A simple synthesis of *N*-vinylpyrrole, *N*-vinylindole and *N*-vinylcarbazole derivatives

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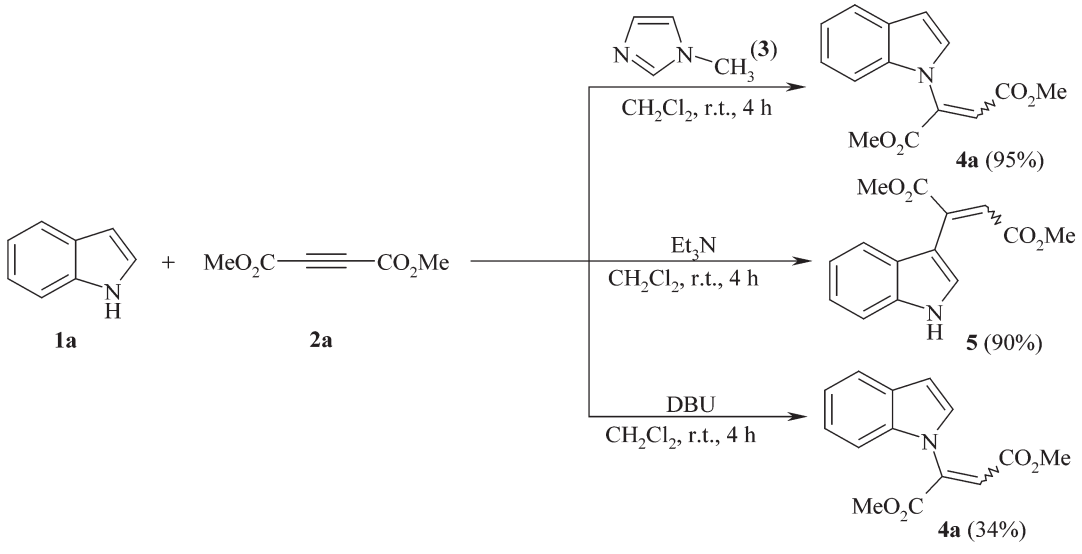
Reaction of pyrrole, indole or carbazole with dialkyl acetylenedicarboxylates catalysed by *N*-methylimidazole provides a simple and efficient route for the synthesis of *N*-vinylpyrrole, *N*-vinylindole and *N*-vinylcarbazole derivatives in high yields.

Keywords: *N*-vinylpyrrole, *N*-vinylindole, *N*-vinylcarbazole, acetylenic esters, *N*-methylimidazole

Indole and pyrrole derivatives are among the most important heterocyclic building blocks, since these ring systems can be widely found in natural products and pharmaceuticals.[1,2] Among these heterocycles, their vinyl derivatives have attracted major attention. Vinylpyrroles and vinylindoles are common structural units in natural products, and are important organic skeletons that are frequently employed in the synthesis of alkaloids and other biologically important heterocycles.[3] In addition, vinylpyrroles have been extensively studied in material science as vinyl monomers, molecular switches, photo- and electroconducting materials.[4,10] As a result, much effort has been devoted to the development of new methodologies for efficient synthesis of vinylpyrroles and vinylindoles.[5–18] Because of their electron-rich characteristics, pyrrole and indole react readily with a wide range of electrophiles. Substitution of pyrrole usually takes place most readily at the 2-position while indole almost always reacts with electrophiles at the 3-position.[5] Pyrrole and its derivatives were reported to react with electron-deficient acetylenes to produce 2-vinylpyrrole derivatives, without observing any traces of *N*-vinylpyrrole derivatives.[6–8,11] The reaction of indole was also reported with different electron-deficient acetylenes,[5,9] all of them afforded 3-vinylindole derivatives. Introduction of the vinyl group in the pyrrole ring, in particular at the nitrogen atom, permits a substantial increase in the potential of these compounds by converting them into monomers and also reveals them as reactive building blocks for selective synthesis of important technological materials. Poly-*N*-vinylazopyrroles, as well as poly-*N*-vinylcarbazole, can be photoconductors of interest for the creation of electrophotographic materials.[10] *N*-vinylpyrrole can be prepared by the reaction of pyrrole with acetylene in the presence of strong bases.[10] *N*-vinylation of pyrrole and indole derivatives with vinyl triflates catalysed by palladium complexes has also been reported.[9] The reaction of indole derivatives with dimethyl acetylenedicarboxylate in the presence of bases such as isoquinoline or quinoline is reported to produce a triadduct 3-indolyl-1,2-dihydro-2-isoquinolinyl-2-butenedioates.[12] Similar products were obtained from the reaction between pyrrole, DMAD and isoquinoline. Here we report the results of our study on the reaction between pyrrole, indole or carbazole and acetylene diesters in the presence of *N*-methylimidazole.

Results and discussion

Treatment of indole (**1a**) with DMAD (**2a**) and *N*-methylimidazole (**3**) in dichloromethane at room temperature for 4 h, after silica gel column chromatography afforded 2-(1-indolyl)-2-butene-1,4-dicarboxylate **4a** as a mixture of geometrical isomers in 95% yield as the only product (Scheme 1). The isomer ratio *E*/*Z* can be obtained from the ^{1}H NMR spectrum of compound **4a** to be 73/27. The vinyl proton of the Z isomer is expected to resonate at higher fields than the proton of the *E* isomer.[19]



Scheme 1 Reaction of indole with DMAD catalysed by *N*-methyimidazole, triethylamine or DBU.

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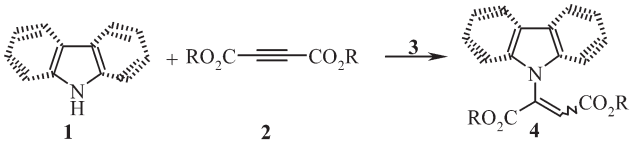
We also examined the reaction of indole and DMAD in the presence of other nitrogen bases such as diaza[5,3,0]bicycloun decane (DBU) and triethylamine. As shown in Scheme 1, the reaction of indole, AMAD and DBU led to a complex mixture of products from which *N*-vinylindole **4a** was isolated in 34% yield, while the reaction of indole and DMAD in the presence of 1 equiv. of triethylamine afforded 3-vinylindole **5** in 90% yield as the sole product.

With regard to the above results and our interest in preparing *N*-vinylheterocycles, we chose *N*-methylimidazole as the base and investigated the reaction of heterocyclic compounds such as indole, pyrrole, carbazole, benzotriazole and saccharin with dialkyl acetylenedicarboxylates (DAADs) in the presence of this compound. As shown in Table 1, indole underwent a smooth reaction with DMAD, diethyl acetylenedicarboxylate (DEAD), and ditert-butyl acetylenedicarboxylate (DTAD) in the presence of *N*-methylimidazole to produce the corresponding *N*-vinylindole derivatives in high yields. Under similar conditions, pyrrole reacted with DAADs to produce *N*-vinylpyrroles in good yields. Similar reaction between carbazole and acetylene diesters afforded *N*-vinylcarbazoles as the only product in good yields. When benzotriazole was treated with DMAD and *N*-methylimidazole a complex mixture was obtained from which no product was isolated. We also could not obtain any product from the complex mixture of the reaction between saccharin, DMAD and *N*-methylimidazole.

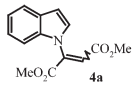
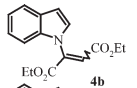
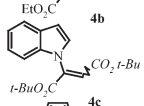
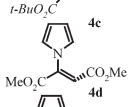
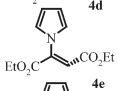
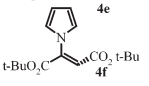
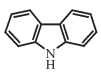
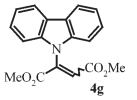
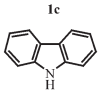
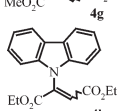
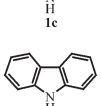
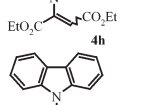
The structure of products could be easily deduced from their NMR, IR and mass spectral and elemental analytical data. For example the ^{1}H NMR spectrum of dimethyl 2-(indole-1-yl)-2-butane-1,4 dicarboxylate (**4a**) showed two sets of signals due to two geometric isomers. The methoxy protons of the major isomer were observed at δ = 3.58 and 3.89 ppm as two sharp singlets. The vinyl proton for the major isomer resonated at δ = 7.10 ppm which is in agreement with the *Z*-geometry of the double bond. The indole protons resonated at δ = 6.71 (1 H, doublet, J = 4 H_Z), 7.12–7.31 (4 H, multiplets) and 7.63 (1 H, d, J = 8 H_Z). The corresponding signals for the *E*-isomer were observed at δ = 3.86, 4.05 (methoxy groups), 6.35 (vinyl proton), 6.74 (d, J = 8 H_Z, C-3 indole proton), 7.12–7.31 (4 CH of indole) and 7.62 (d, J = 4 H_Z, C-2 indole proton). ^{13}C NMR of compound **4a** exhibited 14 distinct signals for each isomer, consistent with the proposed structure.

In conclusion, we report here a simple and efficient method for the synthesis of *N*-vinylpyrrole, *N*-vinylindole or *N*-vinylcarbazole by the addition reaction of pyrrole, indole or carbazole with dialkyl acetylenedicarboxylates catalysed by *N*-methylimidazole. The reported method has the advantages that the reaction is performed under neutral conditions and the starting materials are mixed without any activation or modifications.

Table 1 Reaction of pyrrole, indole or carbazole with dialkyl acetylenedicarboxylates catalysed by *N*-methylimidazole



1 2 4

Entry	1	R	Product	Yield*(%)	E:Z Ratio**
1	 1a	Me	 4a	95	95
2	 1a	Et	 4b	95	95
3	 1a	*t*-Bu	 4c	100	100
4	 1b	Me	 4d	95	95
5	 1b	Et	 4e	95	95
6	 1b	*t*-Bu	 4f	98	98
7	 1c	Me	 4g	98	98
8	 1c	Et	 4h	100	100
9	 1c	*t*-Bu	 4i	100	100
10	 1d	Me	Non		
11	 1e	Me	Non		

*Isolated Yields.
**Determined using ^{1}H NMR spectra.

Experimental

Melting points were determined with an Electrothermal 9100 apparatus. Elemental analyses were performed using a Costech ECS 4010 CHNS-O analyser at analytical laboratory of Islamic Azad University Yazd branch. Mass spectra were recorded on a FINNIGAN-MAT 8430 mass spectrometer operating at an ionisation potential of 70 eV. IR spectra were recorded on a Shimadzu IR-470 spectrometer.^{1}H and ^{13}C NMR spectra were recorded on Bruker DRX-500 Avance spectrometer at solution in $CDCl_3$ using TMS as internal standard. The chemicals used in this work were purchased from Fluka (Buchs, Switzerland) and were used without further purification.

General procedure:
To a magnetically stirred solution of indole (1 mmol) and *N*-methylimidazole (0.2 mmol) in dichloromethane (10ml) was added dropwise a mixture of DMAD (1 mmol) in dichloromethane (5ml) at room temperature. The reaction mixture was then stirred for 4h. The solvent was removed under reduced pressure and the residue was purified by silica gel column chromatography using hexane-ethyl acetate (4:1) as eluent. The solvent was removed under reduced pressure to afford the product as a yellow oil.

Dimethyl 2-(indol-1-yl)-2-butene-1,4-dicarboxylate **(4a):** Yellow oil., IR (KB_r) (ν_{max}, cm^{-1}): 1722 (C=O, ester). Anal. Calcd for $C_{14}H_{13}NO_4$: C, 64.91; H, 5.17; N, 5.44. Found: C, 64.72; H, 4.90; N, 5.51%. MS (*m/z*, %): 259 (M^+, 8). NMR data isomer *Z*: ^{1}H NMR (500 MHz, $CDCl_3$): δ = 3.58 and 3.89 (6 H, 2 s, 2 OCH_3), 6.71 (1H, d, $^3J_{HH}$ = 4 H_Z, 1CH of indole), 7.10 (1 H, s, $CH_{olefine}$), 7.12–7.31 (4 H, m, 4 CH of indole), 7.63 (1H, d, $^3J_{HH}$ = 8 H_Z, 2CH of indole). ^{13}C NMR (125.75 MH_Z, $CDCl_3$): δ = 52.59, 53.80 (2 OCH_3), 105.10, 110.67, 121.37, 121.65, 123.11, 129.15 (6 CH indole), 131.13 and 137.57 (2 C indole), 123.70 (=CH), 107.25 (=C), 164.27 and 164.43 (2 C=O). NMR data isomer *E*: ^{1}H NMR (500 MHz, $CDCl_3$): δ = 3.86 and 4.05 (6 H, 2 s, 2 OCH_3), 6.35 (1 H, s, $CH_{olefine}$), 6.74 (1H, d, $^3J_{HH}$ = 4 H_Z, 2CH of indole), 7.12–7.31 (4 H, m, 4 CH of indole), 7.62 (1H, d, $^3J_{HH}$ = 8 H_Z, 1CH of indole),. ^{13}C NMR (125.75 MH_Z, $CDCl_3$): δ = 52.46, 53.83 (2 OCH_3), 108.17, 112.47, 122.19, 122.94, 129.33 (6 CH indole), 135.33 and 136.95 (2 C indole), 124.46 (=CH), 111.52 (=C), 164.87 and 166.23 (2 C=O).

Diethyl 2-(indol-1-yl)- 2-butene-1,4-dicarboxylate **(4b):** Yellow oil., IR (KBr)(ν_{max}, cm^{-1}): 1719 (C=O, ester). Anal. Calcd for $C_{16}H_{17}NO_4$: C, 66.95; H, 6.02; N, 4.94. Found: C, 67.06; H, 6.22; N, 4.63%. MS (*m/z*, %): 287 (M^+, 15). NMR data isomer *Z*: ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.71 and 1.10 (6 H, 2 t, $^3J_{HH}$ = 7 H_Z, 2 CH_3), 3.75 and 4.11 (4 H, 2 q, $^3J_{HH}$ = 7 H_Z, 2 OCH_2), 6.46 (1H, d, $^3J_{HH}$ = 4 H_Z, 1CH of indole), 6.86 (1 H, s, $CH_{olefine}$), 6.87–7.26 (4 H, m, 4 CH of indole), 7.41 (1H, d, $^3J_{HH}$ = 8 H_Z, 2CH of indole),. ^{13}C NMR (125.75 MH_Z, $CDCl_3$): δ = 14.06, 14.47 (2 CH3), 61.73, 63.16 (2 OCH_2), 104.92, 110.85, 121.29, 121.56, 122.98, 129.19 (6 CH indole), 131.13

and 137.40 (2 C indole), 124.28 (=CH), 107.85 (=C), 163.93 and 164.46 (2 C=O). NMR data isomer *E*: ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.16 and 1.20 (6 H, 2 t, $^3J_{HH}$ = 7 H_Z, 2 CH_3), 4.07 and 4.28 (4 H, 2 q, $^3J_{HH}$ = 7 H_Z, 2 OCH_2), 6.04 (1 H, s, $CH_{olefine}$), 6.51 (1H, d, $^3J_{HH}$ = 4 H_Z, 1CH of indole), 6.87-7.26 (4 H, m, 4 CH of indole), 7.47 (1H, d, $^3J_{HH}$ = 8 H_Z, 2CH of indole). ^{13}C NMR (125.75 MH_Z, $CDCl_3$): δ = 14.39, 14.50 (2 CH3), 61.77, 63.08 (2 OCH_2), 107.98, 112.59, 122.18, 122.86, 124.37, 129.35 (6 CH indole), 135.81 and 137.15 (2 C indole), 126.70 (=CH), 111.56 (=C), 164.46 and 165.77 (2 C=O).

Di t-butyl 2-(indol -1-yl)- 2-butene-1,4-dicarboxylate **(4c):** Yellow oil., IR (KBr)(ν_{max}, cm^{-1}): 1709 (C=O, ester). Anal. Calcd for $C_{20}H_{25}NO_4$: C, 69.97; H, 7.32; N, 4.14. Found: C, 70.26; H, 7.50; N, 4.35%. MS (*m/z*, %): 343 (M$^+$, 11). NMR data isomer *Z*: ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.12 and 1.54 (18 H, 2 s, 6 CH_3), 6.68 (1H, d, $^3J_{HH}$ = 4 H_Z, 1CH of indole), 6.99 (1 H, s, $CH_{olefine}$), 7.16–7.34 (4 H, m, 4 CH of indole), 7.65 (1H, d, $^3J_{HH}$ = 8 H_Z, 2CH of indole),. ^{13}C NMR (125.75 MH_Z, $CDCl_3$): δ = 27.90, 28.27 (6 CH3), 82.72, 83.96 (2 C), 104.36, 111.00, 120.94, 121.31, 122.72, 129.02 (6 CH indole), 130.83 and 137.34 (2 C indole), 126.32 (=CH), 110.78 (=C), 162.91 and 163.68 (2 C=O). NMR data isomer *E*: ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.59 and 1.65 (18 H, 2 s, 6 CH_3), 6.20 (1 H, s, $CH_{olefine}$), 6.71 (1H, d, $^3J_{HH}$ = 4 H_Z, 1CH of indole), 7.16-7.34 (4 H, m, 4 CH of indole), 7.67 (1H, d, $^3J_{HH}$ = 8 H_Z, 2CH of indole),. ^{13}C NMR (125.75 MH_Z, $CDCl_3$): δ = 28.29, 28.63 (6 CH3), 81.64, 84.60 (2 C), 106.99, 112.69, 121.91, 122.37, 123.83, 129.14 (6 CH indole), 135.90 and 136.99 (2 C indole), 126.82 (=CH), 104.62 (=C), 163.31 and 164.86 (2 C=O).

Dimethyl 2-(pyrrol-1-yl)- 2-butene-1,4-dicarboxylate **(4d):** Yellow oil. IR (KBr)(ν_{max}, cm^{-1}): 1726 (C=O, ester). Anal. Calcd for $C_{10}H_{11}NO_4$: C, 57.42; H, 5.48; N, 6.71. Found: C, 57.55; H, 5.60; N, 6.92%. MS (*m/z*, %): 209 (M$^+$, 10). NMR data isomer *Z*: ^{1}H NMR (500 MHz, $CDCl_3$) : δ = 3.58 and 3.89 (6 H, 2 s, 2 OCH_3), 6.10 (2 H, d, $^3J_{HH}$ = 1.6 H_Z, 2 CH of pyrrole), 6.57 (2 H, d, $^3J_{HH}$ = 1.2 H_Z, 2 CH of pyrrole), 6.69 (1 H, s, $CH_{olefine}$). ^{13}C NMR (125.75 MH_Z, $CDCl_3$): δ = 52.59, 53.80 (2 OCH_3), 110.36, 122.88 (4 CH pyrrole), 119.65 (=CH), 138.35 (=C), 163.62 and 164.44 (2 C=O). NMR data isomer *E*: ^{1}H NMR (500 MHz, $CDCl_3$): δ = 3.58 and 3.89 (6 H, 2 s, 2 OCH_3), 6.10 (2 H, d, $^3J_{HH}$ = 1.6 H_Z, 2 CH of pyrrole), 6.57 (2 H, d, $^3J_{HH}$ = 1.2 H_Z, 2 CH of pyrrole), 6.69 (1 H, s, $CH_{olefine}$). ^{13}C NMR (125.75 MH_Z, $CDCl_3$): δ = 52.59, 53.80 (2 OCH_3), 110.36, 122.88 (4 CH pyrrole), 119.65 (=CH), 138.35 (=C), 163.62 and 164.44 (2 C=O).

Diethyl 2-(pyrrol-1-yl)- 2-butene-1,4-dicarboxylate **(4e):** Yellow oil.. IR (KBr)(vmax , cm^{-1}): 1722 (C=O, ester). Anal. Calcd for $C_{12}H_{15}NO_4$: C, 60.81; H, 6.44; N, 5.90. Found: C, 60.65; H, 6.32; N, 6.11%. MS (*m/z*, %): 237 (M$^+$, 8). NMR data isomer *Z*: ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.99 and 1.15 (6 H, 2 t, $^3J_{HH}$ = 7 H_Z, 2 CH_3), 3.94 and 4.14 (4 H, 2 q, $^3J_{HH}$ = 7 H_Z, 2 OCH_2), 6.10 (2 H, d, $^3J_{HH}$ = 1.6 H_Z,2 CH of pyrrole), 6.57 (2 H, d, $^3J_{HH}$ = 1.2 H_Z,2 CH of pyrrole), 6.69 (1 H, s, $CH_{olefine}$). ^{13}C NMR (125.75 MH_Z, $CDCl_3$): δ = 14.39, 14.50 (2 CH3), 61.77, 63.08 (2 OCH_2), 110.36, 122.88 (4 CH pyrrole), 119.65 (=CH), 138.35 (=C), 163.62 and 164.44 (2 C=O). NMR data isomer *E*: ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.08 and 1.21 (6 H, 2 t, $^3J_{HH}$ = 7 H_Z, 2 CH_3), 4.02 and 4.27 (4 H, 2 q, $^3J_{HH}$ = 7 H_Z, 2 OCH_2), 5.72 (1 H, s, $CH_{olefine}$), 6.13 (2 H, d, $^3J_{HH}$ = 1.6 H_Z, 2 CH of pyrrole), 6.60 (2 H, d, $^3J_{HH}$ = 1.2 H_Z,2 CH of pyrrole). ^{13}C NMR (125.75 MH_Z, $CDCl_3$): δ = 14.30, 14.62 (2 CH3), 61.25, 63.19 (2 OCH_2), 113.31, 121.60 (4CH pyrrole), 102.98 (=CH), 144.21 (=C), 164.12 and 165.52 (2 C=O).

Di t-butyl 2-(pyrrol-1-yl)- 2-butene-1,4-dicarboxylate **(4f):** Yellow oil., IR (KB_r) (ν_{max}, cm^{-1}): 1724 (C=O, ester). Anal. Calcd for $C_{16}H_{23}NO_4$: C, 65.50; H, 7.92; N, 4.84. Found: C, 65.72; H, 7.81; N, 4.95%. MS (*m/z*, %): 293 (M$^+$, 6). NMR data isomer *Z*: ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.40 and 1.56 (18 H, 2 s, 6 CH_3), 6.27 (2 H, d, $^3J_{HH}$ = 1.6 H_Z, 2 CH of pyrrole), 6.72 (1 H, s, $CH_{olefine}$), 6.75 (2 H, d, $^3J_{HH}$ = 1.2 H_Z,2 CH of pyrrole). ^{13}C NMR (125.75 MH_Z, $CDCl_3$): δ = 28.18, 28.23 (6 CH3), 82.93, 83.81 (2 C), 109.87, 122.87 (4 CH pyrrole), 123.50 (=CH), 138.09 (=C), 162.66 and 164.00 (2 C=O). NMR data isomer *E*: ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.53 and 1.67 (18 H, 2 s, 6 CH_3), 5.85 (1 H, s, $CH_{olefine}$), 6.32 (2 H, d, $^3J_{HH}$ = 1.6 H_Z,2 CH of pyrrole), 6.93 (2 H, d, $^3J_{HH}$ = 1.2 H_Z,2 CH of pyrrole). ^{13}C NMR (125.75 MH_Z, $CDCl_3$): δ = 28.26, 28.31 (6 CH3), 81.25, 84.53 (2 C), 112.69, 119.50 (4 CH pyrrole), 104.52 (=CH), 144.45 (=C), 162.99 and 164.73 (2 C=O).

Dimethyl 2-(carbazol-9-yl)- 2-butene-1,4-dicarboxylate **(4g):** Yellow oil., IR (KBr) (ν_{max}, cm^{-1}): 1728 (C=O, ester). Anal. Calcd for $C_{18}H_{15}NO_4$: C, 69.93; H, 4.97; N, 4.94. Found: C, 69.69; H, 4.83; N, 5.10%. MS (*m/z*, %): 309 (M$^+$, 10). NMR data isomer *Z*: ^{1}H NMR (500 MHz, $CDCl_3$): δ = 3.23 and 3.57 (6 H, 2 s, 2 OCH_3), 7.14 (1 H, s, $CH_{olefine}$), 6.91-7.89 (8 H, m, 8 CH of carbazole). ^{13}C NMR (125.75 MH_Z, $CDCl_3$): δ = 52.64, 53.73 (2 OCH_3), 110.46, 120.94, 121.26, 126.64 (8 CH carbazole), 127.23 and 136.42 (4 C carbazole), 124.52 (=CH), 140.79 (=C), 164.02 and 164.52 (2 C=O). NMR data isomer *E*: ^{1}H NMR (500 MHz, $CDCl_3$): δ = 3.68 and 3.70 (6 H, 2 s, 2 OCH_3), 6.31 (1 H, s, $CH_{olefine}$), 6.91-7.89 (8 H, m, 8 CH of carbazole). ^{13}C NMR (125.75 MH_Z, $CDCl_3$): δ = 52.46, 53.83 (2 OCH_3), 111.23, 119.08, 122.33, 127.76 (8 CH carbazole), 125.14 and 140.34 (4 C carbazole), 120.97 (=CH), 140.08 (=C), 164.61 and 165.71 (2 C=O).

Diethyl 2-(carbazol-9-yl)- 2-butene-1,4-dicarboxylate **(4h):** Yellow oil., IR (KBr)(ν_{max}, cm^{-1}): 1709 (C=O, ester). Anal. Calcd for $C_{20}H_{19}NO_4$: C, 71.21; H, 5.70; N, 4.24. Found: C, 71.53; H, 5.92; N, 4.40%. MS (*m/z*, %): 337 (M$^+$, 15). NMR data isomer *Z*: ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.99 and 1.05 (6 H, 2 t, $^3J_{HH}$ = 7 H_Z, 2 CH_3), 3.52 and 3.63 (4 H, 2 q, $^3J_{HH}$ = 7 H_Z, 2 OCH_2), 7.13 (1 H, s, $CH_{olefine}$), 6.93–7.88 (8 H, m, 8 CH of carbazole). ^{13}C NMR (125.75 MH_Z, $CDCl_3$) 13.75, 14.37 (2 CH3), 61.67, 63.03 (2 OCH_2), 110.52, 120.75, 121.03, 126.44 (8 CH carbazole), 127.03 and 136.34 (4 C carbazole), 124.38 (=CH), 140.86 (=C), 163.82 and 163.93 (2 C=O). NMR data isomer *E*: ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.08 and 1.18 (6 H, 2 t, $^3J_{HH}$ = 7 H_Z, 2 CH_3), 4.08 and 4.15 (4 H, 2 q, $^3J_{HH}$ = 7 H_Z, 2 OCH_2), 6.29 (1 H, s, $CH_{olefine}$), 6.93-7.88 (8 H, m, 8 CH of carbazole). ^{13}C NMR (125.75 MH_Z, $CDCl_3$): δ = 14.37, 14.59 (2 CH3), 61.83, 62.99 (2 OCH_2), 111.28, 120.83, 122.10, 128.21 (8 CH carbazole), 119.60 and 140.27 (4 C carbazole), 125.03 (=CH), 140.10 (=C), 164.08 and 165.26 (2 C=O).

Di t-butyl 2-(carbazol-9-yl)- 2-butene-1,4-dicarboxylate **(4i):** Yellow oil., IR (KBr)(ν_{max}, cm^{-1}):1716 (C=O, ester). Anal. Calcd for $C_{24}H_{27}NO_4$: C, 73.32; H, 6.90; N, 3.63. Found: C, 73.56; H, 7.11; N, 3.82%. MS (*m/z*, %): 393 (M$^+$, 10). NMR data isomer *Z*: ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.93 and 1.47 (18 H, 2 s, 6 CH_3), 7.32 (1 H, s, $CH_{olefine}$), 7.27–8.13 (8 H, m, 8 CH of carbazole). ^{13}C NMR (125.75 MH_Z, $CDCl_3$): δ = 27.56, 28.19 (6 CH3), 82.68, 83.81 (2 C), 110.67, 120.62, 120.77, 126.35 (8 CH carbazole), 126.73 and 136.18 (4 C carbazole), 124.81 (=CH), 141.12 (=C), 162.83 and 163.54 (2 C=O). NMR data isomer *E*: ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.55 and 1.67 (18 H, 2 s, 6 CH_3), 6.49 (1 H, s, $CH_{olefine}$), 7.27-8.13 (8 H, m, 8 CH of carbazole). ^{13}C NMR (125.75 MH_Z, $CDCl_3$): δ = 28.42, 28.60 (6 CH3), 82.42, 84.27 (2 C),111.29, 121.73, 124.21, 130.11 (8 CH carbazole), 124.65 and 139.90 (4 C carbazole), 122.18 (=CH), 140.37 (=C), 162.95 and 164.46 (2 C=O).

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