Supporting Information

Direct access to substituted benzo[*b*]carbazoles through cascade annulation of 2-vinylbenzaldehydes with indoles

Deng-Yuan Li, An Wang, Xiao-Ping Zhu, Wei Feng, and Pei-Nian Liu*

Shanghai Key Laboratory of Functional Materials Chemistry, Key Lab for Advanced Materials and School of Chemistry & Molecular Engineering, East China University of Science & Technology, Meilong Road 130, Shanghai 200237, China

liupn@ecust.edu.cn

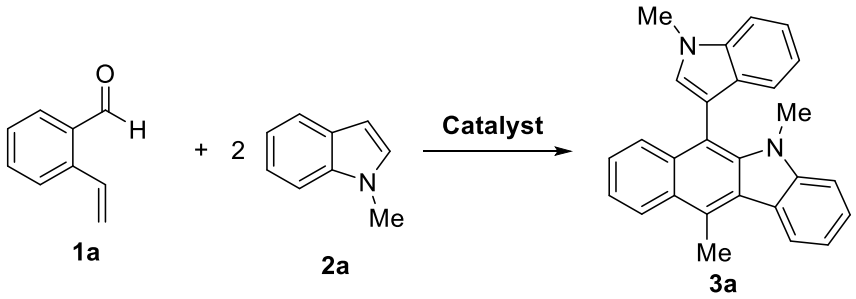
Table of contents

1 General information

All manipulations were carried out under a nitrogen atmosphere using standard Schlenk techniques, unless otherwise stated. Solvents were distilled under nitrogen from sodium-benzophenone (THF, benzene, toluene) or calcium hydride (dichloromethane, MeCN, DMF, DMSO, 1,2-DCE). Other chemicals were obtained from commercial sources, and were used without further purification. Chemical shifts (δ, ppm) in the ^{1}H NMR spectra were recorded using TMS as internal standard or referenced to $CHCl_3$ (δ = 7.26 ppm). Chemical shifts in ^{13}C {^{1}H} NMR spectra were internally referenced to $CHCl_3$ (δ = 77.16 ppm).

2 Screening of other catalysts and solvents for the cascade annulation of 2-vinylbenzaldehyde 1a with indole 2a

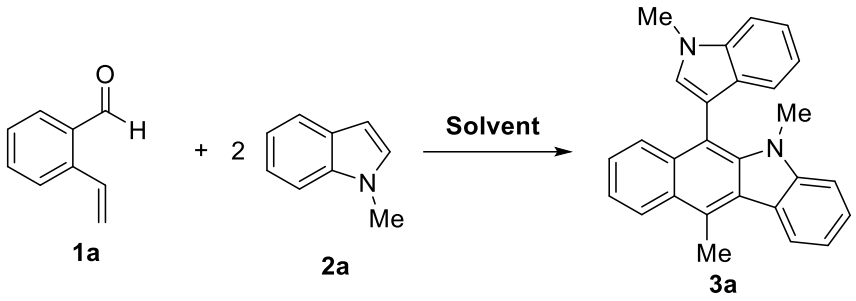
Table S1. Screening of other catalysts[a]



Entry	Catalyst	Yield (**3a**, %)[b]
1	$(MeCN)_4Pd(OTf)_2$	96
2	$Cu(OTf)_2$	trace
3	$Sc(OTf)_3$	3
4	$Fe(OTf)_3$	trace

[a]Reaction conditions: [a] Reaction conditions: **1a** (0.2 mmol), **2a** (0.6 mmol), catalyst (0.02 mmol), $K_2S_2O_8$ (0.34 mmol), MeCN:AcOH = 2:1 (v/v, 1.5 mL), at 60 ºC for 18 h under N_2. [b] Determined by ^{1}H NMR using CH_2Br_2 as the internal standard.

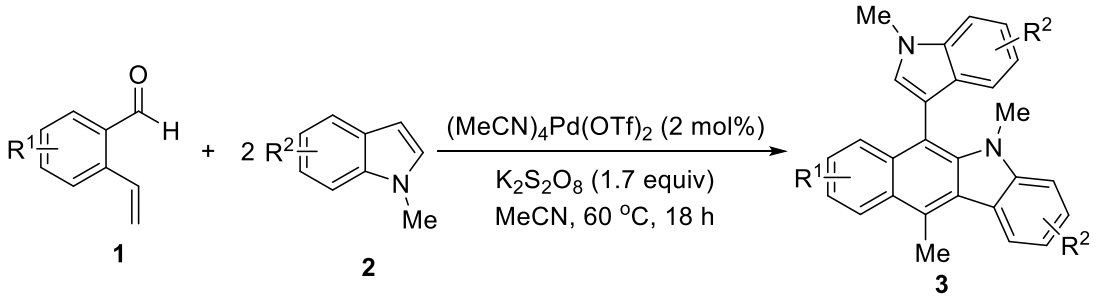
Table S2. Screening of other solvents[a]



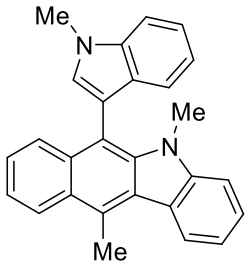
Entry	Solvent	Yield (**3a**, %)[b]
1	MeCN	96
2	toluene	5
3	THF	4
4	MeOH	4
5	DCE	8
6	CH_2Cl_2	4
7	DMF	12

[a] Reaction conditions: **1a** (0.2 mmol), **2a** (0.6 mmol), $(MeCN)_4Pd(OTf)_2$ (0.01 mmol), $K_2S_2O_8$ (0.34 mmol), solvent (1.5 mL), at 60 °C for 18 h under N_2. [b] Determined by ^1H NMR using CH_2Br_2 as the internal standard.

3 General procedure for the cascade annulation of 2-vinylbenzaldehydes with indoles

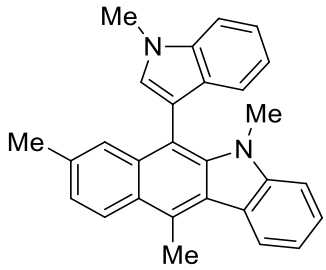


A mixture of 2-vinylbenzaldehydes **1** (0.2 mmol), indoles **2** (0.6 mmol), $(MeCN)_4Pd(OTf)_2$ (2.4 mg, 0.004 mmol), $K_2S_2O_8$ (92 mg, 0.34 mmol) in MeCN (1.5 mL) was stirred at 60 °C (oil bath temperature) in a sealed tube under nitrogen atmosphere. After 18 h, it was cooled down to room temperature and then transferred to a round bottom flask. Silica gel was added to the flask and volatiles were evaporated under reduced pressure. The purification was performed by flash column chromatography on silica gel (see below for specific eluents) to afford the desired products **3**.

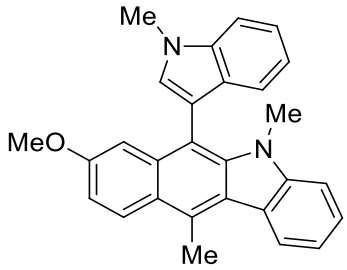


5,11-Dimethyl-6-(1-methyl-1*H*-indol-3-yl)-5*H*-benzo[*b*]carbazole (3a). The compound was prepared from 2-vinylbenzaldehyde (26.4 mg, 0.2 mmol) and 1-methyl-1*H*-indole (78.7 mg, 0.6 mmol) following the general procedure. The product **3a** was obtained in 92% yield (69 mg) as a yellow solid after column chromatography (eluent = petroleum ether/ethyl acetate 100:1 v/v). **Mp:** 226-228 °C; **^{1}H NMR (400 MHz, $CDCl_3$, 25 °C):** δ 8.47 (d, J = 7.80 Hz, 1H), 8.38 (d, J = 8.24 Hz, 1H), 7.79 (d, J = 8.08 Hz, 1H), 7.49-7.54 (m, 2H), 7.42-7.46 (m, 1H), 7.27-7.35 (m, 4H), 7.22 (d, J = 7.92 Hz, 1H), 7.18 (s, 1H), 7.04-7.08 (m, 1H), 3.99 (s, 3H), 3.35 (s, 3H), 3.27 (s, 3H); **^{13}C NMR (100.6 MHz, $CDCl_3$, 25 °C):** δ 144.90, 139.83, 136.76, 134.04, 130.85, 129.78, 128.88, 127.21, 126.57, 126.09, 124.58, 124.00, 123.91, 123.83, 123.73, 122.37, 122.15,

120.73, 119.84, 118.87, 111.59, 109.41, 108.49, 108.10, 33.18, 31.70, 15.88; **HRMS (EI, TOF):** calcd for $C_{27}H_{22}N_2^+$ $[M]^+$: 374.1783 , found: 374.1784 .

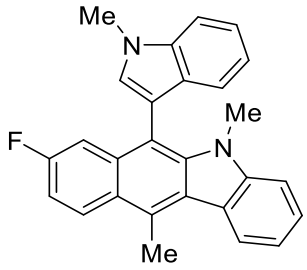


5,8,11-Trimethyl-6-(1-methyl-1*H*-indol-3-yl)-5*H*-benzo[*b*]carbazole (3b). The compound was prepared from 5-methyl-2-vinylbenzaldehyde (29.2 mg, 0.2 mmol) and 1-methyl-1*H*-indole (78.7 mg, 0.6 mmol) following the general procedure. The product **3b** was obtained in 87% yield (68 mg) as a yellow solid after column chromatography (eluent = petroleum ether/ethyl acetate 100:1 v/v). **Mp:** 212-214 °C; **^{1}H NMR (400 MHz, $CDCl_3$, 25 °C):** δ 8.52 (d, J = 7.80 Hz, 1H), 8.36 (d, J = 8.72 Hz, 1H), 7.67 (s, 1H), 7.57 (t, J = 7.38 Hz, 2H), 7.40 (t, J = 7.62 Hz, 1H), 7.35 (t, J = 7.88 Hz, 2H), 7.31 (t, J = 7.48 Hz, 2H), 7.20 (s, 1H), 7.15 (t, J = 7.42 Hz, 1H), 4.01 (s, 3H), 3.39 (s, 3H), 3.27 (s, 3H), 2.45 (s, 3H); **^{13}C NMR (100.6 MHz, $CDCl_3$, 25 °C):** δ 144.78, 140.03, 136.74, 134.29, 134.09, 130.95, 129.75, 128.74, 126.28, 125.61, 124.85, 124.74, 123.96, 123.83, 123.68, 123.08, 122.05, 120.75, 119.77, 118.78, 111.66, 109.35, 108.01, 107.80, 33.11, 31.54, 22.01, 15.86; **HRMS (EI, TOF):** calcd for $C_{28}H_{24}N_2^+$ $[M]^+$: 388.1939, found: 388.1938.

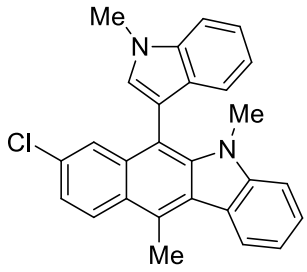


8-Methoxy-5,11-dimethyl-6-(1-methyl-1*H*-indol-3-yl)-5*H*-benzo[*b*]carbazole (3c). The compound was prepared from 5-methoxy-2-vinylbenzaldehyde (32.4 mg, 0.2 mmol) and 1-methyl-1*H*-indole (78.7 mg, 0.6 mmol) following the general procedure. The product **3c** was obtained in 76% yield (62 mg) as a yellow solid after column chromatography (eluent = petroleum ether/ethyl acetate 50:1 v/v). **Mp:** 210-212 °C; **^{1}H**

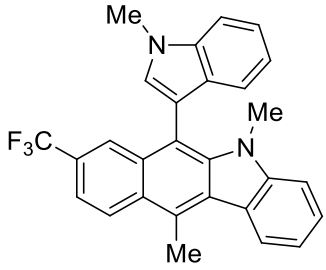
NMR (400 MHz, $CDCl_3$, 25 °C): δ 8.35 (d, J = 7.84 Hz, 1H), 8.23 (dd, J_1 = 10.00 Hz, J_2 = 6.00 Hz, 1H), 7.42(t, J = 8.12 Hz 2H), 7.23-7.27 (m, 1H), 7.19 (t, J = 7.60 Hz, 3H), 7.06-7.11 (m, 3H), 6.99-7.03 (m, 1H), 3.92 (s, 3H), 3.56 (s, 3H), 3.24 (s, 3H), 3.16 (s, 3H); **^{13}C NMR (100.6 MHz, $CDCl_3$, 25 °C):** δ 156.87, 144.63, 140.58, 136.86, 135.42, 130.49, 129.60, 129.02, 126.06, 125.80, 123.98, 123.45, 123.06, 122.11, 120.82, 119.78, 118.88, 114.78, 111.78, 109.40, 108.07, 107.36, 104.70, 55.22, 33.21, 31.82, 15.99; **HRMS (EI, TOF):** calcd for $C_{28}H_{24}N_2O^+$ $[M]^+$: 404.1889, found: 404.1888.



8-Fluoro-5,11-dimethyl-6-(1-methyl-1*H*-indol-3-yl)-5*H*-benzo[*b*]carbazole (3d). The compound was prepared from 5-fluoro-2-vinylbenzaldehyde (30.0 mg, 0.2 mmol) and 1-methyl-1*H*-indole (78.7 mg, 0.6 mmol) following the general procedure. The product **3d** was obtained in 91% yield (71 mg) as a yellow solid after column chromatography (eluent = petroleum ether/ethyl acetate 100:1 v/v). **Mp:** 248-250 °C; **^{1}H NMR (400 MHz, $CDCl_3$, 25 °C):** δ 8.44 (d, J = 7.80 Hz, 1H), 8.33-8.37 (m, 1H), 7.49-7.54 (m, 2H), 7.36-7.39 (m, 1H), 7.28-7.35 (m, 3H), 7.18-7.22 (m, 3H), 7.05-7.08(m, 1H), 3.99 (s, 3H), 3.32 (s, 3H), 3.26 (s, 3H); **^{13}C NMR (100.6 MHz, $CDCl_3$, 25 °C):** δ 160.9 (d, $J_{C\text{-}F}$ = 43.06 Hz), 144.70, 140.55, 136.82, 135.33 (d, $J_{C\text{-}F}$ = 8.70 Hz), 130.61, 129.68, 129.9, 126.59, 126.57 (d, $J_{C\text{-}F}$ = 9.07 Hz), 124.37, 123.75, 123.64, 123.30 (d, $J_{C\text{-}F}$ = 2.12 Hz), 122.28, 120.50, 119.99, 119.10, 112.70 (d, $J_{C\text{-}F}$ = 25.75 Hz), 111.17, 109.50, 108.87 (d, $J_{C\text{-}F}$ = 22.18 Hz), 108.21, 107.96 (d, $J_{C\text{-}F}$ = 5.69 Hz), 33.23, 31.58, 16.10; **HRMS (EI, TOF):** calcd for $C_{27}H_{21}FN_2^+$ $[M]^+$: 392.1689, found: 392.1692.

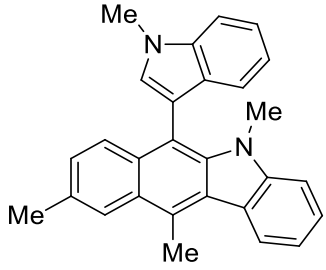


8-Chloro-5,11-dimethyl-6-(1-methyl-1*H*-indol-3-yl)-5*H*-benzo[*b*]carbazole (3e). The compound was prepared from 5-chloro-2-vinylbenzaldehyde (33.3 mg, 0.2 mmol) and 1-methyl-1*H*-indole (78.7 mg, 0.6 mmol) following the general procedure. The product **3e** was obtained in 78% yield (64 mg) as a yellow solid after column chromatography (eluent = petroleum ether/ethyl acetate 50:1 v/v). **Mp:** 207-209 °C; **^{1}H NMR (400 MHz, $CDCl_3$, 25 °C):** δ 8.52 (d, J = 7.72 Hz, 1H), 8.28 (d, J = 9.08 Hz, 1H), 7.77 (s, 1H), 7.50-7.54 (m, 2H), 7.32-7.36 (m, 3H), 7.27 (d, J = 8.56 Hz, 1H), 7.18 (s, 2H), 7.07 (t, J = 7.28 Hz, 1H), 4.00 (s, 3H), 3.31 (s, 3H), 3.23 (s, 3H); **^{13}C NMR (100.6 MHz, $CDCl_3$, 25 °C):** δ 144.86, 140.38, 136.77, 134.89, 130.79, 130.76, 129.81, 129.02, 126.77, 125.83, 125.47, 124.50, 123.98, 123.89, 123.49, 123.13, 122.29, 120.48, 120.03, 119.15, 110.81, 109.52, 108.26, 107.98, 33.28, 31.51, 15.96; **HRMS (EI, TOF):** calcd for $C_{27}H_{21}ClN_2^+$ $[M]^+$: 408.1393, found: 408.1391.

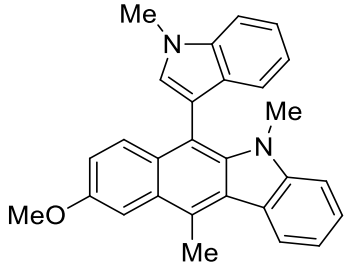


5,11-Dimethyl-6-(1-methyl-1*H*-indol-3-yl)-8-(trifluoromethyl)-5*H*-benzo[*b*]carbazole (3f). The compound was prepared from 5-(trifluoromethyl)-2-vinylbenzaldehyde (40.0 mg, 0.2 mmol) and 1-methyl-1*H*-indole (78.7 mg, 0.6 mmol) following the general procedure. The product **3f** was obtained in 61% yield (54 mg) as a yellow solid after column chromatography (eluent = petroleum ether/ethyl acetate 100:1 v/v). **Mp:** 233-235 °C; **^{1}H NMR (400 MHz, $CDCl_3$, 25 °C):** δ 8.48 (t, J = 7.84 Hz, 2H), 8.17 (s, 1H), 7.54-7.59 (m, 2H), 7.52 (d, J = 8.32 Hz, 1H), 7.32-7.36 (m, 2H), 7.30 (d, J = 8.16 Hz, 1H), 7.21(s, 1H), 7.16 (d, J = 7.88 Hz, 1H), 7.07 (t, J = 7.20 Hz,

1H), 4.01 (s, 3H), 3.36 (s, 3H), 3.24 (s, 3H); **^{13}C NMR (100.6 MHz, $CDCl_3$, 25 °C):** δ 145.09, 140.35, 136.79, 132.68, 130.75, 129.84, 128.85, 128.07, 127.25, 126.13 (q, $J_{C\text{-}F}$ = 45.17 Hz), 125.48, 125.20, 124.22, 123.96, 123.84 (q, $J_{C\text{-}F}$ = 4.67 Hz), 123.29, 122.40, 120.40, 120.13, 119.30, 117.67 (q, $J_{C\text{-}F}$ = 3.20 Hz), 110.47, 110.02, 109.61, 108.45, 33.32, 31.58, 15.99; **HRMS (EI, TOF):** calcd for $C_{28}H_{21}F_3N_2^+$ $[M]^+$: 442.1657, found: 442.1656.

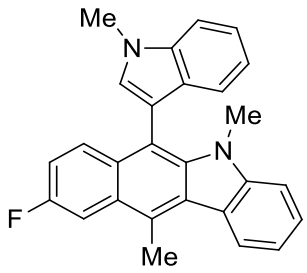


5,9,11-Trimethyl-6-(1-methyl-1*H*-indol-3-yl)-5*H*-benzo[*b*]carbazole (3g). The compound was prepared from 4-methyl-2-vinylbenzaldehyde (29.2 mg, 0.2 mmol) and 1-methyl-1*H*-indole (78.7 mg, 0.6 mmol) following the general procedure. The product **3g** was obtained in 72% yield (56 mg) as a yellow solid after column chromatography (eluent = petroleum ether/ethyl acetate 100:1 v/v). **Mp:** 239-241 °C; **^{1}H NMR (400 MHz, $CDCl_3$, 25 °C):** δ 8.46 (d, J = 7.80 Hz, 1H), 8.13 (s, 1H), 7.68 (d, J = 8.72 Hz, 1H), 7.49-7.52 (m, 2H), 7.29-7.34 (m, 1H), 7.27 (d, J = 1.04 Hz, 1H), 7.25 (t, J = 1.88 Hz, 1H), 7.22 (d, J = 7.92 Hz, 1H), 7.17 (s, 1H), 7.15 (dd, J_1 = 8.76 Hz, J_2 = 1.56 Hz,1H), 7.29-7.34 (m, 1H), 3.98 (s, 3H), 3.32 (s, 3H), 3.25 (s, 3H), 3.58 (s, 3H); **^{13}C NMR (100.6 MHz, $CDCl_3$, 25 °C):** δ 144.88, 139.36, 136.74, 132.33, 131.61, 130.86, 129.73, 128.07, 127.39, 126.97, 126.45, 126.04, 123.88, 123.79, 122.94, 122.11, 120.75, 119.81, 118.72, 111.73, 109.38, 108.42, 108.04, 33.17, 31.70, 22.04, 15.84; **HRMS (EI, TOF):** calcd for $C_{28}H_{24}N_2^+$ $[M]^+$: 388.1939, found: 388.1942.



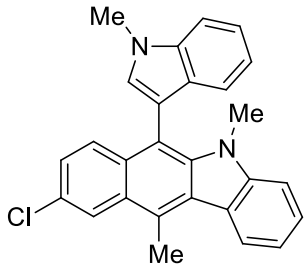
9-Methoxy-5,11-dimethyl-6-(1-methyl-1*H*-indol-3-yl)-5*H*-benzo[*b*]carbazole (3h).

The compound was prepared from 4-methoxy-2-vinylbenzaldehyde (32.4 mg, 0.2 mmol) and 1-methyl-1*H*-indole (78.7 mg, 0.6 mmol) following the general procedure. The product **3h** was obtained in 40% yield (32 mg) as a yellow solid after column chromatography (eluent = petroleum ether/ethyl acetate 50:1 v/v). **Mp:** 216-218 °C; **^{1}H NMR (400 MHz, $CDCl_3$, 25 °C):** δ 8.47 (d, J = 7.64 Hz, 1H), 7.71 (d, J = 9.36 Hz, 1H), 7.61 (d, J = 2.52 Hz, 1H), 7.50 (t, J = 8.44 Hz, 2H), 7.28-7.34 (m, 1H), 7.25 (d, J = 7.72 Hz, 2H), 7.21 (d, J = 7.84 Hz, 1H), 7.18 (s, 1H), 7.06 (dt, J_1 = 7.80 Hz, J_2 = 0.72 Hz,1H), 7.01 (dd, J_1 = 9.36 Hz, J_2 = 2.52 Hz,1H), 4.01 (s, 3H), 3.98 (s, 3H), 3.29 (s, 3H), 3.25 (s, 3H); **^{13}C NMR (100.6 MHz, $CDCl_3$, 25 °C):** δ 155.40, 144.87, 138.64, 136.75, 130.83, 129.74, 129.68, 127.98, 127.82, 127.17, 126.50, 124.25, 123.91, 123.59, 122.18, 120.72, 119.87, 118.64, 117.44, 111.69, 109.41, 108.93, 108.09, 102.25, 55.49, 33.23, 31.73, 16.08; **HRMS (EI, TOF):** calcd for $C_{28}H_{24}N_2O^+$ $[M]^+$: 404.1889, found: 404.1896.

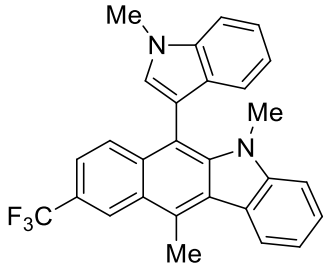


9-Fluoro-5,11-dimethyl-6-(1-methyl-1*H*-indol-3-yl)-5*H*-benzo[*b*]carbazole (3i). The compound was prepared from 4-fluoro-2-vinylbenzaldehyde (30.0 mg, 0.2 mmol) and 1-methyl-1*H*-indole (78.7 mg, 0.6 mmol) following the general procedure. The product **3i** was obtained in 82% yield (64 mg) as a yellow solid after column chromatography (eluent = petroleum ether/ethyl acetate 50:1 v/v). **Mp:** 205-207 °C; **^{1}H NMR (400 MHz, $CDCl_3$, 25 °C):** δ 8.48 (d, J = 7.84 Hz, 1H), 7.98 (dd, J_1 = 11.48 Hz, J_2 = 2.26 Hz, 1H), 7.81 (dd, J_1 = 9.44 Hz, J_2 = 6.12 Hz, 1H), 7.51-7.57 (m, 2H), 7.33-7.38 (m, 1H), 7.29 (t, J = 7.88 Hz, 2H), 7.23 (d, J = 7.84 Hz, 1H), 7.17 (s, 1H), 7.08-7.14 (m, 2H), 3.99 (s, 3H), 3.29 (s, 3H), 3.26 (s, 3H); **^{13}C NMR (100.6 MHz, $CDCl_3$, 25 °C):** δ 159.05 (d, $J_{C\text{-}F}$ = 241.31 Hz), 144.96, 139.33, 139.31, 136.73, 130.86 (d, $J_{C\text{-}F}$ = 29.42 Hz), 129.75, 128.55 (d, $J_{C\text{-}F}$ = 8.44 Hz), 127.88 (d, $J_{C\text{-}F}$ = 5.89 Hz), 127.67 (d, $J_{C\text{-}F}$ = 7.95 Hz), 126.89, 124.73, 124.01, 123.27, 122.29, 120.57, 119.98, 118.94, 114.86

(d, $J_{C\text{-}F}$ = 25.32 Hz), 111.32, 109.49, 108.96, 108.19, 106.99 (d, $J_{C\text{-}F}$ = 21.34 Hz), 33.20, 31.69, 16.03; **HRMS (EI, TOF):** calcd for $C_{27}H_{21}FN_2^+$ $[M]^+$: 392.1689, found: 392.1691.

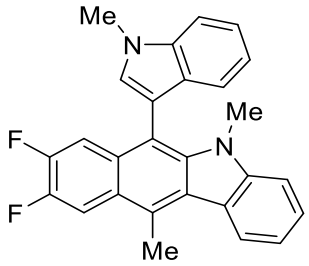


9-Chloro-5,11-dimethyl-6-(1-methyl-1*H*-indol-3-yl)-5*H*-benzo[*b*]carbazole (3j). The compound was prepared from 4-chloro-2-vinylbenzaldehyde (33.3 mg, 0.2 mmol) and 1-methyl-1*H*-indole (78.7 mg, 0.6 mmol) following the general procedure. The product **3j** was obtained in 90% yield (74 mg) as a yellow solid after column chromatography (eluent = petroleum ether/ethyl acetate 50:1 v/v). **Mp:** 209-211 °C; **^{1}H NMR (400 MHz, $CDCl_3$, 25 °C):** δ 8.46 (d, J = 7.84 Hz, 1H), 8.32 (d, J = 2.08 Hz, 1H), 7.72 (d, J = 9.16 Hz, 1H), 7.49-7.55 (m, 2H), 7.33 (dt, J_1 = 8.08 Hz, J_2 = 1.00 Hz, 1H), 7.28 (t, J = 3.84 Hz, 1H), 7.26 (s, 1H), 7.21 (dd, J_1 = 9.20 Hz, J_2 = 2.12 Hz,1H), 7.17 (s, 2H), 7.06 (dt, J_1 = 7.68 Hz, J_2 = 0.64 Hz, 1H), 3.99 (s, 3H), 3.29 (s, 3H), 3.25 (s, 3H); **^{13}C NMR (100.6 MHz, $CDCl_3$, 25 °C):** δ 144.96, 139.82, 136.75, 132.25, 130.69, 129.76, 128.26, 128.00, 127.91, 127.86, 126.96, 125.22, 124.66, 124.04, 123.39, 122.88, 122.32, 120.55, 120.02, 119.11, 111.09, 109.51, 108.82, 108.27, 33.24, 31.69, 15.91; **HRMS (EI, TOF):** calcd for $C_{27}H_{21}ClN_2^+$ $[M]^+$: 408.1393, found: 408.1395.

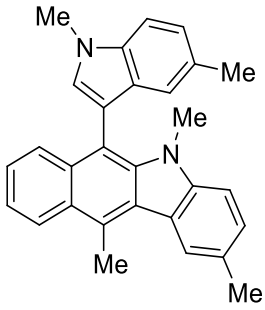


5,11-Dimethyl-6-(1-methyl-1*H*-indol-3-yl)-9-(trifluoromethyl)-5*H*-benzo[*b*]carbazole (3k). The compound was prepared from 4-(trifluoromethyl)-2-vinylbenzaldehyde (40.0 mg, 0.2 mmol) and 1-methyl-1*H*-indole (78.7 mg, 0.6 mmol)

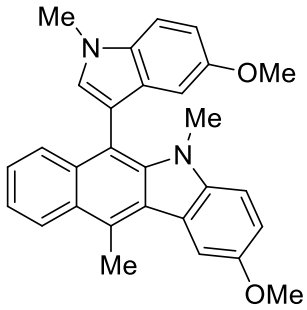
following the general procedure. The product **3k** was obtained in 75% yield (66 mg) as a yellow solid after column chromatography (eluent = petroleum ether/ethyl acetate 50:1 v/v). **Mp:** 224-226 °C; **^{1}H NMR (400 MHz, $CDCl_3$, 25 °C):** δ 8.69 (s, 1H), 8.49 (d, J = 7.80 Hz, 1H), 7.90 (d, J = 9.00 Hz, 1H), 7.57 (dt, J_1 = 8.12 Hz, J_2 = 0.84 Hz, 1H), 7.53 (d, J = 7.32 Hz, 1H), 7.45 (dd, J_1 = 9.04 Hz, J_2 = 1.56 Hz, 1H), 7.30-7.38 (m, 3H), 7.20 (d, J = 7.92 Hz, 1H), 7.18 (s, 1H), 7.09 (dt, J_1 = 7.72 Hz, J_2 = 0.64 Hz, 1H), 4.00 (s, 3H), 3.38 (s, 3H), 3.29 (s, 3H); **^{13}C NMR (100.6 MHz, $CDCl_3$, 25 °C):** δ 144.89, 140.94, 136.79, 135.11, 130.67, 130.10, 129.80, 127.15, 127.13, 123.90 (q, J_{C-F} = 31.71 Hz), 125.70 124.81, 124.10, 123.31, 122.40, 122.06 (q, J_{C-F} = 4.80 Hz), 120.49, 120.10, 119.83 (q, J_{C-F} = 2.84 Hz), 119.43, 110.93, 109.58, 108.80, 108.40, 33.25, 31.69, 15.95; **HRMS (EI, TOF):** calcd for $C_{28}H_{21}F_3N_2^+$ $[M]^+$: 442.1657, found: 442.1655.



8,9-Difluoro-5,11-dimethyl-6-(1-methyl-1*H*-indol-3-yl)-5*H*-benzo[*b*]carbazole (3l). The compound was prepared from 4,5-difluoro-2-vinylbenzaldehyde (33.6 mg, 0.2 mmol) and 1-methyl-1*H*-indole (78.7 mg, 0.6 mmol) following the general procedure. The product **3l** was obtained in 60% yield (49 mg) as a yellow solid after column chromatography (eluent = petroleum ether/ethyl acetate 50:1 v/v). **Mp:** 242-243 °C; **^{1}H NMR (400 MHz, $CDCl_3$, 25 °C):** δ 8.44 (d, J = 7.84 Hz, 1H), 8.04 (dd, J_1 = 13.00 Hz, J_2 = 8.28 Hz, 1H), 7.47-7.55 (m, 3H), 7.26-7.36 (m, 3H), 7.18 (d, J = 8.16 Hz, 1H), 7.17 (s, 1H), 7.08 (dt, J_1 = 7.64 Hz, J_2 = 0.48 Hz, 1H), 3.99 (s, 3H), 3.26 (s, 3H), 3.25 (s, 3H); **^{13}C NMR (100.6 MHz, $CDCl_3$, 25 °C):** δ 149.78 (d, J_{C-F} = 247.32 Hz), 149.29, 149.13, 146.86, 144.67, 139.97, 136.80, 131.37 (d, J_{C-F} = 6.66 Hz), 130.48, 129.66, 128.16 (d, J_{C-F} = 3.99 Hz), 126.88, 124.13, 123.85, 123.23, 122.43, 120.38, 120.13, 119.16, 111.65 (d, J_{C-F} = 18.22 Hz), 110.99, 109.88 (d, J_{C-F} = 17.67 Hz), 109.59, 108.29, 33.28, 31.59, 16.29; **HRMS (EI, TOF):** calcd for $C_{27}H_{20}F_2N_2^+$ $[M]^+$: 410.1595, found: 410.1598.

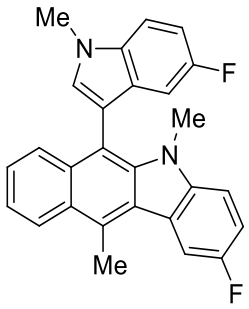


6-(1,5-Dimethyl-1*H*-indol-3-yl)-2,5,11-trimethyl-5*H*-benzo[*b*]carbazole (3m). The compound was prepared from 2-vinylbenzaldehyde (26.4 mg, 0.2 mmol) and 1,5-dimethyl-1*H*-indole (87.1 mg, 0.6 mmol) following the general procedure. The product **3m** was obtained in 60% yield (48 mg) as a yellow solid after column chromatography (eluent = petroleum ether/ethyl acetate 100:1 v/v). **Mp:** 234-236 °C; **^{1}H NMR (400 MHz, $CDCl_3$, 25 °C):** δ 8.40 (dd, J_1 = 8.44 Hz, J_2 = 2.44 Hz,1H), 8.30 (s, 1H), 7.83 (dd, J_1 = 8.48 Hz, J_2 = 3.12 Hz,1H), 7.43-7.47 (m, 1H), 7.39 (d, J = 8.40 Hz,1H), 7.31-7.41 (m, 3H), 7.18 (t, J = 8.36 Hz, 2H), 7.13 (s, 1H), 7.03 (s, 1H), 3.96 (s, 3H), 3.37 (d, J = 2.84 Hz, 3H), 3.27 (d, J = 2.16 Hz, 3H), 2.64 (d, J = 2.84 Hz, 3H), 3.27 (d, J = 3.08 Hz, 3H); **^{13}C NMR (100.6 MHz, $CDCl_3$, 25 °C):** δ 143.21, 140.12, 135.22, 134.01, 131.16, 129.83, 129.09, 128.73, 127.95, 127.59, 127.08, 126.13, 124.48, 124.20, 123.99, 123.86, 123.78, 122.21, 120.27, 111.07, 109.06, 108.56, 107.79, 33.20, 31.75, 21.75, 21.44, 15.93; **HRMS (EI, TOF):** calcd for $C_{29}H_{26}N_2^+$ $[M]^+$: 402.2096 , found: 402.2098.



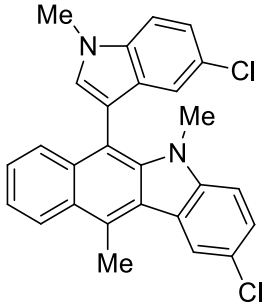
2-Methoxy-6-(5-methoxy-1-methyl-1*H*-indol-3-yl)-5,11-dimethyl-5*H*-benzo[*b*]carbazole (3n). The compound was prepared from 2-vinylbenzaldehyde (26.4 mg, 0.2 mmol) and 5-methoxy-1-methyl-1*H*-indole (96.7 mg, 0.6 mmol) following the general procedure. The product **3n** was obtained in 54% yield (47 mg) as a yellow solid after column chromatography (eluent = petroleum ether/ethyl acetate 30:1 v/v). **Mp:**

228-230 °C; **^{1}H NMR (400 MHz, $CDCl_3$, 25 °C):** δ 8.38 (d, J = 8.56 Hz, 1H), 8.05 (s, 1H), 7.83 (d, J = 8.60 Hz, 1H), 7.45 (t, J = 7.24 Hz, 1H), 7.38 (d, J = 8.88 Hz, 1H), 7.34 (t, J = 7.64 Hz, 1H), 7.18 (s, 2H), 7.12 (s, 1H), 6.98 (dd, J_1 = 8.84 Hz, J_2 = 2.24 Hz, 1H), 8.66 (d, J = 2.28 Hz, 1H), 4.00 (s, 3H), 3.94 (s, 3H), 3.61 (s, 3H), 3.35 (s, 3H), 3.26 (s, 3H); **^{13}C NMR (100.6 MHz, $CDCl_3$, 25 °C):** δ 154.58, 153.37, 140.44, 140.01, 134.10, 132.05, 131.13, 130.28, 128.91, 126.91, 126.09, 124.64, 124.15, 124.00, 123.77, 122.25, 113.92, 112.80, 111.08, 110.27, 109.13, 108.58, 108.36, 101.59, 56.58, 55.85, 33.33, 31.75, 15.79; **HRMS (EI, TOF):** calcd for $C_{29}H_{26}N_2O_2^+$ $[M]^+$: 434.1994, found: 434.1993.

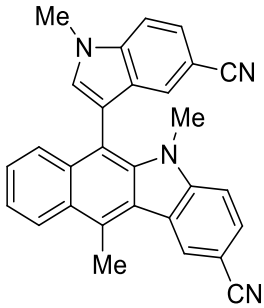


2-Fluoro-6-(5-fluoro-1-methyl-1*H*-indol-3-yl)-5,11-dimethyl-5*H*-benzo[*b*]carbazole (3o). The compound was prepared from 2-vinylbenzaldehyde (26.4 mg, 0.2 mmol) and 5-fluoro-1-methyl-1*H*-indole (89.5 mg, 0.6 mmol) following the general procedure. The product **3o** was obtained in 76% yield (63 mg) as a yellow solid after column chromatography (eluent = petroleum ether/ethyl acetate 50:1 v/v). **Mp:** 225-227 °C; **^{1}H NMR (400 MHz, $CDCl_3$, 25 °C):** δ 8.39 (d, J = 8.52 Hz, 1H), 8.14 (dd, J_1 = 9.88 Hz, J_2 = 2.20 Hz, 1H), 7.79 (d, J = 8.16 Hz, 1H), 7.47 (t, J = 6.88 Hz, 1H), 7.40 (dd, J_1 = 8.92 Hz, J_2 = 4.16 Hz, 1H), 7.36 (t, J = 7.08 Hz, 1H), 7.26 (dt, J_1 = 8.88 Hz, J_2 = 2.36 Hz, 1H), 7.14-7.19 (m, 2H), 7.08 (dt, J_1 = 8.92 Hz, J_2 = 2.28 Hz, 1H), 6.87 (t, J = 7.32 Hz, 1H), 3.96 (s, 3H), 3.29 (s, 3H), 3.24 (s, 3H); **^{13}C NMR (100.6 MHz, $CDCl_3$, 25 °C):** δ 158.35 (d, $J_{C\text{-}F}$ = 235.38 Hz), 157.12 (d, $J_{C\text{-}F}$ = 233.86 Hz), 141.17, 140.30, 134.12, 133.41, 131.32, 130. 97 (d, $J_{C\text{-}F}$ = 9.58 Hz), 129.53, 127.05, 125.82, 125.04, 124.18, 123.94 (d, $J_{C\text{-}F}$ = 9.06 Hz), 123.37 (d, $J_{C\text{-}F}$ = 3.69 Hz), 122.57, 113.72 (d, $J_{C\text{-}F}$ = 24.80 Hz), 111.32 (d, $J_{C\text{-}F}$ = 4.97 Hz), 110.75 (d, $J_{C\text{-}F}$ = 26.54 Hz), 110.27 (d, $J_{C\text{-}F}$ = 9.58 Hz), 110.05 (d, $J_{C\text{-}F}$ = 25.04 Hz), 108.31,108.17 (d, $J_{C\text{-}F}$ = 10.09

Hz), 105.27 (d, $J_{C\text{-}F}$ = 23.47 Hz), 33.45, 31.81, 15.67; **HRMS (EI, TOF):** calcd for $C_{27}H_{20}F_2N_2^+$ $[M]^+$: 410.1595, found: 410.1598.

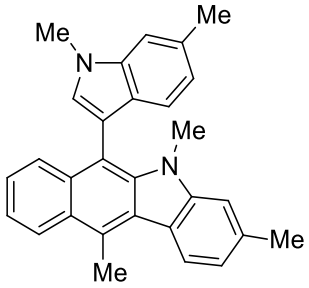


2-Chloro-6-(5-chloro-1-methyl-1*H*-indol-3-yl)-5,11-dimethyl-5*H*-benzo[*b*]carbazole (3p). The compound was prepared from 2-vinylbenzaldehyde (26.4 mg, 0.2 mmol) and 5-chloro-1-methyl-1*H*-indole (99.4 mg, 0.6 mmol) following the general procedure. The product **3p** was obtained in 82% yield (73 mg) as a yellow solid after column chromatography (eluent = petroleum ether/ethyl acetate 30:1 v/v). **Mp:** 234-236 °C; **^{1}H NMR (400 MHz, $CDCl_3$, 25 °C):** δ 8.39 (d, J = 2.00 Hz, 1H), 8.37 (d, J = 8.76 Hz, 1H), 7.70 (d, J = 8.08 Hz, 1H), 7.45 (dt, J_1 = 8.60 Hz, J_2 = 2.00 Hz, 2H), 7.40 (d, J = 8.68 Hz, 1H), 7.32-7.36 (m, 1H), 7.25 (dd, J_1 = 8.60 Hz, J_2 = 1.96 Hz, 2H), 7.15-7.18 (m, 3H), 3.97 (s, 3H), 3.29 (s, 3H), 3.23 (s, 3H); **^{13}C NMR (100.6 MHz, $CDCl_3$, 25 °C):** δ 143.19, 139.94, 135.19, 134.20, 131.69, 131.02, 129.79, 127.25, 126.48, 125.98, 125.83, 125.19, 124.79, 124.22, 123.55, 122.91, 122.76, 122.73, 119.88, 111.07, 110.69, 108.94, 107.90, 33.45, 31.89, 15.88; **HRMS (EI, TOF):** calcd for $C_{27}H_{20}Cl_2N_2^+$ $[M]^+$: 442.1004, found: 442.1008.

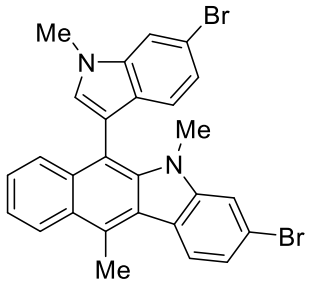


6-(5-Cyano-1-methyl-1*H*-indol-3-yl)-5,11-dimethyl-5*H*-benzo[*b*]carbazole-2-carbonitrile (3q). The compound was prepared from 2-vinylbenzaldehyde (26.4 mg, 0.2 mmol) and 1-methyl-1*H*-indole-5-carbonitrile (93.7 mg, 0.6 mmol) following the general procedure. The product **3q** was obtained in 35% yield (30 mg) as a yellow solid

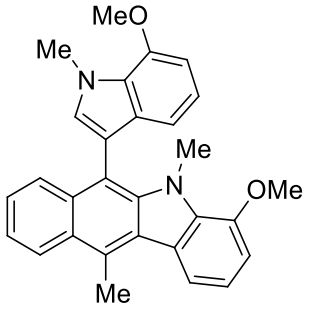
after column chromatography (eluent = petroleum ether/ethyl acetate 100:1 v/v). **Mp:** 287-289 °C; **^{1}H NMR (400 MHz, $CDCl_3$, 25 °C):** δ 8.66 (d, J = 1.24 Hz, 1H), 8.39 (d, J = 8.44 Hz, 1H), 7.74 (dd, J_1 = 8.44 Hz, J_2 = 1.48 Hz, 1H), 7.63 (d, J = 8.56 Hz, 1H), 7.49-7.53 (m, 4H), 7.36-7.40 (m, 1H), 7.34 (s, 1H), 7.26 (d, J = 8.52 Hz, 1H), 4.04 (s, 3H), 3.26 (s, 3H), 3.24 (s, 3H); **^{13}C NMR (100.6 MHz, $CDCl_3$, 25 °C):** δ 146.60, 139.61, 138.19, 134.26, 131.95, 130.76, 130.29, 130.27, 128.06, 127.83, 125.97, 125.87, 125.61, 125.44, 124.41, 123.93, 123.54, 122.36, 120.91, 120.36, 112.22, 110.76, 108.66, 107.66, 103.45, 101.62, 33.57, 32.08, 15.93; **HRMS (EI, TOF):** calcd for $C_{29}H_{20}N_4^+$ $[M]^+$: 424.1688, found: 424.1689.



6-(1,6-Dimethyl-1*H*-indol-3-yl)-3,5,11-trimethyl-5*H*-benzo[*b*]carbazole (3r). The compound was prepared from 2-vinylbenzaldehyde (26.4 mg, 0.2 mmol) and 1,6-dimethyl-1*H*-indole (87.1 mg, 0.6 mmol) following the general procedure. The product **3r** was obtained in 87% yield (70 mg) as a yellow solid after column chromatography (eluent = petroleum ether/ethyl acetate 100:1 v/v). **Mp:** 196-198 °C; **^{1}H NMR (400 MHz, $CDCl_3$, 25 °C):** δ 8.36 (d, J = 8.48 Hz, 1H), 8.33 (d, J = 8.04 Hz, 1H), 7.80 (d, J = 8.56 Hz, 1H), 7.43 (dt, J_1 = 6.52 Hz, J_2 = 1.20 Hz, 1H), 7.30 (dt, J_1 = 6.36 Hz, J_2 = 1.08 Hz, 2H), 7.08-7.14 (m, 4H), 6.91 (dd, J_1 = 8.04 Hz, J_2 = 0.68 Hz, 1H), 3.95 (s, 3H), 3.32 (s, 3H), 3.27 (s, 3H), 2.58 (s, 3H), 2.57 (s, 3H); **^{13}C NMR (100.6 MHz, $CDCl_3$, 25 °C):** δ 145.36, 139.96, 137.15, 136.79, 133.84, 131.96, 129.22, 128.85, 128.08, 127.23, 126.10, 124.33, 123.92, 123.87, 123.56, 122.28, 121.59, 121.38, 120.42, 120.19, 111.49, 109.38, 108.59, 108.53, 33.01, 31.62, 22.30, 22.08, 15.78; **HRMS (EI, TOF):** calcd for $C_{29}H_{26}N_2^+$ $[M]^+$: 402.2096, found: 402.2098.

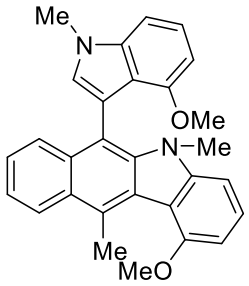


3-bromo-6-(6-bromo-1-methyl-1H-indol-3-yl)-5,11-dimethyl-5*H*-benzo[*b*]carbazole (3s). The compound was prepared from 2-vinylbenzaldehyde (26.4 mg, 0.2 mmol) and 6-bromo-1-methyl-1*H*-indole (126 mg, 0.6 mmol) following the general procedure. The product **3s** was obtained in 62% yield (41 mg) as a yellow solid after column chromatography (eluent = petroleum ether/ethyl acetate 30:1 v/v). **Mp:** 235-237 ºC; **^{1}H NMR (400 MHz, $CDCl_3$, 25 ºC):** δ 8.33 (d, J = 8.44 Hz, 1H), 8.22 (d, J = 8.16 Hz, 1H), 7.68 (d, J = 8.20 Hz, 1H), 7.64 (d, J = 1.48 Hz, 1H), 7.41-7.45 (m, 1H), 7.29-7.36 (m, 3H), 7.13 (dd, J_1 = 8.44 Hz, J_2 = 1.64 Hz, 1H), 7.09 (s, 1H), 7.02 (d, J = 8.40 Hz, 1H), 3.91 (s, 3H), 3.23 (s, 3H), 3.16 (s, 3H); **^{13}C NMR (100.6 MHz, $CDCl_3$, 25 ºC):** δ 145.76, 139.67, 137.56, 134.05, 130.30, 129.53, 129.31, 127.43, 125.85, 125.03, 124.83, 124.09, 123.31, 123.15, 122.82, 122.66, 121.97, 121.86, 120.61, 116.11, 112.69, 111.62, 111.27, 108.04, 33.34, 31.80, 15.86; **HRMS (EI, TOF):** calcd for $C_{27}H_{20}Br_2N_2^+$ $[M]^+$: 529.9993, found: 529.9992.

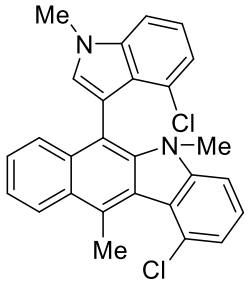


4-Methoxy-6-(7-methoxy-1-methyl-1*H*-indol-3-yl)-5,11-dimethyl-5*H*-benzo[*b*]carbazole (3t). The compound was prepared from 2-vinylbenzaldehyde (26.4 mg, 0.2 mmol) and 7-methoxy-1-methyl-1*H*-indole (96.7 mg, 0.6 mmol) following the general procedure. The product **3t** was obtained in 75% yield (65 mg) as a yellow solid after column chromatography (eluent = petroleum ether/ethyl acetate 30:1 v/v). **Mp:** 195-197 ºC; **^{1}H NMR (400 MHz, $CDCl_3$, 25 ºC):** δ 8.39 (d, J = 8.56 Hz, 1H), 8.14 (d, J = 7.88 Hz, 1H), 7.89 (d, J = 8.56 Hz, 1H), 7.46 (t, J = 6.88 Hz, 1H), 7.33 (t, J = 7.68

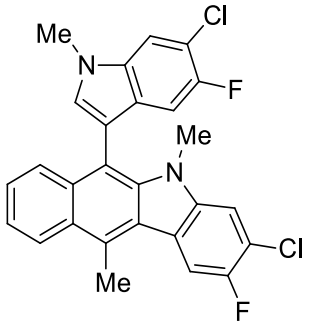
Hz, 1H), 7.23 (d, *J* = 7.96 Hz, 1H), 7.08 (s, 1H), 7.03 (d, *J* = 7.88 Hz, 2H), 6.97 (t, *J* = 7.80 Hz, 1H), 6.87 (d, *J* = 7.88 Hz, 1H), 6.72 (d, *J* = 7.56 Hz, 1H), 4.24 (s, 3H), 4.04 (s, 3H), 3.94 (s, 3H), 3.58 (s, 3H), 3.34 (s, 3H); **^{13}C NMR (100.6 MHz, $CDCl_3$, 25 °C):** δ 147.86, 146.75, 141.64, 134.91, 133.81, 132.82, 130.79, 128.37, 127.43, 126.40, 126.29, 126.16, 124.54, 124.44, 123.96, 122.37, 120.19, 119.48, 116.89, 113.65, 111.89, 109.74, 109.27, 102.58, 55.99, 55.46, 36.77, 35.34, 15.82; **HRMS (EI, TOF):** calcd for $C_{29}H_{26}N_2O_2^+$ $[M]^+$: 434.1994, found: 434.1995.



1-Methoxy-6-(4-methoxy-1-methyl-1*H*-indol-3-yl)-5,11-dimethyl-5*H*-benzo[*b*]carbazole (3u). The compound was prepared from 2-vinylbenzaldehyde (26.4 mg, 0.2 mmol) and 4-methoxy-1-methyl-1*H*-indole (96.7 mg, 0.6 mmol) following the general procedure. The product **3u** was obtained in 38% yield (33 mg) as a yellow solid after column chromatography (eluent = petroleum ether/ethyl acetate 30:1 v/v). **Mp:** 258-260 °C; **^{1}H NMR (400 MHz, $CDCl_3$, 25 °C):** δ 8.40 (d, *J* = 8.52 Hz, 1H), 7.76 (d, *J* = 8.56 Hz, 1H), 7.47 (t, *J* = 8.04 Hz, 1H), 7.42 (dt, J_1 = 8.04 Hz, J_2 = 1.20 Hz, 1H), 7.29-7.33 (m, 1H), 7.28 (d, *J* = 2.92 Hz, 1H), 7.13 (d, *J* = 8.24 Hz, 1H), 6.96 (s, 1H), 6.93 (d, *J* = 8.04 Hz, 1H), 6.77 (d, *J* = 8.00 Hz, 1H), 6.53 (d, *J* = 7.72 Hz, 1H), 4.12 (s, 3H), 3.93 (s, 3H), 3.53 (s, 3H), 3.36 (s, 3H), 3.35 (s, 3H); **^{13}C NMR (100.6 MHz, $CDCl_3$, 25 °C):** δ 155.45, 147.06, 139.77, 138.62, 134.16, 128.80, 128.56, 128.02, 127.81, 126.19, 124.52, 124.26, 123.93, 122.94, 121.86, 120.76, 112.11, 111.23, 110.29, 102.66, 101.44, 100.39, 55.61, 55.52, 33.32, 32.58, 18.95; **HRMS (EI, TOF):** calcd for $C_{29}H_{26}N_2O_2^+$ $[M]^+$: 434.1994, found: 434.1995.

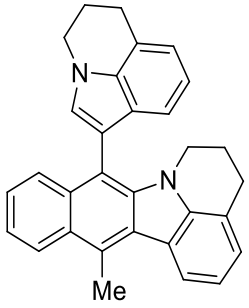


1-Chloro-6-(4-chloro-1-methyl-1*H*-indol-3-yl)-5,11-dimethyl-5*H*-benzo[*b*]carbazole (3v). The compound was prepared from 2-vinylbenzaldehyde (26.4 mg, 0.2 mmol) and 4-chloro-1-methyl-1*H*-indole (99 mg, 0.6 mmol) following the general procedure. The product **3v** was obtained in 44% yield (39 mg) as a yellow solid after column chromatography (eluent = petroleum ether/ethyl acetate 30:1 v/v). **Mp:** 238-240 ºC; **^{1}H NMR (400 MHz, $CDCl_3$, 25 ºC):** δ 8.33 (d, J = 8.56 Hz, 1H), 7.58 (d, J = 8.52 Hz, 1H), 7.42 (dt, J_1 = 7.96 Hz, J_2 = 1.16 Hz, 1H), 7.38 (t, J = 7.92 Hz, 2H), 7.33 (dt, J_1 = 6.56 Hz, J_2 = 0.96 Hz, 1H), 7.21-7.25 (m, 2H), 7.14 (d, J = 8.08Hz, 1H), 7.09 (s, 1H), 7.06 (d, J = 7.56 Hz, 1H), 3.94 (s, 3H), 3.45 (s, 3H), 3.30 (s, 3H); **^{13}C NMR (100.6 MHz, $CDCl_3$, 25 ºC):** δ 146.97, 140.35, 138.13, 135.11, 131.02, 129.72, 128.52, 128.22, 127.48, 127.46, 127.17, 125.83, 125.11, 124.73, 123.32, 122.82, 122.56, 121.45, 121.10, 120.74, 111.29, 108.61, 108.37, 106.36, 33.49, 32.35, 22.40; **HRMS (EI, TOF):** calcd for $C_{27}H_{20}Cl_2N_2^+$ $[M]^+$: 442.1004, found: 442.1003.



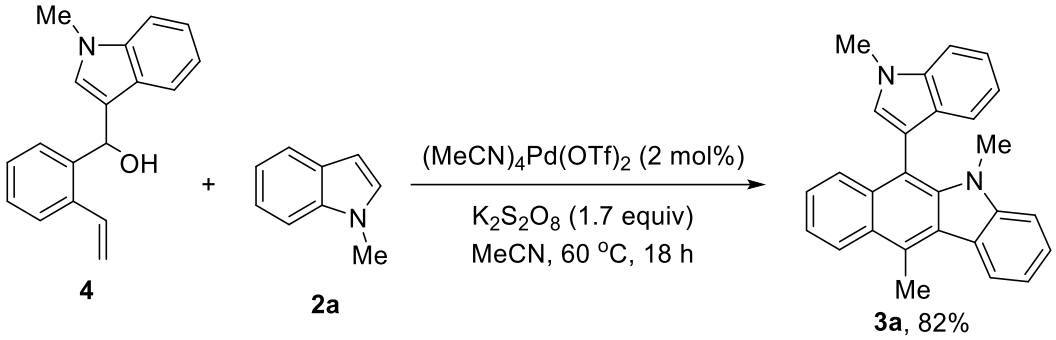
3-Chloro-6-(6-chloro-5-fluoro-1-methyl-1*H*-indol-3-yl)-2-fluoro-5,11-dimethyl-5*H*-benzo[*b*]carbazole (3w). The compound was prepared from 2-vinylbenzaldehyde (26.4 mg, 0.2 mmol) and 6-chloro-5-fluoro-1-methyl-1*H*-indole (110.2 mg, 0.6 mmol) following the general procedure. The product **3w** was obtained in 67% yield (64 mg) as a yellow solid after column chromatography (eluent = petroleum ether/ethyl acetate 30:1 v/v). **Mp:** 257-259 ºC; **^{1}H NMR (400 MHz, $CDCl_3$, 25 ºC):** δ 8.35 (d, J = 8.44 Hz, 1H), 8.16 (d, J = 10.00 Hz, 1H), 7.67 (d, J = 8.16 Hz, 1H), 7.51 (d, J = 5.88 Hz,

1H), 7.46 (dt, J_1 = 6.56 Hz, J_2 = 1.16 Hz, 1H), 7.35 (dt, J_1 = 6.60 Hz, J_2 = 1.08 Hz, 1H), 7.23 (d, J = 6.08 Hz, 1H), 7.19 (s, 1H), 6.91 (d, J = 9.36 Hz, 1H), 3.95 (s, 3H), 3.23 (s, 3H), 3.20 (s, 3H); **^{13}C NMR (100.6 MHz, $CDCl_3$, 25 °C):** δ 153.51 (d, J_{C-F} = 239.25 Hz), 152.28 (d, J_{C-F} = 236.93Hz), 141.24, 140.09, 134.14, 133.21, 131.63, 129.84, 129.36 (d, J_{C-F} = 8.50Hz), 127.28, 125.64, 125.43, 124.24, 122.98, 122.89 (d, J_{C-F} = 3.60 Hz), 122.50 (d, J_{C-F} = 8.01 Hz), 119.50 (d, J_{C-F} = 20.28 Hz), 116.51 (d, J_{C-F} = 21.54 Hz), 111.38 (d, J_{C-F} = 4.73 Hz), 111.07, 110.80, 109.06, 107.78, 106.40 (d, J_{C-F} = 23.40 Hz), 33.62, 31.96, 15.66; **HRMS (EI, TOF):** calcd for $C_{27}H_{18}Cl_2F_2N_2^+$ $[M]^+$: 478.0815, found: 478.0820.

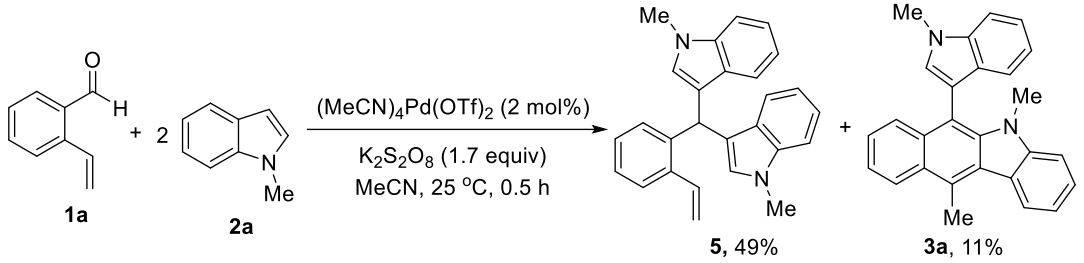


8-(5,6-dihydro-4*H*-pyrrolo[3,2,1-*ij*]quinolin-1-yl)-13-methyl-5,6-dihydro-4*H*-benzo[*b*]pyrido[3,2,1-*jk*]carbazole (3x). The compound was prepared from 2-vinylbenzaldehyde (26.4 mg, 0.2 mmol) and 5,6-dihydro-4*H*-pyrrolo[3,2,1-ij]quinoline (94.3 mg, 0.6 mmol) following the general procedure. The product **3x** was obtained in 91% yield (78 mg) as a yellow solid after column chromatography (eluent = petroleum ether/ethyl acetate 50:1 v/v). **Mp:** 230-232°C; **^{1}H NMR (400 MHz, $CDCl_3$, 25 °C):** δ 8.39 (d, J = 8.96 Hz, 1H), 8.16 (d, J = 7.56 Hz, 1H), 7.72 (d, J = 8.60 Hz, 1H), 7.30-7.34 (m, 1H), 7.18-7.22 (m, 1H), 7.06-7.12 (m, 3H), 6.97 (d, J = 7.64 Hz, 1H), 6.86-6.92 (m, 2H), 4.22 (t, J = 5.64 Hz, 2H), 3.66-3.72 (m, 1H), 3.37-3.43 (m, 1H), 3.24 (s, 3H), 3.05 (t, J = 6.04 Hz, 2H) , 2.80 (t, J = 5.40 Hz, 2H), 2.28-2.34 (m, 2H), 1.73-1.88 (m, 2H); **^{13}C NMR (100.6 MHz, $CDCl_3$, 25 °C):** δ 140.95, 139.01, 134.24, 133.83, 128.89, 128.46, 127.10, 126.98, 126.06, 124.43, 124.37, 123.99, 122.10, 121.88, 121.79, 121.47, 120.83, 120.05, 118.90, 118.48, 118.15, 111.27, 108.71, 44.38, 43.83, 25.29, 24.90, 23.28, 22.98, 15.81; **HRMS (EI, TOF):** calcd for $C_{31}H_{26}N_2^+$ $[M]^+$: 426.2096, found: 426.2097.

4 Mechanism studies for the cascade annulation of 2-vinylbenzaldehydes with indoles



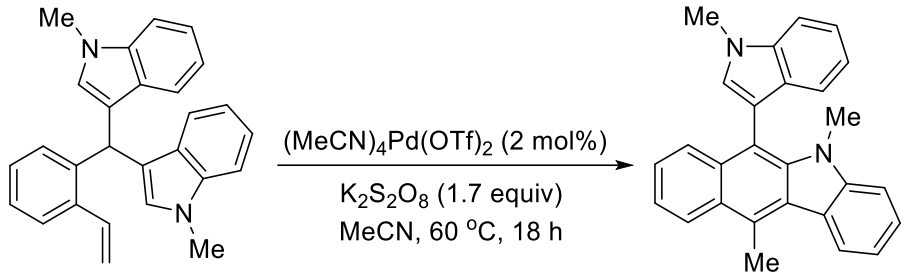
A mixture of (1-methyl-1*H*-indol-3-yl)(2-vinylphenyl)methanol **4** (26.3 mg, 0.1 mmol), 1-methyl-1*H*-indole **2a** (39.4 mg, 0.3 mmol), $Pd(MeCN)_4(OTf)_2$ (1.2 mg, 0.002 mmol), $K_2S_2O_8$ (46 mg, 0.17 mmol), in MeCN (1.0 mL) was stirred at 60 °C (oil bath temperature) in a sealed tube under nitrogen atmosphere. After 18 h, the reaction mixture was cooled down to room temperature and then transferred to a round bottom flask. Silica gel was added to the flask and volatiles were evaporated under reduced pressure. The purification was performed by flash column chromatography on silica gel to afford the addition product **3a** (31 mg, 82% yield).



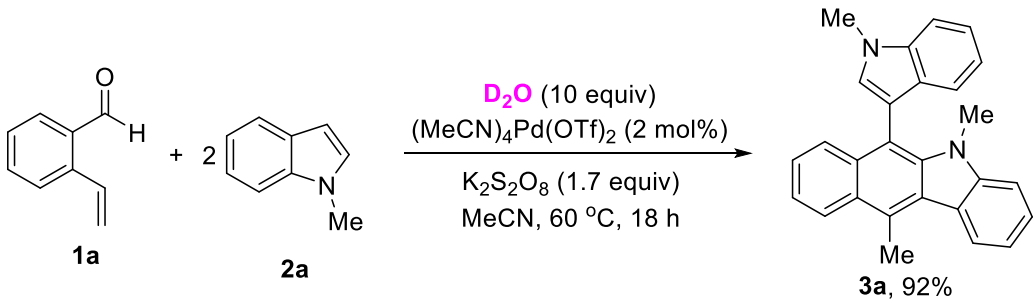
A mixture of 2-vinylbenzaldehyde **1a** (26.4 mg, 0.2 mmol), 1-methyl-1*H*-indole **2a** (78.7 mg, 0.6 mmol), $Pd(MeCN)_4(OTf)_2$ (2.4 mg, 0.004 mmol), $K_2S_2O_8$ (92 mg, 0.34 mmol), in MeCN (1.5 mL) was stirred at 25 °C in a sealed tube under nitrogen atmosphere. After 0.5 h, the reaction mixture was filtered and ransferred to a round bottom flask. Silica gel was added to the flask and volatiles were evaporated under reduced pressure. The purification was performed by flash column chromatography on silica gel to afford the addition product **5** (37 mg, 49% yield) and **3a** (8 mg, 11% yield).

3,3'-((2-Vinylphenyl)methylene)bis(1-methyl-1*H*-indole) (5). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ 7.55 (d, J = 7.56 Hz, 1H), 7.28-7.34 (m, 4H), 7.17-7.21 (m, 3H), 7.06-

7.13 (m, 3H), 6.98 (dt, J_1 = 7.88 Hz, J_2 = 0.92 Hz, 2H), 6.45 (d, J = 0.32 Hz, 2H), 6.13 (s, 1H), 5.66 (dd, J_1 = 17.36 Hz, J_2 = 1.56 Hz, 1H), 5.51 (dd, J_1 = 10.96 Hz, J_2 = 1.56 Hz, 1H), 3.66 (s, 6H); **^{13}C NMR (100.6 MHz, $CDCl_3$, 25 °C)**: δ 141.45, 137.59, 136.76, 135.20, 128.90, 128.82, 128.32, 127.74, 127.58, 126.39, 126.04, 121.55, 120.12, 118.75, 117.81, 116.02, 109.16, 36.05, 32.83; **HRMS (EI, TOF):** calcd for $C_{27}H_{24}N_2^+$ $[M]^+$: 376.1939, found: 376.1943.

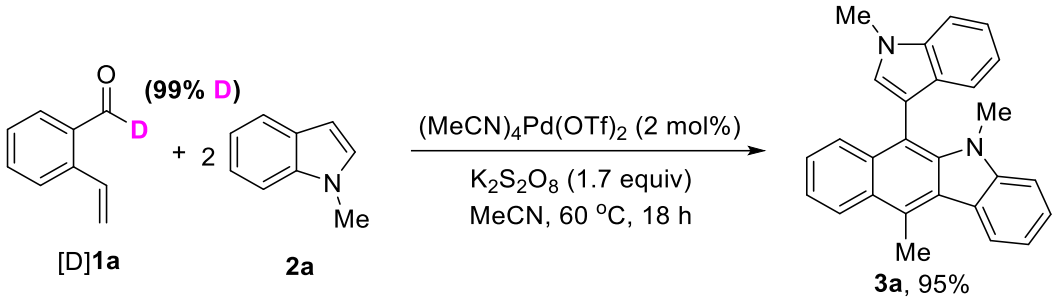


Then a mixture of 3,3'-((2-vinylphenyl)methylene)bis(1-methyl-1*H*-indole) **5** (37.8 mg, 0.1 mmol), $Pd(MeCN)_4(OTf)_2$ (1.2 mg, 0.002 mmol), $K_2S_2O_8$ (46 mg, 0.17 mmol), in MeCN (1 mL) was stirred at 60 °C (oil bath temperature) in a sealed tube under nitrogen atmosphere. After 18 h, the reaction mixture was cooled down to room temperature and then transferred to a round bottom flask. Silica gel was added to the flask and volatiles were evaporated under reduced pressure. The purification was performed by flash column chromatography on silica gel to afford the addition product **3a** (17 mg, 45% yield).

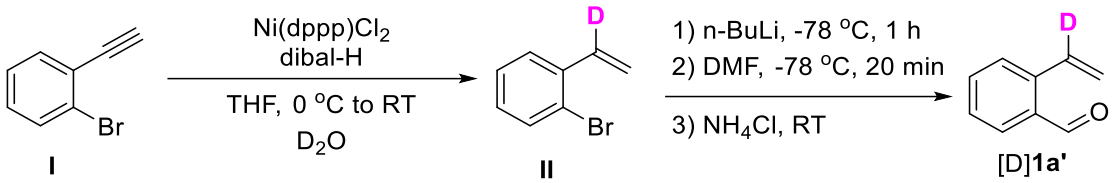


A mixture of **1a** (26.4 mg, 0.2 mmol), 1-methyl-1*H*-indole **2a** (78.7 mg, 0.6 mmol), $Pd(MeCN)_4(OTf)_2$ (2.4 mg, 0.004 mmol), $K_2S_2O_8$ (92 mg, 0.34 mmol) and **D_2O** (10 equiv) in MeCN (1.5 mL) was stirred at 60 °C (oil bath temperature) in a sealed tube under nitrogen atmosphere. After 18 h, the reaction mixture was cooled down to room temperature and then transferred to a round bottom flask. Silica gel was added to the

flask and volatiles were evaporated under reduced pressure. The purification was performed by flash column chromatography on silica gel to afford the addition product **3a** (69 mg, 92% yield) without any deuterated product.



A mixture of [D]**1a** (26.6 mg, 0.2 mmol), 1-methyl-1*H*-indole **2a** (78.7 mg, 0.6 mmol), $Pd(MeCN)_4(OTf)_2$ (2.4 mg, 0.004 mmol), $K_2S_2O_8$ (92 mg, 0.34 mmol), in MeCN (1.5 mL) was stirred at 60 °C (oil bath temperature) in a sealed tube under nitrogen atmosphere. After 18 h, the reaction mixture was cooled down to room temperature and then transferred to a round bottom flask. Silica gel was added to the flask and volatiles were evaporated under reduced pressure. The purification was performed by flash column chromatography on silica gel to afford the addition product **3a** (69.1mg, 92% yield) without any deuterated product.



$Ni(dppp)Cl_2$ (162.6 mg, 0.3 mmol) is placed in an oven-dried Schlenk tube equipped with a stirring bar. The Schlenk tube was sealed with a septum and purged with argon for approximately ten minutes. Tetrahydrofuran (10 mL) was added with a syringe, followed by dropwise addition of commercial grade 1M di-iso-butylaluminum hydride in THF (13 mL, 13 mmol) at 22 °C (gas evolution occurs as dibal-H was added). The resulting black solution was allowed to cool to 0 °C (ice bath) before **I** (1.2 mL, 10 mmol) was slowly added over 30 minutes (please note that reaction was exothermic). The resulting black solution was allowed to warm to 22 °C and stirred for additional two hours. The reaction mixture was subjected to dropwise addition of D_2O (1 mL) at 0 °C (ice bath) and the resulting mixture was allowed to stir at 0 °C for additional 30

minutes. The aqueous layer was washed with methyl tert-butyl ether (10 mL x 3) and the combined organic layers were passed through a plug of anhydrous Na_2SO_4 and concentrated in vacuo. The crude product was purified by silica gel chromatography (100% *n*-pentane) to yield **II** (1.8 g, 98% ,deuteration level: >98% based on ^{1}HNMR).

n-BuLi (2.5 M solution in hexanes, 22 mmol) was added slowly to a solution of **II** (2 mmol) in THF (15 mL) at -78 °C , then stirred for 1 hour at this temperature. DMF (2.5 mmol) was then added dropwise to the mixture and stirred for a further 20 min. Saturated aqueous NH_4Cl (6 mL) was added and the mixture was extracted with Et_2O (3 x 10 mL). The combined organic phase was washed with saturated aqueous NaCl and dried over $MgSO_4$, then concentrated in vacuo. The crude residue was purified by silica chromatography (EtOAc: Petroleum ether = 1:25) to give the desired [D]**1a'** (178 mg, 67% yield, deuteration level: >95% based on ^{1}HNMR in Fugure S1) as a pale yellow oil.

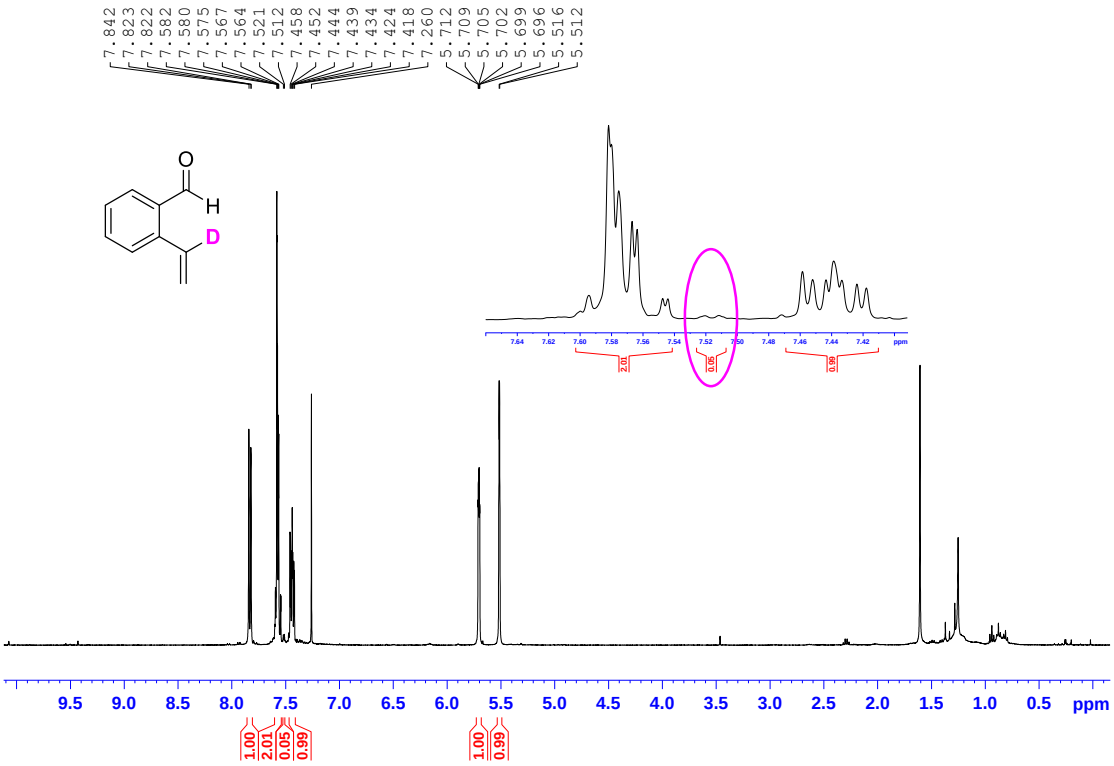
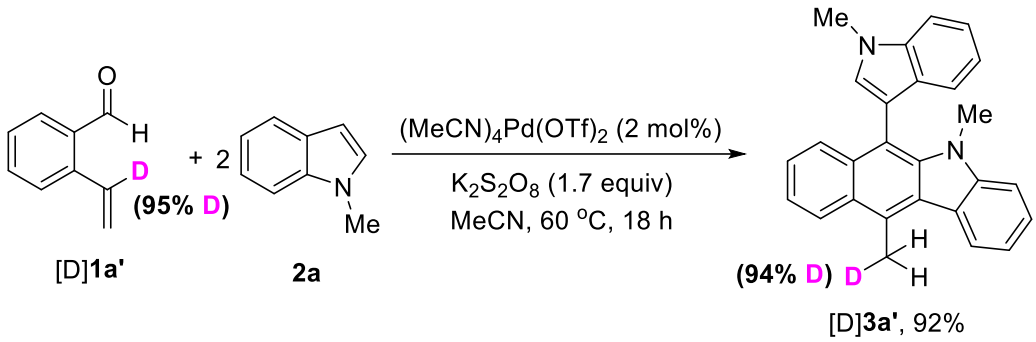


Figure S1. ^{1}H NMR spectra analysis of deuterated products [D]**1a'**



A mixture of [D]**1a'** (26.6 mg, 0.2 mmol), 1-methyl-1*H*-indole **2a** (78.7 mg, 0.6 mmol), $Pd(MeCN)_4(OTf)_2$ (2.4 mg, 0.004 mmol), $K_2S_2O_8$ (92 mg, 0.34 mmol), in MeCN (1.5 mL) was stirred at 60 °C (oil bath temperature) in a sealed tube under nitrogen atmosphere. After 18 h, the reaction mixture was cooled down to room temperature and then transferred to a round bottom flask. Silica gel was added to the flask and volatiles were evaporated under reduced pressure. The purification was performed by flash column chromatography on silica gel to afford the addition product [D]**3a'** (69 mg, 92% yield). Deuterated ratio of [D]**3a'** was determined by ^{1}H NMR (Figure S2).

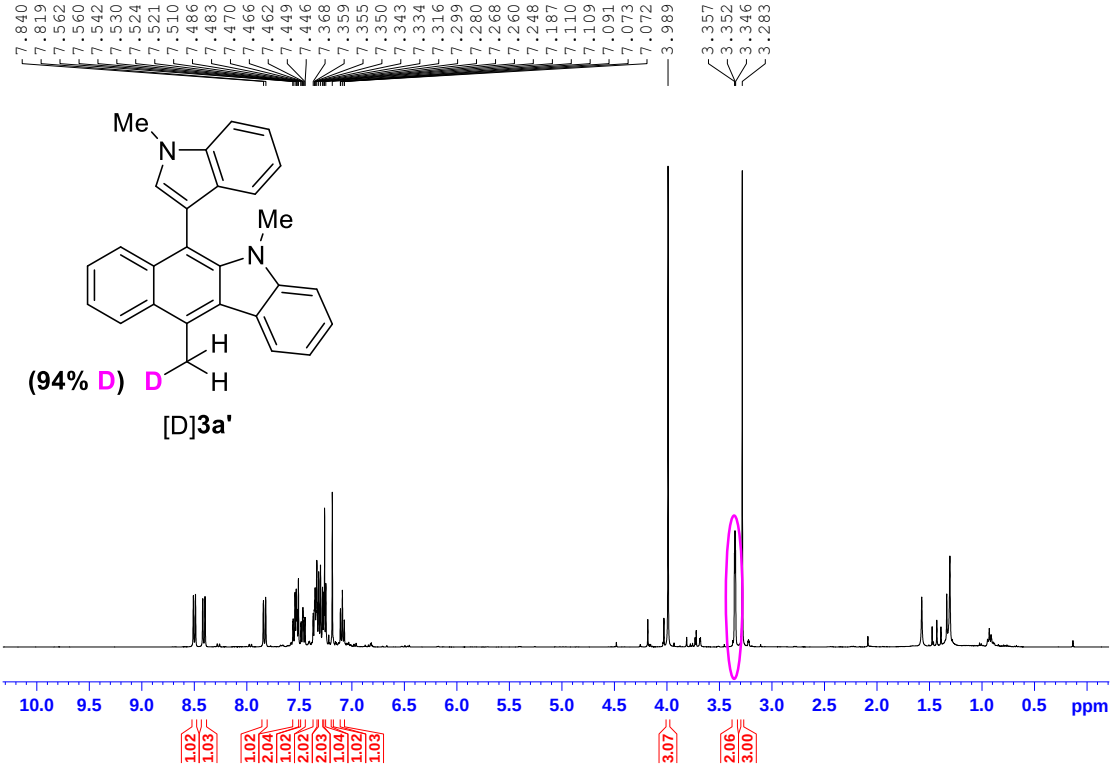
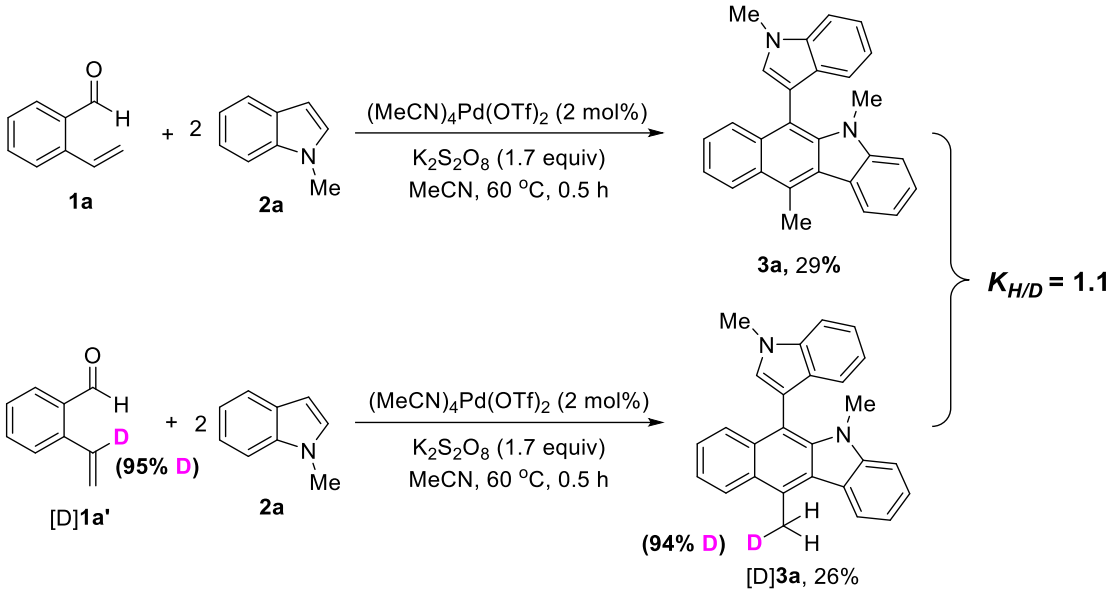


Figure S2. ^{1}H NMR spectra analysis of deuterated products [D]**3a'**



A mixture of 2-vinylbenzaldehydes **1a** (26.4 mg, 0.2 mmol) or [D]**1a**' (26.4 mg, 0.2 mmol), 1-methyl-1*H*-indoles **2a** (78.7 mg, 0.6 mmol), $(MeCN)_4Pd(OTf)_2$ (2.4 mg, 0.004 mmol), $K_2S_2O_8$ (92 mg, 0.34 mmol) in MeCN (1.5 mL) was stirred at 60 °C (oil bath temperature) in a sealed tube under nitrogen atmosphere. After 30 min, they were cooled down to room temperature and then the two parallel reaction mixtures were transferred to a round bottom flask respectively. Silica gel was added to the flask and volatiles were evaporated under reduced pressure. The purification was performed by flash column chromatography on silica gel (see below for specific eluents) to afford the desired products **3a** (22 mg, 29%) and [D]**3a** (20 mg, 26%), $K_{H/D}$ = 1.1.

5 Crystal data and structure refinement of product 3u

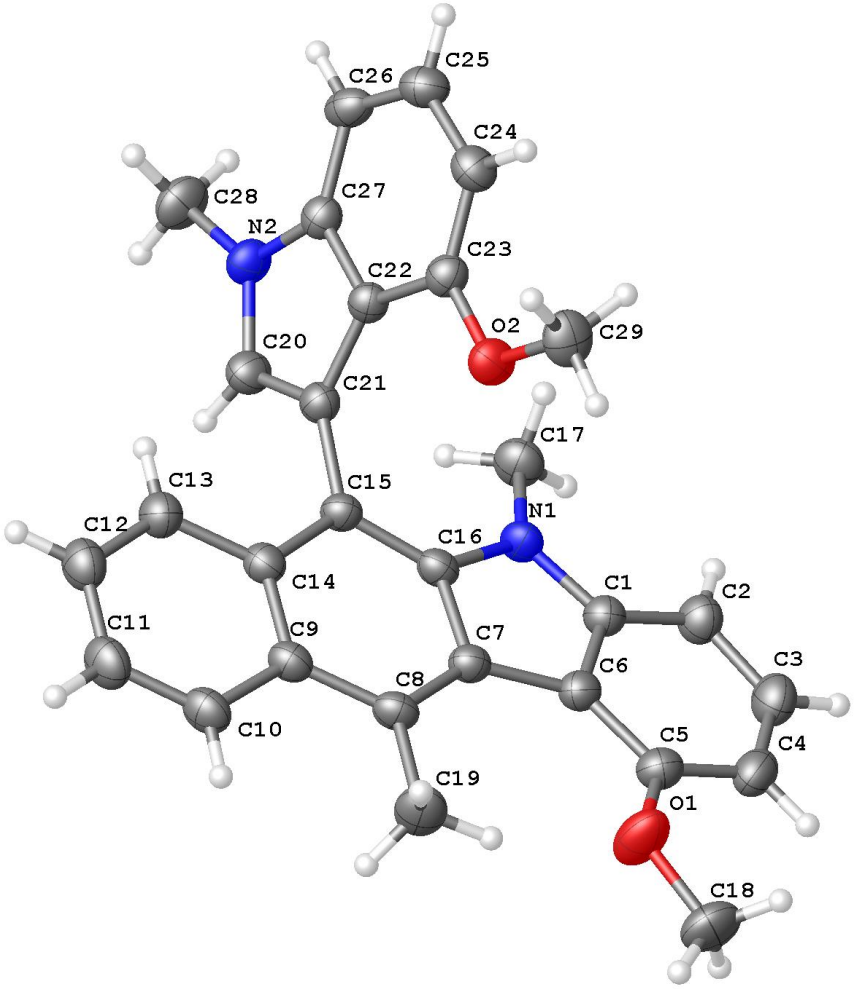


Figure S5. Crystal data and structure refinement of product **3u**.

Table S3. Crystal data and structure refinement for **3u**

Identification code	**3u**
CCDC	1885278
Empirical formula	$C_{29}H_{26}N_2O_2$
Formula weight	434.52
Temperature	296.15 K
Wavelength	0.71073 Å
Crystal system	Triclinic
Space group	P -1
Unit cell dimensions	a = 6.816(3) Å = 64.897(7) °.

	b = 12.787(6) Å = 85.931(9) °.
	c = 14.108(6) Å = 82.683(7) °.
Volume	1104.2(8) $Å^3$
Z	2
Density (calculated)	1.307 Mg/m^3
Absorption coefficient	0.082 mm^{-1}
F(000)	460
Crystal size	0.08 x 0.05 x 0.03 mm^3
Theta range for data collection	1.769 to 25.997 °.
Index ranges	-8<=h<=8, -15<=k<=15, -17<=l<=17
Reflections collected	8072
Independent reflections	4348 [R(int) = 0.0451]
Completeness to theta = 25.242 °	99.9 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7456 and 0.5243
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4348 / 0 / 303
Goodness-of-fit on F^2	0.927
Final R indices [I>2sigma(I)]	R1 = 0.0614, wR2 = 0.1469
R indices (all data)	R1 = 0.1392, wR2 = 0.1865
Extinction coefficient	n/a
Largest diff. peak and hole	0.242 and -0.241 e.$Å^{-3}$

Table S4. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **3u**.

U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
O(1)	-3056(4)	103(2)	-2550(2)	93(1)
O(2)	-4565(3)	-4905(2)	-1511(2)	61(1)
N(1)	-7828(3)	-2367(2)	-2150(2)	51(1)
N(2)	-9979(4)	-5268(2)	-3086(2)	55(1)
C(1)	-7268(4)	-1583(2)	-1816(2)	51(1)
C(2)	-8225(5)	-1285(3)	-1043(3)	62(1)
C(3)	-7418(5)	-491(3)	-811(3)	71(1)
C(4)	-5708(5)	-20(3)	-1307(3)	66(1)
C(5)	-4780(5)	-318(3)	-2075(3)	58(1)
C(6)	-5561(4)	-1098(2)	-2371(2)	50(1)
C(7)	-5121(4)	-1573(2)	-3153(2)	46(1)
C(8)	-3774(4)	-1369(2)	-3990(2)	50(1)
C(9)	-3891(4)	-1980(2)	-4630(2)	50(1)
C(10)	-2674(5)	-1744(3)	-5553(2)	61(1)
C(11)	-2730(5)	-2344(3)	-6151(3)	69(1)
C(12)	-3983(5)	-3209(3)	-5879(3)	67(1)
C(13)	-5196(5)	-3458(3)	-5009(2)	59(1)
C(14)	-5229(4)	-2833(2)	-4380(2)	49(1)
C(15)	-6564(4)	-3074(2)	-3502(2)	45(1)
C(16)	-6547(4)	-2388(2)	-2966(2)	46(1)
C(17)	-9653(5)	-2902(3)	-1804(3)	67(1)
C(18)	-2332(6)	1004(3)	-2399(3)	93(1)
C(19)	-2224(5)	-542(3)	-4253(3)	79(1)
C(20)	-9335(5)	-4187(3)	-3618(3)	57(1)
C(21)	-7733(4)	-4074(2)	-3159(2)	48(1)

C(22)	-7321(4)	-5179(2)	-2270(2)	44(1)
C(23)	-5897(4)	-5642(3)	-1476(2)	50(1)
C(24)	-5908(5)	-6771(3)	-733(2)	58(1)
C(25)	-7332(5)	-7451(3)	-760(3)	61(1)
C(26)	-8763(5)	-7045(2)	-1499(3)	58(1)
C(27)	-8736(4)	-5896(2)	-2256(2)	49(1)
C(28)	-11626(5)	-5680(3)	-3369(3)	73(1)
C(29)	-3044(5)	-5350(3)	-755(3)	72(1)

Table S5. Bond lengths [Å] and angles [°] for **3u**.

O(1)-C(5)	1.364(4)
O(1)-C(18)	1.410(4)
O(2)-C(23)	1.374(3)
O(2)-C(29)	1.424(4)
N(1)-C(1)	1.376(4)
N(1)-C(16)	1.402(4)
N(1)-C(17)	1.450(4)
N(2)-C(20)	1.377(4)
N(2)-C(27)	1.379(4)
N(2)-C(28)	1.446(4)
C(1)-C(2)	1.396(4)
C(1)-C(6)	1.412(4)
C(2)-H(2)	0.9300
C(2)-C(3)	1.376(4)
C(3)-H(3)	0.9300
C(3)-C(4)	1.385(5)
C(4)-H(4)	0.9300
C(4)-C(5)	1.382(5)
C(5)-C(6)	1.404(4)

C(6)-C(7)	1.467(4)
C(7)-C(8)	1.396(4)
C(7)-C(16)	1.445(4)
C(8)-C(9)	1.434(4)
C(8)-C(19)	1.506(4)
C(9)-C(10)	1.434(4)
C(9)-C(14)	1.423(4)
C(10)-H(10)	0.9300
C(10)-C(11)	1.363(4)
C(11)-H(11)	0.9300
C(11)-C(12)	1.391(5)
C(12)-H(12)	0.9300
C(12)-C(13)	1.372(4)
C(13)-H(13)	0.9300
C(13)-C(14)	1.423(4)
C(14)-C(15)	1.430(4)
C(15)-C(16)	1.382(4)
C(15)-C(21)	1.478(4)
C(17)-H(17A)	0.9600
C(17)-H(17B)	0.9600
C(17)-H(17C)	0.9600
C(18)-H(18A)	0.9600
C(18)-H(18B)	0.9600
C(18)-H(18C)	0.9600
C(19)-H(19A)	0.9600
C(19)-H(19B)	0.9600
C(19)-H(19C)	0.9600
C(20)-H(20)	0.9300
C(20)-C(21)	1.361(4)
C(21)-C(22)	1.446(4)

C(22)-C(23)	1.412(4)
C(22)-C(27)	1.407(4)
C(23)-C(24)	1.379(4)
C(24)-H(24)	0.9300
C(24)-C(25)	1.395(4)
C(25)-H(25)	0.9300
C(25)-C(26)	1.365(4)
C(26)-H(26)	0.9300
C(26)-C(27)	1.406(4)
C(28)-H(28A)	0.9600
C(28)-H(28B)	0.9600
C(28)-H(28C)	0.9600
C(29)-H(29A)	0.9600
C(29)-H(29B)	0.9600
C(29)-H(29C)	0.9600

C(5)-O(1)-C(18)	120.6(3)
C(23)-O(2)-C(29)	117.8(2)
C(1)-N(1)-C(16)	108.8(2)
C(1)-N(1)-C(17)	122.8(3)
C(16)-N(1)-C(17)	127.6(3)
C(20)-N(2)-C(27)	107.7(3)
C(20)-N(2)-C(28)	125.9(3)
C(27)-N(2)-C(28)	126.4(3)
N(1)-C(1)-C(2)	126.0(3)
N(1)-C(1)-C(6)	110.6(3)
C(2)-C(1)-C(6)	123.4(3)
C(1)-C(2)-H(2)	121.4
C(3)-C(2)-C(1)	117.2(3)
C(3)-C(2)-H(2)	121.4

C(2)-C(3)-H(3)	119.2
C(2)-C(3)-C(4)	121.6(3)
C(4)-C(3)-H(3)	119.2
C(3)-C(4)-H(4)	119.7
C(5)-C(4)-C(3)	120.6(3)
C(5)-C(4)-H(4)	119.7
O(1)-C(5)-C(4)	121.7(3)
O(1)-C(5)-C(6)	117.7(3)
C(4)-C(5)-C(6)	120.6(3)
C(1)-C(6)-C(7)	106.1(3)
C(5)-C(6)-C(1)	116.5(3)
C(5)-C(6)-C(7)	137.4(3)
C(8)-C(7)-C(6)	134.8(3)
C(8)-C(7)-C(16)	119.1(3)
C(16)-C(7)-C(6)	106.0(2)
C(7)-C(8)-C(9)	117.8(3)
C(7)-C(8)-C(19)	123.5(3)
C(9)-C(8)-C(19)	118.8(3)
C(10)-C(9)-C(8)	121.0(3)
C(14)-C(9)-C(8)	121.5(3)
C(14)-C(9)-C(10)	117.5(3)
C(9)-C(10)-H(10)	119.2
C(11)-C(10)-C(9)	121.5(3)
C(11)-C(10)-H(10)	119.2
C(10)-C(11)-H(11)	119.7
C(10)-C(11)-C(12)	120.7(3)
C(12)-C(11)-H(11)	119.7
C(11)-C(12)-H(12)	120.0
C(13)-C(12)-C(11)	120.1(3)
C(13)-C(12)-H(12)	120.0

C(12)-C(13)-H(13)	119.4
C(12)-C(13)-C(14)	121.2(3)
C(14)-C(13)-H(13)	119.4
C(9)-C(14)-C(15)	120.8(3)
C(13)-C(14)-C(9)	118.9(3)
C(13)-C(14)-C(15)	120.3(3)
C(14)-C(15)-C(21)	120.1(3)
C(16)-C(15)-C(14)	116.0(3)
C(16)-C(15)-C(21)	123.6(3)
N(1)-C(16)-C(7)	108.3(3)
C(15)-C(16)-N(1)	127.4(3)
C(15)-C(16)-C(7)	124.2(3)
N(1)-C(17)-H(17A)	109.5
N(1)-C(17)-H(17B)	109.5
N(1)-C(17)-H(17C)	109.5
H(17A)-C(17)-H(17B)	109.5
H(17A)-C(17)-H(17C)	109.5
H(17B)-C(17)-H(17C)	109.5
O(1)-C(18)-H(18A)	109.5
O(1)-C(18)-H(18B)	109.5
O(1)-C(18)-H(18C)	109.5
H(18A)-C(18)-H(18B)	109.5
H(18A)-C(18)-H(18C)	109.5
H(18B)-C(18)-H(18C)	109.5
C(8)-C(19)-H(19A)	109.5
C(8)-C(19)-H(19B)	109.5
C(8)-C(19)-H(19C)	109.5
H(19A)-C(19)-H(19B)	109.5
H(19A)-C(19)-H(19C)	109.5
H(19B)-C(19)-H(19C)	109.5

N(2)-C(20)-H(20)	124.2
C(21)-C(20)-N(2)	111.6(3)
C(21)-C(20)-H(20)	124.2
C(20)-C(21)-C(15)	128.6(3)
C(20)-C(21)-C(22)	105.4(3)
C(22)-C(21)-C(15)	125.9(3)
C(23)-C(22)-C(21)	134.9(3)
C(27)-C(22)-C(21)	107.3(2)
C(27)-C(22)-C(23)	117.8(3)
O(2)-C(23)-C(22)	115.8(2)
O(2)-C(23)-C(24)	124.4(3)
C(24)-C(23)-C(22)	119.8(3)
C(23)-C(24)-H(24)	119.9
C(23)-C(24)-C(25)	120.2(3)
C(25)-C(24)-H(24)	119.9
C(24)-C(25)-H(25)	118.6
C(26)-C(25)-C(24)	122.7(3)
C(26)-C(25)-H(25)	118.6
C(25)-C(26)-H(26)	121.6
C(25)-C(26)-C(27)	116.8(3)
C(27)-C(26)-H(26)	121.6
N(2)-C(27)-C(22)	108.0(2)
N(2)-C(27)-C(26)	129.3(3)
C(26)-C(27)-C(22)	122.7(3)
N(2)-C(28)-H(28A)	109.5
N(2)-C(28)-H(28B)	109.5
N(2)-C(28)-H(28C)	109.5
H(28A)-C(28)-H(28B)	109.5
H(28A)-C(28)-H(28C)	109.5
H(28B)-C(28)-H(28C)	109.5

O(2)-C(29)-H(29A)	109.5
O(2)-C(29)-H(29B)	109.5
O(2)-C(29)-H(29C)	109.5
H(29A)-C(29)-H(29B)	109.5
H(29A)-C(29)-H(29C)	109.5
H(29B)-C(29)-H(29C)	109.5

Symmetry transformations used to generate equivalent atoms:

Table S6. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for **3u**. The anisotropic displacement factor exponent takes the form: $-2\ ^2[\ h^2\ a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
O(1)	94(2)	107(2)	112(2)	-70(2)	29(2)	-56(2)
O(2)	58(1)	68(1)	60(1)	-24(1)	-8(1)	-18(1)
N(1)	50(2)	55(1)	48(2)	-22(1)	12(1)	-18(1)
N(2)	48(2)	61(2)	62(2)	-30(1)	-3(1)	-14(1)
C(1)	55(2)	48(2)	49(2)	-20(2)	1(2)	-8(1)
C(2)	64(2)	68(2)	61(2)	-33(2)	7(2)	-10(2)
C(3)	80(3)	74(2)	67(2)	-40(2)	3(2)	-5(2)
C(4)	81(3)	59(2)	67(2)	-33(2)	-10(2)	-7(2)
C(5)	62(2)	52(2)	61(2)	-23(2)	1(2)	-12(2)
C(6)	54(2)	46(2)	49(2)	-18(2)	-2(2)	-8(1)
C(7)	47(2)	44(2)	47(2)	-16(1)	0(1)	-10(1)
C(8)	47(2)	48(2)	50(2)	-13(2)	5(2)	-13(1)
C(9)	49(2)	50(2)	46(2)	-14(1)	5(1)	-7(1)
C(10)	60(2)	64(2)	53(2)	-19(2)	12(2)	-10(2)

C(11)	73(2)	79(2)	54(2)	-29(2)	16(2)	-7(2)
C(12)	74(2)	75(2)	56(2)	-32(2)	4(2)	-5(2)
C(13)	65(2)	59(2)	55(2)	-26(2)	3(2)	-9(2)
C(14)	52(2)	47(2)	45(2)	-16(1)	2(2)	-4(1)
C(15)	46(2)	44(2)	46(2)	-17(1)	4(1)	-11(1)
C(16)	46(2)	45(2)	41(2)	-12(1)	3(1)	-10(1)
C(17)	60(2)	75(2)	66(2)	-29(2)	13(2)	-20(2)
C(18)	103(3)	81(3)	112(3)	-47(2)	-2(3)	-42(2)
C(19)	81(3)	91(3)	76(3)	-39(2)	26(2)	-45(2)
C(20)	61(2)	53(2)	56(2)	-19(2)	-7(2)	-7(2)
C(21)	50(2)	50(2)	46(2)	-21(1)	3(1)	-9(1)
C(22)	40(2)	49(2)	46(2)	-21(1)	4(1)	-10(1)
C(23)	47(2)	53(2)	54(2)	-26(2)	3(2)	-9(2)
C(24)	57(2)	59(2)	52(2)	-19(2)	-2(2)	-3(2)
C(25)	64(2)	51(2)	62(2)	-18(2)	5(2)	-11(2)
C(26)	61(2)	50(2)	66(2)	-28(2)	19(2)	-19(2)
C(27)	45(2)	54(2)	52(2)	-27(2)	3(2)	-8(1)
C(28)	59(2)	82(2)	90(3)	-45(2)	-10(2)	-18(2)
C(29)	50(2)	96(3)	74(2)	-38(2)	-6(2)	-14(2)

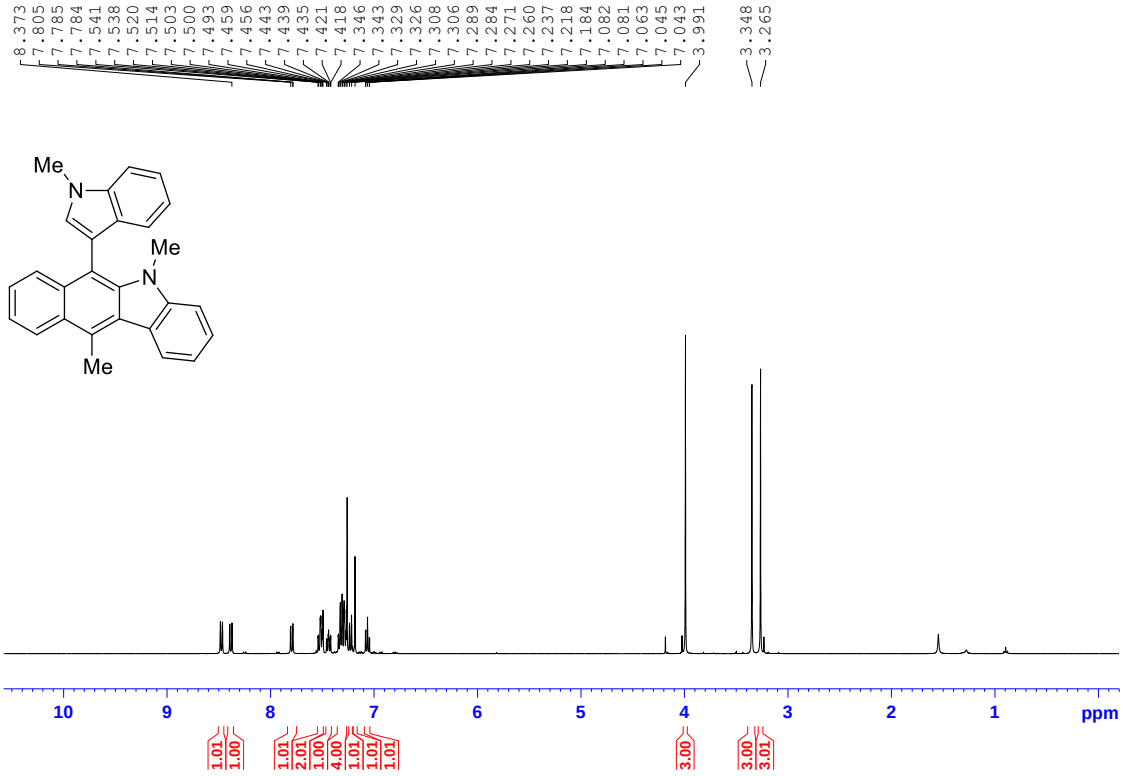
Table S7. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for **3u**.

	x	y	z	U(eq)
H(2)	-9361	-1610	-700	75
H(3)	-8036	-265	-308	85
H(4)	-5179	501	-1123	80

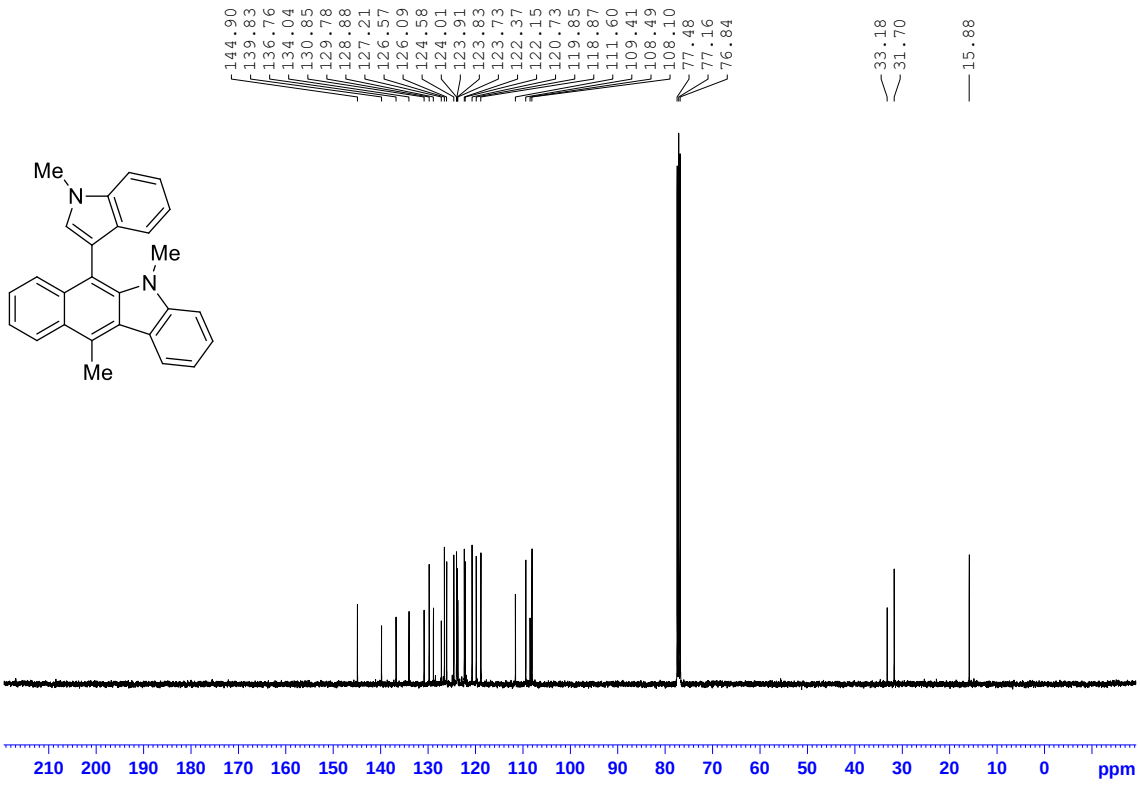
H(10)	-1825	-1169	-5750	73
H(11)	-1923	-2172	-6746	83
H(12)	-3999	-3618	-6288	81
H(13)	-6011	-4047	-4827	71
H(17A)	-10240	-2945	-2383	100
H(17B)	-10552	-2445	-1537	100
H(17C)	-9376	-3671	-1262	100
H(18A)	-1241	1278	-2874	140
H(18B)	-1897	718	-1692	140
H(18C)	-3365	1631	-2528	140
H(19A)	-2401	-144	-3803	119
H(19B)	-2350	15	-4969	119
H(19C)	-933	-968	-4153	119
H(20)	-9922	-3606	-4216	69
H(24)	-4964	-7081	-213	70
H(25)	-7305	-8212	-253	73
H(26)	-9710	-7508	-1500	69
H(28A)	-11153	-6320	-3540	109
H(28B)	-12269	-5063	-3965	109
H(28C)	-12551	-5929	-2791	109
H(29A)	-2284	-4737	-829	107
H(29B)	-2195	-5952	-862	107
H(29C)	-3627	-5663	-65	107

6 Copies of the ^{1}H NMR and ^{13}C NMR spectra

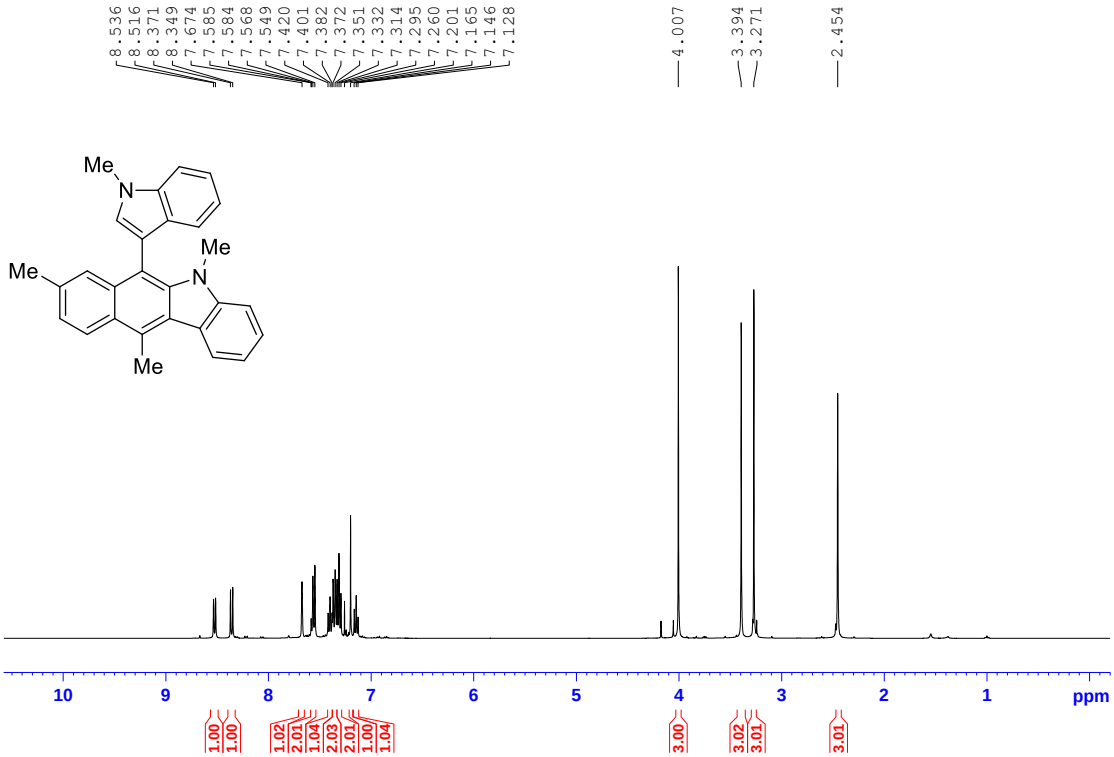
^{1}H NMR of 5,11-Dimethyl-6-(1-methyl-1*H*-indol-3-yl)-5*H*-benzo[*b*]carbazole (3a)



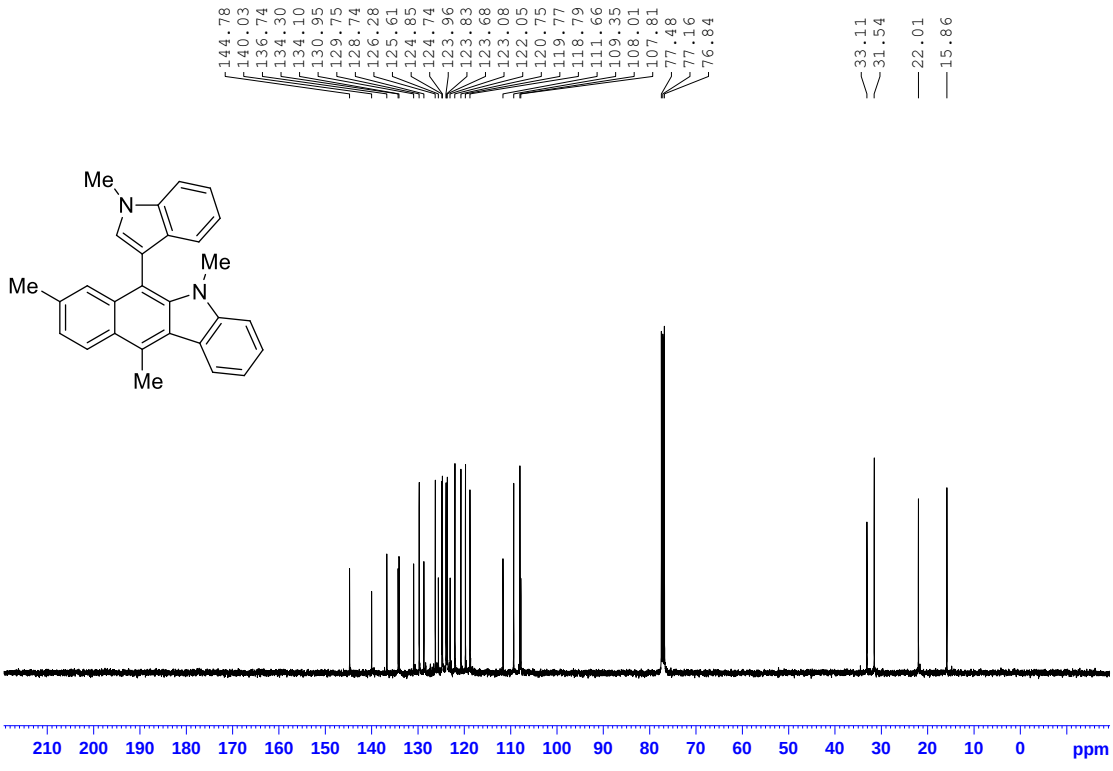
^{13}C NMR of 5,11-Dimethyl-6-(1-methyl-1*H*-indol-3-yl)-5*H*-benzo[*b*]carbazole (3a)



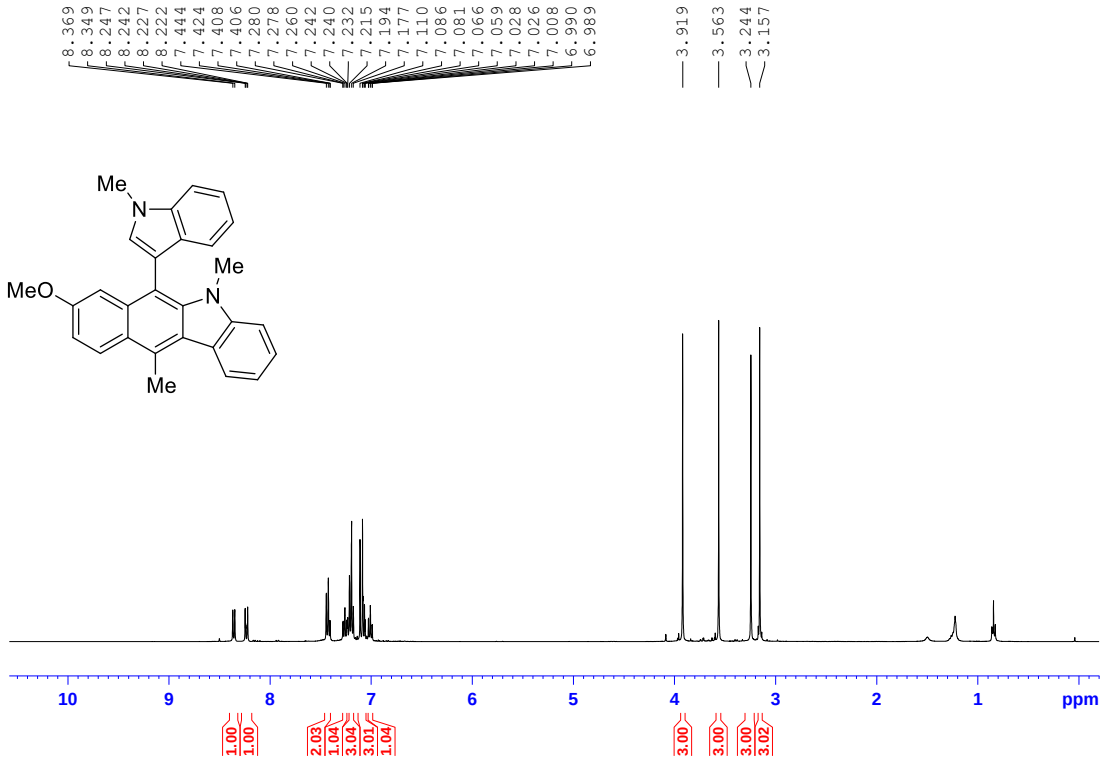
^{1}H NMR of 5,8,11-Trimethyl-6-(1-methyl-1*H*-indol-3-yl)-5*H*-benzo[*b*]carbazole (3b)



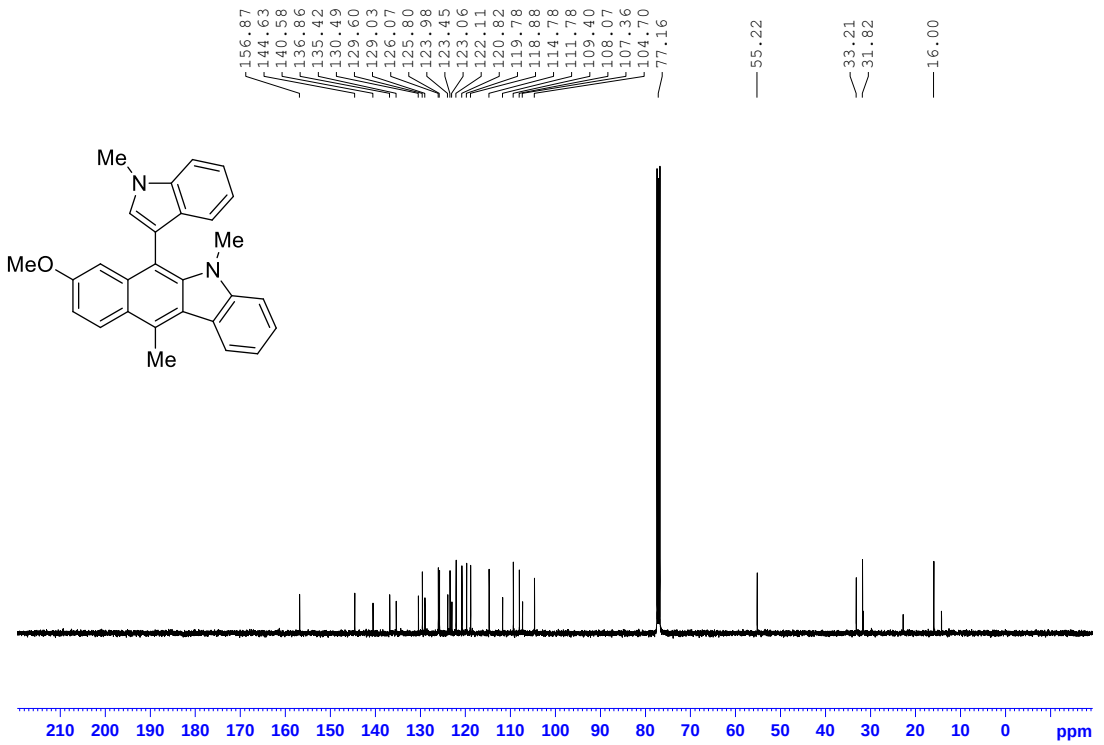
^{13}C NMR of 5,8,11-Trimethyl-6-(1-methyl-1*H*-indol-3-yl)-5*H*-benzo[*b*]carbazole (3b)



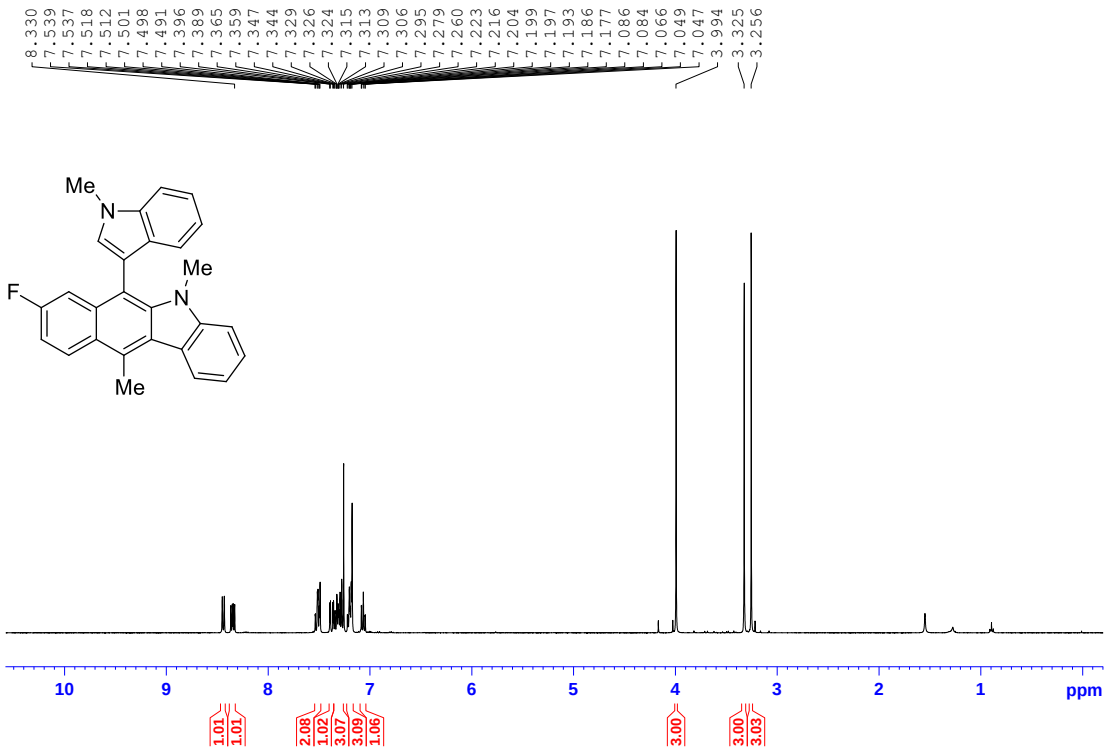
^{1}H NMR of 8-Methoxy-5,11-dimethyl-6-(1-methyl-1*H*-indol-3-yl)-5*H*-benzo[*b*]carbazole (3c)



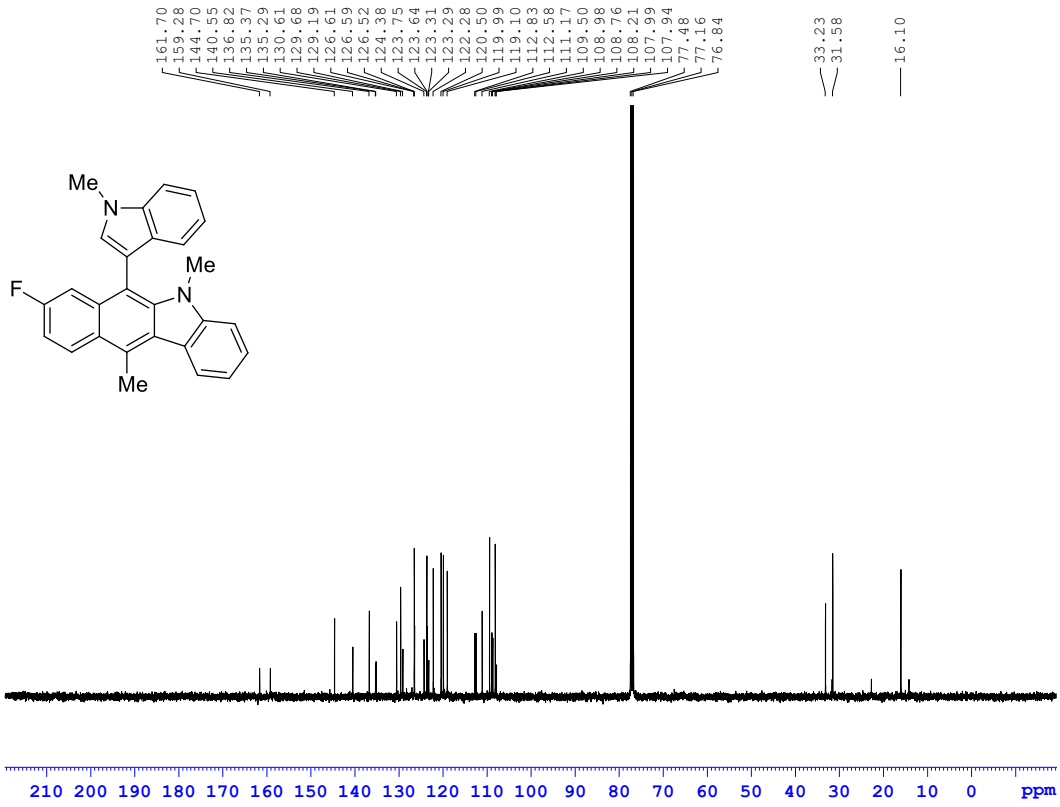
^{13}C NMR of 8-Methoxy-5,11-dimethyl-6-(1-methyl-1*H*-indol-3-yl)-5*H*-benzo[*b*]carbazole (3c)



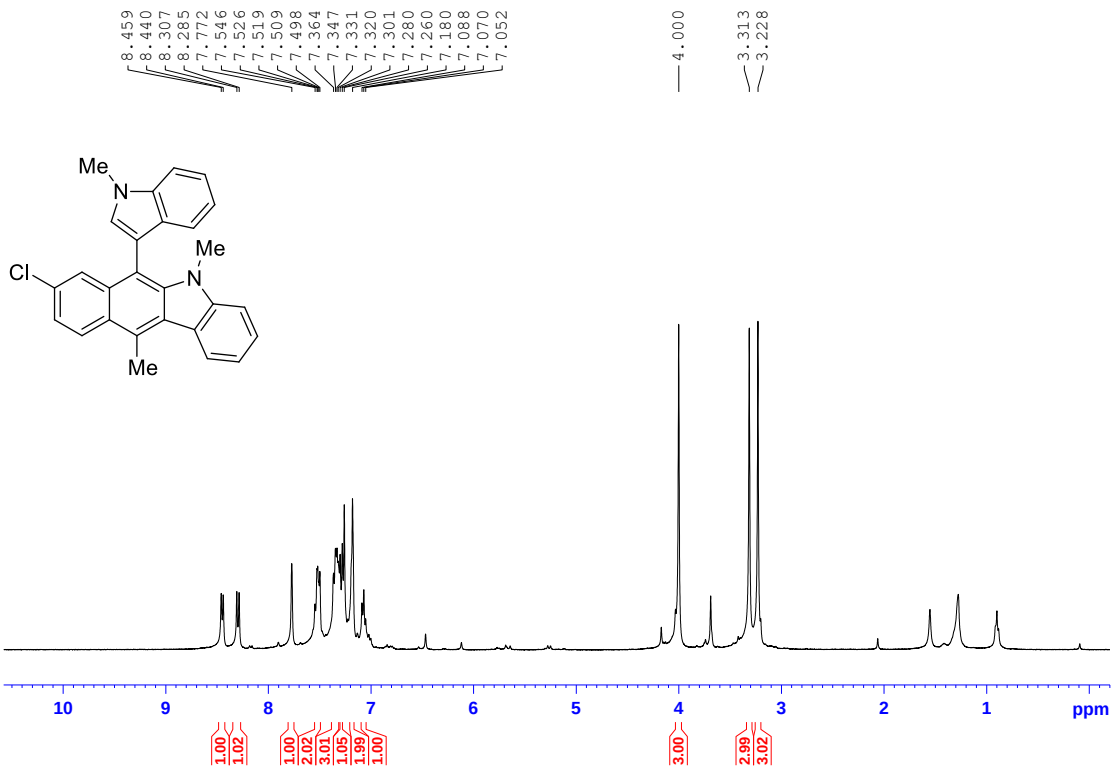
^{1}H NMR of 8-Fluoro-5,11-dimethyl-6-(1-methyl-1*H*-indol-3-yl)-5*H*-benzo[*b*]carbazole (3d)



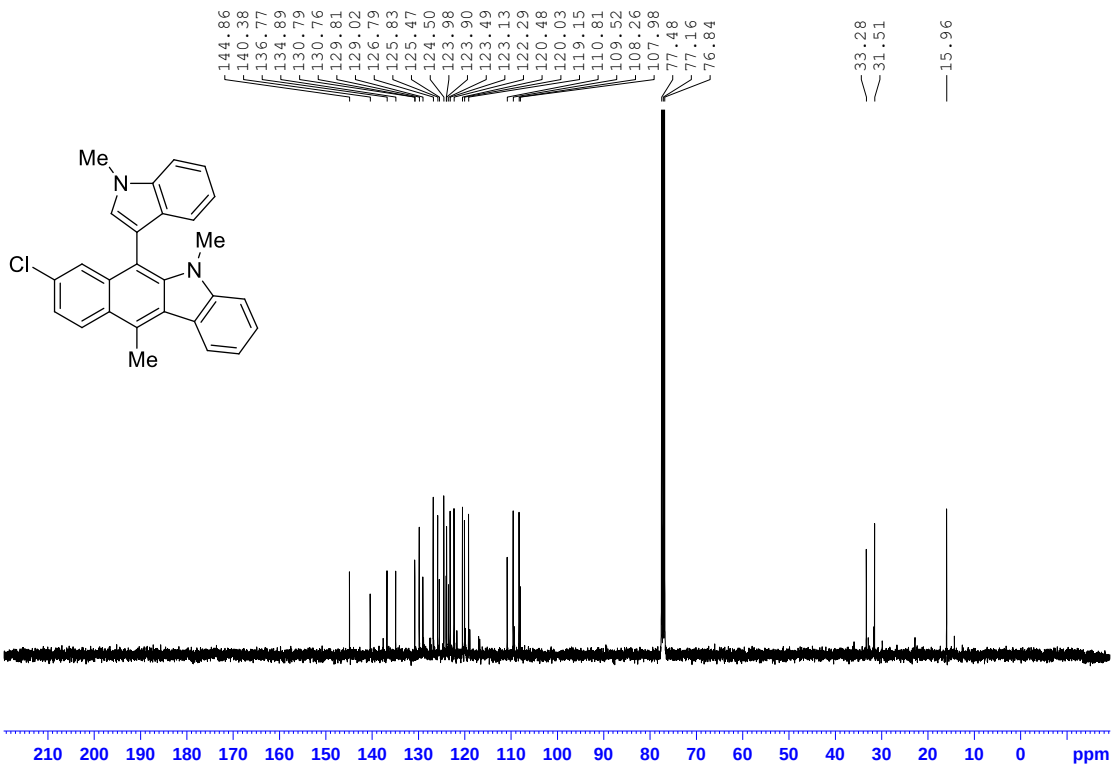
^{13}C NMR of 8-Fluoro-5,11-dimethyl-6-(1-methyl-1*H*-indol-3-yl)-5*H*-benzo[*b*]carbazole (3d)



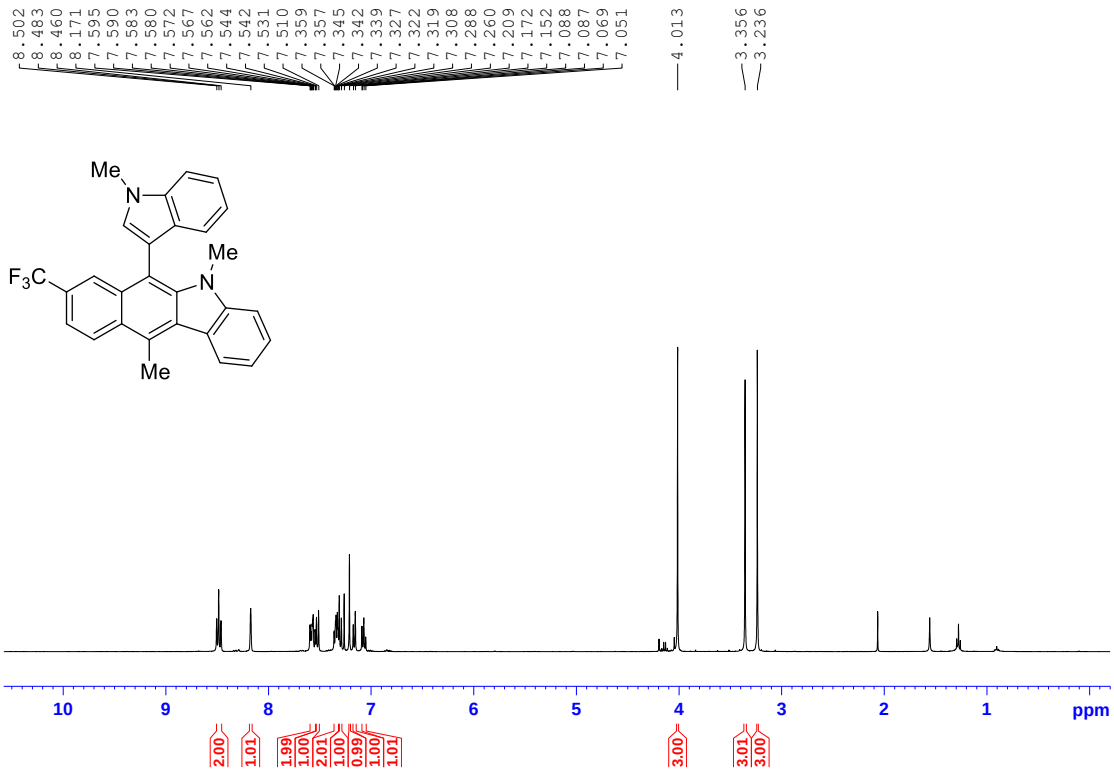
^{1}H NMR of 8-Chloro-5,11-dimethyl-6-(1-methyl-1*H*-indol-3-yl)-5*H*-benzo[*b*]carbazole (3e)



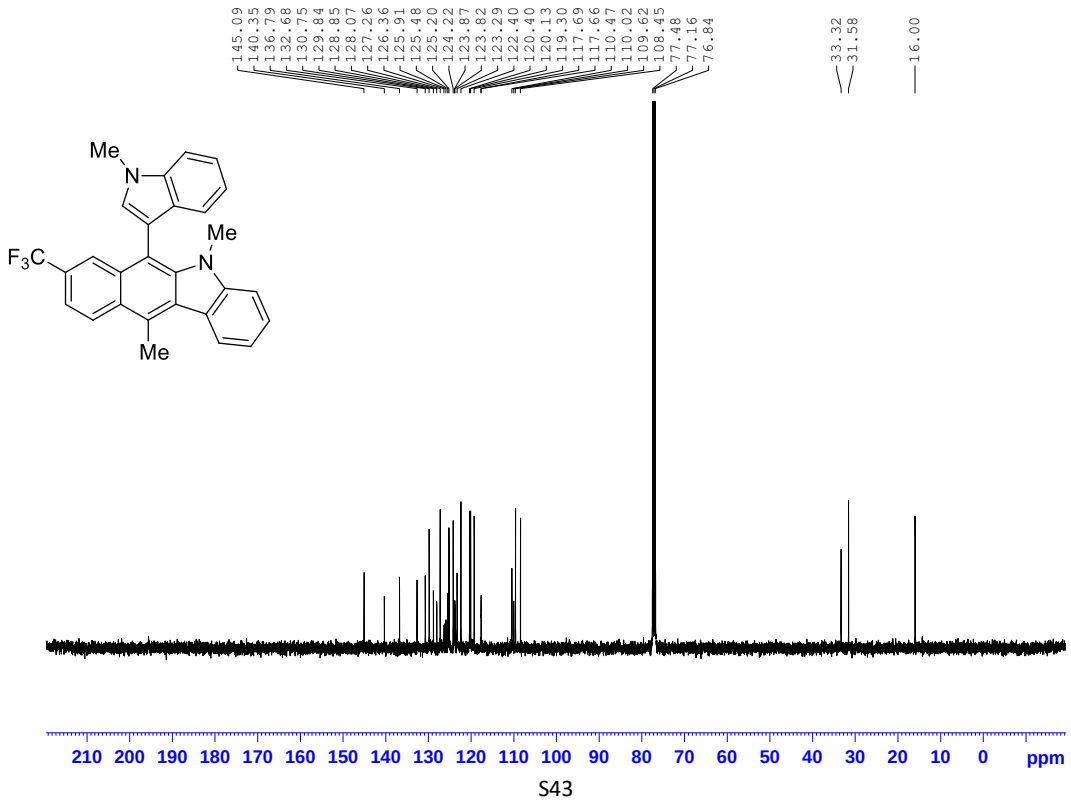
^{13}C NMR of 8-Chloro-5,11-dimethyl-6-(1-methyl-1*H*-indol-3-yl)-5*H*-benzo[*b*]carbazole (3e)



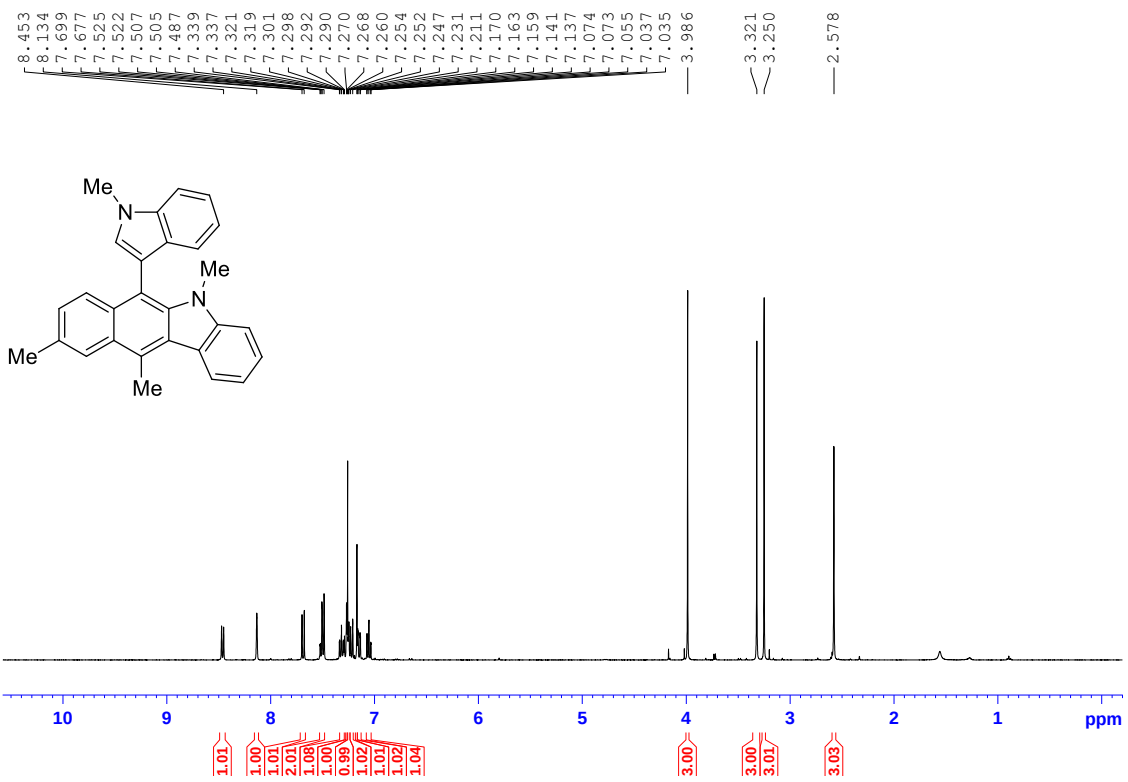
^{1}H NMR of 5,11-Dimethyl-6-(1-methyl-1*H*-indol-3-yl)-8-(trifluoromethyl)-5*H*-benzo[*b*]carbazole (3f)



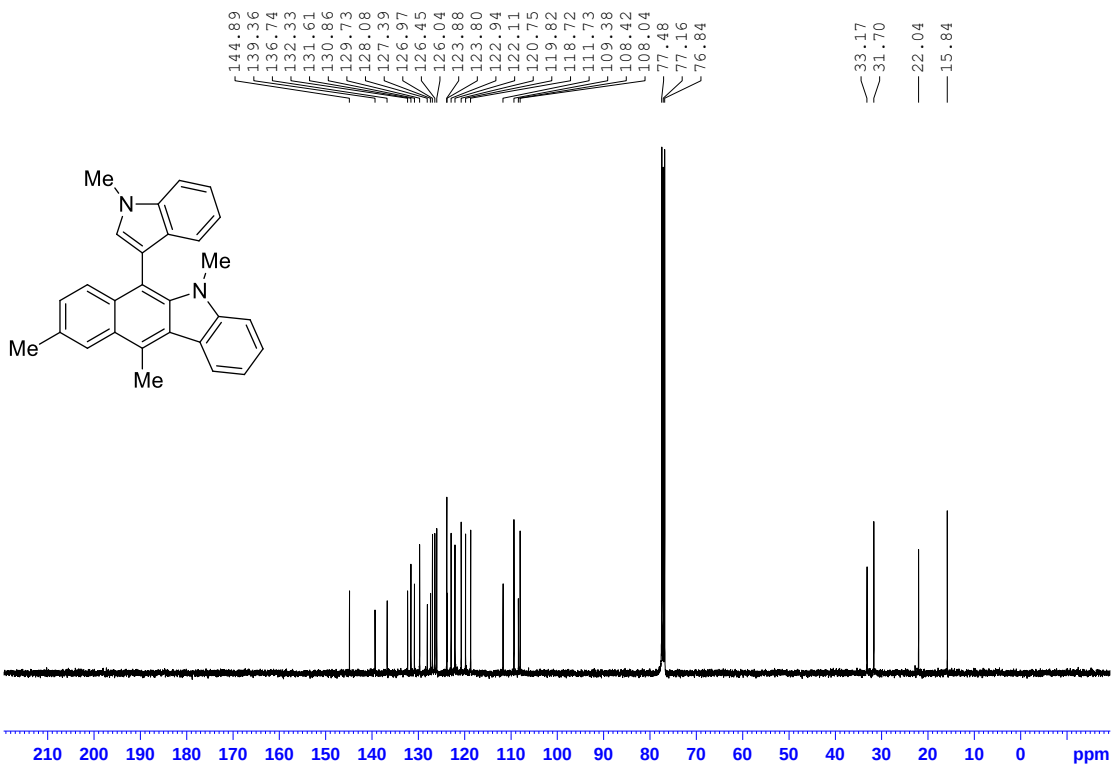
^{13}C NMR of 5,11-Dimethyl-6-(1-methyl-1*H*-indol-3-yl)-8-(trifluoromethyl)-5*H*-benzo[*b*]carbazole (3f)



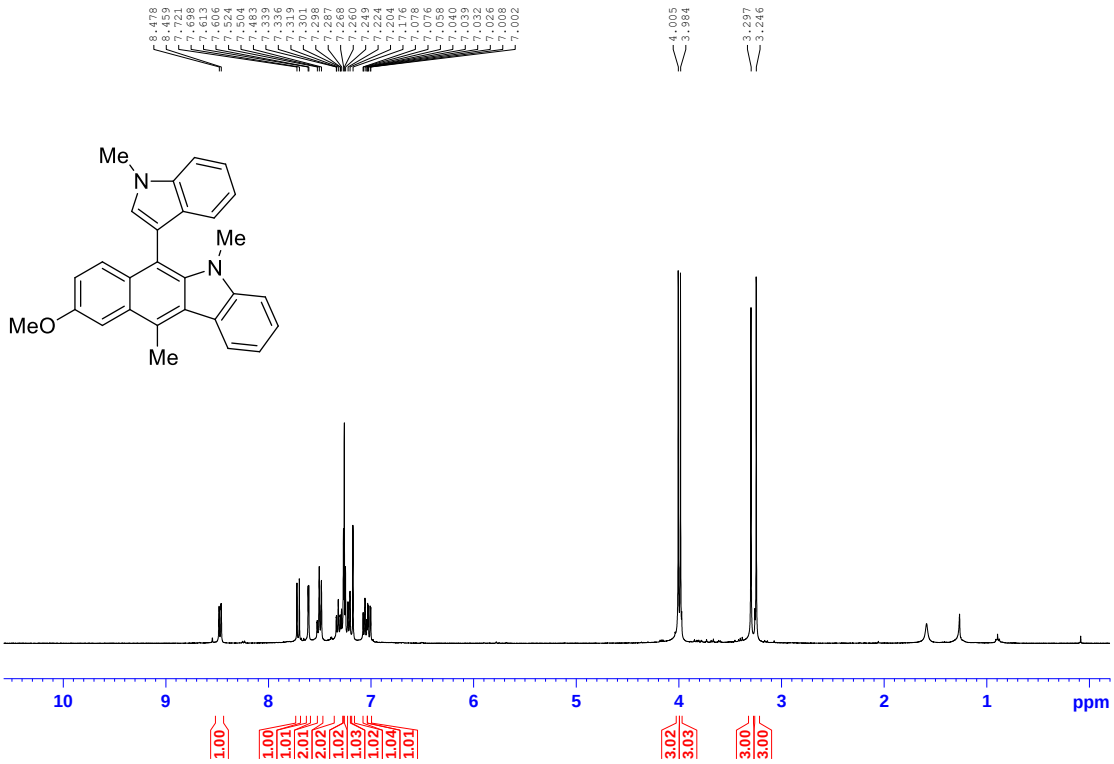
^{1}H NMR of 5,9,11-Trimethyl-6-(1-methyl-1*H*-indol-3-yl)-5*H*-benzo[*b*]carbazole (3g)



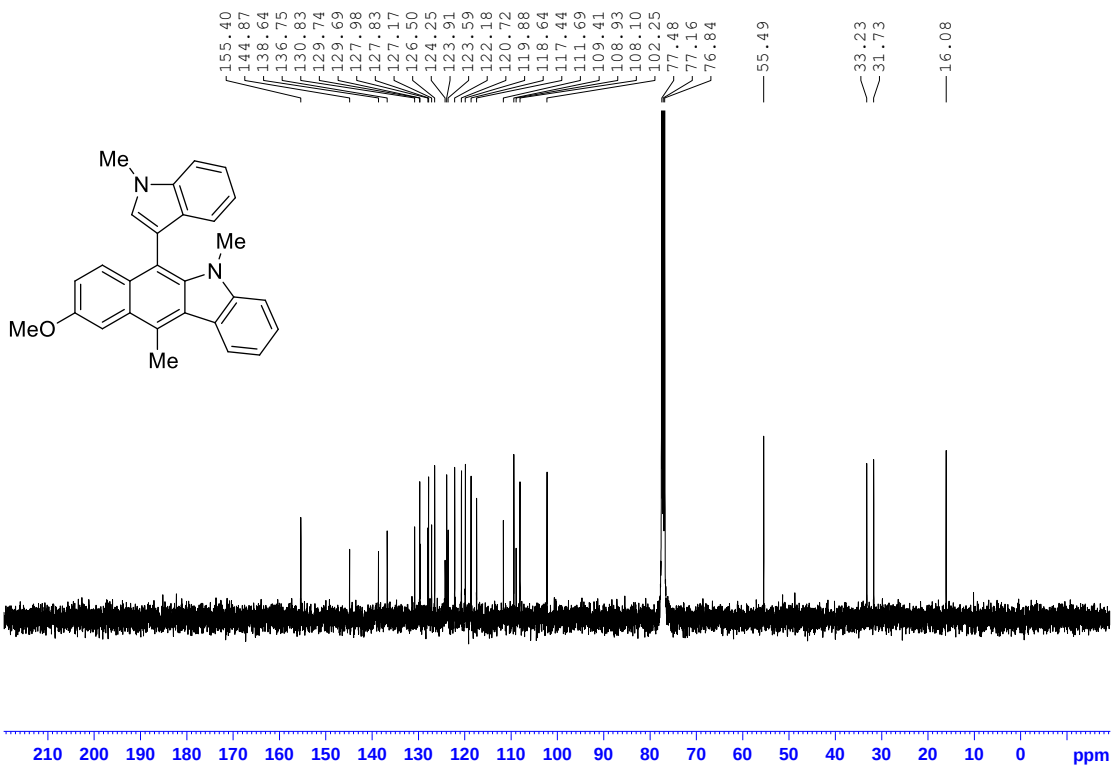
^{13}C NMR of 5,9,11-Trimethyl-6-(1-methyl-1*H*-indol-3-yl)-5*H*-benzo[*b*]carbazole (3g)



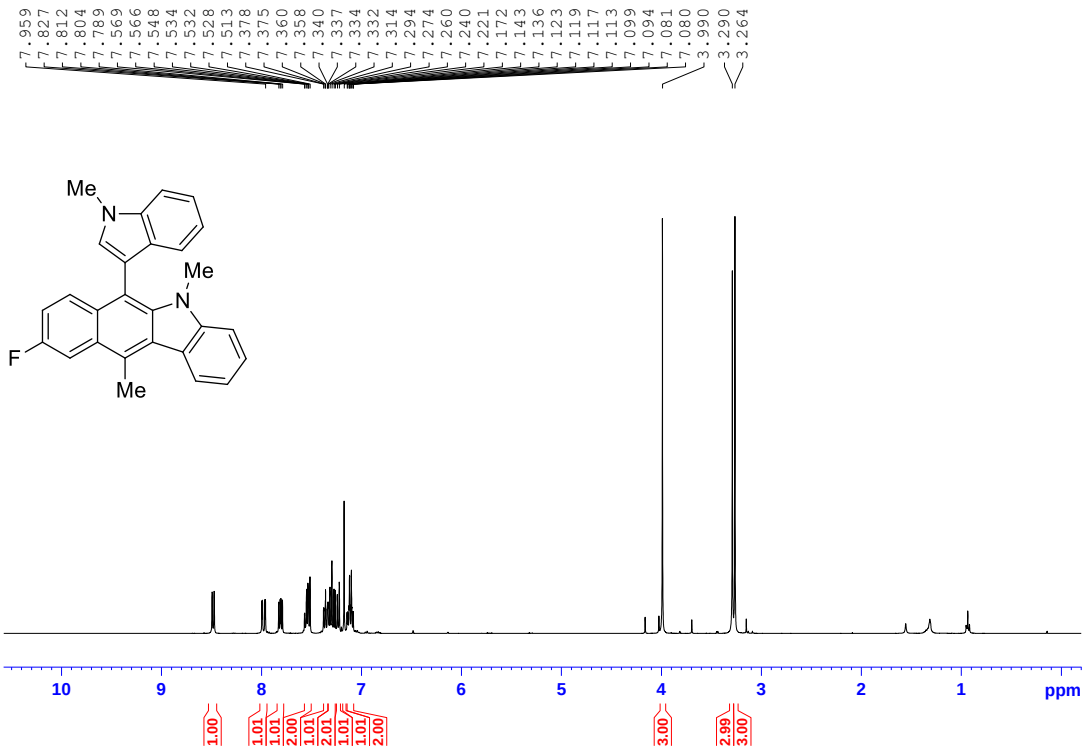
^{1}H NMR of 9-Methoxy-5,11-dimethyl-6-(1-methyl-1*H*-indol-3-yl)-5*H*-benzo[*b*]carbazole (3h)



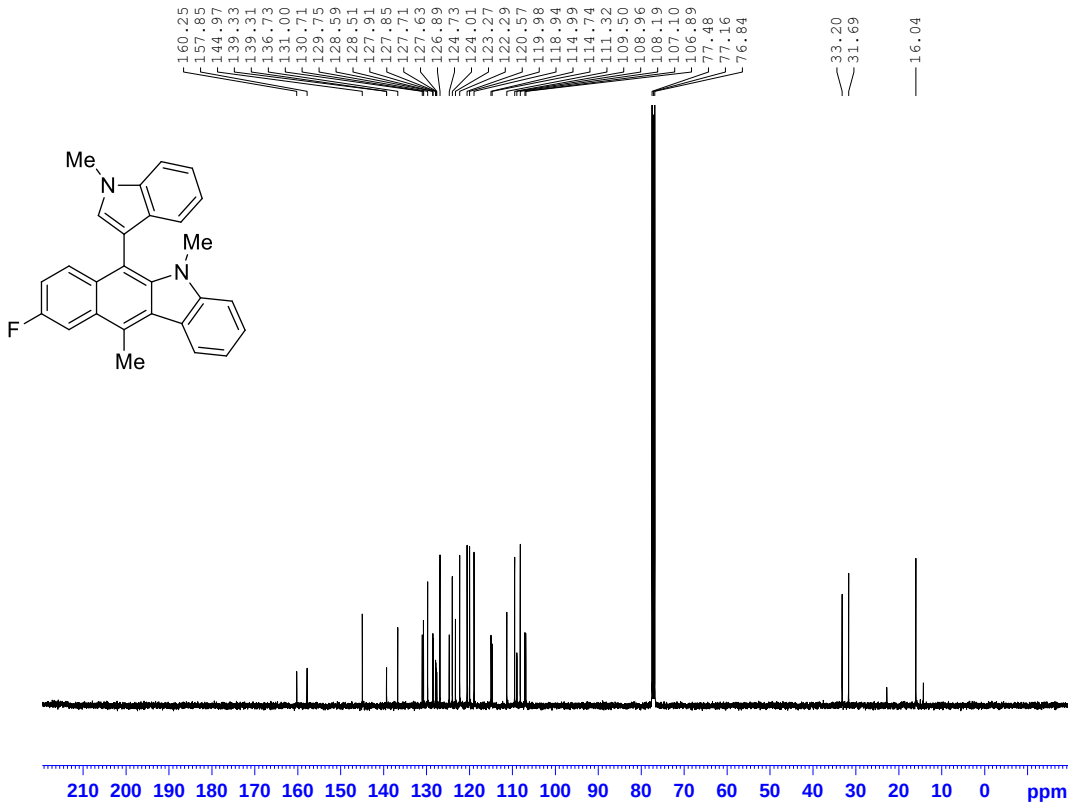
^{13}C NMR of 9-Methoxy-5,11-dimethyl-6-(1-methyl-1*H*-indol-3-yl)-5*H*-benzo[*b*]carbazole (3h)



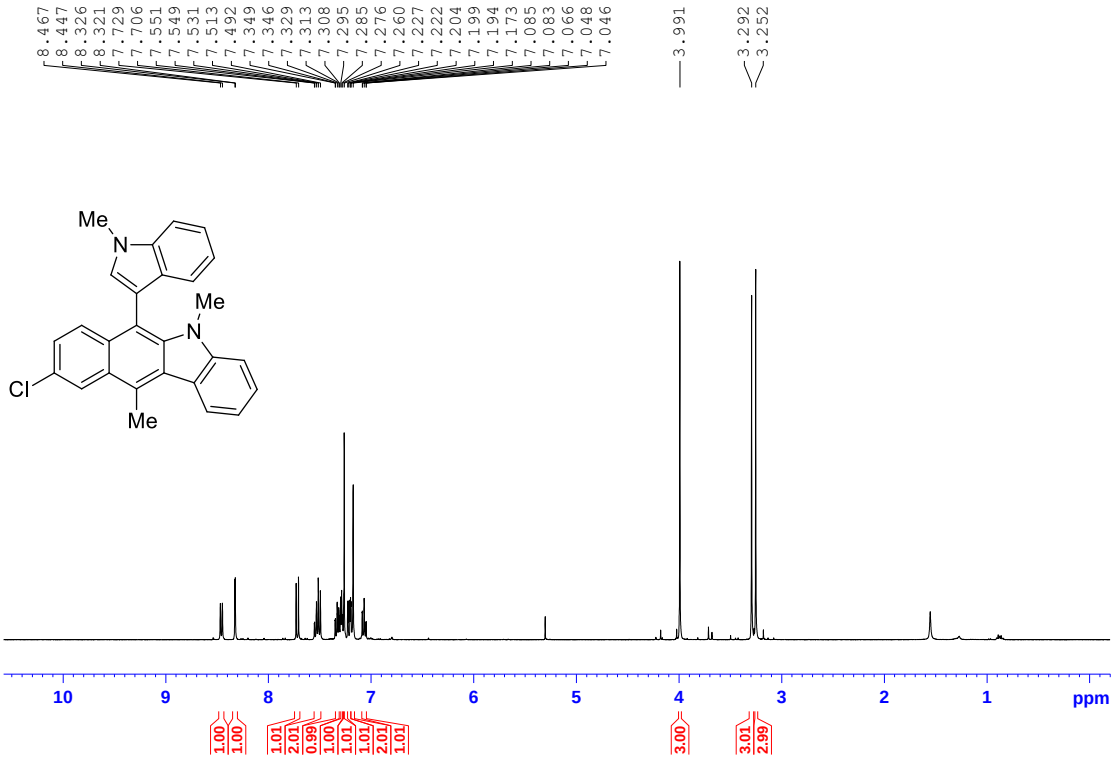
^{1}H NMR of 9-Fluoro-5,11-dimethyl-6-(1-methyl-1*H*-indol-3-yl)-5*H*-benzo[*b*]carbazole (3i)



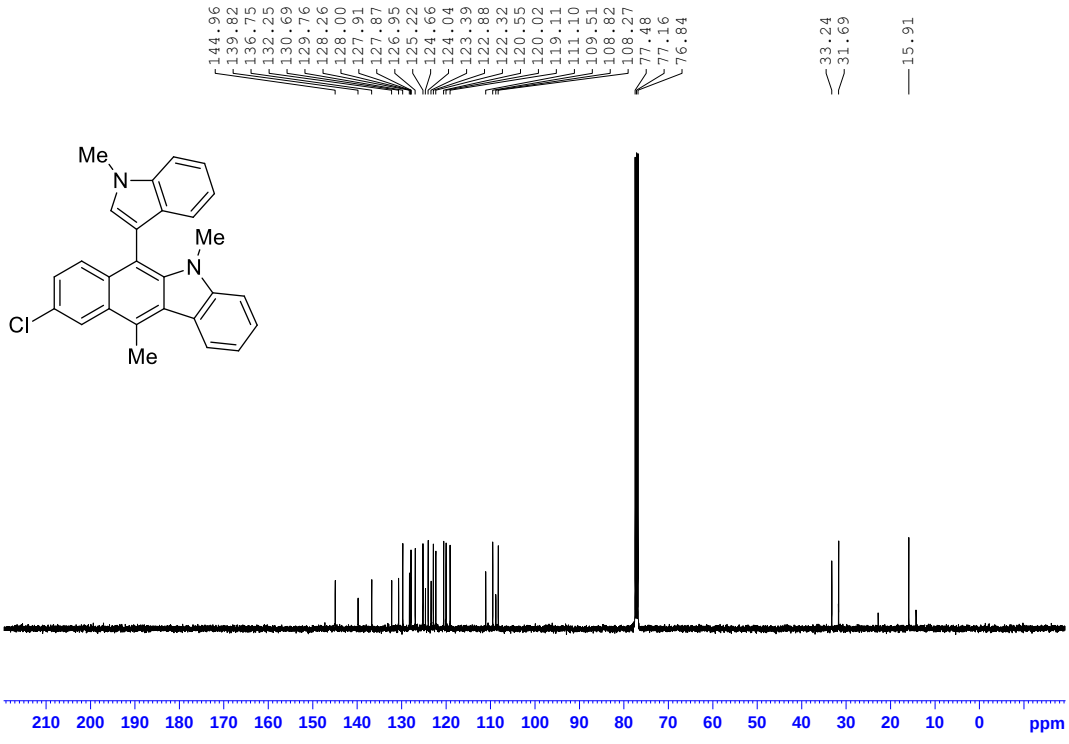
^{13}C NMR of 9-Fluoro-5,11-dimethyl-6-(1-methyl-1*H*-indol-3-yl)-5*H*-benzo[*b*]carbazole (3i)



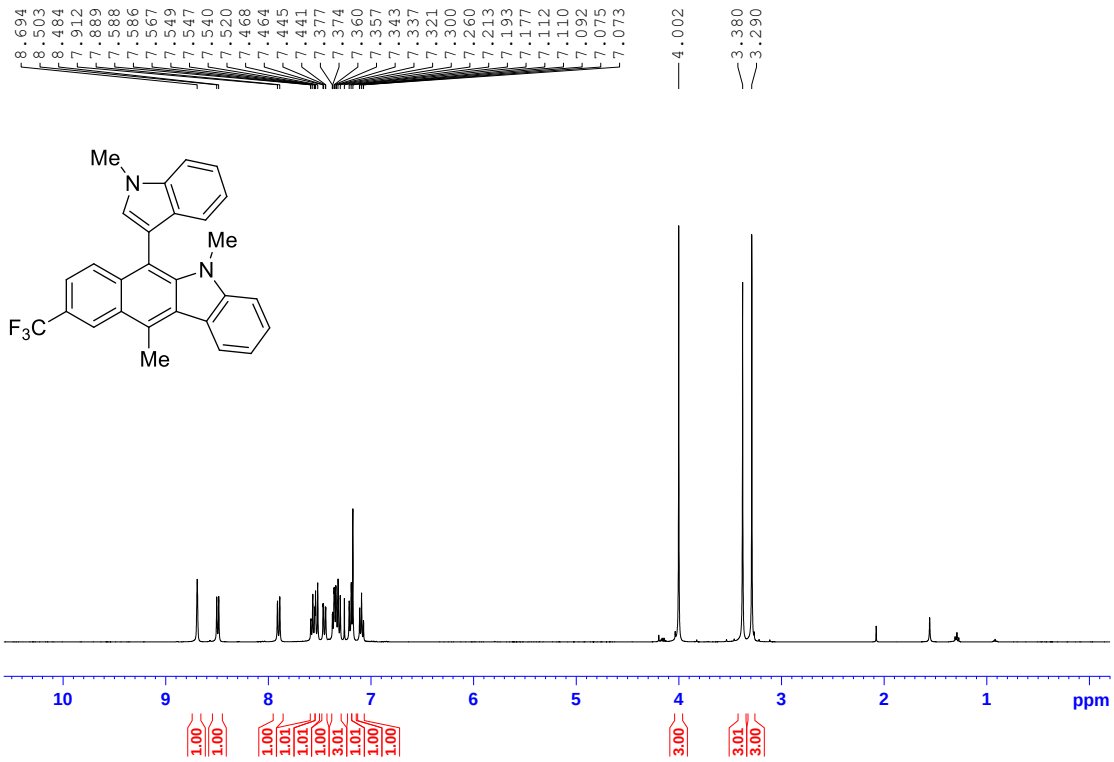
^{1}H NMR of 9-Chloro-5,11-dimethyl-6-(1-methyl-1*H*-indol-3-yl)-5*H*-benzo[*b*]carbazole (3j)



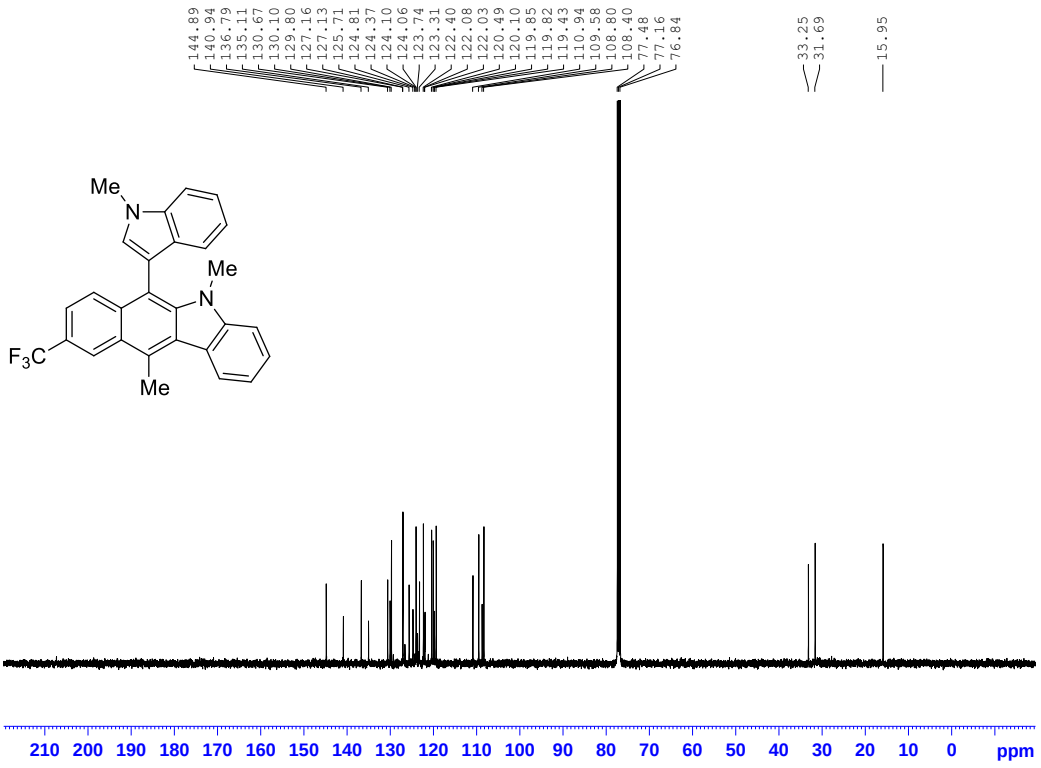
^{13}C NMR of 9-Chloro-5,11-dimethyl-6-(1-methyl-1*H*-indol-3-yl)-5*H*-benzo[*b*]carbazole (3j)



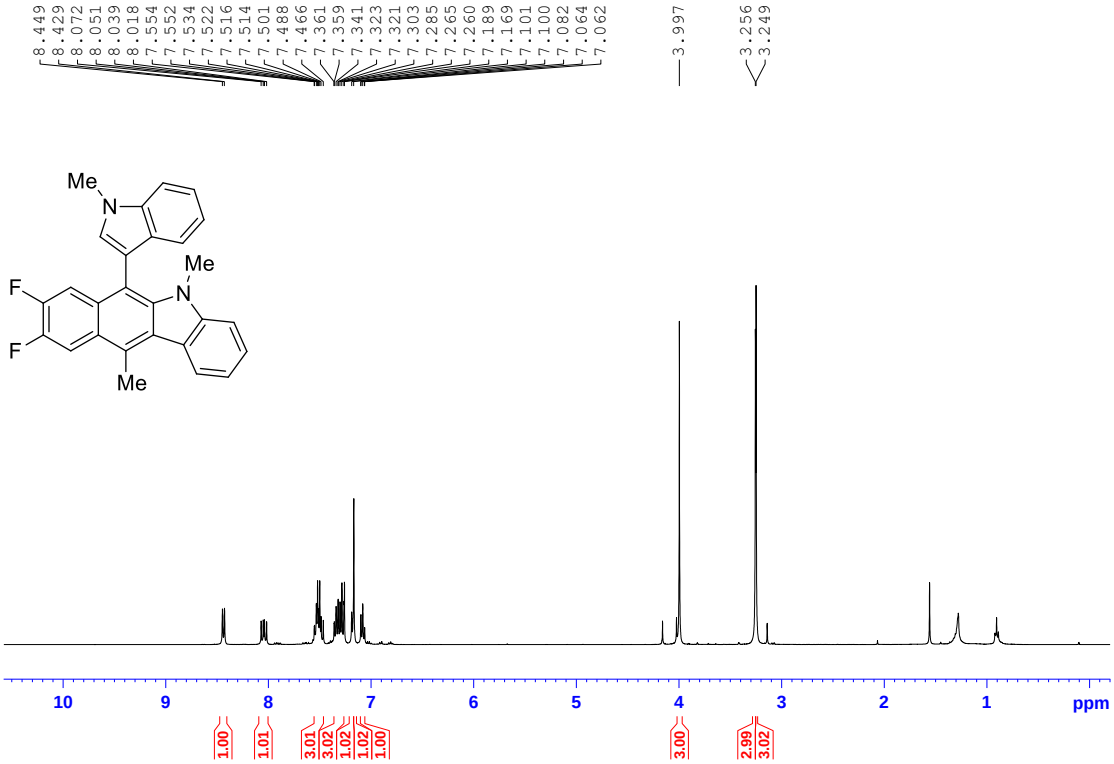
^{1}H NMR of 5,11-Dimethyl-6-(1-methyl-1*H*-indol-3-yl)-9-(trifluoromethyl)-5H-benzo[*b*]carbazole (3k)



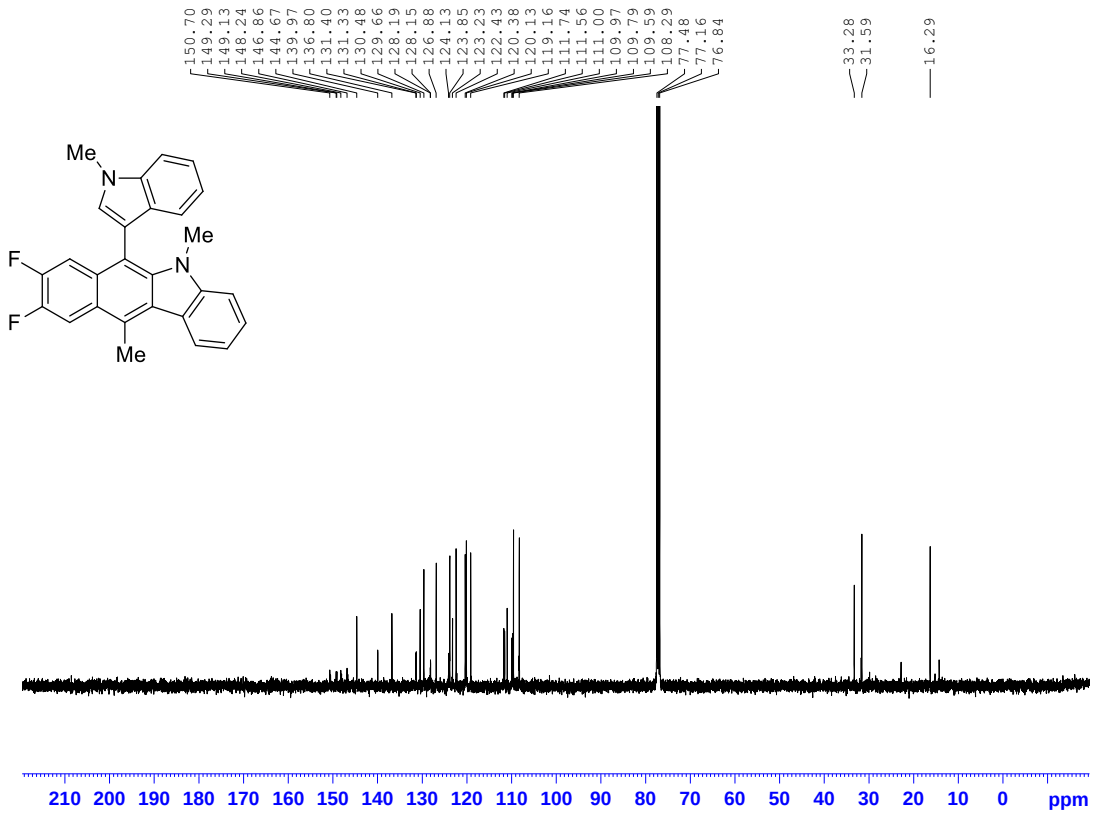
^{13}C NMR of 5,11-Dimethyl-6-(1-methyl-1*H*-indol-3-yl)-9-(trifluoromethyl)-5H-benzo[*b*]carbazole (3k)



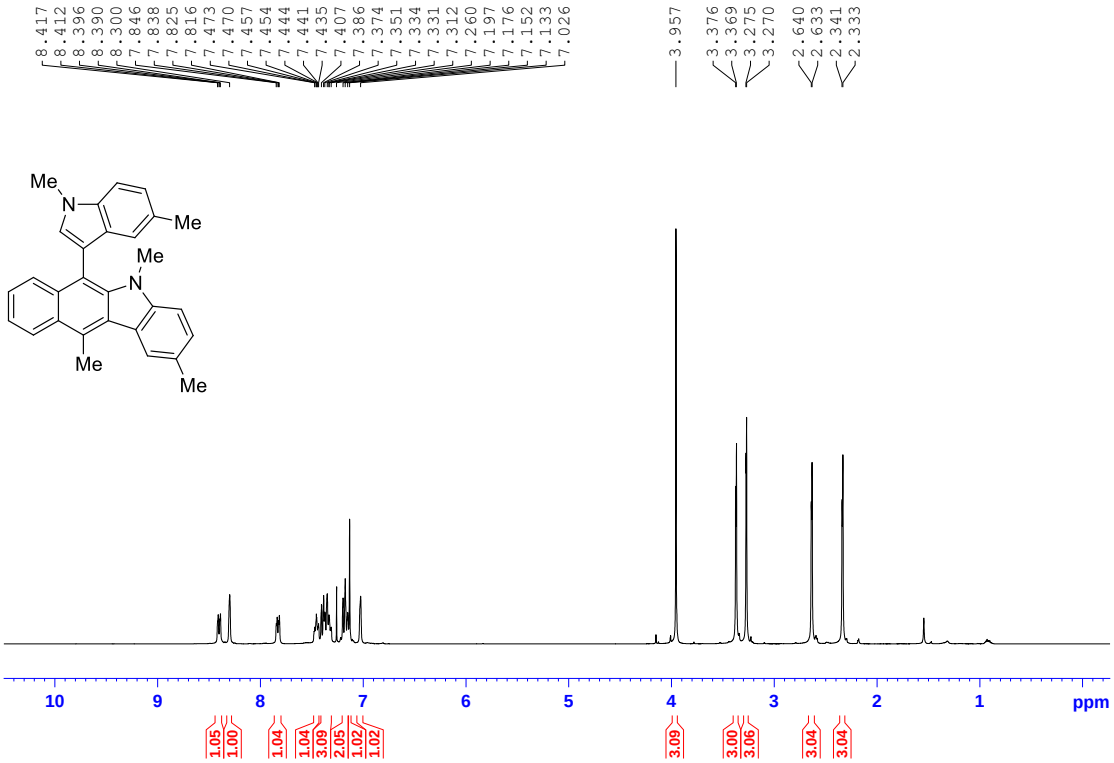
^{1}H NMR of 8,9-Difluoro-5,11-dimethyl-6-(1-methyl-1*H*-indol-3-yl)-5*H*-benzo[*b*]carbazole (3l)



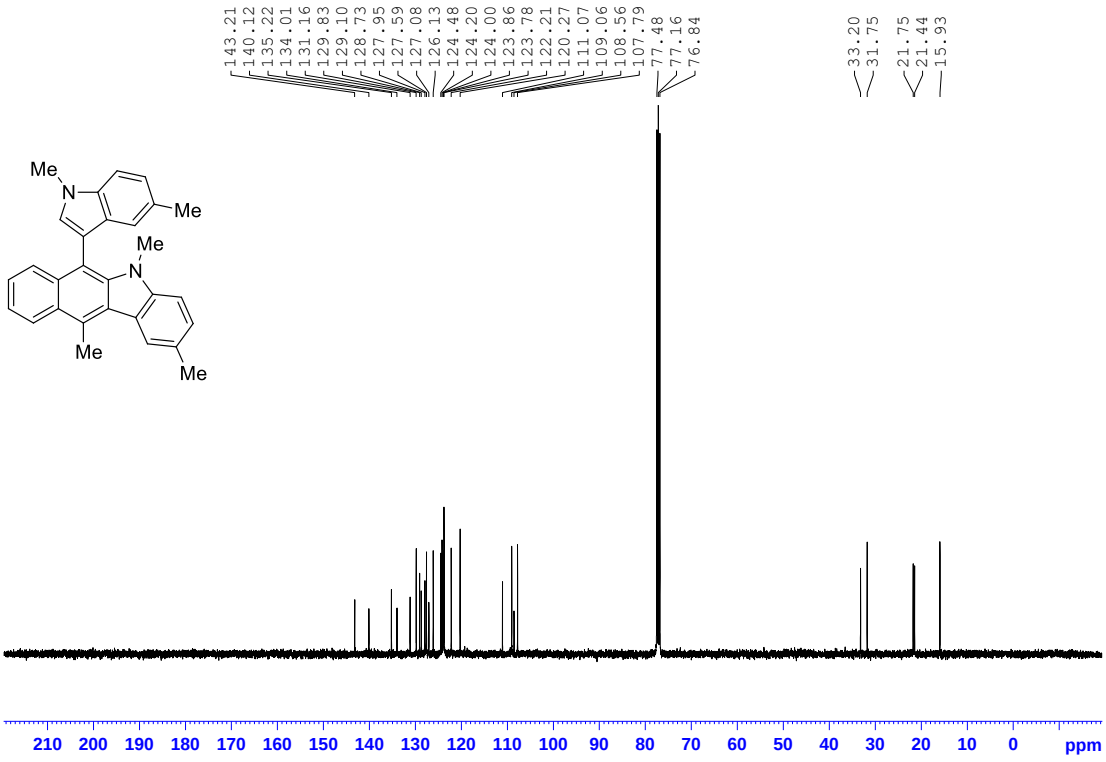
^{13}C NMR of 8,9-Difluoro-5,11-dimethyl-6-(1-methyl-1*H*-indol-3-yl)-5*H*-benzo[*b*]carbazole (3l)



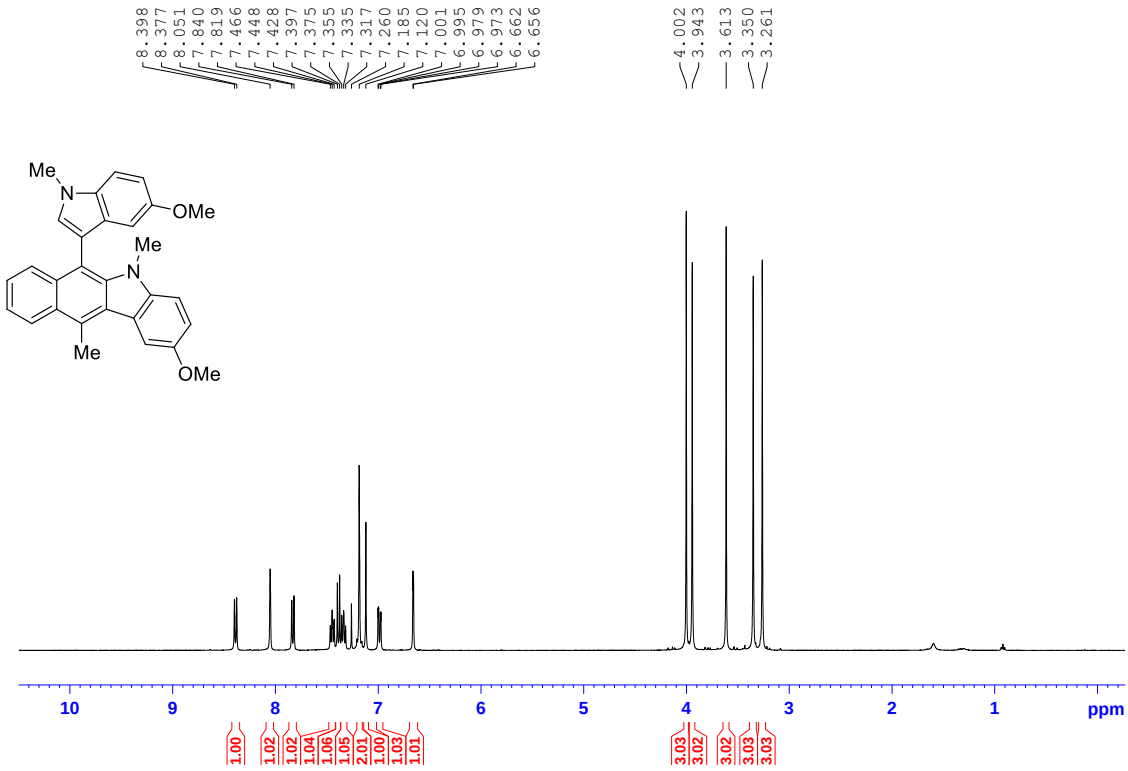
^{1}H NMR of 6-(1,5-Dimethyl-1*H*-indol-3-yl)-2,5,11-trimethyl-5*H*-benzo[*b*]carbazole (3m)



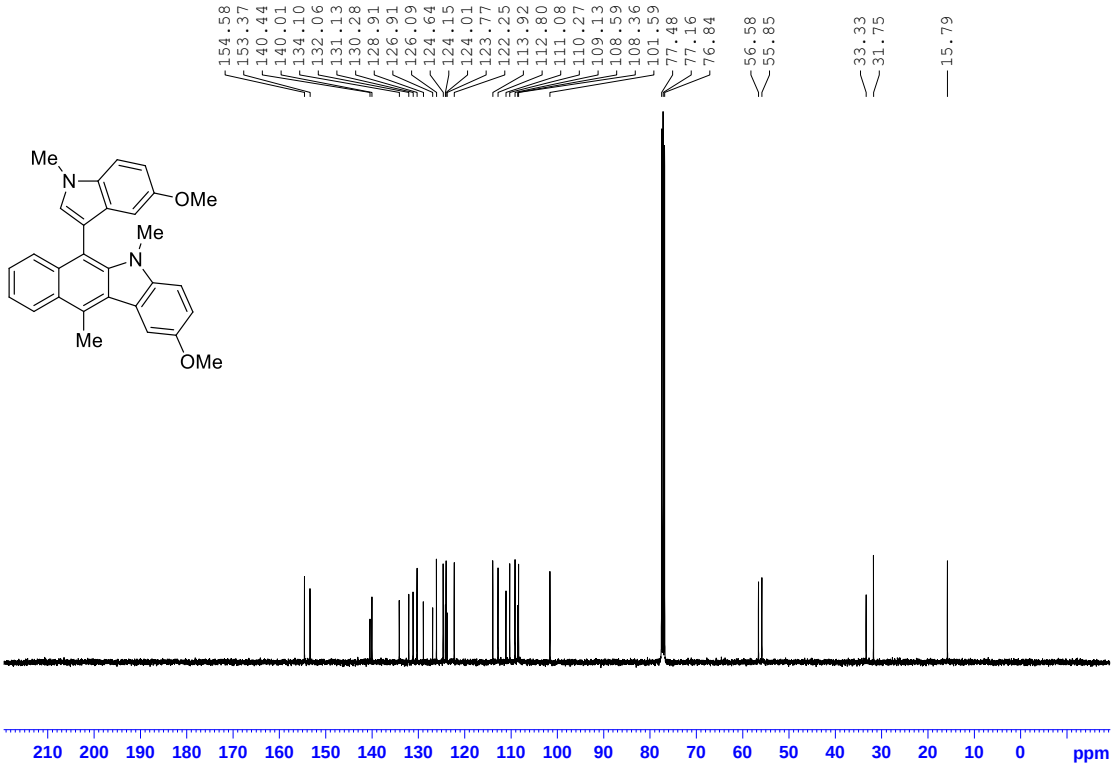
^{13}C NMR of 6-(1,5-Dimethyl-1*H*-indol-3-yl)-2,5,11-trimethyl-5*H*-benzo[*b*]carbazole (3m)



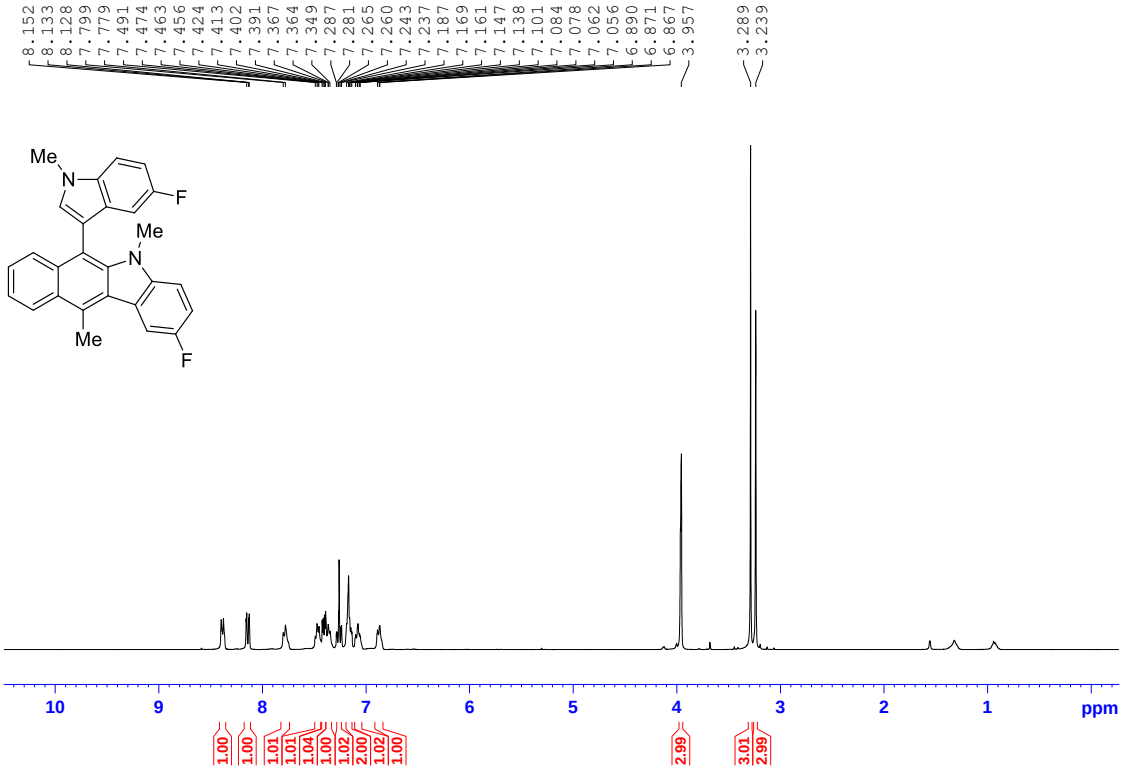
^{1}H NMR of 2-Methoxy-6-(5-methoxy-1-methyl-1*H*-indol-3-yl)-5,11-dimethyl-5*H*-benzo[*b*]carbazole (3n)



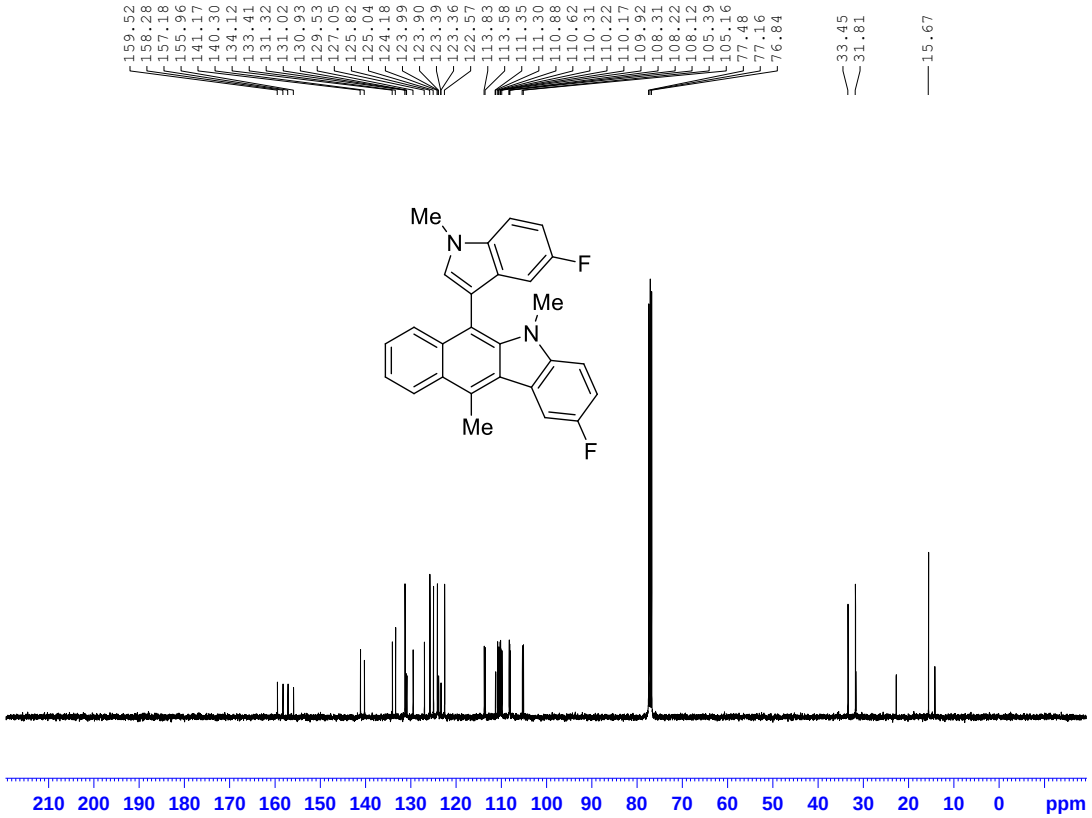
^{13}C NMR of 2-Methoxy-6-(5-methoxy-1-methyl-1*H*-indol-3-yl)-5,11-dimethyl-5*H*-benzo[*b*]carbazole (3n)



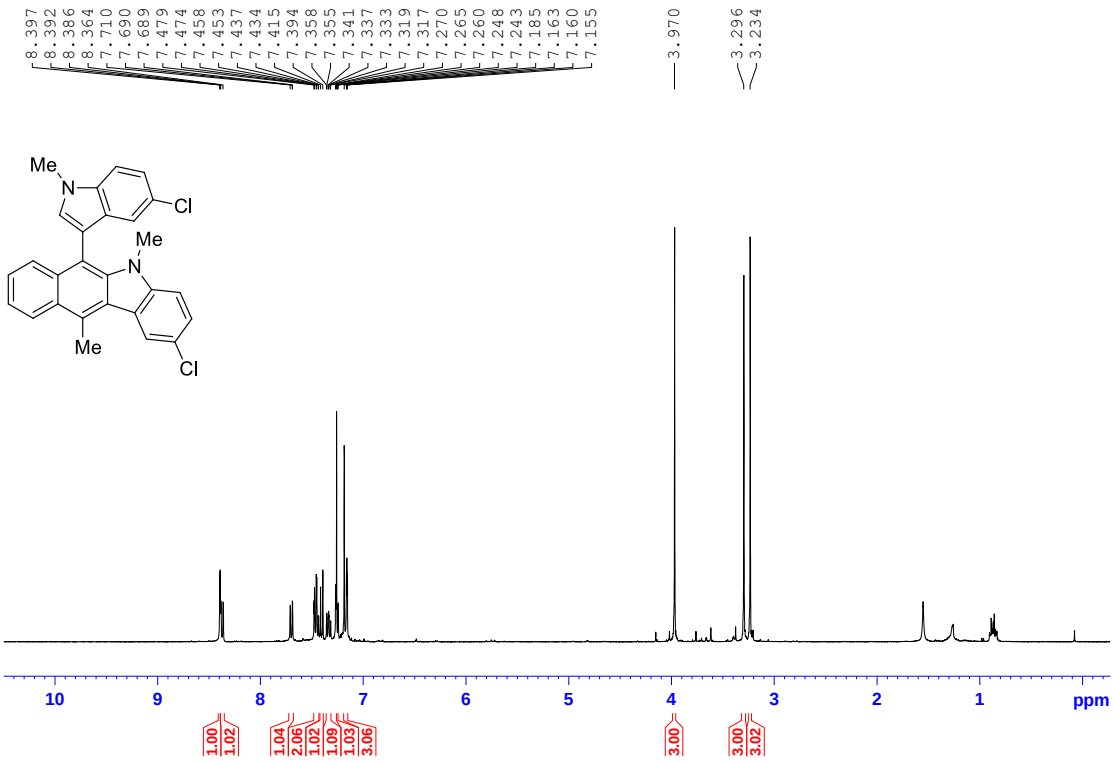
^{1}H NMR of 2-Fluoro-6-(5-fluoro-1-methyl-1*H*-indol-3-yl)-5,11-dimethyl-5*H*-benzo[*b*]carbazole (3o)



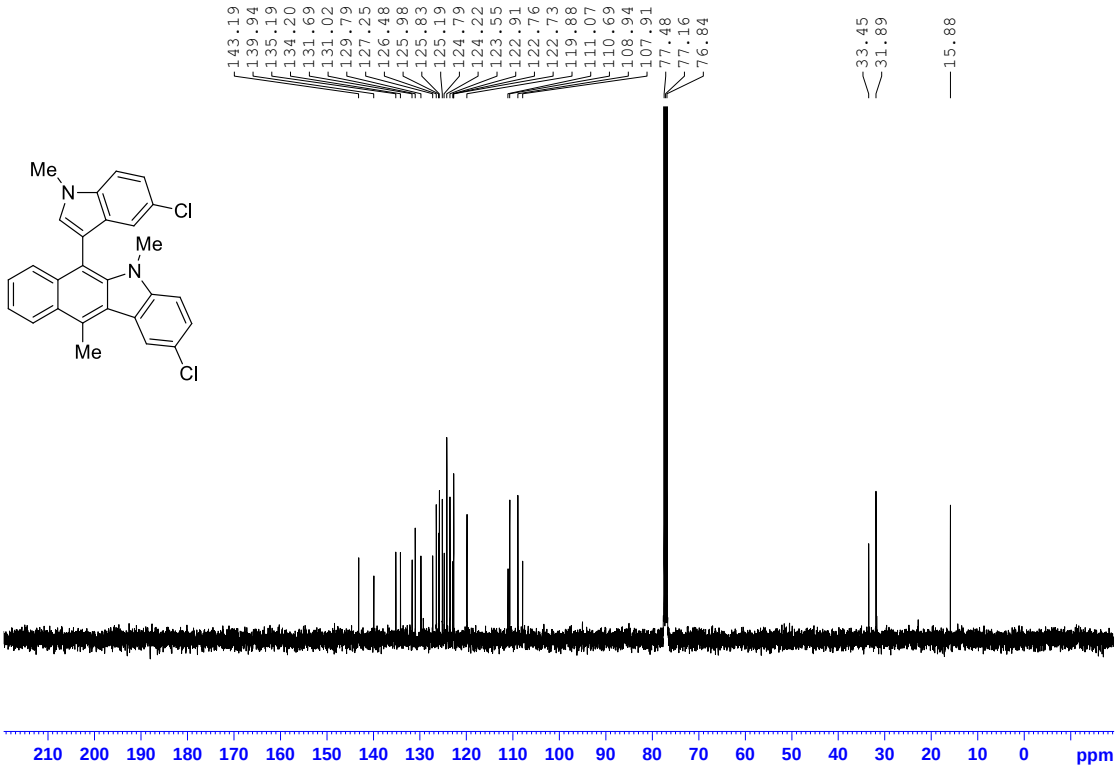
^{13}C NMR of 2-Fluoro-6-(5-fluoro-1-methyl-1*H*-indol-3-yl)-5,11-dimethyl-5*H*-benzo[*b*]carbazole (3o)



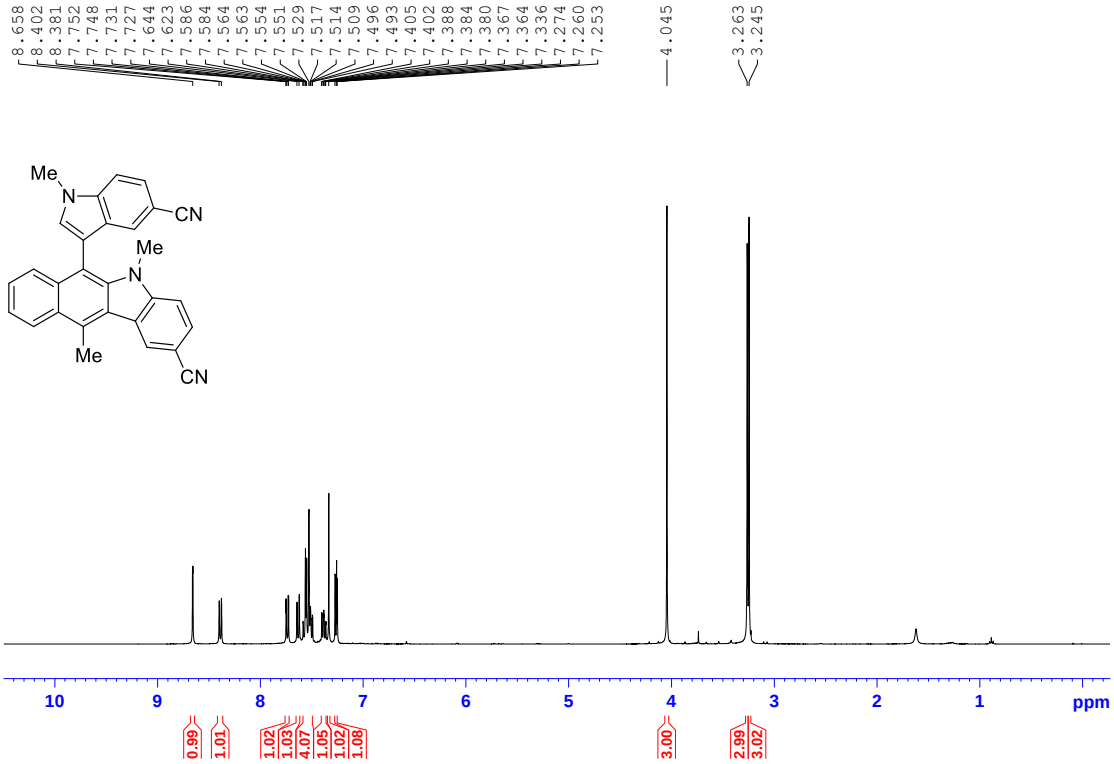
^{1}H NMR of 2-Chloro-6-(5-chloro-1-methyl-1*H*-indol-3-yl)-5,11-dimethyl-5*H*-benzo[*b*]carbazole (3p)



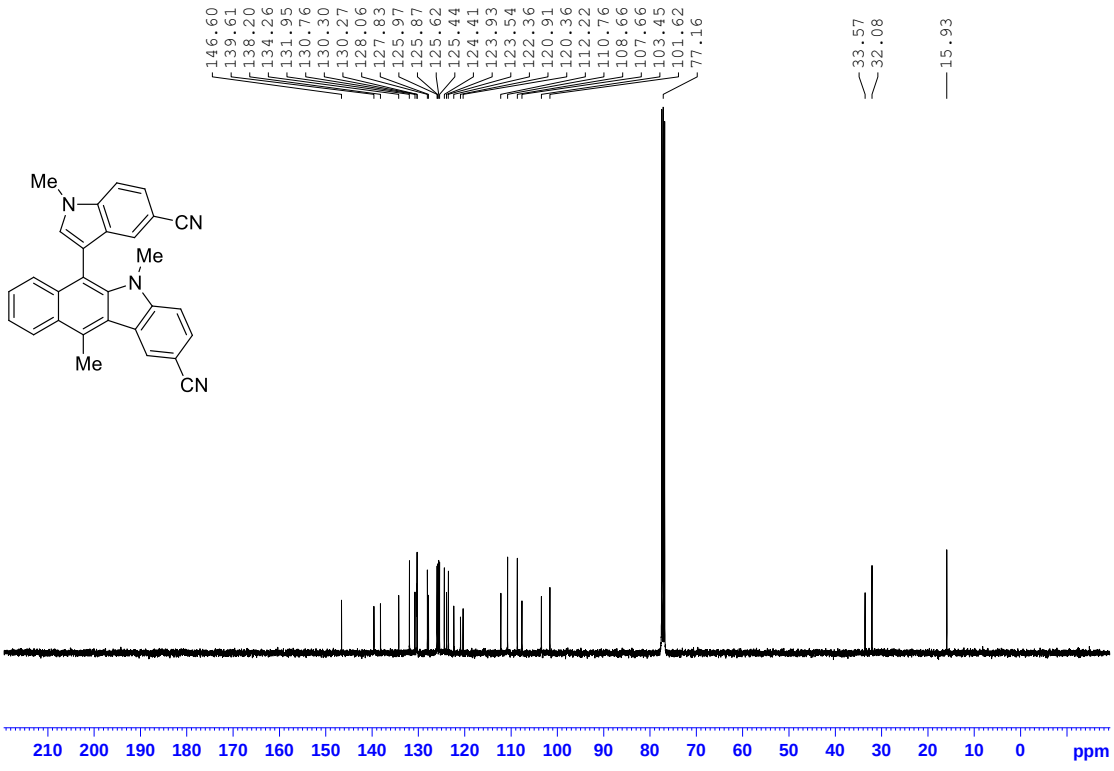
^{13}C NMR of 2-Chloro-6-(5-chloro-1-methyl-1*H*-indol-3-yl)-5,11-dimethyl-5*H*-benzo[*b*]carbazole (3p)



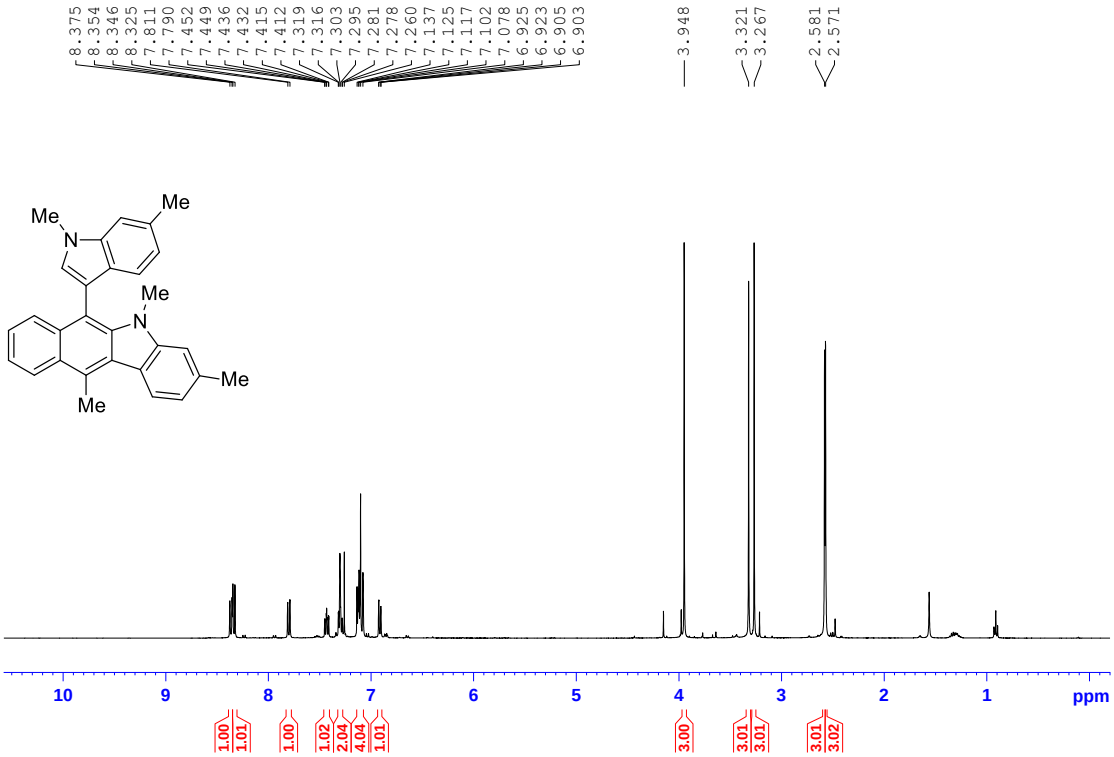
^{1}H NMR of 6-(5-Cyano-1-methyl-1*H*-indol-3-yl)-5,11-dimethyl-5*H*-benzo[*b*]carbazole-2-carbonitrile (3q)



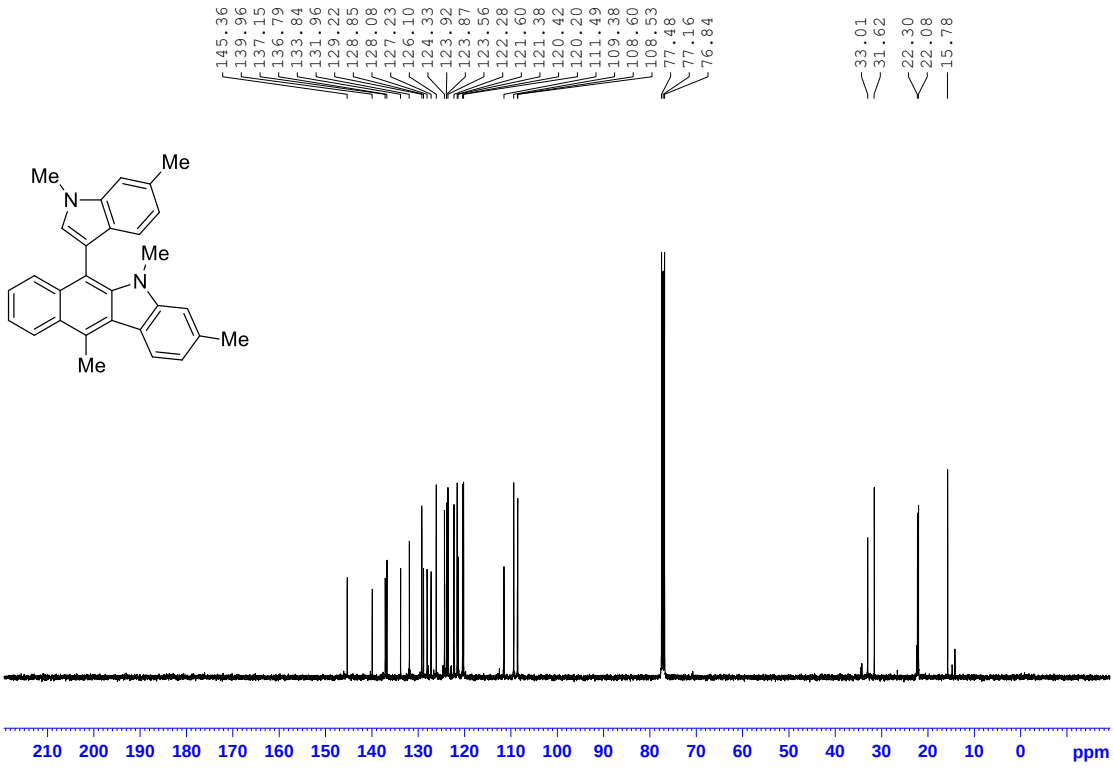
^{13}C NMR of 6-(5-Cyano-1-methyl-1*H*-indol-3-yl)-5,11-dimethyl-5*H*-benzo[*b*]carbazole-2-carbonitrile (3q)



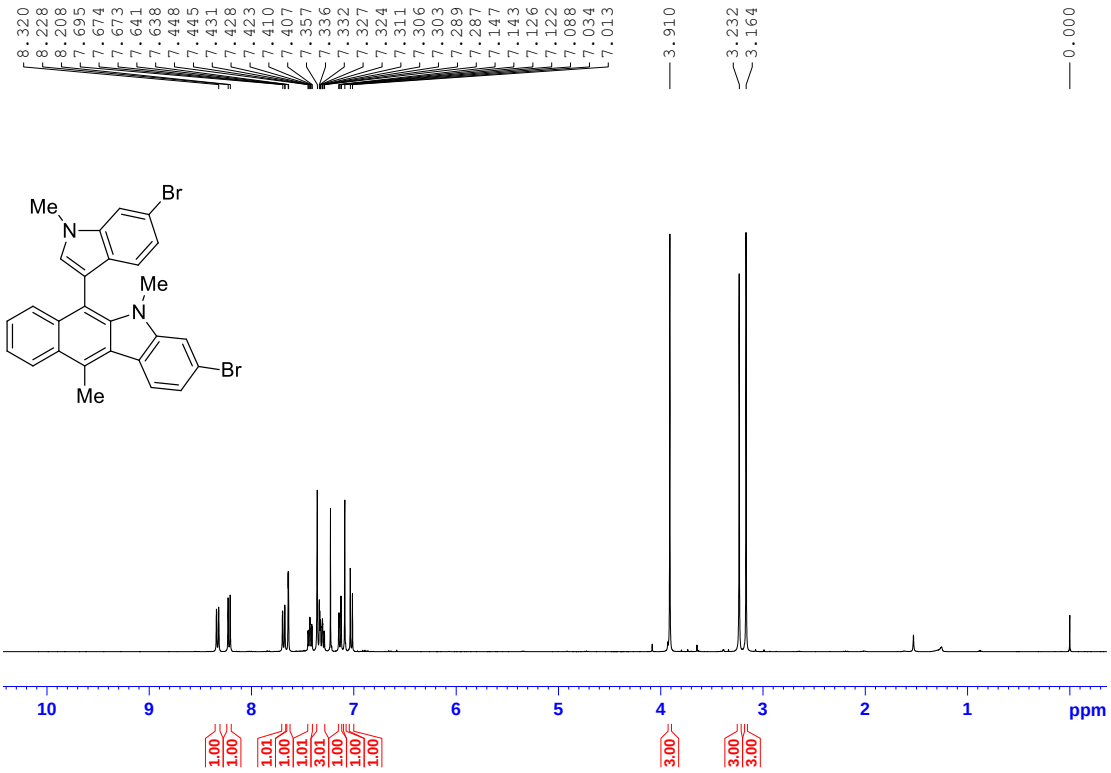
^{1}H NMR of 6-(1,6-Dimethyl-1*H*-indol-3-yl)-3,5,11-trimethyl-5*H*-benzo[*b*]carbazole (3r)



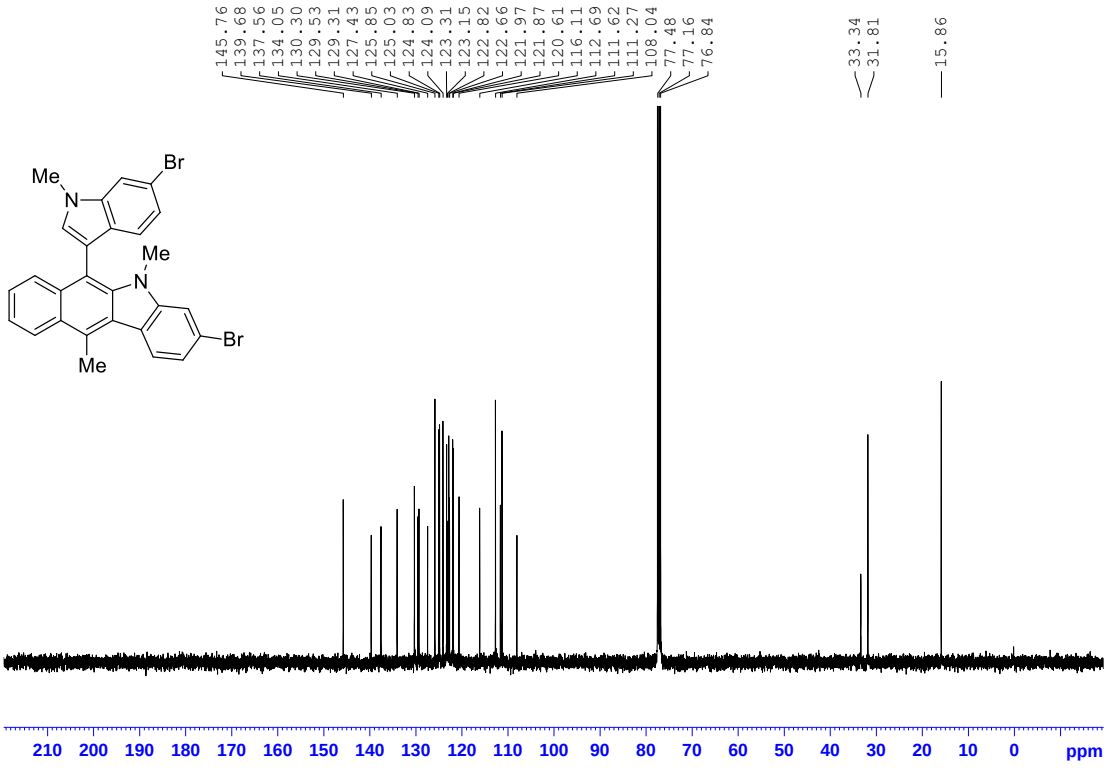
^{13}C NMR of 6-(1,6-Dimethyl-1*H*-indol-3-yl)-3,5,11-trimethyl-5*H*-benzo[*b*]carbazole (3r)



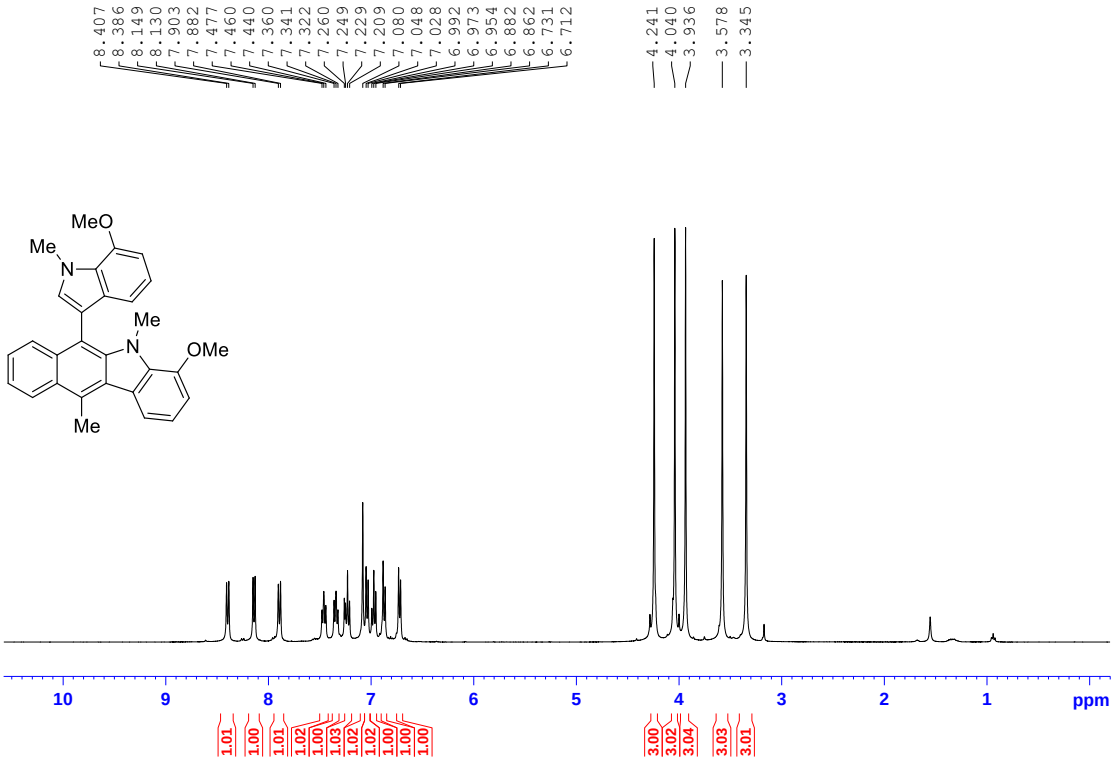
^{1}H NMR of 3-Bromo-6-(6-bromo-1-methyl-1H-indol-3-yl)-5,11-dimethyl-5*H*-benzo[*b*]carbazole (3s)



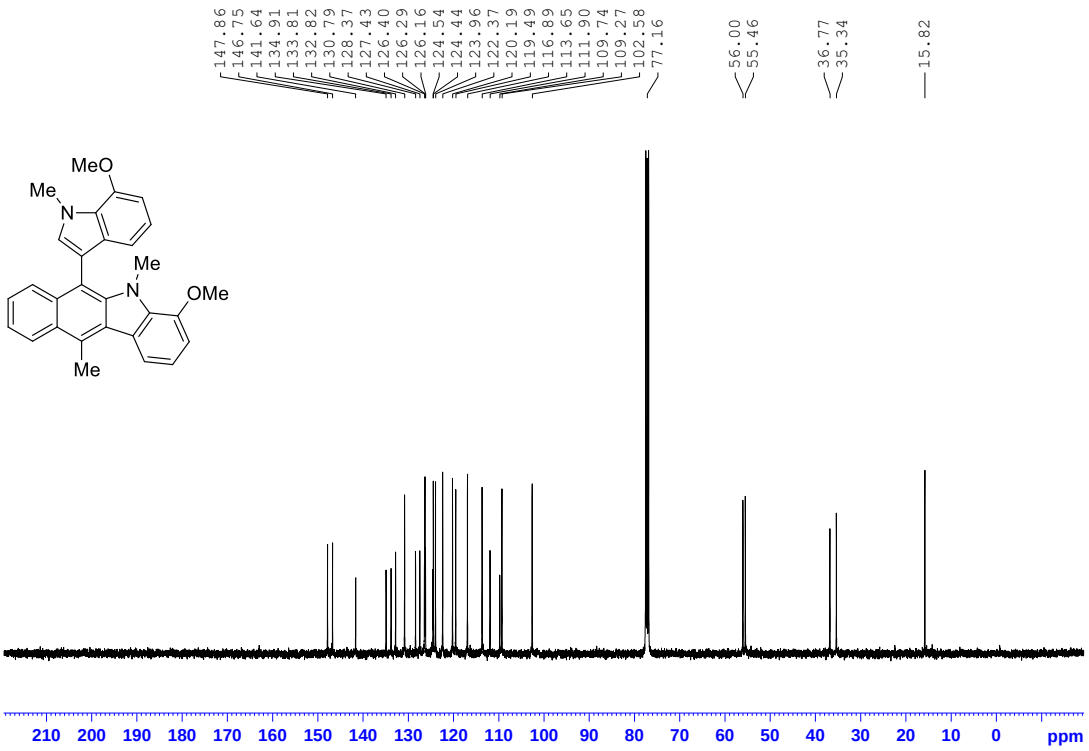
^{13}C NMR of 3-Bromo-6-(6-bromo-1-methyl-1H-indol-3-yl)-5,11-dimethyl-5H-benzo[b]carbazole (3s)



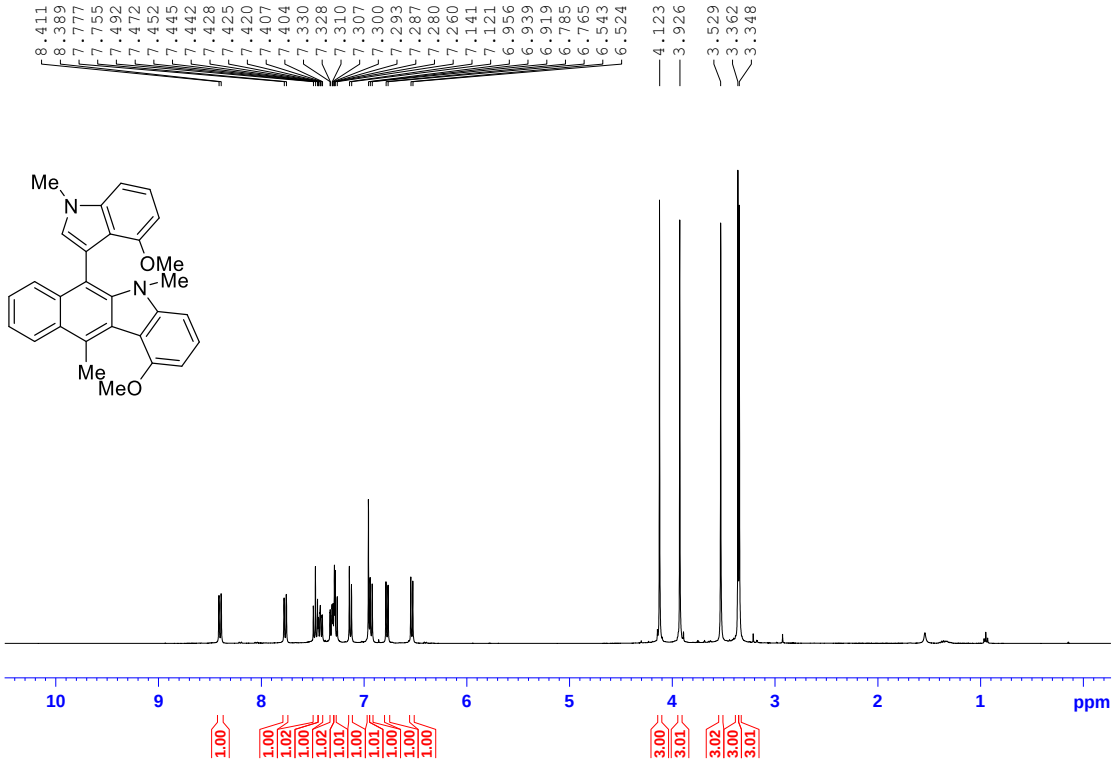
^{1}H NMR of 4-Methoxy-6-(7-methoxy-1-methyl-1*H*-indol-3-yl)-5,11-dimethyl-5*H*-benzo[*b*]carbazole (3t)



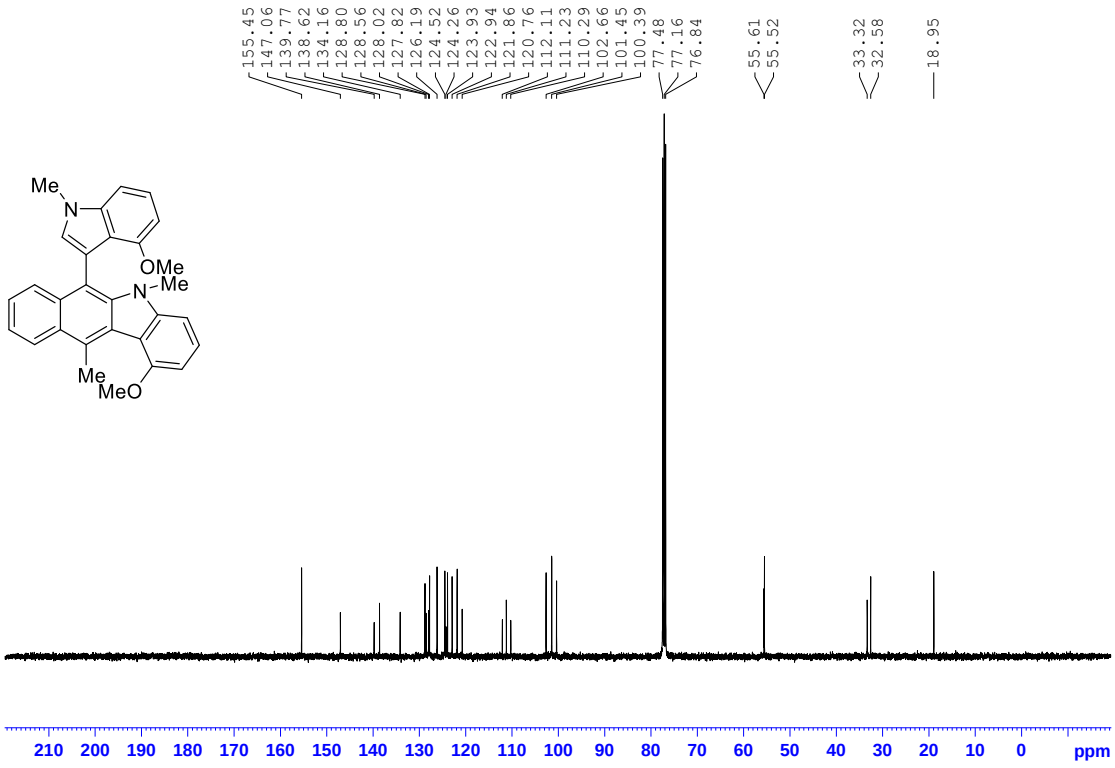
^{13}C NMR of 4-Methoxy-6-(7-methoxy-1-methyl-1*H*-indol-3-yl)-5,11-dimethyl-5*H*-benzo[*b*]carbazole (3t)



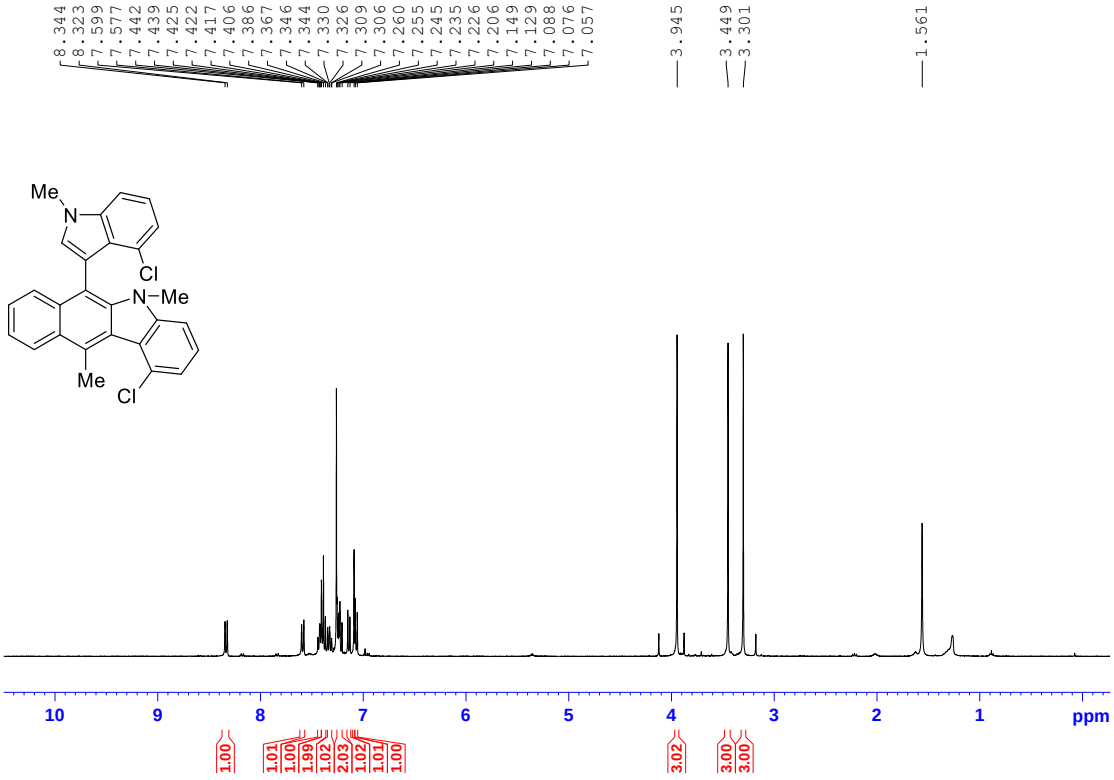
^{1}H NMR of 1-Methoxy-6-(4-methoxy-1-methyl-1*H*-indol-3-yl)-5,11-dimethyl-5*H*-benzo[*b*]carbazole (3u)



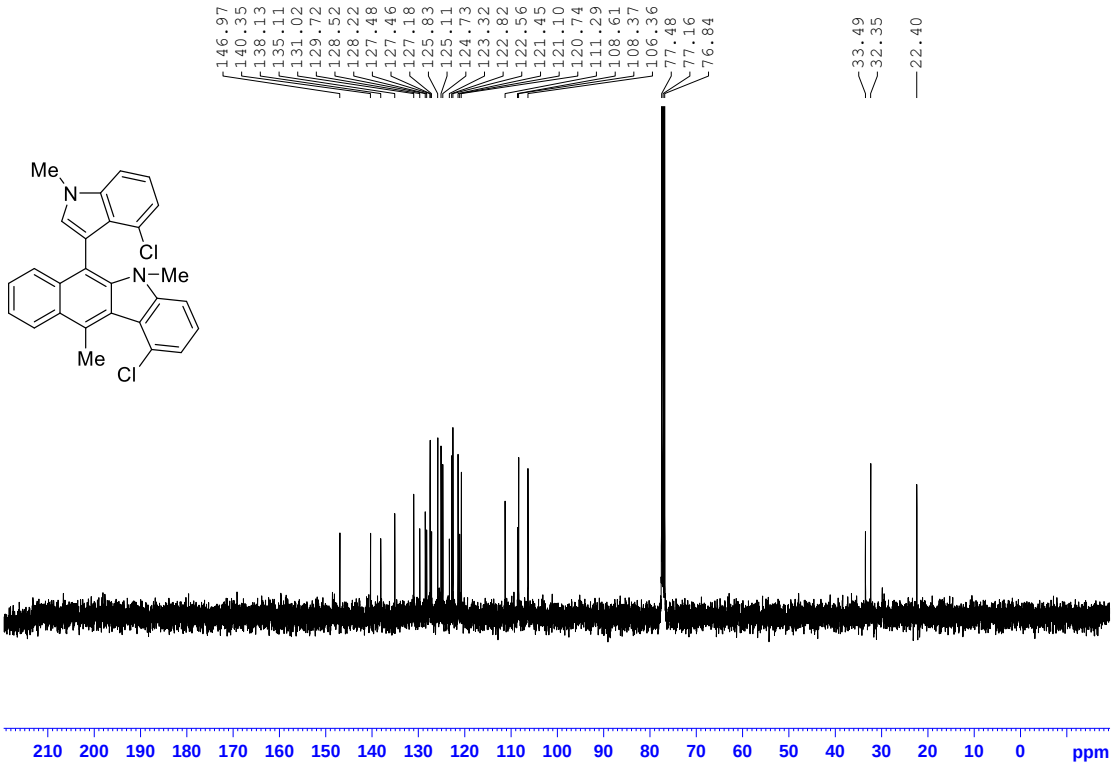
^{13}C NMR of 1-Methoxy-6-(4-methoxy-1-methyl-1*H*-indol-3-yl)-5,11-dimethyl-5*H*-benzo[*b*]carbazole (3u)



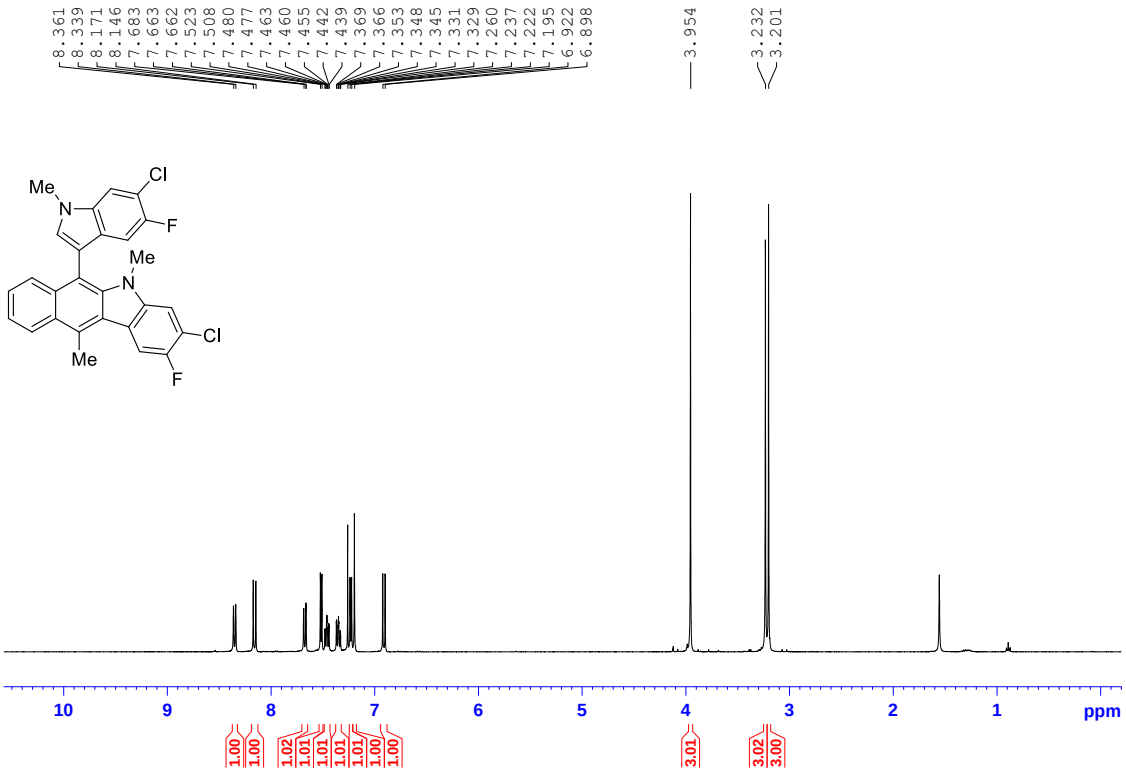
^{1}H NMR of 1-Chloro-6-(4-chloro-1-methyl-1*H*-indol-3-yl)-5,11-dimethyl-5*H*-benzo[*b*]carbazole (3v)



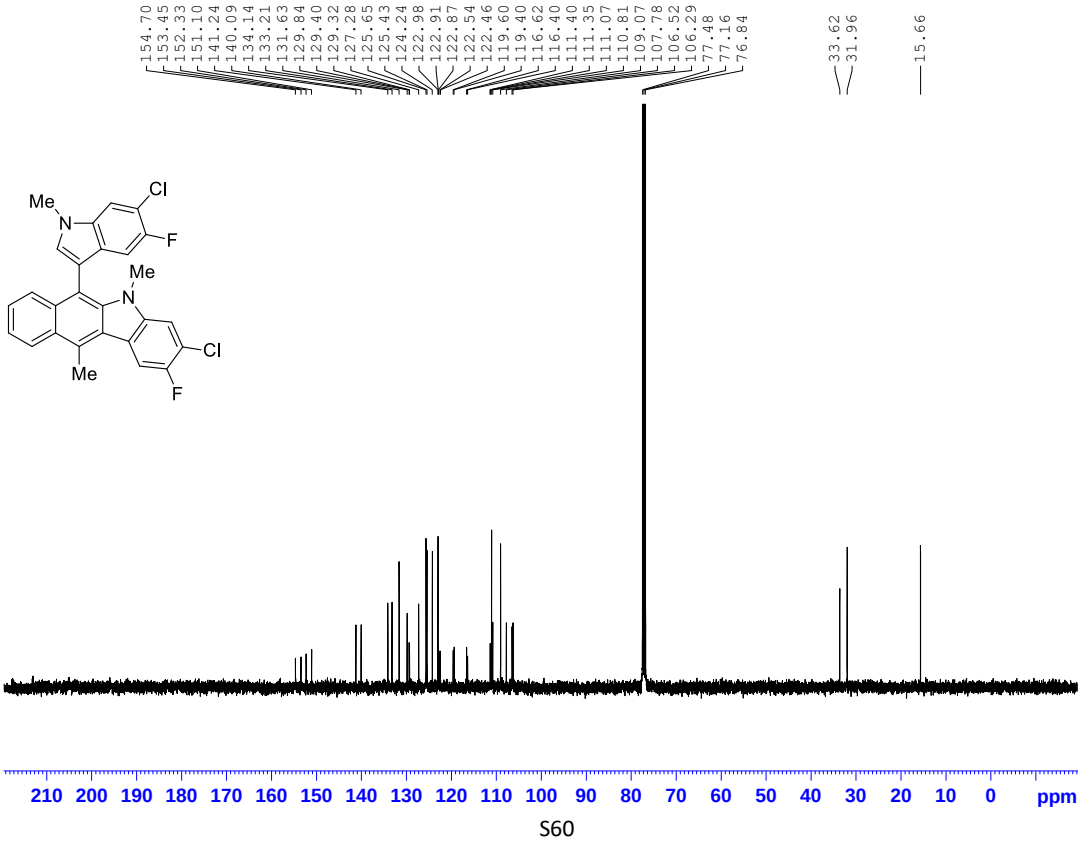
^{13}C NMR of 1-Chloro-6-(4-chloro-1-methyl-1*H*-indol-3-yl)-5,11-dimethyl-5*H*-benzo[*b*]carbazole (3v)



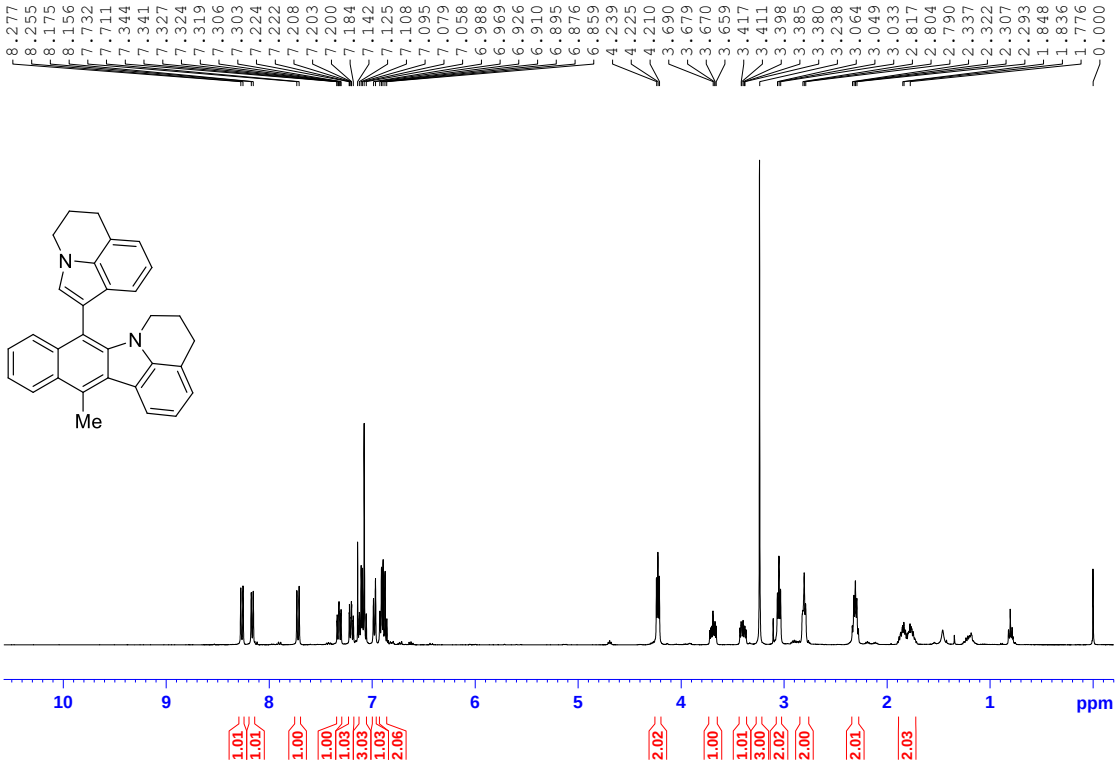
^{1}H NMR of 3-Chloro-6-(6-chloro-5-fluoro-1-methyl-1*H*-indol-3-yl)-2-fluoro-5,11-dimethyl-5*H*-benzo[*b*]carbazole (3w)



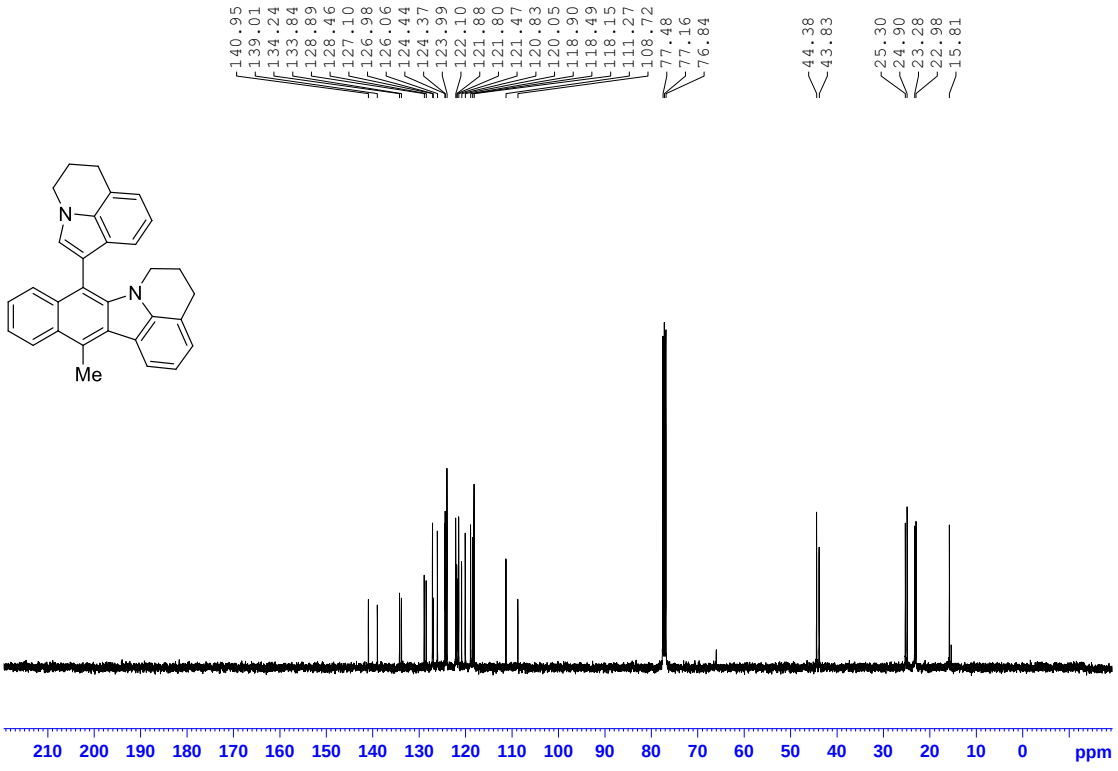
^{13}C NMR of 3-Chloro-6-(6-chloro-5-fluoro-1-methyl-1*H*-indol-3-yl)-2-fluoro-5,11-dimethyl-5*H*-benzo[*b*]carbazole (3w)



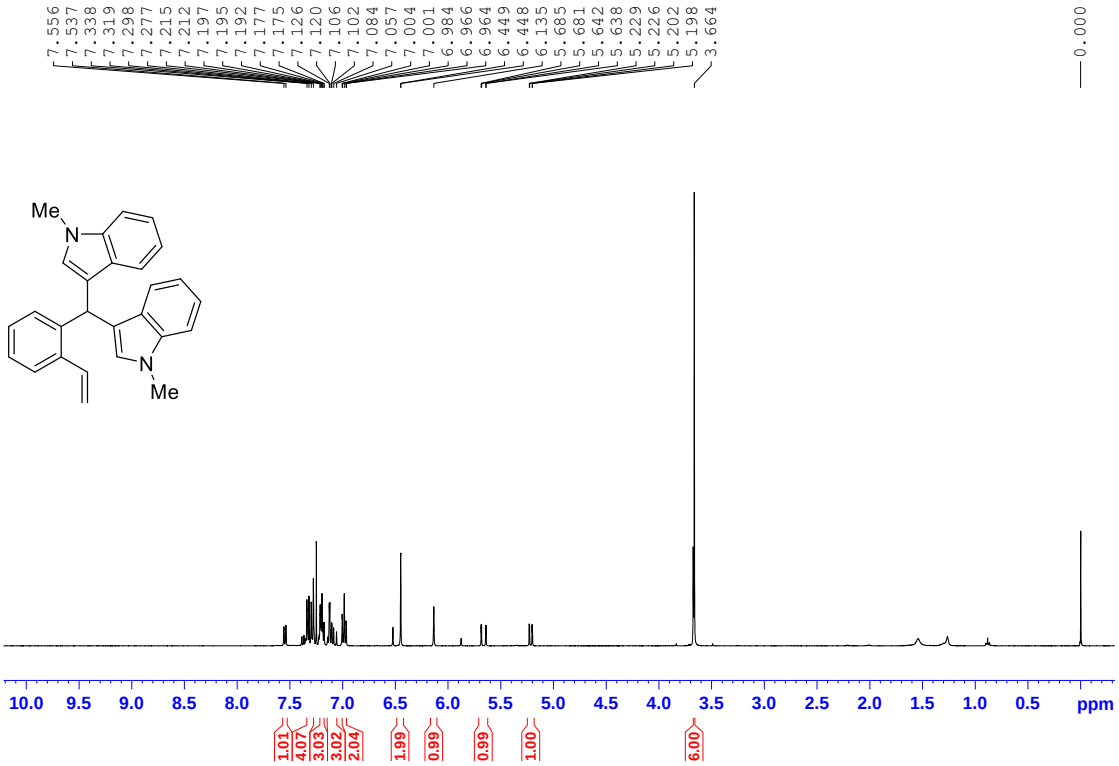
^{1}H NMR of 8-(5,6-Dihydro-4*H*-pyrrolo[3,2,1-*ij*]quinolin-1-yl)-13-methyl-5,6-dihydro-4*H*-benzo[*b*]pyrido[3,2,1-*jk*]carbazole (3x)



^{13}C NMR of 8-(5,6-Dihydro-4*H*-pyrrolo[3,2,1-*ij*]quinolin-1-yl)-13-methyl-5,6-dihydro-4*H*-benzo[*b*]pyrido[3,2,1-*jk*]carbazole (3x)



^{1}H NMR of 3,3'-((2-Vinylphenyl)methylene)bis(1-methyl-1*H*-indole) (5)



^{13}C NMR of 3,3'-((2-Vinylphenyl)methylene)bis(1-methyl-1*H*-indole) (5)