SUPPORTING INFORMATION FOR

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GENERAL REVIEW

Chemicals and solvents received from commercial sources were used without further purification. All solvents that were used were stored on oven-dried molecular sieves (4A). Thin layer chromatography was performed on F254 aluminium coated plates. All the compounds were purified by column chromatography using silica gel (60-120 mesh). Photoreactions were performed in an immersion well photoreactor with a water jacket for cooling with a 250 W high pressure mercury vapour lamp. All reactions were carried out under an inert atmosphere (nitrogen) unless other conditions are specified. ¹H NMR spectra were recorded on a 400 MHz spectrometer (100 MHz for ¹³C ) in CDCl₃ as solvent and TMS as internal standard. IR spectra were recorded as KBr pellets. HRMS was recorded with an electrospray ion source and controlled by Xcalibur software, and fluorescence and UV-Vis spectra were recorded at room temperature.

9-butyl-3-(4-methylstyryl)-6-(styryl)-9H-carbazole (4a)

¹H- NMR SPECTRA OF 4a
$^{13}$C- NMR SPECTRA OF 4a

9-butyl-3-(4-chlorostyryl)-6-(styryl)-9H-carbazole (4b)

$^1$H- NMR SPECTRA OF 4b
$^{13}$C- NMR SPECTRA OF 4b

9-butyl-3-(4-methoxystyryl)-6-(styryl)-9H-carbazole (4c)

$^1$H- NMR SPECTRA OF 4c
$^1$H-NMR SPECTRA OF 4d

9-butyl-3-(4-chlorostyryl)-6-(methylstyrlyl)-9H-carbazole (4d)
$^{13}$C-NMR SPECTRA OF 4d

9-butyl-3-(4-chlorostyryl)-6-(methoxystyryl)-9H-carbazole (4e)

$^1$H-NMR SPECTRA OF 4e
General procedure for photocyclodehydrogenation:

Synthesis of 2-methyl-9-butyl-9H-aza[7]helicene (6a): A solution of 3,6-distyryl-N-butylcarbazole 4a (0.200 g, 0.45 mmol), iodine (0.253 g, 0.99 mmol), dry THF (3.26 g, 3.67 mL, 45.3 mmol), and toluene (610 mL) was irradiated using a 250W HPMV lamp (10 h monitored by TLC). After the completion of the reaction, the excess of iodine was removed by washing the solution with aqueous Na2S2O3 and water. The organic layer was concentrated under reduced pressure to obtain the crude product. The crude product was purified by column chromatography over silica gel using petroleum ether—ethyl acetate (98:2) as eluent to obtain a pale yellow solid. 0.0597 g (30%).

Rf = 0.4 (5:95 EtOAc/petroleum ether). Physical state = yellow solid. M.p.: >200°C.

1H NMR (400 MHz, CDCl3): δ = 8.14 (d, J = 8.8 Hz, 2H), 8.06 (d, J = 8.4 Hz, 2H), 7.99–7.96 (m, 3H), 7.90–7.88 (d, J = 8.4 Hz, 1H), 7.83–7.79 (m, 2H), 7.75 (d, J = 8 Hz, 1H), 7.40 (d, J = 8.4 Hz, 1H), 7.22–7.18 (m, 2H), 7.05–7.03 (dd, J = 8.1, 1.2 Hz, 1H), 6.28–6.24 (m, 1H), 4.79 (t, J = 7.2 Hz, 2H), 1.44 (s, 3H), 1.04 (t, J = 7.2 Hz, 3H) ppm.

13C NMR (100 MHz, CDCl3): δ = 139.23, 132.47, 131.49, 130.11, 129.91, 129.43, 128.34, 127.74, 127.43, 127.20, 126.82, 126.73, 126.61, 126.57, 126.53, 126.40, 126.14, 126.10, 125.91, 125.78, 124.03, 123.96, 122.34, 120.18, 116.75, 116.70, 109.57, 109.45, 43.44, 31.96, 20.77, 20.71, 13.98

HRMS (ESI-TOF): m/z calcld for C33H27N is 437.2143; found, 437.2140

IR (KBr): t = 3427, 3042, 2952, 2927, 2867, 1725, 1660, 1588, 1522, 1495, 1450, 1339, 1283, 1218, 795, 746, 645 cm−1
2-methyl-9-butyl-9H-aza[7]helicene (6a)

$^1$H-NMR SPECTRA OF 6a

$^{13}$C-NMR SPECTRA OF 6a

R_f = 0.3 (5:95 EtOAc/petroleum ether). Physical state = yellow solid. M.p. = 168^oC.

^1H NMR (400 MHz, CDCl_3): δ = 8.07 (d, J = 8.8 Hz, 2H), 8.03 (m, 2H), 7.54-7.47 (m, 3H), 7.41-7.29 (m, 5H), 7.22-7.11 (m, 4H), 4.33 (t, J = 7.2 Hz, 2H), 2.39 (s, 3H), 1.93-1.85 (m, 2H), 1.47-1.39 (m, 2H), 0.97 (t, J = 7.2 Hz, 3H) ppm.

^13C NMR (100 MHz, CDCl_3): δ = 139.38, 139.28, 132.06, 130.96, 129.57, 129.53, 129.51, 128.90, 127.74, 127.55, 127.43, 127.13, 126.90, 126.88, 126.83, 126.81, 126.65, 126.40, 126.06, 125.95, 125.83, 124.56, 123.54, 122.35, 116.62, 116.25, 110.26, 109.61, 43.48, 31.95, 20.70, 13.96.

HRMS(ESI-TOF): m/z calcd for C_{33}H_{25}NCl is 458.1672; found, 458.1670

IR (KBr): v 3010, 2956, 1682, 1599, 1500, 1220, 838, 762, 674 cm^{-1}

Rf = 0.2 (5:95 EtOAc/petroleum ether). Physical state = yellow solid. M.p. = 182°C.

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 8.07 (d, $J$ = 8.8 Hz, 2H), 8.03 (m, 2H), 7.54-7.47 (m, 3H), 7.41-7.29 (m, 5H), 7.22-7.11 (m, 4H), 4.33 (t, $J$ = 7.2 Hz, 2H), 2.39 (s, 3H), 1.93-1.85 (m, 2H), 1.47-1.39 (m, 2H), 0.97 (t, $J$ = 7.2 Hz, 3H).


HRMS (ESI-TOF): m/z calcd for $C_{33}H_{27}NO$ is 476.1986; found, 476.1985 [M+Na]$^+$

IR (KBr): v 3430, 3040, 2956, 2929, 2870, 1728, 1665, 1592, 1525, 1498, 1454, 1343, 1286, 1223, 798, 749, 647 cm$^{-1}$
$^1$H- NMR SPECTRA OF 6c

$^{13}$C- NMR SPECTRA OF 6c

R<sub>f</sub>=0.4 (5:95 EtOAc/petroleum ether). Physical state = yellow solid. M.p.: >200°C. 

1H NMR (400 MHz, CDCl<sub>3</sub>): δ 8.16 (d, J=8.4 Hz, 1H), 8.14 (d, J=8.4 Hz, 1H), 8.07 (d, J=8.8 Hz, 1H), 8.02 (dd, J=8.4, 1.2 Hz, 2H), 7.97 (d, J=8.4 Hz, 1H), 7.91 (d, J=8.8 Hz, 1H), 7.85 (d, J=8.8 Hz, 1H), 7.79 (d, J=7.6 Hz, 1H), 7.74 (d, J=8.8 Hz, 1H), 7.31 (d, J=2.4), 7.16 (dd, J=8.4, 1.2 Hz, 1H), 7.12-7.08 (m, 2H), 4.80 (t, J=7.2 Hz, 2H), 2.11-2.09 (m, 2H), 1.59-1.55 (m, 2H), 1.53 (s, 3H), 1.04 (t, J=7.2 Hz, 3H).


HRMS(ESI-TOF): m/z calcd for C<sub>33</sub>H<sub>26</sub>NCl is 494.1641; found, 494.1646[M+Na]<sup>+</sup>

IR (KBr): v 3430, 3036, 2948, 2924, 2854, 1730, 1650, 1595, 1532, 1495, 1450, 1342, 1285, 1222, 792, 741, 640 cm<sup>-1</sup>

1H-NMR SPECTRA OF 6d

Rf = 0.2 (5:95 EtOAc/petroleum ether). Physical state = yellow solid. M.p.: >200°C.
1H NMR (400 MHz, CDCl3): δ = 8.16 (d, J = 8.8 Hz, 1H), 8.11 (d, J = 8.4 Hz, 1H), 8.05 (d, J = 8.4 Hz, 1H), 8.02 (d, J = 8.8 Hz, 1H), 7.97 (d, J = 8.8 Hz, 2H), 7.91 (d, J = 8.8 Hz, 1H), 7.83 (d, J = 7.6 Hz, 1H), 7.81 (d, J = 8.4 Hz, 1H), 7.77 (d, J = 8.4 Hz, 1H), 7.39 (s, 1H), 7.20-7.17 (m, 1H), 6.90-6.87 (m, 1H), 6.77 (d, J = 2 Hz, 1H), 4.80 (t, J = 7.2 Hz, 2H), 2.47 (s, 3H), 2.47-2.11 (m, 2H), 1.60-1.55 (m, 2H), 1.05 (t, J = 7.2 Hz, 3H).

13C NMR: δ = 155.04, 139.16, 130.91, 130.72, 129.44, 129.03, 128.42, 127.67, 127.26, 127.11, 126.96, 126.82, 126.77, 126.28, 126.23, 125.66, 124.25, 124.22, 123.51, 117.61, 116.29, 116.05, 110.43, 109.71, 106.71, 53.48, 43.54, 32.05, 20.72, 13.98.
HRMS(ESI-TOF): m/z calcd for C33H26NClO is 510.1593; found, 510.1595[M+Na]^+.
IR (KBr): ν = 3445, 3030, 2900, 2870, 1725, 1670, 1591, 1523, 1500, 1447, 1334, 1284, 1218, 787, 749, 638 cm⁻¹.
$^1$H- NMR SPECTRA OF 6e

$^{13}$C- NMR SPECTRA OF 6e
NMR STUDY OF CRUDE REACTION MIXTURE OF COMPOUND 6a

Singlet peaks not observed as expected for protons HL1 and HL2 of the linear regiomer of compound 6a

The angular regiomer
X-RAY CRYSTALLOGRAPHIC DATA OF 6a

(The atom numbers in the above figure correspond to the ones obtained during X-Ray analysis and are different compared to IUPAC numbers given in the Figure in text.)

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U.V-Vis and Fluorescence spectra of compounds 6a-6e in Chloroform at room temperature with concentration of $1 \times 10^{-5}$ mol