Supporting Information

Silver(I)-Catalyzed Annulation for the Regioselective Synthesis of N-Imino-γ-Carbolinium Ylides from Hydrazones of Indole-3-Carbonyl Derivatives and Propargylic Alcohols

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1. General Information

Tetrahydrofuran was freshly distilled from Na prior to use. Unless otherwise noted, all reagents and solvents were obtained commercially and used without further purification. Propargylic alcohol and indole-3-hydrazone were prepared according to literature procedures. All reaction mixtures were stirred with a magnetic bar in flame-dried glassware.

Chromatography

Thin layer chromatography (TLC) was performed on Huanghai pre-coated glass-backed TLC plates and visualized by UV lamp (254 nm). Column chromatography on silica gel (300-400 mesh) was carried out using analytical grade dichloromethane (without further purification) and analytical grade EtOAc (without further purification). Concentration under reduced pressure was performed by rotary evaporation. Purified compounds were further addressed under high vacuum (3-5 mmHg). Yields refer to chromatographically purified compounds.

Nuclear magnetic resonance spectra

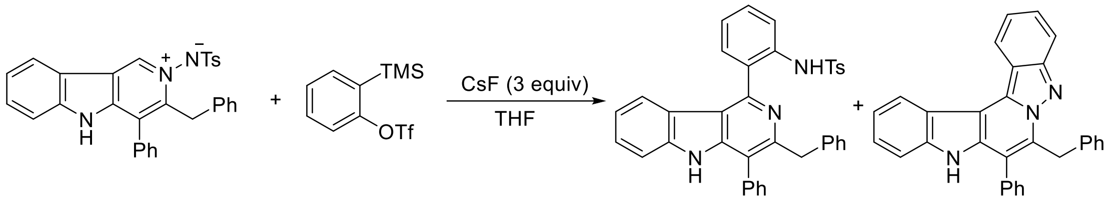
^{1}H and **^{13}C** spectra were recorded on a Bruker AV-500 spectrometer. Chemical shifts were reported in ppm. ^{1}H-NMR spectra were referenced to d6-DMSO (2.50 ppm), and ^{13}C-NMR spectra were referenced to d6-DMSO (39.5 ppm).. All ^{13}C-NMR spectra were measured with complete proton decoupling. Peak multiplicities were designated by the following abbreviations: s, singlet; d, doublet; t, triplet; m, multiplet; brs, broad singlet and J, coupling constant in Hz.

IR spectra, Mass spectroscopy

IR spectra were recorded on a Nicolet AVATER FTIR360 spectrometer as thin film. Absorptions were given in wavenumbers (cm^{-1}).

Mass spectroscopy: HRMS data were obtained via Ultra-high Resolution Hybrid Qh-Fourier Transform Mass Spectrometer(En Apex ultra 7.0 FT-MS) operated by the Department of Chemistry, Xiamen University

2. The attempt of [3+2] reaction of 3aa with aryne



3aa **5aa**, 75% yield **6aa**, not detected

The attempt of [3+2] reaction of **3aa** with aryne has been conducted, unfortunately, only N-N cleavage product **5aa** was obtained in 75% yield, no [3+2] cycloaddition product **6aa** was detected in this transformation. The synthesis procedure of **5aa** was followed: To a 10 mL round-bottom flask equipped with a stir bar was added **3aa** (0.3 mmol, 150 mg), followed by the aryne precursor 2-(Trimethylsilyl)phenyl trifluoromethanesulfonate (0.36 mmol, 107 mg) and THF (4 mL). Then CsF (0.9 mmol, 137 mg) was added. The flask was fitted with a reflux condenser and sealed with a septum. A balloon was added on top, and the mixture was stirred at 70 ^{o}C for 24 h. Upon completion as judged by TLC, the mixture was diluted with brine (20 mL), extracted with EtOAc (20 mL*3). Combined extracts were dried over Na_2SO_4, filtered, and concentrated in vacuo. The residue was purified by silica gel column chromatography eluting with PE and ethyl acetate (v/v, 5:1) to afford the product **5aa** (130 mg).

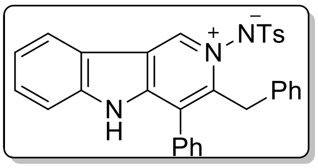
N-(2-(3-benzyl-4-phenyl-5H-pyrido[4,3-b]indol-1-yl)phenyl)-4-methylbenzenesulfonamide (**5aa**): (mp: 248-249 ^{o}C); **^{1}H NMR** (500 MHz, dmso-d6) δ 1.44 (s, 3H), 4.10 (s, 2H), 6.26 (d, 2H, *J* = 7.8 Hz), 6.68 (d, 2H, *J* = 7.8 Hz), 7.04 (t, 1H, *J* = 7.5 Hz), 7.11 (d, 2H, *J* = 7.4 Hz), 7.18 (t, 1H, *J* = 7.4 Hz), 7.24-7.34 (m, 3H), 7.38-7.46 (m, 2H), 7.49 (d, 1H, *J* = 8.1 Hz), 7.53-7.65 (m, 5H), 7.66-7.73 (m, 3H), 9.67-10.00 (brs, 1H), 11.14 (s, 1H); **^{13}C NMR** (125 MHz, dmso-d6) δ 20.5, 40.8, 112.3, 116.0, 119.0, 119.9, 120.7, 122.3, 125.7, 126.3, 126.5, 126.7, 128.0, 128.6, 129.0, 129.1, 129.7, 130.2, 130.6, 130.8, 132.6, 134.9, 135.4, 135.5, 140.5, 141.1, 142.7, 145.5, 149.2, 151.1; **IR** (film): 3120, 3056, 1610 cm^{-1}; **HRMS** (ESI) *m/z* Calculated for C37H29N3NaO2S [M+Na]$^{+}$ 602.1873, found: 602.1877.

3. Procedure for the synthesis of 3aa-3ak, 3ba-ha, and 4ja-4la. ^{1}H, ^{13}C-NMR, IR, MP and MS Data of 3aa-3ak, 3ba-ha, and 4ja-4la

General procedure for the synthesis of *N*-Imino-γ-Carbolinium Ylides.

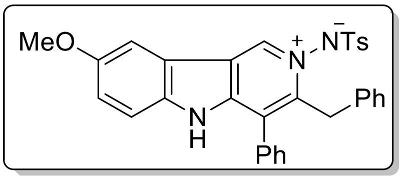
A 15 mL sealed tube was charged with a stir bar, propargylic alcohol (0.45 mmol), indole-3-hydrazone (0.3 mmol), AgOTf (0.06 mmol, 15 mg), and freshly distilled THF (3 mL). The tube was then quickly sealed with a screw cap then heated while stirring in a oil bath at 100 ℃ for 12 hrs and analyzed by TLC. The tube was cooled to ambient temperature, then again concentrated under reduced pressure and purified by silica gel chromatography eluting with dichloromethane and ethyl acetate (v/v, 5:1) to give the corresponding products.

(3-benzyl-4-phenyl-5H-pyrido[4,3-b]indol-2-ium-2-yl)(tosyl)amide (**3aa)**



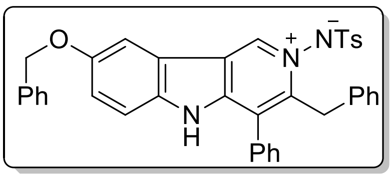
The general procedure was followed to afford the product as brown solid in 78% yield (mp: 247-248 °C); **^{1}H NMR** (500 MHz, dmso-d6) δ 2.37 (s, 3H), 3.67 (s, 2H), 6.62-6.70 (m, 2H), 7.04-7.12 (m, 2H), 7.15-7.23 (m, 2H), 7.26-7.34 (m, 4H), 7.40-7.45 (m, 1H), 7.47-7.56 (m, 3H), 7.57-7.67 (m, 2H), 7.96 (s, 1H), 8.38 (d, 1H, *J* = 7.8 Hz), 9.60 (s, 1H), 12.02 (s, 1H); **^{13}C NMR** (125 MHz, dmso-d6) δ 21.4, 34.1, 113.3, 118.8, 120.9, 122.3, 122.5, 123.1, 126.5, 128.3, 128.5, 129.2, 129.5, 129.6, 129.7, 129.9, 133.0, 138.1, 141.0, 141.4, 141.5, 142.1, 143.6, 149.2, 162.8; **IR** (film): 3055, 1645, 1600 cm^{-1}; **HRMS** (ESI) *m/z* Calculated for $C_{31}H_{25}N_3NaO_2S$ $[M+Na]^+$ 526.1565, found: 526.1560.

(3-benzyl-8-methoxy-4-phenyl-5H-pyrido[4,3-b]indol-2-ium-2-yl)(tosyl)amide (**3ab**)



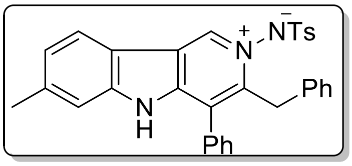
The general procedure was followed to afford the product as gray solid in 82% yield (mp: 285-286 °C); **^{1}H NMR** (500 MHz, dmso-d6) δ 2.37 (s, 3H), 3.61 (s, 2H), 3.89 (s, 3H), 6.60-6.69 (m, 2H), 7.04-7.11 (m, 3H), 7.14-7.20 (m, 2H), 7.20-7.25 (m, 1H), 7.25-7.35 (m, 4H), 7.48-7.55 (m, 4H), 8.04 (d, 1H, *J* = 2.36 Hz), 9.63 (s, 1H), 11.87 (s, 1H); **^{13}C NMR** (125 MHz, dmso-d6) δ 21.4, 34.0, 56.2, 104.6, 114.1, 118.7, 121.6, 122.9, 126.4, 126.5, 128.2, 128.5, 129.5, 129.7, 129.8, 133.1, 136.6, 138.2, 140.9, 141.4, 141.8, 143.6, 148.5, 155.7; **IR** (film): 3103, 1660, 1622 cm^{-1}; **HRMS** (ESI) *m/z* Calculated for $C_{32}H_{27}N_3NaO_3S$ $[M+Na]^+$ 556.1671, found: 556.1673.

(3-benzyl-8-(benzyloxy)-4-phenyl-5H-pyrido[4,3-b]indol-2-ium-2-yl)(tosyl)amide (**3ac**)



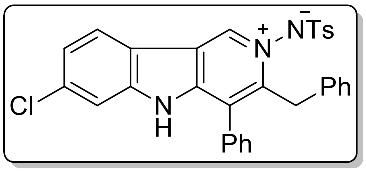
The general procedure was followed to afford the product as gray solid in 78% yield (mp: 200-201 °C); **^{1}H NMR** (500 MHz, dmso-d6) δ 2.38 (s, 3H), 3.60 (s, 2H), 5.24 (s, 2H), 6.61-6.70 (m, 2H), 7.05-7.12 (m, 3H), 7.14-7.20 (m, 2H), 7.26-7.33 (m, 5H), 7.33-7.39 (m, 1H), 7.40-7.46 (m, 2H), 7.48-7.56 (m, 6H), 8.18 (d, 1H, *J* = 2.2 Hz), 9.62 (s, 1H), 11.89 (s, 1H); **^{13}C NMR** (125 MHz, dmso-d6) δ 21.4, 34.0, 70.5, 106.1, 114.2, 118.8, 119.4, 121.6, 123.0, 126.5, 128.2, 128.3, 128.4, 128.5, 128.9, 129.5, 129.6, 129.7, 129.8, 133.1, 136.8, 137.5, 138.2, 141.0, 141.3, 141.8, 143.8, 148.6, 154.6; **IR** (film): 3060, 1625 cm^{-1}; **HRMS** (ESI) *m/z* Calculated for $C_{38}H_{31}N_3NaO_3S$ $[M+Na]^+$ 632.1984, found: 632.1979.

(3-benzyl-7-methyl-4-phenyl-5H-pyrido[4,3-b]indol-2-ium-2-yl)(tosyl)amide (**3ad**)



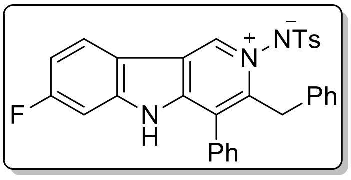
The general procedure was followed to afford the product as white solid in 83% yield (mp: 189-190 ^oC); ^{1}**H NMR** (500 MHz, dmso-d6) δ 2.37 (s, 3H), 2.50 (s, 3H), 3.67 (s, 2H), 6.63-6.69 (m, 2H), 7.05-7.11 (m, 3H), 7.14-7.20 (m, 2H), 7.23-7.29 (m, 3H), 7.29-7.34 (m, 2H), 7.38 (s, 1H), 7.48-7.56 (m, 3H), 8.23 (d, 1H, *J* = 8.2 Hz), 9.48 (s, 1H), 11.90 (s, 1H); ^{13}**C NMR** (125 MHz, dmso-d6) δ 21.4, 22.3, 34.0, 113.0, 118.5, 118.8, 121.9, 122.9, 124.0, 126.5, 128.3, 128.5, 129.5, 129.7, 129.9, 133.1, 138.2, 139.3, 140.8, 140.9, 141.4, 142.6, 143.6, 148.8; **IR** (film): 3100, 1611, 1580 cm^{-1}; **HRMS** (ESI) *m/z* Calculated for $C_{32}H_{27}N_3NaO_2S$ $[M+Na]^+$ 540.1722, found: 540.1725.

(3-benzyl-7-chloro-4-phenyl-5H-pyrido[4,3-b]indol-2-ium-2-yl)(tosyl)amide (**3ae**)



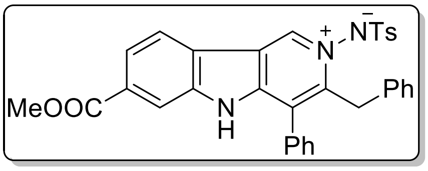
The general procedure was followed to afford the product as white solid in 81% yield (mp: 271-272 ^oC); ^{1}**H NMR** (500 MHz, dmso-d6) δ 2.37 (s, 3H), 3.65 (s, 2H), 6.59-6.71 (m, 2H), 7.04-7.13 (m, 3H), 7.16-7.23 (m, 2H), 7.24-7.36 (m, 4H), 7.43-7.49 (m, 1H), 7.50-7.56 (m, 3H), 7.56-7.61 (m, 1H), 8.45 (d, 1H, *J* = 8.4 Hz), 9.68 (s 1H), 12.09 (s, 1H); ^{13}**C NMR** (125 MHz, dmso-d6) δ 21.4, 34.1, 112.9, 118.3, 122.8, 123.3, 124.0, 126.4, 126.5, 128.2, 128.5, 129.6, 129.7, 129.8, 132.8, 133.5, 137.9, 141.0, 141.3, 142.0, 142.8, 144.1, 149.7; **IR** (film): 3063, 1655, 1600 cm^{-1}; **HRMS** (ESI) *m/z* Calculated for $C_{31}H_{24}ClN_3NaO_2S$ $[M+Na]^+$ 560.1175, found: 560.1177.

(3-benzyl-7-fluoro-4-phenyl-5H-pyrido[4,3-b]indol-2-ium-2-yl)(tosyl)amide (**3af**)



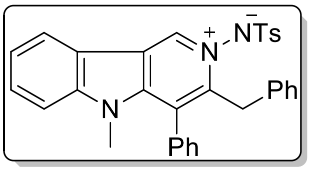
The general procedure was followed to afford the product as white solid in 90% yield (mp: 284-285 ^oC); ^{1}**H NMR** (500 MHz, dmso-d6) δ 2.37 (s, 3H), 3.65 (s, 2H), 6.61-6.71 (m, 2H), 7.05-7.12 (m, 3H), 7.14-7.22 (m, 2H), 7.25-7.35 (m, 6H), 7.46-7.58 (m, 3H), 8.39-8.53 (m, 1H), 9.64 (s 1H), 12.09 (s, 1H); ^{13}**C NMR** (125 MHz, dmso-d6) δ 21.4, 34.0, 99.8 ($^2J_{C-F}$ = 26 Hz), 110.7, 110.9, 117.6, 118.5, 123.1, 124.3, 124.4, 126.5, 128.3, 128.5, 129.6, 129.7, 129.8, 129.9, 138.0, 141.0, 141.4, 141.5, 143.1, 143.2, 144.3, 149.2, 162.9 ($^1J_{C-F}$ = 248 Hz); **IR** (film): 3060, 1610 cm^{-1}; **HRMS** (ESI) *m/z* Calculated for $C_{31}H_{24}FN_3NaO_2S$ $[M+Na]^+$ 544.1471, found: 544.1468.

(3-benzyl-7-(methoxycarbonyl)-4-phenyl-5H-pyrido[4,3-b]indol-2-ium-2-yl)(tosyl)amide (**3ag)**



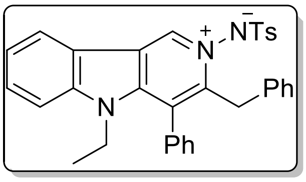
The general procedure was followed to afford the product as white soild in 73% yield (mp: 252-253 ^oC); **^{1}H NMR** (500 MHz, dmso-d6) δ 2.37 (s, 3H), 3.67 (s, 2H), 3.91 (s, 3H), 6.58-6.77 (m, 2H), 7.00-7.14 (m, 3H), 7.18-7.43 (m, 6H), 7.46-7.67 (m, 3H), 7.85-8.09 (m, 1H), 8.20 (s, 1H), 8.54 (d, 1H, *J* = 8.2 Hz), 9.74 (s, 1H), 12.22 (s, 1H); **^{13}C NMR** (125 MHz, dmso-d6) δ 21.4, 34.1, 52.9, 114.4, 118.1, 122.6, 123.5, 124.7, 126.5, 126.6, 128.3, 128.5, 129.7, 129.8, 132.7, 137.9, 141.0, 141.3, 141.7, 142.8, 144.7, 150.2, 166.6; **IR** (film): 3030, 1600 cm^{-1}; **HRMS** (ESI) *m/z* Calculated for $C_{33}H_{27}N_3NaO_4S$ $[M+Na]^+$ 584.1620, found: 584.1622.

(3-benzyl-5-methyl-4-phenyl-5H-pyrido[4,3-b]indol-2-ium-2-yl)(tosyl)amide (**3ah**)



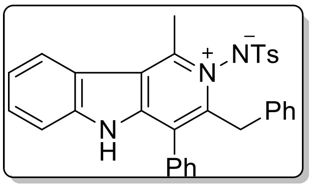
The general procedure was followed to afford the product as white solid in 82% yield (mp: 246-247 ^oC); **^{1}H NMR** (500 MHz, dmso-d6) δ 2.37 (s, 3H), 3.16 (s, 3H), 3.57 (s, 2H), 6.57-6.67 (m, 2H), 7.05-7.11 (m, 3H), 7.14-7.20 (m, 2H), 7.26-7.32 (m, 4H), 7.42-7.54 (m, 4H), 7.65-7.75 (m, 2H), 8.45 (d, 1H, *J* = 8.0 Hz), 9.65 (s, 1H); **^{13}C NMR** (125 MHz, dmso-d6) δ 14.5, 21.3, 34.2, 111.5, 119.1, 120.2, 122.1, 122.9, 126.4, 126.5, 128.2, 128.5, 128.9, 129.4, 129.7, 130.8, 133.4, 138.1, 140.9, 141.3, 142.4, 143.5, 150.1, 162.7; **IR** (film): 3130, 1618 cm^{-1}; **HRMS** (ESI) *m/z* Calculated for $C_{32}H_{27}N_3NaO_2S$ $[M+Na]^+$ 540.1722, found: 540.1725.

(3-benzyl-5-ethyl-4-phenyl-5H-pyrido[4,3-b]indol-2-ium-2-yl)(tosyl)amide (**3ai**)



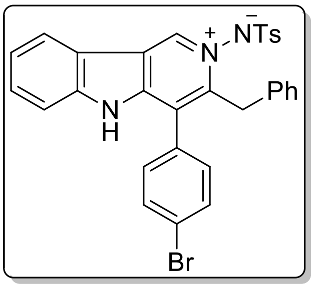
The general procedure was followed to afford the product as gray solid in 83% yield (mp: 223-224 ^oC); **^{1}H NMR** (500 MHz, dmso-d6) δ 0.94 (t, 3H, *J* = 7.3 Hz), 2.3 (s, 3H), 3.55 (s, 2H), 3.67 (q, 2H, *J* = 7.3 Hz), 6.58-6.69 (m, 2H), 7.00-7.13 (m, 3H), 7.15-7.24 (m, 2H), 7.24-7.36 (m, 4H), 7.41-7.57 (m, 4H), 7.64-7.77 (m, 2H), 8.45 (d, 1H, *J* = 7.8 Hz), 9.65 (s, 1H); **^{13}C NMR** (125 MHz, dmso-d6) δ 14.4, 21.4, 34.3, 39.2, 111.6, 119.5, 12.5, 122.2, 122.8, 123.1, 126.5, 128.2, 128.5, 129.1, 129.7, 129.9, 130.1, 133.4, 138.0, 140.9, 141.1, 141.7, 142.3, 150.1, 162.7; **IR** (film): 3130, 1620 cm^{-1}; **HRMS** (ESI) *m/z* Calculated for $C_{33}H_{29}N_3NaO_2S$ $[M+Na]^+$ 554.1878, found: 554.1877.

(3-benzyl-1-methyl-4-phenyl-5H-pyrido[4,3-b]indol-2-ium-2-yl)(tosyl)amide (**3aj**)



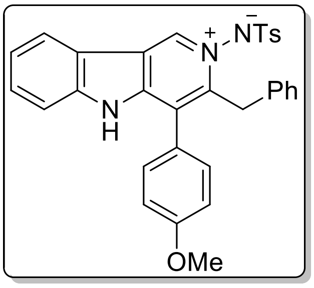
The general procedure was followed to afford the product as yellow solid in 70% yield (mp: 268-269 ^oC); **^{1}H NMR** (500 MHz, dmso-d6) δ 2.37 (s, 3H), 3.15 (s, 3H), 3.62 (s, 2H), 6.66-6.69 (m, 2H), 7.01-7.10 (m, 3H), 7.28-7.32 (m, 2H), 7.34-7.45 (m, 4H), 7.51-7.68 (m, 4H), 7.95 (s, 1H), 8.22 (d, 1H, *J* = 7.9 Hz), 12.03 (s, 1H); **^{13}C NMR** (125 MHz, dmso-d6) δ 19.8, 21.4, 35.5, 113.3, 117.9, 121.7, 121.8, 122.5, 123.0, 126.4, 126.5, 128.3, 128.4, 128.5, 129.5, 129.7, 130.1, 133.4, 138.4, 140.8, 141.8, 142.4, 142.8, 150.9, 153.7, 162.7; **IR** (film): 3065, 1615 cm^{-1}; **HRMS** (ESI) *m/z* Calculated for $C_{32}H_{27}N_3NaO_2S$ $[M+Na]^+$ 540.1722, found: 540.1723.

(3-benzyl-4-(4-bromophenyl)-5H-pyrido[4,3-b]indol-2-ium-2-yl)(tosyl)amide (**3ba**)



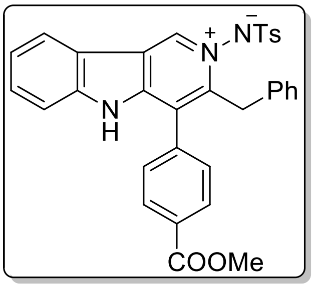
The general procedure was followed to afford the product as white solid in 81% yield (mp: 275-276 ^oC); **^{1}H NMR** (500 MHz, dmso-d6) δ 2.37 (s, 3H), 3.67 (s, 2H), 6.62-6.74 (m, 2H), 7.03-7.17 (m, 5H), 7.25-7.33 (m, 4H), 7.40-7.45 (m, 1H), 7.56-7.64 (m, 2H), 7.66-7.77 (m, 2H), 8.45 (d, 1H, *J* = 7.8 Hz), 9.60 (s, 1H), 12.07 (s, 1H); **^{13}C NMR** (125 MHz, dmso-d6) δ 21.4, 34.1, 113.2, 118.9, 120.9, 121.9, 122.4, 122.5, 123.2, 126.5, 126.6, 128.3, 128.6, 129.3, 129.7, 132.1, 132.2, 132.7, 138.0, 141.0, 141.4, 141.7, 142.1, 143.6, 149.0, 162.7; **IR** (film): 3066, 1660, 1610 cm^{-1}; **HRMS** (ESI) *m/z* Calculated for $C_{31}H_{24}BrN_3NaO_2S$ $[M+Na]^+$ 604.0670 and 606.0650, found: 604.0667 and 606.0648.

(3-benzyl-4-(4-methoxyphenyl)-5H-pyrido[4,3-b]indol-2-ium-2-yl)(tosyl)amide (**3ca**)



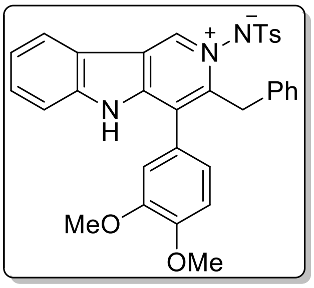
The general procedure was followed to afford the product as gray solid in 85% yield (mp: 265-266 ^{o}C); **^{1}H NMR** (500 MHz, dmso-d6) δ 2.37 (s, 3H), 3.69 (s, 2H), 3.89 (s, 3H), 6.62-6.75 (m, 2H), 7.05-7.14 (m, 7H), 7.23-7.24 (m, 4H), 7.37-7.45 (m, 1H), 7.55-7.64 (m, 2H), 8.37 (d, 1H, *J* = 7.8 Hz), 9.55 (s, 1H), 12.00 (s, 1H); **^{13}C NMR** (125 MHz, dmso-d6) δ 21.4, 34.1, 55.8, 113.3, 115.2, 118.6, 120.9, 122.3, 122.4, 122.9, 125.0, 126.5, 128.3, 128.6, 129.1, 129.7, 131.2, 138.2, 140.9, 141.3, 141.4, 142.1, 144.0, 149.4, 160.2, 162.7; **IR** (film): 3100, 1654 cm^{-1}; **HRMS** (ESI) *m/z* Calculated for $C_{32}H_{27}N_3NaO_3S$ [M+Na]$^+$ 556.1671, found: 556.1676.

(3-benzyl-4-(4-(methoxycarbonyl)phenyl)-5H-pyrido[4,3-b]indol-2-ium-2-yl)(tosyl)amide (**3da**)



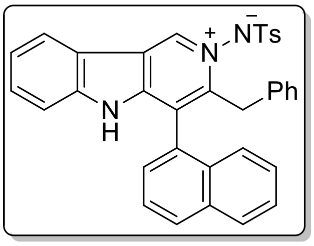
The general procedure was followed to afford the product as brown solid in 67% yield (mp: 195-196 ^{o}C); **^{1}H NMR** (500 MHz, dmso-d6) δ 2.38 (s, 3H), 3.69 (s, 2H), 3.91 (s, 3H), 6.59-6.73 (m, 2H), 7.04-7.14 (m, 3H), 7.25-7.37 (m, 6H), 7.56-7.64 (m, 2H), 7.95 (s, 1H),8.07 (d, 2H, *J* = 8.0 Hz), 8.39 (d, 1H, *J* = 7.8 Hz), 9.61 (s, 1H), 12.07 (s, 1H); **^{13}C NMR** (125 MHz, dmso-d6) δ 21.4, 34.1, 52.8, 113.2, 118.9, 120.8, 122.1, 122.4, 122.6, 126.5, 128.3, 128.6, 129.3, 129.7, 130.4, 130.5, 130.6, 137.8, 137.9, 141.1, 141.3, 141.8, 142.1, 143.4, 149.0, 162.7, 166.3; **IR** (film): 3133, 1628 cm^{-1}; **HRMS** (ESI) *m/z* Calculated for $C_{33}H_{27}N_3NaO_4S$ [M+Na]$^+$ 584.1620, found: 584.1622.

(3-benzyl-4-(3,4-dimethoxyphenyl)-5H-pyrido[4,3-b]indol-2-ium-2-yl)(tosyl)amide (**3ea**)



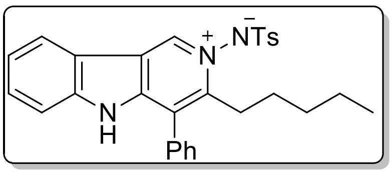
The general procedure was followed to afford the product as brown solid in 70% yield (mp: 255-256 °C); **^{1}H NMR** (500 MHz, dmso-d6) δ 2.36 (s, 3H), 3.57 (s, 3H), 3.58 (d, 1H, J = 15.2 Hz), 3.80 (d, 1H, J = 15.2 Hz), 3.82 (s, 3H), 6.62-6.67 (m, 1H), 6.69-6.73 (m, 2H), 6.73-6.78 (m, 1H), 7.06-7.14 (m, 4H), 7.26-7.33 (m, 4H), 7.38-7.44 (m, 1H), 7.58-7.65 (m, 2H), 8.38 (d, 1H, *J* = 7.8 Hz), 9.58 (s, 1H), 12.02 (s, 1H); **^{13}C NMR** (125 MHz, dmso-d6) δ 21.4, 36.2, 55.7, 56.1, 112.7, 113.2, 113.4, 118.6, 120.9, 122.1, 122.3, 122.4, 123.1, 125.0, 126.4, 126.5, 128.3, 128.5, 129.1, 129.7, 138.5, 140.9, 141.3, 141.4, 142.1, 143.9, 149.4, 149.7, 162.7; **IR** (film): 3100, 1622 cm^{-1}; **HRMS** (ESI) *m/z* Calculated for $C_{33}H_{29}N_3NaO_4S$ [M+Na]$^+$ 586.1776, found: 586.1773.

(3-benzyl-4-(naphthalen-1-yl)-5H-pyrido[4,3-b]indol-2-ium-2-yl)(tosyl)amide (**3fa**)



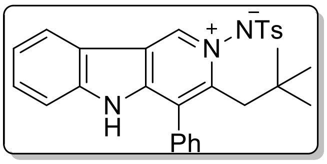
The general procedure was followed to afford the product as yellow solid in 88% yield (mp: 292-293 °C); **^{1}H NMR** (500 MHz, dmso-d6) δ 2.33 (s, 3H), 3.05 (d, 1H, *J* = 15.1 Hz), 3.73 (d, 1H, *J* = 15.1 Hz), 6.53- 6.61 (m, 2H), 6.96-7.05 (m, 4H), 7.21-7.28 (m, 1H), 7.28-7.33 (m, 2H), 7.37-7.46 (m, 4H), 7.46-7.51 (m, 1H), 7.52-7.64 (m, 3H), 8.01-8.18 (m, 2H), 8.48 (d, 1H, *J* = 7.8 Hz), 9.84 (s, 1H), 11.92 (s, 1H); **^{13}C NMR** (125 MHz, dmso-d6) δ 21.4, 34.4, 113.1, 118.9, 120.8, 120.9, 122.5, 124.5, 126.2, 126.4, 126.9, 127.5, 128.2, 128.4, 129.1, 129., 129.7, 129.9, 130.1, 131.1, 133.9, 137.9, 140.8, 141.4, 141.9, 142.1, 144.3, 149.6; **IR** (film): 3031, 1644 cm^{-1}; **HRMS** (ESI) *m/z* Calculated for $C_{35}H_{27}N_3NaO_2S$ [M+Na]$^+$ 576.1722, found: 576.1721.

(3-pentyl-4-phenyl-5H-pyrido[4,3-b]indol-2-ium-2-yl)(tosyl)amide (**3ga**)



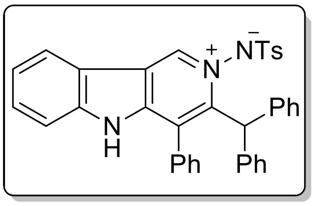
The general procedure was followed to afford the product as brown solid in 40% yield (mp: 246-247 °C); **^{1}H NMR** (500 MHz, dmso-d6) δ 0.67 (t, 3H, *J* = 7.24 Hz), 0.85-0.99 (m, 4H), 1.26-1.37 (m, 2H), 2.22 (t, 2H, *J* = 8.2 Hz), 2.32 (s, 3H), 7.19-7.24 (m, 2H), 7.25-7.30 (m, 2H), 7.32-7.41 (m, 3H), 7.55-7.63 (m, 5H), 8.34 (d, 1H, *J* = 7.8 Hz), 9.51 (s, 1H), 11.91 (s, 1H); **^{13}C NMR** (125 MHz, dmso-d6) δ 13.9, 21.3, 21.6, 27.2 28.8, 31.4, 113.2, 118.3, 120.8, 122.0, 122.2, 122.3, 126.4, 129.0, 129.4, 129.5, 129.7, 129.9, 133.4, 140.7, 141.2, 141.7, 142.0, 143.5, 151.6; **IR** (film): 3100, 1625 cm^{-1}; **HRMS** (ESI) *m/z* Calculated for $C_{29}H_{29}N_3NaO_2S$ [M+Na]$^+$ 506.1878, found: 506.1874.

(3-neopentyl-4-phenyl-5H-pyrido[4,3-b]indol-2-ium-2-yl)(tosyl)amide (**3ha**)



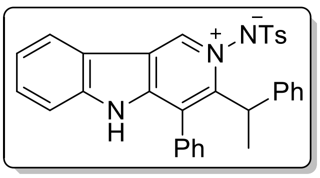
The general procedure was followed to afford the product as white solid in 75% yield (mp: 322-323 °C); **^{1}H NMR** (500 MHz, dmso-d6) δ0.58 (s, 9H), 2.38 (s, 3H), 2.50 (s, 2H), 7.17-7.31 (m, 5H), 7.38-7.43 (m, 1H), 7.49-7.67 (m, 6H), 8.39 (d, 1H, *J* = 7.8 Hz), 9.61 (s, 1H), 11.88 (s, 1H); **^{13}C NMR** (125 MHz, dmso-d6) δ 21.4, 30.7, 35.2, 38.8, 113.3, 118.1, 121.0, 122.3, 122.4, 123.3, 126.6, 129.0, 129.3, 129.5, 129.7, 134.1, 140.7, 141.6, 141.9, 142.1, 143.4, 150.0; **IR** (film): 3133, 1622 cm^{-1}; **HRMS** (ESI) *m/z* Calculated for $C_{29}H_{29}N_3NaO_2S$ $[M+Na]^+$ 506.1878, found: 506.1875.

(3-benzhydryl-4-phenyl-5H-pyrido[4,3-b]indol-2-ium-2-yl)(tosyl)amide (**4ja**)



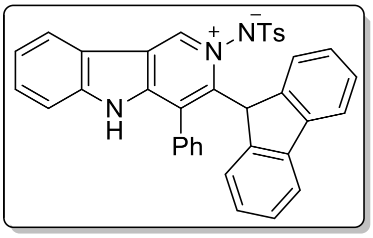
The general procedure was followed to afford the product as gray solid in 67% yield (mp: 196-197 °C); **^{1}H NMR** (500 MHz, dmso-d6) δ 2.35 (s, 3H), 6.36-6.45 (m, 4H), 6.64-6.74 (m, 2H), 6.83 (s, 1H), 6.95-7.02 (m, 6H), 7.02-7.09 (m, 2H), 7.12-7.19 (m, 21), 7.25-7.31 (m, 2H), 7.37-7.43 (m, 1H), 7.55-7.61 (m, 3H), 7.96 (s, 1H), 8.30 (d, 1H, *J* = 7.8 Hz), 9.64 (s, 1H), 11.52 (s, 1H); **^{13}C NMR** (125 MHz, dmso-d6) δ 21.4, 51.0, 113.3. 118.2, 120.7, 122.1, 122.5, 124.5, 126.3, 127.1, 127.9, 128.0, 128.6, 129.2, 129.5, 129.6, 130.0, 132.3, 140.6, 140.9, 141.4, 142.0, 142.1, 144.9, 150.2, 162.7; **IR** (film): 3066, 1615 cm^{-1}; **HRMS** (ESI) *m/z* Calculated for $C_{37}H_{29}N_3NaO_2S$ $[M+Na]^+$ 602.1878, found: 602.1877.

(4-phenyl-3-(1-phenylethyl)-5H-pyrido[4,3-b]indol-2-ium-2-yl)(tosyl)amide (**4ka**)



The general procedure was followed to afford the product as brown solid in 70% yield (mp: 187-188 °C); **^{1}H NMR** (500 MHz, dmso-d6) δ 0.91 (d, 3H, *J* = 7.3 Hz), 2.32 (s, 3H), 5.53 (q, 1H, *J* = 7.3 Hz), 6.07-6.17 (m, 1H), 6.45-6.57 (m, 2H), 6.92-7.10 (m, 4H), 7.20-7.26 (m, 2H), 7.28-7.42 (m, 3H), 7.43-7.51 (m, 3H), 7.52-7.60 (m, 2H), 8.28 (d, 1H, J = 7.8 Hz), 9.60 (s, 1H), 11.61 (s, 1H); **^{13}C NMR** (125 MHz, dmso-d6) δ 16.8, 21.3, 60.2, 113.2, 118.2, 120.6, 122.1, 122.4, 122.8, 126.1, 126.9, 127.0, 128.1, 128.6, 128.7, 128.8, 129.8, 129.9, 130.7, 131.9, 140.5, 141.1, 141.7, 142.1, 143.0, 144.7, 154.0, 162.7; **IR** (film): 3033, 1611, 1600 cm^{-1}; **HRMS** (ESI) *m/z* Calculated for $C_{32}H_{27}N_3NaO_2S$ $[M+Na]^+$ 540.1722, found: 540.1721.

(3-(9H-fluoren-9-yl)-4-phenyl-5H-pyrido[4,3-b]indol-2-ium-2-yl)(tosyl)amide (**4la**)



The general procedure was followed to afford the product as black solid in 40% yield (mp: 278-279 ^{o}C); **^{1}H NMR** (500 MHz, dmso-d6) δ 2.32 (s, 3H), 6.00-6.07 (m, 2H), 6.65-6.72 (m, 2H), 6.72-6.77 (m, 1H), 6.85-6.90 (m, 2H), 6.94-7.00 (m, 1H), 7.08-7.13 (m, 2H), 7.17-7.26 (m, 4H), 7.37-7.46 (m, 3H), 7.47-7.52 (m, 1H), 7.52-7.60 (m, 3H), 8.29 (d, 1H, *J* = 7.8 Hz), 9.66 (s, 1H), 11.58 (s, 1H); **^{13}C NMR** (125 MHz, dmso-d6) δ 21.3, 48.1, 113.3, 118.7, 120.3, 120.6, 122.2, 122.5, 123.1, 125.0, 127.1, 127.2, 127.5, 128.0, 129.4, 129.5, 129.7, 130.0, 140.6, 140.8, 141.3, 142.1, 144.2, 145.6, 149.5, 162.7; **IR** (film): 3160, 3066, 1615 cm^{-1}; **HRMS** (ESI) *m/z* Calculated for $C_{37}H_{27}N_3NaO_2S$ [M+Na]$^+$ 600.1722, found: 600.1720.

4. X-Ray analysis of 3aa

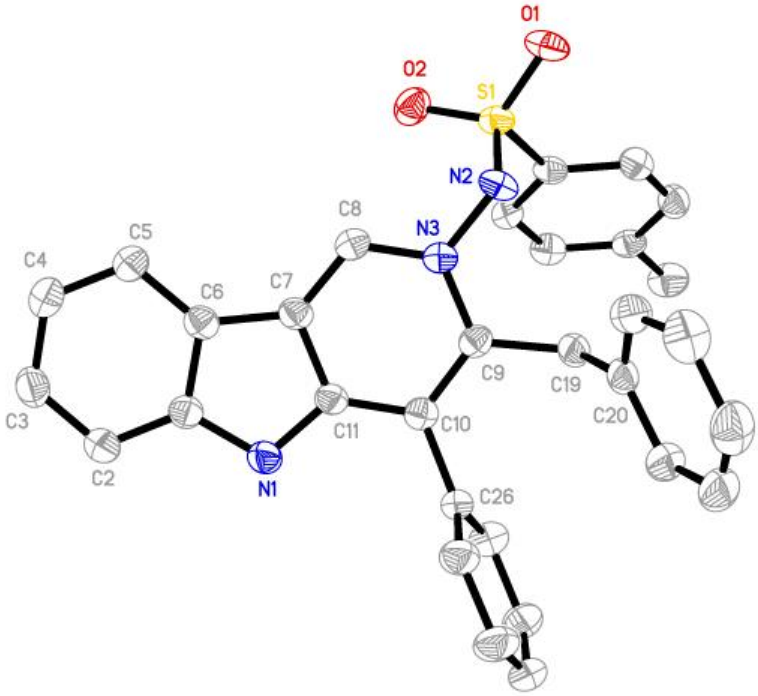


Table 1. Crystal data and structure refinement for **3aa**.

Identification code	**3aa** (including a molecule of DMSO)	
Empirical formula	C33 H30 N3 O3 S2	
Formula weight	580.72	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	p-1	
Unit cell dimensions	a = 7.8264(16) Å	= 96.36(3)°.
	b = 11.561(2) Å	= 95.09(3)°.
	c = 16.718(3) Å	= 102.82(3)°.
Volume	1455.8(5) $Å^3$	
Z	2	
Density (calculated)	1.325 Mg/m^3	
Absorption coefficient	0.222 mm^{-1}	
F(000)	610	
Crystal size	0.5 x 0.4 x 0.4 mm^3	
Theta range for data collection	3.09 to 26.00 °.	
Index ranges	-9<=h<=9, -14<=k<=14, -20<=l<=20	
Reflections collected	12592	
Independent reflections	5699 [R(int) = 0.0300]	
Completeness to theta = 26.00 °	99.4 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.0000 and 0.5493	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5699 / 0 / 370	
Goodness-of-fit on F^2	0.970	
Final R indices [I>2sigma(I)]	R1 = 0.0502, wR2 = 0.1727	
R indices (all data)	R1 = 0.0684, wR2 = 0.2362	
Largest diff. peak and hole	0.643 and -0.674 e.$Å^{-3}$	

5. X-Ray analysis of 3fa

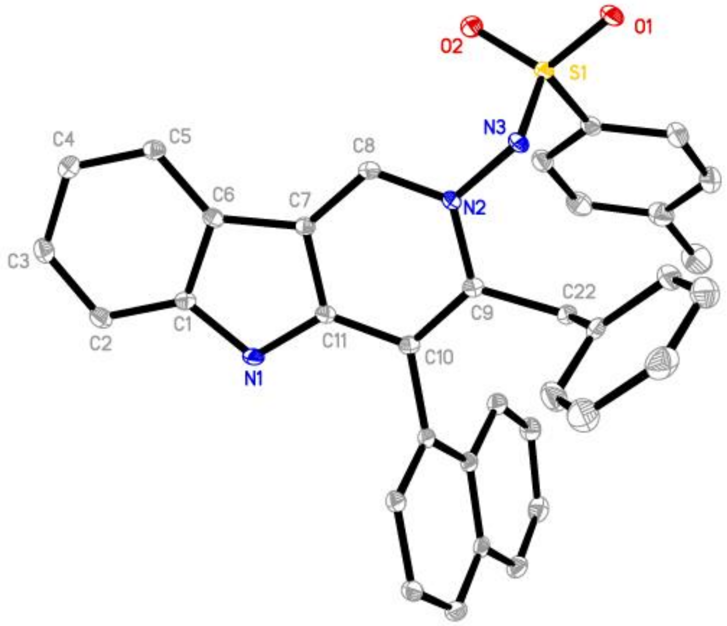
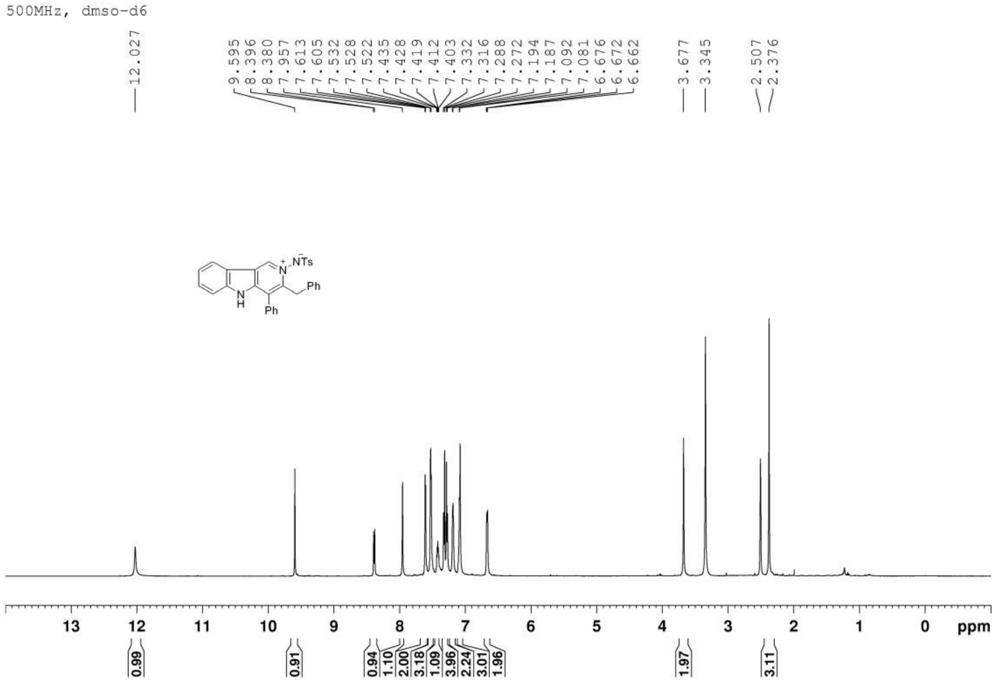


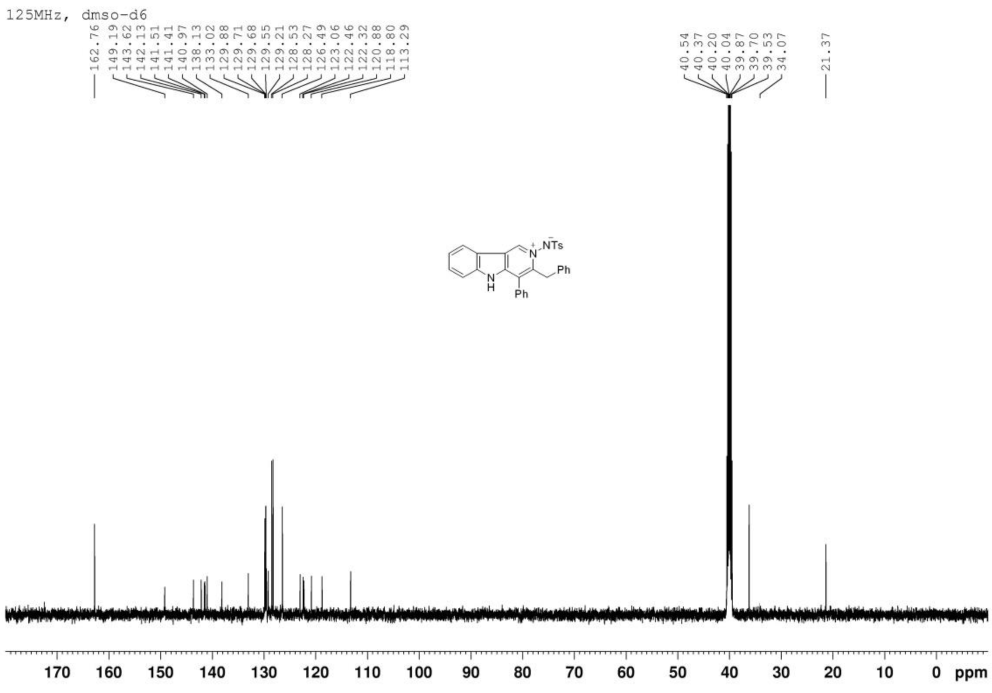
Table 2. Crystal data and structure refinement for **3fa**.

Identification code	**3fa**	
Empirical formula	C35 H27 N3 O2 S	
Formula weight	553.66	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P21/c	
Unit cell dimensions	a = 10.2471(5) Å	α= 90°.
	b = 15.4948(8) Å	β= 105.211(5)°.
	c = 17.7996(9) Å	γ = 90°.
Volume	2727.1(2) Å^3	
Z	4	
Density (calculated)	1.348 Mg/m^3	
Absorption coefficient	0.158 mm^{-1}	
F(000)	1160	
Crystal size	? x ? x ? mm^3	
Theta range for data collection	3.34 to 25.99°.	
Index ranges	-11<=h<=12, -19<=k<=15, -18<=l<=21	
Reflections collected	14289	
Independent reflections	5273 [R(int) = 0.0406]	
Completeness to theta = 25.99°	98.4 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.00000 and 0.77392	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5273 / 0 / 370	
Goodness-of-fit on F^2	1.029	
Final R indices [I>2sigma(I)]	R1 = 0.0450, wR2 = 0.1074	
R indices (all data)	R1 = 0.0616, wR2 = 0.1175	
Largest diff. peak and hole	0.319 and -0.516 e.Å^{-3}	

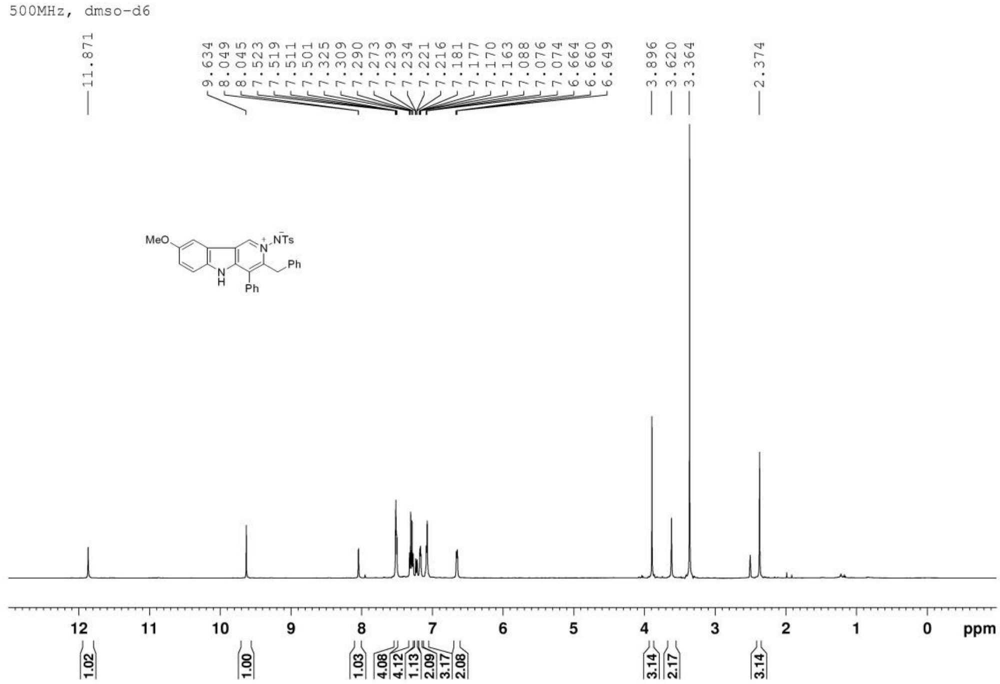
6. ^{1}H, ^{13}C-NMR spectra of products 3aa-3ak, 3ba-ha, 4ja-4la, 5aa and ^{1}H-^{13}C HSQC of 3fa

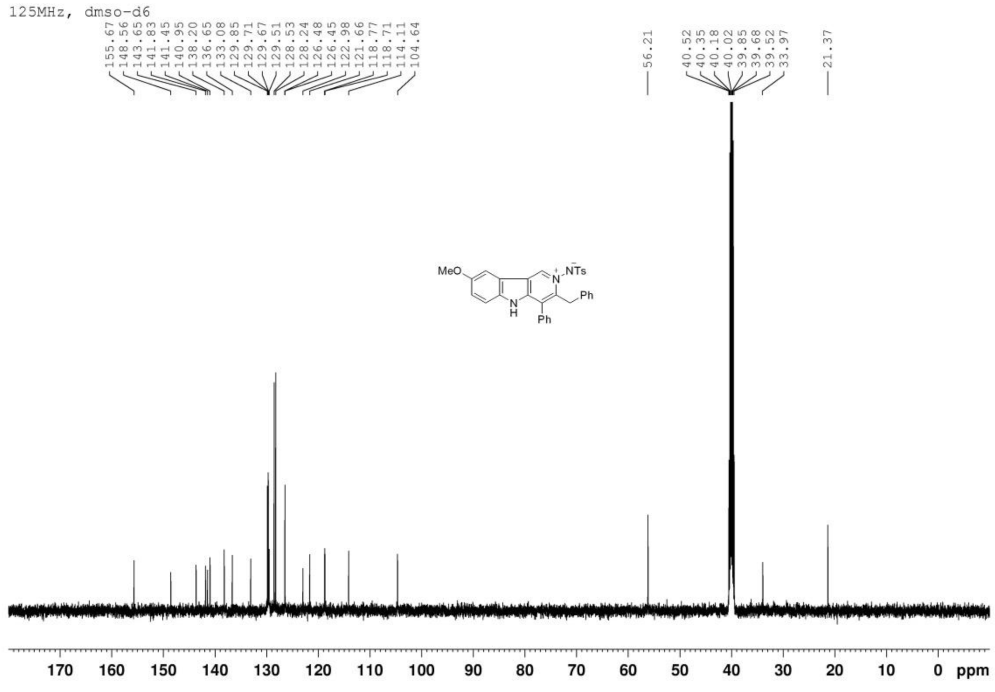
(3-benzyl-4-phenyl-5H-pyrido[4,3-b]indol-2-ium-2-yl)(tosyl)amide (**3aa)**



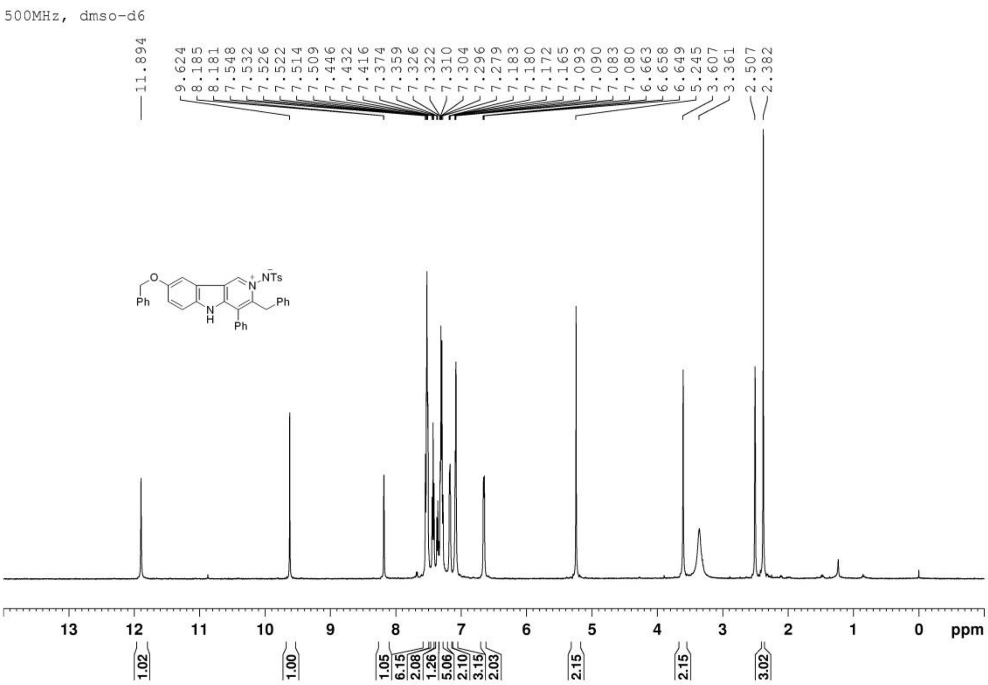


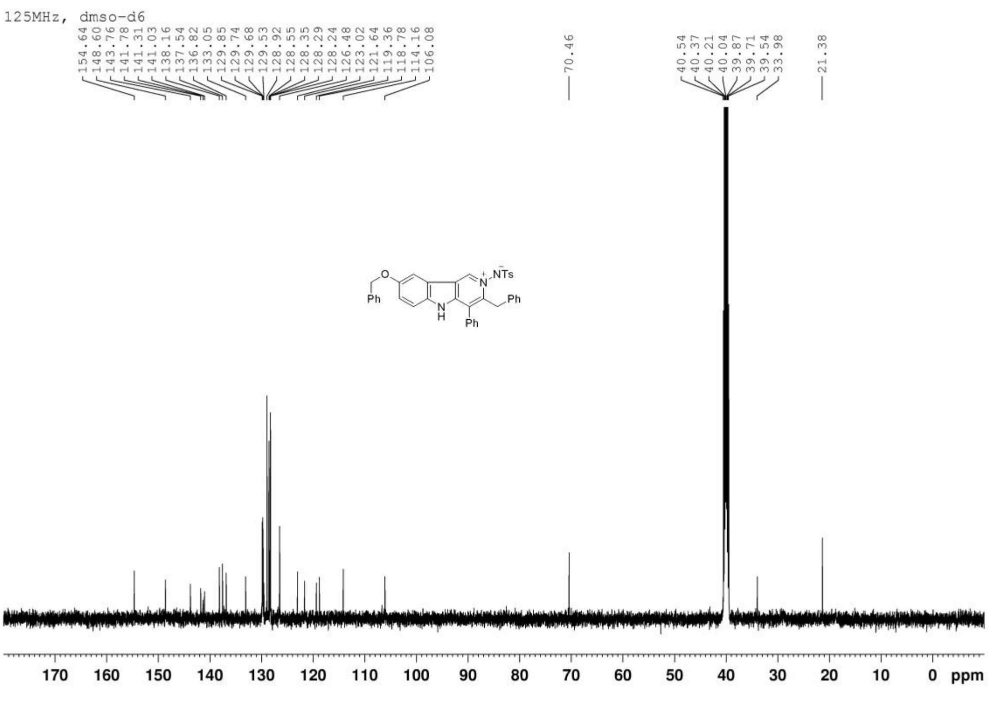
(3-benzyl-8-methoxy-4-phenyl-5H-pyrido[4,3-b]indol-2-ium-2-yl)(tosyl)amide (**3ab**)



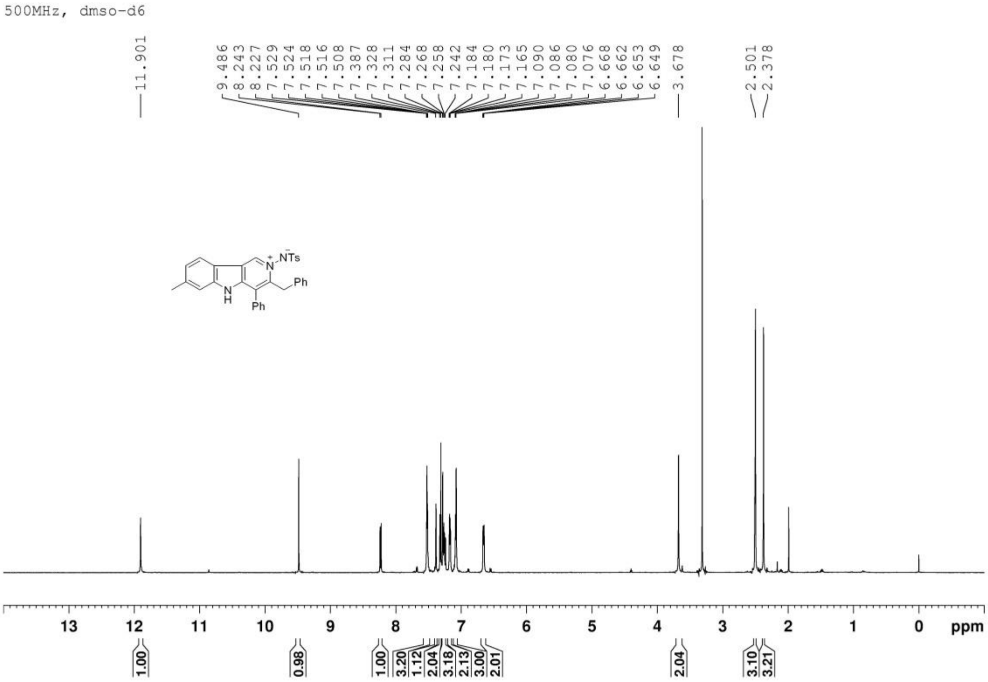


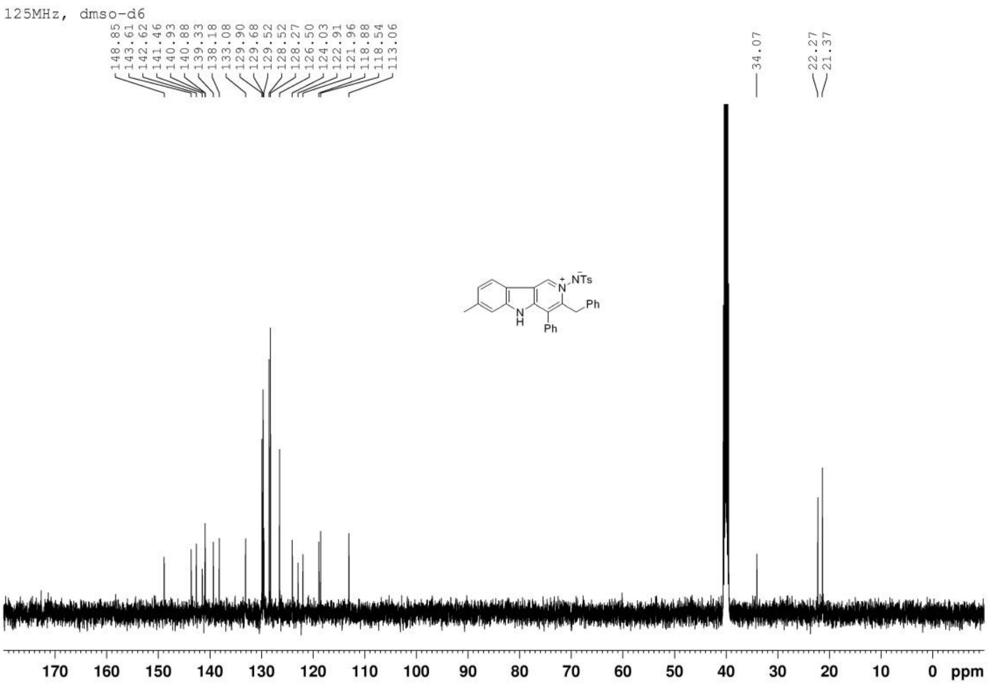
(3-benzyl-8-(benzyloxy)-4-phenyl-5H-pyrido[4,3-b]indol-2-ium-2-yl)(tosyl)amide (**3ac**)



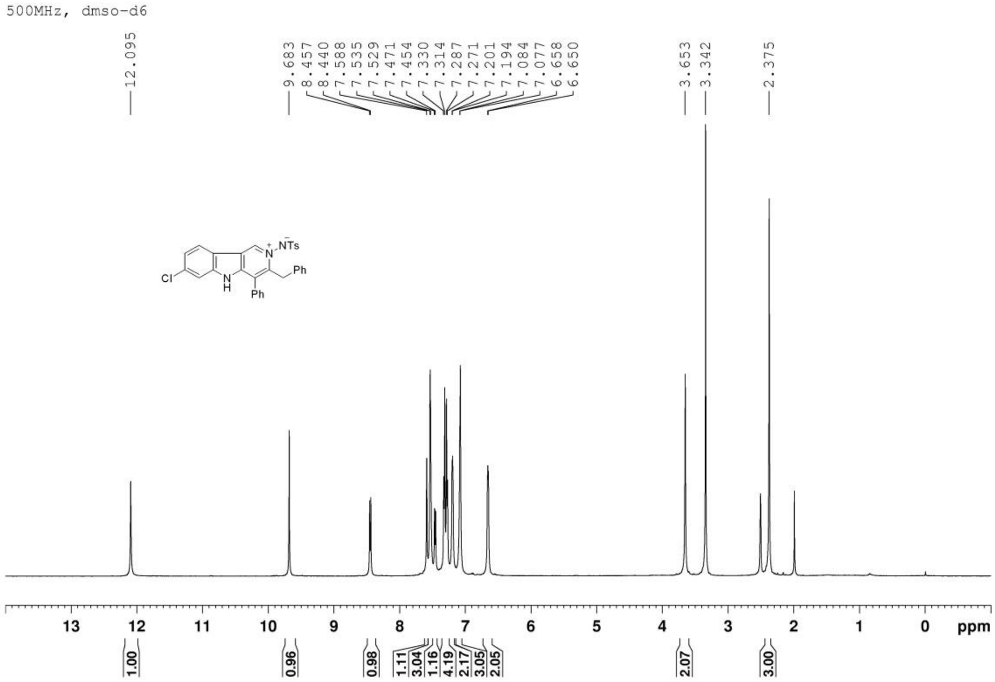


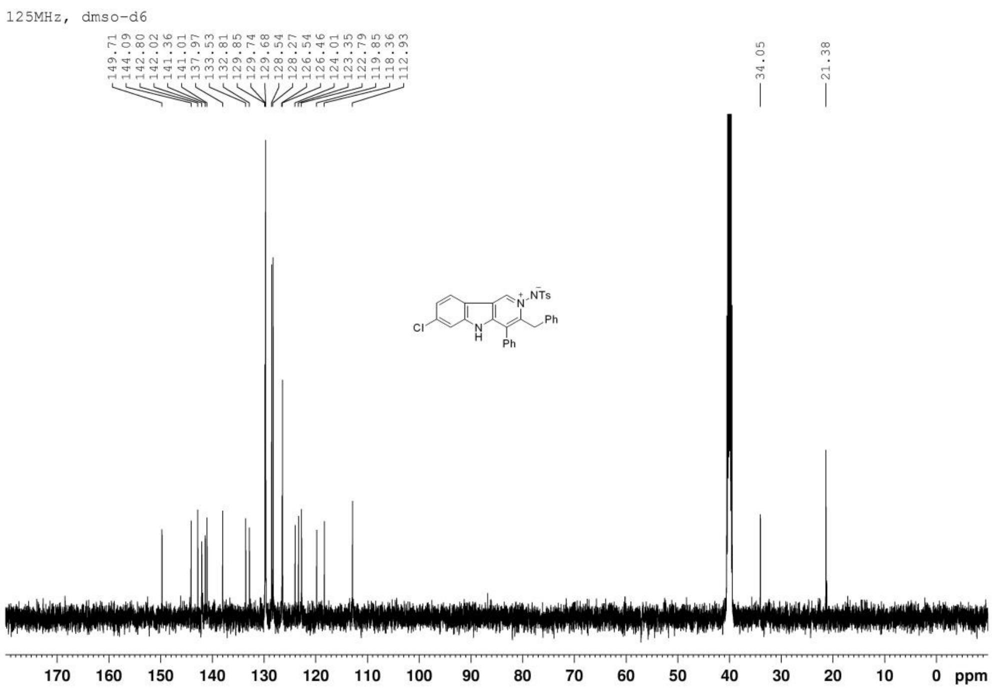
(3-benzyl-7-methyl-4-phenyl-5H-pyrido[4,3-b]indol-2-ium-2-yl)(tosyl)amide (**3ad**)



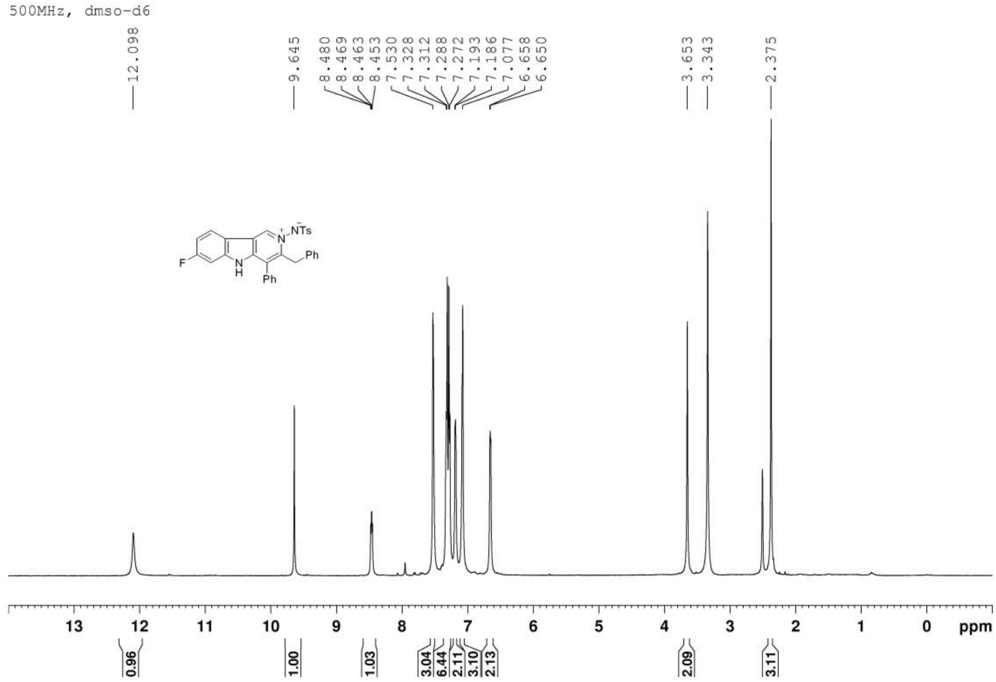


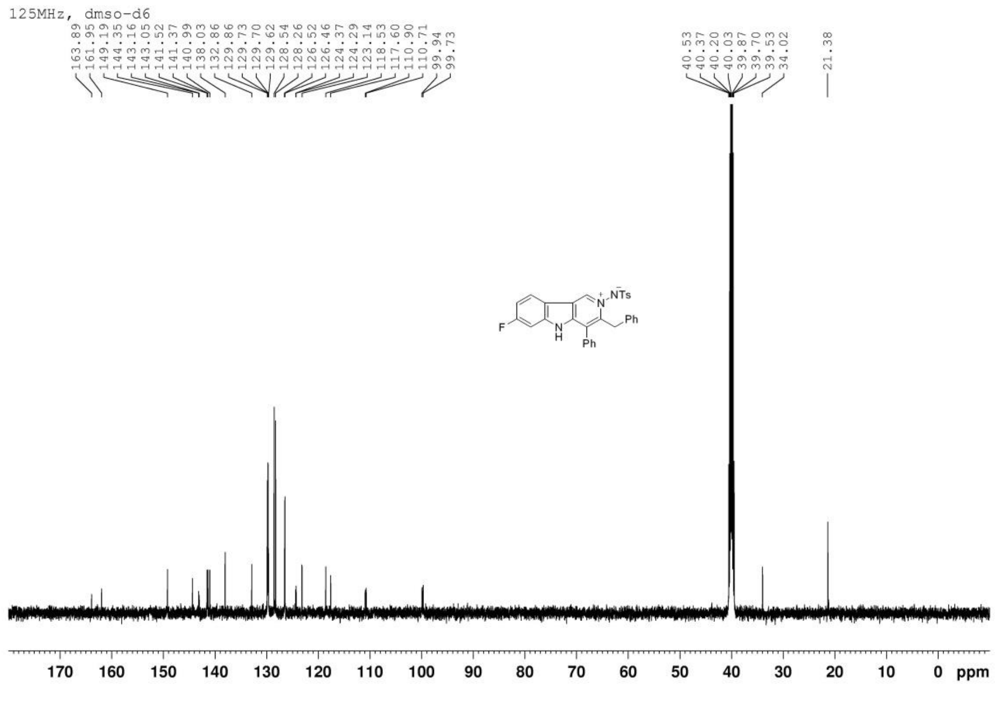
(3-benzyl-7-chloro-4-phenyl-5H-pyrido[4,3-b]indol-2-ium-2-yl)(tosyl)amide (**3ae**)



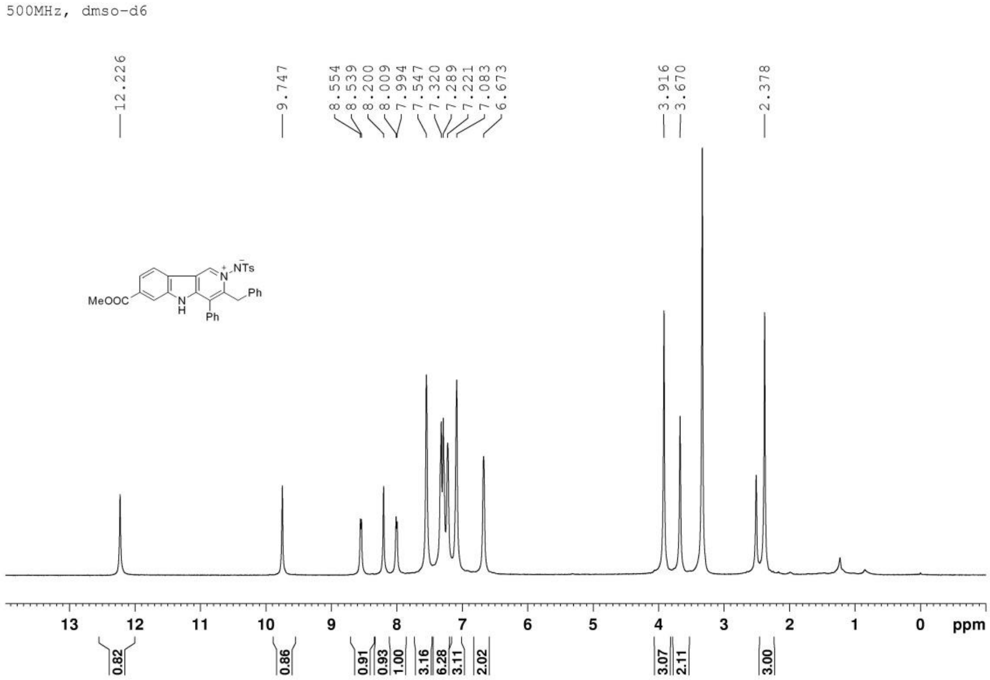


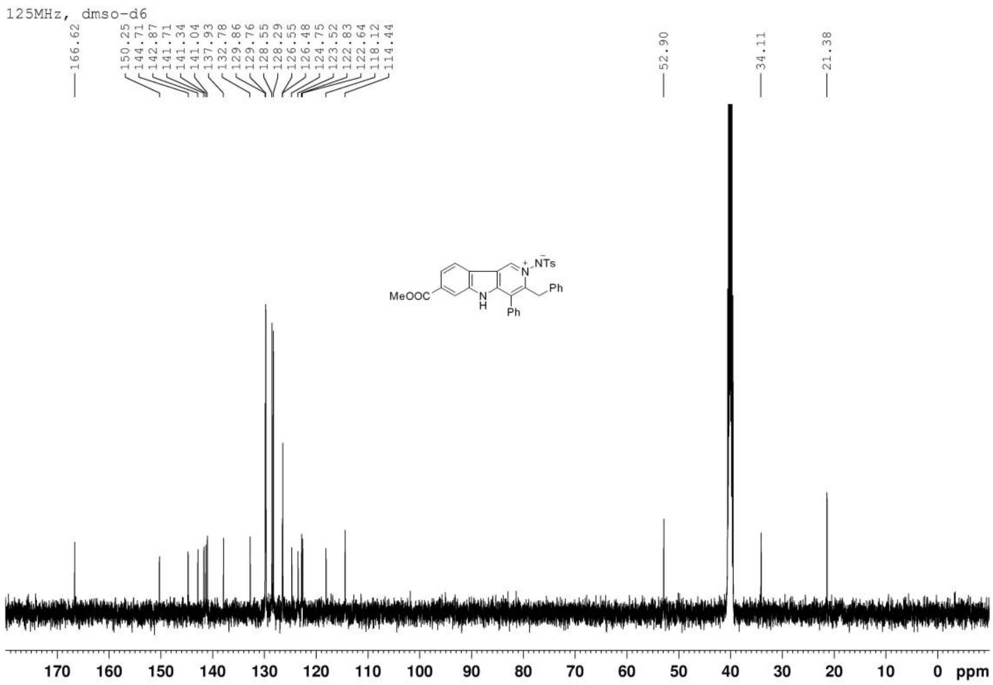
(3-benzyl-7-fluoro-4-phenyl-5H-pyrido[4,3-b]indol-2-ium-2-yl)(tosyl)amide (**3af**)



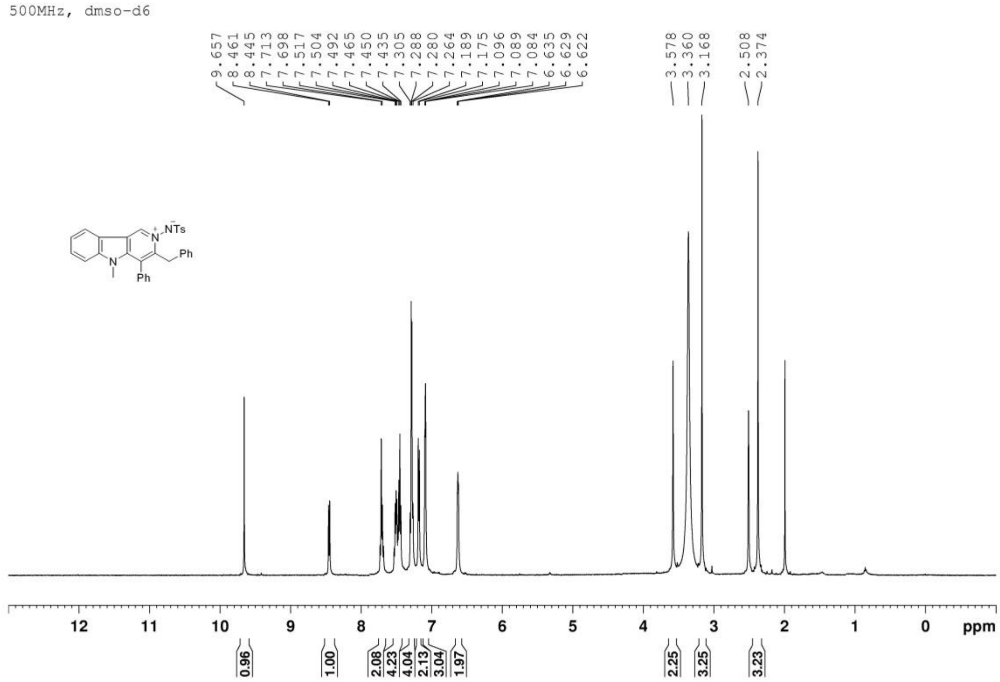


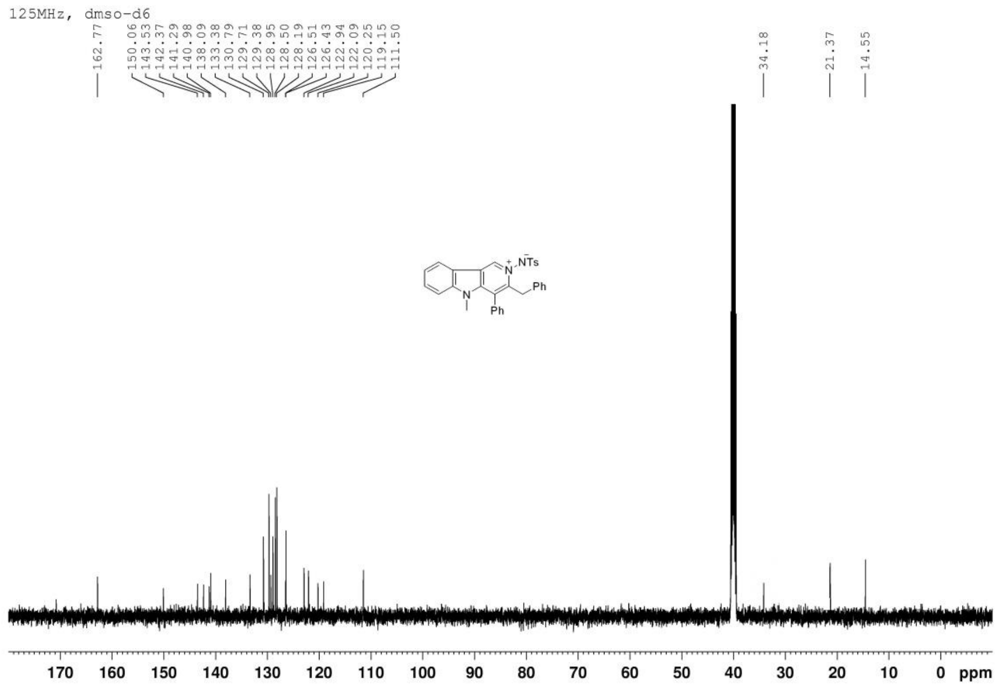
(3-benzyl-7-(methoxycarbonyl)-4-phenyl-5H-pyrido[4,3-b]indol-2-ium-2-yl)(tosyl)amide (**3ag)**



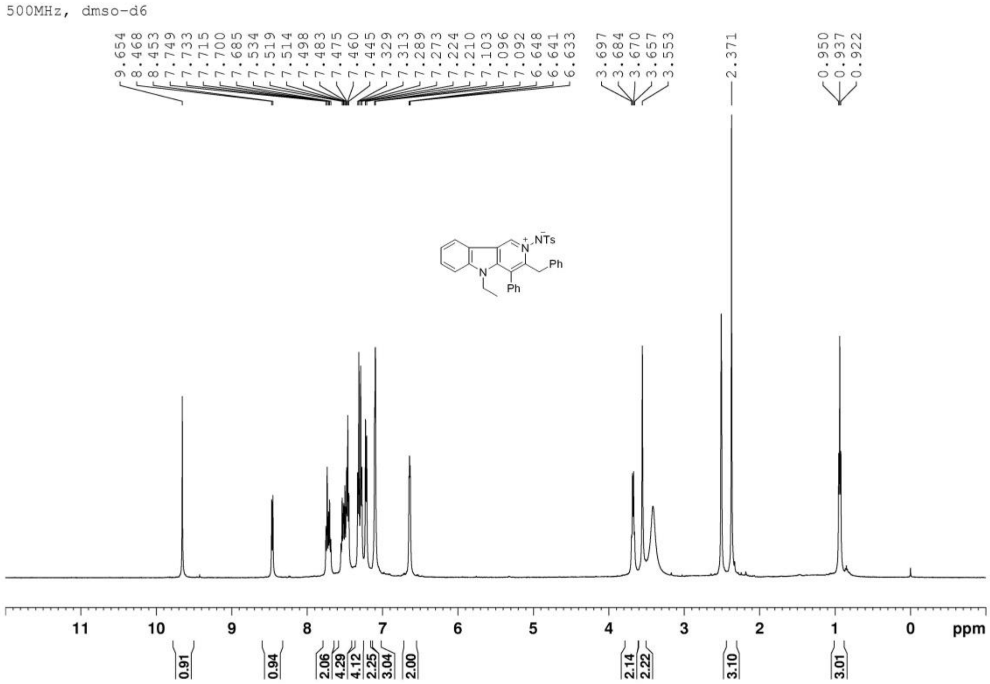


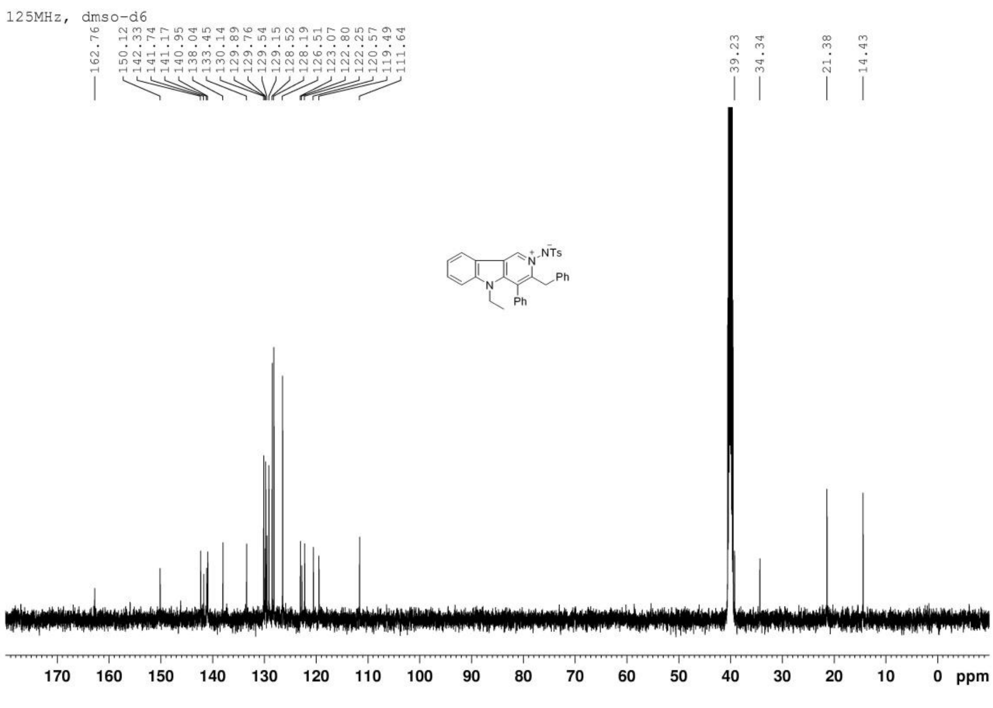
(3-benzyl-5-methyl-4-phenyl-5H-pyrido[4,3-b]indol-2-ium-2-yl)(tosyl)amide (**3ah**)



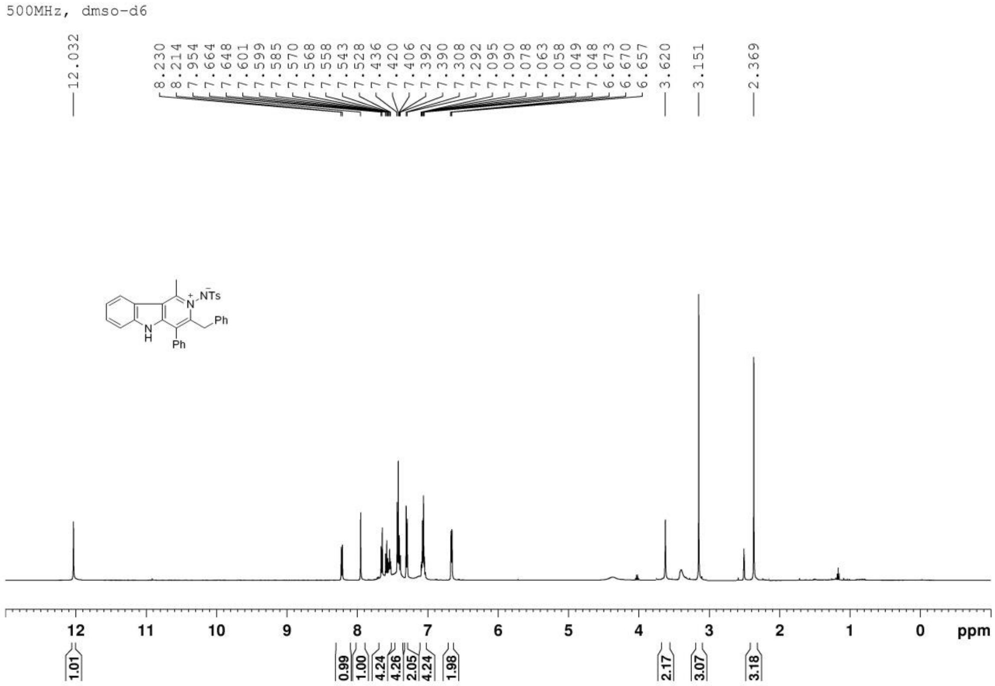


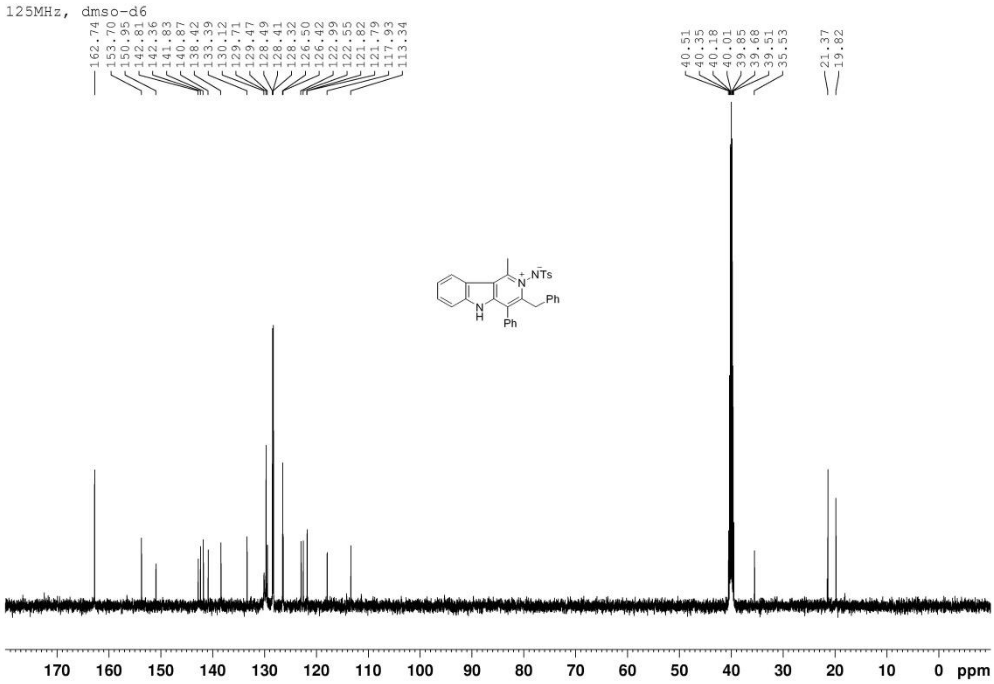
(3-benzyl-5-ethyl-4-phenyl-5H-pyrido[4,3-b]indol-2-ium-2-yl)(tosyl)amide (**3ai**)



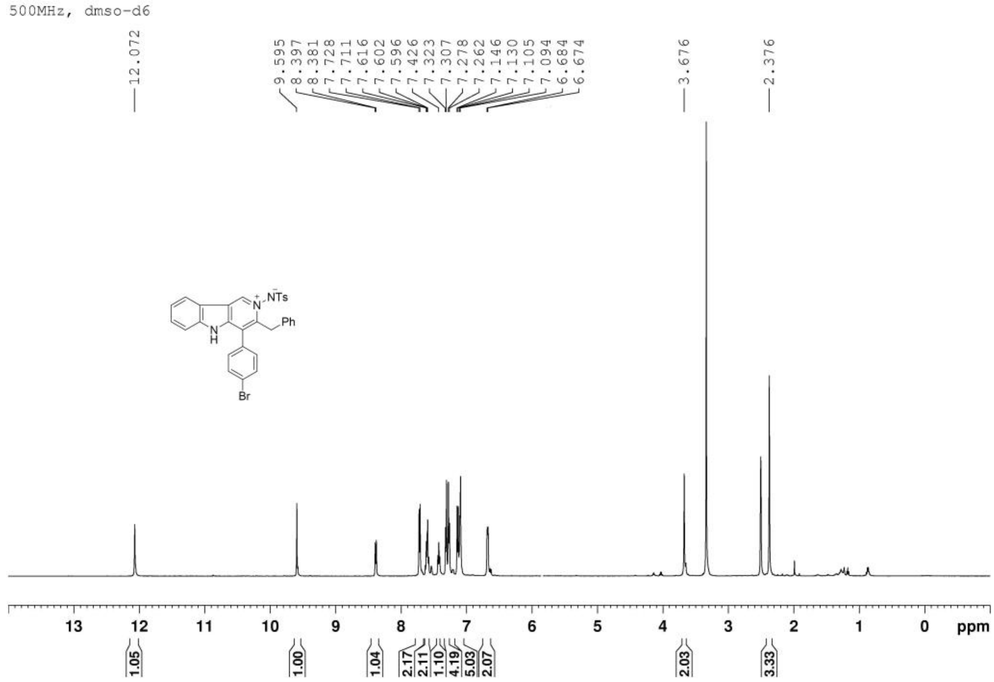


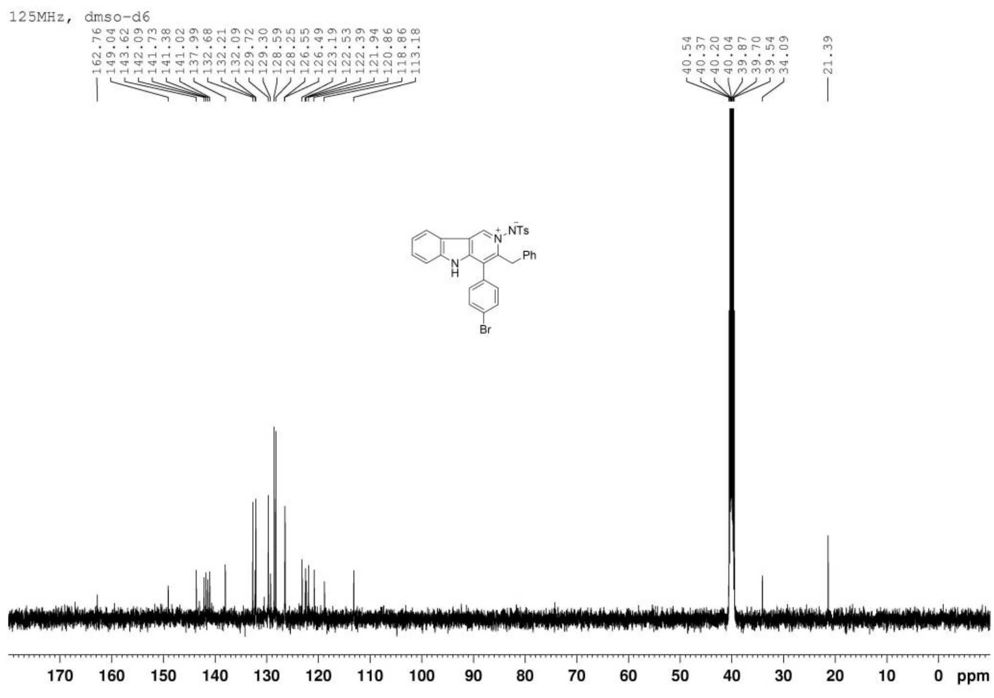
(3-benzyl-1-methyl-4-phenyl-5H-pyrido[4,3-b]indol-2-ium-2-yl)(tosyl)amide (**3aj**)



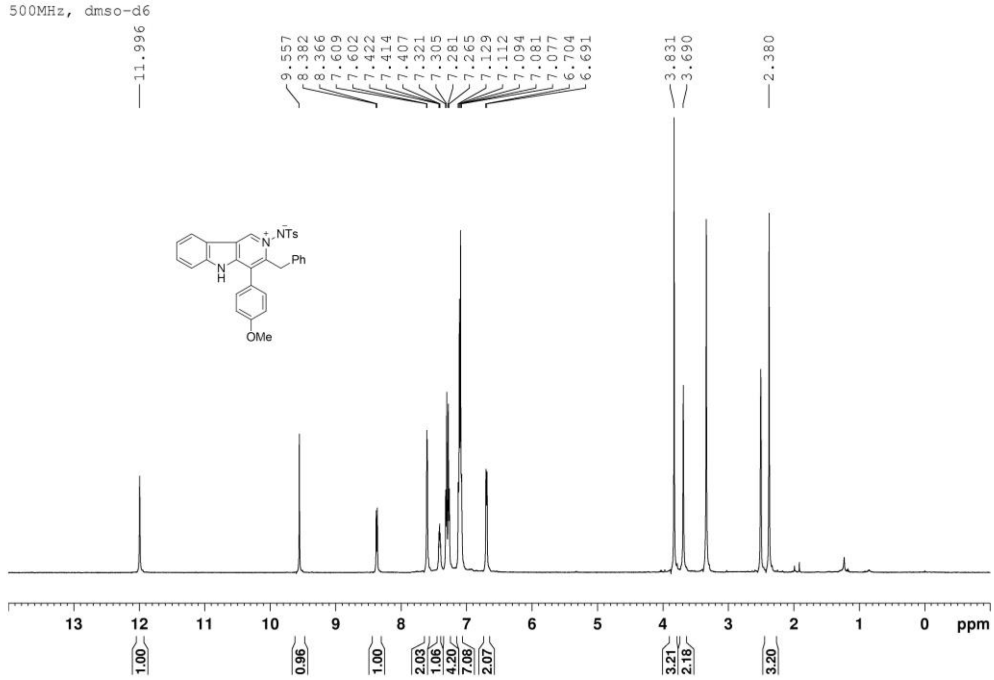


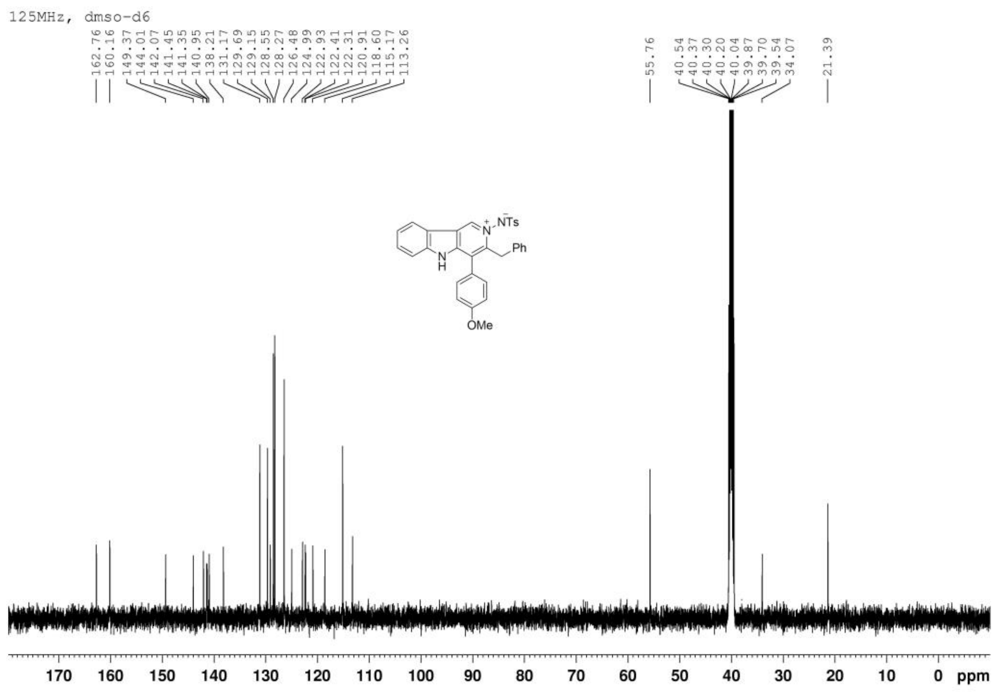
(3-benzyl-4-(4-bromophenyl)-5H-pyrido[4,3-b]indol-2-ium-2-yl)(tosyl)amide (**3ba**)



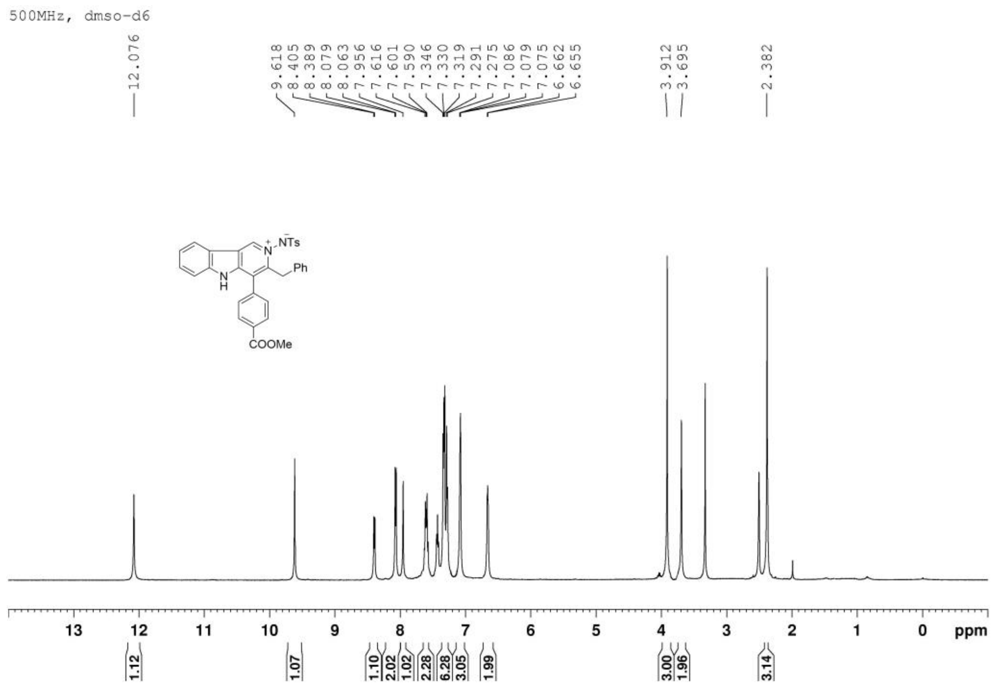


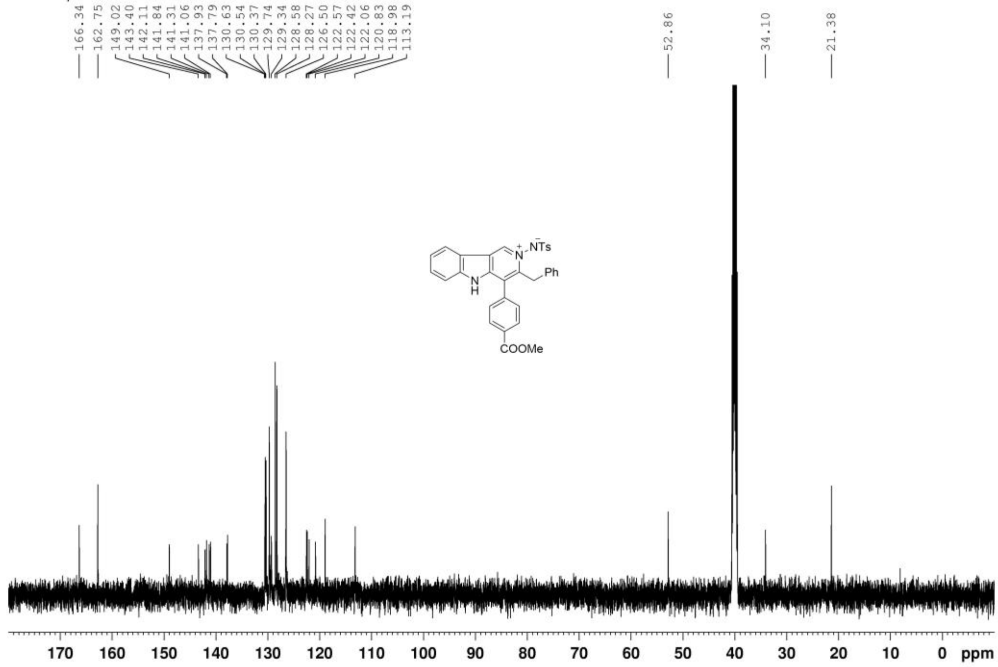
(3-benzyl-4-(4-methoxyphenyl)-5H-pyrido[4,3-b]indol-2-ium-2-yl)(tosyl)amide (**3ca**)



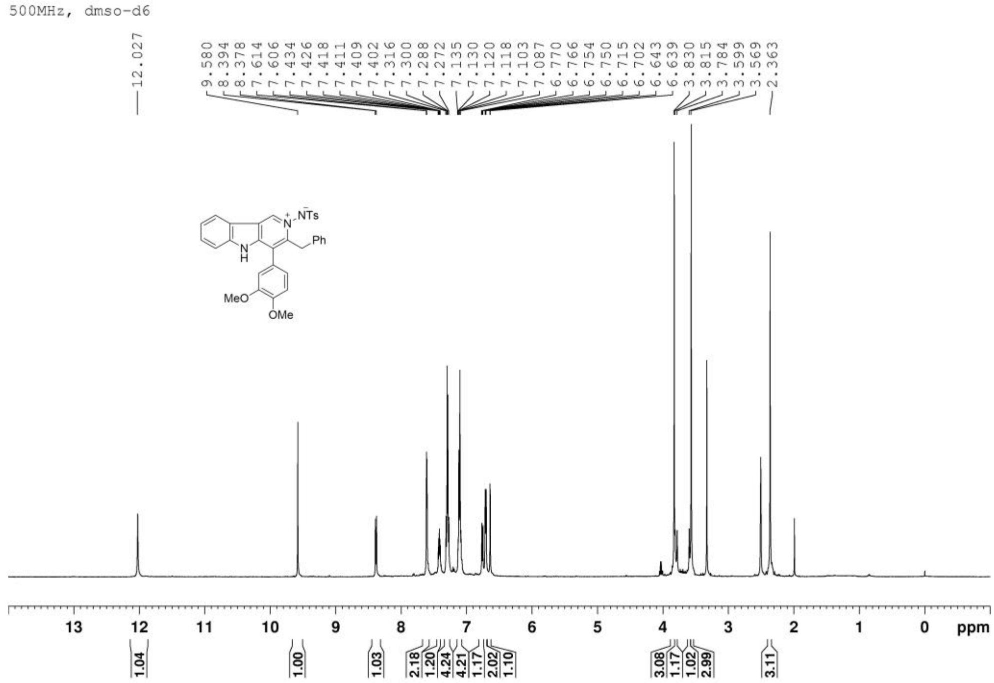


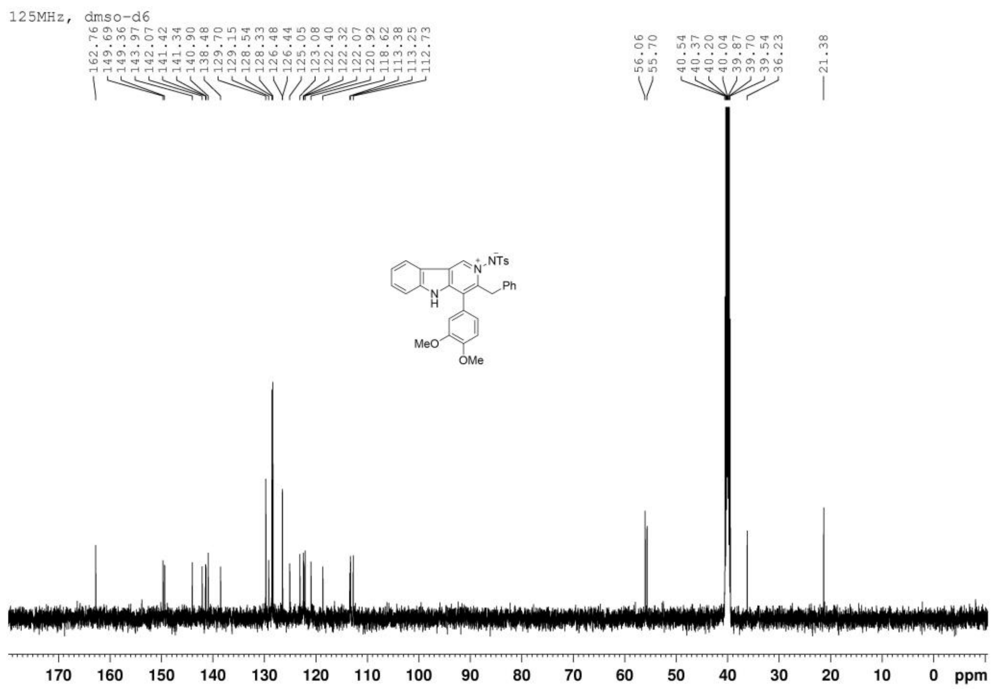
(3-benzyl-4-(4-(methoxycarbonyl)phenyl)-5H-pyrido[4,3-b]indol-2-ium-2-yl)(tosyl)amide (**3da**)



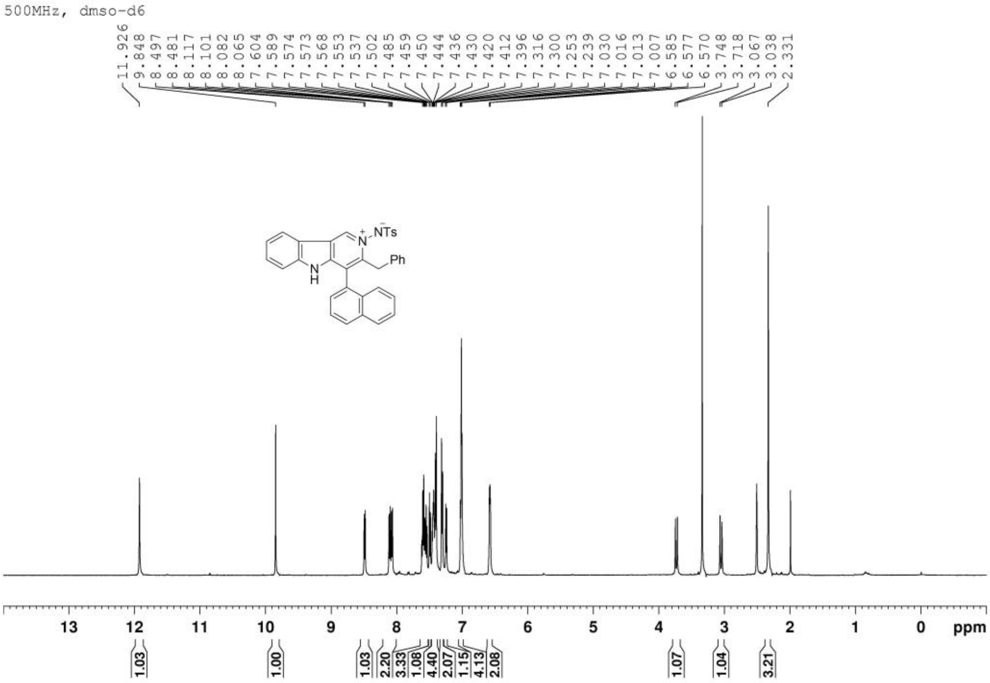


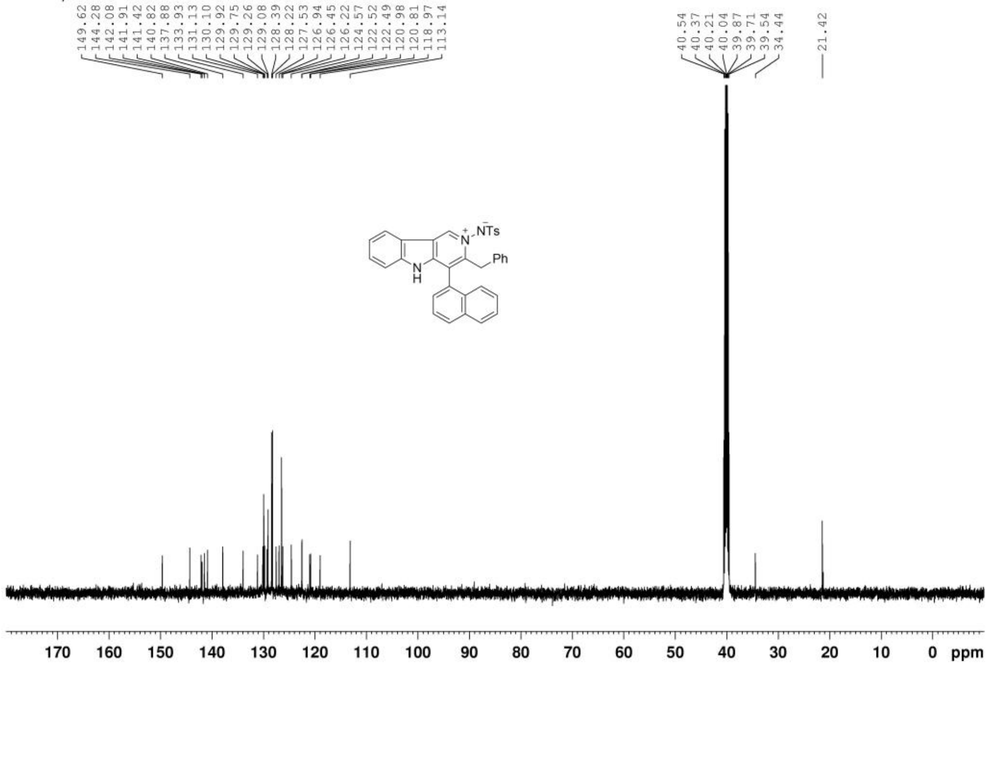
(3-benzyl-4-(3,4-dimethoxyphenyl)-5H-pyrido[4,3-b]indol-2-ium-2-yl)(tosyl)amide (**3ea**)





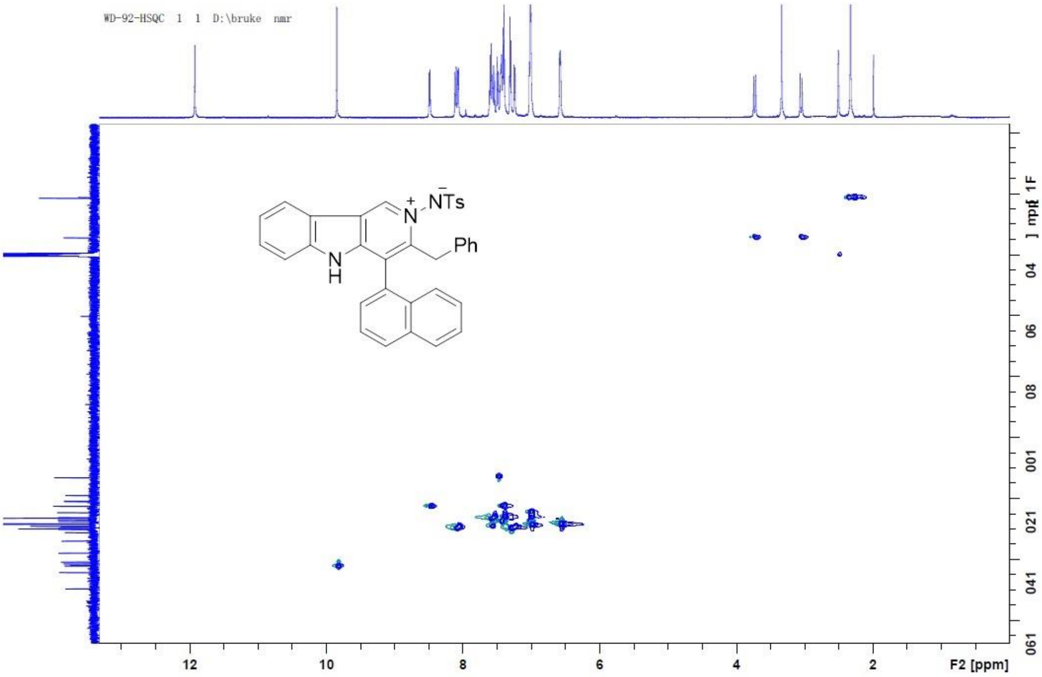
(3-benzyl-4-(naphthalen-1-yl)-5H-pyrido[4,3-b]indol-2-ium-2-yl)(tosyl)amide (**3fa**)



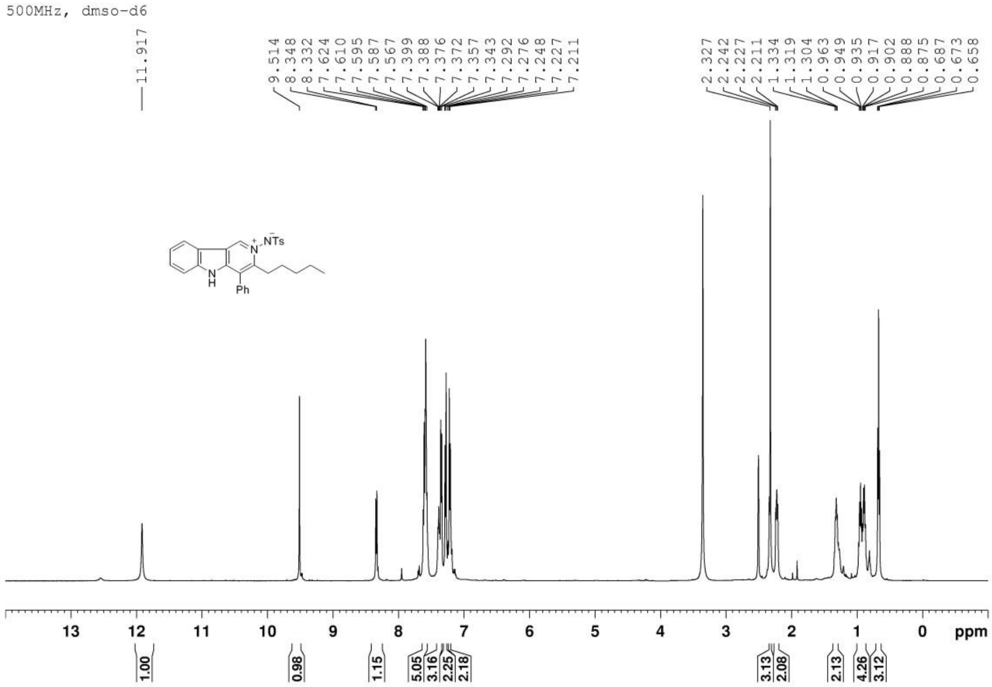


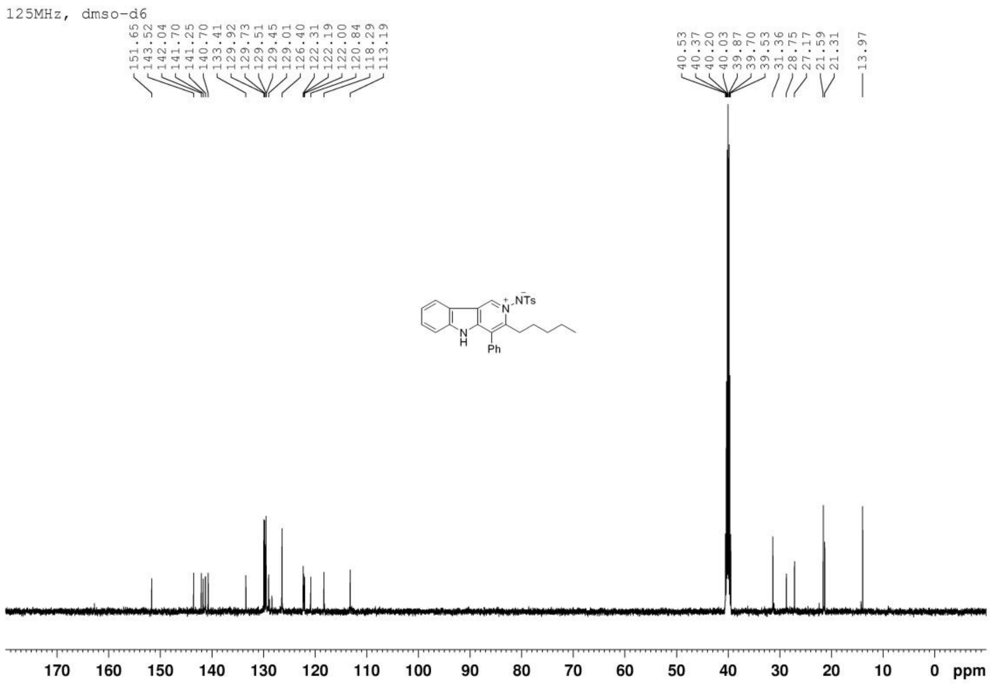
(3-benzyl-4-(naphthalen-1-yl)-5H-pyrido[4,3-b]indol-2-ium-2-yl)(tosyl)amide (**3fa**)

1H-13C HSQC

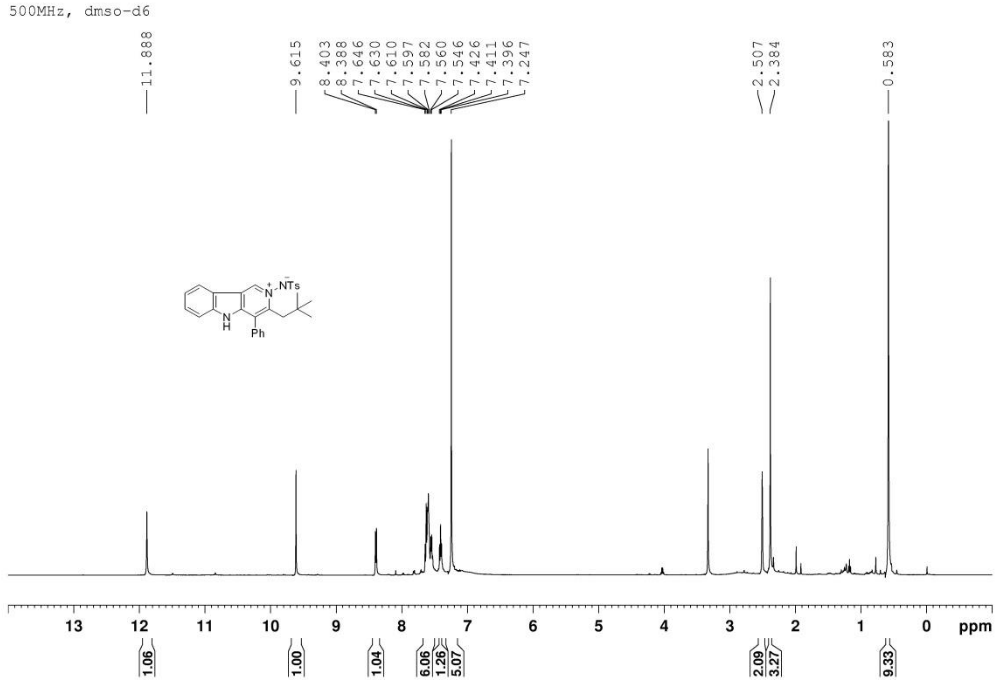


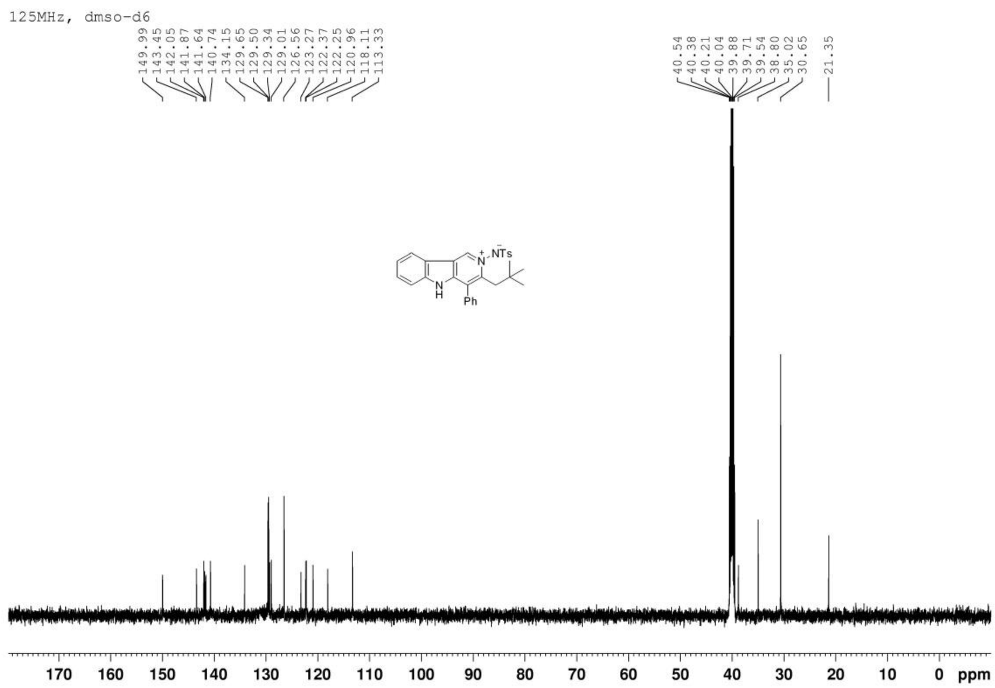
(3-pentyl-4-phenyl-5H-pyrido[4,3-b]indol-2-ium-2-yl)(tosyl)amide (**3ga**)



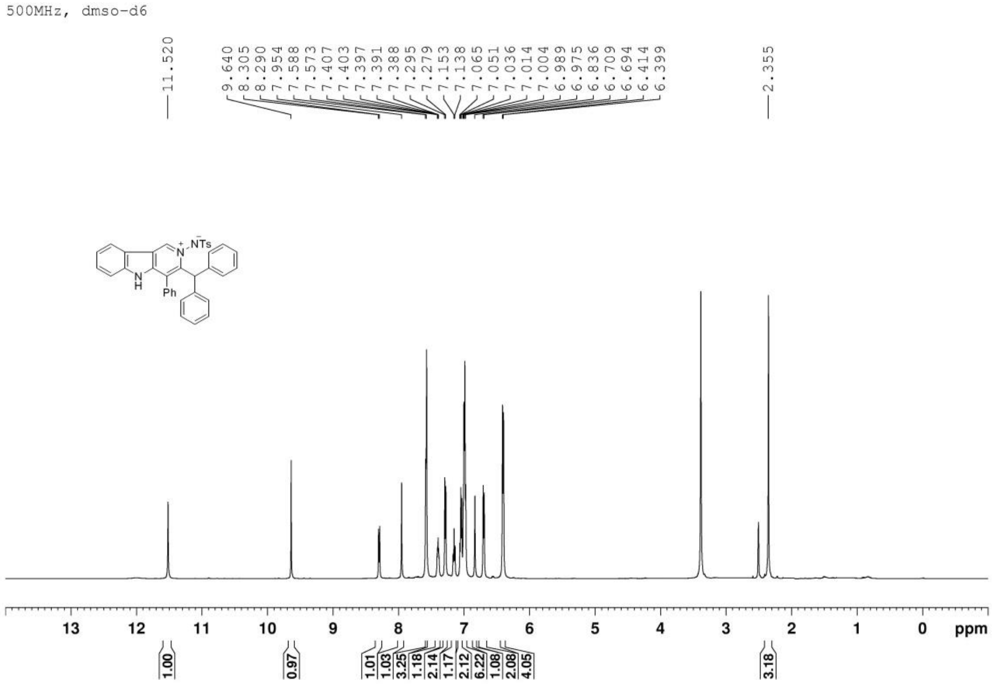


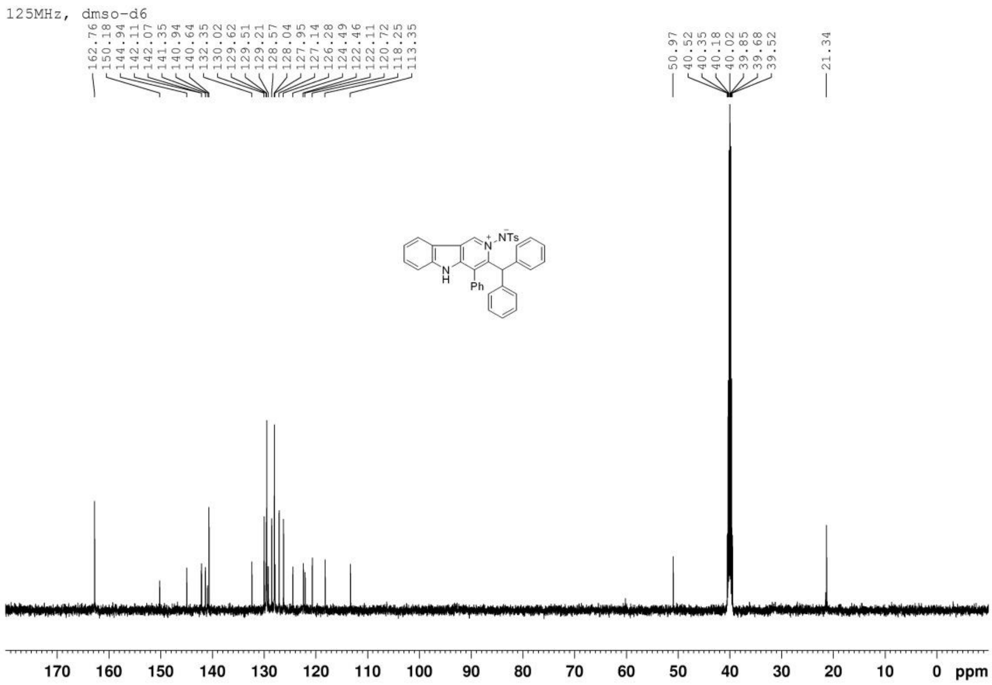
(3-neopentyl-4-phenyl-5H-pyrido[4,3-b]indol-2-ium-2-yl)(tosyl)amide (**3ha**)



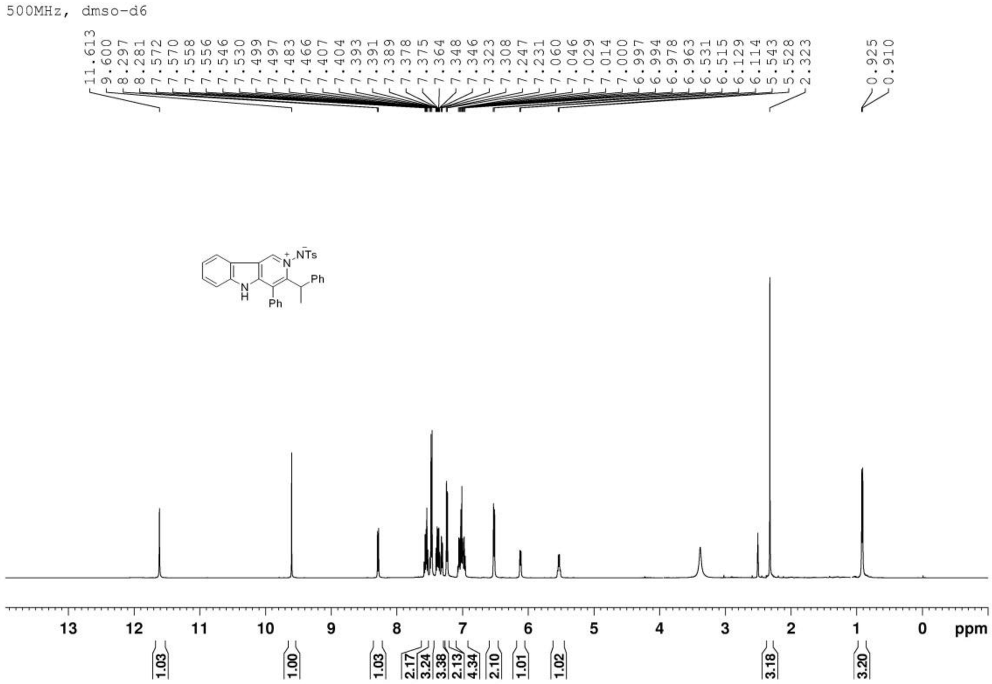


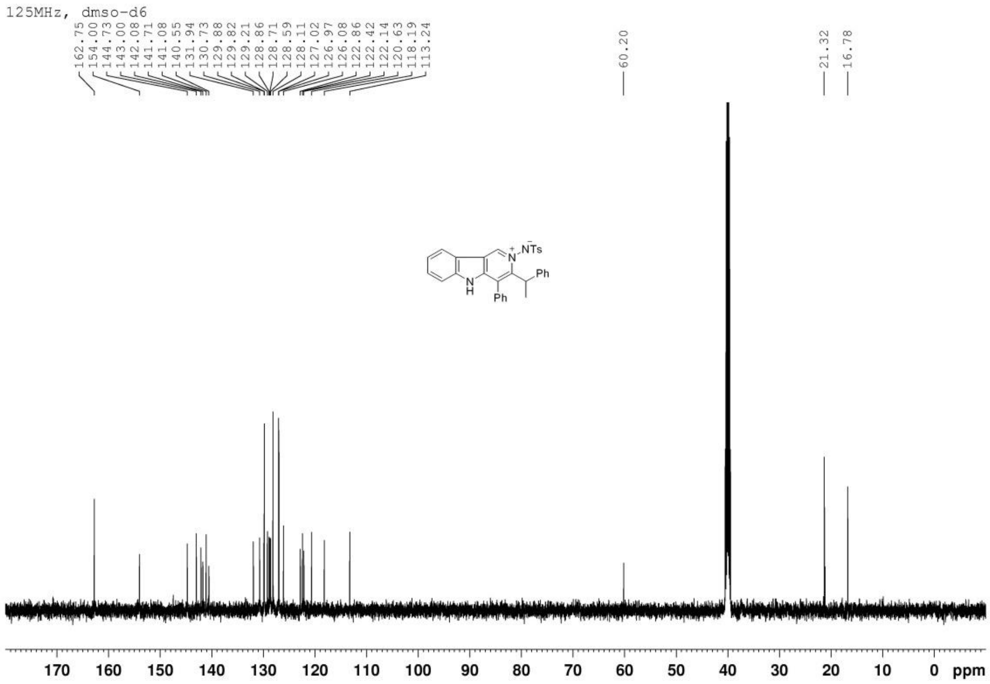
(3-benzhydryl-4-phenyl-5H-pyrido[4,3-b]indol-2-ium-2-yl)(tosyl)amide (**4ja**)



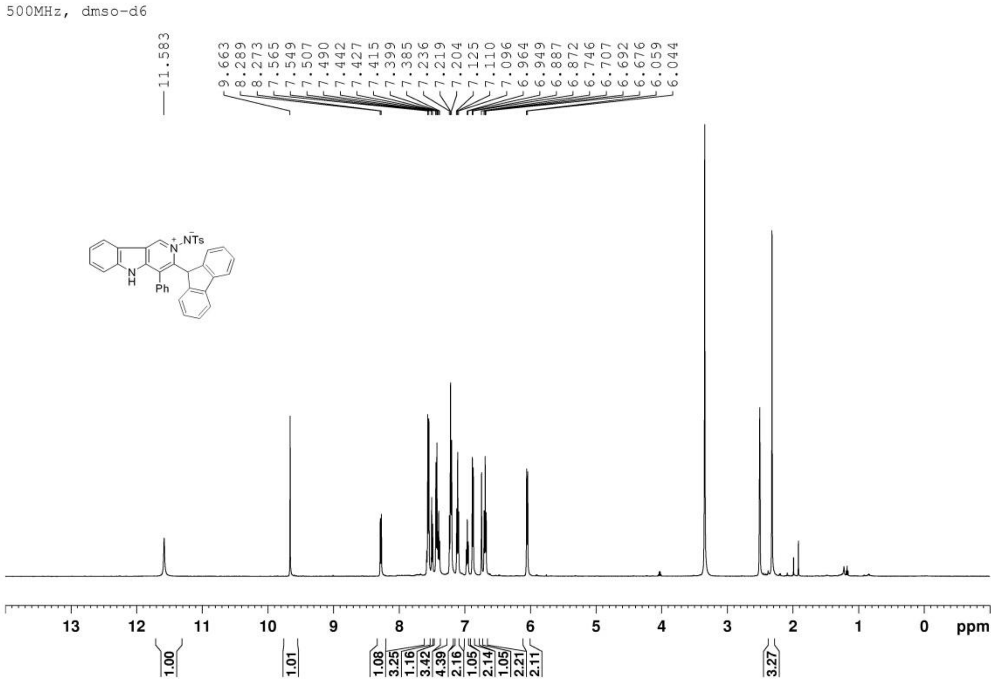


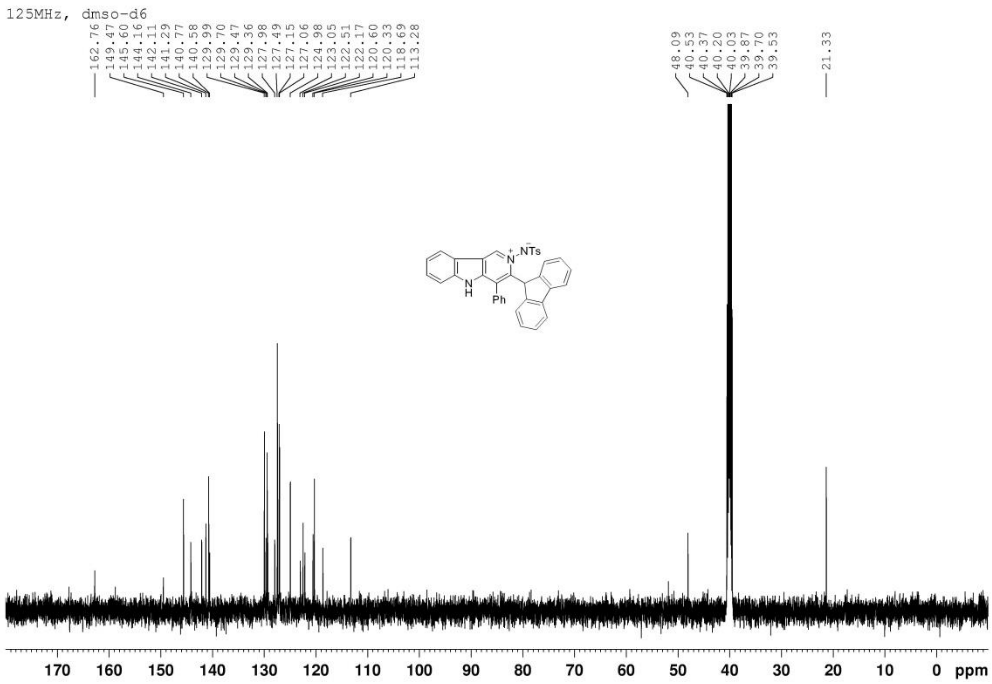
(4-phenyl-3-(1-phenylethyl)-5H-pyrido[4,3-b]indol-2-ium-2-yl)(tosyl)amide (**4ka**)





(3-(9H-fluoren-9-yl)-4-phenyl-5H-pyrido[4,3-b]indol-2-ium-2-yl)(tosyl)amide (**4la**)





N-(2-(3-benzyl-4-phenyl-5H-pyrido[4,3-b]indol-1-yl)phenyl)-4-methylbenzenesulfonamide (**5aa**)