Supporting Informatiom

A Micelle-mediated Approach Enables Facile Access to Bridged Oxabicyclo[n.3.1]alkene Scaffolds

Mohmad Muzafar Wani,[†‡] Auqib Rashid[†‡] and Bilal A. Bhat[†‡]*

CSIR-Indian Institute of Integrative Medicine, Sanatnagar Srinagar-190005, India;
+91-1942431253;
[‡]Academy of Scientific and Innovative Research (AcSIR), Ghaziabad-201002, India
E-mail: bilal@iiim.res.in

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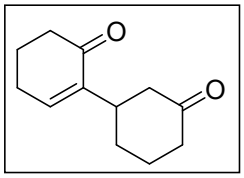
General information

All the commercially available chemicals and reagents were used without further purification unless otherwise stated. All the reactions were monitored by thin layer chromatography (TLC) using silica gel 60 F254 pre-coated plates and visualized under UV light. Further visualisation was carried out by $KMnO_4$ and other staining solution. Commercial silica gel with mesh size 100 and 200 was utilised for column chromatography. NMR was recorded on a 400 MHz instrument in $CDCl_3$ solvent. Tetramethylsilane was used as an internal standard, and chemical shifts were reported in parts per million. Standard abbreviations for singlet (s), doublet (d), triplet (t), quartet (q), doublet of doublet (dd), and multiplet (m) were used. Coupling constant (J) was measured in Hz. Mass spectra were measured using HRMS (ESI-TOF analyser) equipment.

Preparation of micellar stock solution: In a 250 ml RB, 53 mg (1.6 mmol) cetyltrimethylammonium chloride (CTAC) surfactant was added to 100 ml double-distilled water and stirred for half an hour to prepare CTAC micelles just above CMC. Similarly, for CTAB micellar solution, cetyltrimethylammonium bromide (49 mg, 1.3 mmol) was added to 100 ml double distilled water in a 250ml RB with constant stirring for half an hour. Both the solutions were continuously shacked for one hour at or above their Kraft's temperature to get required micellar assemblies which were stored in reagent bottles for different reactions. The same method was used to create the stock solutions of other micelles used in the study.

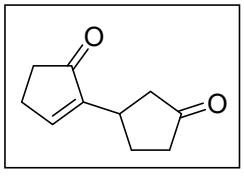
General procedure for the synthesis of compounds (2-5): In a clean RB, 5 ml of CTAB stock micellar solution was taken. To it, 1 mmol of 2-cycloalkenone (2-cyclohexenone, 2-cyclopentenone, 2-cycloheptenone, 4,4-dimethyl-2-cyclohexenone) was added at constant stirring at or above the Kraft temperature. DBU (30mg, 0.2mmol) was also added to the reaction mixture and stirred till its completion confirmed by TLC. Ethyl acetate and water (10 ml; 2:1 v/v) were added to the reaction mixture followed by brine solution. The organic layer was partitioned and further extracted with ethyl acetate and dried over sodium sulphate. Solvent was removed under the reduced pressure and the pure compounds were isolated using column chromatography with hexane and ethyl acetate (9:1 v/v).

[1,1'-bi(cyclohexan)]-6-ene-2,3'-dione (2):



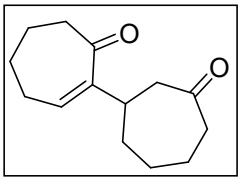
Viscous colourless liquid, Yield : 85%; ^{1}H NMR (CDCl3, 400 MHz): δ 1.59 (m, 1H), 1.73 (m, 1H), 1.89 (m, 1H), 2.00 (m, 3H), 2.39 (m, 8H), 2.99 (m, 1H), 6.72 (t, J = 4.0 Hz, 1H); ^{13}C NMR ($CDCl_3$, 101 MHz): δ 22.7, 25.0, 26.0, 30.6, 37.5, 38.7, 41.2, 46.3, 141.7, 144.5, 198.5, 211.4; HRMS calcd. for $C_{12}H_{17}O_2$ $[M+H]^+$: 193.1223; Found 193.1231.

[1,1'-bi(cyclopentan)]-5-ene-2,3'-dione (3):



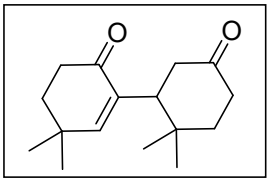
Viscous colourless liquid, Yield : 65%; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.88 (m, 1H), 2.28 (m, 4H), 2.45 (m, 2H), 2.53 (m, 1H), 2.62 (m, 2H), 3.13 (m, 1H), 7.36 (t, J = 4.0 Hz, 1H); ^{13}C NMR ($CDCl_3$, 101 MHz): δ 26.5, 28.1, 33.3, 35.0, 38.1, 43.2, 147.5, 157.0, 209.2, 218.3; HRMS calcd. for $C_{10}H_{13}O_2$ $[M+H]^+$: 165.0916; Found 165.0922.

[1,1'-bi(cycloheptan)]-7-ene-2,3'-dione (4):



Viscous colourless liquid, Yield : 70%; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.25 (m, 4H), 1.75 (m, 5H), 2.35 (m, 9H), 2.79 (m, 1H), 6.51 (t, J = 4.0 Hz, 1H); ^{13}C NMR ($CDCl_3$, 101 MHz): δ 21.4, 24.3, 24.8, 27.2, 29.5, 37.5, 38.1, 42.7, 43.8, 50.0, 139.9, 148.4, 204.9, 214.1; HRMS calcd. for $C_{14}H_{20}NaO_2$ $[M+Na]^+$: 243.1356; Found 243.1363.

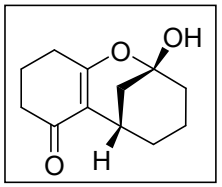
5,5,6',6'-tetramethyl-[1,1'-bi(cyclohexan)]-6-ene-2,3'-dione (5):



Viscous colourless liquid, Yield : 70%; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.18 (s, 3H), 1.40 (m, 2H), 1.55 (m, 2H), 1.66 (m, 4H), 1.87 (m, 2H), 2.07 (s, 1H), 2.11 (s, 1H), 2.31 (m, 2H), 2.40 (m, 2H), 2.49 (m, 2H), 2.61 (m, 1H), 2.82 (t, J = 8.0 Hz, 1H), 6.36 (s, 1H); ^{13}C NMR ($CDCl_3$, 101 MHz): δ 21.4, 24.4, 24.9, 27.2, 29.5, 37.5, 38.1, 42.7, 43.8, 50.0, 139.9, 148.5, 204.9, 214.0; HRMS calcd. for $C_{16}H_{25}O_2$ $[M+H]^+$: 249.1849; Found 249.1857.

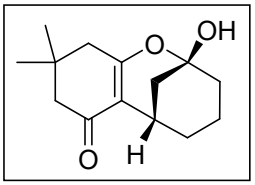
General procedure for the synthesis of compounds (8a-8n): To a micellar stock solution of CTAC (5 ml) taken in a clean RB was added 2-cycloalkenone (1.0 mmol) and 1,3-cycloalkanedione (1.0 mmol). The reaction mixture was stirred at 25-30 °C (at or above the CTAC surfactant's Kraft temperature) and DBU (30mg, 0.2 mmol) was added and reaction was continued till its completion monitored by TLC. Ethyl acetate (10 ml) was added to the reaction mixture, followed by brine solution. Partitioning of the two layers was allowed and the organic layer was further extracted with ethyl acetate (2 × 10ml) and the combined organic layer was dried over sodium sulphate. The solvent was removed under reduced pressure and the pure compound was isolated by column chromatography using hexane and ethyl acetate (8:2, v/v).

(2*R,6*S**)-2-hydroxy-2,3,4,5,6,8,9,10-octahydro-7H-2,6-methanobenzo[b]oxocin-7-one (8a):**



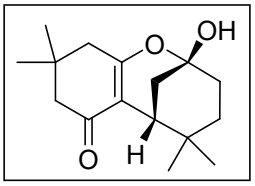
White solid, Yield : 78%; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.20 (m, 2H), 1.41 (m, 2H), 1.52 (m, 2H), 1.77 (m, 4H), 2.15 (m, 2H), 2.24 (m, 2H), 3.0 (t, , J = 4.0 Hz, 1H), 3.70 (s, 1H); ^{13}C NMR ($CDCl_3$, 101 MHz): δ 19.2, 21.3, 27.2, 28.3, 28.4, 36.3, 36.6, 38.8, 101.2, 113.7, 172.9, 197.1; HRMS calcd. for $C_{12}H_{17}O_3$ $[M+H]^+$: 209.1172; Found 209.1182.

(2*R,6*S**)-2-hydroxy-9,9-dimethyl-2,3,4,5,6,8,9,10-octahydro-7H-2,6-methanobenzo[b]oxocin-7-one (8b):**



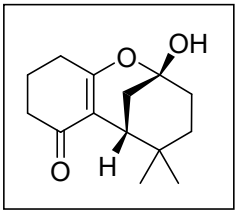
White solid, Yield : 82%; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 0.87 (s, 6H), 1.22 (m, 2H), 1.43 (m, 2H), 1.55 (m, 2H), 1.78 (m, 2H), 2.02(s, 2H), 2.10 (s, 2H), 2.99 (t, J = 4.0 Hz, 1H), 3.72 (s, 1H); ^{13}C NMR ($CDCl_3$, 101 MHz): δ 19.3, 27.0, 28.3, 28.5, 28.6, 32.4, 36.3, 38.8, 42.0, 50.4, 101.3, 112.4, 171.1, 196.7; HRMS calcd. for $C_{14}H_{21}O_3$ $[M+H]^+$: 237.1494; Found 237.1494.

(2*R,6*R**)-2-hydroxy-5,5,9,9-tetramethyl-2,3,4,5,6,8,9,10-octahydro-7H-2,6-methanobenzo[b]oxocin-7-one (8c):**



White solid, Yield : 65%; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 0.71 (s, 3H), 1.00 (s, 3H), 1.01 (s, 3H), 1.03 (s, 3H), 1.18 (m, 4H), 1.44 (m, 1H), 1.81 (m, 1H), 2.17 (m, 4H), 2.72 (s, 1H), 3.42 (s, 1H); ^{13}C NMR ($CDCl_3$, 101 MHz): δ 25.0, 27.9, 29.1, 29.3, 32.0, 32.5, 32.7, 34.5, 34.8, 36.2, 42.4, 50.5, 101.4, 113.0, 170.5, 196.7; HRMS calcd. for $C_{16}H_{25}O_3$ $[M+H]^+$: 265.1798 Found 265.1805.

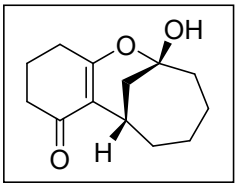
(2*R,6*R**)-2-hydroxy-5,5-dimethyl-2,3,4,5,6,8,9,10-octahydro-7H-2,6-methanobenzo[b]oxocin-7-one (8d):**



White solid, Yield : 70%; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 0.65 (s, 3H), 0.78 (m, 1H), 0.99 (s, 3H), 1.21 (m, 2H), 1.38 (m, 1H), 1.75 (m, 4H),

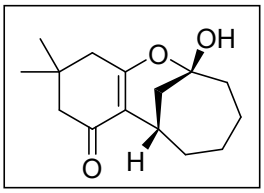
2.13 (m, 1H), 2.46 (m, 2H), 2.58 (m, 2H), 2.88 (t, J = 4.0 Hz, 1H); ^{13}C NMR ($CDCl_3$, 101 MHz): δ 20.9, 23.4, 24.8, 29.2, 32.1, 34.3, 34.8, 38.4, 41.1, 100.8, 116.3, 170.5, 201.3; HRMS calcd. for $C_{14}H_{21}O_3$ $[M+H]^+$: 237.1485; Found 237.1493.

(2*R,7*S**)-2-hydroxy-3,4,5,6,7,9,10,11-octahydro-2,7-methanobenzo[b]oxonin-8(2H)-one (8e):**



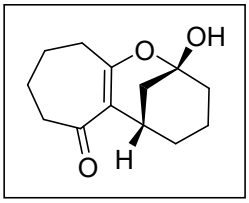
White solid, Yield : 79%; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.54 (m, 4H), 1.96 (m, 7H), 2.27(m, 1H), 2.40 (m, 4H), 3.00 (t, J = 4.0 Hz, 1H), 3.76(s, 1H); ^{13}C NMR ($CDCl_3$, 101 MHz): δ 21.1, 22.0, 25.7, 26.2, 29.0, 31.4, 36.5, 37.1, 43.6, 102.6, 114.6, 170.6, 198.0; HRMS calcd. for $C_{13}H_{19}O_3$ $[M+H]^+$: 223.1329; Found 223.1330.

(2*R,7*S**)-2-hydroxy-10,10-dimethyl-3,4,5,6,7,9,10,11-octahydro-2,7-methanobenzo[b]oxonin-8(2H)-one (8f):**



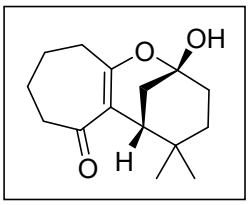
White solid, Yield : 80%; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 0.86 (s, 3H), 0.88 (s, 3H), 1.30 (m, 6H), 1.67 (m, 2H), 1.80 (m, 2H), 2.08 (m, 4H), 2.79 (t, J = 4.0 Hz, 1H), 3.42 (s, 1H); ^{13}C NMR ($CDCl_3$, 101 MHz): δ 22.0, 25.8, 26.1, 28.4, 31.5, 32.2, 36.6, 42.7, 43.6, 50.9, 102.7, 113.3, 168.8, 197.5; HRMS calcd. for $C_{15}H_{23}O_3$ $[M+H]^+$: 251.1642; Found 251.1645.

(2*R,6*S**)-2-hydroxy-3,4,5,6,8,9,10,11-octahydro-2,6-methanocyclohepta[b]oxocin-7(2H)-one (8g):**



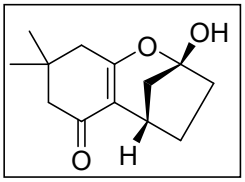
White solid, Yield : 73%; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.20 (m, 2H), 1.41 (m, 2H), 1.60 (m, 7H), 1.79 (m, 1H), 2.39 (m, 4H), 3.03 (t, J = 4.0 Hz, 1H), 3.10 (s, 1H); ^{13}C NMR ($CDCl_3$, 101 MHz): δ 19.3, 20.9, 23.4, 28.8, 29.6, 32.0, 36.0, 39.0, 41.4, 100.5, 116.0, 171.8, 200.3; HRMS calcd. for $C_{13}H_{19}O_3$ $[M+H]$: 223.1334; Found 223.1339.

(2*R,6*R**)-2-hydroxy-5,5-dimethyl-3,4,5,6,8,9,10,11-octahydro-2,6-methanocyclohepta[b]oxocin-7(2H)-one (8h):**



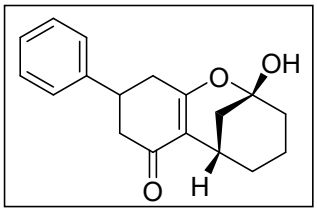
White solid, Yield : 57%; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 0.65 (s, 3H), 0.78 (m, 1H), 0.99 (s, 3H), 1.21 (m, 4H), 1.38 (m, 1H), 1.75 (m, 4H), 2.13 (m, 1H), 2.46 (m, 2H), 2.58 (m, 2H), 2.88 (t, J = 4.0 Hz, 1H); ^{13}C NMR ($CDCl_3$, 101 MHz): δ 20.9, 23.4, 24.8, 29.2, 29.7, 32.1, 34.3, 34.8, 38.4, 41.1, 100.8, 116.3, 170.5, 201.3; HRMS calcd. for $C_{15}H_{23}O_3$ $[M+H]^+$: 251.1642; Found 251.1647.

(2*R,5*S**)-2-hydroxy-8,8-dimethyl-3,4,5,7,8,9-hexahydro-2,5-methanobenzo[b]oxepin-6(2H)-one (8i):**



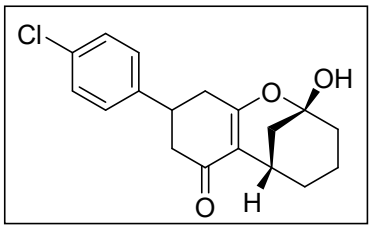
Colourless liquid, Yield : 30%; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.01 (s, 3H), 1.06 (s, 3H), 1.54 (m, 2H), 1.82 (m, 2H), 2.16 (m, 2H), 2.24 (m, 4H), 4.14 (t, J = 4.0 Hz, 1H), 4.62 (s, 1H); ^{13}C NMR ($CDCl_3$, 101 MHz): δ 14.1, 22.7, 28.3, 28.9, 32.8, 34.4, 36.0, 37.8, 51.2, 100.3, 115.8, 177.6, 195.5; HRMS calcd. for $C_{13}H_{19}O_3$ $[M+H]^+$:223.1334 ; Found 223.1353.

(2*R,6*S**)-2-hydroxy-9-phenyl-2,3,4,5,6,8,9,10-octahydro-7H-2,6-methanobenzo[b]oxocin-7-one (8j):**



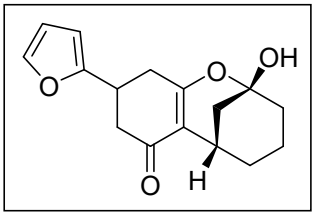
White solid, Yield : 67%; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.05 (s, 1H), 1.27 (m, 1H), 1.52 (m, 4H), 1.72 (m, 1H), 1.85 (m, 1H), 2.44 (m, 4H), 3.03 (t, J = 4.0 Hz, 1H), 3.14 (m, 1H), 4.09 (s, 1H), 7.01 (d, J = 8.0 Hz, 2H), 7.05 (t, J = 4.0 Hz, 1H), 7.12 (t, J = 8.0 Hz, 2H); ^{13}C NMR ($CDCl_3$, 101 MHz): δ 19.2, 27.0 (27.3), 28.3 (28.6), 35.6 (35.9), 36.2, 38.8 (38.9), 39.3 (39.4), 43.5 (43.7), 101.6 (101.7), 113.2 (113.6), 126.6 (126.7), 127.0, 128.8, 142.7 (142.8), 172.0 (172.3), 196.1 (196.2); HRMS calcd. for $C_{18}H_{21}O_3$ $[M+H]^+$: 285.1485; Found 285.1494.

(2*R*,6*S*)-9-(4-chlorophenyl)-2-hydroxy-2,3,4,5,6,8,9,10-octahydro-7H-2,6-methanobenzo[b]oxocin-7-one (8k):



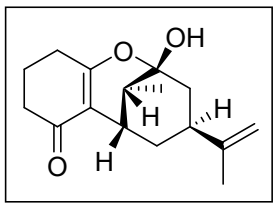
White solid, Yield : 78%; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.26 (s, 1H), 1.44 (m, 1H), 1.76 (m, 4H), 2.04 (m, 2H), 2.55 (m, 4H), 3.19 (s, 1H), 3.28 (t, J = 4.0 Hz, 1H), 5.28 (s, 1H), 7.12 (d, J = 4.0 Hz, 2H), 7.28 (d, J = 8.0 Hz, 2H); ^{13}C NMR ($CDCl_3$, 101 MHz): δ 19.2, 27.0 (27.3), 28.3 (28.6), 29.7, 35.6 (35.8), 36.2, 38.7 (38.8), 43.2 (43.4), 102.0, 113.3 (113.6), 128.0 (128.1), 128.9, 132.7, 141.1 (141.2), 172.2 (172.4), 196.0; HRMS calcd. for $C_{18}H_{20}ClO_3$ $[M+H]^+$: 319.1095; Found 319.1102.

(2*R,6*S**)-9-(furan-2-yl)-2-hydroxy-2,3,4,5,6,8,9,10-octahydro-7H-2,6-methanobenzo[b]oxocin-7-one (8l):**



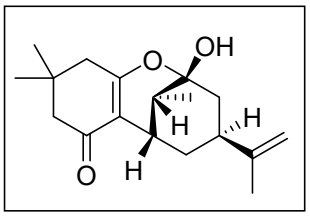
Light yellowish solid, Yield : 73%; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.18 (m, 1H), 1.36 (m, 1H), 1.51 (m, 2H), 1.67 (m, 2H), 1.84 (m, 1H), 1.98 (m, 1H), 2.49 (m, 1H), 2.64 (m, 3H), 3.11 (s, 1H), 3.35 (m, 1H), 4.50 (s, 1H), 5.95 (d, J = 4.0 Hz, 1H), 6.20 (dd, J = 4.0 Hz, 1H), 7.23 (d, J = 4.0 Hz, 1H); ^{13}C NMR ($CDCl_3$, 101 MHz): δ 19.0 (19.1), 27.0 (27.3), 28.3 (28.5), 32.7 (32.8), 33.2, 36.1, 38.7, 40.7 (40.8), 101.8, 104.7, 110.1, 113.4 (113.6), 141.5, 155.9, 171.7 (172.0), 195.6; HRMS calcd. for $C_{16}H_{19}O_4$ $[M+H]^+$: 275.1278; Found 275.1290.

(2*R,4*S**,6*S**,11*R**)-2-hydroxy-11-methyl-4-(prop-1-en-2-yl)-2,3,4,5,6,8,9,10-octahydro-7H-2,6-methanobenzo[b]oxocin-7-one (8m):**



Colourless semi-solid, Yield : 53%; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.11 (d, J = 8 Hz, 3H), 1.19 (m, 4H), 1.34 (m,,1H), 1.51 (m, 1H), 1.62 (s, 3H), 1.90 (m, 3H), 2.35 (m, 4H), 2.94 (s, 1H), 4.62 (s, 1H), 4.66 (s, 1H); ^{13}C NMR ($CDCl_3$, 101 MHz): δ 13.0, 14.2, 21.0, 21.3, 27.3, 31.9, 37.3, 37.5, 37.8, 60.5, 105.4, 109.7, 116.1, 147.5, 171.3, 196.8; HRMS calcd. for $C_{16}H_{23}O_3$ $[M+H]^+$: 263.1642; Found 263.1651.

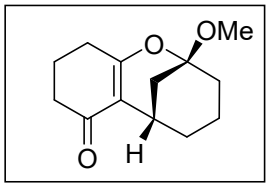
(2*R,4*S**,6*S**,11*R**)-2-hydroxy-9,9,11-trimethyl-4-(prop-1-en-2-yl)-2,3,4,5,6,8,9,10-octahydro-7H-2,6-methanobenzo[b]oxocin-7-one (8n):**



Colourless semi-solid, Yield : 56%; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.01 (s, 6H), 1.11 (d, J = 8.0 Hz, 3H), 1.18 (s, 4H), 1.52 (m, 1H), 1.62 (s, 3H), 1.83 (m, 1H), 2.16 (s, 2H), 2.24 (s, 2H), 2.93 (t, J = 4.0 Hz, 1H), 3.42 (s, 1H), 4.61 (s, 1H), 4.66 (s, 1H); ^{13}C NMR ($CDCl_3$, 101 MHz): δ 13.0, 21.1, 27.5, 28.2, 28.6, 31.8, 32.5, 37.4, 37.8, 37.9, 41.8, 50.4, 104.9, 109.6, 114.8, 147.5, 170.2, 196.2; HRMS calcd. for $C_{18}H_{27}O_3$ $[M+H]^+$: 291.1955; Found 291.1963.

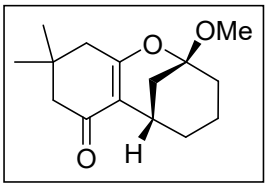
Procedure for the synthesis of compounds 9a and 9b: Compounds **8a** and **8b** (50 mg each; 0.21-0.24 mmol) were dissolved in 3 ml of methanol in two separate round bottom flasks. Hydrochloric acid (0.12 mmol, 10 µl) was added to each on stirring and the reaction was monitored by TLC. After completion, the reaction was diluted with brine solution (10 ml) and extracted with ethyl acetate 2 × 10ml) and dried over sodium sulphate. The combined organic layer was evaporated under reduced pressure and the pure compounds were isolated by column chromatography using hexane and ethyl acetate (8:2; v/v).

(2R*,6S*)-2-methoxy-2,3,4,5,6,8,9,10-octahydro-7H-2,6-methanobenzo[b]oxocin-7-one (9a):



Colourless liquid, Yield : 80%; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.35 (m, 2H), 1.58 (m, 4H), 1.90 (m, 4H), 2.28 (m, 2H), 2.40 (m, 2H), 3.14 (s, 1H), 3.30 (s, 3H); ^{13}C NMR ($CDCl_3$, 101 MHz): δ 19.1, 21.2, 26.9, 28.0, 28.8, 32.5, 36.6, 37.0, 49.3, 103.6, 113.9, 172.7, 196.5; HRMS calcd. for $C_{13}H_{19}O_3$ $[M+H]^+$: 223.1334; Found 223.1341.

(*2R*,6S)-2-methoxy-9,9-dimethyl-2,3,4,5,6,8,9,10-octahydro-7H-2,6-methanobenzo[b]oxocin-7-one (9b):**

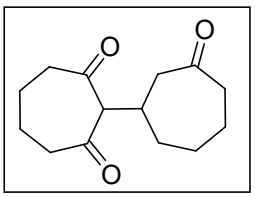


Colourless liquid, Yield : 85%; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.01 (s, 6H), 1.36 (m, 2H), 1.55 (m, 2H), 1.62 (m, 2H), 1.84 (m, 1H), 2.01 (s, 1H), 2.15 (s, 2H), 2.27 (d, J = 8.0 Hz, 2H), 3.14 (s, 1H), 3.30 (s, 3H); ^{13}C NMR ($CDCl_3$, 101 MHz): δ 19.3, 26.8, 28.2, 28.7, 28.9, 32.3, 32.7, 36.9, 41.9, 49.3, 50.5, 103.8, 112.6, 171.1, 196.4; HRMS calcd. for $C_{15}H_{23}O_3$ $[M+H]^+$: 251.1647; Found 251.1653.

General procedure for the synthesis of compounds (7b-7d):

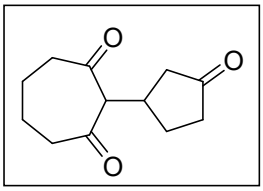
To a micellar stock solution of CTAC (5 ml) taken in a clean RB was added 2-cycloalkenone (2-cyclopenenone, 2-cycloheptenone or 2-cyclohexenone; 1.0 mmol) and 1,3-cycloalkanedione (1,3-cyclopentadione or 1H-indene-1,3(2*H*)-dione; 1.0 mmol). The reaction mixture was stirred at 25-30 °C and DBU (30mg, 0.2 mmol) was added and reaction was continued till its completion monitored by TLC. Ethyl acetate (10 ml) was added to the reaction mixture, followed by brine solution. Partitioning of the two layers was allowed and the organic layer was further extracted with ethyl acetate (2 × 10 ml) and the combined organic layer was dried over sodium sulphate. The solvent was removed under reduced pressure and the pure compound was isolated by column chromatography using hexane and ethyl acetate (9:1, v/v).

[1,1'-bi(cycloheptane)]-2,3',7-trione (7b):



White solid, Yield : 95%; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.23 (m, 4H), 1.51 (m, 2H), 1.79 (m, 5H), 2.04 (m, 2H), 2.42 (m, 3H), 2.49 (m, 2H), 2.69 (m, 1H), 3.85 (d, J = 8.0 Hz, 1H); ^{13}C NMR ($CDCl_3$, 101 MHz): δ 24.5, 25.1, 25.2, 28.4, 33.5, 33.7, 43.6, 45.0, 45.1, 46.9, 70.9, 205.9, 206, 213.6; HRMS calcd. for $C_{14}H_{21}O_3$ $[M+H]^+$: 237.1491; Found 237.1497.

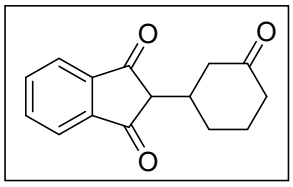
2-(3-oxocyclopentyl)cycloheptane-1,3-dione (7c):



White solid, Yield : 93%; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.50 (m, 3H), 1.84 (m, 3H), 2.10 (m, 4H), 2.44 (m, 2H), 2.53 (m, 2H), 2.87 (m, 1H), 3.82 (d, J = 8.0 Hz, 1H); ^{13}C NMR ($CDCl_3$, 101 MHz): δ 25.5,

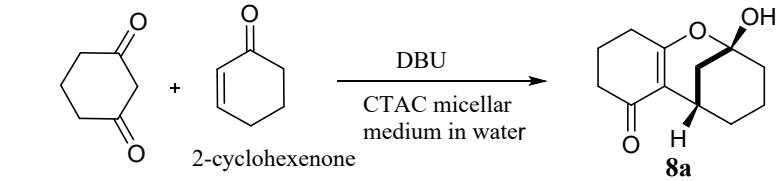
25.7, 27.4, 34.4, 38.1, 42.9, 44.4, 44.5, 71.6, 205.8, 205.9, 217.9; HRMS calcd. for $C_{12}H_{17}O_3$ $[M+H]^+$: 209.1178; Found 209.1183.

2-(3-oxocyclohexyl)-1H-indene-1,3(2H)-dione (7d):



White solid, Yield : 70%; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.53 (m, 2H), 2.25 (m, 3H), 2.53 (m, 2H), 2.73 (s, 1H), 2.91 (m, 1H), 3.78 (d, J = 5.5 Hz, 1H), 7.54 (d, J = 5.5 Hz, 1H), 7.79 (m, 3H); ^{13}C NMR ($CDCl_3$, 101 MHz): δ 18.9, 21.6, 25.2, 39.0, 46.3, 56.5, 122.8, 130.1, 136.5, 206.8, 206.9, 211.3; HRMS calcd. for $C_{15}H_{15}O_3$ $[M+H]^+$: 243.1021; Found 243.1033.

Gram scale synthesis of compound 8a: To a clean 100 ml RB was added CTAC stock micellar solution (30 ml). To this was added 1,3-cyclohexanedione (1g, 8.9 mmol), 2-cyclohexenone (857 mg, 8.9 mmol) and DBU (270mg, 1.76 mmol) and the reaction was stirred at 25-30 °C till its completion confirmed by TLC. After the completion of reaction, ethyl acetate (30 ml) was added to it and allowed to partition. Aqueous layer was further extracted with ethyl acetate (2 × 20 ml) and the combined organic layer was dried over sodium sulphate. Solvent was removed under the reduced pressure and the pure compound was isolated by column chromatography using hexane and ethyl acetate (8:2) to furnish 1.46 gram of compound **8a**.



Recycling and reuse of micellar medium:

Micellar solution employed in the above reaction was reused in synthesizing the compound **8b**. Dimedone (140mg, 1 mmol) and 2-cyclohexenone (96 mg, 1 mmol) was dissolved in 5 ml of above recovered micellar solution (5 ml). To it was added DBU (30 mg, 0.2 mmol) and the reaction was stirred till its completion. Ethyl acetate (2×10 ml) was added to the reaction and allowed to partition. Combined organic layer was dried over sodium sulphate, solvent was removed and the pure compound was purified by column chromatography. The recovered micellar solution was further used in synthesising the compound **8b** without the loss of efficiency.

Figure S1: ORTEP view (30% probability ellipsoid) and crystallographic data for **8l (CCDC 2255197)**

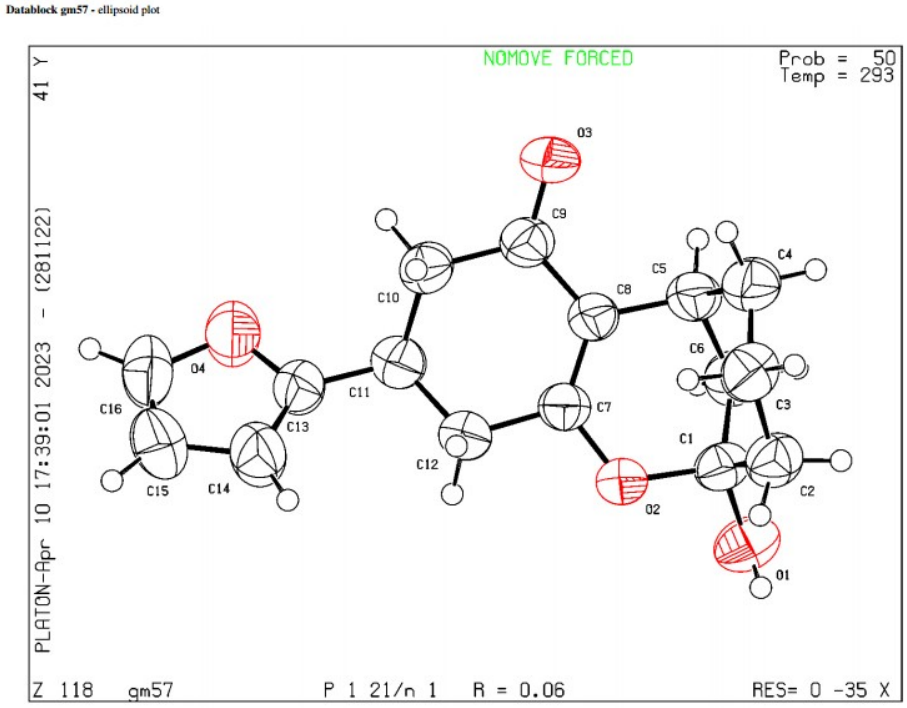
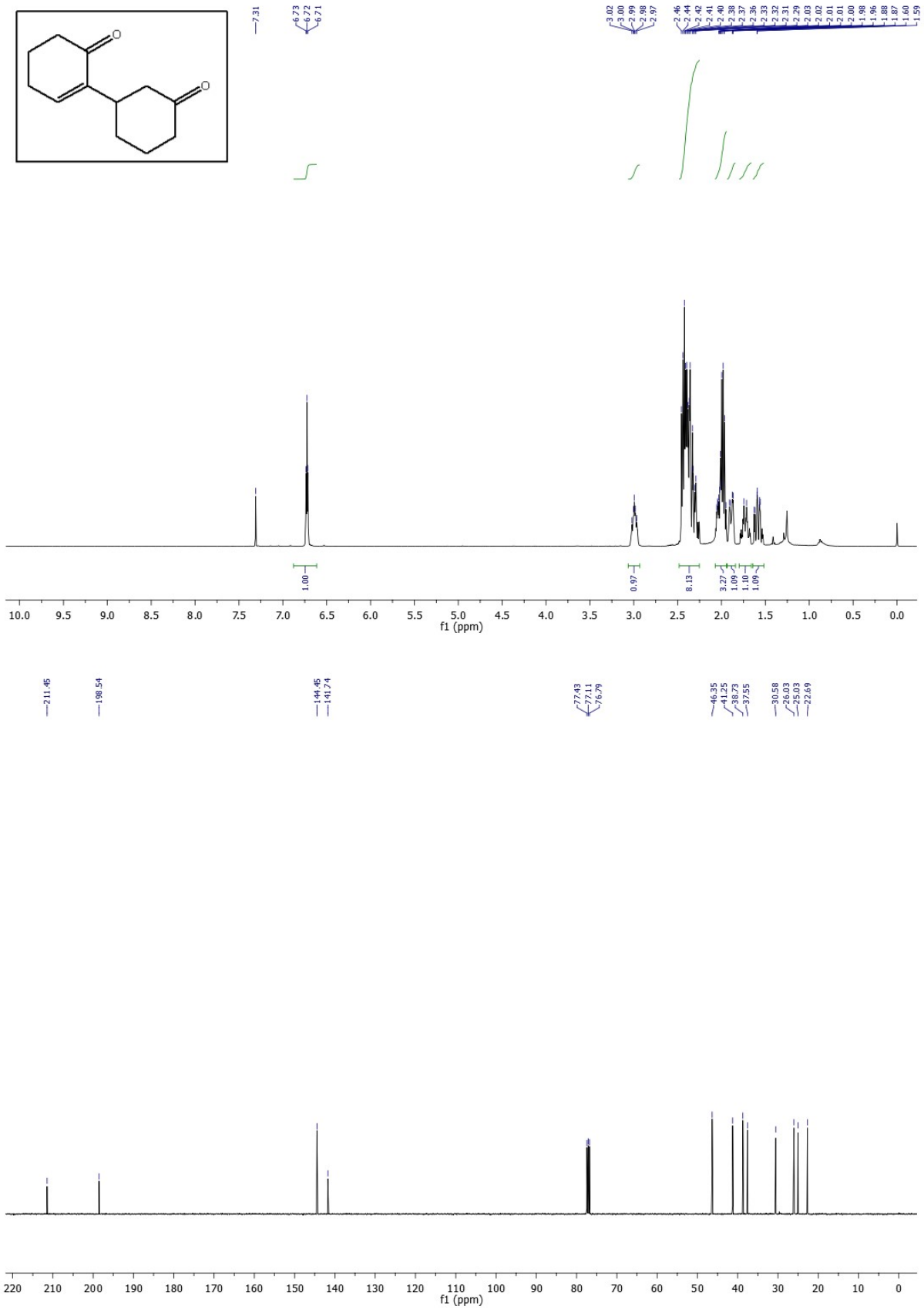


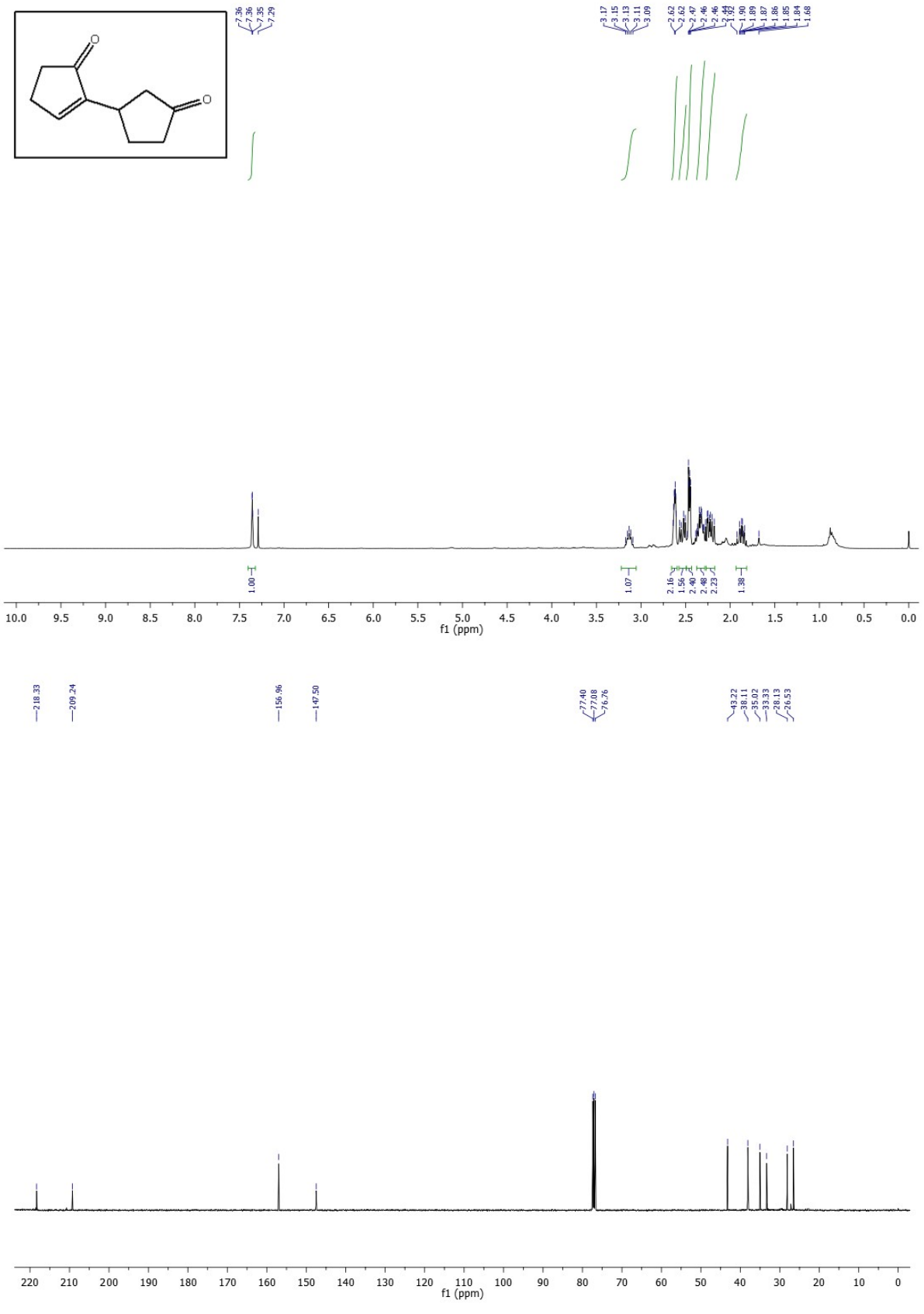
Table S1: Crystal data and structure refinement details for compound 8l

Identification code	**GM-57**
Compound	**8l**
Empirical formula	$C_{16}H_{18}O_4$
Formula weight	274.32
Space group	P 21/n
T (K)	293
a (Å)	5.8721 (2)
b (Å)	21.5158 (7)
c (Å)	12.7252 (4)
α (°)	90
β (°)	98.689 (3)
γ (°)	90
Z	4
V (A^3)	1589.29 (9)
Density calculated (g/cm^3)	1.146
μ (mm^{-1})	0.082
F (000)	584.0
h, k, l	7, 27, 16
Radiation	MoKα (λ=0.71073)
R_1	0.0607
wR_2	0.1994
CCDC No.	**2255197**

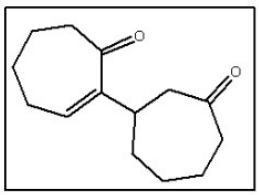
^{1}H and ^{13}C NMR in $CDCl_3$ of compound **2**

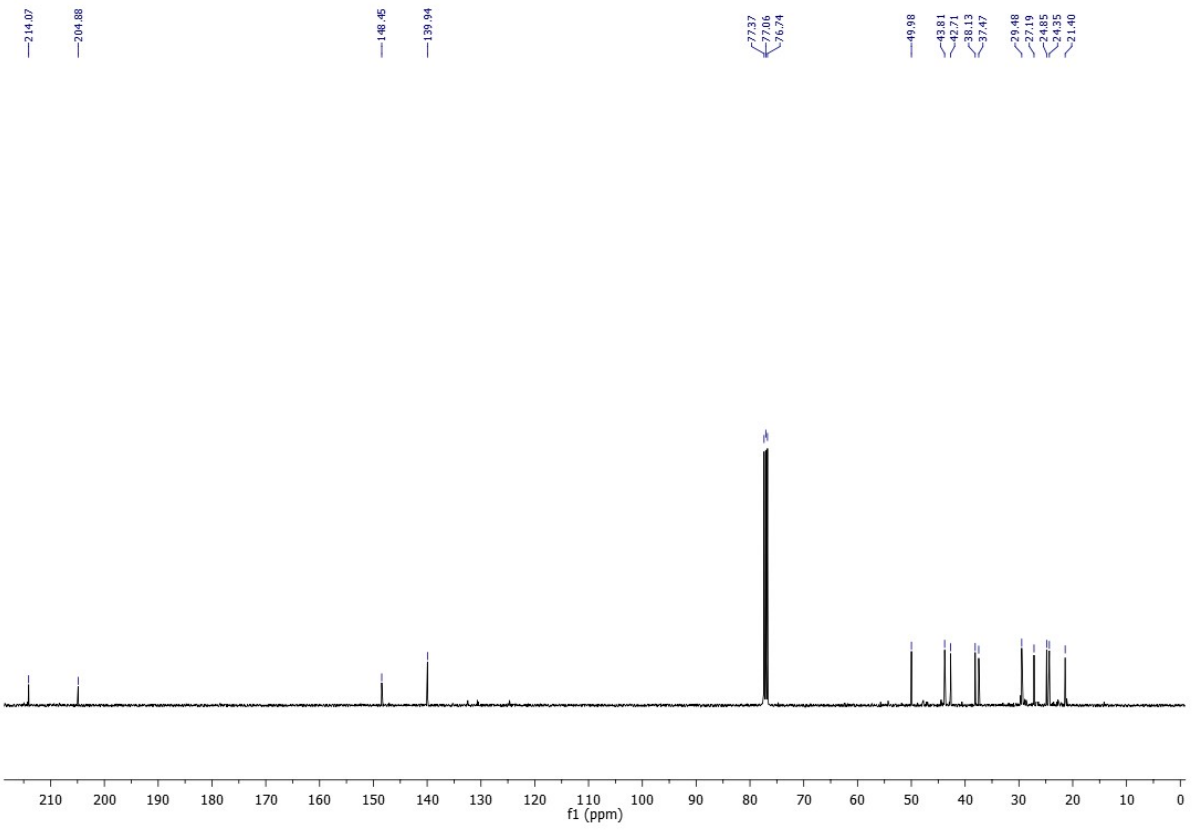


^{1}H and ^{13}C NMR in $CDCl_3$ of compound **3**

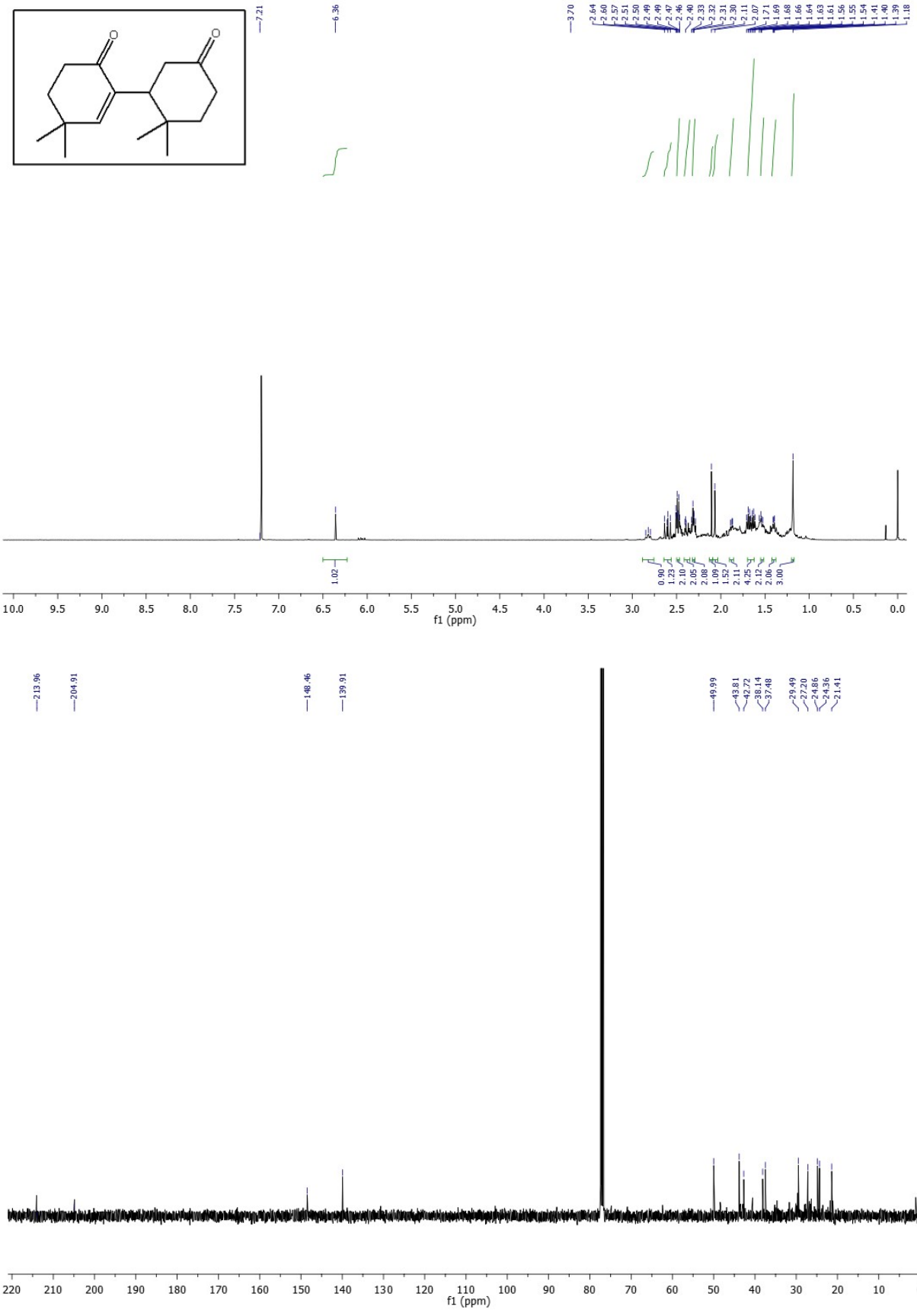


^{1}H and ^{13}C NMR in $CDCl_3$ of compound **4**

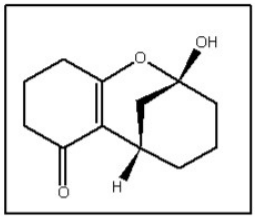


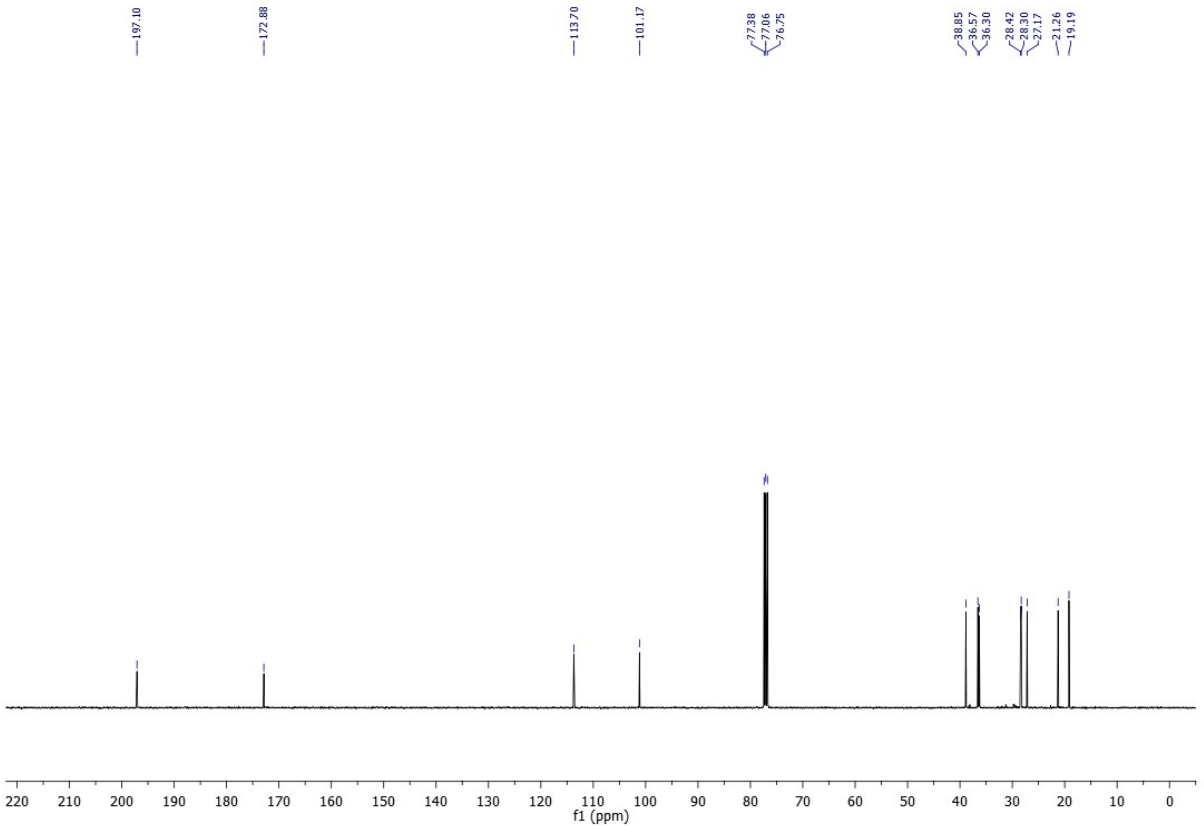


^{1}H and ^{13}C NMR in $CDCl_3$ of compound **5**

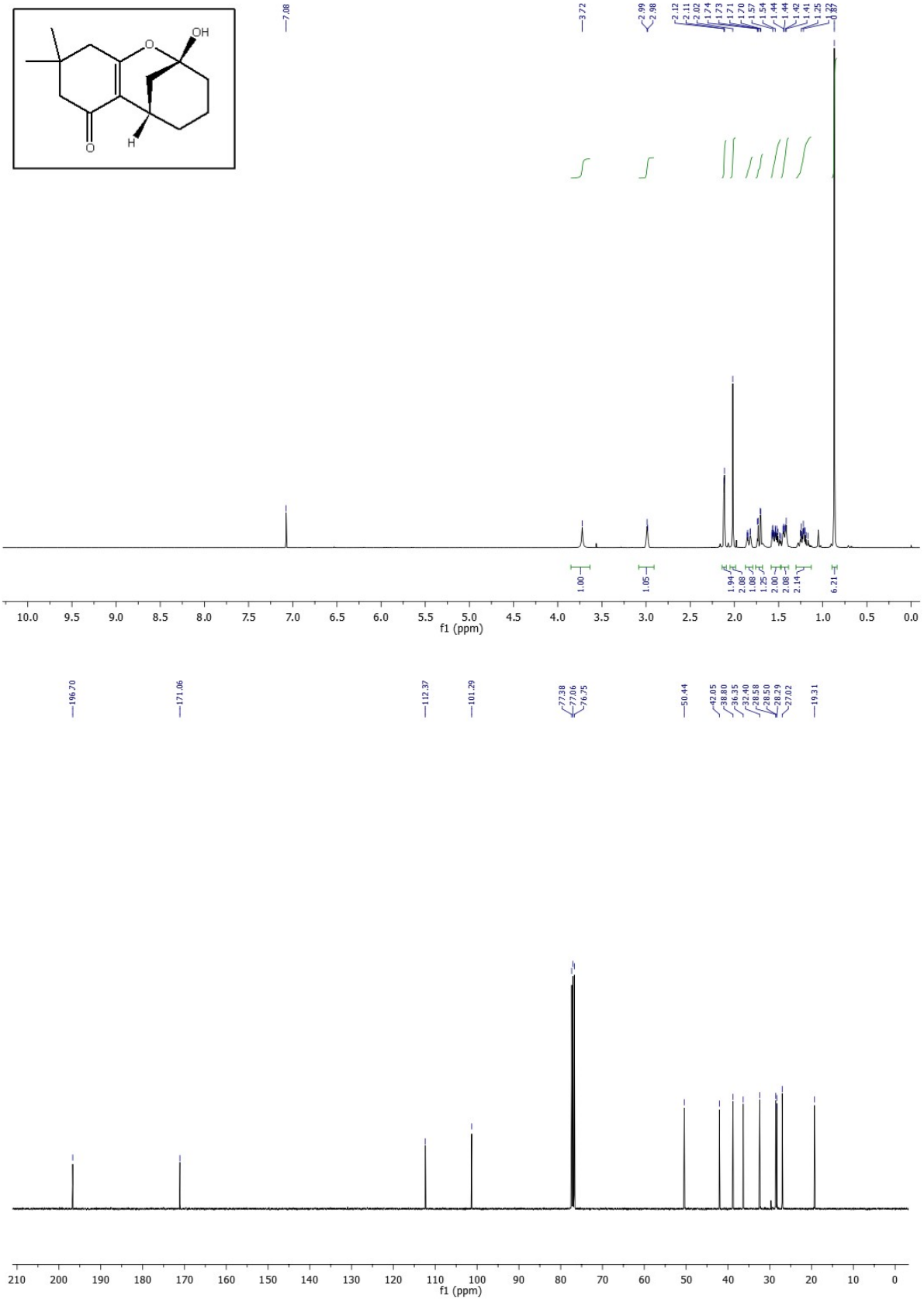


^{1}H and ^{13}C NMR in $CDCl_3$ of compound **8a**

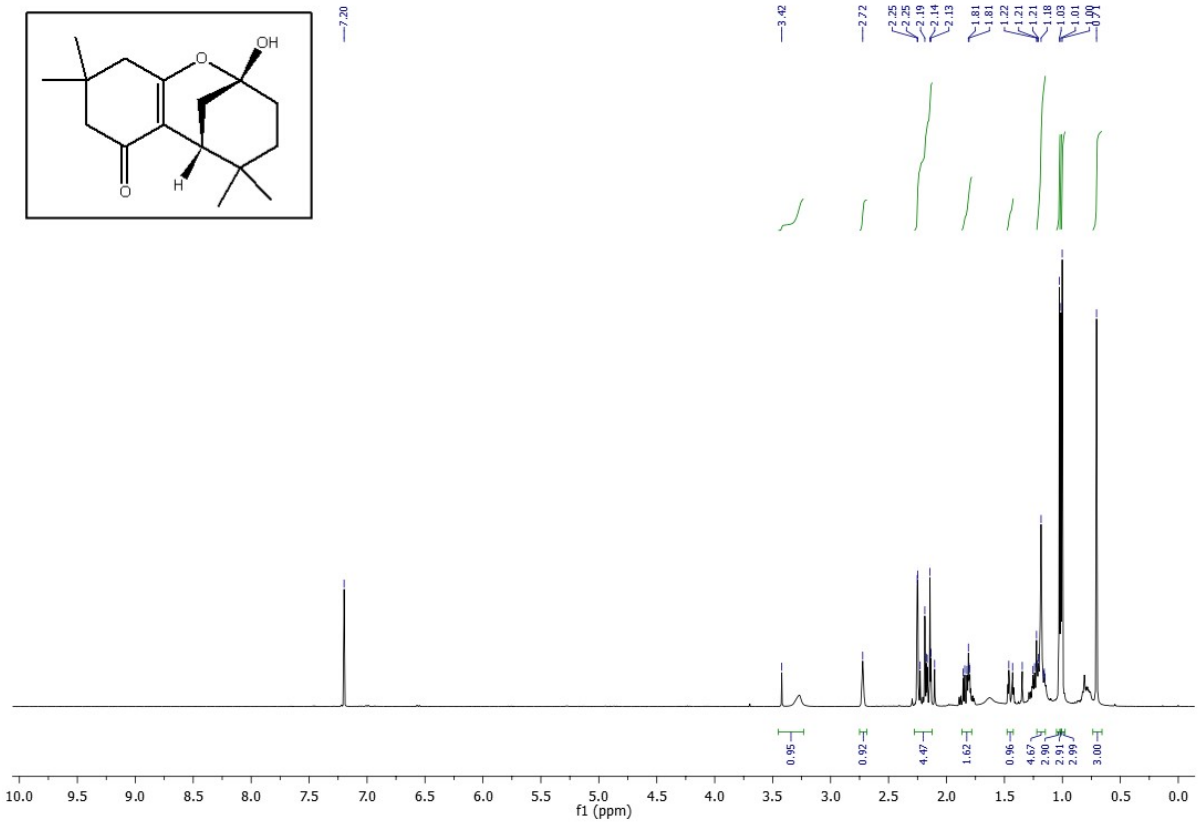


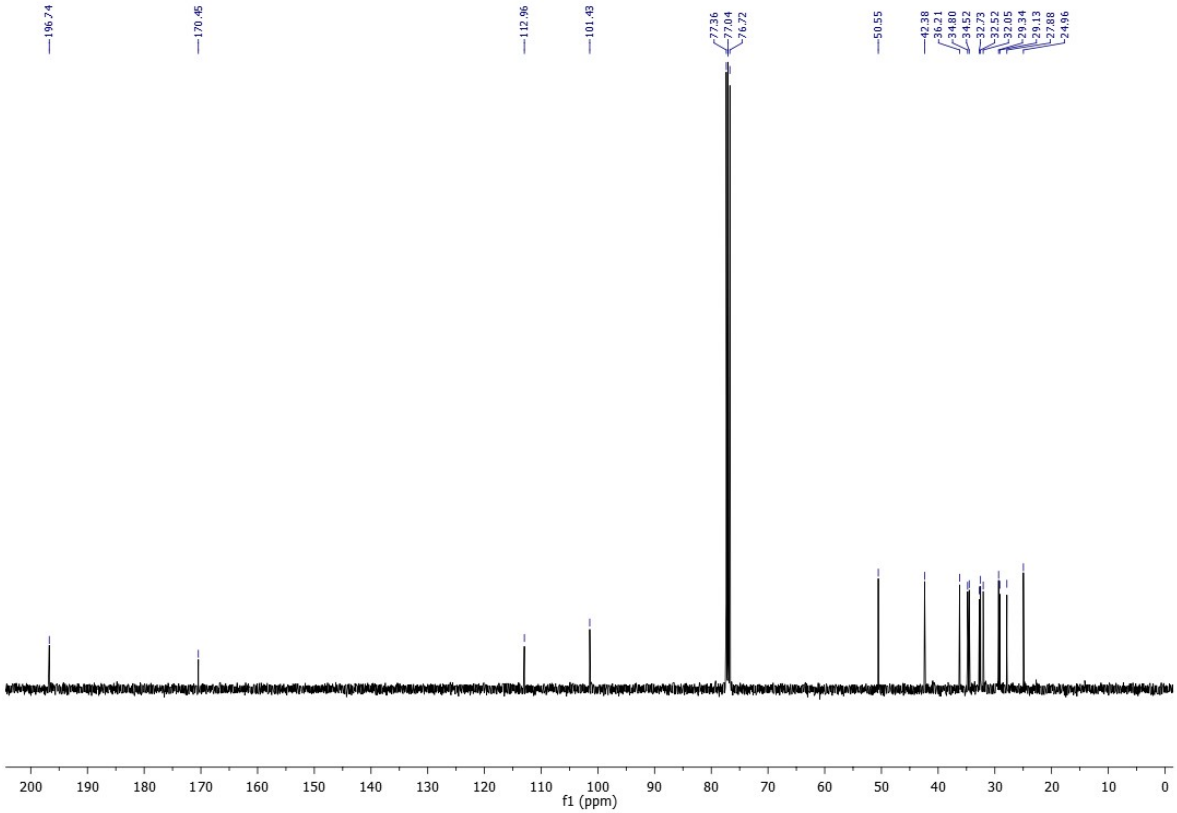


^{1}H and ^{13}C NMR in $CDCl_3$ of compound **8b**

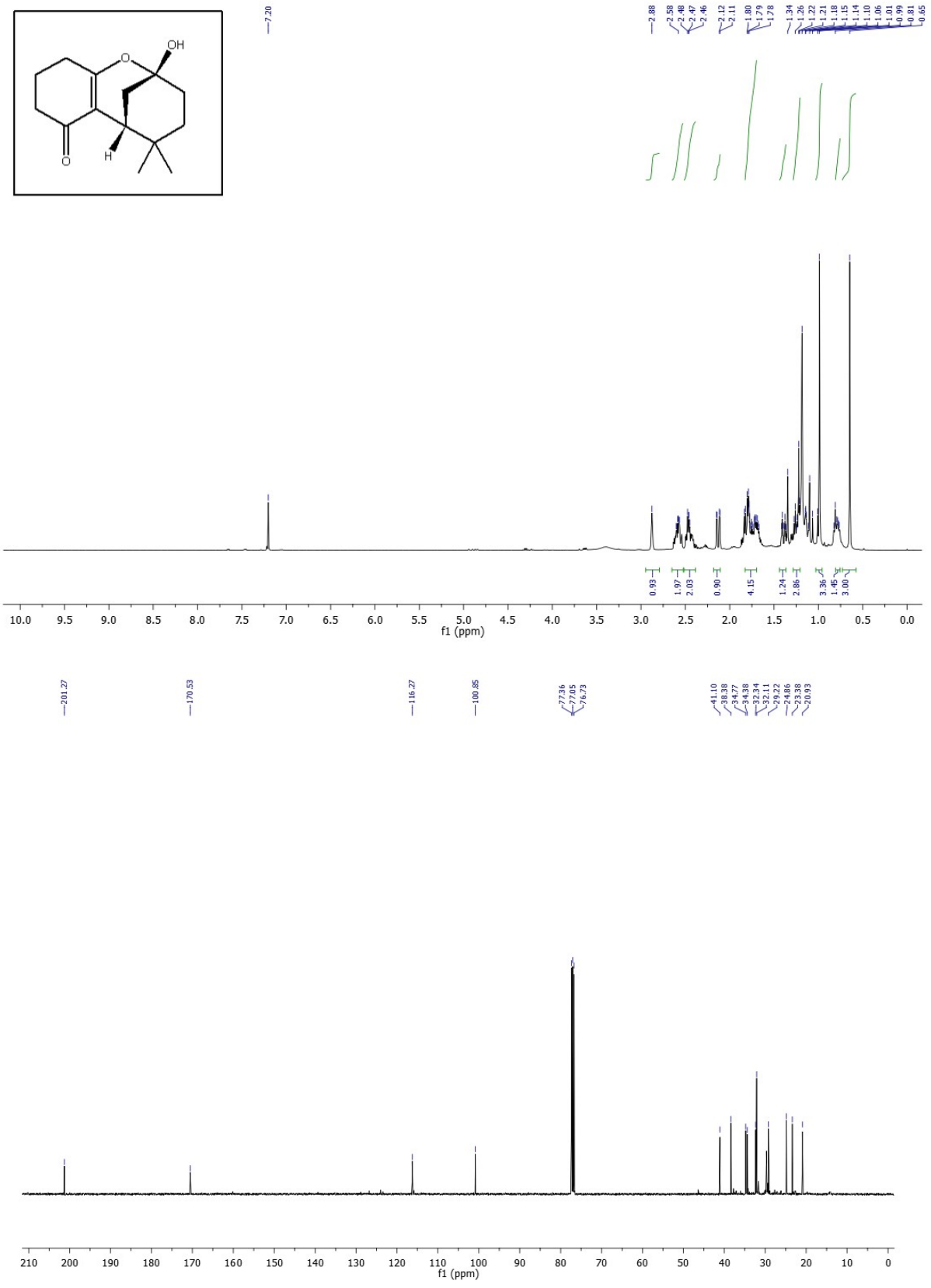


^{1}H & ^{13}C NMR in CD_3OD of compound **8c**

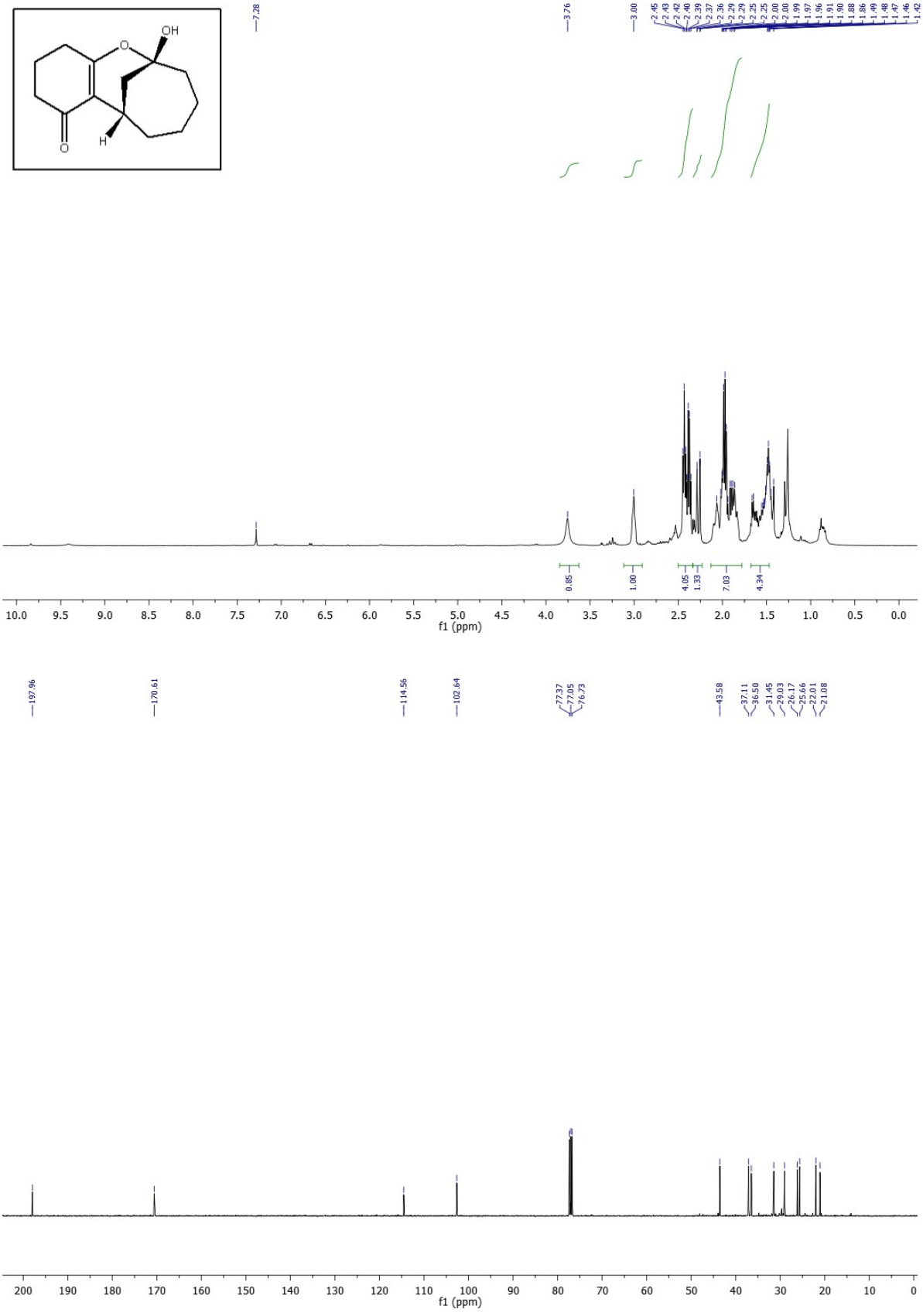




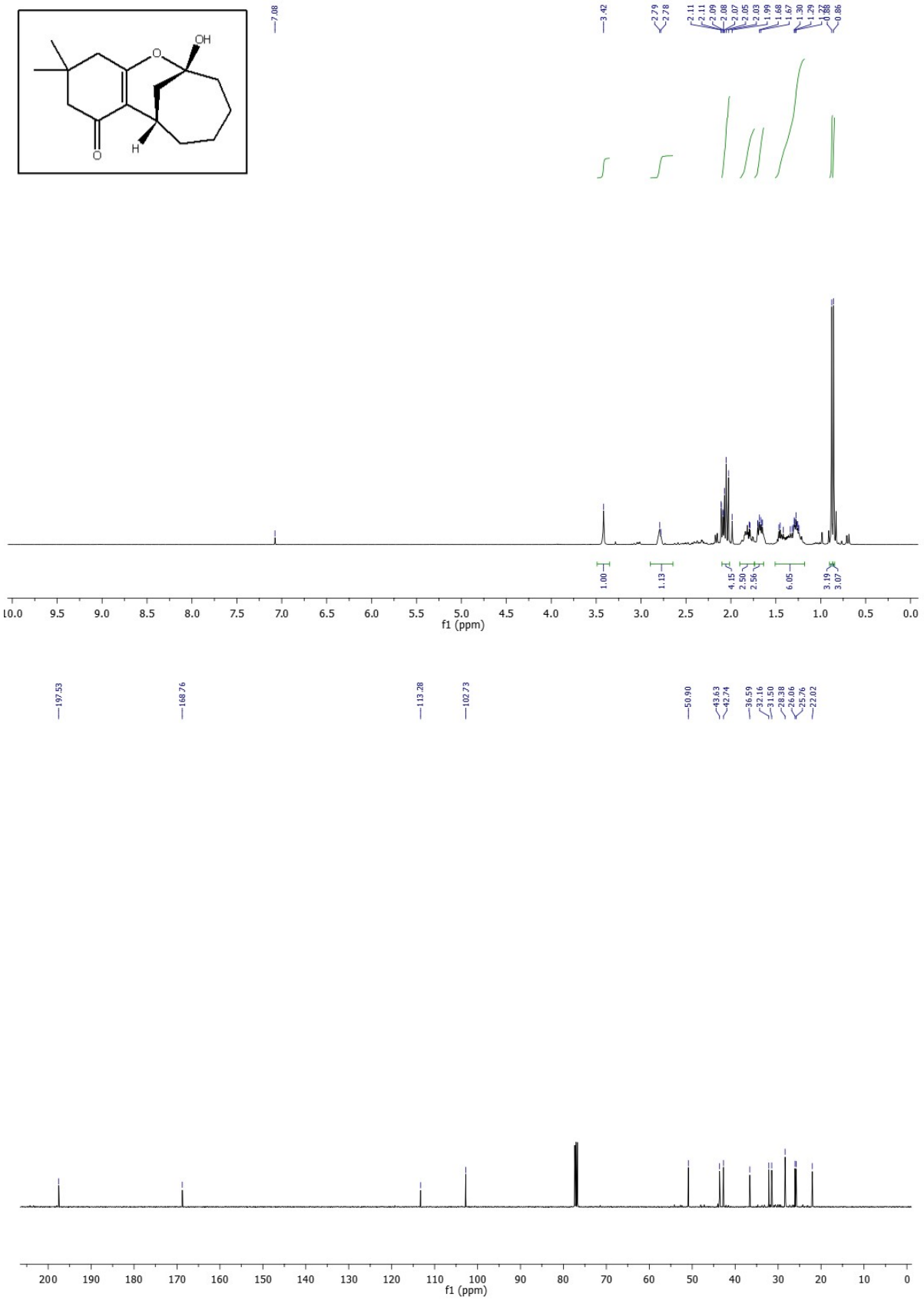
^{1}H and ^{13}C NMR in $CDCl_3$ of compound **8d**



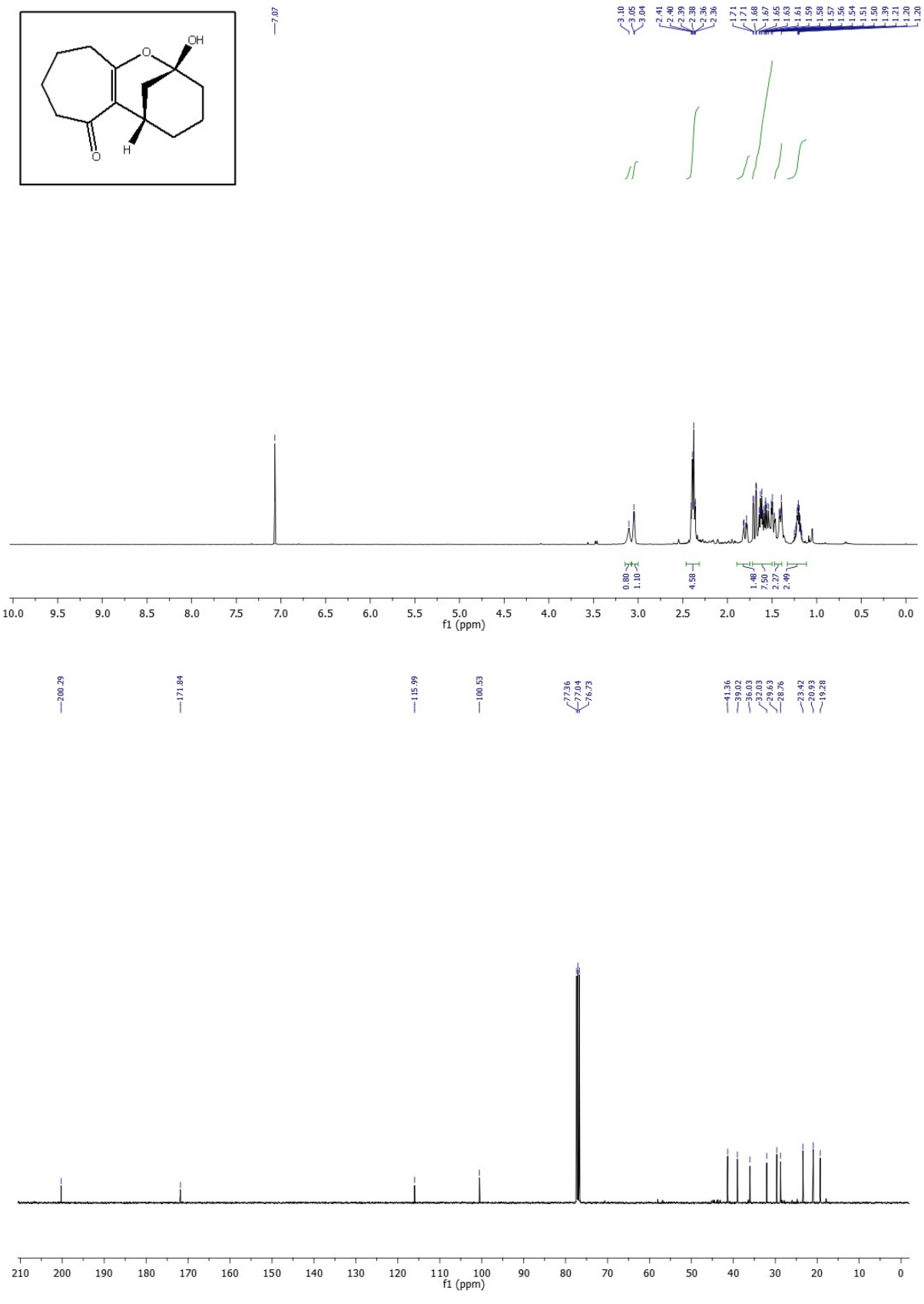
^{1}H and ^{13}C NMR in $CDCl_3$ of compound **8e**



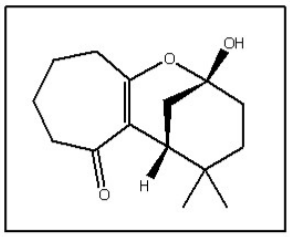
^{1}H and ^{13}C NMR in $CDCl_3$ of compound **8f**

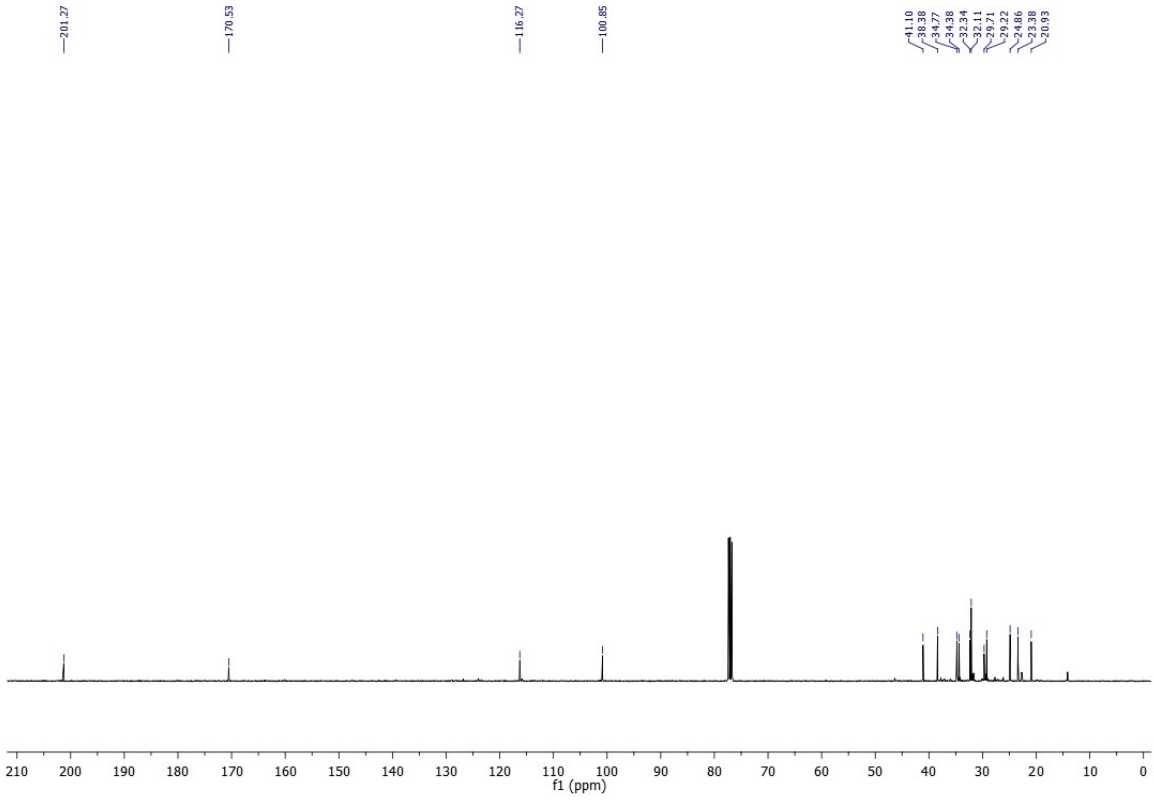


^{1}H and ^{13}C NMR in $CDCl_3$ of Compound **8g**

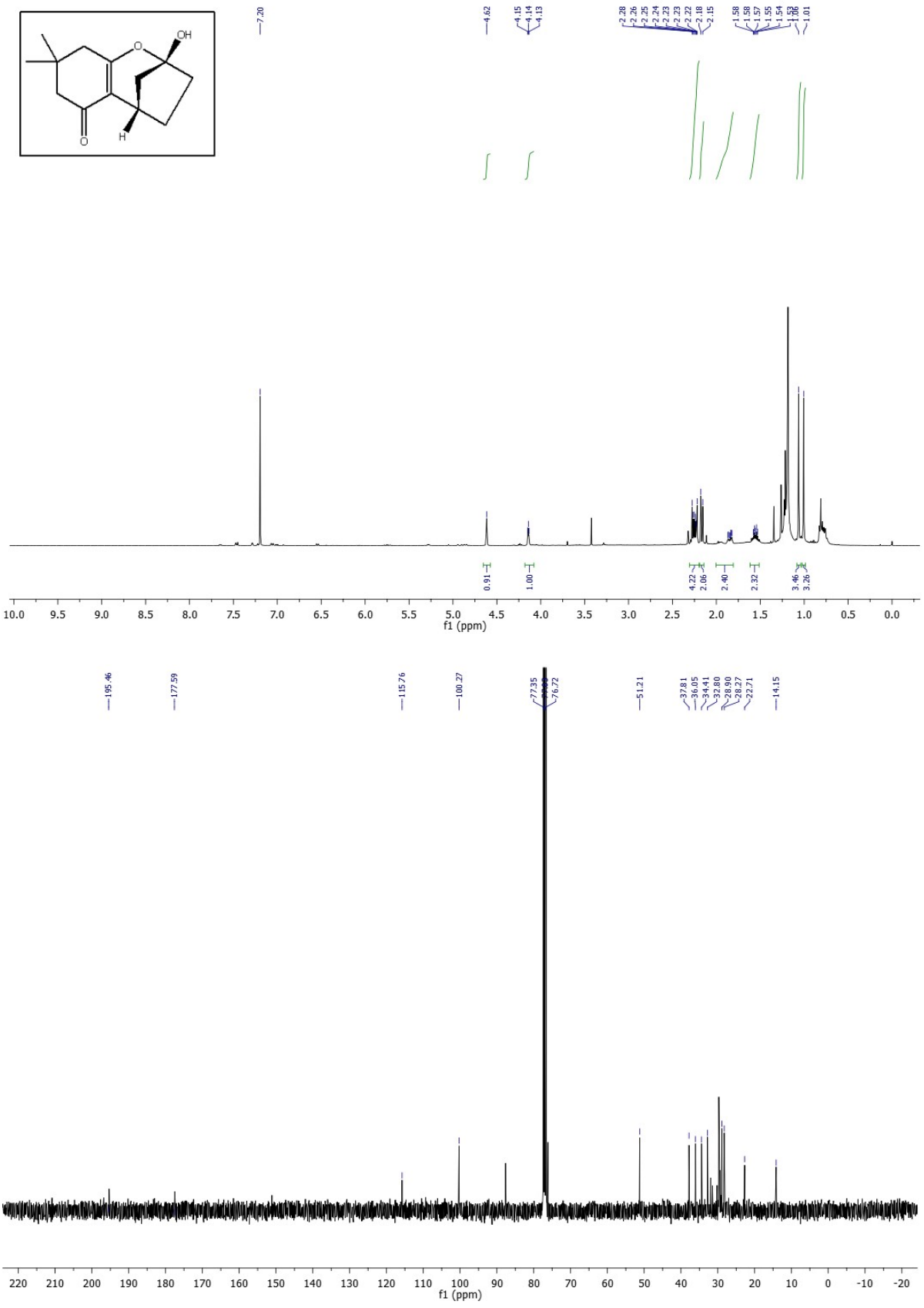


^{1}H and ^{13}C NMR in $CDCl_3$ of compound **8h**

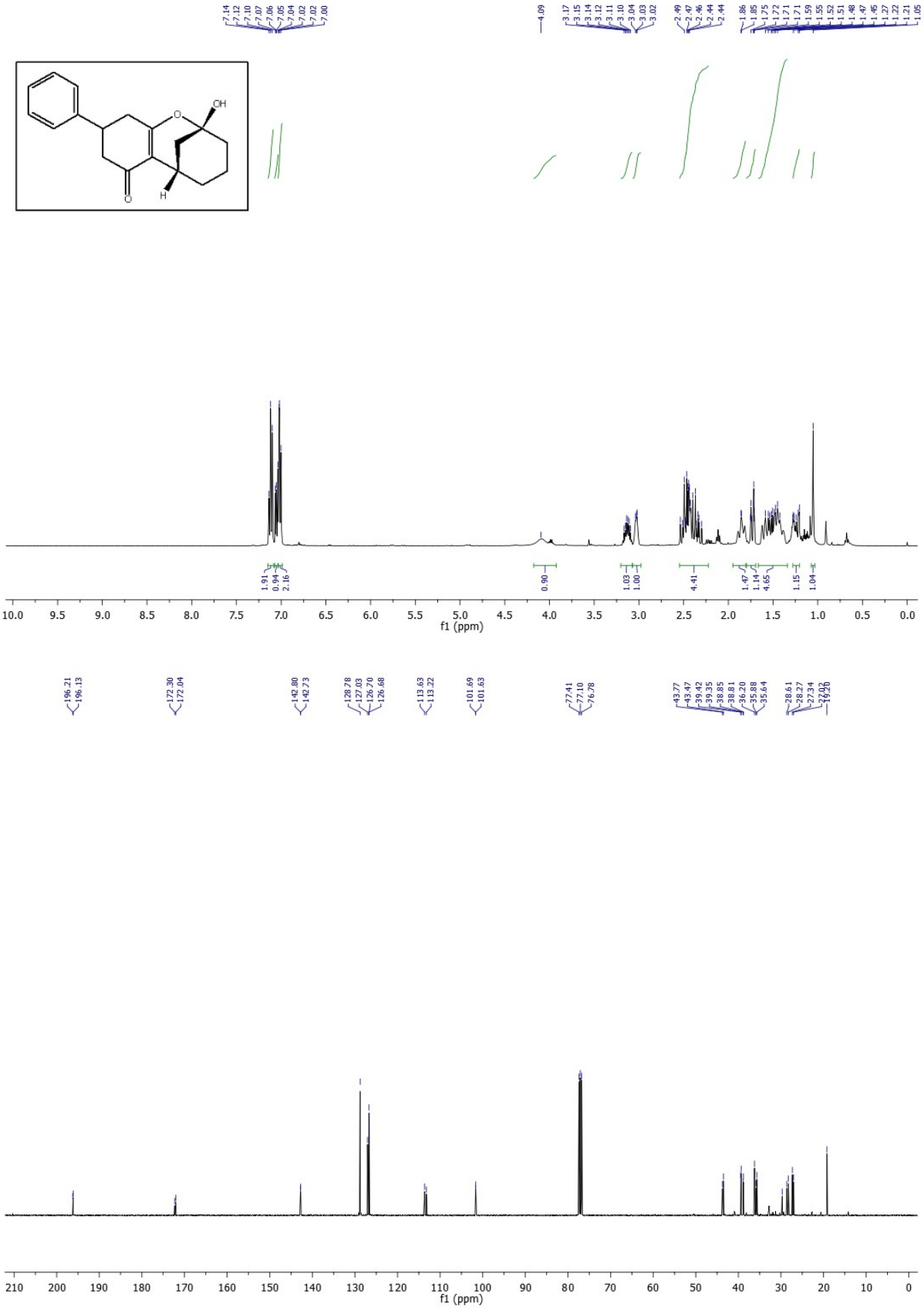




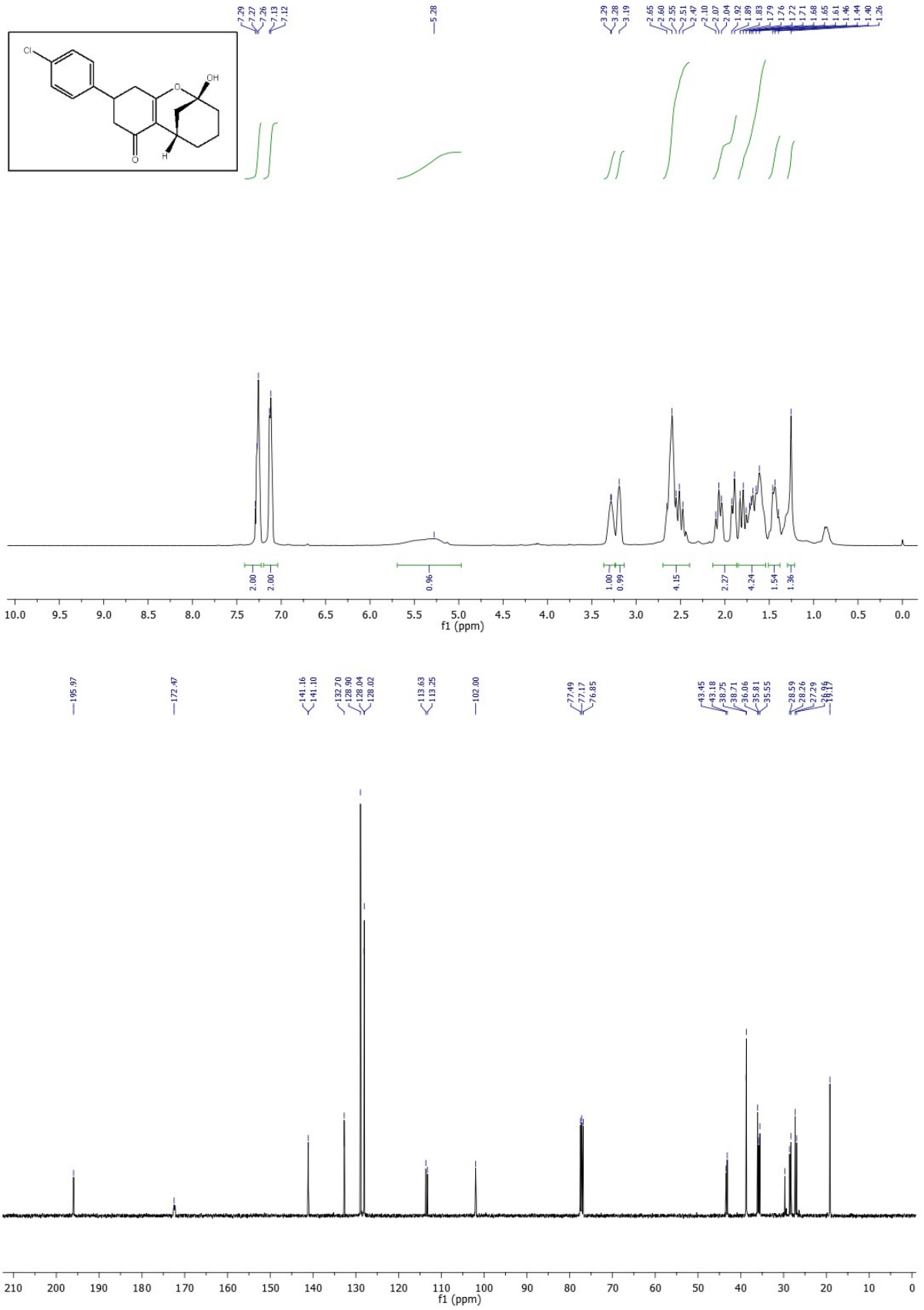
^{1}H and ^{13}C NMR in $CDCl_3$ of compound **8i**



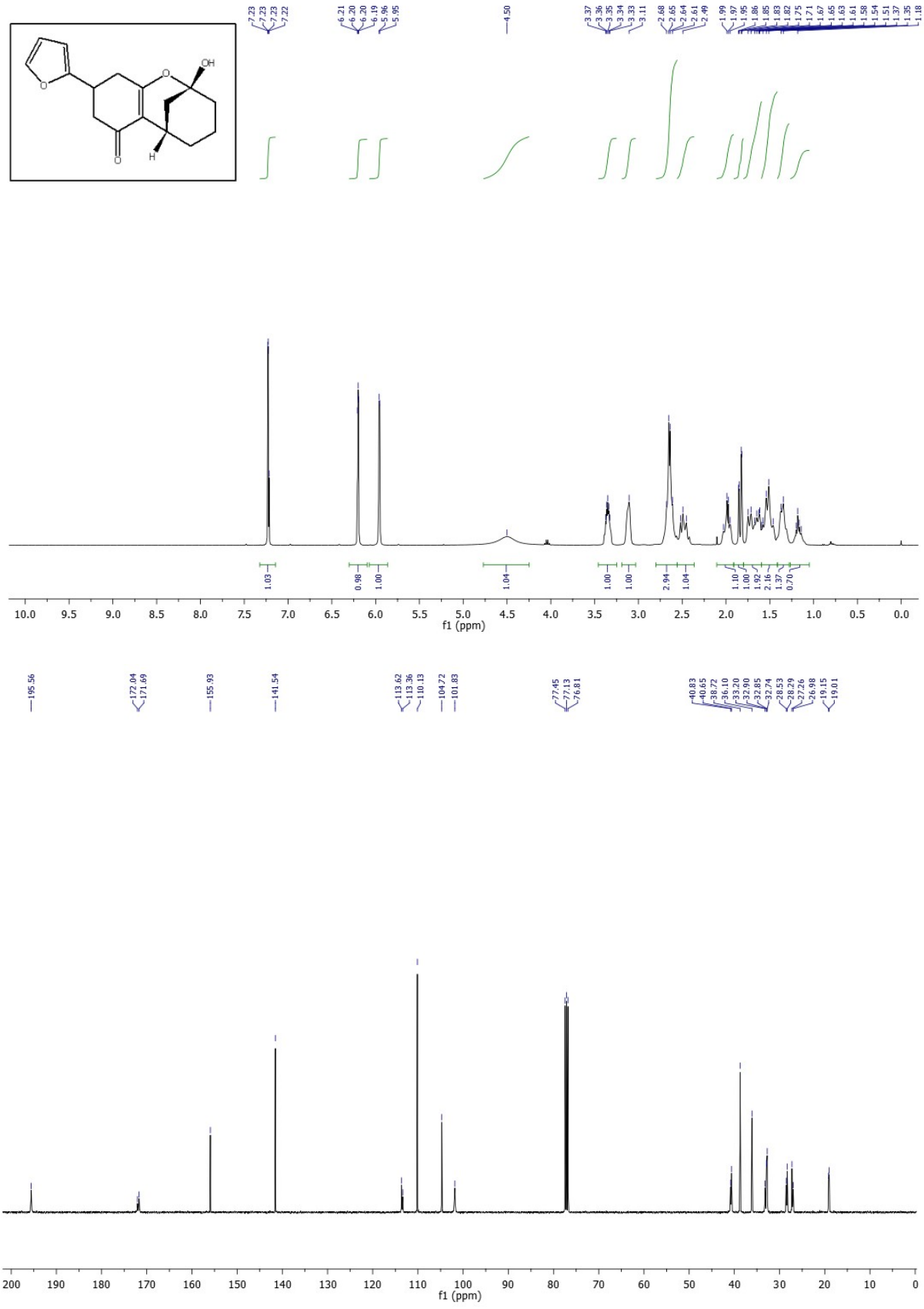
^{1}H and ^{13}C NMR in $CDCl_3$ of compound **8j**



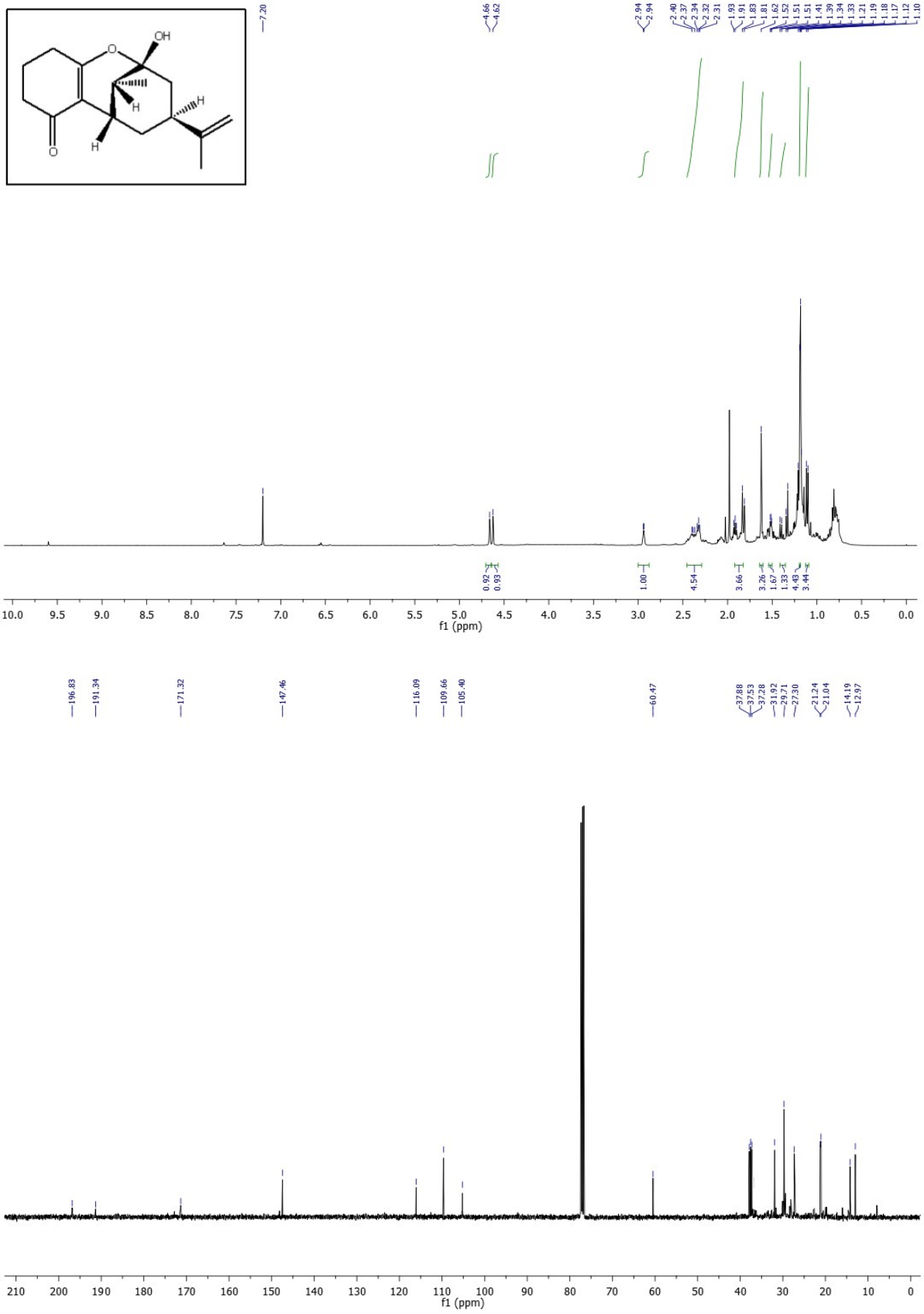
^{1}H and ^{13}C NMR in $CDCl_3$ of compound **8k**



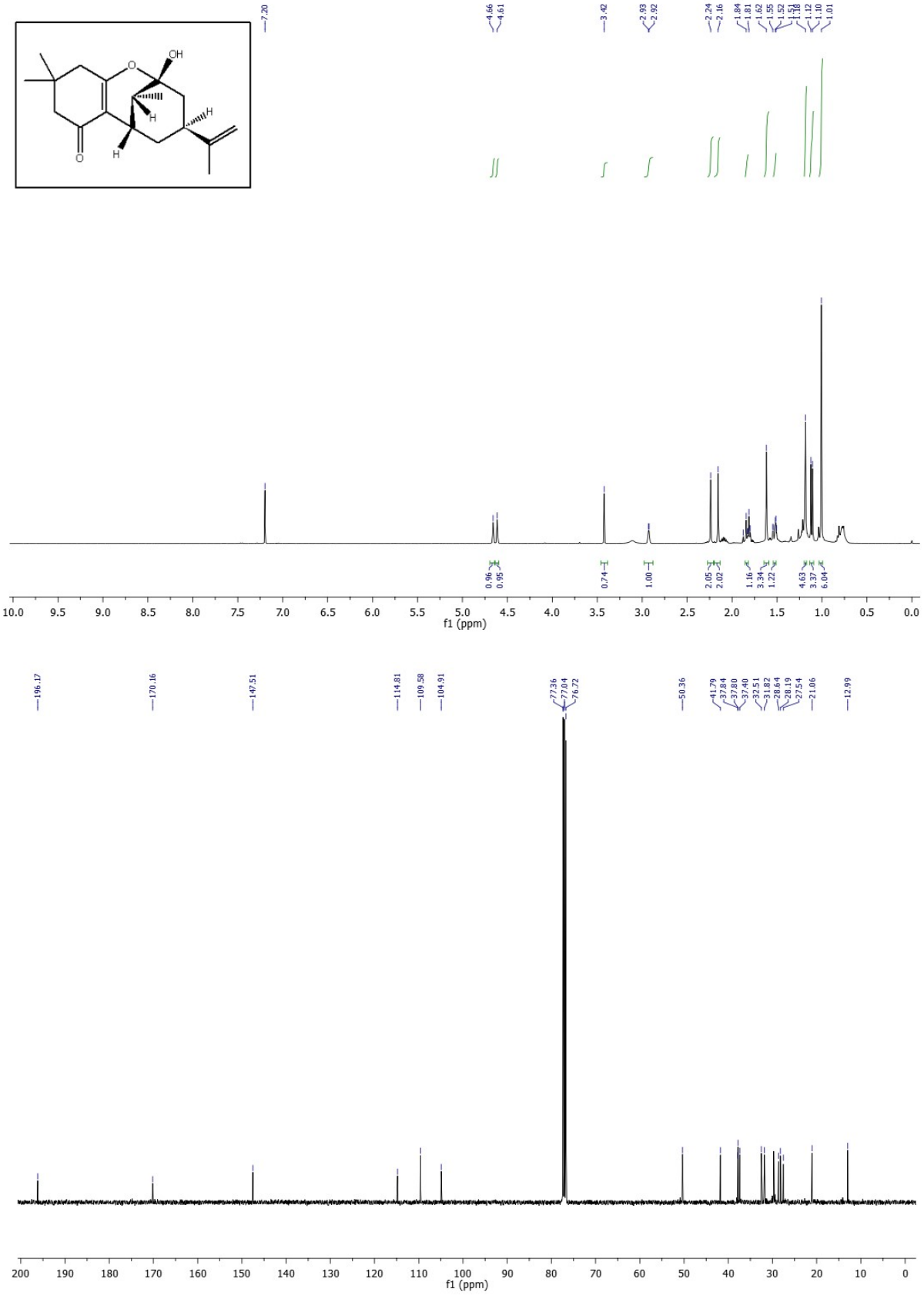
^{1}H and ^{13}C NMR in $CDCl_3$ of compound **8l**



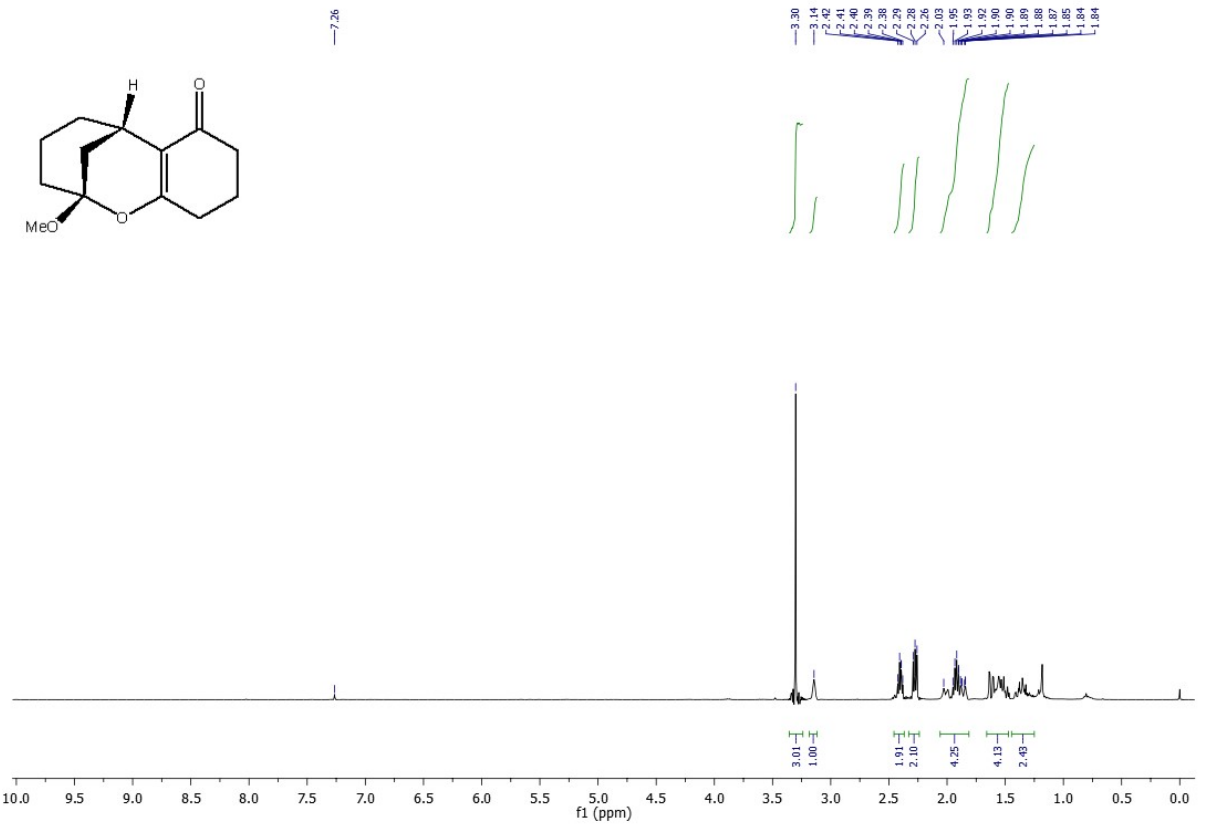
^{1}H and ^{13}C NMR in $CDCl_3$ of compound **8m**

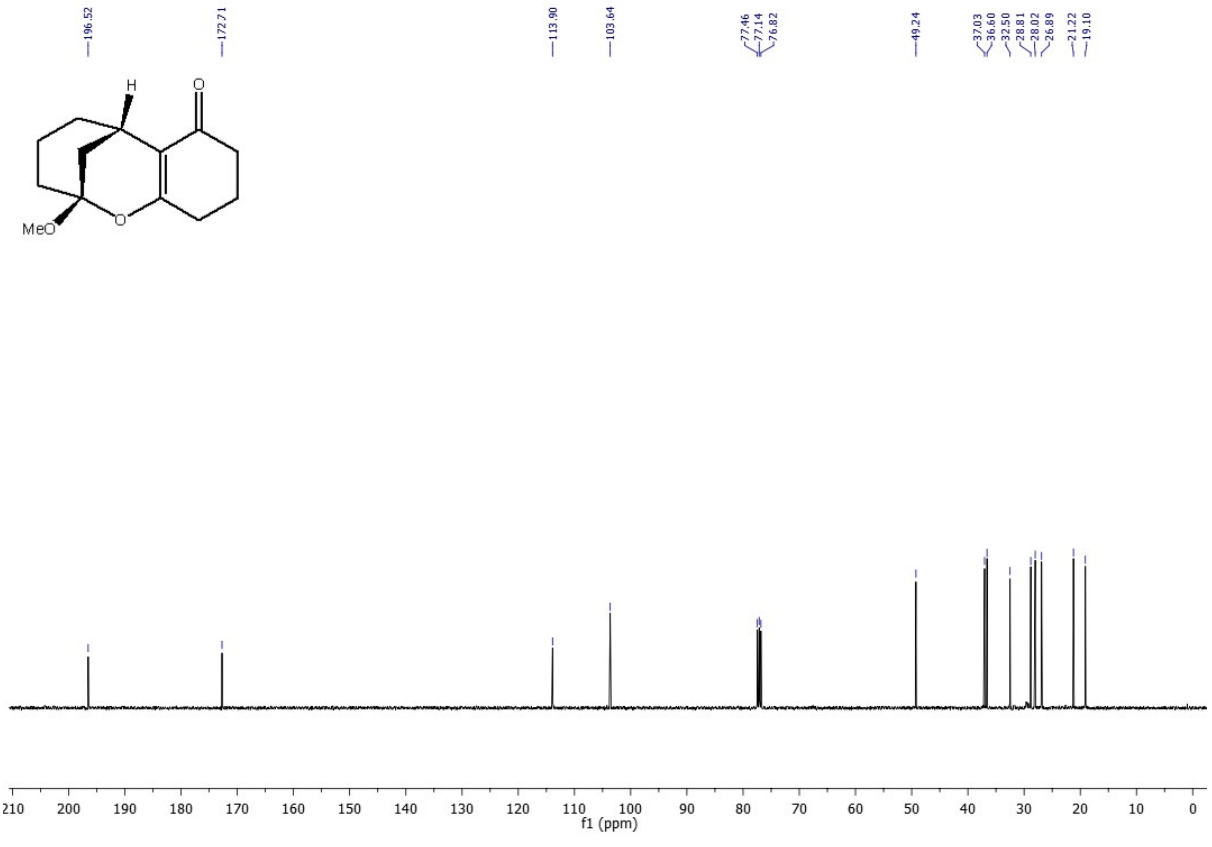


^{1}H and ^{13}C NMR in $CDCl_3$ of compound **8n**

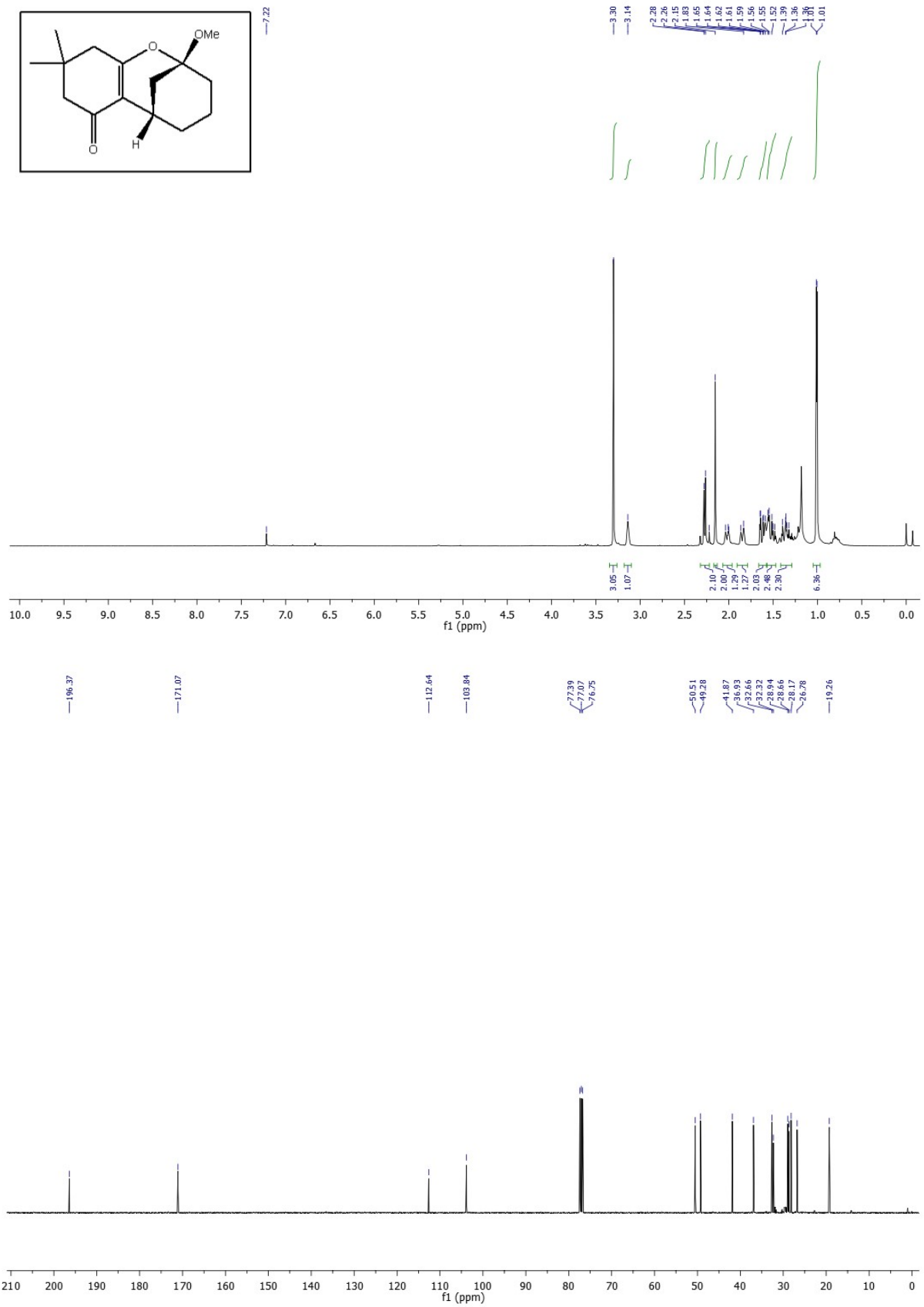


^{1}H and ^{13}C NMR in $CDCl_3$ of compound **9a**

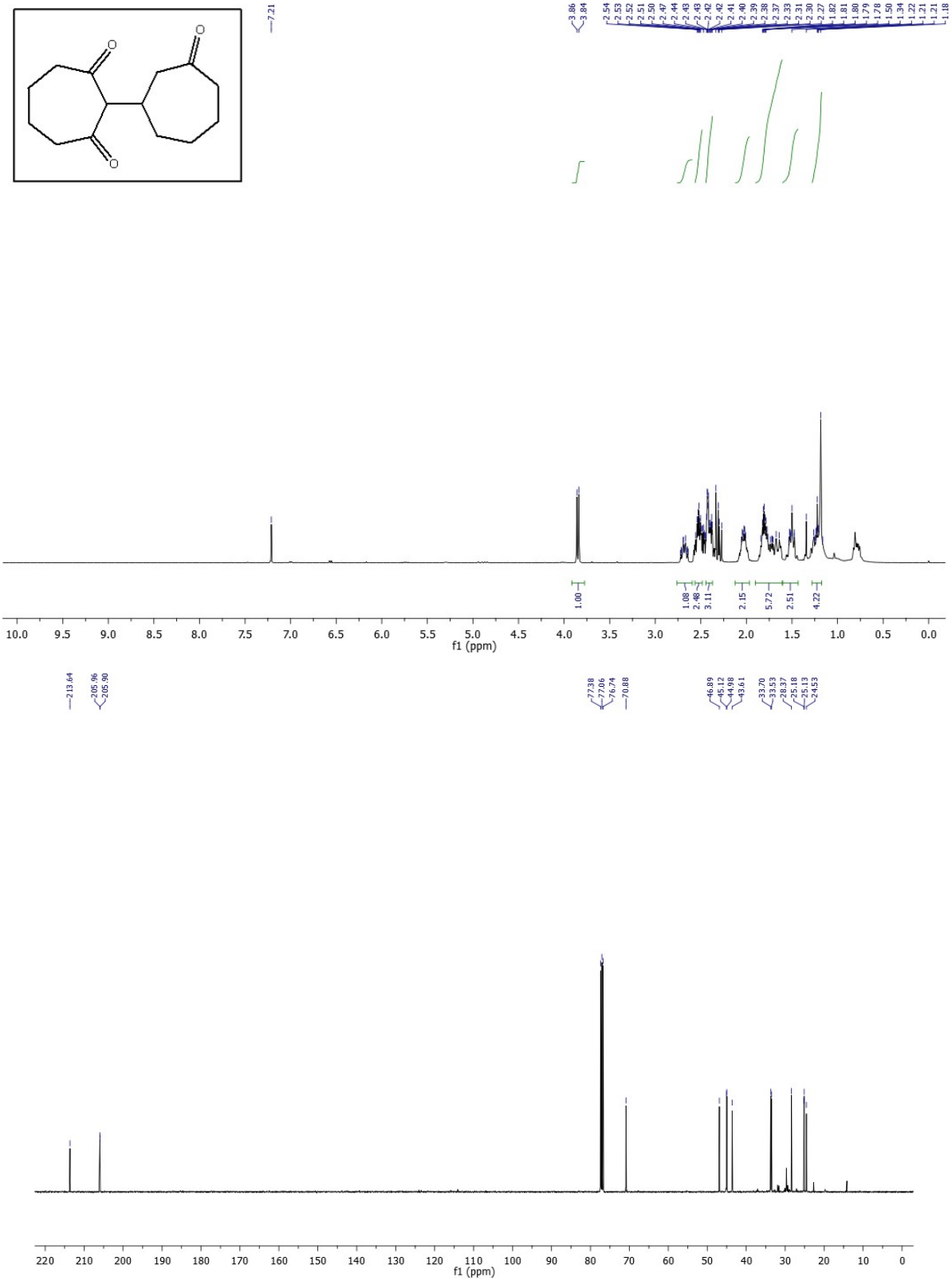




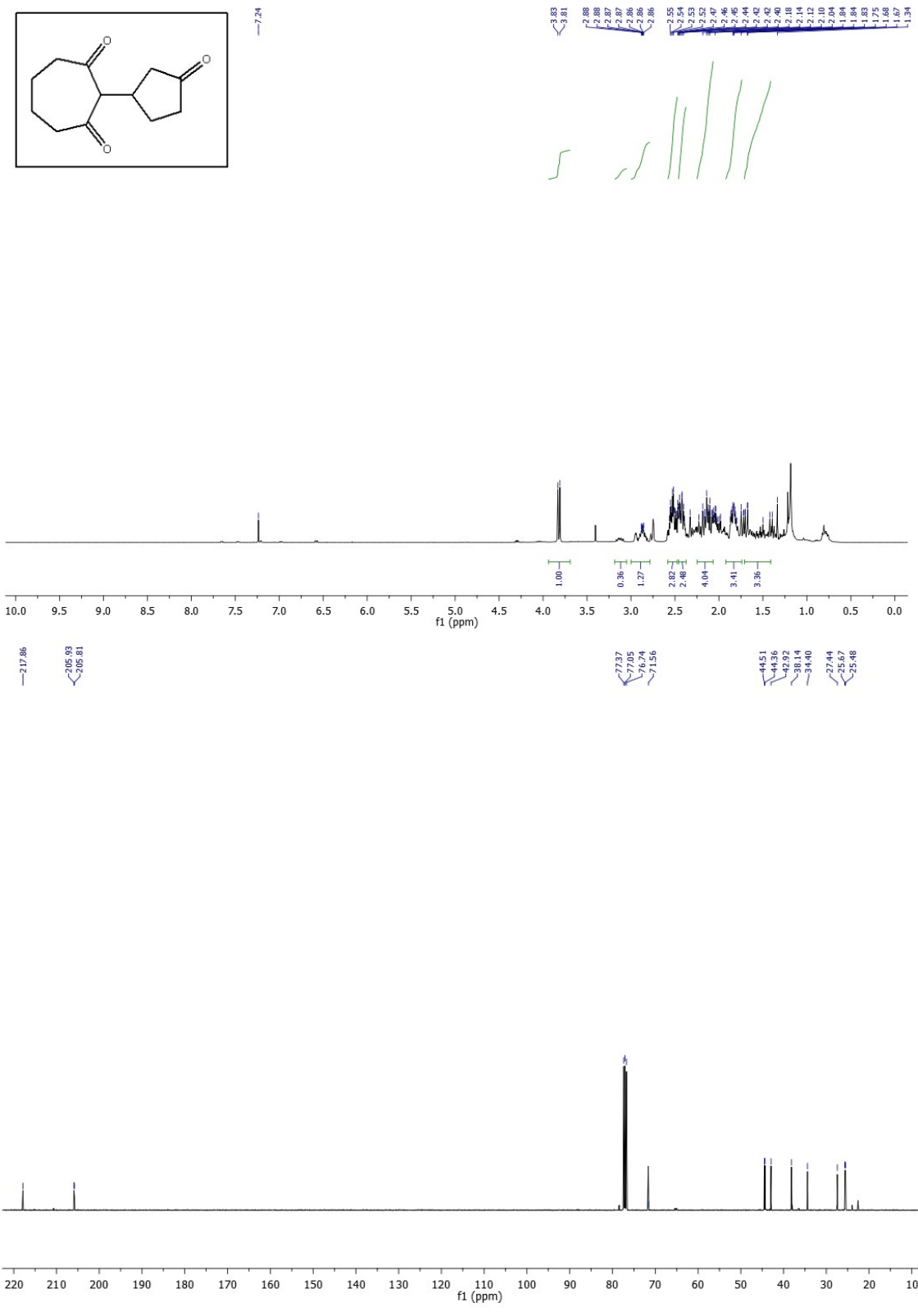
^{1}H and ^{13}C NMR in $CDCl_3$ of compound **9b**



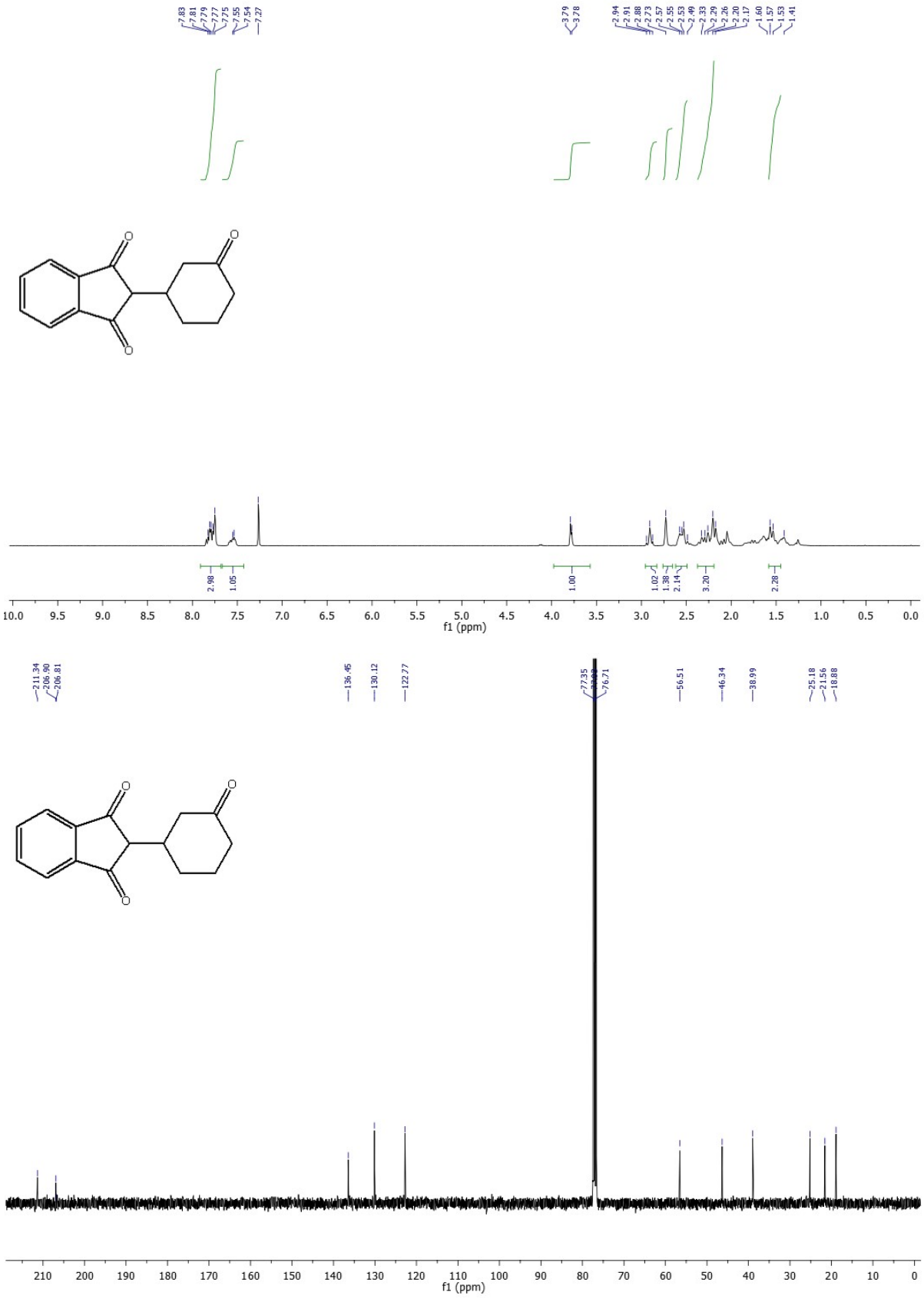
^{1}H and ^{13}C NMR in $CDCl_3$ of compound **7b**



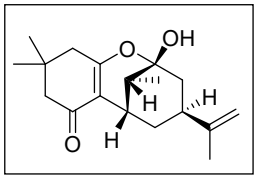
^{1}H and ^{13}C NMR in $CDCl_3$ of compound **7c**

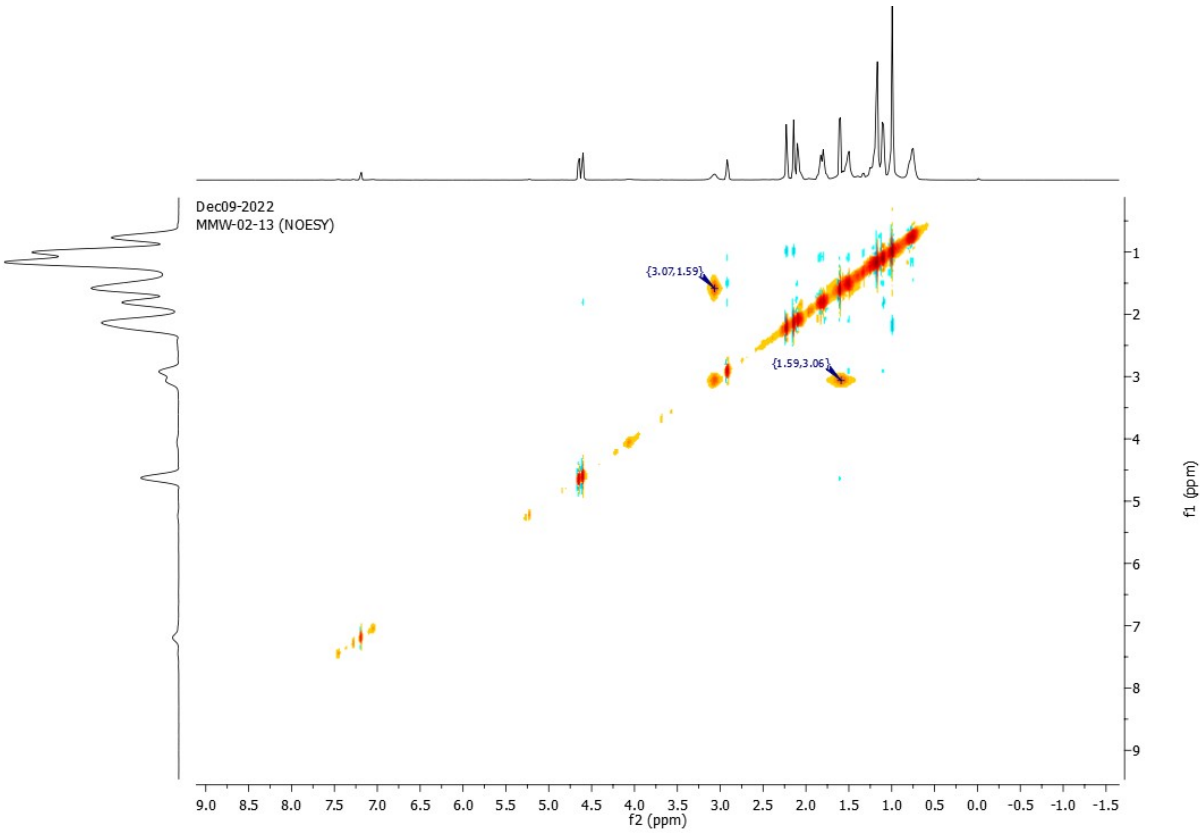


^{1}H and ^{13}C NMR in $CDCl_3$ of compound **7d**



COSY and NOESY of compound **8n**

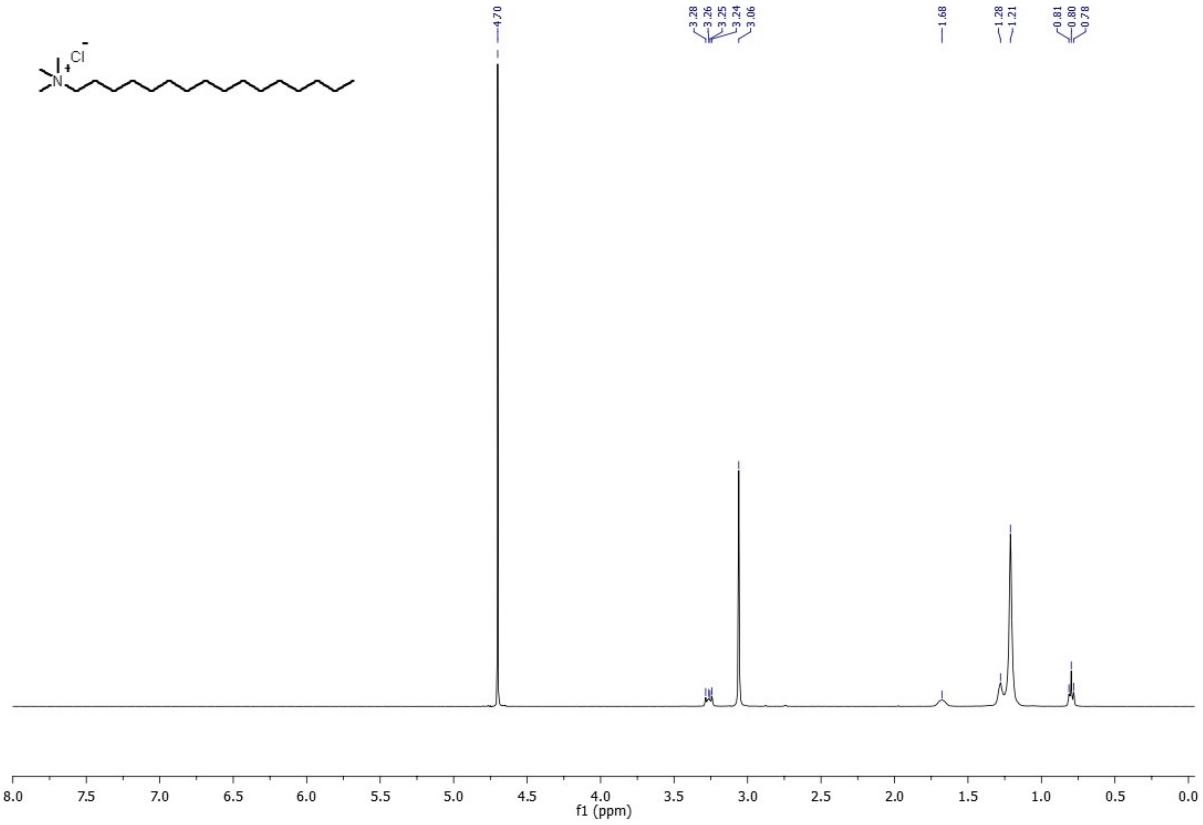




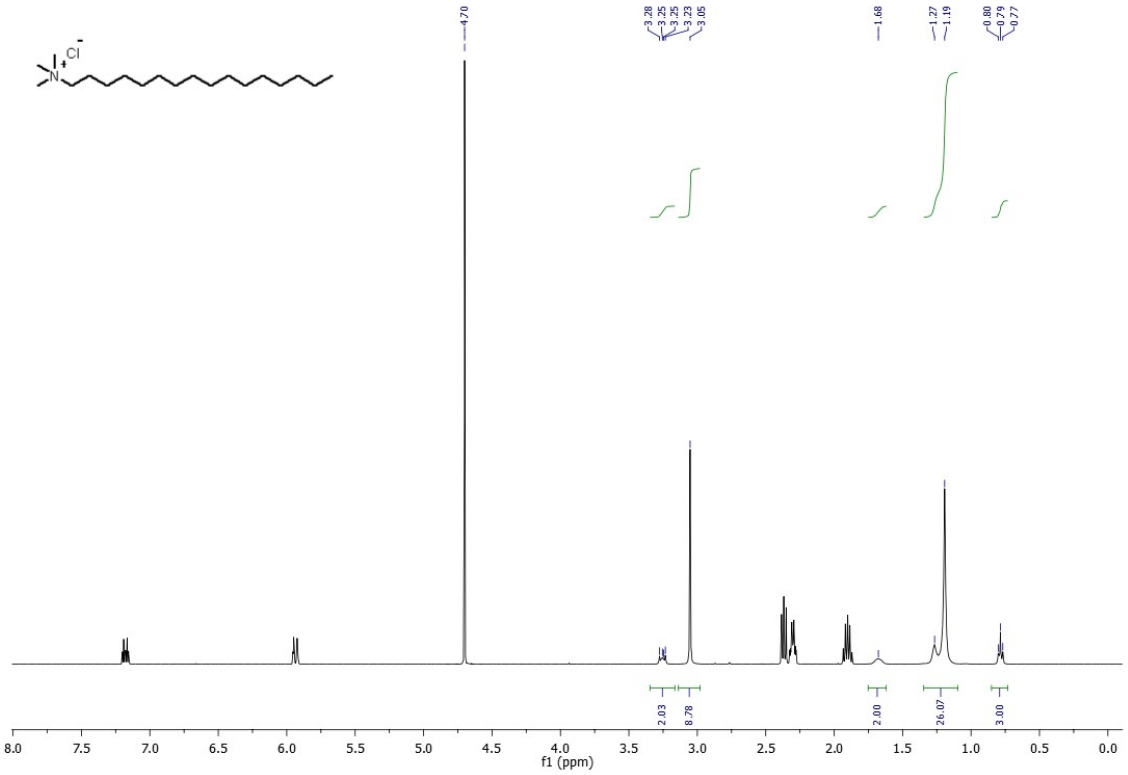
Locus of solubilisation:

To find out the locus of reaction site, 1.6 mM CTAC solution was prepared in D_2O by dissolving 5.3 mg of CTAC in 10 ml of D_2O on constant stirring in a clean RB flask. Various concentrations of 2-cyclohexenone, 0.2, 0.4, 0.8, 1.6 and 3.2 mM was prepared from it and their proton NMR was recorded and compared with pure CTAC solution in D_2O. With increase in the concentration of solubilizate, 2-cyclohexenone, the chemical shifts were tabulated and plotted in a graph to investigate its locus. Similarly, the same experiment was carried out to know the locus of other solubilizate, 1-3-cyclohexdione. Proton NMR of 1.6 mM CTAC micellar solution in D_2O was recorded and compared with NMRs of 0.2, 0.4, 0.8, 1.6 and 3.2 mM solutions of 1,3-cyclohexadione in CTAC solution. Change in chemical shifts were analysed to determine its locus in micellar assembly.

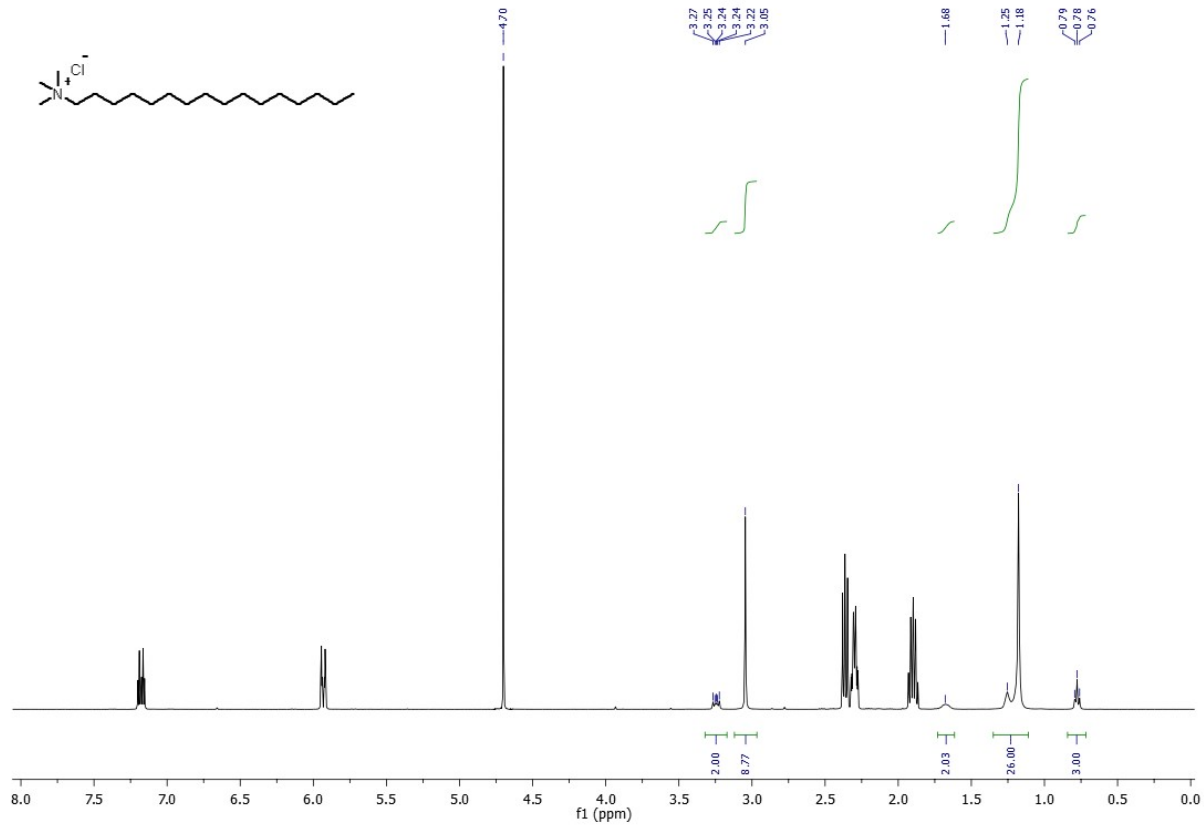
^1H NMR of 1.6 mM CTAC micellar solution in D_2O



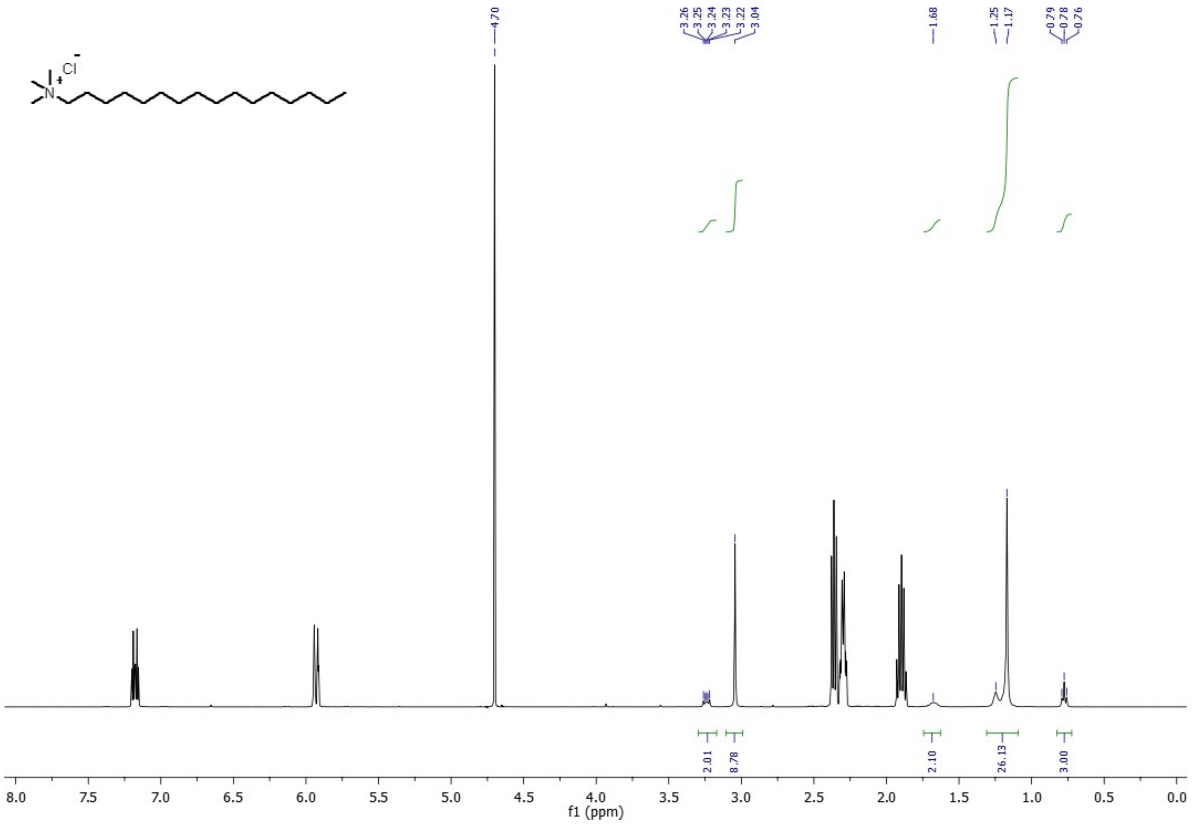
^{1}H NMR of 1.6 mM CTAC micellar and 0.2 mM 2-cyclohexenone solution in D_2O



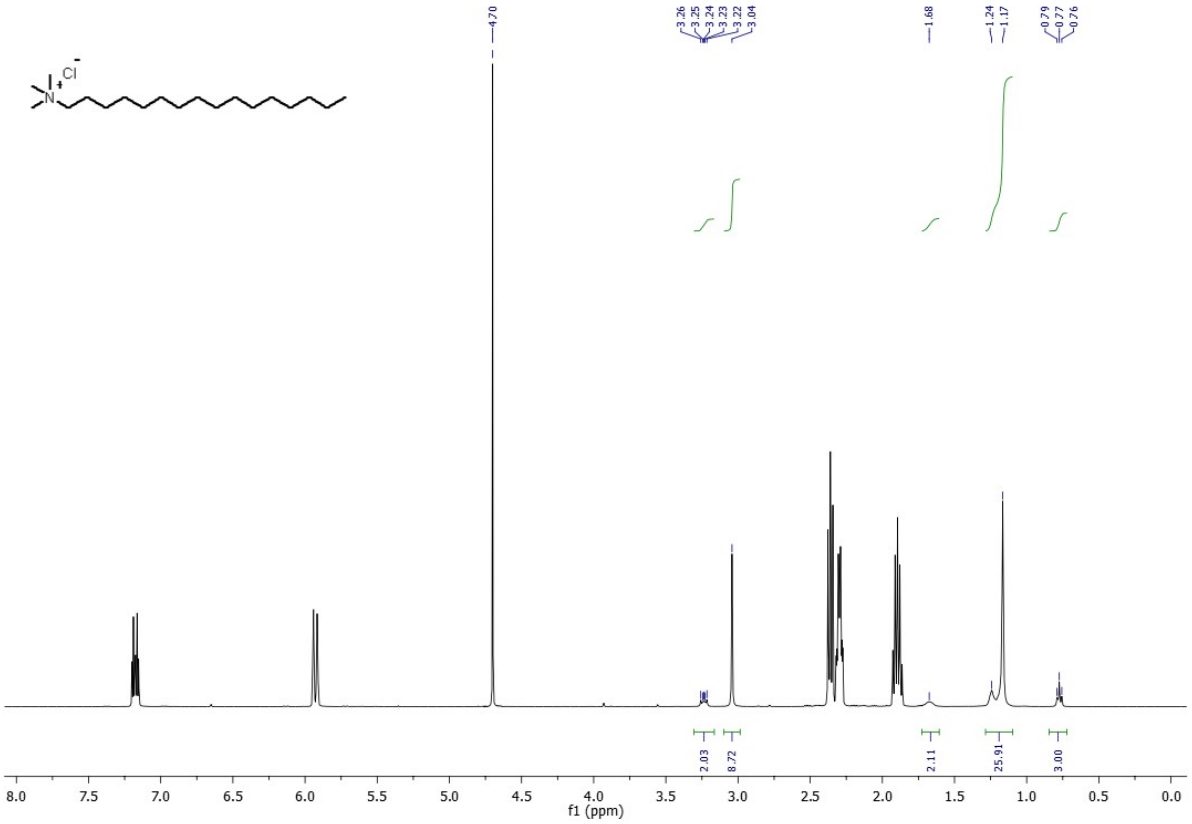
^{1}H NMR of 1.6 mM CTAC micellar and 0.4 mM 2-cyclohexenone solution in D_2O



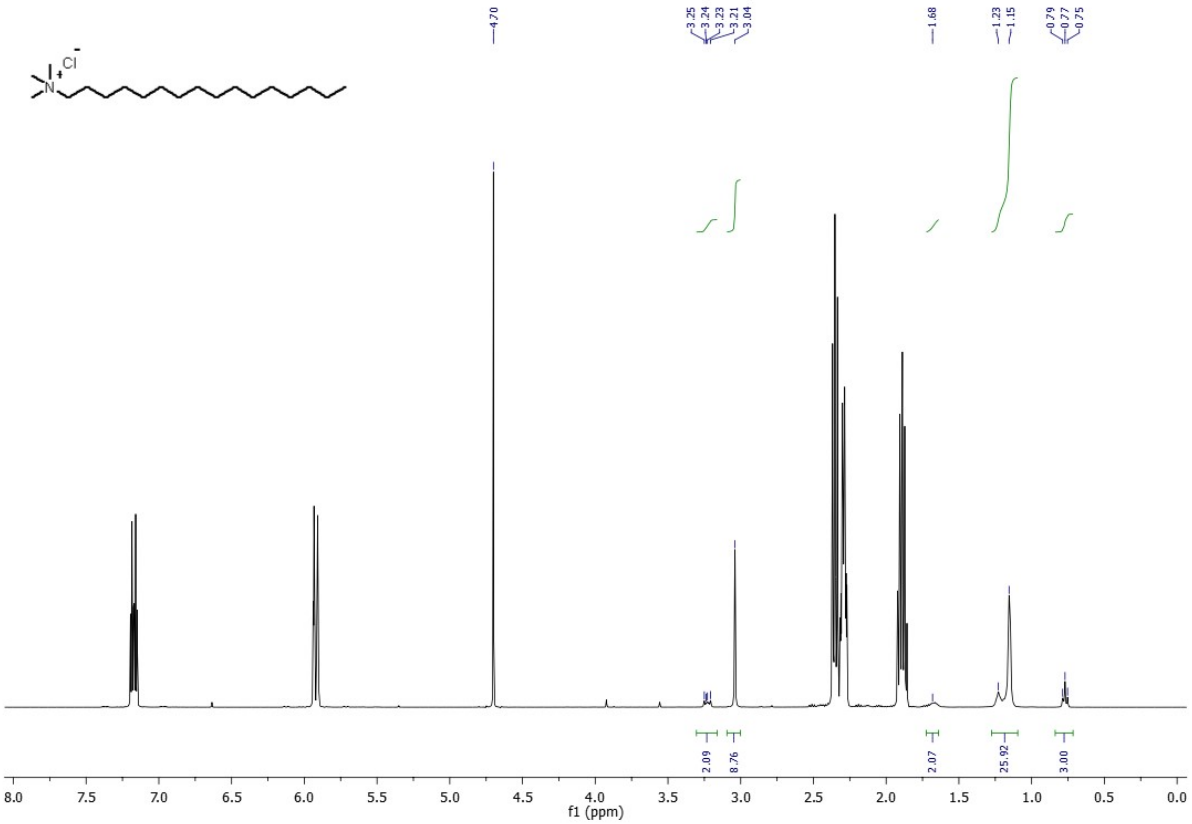
^{1}H NMR of 1.6 mM CTAC micellar and 0.8 mM 2-cyclohexenone solution in D_2O



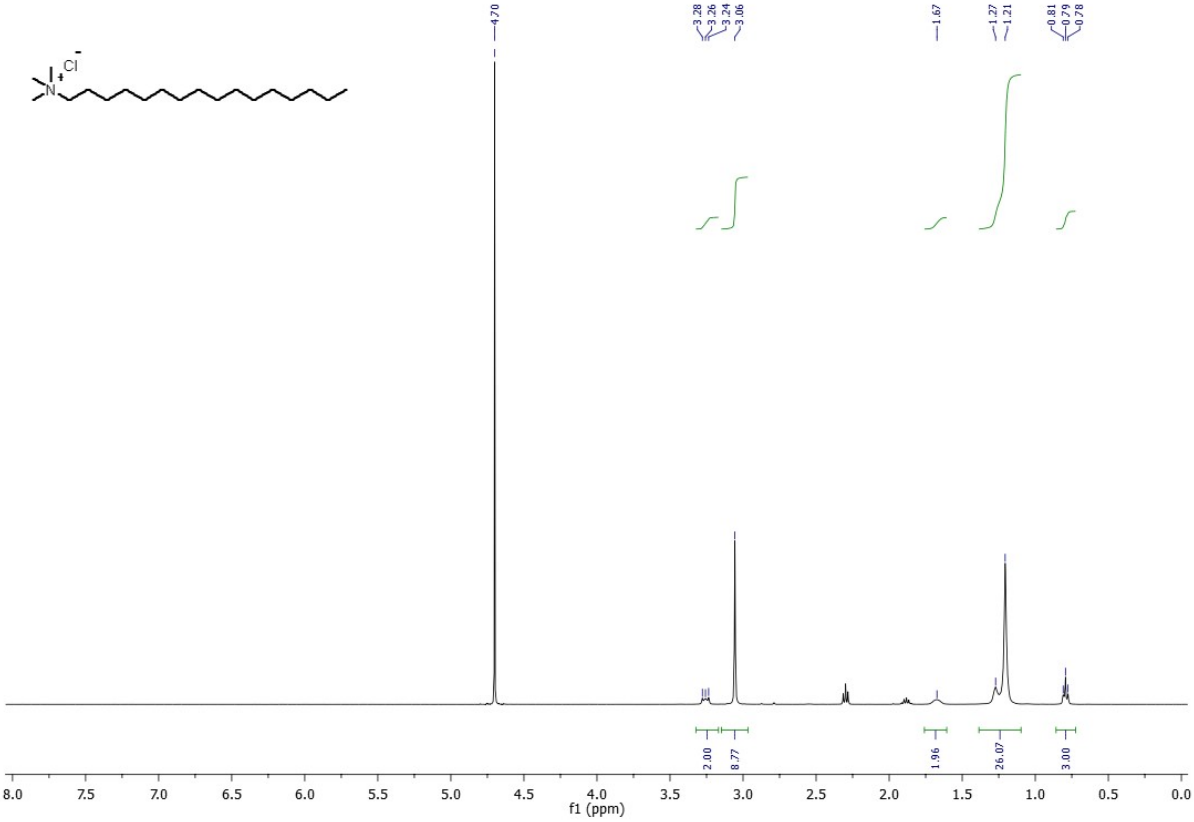
^{1}H NMR of 1.6 mM CTAC micellar and 1.6 mM 2-cyclohexenone solution in D_2O



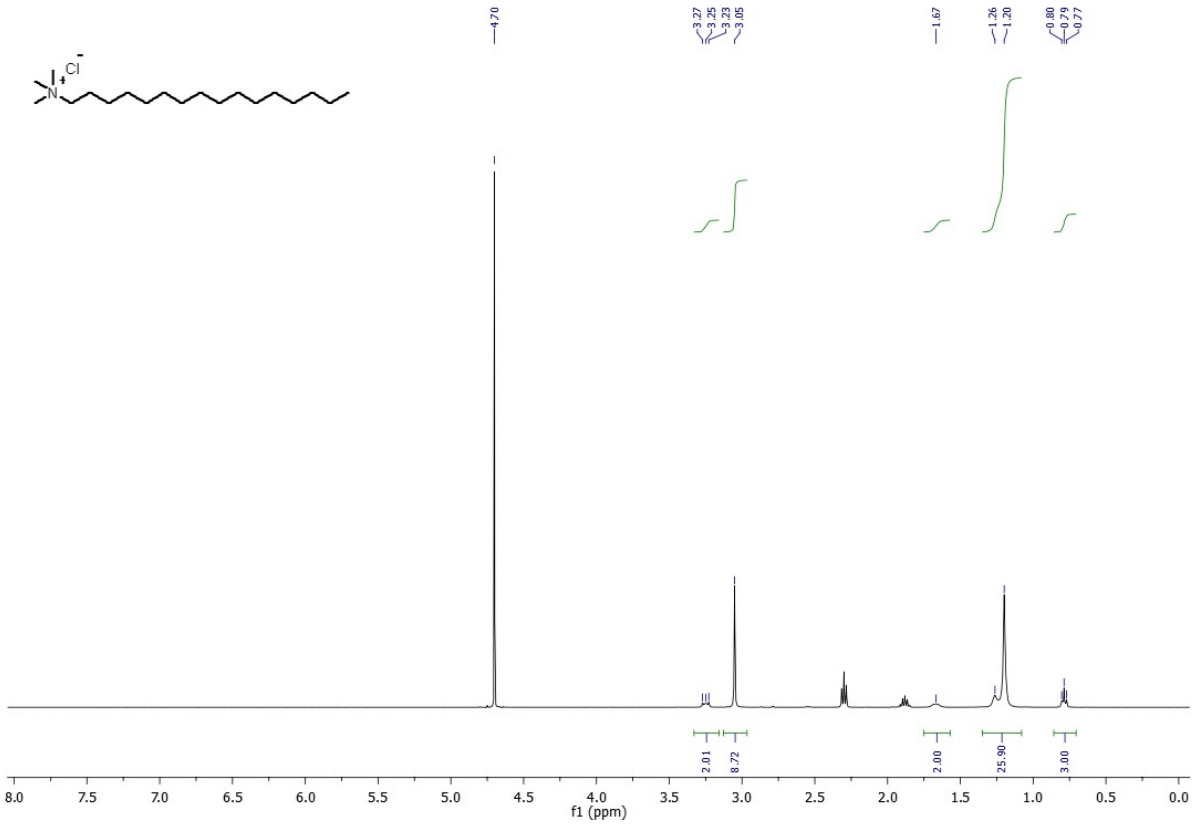
^{1}H NMR of 1.6 mM CTAC micellar and 3.2 mM 2-cyclohexenone solution in D_2O



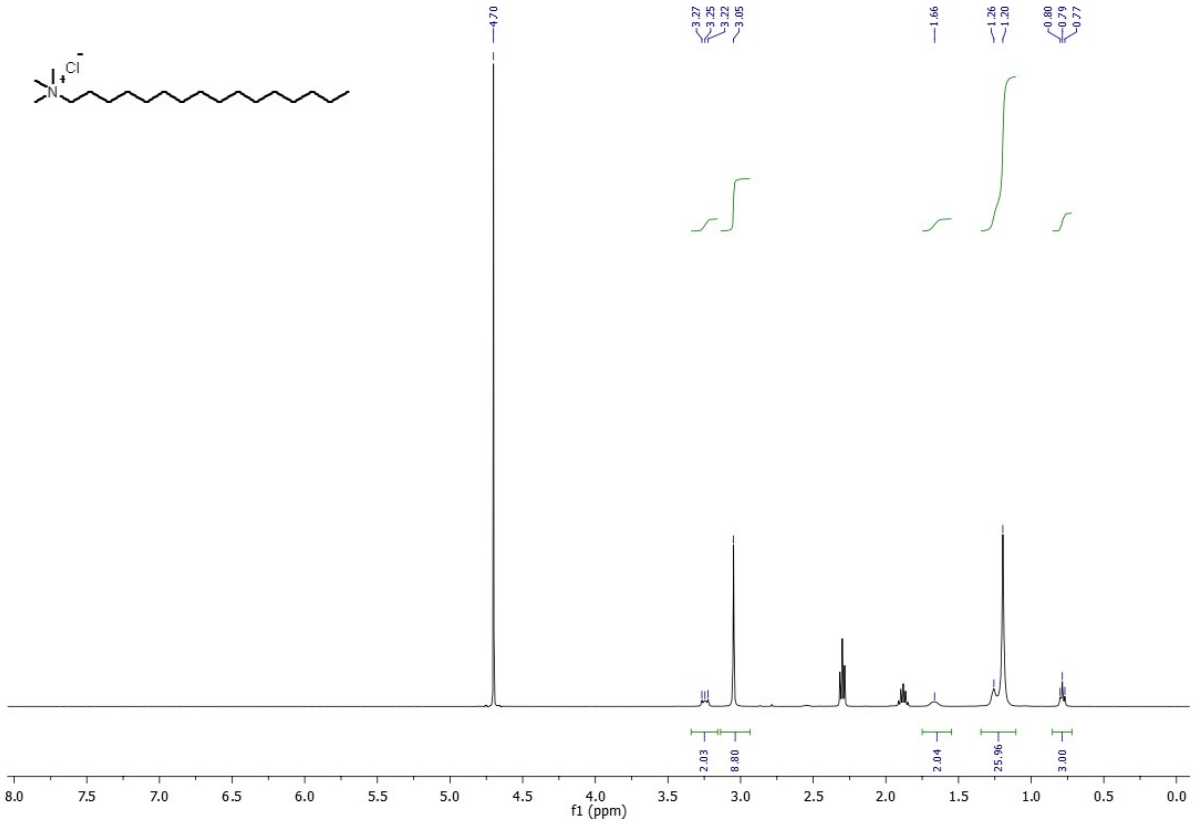
^{1}H NMR of 1.6 mM CTAC micellar and 0.2 M cyclohexane-1,3-dione solution in D_2O



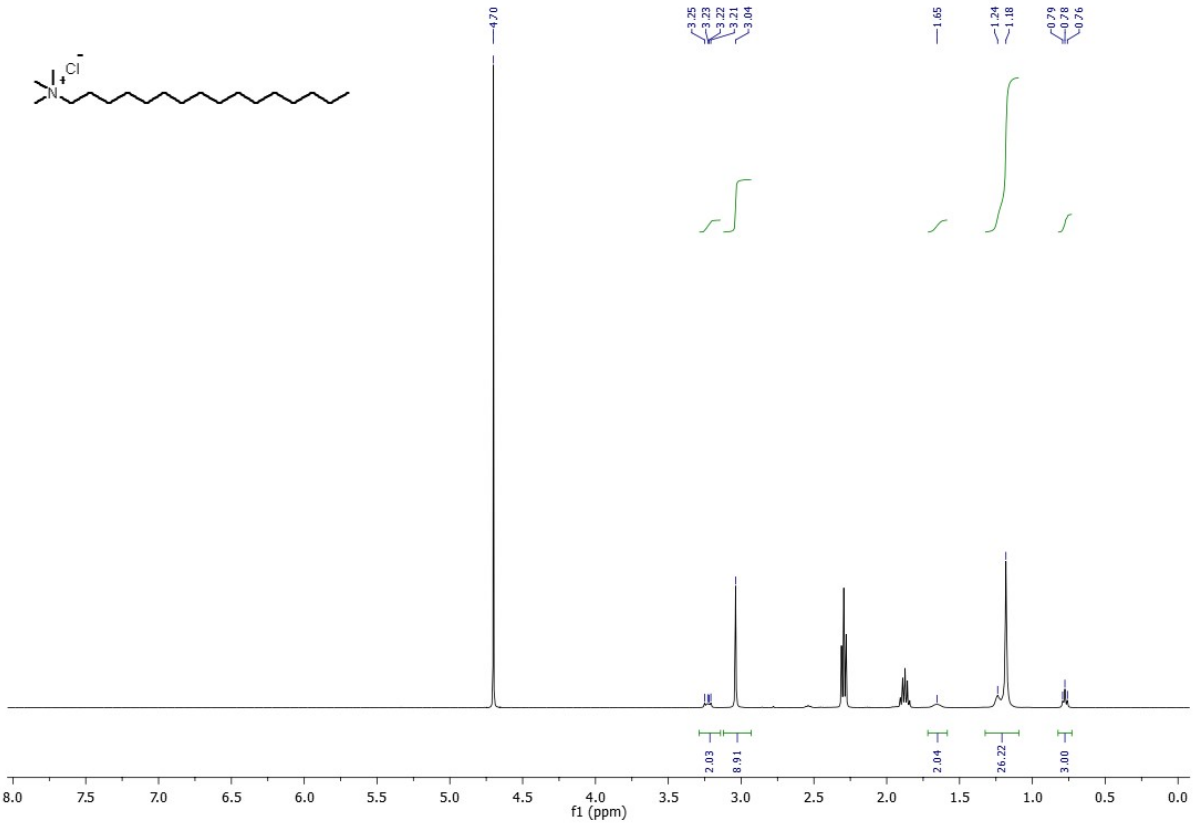
^{1}H NMR of 1.6 mM CTAC micellar and 0.4 mM cyclohexane-1,3-dione solution in D_2O



^{1}H NMR of 1.6 mM CTAC micellar and 0.8 mM cyclohexane-1,3-dione solution in D_2O



^{1}H NMR of 1.6 mM CTAC micellar and 1.6 mM cyclohexane-1,3-dione solution in D_2O



^{1}H NMR of 1.6 mM CTAC micellar and 3.2 mM cyclohexane-1,3-dione solution in D_2O

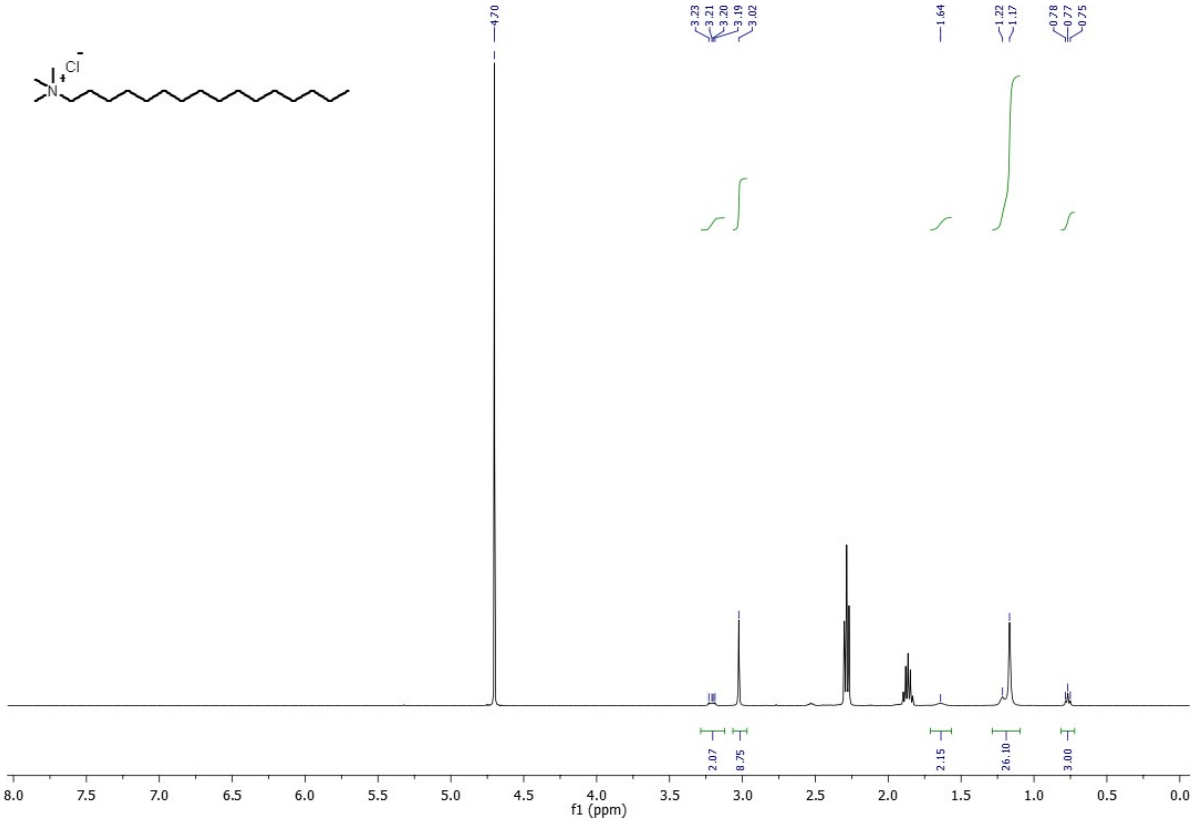


Figure S2: Chemical shift in the protons of 1.6 mM CTAC/D_2O solution at different concentrations of 2-cyclohexenone

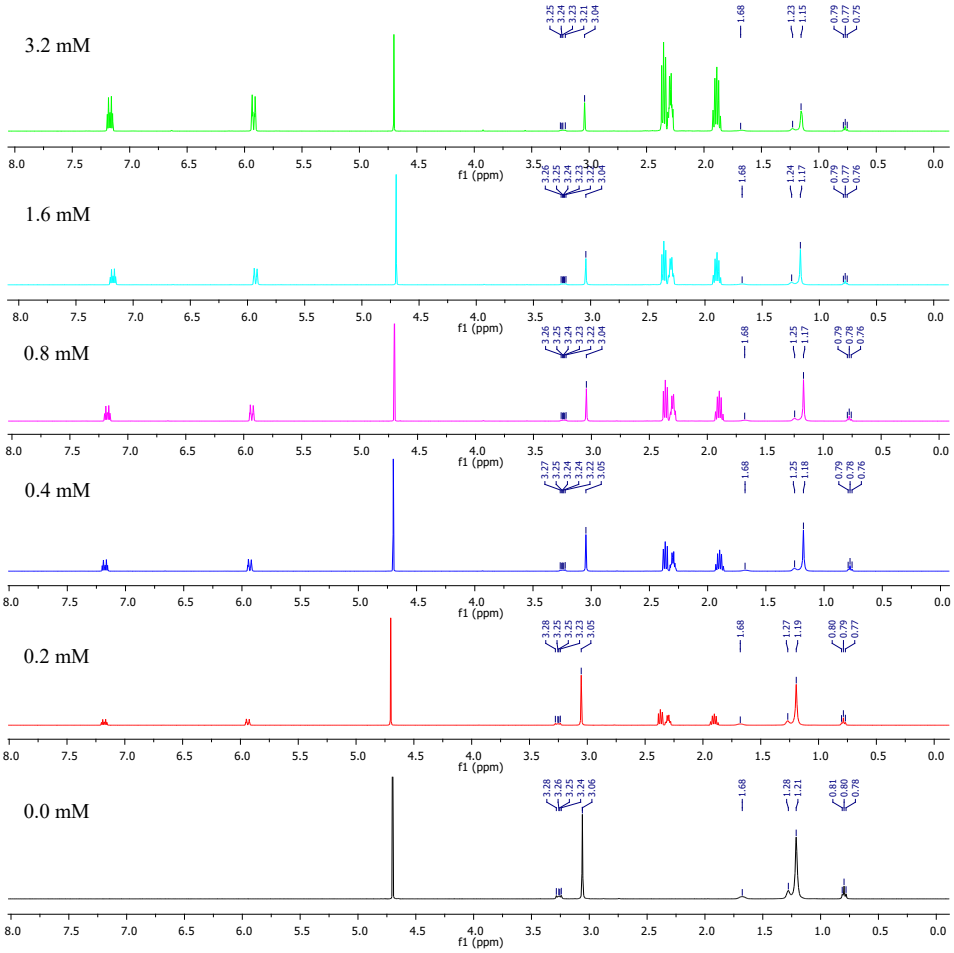


Table S2: A shift of protons in CTAC in D_2O at various concentrations of 2-cyclohexenone.

Conc. of 2-cyclohexenone (mM)	Chemical shift of protons in 1.6 mM CTAC micellar solution					
	A $N(CH_3)_3$	B $\alpha(CH_2)$	C $\beta(CH_2)$	D $\gamma(CH_2)$	E $\delta(CH_2)_{12}$	F ωCH_3
0.0	3.06	3.26	1.68	1.28	1.21	0.79
0.2	3.05	3.25	1.68	1.27	1.19	0.78
0.4	3.05	3.24	1.68	1.25	1.18	0.77
0.8	3.04	3.24	1.68	1.25	1.17	0.77
1.6	3.04	3.24	1.68	1.24	1.17	0.77
3.2	3.04	3.23	1.68	1.23	1.15	0.77

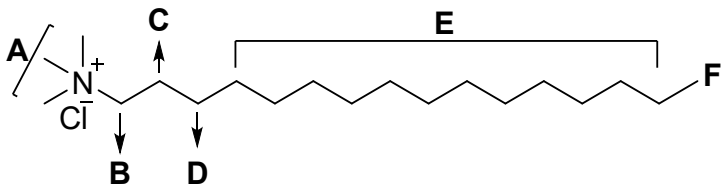


Figure S3: Structure of CTAC surfactant

Figure S4: A plot of chemical shift of CTAC surfactant protons with the change in the concentration of 2-cyclohexenone.

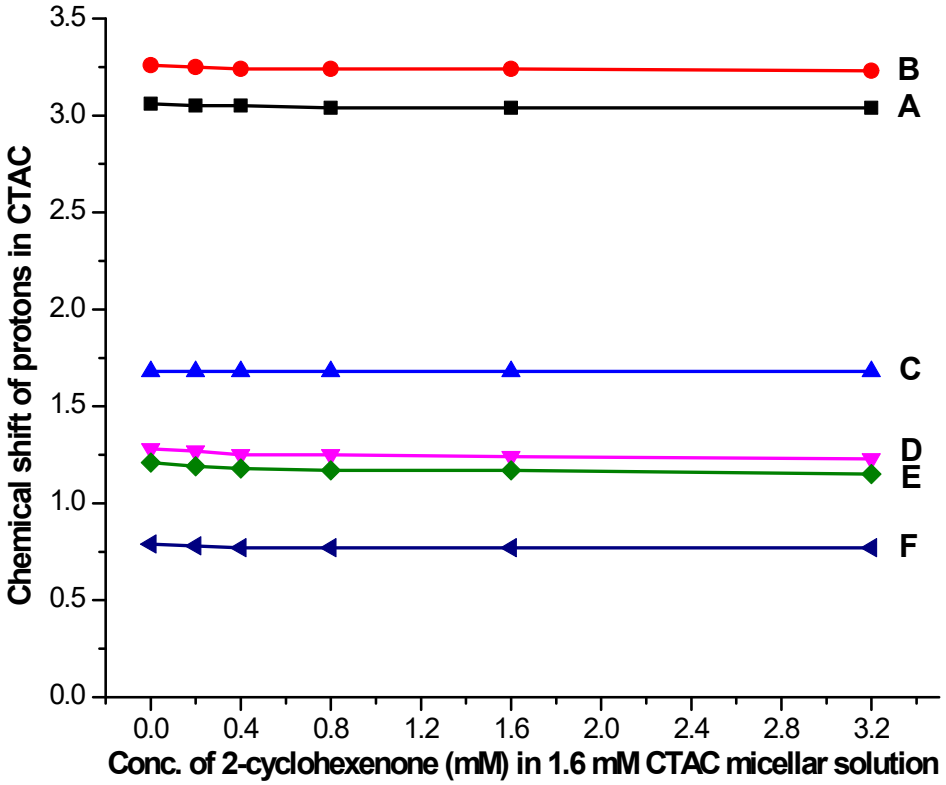


Figure S5: Shift in the protons of 1.6 mM CTAC/D_2O solution at different concentrations of 1,3-cyclohexanedione

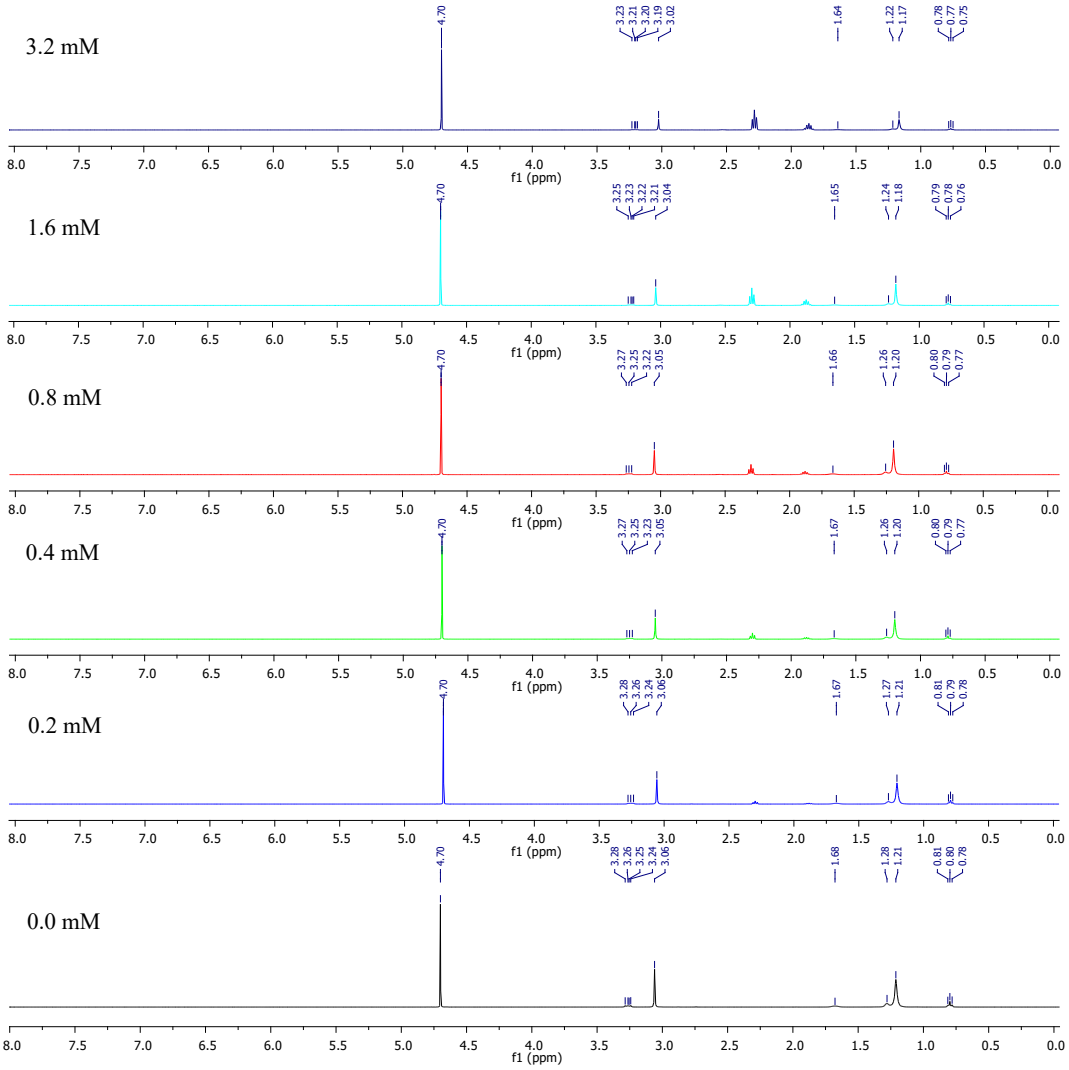


Table S3: A shift of protons in CTAC/D_2O solution at various concentrations of 1,3-cyclohexadione

Conc. of 1,3-cyclohexanedione (mM)	Chemical shift of protons in 1.6 mM CTAC micellar solution					
	A $N(CH_3)_3$	B $\alpha(CH_2)$	C $\beta(CH_2)$	D $\gamma(CH_2)$	E $\delta(CH_2)_{12}$	F ωCH_3
0.0	3.06	3.26	1.68	1.28	1.21	0.79
0.2	3.06	3.26	1.67	1.27	1.21	0.79
0.4	3.05	3.25	1.67	1.26	1.20	0.78
0.8	3.05	3.24	1.66	1.26	1.20	0.78
1.6	3.04	3.23	1.65	1.24	1.18	0.77
3.2	3.02	3.21	1.64	1.22	1.17	0.77

Figure S6: A plot of chemical shift of CTAC surfactant protons with the change in the concentration of 1,3-cyclohexadione.