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Synthesis of vinylpyrroles, vinylfurans and vinylindoles via a Brønsted acid catalyzed highly regio- and stereoselective cis-hydroarylation of ynamides☆

Yanshi Zhang*

GE Global Research Center, One Research Circle, CEB-1599, Niskayuna, NY 12308, USA

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Abstract—A highly regio- and stereoselective Brønsted acid-catalyzed coupling of ynamides and aromatic heterocycles, such as pyrroles, furans, and indoles is described. This process is the equivalent of hydroarylation of ynamides, and leads to the efficient syntheses of an array of vinylheterocycles. Diels–Alder reaction between the vinylindoles and DMAD afforded carbazole derivatives in good yields.

1. Introduction

Serving as a powerful electrophile, iminium ions have been extensively investigated in organic synthesis. These efforts have led to the discovery of a wide range of bond-forming methods, which can be exemplified by some of the most classical reactions, such as Pictet–Spengler reactions, Mannich reactions, and Alder-ene reactions.[1] Ketene iminium ions, a sub-class of highly functionalized iminium ions, however, received very little attention.[2] This lack of interest can be partly attributed to the synthetic availability of this class of compounds as well as their highly reactive nature.

The existing methods for the synthesis of ketene iminium ions are rather limited. Commonly, they can be generated as reactive intermediates through either dehydration of amide or dehydrohalogenation of α-haloenamines.[2] Relative harsh reaction conditions and low reaction yields were encountered in most cases. An alternative, however, less common approach for the generation of ketene iminium ions, is through the protonation of ynamine or ynamides.

Ynamides have recently attracted major attention from the synthetic organic community, leading to the discovery of a large number of novel methods for the synthesis of structurally diverse heterocycles, carbocycles, and an array of useful organic functional groups.[3,4,5] Generating followed by trapping the ketene iminium intermediates with nucleophiles represents a novel bond-forming process, and offers expedite approaches for the synthesis of highly functionalized organic building blocks. Among the wide range of nucleophiles, electron rich heterocycles, such as indoles and pyrroles are particularly appealing.[4a]

Development of efficient methodologies for regioselective functionalization of indoles and pyrroles are of great importance, since these ring systems can be found as structural motifs in numerous biologically active natural products and pharmaceuticals.[6] Among these heterocycles, their vinyl derivatives have attracted major attentions. Vinylpyrroles and vinylindoles are not only common structural features in natural products, but also are viable key building blocks that are frequently employed in the synthesis of alkaloids and other biologically important heterocycles.[7,8] In addition, vinylpyrroles have found extensive applications in material science as vinyl monomers, molecular switches, photo- and electroconducting materials.[8g] As a result, considerable amount of efforts has been devoted to the development of new methodologies for efficient synthesis of vinylpyrroles and vinylindoles.[9] Though significant progresses have been made in this field, there remain serious limitations among these methods, which are characterized by the necessity of introducing electron-withdrawing nitrogen protecting groups and/or other reactive functional groups such as halogen, acyl groups, phosphrances, or amines on to the heterocycles in order to facilitate the key vinylation step.[8g,9a] Thus, developing a general method, which can realize direct vinylation of unfunctionalized indoles or pyrroles, still holds great synthetic potential.

☆ Note: Contribution from the Department of Chemistry, University of Minnesota

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* Tel.: +1 5183877634; fax: +1 5183875592;
e-mail: zhangy@research.ge.com

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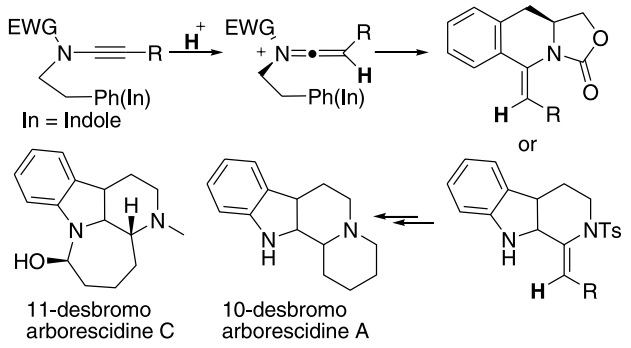
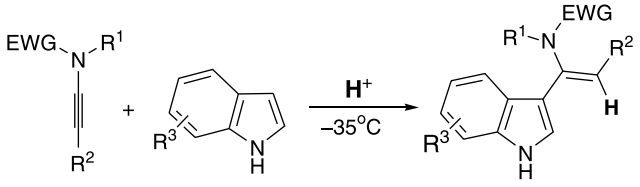
Early this year, we reported a Brønsted acid-catalyzed highly stereoselective intramolecular ynamide-arene cyclization by trapping the in situ generated active ketene iminium intermediates with internally tethered arenes. Both aromatic carbocycles and heterocyles are demonstrated to the efficient nucleophiles for the transformation, leading to the synthesis of isoquinoline and carboline derivatives, respectively. Furthermore, this novel ketene imminium Pictet–spengler cyclization process was successfully applied as the corner stone step in the total synthesis of β-carboline indole alkaloids desbromoarborescidine A and C (Scheme 1).[5a]



Scheme 1. Ketene iminium Pictet–Spengler cyclizations.

As an extension of this work, intermolecular trapping of the in situ generated ketene iminium intermediates with indoles was then investigated. Recently, we reported a Brønsted acid-catalyzed highly regio- and stereoselective cis-hydroarylation of ynamides. This process features nucleophilic attack on the in situ generated ketene iminium intermediates with indoles, and provides an efficient method for the direct construction of vinyl indoles (Scheme 2).[4a] These vinylindole derivatives are synthetic equivalents to masked dienamides, and react efficiently with dienylphiles such as DMAD in a [4+2] fashion to afford carbazole derivatives. Herein, we disclose the scope and limitation of this novel hydroarylation protocol in full account.



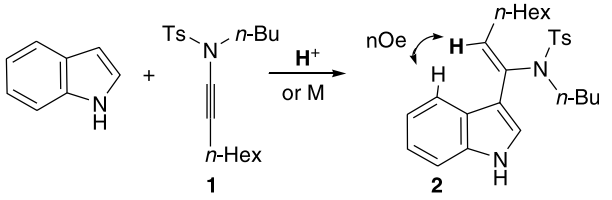
Scheme 2. cis-Hydroarylation of ynamides.

2. Results and discussions

2.1. Feasibility establishment

Given the lack of literature precedents, our initial effort was orientated toward the establishment of the feasibility of this new design. Employing the readily made ynamids **1** (1.0 equiv) and indole (1.4 equiv) as the model substrates, a series of transitional metal π-acids and Brønsted acids were investigated as summarized in Table 1.

Table 1. Catalyst screening

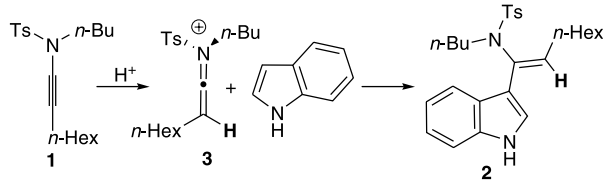


Entry	M^+ (mol%)	Solvent	Temperature (°C)	Yield (%)[a]
1	$PtCl_2$ (10)	Toluene	80	ND
2	$PtCl_4$ (10)	Toluene	80	ND
3	$Pd(Ac)_2$(10)	Toluene	80	ND
4	$PdCl_2$ (10)	Toluene	80	ND
5	PNBSA (10)[b]	Toluene	80	ND
6	Tf_2NH (5)	CH_2Cl_2	Room temperature	84[c]
7	Tf_2NH (10)	CH_2Cl_2	−35	81[d]
8	TfOH (10)	CH_2Cl_2	−35	ND

[a] Isolated yields.
[b] PNBSA, *p*-nitrobenzenesulfonicacid.
[c] *Z*/*E*=6:1 by ^{1}H NMR.
[d] *Z*/*E*>30:1 by ^{1}H NMR.

Initial screenings employing alkynophilic transition metal π-acids including platinum salts and palladium salts turned out to be very unsuccessful (entry 1–4). Though ynamide **1** was totally consumed in all these cases, very complex reaction mixtures were obtained, in which only trace amount of the desired products were observed by ^{1}H NMR analysis of the crude reaction mixtures. At this point, we turned our attention to Brønsted acid. Based on our previous experiences, *para*-nitrobenzenesulfonic acid (PNBSA) and trifluoromethanesulfone imide (Tf_2NH) were tested. Tf_2NH was proved to be the most active catalyst for this transformation (entries 5 and 6). At room temperature, with 5% loading of the catalyst, the desired vinylindole **2** was separated in 84% yield. This hydroarylation reaction is highly regioselective furnishing exclusively C-3 vinylation product **6** as expected.[6b] The fact that Tf_2NH is a better catalyst for this transformation is quite surprising, since PNBSA gave superior results in the intramolecular version of this transformation.[5a]

More interestingly, this reaction is moderately stereoselective when conducted at room temperature favoring the formation of (*Z*)-enamide as the major isomer with a *Z*/*E* ratio of 6:1, which was confirmed by NOE studies. This stereoselectivity outcome is not surprising, and can be explained by the rationale that indole nucleophile would prefer to approach the ketene iminium intermediate **3** from the less hinder side—the hydrogen side, in order to avoid to the unnecessary steric interaction with the hexyl group (Scheme 3). Based on this model, an improved selectivity



Scheme 3. Stereoselectivity rationale.

was expected when the reaction was conducted at relatively lower temperature. To our delight, when conducted at −35 °C with 10% catalyst loading, the reaction proceeded at a reasonable speed, leading to the formation of (*Z*)-enamide almost exclusively.

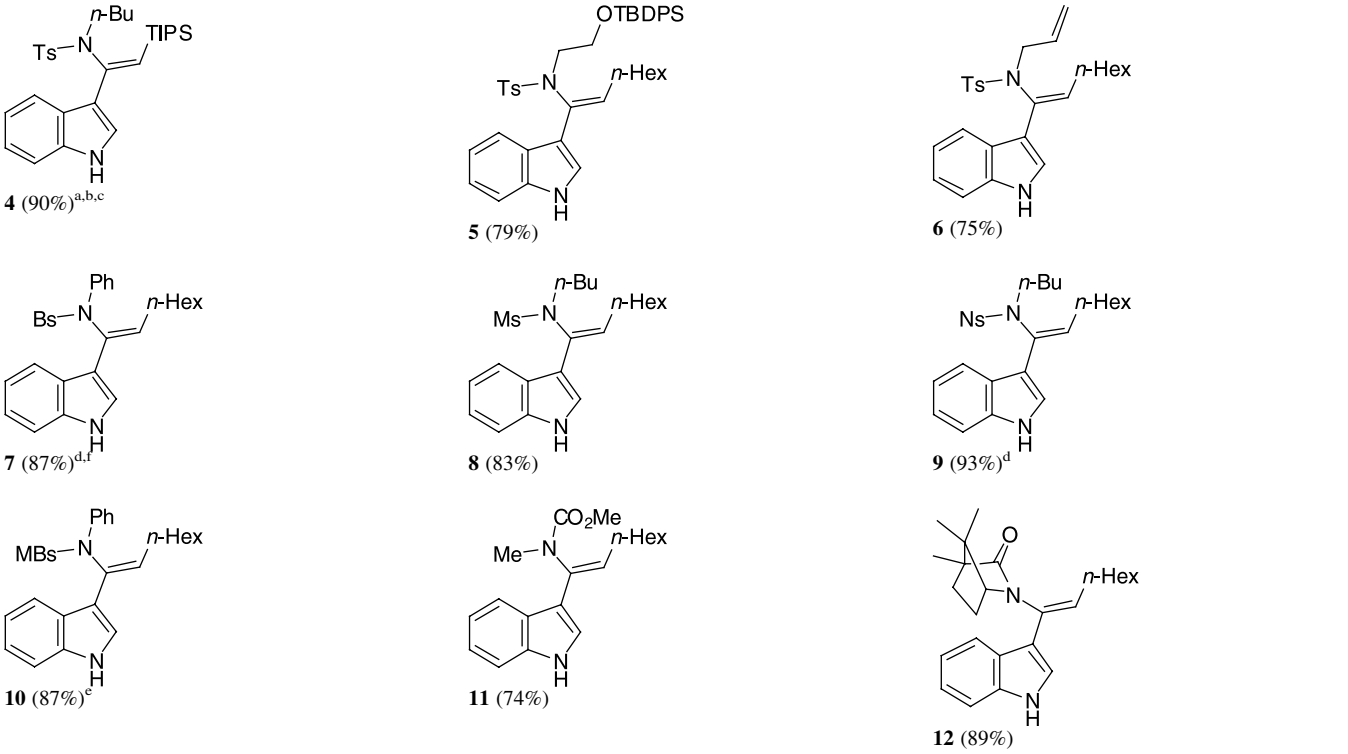
2.2. Reaction of indole with different ynamides

In order to establish the scope of this novel hydroarylation protocol, we first tested the reaction of indole with various types of ynamides under the optimized reaction conditions. This protocol is proved to be quite general with respect to variations on ynamides as summarized in Table 2. In addition to alkyl substituted alkynes, silyl substituted alkyne also survived the acidic reaction condition giving vinylindole **4** in excellent yield. Potentially useful functional groups such as silyl protected alcohol and allyl group were successfully introduced into the reaction system (**5** and **6**). Sulfonyl groups with different degree of electron withdrawing power, including Bs, Ms, Ns, and MBs, were all viable substrates for this transformation, furnishing the vinyl indole derivatives in comparable efficiency (**7**–**10**). For vinylindole **9** and **10**, however, the reactions were observed to be much slower, and resulted in a relatively larger amount of the (*E*)-isomers. This can be attributed to the relatively stronger electron withdrawing power of nitro and phenyl substituents, which resulted in the further delocalization of the lone pair electrons on the ynamide nitrogens. As a result, relatively higher energy was required to generate the ketene iminium intermediates from protonation of these two ynamide precursors. In addition to sulfonyl-substituted ynamides, carbamate-derived and aza-camphor-derived ynamides also underwent the desired transformation, giving the vinylindole derivatives in good yield (**11** and **12**).

2.3. Reaction of substituted indoles with ynamide 1

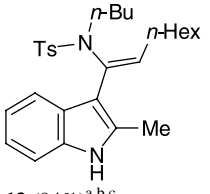
We then turned our attention to study the scope of this transformation toward various substituted indoles employing ynamide **1** as the model substrate (Table 3). Indoles with electronically neutral alkyl and aryl substitutions, including 2-methylindole, 2-phenylindole, 7-methyldindole, 2-methyl-7-isopropylindole, were investigated. The hydroarylation processes were very efficient for all these substrates affording the desired vinylindoles in good to excellent yields. It was also observed that sterically demanding C-2 substituted indoles are less reactive for the vinylation process (**13**, **14**, and **16**). Much higher reaction temperature (25 °C) had to be employed for the reaction to proceed at a reasonable speed. Interestingly, though conducted at room temperature, the desired (*Z*)-enamides were the exclusive product in these reactions, which can be attributed to the increased steric interaction between the C-2 substituents and the approaching ketene iminium intermediate **3**. Electron-donating methoxy group and weak electron-withdrawing groups, such as chloride and bromide,

Table 2. Coupling of indole with different ynamides

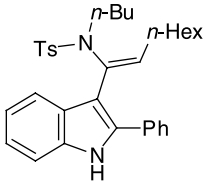


[a] All reactions were conducted at −35 °C, using ynamides and indole at the ratio of 1:1.4 with 10 mol% Tf_2NH in CH_2Cl_2 (0.1 M).
[b] Isolated yields for all entries.
[c] *Z*/*E*>25:1 by ^1H NMR unless otherwise indicated.
[d] *Z*/*E*=10:1 by ^1H NMR.
[e] *Z*/*E*=13:1 by ^1H NMR.
[f] Bs, Benzenesulfonyl; PMBs, *p*-methoxybenzenesulfonyl.

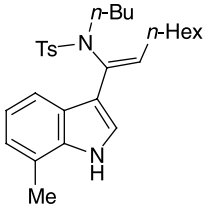
Table 3. Coupling of ynamide **1** with substituted indoles



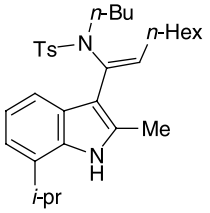
13 (94%)[a,b,c]



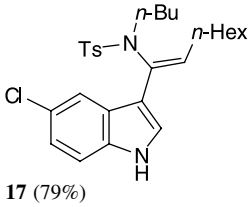
14 (91%)[a]



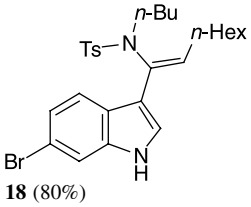
15 (88%)[d]



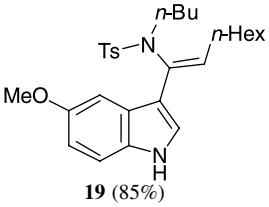
16 (84%)[a]



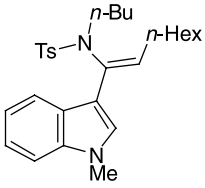
17 (79%)



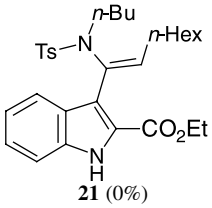
18 (80%)



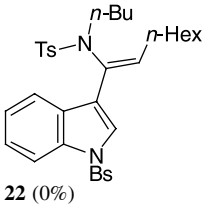
19 (85%)



20 (85%)



21 (0%)



22 (0%)

[a] Reactions were conducted at room temperature.
[b] Isolated yields for all entries.
[c] *Z*/*E*>25:1 by ^{1}HNMR.
[d] Reactions were conducted at −35 °C unless otherwise indicated.

can also be tolerated in this transformation (**17**, **18**, and **19**). *N*-Methyl indole should similar reactivity, affording vinylindole **20** in good yield. Strong electron-withdrawing substitutions, such as carbonyl and sulfonyl groups, had detrimental effect on this transformation (**21** and **22**). No desired vinylation products were observed even after prolonged reaction time at room temperature. Diminished electrophilicity of the substituted indoles caused by the electron-withdrawing groups are responsible for these results.

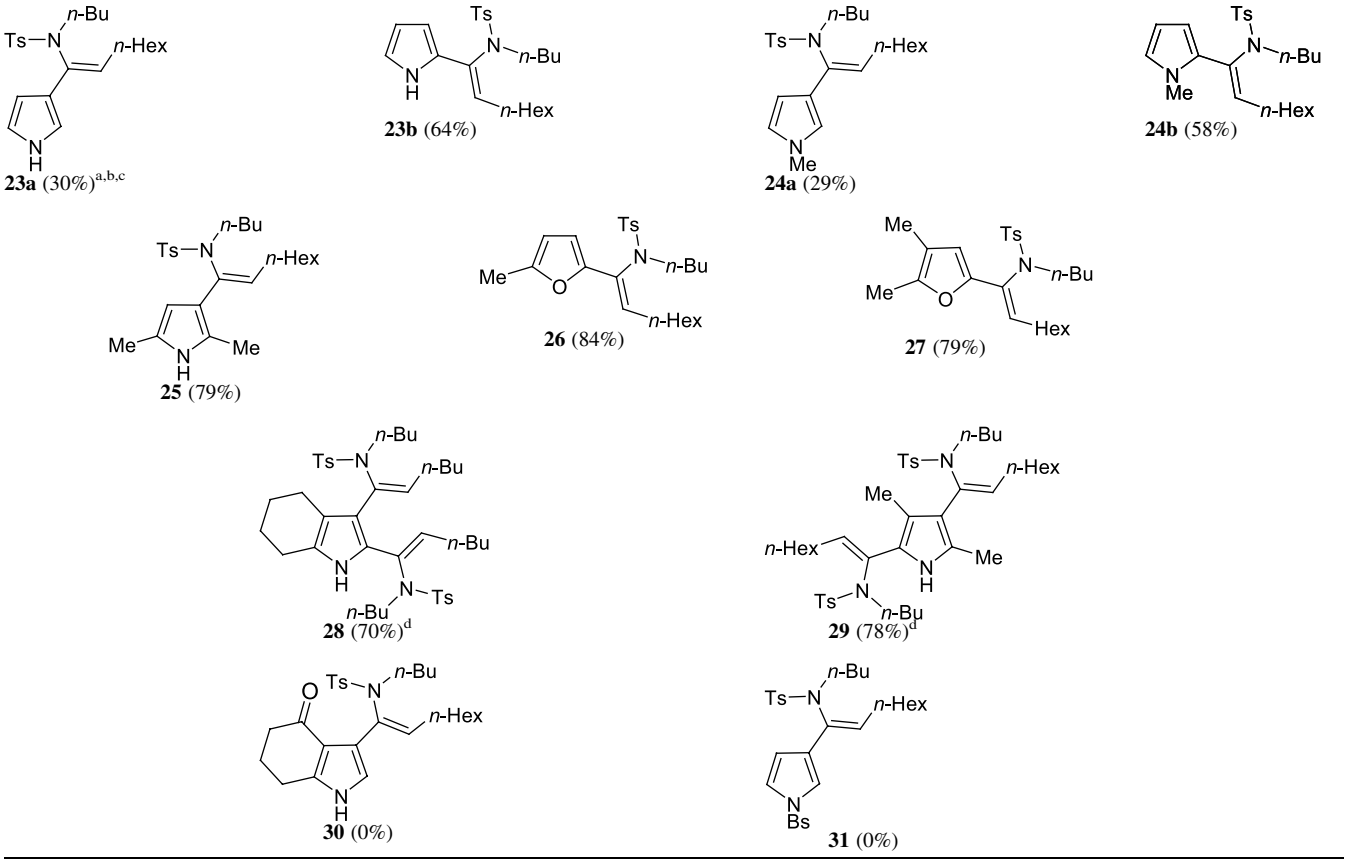
2.4. Couplings of pyrroles and furans with ynamide 1

Other nucleophilic heterocycles including furans and pyrroles were then investigated as summarized in Table 4. We were intrigued to discover that pyrroles also participated well in this vinylation process (**23**–**25**). Unfortunately, the hydroarylation involving pyrroles was only slightly regioselective affording C-3 and C-2 vinylation products in roughly 1/2 ratio. This result is somewhat unexpected, since C-2 carbon is generally believed to be the more nucleophilic site.[9d] Variation on the reaction temperature does not have significant affect on the ratio of C-2 and C-3 isomers.

When C-2 carbon was blocked, as with 2,3-dimethylpyrrole, C-3 vinylpyrrole **25** was produced as the only product in 79% yield. Vinylation of furans, on the other hand, showed excellent regioselectivity affording exclusively 2-vinylfurans in good yields (**26**,**27**). Following the lead that both the C-2 and C-3 positions of pyrroles can undergo the vinylation process, 2,3-divinylpyrrole, known to be excellent substrates for electrocyclic reactions, was prepared accordingly in good yields by simply employing an excess of the ynamides (**28**). Again, this vinylation protocol is not efficient for pyrroles with electron withdrawing substituents (**30**,**31**).

This new methodology has some distinct advantages over the existing methods: (1) There is no need to introduce protecting group on the indole nitrogen, (2) the hydroarylation employs unfunctionalized indoles, which circumvents the needs to introduce other functional groups, (3) the reaction is catalyzed by a Brønsted acid, which is more environmentally friendly than transition metals, and (4) more importantly, an enamide motif, which is otherwise difficult to introduce, is conveniently generated and can be employed for further transformations.

Table 4. Vinylation reactions involving pyrroles and furans

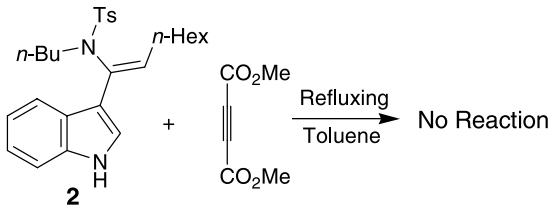


[a] All reactions were conducted at −35 °C, using ynamides and heteroarenes at the ratio of 1:2.5 with 10 mol% Tf_2NH in CH_2Cl_2 (0.1 M).
[b] Isolated yields for all entries.
[c] *Z*/*E*>20:1 by ^1H NMR unless otherwise indicated.
[d] Reactions were conducted at room temperature using ynamides and pyrroles at the ratio of 2:1.

2.5. Diels–Alder reaction of vinylindoles with DMAD

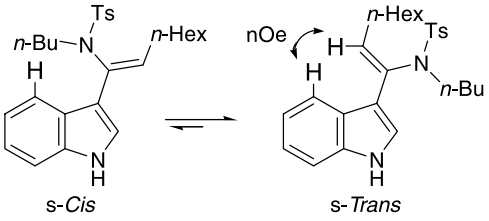
One of the most attractive features of this methodology is that the products can be considered synthetic equivalents to masked dienamides, which are excellent substrates for [4+2] cycloaddition reactions.[10,11,12,13,6b] In order to further demonstrate the synthetic utility of the new methodology, we investigated the Diels–Alder activity of these novel vinylindoles. Vinylindoles have been extensively studies for the Diels–Alder reactivations, which efficiently lead to the construction of polycyclic systems.[14]

Initial result was actually quite disappointing. No cycloaddition product was detected after refluxing a 0.1 M mixture of vinylindole **2** and DMAD in toluene for 24 h (Scheme 4).



Scheme 4. Attempted Diels–Alder reactions between vinylindole **2** and DMAD.

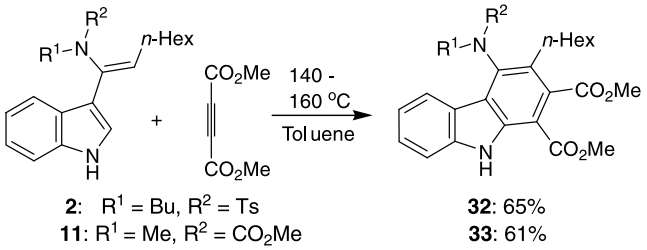
We attributed this unexpected lack of reactivity to the unfavorable configuration of the diene moiety.[14] The diene moiety of vinylindole **2** are expected to have two possible resonance stabilized configurations, *s*-cis and *s*-trans. Strong steric interaction between the butyl (or Ts) group on the nitrogen and the C-4 hydrogen seriously destabilizes the *s*-cis configuration, which is required for the Diels–Alder reaction. More importantly, the steric interaction between the bulky *N*-substituent and indole significant resist the rotation of the free diene single bond (Scheme 5).



Scheme 5. Configurations of vinylindole **2**.

Based on this rationale, we speculated that higher energy was required to access the *s*-cis configuration, and facilitate the intramolecular Diels–Alder reaction. To our delight, Diels–Alder reaction between vinylindole **2** and DMAD

proceeded smoothly in toluene at 160 °C, furnishing the oxidized cycloadduct carbazole **32** in good yield. Theoretically, reducing the steric bulkyness of the substitutions on the nitrogen would, to certain extend, favors the rotation of the diene single bond, and thus shift the resonance toward the *s*-cis configuration. This would in turn facilitate the cycloaddition reaction. As expected, vinylindole **11**, which has sterically less hindered substituents on the nitrogen, underwent Diels–Alder reaction at a lower temperature (140 °C) to afford carbazole **33** in 61% yield (Scheme 6).



Scheme 6. Diels–Alder reactions between vinylindoles and DMAD.

3. Conclusion

In conclusion, a Brønsted acid catalyzed hydroarylation of ynamide was developed, leading to the efficient construction of biologically and synthetically useful vinylpyrroles, vinylindoles, and vinylfurans with high regio- and stereocontrol. Diels–Alder reactivity of the vinylindole derivatives was probed and found to be efficient. Further applications of the methodology to the synthesis of alkaloids are currently under investigation.

4. Experimental

All reactions performed in flame-dried glassware under nitrogen atmosphere. Solvents were distilled prior to use. Reagents were used as purchased. ^{1}H and ^{13}C NMR spectra were obtained on Varian VI-300, VX-300, and VI-500 spectrometers using $CDCl_3$ or CD_2Cl_2 (except where noted) with TMS as standard. Melting points were determined using a Laboratory Devices MEL-TEMP. Infrared spectra were obtained using NaCl plates on a Midac M2000 FTIR. Low-resolution mass spectra were obtained using an Agilent 1100 series LS/MSD and are APCI. High-resolution mass spectral analyses performed at University of Minnesota Department of Chemistry Mass Spectrometry Laboratory. All spectral data obtained for new compounds are reported here.

4.1. General procedure for the hydroarylation reactions: synthesis of vinylindole 2

A solution of ynamide **1** (168.0 mg, 0.5 mmol) and indole (82.0 mg, 0.7 mmol) in 5 mL of dry methylene chloride was cooled to −35 °C. To this stirring mixture, a solution of Tf_2NH (14.0 mg, 0.05 mmol) in 0.35 mL of CH_2Cl_2 was added slowly, leading to a bright yellow solution, which became darker as reaction proceeded. The reaction was kept at −35 °C for 1 h with the reaction process monitored by TLC analysis. Upon completion, the reaction mixture was warmed up to room temperature, and the stir was continued for another 30 min. Several drops of triethylamine were then added to the reaction mixture to neutralize the acid, resulting in a colorless solution. The solution was concentrated in vacuo, and the reside was purified by silica gel column flash chromatography [gradient eluent: 10–25% EtOAc in hexane] to give vinylindole **2** (183.0 mg, 81%) as a white solid.

4.1.1. Vinylindole 2. (183 mg, 81% yield) R_f=0.30 (20% EtOAc in hexane); mp 140–142 °C; ^{1}H NMR (500 MHz, CD_2Cl_2) δ 8.47 (br s, 1H), 7.82 (d, 1H, J=8.0 Hz), 7.77 (d, 2H, J=8.0 Hz), 7.39 (d, 1H, J=8.0 Hz), 7.33 (d, 2H, J=8.0 Hz), 7.22 (t, 1H, J=8.0 Hz), 7.19 (t, 1H, J=8.0 Hz), 6.86 (d, 1H, J=2.5 Hz), 6.16 (t, 1H, J=7.5 Hz), 3.50–3.38 (m, 2H), 2.48 (s, 3H), 2.32–2.05 (m, 2H), 1.59–1.42 (m, 4H), 1.42–1.21 (m, 8H), 0.96 (t, 3H, J=7.0 Hz), 0.86 (t, 3H, J=7.0 Hz); ^{13}C NMR (125 MHz, CD_2Cl_2) δ 143.9, 138.9, 137.2, 132.7, 130.7, 130.1, 128.0, 126.1, 124.7, 122.8, 120.8, 120.4, 115.5, 112.0, 49.5, 32.3, 31.6, 30.1, 29.9, 29.7, 23.2, 21.8, 20.6, 14.4, 14.0; IR (film) cm^{-1} 3385 (m), 2958 (s), 2927 (s), 1459 (w), 1338 (m), 1159 (s), 1089 (m); mass spectrum (ESI): *m/e* (% relative intensity) 475.4 (100) (M+Na)$^+$, 453.4 (16) (M+H)$^+$, 365.2 (27), 337.2 (23), 285.2 (15); *m/e* calcd for $C_{27}H_{36}N_2O_2SNa$ 475.2390, found 475.2398.

4.1.2. Vinylindole 4. (58 mg, 90% yield) R_f=0.33 (20% EtOAc in hexane); mp 160–162 °C; ^{1}H NMR (300 MHz, CD_2Cl_2) δ 8.17 (br s, 1H), 7.96–7.90 (m, 1H), 7.44 (d, 2H, J=8.1 Hz), 7.44–7.33 (m, 1H), 7.25–7.18 (m, 4H), 6.13 (s, 1H), 6.08 (d, 1H, J=2.7 Hz), 3.61 (t, 2H, J=7.8 Hz), 2.45 (s, 3H), 1.76–1.46 (m, 5H), 1.29 (d, 18H, J=7.5 Hz), 0.89 (t, 3H, J=7.2 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 167.3, 167.0, 161.4, 159.8, 152.9, 151.4, 150.6, 146.6, 146.1, 144.3, 143.6, 140.5, 135.0, 73.9, 54.4, 45.0, 44.0, 43.1, 37.3, 36.0; IR (film) cm^{-1} 3378 (m), 2942 (s), 2866 (s), 1596 (m), 1344 (m), 1156 (s), 773 (s); mass spectrum (ESI): *m/e* (% relative intensity) 547.3 (100) (M+Na)$^+$, 525.3 (23) (M+H)$^+$; *m/e* calcd for $C_{30}H_{44}N_2O_2SSiNa$ 547.2785, found 547.2784.

4.1.3. Vinylindole 5. (75 mg, 79% yield) R_f=0.36 (20% EtOAc in hexane); light yellow oil; ^{1}H NMR (300 MHz, CD_2Cl_2) δ 8.34 (br s, 1H), 7.83 (d, 1H, J=7.2 Hz), 7.78 (d, 2H, J=8.4 Hz), 7.70–7.58 (m, 4H), 7.51–7.30 (m, 9H), 7.27 (dt, 1H, J=1.5, 7.2 Hz), 7.22 (dt, 1H, J=1.5, 7.2 Hz), 6.19 (t, 1H, J=7.5 Hz), 3.95–3.73 (m, 2H), 3.73–3.57 (m, 2H), 2.49 (s, 3H), 2.17–1.93 (m, 2H), 1.48–1.20 (m, 8H), 1.08 (s, 9H), 0.96 (t, 3H, J=6.9 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 144.0, 138.3, 137.3, 136.1, 136.0, 133.9, 132.0, 131.2, 130.1, 128.2, 128.1, 125.9, 125.0, 122.8, 120.8, 120.4, 115.2, 112.0, 62.6, 51.4, 32.3, 30.0, 29.9, 29.6, 27.1, 23.2, 21.8, 19.5, 14.5; IR (film) cm^{-1} 3391 (m), 2957 (m), 2930 (s), 2857 (m), 1428 (m), 1345 (m), 1161 (s), 1110 (s), 1090 (s); mass spectrum (ESI): *m/e* (% relative intensity) 701.8 (100) (M+Na)$^+$; *m/e* calcd for $C_{41}H_{50}N_2O_3SSiNa$ 701.3204, found 701.3218.

4.1.4. Vinylindole 6. (41 mg, 75% yield) R_f=0.28 (20% EtOAc in hexane); mp 131–132 °C; ^{1}H NMR (500 MHz, CD_2Cl_2) δ 8.36 (br s, 1H), 7.81 (d, 1H, J=8.0 Hz), 7.79 (d, 2H, J=8.0 Hz), 7.38 (d, 1H, J=8.0 Hz), 7.34 (d, 2H,

J=8.0 Hz), 7.22 (dt, 1H, J=1.0, 8.0 Hz), 7.17 (dt, 1H, J=1.0, 8.0 Hz), 6.95 (d, 1H, J=3.0 Hz), 6.15 (t, 1H, J=7.5 Hz), 6.88 (ddt, 1H, J=7.0, 10.5, 14.0 Hz), 5.05 (dd, 1H, J=1.5, 10.5 Hz), 5.03 (dd, 1H, J=1.5, 14.0 Hz), 4.18–4.00 (m, 2H), 2.47 (s, 3H), 2.16–1.96 (m, 2H), 1.50–1.25 (m, 8H), 0.95 (t, 3H, J=7.0 Hz); ^{13}C NMR (125 MHz, CD_2Cl_2) δ 144.0, 138.6, 137.3, 134.1, 132.4, 130.9, 130.1, 128.0, 125.9, 124.8, 122.8, 120.7, 120.4, 118.9, 112.0, 53.0, 32.3, 30.1, 29.9, 29.7, 23.2, 21.8, 14.5; IR (thin film) cm^{-1} 3393 (m), 2935 (w), 2926 (s), 1344 (s), 1159 (s); mass spectrum (ESI): *m/e* (% relative intensity) 459.6 (100) $(M+Na)^+$, 437.6 (22) $(M+H)^+$, 340.5 (55); HRMS (ESI) calcd for $C_{26}H_{32}N_2O_2SNa$ 459.2077, found 459.2075.

4.1.5. Vinylindole 7. (115 mg, 87% yield) R_f=0.23 (20% EtOAc in hexane); light yellow oil; ^{1}H NMR (300 MHz, CD_2Cl_2) δ 8.48 (br s, 1H), 7.93 (d, 1H, J=7.8 Hz), 7.91 (d, 2H, J=7.8 Hz), 7.66–7.56 (m, 3H), 7.48 (t, 1H, J=7.8 Hz), 7.42–7.25 (m, 7H), 7.18 (d, 1H, J=2.4 Hz), 6.37 (t, 1H, J=7.2 Hz), 2.30 (q, 2H, J=7.5 Hz), 1.58–1.20 (m, 8H), 0.99 (t, 3H, J=6.9 Hz); ^{13}C NMR (75 MHz, CD_2Cl_2) δ 141.9, 141.2, 137.2, 133.4, 133.3, 132.3, 129.5, 129.3, 128.3, 125.9, 125.7, 125.3, 124.0, 122.9, 120.9, 120.3, 116.1, 112.2, 32.2, 29.8, 29.6, 29.5, 23.1, 14.5; IR (thin film) cm^{-1} 3402 (s), 2955 (m), 2926 (s), 1353 (m), 1165 (s), 1092 (m); mass spectrum (ESI): *m/e* (% relative intensity) 481.2 (100) $(M+Na)^+$, 459.3 (14) $(M+H)^+$, 235.1 (8); HRMS (ESI) calcd for $C_{28}H_{31}N_2O_2S$ 459.2101, found 459.2113.

4.1.6. Vinylindole 8. (47 mg, 83% yield) R_f=0.12 (20% EtOAc in hexane); light yellow oil; ^{1}H NMR (300 MHz, CD_2Cl_2) δ 8.61 (br s, 1H), 7.88 (d, 1H, J=7.8 Hz), 7.44 (d, 1H, J=7.8 Hz), 7.33 (d, 1H, J=2.7 Hz), 7.26 (dt, 1H, J=2.7, 7.8 Hz), 7.22 (dt, 1H, J=2.7, 7.8 Hz), 6.21 (t, 1H, J=7.5 Hz), 3.53–3.37 (m, 2H), 3.06 (s, 3H), 2.55–2.40 (m, 2H), 1.70–1.28 (m, 12H), 1.00 (t, 3H, J=6.9 Hz), 0.93 (t, 3H, J=7.2 Hz); ^{13}C NMR (75 MHz, CD_2Cl_2) δ 137.3, 132.7, 130.9, 126.1, 124.6, 122.8, 120.8, 120.3, 115.1, 112.1, 49.3, 40.7, 32.4, 31.6, 29.9, 29.6, 23.2, 20.7, 14.4, 14.1; IR (thin film) cm^{-1} 3381 (m), 2958 (m), 2929 (m), 1326 (s), 1150 (m); mass spectrum (ESI): *m/e* (% relative intensity) 399.2 (100) $(M+Na)^+$, 377.3 (10) $(M+H)^+$; HRMS (ESI) calcd for $C_{21}H_{32}N_2O_2SNa$ 399.2077, found 399.2064.

4.1.7. Vinylindole 9. (54 mg, 93% yield) R_f=0.36 (20% EtOAc in hexane); mp 122–124 °C; ^{1}H NMR (300 MHz, CD_2Cl_2) δ 8.38 (br s, 1H), 8.34 (d, 2H, J=9.3 Hz), 8.04 (d, 2H, J=9.3 Hz), 7.85 (dd, 1H, J=1.5, 7.5 Hz), 7.42 (d, 1H, J=1.5, 7.5 Hz), 7.25 (dt, 1H, J=1.5, 7.5 Hz), 7.24 (dt, 1H, J=1.5, 7.5 Hz), 6.83 (d, 1H, J=2.7 Hz), 6.25 (t, 1H, J=7.5 Hz), 3.52 (t, 2H, J=7.5 Hz), 2.23–2.04 (m, 2H), 1.70–1.20 (m, 12H), 0.98 (t, 3H, J=6.3 Hz), 0.91 (t, 3H, J=7.2 Hz); ^{13}C NMR (75 MHz, CD_2Cl_2) δ 150.3, 146.9, 137.1, 133.1, 130.3, 129.2, 125.9, 124.6, 124.3, 123.0, 121.0, 120.3, 115.2, 112.1, 50.4, 32.3, 31.7, 30.0, 29.9, 29.8, 23.2, 20.6, 14.4, 14.0; IR (thin film) cm^{-1} 3408 (m), 2958 (m), 2929 (m), 1532 (s), 1351 (s), 1161 (m); mass spectrum (ESI): *m/e* (% relative intensity) 506.3 (100) $(M+Na)^+$, 484.3 (3) $(M+H)^+$; HRMS (ESI) calcd for $C_{26}H_{33}N_3O_4SNa$ 506.2084, found 506.2089.

4.1.8. Vinylindole 10. (46 mg, 87% yield) R_f=0.22 (20% EtOAc in hexane); mp 102–103 °C; ^{1}H NMR (300 MHz, CD_2Cl_2) δ 8.39 (br s, 1H), 7.90–7.83 (m, 3H), 7.42 (d, 1H, J=6.9 Hz), 7.24 (t, 1H, J=6.9 Hz), 7.20 (t, 1H, J=6.9 Hz), 7.03 (d, 2H, J=8.7 Hz), 6.92 (d, 1H, J=2.7 Hz), 6.20 (t, 1H, J=7.5 Hz), 3.92 (s, 3H), 3.45–3.31 (m, 2H), 2.29–2.09 (m, 2H), 1.60–1.20 (m, 12H), 0.98 (t, 2H, J=6.6 Hz), 0.86 (t, 3H, J=7.2 Hz); ^{13}C NMR (75 MHz, CD_2Cl_2) δ 163.4, 137.2, 133.3, 132.7, 130.8, 130.1, 126.1, 124.7, 122.7, 120.7, 120.4, 115.4, 114.5, 112.0, 56.2, 49.4, 32.3, 31.6, 30.1, 30.0, 29.7, 23.2, 20.6, 14.4, 14.0; IR (thin film) cm^{-1} 3392 (m), 2957 (m), 2927 (m), 1596 (m), 1334 (m), 1260 (m), 1153 (s); mass spectrum (ESI): *m/e* (% relative intensity) 491.6 (100) $(M+Na)^+$, 469.6 (33) $(M+H)^+$; HRMS (ESI) calcd for $C_{27}H_{37}N_2O_3S$ 469.2519, found 469.2523.

4.1.9. Vinylindole 11. (14 mg, 74% yield) R_f=0.10 (20% EtOAc in hexane); colorless oil; ^{1}H NMR (500 MHz, CD_2Cl_2) δ 8.50 (br s, 1H), 7.76 (d, 1H, J=8.0 Hz), 7.41 (d, 1H, J=8.0 Hz), 7.23 (t, 1H, J=7.5 Hz), 7.17 (t, 1H, J=7.5 Hz), 7.12 (d, 1H, J=3.0 Hz), 5.95 (t, 1H, J=7.5 Hz), 3.81 (s, J=3 Hz), 3.09 (s, 3H), 2.19 (q, 2H, J=7.5 Hz), 1.60–1.31 (m, 8H), 0.93 (t, 3H, J=7.0 Hz); ^{13}C NMR (75 MHz, CD_2Cl_2) δ 157.1, 137.6, 134.9, 126.2, 125.7, 125.3, 123.4, 123.3, 122.8, 120.8, 120.5, 115.0, 112.1, 36.4, 32.3, 29.8, 29.7, 28.1, 28.0, 23.2, 14.4; IR (thin film) cm^{-1} 3311 (m), 2955 (m), 2927 (m), 1686 (s), 1458 (m), 1374 (w), 1163 (w); mass spectrum (ESI): *m/e* (% relative intensity) 337.2 (100) $(M+Na)^+$, 315.2 (24) $(M+H)^+$; HRMS (ESI) calcd for $C_{19}H_{26}N_2O_2Na$ 337.1886, found 337.1887.

4.1.10. Vinylindole 12. (49 mg, 89% yield) R_f=0.16 (25% EtOAc in hexane); colorless oil; ^{1}H NMR (300 MHz, CD_2Cl_2) δ 9.26 (br s, 1H), 7.77 (d, 1H, J=8.1 Hz), 7.43 (d, 1H, J=8.1 Hz), 7.21 (dt, 1H, J=1.2, 7.2 Hz), 7.14 (dt, 1H, J=1.2, 7.2 Hz), 7.11 (d, 1H, J=2.7 Hz), 5.77 (dd, 1H, J=5.4, 8.7 Hz), 3.36 (s, 1H), 2.31–2.18 (m, 1H), 2.04–1.72 (m, 3H), 1.70–1.32 (m, 10H), 1.14 (s, 3H), 1.09 (s, 3H), 0.96 (t, 3H, J=6.9 Hz), 0.86 (s, 3H); ^{13}C NMR (75 MHz, CD_2Cl_2) δ 178.0, 137.0, 127.7, 127.5, 126.9, 123.9, 122.5, 120.3, 120.2, 115.0, 112.1, 68.4, 55.7, 49.8, 32.4, 31.2, 30.2, 29.9, 29.2, 27.3, 23.2, 19.7, 18.5, 14.5, 10.0; IR (thin film) cm^{-1} 3249 (m), 2959 (s), 2926 (s), 1686 (s), 1404 (w); mass spectrum (ESI): *m/e* (% relative intensity) 401.6 (100) $(M+Na)^+$, 379.5 (38) $(M+H)^+$, 318.5 (48); HRMS (ESI) calcd for $C_{25}H_{34}N_2ONa$ 401.2563, found 401.2563.

4.1.11. Vinylindole 13. (22 mg, 94% yield) R_f=0.35 (20% EtOAc in hexane); mp 89–90 °C; ^{1}H NMR (300 MHz, CD_2Cl_2) δ 8.16 (br s, 1H), 7.67 (d, 1H, J=7.8 Hz), 7.65 (d, 2H, J=8.1 Hz), 7.33 (d, 1H, J=7.8 Hz), 7.22 (d, 2H, J=8.1 Hz), 7.13 (dt, 1H, J=0.9, 7.2 Hz), 7.05 (dt, 1H, J=0.9, 7.2 Hz), 5.69 (t, 1H, J=7.2 Hz), 3.36 (t, 2H, J=7.8 Hz), 2.48 (s, 3H), 2.41 (s, 3H), 2.19 (q, 2H, J=7.2 Hz), 1.71–1.58 (m, 2H), 1.56–1.20 (m, 10H), 0.96 (t, 3H, J=6.9 Hz), 0.90 (t, 3H, J=7.5 Hz); ^{13}C NMR (75 MHz, CD_2Cl_2) δ 143.5, 138.6, 136.0, 135.4, 135.1, 130.0, 129.7, 128.6, 127.7, 121.7, 120.2, 119.8, 111.9, 110.7, 49.7, 32.2, 31.4, 30.0, 29.9, 29.8, 23.2, 21.7, 20.7, 14.4, 14.1, 13.2; IR (thin film) cm^{-1} 3385 (m), 2958 (s), 2928 (s), 1460 (m), 1334 (m), 1152 (s); mass spectrum (ESI): *m/e* (% relative intensity) 489.4 (100) $(M+Na)^+$, 467.4 (20) $(M+H)^+$; HRMS (ESI) calcd for $C_{28}H_{39}N_2O_2S$ 467.2727, found 467.2726.

4.1.12. Vinylindole 14. (24 mg, 91% yield) R_f=0.40 (20% EtOAc in hexane); mp 134–136 °C; ^{1}H NMR (300 MHz, CD_2Cl_2) δ 8.33 (br s, 1H), 7.86 (d, 1H, J=8.1 Hz), 7.65 (d, 2H, J=8.4 Hz), 7.50–7.38 (m, 4H), 7.33 (d, 2H, J=8.4 Hz), 7.24 (t, 1H, J=7.8 Hz), 7.15 (t, 1H, J=7.8 Hz), 7.03 (d, 2H, J=7.8 Hz), 6.00 (t, 1H, J=7.2 Hz), 2.93 (t, 2H, J=8.1 Hz), 2.39 (t, 2H, J=7.2 Hz), 2.34 (s, 3H), 1.60–1.20 (m, 10H), 0.97 (t, 3H, J=6.9 Hz), 0.93–0.80 (m, 2H), 0.74 (t, 3H, J=6.9 Hz); ^{13}C NMR (75 MHz, CD_2Cl_2) δ 142.5, 139.5, 137.5, 135.9, 135.0, 133.3, 129.4, 128.7, 128.5, 128.4, 128.1, 127.0, 122.3, 120.5, 120.0, 112.2, 110.3, 48.8, 31.6, 30.5, 29.2, 29.1, 28.8, 22.5, 20.9, 19.6, 13.7, 13.3; IR (thin film) cm^{-1} 3362 (m), 2958 (s), 2929 (s), 1456 (m), 1329 (m), 1152 (s); mass spectrum (ESI): *m/e* (% relative intensity) 551.4 (100) $(M+Na)^+$, 429.4 (26) $(M+H)^+$; HRMS (ESI) calcd for $C_{33}H_{40}N_2O_2SNa$ 551.2703, found 551.2722.

4.1.13. Vinylindole 15. (59 mg, 88%) R_f=0.88 (20% EtOAc in hexane); mp 100–102 °C; ^{1}H NMR (300 MHz, CD_2Cl_2) δ 8.35 (br s, 1H), 7.84 (d, 2H, J=8.4 Hz), 7.70 (d, 1H, J=7.5 Hz), 7.38 (d, 2H, J=8.4 Hz), 7.13 (t, 1H, J=7.5 Hz), 7.05 (d, 1H, J=7.5 Hz), 6.93 (d, 1H, J=2.4 Hz), 6.20 (t, 1H, J=7.2 Hz), 3.53–3.38 (m, 2H), 2.50 (s, 6H), 2.28–2.03 (m, 2H), 1.60–1.20 (m, 12H), 0.98 (t, 3H, J=6.6 Hz), 0.87 (t, 3H, J=7.2 Hz); ^{13}C NMR (75 MHz, CD_2Cl_2) δ 143.9, 138.6, 136.7, 132.5, 130.9, 130.1, 128.0, 125.6, 124.5, 123.3, 121.3, 120.9, 118.0, 115.9, 49.5, 32.3, 31.6, 30.1, 29.9, 29.7, 23.2, 21.8, 20.6, 16.8, 14.5, 14.1; IR (thin film) cm^{-1} 3372 (m), 2958 (s), 2927 (s), 1439 (w), 1347 (m), 1159 (s); mass spectrum (ESI): *m/e* (% relative intensity) 489.3 (100) $(M+Na)^+$, 467.3 (15) $(M+H)^+$; HRMS (ESI) calcd for $C_{28}H_{38}N_2O_2SNa$ 489.2546, found 489.2552.

4.1.14. Vinylindole 16. (51 mg, 84% yield) R_f=0.45 (20% EtOAc in hexane); mp 107–109 °C; ^{1}H NMR (300 MHz, CD_2Cl_2) δ 8.12 (br s, 1H), 7.57 (d, 2H, J=8.4 Hz), 7.42 (quint, 1H, J=4.5 Hz), 7.15 (d, 2H, J=8.4 Hz), 6.97 (d, 2H, J=4.5 Hz), 5.64 (t, 1H, J=7.2 Hz), 3.33 (t, 2H, J=7.8 Hz), 3.20 (m, 1H, J=6.9 Hz), 2.46 (s, 3H), 2.34 (s, 3H), 2.16 (q, 2H, J=7.8 Hz), 1.70–1.56 (m, 2H), 1.52–1.18 (m, 10H), 1.38 (s, 3H), 1.35 (s, 3H), 0.93 (t, 3H, J=6.9 Hz), 0.88 (t, 3H, J=7.5 Hz); ^{13}C NMR (75 MHz, CD_2Cl_2) δ 143.4, 138.5, 136.1, 134.6, 133.4, 130.9, 130.3, 129.6, 128.6, 127.7, 120.5, 117.6, 117.4, 112.4, 49.9, 32.3, 31.4, 30.0, 29.9, 29.9, 29.5, 23.2, 23.2, 21.7, 20.7, 14.4, 14.2, 13.2; IR (film) cm^{-1} 3379 (m), 2959 (s), 2928 (s), 1457 (w), 1335 (w), 1152 (m), 1089 (w); mass spectrum (ESI): *m/e* (% relative intensity) 531.4 (100) $(M+Na)^+$, 509.4 (36) $(M+H)^+$, 393.2 (4), 282.2 (8); *m/e* calcd for $C_{31}H_{45}N_2O_2S$ 509.3202, found 509.3218.

4.1.15. Vinylindole 17. (46 mg, 79% yield) R_f=0.22 (20% EtOAc in hexane); mp 105–107 °C; ^{1}H NMR (500 MHz, CD_2Cl_2) δ 8.55 (br s, 1H), 7.78 (d, 2H, J=8.0 Hz), 7.77 (d, 1H, J=2.0 Hz), 7.35 (d, 2H, J=8.0 Hz), 7.30 (d, 1H, J=8.5 Hz), 7.15 (dd, 1H, J=2.0, 8.5 Hz), 7.01 (d, 1H, J=2.0 Hz), 6.07 (t, 1H, J=7.5 Hz), 3.38 (t, 2H, J=7.5 Hz), 2.46 (s, 3H), 2.17–1.98 (m, 2H), 1.56–1.21 (m, 12H), 0.94 (t, 3H, J=7.2 Hz), 0.83 (t, 3H, J=7.5 Hz); ^{13}C NMR (125 MHz, CD_2Cl_2) δ 144.1, 138.3, 135.6, 132.8, 130.4, 130.1, 128.0, 127.1, 126.4, 126.2, 122.9, 119.8, 11.5, 113.2, 49.7, 32.3, 31.6, 30.0, 29.7, 23.2, 21.8, 20.6, 14.4, 14.0; IR (film) cm^{-1} 3374 (m), 2958 (s), 2928 (s), 1463 (m), 1344 (m), 1159 (s), 1090 (w); mass spectrum (ESI): *m/e* (% relative intensity) 509.3 (100) $(M+Na)^+$, 487.3 (6) $(M+H)^+$; *m/e* calcd for $C_{27}H_{35}ClN_2O_2SNa$ 509.2000, found 509.2010.

4.1.16. Vinylindole 18. (64 mg, 80% yield) R_f=0.31 (20% EtOAc in hexane); mp 141–143 °C; ^{1}H NMR (300 MHz, CD_2Cl_2) δ 8.64 (br s, 1H), 7.82 (d, 2H, J=8.1 Hz), 7.72 (d, 1H, J=8.7 Hz), 7.54 (d, 1H, J=2.5 Hz), 7.38 (d, 2H, J=8.1 Hz), 7.29 (dd, 1H, J=2.5, 8.7 Hz), 6.97 (d, 1H, J=2.7 Hz), 6.13 (t, 1H, J=7.0 Hz), 3.42 (t, 2H, J=7.5 Hz), 2.49 (s, 3H), 2.23–1.91 (m, 2H), 1.59–1.20 (m, 12H), 0.96 (t, 3H, J=6.9 Hz), 0.86 (t, 3H, J=7.2 Hz); ^{13}C NMR (75 MHz, CD_2Cl_2) δ 144.1, 138.3, 138.0, 132.9, 130.5, 130.1, 128.0, 125.4, 125.0, 123.8, 121.6, 116.0, 115.8, 115.0, 49.6, 32.3, 31.6, 30.0, 29.9, 29.6, 23.2, 21.8, 20.5, 14.4, 14.0; IR (film) cm^{-1} 3369 (m), 2959 (s), 2928 (s), 1455 (w), 1340 (m), 1158 (s), 1089 (w); mass spectrum (ESI): *m/e* (% relative intensity) 553.2 (100) $(M+Na)^+$, 531.2 (9) $(M+H)^+$, 376.2 (25); *m/e* calcd for $C_{27}H_{35}BrN_2O_2SNa$ 553.1495, found 553.1503.

4.1.17. Vinylindole 19. (41 mg, 85% yield) R_f=0.21 (20% EtOAc in hexane); mp 95–96 °C; ^{1}H NMR (300 MHz, CD_2Cl_2) δ 8.35 (br s, 1H), 7.81 (d, 2H, J=8.4 Hz), 7.37 (d, 2H, J=8.4 Hz), 7.31 (d, 1H, J=2.4 Hz), 7.30 (d, 1H, J=8.4 Hz), 6.89 (dd, 1H, J=2.4, 8.4 Hz), 6.86 (d, 1H, J=2.4 Hz), 6.12 (t, 1H, J=7.5 Hz), 3.90 (s, 3H), 3.48–3.32 (m, 2H), 2.49 (s, 3H), 2.28–2.04 (m, 2H), 1.59–1.20 (m, 12H), 0.96 (t, 3H, J=6.6 Hz), 0.86 (t, 3H, J=7.2 Hz); ^{13}C NMR (75 MHz, CD_2Cl_2) δ 154.5, 143.3, 137.9, 131.6, 130.1, 129.4, 127.4, 125.9, 124.8, 114.4, 111.9, 111.7, 102.0, 55.5, 48.7, 31.6, 30.9, 29.4, 29.2, 28.9, 22.5, 21.1, 19.8, 13.7, 13.3; IR (film) cm^{-1} 3387 (m), 2957 (m), 2929 (s), 1340 (m), 1158 (s); mass spectrum (ESI): *m/e* (% relative intensity) 505.3 (100) $(M+Na)^+$, 483.3 (45) $(M+H)^+$, 453.3 (6); *m/e* calcd for $C_{28}H_{39}N_2O_3S$ 483.2676, found 483.2687.

4.1.18. Vinylindole 20. (59 mg, 85% yield) R_f=0.48 (20% EtOAc in hexane); mp 109–110 °C; ^{1}H NMR (500 MHz, CD_2Cl_2) δ 7.82 (d, 1H, J=7.5 Hz), 7.78 (d, 2H, J=8.1 Hz), 7.35 (d, 2H, J=8.1 Hz), 7.32 (d, 1H, J=7.5 Hz), 7.27 (t, 1H, J=7.5 Hz), 7.19 (t, 1H, J=7.5 Hz), 6.57 (s, 1H), 6.15 (t, 1H, J=7.2 Hz), 3.65 (s, 3H), 3.58–3.33 (m, 2H), 2.48 (s, 3H), 2.32–2.04 (m, 2H), 1.59–1.20 (m, 12H), 0.96 (t, 3H, J=7.5 Hz), 0.86 (t, 3H, J=7.5 Hz); ^{13}C NMR (75 MHz, CD_2Cl_2) δ 143.8, 138.3, 137.8, 132.3, 130.7, 130.0, 129.3, 128.1, 126.7, 122.4, 120.5, 120.4, 113.6, 110.1, 49.6, 33.2, 32.4, 31.7, 30.1, 30.0, 23.3, 21.8, 20.6, 14.5, 14.1; IR (film) cm^{-1} 2957 (s), 2927 (s), 1349 (m), 1160 (s); mass spectrum (ESI): *m/e* (% relative intensity) 489.3 (100) $(M+Na)^+$, 467.3 (15) $(M+H)^+$, 242.3 (5); *m/e* calcd for $C_{28}H_{38}N_2O_2SNa$ 489.2546, found 489.2552.

4.1.19. Vinylpyrrole 23a. (12 mg, 30% yield) R_f=0.28 (20% EtOAc in hexane); yellow oil; ^{1}H NMR (300 MHz, CD_2Cl_2) δ 8.23 (br s, 1H), 7.76 (d, 2H, J=8.7 Hz), 7.34 (d, 2H, J=8.7 Hz), 6.68 (dd, 1H, J=2.7, 4.8 Hz), 6.45 (dd, 1H, J=1.8, 4.5 Hz), 6.14 (ddd, 1H, J=1.8, 2.7, 4.5 Hz), 5.94 (t, 1H, J=7.5 Hz), 3.52–3.26 (m, 2H), 2.47 (s, 3H), 2.20–1.86

(m, 2H), 1.59–1.44 (m, 2H), 1.44–1.20 (m, 10H), 0.96 (t, 3H, J=6.6 Hz), 0.88 (t, 3H, J=7.5 Hz); ^{13}C NMR (75 MHz, CD_2Cl_2) δ 143.7, 138.8, 131.8, 129.9, 129.5, 128.0, 123.5, 118.8, 117.0, 106.9, 49.7, 32.3, 31.7, 29.9, 29.8, 29.3, 23.2, 21.8, 20.6, 14.4, 14.1; IR (film) cm^{-1} 3399 (m), 2959 (s), 2928 (s), 1340 (m), 1276 (s), 1261 (s); mass spectrum (ESI): *m/e* (% relative intensity) 425.3 (100) (M+Na)$^+$, 403.3 (17) (M+H)$^+$, 393.3 (7), 349.2 (5); *m/e* calcd for $C_{23}H_{34}N_2O_2SNa$ 425.2233, found 425.2223.

4.1.20. Vinylpyrrole 23b. (26 mg, 64% yield) R_f=0.57 (20% EtOAc in hexane); light yellow oil; ^{1}H NMR (300 MHz, CD_2Cl_2) δ 8.81 (br s, 1H), 7.80 (d, 2H, J=8.4 Hz), 7.38 (d, 2H, J=8.4 Hz), 6.80–6.74 (m, 1H), 6.15–6.06 (m, 2H), 5.93 (t, 1H, J=7.5 Hz), 3.37 (t, 2H, J=7.5 Hz), 2.49 (s, 3H), 2.00–1.81 (m, 1H), 1.80–1.58 (m, 1H), 1.58–1.40 (m, 2H), 1.40–1.16 (m, 10H), 0.93 (t, 3H, J=7.2 Hz), 0.86 (t, 3H, J=7.2 Hz); ^{13}C NMR (75 MHz, CD_2Cl_2) δ 144.3, 137.6, 131.0, 130.8, 130.2, 129.4, 128.2, 118.6, 109.5, 107.8, 50.1, 32.2, 31.6, 29.8, 29.5, 28.9, 23.2, 21.8, 20.4, 14.4, 14.0; IR (film) cm^{-1} 3389 (m), 2957 (s), 2927 (s), 1343 (m), 1276 (s), 1261 (s), 1159 (s); mass spectrum (ESI): *m/e* (% relative intensity) 425.3 (100) (M+Na)$^+$, 403.3 (39) (M+H)$^+$, 393.3 (8), 349.2 (6); *m/e* calcd for $C_{23}H_{34}N_2O_2SNa$ 425.2233, found 425.2222.

4.1.21. Vinylpyrrole 24a. (12 mg, 29% yield) R_f=0.29 (20% EtOAc in hexane); light yellow oil; ^{1}H NMR (500 MHz, CD_2Cl_2) δ 7.71 (d, 2H, J=8.5 Hz), 7.31 (d, 2H, J=8.5 Hz), 6.44 (t, 1H, J=2.5 Hz), 6.14 (t, 1H, J=2.0 Hz), 5.98 (t, 1H, J=2.5 Hz), 5.86 (t, 1H, J=7.0 Hz), 3.49 (s, 3H), 3.48–3.37 (m, 1H), 3.37–3.27 (m, 1H), 2.45 (s, 3H), 2.14–2.05 (m, 1H), 2.05–1.90 (m, 1H), 1.57–1.42 (m, 2H), 1.42–1.20 (m, 10H), 0.92 (t, 3H, J=7.0 Hz), 0.87 (t, 3H, J=7.0 Hz); ^{13}C NMR (125 MHz, CD_2Cl_2) δ 143.6, 138.9, 131.8, 129.9, 128.8, 128.0, 122.5, 120.9, 106.8, 49.7, 36.5, 32.3, 31.8, 29.9, 29.3, 23.2, 21.8, 20.6, 14.4, 14.1; IR (film) cm^{-1} 2957 (m), 2928 (m), 1345 (m), 1276 (s), 1261 (m), 1158 (m); mass spectrum (ESI): *m/e* (% relative intensity) 439.3 (100) (M+Na)$^+$, 417.3 (78) (M+H)$^+$; *m/e* calcd for $C_{24}H_{36}N_2O_2SNa$ 439.2390, found 439.2384.

4.1.22. Vinylpyrrole 24b. (24 mg, 58% yield) R_f=0.63 (20% EtOAc in hexane); light yellow oil; ^{1}H NMR (300 MHz, CD_2Cl_2) δ 7.59 (d, 2H, J=8.4 Hz), 7.31 (d, 2H, J=8.4 Hz), 6.34 (t, 1H, J=2.1 Hz), 5.97 (dd, 1H, J=2.7, 3.6 Hz), 5.68 (t, 1H, J=7.2 Hz), 5.67–5.63 (m, 1H), 3.70 (s, 3H), 3.30 (t, 2H, J=7.2 Hz), 2.46 (s, 3H), 2.31 (q, 2H, J=7.2 Hz), 1.64–1.24 (m, 12H), 0.96 (t, 3H, J=6.6 Hz), 0.92 (t, 3H, J=7.2 Hz); ^{13}C NMR (75 MHz, CD_2Cl_2) δ 143.7, 138.2, 136.9, 130.8, 129.9, 127.9, 123.9, 109.7, 107.5, 49.0, 35.5, 32.3, 31.4, 29.9, 29.8, 23.2, 21.8, 20.6, 14.4, 14.1; IR (film) cm^{-1} 2957 (m), 2928 (m), 1467 (w), 1346 (m), 1159 (m); mass spectrum (ESI): *m/e* (% relative intensity) 439.3 (100) (M+Na)$^+$, 417.3 (35) (M+H)$^+$; *m/e* calcd for $C_{24}H_{36}N_2O_2SNa$ 439.2390, found 439.2402.

4.1.23. Vinylpyrrole 25. (51 mg, 79% yield) R_f=0.35 (20% EtOAc in hexane); light yellow oil; ^{1}H NMR (300 MHz, CD_2Cl_2) δ 7.71 (d, 2H, J=8.4 Hz), 7.31 (d, 2H, J=8.4 Hz), 5.51 (t, 1H, J=7.2 Hz), 5.14 (br s, 1H), 3.55–3.05 (m, 2H), 2.47 (s, 3H), 2.27 (s, 3H), 2.27–2.10 (m, 2H), 2.08 (s, 3H), 1.56–1.24 (m, 12H), 0.95 (t, 3H, J=6.6 Hz), 0.88 (t, 3H, J=7.2 Hz); ^{13}C NMR (75 MHz, CD_2Cl_2) δ 143.5, 138.8, 132.8, 131.3, 129.8, 128.0, 125.4, 125.2, 118.4, 106.2, 48.8, 32.3, 31.4, 30.1, 29.9, 29.7, 23.2, 21.7, 20.5, 14.4, 14.1, 12.9, 12.8; IR (film) cm^{-1} 3378 (m), 2957 (m), 2926 (m), 1337 (m), 1154 (m); mass spectrum (ESI): *m/e* (% relative intensity) 453.3 (100) (M+Na)$^+$, 431.3 (42) (M+H)$^+$; *m/e* calcd for $C_{25}H_{39}N_2O_2S$ 431.2727, found 431.2706.

4.1.24. Vinylfuran 26. (35 mg, 84% yield) R_f=0.64 (20% EtOAc in hexane); light yellow oil; ^{1}H NMR (500 MHz, CD_2Cl_2) δ 7.70 (d, 2H, J=8.5 Hz), 7.30 (d, 2H, J=8.5 Hz), 6.20 (t, 1H, J=7.5 Hz), 5.86 (d, 1H, J=3.5 Hz), 5.72 (d, 1H, J=3.5 Hz), 3.52–3.42 (m, 1H), 3.38–3.26 (m, 1H), 2.45 (s, 3H), 2.19 (s, 3H), 2.25–2.05 (m, 2H), 1.60–1.24 (m, 12H), 0.92 (t, 3H, J=7.0 Hz), 0.89 (t, 3H, J=7.5 Hz); ^{13}C NMR (75 MHz, CD_2Cl_2) δ 152.3, 150.6, 143.9, 138.3, 132.1, 129.9, 128.1, 128.0, 108.7, 107.6, 50.0, 32.3, 31.7, 29.9, 29.6, 29.0, 23.2, 21.8, 20.6, 14.4, 14.1, 13.8; IR (film) cm^{-1} 2958 (s), 2928 (s), 1350 (m), 1162 (m); mass spectrum (ESI): *m/e* (% relative intensity) 440.3 (100) (M+Na)$^+$, 418.3 (28) (M+H)$^+$, 376.2 (18); *m/e* calcd for $C_{24}H_{35}NO_3SNa$ 440.2230, found 440.2241.

4.1.25. Vinylfuran 27. (41 mg, 79% yield) R_f=0.68 (20% EtOAc in hexane); light yellow oil; ^{1}H NMR (300 MHz, CD_2Cl_2) δ 7.72 (d, 2H, J=8.4 Hz), 7.33 (d, 2H, J=8.4 Hz), 6.18 (t, 1H, J=7.5 Hz), 5.60 (s, 1H), 3.55–3.24 (m, 2H), 2.46 (s, 3H), 2.28–2.00 (m, 2H), 2.12 (s, 3H), 1.84 (s, 3H), 1.60–1.24 (m, 12H), 0.96 (t, 3H, J=6.6 Hz), 0.91 (t, 3H, J=7.2 Hz); ^{13}C NMR (75 MHz, CD_2Cl_2) δ 149.1, 147.5, 143.8, 138.3, 131.4, 129.9, 128.1, 127.9, 116.2, 111.3, 50.0, 32.3, 31.7, 29.9, 29.6, 29.0, 23.2, 21.7, 20.6, 14.4, 14.1, 11.6, 10.0; IR (film) cm^{-1} 2958 (s), 2927 (s), 1352 (m), 1162 (s); mass spectrum (ESI): *m/e* (% relative intensity) 454.3 (100) (M+Na)$^+$, 432.3 (40) (M+H)$^+$; *m/e* calcd for $C_{25}H_{37}N_2O_3SNa$ 454.2386, found 454.2395.

4.1.26. Divinylpyrrole 28. (38 mg, 70% yield) R_f=0.55 (20% EtOAc in hexane); yellow oil; ^{1}H NMR (300 MHz, CD_2Cl_2) δ 8.55 (br s, 1H), 7.83 (d, 2H, J=8.1 Hz), 7.55 (d, 2H, J=8.1 Hz), 7.40 (d, 2H, J=8.1 Hz), 7.23 (d, 2H, J=8.1 Hz), 6.33 (t, 1H, J=7.2 Hz), 5.62 (t, 1H, J=7.2 Hz), 3.43–3.23 (m, 4H), 2.49 (s, 3H), 2.55–2.48 (m, 2H), 2.42 (s, 3H), 2.40–2.18 (m, 4H), 1.80–1.09 (m, 22H), 1.09–0.81 (m, 12H); ^{13}C NMR (75 MHz, CD_2Cl_2) δ 144.6, 143.2, 138.7, 137.7, 136.0, 134.1, 131.8, 130.3, 129.5, 128.3, 127.9, 126.8, 126.2, 119.4, 51.0, 50.5, 32.1, 32.0, 31.9, 31.6, 29.8, 29.1, 24.2, 23.5, 23.3, 23.1, 21.8, 21.7, 20.8, 20.5, 14.4, 14.2, 14.1, 14.0; IR (film) cm^{-1} 3360 (w), 2957 (m), 2930 (m), 1339 (m), 1157 (m); mass spectrum (ESI): *m/e* (% relative intensity) 758.4 (100) (M+Na)$^+$, 736.4 (39) (M+H)$^+$, 580.4 (28); *m/e* calcd for $C_{42}H_{61}N_3O_4S_2Na$ 758.3996, found 758.4005.

4.1.27. Divinylpyrrole 29. (57 mg, 78% yield) R_f=0.56 (20% EtOAc in hexane); yellow oil; ^{1}H NMR (300 MHz, CD_2Cl_2) δ 8.22 (br s, 1H), 7.84 (d, 2H, J=8.1 Hz), 7.56 (d, 2H, J=8.1 Hz), 7.44 (d, 2H, J=8.1 Hz), 7.29 (d, 2H, J=8.1 Hz), 5.48 (t, 2H, J=7.5 Hz), 5.42 (t, 1H, J=7.5 Hz), 3.56–3.00 (m, 4H), 2.51 (s, 3H), 2.44 (s, 3H), 2.28–2.16 (m, 2H), 2.11 (s, 3H), 1.94 (s, 3H), 1.80–1.09 (m, 26H),

1.02–0.80 (m, 12H); ^{13}C NMR (75 MHz, CD_2Cl_2) δ 144.6, 143.2, 139.1, 137.8, 135.9, 135.3, 131.4, 130.4, 129.6, 128.3, 127.7, 127.4, 127.2, 124.1, 119.5, 119.1, 50.0, 49.3, 32.2, 32.1, 31.5, 31.3, 30.0, 29.9, 29.8, 29.8, 29.1, 23.2, 23.2, 21.8, 21.7, 20.7, 20.4, 14.4, 14.1, 14.0, 12.6, 12.4; IR (film) cm^{-1} 3435 (w), 2958 (s), 2928 (s), 1341 (s), 1157 (s); mass spectrum (ESI): *m/e* (% relative intensity) 788.6 (100) $(M+Na)^+$; *m/e* calcd for $C_{44}H_{67}N_3O_4S_2Na$ 788.4465, found 788.4480.

4.1.28. Carbazole 32. A solution of vinylindole **2** (21.0 mg, 0.044 mmol) and DMAD (13.0 mg, 0.09 mmol) in toluene (0.45 mL) was heated at 160 °C in a seal tube. The reaction was monitored by TLC analysis. Upon completion, the solution was cooled to room temperature with stirring. White precipitation formed at this point, which was filtered and washed with cold toluene. The white powder was dried under vacuo to afford carbazole **32** (17.1 mg, 65% yield). R_f=0.44 (33% EtOAc in hexane); mp 258–260 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.76 (s, 1H), 8.28 (d, 1H, J=8.0 Hz), 7.27 (d, 2H, J=8.0 Hz), 7.42 (t, 1H, J=7.5 Hz), 7.40–7.29 (m, 3H, J=7.5 Hz), 4.22–4.01 (m, 1H), 4.05 (s, 3H), 3.94 (s, 3H), 3.55–3.44 (m, 1H), 2.45 (s, 3H), 2.44–2.32 (m, 1H), 2.13–1.98 (m, 1H), 1.82–1.66 (m, 1H), 1.66–1.39 (m, 2H), 1.39–1.03 (m, 9H), 0.89 (t, 3H, J=7.0 Hz), 0.81 (t, 3H, J=7.0 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 169.9, 166.4, 143.8, 140.5, 139.0, 137.9, 136.2, 134.4, 131.5, 130.0, 127.7, 127.5, 126.6, 124.1, 121.0, 120.3, 110.9, 110.0, 52.9, 52.6, 51.5, 31.2, 30.6, 30.5, 30.2, 28.8, 22.8, 21.7, 20.4, 14.2, 13.8; IR (film) cm^{-1} 3409 (m), 2956 (m), 1731 (s), 1722 (s), 1341 (m), 1210 (m), 1161 (m); mass spectrum (ESI): *m/e* (% relative intensity) 615.1 (70) $(M+Na)^+$, 561.1 (100); *m/e* calcd for $C_{33}H_{40}N_2O_6SNa$ 615.2500, found 615.2524.

4.1.29. Carbazole 33. A solution of vinylindole **11** (15.0 mg, 0.048 mmol) and DMAD (14.0 mg, 0.10 mmol) in toluene (0.5 mL) was heated at 140 °C in a seal tube. The reaction was monitored by TLC analysis. Upon completion, the solution was cooled to room temperature. Evaporation of the solvent under reduced pressure afforded a residue, which was purified by silica gel flash chromatograph to afford carbazole **33** as a light yellow solid (13.2 mg, 61% yield). R_f=0.56 (33% EtOAc in hexane); mp 186–187 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.97 (br s, 1H), 7.87 (d, 1H, J=8.1 Hz), 7.60–7.50 (m, 2H), 7.36–7.30 (m, 1H), 4.06 (s, 3H), 4.02 (s, 3H), 3.58 (s, 3H), 3.40 (s, 3H), 2.78–2.58 (m, 2H), 1.64–1.26 (m, 8H), 0.94 (t, 3H, J=6.9 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.0, 166.4, 156.6, 140.4, 139.9, 139.5, 134.5, 129.1, 127.6, 122.7, 122.0, 121.2, 120.5, 111.4, 108.6, 53.3, 52.9, 52.7, 36.5, 31.7, 31.3, 30.2, 29.2, 22.7, 14.3; IR (film) cm^{-1} 3346 (w), 2953 (m), 1696 (br s), 1210 (m); mass spectrum (ESI): *m/e* (% relative intensity) 477.2 (100) $(M+Na)^+$; *m/e* calcd for $C_{25}H_{30}N_2O_6Na$ 477.1996, found 477.1994.

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