Electronic Supplementary Information

Synthesis, Photophysical Properties and DFT analysis of Highly substituted Pyrido Carbazole-based "push pull" chromophores

Karunanidhi Murali [a], Hazel A. Sparkes [b], Baskaran Vijaya Pandiyan [c],
Karnam Jayarampillai Rajendra Prasad [a*]

[a*] Department of Chemistry, Bharathiar University, Coimbatore 641046, India.

[b] School of Chemistry, University of Bristol, Cantock's Close, Bristol, BS8 1TS, United Kingdom.

[c] Department of Physics, Bharathiar University, Coimbatore 641046, India.

4. Experimental section

4.1. General

All the chemicals were bought from Sigma-Aldrich and Merck and were utilized for the process without further purification. Melting points (m.p.) were determined on a Mettler FP 51 apparatus (Mettler Instruments, Switzerland) and are uncorrected. They are expressed in degree centigrade (°C). FT-IR spectra were recorded on Avatar Model FT-IR (4000–400 cm^{-1}) spectrophotometer. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Agilent- 400 MHz (^{1}H) and 100 MHz (^{13}C) spectrometers respectively in $CDCl_3$ using TMS (tetramethylsilane) as internal reference; chemical shifts are expressed in parts per million (ppm); coupling constants (*J*) are reported in hertz (Hz) and the terms J_o and J_m refer to ortho coupling constant and meta coupling constant. The signals were characterized as s (singlet), d (doublet), t (triplet), m (multipiet), bs (broad singlet) and dd (doublet, and doublet). Microanalyses were carried out using Vario EL III model CHNS analyzer (Vario, Germany). Absorption spectral measurements were carried out using JASCO V-630 UV–Visible spectrophotometer. Quartz cuvettes of path length 1cm were used to record the absorption spectra. The emission spectral studies were performed with JASCO FP-6600 spectrofluorometer equipped with a 1cm quartz cuvette at the Department of Chemistry, Bharathiar University. When known compounds had to be prepared according to literature procedures and pertinent references are given. The purity of the products was tested by TLC plates coated with silica gel-G using petroleum ether and ethyl acetate in the ratio of 1:1 as developing solvents.

4.2. General procedure for the preparation of pyrido[2,3-*a*]carbazole 5 (a-q)

A mixture of 2,3,4,9-tetrahydro-1*H*-carbazol-1-one **1** (1.0 mmol), malononitrile **2**, (1.0 mmol), aryl /heteroaryl aldehyde **3** (1.0 mmol) and sodum ethoxide (0.023g in 1mL EtOH) in 15 mL of methanol was refluxed for 3 h. The reaction was monitored by TLC which indicated the formation of product. The excess of solvent was removed by distillation and the mixture was poured into ice-water. The reaction mixture was then neutralized with 5N HCl and extracted with ethyl acetate. The organic layer was thoroughly washed with water and dried over anhydrous Na_2SO_4. Upon removal of the solvent a brown crude mixture was obtained. It was purified by column chromatography over silica gel using petroleum ether: ethyl acetate (96:4) mixture as eluant to afford the corresponding product, 2-methoxy-4-aryl/heteroaryl-5,6-dihydro-11*H*-pyrido[2,3-*a*]carbazole-3-carbonitrile **5** (**a-q**).

2-Methoxy-10-methyl-4-phenyl-5,6-dihydro-11*H*-pyrido[2,3-a]carbazole-3-carbonitrile (5a). Yellow solid; yield: 310 mg (85%); m.p. 267-269 °C; FT-IR (KBr, cm^{-1}) ν_{max}: 3337 (NH), 2217 (CN), 1556 (C=N); ^{1}H NMR (400 MHz, $CDCl_3$) (ppm) δ_H: 8.65 (b s, 1H, N_{11}-H), 7.52-7.44 (m, 3H, C_9, C_8 & C_7-H), 7.43-7.41 (m, 1H, C_4'), 7.34-7.31 (m, 2H, C_6' & C_2'-H), 7.10-7.04 (m, 2H, C_5' & C_3') 4.18 (s, 3H, C_2-OCH_3), 2.96-2.91 (m, 2H, C_6-2H), 2.87-2.82 (m, 2H, C_5-2H), 2.57 (s, 3H, C_{10}-CH_3); ^{13}C NMR(100 MHz, $CDCl_3$) (ppm) δ_C: 163.7 (C_2), 154.2 (C_{11b}), 148.8 (C_4), 137.5 (C_{10a}), 135.5 (C_1'), 131.9 (C_{11a}), 129.0 (C_5'), 128.7 (C_4'), 128.4 (C_3'), 126.3 (C_6'), 125.2 (C_2'), 124.6 (C_{6b}), 121.5 (C_{4a}), 121.0 (C_8), 120.5 (C_{10}), 120.2 (C_9), 119.7 (C_7), 117.5 (CN), 115.7 (C_{6a}), 93.1 (C_3), 54.4 (OCH_3), 25.3 (C_5), 19.5 (C_6), 16.7 (CH_3); HRMS (ESI) m/z: $[M]^+$ Calcd for $C_{24}H_{19}N_3O$: 365.1530; Found: 365.1525; Anal. calcd. for $C_{24}H_{19}N_3O$: C, 78.88; H, 5.24; N, 11.50. Found: C, 78.79; H, 5.19; N, 11.54 %.

2-Methoxy-8-methyl-4-phenyl-5,6-dihydro-11*H*-pyrido[2,3-a]carbazole-3-carbonitrile (5b).Yellow solid; yield: 295 mg (81%); m.p. 265-267 °C; FT-IR (KBr, cm^{-1}) ν_{max}: 3337 (NH), 2215 (CN), 1553 (C=N); ^{1}H NMR (400 MHz, $CDCl_3$) (ppm) δ_H: 8.74 (b s, 1H, N_{11}-H), 7.52-7.46 (m, 3H, C_{10}, C_9 & C_7 -H), 7.35-7.31 (m, 4H, C_6', C_5', C_4' & C_2'-H), 7.11 (d d, 1H, C_2'-H, J_m = 1.6 & J_o = 8.2 Hz) 4.15 (s, 3H, C_2-OCH_3), 2.91-2.89 (m, 2H, C_6-2H), 2.86-2.84 (m, 2H, C_5-2H), 2.44 (s, 3H, C_8-CH_3); Anal. calcd. for $C_{24}H_{19}N_3O$: C, 78.88; H, 5.24; N, 11.50. Found: C, 78.96; H, 5.27; N, 11.46 %.

2-Methoxy-8-chloro-4-phenyl-5,6-dihydro-11*H*-pyrido[2,3-a]carbazole-3-carbonitrile (5c). Yellow solid; yield: 284 mg (74%); m.p. 270-272 °C; FT-IR (KBr, cm^{-1}) ν_{max}: 3367 (NH), 2211 (CN), 1558 (C=N); ^{1}H NMR (400 MHz, $CDCl_3$) (ppm) δ_H: 8.83 (b s, 1H, N_{11}-H), 7.62-7.50 (m, 2H, C_{10} & C_7-H), 7.37-7.32 (m, 4H, C_6', C_5', C_3' & C_2'-H), 7.23-7.21 (m, 2H, C_9 & C_4'-H), 4.15 (s, 3H, C_2-OCH_3), 2.97-2.85 (m, 4H, C_6 & C_5-2H); Anal. calcd. for $C_{23}H_{16}ClN_3O$: C, 71.59; H, 4.18; N, 10.89. Found: C, 71.51; H, 4.25; N, 10.84 %.

2-Methoxy-4-phenyl-5,6-dihydro-11*H*-pyrido[2,3-a]carbazole-3-carbonitrile (5d). Yellow solid; yield: 280 mg (80%); m.p. 268-271 °C; FT-IR (KBr, cm^{-1}) ν_{max}: 3381 (NH), 2204 (CN), 1552 (C=N); ^{1}H NMR (400 MHz, $CDCl_3$) (ppm) δ_H: 11.59 (b s, 1H, N_{11}-H), 7.61-7.55 (m, 4H, C_{10}, C_9, C_8 & C_4'-H), 7.51 (d, 1H, C_7-H, J_o = 8.0 Hz), 7.46-7.44 (m, 2H, C_6' & C_2'-H), 7.24 (t, C_5'-H, J_o = 7.8 Hz), 7.06 (t, C_3'-H, J_o = 7.8 Hz) 4.20 (s, 3H, C_2-OCH_3), 2.94-2.90 (m, 2H, C_6-2H), 2.80-2.76 (m, 2H, C_5-2H); Anal. calcd. for $C_{23}H_{17}N_3O$: C, 78.61; H, 4.88; N, 11.96. Found: C, 78:54; H, 4.83; N, 11.90 %.

2-Methoxy-10-methyl-4-(thiophen-2'-yl)-5,6-dihydro-11*H*-pyrido[2,3-a]carbazole-3-carbonitrile (5e). Yellow solid; yield: 385 mg (77%); m.p. 271-273 °C; FT-IR (KBr, cm^{-1}) ν_{max}: 3342 (NH), 2217 (CN), 1553 (C=N); ^{1}H NMR (400 MHz, $CDCl_3$) (ppm) δ_H: 8.71 (b s, 1H, N_{11}-H), 7.53 (d d, 1H, C_7-H, J_m = 1.6 & J_o = 8.0 Hz), 7.35-7.31 (m, 2H, C_8 & C_3-H), 7.20-7.16 (m, 2H, C_4' & C_2'-H), 7.11 (d d, 1H, C_9-H, J_m = 1.6 & J_o = 8.0 Hz), 4.14 (s, 3H, C_2-OCH_3), 3.03-2.99 (m, 2H, C_6-2H), 2.96-2.92 (m, 2H, C_5-2H), 2.44 (s, 3H, C_{10}-CH_3); Anal. calcd. for $C_{22}H_{17}N_3OS$: C, 71.14; H, 4.61; N, 11.31. Found: C, 71.22; H, 4.65; N, 11.28 %.

2-Methoxy-8-methyl-4-(thiophen-2'-yl)-5,6-dihydro-11*H*-pyrido[2,3-a]carbazole-3-carbonitrile (5f). Yellow solid; yield: 278 mg (75%); m.p. 270-272 °C; FT-IR (KBr, cm^{-1}) ν_{max}: 3367 (NH), 2205 (CN), 1554 (C=N); ^{1}H NMR (400 MHz, $CDCl_3$) (ppm) δ_H: 8.61 (b s, 1H, N_{11}-H), 7.54-7.52 (m, 1H, C_7-H), 7.45-7.42 (m, 1H, 1H, C_{10}-H), 7.21-7.17 (m, 2H, C_9 & C_3'-H), 7.09-7.06 (m, 2H, C_4' & C_2'-H), 4.18 (s, 3H, C_2-OCH_3), 3.04-3.00 (m, 2H, C_6-2H), 2.99-2.94 (m, 2H, C_5-2H), 2.57 (s, 3H, C_8-CH_3); ^{13}C NMR(100 MHz, $CDCl_3$) (ppm) δ_C: 163.8 (C_2), 148.8 (C_{11b}), 146.9 (C_4), 136.4 (C_1'), 134.8 (C_{10a}), 132.1 (C_{11a}), 129.7 (C_8), 129.0 (C_4'), 127.8 (C_3), 126.8 (C_2'), 124.6 (C_{6b}), 122.8 (C_{4a}), 119.4 (C_9), 118.8 (C_{6a}), 118.3 (CN), 115.6 (C_7), 111.4 (C_9),

110.9 (C_3), 54.4 (OCH_3), 25.4 (C_5), 21.4 (C_6), 20.6 (CH_3); Anal. calcd. for $C_{22}H_{17}N_3OS$: C, 71.14; H, 4.61; N, 11.31. Found: C, 71.08; H, 4.66; N, 11.27 %.

2-Methoxy-8-chloro-4-(thiophen-2'-yl)-5,6-dihydro-11*H*-pyrido[2,3-a]carbazole-3-carbonitrile (5g). Yellow solid; yield: 265 mg (68%); m.p. 275-278 °C; FT-IR (KBr, cm^{-1}) ν_{max}: 3350 (NH), 2211 (CN), 1555 (C=N); ^{1}H NMR (400 MHz, $CDCl_3$) (ppm) δ_H: 8.82 (b s, 1H, N_{11}-H), 7.54 (s, 1H, C_7-H), 7.36 (d, 1H, C_{10}-H, J_o = 8.8 Hz), 7.25-7.19 (m, 4H, C_9, C_4', C_3' & C_2'-H), 4.15 (s, 3H, C_2-OCH_3), 3.05-3.01 (m, 2H, C_6-2H), 2.96-2.94 (m, 2H, C_5-2H); ^{13}C NMR(100 MHz, $CDCl_3$) (ppm) δ_C: 163.7 (C_2), 148.2 (C_{11b}), 136.1 (C_4), 134.5 (C_1'), 129.1 (C_{10a} & C_{11a}), 127.9 (C_8), 127.6 (C_4' & C_2'), 127.5 (C_3'), 126.1 (C_{6b}), 125.0 (C_{4a}), 123.0 (C_9 & C_7), 119.3 (C_{6a}), 118.3 (CN), 115.3 (C_{10}), 112.7 (C_3), 54.4 (OCH_3), 25.3 (C_5), 19.2 (C_6); Anal. calcd. for $C_{21}H_{14}ClN_3OS$: C, 64.36; H, 3.60; N, 10.72. Found: C, 64.29; H, 3.55; N, 10.76 %.

2-Methoxy-4-(thiophen-2'-yl)-5,6-dihydro-11*H*-pyrido[2,3-a]carbazole-3-carbonitrile (5h). Yellow solid; yield: 253 mg (71%); m.p. 272-274 °C; FT-IR (KBr, cm^{-1}) ν_{max}: 3297 (NH), 2225 (CN), 1558 (C=N); ^{1}H NMR (400 MHz, $CDCl_3$) (ppm) δ_H: 8.79 (b s, 1H, N_{11}-H), 7.58 (d, 1H, C_7-H, J_o = 7.6 Hz), 7.54-7.52 (m, 1H, C_8-H), 7.45-7.42 (m, 1H, C_{10}-H), 7.28 (t, 1H, C_9-H, J = 7.6 Hz), 7.21-7.12 (m, 3H, C_4', C_3' & C_2'-H), 4.15 (s, 3H, C_2-OCH_3), 3.04-2.96 (m, 4H, C_6 & C_5-2H); ^{13}C NMR(100 MHz, $CDCl_3$) (ppm) δ_C: 163.8 (C_2),148.7 (C_{11b}), 147.0 (C_4), 138.0 (C'_1), 134.8 (C_{10a}), 132.0 (C_{11a}), 129.1 (C_4'), 127.8 (C_3'), 127.4 (C_2'), 126.7 (C_{6b}), 124.8 (C_{4a}), 122.8 (C_9), 120.3 (C_8), 119.9 (C_7), 119.2 (CN), 115.4 (C_{6a}), 111.7 (C_{10}), 93.9 (C_3), 54.3 (OCH_3), 25.4 (C_5), 19.3 (C_6); HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{21}H_{15}N_3OS$: 358.1015; Found: 358.1009; Anal. calcd. for $C_{21}H_{15}N_3OS$: C, 70.57; H, 4.23; N, 11.76. Found: C, 70.66; H, 4.25; N, 11.71 %.

2-Methoxy-10-methyl-4-(4'-methyl-phenyl)-5,6-dihydro-11*H*-pyrido[2,3-a]carbazole-3-carbonitrile (5i). Yellow solid; yield: 295 mg (78%); m.p. 263-266 °C; FT-IR (KBr, cm^{-1}) ν_{max}: 3339 (NH), 2219 (CN), 1556 (C=N); ^{1}H NMR (400 MHz, $CDCl_3$) (ppm) δ_H: 8.73 (b s, 1H, N_{11}-H), 7.42 (d, 1H, C_7-H, J_o = 8.4 Hz), 7.39-7.29 (m, 3H, C_8, C_4' & C_2'-H), 7.25-7.21 (m, C_5' & C_3'-H), 7.11-7.09 (d, 1H, C_9-H, J_o = 8.4 Hz), 4.14 (s, 3H, C_2-OCH_3), 2.93-2.83 (m, 4H, C_6 & C_5-2H), 2.44 (s, 3H, C'_4-CH_3), 2.42 (s, 3H, C_{10}-CH_3); ^{13}C NMR(100 MHz, $CDCl_3$) (ppm) δ_C: 163.7 (C_2),

154.3 (C_{11b}), 148.6 (C_4), 139.0 (C_{10a}), 136.3 (C_4'), 132.5 (C_{11a}), 129.5 (C_1'), 129.3 (C_5'), 128.3 (C_3'), 126.9 (C_6'), 126.4 (C_2'), 121.6 (C_{6b}), 120.5 (C_{4a}), 119.5 (C_8), 118.4 (C_{10}), 118.2 (C_9), 117.8 (CN), 115.9 (C_7), 111.3 (C_{6a}), 93.0 (C_3), 54.4 (OCH_3), 25.3 (C_5), 23.7 (C_6), 21.4 (C_4'-CH_3), 19.4 (C_{10}-CH_3); HRMS (ESI) m/z: $[M]^+$ Calcd for: $C_{25}H_{21}N_3O$: 379.1686; Found: 379.1642; Anal. calcd. for $C_{25}H_{21}N_3O$: C, 79.13; H, 5.58; N, 11.07. Found: C, 79.21; H, 5.61; N, 11.11 %.

2-Methoxy-8-methyl-4-(4'-methyl-phenyl)-5,6-dihydro-11*H*-pyrido[2,3-a]carbazole-3-carbonitrile (5j). Yellow solid; yield: 288 mg (76%); m.p. 265-268 °C; FT-IR (KBr, cm^{-1}) ν_{max}: 3315 (NH), 2225 (CN), 1559 (C=N); ^{1}H NMR (400 MHz, $CDCl_3$) (ppm) δ_H: 8.62 (b s, 1H, N_{11}-H), 7.42 (d, 1H, C_{10}-H, J_o = 7.2 Hz), 7.32-7.30 (m, 2H, C_7 & C_9-H), 7.25-7.22 (m, 2H, C_6' & C_2'-H), 7.08-7.04 (m, 2H, C_5' & C_3'-H), 4.18 (s, 3H, C_2-OCH_3), 2.94-2.91 (m, 2H, C_6-2H), 2.89-2.85 (m, 2H, C_5-2H), 2.58 (s, 3H, C'_4-CH_3), 2.42 (s, 3H, C_8-CH_3); ^{13}C NMR(100 MHz, $CDCl_3$) (ppm) δ_C: 163.7 (C_2), 154.3 (C_{11b}), 148.6 (C_4), 139.0 (C_{10a}), 136.2 (C_4'), 132.5 (C_{11a}), 129.7 (C_1'), 129.3 (C_5'), 128.3 (C_3'), 126.9 (C_8), 126.4 (C_6'), 126.1 (C_2'), 121.6 (C_{6b}), 120.6 (C_{4a}), 119.4 (C_9), 118.5 (C_7), 117.8 (CN), 115.9 (C_{6a}), 112.0 (C_3), 111.3 (C_{10}), 54.3 (OCH_3), 25.3 (C_8-CH_3), 24.9 (C_4'-CH_3), 21.4 (C_5), 19.4 (C_6); Anal. calcd. for $C_{25}H_{21}N_3O$: C, 79.13; H, 5.58; N, 11.07. Found: C, 79.20; H, 5.53; N, 11.10 %.

2-Methoxy-4-(4'-methyl-phenyl)-5,6-dihydro-11*H*-pyrido[2,3-a]carbazole-3-carbonitrile (5k). Yellow solid; yield: 262 mg (72%); m.p. 267-270 °C; FT-IR (KBr, cm^{-1}) ν_{max}: 3303 (NH), 2226 (CN), 1557 (C=N); ^{1}H NMR (400 MHz, $CDCl_3$) (ppm) δ_H: 8.82 (b s, 1H, N_{11}-H), 7.57 (d, 1H, C_7-H, J_o = 7.6 Hz), 7.45-7.40 (m, 1H, C'_2-H), 7.32-7.30 (m, 3H, C_{10}, C_8 & C_6'-H), 7.26-7.22 (m, 2H, C_5' & C_3'-H), 7.15-7.11 (m, 1H, C_9-H), 4.15 (s, 3H, C_2-OCH_3), 2.96-2.92 (m, 2H, C_6-2H), 2.89-2.86 (m, 2H, C_5-2H) 2.42 (s, 3H, C_4'-CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) (ppm) δ_C: 163.7 (C_2), 154.4 (C_{11b}), 148.5 (C_4), 139.0 (C_{10a}), 137.8 (C'_4), 132.4 (C_{11a}), 132.2 (C_1'), 129.3 (C_5'), 128.3 (C_3'), 126.7 (C_2'), 124.6 (C_6'), 121.6 (C_{6b}), 120.8 (C_{4a}), 120.2 (C_9), 119.9 (C_8), 118.9 (C_7), 118.0 (CN), 115.8 (C_{6a}), 111.7 (C_{10}), 93.3 (C_3), 54.3 (OCH_3), 25.2 (C_5), 21.3 (C_6), 19.4 (C_4'-CH_3); Anal. calcd. for $C_{24}H_{19}N_3O$: C, 78.88; H, 5.24; N, 11.50. Found: C, 78.96; H, 5.28; N, 11.46 %.

2-Methoxy-10-methyl-4-(4'-chloro-phenyl)-5,6-dihydro-11*H*-pyrido[2,3-a]carbazole-3-carbonitrile (5l). Yellow solid; yield: 263 mg (66%); m.p. 280-282 °C; FT-IR (KBr, cm^{-1}) ν_{max}: 3386 (NH), 2217 (CN), 1544 (C=N); ^{1}H NMR (400 MHz, $CDCl_3$) (ppm) δ_H: 8.61 (b s, 1H, N_{11}-H), 7.51-7.49 (m, 2H, C_8 & C_7-H), 7.43(d, 1H, C_9-H, J_o = 8.0 Hz), 7.30-7.28 (m, 2H, C_6' & C_2'-H), 7.10-7.04 (m, 2H, C_5' & C_3'-H), 4.18 (s, 3H, C_2-OCH_3), 2.96-2.92 (m, 2H, C_6-2H), 2.85-2.81 (m, 2H, C_5-2H), 2.58 (s, 3H, C_{10}-CH_3); HRMS (ESI) m/z: $[M]^+$ Calcd for $C_{24}H_{18}ClN_3O$: 399.1140; Found: 399.1101; Anal. calcd. for $C_{24}H_{18}ClN_3O$: C, 72.09; H, 4.54; N, 10.51. Found: C, 72.01; H, 4.59; N, 10.46 %.

2-Methoxy-8-chloro-4-(4'-chloro-phenyl)-5,6-dihydro-11*H*-pyrido[2,3-a]carbazole-3-carbonitrile (5m). Yellow solid; yield: 243 mg (58%); m.p. 287-289 °C; FT-IR (KBr, cm^{-1}) ν_{max}: 3349 (NH), 2221 (CN), 1552 (C=N); ^{1}H NMR (400 MHz, $CDCl_3$) (ppm) δ_H: 8.82 (b s, 1H, N_{11}-H), 7.53-7.22 (m, 7H, C_{10}, C_9, C_7, C_6', $_5$C', C_3' & C_2'-H), 4.15 (s, 3H, C_2-OCH_3), 2.91-2.89 (m, 2H, C_6-2H), 2.86-2.84 (m, 2H, C_5-2H); Anal. calcd. for $C_{23}H_{15}Cl_2N_3O$: C, 65.73; H, 3.60; N, 10.00. Found: C, 65.81; H, 3.54; N, 10.07 %.

2-Methoxy-4-(4'-chloro-phenyl)-5,6-dihydro-11*H*-pyrido[2,3-a]carbazole-3-carbonitrile (5n). Yellow solid; yield: 231 mg (60%); m.p. 283-285 °C; FT-IR (KBr, cm^{-1}) ν_{max}: 3346 (NH), 2224 (CN), 1554 (C=N); ^{1}H NMR (400 MHz, $CDCl_3$) (ppm) δ_H: 8.80 (b s, 1H, N_{11}-H), 7.58 (d, 1H, C_7-H, J_o = 7.6 Hz), 7.51-7.48 (m, 2H, C_8 & C_6'-H), 7.45 (d, 1H, C_{10}-H, J_o = 7.6 Hz), 7.30-7.27 (m, 3H, C_5', C_3' & C_2'-H), 7.14 (t, 1H, C_9-H, J_o = 7.6 Hz), 4.16 (s, 3H, C_2-OCH_3), 2.97-2.93 (m, 2H, C_6-2H), 2.86-2.82 (m, 2H, C_5-2H); Anal. calcd. for $C_{23}H_{16}ClN_3O$: C, 71.59; H, 4.18; N, 10.89. Found: C, 71.49; H, 4.23; N, 10.83 %.

2-Methoxy-10-methyl-4-(4'-methoxy-phenyl)-5,6-dihydro-11*H*-pyrido[2,3-a]carbazole-3-carbonitrile (5o). Yellow solid; yield: 264 mg (67%); m.p. 271-274 °C; FT-IR (KBr, cm^{-1}) ν_{max}: 3353 (NH), 2216 (CN), 1544 (C=N); ^{1}H NMR (400 MHz, $CDCl_3$) (ppm) δ_H: 8.61 (b s, 1H, N_{11}-H), 7.42 (d, 1H, C_7-H, J_o = 8.0 Hz), 7.30-7.25 (m, C_9 & C_8-H), 7.08-7.01 (m, 4H, C_6', C_5', C_3' & C_2'-H), 4.18 (s, 3H, C_2-OCH_3), 3.28 (s, 3H, C_4'-OCH_3) 2.94-2.87 (m, 4H, C_6 & C_5-2H), 2.58 (s, 3H, C_{10}-CH_3); ^{13}C NMR(100 MHz, $CDCl_3$) (ppm) δ_C: 163.8 (C_2), 160.1 (C'_4), 154.0 (C_{11b}), 148.7 (C_4), 137.5 (C_{10a}), 131.9 (C_{11a}), 129.9 (C_6' & C_2'), 127.5 (C_{6b}), 126.3 (C_1'), 125.1 (C_8), 121.7

(C_{10}), 120.9 (C_9), 120.5 (C_{4a}), 119.5 (C_7 & C_{6a}), 117.5 (CN), 115.9 (C_5' & C_3'), 114.1 (C_3), 55.3 (C_4'-OCH_3), 54.3 (OCH_3), 25.3 (C_5), 19.5 (C_6), 16.7 (CH_3); HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{25}H_{21}N_3O_2$: 396.1713; Found: 396.1708; Anal. calcd. for $C_{25}H_{21}N_3O_2$: C, 75.93; H, 5.35; N, 10.63. Found: C, 75.84; H, 5.39; N, 10.58 %.

2-Methoxy-8-methyl-4-(4'-methoxy-phenyl)-5,6-dihydro-11*H*-pyrido[2,3-a]carbazole-3-carbonitrile (5p). Yellow solid; yield: 256 mg (65%); m.p. 273-275 °C; FT-IR (KBr, cm^{-1}) ν_{max}: 3380 (NH), 2219 (CN), 1544 (C=N); ^{1}H NMR (400 MHz, $CDCl_3$) (ppm) δ_H: 8.70 (b s, 1H, N_{11}-H), 7.34-7.01 (m, 7H, C_{10}, C_9, C_7, C_6', C_5', C_3' & C_2'-H), 4.14 (s, 3H, C_2-OCH_3), 3.86 (s, 3H, C_4'-OCH_3) 2.91-2.89 (m, 4H, C_6 & C_5-2H), 2.44 (s, 3H, C_8-CH_3); Anal. calcd. for $C_{25}H_{21}N_3O_2$: C, 75.93; H, 5.35; N, 10.63. Found: C, 75.94; H, 5.31; N, 10.69 %.

2-Methoxy-8-chloro-4-(4'-methoxy-phenyl)-5,6-dihydro-11*H*-pyrido[2,3-a]carbazole-3-carbonitrile (5q). Yellow solid; yield: 244 mg (59%); m.p. 275-278 °C; FT-IR (KBr, cm^{-1}) ν_{max}: 3386 (NH), 2241 (CN), 1553 (C=N); ^{1}H NMR (400 MHz, $CDCl_3$) (ppm) δ_H: 8.82 (b s, 1H, N_{11}-H), 7.52 (d, 1H, J_m = 2.0 Hz), 7.36 (d, 1H, C_{10}-H, J_o = 8.8 Hz), 7.28-7.26 (m, 2H, C_6' & C_2'-H), 7.22 (d d, 1H, C_9-H, J_m = 2.0 & J_o = 8.8 Hz), 7.04-7.02 (m, 2H, C'$_5$ & C_3-H), 4.14 (s, 3H, C_2-OCH_3), 3.87 (s, 3H, C_4'-OCH_3) 2.90-2.85 (m, 4H, C_6 & C_5-2H); Anal. calcd. for $C_{24}H_{18}ClN_3O_2$: C, 69.31; H, 4.36; N, 10.10. Found: C, 69.40 H, 4.31; N, 10.04 %.

4.3. Computational methods

All the theoretical calculations were performed with the Gaussian 09 package.[40] DFT method was used for the ground state optimization. In the present study, all the computations were performed by DFT theory in the frame work of M06-2X/6-31G** level of theory. Shang *et. al*.,[41] reported the M06-2X/6-31G** functional gave more satisfactory results for photochemistry calculations. All these molecules are first optimized with that level of theories. Then, all the optimized model structures correspond to the minima in the potential energy surface. Molecular orbital (MO) compositional analyses were carried out by chemissian software.

ESI-Table 1. Crystal data and structure refinement for **5a**, **5d**, **5h**, **5j** and **5k**.

	5a	**5d**	**5h**	**5j**	**5k**
Empirical formula	$C_{24}H_{19}N_3O$	$C_{23}H_{17}N_3O$	$C_{21}H_{15}N_3OS$	$C_{25}H_{21}N_3O$	$C_{24}H_{19}N_3O$
Formula weight	365.42	351.39	357.42	379.45	365.42
Temperature/K	100(2)	100(2)	100(2)	100(2)	100(2)
Crystal system	Monoclinic	Monoclinic	Monoclinic	monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1$	$P2_1/c$	$P2_1/n$	$P2_1/c$
a/Å	10.0881(4)	13.4283(10)	10.7239(11)	9.9044(6)	14.1159(6)
b/Å	15.1974(6)	15.7465(11)	15.4965(15)	16.2434(9)	15.3254(7)
c/Å	12.2090(5)	16.5327(11)	10.3257(10)	12.9264(8)	18.2305(9)
α/°	90	90	90	90	90
β/°	98.801(3)	92.893(6)	91.507(8)	106.592(4)	112.383(3)
γ/°	90	90	90	90	90
Volume/Å^3	1849.76(13)	3491.4(4)	1715.4(3)	1993.0(2)	3646.7(3)
Z	4	8	4	4	8
ρ_{calc} g/cm^3	1.312	1.337	1.384	1.265	1.331
μ/mm^{-1}	0.082	0.084	0.204	0.079	0.083
F(000)	768.0	1472.0	744.0	800.0	1536.0
Crystal size/mm^3	0.43×0.41×0.33	0.33×0.27×0.13	0.39×0.25×0.09	0.44×0.4×0.25	0.28×0.22×0.13
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
2θ range for data collection/°	4.086 to 55.824	2.466 to 52.746	3.8 to 52.742	4.134 to 56.076	3.12 to 55.942
Index ranges	$-13 \le h \le 13$, $-19 \le k \le 19$, $-16 \le l \le 15$	$-16 \le h \le 16$, $-19 \le k \le 19$, $-20 \le l \le 20$	$-13 \le h \le 13$, $-19 \le k \le 19$, $-11 \le l \le 12$	$-13 \le h \le 13$, $-21 \le k \le 21$, $-17 \le l \le 12$	$-18 \le h \le 18$, $-14 \le k \le 20$, $-23 \le l \le 24$
Reflections collected	16608	28602	13590	17960	32948
R_{int}	0.0305	0.0767	0.0760	0.0318	0.0808
Data/restraints/parameters	4404/0/259	13203/1/977	3492/0/240	4780/0/269	8712/0/509
Goodness-of-fit on F^2	1.040	0.993	1.161	1.031	1.083
Final R indexes [I>=2σ (I)]	R_1 = 0.0408, wR_2 = 0.0998	R_1 = 0.0592, wR_2 = 0.0966	R_1 = 0.0857, wR_2 = 0.2348	R_1 = 0.0449, wR_2 = 0.1123	R_1 = 0.0801, wR_2 = 0.1874
Final R indexes [all data]	R_1 = 0.0537, wR_2 = 0.1072	R_1 = 0.1143, wR_2 = 0.1160	R_1 = 0.1173, wR_2 = 0.2495	R_1 = 0.0594, wR_2 = 0.1220	R_1 = 0.1235, wR_2 = 0.2063
Largest diff. peak/hole / e Å^{-3}	0.33/-0.28	0.22/-0.28	0.77/-0.43	0.33/-0.37	0.32/-0.37

ESI-Table 2. Photophysical properties of pyrido[2,3-*a*]carbazoles **5** (**a-q**) in $CHCl_3$

	$CHCl_3$				
Compounds	λ_{abs} (nm)	λ_{emi} (nm)	Φ_{fl}	$\Delta\nu$ (cm^{-1})	**ε** (L mol^{-1} cm^{-1})
5a	393	459	0.55±0.07	3659	39970
5b	398	456	0.58±0.055	3196	40170
5c	396	458	0.43±0.055	3418	41560
5d	395	461	0.49±0.04	3625	45490
5e	401	466	0.56±0.075	3478	46480
5f	399	459	0.53±0.06	3276	43430
5g	400	467	0.47±0.04	3587	42790
5h	403	458	0.48±0.06	2979	40670
5i	394	453	0.29±0.045	3305	42470
5j	395	454	0.38±0.07	3290	41390
5k	401	457	0.27±0.055	3056	40276
5l	396	448	0.29±0.06	2931	41340
5m	397	457	0.36±0.04	3307	43260
5n	401	463	0.34±0.055	3339	42480
5o	392	456	0.51±0.07	3581	40390
5p	393	460	0.42±0.05	3706	41780
5q	390	461	0.45±0.05	3950	43170

ESI-Table 3. Photophysical properties of pyrido[2,3-*a*]carbazoles **5** (**a-q**) in MeOH

			MeOH		
Compounds	λ_{abs} (nm)	λ_{emi} (nm)	Φ_{fl}	$\Delta\nu$ (cm^{-1})	**ε** (L mol^{-1} cm^{-1})
5a	394	460	0.59±0.04	3641	36910
5b	397	459	0.59±0.045	3402	37130
5c	398	466	0.48±0.06	3666	37980
5d	397	464	0.51±0.04	3637	38130
5e	400	469	0.61±0.04	3679	37710
5f	402	463	0.55±0.045	3277	38680
5g	402	470	0.46±0.035	3599	39470
5h	400	465	0.51±0.04	3495	39290
5i	399	455	0.29±0.05	3084	40110
5j	399	459	0.35±0.06	3276	39460
5k	394	456	0.30±0.045	3451	38360
5l	398	451	0.33±0.05	2953	41240
5m	399	459	0.37±0.05	3276	37320
5n	400	466	0.35±0.06	3541	36940
5o	390	453	0.53±0.055	3566	37290
5p	392	457	0.41±0.05	3629	38110
5q	391	467	0.48±0.04	4162	39310

ESI-Table 4. Photophysical properties of pyrido[2,3-*a*]carbazoles **5** (**a-q**) in DMF

	DMF				
Compounds	λ_{abs} (nm)	λ_{emi} (nm)	Φ_{fl}	$\Delta\nu$ (cm^{-1})	ε (L mol^{-1} cm^{-1})
5a	395	478	0.56±0.05	4396	36430
5b	403	483	0.61±0.045	4110	35780
5c	403	481	0.51±0.3	4023	36370
5d	399	483	0.54±0.05	4359	38410
5e	405	497	0.62±0.05	4571	37620
5f	404	493	0.56±0.055	4469	38590
5g	406	489	0.48±0.03	4590	3660
5h	407	504	0.65±0.035	4729	38190
5i	401	464	0.39±0.04	3386	36180
5j	400	469	0.48±0.04	3679	35470
5k	402	467	0.32±0.055	3462	35910
5l	401	476	0.34±0.06	3929	35270
5m	398	486	0.41±0.05	4549	34685
5n	403	486	0.38±0.055	4237	36390
5o	398	466	0.58±0.04	3660	35470
5p	395	467	0.49±0.05	3903	37250
5q	394	477	0.53±0.05	4416	36430

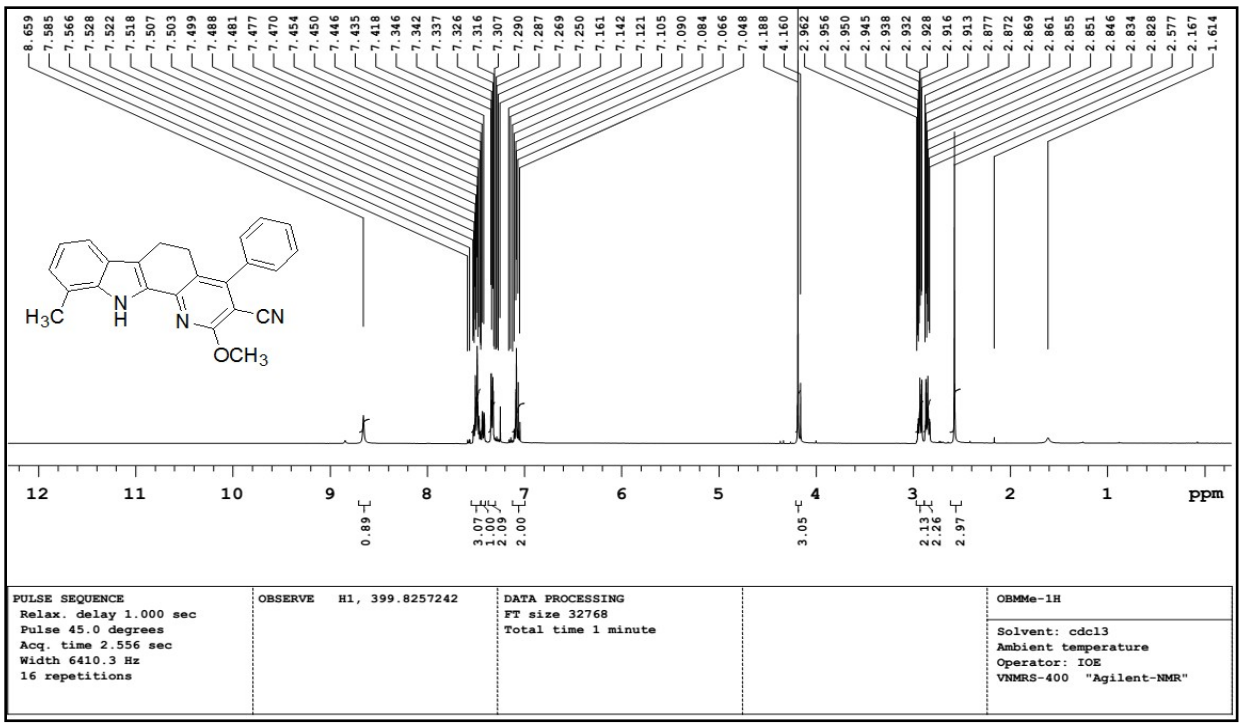

Fig.S1 ^{1}H NMR spectrum of 2-methoxy-10-methyl-4-phenyl-5,6-dihydro-11*H*-pyrido[2,3-*a*]carbazole-3-carbonitrile (5a)

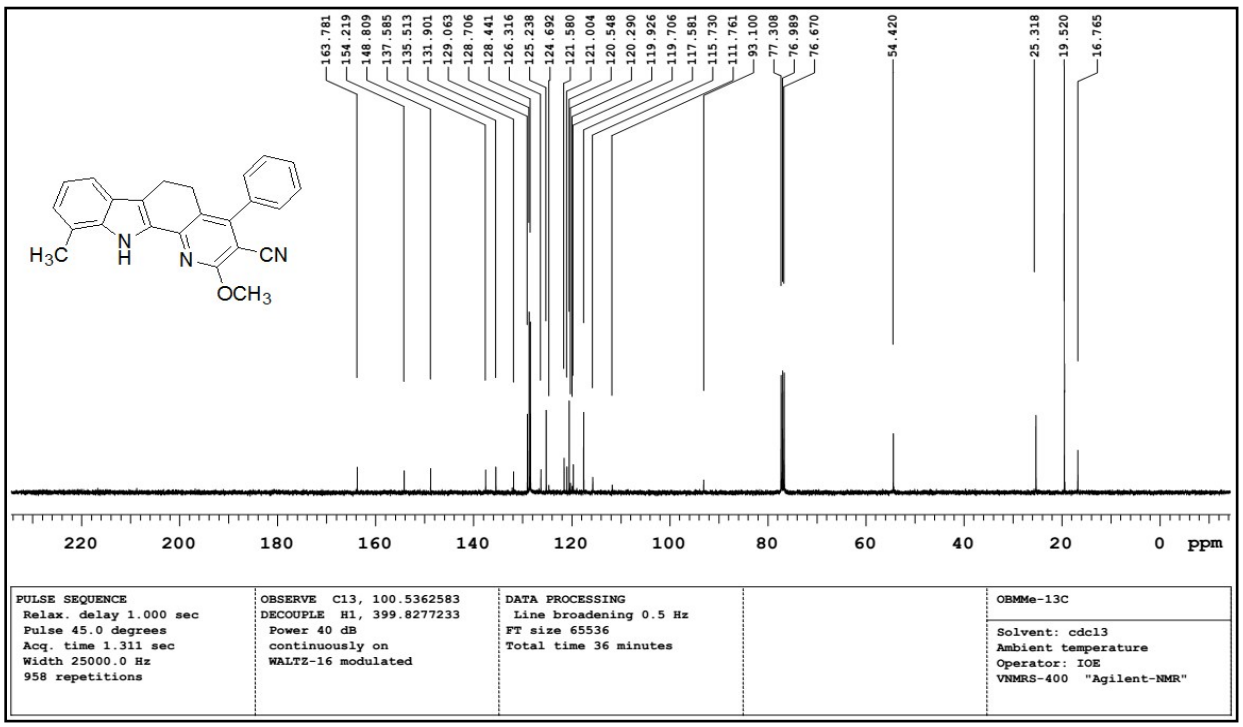

Fig.S2 ^{13}C NMR spectrum of 2-methoxy-10-methyl-4-phenyl-5,6-dihydro-11*H*-pyrido[2,3-*a*]carbazole-3-carbonitrile (5a)

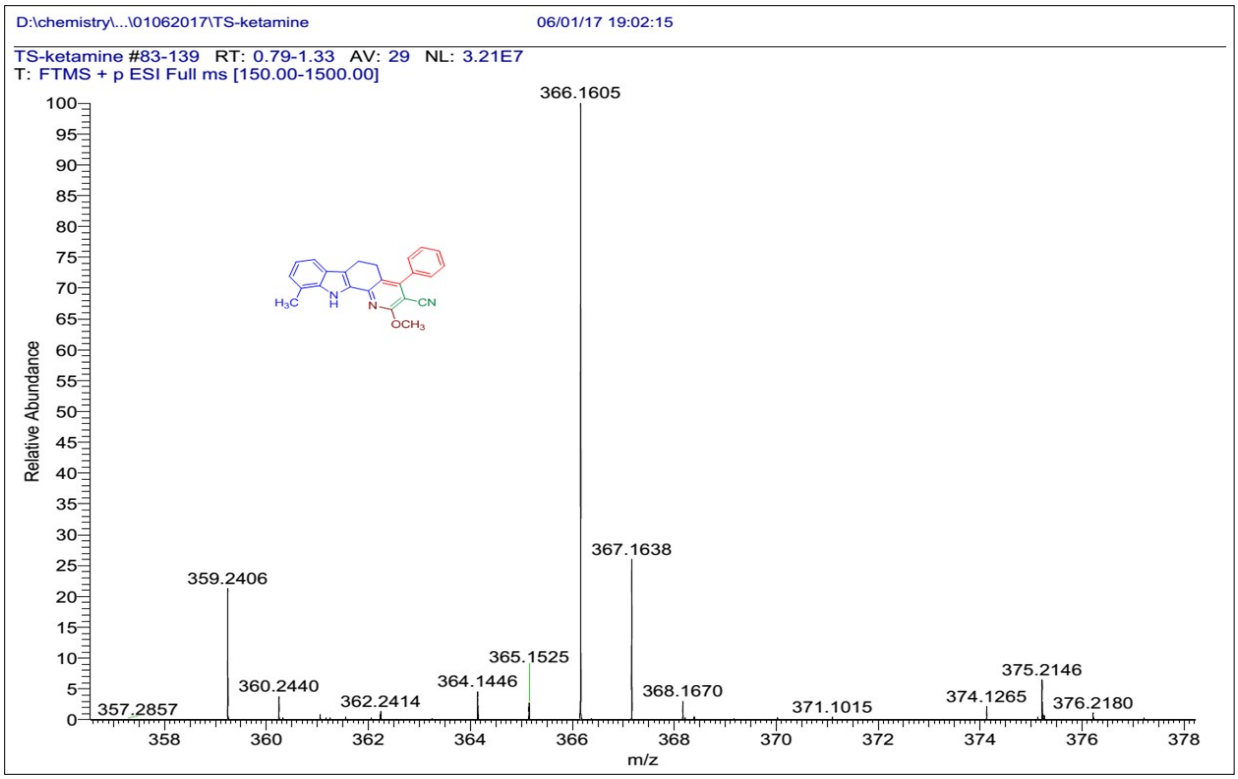

Fig. S3. HRMS spectrum of 2-methoxy-10-methyl-4-phenyl-5,6-dihydro-11*H*-pyrido[2,3-*a*]carbazole-3-carbonitrile (5a)

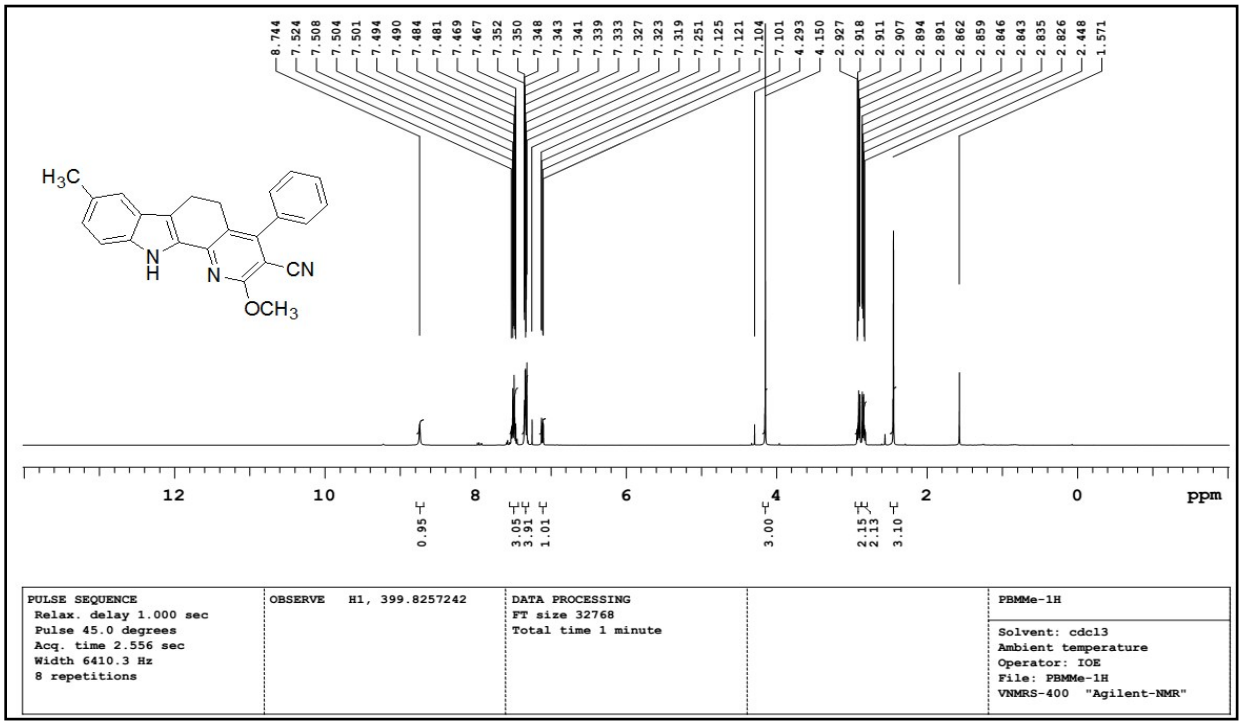

Fig. S4. ^{1}H NMR spectrum of 2-methoxy-8-methyl-4-phenyl-5,6-dihydro-11*H*-pyrido[2,3-*a*]carbazole-3-carbonitrile (5b)

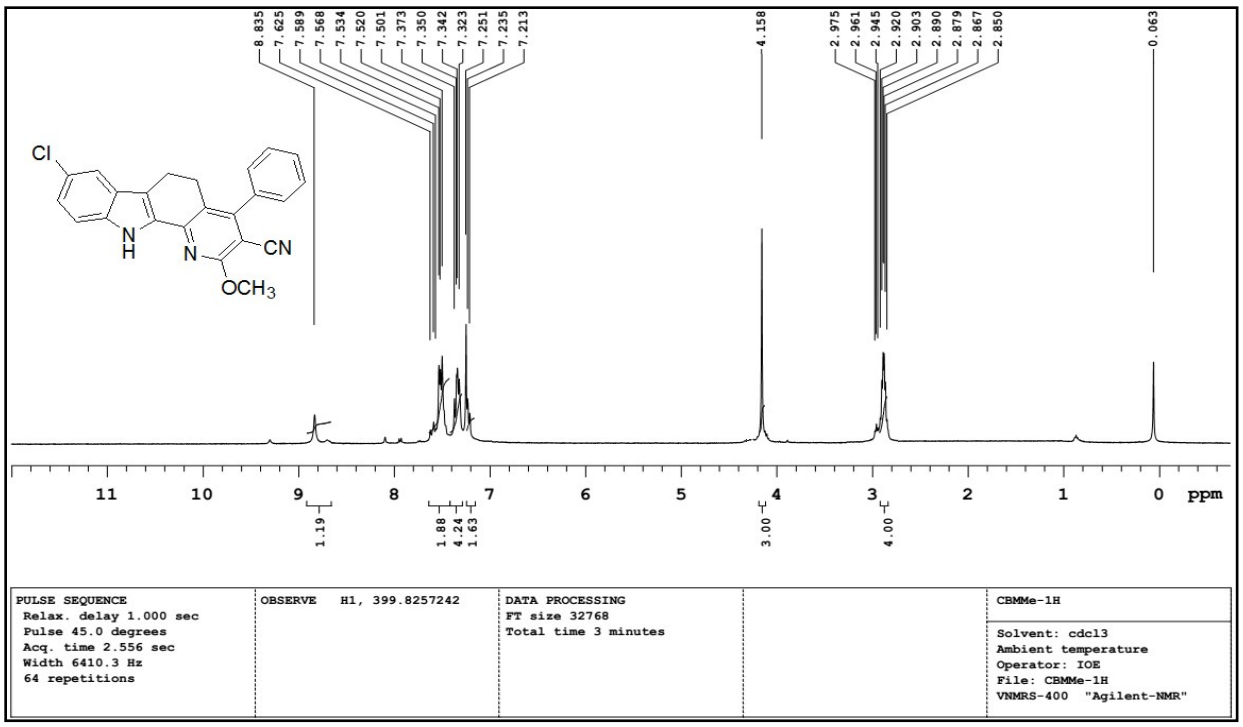

Fig. S5. ^{1}H NMR spectrum of 2-methoxy-8-chloro-4-phenyl-5,6-dihydro-11*H*-pyrido[2,3-*a*]carbazole-3-carbonitrile (5c)

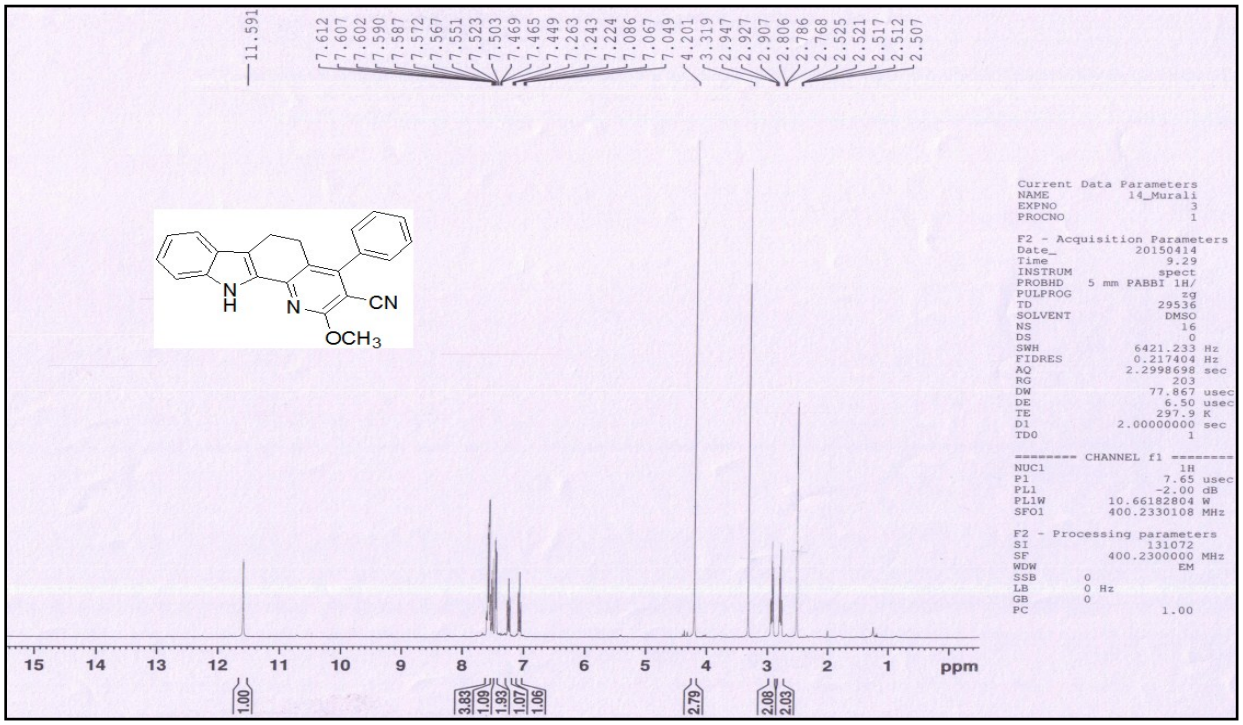

Fig. S6. ^{1}H NMR spectrum of 2-methoxy-4-phenyl-5,6-dihydro-11*H*-pyrido[2,3-*a*]carbazole-3-carbonitrile (5d)

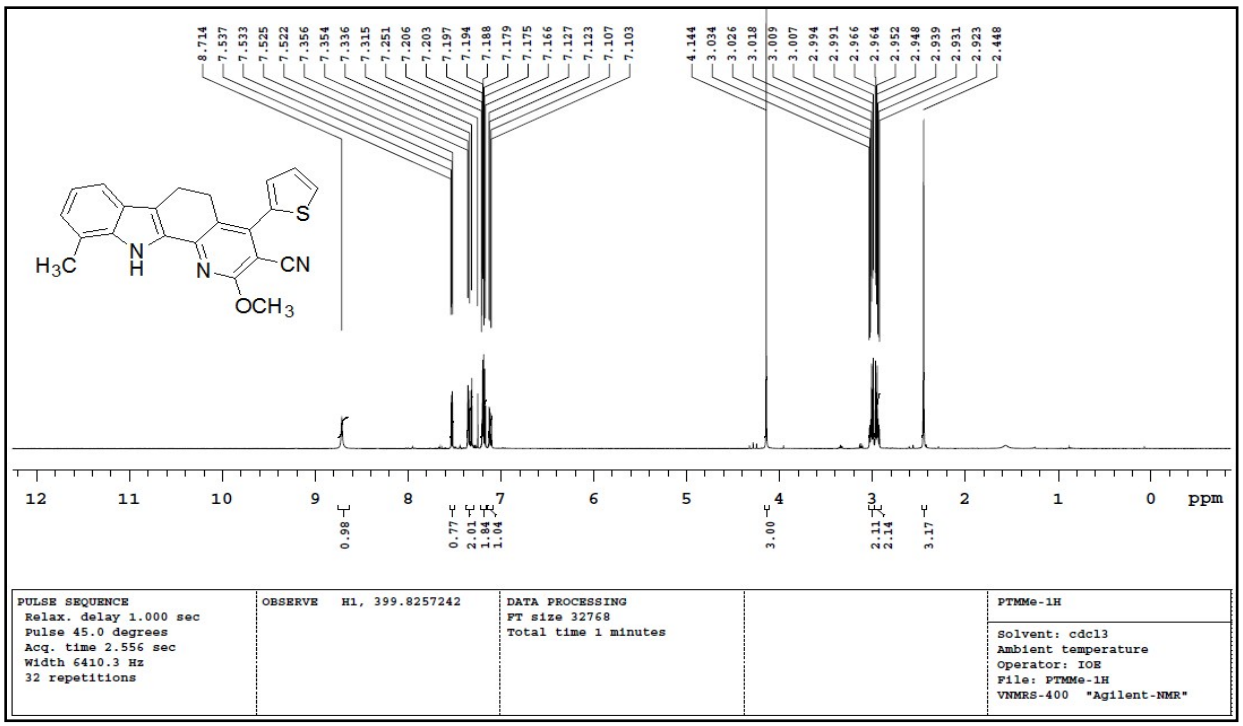

Fig. S7. [1]H NMR spectrum of 2-methoxy-10-methyl-4-(thiophen-2'-yl)-5,6-dihydro-11*H*-pyrido[2,3-*a*]carbazole-3-carbonitrile (5e)

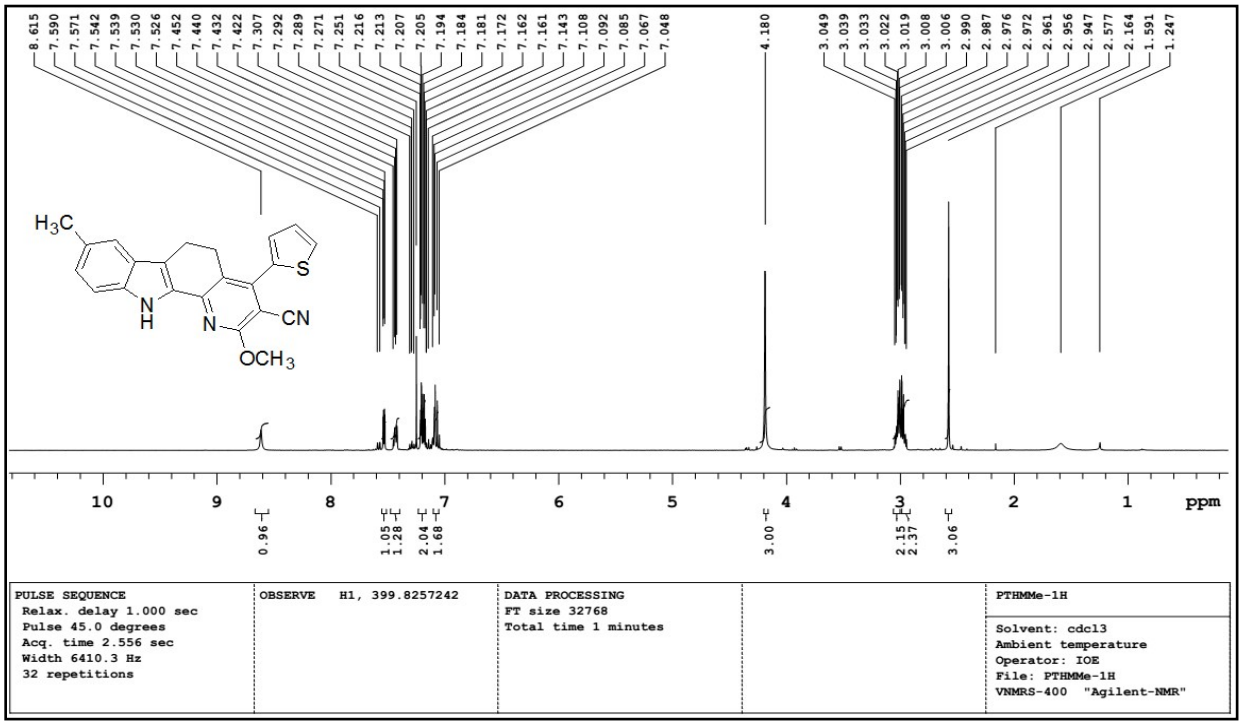

Fig. S8. [1]H NMR spectrum of 2-methoxy-8-methyl-4-(thiophen-2'-yl)-5,6-dihydro-11*H*-pyrido[2,3-*a*]carbazole-3-carbonitrile (5f)

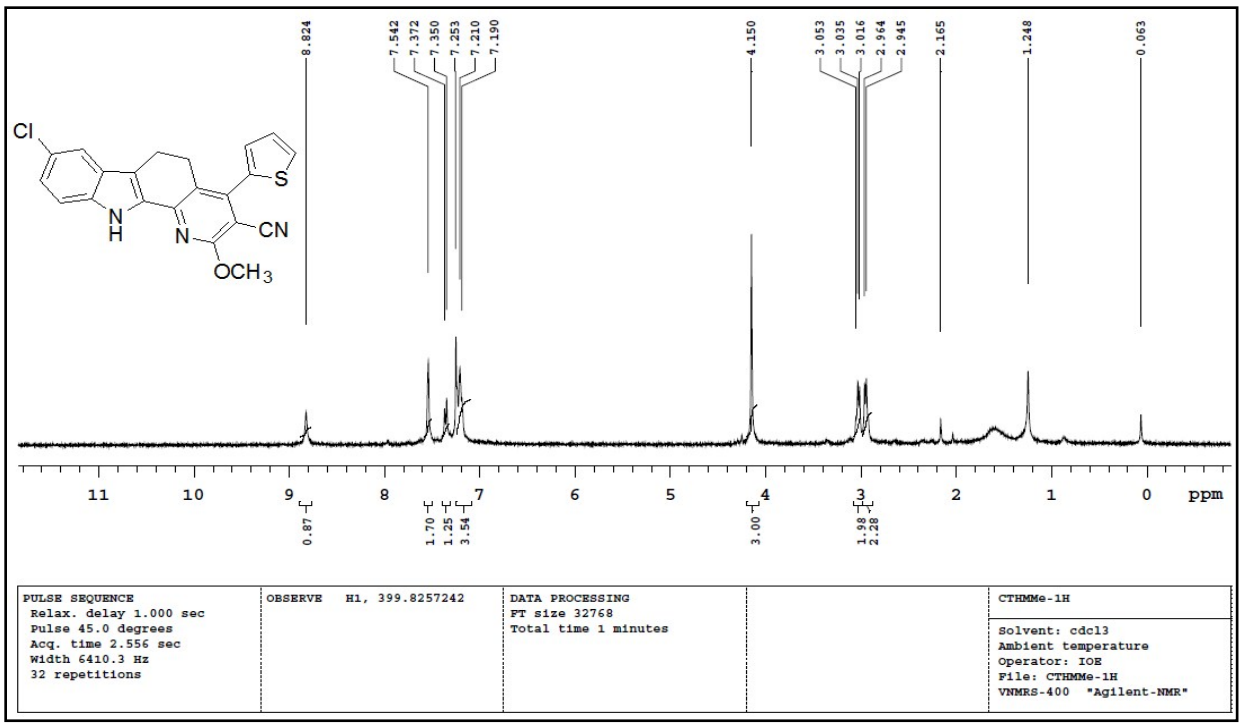

Fig. S9. [1]H NMR spectrum of 2-methoxy-8-chloro-4-(thiophen-2'-yl)-5,6-dihydro-11*H*-pyrido[2,3-*a*]carbazole-3-carbonitrile (5g)

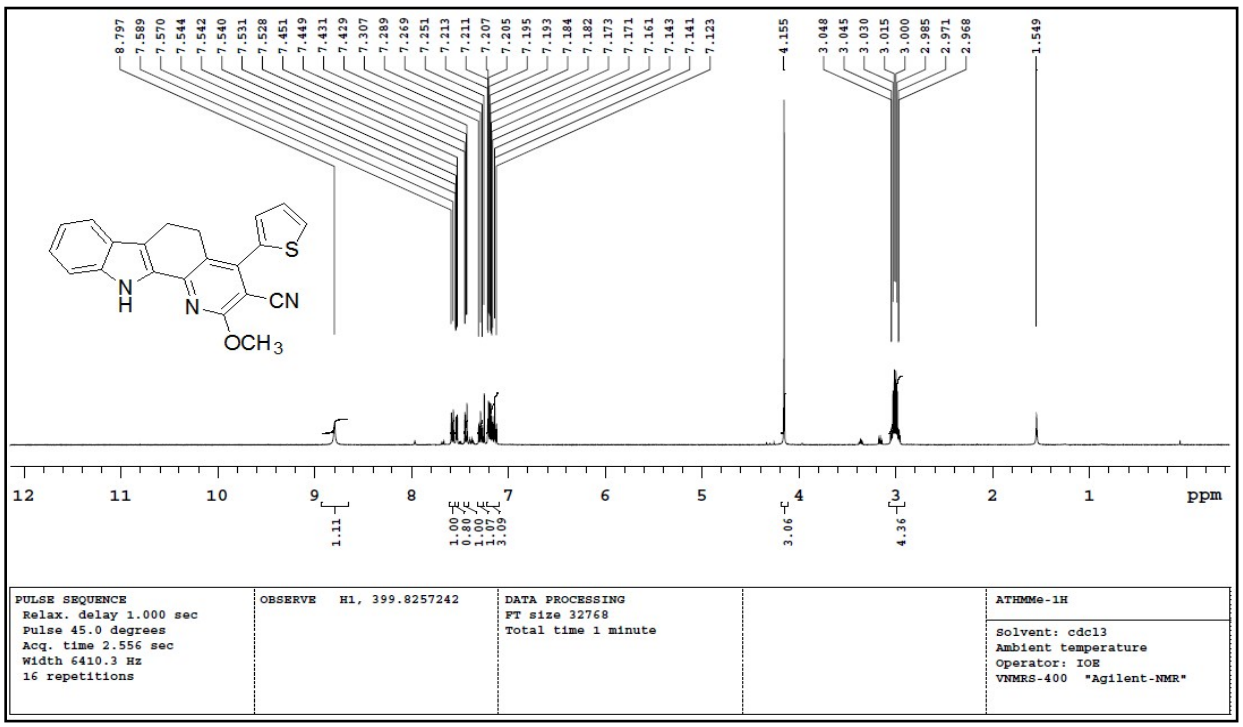

Fig. S10. [1]H NMR spectrum of 2-methoxy-4-(thiophen-2'-yl)-5,6-dihydro-11*H*-pyrido[2,3-*a*]carbazole-3-carbonitrile (5h)

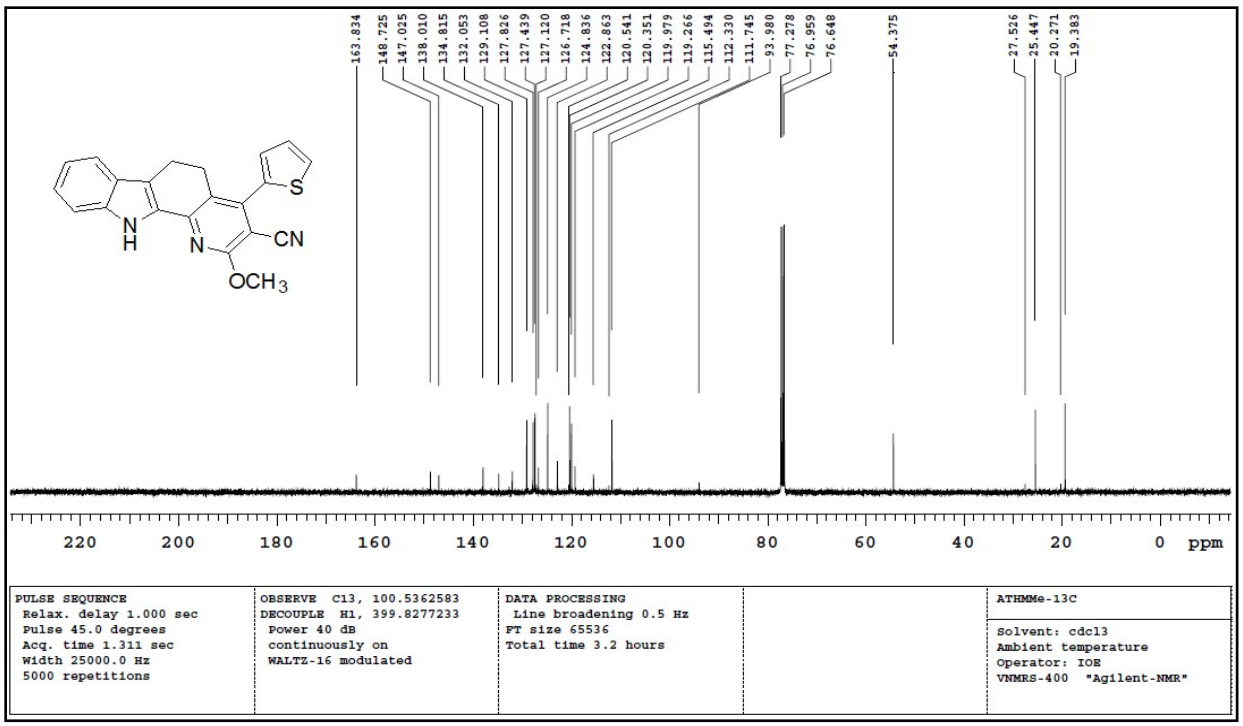

Fig. S11. ^{13}C NMR spectrum of 2-methoxy-4-(thiophen-2'-yl)-5,6-dihydro-11*H*-pyrido[2,3-*a*]carbazole-3-carbonitrile (5h)

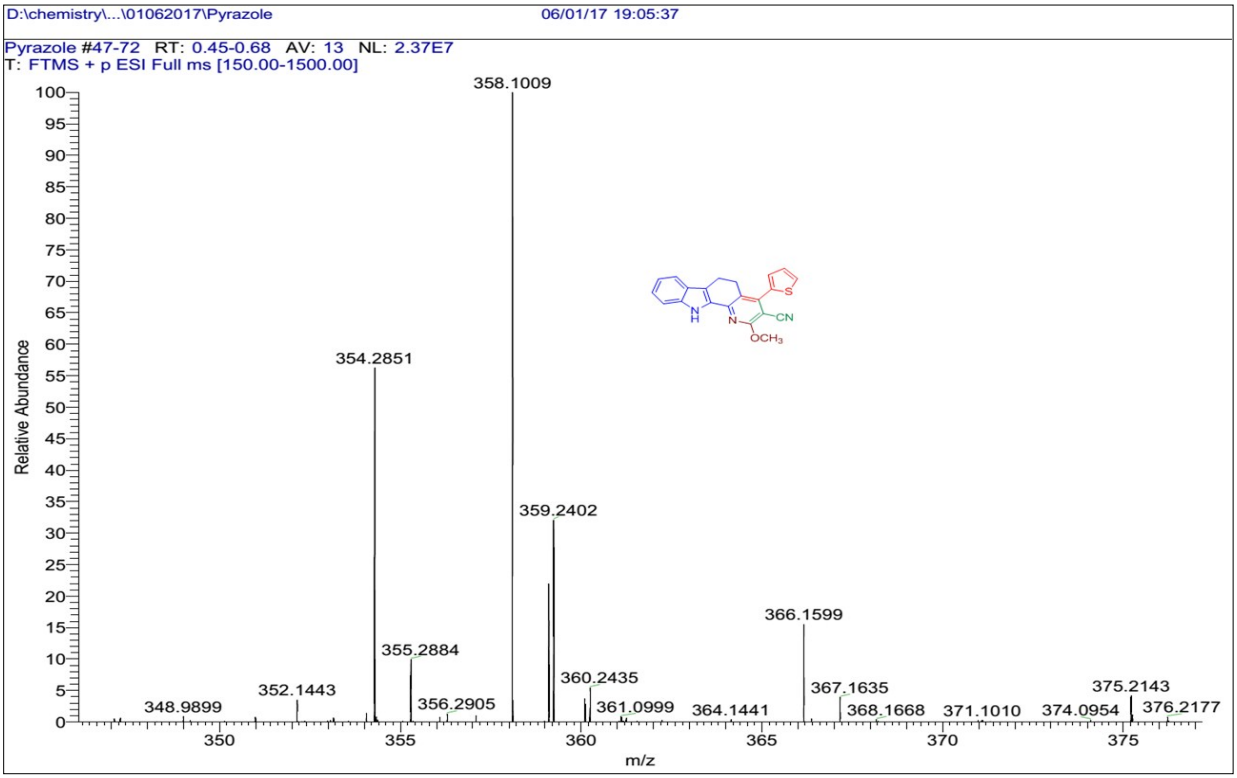

Fig. S12. HRMS spectrum of 2-methoxy-4-(thiophen-2'-yl)-5,6-dihydro-11*H*-pyrido[2,3-*a*]carbazole-3-carbonitrile (5h)

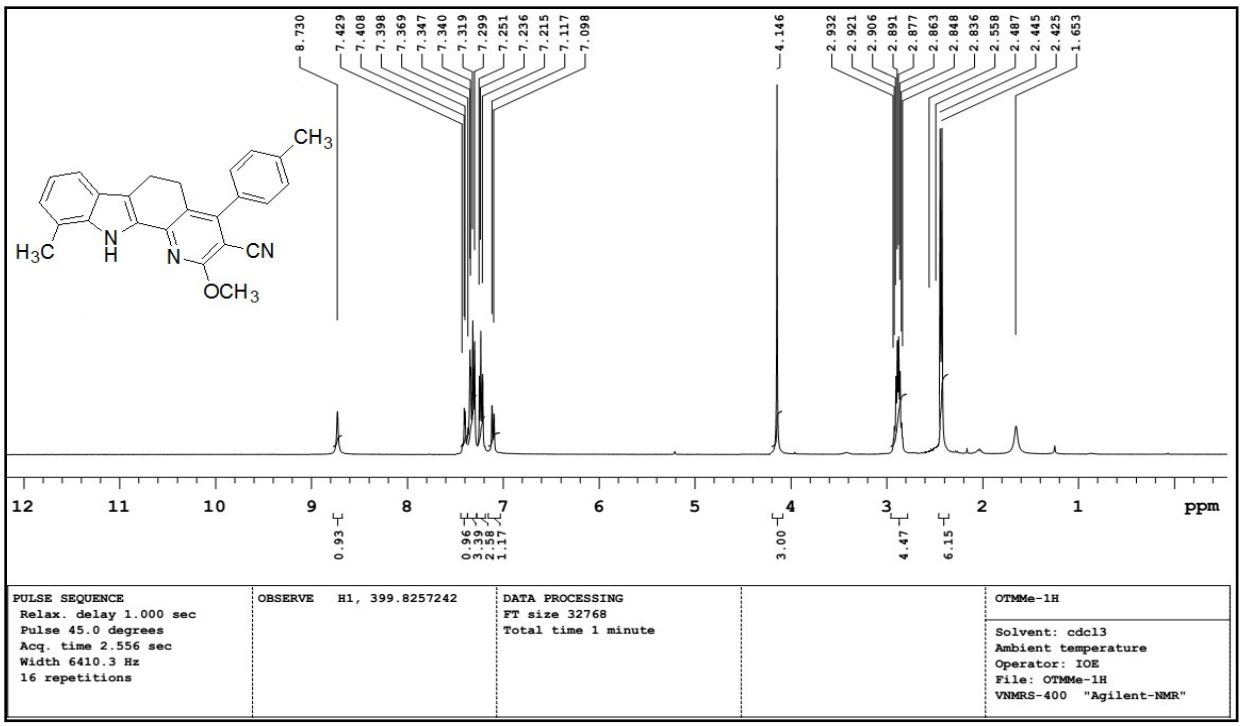

Fig. S13. ^{1}H NMR spectrum of 2-methoxy-10-methyl-4-(4'-methyl-phenyl)-5,6-dihydro-11*H*-pyrido[2,3-*a*]carbazole-3-carbonitrile (5i)

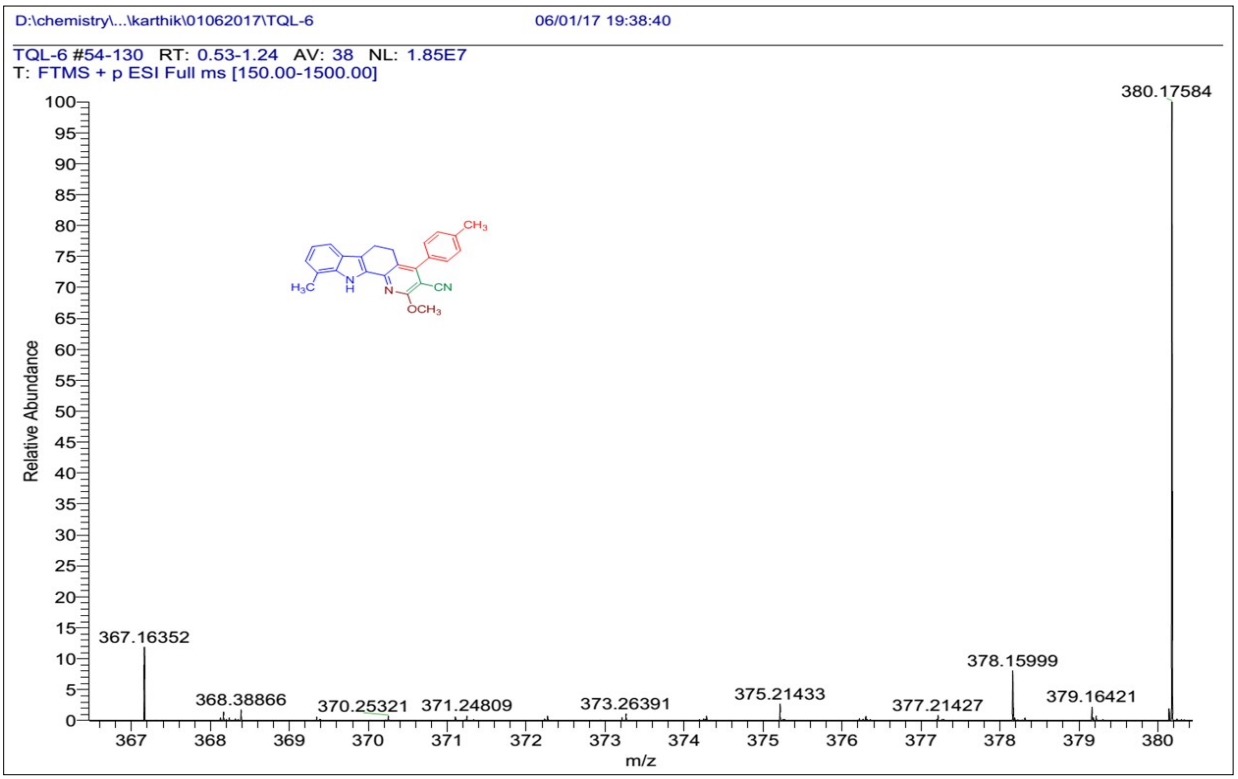

Fig. S14. HRMS spectrum of 2-methoxy-10-methyl-4-(4'-methyl-phenyl)-5,6-dihydro-11*H*-pyrido[2,3-*a*]carbazole-3-carbonitrile (5i)

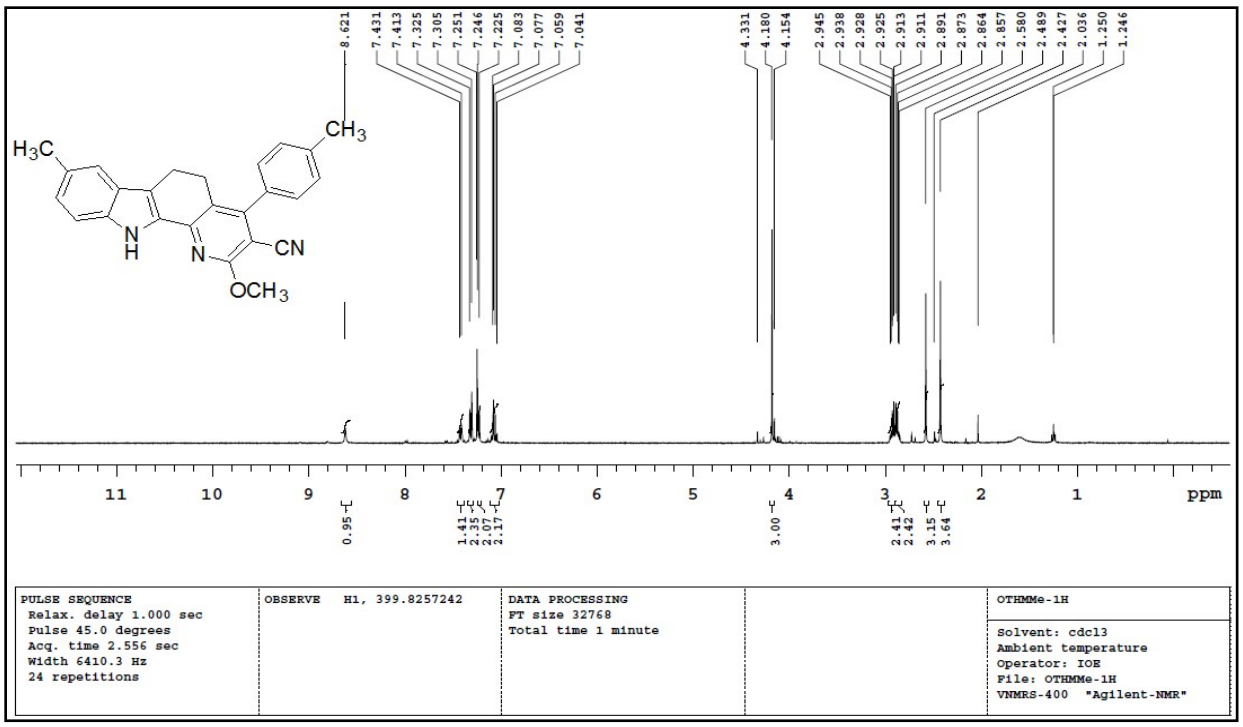

Fig. S15. ^{1}H NMR spectrum of 2-methoxy-8-methyl-4-(4'-methyl-phenyl)-5,6-dihydro-11*H*-pyrido[2,3-*a*]carbazole-3-carbonitrile (5j)

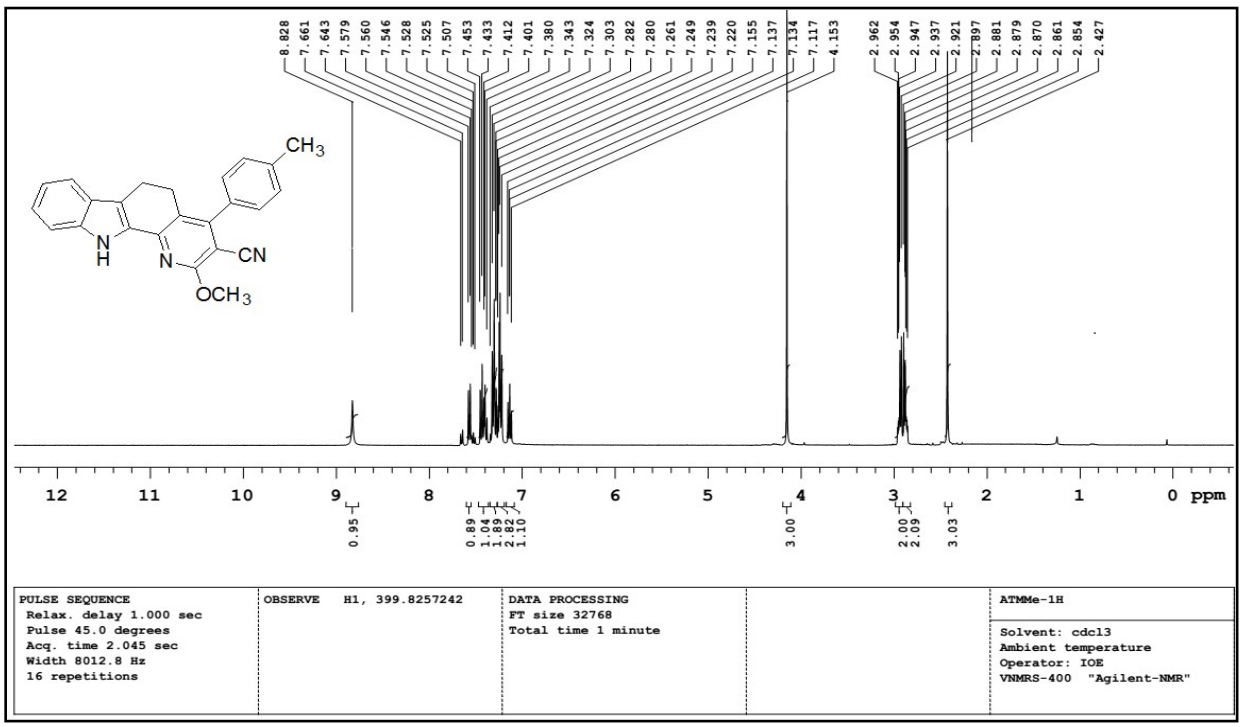

Fig. S16. ^{1}H NMR spectrum of 2-methoxy-4-(4'-methyl-phenyl)-5,6-dihydro-11*H*-pyrido[2,3-*a*]carbazole-3-carbonitrile (5k)

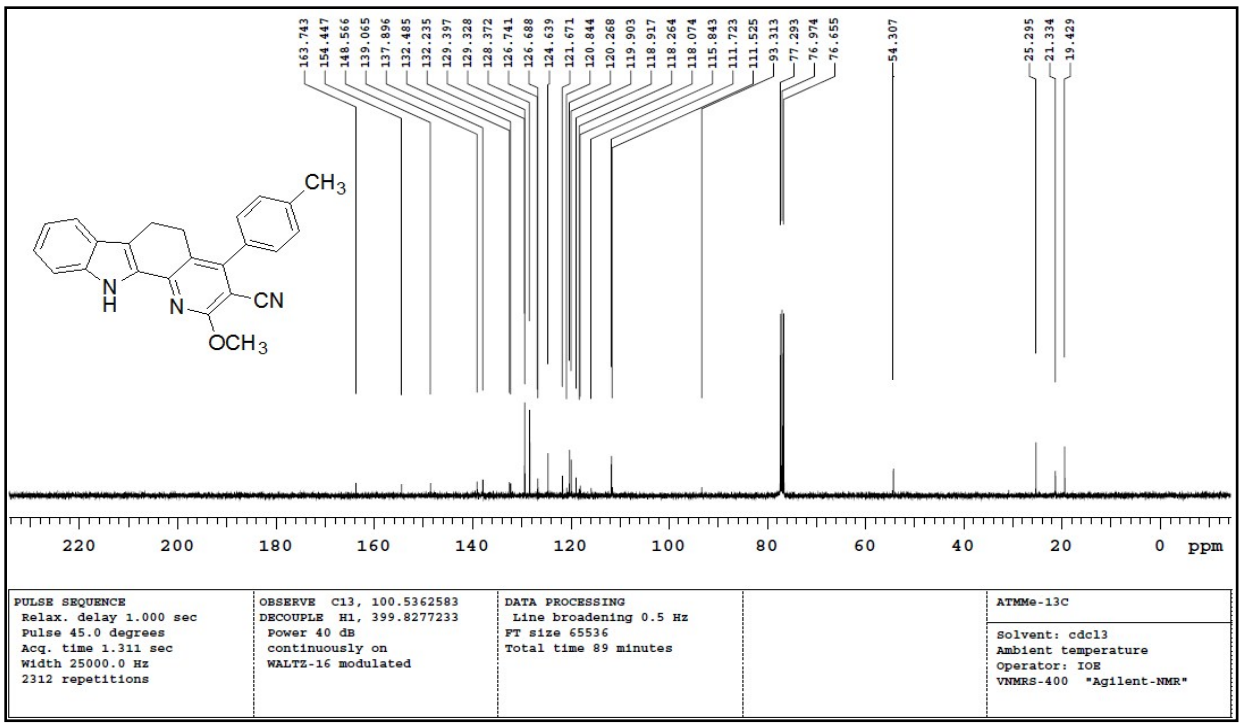

Fig. S17. ^{13}C NMR spectrum of 2-methoxy-4-(4'-methyl-phenyl)-5,6-dihydro-11*H*-pyrido[2,3-*a*]carbazole-3-carbonitrile (5k)

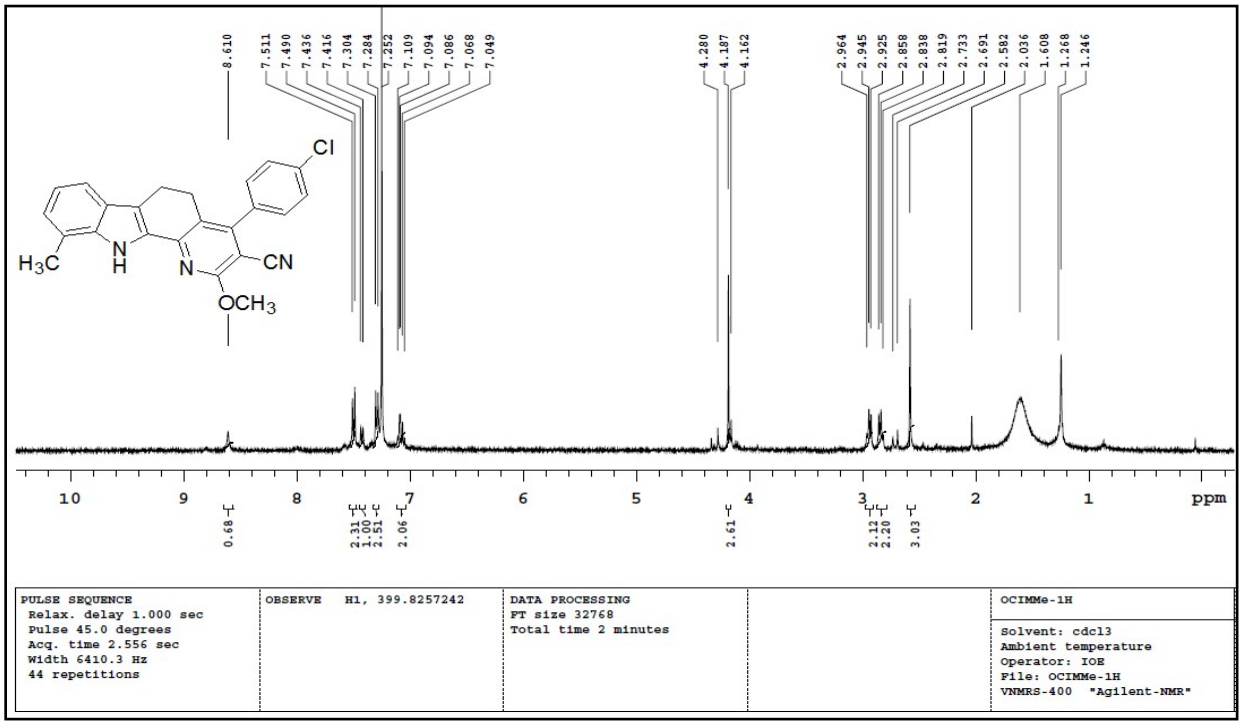

Fig. S18. ^{1}H NMR spectrum of 2-methoxy-10-methyl-4-(4'-chloro-phenyl)-5,6-dihydro-11*H*-pyrido[2,3-*a*]carbazole-3-carbonitrile (5l)

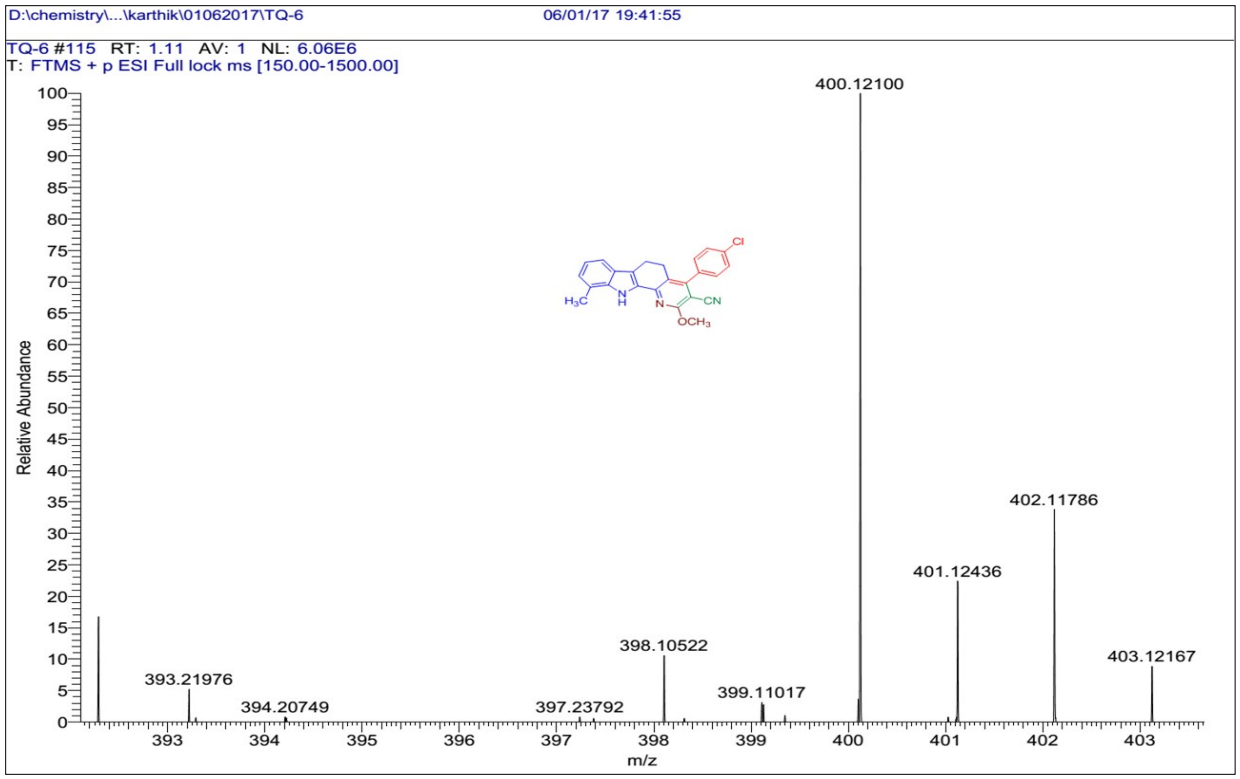

Fig. S19. HRMS spectrum of 2-methoxy-10-methyl-4-(4'-chloro-phenyl)-5,6-dihydro-11*H*-pyrido[2,3-*a*]carbazole-3-carbonitrile (5l)

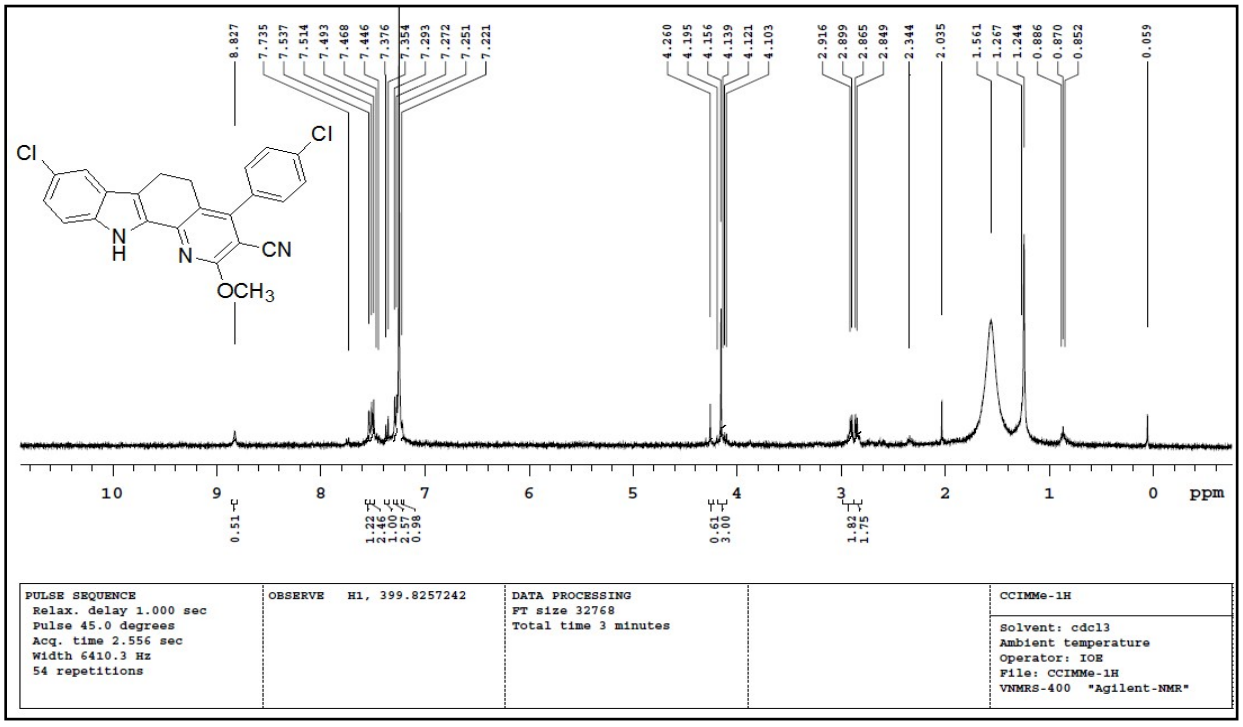

Fig. S20. ^{1}H NMR spectrum of 2-methoxy-8-chloro-4-(4'-chloro-phenyl)-5,6-dihydro-11*H*-pyrido[2,3-*a*]carbazole-3-carbonitrile (5m)

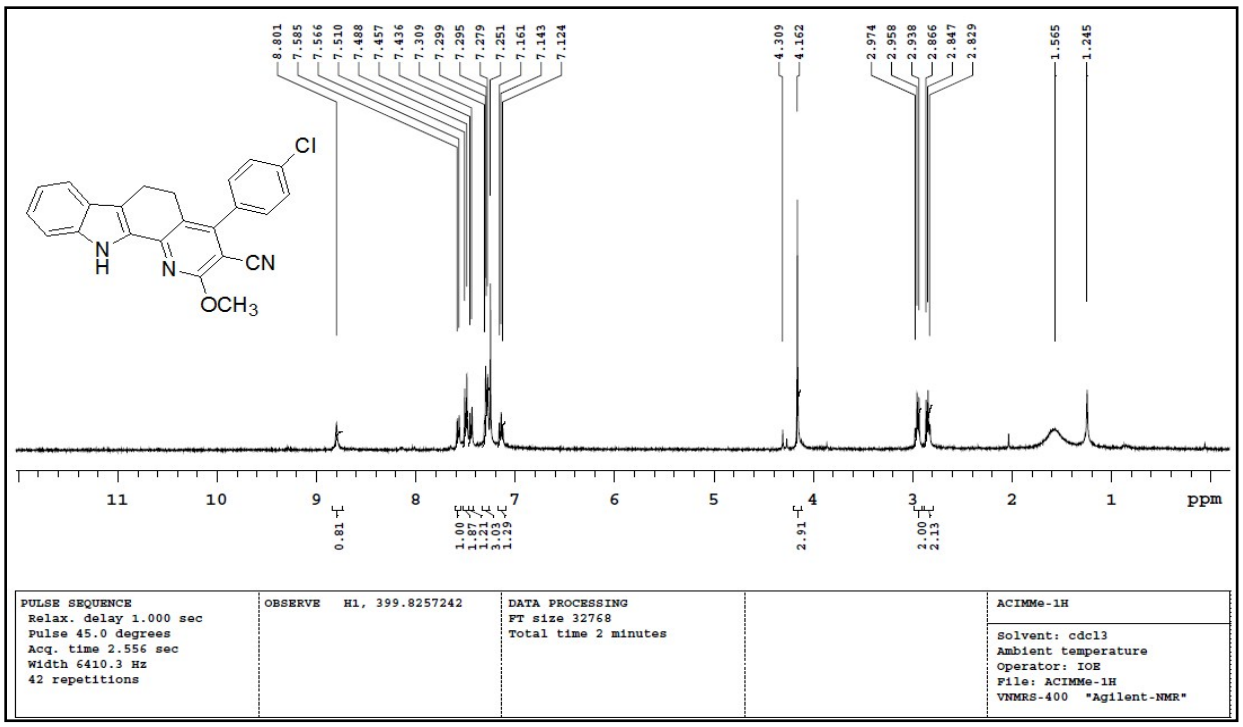

Fig. S21. ^{1}H NMR spectrum of 2-methoxy-4-(4'-chloro-phenyl)-5,6-dihydro-11*H*-pyrido[2,3-*a*]carbazole-3-carbonitrile (5n)

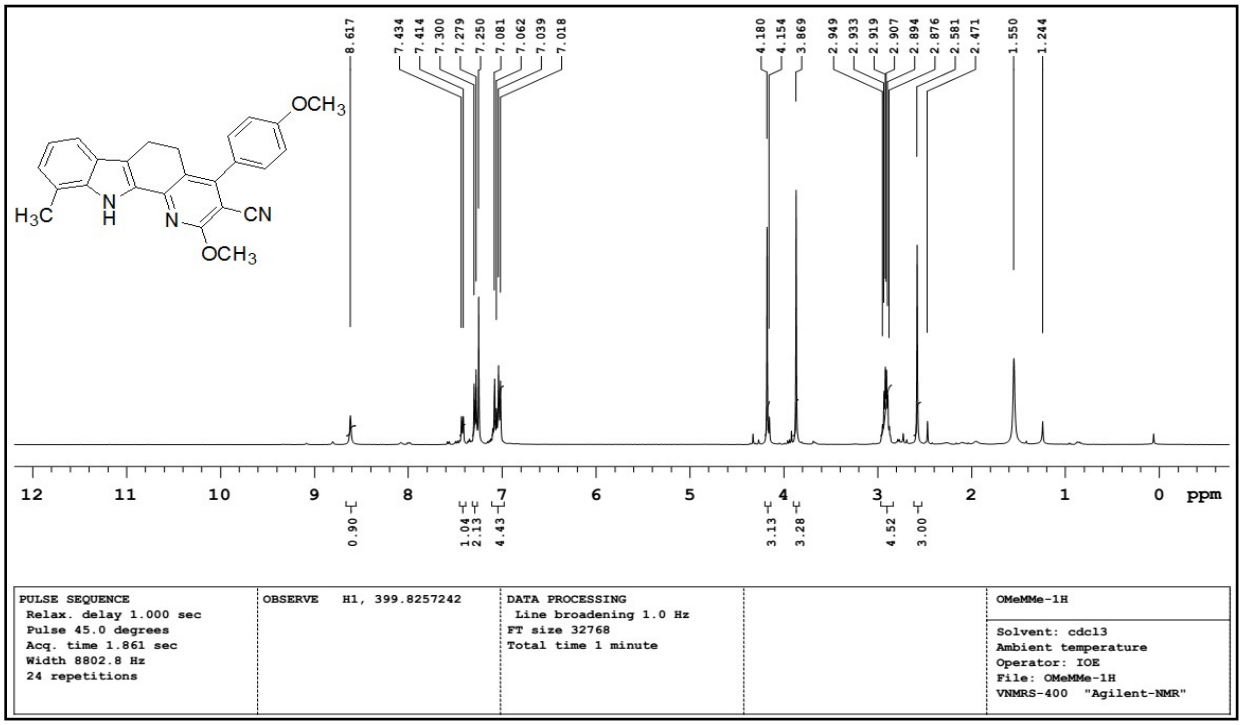

Fig. S22. ^{1}H NMR spectrum of 2-methoxy-10-methyl-4-(4'-methoxy-phenyl)-5,6-dihydro-11*H*-pyrido[2,3-*a*]carbazole-3-carbonitrile (5o)

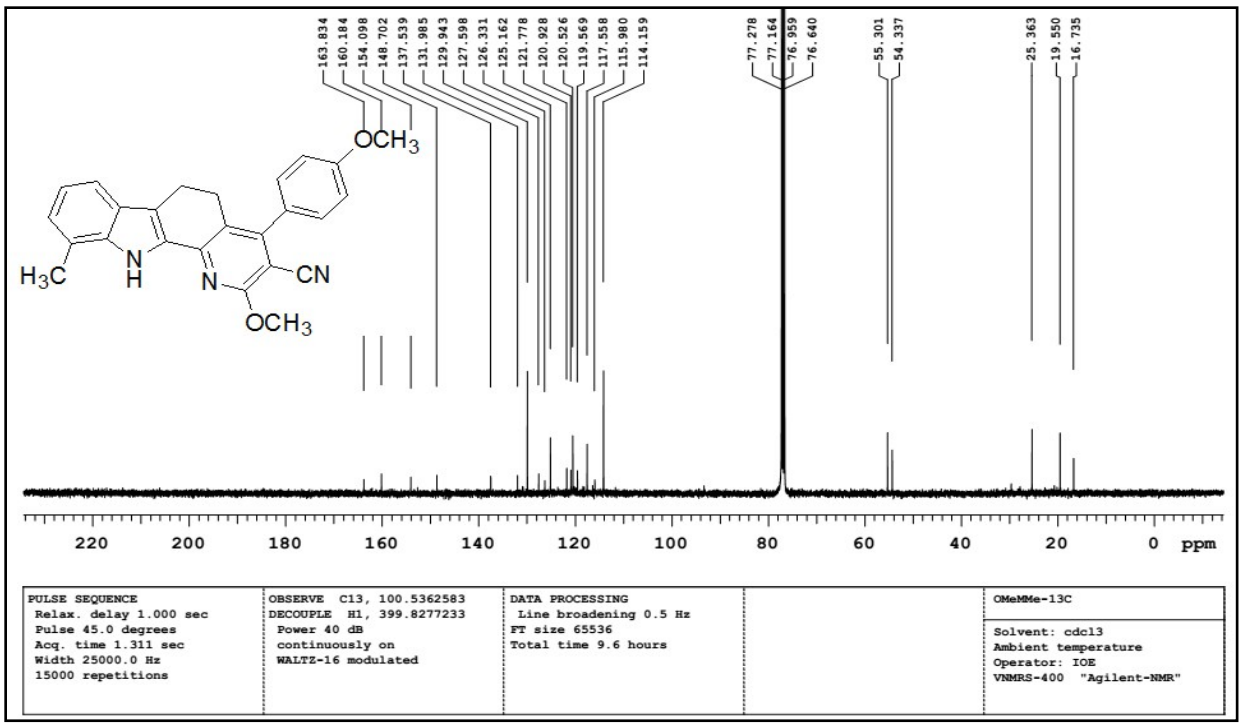

Fig. S23. ^{13}C NMR spectrum of 2-methoxy-10-methyl-4-(4'-methoxy-phenyl)-5,6-dihydro-11*H*-pyrido[2,3-*a*]carbazole-3-carbonitrile (5o)

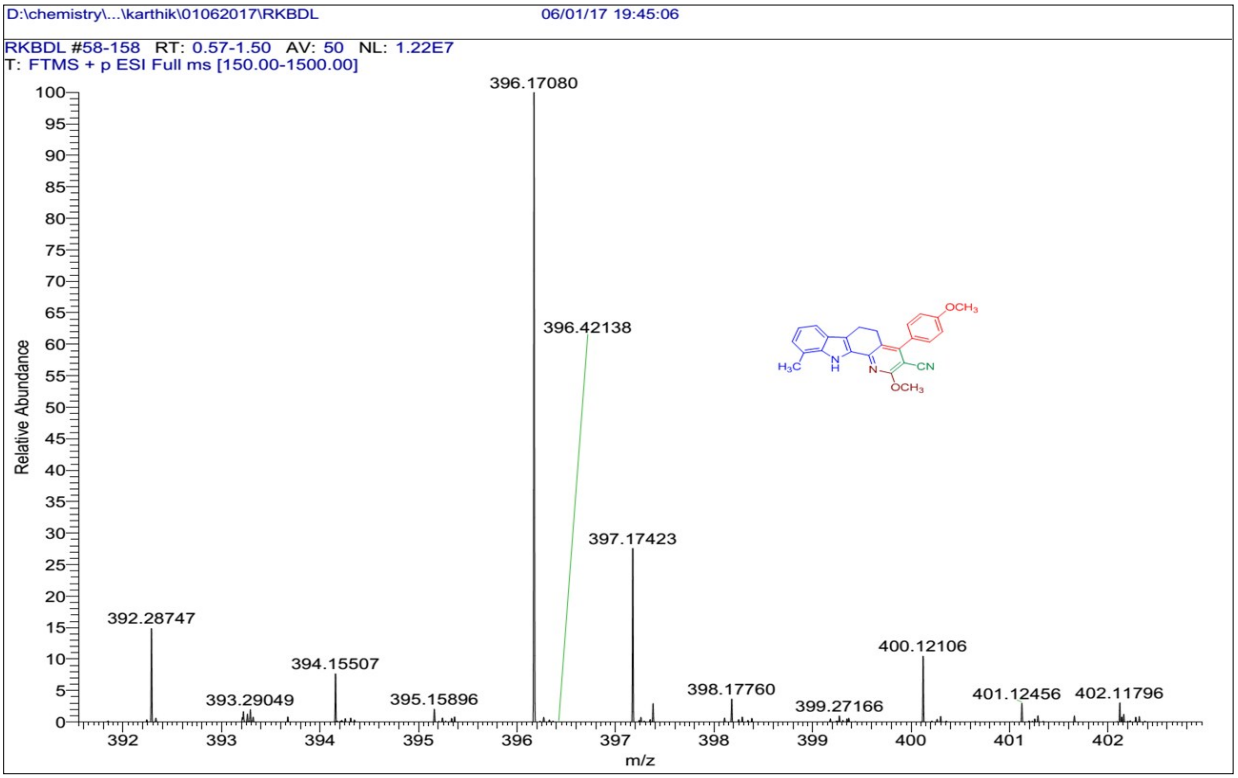

Fig. S24. HRMS spectrum of 2-methoxy-10-methyl-4-(4'-methoxy-phenyl)-5,6-dihydro-11*H*-pyrido[2,3-*a*]carbazole-3-carbonitrile (5o)

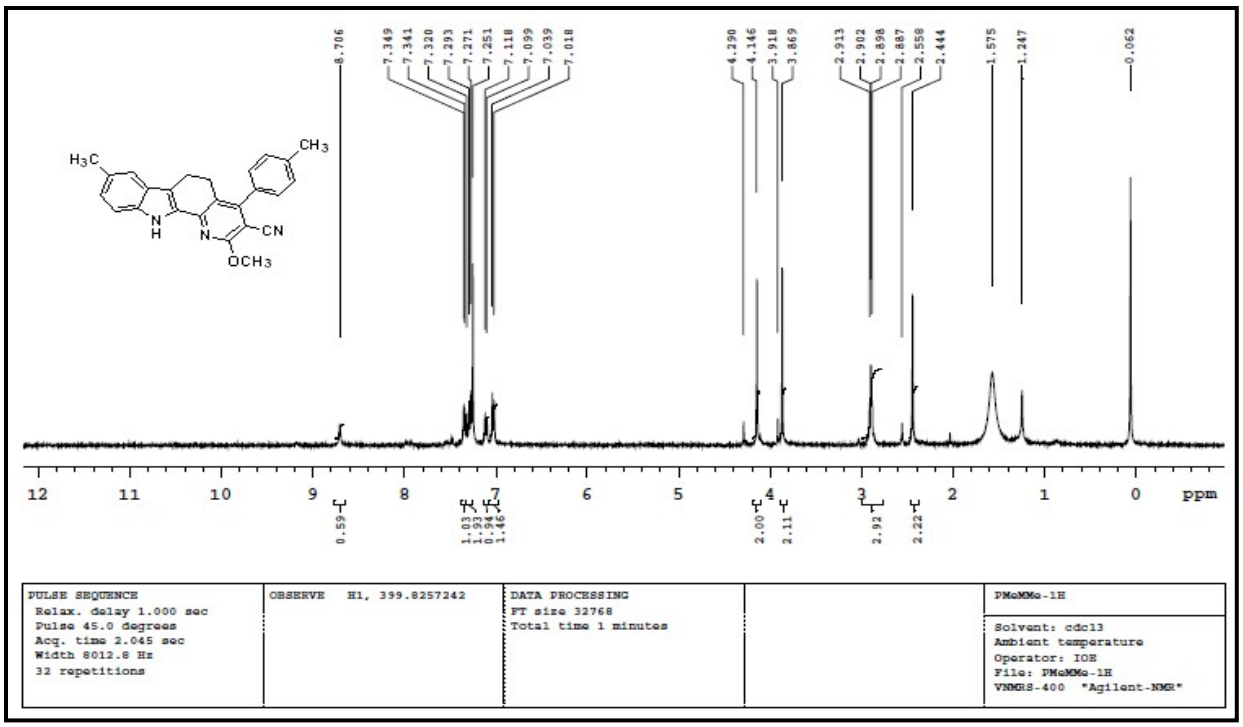

Fig. S25. ^{1}H NMR spectrum of 2-methoxy-8-methyl-4-(4'-methoxy-phenyl)-5,6-dihydro-11*H*-pyrido[2,3-*a*]carbazole-3-carbonitrile (5p)

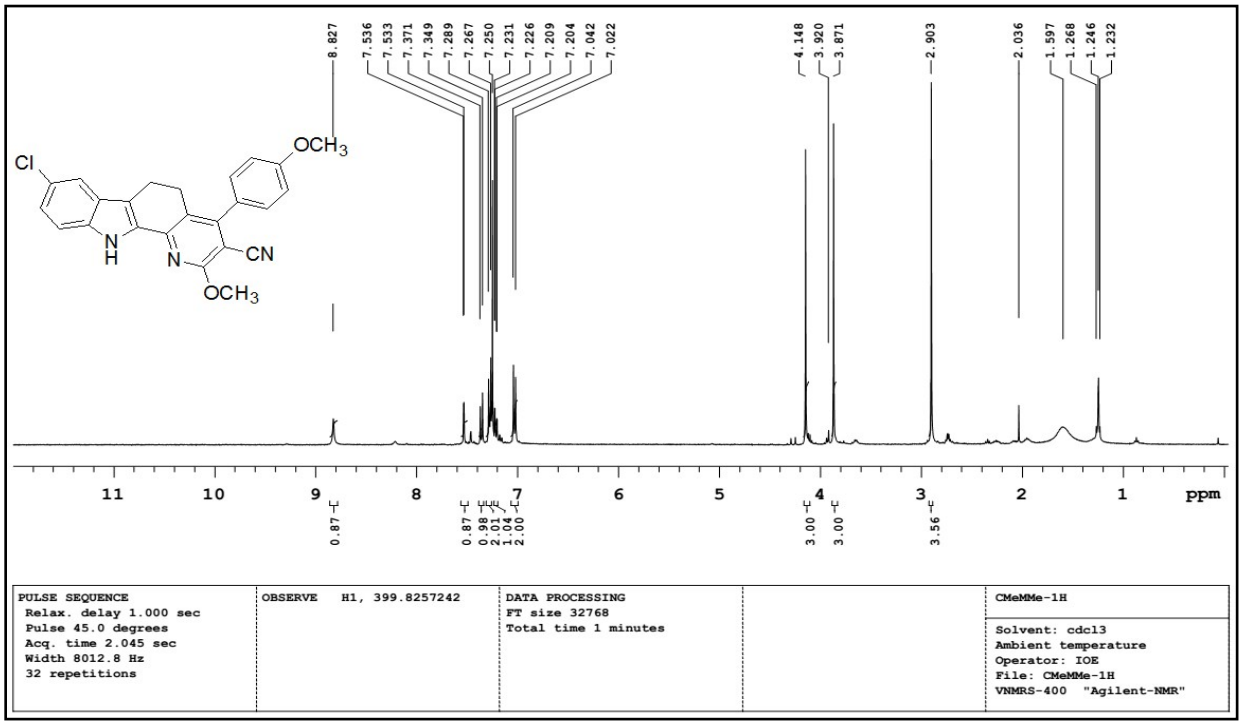

Fig. S26. ^{1}H NMR spectrum of 2-methoxy-8-chloro-4-(4'-methoxy-phenyl)-5,6-dihydro-11*H*-pyrido[2,3-*a*]carbazole-3-carbonitrile (5q)