Supporting Information for

Tandem Prins-type cyclization for the stereoselective construction of fused polycyclic ring systems

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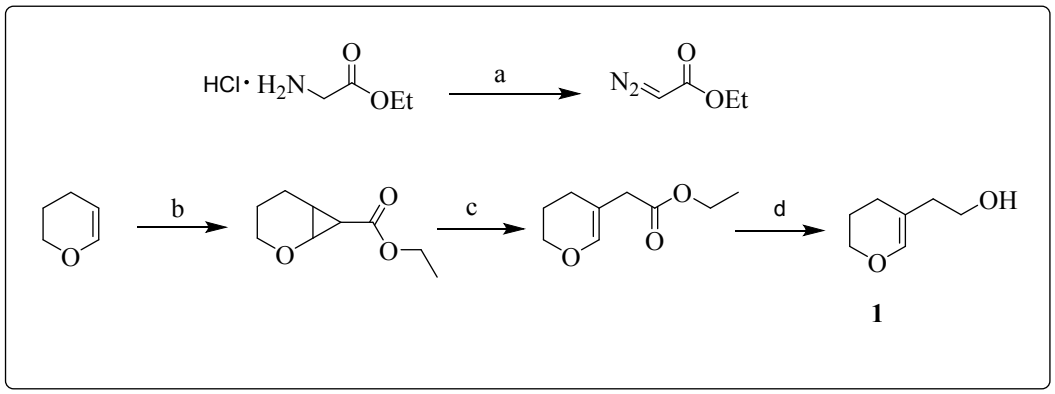
Experimental Section

General. IR spectra were recorded on FT-IR spectrometer (KBr) and reported in reciprocal centimetres (cm^{-1}). ^1H NMR spectra were recorded at 500 MHz and ^{13}C NMR at 125 MHz. For ^1H NMR, tetramethylsilane (TMS) was used as internal standard ($\delta = 0$) and the values are reported as follows: chemical shift, integration, multiplicity (s = singlet, d = doublet, t= triplet, q = quartet, m = multiplet), and the coupling constants in Hz. For ^{13}C NMR, $CDCl_3$ ($\delta = 77.27$) was used as internal standard and spectra were obtained with complete proton decoupling. HRMS data were obtained using EI ionization.

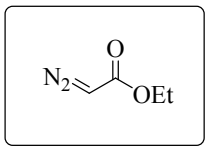
Preparation of starting materials

The synthetic route for the preparation of starting material is depicted in Scheme 1.



Reagents & conditions: (a) $NaNO_2$, H_2SO_4, H_2O, CH_2Cl_2, 0-25 °C, 15 min. (b) $CuSO_4$, N_2CHCO_2Et, reflux, 90%, 5h. (c) Copper bronze, reflux (150 °C), 4h. (c) LAH, THF.

Ethyl 2-diazoacetate

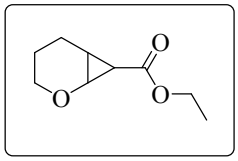


Diazoacetic esters are potentially explosive and therefore must be handled with caution. They are also toxic and prone to cause development of specific sensitivity. A well-ventilated hood should be used for the entire procedure.

A solution of 14 g (0.1 mol) of ethyl glycinate hydrochloride in 25 mL of water was mixed with 60 mL of methylenechloride in a four-necked round-bottomed flask fitted with a stirrer, dropping funnel, thermometer, and nitrogen inlet tube, and cooled to −5 °C. The flask was flushed with

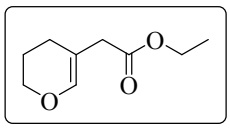
nitrogen and then ice-cold solution of 8.3 g (0.12 mol) of sodium nitrite in 25 mL of water was added under vigorous stirring. The temperature was lowered to −9 °C and then 9.5 g. of 5% (by weight) sulfuric acid was added from a dropping funnel during a period of about 3 min. The temperature may rise to a maximum of +1 °C with the cooling bath at −23 °C. The reaction terminates within 10 min, when heat is no longer evolved. The reaction mixture was transferred to an ice-cold. separatory funnel, and the yellow-green methylenechloride layer was poured into a cold 5% sodium bicarbonate solution. The aqueous layer was extracted once with 15 mL of methylenechloride. The methylenechloride and sodium bicarbonate solutions were transferred to the separatory funnel and shaken until no trace of acid remains, as shown by pH paper. The golden yellow organic layer was separated and transferred to a dry separatory funnel and shaken for 5 min with 10 g of granular anhydrous sodium sulfate. The dried ethyl diazoacetate solution was filtered through a cotton plug inserted in the separatory funnel and the solvent was distilled through a column at a pressure of about 350 mm. The traces of solvent are removed at a pressure of 20 mm at a maximum temperature of 35 °C. The desired diazoester was obtained in 10 g yield (88%) as yellow oil.[1]

7-Carbethoxy-2-oxabicyclo[4.1.0]heptane



To a refluxing solution of freshly distilled 3,4-dihydropyran (37.8 g, 45 mmol) and $CuSO_4$ (0.6 g) were added slowly a mixture of ethyl diazoacetate (8.5 g, 85 mmol) and 3,4-dihydropyran (12.6 g, 150 mmol) over 2.5 h. The reaction mixture was heated under reflux for another 2h. Excess of 3,4-dihydropyran was removed at atmospheric pressure and the crude product was distilled (b.p. 88-92 °C/3 mmHg) to give the cyclopropyl ester (11.4 g, 90%) as a colorless oil.[2]

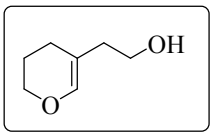
Ethyl 2-(3,4-dihydro-2*H*-pyran-5-yl)acetate



A mixture of 441 mg of cyclopropane compound (2.59 mmol) and 30 mg of Cupper Bronze (0.48 mmol) was heated under reflux (150 °C) with stirring for 4h and then directly distilled in a

Buchi Kugelrohr apparatus under reduce pressure to yield the ester (352 mg) in 80% isolated yield.[3]

2-(3,4-Dihydro-2*H*-pyran-5-yl)ethan-1-ol



To a stirred solution of $LiAlH_4$ (205 mg, 5.42mmol) in THF (10 mL), was added drop wise a solution of olefin ester (0.5g, 3.9 mmol in THF (10mL) at 0°C. The resulting mixture was stirred at room temperature for 2 hrs. After completion, the reaction mixture was quenched with aq.Na_2SO_4, filtrates and concentrated under reduced pressure. Purification by flash column chromatography (hexanes/EtOAc 1:1) to give the compound (**22**) as a yellow oil in 90% yield.

Yellow liquid; ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.31 (s, 1H), 3.96 – 3.87 (m, 2H), 3.62 (t, *J* = 6.3 Hz, 2H), 2.13 (t, *J* = 6.2 Hz, 2H), 1.98 (t, *J* = 6.1 Hz, 2H), 1.92 - 1.81 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 140.9, 108.4, 65.3, 60.1, 36.4, 22.8, 22.4; IR (KBr): ν 3377, 2925, 1648, 1439, 1044, 778.

3a: **2,3,5,6-Tetrahydro-4*H*,7a*H*,12b*H*-furo[3,2-*c*]pyrano[2,3-*b*]chromene**:

Yellow semisolid; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.36 (dd, *J* = 7.8, 1.2 Hz, 1H), 7.31 – 7.19 (m, 1H), 6.98 (t, *J* = 7.0 Hz, 2H), 4.97 (s, 1H), 4.24 (s, 1H), 4.12 – 3.84 (m, 3H), 3.83 – 3.72 (m, 1H), 2.49 - 2.33 (m, 1H), 2.01 – 1.55 (m, 4H), 1.42 (d, *J* = 12.4 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 152.6, 130.8, 129.7, 121.4, 119.7, 117.0, 97.1, 80.5, 65.4, 61.5, 42.2, 34.8, 26.3, 22.7; IR (KBr): ν 2955, 2349, 1768, 1420, 1207, 951, 748; HRMS (*m/z*) calcd for $C_{14}H_{17}O_3(M–H)^+$: 231.1009, found: 231.1015.

3b: **2,3,5,6-Tetrahydro-4*H*,7a*H*,14b*H*-benzo[*g*]furo[3,2-*c*]pyrano[2,3-*b*]chromene:**

White solid; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.07 (d, *J* = 8.4 Hz, 1H), 7.76 (t, *J* = 7.6 Hz, 2H), 7.59 – 7.46 (m, 1H), 7.37 (t, *J* = 7.5 Hz, 1H), 7.16 (d, *J* = 9.0 Hz 1H), 5.08 (s, 1H), 4.66 (s, 1H), 4.18 – 3.95 (m, 3H), 3.87 - 3.78 (m, 1H), 2.57 – 2.42 (m, 1H), 2.12 – 1.99 (m, 1H), 1.97 - 1.82 (m, 1H), 1.78 - 1.55 (m, 2H), 1.44 (d, *J* = 12.9 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 150.6, 133.6, 130.7, 129.4, 128.3, 127.1, 123.9, 123.3, 118.5, 111.9, 97.1, 78.8, 65.5, 61.4, 41.7, 34.8, 26.1, 22.8; IR (KBr): ν 2921, 2855, 2361, 1761, 1668, 1457, 1320, 1273, 1081, 901, 710; HRMS (*m/z*) calcd for $C_{18}H_{19}O_3(M+H)^+$: 283.1333, found: 283.1329.

3c: **11-Bromo-2,3,5,6-tetrahydro-4*H*,7a*H*,12b*H*-furo[3,2-*c*]pyrano[2,3-*b*]chromene**:

White solid; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.49 (d, *J* = 2.3 Hz, 1H), 7.34 (dd, *J* = 8.7, 2.4 Hz, 1H), 6.86 (d, *J* = 8.7 Hz, 1H), 4.94 (s, 1H), 4.20 (s, 1H), 4.08 – 3.84 (m, 3H), 3.84 - 3.71 (m,

1H), 2.40 (m, 1H), 1.99 – 1.58 (m, 4H), 1.51 – 1.33 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 151.7, 133.3, 132.7, 121.9, 118.9, 113.4, 97.3, 79.8, 65.5, 61.7, 42.1, 34.6, 26.3, 22.6; IR (KBr): ν 2927, 1723, 1682, 1601, 1450, 1382, 1220, 1182, 1074, 928, 754; HRMS (*m/z*) calcd for $C_{14}H_{14}BrO_3(M\text{-}H)^+$: 309.0119, found: 309.0119.

3d: **9,11-Di-tert-butyl-2,3,5,6-tetrahydro-4*H*,7a*H*,12b*H*-furo[3,2-*c*]pyrano[2,3-*b*]chromene**:

White solid; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.30 (d, *J* = 2.4 Hz, 1H), 7.22 (d, *J* = 2.4 Hz, 1H), 4.92 (s, 1H), 4.21 (s, 1H), 4.09 – 3.99 (m, 2H), 3.93 - 3.85 (m, 1H), 3.85 - 3.78 (m, 1H), 2.46 - 2.37 (m, 1H), 2.00 - 1.92 (m, 1H), 1.91 - 1.80 (m, 1H), 1.64 - 1.55 (m, 1H), 1.64 - 1.56 (m, 2H), 1.42 (s, 9H), 1.30 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 149.0, 143.1, 137.4, 124.9, 124.2, 119.1, 96.9, 81.9, 65.4, 61.5, 41.8, 35.1, 34.8, 34.3, 31.5, 29.8, 26.0, 22.8; IR (KBr): ν 2921, 1693, 1467, 1354, 1271, 1195, 1022, 945, 846; HRMS (*m/z*) calcd for $C_{22}H_{33}O_3(M+H)^+$: 343.2264, found: 343.2267.

5a: **2,3,5,6-Tetrahydro-4*H*,7a*H*,13b*H*-furo[3,2-*e*]naphtho[1,8-*gh*]chromene**:

White solid; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.87 - 7.78 (m, 2H), 7.66 (d, *J* = 7.0 Hz, 1H), 7.61 (d, *J* = 6.9 Hz, 1H), 7.55 – 7.48 (m, 2H), 4.88 (s, 1H), 4.78 (s, 1H), 4.08 - 4.01 (m, 1H), 3.94 (q, *J* = 15.7, 8.6 Hz, 1H), 3.85 – 3.73 (m, 2H), 2.53 - 2.41 (m, 1H), 1.89 - 1.75 (m, 2H), 1.71 – 1.55 (m, 2H), 1.50 – 1.41 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 133.3, 132.1, 130.8, 128.2, 128.0, 127.8, 127.4, 125.8, 125.8, 124.8, 82.0, 75.8, 65.4, 63.6, 44.0, 35.9, 31.8, 29.1, 23.8; IR (KBr): ν 3051, 2934, 2851, 2373, 1959, 1596, 1452, 1383, 1265, 1162, 1083, 912, 853, 783; HRMS (*m/z*) calcd for $C_{18}H_{19}O_2[M+H]^+$: 267.1382, found: 267.1380.

5b: **11-Methoxy-2,3,5,6-tetrahydro-4*H*,7a*H*,13b*H*-furo[3,2-*e*]naphtho[1,8-*gh*] chromene**:

Yellow semisolid; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.27 – 8.18 (m, 1H), 7.75 - 7.66 (m, 1H), 7.53 (dd, *J* = 8.2, 7.0 Hz, 2H), 6.87 (d, *J* = 7.9 Hz, 1H), 4.88 (s, 1H), 4.67 (s, 1H), 4.09–3.92 (m, 5H), 3.83 – 3.70 (m, 2H), 2.60 – 2.45 (m, 1H), 1.94 – 1.76 (m, 2H), 1.60 - 1.51 (m, 2H), 1.49 - 1.37 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 155.7, 131.9, 129.0, 128.3, 125.2, 125.2, 125.1, 122.5, 121.4, 103.9, 82.5, 75.5, 65.3, 63.1, 55.5, 43.9, 36.1, 28.7, 23.8; IR (KBr): ν 3013, 2856, 1726, 1674, 1584, 1461, 1376, 1178, 1077, 823, 755; HRMS (*m/z*) Calcd for $C_{19}H_{21}O_3[M+H]^+$: 297.1583, found: 297.1492.

5c: **2,3,14,15-Tetrahydro-1*H*,4a*H*,12c*H*-anthra [9,1-*gh*]furo[3,2-*e*]chromene**:

Brown solid; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.50 – 8.38 (m, 2H), 8.02 (d, *J* = 8.8 Hz, 1H), 7.94 (d, *J* = 8.5 Hz, 1H), 7.68 (d, *J* = 9.1 Hz, 1H), 7.62 – 7.44 (m, 3H), 5.34 (s, 1H), 5.02 (s, 1H), 4.23 - 4.14 (m, 1H), 4.14 – 4.04 (m, 1H), 3.95 – 3.77 (m, 2H), 2.86 – 2.71 (m, 1H), 2.12 – 2.00 (m, 1H), 1.99 – 1.80 (m, 1H), 1.60 – 1.40 (m, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 132.4, 131.7, 131.2, 128.7, 128.1, 127.7, 126.5, 126.3, 125.4, 125.3, 125.0, 124.7, 124.0, 80.4, 75.2, 65.9, 62.4,

44.1, 36.4, 29.0, 24.0; IR (KBr): ν 3326, 2932, 1724, 1672, 1597, 1448, 1319, 1249, 1182, 1077, 979, 755; HRMS (*m/z*) calcd for $C_{22}H_{21}O_2(M+H)^+$: 317.1692, found: 317.1697.

5d: **3,4,5,6,8,12b-Hexahydro-2*H*,7a*H*-benzo[*h*]furo[3,2-*e*]chromene**:

Yellow liquid; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.24 (td, *J* = 6.8, 3.4 Hz, 2H), 7.22 – 7.16 (m, 2H), 4.29 (s, 1H), 4.16-4.20 (m, 1H), 4.03 – 3.90 (m, 1H), 3.65 – 3.52 (m, 2H), 3.52 – 3.39 (m, 1H), 3.33 (dd, *J* = 15.4, 4.7 Hz, 1H), 2.85 (dd, *J* = 15.4, 1.9 Hz, 1H), 2.12 – 2.01 (m, 1H), 1.78 – 1.58 (m, 2H), 1.55 – 1.41 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 136.4, 135.9, 129.0, 128.6, 128.4, 126.2, 81.8, 80.6, 67.0, 65.8, 44.8, 39.4, 35.5, 34.8, 23.2; IR (KBr): ν 2925, 2852, 2379, 1628, 1449, 1370, 1155, 1074, 871, 756, 654; HRMS (*m/z*) calcd for $C_{15}H_{19}O_2$ $[M+H]^+$: 231.1386, found: 231.1380.

5e: **2,3,5,6,7a,13c-Hexahydro-4*H*-benzo[4,5]furo[3',2':2,3]indeno[1,2-*b*]pyran**:

White semisolid; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.07 (d, *J* = 8.3 Hz, 1H), 7.91 – 7.81 (m, 2H), 7.59 – 7.51 (m, 2H), 7.51 – 7.45 (m, 1H), 5.43 (s, 1H), 5.27 (s, 1H), 4.01 – 3.94 (m, 1H), 3.93 – 3.85 (m, 1H), 3.75 – 3.66 (m, 1H), 3.48 (dd, *J* = 16.0, 7.8 Hz, 1H), 2.28 – 2.18 (m, 1H), 1.88 – 1.68 (m, 5H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 140.9, 137.8, 134.1, 130.3, 130.1, 128.5, 126.7, 125.9, 124.3, 123.0, 89.3, 82.0, 66.6, 65.1, 52.7, 39.1, 30.6, 22.8; IR (KBr): ν 2974, 2849, 2389, 1960, 1564, 1483, 1262, 1183, 893, 781; HRMS (*m/z*) calcd for $C_{18}H_{19}O_2$ $(M+H)^+$: 267.1382, found: 267.1380.

5f: **9,11-Dimethoxy-2,3,5,6,7a,11b-hexahydro-4*H*-furo[3',2':2,3]indeno[1,2-*b*]pyran**:

Yellow liquid; ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.93 (s, 1H), 6.90 (s, 1H), 5.21 (s, 1H), 4.68 (s, 1H), 3.99 - 3.91 (m, 1H), 3.89 (d, *J* = 1.0 Hz, 6H), 3.87 - 3.83 (m, 1H), 3.64 – 3.50 (m, 2H), 2.15 – 2.06 (m, 1H), 1.82 – 1.66 (m, 5H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 150.5, 150.0, 135.1, 134.2, 107.7, 107.5, 88.7, 83.5, 66.7, 64.9, 56.0, 55.9, 53.1, 38.7, 30.5, 22.8; IR (KBr): ν 2979, 2867, 1725, 1564, 1467, 1267, 1037, 855, 689; HRMS (*m/z*) calcd for $C_{16}H_{21}O_4(M+H)^+$: 277.1431, found: 277.1434.

5g: **3,4,5,6,7a,10b-Hexahydro-2*H*-furo [3',2':2,3]thieno[2',3':4,5]cyclopenta[1,2-*b*]pyran**:

Yellow liquid; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.38 (dd, *J* = 4.9, 0.6 Hz, 1H), 6.94 (d, *J* = 4.9 Hz, 1H), 5.29 (s, 1H), 4.66 (s, 1H), 4.03 - 3.92 (m, H), 3.90 – 3.77 (m, 1H), 3.69 - 3.51 (m, 2H), 2.16 – 2.04 (m, 1H), 1.98 – 1.66 (m, 5H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 147.3, 145.8, 131.8, 121.8, 85.9, 80.3, 67.0, 63.9, 59.2, 39.3, 30.4, 22.0; IR (KBr): ν 2931, 2845, 1741, 1593, 1459, 1348, 1168, 1094, 950, 826, 762; HRMS (*m/z*) calcd for $C_{12}H_{13}O_2S(M–H)^+$: 221.0632, found: 221.0632.

5h: **9-Methyl-2,3,5,6,7a,11b-hexahydro-4*H*-furo[3',2':2,3]indeno[1,2-*b*]pyran**:

Light yellow liquid; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.27 – 7.20 (m, 2H), 7.14 – 7.10 (m, 1H), 5.30 (s, 1H), 4.74 (s, 1H), 3.99 – 3.92 (m, 1H), 3.88 – 3.81 (m, 1H), 3.64 – 3.52 (m, 2H), 2.41 (s, 3H), 2.14 – 2.06 (m, 1H), 1.86 – 1.67 (m, 5H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 142.4, 140.7, 136.8, 130.4, 129.1, 122.6, 88.3, 83.3, 66.9, 65.1, 52.2, 38.4, 30.3, 22.9, 18.0; IR (KBr): ν 2955, 2852, 1735, 1597, 1494, 1284, 1167, 1089, 969, 815, 755; HRMS (*m/z*) calcd for $C_{15}H_{19}O_2(M+H)^+$: 231.1386, found: 231.1380.

6a: **8-(4-Nitrophenyl)-2,3,4,6,8,8a-hexahydropyrano[3,4-*b*]pyran**:

White Solid; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.32 – 8.13 (m, 2H), 7.69 – 7.56 (m, 2H), 5.74 (d, *J* = 2.7 Hz, 1H), 4.23 – 4.09 (m, 2H), 3.91 (dd, *J* = 11.1, 6.0 Hz, 2H), 3.59 – 3.42 (m, 2H), 2..60-2.46 (m, 1H), 2.45-2.31 (m, 1H), 2.27 (dd, *J* = 14.1, 2.0 Hz, 1H), 2.01 – 1.88 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 147.5, 147.4, 135.1, 128.1, 123.2, 119.4, 82.5, 76.6, 68.7, 63.5, 33.8, 25.3; IR (KBr): ν 3011, 2957, 2853, 1547, 1535, 1363, 987, 784; HRMS (*m/z*) calcd for $C_{14}H_{16}NO_4(M+H)^+$: 262.1071, found: 262.1073.

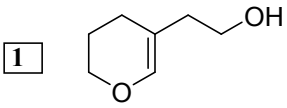
6b: **4-(2,3,4,6,8,8a-Hexahydropyrano[3,4-*b*]pyran-8-yl)benzonitrile**:

Yellow liquid; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.68 – 7.61 (m, 2H), 7.59 – 7.52 (m, 2H), 5.73 (d, *J* = 2.6 Hz, 1H), 4.19-4.02 (m, 2H), 3.91 (dd, *J* = 9.8, 7.1 Hz, 2H), 3.62 – 3.38 (m, 2H), 2.59 – 2.45 (m, 1H), 2.43 – 2.30 (m, 1H), 2.26 (dd, *J* = 14.1, 2.0 Hz, 1H), 1.94 (ddd, *J* = 11.9, 6.6, 4.0 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 145.4, 135.2, 131.9, 128.0, 119.4, 119.0, 111.6, 82.7, 76.5, 68.7, 63.5, 33.8, 25.3; IR (KBr): ν 2962, 2855, 2227, 1636, 1423, 1165, 932, 800; HRMS (*m/z*) calcd for $C_{15}H_{16}NO_2(M+H)^+$: 242.1183, found: 242.1181.

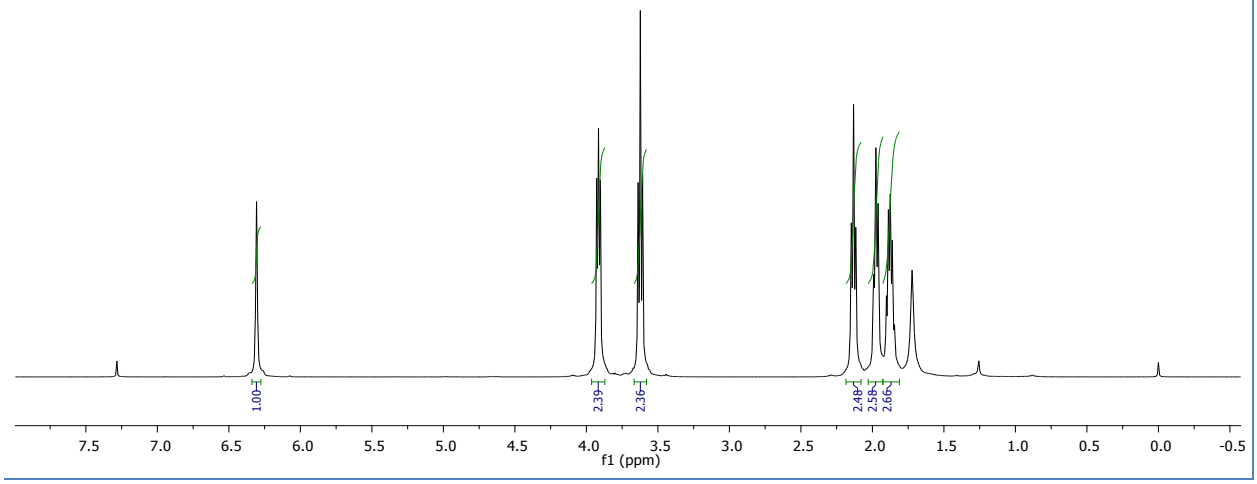
6c: **8-(2-Bromophenyl)-2,3,4,6,8,8a-hexahydropyrano[3,4-*b*]pyran**:

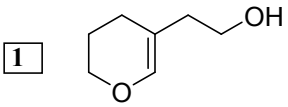
Yellow liquid; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.57 (dt, *J* = 8.0, 4.0 Hz, 1H), 7.52 (dd, *J* = 7.8, 1.7 Hz, 1H), 7.38 – 7.32 (m, 1H), 7.19 – 7.12 (m, 1H), 5.74 (d, *J* = 2.1 Hz, 1H), 4.60 (d, *J* = 9.4 Hz, 1H), 4.20 (d, *J* = 9.4 Hz, 1H), 4.12 – 4.04 (m, 1H), 3.92 (ddd, *J* = 11.0, 5.4, 3.1 Hz, 1H), 3.61 – 3.51 (m, 2H), 2.58 – 2.47 (m, 1H), 2.36-2.34 (m, 2H), 2.04 – 1.95 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 138.8, 135.7, 132.8, 129.5, 128.4, 127.6, 125.1, 119.1, 81.5, 76.0, 68.9, 63.3, 34.2, 25.3; IR (KBr): ν 3061, 2960, 2852, 1636, 1432, 1106, 998, 753; HRMS (*m/z*) calcd for $C_{14}H_{16}O_2Br(M+H)^+$: 295.0334, found: 295.0334.

^{1}H & ^{13}C NMR spectra of compound 1

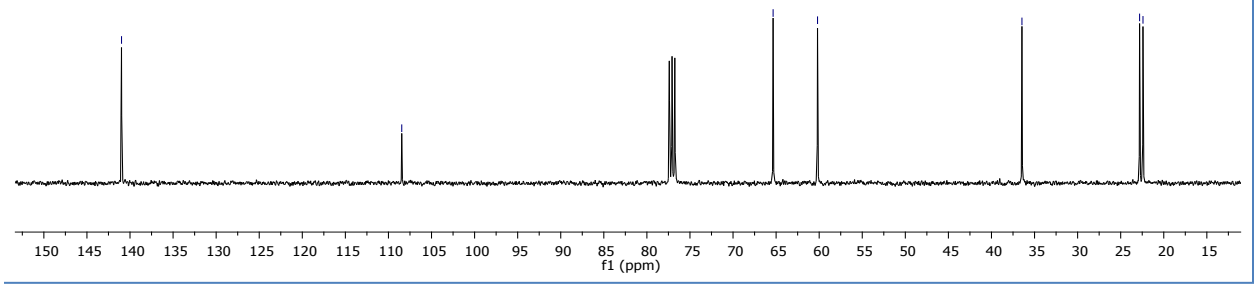


^{1}H, $CDCl_3$, 500 MHz

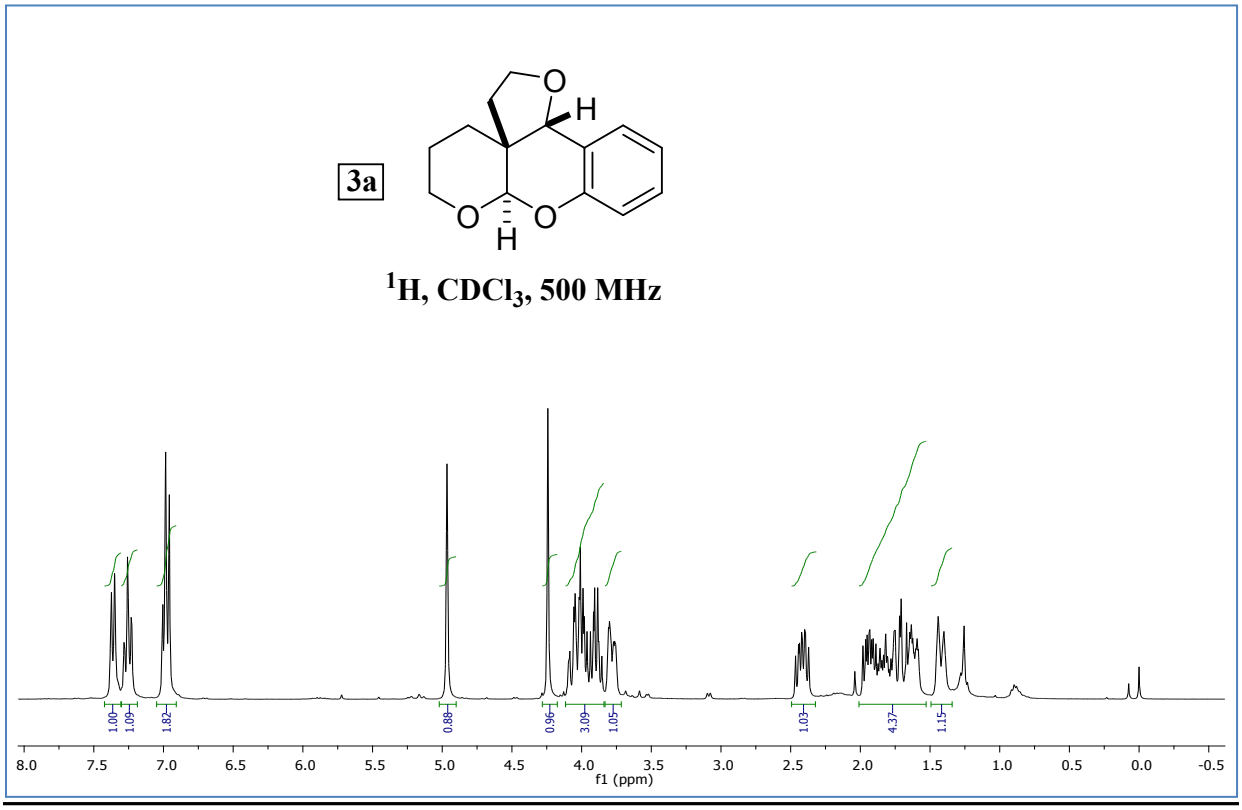


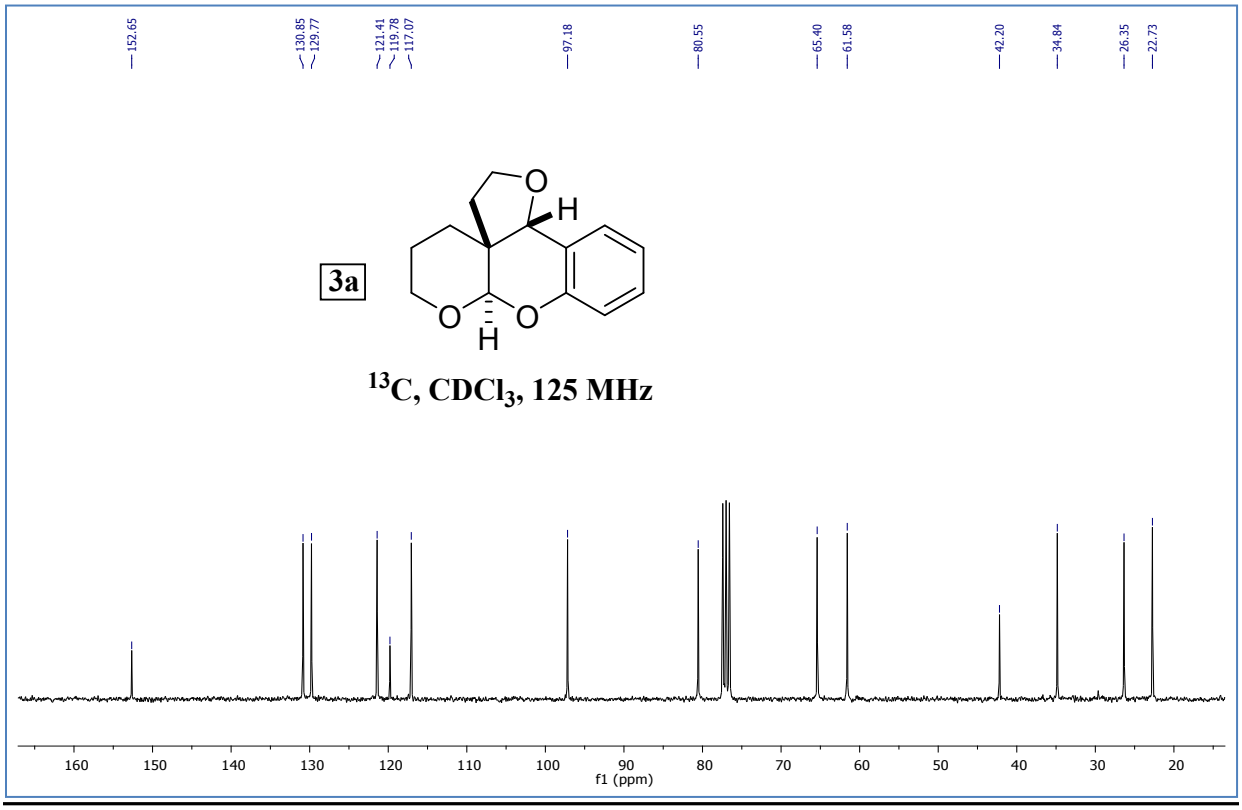


^{13}C, $CDCl_3$, 125 MHz

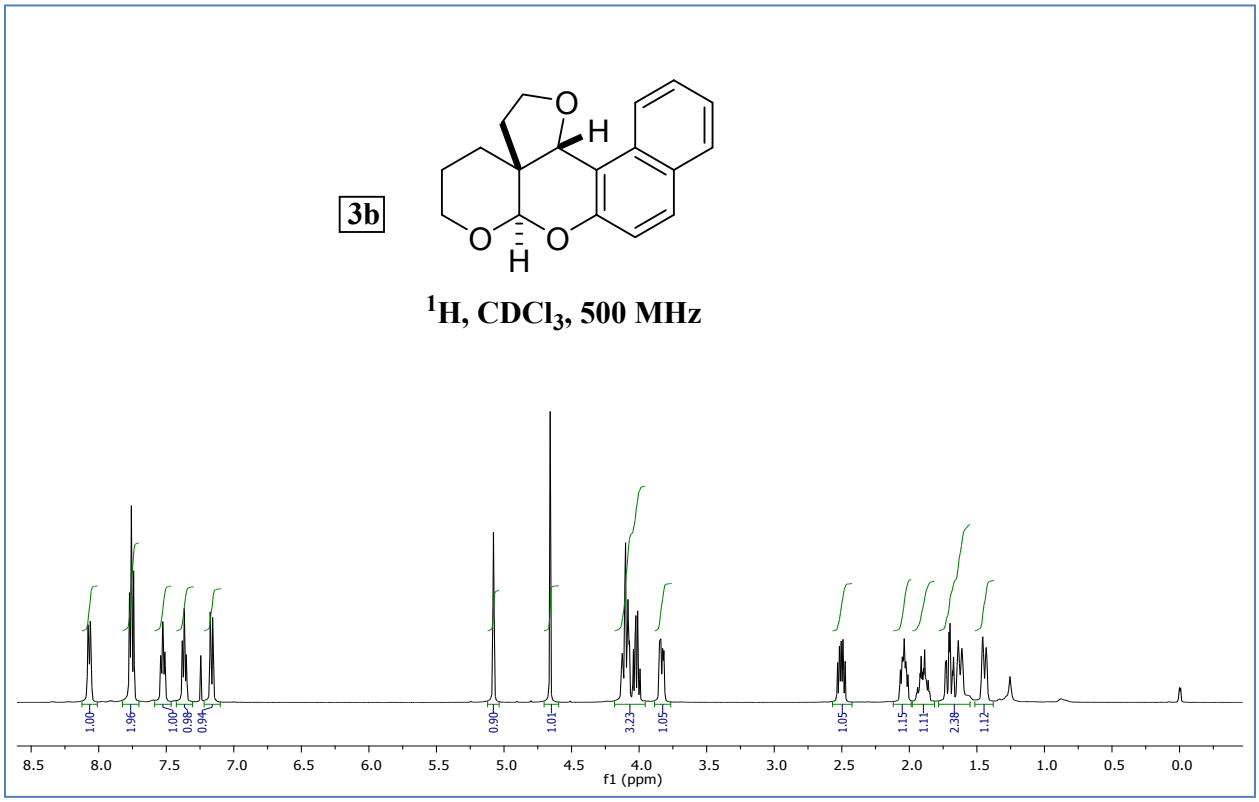


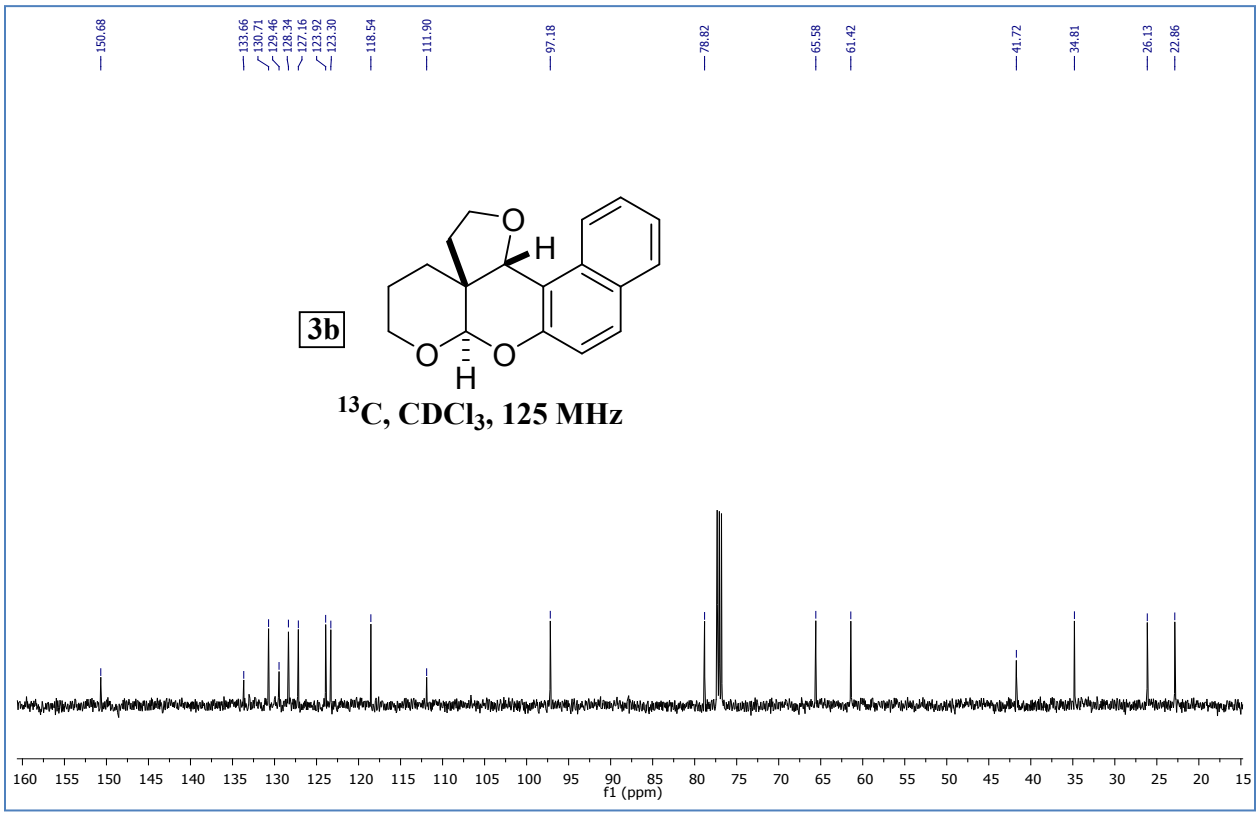
^{1}H and ^{13}C NMR spectra of compound 3a (Table 1, entry a):



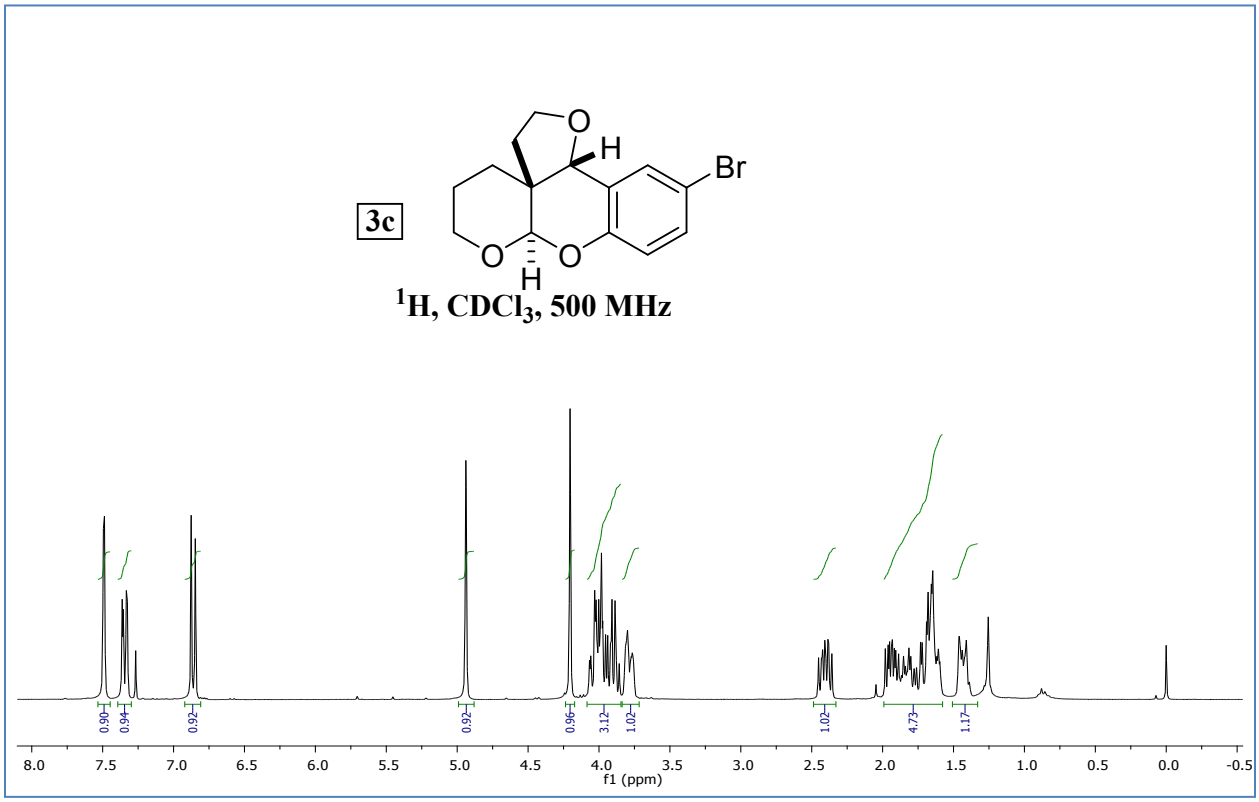


^{1}H and ^{13}C NMR spectra of compound 3b (Table 1 entry b):

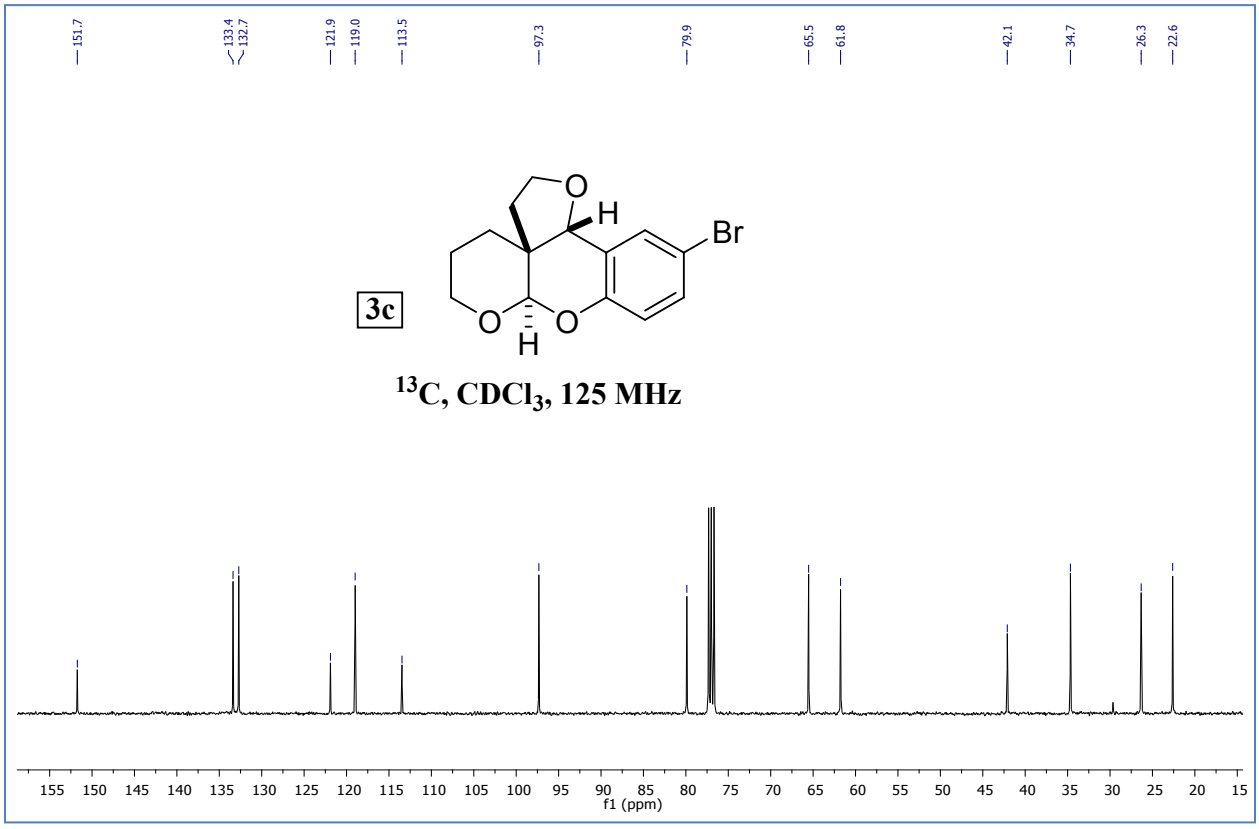




^{1}H and ^{13}C NMR spectra of compound 3c (Table 1 entry c):

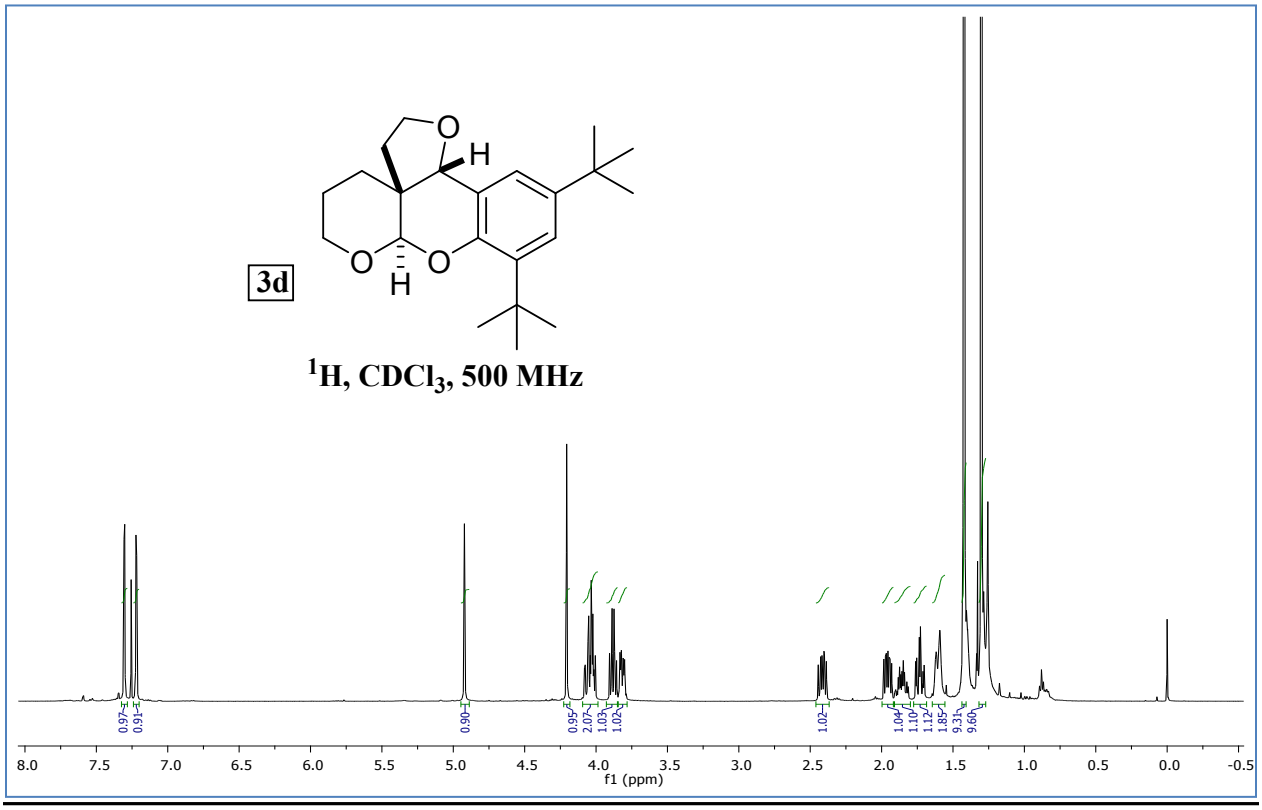


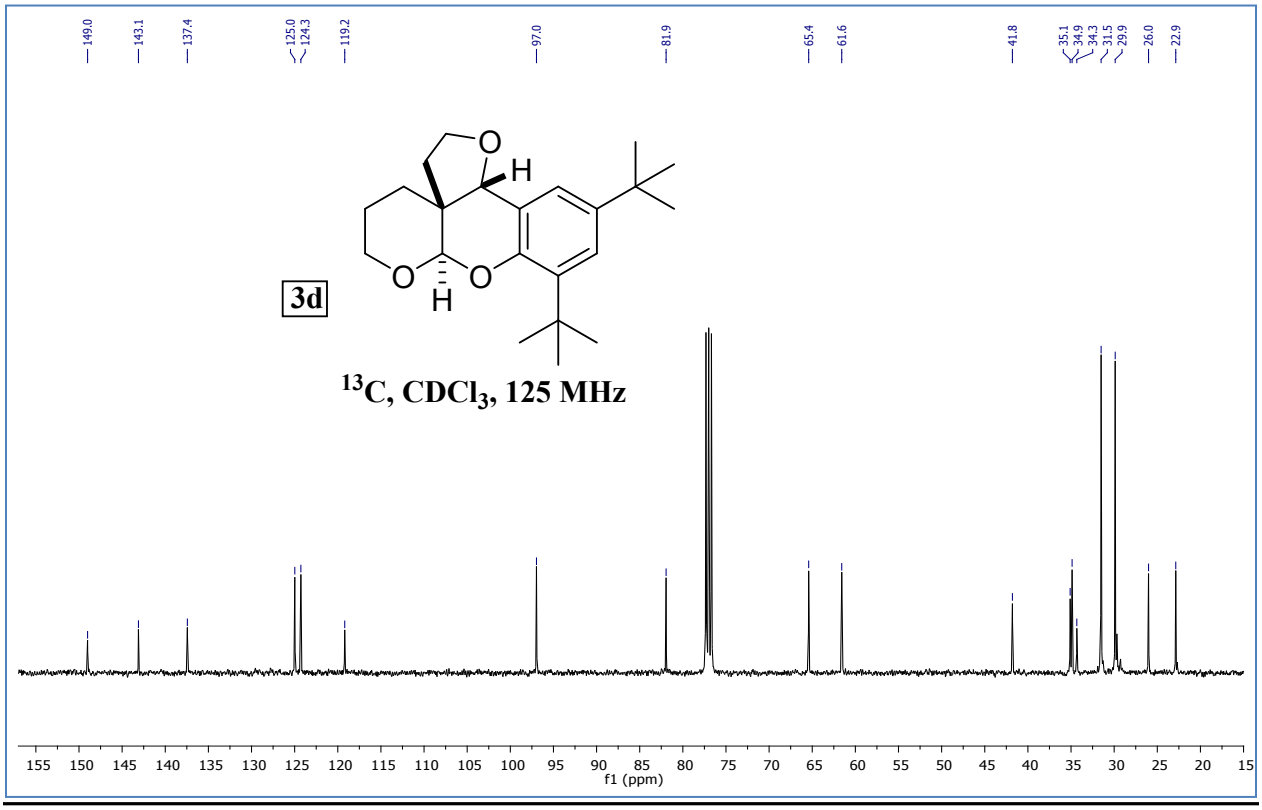
^{1}H, $CDCl_3$, 500 MHz



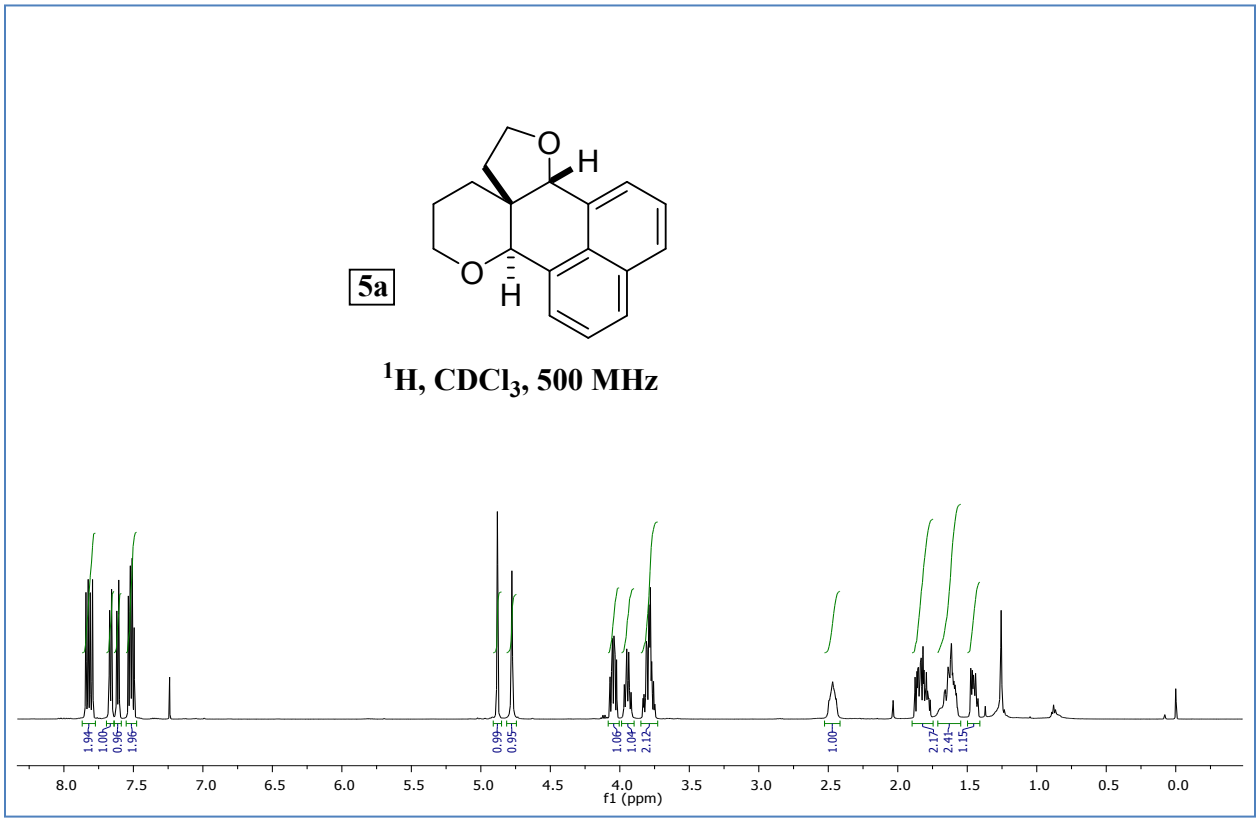
^{13}C, $CDCl_3$, 125 MHz

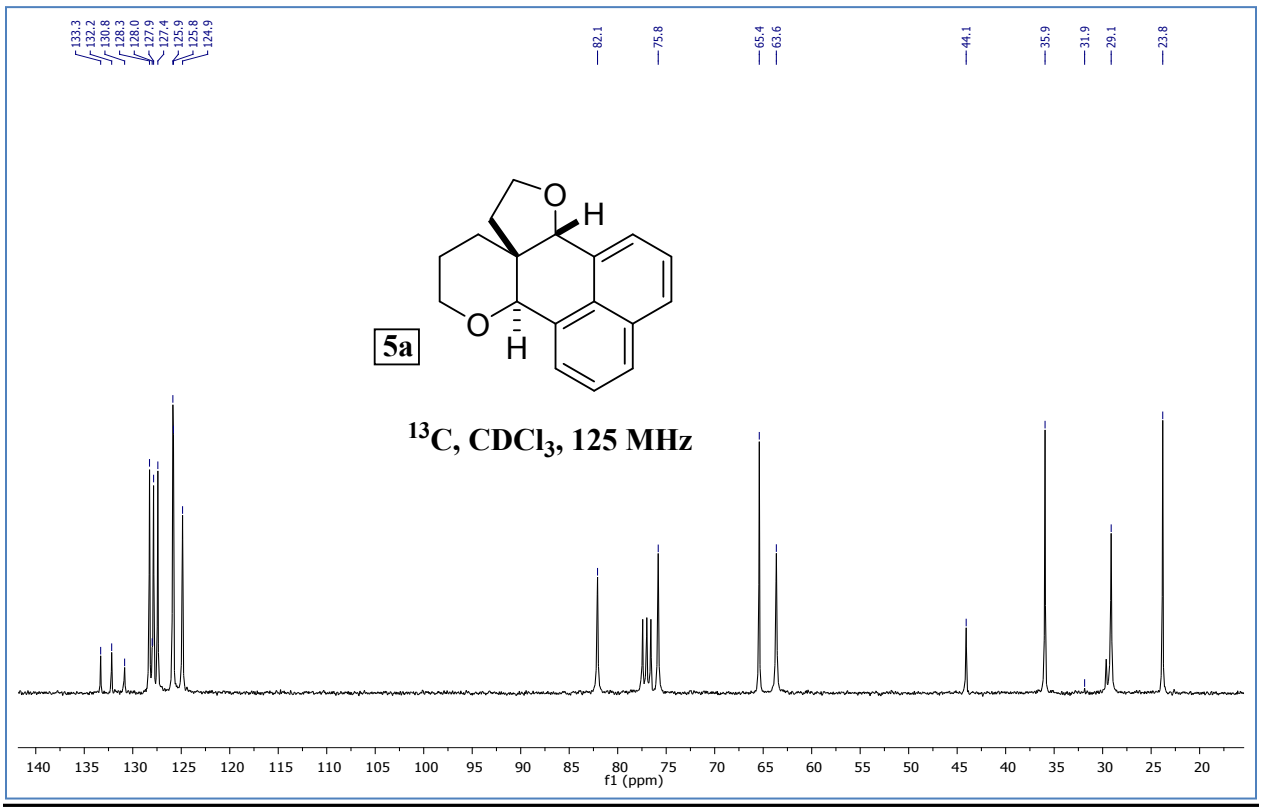
^{1}H and ^{13}C NMR spectra of compound 3d (Table 1 entry d):



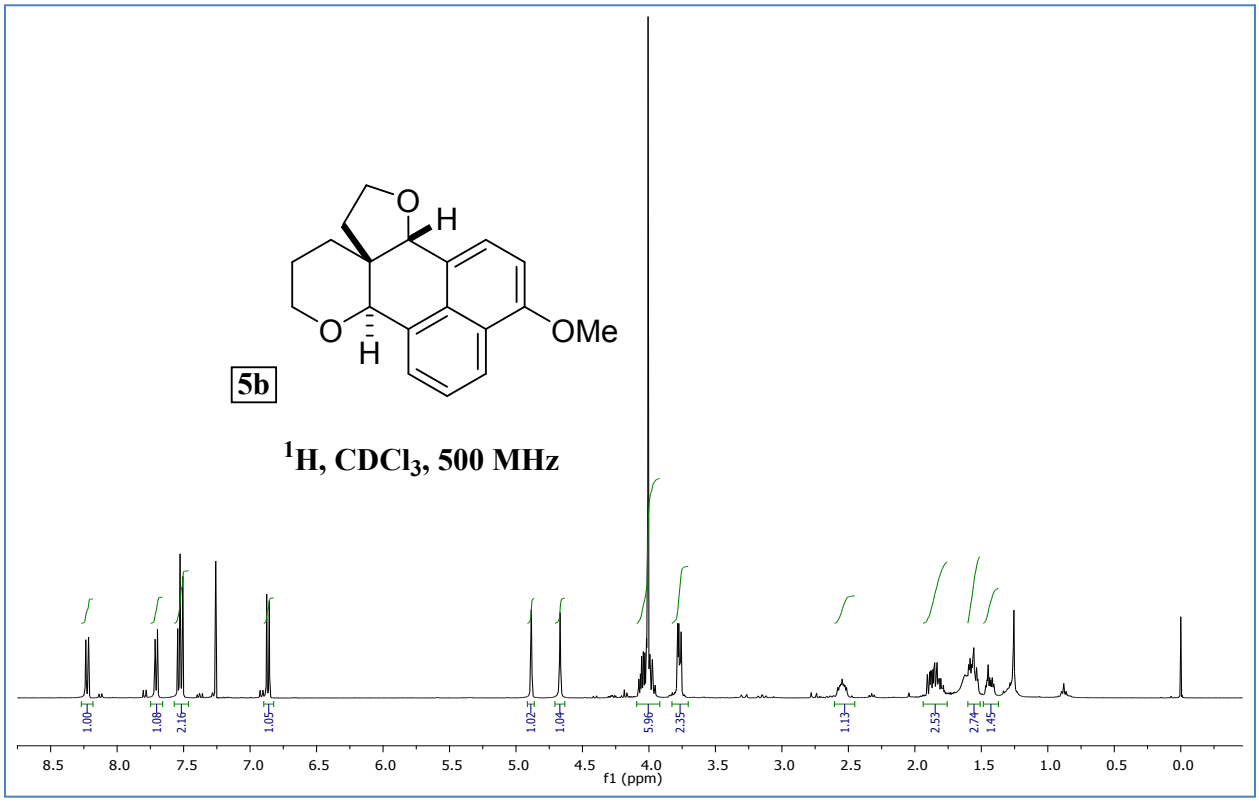


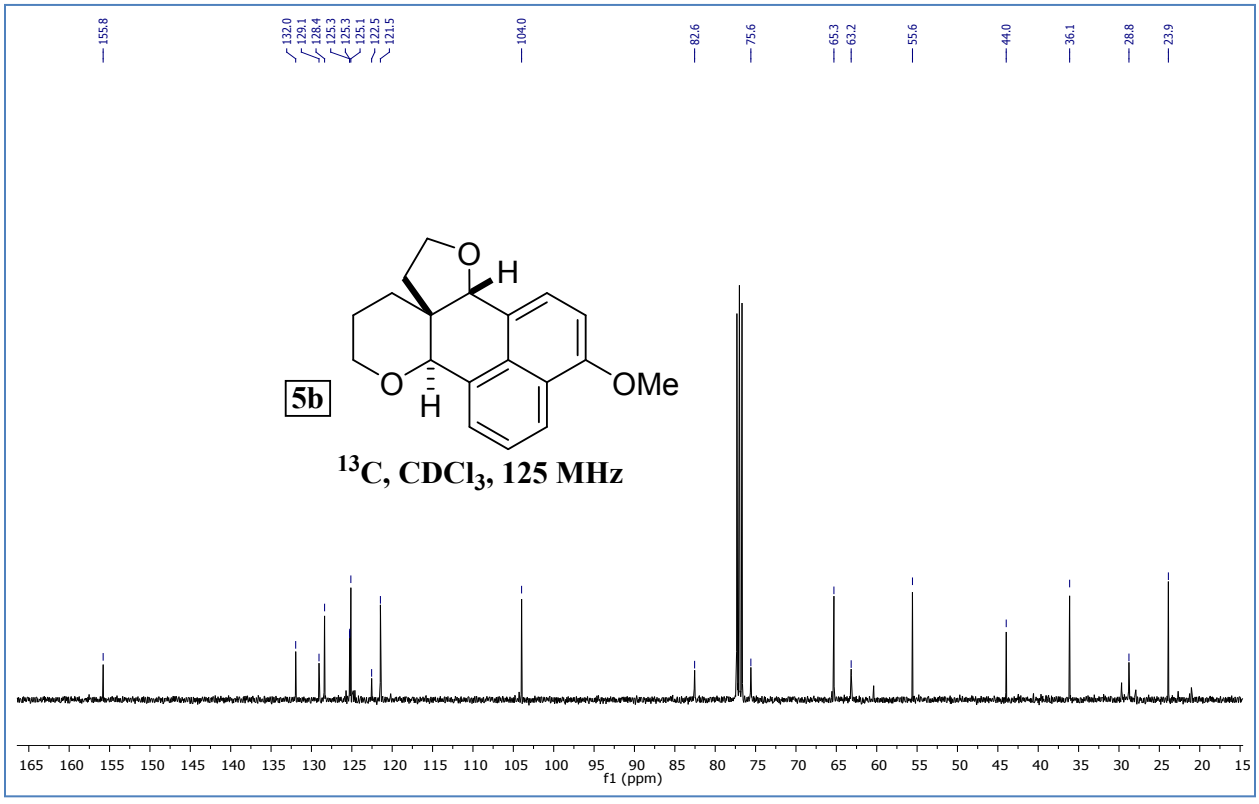
^{1}H and ^{13}C NMR spectra of compound 5a (Table 2 entry a):



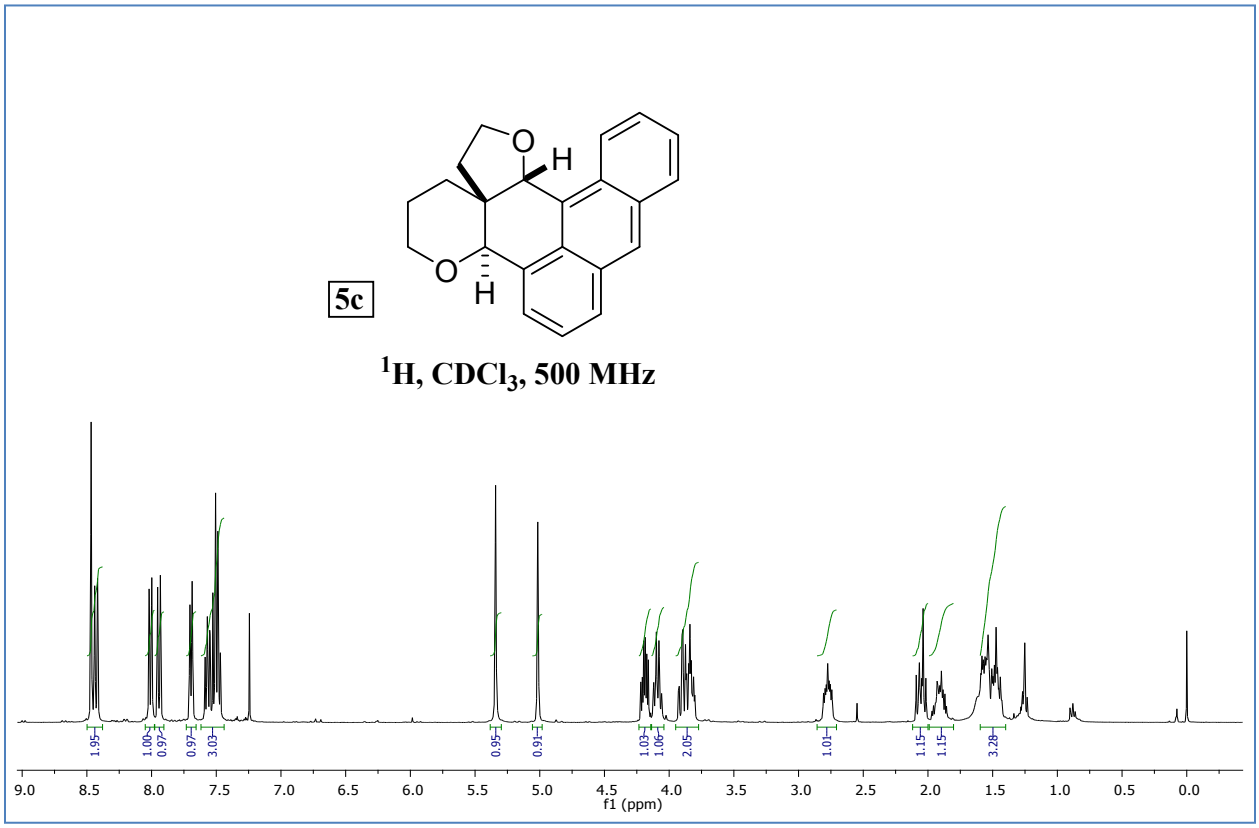


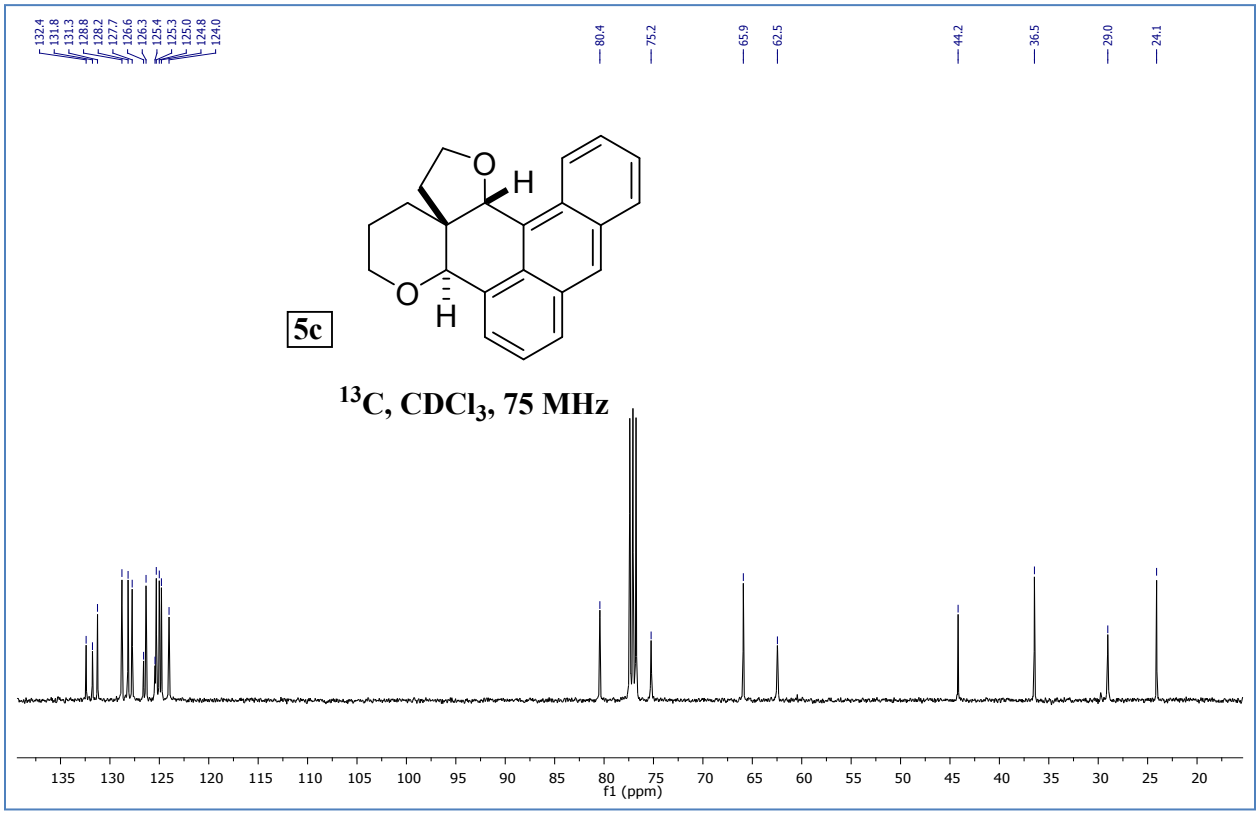
^{1}H and ^{13}C NMR spectra of compound 5b (Table 2 entry b):



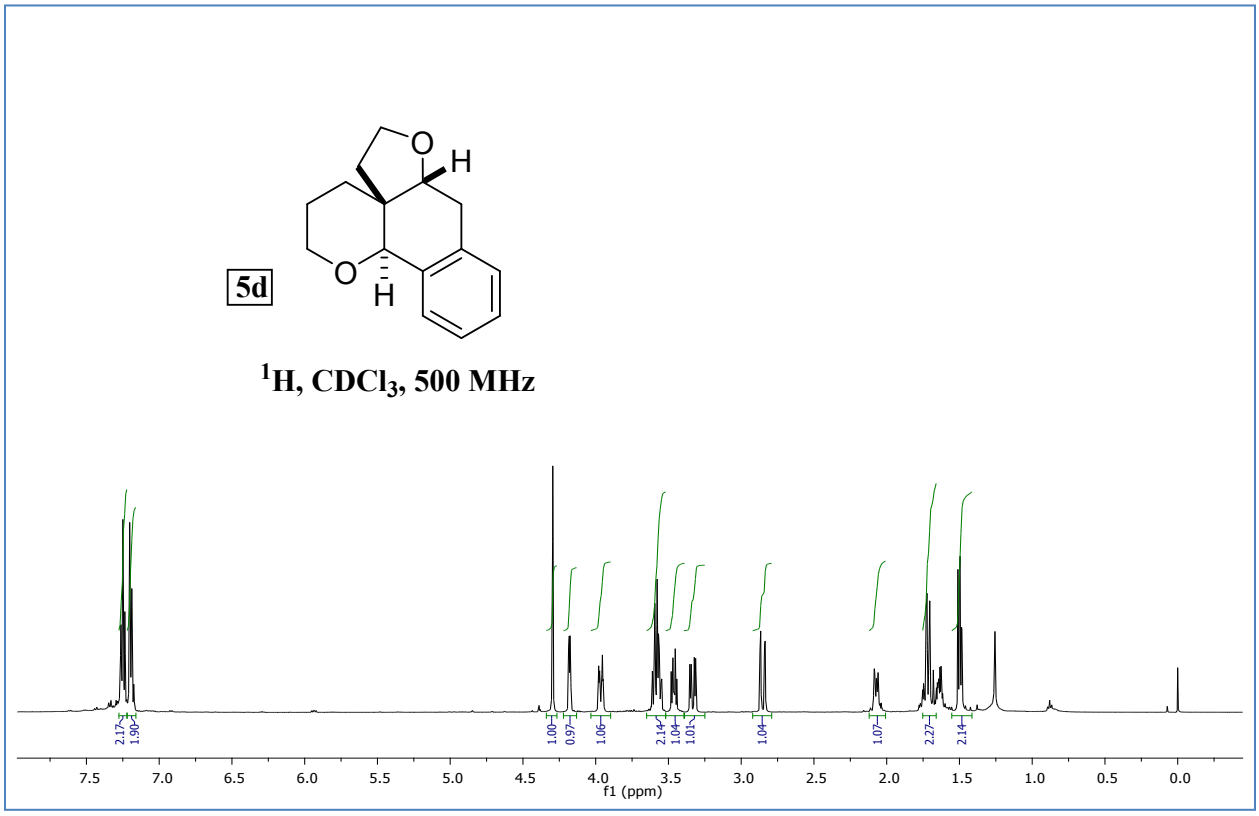


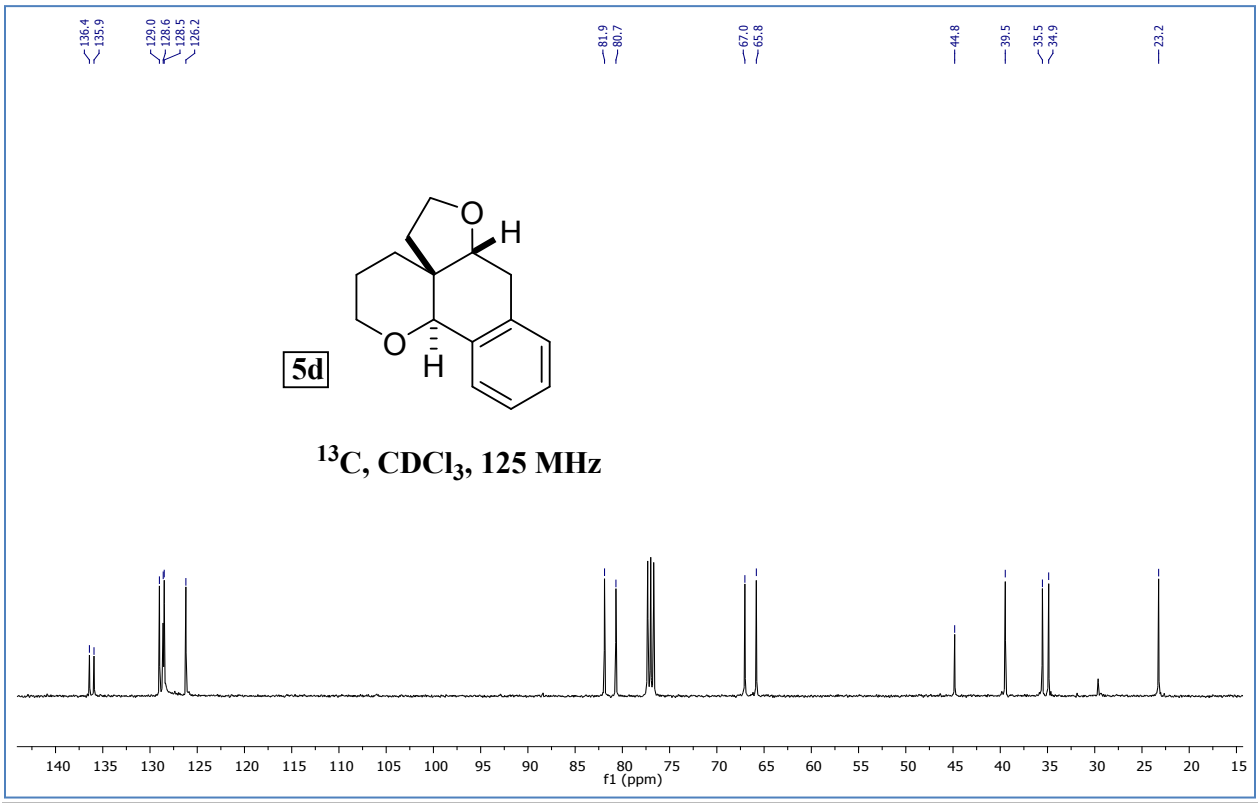
^{1}H and ^{13}C NMR spectra of compound 5c (Table 2 entry c):



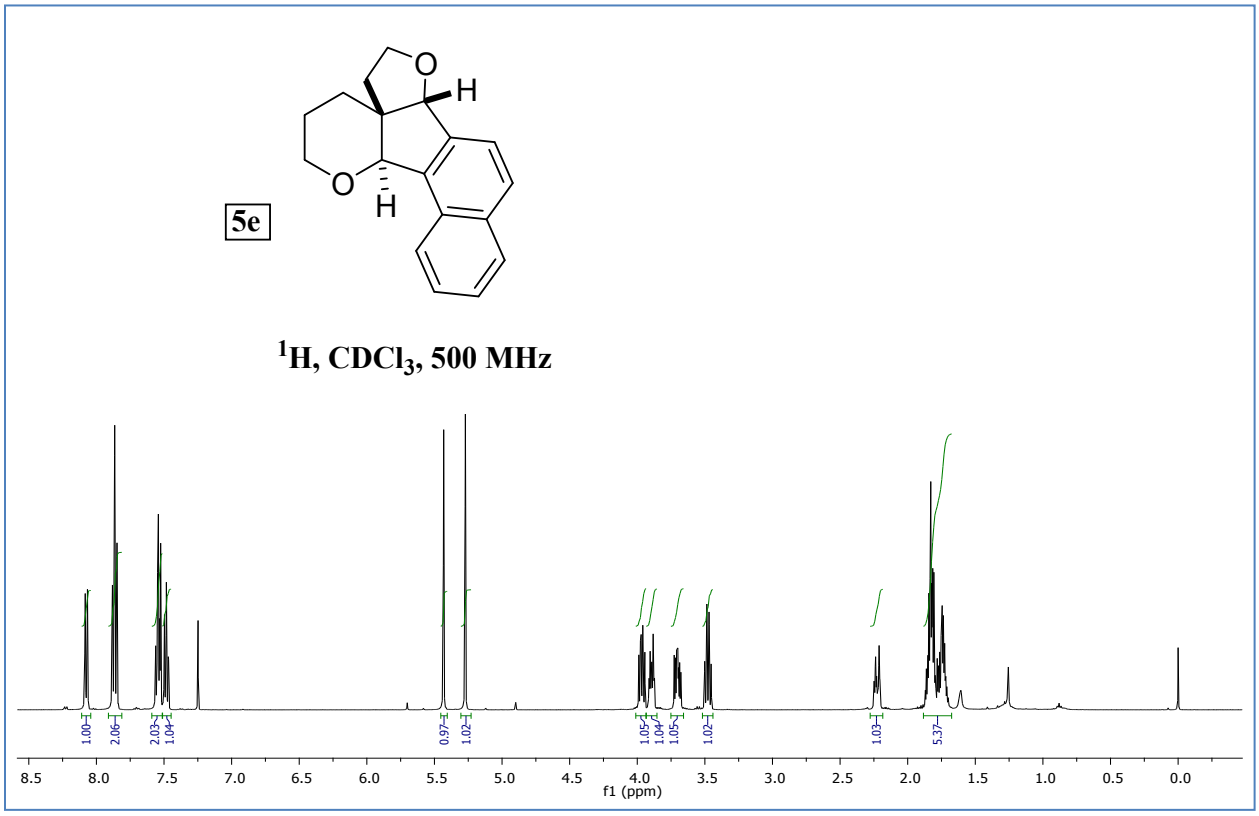


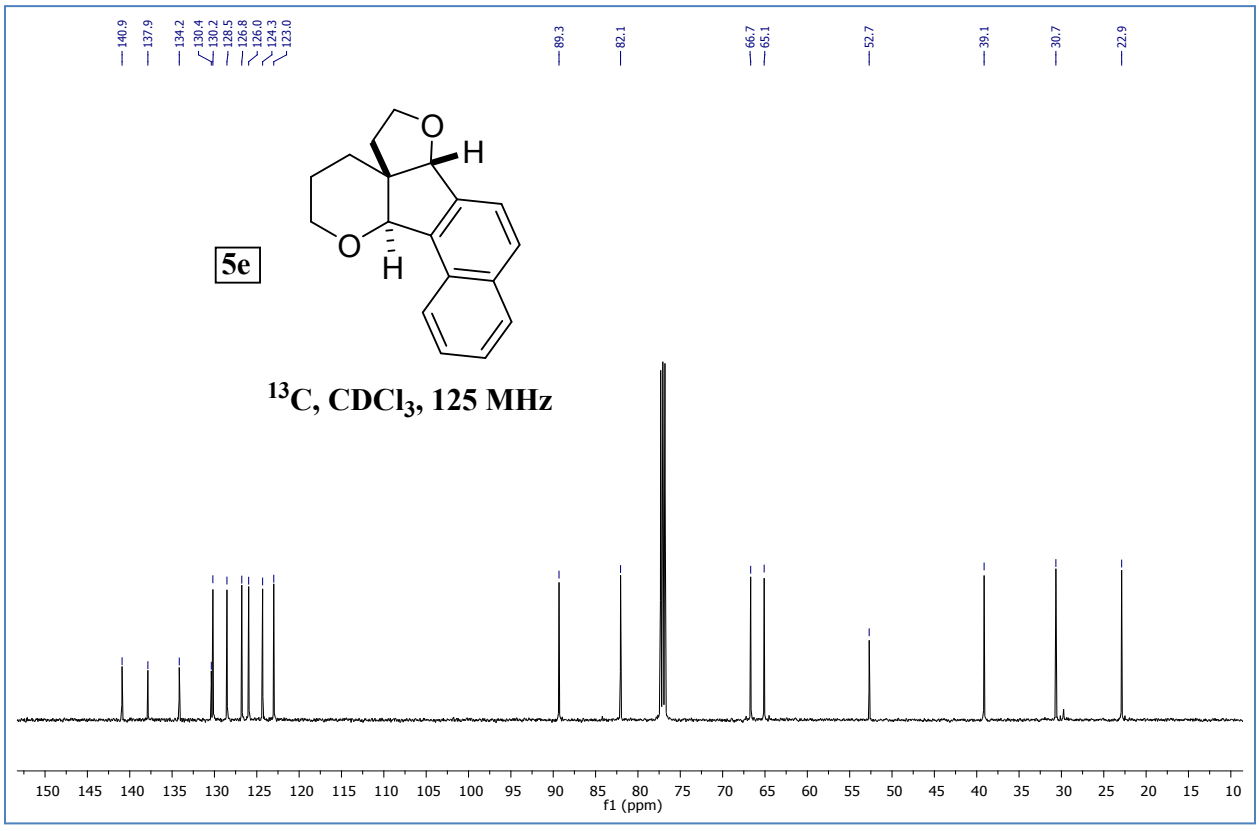
^{1}H and ^{13}C NMR spectra of compound 5d (Table 2 entry e):



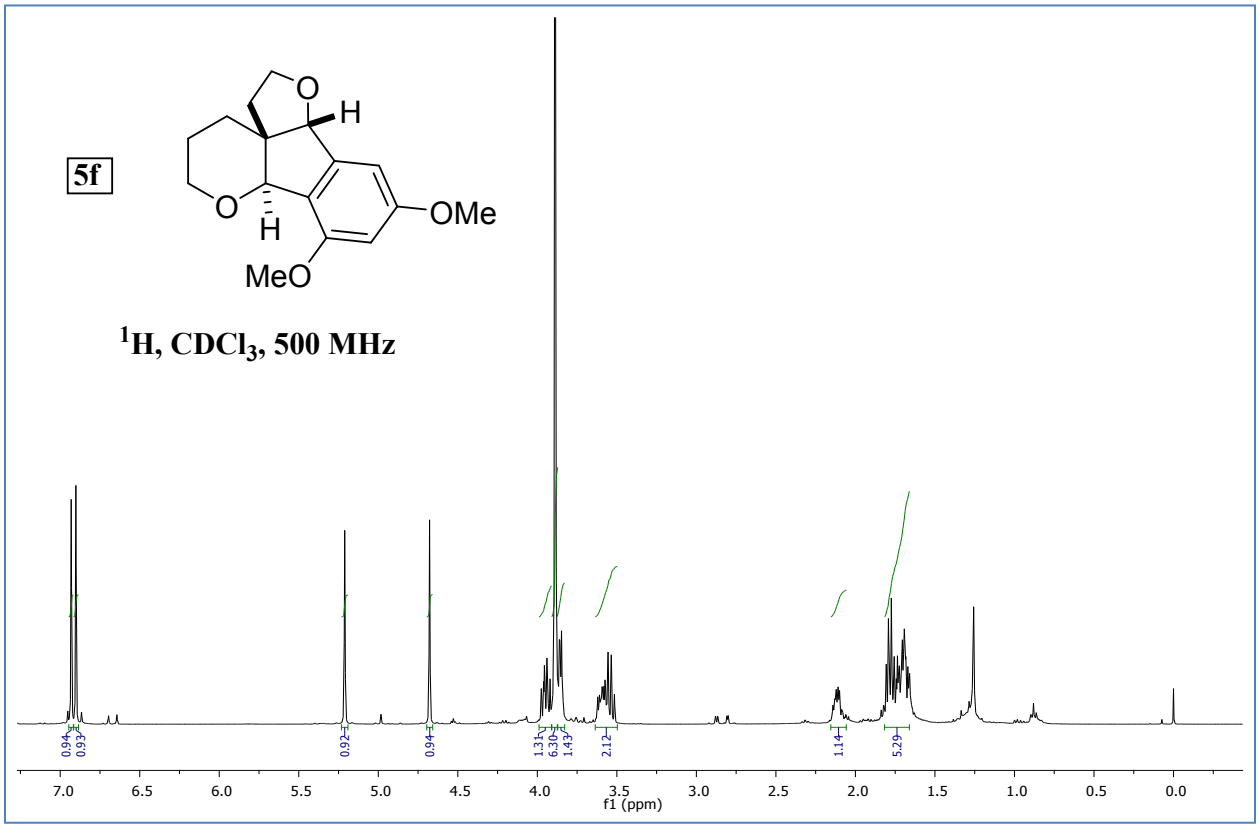


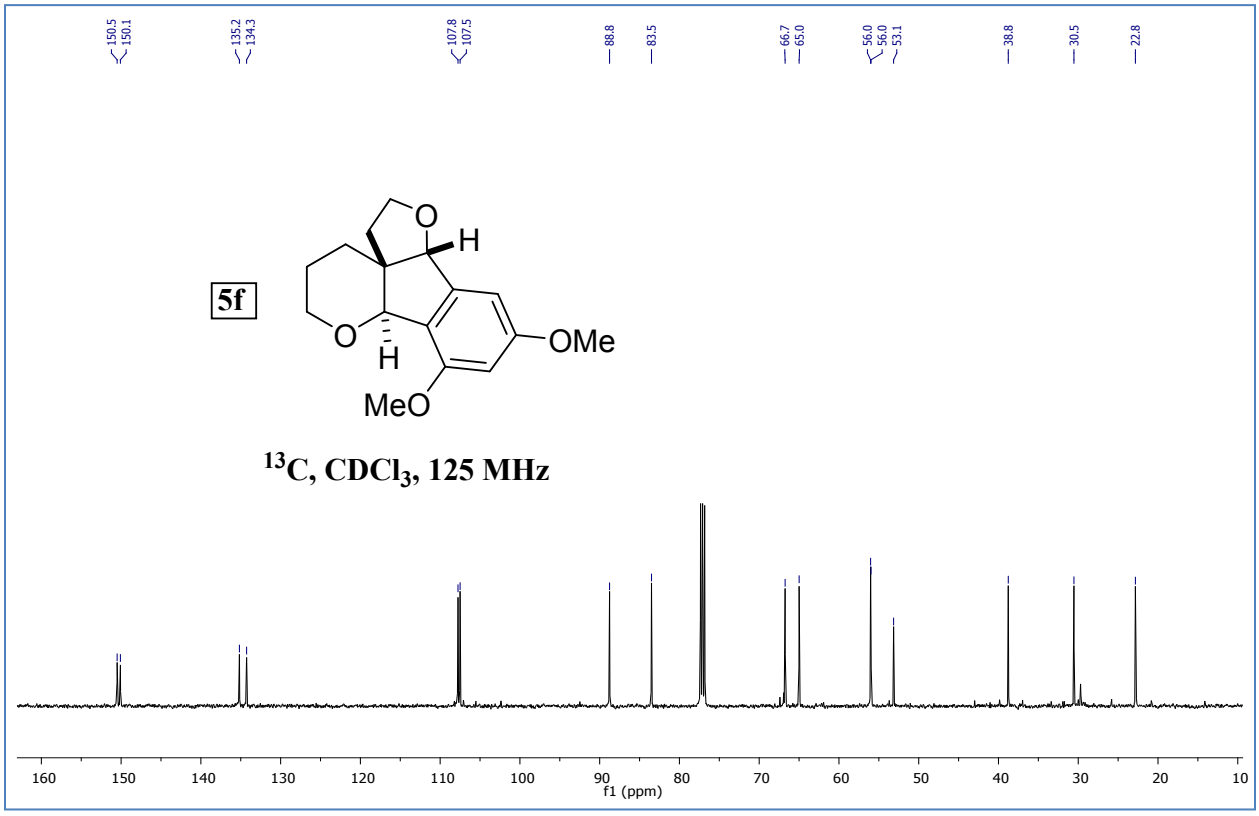
^{1}H and ^{13}C NMR spectra of compound 5e (Table 2 entry f):



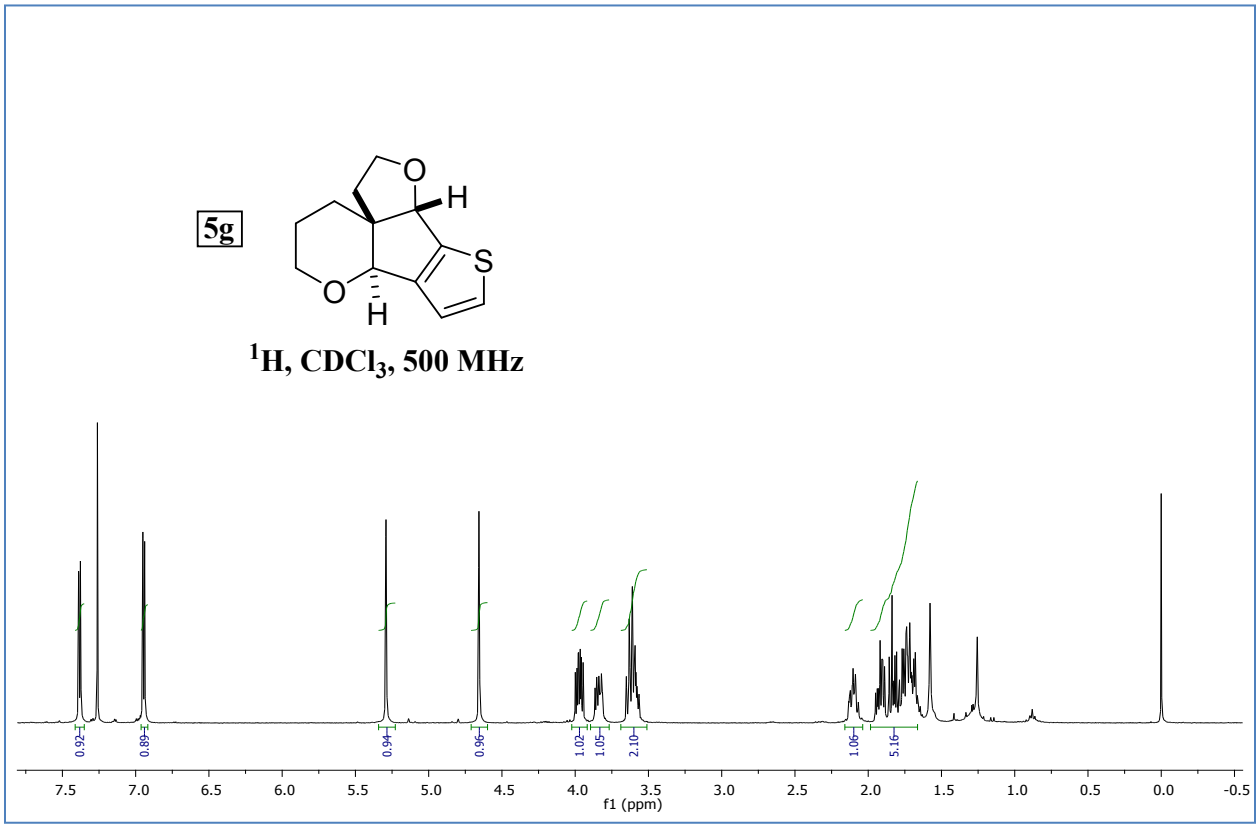


^{1}H and ^{13}C NMR spectra of compound 5f (Table 2 entry g):

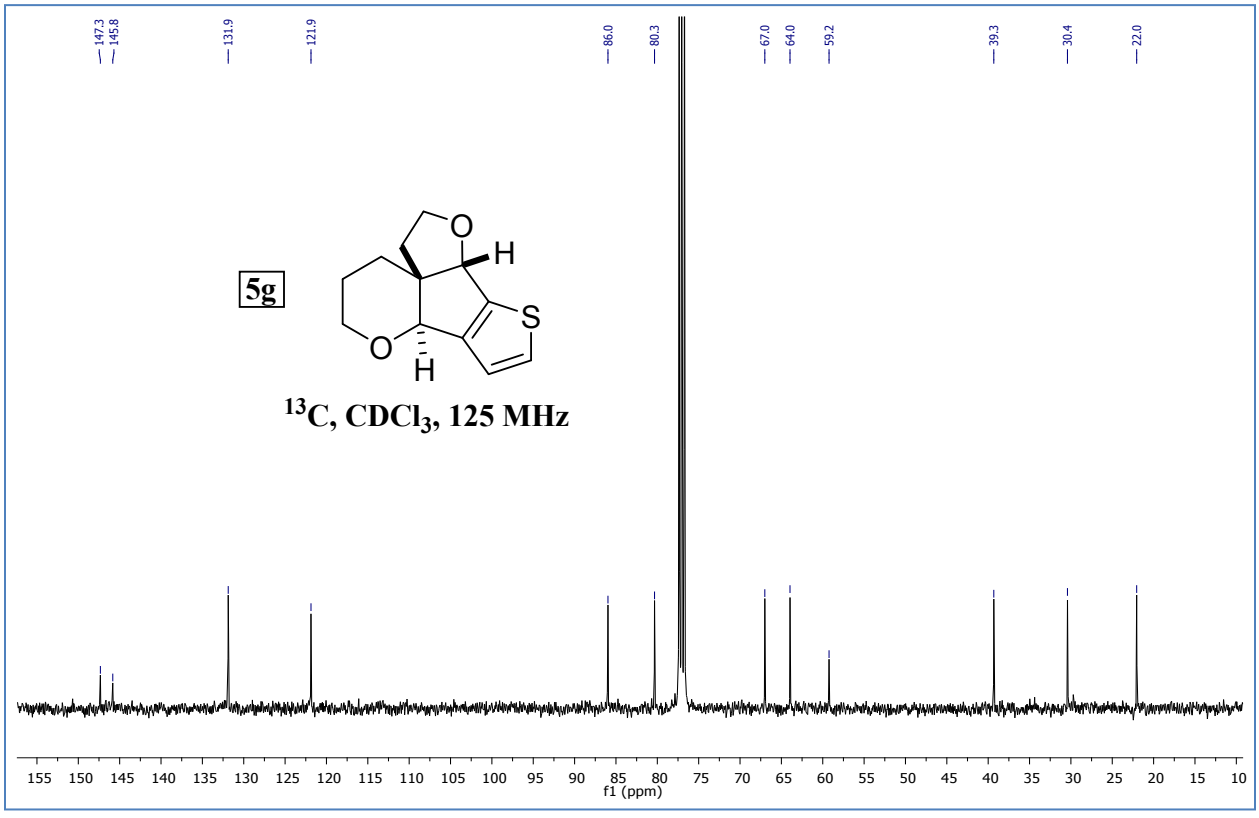




^{1}H and ^{13}C NMR spectra of compound 5g (Table 2 entry h):

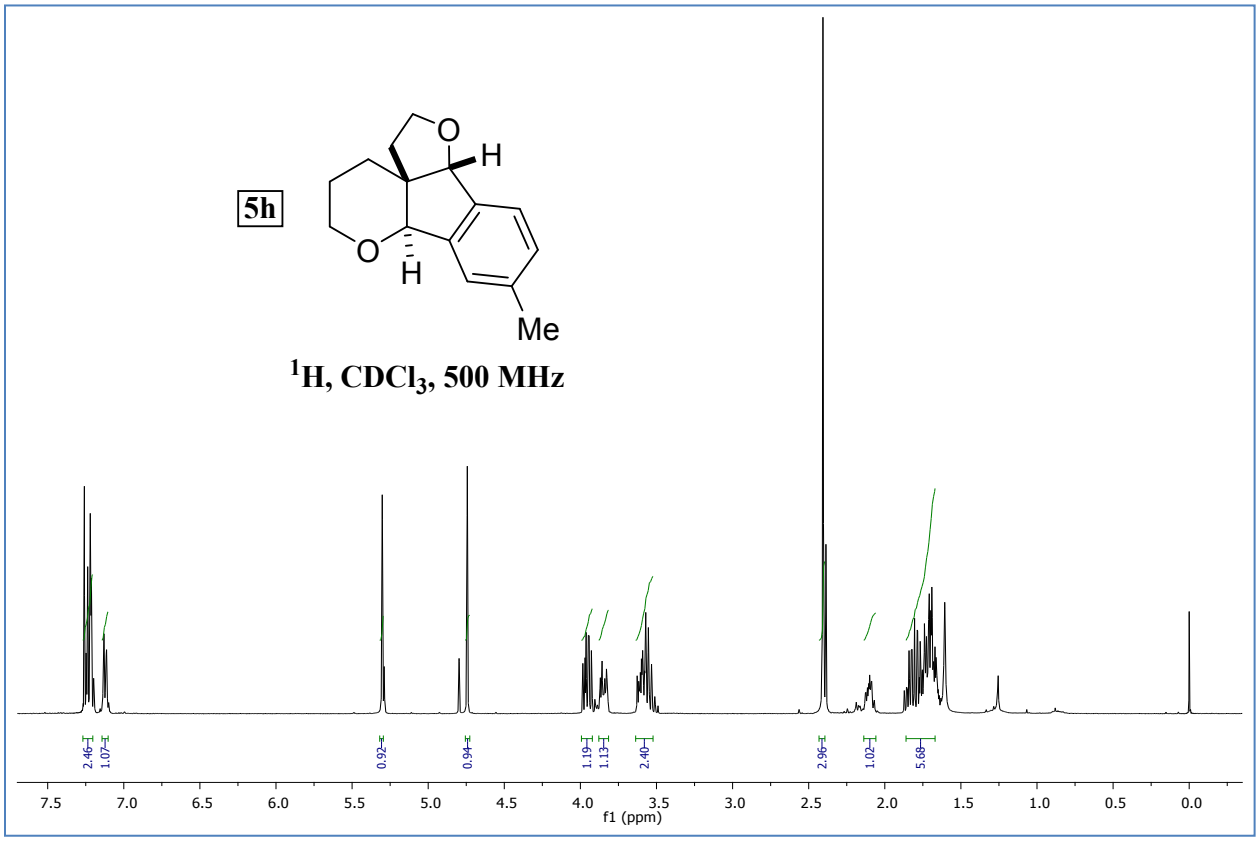


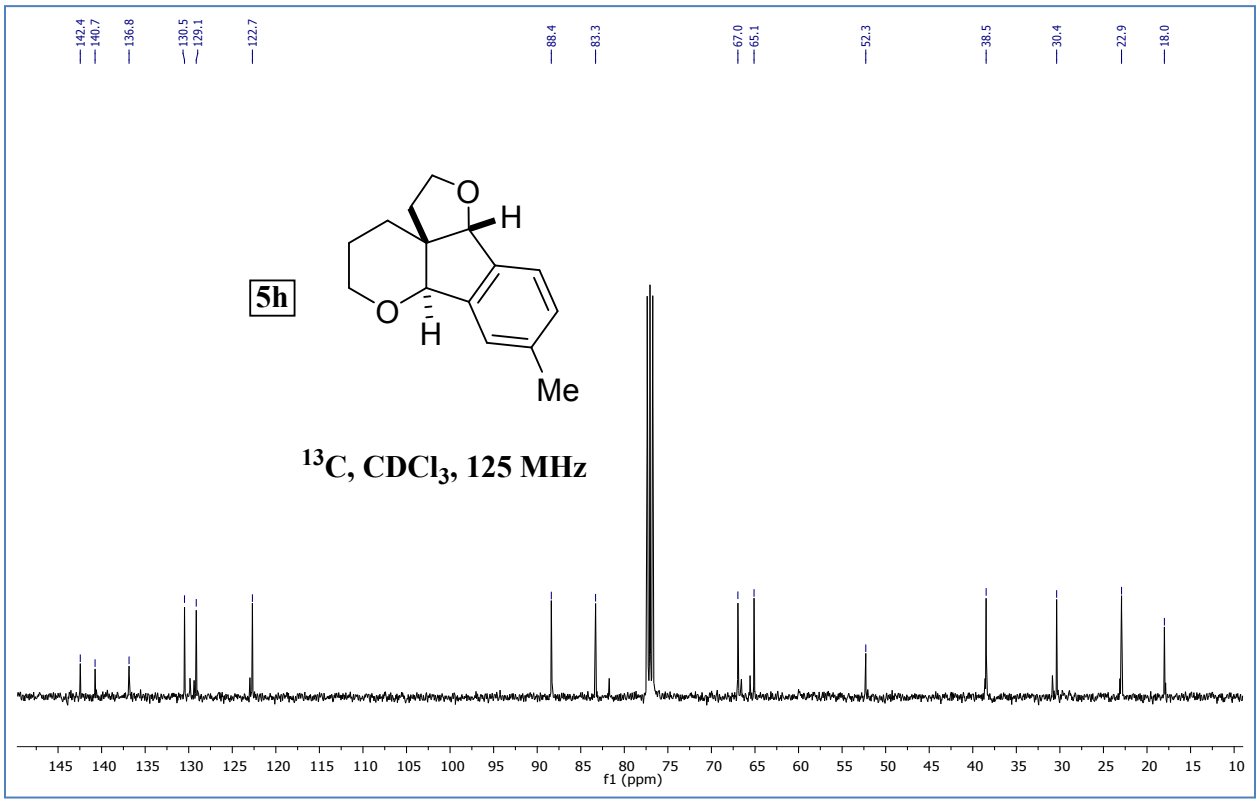
^{1}H, $CDCl_3$, 500 MHz



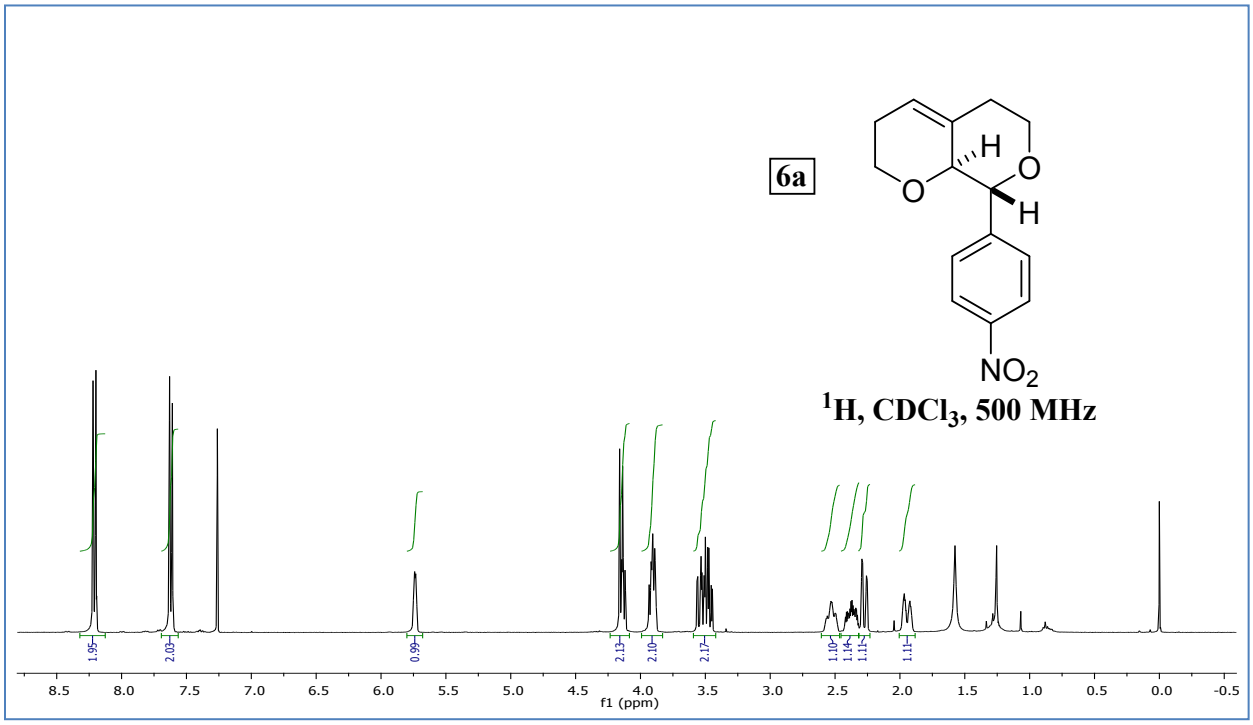
^{13}C, $CDCl_3$, 125 MHz

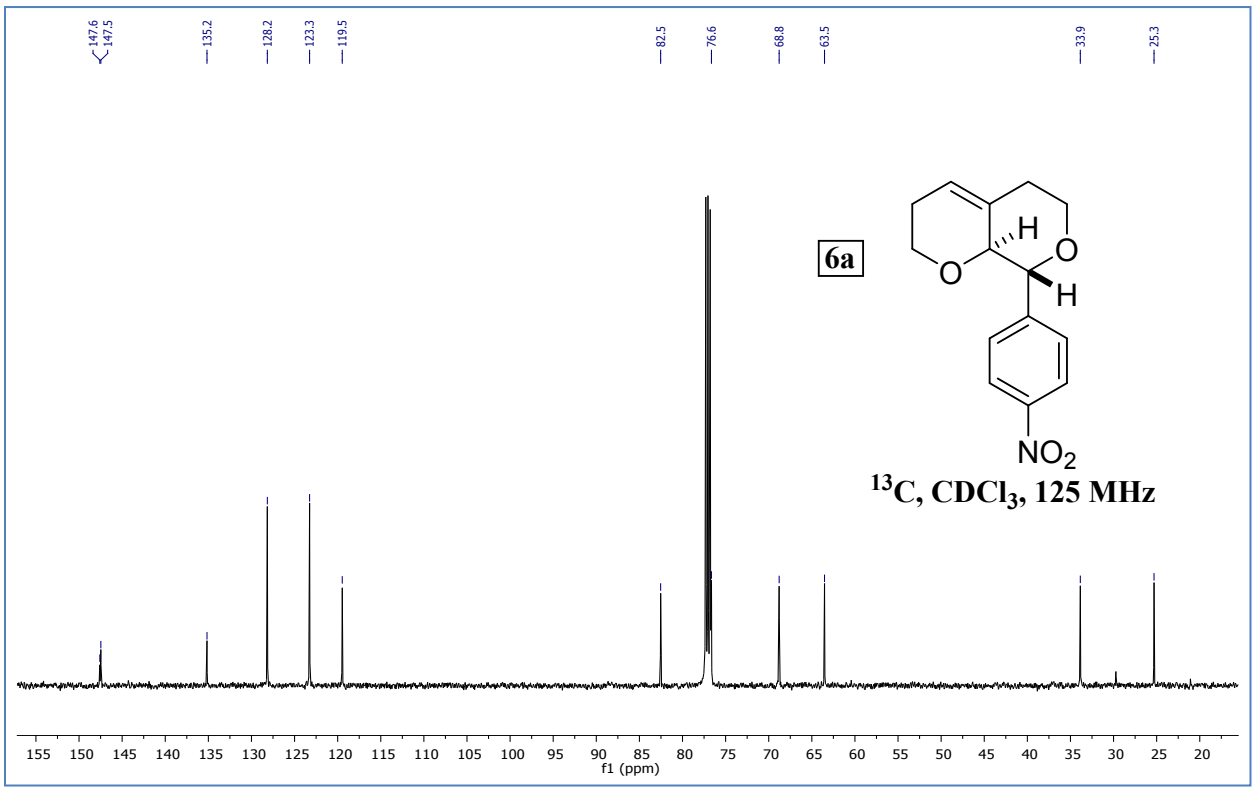
^{1}H and ^{13}C NMR spectra of compound 5h (Table 2 entry i):



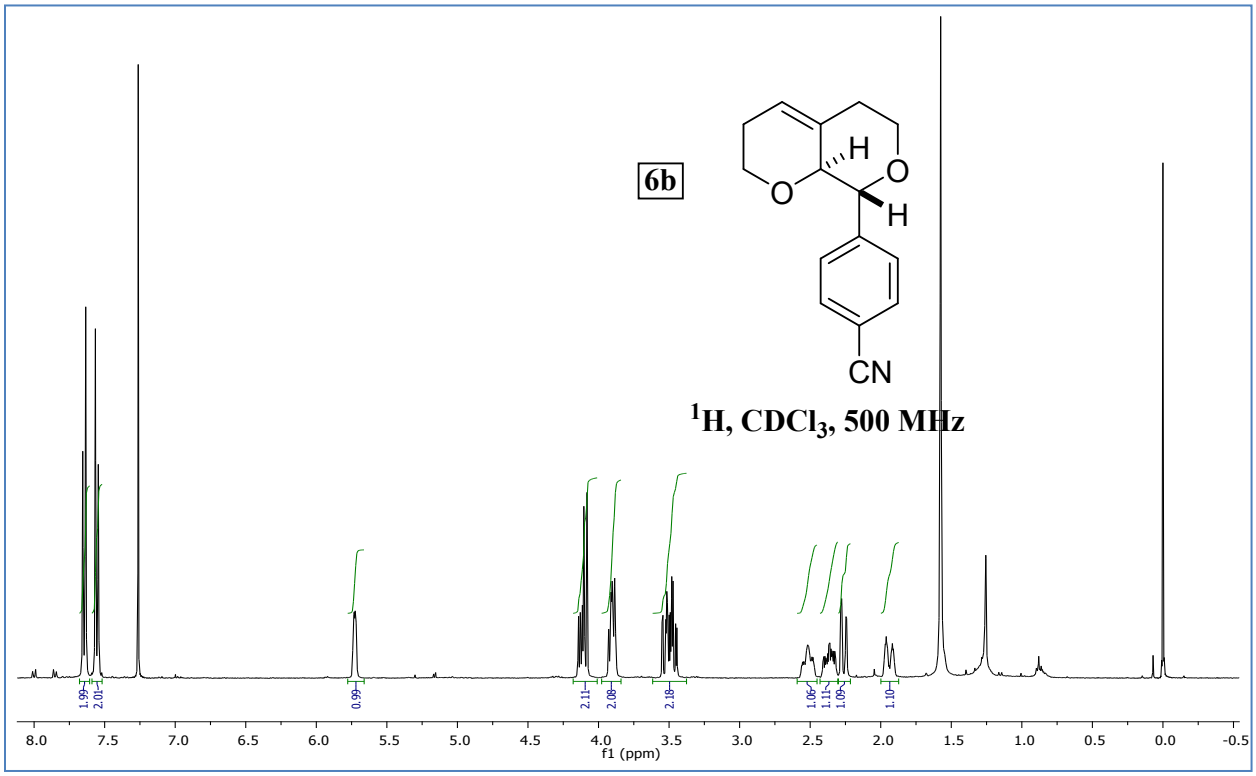


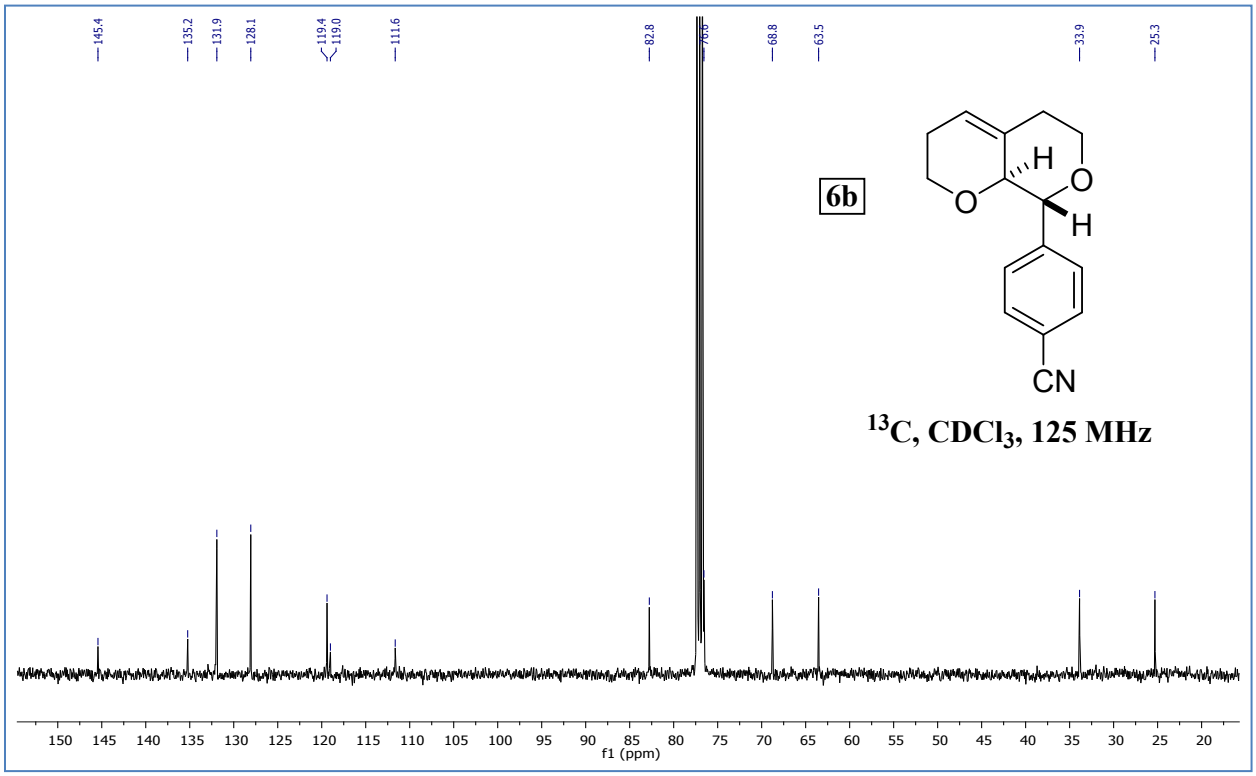
^{1}H and ^{13}C NMR spectra of compound 6a (Table 3 entry a):



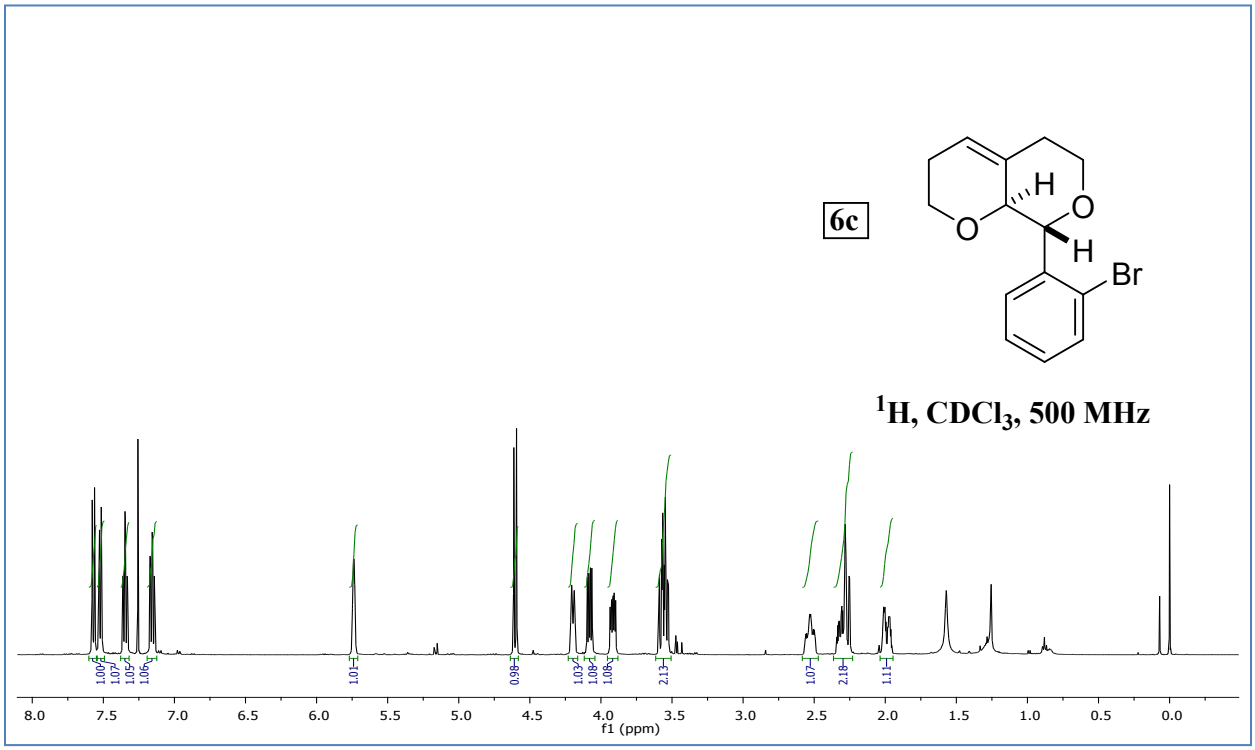


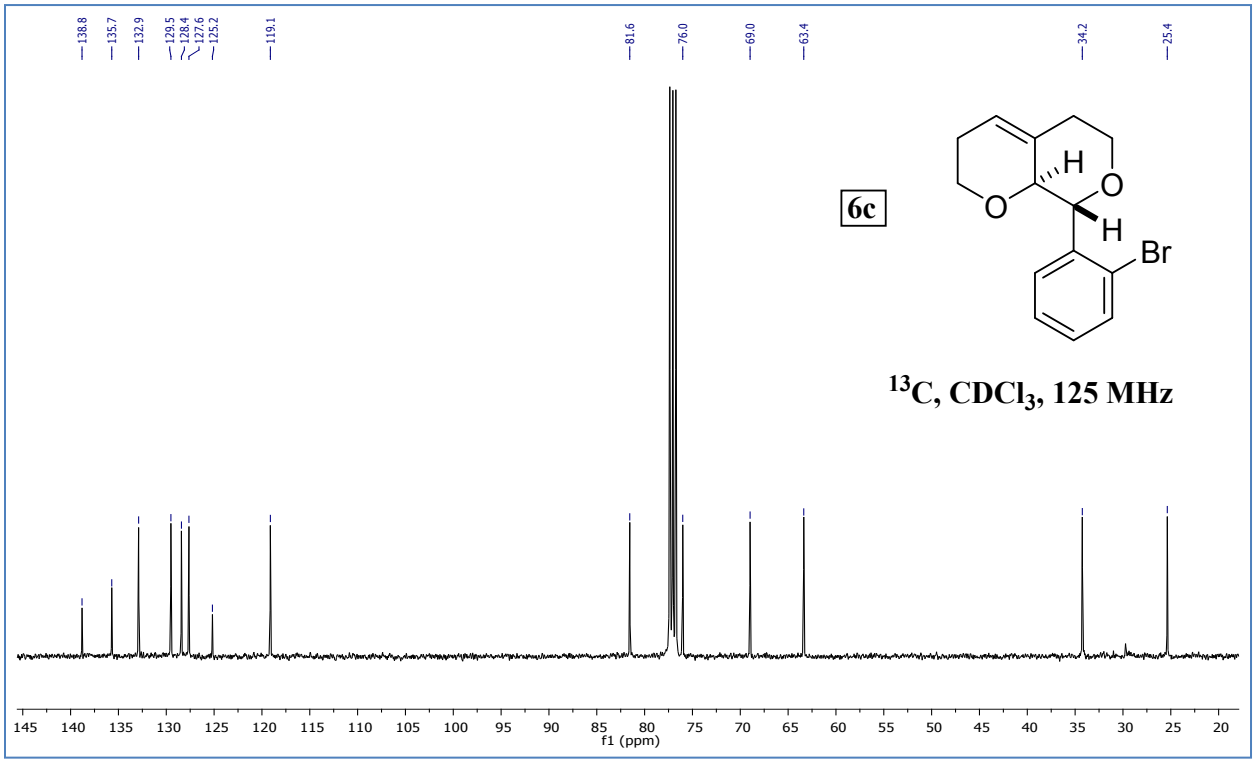
^{1}H and ^{13}C NMR spectra of compound 6b (Table 3 entry b):





^{1}H and ^{13}C NMR spectra of compound 6c (Table 3 entry c):





(3) X-ray Crystallography

X-ray data for the compounds (**3b,5a and 6a**) were collected at room temperature using a Bruker Smart Apex CCD diffractometer with graphite monochromated MoKα radiation (λ=0.71073Å) with ω-scan method [4]. Preliminary lattice parameters and orientation matrices were obtained from four sets of frames.

Integration and scaling of intensity data was accomplished using SAINT program [4]. The structure was solved by direct methods using SHELXS [5] and refinement was carried out by full-matrix least-squares technique using SHELXL [5]. Anisotropic displacement parameters were included for all non-hydrogen atoms. All H atoms were positioned geometrically and treated as riding on their parent C atoms [C-H = 0.93-0.97 Å and $U_{iso}(H) = 1.2U_{eq}(c)$ for other H atoms].

Crystal Data for 3b: $C_{18}H_{18}O_3$ (M =282.34 g/mol): monoclinic, space group $P2_1/c$ (no. 14), a = 12.6396(10) Å, b = 9.6186(8) Å, c = 11.8318(9) Å, β = 103.394(1)°, V = 1399.33(19) Å^3, Z = 4, T = 294.15 K, μ(Mo Kα) = 0.090 mm^{-1}, $Dcalc$ = 1.3401 g/cm^3, 16004 reflections measured (5.38° ≤ 2Θ ≤ 56.58°), 3379 unique (R_{int} = 0.0217, R_{sigma} = 0.0167) which were used in all calculations. The final R_1 was 0.0463 (I>2σ(I)) and wR_2 was 0.1493 (all data). CCDC 1566995 contains supplementary Crystallographic data for the structure.

Crystal Data for 5a: $C_{18}H_{18}O_2$ (M =266.34 g/mol): orthorhombic, space group $P2_12_12_1$ (no. 19), a = 7.9384(9) Å, b = 9.9744(12) Å, c = 17.126(2) Å, V = 1356.0(3) Å^3, Z = 4, T = 294.15 K, μ(Mo Kα) = 0.084 mm^{-1}, $Dcalc$ = 1.3045 g/cm^3, 15919 reflections measured (4.72° ≤ 2Θ ≤ 56.5°), 3293 unique (R_{int} = 0.0395, R_{sigma} = 0.0267) which were used in all calculations. The final R_1 was 0.0707 (I>2σ(I)) and wR_2 was 0.1618 (all data). CCDC 1566994 contains supplementary Crystallographic data for the structure.

Crystal Data for **6a**: $C_{14}H_{15}NO_4$ (M =261.28 g/mol): monoclinic, space group $P2_1/c$ (no. 14), a = 13.13(4) Å, b = 12.87(4) Å, c = 7.80(2) Å, β = 105.51(2)°, V = 1270(7) Å^3, Z = 4, T = 294.15 K, μ(Mo Kα) = 0.101 mm^{-1}, $Dcalc$ = 1.3664 g/cm^3, 19377 reflections measured (4.52° ≤ 2Θ ≤ 61.52°), 3941 unique (R_{int} = 0.0683, R_{sigma} = 0.0600) which were used in all calculations. The final R_1 was 0.0677 (I>2σ(I)) and wR_2 was 0.2064 (all data).

CCDC 1578489 contains supplementary Crystallographic data for the structure. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge

Crystallographic Data Centre (CCDC), 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44(0) 1223 336 033; email: deposit@ccdc.cam.ac.uk].

References

1. Searle, N. E.; Newman, M. S.; Ottmann, G. F.; C. F. Grundmann, *Org. Synth.,* 1956, *36*, 25.
2. Oliver Temme,; Shabbir-Ali Taj,; Pher G. Andersson, *J. Org. Chem*., 1998, *63*, 6007.
3. Michael P. Doyle,; Daan Van Leusen, *J. Org. Chem*., 1982, *47*, 5326.
4. Bruker (2001). SAINT (Version 6.28a) & SMART (Version 5.625). Bruker AXS Inc., Madison, Wisconsin, USA.
5. Sheldrick G. M. (2015) Acta Crystallogr C71: 3-8.