″E,2‴E)-Tetraethyl 3,3′,3″,3‴-(1-methyl-1H-indole-2,3,5,6-tetrayl) tetraacrylate (**17b**).* Product **17b** was prepared starting with **2c** (446 mg, 1.0 mmol), ethyl acrylate (0.6 mL, 5.0 mmol), $Pd(OAc)_2$ (11 mg, 5 mol %), SPhos (10 mol %), NEt_3 (1.10 mL, 8.0 mmol), DMF (5 mL) at 90 °C for 36 h following general procedure A, as a yellow highly viscous oil (397 mg, 76%). ^{1}H NMR (300 MHz, $CDCl_3$): δ=1.3 (t, 6H, J=6.8 Hz, $2CH_3$), 1.3 (t, 6H, J=7.0 Hz, $2CH_3$), 3.8 (s, 3H, CH_3N), 4.2–4.3 (m, 8H, $4CH_2O$), 6.2 (d, 1H, J=15.8 Hz, CH), 6.3 (d, 1H, J=15.7 Hz, CH), 6.3 (d, 1H, J=15.4 Hz, CH), 6.4 (d, 1H, J=16.0 Hz, CH), 7.4 (s, 1H, ArH), 7.8 (d, 1H, J=16.0 Hz), 7.9 (d, 1H, J=16.0 Hz), 8.0 (s, 1H, ArH), 8.0 (d, 1H, J=15.8 Hz), 8.1 (d, 1H, J=15.8 Hz). ^{13}C NMR (62.9 MHz, $CDCl_3$): δ=13.2 (CH_3), 13.3 ($2CH_3$), 13.4 (CH_3), 30.4 (CH_3N), 59.5, 59.6, 59.7, 60.2 (CH_2O), 107.9 (CH), 113.2 (C), 116.7, 119.4, 119.7, 120.1, 125.1, (CH), 125.7, 127.8 (C), 129.3 (CH), 130.0 (C), 134.7 (CH), 138.1, 138.4 (C), 141.2, 141.3 (CH), 164.7, 165.4, 165.6, 166.5 (CO). IR (KBr): ν=2979, 2930, 2872 (w), 1704, 1613 (s), 1463, 1445, 1367 (m), 1259, 1160, 1093, 1028, 974, 855 (s), 809, 785, 770, 727, 702, 607 (m) cm^{-1}. GC–MS (EI, 70 eV): m/z (%)=523 (M^+, 100), 477 (18), 452 (88), 402 (84), 375 (23), 350 (70). HRMS: m/z calcd for $C_{29}H_{33}NO_8$ (M^+): 523.22062; found: 523.22073.

*3.15.18. (2E,2′E,2″E,2‴E)-Tetrabutyl 3,3′,3″,3‴-(1-methyl-1H-indole-2,3,5,6-tetrayl)tetraacrylate (**17c**).* Product **17c** was prepared starting with **2c** (446 mg, 1.0 mmol), n-butyl acrylate (0.70 mL, 5.0 mmol), $Pd(OAc)_2$ (11 mg, 5 mol %), SPhos (10 mol %), NEt_3 (1.10 mL, 8.0 mmol), DMF (5 mL) at 90 °C for 36 h following general procedure B, as a yellow highly viscous oil (450 mg, 71%). ^{1}H NMR (300 MHz, $CDCl_3$): δ=0.8–0.9 (m, 12H, $4CH_3$), 1.3–1.5 (m, 8H, $4CH_2$), 1.6–1.7 (m, 8H, $4CH_2$), 3.7 (s, 3H, CH_3N), 4.1 (t, 4H, J=6.9 Hz, $2CH_2O$), 4.2 (t, 4H, J=6.9 Hz, $2CH_2O$), 6.2 (d, 1H, J=16.4 Hz, CH), 6.2 (d, 1H, J=15.4 Hz, CH), 6.3 (d, 1H, J=15.8 Hz, CH), 6.4 (d, 1H, J=16.2 Hz, CH), 7.4 (s, 1H, ArH), 7.7 (d, 1H, J=16.2 Hz, CH), 7.8 (d, 1H, J=16.2 Hz, CH), 7.9 (s, 1H, ArH), 8.0 (d, 1H, J=15.4 Hz, CH), 8.0 (d, 1H, J=15.4 Hz, CH). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ=13.7 (CH_3), 13.7 ($2CH_3$), 13.8 (CH_3), 19.1, 19.1, 19.2, 19.2, 30.6, 30.7, 30.8, 30.8 (CH_2), 31.4 (CH_3N), 64.4, 64.5, 64.5, 65.0 (CH_2O), 108.9 (CH), 114.1 (C), 117.6, 120.3, 120.6, 121.0, 125.9 (CH), 126.6, 128.6 (C), 130.3 (CH), 130.9 (C), 135.5 (CH), 139.0, 139.3, 142.0, 142.1 (C), 165.7, 166.3, 166.6, 167.4 (CO). IR (KBr): ν=2932 (w), 1699, 1622, 1548 (s), 1463 (m), 1416, 1379, (s), 1273 (m), 1243, 1212, 1168, 1062, 1025, 956, 864, 780 (s), 738 (m), 694, 647, 588 (s) cm^{-1}. (EI, 70 eV): m/z (%)=635 (M^+, 100), 591 (18), 562 (16), 534 (14), 509 (14), 507 (11), 478 (33), 460 (46), 431 (11), 360 (11), 334 (12), 304 (13), 260 (19), 231 (15), 57 (21). HRMS: m/z calcd for $C_{37}H_{49}NO_8$ (M^+): 635.34527; found: 635.34554.

*3.15.19. (2E,2′E,2″E,2‴E)-tert-Butyl 3,3′,3″,3‴-(1-methyl-1H-indole-2,3,5,6-tetrayl) tetraacrylate (**17e**).* Product **17e** was prepared starting with **2c** (446 mg, 1.0 mmol), *tert*-butyl acrylate (0.7 mL, 5.0 mmol), $Pd(OAc)_2$ (11 mg, 5 mol %), SPhos (10 mol %), NEt_3 (1.10 mL, 8.0 mmol), DMF (5 mL) at 90 °C for 36 h following general procedure A, as a yellow highly viscous oil (559 mg, 88%). ^{1}H NMR (300 MHz, $CDCl_3$): δ=1.5 (s, 9H, $3CH_3$), 1.5 (s, 9H, $3CH_3$), 1.5 (s, 9H, $3CH_3$), 1.5 (s, 9H, $3CH_3$), 3.8 (s, 3H, CH_3N), 6.2 (d, 1H, J=16.1 Hz, CH), 6.3 (d, 1H, J=15.7 Hz, CH), 6.3 (d, 1H, J=15.7 Hz, CH), 6.4 (d, 1H, J=16.0 Hz, CH), 7.4 (s, 1H, ArH), 7.7 (d, 1H, J=16.0 Hz, CH), 7.8 (d, 1H, J=16.0 Hz, CH), 7.9 (d, 1H, J=15.8 Hz, CH), 8.0 (d, 1H, J=14.2 Hz, CH), 8.0 (s, 1H, ArH). ^{13}C NMR (62.9 MHz, $CDCl_3$): δ=28.1 (CH_3), 28.2 (CH_3), 28.3 (CH_3), 30.9 (CH_3CN), 80.4, 80.6, 80.7, 81.5 (C–O), 108.7 (CH), 114.1 (C), 119.3, 120.5, 122.6, 122.7 (CH), 126.6 (C), 127.7 (CH), 128.8 (C), 129.6 (CH), 131.0 (C), 134.9 (CH) 139.0, 139.3 (C), 141.5 (CH), 165.0, 165.7, 165.9, 166.9 (CO). IR (KBr): ν=2976, 2931 (w), 1694, 1621, 1548, 1475, 1455, 1390, 1365, 1289, 1254, 1217, 1140, 965, 846, 764 (s) cm^{-1}. EI$^+$ (70 eV): m/z (%)=635 (M^+, 15), 579 (04), 523 (07), 478 (17), 766 (20), 304 (28). HRMS: m/z calcd for $C_{37}H_{49}NO_8$ (M^+): 635.34582; found: 635.34532.

*3.15.20. (2E,2′E,2″E,2‴E)-Tetrakis(2-ethylhexyl) 3,3′,3″,3‴-(1-methyl-1H-indole-2,3,5,6-tetrayl) tetraacrylate (**17g**).* Product **17g** was prepared starting with **2c** (446 mg, 1.0 mmol), 2-ethylhexyl acrylate (1.10 mL, 5.0 mmol), $Pd(OAc)_2$ (11 mg, 5 mol %), SPhos (10 mol %), NEt_3 (1.10 mL, 8.0 mmol), DMF (5 mL) at 90 °C for 36 h following general procedure A, as a yellow highly viscous oil (645 mg, 75%). ^{1}H NMR (300 MHz, $CDCl_3$): δ=0.81–0.92 (m, 24H, $8CH_3$), 1.23–1.44 (m, 32H, CH_2-aliphatic), 1.52–1.61 (m, 4H, CH), 3.83 (s, 3H, CH_3N), 4.01–4.12 (m, 8H, $4CH_2O$), 6.21 (d, 1H, J=16.1 Hz), 6.32 (d, 1H, J=15.6 Hz), 6.33 (d, 1H, J=15.7 Hz), 6.41 (d, 1H, J=16.0 Hz), 7.52 (s, 1H, ArH), 7.74 (d, 1H, J=16.0 Hz), 7.81 (d, 1H, J=16.0 Hz), 8.01 (s, 1H, ArH), 8.02 (d, 2H, J=16.0 Hz). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ=10.9 (CH_3), 11.0 ($3CH_3$), 14.0 ($4CH_3$), 22.9 ($4CH_2$), 23.7 (CH_2), 23.8 ($2CH_2$), 23.9, 28.1, 28.9 (CH_2), 29.0 ($2CH_2$), 30.3 (CH_2), 30.4 ($2CH_2$), 30.5 (CH_2), 31.3 (CH_3N), 38.8 (CH), 38.9 (3CH), 66.9, 67.0, 67.1, 67.6 (CH_2O), 108.9 (CH), 114.1 (C), 117.8, 120.4, 120.7, 121.0, 125.9 (CH), 126.7, 128.8 (C), 130.4 (CH), 131.0 (C), 135.5 (CH), 139.0, 139.4 (C), 142.1, 142.2 (CH), 165.8, 166.4, 166.6, 167.5 (CO). IR (KBr): ν=2957, 2927, 2872, 2858 (w), 1706, 1691, 1624 (s), 1600, 1548, 1460, 1379, 1283, 1254, 1215 (w), 1164 (s), 1029, 970, 864 (m), 769, 727, 695, 639, 595 (w) cm^{-1}. EI$^+$ (70 eV): m/z (%)=859 (M^+, 46), 703 (11), 701 (14), 591 (13), 590 (32), 571 (11), 572 (28), 543 (15), 460 (14), 432 (21), 431 (13), 416 (10), 414 (13), 304 (19), 276 (19), 71 (31), 70 (20), 57 (100), 44 (19), 43 (44). HRMS (ESI$^+$): m/z calcd for $C_{53}H_{82}NO_8$ [M^++H]: 860.6035; found: 860.6029.

*3.15.21. (2E,2′E)-Diethyl 3,3′-(1-methyl-1H-indole-5,6-diyl)diacrylate (**18**).* By heating **17b** in xylene side-product **18** was derived. ^{1}H NMR (250 MHz, $CDCl_3$): δ=1.3 (t, 3H, J=7.1 Hz, CH_3), 1.3 (t, 3H, J=7.1 Hz, CH_3), 3.7 (s, 3H, CH_3N), 4.2 (q, 2H, J=7.2 Hz, CH_2O), 4.2 (q, 2H, J=7.2 Hz, CH_2O), 6.2 (d, 1H, J=15.9 Hz, CH), 6.3 (d, 1H, J=15.9 Hz, CH), 6.4 (d, 1H, J=3.0 Hz, ArH), 7.0 (d, 1H, J=3.0 Hz, ArH), 7.5 (s, 1H, ArH), 7.8 (s, 1H, ArH), 8.1 (d, 1H, J=15.9 Hz, CH), 8.2 (d, 1H, J=15.9 Hz, CH). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ=14.4 ($2CH_3$), 33.0 (CH_3N), 60.4 (CH_2O), 60.5 (CH_2O), 102.0, 108.3, 119.1, 119.5, 120.5 (CH), 126.4, 128.4, 130.0 (C), 132.0 (CH), 137.5 (C), 143.2, 143.4 (CH), 166.8, 167.0 (CO). IR (KBr): ν=2925 (w), 1703, 1626, 1604, 1505, 1462, 1446, 1422, 1366, 1349, 1303, 1260, 1174, 1159, 1094, 1030, 974, 856, 761, 748, 718, 655, 590 (s) cm^{-1}. GC–MS (EI, 70 eV): m/z (%)=327 ([M]$^+$, 100), 298 (52), 277 (33). HRMS (EI): m/z calcd for $C_{19}H_{21}NO_4$ [M^+]: 327.14706; found: 327.147666.

3.16. General procedure D for Sonogashira cross-coupling reactions of 2a

A mixture of $Pd(OAc)_2$ (11 mg, 5 mol %), the ligand XPhos (**L_2**) (48 mg, 10 mol %) and 20 ml xylene was stirred at room temperature for 30 min under an argon atmosphere. Then, CuI (19 mg, 10 mol %), (^{i}Pr)$_2$NH (5 ml), 1-methyl-2,3-dibromoindole (290 mg, 1 mmol) and phenylacetylene (0.12 ml, 2.2 mmol) were added and the mixture was stirred for 36 h at 120 °C. The organic layer was washed with

water and extracted with CH_2Cl_2. The crude product was purified by column chromatography (*n*-heptane/ethylacetate 10:1).

*3.16.1. 1-Methyl-2,3-bis(phenylethynyl)-1H-indole (**19**).* Compound **19** was synthesized according to the general procedure D starting with **2a** (290 mg, 1.0 mmol) as a brown, unstable semisolid (199 mg, 60%). ^{1}H NMR ($CDCl_3$, 250 MHz): δ=3.81 (s, 3H, CH_3), 7.12–7.34 (m, 9H, ArH), 7.52–7.57 (m, 4H, ArH), 7.70–7.74 (m, 1H, ArH). ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ=30.1 (CH_3), 78.9, 81.8, 93.5, 98.4 (C≡*C*), 102.2 (C), 108, 119.3, 119.9 (CH), 121.5 (C), 123.1 (CH), 123.2 (C), 124.7 (C), 126.6 (CH), 127.0 (C), 127.3, 127.5, 127.8, 130.3, 130.6 (CH), 135.7 (C). IR (ATR, cm^{-1}): ν=3050 (w), 2962 (w), 2210 (w), 2195 (w), 1594 (w), 1569 (w), 1494 (w), 1477 (m), 1464 (m), 1439 (w), 1413 (w), 1372 (m), 1329 (m), 1259 (s), 1086 (s), 1067 (s), 1011 (s). MS (EI, 70 eV): *m*/*z* (%)=331 (M^+, 100), 314 (4), 254 (4), 226 (1), 187 (1), 164 (3), 150 (2), 77 (1). HRMS (EI): calcd for $C_{25}H_{17}N$ (M^+) 331.13555, found 331.13528.

References and notes

1. Reviews: (a) Brossi, A. In *The Alkaloids*; Cordell, G. A., Ed.; Academic: New York, NY, 1985; Vol. 26, p 1; (b) Bhattacharrya, P.; Chakraborthy, D. P. *Prog. Chem. Org. Nat. Prod.* **1987**, *52*, 160; (c) Maryanoff, B. E.; Reitz, A. B. *Chem. Rev.* **1989**, *89*, 863; (d) Knölker, H.-J.; Reddy, K. R. *Chem. Rev.* **2002**, *102*, 4303; (e) Chakraborty, D. P.; Roy, S. *Prog. Chem. Org. Nat. Prod.* **1991**, *57*, 71; (f) Chakraborty, D. P. In *The Alkaloids*; Cordell, G. A., Ed.; Academic: New York, NY, 1993; Vol. 44, p 257; (g) Knölker, H.-J. *Top. Curr. Chem.* **2005**, *244*, 115; (h) Knölker, H.-J.; Reddy, K. R. In *The Alkaloids*; Cordell, G. A., Ed.; Academic: Amsterdam, 2008; Vol. 65, p 1; (i) Pindur, U. *Chimia* **1990**, *44*, 406; (j) Bergman, J.; Pelcman, B. *Pure Appl. Chem.* **1990**, *62*, 1967; (k) Moody, C. J. *Synlett* **1994**, 681; (l) Kirsch, G. H. *Curr. Org. Chem.* **2001**, *5*, 507; (m) Lemster, T.; Pindur, U. *Recent Res. Dev. Org. Bioorg. Chem.* **2002**, *5*, 99; (n) Knölker, H.-J. *Curr. Org. Synth.* **2004**, *1*, 309.
2. For some recent contributions, see: (a) Bedford, R. B.; Betham, M. *J. Org. Chem.* **2006**, *71*, 9403; (b) Lebold, T. P.; Kerr, M. A. *Org. Lett.* **2007**, *9*, 1883; (c) Watanabe, T.; Ueda, S.; Inuki, S.; Oishi, S.; Fujii, N.; Ohno, H. *Chem. Commun.* **2007**, 4516; (d) Jean, D. J., Jr.; Poon, S. F.; Schwarzbach, J. L. *Org. Lett.* **2007**, *9*, 4893; (e) Liu, C.-Y.; Knochel, P. *J. Org. Chem.* **2007**, *72*, 7106; (f) Naffziger, M. R.; Ashburn, B. O.; Perkins, J. R.; Carter, R. G. *J. Org. Chem.* **2007**, *72*, 9857.
3. (a) Forke, R.; Krahl, M. P.; Däbritz, F.; Jäger, A.; Knölker, H.-J. *Synlett* **2008**, 1870; (b) Forke, R.; Krahl, M. P.; Krause, T.; Schlechtingen, G.; Knölker, H.-J. *Synlett* **2007**, 268.
4. Ackermann, L.; Althammer, A. *Angew. Chem., Int. Ed.* **2007**, *46*, 1627.
5. Pindur, U. *Heterocycles* **2008**, *27*, 1253.
6. Kano, S.; Sugino, E.; Shibuya, S.; Hibino, S. *J. Org. Chem.* **1981**, *46*, 3856.
7. Pindur, U.; Adam, R. *Helv. Chim. Acta* **1990**, *73*, 827.
8. Voigt, K.; von Zezschwitz, P.; Rosauer, K.; Lansky, A.; Adams, A.; Reiser, O.; de Meijere, A. *Eur. J. Org. Chem.* **1998**, 1521 and references cited therein.
9. (a) Hussain, M.; Dang, T. T.; Langer, P. *Synlett* **2009**, 1822; (b) Toguem, S.-M. T.; Hussain, M.; Malik, I.; Villinger, A.; Langer, P. *Tetrahedron Lett.* **2009**, *50*, 4962; (c) Hussain, M.; Hung, N. T.; Langer, P. *Tetrahedron Lett.* **2009**, *50*, 3929; (d) Toguem, S.-M. T.; Langer, P. *Synlett* **2010**, 1779.
10. Tang, S.; Li, J.-H.; Xie, Y.-X.; Wang, N.-X. *Synthesis* **2007**, 1535.
11. Ji, N.-Y.; Li, X.-M.; Cui, C.-M.; Wang, B.-G. *Helv. Chim. Acta* **2007**, *90*, 1731.
12. Ji, N.-Y.; Li, X.-M.; Cui, C.-M.; Wang, B.-G. *Helv. Chim. Acta* **2007**, *90*, 385.
13. Carter, G. T.; Rinehart, K. L., Jr.; Li, L. H.; Küntzel, S. L.; Condor, J. L. *Tetrahedron Lett.* **1978**, *19*, 4479.
14. Liu, Y.; Gribble, G. W. *J. Nat. Prod.* **2002**, *65*, 748.
15. Billingsley, K.; Buchwald, S. L. *J. Am. Chem. Soc.* **2007**, *129*, 3358 and references cited therein.
16. Li, H. J.; Wang, L. *Eur. J. Org. Chem.* **2006**, 5099.
17. CCDC-823758 (**5f**), CCDC-823759 (**6a**), CCDC-823760(**7**) and CCDC-823758 (**12c**) contain all crystallographic details of this publication, which are available free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html or can be ordered from the following address: Cambridge Crystallographic Data Centre, 12 Union Road, GB-Cambridge CB21EZ; Fax:(+44)1223-336-033; or deposit@ccdc.cam.ac.uk).
18. Kawasaki, I.; Yamashita, M.; Ohta, S. *Chem. Pharm. Bull.* **1996**, *44*, 1831.