Supporting Information

Chloride-Tolerant Gold(I) Catalyzed Regioselective Hydrochlorination of Alkynes

Rene Ebule,[a]† Shengzong Liang,[a]† Gerald B. Hammond, [a]* Bo Xu [b]*

[a] Department of Chemistry, University of Louisville, Louisville, Kentucky 40292, USA. [b] College of Chemistry, Chemical Engineering and Biotechnology, Donghua University, 2999 North Renmin Lu, Shanghai 201620, China

† These authors contributed equally to this work

Corresponding Authors; gb.hammond@louisville.edu; bo.xu@dhu.edu.cn

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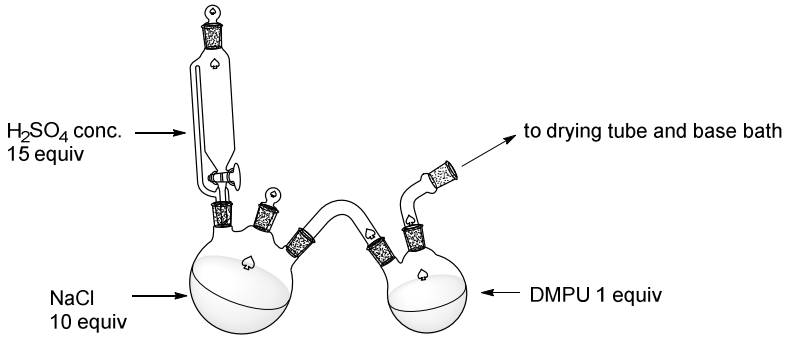
1. General

^{1}H and ^{13}C NMR spectra were recorded at 400 MHz and 101 MHz using $CDCl_3$ as a solvent. The chemical shifts are reported in δ (ppm) values (^{1}H and ^{13}C NMR relative to $CHCl_3$, δ 7.26 ppm for ^{1}H NMR and δ 77.0 ppm for ^{13}C NMR and $CFCl_3$ (δ 0 ppm for ^{19}F NMR), multiplicities are indicated by s (singlet), d (doublet), t (triplet), q (quartet), p (pentet), h (hextet), m (multiplet) and br (broad). Coupling constants (*J*), are reported in Hertz (Hz). All reagents and solvents were employed without further purification. The products were purified using a commercial flash chromatography system. TLC was developed on silica gel 60 F254 aluminum sheets. All reagents were purchased from Sigma-Aldrich or Alfa Aesar and used as received without any further purification.

2. General procedures

2.1 Procedure for generation of HCl/DMPU

A pressure-equalizing dropping funnel and inlet of a drying tube packed with $CaCl_2$ were attached onto a 500 mL of two-neck round-bottom flask. The outlet of the drying tube was attached to one joint of 100 mL two-neck round-bottom flask through tubing; a 5'' pipette was attached to the end of the tubing. The other joint of the same flask was attached to the second drying tube connected to a base bath.



After flushing the whole system by argon for 10 minutes, sodium chloride and a stirring bar were placed in the 500 mL two-neck flask, the dropping funnel was charged with concentrated sulfuric acid, and DMPU and a small stirring bar were placed in a 100 mL receiving flask. Both flasks were cooled in ice-water baths.

Concentrated sulfuric acid was then gradually dropped onto sodium chloride at a rate of one drop per second, and an extremely exothermic reaction took place. During the absorption of HCl, the colorless DMPU turned into a viscous yellowish liquid.

The obtained HCl/DMPU solution was pipetted into an argon-flushed glass vessel with PTFE-lined cap. The concentration of the generated HCl/DMPU was approximately 43% by weight. This solution is slightly fuming but stable over months on a lab bench.

2.2 Synthesis of gold complexes (L-AuCl)

All gold complexes (L-AuCl) were synthesized using a slightly modified version of a literature method.[1] These complexes were prepared via either one of the following general procedures, and the characterization of these gold complexes were previously reported by us.[2]

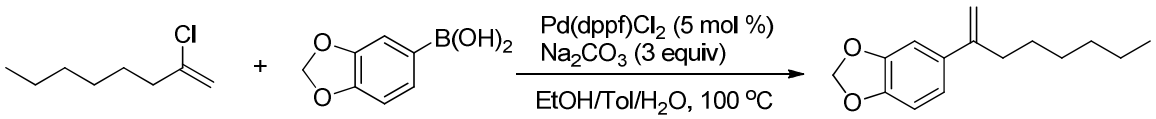
Method 1: Sodium tetrachloroaurate(III) dihydrate (1 mmol) was dissolved in water, and the orange solution was cooled in ice. To this solution, 2,2'-thiodiethanol (3 mmol) was slowly added (ca. 10 min) with stirring. After stirring at 0°C for another 30 min, a solution of the phosphine ligand (1 mmol) in EtOH (if the ligand could not be dissolved, more EtOH was used) was added dropwise to yield a white solid. The solid was filtered off, washed with water followed by EtOH, and ultimately dried in vacuum.

Method 2: Chloro(dimethylsulfide)gold(I) (1 mmol) was dissolved in dichloromethane in a vial and cooled in an ice bath. A solution of phosphine ligand (1 mmol) in dichloromethane was added dropwise, and the resulting solution was allowed to warm to room temperature and stirred at room temperature for 3 h. After TLC indicated complete consumption of the starting material, the reaction solution was concentrated to dryness in the rotovap, and the gold complex product was further dried under high vacuum.

2.3 General procedure for homogeneous gold catalyzed hydrochlorination of alkynes

A glass screw cap vial equipped with a stir bar was charged with alkyne **1** (0.5 mmol). A 1:1 mixture of hexafluoroisopropanol (HFIP) and nitromethane (125 µL) was added to dissolve it. **L6**-Au-Cl (7.3 mg, 2 mol %) was then added followed by HCl/DMPU (48 µL, 0.6 mmol). The reaction mixture was stirred at rt (or 75 °C as the case may demand) and the progress of the reaction was monitored by GCMS or ^{1}H-NMR. Upon completion, reaction mixture was quenched with water and extracted with DCM. It was then dried over anhydrous Na_2SO_4, filtered and solvent evaporated. The crude product was purified by silica gel column chromatography (hexanes/ethyl acetate).

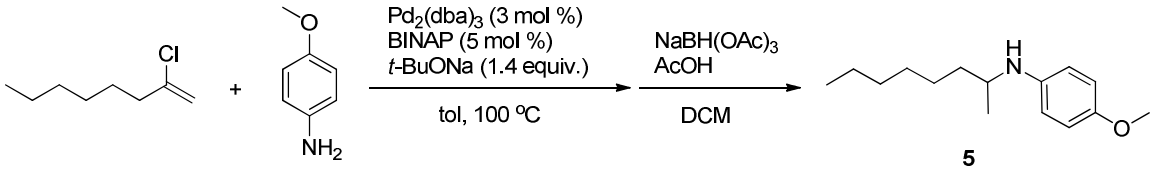
2.4 Procedure for synthesis of 4



4

Boronic acid (0.3 mmol, 49.8 mg), Pd(dppf)Cl_2 (5 mol %) and Na_2CO_3 (0.6 mmol, 63.6 mg) were place into an oven-dried vial, then the vial was vacuumed and purged with argon for three times. Vinylchloride (0.2 mmol, 29.3 mg), EtOH (0.3 ml), toluene (0.3ml) and H_2O (0.3 mL) were injected into the vial through syringe. The vial was placed into a preheated oil bath at 100 °C. The mixture was allowed to stir for overnight. The reaction mixture was cooled down to room temperature and diluted with ethyl acetate (EA) (2 mL). Then the solution was washed with $NaHCO_3$ (aq.). The organic phase was dried over Na_2SO_4. Then Na_2SO_4 was filtered off. After evaporation of solvent, the residue was purified by flash chromatography on silica gel to obtain **4** (EA:Hex=1:15).

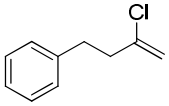
2.5 Procedure for the synthesis of 5



Aniline (0.22 mmol, 27.1 mg), $Pd_2(dba)_3$ (3 mol %, 5.49 mg), BINAP (5 mol %, 6.23 mg) and *t*-BuONa (0.28 mmol, 26.9 mg) were place into an oven-dried vial, then the vial was vacuumed and purged with argon for three times. Vinylchloride (0.2 mmol, 29.3 mg) and toluene (1 mL) were injected into the vial through syringe. The vial was placed into a preheated oil bath at 100 ^{o}C. The mixture was allowed to stir for overnight. The reaction mixture was cooled down to room temperature and toluene was evaporated, followed by adding DCM (1 mL) into the mixture. Then $NaBH(OAc)_3$ (0.4 mmol, 42.4 mg) and AcOH (0.4 mmol, 11.4 µL) were added. The reaction mixture was stirred for 24 h at room temperature, then quenched with 1 M NaOH solution, extracted by DCM (2 mL). The organic phase was washed with H_2O and brine, dried over Na_2SO_4. Na_2SO_4 was then filtered off, the solvent was evaporated and the residue was purified by flash chromatography on silica gel to obtain **5** (EA:Hex=1:8).

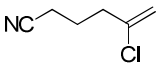
3. Characterization of products

(3-chlorobut-3-en-1-yl) benzene (**2a**)



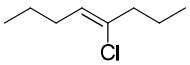
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 – 7.26 (m, 2H), 7.24 – 7.16 (m, 3H), 5.14 (s, 1H), 5.08 (s, 1H), 2.96– 2.80 (t, *J* = 8.0 Hz, 2H), 2.69 – 2.57 (t, *J* = 8.0 Hz, 2H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 141.9, 140.5, 128.4, 126.1, 112.5, 112.7, 41.0, 33.6. Colorless oil, 159.4 mg, 96 % yield.

5-chlorohex-5-enenitrile (**2b**)



^{1}H NMR (400 MHz, $CDCl_3$) δ 5.23 (s, 2H), 2.50 (t, *J* = 7.0 Hz, 2H), 2.36 (t, *J* = 7.0 Hz, 2H), 2.02-1.89 (m, 2H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 139.9, 119.0, 114.3, 37.5, 22.6, 15.7. Colorless oil, 126.4 mg, 98 % yield.

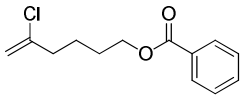
(Z)-4-chlorooct-4-ene (**2c**)



^{1}H NMR (400 MHz, $CDCl_3$) δ 5.42 (t, *J* = 6.9 Hz, 1H), 2.26 (t, *J* = 7.2 Hz, 2H), 2.13 (q, *J* = 7.2 Hz, 2H), 1.55 (dd, *J* = 14.7, 7.4 Hz, 2H), 1.39 (dd, *J* = 14.7, 7.4 Hz, 2H), 0.89 (dt, *J* = 9.7, 7.4 Hz, 6H). **^{13}C**

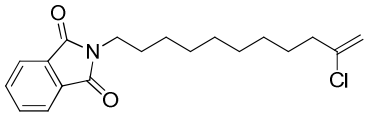
NMR (126 MHz, $CDCl_3$) δ 134.5, 125.1, 41.4, 30.5, 21.9, 20.5, 13.7, 12.9. Colorless oil, 132.9 mg, 91 % yield.

5-chlorohex-5-en-1-yl benzoate (**2d**)



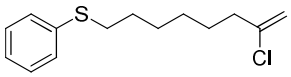
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, *J* = 8.1 Hz, 2H), 7.55 (dd, *J* = 10.8, 4.0 Hz, 1H), 7.44 (t, *J* = 7.6 Hz, 2H), 5.16 (d, *J* = 7.4 Hz, 2H), 4.33 (t, *J* = 6.1 Hz, 2H), 2.41 (t, *J* = 6.9 Hz, 2H), 1.87 – 1.67 (m, 4H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 166.6, 142.3, 132.9, 130.3, 129.5, 128.3, 112.5, 64.5, 38.6, 27.6, 23.6. Colorless oil, 226.2 mg, 95 % yield.

2-(10-chloroundec-10-en-1-yl)isoindoline-1,3-dione (**2e**)



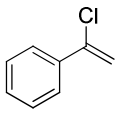
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (dd, *J* = 5.0, 3.0 Hz, 2H), 7.69 (dd, *J* = 5.1, 2.9 Hz, 2H), 5.09 (d, *J* = 8.4 Hz, 2H), 3.65 (t, *J* = 7.2 Hz, 2H), 2.29 (t, *J* = 7.4 Hz, 2H), 1.68 – 1.61 (m, 2H), 1.57 – 1.48 (m, 2H), 1.35 – 1.26 (m, 2H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ168.4, 143.1, 133.8, 132.2, 123.1, 111.7, 39.1, 38.0, 29.3, 29.2, 29.1, 28.5, 28.4, 27.1, 26.8. **HRMS (ESI)** calcd. for [$C_{19}H_{24}NClONa^+$] ([M+Na^+]) 356.1393; found 356.1385. White solid, 303.1 mg, 91 % yield.

(7-chlorooct-7-en-1-yl)(phenyl)sulfane (**2f**)



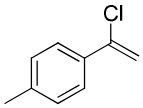
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 – 7.13 (m, 5H), 5.11 (d, *J* = 11.9 Hz, 2H), 2.90 (t, *J* = 7.3 Hz, 2H), 2.31 (t, *J* = 7.4 Hz, 2H), 1.70 – 1.59 (m, 2H), 1.60 – 1.50 (m, 2H), 1.49 – 1.38 (m, 2H), 1.37 – 1.26 (m, 2H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ = 142.9, 136.9, 128.9, 128.8, 125.7, 111.9, 39.0, 33.51, 28.9, 28.4, 28.0, 26.9. Colorless oil, 215.9 mg, 85 % yield.

(1-chlorovinyl) benzene (**2g**)



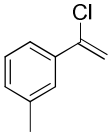
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 – 7.55 (m, 2H), 7.39 – 7.34 (m, 3H), 5.77 (d, *J* = 1.7 Hz, 1H), 5.53 (d, *J* = 1.7 Hz, 1H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 139.9, 136.9, 129.1, 128.3, 126.4, 112.4. Colorless oil, 126.9 mg, 92 % yield.

1-(1-chlorovinyl)-4-methylbenzene (**2h**)



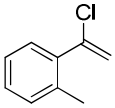
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (d, *J* = 8.1 Hz, 2H), 7.17 (d, *J* = 7.9 Hz, 2H), 5.72 (d, *J* = 1.2 Hz, 1H), 5.47 (d, *J* = 1.1 Hz, 1H), 2.37 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 139.9, 139.2, 134.1, 128.9, 126.27, 111.7, 21.2. Colorless oil, 135.3 mg, 89 % yield.

1-(1-chlorovinyl)-3-methylbenzene (**2i**)



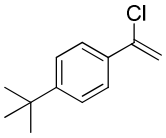
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 – 7.43 (m, 2H), 7.27 – 7.16 (m, 2H), 5.75 (s, 1H), 5.51 (s, 1H), 2.38 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 140.1, 137.9, 136.9, 129.8, 128.2, 127.1, 123.5, 112.5, 21.4. Colorless oil, 121.6 mg, 80 % yield.

1-(1-chlorovinyl)-2-methylbenzene (**2j**)



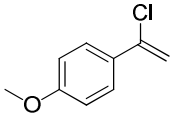
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 – 7.11 (m, 4H), 5.64 (d, *J* = 1.1 Hz, 1H), 5.34 (d, *J* = 1.1 Hz, 1H), 2.42 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 139.5, 138.7, 135.8, 130.4, 128.9, 125.7, 116.5, 116.4, 19.8. Colorless oil, 136.8, 90 % yield.

1-(tert-butyl)-4-(1-chlorovinyl) benzene (**2k**)



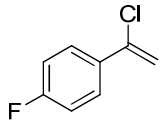
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (d, *J* = 8.3 Hz, 2H), 7.38 (d, *J* = 8.2 Hz, 2H), 5.73 (s, 1H), 5.47 (s, 1H), 1.32 (s, 9H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 152.3, 139.9, 134.1, 126.1, 125.2, 111.8, 34.6, 31.2. Colorless oil, 192.1 mg, 99 % yield.

1-(1-chlorovinyl)-4-methoxybenzene (**2l**)



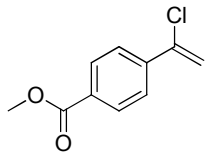
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (d, *J* = 8.0 Hz, 2H), 6.87 (d, *J* = 8.0 Hz, 2H), 5.65 (d, *J* = 1.7 Hz, 1H), 5.41 (d, *J* = 1.7 Hz, 1H), 3.82 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 160.3, 139.6, 129.5, 127.7, 113.6, 110.8, 55.3. Colorless oil, 139.4 mg, 83 % yield.

1-(1-chlorovinyl)-4-fluorobenzene (**2m**)



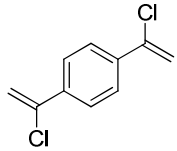
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.64 – 7.61 (m, 2H), 7.08 – 7.05 (m, 2H), 5.72 (d, *J* = 1.8 Hz, 1H), 5.52 (d, *J* = 1.8 Hz, 1H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 163.2 (d, *J* = 199 Hz), 138.9, 133.1, 128.3, 115.3, 112.6. Colorless oil. **^{19}F NMR (376 MHz, $CDCl_3$)** δ -112.28. Pale yellow oil, 135.7 mg, 87 % yield.

methyl 4-(1-chloroethenyl) benzoate (**2n**)



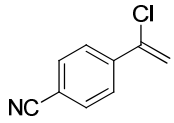
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, *J* = 8.3 Hz, 2H), 7.66 (d, *J* = 8.3 Hz, 2H), 5.85 (d, *J* = 1.5 Hz, 1H), 5.60 (d, *J* = 1.5 Hz, 1H), 3.90 (s, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 166.4, 140.9, 138.9, 130.5, 129.5, 126.3, 114.6, 52.1. Yellow solid, 158.7 mg, 81 % yield.

1,4-di(1-chloroethenyl) benzene (**2o**)



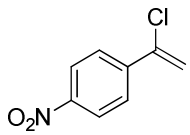
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, *J* = 1.0 Hz, 4H), 5.81 (d, *J* = 1.3 Hz, 2H), 5.56 (d, *J* = 1.3 Hz, 2H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 139.1, 137.4, 126.3, 113.4. White solid, 148.5 mg, 75 % yield.

4-(1-chlorovinyl) benzonitrile (2p)



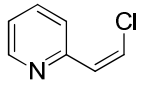
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, *J* = 8.4 Hz, 2H), 7.64 (d, *J* = 8.4 Hz, 2H), 5.88 (d, *J* = 2.0 Hz, 1H), 5.67 (d, *J* = 2.0 Hz, 1H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 138.1, 132.7, 132.2, 126.9, 118.3, 115.8, 112.6. White solid, 130.4 mg, 80 % yield.

1-(1-chlorovinyl)-4-nitrobenzene (**2q**)



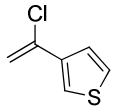
^{1}H NMR (400 MHz, $CDCl_3$) 2r: δ 8.21 (d, *J* = 8.6 Hz, 2H), 7.79 (t, *J* = 9.4 Hz, 2H), 5.99 – 5.86 (m, 1H), 5.72 (d, *J* = 1.7 Hz, 1H). **^{13}C NMR (126 MHz, $CDCl_3$) 2r/2r'**: δ 142.7, 140.4, 129.9, 127.5, 127.3, 123.6, 123.5, 121.8, 116.41. Yellow solid, 135.4 mg, 74 % yield.

(Z)-2-(2-chlorovinyl) pyridine (**2r**)



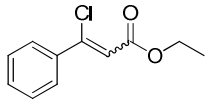
^{1}H NMR (700 MHz, $CDCl_3$) δ 8.62 (d, *J* = 3.5 Hz, 1H), 8.02 (d, *J* = 8.0 Hz, 1H), 7.71 (td, *J* = 7.8, 1.6 Hz, 1H), 7.19 (dd, *J* = 6.5, 4.9 Hz, 1H), 6.85 (d, *J* = 8.4 Hz, 1H), 6.48 (d, *J* = 8.4 Hz, 1H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 153.2, 149.5, 136.1, 130.4, 124.1, 122.6, 120.51. Yellow oil, 97.3 mg, 70 % yield.

3-(1-chlorovinyl) thiophene (**2s**)



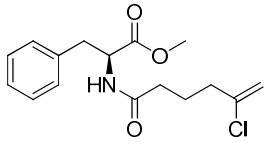
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (s, 1H), 7.33 – 7.20 (m, 2H), 5.69 (s, 1H), 5.43 (s, 1H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 138.9, 134.6, 126.4, 125.0, 124.3, 111.4. Yellow oil, 138.2 mg, 96 % yield.

(Z)-ethyl 3-chloro-3-phenylacrylate and (E)-ethyl 3-chloro-3-phenylacrylate (**2t**)



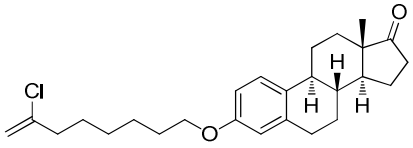
^{1}H NMR (500 MHz, $CDCl_3$) (Z) δ 7.71- 7.69 (m, 2H), 7.57 – 7.34 (m, 3H), 6.56 (s, 1H, *Z*), 6.37 (s, 1H, *E*), 4.29 (q, *J* = 7.1 Hz, 2H, *Z*), 4.07 (q, *J* = 7.1 Hz, 2H, *E*), 1.35 (t, *J* = 7.1 Hz, 3H, *Z*), 1.13 (t, *J* = 7.1 Hz, 3H, *E*). **^{13}C NMR (126 MHz, $CDCl_3$) *Z*/*E***: δ 164.2, 163.8, 149.7, 146.1, 137.3, 130.6, 129.9, 128.6, 128.4, 127.8, 127.2, 119.9, 116.4, 60.6, 14.2, 13.9. Colorless liquid, 138.6 mg, 66 % yield

(S)-methyl 2-(5-chlorohex-5-enamido)-3-phenylpropanoate (**2u**)



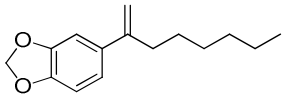
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28-7.25 (m, 3H), 7.09-7.07 (m, 2H), 7.57-7.54 (m, 1H), 5.86 (s, 1H), 5.11 (d, *J* = 24.0 Hz, 2H), 4.92-4.87 (m, 1H), 3.73 (s, 1H), 3.16-3.05 (m, 2H), 2.33 (t, *J* = 8.0 Hz, 2H), 2.18 (t, *J* = 8.0 Hz, 2H), 1.90-1.85 (m, 2H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 172.1, 171.8, 141.8, 135.7, 129.2, 128.6, 127.2, 112.9, 52.9, 52.3, 38.1, 37.8, 34.6, 22.7. **HRMS (ESI)** calcd. for $[C_{16}H_{20}NClO_3Na^+]$ ($[M+Na^+]$) 332.1029; found 332.1031. Colorless oil, 213.3 mg, 69 % yield.

(8R,9S,13S,14S)-3-((7-chlorooct-7-en-1-yl)oxy)-13-methyl-7,8,9,11,12,13,15,16-octahydro-6H-cyclopenta[a]phenanthren-17(14H)-one (**2v**)



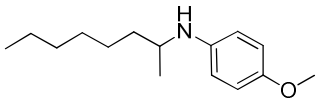
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.18 (d, *J*=8.0 Hz, 1H), 6.71-6.69 (m, 1H), 6.63 (s, 1H), 5.11 (d, *J* = 8.0 Hz, 2H), 3.91 (t, *J* = 8.0 Hz, 2H), 2.90-2.87 (m, 2H), 2.52-2.45 (m, 2H), 2.39-2.31 (m, 3H), 2.26-2.22 (m, 1H), 2.18-1.93 (m, 4H), 1.80-1.73 (m, 2H), 1.64-1.37 (m, 11H), 0.90 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 220.9, 157.1, 142.9, 137.7, 131.9, 126.3, 114.5, 114.5, 112.1, 111.9, 67.7, 50.4, 47.9, 43.9, 39.0, 38.4, 25.9, 31.6, 29.6, 29.2, 28.2, 27.1, 26.6, 25.9, 25.8, 21.6, 13.8. **HRMS (ESI)** calcd. for $[C_{26}H_{35}ClO_2Na^+]$ ($[M+Na^+]$) 437.2223; found 437.2213. White solid, 393.5 mg, 95 % yield.

5-(oct-1-en-2-yl)benzo[d][1,3]dioxole(**4**)



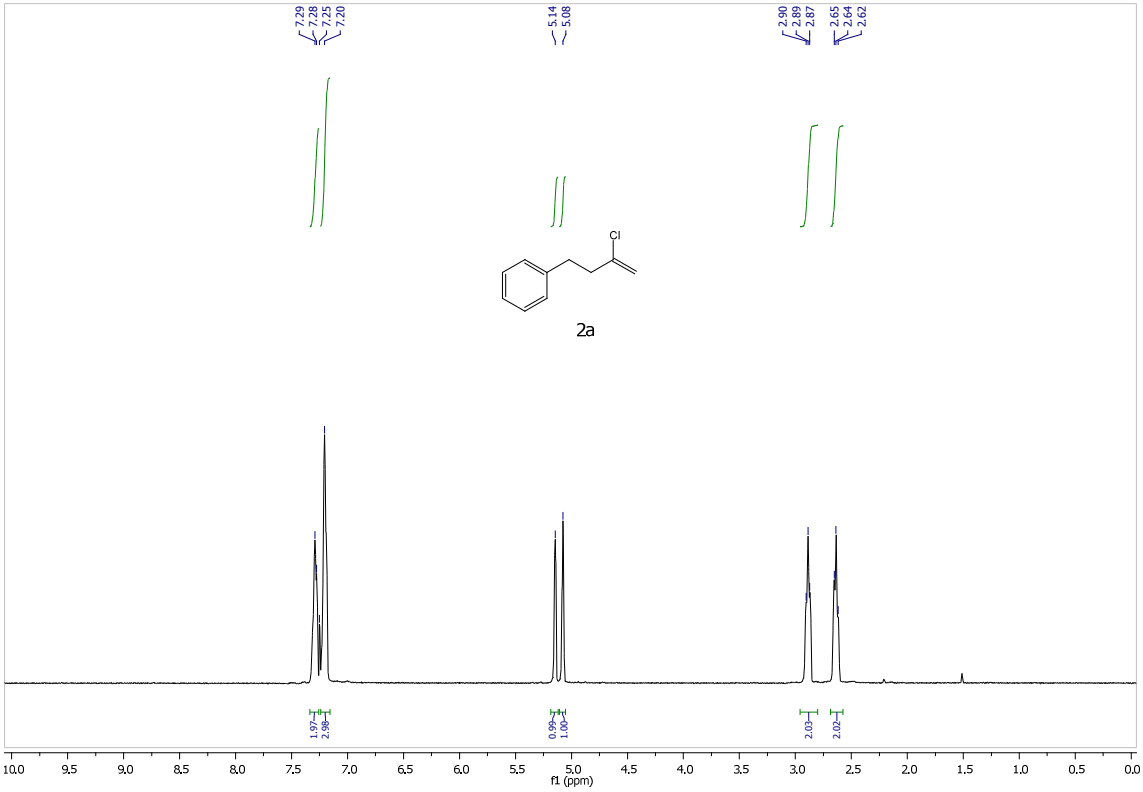
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.90-6.87 (m, 2H), 6.76 (d, *J* = 8.0 Hz, 1H), 5.94 (s, 2H), 5.15 (s, 1H), 4.96 (s, 1H), 2.42 (t, *J* = 8.0 Hz, 2H), 1.42 – 1.19 (m, 8H), 0.87 (t, *J* = 8.0 Hz, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ = 148.2, 147.6, 146.7, 135.8, 119.5, 111.1, 107.9, 106.7, 100.9, 35.6, 31.7, 28.9, 28.3, 22.6, 14.1. Colorless oil, 174.1 mg, 75 % yield.

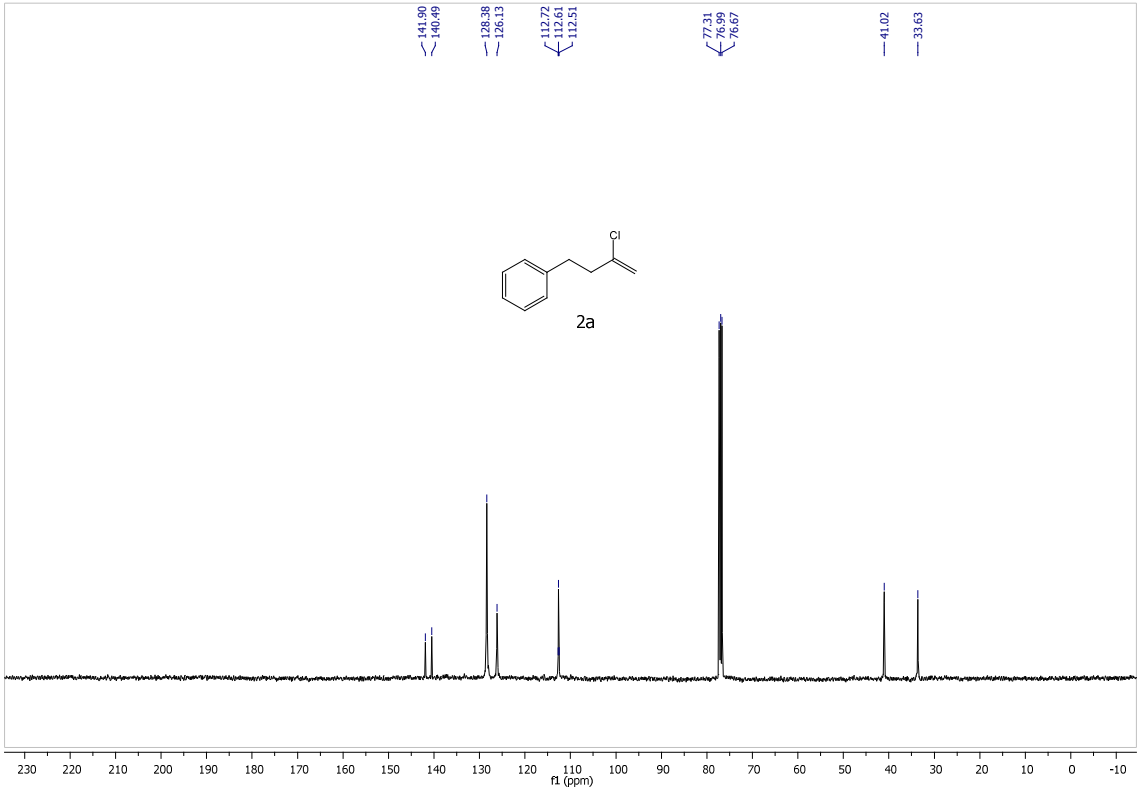
4-methoxy-N-(octan-2-yl)aniline (**5**)

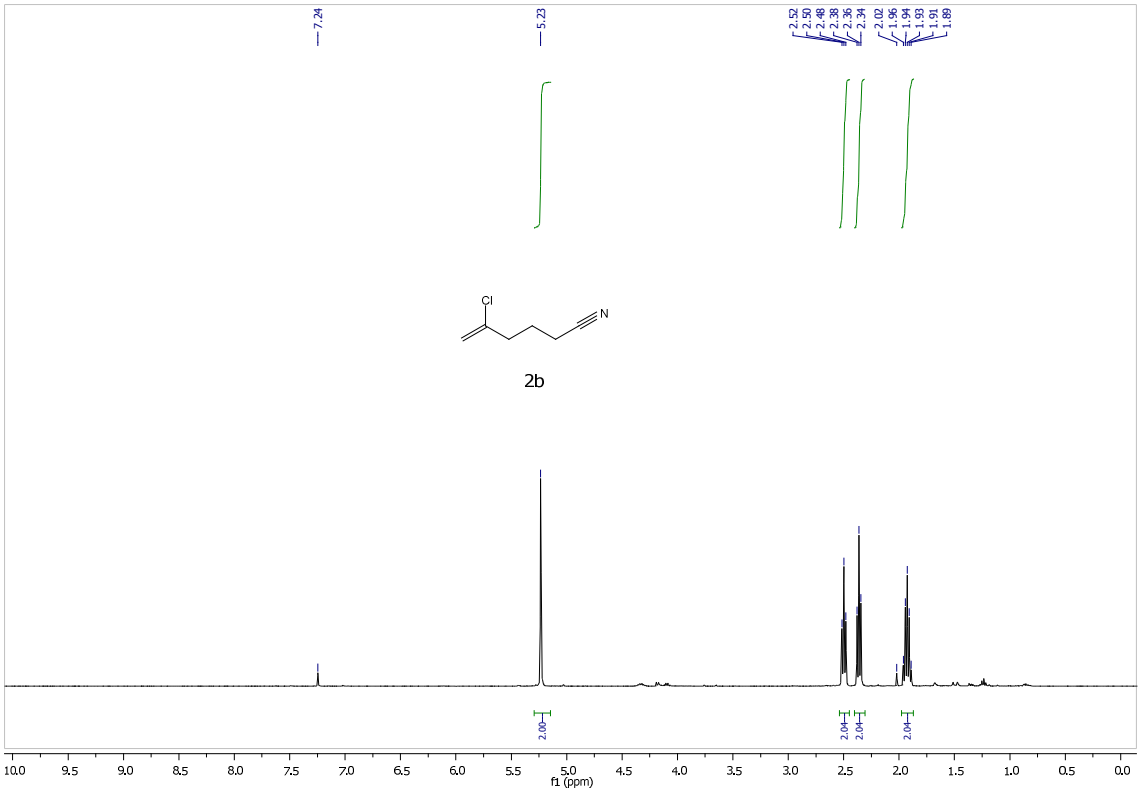


^{1}H NMR (400 MHz, $CDCl_3$) δ 6.76 (d, *J* = 8.0 Hz, 2H), 6.55 (d, *J* = 8.0 Hz, 2H), 3.74 (s, 1H), 3.37-3.33 (m, 1H), 3.05 (s, 1H), 1.36-1.27 (m, 10H), 1.14 (d, *J* = 8.0 Hz, 3H), 0.88 (t, *J* = 8.0 Hz, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 151.8, 141.9, 114.9, 114.6, 55.9, 49.6, 37.2, 31.8, 29.4, 26.1, 22.6, 20.81, 14.0. Colorless oil, 157.6 mg, 67 % yield.

4. Copies of NMR spectra for compounds 2, 4 and 5



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2.50
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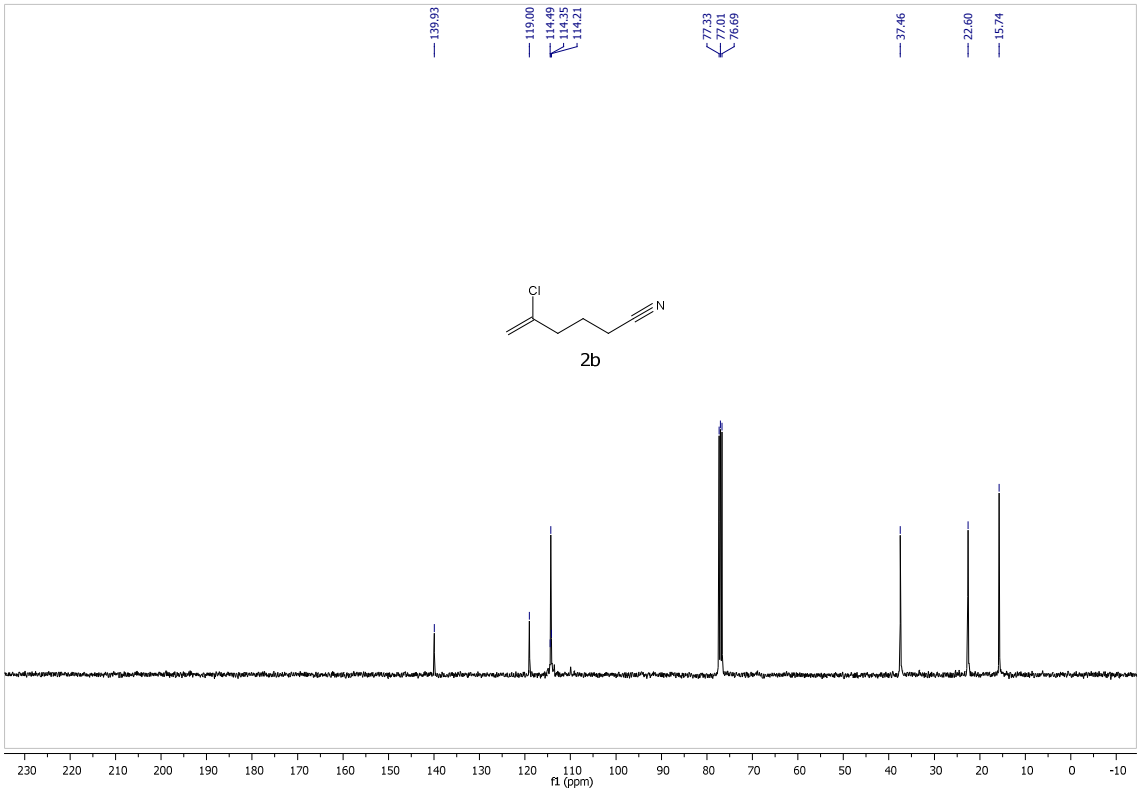
2.36
2.34
2.02
1.96
1.94
1.93
1.91
1.89
Cl
N
2b
2.00
2.04
2.04
2.04
f1 (ppm)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114.49
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114.21
77.33
77.01
76.69
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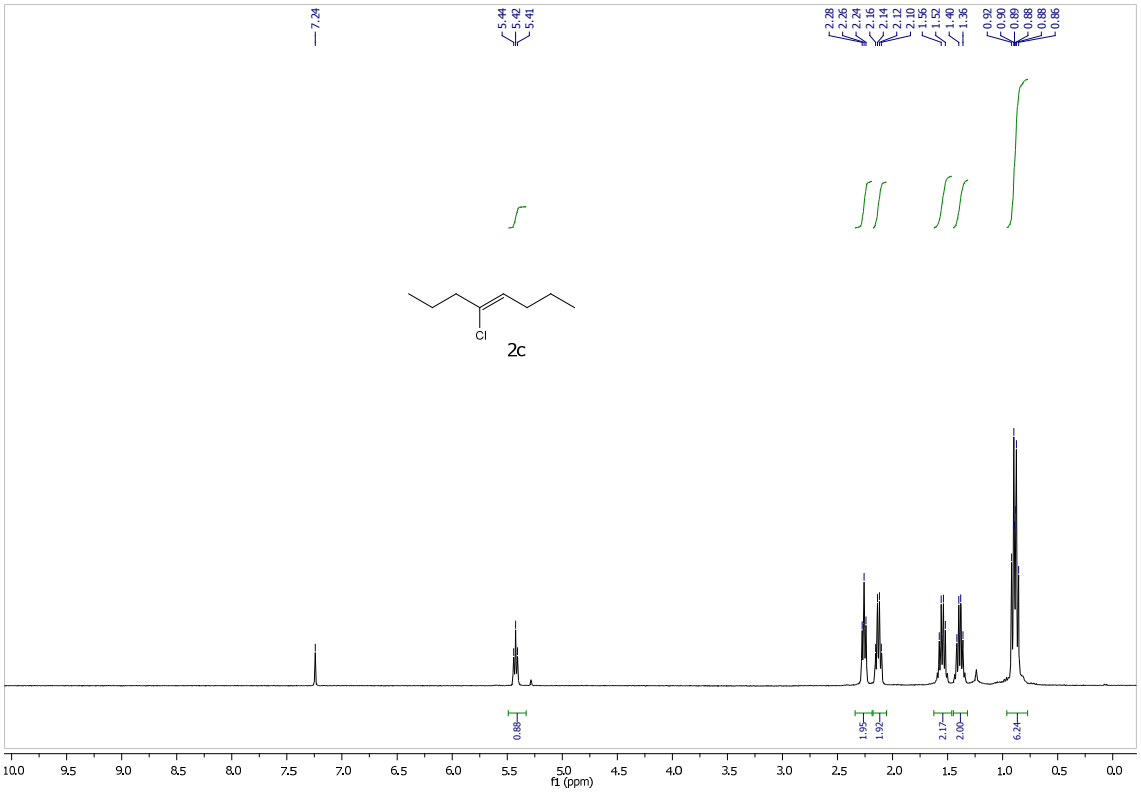
22.60
15.74
Cl
N
2b
f1 (ppm)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5.44
5.42
5.41
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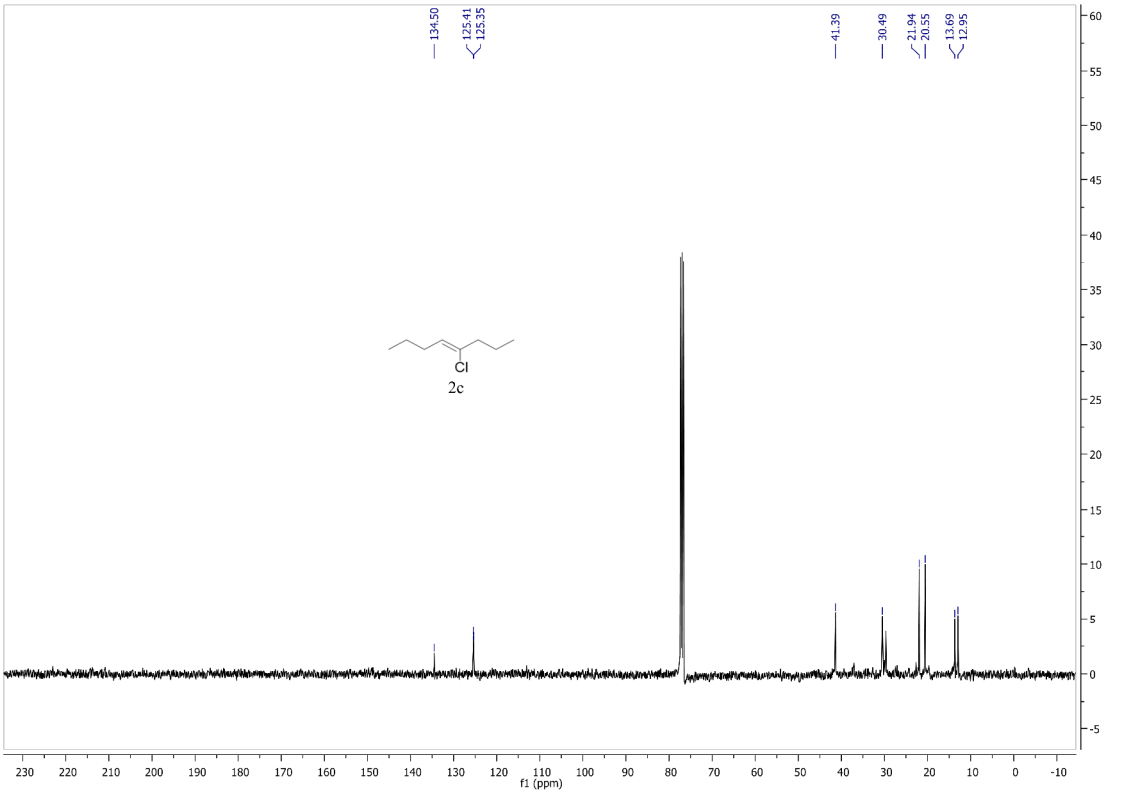
2.26
2.24
2.16
2.14
2.12
2.10
1.56
1.52
1.40
1.36
0.92
0.90
0.89
0.88
0.88
0.86
Cl
2c
0.88
1.99
1.92
2.17
2.00
6.24
f1 (ppm)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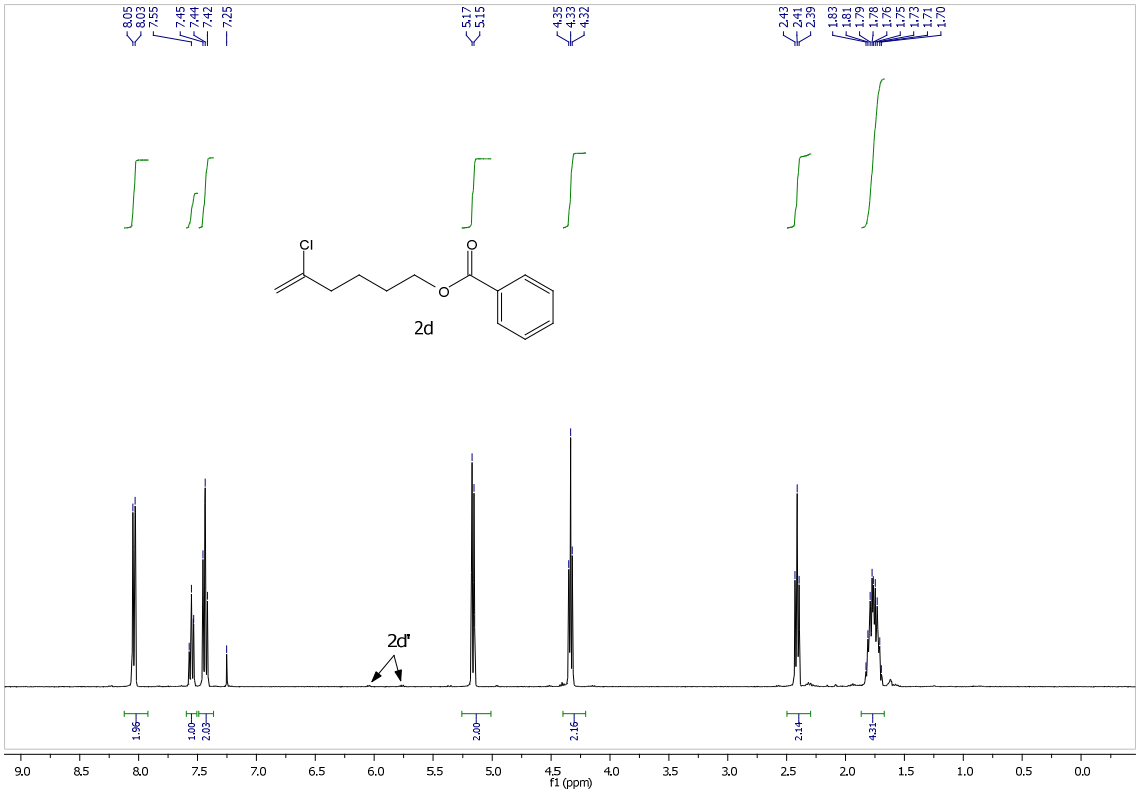
41.39
30.49
21.94
20.55
13.69
12.95
Cl
2c
f1 (ppm)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8.03
7.55
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7.25
5.17
5.15
4.35
4.33
4.32
2.43
2.41
2.39
1.83
1.81
1.79
1.78
1.76
1.75
1.73
1.71
1.70
Cl
O
O
2d
2d'
1.96
1.00
2.03
2.00
2.16
2.14
4.31
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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4.5
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2.0
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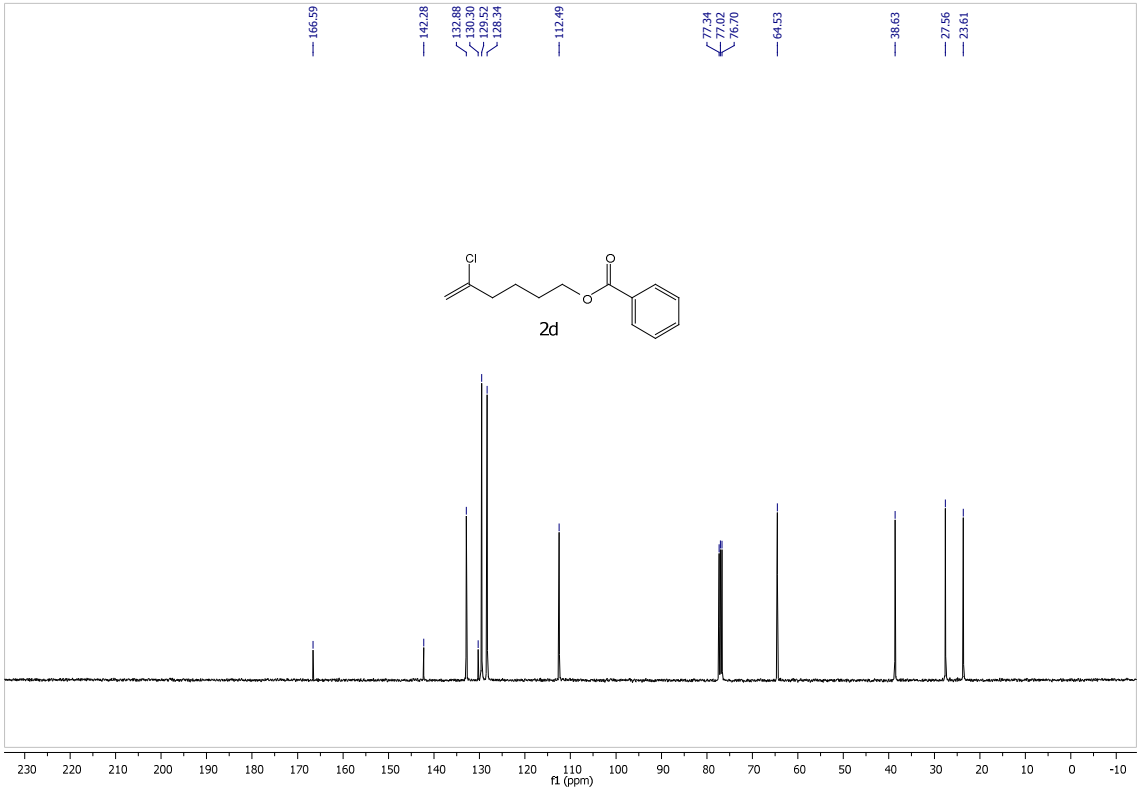
0.0
f1 (ppm)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132.88
130.30
129.52
128.34
112.49
77.34
77.02
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64.53
38.63
27.56
23.61
Cl
O
O
2d
230
220
210
200
190
180
170
160
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120
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100
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80
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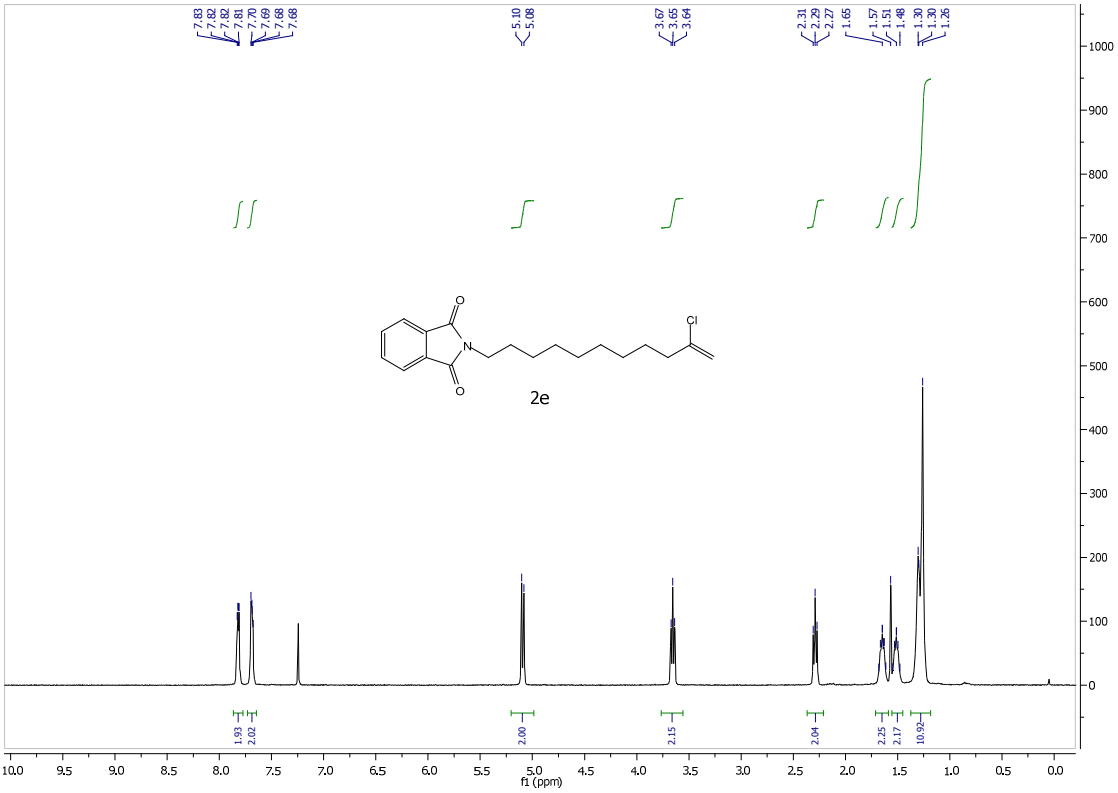
f1 (ppm)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7.69
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7.68
7.68
5.10
5.08
3.67
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3.64
2.31
2.29
2.27
1.65
1.57
1.51
1.48
1.30
1.30
1.26
O
N
O
Cl
2e
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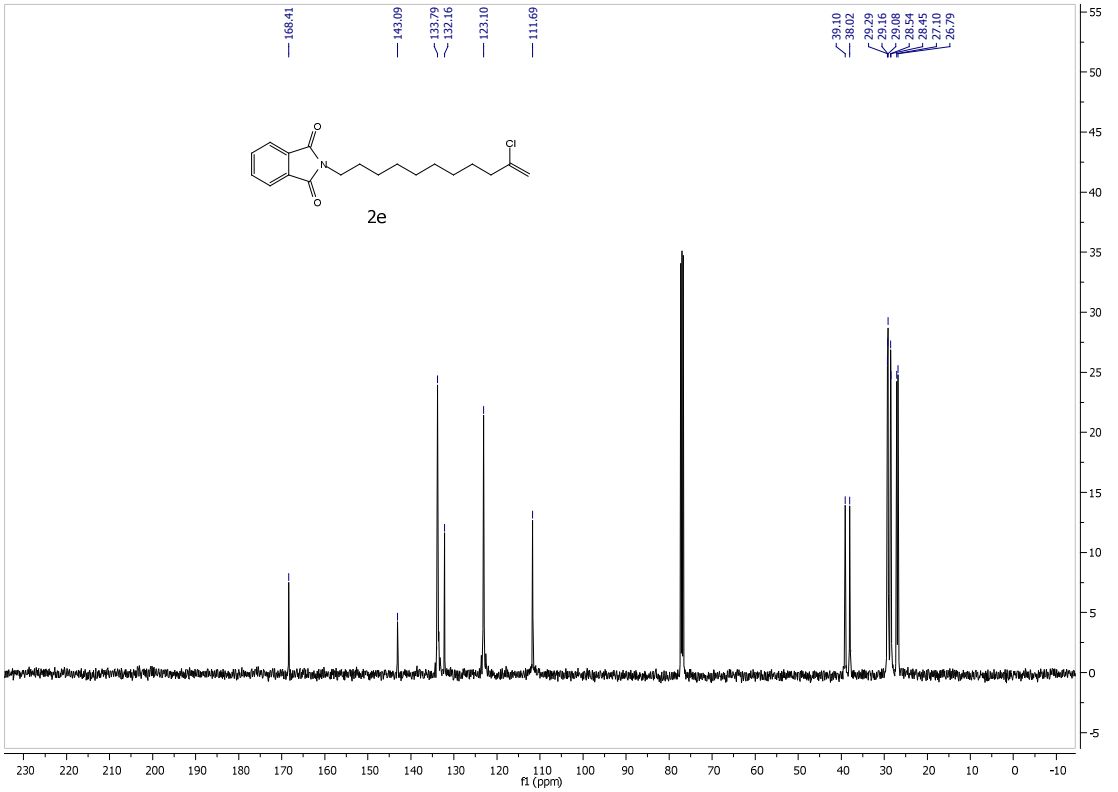
2.02
2.00
2.15
2.04
2.25
2.17
10.92
f1 (ppm)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123.10
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39.10
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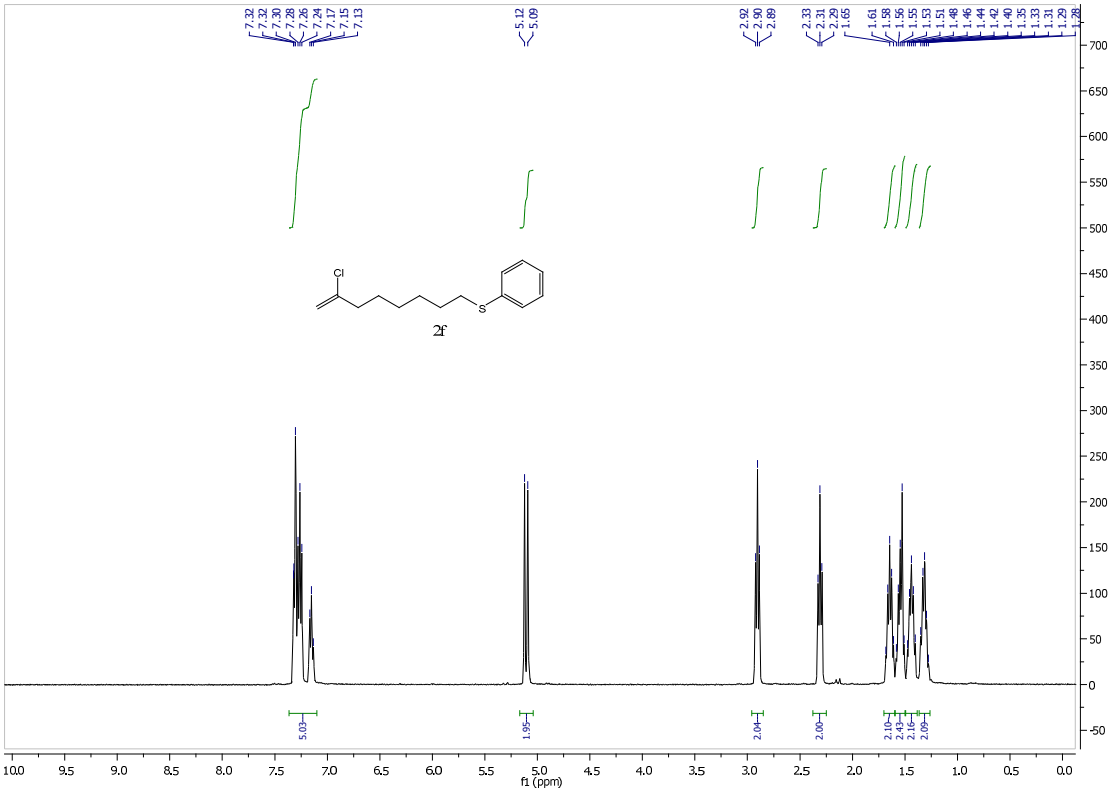
28.54
28.45
27.10
26.79
O
N
O
Cl
2e
f1 (ppm)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5.12
5.09
2.92
2.90
2.89
2.33
2.31
2.29
1.65
1.61
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1.55
1.53
1.51
1.48
1.46
1.44
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1.40
1.35
1.33
1.31
1.29
1.28
Cl
S
2f
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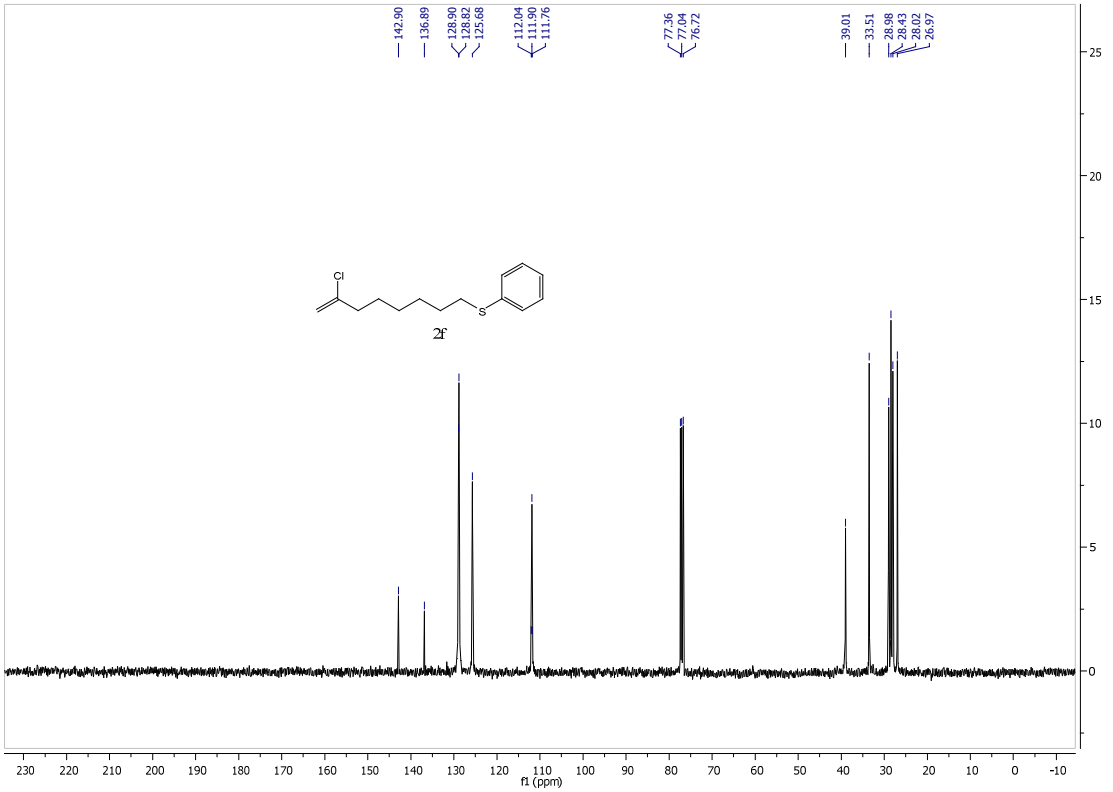
2.04
2.00
2.10
2.43
2.16
2.09
f1 (ppm)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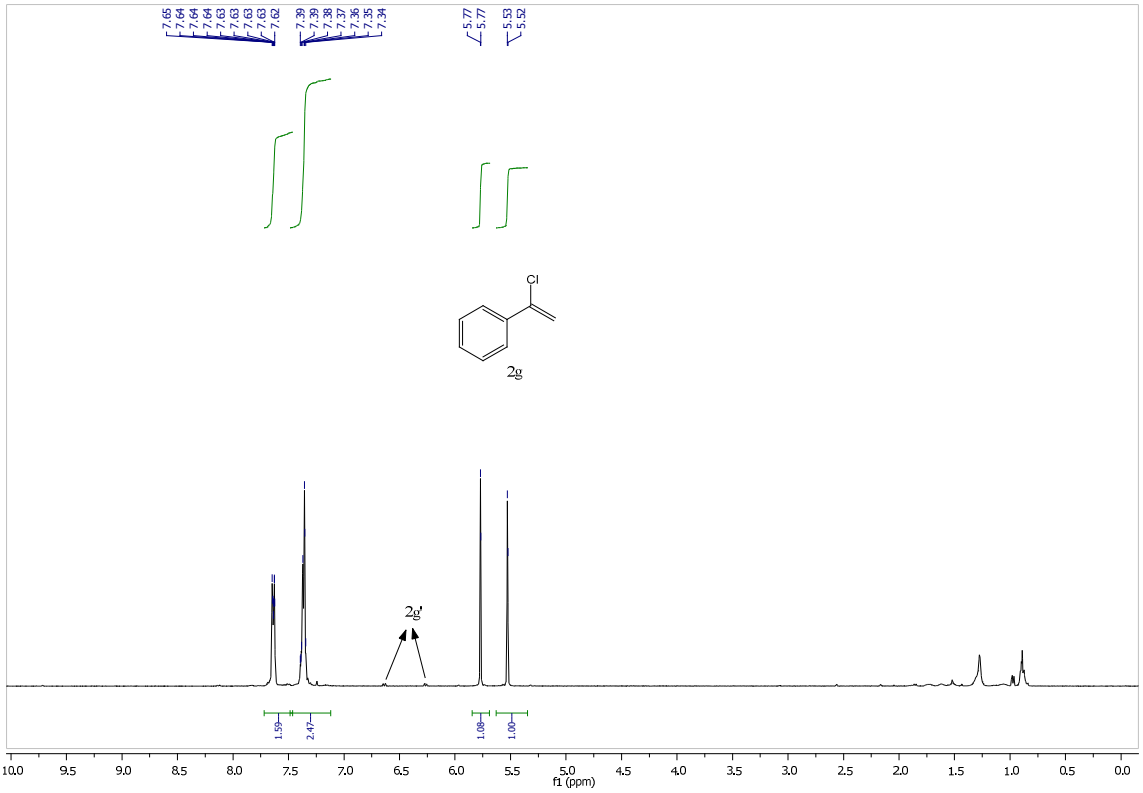
28.02
26.97
Cl
S
2f
f1 (ppm)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7.36
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7.34
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5.53
5.52
Cl
2g
2g'
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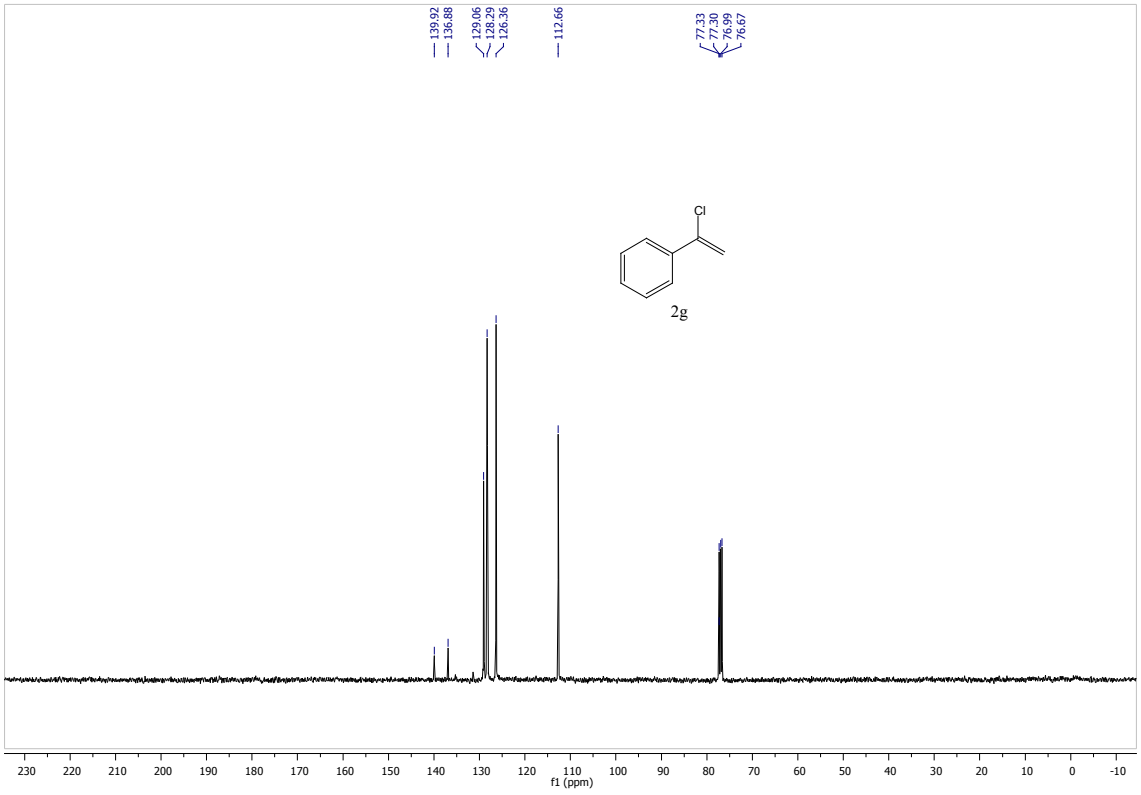
2.47
1.08
1.00
f1 (ppm)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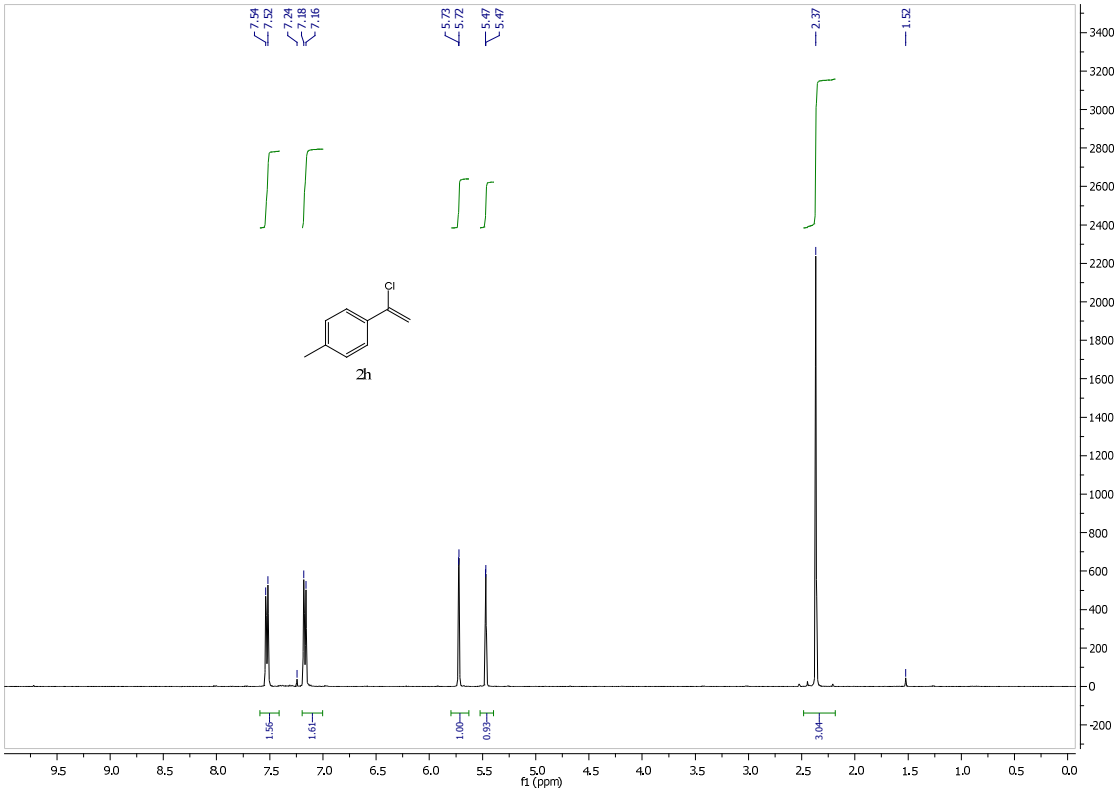
Cl
2g
f1 (ppm)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Cl
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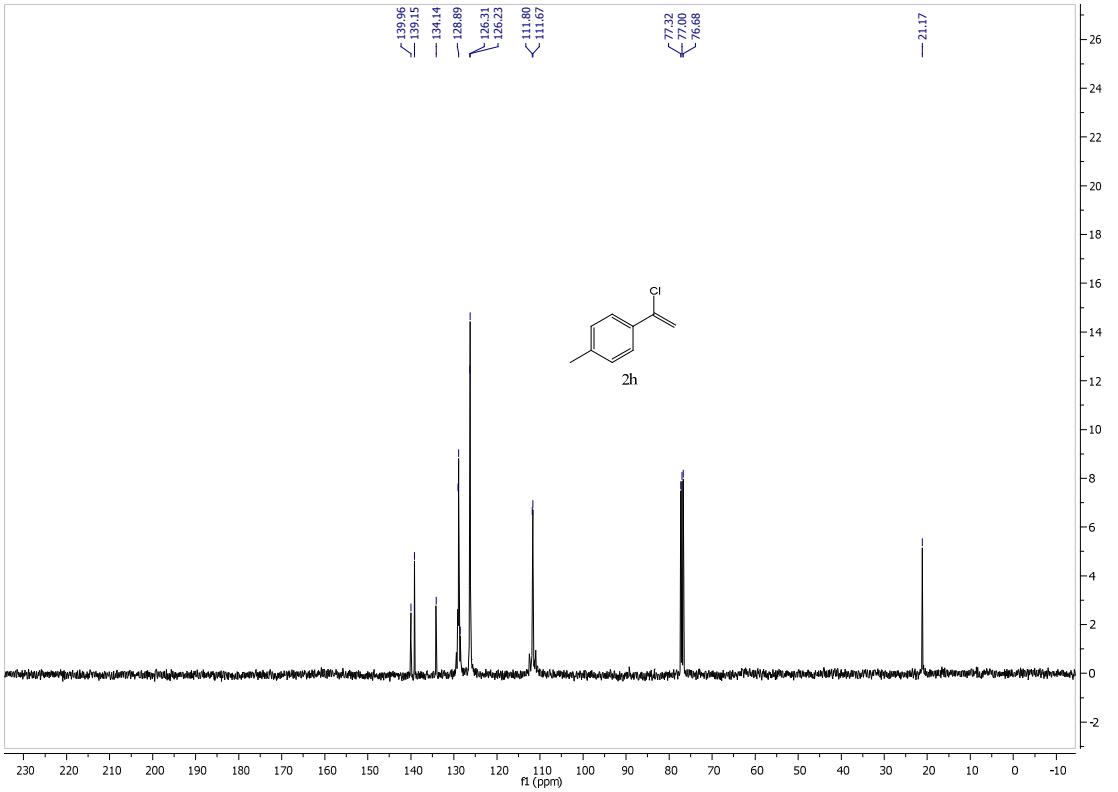
f1 (ppm)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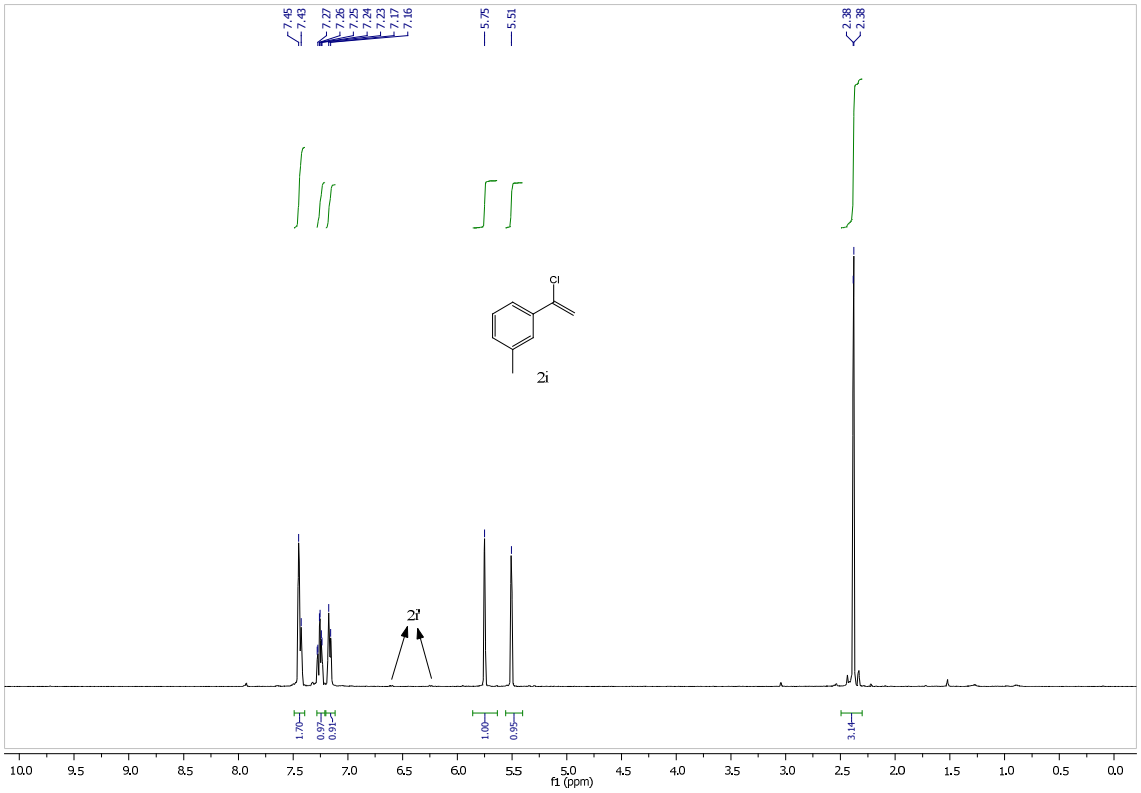
Cl
2h
f1 (ppm)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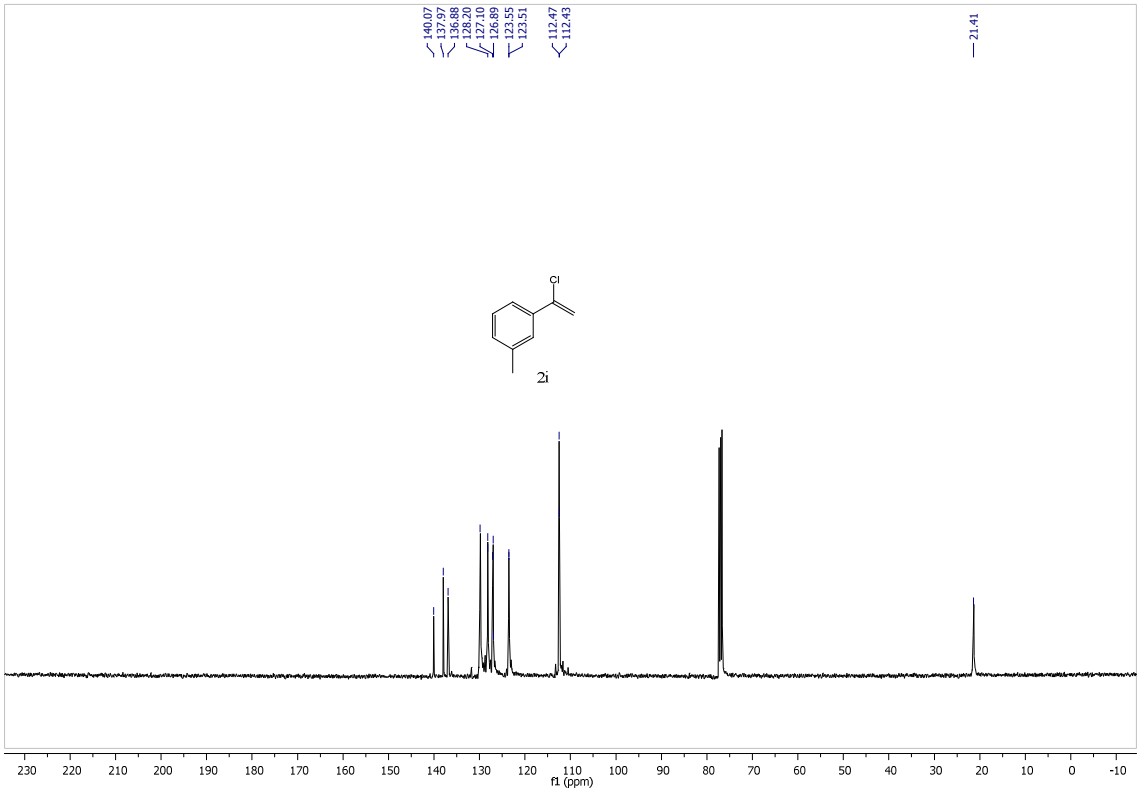
Cl
2i
2i'
1.70
0.97
0.91
1.00
0.95
3.14
f1 (ppm)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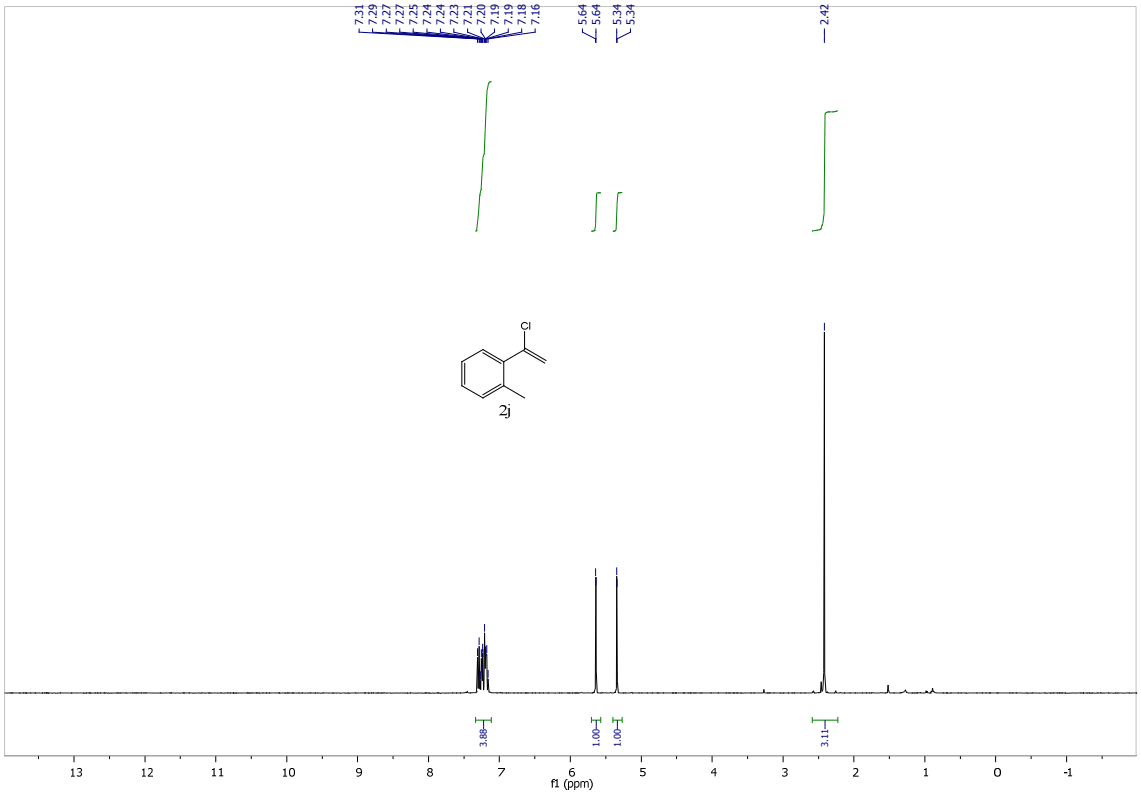
Cl
2i
f1 (ppm)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5.34
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Cl
2j
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11
10
9
8
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4
3
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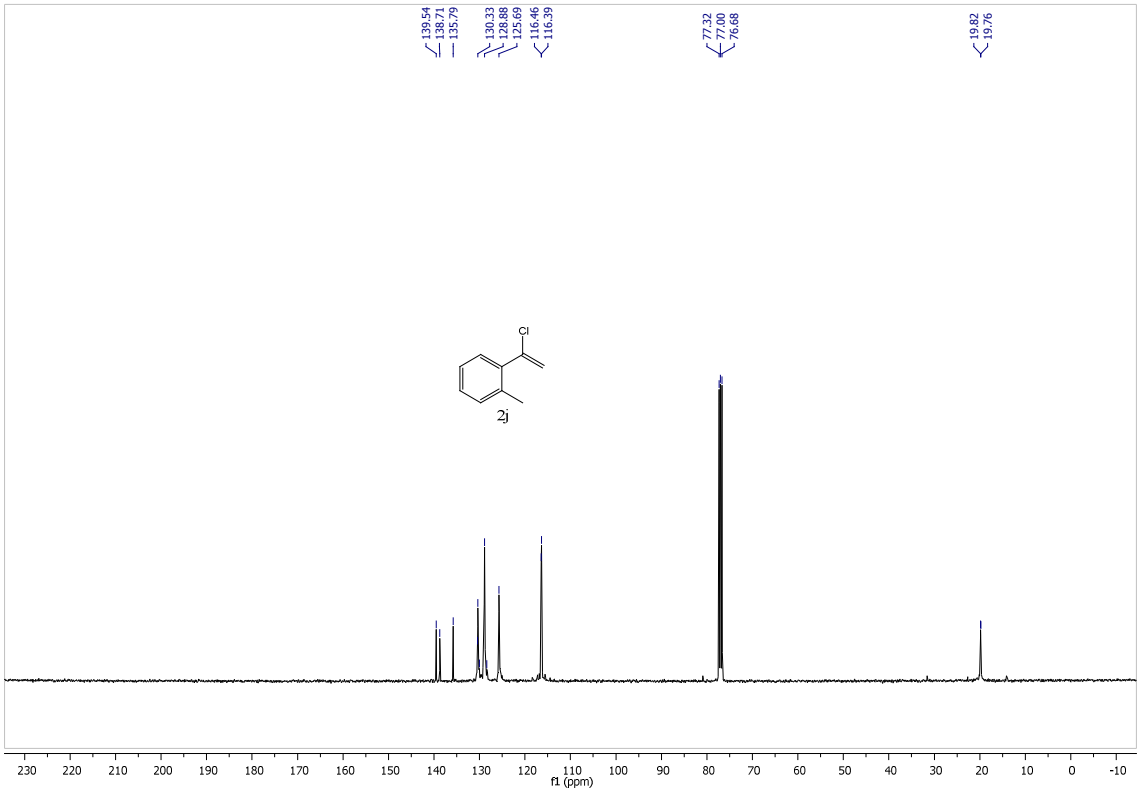
f1 (ppm)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19.76
Cl
2j
230
220
210
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190
180
170
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100
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80
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40
30
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0
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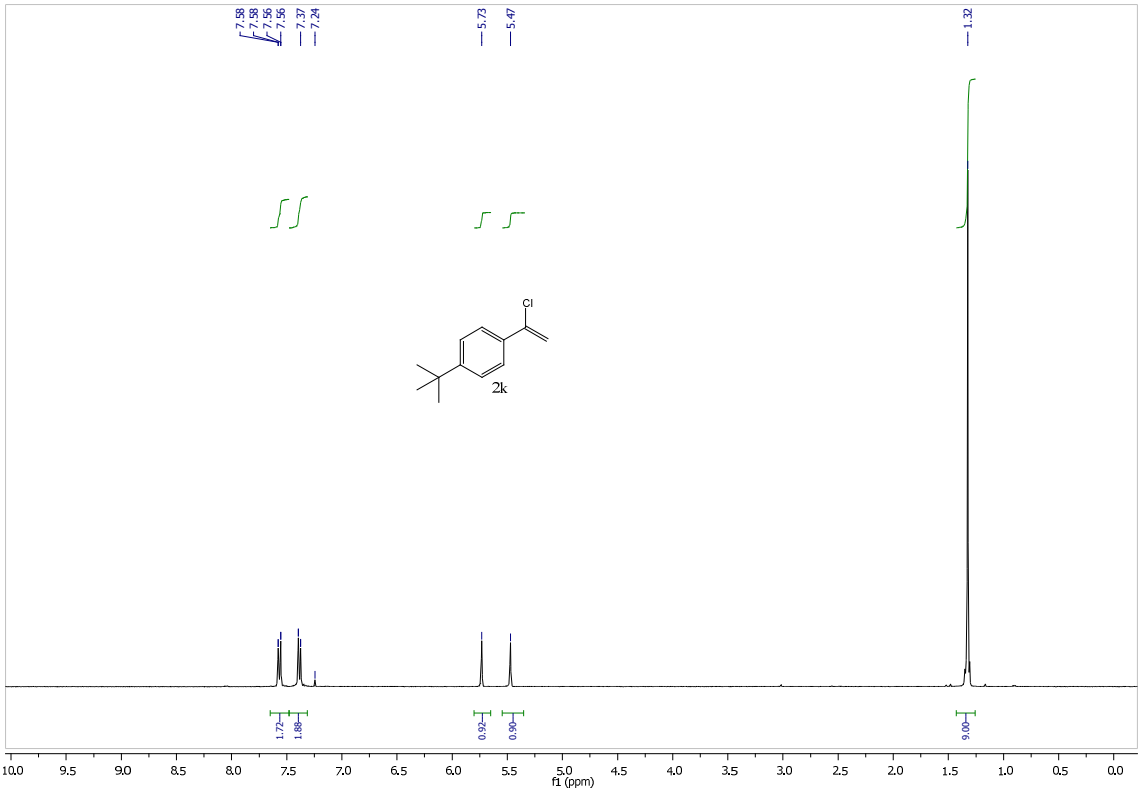
f1 (ppm)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5.47
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Cl
2k
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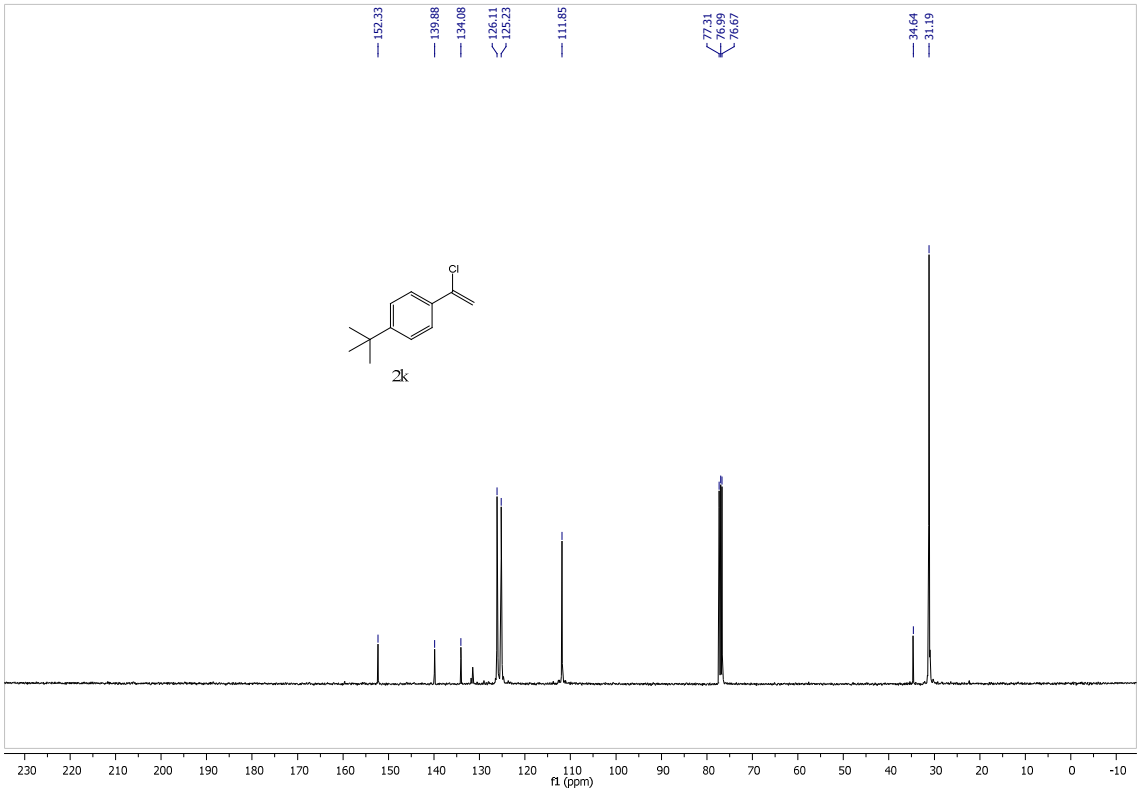
0.92
0.90
9.00
f1 (ppm)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34.64
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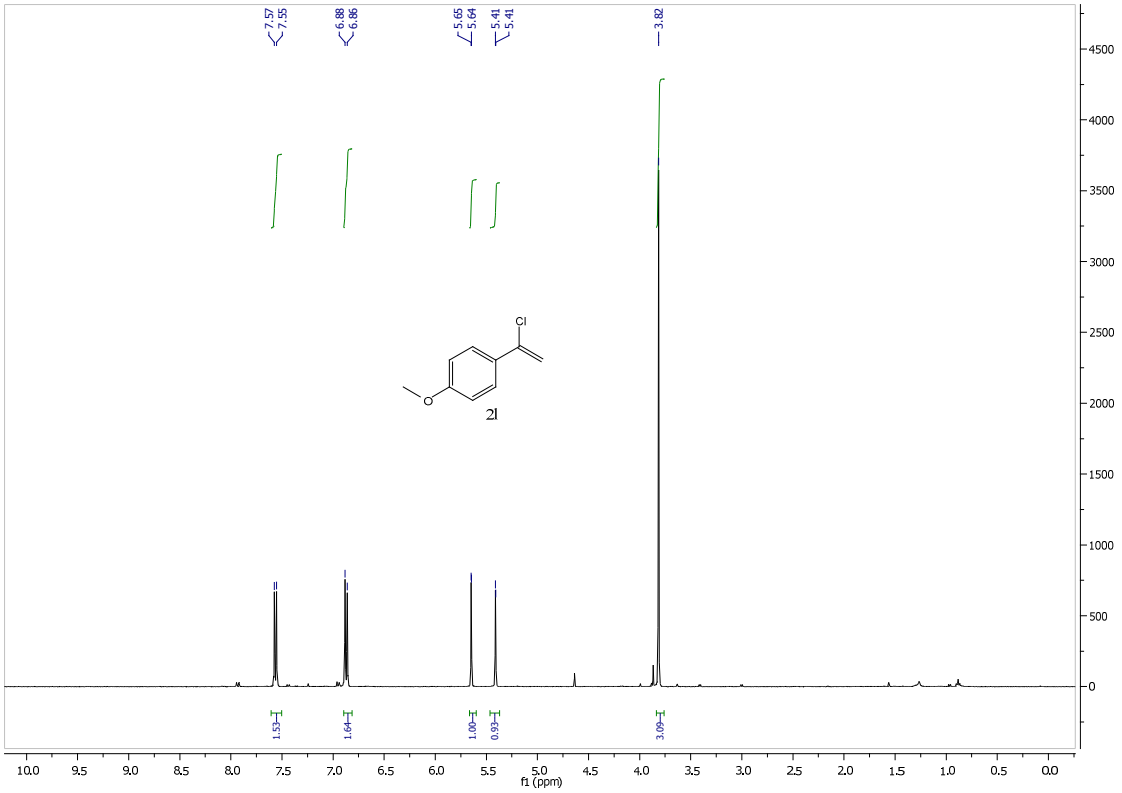
Cl
2k
f1 (ppm)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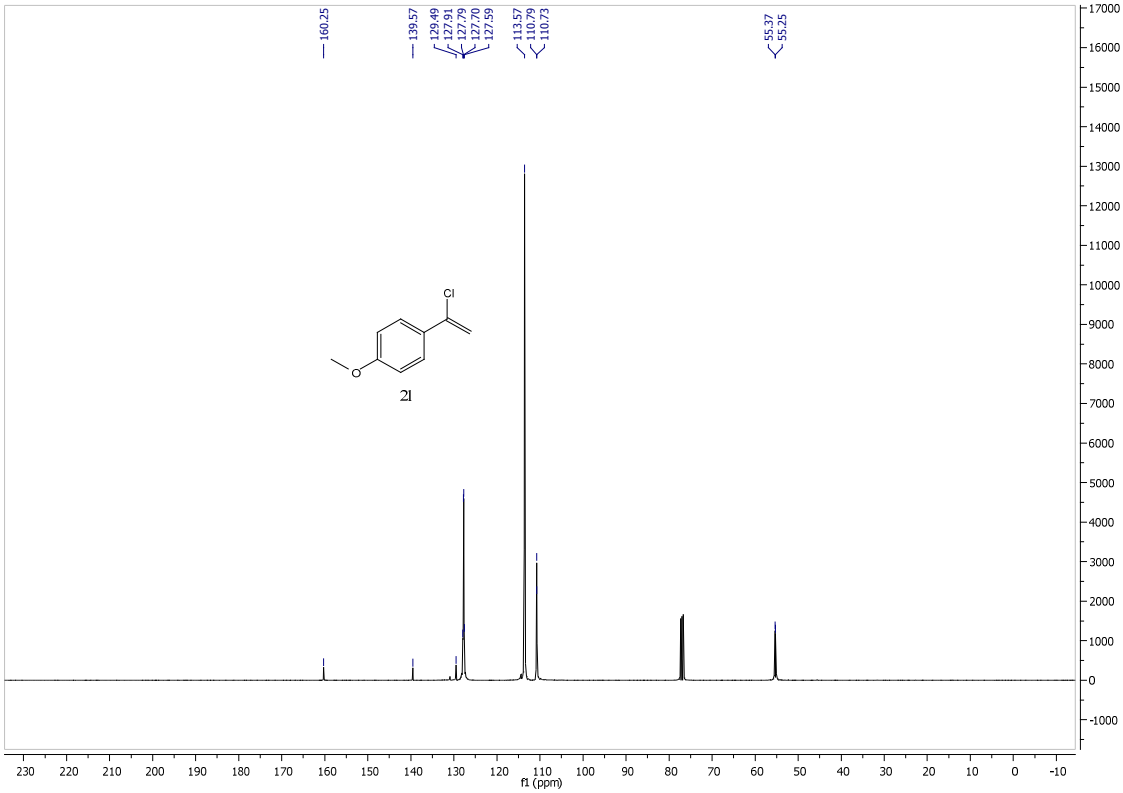
5.41
3.82
Cl
O
2l
1.53
1.64
1.00
0.93
3.09
f1 (ppm)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139.57
129.49
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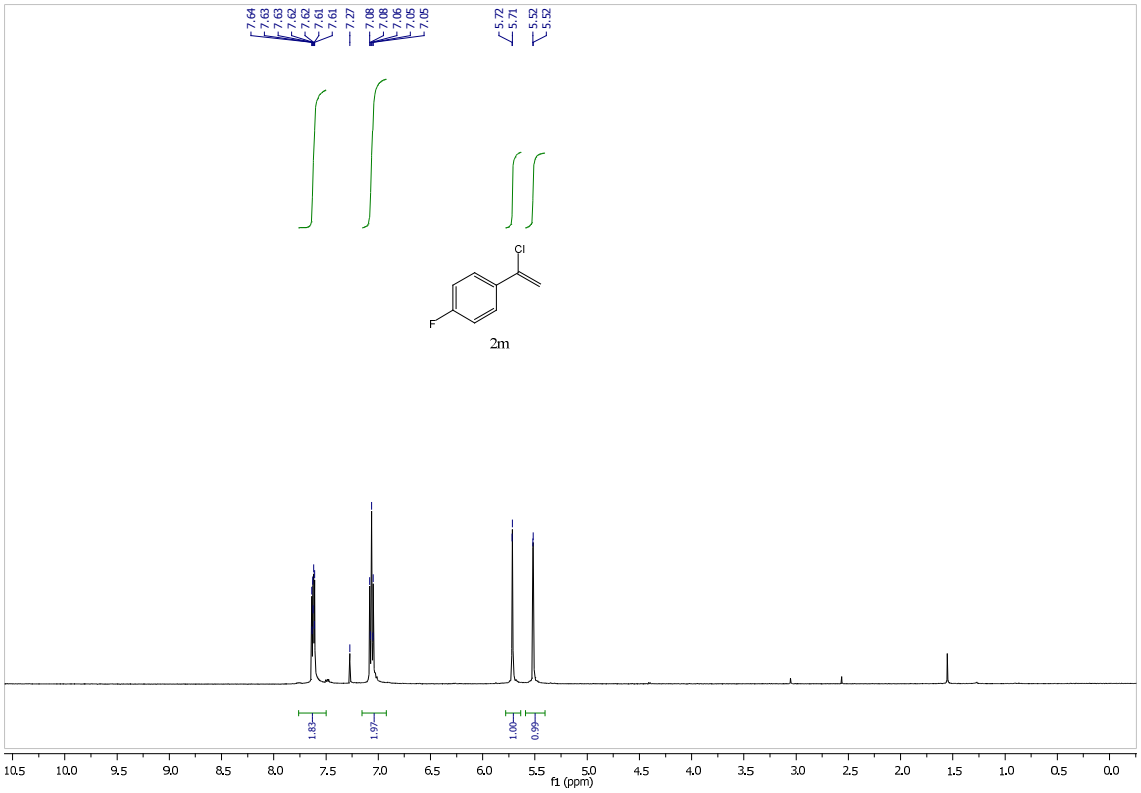
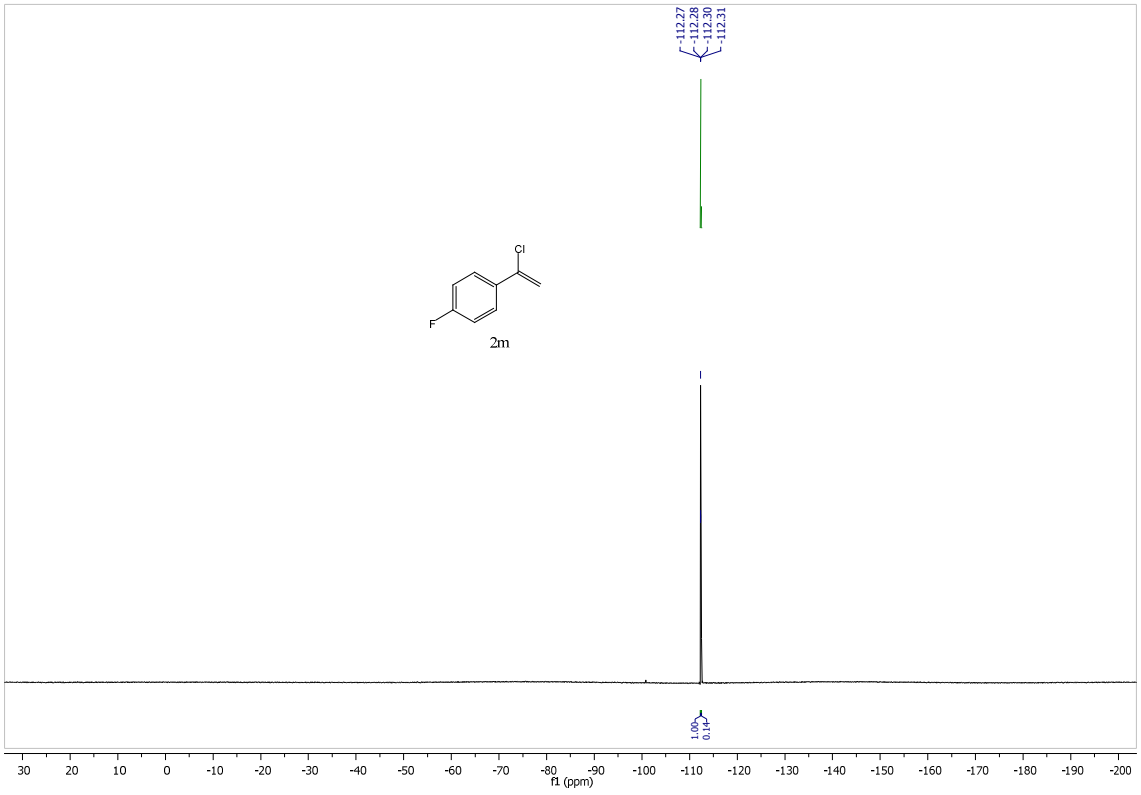
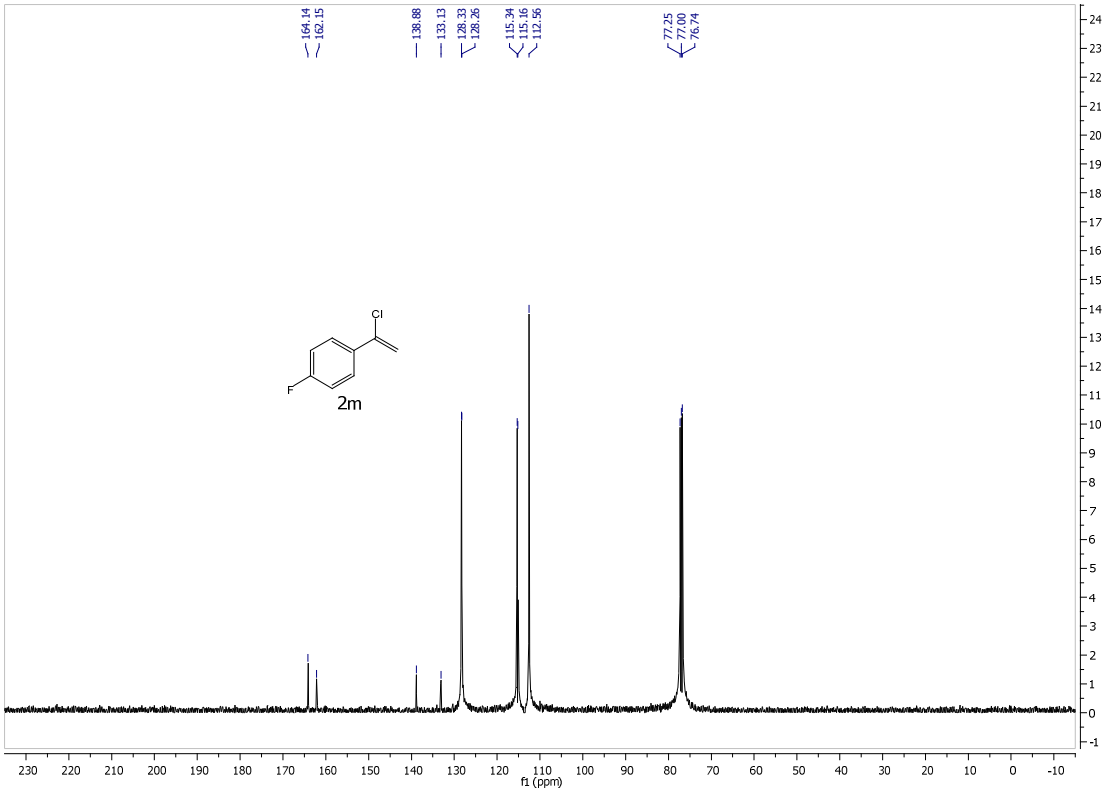
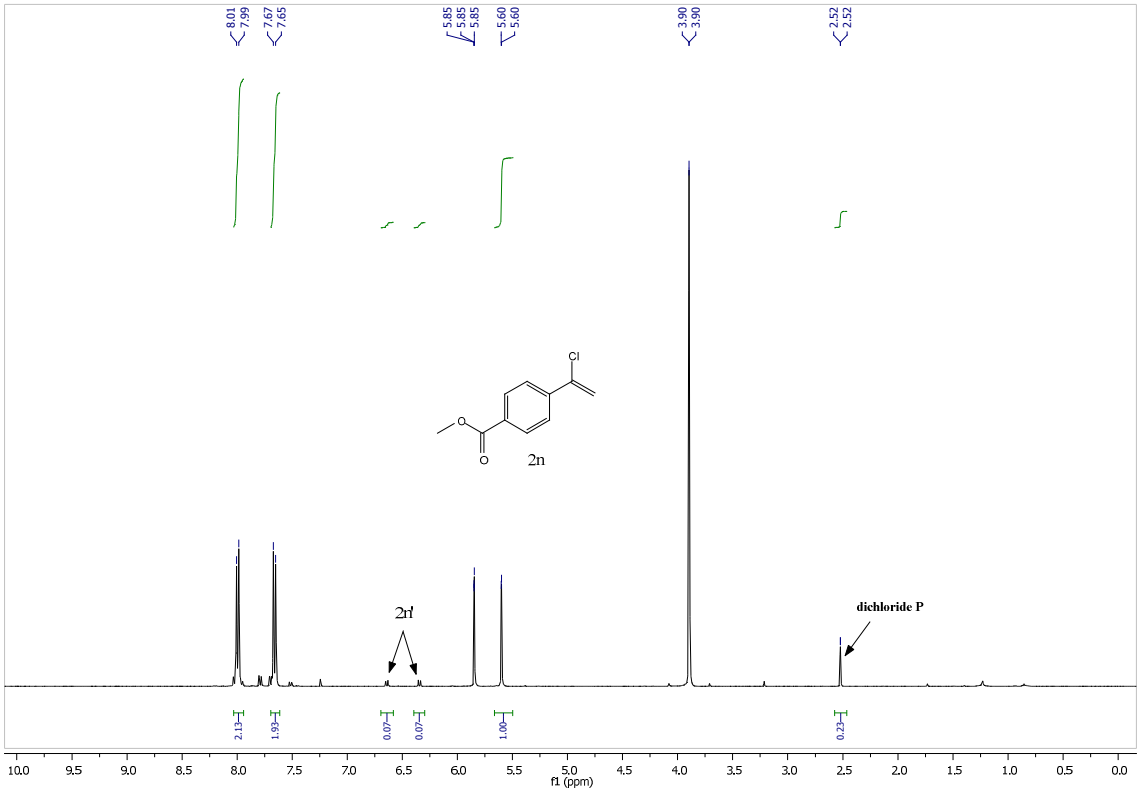
127.59
113.57
110.79
110.73
55.37
55.25
Cl
O
2l
f1 (ppm)


7.64
7.63
7.63
7.62
7.62
7.61
7.61
7.27
7.08
7.06
7.05
7.05
5.72
5.71
5.52
5.52
Cl
F
2m
1.83
1.97
1.00
0.99
f1 (ppm)


-112.27
-112.28
-112.30
-112.31
Cl
F
2m
1.00
0.14
f1 (ppm)


164.14
162.15
138.88
133.13
128.33
128.26
115.34
115.16
112.96
77.25
77.00
76.74
Cl
F
2m
f1 (ppm)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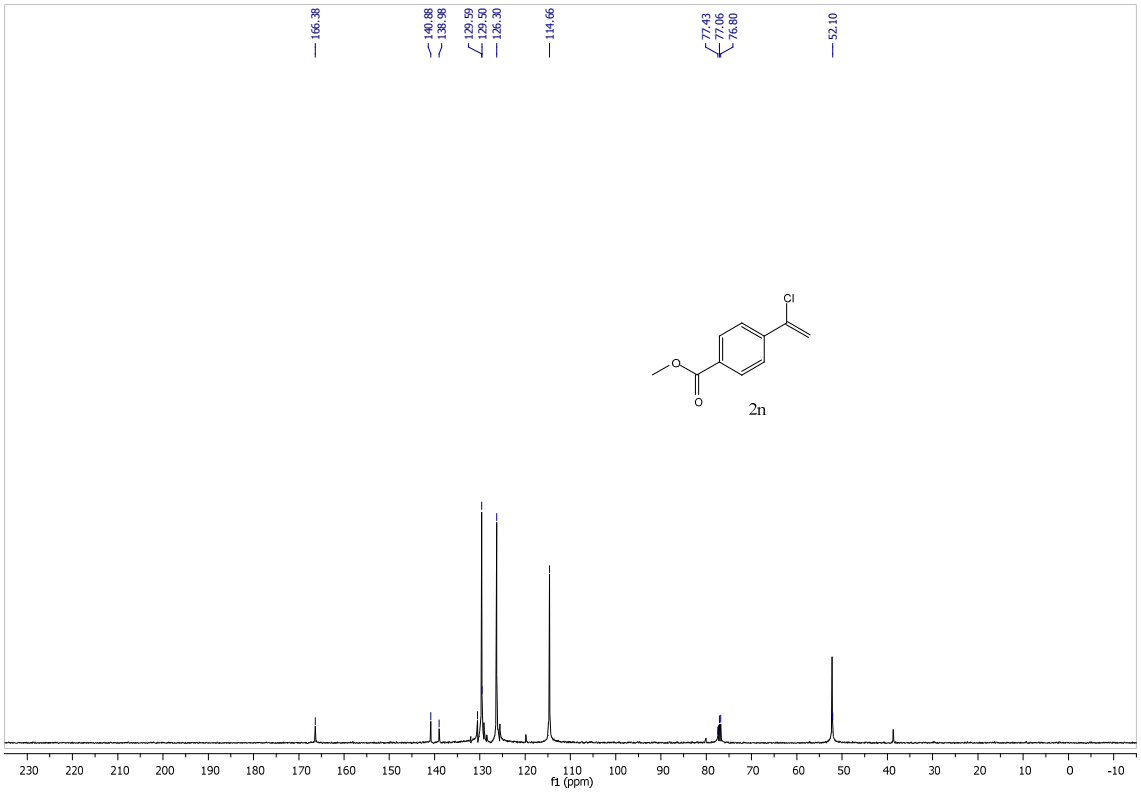
7.99
7.67
7.65
5.85
5.85
5.85
5.60
5.60
3.90
3.90
2.52
2.52
Cl
O
O
2n
2n'
dichloride P
2.13
1.93
0.07
0.07
1.00
0.23
f1 (ppm)


166.38
140.88
138.98
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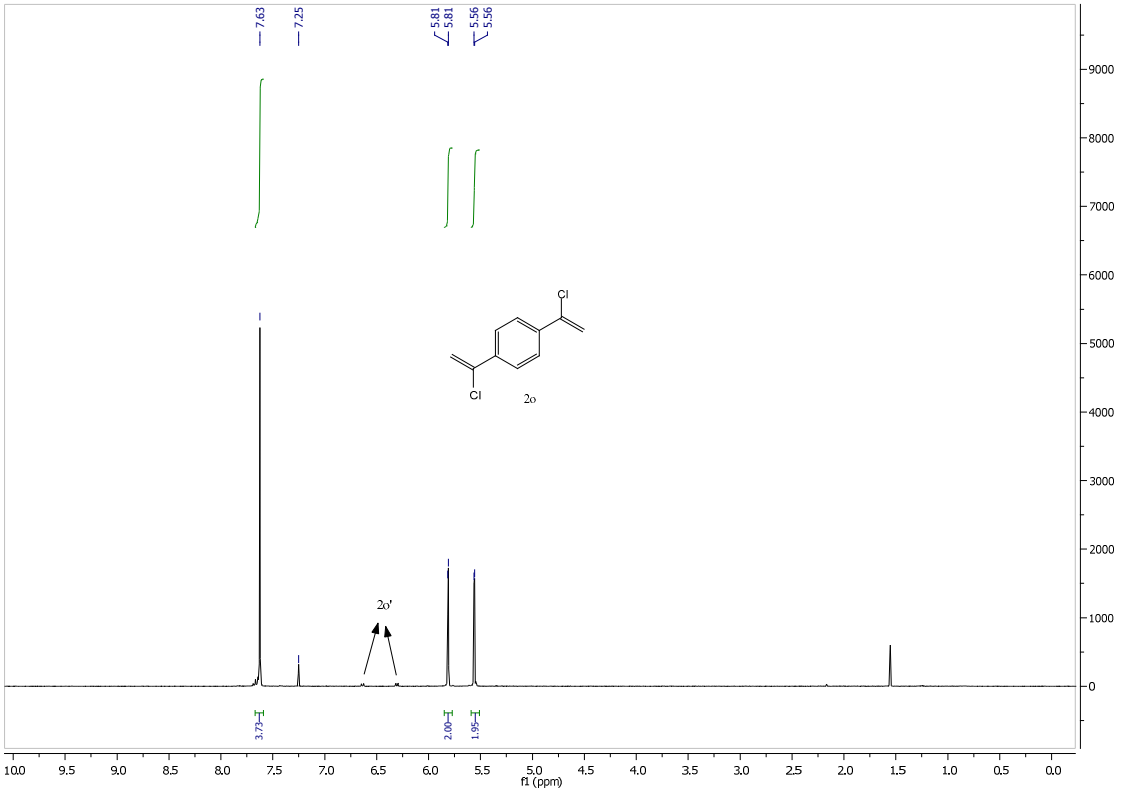
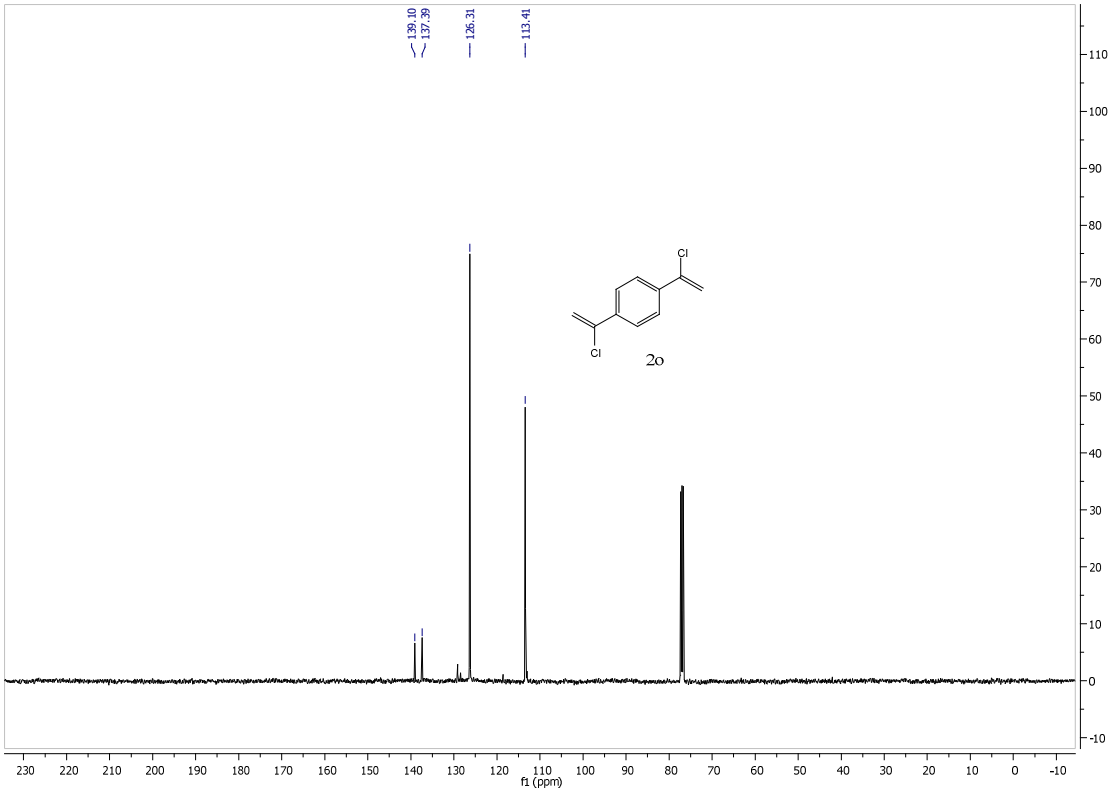
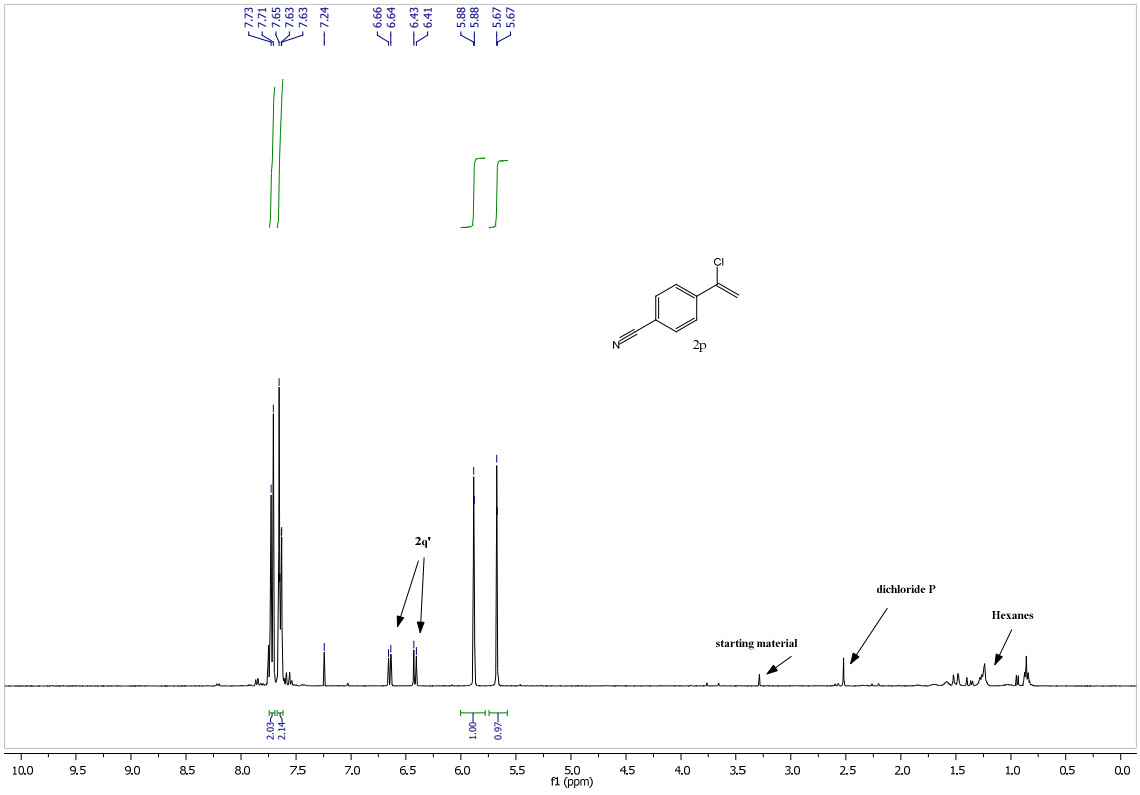
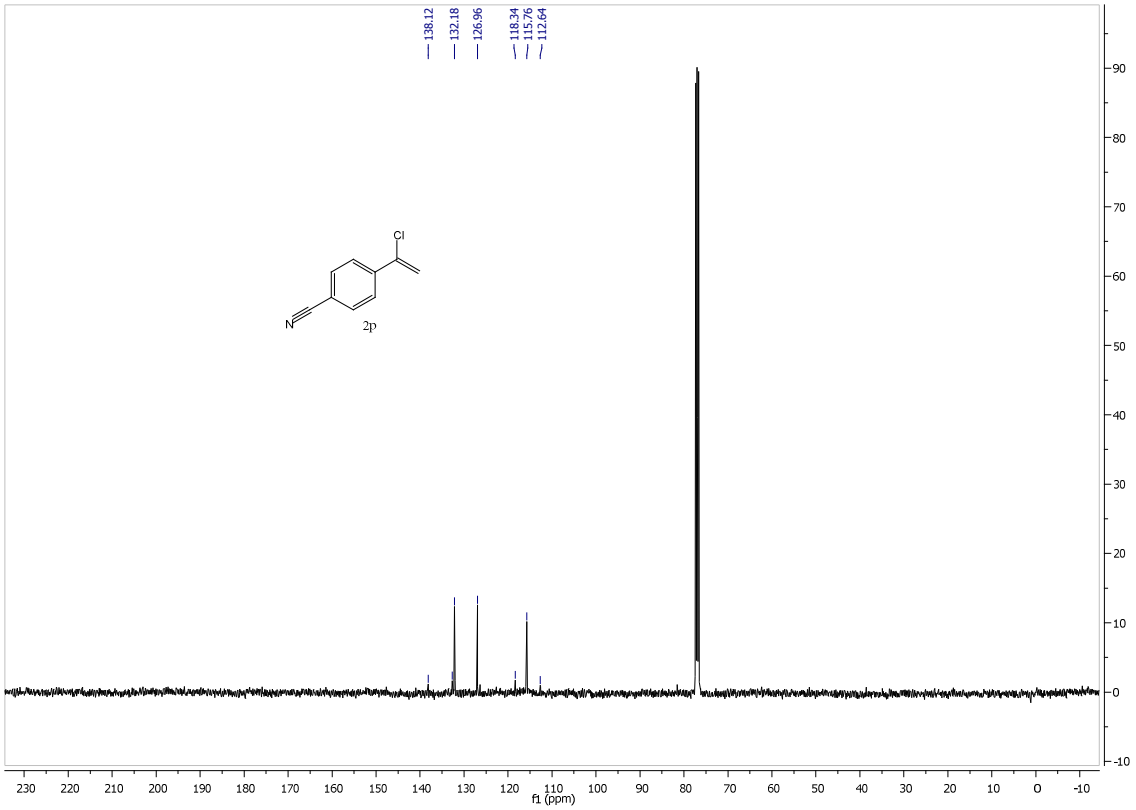
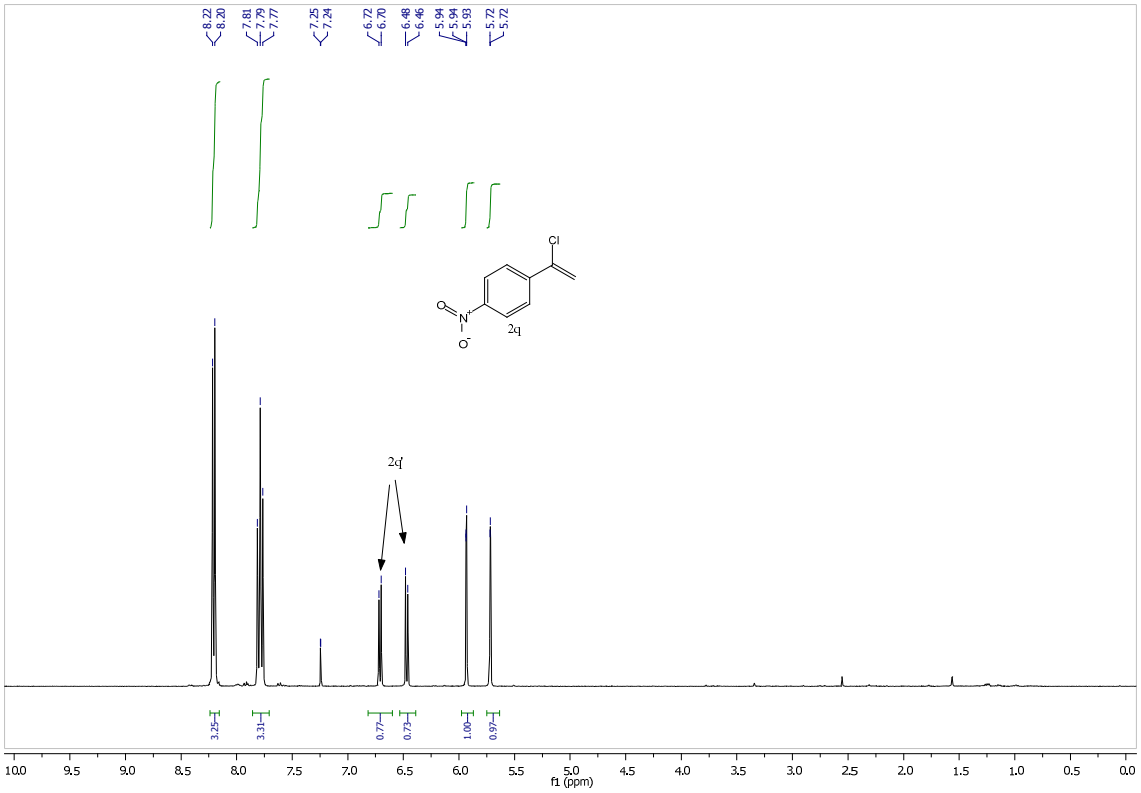
126.30
114.66
77.43
77.06
76.80
52.10
Cl
O
O
2n
f1 (ppm)

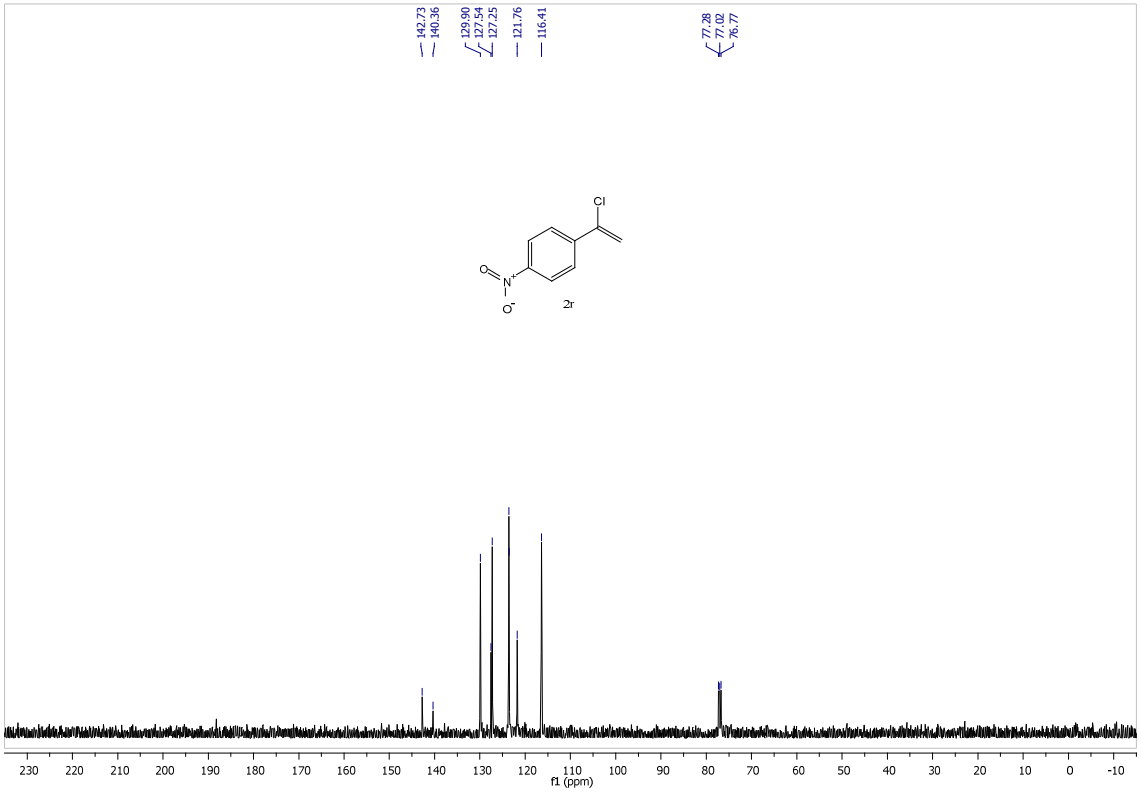

7.63
7.25
5.81
5.81
5.56
5.56
Cl
Cl
2o
2o'
3.73
2.00
1.95
f1 (ppm)

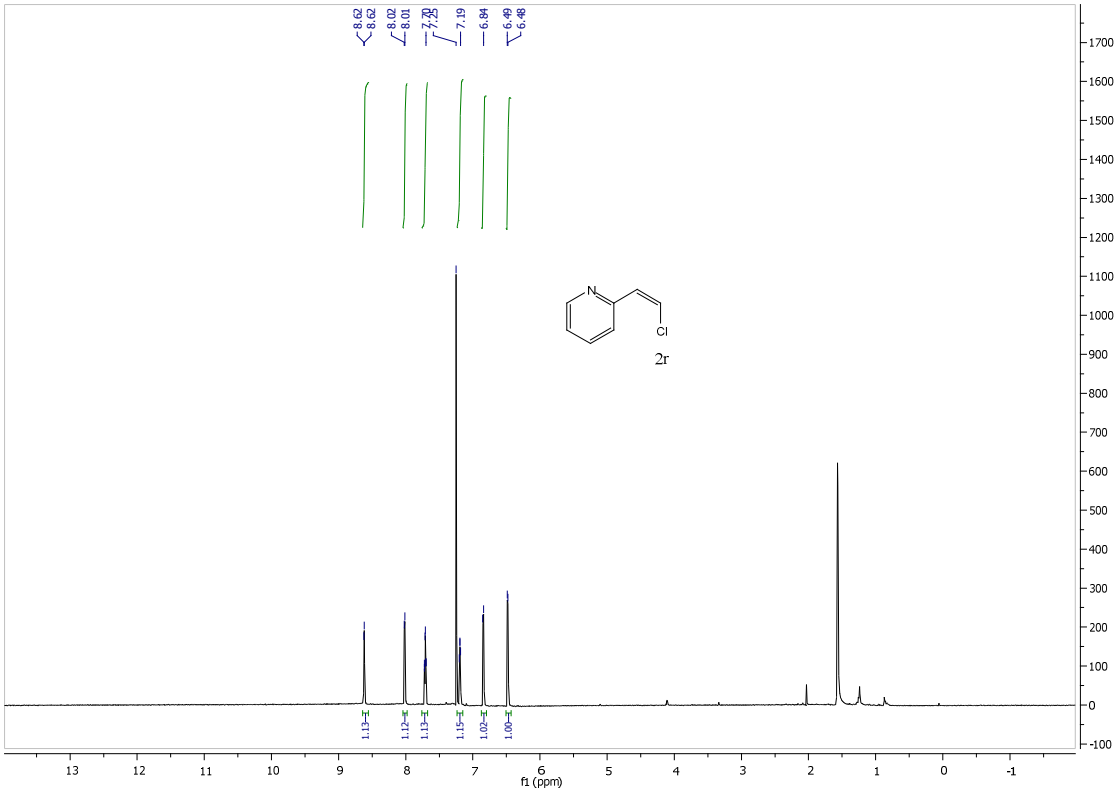

139.10
137.39
126.31
113.41
Cl
Cl
2o
f1 (ppm)

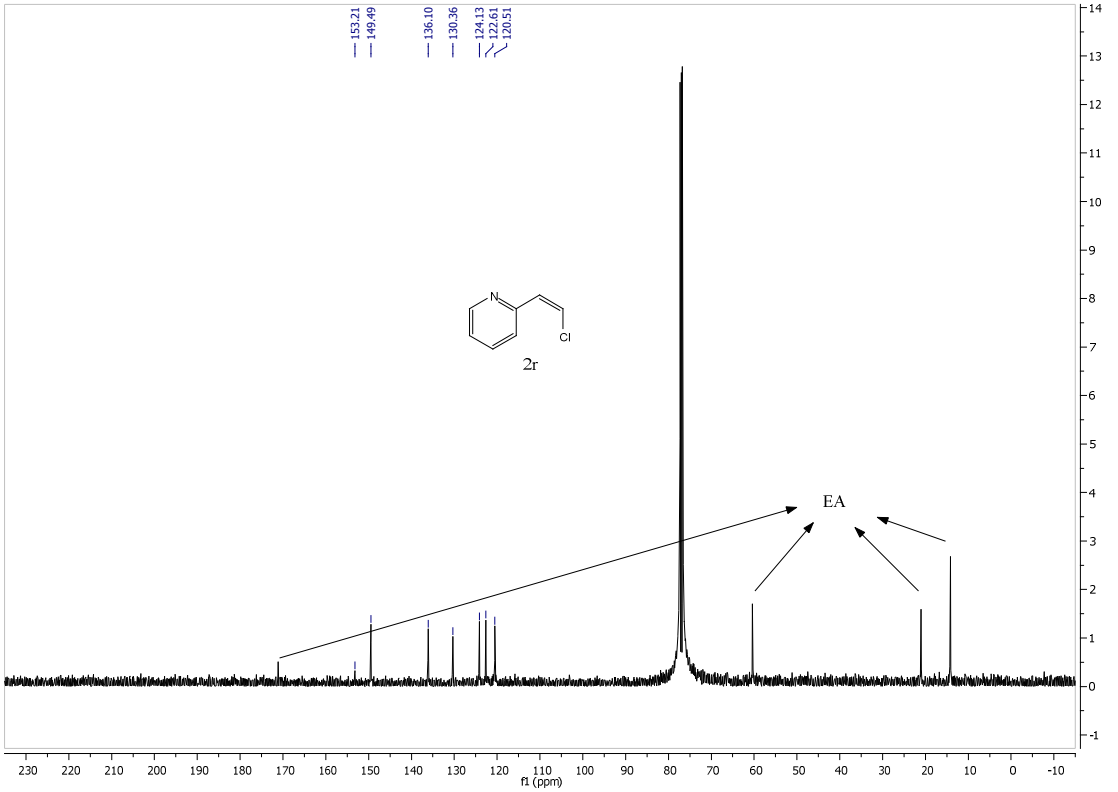

7.73
7.71
7.65
7.63
7.63
7.24
6.66
6.64
6.43
6.41
5.88
5.88
5.67
5.67
Cl
N
2p
2q'
dichloride P
Hexanes
starting material
2.03
2.14
1.00
0.97
f1 (ppm)

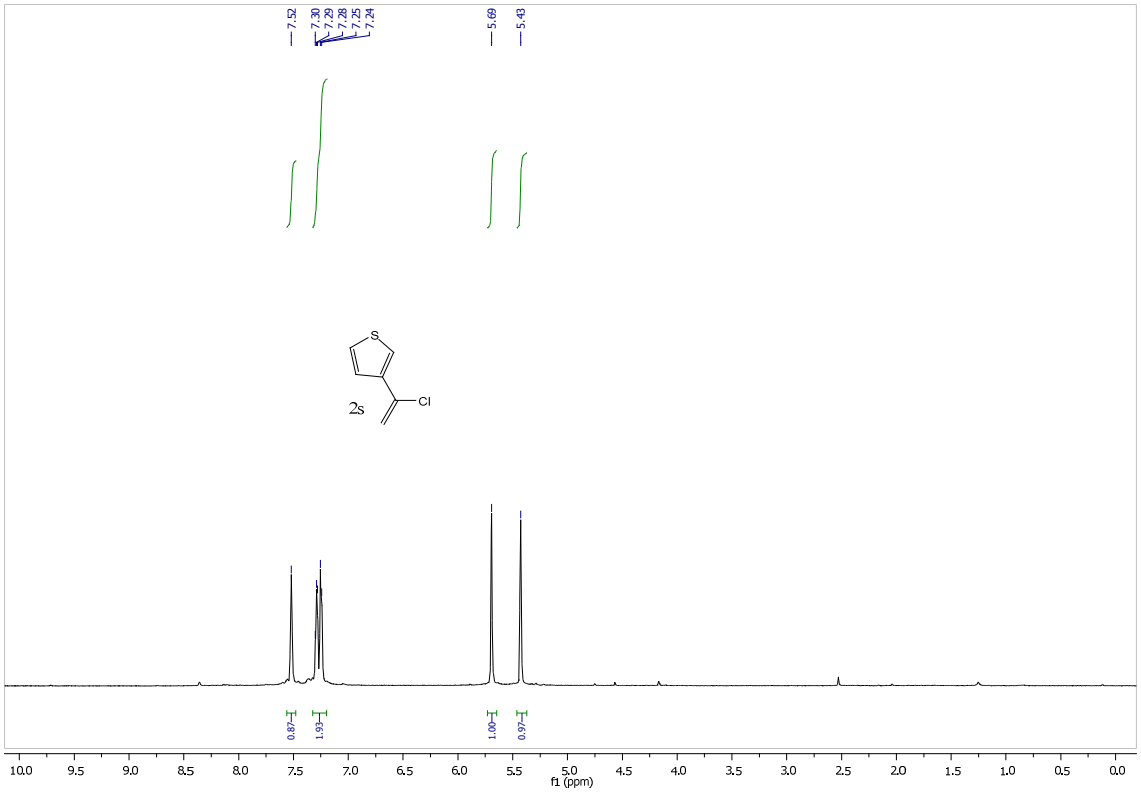

138.12
132.18
126.96
118.34
115.76
112.64
Cl
N
2p
f1 (ppm)

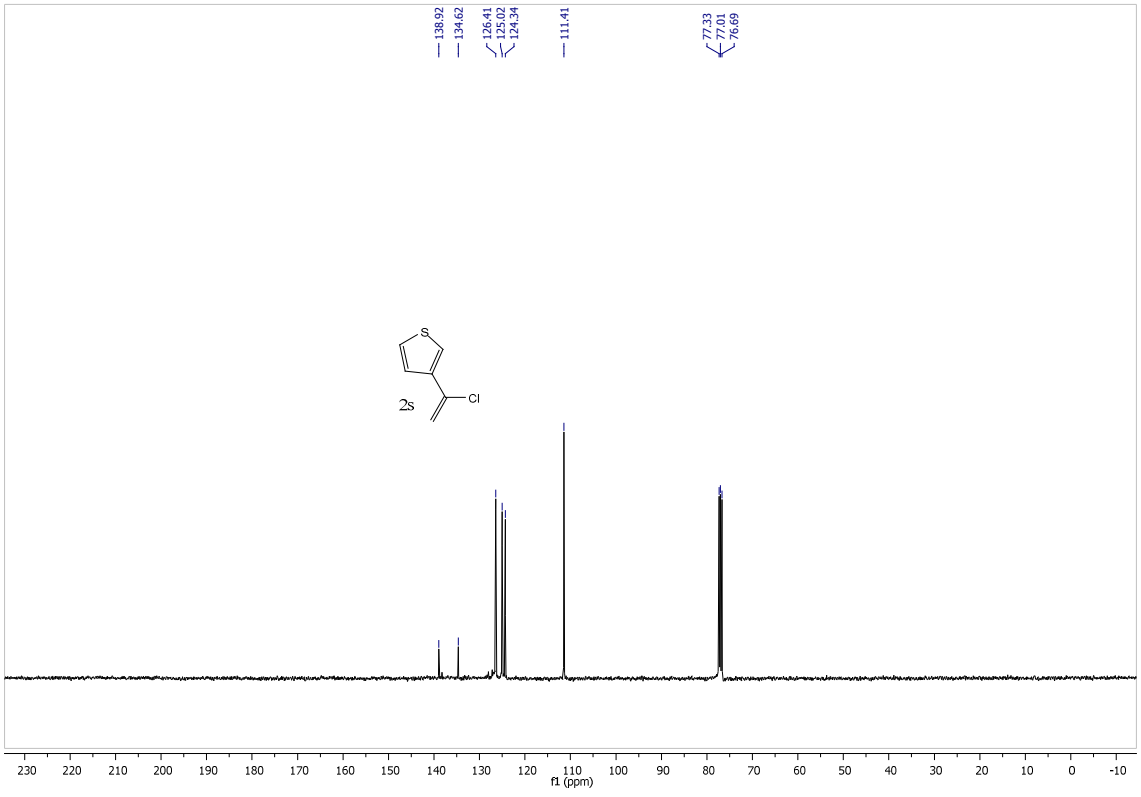

8.22
8.20
7.81
7.79
7.77
7.25
7.24
6.72
6.70
6.48
6.46
5.94
5.94
5.93
5.72
5.72
Cl
O
N+
O-
2q
2q'
3.25
3.31
0.77
0.73
1.00
0.97
f1 (ppm)

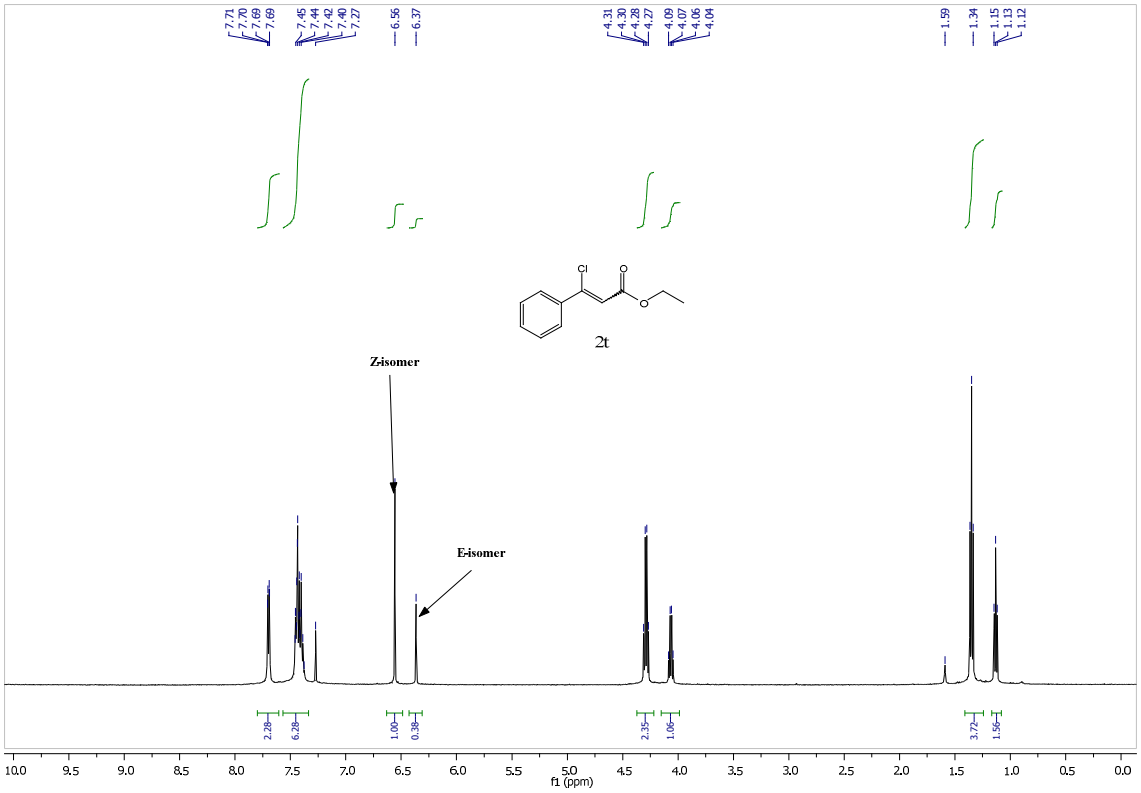

142.73
140.36
129.90
127.54
127.25
121.76
116.41
77.28
77.02
76.77
Cl
O
N+
O-
2r
f1 (ppm)

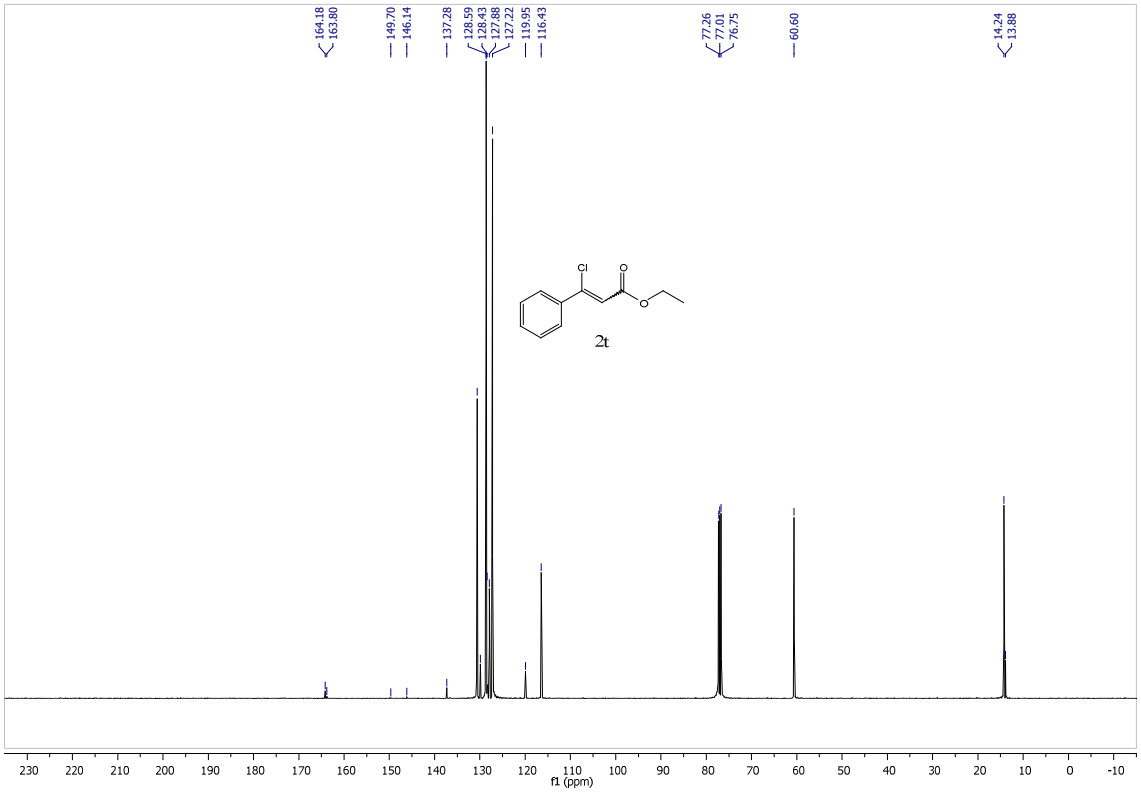

8.62
8.62
8.02
8.01
7.20
7.19
6.49
6.48
N
Cl
2r
f1 (ppm)

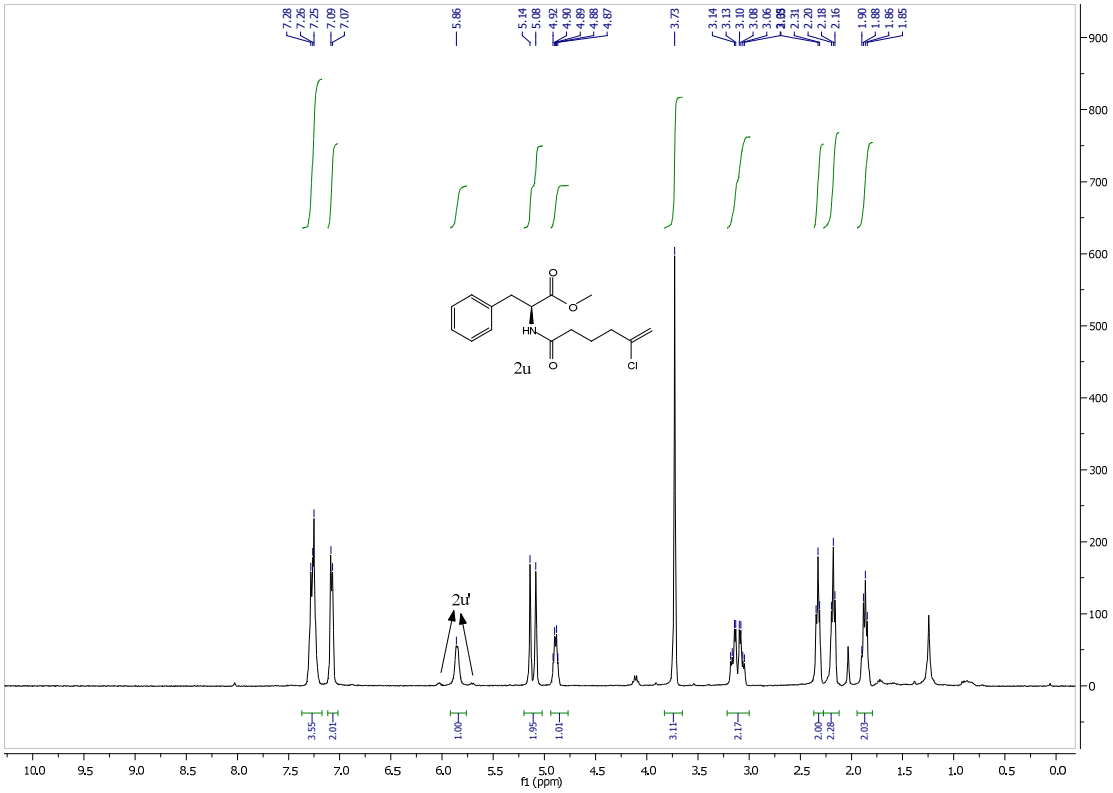

153.21
149.49
136.10
130.36
124.13
122.61
120.51
N
Cl
2r
EA
f1 (ppm)

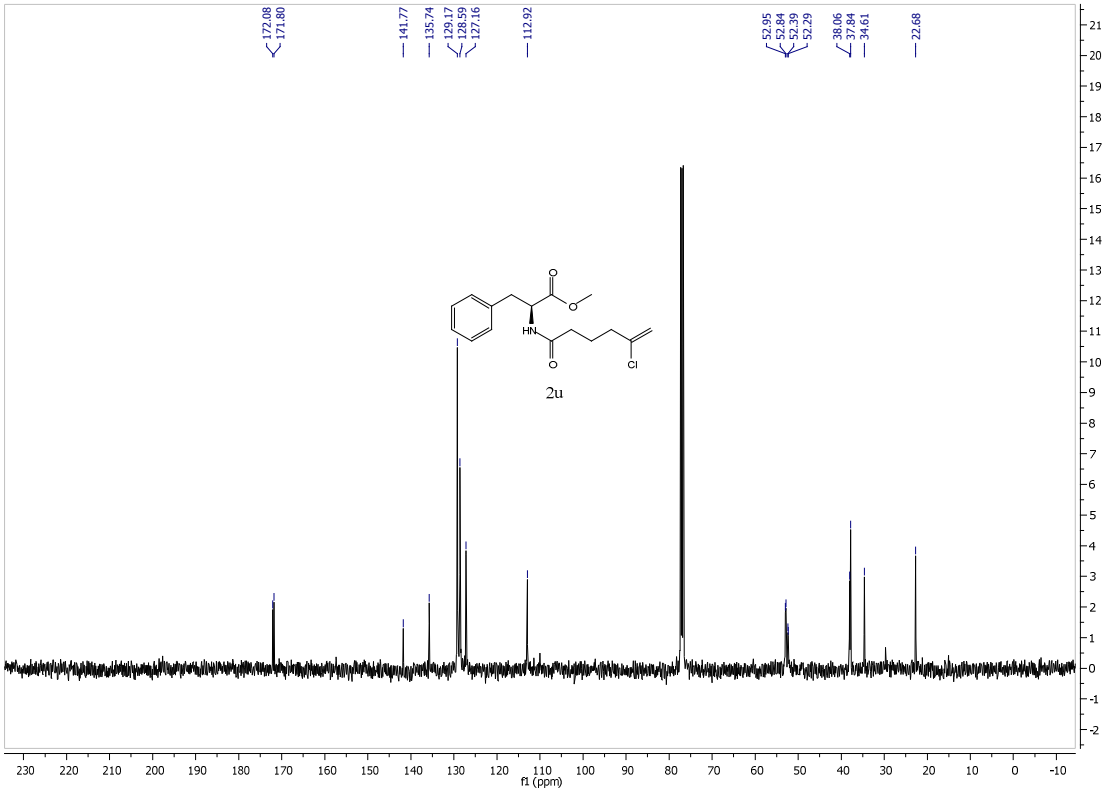

7.52
7.30
7.29
7.28
7.25
7.24
5.69
5.43
S
Cl
2s
0.87
1.93
1.00
0.97
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


138.92
134.62
126.41
125.02
124.34
111.41
77.33
77.01
76.69
S
Cl
2s
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


7.71
7.70
7.69
7.69
7.45
7.44
7.42
7.40
7.27
6.56
6.37
4.31
4.30
4.28
4.27
4.09
4.07
4.06
4.04
1.59
1.34
1.15
1.13
1.12
Cl
O
O
2t
Z-isomer
E-isomer
2.28
6.28
1.00
0.38
2.35
1.06
3.72
1.56
f1 (ppm)


164.18
163.80
149.70
146.14
137.28
128.59
128.43
127.88
127.22
119.95
116.43
77.26
77.01
76.75
60.60
14.24
13.88
Cl
O
O
2t
f1 (ppm)


7.28
7.26
7.25
7.09
7.07
5.86
5.14
5.08
4.92
4.90
4.89
4.88
4.87
3.73
3.14
3.13
3.10
3.08
3.06
2.31
2.20
2.18
2.16
1.90
1.88
1.86
1.85
2u
2u'
3.55
2.01
1.00
1.95
1.01
3.11
2.17
2.03
2.28
2.03
f1 (ppm)


172.08
171.80
141.77
135.74
129.17
128.59
127.16
112.92
52.95
52.84
52.39
52.29
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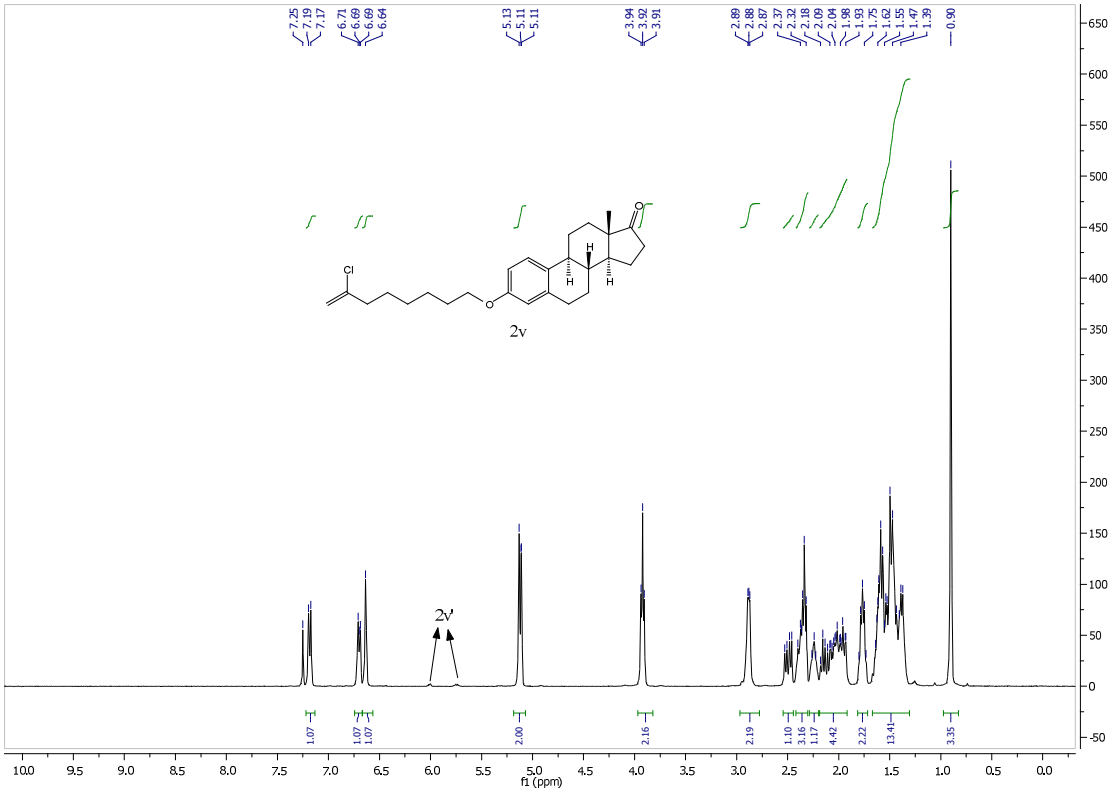
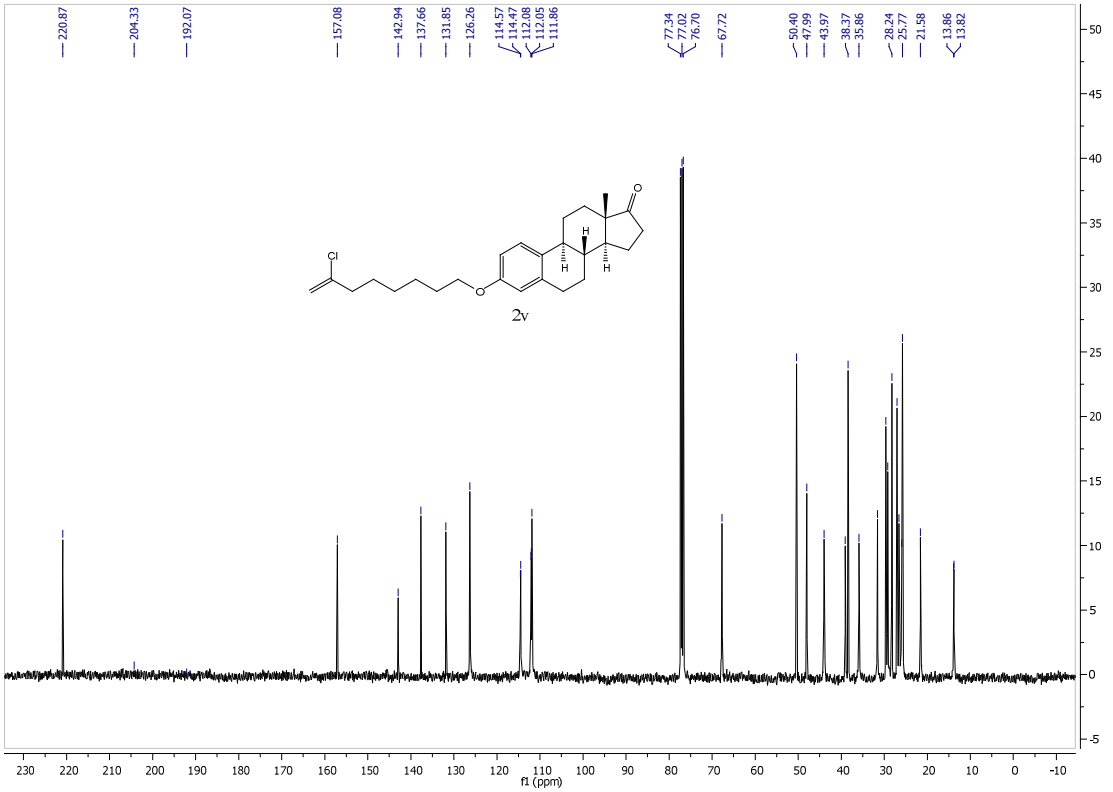
37.84
34.61
22.68
2u
f1 (ppm)


7.25
7.19
7.17
6.71
6.69
6.69
6.64
5.13
5.11
5.11
3.94
3.92
3.91
2.89
2.88
2.87
2.37
2.32
2.18
2.09
2.04
1.98
1.93
1.75
1.62
1.55
1.47
1.39
0.90
Cl
O
H
H
H
O
2v
2v'
1.07
1.07
1.07
2.00
2.16
2.19
1.10
3.16
1.17
4.42
2.22
13.41
3.35
f1 (ppm)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192.07
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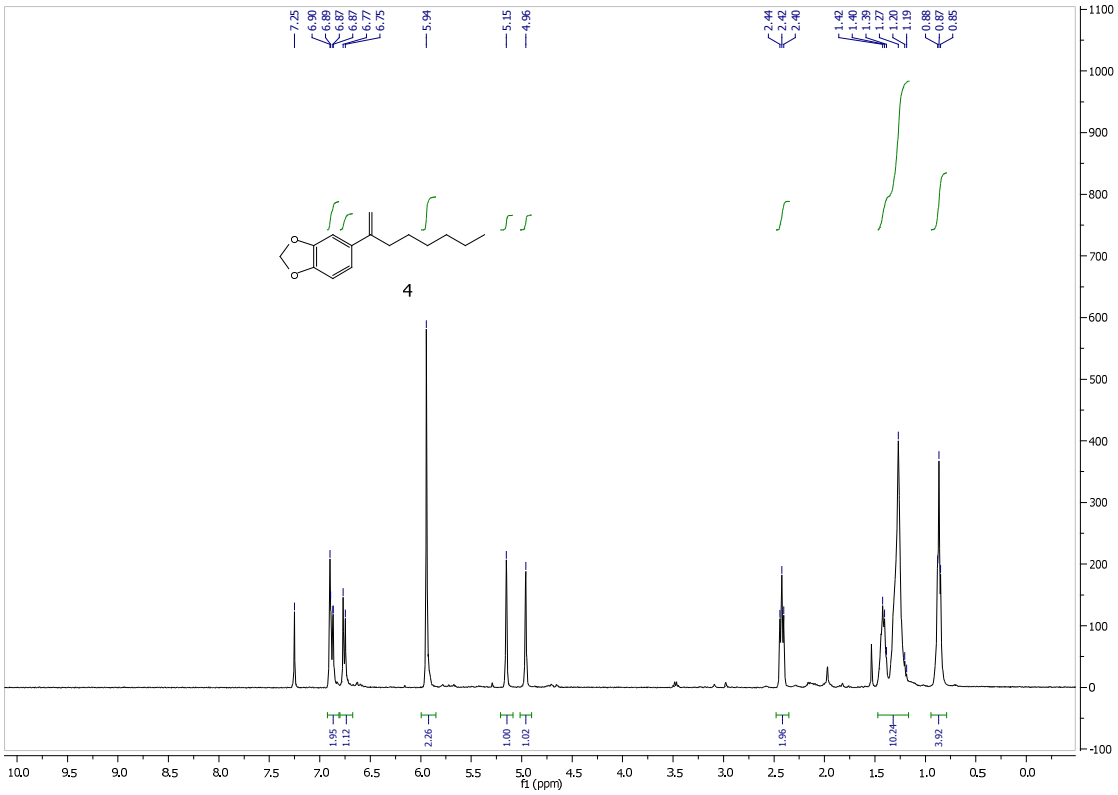
131.85
126.26
114.57
114.47
112.08
112.05
111.86
77.34
77.02
76.70
67.72
50.40
47.99
43.97
38.37
35.86
28.24
25.77
21.58
13.86
13.82
Cl
O
H
H
H
O
2v
f1 (ppm)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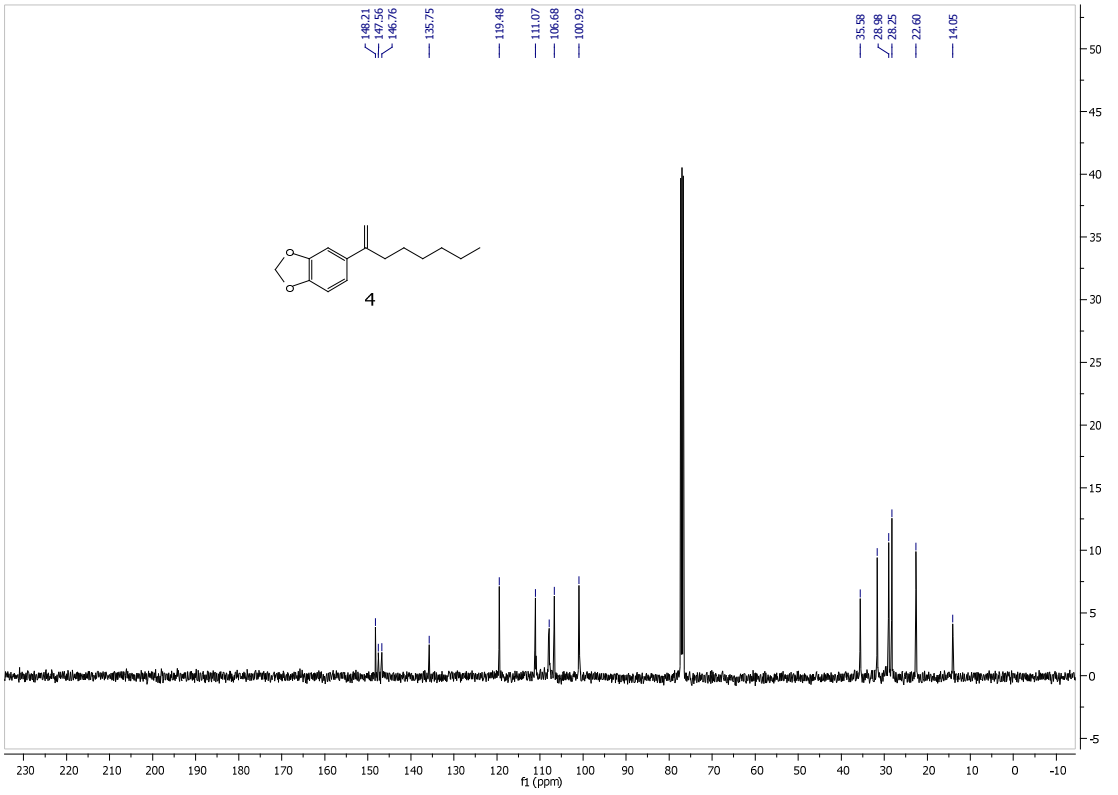
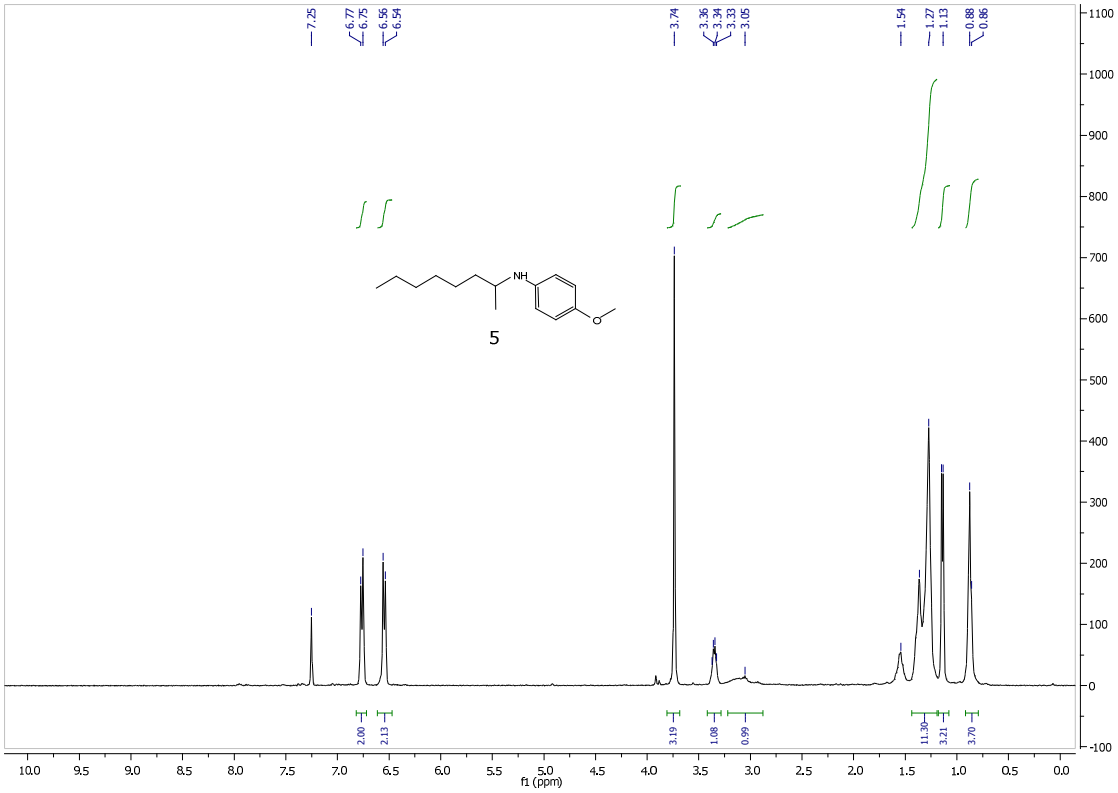
6.90
6.89
6.87
6.87
6.77
6.75
5.94
5.15
4.96
2.44
2.42
2.40
1.42
1.40
1.39
1.27
1.20
1.19
0.88
0.87
0.85
4
1.95
1.12
2.26
1.00
1.02
1.96
10.24
3.92
f1 (ppm)


148.21
147.56
146.76
135.75
119.48
111.07
106.68
100.92
35.58
28.98
28.25
22.60
14.05
4
f1 (ppm)


7.25
6.77
6.75
6.56
6.54
3.74
3.36
3.34
3.33
3.05
1.54
1.27
1.13
0.88
0.86
NH
O
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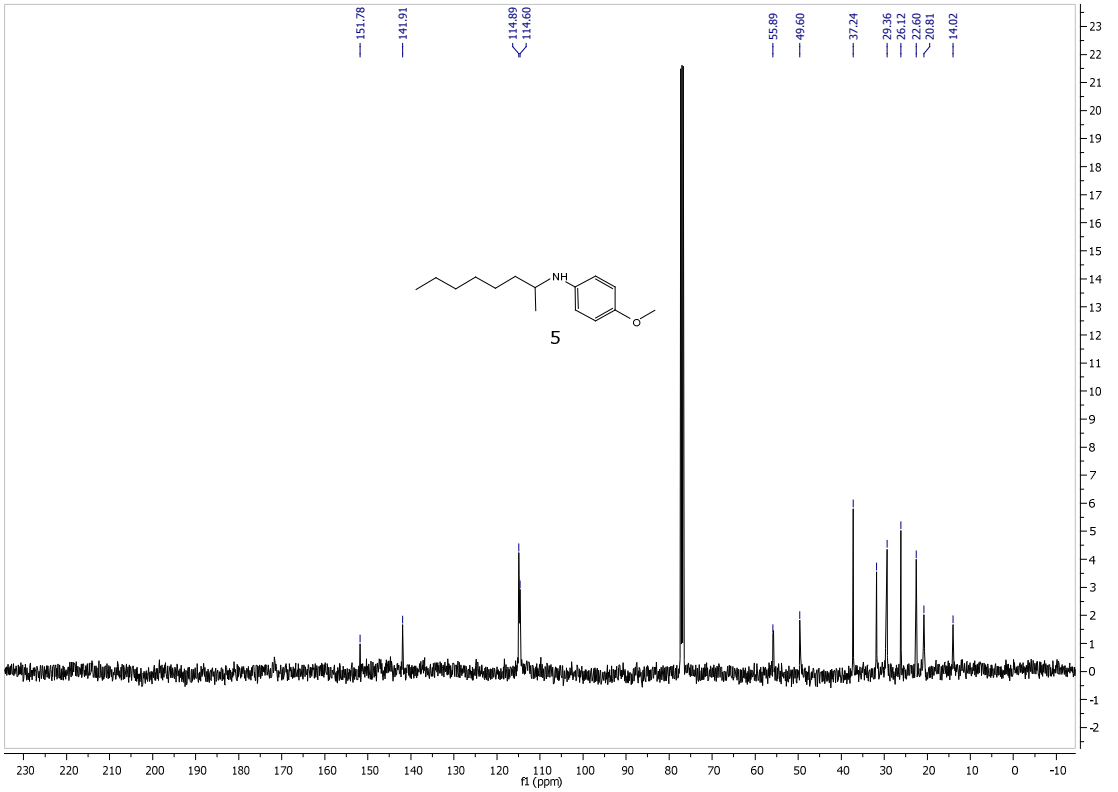
2.00
2.13
3.19
1.08
0.99
11.30
3.21
3.70
f1 (ppm)


151.78
141.91
114.89
114.60
55.89
49.60
37.24
29.36
26.12
22.60
20.81
14.02
NH
O
5
f1 (ppm)

5. References

1. Nieto-Oberhuber, C.; López, S.; Echavarren, A. M. *J. Am. Chem. Soc.* **2005,** *127*, 6178-6179.
2. Ebule, R. E.; Malhotra, D.; Hammond, G. B.; Xu, B. *Adv. Synth. Catal.* **2016,** *358*, 1478-1481.