Electronic Supporting Information (ESI) for

Trifluoroethanol-promoted ring-opening cyclization of 4-(2-oxiranylmethoxy)indoles: access to 4,5-fused indoles

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1. General Experimental Remarks

All reactions were carried out in oven-dried glassware and under nitrogen atmosphere. *N*,*N*-Dimethylformamide (DMF) was dried over 3 Å molecular sieves for 1 day prior to use. Thin-layer chromatography (TLC) was performed on pre-coated Merck silica gel plates (60 F254). Compounds were visualized with UV light (λ = 254 nm). Column chromatography was performed using silica gel (60–120 mesh) procured from Merck using freshly distilled solvents. Perkin Elmer 20 analyzer was utilized for elemental analysis of all compounds. HRMS data were recorded by electron spray ionization with a Q-TOF mass analyzer. ^{1}H NMR and ^{13}C NMR spectra were run on JEOL 400 MHz spectrometer and Bruker Advance III 400 MHz spectrometer in $CDCl_3$ as solvent. Chemical shifts are expressed in δ ppm using residual solvent as the internal standard. Coupling constants (*J*) are reported in Hz with the splitting abbreviations s, d, t, q, dd, dt, td and m denoting singlet, doublet, triplet, quartet, doublet of doublets, doublet of triplets, triplet of doublets and multiplet, respectively.

2. Synthesis of Compounds

We have employed 2,3-epoxy tosylates **20a–d** (Figure SI-1**)** for the synthesis of all of the cyclized products. These epoxy tosylates were prepared following our previously reported procedure (H. Borgohain, K. Talukdar, B. Sarma, S. K. Das, *Org. Biomol. Chem*., 2020, **18**, 7401–7413).

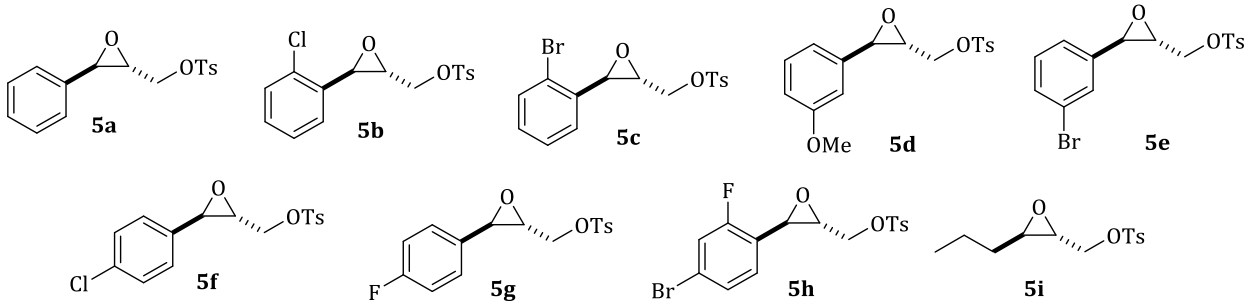


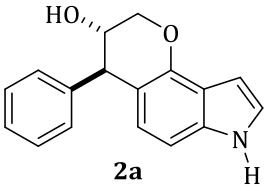
Figure SI-1. Structures of 2,3-epoxy tosylates utilized in the synthesis

General procedure A: Synthesis of 2a–j (Table 2, main manuscript)

A mixture of 4-hydroxyindole **4** (27 mg, 0.2 mmol, 1.0 equiv), appropriate epoxy tosylate **5** (1.0 equiv) and anhydrous K_2CO_3 (42 mg, 0.3 mmol, 1.5 equiv) in anhydrous DMF (5 mL) under an atmosphere of nitrogen was heated at 70 °C for 12 h. After removing most of DMF under reduced pressure, the resulting residue was dissolved in water (5 mL) and ethyl

acetate (10 mL). The organic layer was separated, dried ($MgSO_4$) and concentrated under reduced pressure. The resulting crude product was quickly purified by silica gel column chromatography (roughly filtered on a silica gel-plug) to obtain the corresponding 4-(2-oxiranylmethoxy)indole **1** which was immediately used for the next step. Compound **1** thus obtained was dissolved in trifluoroethanol (3 mL) was refluxed for 1.5 h. The solvent was removed under reduced pressure and the resulting crude product was purified by a silica gel column chromatography (ethyl acetate/hexanes) to furnish the corresponding pyrano[2,3-*e*]indol-3-ol **2**.

(3*S,4*R**)-4-Phenyl-2,3,4,7-tetrahydropyrano[2,3-*e*]indol-3-ol (2a)**

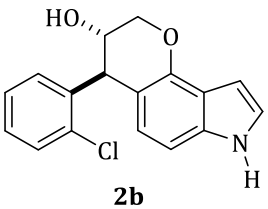


2a

Following the **general procedure A**, the title compound was synthesized from 4-hydroxyindole **4** (27 mg, 0.2 mmol, 1.0 equiv) and epoxy tosylate **5a** (61 mg, 0.2 mmol, 1.0 equiv). Colorless semi-solid. Yield: 76% (40 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.21 (s, 1H), 7.31–7.20 (m, 3H), 7.15–7.12 (m, 3H), 6.93 (d, *J* = 8.2 Hz, 1H), 6.67 (d, *J* = 8.2 Hz, 2H), 4.28-4.13 (m, 4H), 2.32 (br s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.2, 143.7, 136.3, 129.1, 128.5, 126.8, 125.4, 123.1, 117.7, 110.3, 105.2, 99.7, 70.2, 66.5, 49.7. HRMS (TOF MS ES$^+$) calcd for $C_{17}H_{16}NO_2$ $[M + H]^+$: 266.1181, found 266.1190. Anal. Calcd for $C_{17}H_{15}NO_2$: C, 76.96; H, 5.70; N, 5.28, found: C, 77.08; H, 5.79; N, 5.35.

We also repeated the reaction sequence starting with 4-hydroxyindole **4** (1.33 g, 10 mmol, 1.0 equiv) and epoxy tosylate **5a** (3.04 g, 10.0 mmol, 1.0 equiv) to afford compound **2a** in 72% (1.91 g) yield.

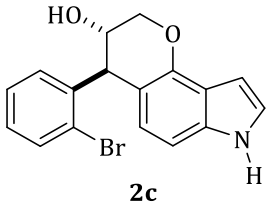
(3*S,4*R**)-4-(2-Chlorophenyl)-2,3,4,7-tetrahydropyrano[2,3-*e*]indol-3-ol (2b)**



2b

Following **the general procedure A**, the title compound was synthesized from 4-hydroxyindole **4** (27 mg, 0.2 mmol, 1.0 equiv) and epoxy tosylate **5b** (68 mg, 0.2 mmol, 1.0 equiv). Colorless semi-solid. Yield: 70% (42 mg) over two steps. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.22 (s, 1H), 7.42 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.19–7.08 (m, 3H), 6.99 (d, *J* = 8.2 Hz, 1H), 6.82 (dd, *J* = 7.8, 1.4 Hz, 1H), 6.68 (d, *J* = 8.2 Hz, 2H), 4.67 (s, 1H), 4.24–4.11 (m, 3H), 2.33 (d, *J* = 6.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.5, 141.1, 136.4, 134.1, 131.4, 129.5, 128.0, 126.9, 125.5, 123.2, 117.7, 109.0, 105.5, 99.8, 67.8, 65.8, 45.9. HRMS (TOF MS ES$^+$) calcd for $C_{17}H_{15}ClNO_2$ [M + H]$^+$: 300.0791, found 300.0783. Anal. Calcd for $C_{17}H_{14}ClNO_2$: C, 68.12; H, 4.71; N, 4.67, found: C, 68.25; H, 4.61; N, 4.77.

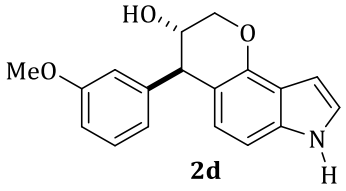
(3*S,4*R**)-4-(2-Bromophenyl)-2,3,4,7-tetrahydropyrano[2,3-*e*]indol-3-ol (2c)**



2c

Following the **general procedure A**, the title compound was synthesized from 4-hydroxyindole **4** (27 mg, 0.2 mmol, 1.0 equiv) and epoxy tosylate **5c** (77 mg, 0.2 mmol, 1.0 equiv). Colorless semi-solid. Yield: 68% (47 mg) over two steps. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.23 (s, 1H), 7.43 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.20–7.09 (m, 3H), 7.00 (d, *J* = 8.2 Hz, 1H), 6.83 (dd, *J* = 7.8, 1.4 Hz, 1H), 6.70–6.68 (m, 2H), 4.68 (s, 1H), 4.25–4.10 (m, 3H), 2.34 (d, *J* = 6.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.5, 142.7, 136.4, 132.9, 131.6, 128.3, 127.6, 125.5, 124.9, 123.2, 117.7, 109.2, 105.5, 99.8, 68.0, 65.7, 48.3. HRMS (TOF MS ES$^+$) calcd for $C_{17}H_{15}BrNO_2$ [M + H]$^+$: 344.0286, found 344.0282. Anal. Calcd for $C_{17}H_{14}BrNO_2$: C, 59.32; H, 4.10; N, 4.07, found: C, 59.19; H, 4.18; N, 4.15.

(3*S,4*R**)-4-(3-Methoxyphenyl)-2,3,4,7-tetrahydropyrano[2,3-*e*]indol-3-ol (2d)**

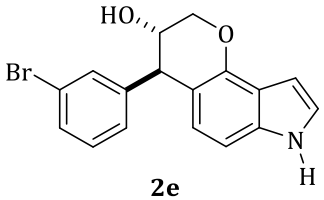


2d

Following the **general procedure A**, the title compound was synthesized from 4-hydroxyindole **4** (27 mg, 0.2 mmol, 1.0 equiv) and epoxy tosylate **5d** (67 mg, 0.2 mmol, 1.0

equiv). Colorless semi-solid. Yield: 74% (44 mg) over two steps. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.21 (s, 1H), 7.23 (t, *J* = 8.1 Hz, 1H), 7.15 (t, *J* = 2.7 Hz, 1H), 6.95 (d, *J* = 8.2 Hz, 1H), 6.81–6.67 (m, 5H), 4.31–4.27 (m, 1H), 4.19–4.15 (m, 3H), 3.76 (s, 3H), 2.33 (br s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.8, 147.2, 145.4, 136.3, 129.5, 125.4, 123.1, 121.5, 117.7, 115.0, 112.0, 110.2, 105.2, 99.7, 70.1, 66.6, 55.2, 49.7. Anal. Calcd for $C_{18}H_{17}NO_3$: C, 73.20; H, 5.80; N, 4.74, found: C, 73.38; H, 5.66; N, 4.77.

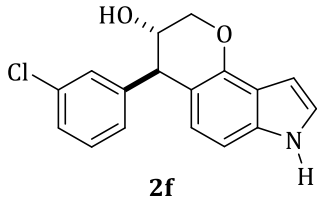
(3*S,4*R**)-4-(3-Bromophenyl)-2,3,4,7-tetrahydropyrano[2,3-*e*]indol-3-ol (2e)**



2e

Following the **general procedure A**, the title compound was synthesized from 4-hydroxyindole **4** (27 mg, 0.2 mmol, 1.0 equiv) and epoxy tosylate **5e** (77 mg, 0.2 mmol, 1.0 equiv). Colorless semi-solid. Yield: 73% (50 mg) over two steps. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.26 (s, 1H), 7.38 (d, *J* = 8.2 Hz, 1H), 7.31 (s, 1H), 7.19–7.15 (m, 2H), 7.09 (d, *J* = 7.8 Hz, 1H), 6.97 (d, *J* = 8.2 Hz, 1H), 6.68–6.65 (m, 2H), 4.25–4.11 (m, 4H), 2.38 (br s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.2, 146.2, 136.3, 132.0, 130.1, 129.9, 127.8, 125.2, 123.3, 122.7, 117.7, 109.6, 105.5, 99.7, 70.0, 66.3, 49.3. Anal. Calcd for $C_{17}H_{14}BrNO_2$: C, 59.32; H, 4.10; N, 4.07, found: C, 59.49; H, 4.19; N, 4.17.

(3*S,4*R**)-4-(3-Chlorophenyl)-2,3,4,7-tetrahydropyrano[2,3-*e*]indol-3-ol (2f)**

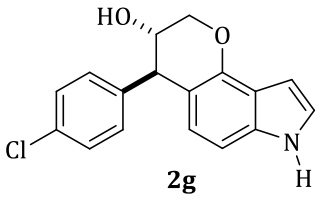


2f

Following the **general procedure A**, the title compound was synthesized from 4-hydroxyindole **4** (27 mg, 0.2 mmol, 1.0 equiv) and epoxy tosylate **5f** (68 mg, 0.2 mmol, 1.0 equiv). Colorless semi-solid. Yield: 73% (44 mg) over two steps. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.22 (s, 1H), 7.25–7.21 (m, 2H), 7.17 (t, *J* = 2.3 Hz, 1H), 7.15 (s, 1H), 7.08–7.06 (m, 1H), 6.99 (d, *J* = 8.2 Hz, 1H), 6.67–6.66 (m, 2H), 4.26–4.11 (m, 4H), 2.29 (br s, 1H). ^{13}C NMR (100

MHz, $CDCl_3$): δ 147.2, 145.9, 136.4, 134.5, 129.8, 129.2, 127.3, 127.0, 125.2, 123.2, 117.7, 109.6, 105.4, 99.8, 70.0, 66.4, 49.3. HRMS (TOF MS ES$^+$) calcd for $C_{17}H_{15}ClNO_2$ [M + H]$^+$: 300.0791, found 300.0783. Anal. Calcd for $C_{17}H_{14}ClNO_2$: C, 68.12; H, 4.71; N, 4.67, found: C, 68.31; H, 4.78; N, 4.74.

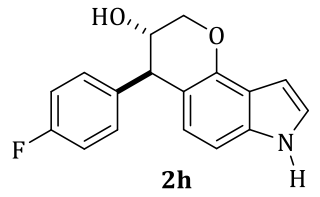
(3*S,4*R**)-4-(4-Chlorophenyl)-2,3,4,7-tetrahydropyrano[2,3-*e*]indol-3-ol (2g)**



2g

Following the **general procedure A**, the title compound was synthesized from 4-hydroxyindole **4** (27 mg, 0.2 mmol, 1.0 equiv) and epoxy tosylate **5g** (68 mg, 0.2 mmol, 1.0 equiv). Colorless semi-solid. Yield: 74% (45 mg) over two steps. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.22 (s, 1H), 7.25 (d, *J* = 8.2 Hz, 2H), 7.13 (t, *J* = 2.4 Hz, 1H), 7.06 (d, *J* = 8.2 Hz, 2H), 6.94 (d, *J* = 8.2 Hz, 1H), 6.65 (app. s, 1H), 6.63 (d, *J* = 8.2 Hz, 1H), 4.22–4.08 (m, 4H), 2.35 (br s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.2, 142.3, 136.3, 132.6, 130.4, 128.7, 125.1, 123.2, 117.7, 109.9, 105.4, 99.7, 70.0, 66.3, 49.0. Anal. Calcd for $C_{17}H_{14}ClNO_2$: C, 68.12; H, 4.71; N, 4.67. Found: C, 68.03; H, 4.78; N, 4.74.

(3*S,4*R**)-4-(4-Fluorophenyl)-2,3,4,7-tetrahydropyrano[2,3-*e*]indol-3-ol (2h)**

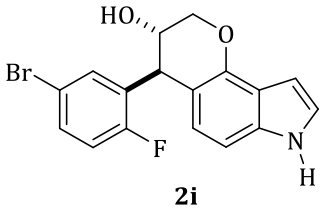


2h

Following the general procedure A, the title compound was synthesized from 4-hydroxyindole **4** (27 mg, 0.2 mmol, 1.0 equiv) and epoxy tosylate **5h** (64 mg, 0.2 mmol, 1.0 equiv). Colorless semi-solid. Yield: 75% (42 mg) over two steps. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.22 (s, 1H), 7.17–7.11 (m, 3H), 7.02–6.97 (m, 3H), 6.68–6.66 (m, 2H), 4.27–4.12 (m, 4H), 2.28 (br s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.7 (d, *J* = 245.4 Hz), 147.2, 139.4 (d, *J* = 2.9 Hz), 136.3, 130.5 (d, *J* = 10.5 Hz), 125.2, 123.3, 117.7, 115.4 (d, *J* = 23 Hz), 110.2, 105.4, 99.8, 68.2, 66.2, 42.5. HRMS (TOF MS ES$^+$) calcd for $C_{17}H_{15}FNO_2$ [M + H]$^+$: 284.1087, found

284.1085. Anal. Calcd for $C_{17}H_{14}FNO_2$: C, 72.07; H, 4.98; N, 4.94. Found: C, 72.21; H, 4.90; N, 5.03.

(3*S,4*R**)-4(5-Bromo-2-fluorophenyl)-2,3,4,7-tetrahydropyrano[2,3-*e*]indol-3-ol (2i)**



2i

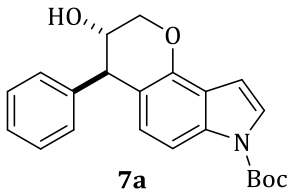
Following the **general procedure A**, the title compound was synthesized from 4-hydroxyindole **4** (27 mg, 0.2 mmol, 1.0 equiv) and epoxy tosylate **5i** (80 mg, 0.2 mmol, 1.0 equiv). Colorless semi-solid. Yield: 67% (48 mg) over two steps. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.31 (s, 1H), 7.36–7.32 (m, 1H), 7.18 (t, *J* = 2.7 Hz, 1H), 7.01–6.93 (m, 3H), 6.66–6.65 (m, 2H), 4.51 (s, 1H), 4.22–4.10 (m, 3H), 2.44 (br s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.9 (d, *J* = 247.3 Hz), 147.4, 136.5, 133.8 (d, *J* = 3.8 Hz), 133.1 (d, *J* = 15.3 Hz), 131.4 (d, *J* = 7.7 Hz), 125.0, 123.3, 117.7, 117.0 (d, *J* = 23.9 Hz), 116.8 (d, *J* = 2.9 Hz), 107.9, 105.7, 99.7, 68.2, 66.2, 42.5. Anal. Calcd for $C_{17}H_{13}BrFNO_2$: C, 56.37; H, 3.62; N, 3.87. Found: C, 56.55; H, 3.69; N, 3.83.

General procedure B: Synthesis of 7a–d (Table 3, main manuscript)

A mixture of 4-hydroxyindole **4** (27 mg, 0.2 mmol, 1.0 equiv), epoxy tosylate **5a** (1.0 equiv) and anhydrous K_2CO_3 (42 mg, 0.3 mmol, 1.5 equiv) in anhydrous DMF (5 mL) under an atmosphere of nitrogen was heated at 70 °C for 12 h. NaH (60 % in mineral oil, 0.3 mmol, 10 mg) and Boc_2O/alkyl bromide (1.0 equiv) were sequentially added to the reaction mixture after cooling it to rt. The reaction mixture was stirred for additional 6 h. The reaction was quenched by adding cold water (5 mL) and ethyl acetate (10 mL). The organic layer was separated, dried ($MgSO_4$) and concentrated under reduced pressure. The resulting crude product was quickly purified by silica gel column chromatography (roughly filtered on a silica gel-plug) to obtain the corresponding 4-(2-oxiranylmethoxy)indole **6** which was immediately used for the next step. Compound **6** thus obtained was dissolved in trifluoroethanol (3 mL) was refluxed for 1.5 h. The solvent was removed under reduced pressure and the resulting crude product was purified by a silica gel column

chromatography (ethyl acetate/hexanes) to furnish the corresponding pyrano[2,3-*e*]indol-3-ol **7**.

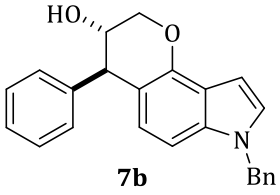
tert-Butyl (3*S,4*R**)-3-hydroxy-4-phenyl-3,4-dihydropyrano[2,3-*e*]indole-7(2*H*)-carboxylate (7a)**



7a

Following the **general procedure B**, the title compound was synthesized from 4-hydroxyindole **4** (27 mg, 0.2 mmol, 1.0 equiv), epoxy tosylate **5a** and (61 mg, 0.2 mmol, 1.0 equiv) and Boc_2O (43 mg, 0.2 mmol, 1.0 equiv). Colorless semi-solid. Yield: 65% (48 mg) over two steps. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.66 (d, *J* = 8.2, 1H), 7.53 (d, J = 3.6 Hz, 1H), 7.32-7.22 (m, 3H), 7.13 (d, *J* = 7.3 Hz, 2H), 6.80 (d, *J* = 8.7 Hz, 1H), 6.70 (d, *J* = 3.6 Hz, 1H), 4.27–4.13 (m, 4H), 2.25 (br s, 1H), 1.65 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 149.8, 147.0, 143.1, 135.5, 129.1, 128.6, 127.4, 127.0, 124.8, 119.9, 114.2, 109.0, 104.1, 83.7, 70.0, 66.7, 49.6, 28.2. Anal. Calcd for $C_{22}H_{23}NO_4$: C, 72.31; H, 6.34; N, 3.83, found: C, 72.42; H, 6.38; N, 3.89.

(3*S,4*R**)-7-Benzyl-4-phenyl-2,3,4,7-tetrahydropyrano[2,3-*e*]indol-3-ol (7b)**

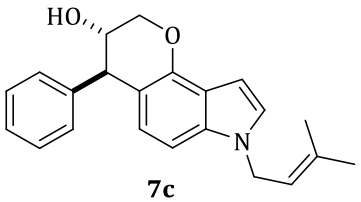


7b

Following the **general procedure B**, the title compound was synthesized from 4-hydroxyindole **4** (27 mg, 0.2 mmol, 1.0 equiv), epoxy tosylate **5a** and (61 mg, 0.2 mmol, 1.0 equiv) and BnBr (24 μL, 0.2 mmol, 1.0 equiv). Colorless semi-solid. Yield: 66% (47 mg) over two steps. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.31–7.20 (m, 6H), 7.16–7.11 (m, 4H), 7.07 (d, *J* = 3.2 Hz, 1H), 6.84 (d, *J* = 8.2 Hz, 1H), 6.66–6.64 (m, 2H), 5.27 (s, 2H), 4.29–4.15 (m, 1H), 4.20-4.15 (m, 3H), 2.23 (br s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.3, 143.7, 137.5, 136.9, 129.2, 128.7, 128.6, 127.7, 127.2, 127.1, 126.8, 125.1, 118.3, 110.3, 103.9, 98.8, 70.3, 66.5,

50.3, 49.8. Anal. Calcd for $C_{24}H_{21}NO_2$: C, 81.10; H, 5.96; N, 3.94, found: C, 81.01; H, 6.05; N, 3.98.

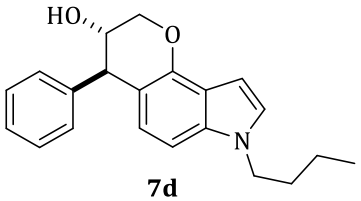
(3*S,4*R**)-7-(3-Methylbut-2-en-1-yl)-4-phenyl-2,3,4,7-tetrahydropyrano[2,3-*e*]indol-3-ol (7c)**



7c

Following the **general procedure B**, the title compound was synthesized from 4-hydroxyindole **4** (27 mg, 0.2 mmol, 1.0 equiv), epoxy tosylate **5a** and (61 mg, 0.2 mmol, 1.0 equiv) and prenyl bromide (27 μL, 0.2 mmol, 1.0 equiv). Colorless semi-solid. Yield: 68% (45 mg) over two steps. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.31–7.20 (m, 4H), 7.16 (d, *J* = 7.3 Hz, 2H), 7.04 (d, *J* = 3.2 Hz, 1H), 6.89 (d, *J* = 8.2 Hz, 1H), 6.68 (d, *J* = 8.2 Hz, 1H), 6.59 (d, *J* = 3.2 Hz, 1H), 5.38 (t, *J* = 6.8 Hz, 1H), 4.64 (d, *J* = 6.8 Hz, 2H), 4.28–4.12 (m, 4H), 2.27 (br s, 1H), 1.80 (s, 3H), 1.75 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.2, 143.8, 136.6, 136.3, 129.1, 128.5, 126.7, 126.4, 124.8, 119.9, 118.3, 109.9, 103.8, 98.0, 70.2, 66.5, 49.7, 44.3, 25.6, 18.0. HRMS (TOF MS ES$^+$) calcd for $C_{22}H_{24}NO_2$ $[M + H]^+$: 334.1807, found 334.1804. Anal. Calcd for $C_{22}H_{23}NO_2$: C, 79.25; H, 6.95; N, 4.20, found: C, 79.42; H, 7.06; N, 4.25.

(3*S,4*R**)-7-Butyl-4-phenyl-2,3,4,7-tetrahydropyrano[2,3-*e*]indol-3-ol (7d)**

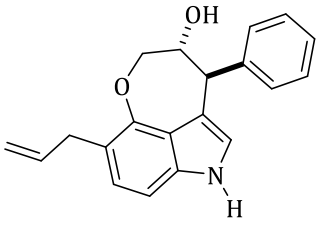


7d

Following the general procedure B, the title compound was synthesized from 4-hydroxyindole **4** (27 mg, 0.2 mmol, 1.0 equiv), epoxy tosylate **5a** and (61 mg, 0.2 mmol, 1.0 equiv) and 1-bromobutane (28 mg, 0.2 mmol, 1.0 equiv). Colorless semi-solid. Yield: 65% (42 mg) over two steps. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.33–7.24 (m, 3H), 7.18 (d, *J* = 7.3 Hz, 2H), 7.04 (d, *J* = 3.2 Hz, 1H), 6.91 (d, *J* = 8.7 Hz, 1H), 6.69 (d, *J* = 8.2 Hz, 1H), 6.59 (d, *J* = 2.7 Hz, 1H), 4.28–4.06 (m, 7H), 2.26 (br s, 1H), 1.85–1.78 (m, 2H), 1.40–1.29 (m, 2H), 0.95 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.3, 143.8, 136.6, 129.1, 128.5, 126.8, 126.7,

124.7, 118.1, 109.8, 103.7, 97.9, 70.3, 66.5, 49.7, 46.3, 32.4, 20.1, 13.7. Anal. Calcd for $C_{21}H_{23}NO_2$: C, 78.47; H, 7.21; N, 4.36, found: C, 78.66; H, 7.28; N, 4.40.

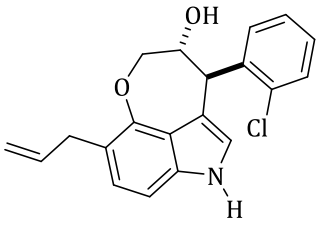
(3*R,4*R**)-9-Allyl-4-phenyl-2,3,4,6-tetrahydrooxepino[4,3,2-*cd*]indol-3-ol (10a)**



10a

Following the **general procedure A**, the title compound was synthesized from 5-allyl-4-hydroxyindole **8** (35 mg, 0.2 mmol, 1.0 equiv) and epoxy tosylate **5a** (61 mg, 0.2 mmol, 1.0 equiv). Colorless semi-solid. Yield: 73% (45 mg) over two steps. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.28 (s, 1H), 7.34–7.23 (m, 3H), 7.19–7.15 (m, 3H), 6.68–6.66 (m, 1H), 6.51 (s, 1H), 6.03–5.96 (m, 1H), 5.23–5.18 (m, 1H), 5.14–5.11 (m, 1H), 4.27–4.13 (m, 4H), 3.48 (d, *J* = 6.4 Hz, 2H), 2.28 (br s, 1H). Anal. Calcd for $C_{20}H_{19}NO_2$: C, 78.66; H, 6.27; N, 4.59, found: C, 78.55; H, 6.32; N, 4.55.

(3*R,4*R**)-9-Allyl-4-(2-chlorophenyl)-2,3,4,6-tetrahydrooxepino[4,3,2-*cd*]indol-3-ol (10b)**

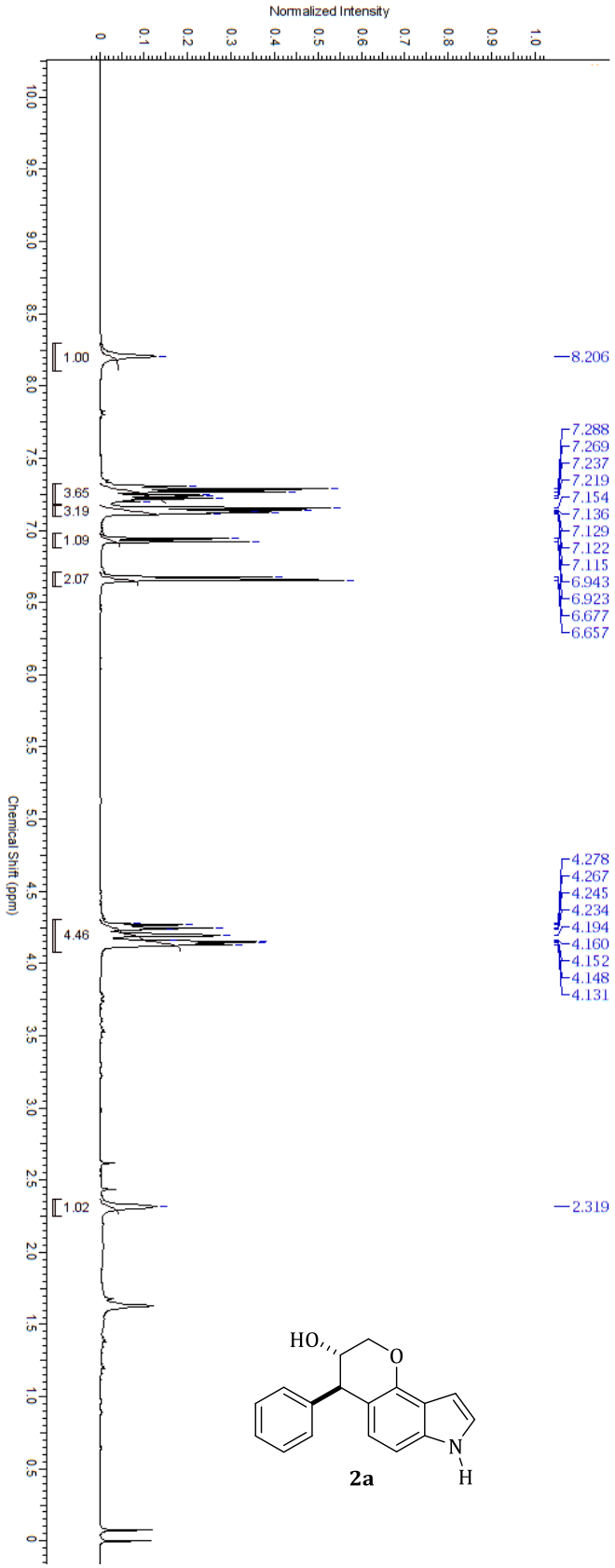


10b

Following the **general procedure A**, the title compound was synthesized from 5-allyl-4-hydroxyindole **4** (35 mg, 0.2 mmol, 1.0 equiv) and epoxy tosylate **5b** (68 mg, 0.2 mmol, 1.0 equiv). Colorless semi-solid. Yield: 66% (45 mg) over two steps. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.32 (br s, 1H), 7.43 (d, *J* = 7.8 Hz, 1H), 7.20–7.10 (m, 3H), 6.85 (d, *J* = 7.3 Hz, 1H), 6.69 (t, *J* = 2.3 Hz, 1H), 6.50 (s, 1H), 6.05–5.95 (m, 1H), 5.21 (dd, *J* = 17.4, 1.8 Hz, 1H), 5.14 (dd, *J* = 10.0, 1.4 Hz, 1H), 4.66 (s, 1H), 4.23–4.11 (m, 3H), 3.50 (d, *J* = 6.4 Hz, 2H), 2.37 (d, *J* = 6.8 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 146.3, 141.2, 137.1, 135.7, 134.1, 131.5, 129.5, 128.0,

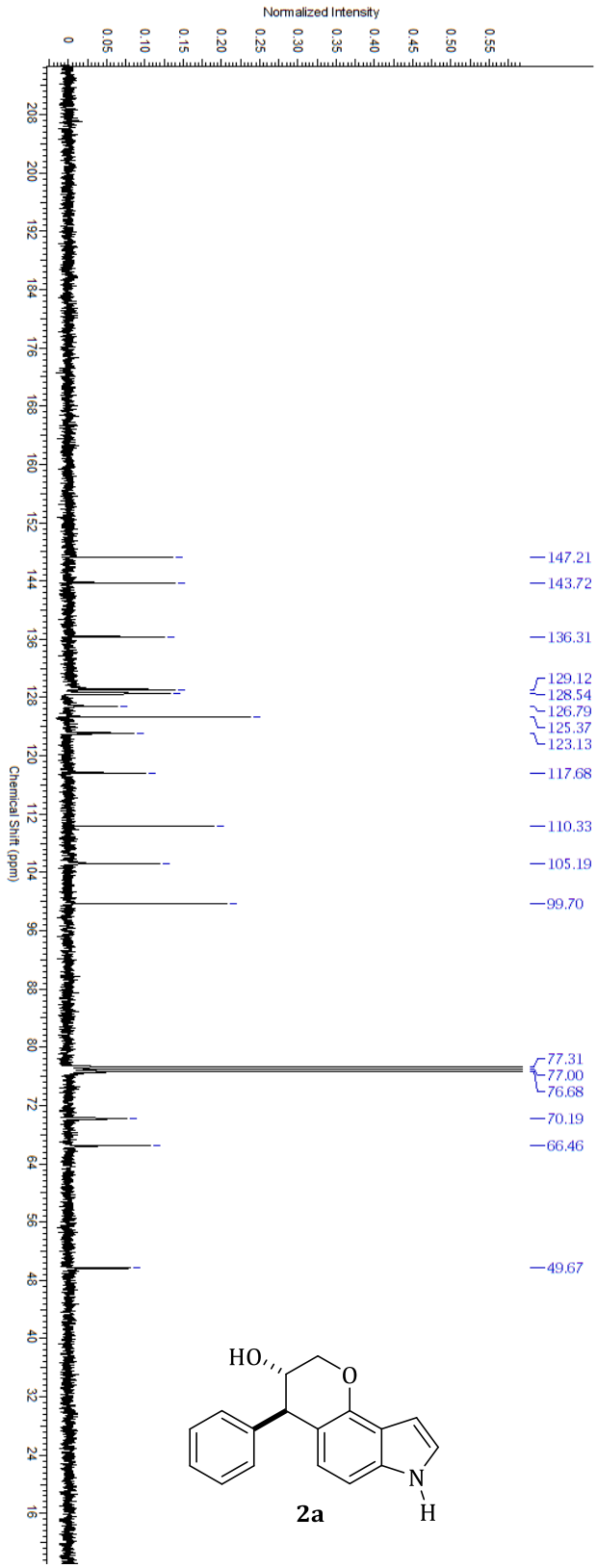
126.9, 125.2, 123.0, 117.7, 116.4, 116.1, 108.8, 100.0, 67.8, 65.6, 45.8, 36.3. Anal. Calcd for $C_{20}H_{18}ClNO_2$: C, 70.69; H, 5.34; N, 4.12. Found: C, 70.90; H, 5.44; N, 4.18.

3. Figures of ^{1}H and ^{13}C NMR Spectra of Compounds

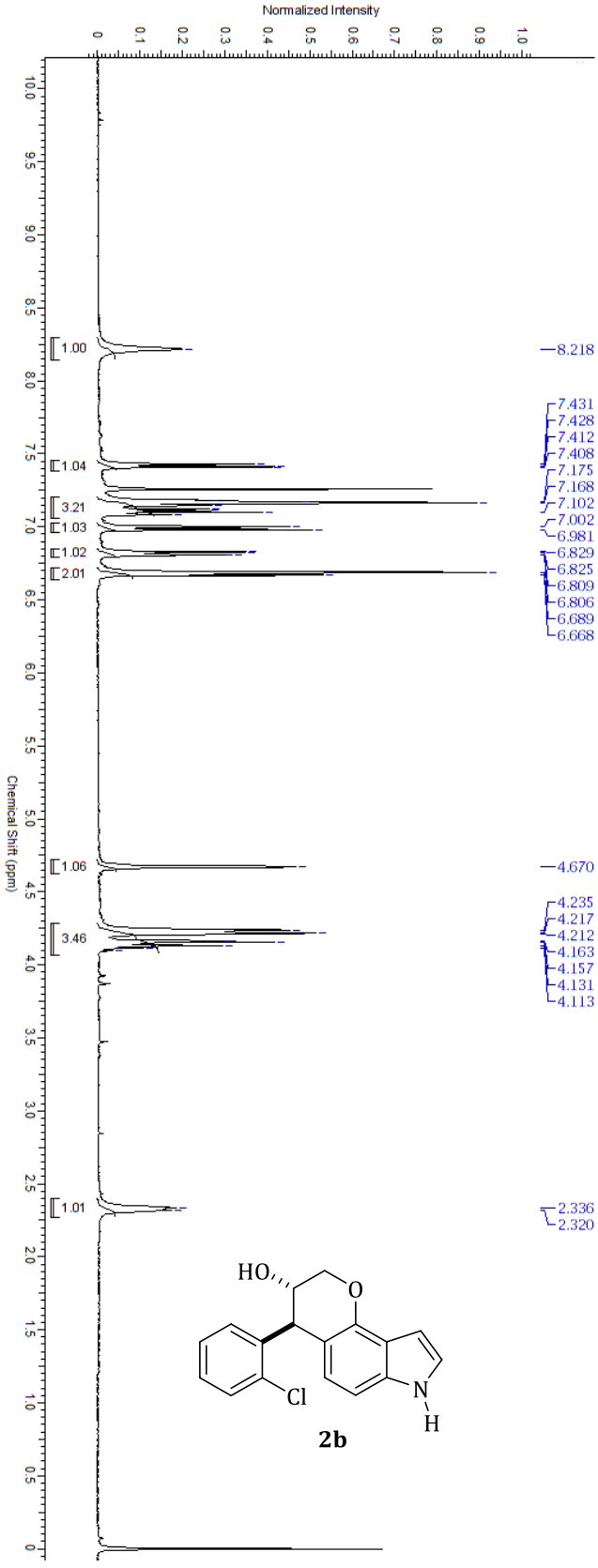


2a

^{1}H NMR (400 MHz, $CDCl_3$) of compound **2a**.

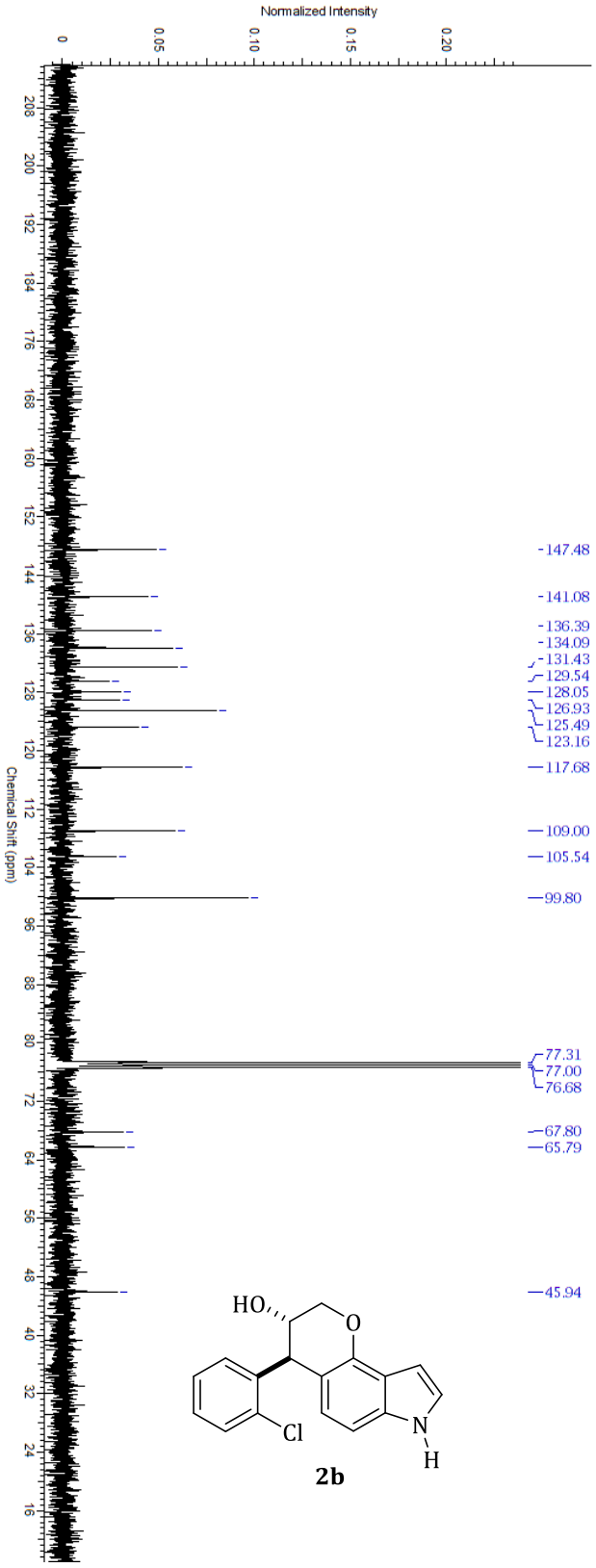


^{13}C NMR (100 MHz, $CDCl_3$) of compound **2a**.



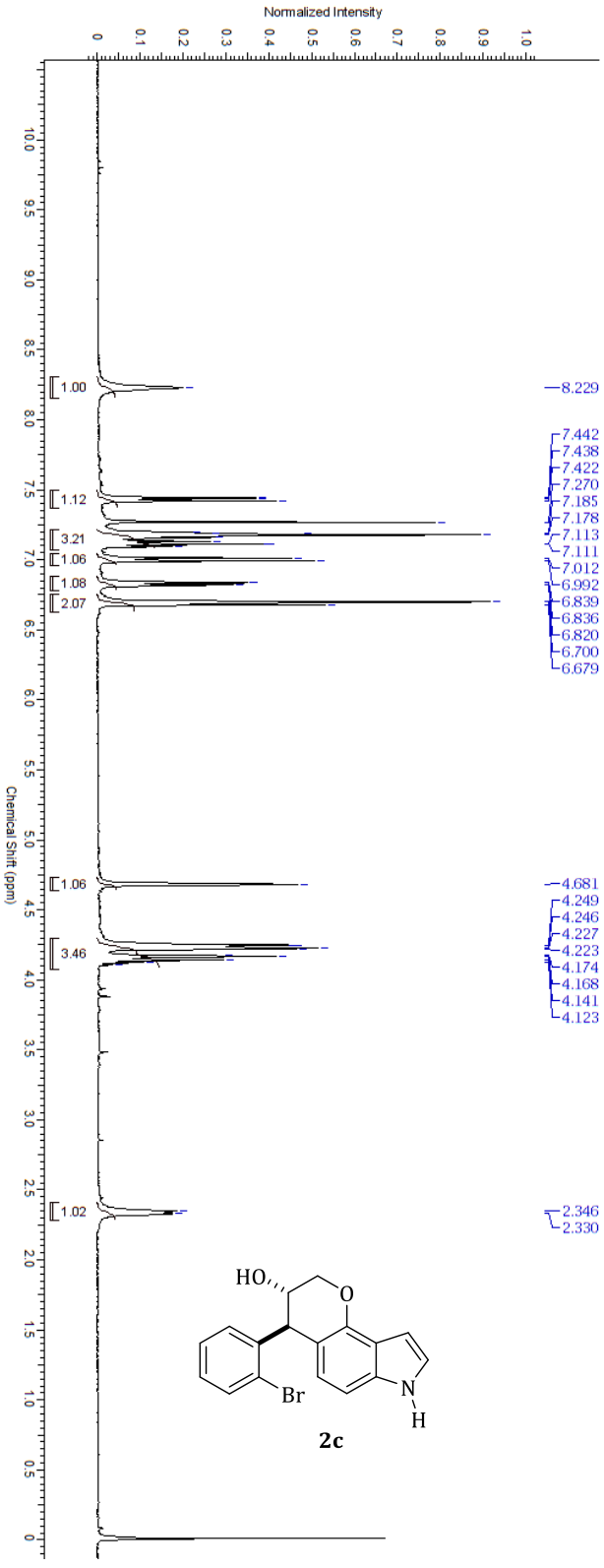
2b

^{1}H NMR (400 MHz, $CDCl_3$) of compound **2b**,



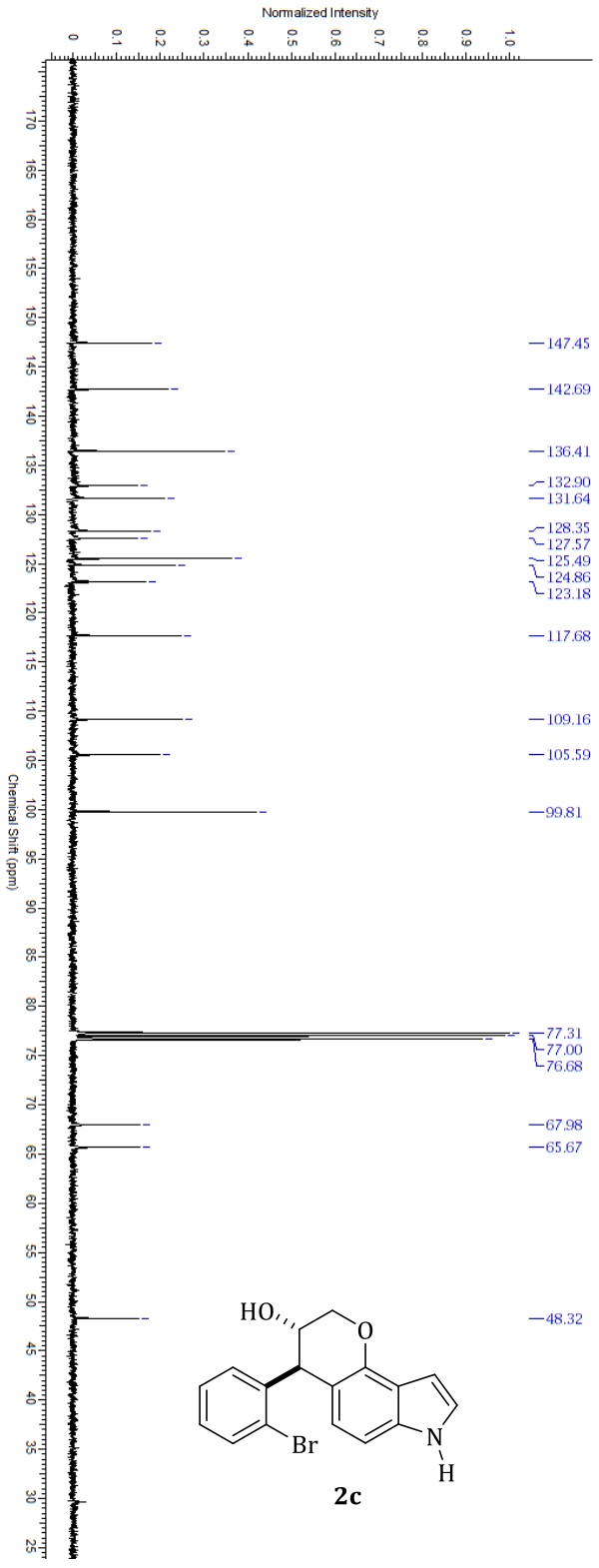
2b

^{13}C NMR (100 MHz, $CDCl_3$) of compound **2b**.

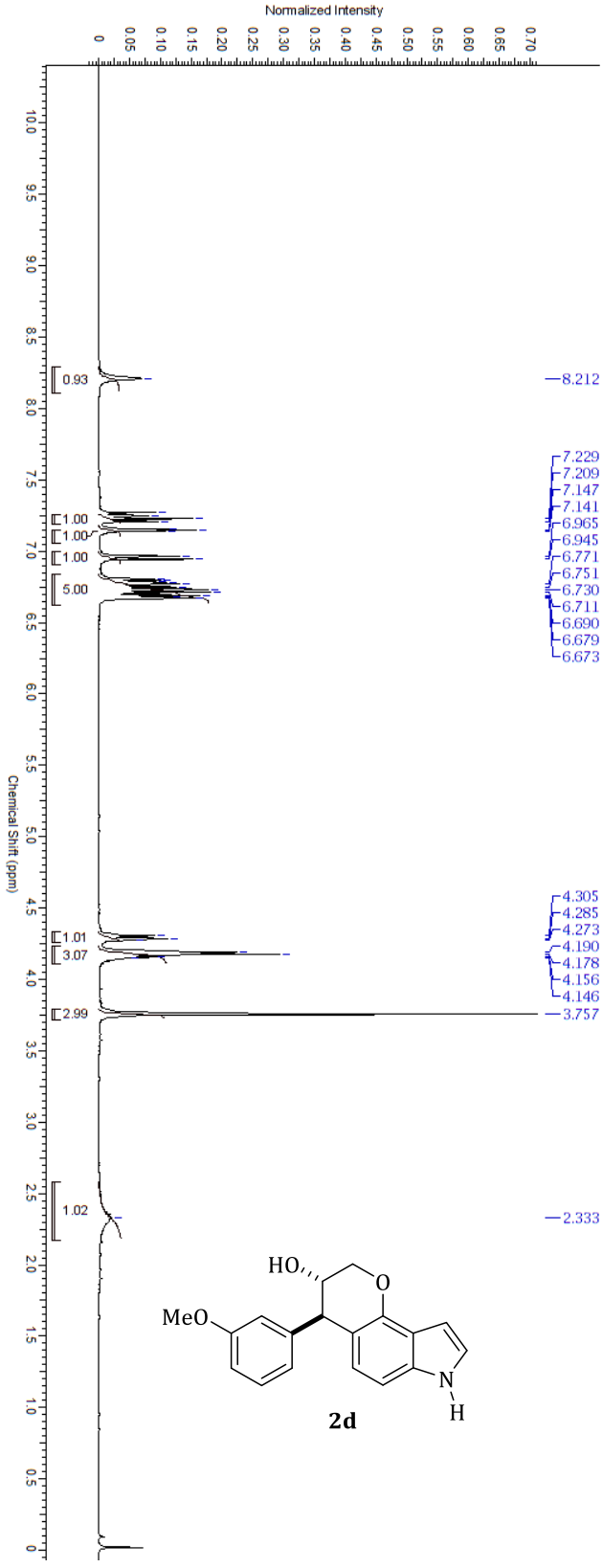


2c

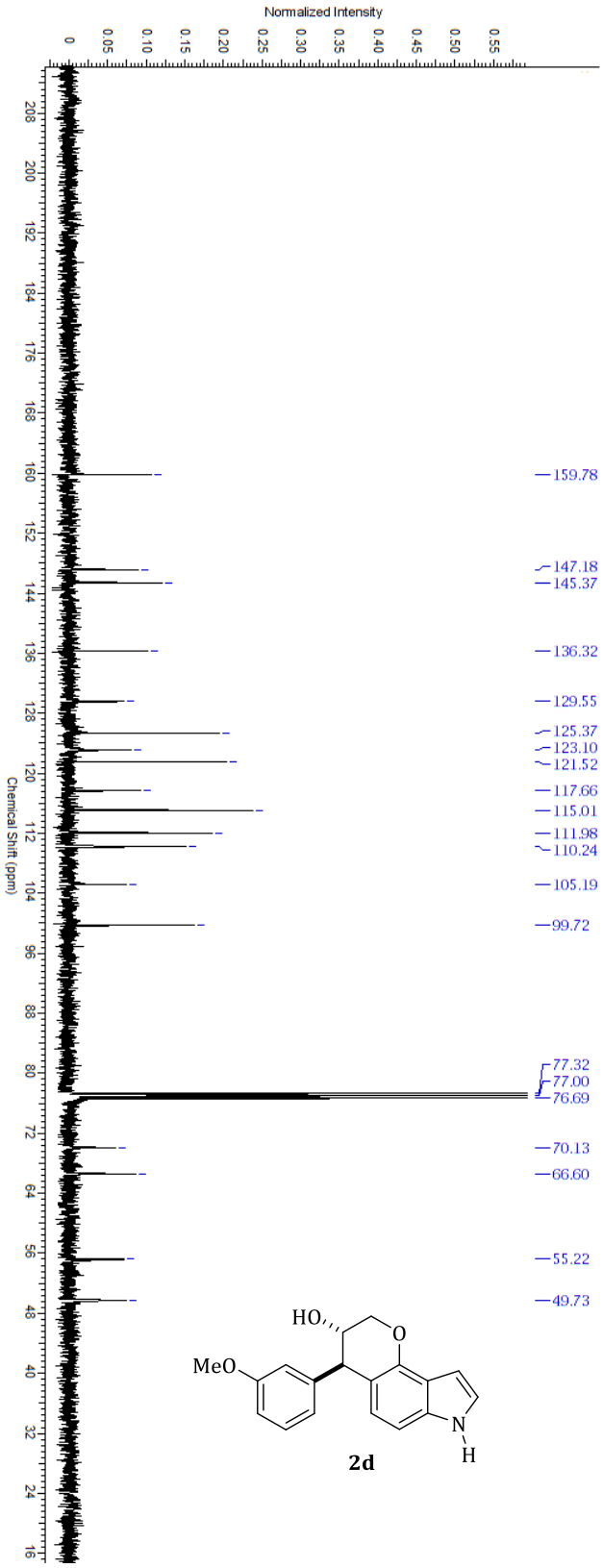
^{1}H NMR (400 MHz, $CDCl_3$) of compound **2c**.



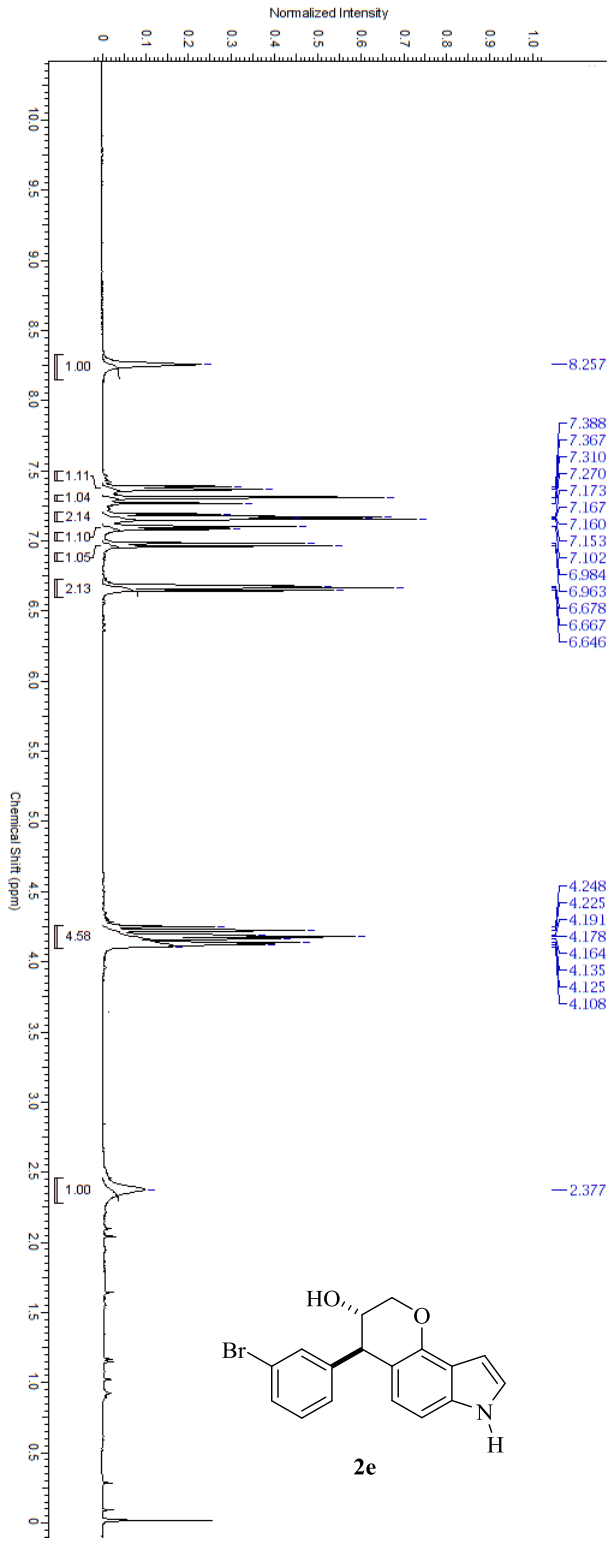
^{13}C NMR (100 MHz, $CDCl_3$) of compound **2c**.



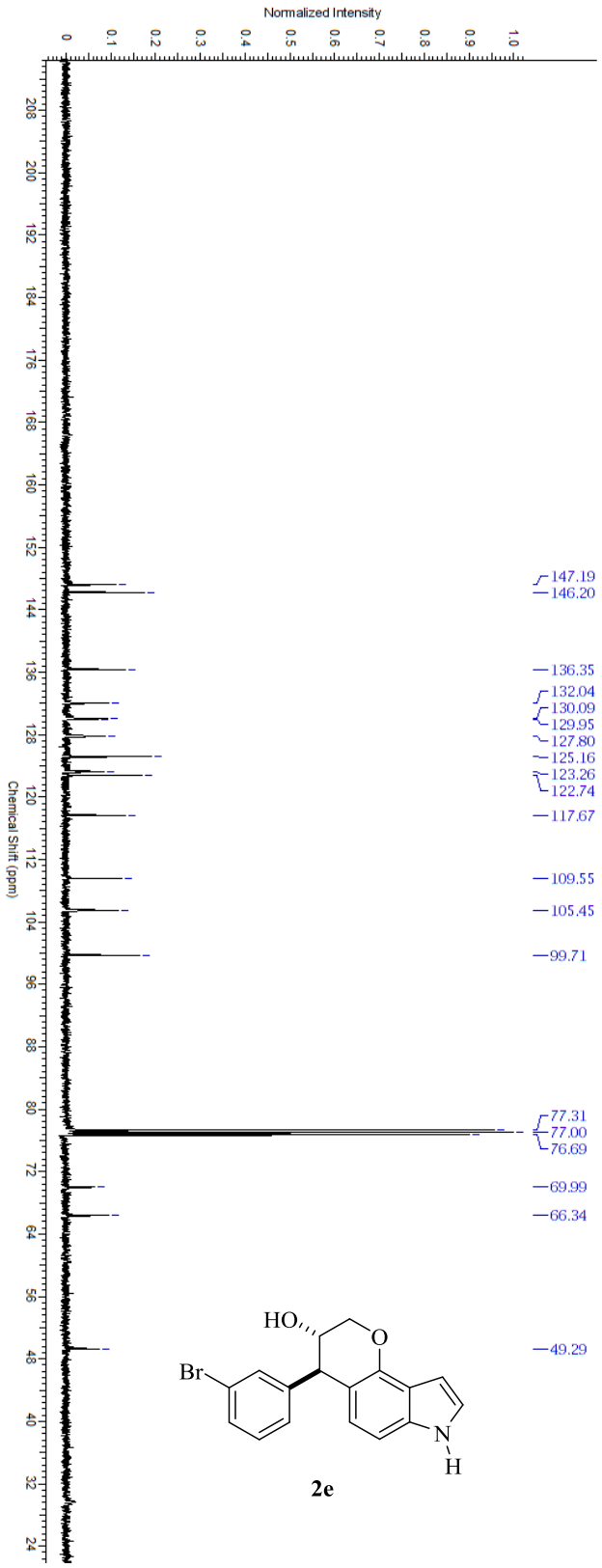
^{1}H NMR (400 MHz, $CDCl_3$) of compound **2d**.



^{13}C NMR (100 MHz, $CDCl_3$) of compound **2d**.

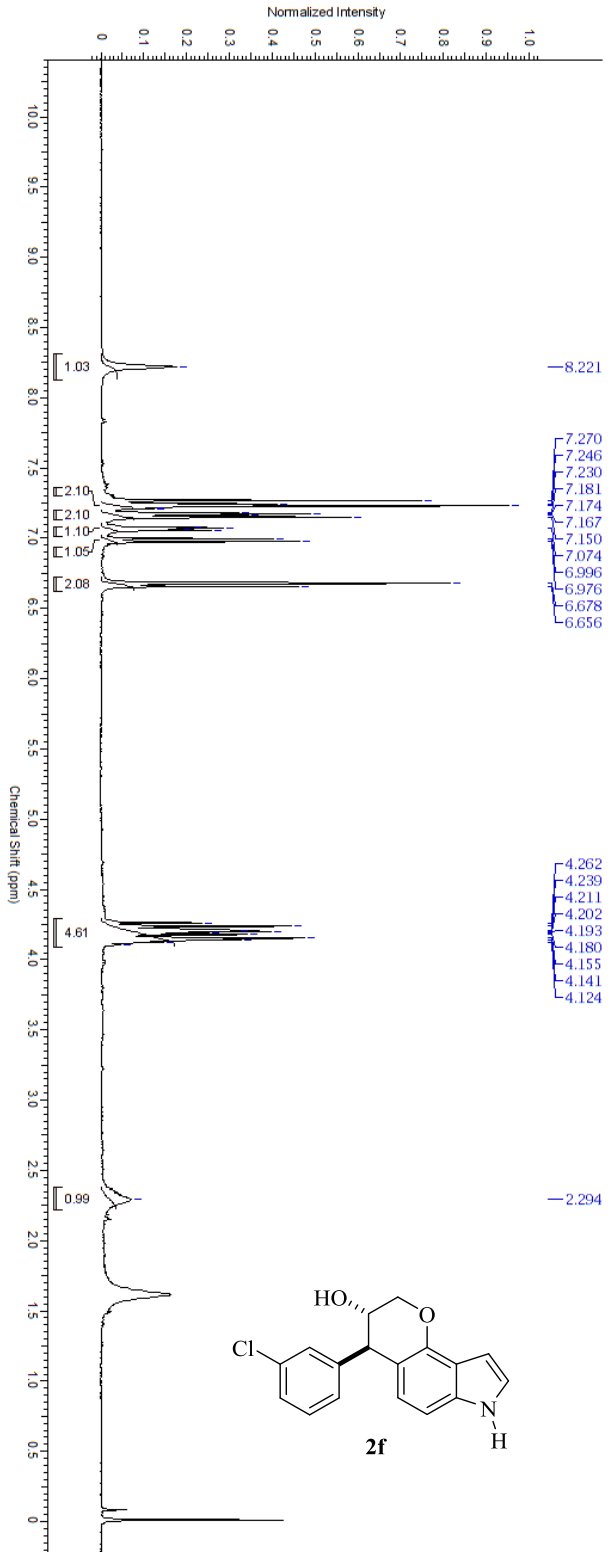


^{1}H NMR (400 MHz, $CDCl_3$) of compound **2e**.

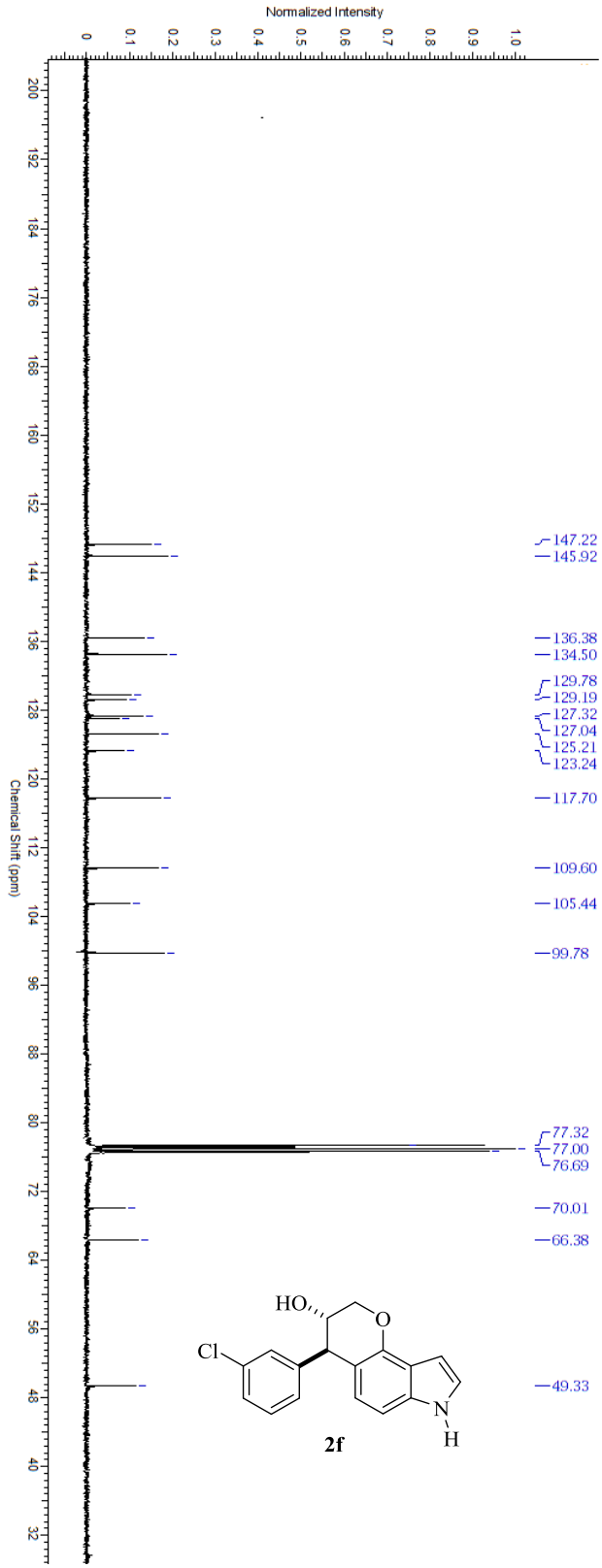


2e

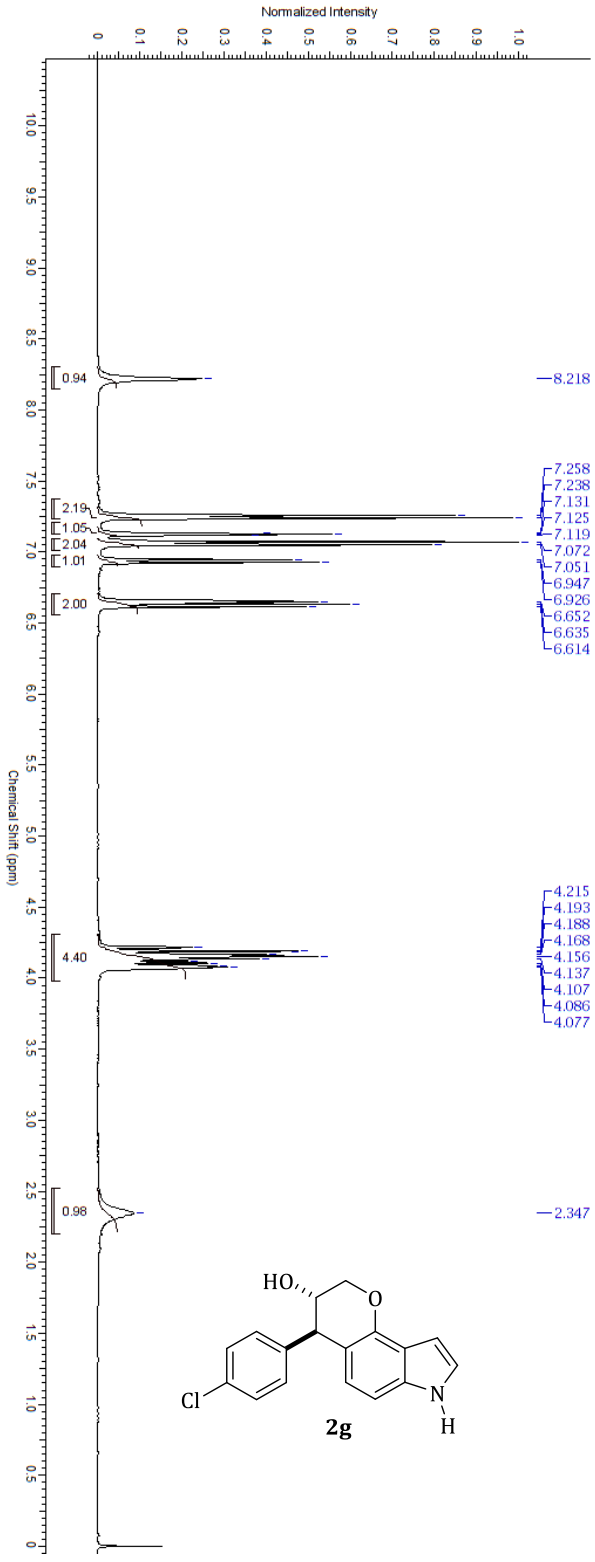
^{13}C NMR (100 MHz, $CDCl_3$) of compound **2e**.



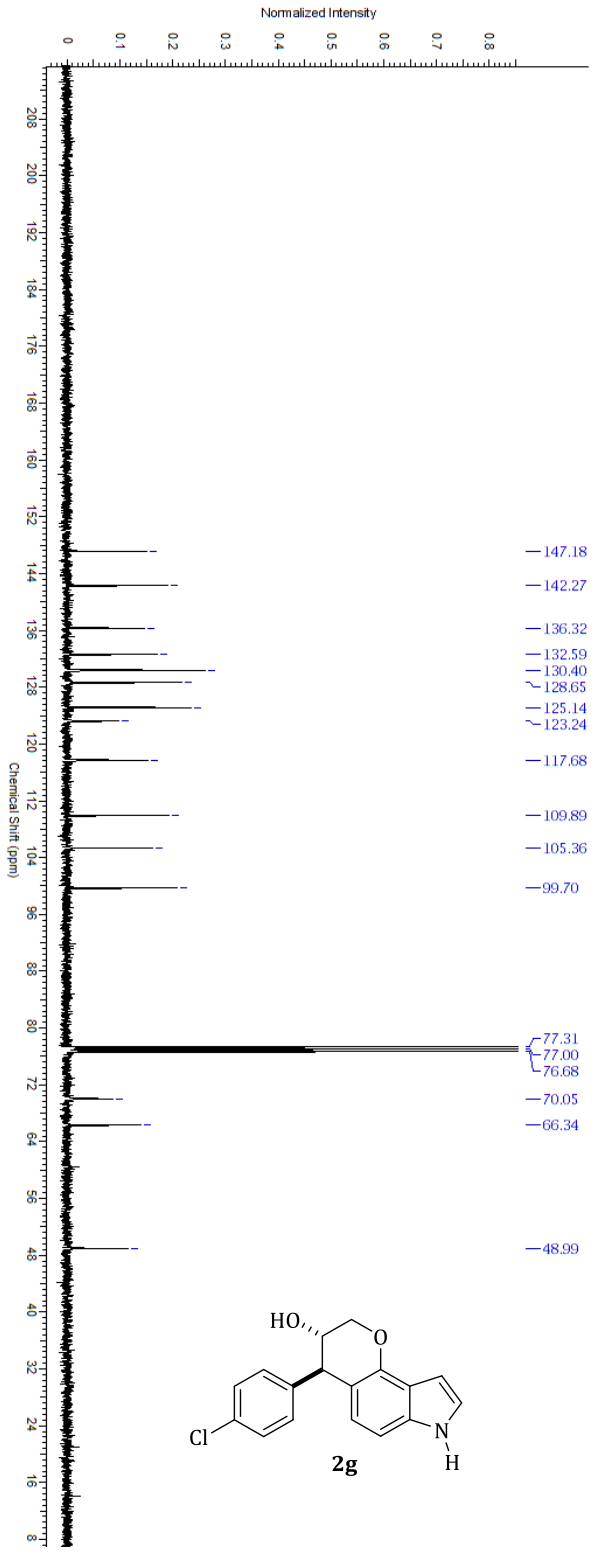
^{1}H NMR (400 MHz, $CDCl_3$) of compound **2f**.



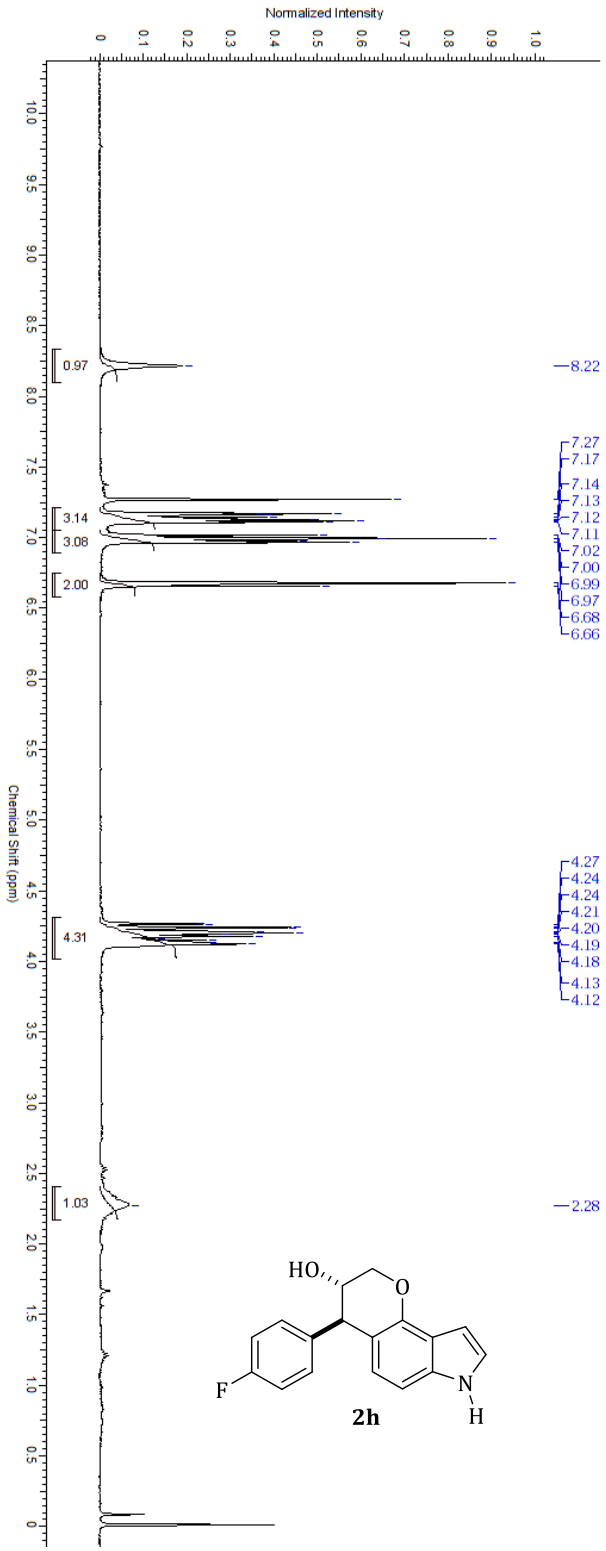
^{13}C NMR (100 MHz, $CDCl_3$) of compound **2f**.



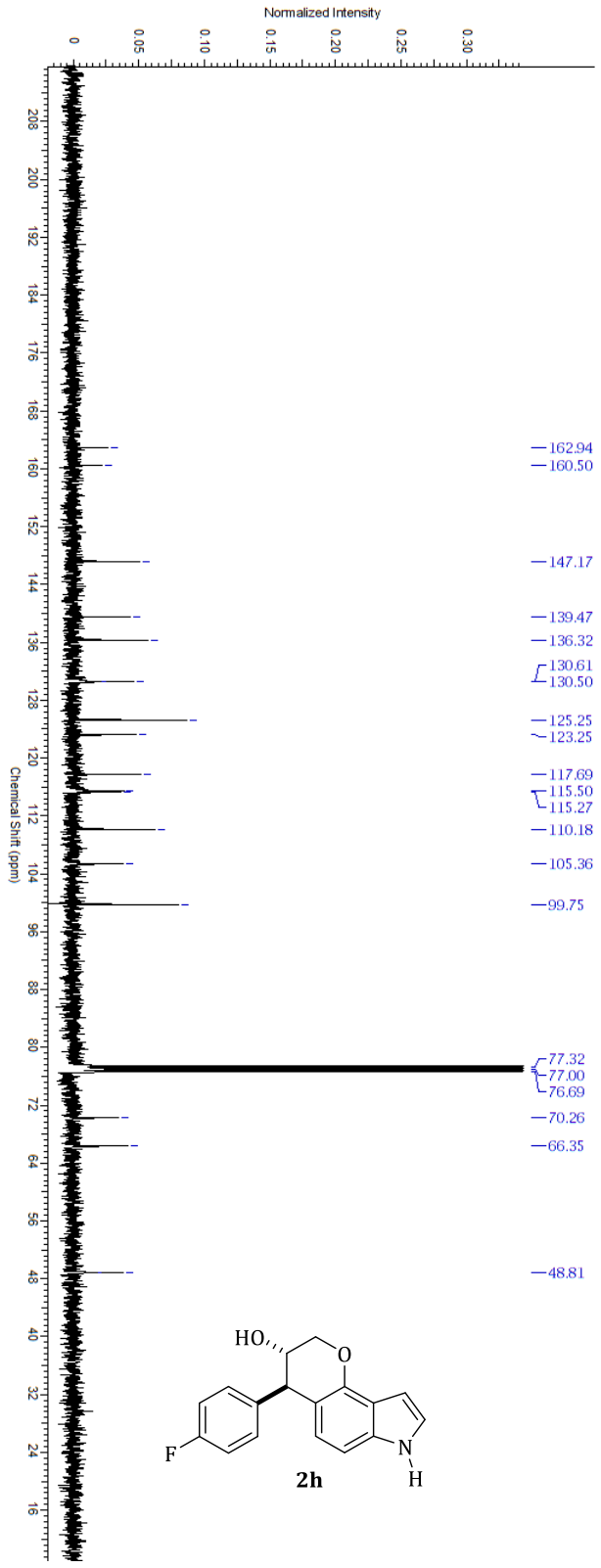
^{1}H NMR (400 MHz, $CDCl_3$) of compound **2g**.



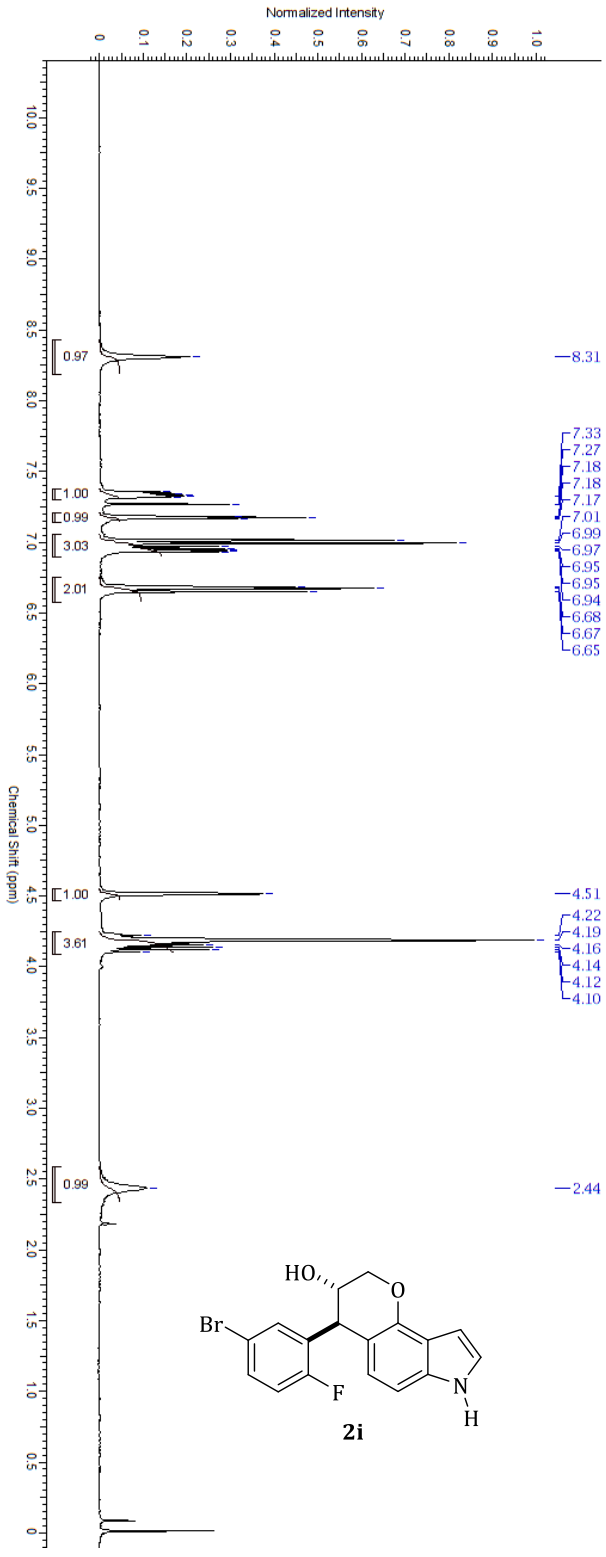
^{13}C NMR (100 MHz, $CDCl_3$) of compound **2g**.



^{1}H NMR (400 MHz, $CDCl_3$) of compound **2h**.

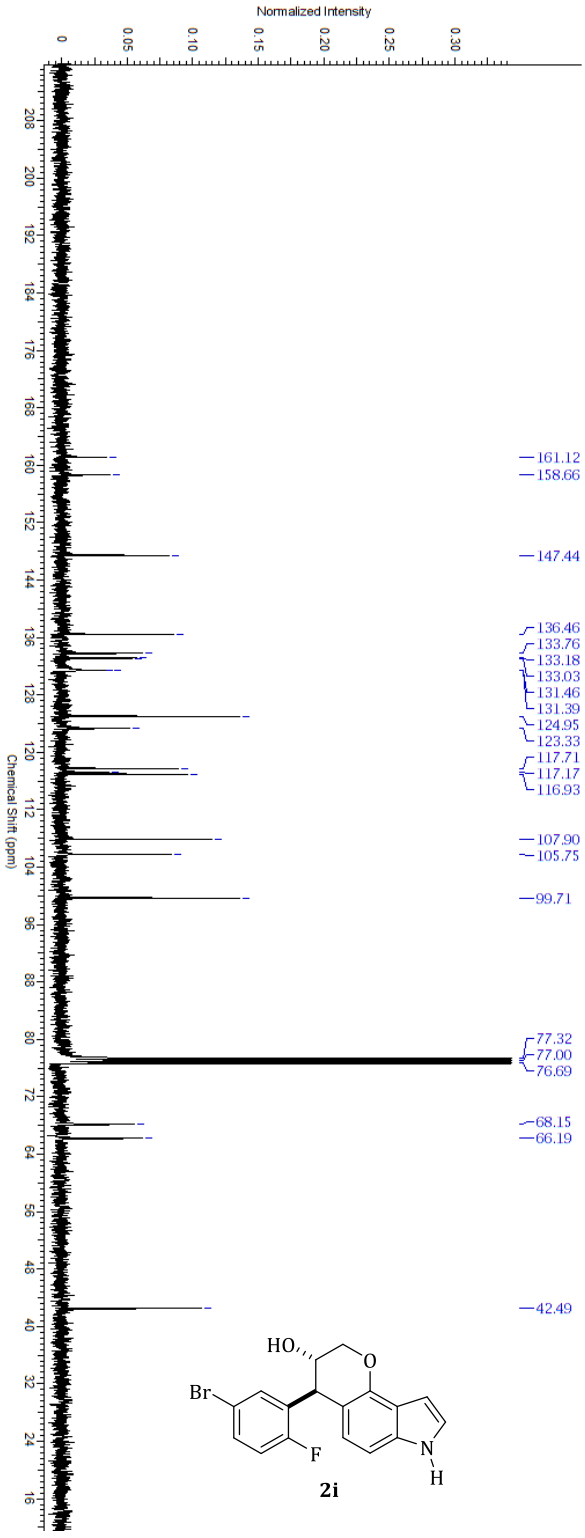


^{13}C NMR (100 MHz, $CDCl_3$) of compound **2h**.

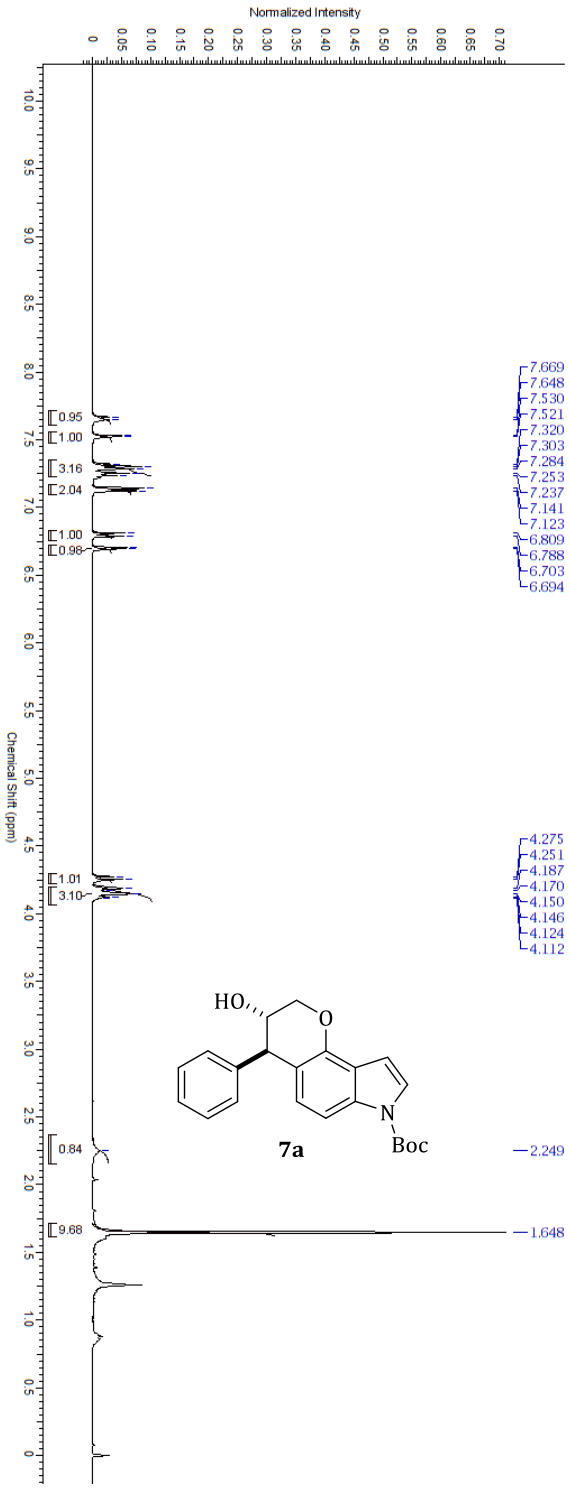


2i

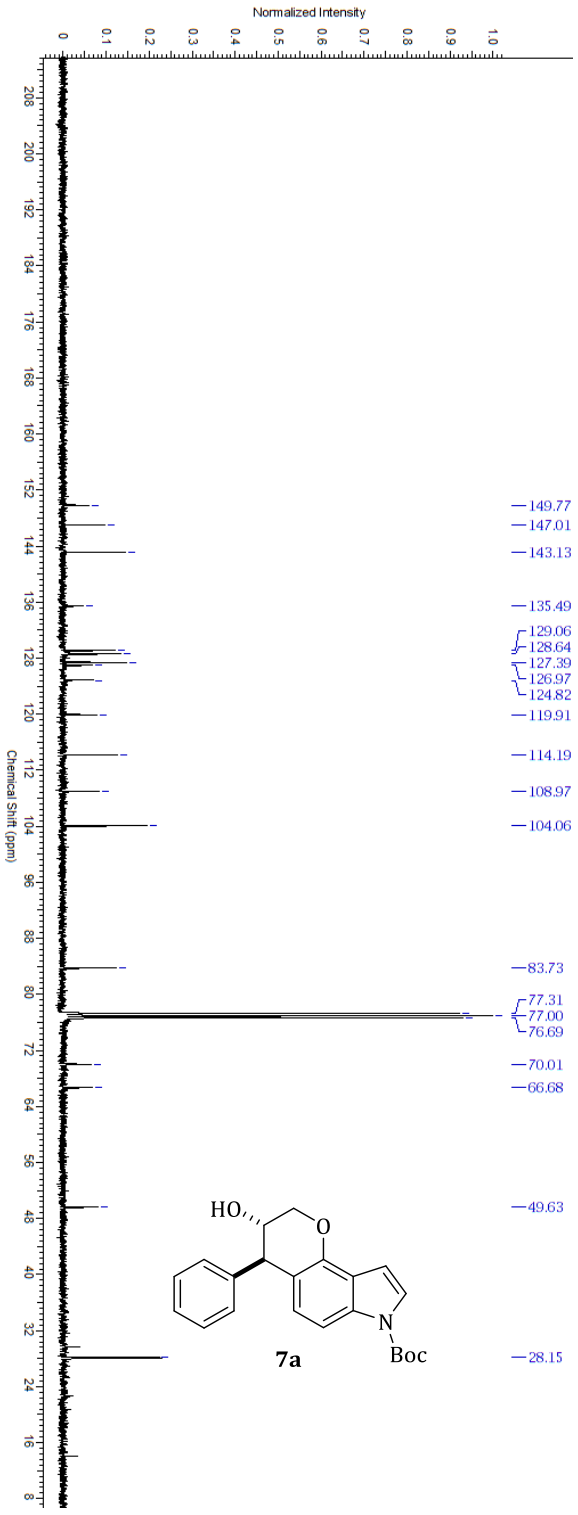
^{1}H NMR (400 MHz, $CDCl_3$) of compound **2i**.



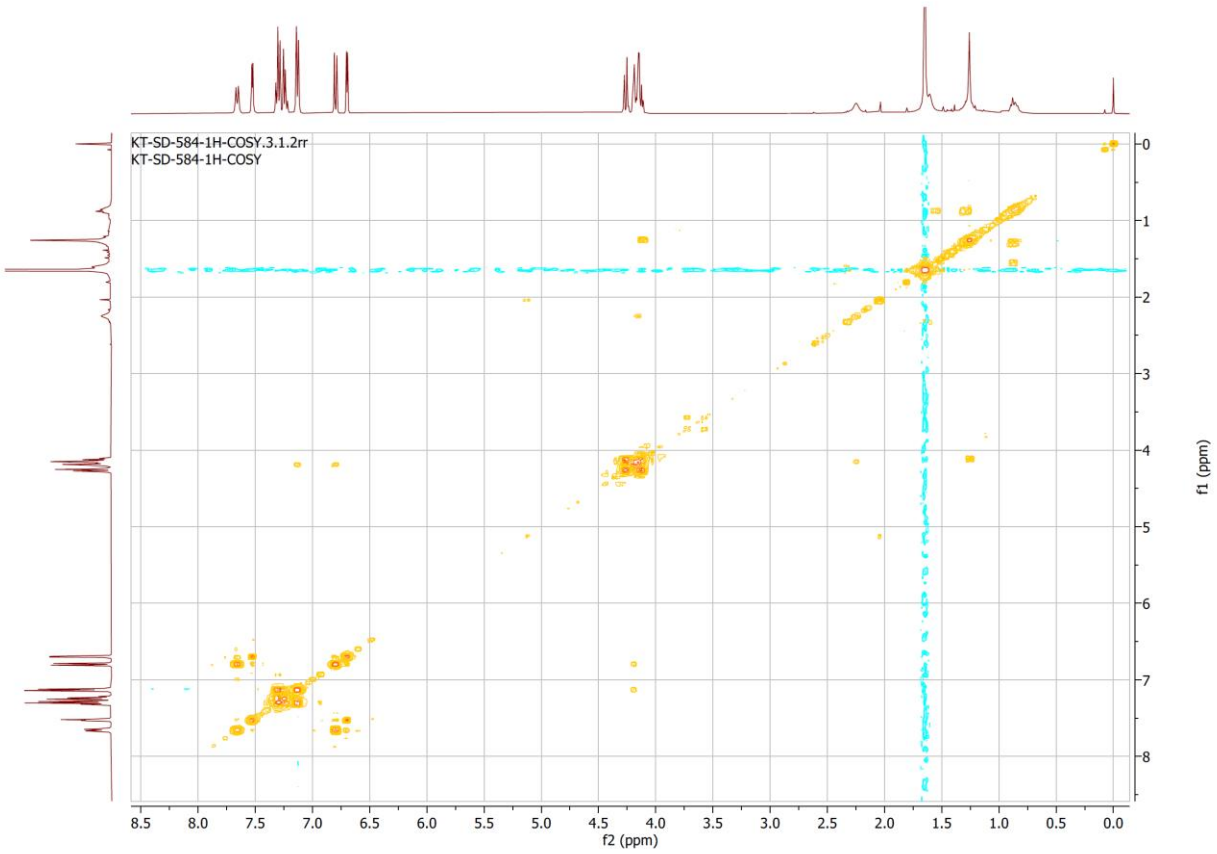
^{13}C NMR (100 MHz, $CDCl_3$) of compound **2i**.



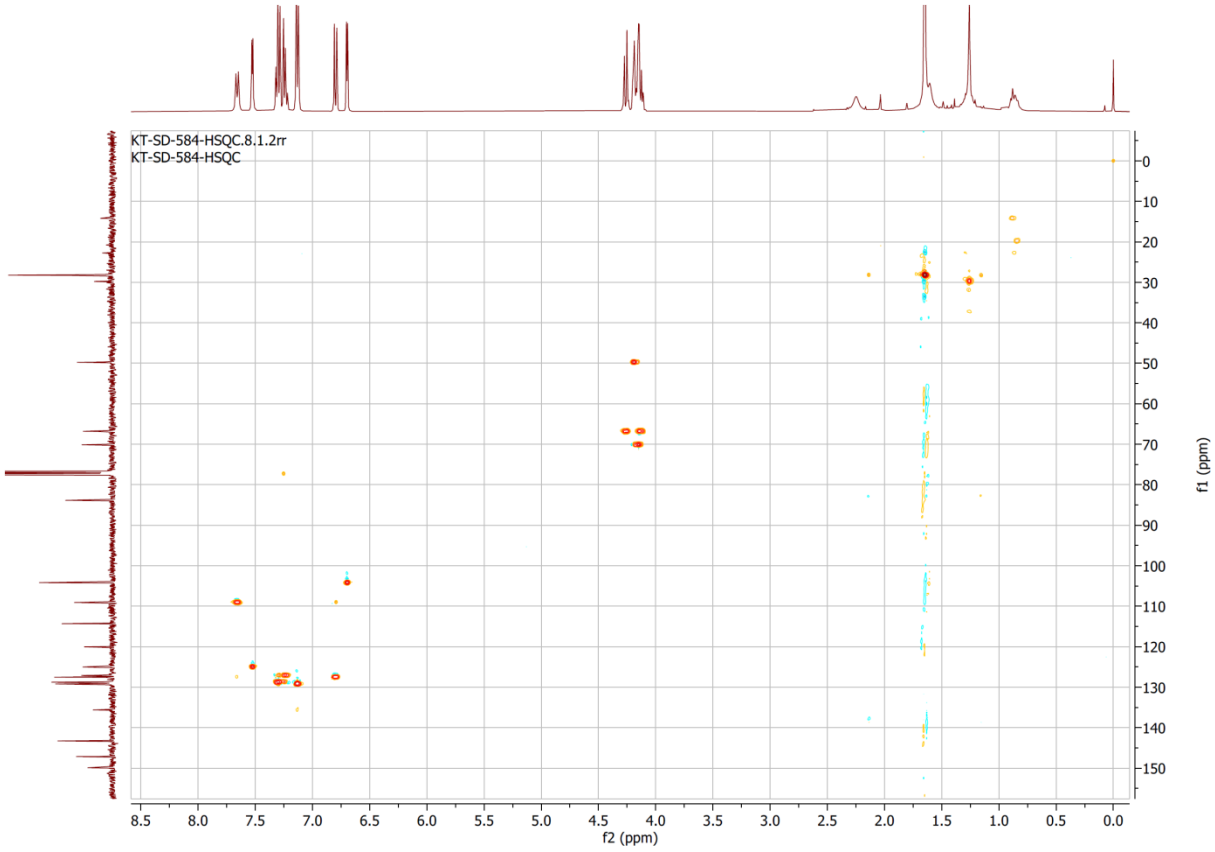
^{1}H NMR (400 MHz, $CDCl_3$) of compound **7a**.



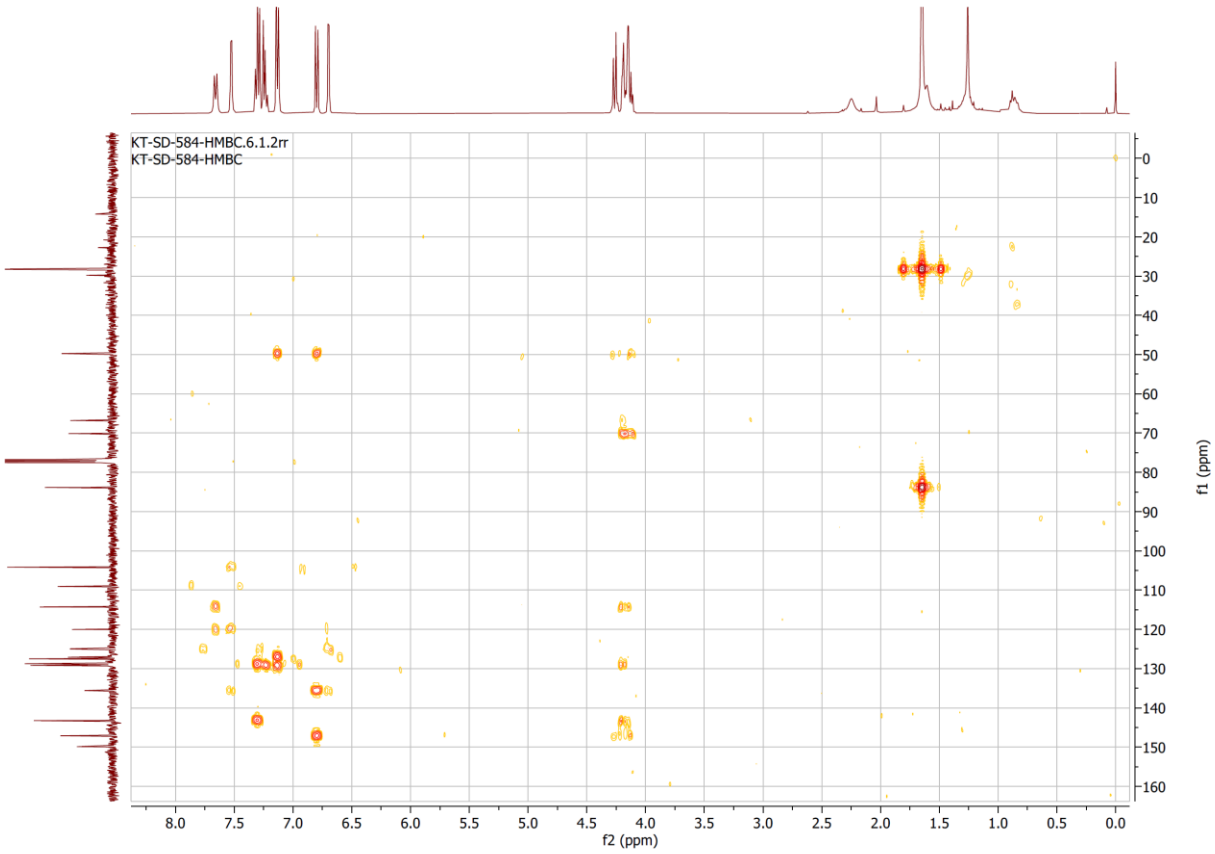
^{13}C NMR (100 MHz, $CDCl_3$) of compound **7a**.



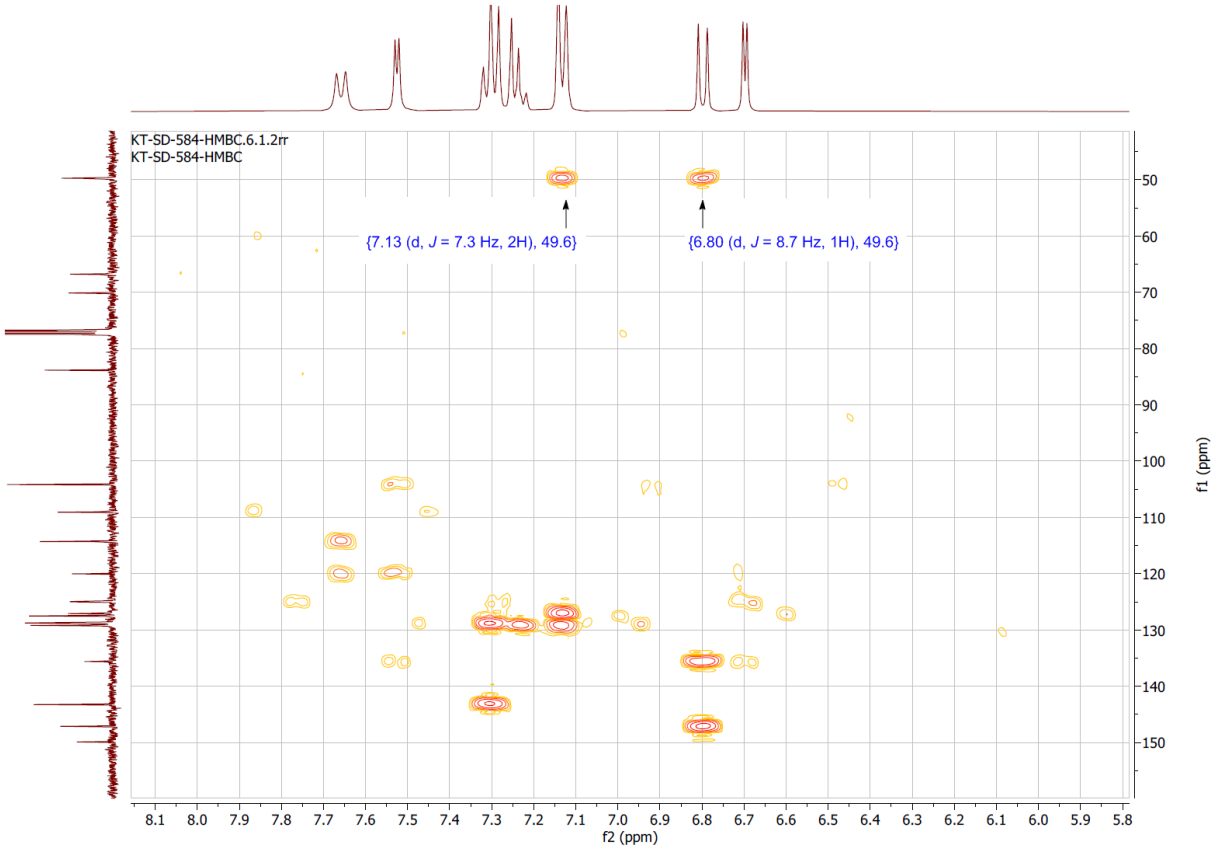
^{1}H-^{1}H COSY NMR spectrum (400 MHz, $CDCl_3$) of **7a**



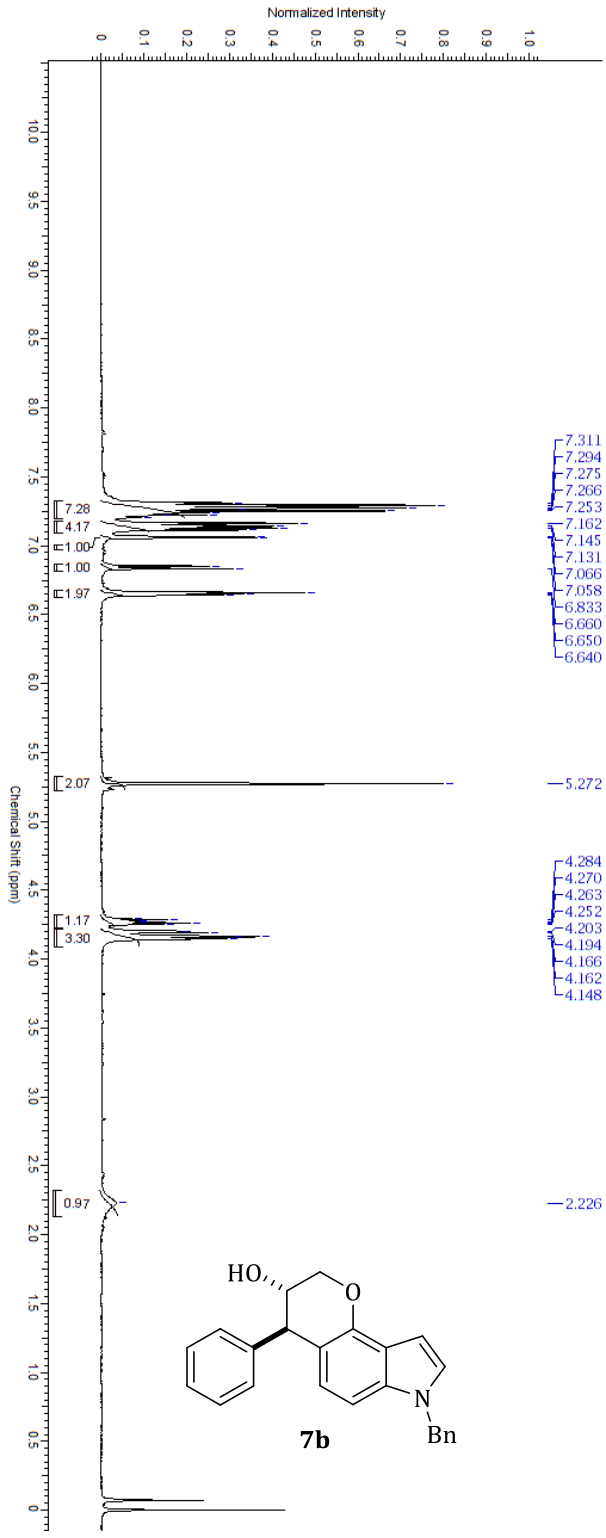
^{1}H-^{13}C HSQC NMR spectrum (400 MHz, $CDCl_3$) of **7a**



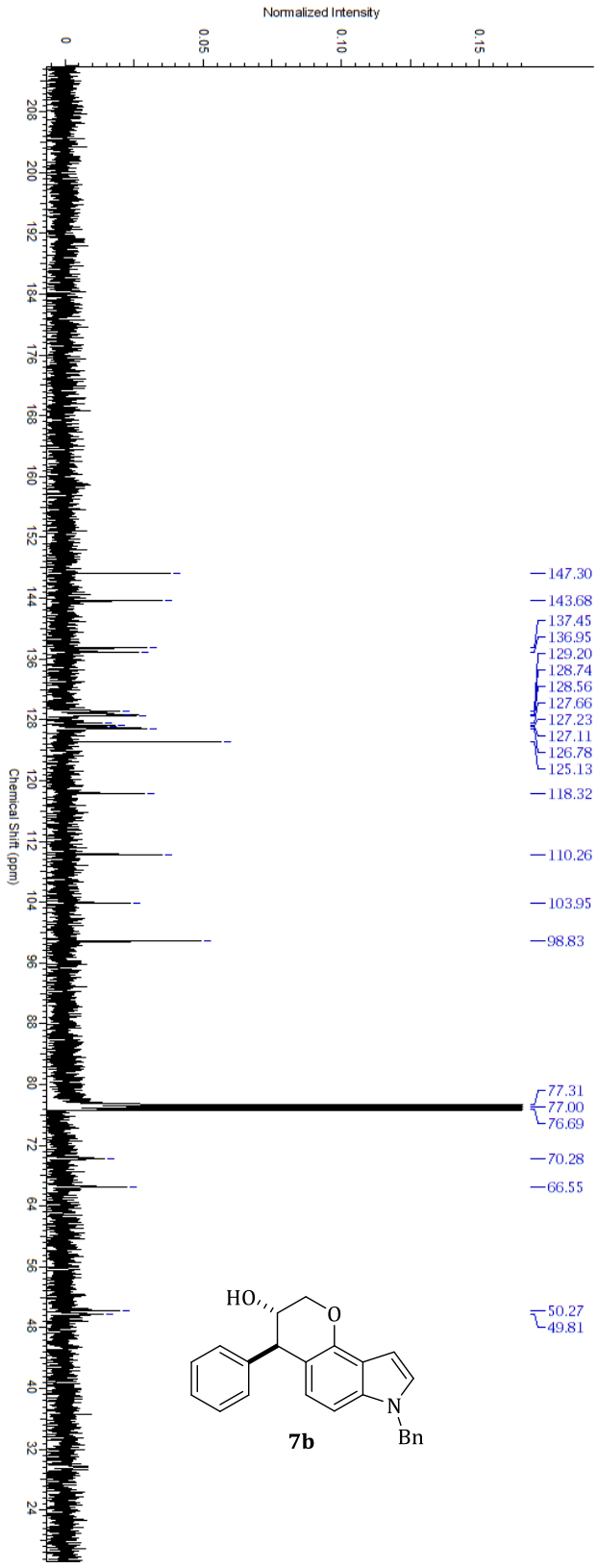
^{1}H-^{13}C HMBC NMR spectrum (400 MHz, $CDCl_3$) of **7a**



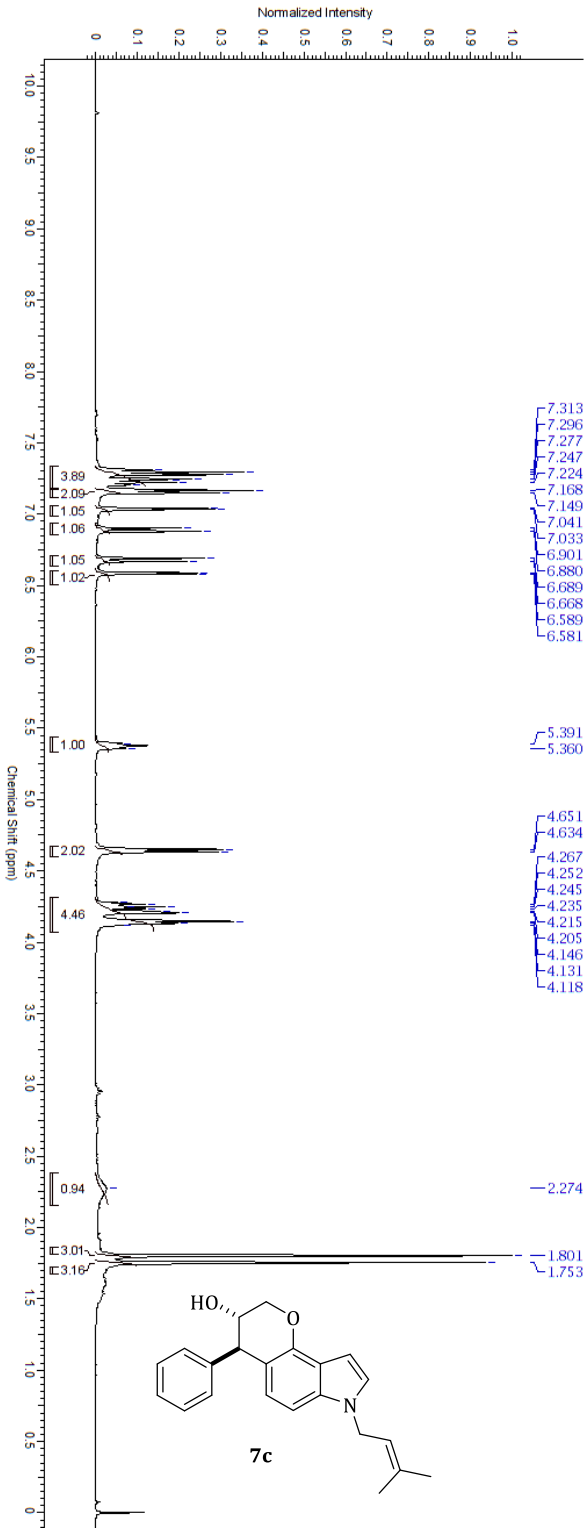
^{1}H-^{13}C HMBC NMR spectrum (expanded) (400 MHz, $CDCl_3$) of **7a**



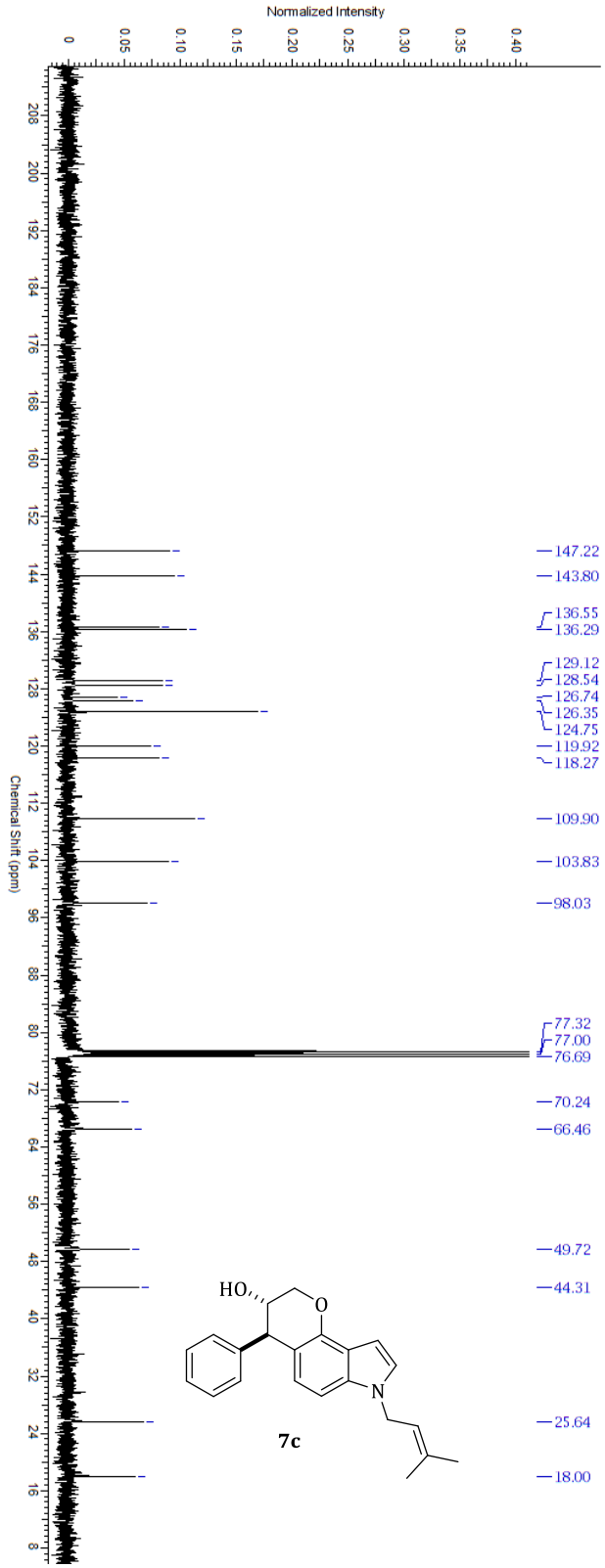
^{1}H NMR (400 MHz, $CDCl_3$) of compound **7b**.



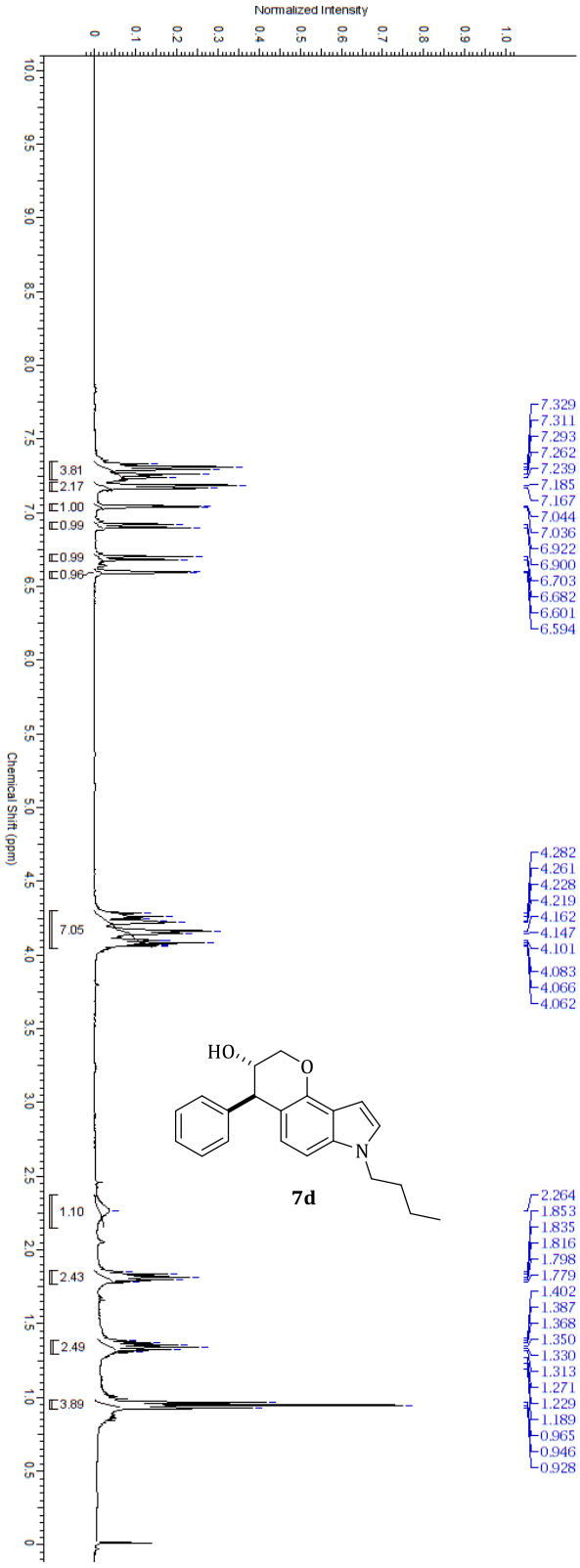
^{13}C NMR (100 MHz, $CDCl_3$) of compound **7b**.



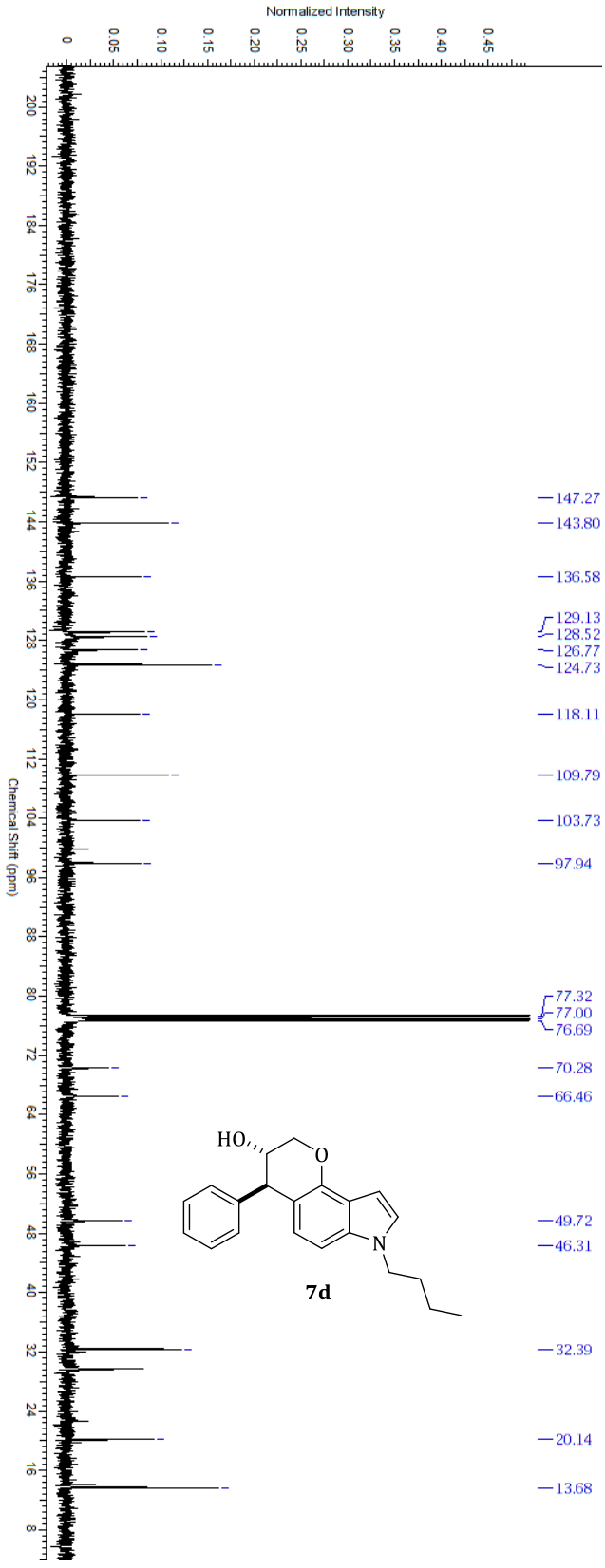
^{1}H NMR (400 MHz, $CDCl_3$) of compound **7c**.



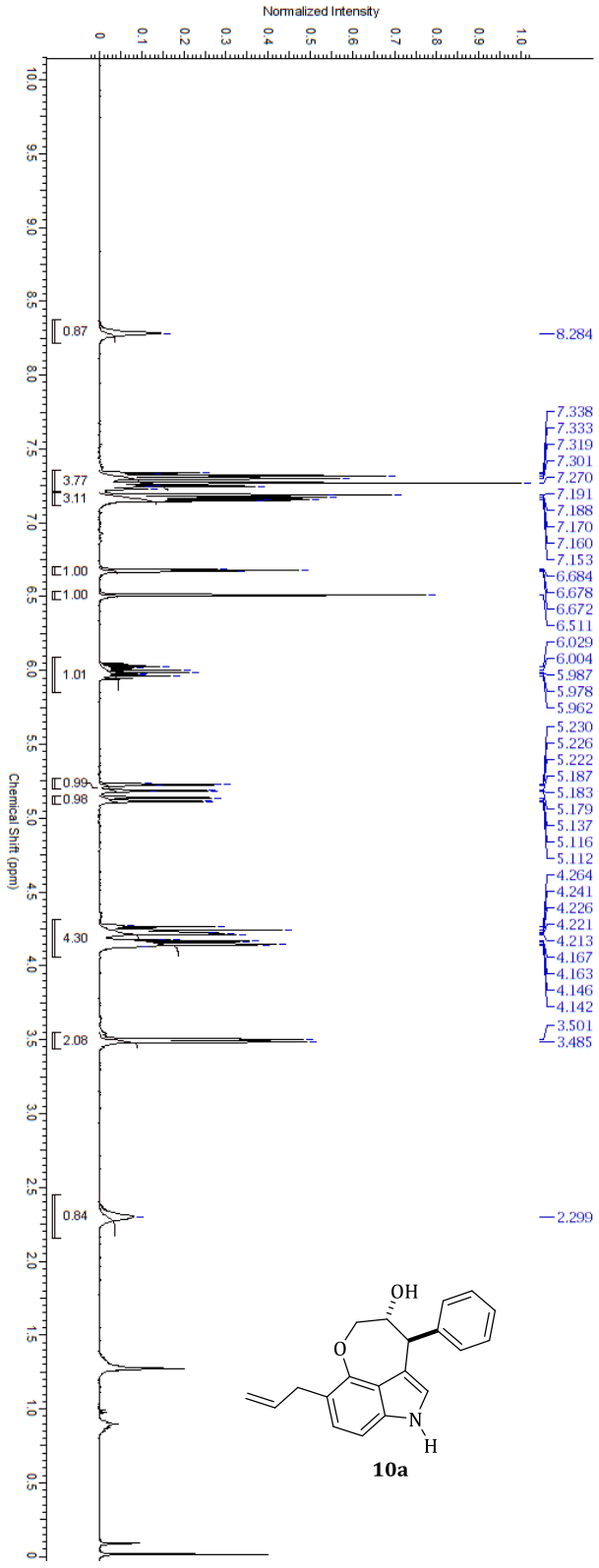
^{13}C NMR (100 MHz, $CDCl_3$) of compound **7c**.



^{1}H NMR (400 MHz, $CDCl_3$) of compound **7d**.

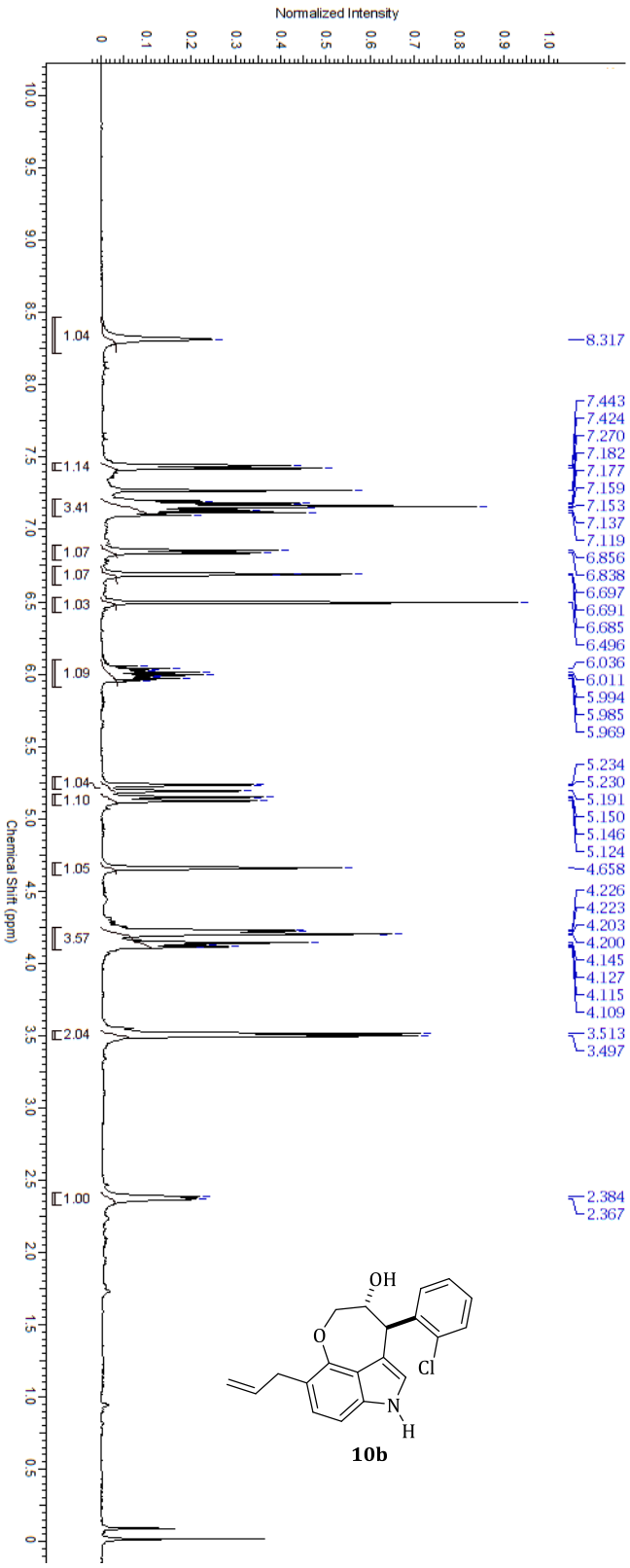


^{13}C NMR (100 MHz, $CDCl_3$) of compound **7d**.



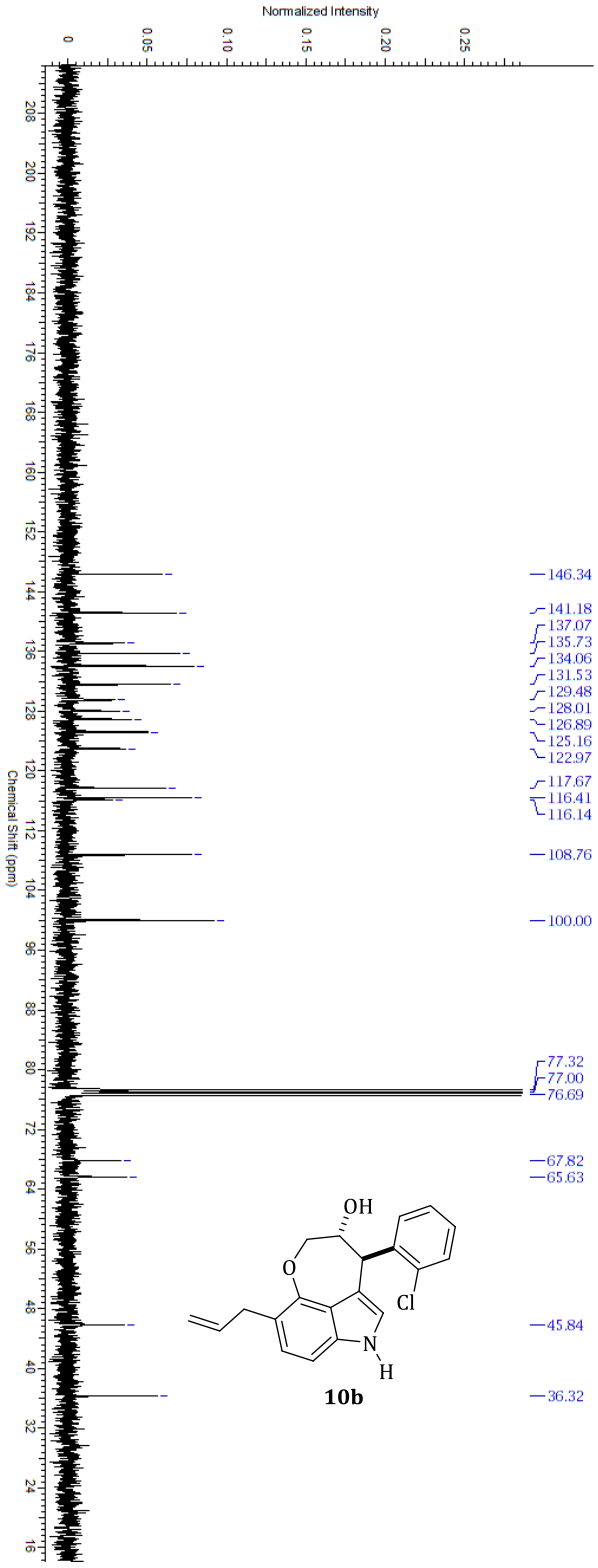
10a

^{1}H NMR (400 MHz, $CDCl_3$) of compound **10a**.



10b

^{1}H NMR (100 MHz, $CDCl_3$) of compound **10b**.



10b

^{13}C NMR (100 MHz, $CDCl_3$) of compound **10b**.