Supporting Information

Multicomponent Prins-cyclization from allylsilyl alcohols leading to dioxaspirodecanes

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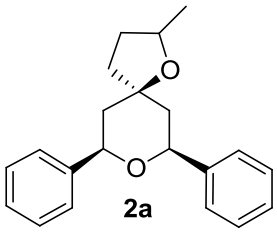
General remarks: spectroscopic data were recorded as follows: ^{1}H NMR and ^{13}C NMR spectra were run at 400 and 100 MHz respectively. Peak asignments were performed with the aid of the DEPT technique and 2D-COSY spectra. High resolution mass spectra were recorded on Bruker Maxis Impact using ESI-TOF (electrospray ionization-time of flight). Tetrahydrofuran was dried over molecular sieves prior to use. The stereochemistry of the compounds has been asigned on the basis of NOESY experiments.

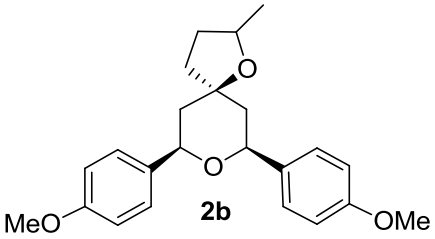
General procedure for Prins cyclization of hydroxysilanes. To a stirred solution of the allylsilyl alcohol (1 mmol) and the aldehyde (2.2 mmol) in CH_2Cl_2 (13 mL) at -78 °C was added dropwise TMSOTf (1.2 mmol). The mixture was stirred for 10 min at -78 °C. Aqueous NaOH (2 M) was added and the mixture extracted with ether. The combined organic layer was dried, concentrated to dryness and cromatographied on silica gel (hexanes/ethyl acetate, 20:1/15:1, v/v) to afford the following products:



2a

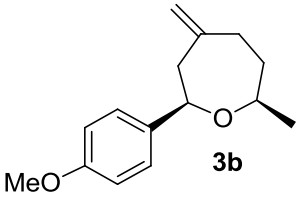
(*5s,7R*,9S)-2-methyl-7,9-diphenyl-1,8-dioxaspiro[4.5]decane (2a)**

Yellow solid; mp 68.1-68.5 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48-7.41 (m, 4H), 7.40-7.32 (m, 4H), 7.31-7.26 (m, 2H), 4.64-4.49 (m, 2H), 4.23-4.09 (m, 1H), 2.24-2.13 (m, 2H), 2.11-2.04 (m, 1H), 2.03-1.95 (m, 2H), 1.95-1.85 (m, 2H), 1.75-1.59 (m, 1H), 1.27 (d, J = 6.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.4 (C), 128.4 (CH), 127.6 (CH), 126.2 (CH), 81.6 (C), 78.5 (CH), 78.0 (CH), 74.0 (CH), 46.6 (CH_2), 46.2 (CH_2), 35.3 (CH_2), 33.8 (CH_2), 21.8 (CH_3); HRMS (ESI) m/z calcd for $C_{21}H_{24}O_2Na$ ($[M + Na]^+$): 331.1669, found 331.1671.



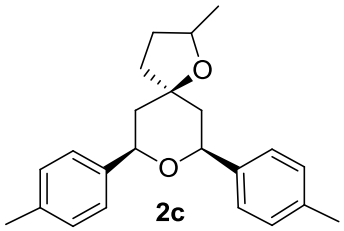
(*5s,7R*,9S)-7,9-di(4-methoxyphenyl)-2-methyl-1,8-dioxaspiro[4.5]decane (2b)**

Yellow viscous liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 (dd, *J* = 8.5 and 4.6 Hz, 4H), 6.86 (d, *J* = 8.5 Hz, 4H), 4.49 (dd, *J* = 11.8 and 2.2 Hz, 1H), 4.46 (dd, *J* = 11.5 and 2.4 Hz, 1H), 4.17-4.10 (m, 1H), 3.79 (s, 6H), 2.17-2.11 (m, 2H), 2.05-1.98 (m, 1H), 1.96-1.80 (m, 4H), 1.69-1.55 (m, 1H), 1.24 (d, *J* = 6.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.1 (C), 134.7 (C), 127.6 (CH), 113.8 (CH), 81.7 (C), 78.1 (CH), 77.5 (CH), 74.0 (CH), 55.4 (CH_3), 46.3 (CH_2), 46.0 (CH_2), 35.3 (CH_2), 33.8 (CH_2), 21.8 (CH_3), 21.3 (CH_3); HRMS (ESI) m/z calcd for $C_{23}H_{28}O_4Na$ ($[M + Na]^+$): 391.1882, found 391.1880.



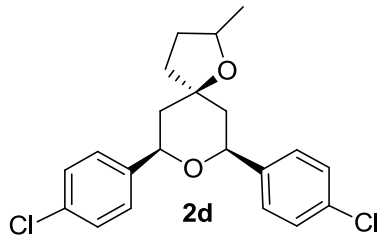
(2*R,7*R**)-2-(4-methoxyphenyl)-7-methyl–4-methyleneoxepane (3b)**

Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (d, *J* = 8.7 Hz, 2H), 6.87 (d, *J* = 8.7 Hz, 2H), 4.84 (s, 1H), 4.76 (s, 1H), 4.52 (dd, *J* = 10.5 and 3.2 Hz, 1H), 3.80 (s, 3H), 3.78 – 3.74 (m, 1H), 2.71 (dd, *J* = 14.9 and 3.2 Hz, 1H), 2.60 (dd, *J* = 14.9 and 10.5 Hz, 1H), 2.51 – 2.36 (m, 2H), 1.90 – 1.83 (m, 1H), 1.72 – 1.61 (m, 1H), 1.24 (d, *J* = 6.3 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.8 (C), 148.4 (C), 136.5 (C), 127.0 (CH), 113.8 (CH), 112.5 (CH_2), 80.9 (CH), 77.7 (CH), 55.4 (CH_3), 47.0 (CH_2), 37.8 (CH_2), 33.7 (CH_2), 23.1 (CH_3). M. S. *m/z* 233 (M^++1), 217 (M^+-Me), 125 (M^+-MeOPh).



(*5s,7R*,9S)-2-methyl-7,9-di(4-tolyl)-1,8-dioxaspiro[4.5]decane (2c)**

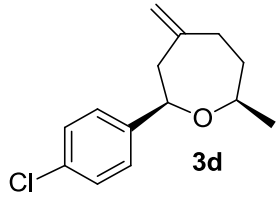
Yellow viscous liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34-7.29 (m, 4H), 7.17-7.13 (m, 4H), 4.58-4.43 (m, 2H), 4.20-4.09 (m, 1H), 2.34 (s, 6H), 2.20-2.11 (m, 2H), 2.09-2.00 (m, 1H), 1.98-1.83 (m, 4H), 1.70-1.60 (m, 1H), 1.25 (d, *J* = 6.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.6 (C), 137.2 (C), 129.1 (CH), 126.2 (CH), 81.7 (C), 78.3 (CH), 77.8 (CH), 74.0 (CH), 46.5 (CH_2), 46.1 (CH_2), 35.3 (CH_2), 33.8 (CH_2), 21.8 (CH_3), 21.3 (CH_3); HRMS (ESI) m/z calcd for $C_{23}H_{28}O_2Na$ ($[M + Na]^+$): 359.1982, found 359.1981.



2d

(*5s,7R*,9S)-7,9-di(4-chlorophenyl)-2-methyl-1,8-dioxaspiro[4.5]decane (2d)**

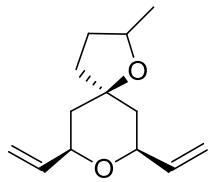
Yellow solid; mp 116.0-116.2 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38-7.28 (m, 8H), 4.54-4.47 (m, 2H), 4.18-4.10 (m, 1H), 2.20-2.11 (m, 2H), 2.06-1.92 (m, 2H), 1.87-1.77 (m, 3H), 1.70-1.59 (m, 1H), 1.24 (d, *J* = 6.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.8 (C), 133.4 (C), 128.7 (CH), 127.5 (CH), 81.4 (C), 77.9 (CH), 77.3 (CH), 74.2 (CH), 46.4 (CH_2), 46.1 (CH_2), 35.4 (CH_2), 33.8 (CH_2), 21.8 (CH_3); HRMS (ESI) m/z calcd for $C_{21}H_{22}O_2Cl_2Na$ ($[M + Na]^+$): 399.0889, found 399.0882.



3d

(*2R*,7R)-2-(4-chlorophenyl)-7-methyl-4-methylenoxepane (3d)**

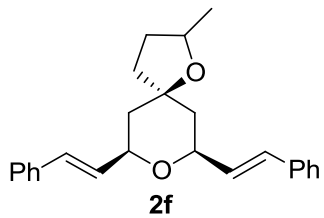
Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37-7.23 (m, 4H), 4.82 (s, 1H), 4.72 (s, 1H), 4.52 (dd, *J* = 10.5 and 3.3 Hz, 1H), 3.78-3.70 (m, 1H), 2.68 (dd, *J* = 15.0 and 3.3 Hz, 1H), 2.50 (dd, *J* = 15.0 and 10.5 Hz, 1H), 2.43-2.32 (m, 2H), 1.84 (dddd, *J* = 14.1, 7.5, 4.5 and 3.2 Hz, 1H), 1.67-1.58 (m, 1H), 1.21 (d, *J* = 6.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.8 (C), 142.6 (C), 139.9 (C), 133.1 (CH), 127.8 (CH), 112.9 (CH_2), 80.4 (CH), 77.8 (CH), 46.9 (CH_2), 37.8 (CH_2), 33.7 (CH_2), 23.1 (CH_3).



2e

(*5s,7R*,9S)-2-methyl-7,9-divinyl-1,8-dioxaspiro[4.5]decane (2e)**

Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.88 (dddd, *J* = 17.4, 10.5, 5.5 and 1.0 Hz, 2H), 5.27 (ddd, *J* = 17.4, 2.7 and 1.4 Hz, 2H), 5.14-5.09 (m, 2H), 4.16-4.06 (m, 1H), 3.92-3.82 (m, 2H), 2.12-2.04 (m, 1H), 1.98-1.91 (m, 1H), 1.85 (dt, *J* = 12.4 and 8.3 Hz, 1H), 1.72 (dd, *J* = 12.6 and 0.8 Hz, 1H), 1.63-1.49 (m, 4H), 1.24 (d, *J* = 6.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.8 (CH), 115.4 (CH_2), 81.2 (C), 76.6 (CH), 76.1 (CH), 74.0 (CH), 44.2 (CH_2), 43.8 (CH_2), 35.2 (CH_2), 33.7 (CH_2), 21.8 (CH_3).

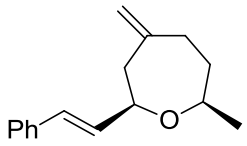


2f

(*5s,7R*,9S)-2-methyl-7,9-(*E*)-distyryl-1,8-dioxaspiro[4.5]decane (2f)**

Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43-7.37 (m, 4H), 7.35-7.27 (m, 4H), 7.26-7.17 (m, 2H), 6.66 (dd, *J* = 16.0 and 2.8 Hz, 2H), 6.28 (ddd, *J* = 16.0, 6.1 and 1.5 Hz, 2H), 4.21-4.00 (m, 3H), 2.17-2.07 (m, 1H), 2.07-1,99 (m, 1H),

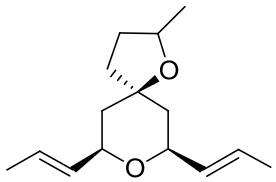
1.98-1.56 (m, 6H), 1.27 (d, J = 6.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.9 (C), 130.8 (CH), 129.8 (CH), 128.6 (CH), 127.7 (CH), 126.6 (CH), 81.1 (C), 76.5 (CH), 76.1 (CH), 74.0 (CH), 44.5 (CH_2), 44.1 (CH_2), 35.2 (CH_2), 33.6 (CH_2), 21.8 (CH_3); HRMS (ESI) m/z calcd for $C_{25}H_{28}O_2Na$ ([M + Na]$^+$): 383.1982, found 383.1983.



3f

(2*R,7*R**)-7-methyl-4-methylene-2-(*E*)-styryloxepane (3f)**

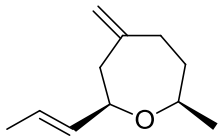
Pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72-7.51 (m, 2H), δ 7.35-7.27 (m, 3H), 6.60 (d, J = 16.0 Hz, 1H), 6.25 (dd, J = 16.0 and 5.6 Hz, 1H), 4.84 (s, 1H), 4.79 (s, 1H), 4.24-4.17 (m, 1H), 3.79-3.69 (m, 1H), 2.63 (dd, J = 15.0 and 2.4 Hz, 1H), 2.54-2.48 (m, 1H), 2.46-2.34 (m, 2H), 1.88-1.80 (m, 1H), 1.65-1.58 (m, 1H), 1.26 (d, J = 6.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.0 (C), 137.3 (C), 132.8 (CH), 129.3 (CH), 128.6 (CH), 127.5 (CH), 126.6 (CH), 112.6 (CH_2), 79.7 (CH), 77.4 (CH), 45.2 (CH_2), 37.8 (CH_2), 33.8 (CH_2), 23.1 (CH_3). M. S. *m/z* 228 (M^++1), 125 (M^+-PhCH=CH).



2g

(*5s,7R*,9S)-2-methyl-7,9-di((*E*)-prop-1-enyl)-1,8-dioxaspiro[4.5]decane (2g)**

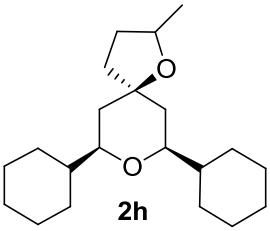
Pale yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.75-5.64 (m, 2H), 5.55-5.47 (m, 2H), 4.12-4.06 (m, 1H), 3.85-3.74 (m, 2H), 2.10-2.01 (m, 1H), 1.92 (ddd, J = 12.4, 8.6 and 4.1 Hz, 1H), 1.81 (dt, J = 12.4 and 8.4 Hz, 1H), 1.69-1.64 (m, 7H), 1.60-1.49 (m, 4H), 1.23 (d, J = 6.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 131.9 (CH), 127.7 (CH), 81.2 (C), 76.5 (CH), 76.0 (CH), 73.9 (CH), 44.4 (CH_2), 44.0 (CH_2), 35.2 (CH_2), 33.7 (CH_2), 21.9 (CH_3), 17.9 (CH_3); HRMS (ESI) m/z calcd for $C_{15}H_{24}O_2Na$ ([M + Na]$^+$): 259.1669, found 259.1669.



3g

(*2R*,7R)-7-methyl-4-methylene-2-((*E*)-prop-1-enyl)oxepane (3g)**

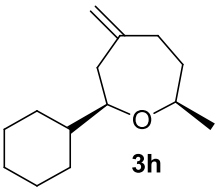
Pale yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.75-5.66 (m, 1H), 5.61-5.53 (m, 1H), 4.83 (s, 1H), 4.77 (s, 1H), 4.02-3.95 (m, 1H), 3.73-3.65 (m, 1H), 2.56-2.50 (m, 1H), 2.47-2.33 (m, 3H), 1.85-1.77 (m, 1H), 1.72 (d, J = 6.4 Hz, 3H), 1.64-1.56 (m, 1H), 1.24 (d, J = 6.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.2 (C), 133.0 (CH), 125.6 (CH), 112.3 (CH_2), 79.8 (CH), 77.0 (CH), 45.1 (CH_2), 37.7 (CH_2), 33.8 (CH_2), 30.5 (CH_3), 17.9 (CH_3). M. S. *m/z* 167 (M^++1), 151 (M^+-Me), 125 (M^+-MeCH=CH).



2h

(*5s,7R*,9S)-7,9-dicyclohexyl-2-methyl-1,8-dioxaspiro[4.5]decane (2h)**

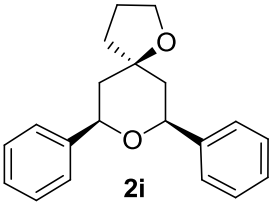
Pale yellow solid; mp 48.8-49.1 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.11-4.00 (m, 1H), 2.95-2.79 (m, 2H), 2.07-1.89 (m, 3H), 1.80 (ddd, *J* = 12.5, 8.8 and 3.9 Hz, 1H), 1.76-1.57 (m, 10H), 1.57-1.44 (m, 2H), 1.44-1.38 (m, 1H), 1.38-1.27 (m, 3H), 1.27-1.02 (m, 6H), 1.21 (d, *J* = 6.2 Hz, 3H) 1.02-0.84 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 82.1 (C), 80.1 (CH), 79.6 (CH), 73.6 (CH), 43.1 (CH), 42.1 (CH_2), 41.6 (CH_2), 35.6 (CH_2), 33.7 (CH_2), 29.4 (CH_2), 29.1 (CH_2), 26.8 (CH_2), 26.3 (CH_2), 26.2 (CH_2), 21.8 (CH_3); HRMS (ESI) m/z calcd for $C_{21}H_{36}O_2Na$ ($[M + Na]^+$): 343.2608, found 343.2613.



3h

(*2R*,7R)-2-cyclohexyl-7-methyl-4-methylenoxepane (3h)**

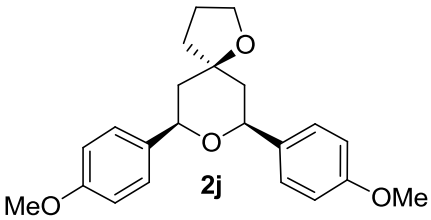
Pale yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.77 (s, 1H), 4.71 (s, 1H), 3.54-3.45 (m, 1H), 3.15 (ddd, *J* = 10.9, 7.3, 3.6 Hz, 1H), 2.53-2.44 (m, 1H), 2.37-2.21 (m, 3H), 2.04-1.97 (m, 1H), 1.81-1.69 (m, 5H), 1.53-1.43 (m, 1H), 1.34-1.28 (m, 1H), 1.27-1.12 (m, 4H), 1.16 (d, *J* = 6.3 Hz, 3H), 0.98-0.92 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.4 (C), 112.0 (CH_2), 84.1 (CH), 78.5 (CH), 43.9 (CH), 42.4 (CH_2), 38.8 (CH_2), 33.7 (CH_2), 29.7 (CH_2), 29.3 (CH_2), 26.8 (CH_2), 26.4 (CH_2), 26.2 (CH_2), 22.6 (CH_3).



2i

(*5s,7R*,9S)-7,9-diphenyl-1,8-dioxaspiro[4.5]decane (2i)**

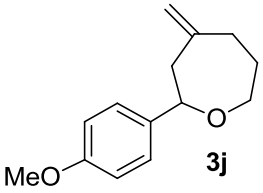
Yellow viscous liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55-7.45 (m, 4H), 7.46-7.38 (m, 4H), 7.35-7.30 (m, 2H), 4.61 (dd, *J* = 10.6 and 3.1 Hz, 2H), 3.94-3.89 (m, 2H), 2.14-2.06 (m, 4H), 2.01-1.91 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.3 (C), 128.4 (CH), 127.5 (CH), 126.0 (CH), 81.5 (C), 78.2 (CH), 66.4 (CH_2), 45.5 (CH_2), 34.6 (CH_2), 26.1 (CH_2); HRMS (ESI) m/z calcd for $C_{20}H_{22}O_2Na$ ($[M + Na]^{\pm}$): 317.1512, found 317.1512.



2j

(*5s,7R*,9S)-7,9-di(4-methoxyphenyl)-1,8-dioxaspiro[4.5]decane (2j)**

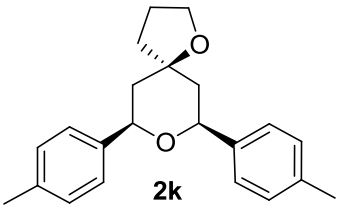
Yellow solid; mp 126.0-126.2 ºC; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37 (d, *J* = 8.8 Hz, 4H), 6.90 (d, *J* = 8.8 Hz, 4H), 4.53-4.48 (m, 2H), 3.89 (t, *J* = 6.3 Hz, 2H), 3.80 (s, 6H), 2.08-2.02 (m, 4H), 1.92-1.88 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.1 (C), 134.6 (C), 127.5 (CH), 113.8 (CH), 81.6 (C), 77.9 (CH), 66.5 (CH_2), 55.4 (CH_3), 45.3 (CH_2), 34.6 (CH_2), 26.2 (CH_2); HRMS (ESI) m/z calcd for $C_{22}H_{26}O_4Na$ ([M + Na]$^+$): 377.1723, found 377.1729.



3j

2-(4-methoxyphenyl)-4-methylenoxepane (3j)

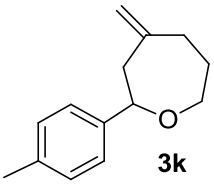
Yellow viscous liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (d, *J* = 8.8 Hz, 2H), 6.88 (d, *J* = 8.8 Hz, 2H), 4.87 (s, 1H), 4.79 (s, 1H), 4.45 (dd, *J* = 10.1 and 3.4 Hz, 1H), 4.12 (dt, *J* = 12.6 and 4.6 Hz, 1H), 3.80 (s, 3H), 3.64 (ddd, *J* = 12.6, 9.5 and 3.4 Hz, 1H), 2.70 (dd, *J* = 14.8 and 3.4 Hz, 1H), 2.61 (ddd, *J* = 14.8, 10.1 and 0.7 Hz, 1H), 2.53-2.40 (m, 2H), 1.98-1.85 (m, 1H), 1.84-1.77 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.9 (C), 148.0 (C), 136.1 (C), 127.0 (CH), 113.8 (CH), 112.9 (CH_2), 82.0 (CH), 70.7 (CH_2), 55.4 (CH_3), 46.7 (CH_2), 34.7 (CH_2), 30.2 (CH_2). M. S. *m/z* 218 (M^++1), 111 (M^+-MeOPh), 187 (M^+-OMe).



2k

(*5s,7R*,9S)-7,9-di(4-tolyl)-1,8-dioxaspiro[4.5]decane (2k)**

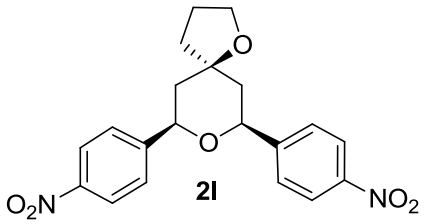
Pale yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33 (d, *J* = 8.2 Hz, 4H), 7.16 (d, *J* = 8.2 Hz, 4H), 4.52 (dd, *J* = 10.7 and 3.2 Hz, 2H), 3.91-3.87 (m, 2H), 2.35 (s, 6H), 2.09-2.04 (m, 4H), 1.93-1.85 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.5 (C), 137.2 (C), 129.1 (CH), 126.1 (CH), 81.6 (C), 78.2 (CH), 66.5 (CH_2), 45.5 (CH_2), 34.6 (CH_2), 26.2 (CH_2), 21.3 (CH_3); HRMS (ESI) m/z calcd for $C_{22}H_{26}O_2Na$ ([M + Na]$^+$): 345.1825, found 345.1827.



3k

4-methylene-2-(4-tolyl)oxepane (3k)

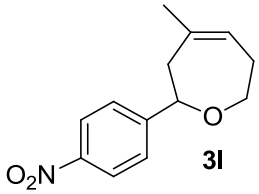
Pale yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 (d, *J* = 8.0 Hz, 2H), 7.17 (d, *J* = 8.0 Hz, 2H), 4.89 (s, 1H), 4.81 (s, 1H), 4.49 (dd, *J* = 10.2 and 3.1 Hz, 1H), 4.14 (dt, *J* = 12.3 and 4.6 Hz, 1H), 3.70-3.63 (m, 1H), 2.73 (dd, *J* = 14.7 and 3.1 Hz, 1H), 2.63 (dd, *J* = 14.7 and 10.2 Hz, 1H), 2.55-2.44 (m, 2H), 2.36 (s, 3H), 2.01-1.78 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.1 (C), 140.9 (C), 136.8 (C), 129.1 (CH), 125.7 (CH), 112.9 (CH_2), 82.3 (CH), 70.7 (CH_2), 46.8 (CH_2), 34.7 (CH_2), 30.3 (CH_2), 21.2 (CH_3); HRMS (ESI) m/z calcd for $C_{14}H_{18}ONa$ ([M + Na]$^+$): 225.1250, found 225.1244.



2l

(*5s,7R*,9S)-7,9-di(4-nitrophenyl)-1,8-dioxaspiro[4.5]decane (2l)**

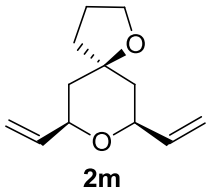
Yellow solid; mp 98.4-98.5 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 (d, *J* = 8.9 Hz, 4H), 7.58 (d, *J* = 8.9 Hz, 4H), 4.68 (d, *J* = 10.7 Hz, 2H), 3.89 – 3.83 (m, 2H), 2.11 – 2.05 (m, 4H), 1.96 (d, *J* = 12.6 Hz, 2H), 1.77 (dd, *J* = 12.6 and 10.7 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.0 (C), 147.4 (C), 126.6 (CH), 123.7 (CH), 80.9 (C), 77.3 (CH), 66.7 (CH_2), 45.2 (CH_2), 34.6 (CH_2), 26.1 (CH_2).



3l

4-methyl-2-(4-nitrophenyl)-2,3,6,7-tetrahydrooxepine (3l)

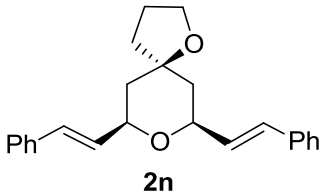
Brown oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 (d, *J* = 8.8 Hz, 2H), 7.52 (d, *J* = 8.8 Hz, 2H), 5.70 – 5.65 (m, 1H), 4.60 (d, *J* = 9.8 Hz, 1H), 4.13 (ddd, *J* = 12.0, 4.7, 3.3 Hz, 1H), 3.63 (ddd, *J* = 12.0, 10.6, 1.7 Hz, 1H), 2.73 (dd, *J* = 16.3, 10.3 Hz, 1H), 2.57 – 2.46 (m, 1H), 2.26 – 2.20 (m, 1H), 2.17 (d, *J* = 16.3 Hz, 1H), 1.78 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.3 (C), 147.1 (C), 137.3 (C), 126.7 (CH), 125.6 (CH), 123.7 (CH), 80.0 (CH), 70.3 (CH_2), 45.0 (CH_2), 31.2 (CH_2), 26.6 (CH_3). M. S. *m/z* 234 (M^++1), 111 (M^+-$PhNO_2$).



2m

(*5s,7R*,9S)-7,9-divinyl-1,8-dioxaspiro[4.5]decane (2m)**

Pale yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.88 (ddd, *J* = 17.2, 10.6 and 5.5 Hz, 2H), 5.27 (d, *J* = 17.2 Hz, 2H), 5.12 (d, *J* = 10.6 Hz, 2H), 3.91-3.82 (m, 4H), 2.03-1.94 (m, 2H), 1.89-1.81 (m, 2H), 1.66 (d, *J* = 12.4 Hz, 2H), 1.54 (t, *J* = 12.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.6 (CH), 115.4 (CH_2), 81.0 (C), 76.4 (CH), 66.5 (CH_2), 43.1 (CH_2), 34.5 (CH_2), 26.1 (CH_2); HRMS (ESI) m/z calcd for $C_{12}H_{18}O_2Na$ ($[M + Na]^+$): 217.1199, found 217.1194.

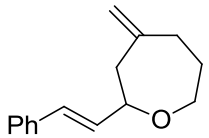


2n

(*5s,7R*,9S)-7,9-distyryl-1,8-dioxaspiro[4.5]decane (2n)**

Yellow solid; mp 40.5-40.7 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 (d, *J* = 7.4 Hz, 4H), 7.21 (t, *J* = 7.4 Hz, 4H), 7.13 (t, *J* = 7.2 Hz, 2H), 6.56 (d, *J* = 16.0 Hz, 2H), 6.18 (dd, *J* = 16.0 and 6.1 Hz, 2H), 4.05-3.99 (m, 2H), 3.79-3.72 (m, 2H), 1.96-1.88 (m, 2H), 1.83-1.80 (m, 2H), 1.70-1.59 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.8 (C), 130.8

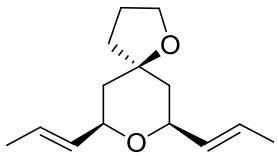
(CH), 129.7 (CH), 128.6 (CH), 127.7 (CH), 126.6 (CH), 81.0 (C), 76.4 (CH), 66.5 (CH_2), 43.4 (CH_2), 34.6 (CH_2), 26.1 (CH_2); HRMS (ESI) m/z calcd for $C_{24}H_{26}O_2Na$ ([M + Na]$^+$): 369.1825, found 369.1824.



3n

4-methylene-2-styryloxepane (3n)

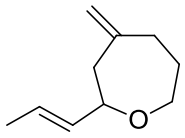
Pale yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41-7.37 (m, 2H), 7.34-7.28 (m, 2H), 7.26-7.20 (m, 1H), 6.61 (dd, *J* = 16.0 and 1.3 Hz, 1H), 6.25 (dd, *J* = 16.0 and 5.8 Hz, 1H), 4.87 (s, 1H), 4.82 (s, 1H), 4.15 (dddd, *J* = 10.0, 5.8, 3.3 and 1.3 Hz, 1H), 4.08 (dt, *J* = 12.4 and 4.6 Hz, 1H), 3.62 (ddd, *J* = 12.4, 9.2 and 3.4 Hz, 1H), 2.63 (dd, *J* = 14.7 and 3.3 Hz, 1H), 2.48 (dd, *J* = 14.7 and 10.0 Hz, 1H), 2.43-2.36 (m, 2H), 1.92-1.73 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.6 (C), 137.1 (C), 130.9 (CH), 129.6 (CH), 128.6 (CH), 127.6 (CH), 126.6 (CH), 113.0 (CH_2), 80.3 (CH), 70.1 (CH_2), 44.7 (CH_2), 34.9 (CH_2), 30.3 (CH_2). M. S. *m/z* 215 (M^++1), 111 (M^+-PhCH=CH).



2o

(*5s,7R*,9S)-7,9-di((*E*)-prop-1-enyl)-1,8-dioxaspiro[4.5]decane (2o)**

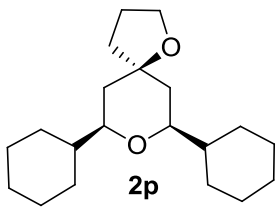
Pale yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.69 (dqd, *J* = 15.3, 6.4 and 1.0 Hz, 2H), 5.51 (ddq, *J* = 15.3, 6.7 and 1.5 Hz, 2H), 3.84-3.76 (m, 4H), 2.00-1.92 (m, 2H), 1.83-1.79 (m, 2H), 1.67 (dd, *J* = 6.4 and 1.5 Hz, 6H), 1.59-1.48 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 131.8 (CH), 127.7 (CH), 81.1 (C), 76.4 (CH), 66.4 (CH_2), 43.3 (CH_2), 34.5 (CH_2), 26.1 (CH_2), 17.9 (CH_3); HRMS (ESI) m/z calcd for $C_{14}H_{22}O_2Na$ ([M + Na]$^+$): 245.1512, found 245.1515.



3o

4-methylene-2-((*E*)-prop-1-enyl)oxepane (3o)

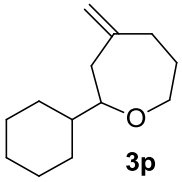
Pale yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.77-5.65 (m, 1H), 5.61-5.52 (m, 1H), 4.84 (s, 1H), 4.79 (s, 1H), 4.04 (dt, *J* = 12.4 and 4.6 Hz, 1H), 3.96-3.89 (m, 1H), 3.59-3.52 (m, 1H), 2.52 (dd, *J* = 14.6 and 2.9 Hz, 1H), 2.44-2.35 (m, 3H), 1.88-1.79 (m, 1H), 1.78-1.75 (m, 1H), 1.72 (d, *J* = 6.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.9 (C), 132.6 (CH), 126.2 (CH), 112.7 (CH_2), 80.6 (CH), 69.9 (CH_2), 44.8 (CH_2), 34.9 (CH_2), 30.2 (CH_2), 17.9 (CH_3). M. S. *m/z* 153 (M^++1), 111 (M^+-MeCH=CH).



2p

(*5s,7R*,9S)-7,9-dicyclohexyl-1,8-dioxaspiro[4.5]decane (2p)**

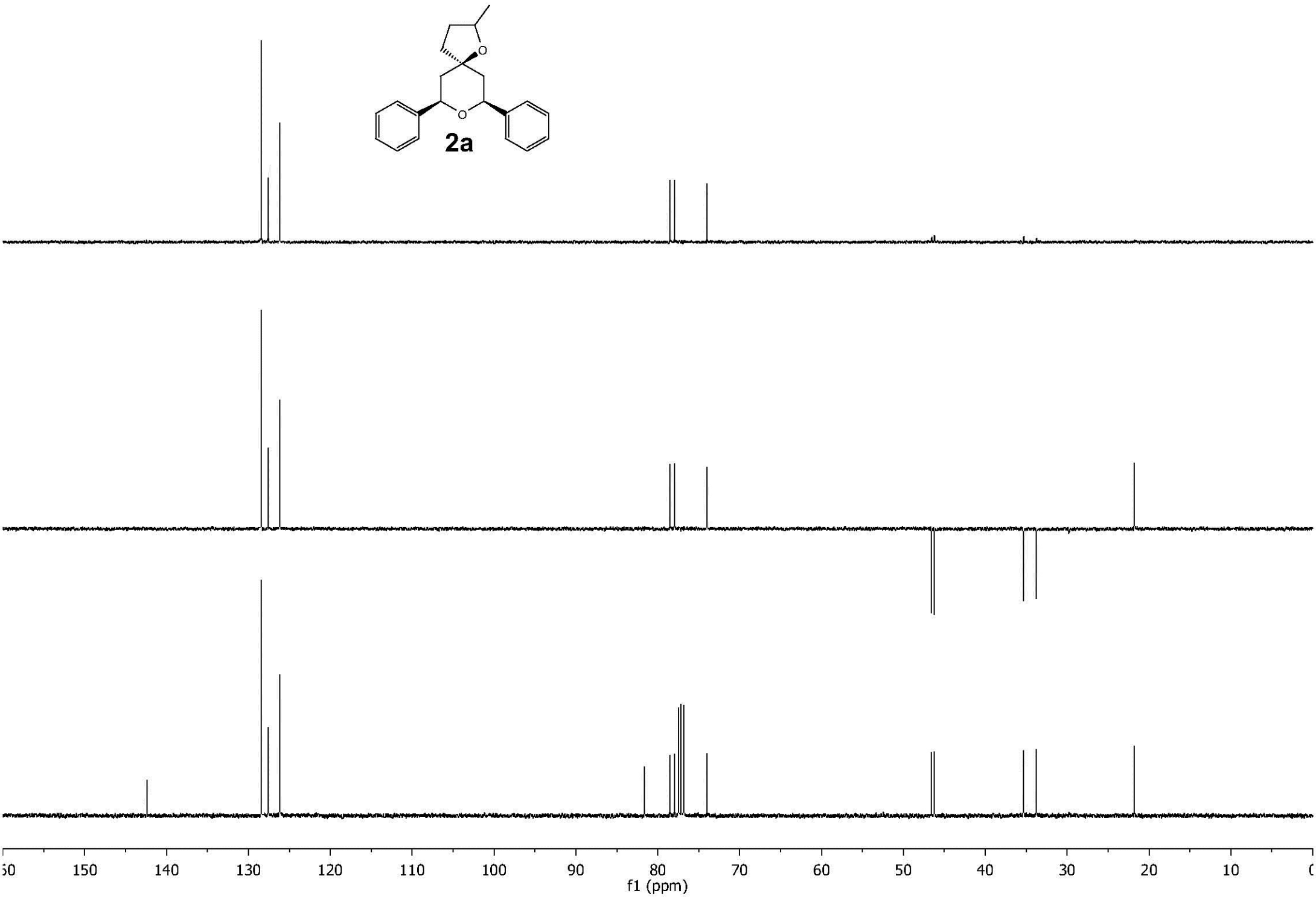
Pale yellow solid; mp 60.7-60.9 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.81 (t, *J* = 6.7 Hz, 2H), 2.94-2.86 (m, 2H), 2.00-1.88 (m, 4H), 1.73-1.56 (m, 12H), 1.39-1.30 (m, 4H), 1.25-1.09 (m, 6H), 1.01-0.81 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 82.1 (C), 80.1 (CH), 66.3 (CH_2), 43.1 (CH), 41.0 (CH_2), 34.9 (CH_2), 29.4 (CH_2), 29.1 (CH_2), 26.8 (CH_2), 26.3 (CH_2), 26.2 (CH_2); HRMS (ESI) m/z calcd for $C_{20}H_{34}O_2Na$ ($[M + Na]^+$): 329.2451, found 329.2450.



3p

4-methylene-2-cyclohexyloxepane (3p)

Pale yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.45 (s, 1H), 4.39 (s, 1H), 3.78-3.57 (m, 1H), 3.17-2.99 (m, 1H), 2.90-2.66 (m, 1H), 2.18-1.50 (m, 5H), 1.43-1.28 (m, 7H), 1.06-0.97 (m, 1H), 0.85-0.64 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.2 (C), 112.1 (CH_2), 84.5 (CH), 71.2 (CH_2), 43.8 (CH), 41.8 (CH_2), 34.7 (CH_2), 30.9 (CH_2), 29.5 (CH_2), 28.9 (CH_2), 26.7 (CH_2), 26.5 (CH_2), 26.4 (CH_2). M. S. *m/z* 195 (M^++1), 112 (M^+-Cy).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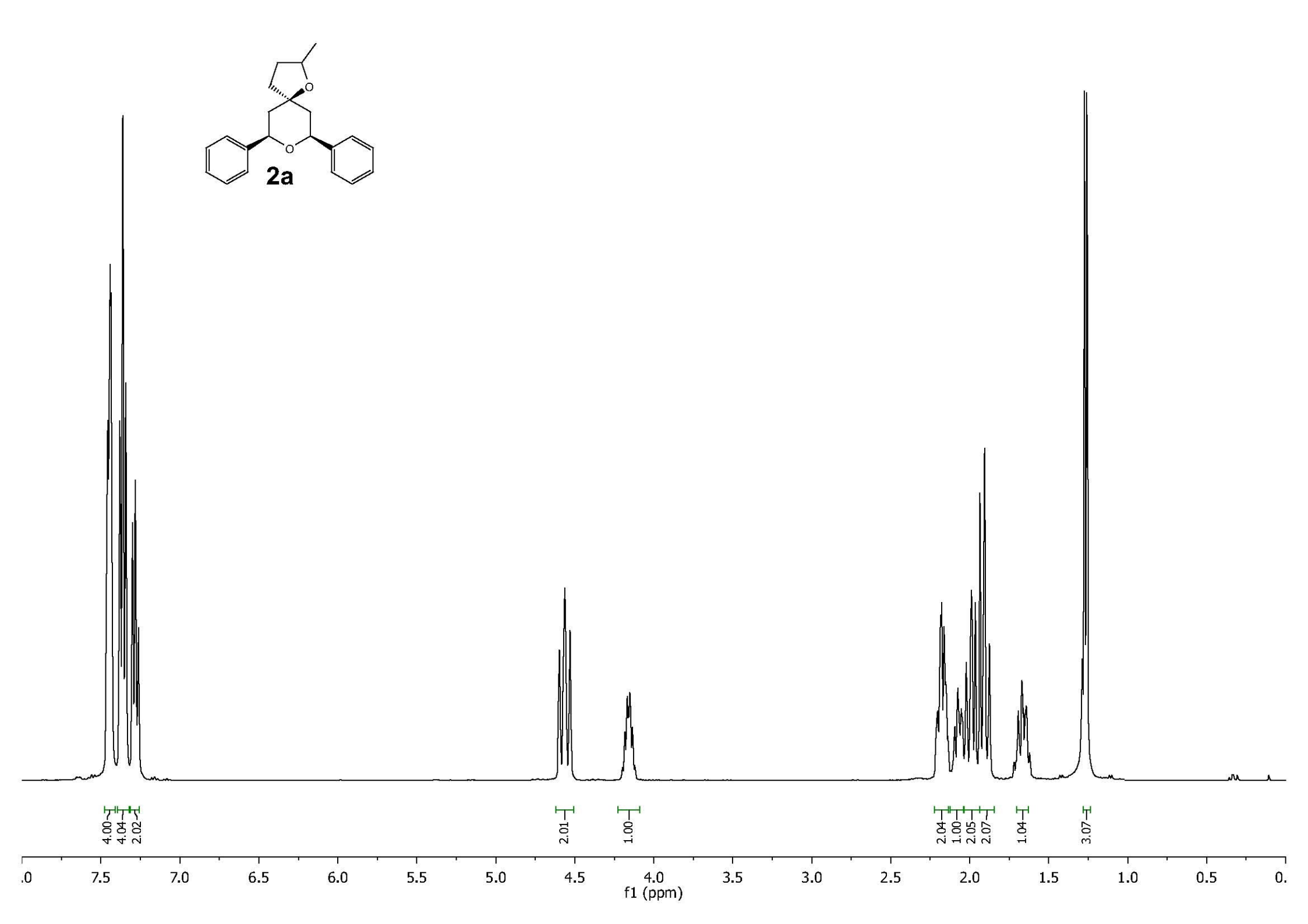
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


2a
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4.04
2.02
2.01
1.00
2.04
1.00
2.05
2.07
1.04
3.07
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6.5
6.0
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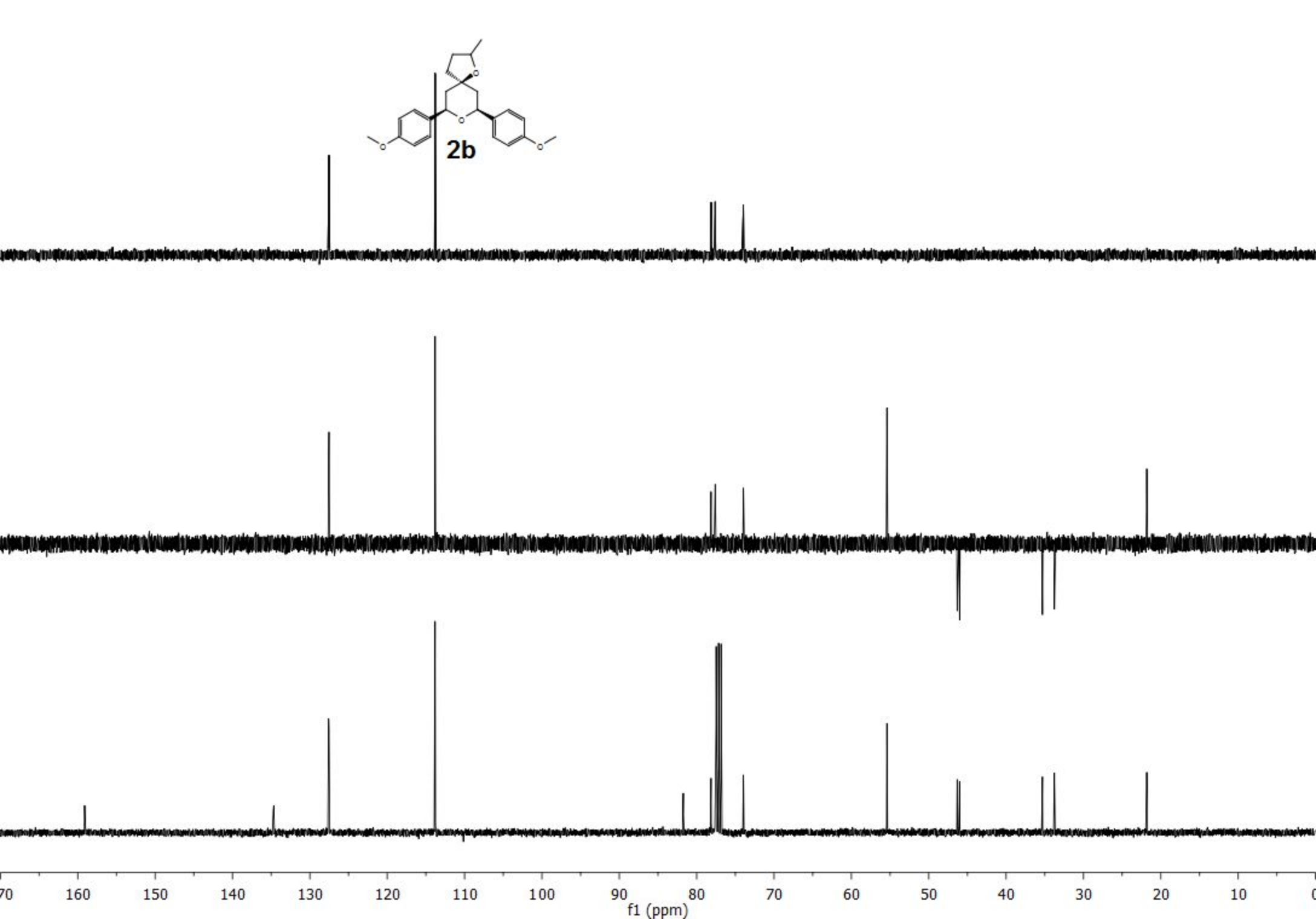
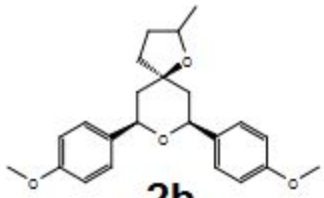
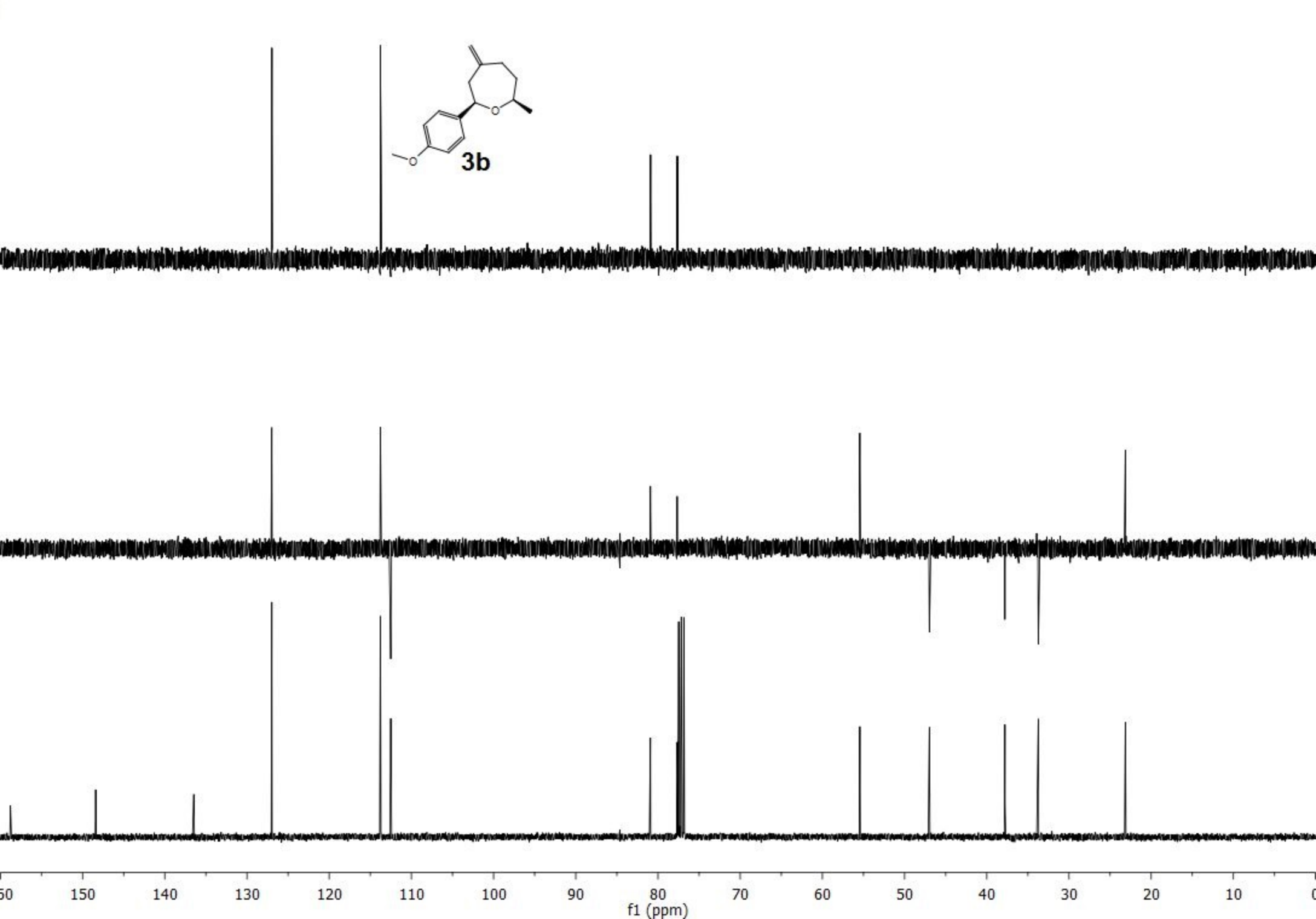
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

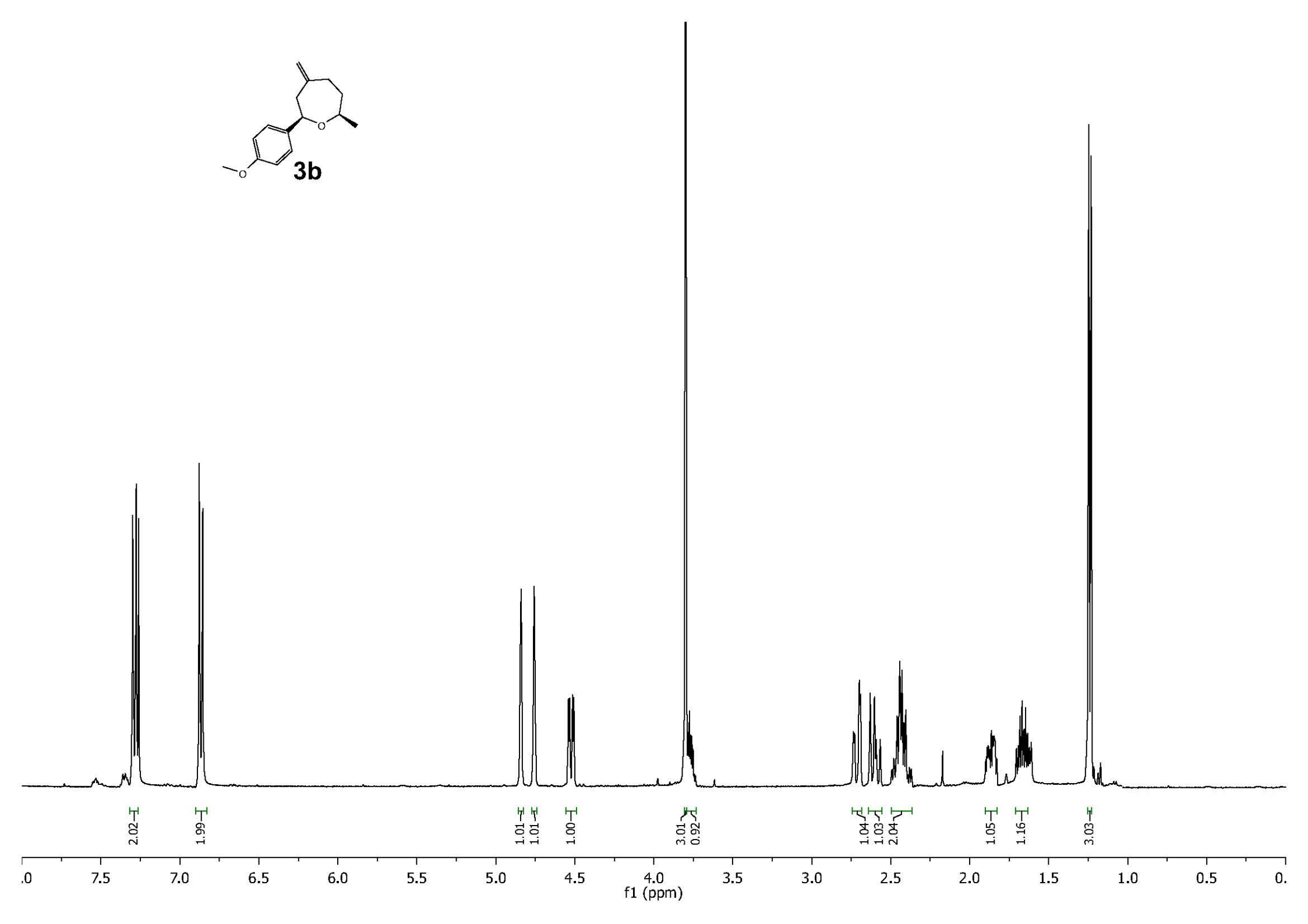

2b
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)



2b

4.00
4.00
2.04
1.00
6.07
2.06
1.08
4.11
1.63
3.01
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)


3b
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


3b
2.02
1.99
1.01
1.01
1.00
3.01
0.92
1.04
1.03
2.04
1.05
1.16
3.03
7.5
7.0
6.5
6.0
5.5
5.0
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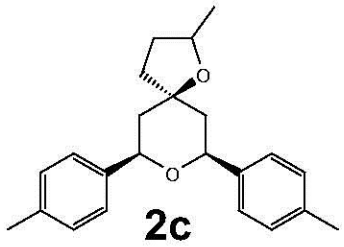
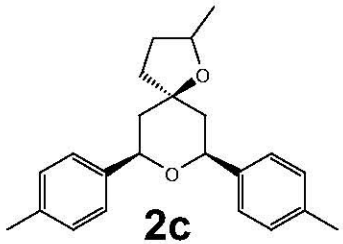
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)



2c



2c

4.11
4.01
2.01
0.97
6.04
2.08
1.03
4.09
1.26
3.01
.5
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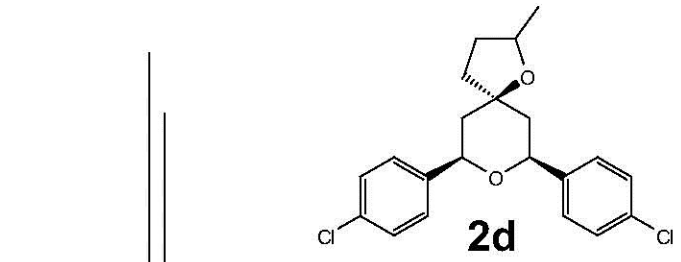
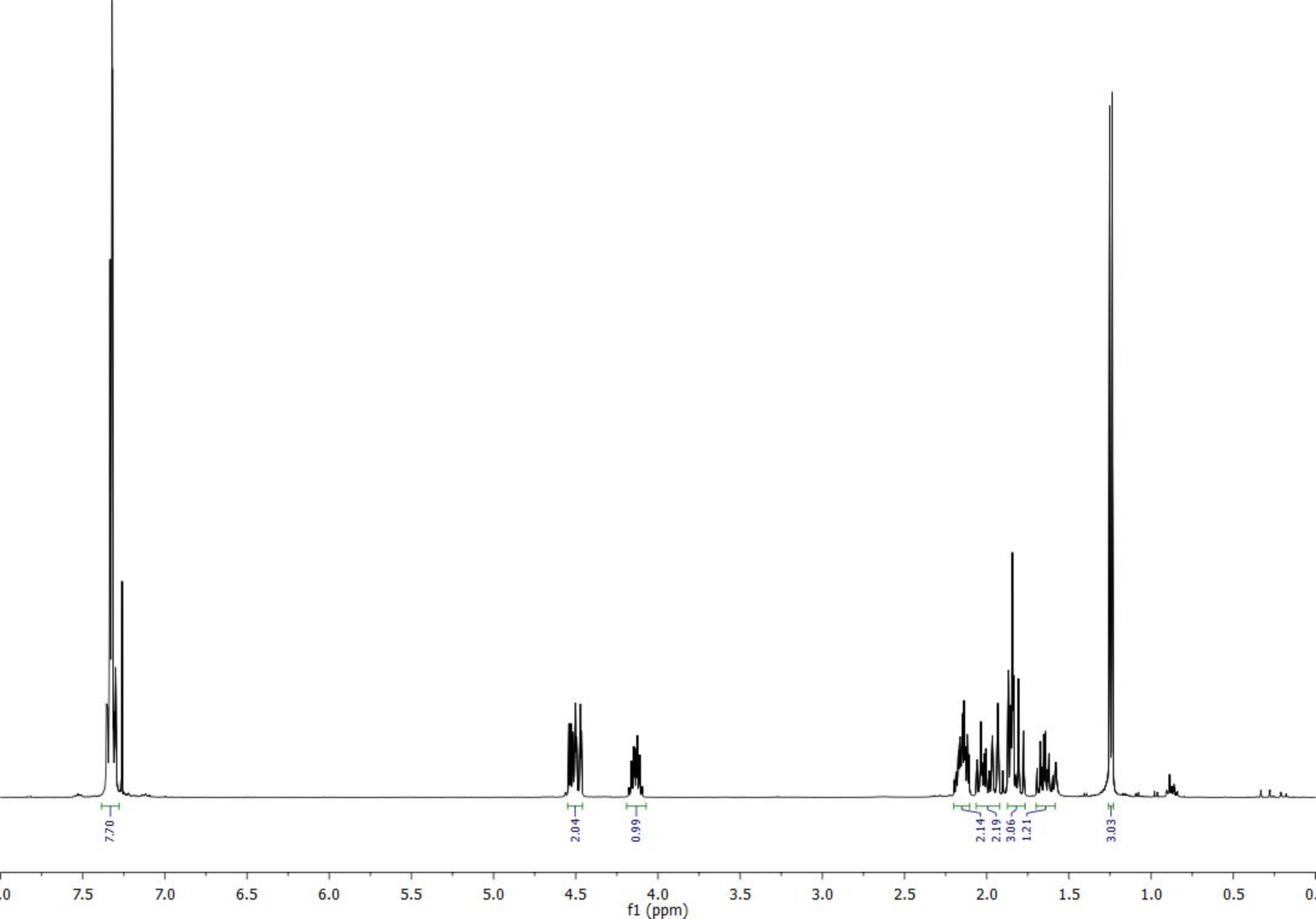
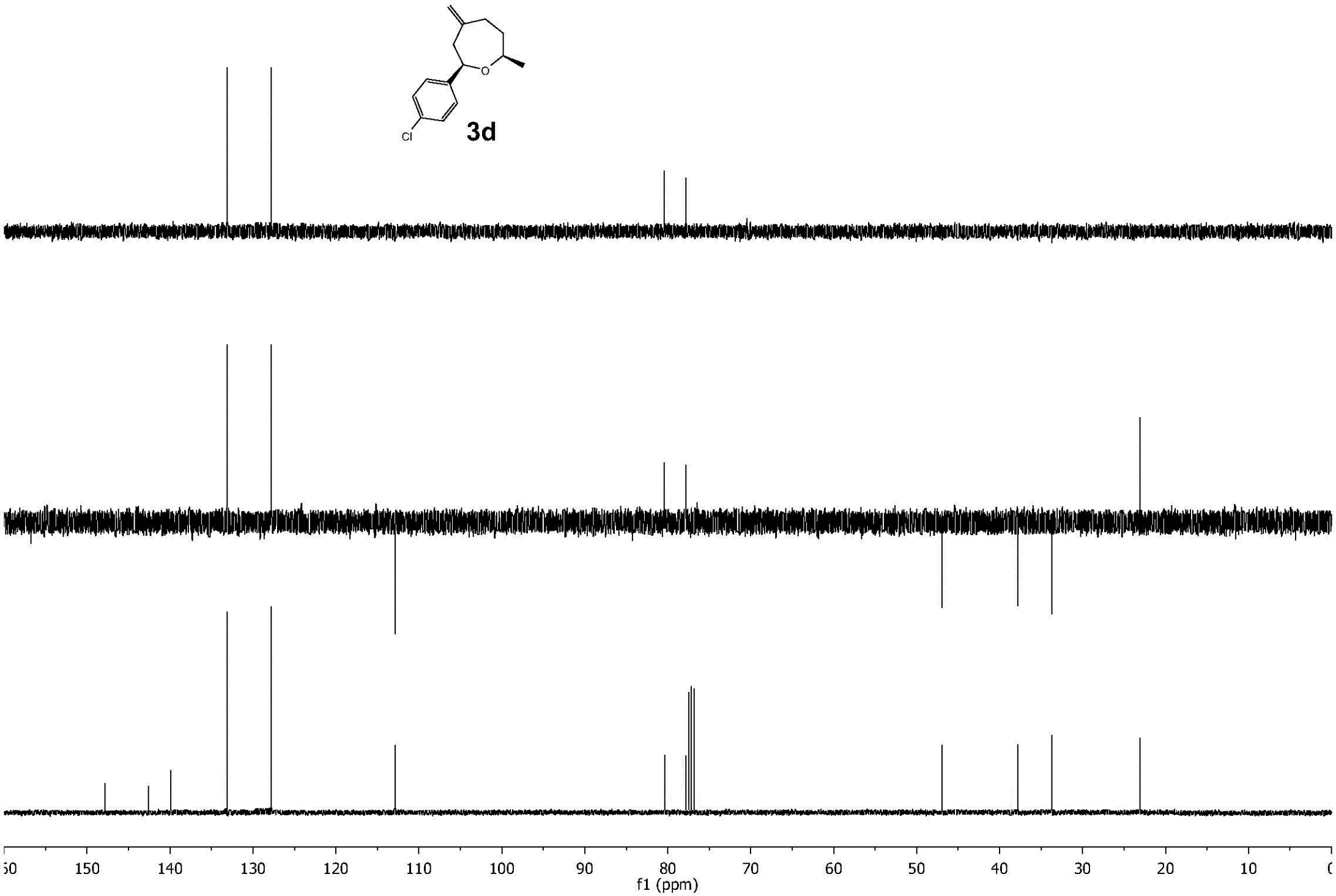
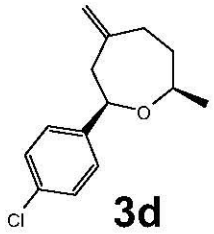
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)



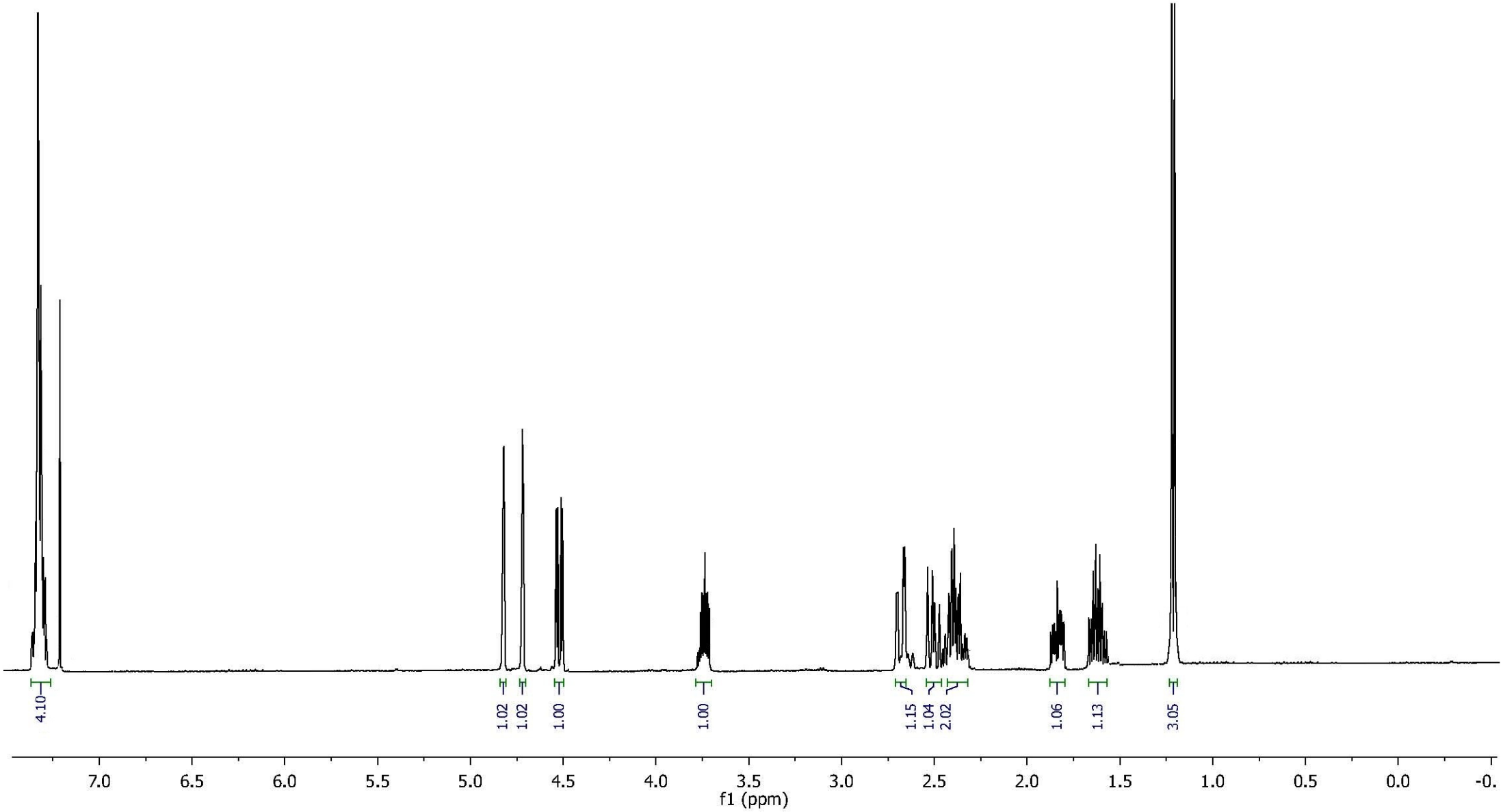
2d

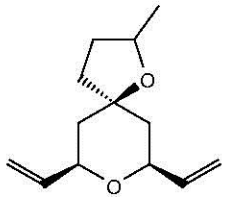

7.70
2.04
0.99
2.14
2.19
3.06
1.21
3.03
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)


O
Cl
3d
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


O
Cl

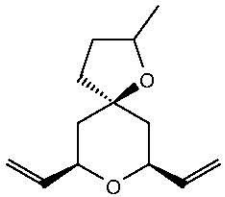
3d


4.10
1.02
1.02
1.00
1.00
1.15
1.04
2.02
1.06
1.13
3.05
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.
f1 (ppm)



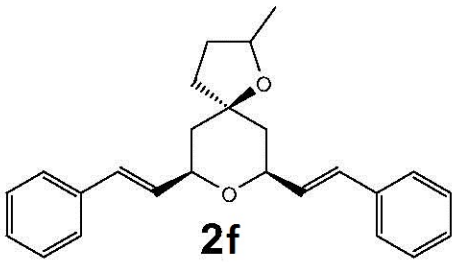
2e

50 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5
f1 (ppm)

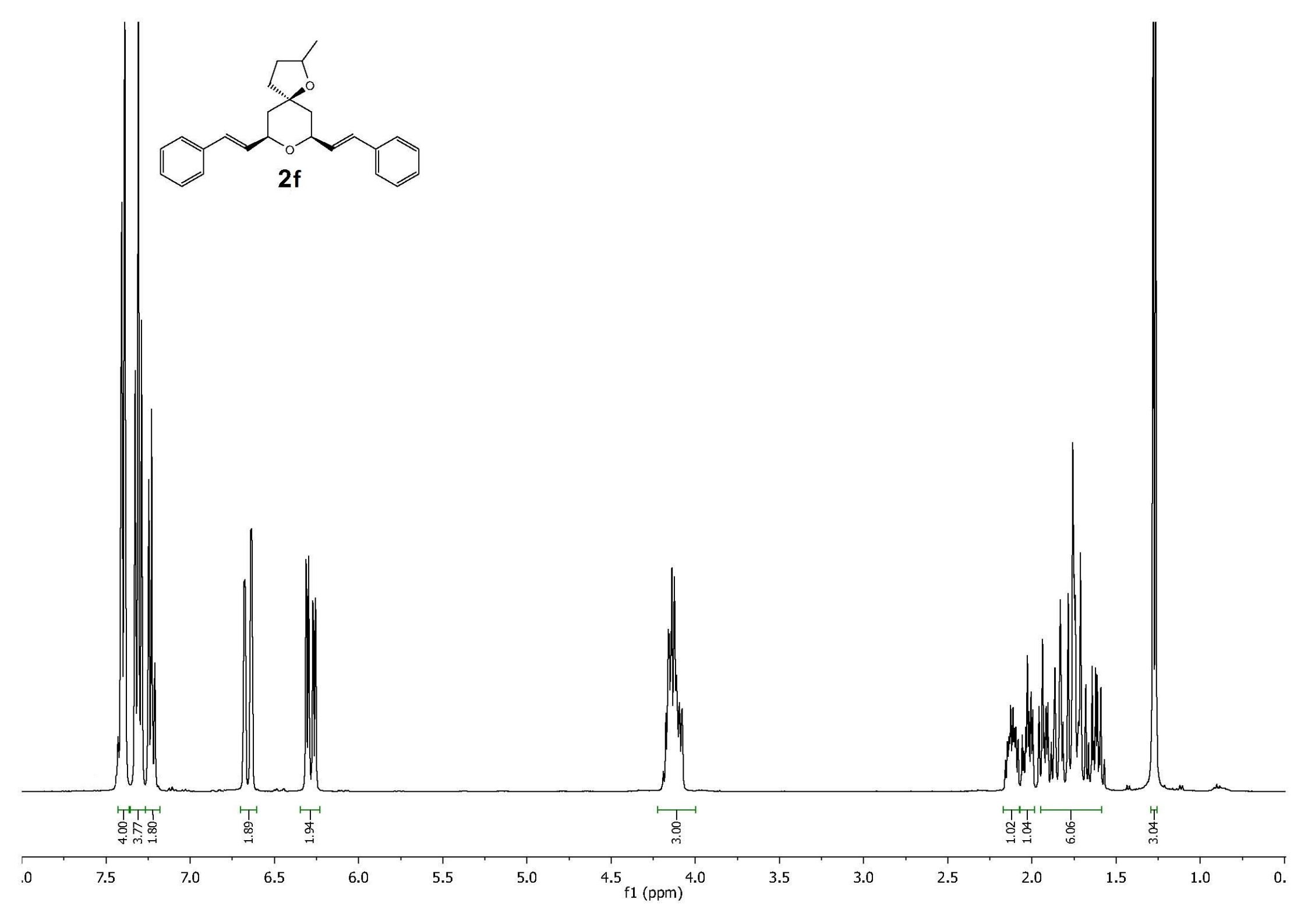


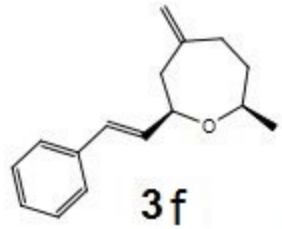
2e

1.80
2.01
2.00
1.01
2.00
1.00
1.05
1.08
1.05
5.00
3.01
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

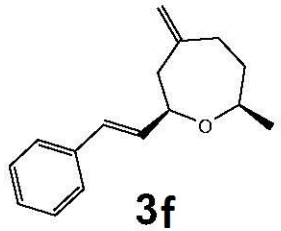


2f

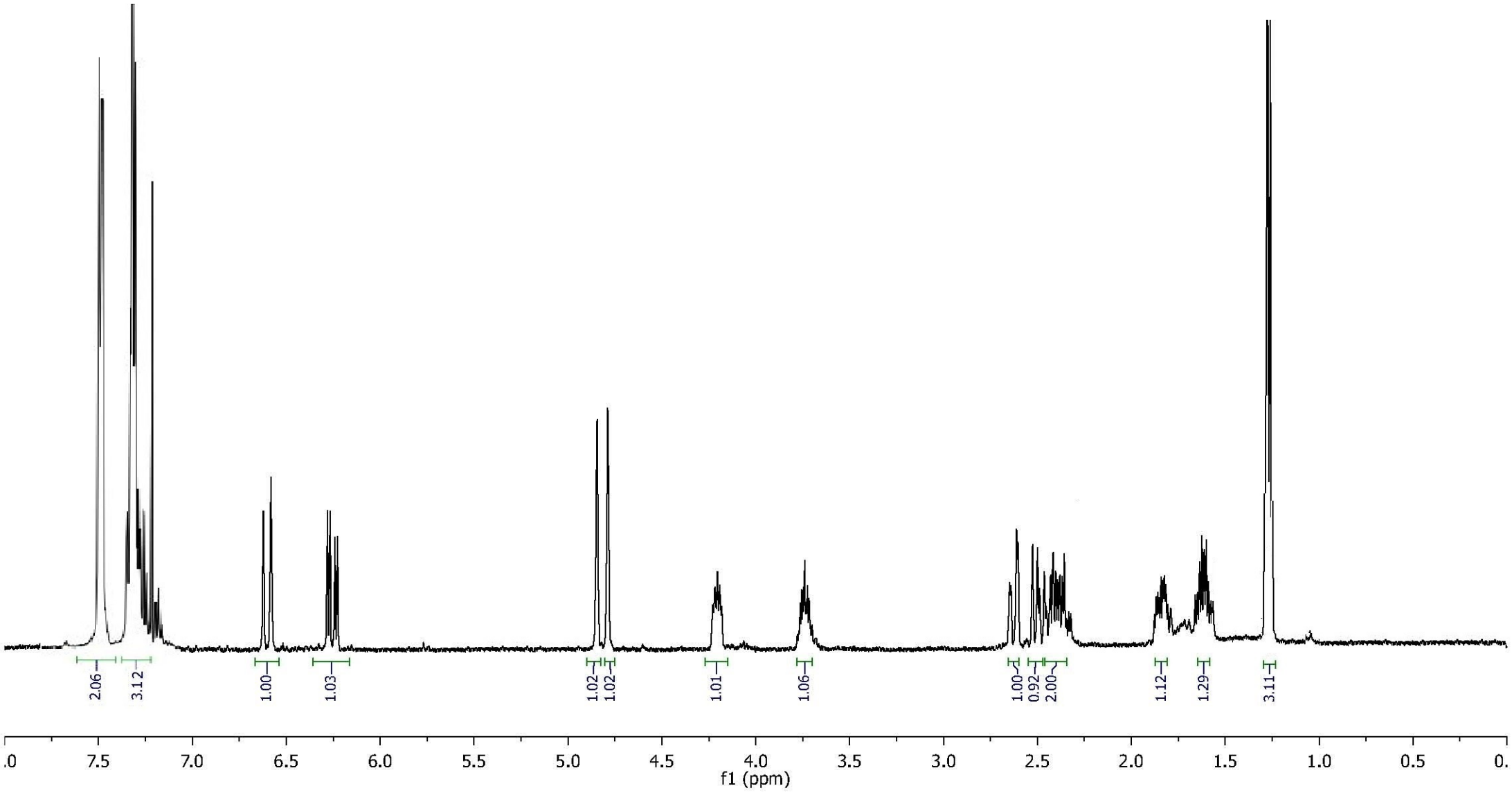

2f
4.00
3.77
1.80
1.89
1.94
3.00
1.02
1.04
6.06
3.04
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
f1 (ppm)

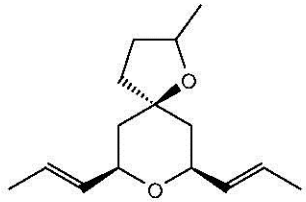


3f

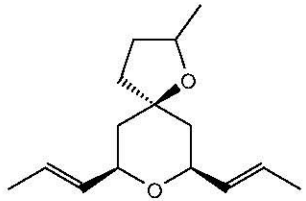


3f



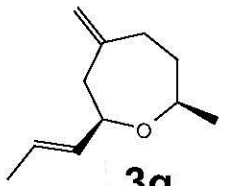


2g

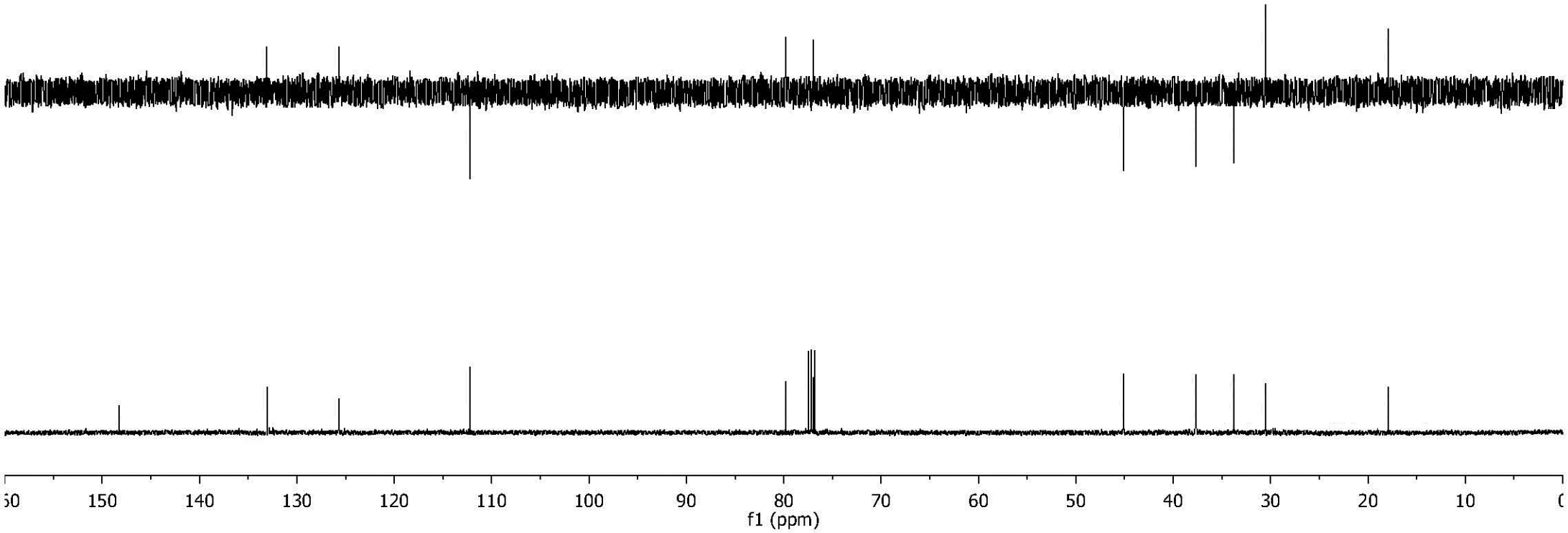


2g

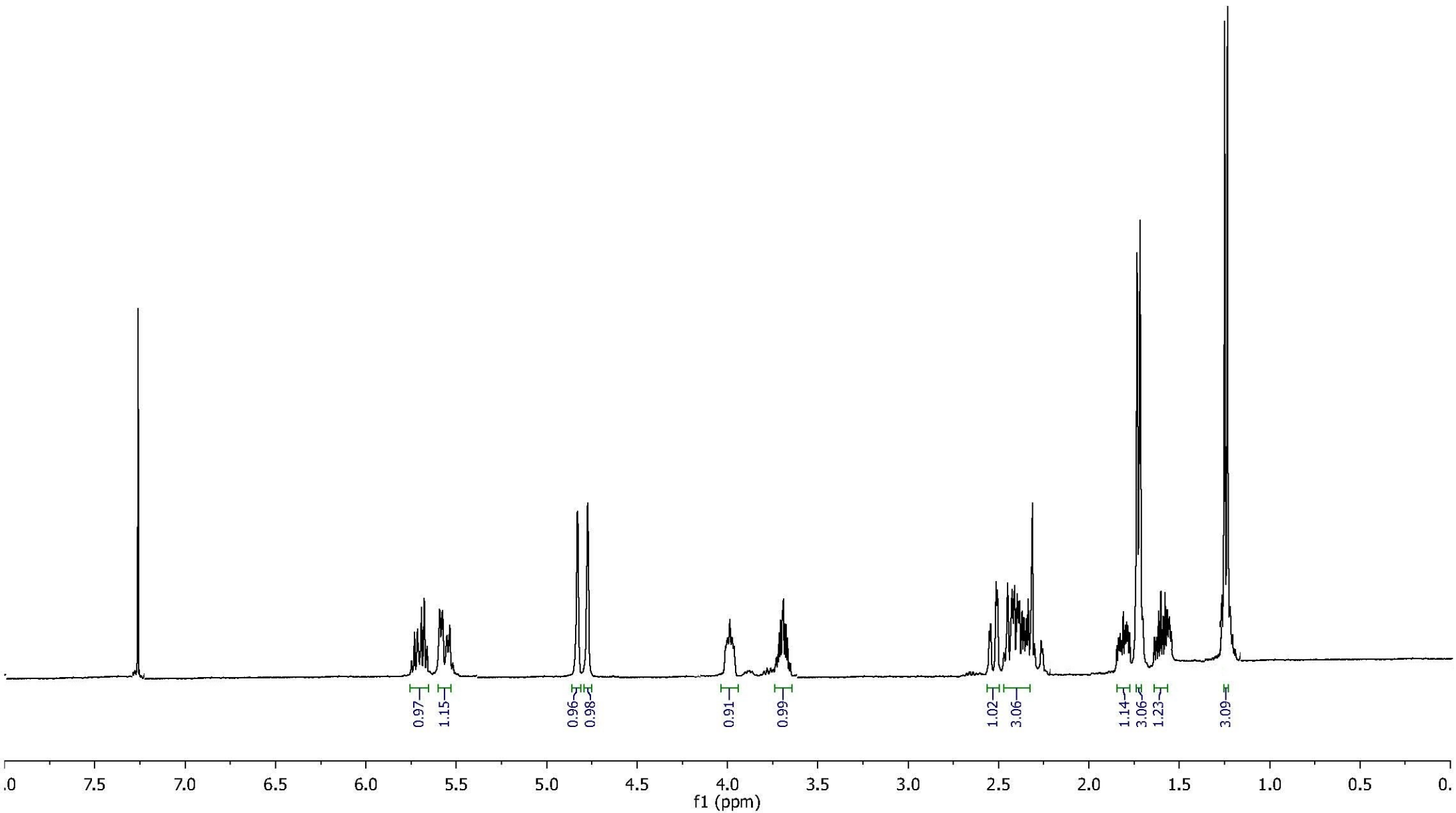
1.82
1.86
1.00
1.97
1.12
1.06
1.14
6.07
1.00
4.18
3.10
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

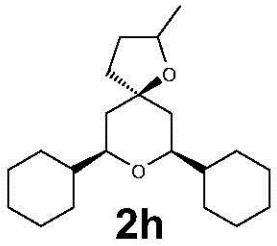


3g

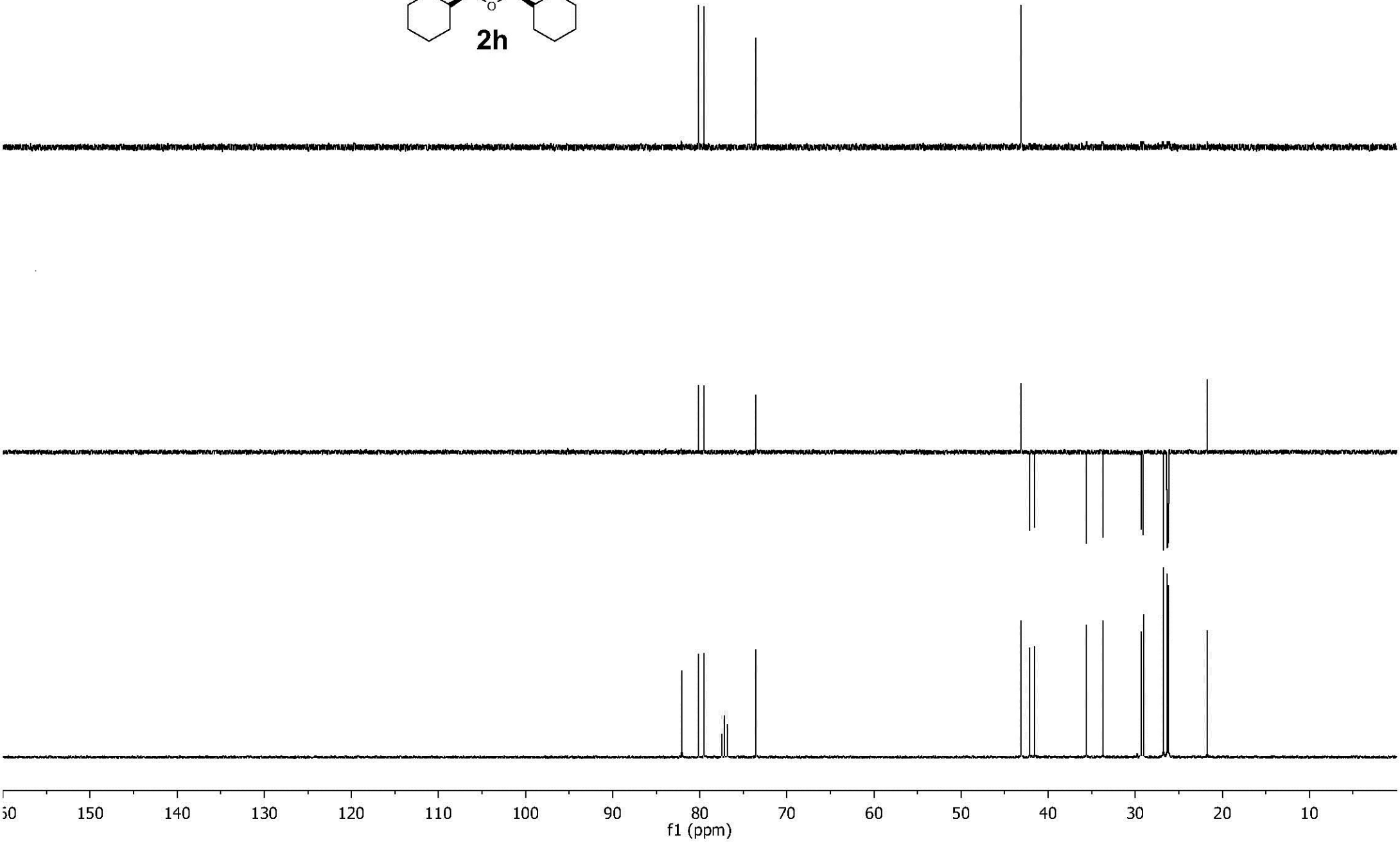


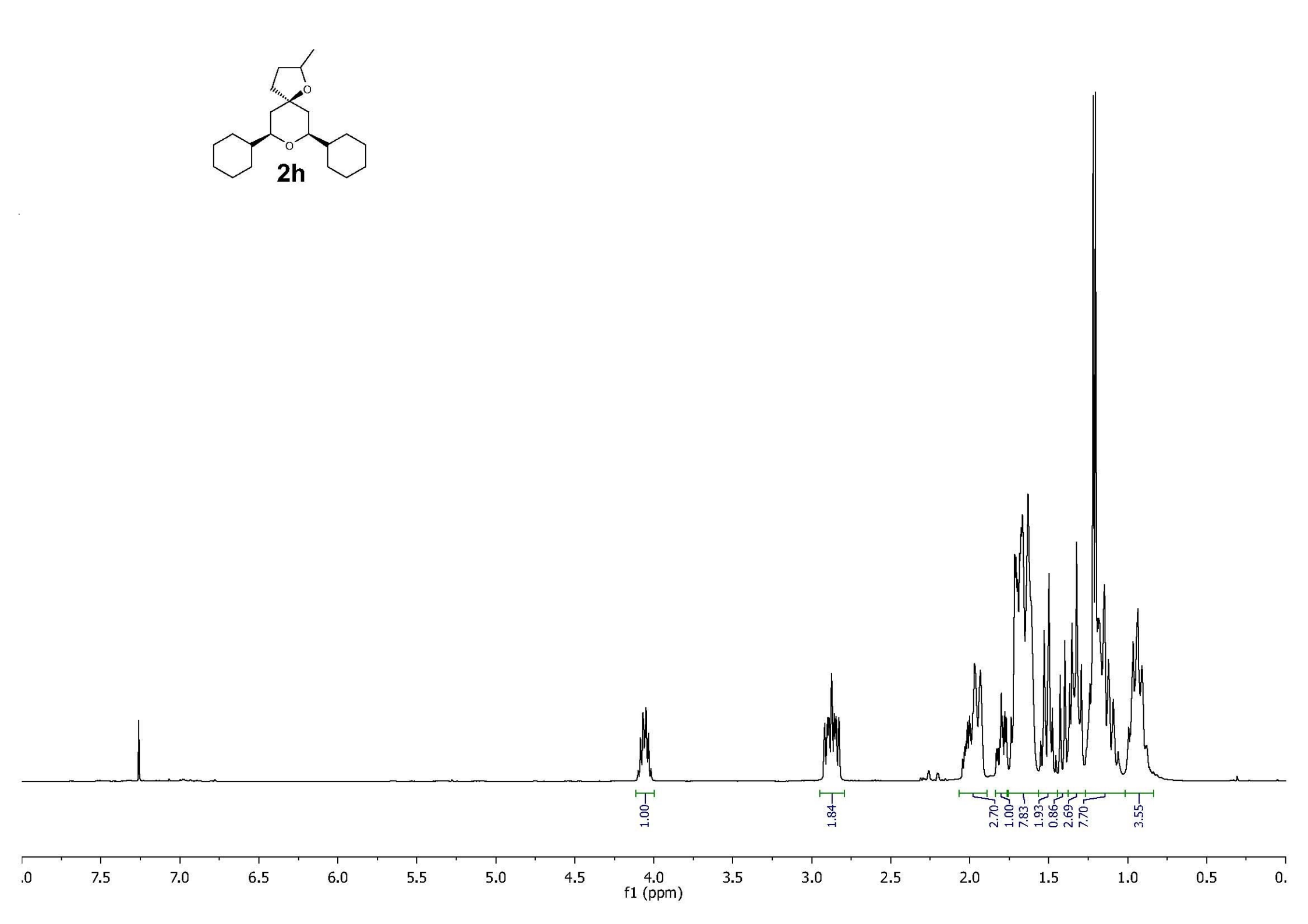
3g

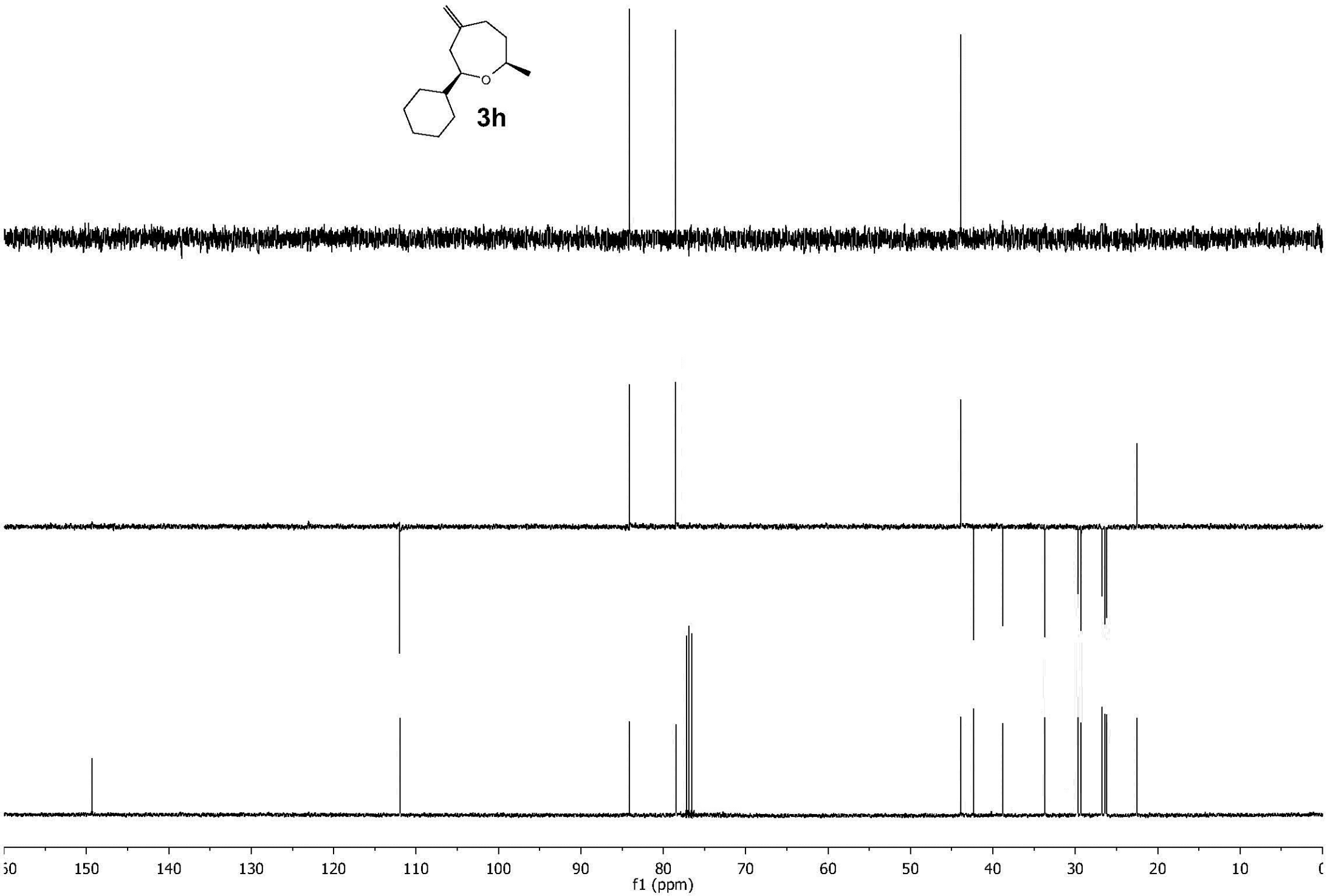

0.97
1.15
0.96
0.98
0.91
0.99
1.02
3.06
1.14
3.06
1.23
3.09
.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.
f1 (ppm)

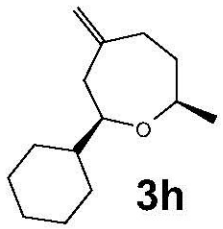


2h



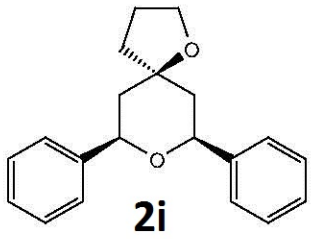

2h
1.00
1.84
2.70
1.00
7.83
1.93
0.86
2.69
7.70
3.55
f1 (ppm)


3h
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

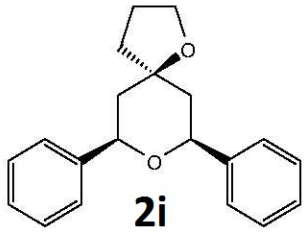


3h

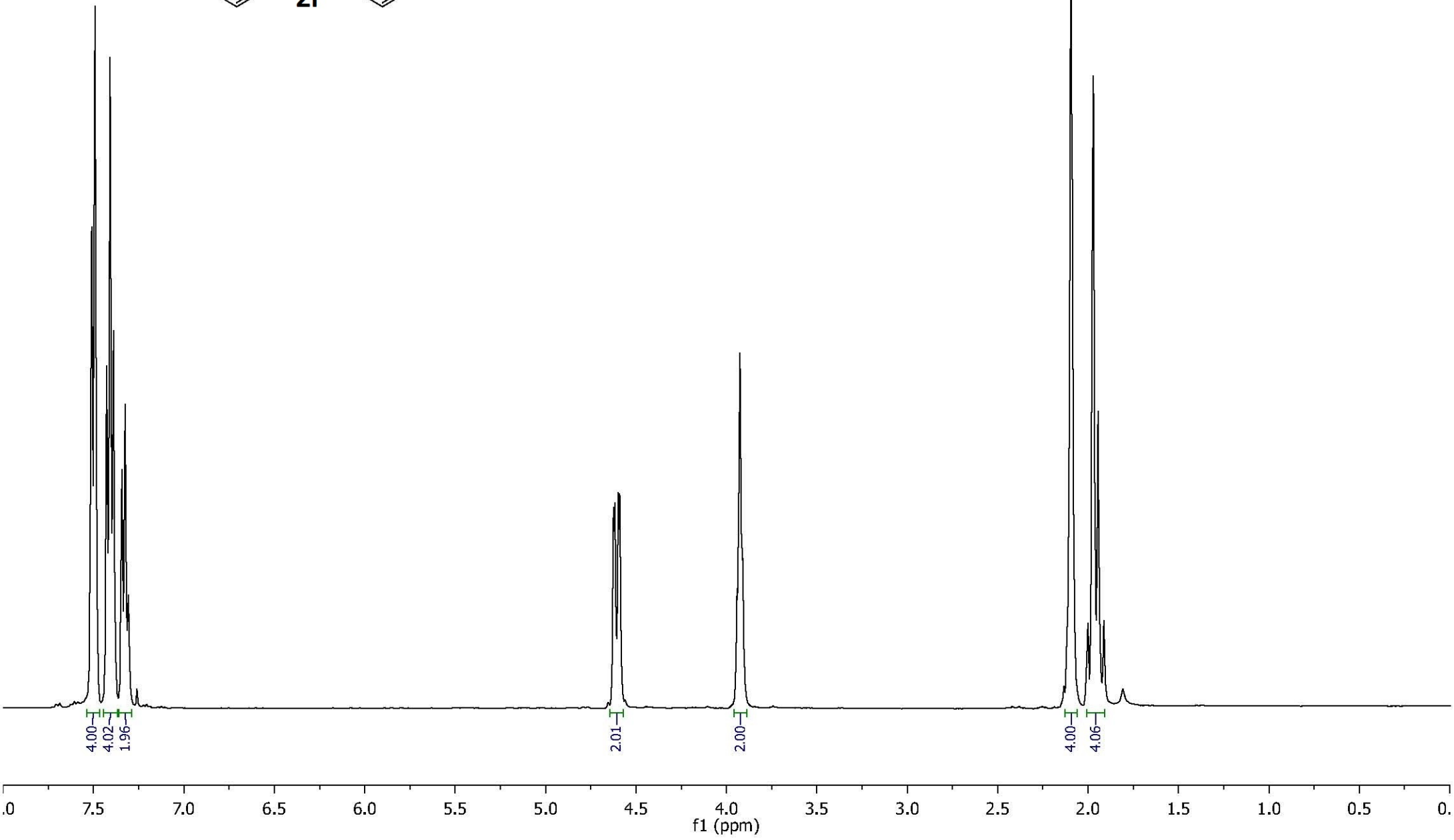
0.99
1.00
1.05
0.99
1.04
3.01
1.06
1.08
2.18
2.16
1.01
1.12
3.01
3.25
1.01
1.06
.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)



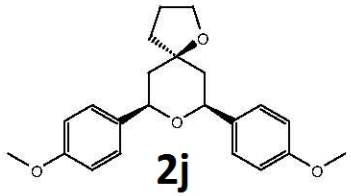
2i



2i

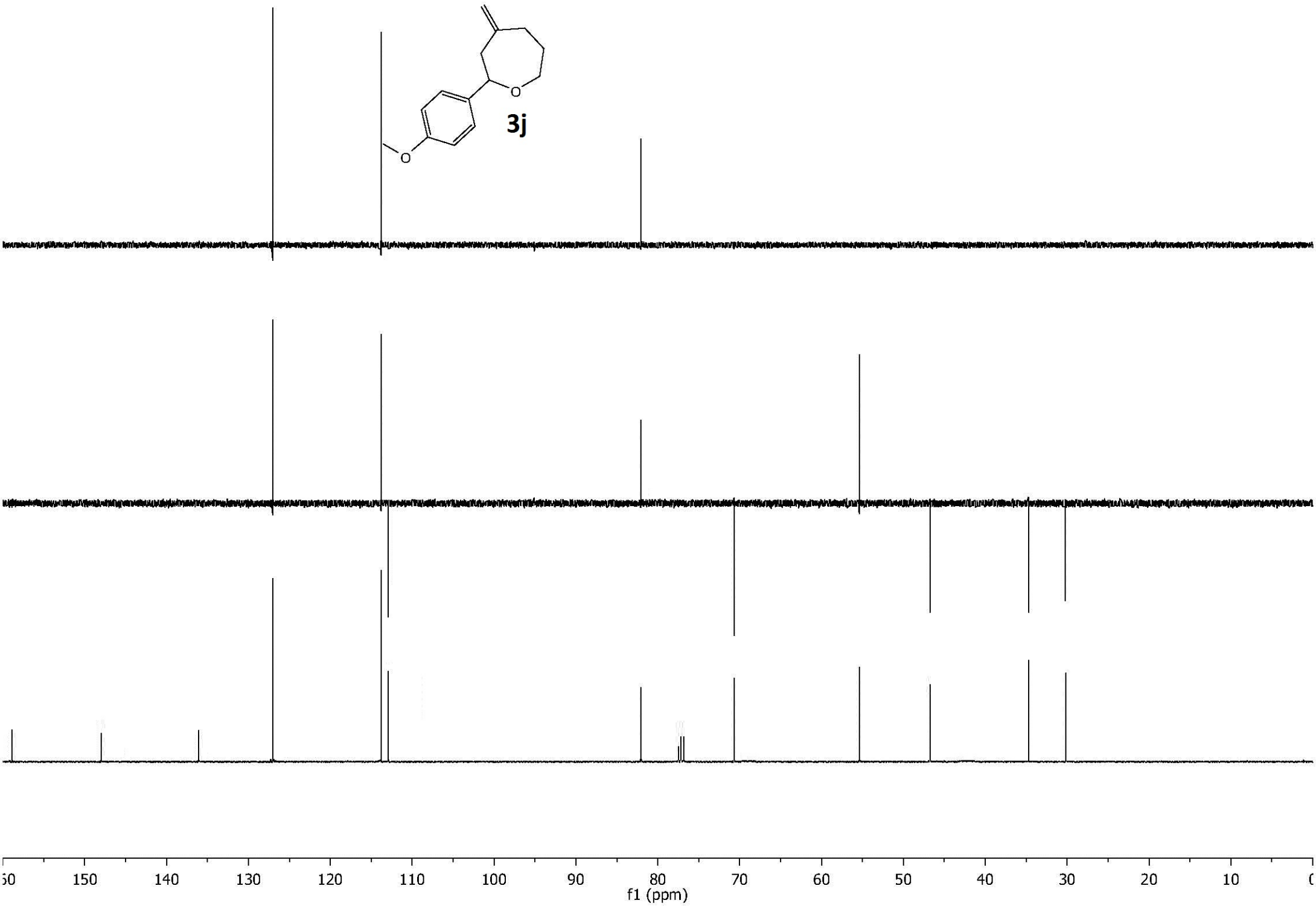

4.00
4.02
1.96
2.01
2.00
4.00
4.06
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

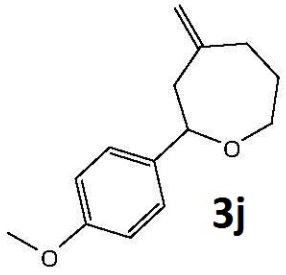
2j



2j

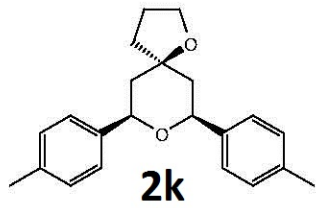
4.00
4.08
2.15
2.08
6.06
4.07
4.08
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)


O
O
3j
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)



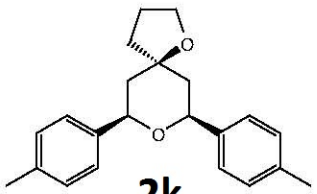
3j

2.15
2.07
1.03
1.05
1.00
1.03
3.09
1.04
2.03
2.25
1.03
1.06
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)



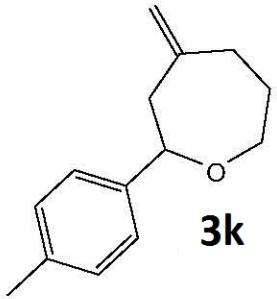
2k

f1 (ppm)

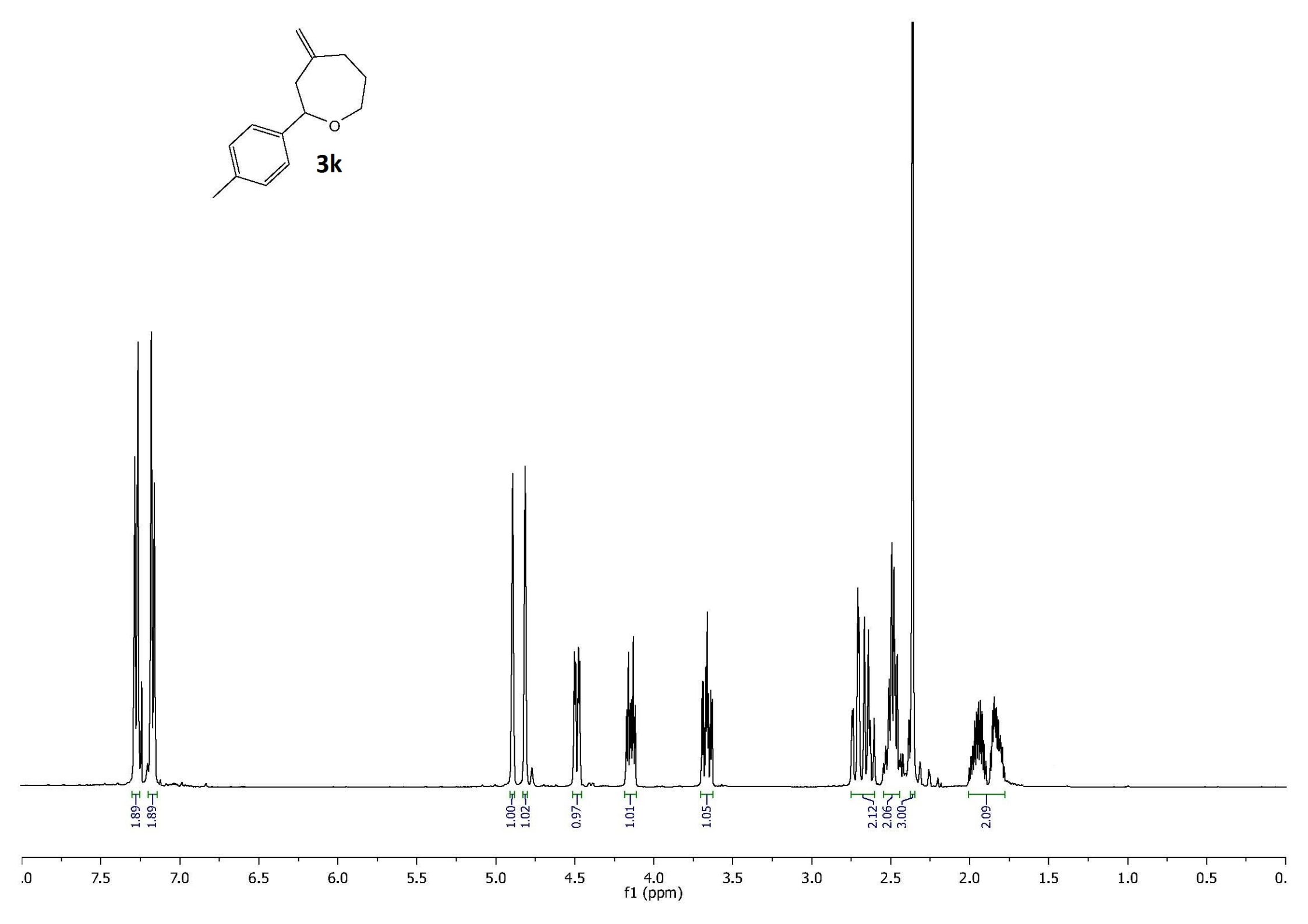


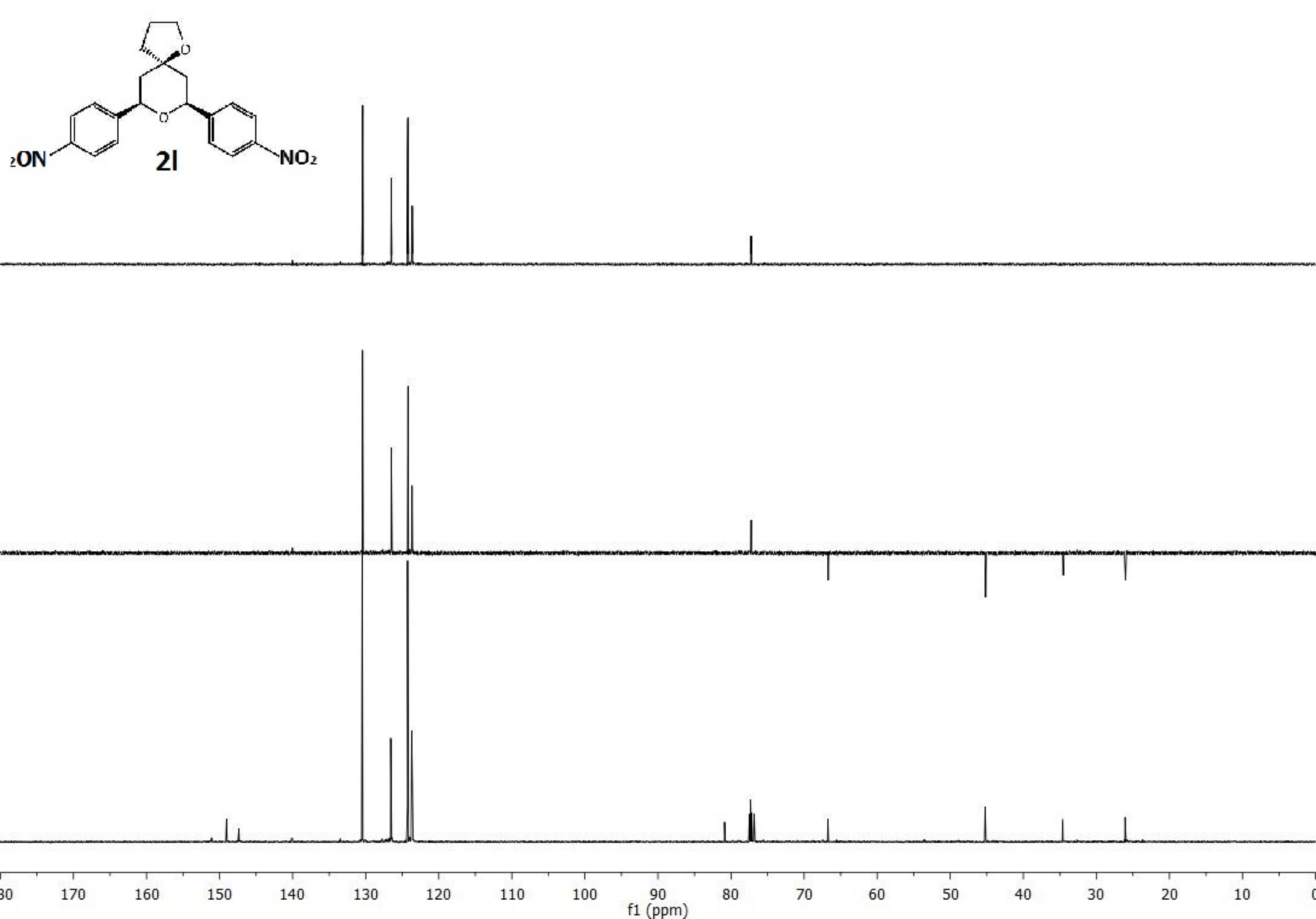
2k

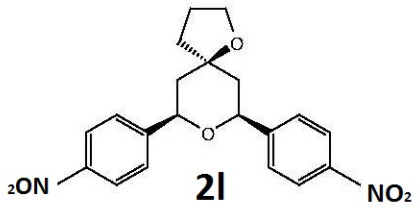
4.00
3.98
2.00
2.02
6.01
4.01
4.16
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)



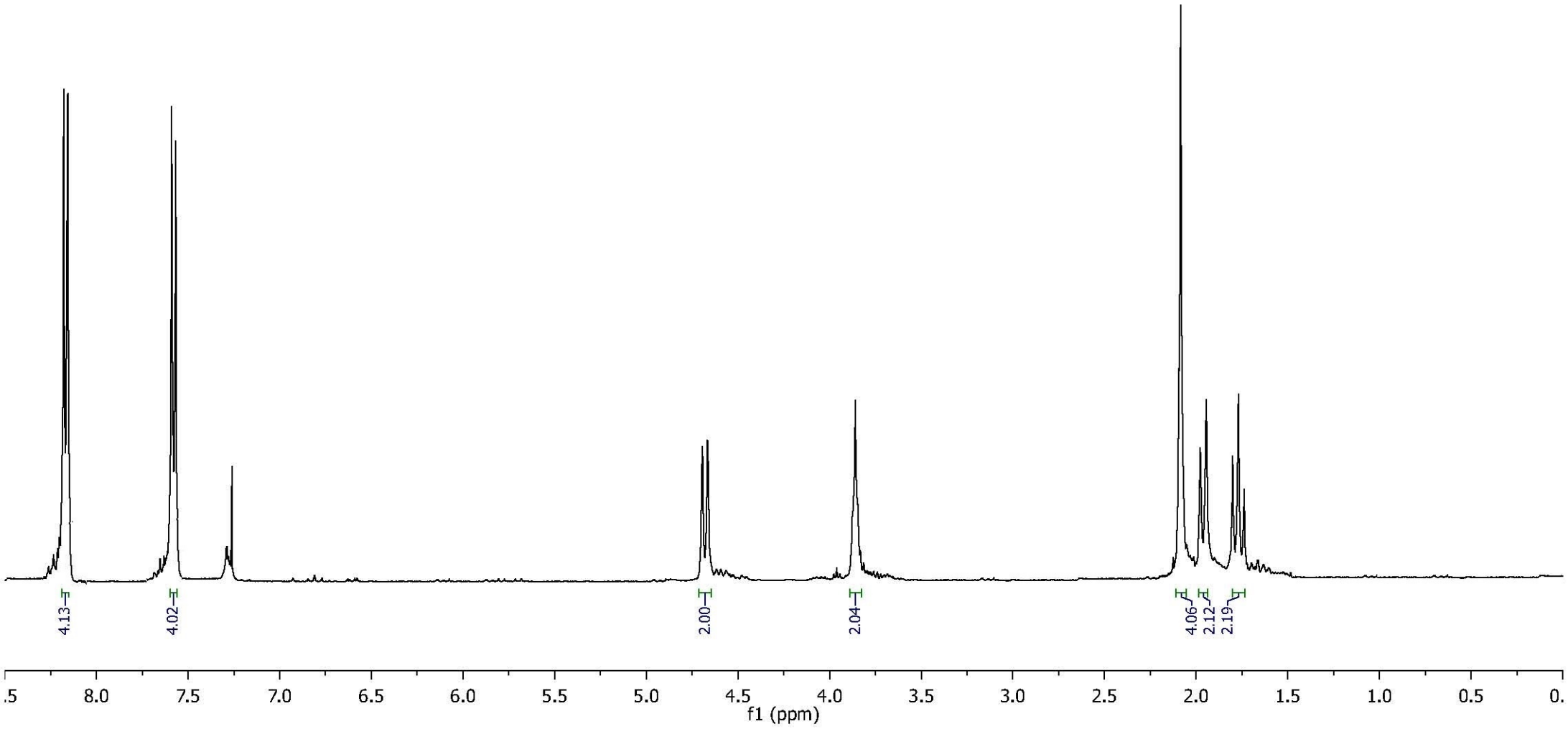
3k

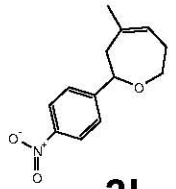

3k
1.89
1.89
1.00
1.02
0.97
1.01
1.05
2.12
2.06
3.00
2.09
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)


2ON
NO2
2l
f1 (ppm)

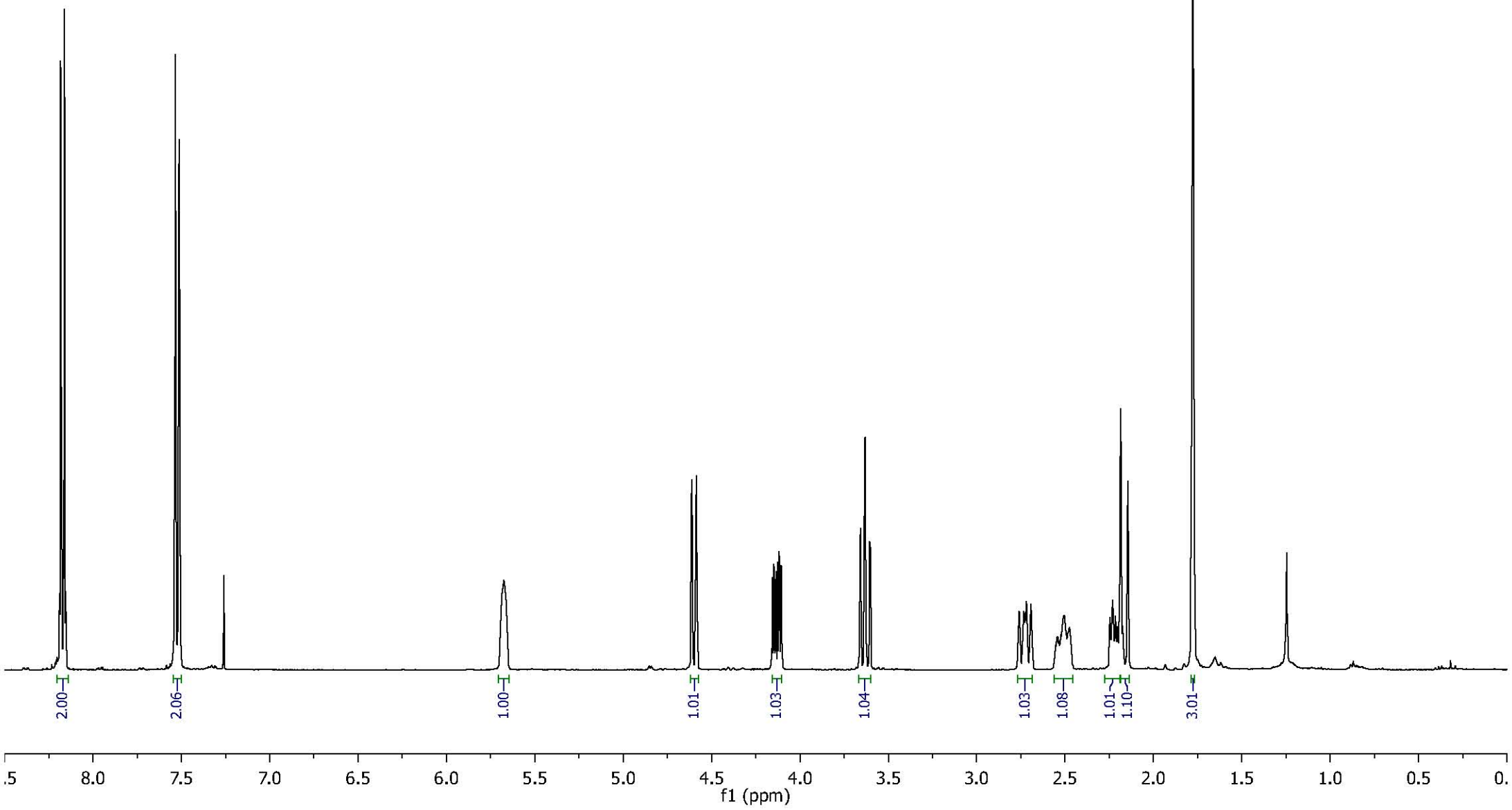

O
O
$_2$ON
NO$_2$

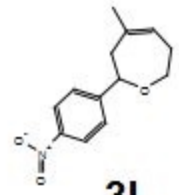
2l


4.13
4.02
2.00
2.04
4.06
2.12
2.19
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

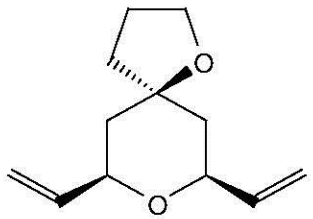


3l

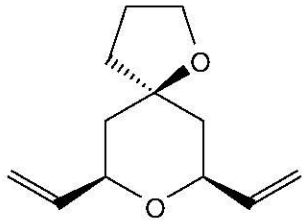

2.00
2.06
1.00
1.01
1.03
1.04
1.03
1.08
1.01
1.10
3.01
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)



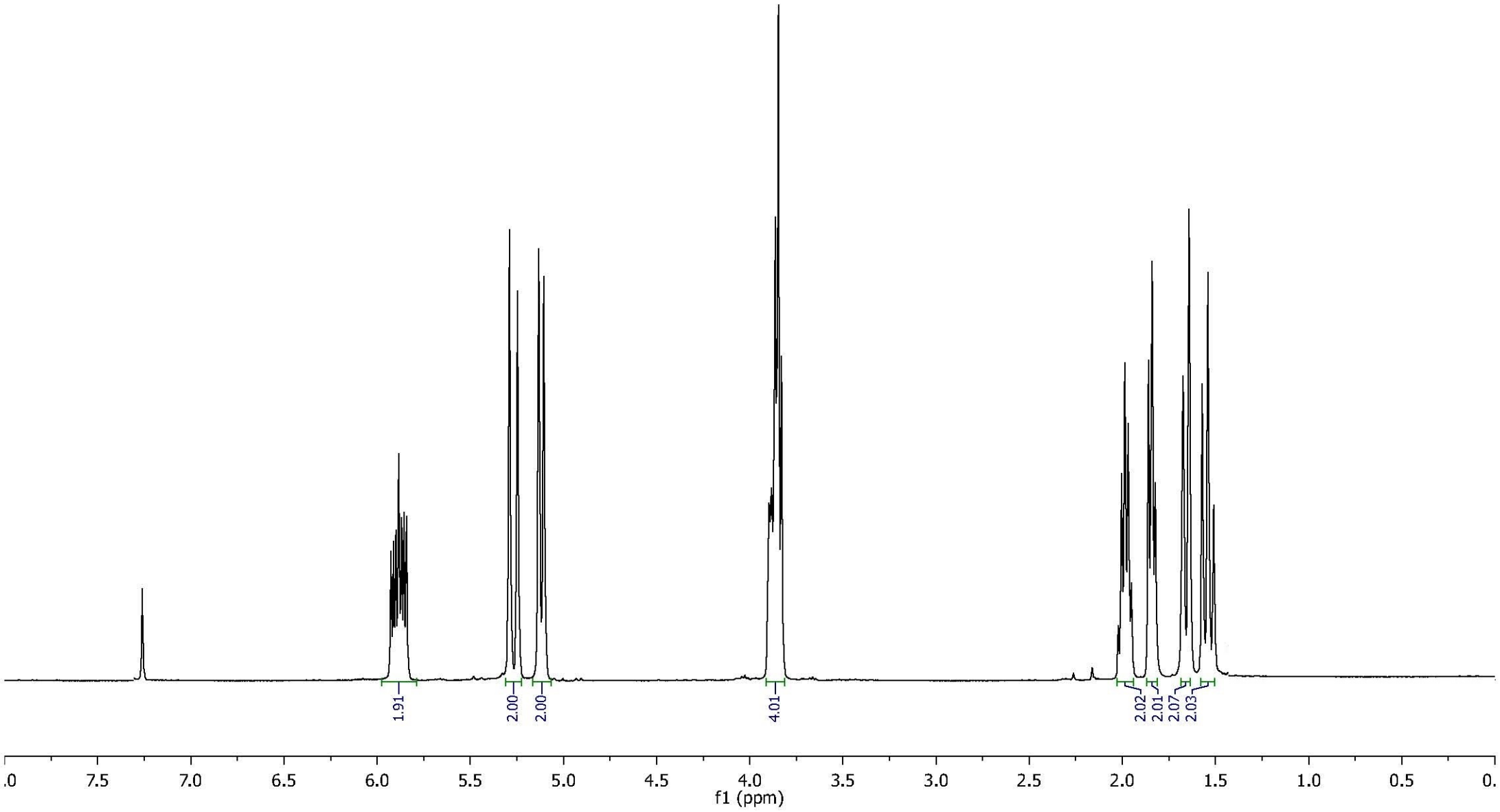
3l

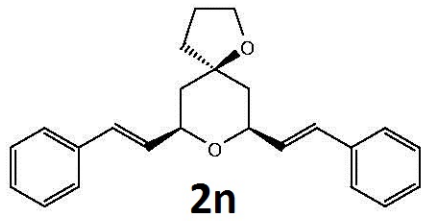


2m

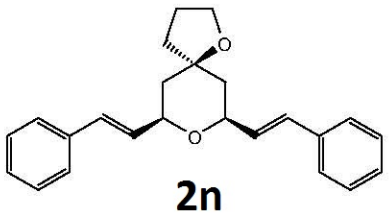


2m

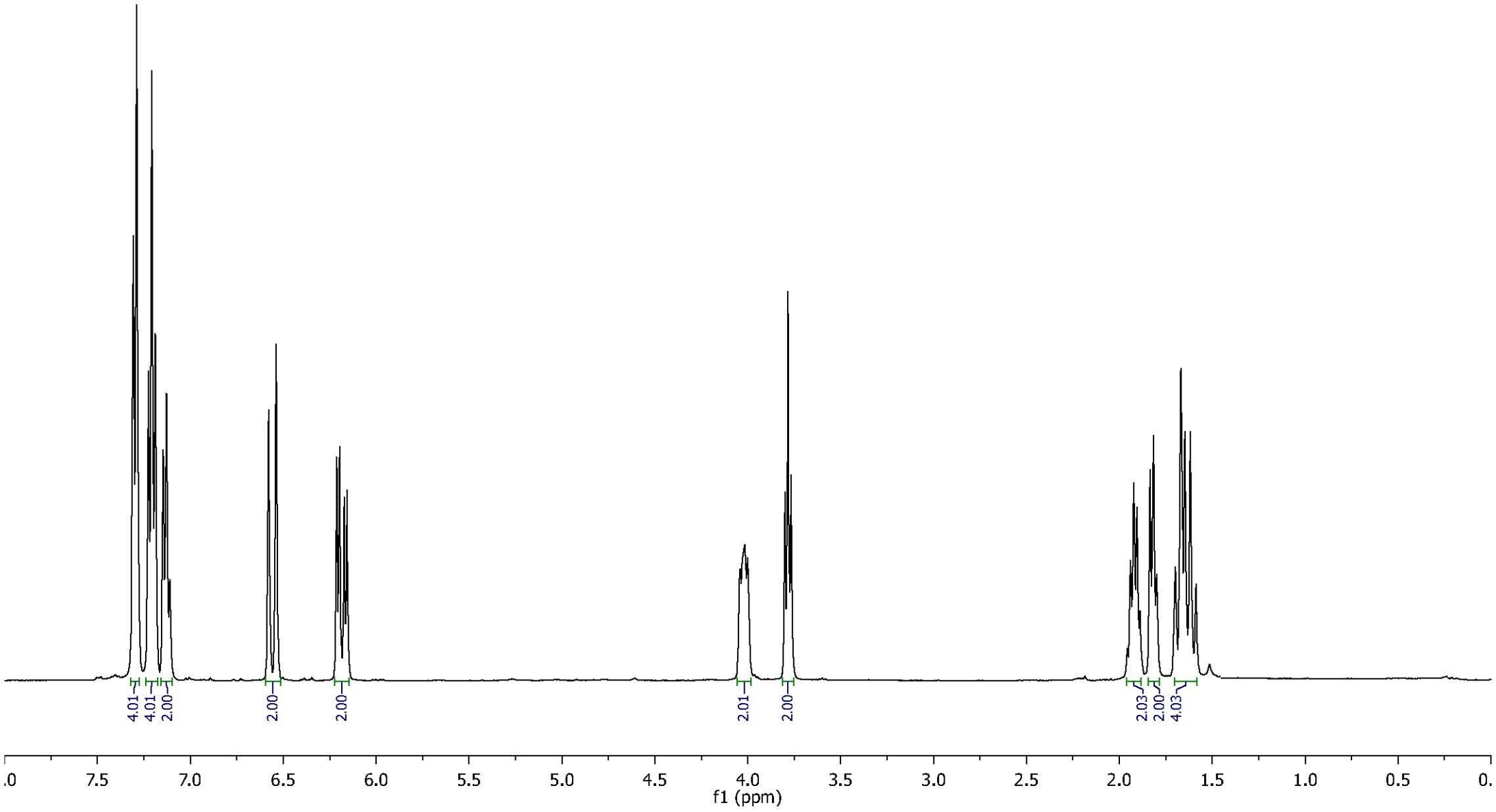

1.91
2.00
2.00
4.01
2.02
2.01
2.07
2.03
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

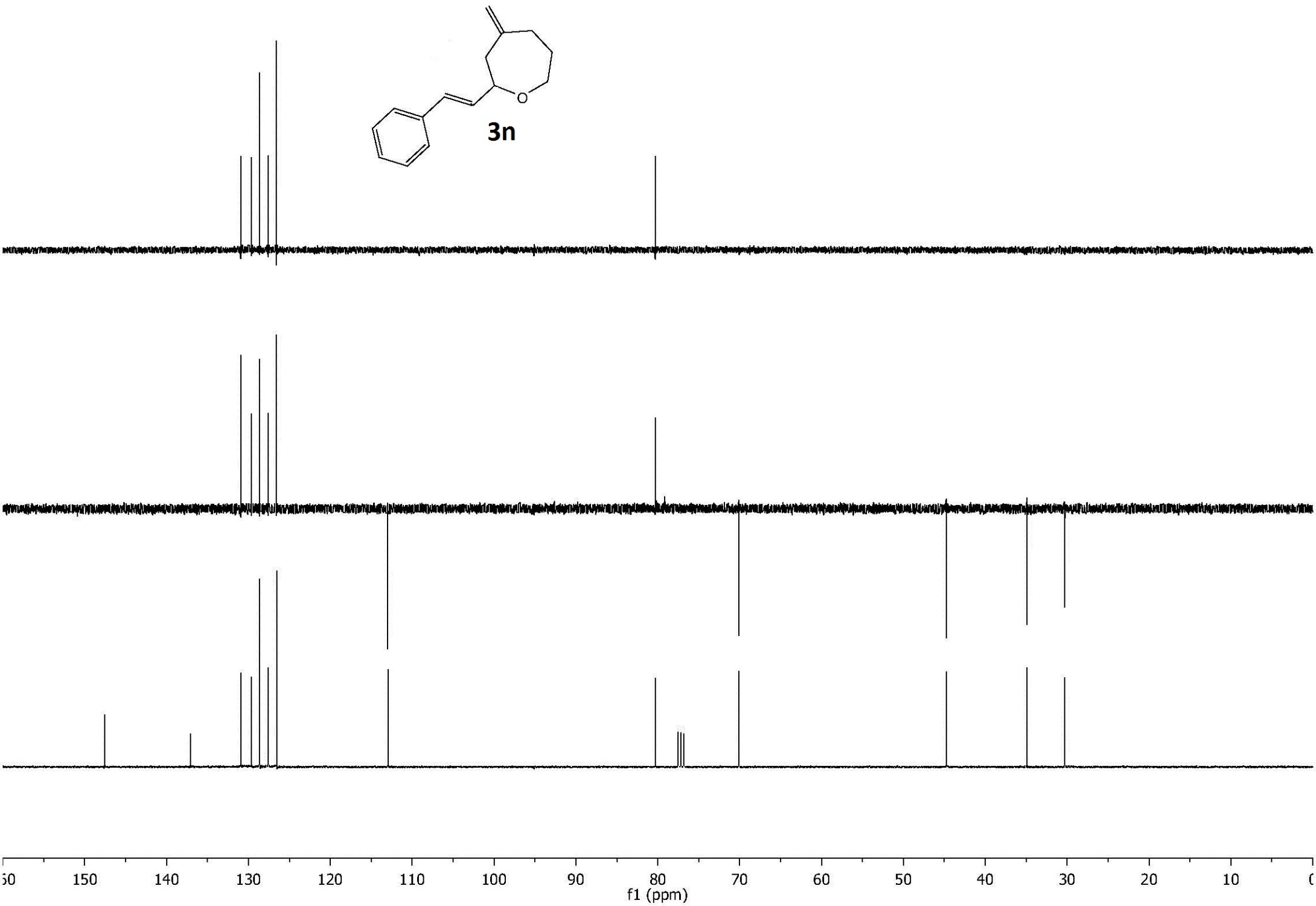


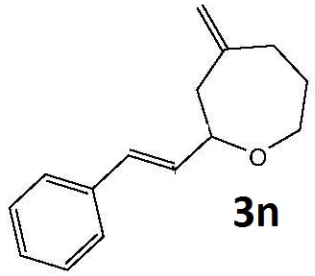
2n



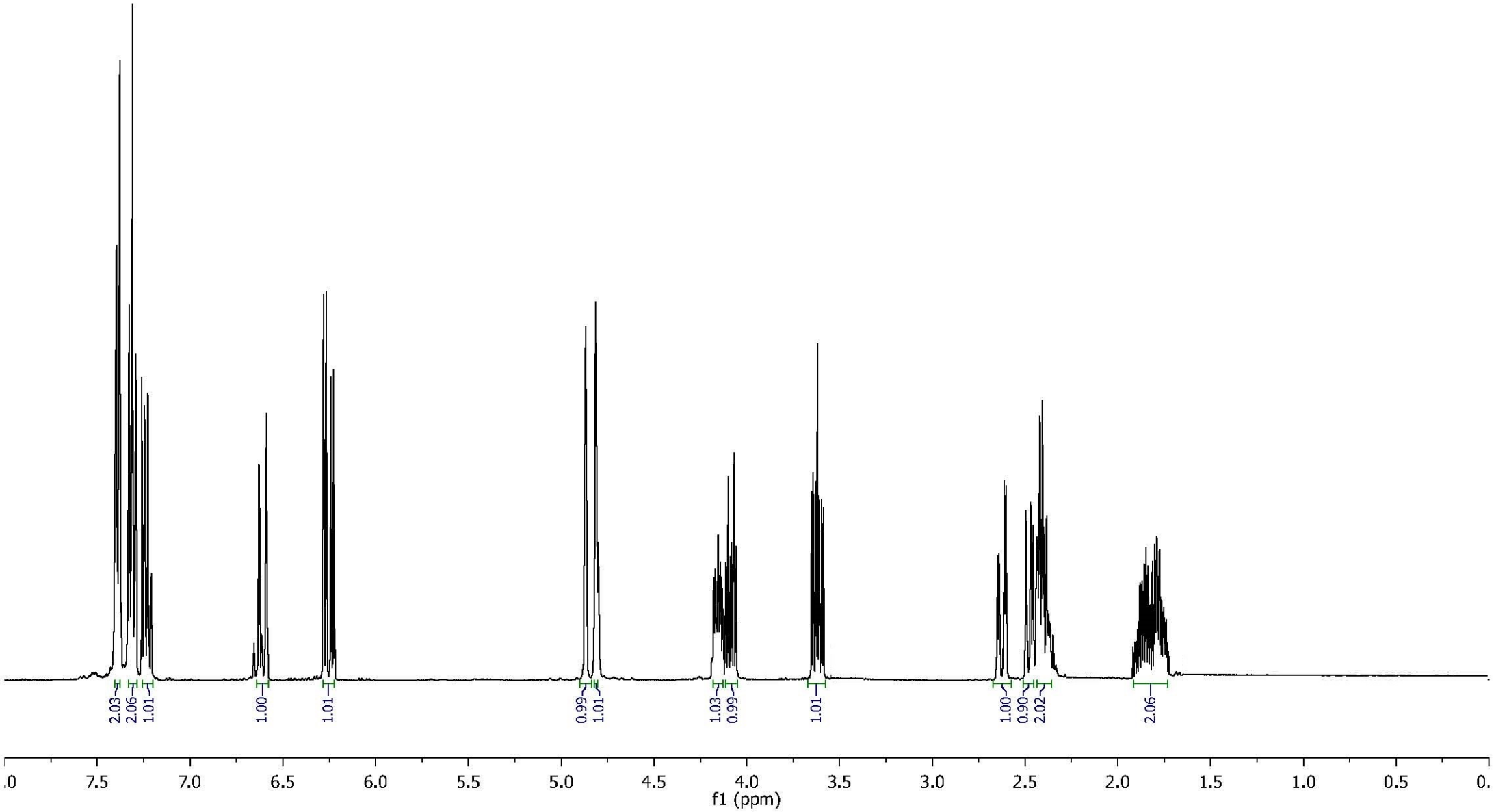
2n

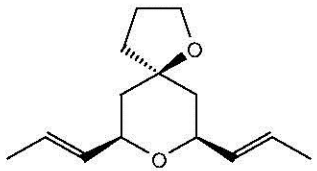



O
3n
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

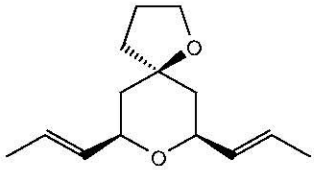

O

3n

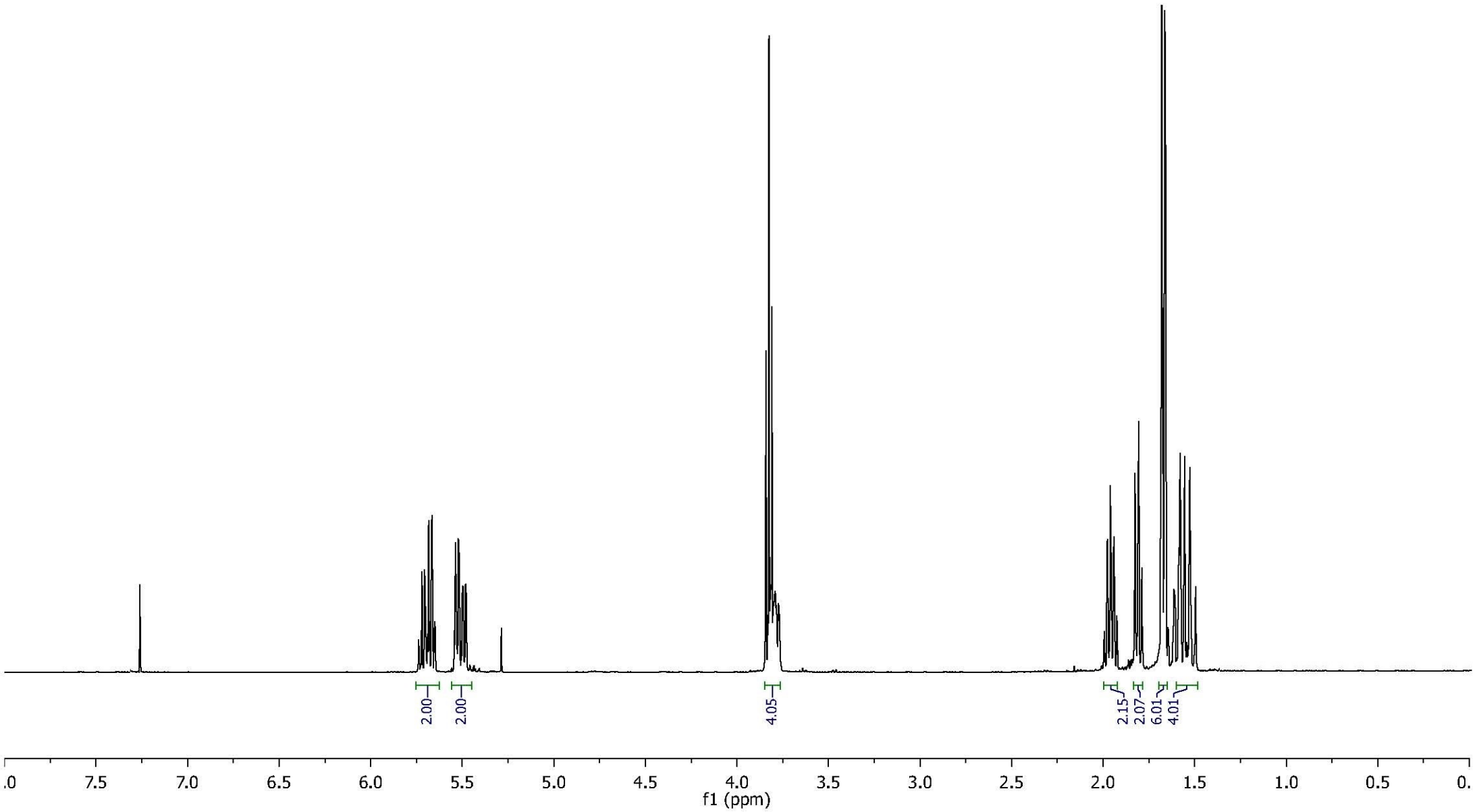

2.03
2.06
1.01
1.00
1.01
0.99
1.01
1.03
0.99
1.01
1.00
0.90
2.02
2.06
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

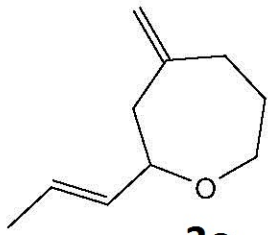


2o

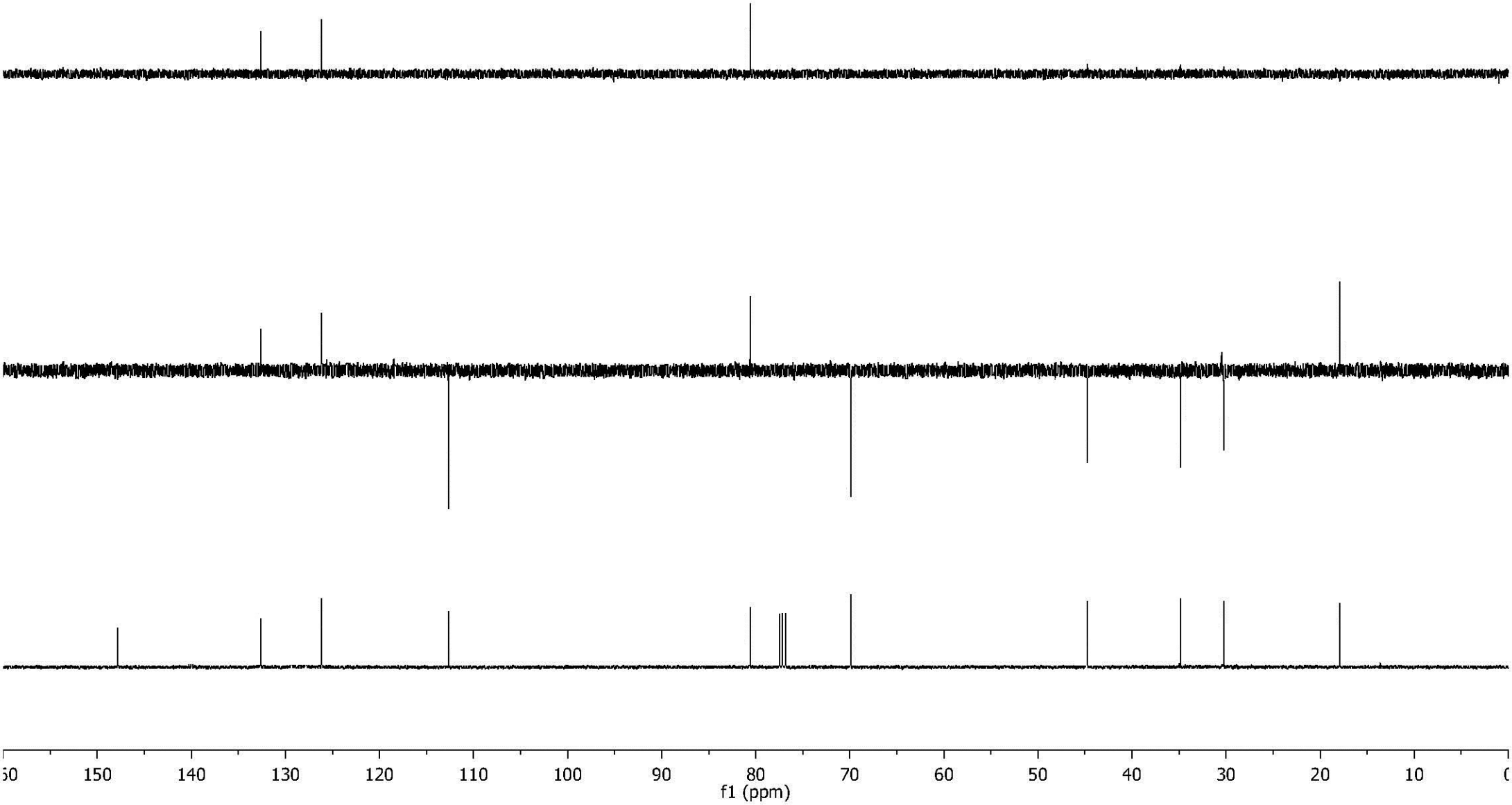


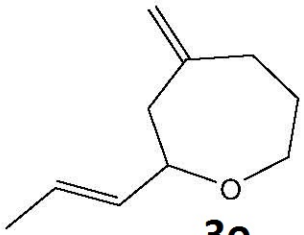
2o


2.00
2.00
4.05
2.15
2.07
6.01
4.01
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

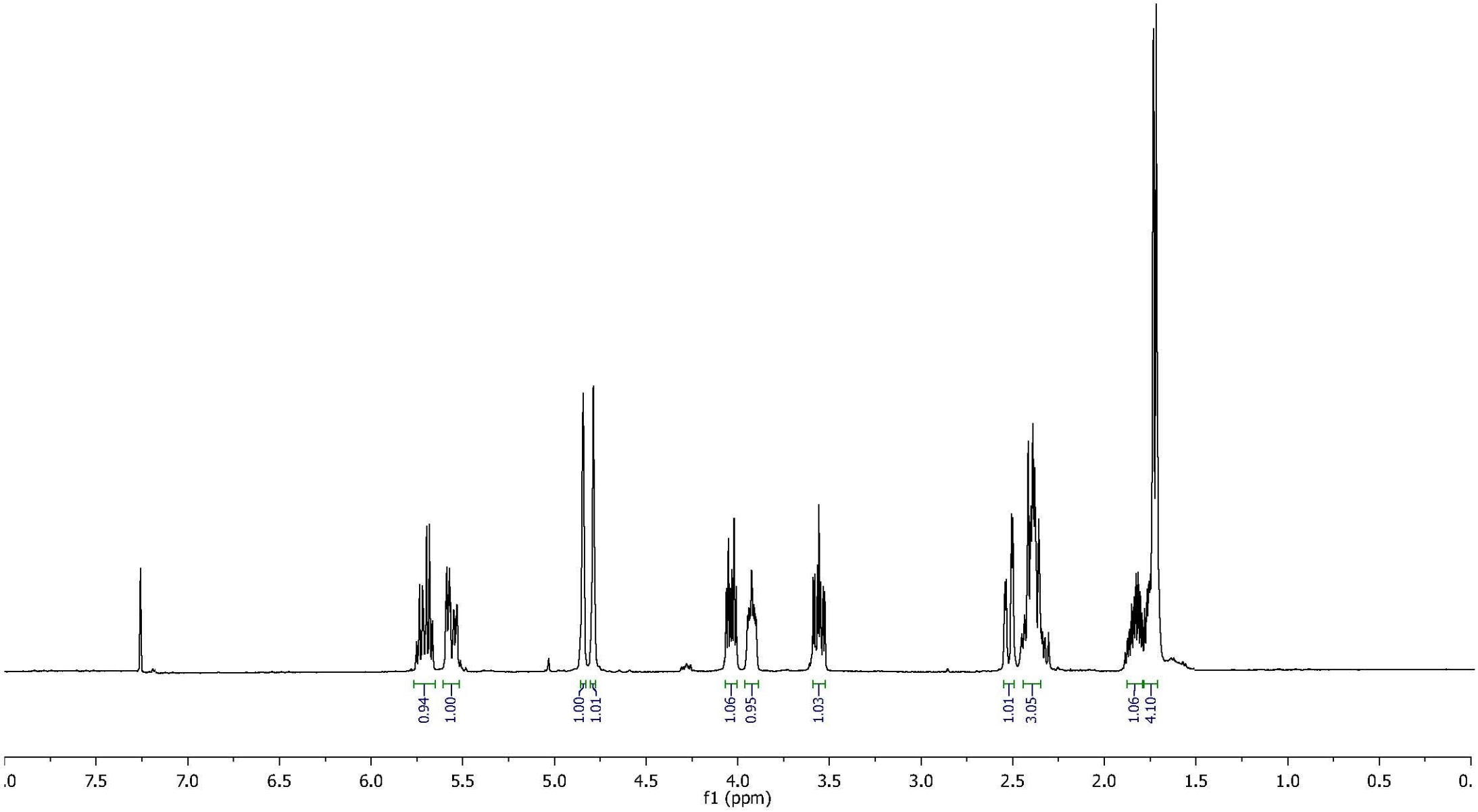


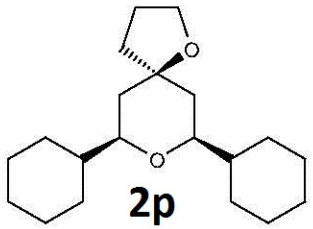
3o



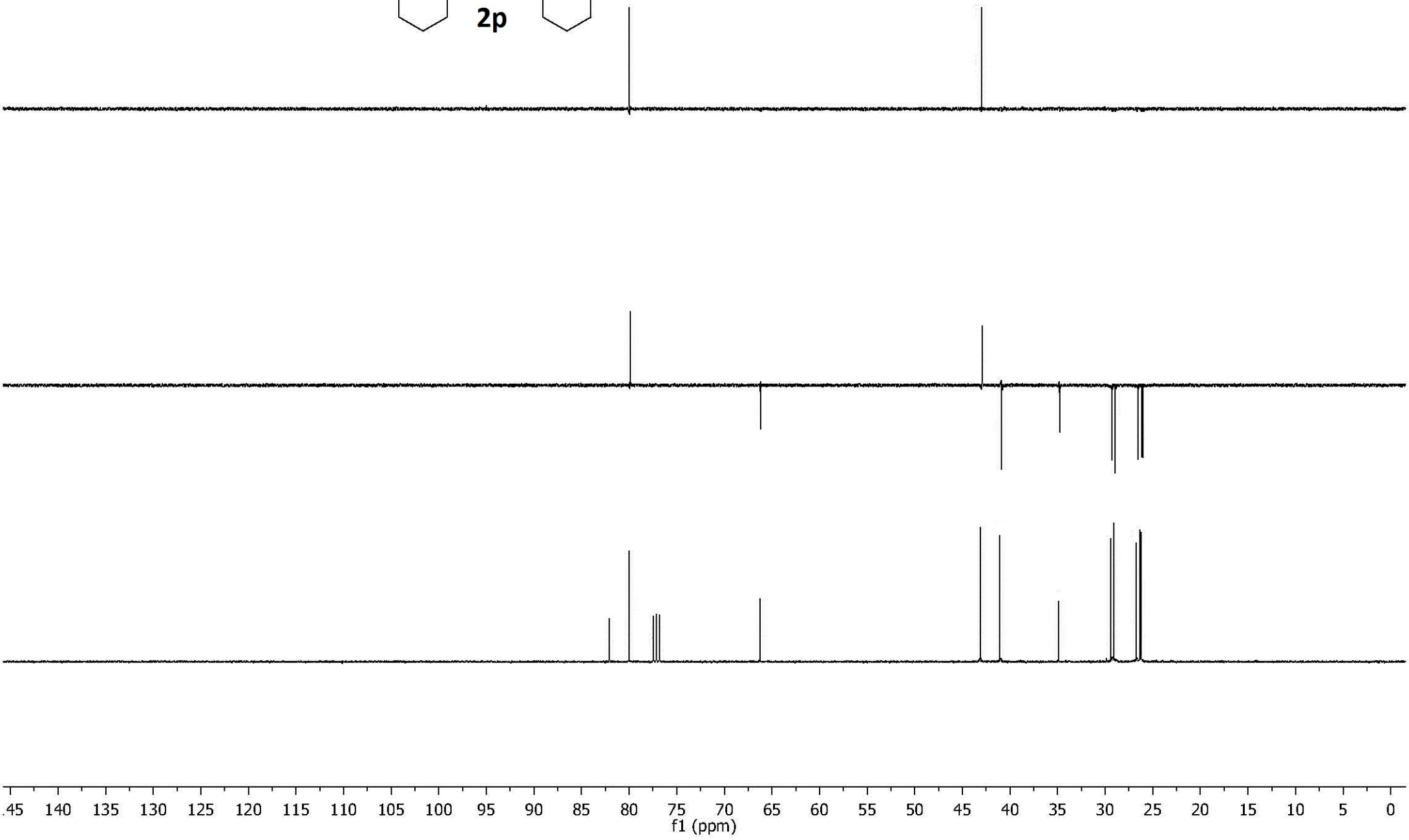


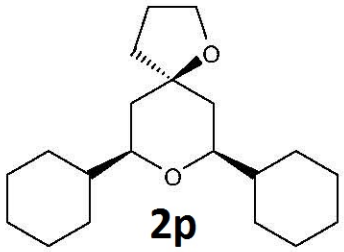
3o


0.94
1.00
1.00
1.01
1.06
0.95
1.03
1.01
3.05
1.06
4.10
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

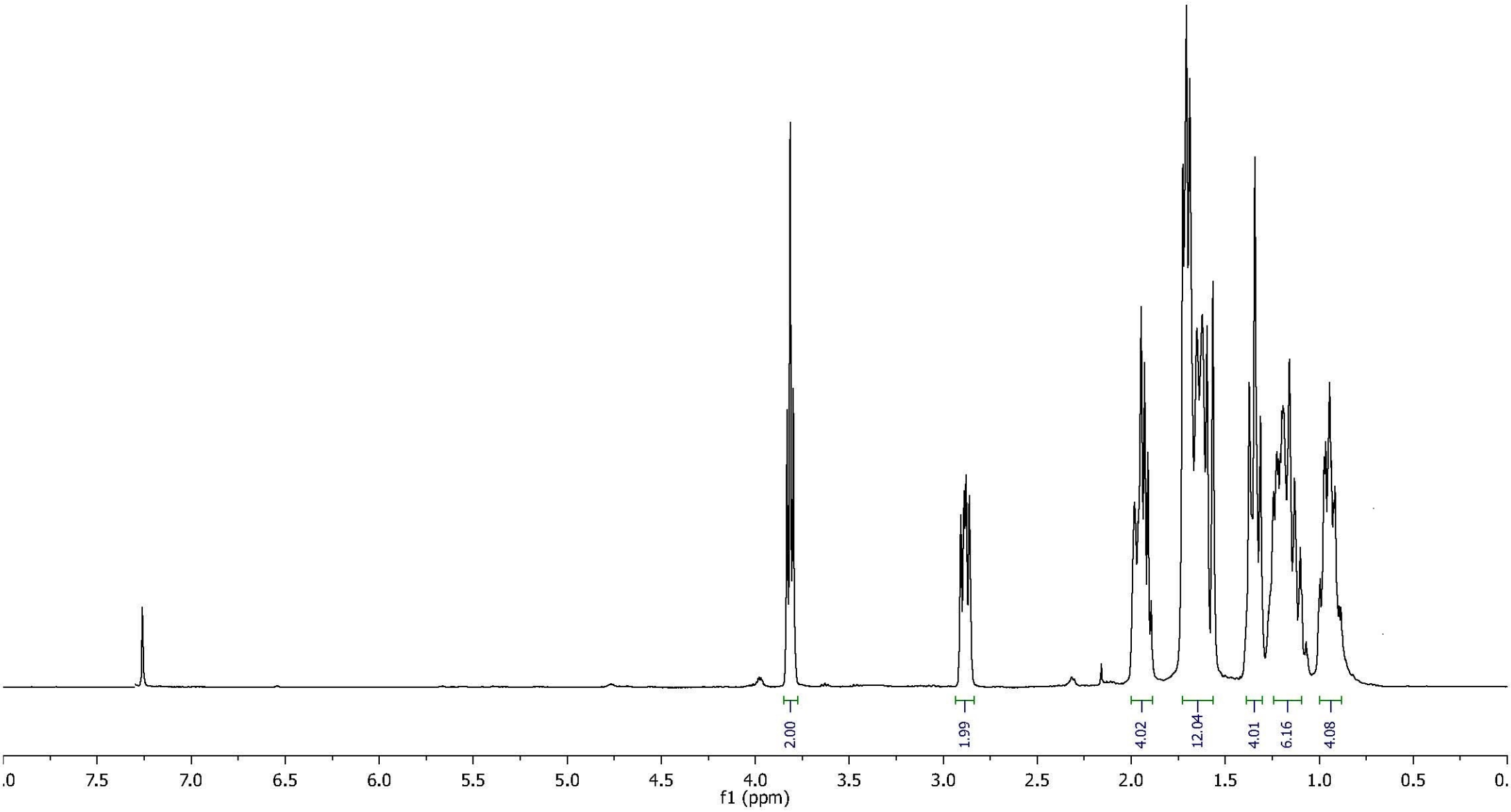


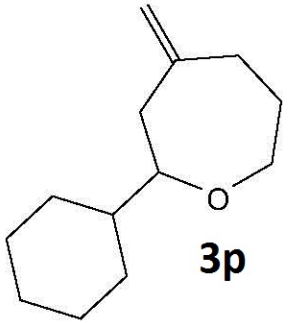
2p


.45 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0
f1 (ppm)

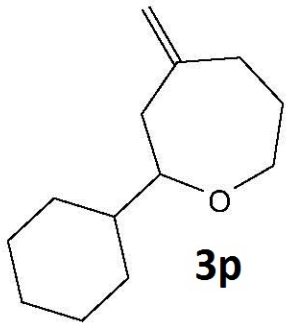


2p

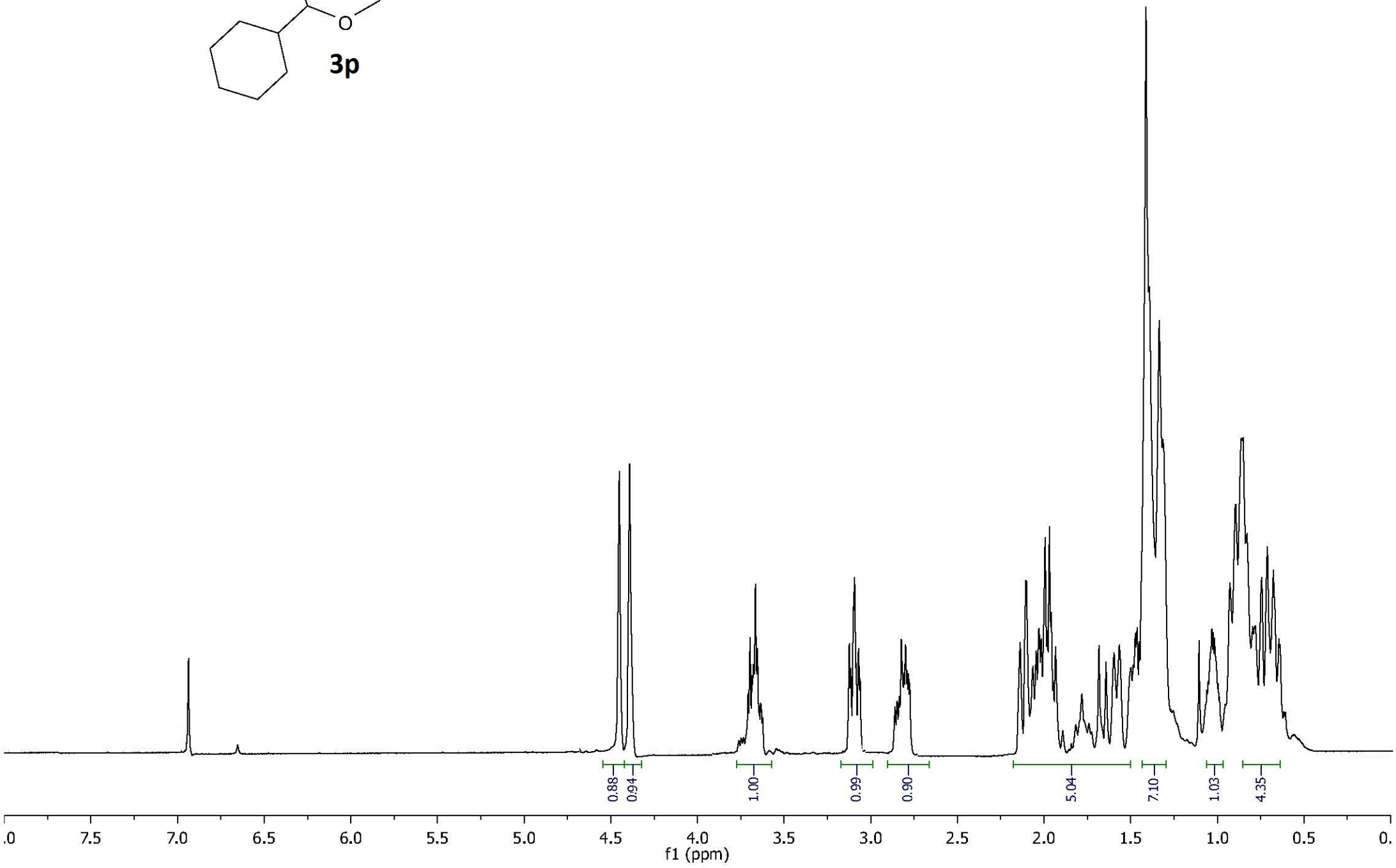

2.00
1.99
4.02
12.04
4.01
6.16
4.08
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)



3p


O

3p


0.88
0.94
1.00
0.99
0.90
5.04
7.10
1.03
4.35
.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.
f1 (ppm)