**Supporting Information**

# A novel bicyclization for the stereoselective synthesis of indeno[2,1-*c*]pyran and cyclopenta[*c*]pyran derivatives

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**Table of contents**

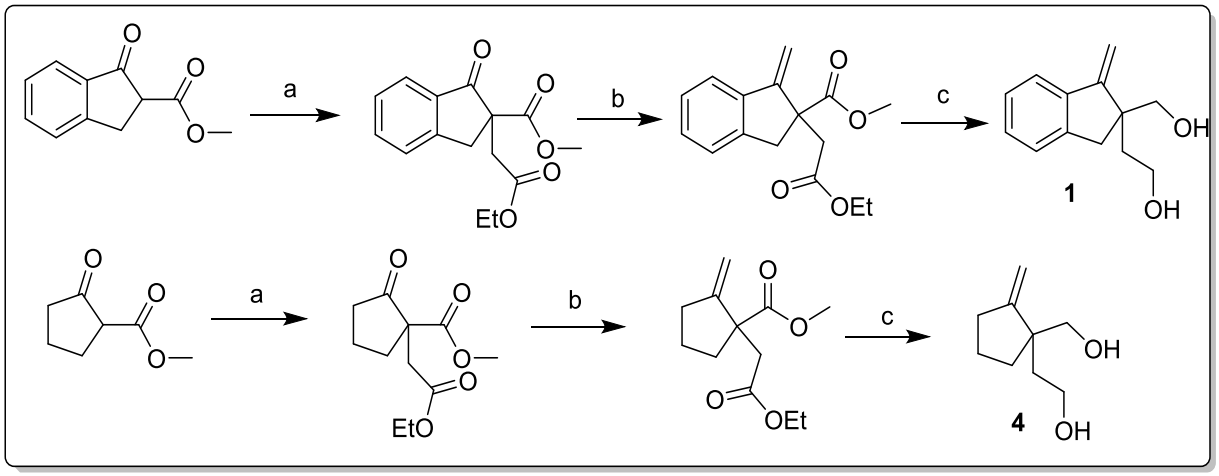


## General methods

IR spectra were recorded on FT-IR spectrometer (KBr) and reported in reciprocal centimeters ($cm^{-1}$). $^{1}$HNMR spectra were recorded at 500 MHz and 600 MHz. $^{13}$C NMR at 125 MHz, 150 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 APCI ionization.

## General procedure:

**Scheme 1.** Synthetic procedure for **1** and **4**:




**Reagents & conditions:** (a) 60% NaH, Ethyl bromoacetate, THF, 0-25 °C, **2**; (b) $PPh_3$, $CH_3Br$, $(CH_3)_3COK$, THF, 0-25 °C, 3-4 h; (c) $LiAlH_4$, THF, 0-25°C, 1h.

**Typical procedure for Prins bicyclization:**

To a mixture of aldehyde (1.1 mmol) and 1 or 4 (1.0 mmol) in dichloromethane (5.0 mL), was added $BF_3.OEt_2$ (10 mol%) slowly drop by drop at 0 $^oC$. The resulting mixture was allowed to stir at the 25 °C under nitrogen atmosphere for the specified time (Table 1 and 2). After completion of the reaction, the reaction was quenched with $NaHCO_3$ solution (5 mL) and then extracted with dichloromethane (2x5 mL). The organic phases were washed with brine (3x2 mL), 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 (1:19) to afford the pure products 3(a-g) or 5(a-g).

**NMR studies of products 3d & 5k:**

**Table 1.** $^1H$ NMR chemical shift (ppm) and coupling constant (Hz) values of **3d** in $CDCl_3$ (298 K, 600 MHz):

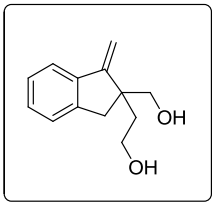
| Proton | (δ) ppm | multiplicity | $^3J$ values (Hz) |
|---|---|---|---|
| 1-H | 3.98 | dd | $^3J_{1\text{-H/2-H(pro-}S\text{)}}$ = 12.2<br>$^3J_{1\text{-H/2-H(pro-}R\text{)}}$ = 2.2 |
| 2-H(pro-*S*) | 2.11 | dd | $^3J_{1\text{-H/2-H(pro-}S\text{)}}$ = 12.2<br>$^3J_{2\text{-H(pro-}S\text{)/2-H(pro-}R\text{)}}$ =14.0 |
| 2-H(pro-*R*) | 2.65 | dd | $^3J_{1\text{-H/2-H(pro-}R\text{)}}$ =2.2<br>$^3J_{2\text{-H(pro-}S\text{)/2-H(pro-}R\text{)}}$ =14.0 |
| 3-H(pro-*R*) | 4.21 | d | $^3J_{3\text{-H(pro-}S\text{)/3-H(pro-}R\text{)}}$ = 12.0 |
| 3-H(pro-*S*) | 3.36 | d | $^3J_{3\text{-H(pro-}S\text{)/3-H(pro-}R\text{)}}$ = 12.0 |
| 4-H(pro-*S*) | 2.65 | d | $^3J_{4\text{-H(pro-}S\text{)/4-H(pro-}R\text{)}}$ = 16.2 |
| 4-H(pro-*R*) | 3.03 | d | $^3J_{4\text{-H(pro-}S\text{)/4-H(pro-}R\text{)}}$ = 16.2 |
| 5-H(pro-*S*) | 4.06 | ddd | $^3J_{5\text{-H(pro-}R\text{)/6-H(pro-}R\text{)}}$ = 7.2<br>$^3J_{5\text{-H(pro-}R\text{)/6-H(pro-}S\text{)}}$ = 9.4<br>$^3J_{5\text{-H(pro-}R\text{)/5-H(pro-}S\text{)}}$ = 8.9 |
| 5-H(pro-*R*) | 4.10 | td | $^3J_{5\text{-H(pro-}S\text{)/6-H(pro-}R\text{)}}$ = 3.0<br>$^3J_{5\text{-H(pro-}S\text{)/6-H(pro-}S\text{)}}$ = 8.9<br>$^3J_{5\text{-H(pro-}S\text{)/5-H(pro-}R\text{)}}$ =8.9 |
| 6-H(pro-*R*) | 2.54 | ddd | $^3J_{5\text{-H(pro-}S\text{)/6-H(pro-}S\text{)}}$ = 8.9<br>$^3J_{5\text{-H(pro-}R\text{)/6-H(pro-}S\text{)}}$ = 9.4<br>$^3J_{6\text{-H(pro-}S\text{)/6-H(pro-}R\text{)}}$ =12.6 |
| 6-H(pro-*S*) | 2.07 | ddd | $^3J_{5\text{-H(pro-}S\text{)/6-H(pro-}R\text{)}}$ = 3.0<br>$^3J_{5\text{-H(pro-}R\text{)/6-H(pro-}R\text{)}}$ = 7.2<br>$^3J_{6\text{-H(pro-}S\text{)/6-H(pro-}R\text{)}}$ =12.6 |
| 8-H | 2.89 | sp | $^3J_{8\text{-H/(CH3)2}}$ = 7.1 |

**Table 2**. $^1$H NMR chemical shift (ppm) and coupling constant (Hz) values of **5k** in $CDCl_3$ (298 K, 500 MHz):

| Proton | (δ) ppm | multiplicity | $^3J$ values (Hz) |
|---|---|---|---|
| 1-H | 4.36 | dd | $^3J_{1\text{-H/2-H(pro-}S\text{)}}$ = 12.2<br>$^3J_{1\text{-H/2-H(pro-}R\text{)}}$ = 2.9 |
| 2-H(pro-*S*) | 1.67 | dd | $^3J_{1\text{-H/2-H(pro-}S\text{)}}$ = 12.2<br>$^3J_{2\text{-H(pro-}S\text{)/2-H(pro-}R\text{)}}$ =13.8 |
| 2-H(pro-*R*) | 2.04 | dd | $^3J_{1\text{-H/2-H(pro-}R\text{)}}$ =2.9<br>$^3J_{2\text{-H(pro-}S\text{)/2-H(pro-}R\text{)}}$ =13.8 |
| 3-H(pro-*S*) | 4.05 | d | $^3J_{3\text{-H(pro-}S\text{)/3-H(pro-}R\text{)}}$ = 12.0 |
| 3-H(pro-*R*) | 3.43 | d | $^3J_{3\text{-H(pro-}S\text{)/3-H(pro-}R\text{)}}$ = 12.0 |
| 4-H(pro-*S*) | 1.93 | m | --- |
| 4-H(pro-*R*) | 1.76 | m | --- |
| 5-H(pro-*R*) | 2.01 | m | --- |
| 5-H(pro-*S*) | 1.96 | m | --- |
| 6-H(pro-*S*) | 1.70 | ddd | $^3J_{6\text{-H(pro-}S\text{)/5-H(pro-}S\text{)}}$ = 9.5<br>$^3J_{6\text{-H(pro-}S\text{)/5-H(pro-}R\text{)}}$ =5.5<br>$^3J_{6\text{-H(pro-}R\text{)/6-H(pro-}S\text{)}}$ =13.5 |
| 6-H(pro-*R*) | 1.57 | ddd | $^3J_{6\text{-H(pro-}R\text{)/5-H(pro-}S\text{)}}$ = 6.5<br>$^3J_{6\text{-H(pro-}R\text{)/5-H(pro-}R\text{)}}$ =8.5<br>$^3J_{6\text{-H(pro-}R\text{)/6-H(pro-}S\text{)}}$ =13.5 |
| 7-H(pro-*S*) | 3.96 | dt | $^3J_{7\text{-H(pro-}S\text{)/8-H(pro-}R\text{)}}$ = 9.0<br>$^3J_{7\text{-H(pro-}S\text{)/8-H(pro-}S\text{)}}$ = 7.5<br>$^3J_{7\text{-H(pro-}S\text{)/7-H(pro-}R\text{)}}$ =9.0 |
| 7-H(pro-*R*) | 3.91 | dt | $^3J_{7\text{-H(pro-}R\text{)/8-H(pro-}R\text{)}}$ = 9.0<br>$^3J_{7\text{-H(pro-}R\text{)/8-H(pro-}S\text{)}}$ = 3.6<br>$^3J_{7\text{-H(pro-}S\text{)/7-H(pro-}R\text{)}}$ = 9.0 |
| 8-H(pro-*R*) | 2.34 | dt | $^3J_{7\text{-H(pro-}R\text{)/8-H(pro-}R\text{)}}$ = 9.0<br>$^3J_{7\text{-H(pro-}S\text{)/8-H(pro-}R\text{)}}$ = 9.0<br>$^3J_{8\text{-H(pro-}S\text{)/8-H(pro-}R\text{)}}$ = 12.3 |
| 8-H(pro-*S*) | 1.87 | dt | $^3J_{7\text{-H(pro-}R\text{)/8-H(pro-}S\text{)}}$ = 3.6<br>$^3J_{7\text{-H(pro-}S\text{)/8-H(pro-}S\text{)}}$ = 7.5<br>$^3J_{8\text{-H(pro-}S\text{)/8-H(pro-}R\text{)}}$ = 12.3 |

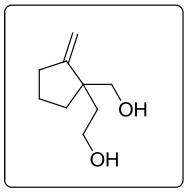
## Characterization data for compounds 1,4 and 3a-g (Table 1) and 5h-n (Table 2):

**2-(2-(Hydroxymethyl)-1-methylene-2,3-dihydro-1*H*-inden-2-yl)ethanol (1)**:



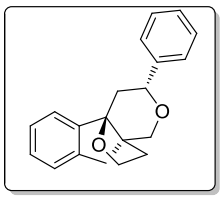

$^1$H NMR (500 MHz, $CDCl_3$): δ 7.47 (d, *J* = 7.1Hz, 1H), 7.25-7.17 (m, 3H), 5.60 (s, 1H), 5.00 (s, 1H), 3.77-3.68 (m, 2H), 3.06 (d, *J* = 16.6 Hz, 1H), 2.88 (d, *J* =16.6 Hz, 1H), 2.04-1.97 (m, 1H), 1.88-1.83 (m, 1H), 1.26 (t, *J* = 7.1 Hz, 2H) ppm; $^{13}$C NMR (125 MHz, $CDCl_3$): δ 154.7, 143.6, 129.0, 126.7, 125.4, 120.9, 103.8, 69.1, 59.6, 50.7, 40.1, 39.3, 29.7 ppm; IR (KBr): υ 3416.3, 2924.3, 1646.3, 1037, 729.3 cm$^{-1}$; HRMS (*APCI*) calculated for $C_{13}H_{16}O_2$: 203.1066 $(M-H)^+$, Found, 203.1068.

**2-(1-(Hydroxymethyl)-2-methylenecyclopentyl)ethanol (4)**:



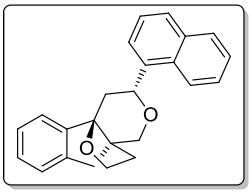

$^1$H NMR (500 MHz, $CDCl_3$): δ 4.99 (t, *J* = 1.9Hz, 1H), 4.81 (t, *J* = 2.1Hz, 1H), 3.80-3.69 (m, 2H), 3.41 (q, *J* =11.2 Hz, 2H), 2.43-2.28 (m, 2H), 1.89-1.81 (m, 2H), 1.71-1.56 (m, 4H) ppm; $^{13}$C NMR (125 MHz, $CDCl_3$): δ 157.6, 105.6, 68.1, 59.7, 49.7, 40.5, 34.1, 33.9, 22.7 ppm; IR (KBr): υ 2923.5, 1651.4, 1047.79, 752.8 cm$^{-1}$; HRMS (*APCI*) calculated for $C_9H_{16}O_2$: 157.1223 $(M+H)^+$, Found, 157.1222.

**(3*R*, 4a*R*,9a*R*)-3-Phenyl-1,3,4,9-tetrahydro-4a,9a-(epoxyethano)indeno[2,1-c]pyran (3a):**



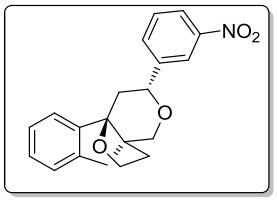

$^1$H NMR (500 MHz, $CDCl_3$): δ 7.40 (d, *J* = 6.9Hz, 1H), 7.37-7.27 (m, 8H), 4.24 (d, *J* = 12.0Hz, 1H), 4.07 (m, 3H), 3.39 (d, *J* = 12.0Hz, 1H), 3.06 (d, *J* = 16.2Hz, 1H), 2.68 (d, *J* = 16.3Hz, 1H), 2.64-2.52 (m, 2H), 2.14-2.06 (m, 2H) ppm; $^{13}$C NMR (125MHz, $CDCl_3$): δ 143.3, 142.4, 141.9, 129.3, 128.3, 127.5, 127.2, 125.7, 125.6, 123.3, 90.5, 76.4, 71.4, 67.4, 52.3, 40.1, 37.8, 33.6 ppm; IR (KBr): υ 3054.0, 2925.2, 1098.9, 777.7 cm$^{-1}$; HRMS (*APCI*) calculated for $C_{20}H_{20}O_2$: 293.1536 $(M+H)^+$, Found 293.1536.

**(3*R*,4a*R*,9a*R*)-3-(Naphthalen-1-yl)-1,3,4,9-tetrahydro-4a,9a-(epoxyethano)indeno[2,1-c]pyran (3b):**



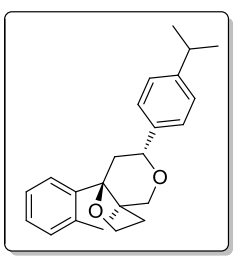
$^1$H NMR (500 MHz, $CDCl_3$): δ 7.96-7.68 (m, 4H), 7.59-7.32 (m, 7H), 4.76 (d, *J* = 11.6 Hz, 1H), 4.38 (d, *J* = 12.0Hz, 1H), 4.24-4.06 (m, 2H), 3.56 (d, *J* = 12.0Hz, 1H), 3.13 (d, *J* = 16.3Hz, 1H), 2.95-2.59 (m, 3H), 2.32-2.11 (m, 2H) ppm; $^{13}$C NMR (125 MHz, $CDCl_3$): δ 143.4, 142.5, 137.5, 133.6, 130.2, 129.5, 128.8, 128.0, 127.4, 126.0, 125.8, 125.4, 123.2, 122.8, 122.7, 90.8, 73.5, 71.8, 67.4, 52.6, 40.2, 37.1, 33.7 ppm; IR (KBr): υ 3024.0, 2925.2, 1092.2, 757.6 cm$^{-1}$; HRMS (*APCI*) calculated for $C_{24}H_{22}O_2$: 343.3420 $(M+H)^+$, Found 343.3426.

**(3*R*,4a*R*,9a*R*)-3-(3-Nitrophenyl)-1,3,4,9-tetrahydro-4a,9a-(epoxyethano)indeno[2,1-c]pyran (3c):**



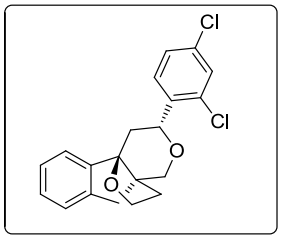

$^1$H NMR (500 MHz, $CDCl_3$): δ 8.36 (d, *J* = 1.8Hz, 1H), 8.17 (m, 1H), 7.78 (d, *J* = 7.7Hz, 1H), 7.56 (t, *J* = 7.9Hz, 1H), 7.43 (d, *J* = 7.3Hz, 1H), 7.32-7.27 (m, 1H), 7.22-7.14 (m, 2H), 4.74 (dd, *J* = 10.8, 1.6Hz, 1H), 4.41-4.36 (m, 1H), 3.81 (dt , *J* = 1.9, 11.9Hz, 1H), 3.43 (d, *J* = 3.0Hz, 2H), 3.12-3.02 (m, 3H), 2.94-2.84 (m, 2H), 2.66 (d, *J* = 17.1Hz, 1H) ppm; $^{13}$C NMR (125 MHz, $CDCl_3$): δ 148.3, 146.4, 145.7, 143.4, 142.1, 135.7, 131.9, 129.2, 126.2, 124.1, 123.3, 122.3, 120.9, 117.7, 82.0, 70.8, 42.9, 36.6, 33.2, 29.6 ppm; IR (KBr): υ 3449.1, 2923.2, 1113.3, 758.7 cm$^{-1}$; HRMS (*APCI*) calculated for $C_{20}H_{19}NO_4$: 338.0604 $(M+H)^+$, Found, 338.0603.

**(3*R*,4a*R*,9a*R*)-3-(4-Isopropylphenyl)-1,3,4,9-tetrahydro-4a,9a-(epoxyethano)indeno[2,1-c]pyran (3d)**:



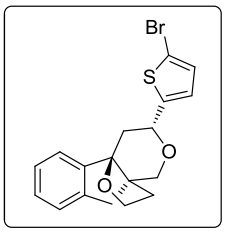
$^1$H NMR (600 MHz, $CDCl_3$): δ 7.38 (d, *J* = 7.3Hz, 1H), 7.34-7.24 (m, 5H), 7.20 (d, *J* = 8.1 Hz, 2H), 4.21(d, *J* = 12.2Hz, 1H), 4.10 (td, *J* = 3.0, 8.9, 8.9Hz, 1H), 4.06 (ddd, *J* = 7.2, 9.4, 8.9, Hz, 1H ), 3.98 (dd, *J* = 12.2, 2.2Hz, 1H), 3.36 (d, *J* = 12.0Hz, 1H), 3.03 (d, *J* = 16.2 Hz, 1H), 2.89 (sp, *J* = 7.1Hz, 1H), 2.65 (dd, *J* =2.2, 14.0 Hz, 1H), 2.65 (d, *J* = 16.2Hz, 1H), 2.54 (ddd, *J* = 8.9, 9.4, 12.6 Hz, 1H), 2.11 (dd, *J* = 12.2, 14.0 Hz, 1H), 2.07 (ddd, d, *J* = 3.0, 7.2, 12.6Hz, 1H), 1.23 (d, *J* = 6.9 Hz, 6H) ppm; $^{13}$C NMR (150 MHz, $CDCl_3$): δ 148.3, 143.3, 142.5, 139.1, 129.3, 127.2, 126.4, 125.9, 125.6, 123.3, 90.6, 76.3, 71.4, 67.4, 52.3, 40.2, 37.4, 33.8, 33.6, 29.6, 23.9 ppm; DEPT-135: δ 129.4 (CH), 127.3 (CH), 126.5 (CH), 126.0 (CH), 125.7 (CH), 123.4 (CH), 76.4 (CH), 71.5 ($CH_2$), 67.5 ($CH_2$), 40.3 ($CH_2$), 37.5 ($CH_2$), 33.9 (CH), 33.7 ($CH_2$), 24.0 ($CH_2$) ppm; IR (KBr): υ 3022.0, 2957, 1100.1, 760.1 cm$^{-1}$; HRMS (*APCI*) calculated for $C_{23}H_{26}O_2$: 335.2005 $(M+H)^+$, Found, 335.2001.

**((3*R*,4a*R*,9a*R*)-3-(2,4-Dichlorophenyl)-1,3,4,9-tetrahydro-4a,9a(epoxyethano)indeno[2,1-c]pyran (3e):**




$^1$H NMR (500 MHz, $CDCl_3$): δ 7.54(d, *J* = 8.3 Hz, 1H), 7.45 (d, *J* = 7.0 Hz, 1H), 7.38-7.21 (m, 5H), 4.30 (dd, *J* = 1.6, 10.0 Hz, 1H), 4.25 (d, *J* = 12.0 Hz, 1H), 4.12-4.04 (m, 2H), 3.38 (d, *J* = 12.0 Hz, 1H), 3.06 (d, *J* =16.1 Hz, 1H), 2.76 (dd, *J* = 1.9, 11.9 Hz, 1H), 2.65 (d, *J* = 16.1 Hz, 1H), 2.59-2.49 (m, 1H), 2.15-2.07 (m, 1H), 1.81-1.72 (m, 1H) ppm; $^{13}$C NMR (125 MHz, $CDCl_3$): δ 143.2, 142.0, 138.7, 133.4, 131.8, 129.6, 129.1, 127.8, 125.7, 123.7, 90.5, 73.3, 71.5, 67.6, 52.5, 40.2, 36.3, 33.4 ppm; IR (KBr) :υ 3070.1, 2928.5, 1097.2, 757.7 cm$^{-1}$; HRMS (*APCI*) calculated for $C_{20}H_{18}O_2Cl_2$: 361.0756$(M)^+$, Found, 361.0761.

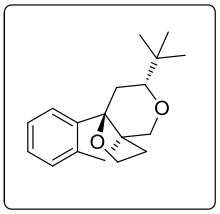
**(3*R*,4a*R*,9a*R*)-3-(5-Bromothiophen-2-yl)-1,3,4,9-tetrahydro-4a,9a-(epoxyethano)indeno[2,1-c]pyran (3f):**




$^1$H NMR (500 MHz, $CDCl_3$): δ 7.33-7.29 (m, 1H), 7.27-7.21 (m, 3H), 6.86 (d, *J* = 4.4Hz, 1H), 6.69 (d, *J* = 3.8Hz, 1H), 4.71 (d, *J* = 11.6Hz, 1H), 4.12 (d, *J* = 9.9Hz, 1H), 4.04 (q, *J* = 15.6Hz, 1H), 3.71-3.66 (m, 1H), 3.65 (d, *J* = 9.1Hz, 1H), 3.19 (d, *J* = 15.7Hz, 1H), 2.90 (d, *J* = 15.7Hz, 1H), 2.54 (d, *J* = 14.5Hz, 1H), 1.87-1.81 (m, 1H), 1.80-1.64 (m, 2H) ppm; $^{13}$C

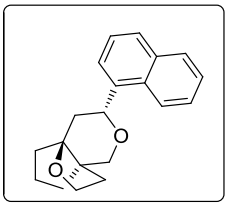
NMR (125 MHz, $CDCl_3$): δ 147.0, 146.4, 139.6, 129.2, 128.2, 127.2, 125.6, 123.7, 122.8, 111.3, 90.2, 70.9, 70.7, 66.2, 49.5, 40.1, 38.0, 36.1 ppm; IR (KBr): υ 3069.1, 2925.9, 1091.4, 765.6 $cm^{-1}$; HRMS (*APCI*) calculated for $C_{18}H_{17}BrO_2S$: 377.0037 $(M)^+$, Found, 377.0025.

**(3*R*,4a*R*,9a*R*)-3-(*tert*-Butyl)-1,3,4,9-tetrahydro-4a,9a-(epoxyethano)indeno[2,1-*c*]pyran (3g)**:



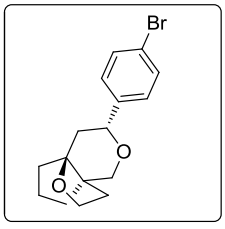
$^1H$ NMR (500 MHz, $CDCl_3$): δ 7.36 – 7.17 (m, 4H), 4.06 (m, 2H), 4.01-3.95 (m, 1H), 3.17 (d, *J* = 11.8Hz, 1H), 2.97 (d, *J* = 16.3Hz, 1H), 2.65-2.53 (m, 2H), 2.42-2.32 (m, 2H), 2.03-1.94 (m, 1H), 1.78-1.70 (m, 1H), 0.89 (s, 9H) ppm; $^{13}C$ NMR (125 MHz, $CDCl_3$): δ 143.2, 142.8, 129.0, 127.1, 125.4, 123.1, 91.0, 81.8, 71.3, 67.2, 52.2, 40.1, 33.9, 33.8, 30.3, 25.7 ppm; IR (KBr): υ 3024.0, 2955.2, 1102.3, 759.3 $cm^{-1}$; HRMS (*APCI*) calculated for $C_{18}H_{24}O_2$: 273.1849 $(M+H)^+$, Found, 273.1843.

**(3*R*,4a*S*,7a*R*)- Naphthalen-1-yl)hexahydro-4a,7a-(epoxyethano)cyclopenta[c]pyran (5h)**:



$^1H$ NMR (500 MHz, $CDCl_3$): δ 7.95 (d, *J* = 8.0 Hz, 1H), 7.87 (d, *J* = 7.4 Hz, 1H), 7.79 (d, *J* = 8.1 Hz, 1H), 7.66 (d, *J* = 7.0 Hz, 1H), 7.50 (m, 3H), 5.03 (d, *J* = 10.4 Hz, 1H), 4.17 (d, *J* = 12.0 Hz, 1H), 4.09-3.89 (m, 2H), 3.60 (d, *J* = 12.0 Hz, 1H), 2.57-2.39 (m, 1H), 2.28-2.04 (m, 3H), 2.01-1.55 (m, 6H) ppm; $^{13}C$ NMR (125MHz, $CDCl_3$): δ 137.6, 133.6, 130.2, 128.8, 127.9, 126.0, 125.4, 125.3, 122.8, 122.6, 90.1, 74.5, 71.9, 65.5, 50.3, 38.2, 35.1, 34.8, 34.6, 22.4 ppm; IR (KBr): υ 3027.8, 2925, 1100.0, 759.9 $cm^{-1}$; HRMS (*APCI*) calculated for $C_{20}H_{22}O_2$: 295.1692 $(M+H)^+$, Found, 295.1692.

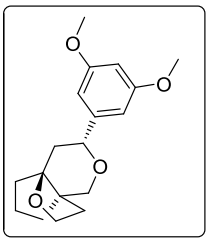
**(3*R*,4a*S*,7a*R*)-3-(4-Bromophenyl)hexahydro-4a,7a-(epoxyethano)cyclopenta[c]pyran (5i)**:




$^1H$ NMR (500 MHz, $CDCl_3$): δ 7.46 (d, *J* = 8.3 Hz, 2H), 7.22 (d, *J* = 8.3 Hz, 2H), 4.26 (dd, *J* = 12.2, 2.7 Hz, 1H), 4.03 (d, *J* = 12.0 Hz, 1H), 3.98-3.88 (m, 2H), 3.41 (d, *J* = 12.0 Hz, 1H),

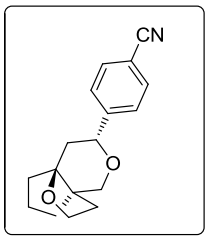
2.40-2.32 (m, 1H), 2.05-1.81 (m, 5H), 1.78-1.64 (m, 3H), 1.59-1.51 (m, 1H) ppm; $^{13}$C NMR (125 MHz, $CDCl_3$): δ 141.3, 131.3, 127.3, 121.1, 89.7, 76.6, 71.4, 65.5, 50.0, 39.1, 35.1, 34.7, 29.6, 22.3 ppm; IR (KBr): υ 3071.6, 2954.7, 1183.0, 763.5 cm$^{-1}$; HRMS (*APCI*) calculated for $C_{16}H_{19}BrO_2$: 323.0461 $(M)^+$, Found, 323.0459.

**(3*R*,4a*S*,7a*R*)-3-(3,5-Dimethoxyphenyl)hexahydro-4a,7a-(epoxyethano)cyclopenta [c]pyran (5j):**



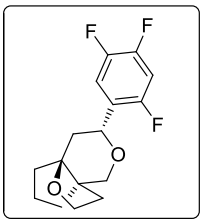
$^1$H NMR (500 MHz, $CDCl_3$): δ 6.51 (d, *J* = 2.2 Hz, 2H), 7.22 (m, 1H), 4.25 (dd, *J* = 9.4, 2.6 Hz, 1H), 4.04 (d, *J* = 12.0 Hz, 1H), 3.99-3.89 (m, 2H), 3.79 (s, 6H), 3.41 (d, *J* = 12.0 Hz, 1H), 2.43-2.31 (m, 1H), 2.06-1.50 (m, 9H) ppm; $^{13}$C NMR (125MHz, $CDCl_3$): δ 160.5, 144.5, 103.3, 90.0, 89.6, 76.3, 71.1, 65.2, 55.0, 49.9, 38.8, 34.9, 34.5, 29.4, 22.1 ppm; IR(KBr): υ 3091.7, 2927.7, 1154.5, 836.2 cm$^{-1}$; HRMS (*APCI*) calculated for $C_{18}H_{24}O_4$: 305.1747 $(M+H)^+$, Found, 305.1736.

**4-((3*R*,4a*S*,7a*R*)-Hexahydro-4a,7a-(epoxyethano)cyclopenta[c]pyran-3-yl)benzonitrile (5k):**



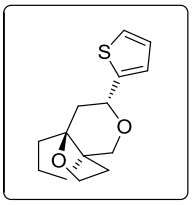
$^1$H NMR (500 MHz, $CDCl_3$): δ 7.64 (d, *J* = 8.3 Hz, 2H), 7.46 (d, *J* = 8.2 Hz, 2H), 4.36 (dd, *J* = 12.2, 2.9Hz, 1H), 4.05 (d, *J* = 12.0Hz, 1H), 3.96 (dt, *J* =9.0, 7.5, 9.0Hz, 1H), 3.91 (dt, *J* =9.0, 3.6, 9.0Hz, 1H), 3.43 (d, *J* = 12.0Hz, 1H), 2.34 (dt, *J* = 9.0, 9.0, 12.3Hz, 1H), 2.04 (dd, *J* =2.9, 13.8Hz, 1H), 2.01 (m, 1H), 1.96 (m, 1H), 1.93 (m, 1H), 1.87 (dt, *J* = 3.6, 7.5 12.3Hz, 1H), 1.76 ( m, 1H), 1.70 ( ddd, *J* = 9.5, 5.5, 13.5Hz, 1H), 1.67 (dd, *J* =12.2,13.8 Hz, 1H), 1.57 (ddd, *J* = 6.5, 5.5, 13.5Hz, 1H) ppm; $^{13}$C NMR (125 MHz, $CDCl_3$): δ 148.1, 132.5, 126.3, 118.9, 111.3, 89.5, 71.4, 65.5, 50.2, 39.2, 35.2, 34.7, 29.7, 22.4 ppm; IR(KBr): υ 3051.9, 2924.9, 2227.6, 1097.4, 833.5 cm$^{-1}$; HRMS (*APCI*) calculated for $C_{17}H_{19}NO_2$: 270.1488 $(M+H)^+$, Found, 270.1492.

**(3*R*,4a*S*,7a*R*)-3-(2,4,5-Trifluorophenyl)hexahydro-4a,7a-(epoxyethano)cyclopenta [c]pyran (5l):**



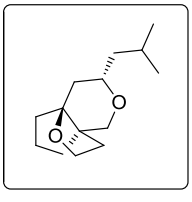

$^1$H NMR (500 MHz, $CDCl_3$): δ 7.42-7.27 (m, 1H), 6.96-6.81 (m, 1H), 4.55 (d, *J* = 10.7 Hz, 1H), 4.04-3.88 (m, 3H), 3.44 (d, *J* = 12.0 Hz, 1H), 2.41-2.28 (m, 1H), 2.09-1.82 (m, 5H), 1.80-1.52 (m, 4H) ppm; $^{13}$C NMR (125 MHz, $CDCl_3$): δ 115.2, 115.1, 114.9, 105.6, 105.3, 105.2, 104.9, 89.5, 71.4, 70.6, 65.6, 50.2, 38.2, 35.1, 34.8, 34.7, 29.7, 22.3 ppm; IR (KBr): υ 3071.1, 2925.8, 1111.0, 779.4 cm$^{-1}$; HRMS (*APCI*) calculated for $C_{16}H_{17}F_3O_2$: 297.1096 $(M-H)^+$, Found, 297.1095.

**(3*R*,4a*S*,7a*R*)-3-(Thiophen-2-yl)hexahydro-4a,7a-(epoxyethano)cyclopenta[*c*]pyran (5m)**:



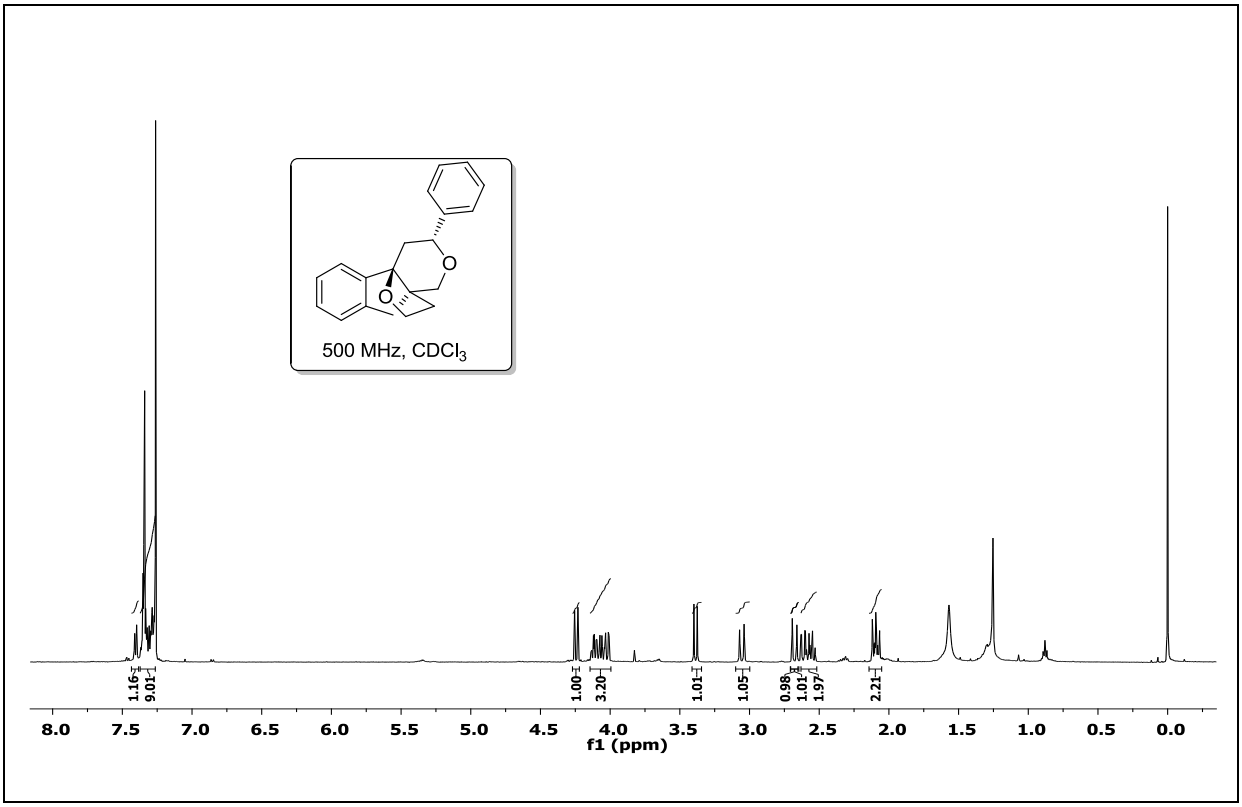

$^1$H NMR (500 MHz, $CDCl_3$): δ 7.26-7.22 (m, 1H), 6.99-6.95 (m, 2H), 4.57 (dd, *J* = 9.3, 2.7 Hz, 1H), 4.02-3.93 (m, 3H), 3.45 (d, *J* = 12.0 Hz, 1H), 2.39-2.27 (m, 1H), 2.19 (dd, *J* = 10.8, 2.7 Hz, 1H), 2.0-1.81 (m, 5H), 1.77-1.65 (m, 3H) ppm; $^{13}$C NMR (125 MHz, $CDCl_3$): δ 126.6, 124.8, 124.3, 123.5, 89.7, 73.2, 71.4, 65.7, 50.4, 39.5, 38.6, 34.8, 32.9, 22.4 ppm; IR (KBr): υ 3051.6, 2925.9, 1088.8, 760.5 cm$^{-1}$; HRMS (*APCI*) calculated for $C_{14}H_{18}O_2S$: 251.1100 $(M+H)^+$, Found, 251.1099.

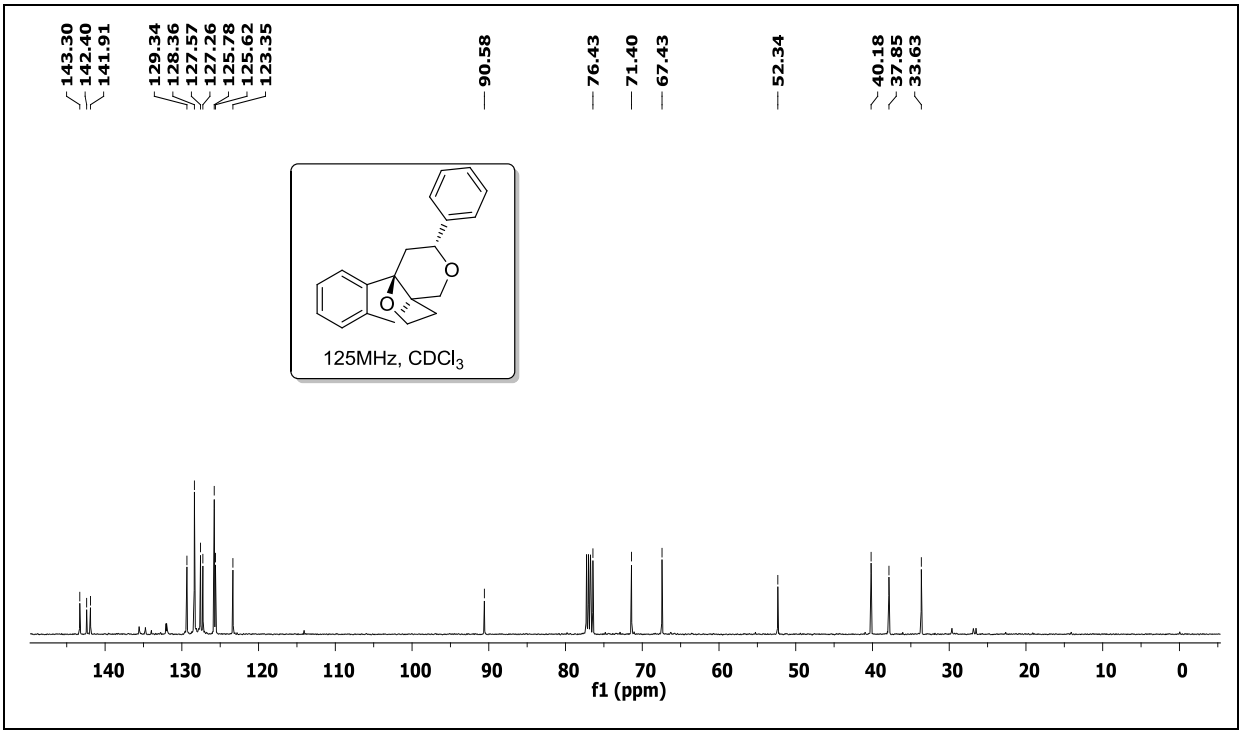
**(3*S*,4a*S*,7a*R*)-3-Isobutylhexahydro-4a,7a-(epoxyethano)cyclopenta[*c*]pyran (5n)**:



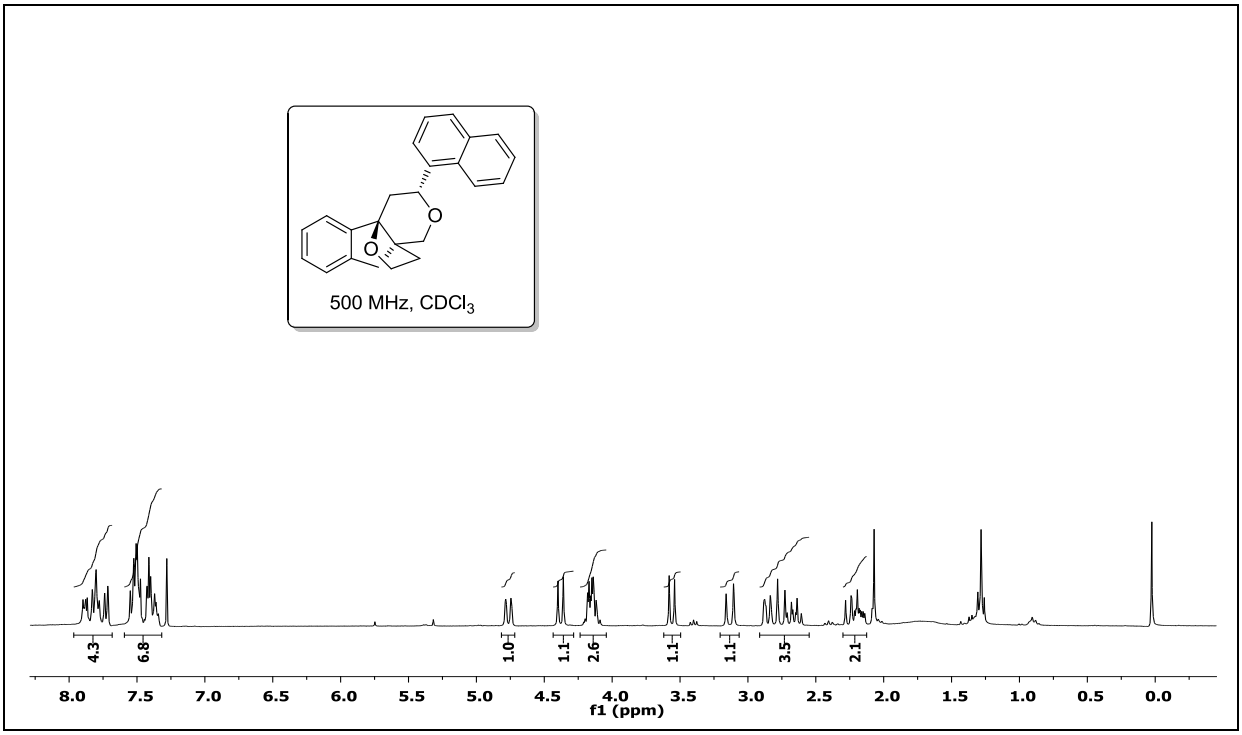

$^1$H NMR (500 MHz, $CDCl_3$): δ 3.96-3.90 (m, 2H), 3.87 (d, *J* = 12.2 Hz, 1H), 3.33-3.23 (m, 1H), 3.20 (d, *J* = 11.8 Hz, 1H), 2.25-2.21 (m, 1H), 1.97-1.57 (m, 8H), 1.55-1.37 (m, 3H), 1.23-1.13 (m, 1H), 0.89 (d, *J* = 6.6 Hz, 6H) ppm; $^{13}$C NMR (125 MHz, $CDCl_3$): δ 89.7, 73.7, 71.2, 65.5, 50.1, 45.3, 37.9, 35.3, 34.8, 29.64, 24.3, 23.1, 22.3 ppm; IR (KBr): υ 2925.8, 1109.1, 807.7 cm$^{-1}$; HRMS (*APCI*) calculated for $C_{14}H_{24}O_2$: 225.1849 $(M+H)^+$, Found, 225.1848.

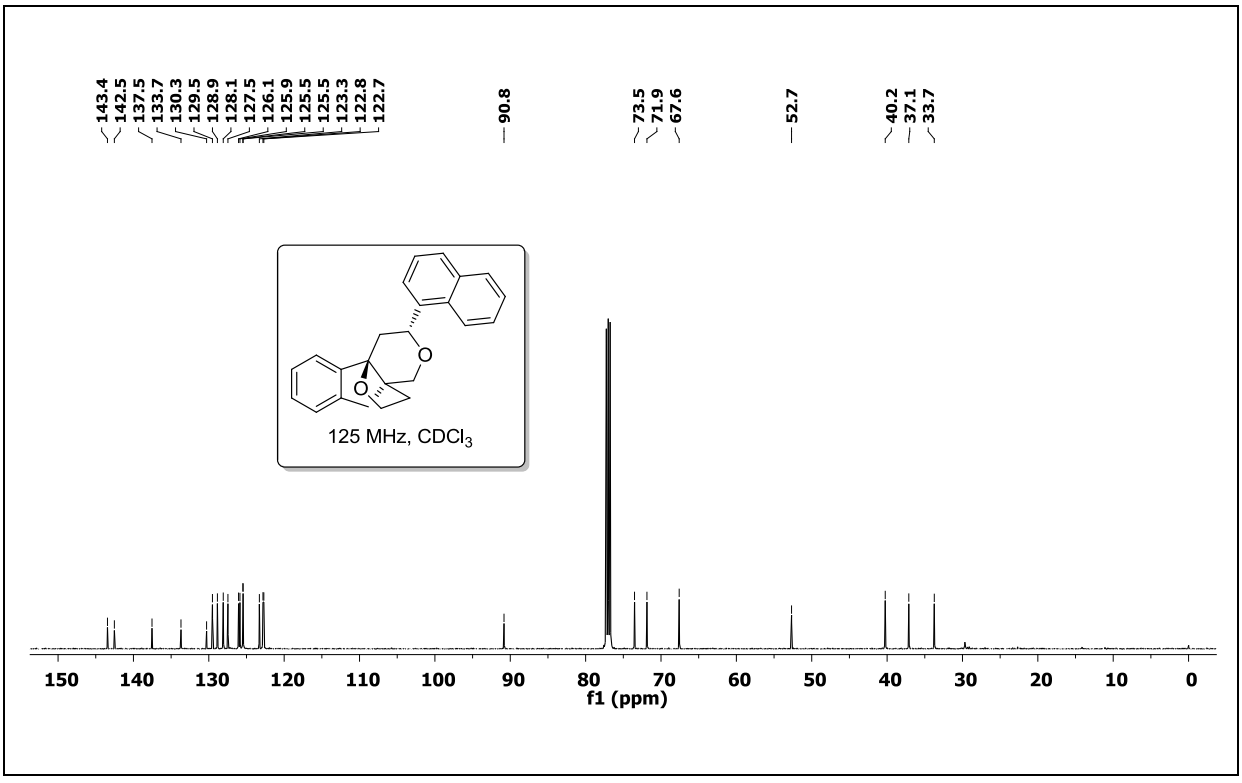
**$^{1}$H and $^{13}$C NMR Spectra of compound 3a (Table 1 entry a):**



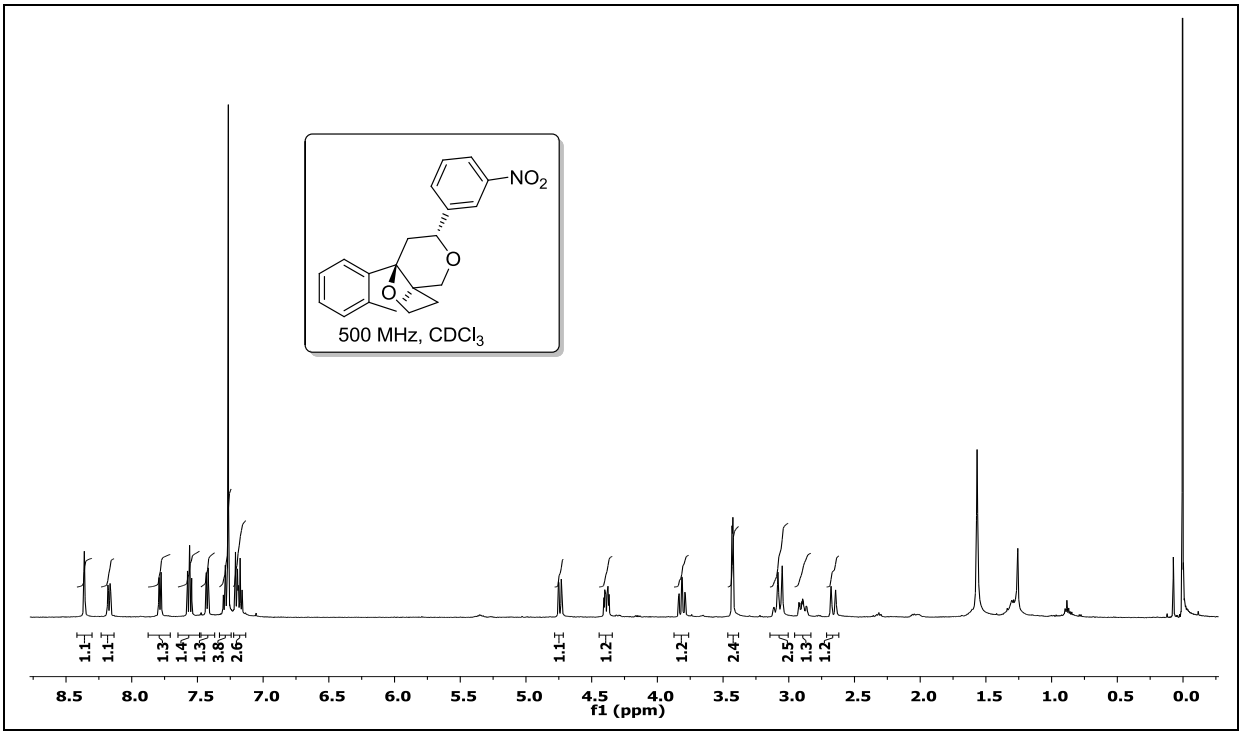



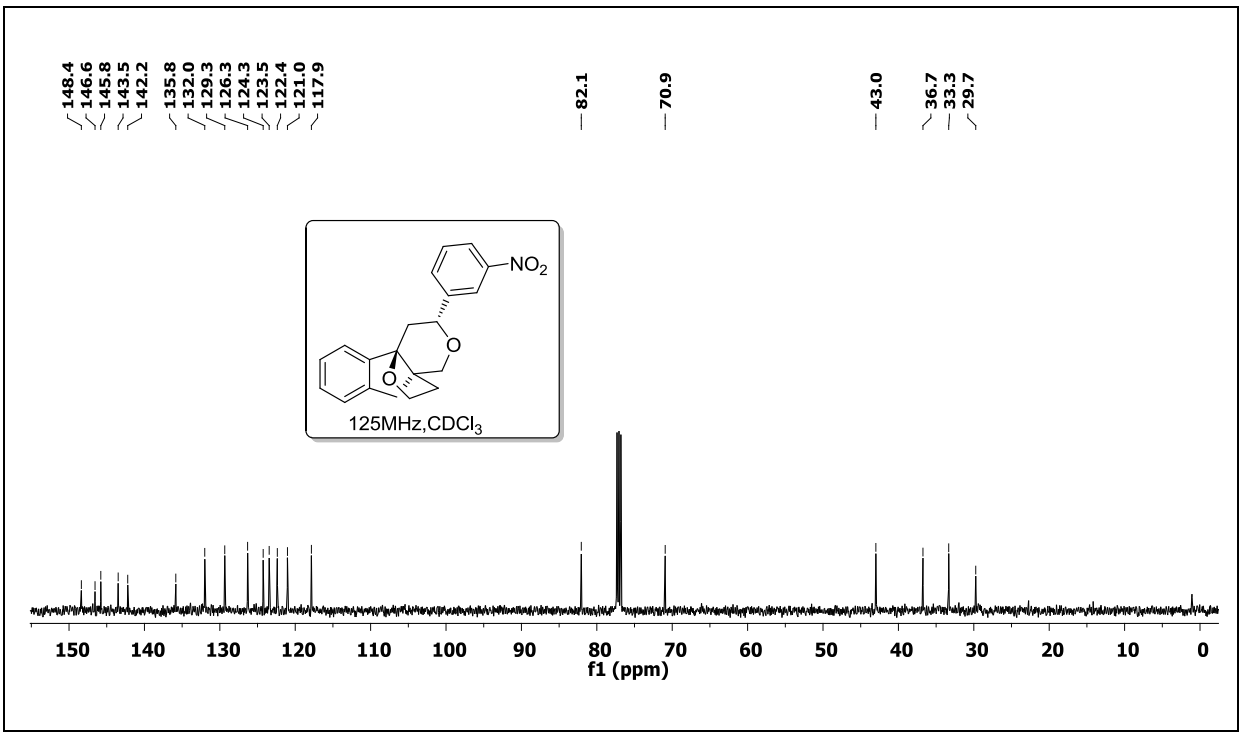
**$^{1}$H and $^{13}$C NMR Spectra of compound 3b (Table 1 entry b):**



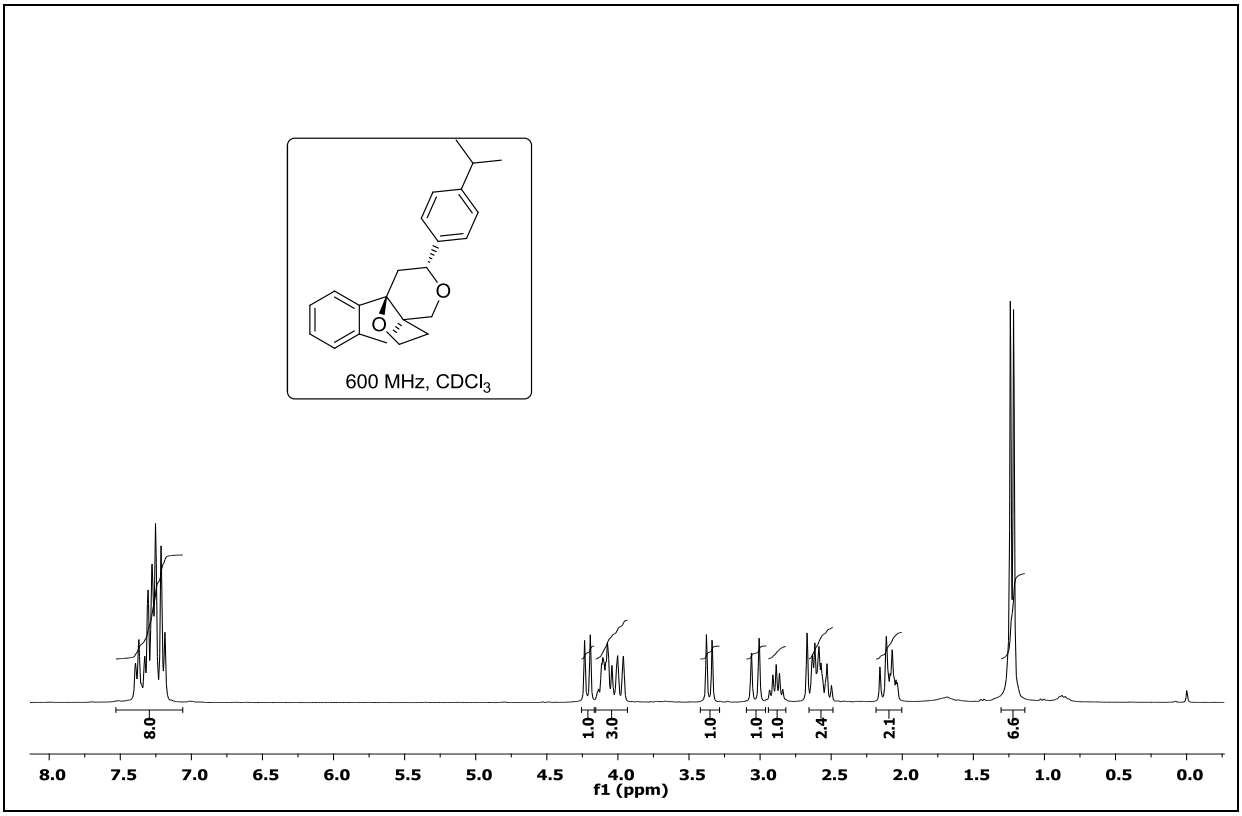



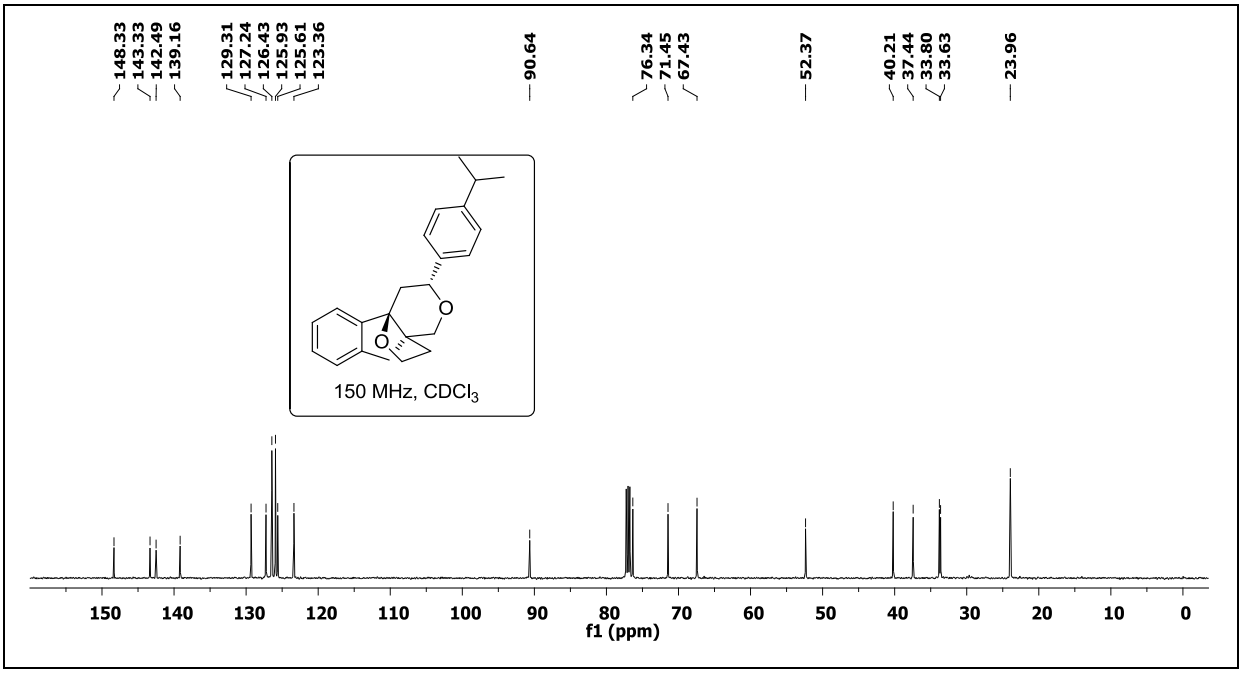
**$^{1}$H and $^{13}$C NMR Spectra of compound 3c (Table1 entry c):**



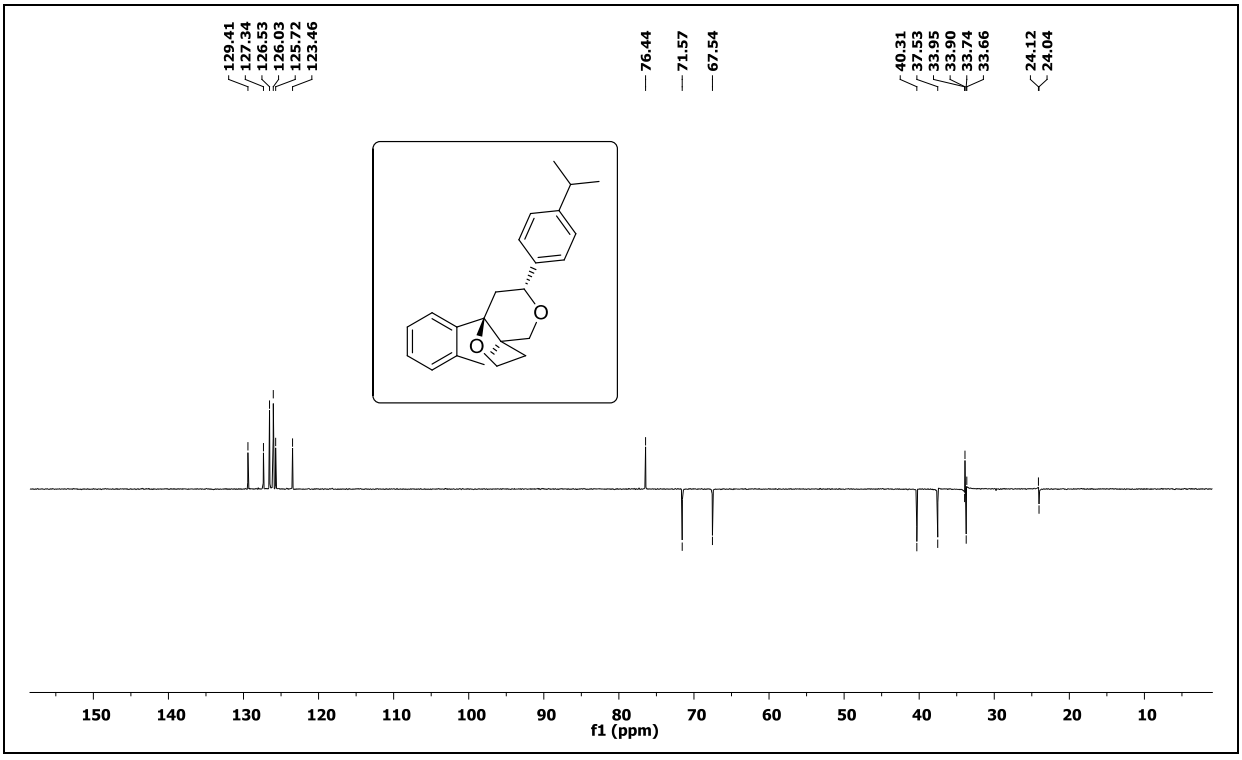



**$^{1}$H and $^{13}$C NMR Spectra of compound 3d (Table 1 entry d):**

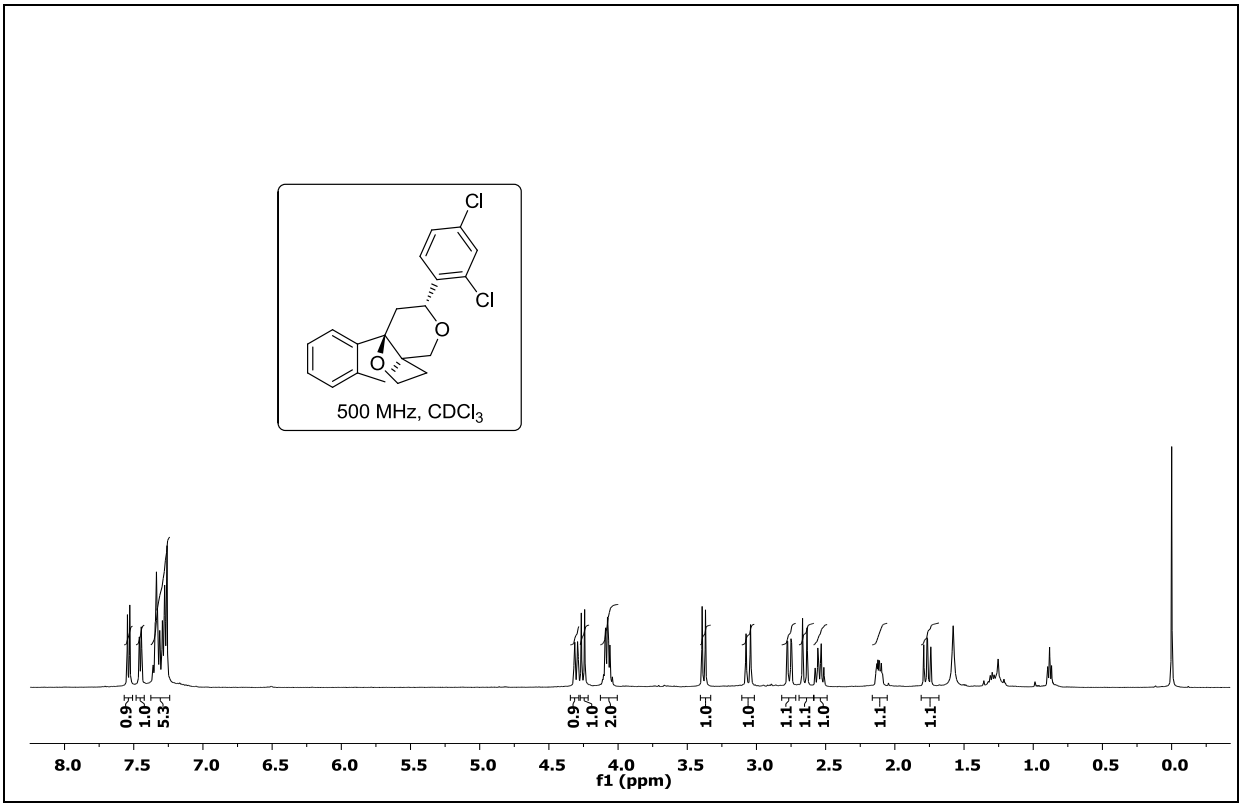


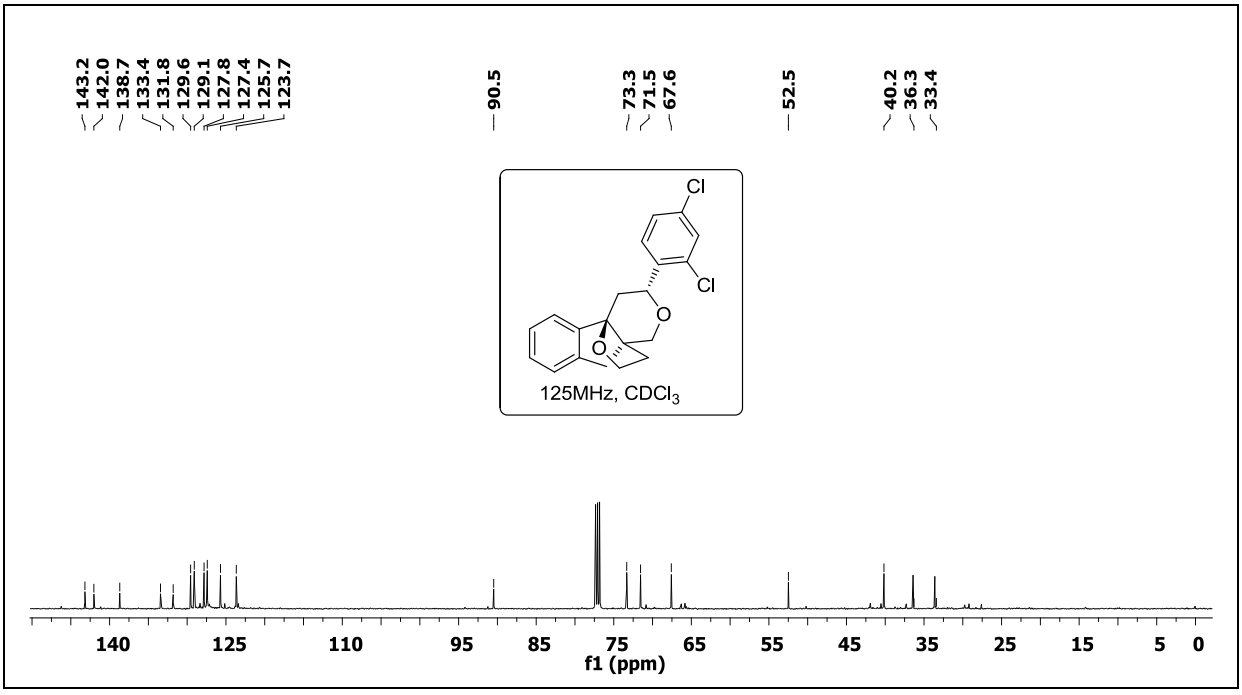



**DEPT-135 NMR Spectra of compound 3d (Table 1 entry d):**

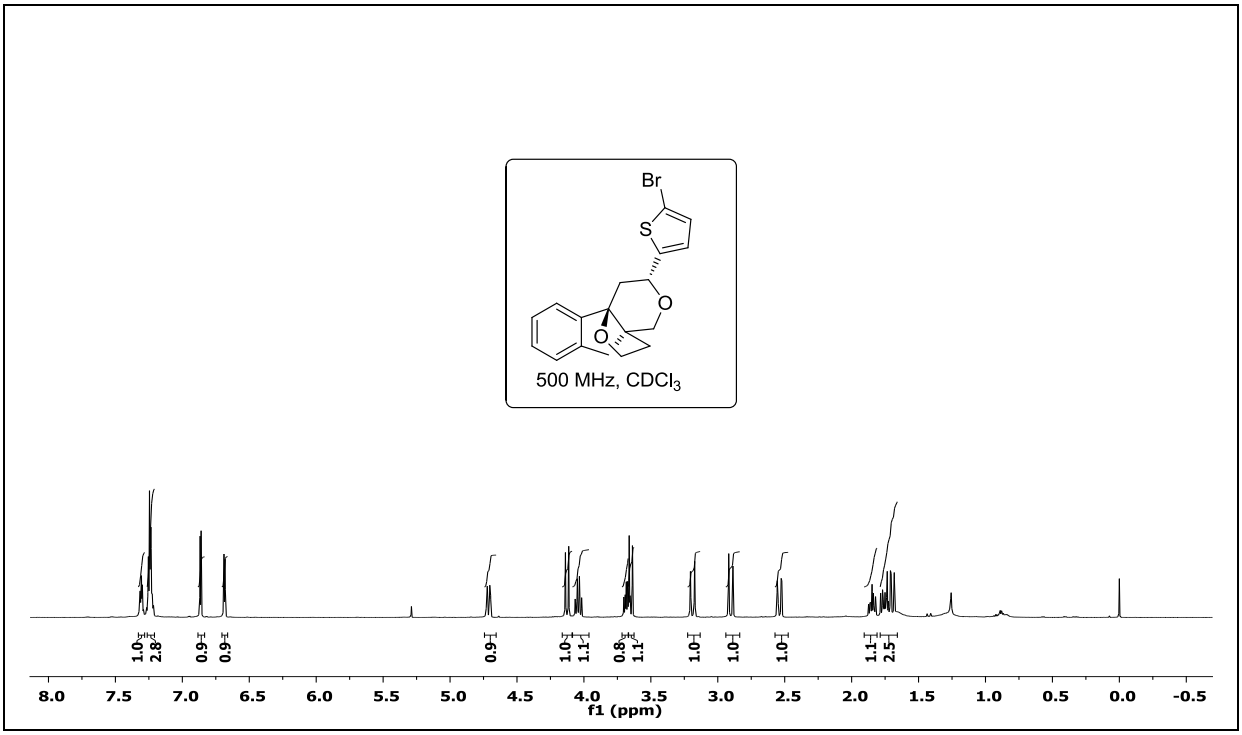


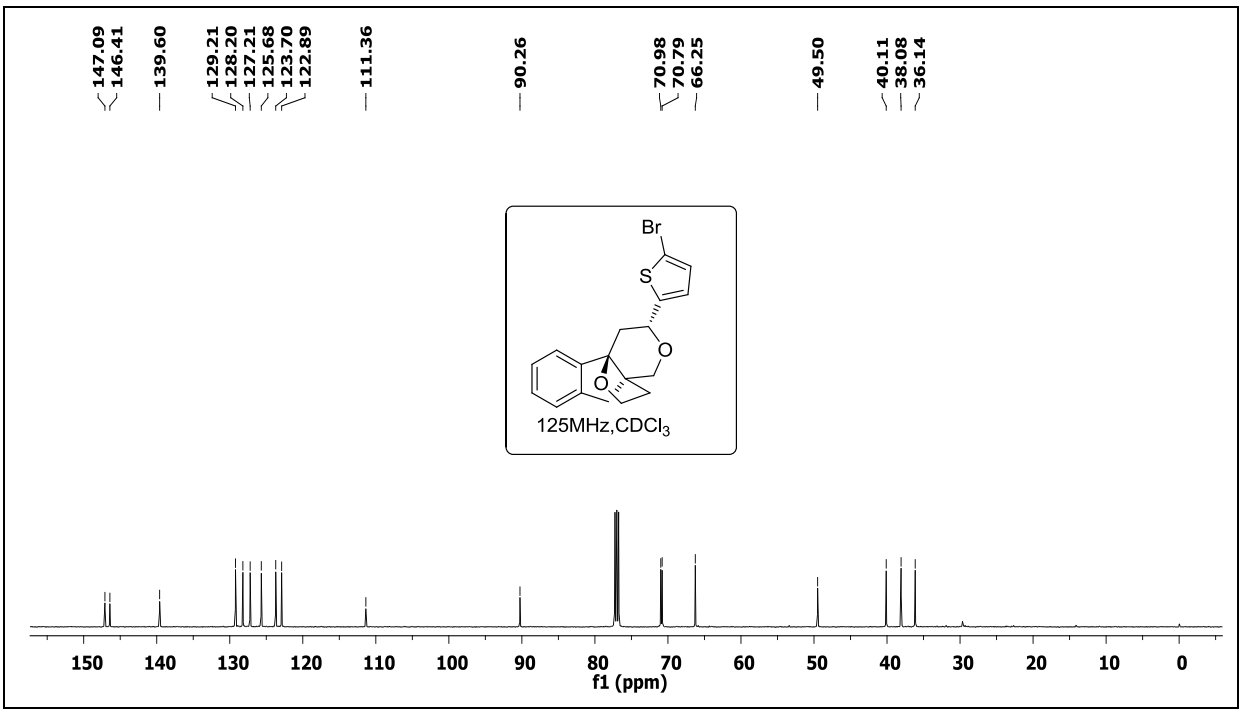
**$^{1}$H and $^{13}$C NMR Spectra of compound 3e (Table 1 entry e):**



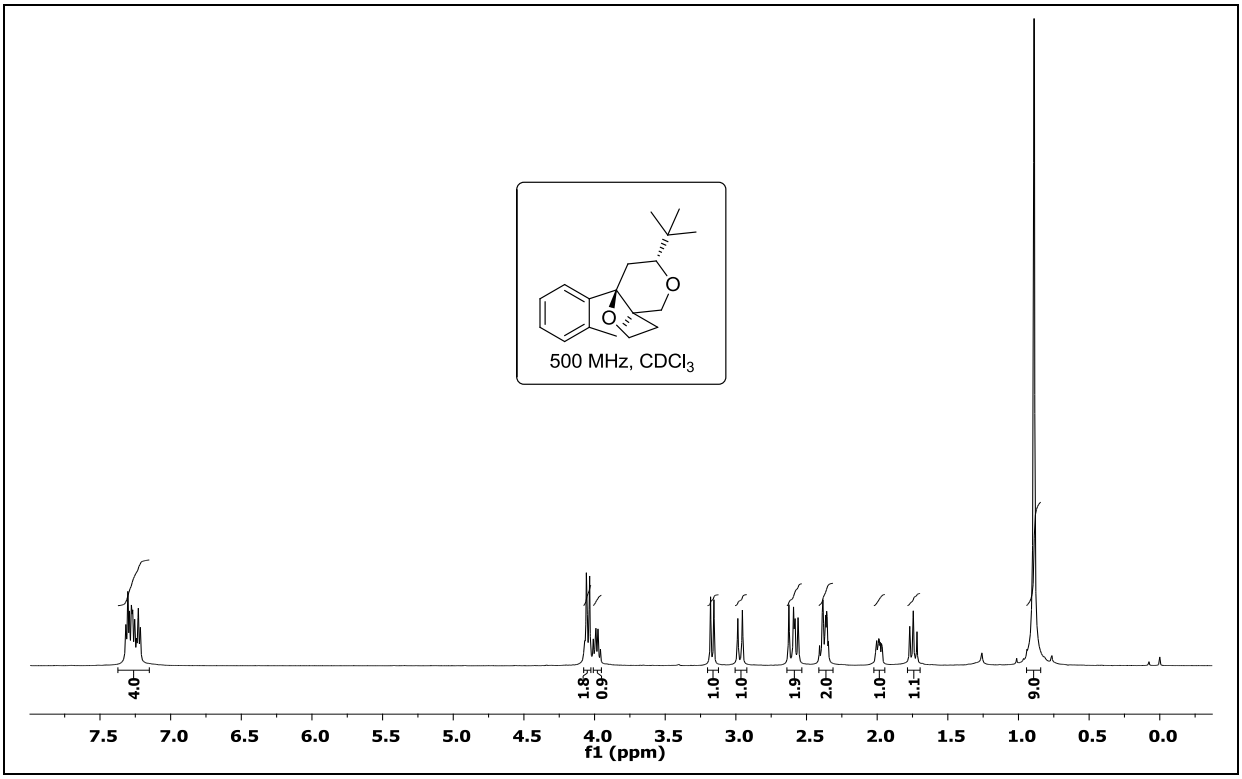



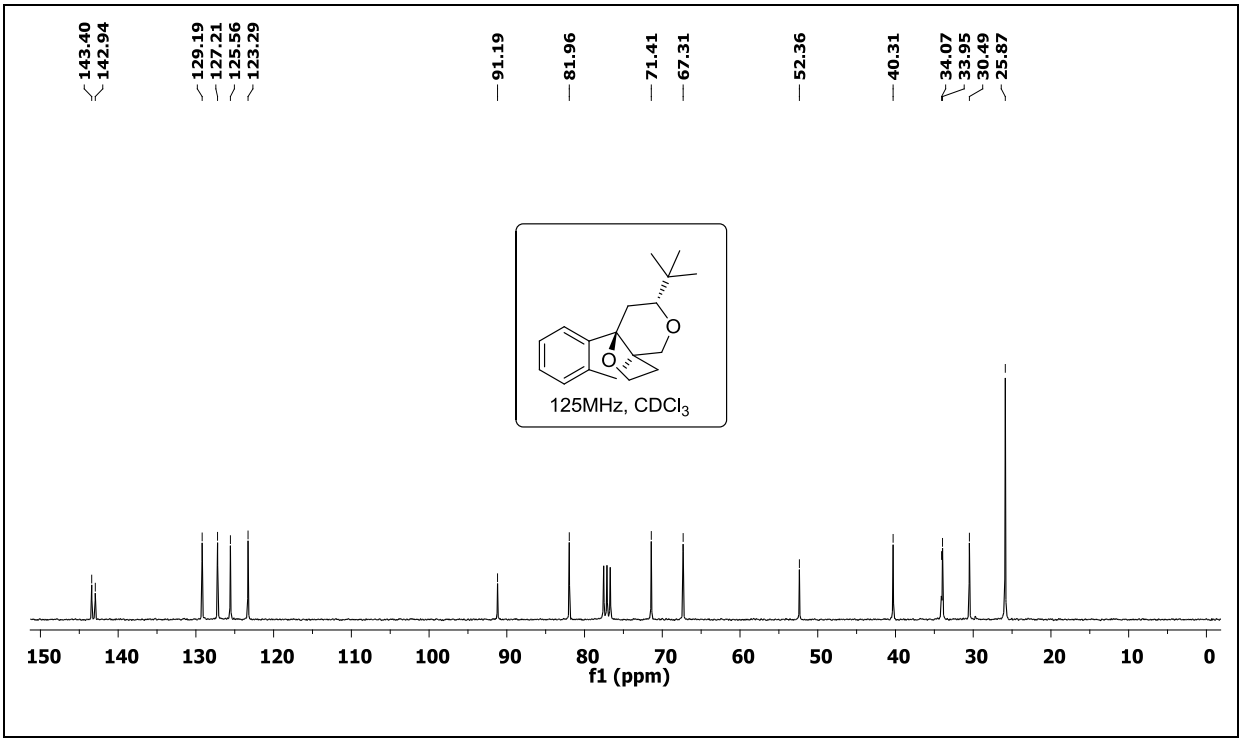
**$^{1}$H and $^{13}$C NMR Spectra of compound 3f (Table 1 entry f):**



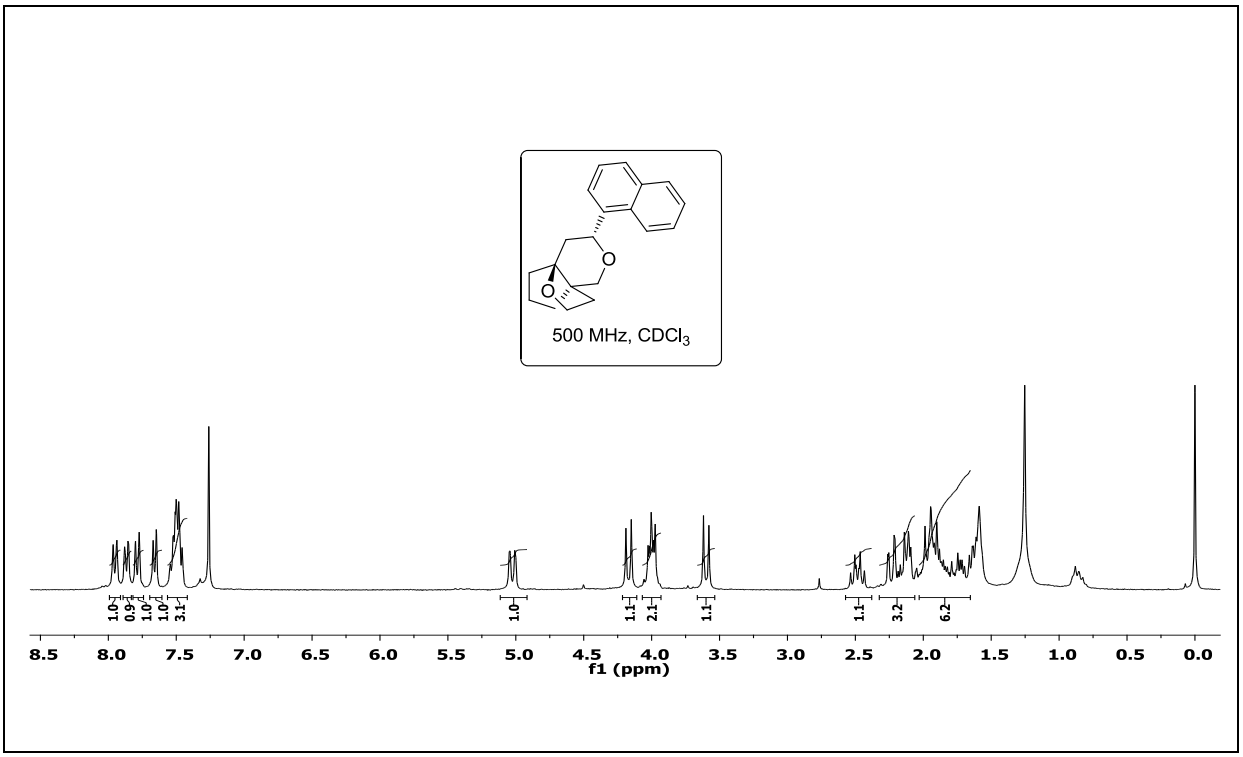



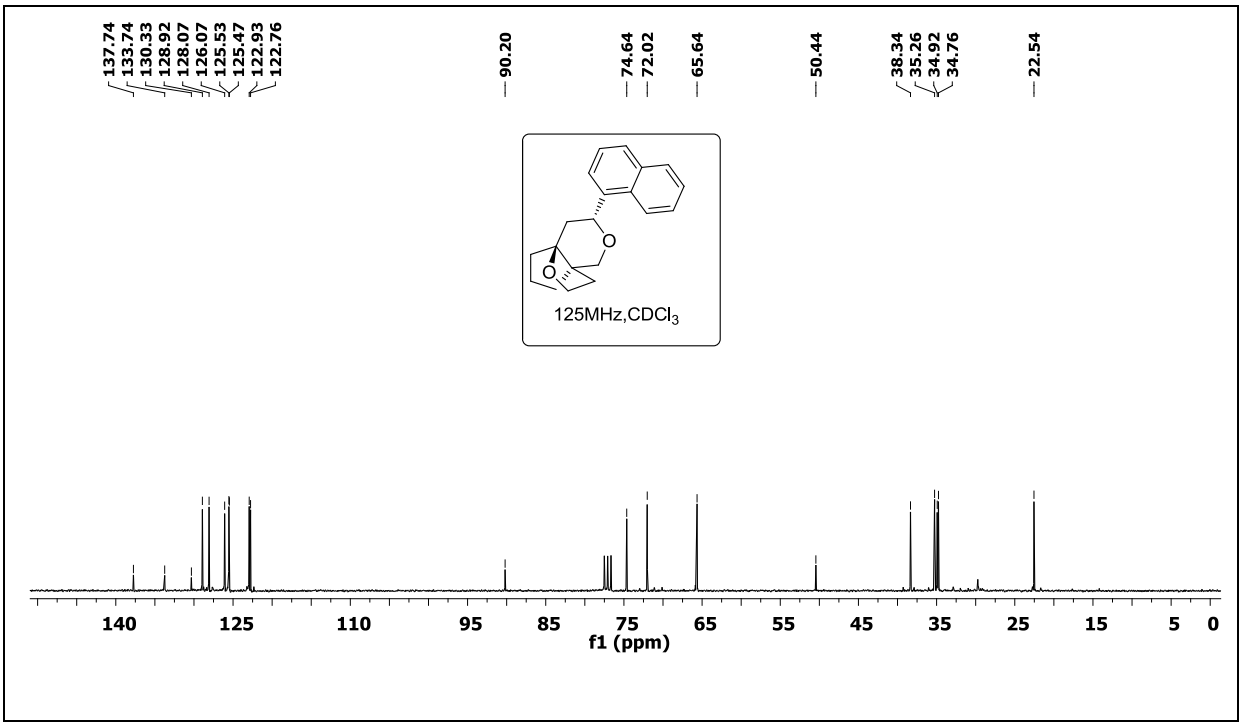
**$^{1}$H and $^{13}$C NMR Spectra of compound 3g (Table 1 entry g):**



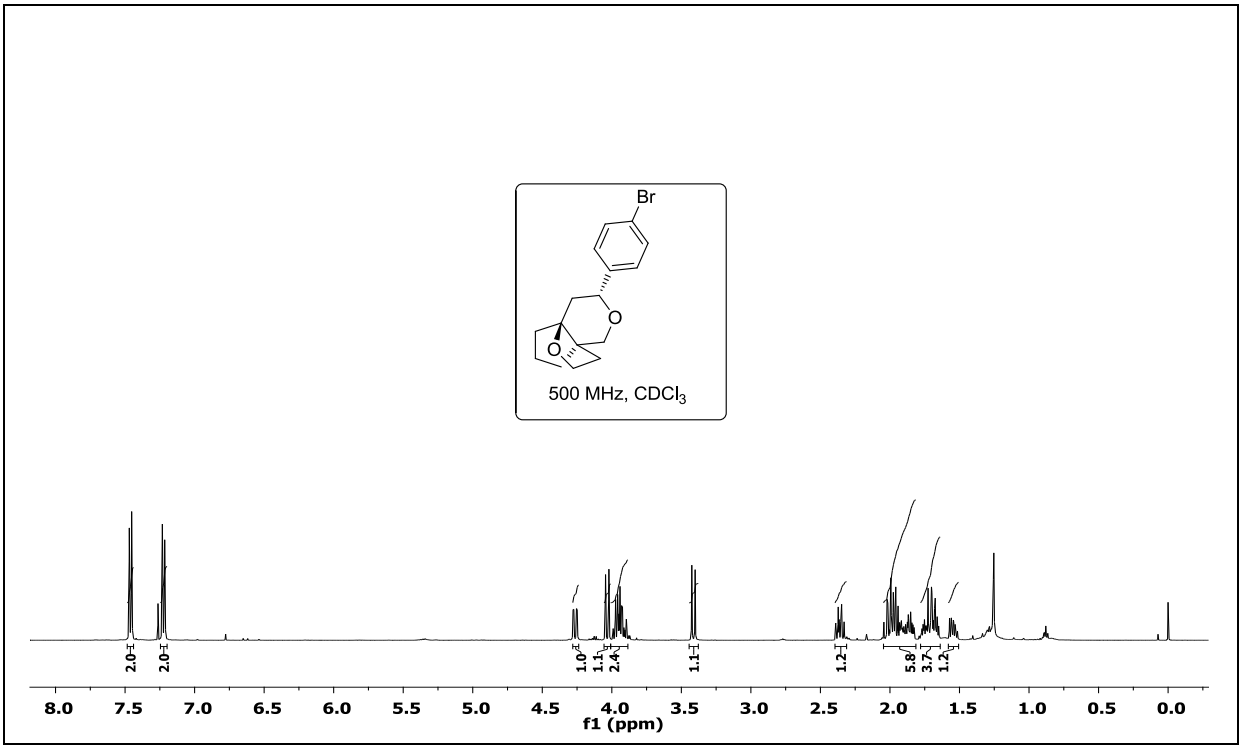



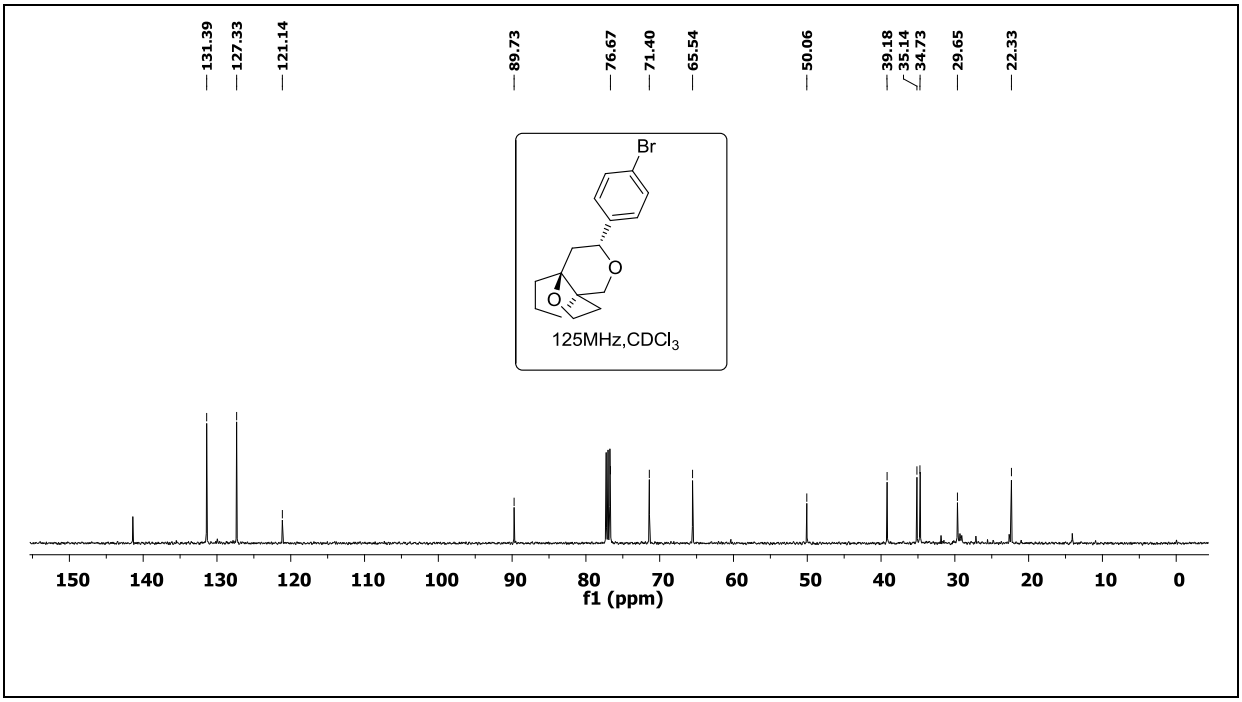
**$^{1}$H and $^{13}$C NMR Spectra of compound 5h (Table 2 entry h):**



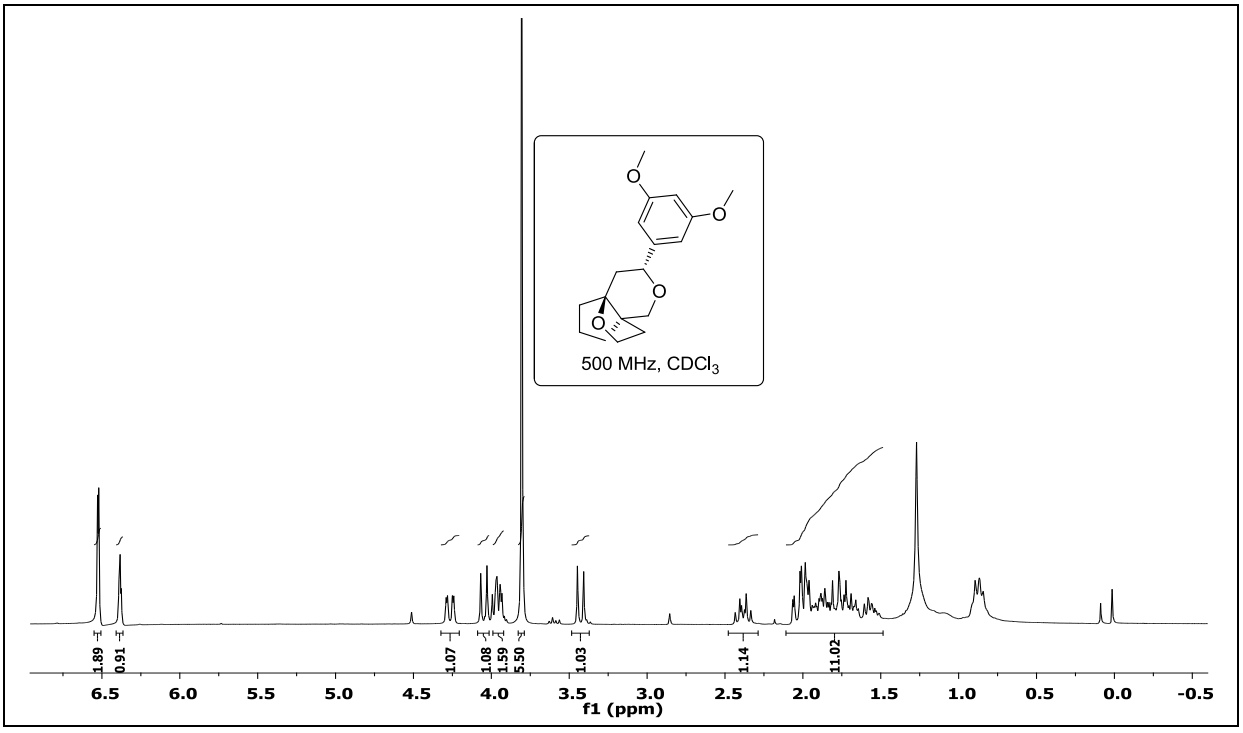



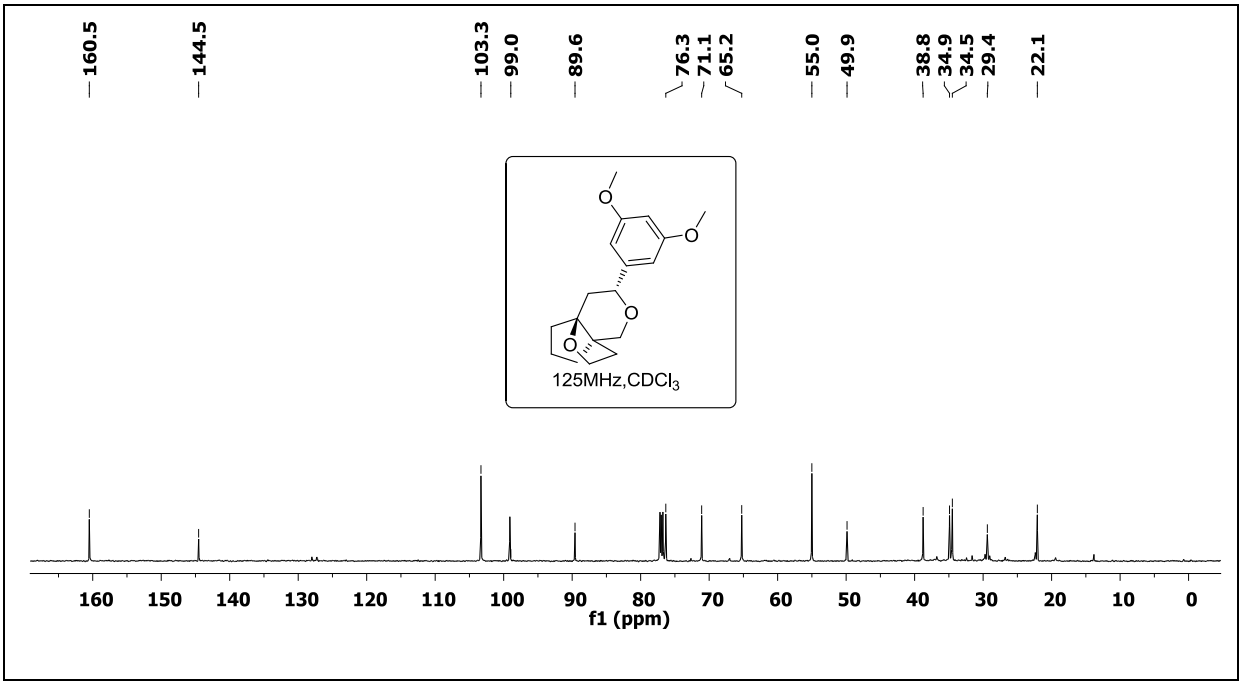
**$^{1}$H and $^{13}$C NMR Spectra of compound 5i (Table 2 entry i):**



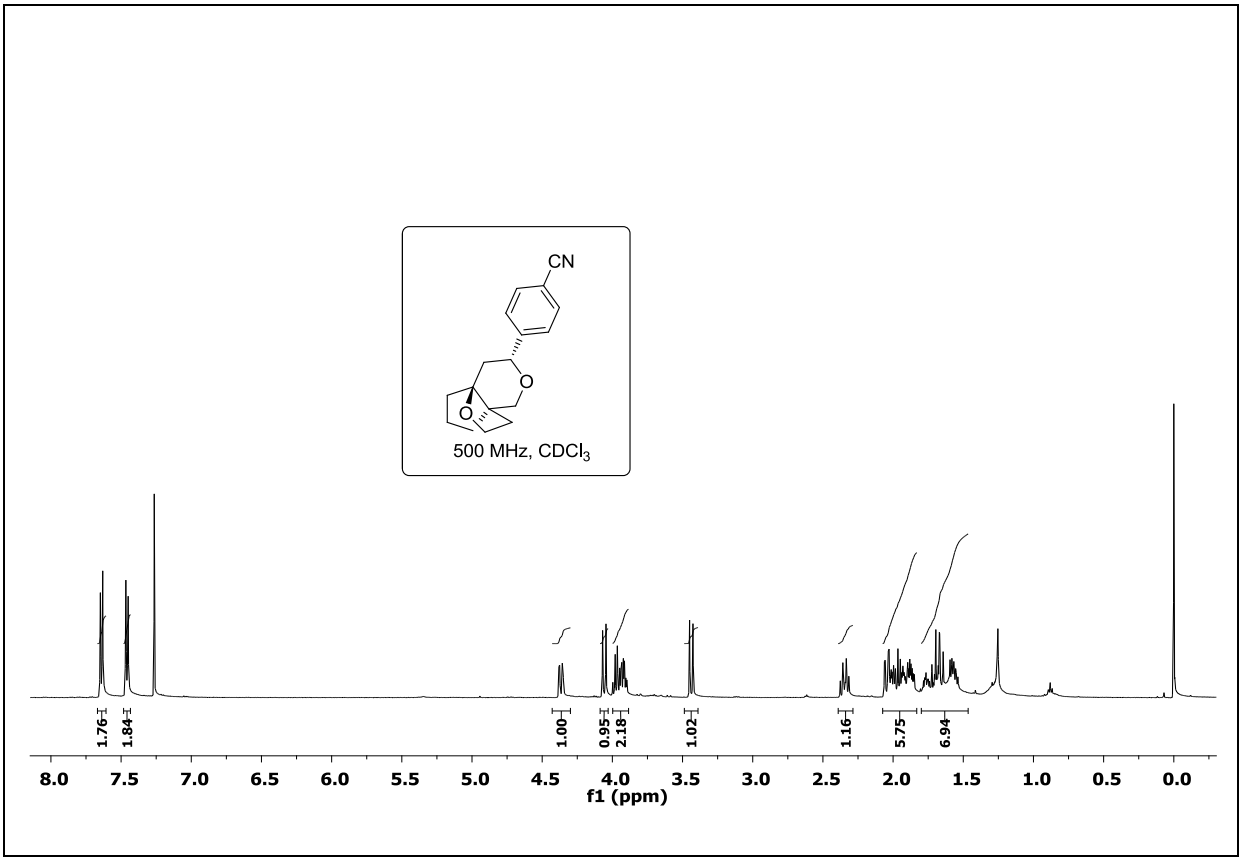



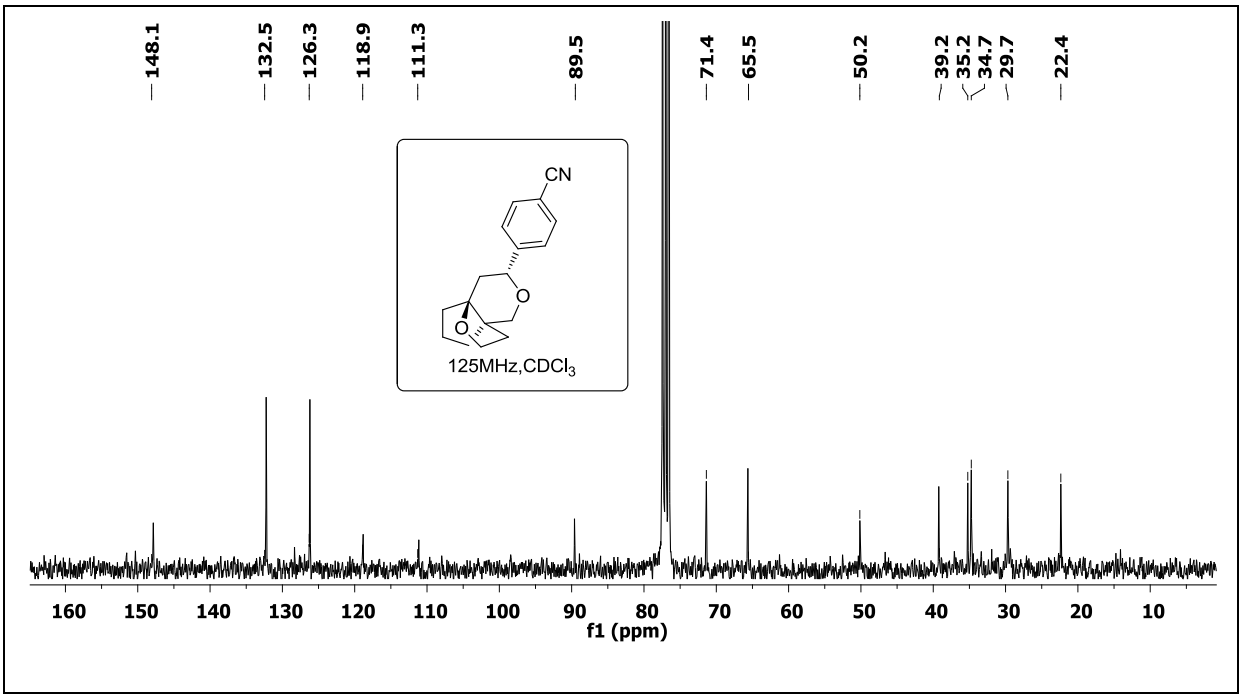
**$^{1}$H and $^{13}$C NMR Spectra of compound 5j (Table 2 entry j):**



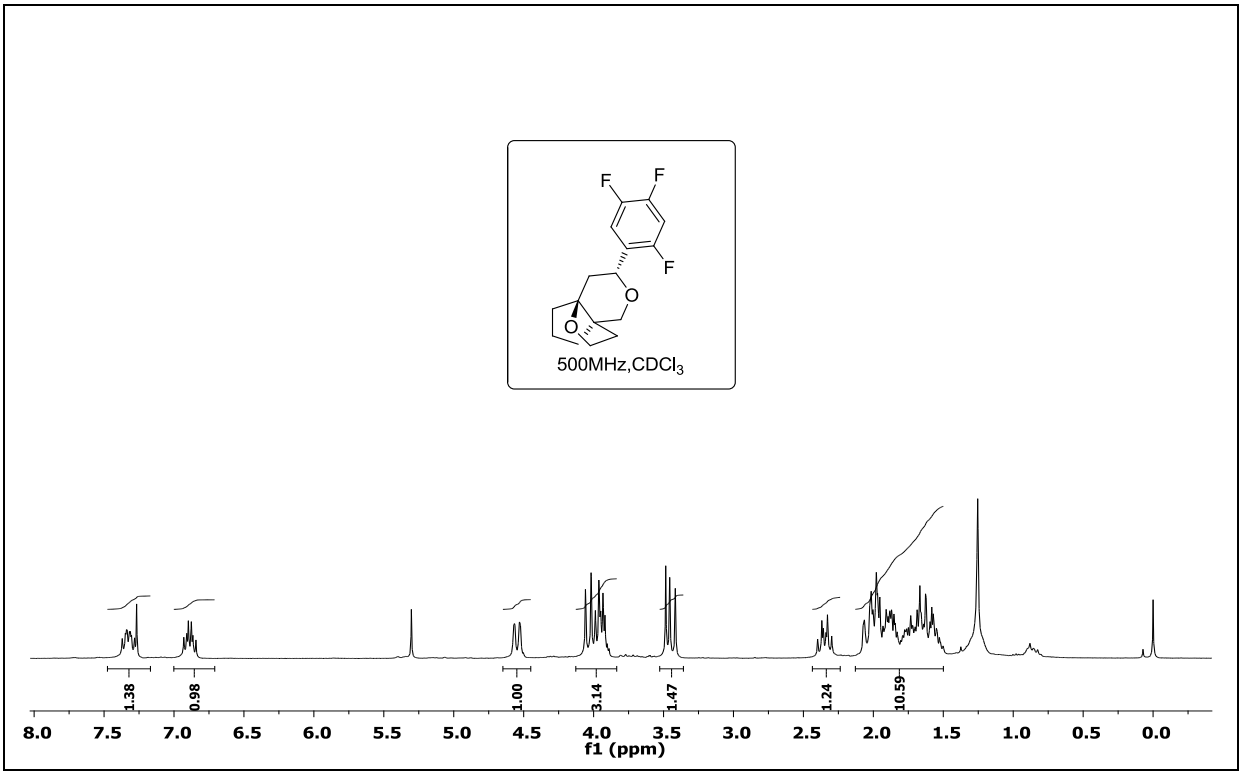



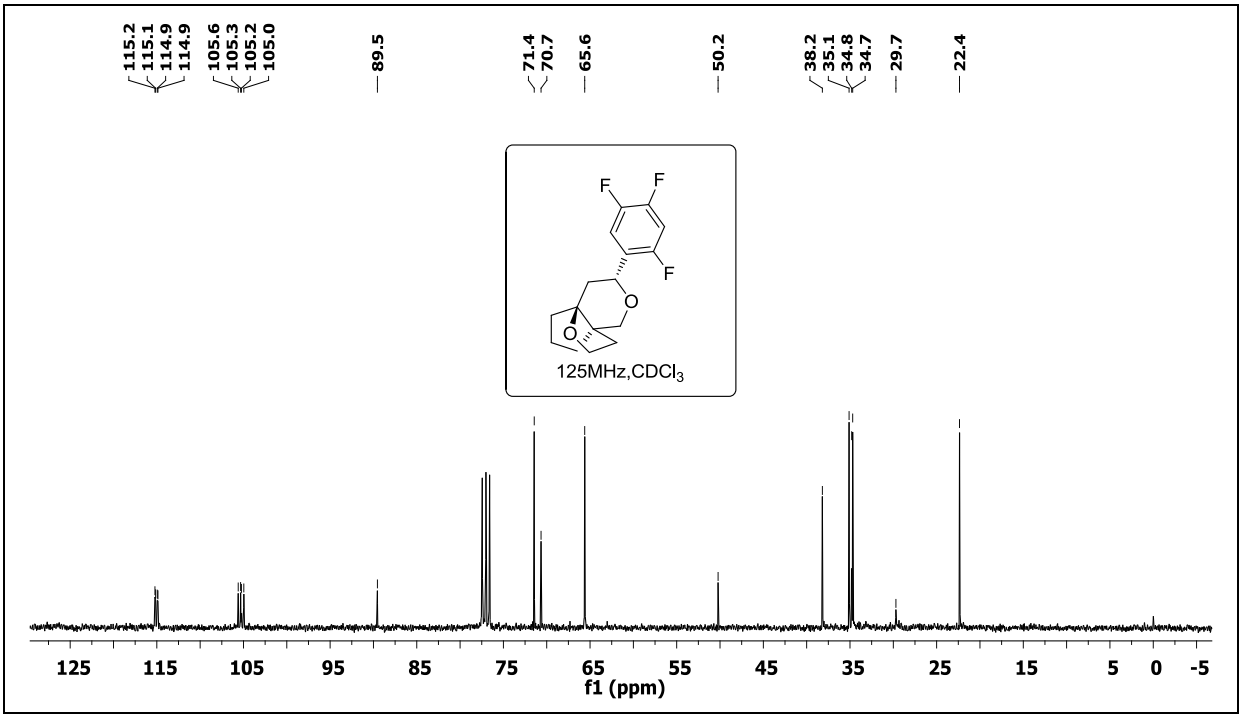
**$^{1}$H and $^{13}$C NMR Spectra of compound 5k (Table 2 entry k):**



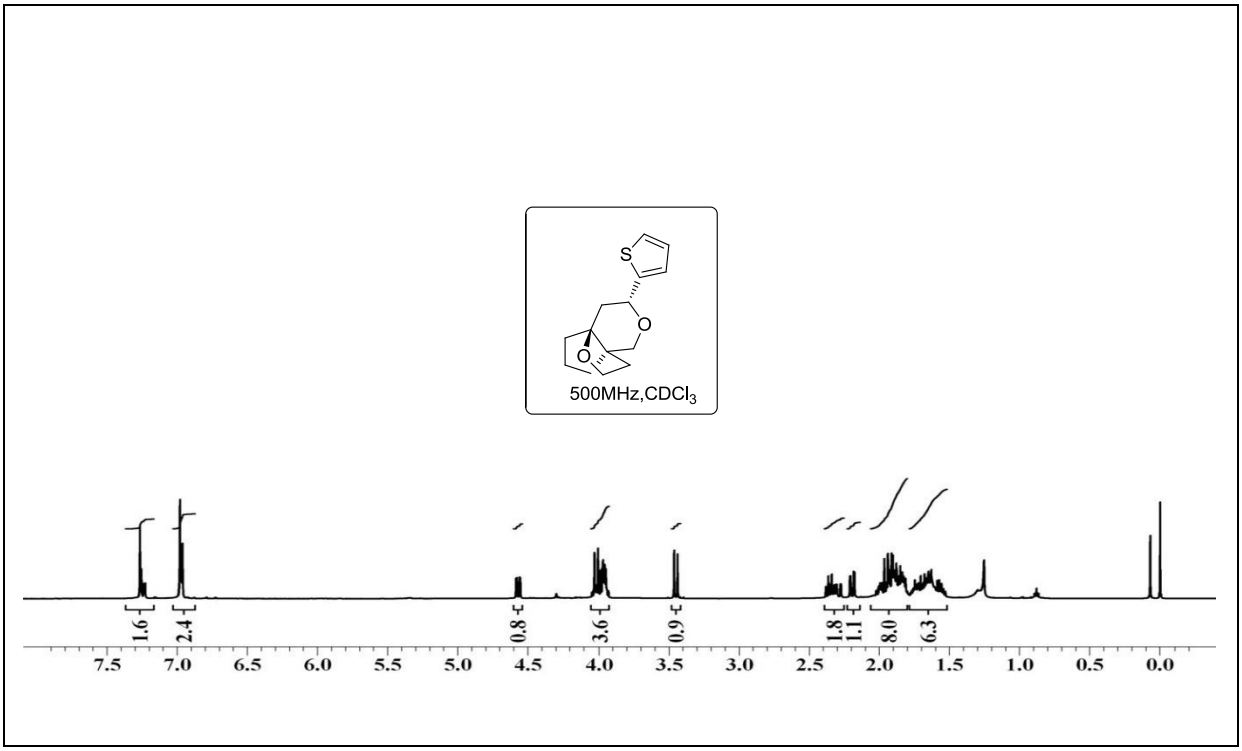



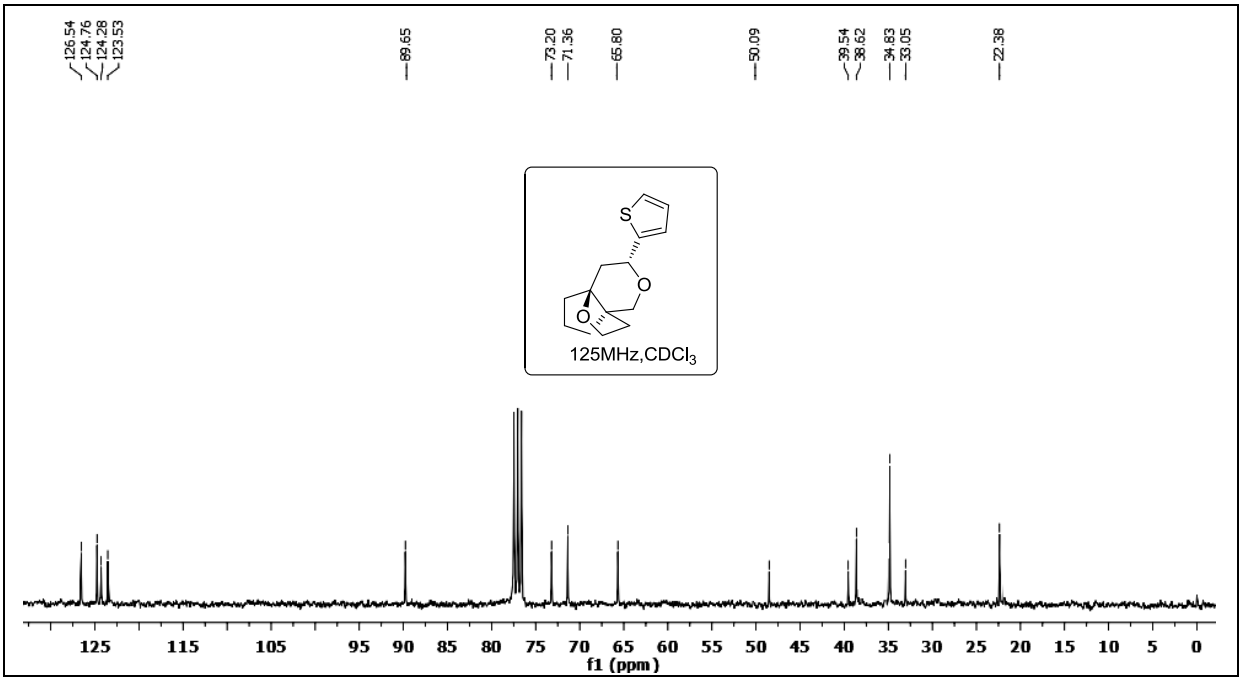
**$^{1}$H and $^{13}$C NMR Spectra of compound 5l (Table 2 entry l):**



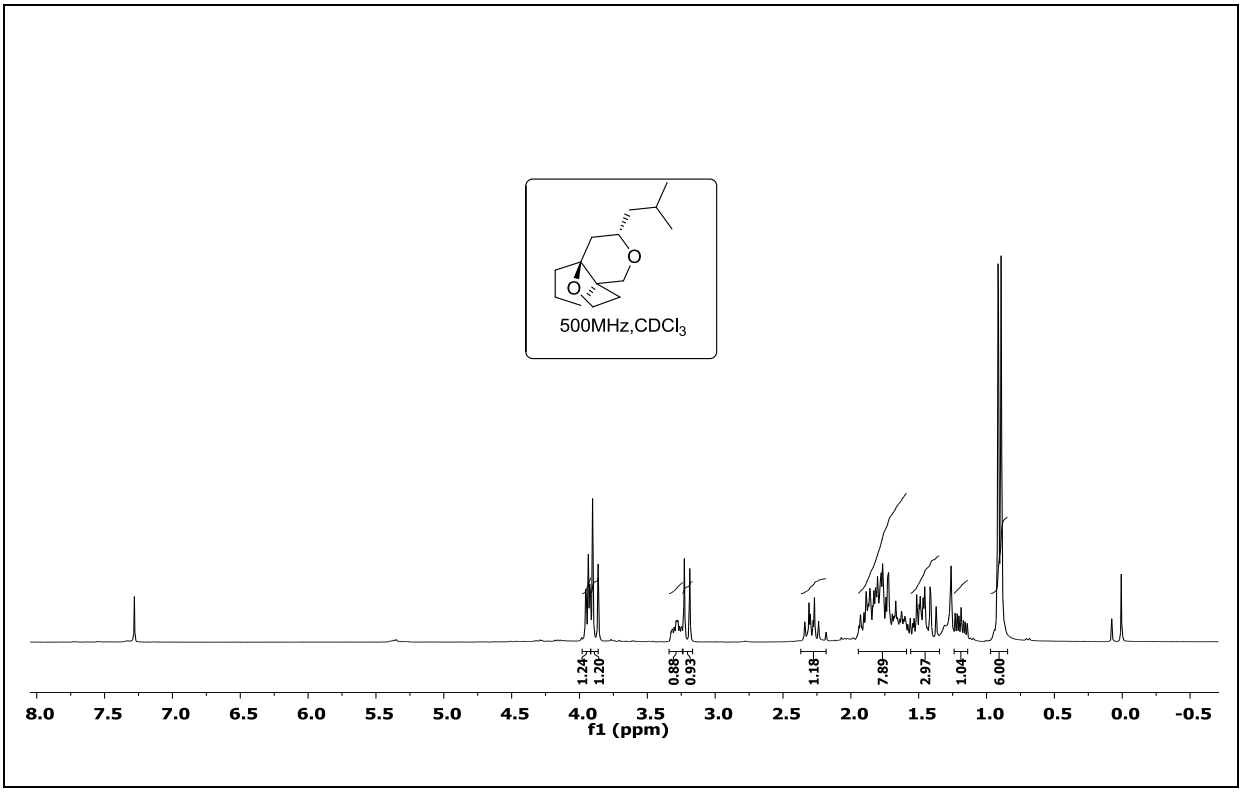



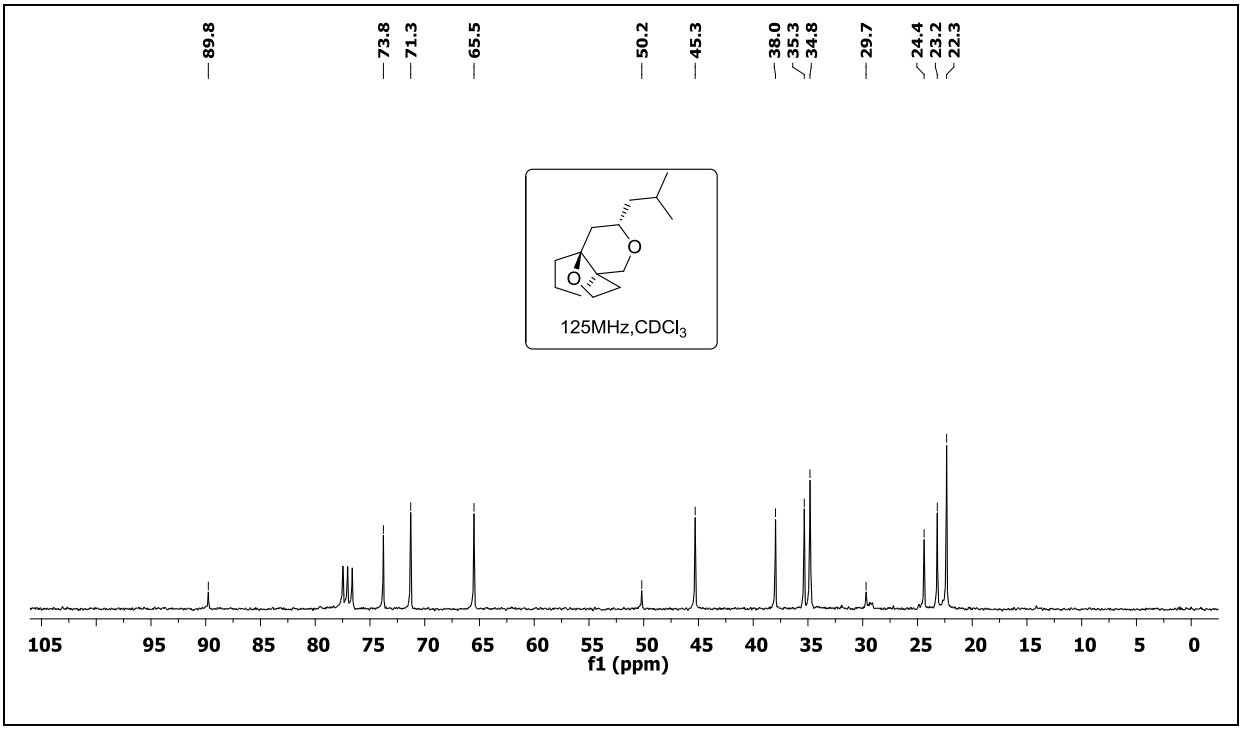
**$^{1}$H and $^{13}$C NMR Spectra of compound 5m (Table 2 entry m):**



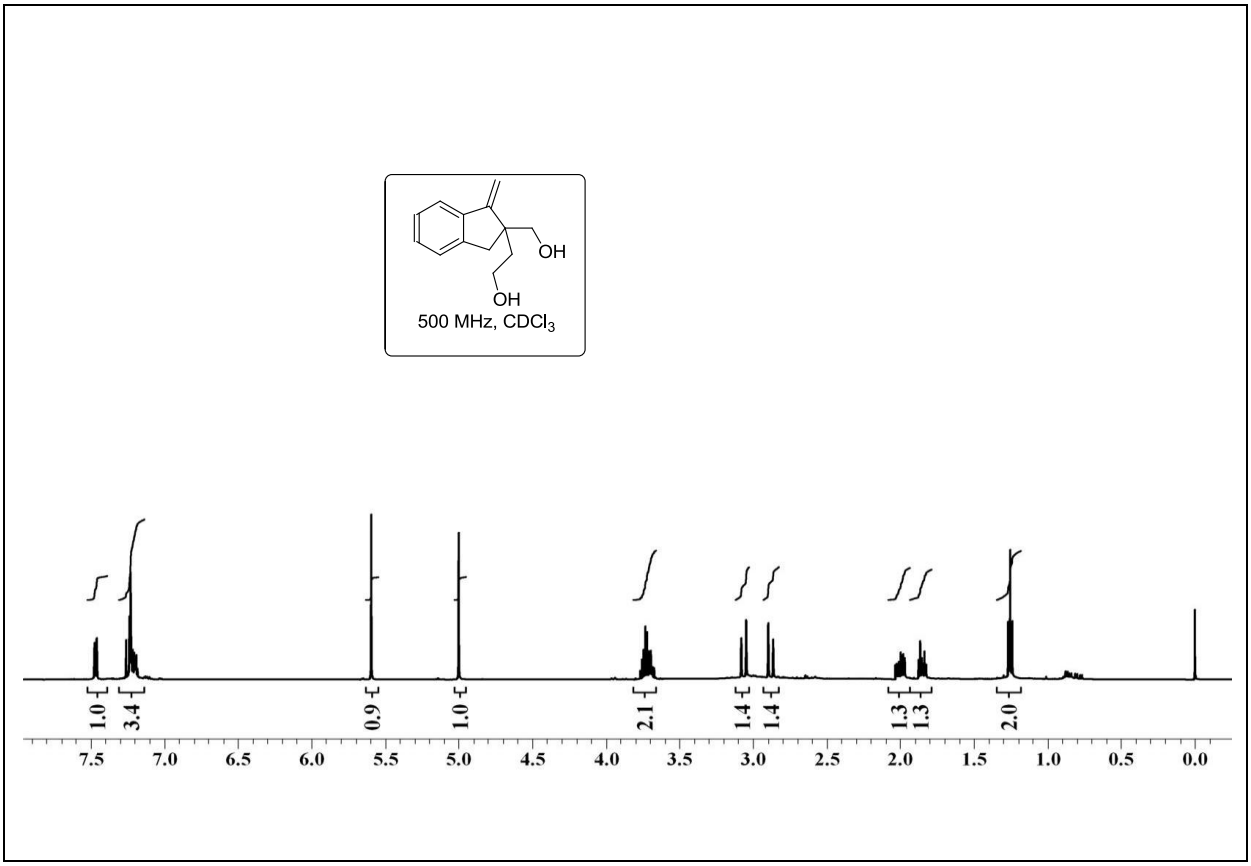



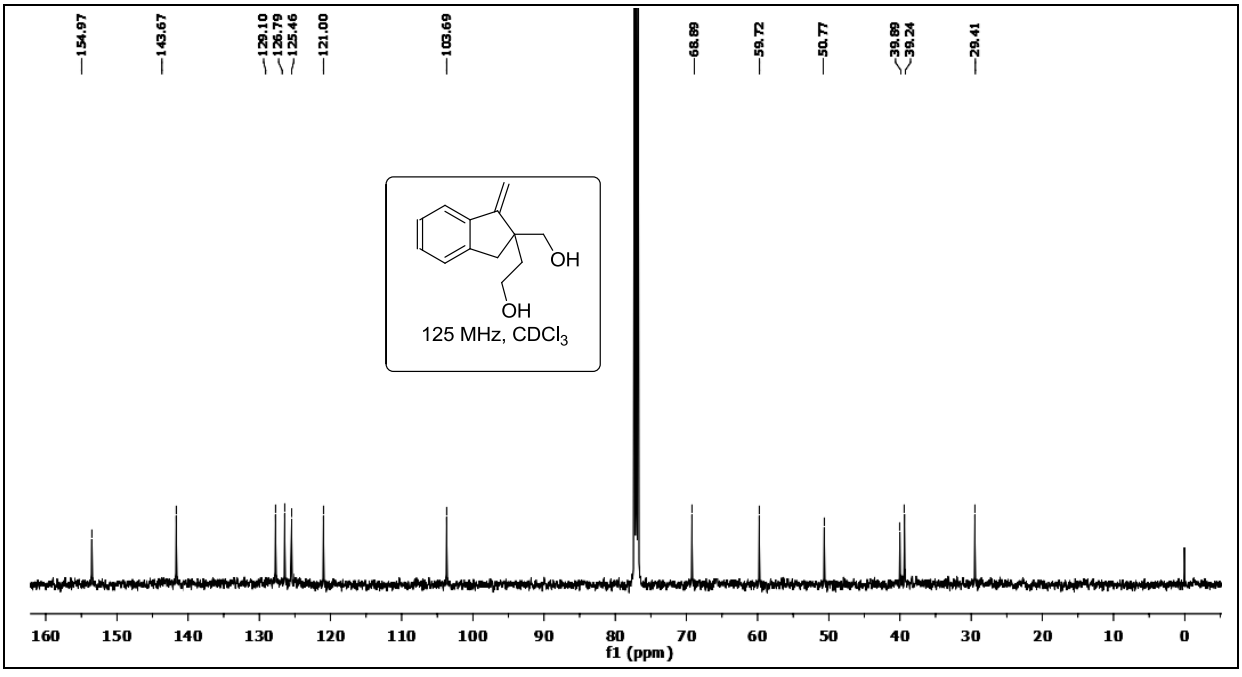
**$^{1}$H and $^{13}$C NMR Spectra of compound 5n (Table 2 entry n):**



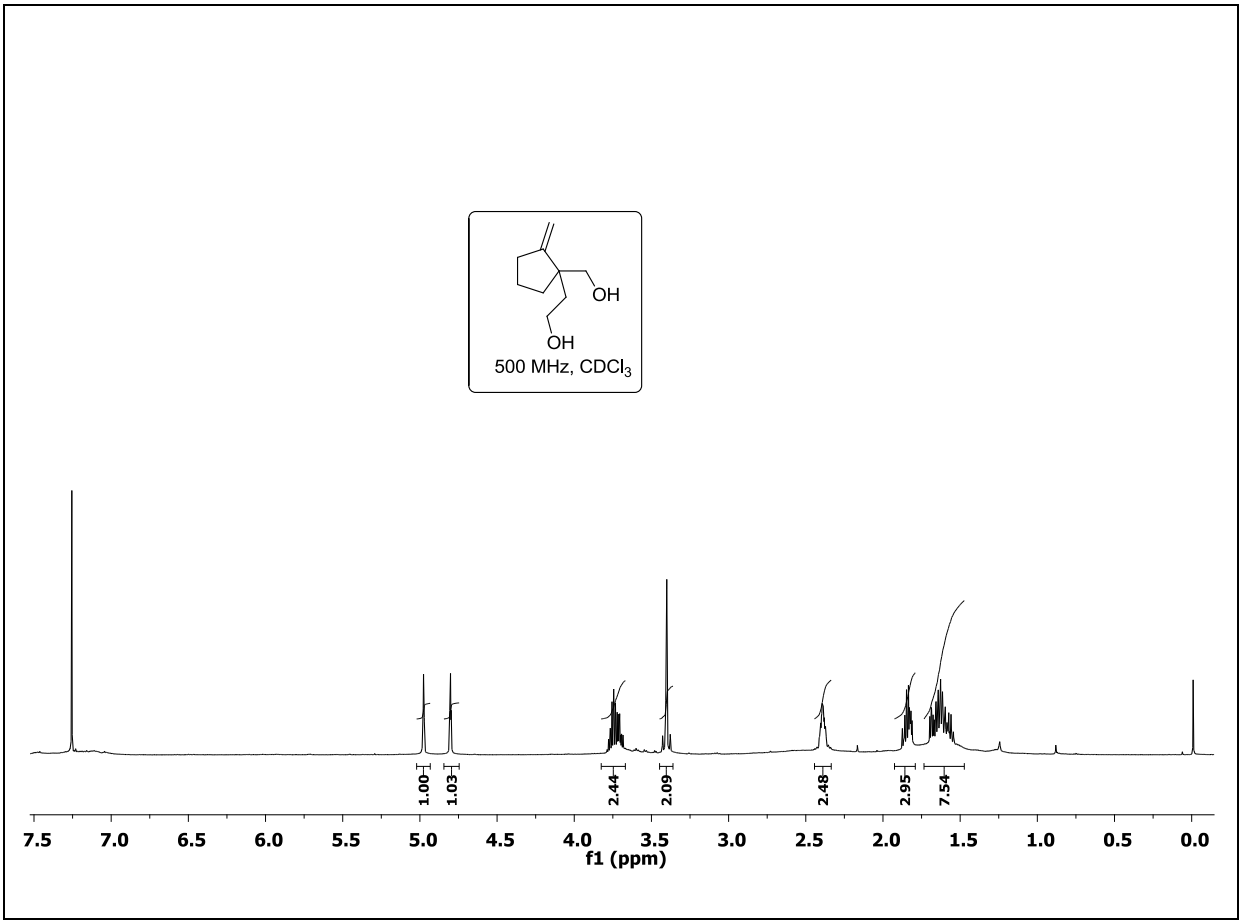



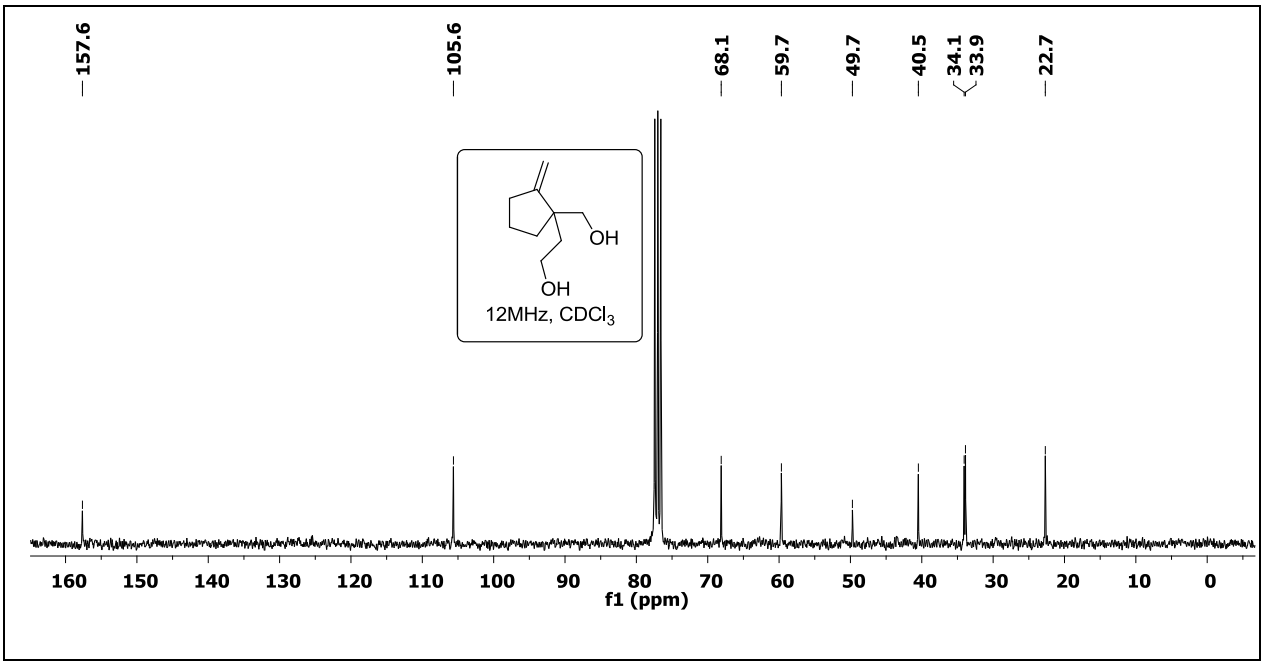
**$^{1}$H and $^{13}$C NMR Spectra of compound 1:**



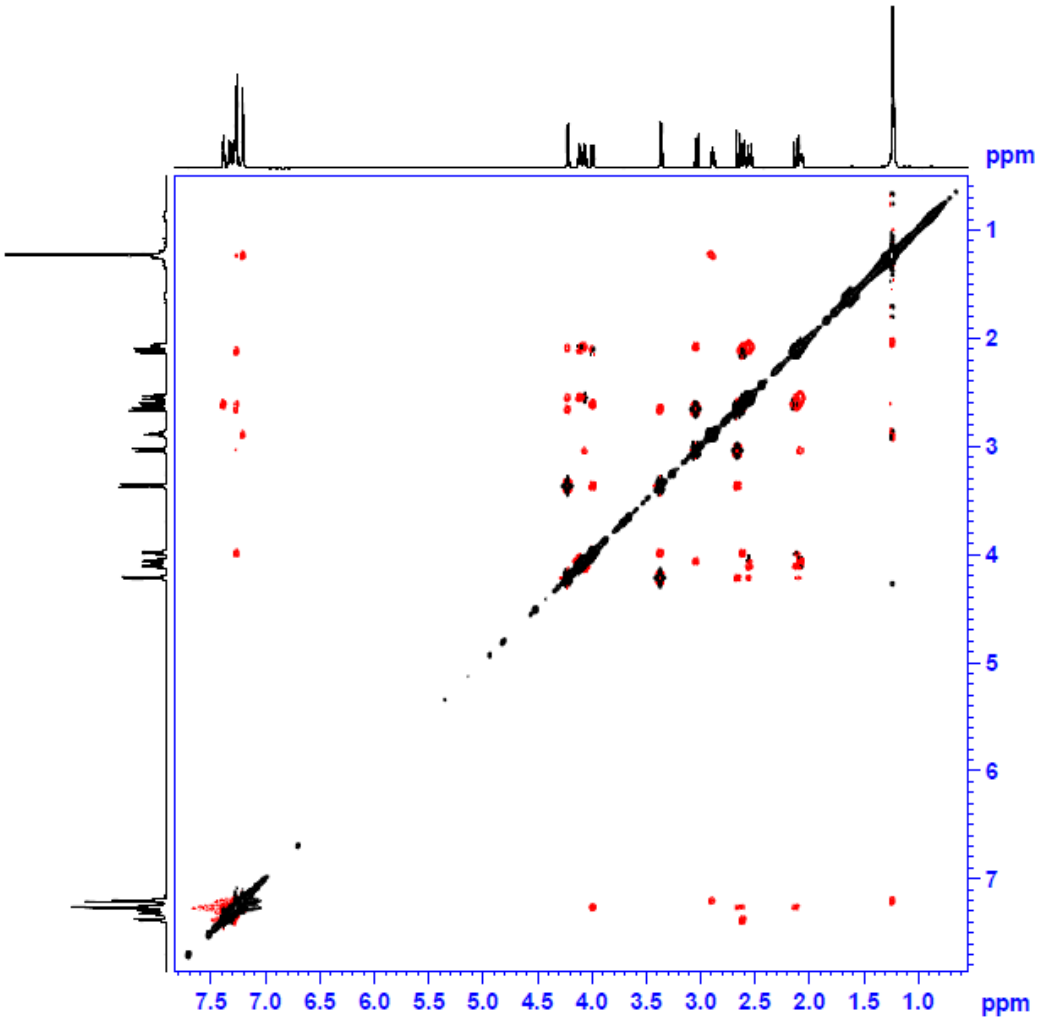



**$^{1}$H and $^{13}$C NMR Spectra of compound 4:**

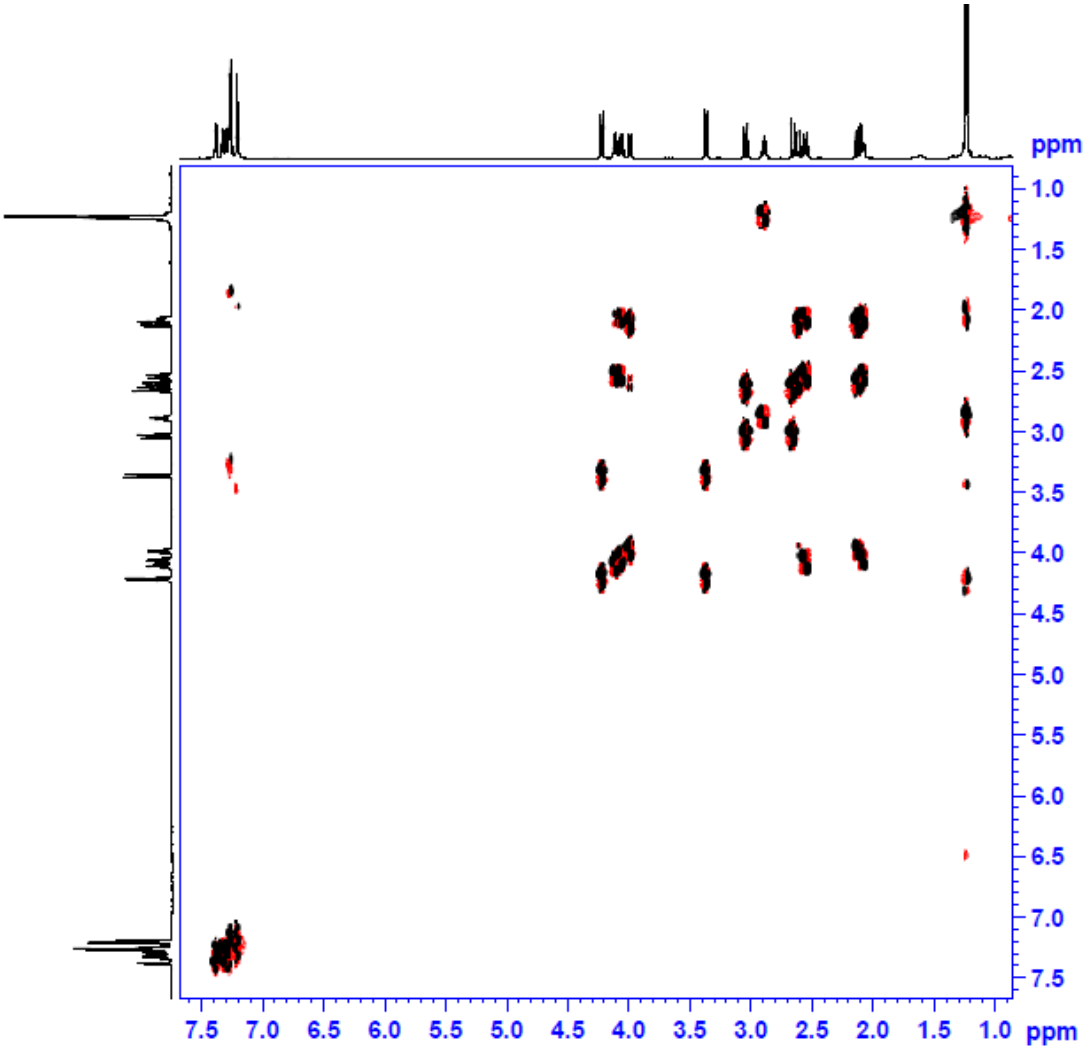


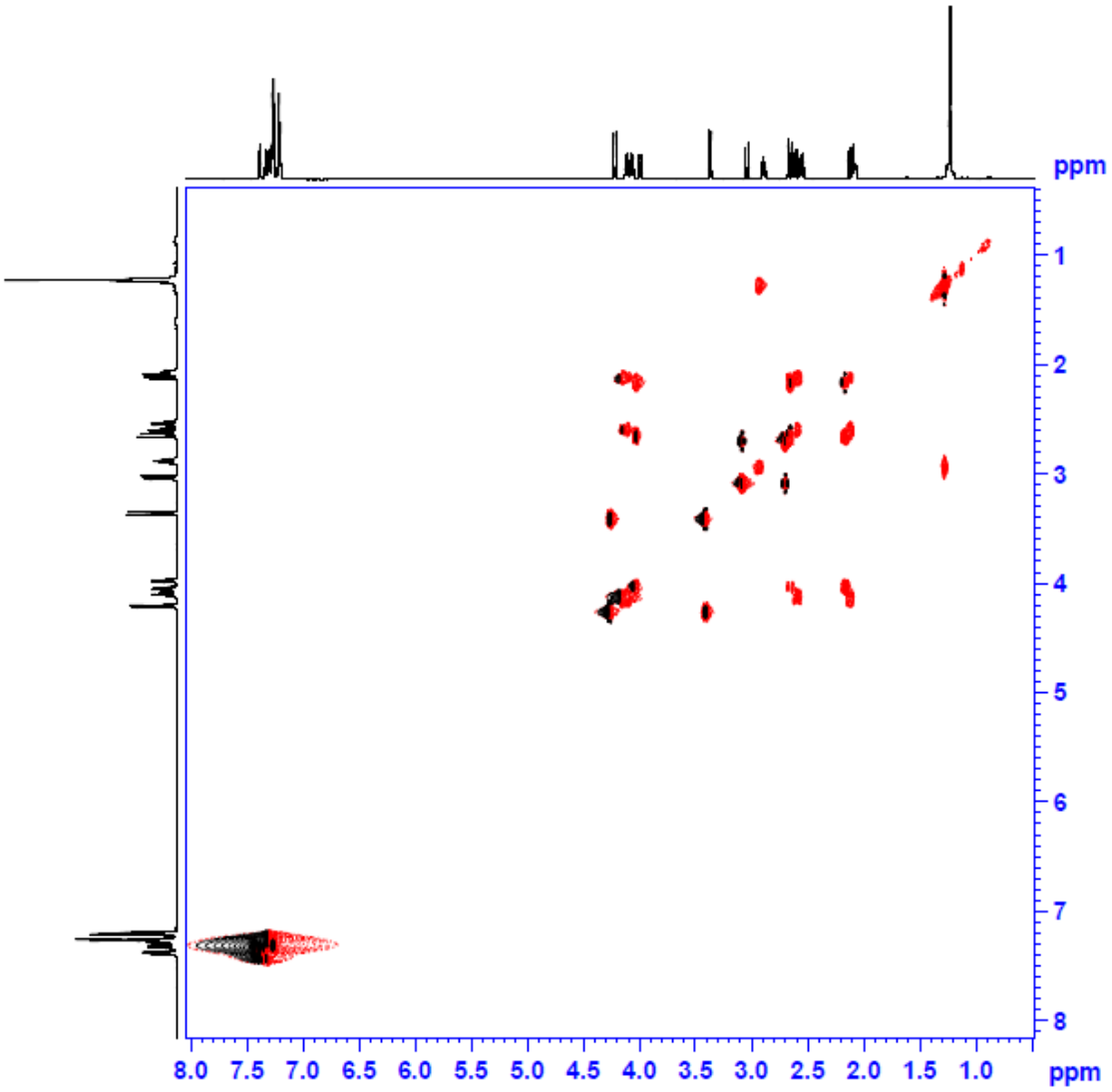
**NOESY spectrum of 3d**



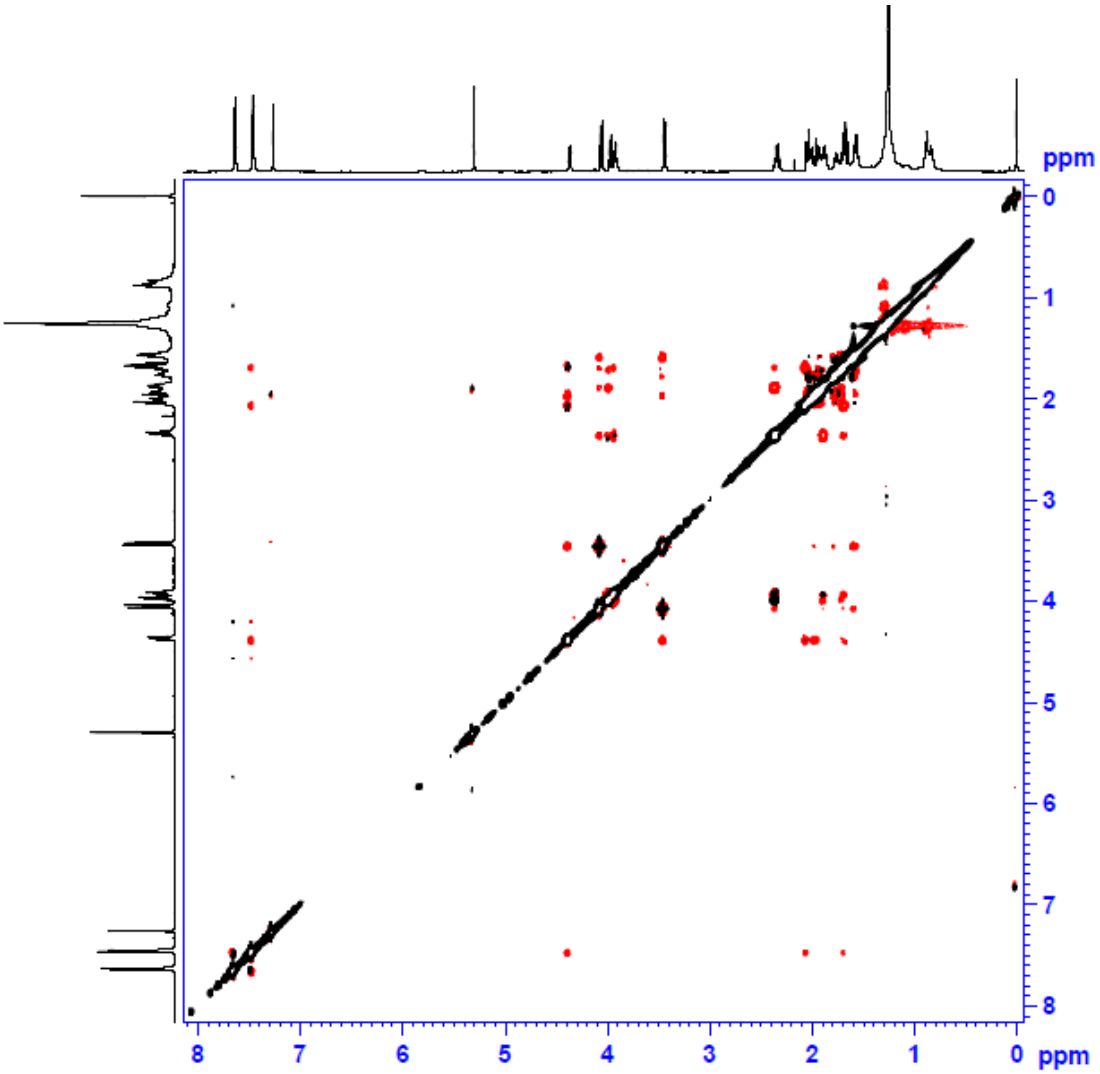
**COSY spectrum of 3d**



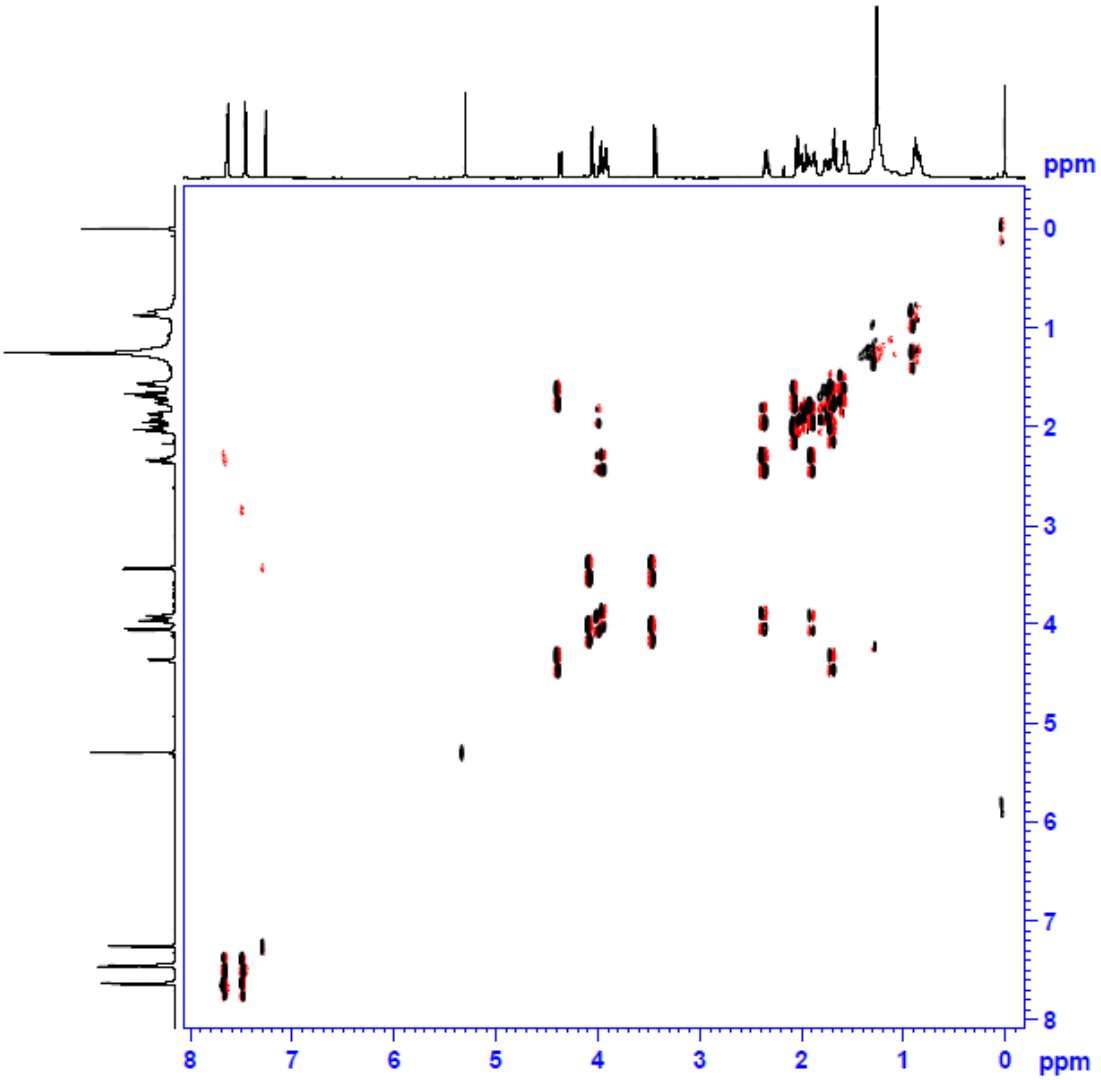
**TOCSY spectrum of 3d**



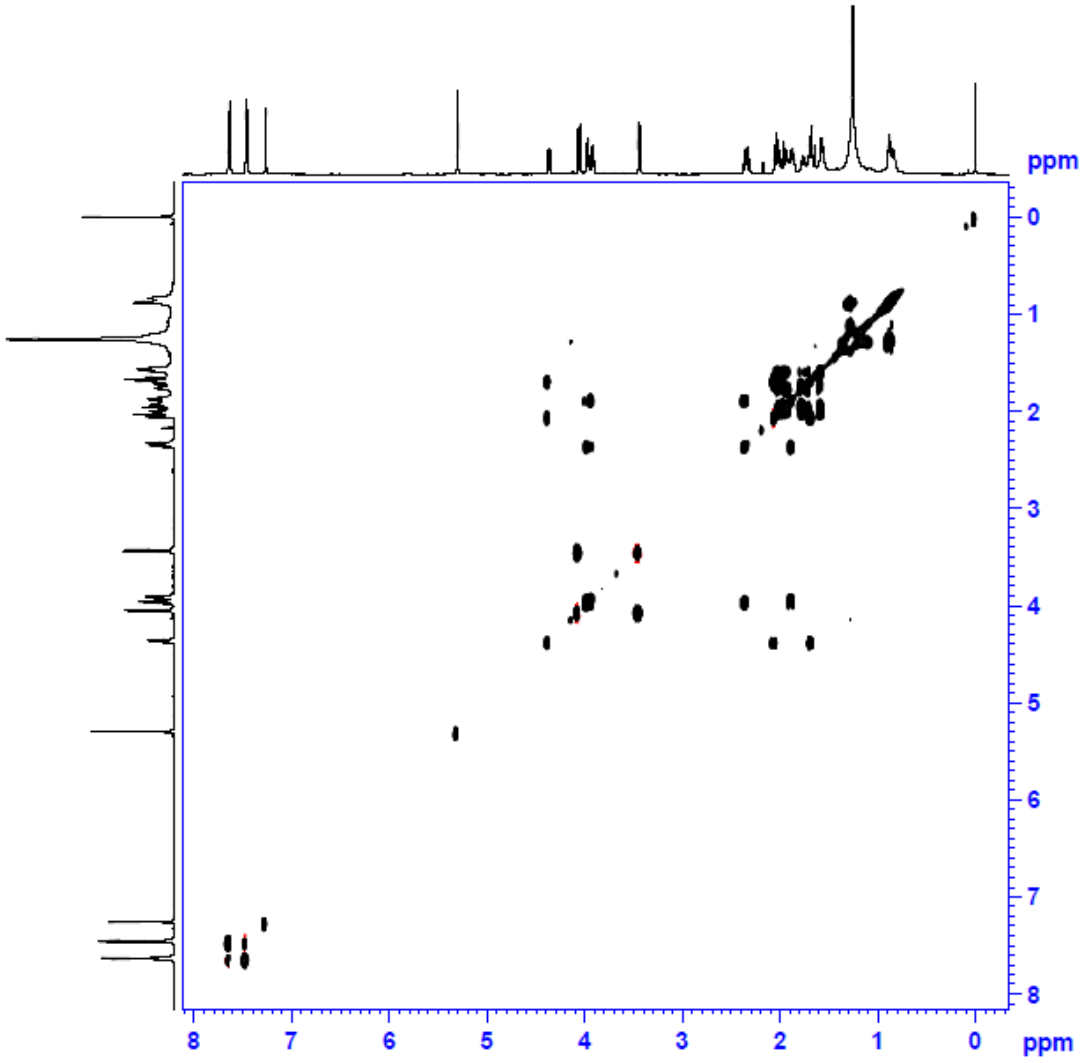
**NOESY spectrum of 5k**



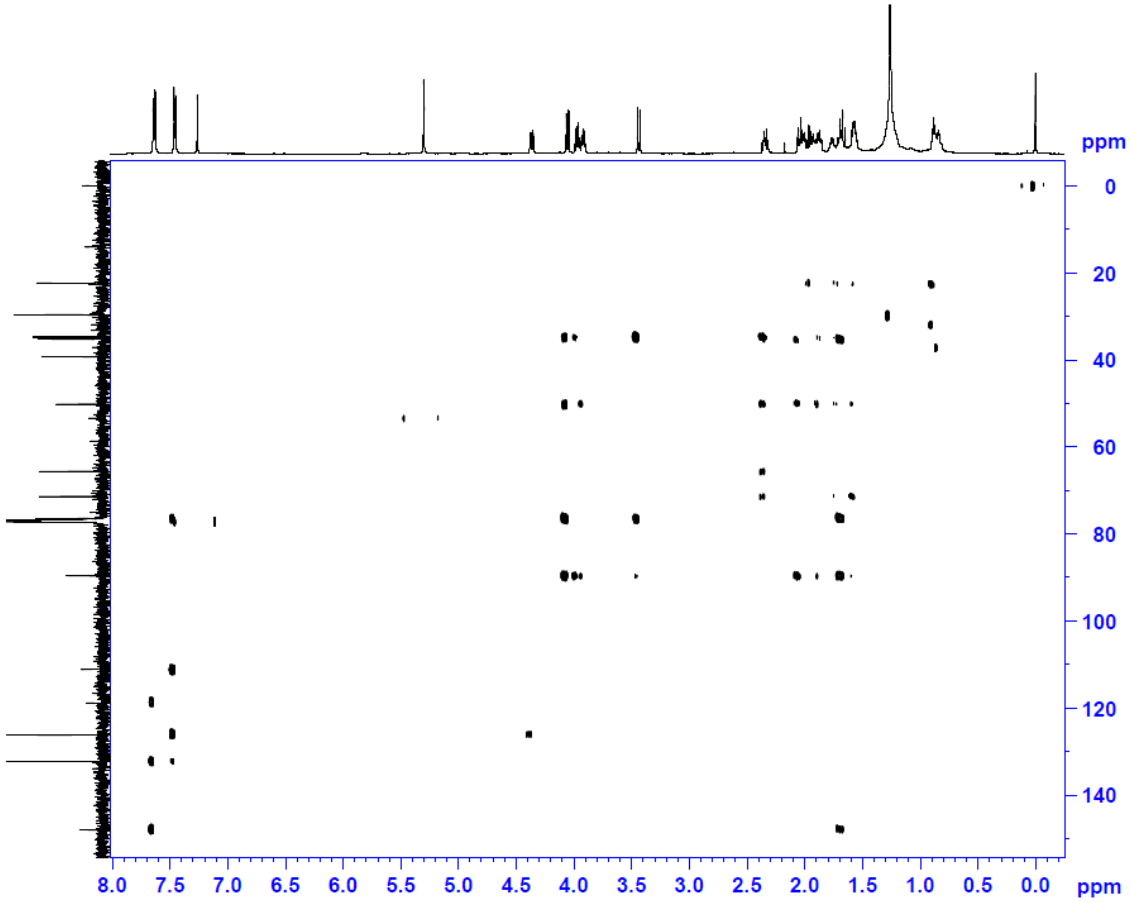
**COSY spectrum of 5k**



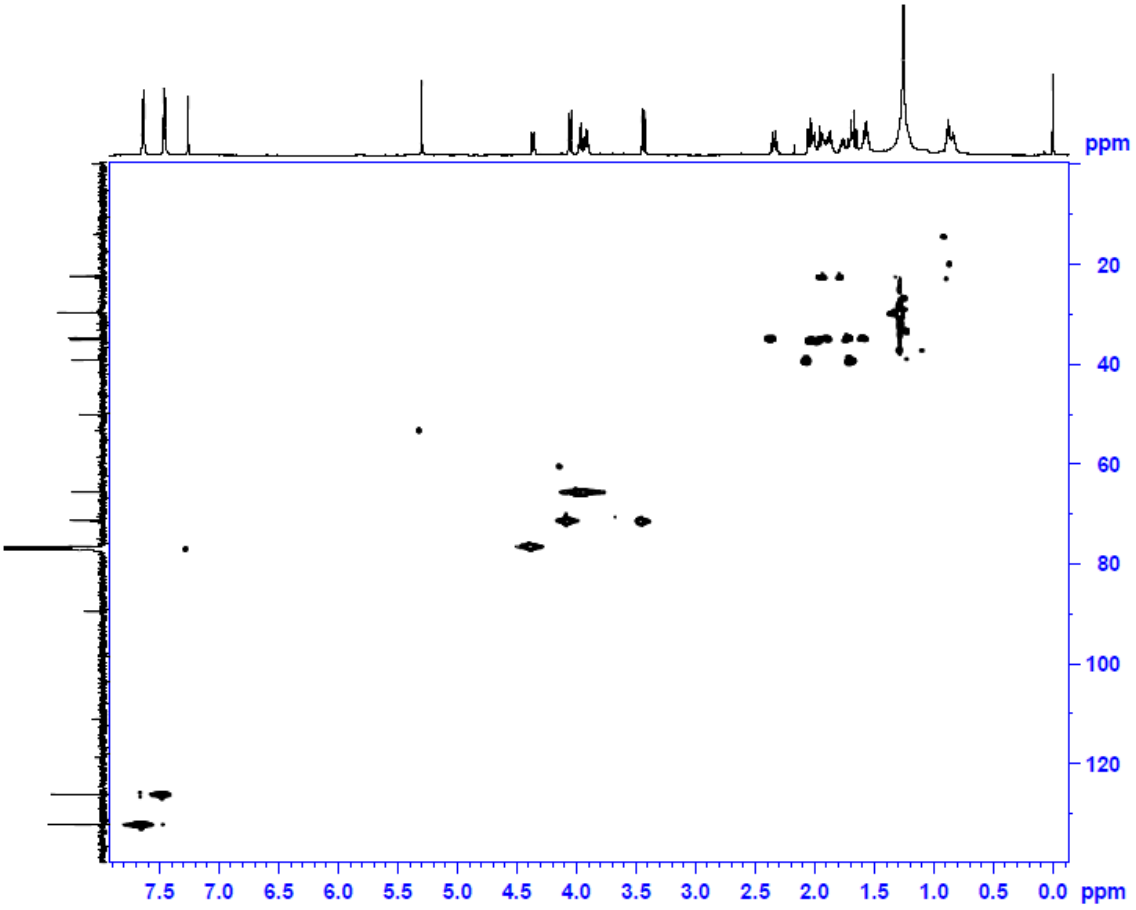
**TOCSY spectrum of 5k**



## HMBC spectrum of 5k



## HSQC spectrum of 5k



# Crystal data for 3e:

**X-ray Crystallography**.

X-ray data for the compounds were collected at room temperature using a Bruker Smart Apex CCD diffractometer with graphite monochromated MoKα radiation (λ=0.71073Å) with ω-scan method [1]. Preliminary lattice parameters and orientation matrices were obtained from four sets of frames.

Integration and scaling of intensity data were accomplished using SAINT program [1]. The structure was solved by direct methods using SHELXS97 [2] and refinement was carried out by full-matrix least-squares technique using SHELXL97 [2]. 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 $U_{iso}(H) = 1.2U_{eq}(c)$].

Crystal data for **3e**: $C_{20}H_{18}Cl_2O_2$, $M$ = 361.24, 0.21 x0.17 x 0.09 $mm^3$, monoclinic, space group $P2_1/n$ (No. 14), $a$ = 11.7351(14), $b$ = 10.1832(12), $c$ = 14.5872(18) Å, $\beta$ = 99.078(2)°, $V$ = 1721.3(4) $Å^3$, $Z$ = 4, $D_c$ = 1.394 $g/cm^3$, $F_{000}$ = 752, MoKα radiation, λ = 0.71073 Å, $T$ = 294(2)K, $2\theta_{max}$ = 52.5º, 17811 reflections collected, 3468 unique ($R_{int}$ = 0.0315). Final *GooF* = 1.119, *R1* = 0.0518, *wR2* = 0.1187, *R* indices based on 2896 reflections with I >2σ(I) (refinement on $F^2$), 217 parameters, 0 restraints, μ = 0.386 $mm^{-1}$. CCDC 1044784 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].

Figure Caption

A view of **3e**, showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are represented by circles of arbitrary radii.


1. Bruker (2001). SAINT (Version 6.28a) & SMART (Version 5.625). Bruker AXS Inc., Madison, Wisconsin, USA.
2. Sheldrick GM. (2008**)** Acta Crystallogr A64: 112-122.