Supplementary Material (ESI) for Chemical Communications

Supporting Information

Cesium fluoride-promoted Stille coupling reaction: an efficient synthesis of 9*Z*-retinoic acid and its analogues using a practical building block

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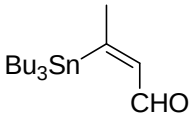
Table of Contents

General. Optical rotations were measured on a JASCO DIP-370 polarimeter ($[\alpha]_D$ values are in units of 10^{-1} deg cm^2 g^{-1}). IR spectra were measured on a Perkin Elmer FT-IR spectrometer, model Paragon 1000, using $CHCl_3$. ^{1}H NMR and ^{13}C NMR spectra were determined on a Varian Gemini-300 or a Varian Mercury-300 or a Varian VXR-500 superconducting FT-NMR spectrometer in $CDCl_3$ unless otherwise noted (tetramethylsilane as internal reference). *J*-Values are given in Hz. Mass spectra were taken on a Hitachi M-4100 spectrometer. Column chromatography was performed using Kanto Silica Gel 60 N (spherical, neutral). All reactions were carried out under Ar or N_2 atmosphere. All reagents were used directly as obtained commercially unless otherwise noted.

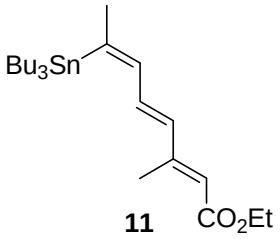
(*Z*)-3-Tributylstannylbut-2-en-1-al (12)



12

To a solution of stannyl alcohol **9**[1)] (5.50 g, 15.2 mmol) in CH_2Cl_2 (75 mL) was added Dess-Martin periodinane (7.11 g, 16.8 mmol) and the mixture was stirred for 30 min. The reaction mixture was cooled to 0 ^{o}C, and then quenched with saturated aqueous solution of $NaHCO_3$, and $Na_2S_2O_3$. The reaction mixture was extracted with CH_2Cl_2, dried over Na_2SO_4, filtered, and evaporated in *vacuo*. The residue was purified by flash column chromatography on silica gel eluting with hexane/AcOEt = 10/1 to give **12** as a colorless oil (4.62 g, 84%): ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.47 (d, *J* = 6.9 Hz, 1H), 6.69 (dd, *J* = 6.9, 1.5 Hz, 1H), 2.24 (d, *J* = 1.5 Hz, 3H), 1.37-1.30 (m, 6H), 1.55-1.44 (m, 6H), 1.27-1.01 (m, 6H), 0.89 (t, *J* = 7.5 Hz, 9H). The spectral data of this compound were identical with those of the literature.[2)]

Ethyl (2*E*,4*E*,6*Z*)-7-tributylstannyl-3-methyl-2,4,6-octatrienoate (11)



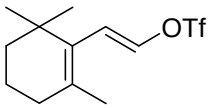
11

A solution of triethyl 3-methyl-4-phosphonocrotonate (15.7 g, 14.5 mmol) in dry THF (100 mL) was cooled to 0 ^{o}C and treated with DMPU (9.58 mL, 79.4 mmol) and *n*-BuLi (36.1 mL of 1.65 M solution in *n*-hexane). The mixture was stirred at the same temperature for 20 min and then cooled to -78 ^{o}C. A solution of aldehyde **12** (7.13 g, 19.9 mmol) in THF (40 mL) was slowly added, and the reaction mixture was allowed to warm to room temperature overnight. The reaction mixture was diluted with saturated aqueous solution of NH_4Cl, and extracted with Et_2O. The organic layer was washed with brine, dried over Na_2SO_4, filtered, and evaporated in *vacuo*. The residue was purified by flash column chromatography on silica gel eluting with hexane/AcOEt = 20/1 to give **11** as a yellow oil (8.68 g, 93%): IR 2959, 2929, 1701, 1605, 1218, 1157 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.76 (dd, *J* = 10.8, 1.2 Hz, 1H), 6.54 (dd, *J* = 15.0, 10.8 Hz, 1H), 6.18 (d, *J* = 15.0 Hz, 1H), 4.17 (q, *J* = 7.2 Hz, 2H), 2.29 (d, *J* = 1.2 Hz, 3H) 2.07 (d, *J* = 1.2 Hz, 3H) 1.54-1.45 (m, 6H), 1.30 (sext, *J* = 7.2 Hz, 6H), 1.26 (t, *J* = 7.2 Hz, 3H), 1.03-0.97 (m, 6H), 0.89 (t, *J* = 7.2 Hz, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 167.1, 153.8, 152.5, 140.4 (t, $^2J_{CSn}$ = 10.1, 9.8 Hz), 136.2 (t, $^3J_{CSn}$ = 20.4 Hz), 134.3, 118.5, 59.6, 29.1 (t, $^2J_{CSn}$ = 10.0 Hz), 27.8, 27.3 (t, $^3J_{CSn}$ = 28.9 Hz), 14.3, 13.7, 13.6, 10.3 (t, $^1J_{CSn}$ = 162 Hz); HR-EIMS Calcd for $C_{23}H_{42}O_2Sn$ (M^+) 470.2207. Found 470.2210.

General Procedure for the Triflation of Carbonyl Compounds

A solution of *i*-Pr_2NH (1.1 equiv) in dry THF (1 M) was cooled at -78 ^oC and *n*-BuLi (1.1 equiv) was added dropwise. The reaction mixture was stirred for 10 min at the same temperature, then for 30 min at 0 ^oC, and recooled at -78 ^oC. A solution of carbonyl compound (1 equiv) in THF (1 M) was added and the reaction mixture was stirred for 2 h at the same temperature. After $PhNTf_2$ (1.5 equiv) was added to the reaction mixture, it was allowed to warm to room temperature in cooling bath for overnight. The solution was evaporated in *vacuo*, then the residue was purified by flash column chromatography on silica gel to give a vinyl triflate.

(*E*)-2-(2,2,6-Trimethylcyclohexen-1-yl)ethenyl trifluoromethanesulfonate (8)

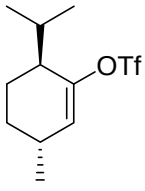


8

According to general procedure for the triflation of carbonyl compounds, **8** was obtained from *i*-Pr_2NH (465 μL, 3.31 mmol), *n*-BuLi (2.01 mL, 1.65 M in *n*-hexane, 3.31 mmol), 2,2,6-trimethyl-cyclohexene-1-acetaldehyde (**13**) (purified by flash column chromatography eluting with hexane/Et_2O = 30/1 before use, 501 mg, 3.01 mmol) and $PhNTf_2$ (1.62 g, 4.52 mmol). Eluent: hexane.

8: colorless oil (658 mg, 73%); ^1H NMR (300 MHz, $CDCl_3$) δ 6.41 (d, *J* = 12.0 Hz, 1H), 6.22 (br d, *J* = 12.0 Hz, 1H), 2.00 (br t, *J* = 6.0 Hz, 2H), 1.68 (d, *J* = 0.6 Hz, 3H), 1.65-1.57 (m, 2H), 1.49-1.45 (m, 2H), 0.98 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 137.7, 133.1, 130.2, 120.4, 118.7 (q, J_{CF} = 319 Hz), 38.9, 33.9, 32.6, 28.3, 21.2, 18.9. The ^1H NMR spectral data of this compound were identical with those of the literature.[3)]

(6*S*)-Isopropyl-(3*R*)-methylcyclohex-1-enyl trifluoromethanesulfonate (14a)

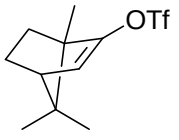


14a

According to general procedure for the triflation of carbonyl compounds, **14a** was obtained from *i*-Pr_2NH (1.00 mL, 7.13 mmol), *n*-BuLi (4.32 mL, 1.65 M in *n*-hexane, 7.13 mmol), (-)-menthone (1.00 g, 6.48 mmol) and $PhNTf_2$ (3.47 g, 9.72 mmol). Eluent: hexane.

14a: colorless oil (1.10 g, 59%); ^1H NMR (300 MHz, $CDCl_3$) δ 5.64 (br s, 1H), 2.50-2.45 (m, 1H), 2.36-2.28 (m, 1H), 2.21-2.10 (m, 1H), 1.86-1.77 (m, 2H), 1.48-1.36 (m, 1H), 1.19-1.11 (m, 1H), 1.04 (d, *J* = 6.9 Hz, 3H), 0.95 (d, *J* = 6.6 Hz, 3H), 0.82 (d, *J* = 6.9 Hz, 3H). The ^1H NMR spectral data of this compound were identical with those of the literature.[4)]

(1*R*,4*R*)-1,7,7-Trimethylbicyclo[2.2.1]hept-2-en-2-yl trifluoromethanesulfonate (14b)



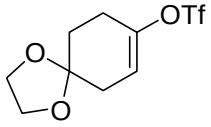
14b

According to general procedure for the triflation of carbonyl compounds, **14b** was obtained from *i*-Pr_2NH (1.01 mL, 7.23 mmol), *n*-BuLi (4.38 mL, 1.65 M in *n*-hexane, 7.23 mmol), (+)-camphor (1.00 g, 6.57 mmol) and $PhNTf_2$ (3.52 g, 9.85 mmol). Eluent: hexane.

14b: colorless oil (1.43 g, 76%); ^1H NMR (300 MHz, $CDCl_3$) δ 5.66 (d, *J* = 3.9 Hz, 1H), 2.45 (t, *J* = 3.6 Hz, 1H), 1.93 (ddd, *J* = 15.6, 8.4, 3.6 Hz, 1H), 1.65 (ddd, *J* = 12.0, 8.4, 3.6 Hz, 1H), 1.33 (ddd, *J*

= 12.0, 9.0, 3.6 Hz, 1H), 1.15 (ddd, *J* = 12.0, 9.0, 3.6 Hz, 1H), 1.03 (s, 3H), 0.92 (s, 3H), 0.79 (s, 3H). The ^{1}H NMR spectral data of this compound were identical with those of the literature.[5)]

1,4-Dioxaspiro[4.5]dec-7-en-8-yl trifluoromethanesulfonate (14c)

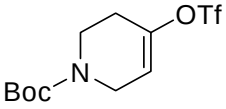


14c

According to general procedure for the triflation of carbonyl compounds, **14c** was obtained from *i*-Pr_2NH (790 μL 5.63 mmol), *n*-BuLi (3.39 mL, 1.66 M in *n*-hexane, 5.63 mmol), 1,4-cyclohexanedione mono(ethylene ketal) (800 mg, 5.12 mmol) and $PhNTf_2$ (2.74 g, 7.68 mmol). Eluent: hexane/AcOEt = 9/1.

14c: colorless oil (488 mg, 33%); ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.67-5.65 (m, 1H), 4.01-3.97 (m, 4H), 2.57-2.51 (m, 2H), 2.42-2.39 (m, 2H), 1.90 (t, *J* = 6.6 Hz, 2H); *Anal*. Calcd for $C_9H_{11}F_3O_3S$: C, 37.50; H, 3.85; F, 19.77. Found: C, 37.72; H, 4.07; F, 19.50. The ^{1}H NMR spectral data of this compound were identical with those of the literature.[6)]

1-*tert*-Butoxycarbonyl-5,6-dihydro-2*H*-pyridin-4-yl trifluoromethanesulfonate (14d)

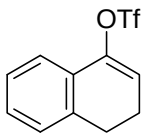


14d

According to general procedure for the triflation of carbonyl compounds, **14d** was obtained from *i*-Pr_2NH (619 μL 4.42 mmol), *n*-BuLi (2.66 mL, 1.66 M in *n*-hexane, 4.42 mmol), 1-Boc-4-piperidone (800 mg, 4.02 mmol) and $PhNTf_2$ (2.15 g, 6.02 mmol). Eluent: hexane/AcOEt = 9/1.

14d: colorless oil (651 mg, 49%); ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.76 (br s, 1H), 4.06-4.03 (m, 2H), 3.63 (t, *J* = 5.7 Hz, 2H), 2.46-2.42 (m, 2H), 1.47 (s, 9H). The ^{1}H NMR spectral data of this compound were identical with those of the literature.[6)]

3,4-Dihydronaphthalen-1-yl trifluoromethanesulfonate (14e)

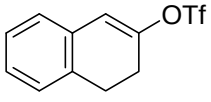


14e

According to general procedure for the triflation of carbonyl compounds, **14e** was obtained from *i*-Pr_2NH (1.05 mL 7.52 mmol), *n*-BuLi (4.85 mL, 1.55 M in *n*-hexane, 7.52 mmol), α-tetralone (1.00 g, 6.84 mmol) and $PhNTf_2$ (3.66 g, 10.3 mmol). Eluent: hexane.

14e: yellow oil (1.50 g, 80%); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.36-7.31 (m, 1H), 7.27-7.21 (m, 2H), 7.18-7.13 (m, 1H), 5.99 (t, *J* = 4.5 Hz, 1H), 2.84 (t, *J* = 8.4 Hz, 2H), 2.47 (td, *J* = 8.4, 4.5 Hz, 2H). The ^{1}H NMR spectral data of this compound were identical with those of the literature.[7)]

3,4-Dihydronaphthalen-2-yl trifluoromethanesulfonate (14f)



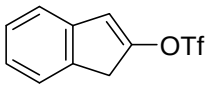
14f

According to general procedure for the triflation of carbonyl compounds, **14f** was obtained from *i*-Pr_2NH (1.05 mL 7.52 mmol), *n*-BuLi (4.56 mL, 1.65 M in *n*-hexane, 7.52 mmol), β-tetralone (1.00 g, 6.84 mmol) and $PhNTf_2$ (3.66 g, 10.3 mmol). Eluent: hexane / Et_2O = 50/1.

14f: colorless oil (1.85 g, 97%); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.23-7.19 (m, 2H), 7.18-7.13 (m, 1H), 7.11-7.06 (m, 1H), 6.48 (s, 1H), 3.07 (t, *J* = 8.7 Hz, 2H), 2.70 (t, *J* = 8.7 Hz, 2H); *Anal*. Calcd

for $C_{11}H_9F_3O_3S$: C, 47.48; H, 3.26; F, 20.48. Found: C, 47.30; H, 3.47; F, 20.59. The ^{1}H NMR spectral data of this compound were identical with those of the literature.[6)]

2-Indenyl trifluoromethanesulfonate (14g)

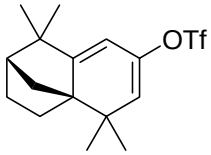


14g

According to general procedure for the triflation of carbonyl compounds, **14g** was obtained from *i*-Pr_2NH (349 μL 2.49 mmol), *n*-BuLi (1.50 mL, 1.66 M in *n*-hexane, 2.49 mmol), 2-indanone (300 mg, 2.26 mmol) and $PhNTf_2$ (1.21 g, 3.39 mmol). Eluent: hexane.

14g: colorless oil (394 mg, 66%); IR 3030, 1619, 1610, 1578, 1427, 1204, 1141, 1092 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.41-7.24 (m, 4H), 6.70 (s, 1H), 3.67 (s, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 153.2, 140.1, 137.3, 127.2, 126.1, 123.7, 122.1, 119.5, 118.7 (q, J_{CF} = 319 Hz), 37.6; *Anal*. Calcd for $C_{10}H_7F_3O_3S$: C, 45.46; H, 2.67; F, 21.57. Found: C, 45.34; H, 2.81; F, 21.53; HR-EIMS Calcd for $C_{10}H_7F_3O_3S$ (M^+) 264.0068. Found 264.0041.

(2*S*,4*aR*)-1,2,3,4,4a,5-Hexahydro-1,1,5,5-tetramethyl-2,4a-methanonaphthalen-7-yl trifluoromethanesulfonate (14h)

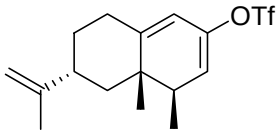


14h

According to general procedure for the triflation of carbonyl compounds, **14h** was obtained from *i*-Pr_2NH (247 μL 1.76 mmol), *n*-BuLi (1.14 mL, 1.55 M in *n*-hexane, 1.76 mmol), (-)-isolongifolen-9-one (350 mg, 1.60 mmol) and $PhNTf_2$ (859 mg, 2.41 mmol). Eluent: hexane.

14h: yellow oil (469 mg, 83%); $[\alpha]_D^{29}$ -290 (*c* 0.980, MeOH); IR 2965, 2871, 1662, 1613, 1417, 1204, 1142, 1066 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.40 (d, *J* = 2.1 Hz, 1H), 5.19 (d, *J* = 2.1 Hz, 1H), 1.93 (br t, *J* = 2.1 Hz, 1H), 1.79-1.74 (dq, *J* = 7.8, 2.1 Hz, 1H), 1.72-1.60 (m, 2H), 1.55-1.43 (m, 1H), 1.28 (d, *J* = 6.9 Hz, 1H), 1.19-1.10 (m, 1H), 1.13 (s, 3H), 1.12 (s, 3H), 1.05 (s, 3H), 0.99 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.4, 146.2, 121.9, 118.6 (q, J_{CF} = 319 Hz), 106.4, 56.7, 46.6, 43.7, 35.5, 34.1, 28.6, 27.1, 24.4, 24.3, 24.0, 23.9; *Anal*. Calcd for $C_{16}H_{21}F_3O_3S$: C, 54.84; H, 6.04; F, 16.27. Found: C, 55.55; H, 6.09; F, 16.13; HR-EIMS Calcd for $C_{16}H_{21}F_3O_3S$ (M^+) 350.1163. Found 350.1159.

(4*R*,4*aS*,6*R*)-4,4a,5,6,7,8-Hexahydro-4,4a-dimethyl-6-(1-methylethenyl)-naphthalen-2-yl trifluoromethanesulfonate (14i)



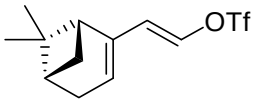
14i

According to general procedure for the triflation of carbonyl compounds, **14i** was obtained from *i*-Pr_2NH (565 μL 4.03 mmol), *n*-BuLi (2.44 mL, 1.65 M in *n*-hexane, 4.03 mmol), (+)-nootkatone (800 mg, 3.66 mmol) and $PhNTf_2$ (1.96 g, 5.50 mmol). Eluent: hexane.

14i: colorless oil (1.08 g, 84%); $[\alpha]_D^{28}$ +152 (*c* 1.14, MeOH); IR 2936, 2861, 1655, 1607, 1418, 1204, 1142, 1082 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.53 (br s, 1H), 5.27 (br t, *J* = 2.4 Hz, 1H), 4.74-4.72 (m, 2H), 2.59-2.52 (m, 1H), 2.40-2.32 (m, 2H), 2.17 (tt, *J* = 12.3, 3.0 Hz, 1H), 1.92 (dt, *J*

= 12.9, 2.4 Hz, 1H), 1.87-1.79 (m, 1H), 1.74 (t, *J* = 1.2 Hz, 3H), 1.36-1.09 (m, 2H), 1.07 (d, *J* = 7.8 Hz, 3H), 0.90 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 152.1, 149.4, 144.7, 118.6 (q, J_{CF} = 319 Hz), 117.8, 114.2, 109.0, 45.2, 41.4, 41.0, 38.9, 31.4, 30.8, 20.8, 14.4, 13.5; *Anal*. Calcd for $C_{16}H_{21}F_3O_3S$: C, 54.84; H, 6.04; F, 16.27. Found: C, 54.78; H, 6.31; F, 16.07; HR-EIMS Calcd for $C_{16}H_{21}F_3O_3S$ (M^+) 350.1163. Found 350.1178.

2-((1*R*)-6,6-Dimethylbicyclo[3.1.1]hept-2-ene)ethenyl trifluoromethanesulfonate (14j)



14j

According to general procedure for the triflation of carbonyl compounds, **14j** was obtained from *i*-Pr_2NH (685 μL 4.89 mmol), *n*-BuLi (2.96 mL, 1.65 M in *n*-hexane, 4.89 mmol), aldehyde[8] (730 mg, 4.45 mmol) and $PhNTf_2$ (2.38 g, 6.67 mmol). Eluent: hexane.

14j: colorless oil (666 mg, 51%); $[\alpha]_D^{30}$ +1.04 (*c* 0.964, MeOH); IR 2952, 2889, 1644, 1605, 1423, 1206, 1142, 1018 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.66 (d, *J* = 12.0 Hz, 1H), 6.21 (d, *J* = 12.0 Hz, 1H), 5.72 (br s, 1H), 2.49-2.35 (m, 3H), 2.26 (td, *J* = 5.7, 1.5 Hz, 1H), 2.17-2.13 (m, 1H), 1.33 (s, 3H), 1.18 (d, *J* = 8.7 Hz, 1H), 0.80 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 140.2, 134.8, 128.6, 123.8, 118.6 (q, J_{CF} = 319 Hz), 41.9, 40.5, 37.9, 32.2, 31.1, 26.1, 20.6; HR-EIMS Calcd for $C_{12}H_{15}F_3O_3S$ (M^+) 296.0694. Found 296.0674.

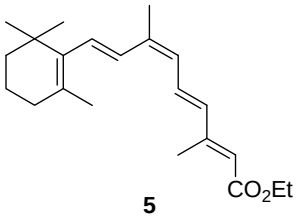
General Procedure for the Stille Coupling (Method A)

A mixture of the vinyl triflate (1.1 equiv), stannanyl ester **11** (1.0 equiv), $Pd_2(dba)_3{\cdot}CHCl_3$ (4 mol%), and $AsPh_3$ (16 mol%) was dissolved in dry DMF (0.1 M), then CsF (2.0 equiv) was added. The flask was evacuated and refulled with argon five times. After the mixture was stirred at 45 °C for the required time, cooled to room temperature, quenched with water, and extracted with Et_2O. The organic phase was dried over Na_2SO_4, filtrated, and evaporated in *vacuo*. The residue was purified by column chromatography using neutralized SiO_2/powdered KF (9/1) to give a coupled product.

General Procedure for the Stille Coupling (Method B)

According to Baldwin's procedure,[9] a mixture of the vinyl triflate (1.0 equiv) and the stannanyl ester **11** (1.3 equiv) was dissolved in dry DMF (0.1 M), then CsF (2.0 equiv), $Pd(PPh_3)_4$ (10 mol%), and CuI (20 mol%) was added. The flask was evacuated and refulled with argon five times. After the mixture was stirred at 45 °C for the required time, cooled to room temperature, and diluted with CH_2Cl_2 and water. After vigorous stirring, the mixture was filtered through Celite with CH_2Cl_2/AcOEt (1/1). The organic layer was separated, dried over Na_2SO_4, filtrated, and evaporated in *vacuo*. The residue was purified by column chromatography using neutralized SiO_2/powdered KF (9/1) to give a coupled product.

Ethyl (9*Z*)-retinoate (5)

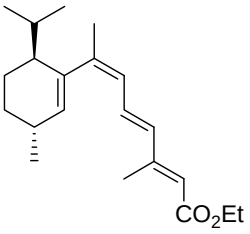


5

According to Method A, **5** (49.8 mg, 88%) was obtained from vinyl triflate **8** (56.6 mg, 0.190 mmol), stannanyl ester **11** (81.0 mg, 0.173 mmol), $Pd_2(dba)_3{\cdot}CHCl_3$ (7.1 mg, 6.90 μmol), $AsPh_3$ (8.5 mg, 27.6 μmol), and CsF (52.4 mg, 0.345 mmol). Eluent: hexane/AcOEt = 30/1. Reaction time: 1.5 h.

5: yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.08 (dd, *J* = 15.0, 11.4 Hz, 1H), 6.65 (d, *J* = 15.9 Hz, 1H), 6.27 (d, *J* = 16.5 Hz, 1H), 6.21 (d, *J* = 15.0 Hz, 1H), 6.05 (d, *J* = 11.4 Hz, 1H), 5.76 (s, 1H), 4.16 (q, *J* = 7.2 Hz, 2H), 2.35 (d, *J* = 0.9 Hz, 3H), 2.05 (t, *J* = 6.3 Hz, 2H), 1.99 (s, 3H) 1.74 (s, 3H), 1.68-1.60 (m, 2H), 1.50-1.46 (m, 2H), 1.28 (t, *J* = 7.2 Hz, 3H), 1.04 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 167.1, 152.7, 138.3, 138.0, 134.4, 130.1, 130.0, 129.7, 129.5, 128.0, 118.5, 113.8, 59.6, 39.5, 34.2, 33.0, 29.0, 21.8, 20.8, 19.2, 14.3. The ^{1}H NMR spectral data of this compound were identical with those of the literature.[10)]

Ethyl (2*E*,4*E*,6*Z*)-7-[(6*S*)-isopropyl-(3*R*)-methylcyclohex-1-enyl]-3-methyl-2,4,6-octatrienoate (15a)

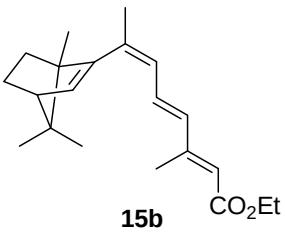


15a

According to Method A, **15a** (243 mg, 77%) was obtained from vinyl triflate **14a** (310 mg, 1.08 mmol), stannanyl ester **11** (465 mg, 0.991 mmol), $Pd_2(dba)_3{\cdot}CHCl_3$ (41.0 mg, 39.6 μmol), $AsPh_3$ (48.5 mg, 0.158 mmol) and CsF (300 mg, 1.97 mmol). Eluent: hexane/Et_2O = 30/1. Reaction time: 4 h.

15a: yellow oil; $[\alpha]_D^{26}$ +215 (*c* 0.858, MeOH); IR 2960, 2852, 1698, 1600, 1241, 1156 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.98 (dd, *J* = 15.3, 11.1 Hz, 1H), 6.15 (d, *J* = 15.3 Hz, 1H), 5.97 (d, *J* = 10.8 Hz, 1H), 5.72 (s, 1H), 5.42 (br s, 1H), 4.15 (q, *J* = 7.2 Hz, 2H), 2.34-2.18 (m, 2H), 2.27 (d, *J* = 1.2 Hz, 3H), 1.88 (s, 3H), 1.88-1.69 (m, 3H), 1.47-1.34 (m, 1H), 1.27 (t, *J* = 7.2 Hz, 3H), 1.12-0.99 (m, 1H), 0.96 (d, *J* = 7.2 Hz, 3H), 0.90 (d, *J* = 7.2 Hz, 3H), 0.67 (d, J = 6.6 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 167.3, 153.3, 146.8, 141.1, 135.1, 133.1, 132.7, 126.3, 117.6, 59.5, 41.7, 31.2, 30.8, 28.9, 23.9, 22.0, 21.20, 21.16, 16.6, 14.3, 13.8; HR-EIMS Calcd for $C_{21}H_{32}O_2$ (M^+) 316.2402. Found 316.2420.

Ethyl (2*E*,4*E*,6*Z*)-3-methyl-7-[(1*R*,4*R*)-1,7,7-trimethylbicyclo[2.2.1]hept-2-en-2-yl]-2,4,6-octatrienoate (15b)



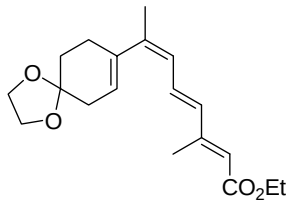
15b

According to Method B, **15b** (81.6 mg, 76%) was obtained from vinyl triflate **14b** (98.0 mg, 0.345 mmol), stannanyl ester **11** (210 mg, 0.448 mmol), CsF (300 mg, 1.97 mmol), $Pd(PPh_3)_4$ (39.9 mg, 34.5 μmol) and CuI (13.1 mg, 68.9 μmol). Eluent: hexane/Et_2O = 40/1. Reaction time: 1.5 h.

15b: yellow oil; $[\alpha]_D^{26}$ -185 (*c* 1.63, MeOH); IR 2960, 2875, 1698, 1600, 1241, 1156 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.91 (dd, *J* = 15.0, 11.0 Hz, 1H), 6.16 (d, *J* = 15.0 Hz, 1H), 6.07 (d, *J* = 11.0 Hz, 1H), 5.76 (d, *J* = 3.5 Hz, 1H), 5.71 (s, 1H), 4.15 (q, *J* = 7.0 Hz, 2H), 2.38 (br t, *J* = 3.5 Hz, 1H), 2.27 (d, *J* = 1.0 Hz, 3H), 1.94-1.89 (m, 1H), 1.91 (s, 3H), 1.60 (ddd, *J* = 12.0, 8.5, 3.5 Hz, 1H), 1.28

(t, *J* = 7.0 Hz, 3H), 1.20 (ddd, *J* = 12.5, 9.0, 3.5 Hz, 1H), 1.07 (ddd, *J* = 12.0, 9.0, 3.5 Hz, 1H), 1.01 (s, 3H), 0.93 (s, 3H), 0.80 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 167.3, 153.3, 148.8, 141.9, 133.3, 133.03, 132.97, 128.0, 117.8, 59.5, 56.9, 55.8, 51.9, 31.5, 25.5, 23.9, 19.78, 19.76, 14.3, 13.7, 12.2; HR-EIMS Calcd for $C_{21}H_{30}O_2$ (M^+) 314.2246. Found 314.2242.

Ethyl (2*E*,4*E*,6*Z*)-7-(1,4-dioxaspiro[4.5]dec-7-en-8-yl)-3-methyl-2,4,6-octatrienoate (15c)

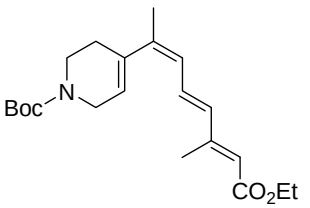


15c

According to Method A, **15c** (31.1 mg, 47%) was obtained from vinyl triflate **14c** (66.2 mg, 0.230 mmol), stannanyl ester **11** (98.0 mg, 0.209 mmol), $Pd_2(dba)_3{\cdot}CHCl_3$ (8.6 mg, 8.35 μmol), $AsPh_3$ (10.2 mg, 33.4 μmol) and CsF (63.4 mg, 0.418 mmol). Eluent: hexane/AcOEt = 10/1. Reaction time: 3.5 h.

15c: yellow oil; IR 2985, 2889, 1700, 1601, 1242, 1157 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.88 (dd, *J* = 15.6, 11.1 Hz, 1H), 6.16 (d, *J* = 15.6 Hz, 1H), 5.95 (d, *J* = 11.4 Hz, 1H), 5.72 (s, 1H), 5.42 (br s, 1H), 4.15 (q, *J* = 7.2 Hz, 2H), 2.34-2.18 (m, 2H), 2.27 (d, *J* = 1.2 Hz, 3H), 1.88 (s, 3H), 1.88-1.69 (m, 3H), 1.47-1.34 (m, 1H), 1.27 (t, *J* = 7.2 Hz, 3H), 1.12-0.99 (m, 1H), 0.96 (d, *J* = 7.2 Hz, 3H), 0.90 (d, *J* = 7.2 Hz, 3H), 0.67 (d, *J* = 6.6 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 167.3, 153.2, 145.5, 137.5, 133.3, 132.8, 126.0, 123.3, 117.9, 107.6, 64.4 (2C), 59.5, 35.8, 31.1, 27.1, 23.4, 14.3, 13.8; HR-EIMS Calcd for $C_{19}H_{26}O_4$ (M^+) 318.1831. Found 318.1831.

Ethyl (2*E*,4*E*,6*Z*)-7-(1-*tert*-butoxycarbonyl-5,6-dihydro-2*H*-pyridine-4-yl)-3-methyl-2,4,6-octatrienoate (15d)

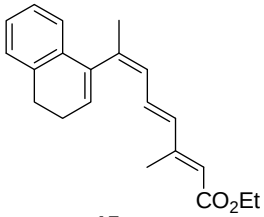


15d

According to Method A, **15d** (37.0 mg, 65%) was obtained from vinyl triflate **14d** (57.1 mg, 0.172 mmol), stannanyl ester **11** (73.5 mg, 0.157 mmol), $Pd_2(dba)_3{\cdot}CHCl_3$ (6.5 mg, 6.27 μmol), $AsPh_3$ (7.7 mg, 25.1 μmol) and CsF (47.6 mg, 0.313 mmol). Eluent: hexane/AcOEt = 10/1. Reaction time: 3.5 h.

15d: yellow oil; IR 2982, 2933, 1689, 1602, 1241, 1159 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.81 (dd, *J* = 15.0, 11.0 Hz, 1H), 6.17 (d, *J* = 15.0 Hz, 1H), 5.98 (d, *J* = 11.0 Hz, 1H), 5.72 (s, 1H), 5.53 (br s, 1H), 4.15 (q, *J* = 7.0 Hz, 2H), 3.99 (br d, *J* = 2.5 Hz, 2H), 3.54 (br t, *J* = 5.0 Hz, 2H), 2.25 (s, 3H), 2.20 (br s, 2H), 1.89 (s, 3H), 1.47 (s, 9H), 1.27 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 167.3, 155.1, 152.9, 144.0, 136.8, 134.3, 132.1, 126.6, 123.2, 118.6, 79.9, 59.8, 43.5, 40.8, 28.7 (3C), 28.1, 23.4, 14.6, 14.1; HR-EIMS Calcd for $C_{21}H_{31}N_1O_4$ (M^+) 361.2253. Found 361.2256.

Ethyl (2*E*,4*E*,6*Z*)-7-(3,4-dihydronaphthalen-1-yl)-3-methyl-2,4,6-octatrienoate (15e)



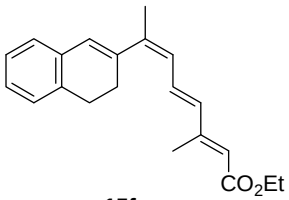
15e

According to Method B, **15e** (160 mg, 88%) was obtained from vinyl triflate **14e** (163 mg, 0.586 mmol), stannanyl ester **11** (357 mg, 0.762 mmol), CsF

(178 mg, 1.17 mmol), $Pd(PPh_3)_4$ (67.7 mg, 58.6 μmol) and CuI (22.3 mg, 0.117 mmol). Eluent: hexane/Et_2O = 30/1. Reaction time: 1.5 h.

15e: yellow oil; IR 2940, 2834, 1700, 1603, 1242, 1157 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.18-7.15 (m, 3H), 6.99 (br t, *J* = 4.2 Hz, 1H), 6.66 (dd, *J* = 15.3, 10.8 Hz, 1H), 6.28 (d, *J* = 10.8 Hz, 1H), 6.22 (d, *J* = 15.3 Hz, 1H), 5.89 (td, *J* = 4.2, 1.5 Hz, 1H), 5.74 (s, 1H), 4.16 (qd, *J* = 7.2, 1.5 Hz, 2H), 2.82 (br d, *J* = 7.8 Hz, 2H), 2.39 (br q, *J* = 7.8 Hz, 2H), 2.15 (br q, *J* = 1.2 Hz, 3H), 2.02 (s, 3H), 1.28 (td, *J* = 7.2, 1.5 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 167.1, 152.9, 143.0, 138.6, 136.3, 133.8, 133.7, 132.5, 128.6, 127.6, 127.1 (2C), 126.5, 124.5, 118.2, 59.5, 28.0, 24.7, 22.9, 14.3, 13.7; HR-EIMS Calcd for $C_{21}H_{24}O_2$ (M^+) 308.1776. Found 308.1789.

Ethyl (2*E*,4*E*,6*Z*)-7-(3,4-dihydronaphthalen-2-yl)-3-methyl-2,4,6-octatrienoate (15f)

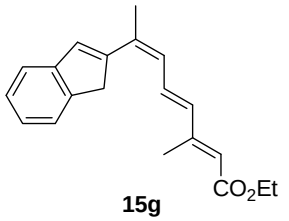


15f

According to Method B, **15f** (50.2 mg, 65%) was obtained from vinyl triflate **14f** (70.0 mg, 0.252 mmol), stannanyl ester **11** (153 mg, 0.327 mmol), CsF (76.4 mg, 0.503 mmol), $Pd(PPh_3)_4$ (29.1 mg, 25.2 μmol), and CuI (9.6 mg, 50.3 μmol). Eluent: hexane/Et_2O = 30/1. Reaction time: 1.5 h.

15f: yellow oil; IR 2939, 2892, 1698, 1605, 1239, 1154 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.20-7.13 (m, 3H), 7.08-7.04 (m, 1H), 7.00 (dd, *J* = 15.3, 11.1 Hz, 1H), 6.40 (s, 1H), 6.24 (d, *J* = 15.3 Hz, 1H), 6.09 (d, *J* = 11.1 Hz, 1H), 5.75 (s, 1H), 4.16 (q, *J* = 7.2 Hz, 2H), 2.89 (br t, *J* = 7.8 Hz, 2H), 2.46-2.37 (m, 2H), 2.24 (d, *J* = 0.9 Hz, 3H), 1.99 (s, 3H), 1.28 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 167.2, 153.0, 143.9, 139.8, 134.9, 134.09, 134.06, 132.5, 127.3, 127.2, 127.0, 126.9, 126.7, 126.4, 118.2, 59.6, 28.0, 26.8, 22.8, 14.3, 13.9; HR-EIMS Calcd for $C_{21}H_{24}O_2$ (M^+) 308.1776. Found 308.1751.

Ethyl (2*E*,4*E*,6*Z*)-7-(2-indenyl)-3-methyl-2,4,6-octatrienoate (15g)

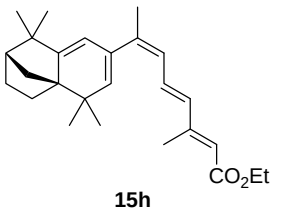


15g

According to Method B, **15g** (32.9 mg, 59%) was obtained from vinyl triflate **14g** (50.2 mg, 0.190 mmol), stannanyl ester **11** (116 mg, 0.247 mmol), CsF (57.7 mg, 0.380 mmol), $Pd(PPh_3)_4$ (22.0 mg, 19.0 μmol), and CuI (7.2 mg, 38.0 μmol). Eluent: hexane/Et_2O = 35/1. Reaction time: 1.5 h.

15g: yellow oil; IR 3011, 2984, 1699, 1604, 1243, 1157 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.48 (d, *J* = 6.6 Hz, 1H), 7.41 (m, *J* = 7.2 Hz, 1H), 7.32-7.18 (m, 3H), 6.94 (s, 1H), 6.31 (d, *J* = 15.0 Hz, 1H), 6.21 (d, *J* = 11.4 Hz, 1H), 5.80 (s, 1H), 4.18 (q, *J* = 7.2 Hz, 2H), 3.69 (s, 2H), 2.36 (d, *J* = 0.9 Hz, 3H), 2.15 (s, 3H), 1.30 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 167.1, 152.6, 145.0, 144.1, 143.4, 136.3, 135.9, 131.9 (2C), 128.5, 126.7, 125.2, 123.6, 121.3, 118.9, 59.6, 41.0, 24.5, 14.3, 14.0; HR-EIMS Calcd for $C_{20}H_{22}O_2$ (M^+) 294.1616. Found 294.1618.

Ethyl (2*E*,4*E*,6*Z*)-7-[(2*S*,4*aR*)-1,2,3,4,4a,5-hexahydro-1,1,5,5-tetramethyl-2,4a-methanonaphthalen-7-yl]-3-methyl-2,4,6-octatrienoate



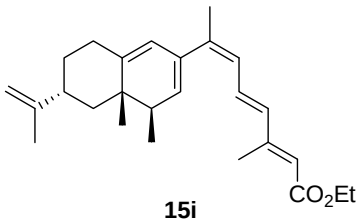
15h

(15h)

According to Method A, **15h** (42.3 mg, 75%) was obtained from vinyl triflate **14h** (56.9 mg, 0.162 mmol), stannanyl ester **11** (69.3 mg, 0.148 mmol), $Pd_2(dba)_3{\cdot}CHCl_3$ (6.1 mg, 5.91 μmol), $AsPh_3$ (7.2 mg, 23.6 μmol) and CsF (44.9 mg, 0.295 mmol). Eluent: hexane/Et_2O = 40/1. Reaction time: 3 h.

15h: yellow oil; $[\alpha]_D^{27}$ -164 (*c* 1.04, MeOH); IR 2961, 2868, 1698, 1603, 1242, 1157 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 6.90 (dd, *J* = 15.3, 11.1 Hz, 1H), 6.14 (d, *J* = 15.3 Hz, 1H), 6.00 (d, *J* = 11.1 Hz, 1H), 5.72 (s, 1H), 5.42 (d, *J* = 0.6 Hz, 1H), 5.11 (d, *J* = 1.2 Hz, 1H), 4.15 (q, *J* = 7.2 Hz, 2H), 2.24 (d, *J* = 0.9 Hz, 3H), 1.95-1.89 (m, 1H), 1.93 (s, 3H), 1.79-1.75 (m, 1H), 1.70-1.62 (m, 2H), 1.54-1.46 (m, 1H), 1.30-1.25 (m, 4H), 1.16-1.06 (m, 1H), 1.13 (s, 3H), 1.09 (s, 3H), 1.04 (s, 3H), 0.97 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 167.3, 159.0, 153.2, 144.7, 134.0, 133.44, 133.40, 132.6, 126.0, 117.8, 111.1, 59.5, 56.0, 46.6, 43.2, 35.8, 33.7, 28.9, 27.5, 24.9, 24.8, 24.3, 24.2, 24.0, 14.3, 13.6; *Anal*. Calcd for $C_{26}H_{36}O_2$: C, 82.06; H, 9.53. Found: C, 81.80; H, 9.70; HR-EIMS Calcd for $C_{26}H_{36}O_2$ (M^+) 380.2715. Found 380.2727.

Ethyl (2*E*,4*E*,6*Z*)-7-[(4*R*,4*aS*,6*R*)-4,4a,5,6,7,8-hexahydro-4,4a-dimethyl-6-(1-methylethenyl)-naphthalen-2-yl]-3-methyl-2,4,6-octatrienoate (15i)

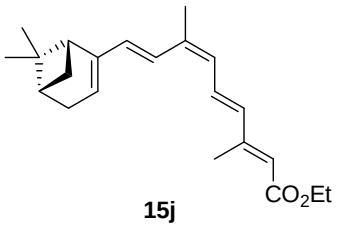


15i

According to Method B, **15i** (72.3 mg, 84%) was obtained from vinyl triflate **14i** (79.0 mg, 0.225 mmol), stannanyl ester **11** (138 mg, 0.293 mmol), CsF (68.5 mg, 0.451 mmol), $Pd(PPh_3)_4$ (26.1 mg, 22.6 μmol) and CuI (8.6 mg, 45.1 μmol). Eluent: hexane/Et_2O = 40/1. Reaction time: 1.5 h.

15i: yellow oil; $[\alpha]_D^{25}$ +81.9 (*c* 1.44, MeOH); IR 2966, 2933, 1698, 1601, 1242, 1157 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 6.89 (dd, *J* = 15.5, 11.0 Hz, 1H), 6.13 (d, *J* = 15.5 Hz, 1H), 5.99 (d, *J* = 11.0 Hz, 1H), 5.70 (s, 1H), 6.58 (br s, 1H), 5.23 (br s, 1H), 4.71 (s, 2H), 4.13 (q, *J* = 7.0 Hz, 2H), 2.37 (br td, *J* = 7.5, 2.5 Hz, 1H), 2.32 (br t, *J* = 2.5 Hz, 2H), 2.22 (s, 3H), 2.16 (br tt, *J* = 12.5, 2.5 Hz, 1H), 1.93-1.90 (m, 1H), 1.91 (s, 3H), 1.80 (br dq, *J* = 12.5, 2.5 Hz, 1H), 1.73 (s, 3H), 1.29-1.24 (m, 1H), 1.26 (t, *J* = 7.0 Hz, 3H), 1.15 (t, *J* = 12.5 Hz, 1H), 1.03 (d, *J* = 7.5 Hz, 3H), 0.87 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 167.2, 153.1, 150.2, 146.1, 143.4, 135.3, 133.1, 132.9, 129.7, 126.2, 119.8, 118.0, 108.6, 59.5, 45.7, 42.2, 41.4, 38.4, 31.6, 31.4, 23.8, 20.9, 14.3 (2C), 13.64, 13.60; HR-EIMS Calcd for $C_{26}H_{36}O_2$ (M^+) 380.2715. Found 380.2707.

Ethyl (2*E*,4*E*,6*Z*,8*E*)-3,7-dimethyl-9-[(1*R*)-6,6-dimethylbicyclo-[3,1,1]hept-2-ene-2-yl]-2,4,6,8-nonatetraenoate (15j)



15j

According to Method B, **15j** (36.4 mg, 29%) was obtained from vinyl triflate **14j** (114 mg, 0.385 mmol), stannanyl ester **11** (235 mg, 0.500 mmol), CsF (117 mg, 0.769 mmol), $Pd(PPh_3)_4$ (44.5 mg, 38.5 μmol) and CuI (14.7 mg, 77.0 μmol). Eluent: hexane/Et_2O = 40/1. Reaction time: 15 h.

15j: yellow oil; $[\alpha]_D^{25}$ +117 (*c* 1.56, MeOH); IR 2983, 2929, 1701, 1608, 1242, 1158 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.10 (dd, *J* = 15.0, 11.4 Hz, 1H), 6.71 (d, *J* = 15.9 Hz, 1H), 6.39 (d, *J* = 15.6 Hz, 1H), 6.12 (d, *J* = 15.0 Hz, 1H), 6.05 (d, *J* = 11.4 Hz, 1H) 5.77 (s, 1H), 5.73 (br s, 1H), 4.17 (q, *J* = 7.2 Hz, 2H), 2.67 (br t, *J* = 5.4 Hz, 1H), 2.53-2.47 (m, 1H), 2.42-2.34 (m, 1H), 2.38 (s, 3H), 2.15 (br s, 1H), 1.98 (s, 3H), 1.38 (s, 3H), 1.37-1.25 (m, 1H), 1.29 (t, *J* = 7.2 Hz, 3H), 1.17 (d, *J* = 8.7 Hz, 1H), 0.82 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 167.2, 152.7, 146.9, 138.2, 134.6, 132.4, 129.6, 128.7, 127.3, 120.9, 118.6, 59.6, 41.1, 40.9, 37.9, 32.3, 31.4, 26.4, 21.1, 20.9, 14.3, 13.9; HR-EIMS Calcd for $C_{22}H_{30}O_2$ (M^+) 326.2246. Found 326.2226.

References

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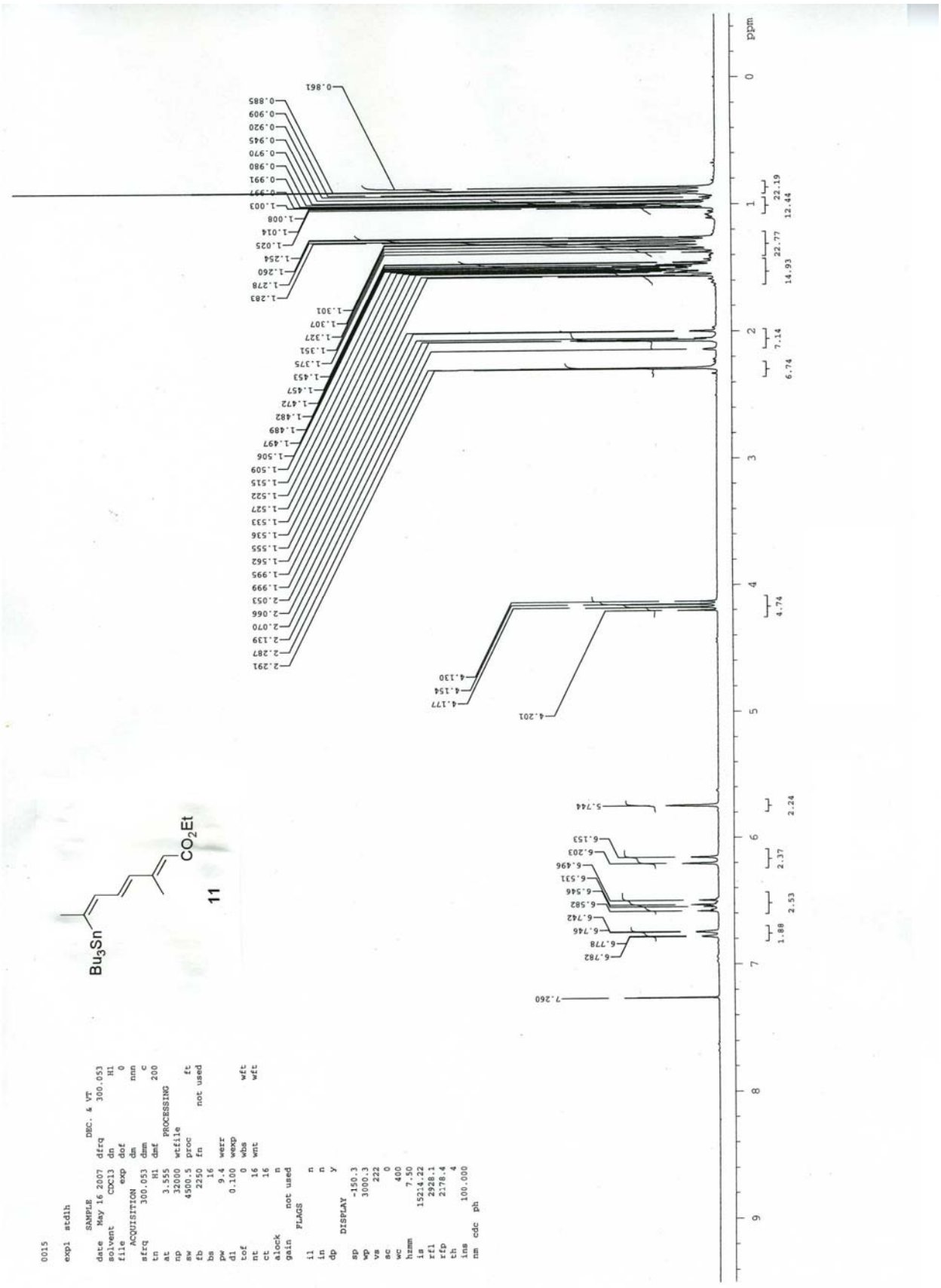


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N-712
C-13

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file          exp   spin        16        np         79298  FLAGS
                    hat          0.008     fb         17000  il          n
ACQUISITION                              bs            32  in          n
                                         d1         1.000  dp          y
                                         nt          2200  hs          nn
                                         ct           352  PROCESSING
TRANSMITTER                                   lb          1.00
tn          C13  fn      not used
sfrq    125.670  DISPLAY
tof      1285.1  sp         -0.3
tpwr         54  wp      25130.9
pw        4.450  rf1     11727.9
DECOUPLER        rfp      9675.6
dn          H1   rp         72.1
dof          0   lp         17.7
dm          yyy  PLOT
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dmf       12338  vs         6222
                 th           62
                 al  cdc  ph
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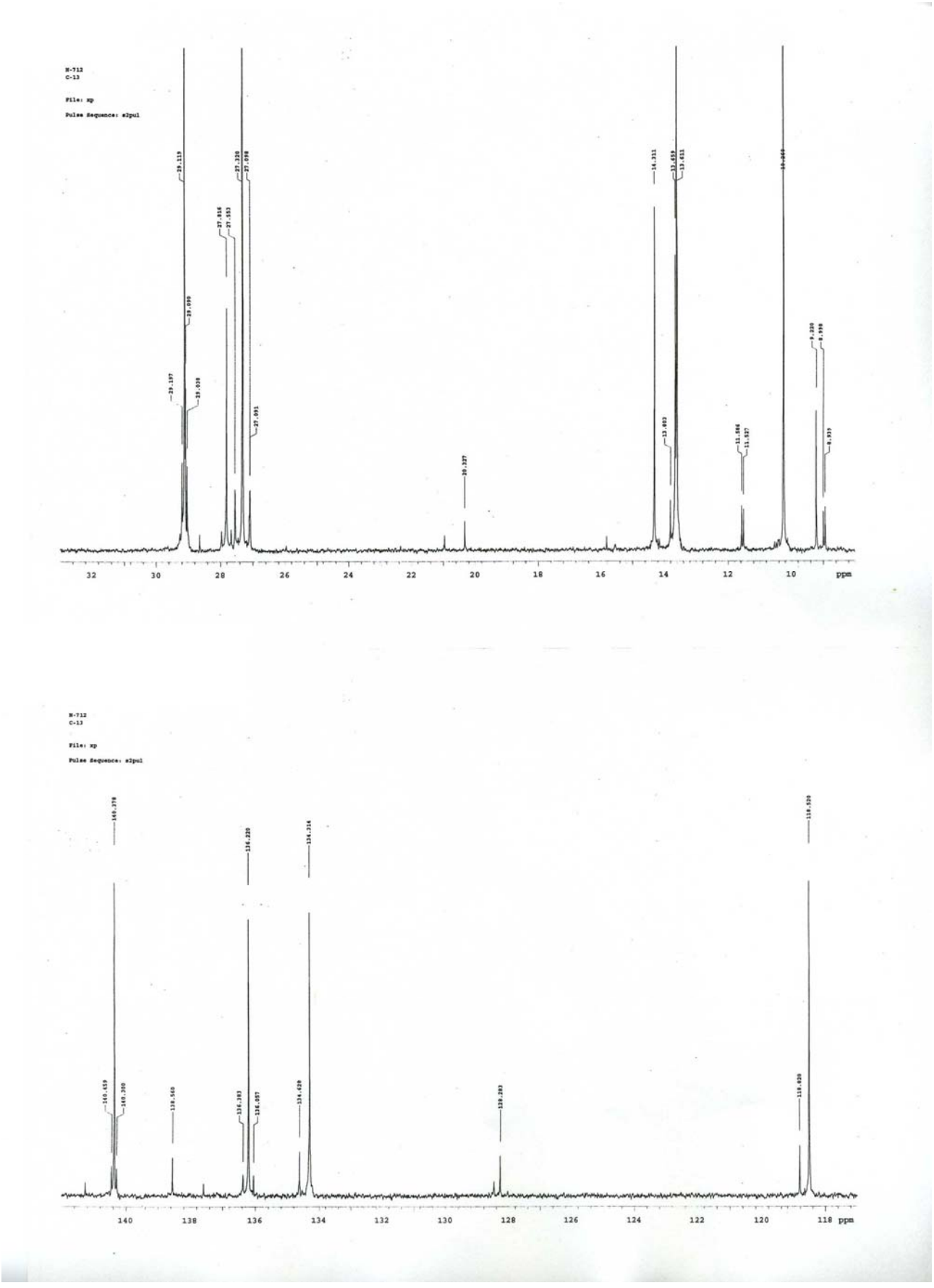

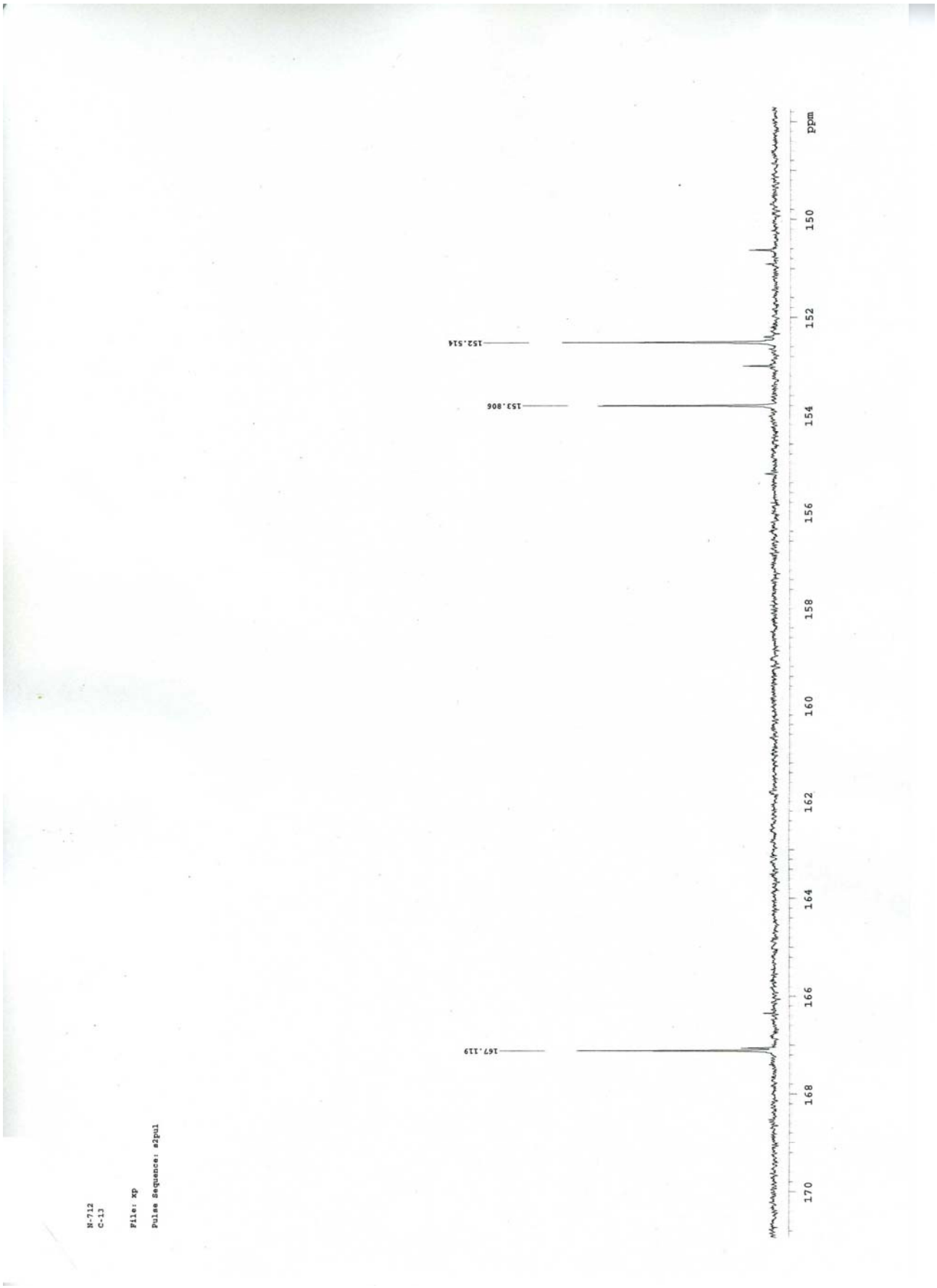

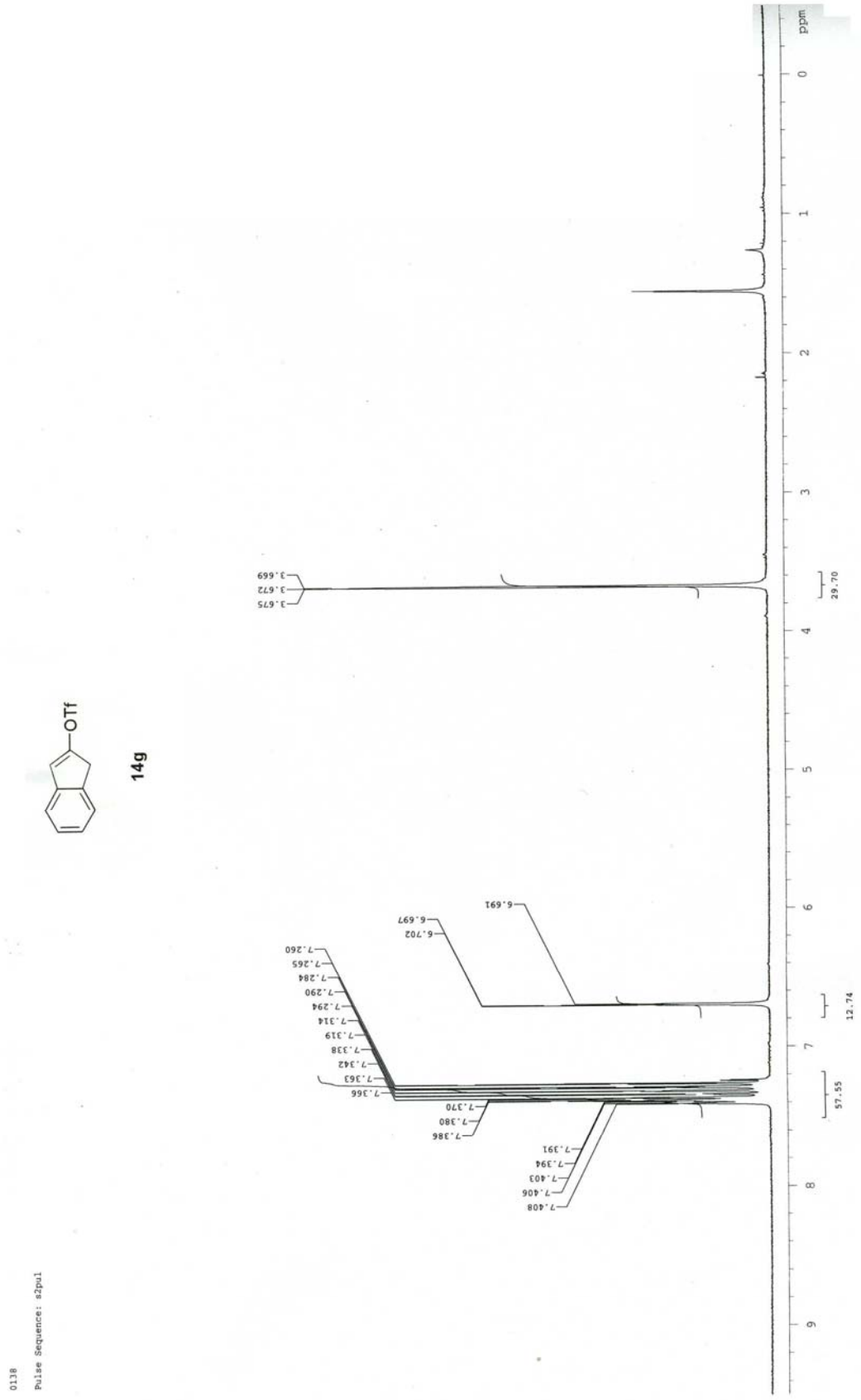

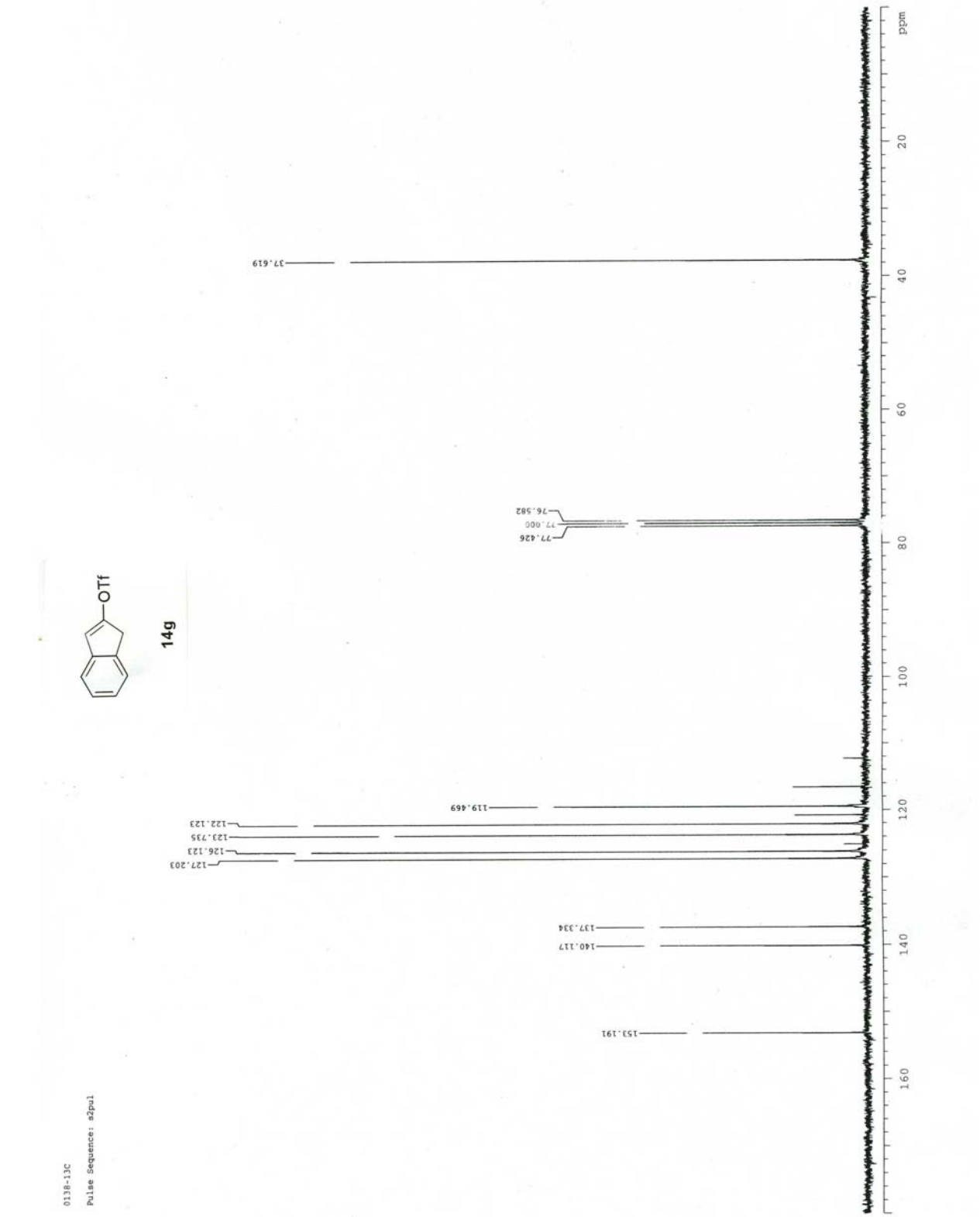

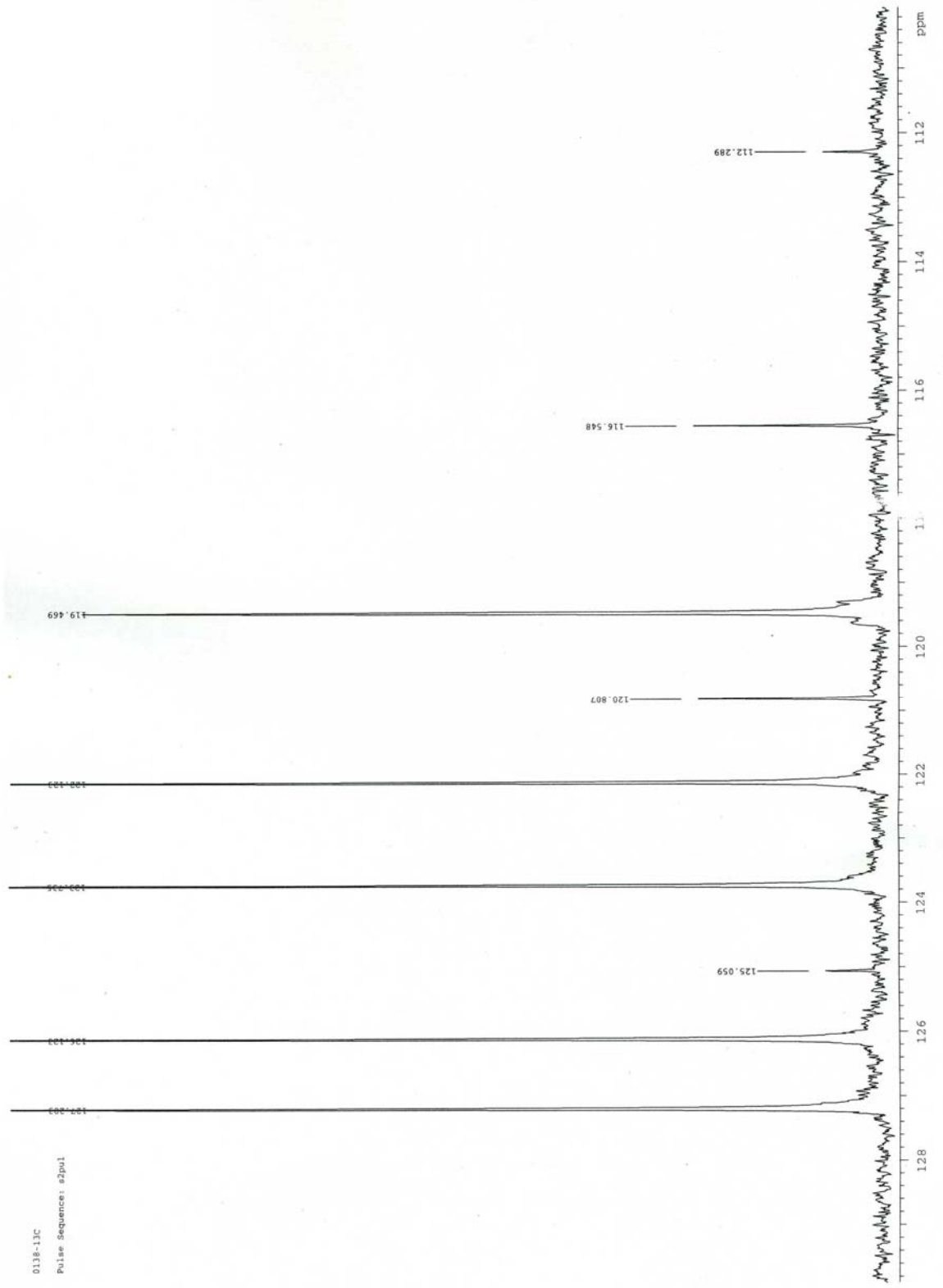

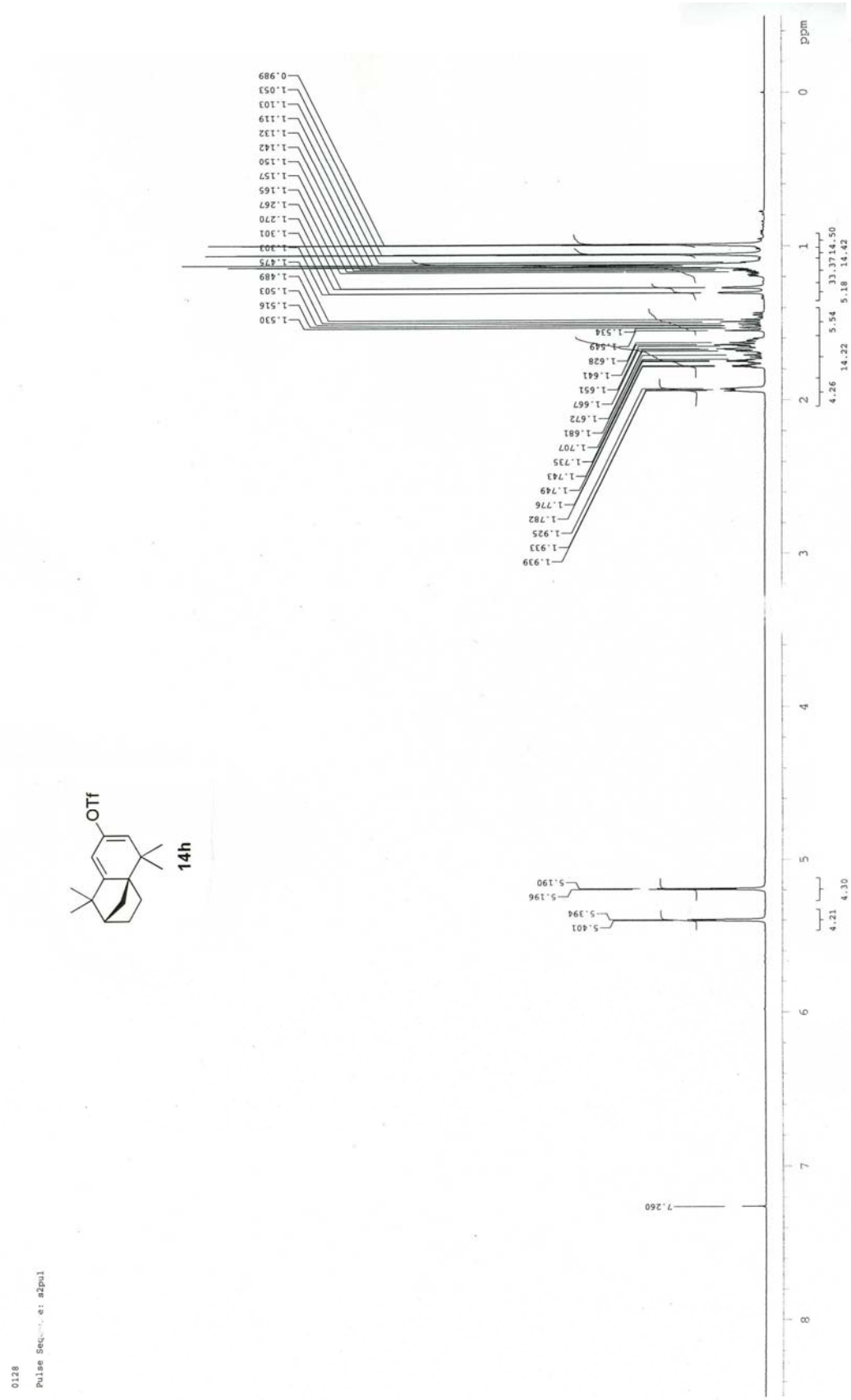

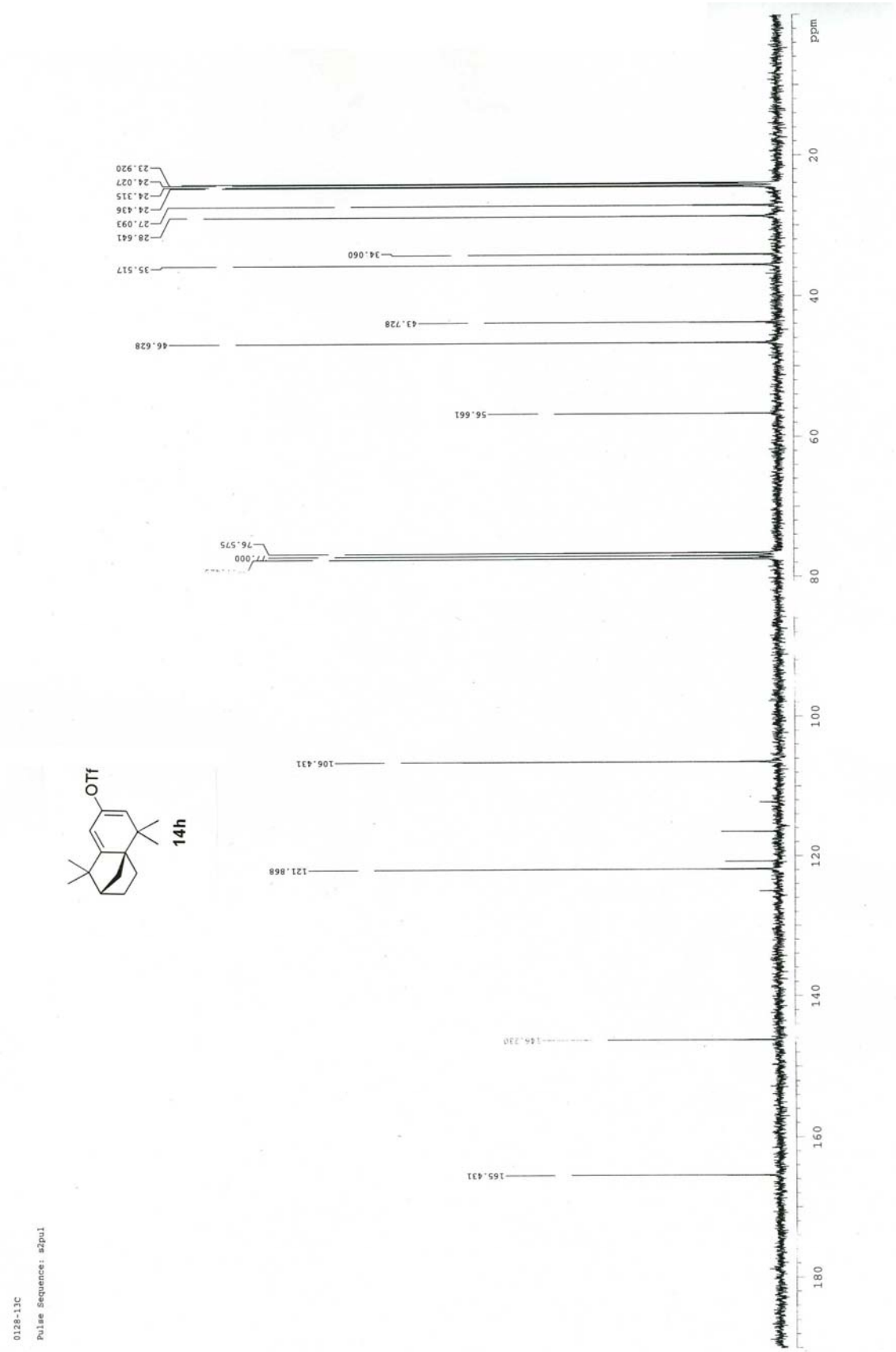

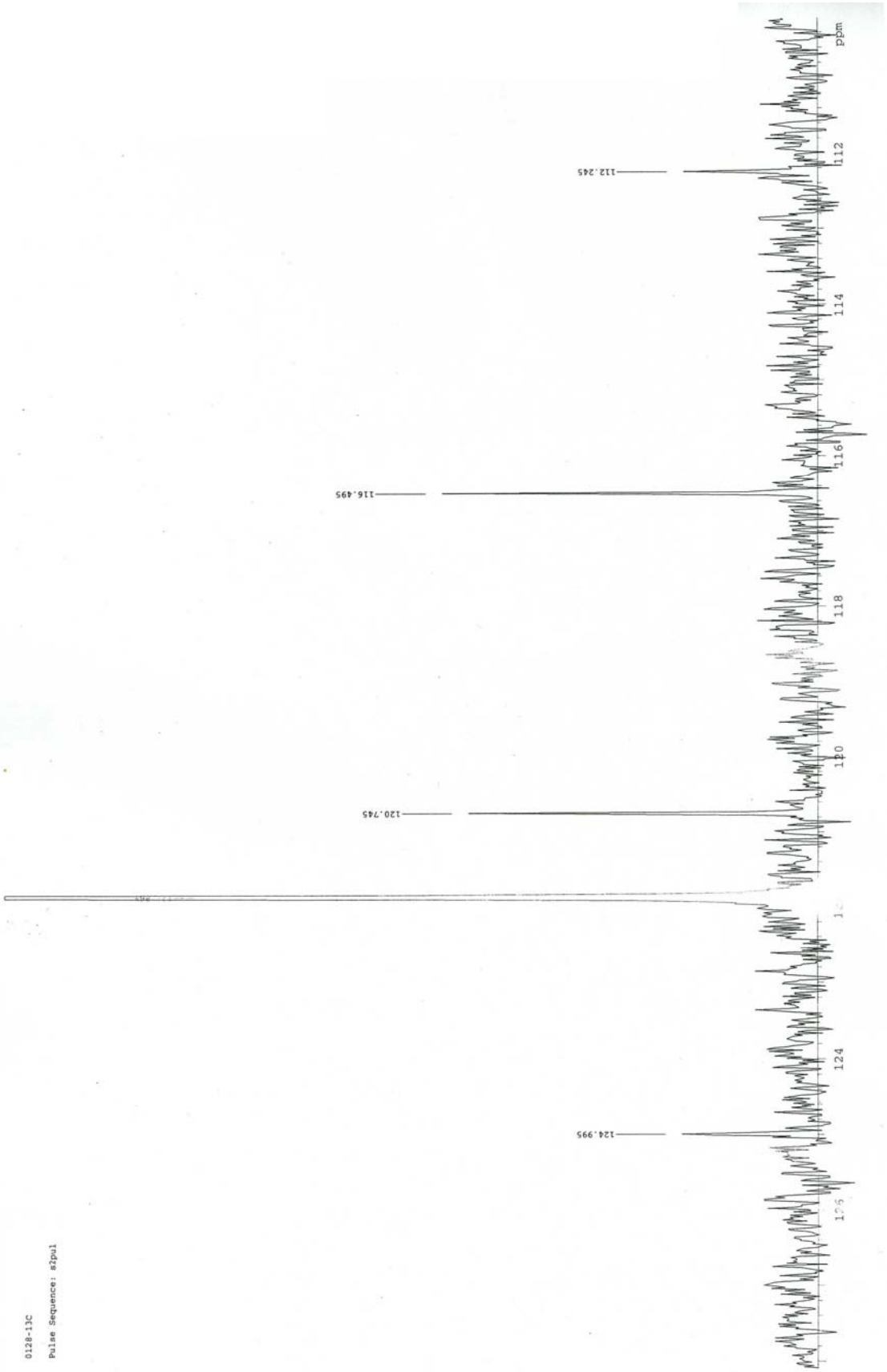

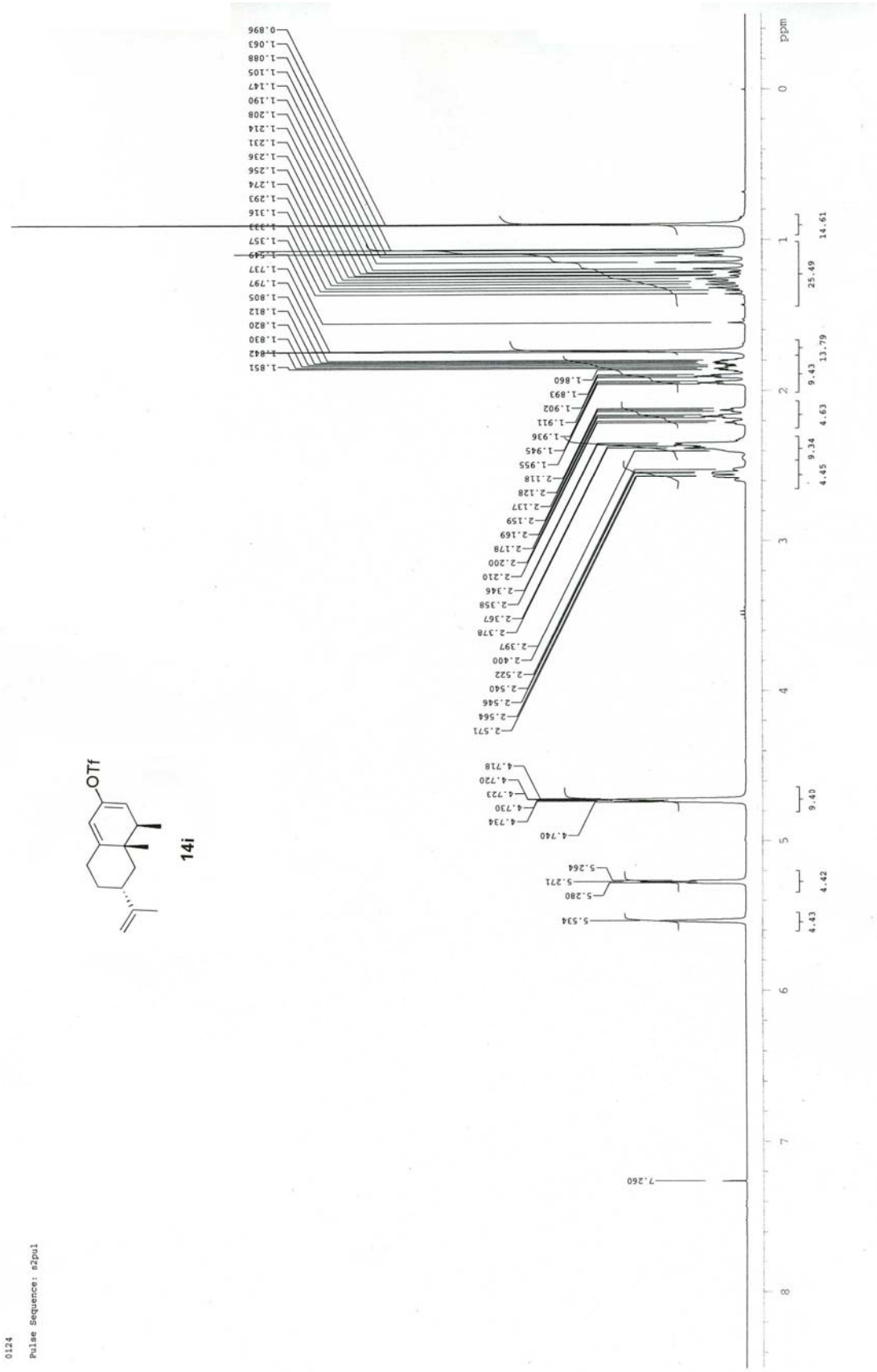

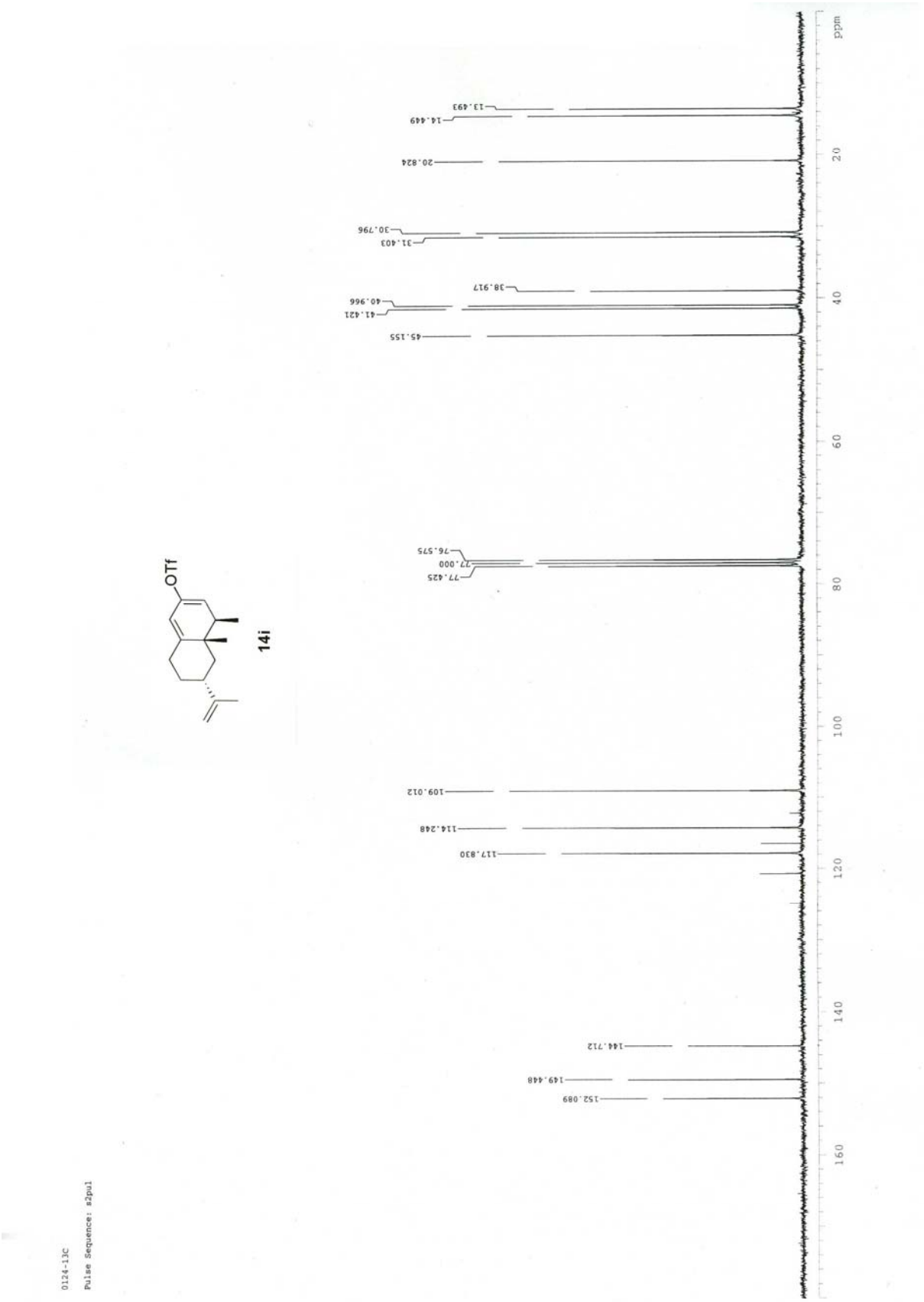

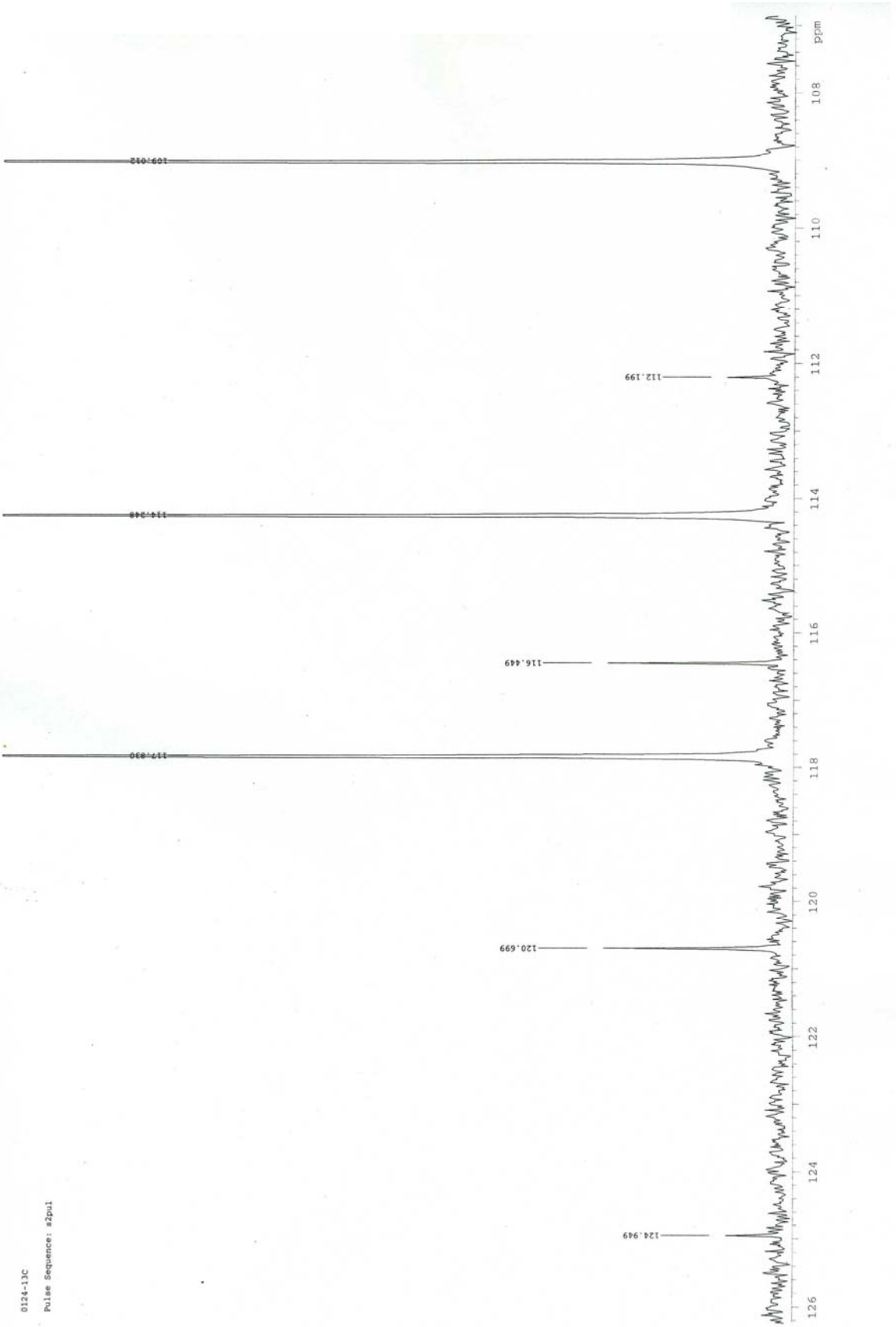

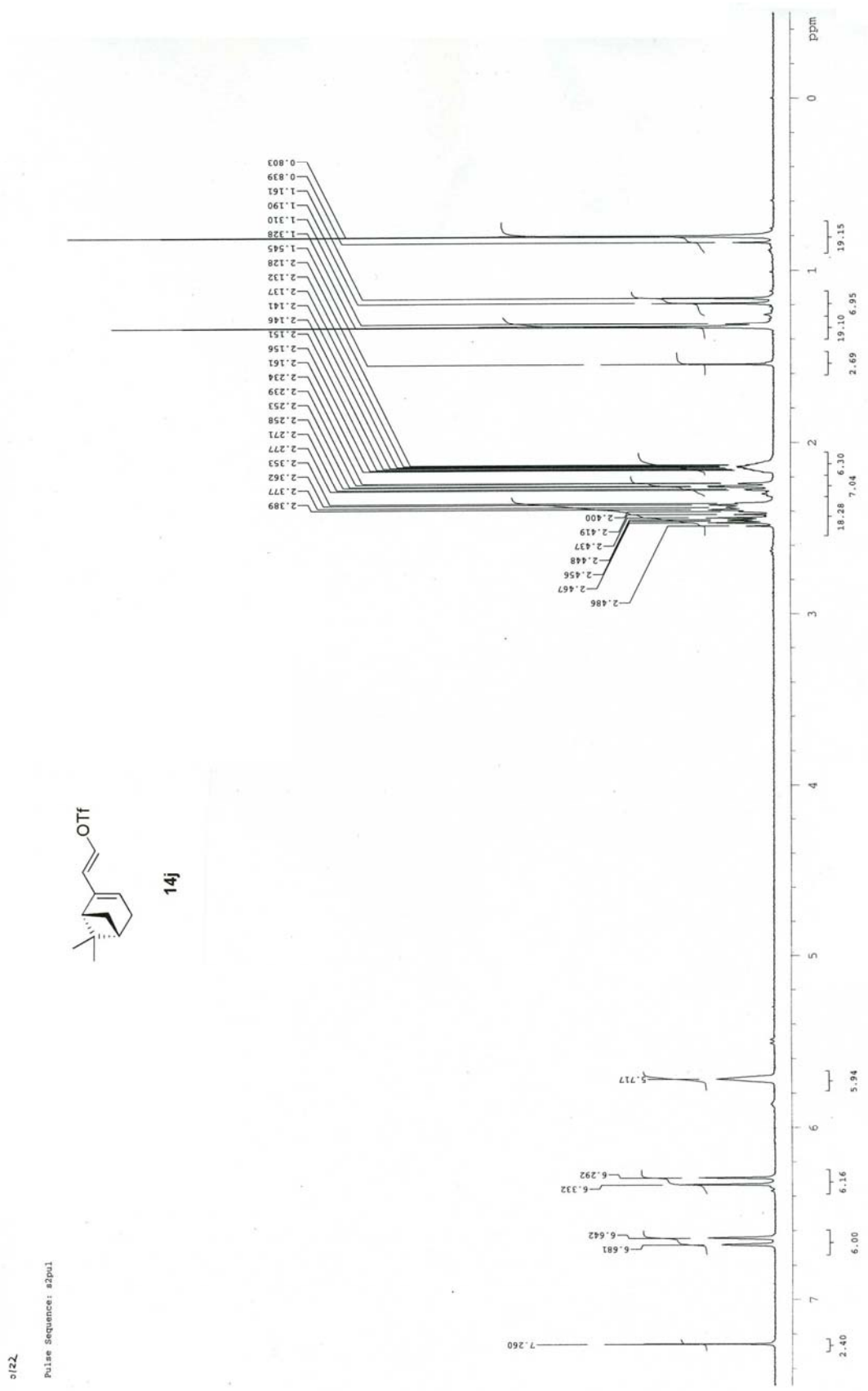

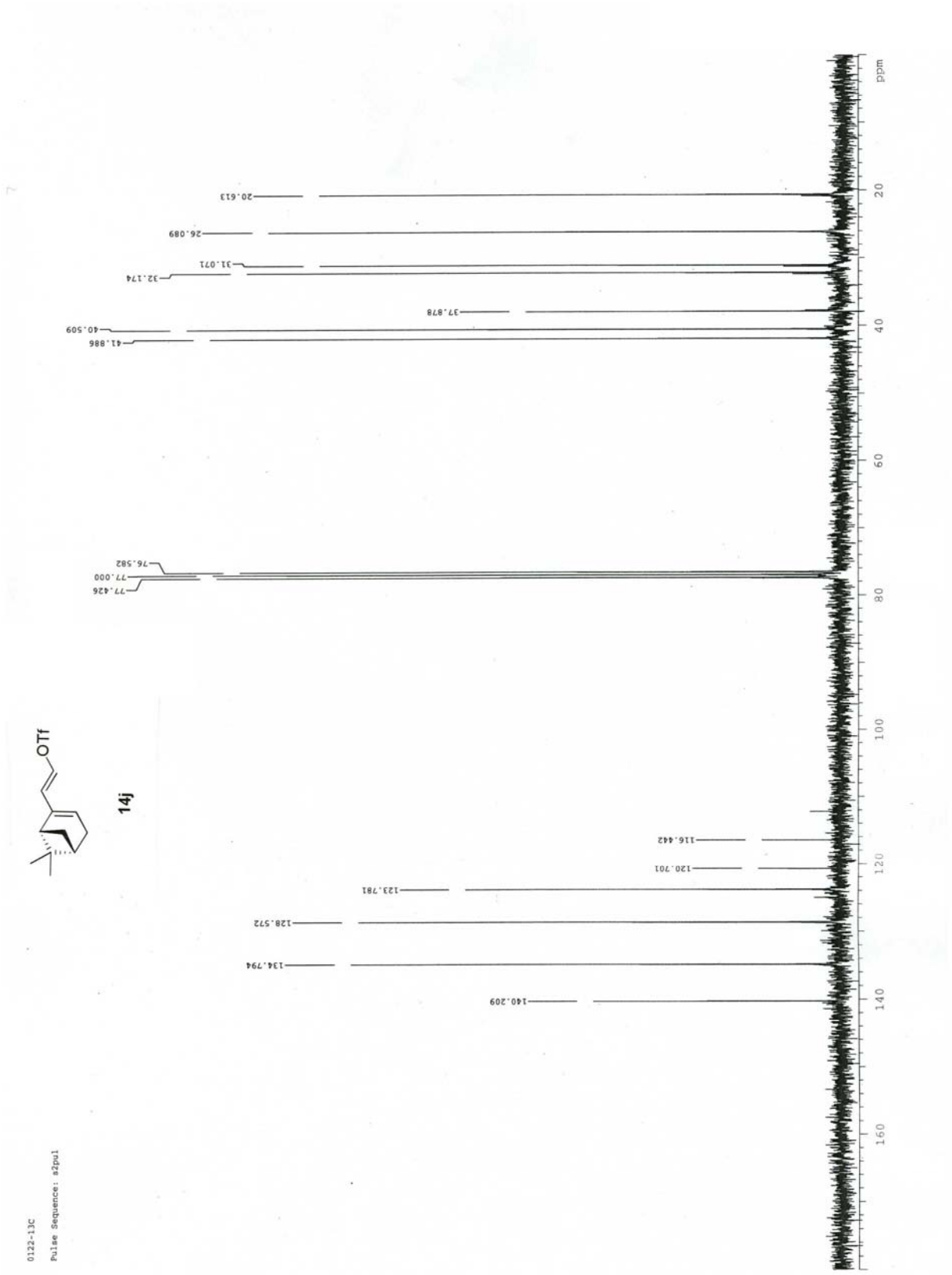

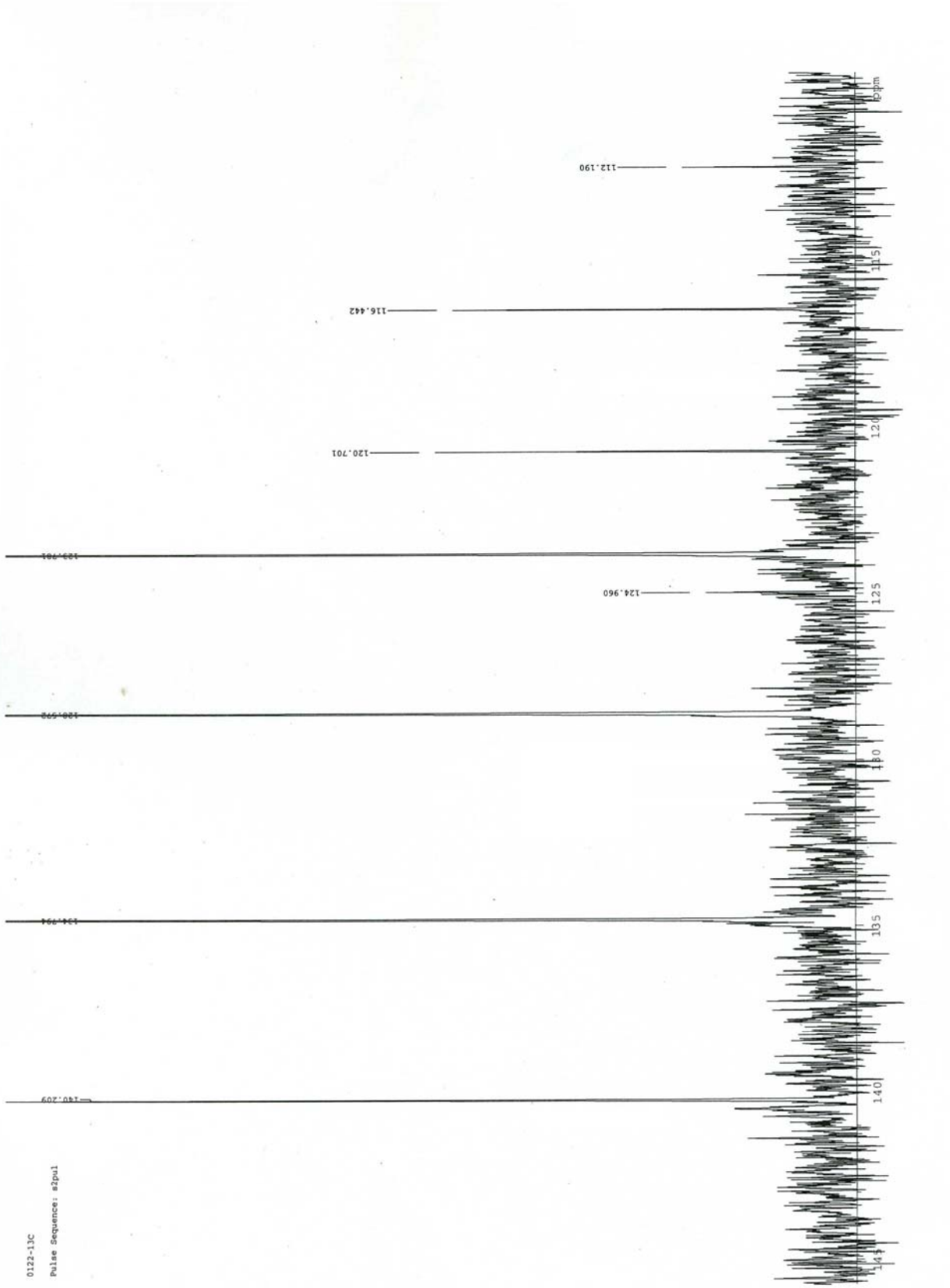

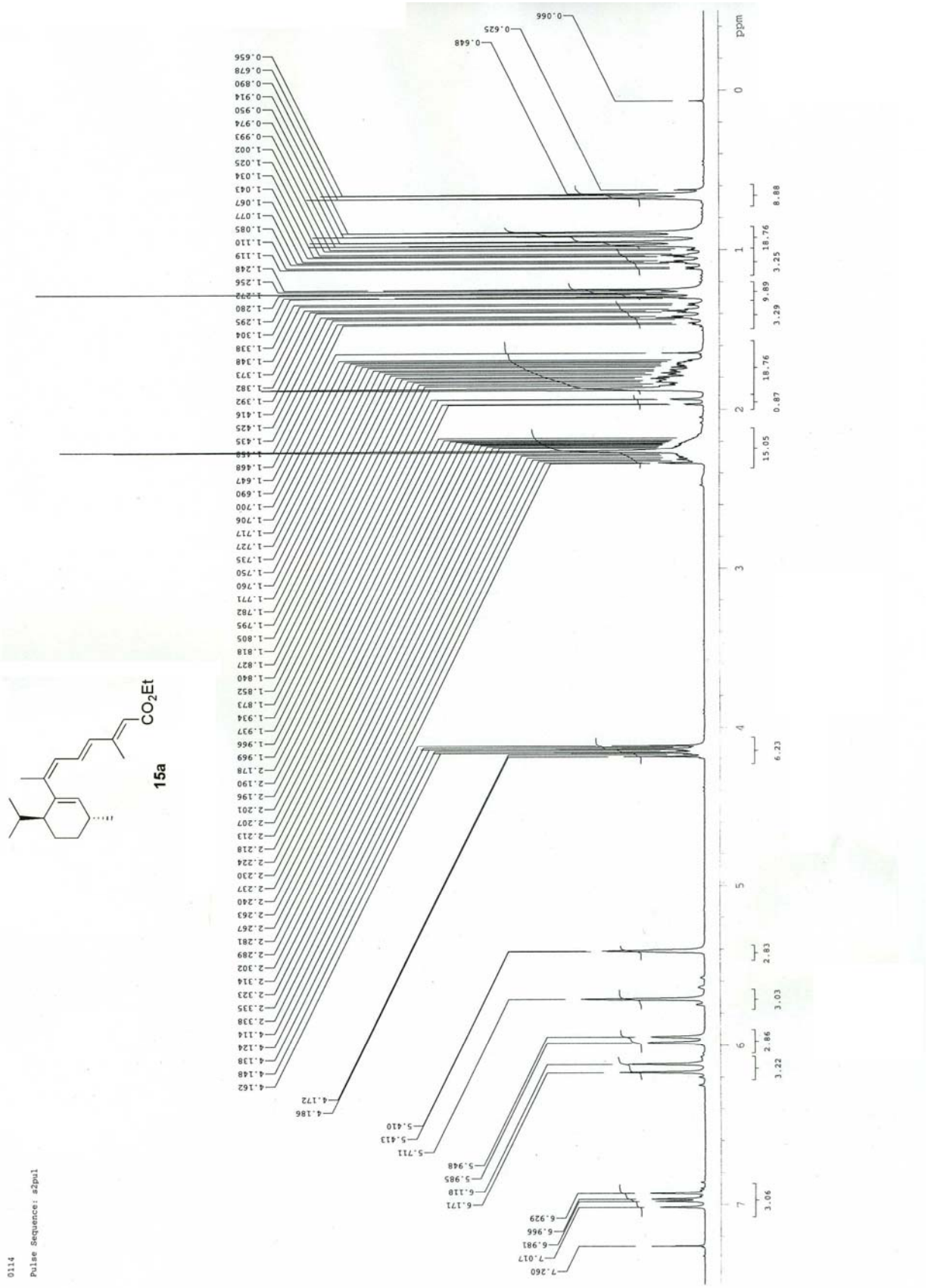

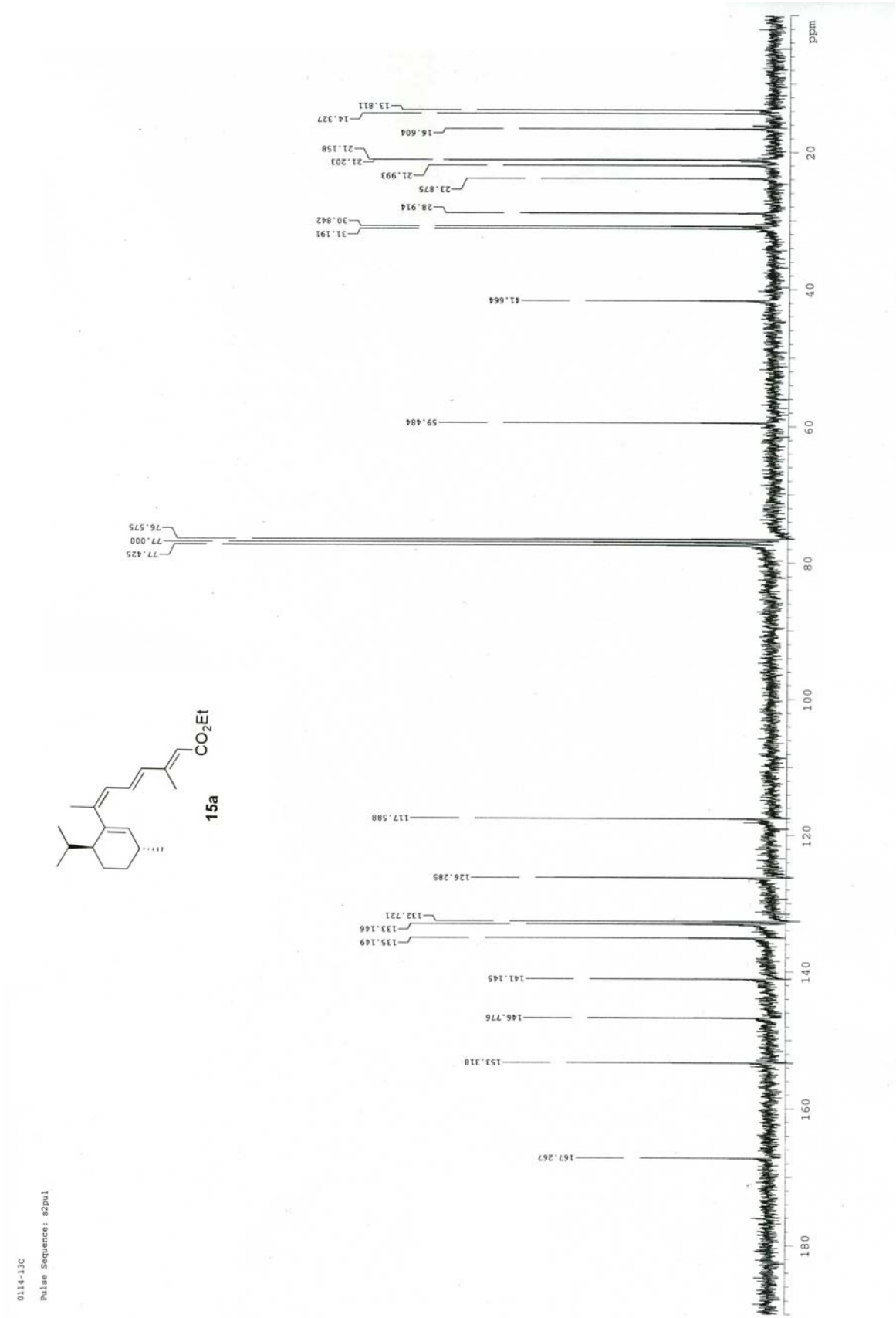

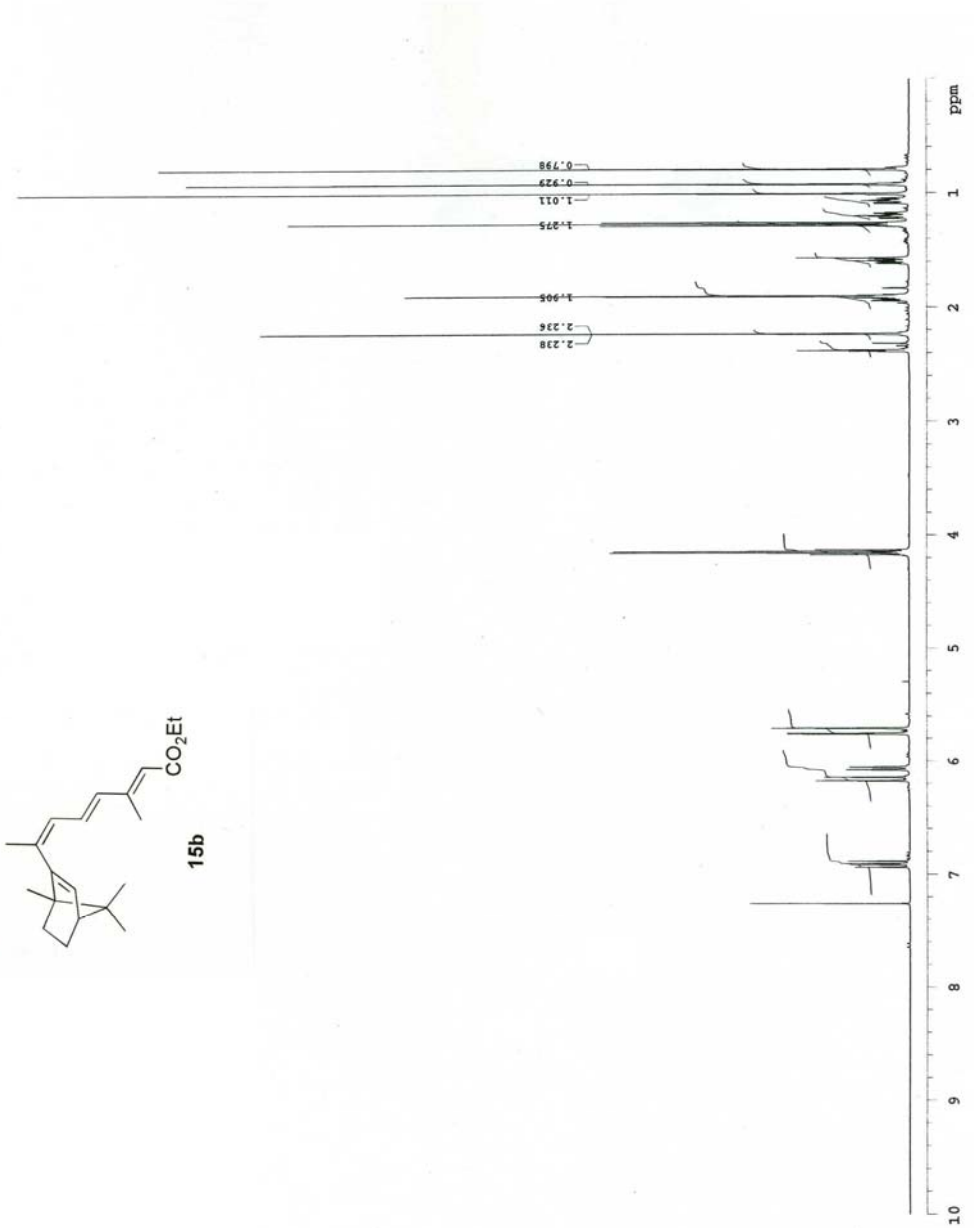


```
N-693
H-1

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        at         3.500  alfa       10.000
        np         56090         FLAGS
        fb          4000  il              n
        hs            32  in              n
        d1         1.500  dp              y
        nt             4  hs             nn
        ct             4         PROCESSING
     TRANSMITTER     H1  lb          0.30
        tn                   fn    not used
      sfrq       499.737         DISPLAY
       tof          499.7  sp           -0.0
      tpwr             59  wp         4997.3
        pw          5.600  rf1        4641.9
       DECOUPLER          rfp        3628.1
        dn             C13  rp          -52.0
       dof               0  lp           7.3
        dm             nnn         PLOT
       dmm               c  wc            270
      dpwr              41  sc              0
       daf           24000  vs            284
                            th             96
                                ai  cdc  ph
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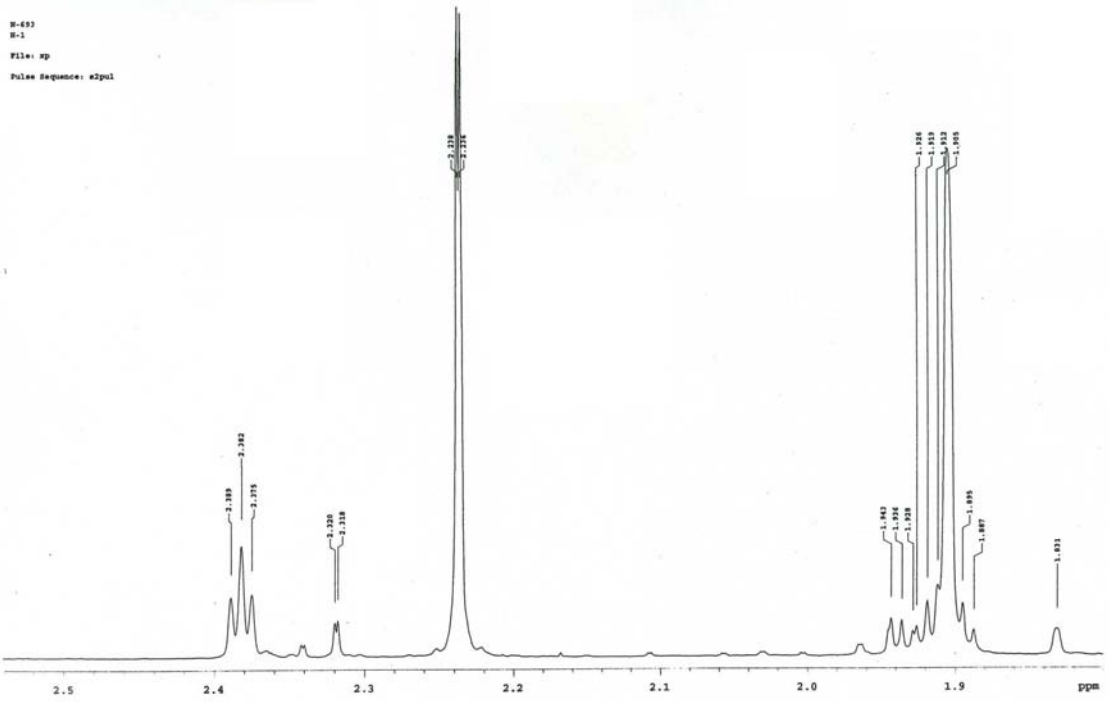

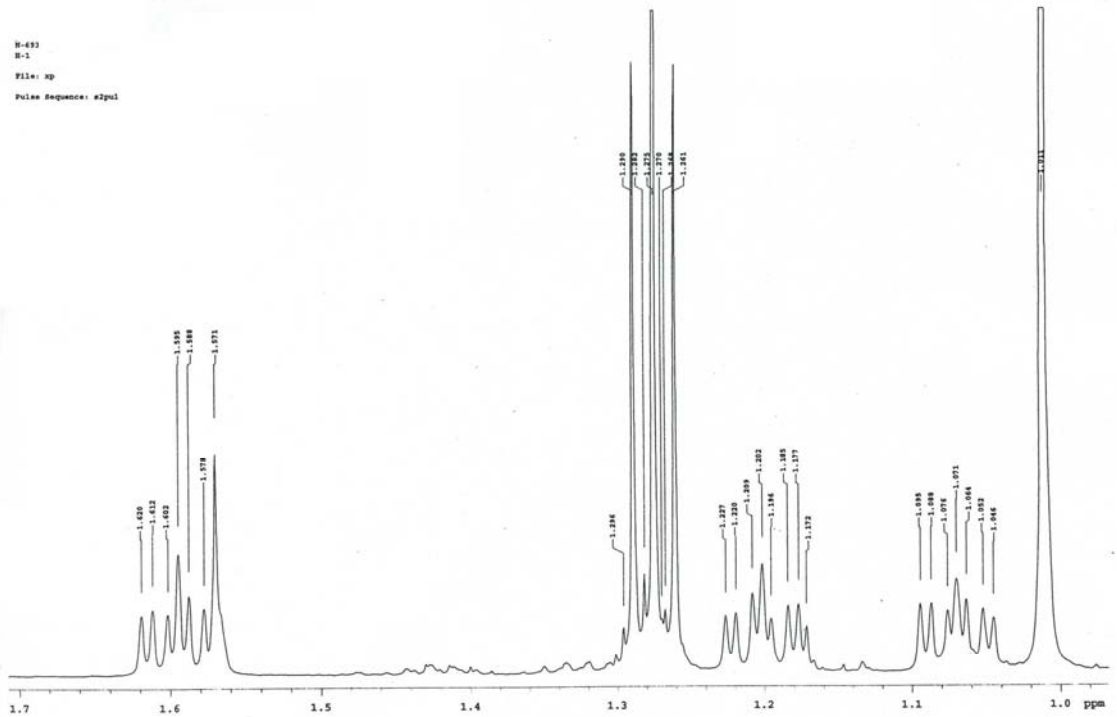

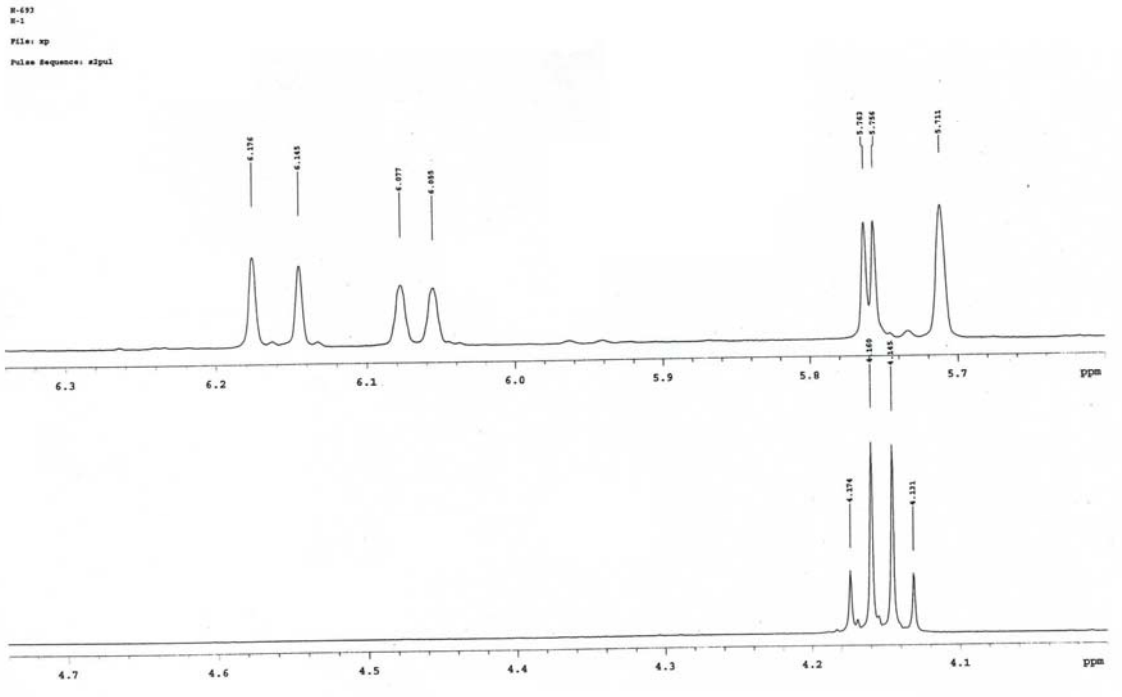

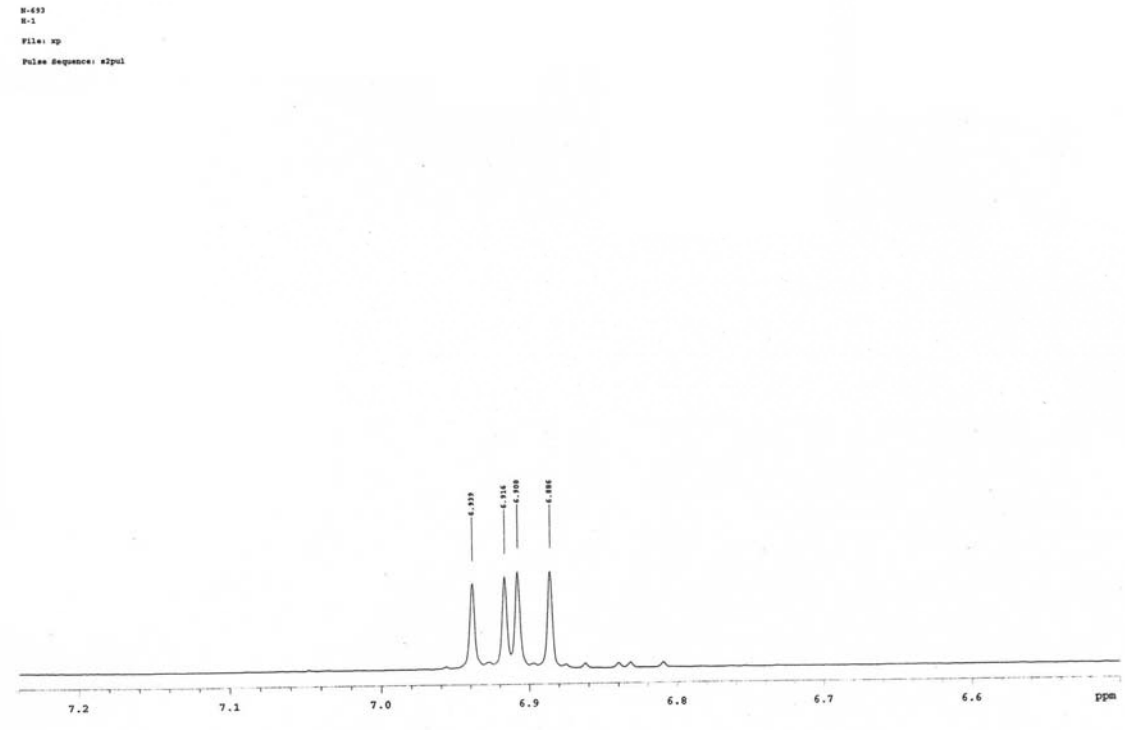

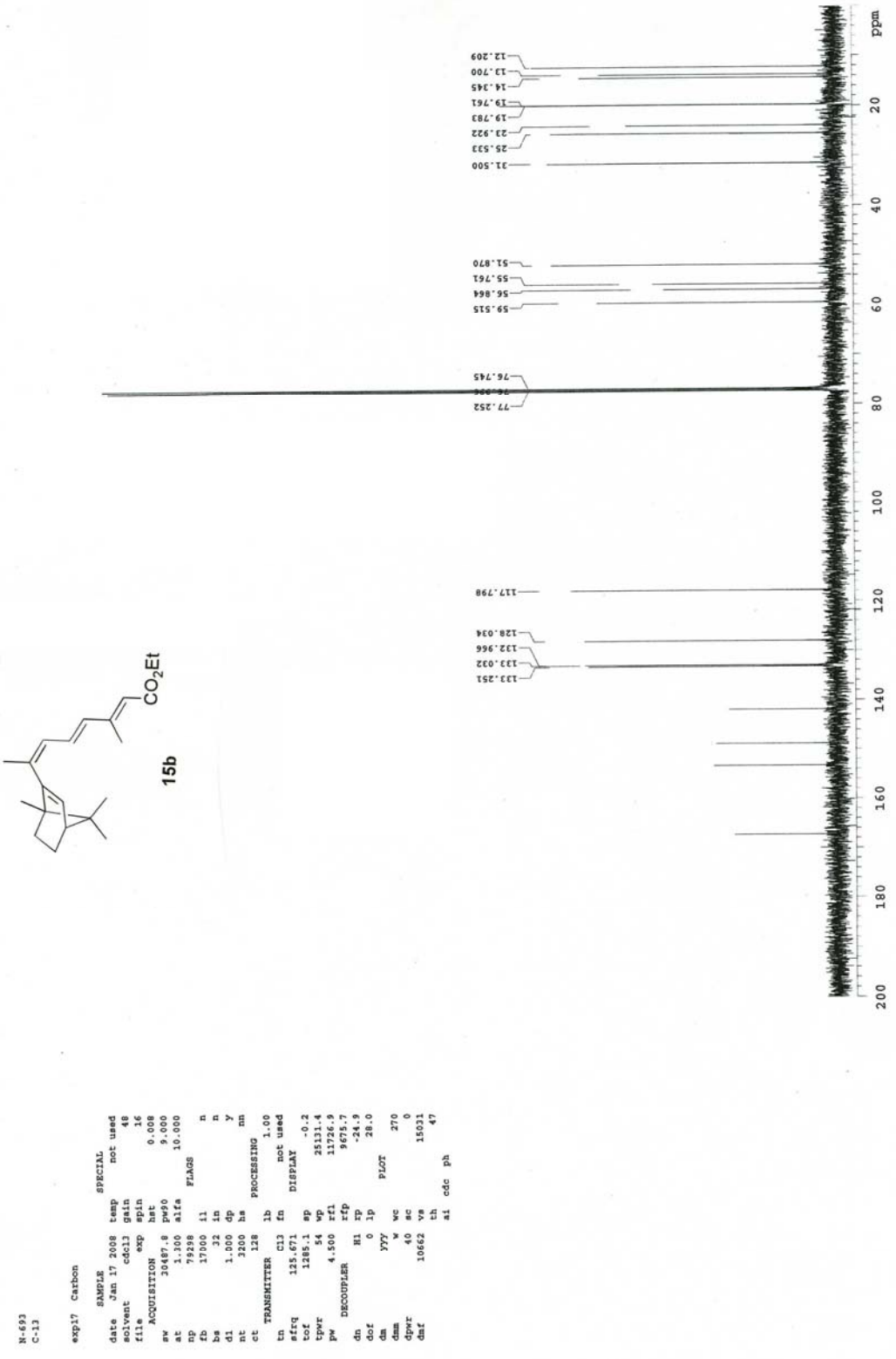

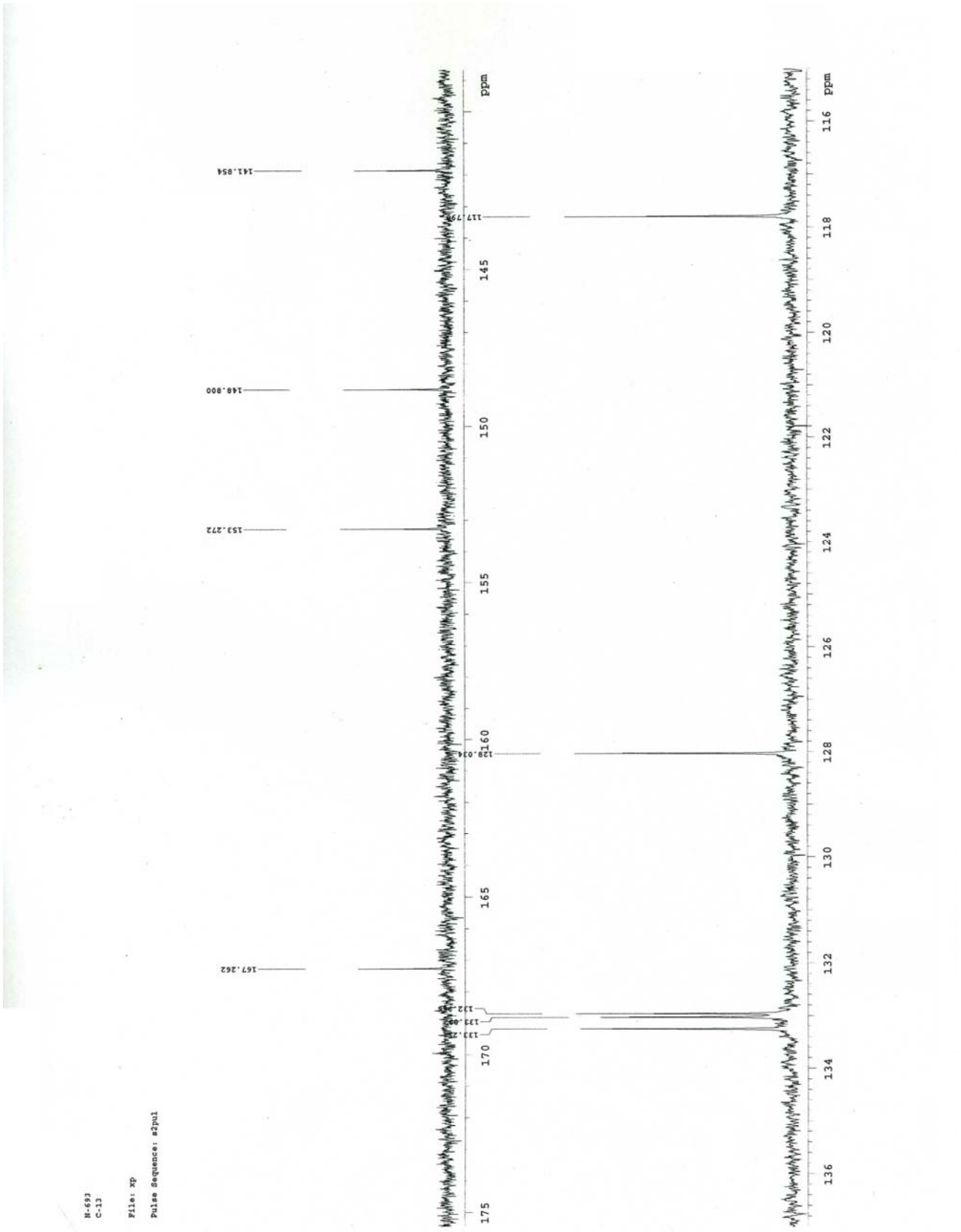

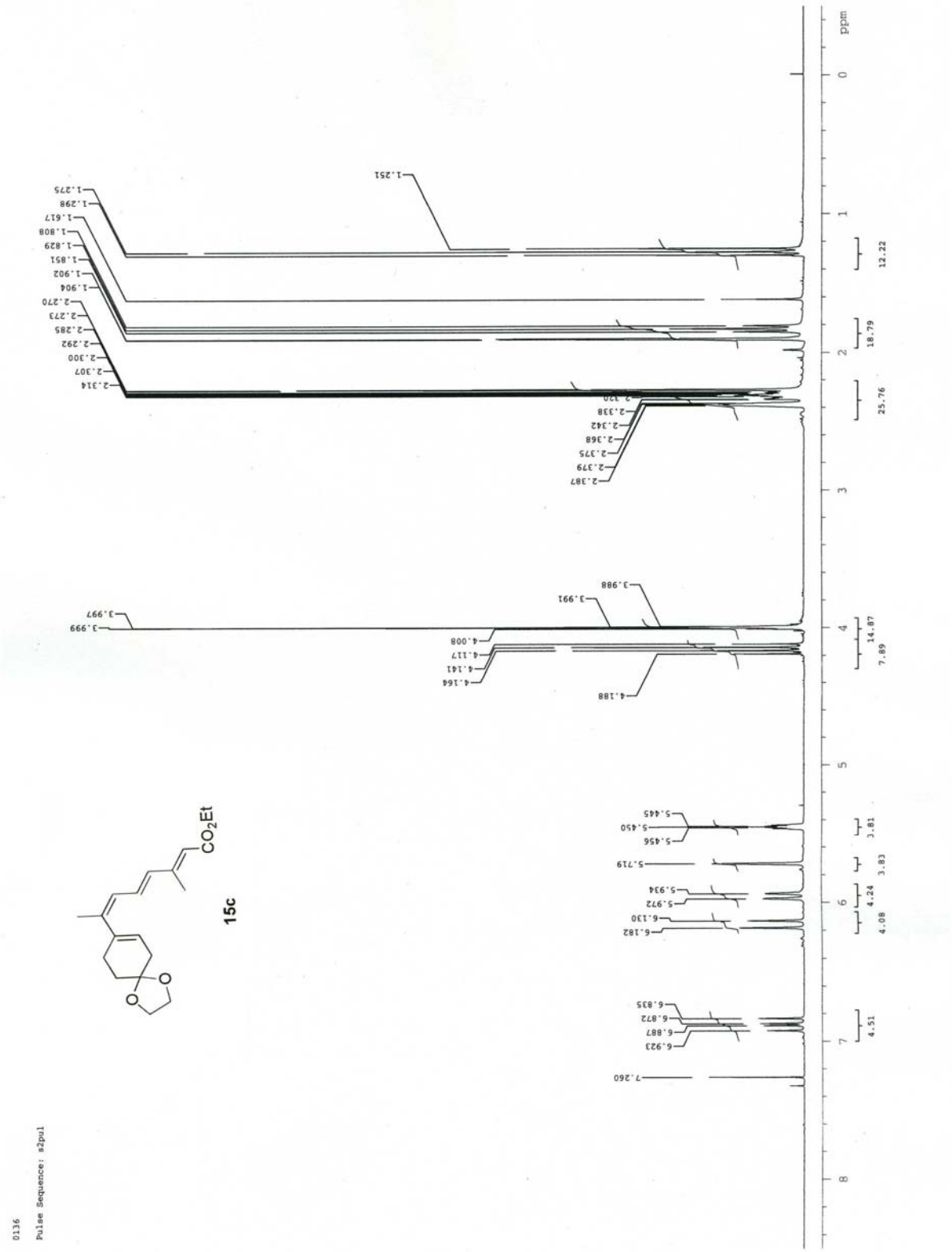

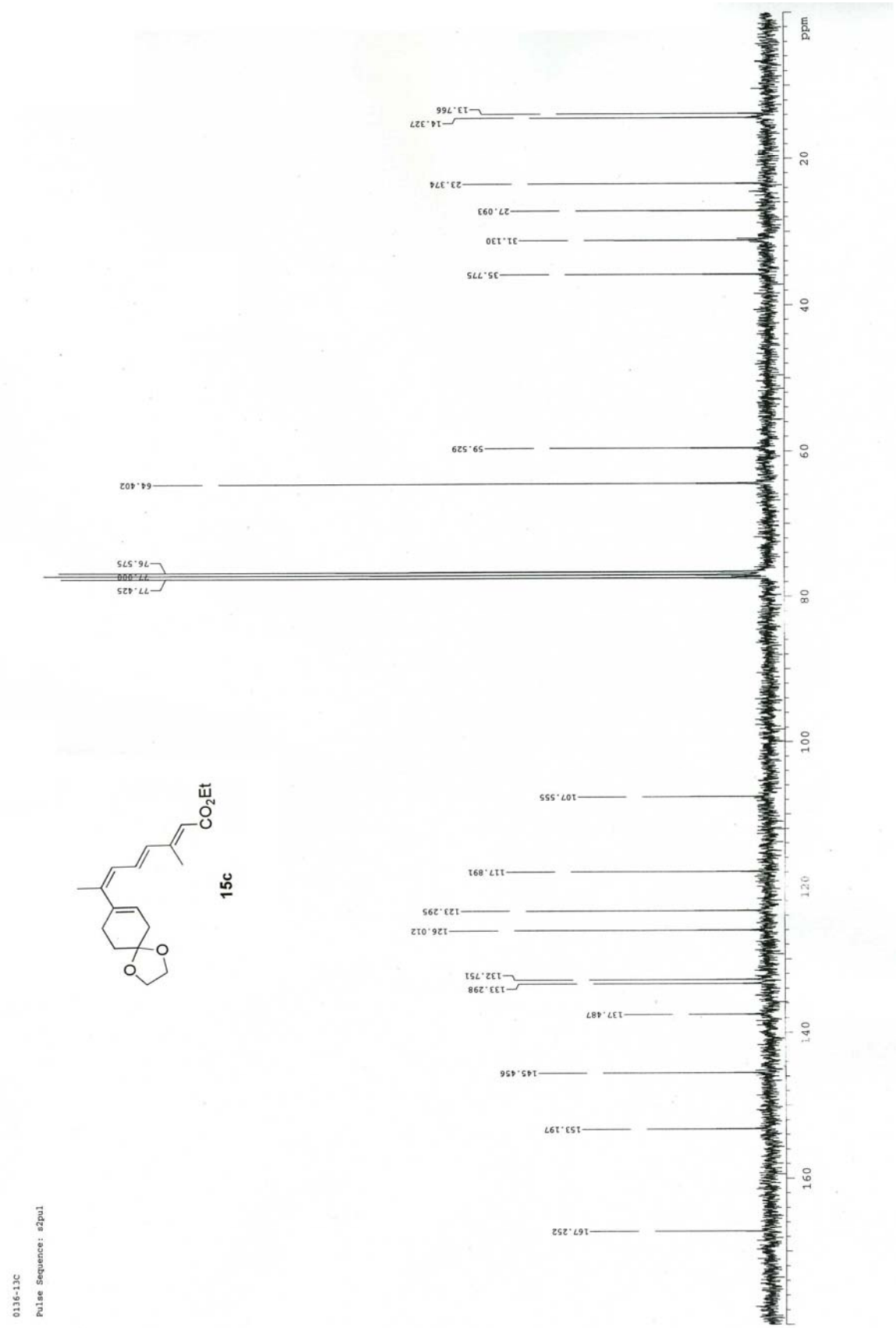

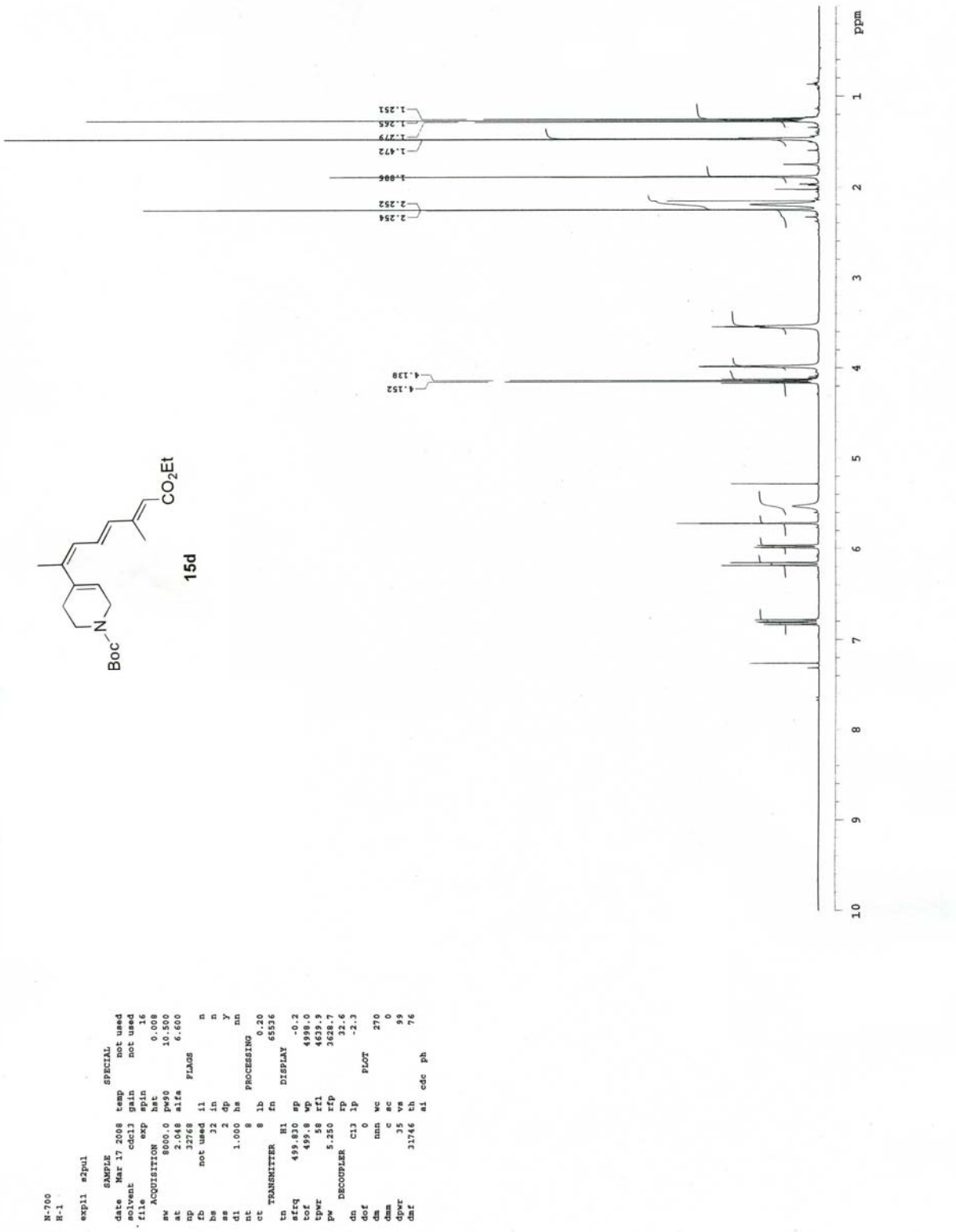


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N-700
H-1
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            bs            32   in             n
            ss             2   dp             y
            d1         1.000   hs            nn
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            ct             8   lb          0.20
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                    H1                DISPLAY
            tn
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            tpwr           58   rf1       4639.9
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                DECOUPLER       rp         32.6
            dn             C13  lp         -2.3
            dof              0                PLOT
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            dmf          31746   th            76
                                 ai   cdc  ph
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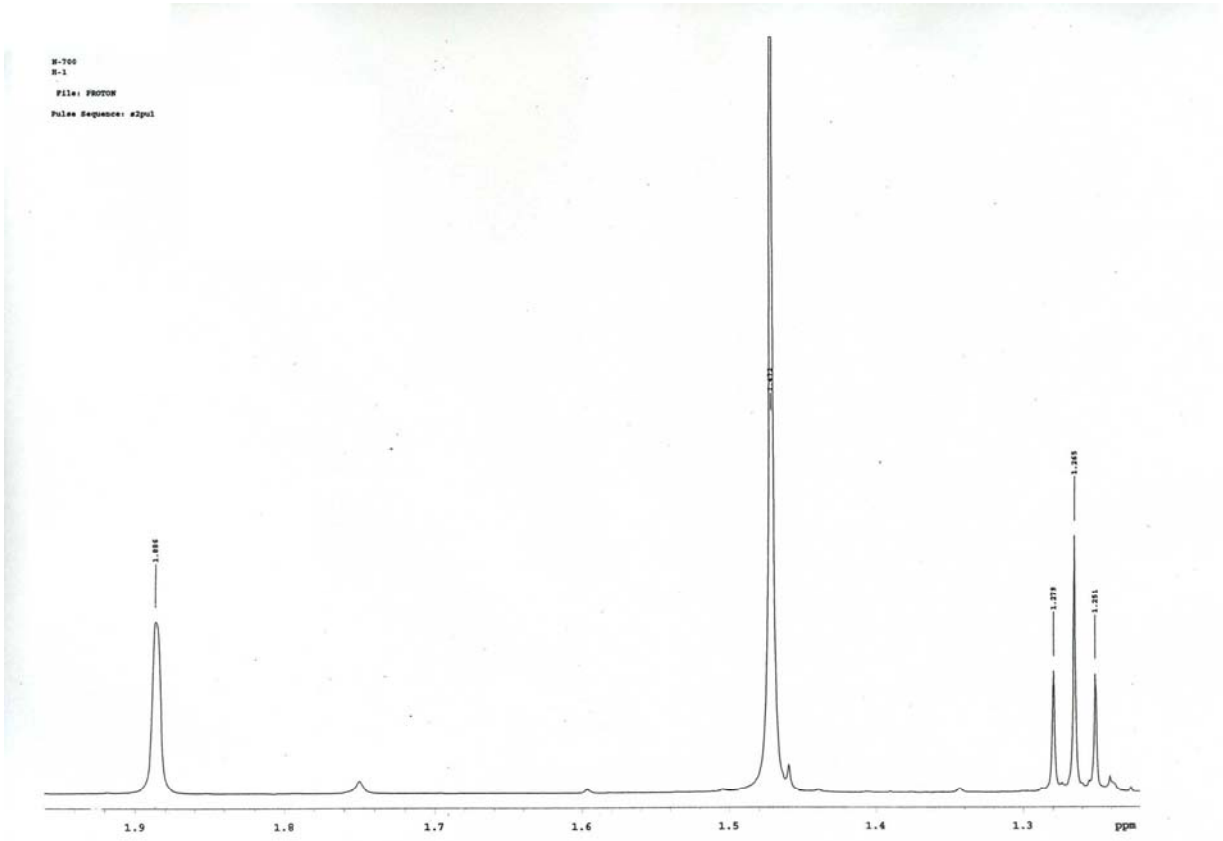

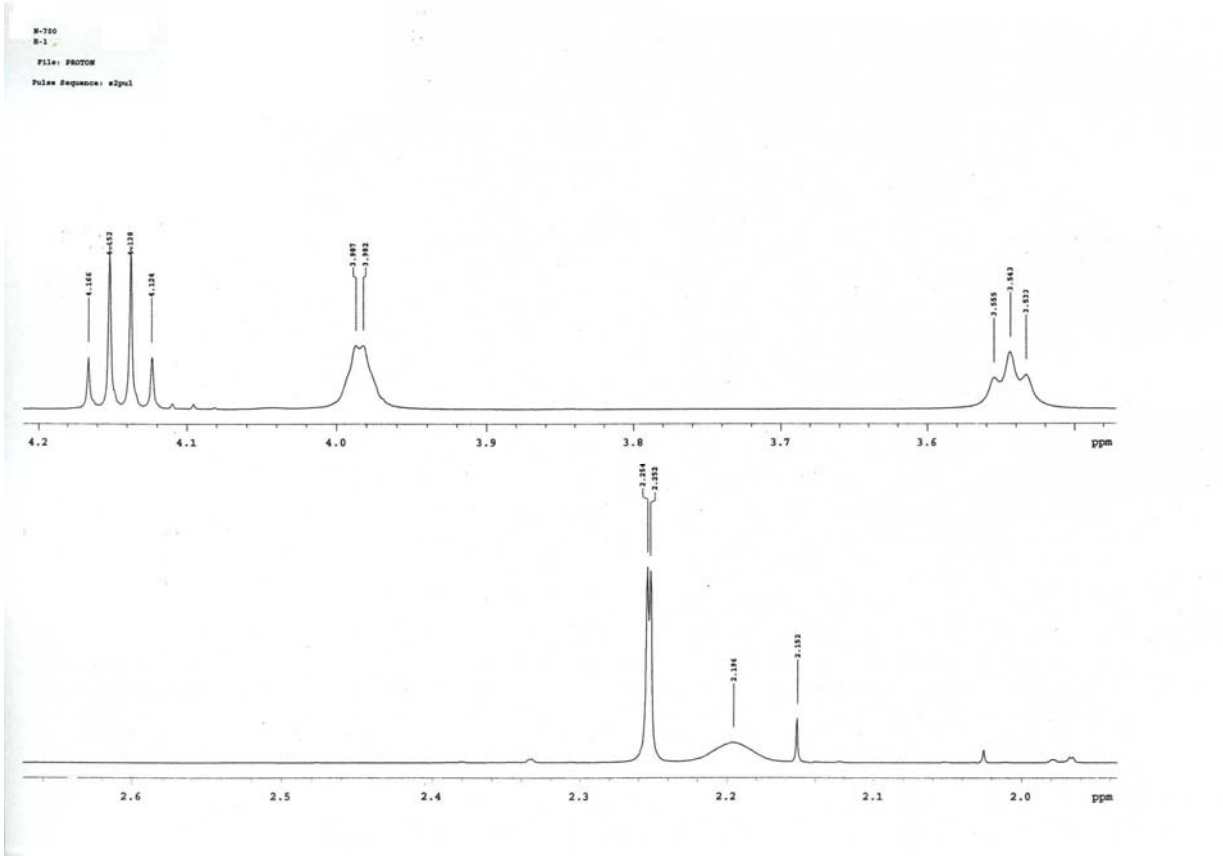

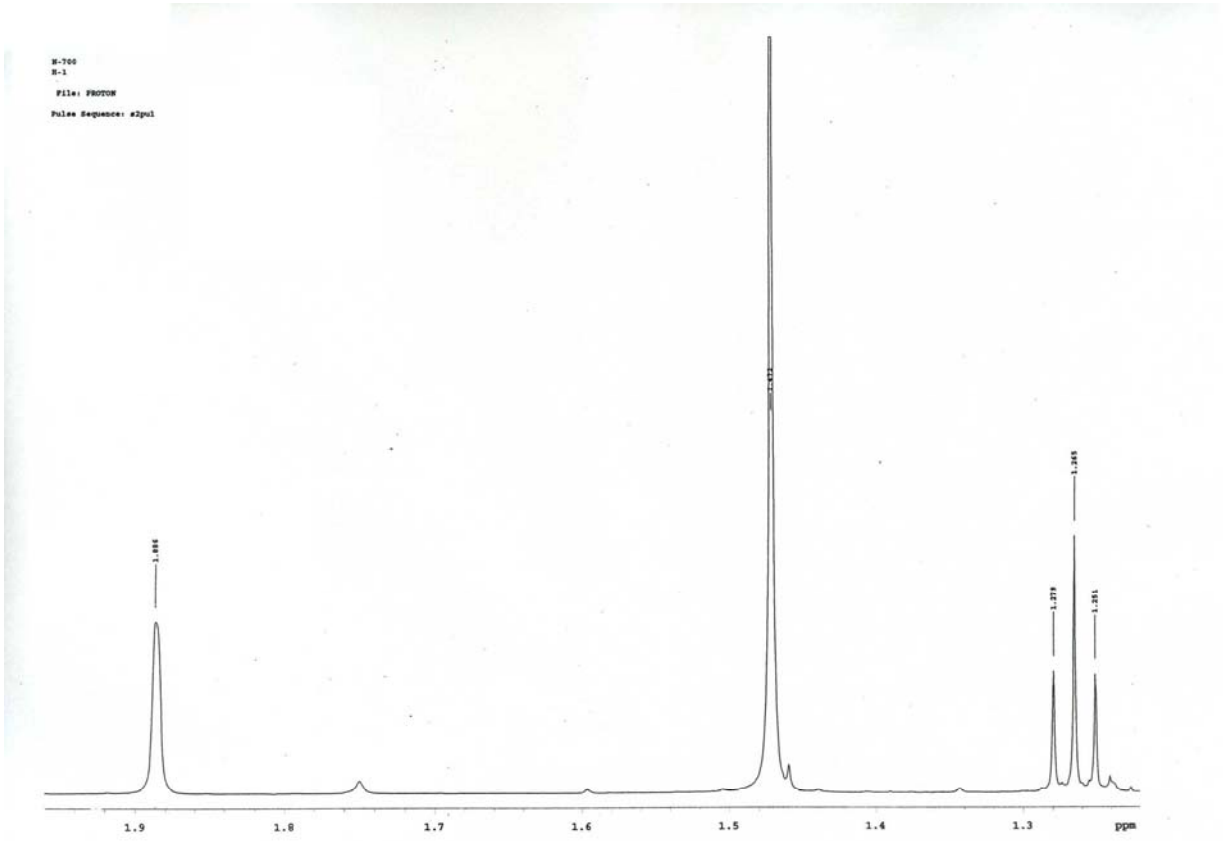

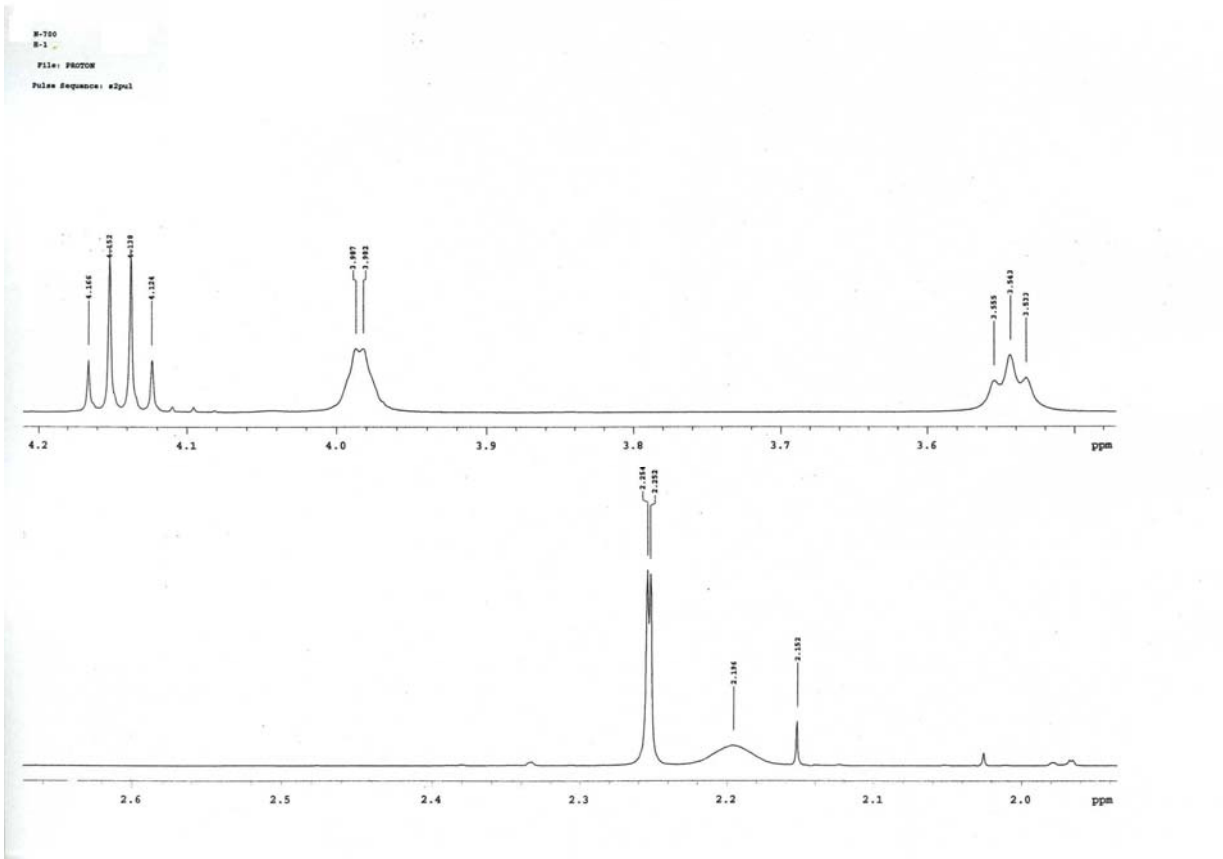

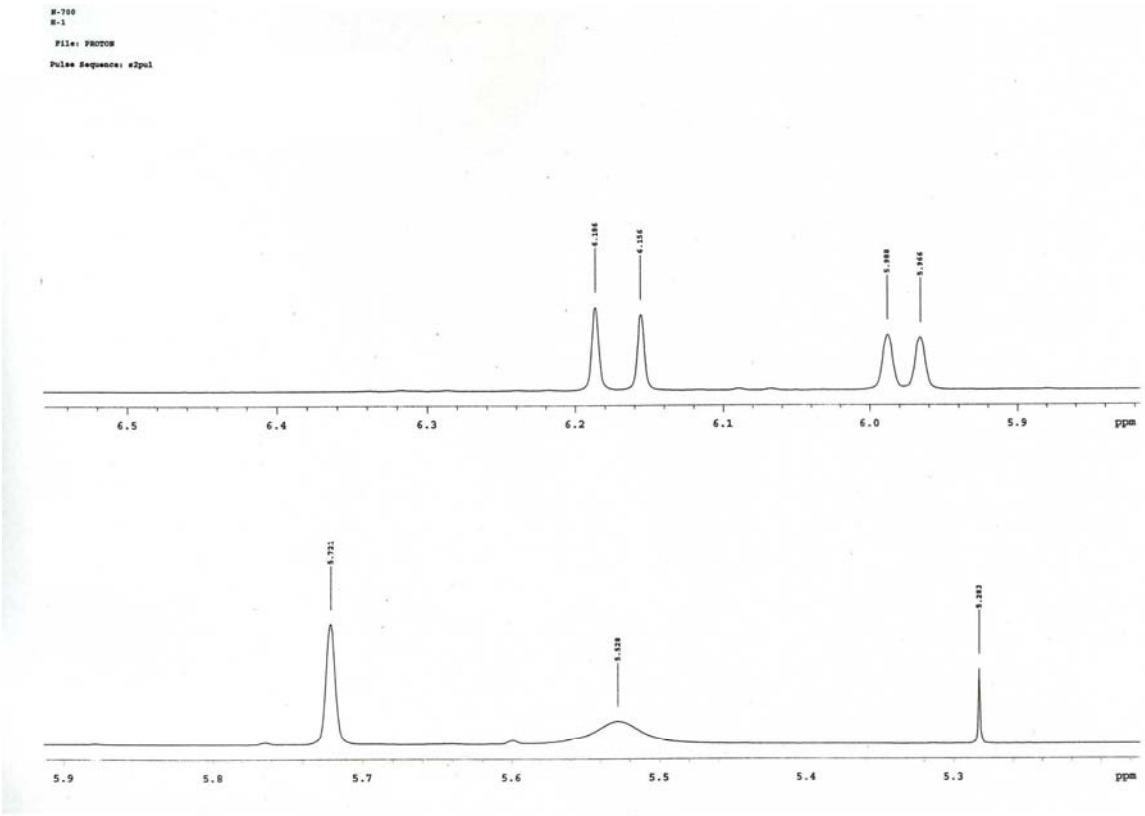

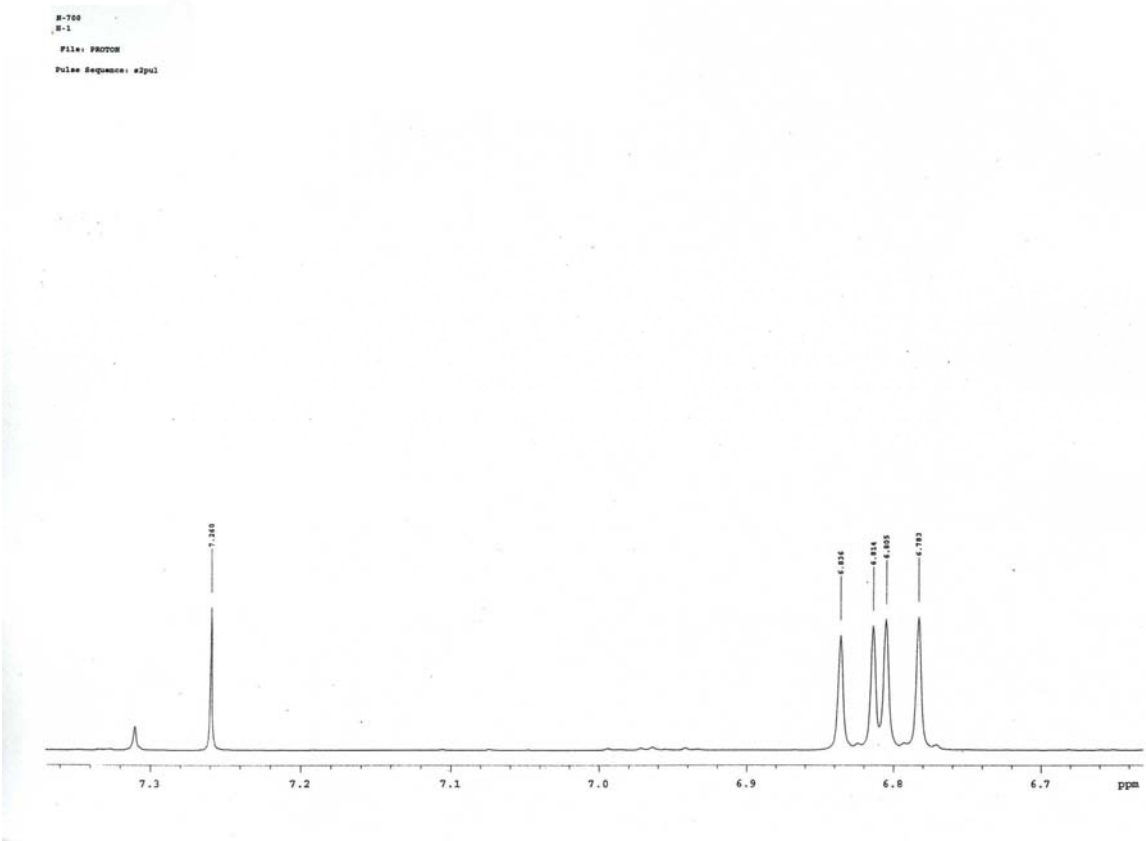

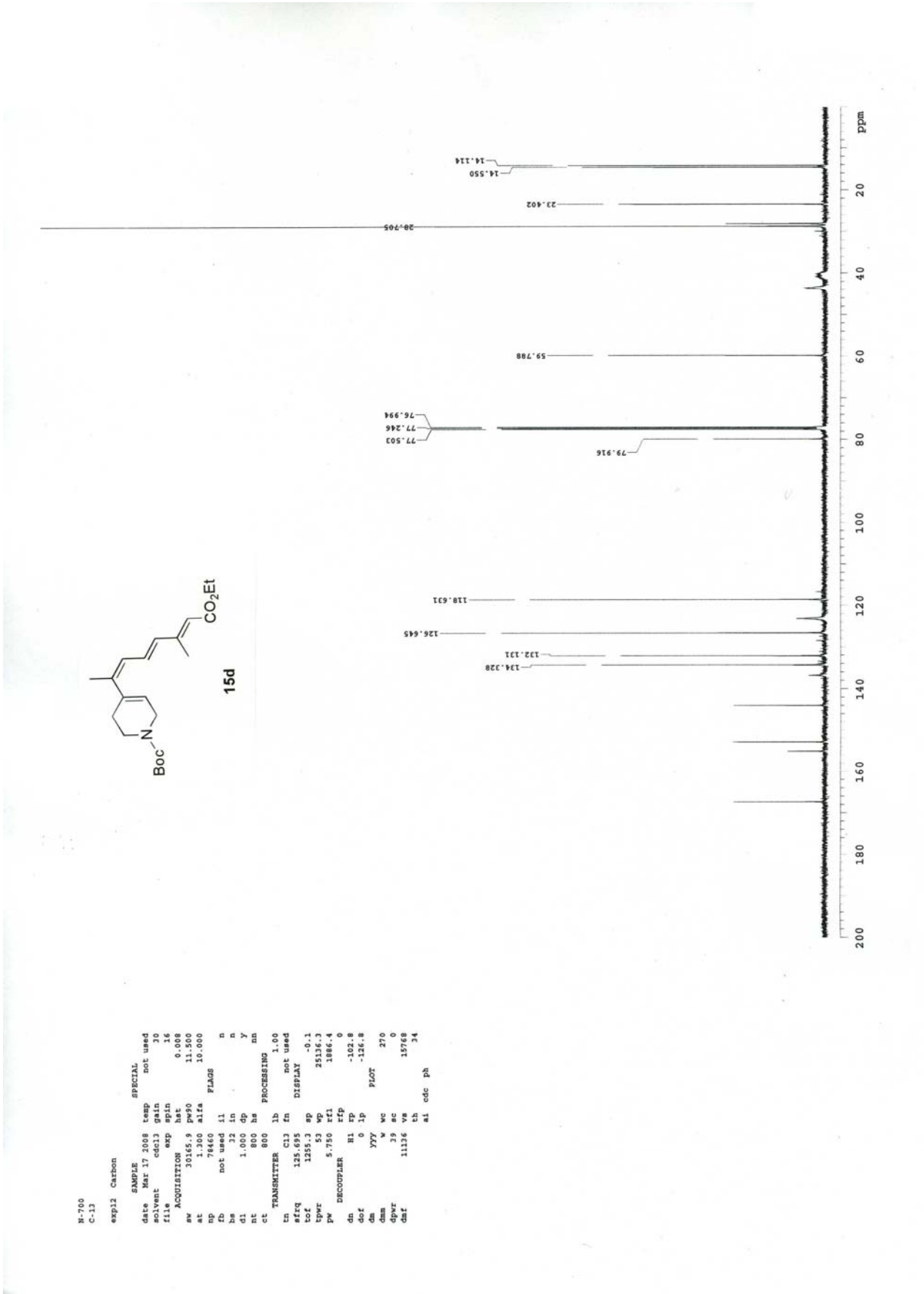

N-700
C-13
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d1 1.000 dp y
nt 800 hs nn
ct 800 PROCESSING 1.00
TRANSMITTER C13 fn not used
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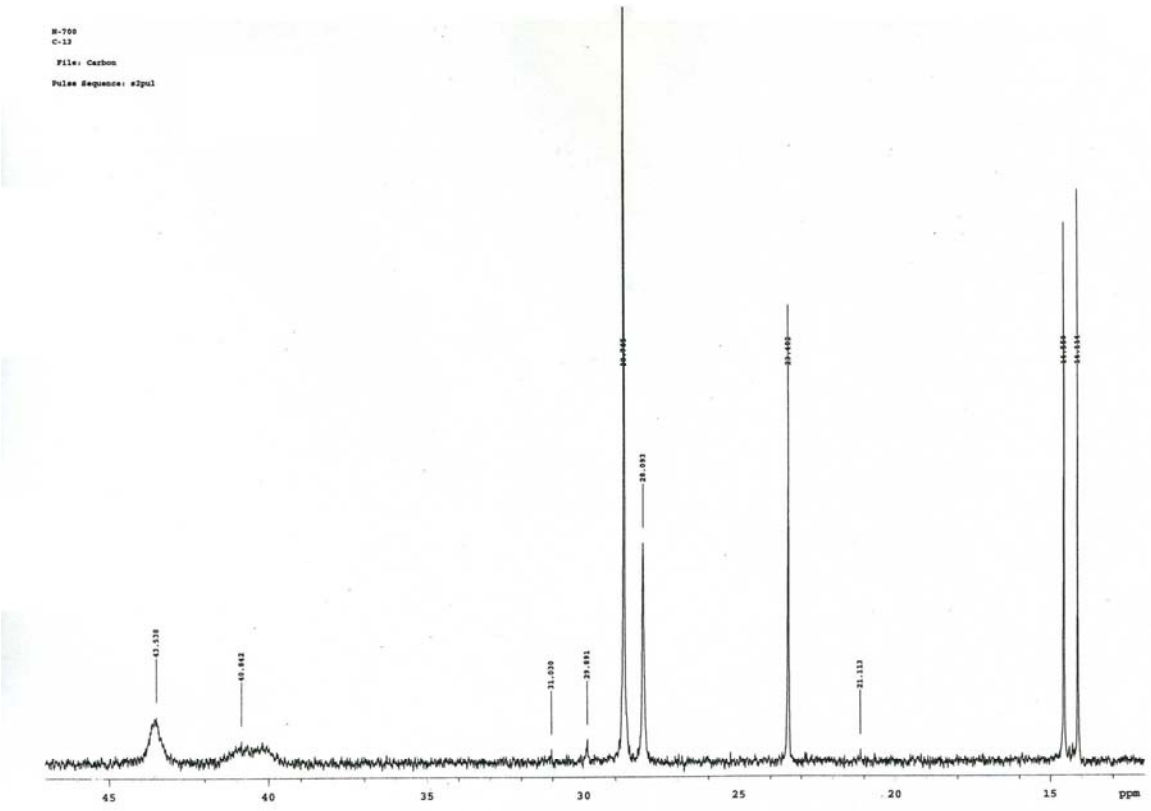
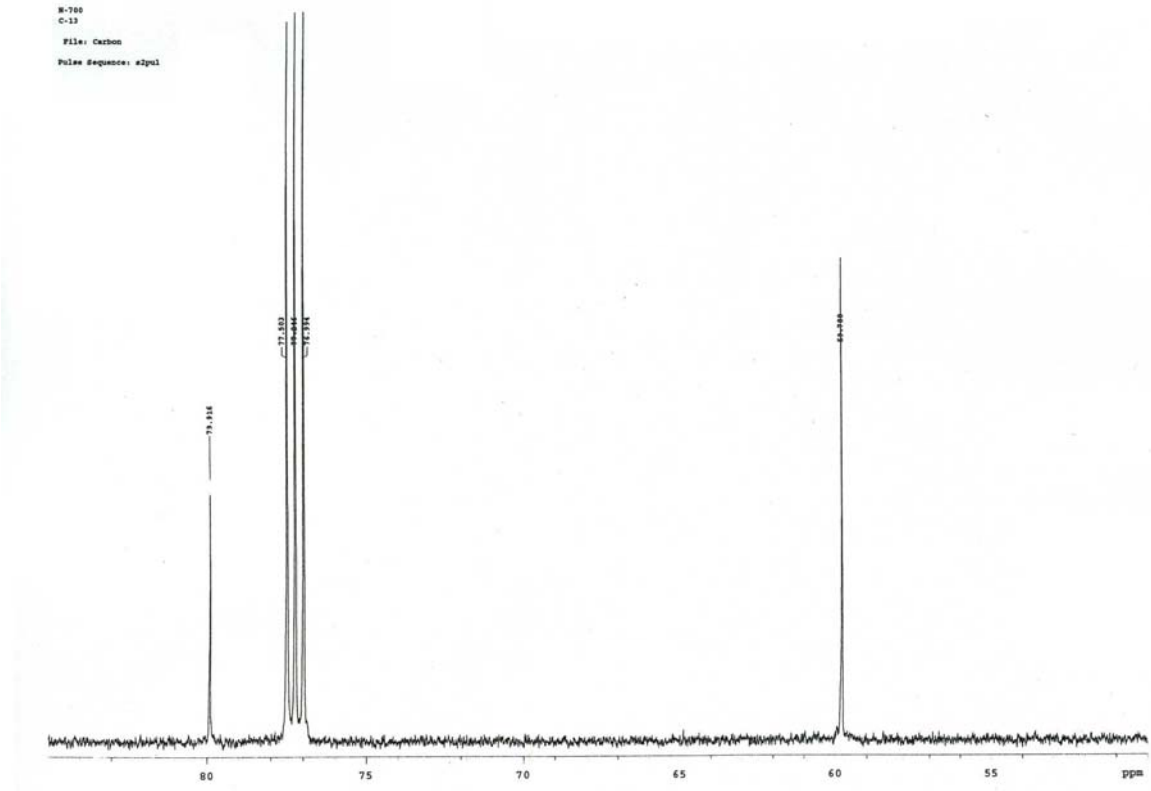
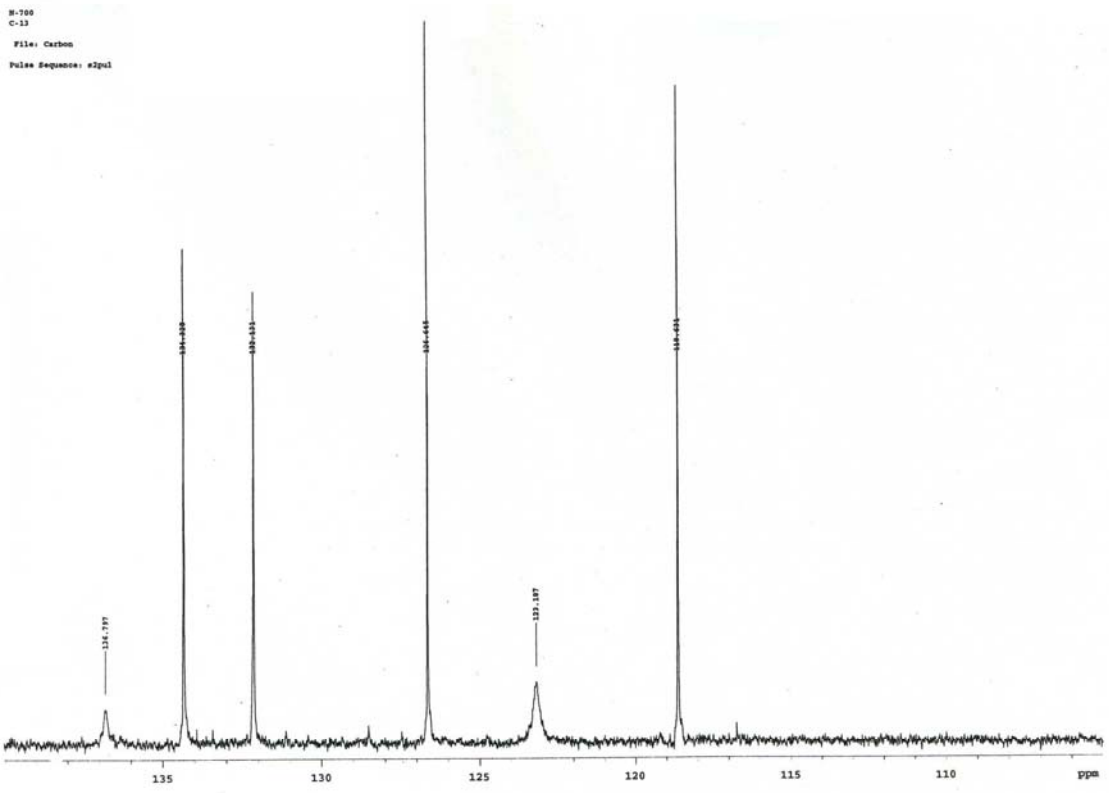
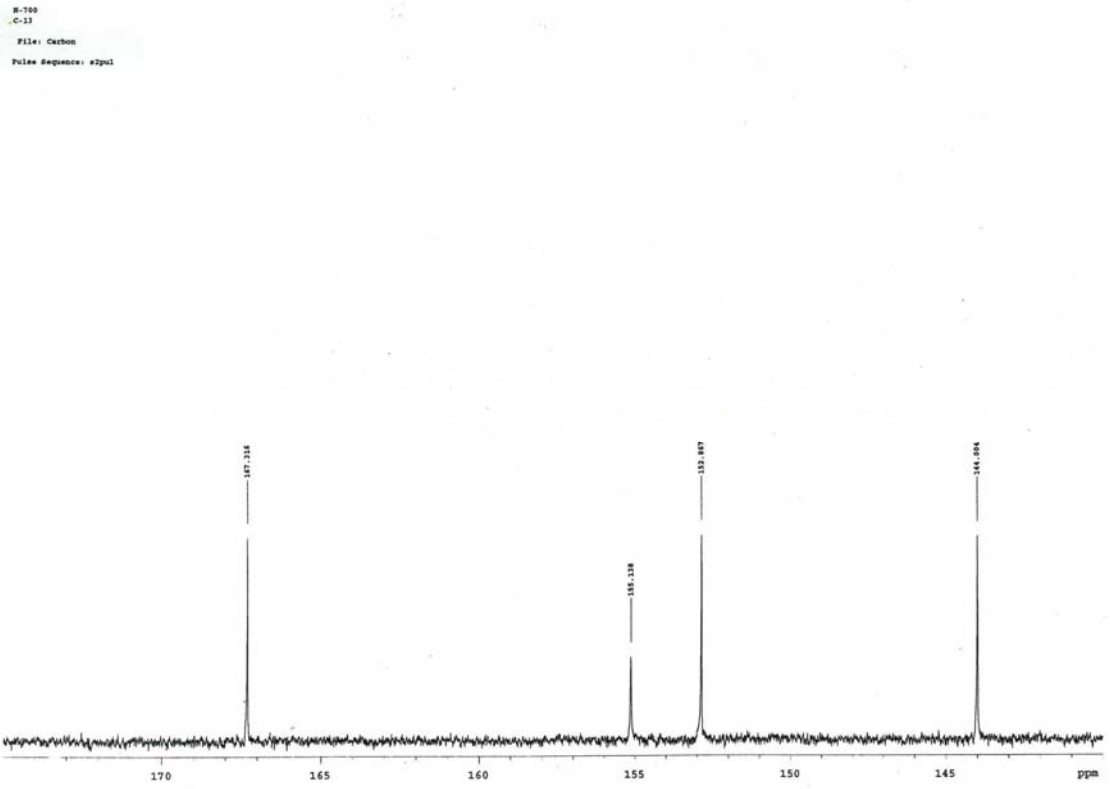
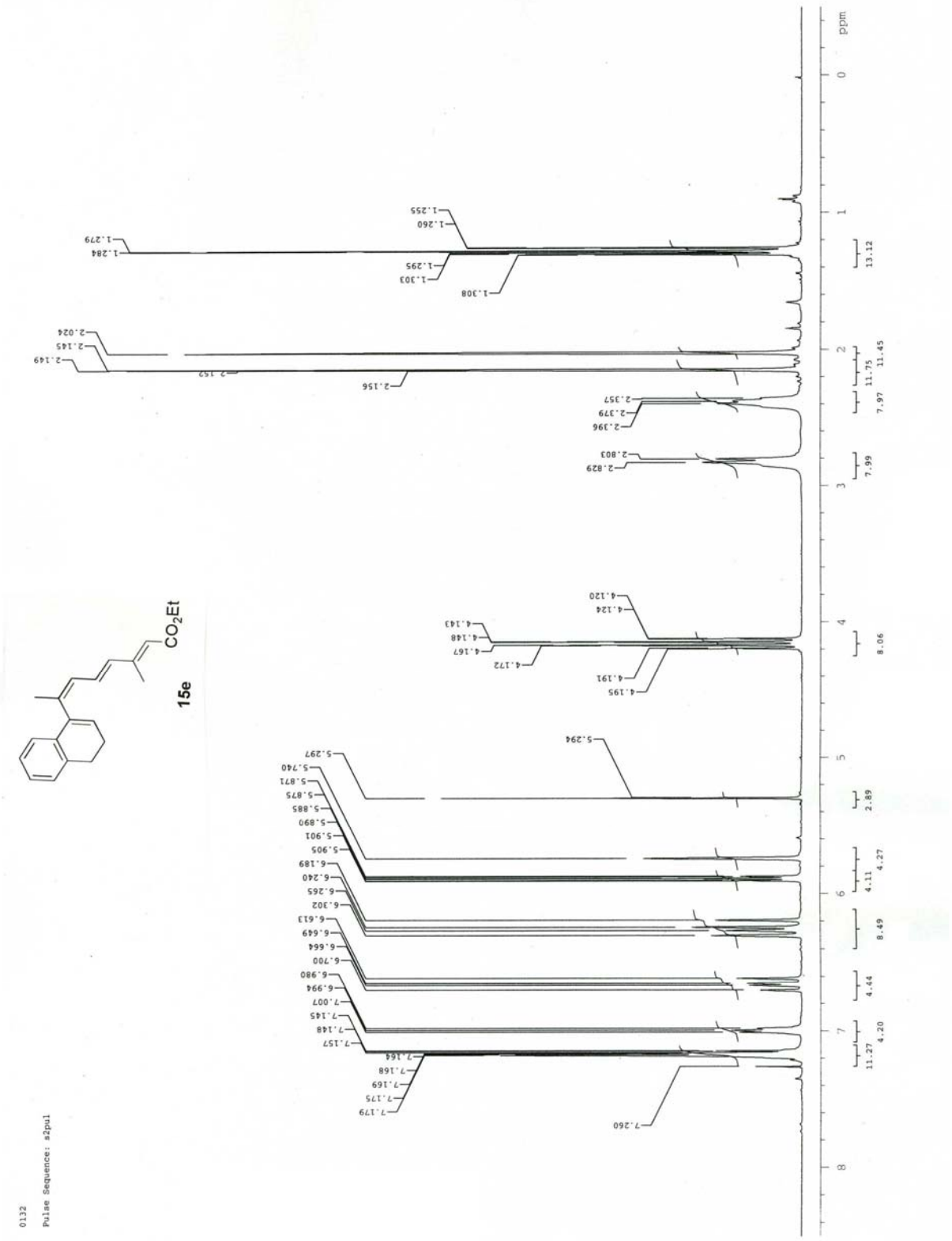
al cdc ph

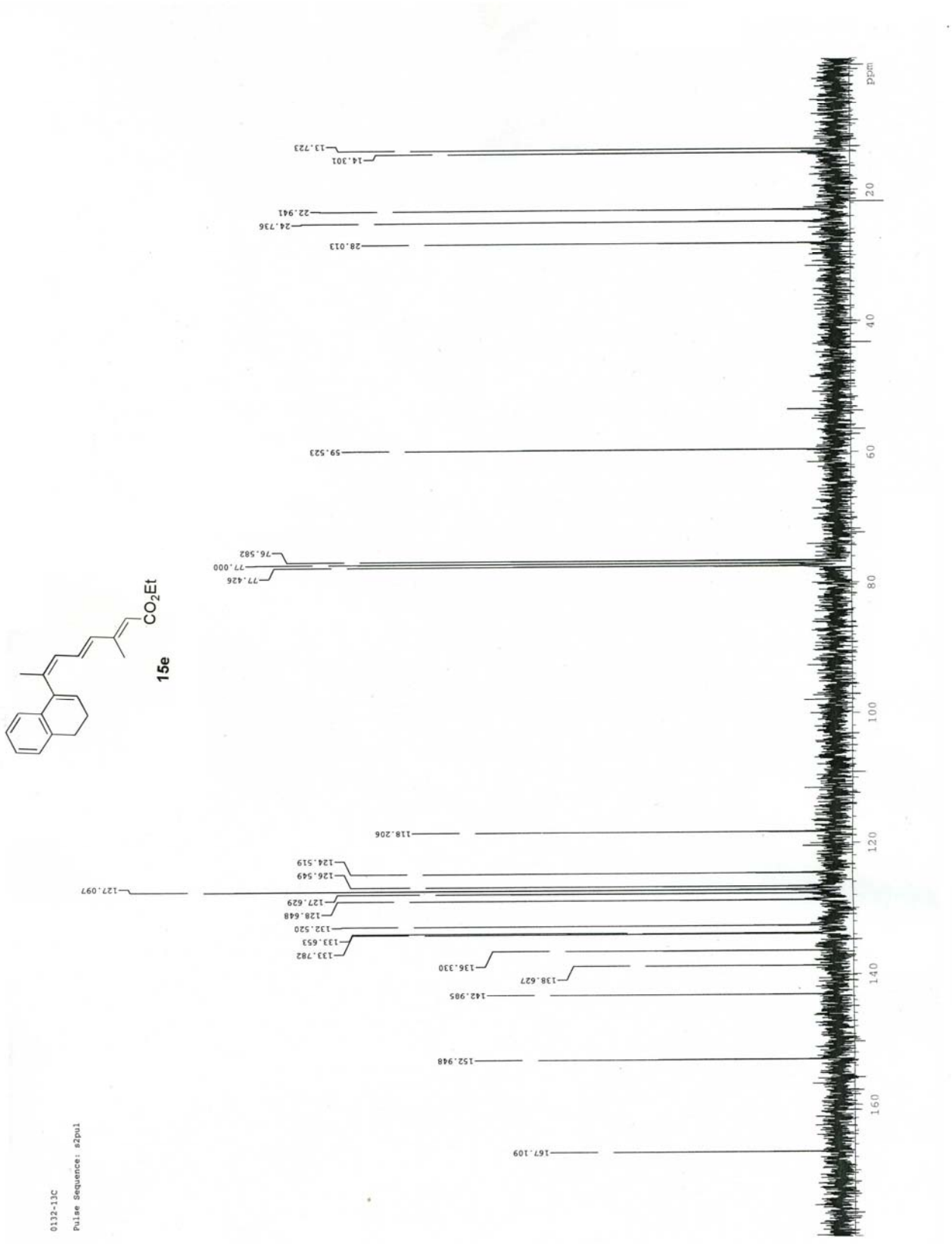


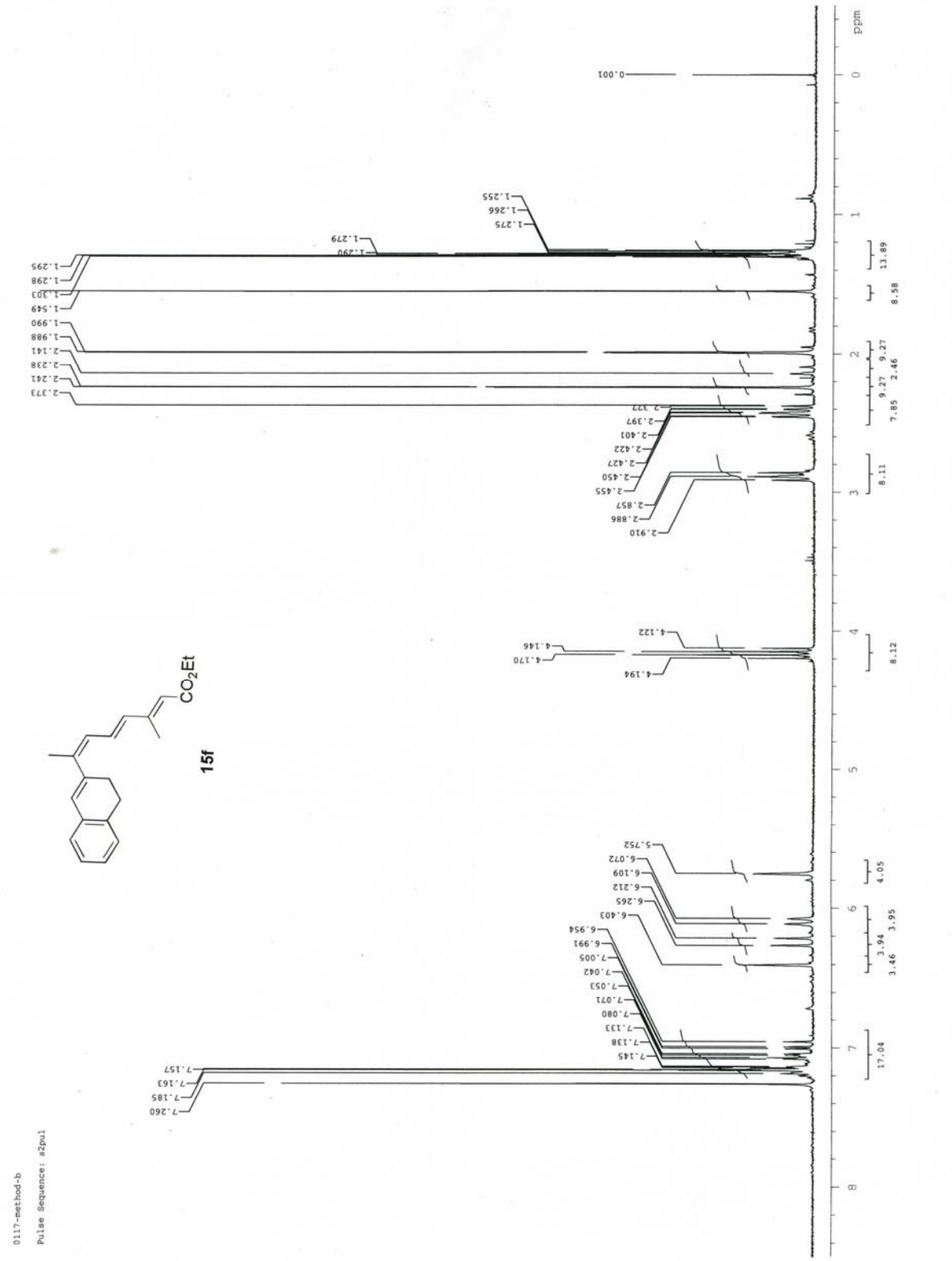


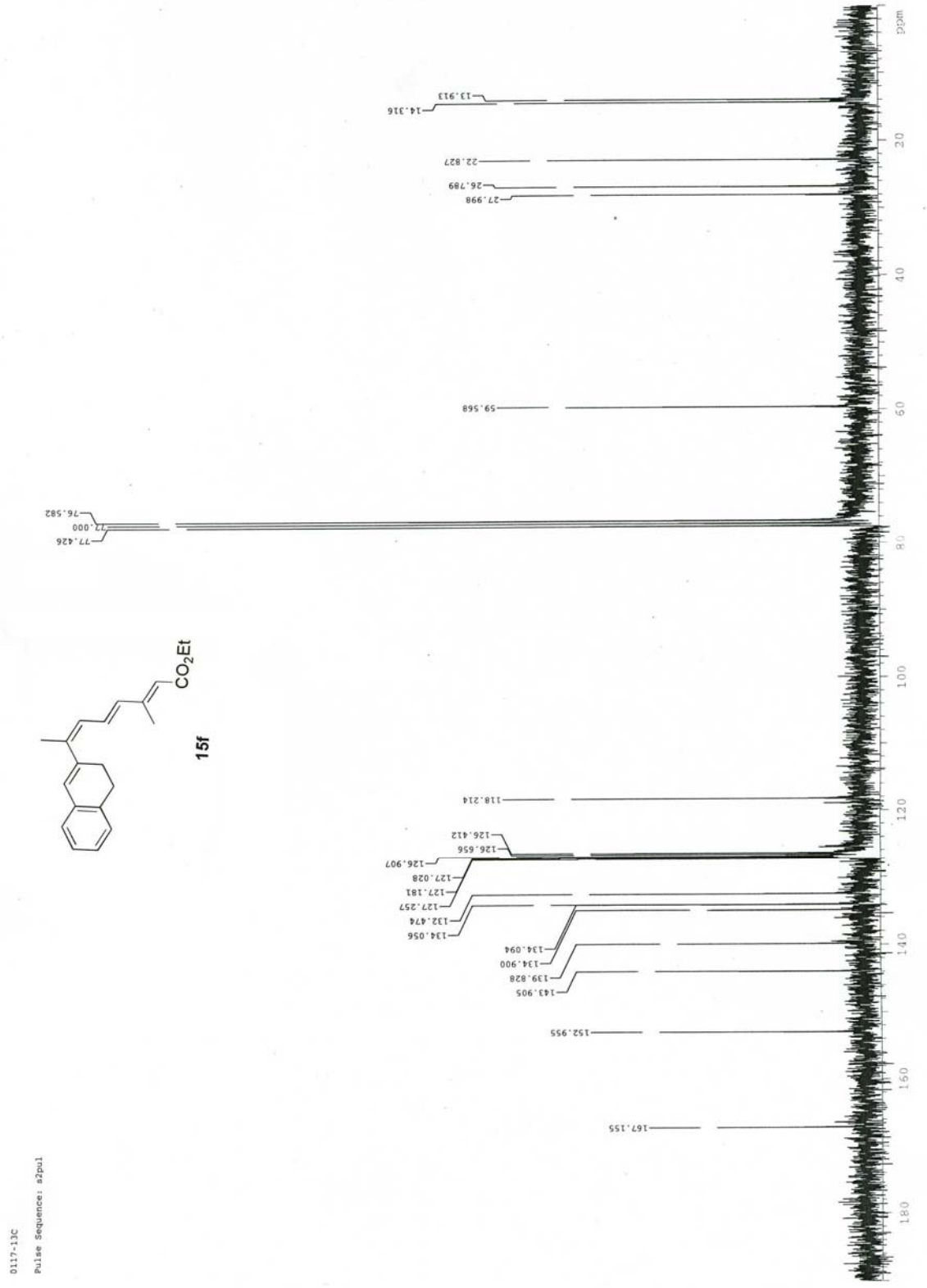


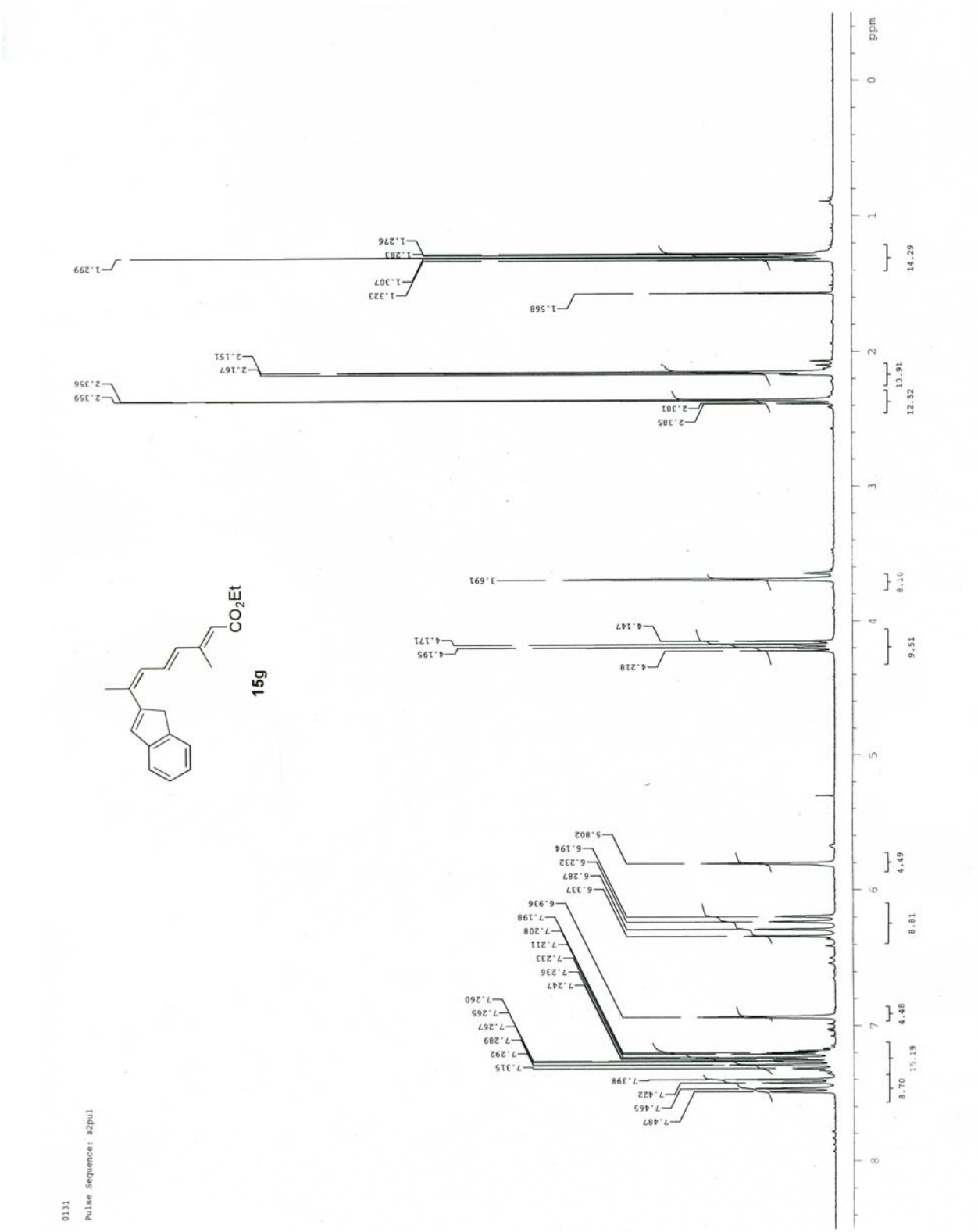


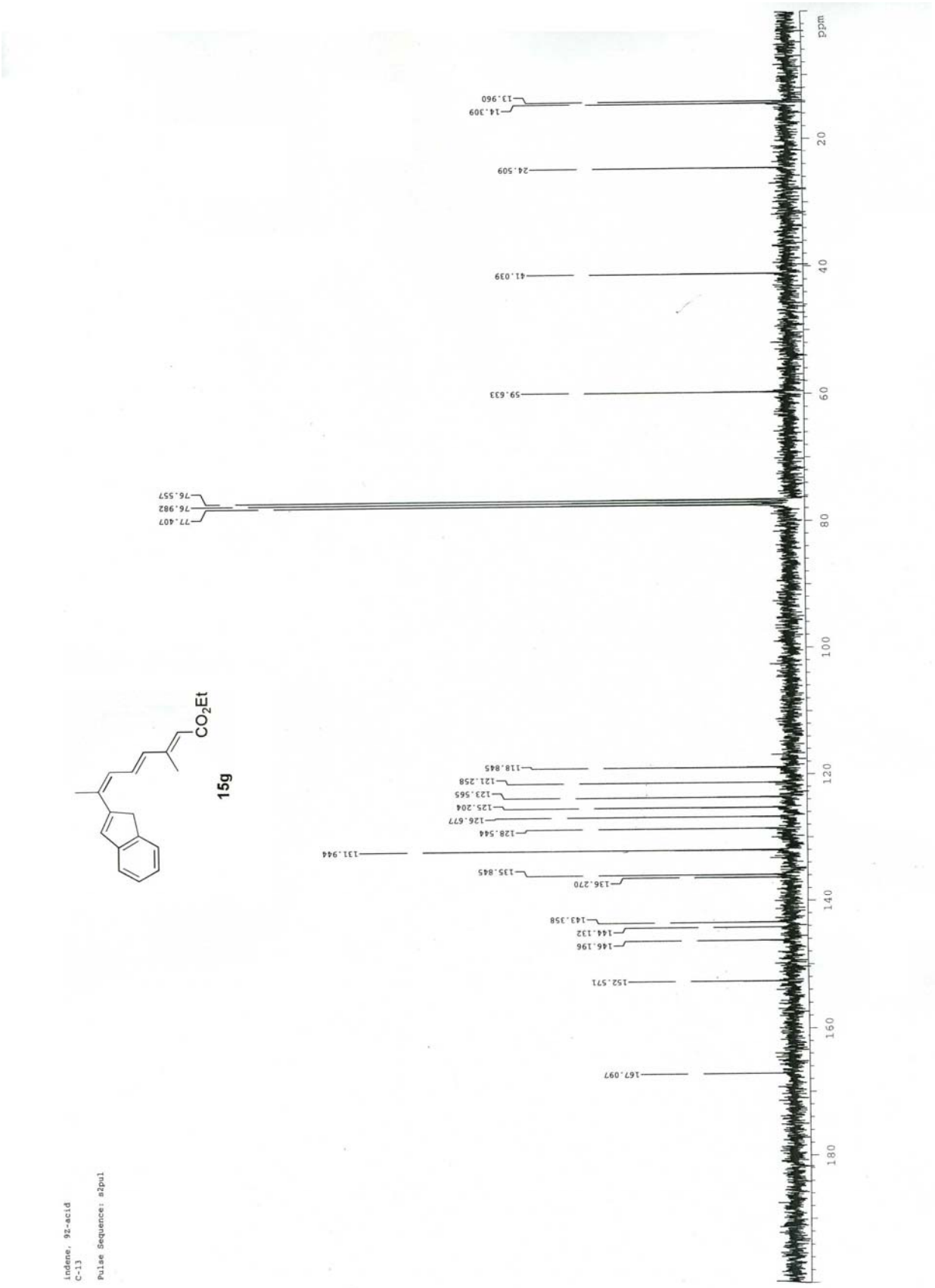


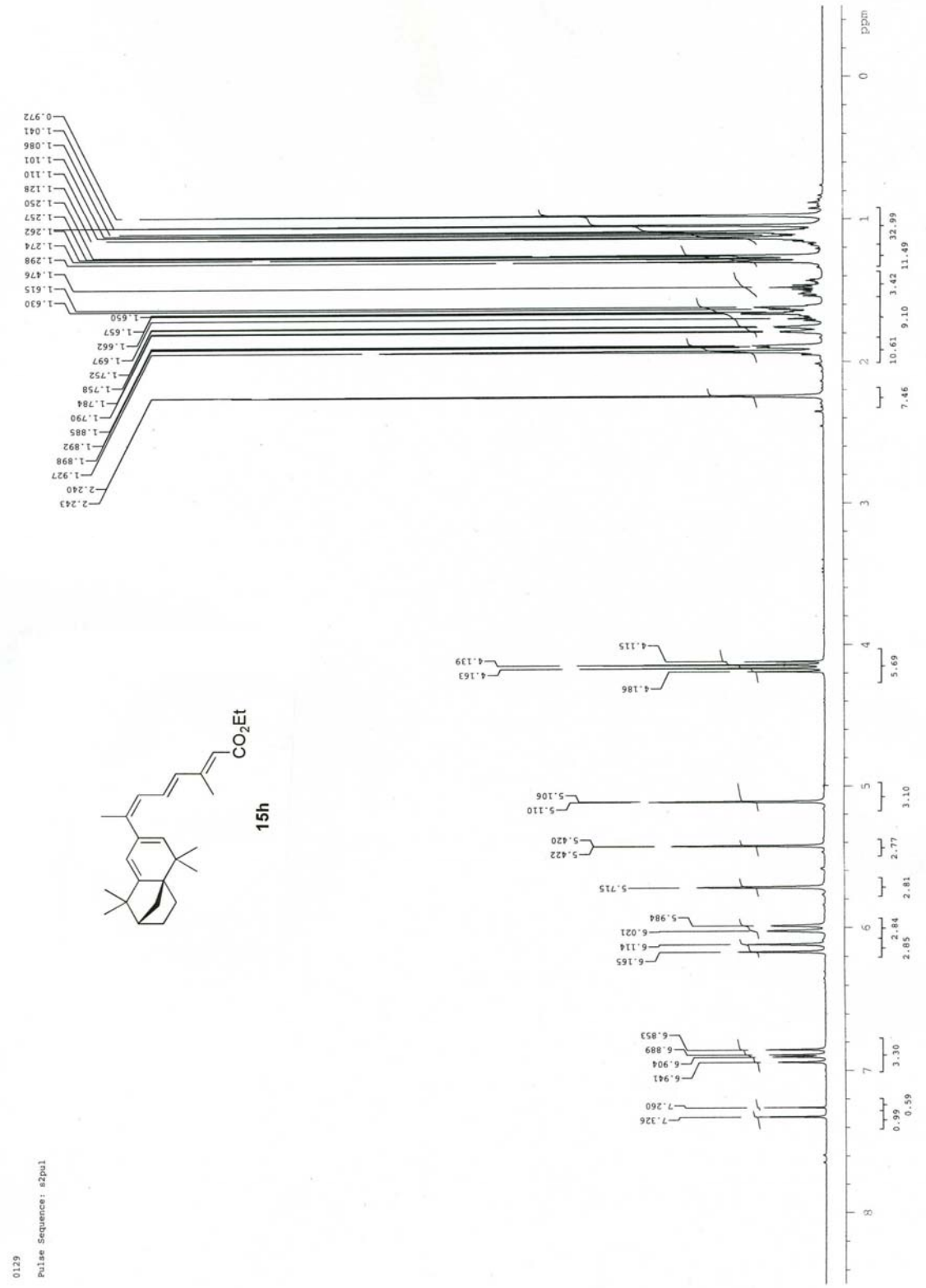


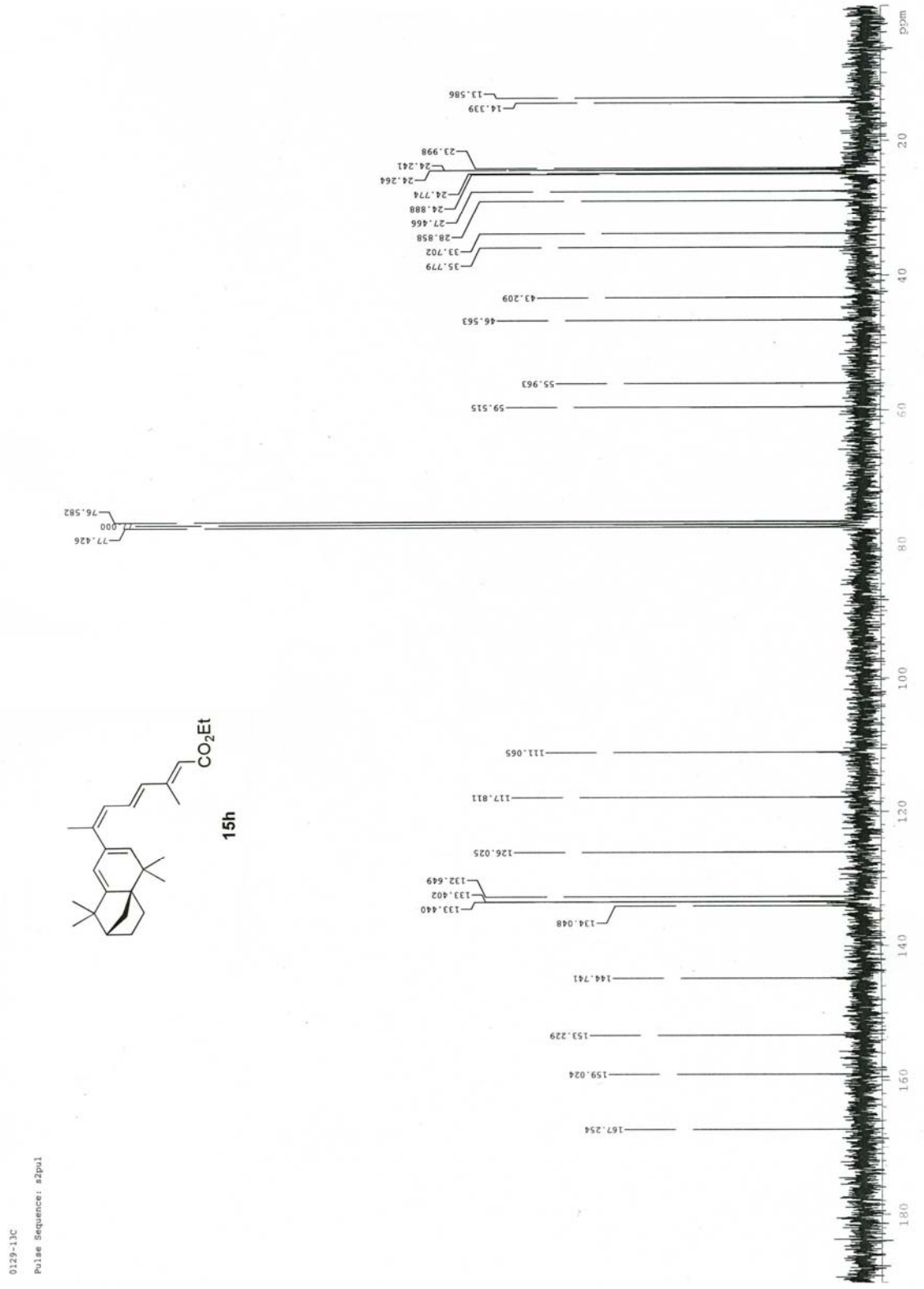


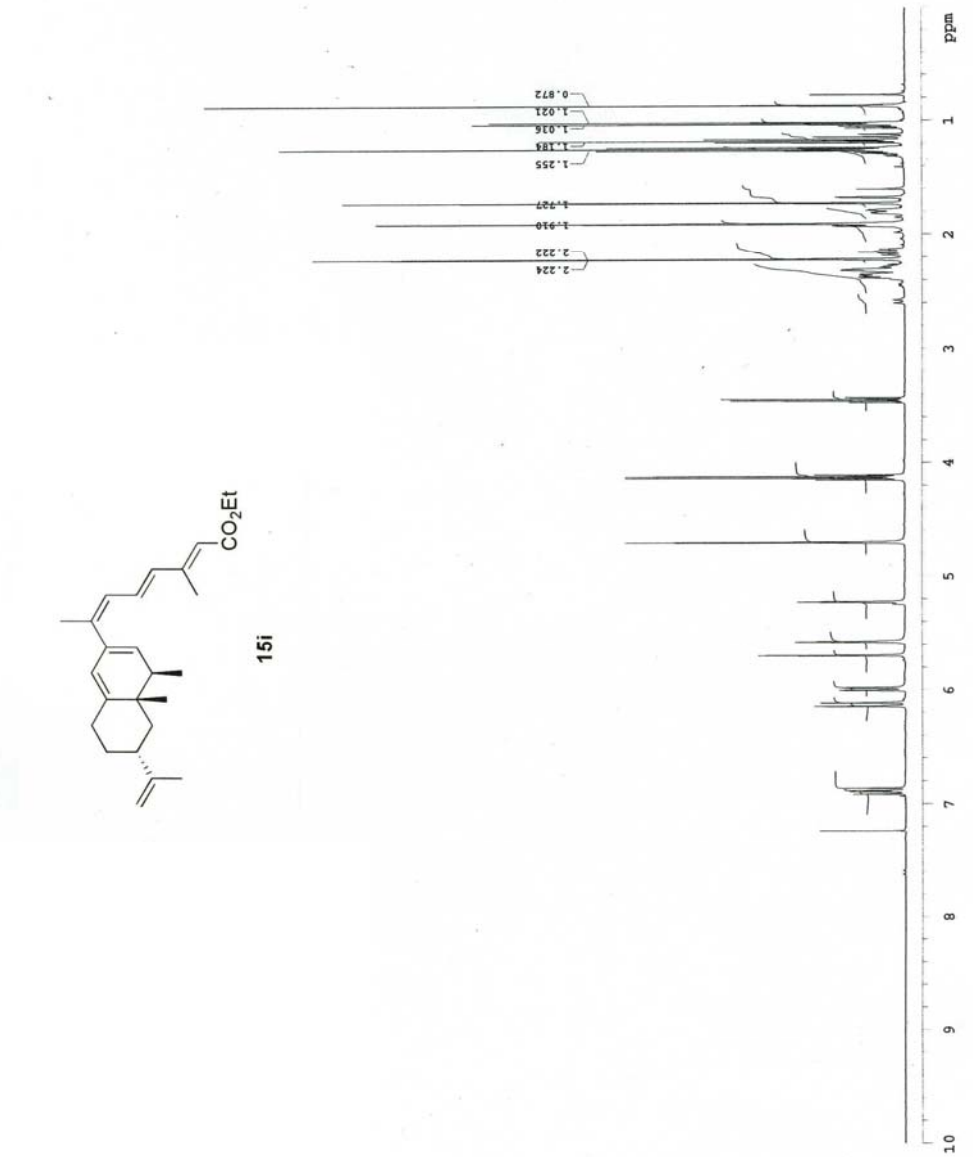










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N-695
E-1

exp12  #2pul

                SAMPLE                          SPECIAL
date   Feb 29 2008  temp      not used      not used
solvent     cdcl3    gain        20
file          exp    spin        16
    ACQUISITION      hat      0.008
sw          8012.8   pw90      10.600
at             3.500 alfa      10.000
np            56090              FLAGS
fb             4000  il                n
bs               32  in                n
d1            1.500  dp                y
nt               4   hs               nn
ct               4            PROCESSING
    TRANSMITTER      lb         0.30
tn               H1  fn      not used
sfrq        499.732              DISPLAY
tof            499.7  sp         -0.1
tpwr              59  wp       4997.3
pw             5.300  rf1      4641.9
    DECOUPLER        rfp      3618.0
dn               C13  rp       -49.7
dof                0  lp       -14.4
dm               nnn              PLOT
dmm                c  wc          270
dpwr              34  sc            0
dmf            32258  vs          371
                      th           93
                      ai  cdc  ph
```