Electronic Supplementary Material (ESI) for ChemComm.

Electronic Supporting Information

Methylation of secondary amines with dialkylcarbonates and hydrosilanes catalysed by iron complexes

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I. General information.

All reagents were obtained from commercial sources and used as received. All reactions were carried out with oven-dried glassware using standard Schlenk techniques under an inert atmosphere of dry argon. Toluene, THF, diethyl ether (Et_2O), and CH_2Cl_2 were dried over Braun MB-SPS-800 solvent purification system. Technical grade pentane, diethyl ether were used for chromatography column. Analytical TLC was performed on Merck 60F254 silica gel plates (0.25 mm thickness). Column chromatography was performed on Acros Organics Ultrapure silica gel (mesh size 40-60 m, 60Å).

^{1}H NMR spectra were recorded in $CDCl_3$ at ambient temperature on Bruker AVANCE 400 spectrometers at 400.1 MHz, using the solvent as internal standard ($CDCl_3$ 7.26 ppm). ^{13}C NMR spectra were obtained at 100.6 MHz and referenced to the internal solvent signals ($CDCl_3$, central peak is 77.00 ppm). ^{19}F NMR spectra were obtained at 376 MHz. Chemical shift (δ) and coupling constants (J) are given in ppm and in Hz respectively. The peak patterns are indicated as follows: (s, singlet; d, doublet; t, triplet; q, quartet; quin, quintet; m, multiplet, and br. for broad).

GCMS were measured by GCMS-QP2010S (Shimadzu) with GC-2010 equipped with a 30-m capillary column (Supelco, SLBTM-5ms, fused silica capillary column, 30 M × 0.25 mm × 0.25 mm film thickness), which was used with helium as vector gas. The following GC-MS conditions were used: Initial temperature 100 °C, for 2 minutes, then rate 10 °C/min. until 250 °C and 250 °C for 10 minutes.

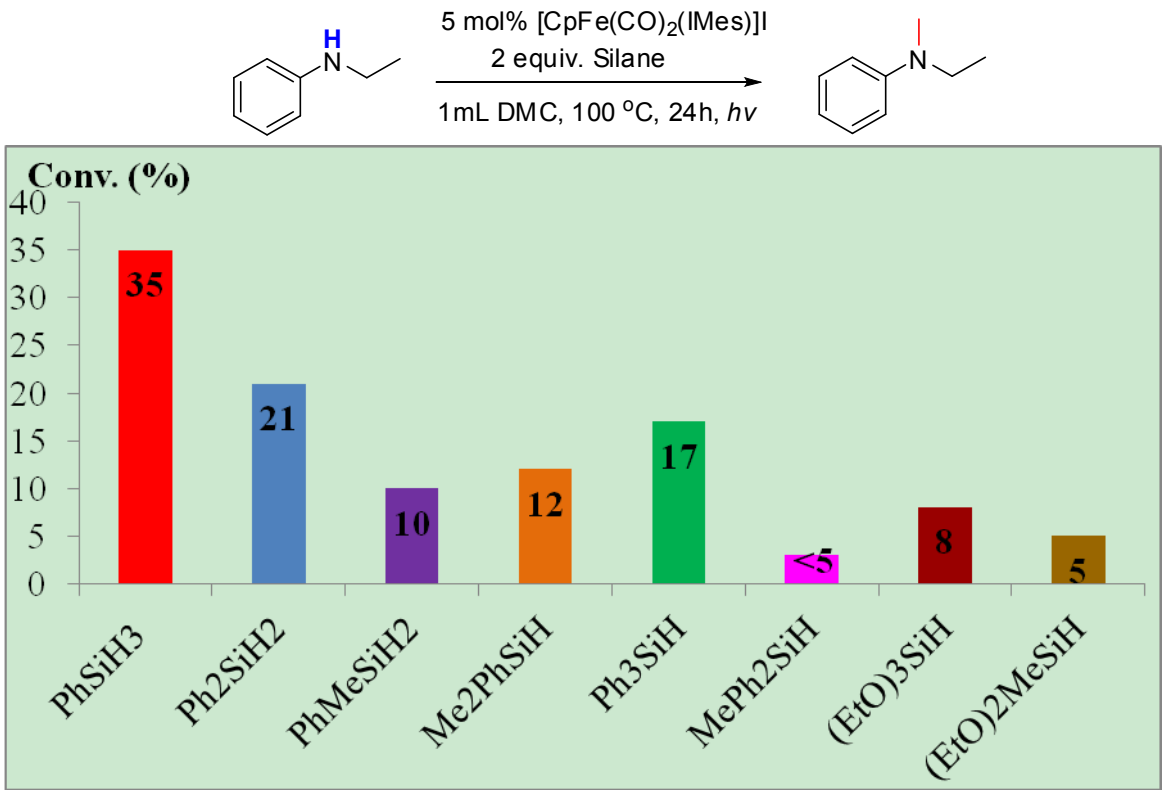
$Fe(CO)_5$, $Fe_2(CO)_9$ were purchased from commercial supply, Stream and used as received. All the well-defined iron complexes were prepared as described in the literature: $[CpFe(CO)_2(IMes)][I]$[1], $[CpFe(CO)_2(PCy)_3][I]$[2], $[CpFe(CO)_2(PCy)_3][PF_6]$[2], $[CpFe(CO)_2(PCy)_3][BF_4]$[3], $Fe(CO)_4(IMes)$ [4].

II. General procedures for the iron-catalyzed methylation reactions

A 20 mL oven dried Schlenk tube, containing a stirring bar, was charged with $[CpFe(CO)_2(IMes)]I$ (12 mg, 0.025 mmol). After purging with argon (argon-vacuum three cycles), dimethyl carbonate or diethyl carbonate (1.5 mL) was added followed by amine (0.5 mmol) and $PhSiH_3$ (309 µL, 2.5 mmol). The reaction mixture was stirred at 100 ^{o}C for 24 h or 48 h under visible light irradiation (24 Watt compact fluorescent lamp). At the end of the reaction, the crude reaction mixture was filtered through a plug of silica gel with CH_2Cl_2 as an eluent. The filtrate was evaporated and then analyzed by ^{1}H NMR using 1,3,5-trimethoxybenzene or pyridine as internal standard to determine the yield. The residue was purified by silica gel column chromatography using diethyl ether-pentane mixture as the eluent to achieve the desired product.

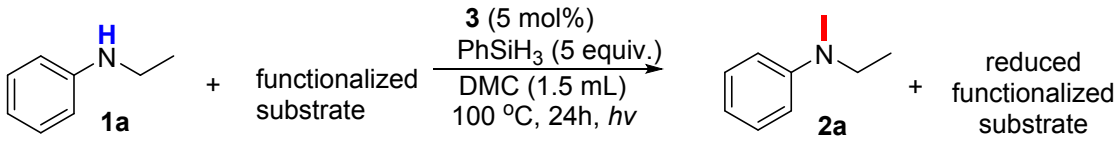
III Optimization

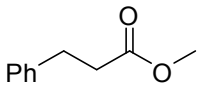
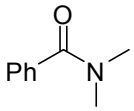
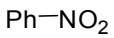
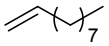
III.1 Optimization table for the silane



III.2

Table S1 : Competitive experiments[a]



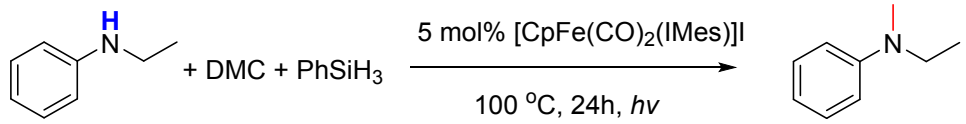
Entry	Functionalized substrate	Yield of 2a (%)[b]	Others observed products
1		30	100% $PhCH(OH)CH_3$.
2		31	17% $Ph\text{-}(CH_2)_3\text{-}OH$ 83% unreacted ester
3		< 5	62% $PhCH_2NMe_2$ 38% unreacted amide
4		10	100% unreacted PhCN
5		< 5	50% $PhNH_2$ 50% unreacted $PhNO_2$.
6		88	100% unreacted 1-decene

a. 0.5 mmol of *N*-ethylaniline, 0.5 mmol competitive substrate, 5 mol% catalyst **3,** 5 equiv. $PhSiH_3$, 1.5 mL DMC, at 100 °C for 24 h under visible light irradiation.

b. Yield was determined by ^1H NMR of the crude mixture after the evaporation of the solvent using 1,3,5-trimethoxybenzene

as internal standard.

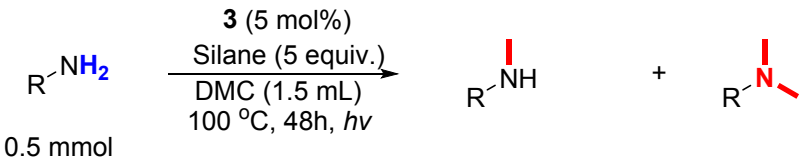
Table S2: Supplementary catalytic results.[a]



Entry	DMC	$PhSiH_3$	Yield (%)[b]
1	42 μL (1 equiv.)	5 equiv.	60
2	1.5 mL (36 equiv.)	2 equiv.	35
3	1.5 mL (36 equiv.)	4 equiv.	78
4	1.5mL (36 equiv.)	5 equiv.	96

a. 0.5 mmol of *N*-ethylaniline, 5 mol% catalyst **3,** at 100 °C for 24 h under visible light irradiation.
b. Yield was determined by ^{1}H NMR of the crude mixture after the evaporation of the solvent using 1,3,5-trimethoxybenzene as internal standard.

Table S3: methylation of primary amines.



0.5 mmol
8

1

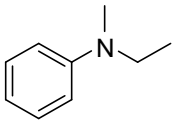
2

Entry	**Functionalized substrates**	**Yield of 1 (%)[a]**	**Yield of 2 (%)[a]**
1	R = Ph	10 (**1e**)	20 (**2e**)
2	R = 4-(CH_3O)-Ph	11 (**1f**)	11 (**2f**)
3	R = $PhCH_2$-	0 (**1r**)	8 (**2r**)

a. Yield was determined by ^{1}H NMR of the crude mixture after the evaporation of the solvent using 1,3,5-trimethoxybenzene as internal standard and confirmed by GC/GC-MS.

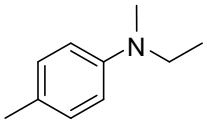
IV. Characterization of the methylated products

N-Ethyl-*N*-methylaniline[5]



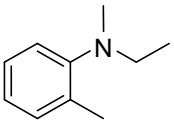
The compound was prepared as described in the general procedure (m = 57 mg, 84% isolated yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.25-7.21 (m, 2H), 6.73-6.66 (m, 3H), 3.40 (q, *J* = 7.1, 2H), 2.91 (s, 3H), 1.12 (t, *J* = 7.1, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 149.1, 129.1(2C), 116.0, 112.4(2C), 46.8, 37.4, 11.2.

N-Ethyl-*N*-methyl-4-methylaniline



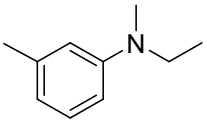
The compound was prepared as described in the general procedure (m = 71 mg, 95% isolated yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.04 (d, *J* = 8.4, 2H), 6.66 (d, *J* = 8.4, 2H), 3.36 (q, *J* = 7.0, 2H), 2.87 (s, 3H), 2.25 (s, 3H), 1.10 (t, *J* = 7.0, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 147.2, 129.6(2C), 125.4, 113.0(2C), 47.1, 37.6, 20.2, 11.0. GC-MS: m/z (%) 149 (M^+, 26), 134(100), 119(18), 105(3), 91(22), 77(6), 65(12), 51(5).

***N*-Ethyl-*N*-methyl-2-methylaniline**



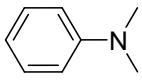
The compound was prepared as described in the general procedure (m = 59 mg, 79% isolated yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.18-7.13 (m, 2H), 7.05-7.03 (m, 1H), 6.97-6.93 (m, 1H), 2.91 (q, *J* = 7.1, 2H), 2.68 (s, 3H), 2.31 (s, 3H), 1.10 (t, *J* = 7.1, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 152.2, 133.1, 131.0, 126.2, 122.6, 119.8, 50.4, 40.9, 18.3, 12.8. GC-MS: m/z (%) 149 (M^+, 22), 134(100), 118(20), 106(3), 91(22), 77(9), 65(16), 51(11).

***N*-Ethyl-*N*-methyl-3-methylaniline**



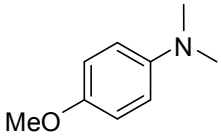
The compound was prepared as described in the general procedure (m = 45 mg, 60% isolated yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.14-7.10 (m, 1H), 6.55-6.51 (m, 3H), 3.38 (q, *J* = 7.1, 2H), 2.89 (s, 3H), 2.31 (s, 3H), 1.12 (t, *J* = 7.1, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 149.2, 138.8, 129.0, 117.0, 113.2, 109.7, 46.8, 37.5, 21.9, 11.2. GC-MS: m/z (%) 149 (M^+, 28), 134(100), 119(14), 105(3), 91(23), 77(6), 65(13), 51(4).

***N,N*-Dimethylaniline[6]**



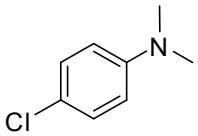
The compound was prepared as described in the general procedure (m = 45 mg, 75% isolated yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.27-7.24 (m, 2H), 6.76-6.71 (m, 3H), 2.95 (s, 6H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 150.6, 129.0(2C), 116.6, 112.6(2C), 40.6(2C).

4-Methoxy-*N,N*-dimethylaniline[7]



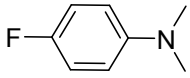
The compound was prepared as described in the general procedure (m = 55 mg, 72% isolated yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.86-6.82 (m, 2H), 6.77-6.73 (m, 2H), 3.76 (s, 3H), 2.87 (s, 6H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 151.9, 145.7, 114.8(2C), 114.6(2C), 55.7, 41.8(2C).

4-Chloro-*N,N*-dimethylaniline[8]



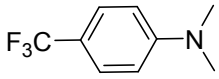
The compound was prepared as described in the general procedure (m = 78 mg, 98% isolated yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.19-7.15 (m, 2H), 6.66-6.62 (m, 2H), 2.93 (s, 6H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$): δ 149.2, 128.8(2C), 121.4, 113.7(2C), 40.7.

4-Fluoro-*N,N*-dimethylaniline*(ZJX1775 redo After c)*[9]



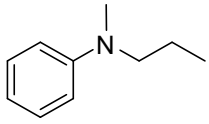
The compound was prepared as described in the general procedure (m = 52 mg, 75% isolated yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.97-6.91 (m, 2H), 6.71-6.66 (m, 2H), 2.90 (s, 6H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$): δ 155.6 (d, J_{C-F} = 235.2), 147.5 (d, J_{C-F} = 1.7), 115.3 (d, J_{C-F} = 22.0, 2C), 113.9 (d, J_{C-F} = 7.3, 2C), 41.3. ^{19}F NMR (376 MHz. $CDCl_3$): δ -129.0.

***N,N*-Dimethyl-4-(trifluoromethyl)aniline[10]**



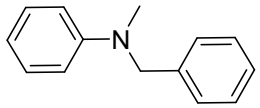
The compound was prepared as described in the general procedure (m = 71 mg, 75% isolated yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.45 (d, J = 8.8, 2H), 6.70 (d, J = 8.8, 2H), 3.01 (s, 6H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$): δ 152.3, 125.2 (q, J_{C-F} = 270.0), 126.3 (q, J_{C-F} = 3.8), 117.4 (q, J_{C-F} = 32.6), 111.1, 40.0(2C). ^{19}F NMR (376 MHz. $CDCl_3$): δ -60.8.

***N*-Methyl-*N*-propylaniline[11]**



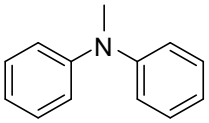
The compound was prepared as described in the general procedure (m = 40 mg, 54% isolated yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.24-7.20 (m, 2H), 6.71-6.65 (m, 3H), 3.27 (t, J = 7.4, 2H), 2.93 (s, 3H), 1.61 (m, 2H), 0.92 (t, J = 7.4, 3H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$): δ 149.4, 129.1(2C), 115.7, 112.0(2C), 54.5, 38.3, 19.9, 11.5.

***N*-Benzyl-*N*-methylaniline[8]**



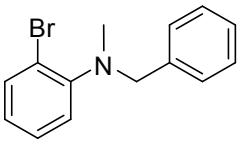
The compound was prepared as described in the general procedure (m = 85 mg, 86% isolated yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.32-7.30 (m, 2H), 7.25-7.20 (m, 5H), 6.77-6.70 (m, 3H), 4.54 (s, 2H), 3.02 (s, 3H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$): δ 149.7, 139.0, 129.1(2C), 128.5(2C), 126.8, 126.7(2C), 116.5, 112.3(2C), 56.6, 38.4.

***N*-Methyl-*N*-phenylaniline[12]**



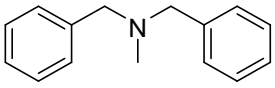
The compound was prepared as described in the general procedure (m = 79 mg, 86% isolated yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.30-7.26 (m, 4H), 7.04-7.02 (m, 4H), 6.98-6.94 (m, 2H), 3.32 (s, 3H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$): δ 149.0(2C), 129.2(4C), 121.2(2C), 120.4(4C), 40.2.

***N*-Benzyl-2-bromo-*N*-methylaniline[13]**



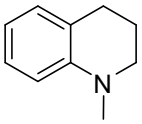
The compound was prepared as described in the general procedure (m = 89 mg, 64% isolated yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.59-7.57 (m, 1H), 7.24-7.20 (m, 3H), 7.14-7.10 (m, 2H), 6.74-6.66 (m, 3H), 4.55 (s, 2H), 3.09 (s, 3H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$): δ 149.1, 137.3, 132.8, 129.2(2C), 128.3, 127.8, 127.5, 122.7, 116.6, 111.9(2C), 57.3, 38.7.

***N*-Benzyl-*N*-methyl-1-phenylmethanamine[14]**



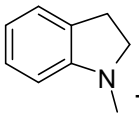
The compound was prepared as described in the general procedure (m = 60 mg, 57% isolated yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.38-7.22 (m, 10H), 3.53 (s, 4H), 2.19 (s, 4H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$): δ 139.3(2C), 128.9(4C), 1281.2(4C), 126.9(2C), 61.8(2C), 42.2.

1-Methyl-1,2,3,4-tetrahydroquinoline[15]



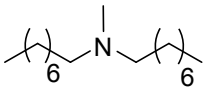
The compound was prepared as described in the general procedure (m = 44 mg, 60% isolated yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.09-7.05 (m, 1H), 6.96-6.94 (m, 1H), 6.62-6.58 (m, 2H), 3.22 (t, *J* = 5.6, 2H), 2.88 (s, 3H), 2.77 (t, *J* = 6.4, 2H), 1.98 (m, 2H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$): δ 146.7, 128.8, 127.0, 122.8, 116.2, 110.9, 51.2, 39.1, 27.8, 22.4.

1-Methylindoline[8]



The compound was prepared as described in the general procedure (m = 41 mg, 61% isolated yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.10-7.07 (m, 2H), 6.99-6.95 (m, 1H), 6.50-6.48 (m, 1H), 3.29 (t, *J* = 8.1, 2H), 2.94 (t, *J* = 8.1, 2H), 2.76 (s, 3H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$): δ 153.4, 130.3, 127.3, 124.2, 117.7, 107.2, 56.1, 36.2, 28.7.

***N*-methyl-*N*-octyloctan-1-amine[16]**



The compound was prepared as described in the general procedure (m = 84 mg, 66% isolated yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.31-2.27 (m, 4H), 2.20 (s, 3H), 1.48-1.27 (m, 26H), 0.88 (t, *J* = 6.8, 3H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$): δ 58.0(2C), 42.4, 31.8(2C), 29.6(2C), 29.3(2C), 27.6(2C), 27.3(2C), 22.6(2C), 14.1(2C).

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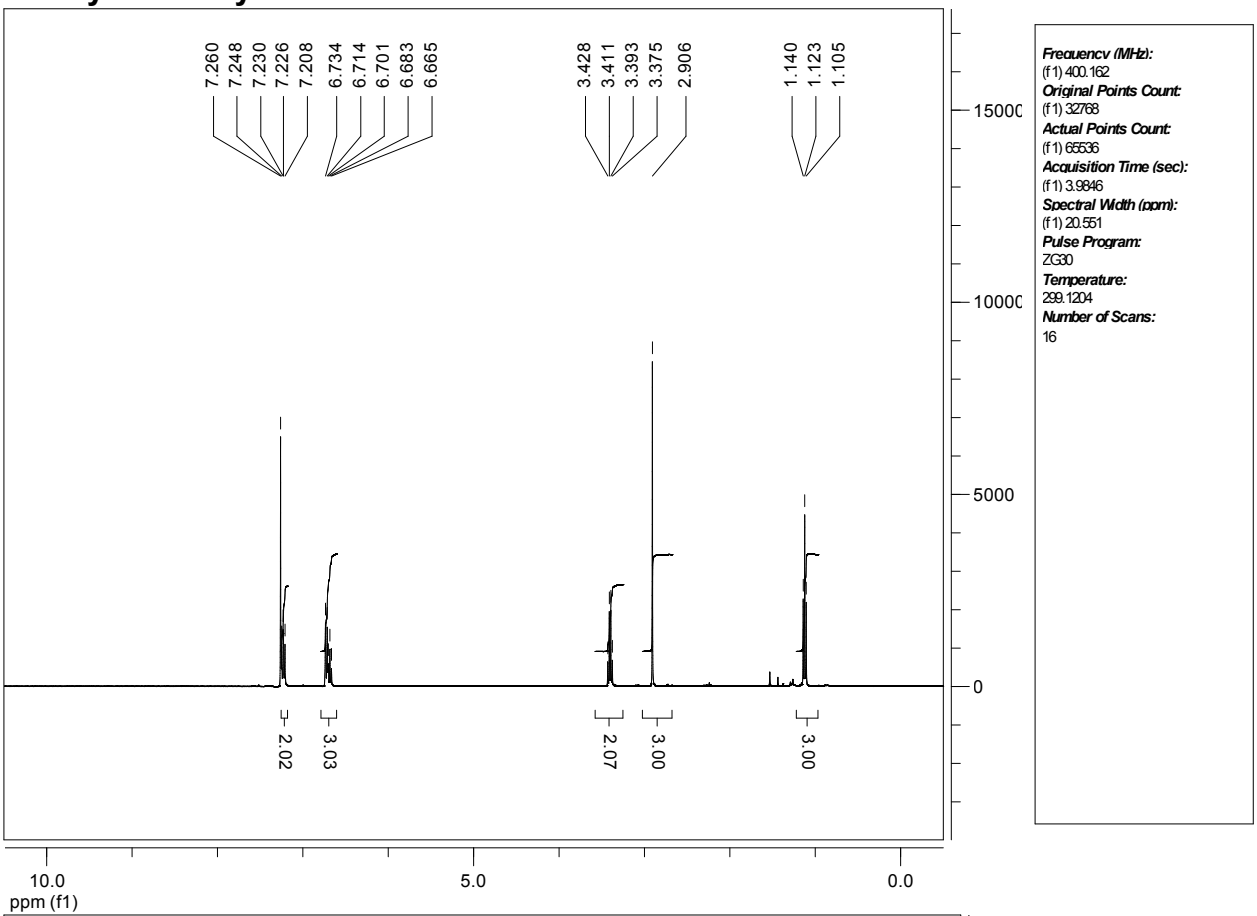
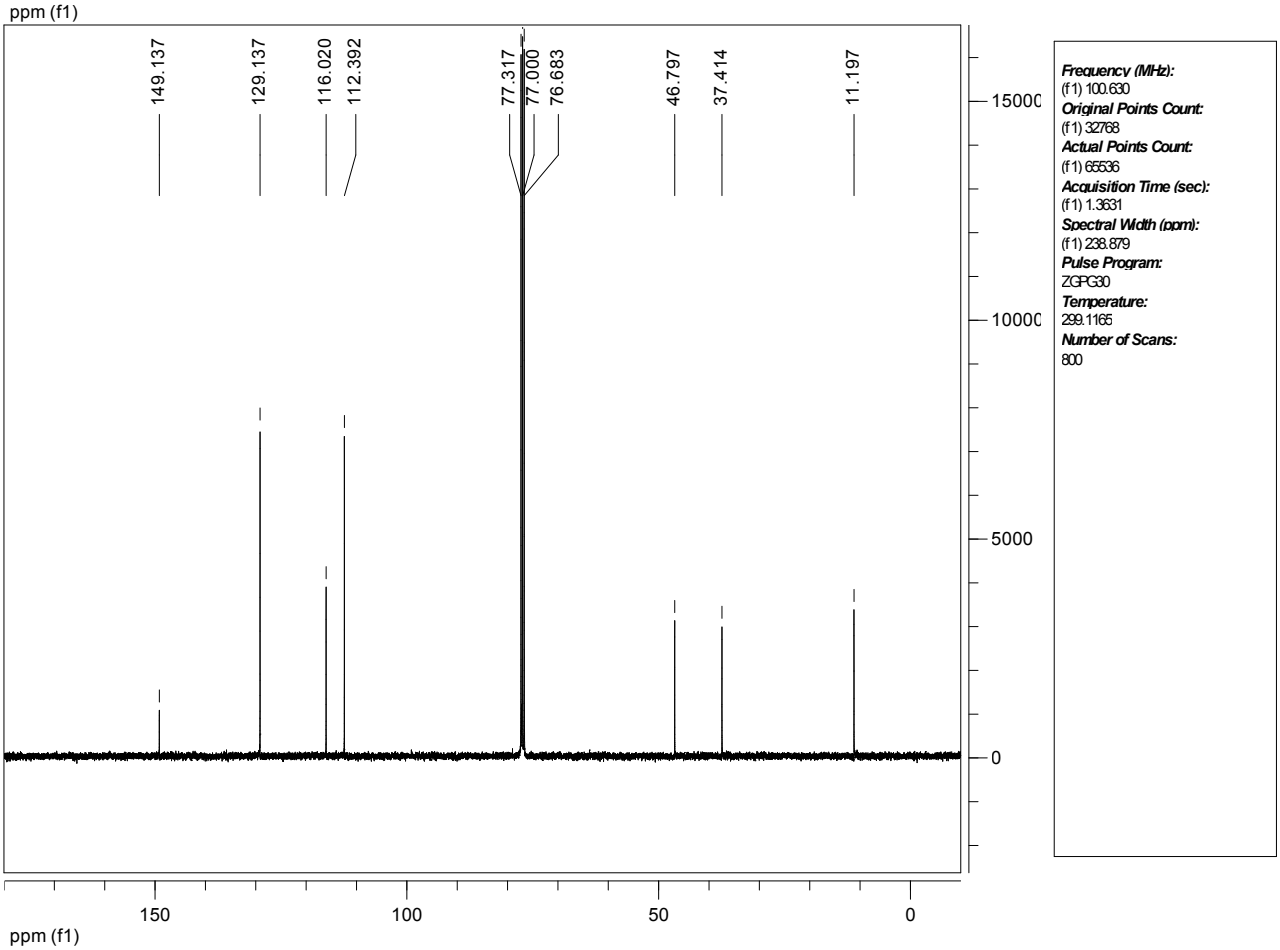
N-Ethyl-*N*-methylaniline





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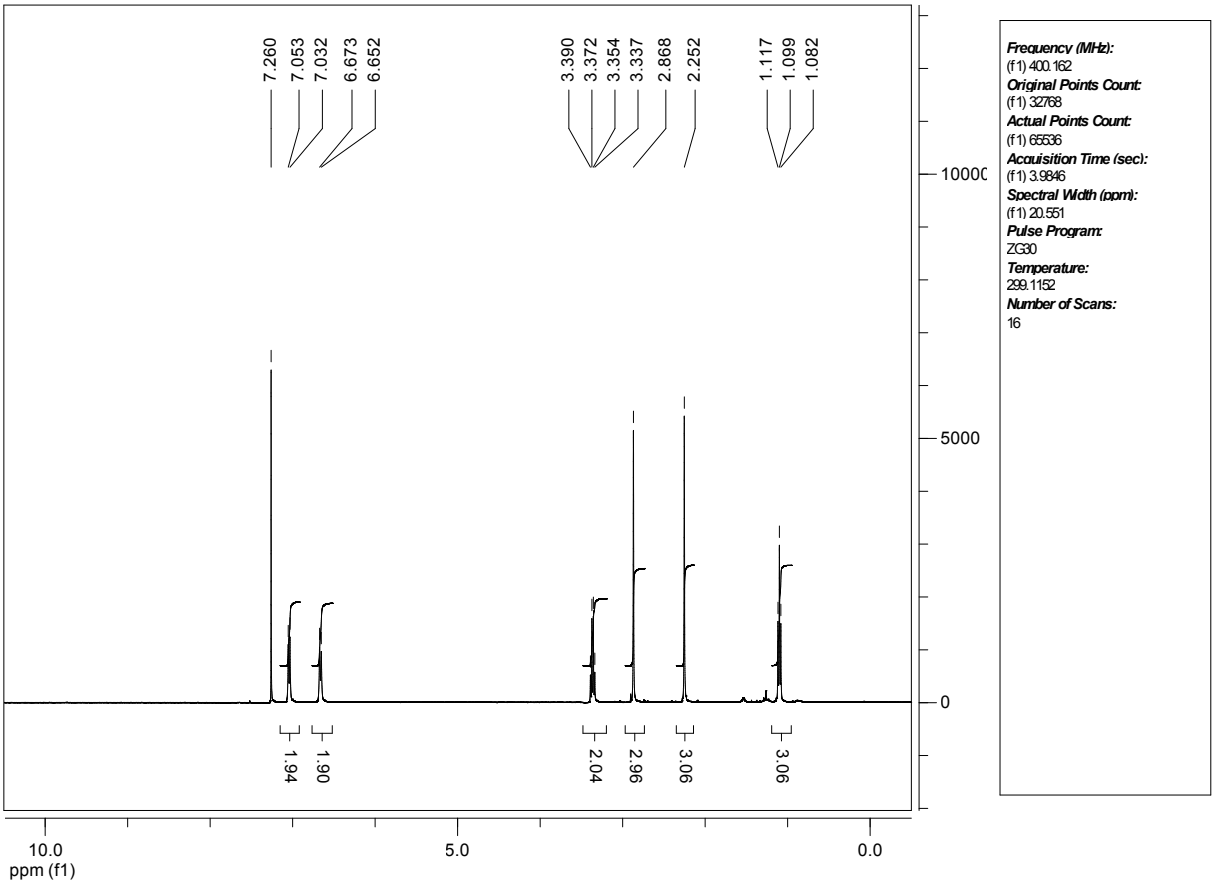

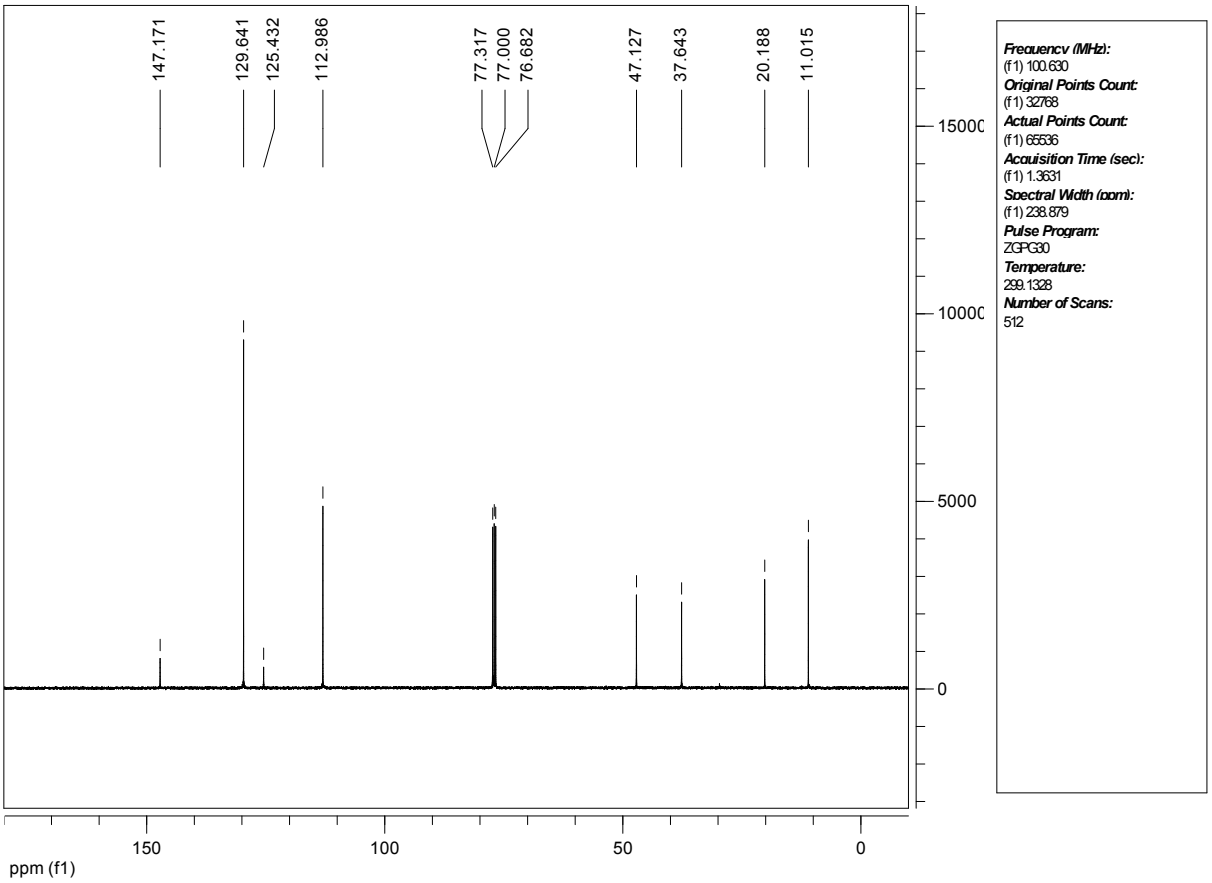

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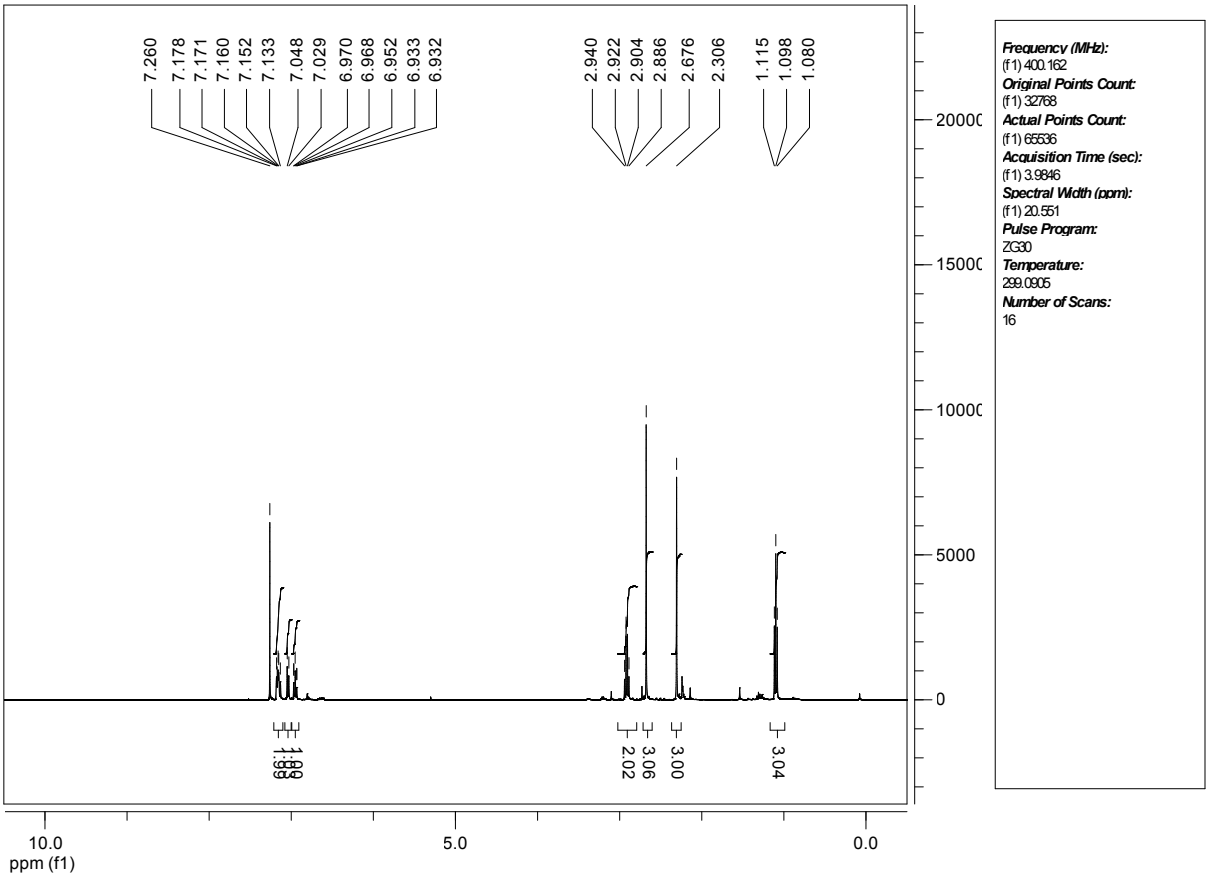

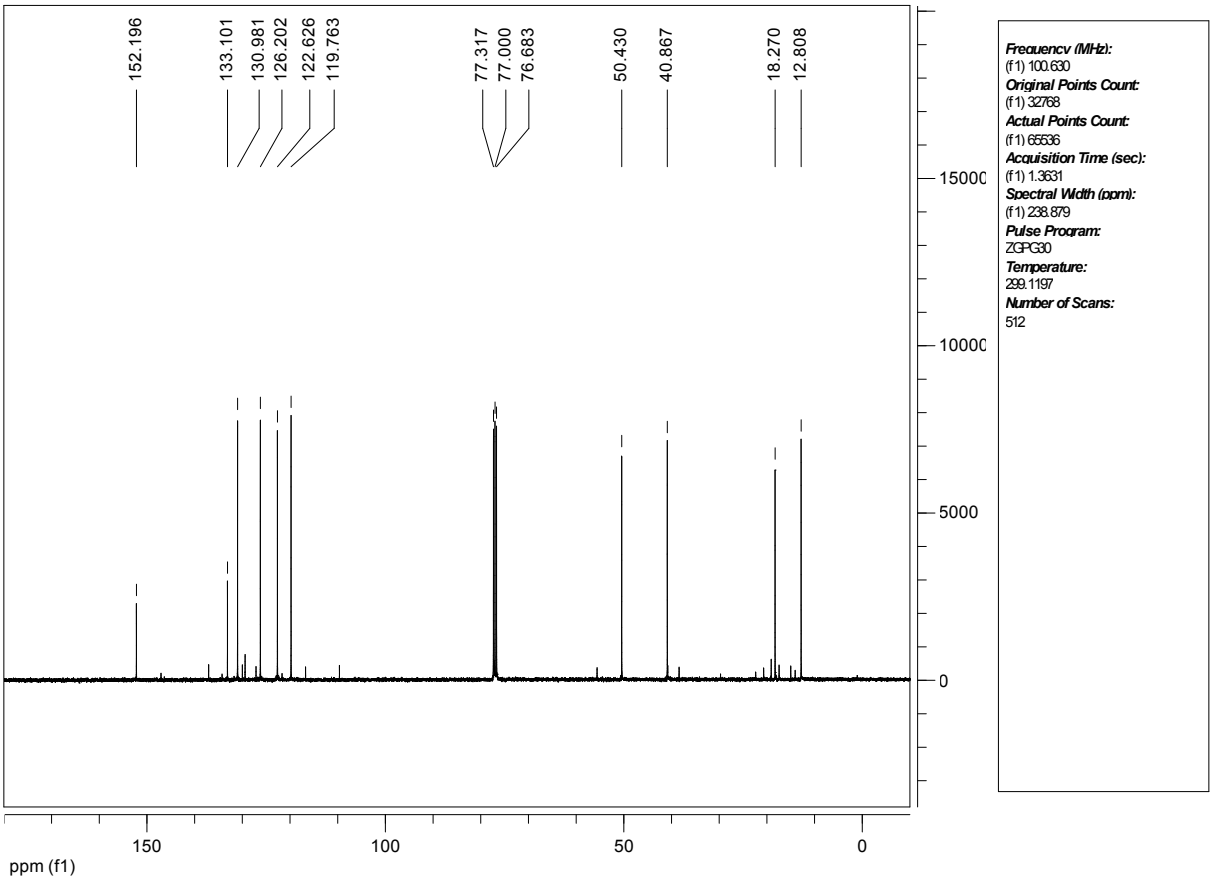

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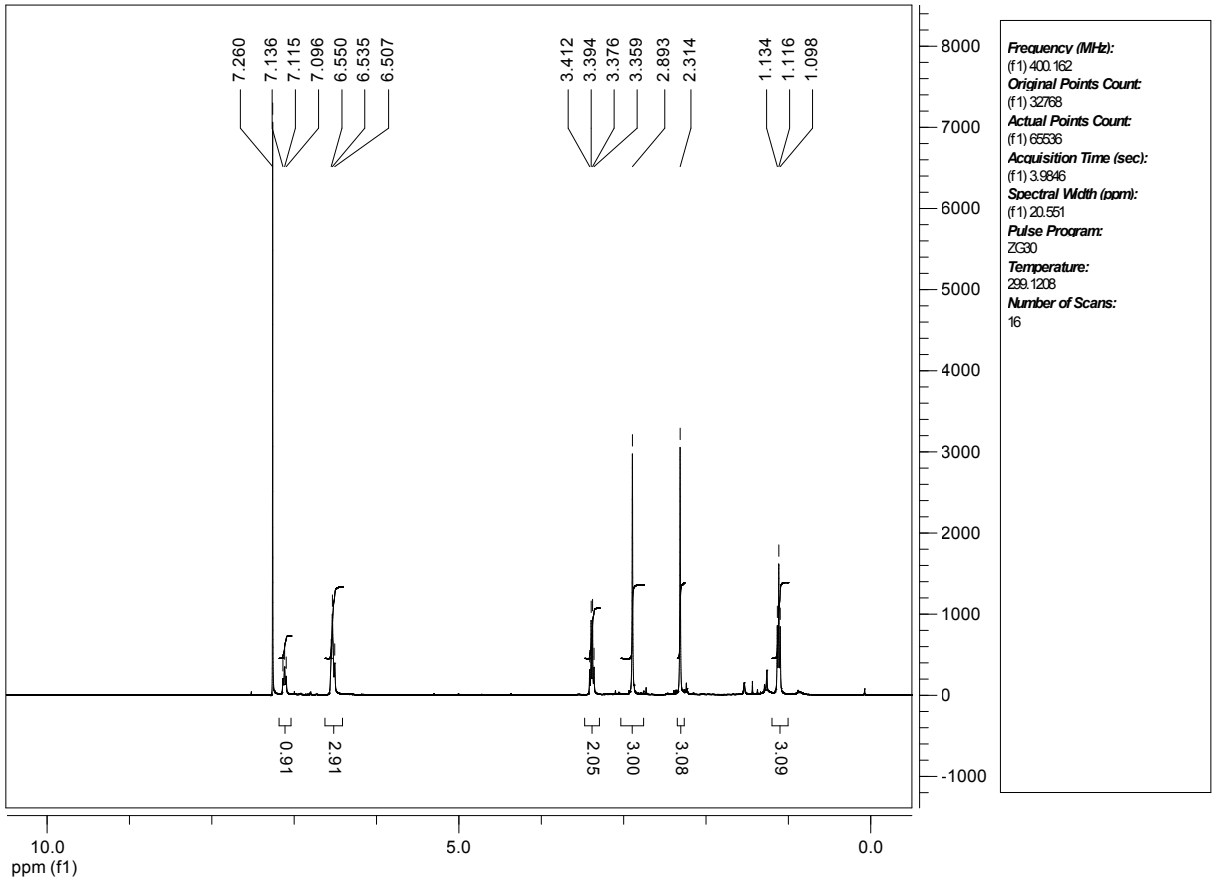

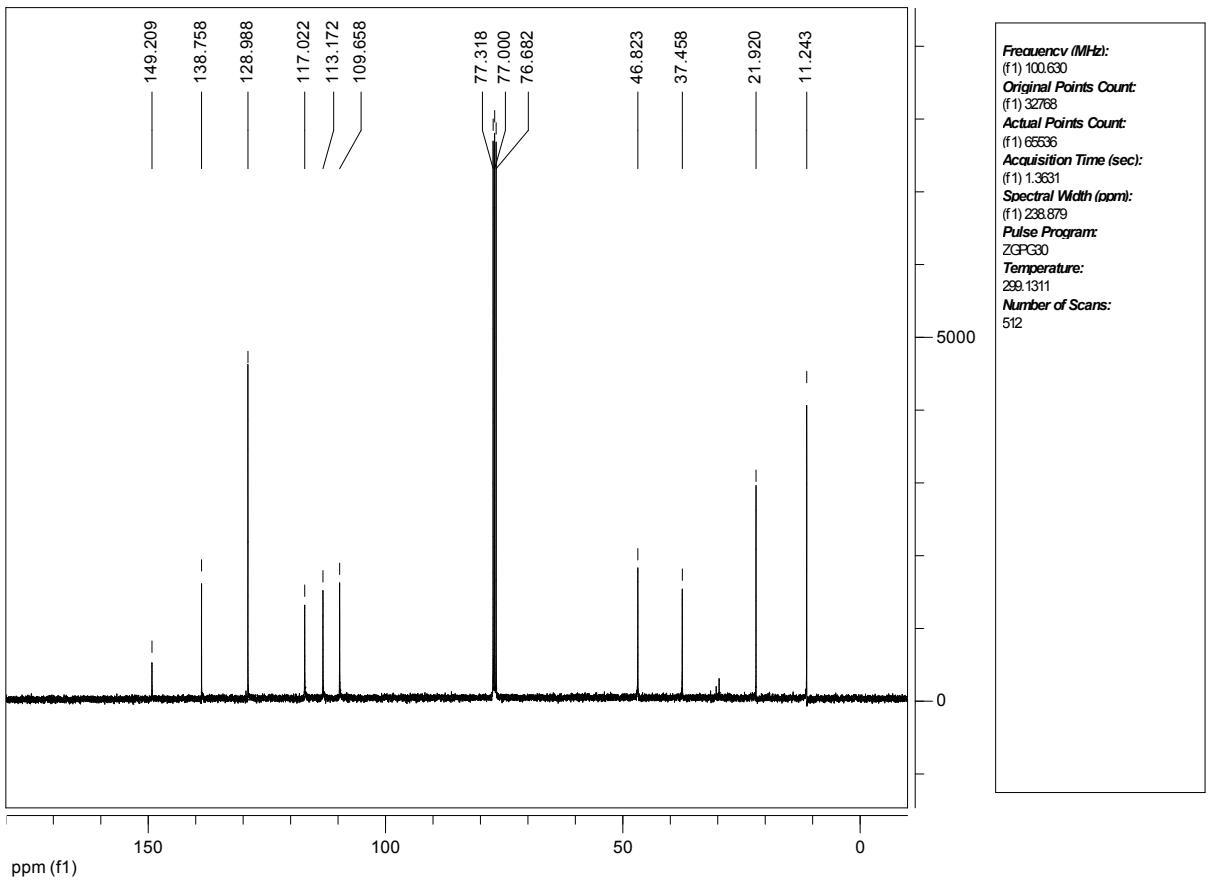

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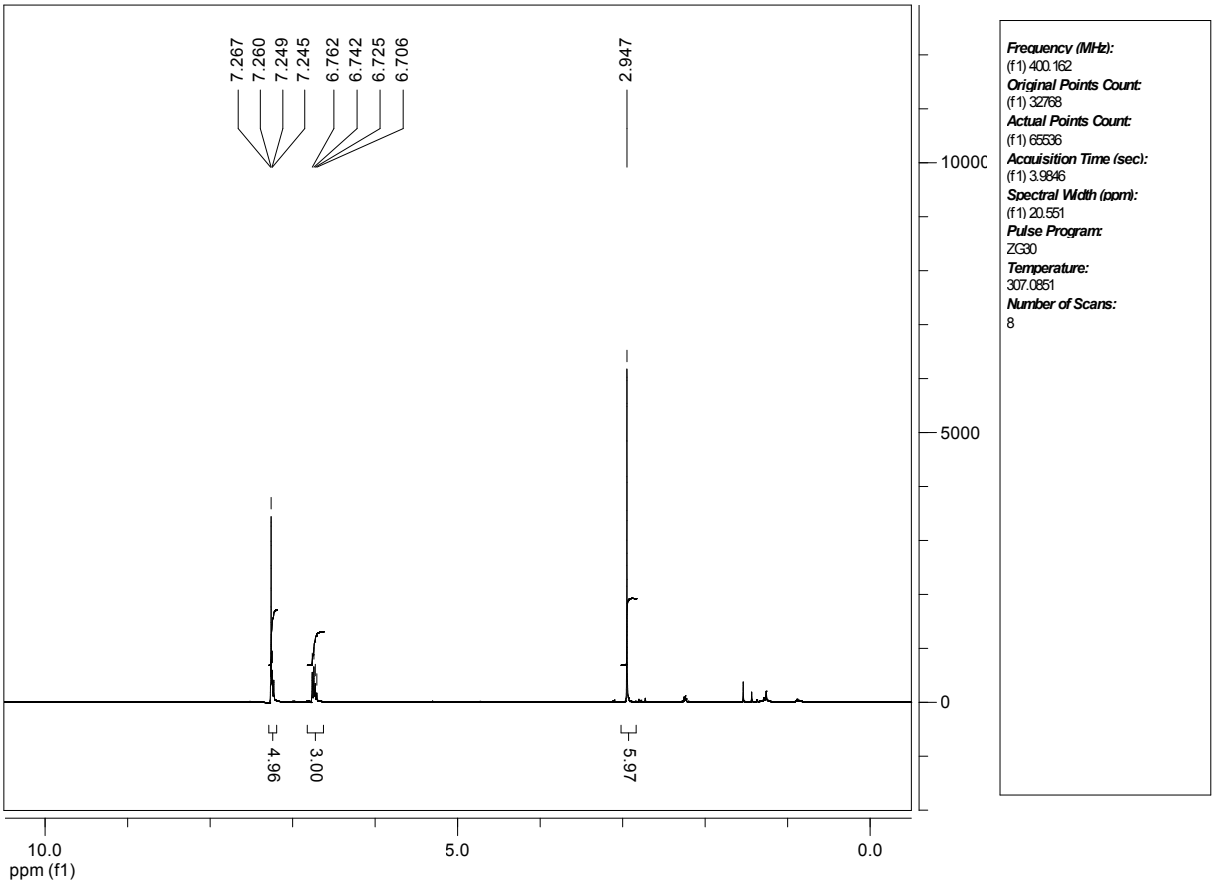

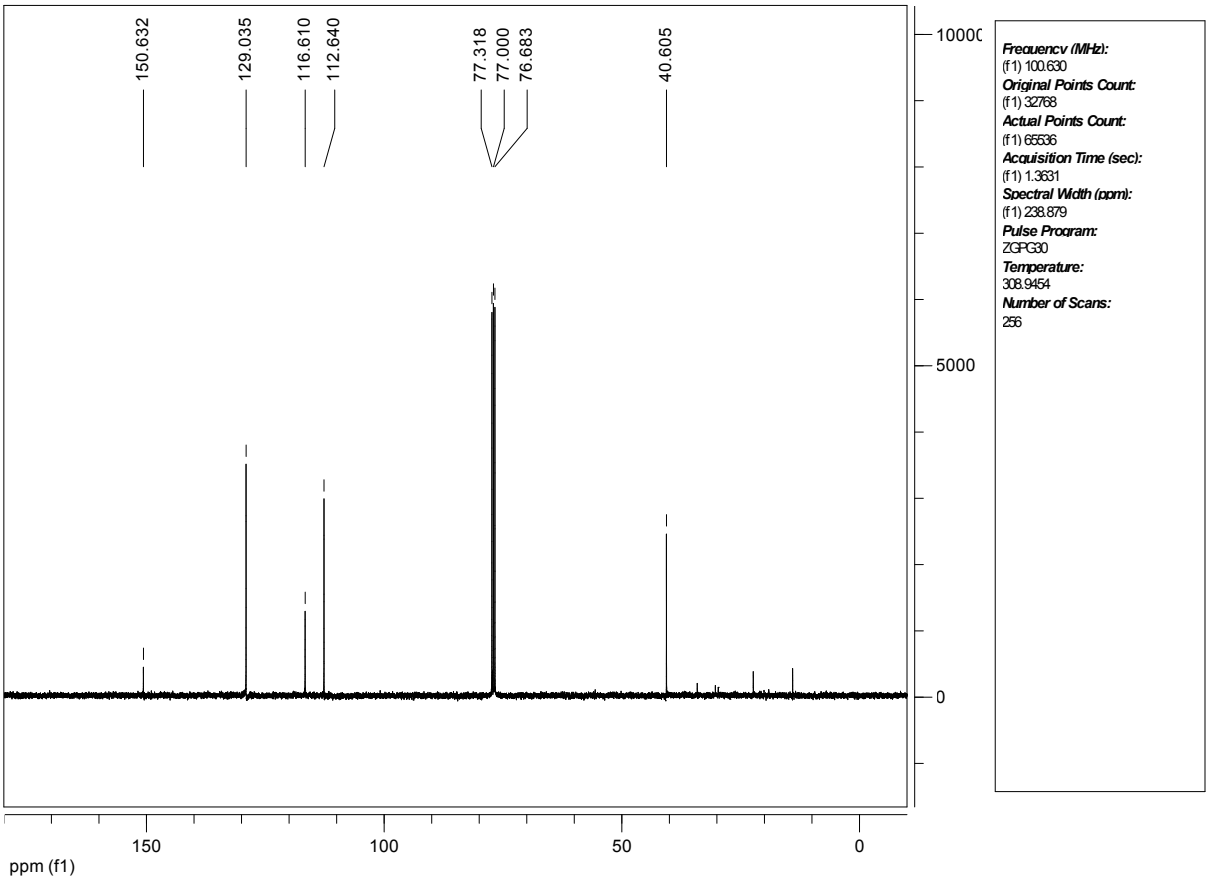

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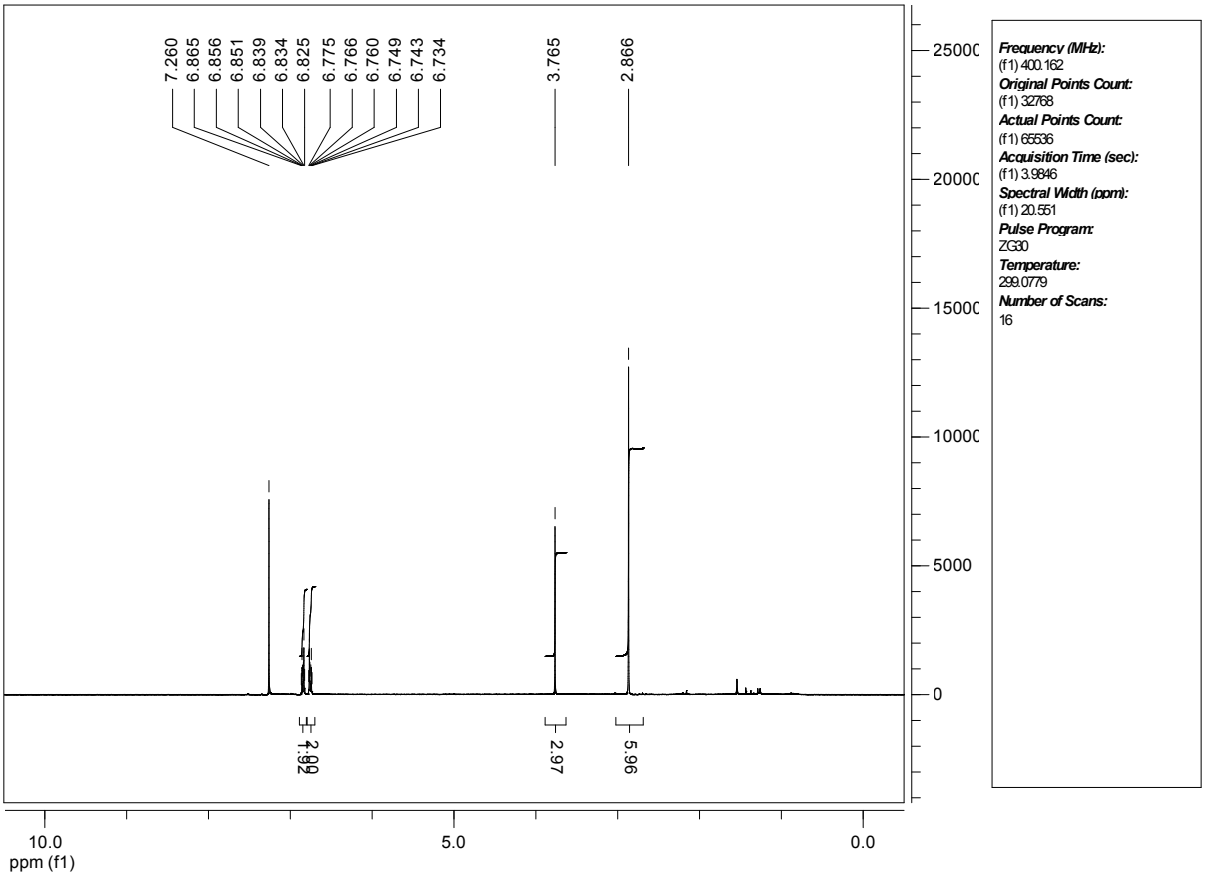

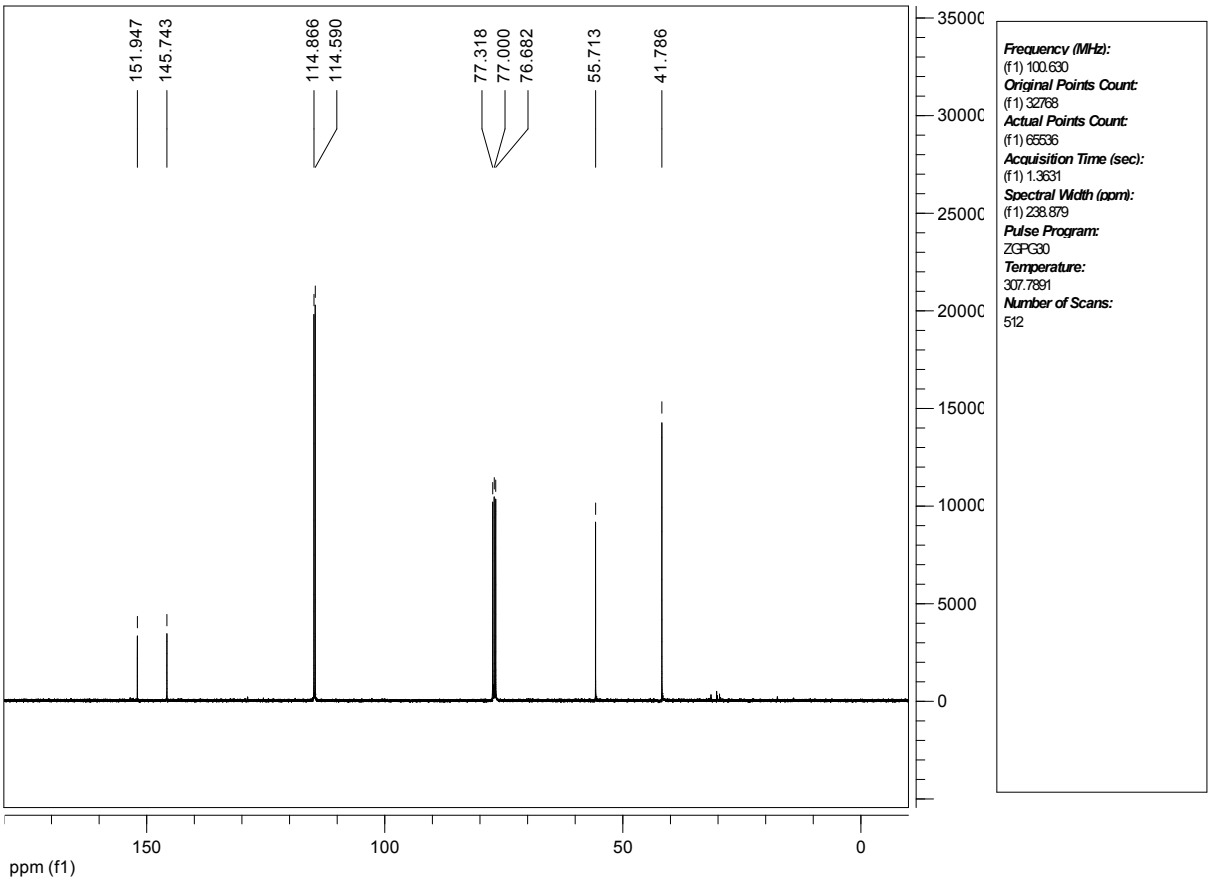

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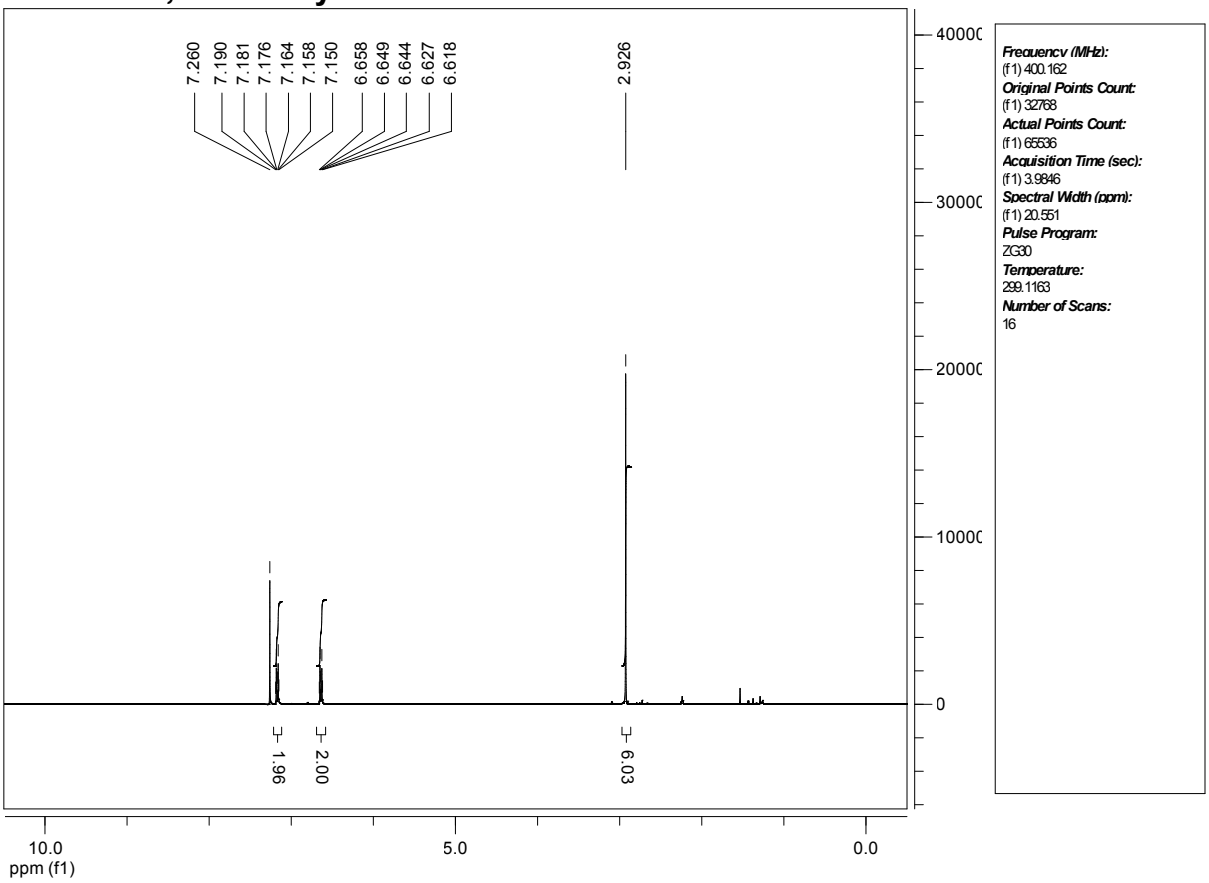

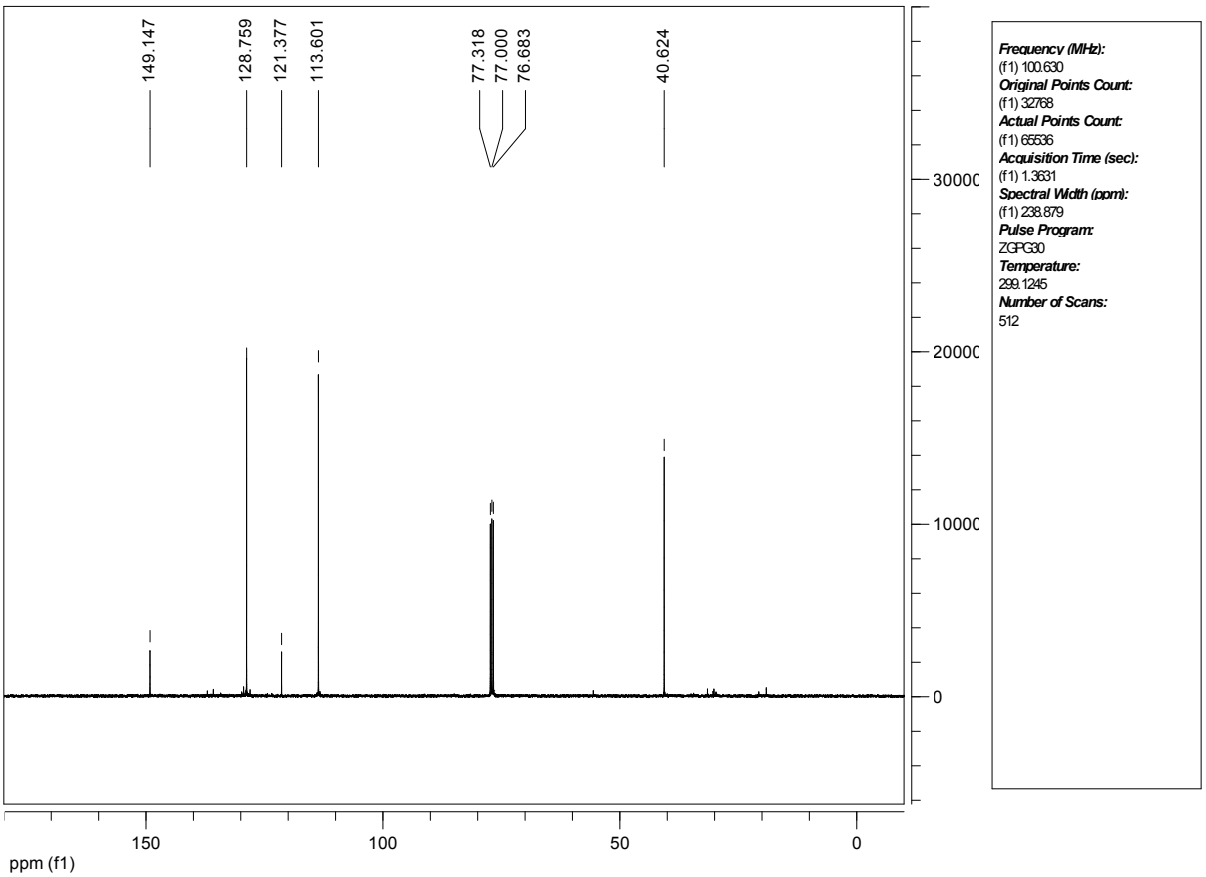

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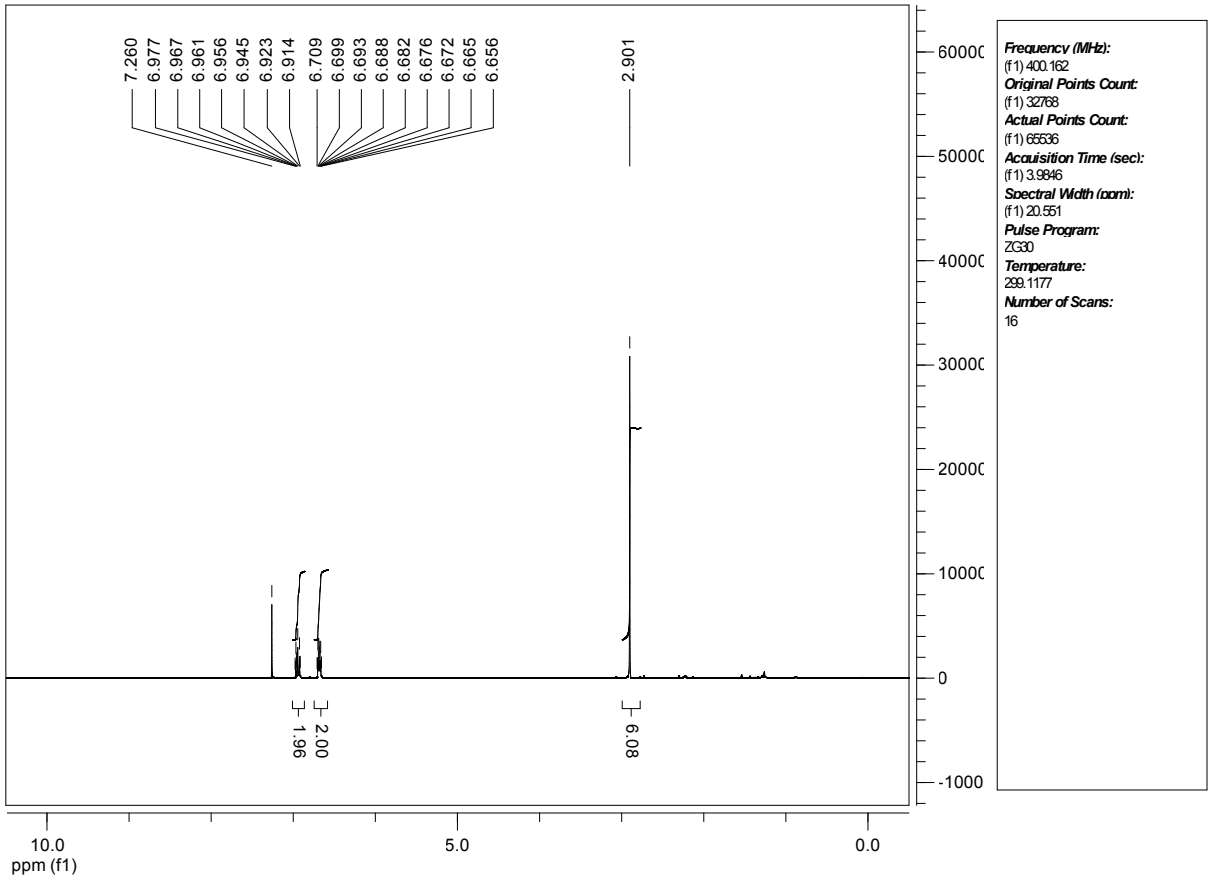

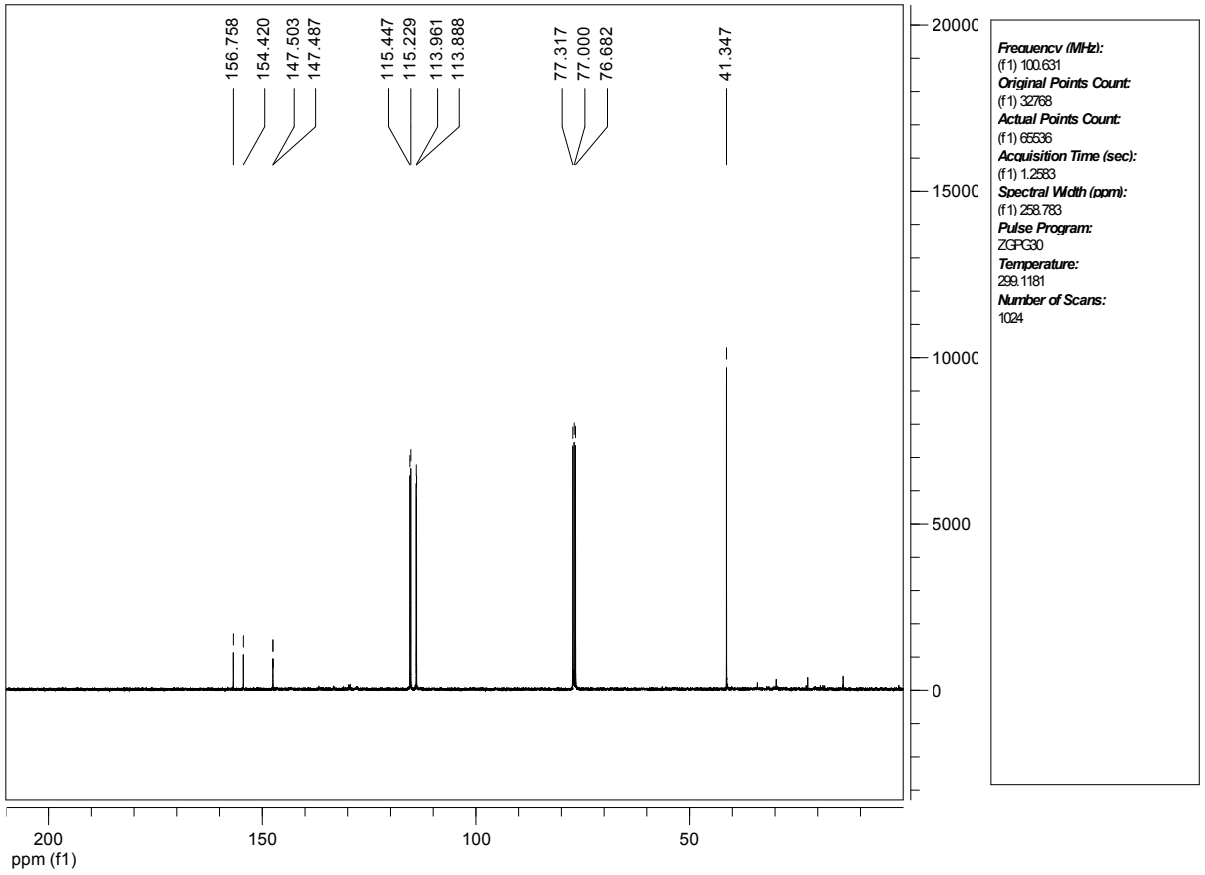

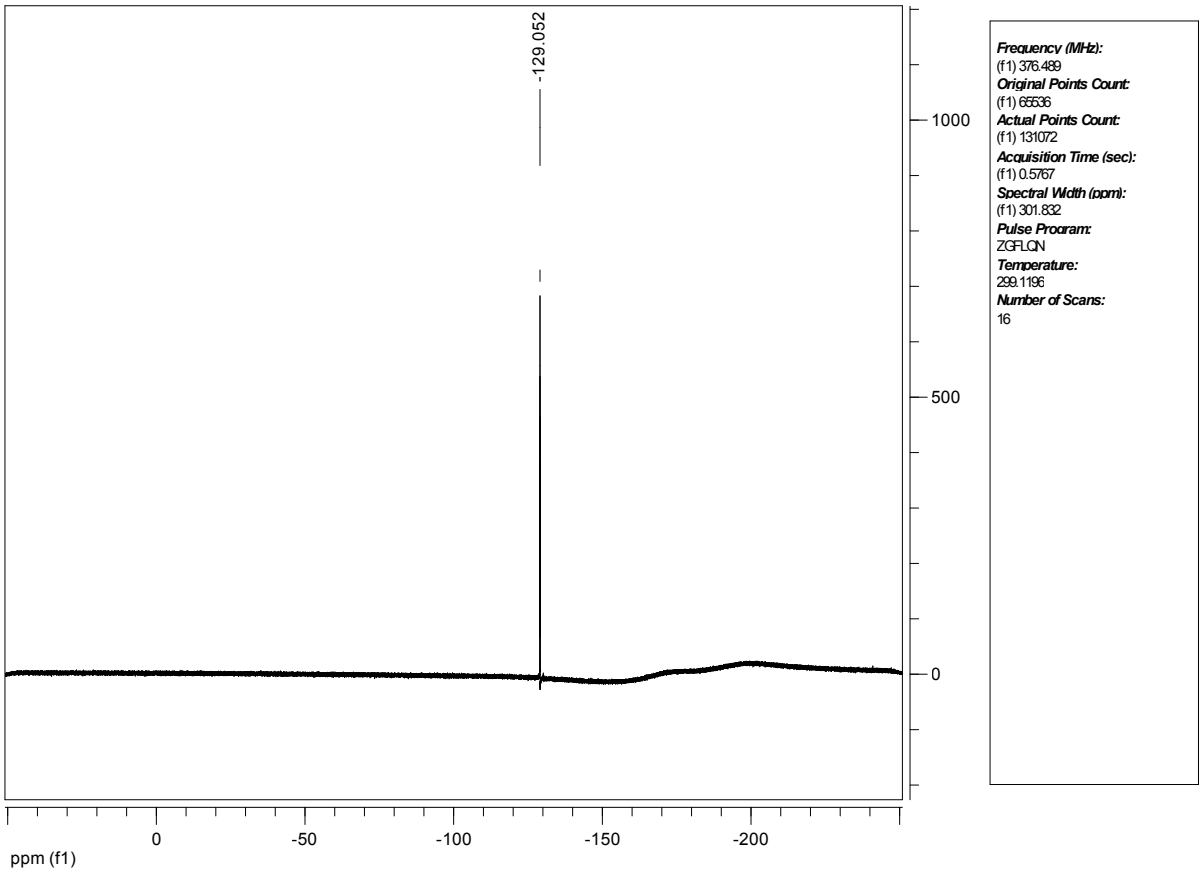

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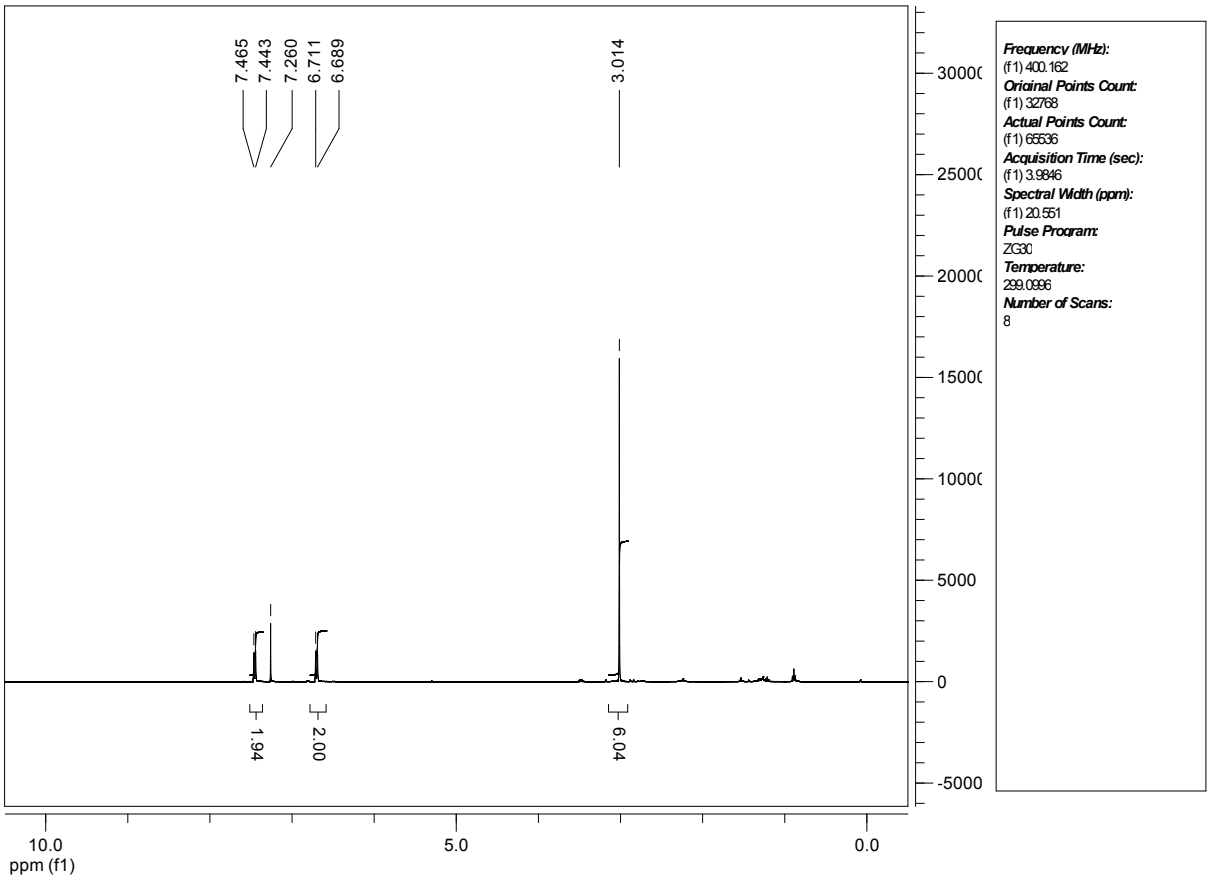

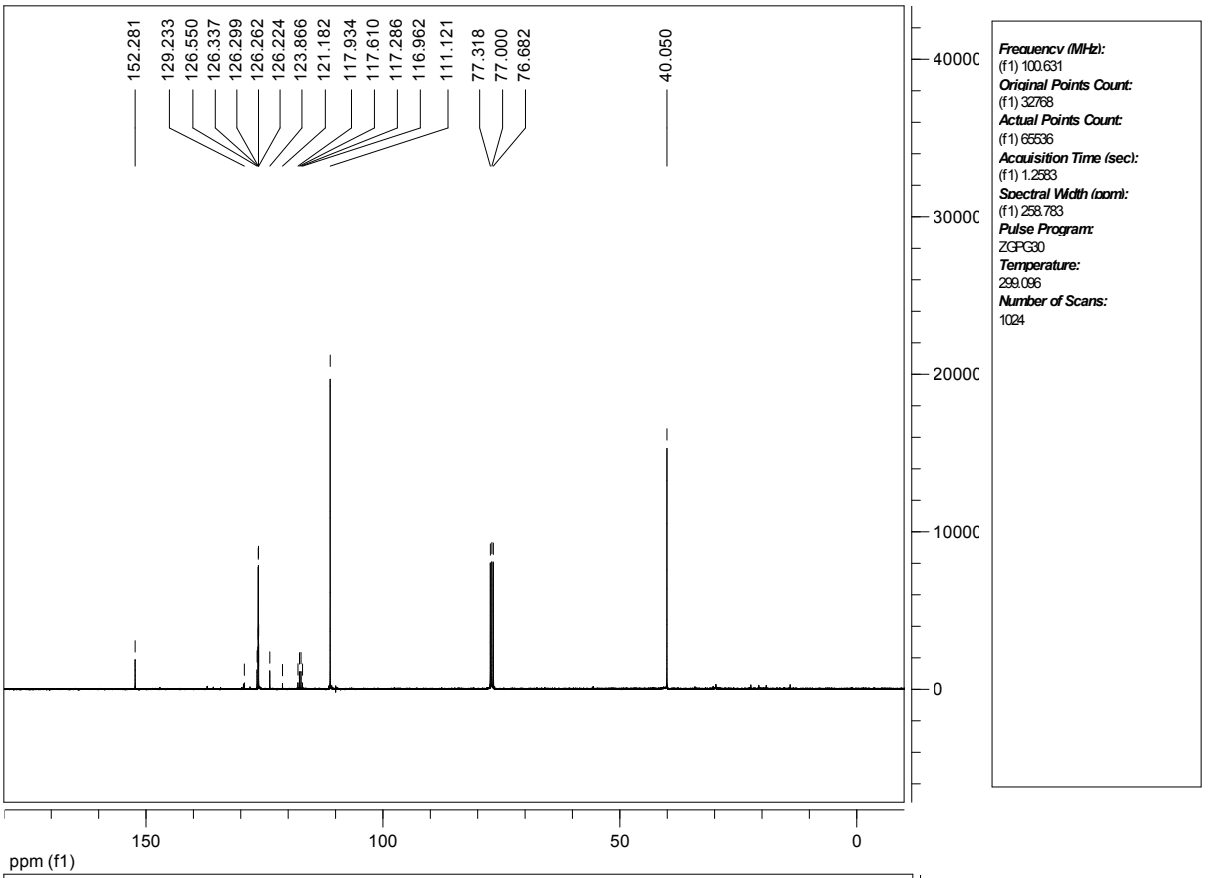
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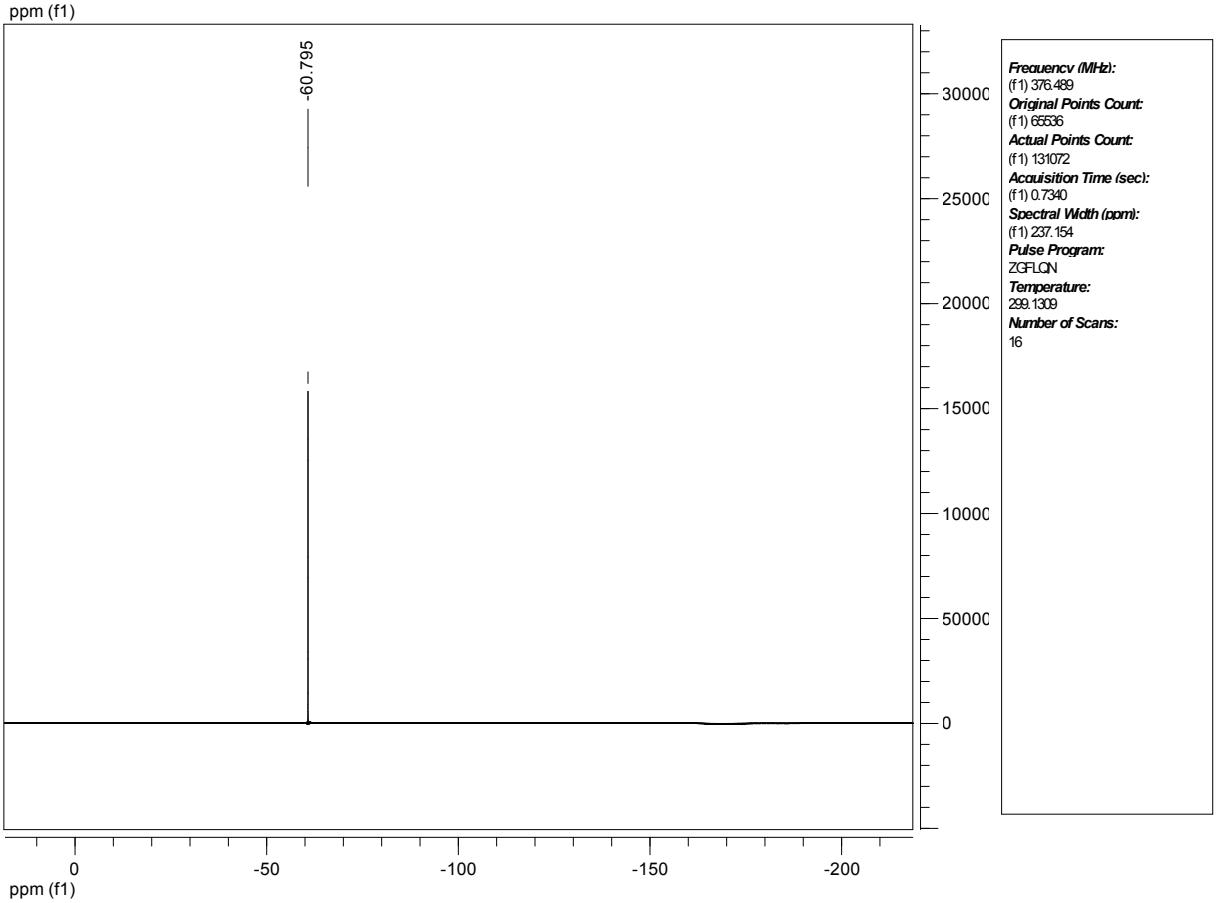
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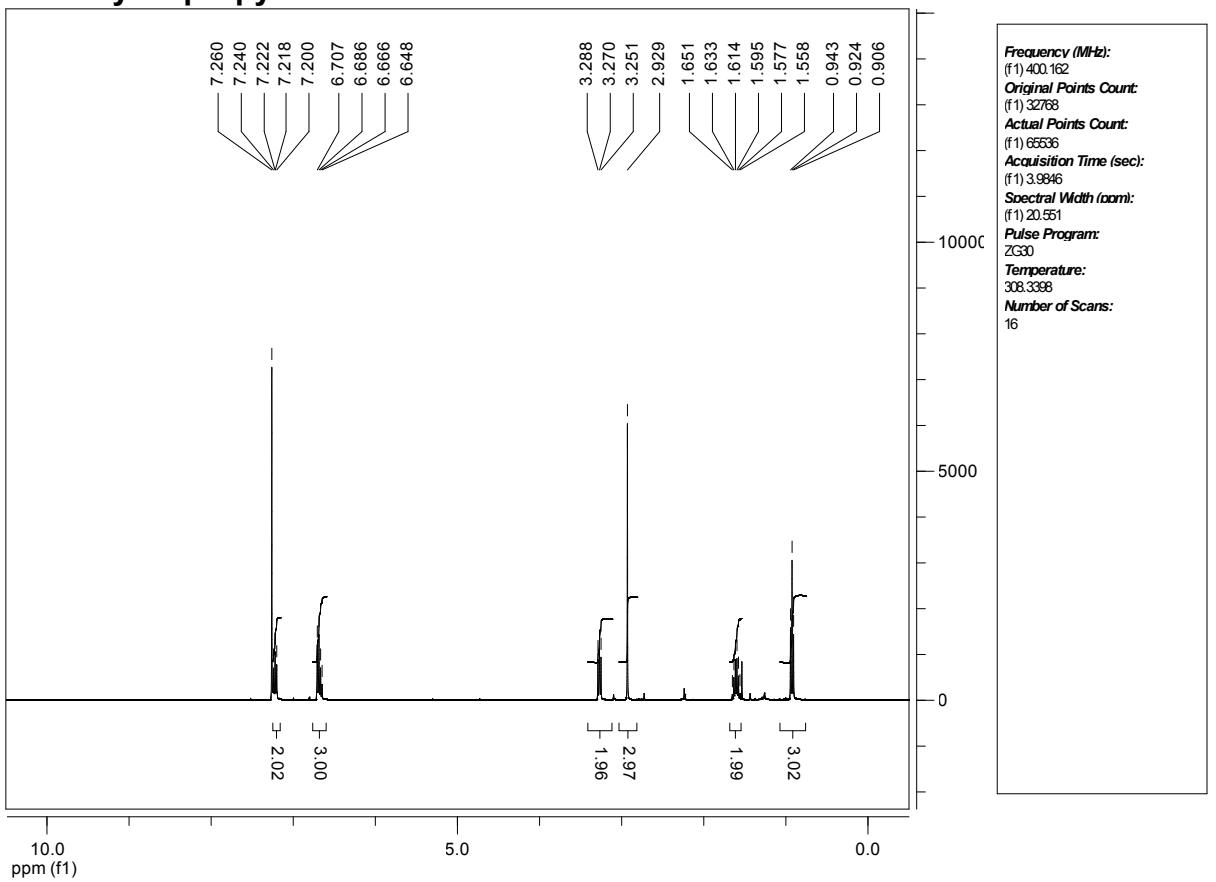

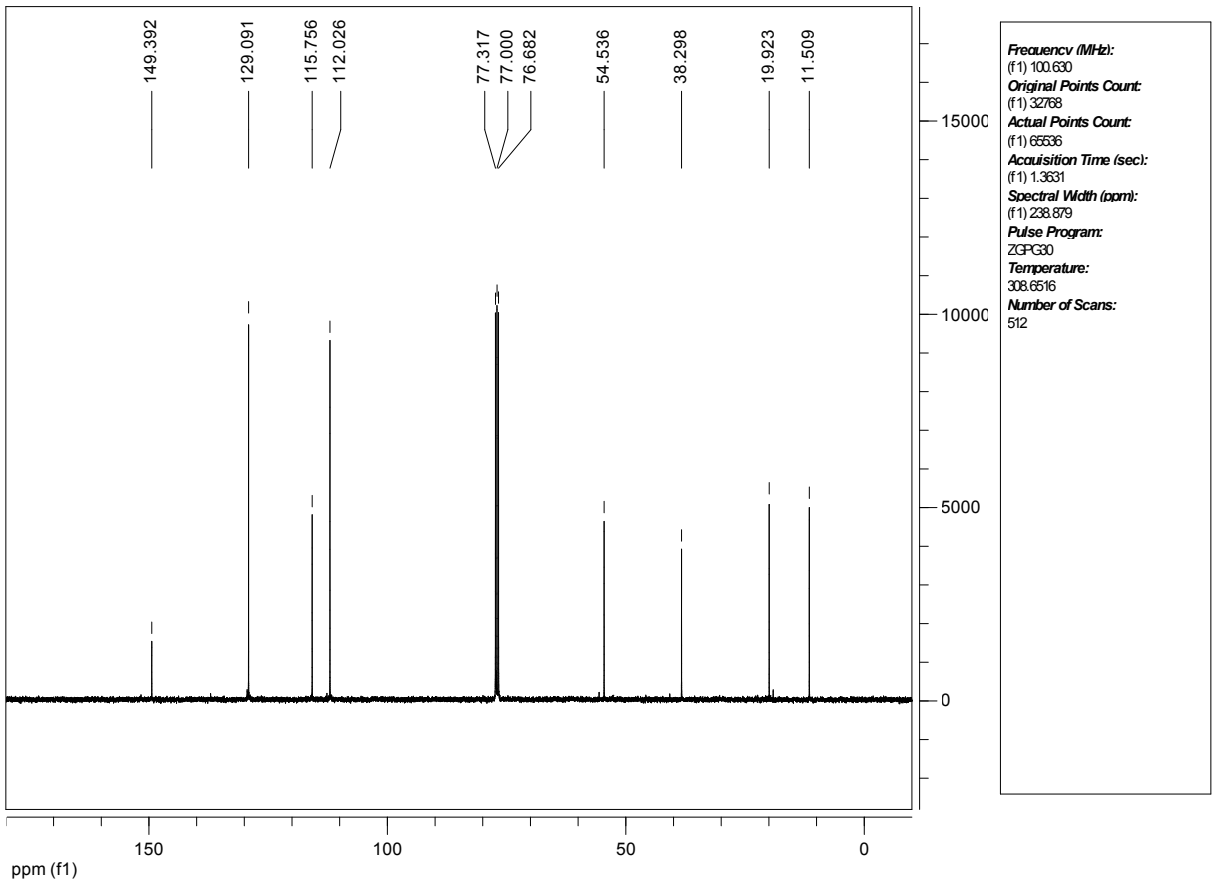

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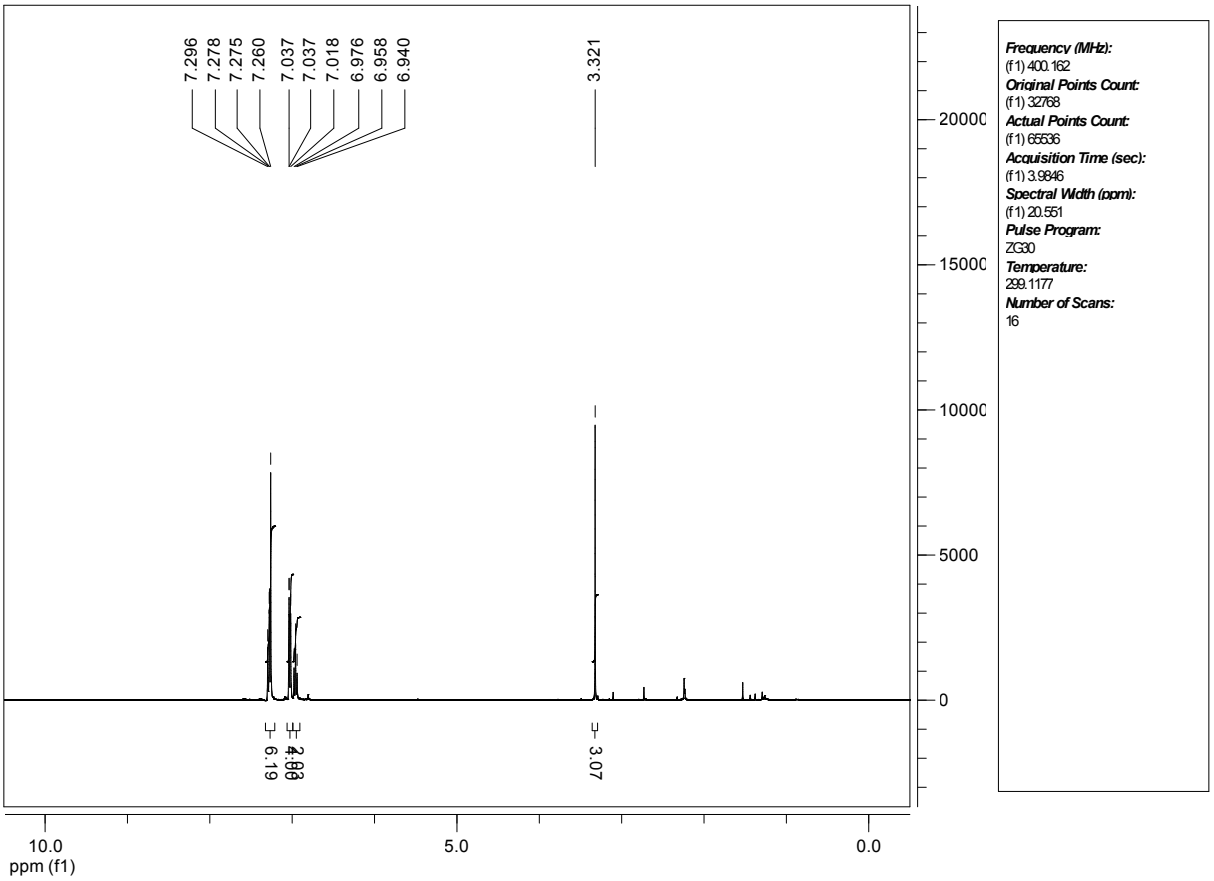

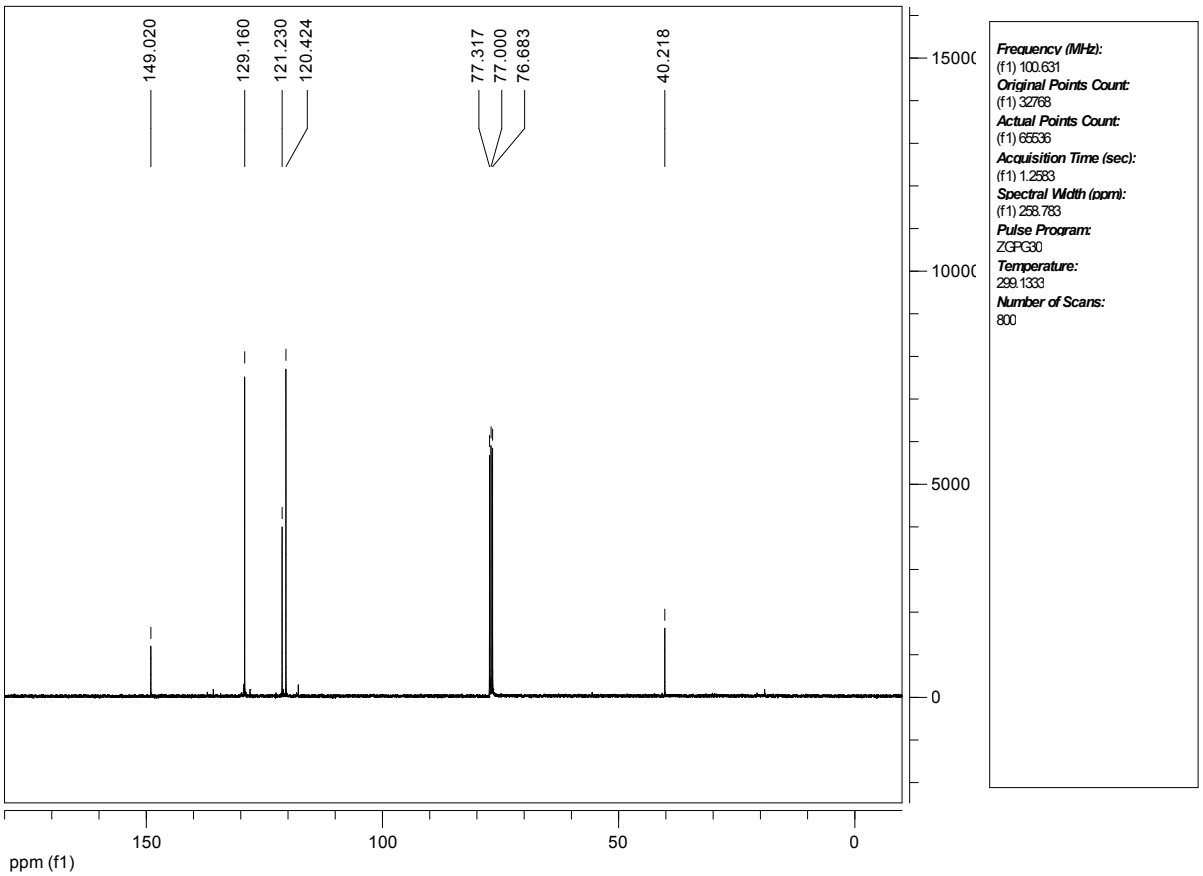

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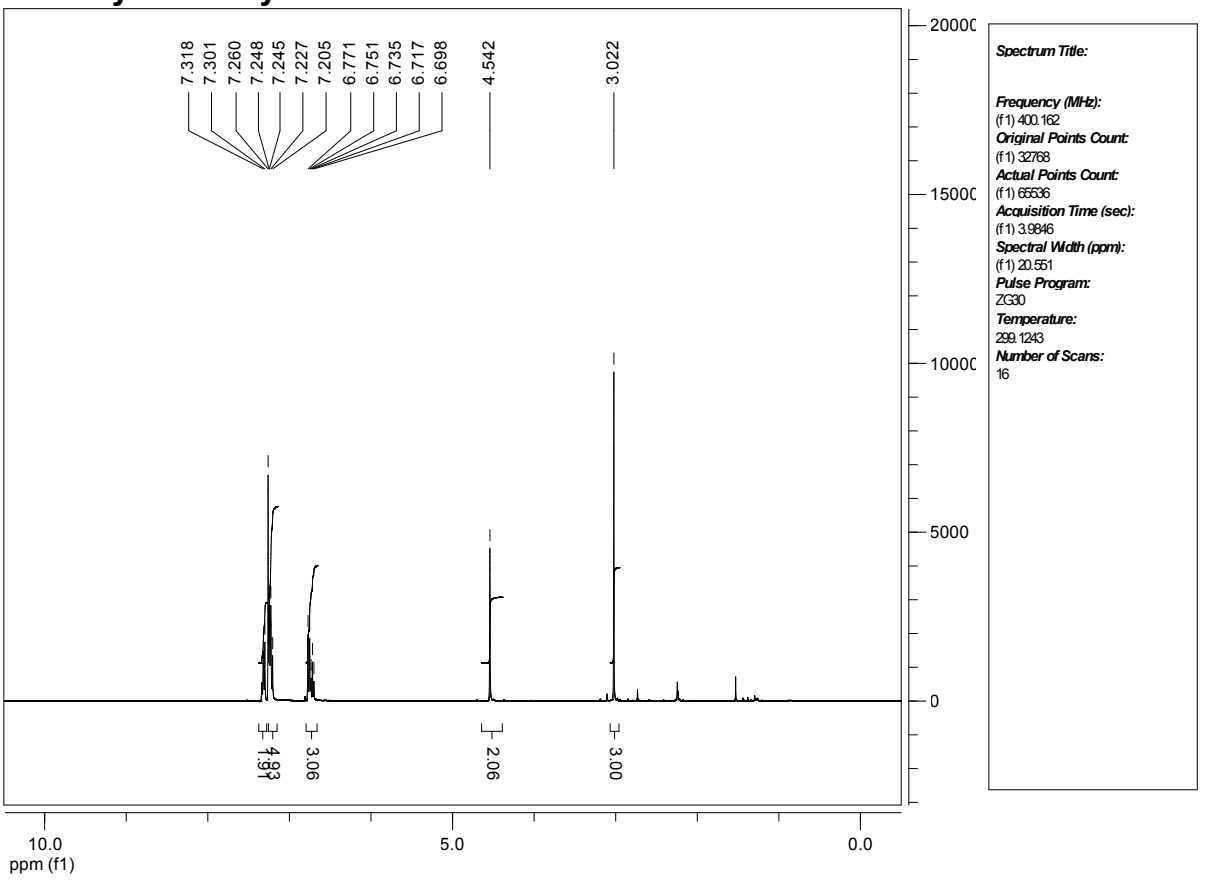

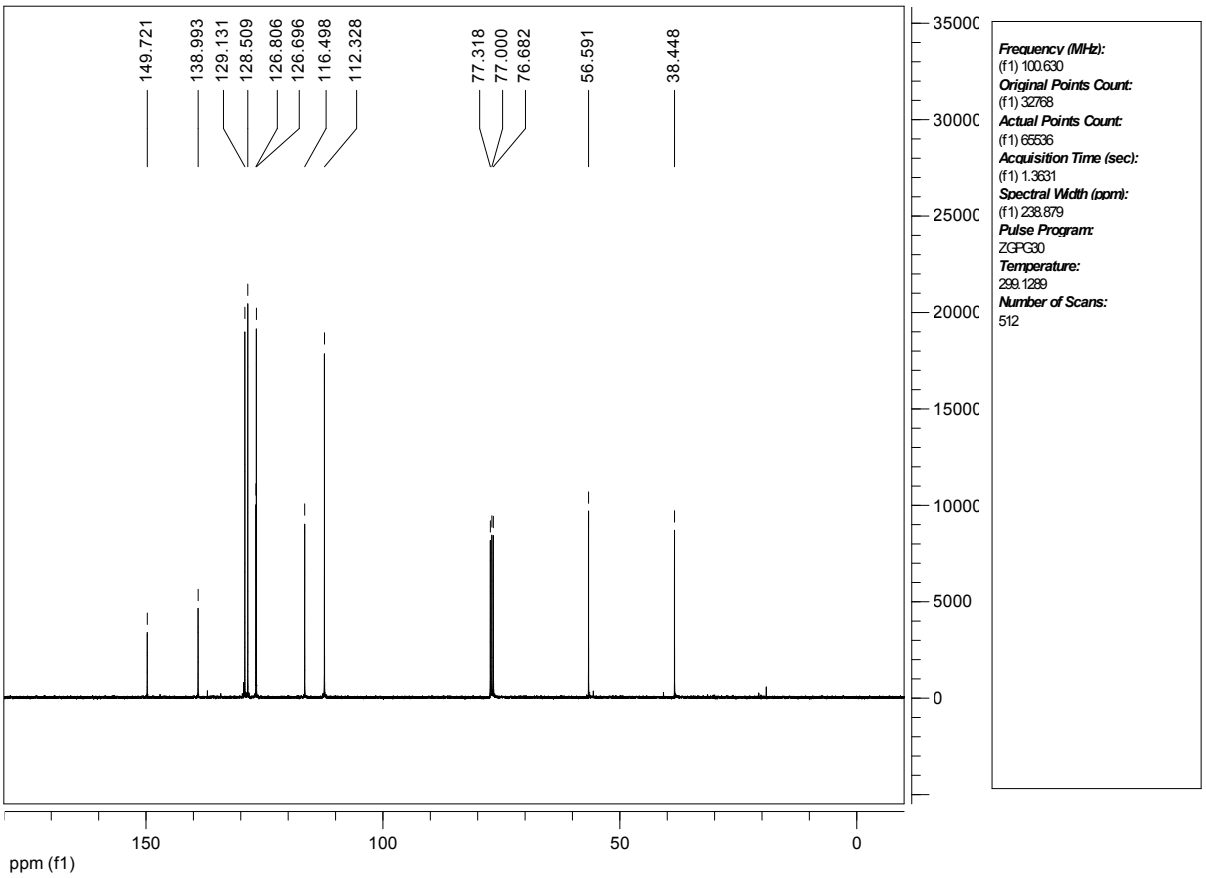

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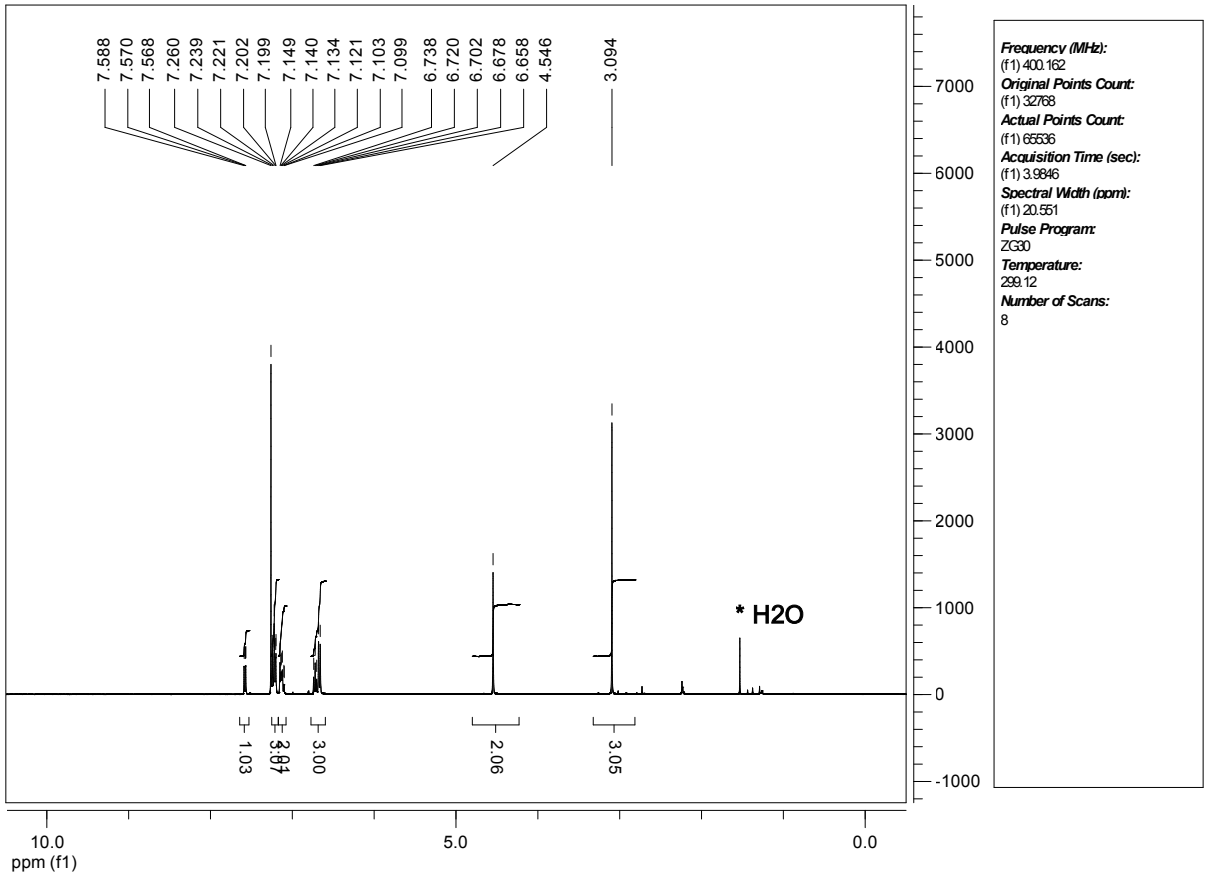

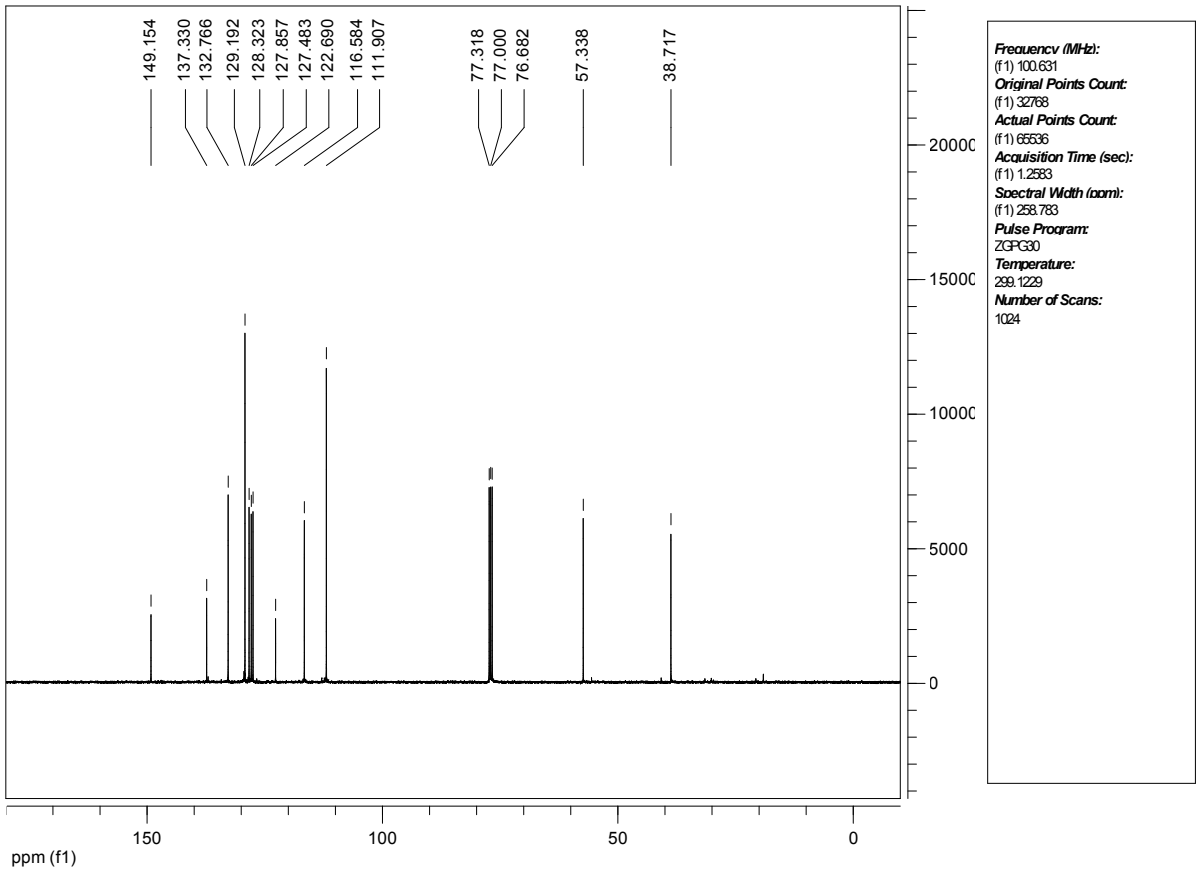

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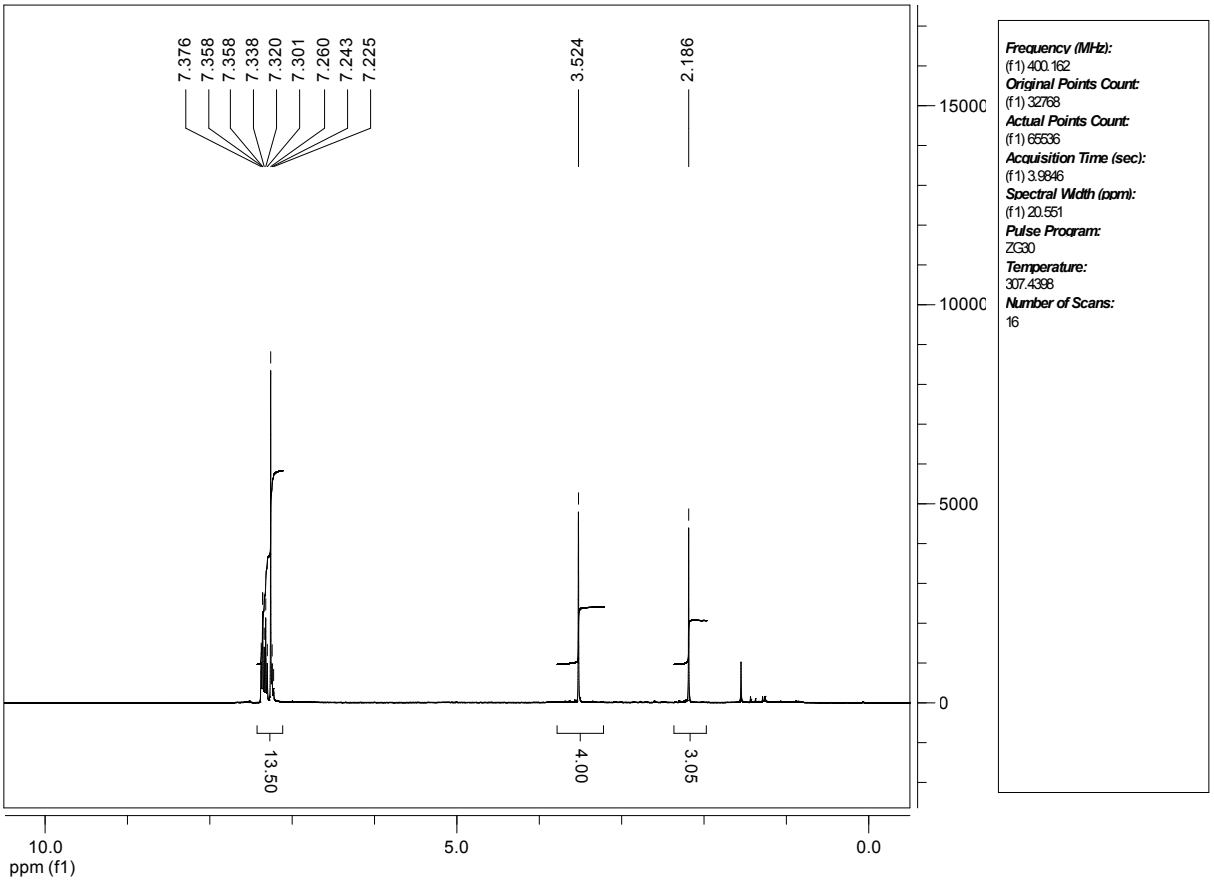

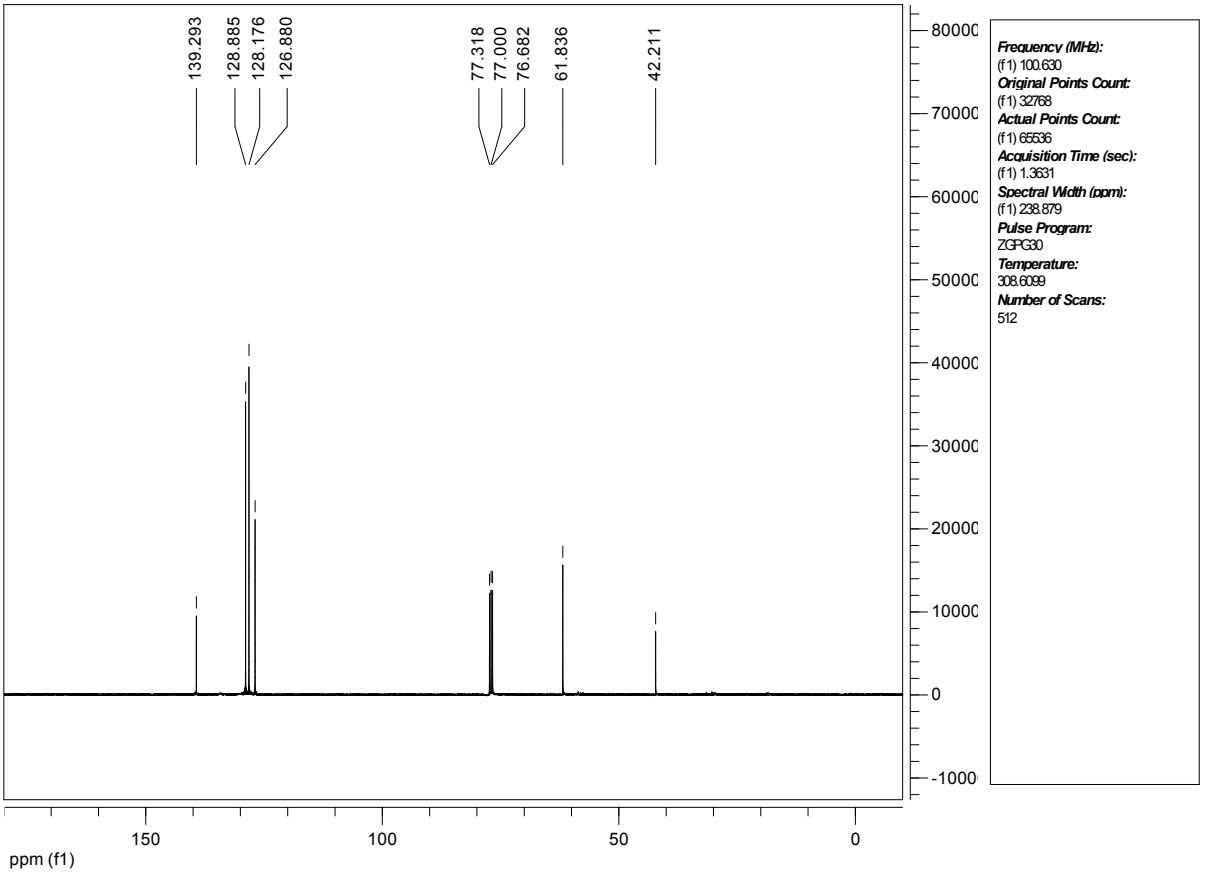

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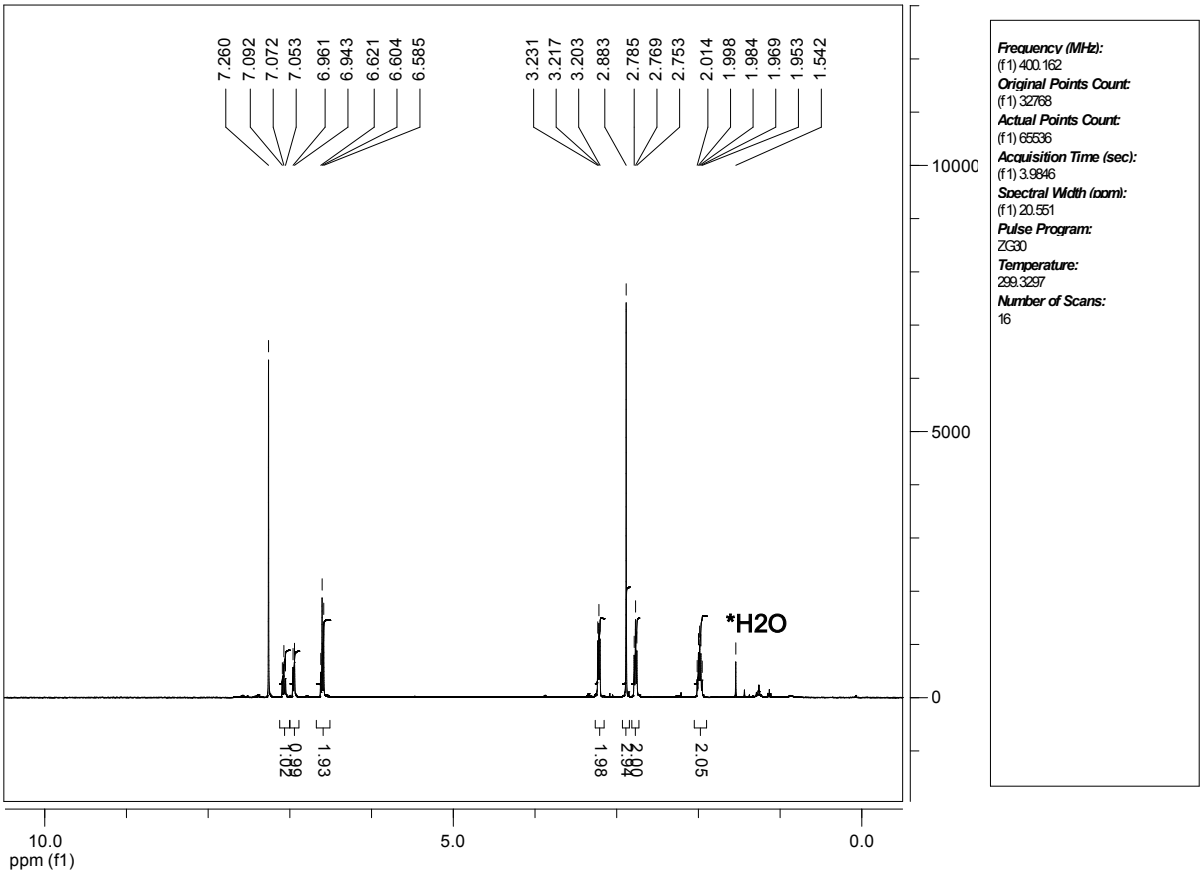

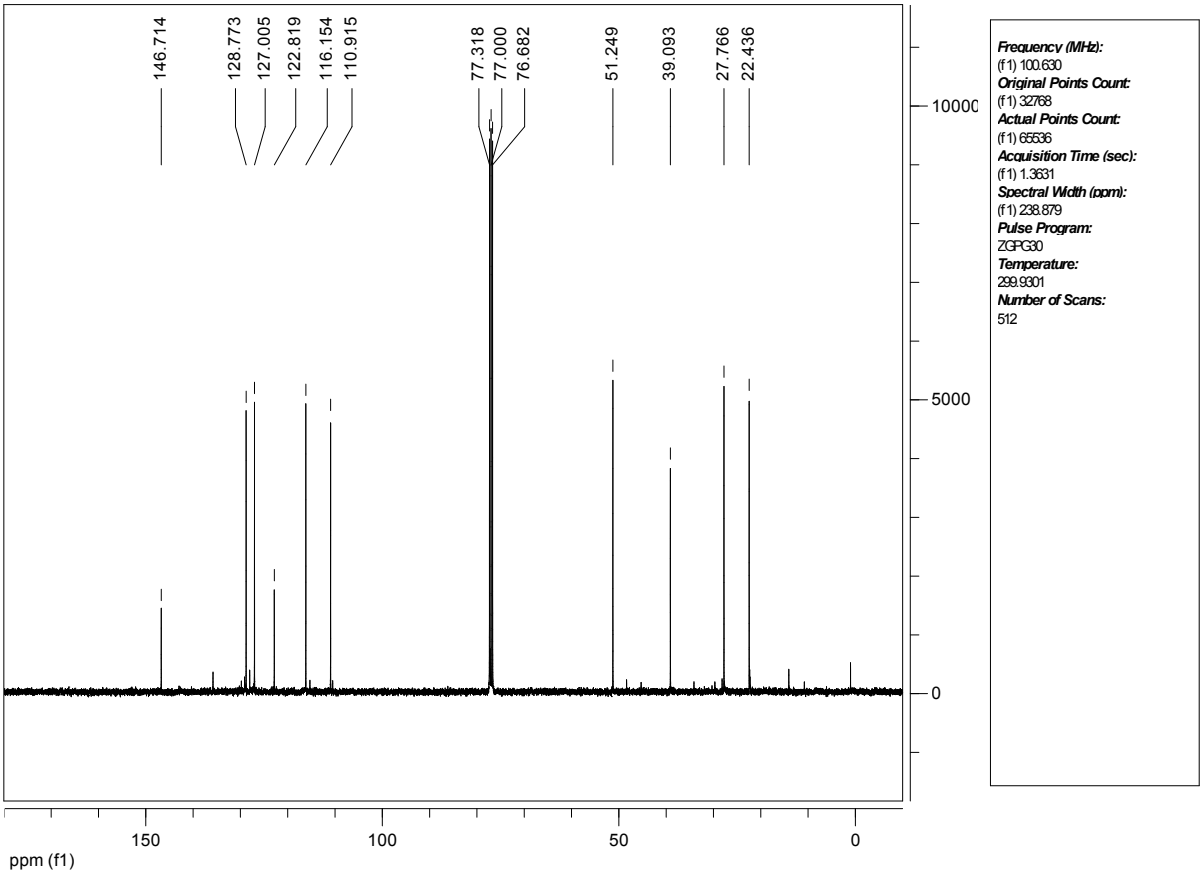

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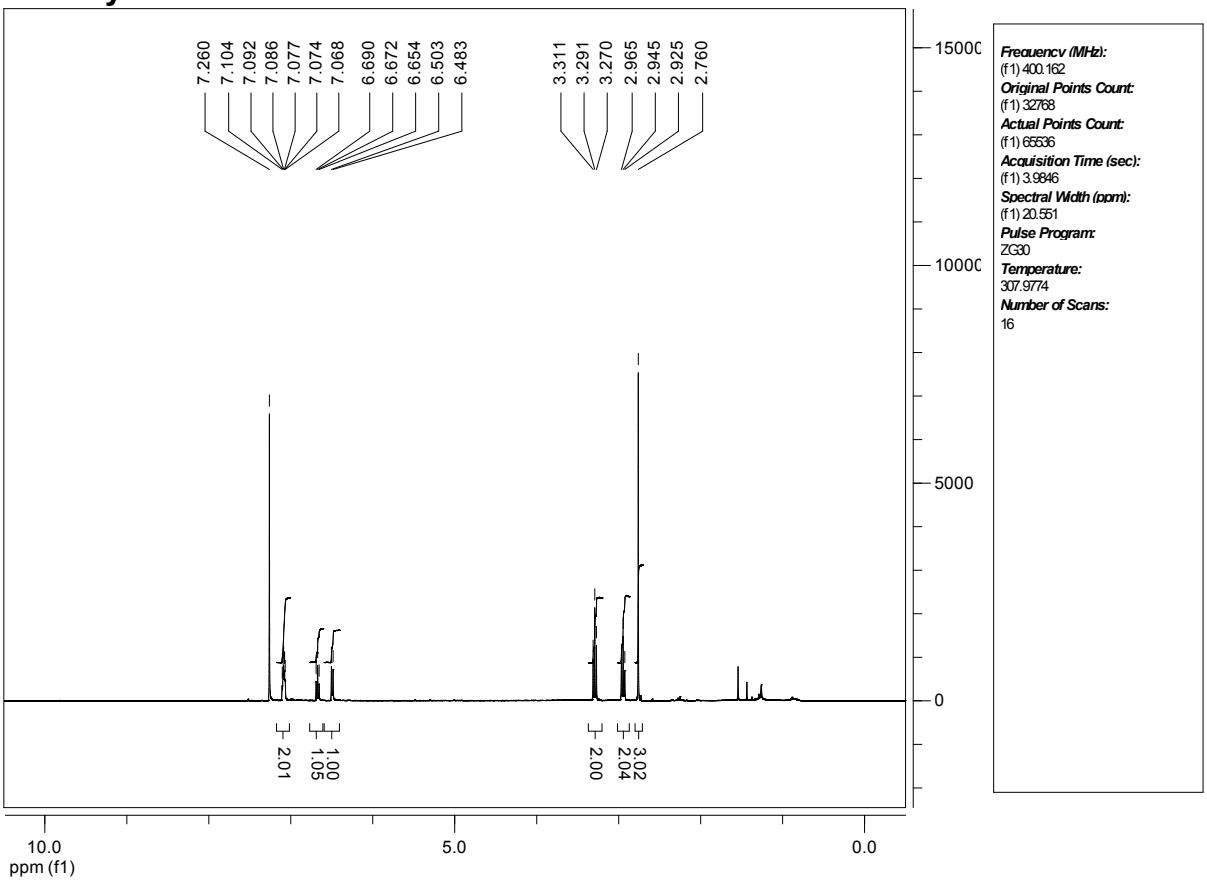

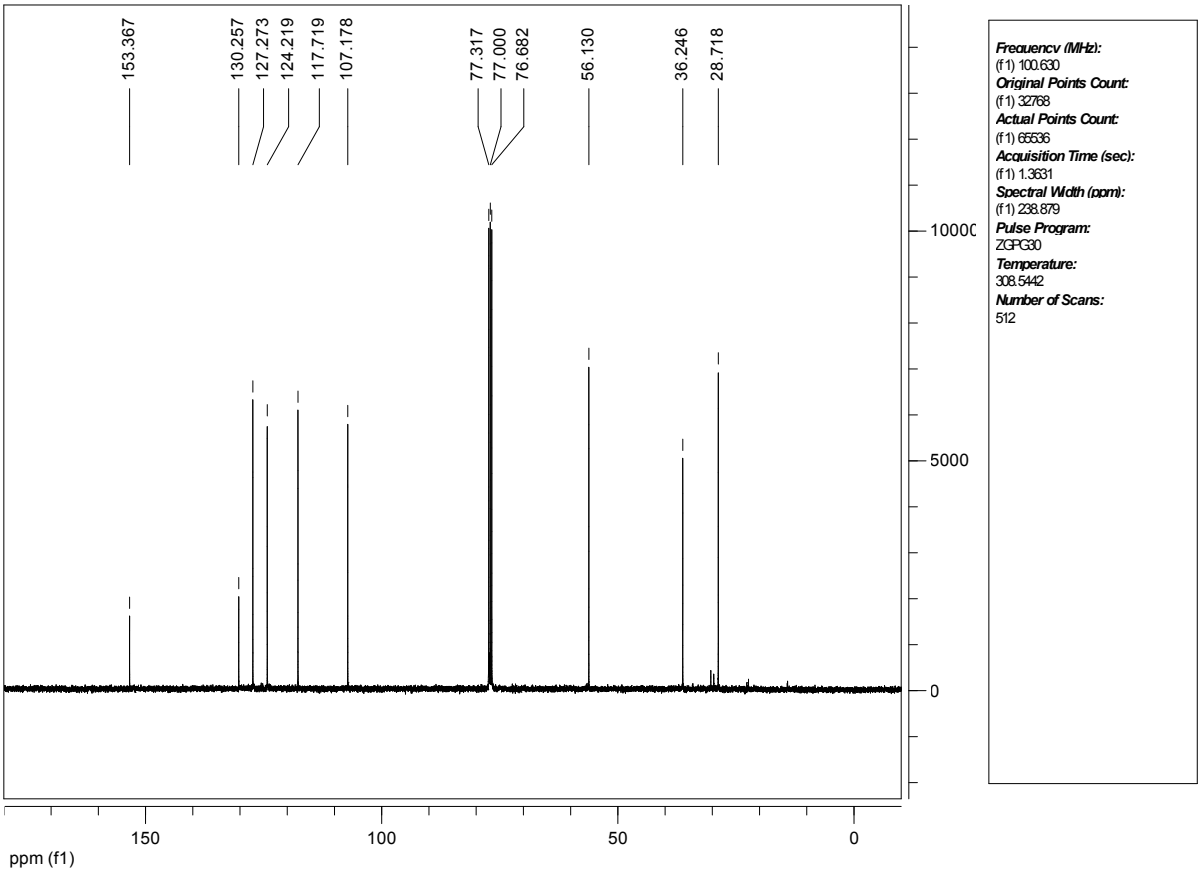

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