Supporting Information

Accessing pyrrolo[1,2-*a*]indole derivatives via visible-light-induced dearomatizative cyclization of indoles

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1. General information

All reactions were carried out under an atmosphere of nitrogen unless otherwise noted. Colum chromatography was performed using silica gel (200-300 mesh) and thin layer chromatography was performed using silica gel (GF254). ^{1}H NMR and ^{13}C NMR spectra were recorded on Bruker-AV (400 and 100 MHz, respectively) instrument using $CDCl_3$, acetone-d_6 or dimethyl sulfoxide-d_6 as solvent. Mass spectra were measured on Agilent 5975 GC-MS instrument (EI). High-resolution mass spectra (ESI) were obtained with the Thermo Scientific LTQ Orbitrap XL mass spectrometer. The structures of known compounds were further corroborated by comparing their ^{1}H NMR, ^{13}C NMR data and HRMS data with those of literature. Melting points were measured with a YUHUA X-5 melting point instrument and were uncorrected. Reagents were used as received or prepared in our laboratory.

2. General procedure for hydroarylation

Standard conditions A: A 10 mL reaction vessel was charged with 2-methyl-1-(1,2,3,4-tetrahydro-9H-carbazol-9-yl)prop-2-en-1-one (**1a**, 48 mg, 0.2 mmol), NaBr (23 mg, 0.2 mmol, 1 equiv), $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (5 mg, 0.004 mmol), $CF_3SO_3H{\cdot}5H_2O$ (5.4 M, 36 μL, 0.2 mmol), H_2O (54 μL, 15 equiv), 2,2'-bipyridine (15 mg, 0.5 equiv), PhCl (1 mL). The atmosphere was exchanged by applying vacuum and backfilling with argon (this process was conducted for three times). The resulting mixture was stirred at 2000 RPM for 48 hours under irradiation with a 35 W blue LED. The crude reaction mixture was quenched with saturated sodium carbonate and extracted with ethyl acetate (3 × 20 mL). The extracts were combined, dried over sodium sulfate, filtered and the volatiles were removed under reduced pressure. The reaction yield was quantified by separation, and then column chromatography was performed using silica gel (200-300 mesh) or thin layer chromatography was performed using silica gel (GF254) to give product **2a**.

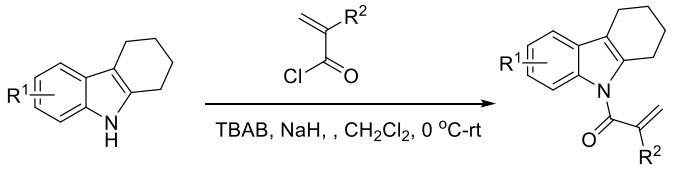
Standard conditions B: A 10 mL reaction vessel was charged with 2-methyl-1-(1,2,3,4-tetrahydro-9H-carbazol-9-yl)prop-2-en-1-one (**1a**, 48 mg, 0.2 mmol), $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (5 mg, 0.004 mmol), $CF_3SO_3H{\cdot}5H_2O$ (5.4 M, 36 μL, 0.2 mmol), CH_3OH (96 μL, 15 equiv), 2,2'-bipyridine (37 mg, 1.2 equiv), PhCl (1 mL). The atmosphere was exchanged by applying vacuum and backfilling with argon (this process was conducted for three times). The resulting mixture was stirred

at 2000 RPM for 48 hours under irradiation with a 35 W blue LED. The crude reaction mixture was quenched with saturated sodium carbonate and extracted with ethyl acetate (3 × 20 mL). The extracts were combined, dried over sodium sulfate, filtered and the volatiles were removed under reduced pressure. The reaction yield was quantified by separation, and then column chromatography was performed using silica gel (200-300 mesh) or thin layer chromatography was performed using silica gel (GF254) to give product **4a**.

3. Procedures for the preparation of acrylamides

3.1 General Procedure for preparation of substrates:

To a solution of aniline **S1** (8.0 mmol) in CH_2Cl_2 (20 mL) was added TBAB (1.03 g, 0.4 equiv) and NaH (640 mg, 2 equiv) at 0℃. Methacryloyl chloride (0.93 mL, 9.6 mmol) was added by dropwise and the resulting solution was stirred at rt for 24 h. Then the reaction mixture was poured into water and the aqueous layer was extracted with CH_2Cl_2 (3×15 mL). The combined organic layers were dried over Na_2SO_4, filtered and concentrated under reduced pressure. The crude product was purified by flash column chromatography (SiO_2; gradient eluent: petroleum ether to 3% EtOAc in petroleum ether) to provide amide **S2** as yellow oil.



S1 **S2**

4. Mechanistic studies

4.1. Stern–Volmer Quenching

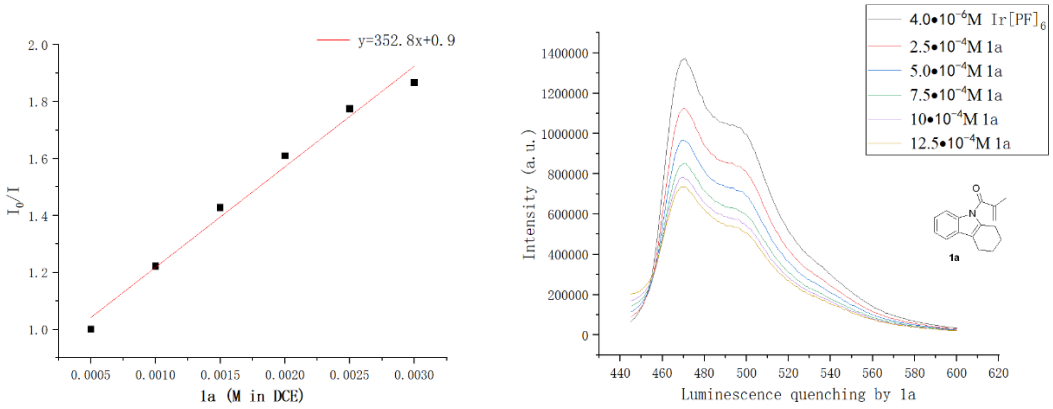
Formulation solution:

2-methyl-1-(1,2,3,4-tetrahydro-9H-carbazol-9-yl)prop-2-en-1-one (**1a**, 597.5 mg) was dissolved in DCE in a 25 mL volumetric flask to set the concentration to be 0.1 M. 2,2'-bipyridine (390 mg) was dissolved in DCE in a 25 mL volumetric flask to set the concentration to be 0.1 M. TfOH (220 μL) was dissolved in acetone in a 25 mL volumetric flask to set the concentration to be 0.1 M. CH_3OH (80 mg) was dissolved

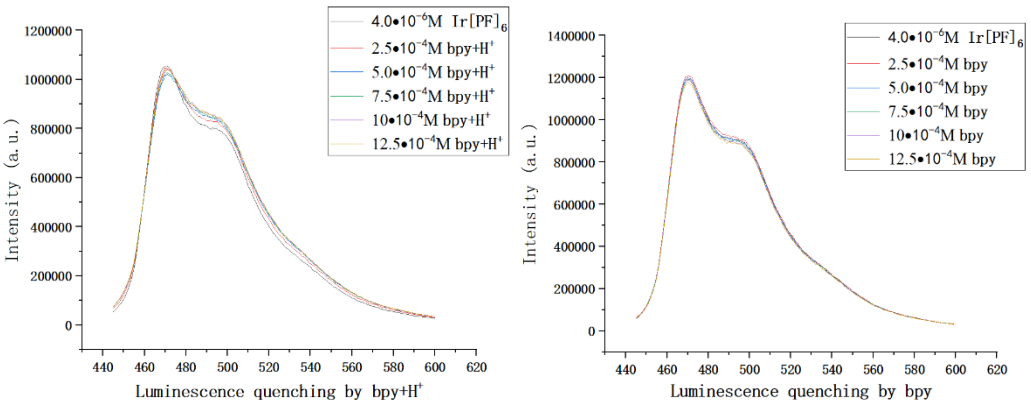
in DCE in a 25 mL volumetric flask to set the concentration to be 0.1 M. Photocatalyst Ir[dF(CF_3)ppy]$_2$(dtbbpy)PF_6 (2.5 mg) was dissolved in DCE (25.0 mL) to set the concentration to be 0.1 mM.

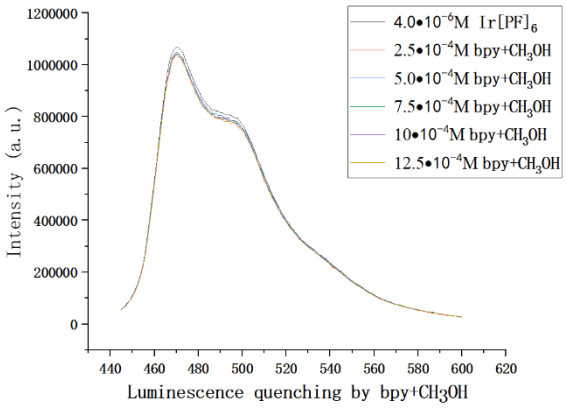
Experimental procedure: The resulting 0.1 M solution (50 μL) was added to cuvette to obtain different concentrations of catalyst solution. This solution was then diluted to a volume of 2.0 mL by adding further solvent (acetone) to prepare a 2.5 μM solution. The resulting mixture was sparged with nitrogen for 3 minutes and then irradiated at 425 nm. Fluorescence emission spectra were recorded (3 trials per sample). Into this solution, 10.0 μL of a **1a** solution was successively added and uniformly stirred, and the resulting mixture was bubbled with nitrogen for 3 minutes and irradiated at 425 nm. Fluorescence emission spectra of 0 μL, 5.0 μL, 10.0 μL, 15.0 μL, 20.0 μL, 25.0 μL, 30.0μL fluorescence intensity. Follow this method and make changes to the amount to obtain the Stern–Volmer relationship in turn.

(a) Ir[dF(CF_3)ppy]$_2$(dtbbpy)PF_6 quenched by **1a**.

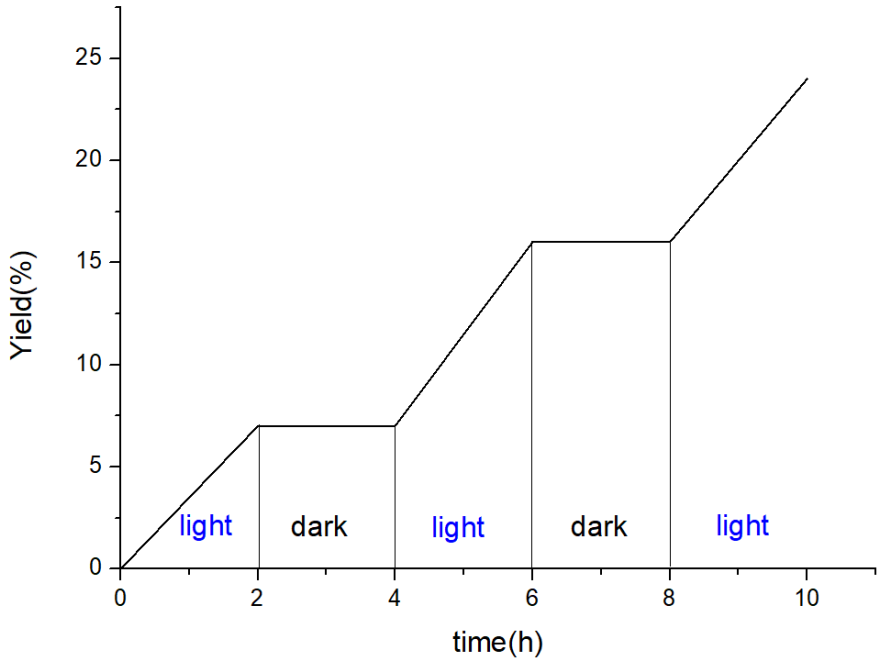


(b) Ir[dF(CF_3)ppy]$_2$(dtbbpy)PF_6 quenched by bpy, bpy + TfOH and bpy + CH_3OH. Linear quenching is not observed.



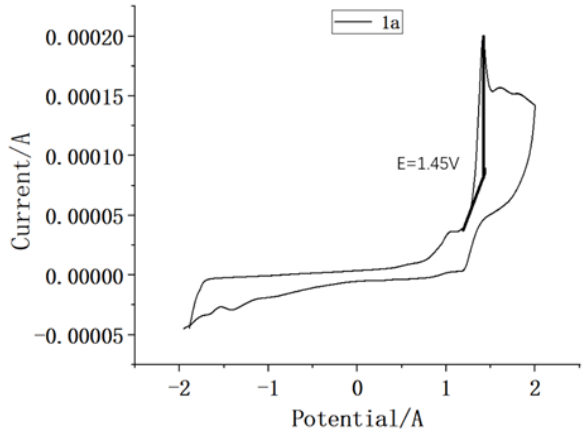


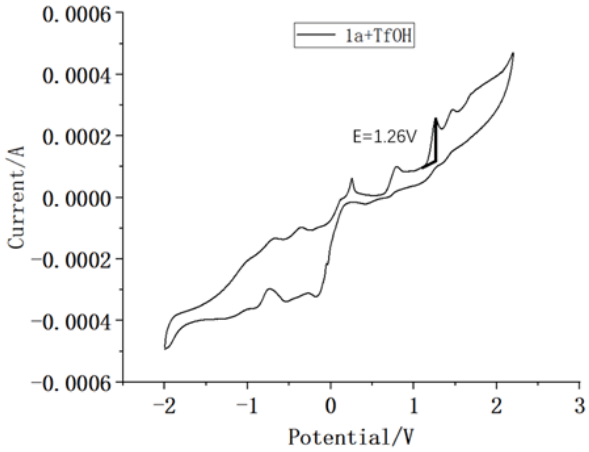
4.2. Switched light on/off experiment



4.3. Cyclic Voltammetry

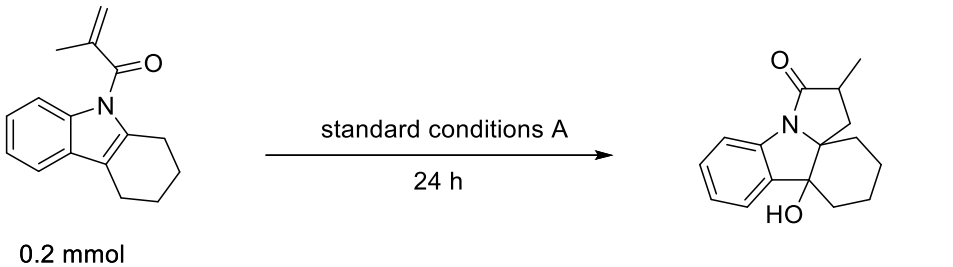
Cyclic voltammograms were recorded with a CHI830b potentiostat at room temperature in MeCN. *n*-Bu_4NBF_4 (0.1 M) was used as the supporting electrolyte, and a glass carbon electrode was used as the working electrode. The auxiliary electrode was a platinum wire electrode. All potentials are referenced against the Hg/Hg_2Cl_2 (SCE) redox couple. The scan rate was 100 $mV \cdot s^{-1}$.





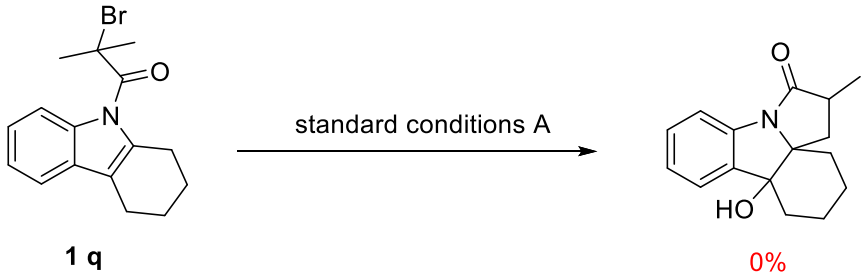
4.4 Radical quenching experiment

The following reaction was carried out under standard condition: A 10 mL reaction vessel was charged with 2-methyl-1-(1,2,3,4-tetrahydro-9H-carbazol-9-yl)prop-2-en-1-one (**1a**, 48 mg, 0.2 mmol), NaBr (23 mg, 0.2 mmol, 1 equiv), $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (5 mg, 0.004 mmol), CF_3SO_3H (5.4 M, 36 μL, 0.2 mmol), 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) (94 mg, 0.6 mmol, 3.0 equiv) or 1,1-Diphenylethylene (108 mg, 0.6 mmol, 3.0 equiv) or 2,6-di-tert-butyl-4-methylphenol (BHT) (132 mg, 3.0 equiv), H_2O (54 μL, 15 equiv), 2,2'-bipyridine (15 mg, 0.5 equiv), PhCl (1 mL). The atmosphere was exchanged by applying vacuum and backfilling with Ar (this process was conducted for three times). The resulting mixture was stirred at 2000 RPM for 24 hours under irradiation with a 35 W blue LED. After completion, the consequence was detected by GC-MS.



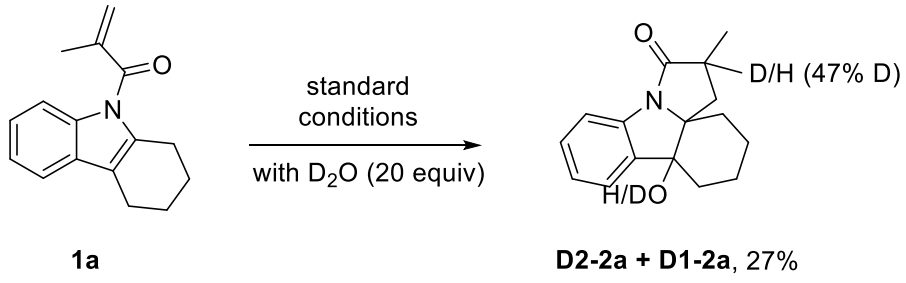
4.5 Possible intermediate

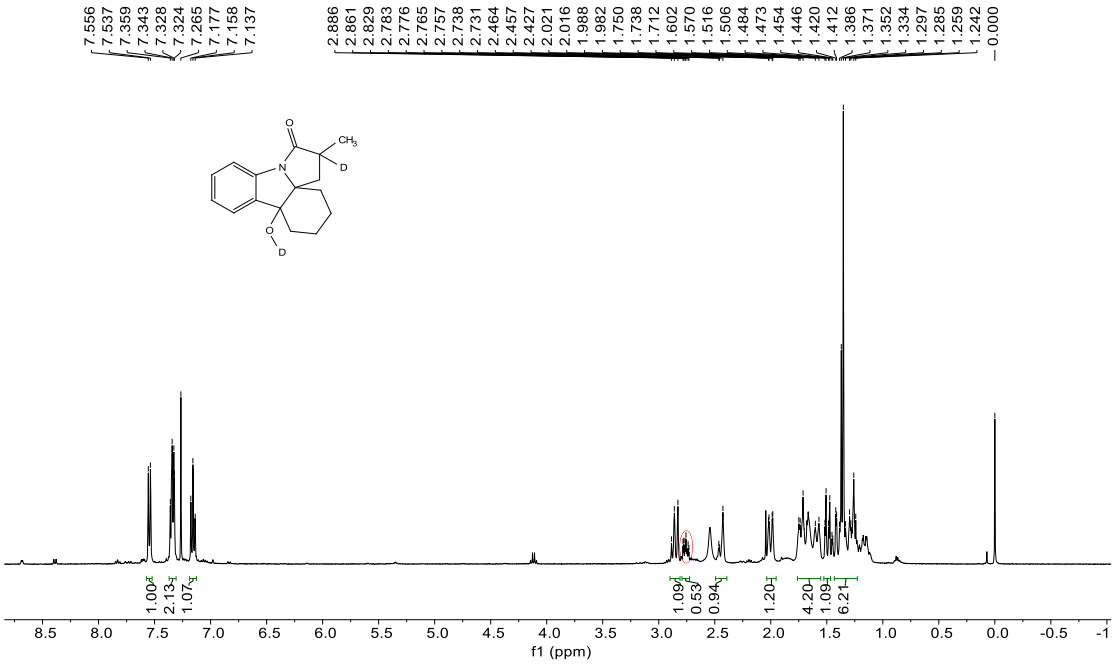
Formation of bromine in ring: A 10 mL reaction vessel was charged with 2-methyl-2-bromo-2-methyl-1-(1,2,3,4-tetrahydro-9H-carbazol-9-yl)propan-1-one (**1q**, 64 mg, 0.2 mmol), NaBr (23 mg, 0.2 mmol, 1 equiv), $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (5 mg, 0.004 mmol), $CF_3SO_3H{\cdot}5H_2O$ (5.4 M, 36 μL, 0.2 mmol), H_2O (54 μL, 15 equiv), 2,2'-bipyridine (15 mg, 0.5 equiv), PhCl (1 mL). The atmosphere was exchanged by applying vacuum and backfilling with argon (this process was conducted for three times). The resulting mixture was stirred at 2000 RPM for 48 hours under irradiation with a 35 W blue LED. The crude reaction mixture was quenched with saturated sodium carbonate and extracted with ethyl acetate (3 × 20 mL). The extracts were combined, dried over sodium sulfate, filtered and the volatiles were removed under reduced pressure. No target product was obtained by TLC analysis.



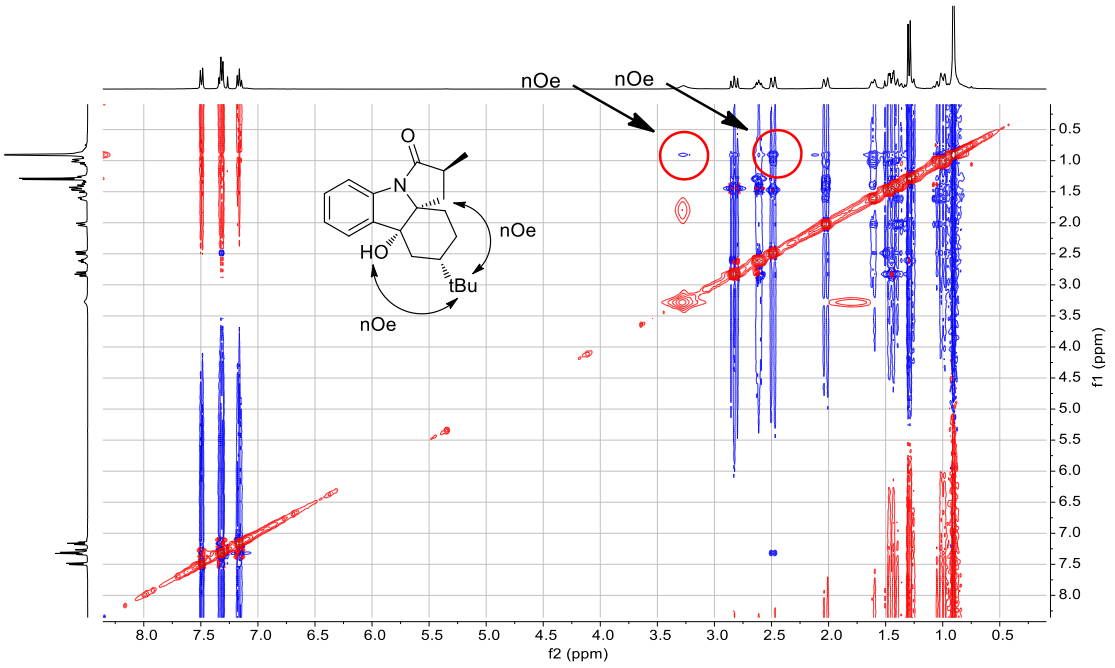
4.6 H/D exchange

Using **D_2O** under standard condition



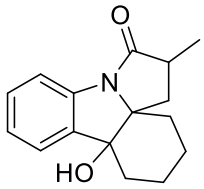


4.7 NOESY spectra of 2-(tert-butyl)-12b-hydroxy-6-methyl-1,3,4,5,6,12b-hexahydro-2H,7H-pyrrolo[2,1-k]carbazol-7-one (2n)



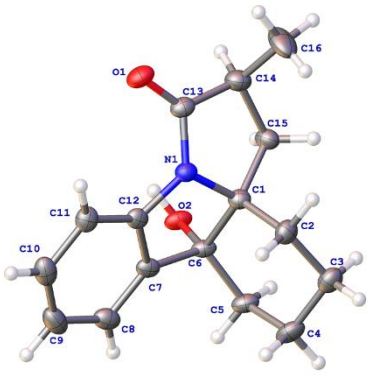
5. Characterization data of products

12b-hydroxy-6-methyl-1,3,4,5,6,12b-hexahydro-2H,7H-pyrrolo[2,1-k]carbazol-7-one (2a)



Prepared according to standard conditions A. Purification by thin layer chromatography was performed (PE/EA: 3/1) to yield **2a** (31 mg, 61%) as a solid. mp: 155 – 157 °C. dr 6:1 (by GC-MS).

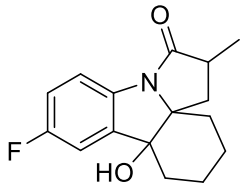
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.51 (d, *J* = 7.6 Hz, 1H), 7.32 (t, *J* = 7.7 Hz, 2H), 7.15 (t, *J* = 7.5 Hz, 1H), 2.88 – 2.78 (m, 1H), 2.70 – 2.61 (m, 1H), 2.44 (d, *J* = 14.5 Hz, 1H), 1.98 (d, *J* = 11.3 Hz, 1H), 1.76 – 1.67 (m, 2H), 1.60 – 1.52 (m, 1H), 1.46 (dd, *J* = 13.0, 3.0 Hz, 1H), 1.38 (dd, *J* = 13.4, 3.0 Hz, 1H), 1.30 (d, *J* = 7.6 Hz, 3H), 1.27 – 1.07 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 175.8, 139.2, 138.9, 129.6, 125.1, 123.0, 117.7, 78.1, 74.6, 42.2, 38.6, 30.6, 30.2, 22.8, 21.8, 19.6. HRMS (ESI): m/z calcd for $C_{16}H_{20}NO_2^+$ $(M+H)^+$: 258.1489; found: 258.1489.



CCDC 2338949

Crystal Data for **2a**: $C_{16}H_{19}NO_2$ (*M* =257.32 g/mol): monoclinic, space group $P2_1/c$ (no. 14), *a* = 16.3685(3) Å, *b* = 10.1416(2) Å, *c* = 33.0222(7) Å, *β* = 92.147(2)°, *V* = 5477.93(19) Å^3, *Z* = 16, *T* = 295.62(13) K, μ(Cu Kα) = 0.652 mm^{-1}, *Dcalc* = 1.248 g/cm^3, 39310 reflections measured (5.356° ≤ 2Θ ≤ 133.196°), 9638 unique (R_{int} = 0.0723, R_{sigma} = 0.0562) which were used in all calculations. The final R_1 was 0.0728 (I > 2σ(I)) and wR_2 was 0.2424 (all data).

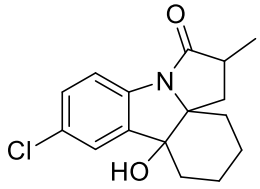
11-fluoro-12b-hydroxy-6-methyl-1,3,4,5,6,12b-hexahydro-2H,7H-pyrrolo[2,1-k]carbazol-7-one (2b)



Prepared according to standard conditions A. Purification by thin layer chromatography was performed (PE/EA: 3/1) to yield **2b** (45 mg, 69%) as a solid. mp: 139 – 140 ^{o}C. dr 4.8:1 (by GC-MS).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.37 (dd, *J* = 8.5, 4.5 Hz, 1H), 7.05 (dd, *J* = 7.9, 2.5 Hz, 1H), 6.97 (dd, *J* = 8.7, 2.5 Hz, 1H), 3.69 (brs, 1H), 2.85 – 2.75 (m, 1H), 2.61 – 2.48 (m, 1H), 2.42 – 2.30 (m, 1H), 1.96 (d, *J* = 13.3 Hz, 1H), 1.78 – 1.62 (m, 2H), 1.58 (d, *J* = 12.6 Hz, 1H), 1.44 (dd, J = 13.1, 3.0 Hz, 1H), 1.34 (dd, J = 13.5, 2.7 Hz, 1H), 1.26 (d, *J* = 7.7 Hz, 3H), 1.21 – 1.07 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 175.8, 160.3 (J_{C-F} = 243 Hz), 141.5 (J_{C-F} = 7 Hz), 134.9, 118.6 (J_{C-F} = 8 Hz), 115.9 (J_{C-F} = 24 Hz), 110.7 (J_{C-F} = 24 Hz), 78.0, 75.0, 42.0, 38.3, 30.6, 30.1, 22.7. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -116.14. HRMS (ESI): m/z calcd for $C_{16}H_{19}FNO_2^+$ $(M+H)^+$: 276.1394; found: 276.1397.

11-chloro-12b-hydroxy-6-methyl-1,3,4,5,6,12b-hexahydro-2H,7H-pyrrolo[2,1-k]carbazol-7-one (2c)

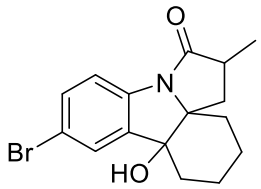


Prepared according to standard conditions A. Purification by thin layer chromatography was performed (PE/EA: 3/1) to yield **2c** (44 mg, 76%) as a solid. mp: 144 – 146 ^{o}C. dr 3:1.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.44 (d, *J* = 8.0 Hz, 0.25H), 7.34 (d, *J* = 8.0 Hz, 0.75H), 7.31 – 7.23 (m, 2H), 3.66 (brs, 1H), 3.11 – 2.98 (m, 0.25H), 2.80 (dd, *J* = 12.8,

11.0 Hz, 0.75H), 2.62 – 2.50 (m, 0.75H), 2.45 – 2.33 (m, 1H), 2.23 (t, *J* = 12.2 Hz, 0.25H), 2.08 – 1.92 (m, 0.25H), 1.79 – 1.53 (m, 3H), 1.45 (dd, *J* = 13.1, 3.0 Hz, 0.75H), 1.35 – 1.10 (m, 6H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 175.9, 172.8, 141.3, 140.8, 137.4, 136.3, 130.2, 129.8, 129.4, 123.7, 118.7, 117. 8, 78.1, 74.9, 72.9, 42.1, 40.5, 38.3, 31.4, 30.9, 30.5, 30.1, 22.8, 22.7, 21.9, 21.7, 19.5, 15.2. HRMS (ESI): m/z calcd for $C_{16}H_{19}ClNO_2^+$ $(M+H)^+$: 292.1099; found: 292.1099.

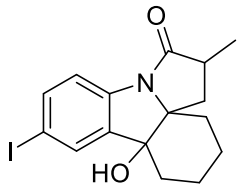
11-bromo-12b-hydroxy-6-methyl-1,3,4,5,6,12b-hexahydro-2H,7H-pyrrolo[2,1-k]carbazol-7-one (2d)



Prepared according to standard conditions A. Purification by thin layer chromatography was performed (PE/EA: 3/1) to yield **2d** (51 mg, 77%) as a solid. mp: 147 – 150 °C. dr 5.7:1.

^{1}H NMR (400 MHz, Chloroform-*d*) δ7.44 (d, *J* = 8.0 Hz, 0.15H), 7.34 (d, J = 8.2 Hz, 0.85H), 7.30 (t, J = 2.4 Hz, 1H), 7.25 (d, J = 8.3, 0.7H), 7.24 (d, J = 8.0 Hz, 0.3H), 3.67 (brs, 1H), 3.12 – 2.97 (m, 0.15H), 2.80 (dd, *J* = 13.1, 10.7 Hz, 1H), 2.63 – 2.52 (m, 0.85H), 2.42 – 2.34 (m, 1H), 2.23 (t, *J* = 11.8 Hz, 0.15H), 2.05-1.95 (m, 1H), 1.75 – 1.53 (m, 3H), 1.45 (dd, *J* = 13.1, 3.0 Hz, 1H), 1.39 – 1.10 (m, 6H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 175.8, 172.8, 141.5, 137.4, 130.2, 129.4, 123.7, 118.6, 117.8, 78.0, 74.8, 42.1, 38.3, 30.5, 30.1, 22. 6, 21.6, 19.4. HRMS (ESI): m/z calcd for $C_{16}H_{19}BrNO_2^+$ $(M+H)^+$: 336.0594; found: 336.0594.

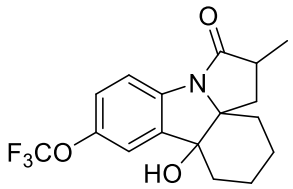
12b-hydroxy-11-iodo-6-methyl-1,3,4,5,6,12b-hexahydro-2H,7H-pyrrolo[2,1-k]carbazol-7-one (2e)



Prepared according to standard conditions A. Purification by thin layer chromatography was performed (PE/EA: 3/1) to yield **2e** (48 mg, 63%) as a solid. mp: 190 – 194 °C. dr 10:1.

^{1}H NMR (400 MHz, Chloroform-*d*) δ7.62 (d, J = 2.4 Hz, 1.8H), 7.60 (d, J = 1.7 Hz, 0.2H), 7.29 (d, J = 8.6 Hz, 0.1H), 7.19 (d, *J* = 8.1 Hz, 0.9H), 3.55 (brs, 1H), 3.04 (m, 0.1H), 2.79 (dd, *J* = 12.8, 11.0 Hz, 1H), 2.58 (m, 0.9H), 2.37 (d, *J* = 12.7 Hz, 1H), 1.96 (d, *J* = 13.4 Hz, 1H), 1.77 – 1.53 (m, 3H), 1.45 (dd, *J* = 13.1, 3.0 Hz, 1H), 1.39 – 1.07 (m, 6H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 175.9, 170.9, 141.9, 138.5, 138.2, 132.4, 119.6, 88.2, 78.0, 74.7, 42.2, 38.4, 30.5, 30.0, 22.7, 21.6, 19. 5. HRMS (ESI): m/z calcd for $C_{16}H_{19}INO_2^+$ $(M+H)^+$: 384.0455; found: 384.0456.

12b-hydroxy-6-methyl-11-(trifluoromethoxy)-1,3,4,5,6,12b-hexahydro-2H,7H-pyrrolo[2,1-k]carbazol-7-one (2f)

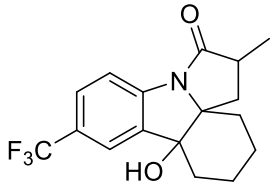


Prepared according to standard conditions A. Purification by thin layer chromatography was performed (PE/EA: 3/1) to yield **2f** (73 mg, 63%) as a solid. mp: 133 – 135 °C. dr 9:1.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.49 (d, J = 8.3 Hz, 0.1H), 7.41 (d, *J* = 8.4 Hz, 0.9H), 7.20 (s, 1H), 7.15 (d, *J* = 8.4 Hz, 1H), 4.22 (brs, 1H), 3.02 (m, 0.1H), 2.84 – 2.70 (m, 1H), 2.39 – 2.32 (m, 1.9H), 2.23 (t, J = 11.8 Hz, 0.1H), 1.95 (d, *J* = 12.9 Hz, 1H), 1.77 – 1.53 (m, 2H), 1.57 (d, J = 12.5 Hz, 1H), 1.42 (dd, *J* = 13.2, 2.9 Hz, 1H), 1.38 – 1.06 (m, 6H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 176.1, 146.3, 141.5, 137.4,

122.3, 120.3 ($J_{C\text{-}F}$ = 255 Hz), 118.3, 77.9, 75.0, 42.0, 38.4, 30.5, 30.1, 22.6, 21.6, 19.2. HRMS (ESI): m/z calcd for $C_{17}H_{18}F_3KNO_3^+$ $(M+K)^+$: 380.0870; found: 380.0875.

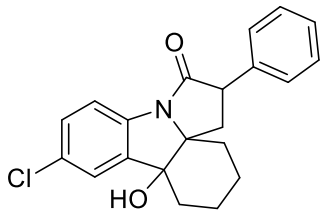
12b-hydroxy-6-methyl-11-(trifluoromethyl)-1,3,4,5,6,12b-hexahydro-2H,7H-pyrrolo[2,1-k]carbazol-7-one (2g)



Prepared according to standard conditions A. Purification by thin layer chromatography was performed (PE/EA: 3/1) to yield **2g** (32 mg, 51%) as a solid. mp: 194 – 196 °C. dr 10:1 (by GC-MS).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.59 (d, *J* = 8.3 Hz, 2H), 7.54 (d, *J* = 7.9 Hz, 1H), 3.35 (s, 1H), 2.84 (dd, *J* = 12.9, 11.0 Hz, 1H), 2.64 – 2.55 (m, 1H), 2.46 (d, *J* = 14.6 Hz, 1H), 2.01 (d, *J* = 15.1 Hz, 1H), 1.81 – 1.71 (m, 2H), 1.60 (d, *J* = 13.8 Hz, 1H), 1.49 (dd, *J* = 13.1, 3.1 Hz, 1H), 1.35 – 1.08 (m, 6H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 176.1, 141.7, 140.1, 127.2 ($J_{C\text{-}F}$ = 32 Hz), 127.1 ($J_{C\text{-}F}$ = 4 Hz), 124.1 ($J_{C\text{-}F}$ = 270 Hz), 120.4 ($J_{C\text{-}F}$ = 4 Hz), 117.5, 77.9, 74.7, 42.2, 38.4, 30.5, 30.0, 22.6, 21.5, 19.3. HRMS (ESI): m/z calcd for $C_{17}H_{18}F_3KNO_2^+$ $(M+K)^+$: 364.0921; found: 364.0926.

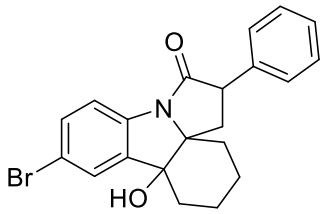
11-chloro-12b-hydroxy-6-phenyl-1,3,4,5,6,12b-hexahydro-2H,7H-pyrrolo[2,1-k]carbazol-7-one (2h)



Prepared according to standard conditions A. Purification by thin layer chromatography was performed (PE/EA: 3/1) to yield **2h** (47 mg, 70%) as a solid. mp: 233 – 237 °C. dr >20:1 (by GC-MS).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.48 (d, *J* = 7.9 Hz, 1H), 7.36 – 7.28 (m, 4H), 7.23 (d, *J* = 7.3 Hz, 1H), 7.19 (d, *J* = 7.3 Hz, 2H), 3.82 (dd, *J* = 11.4, 3.3 Hz, 1H), 3.72 (s, 1H), 3.17 – 3.08 (m, 1H), 2.38 (d, *J* = 14.7 Hz, 1H), 1.98 – 1.85 (m, 2H), 1.69 (t, *J* = 11.9 Hz, 2H), 1.51 (d, *J* = 8.7 Hz, 1H), 1.38 – 1.07 (m, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 172.9, 141.5, 140.4, 137.4, 130.6, 129.6, 128.8, 127.4, 126.9, 123.8, 118.9, 78.1, 75.0, 52.7, 37.5, 30.9, 30. 6, 22.6, 21.6

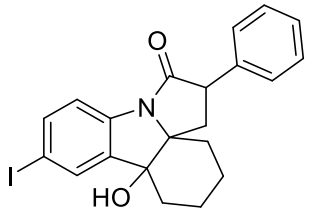
11-bromo-12b-hydroxy-6-phenyl-1,3,4,5,6,12b-hexahydro-2H,7H-pyrrolo[2,1-k]carbazol-7-one (2i)



Prepared according to standard conditions A. Purification by thin layer chromatography was performed (PE/EA: 3/1) to yield **2i** (59 mg, 74%) as a solid. mp: 204 – 209 ºC. dr >20:1 (by GC-MS).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.52 – 7.42 (m, 3H), 7.33 (t, *J* = 7.4 Hz, 2H), 7.26 (d, *J* = 7.6 Hz, 1H), 7.18 (d, *J* = 7.6 Hz, 2H), 3.80 (dd, *J* = 11.3, 2.9 Hz, 1H), 3.73 (s, 1H), 3.12 (t, *J* = 12.4 Hz, 1H), 2.38 (d, *J* = 14.9 Hz, 1H), 1.98 – 1.85 (m, 2H), 1.70 (dd, *J* = 19.0, 9.0 Hz, 2H), 1.52 (d, *J* = 10.9 Hz, 1H), 1.35 – 1.11 (m, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 173.0, 141.9, 140.4, 137.9, 132.6, 128.8, 127.5, 126.7, 118.2, 78.2, 74.9, 52.8, 37.6, 30.9, 30.6, 22.7, 21.6. HRMS (ESI): m/z calcd for $C_{21}H_{21}BrNO_2^+$ $(M+H)^+$: 398.0750; found: 398.0752.

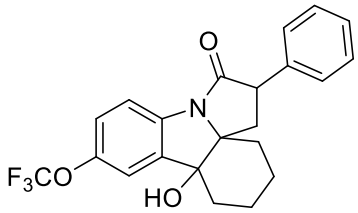
12b-hydroxy-11-iodo-6-phenyl-1,3,4,5,6,12b-hexahydro-2H,7H-pyrrolo[2,1-k]carbazol-7-one (2j)



Prepared according to standard conditions A. Purification by thin layer chromatography was performed (PE/EA: 3/1) to yield **2j** (66 mg, 75%) as a solid. mp: 182 – 185 °C. dr >20:1 (by GC-MS).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.70 – 7.64 (m, 2H), 7.34 (t, *J* = 8.0 Hz, 3H), 7.23 (d, *J* = 7.4 Hz, 1H), 7.17 (d, *J* = 7.3 Hz, 2H), 3.79 (dd, *J* = 11.4, 3.3 Hz, 1H), 3.71 (s, 1H), 3.17 – 3.05 (m, 1H), 2.37 (d, *J* = 14.8 Hz, 1H), 1.99 – 1.83 (m, 2H), 1.75 – 1.62 (m, 2H), 1.55 – 1.45 (m, 1H), 1.37 – 1.08 (m, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 173.0, 142.1, 138.5, 128.9, 127.5, 127.0, 119. 9, 88.8, 78.2, 74.8, 52.8, 37.6, 30.9, 30.6, 22. 7, 21.6. HRMS (ESI): m/z calcd for $C_{21}H_{20}INNaO_2^+$ $(M+Na)^+$: 468.0431; found: 468.0432.

12b-hydroxy-6-phenyl-11-(trifluoromethoxy)-1,3,4,5,6,12b-hexahydro-2H,7H-pyrrolo[2,1-k]carbazol-7-one (2k)

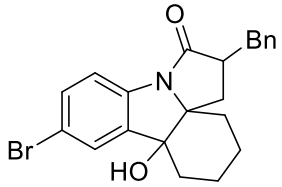


Prepared according to standard conditions A. Purification by thin layer chromatography was performed (PE/EA: 3/1) to yield **2k** (50 mg, 62%) as a solid. mp: 170 – 173 °C. dr >20:1 (by GC-MS).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.60 (d, *J* = 8.1 Hz, 1H), 7.33 (t, *J* = 7.4 Hz, 2H), 7.25 – 7.18 (m, 5H), 3.90 (dd, *J* = 11.3, 3.3 Hz, 1H), 3.33 (s, 1H), 3.20 – 3.10 (m, 1H), 2.40 (d, *J* = 14.8 Hz, 1H), 2.00 – 1.90 (m, 2H), 1.70 (dd, *J* = 28.5, 15.8 Hz, 2H), 1.53 (d, *J* = 11.9 Hz, 1H), 1.40 – 1.08 (m, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 173.1, 146.4, 141.4, 140.3, 137. 5, 128.8, 127.4, 127.0, 122. 6,120.4 (J_{C-F} = 255 Hz),

116.6, 78.2, 75.1, 52.7, 37. 5, 31.0, 30.6, 22.6, 21.5. HRMS (ESI): m/z calcd for $C_{22}H_{20}F_3NNaO_3^+$ $(M+Na)^+$: 426.1287; found: 426.1289.

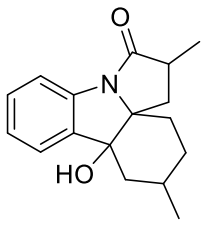
6-benzyl-11-bromo-12b-hydroxy-1,3,4,5,6,12b-hexahydro-2H,7H-pyrrolo[2,1-k]carbazol-7-one (2l)



Prepared according to standard conditions A. Purification by thin layer chromatography was performed (PE/EA: 3/1) to yield **2l** (49 mg, 60%) as a solid. mp: 210 – 213 °C. dr >20:1 (by GC-MS).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.48 – 7.41 (m, 3H), 7.33 (t, *J* = 7.4 Hz, 2H), 7.25 (d, *J* = 10.0 Hz, 2H), 7.15 (d, *J* = 7.4 Hz, 2H), 3.18 (s, 1H), 3.10 (dd, *J* = 13.5, 4.0 Hz, 1H), 2.96 – 2.87 (m, 1H), 2.80 (dd, *J* = 13.4, 10.2 Hz, 1H), 2.65 – 2.56 (m, 1H), 2.36 (d, *J* = 12.9 Hz, 1H), 1.75 – 1.48 (m, 4H), 1.28 – 1.10 (m, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 174.6, 141.6, 138.9, 138.1, 132.5, 129.1, 128.6, 126.5, 126.5, 119.2, 117.9, 78.3, 74.7, 48.8, 38.7, 37.9, 30.5, 26.5, 22.7, 21.5. HRMS (ESI): m/z calcd for $C_{22}H_{22}BrNNaO_2^+$ $(M+Na)^+$: 434.0726; found: 434.0727.

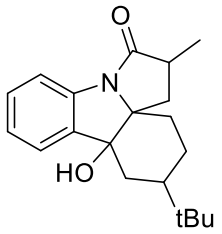
12b-hydroxy-2,6-dimethyl-1,3,4,5,6,12b-hexahydro-2H,7H-pyrrolo[2,1-k]carbazol-7-one (2m)



Prepared according to standard conditions A. Purification by thin layer chromatography was performed (PE/EA: 3/1) to yield **2m** (33 mg, 61%) as a solid. mp: 190 – 196 °C. dr 6:1 (by GC-MS).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.47 (d, *J* = 7.7 Hz, 1H), 7.36 – 7.28 (m, 2H), 7.15 (t, *J* = 7.4 Hz, 1H), 2.85 – 2.76 (m, 1H), 7.18 – 7.11 (m, 1H), 2.41 (dd, *J* = 10.4, 1.8 Hz, 1H), 1.95 (d, *J* = 13.2 Hz, 1H), 1.54 – 1.30 (m, 5H), 1.26 (d, *J* = 7.7 Hz, 3H), 0.97 (d, *J* = 5.9 Hz, 3H), 0.84 (d, *J* = 6.8 Hz, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 175.9, 139.5, 138.8, 129.5, 125.1, 123.0, 117.6, 78.2, 74.2, 42.2, 39.3, 38.1, 30.3, 30.2, 29.5, 21.9, 19.5. HRMS (ESI): m/z calcd for $C_{17}H_{21}NO_2^+$ $(M+H)^+$: 272.1645; found: 272.1645.

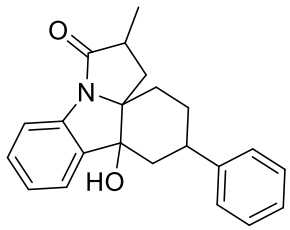
2-(tert-butyl)-12b-hydroxy-6-methyl-1,3,4,5,6,12b-hexahydro-2H,7H-pyrrolo[2,1-k]carbazol-7-one (2n)



Prepared according to standard conditions A. Purification by thin layer chromatography was performed (PE/EA: 3/1) to yield **2n** (39 mg, 62%) as a solid. mp: 183 – 185 ^{o}C. dr 5:1 (by GC-MS).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.47 (d, *J* = 7.9 Hz, 1H), 7.31 (t, *J* = 7.1 Hz, 2H), 7.15 (t, *J* = 7.5 Hz, 1H), 3.56 (s, 1H), 2.87 – 2.76 (m, 1H), 2.62 – 2.44 (m, 2H), 2.01 (d, *J* = 13.7 Hz, 1H), 1.60 (d, *J* = 10.6 Hz, 1H), 1.51 – 1.33 (m, 3H), 1.26 (d, *J* = 7.6 Hz, 3H), 1.06 – 0.96 (m, 2H), 0.90 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 175.8, 139.5, 138.6, 129.4, 125.1, 117.6, 78.7, 74.2, 44.5, 42.2, 38.3, 32.1, 31.9, 30.2, 27.3, 22.8, 19.5. HRMS (ESI): m/z calcd for $C_{20}H_{28}NO_2^+$ $(M+H)^+$: 314.2115; found: 314.2115.

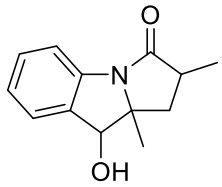
12b-hydroxy-6-methyl-2-phenyl-1,3,4,5,6,12b-hexahydro-2H,7H-pyrrolo[2,1-k]carbazol-7-one (2o)



Prepared according to standard conditions A. Purification by thin layer chromatography was performed (PE/EA: 3/1) to yield **2o** (37 mg, 56%) as a solid. mp: 180 – 183 °C. dr 7:1 (by GC-MS).

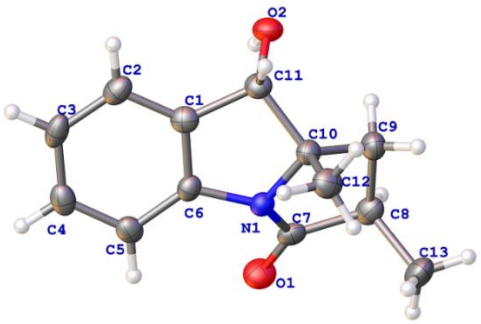
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.56 (d, *J* = 7.7 Hz, 1H), 7.36 (dt, *J* = 24.2, 7.3 Hz, 4H), 7.27 – 7.20 (m, 4H), 3.04 (s, 1H), 2.98 – 2.88 (m, 1H), 2.75 – 2.60 (m, 2H), 2.52 (t, *J* = 12.3 Hz, 1H), 2.12 (d, *J* = 13.3 Hz, 1H), 2.05 – 1.93 (m, 1H), 1.81 – 1.48 (m, 4H), 1.34 (d, *J* = 7.6 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 175.9, 145.0, 139.0, 129.8, 128.6, 126.7, 126.5, 125.3, 122.9, 117.8, 78.5, 74.0, 42.2, 40.7, 38.4, 37.9, 30.3, 29.7, 19.6. HRMS (ESI): m/z calcd for $C_{22}H_{23}KNO_2^+$ $(M+K)^+$: 372.1360; found: 372.1361.

9-hydroxy-2,9a-dimethyl-1,2,9,9a-tetrahydro-3H-pyrrolo[1,2-a]indol-3-one (2p)



Prepared according to standard conditions A. Purification by thin layer chromatography was performed (PE/EA: 3/1) to yield **2p** (24 mg, 56%) as a solid. mp: 207 – 210 °C. dr 10:1 (by GC-MS).

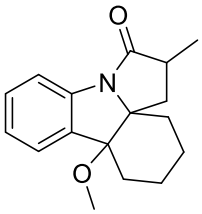
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.51 (t, *J* = 6.6 Hz, 2H), 7.33 (td, *J* = 7.7, 1.0 Hz, 1H), 7.22 – 7.10 (m, 1H), 4.28 (s, 1H), 2.84 (dd, *J* = 13.3, 10.5 Hz, 1H), 2.31 – 2.22 (m, 1H), 1.44 (dd, *J* = 13.3, 2.3 Hz, 1H), 1.32 (s, 3H), 1.26 (d, *J* = 7.7 Hz, 4H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 176.8, 138.5, 136.2, 129.9, 126.8, 125.1, 116.5, 76.4, 71.4, 41.7, 31.9, 26.8, 19.0. HRMS (ESI): m/z calcd for $C_{13}H_{15}NNaO_2^+$ $(M+Na)^+$: 240.0995; found: 240.1384.



CCDC 2338950

Crystal Data for **2p**: $C_{13}H_{15}NO_2$ (*M* =217.26 g/mol): monoclinic, space group $P2_1/c$ (no. 14), *a* = 19.4445(16) Å, *b* = 8.0850(5) Å, *c* = 15.4094(13) Å, *β* = 111.936(10)°, *V* = 2247.1(3) $Å^3$, *Z* = 8, *T* = 149.99(10) K, μ(Mo Kα) = 0.087 mm^{-1}, *Dcalc* = 1.284 g/cm^3, 10183 reflections measured (4.516° ≤ 2Θ ≤ 50°), 3955 unique (R_{int} = 0.0447, R_{sigma} = 0.0615) which were used in all calculations. The final R_1 was 0.0753 (I > 2σ(I)) and wR_2 was 0.2340 (all data).

12b-methoxy-6-methyl-1,3,4,5,6,12b-hexahydro-2H,7H-pyrrolo[2,1-k]carbazol-7-one (4a)

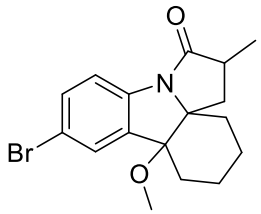


Prepared according to standard conditions B. Purification by thin layer chromatography was performed (PE/EA: 6/1) to yield **4a** (33 mg, 60%) as a colorless liquid. dr 2:1.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.63 (d, J = 7.8 Hz, 0.3H), 7.61 (dd, *J* = 17.8, 7.8 Hz, 0.6H), 7.38 – 7.33 (m, 1H), 7.25 (d, *J* = 7.2 Hz, 2H), 7.15 – 7.10 (m, 1H), 7.09 (d, J = 7.5 Hz, 0.3H), 3.13 – 3.07 (m, 0.3H), 2.97 – 2.90 (m, 1H), 2.84 (s, 3H), 2.57 (d, *J* = 15.2 Hz, 1H), 2.34 (t, *J* = 11.8 Hz, 0.3H), 2.05 – 1.89 (m, 0.7H), 1.79 – 1.69 (m, 1H), 1.68 – 1.38 (m, 5H), 1.34 – 1.22 (m, 2H), 1.13 (m, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 176.3, 140.5, 134.5, 129.7, 124.6, 123.6, 123.2, 118.1, 82.0,

74.8, 49.5, 42.1, 40.6, 38.9, 35.1, 27.7, 26.9, 22.5, 22.4, 21.9, 21.7, 15.6. HRMS (ESI): m/z calcd for $C_{17}H_{22}NO_2^+$ $(M+H)^+$: 272.1645; found: 272.1646.

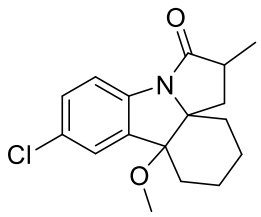
11-bromo-12b-methoxy-6-methyl-1,3,4,5,6,12b-hexahydro-2H,7H-pyrrolo[2,1-k] carbazol-7-one (4b)



Prepared according to standard conditions B. Purification by thin layer chromatography was performed (PE/EA: 6/1) to yield **4b** (40 mg, 57%) as a colorless liquid. dr 3:1.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.50 (d, J = 8.3 Hz, 0.25H), 7.52 – 7.42 (m, 2H), 7.36 (d, J = 1.7 Hz, 0.25H), 7.35 (d, J = 1.7 Hz, 0.75H), 3.10 – 3.03 (m, 0.25H), 2.94 – 2.83 (m, 4H), 2.51 (d, *J* = 13.5 Hz, 1H), 2.36 – 2.30 (t, *J* = 12.1 Hz, 0.25H), 2.04 – 1.90 (m, 0.75H), 1.75 (d, *J* = 11.0 Hz, 1H), 1.65 – 1.54 (m, 1H), 1.52 – 1.36 (m, 5H), 1.27 – 1.22 (m, 2H), 1.16 – 1.08 (m, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 176.3, 139.5, 137.1, 132.6, 127.6, 119.5, 118.2, 116.4, 82.2, 80.8, 75.0, 73.1, 49.5, 41.95, 38.8, 35.1, 30.9, 30.5, 27.4, 26.6, 22.3, 21.8, 21.5, 19.5, 15.5. HRMS (ESI): m/z calcd for $C_{17}H_{21}BrNO_2^+$ $(M+H)^+$: 350.0750; found: 350.0753.

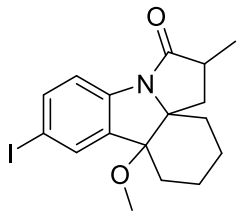
11-chloro-12b-methoxy-6-methyl-1,3,4,5,6,12b-hexahydro-2H,7H-pyrrolo[2,1-k]carbazol-7-one (4c)



Prepared according to standard conditions B. Purification by thin layer chromatography was performed (PE/EA: 6/1) to yield **4c** (39 mg, 64%) as a colorless liquid. dr 3:1.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.55 (d, J = 8.3 Hz, 0.25H), 7.50 (d, *J* = 8.3 Hz, 0.75H), 7.32 (dt, *J* = 8.3, 2.6 Hz, 1H), 7.22 (d, J = 2.0 Hz, 0.25H), 7.20 (d, *J* = 2.0 Hz, 0.75H), 3.10 – 3.02 (m, 0.25H), 2.95 – 2.88 (m, 1H), 2.87 (d, *J* = 1.6 Hz, 3H), 2.51 (d, *J* = 13.6 Hz, 1H), 2.36 – 2.30 (t, *J* = 12.1 Hz, 0.25H), 2.04 – 1.90 (m, 0.75H), 1.80 – 1.70 (m, 1H), 1.66 – 1.55 (m, 1H), 1.54 – 1.36 (m, 5H), 1.27 – 1.22 (m, 2H), 1.17 – 1.08 (m, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 176.3, 139.0, 136.6, 129.6, 128.9, 124.8, 119.0, 117.7, 82.1, 75.0, 49.5, 41.9, 40.4, 38.7, 35.0, 30.9, 30.5, 22.3, 22.3, 21.7, 21.4, 19.5, 15.5. HRMS (ESI): m/z calcd for $C_{17}H_{21}ClNO_2^+$ $(M+H)^+$: 306.1225; found: 306.1258.

11-iodo-12b-methoxy-6-methyl-1,3,4,5,6,12b-hexahydro-2H,7H-pyrrolo[2,1-k]carbazol-7-one (4d)

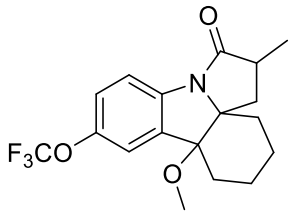


Prepared according to standard conditions B. Purification by thin layer chromatography was performed (PE/EA: 6/1) to yield **4d** (37 mg, 47%) as a colorless liquid. dr 3:1.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.70 – 7.64 (m, 1H), 7.55 (d, J = 1.4 Hz, 0.25H), 7.53 (d, J = 1.3 Hz, 0.75H), 7.40 (d, J = 8.2 Hz, 0.25H), 7.35 (d, *J* = 8.1 Hz, 0.75H), 3.12 – 3.01 (m, 0.25H), 2.96 – 2.83 (m, 4H), 2.50 (d, *J* = 13.4 Hz, 1H), 2.33 (t, *J* = 11.5 Hz, 0.25H), 2.03 – 1.90 (m, 0.75H), 1.76 (d, *J* = 13.3 Hz, 1H), 1.59 (d, *J* = 11.8 Hz, 1H), 1.52 – 1.37 (m, 5H), 1.31 – 1.21 (m, 2H), 1.17 – 1.08 (m, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 176.2, 140.1, 138.5, 137.3, 133.3, 119.9, 118.7, 86.8, 82.1, 74.8, 49.5, 41.9, 40.5, 38.7, 35.0, 30.9, 30.4, 27.3, 26.6, 22.3, 22.2, 21.7, 21.4,

19.5, 15.4. HRMS (ESI): m/z calcd for $C_{17}H_{21}INO_2^+$ $(M+H)^+$: 398.0611; found: 398.0613.

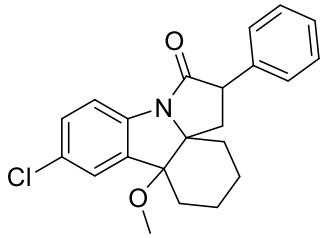
12b-methoxy-6-methyl-11-(trifluoromethoxy)-1,3,4,5,6,12b-hexahydro-2H,7H-pyrrolo[2,1-k]carbazol-7-one (4e)



Prepared according to standard conditions B. Purification by thin layer chromatography was performed (PE/EA: 6/1) to yield **4e** (43 mg, 61%) as a colorless liquid. dr 3:1.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.61 (d, J = 8.5 Hz, 0.25H), 7.57 (d, J = 8.4 Hz, 0.75H), 7.22 (d, J = 8.5 Hz, 1H), 7.10 (s, 1H), 6.97 (d, *J* = 9.7 Hz, 1H), 4.18 (dd, *J* = 11.5, 5.0 Hz, 1H), 3.14 – 3.02 (m, 0.25H), 2.96 – 2.89 (m, 1H), 2.94 (s, 3H), 2.69 (dd, *J* = 10.7, 5.2 Hz, 2H), 2.58 (d, *J* = 13.8 Hz, 1H), 2.53 (d, J = 13.7 Hz, 1H), 2.35 (t, J = 11.6 Hz, 0.25H), 2.04 – 1.89 (m, 0.75H), 1.77 (d, J = 16.4 Hz, 1H), 1.61 (d, J = 14.0 Hz, 1H), 1.56 – 1.32 (m, 5H), 1.30 – 1.20 (m, 2H), 1.18 – 1.00 (m, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 174.1, 145.4, 141.0, 139.3, 136.8, 128.9, 127.7, 127.0, 122.7, 119.4, 114.6, 110.7, 110.3, 82.5, 75.3, 52.8, 49.5, 38.2, 32.1, 26.4, 23.3, 22.3, 21.5, 20.8. HRMS (ESI): m/z calcd for $C_{23}H_{23}F_3NO_3^+$ $(M+H)^+$: 418.1625; found: 418.1626.

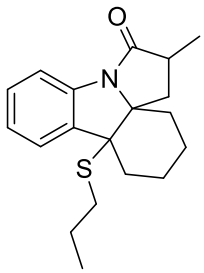
11-chloro-12b-methoxy-6-phenyl-1,3,4,5,6,12b-hexahydro-2H,7H-pyrrolo[2,1-k]carbazol-7-one (4f)



Prepared according to standard conditions B. Purification by thin layer chromatography was performed (PE/EA: 6/1) to yield **4f** (43 mg, 58%) as a colorless liquid. dr 5.7:1.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.58 (d, *J* = 8.2 Hz, 1H), 7.34 (d, *J* = 10.5 Hz, 7H), 7.27 (d, *J* = 10.8 Hz, 4H), 4.26 (dd, J = 11.2, 8.7 Hz, 0.15H), 4.17 (dd, J = 11.5, 4.9 Hz, 0.85H), 3.28 – 3.17 (m, 1H), 2.97 (s, 0.4H), 2.94 (s, 2.6H), 2.73 – 2.62 (m, 0.15H), 2.56 (d, *J* = 14.2 Hz, 1H), 2.38 – 2.31 (m, 0.15H), 2.24 (dd, *J* = 12.6, 8.6 Hz, 0.15H), 2.16 (d, *J* = 16.3 Hz, 0.15H), 2.00 – 1.82 (m, 3H), 1.81 – 1.62 (m, 1H), 1.61 – 1.42 (m, 3H), 1.31 – 1.07 (m, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 173.7, 141.0, 139.2, 136.8, 129.8, 129.7, 129.3, 129.1, 128.8, 128.7, 128.6, 128.1, 127.7, 126.9, 124.9, 124.8, 112.0, 119.6, 117.9, 82.5, 81.0, 75.1, 52.8, 49.6, 49.5, 38.2, 35.0, 31.9, 27.0, 26.5, 21.8, 21.5. HRMS (ESI): m/z calcd for $C_{22}H_{22}ClKNO_2^+$ $(M+K)^+$: 406.0971; found: 406.0972.

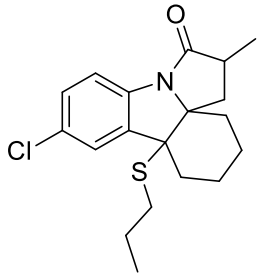
6-methyl-12b-(propylthio)-1,3,4,5,6,12b-hexahydro-2H,7H-pyrrolo[2,1-k]carbazol-7-one (4g)



Prepared according to standard conditions C. Purification by thin layer chromatography was performed (PE/EA: 6/1) to yield **4g** (47 mg, 60%) as a colorless liquid, dr 5.7:1..

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.60 – 7.52 (m, 1H), 7.30-7.22 (m, 1H), 7.20 – 7.08 (m, 2H), 3.15 – 2.96 (m, 2H), 2.60 (d, *J* = 15.4 Hz, 1H), 2.53 (t, *J* = 11.1 Hz, 0.15H), 2.19 (dd, *J* = 12.6, 8.2 Hz, 0.15H), 1.98 – 1.71 (m, 4.7H), 1.70 – 1.54 (m, 3H), 1.44 (d, *J* = 7.2 Hz, 2.6H), 1.34 – 1.16 (m, 4.4H), 0.78 – 0.70 (m, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 174.8, 139.0, 137.7, 128.4, 124.5, 123.1, 117.3, 116.0, 74.9, 60.8, 42.3, 32.2, 31.0, 23.0, 22.5, 21.6, 19.7, 15.6, 13.5. HRMS (ESI): m/z calcd for $C_{19}H_{26}NOS^{+}$ $(M+H)^{+}$: 316.1730; found: 316.1731.

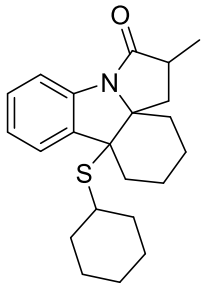
11-chloro-6-methyl-12b-(propylthio)-1,3,4,5,6,12b-hexahydro-2H,7H-pyrrolo[2,1-k]carbazol-7-one (4h)



Prepared according to standard conditions C. Purification by thin layer chromatography was performed (PE/EA: 6/1) to yield **4h** (57 mg, 65%) as a colorless liquid. dr 3:1.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.53 – 7.44 (m, 1H), 7.27 – 7.19 (m, 1H), 7.17 (d, J = 1.8 Hz, 0.25H), 7.13 (d, J = 1.8 Hz, 0.75H), 3.14 – 2.97 (m, 2H), 2.53 (d, *J* = 14.2 Hz, 2H), 2.19 (dd, *J* = 12.6, 8.2 Hz, 0.25H), 2.07 – 1.77 (m, 4.75H), 1.76 – 1.53 (m, 3H), 1.43 (d, *J* = 7.1 Hz, 3H), 1.35 – 1.19 (m, 4H), 0.83 – 0.74 (m, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 174.8, 137.5, 129.7, 123.4, 118.2, 116.9, 75.0, 60.7, 42.2, 40.7, 39.0, 35.3, 35.0, 33.4, 32.0, 31.2, 31.0, 22.9, 22.4, 21.5, 19.6, 15.6, 13.5. HRMS (ESI): m/z calcd for $C_{19}H_{25}ClNOS^{+}$ $(M+H)^{+}$: 350.1340; found: 350.1342.

12b-(cyclohexylthio)-6-methyl-1,3,4,5,6,12b-hexahydro-2H,7H-pyrrolo[2,1-k]carbazol-7-one (4i)

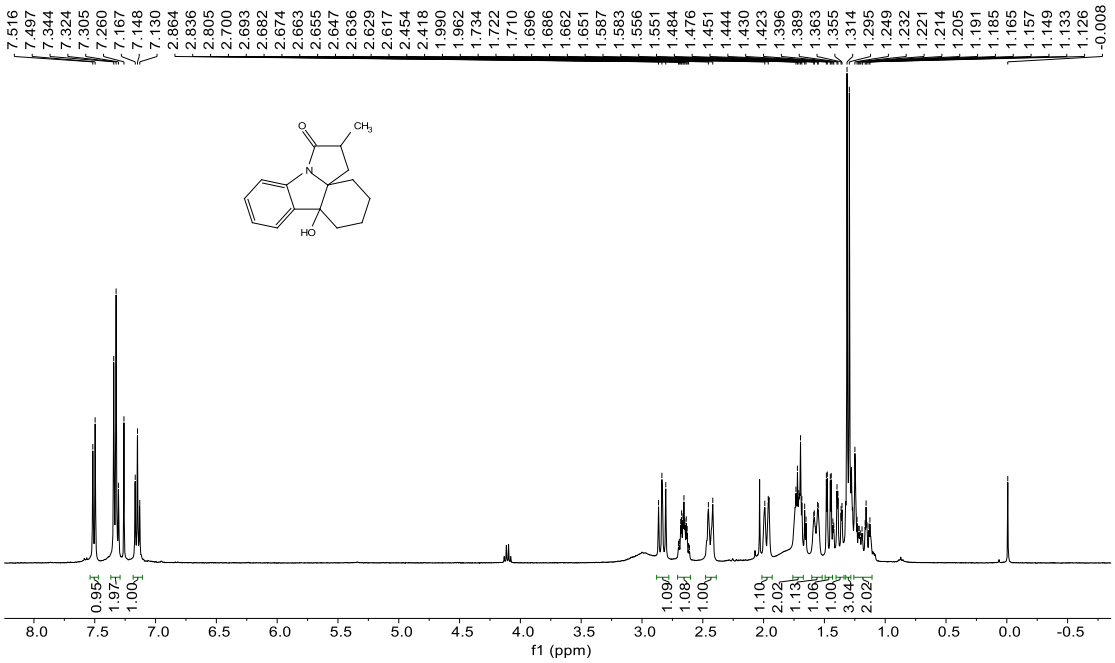


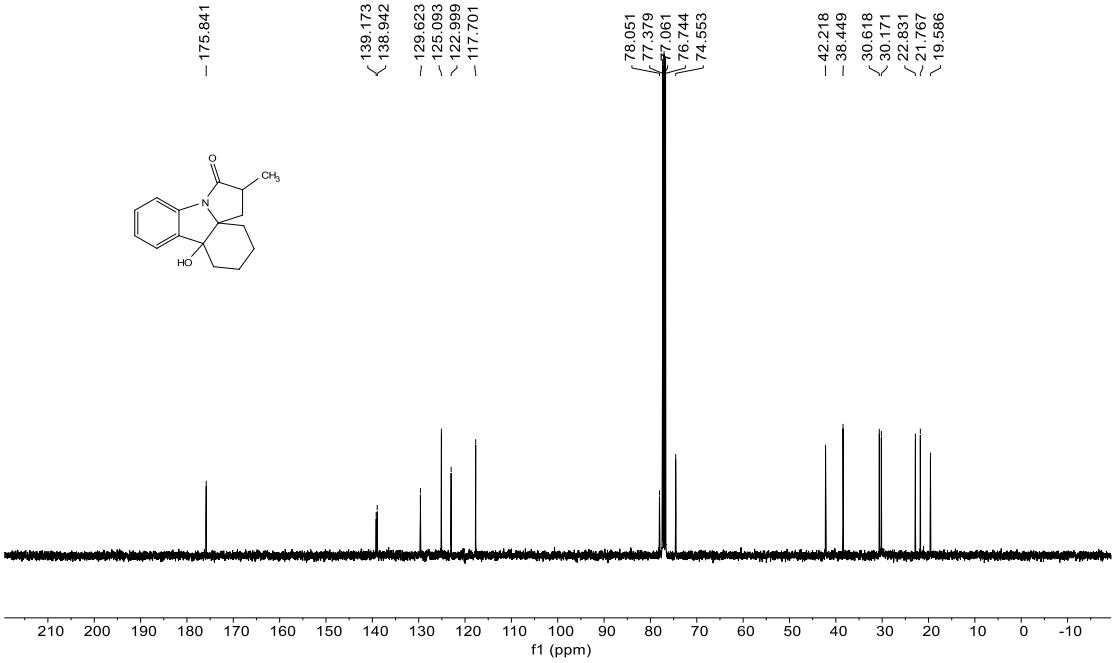
Prepared according to standard conditions C. Purification by thin layer chromatography was performed (PE/EA: 6/1) to yield **4i** (40 mg, 56%) as a colorless liquid. dr 4:1.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.59 (d, J = 7.8 Hz, 0.2H), 7.55 (d, J = 7.7 Hz, 0.8H), 7.30 – 7.19 (m, 2H), 7.11 (t, *J* = 7.6 Hz, 1H), 3.08 – 2.98 (m, 2H), 2.61 (d, *J* = 14.4 Hz, 1H), 2.52 (t, *J* = 11.7 Hz, 0.2H), 2.17 (dd, *J* = 12.6, 8.2 Hz, 0.2H), 1.98 – 1.79 (m, 3H), 1.71 – 1.55 (m, 3H), 1.55 – 1.34 (m, 6H), 1.28 (dd, *J* = 19.9, 8.0 Hz, 3H), 1.20 – 0.89 (m, 6H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 174.9, 139.2, 137.9, 128.4, 124.3, 123.0, 117.5, 75.1, 61.9, 42.4, 42.3, 40.9, 39.0, 36.3, 35.8, 35.4, 34.9, 33.3, 33.3, 26.4, 25.3, 23.1, 23.0, 21.6, 19.8, 15.4. HRMS (ESI): m/z calcd for $C_{22}H_{30}NOS^{+}$ $(M+H)^{+}$: 356.2043; found: 356.2044.

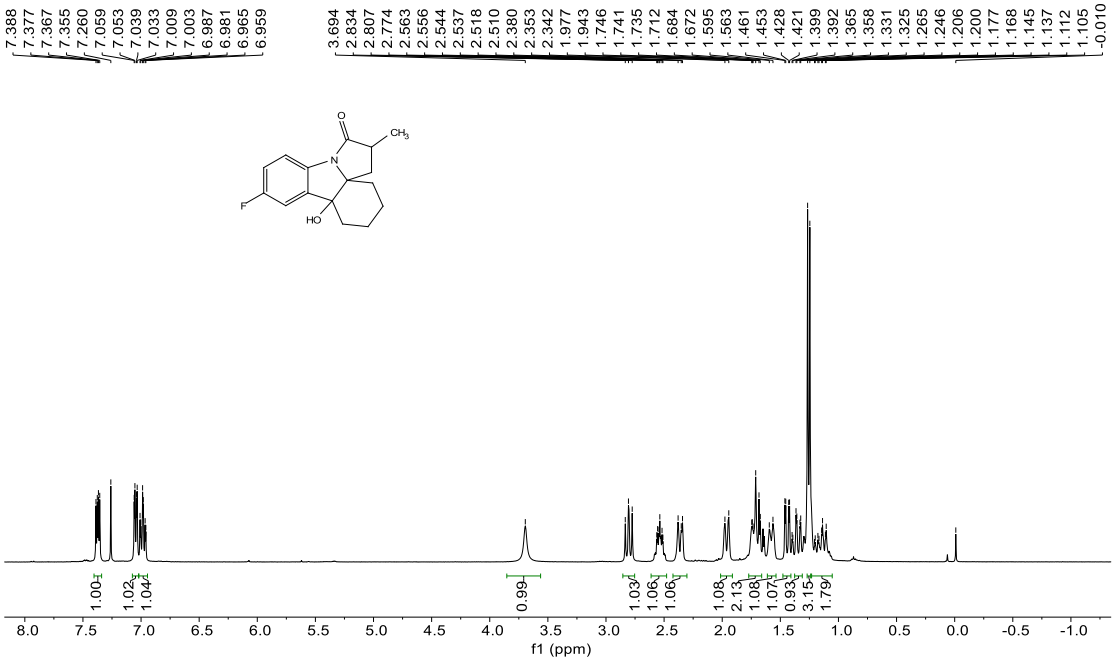
6. Copies of ^{1}H and ^{13}C NMR spectra of all products

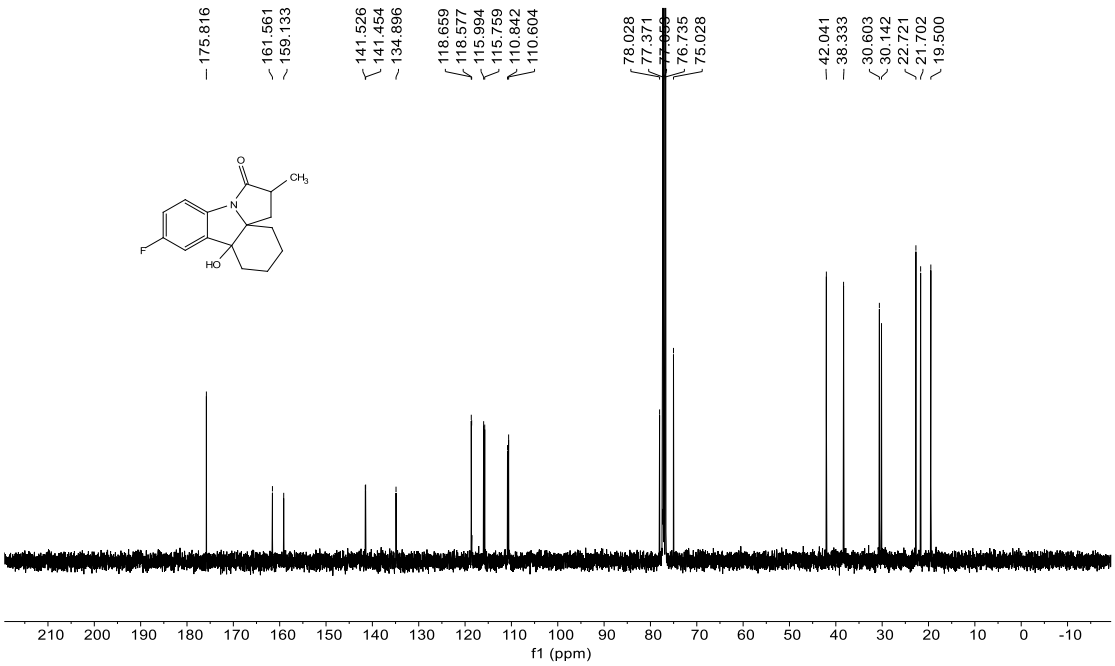
^{1}H and ^{13}C NMR spectra of 2a

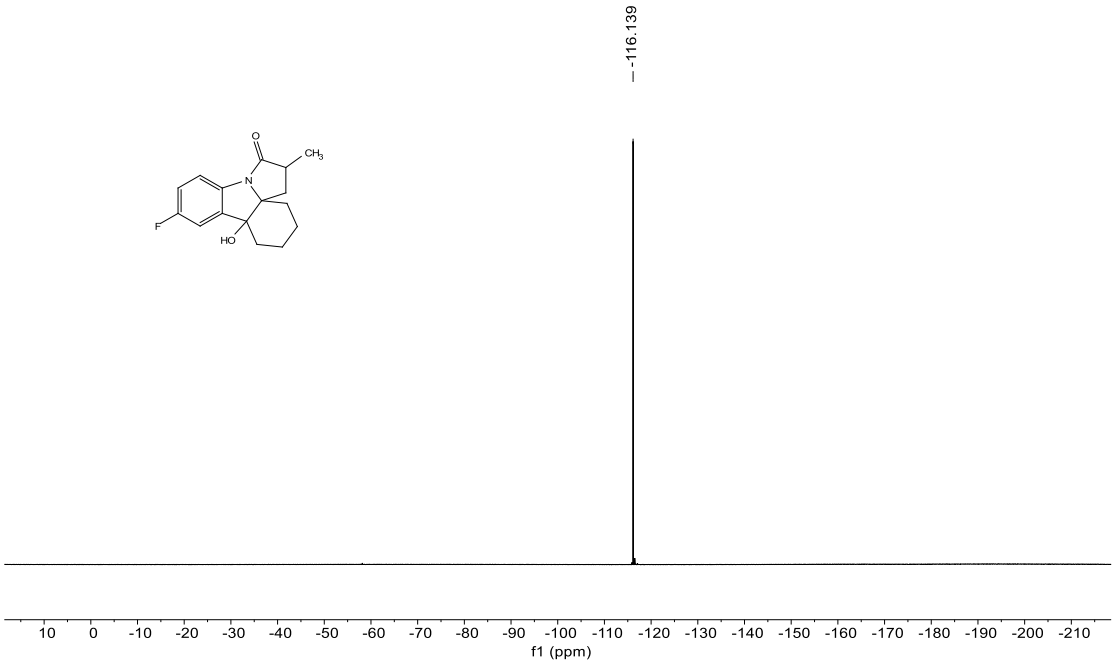




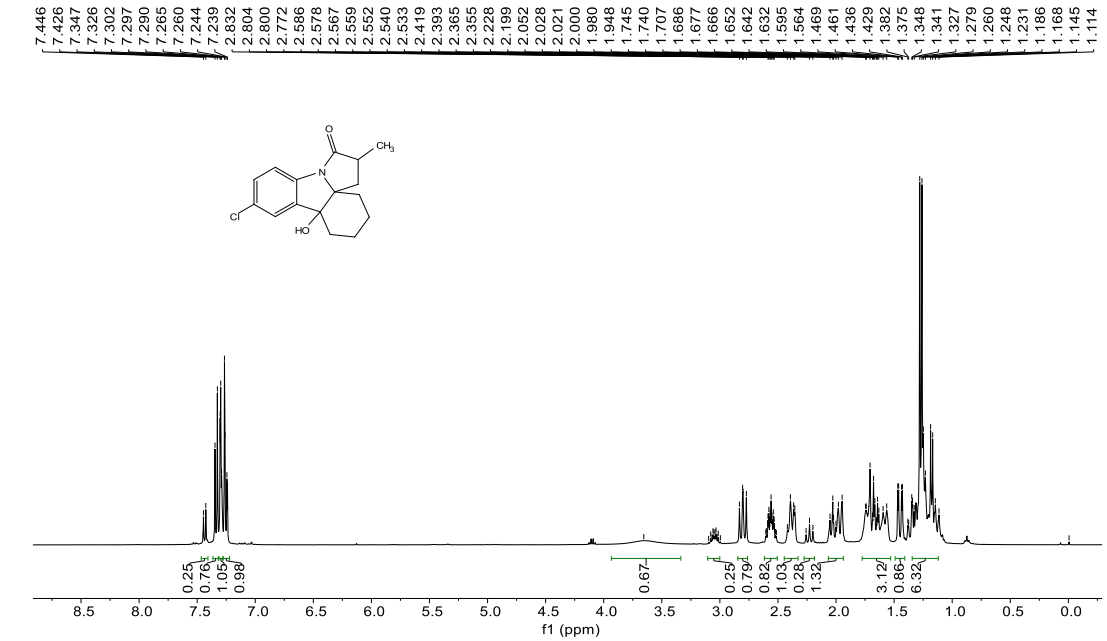
^{1}H, ^{19}F and ^{13}C NMR spectra of 2b

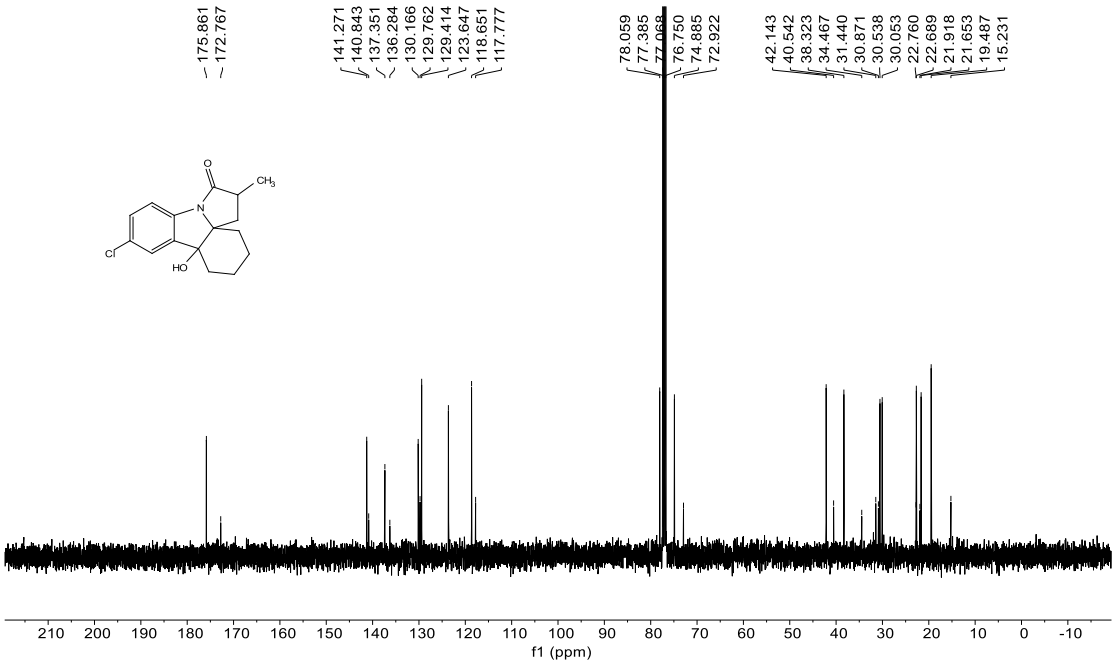




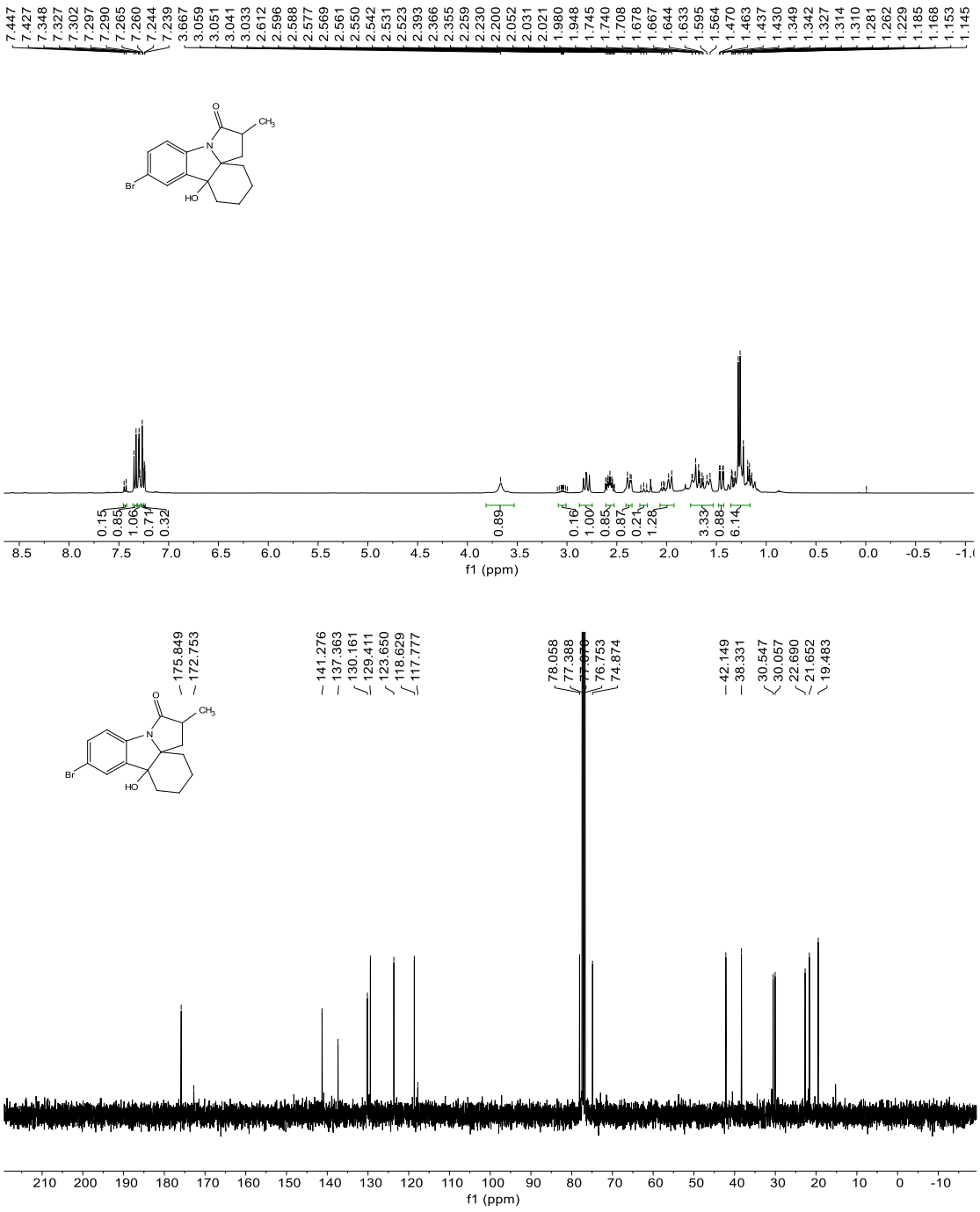

-116.139
O
CH3
N
F
HO
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

^{1}H and ^{13}C NMR spectra of 2c

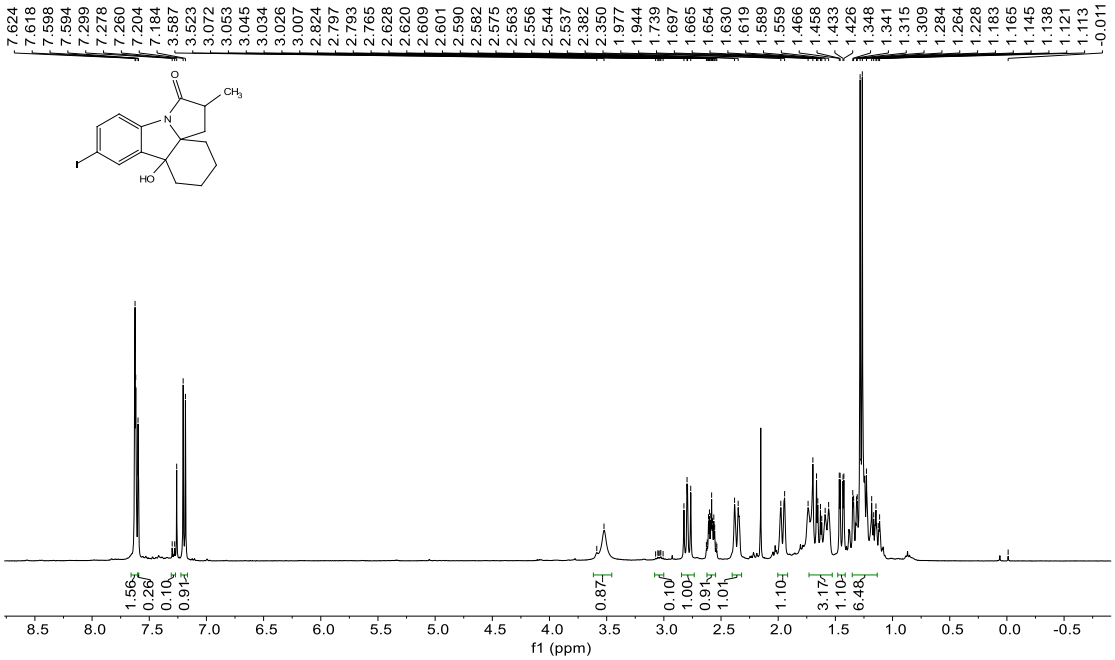


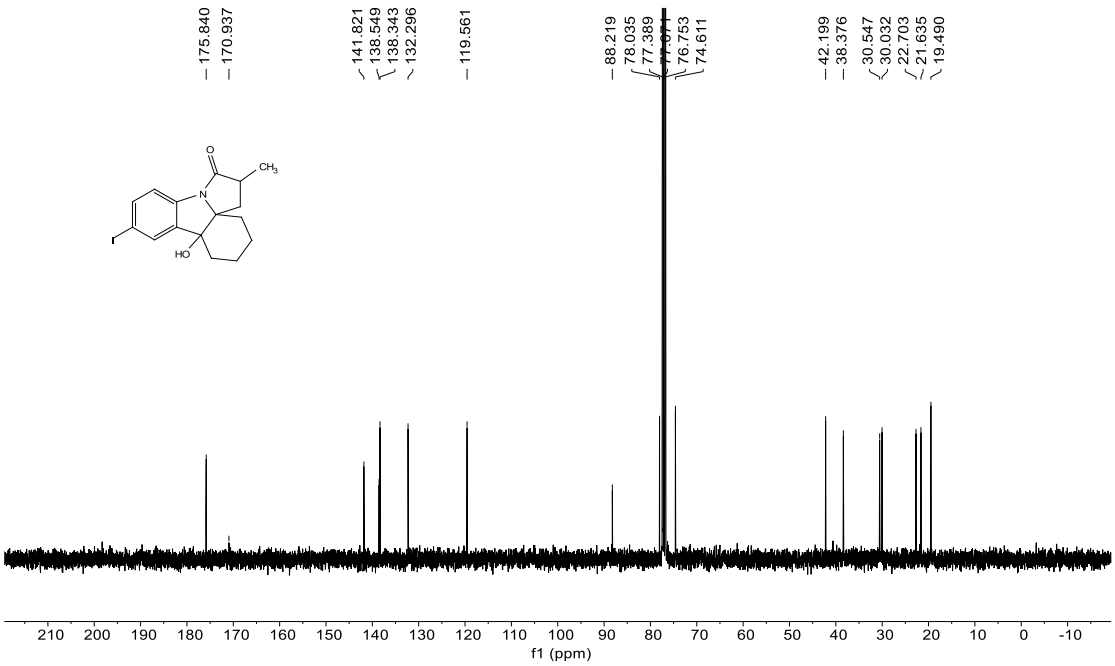


^{1}H and ^{13}C NMR spectra of 2d

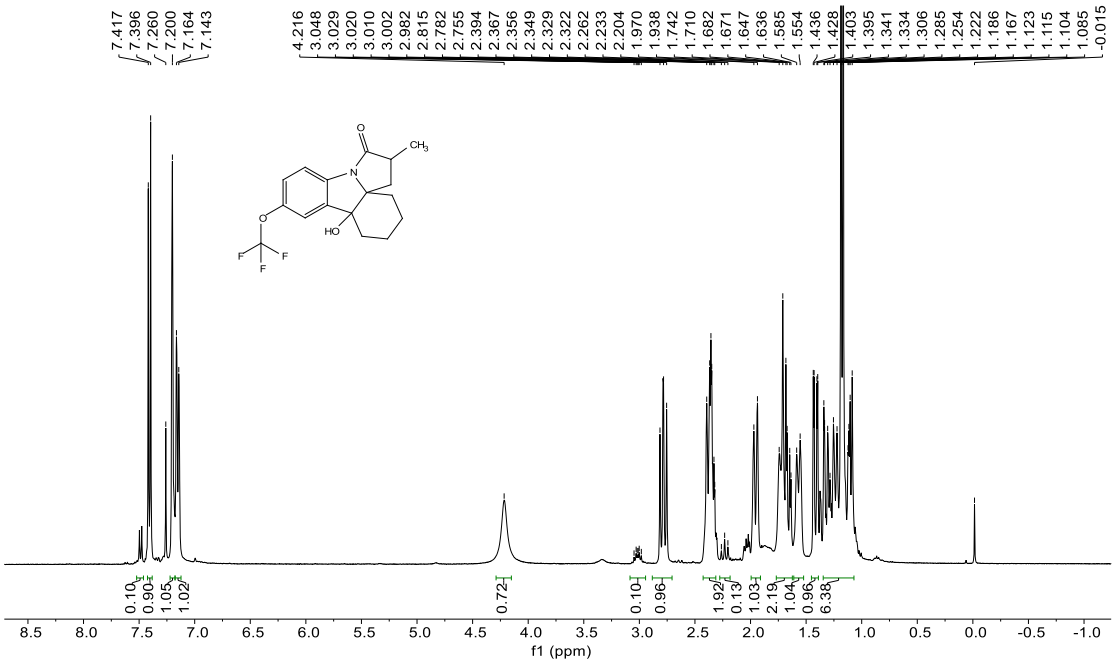


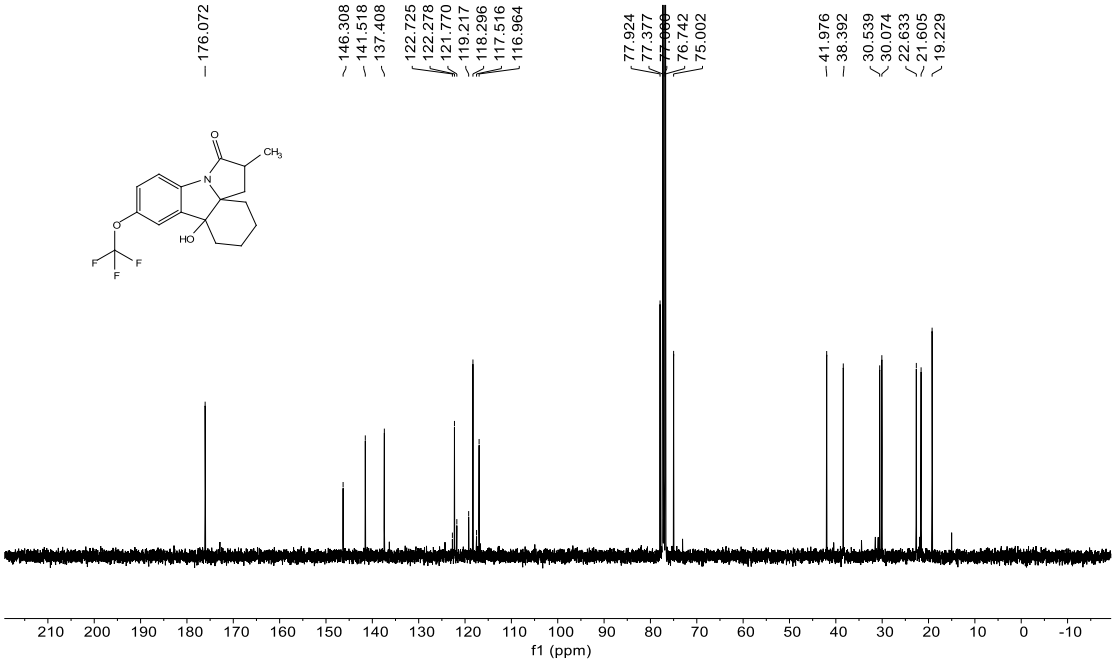
^{1}H and ^{13}C NMR spectra of 2e



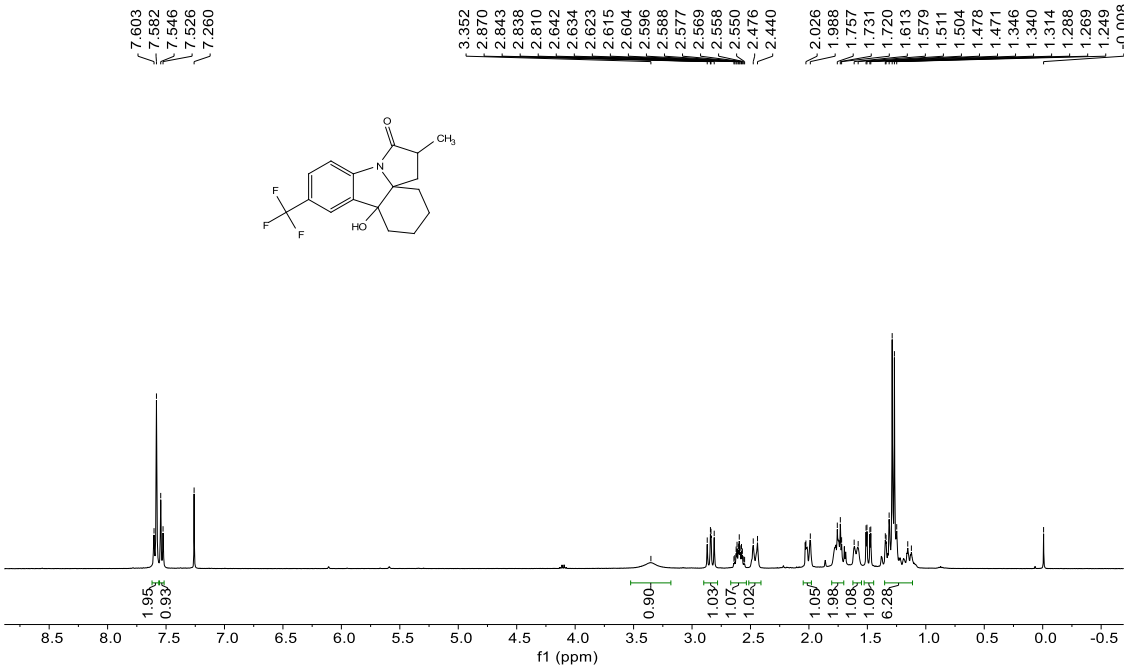


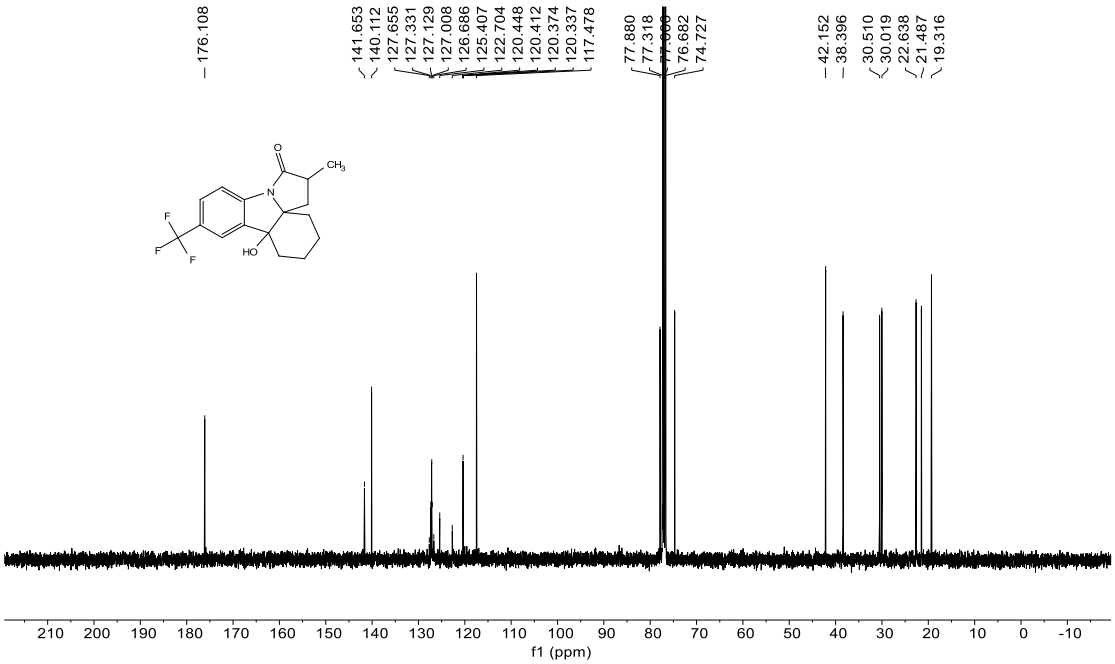
^{1}H and ^{13}C NMR spectra of 2f



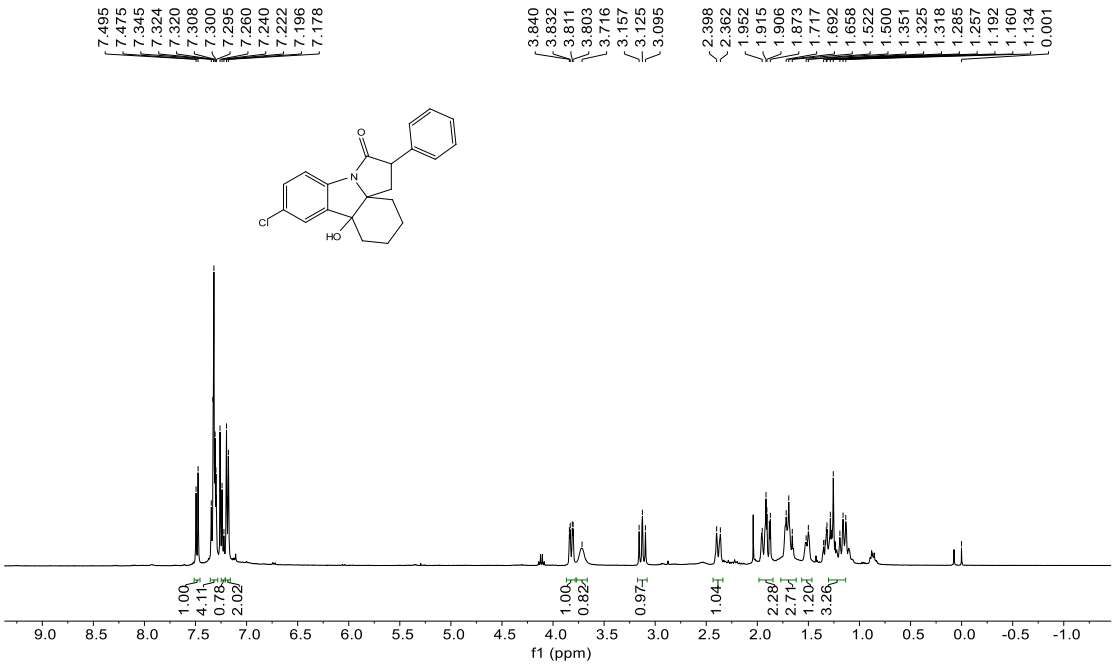


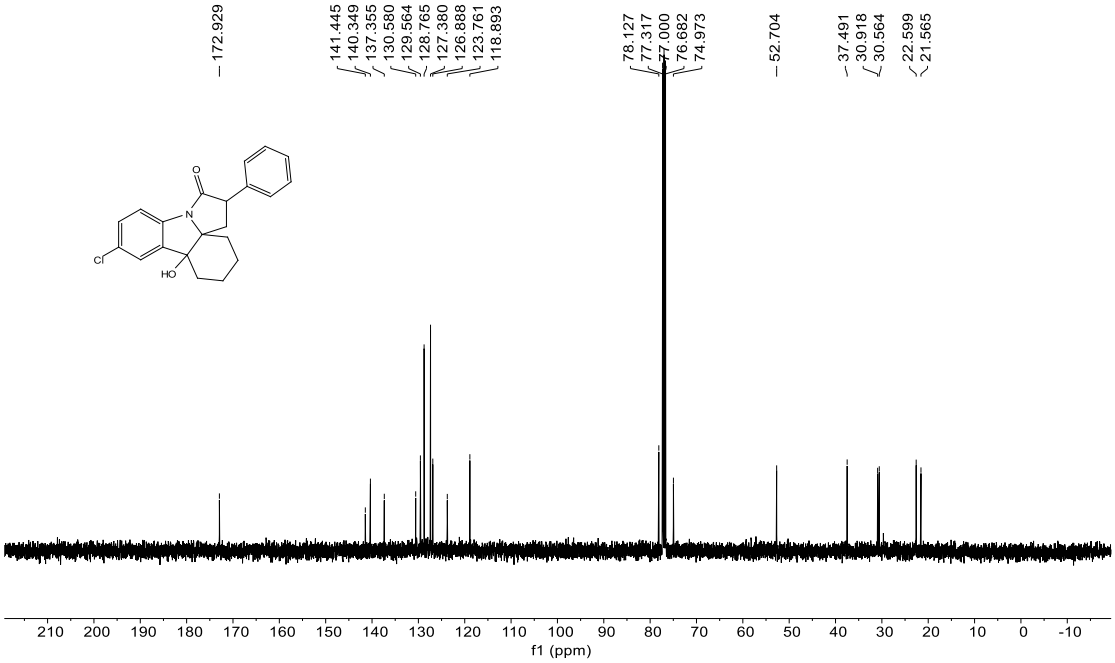
^{1}H and ^{13}C NMR spectra of 2g



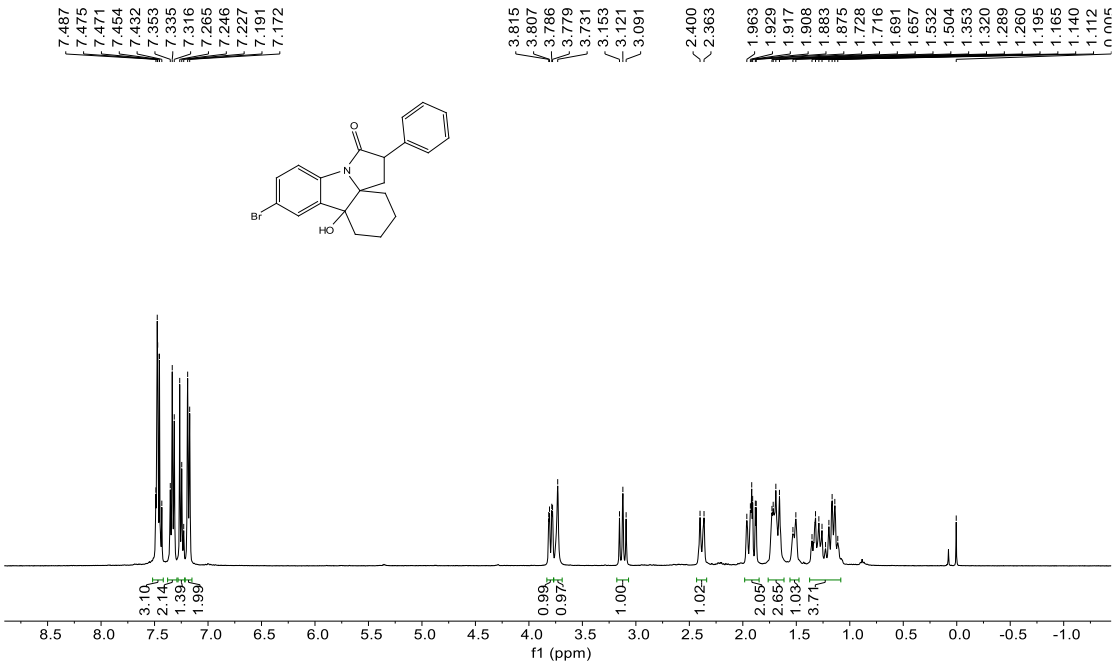


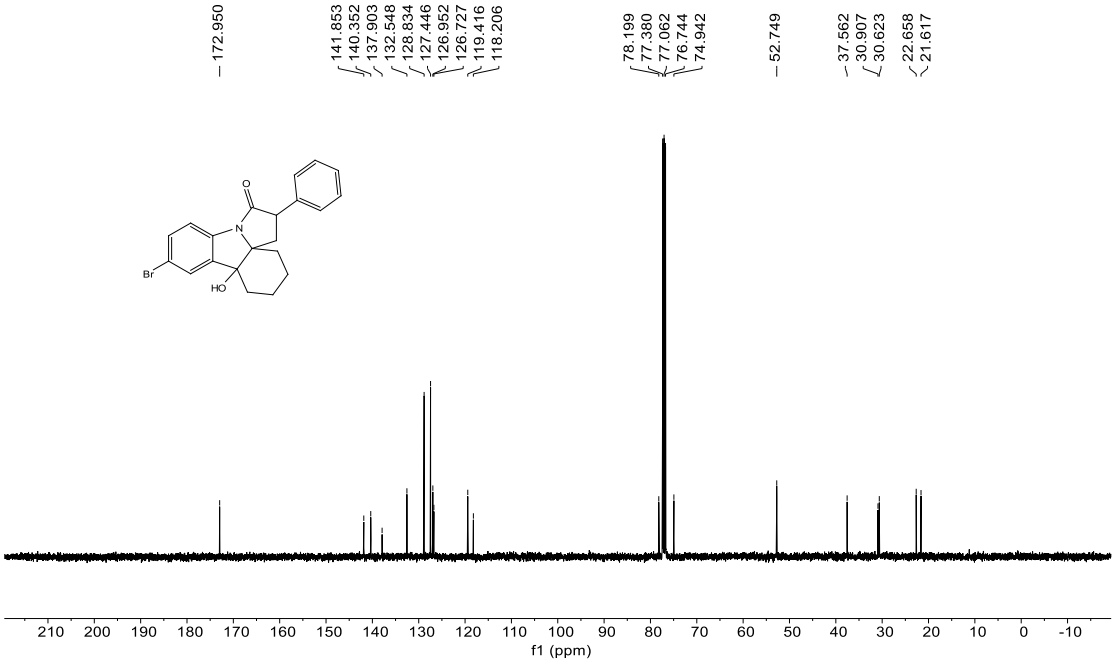
^{1}H and ^{13}C NMR spectra of 2h



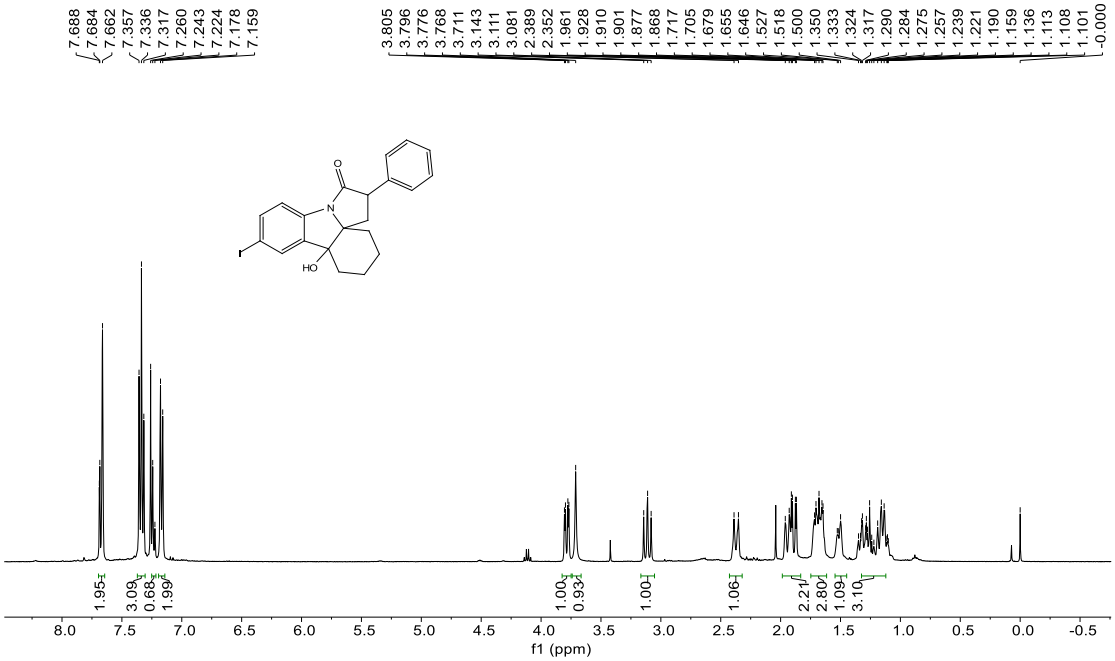


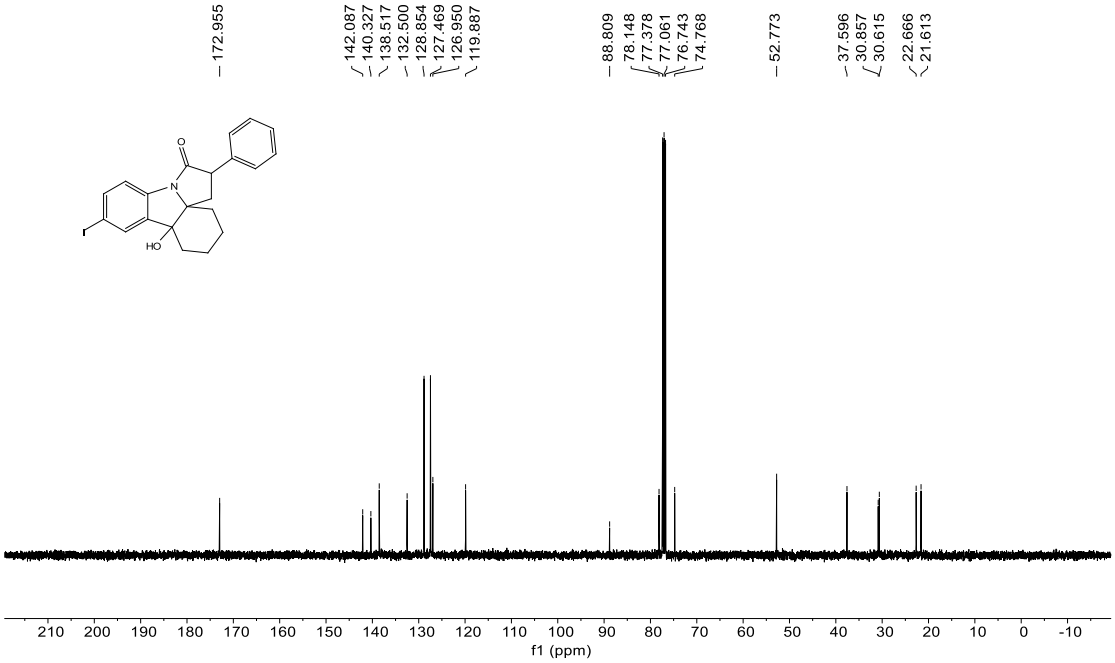
^{1}H and ^{13}C NMR spectra of 2i



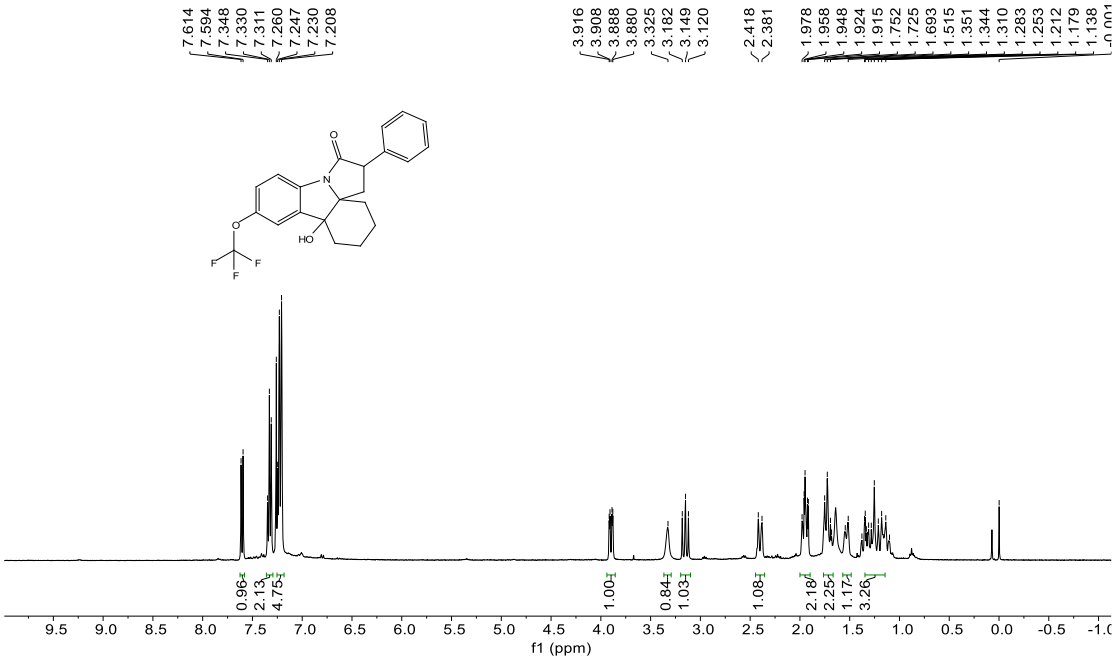


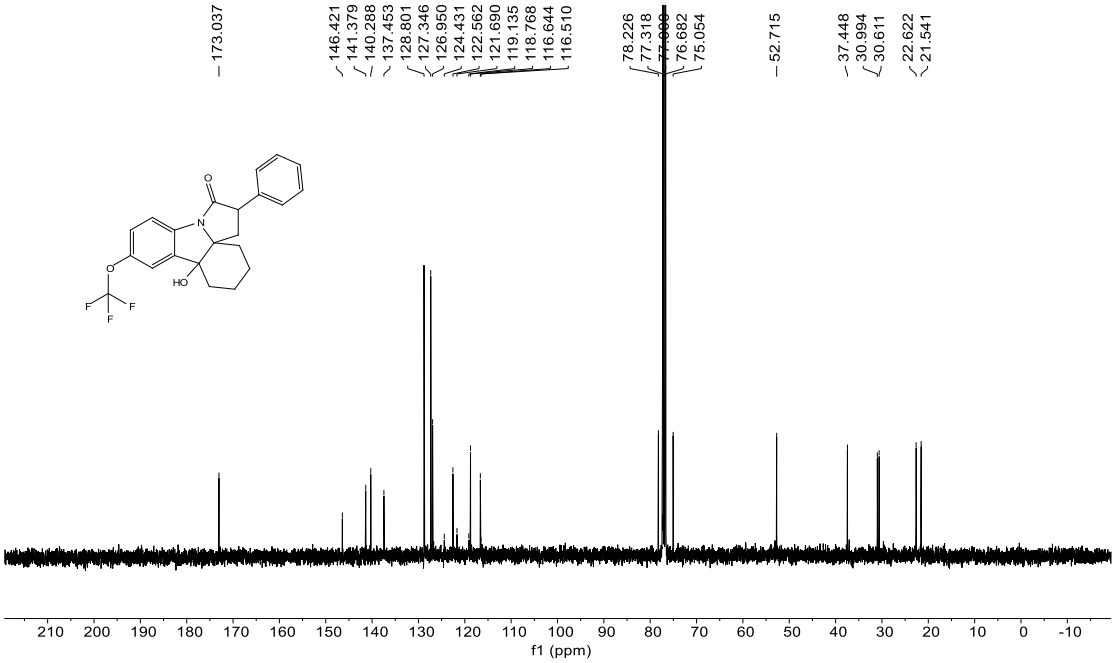
^{1}H and ^{13}C NMR spectra of 2j



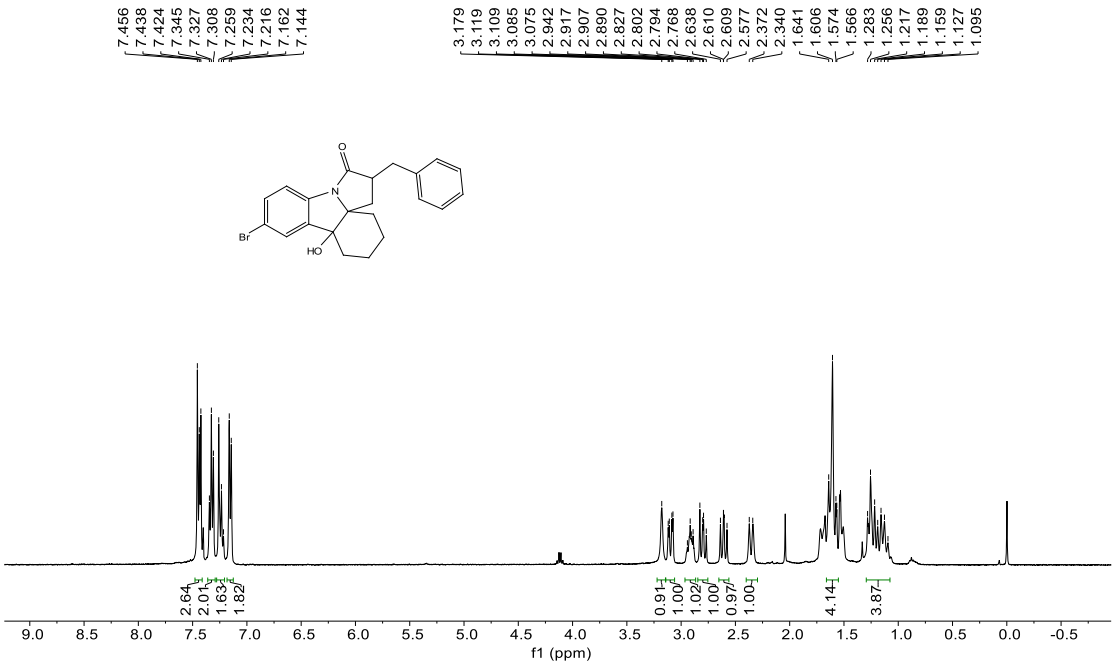


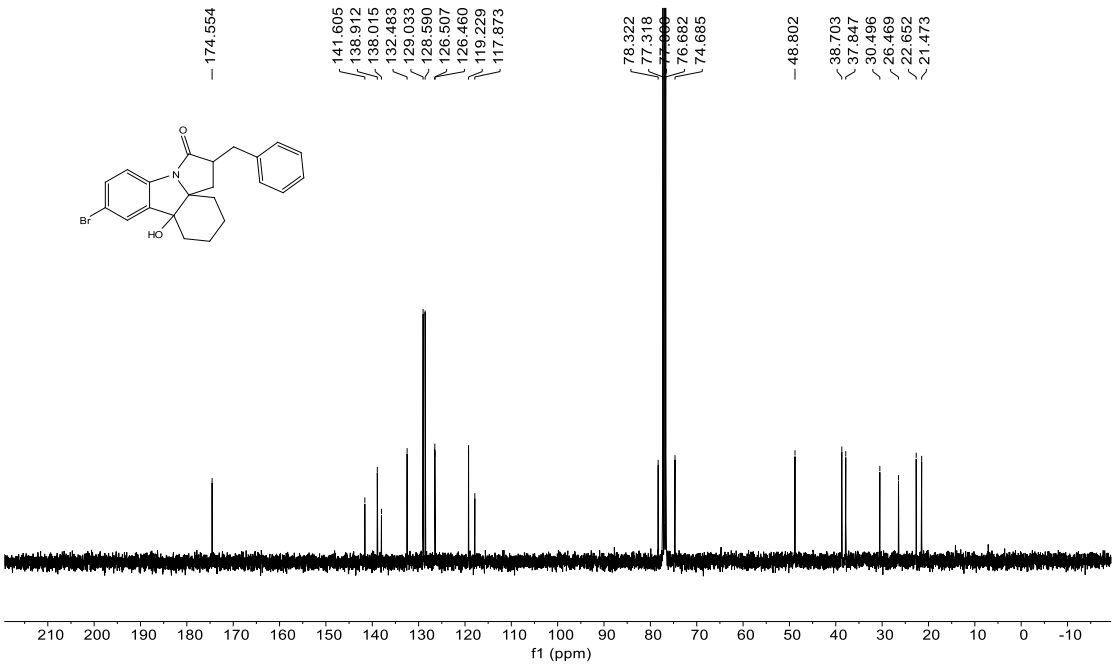
^{1}H and ^{13}C NMR spectra of 2k



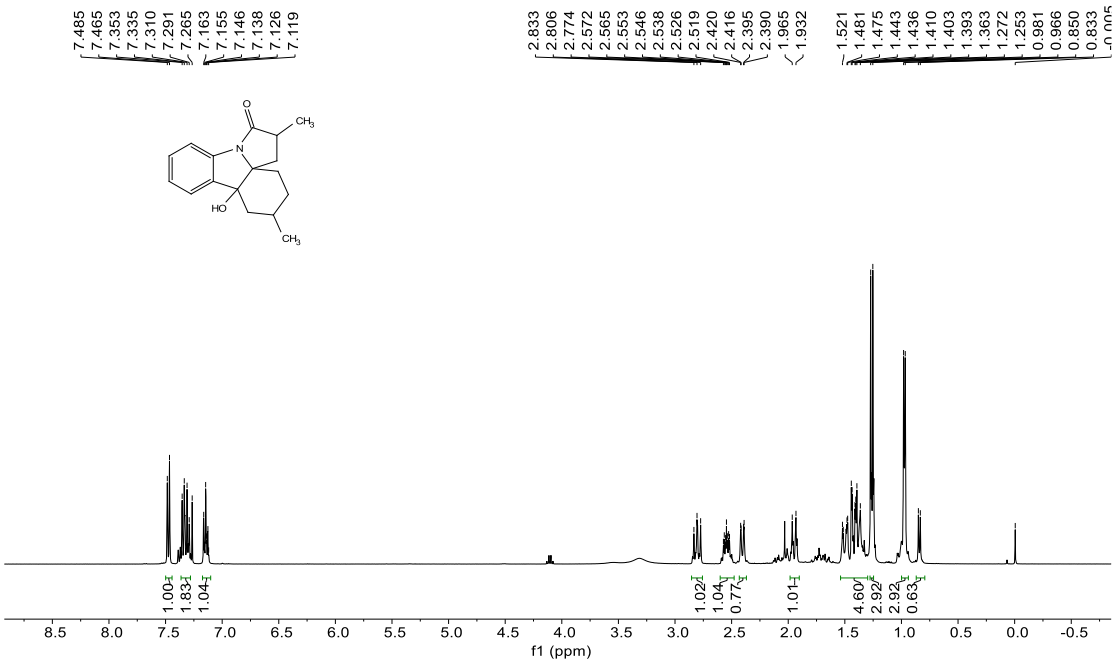


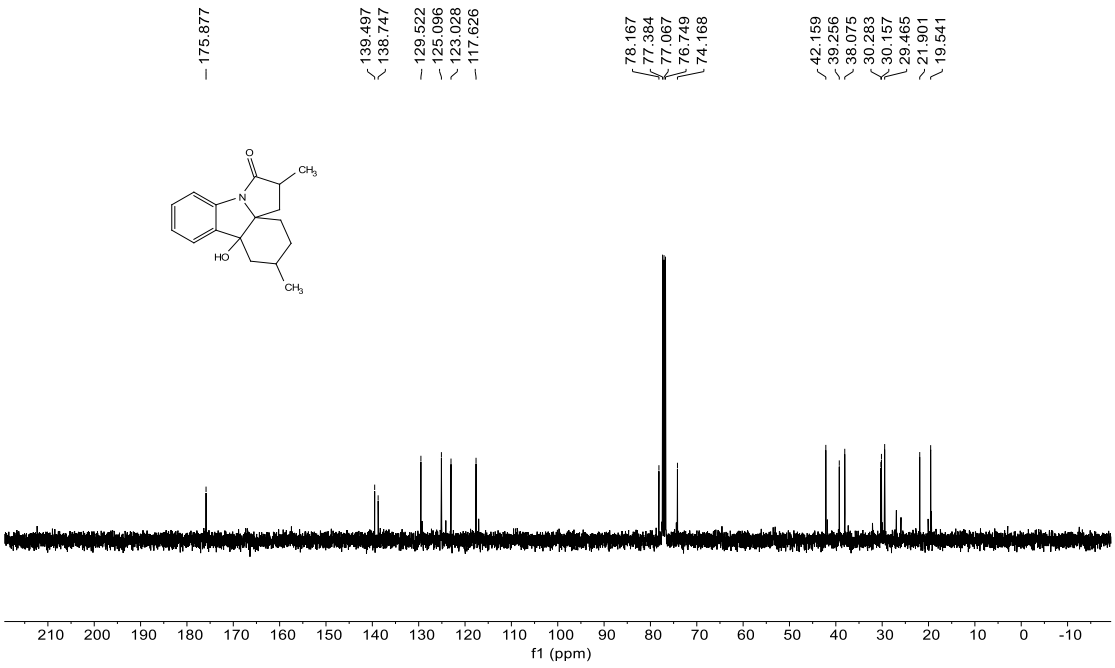
^{1}H and ^{13}C NMR spectra of 2l



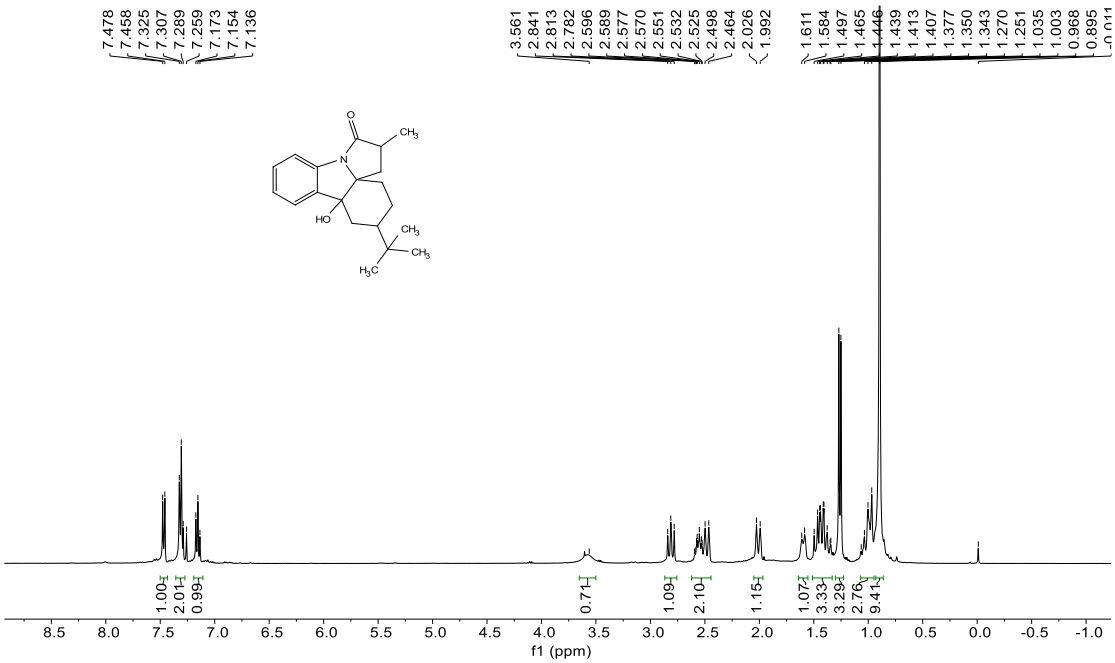


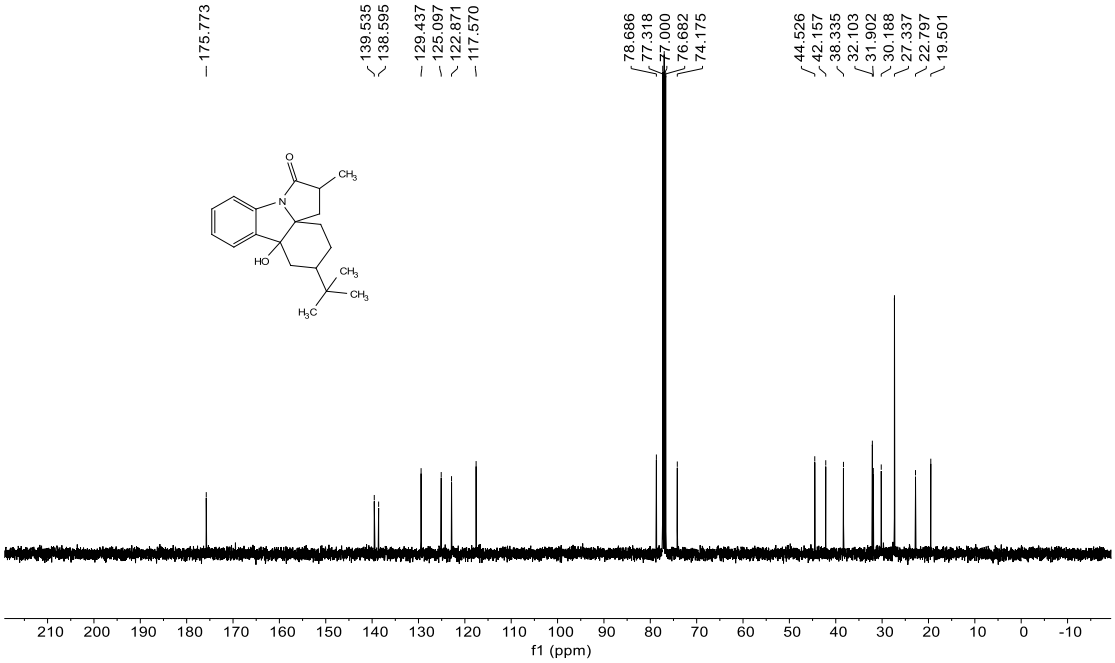
^{1}H and ^{13}C NMR spectra of 2m



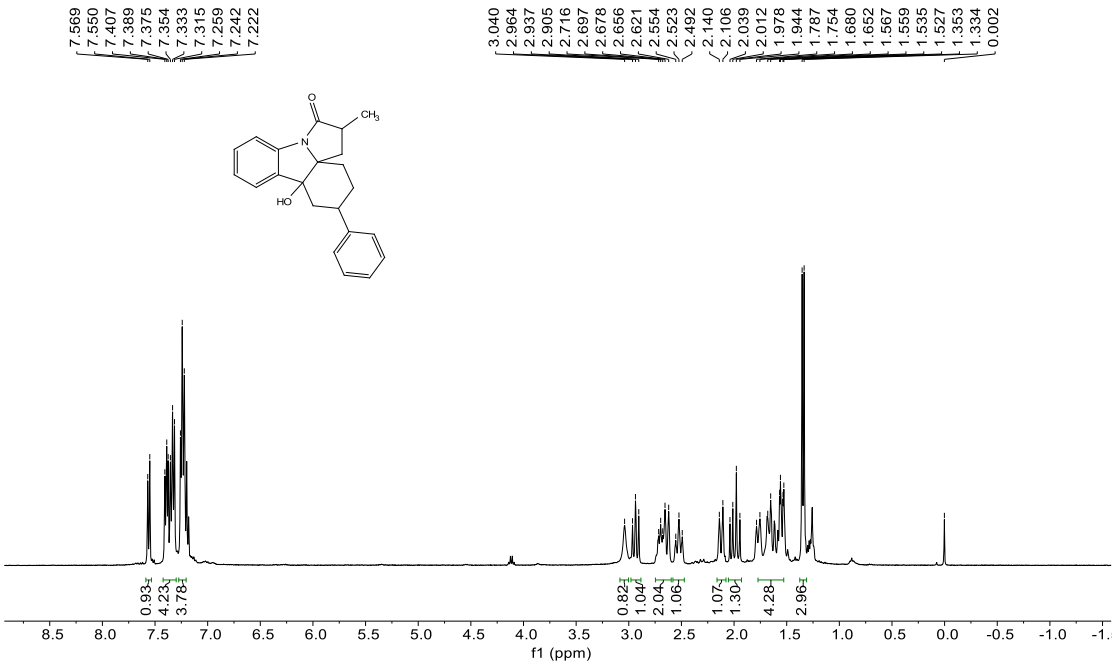


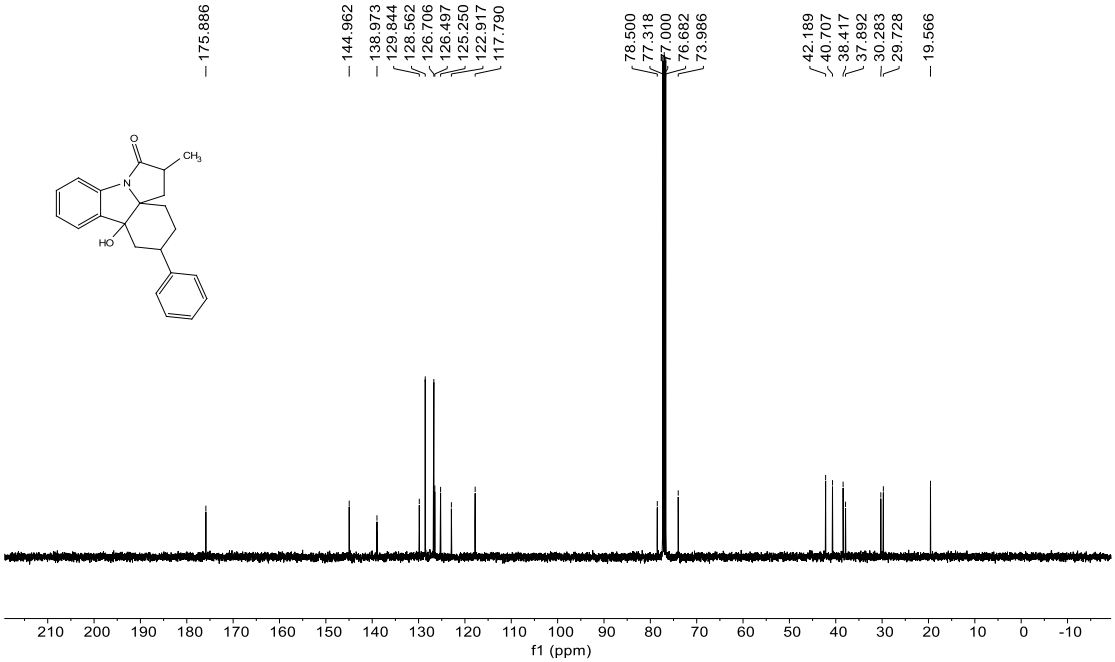
^{1}H and ^{13}C NMR spectra of 2n



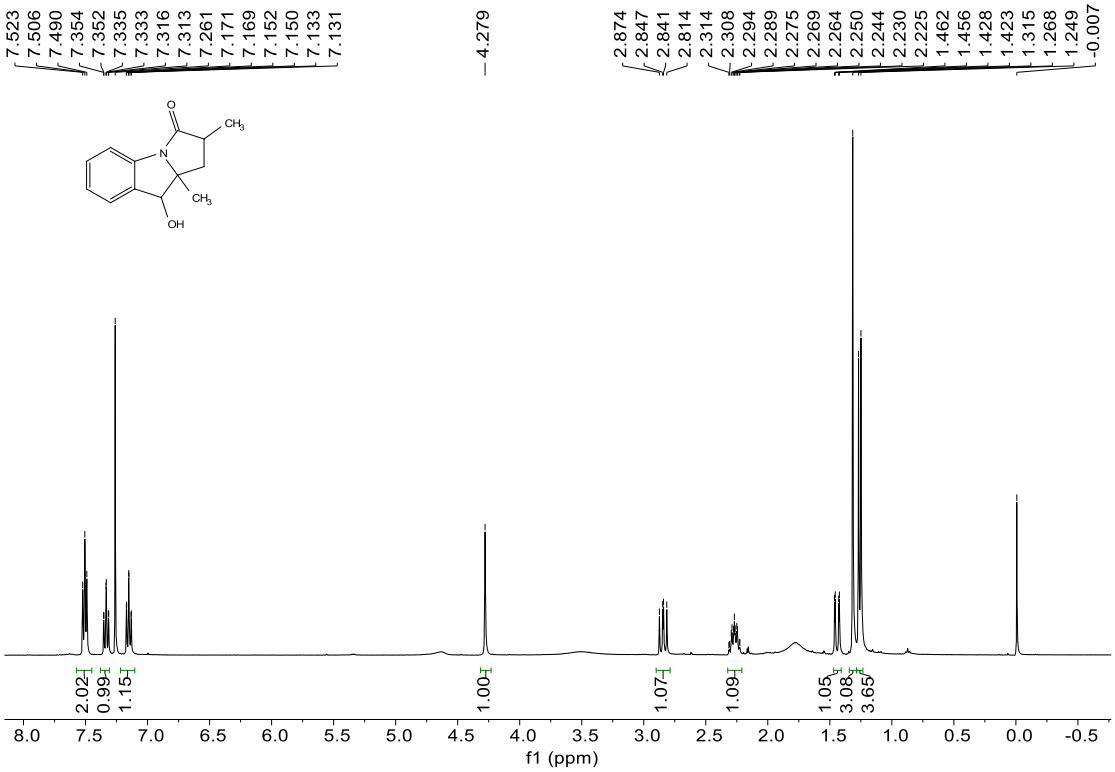


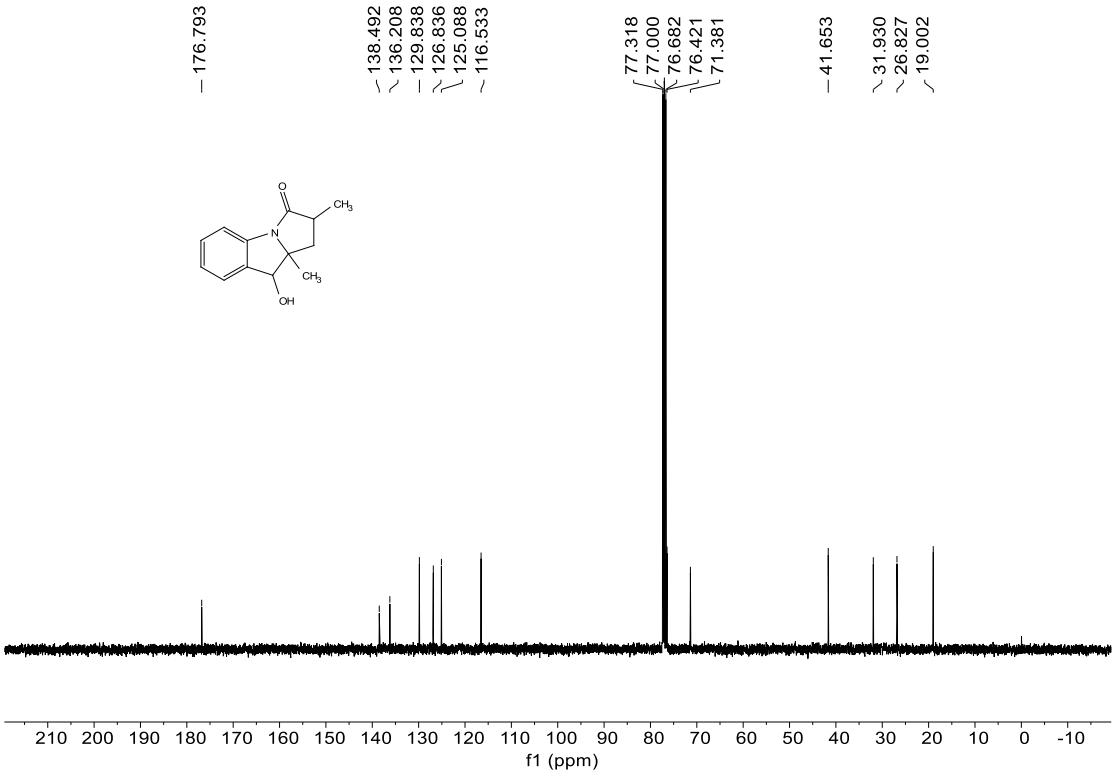
^{1}H and ^{13}C NMR spectra of 2o



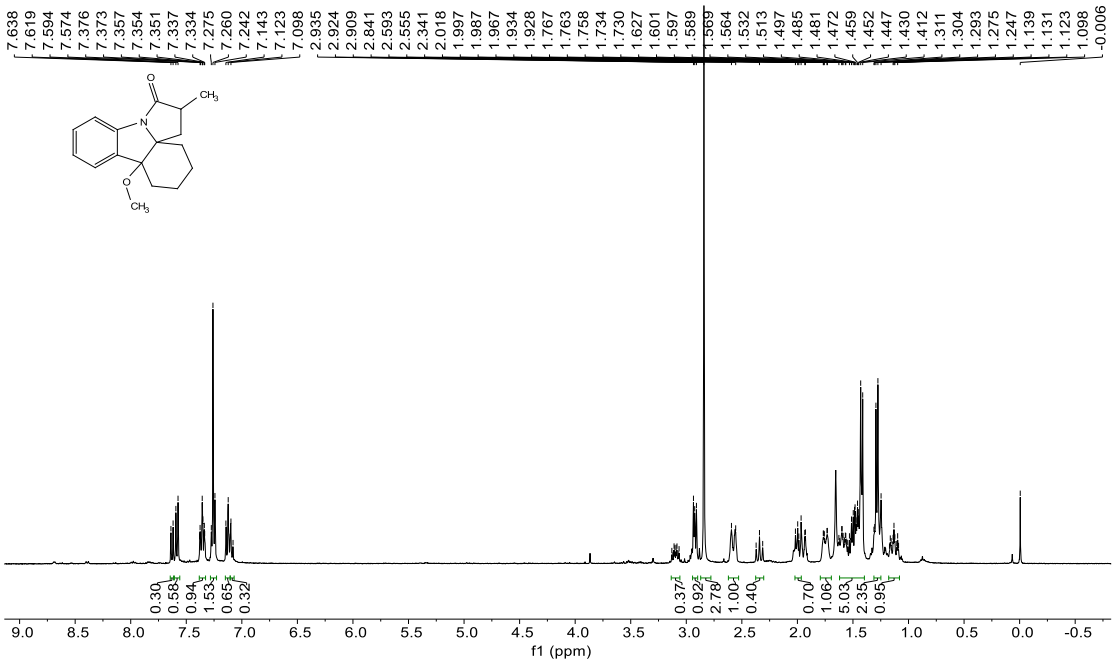


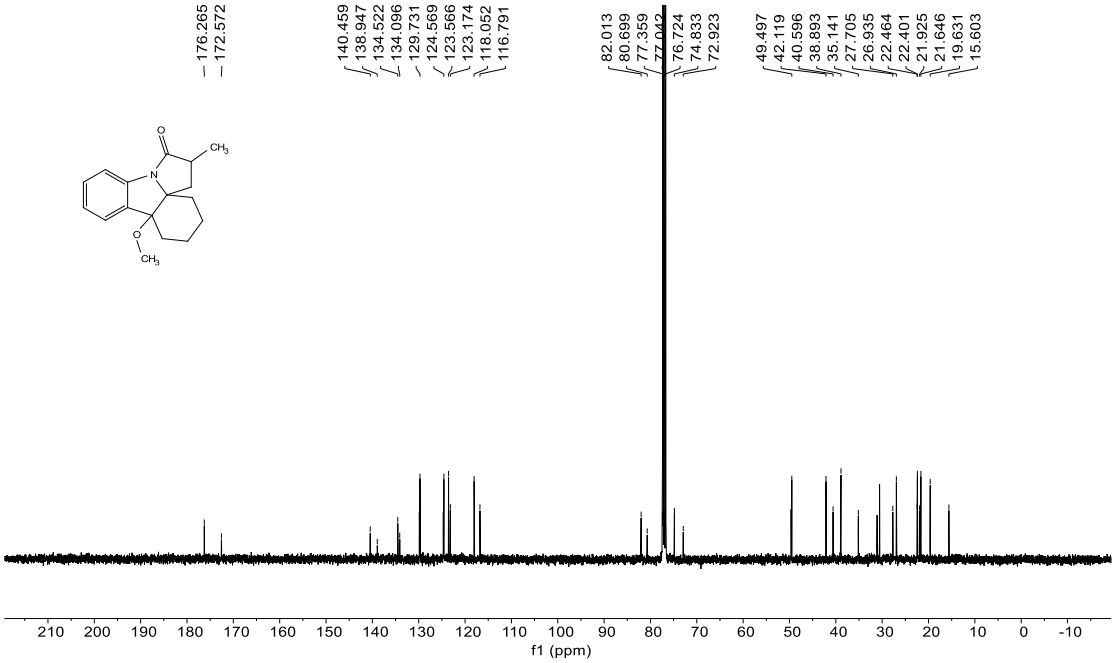
^{1}H and ^{13}C NMR spectra of 2p



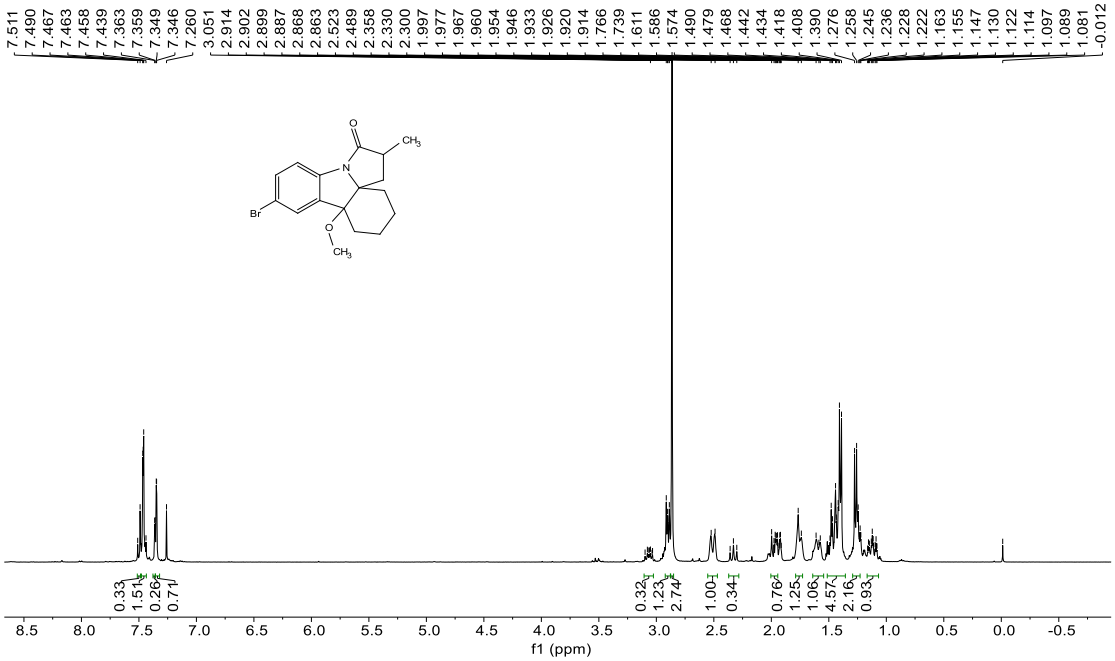


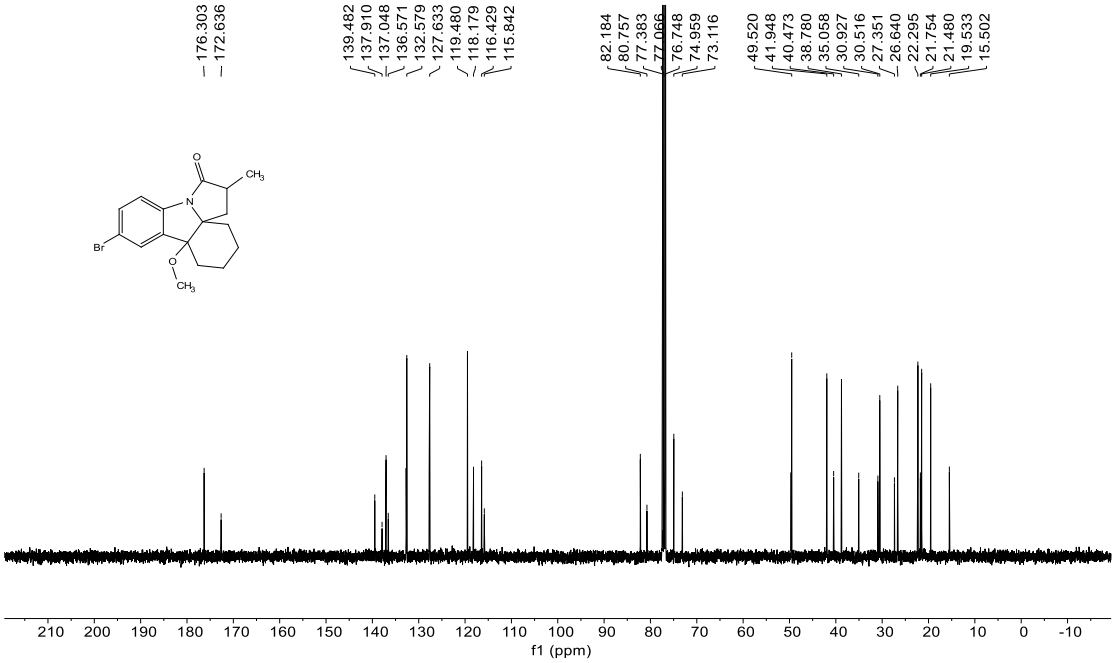
^{1}H and ^{13}C NMR spectra of 4a



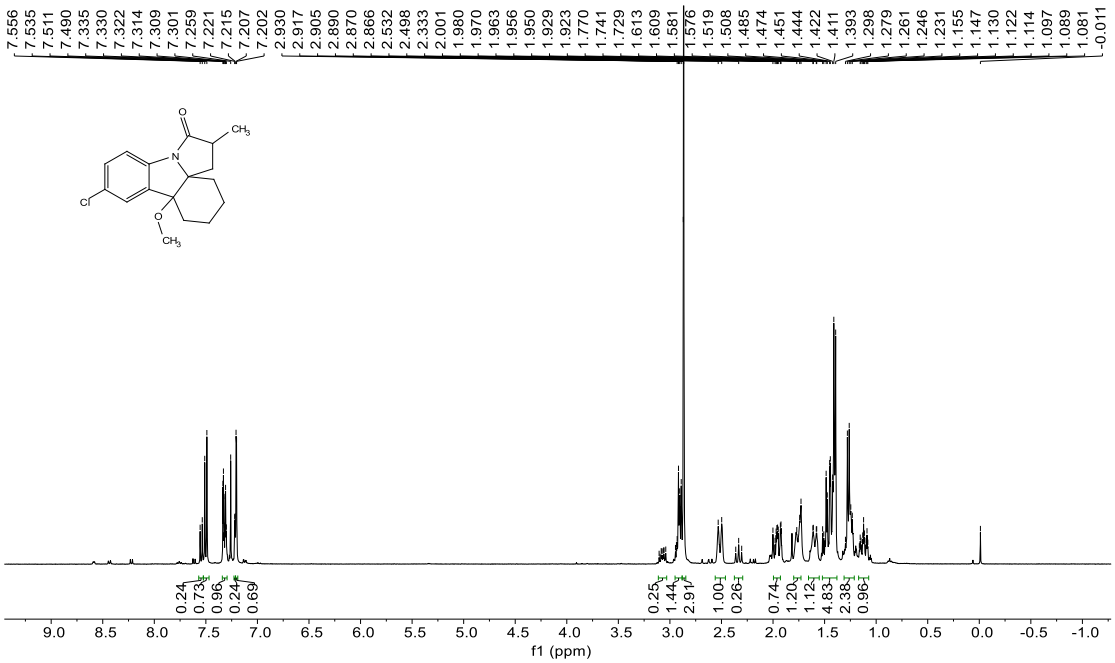


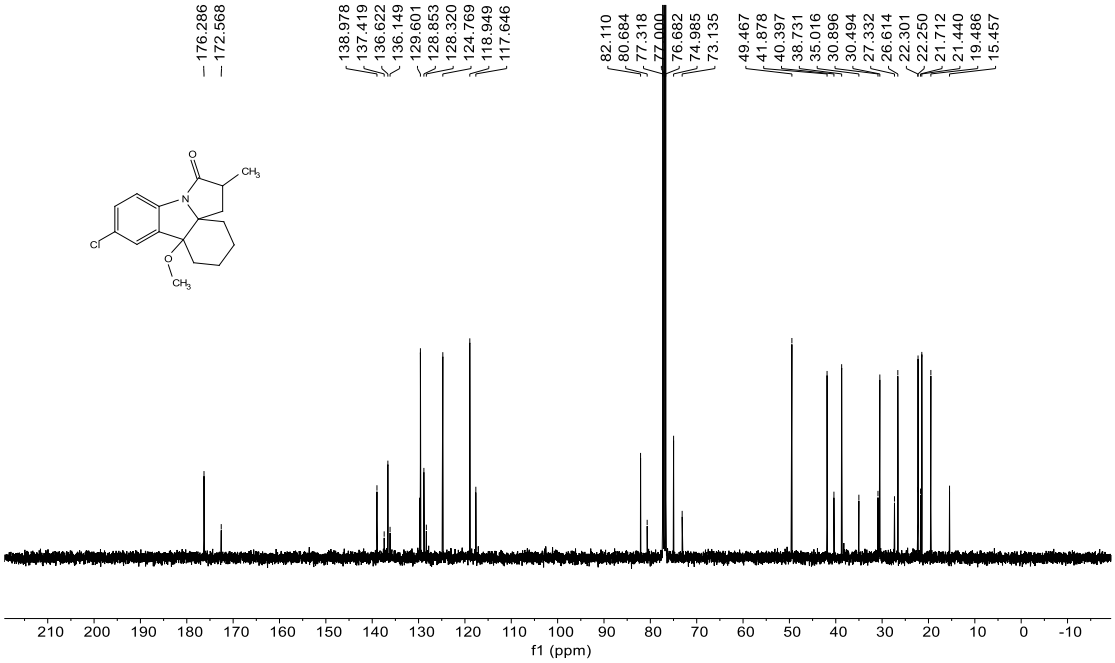
^{1}H and ^{13}C NMR spectra of 4b



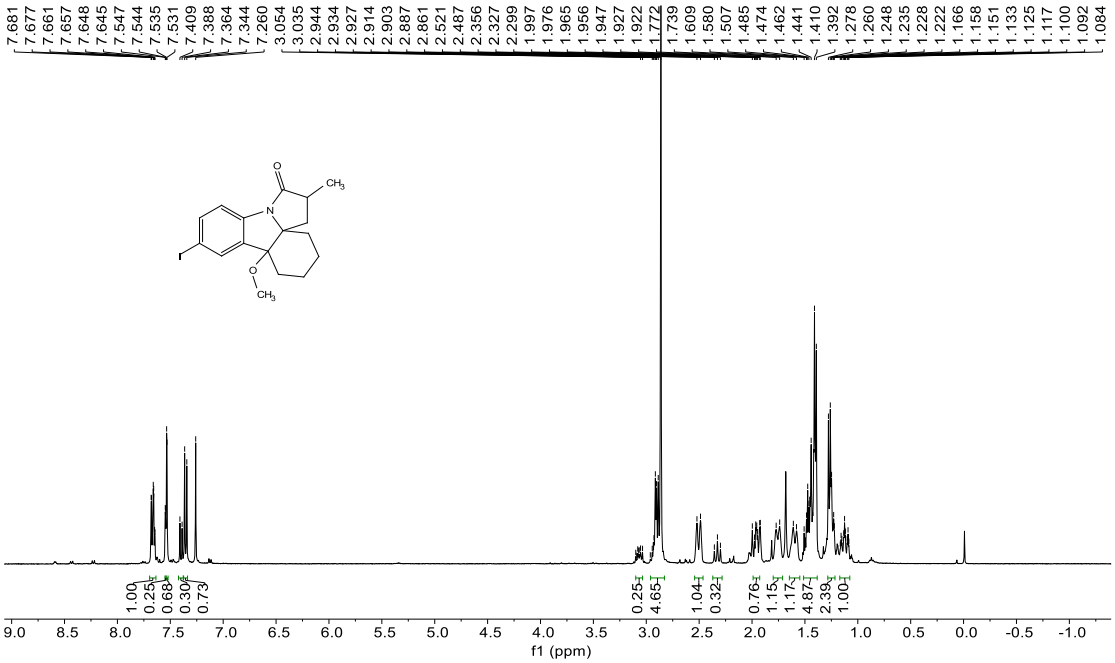


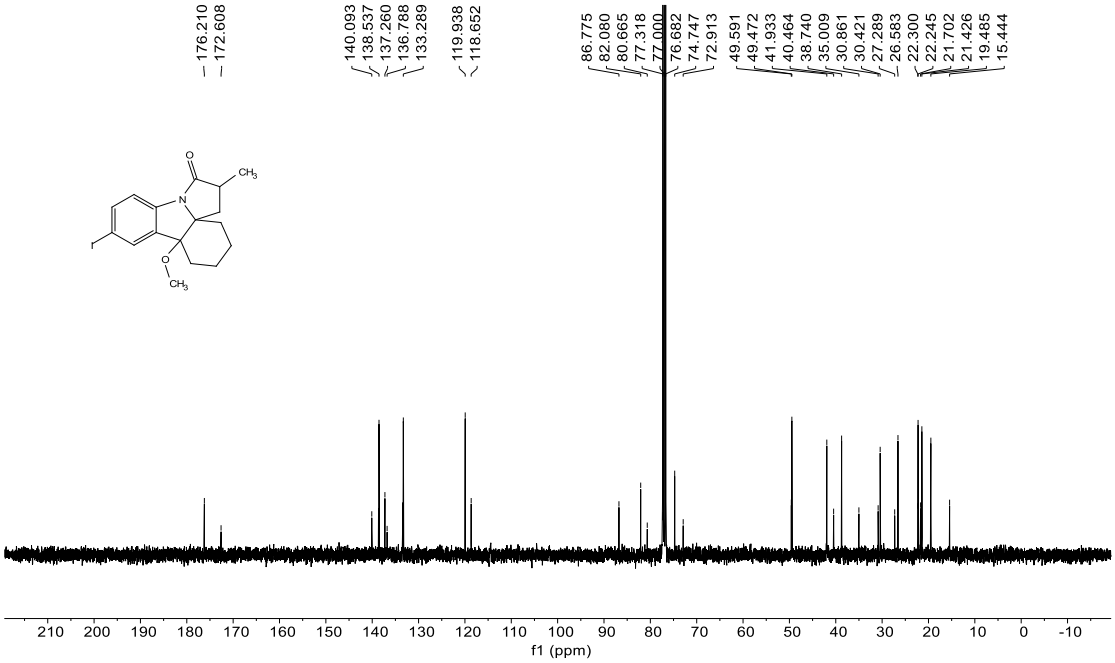
^{1}H and ^{13}C NMR spectra of 4c



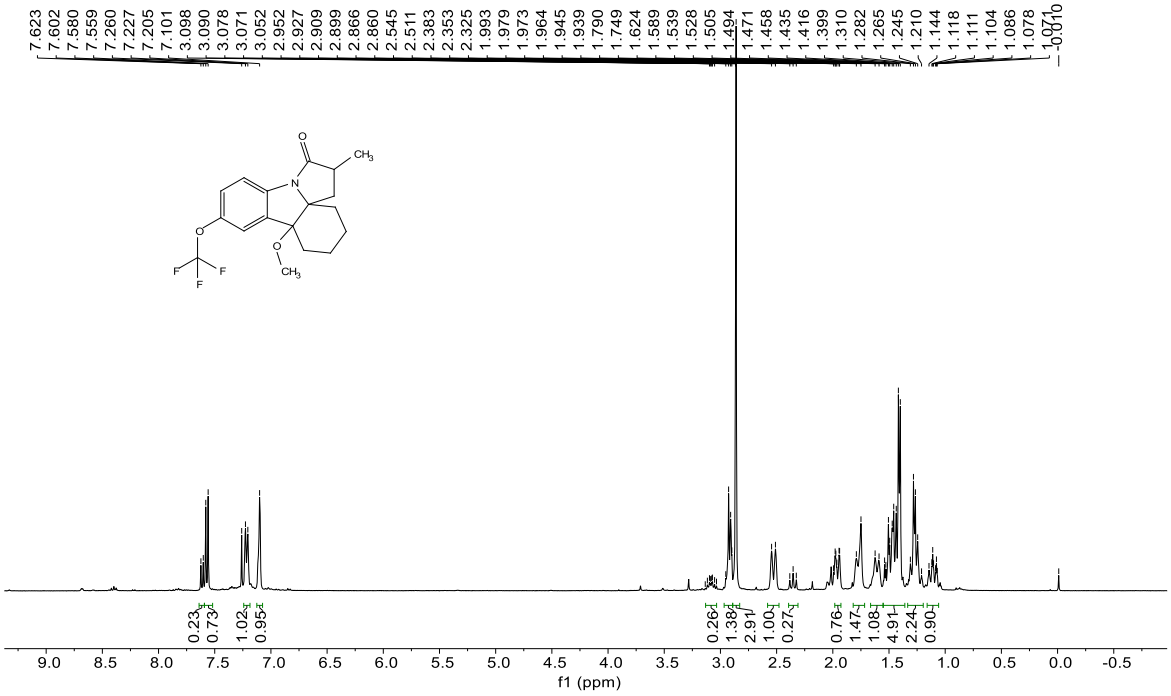


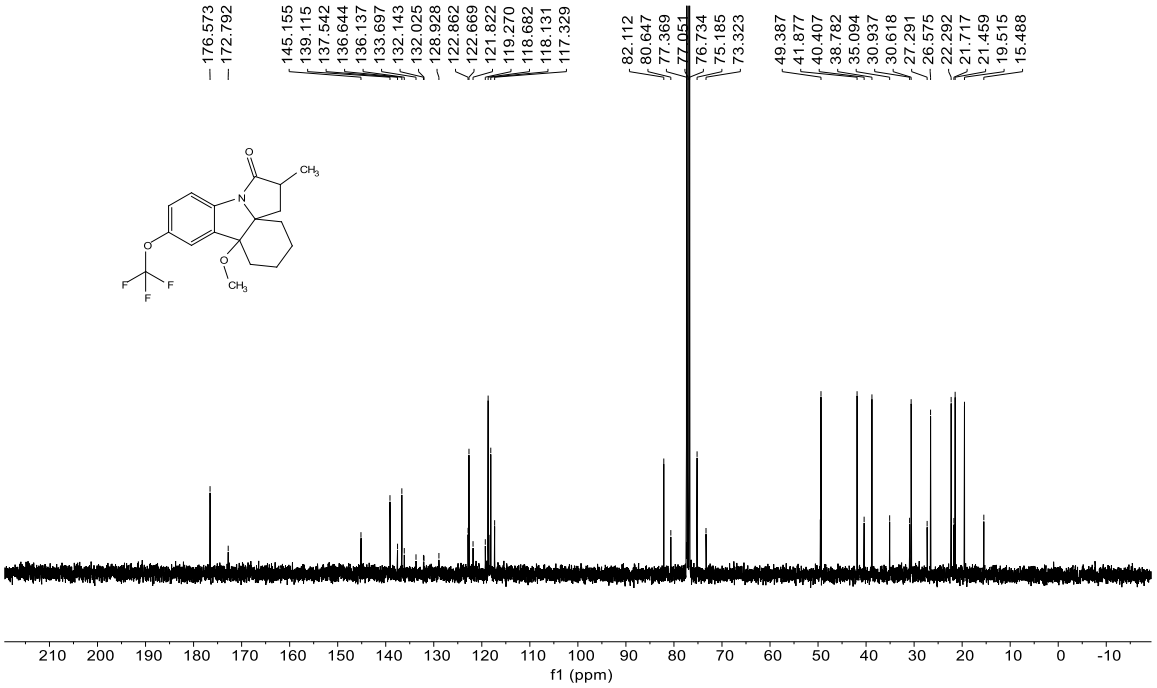
^{1}H and ^{13}C NMR spectra of 4d



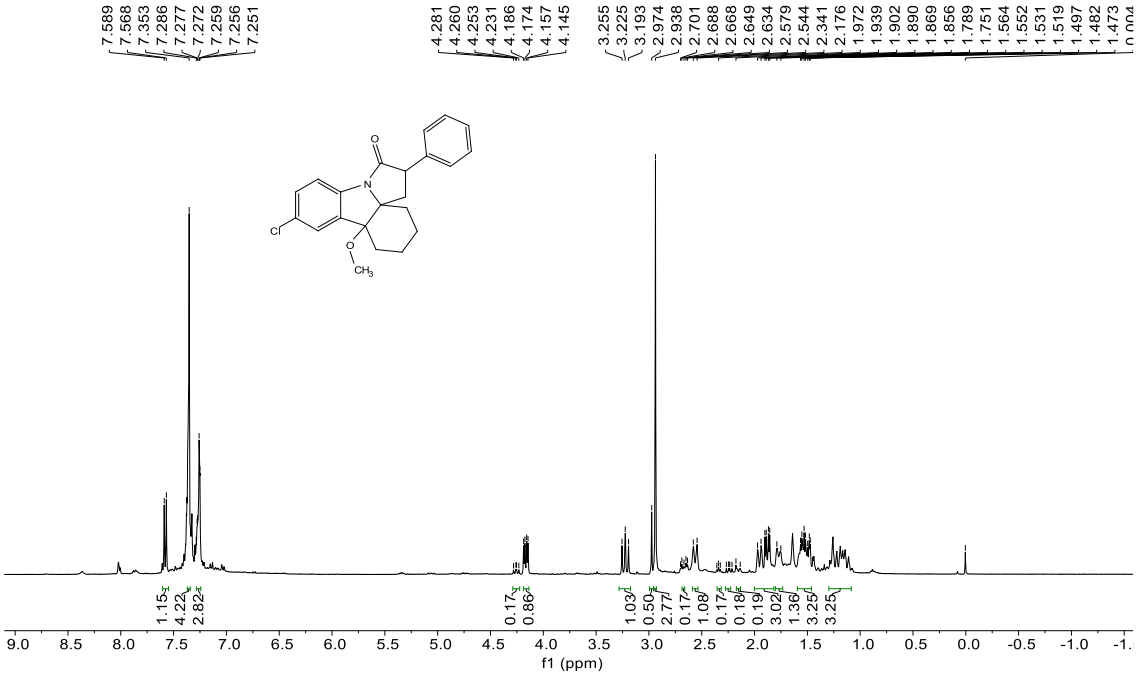


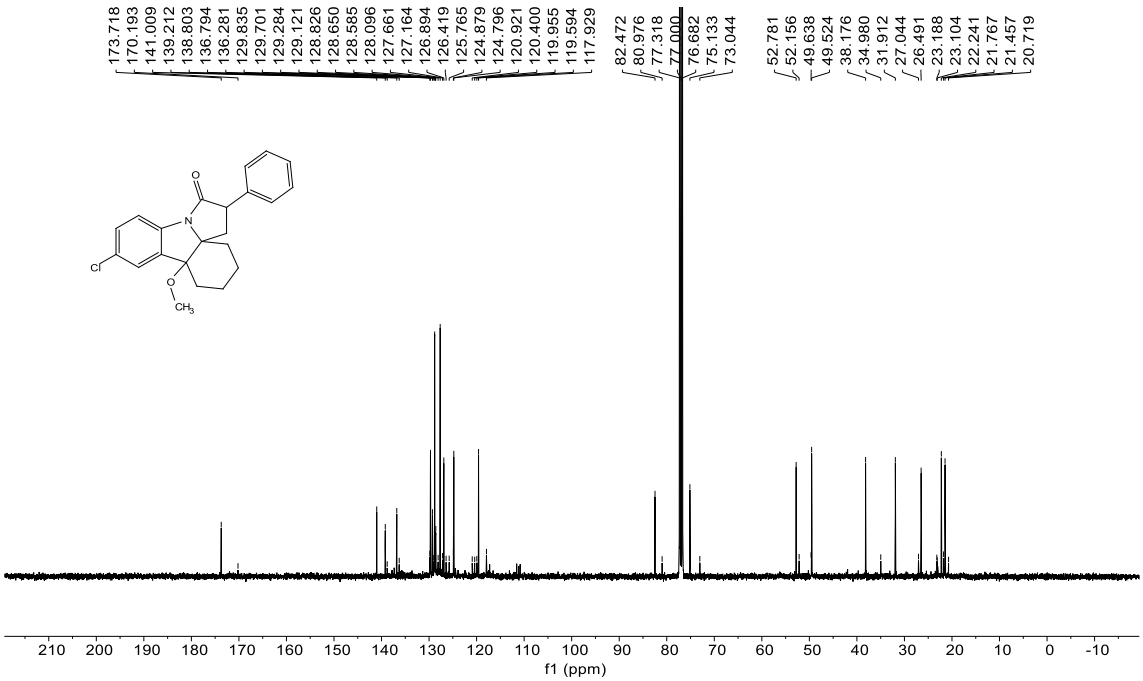
^{1}H and ^{13}C NMR spectra of 4e



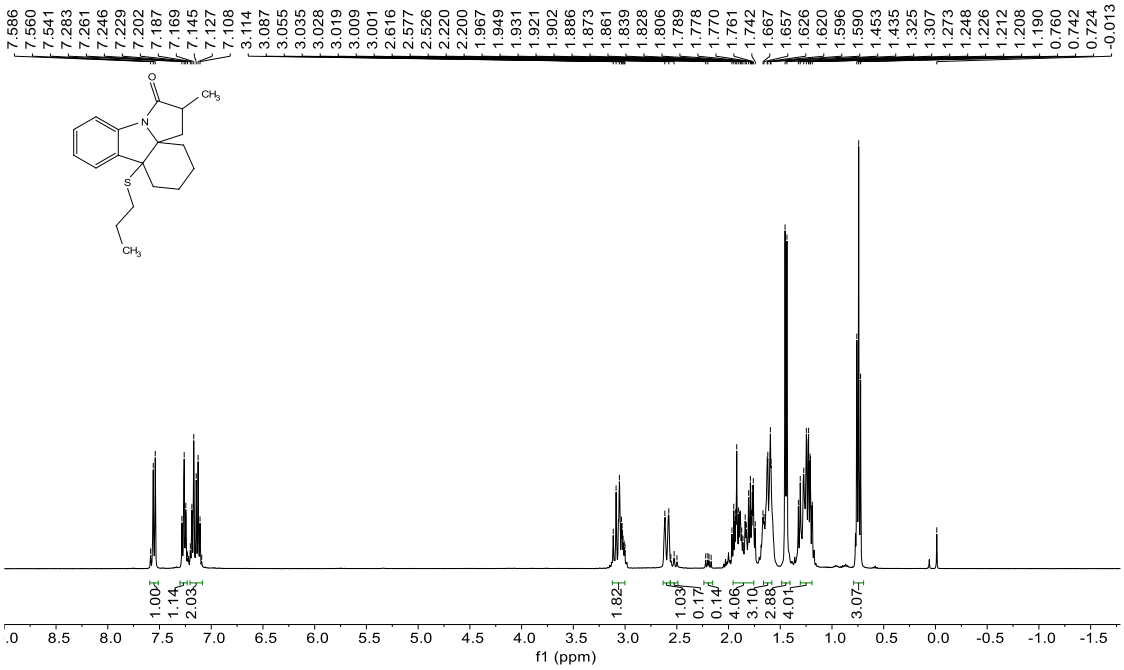


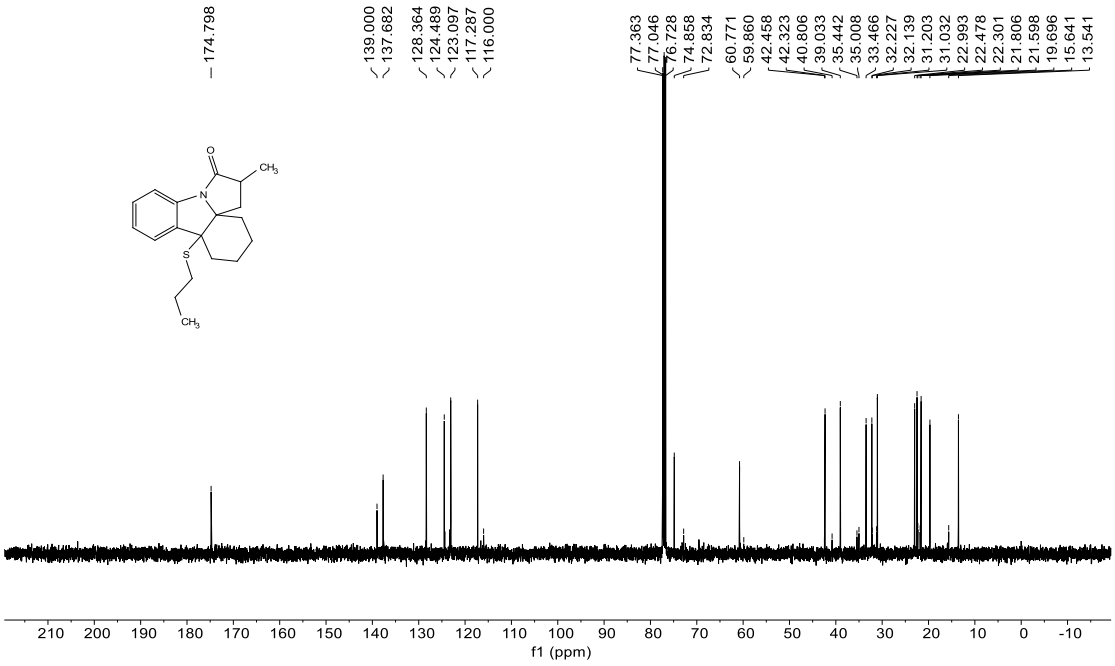
^{1}H and ^{13}C NMR spectra of 4f



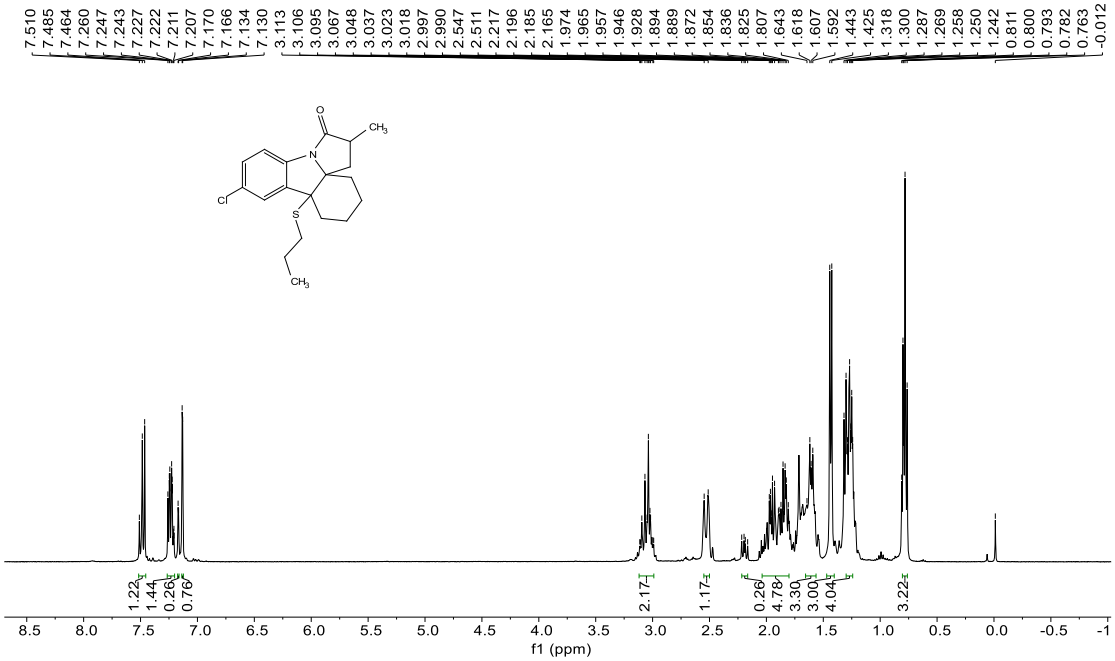


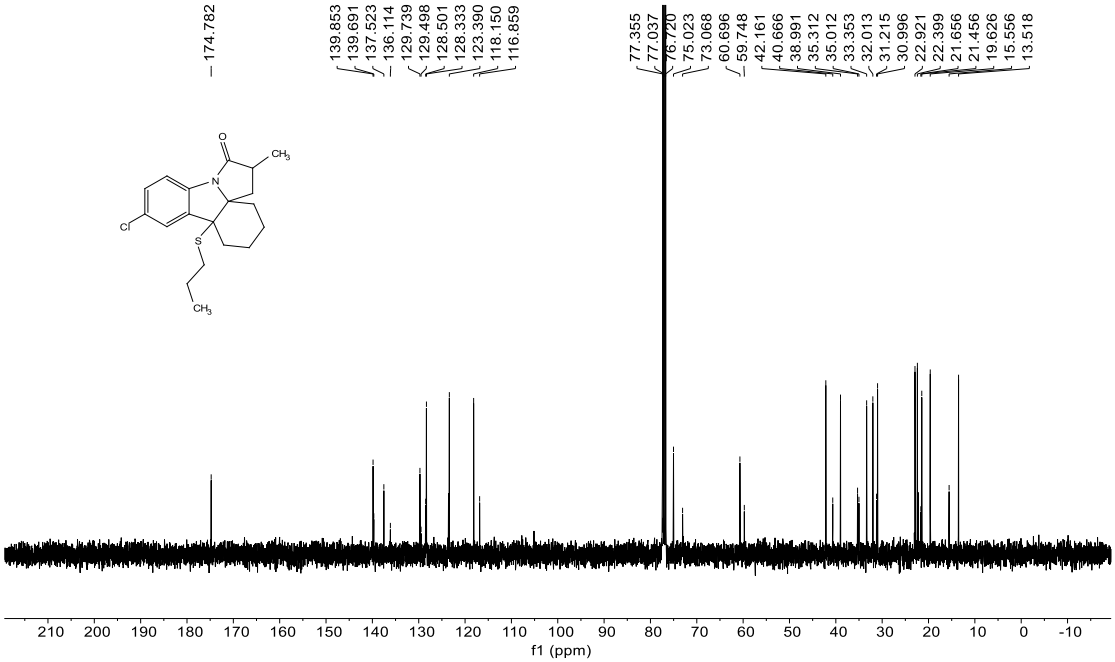
^{1}H and ^{13}C NMR spectra of 4g





^{1}H and ^{13}C NMR spectra of 4h





^{1}H and ^{13}C NMR spectra of 4i