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Supporting Information

$InCl_3$-catalyzed Prins bicyclization for the synthesis of spirotetrahydropyran derivatives

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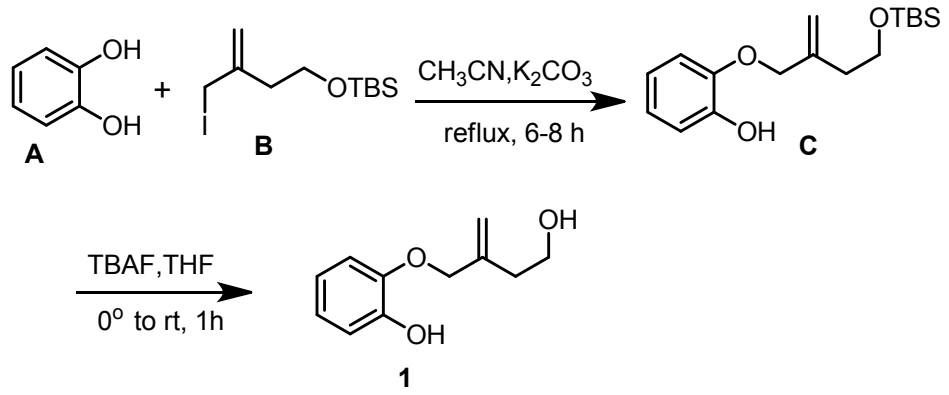
Experimental section:

General. All solvents were dried according to standard literature procedures. Reactions were performed in oven-dried round bottom flasks, and the flasks were fitted with rubber septa and the reactions were conducted under a nitrogen atmosphere. Glass syringes were used to transfer solvents. Crude products were purified by column chromatography on silica gel of 60–120 or 100-200 mesh. Thin layer chromatography plates were visualized by exposure to ultraviolet light and/or by exposure to iodine vapours and/or by exposure to methanolic acidic solution of *p*-anisaldehyde followed by heating (<1 min) on a hot plate (~250°C). Organic solutions were concentrated on rotary evaporator at 35–40 °C. IR spectra were recorded on FT-IR spectrometer. ^{1}H and ^{13}C NMR (proton-decoupled) spectra were recorded in $CDCl_3$ solvent on 200, 300, 400 or 500 MHz NMR spectrometer. Chemical shifts (δ) were reported in parts per million (ppm) with respect to TMS as an internal standard. Coupling constants (*J*) are quoted in hertz (Hz). Mass spectra were recorded on mass spectrometer by Electrospray ionization (ESI) or Atmospheric pressure chemical ionization (APCI) technique.

Preparation of the starting material for Table 1:



To a stirred mixture of **A** (3.0 g, 9.2 mmol), **B** (1.01 g , 9.2 mmol) in 30 mL of dry acetonitrile was added potassium carbonate (2.50 g, 18.4 mmol). The resulting mixture was stirred under reflux for 8 h. After completion of the reaction, as indicated by TLC, the mixture was filtered and the filtrate was evoporated on rotary evaporator. The resulting crude product was purified by column chromatography (silica gel, 60-120 mesh) using ethyl acetate/*n*-hexane gradient mixture to afford the pure product **C** in 75% yield as colorless liquid; Yield 2.12 g, 75%; ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.98-675 (m, 4H), 5.17 (s,1H), 5.06 (s, 1H), 5.81 (s, 1H), 4.57 (s, 2H), 3.79 (t, J = 6.6 Hz, 2H), 2.37 (t, J = 6.2Hz, 2H), 0.9 (s, 9H), 0.06 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): δ145.9, 145.7, 142.1, 121.6, 119.9, 114.6, 114.0, 112.4, 72.0, 62.3, 36.6, 25.8, 18.2, -5.3; IR (KBr): ν 3446, 2950, 2904, 2840, 1735, 1656,1516, 1282, 1037, 793, 745, 548; MS-ESI: *m/z* 309.1 $[M+H]^+$.

To a solution of **C** (2.0 g, 6.4 mmol) in THF at 0 ^{o}C was added TBAF (9.7 mmol) drop wise and the resulting mixture was allowed to stir at rt for 1 h. After completion of the reaction, as indicated by TLC, the reaction mixture was quenched with a sat. solution of $NaHCO_3$ and the aqueous layer was extracted with ethyl acetate. Removal of the solvent followed by purification on silica gel column chromatography (silica gel, 60-120 mesh) using ethyl acetate/*n*-hexane gradient mixture afforded the pure product **1** in 95% yield as a white solid; Yield 1.18 g, 95%; m.p. 90-92˚C; ^{1}H NMR (300 MHz, $CDCl_3$): ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.91-6.70 (m, 4H), 6.23 (b s, 1H), 5.23 (s, 1H), 5.12 (s, 1H), 4.53 (s, 2H), 3.82 (t, J = 6.0Hz, 2H), 2.44 (t, J = 6.0Hz, 2H), 1.91 (b s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 146.1, 145.7, 141.6, 121.9, 119.9, 115.7, 115.0, 112.7, 72.3, 61.2, 36.3; IR (neat): ν 3480, 3115, 2925, 1743, 1595, 1394, 1245, 1109, 1006, 901, 741,557; MS-ESI: *m/z* 195.1 $[M+H]^+$; HRMS (ESI) calcd for $C_{11}H_{15}O_3$ $[M+H]^+$: 195.1015 Found: 195.1020.

General experimental procedure for the Prins Cyclisation Table 1:

To a mixture of 2-(4-hydroxy-2-methylenebutoxy)phenol (0.5 mmol) and benzaldehyde (0.6 mmol) in anhydrous 1,2-DCE (5 mL) was added $InCl_3$ (10 mol%) at 0 °C. The resulting mixture was allowed to stir at room temperature under nitrogen atmosphere for the specified time (Table 1). After completion of the reaction, the reaction mixture was quenched with $NaHCO_3$ solution and then extracted with dichloromethane (2x5 mL). The organic phase was dried over anhydrous Na_2SO_4 and concentrated on rotary evaporator. The resulting crude product was purified by silica gel column chromatography (100-200 mesh) using ethyl acetate/hexane gradient mixture to afford the pure product **3a** (Table 1, entry a).

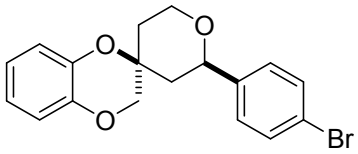


Table 1, **3a**

3a: 2'-(4-Bromophenyl)-2',3',5',6'-tetrahydro-3*H*-spiro[benzo[b][1,4]dioxine-2,4'-pyran]:

Solid; Yield 81%; m.p. 160-162˚C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.46 (d, *J* = 7.9 Hz, 2H), 7.23 (d, *J* = 7.9Hz, 2H), 6.91-6.80 (m, 4H), 4.41 (dd, *J* = 11.9, 2.0 Hz, 1H), 4.31 (d, *J* = 10.9 Hz, 1H), 4.24-4.16 (m, 2H), 3.68 (td, *J* = 12.9, 2.9Hz, 1H), 2.17-2.12 (m, 1H), 2.05-1.97 (m, 1H), 1.84-1.76 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 142.2, 142.0, 140.3, 131.5, 127.5, 122.0, 121.6, 121.2, 117.6, 116.8, 76.0, 72.1, 67.1, 64.8, 39.8, 32.6; IR (KBr): ν 3446, 2923, 2853, 1591, 1491, 1247, 1088, 927, 758; MS-ESI: *m/z* 383.3 $[M+Na]^+$; HRMS (ESI) calcd for $C_{18}H_{18}BrO_3$ $[M+H]^+$: 361.0432 Found: 361.0427.

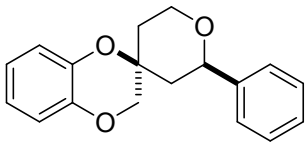


Table 1, **3b**

3b: 2'-Phenyl-2',3',5',6'-tetrahydro-3*H*-spiro[benzo[b][1,4]dioxine-2,4'-pyran]:

Viscous liquid; Yield 75%; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.43-7.25 (m, 5H), 6.93-6.81 (m, 4H), 4.46 (d, *J* = 11.0 Hz, 1H), 4.34 (d, *J* = 11.0 Hz, 1H), 4.28-4.19 (m, 2H), 3.71 (td, *J* = 12.2, 2.2 Hz, 1H), 2.21-2.15 (m, 1H), 2.09-1.99 (m, 1H), 1.98-1.85 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 142.3, 142.1, 141.2, 128.4, 127.8, 125.8, 121.9, 121.3, 117.6, 116.7, 76.8, 72.3, 67.2, 64.8, 39.9, 32.6; IR (KBr): ν 3442, 2924, 2854, 1743, 1594, 1492, 1263, 1091, 1042, 802, 755; MS-ESI: *m/z* 305.3 $[M+Na]^+$; HRMS (ESI) calcd for $C_{18}H_{19}O_3$ $[M+H]^+$: 283.1072 Found: 283.1077.

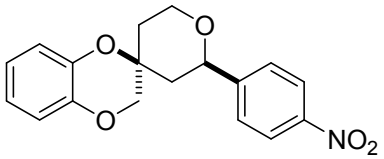


Table 1, **3c**

3c: 2'-(4-Nitrophenyl)-2',3',5',6'-tetrahydro-3H-spiro[benzo[b][1,4]dioxine-2,4'-pyran]:

Solid; Yield 70%; m.p. 120-122˚C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.20 (d, *J* = 8.5 Hz, 2H), 7.47 (d, *J* = 8.6 Hz, 2H), 7.02-6.96 (m, 3H), 6.91-6.86 (m, 1H), 4.58 (dd, *J* = 11.7, 2.1 Hz, 1H), 4.53 (d, *J* = 10.6 Hz, 1H), 4.43 (d, *J* = 10.6 Hz, 1H), 4.17 (ddd, *J* = 12.5, 4.8, 1.9 Hz, 1H), 3.77 (td, *J* = 12.0, 3.3 Hz, 1H), 2.60 (dt, *J* = 13.8, 4.1Hz, 1H), 2.45-2.34 (m, 2H), 2.19-2.12 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 148.0, 147.4, 146.4, 145.4, 126.3, 123.7, 123.3, 120.3, 115.6, 114.0, 75.6, 72.8, 67.4, 65.0, 44.8, 37.3; IR (KBr): ν 3445, 2956, 2856, 1596, 1491, 1355, 1249,

1166, 1091, 946, 752, 664, 575, 541; MS-ESI: *m/z* 327.1 $[M+H]^+$; HRMS (ESI) calcd for $C_{18}H_{18}O_5N$ $[M+H]^+$: 328.1174 Found: 328.1162.

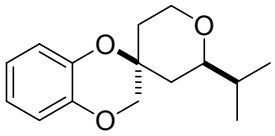


Table 1, **3d**

3d: 2'-Isopropyl-2',3',5',6'-tetrahydro-3*H*-spiro[benzo[b][1,4]dioxine-2,4'-pyran]:

Liquid; Yield 72%; ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.92-6.80 (m, 4H), 4.22-4.09 (m, 2H), 4.08-3.99 (m, 1H), 3.54-3.43 (m, 1H) 3.11 (ddd, *J* = 12.0, 6.0, 2.2 Hz,1H), 1.94-1.81(m, 2H), 1.79-1.67 (m, 1H), 1.63-1.52 (m, 2H), 0.93 (dd, *J* = 12.0, 6.7 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 142.4, 142.3, 121.9, 120.9, 117.6, 116.7, 79.4, 72.5, 67.4, 64.3, 35.1, 32.9, 32.7, 18.3, 18.2; IR (KBr): ν 3446, 2958, 2924, 2852, 1594, 1493, 1465, 1262, 1107, 1044, 747, 619; MS-ESI: *m/z* 249.1 $[M+H]^+$; HRMS (Orbitrap ESI) calcd for $C_{15}H_{21}O_3$ $[M+H]^+$: 249.1495 Found: 249.1437.

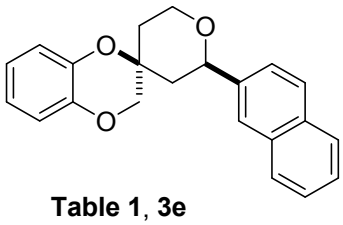


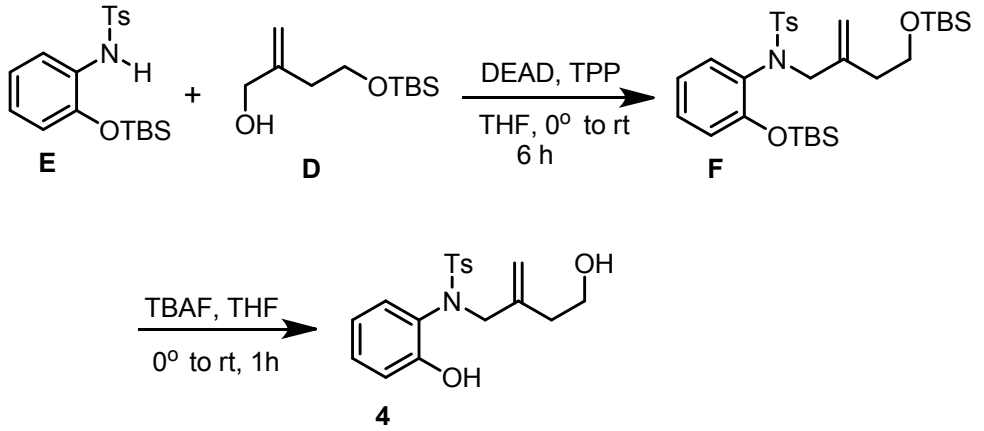
Table 1, **3e**

3e: 2'-(Naphthalen-2-yl)-2',3',5',6'-tetrahydro-3*H*-spiro[benzo[*b*][1,4]dioxine-2,4'-pyran]:

Solid; Yield 70%; m.p. 159-161˚C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.84-7.78 (m, 4H), 7.50-7.43 (m, 3H), 6.93-6.81 (m, 4H), 4.62 (dd, *J* = 12.1, 1.73 Hz, 1H), 4.37 (d, *J* = 12.1 Hz, 1H), 4.31-4.22 (m, 2H) 3.76 (td, *J* = 12.9, 2.5 Hz, 1H), 2.29-2.23 (m, 1H), 2.12-2.02 (m, 1H), 2.01-1.93 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 142.6, 141.7, 139.4, 133.2, 132.9, 128.1, 127.9,

127.6, 126.0, 125.7, 124.4, 124.0, 121.9, 121.3, 117.7, 117.0, 74.2, 71.8, 71.4, 63.3, 39.2, 31.1; IR (KBr): ν 3443, 3051, 2962, 2853, 1592, 1504, 1338, 1164, 1092, 975, 890, 766, 652, 542; MS-ESI: *m/z* 333.1 $[M+H]^+$; HRMS (ESI) calcd for $C_{22}H_{21}O_3$ $[M+H]^+$: 333.1480 Found: 333.1462.

Preparation of the starting material for Table 3:



To a solution of **D** (2.5 g,11.5 mmol), **E** (8.2 g.13.8 mmol) and triphenylphosphine (3.6 g, 13.8 mmol) in dry THF at 0 °C was added diethyl azodicarboxylate (2.4 g,13.8 mmol) dropwise over 10 min. The resulting mixture was stirred at rt for 6h. After completion of the reaction, as indicated by TLC, the solvent was evaporated on rotary evaporator and the resulting crude product was purified by column chromatography (silica gel, 60-120 mesh) using ethyl acetate/hexane gradient mixture to afford the pure product **F** in 64% yield as a colourless liquid. Yield 4.21 g, 64%; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.56 (d, *J* = 8.2Hz, 2H), 7.22 (d, *J* = 7.9 Hz, 2H), 7.17-7.12 (m, 1H), 6.99-6.96 (m, 1H), 6.84-6.80 (m, 2H), 4.84 (s, 1H), 4.77 (s, 1H), 4.17 (s, 2H), 3.68 (t, *J* = 6.4 Hz, 2H), 2.40 (s, 3H), 2.26 (t, *J* = 6.1 Hz, 2H), 0.95 (s, 9H), 0.86 (s, 9H), 0.22 (s, 6H), 0.02 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 153.5, 142.7, 141.7, 137.4, 131.4, 129.2, 129.0, 128.9, 127.6, 120.4, 119.1, 115.1, 61.5, 54.9, 36.4, 25.9, 25.8, 21.4, 18.3, 18.2, -

5.3,-4.2;. IR (KBr): ν 3447, 3070, 2931, 2858, 1492, 1339, 1159, 1108, 818, 704, 581, 505; MS-ESI: *m/z* 576.29 [M+H$^+$].

To a solution of **F** (4.0 g, 6.9 mmol) in dry THF at 0 ^{o}C was added TBAF (20.8 mmol) dropwise and the mixture was allowed to stir at rt for 1h. After completion of the reaction indicated by TLC, the reaction mixture was quenched with a sat.solution of $NaHCO_3$ and the aqueous layer was extracted with ethyl acetate. Removal of the solvent followed by purification on silica gel column chromatography (silica gel, 60-120 mesh) using ethyl acetate/hexane gradient mixture afforded the pure product **4** in 90% yield as pale yellow solid; Yield 2.17 g, 90%; m.p. 103-105˚C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.52 (d, *J* = 8.2 Hz, 2H), 7.28 (d, *J* = 7.9 Hz, 2H), 7.20-7.15 (m, 1H), 7.02 (dd, *J* = 8.0, 1.3Hz, 1H), 6.72-6.67 (m, 1H), 6.37 (dd, *J* = 8.0, 1.5, Hz, 1H), 4.89 (s, 1H), 4.79 (s, 1H), 3.91-3.81 (m, 2H), 2.47-2.37 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 155.1, 144.2, 140.1, 133.5, 129.7, 129.5, 128.0, 127.3, 125.9, 120.2, 117.9, 117.5, 60.8, 56.8, 36.6, 21.5; IR (neat): ν 3575, 3267, 2958, 2925, 1592, 1492, 1339, 1215, 1156, 1040, 891, 757, 699, 579; MS-ESI: *m/z* 348.07 [M+H]$^+$; HRMS (ESI) calcd for $C_{18}H_{22}NO_4S$ [M+H]$^+$: 348.1269 Found: 348.1249.

General procedure for the Prins cyclisation for Table 3:

To a mixture of *N*-(4-hydroxy-2-methylenebutyl)-*N*-(2-hydroxyphenyl)-4-methylbenzenesulfonamide (0.5 mmol) and benzaldehyde (0.6 mmol) in anhydrous 1,2-DCE (5 ml) was added at $InCl_3$ (10 mol%) at -20 ^{o}C. The resulting mixture was allowed to stir at the same temperature under nitrogen atmosphere for the specified time (Table 3). After completion, the reaction mixture was quenched with $NaHCO_3$ solution and then extracted with dichloromethane. The organic phase was dried over anhydrous Na_2SO_4 and concentrated on

rotary evaporator. The crude product was purified by silica gel column chromatography (100-200 mesh) using ethyl acetate/hexane gradient mixture to afford the pure product **5a** (Table 2, entry a).

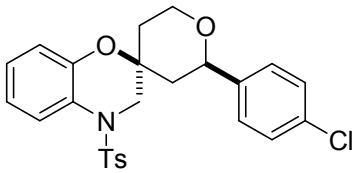


Table 3, **5a**

5a: 2'-(4-Chlorophenyl)-4-tosyl-2'3,3'4,5'6'-hexahydrospiro[benzo[*b*][1,4]oxazine-2,4'-pyran] (major diastereomer):

Solid; Yield 85%; m.p. 107-109˚C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.82 (d, *J* = 8.2 Hz, 2H), 7.40 (dd, *J* = 8.2, 1.3 Hz, 1H), 7.35-7.28 (m, 6H), 6.96-6.92 (m, 1H), 6.85-6.78 (m, 2H), 4.61 (dd, *J* = 11.8, 1.9 Hz, 1H), 4.32 (d, *J* = 12.9 Hz, 1H), 4.20 (ddd, *J* = 12.3, 5.3, 1.3 Hz, 1H), 3.87-3.74 (m, 2H), 2.43 (s, 3H), 2.17 (dt, *J* = 13.5, 4.42 Hz, 1H), 2.11-2.03 (m, 1H), 1.90-1.77 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 144.1, 144.0, 139.9, 137.5, 133.3, 130.0, 128.5, 127.2, 126.6, 124.6, 124.1, 120.6, 119.0, 118.1, 75.7, 73.5, 64.6, 48.6, 41.0, 33.9, 21.5; IR (KBr): ν 3453, 2925, 2855, 1593, 1491, 1350, 1253, 1164, 1090, 947, 751, 661, 573, 543; MS-ESI: *m/z* 470.06 $[M+H]^+$; HRMS (ESI) calcd for $C_{25}H_{25}O_4NClS$ $[M+H]^+$: 470.0987 Found: 470.0999.

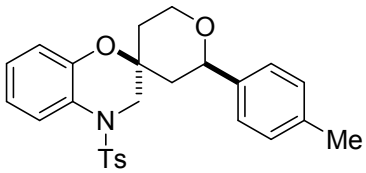


Table 3, **5b**

5b: 2'-(*p*-Tolyl)-4-tosyl-2'3,3'4,5'6'-hexahydrospiro[benzo[*b*][1,4]oxazine-2,4'-pyran] (major diastereomer):

Solid; Yield 82%; m.p. 146-148˚C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.81 (d, *J* = 8.3 Hz, 2H), 7.46 (dd, *J* = 8.3, 1.5 Hz, 1H), 7.32-7.25 (m, 4H), 7.15 (d, *J* = 7.7 Hz, 2H), 6.95-6.91 (m, 1H), 6.85-6.78 (m, 2H), 4,56 (dd, *J* = 12.0, 1.9 Hz, 1H) 4.21-4.15 (m, 2H), 3.96 (d, *J* = 12.8 Hz, 1H), 3.80 (td, *J* = 12.8, 2.2 Hz, 1H), 2.41 (s, 3H), 2.33 (s, 3H), 2.11 (dt, *J* = 13.7, 4.4 Hz, 1H), 2.07-2.00 (m, 1H), 1.93-1.84 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 144.1, 138.2, 137.4, 137.3, 129.9, 129.0, 126.7, 125.8, 124.5, 124.2, 120.6, 118.9, 118.1, 76.4, 73.6, 64.7, 48.7, 41.1, 33.8, 21.5, 21.1; IR (KBr): ν 3456, 2924, 2855, 1589, 1492, 1350, 1253, 1164, 1094, 812, 751, 662, 572, 540; MS-ESI: *m/z* 450.07 $[M+H]^+$; HRMS (ESI) calcd for $C_{26}H_{28}O_4NS$ $[M+H]^+$: 450.1734 Found: 450.1740.

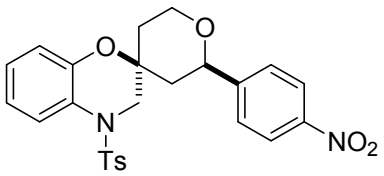


Table 3, **5c**

5c: 2'-(4-Nitrophenyl)-4-tosyl-2'3,3'4,5'6'-hexahydrospiro[benzo[*b*][1,4]oxazine-2,4'-pyran] (major diastereomer):

Solid; Yield 78%; m.p. 185-187˚C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.19 (d, *J* = 8.6 Hz, 2H), 7.85 (d, *J* = 8.3 Hz, 2H), 7.58 (d, *J* = 8.6 Hz, 2H), 7.37 (d, *J* = 8.0 Hz, 2H), 7.32 (dd, *J* = 11.8, 1.3Hz, 1H), 6.97-6.93 (m, 1H), 6.84-6.78 (m, 2H), 4.79 (dd, *J* = 11.8, 1.8 Hz, 1H), 4.52 (d, *J* = 13.1 Hz, 1H), 4.26 (ddd, *J* = 12.3, 5.3 ,1.3 Hz.1H), 3.83 (td, *J* = 12.8, 2.2 Hz, 1H), 3.69 (dd, *J* = 13.1, 0.7 Hz, 1H), 2.45 (s, 3H), 2.31 (dt, *J* = 13.5, 4.2 Hz 1H), 2.18-2.10 (m, 1H), 1.91-1.86 (m,

1H), 1.77-1.70 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 148.8, 147.2, 144.3, 144.0, 137.7, 130.1, 126.6, 126.4, 124.7, 124.0, 123.6, 120.7, 119.2, 118.1, 75.3, 73.3, 64.6, 48.5, 40.8, 39.1, 21.5; IR (KBr): ν 3448, 2997, 2859, 1521, 1493, 1346, 1160, 1091, 809, 658, 578, 543; MS-ESI: *m/z* 481.21 $[M+H]^+$; HRMS (ESI) calcd for $C_{25}H_{24}N_2O_6NaS$ $[M+Na]^+$: 503.1252 Found: 503.1270.

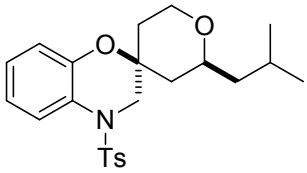


Table 3, **5d**

5d: **2'-Isobutyl-4-tosyl-2'3,3'4,5'6'-hexahydrospiro[benzo[*b*][1,4]oxazine-2,4'-pyran] (major diastereomer):**

Solid; Yield 75%; m.p. 121-123˚C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.79 (d, *J* = 8.3 Hz, 2H), 7.47 (dd, *J* = 8.3, 1.5 Hz, 1H), 7.32 (d, *J* = 7.9 Hz, 2H), 6.96-6.92 (m, 1H), 6.86-6.78 (m, 2H), 4.04-3.95 (m, 3H), 3.64-3.54 (m, 2H), 2.42 (s, 3H), 1.88-1.77 (m, 3H), 1.58-1.50 (m, 2H), 1.26-1.17 (m, 2H), 0.95-0.96 (d, *J* =6.5 Hz, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 144.1, 144.0, 137.3, 129.9, 126.7, 124.4, 124.2, 120.5, 118.8, 118.1, 73.4, 72.5, 64.1, 48.9, 45.2, 39.9, 33.9, 24.3, 23.2, 22.2, 21.5; IR (KBr): ν 3450, 2955, 2925, 2867, 1599, 1492, 1353, 1261, 1166, 1093, 947, 813, 750, 665, 574, 541; MS-ESI: *m/z* 416.1 $[M+H]^+$; HRMS (ESI) calcd for $C_{23}H_{30}O_4NS$ $[M+H]^+$: 416.1881 Found: 416.1890.

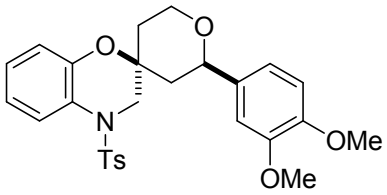
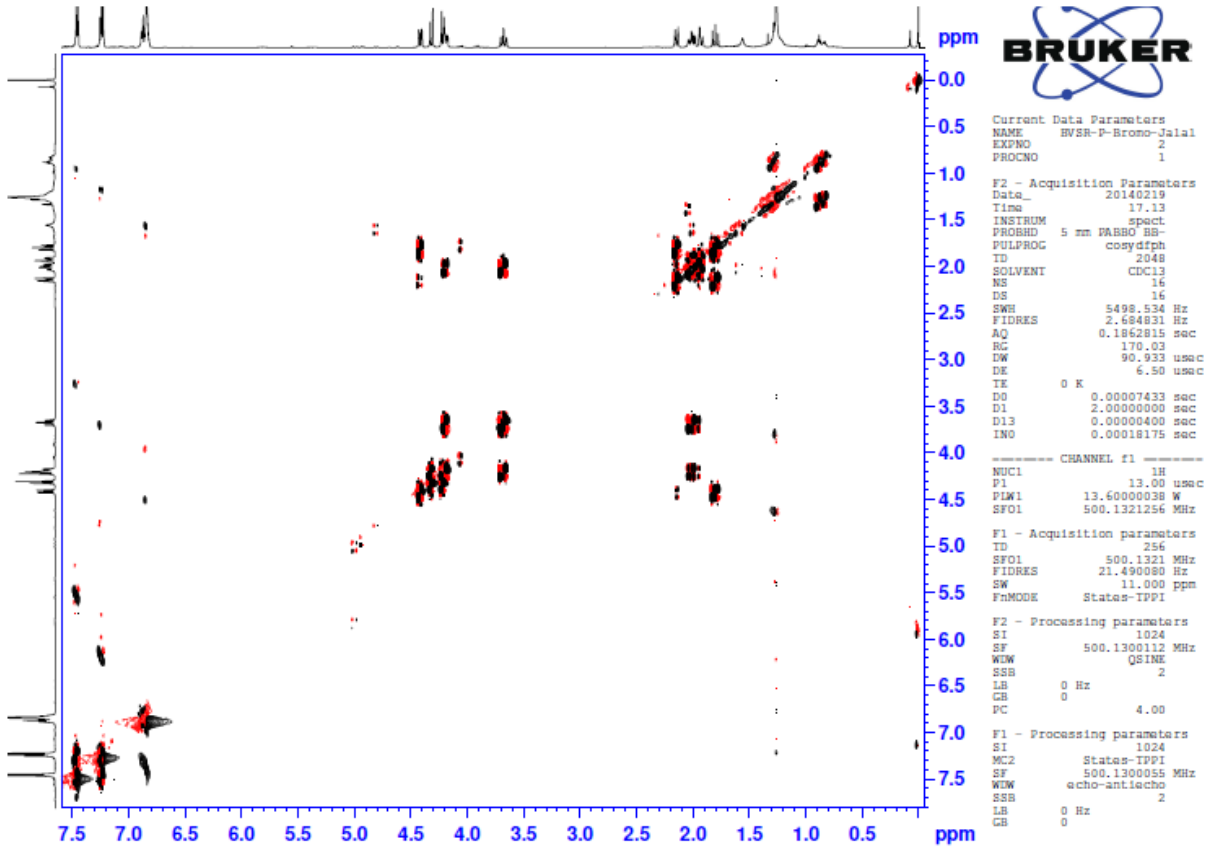


Table 3, **5e**

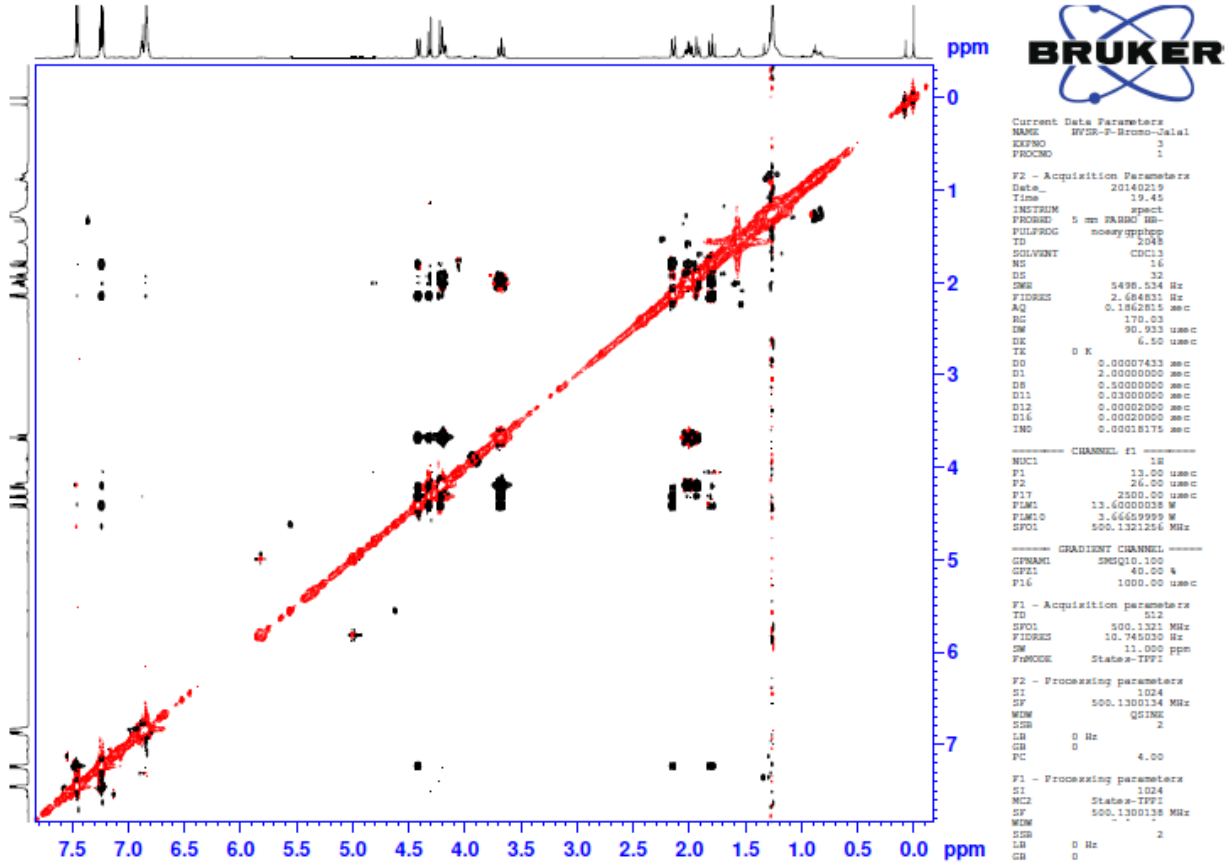
5e: **2'-(3,4-Dimethoxyphenyl)-4-tosyl-2'3,3'4,5'6'-hexahydrospiro[benzo[*b*][1,4]oxazine-2,4'-pyran] (major diastereomer):**

Semisolid; Yield 65%; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.81 (d, *J* = 8.2Hz, 2H), 7.42 (dd, *J* = 8.3, 1.3Hz, 1H), 7.32 (d, *J* = 8.2Hz, 2H), 6.99-6.90 (m, 3H), 6.87-6.78 (m, 3H), 4.57 (dd, *J* = 11.9, 1.8 Hz, 1H), 4.25 (d, *J* = 12.9 Hz, 1H), 4.22-4.17 (m, 1H), 4.04-3.99 (m, 1H), 3.90 (s, 3H), 3.87 (s, 3H), 3.85-3.80 (m, 1H), 2.42 (s, 3H), 2.17-2.12 (m, 1H), 2.10-2.0 (m, 1H), 1.91-1.79 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 148.9, 148.4, 144.1, 143.6, 136.9, 134.4, 129.8, 126.8, 124.5, 120.9, 124.4, 119.4, 118.2, 110.9, 109.2, 74.2, 72.3, 63.2, 55.9, 53.1, 55.8, 40.5, 32.4, 21.4; IR (KBr): ν 3450, 2925, 2859, 1594, 1491, 1350, 1256, 1164, 1088, 1032, 810, 753, 665, 572, 542; MS-ESI: *m/z* 496.1 $[M+H]^+$; HRMS (ESI) calcd for $C_{27}H_{29}NO_6NaS$ $[M+Na]^+$:518.1613 Found: 518.1632.

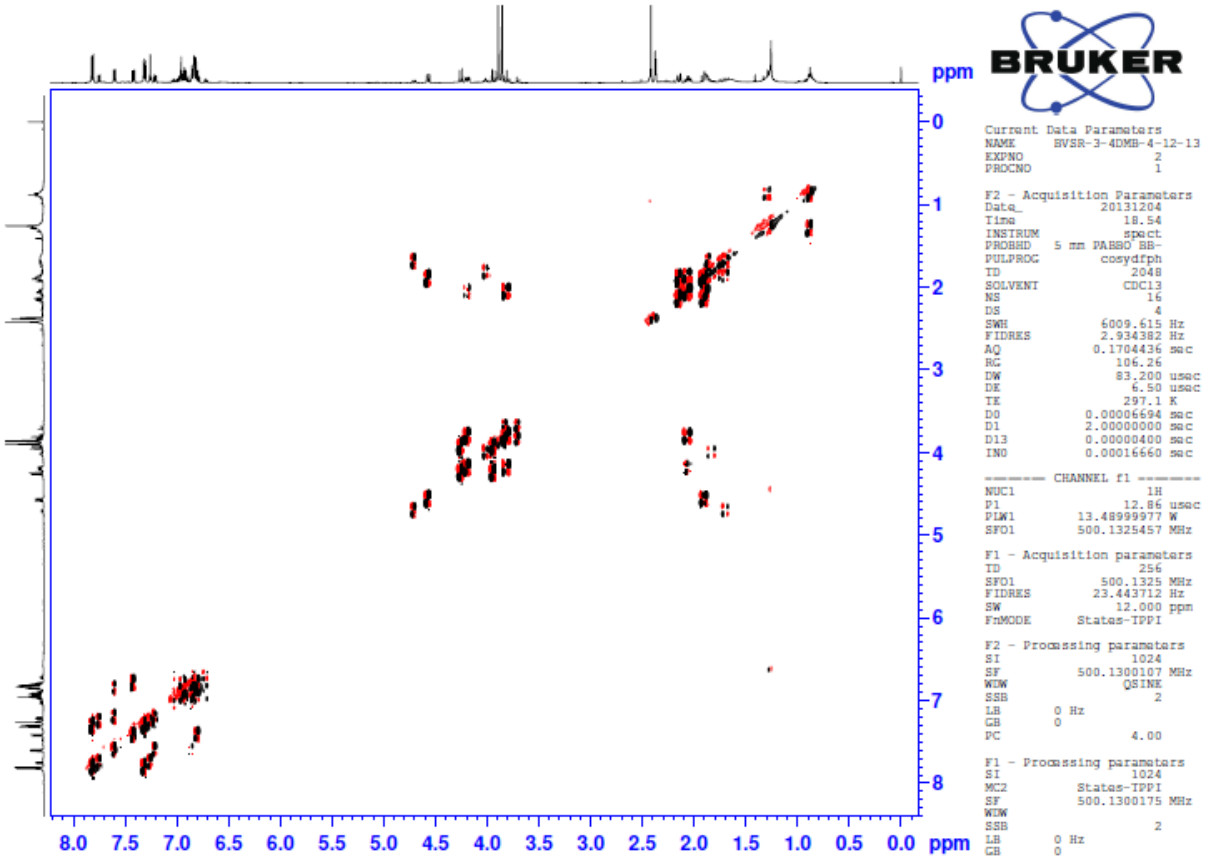
2D Double Quantum Coherence Spectrum (DQFCOSY) of compound 3a



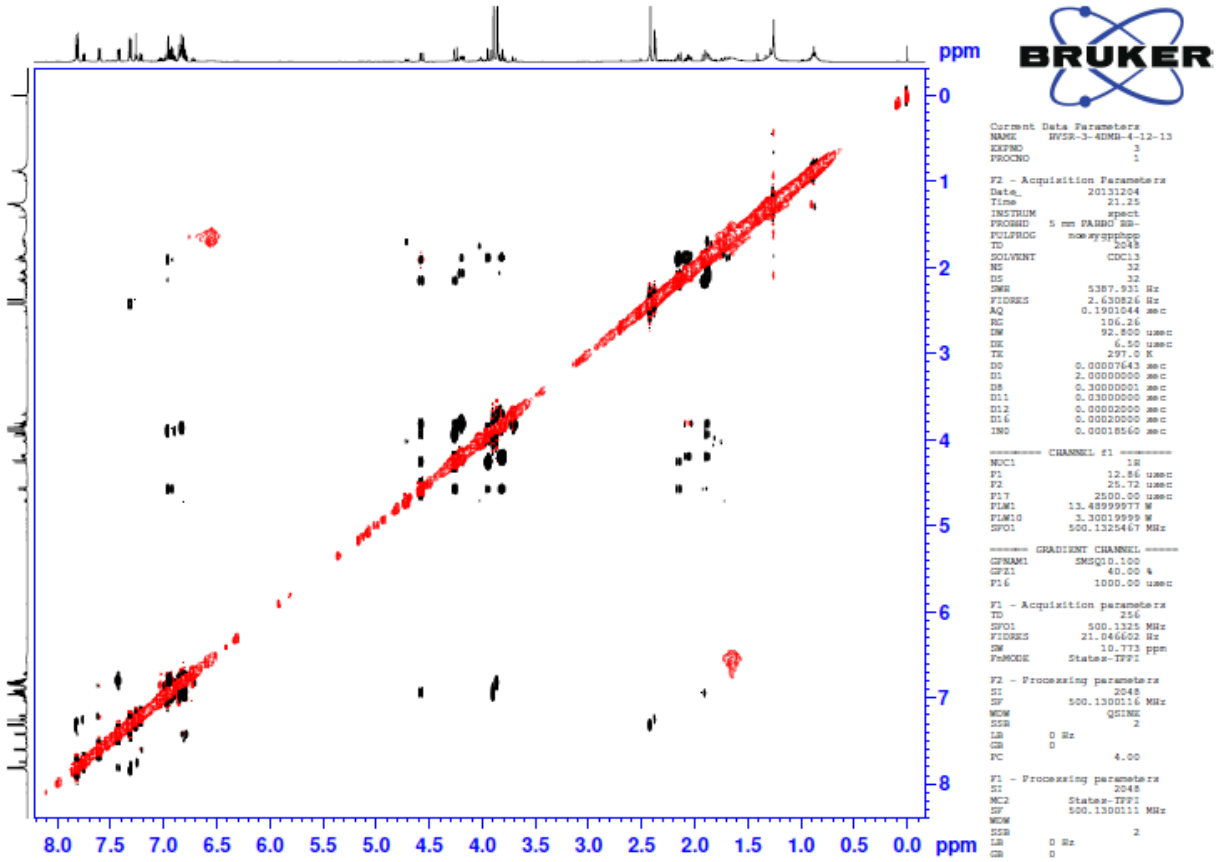
2D Nuclear Overhauser effect spectrum (NOESY) of compound 3a

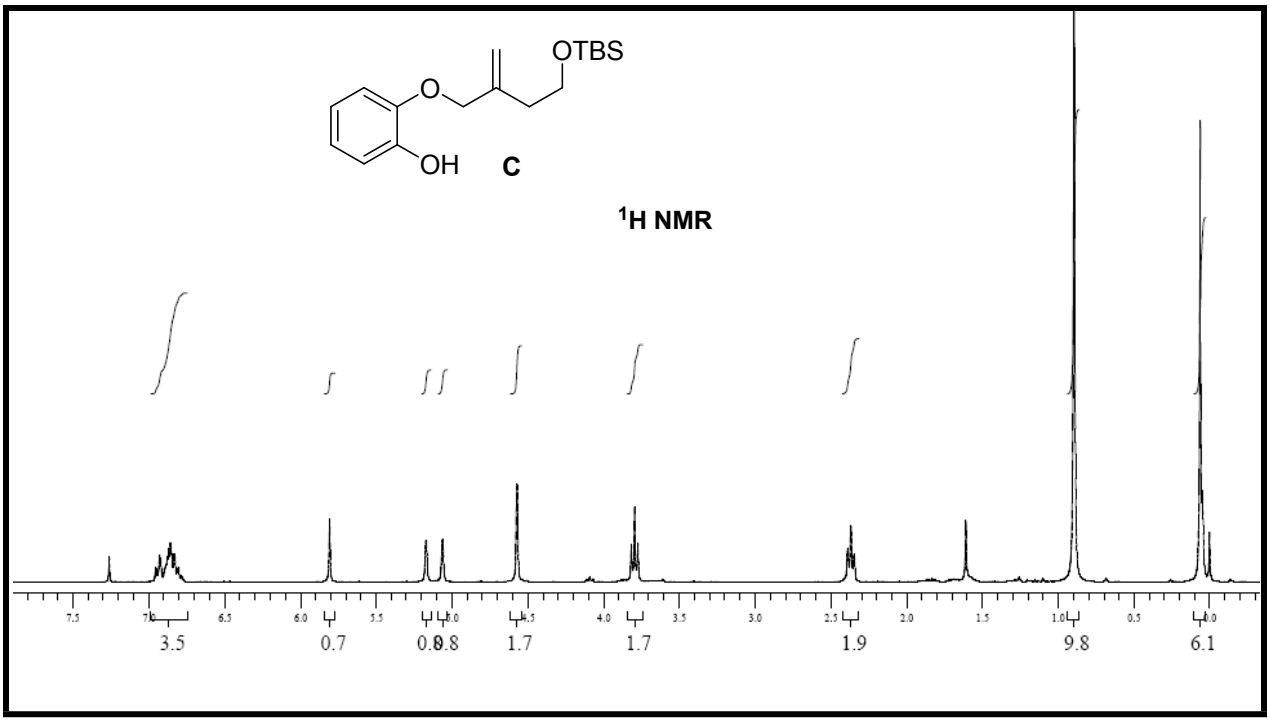


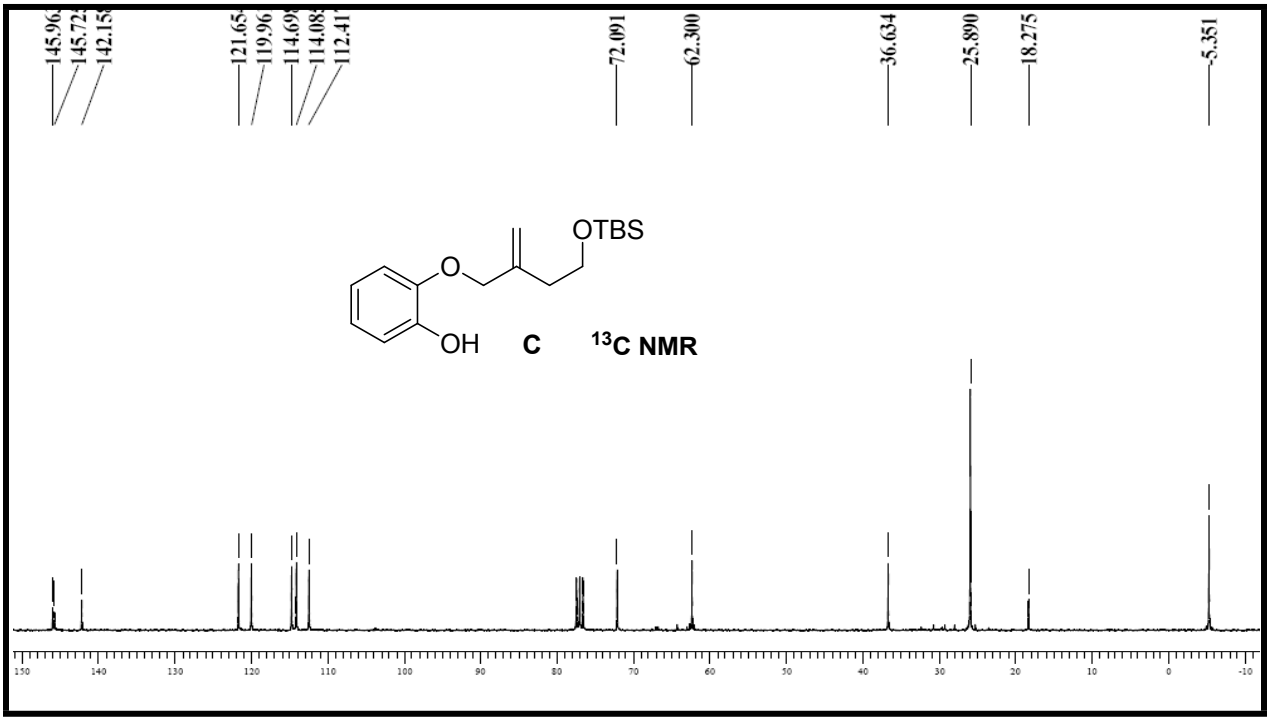
2D Double Quantum Coherence Spectrum (DQFCOSY) of compound 5e

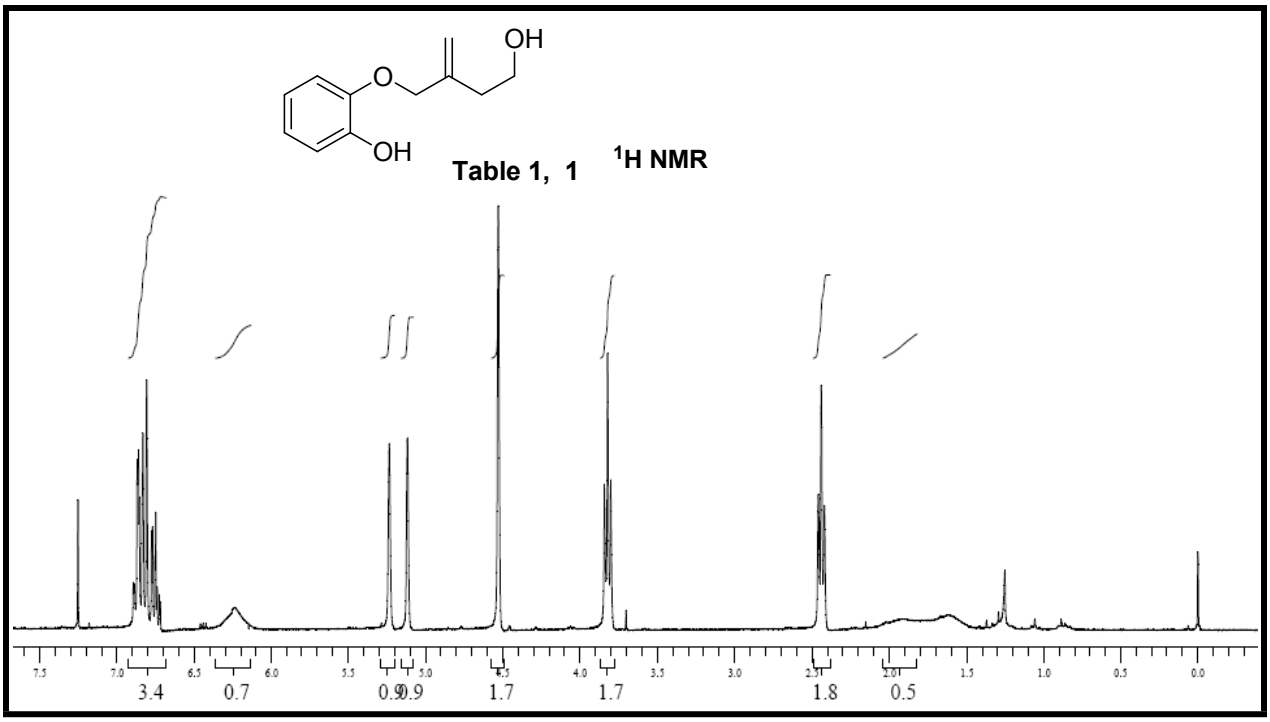


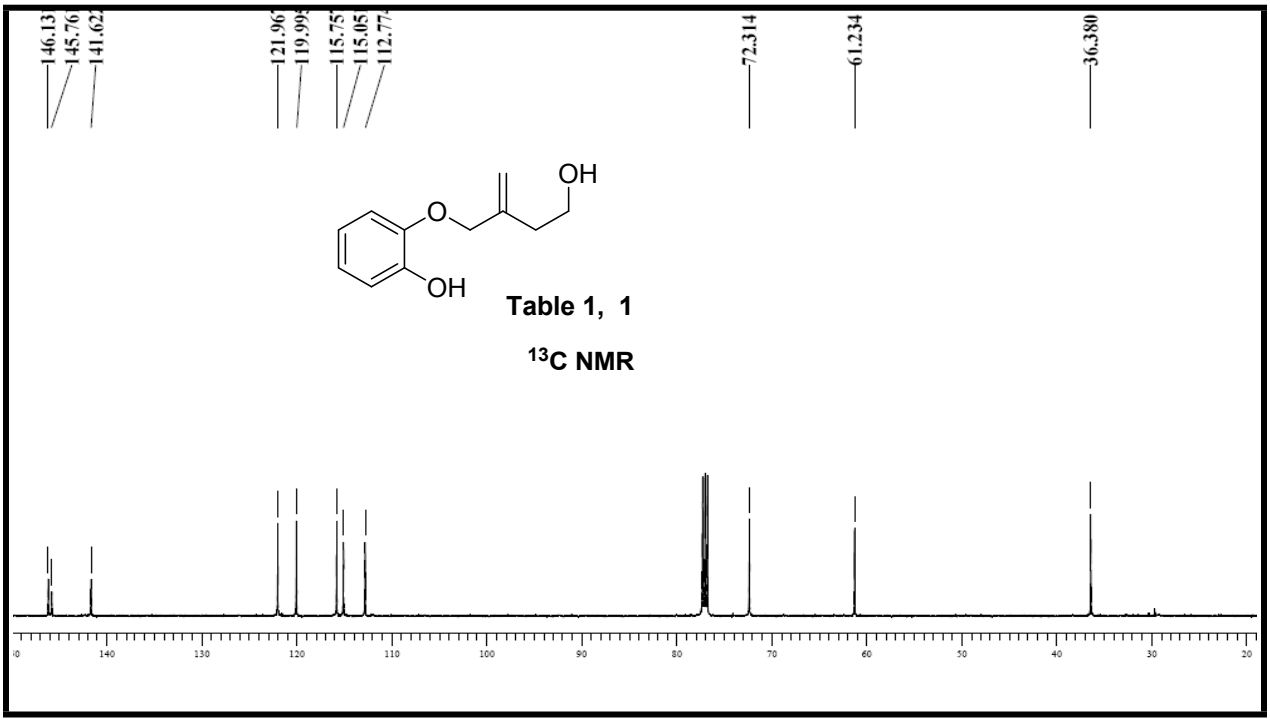
2D Nuclear Overhauser effect spectrum (NOESY) of compound 5e

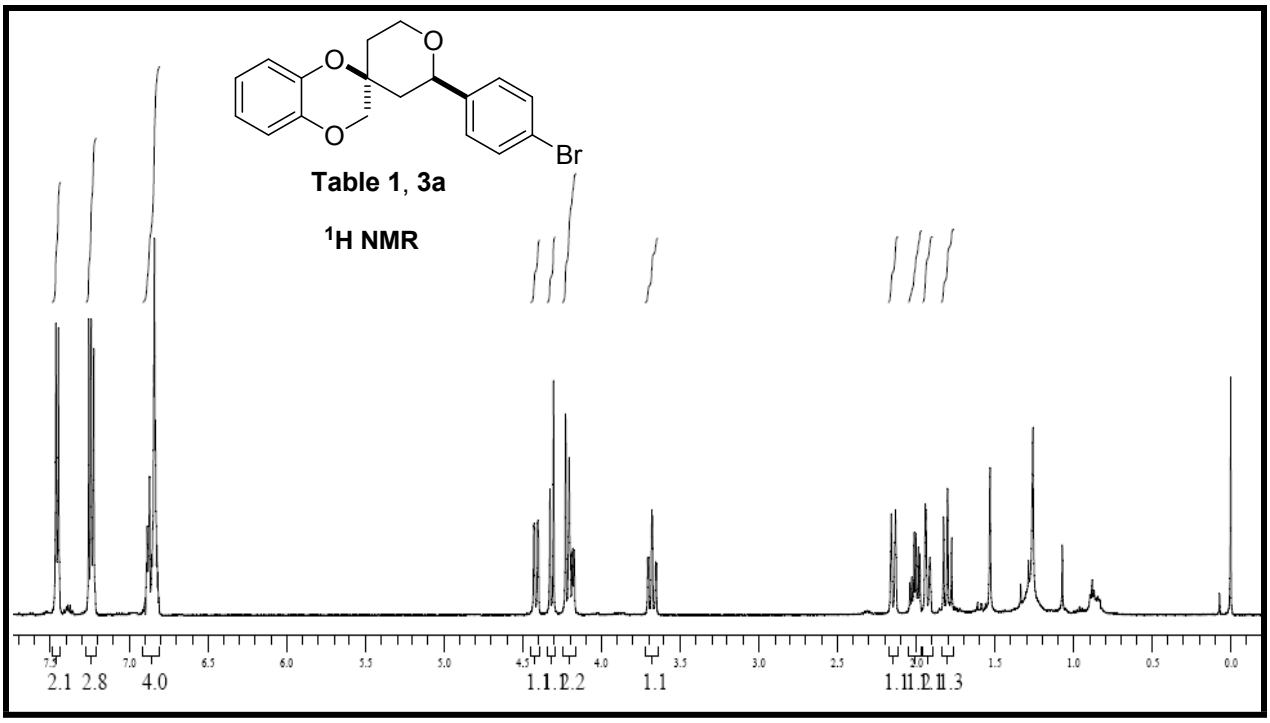


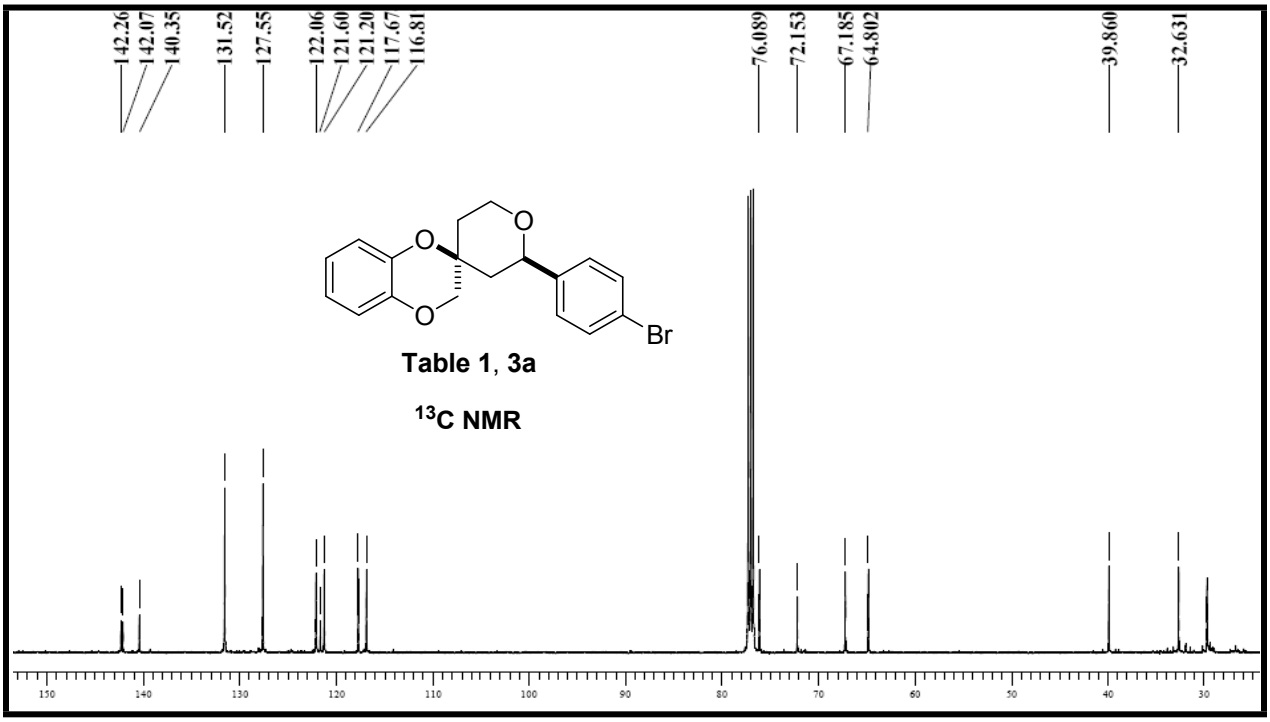

OTBS
O
OH
C
1H NMR
3.5
0.7
0.8
1.7
1.7
1.9
9.8
6.1


145.96
145.72
142.15
121.65
119.96
114.69
114.08
112.41
72.091
62.300
36.634
25.890
18.275
-5.351
OTBS
O
OH
C
13C NMR


OH
O
OH
Table 1, 1 ¹H NMR
3.4
0.7
0.9
0.9
1.7
1.7
1.8
0.5


146.13
145.76
141.62
121.96
119.99
115.75
115.05
112.77
72.314
61.234
36.380
OH
O
OH
Table 1, 1
¹³C NMR


Br
Table 1, 3a
1H NMR
2.1 2.8 4.0
1.1 1.2 2.2
1.1
1.1 1.2 1.1 3


142.26
142.07
140.35
131.52
127.55
122.06
121.60
121.20
117.67
116.81
76.089
72.153
67.185
64.802
39.860
32.631
Br
Table 1, 3a
13C NMR

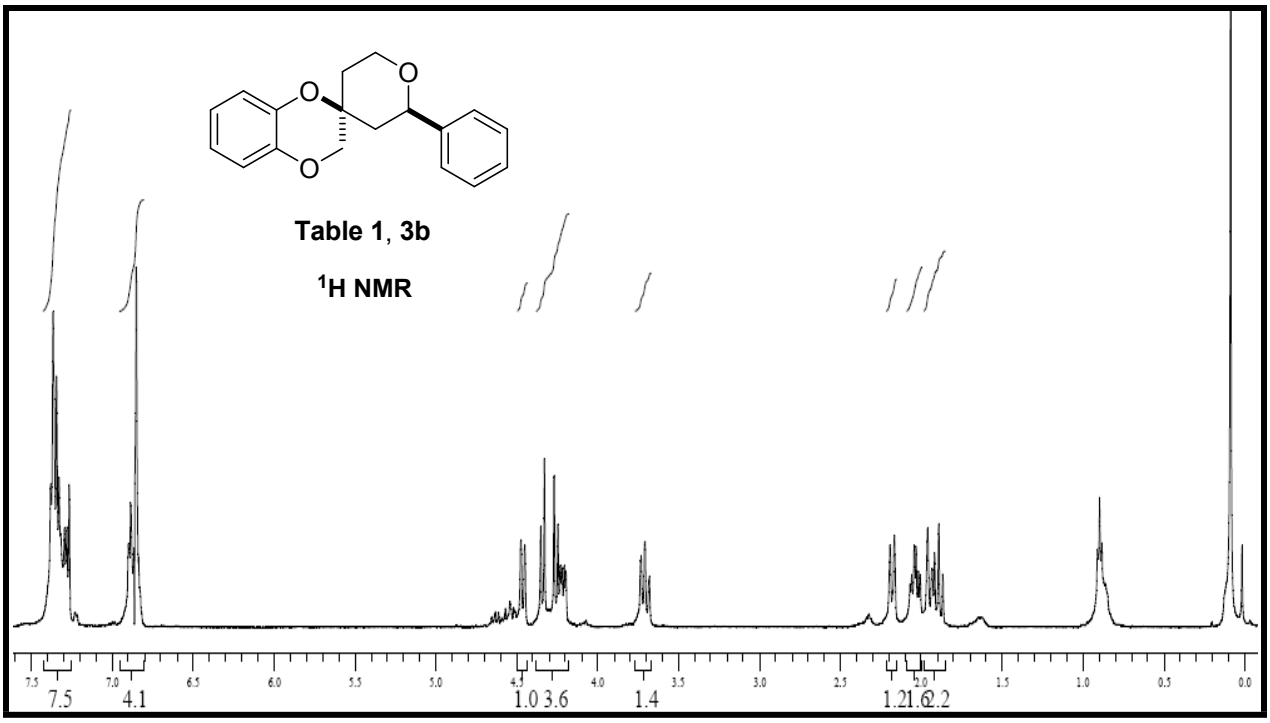
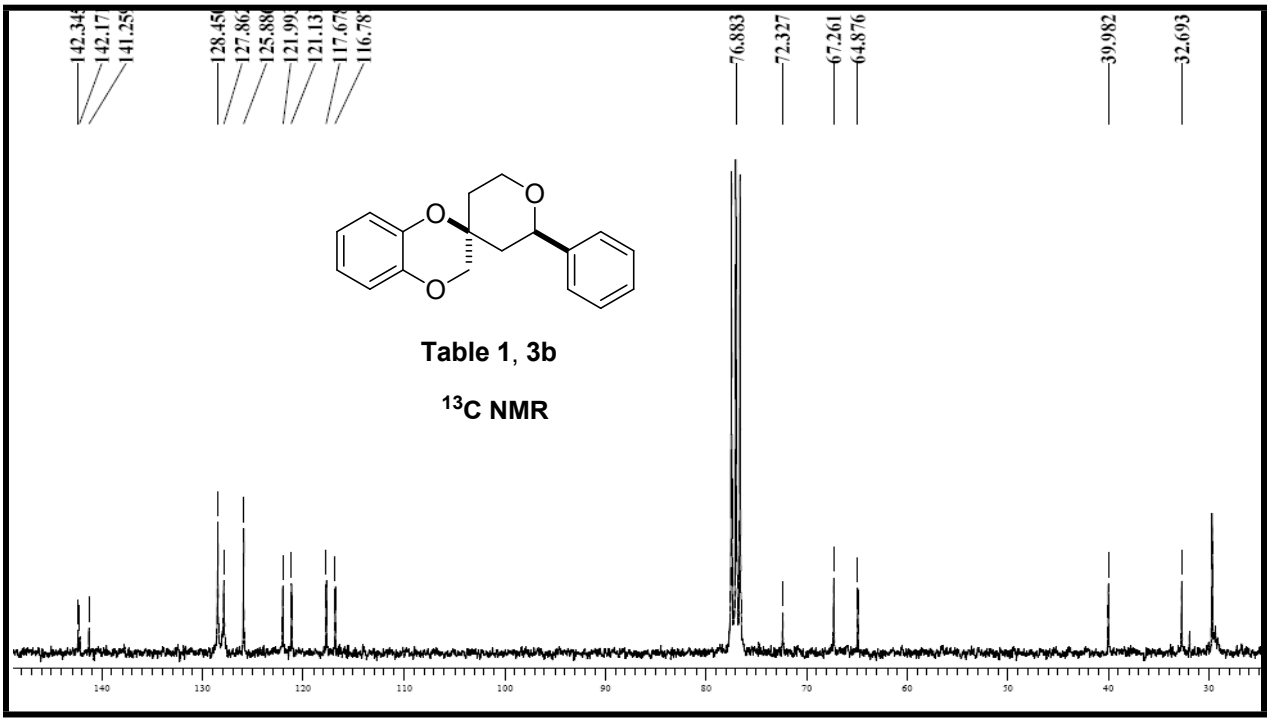


Table 1, 3b
1H NMR
7.5
4.1
1.0
3.6
1.4
1.2
1.6
2.2


142.34
142.17
141.25
128.45
127.86
125.88
121.99
121.13
117.67
116.78
76.883
72.327
67.261
64.876
39.982
32.693
Table 1, 3b
13C NMR

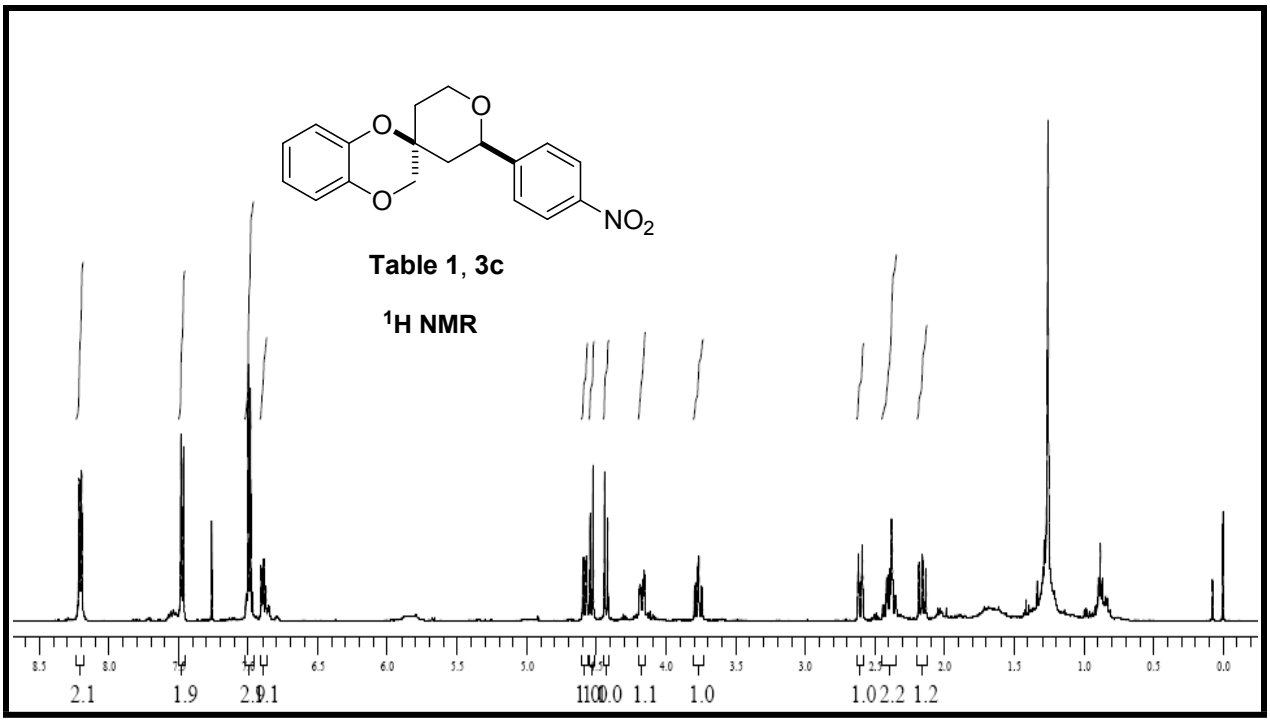


Table 1, **3c**

^{1}H NMR

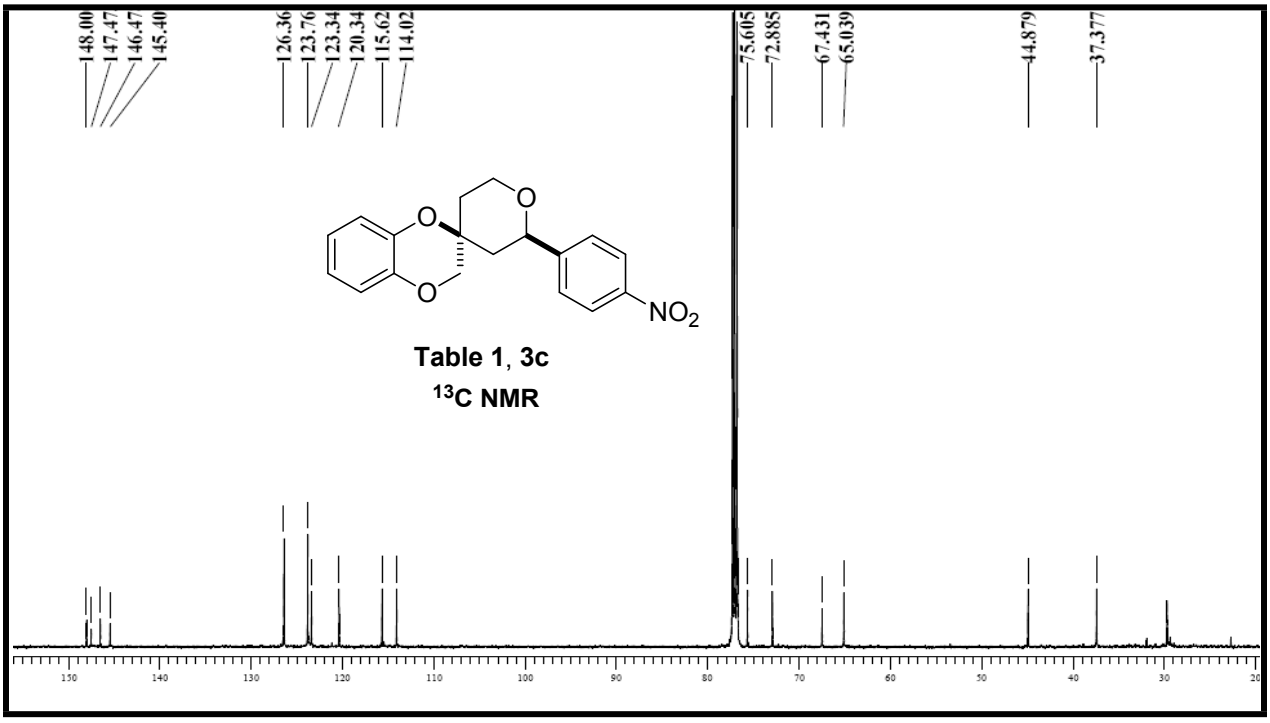


Table 1, **3c**

^{13}C NMR

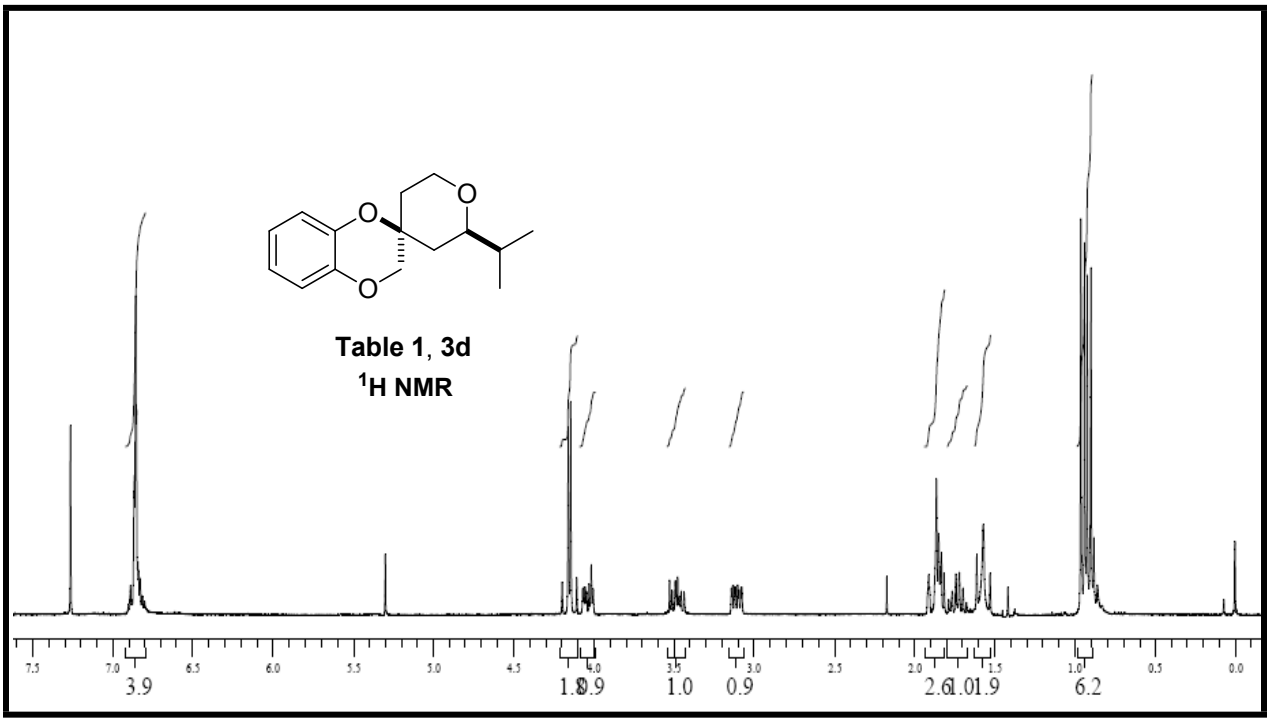
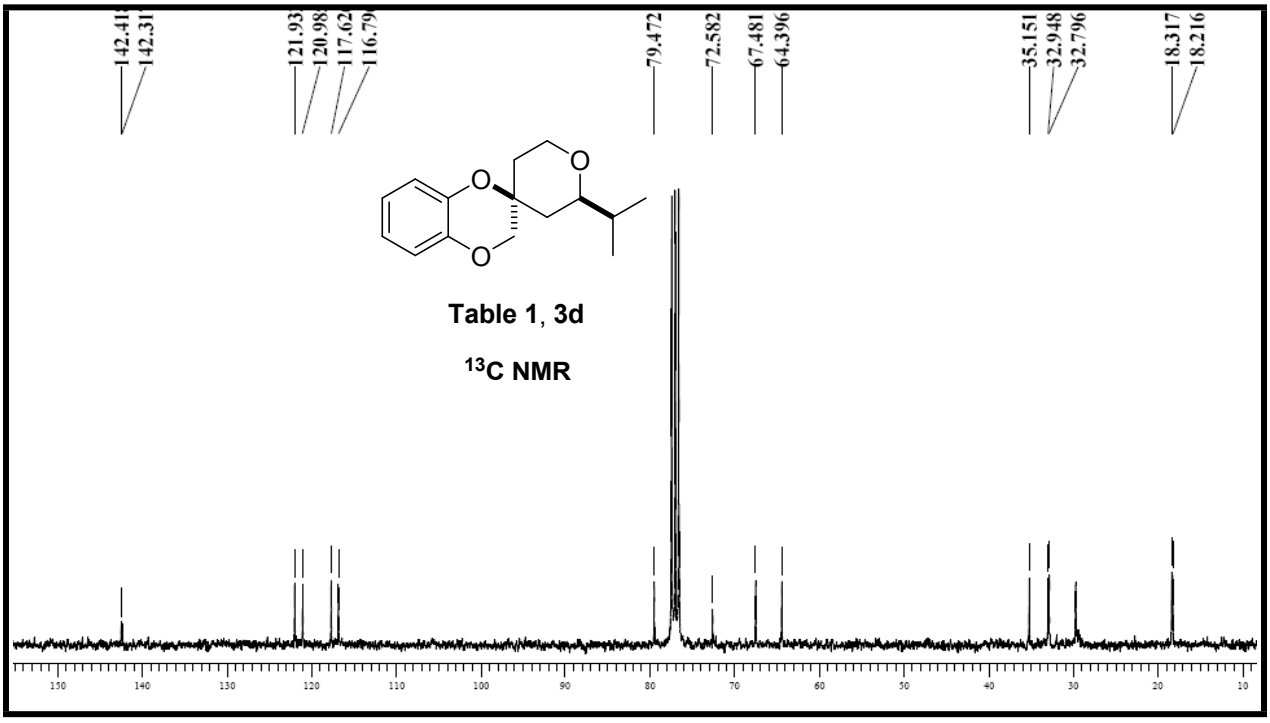


Table 1, 3d
1H NMR
3.9
1.0
0.9
6.2


142.31
121.93
120.98
117.62
79.472
72.582
67.481
64.396
35.151
32.948
32.796
18.317
18.216
Table 1, 3d
13C NMR

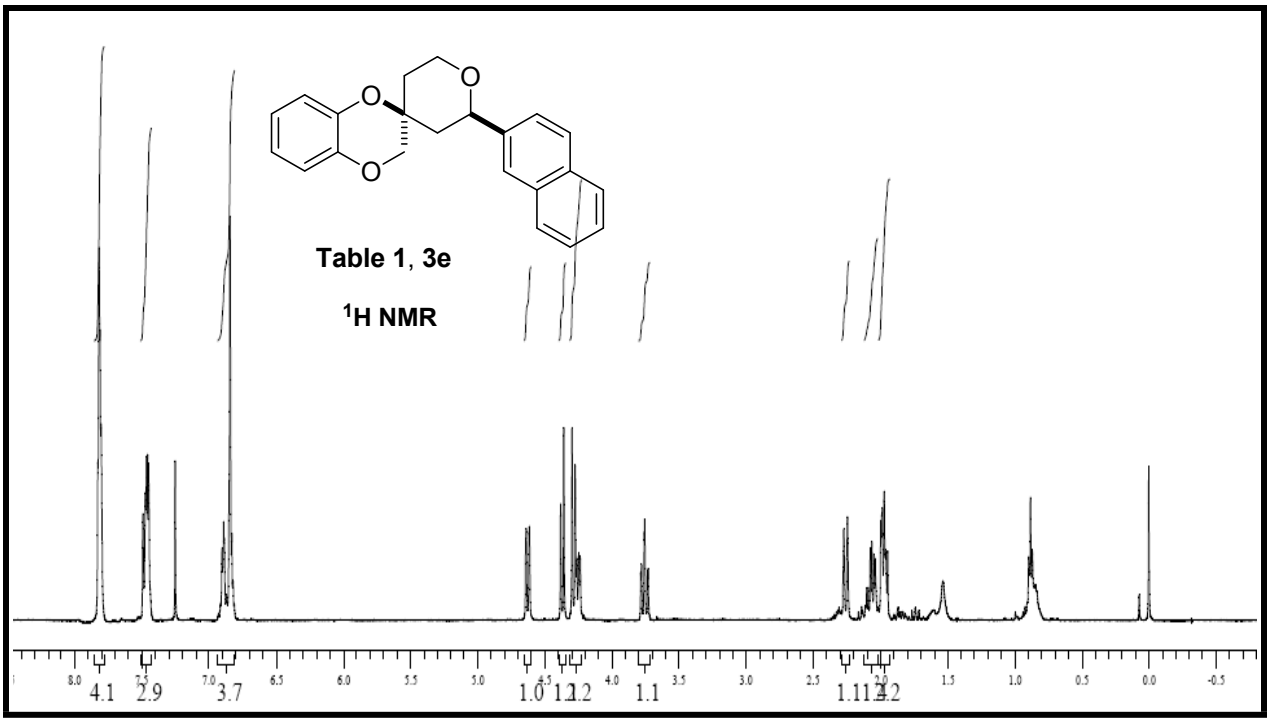
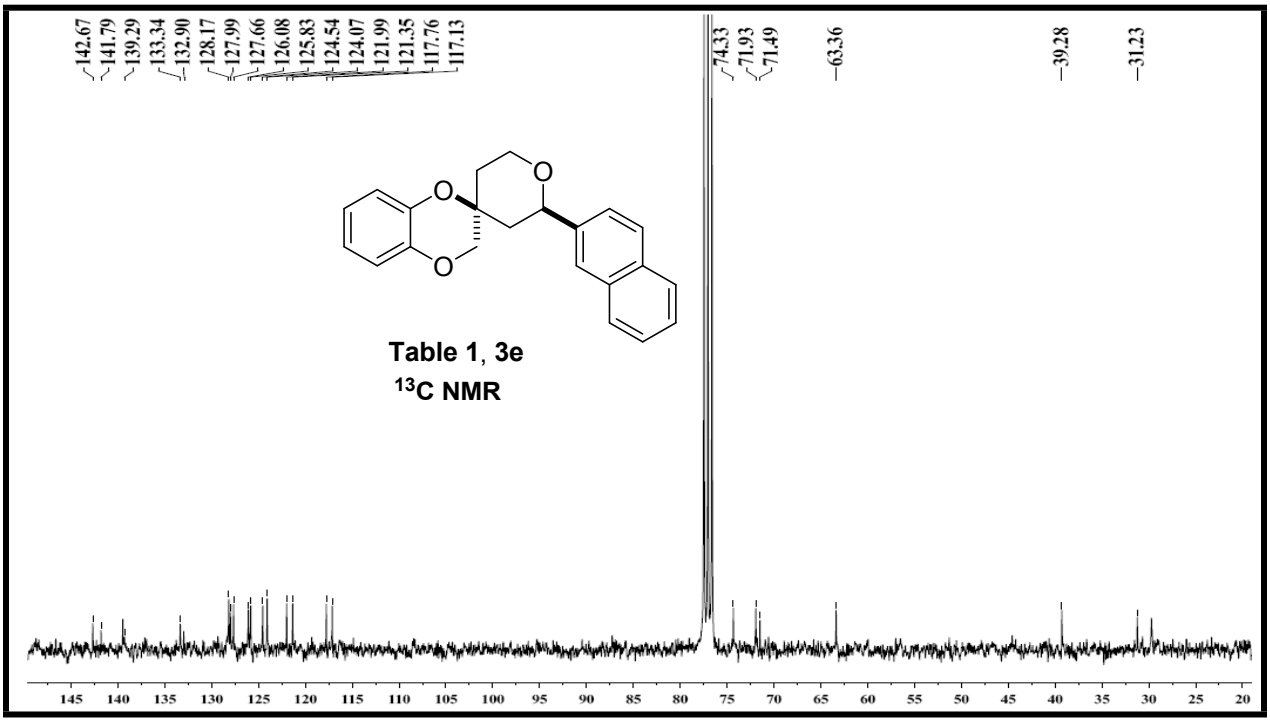
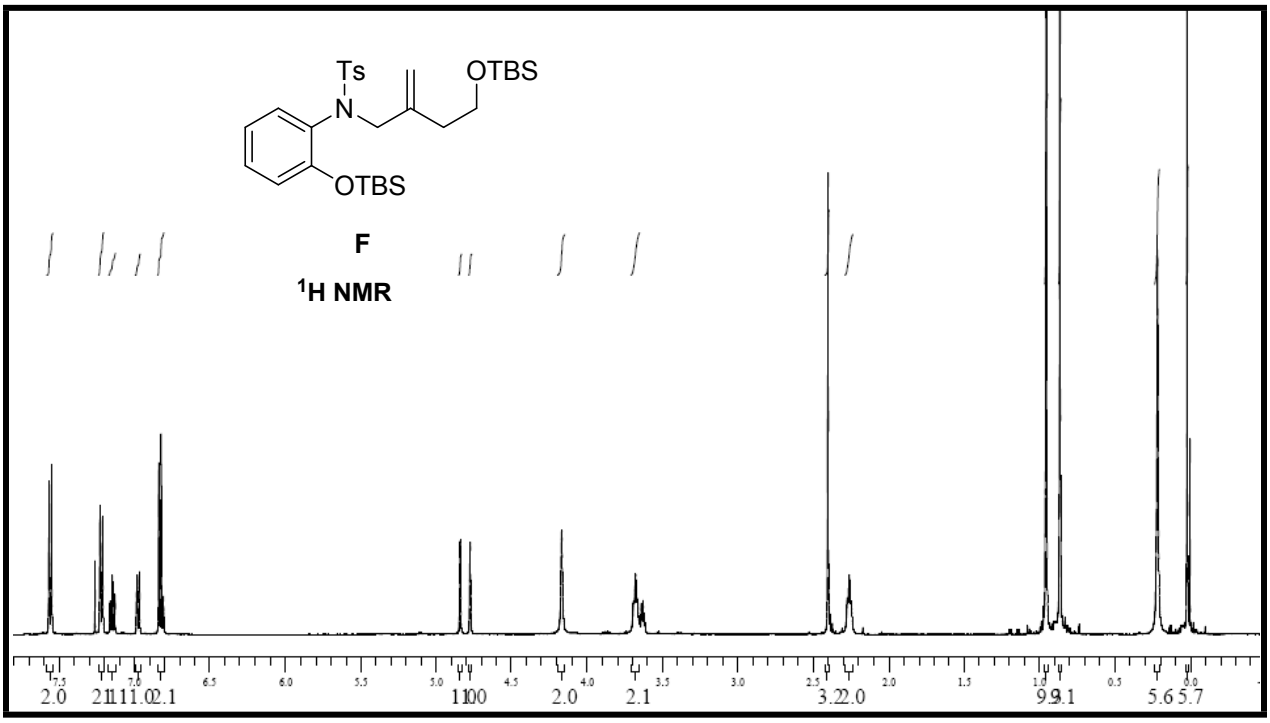
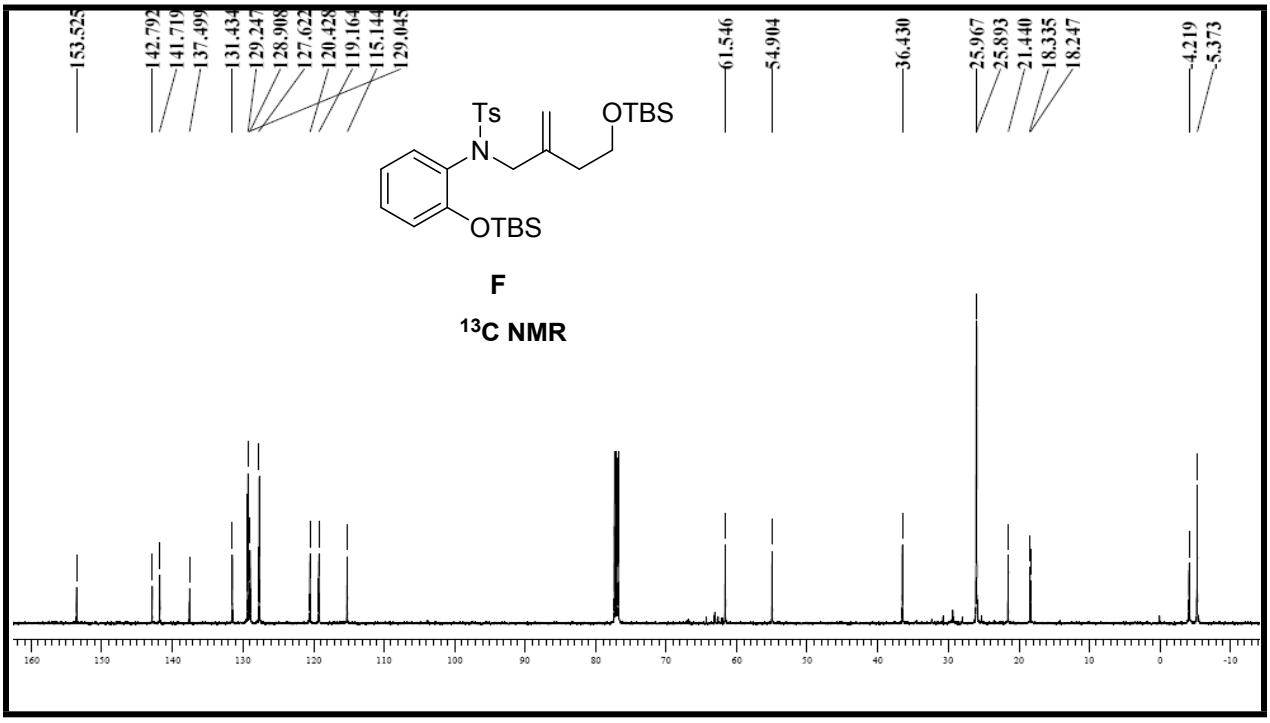


Table 1, 3e
1H NMR
4.1
2.9
3.7
1.0
1.2
1.1
1.1
2.2


142.67
141.79
139.29
133.34
132.90
128.17
127.99
127.66
126.08
125.83
124.54
124.07
121.99
121.35
117.76
117.13
74.33
71.93
71.49
63.36
39.28
31.23
Table 1, 3e
13C NMR


Ts
N
OTBS
OTBS
F
1H NMR
2.0 2.1 1.1 1.0 2.1 1.1 0.0 2.0 2.1 3.2 2.0 9.2 9.1 5.6 5.7


153.525
142.792
141.719
137.499
131.434
129.247
128.908
127.622
120.428
119.164
115.144
129.045
61.546
54.904
36.430
25.967
25.893
21.440
18.335
18.247
-4.219
-5.373
Ts
N
OTBS
OTBS
F
13C NMR

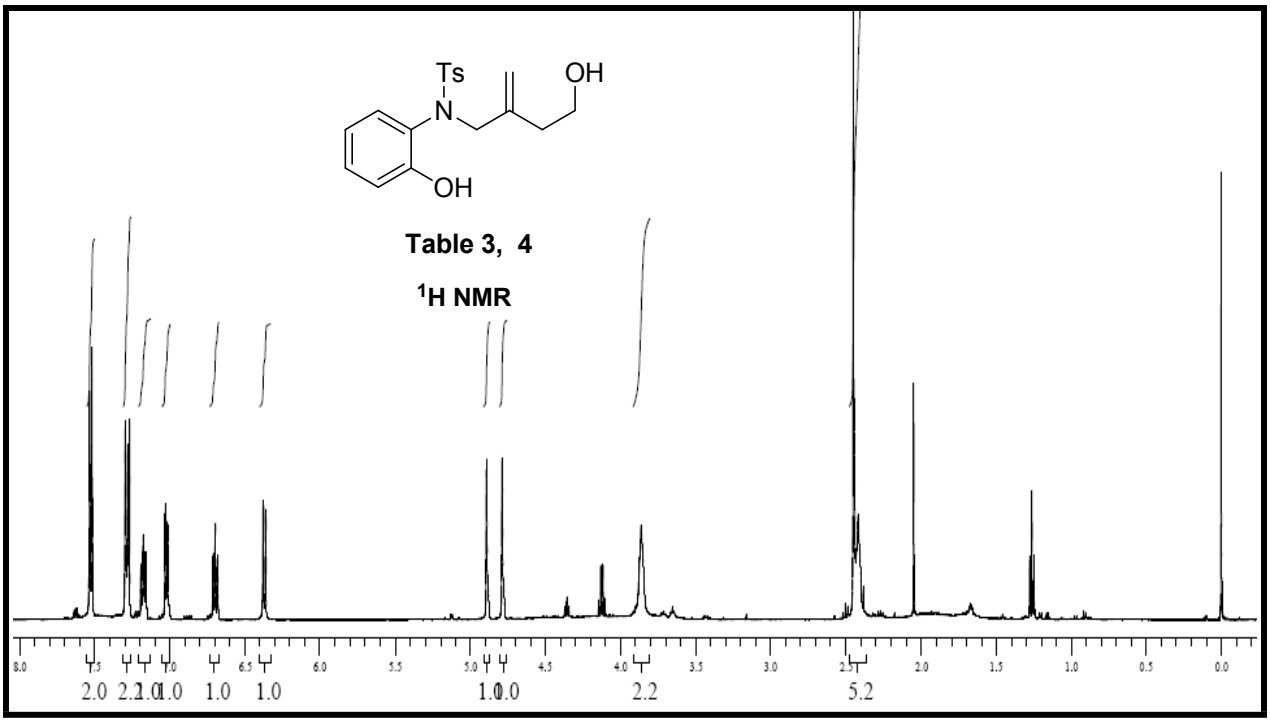


Table 3, 4

^{1}H NMR

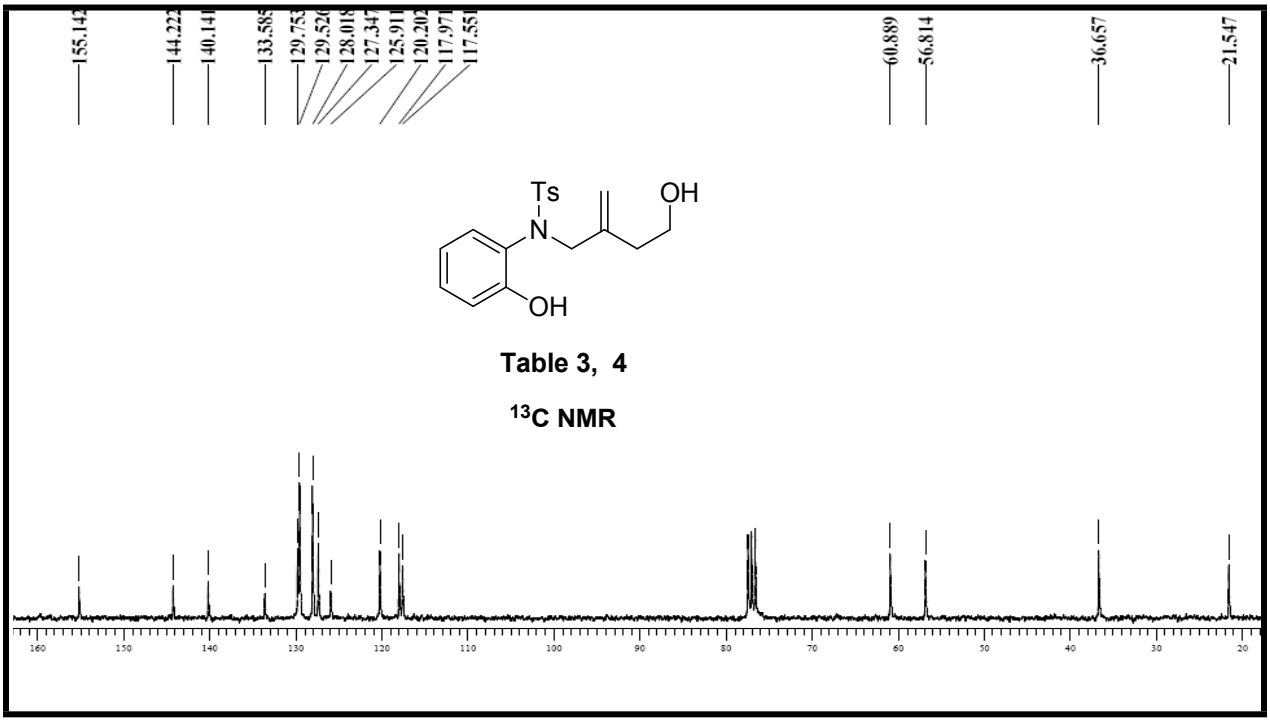
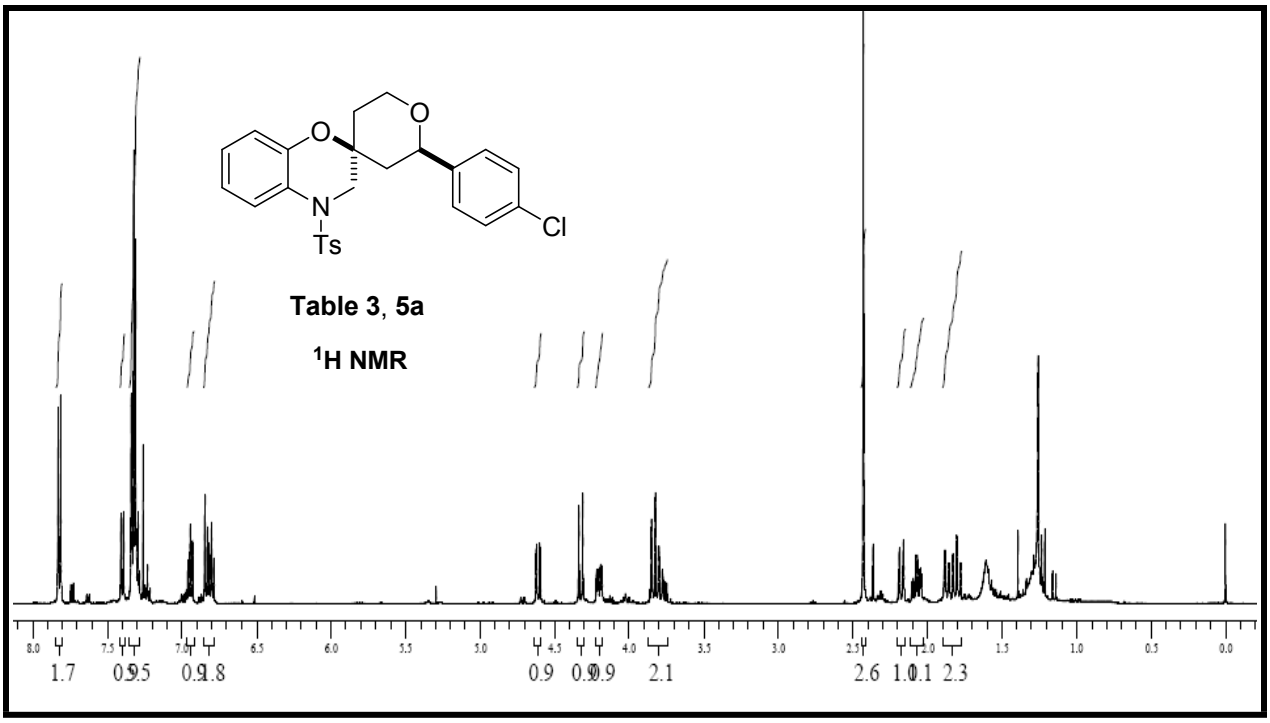
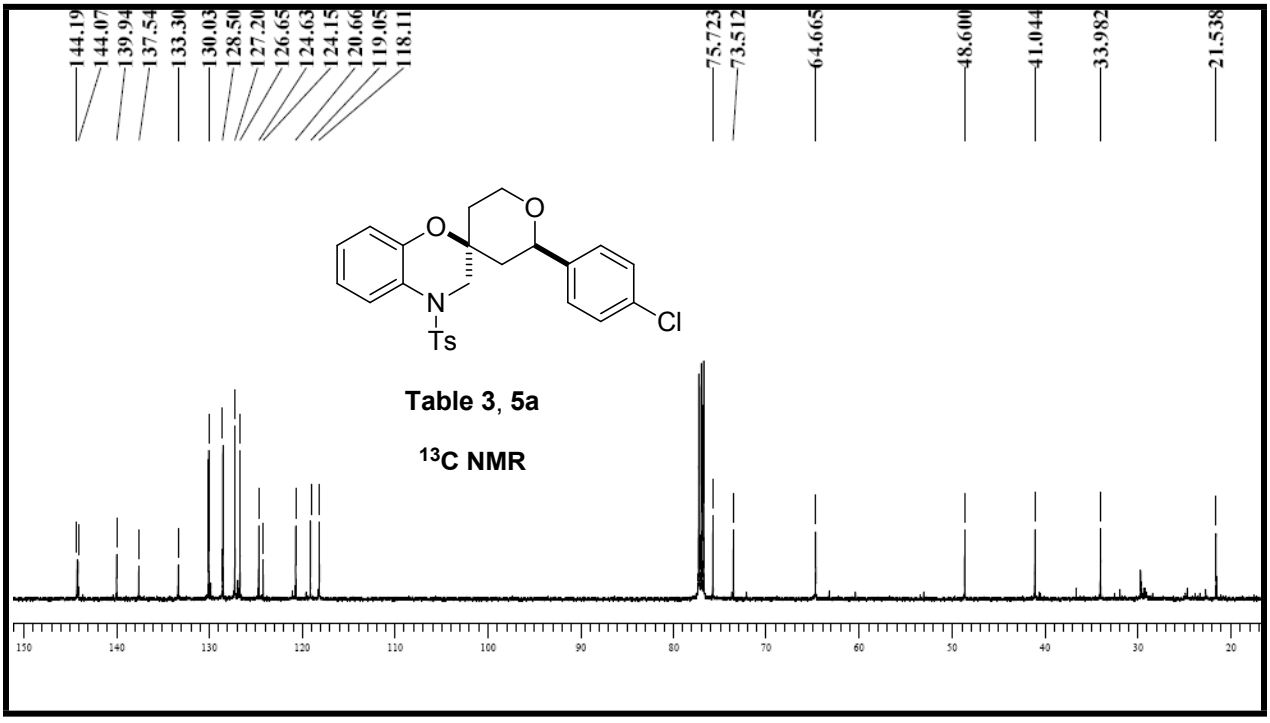


Table 3, 4

^{13}C NMR


O
O
N
Ts
Cl
Table 3, 5a
1H NMR
1.7
0.9
2.1
2.6
2.3


144.19
144.07
139.94
137.54
133.30
130.03
128.50
127.20
126.65
124.63
124.15
120.66
119.05
118.11
75.723
73.512
64.665
48.600
41.044
33.982
21.538
O
O
N
Ts
Cl
Table 3, 5a
13C NMR

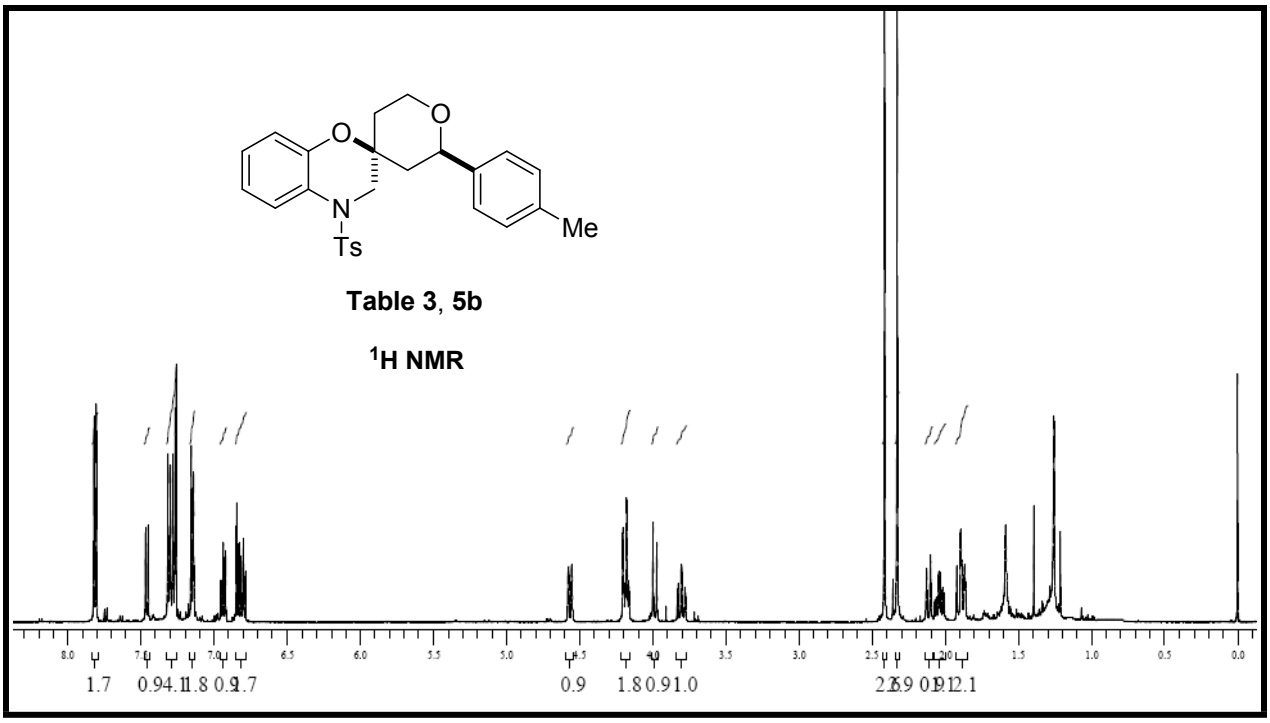


Table 3, **5b**

^{1}H NMR

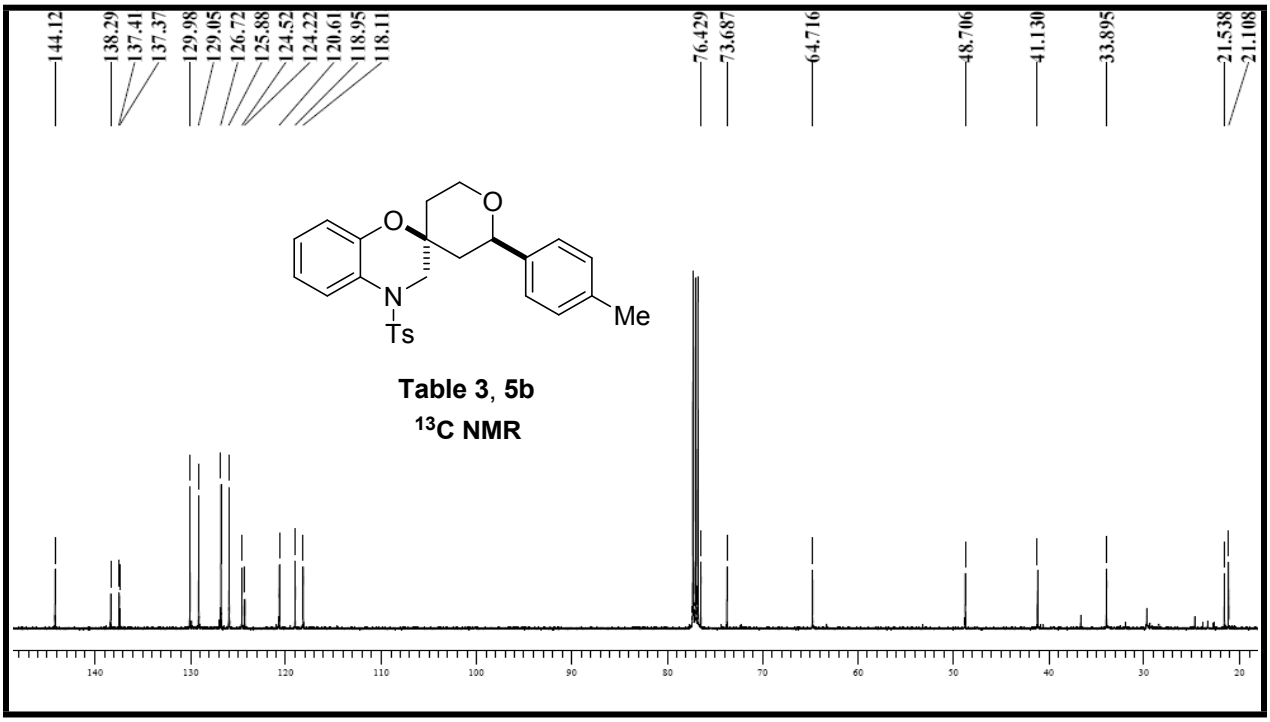


Table 3, **5b**

^{13}C NMR

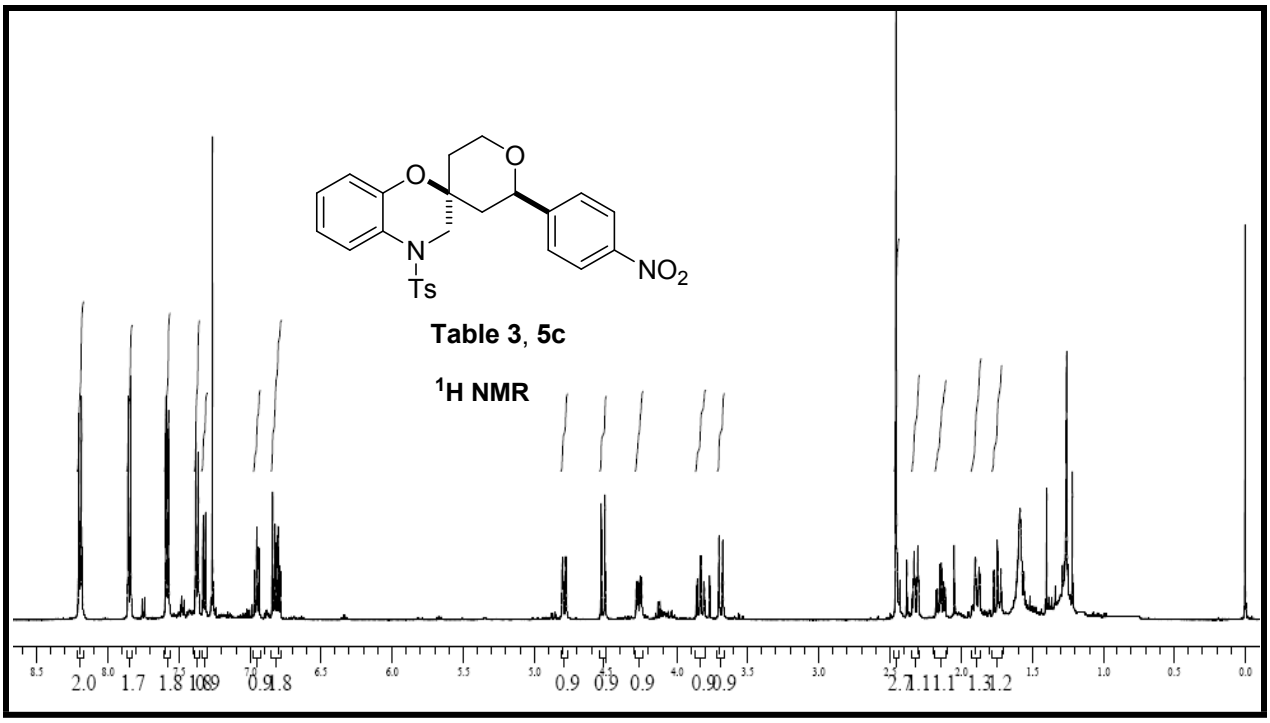


Table 3, **5c**

^{1}H NMR

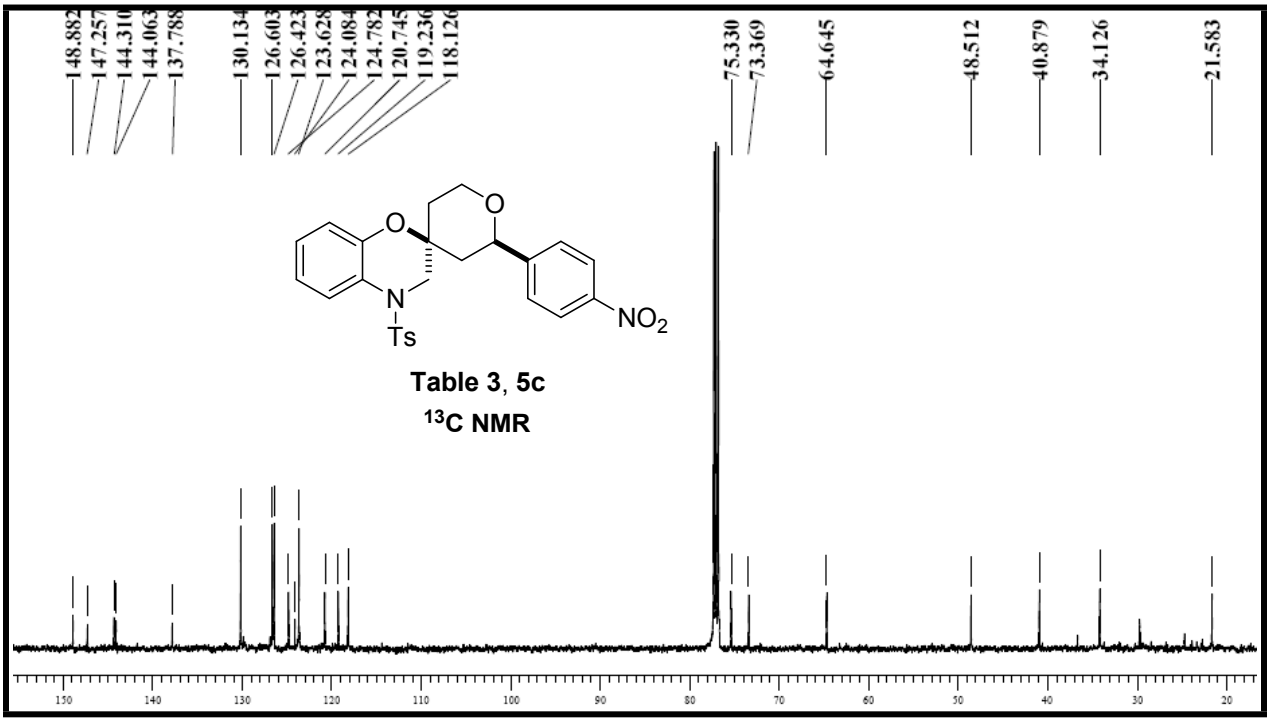


Table 3, **5c**

^{13}C NMR

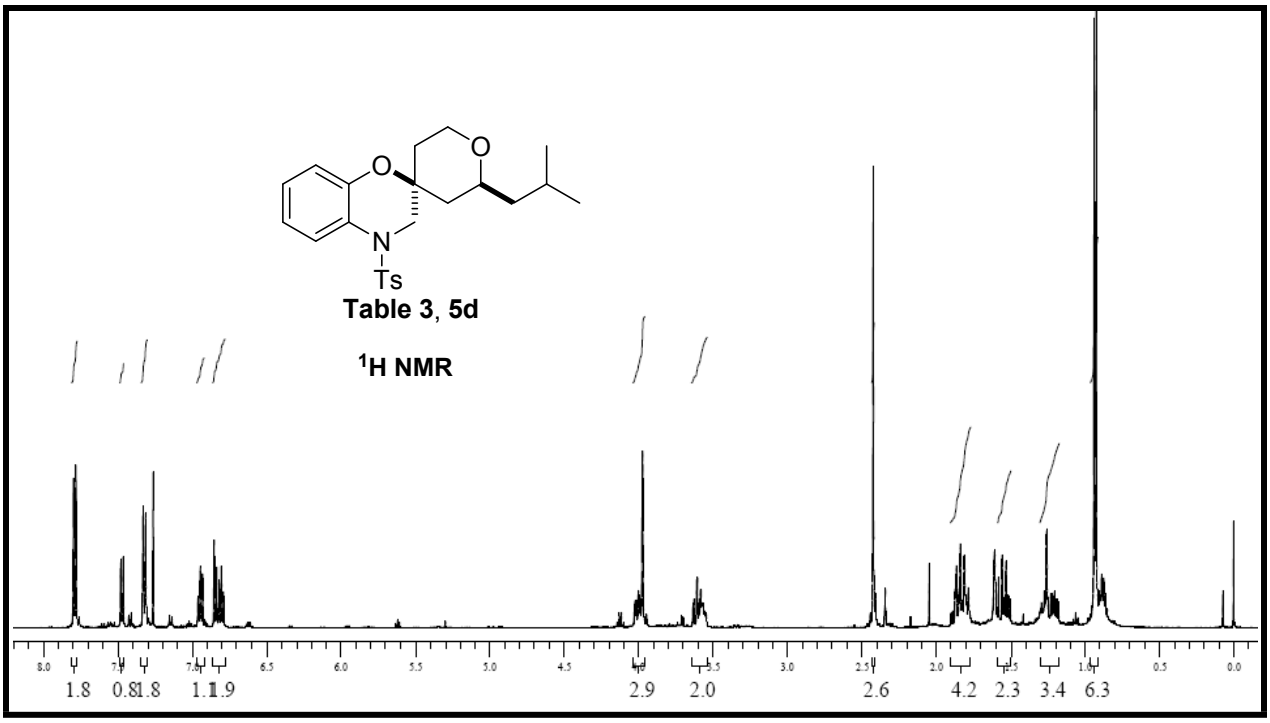


Table 3, **5d**

^{1}H NMR

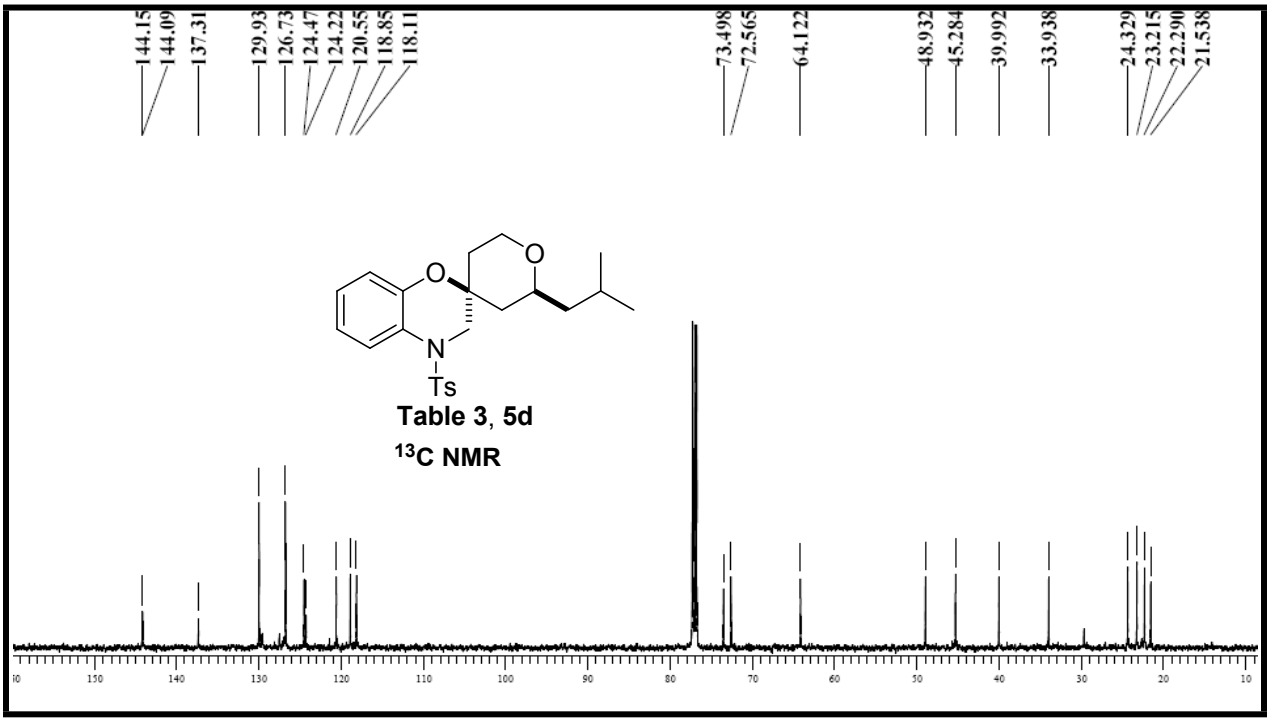


Table 3, **5d**

^{13}C NMR

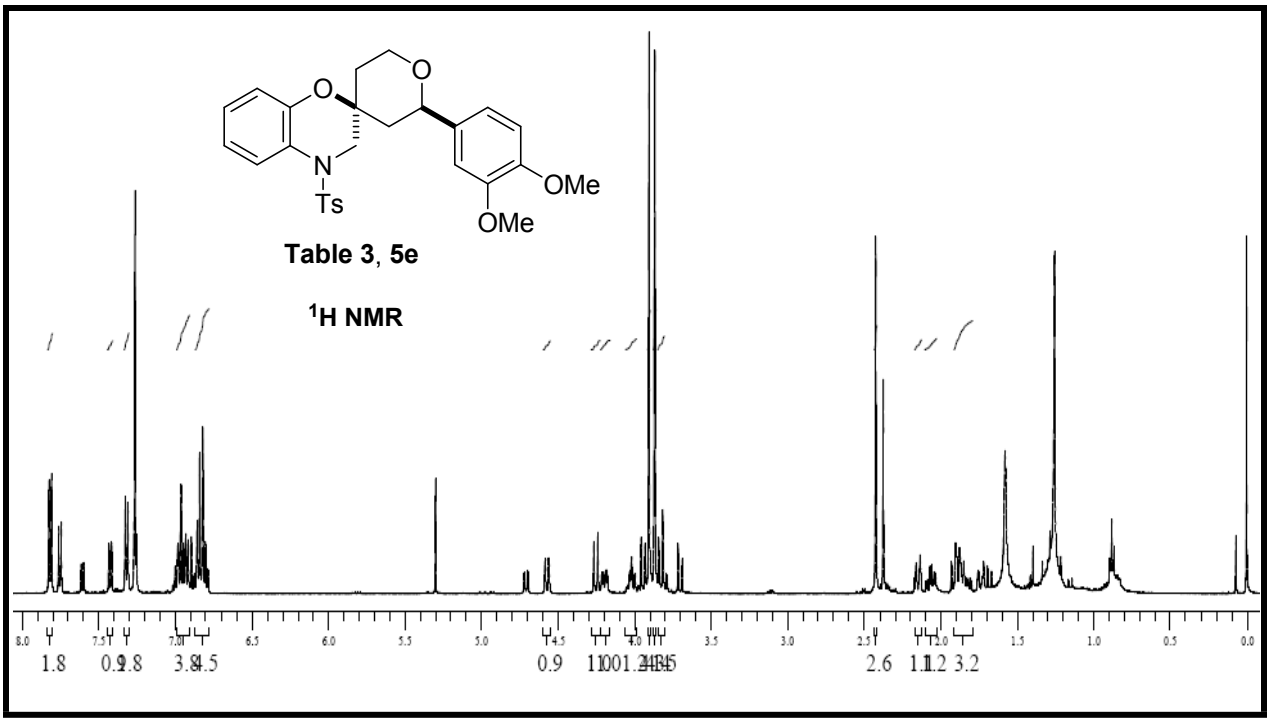


Table 3, **5e**

^{1}H NMR

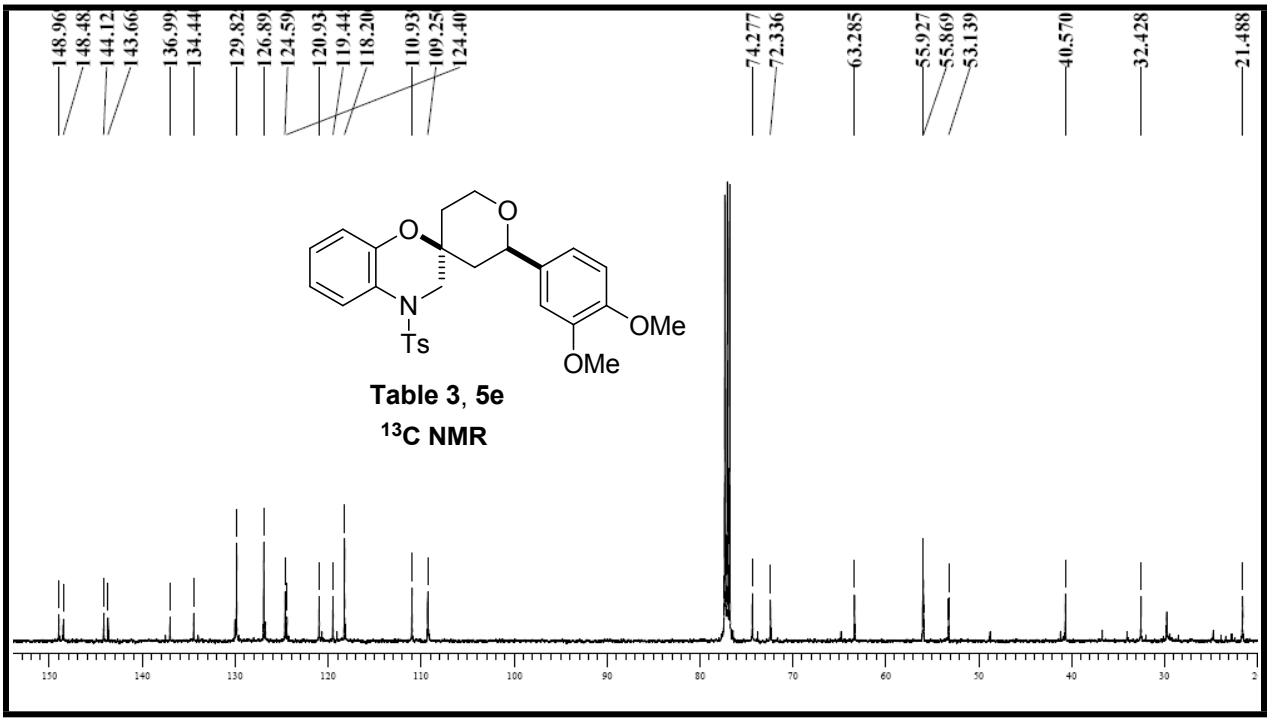


Table 3, **5e**

^{13}C NMR