Electronic supplementary information for

Tandem ene-reaction/hydroamination of amino-olein and -allene compounds catalyzed by $Bi(OTf)_3$

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General

Nuclear magnetic resonance spectra were taken on JEOL EX-270 (^{1}H NMR: 270.05 MHz; ^{13}C NMR: 67.8 MHz) spectrometer or JEOL Lambda-400 (^{1}H NMR: 395.75 MHz; ^{13}C NMR: 99.5 MHz) spectrometer using residual chloroform (for ^{1}H NMR, 7.26 ppm) and $CDCl_3$ (for ^{13}C NMR, 77.0 ppm) as an internal standard. Low-resolution mass spectra (EI) were obtained at 70 eV on a Shimadzu QP-5050. High-resolution mass experiments (EI) were performed on JEOL-SX102A at the Natural Science Center for Basic Research and Development (N-BARD) of Hiroshima University. Melting points were recorded on YANAKO micro melting point apparatus, and uncorrected. Flash column chromatography was performed with silica gel 60 (KANTO, 40-50 μm). TLC monitoring was carried out with silica gel aluminum sheets (Merck, type 60 F_{254}). 1,4-Dioxane and THF were distilled from Na/benzophenone ketyl. Acetonitrile were distilled from P_2O_5 and stored over molecular sieves. DCE was distilled from CaH_2. $MeNO_2$ was dried over crashed $CaCl_2$ and distilled prior to use. Catalysts were purchased, except for $Fe(OTf)_3$[1]. Substrates **1a-c** and **10** were prepared by known methods.[2] Some of alcohols **2** were prepared by $NaBH_4$ reduction of the corresponding ketones. Aryl vinyl ketones **8b-e** were obtained from the addition of vinyl magnesium chloride to aldehydes and sequent oxidation by MnO_2. Unless otherwise noted, commercially available reagents were used without further

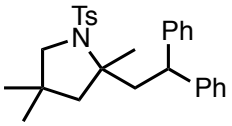
(1) S. Ichikawa, I. Tomita, A. Hosaka, T. Sato, *Bull. Chem. Soc. Jpn.*, 1988, **61**, 513.
(2) (a) Y. Tamaru, M. Hojo, H. Higashimura, Z.-I, Yoshida, *J. Am. Chem. Soc.* 1988, **110**, 3994. (b) K. E. Harding, S. R, Burks, *J. Org. Chem.* 1981, **46**, 3920.

purification.

Representative procedure for the tandem reaction (Table 2, entry 4): Reactions were carried out under N_2 atmosphere. Oven-dried 20 mL-Schlenk tune was added $Bi(OTf)_3$ (8.2 mg, 12 μmol) and cooled $MeNO_2$ solution (2.2 mL at 10 ºC) of **1a** (61.6 mg, 0.22 mmol) and **2e** (45.2 mg, 0.33 mmol). After stirring at 10 ºC for 3 h the reaction mixture was passed through a short silica-gel column with ether as an eluent, and then removed solvent. The crude product was purified by flash column chromatography to provide **3e** (45 mg, 51% yield).

Data of new products

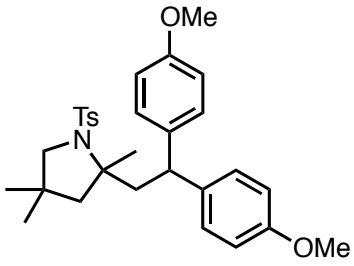
2-(Diphenylmethylmethyl)-2,4,4-trimethyl-1-tosylpyrrolidine (3a)



Chemical Formula: $C_{28}H_{33}NO_2S$
Exact Mass: 447.2232
Molecular Weight: 447.6321

This compound was isolated as a colorless oil; R_f value (Hexane/EtOAc = 5:1, SiO_2) = 0.6; ^{1}H NMR (270.05 MHz, $CDCl_3$) δ 0.76 (3H, s), 0.78 (3H, s), 1.26 (3H, s), 1.28 (1H, d, *J* = 19.3 Hz), 1.71 (1H, d, *J* = 19.3 Hz), 2.32 (3H, s), 2.37 (1H, dd, *J* = 13.5, 4.8 Hz), 2.97 (2H, s), 3.14 (1H, dd, *J* = 13.5, 8.7 Hz), 3.97 (1H, dd, *J* = 8.7, 4.8 Hz), 7.04 (2H, m), 7.17-7.27 (10H, m), 7.66 (2H, d, *J* = 8.7 Hz); ^{13}C NMR (67.80 MHz, $CDCl_3$) δ 21.4, 27.2, 27.9, 36.2, 47.5, 48.6, 52.8, 61.0, 127.2, 127.5, 128.0, 128.4, 129.2, 138.4, 142.6, 145.0, 146.2; HRMS Calcd for $C_{28}H_{33}NO_3S$: 447.2232, Found: 447.2240.

2-(Dianisylmethylmethyl)-2,4,4-trimethyl-1-tosylpyrrolidine (3b)

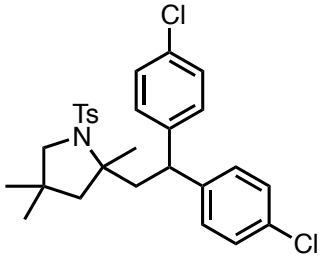


Chemical Formula: $C_{30}H_{37}NO_4S$
Exact Mass: 507.2443
Molecular Weight: 507.6841

This compound was isolated as a colorless oil; R_f value (Hexane/EtOAc = 5:1, SiO_2) = 0.28; ^{1}H NMR (270.05 MHz, $CDCl_3$) δ 0.86 (6H, s), 1.32 (3H, s), 1.36 (1H, d, *J* = 12.9

Hz), 1.80 (1H, d, *J* = 12.9 Hz), 2.37 (1H, dd, *J* = 13.8, 4.6 Hz), 2.42 (3H, s), 3.06 (2H, s), 3.16 (1H, dd, *J* = 13.9, 9.0 Hz), 3.76 (3H, s), 3.78 (3H, s), 3.95 (1H, dd, *J* = 9.0, 4.6 Hz), 6.80 (2H, d, *J* = 8.9 Hz), 6.83 (2H, d, *J* = 8.9 Hz), 7.15 (2H, d, *J* = 8.6 Hz), 7.24 6.80 (2H, d, *J* = 8.8 Hz), 7.27 (2H, d, *J* = 8.8 Hz), 7.75 (2H, d, *J* = 8.2 Hz); ^{13}C NMR (270.05 MHz, $CDCl_3$) δ 21.4, 27.2, 27.4, 27.9, 36.3, 46.8, 47.8, 52.8, 55.2, 61.0, 69.7, 113.8, 113.9, 127.3, 128.3, 128.8, 129.3, 137.6, 138.4, 138.9, 142.6, 157.6, 157.8; HRMS Calcd for $C_{30}H_{37}NO_4S$: 507.2443, Found: 507.2448.

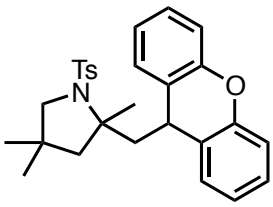
2-(4-Chlorophenylethylmethyl)-2,4,4-trimethyl-1-tosylpyrrolidine (3c).



Chemical Formula: $C_{28}H_{31}Cl_2NO_2S$
Exact Mass: 515.1453
Molecular Weight: 516.5222

This compound was isolated as a colorless oil; R_f value (Hexane/EtOAc = 5:1, SiO_2) = 0.38; ^{1}H NMR ($CDCl_3$, 270.05 MHz) δ 0.85 (6H, s), 1.26 (1H, m), 1.32 (3H, s), 1.35 (1H, d, *J* = 13.2 Hz), 1.74 (1H, d, *J* = 13.2 Hz), 2.41 (3H, s), 1.44 (1H, d, *J* = 13.5 Hz), 1.55 (3H, s), 2.09 (1H, dd, *J* = 14.5, 7.7 Hz), 2.44 (3H, s), 2.71 (1H, d, *J* = 13.5, 6.8 Hz), 3.02 (2H, s), 4.25 (1H, t, *J* = 6.8 Hz), 7.10-7.37 (10H, m), 7.70 (2H, d, *J* = 7.7 Hz); ^{13}C NMR ($CDCl_3$, 99.5 MHz) δ 21.5, 27.3, 27.4, 27.9, 36.3, 47.4, 47.5, 53.0, 61.1, 69.3, 127.3, 128.76, 128.81, 128.83, 129.3, 129.4, 132.0, 132.2, 138.2, 142.9, 143.1, 142.9, 143.1, 144.3; HRMS Calcd for $C_{28}H_{31}Cl_2NO_2S$: 516.1453, Found: 515.1458

2-(9-Xanthenylmethyl)-2,4,4-trimethyl-1-tosylpyrrolidine (3d).

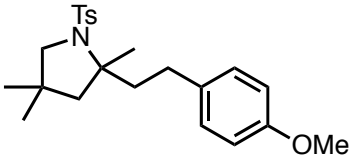


Chemical Formula: $C_{28}H_{31}NO_3S$
Exact Mass: 461.2025
Molecular Weight: 461.6156

This compound was isolated as a yellow oil; R_f value (Hexane/EtOAc = 5:1, SiO_2) = 0.4; ^{1}H NMR ($CDCl_3$, 395.75 MHz) δ 0.87 (3H, s), 0.89 (3H, s), 1.30 (1H, d, *J* = 12.6 Hz), 1.44 (1H, d, *J* = 13.5 Hz), 1.55 (3H, s), 2.09 (1H, dd, *J* = 14.5, 7.7 Hz), 2.44 (3H, s), 2.71 (1H, d, *J* = 13.5, 6.8 Hz), 3.02 (2H, s), 4.25 (1H, t, *J* = 6.8 Hz), 7.10-7.37 (10H, m), 7.70 (2H, d, *J* = 7.7 Hz); ^{13}C NMR ($CDCl_3$, 99.5 MHz) d 21.4, 27.1, 27.5, 27.6, 36.3,

37.8, 51.3, 53.1, 60.5, 69.0, 116.6, 116.6, 123.3, 123.4, 127.2, 127.3, 127.5, 127.5, 127.6, 128.5, 128.6, 129.2, 138.0, 142.7, 153.2, one carbon was obscured; HRMS Calcd for $C_{28}H_{31}NO_2S$: 461.2025, Found: 461.2009.

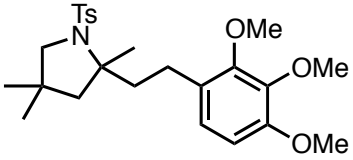
1-(2,4,4-Trimethyl-1-tosylpyrrolidinyl)- 2-anisylethane (3e).



Chemical Formula: $C_{23}H_{31}NO_3S$
Exact Mass: 401.2025
Molecular Weight: 401.5621

This compound was isolated as a colorless oil; R_f value (Hexane/EtOAc = 3:1, SiO_2) = 0.50; ^{1}H NMR ($CDCl_3$, 395.75 MHz) δ 0.98 (3H, s), 1.05 (3H, s), 1.52 (3H, s), 1.58 (1H, d, *J* = 12.5 Hz), 2.00 (1H, d, *J* = 13.5 Hz), 2.11 (1H, dt, *J* = 11.5, 5.6 Hz), 2.22 (1H, dt, *J* = 13.4, 5.7 Hz), 2.40 (3H, s), 2.54-2.67 (2H, m), 3.08 (1H, d. *J* = 9.7 Hz), 3.11 (1H, d. *J* = 9.7 Hz), 3.79 (3H, s), 6.82 (2H, d, *J* = 8.7 Hz), 7.12 (2H, d, *J* = 8.7 Hz), 7.26 (2H, d, *J* = 8.7 Hz), 7.74 (2H, d, *J* = 8.7 Hz), ^{13}C NMR ($CDCl_3$, 99.5 MHz) δ 21.4, 27.3, 27.5, 27.6, 30.5, 36.1, 44.5, 53.1, 55.2, 61.6, 68.8, 113.7, 127.2, 129.2, 129.3, 134.0, 138.4, 142.6, 157.6; HRMS Calcd for $C_{23}H_{31}O_3S$: 401.2025, Found: 401.2018.

1-(2,4,4-Trimethyl-1-tosylpyrrolidinyl)-2-(2,3,4-trimethoxyphenyl)ethane (3f).

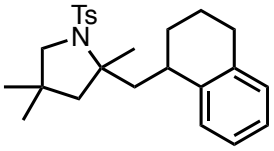


Chemical Formula: $C_{25}H_{35}NO_5S$
Exact Mass: 461.2236
Molecular Weight: 461.6141

This compound was isolated as a colorless oil; R_f value (Hexane/EtOAc = 3:1, SiO_2) = 0.40; ^{1}H NMR ($CDCl_3$, 270.05 MHz) δ 0.98 (3H, s), 1.06 (3H, s), 1.53 (3H, s), 1.60 (1H, d, *J* = 13.1 Hz), 1.57-1.65 (2H, m), 1.95-2.17 (2H, m), 2.59 (2H, dd, *J* = 13.5, 7.9 Hz), 1.63 (1H, d), 2.40 (3H, s), 3.08 (2H, s), 3.84 (3H, s), 3.86 (3H, s), 3.89 (3H, s), 6.60 (1H, d, *J* = 8.5 Hz), 6.87 (1H, d, *J* = 8.5 Hz), 7.24 (2H, d, *J* = 8.2 Hz), 7.74 (2H, d, *J* = 8.2 Hz); ^{13}C NMR ($CDCl_3$, 99.5 MHz) δ 21.4, 25.9, 27.1, 27.5, 27.6, 36.1, 43.6, 53.0, 56.0, 60.7, 60.9, 61.5, 69.0, 107.1, 123.8, 127.3, 128.0, 129.2, 138.4, 142.1, 142.6, 151.7, 151.9; HRMS Calcd for $C_{25}H_{35}O_5S$: 461.2236, Found: 461.2238.

2,4,4-Trimethyl-2-{(1,2,3,4-tetrahydronaphthalen-1-yl)methyl}-1-tosylpyrrolidine

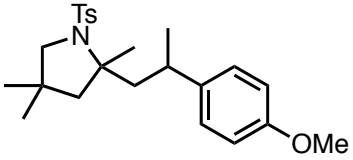
(3g).



Chemical Formula: $C_{25}H_{33}NO_2S$
Exact Mass: 411.2232
Molecular Weight: 411.6000

These compounds were isolated as a mixture of two diastereomers [64:36] (a colorless oil); R_f value (Hexane/EtOAc = 3:1, SiO_2) = 0.40; ^{1}H NMR ($CDCl_3$, 397.75 MHz) Manor & Minor δ 0.96 (3H, s), 1.00 (3H, s), 1.05 (3H, s), 1.09 (3H, s), 1.49-2.21 (14H, m), 1.64 (6H, s), 2.40 (6H, br s), 2.65-2.84 (8H, m), 3.04-3.15 (4H, m), 7.06-7.26 (12H, m), 7.11-7.74 (4H, m); ^{13}C NMR ($CDCl_3$, 99.5 MHz) Major δ 19.2, 27.4, 27.5, 27.7, 28.2, 29.3, 35.2, 36.6, 48.4, 53.7, 60.9, 69.4, 125.4, 125.8, 127.4, 129.1, 129.3, 137.0, 138.3, 141.7, 142.6, Minor δ 19.6, 21.5, 27.1, 27.4, 28.8, 29.7, 34.9, 36.5, 49.1, 54.4, 60.9, 59.8, 125.5, 125.6, 127.3, 128.7, 128.8, 137.1, 138.4, 142.1, 142.6; HRMS Calcd for $C_{25}H_{33}NO_2S$: 411.2232, Found: 411.2227.

1-(2,4,4-Trimethyl-1-tosylpyrrolidie-2-yl)-2-anisylpropane (3h).

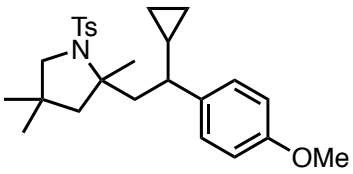


Chemical Formula: $C_{24}H_{33}NO_3S$
Exact Mass: 415.2181
Molecular Weight: 415.5887

These compounds were isolated as a mixture of two diastereomers [64:36] (a colorless oil); R_f value (Hexane/EtOAc = 5:1, SiO_2) = 0.40; ^{1}H NMR ($CDCl_3$, 397.75 MHz) **Major**: δ 0.82 (3H, s), 0.83 (3H, s), 1.12 (1H, d, *J* = 13.4 Hz), 1.27 (3H, d, *J* = 6.8 Hz), 1.44 (1H, d, *J* = 12.9 Hz), 1.57 (3H, s), 2.00 (1H, m), 2.42 (3H, s), 2.67 (1H, dd, *J* = 13.5, 4.2 Hz), 2.78-2.86 (1H, m), 2.92 (1H, d, *J* = 9.7 Hz), 2.94 (1H, d, *J* = 9.7 Hz), 3.79 (3H, s), 6.83 (2H, d, *J* = 6.6 Hz), 7.07 (2H, d, *J* = 8.5 Hz), 7.25 (2H, d, *J* = 6.7 Hz), 7.72 (2H, d, *J* = 8.6 Hz), **Minor**: δ 0.86 (3H, s), 0.91 (3H, s), 1.19 (3H, s), 1.24 (3H, d, *J* = 7.1 Hz), 1.37 (1H, d, *J* = 12.9 Hz), 1.88 (1H, d, *J* = 13.3 Hz), 2.00 (1H, m), 2.40 (3H, s), 2.57 (1H, dd, *J* = 14.3, 9.5 Hz), 2.71-2.77 (1H, m), 3.01 (1H, d, *J* = 9.6 Hz), 3.10 (1H, d, *J* = 9.6 Hz), 3.79 (3H, s), 6.82 (2H, d, *J* = 6.6 Hz), 7.14 (2H, d, *J* = 8.6 Hz), 7.27 (2H, d, *J* = 7.8 Hz), 7.73 (2H, d, *J* = 8.6 Hz); ^{13}C NMR ($CDCl_3$, 99.45 MHz) **Major**: δ 21.5, 25.6, 27.2, 27.3, 27.6, 36.5, 36.6, 50.0, 52.9, 55.2, 60.5, 69.6, 113.8, 127.4, 128.1, 129.22, 140.23, 142.6, 157.8, **Minor**: δ 21.5, 27.1, 26.2, 27.4, 28.1, 36.2, 36.3, 50.1, 52.9, 55.2, 60.5, 69.6, 113.8, 127.4, 128.0, 129.24, 140.20, 142.5, 157.7; HRMS Calcd

for $C_{24}H_{33}NO_3S$: 415.2181, Found: 415.2191.

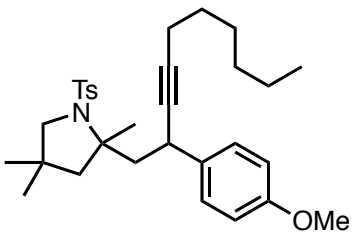
2-{2-Dyclopropyl-2-(4-anisyl)ethyl}-2,4,4-trimethyl-1-tosylpyrrolidine (3i).



Chemical Formula: $C_{26}H_{35}NO_3S$
Exact Mass: 441.2338
Molecular Weight: 441.6260

These compounds were isolated as a mixture of two diastereomers [62:38] (a colorless oil); R_f value (Hexane/EtOAc = 5:1, SiO_2) = 0.35; ^{1}H NMR ($CDCl_3$, 397.75 MHz) Major & Minor δ 0.04-0.06 (2H, m), 0.21-.38 (4H, m), 0.51-0.63 (2H, m), 0.80 (3H, s), 0.81 (3H, s), 0.82 (3H, s), 0.87 (3H, s), 0.91-0.98 (2H, m), 1.03 (1H, d, *J* = 13.2 Hz), 1.15 (3H, s), 1.32 (1H, dd, *J* = 12.9 Hz), 1.40 (1H, d, *J* = 12.9 Hz), 1.52 (3H, s), 1.76 (1H, td, *J* = 9.5, 3.6 Hz), 1.81 (1H, d, *J* = 12.9 Hz), 1.85 (1H, td, *J* = 9.5 Hz), 2.17 (1H, dd, *J* = 13.8 Hz), 2.33 (1H, dd, *J* = 13.8 Hz), 2.39 (3H, s), 2.41 (3H, s), 2.76 (1H, dd, *J* = 13.8, 10.7 Hz), 2.91 (1H, dd, *J* = 10.7, 3.6 Hz), 2.93 (2H, s), 2.97 (1H, d, *J* = 9.6 Hz), 3.09 (1H, d, *J* = 9.6 Hz), 3.788 (3H, s), 3.790 (3H, s), 6.82 (2H, d, *J* = 8.7 Hz), 6.84(2H, d, *J* = 8.7 Hz), 7.05 (2H, d, *J* = 8.7 Hz), 7.13 (2H, d, *J* = 8.7 Hz), 7.24 (2H, d, *J* = 8.4 Hz), 7.27 (2H, d, *J* = 8.4 Hz), 7.72 (2H, d, *J* = 6.0 Hz), (2H, d, *J* = 8.7 Hz), 7.74 (2H, d, *J* = 6.0 Hz); ^{13}C NMR ($CDCl_3$, 99.5 MHz) Major & Minor δ 4.4, 4.6, 5.5, 6.1, 20.0, 20.6, 21.29, 21.31, 27.0, 27.1, 27.3, 27.4, 28.1, 36.0, 36.1, 47.35, 47.43, 48.2, 52.6, 52.8, 55.1, 60.4, 61.2, 69.3, 69.4, 113.74, 113.75, 127.3, 127.4, 128.6, 128.7, 129.28, 129.30, 138.3, 138.5, 142.62, 142.64, 157.96; HRMS Calcd for $C_{26}H_{35}NO_3S$: 441.2338, Found: 441.2339.

2-{2-(4-Anisyl)-4-phenylbut-3-yn-1-yl}-2,4,4-trimethyl-1-tosylpyrrolidine (3j).

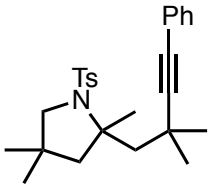


Chemical Formula: $C_{31}H_{43}NO_3S$
Exact Mass: 509.2964
Molecular Weight: 509.7430

These diastereoisomers were separable and isolated as colorless oil each other. The ratio of diastereomers was estimated by ^{1}H NMR of crude mixture; Major: R_f value (Hexane/EtOAc = 5:1, SiO_2) = 0.38; ^{1}H NMR ($CDCl_3$, 397.75 MHz) Major δ 0.88 (3H,

t, *J* = 6.8 Hz), 0.97 (3H, s), 1.03 (3H, s), 1.24-1.41 (6H, m), 1.45-1.52 (3H, m), 1.58 (3H, s), 2.06 (1H, dd, *J* = 13.5 Hz, 10.6 Hz), 2.18 (2H, td, *J* = 6.8, 1.9 Hz), 2.39 (3H, s), 2.53 (1H, d, *J* = 13.5 Hz), 2.77 (1H, dd, *J* = 12.5, 3.8 Hz), 3.00 (2H, m), 3.63-3.67 (1H, m), 3.80 (3H, s), 6.85 (2H, 2H, d, *J* = 8.7 Hz), 7.23 (2H, d, *J* 8.7 Hz), 7.29 (2H, d, *J* = 8.7 Hz), 7.68 (2H, d, *J* = 8.7 Hz); ^{13}C NMR ($CDCl_3$, 99.5 MHz) δ 14.0, 18.9, 21.4, 22.6, 26.3, 27.3, 27.5, 28.6, 28.7, 31.3, 33.8, 36.5, 50.1, 54.0, 55.3, 60.5, 69.0, 82.2, 84.4, 113.8, 127.4, 128.3, 129.2, 135.4, 138.2, 142.6, 158.2; Major: R_f value (Hexane/EtOAc = 5:1, SiO_2) = 0.40; ^{1}H NMR ($CDCl_3$, 397.75 MHz) Major δ 0.878 (3H, s), 0.887 (3H, t, *J* = 6.8 Hz), 1.04 (3H, s), 1.25-1.42 (6H, m), 1.46-1.53 (3H, m), 1.55 (3H, m), 2.15-2.31 (4H, m), 2.41 (3H, s), 2.67 (1H, d, *J* = 13.5 Hz), 3.10 (1H, d, *J* = 9.7 Hz), 3.28 (1H, d, *J* = 9.7 Hz), 3.79 (3H, s), 3.79 (3H, s), 3.88-3.91 (1H, m); 6.85 (2H, d, *J* = 8.7 Hz), 7.26 (2H, d, *J* = 7.8 Hz), 7.36 (2H, d, *J* = 8.7 Hz), 7.75 (2H, d, *J* = 7.8 Hz); ^{13}C NMR ($CDCl_3$, 99.5 MHz) Major 14.1, 19.0, 21.5, 22.6, 27.0, 27.7, 28.5, 28.6, 28.9, 31.3, 33.3, 36.2, 51.3, 51.9, 55.3, 61.9, 69.0, 82.9, 84.2, 113.8, 127.2, 128.4, 129.3, 136.2, 138.6, 142.6, 158.1; HRMS Calcd for $C_{31}H_{43}NO_3S$: 509.2964, Found: 509.2960.

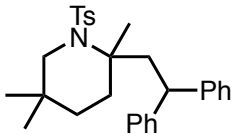
2-(2,2-Dimethyl-4-phenylbut-3-yn-1-yl)-2,4,4-trimethyl-1-tosylpyrrolidine (3k).



Chemical Formula: $C_{26}H_{33}NO_2S$
Exact Mass: 423.2232
Molecular Weight: 423.6107

This compound was isolated as a colorless oil; R_f value (Hexane/EtOAc = 5:1, SiO_2) = 0.38; ^{1}H NMR ($CDCl_3$, 397.75 MHz) Major δ 0.92 (3H, s), 1.02 (3H, s), 1.03 (3H, s), 1.37 (3H, s), 1.42 (3H, s), 1.67 (1H, d, *J* = 14.5 Hz), 1.98 (1H, d, *J* = 13.5 Hz), 2.41 (3H, s), 2.57 (1H, d, *J* = 13.5 Hz), 2.71 (1H, d, *J* = 14.5 Hz), 3.01 (1H, d, *J* = 9.7 Hz), 3.04 (1H, d, *J* = 9.7 Hz), 7.26-7.28 (5H, m), 7.34-7.36 (2H, m), 7.72-7.76 (2H, m); ^{13}C NMR ($CDCl_3$, 67.8 MHz) δ 21.4, 27.4, 27.9, 29.7, 30.2, 32.1, 32.6, 36.7, 53.5, 54.4, 60.3, 70.1, 82.0, 97.4, 124.0, 127.3, 127.5, 128.2, 129.2, 131.1, 138.4, 142.6; HRMS Calcd for $C_{26}H_{33}NO_2S$: 423.2232, Found: 423.2230.

2-(2,2-Diphenylethyl)-2,5,5-trimethyl-1-tosylpiperidine (6a).

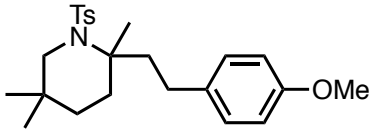


Chemical Formula: $C_{29}H_{35}NO_2S$
Exact Mass: 461.2389
Molecular Weight: 461.6587

This compound was isolated as a colorless oil; R_f (Hexane/EtOAc = 5/1, SiO_2) = 0.45; ^{1}H NMR ($CDCl_3$, 499.828 MHz) δ 0.85 (3H, s), 0.86 (3H, s), 1.10-1.15 (1H, m), 1.20-1.26 (1H, s), 1.28 (3H, s), 1.44-1.46 (2H, m), 2.43 (3H, s), 2.60 (1H, 15.5, 5.0 Hz), 2.70 (1H, dd, *J* = 15.5, 5.0 Hz), 2.96 (1H, *J* = 10.0 Hz), 3.35 (1H, dd, *J* = 15.5, 5.0 H), 3.95 (1H, t, *J* = 10.0 Hz), 7.13-7.16 (2H, m), 7.20-7.28 (12H, m), 7.70 (2H, d, *J* = 5.0 Hz); ^{13}C NMR ($CDCl_3$, 67.80 MHz) δ 21.5, 24.9, 26.9, 28.0, 30.8, 33.1, 33.9, 40.2, 47.7, 53.9, 61.9, 126.08, 126.10, 127.3, 127.6, 127.7, 128.4, 128.5, 129.3, 140.4, 142.6, 145.5, 145.8:

HRMS Calcd for $C_{29}H_{35}NO_2S$, 461.2389; Found, 461.2384.

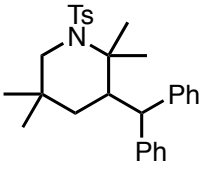
2-(4-Anisylethyl)-2,5,5-trimethyl-1-tosylpiperidine (6e).



Chemical Formula: $C_{24}H_{33}NO_3S$
Exact Mass: 415.2181
Molecular Weight: 415.5887

This compound was isolated as a colorless oil; R_f (Hexane/EtOAc = 5/1, SiO_2) = 0.38; ^{1}H NMR ($CDCl_3$, 499.828 MHz) δ 1.89 (3H, s), 1.91 (3H, s), 2.39 (1H, ddd, *J* = 13.6, 10.4, 4.0 Hz), 2.48 (3H, s), 2.55 (1H, *J* = 14.1, 10.4, 4.2 Hz), 2.70 (1H, *J* = 14.1, 6.6, 4.2 Hz), 3.11 (1H, ddd, *J* = 13.8, 10.8, 9.1 Hz), 2.98 (1H, ddd, *J* = 13.8, 8.2, 6.5 Hz), 3.42 (3H, s), 3.52-3.54 (1H, m), 3.97 (1H, d, *J* = 13.1 Hz), 4.26 (1H, d, *J* = 13.1 Hz), 4.80 (3H, s), 2.37-2.42 (1H, m), 7.82 (2H, d, *J* = 8.6 Hz), 8.10 (2H, d, *J* = 8.6 Hz), 8.26 (2H, d, *J* = 7.5 Hz), 8.73 (2H, *J* = 8.3 Hz); ^{13}C NMR ($CDCl_3$, 67.80 MHz) δ 21.5, 25.3, 25.5, 27.3, 29.7, 30.8, 33.2, 33.9, 38.5, 54.0, 55.3, 60.9, 113.7, 127.4, 129.2, 129.3, 134.2, 140.0, 142.6, 157.7; HRMS Calcd for $C_{24}H_{33}NO_3S$, 415.2181; Found, 415.2179.

3-Benzhydryl-2,2,5,5-tetramethyl-1-tosylpiperidine (7a)

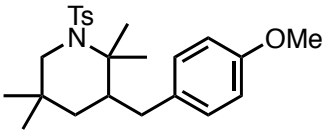


Chemical Formula: $C_{29}H_{35}NO_2S$
Exact Mass: 461.2389
Molecular Weight: 461.6587

This compound was isolated as a colorless oil; R_f value (Hexane/EtOAc = 5:1, SiO_2) =

0.33; ^{1}H NMR ($CDCl_3$, 397.75 MHz) δ 0.83 (3H, s), 1.13 (3H, s), 1.17 (3H, s), 1.20 (3H, s), two protons were overlapped in the former three singlet signals, 2.41 (3H, s), 2.87 (1H, ddd, *J* = 20.3, 7.7, 3.9 Hz), 2.96 (1H, d, *J* = 13.5 Hz), 3.73 (1H, d, 13.5 Hz), 3.85 (1H, d, *J* = 7.7 Hz), 7.15-7.35 (12H, m), 7.70 (2H, d, *J* = 8.7 Hz); ^{13}C NMR ($CDCl_3$, 67.8 MHz) δ 18.6, 21.4, 24.3, 28.0, 28.8, 31.3, 39.4, 45.8, 53.39, 53.41, 63.26, 126.04, 126.09, 126.8, 128.1, 128.4, 128.5, 128.9, 129.3, 141.1, 142.4, 143.5, 145.2; HRMS Calcd for $C_{29}H_{35}NO_2S$: 461.2389, Found: 461.2366.

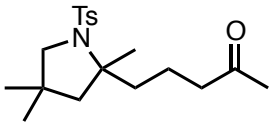
3-(4-Anisyl)-2,2,5,5-tetramethyl-1-tosylpiperidine (7e)



Chemical Formula: $C_{24}H_{33}NO_3S$
Exact Mass: 415.2181
Molecular Weight: 415.5887

This compound was isolated as a colorless oil; R_f value (Hexane/EtOAc = 5:1, SiO_2) = 0.35; ^{1}H NMR ($CDCl_3$, 397.75 MHz) Major δ 0.84 (3H, s), 0.87 (3H, s), 1.06-1.26 (2H, m), 1.11 (3H, s), 1.59 (3H, s), 1.80-1.91 (2H, m), 2.42 (3H, s), 2.78 (1H, d, *J* = 11.6 Hz), 2.87 (1H, d, *J* = 12.5 Hz), 3.64 (1H, d, *J* = 12.5 Hz), 3.78 (3H, s), 6.80 (2H, d, *J* = 8.7 Hz), 6.99 (2H, d, *J* = 7.7 Hz), 7.27 (2H, d, *J* = 8.7 Hz), 7.71 (2H, d, *J* = 7.7 Hz); ^{13}C NMR ($CDCl_3$, 67.8 MHz)δ; 17.1, 21.4, 24.0, 26.5, 28.8, 30.7, 36.3, 39.1, 45.2, 53.7, 55.1, 61.6, 113.6, 126.9, 129.3, 129.7, 132.3, 140.8, 142.5, 157.7; HRMS Calcd for $C_{24}H_{33}NO_3S$: 415.2181, Found: 415.2188.

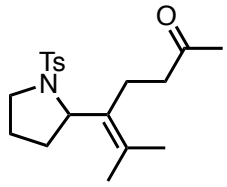
5-(2,4,4-trimethyl-1-tosylpyrrolidin-2-yl)pentan-2-one (9a).



Chemical Formula: $C_{19}H_{29}NO_3S$
Exact Mass: 351.19
Molecular Weight: 351.50

Isolated as colorless oil; R_f value (Hexane/EtOAc = 5:1, SiO_2) = 0.15; ^{1}H NMR ($CDCl_3$, 395.75 MHz) δ 0.92 (3H, s), 1.00 (3H, s), 1.45 (3H, s), 1.48-1.80 (4H, m), 1.93 (2H, dt, *J* = 13.2, 3.9 Hz), 2.13 (3H, s), 2.40 (3H, s), 2.45 (2H, t, *J* = 7.1 Hz), 3.04 (2H, d, *J* = 2.0 Hz), 7.26 (2H, d, *J* = 8.2 Hz), 7.71 (2H, d, *J* = 8.2 Hz); ^{13}C NMR ($CDCl_3$, 67.80 MHz) δ 19.2, 21.4, 27.0, 27.4, 27.5, 30.0, 36.1, 41.7, 43.6, 52.8, 61.5, 68.8, 127.2, 129.3, 138.3, 1427, 208.8; MS *m/z* 336 (M^+–Me, 0.7), 266 (100), 155 (43), 91 (49); HRMS Calcd for $C_{19}H_{29}NO_3S$: 351.1868, Found: 351.1867.

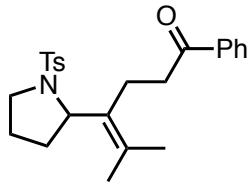
6-Methyl-5-[1-(4-tosyl)-pyrrolidin-2-yl]-hept-5-en-2-one (11a).



Chemical Formula: $C_{19}H_{27}NO_3S$
Exact Mass: 349.1712
Molecular Weight: 349.4876

This compound was isolated as a white solid (mp 80-82 ^{o}C); R_f (Hexane/EtOAc = 5/1, SiO_2) = 0.15; ^{1}H NMR ($CDCl_3$, 270.05 MHz) δ 1.13 (1H, ddd, *J* = 18.4, 18.4, 10.1, Hz), 1.50-1.60 (1H, m,), 1.66 (3H, s), 1.68-1.72 (1H, m), 1.75 (3H, s), 1.79-1.84 (1H, m), 2.08 (1H, ddd, *J* = 11.6, 11.6, 4.8 Hz), 2.18 (3H, s), 2.37-2.40 (1H, m), 2.44 (3H, s), 2.59 (1H, ddd, *J* = 18.4, 11.6, 4.8 Hz), 3.00 (1H, ddd, *J* = 18.4, 11.6, 4.8 Hz), 3.37 (1H, ddd, *J* = 10.2, 10.2, 5.8 Hz), 3.53 (1H, m), 4.45 (1H, t, *J* = 7.8 Hz), 7.33 (2H, d, *J* = 7.7 Hz), 7.71 (2H, d, *J* = 7.7 Hz); ^{13}C NMR ($CDCl_3$, 67.80 MHz) δ 19.9, 21.1, 21.5, 22.0, 24.7, 30.0, 32.3, 43.9, 50.6, 61.5, 127.6, 127.7, 129.6, 131.7, 134.5, 143.4, 209.8; HRMS Calcd for $5C_{19}H_{27}NO_3S$, 349.1712; Found, 349.1705.

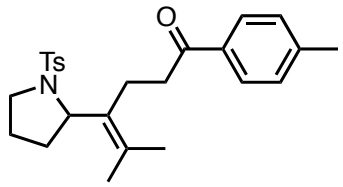
5-Methyl-1-phenyl-4-[1-(4-tosyl)-pyrrolidin-2-yl]-hex-4-en-1-one (11b).



Chemical Formula: $C_{24}H_{29}NO_3S$
Exact Mass: 411.1868
Molecular Weight: 411.5570

This compound was isolated as a white solid (mp: 151-153 ºC); R_f (Hexane/EtOAc = 5/1, SiO_2) = 0.21; ^{1}H NMR ($CDCl_3$, 395.75 MHz) δ 1.14-1.17 (1H, m), 1.55-1.62 (2H, m), 1.71 (3H, s), 1.78 (3H, s), 1.82-1.90 (1H, m), 2.21 (1H, ddd, *J* = 13.5, 11.6, 4.8 Hz), 2.43 (3H, s), 2.55-2.63 (1H, m), 3.03 (1H, ddd, *J* = 16.9, 11.6, 4.8 Hz), 3.38 (1H, dt, *J* = 16.4, 5.8 Hz), 3.55 (1H, ddd, *J* = 11.6, 7.7, 2.9 Hz), 3.65 (1H, ddd, *J* = 16.4, 11.6, 4.8 Hz), 4.51 (1H, t, *J* = 7.7 Hz), 7.32 (2H, d, *J* = 7.7 Hz), 7.46 (2H, t, *J* = 7.7 Hz), 7.54 (1H, t, *J* = 7.7 Hz), 7.73 (2H, d, *J* = 8.7 Hz), 8.03-8.06 (2H, m); ^{13}C NMR ($CDCl_3$, 67.80 MHz) δ 20.0, 21.2, 21.5, 23.0, 24.8, 32.4, 39.0, 50.7, 61.5, 127.6, 128.0, 128.2, 128.5, 129.6, 131.8, 132.8, 134.5, 136.9, 143.4, 201.1; HRMS Calcd for $C_{24}H_{29}NO_3S$, 411.1868; Found, 411.1866.

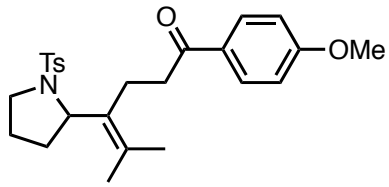
5-Methyl-4-[1-(4-tosyl)-pyrrolidin-2-yl]-1-p-tolyl-hex-4-en-1-one (11c).



Chemical Formula: $C_{25}H_{31}NO_3S$
Exact Mass: 425.2025
Molecular Weight: 425.5835

This compound was isolated as a white solid (mp: 117-118 ºC); R_f (Hexane/EtOAc = 5/1, SiO_2) = 0.21; ^{1}H NMR ($CDCl_3$, 270.05 MHz) δ 1.11-1.29 (1H, m), 1.52-1.68 (2H, m), 1.71 (3H, s), 1.79 (3H, s), 1.84-1.91 (1H, m), 2.20 (1H, ddd, *J* = 14.1, 11.5, 4.6 Hz), 2.41 (3H, s), 2.44 (3H, s), 2.52-2.64 (1H, m), 2.99 (1H, ddd, *J* = 16.8, 11.9, 4.3 Hz), 3.38 (1H, ddd, *J* = 11.4, 9.7, 5.6 Hz), 3.55 (1H, ddd, *J* = 10.2, 7.6, 3.0 Hz), 3.61 (1H, ddd, *J* = 16.5, 11.9, 4.6 Hz), 4.52 (1H, t, *J* = 7.9 Hz), 7.25-7.35 (4H, m), 7.74 (2H, d, *J* = 8.3 Hz), 7.96 (2H, d, *J* = 8.2 Hz); ^{13}C NMR ($CDCl_3$, 67.80 MHz) δ 20.0, 21.2, 21.5, 21.6, 23.2, 24.8, 32.4, 39.0, 50.7, 61.5, 127.6, 128.0, 128.3, 129.2, 129.6, 131.9, 134.4, 134.7, 143.3, 143.5, 200.7; HRMS Calcd for $C_{25}H_{31}NO_3S$, 425.2025; Found, 425.2017.

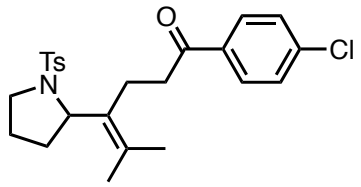
1-(4-Anisyl)-5-methyl-4-[1-(4-tosyl)-pyrrolidin-2-yl]-hex-4-en-1-one (11d).



Chemical Formula: $C_{25}H_{31}NO_4S$
Exact Mass: 441.1974
Molecular Weight: 441.5829

This compound was isolated as a white solid (mp: 116-119 ºC); R_f (Hexane/EtOAc = 5/1, SiO_2) = 0.21; ^{1}H NMR ($CDCl_3$, 270.05 MHz) δ 1.11-1.29 (1H, m), 1.52-1.69 (2H, m), 1.72 (3H, s), 1.79 (3H, s), 1.84-1.91 (1H, m), 2.19 (1H, ddd, *J* = 13.9, 11.9, 4.6 Hz), 2.44 (3H, s), 2.53-2.64 (1H, m), 2.96 (1H, ddd, *J* = 17.0, 11.9, 4.5 Hz), 3.38 (1H, ddd, *J* = 11.4, 9.6, 5.6 Hz), 3.56 (1H, ddd, *J* = 11.7, 7.6, 3.0 Hz), 3.60 (1H, ddd, *J* = 17.1, 11.9, 4.8 Hz), 3.87 (3H, s), 4.52 (1H, t, *J* = 7.9 Hz), 6.94 (2H, d, *J* = 8.9 Hz), 7.33 (2H, d, *J* = 7.9 Hz), 7.74 (2H, d, *J* = 8.2 Hz), 8.05 (2H, d, *J* = 8.9 Hz); ^{13}C NMR ($CDCl_3$, 67.80 MHz) δ 20.0, 21.2, 21.5, 23.3, 24.8, 32.4, 38.6, 50.7, 55.4, 61.5, 113.6, 127.6, 127.9, 129.6, 130.0, 130.5, 131.9, 134.6, 143.4, 163.3, 199.7; HRMS Calcd for $C_{25}H_{31}NO_4S$, 441.1974; Found, 441.1980.

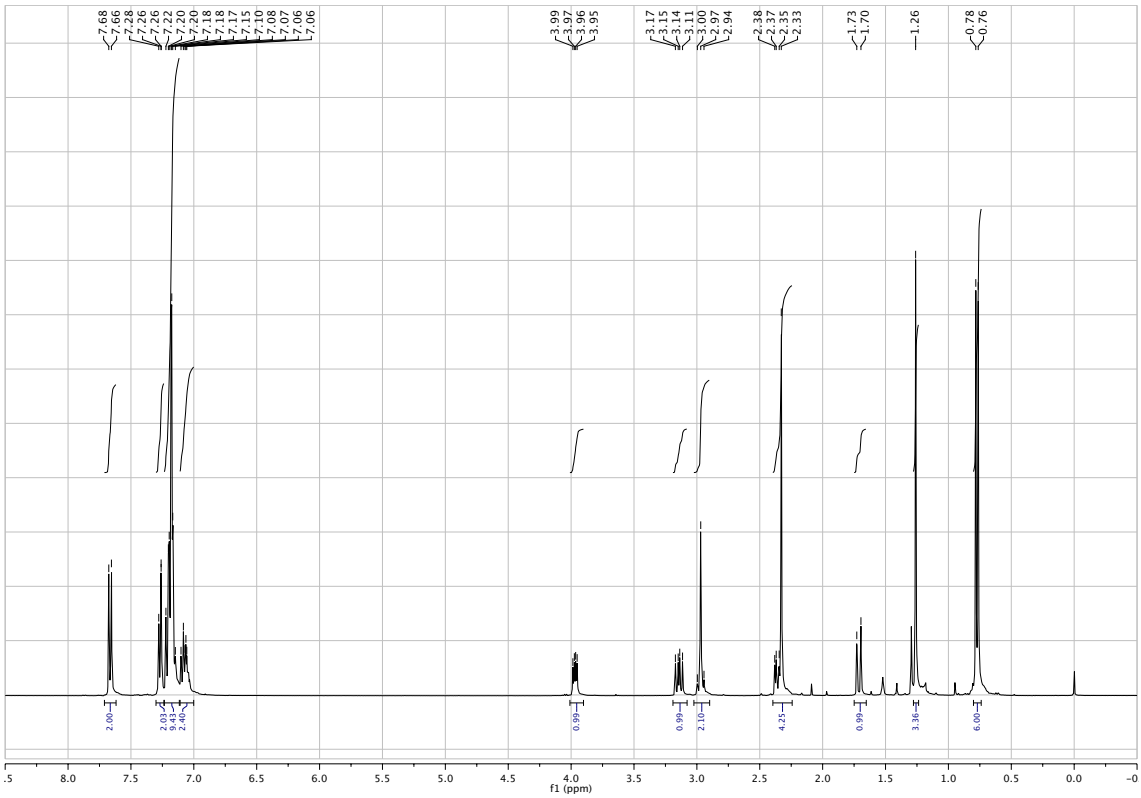
1-(4-Chloro-phenyl)-5-methyl-4-[1-(4-tosyl)-pyrrolidin-2-yl]-hex-4-en-1-one (11e).



Chemical Formula: $C_{24}H_{28}ClNO_3S$
Exact Mass: 445.1478
Molecular Weight: 446.0020

This compound was isolated as a white solid (mp: 121-124 ºC); R_f (Hexane/EtOAc = 7/1, SiO_2) = 0.21; ^{1}H NMR ($CDCl_3$, 270.05 MHz) δ 1.11-1.26 (1H, m), 1.51-1.66 (2H, m), 1.72 (3H, s), 1.78 (3H, s), 1.81-1.90 (1H, m), 2.20 (1H, ddd, *J* = 13.8, 12.0, 4.6 Hz), 2.44 (3H, s), 2.54-2.65 (1H, m), 2.99 (1H, ddd, *J* = 17.4, 11.7, 4.6 Hz), 3.36 (1H, ddd, *J* = 11.5, 9.8, 5.8 Hz), 3.54 (1H, ddd, *J* = 11.7, 7.6, 3.0 Hz), 3.66 (1H, ddd, *J* = 17.5, 11.7, 4.6 Hz), 4.51 (1H, t, *J* = 7.9 Hz), 7.33 (2H, d, *J* = 8.6 Hz), 7.44 (2H, d, *J* = 8.6 Hz), 7.73 (2H, d, *J* = 8.2 Hz), 8.00 (2H, d, *J* = 8.6 Hz); ^{13}C NMR ($CDCl_3$, 67.80 MHz) δ 20.0, 21.2, 21.5, 23.3, 24.7, 32.4, 39.0, 50.7, 61.6, 127.6, 128.0, 128.8, 129.7, 131.7, 134.3, 135.2, 139.2, 143.5, 199.9; HRMS Calcd for $C_{24}H_{28}ClNO_3S$, 445.1478; Found, 445.1485.

3a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7.28
7.26
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7.22
7.20
7.20
7.18
7.18
7.17
7.15
7.10
7.08
7.07
7.06
7.06
3.99
3.97
3.96
3.95
3.17
3.15
3.14
3.11
3.00
2.97
2.94
2.38
2.37
2.35
2.33
1.73
1.70
1.26
0.78
0.76
2.00
2.03
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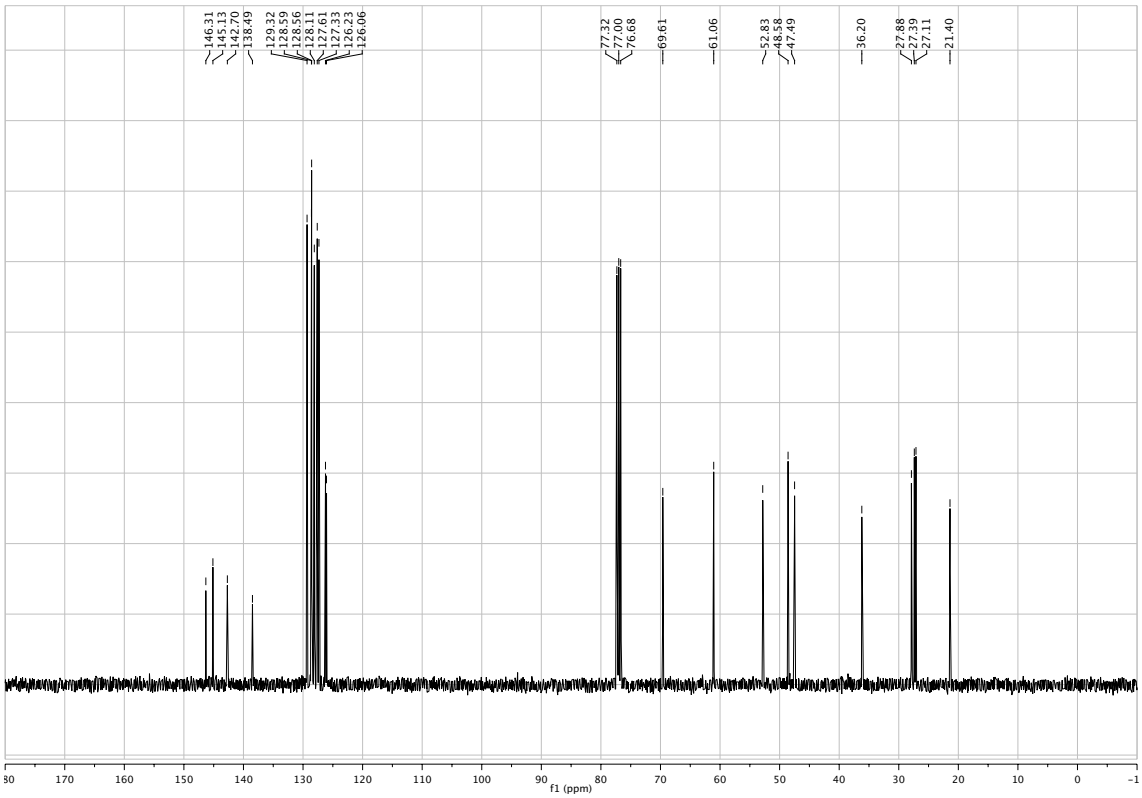
2.40
0.99
0.99
2.10
4.23
0.99
3.36
6.60
f1 (ppm)


146.31
145.13
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138.49
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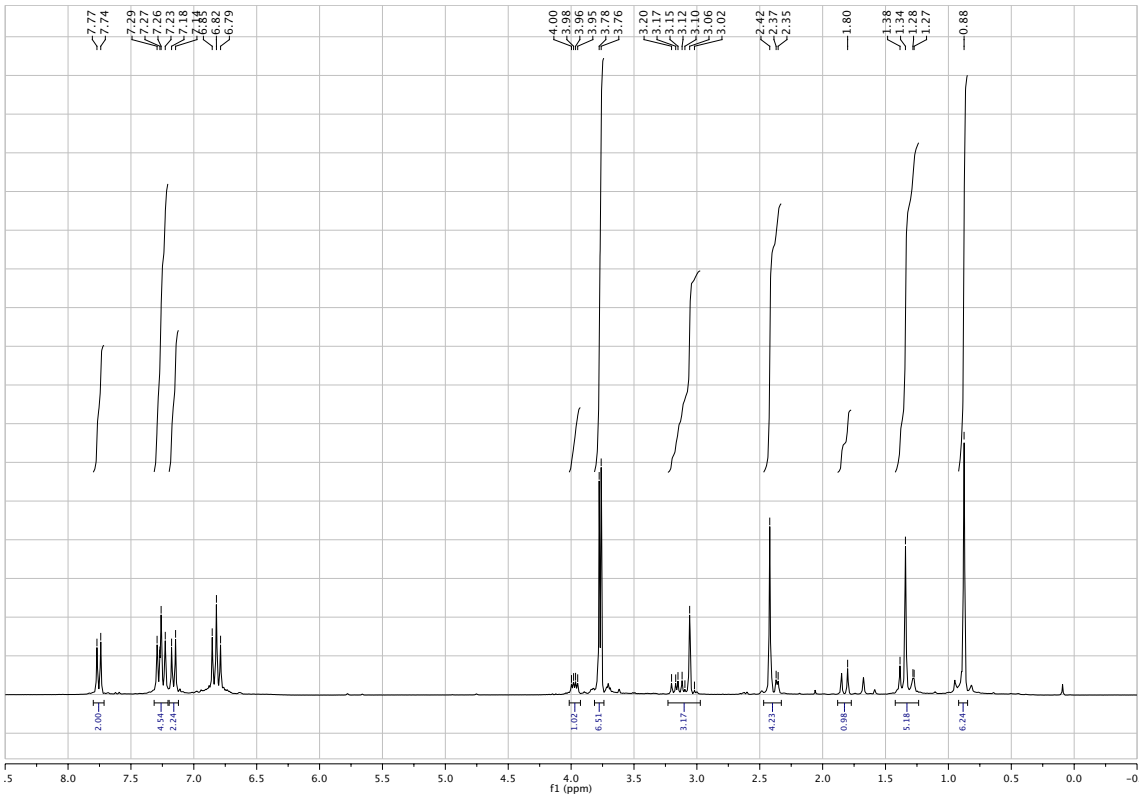
128.59
128.56
128.11
127.61
127.33
126.23
126.06
77.32
77.00
76.68
69.61
61.06
52.83
48.58
47.49
36.20
27.88
27.39
27.11
21.40
f1 (ppm)

3b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7.23
7.18
6.83
6.82
6.79
4.00
3.98
3.96
3.95
3.78
3.76
3.20
3.17
3.15
3.12
3.10
3.06
3.02
2.42
2.37
2.35
1.80
1.38
1.34
1.28
1.27
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2.00
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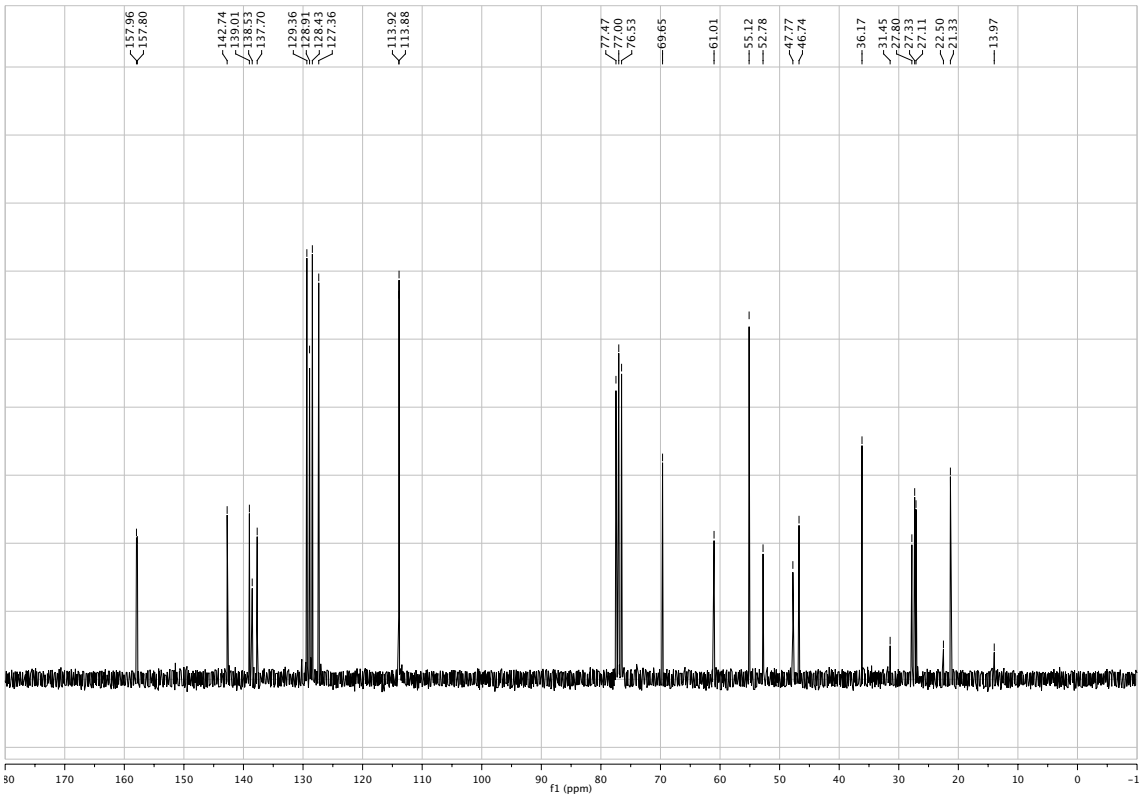
2.24
1.02
6.51
3.17
4.23
0.98
5.18
6.24
f1 (ppm)


157.96
157.80
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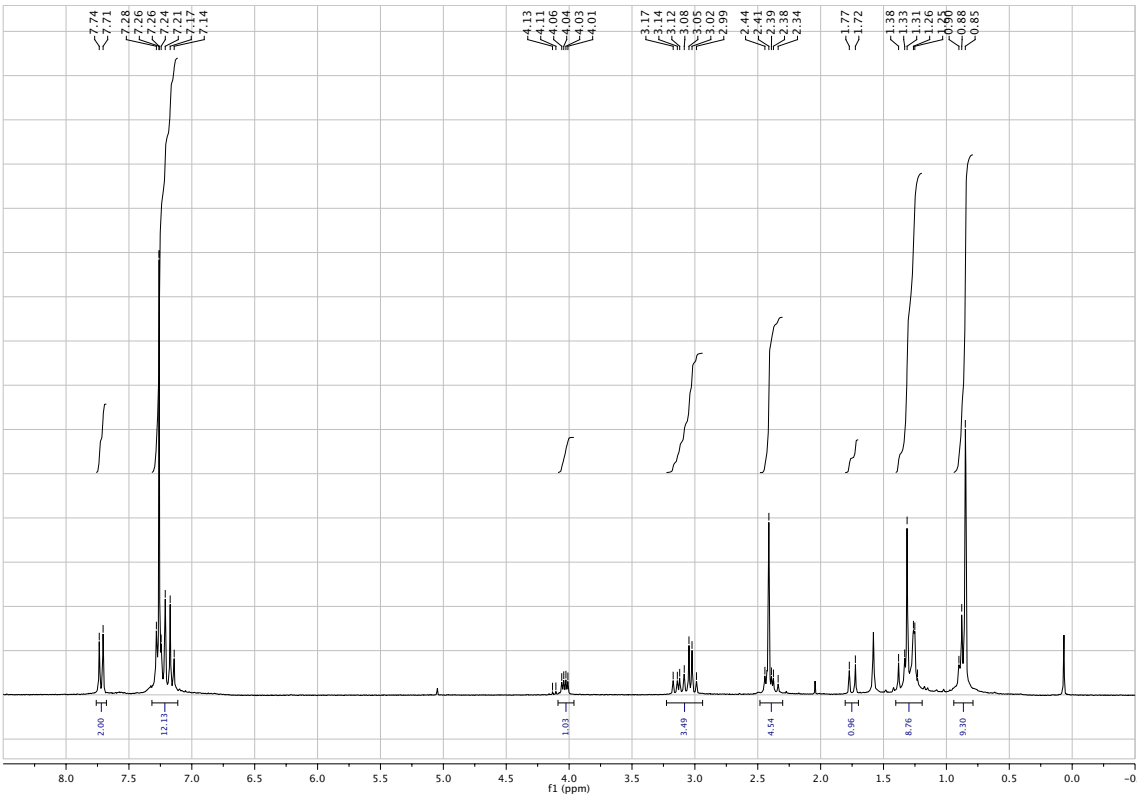
137.70
129.36
128.91
128.43
127.36
113.92
113.88
77.47
77.00
76.53
69.65
61.01
55.12
52.78
47.77
46.74
36.17
31.45
27.80
27.33
27.11
22.50
21.33
13.97
f1 (ppm)

3c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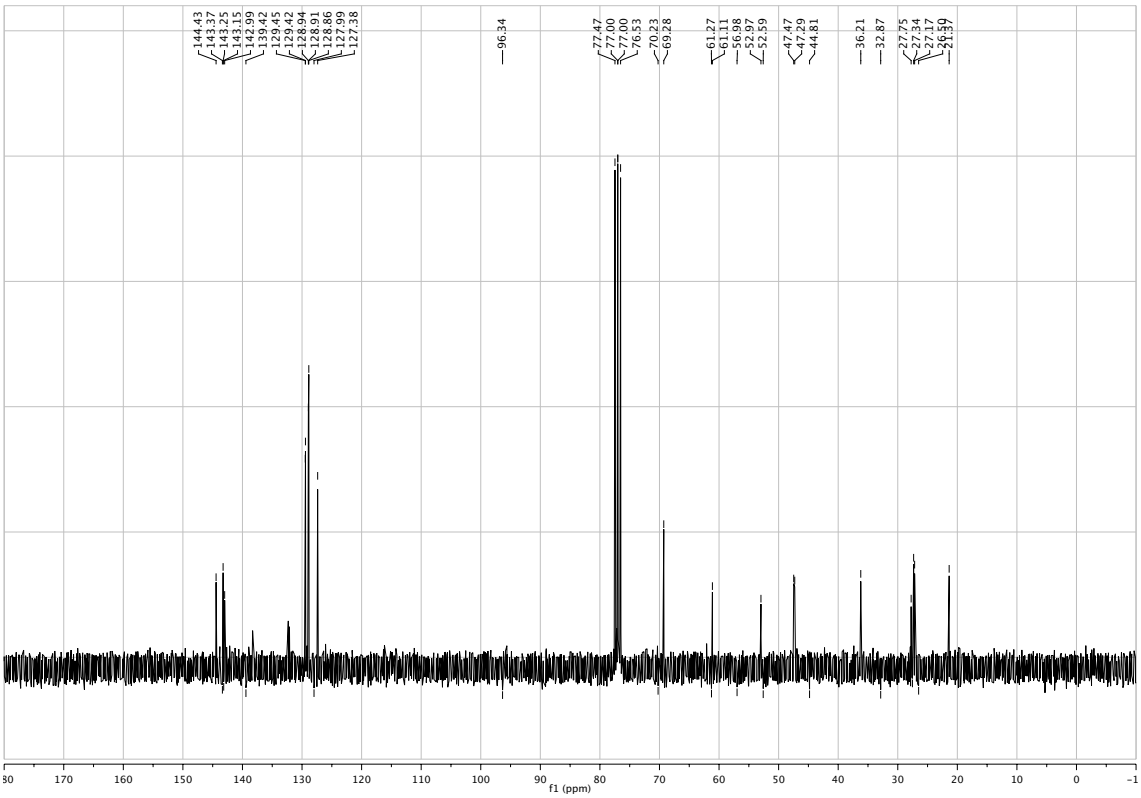
7.17
7.14
4.13
4.11
4.06
4.04
4.03
4.01
3.17
3.14
3.12
3.08
3.05
3.02
2.99
2.44
2.41
2.39
2.38
2.34
1.77
1.72
1.38
1.33
1.31
1.26
1.25
0.90
0.88
0.85
2.00
12.13
1.03
3.49
4.54
0.96
8.76
9.30
f1 (ppm)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143.37
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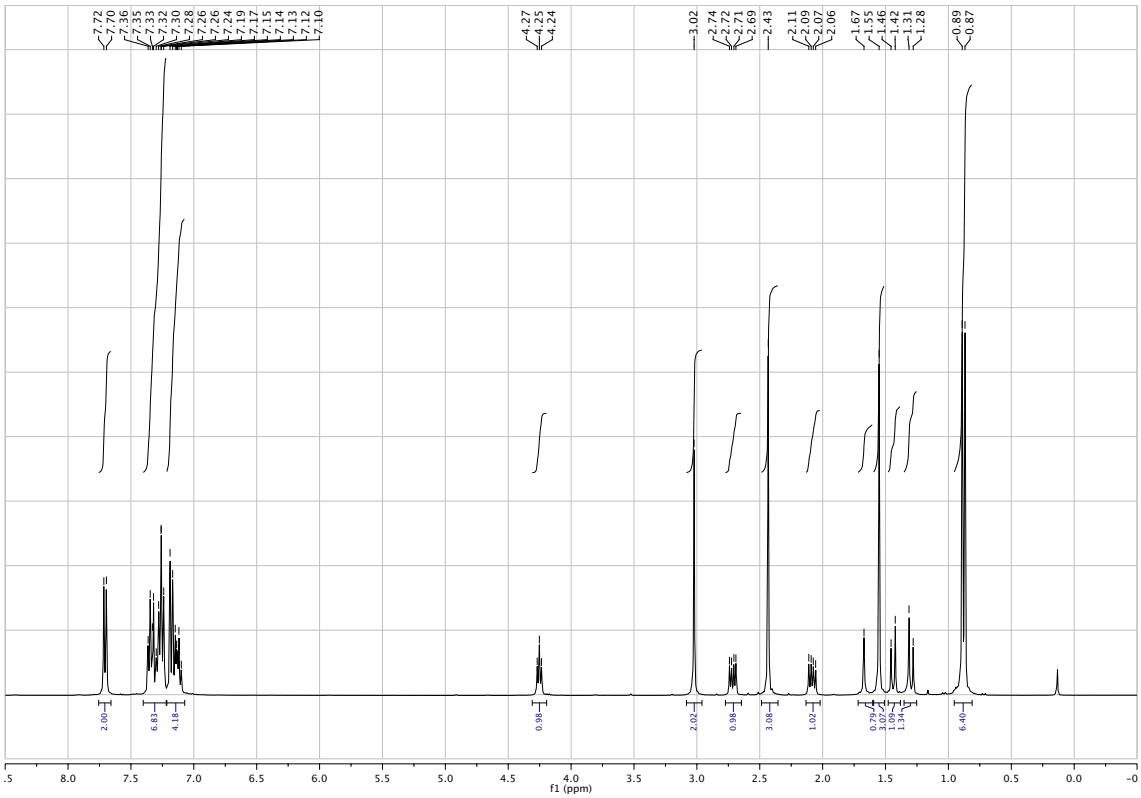
143.15
142.99
139.42
129.45
128.94
128.91
128.86
127.99
127.38
96.34
77.47
77.00
77.00
76.53
70.23
69.28
61.27
61.11
55.98
52.97
52.59
47.47
47.29
44.81
36.21
32.87
27.75
27.34
27.17
26.59
21.37
f1 (ppm)

3d


7.72
7.70
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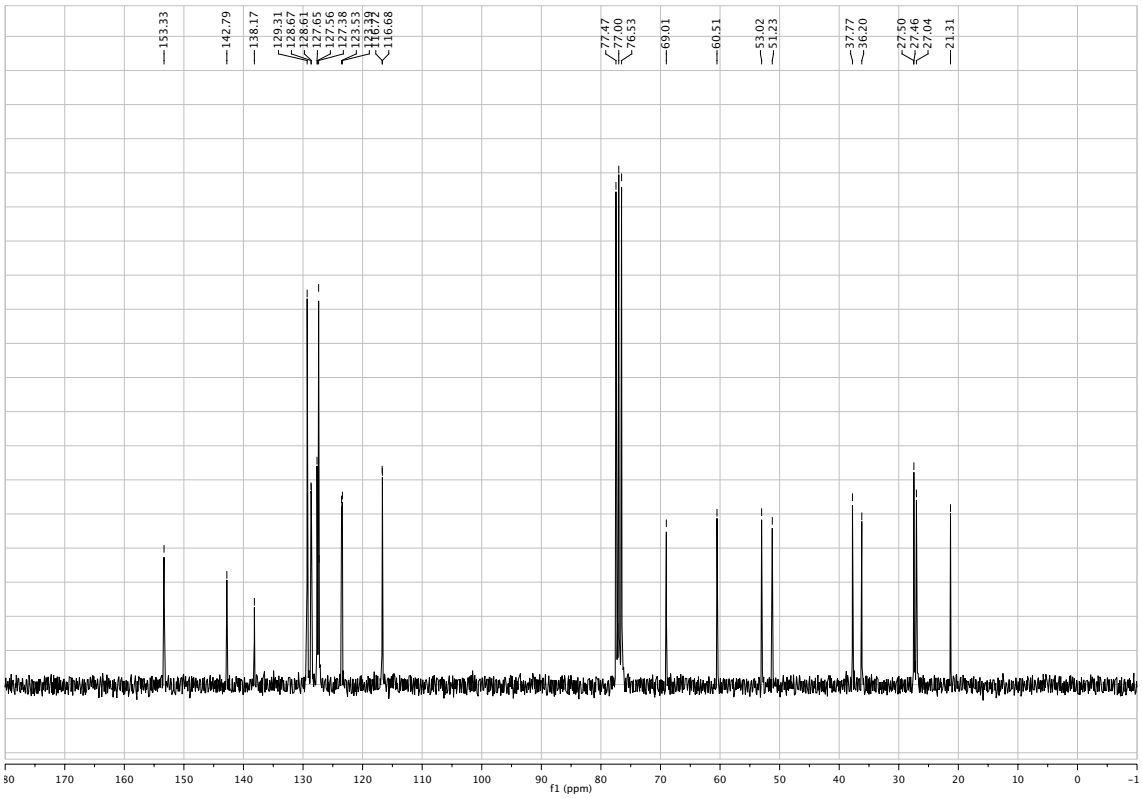
7.35
7.33
7.32
7.30
7.28
7.26
7.26
7.24
7.19
7.17
7.15
7.14
7.13
7.12
7.10
4.27
4.25
4.24
3.02
2.74
2.72
2.71
2.69
2.43
2.11
2.09
2.07
2.06
1.67
1.55
1.46
1.42
1.31
1.28
0.89
0.87
2.00
6.83
4.18
0.98
2.02
0.98
3.08
1.02
0.79
3.07
1.04
1.34
6.40
f1 (ppm)


153.33
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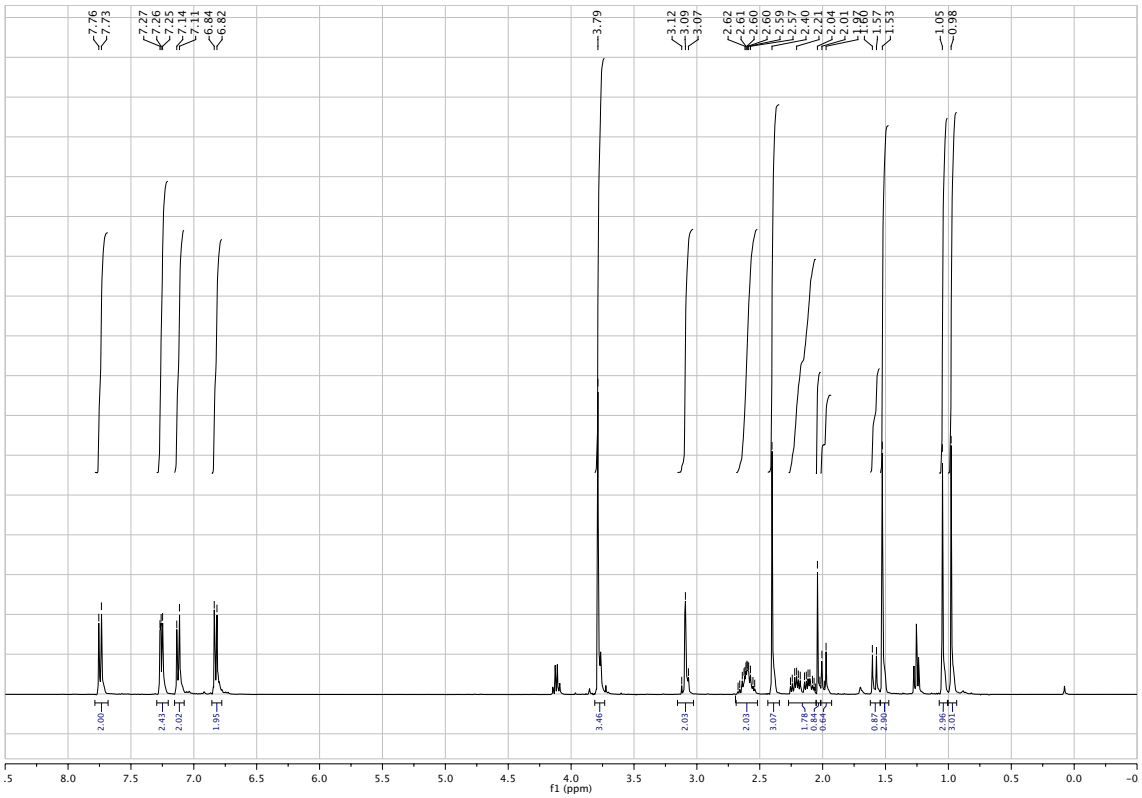
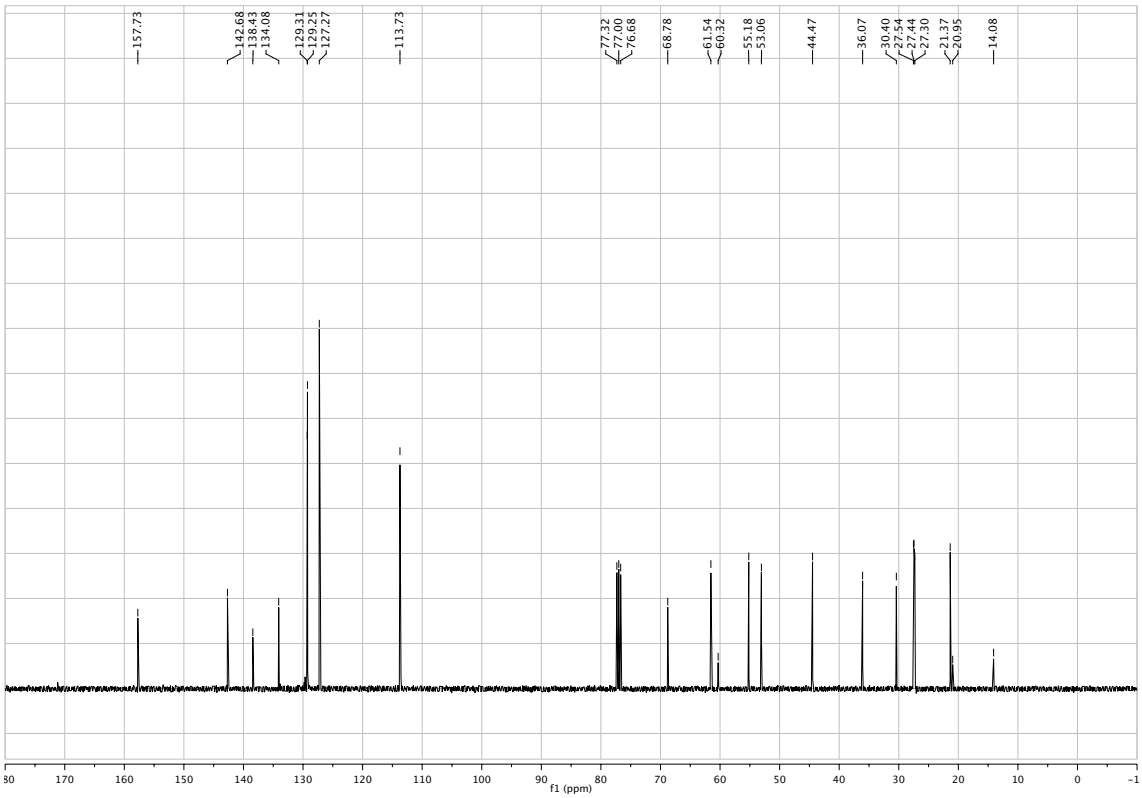
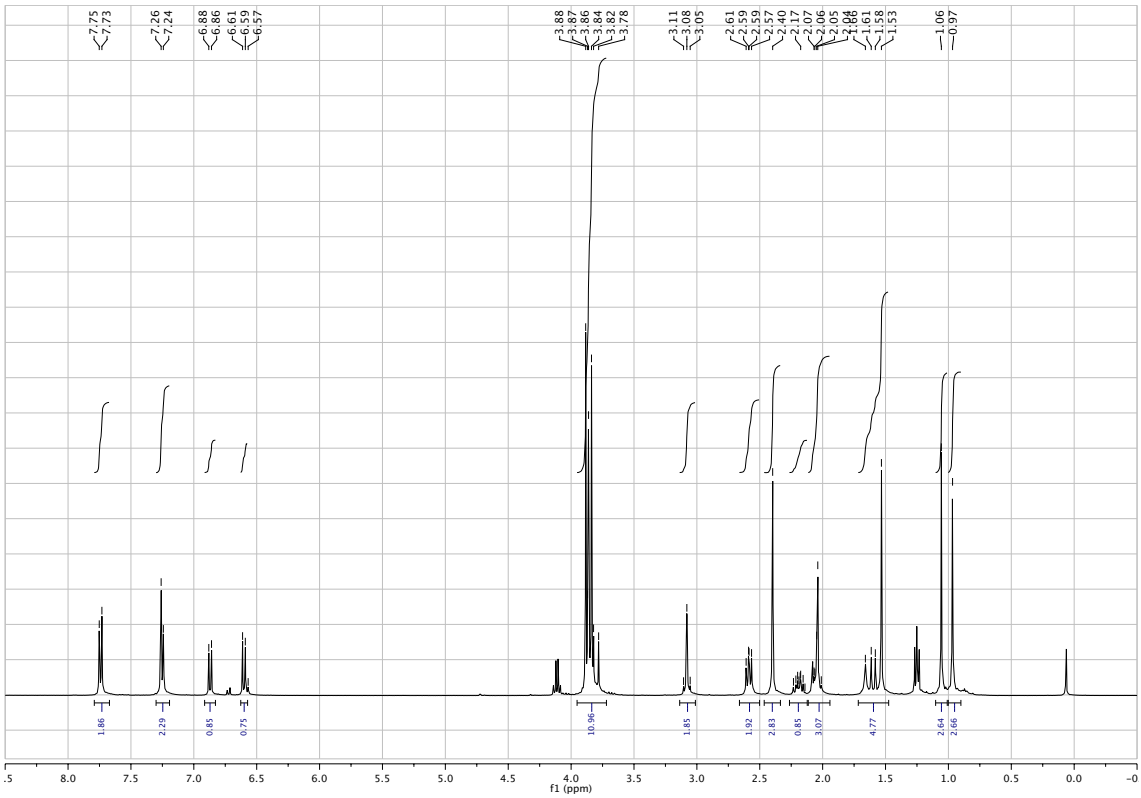
129.31
128.67
128.61
127.65
127.56
127.38
123.53
122.39
122.32
116.72
116.68
77.47
77.00
76.53
69.01
60.51
53.02
51.23
37.77
36.20
27.50
27.46
27.04
21.31
f1 (ppm)

3e


7.76
7.73
7.27
7.26
7.25
7.14
7.11
6.84
6.82
3.79
3.12
3.09
3.07
2.62
2.61
2.60
2.60
2.59
2.57
2.40
2.21
2.04
2.01
1.87
1.60
1.57
1.53
1.05
0.98
2.00
2.43
2.02
1.95
3.46
2.03
2.03
3.07
1.78
0.84
0.64
0.87
2.80
2.96
3.01
f1 (ppm)


157.73
142.68
138.43
134.08
129.31
129.25
127.27
113.73
77.32
77.00
76.68
68.78
61.54
60.32
55.18
53.06
44.47
36.07
30.40
27.54
27.44
27.30
21.37
20.95
14.08
f1 (ppm)

3f


7.75
7.73
7.26
7.24
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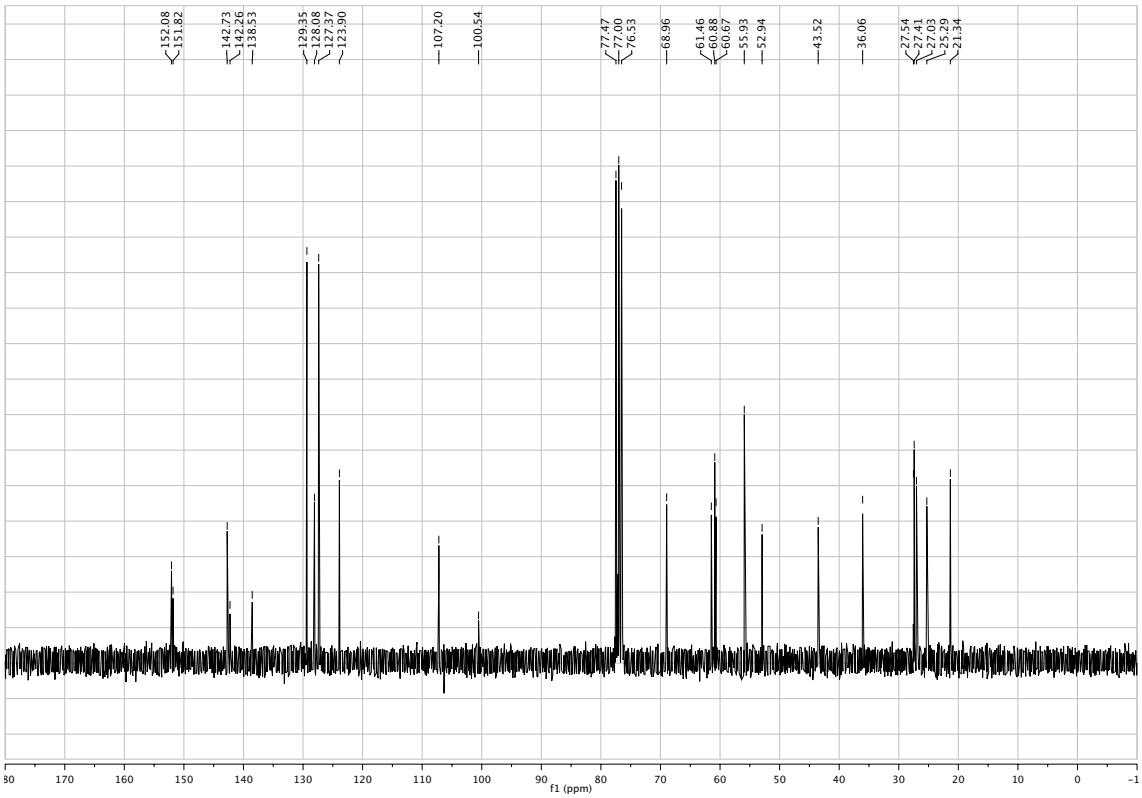
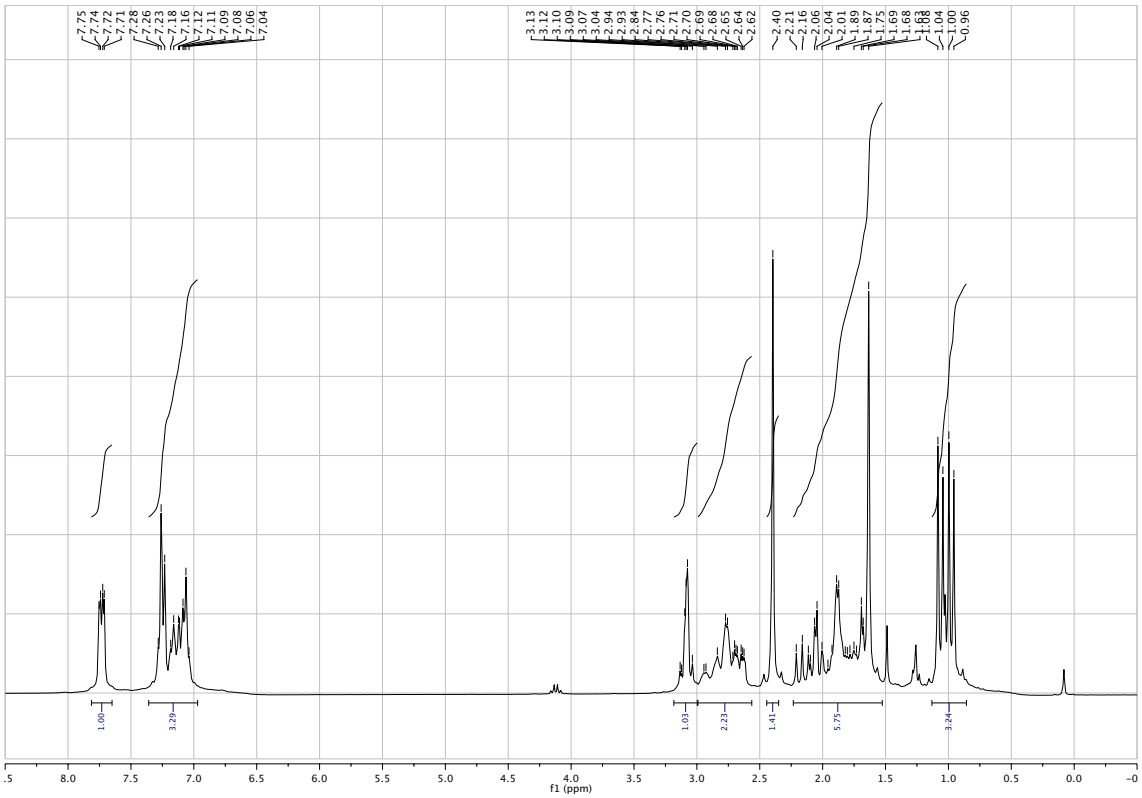
6.86
6.61
6.59
6.57
3.88
3.87
3.86
3.84
3.82
3.78
3.11
3.08
3.05
2.61
2.59
2.59
2.57
2.40
2.17
2.07
2.06
2.05
2.04
1.66
1.61
1.58
1.53
1.06
0.97
1.86
2.29
0.85
0.75
10.86
1.85
1.92
2.83
0.85
3.07
4.77
2.64
2.66
f1 (ppm)


152.08
151.82
142.73
142.26
138.53
129.35
128.08
127.37
123.90
107.20
100.54
77.47
77.00
76.53
68.96
61.46
60.88
60.67
55.93
52.94
43.52
36.06
27.54
27.41
27.03
25.29
21.34
f1 (ppm)

3g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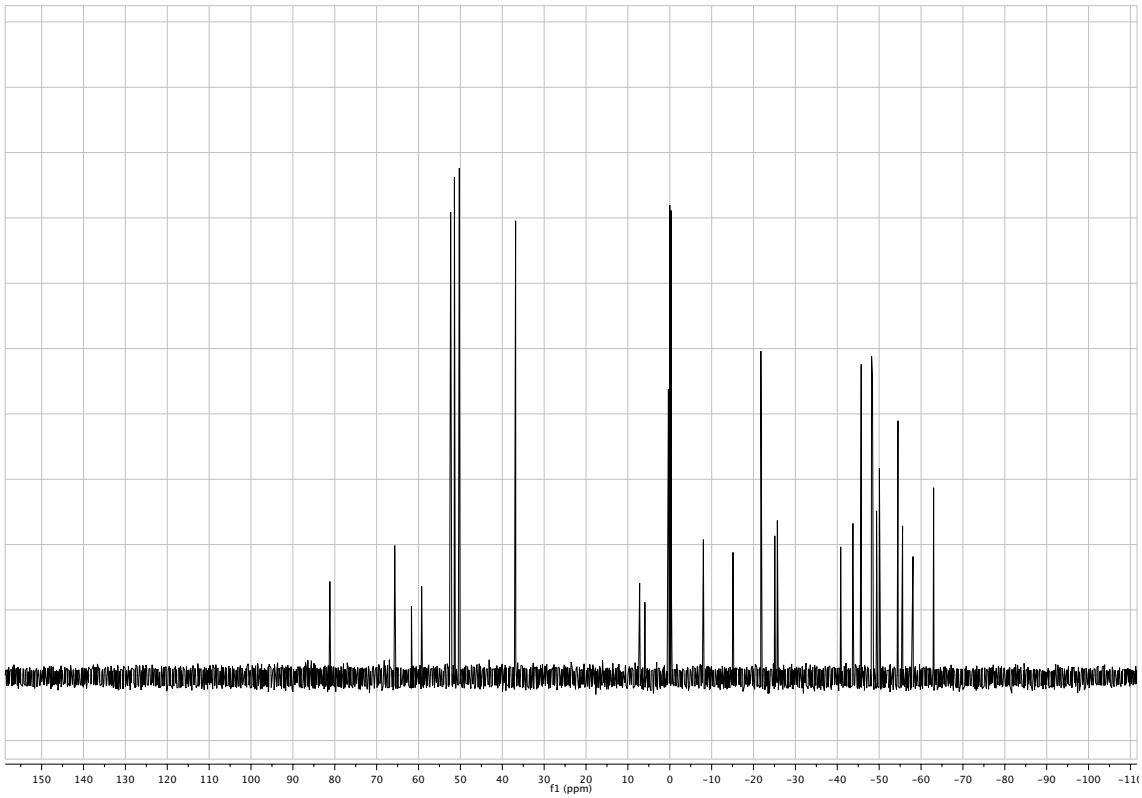
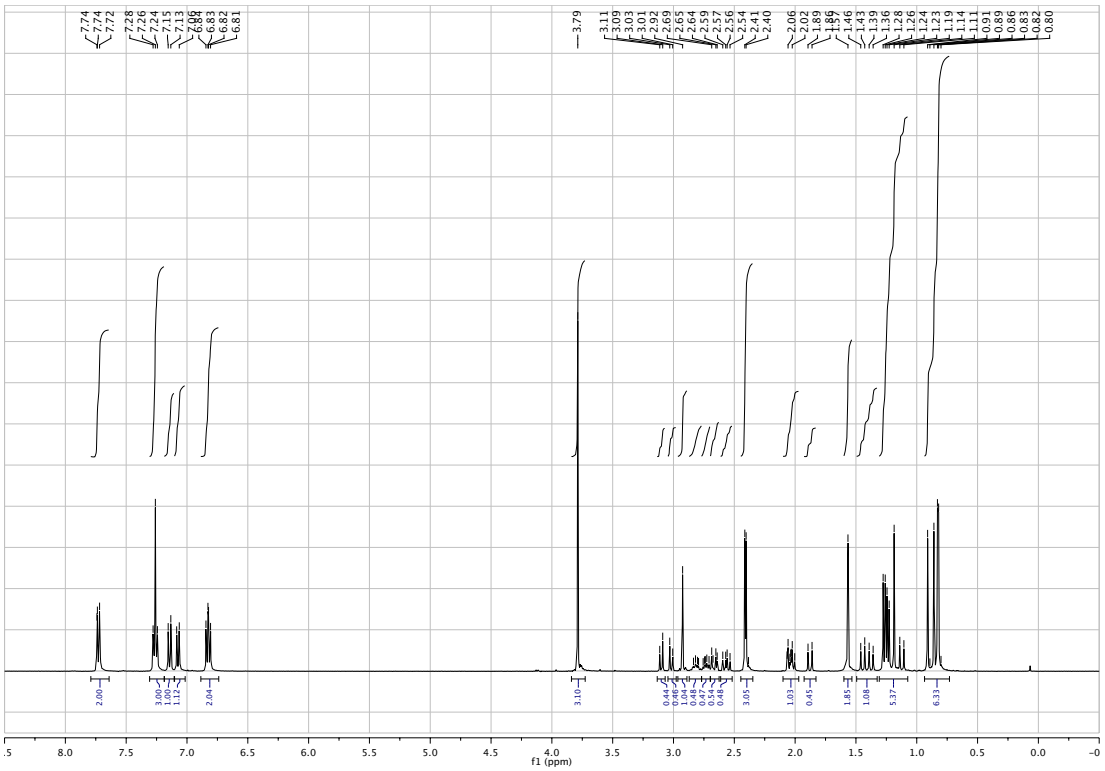
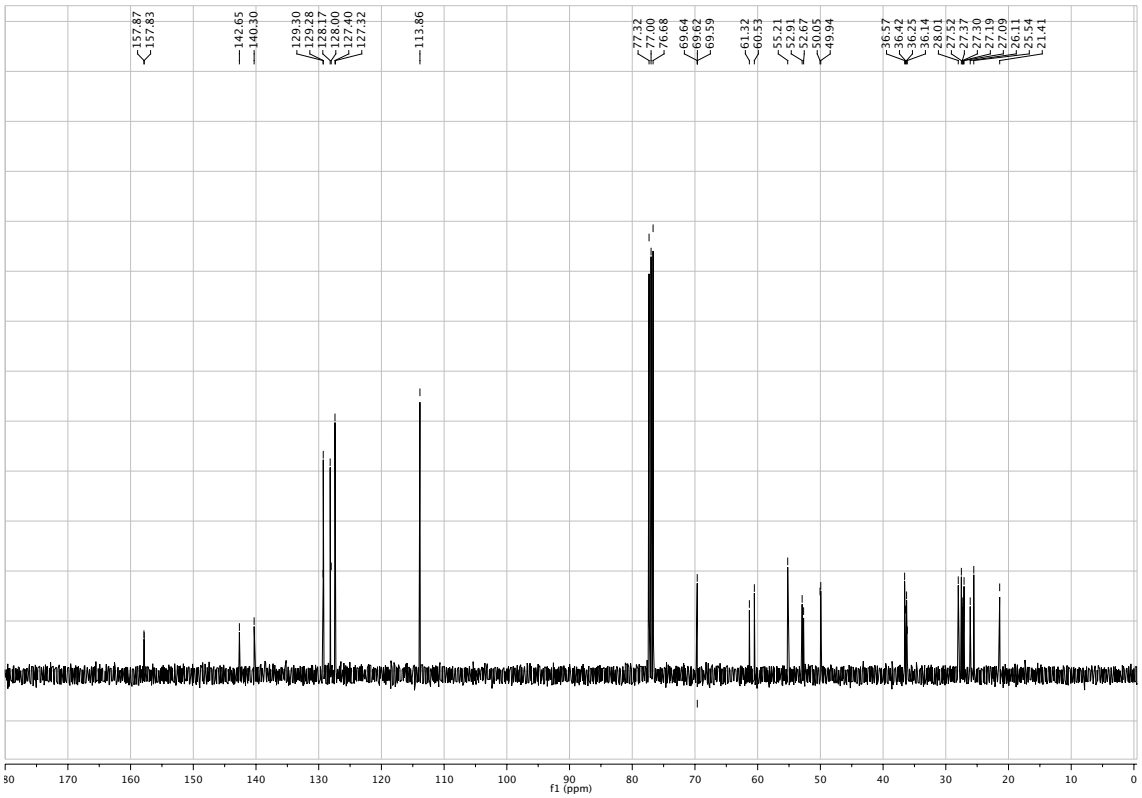
7.74
7.72
7.71
7.28
7.26
7.23
7.18
7.16
7.12
7.11
7.09
7.08
7.06
7.04
3.13
3.12
3.10
3.09
3.07
3.04
2.94
2.93
2.84
2.77
2.76
2.71
2.70
2.69
2.68
2.65
2.64
2.62
2.40
2.21
2.16
2.06
2.04
2.01
1.89
1.87
1.75
1.69
1.68
1.04
1.00
0.96
1.00
3.29
1.03
2.23
1.41
5.75
3.24
f1 (ppm)

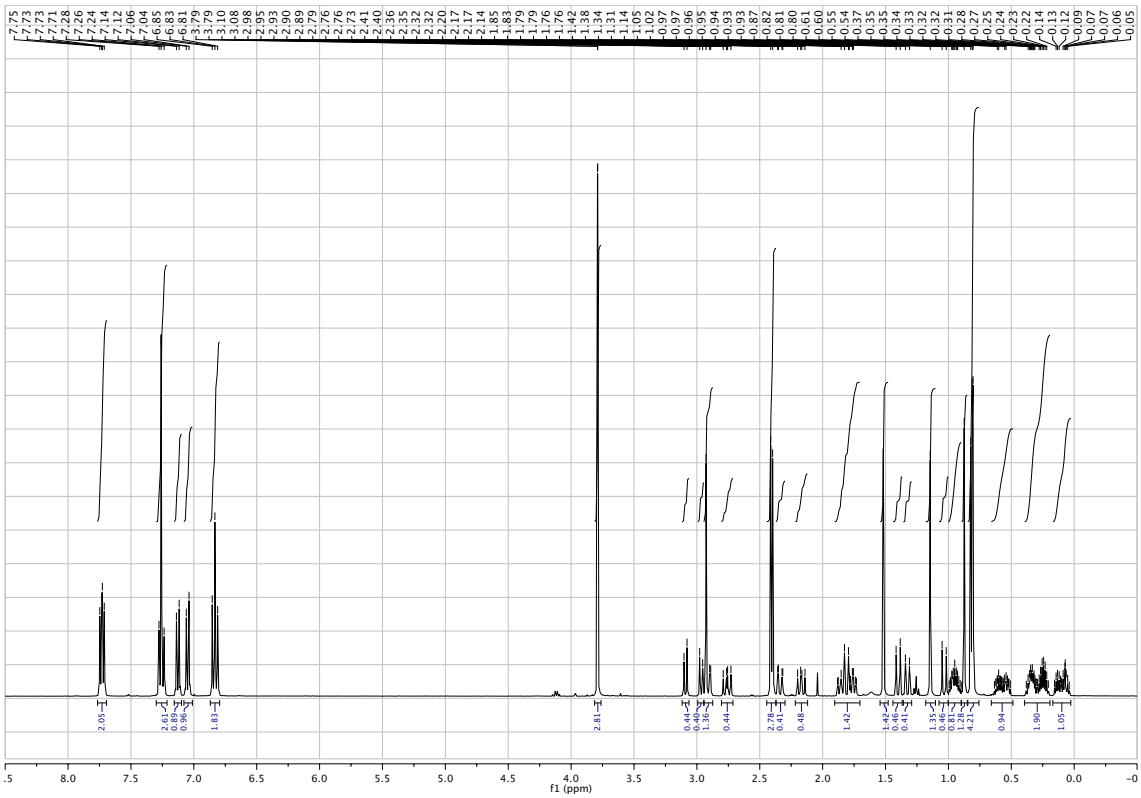

f1 (ppm)

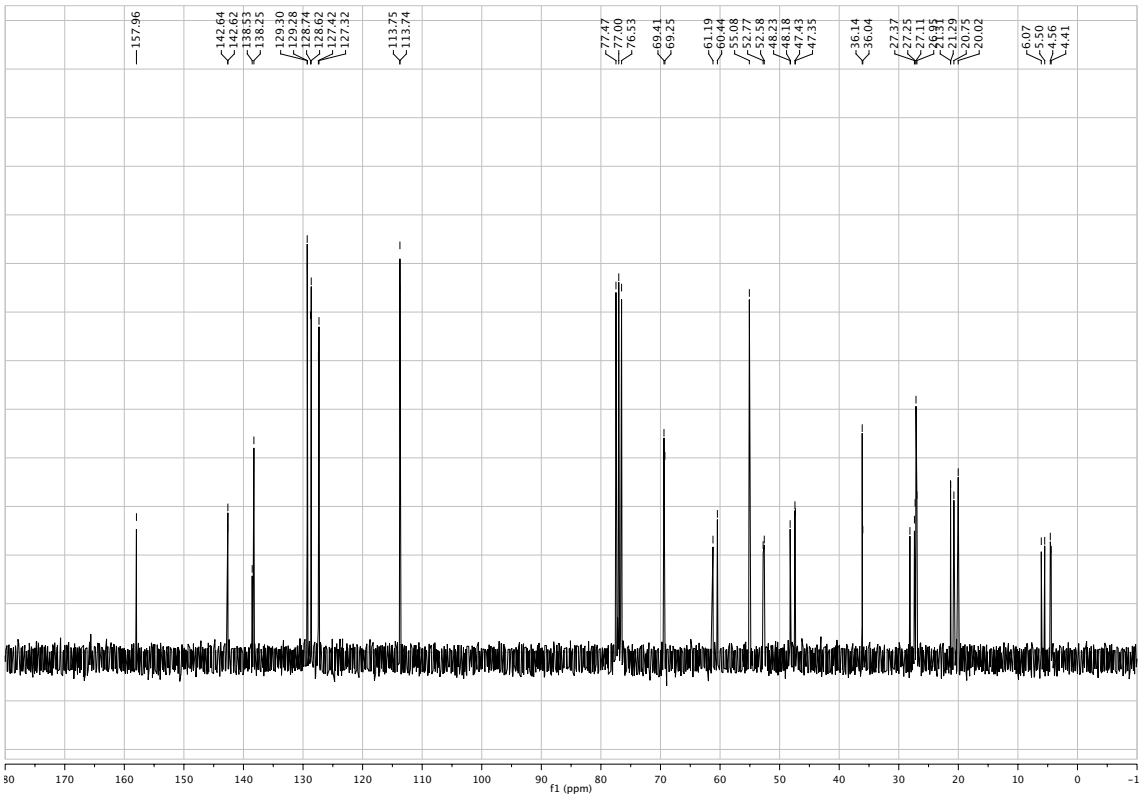
3h





3i


f1 (ppm)


157.96
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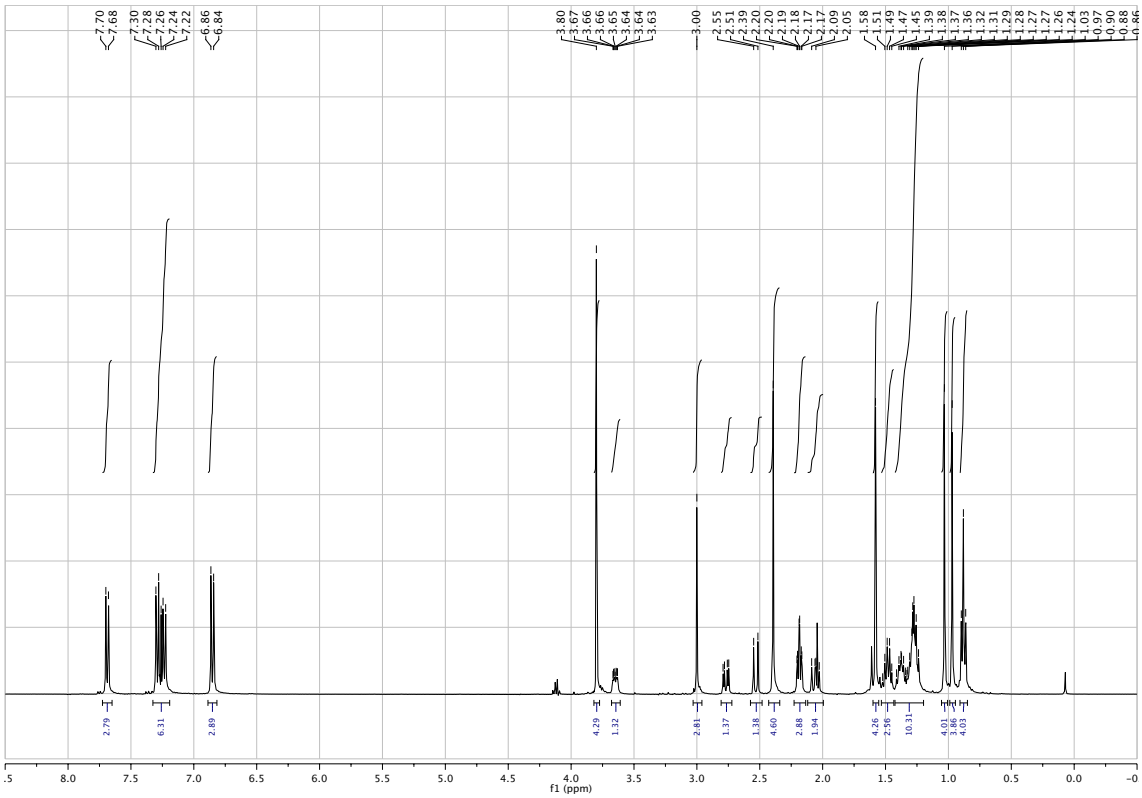
138.25
129.30
129.28
128.74
128.62
127.42
127.32
113.75
113.74
77.47
77.00
76.53
69.41
69.25
61.19
60.44
55.08
52.77
52.58
48.23
48.18
47.43
47.35
36.14
36.04
27.37
27.25
27.11
27.01
21.31
21.29
20.75
20.02
6.07
5.50
4.56
4.41
f1 (ppm)

3j-Major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7.68
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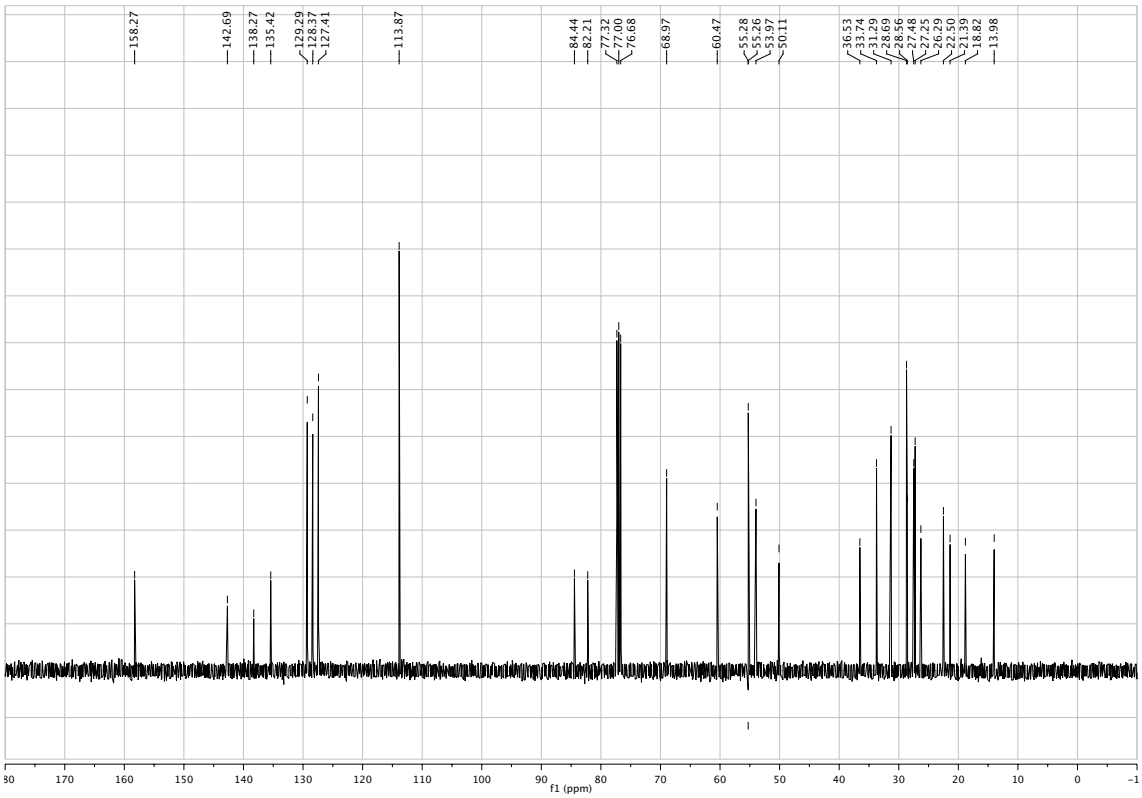
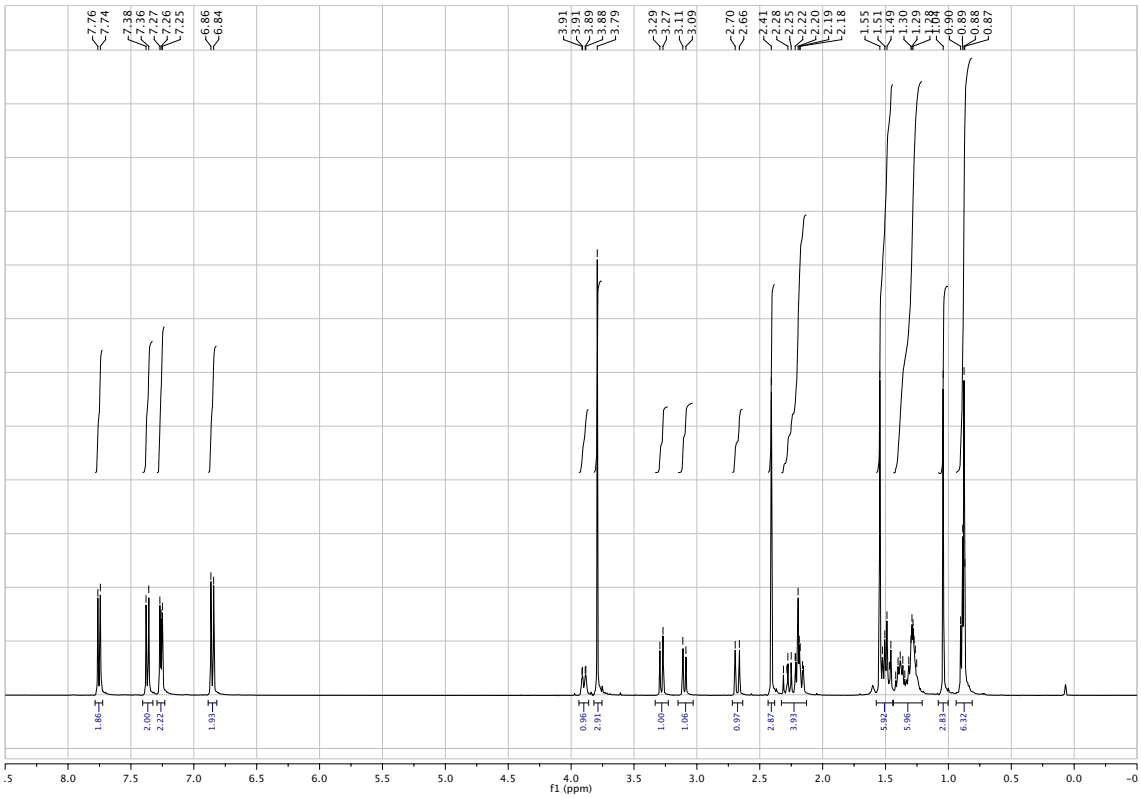
7.24
7.22
6.86
6.84
3.80
3.67
3.66
3.66
3.65
3.64
3.64
3.63
3.00
2.55
2.51
2.39
2.20
2.20
2.19
2.18
2.17
2.17
2.09
2.05
1.58
1.51
1.49
1.47
1.45
1.39
1.38
1.37
1.36
1.32
1.31
1.29
1.28
1.27
1.27
1.26
1.24
1.03
0.97
0.90
0.88
2.79
6.31
2.89
4.29
1.32
2.81
1.37
1.38
4.60
2.88
1.94
4.26
2.56
10.31
4.01
3.86
4.03
f1 (ppm)


158.27
142.69
138.27
135.42
129.29
128.37
127.41
113.87
84.44
82.21
77.32
77.00
76.68
68.97
60.47
55.28
55.26
53.97
50.11
36.53
33.74
31.29
28.69
28.56
27.48
27.25
26.29
22.50
21.39
18.82
13.98
f1 (ppm)

3j-Minor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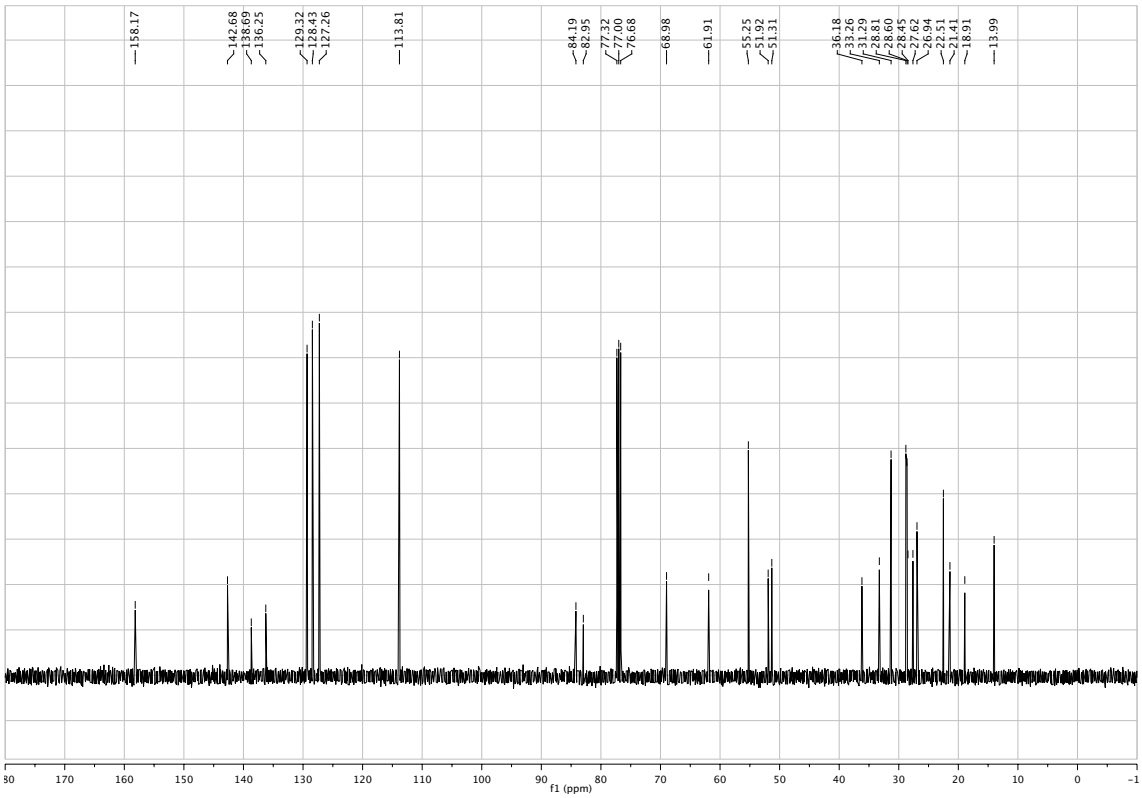
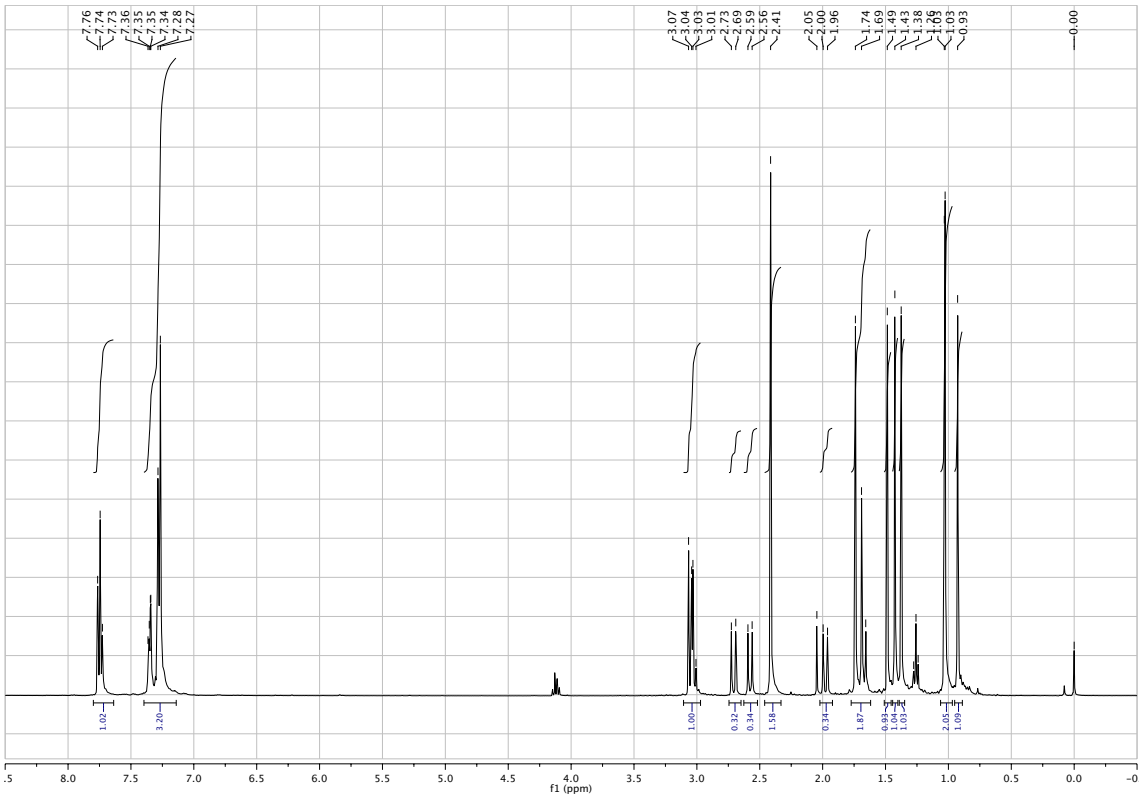
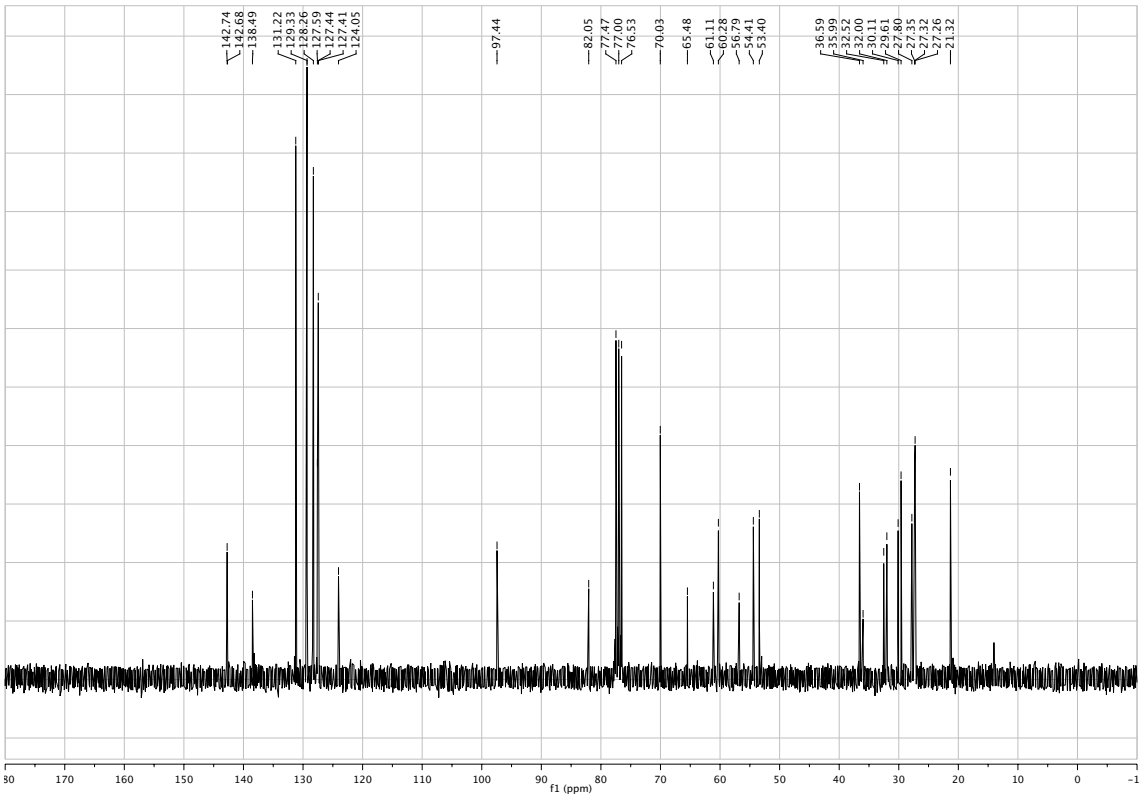
7.74
7.38
7.36
7.27
7.26
7.25
6.86
6.84
3.91
3.91
3.89
3.88
3.79
3.29
3.27
3.11
3.09
2.70
2.66
2.41
2.28
2.25
2.22
2.20
2.19
2.18
1.55
1.51
1.49
1.30
1.29
1.04
1.03
0.90
0.89
0.88
0.87
1.86
2.00
2.22
1.93
0.96
2.91
1.00
1.08
0.97
2.87
3.93
5.92
5.96
2.83
6.32
f1 (ppm)

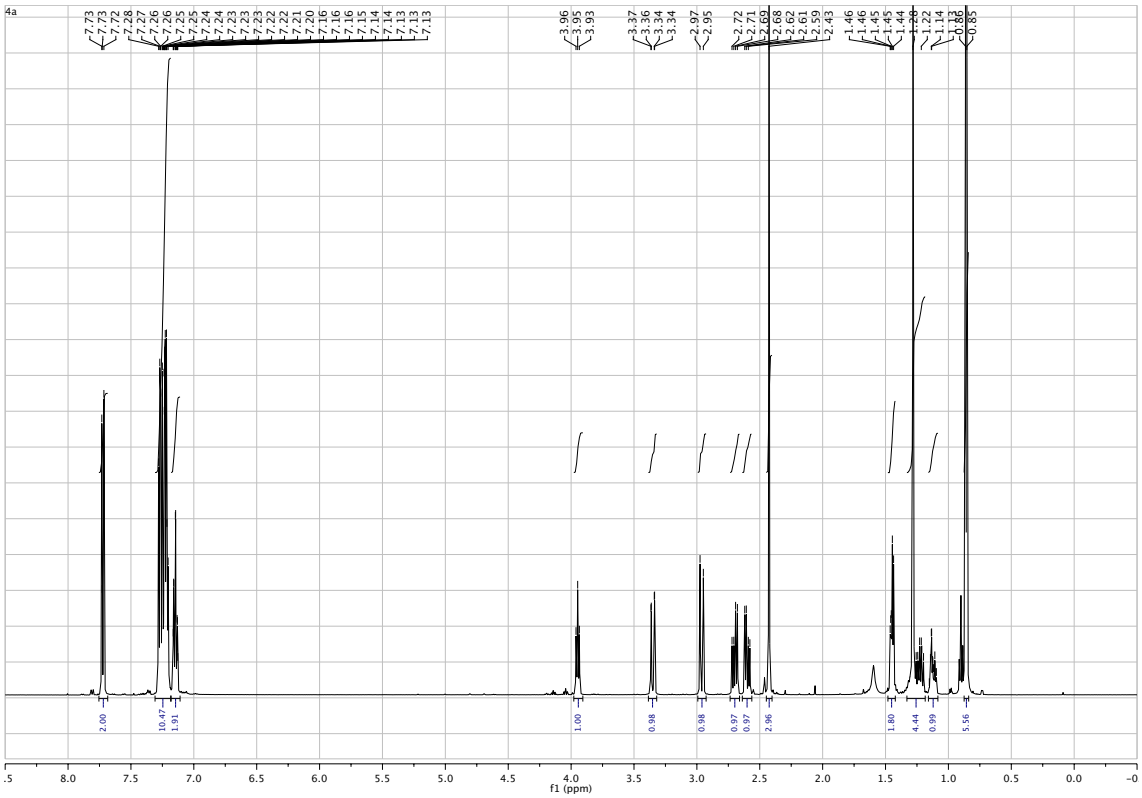

158.17
142.68
135.69
136.25
129.32
128.43
127.26
113.81
84.19
82.95
77.32
77.00
76.68
68.98
61.91
55.25
51.92
51.31
36.18
33.26
31.29
28.81
28.60
28.45
27.62
26.94
22.51
21.41
18.91
13.99
f1 (ppm)

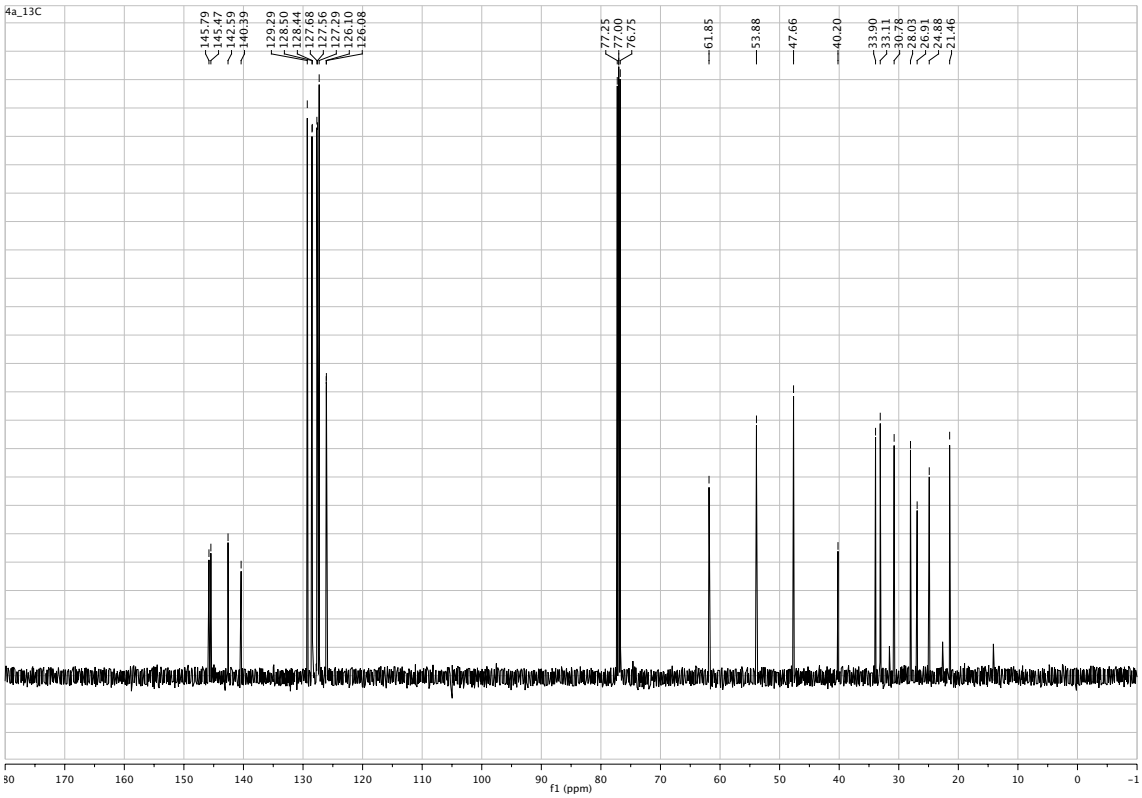
3k


7.76
7.74
7.73
7.36
7.35
7.35
7.34
7.28
7.27
3.07
3.04
3.03
3.01
2.73
2.69
2.59
2.56
2.41
2.05
2.00
1.96
1.74
1.69
1.49
1.43
1.38
1.26
1.03
0.93
0.00
1.02
3.20
1.00
0.32
0.34
1.58
0.34
1.87
0.93
1.04
1.03
2.05
1.09
f1 (ppm)

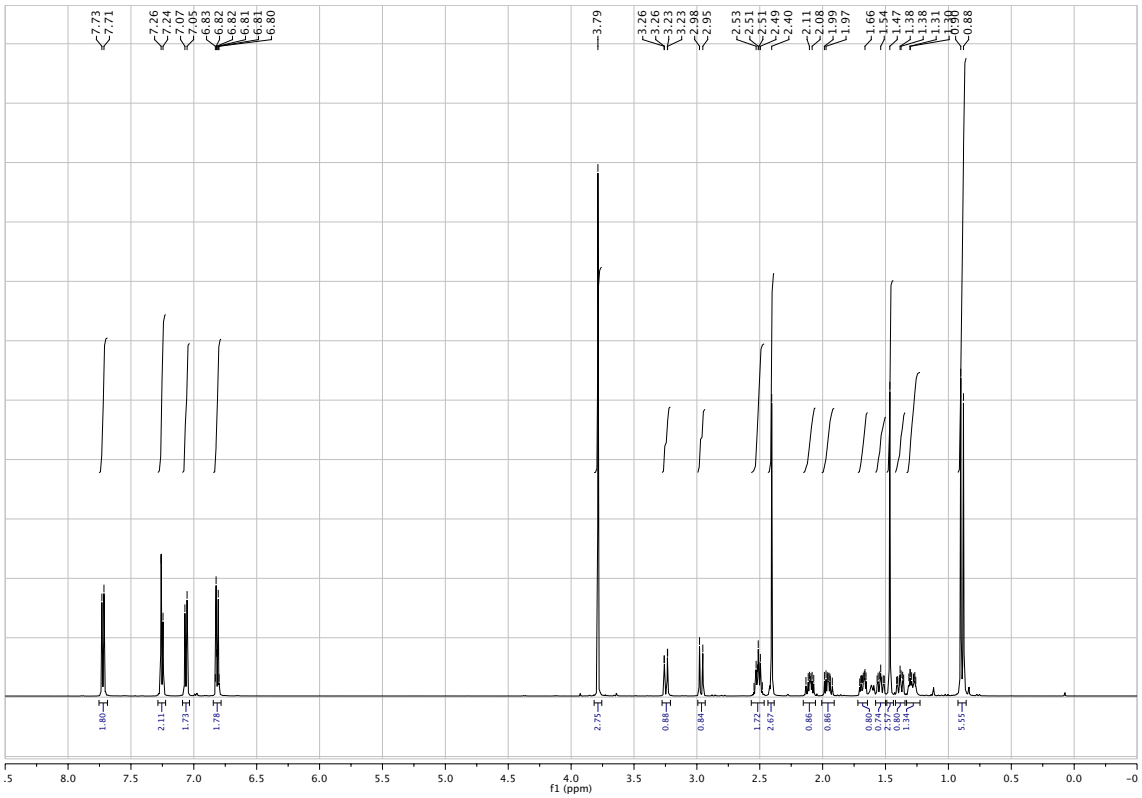

142.74
142.68
138.49
131.22
129.33
128.26
127.59
127.44
127.41
124.05
97.44
82.05
77.47
77.00
76.53
70.03
65.48
61.11
60.28
56.79
54.41
53.40
36.59
35.99
32.52
32.00
30.11
29.61
27.80
27.35
27.32
27.26
21.32
f1 (ppm)

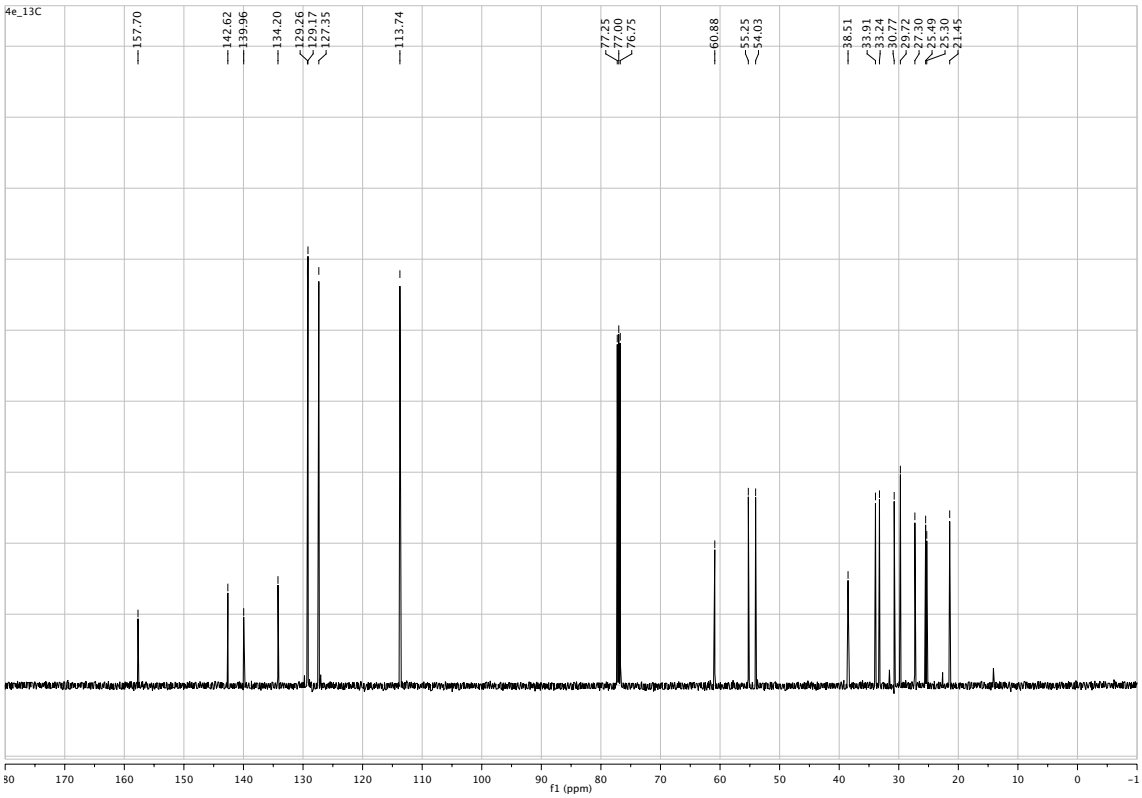
6a


4a
7.73
7.73
7.72
7.28
7.27
7.26
7.26
7.25
7.25
7.24
7.24
7.23
7.23
7.23
7.22
7.22
7.21
7.20
7.16
7.16
7.15
7.14
7.14
7.13
7.13
7.13
3.96
3.95
3.93
3.37
3.36
3.34
3.34
2.97
2.95
2.72
2.71
2.69
2.68
2.62
2.61
2.59
2.43
1.46
1.46
1.45
1.45
1.44
1.28
1.22
1.14
0.88
0.85
2.00
10.47
1.91
1.00
0.98
0.98
0.97
0.97
2.96
1.80
4.44
0.99
5.56
f1 (ppm)

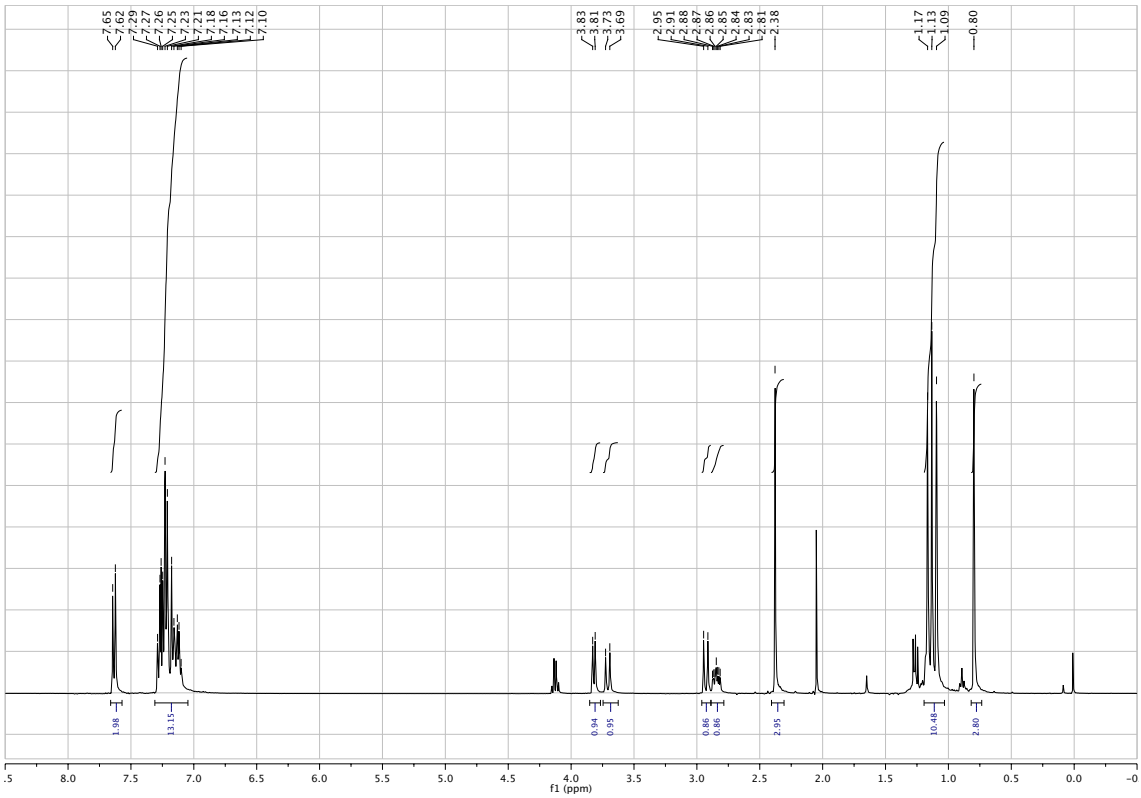

4a_13C
145.79
145.47
142.59
140.39
129.29
128.50
128.44
127.68
127.56
127.29
126.10
126.08
77.25
77.00
76.75
61.85
53.88
47.66
40.20
33.90
33.11
30.78
28.03
26.91
24.88
21.46
f1 (ppm)

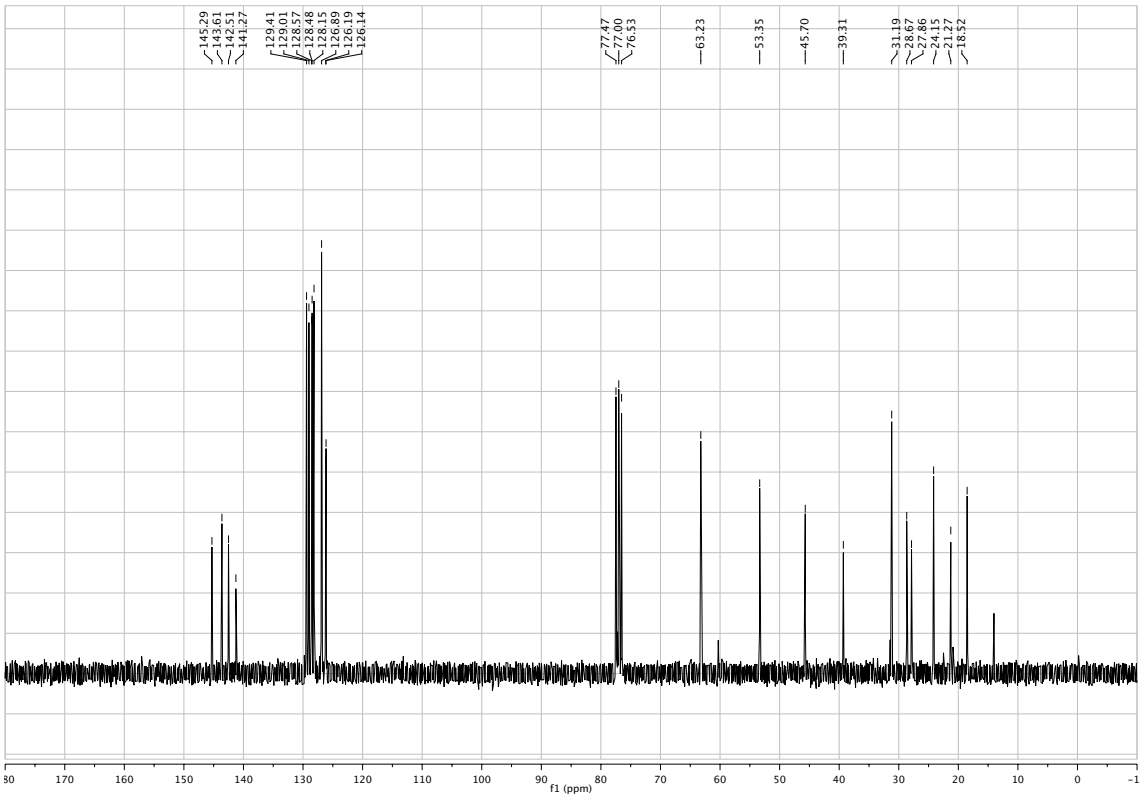
6e


7.73
7.71
7.26
7.24
7.07
7.05
6.83
6.82
6.82
6.81
6.81
6.80
3.79
3.26
3.26
3.23
3.23
3.08
2.95
2.53
2.51
2.51
2.49
2.40
2.11
2.08
1.99
1.97
1.66
1.54
1.47
1.38
1.38
1.31
0.90
0.88
1.80
2.11
1.73
1.78
2.75
0.88
0.84
1.72
2.67
0.86
0.86
0.80
2.57
0.80
1.34
5.55
f1 (ppm)

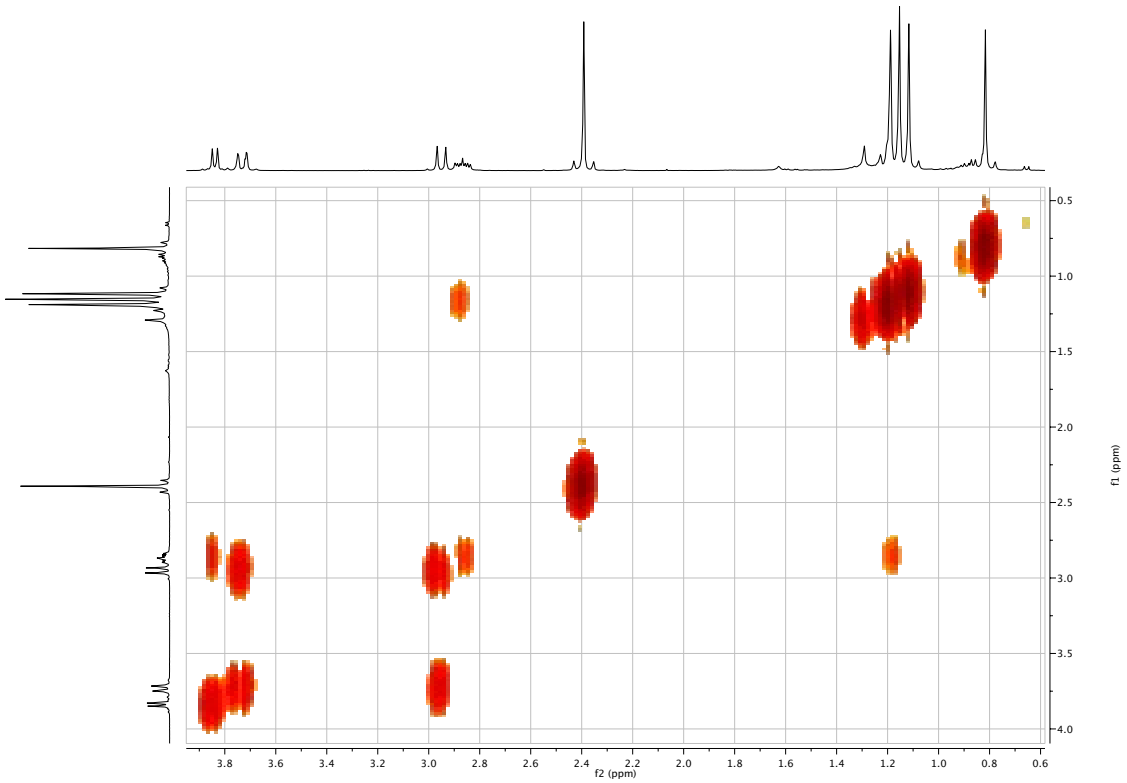

4e_13C
157.70
142.62
139.96
134.20
129.26
129.17
127.35
113.74
77.25
77.00
76.75
60.88
55.25
54.03
38.51
33.91
33.24
30.77
29.72
27.30
25.49
25.30
21.45
f1 (ppm)

7a

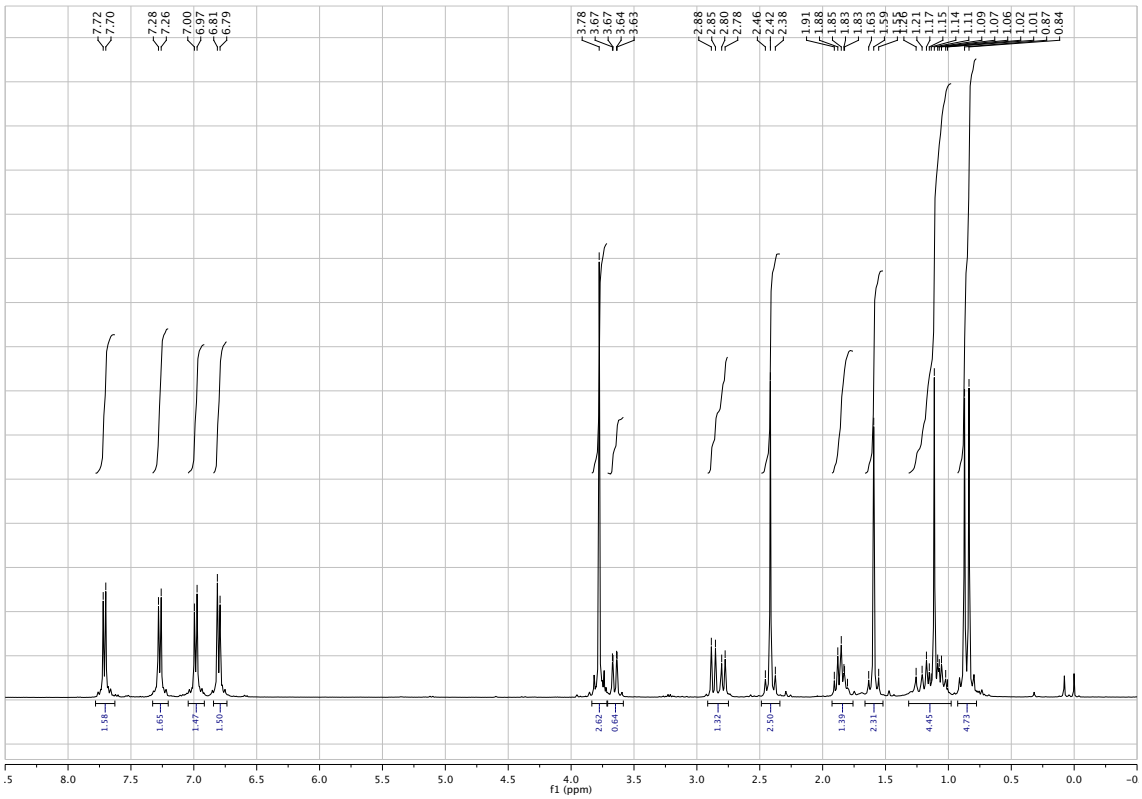

7.65
7.62
7.29
7.27
7.26
7.25
7.23
7.21
7.18
7.16
7.13
7.12
7.10
3.83
3.81
3.73
3.69
2.95
2.91
2.88
2.87
2.86
2.85
2.84
2.83
2.81
2.38
1.17
1.13
1.09
0.80
1.98
13.15
0.94
0.95
0.86
0.86
2.95
10.48
2.80
f1 (ppm)

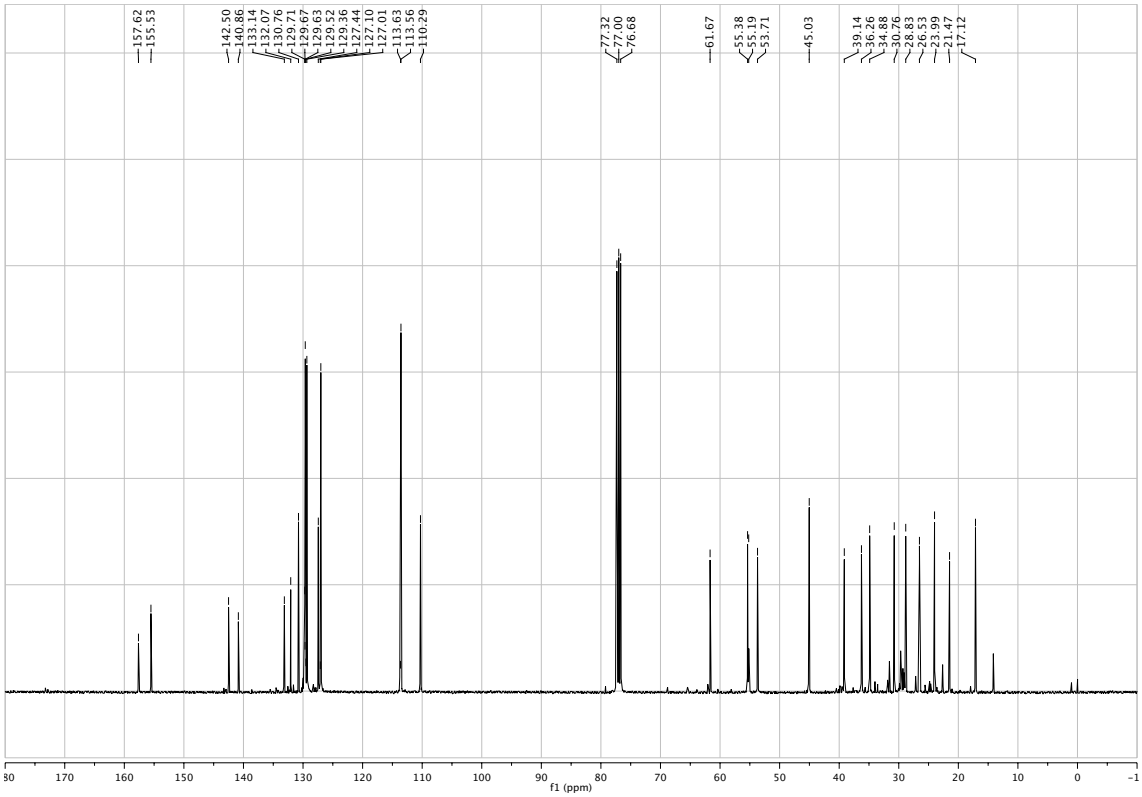

145.29
143.61
142.51
141.27
129.41
129.01
128.57
128.48
128.15
126.89
126.19
126.14
77.47
77.00
76.53
63.23
53.35
45.70
39.31
31.19
28.67
27.86
24.15
21.27
18.52
f1 (ppm)

7a COSY

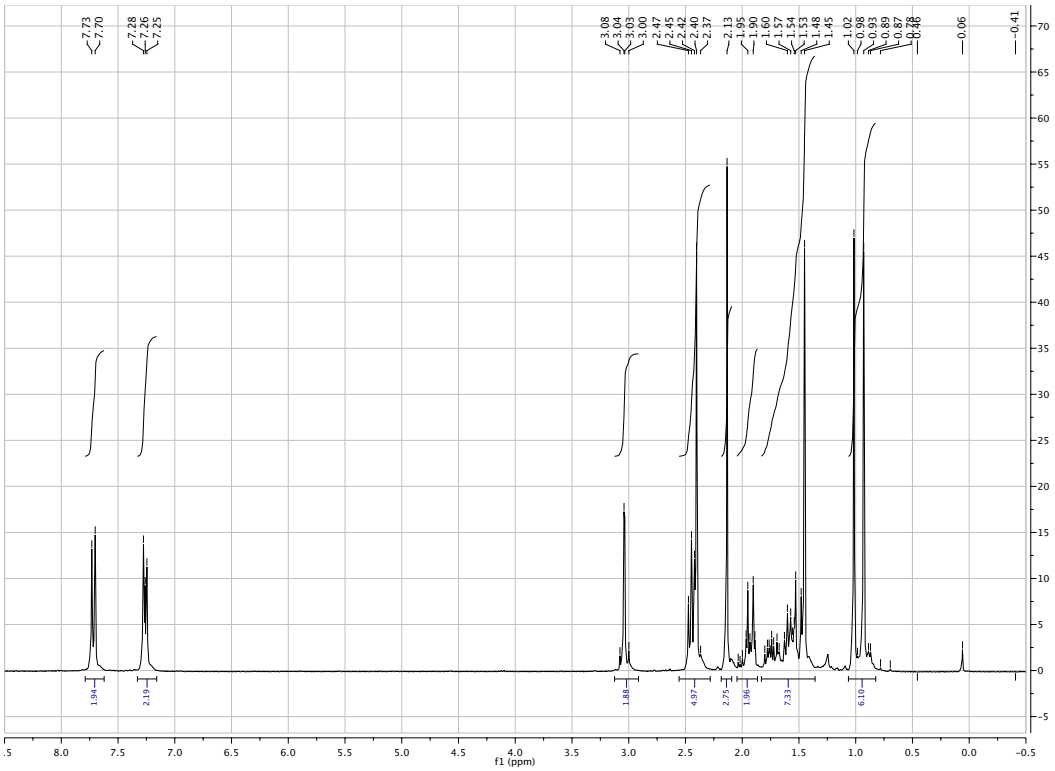


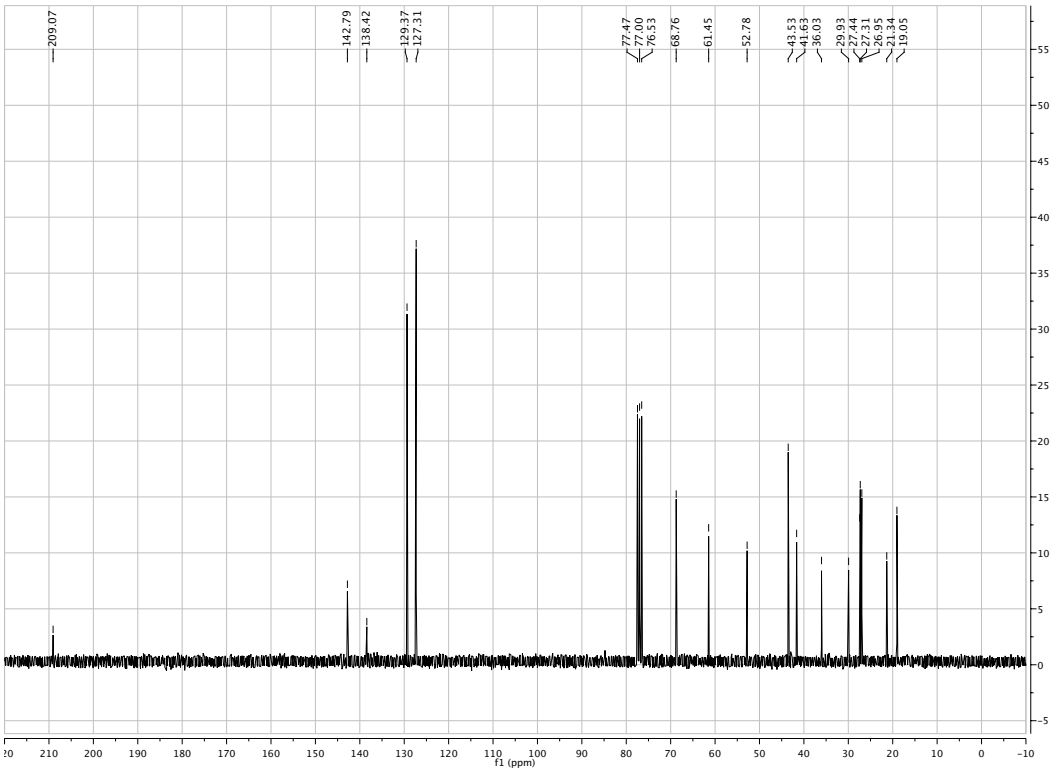
7e


7.72
7.70
7.28
7.26
7.00
6.97
6.81
6.79
3.78
3.67
3.67
3.64
3.63
2.88
2.85
2.80
2.78
2.46
2.42
2.38
1.91
1.88
1.85
1.83
1.83
1.63
1.59
1.25
1.21
1.17
1.15
1.14
1.11
1.09
1.07
1.06
1.02
1.01
0.87
0.84
1.58
1.65
1.47
1.50
2.62
0.64
1.32
2.50
1.39
2.31
4.45
4.73
f1 (ppm)

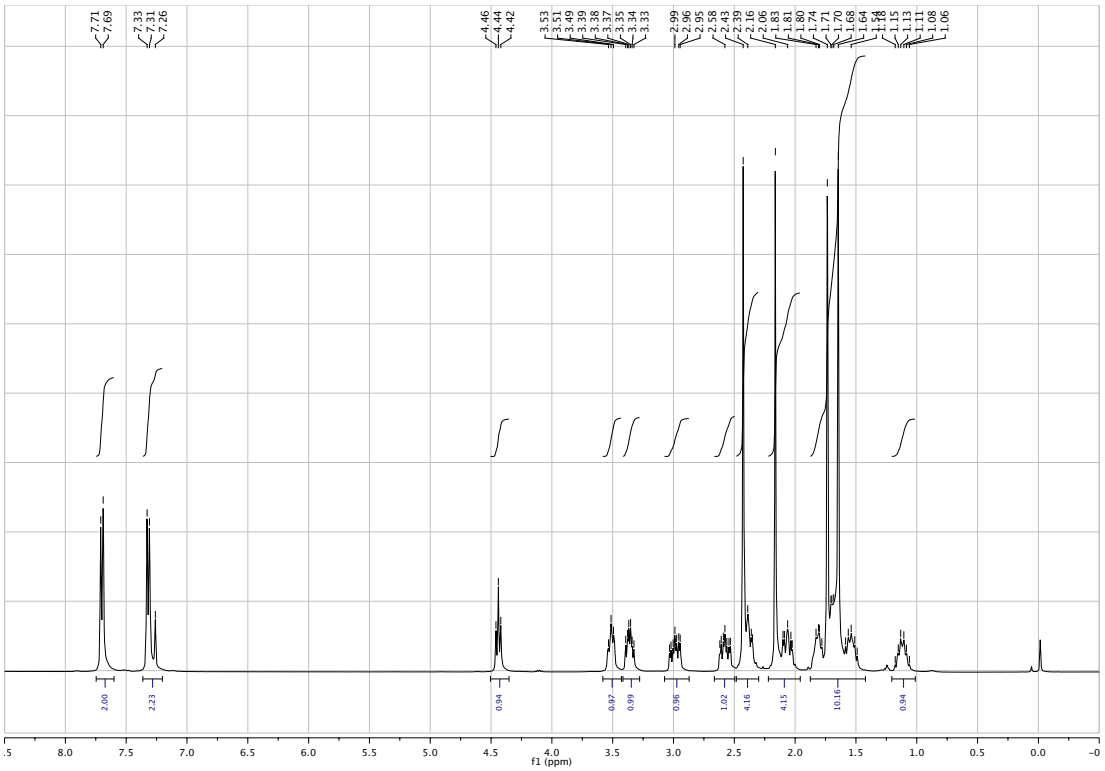

157.62
155.53
142.50
140.86
133.14
132.07
130.76
129.71
129.67
129.52
129.36
127.44
127.10
127.01
113.63
113.56
110.29
77.32
77.00
76.68
61.67
55.38
55.19
53.71
45.03
39.14
36.26
34.88
30.76
28.83
26.53
23.99
21.47
17.12
f1 (ppm)

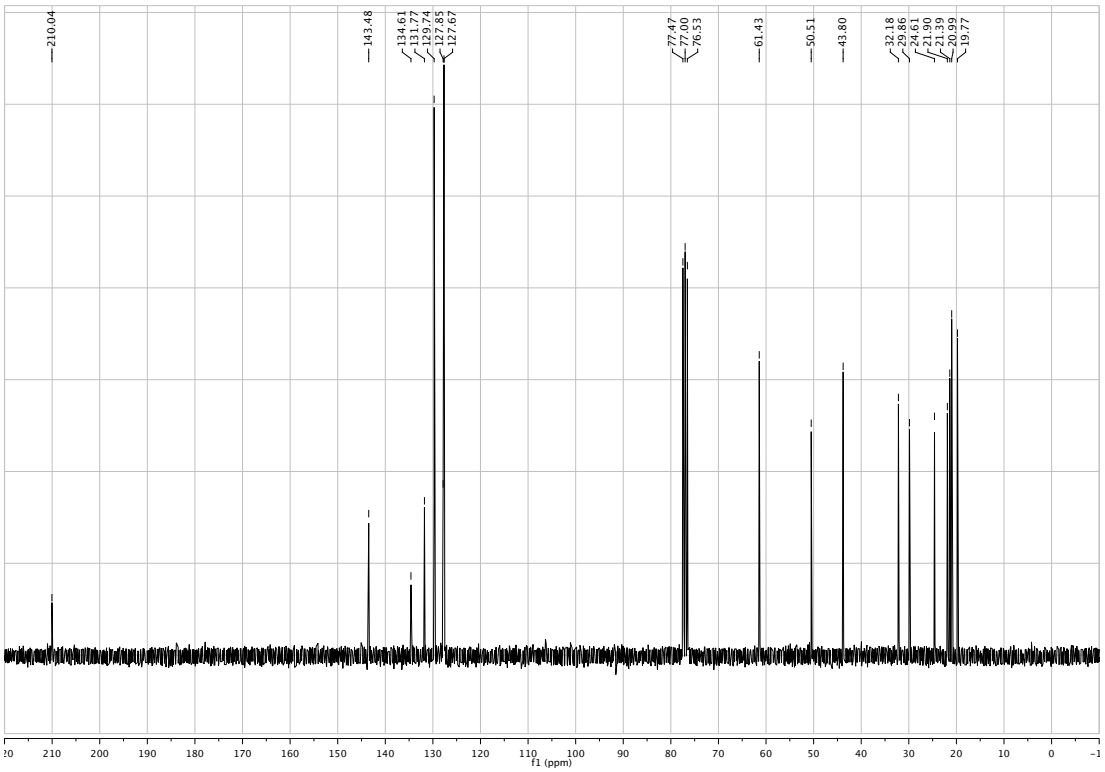
9a


7.73
7.70
7.28
7.26
7.25
3.08
3.04
3.03
3.00
2.47
2.45
2.42
2.40
2.37
2.13
1.95
1.90
1.60
1.57
1.54
1.53
1.48
1.45
1.02
0.98
0.93
0.89
0.87
0.48
0.40
0.06
-0.41
1.94
2.19
1.86
4.97
2.75
1.96
7.33
6.10
f1 (ppm)

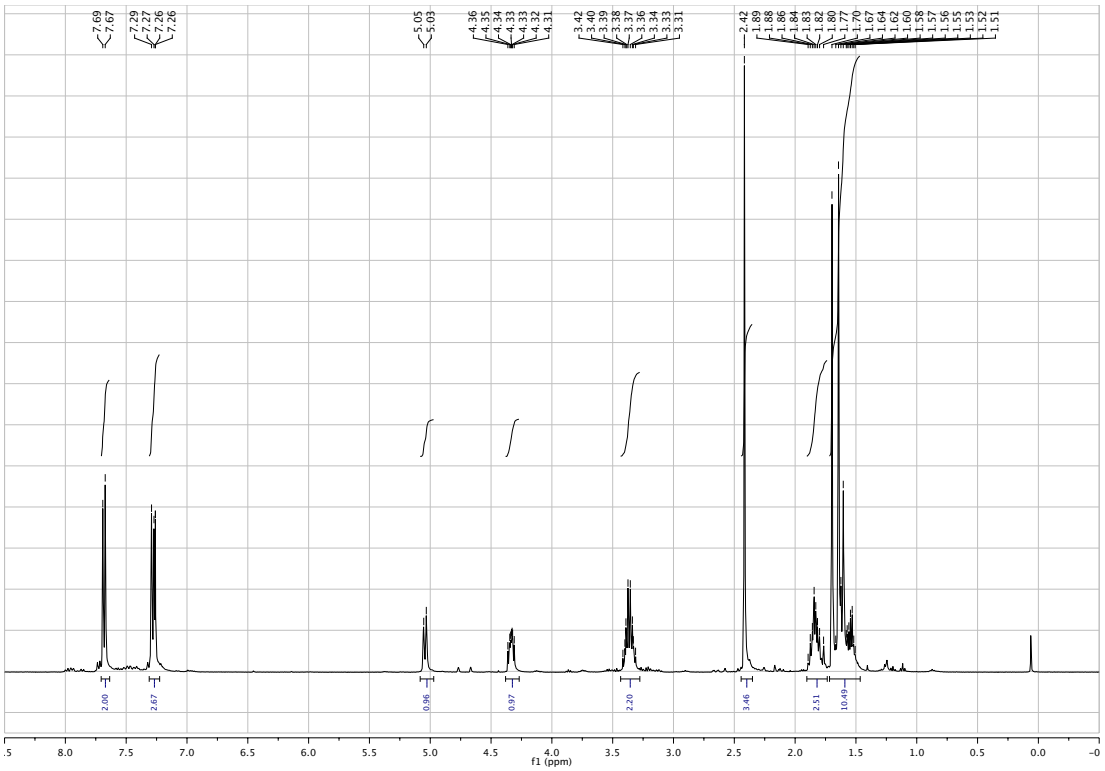

209.07
142.79
138.42
129.37
127.31
77.47
77.00
76.53
68.76
61.45
52.78
43.53
41.63
36.03
29.93
27.44
27.31
26.95
21.34
19.05
f1 (ppm)

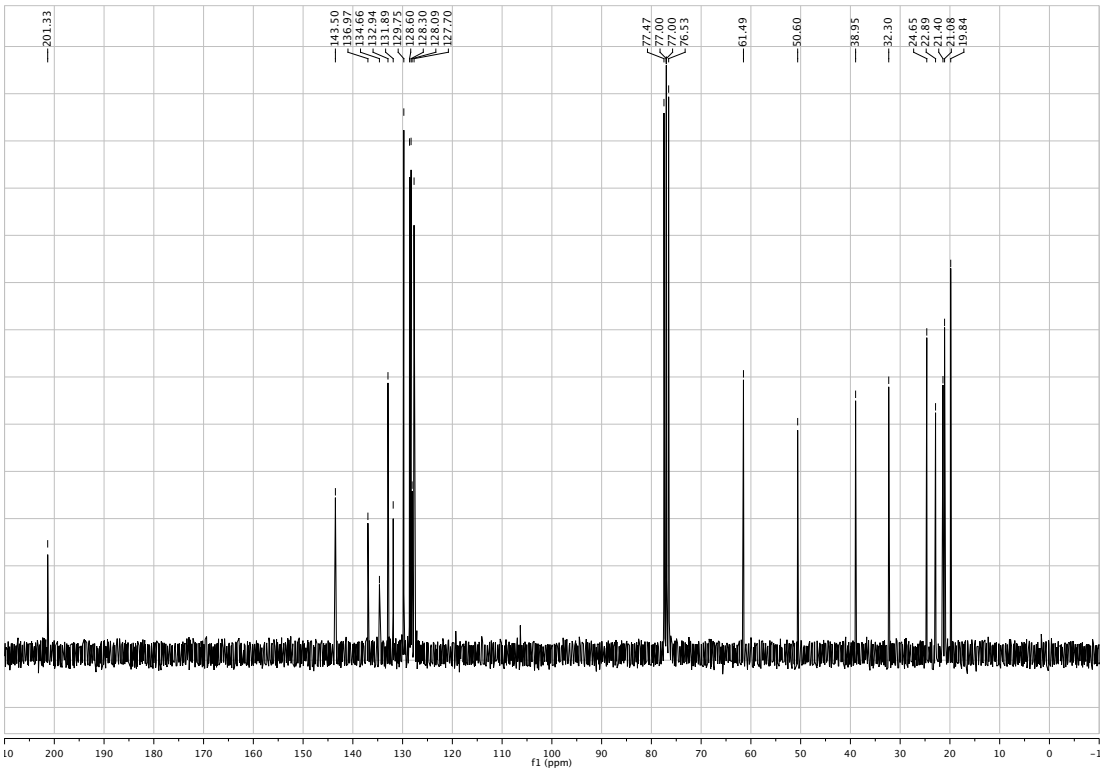
11a


7.71
7.69
7.33
7.31
7.26
4.46
4.44
4.42
3.53
3.51
3.49
3.39
3.38
3.37
3.35
3.34
3.33
2.99
2.96
2.95
2.58
2.43
2.39
2.16
2.06
1.83
1.81
1.80
1.74
1.71
1.70
1.68
1.64
1.54
1.18
1.15
1.13
1.11
1.08
1.06
2.00
2.23
0.94
0.97
0.99
0.96
1.02
4.16
4.15
10.16
0.94
f1 (ppm)

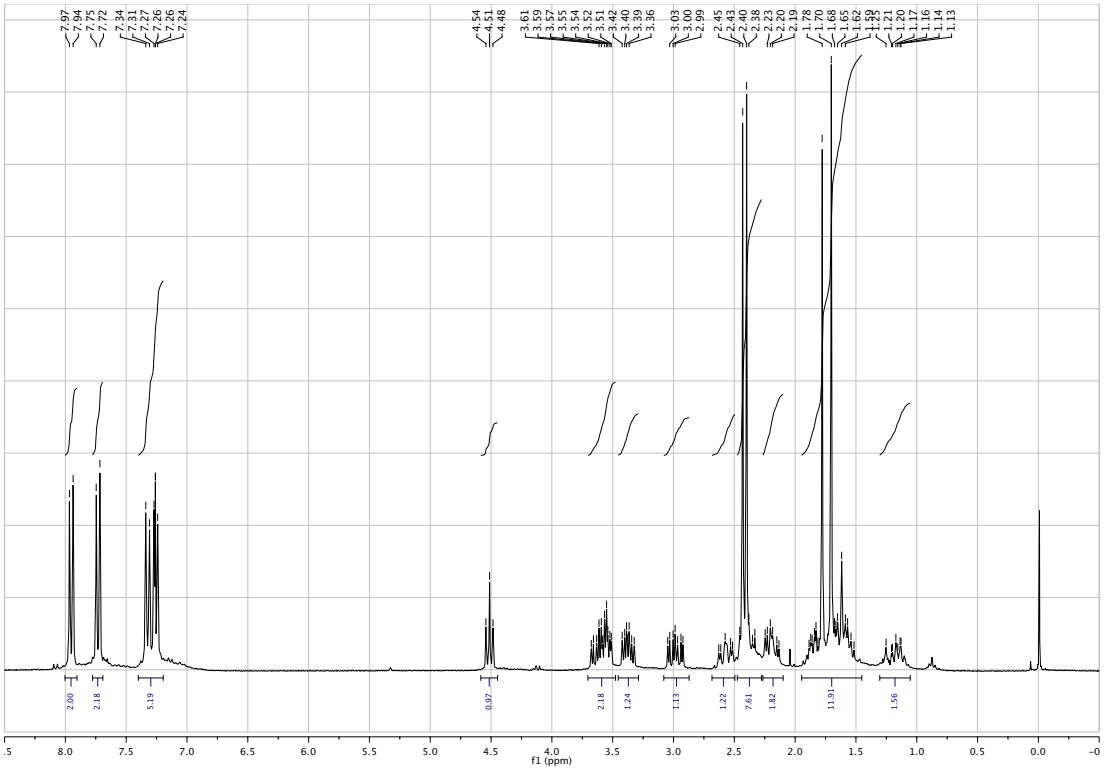

210.04
143.48
134.61
131.77
129.74
127.85
127.67
77.47
77.00
76.53
61.43
50.51
43.80
32.18
29.86
24.61
21.90
21.39
20.99
19.77
f1 (ppm)

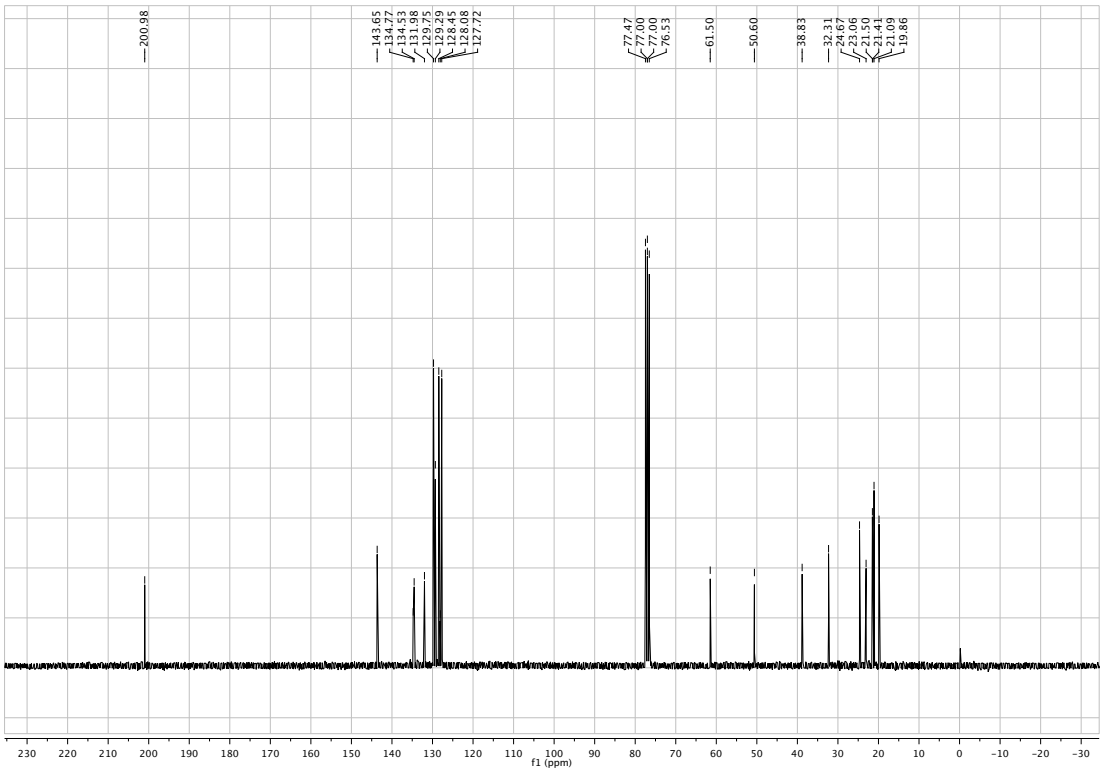
11b


7.69
7.67
7.29
7.27
7.26
7.26
5.05
5.03
4.36
4.35
4.34
4.33
4.33
4.32
4.31
3.42
3.40
3.39
3.38
3.37
3.36
3.34
3.33
3.31
2.42
1.89
1.88
1.86
1.84
1.83
1.82
1.80
1.77
1.70
1.67
1.64
1.62
1.60
1.58
1.57
1.56
1.55
1.53
1.52
1.51
2.00
2.67
0.96
0.97
2.20
3.46
2.51
10.49
f1 (ppm)

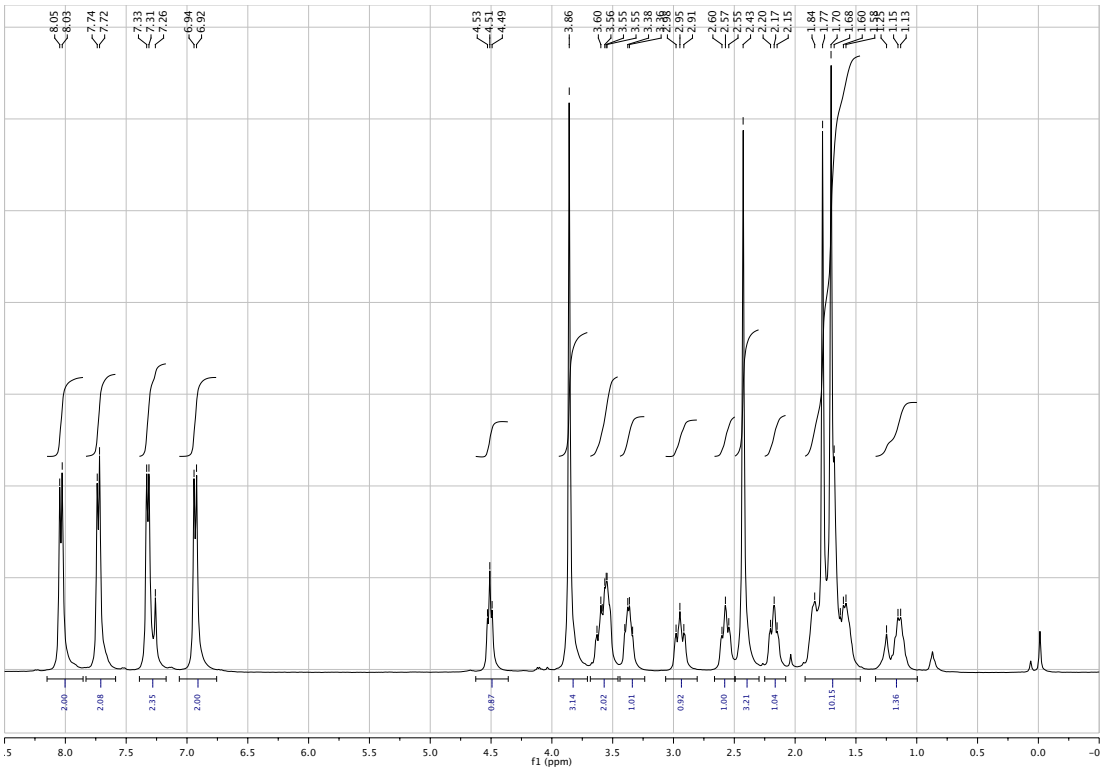

201.33
143.50
136.97
134.66
132.94
131.89
129.75
128.60
128.30
128.09
127.70
77.47
77.00
77.00
76.53
61.49
50.60
38.95
32.30
24.65
22.89
21.40
21.08
19.84
f1 (ppm)

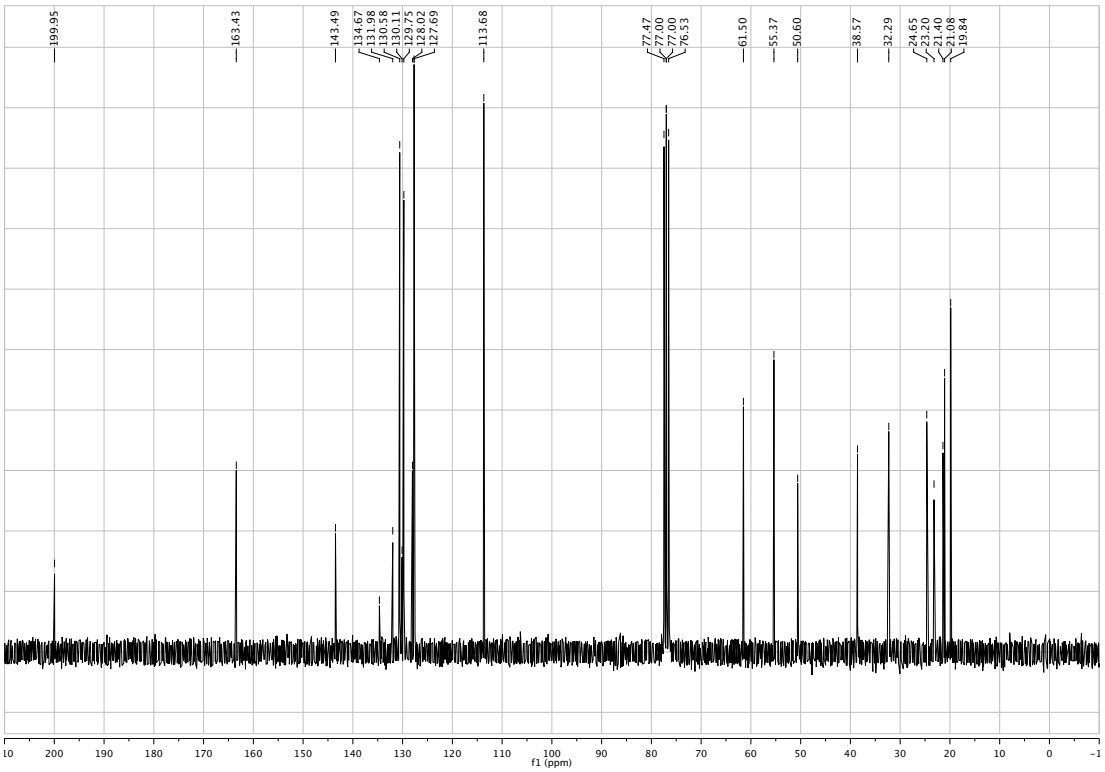
11c


7.97
7.94
7.75
7.72
7.34
7.31
7.27
7.26
7.26
7.24
4.54
4.51
4.48
3.61
3.59
3.57
3.55
3.54
3.52
3.51
3.42
3.40
3.39
3.36
3.03
3.00
2.99
2.45
2.43
2.40
2.38
2.23
2.20
2.19
1.78
1.70
1.68
1.65
1.62
1.58
1.55
1.21
1.20
1.17
1.16
1.14
1.13
2.00
2.18
5.19
0.97
2.18
1.24
1.13
1.22
7.61
1.82
11.91
1.56
f1 (ppm)


200.98
143.65
134.77
134.53
131.98
129.75
129.29
128.45
128.08
127.72
77.47
77.00
77.00
76.53
61.50
50.60
38.83
32.31
24.67
23.06
21.50
21.41
21.01
19.86
f1 (ppm)

11d


8.05
8.03
7.74
7.72
7.33
7.31
7.26
6.94
6.92
4.53
4.51
4.49
3.86
3.60
3.56
3.55
3.55
3.38
2.95
2.91
2.60
2.57
2.55
2.43
2.20
2.17
2.15
1.84
1.77
1.70
1.68
1.60
1.58
1.25
1.15
1.13
2.00
2.08
2.35
2.00
0.87
3.14
2.02
1.01
0.92
1.00
3.21
1.04
10.15
1.36
f1 (ppm)


199.95
163.43
143.49
134.67
131.98
130.58
130.11
129.75
128.02
127.69
113.68
77.47
77.00
77.00
76.53
61.50
55.37
50.60
38.57
32.29
24.65
23.20
21.40
21.08
19.84
f1 (ppm)

11e