

Electronic Supporting Information

Synthesis of Tetrahydropyridine Derivatives Through a Modular Assembly Reaction using 3,4-Dihydropyran as Dual Substrate and Template

Shaohuan Sun, Cheng Cheng, Jian Yang, Amir Taheri, Dan Jiang, Biao Zhang, and Yanlong Gu*

^a Key Laboratory for Large-Format Battery, Materials and System, Ministry of Education, Huazhong University of Science and Technology, Wuhan 430074, China. E-mail: klgyl@hust.edu.cn

^b State Key Laboratory for Oxo Synthesis and Selective Oxidation, Lanzhou Institute of Chemical Physics, Lanzhou, 730000 (P.R. China)

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General remarks:

2-Amino-benzoic acid hydrazide, *p*-anisidine, anhydrous LiBr (99.998 %), 3-ethynylaniline and 2-aminobenzenesulfonamide, were purchased from Alfa Aesar Chemical Company. *p*-Toluidine are purchased from Shanghai Jinshantingxin Industry Co. Ltd. 2-Aminobenzenethiol, methyl 4-methyl-3-oxopentanoate, ethyl 3-oxohexanoate were purchased from Aladdin Industrial Corporation. 2-Aminoacetophenone, *o*-anisidine, 3-aminophenylacetylene, allyl alcohol, propargyl alcohol, 4-morpholinoaniline, dibenzo[*b,d*]furan-3-amine, 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)aniline, benzo[*d*][1,3]dioxol-5-amine, 2,5-dimethoxytetrahydrofuran were purchased from Energy Chemical. Sc(OTf)₃, Methyl 3-cyclopropyl-3-oxopropanoate, TMS-CN, 4-toluenethiol, 3-chloroaniline, 3-aminobenzonitrile, 3,4-difluoroaniline, 4-fluoroaniline, 4-chloroaniline, 4-(trifluoromethoxy)aniline, 4-bromoaniline, 1-(4-aminophenyl)ethanone, *n*-butyl vinyl ether, ethyl 4-aminobenzoate, 2-aminobenzamide were purchased from Shanghai Shaoyuan Co., Ltd. Pentane-2,4-dione, methyl 3-oxobutanoate, ethyl 3-oxobutanoate, FeCl₃, PTSA, ZnCl₂, LiBr·H₂O, Bi(OTf)₃, I₂, H₃BO₃, nitromethane, aniline, 4-nitroaniline, acetophenone and aqueous solution of formaldehyde (30 wt %) were purchased from Sinopharm Chemical Reagent Co. Ltd. 3-Amino-5-(*tert*-butyl)thiophene-2-carboxamide were purchased from Apollo scientific Limited. *Tert*-butyl 6-amino-1H-indole-1-carboxylate was purchased from Adamas Reagent. Co., Ltd. ¹H and ¹³C NMR spectra were recorded on a Bruker AV-400 machine. Chemical shifts are expressed in ppm relative to Me₄Si in CDCl₃. IR spectra were recorded on a FT-IR Bruker (EQUINOX 55) machine using KBr technology. High-resolution mass spectra (HRMS) were obtained on Bruker Bruker Compass DataAnalysis 4.0.

Preparation of 2-butoxy-3,4-dihydropyrans: All the dihydropyrans were prepared through a three-component reaction of 1,3-dicarbonyl compound, formaldehyde and *n*-butyl vinyl ether according to a literature method.^[1] The synthesis was performed in a 25 ml of round bottomed flask equipped with magnetic stirring. Methyl acetoacetate (5.8 g, 50 mmol), *n*-butyl vinyl ether (2.5 g, 25 mmol) and an aqueous solution of formaldehyde (30 wt %, 6.25 g, 62.5 mmol) were mixed, and then stirred at 80 °C for 6 hours. Brine (20 ml) and ethyl acetate (30 ml) were added. The upper organic phase was separated and the bottom aqueous phase was extracted with ethyl acetate (10 ml × 3). The organic phase was combined together and concentrated under vacuum. The residue was subjected to a silica column chromatography by using a mixture of ethyl acetate and petrolether as an eluting solvent (EA/PE_{v/v} = 1/8). The dihydropyran **1a** was obtained in 81 % of yield (4.6 g). The other dihydropyrans were synthesized according to an analogous procedure.

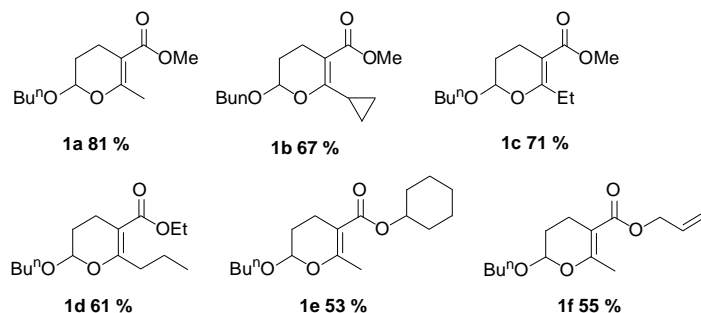
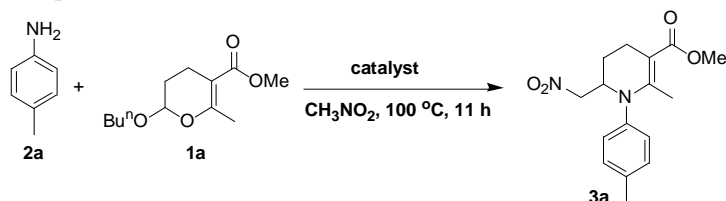


Figure S1. Some 2-butoxy-3,4-dihydropyrans used in this work.

General procedure for the reactions of 2-butoxy 3,4-dihydropyrans, anilines and nitromethane: The prepared starting material **1a** (82.1 mg, 0.36 mmol) was mixed with *p*-toluidine **2a** (32.1 mg, 0.30 mmol) and LiBr H₂O (9.4 mg, 30 mol %) in nitromethane (1.0 mL). The mixture was then stirred for 10 hours at 100 °C. After reaction, the mixture was cooled to room temperature. The desired product, **3a**, was obtained in 99 % of yield (90.3 mg) by isolation with a preparative TLC (eluting solvent: ethyl acetate/petroether = 1/8 (v/v)). Tests for substrate scope were all performed with an analogous procedure. Compound **II-a** was also prepared with an analogous procedure.

Table S1. Three-component reaction of **1a**, *p*-toluidine and nitromethane.^[a]

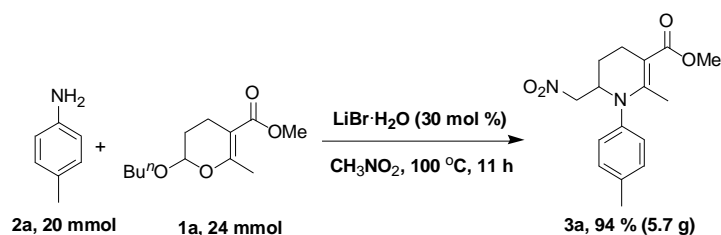


entry	catalyst	yield (%)
1	LiBr·H ₂ O (30 mol %)	99
2	—	0
3	LiBr (30 mol %)	81
4	MnCl ₂ ·4H ₂ O (10 mol %)	12
5	Sc(OTf) ₃ (10 mol %)	< 5
6	CuBr ₂ (10 mol %)	< 5
7	FeCl ₃ ·6H ₂ O (10 mol %)	< 5
8	NiCl ₂ ·6H ₂ O (10 mol %)	0
9	I ₂ (10 mol %)	6
10	LiClO ₄ ·3H ₂ O (30 mol %)	13
11	HBr (<i>aqu.</i> (36 %), 10 mol %)	0
12	HBr (acetic acid solution (33 %), 10 mol %)	0
13	LiBr·H ₂ O (10 mol %)	32
14	LiBr·H ₂ O (20 mol %)	74
15	LiBr·H ₂ O (30 mol %)	77 ^[b]
16	LiBr·H ₂ O (30 mol %)	75 ^[c]
17	LiBr·H ₂ O (30 mol %)	11 ^[d]
18	LiBr·H ₂ O (30 mol %)	48 ^[e]

[a]: **1a**, 0.36 mmol; **2a**, 0.3 mmol; catalyst, 30 mol %; nitromethane, 1.0 ml; 100 °C, yield was calculated with respect to **2a**; 4 h. [b]: **1a/2a** = 1.0/1.0. [c]: **1a/2a** = 1.0/1.2, yield was calculated with respect to **1a**. [d]: 50 °C. [e] 80 °C.

Large scale synthesis of 3a: In a 25 ml of round bottomed flask equipped with magnetic stirring, dihydropyran **1a** (5.5 g, 24 mmol) was mixed with *p*-toluidine **2a** (2.1 g, 20 mmol) in nitromethane (50 ml). LiBr·H₂O (0.63g, 30 mol %) was then added. The solution was stirred at 100 °C for 11 hours. Then, the reaction mixture was cooled to room temperature. Brine (50 ml) and ethyl acetate (20 ml) were added. The upper organic phase was then separated, and the bottom aqueous phase was extracted with ethyl acetate (20 ml × 3). The combined organic phase was

concentrated slowly under reduced pressure. The residue was then subjected to a silica column chromatography by using a mixture of ethyl acetate and petroether as eluting solvent (EA/PE_{v/v} = 10/1). Product **3a** was obtained in 94 % of yield (5.7 g).

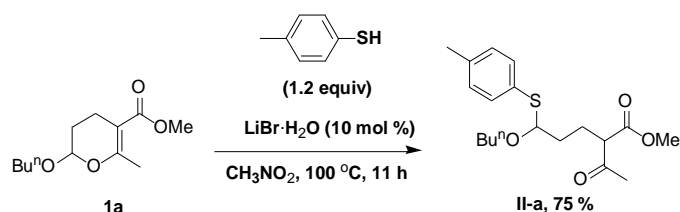


Scheme S1. Large-scale synthesis of THP **3a**.

Preparation of compounds 4a: Dihydropyran **1a** (68.5 mg, 0.30 mmol) and $\text{LiBr}\cdot\text{H}_2\text{O}$ (9.4 mg, 30 mol %) was mixed in nitromethane (1.0 mL), and the mixture was stirred for 10 hours at $100\text{ }^\circ\text{C}$. After reaction, the mixture was cooled to room temperature. The desired product, **4a**, was obtained in 77 % of yield (49.7 mg) by isolation with a preparative TLC (eluting solvent: ethyl acetate/petroether = 1/8 (v/v)).

Reaction of 5a, *p*-toluidine and nitromethane over $\text{LiBr}\cdot\text{H}_2\text{O}$: Methyl acetoacetate (1.0 mmol) was mixed under nitrogen atmosphere with NaY-Zeoline (0.2 g) at $0\text{ }^\circ\text{C}$, and the mixture was stirred at $0\text{ }^\circ\text{C}$ for 15 minutes. After that, acrolein (1.0 mmol) was added, and the mixture was stirred for 2 hours at $0\text{ }^\circ\text{C}$. Then, the mixture was submitted to isolation with a preparative TLC (eluting solvent: ethyl acetate/petroether = 1/5 (v/v)). The desired product, **5a**, was obtained in 60 % of yield (103.2 mg). **5a** (51.7 mg, 0.3 mmol) was mixed under nitrogen atmosphere with *p*-toluidine (32.2 mg, 0.3 mmol) and $\text{LiBr}\cdot\text{H}_2\text{O}$ (9.4 mg, 30 mol %). The mixture was stirred at $100\text{ }^\circ\text{C}$ for 10 hours under the protection of N_2 . After reaction, the mixture was cooled to room temperature. After that, the mixture was subjected to an isolation with a preparative TLC (eluting solvent: ethyl acetate/petroether = 1/8 (v/v)). The products, **3a**, **4a** and **6a**, were obtained in 32 % (22.0 mg), 36 % (23.2 mg) and 17 % (7.9 mg) of yields, respectively.

Preparation of compounds 7a and 3c': Dihydropyran **1b** (91.4 mg, 0.36 mmol) was mixed with **2a** (32.1 mg, 0.30 mmol) and $\text{LiBr}\cdot\text{H}_2\text{O}$ (9.4 mg, 30 mol %) in nitromethane (1.0 mL). The mixture was then stirred for 10 hours at $100\text{ }^\circ\text{C}$. After reaction, the mixture was cooled to room temperature. The desired product, **7a**, was obtained in 66 % of yield (68.9 mg) by isolation with preparative TLC (eluting solvent: ethyl acetate/petroether = 1/5 (v/v)). Compound **7a** can be converted to **3c'** through 5 hours of reaction at $100\text{ }^\circ\text{C}$ in 87% of yield in nitromethane in the presence of ZnI_2 (10 mol%).



Scheme S2. Reaction of **1a** and *p*-toluenethiol over LiBr catalyst.

Preparation of compound 8a: Dihydropyran **1a** (82.1 mg, 0.36 mmol) was mixed with *p*-anisidine **2b** (37.0 mg, 0.30 mmol), TMSCN (89.1 mg, 0.9 mmol) and ZnI₂ (28.7 mg, 30 mol %) in CH₃CN (1.0 mL). Then, the mixture was stirred for 6 hours at 70 °C. Then, the mixture was cooled to room temperature. The desired product, **8a**, was obtained in 74 % of yield (63.5 mg) by isolation with preparative TLC (eluting solvent: ethyl acetate/petroether = 1/8 (v/v)).

Preparation of compounds 10a-10g and 10i: In a typical reaction, dihydropyran **1a** (82.1 mg, 0.36 mmol) was mixed with **9a** (40.8 mg, 0.30 mmol) and LiBr H₂O (9.4 mg, 30 mol %) in nitromethane (1.0 mL). The mixture was then stirred for 10 hours at 100 °C. Then, the mixture was cooled to room temperature. The desired product, **10a**, was obtained in 99 % of yield (80.8 mg) by isolation with preparative TLC (eluting solvent: ethyl acetate/petroether = 1/2 (v/v)). Synthesis of other compounds was performed with an analogous procedure.

Three-component reaction of isatoic anhydride, dihydropyran and amine: In a typical reaction, dihydropyran **1a** (82.1 mg, 0.36 mmol) was mixed with isatoic anhydride (48.8 mg, 0.30 mmol), *n*-butylamine (22.0 mg, 0.3 mmol) and LiBr H₂O (9.4 mg, 30 mol %) in nitromethane (1.0 mL). The mixture was then stirred for 10 hours at 100 °C. Then, the mixture was cooled to room temperature. The desired product, **10b**, was obtained in 88 % of yield (98.8 mg) by isolation with preparative TLC (eluting solvent: ethyl acetate/petroether = 1/2 (v/v)). Three-component reaction of isatoic anhydride, aniline and **1a** was performed with an analogous procedure.

DFT calculation about the molecular properties of 1a. The molecular simulation of **1a** was accomplished by an analytic techniques based on the hybrid density functional approach (DFT) with B3LYP and PBEPBE and ab initio theory with HF method, employing 6-311++g** and 6-31+g* basis sets. The calculation was implemented in GAUSSIAN 98 suit of the program.^[2] Comparison of all the theoretical approaches led us to select B3LYP/6-311++G** level of the theories for analyzing the results (**Table S2**). Vibrational frequencies of the molecules were calculated at the B3LYP/6-311++g** level for the geometry optimization. Additionally, natural bond orbital, NBO, was used for exploring the atomic electron population and the electronic destabilizing effects. After minimization of energy on the molecule **1a** by scrutinizing the geometric properties and electronic interactions, we can see some details of this compound: (i) In the skeleton of **1a**, there is a long conjugate system in one plate, O6-C5-C4-C7-O8-C9 caused to a twisted 6-membered ring; (ii) the angles of C12-O11-C3 and C7-O8-C9 are 115.24° and 115.58°, respectively, whereas the angle of C3-O6-C5 is 119.58°, which is quite unusual; (iii) special configuration of butoxy moiety and electronic interaction between the O11-lone pairs and σ^*_{C3-O6} causes the O11-C3 bond of the donor is shortened, 1.40 Å, and the C3-O6 bond of the acceptor is enlarged, 1.44 Å, $LpO11 \rightarrow \sigma^*_{C3-O6}$. So obviously C3-O6 is weaker than O11-C3, **Figure S3**. This phenomenon can be seen by study of atomic charge of molecule by using natural bond orbital calculation, NBO, **Figure S4**.

Table S2. The structure computation of molecule **1a**.

entry	calculation method	E(Hartree)
1	b3lyp6-311++g	-770.4195061
2	b3lyp/6-31+g(d)	-770.2495121
3	pbepbe/6-31+g(d)	-769.3027242
4	pbepbe/6-311++g(d)	-769.4656482
5	hf/6-311++g(d)	-765.6952077

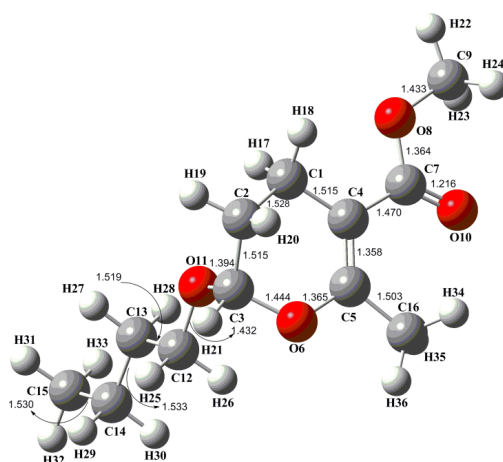


Figure S2. Bond lengths of **1a** (given in Å)

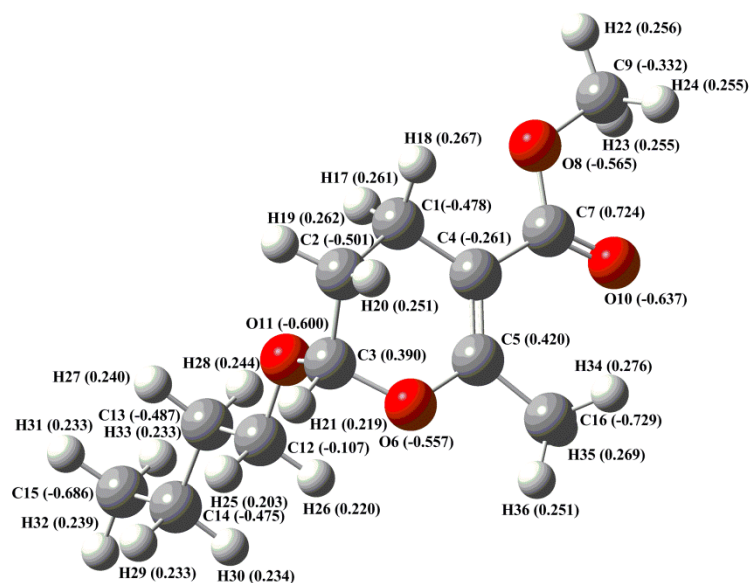


Figure S3. Atomic electron population (in a.u.) and numbering of **1a** by natural bond orbital calculation (NBO).

B3LYP/6-311++G*

A(CI)

HF = -770.4195061

C	-1.31270400	-0.30739400	-1.52117200
C	-0.41174600	-1.51320000	-1.78467400
C	0.65445700	-1.60629900	-0.71280000

C	-1.74326700	-0.26764400	-0.06937900
C	-1.06544900	-0.96611300	0.87824000
O	0.05051400	-1.69949300	0.59579500
C	-2.89346300	0.56167900	0.31883200
O	-3.45037100	1.16861600	-0.76854400
C	-4.57064700	2.02054500	-0.49990700
O	-3.33467900	0.73866500	1.43797500
O	1.48785200	-0.49271500	-0.80225600
C	2.65589200	-0.53938500	0.02553700
C	3.52096700	0.67042000	-0.28631900
C	4.80757300	0.70299700	0.54582300
C	5.68414700	1.91984200	0.24071600
C	-1.38675400	-1.07612600	2.33940300
H	-0.78799600	0.61659300	-1.78617400
H	-2.19090000	-0.35348300	-2.16728400
H	0.06880500	-1.44719100	-2.76338200
H	-0.99547500	-2.43902700	-1.76216500
H	1.24071300	-2.52995300	-0.77527700
H	-4.87078300	2.41983700	-1.46678200
H	-4.28794900	2.82927900	0.17539400
H	-5.38818000	1.45465400	-0.05095600
H	3.20185900	-1.47258200	-0.17662500
H	2.36051300	-0.54848800	1.08033100
H	3.76519000	0.66581600	-1.35471400
H	2.93523600	1.57864200	-0.10540300
H	5.38314000	-0.21367600	0.36657800
H	4.55406500	0.69594800	1.61309900
H	5.98416800	1.94094600	-0.81166000
H	6.59651000	1.91596000	0.84355800
H	5.15482300	2.85466000	0.44975200
H	-2.44884400	-1.23946200	2.51036200
H	-1.12936100	-0.15135400	2.86316300
H	-0.80610500	-1.89362800	2.76861800

B3LYP/6-31+G*

A(CI)

HF = -770.2495121

C	-1.31557300	-0.36418500	-1.51955600
C	-0.41806400	-1.58314500	-1.74782600
C	0.65107000	-1.64757400	-0.67300300
C	-1.73792800	-0.27431300	-0.06577700
C	-1.06278800	-0.95289000	0.90398300
O	0.04672800	-1.70609900	0.63811100
C	-2.87754300	0.58006700	0.30183300

O	-3.43613300	1.16208200	-0.79957300
C	-4.54509500	2.03675800	-0.54565400
O	-3.31120000	0.79592100	1.42554400
O	1.48321600	-0.53306300	-0.79403400
C	2.64991800	-0.54765300	0.03944600
C	3.50574400	0.66312200	-0.30656400
C	4.78938300	0.73585400	0.53279600
C	5.65550100	1.95410400	0.19083800
C	-1.38000800	-1.01818300	2.37133700
H	-0.78766500	0.55019800	-1.82028900
H	-2.20030400	-0.43306100	-2.15957200
H	0.06233800	-1.54606300	-2.73093200
H	-1.00679900	-2.50740900	-1.69449100
H	1.24050400	-2.57308300	-0.71014100
H	-4.85022400	2.40773800	-1.52535000
H	-4.24207400	2.86430100	0.10216700
H	-5.36442200	1.49188200	-0.06805000
H	3.20618800	-1.48300700	-0.13655500
H	2.35058100	-0.52651900	1.09549100
H	3.75788300	0.62638100	-1.37518000
H	2.90797600	1.57192300	-0.15452700
H	5.37705000	-0.18171300	0.38405100
H	4.52801300	0.76321400	1.60053300
H	5.96264700	1.93880300	-0.86260800
H	6.56455700	1.98076400	0.80329600
H	5.10887600	2.88981400	0.36358000
H	-2.44484900	-1.17987100	2.54795600
H	-1.12478700	-0.07349700	2.86558900
H	-0.79408500	-1.82329700	2.82352600

pbepbe/6-311++G*

A(CI)

HF = -769.4656482

C	-1.31678300	-0.34148100	-1.51744500
C	-0.42052900	-1.55661800	-1.75990300
C	0.65694000	-1.62221800	-0.69497200
C	-1.74191000	-0.26958400	-0.06587900
C	-1.05953600	-0.96026500	0.89998400
O	0.05938000	-1.70524700	0.63190500
C	-2.88626300	0.57168000	0.31298100
O	-3.45196900	1.15409900	-0.80183800
C	-4.56945900	2.01545600	-0.52644300
O	-3.32536700	0.78557200	1.43832700
O	1.47893800	-0.49593200	-0.80928300

C	2.65349500	-0.53566600	0.02206100
C	3.51744500	0.67354700	-0.29954200
C	4.80535400	0.71203700	0.53225200
C	5.67972300	1.92921800	0.21971800
C	-1.38328100	-1.04281700	2.36138000
H	-0.78641900	0.58264100	-1.80680600
H	-2.20539100	-0.39597500	-2.16364400
H	0.05431100	-1.51752600	-2.75210800
H	-1.00807700	-2.48841100	-1.70640700
H	1.25762000	-2.54977600	-0.73984500
H	-4.88791900	2.40051900	-1.50264500
H	-4.27265300	2.84195900	0.13562000
H	-5.38673600	1.45624500	-0.04794500
H	3.20421600	-1.47837200	-0.17524000
H	2.35651100	-0.53790500	1.08625100
H	3.76332200	0.66263900	-1.37625200
H	2.92738500	1.59008100	-0.12306900
H	5.38522500	-0.21258900	0.35636300
H	4.54999200	0.70844900	1.60771800
H	5.98181600	1.94495500	-0.84038200
H	6.59883800	1.93300000	0.82635600
H	5.14431400	2.87104900	0.42330400
H	-2.45994300	-1.15235200	2.53625600
H	-1.08023500	-0.11937500	2.88099200
H	-0.83520800	-1.88692300	2.80343300

pbepbe/6-31+G*

A(CI)

HF=-769.3027242

C	-1.30920800	-0.29848500	-1.53224300
C	-0.41619800	-1.51528500	-1.79721700
C	0.66002000	-1.60714800	-0.72867400
C	-1.74529500	-0.26495200	-0.08041500
C	-1.06303500	-0.97565600	0.87694500
O	0.06083900	-1.71216400	0.59655100
C	-2.90104200	0.55391000	0.31518900
O	-3.44512700	1.19726900	-0.77772200
C	-4.57383800	2.03943300	-0.47692400
O	-3.36711500	0.70181900	1.44842400
O	1.48780400	-0.47971200	-0.82158100
C	2.65248400	-0.52748200	0.02554700
C	3.53376700	0.67528700	-0.29024500
C	4.80908400	0.70500300	0.56659200
C	5.70611000	1.91119200	0.25850300

C	-1.39555200	-1.08980400	2.33798300
H	-0.76684300	0.63033300	-1.79294100
H	-2.19470300	-0.33294700	-2.18858400
H	0.06357700	-1.45612200	-2.78868500
H	-1.01061000	-2.44639600	-1.76235700
H	1.25899600	-2.53746500	-0.79036100
H	-4.87313000	2.47669900	-1.44019500
H	-4.29110300	2.82961800	0.23820300
H	-5.39840000	1.44809100	-0.04531100
H	3.19957000	-1.47720900	-0.16205100
H	2.34167800	-0.52022100	1.08830600
H	3.80027800	0.65471000	-1.36437100
H	2.94811900	1.59986000	-0.12609100
H	5.38187900	-0.22987000	0.40696700
H	4.53198900	0.71646200	1.63911700
H	6.02699300	1.91053800	-0.79909000
H	6.61531500	1.90730300	0.88483500
H	5.17465400	2.86211800	0.44447800
H	-2.44893000	-1.37016000	2.49277500
H	-1.26202700	-0.12095800	2.84950100
H	-0.73230000	-1.83816000	2.80022800

hf/6-311++G*

A(CI)

HF=-765.6952077

C	-1.32094000	-0.50603800	-1.48828500
C	-0.42801700	-1.73284600	-1.62647900
C	0.63112600	-1.72055200	-0.55029800
C	-1.70679900	-0.29293400	-0.03820100
C	-1.03841300	-0.89924200	0.95256100
O	0.03131200	-1.68417600	0.72484600
C	-2.81162300	0.63593800	0.27438100
O	-3.39375400	1.09017600	-0.83020400
C	-4.45353100	2.01023200	-0.67399900
O	-3.16907100	0.98427500	1.35622300
O	1.45244900	-0.63504800	-0.74186700
C	2.60167200	-0.56725800	0.06571300
C	3.41781500	0.63957900	-0.35588700
C	4.69678100	0.79819100	0.46553300
C	5.52104700	2.01323000	0.04681500
C	-1.31569400	-0.84918100	2.42819700
H	-0.81265700	0.37098000	-1.87468400
H	-2.21044900	-0.63618900	-2.08985800
H	0.04855900	-1.76754900	-2.59863200

H	-1.01344700	-2.63998600	-1.50997700
H	1.21185100	-2.63532700	-0.53609400
H	-4.77722600	2.25840800	-1.67283200
H	-4.11613800	2.89842800	-0.15947300
H	-5.26666900	1.56625100	-0.11783400
H	3.18063100	-1.48230600	-0.05344900
H	2.31643000	-0.49282100	1.10994800
H	3.66126100	0.54644900	-1.41093100
H	2.79991800	1.52800200	-0.25792200
H	5.30558700	-0.09875000	0.37024100
H	4.44451100	0.88159300	1.52062600
H	5.82271100	1.94542600	-0.99429000
H	6.42229100	2.10271700	0.64471800
H	4.95557800	2.93279200	0.16496000
H	-2.36925700	-0.81889900	2.64519000
H	-0.86928200	0.04074200	2.85896500
H	-0.86224700	-1.71649400	2.88902800

hf/6-31+G*

A(CI)

HF=-765.5373322

C	-1.31737200	-0.50006600	-1.49616800
C	-0.42583400	-1.72897000	-1.63812800
C	0.63230400	-1.72352700	-0.55946500
C	-1.70649700	-0.29457300	-0.04558300
C	-1.03996200	-0.90574900	0.94642400
O	0.02967100	-1.69192700	0.71657300
C	-2.81339100	0.62843600	0.27093900
O	-3.37915300	1.11472600	-0.82977500
C	-4.44114800	2.03413000	-0.66038000
O	-3.18823500	0.94879400	1.36256000
O	1.45497800	-0.63601800	-0.74505900
C	2.59881900	-0.56513900	0.07381100
C	3.42117800	0.63727300	-0.35339000
C	4.69255900	0.80344300	0.48090200
C	5.52152600	2.01481600	0.05523500
C	-1.32373700	-0.85846400	2.42267100
H	-0.80543700	0.37761000	-1.87703600
H	-2.20643300	-0.62794100	-2.10033200
H	0.05343700	-1.75756000	-2.60977900
H	-1.01392800	-2.63544700	-1.52666900
H	1.21277900	-2.63811500	-0.54718400
H	-4.75018500	2.30895400	-1.65724600
H	-4.10581400	2.90589300	-0.11706200

H	-5.26037100	1.57425700	-0.12640800
H	3.17609600	-1.48232700	-0.03432300
H	2.30288700	-0.47854200	1.11388700
H	3.67699100	0.53102700	-1.40445700
H	2.80333900	1.52740300	-0.26970900
H	5.30214000	-0.09462700	0.40023500
H	4.42846300	0.90084600	1.53207300
H	5.83198100	1.93241200	-0.98267500
H	6.41684000	2.11031500	0.66200300
H	4.95237200	2.93452400	0.15744700
H	-2.37948100	-0.91696100	2.63238800
H	-0.96277200	0.07376600	2.84340900
H	-0.80166200	-1.67973900	2.89583400

Spectroscopic data of products

Methyl 2-butoxy-6-cyclopropyl-3,4-dihydro-2H-pyran-5-carboxylate (**1b**): Colorless liquid; ^1H NMR (400 MHz, CDCl_3 , 25 °C, TMS): 0.72-0.80 (m, 2H), 0.87-0.98 (m, 5H), 1.31-1.41 (m, 2H), 1.52-1.59 (m, 2H), 1.71-1.88 (m, 2H), 2.30-2.46 (m, 2H), 3.11-3.18 (m, 1H), 3.45-3.51 (m, 1H), 3.68-3.71 (m, 1H), 3.73 (s, 3H), 4.95-4.97 (m, 1H); ^{13}C NMR (100Mz, CDCl_3): 6.32, 6.82, 12.2, 13.8, 18.5, 19.2, 26.2, 31.6, 51.0, 68.4, 98.0, 101.3, 164.2, 169.2; IR (cm^{-1}): 3096, 3012, 2957, 2871, 1705, 1611, 1435, 1374, 1271, 1130, 1075, 1053, 979, 881, 767, 579, 500; HRMS m/z (ESI) calcd for $\text{C}_{14}\text{H}_{22}\text{NaO}_4$ $[\text{M} + \text{Na}]^+$ 277.1416 found 277.1409.

Methyl 2-butoxy-6-ethyl-3,4-dihydro-2H-pyran-5-carboxylate (**1c**): Colorless liquid; ^1H NMR (400 MHz, CDCl_3 , 25 °C, TMS): 0.89 (t, $J = 7.6$ Hz, 3H), 1.09 (t, $J = 7.6$ Hz, 3H), 1.29-1.38 (m, 2H), 1.51-1.58 (m, 2H), 1.67-1.75 (m, 1H), 1.80-1.87 (m, 1H), 2.24-2.39 (m, 2H), 2.51-2.60 (m, 1H), 2.70-2.79 (m, 1H), 3.49-3.54 (m, 1H), 3.67 (s, 3H), 3.76-3.81 (m, 1H), 5.01-5.02 (m, 1H); ^{13}C NMR (100Mz, CDCl_3): 12.0, 13.7, 17.7, 19.2, 26.0, 26.3, 31.6, 50.8, 68.2, 97.6, 101.0, 166.4, 168.4; IR (cm^{-1}): 2959, 2939, 2874, 1709, 1625, 1435, 1343, 1271, 1188, 1120, 1042, 977, 877, 770, 589; HRMS m/z (ESI) calcd for $\text{C}_{13}\text{H}_{22}\text{NaO}_4$ $[\text{M} + \text{Na}]^+$ 265.1416 found 265.1410.

Ethyl 2-butoxy-6-propyl-3,4-dihydro-2H-pyran-5-carboxylate (**1d**): Colorless liquid; ^1H NMR (400 MHz, CDCl_3 , 25 °C, TMS): 0.90-0.97 (m, 6H), 1.28 (t, $J = 7.2$ Hz, 3H), 1.34-1.39 (m, 2H), 1.53-1.66 (m, 6H), 1.82-1.89 (m, 1H), 2.32-2.35 (m, 1H), 2.54-2.60 (m, 1H), 2.68-2.75 (m, 1H), 4.11-4.22 (m, 4H), 5.03 (t, $J = 3.2$ Hz, 1H); ^{13}C NMR (100Mz, CDCl_3): 13.6, 17.7, 19.1, 21.0, 25.9, 31.5, 34.6, 44.6, 49.0, 59.3, 68.1, 97.5, 101.7, 164.7, 167.9; IR (cm^{-1}): 2961, 2935, 2873, 1744, 1708, 1624, 1461, 1369, 1266, 1091, 1046, 950, 851, 771, 496; HRMS m/z (ESI) calcd for $\text{C}_{15}\text{H}_{26}\text{NaO}_4$ $[\text{M} + \text{Na}]^+$ 293.1729 found 293.1722.

Cyclohexyl 2-butoxy-6-methyl-3,4-dihydro-2H-pyran-5-carboxylate (**1e**): Colorless liquid; ^1H NMR (400 MHz, CDCl_3 , 25 °C, TMS): 0.92 (t, $J = 7.6$ Hz, 3H), 1.26-1.61 (m, 10H), 1.71-1.84 (m, 6H), 2.24 (s, 3H), 2.29-2.38 (m, 2H), 3.51-3.56 (m, 1H), 3.77-3.83 (m, 1H), 4.81-4.85 (m, 1H), 5.02 (s, 1H); ^{13}C NMR (100Mz, CDCl_3): 13.7, 17.9, 19.1, 19.8, 23.5, 25.5, 26.1, 31.6, 31.6, 68.3, 71.3, 97.9, 102.4, 161.1, 167.7; IR (cm^{-1}): 2935, 2860, 1703, 1629, 1451, 1378, 1270, 1119, 1061, 1011, 863, 769, 602; HRMS m/z (ESI) calcd for $\text{C}_{17}\text{H}_{28}\text{NaO}_4$ $[\text{M} + \text{Na}]^+$ 319.1885 found 319.1879.

Allyl 2-butoxy-6-methyl-3,4-dihydro-2H-pyran-5-carboxylate (**1f**): Colorless liquid; ^1H NMR (400 MHz, CDCl_3 , 25 °C, TMS): 0.91 (t, $J = 7.2$ Hz, 3H), 1.33-1.39 (m, 2H), 1.53-1.60 (m, 2H), 1.71-1.79 (m, 1H), 1.83-1.90 (m, 1H), 2.25 (s, 3H), 2.31-2.44 (m, 2H), 3.51-3.56 (m, 1H), 3.76-3.82 (m, 1H), 4.61 (d, $J = 5.2$ Hz, 2H), 5.03-5.04 (m, 1H), 5.18-5.21 (m, 1H), 5.29-5.33 (m, 1H), 5.90-6.00 (m, 1H); ^{13}C NMR (100Mz, CDCl_3): 13.5, 17.5, 18.9, 19.7, 25.9, 31.4, 64.1, 68.1, 97.7, 101.6, 116.9, 132.8, 161.8, 167.5; IR (cm^{-1}): 2959, 2935, 2872, 1709, 1628, 1439, 1379, 1270, 1119, 1061, 1011, 862, 768, 601; HRMS m/z (ESI) calcd for $\text{C}_{14}\text{H}_{22}\text{NaO}_4$ $[\text{M} + \text{Na}]^+$ 277.1416 found 277.1411.

Methyl 2-acetyl-5-oxopentanoate (**5a**):^[3] Colorless liquid; ^1H NMR (400 MHz, CDCl_3 , 25 °C, TMS): $\delta = 2.13$ -2.16 (m, 2H), 2.25 (s, 3H), 2.52-2.55 (m, 2H), 3.52-3.55 (m, 1H), 3.74 (s, 3H), 9.74 ppm (t, $J = 4.8$ Hz, 1H); ^{13}C NMR (100Mz, CDCl_3): $\delta = 20.1$, 29.1, 41.0, 52.5, 57.9, 169.7, 200.8, 202.3 ppm.

Methyl 2-oxocyclohex-3-enecarboxylate (**6a**):^[4] Colorless liquid; ^1H NMR (400 MHz, CDCl_3 , 25 °C, TMS): $\delta = 2.22$ -2.26 (m, 1H), 2.34-2.42 (m, 2H), 2.49-2.54 (m, 1H), 3.44 (q, $J = 4.8$ Hz, 1H), 3.77 (s, 3H), 6.08 (d, $J = 10.0$ Hz, 1H), 7.02-7.07 ppm (m, 1H); ^{13}C NMR (100Mz, CDCl_3): $\delta = 25.5$, 53.2, 61.6, 72.3, 129.0, 150.8, 170.4, 193.9 ppm.

Methyl 2-acetyl-5-butoxy-5-(p-tolylthio)pentanoate (**II-a**): Colorless liquid; ^1H NMR (400 MHz, CDCl_3 , 25 °C, TMS): $\delta = 0.93$ (t, $J = 7.6$ Hz, 3H), 1.35-1.44 (m, 2H), 1.55-1.62 (m, 2H), 1.69-1.75 (m, 2H), 1.97-2.02 (m, 2H), 2.10 (d, $J = 3.2$ Hz, 3H), 2.34 (s, 3H), 3.36-3.44 (m, 2H), 3.71 (s, 3H), 3.92-3.97 (m, 1H), 4.59 (q, $J = 6.4$ Hz, 1H), 7.11 (d, $J = 8.0$ Hz, 2H), 7.35 ppm (d, $J = 8.0$ Hz, 2H); ^{13}C NMR (100Mz, CDCl_3): 13.9, 19.5, 21.1, 24.9 ($J = 5.2$ Hz), 28.9 ($J = 2.7$ Hz), 31.5 ($J = 1.9$ Hz), 33.7 ($J = 13.4$ Hz), 52.4, 59.0 ($J = 14.2$ Hz), 60.4, 68.3 ($J = 9.7$ Hz), 88.8, 129.6, 134.2 ($J = 9.3$ Hz), 137.8, 170.0 ($J = 2.2$ Hz), 202.8 ppm ($J = 6.8$ Hz); IR (cm^{-1}): 2957, 2932, 2869, 1744, 1718, 1492, 1438, 1359, 1246, 1153, 1103, 1084, 811, 645, 607, 496; HRMS m/z (ESI) calcd for $\text{C}_{19}\text{H}_{28}\text{NaO}_4\text{S}$ $[\text{M} + \text{Na}]^+$ 375.1606 found 375.1600.

Methyl 2-methyl-6-(nitromethyl)-1-(p-tolyl)-1,4,5,6-tetrahydropyridine-3-carboxylate (**3a**): yellow liquid; ^1H NMR (400 MHz, CDCl_3 , 25 °C, TMS): $\delta = 1.88$ -1.94 (m, 2 H), 2.09 (t, $J = 1.2$ Hz, 3 H), 2.21-2.29 (m, 1 H), 2.34 (s, 3 H), 2.65-2.71 (m, 1 H), 3.70 (s, 3 H), 4.32-4.36 (m, 1 H), 4.38-4.42 (m, 1 H), 4.58-4.63 (m, 1 H), 6.90 (d, $J = 8.0$ Hz, 2 H), 7.15 ppm (d, $J = 8.0$ Hz, 2 H); ^{13}C NMR (100Mz, CDCl_3): $\delta = 19.7$, 20.3, 20.8, 22.5, 50.7, 58.7, 75.5, 100.7, 126.8, 130.1, 136.5, 142.9, 151.3, 168.7 ppm; IR (cm^{-1}): 3027, 2947, 2862, 1692, 1554, 1511, 1382, 1292, 1238, 1181, 1072, 823, 741, 509; HRMS m/z (ESI) calcd for $\text{C}_{16}\text{H}_{20}\text{N}_2\text{NaO}_4$ $[\text{M} + \text{Na}]^+$ 327.1321 found 327.1316.

Methyl 2-methyl-6-(nitromethyl)-1-phenyl-1,4,5,6-tetrahydropyridine-3-carboxylate (**3b**): yellow liquid; ^1H NMR (400 MHz, CDCl_3 , 25 °C, TMS): $\delta = 1.87$ -1.90 (m, 2 H), 2.10 (s, 3 H), 2.21-2.30 (m, 1 H), 2.64-2.70 (m, 1 H), 3.70 (s, 3 H), 4.37-4.43 (m, 2 H), 4.60-4.63 (m, 1 H), 7.01 (d, $J = 8.0$ Hz, 2 H), 7.34 (d, $J = 7.2$ Hz, 1 H), 7.32-7.36 ppm (m, 2 H); ^{13}C NMR (100Mz, CDCl_3): $\delta = 19.7$, 20.3, 20.8, 22.4, 50.7, 58.7, 75.5, 100.7, 126.8, 130.1, 136.5, 142.8, 151.3, 168.7 ppm; IR (cm^{-1}): 3469, 3369, 3029, 2947, 2860, 1691, 1552, 1493, 1432, 1382, 1292, 1238, 1181, 1070, 957, 920, 767, 701, 649, 497, 419; HRMS m/z (ESI) calcd for $\text{C}_{15}\text{H}_{18}\text{N}_2\text{NaO}_4$ $[\text{M} + \text{Na}]^+$ 313.1164 found 313.1160.

Methyl 1-(4-methoxyphenyl)-2-methyl-6-(nitromethyl)-1,4,5,6-tetrahydropyridine-3-carboxylate (**3c**): yellow liquid; ^1H NMR (400 MHz, CDCl_3 , 25 °C, TMS): δ = 1.90-1.92 (m, 2H), 2.08 (s, 3H), 2.21-2.28 (m, 1H), 2.66-2.71 (m, 1H), 3.70 (s, 3H), 3.80 (s, 3H), 4.30-4.32 (m, 1H), 4.40-4.42 (m, 1H), 4.57-4.60 (m, 1H), 6.87 (d, J = 8.8 Hz, 2H), 6.95 ppm (d, J = 8.8 Hz, 2H); ^{13}C NMR (100Mz, CDCl_3): δ = 19.7, 20.0, 22.6, 50.7, 55.4, 58.7, 75.6, 100.0, 114.7, 128.3, 138.2, 151.6, 158.3, 168.7 ppm; IR (cm^{-1}): 2949, 2860, 2841, 1687, 1557, 1382, 1291, 1239, 1179, 1108, 836, 767, 647, 494; HRMS m/z (ESI) calcd for $\text{C}_{16}\text{H}_{20}\text{N}_2\text{NaO}_5$ [$\text{M} + \text{Na}$] $^+$ 343.1270 found 343.1266.

Methyl 1-(4-fluorophenyl)-2-methyl-6-(nitromethyl)-1,4,5,6-tetrahydropyridine-3-carboxylate (**3d**): yellow liquid; ^1H NMR (400 MHz, CDCl_3 , 25 °C, TMS): δ = 1.88-1.92 (m, 2H), 2.07 (s, 3H), 2.23-2.27 (m, 1H), 2.66-2.70 (m, 1H), 3.71 (s, 3H), 4.31-4.35 (m, 1H), 4.37-4.42 (m, 1H), 4.60-4.63 (m, 1H), 6.98-7.07 ppm (m, 4H); ^{13}C NMR (100Mz, CDCl_3): δ = 19.8, 20.3, 22.3, 50.8, 58.8, 75.6, 102.1, 116.2, 116.4, 128.5 (d, J = 8.4 Hz), 141.7 (d, J = 3.1 Hz), 150.6, 168.5 ppm; IR (cm^{-1}): 3112, 2948, 2862, 1691, 1556, 1506, 1382, 1292, 1210, 1108, 841, 769, 511; HRMS m/z (ESI) calcd for $\text{C}_{15}\text{H}_{17}\text{FN}_2\text{NaO}_4$ [$\text{M} + \text{Na}$] $^+$ 331.1070 found 331.1061.

Methyl 1-(4-chlorophenyl)-2-methyl-6-(nitromethyl)-1,4,5,6-tetrahydropyridine-3-carboxylate (**3e**): yellow liquid; ^1H NMR (400 MHz, CDCl_3 , 25 °C, TMS): δ = 1.85-1.88 (m, 2 H), 2.07 (s, 3 H), 2.17-2.26 (m, 1 H), 2.62-2.67 (m, 1 H), 3.70 (s, 3 H), 4.32-4.40 (m, 2 H), 4.58-4.63 (m, 1 H), 6.93 (d, J = 8.8 Hz, 2 H), 7.29 ppm (d, J = 8.8 Hz, 2 H); ^{13}C NMR (100Mz, CDCl_3): δ = 19.8, 20.5, 22.2, 50.9, 58.7, 75.6, 103.6, 127.8, 129.6, 131.8, 144.3, 150.0, 168.4 ppm; IR (cm^{-1}): 2947, 2860, 1694, 1553, 1432, 1382, 1287, 1239, 1210, 1107, 1070, 1013, 834, 735, 640, 538, 500; HRMS m/z (ESI) calcd for $\text{C}_{15}\text{H}_{17}^{35}\text{ClN}_2\text{NaO}_4$ [$\text{M} + \text{Na}$] $^+$ 347.0775 found 347.0773.

Methyl 1-(4-bromophenyl)-2-methyl-6-(nitromethyl)-1,4,5,6-tetrahydropyridine-3-carboxylate (**3f**): yellow liquid; ^1H NMR (400 MHz, CDCl_3 , 25 °C, TMS): δ = 1.87-1.90 (m, 2H), 2.09 (s, 3H), 2.16-2.28 (m, 1H), 2.63-2.68 (m, 1H), 3.72 (s, 3H), 4.34-4.40 (m, 2H), 4.60-4.65 (m, 1H), 6.89 (d, J = 8.8 Hz, 2H), 7.47 ppm (d, J = 8.8 Hz, 2H); ^{13}C NMR (100Mz, CDCl_3): δ = 19.9, 20.6, 22.2, 50.9, 58.7, 75.6, 103.9, 119.7, 128.1, 132.6, 144.8, 149.9, 168.4 ppm; IR (cm^{-1}): 2947, 2859, 1694, 1556, 1487, 1287, 1239, 1182, 1069, 830, 740, 497; HRMS m/z (ESI) calcd for $\text{C}_{15}\text{H}_{17}^{79}\text{BrN}_2\text{NaO}_4$ [$\text{M} + \text{Na}$] $^+$ 391.0269 found 391.0268.

Methyl 2-methyl-6-(nitromethyl)-1-(4-(trifluoromethoxy)phenyl)-1,4,5,6-tetrahydropyridine-3-carboxylate (**3g**): yellow liquid; ^1H NMR (400 MHz, CDCl_3 , 25 °C, TMS): δ = 1.87-1.90 (m, 2 H), 2.10 (s, 3 H), 2.21-2.29 (m, 1 H), 2.64-2.68 (m, 1 H), 3.72 (s, 3 H), 4.37-4.43 (m, 2 H), 4.62-4.67 (m, 1 H), 7.04 (d, J = 8.8 Hz, 2 H), 7.20 ppm (d, J = 8.8 Hz, 2 H); ^{13}C NMR (100Mz, CDCl_3): δ = 19.9, 20.6, 22.1, 50.9, 58.8, 75.6, 104.1, 119.0, 122.0, 127.7, 144.3, 146.9 (d, J = 1.8 Hz), 149.9, 168.4 ppm; IR (cm^{-1}): 3368, 2949, 2862, 1696, 1581, 1554, 1505, 1433, 1383, 1242, 1203, 1108, 1070, 1017, 921, 736, 676, 560, 497; HRMS m/z (ESI) calcd for $\text{C}_{16}\text{H}_{17}\text{F}_3\text{N}_2\text{NaO}_5$ [$\text{M} + \text{Na}$] $^+$ 397.0987 found 397.0984.

Methyl 1-(4-(ethoxycarbonyl)phenyl)-2-methyl-6-(nitromethyl)-1,4,5,6-tetrahydropyridine-3-carboxylate (**3h**): yellow liquid; ^1H NMR (400 MHz, CDCl_3 , 25 °C, TMS): δ = 1.39 (t, J = 7.2 Hz, 3H), 1.87-1.89 (m, 2H), 2.13 (s, 3H), 2.23-2.30 (m, 1H), 2.63-2.68 (m, 1H), 3.74 (s, 3H), 4.37 (q, J = 7.2 Hz, 2H), 4.41-4.49 (m, 2H), 4.65-4.70 (m, 1H), 7.04 (d, J = 8.8 Hz, 2H), 8.02 ppm (d, J = 8.8 Hz, 2H); ^{13}C NMR (100Mz, CDCl_3): δ = 14.2, 20.0, 21.1, 22.3, 51.0, 60.2, 61.0, 75.5, 106.1, 113.7, 125.3, 131.5, 149.4, 149.7, 165.8, 168.3 ppm; IR (cm^{-1}): 3475, 3372, 2982, 2950, 1705,

1603, 1553, 1437, 1369, 1279, 1176, 1108, 1020, 850, 772, 704, 614, 497; HRMS m/z (ESI) calcd for $C_{18}H_{22}N_2NaO_6$ $[M + Na]^+$ 385.1376 found 385.1375.

Methyl 1-(4-acetylphenyl)-2-methyl-6-(nitromethyl)-1,4,5,6-tetrahydropyridine-3-carboxylate (**3i**): yellow liquid; 1H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 1.88-1.90 (m, 2 H), 2.15 (s, 3 H), 2.21-2.28 (m, 1 H), 2.59-2.68 (m, 1 H), 3.75 (s, 3 H), 4.41-4.45 (m, 1 H), 4.49-4.51 (m, 1 H), 4.67-4.72 (m, 1 H), 7.06 (d, J = 8.4 Hz, 2 H), 7.94 ppm (d, J = 8.4 Hz, 2 H); ^{13}C NMR (100Mz, $CDCl_3$): δ = 18.2, 19.6, 21.9, 26.03, 37.0, 58.2, 75.1, 106.3, 124.8, 129.3, 133.5, 148.7, 149.5, 167.8, 196.4 ppm; IR (cm^{-1}): 3463, 3370, 2949, 2860, 1679, 1594, 1553, 1432, 1360, 1277, 1182, 1142, 958, 840, 734, 597, 480, 427; HRMS m/z (ESI) calcd for $C_{17}H_{20}N_2NaO_5$ $[M + Na]^+$ 355.1270 found 355.1264.

Methyl 2-methyl-6-(nitromethyl)-1-(4-nitrophenyl)-1,4,5,6-tetrahydropyridine-3-carboxylate (**3j**): yellow liquid; 1H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 1.86-1.91 (m, 2H), 2.17 (s, 3H), 2.26-2.29 (m, 1H), 2.66-2.68 (m, 1H), 3.77 (s, 3H), 4.42-4.46 (m, 1H), 4.57-4.60 (m, 1H), 4.70-4.73 (m, 1H), 7.00 (d, J = 8.8 Hz, 2H), 8.20 ppm (d, J = 8.8 Hz, 2H); ^{13}C NMR (100Mz, $CDCl_3$): δ = 20.3, 21.5, 22.4, 51.4, 58.7, 75.4, 109.9, 124.7, 125.1, 144.2, 147.8, 151.5, 167.9 ppm; IR (cm^{-1}): 3082, 2950, 2925, 2852, 1707, 1591, 1553, 1512, 1434, 1341, 1241, 1208, 1185, 1066, 856, 751, 700, 566, 500, 420; HRMS m/z (ESI) calcd for $C_{15}H_{17}N_3NaO_6$ $[M + Na]^+$ 358.1015 found 358.1013.

Methyl 1-(3-chlorophenyl)-2-methyl-6-(nitromethyl)-1,4,5,6-tetrahydropyridine-3-carboxylate (**3k**): yellow liquid; 1H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 1.87-1.89 (m, 2 H), 2.11 (s, 3 H), 2.19-2.26 (m, 1 H), 2.63-2.68 (m, 1 H), 3.73 (s, 3 H), 4.38-4.43 (m, 2 H), 4.61-4.65 (m, 1 H), 6.91-6.93 (m, 1 H), 7.02 (s, 1 H), 7.19-7.21 (m, 1 H), 7.27-7.31 ppm (m, 1 H); ^{13}C NMR (100Mz, $CDCl_3$): δ = 19.8, 20.7, 22.0, 50.9, 58.6, 75.5, 104.5, 124.5, 126.2, 126.4, 130.4, 134.8, 146.9, 149.7, 168.3 ppm; IR (cm^{-1}): 3471, 3371, 2947, 2253, 1696, 1555, 1476, 1431, 1383, 1290, 1211, 1105, 1072, 964, 772, 735, 698, 504, 449; HRMS m/z (ESI) calcd for $C_{15}H_{17}^{35}ClN_2NaO_4$ $[M + Na]^+$ 347.0775 found 347.0770.

Methyl 1-(3-cyanophenyl)-2-methyl-6-(nitromethyl)-1,4,5,6-tetrahydropyridine-3-carboxylate (**3l**): yellow liquid; 1H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 1.85-1.90 (m, 2 H), 2.10 (s, 3 H), 2.19-2.29 (m, 1 H), 2.64-2.69 (m, 1 H), 3.75 (s, 3 H), 4.37-4.42 (m, 2 H), 4.64-4.71 (m, 1 H), 7.00-7.02 (m, 1 H), 7.26-7.28 (m, 2 H), 7.48 ppm (s, 1 H); ^{13}C NMR (100Mz, $CDCl_3$): δ = 20.1, 20.9, 22.0, 51.2, 58.9, 75.6, 107.1, 113.7, 117.4, 119.1, 121.9, 129.2, 130.4, 130.6, 146.8, 168.1 ppm; IR (cm^{-1}): 3472, 3374, 3065, 2949, 2229, 1693, 1552, 1484, 1431, 1382, 1275, 1185, 1108, 969, 866, 789, 733, 686, 590, 475, 427; HRMS m/z (ESI) calcd for $C_{16}H_{17}N_3NaO_4$ $[M + Na]^+$ 338.1117 found 338.1114.

Methyl 1-(2-methoxyphenyl)-2-methyl-6-(nitromethyl)-1,4,5,6-tetrahydropyridine-3-carboxylate (**3m**): yellow liquid; 1H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 1.88-1.91 (m, 2 H), 1.99-2.03 (m, 3 H), 2.18-2.35 (m, 1 H), 2.64-2.72 (m, 1 H), 3.65-3.66 (m, 3 H), 3.78-3.79 (m, 3 H), 4.07-4.21 (m, 1 H), 4.38-4.68 (m, 2 H), 6.90-7.00 (m, 3 H), 7.22-7.29 ppm (m, 1 H); ^{13}C NMR (100Mz, $CDCl_3$): δ = 18.7, 19.2, 22.7, 50.5, 55.1, 55.4, 57.1, 57.5, 75.0, 75.5, 95.6, 97.9, 111.6, 111.9, 120.5, 121.2, 128.5, 128.8, 129.1, 130.6, 133.4, 152.4, 155.5, 155.7, 168.8, 169.0 ppm; IR (cm^{-1}): 3064, 2946, 2842, 2250, 2043, 1686, 1551, 1498, 1434, 1381, 1255, 1177, 1025, 915, 819, 758, 648, 519; HRMS m/z (ESI) calcd for $C_{16}H_{20}N_2NaO_5$ $[M + Na]^+$ 343.1270 found 343.1269.

Methyl 1-(3,4-difluorophenyl)-2-methyl-6-(nitromethyl)-1,4,5,6-tetrahydropyridine-3-carboxylate (**3n**): yellow liquid; $^1\text{H NMR}$ (400 MHz, CDCl_3 , 25 °C, TMS): δ = 1.89-1.91 (m, 2H), 2.09 (s, 3H), 2.21-2.26 (m, 1H), 2.64-2.69 (m, 1H), 3.72 (s, 3H), 4.34-4.41 (m, 2H), 4.61-4.66 (m, 1H), 6.76-6.80 (m, 1H), 6.86-6.92 (m, 1H), 7.11-7.18 ppm (m, 1H); $^{13}\text{C NMR}$ (100Mz, CDCl_3): δ = 19.9, 20.5, 22.0, 50.9, 58.8, 75.6, 104.5, 115.8 (d, J = 17.7 Hz), 117.7 (d, J = 18.1 Hz), 122.7 (dd, J_a = 3.4 Hz, J_b = 6.1 Hz) 142.3 (q, J = 3.6 Hz), 149.5, 168.3 ppm; IR (cm^{-1}): 3058, 2950, 2862, 1696, 1589, 1514, 1294, 1211, 1110, 1069, 971, 772, 460, 440; HRMS m/z (ESI) calcd for $\text{C}_{15}\text{H}_{16}\text{F}_2\text{N}_2\text{NaO}_4$ [$\text{M} + \text{Na}$] $^+$ 349.0976 found 349.0971.

Methyl 1-(benzo[d][1,3]dioxol-5-yl)-2-methyl-6-(nitromethyl)-1,4,5,6-tetrahydropyridine-3-carboxylate (**3o**): yellow liquid; $^1\text{H NMR}$ (400 MHz, CDCl_3 , 25 °C, TMS): δ = 1.89-1.91 (m, 2H), 2.10 (s, 3H), 2.22-2.26 (m, 1H), 2.65-2.70 (m, 1H), 3.70 (s, 3H), 4.30-4.40 (m, 2H), 4.57-4.62 (m, 1H), 6.00 (s, 2H), 6.47-6.50 (m, 1H), 6.53 (d, J = 2.0 Hz, 1H), 6.75-6.77 ppm (m, 1H); $^{13}\text{C NMR}$ (100Mz, CDCl_3): δ = 19.7, 20.2, 22.5, 50.8, 50.9, 58.8, 75.6, 100.6, 101.7, 108.4, 120.6, 139.5, 146.4, 148.4, 151.4, 168.8 ppm; IR (cm^{-1}): 3058, 2950, 2862, 1696, 1589, 1514, 1294, 1211, 1110, 1069, 971, 772, 460, 440; HRMS m/z (ESI) calcd for $\text{C}_{16}\text{H}_{18}\text{N}_2\text{NaO}_6$ [$\text{M} + \text{Na}$] $^+$ 357.1063 found 357.1059.

Methyl 1-(dibenzo[b,d]furan-3-yl)-2-methyl-6-(nitromethyl)-1,4,5,6-tetrahydropyridine-3-carboxylate (**3p**): yellow liquid; $^1\text{H NMR}$ (400 MHz, CDCl_3 , 25 °C, TMS): δ = 1.86-1.94 (m, 2 H), 2.13 (s, 3 H), 2.20-2.29 (m, 1 H), 2.65-2.70 (m, 1 H), 3.71 (s, 3 H), 4.38-4.46 (m, 2 H), 4.63-4.68 (m, 1 H), 6.97 (dd, J_a = 2.0 Hz, J_b = 8.0 Hz, 1H), 7.19-7.20 (m, 1 H), 7.31 (t, J = 7.2 Hz, 1 H), 7.40-7.44 (m, 1 H), 7.51-7.53 (m, 1 H), 7.84-7.89 ppm (m, 2 H); $^{13}\text{C NMR}$ (100Mz, CDCl_3): δ = 19.8, 20.7, 22.2, 50.9, 59.1, 75.6, 103.0, 110.1, 111.6, 120.5, 121.0, 121.6, 122.5, 123.0, 123.4, 127.2, 144.8, 150.6, 156.4, 156.7, 168.5 ppm; IR (cm^{-1}): 3063, 2947, 2857, 2252, 1692, 1552, 1457, 1383, 1291, 1253, 1165, 1071, 969, 911, 730, 670, 453; HRMS m/z (ESI) calcd for $\text{C}_{21}\text{H}_{20}\text{N}_2\text{NaO}_5$ [$\text{M} + \text{Na}$] $^+$ 403.1270 found 403.1266.

Tert-butyl 6-(5-(methoxycarbonyl)-6-methyl-2-(nitromethyl)-3,4-dihydropyridin-1(2H)-yl)-1H-indole-1-carboxylate (**3q**): yellow liquid; $^1\text{H NMR}$ (400 MHz, CDCl_3 , 25 °C, TMS): δ = 1.66 (s, 9H), 1.91-2.00 (m, 2H), 2.13 (s, 3H), 2.26-2.36 (m, 1H), 2.69-2.75 (m, 1H), 3.72 (s, 3H), 4.45-4.49 (m, 2H), 4.62-4.68 (m, 1H), 6.56 (d, J = 3.2 Hz, 1H), 6.91-6.93 (m, 1H), 7.53 (d, J = 8.4 Hz, 1H), 7.61 (d, J = 3.2 Hz, 1H), 7.89 ppm (s, 1H); $^{13}\text{C NMR}$ (100Mz, CDCl_3): δ = 19.7, 20.5, 22.4, 28.1, 50.8, 58.9, 75.3, 84.1, 106.9, 114.4, 121.7, 122.2, 127.0, 129.2, 135.5, 141.9, 149.3, 151.9, 168.8 ppm; IR (cm^{-1}): 2977, 2924, 2853, 1735, 1553, 1439, 1343, 1255, 1179, 1156, 1025, 910, 669, 558, 487, 418; HRMS m/z (ESI) calcd for $\text{C}_{22}\text{H}_{27}\text{N}_3\text{NaO}_6$ [$\text{M} + \text{Na}$] $^+$ 452.1798 found 452.1794.

Methyl 2-methyl-1-(4-morpholinophenyl)-6-(nitromethyl)-1,4,5,6-tetrahydropyridine-3-carboxylate (**3r**): yellow liquid; $^1\text{H NMR}$ (400 MHz, CDCl_3 , 25 °C, TMS): δ = 1.89-1.93 (m, 2 H), 2.08 (s, 3 H), 2.21-2.28 (m, 1 H), 2.66-2.71 (m, 1 H), 3.16 (t, J = 4.8 Hz, 4 H), 3.70 (s, 3 H), 3.86 (t, J = 4.8 Hz, 4 H), 4.29-4.33 (m, 1 H), 4.37-4.42 (m, 1 H), 4.57-4.61 (m, 1 H), 6.85-6.88 (m, 2 H), 6.91-6.93 ppm (m, 2 H); $^{13}\text{C NMR}$ (100Mz, CDCl_3): δ = 19.6, 20.2, 22.6, 48.9, 50.8, 58.7, 66.7, 75.5, 99.5, 116.0, 128.0, 137.2, 149.8, 151.9, 168.9 ppm; IR (cm^{-1}): 2951, 2855, 2249, 1686, 1552, 1513, 1432, 1381, 1294, 1241, 1180, 1114, 1072, 927, 828, 732, 633, 559, 521; HRMS m/z (ESI) calcd for $\text{C}_{19}\text{H}_{26}\text{N}_3\text{O}_5$ [$\text{M} + \text{H}$] $^+$ 376.1872 found 376.1869.

Methyl 2-methyl-6-(nitromethyl)-1-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)-1,4,5,6-tetrahydropyridine-3-carboxylate (**3s**): yellow liquid; ¹H NMR (400 MHz, CDCl₃, 25 °C, TMS): δ = 1.35 (s, 12 H), 1.88-1.92 (m, 2 H), 2.12 (s, 3 H), 2.24-2.31 (m, 1 H), 2.65-2.69 (m, 1 H), 3.73 (s, 3 H), 4.40-4.44 (m, 2 H), 4.58-4.67 (m, 1 H), 7.01 (d, J = 8.0 Hz, 2 H), 7.80 ppm (d, J = 8.0 Hz, 2 H); ¹³C NMR (100Mz, CDCl₃): δ = 19.4, 20.4, 21.8, 24.3, 50.5, 58.1, 75.0, 83.5, 125.1, 127.8, 128.1, 132.6, 135.6, 147.7, 168.1 ppm; IR (cm⁻¹): 2977, 2863, 1688, 1592, 1554, 1434, 1360, 1284, 1238, 1182, 1105, 1019, 961, 857, 660, 590, 530, 497; HRMS *m/z* (ESI) calcd for C₂₁H₂₉BN₂NaO₆ [M + Na]⁺ 439.2016 found 439.2012.

Methyl 1-(3-ethynylphenyl)-2-methyl-6-(nitromethyl)-1,4,5,6-tetrahydropyridine-3-carboxylate (**3t**): yellow liquid; ¹H NMR (400 MHz, CDCl₃, 25 °C, TMS): δ = 1.86-1.91 (m, 2H), 2.10 (s, 3H), 2.20-2.27(m, 1H), 2.63-2.69 (m, 1H), 3.13 (s, 1H), 3.72 (s, 3H), 4.35-4.43 (m, 2H), 4.61-4.66 (m, 1H), 7.01-7.03 (m, 1H), 7.13 (s, 1H), 7.29-7.36 ppm (m, 2H); ¹³C NMR (100Mz, CDCl₃): δ = 19.8, 20.6, 22.1, 50.9, 58.6, 75.5, 78.2, 82.4, 103.7, 123.4, 127.1, 129.6, 129.8, 129.9, 145.7, 150.0, 168.4 ppm; IR (cm⁻¹): 3367, 3291, 2947, 2859, 2252, 1693, 1552, 1480, 1428, 1383, 1292, 1246, 1138, 1108, 1071, 969, 912, 798, 734, 699, 655, 467, 423; HRMS *m/z* (ESI) calcd for C₁₇H₁₈N₂NaO₄ [M + Na]⁺ 337.1164 found 337.1163.

Methyl 2-ethyl-6-(nitromethyl)-1-(p-tolyl)-1,4,5,6-tetrahydropyridine-3-carboxylate (**3u**): yellow liquid; ¹H NMR (400 MHz, CDCl₃, 25 °C, TMS): δ = 0.92 (t, J = 7.6 Hz, 3 H), 1.77-1.91 (m, 2 H), 2.10-2.20 (m, 2 H), 2.30 (s, 3 H), 2.62-2.68 (m, 1 H), 2.78-2.87 (m, 1 H), 3.68 (s, 3 H), 4.27-4.33 (m, 2 H), 4.57-4.62 (m, 1 H), 6.88 (d, J = 8.0 Hz, 2 H), 7.11 ppm (d, J = 8.0 Hz, 2 H); ¹³C NMR (100Mz, CDCl₃): δ = 13.6, 20.0, 20.8, 22.2, 24.7, 50.8, 75.8, 102.0, 126.7, 130.1, 136.3, 143.5, 157.2, 168.2 ppm; IR (cm⁻¹): 3025, 2945, 2870, 1905, 1695, 1555, 1510, 1382, 1261, 1230, 1181, 1080, 996, 823, 719, 554, 505; HRMS *m/z* (ESI) calcd for C₁₇H₂₂N₂NaO₄ [M + Na]⁺ 341.1477 found 341.1476.

Ethyl 6-(nitromethyl)-2-propyl-1-(p-tolyl)-1,4,5,6-tetrahydropyridine-3-carboxylate (**3v**): yellow liquid; ¹H NMR (400 MHz, CDCl₃, 25 °C, TMS): 0.75 (t, J = 7.2 Hz, 3 H), 1.30 (t, J = 7.2 Hz, 3 H), 1.36-1.50 (m, 2 H), 1.79-1.93 (m, 2 H), 2.05-2.23 (m, 2 H), 2.34 (s, 3 H), 2.67-2.73 (m, 1 H), 2.79-2.85 (m, 1 H), 4.18 (q, Ja = 7.2 Hz, Jb = 14.4 Hz, 2 H), 4.32-4.36 (m, 2 H), 4.61-4.66 (m, 1 H), 6.91 (d, J = 8.0 Hz, 2 H), 7.14 (d, J = 8.0 Hz, 2 H); ¹³C NMR (100Mz, CDCl₃): 14.1, 14.4, 20.2, 20.9, 22.1, 22.7, 33.4, 59.0, 59.5, 75.9, 103.0, 126.7, 130.1, 136.2, 143.8, 155.4, 168.0; IR (cm⁻¹): 3027, 2960, 2933, 2869, 1738, 1690, 1554, 1510, 1449, 1381, 1269, 1226, 1179, 1142, 1059, 1021, 822, 738, 652, 511; HRMS *m/z* (ESI) calcd for C₁₈H₂₄N₂NaO₄ [M + Na]⁺ 355.1634 found 355.1630.

Ethyl 2-methyl-6-(nitromethyl)-1-(p-tolyl)-1,4,5,6-tetrahydropyridine-3-carboxylate (**3w**): yellow liquid; ¹H NMR (400 MHz, CDCl₃, 25 °C, TMS): δ = 1.29 (t, J = 7.2 Hz, 3H), 1.88-1.91 (m, 2H), 2.09 (s, 3H), 2.26-2.29 (s, 1H), 2.33 (s, 3H), 2.66-2.71 (m, 1H), 4.16 (q, J = 7.2 Hz, 2H), 4.32-4.36 (m, 1H), 4.38-4.43 (m, 1H), 4.59-4.62 (m, 1H), 6.91 (d, J = 8.0 Hz, 2H), 7.15 ppm (d, J = 8.0 Hz, 2H); ¹³C NMR (100Mz, CDCl₃): δ = 14.3, 19.7, 20.2, 20.7, 22.3, 58.6, 59.2, 75.5, 101.1, 126.7, 130.0, 136.3, 142.9, 150.8, 168.2 ppm; IR (cm⁻¹): 3029, 2979, 2935, 2863, 1687, 1554, 1511, 1382, 1291, 1237, 1068, 822, 721, 510, 427; HRMS *m/z* (ESI) calcd for C₁₇H₂₂N₂NaO₄ [M + Na]⁺ 341.1477 found 341.1473.

1-(2-Methyl-6-(nitromethyl)-1-(p-tolyl)-1,4,5,6-tetrahydropyridin-3-yl)ethanone (**3x**): yellow

liquid; ^1H NMR (400 MHz, CDCl_3 , 25 °C, TMS): δ = 1.95-1.98 (m, 2 H), 2.04 (s, 3 H), 2.22 (s, 3 H), 2.33 (s, 3 H), 2.36-2.42 (m, 1 H), 2.64-2.69 (m, 1 H), 4.32-4.37 (m, 1 H), 4.38-4.43 (m, 1 H), 4.53-4.58 (m, 1 H), 6.89 (d, J = 8.0 Hz, 2 H), 7.15 ppm (d, J = 8.0 Hz, 2 H); ^{13}C NMR (100Mz, CDCl_3): δ = 20.9, 20.9, 21.0, 29.9, 58.3, 75.1, 108.5, 127.1, 130.3, 137.1, 142.2, 151.5, 197.7 ppm; IR (cm^{-1}): 3028, 2929, 2857, 1711, 1642, 1551, 1510, 1380, 1294, 1212, 1185, 1110, 942, 823, 716, 650, 606, 562, 489; HRMS m/z (ESI) calcd for $\text{C}_{16}\text{H}_{20}\text{N}_2\text{NaO}_3$ [$\text{M} + \text{Na}$] $^+$ 311.1372 found 311.1369.

Cyclohexyl 2-methyl-6-(nitromethyl)-1-(p-tolyl)-1,4,5,6-tetrahydropyridine-3-carboxylate (**3y**): yellow liquid; ^1H NMR (400 MHz, CDCl_3 , 25 °C, TMS): δ = 1.29 (t, J = 7.2 Hz, 2H), 1.88-1.91 (m, 1H), 2.09 (s, 3H), 2.26-2.29 (s, 1H), 2.33 (s, 3H), 2.66-2.71 (m, 1H), 4.16 (q, J = 7.2 Hz, 2H), 4.32-4.36 (m, 1H), 4.38-4.43 (m, 1H), 4.59-4.62 (m, 1H), 6.91 (d, J = 8.0 Hz, 2H), 7.15 ppm (d, J = 8.0 Hz, 2H); ^{13}C NMR (100Mz, CDCl_3): δ = 14.3, 19.7, 20.2, 20.7, 22.3, 58.6, 59.2, 75.5, 101.1, 126.7, 130.0, 136.3, 142.9, 150.8, 168.2 ppm; IR (cm^{-1}): 3029, 2979, 2935, 2863, 1687, 1554, 1511, 1382, 1291, 1237, 1068, 822, 721, 510, 427; HRMS m/z (ESI) calcd for $\text{C}_{21}\text{H}_{28}\text{N}_2\text{NaO}_4$ [$\text{M} + \text{Na}$] $^+$ 395.1947 found 395.1942.

2-Methoxyethyl 2-methyl-6-(nitromethyl)-1-(p-tolyl)-1,4,5,6-tetrahydropyridine-3-carboxylate (**3z**): yellow liquid; ^1H NMR (400 MHz, CDCl_3 , 25 °C, TMS): 1.89-1.92 (m, 2H), 2.09 (s, 3H), 2.26-2.31 (m, 1H), 3.34 (s, 3H), 2.70-2.75 (m, 1H), 3.40 (s, 3H), 3.64-3.66 (m, 2H), 4.25-4.27 (m, 2H), 4.32-4.37 (m, 1H), 4.38-4.43 (m, 1H), 4.59-4.61 (m, 1H), 6.90 (d, J = 8.4 Hz, 2H), 7.16 ppm (d, J = 8.4 Hz, 2H); ^{13}C NMR (100Mz, CDCl_3): 19.6, 20.3, 20.8, 22.3, 58.6, 58.8, 62.5, 70.7, 75.4, 100.3, 126.7, 130.1, 136.5, 142.7, 151.6, 168.1; IR (cm^{-1}): 3028, 2932, 2890, 1687, 1552, 1381, 1291, 1209, 1071, 823, 766, 617, 506; HRMS m/z (ESI) calcd for $\text{C}_{18}\text{H}_{24}\text{N}_2\text{NaO}_5$ [$\text{M} + \text{Na}$] $^+$ 371.1583 found 371.1578.

Allyl 2-methyl-6-(nitromethyl)-1-(p-tolyl)-1,4,5,6-tetrahydropyridine-3-carboxylate (**3a'**): yellow liquid; ^1H NMR (400 MHz, CDCl_3 , 25 °C, TMS): δ = 1.89-1.92 (m, 2 H), 2.10 (s, 3 H), 2.22-2.30 (m, 1 H), 2.34 (s, 3 H), 2.70-2.75 (m, 1 H), 4.34-4.43 (m, 2 H), 4.59-4.63 (m, 3 H), 5.21 (dd, J_a = 1.2 Hz, J_b = 10.8 Hz, 1 H), 5.33 (dd, J_a = 1.2 Hz, J_b = 17.2 Hz, 1 H), 5.95-6.02 (m, 1 H), 6.91 (d, J = 8.0 Hz, 2 H), 7.16 ppm (d, J = 8.0 Hz, 2 H); ^{13}C NMR (100Mz, CDCl_3): δ = 19.6, 20.3, 20.7, 22.4, 58.6, 64.1, 75.4, 100.3, 117.0, 126.8, 130.1, 133.1, 136.5, 142.7, 151.6, 167.7 ppm; IR (cm^{-1}): 3083, 3027, 2933, 2862, 1690, 1552, 1510, 1381, 1291, 1236, 1209, 1141, 1062, 822, 766, 722, 552, 512, 421; HRMS m/z (ESI) calcd for $\text{C}_{18}\text{H}_{22}\text{N}_2\text{NaO}_4$ [$\text{M} + \text{Na}$] $^+$ 353.1477 found 353.1472.

Methyl 2-cyclopropyl-6-(nitromethyl)-1-(p-tolyl)-1,4,5,6-tetrahydropyridine-3-carboxylate (**3b'**): yellow liquid; ^1H NMR (400 MHz, CDCl_3 , 25 °C, TMS): 1.86 (s, 2H), 1.98-2.04 (m, 1H), 2.13-2.16 (m, 2H), 2.35 (s, 3H), 4.29-4.34 (m, 2H), 4.58-4.63 (m, 1H), 6.90 (d, J = 6.4 Hz, 2H), 7.17 ppm (d, J = 6.4 Hz, 2H); ^{13}C NMR (100Mz, CDCl_3): 6.2, 20.1, 20.9, 22.1, 32.7, 32.9, 51.1, 59.1, 75.8, 103.3, 126.7, 130.3, 136.7, 143.2, 153.8, 168.2; IR (cm^{-1}): 3376, 2952, 2865, 2254, 1875, 1738, 1698, 1551, 1437, 1383, 1258, 1207, 1066, 912, 813, 733, 507; HRMS m/z (ESI) calcd for $\text{C}_{18}\text{H}_{23}\text{N}_2\text{O}_4$ [$\text{M} + \text{H}$] $^+$ 331.1658 found 331.1650.

Methyl 6-methyl-2-(nitromethyl)-3,4-dihydro-2H-pyran-5-carboxylate (**4a**): yellow liquid; ^1H NMR (400 MHz, CDCl_3 , 25 °C, TMS): δ = 1.61-1.70 (m, 1H), 1.97-2.01 (m, 1H), 2.22 (s, 3H), 2.23-2.39 (m, 1H), 2.43-2.50 (m, 1H), 3.71 (s, 3H), 4.48-4.53 (m, 1H), 4.56-4.65 ppm (m, 2H); ^{13}C NMR (100Mz, CDCl_3): δ = 14.0, 20.5, 23.7, 51.0, 60.2, 72.1, 101.5, 163.2, 168.2 ppm; IR

(cm^{-1}): 3036, 2959, 2859, 1699, 1622, 1553, 1435, 1379, 1275, 1109, 953, 836, 732, 661, 521, 491; HRMS m/z (ESI) calcd for $\text{C}_9\text{H}_{13}\text{NNaO}_5$ [$\text{M} + \text{Na}$] $^+$ 238.0691 found 238.0687.

Methyl 2-(cyclopropanecarbonyl)-6-nitro-5-(*p*-tolylamino)hexanoate (**7a**): yellow liquid; ^1H NMR (400 MHz, CDCl_3 , 25 $^\circ\text{C}$, TMS): δ = 0.92-0.96 (m, 2H), 1.03-1.11 (m, 2H), 1.53-1.62 (m, 1H), 1.66-1.76 (m, 1H), 1.92-2.04 (m, 2H), 2.09-2.17 (m, 1H), 2.22-2.24 (m, 3H), 3.61-3.65 (m, 1H), 3.73-3.76 (m, 4H), 4.01-4.03 (m, 1H), 4.37-4.41 (m, 1H), 4.51-4.55 (m, 1H), 6.58-6.63 (m, 2H), 6.95-7.02 ppm (m, 2H); ^{13}C NMR (100Mz, CDCl_3): δ = 11.8, 11.8, 11.9, 11.9, 19.8, 20.0, 20.3, 24.3, 24.3, 30.2, 30.3, 52.3, 52.4, 58.7, 58.8, 77.7, 77.8, 113.7, 113.8, 128.0, 130.0, 143.3, 169.8, 169.8, 204.7, 204.7 ppm; IR (cm^{-1}): 3376, 2952, 2865, 2254, 1875, 1738, 1698, 1551, 1437, 1383, 1258, 1207, 1066, 912, 813, 733, 507; HRMS m/z (ESI) calcd for $\text{C}_{18}\text{H}_{25}\text{N}_2\text{O}_5$ [$\text{M} + \text{H}$] $^+$ 349.1763 found 349.1763.

Methyl 6-cyano-1-(4-methoxyphenyl)-2-methyl-1,4,5,6-tetrahydropyridine-3-carboxylate (**8a**): yellow liquid; ^1H NMR (400 MHz, CDCl_3 , 25 $^\circ\text{C}$, TMS): δ = 2.08 (s, 3H), 2.11-2.16 (m, 1H), 2.20-2.26 (m, 1H), 2.61-2.76 (m, 2H), 3.70 (s, 3H), 3.83 (s, 3H), 4.44-4.46 (m, 1H), 6.92 (d, J = 9.2 Hz, 2H), 7.12 ppm (d, J = 8.4 Hz, 2H); ^{13}C NMR (100Mz, CDCl_3): δ = 19.2, 20.5, 24.9, 50.8, 52.4, 55.5, 98.5, 114.9, 118.2, 128.9, 136.9, 151.2, 158.9, 168.7 ppm; IR (cm^{-1}): 3343, 2951, 2857, 2215, 1732, 1658, 1512, 1444, 1370, 1234, 1033, 912, 831, 733, 656, 587, 544, 434; HRMS m/z (ESI) calcd for $\text{C}_{16}\text{H}_{18}\text{N}_2\text{NaO}_3$ [$\text{M} + \text{Na}$] $^+$ 309.1215 found 309.1215.

Methyl 1-methyl-6-oxo-4,4a,5,6-tetrahydro-3H-pyrido[1,2-*a*]quinazoline-2-carboxylate (**10a**): Yellow solid; mp. = 191-192 $^\circ\text{C}$; ^1H NMR (400 MHz, CDCl_3 , 25 $^\circ\text{C}$, TMS): δ = 1.87-1.96 (m, 1H), 2.20 (s, 1H), 2.30-2.41 (m, 4H), 2.84 (dt, J_a = 4.4 Hz, J_b = 17.6 Hz, 1H), 3.72 (s, 3H), 5.01 (ddd, J_a = 1.2 Hz, J_b = 6.4 Hz, J_c = 9.2 Hz, 1H), 7.01 (d, J = 8.0 Hz, 1H), 7.19 (td, J_a = 0.8 Hz, J_b = 7.6 Hz, 1H), 7.43-7.48 (m, 1H), 8.00 ppm (dd, J_a = 1.6 Hz, J_b = 7.6 Hz, 1H), 8.21 (s, 1H); ^{13}C NMR (100Mz, CDCl_3): δ = 19.5, 20.0, 27.5, 51.0, 66.3, 106.5, 122.3, 123.5, 123.7, 128.4, 132.0, 143.0, 148.7, 165.7, 168.1 ppm; IR (cm^{-1}): 3198, 3078, 2986, 2947, 2857, 1676, 1604, 1569, 1481, 1434, 1380, 1338, 1291, 1263, 1227, 1187, 1141, 1071, 762, 731; HRMS m/z (ESI) calcd for $\text{C}_{15}\text{H}_{16}\text{N}_2\text{NaO}_3$ [$\text{M} + \text{Na}$] $^+$ 295.1059 found 295.1056.

Methyl 5-butyl-1-methyl-6-oxo-4,4a,5,6-tetrahydro-3H-pyrido[1,2-*a*]quinazoline-2-carboxylate (**10b**): Yellow liquid; ^1H NMR (400 MHz, CDCl_3 , 25 $^\circ\text{C}$, TMS): δ = 0.95 (t, J = 7.2 Hz, 3H), 1.33-1.42 (m, 2H), 1.53-1.67 (m, 2H), 1.94-2.02 (m, 1H), 2.21-2.31 (m, 2H), 2.38 (s, 3H), 2.74 (d, J = 17.2 Hz, 1H), 3.20-3.27 (m, 1H), 3.75 (s, 3H), 3.84-3.92 (m, 1H), 4.83-4.86 (m, 1H), 6.80 (d, J = 8.4 Hz, 1H), 7.09 (t, J = 7.6 Hz, 1H), 7.35-7.39 (m, 1H), 8.00 ppm (dd, J_a = 1.6 Hz, J_b = 7.6 Hz, 1H); ^{13}C NMR (100Mz, CDCl_3): δ = 120.4, 21.8, 26.0, 39.0, 51.1, 71.1, 108.1, 110.4, 119.88, 119.9, 120.0, 122.6, 128.9, 132.2, 141.9, 142.9, 149.2, 150.7, 163.5, 167.8 ppm; IR (cm^{-1}): 3117, 3076, 2949, 2854, 1696, 1660, 1604, 1481, 1433, 1377, 1295, 1268, 1231, 1135, 1073, 1013, 918, 759, 734; HRMS m/z (ESI) calcd for $\text{C}_{19}\text{H}_{24}\text{N}_2\text{NaO}_3$ [$\text{M} + \text{H}$] $^+$ 329.1865 found 329.1862.

Methyl 1-methyl-6-oxo-5-phenyl-4,4a,5,6-tetrahydro-3H-pyrido[1,2-*a*]quinazoline-2-carboxylate (**10c**): yellow liquid; ^1H NMR (400 MHz, CDCl_3 , 25 $^\circ\text{C}$, TMS): δ = 1.62-1.71 (m, 1H), 1.90-1.97 (m, 1H), 2.08-2.11 (m, 1H), 2.43 (s, 3H), 2.60-2.67 (m, 1H), 3.71 (s, 3H), 5.35-5.39 (m, 1H), 6.98 (d, J = 8.0 Hz, 1H), 7.17-7.24 (m, 3H), 7.34-7.38 (m, 1H), 7.41-7.49 (m, 3H), 8.07-8.09 ppm (m, 1H); ^{13}C NMR (100Mz, CDCl_3): δ = 20.1, 20.7, 27.9, 51.1, 72.1, 121.1, 122.7, 123.4, 128.0, 129.0, 129.1, 129.2, 132.2, 138.1, 143.0, 148.8, 164.2, 167.8 ppm; IR (cm^{-1}): 3311, 3063, 2946, 2851,

2245, 1664, 1600, 1484, 1360, 1270, 1232, 1137, 1082, 914, 731, 622, 468; HRMS m/z (ESI) calcd for $C_{21}H_{20}N_2NaO_3$ $[M + Na]^+$ 371.1372 found 371.1369.

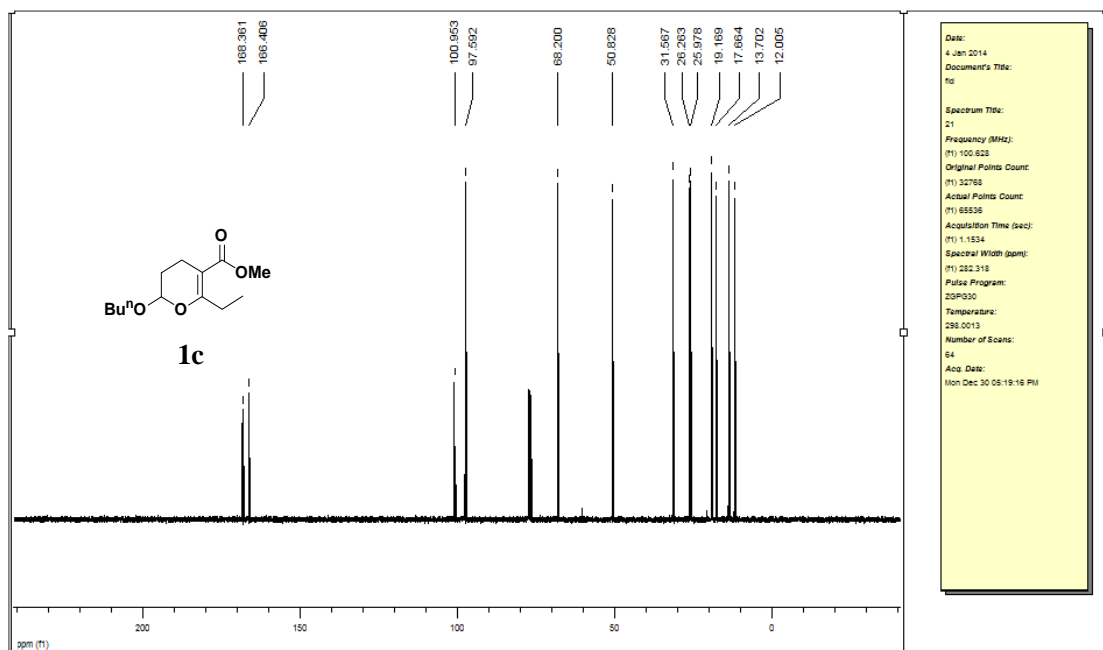
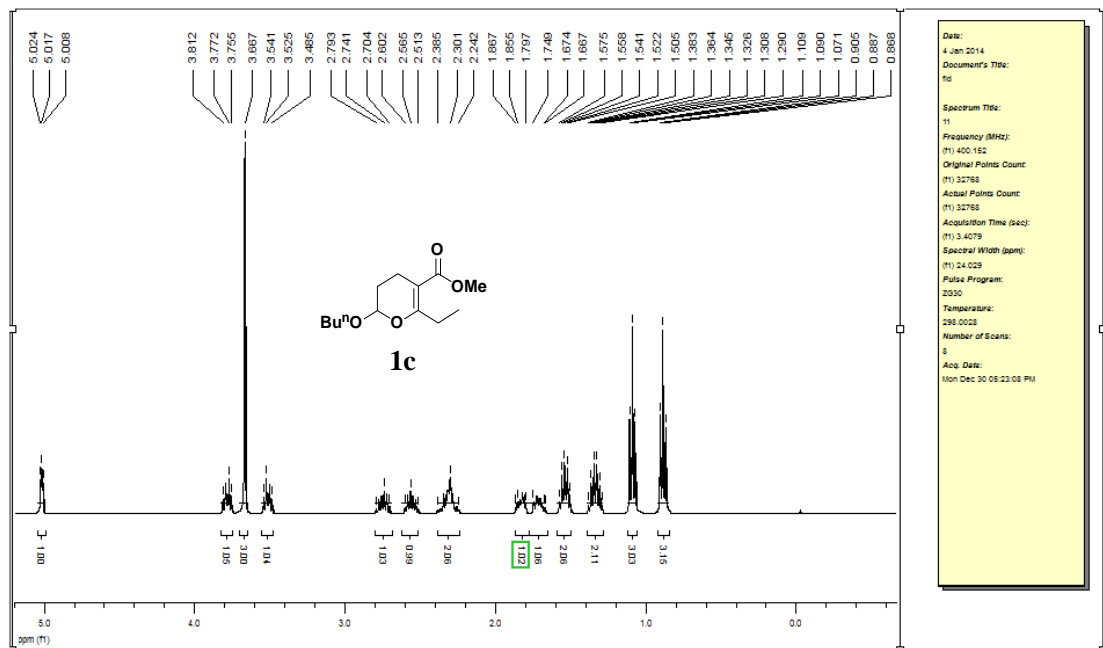
Methyl 10-methyl-6,6a,7,8-tetrahydrobenzo[e]pyrido[2,1-c][1,2,4]thiadiazine-9-carboxylate 5,5-dioxide (**10d**): yellow liquid; 1H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 1.68-1.78 (m, 1 H), 2.18-2.26 (m, 1 H), 2.35 (s, 3 H), 2.44-2.50 (m, 1 H), 2.74-2.80 (m, 1 H), 3.67 (s, 3 H), 5.11-5.18 (m, 1 H), 5.70 (d, J = 12.0 Hz, 1 H), 6.91 (d, J = 8.4 Hz, 1 H), 7.17 (t, J = 8.0 Hz, 1 H), 7.42-7.47 (m, 1 H), 7.80-7.82 ppm (m, 1 H); ^{13}C NMR (100Mz, $CDCl_3$): δ = 14.0, 21.3, 30.1, 51.2, 69.4, 111.7, 123.0, 123.2, 125.1, 129.3, 132.1, 138.5, 148.0, 167.6 ppm; IR (cm^{-1}): 3360, 2932, 2876, 1680, 1592, 1478, 1449, 1328, 1268, 1167, 1134, 1078, 921, 765, 562, 459, 417; HRMS m/z (ESI) calcd for $C_{14}H_{16}N_2O_4S$ $[M]$ 308.0831 found 308.0830.

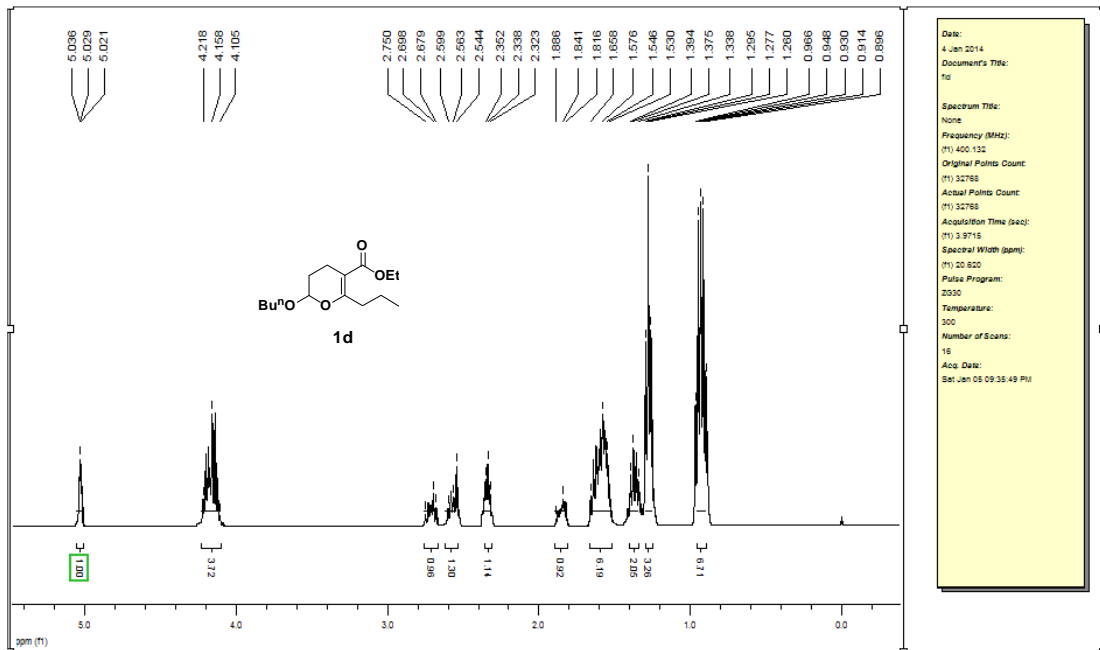
Methyl 2-(tert-butyl)-9-methyl-4-oxo-5,5a,6,7-tetrahydro-4H-pyrido[1,2-a]thieno[3,2-e]pyrimidine-8-carboxylate (**10e**): yellow liquid; 1H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 1.39 (s, 9H), 1.87-1.93 (m, 1H), 2.12-2.17 (m, 1H), 2.32-2.36 (m, 1H), 2.43 (s, 3H), 2.78-2.84 (m, 1H), 3.72 (s, 3H), 5.99-5.03 (m, 1H), 6.63 (s, 1H), 7.66 ppm (s, 1H); ^{13}C NMR (100Mz, $CDCl_3$): δ = 19.1, 20.0, 27.0, 30.7, 31.7, 50.9, 68.3, 105.5, 116.0, 116.7, 146.6, 148.2, 163.2, 163.3, 168.0 ppm; IR (cm^{-1}): 3304, 3188, 2248, 1622, 1527, 1387, 1237, 1091, 910, 738, 646, 612, 448; HRMS m/z (ESI) calcd for $C_{17}H_{22}N_2NaO_3S$ $[M + Na]^+$ 357.1249 found 357.1245.

(*E*)-methyl 1-methyl-6-oxo-5-((1-phenylethylidene)amino)-4,4a,5,6-tetrahydro-3H-pyrido[1,2-a]quinazoline-2-carboxylate (**10f**): yellow liquid; 1H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 1.95-2.00 (m, 1 H), 2.16-2.24 (m, 2 H), 2.30 (s, 3 H), 2.38 (s, 3 H), 2.54-2.59 (m, 1 H), 3.70 (s, 3 H), 5.51-5.54 (m, 1 H), 7.04 (d, J = 8.0 Hz, 1 H), 7.20-7.26 (m, 1 H), 7.40-7.44 (m, 4 H), 7.86-7.88 (m, 2 H), 8.05-8.06 ppm (m, 1 H); ^{13}C NMR (100Mz, $CDCl_3$): δ = 17.9, 19.9, 28.7, 51.2, 61.7, 73.6, 122.7, 123.2, 124.3, 127.1, 127.1, 128.3, 129.0, 129.0, 130.6, 132.0, 137.1, 143.0, 148.5, 168.3, 170.6 ppm; IR (cm^{-1}): 3312, 3065, 2947, 2854, 1667, 1603, 1483, 1435, 1364, 1280, 1136, 1075, 762, 696; HRMS m/z (ESI) calcd for $C_{23}H_{24}N_3O_3$ $[M + H]^+$ 390.1818 found 390.1812.

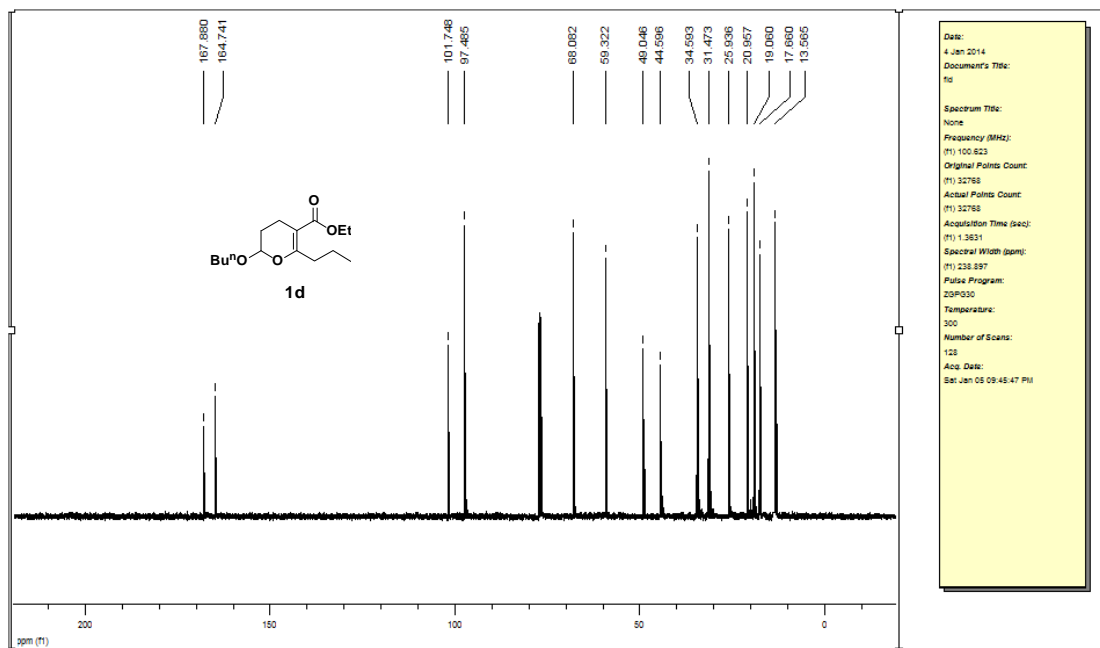
Methyl 10-methyl-13,13a-dihydro-12H-pyrido[1,2-a]pyrrolo[2,1-c]quinoxaline-11-carboxylate (**10g**): yellow liquid; 1H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 1.95-2.05 (m, 1H), 2.24-2.28 (m, 1H), 2.30 (s, 3H), 2.53-2.60 (m, 1H), 2.91-2.97 (m, 1H), 3.71 (s, 3H), 4.42 (q, J = 5.6 Hz, 1H), 6.05-6.06 (m, 1H), 6.31-6.33 (m, 1H), 7.01 (dd, J_a = 1.2 Hz, J_b = 8.0 Hz, 1H), 7.07-7.15 (m, 3H), 7.37 ppm (dd, J_a = 1.2 Hz, J_b = 7.6 Hz, 1H); ^{13}C NMR (100Mz, $CDCl_3$): δ = 20.4, 21.5, 25.5, 50.8, 54.1, 103.5, 105.1, 109.3, 110.5, 114.5, 116.0, 123.7, 123.9, 124.1, 130.8, 132.0, 150.0, 168.5 ppm; IR (cm^{-1}): 3320, 3116, 3070, 2948, 2844, 1686, 1666, 1481, 1433, 1378, 1290, 1261, 1231, 1131, 1073, 918, 759, 734, 551; HRMS m/z (ESI) calcd for $C_{18}H_{18}N_2NaO_2$ $[M + Na]^+$ 317.1266 found 317.1263.

Methyl 1-methyl-4,4a-dihydro-3H-benzo[4,5]thiazolo[3,2-a]pyridine-2-carboxylate (**10h**): yellow liquid; 1H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 2.03-2.10 (m, 1H), 2.23-2.27 (m, 2H), 2.52 (s, 3H), 2.78-2.83 (m, 1H), 3.71 (s, 3H), 5.29 (dd, J_a = 4.0 Hz, J_b = 11.6 Hz, 1H), 6.86-6.93 (m, 2H), 6.96-7.00 (m, 1H), 7.15 ppm (dd, J_a = 1.2 Hz, J_b = 7.6 Hz, 1H); ^{13}C NMR (100Mz, $CDCl_3$): δ = 19.3, 23.9, 27.6, 50.9, 68.5, 104.3, 115.9, 122.8, 123.2, 124.7, 130.3, 140.9, 149.4, 168.4 ppm; IR (cm^{-1}): 3341, 2928, 2851, 1698, 1656, 1481, 1435, 1378, 1295, 1269, 1229, 1188, 1139, 1073, 918, 760, 732, 571; HRMS m/z (ESI) calcd for $C_{14}H_{15}NNaO_2S$ $[M + Na]^+$ 284.0721 found 284.0718.

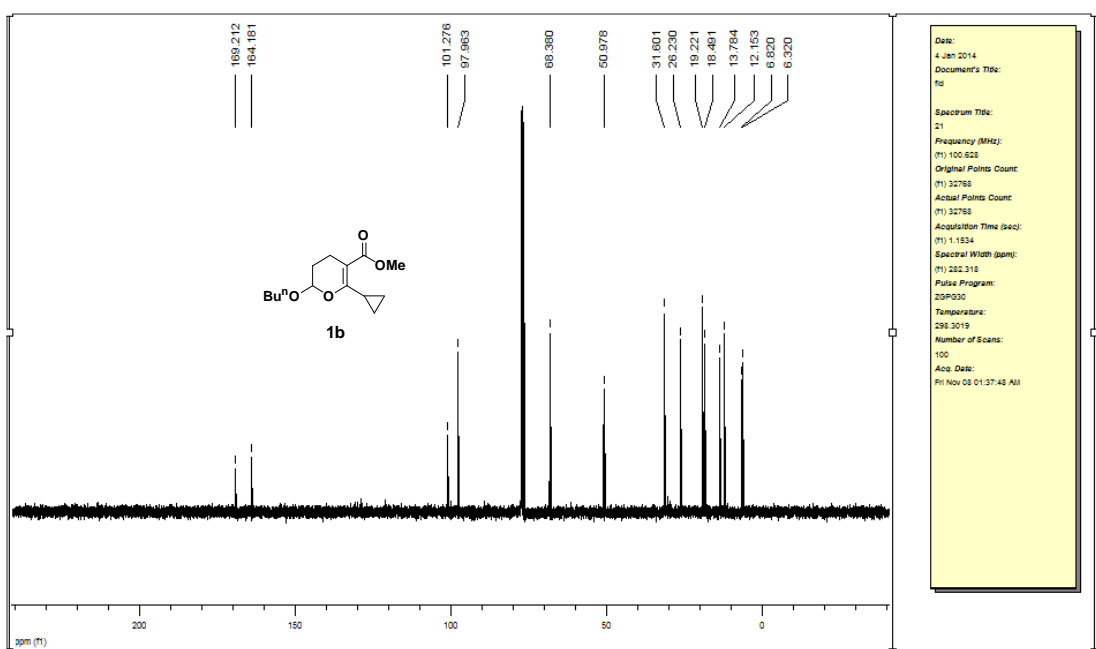
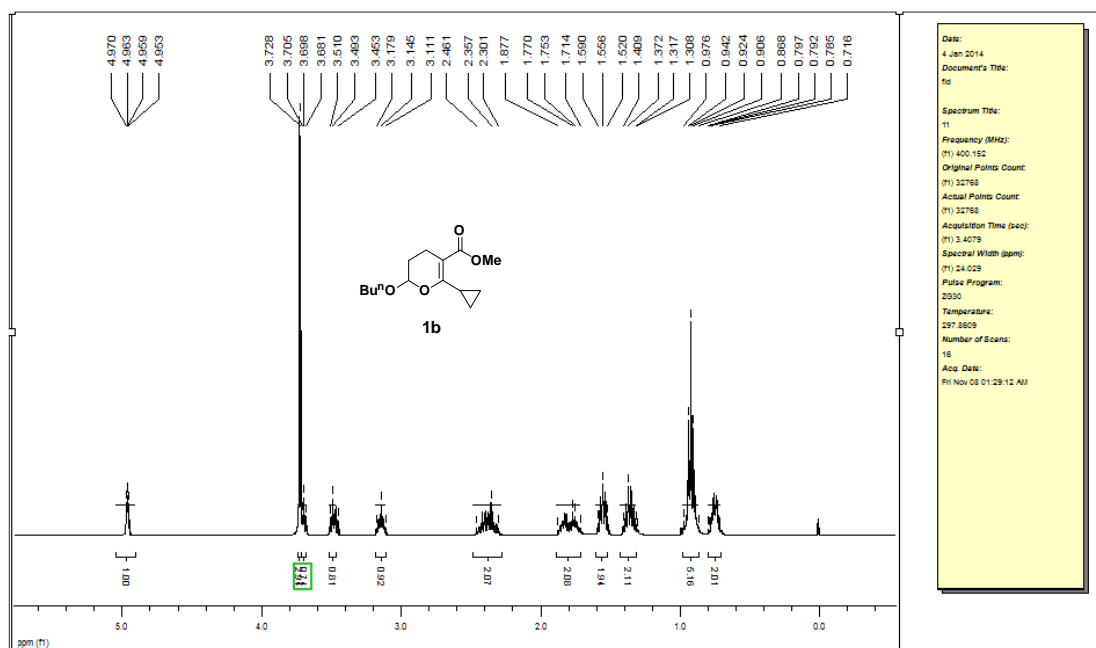


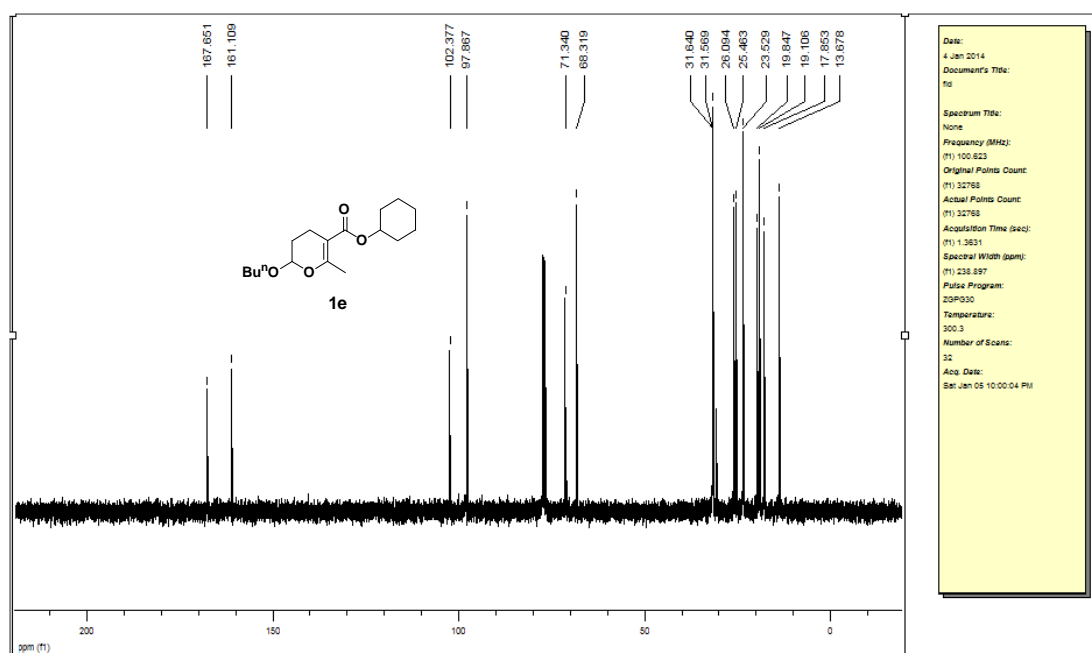
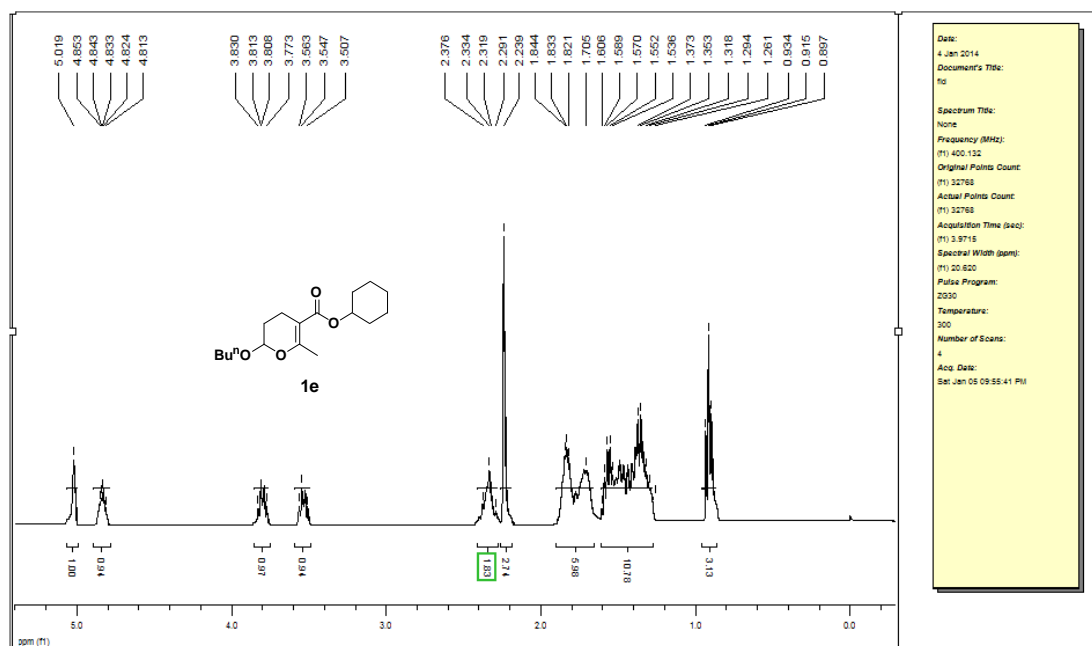


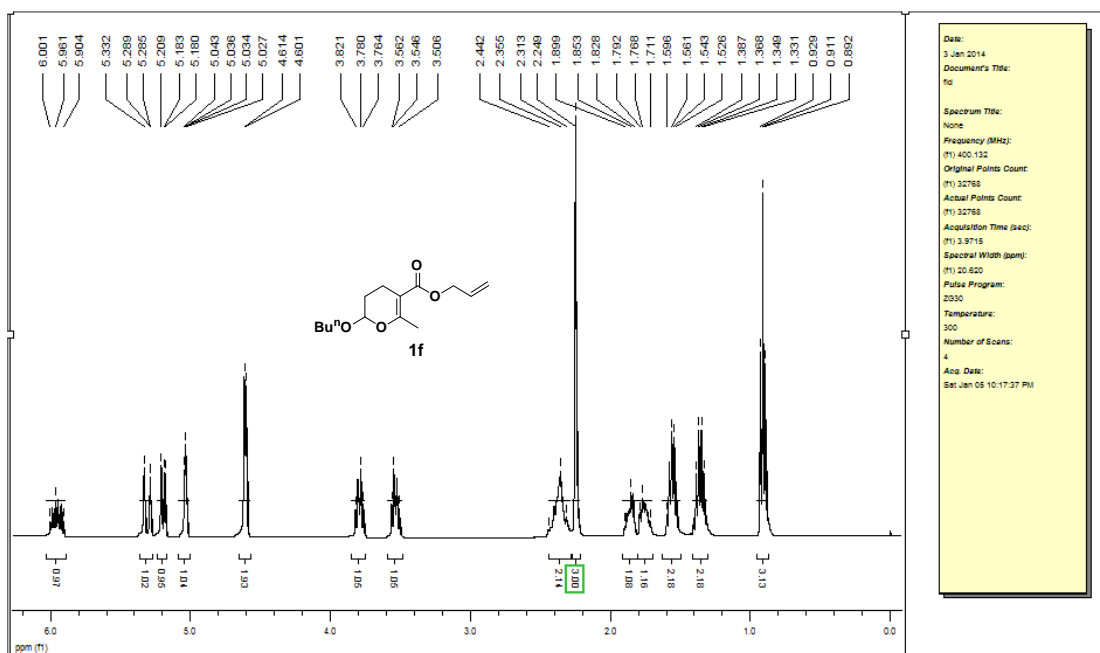
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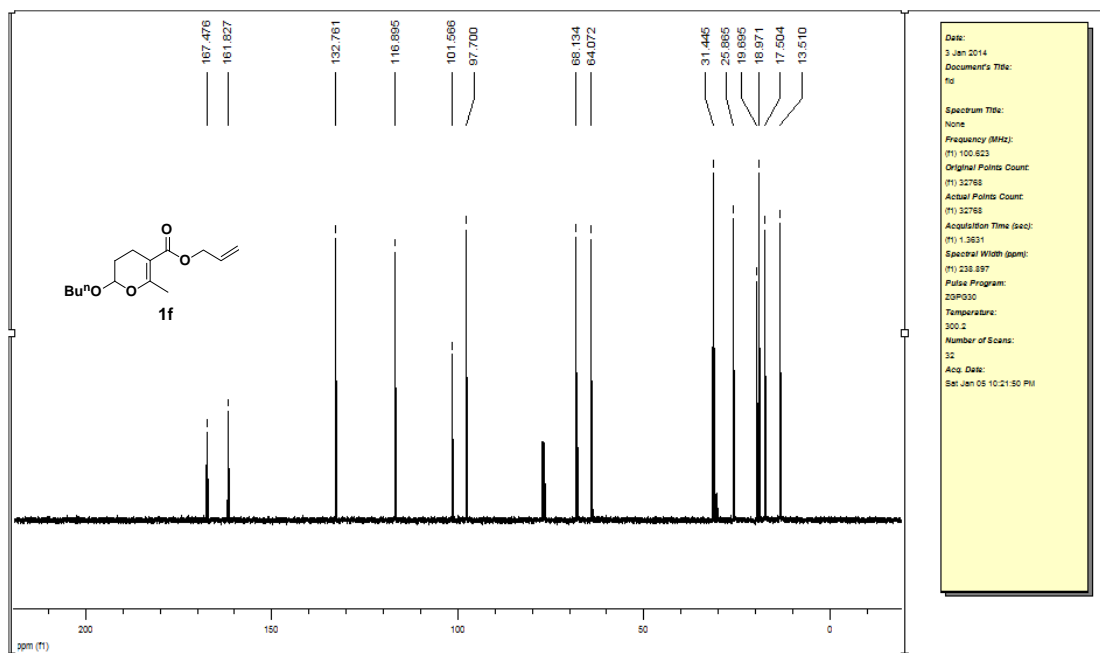
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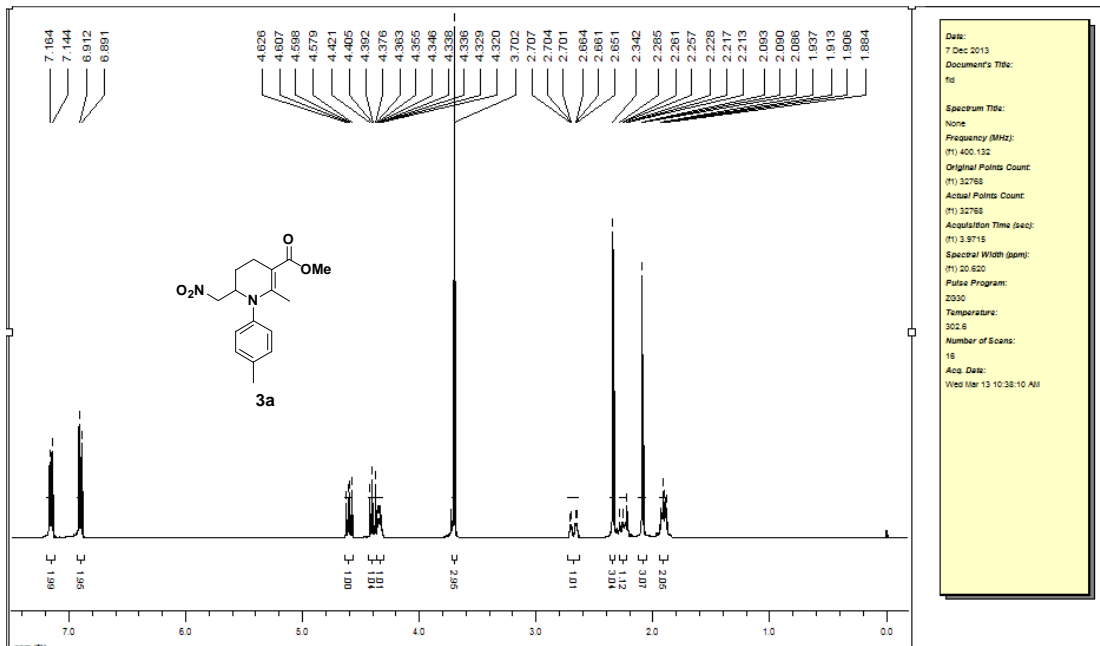




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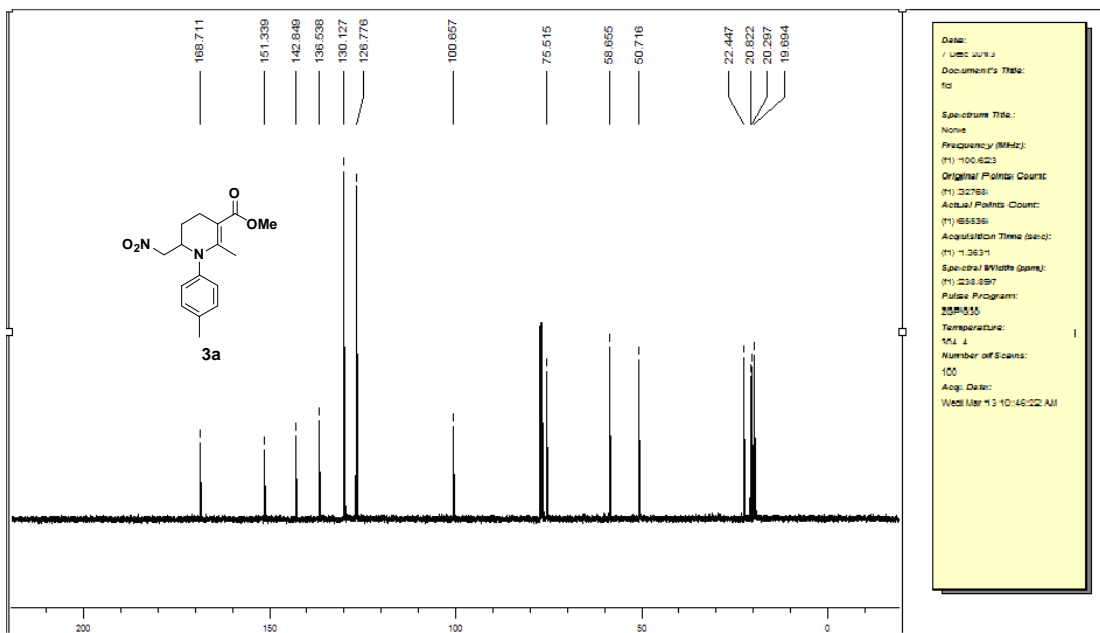


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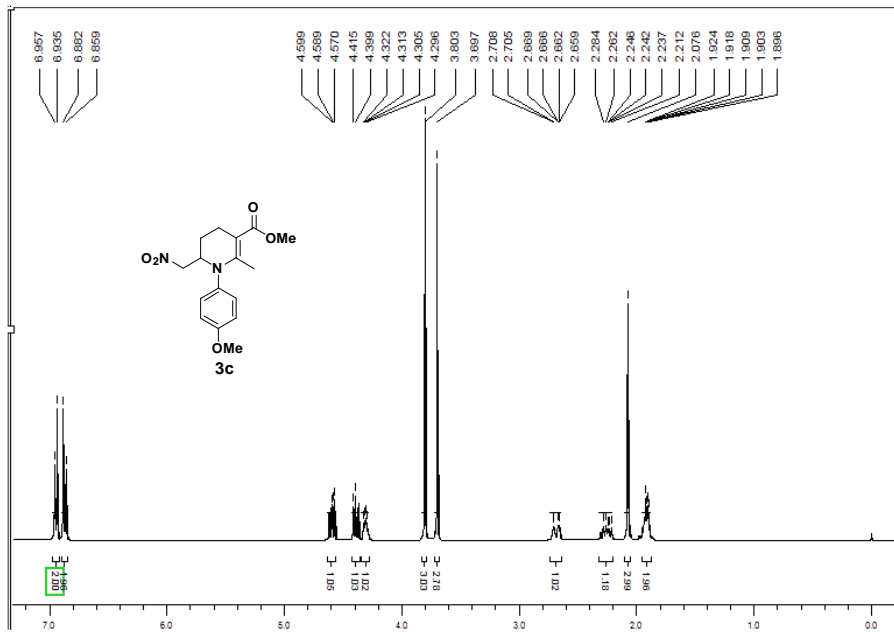
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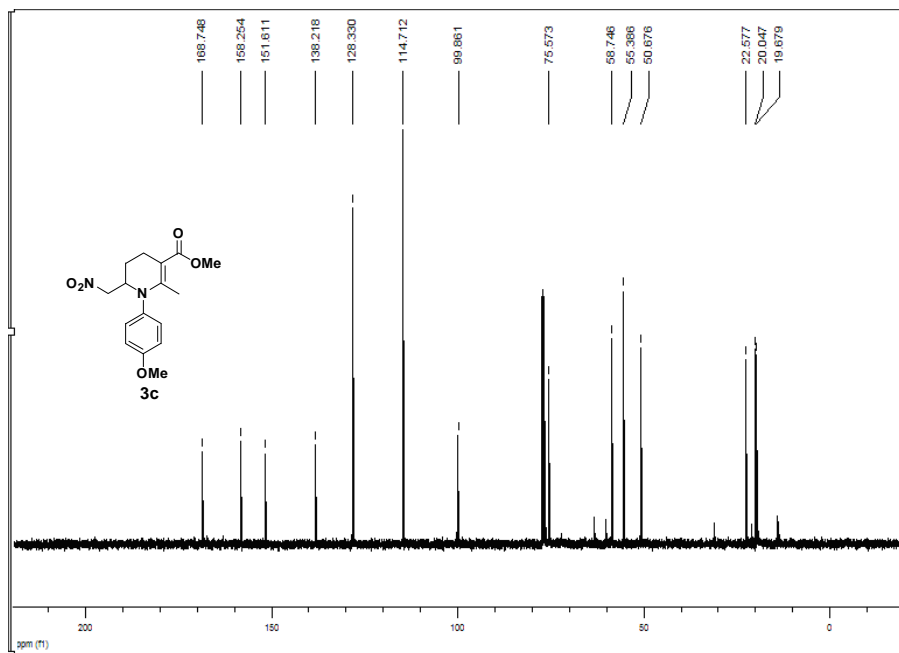


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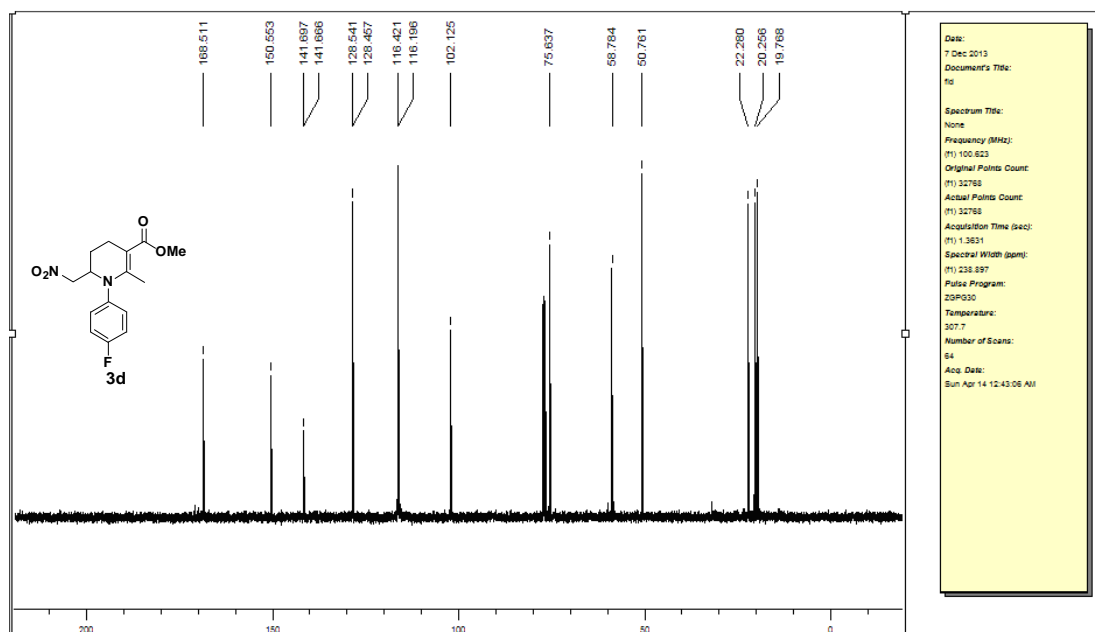
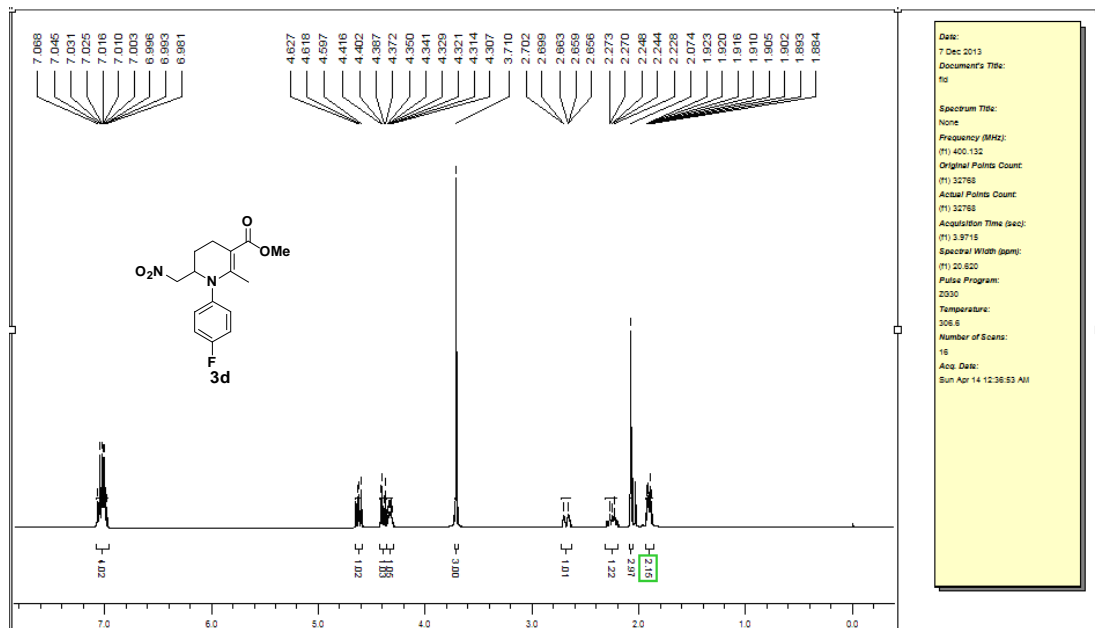
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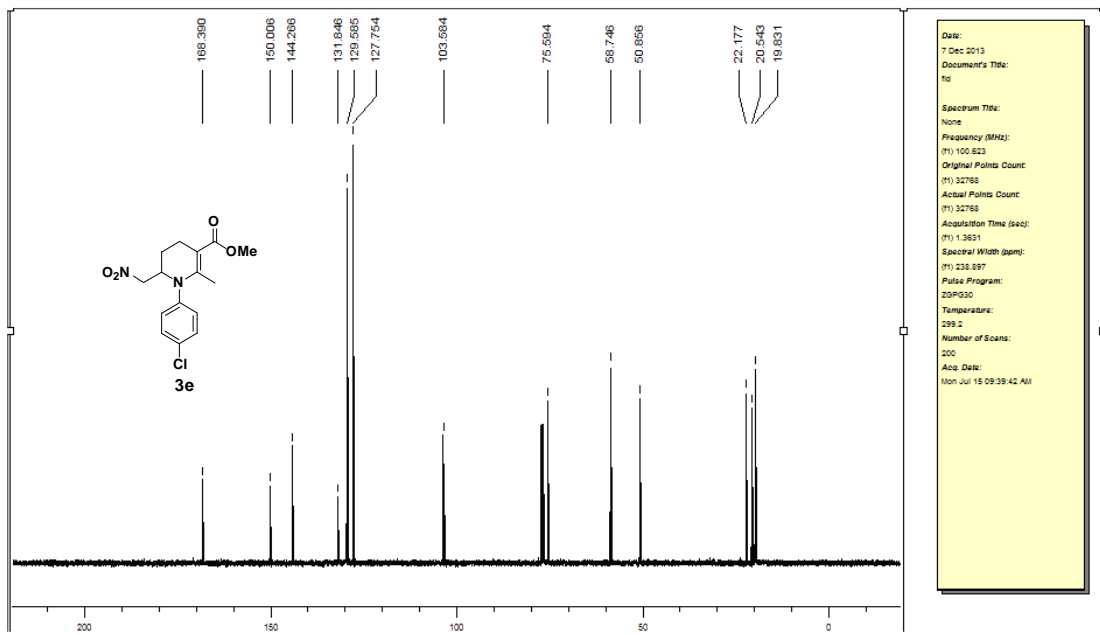
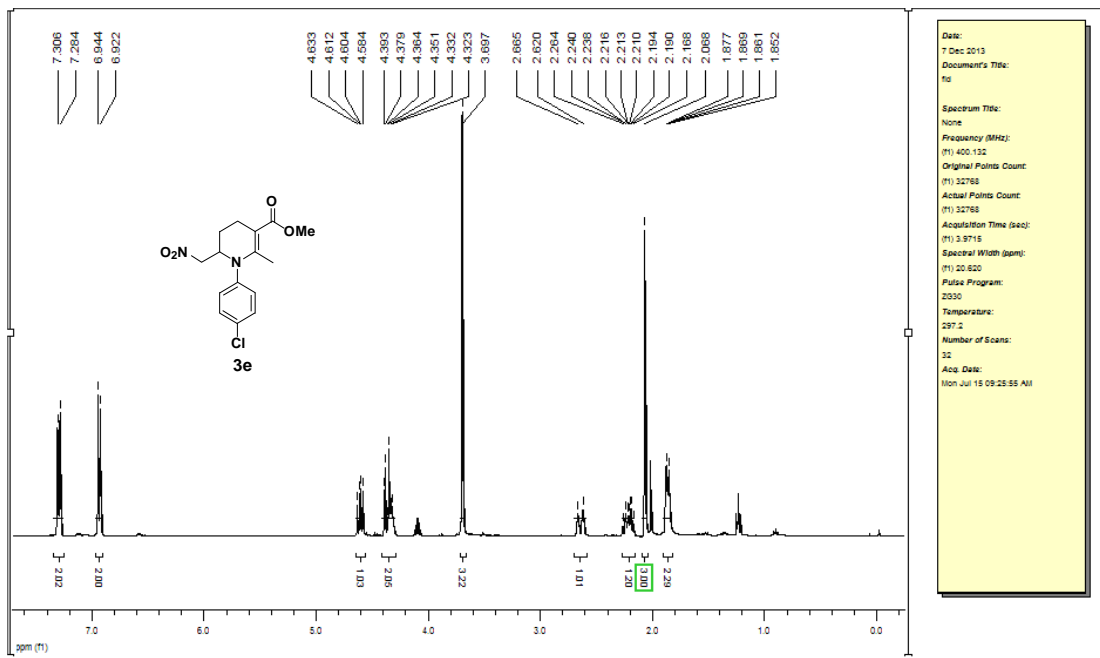


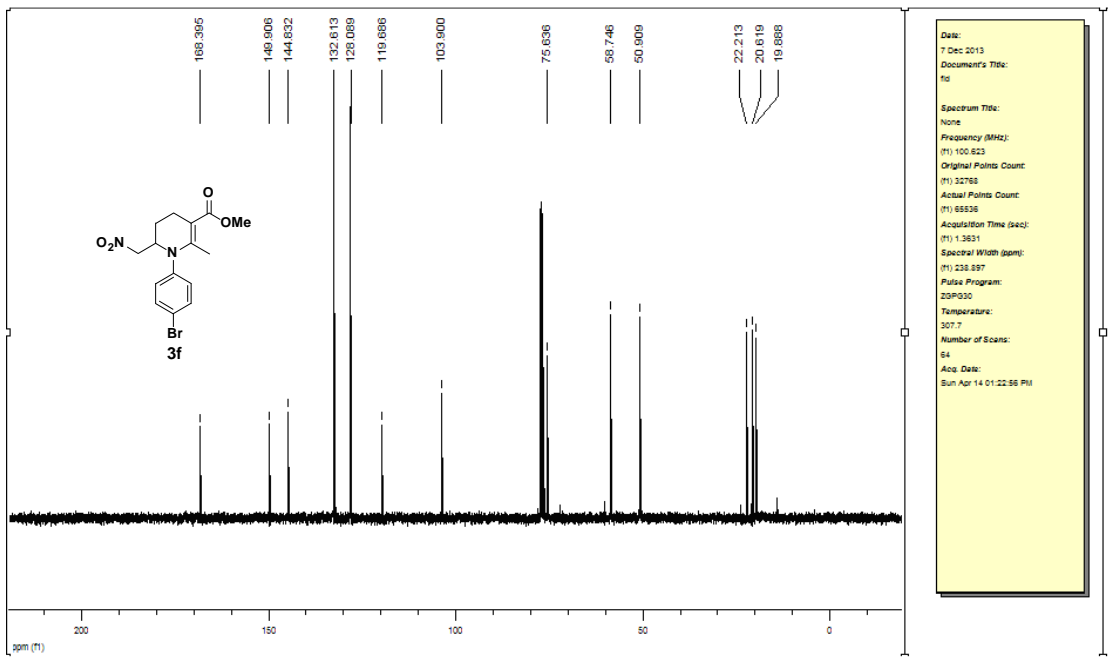
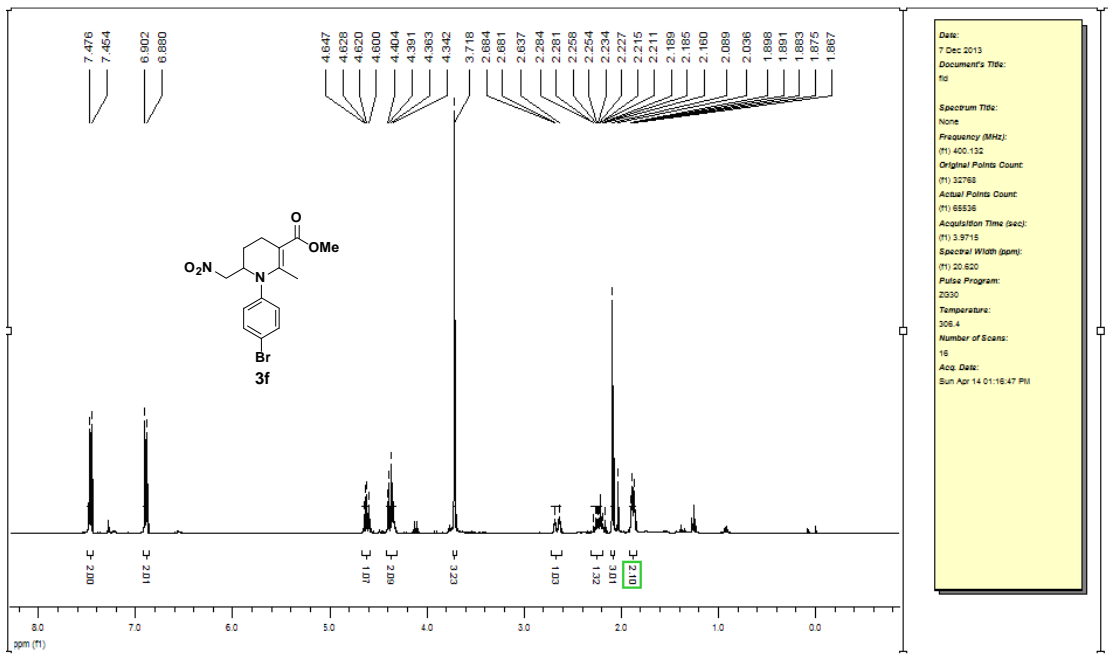
Date: 7 Dec 2013
Document's Title: fd
Spectrum Title: None
Frequency (MHz): (F1) 400.132
Original Points Count: (F1) 32768
Actual Points Count: (F1) 32768
Acquisition Time (sec): (F1) 3.9719
Spectral Width (ppm): (F1) 20.620
Pulse Program: zgpg30
Temperature: 306.5
Number of Scans: 16
Acq. Date: Sun Apr 14 01:04:55 PM

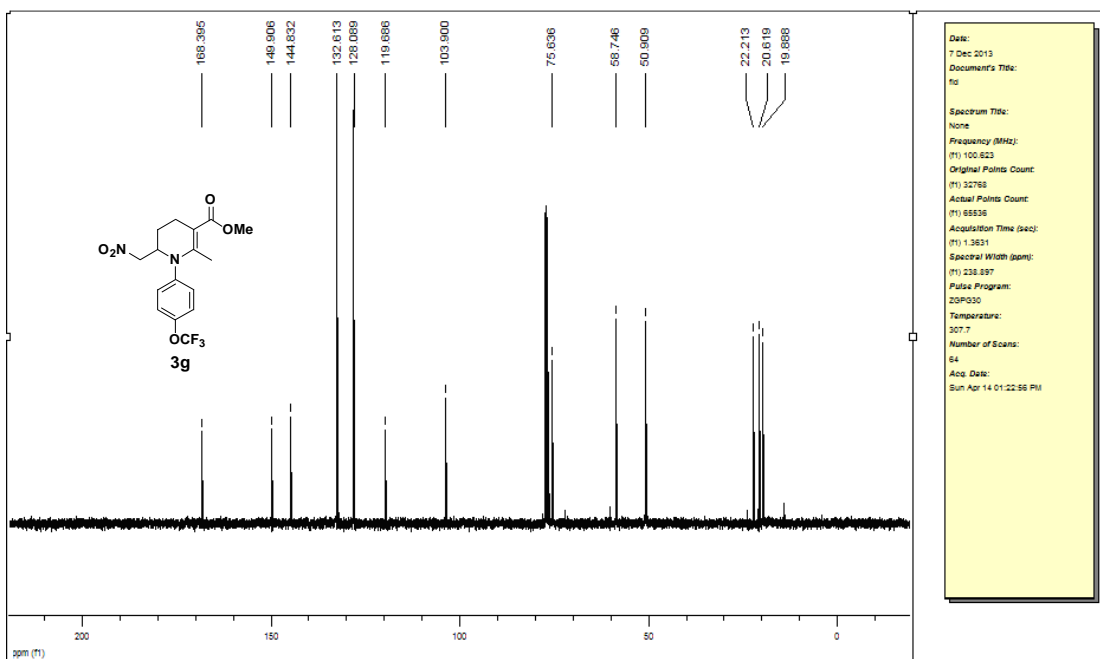
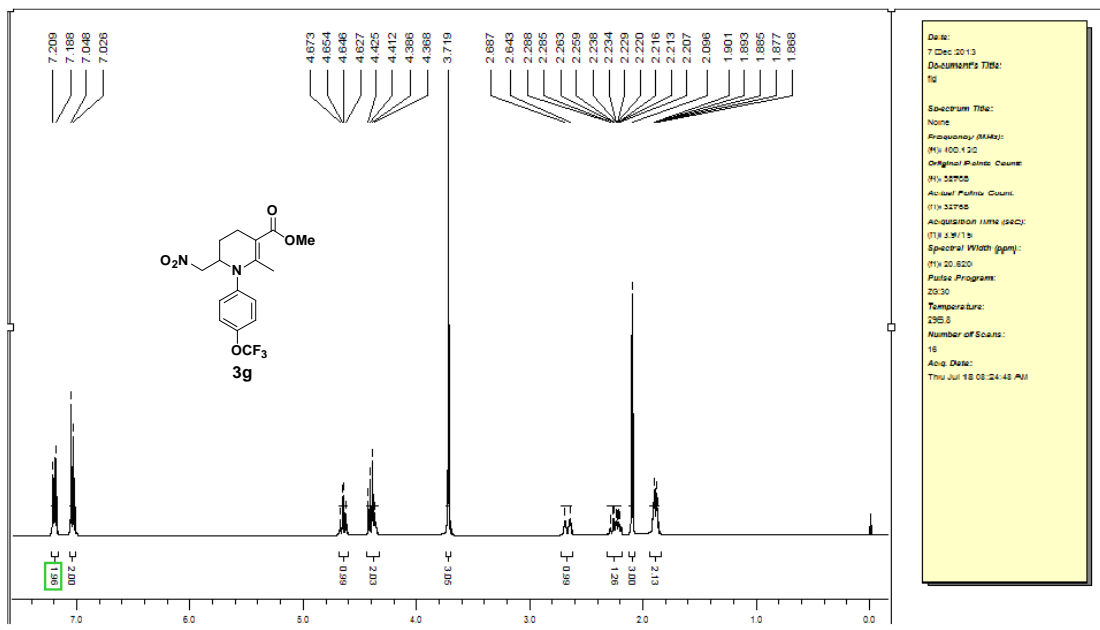


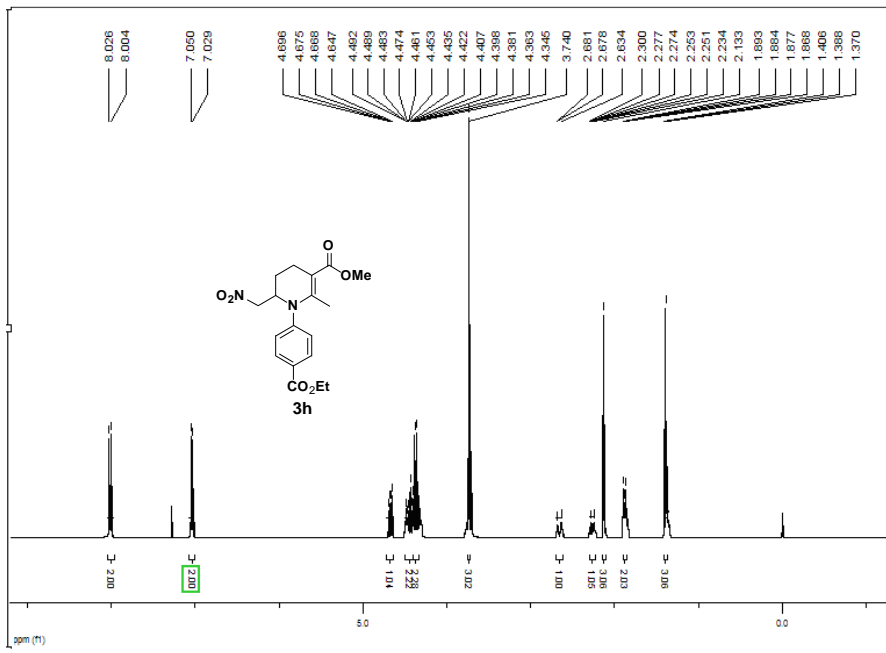
Date: 7 Dec 2013
Document's Title: fd
Spectrum Title: None
Frequency (MHz): (F1) 100.623
Original Points Count: (F1) 32768
Actual Points Count: (F1) 32768
Acquisition Time (sec): (F1) 1.3531
Spectral Width (ppm): (F1) 238.897
Pulse Program: zgpg30
Temperature: 307.7
Number of Scans: 64
Acq. Date: Sun Apr 14 01:11:00 PM



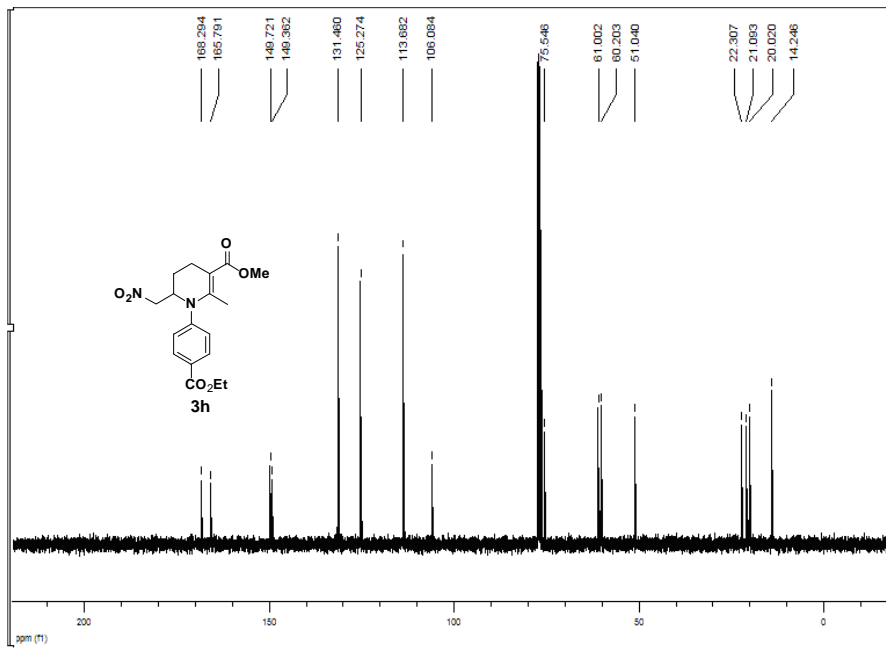




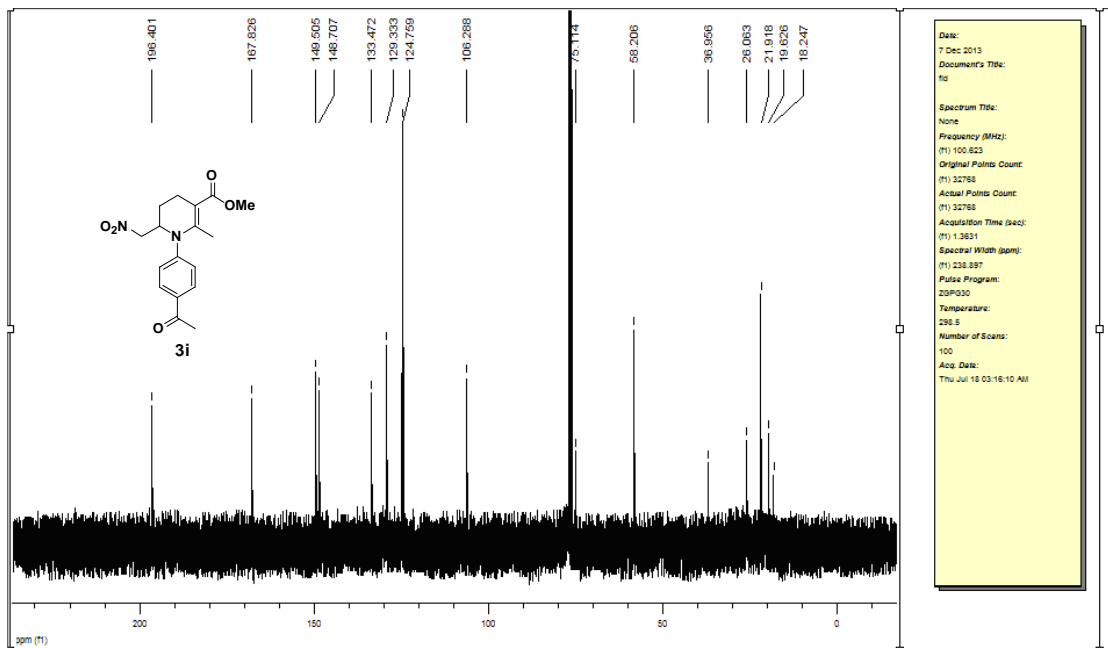
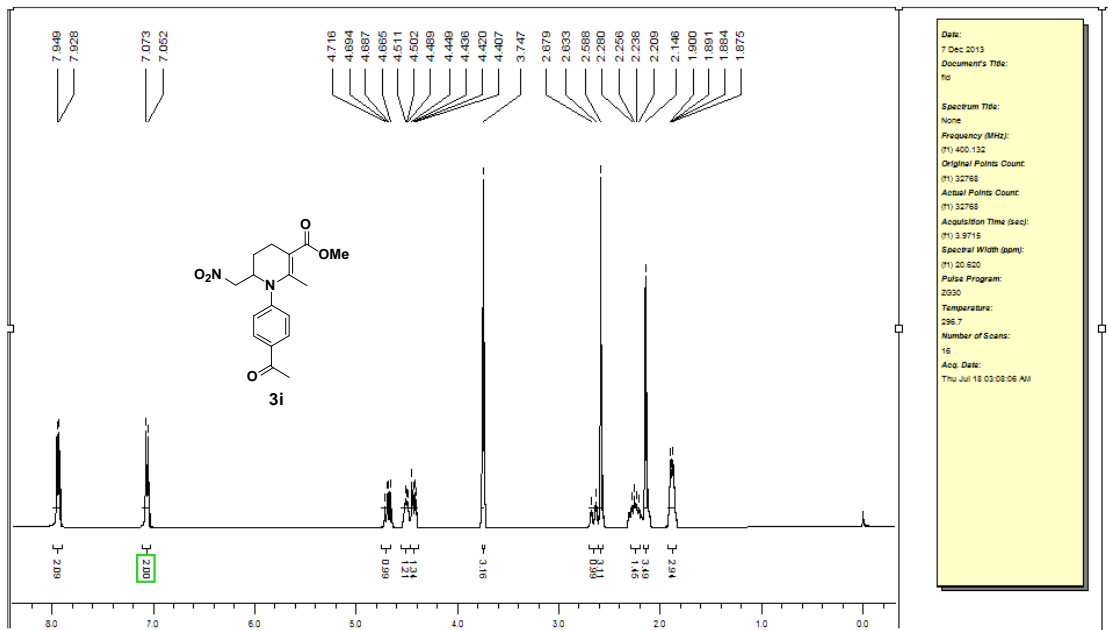


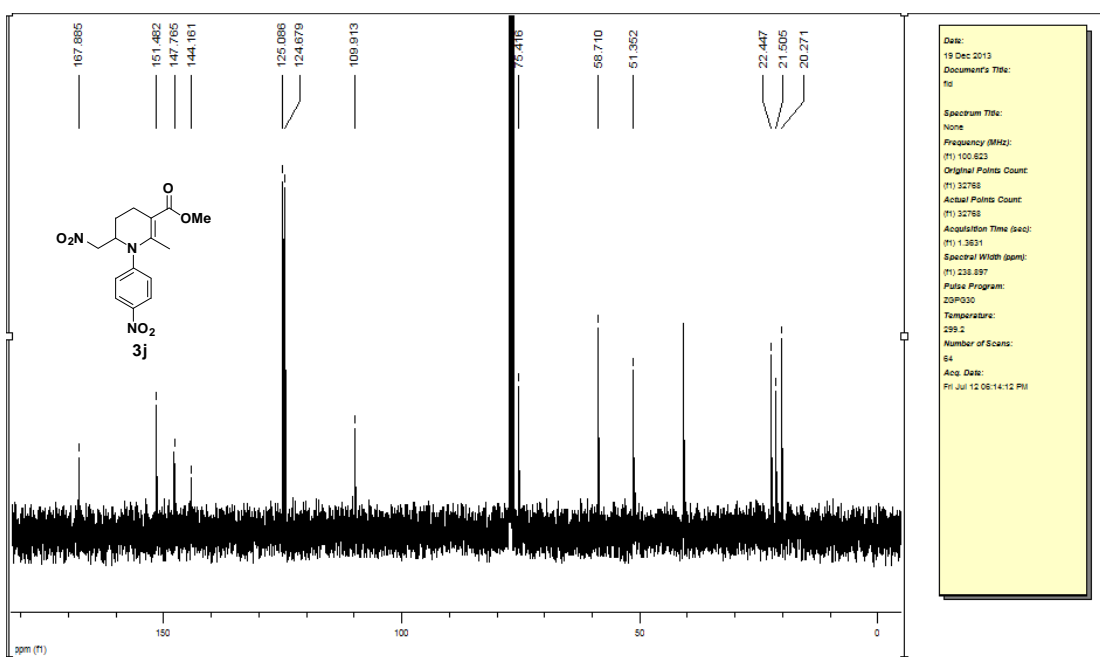
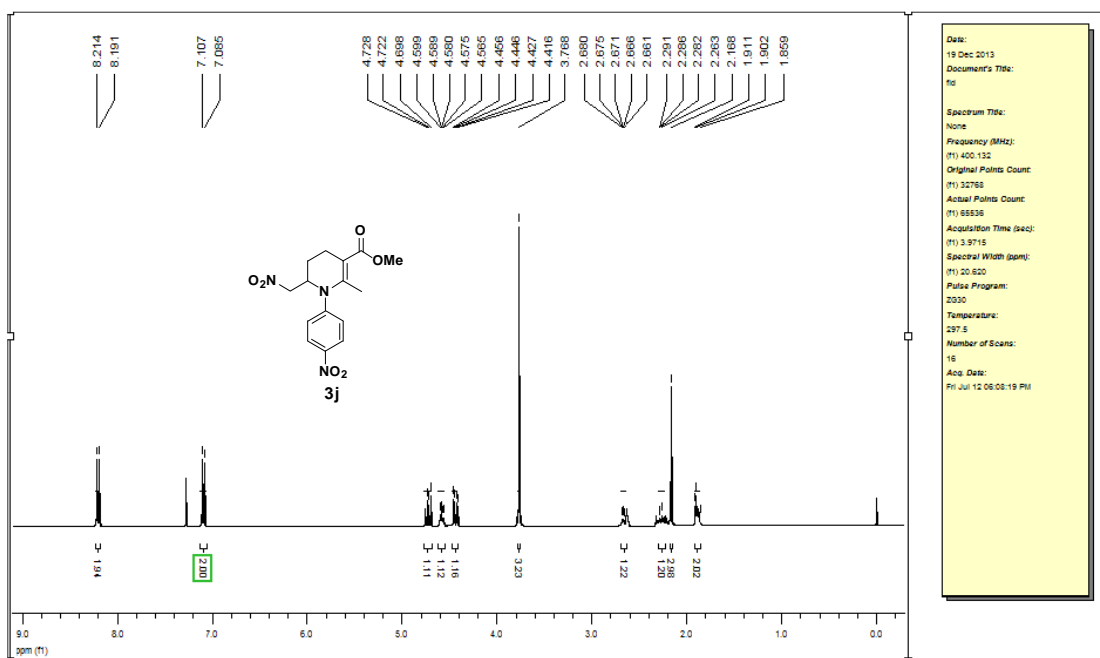


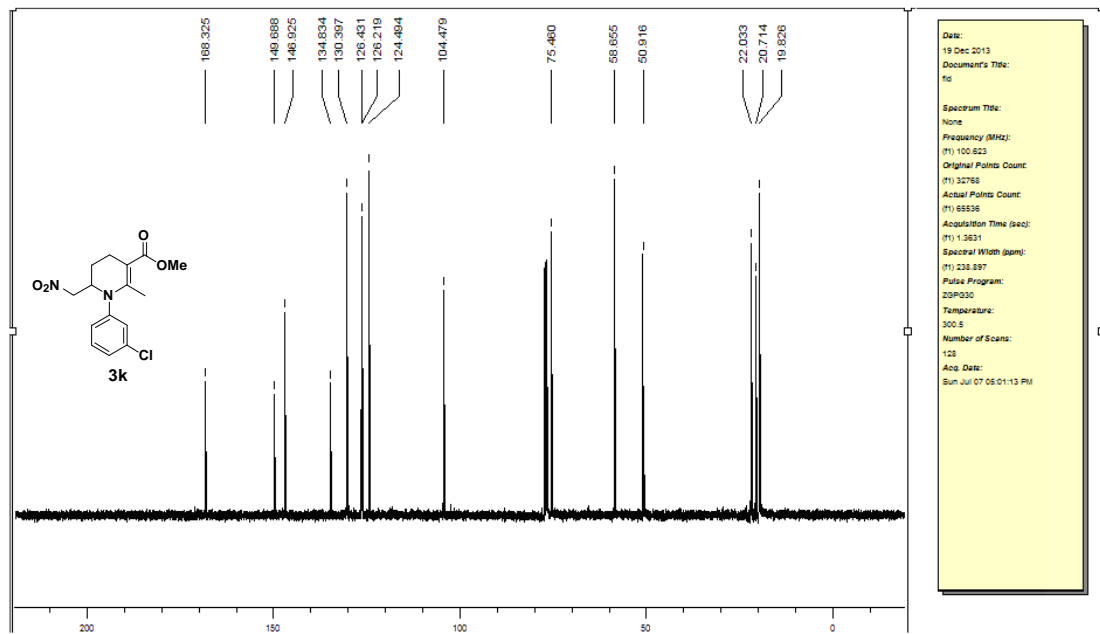
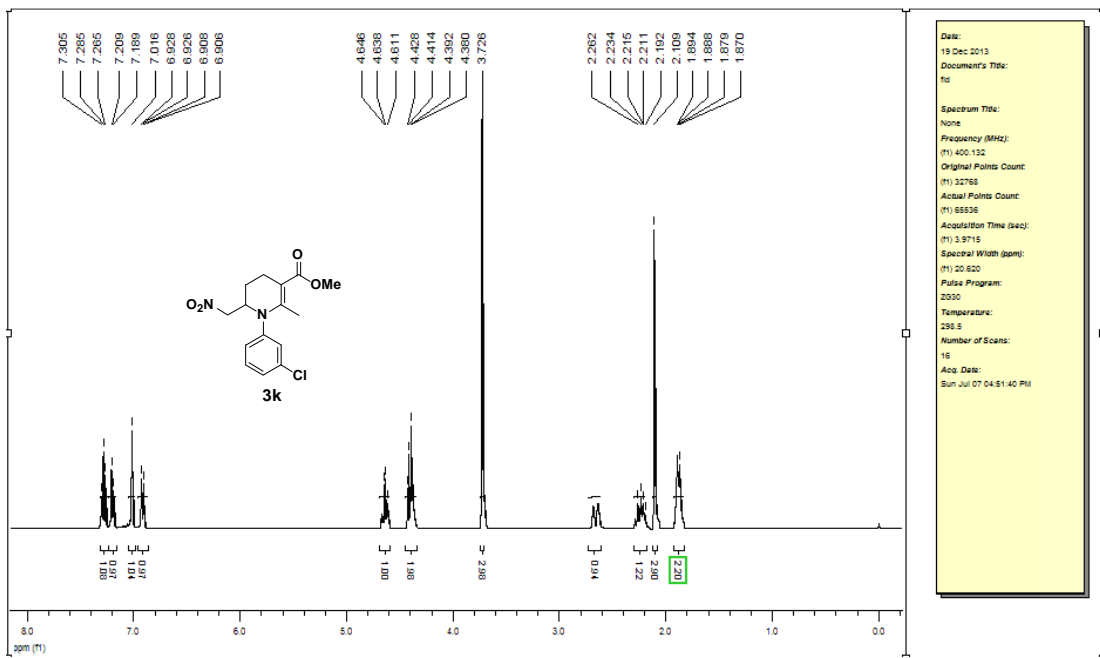
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 Acquisition Time (sec): (f1) 3.9715
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 Pulse Program: zgpg30
 Temperature: 303.4
 Number of Scans: 16
 Acq. Date: Fri Jul 05 06:50:16 PM

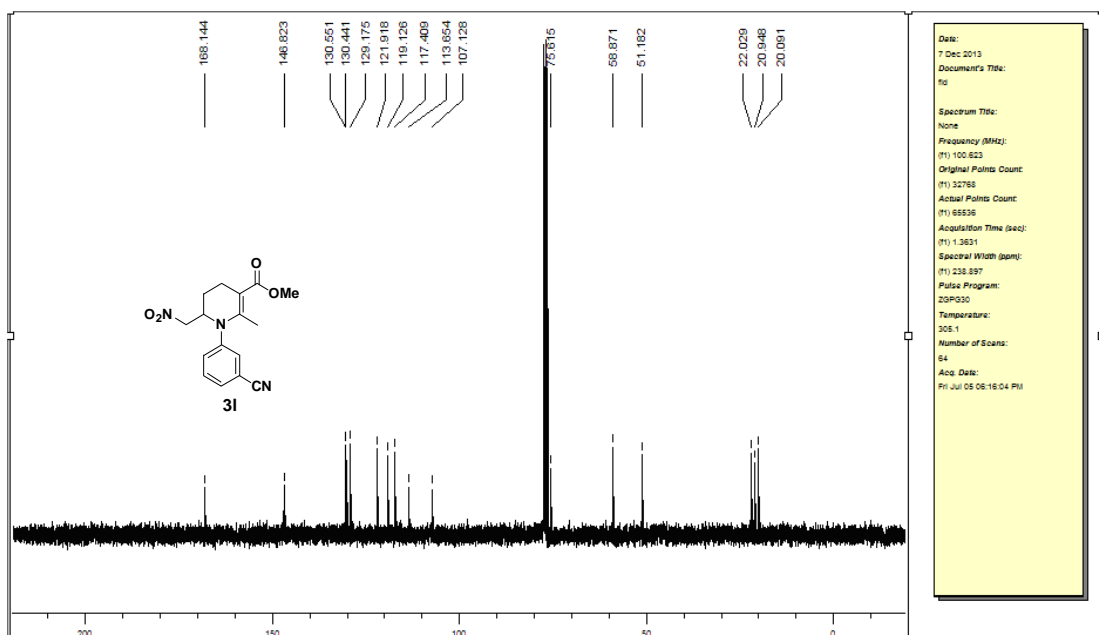
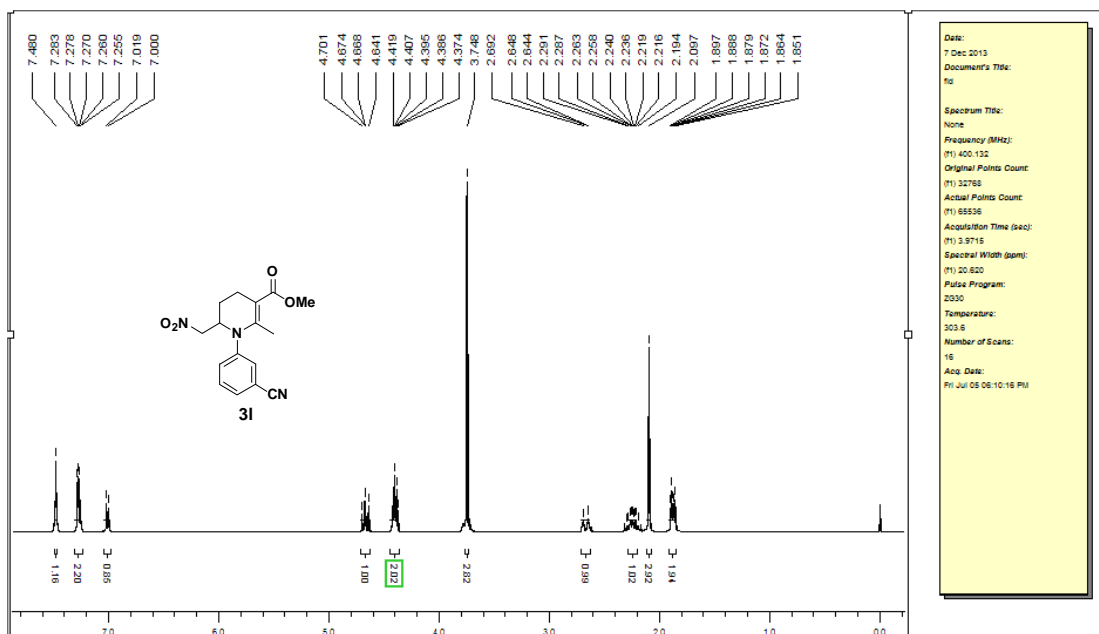


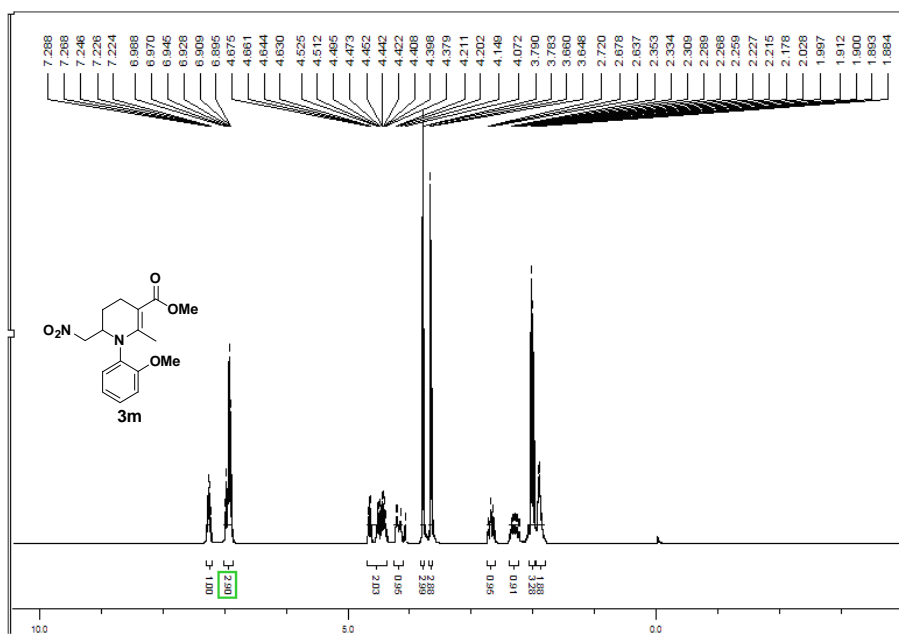
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 Original Points Count: (f1) 32768
 Actual Points Count: (f1) 32768
 Acquisition Time (sec): (f1) 1.3631
 Spectral Width (ppm): (f1) 238.897
 Pulse Program: zgpg30
 Temperature: 305.1
 Number of Scans: 128
 Acq. Date: Fri Jul 05 07:00:51 PM



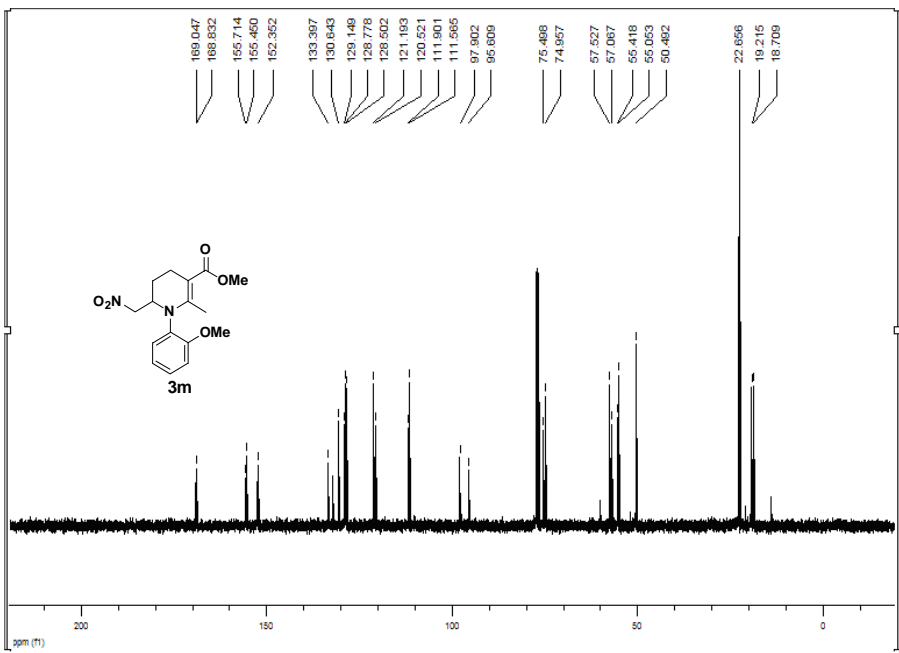




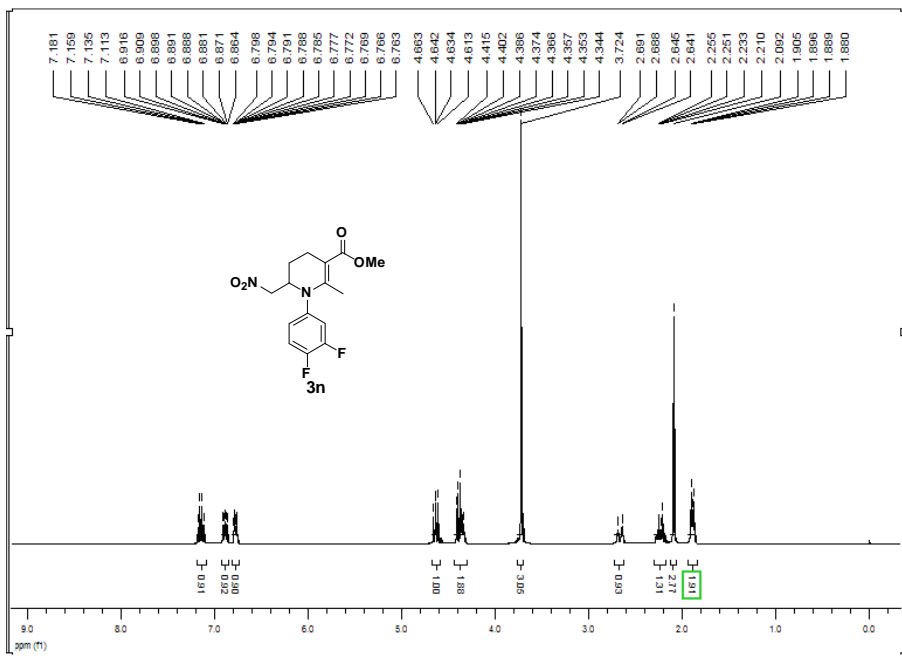




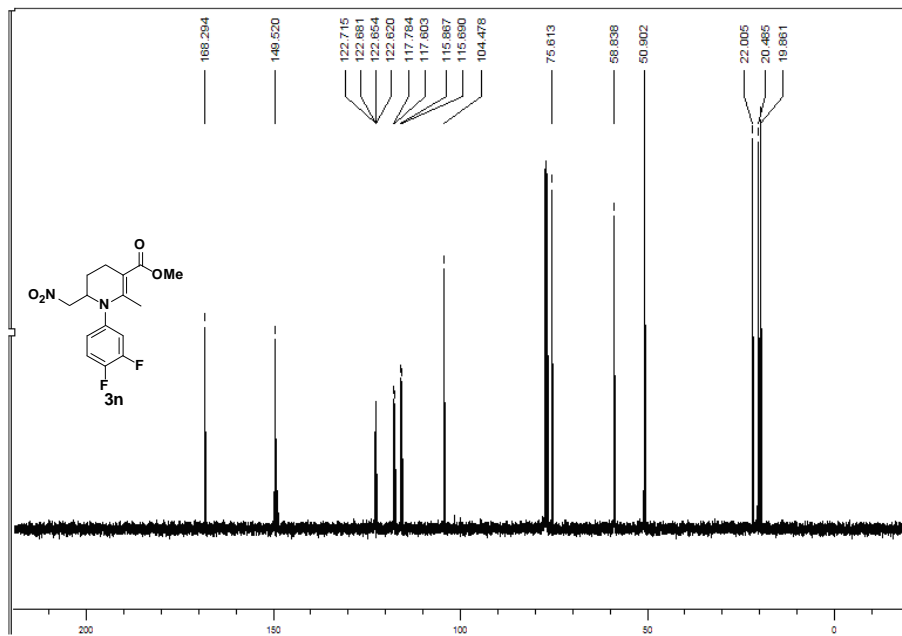
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Document's Title: fa
Spectrum Title: None
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Actual Points Count: (F1) 32788
Acquisition Time (sec): (T1) 3.5715
Spectral Width (ppm): (F1) 20.820
Pulse Program: 2930
Temperature: 303.2
Number of Scans: 16
Acq. Date: Fri Jul 05 08:41:22 PM



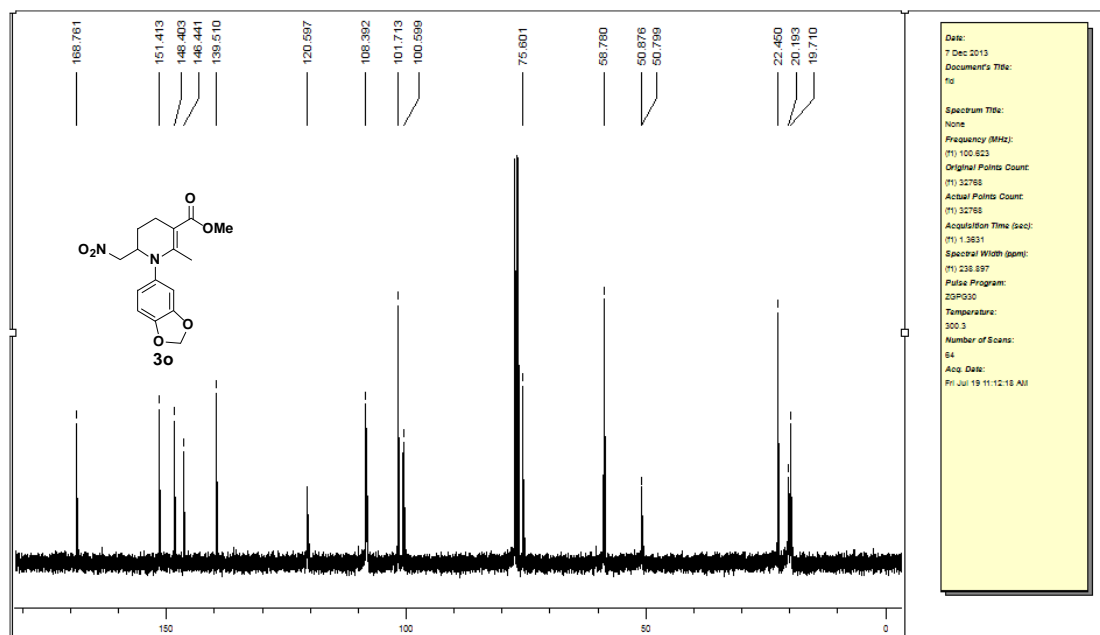
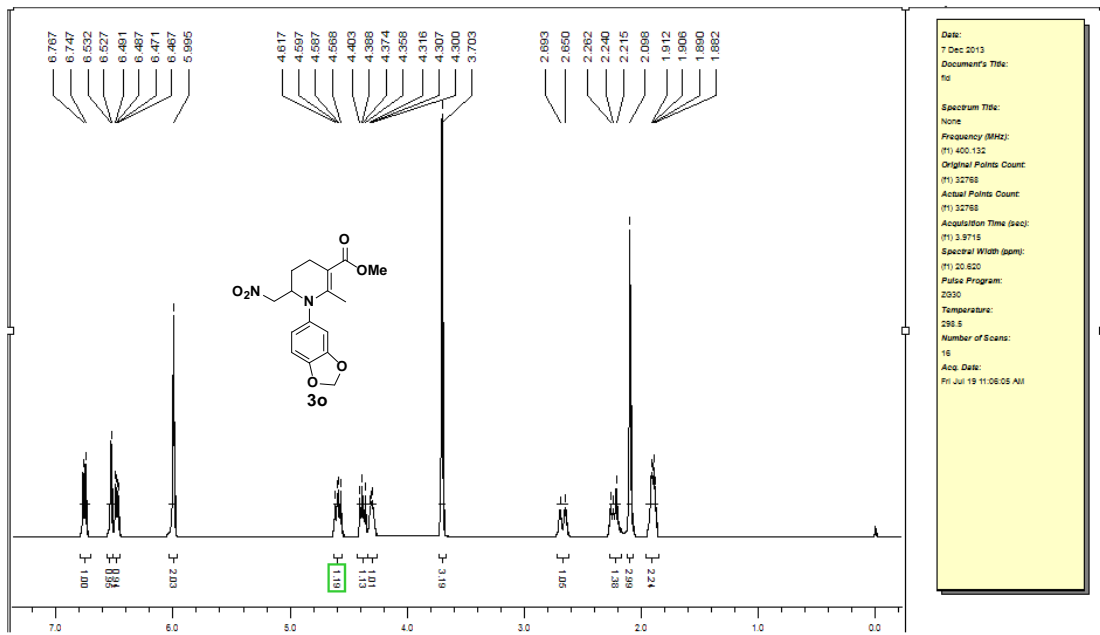
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Document's Title: fa
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Original Points Count: (F1) 32788
Actual Points Count: (F1) 65536
Acquisition Time (sec): (T1) 1.3631
Spectral Width (ppm): (F1) 238.897
Pulse Program: 2930
Temperature: 304.8
Number of Scans: 64
Acq. Date: Fri Jul 05 08:47:43 PM

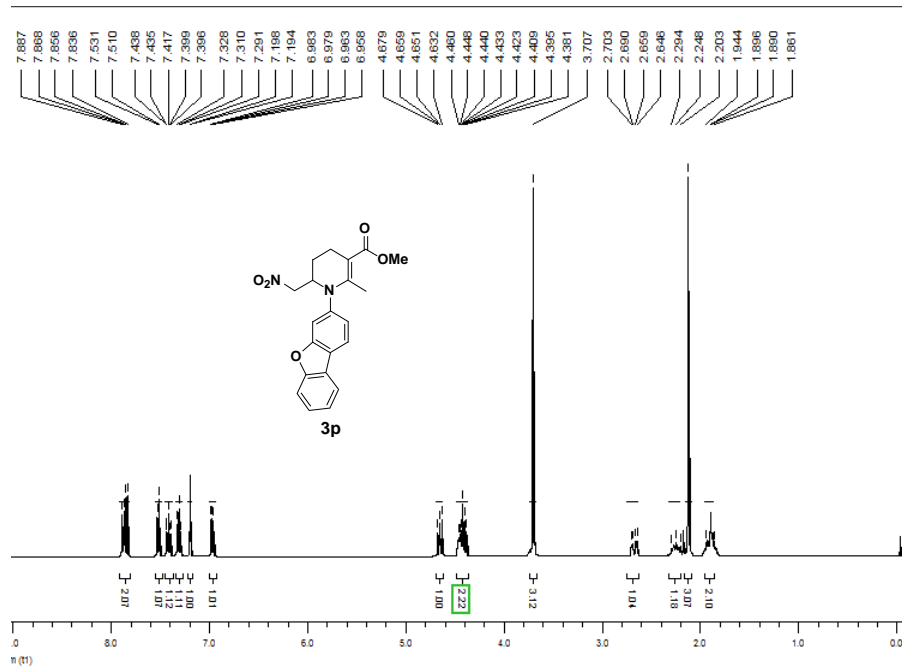


Date: 18 Dec 2013
 Document's Title: f1
 Spectrum Title: None
 Frequency (MHz): (F1) 400.132
 Original Points Count: (F1) 32768
 Actual Points Count: (F1) 65536
 Acquisition Time (sec): (F1) 3.9715
 Spectral Width (ppm): (F1) 20.620
 Pulse Program: 2DPSO
 Temperature: 304.1
 Number of Scans: 16
 Acq. Date: Wed Apr 03 02:50:48 AM

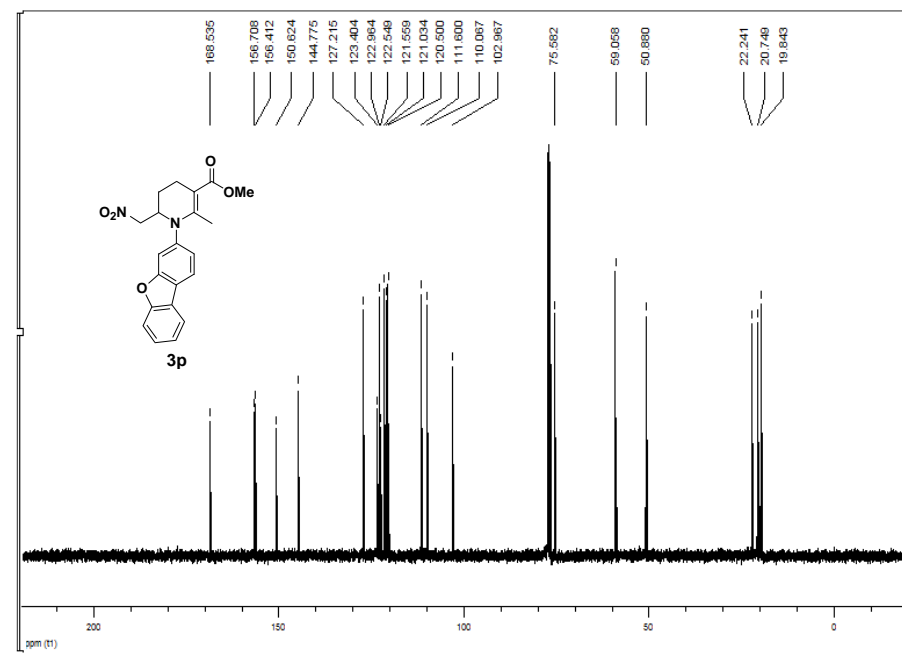


Date: 18 Dec 2013
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 Actual Points Count: (F1) 32768
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 Pulse Program: 2DPSO
 Temperature: 305.1
 Number of Scans: 64
 Acq. Date: Wed Apr 03 02:58:39 AM

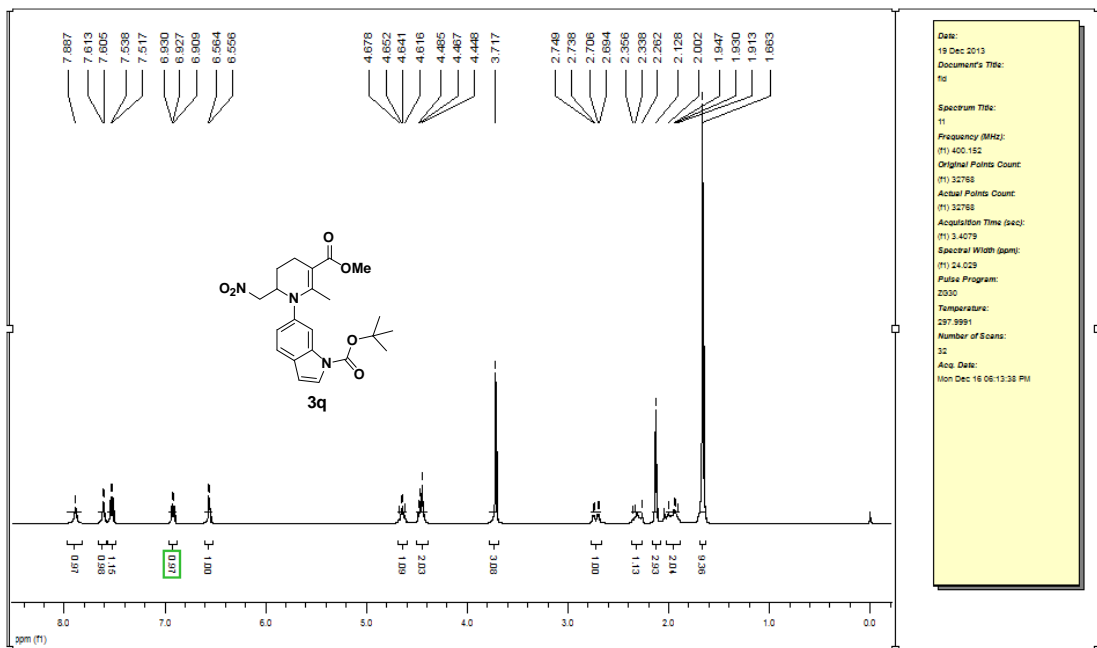




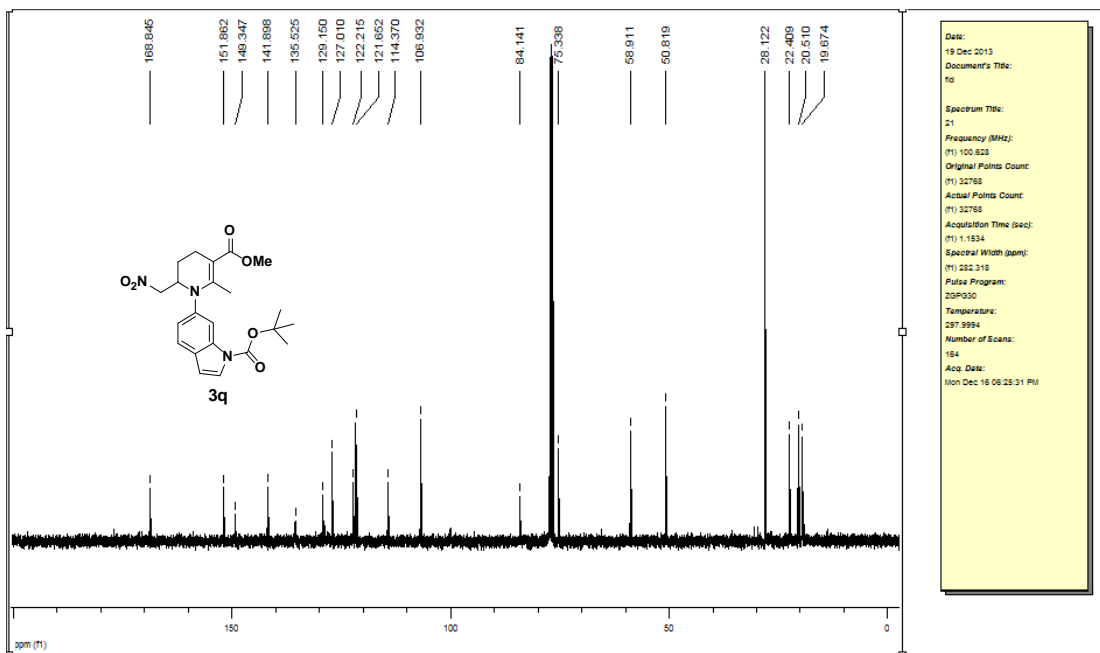
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 Actual Points Count: (F1) 65536
 Acquisition Time (sec): (F1) 3.9715
 Spectral Width (ppm): (F1) 20.620
 Pulse Program: zgpg30
 Temperature: 297.4
 Number of Scans: 16
 Acq. Date: Mon Jun 17 06:11:58 PM



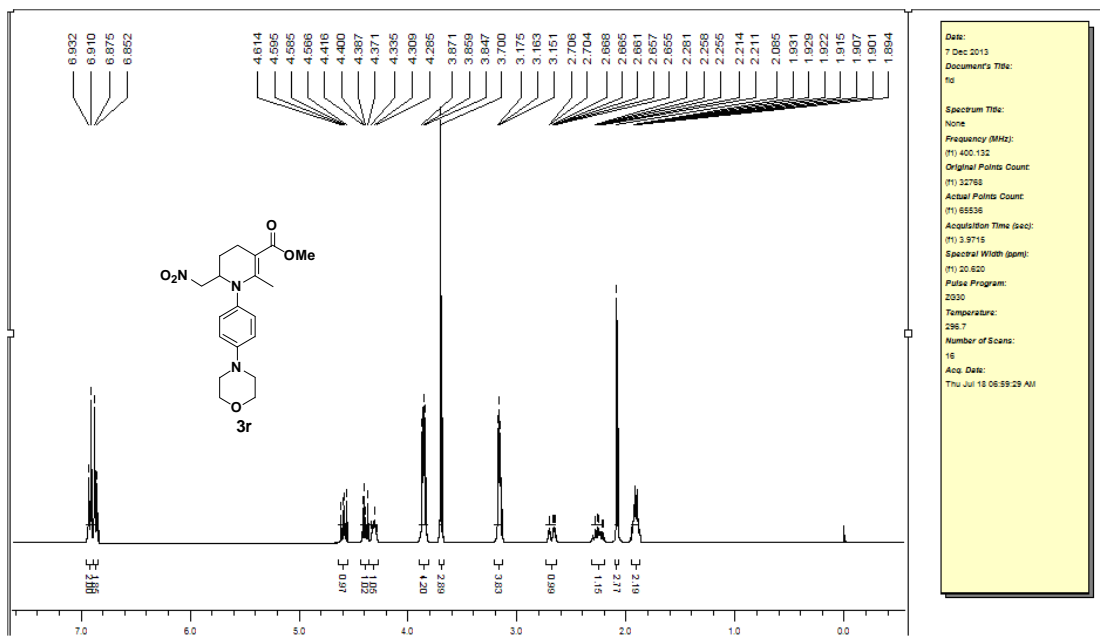
Date: 10 Dec 2013
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 Original Points Count: (F1) 32768
 Actual Points Count: (F1) 65536
 Acquisition Time (sec): (F1) 1.3631
 Spectral Width (ppm): (F1) 238.897
 Pulse Program: zgpg30
 Temperature: 299.2
 Number of Scans: 128
 Acq. Date: Mon Jun 17 06:21:32 PM



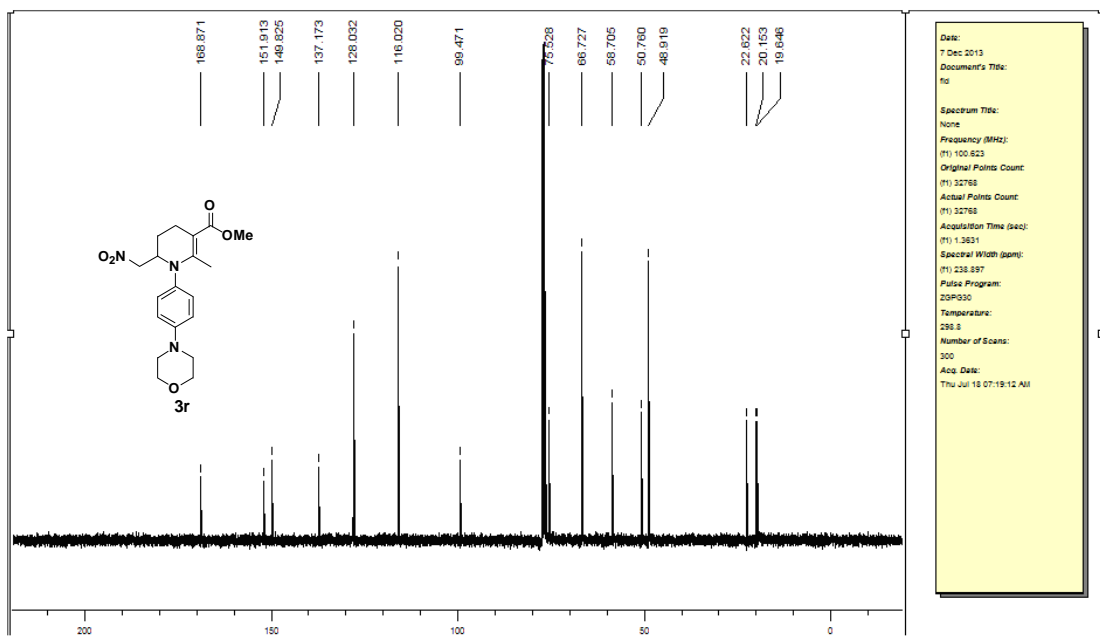
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 Document's Title: 1d
 Spectrum Title: 11
 Frequency (MHz): (F1) 400.152
 Original Points Count: (F1) 32768
 Actual Points Count: (F1) 32768
 Acquisition Time (sec): (F1) 3.4079
 Spectral Width (ppm): (F1) 24.029
 Pulse Program: zgpg30
 Temperature: 297.9991
 Number of Scans: 32
 Acq. Date: Mon Dec 16 08:13:38 PM



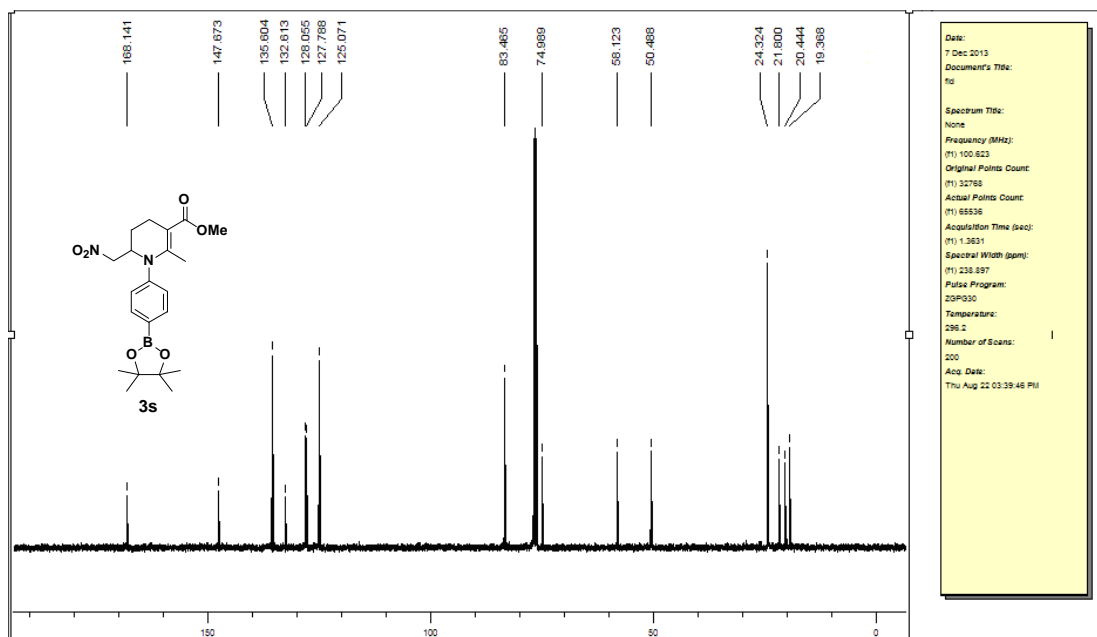
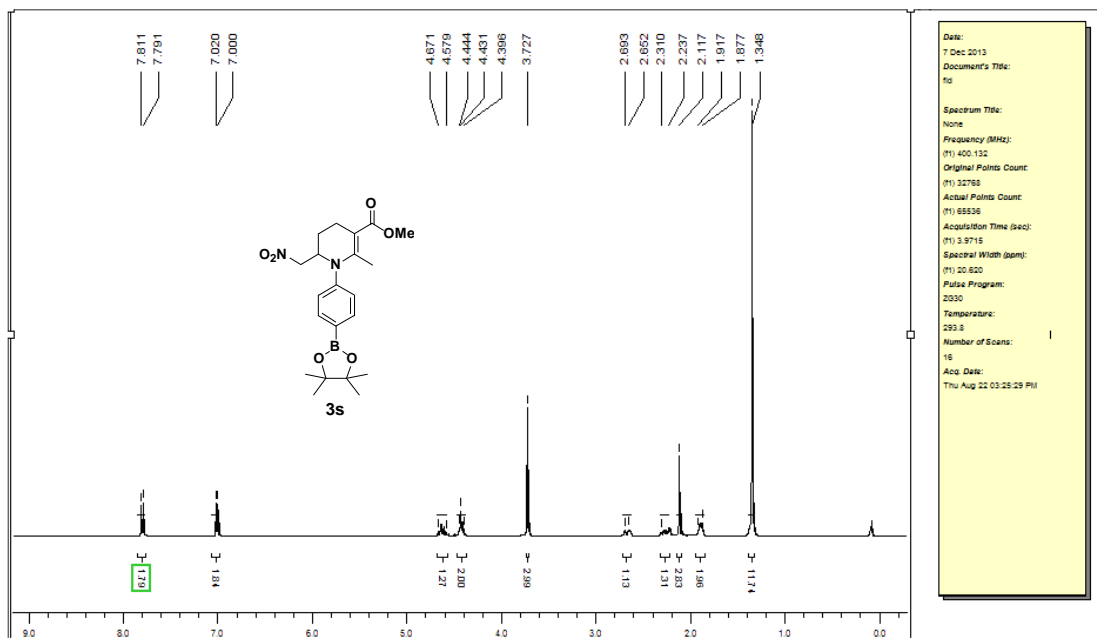
Date: 19 Dec 2013
 Document's Title: 1d
 Spectrum Title: 21
 Frequency (MHz): (F1) 100.623
 Original Points Count: (F1) 32768
 Actual Points Count: (F1) 32768
 Acquisition Time (sec): (F1) 1.1834
 Spectral Width (ppm): (F1) 282.318
 Pulse Program: zgpg30
 Temperature: 297.9994
 Number of Scans: 164
 Acq. Date: Mon Dec 16 08:28:31 PM

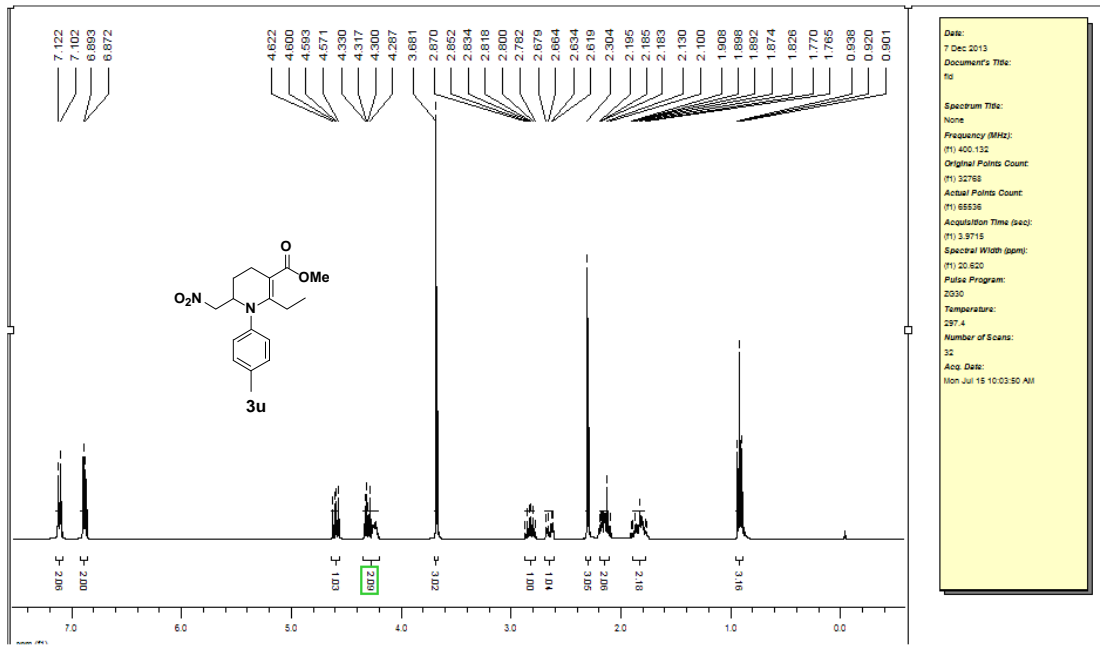


Date: 7 Dec 2013
 Document's Title: fo
 Spectrum Title: None
 Frequency (MHz): (F1) 400.133
 Original Points Count: (P1) 32768
 Actual Points Count: (F1) 65536
 Acquisition Time (sec): (T1) 3.9716
 Spectral Width (ppm): (W1) 20.620
 Pulse Program: zgpg30
 Temperature: 298.7
 Number of Scans: 16
 Acq. Date: Thu Jul 18 06:59:23 AM

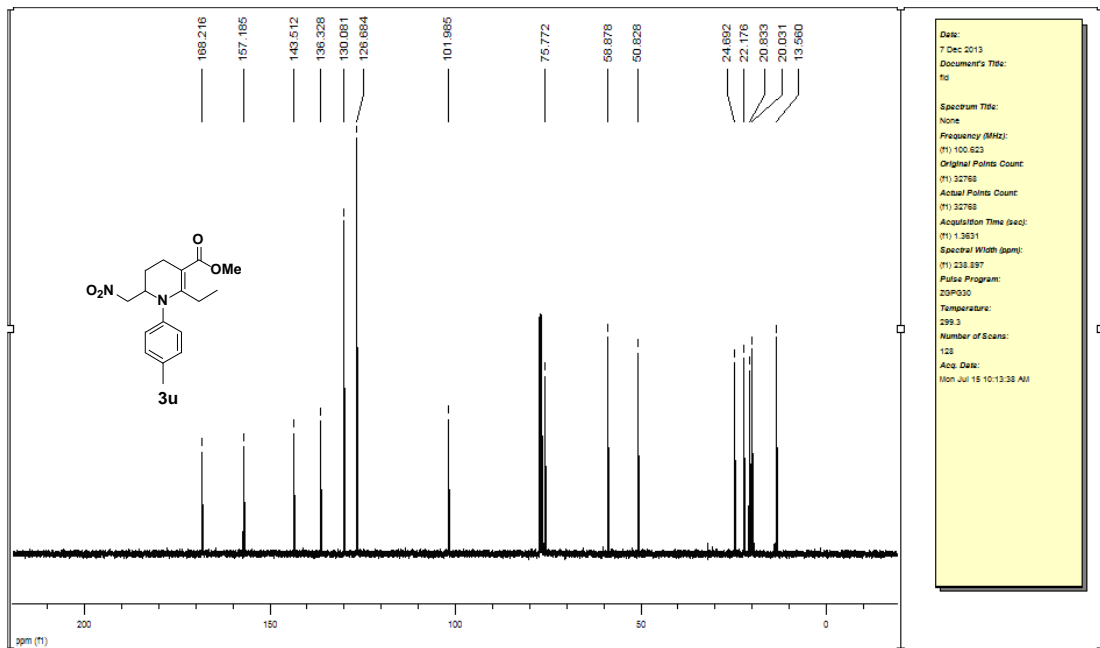


Date: 7 Dec 2013
 Document's Title: fo
 Spectrum Title: None
 Frequency (MHz): (F1) 100.623
 Original Points Count: (P1) 32768
 Actual Points Count: (F1) 32768
 Acquisition Time (sec): (T1) 1.3631
 Spectral Width (ppm): (W1) 238.897
 Pulse Program: zgpg30
 Temperature: 298.8
 Number of Scans: 300
 Acq. Date: Thu Jul 18 07:19:12 AM

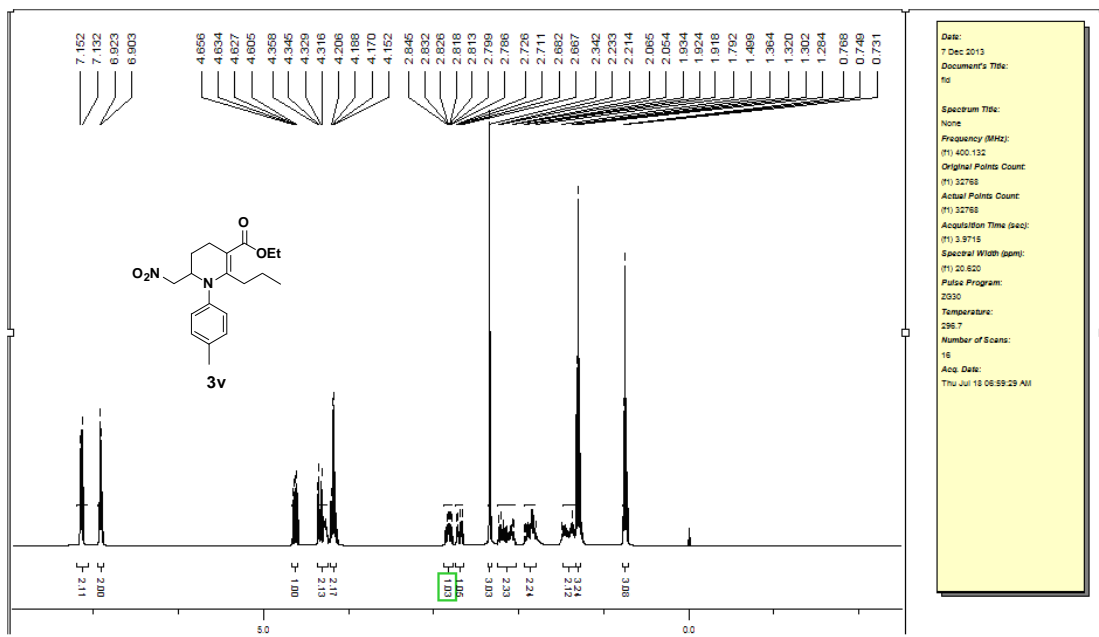




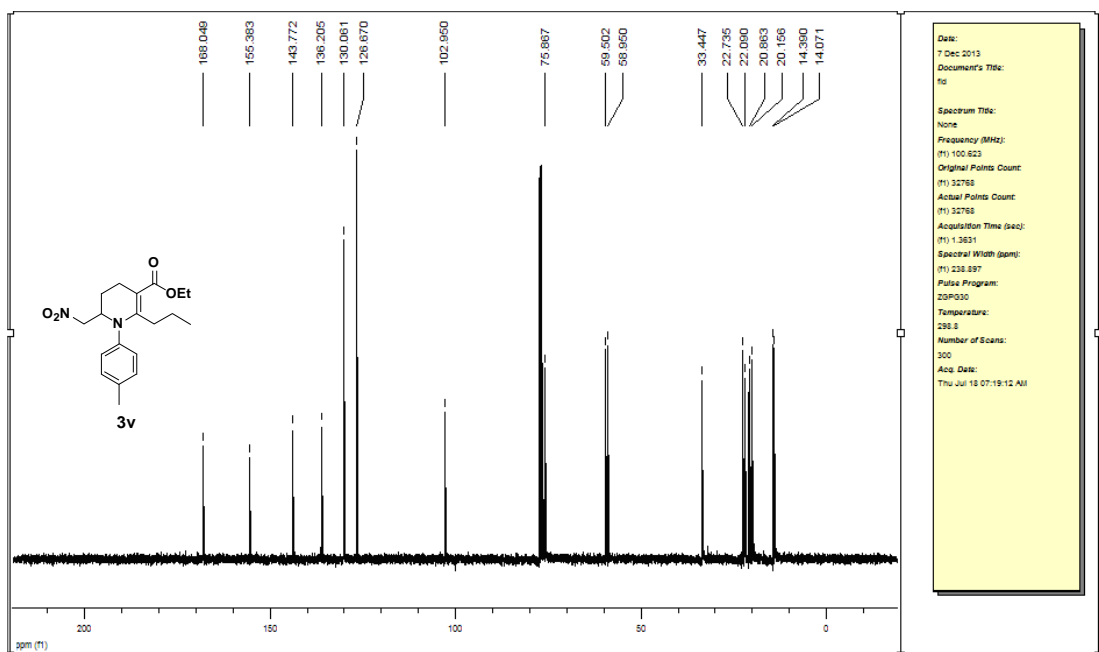
Date: 7 Dec 2013
 Document's Title: fd
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 Frequency (MHz): (F1) 400.132
 Original Points Count: (F1) 32768
 Actual Points Count: (F1) 65536
 Acquisition Time (sec): (F1) 3.9715
 Spectral Width (ppm): (F1) 20.620
 Pulse Program: ZG30
 Temperature: 297.4
 Number of Scans: 32
 Acq. Date: Mon Jul 15 10:03:50 AM



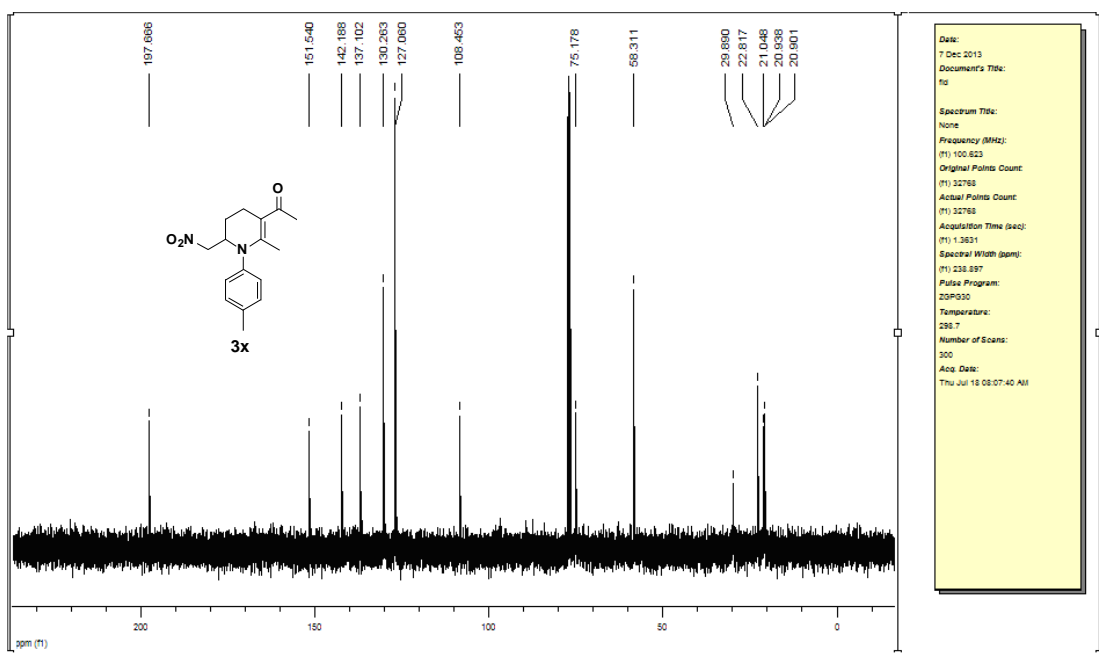
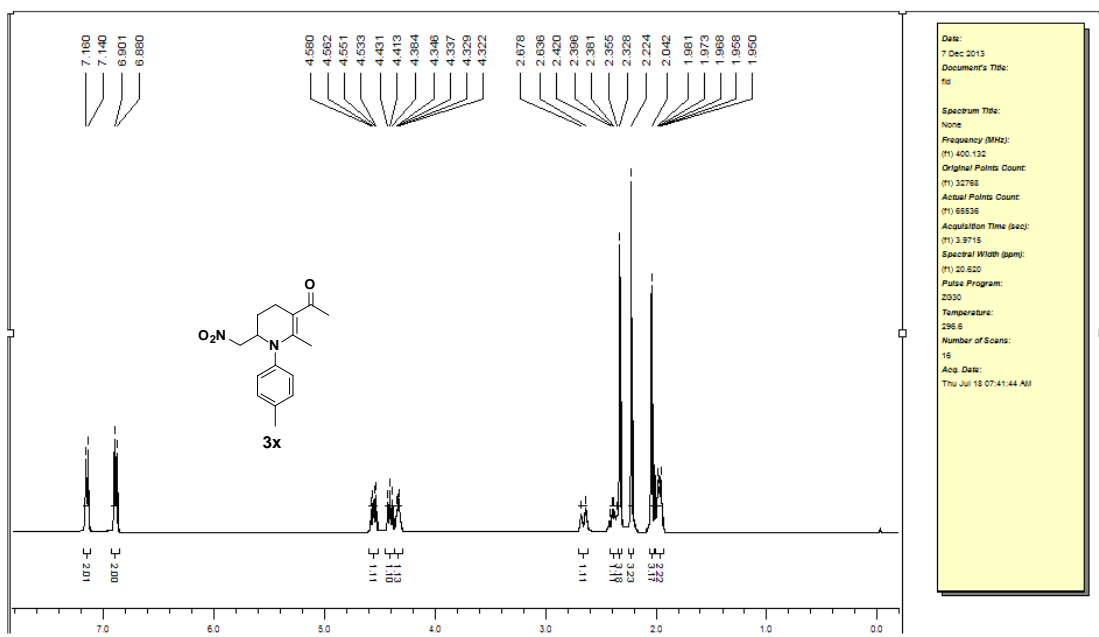
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 Actual Points Count: (F1) 32768
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 Spectral Width (ppm): (F1) 238.997
 Pulse Program: zgpg30
 Temperature: 299.3
 Number of Scans: 128
 Acq. Date: Mon Jul 15 10:13:38 AM

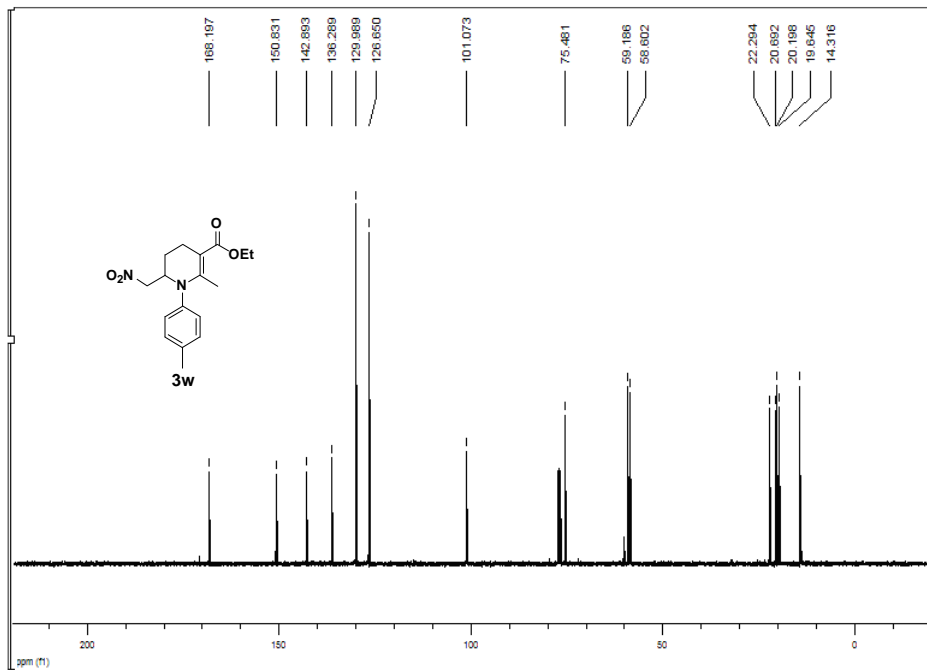
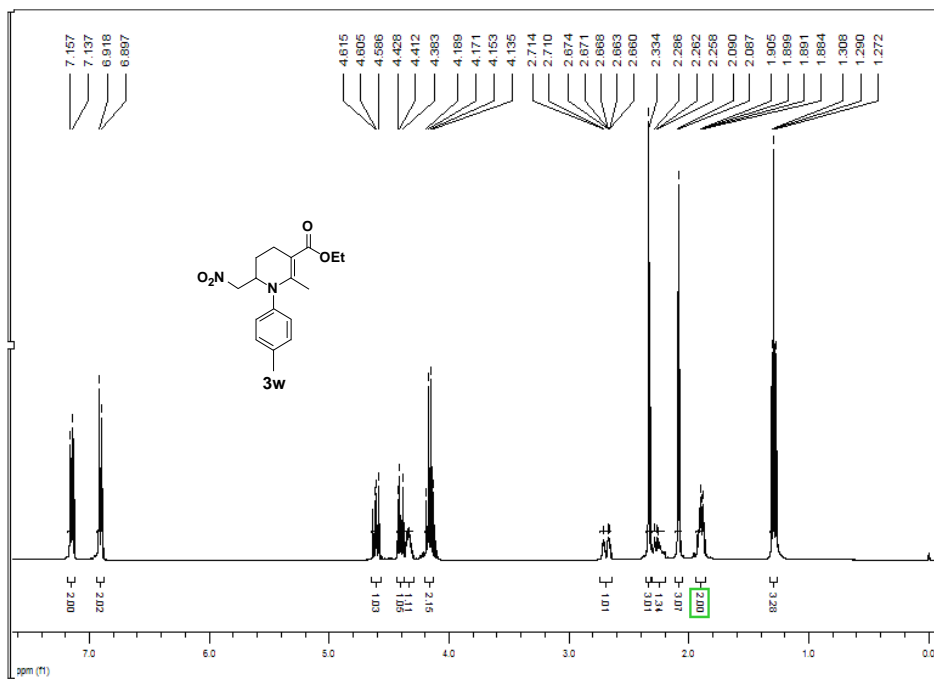


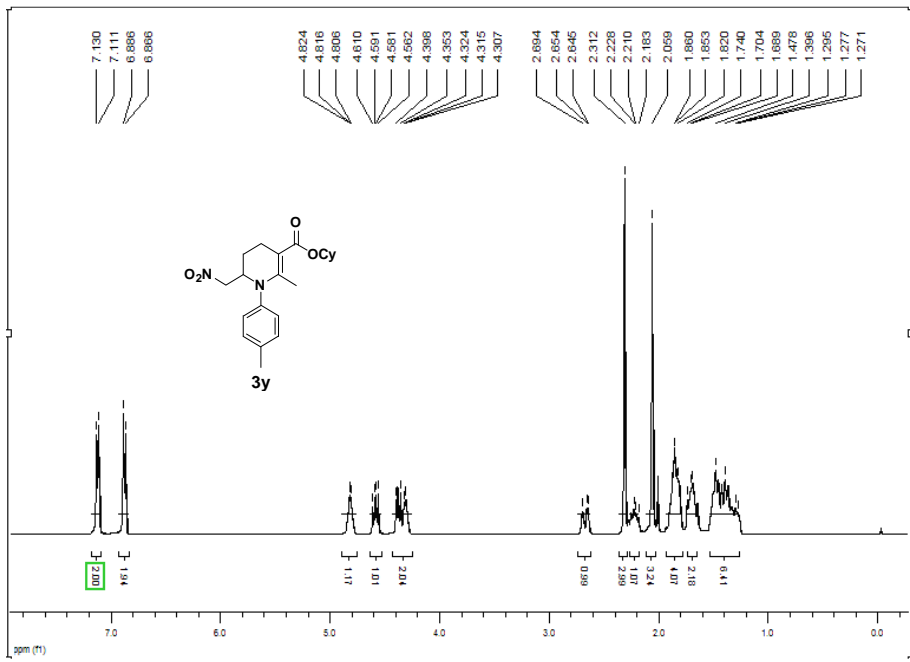
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 Actual Points Count: (F1) 32768
 Acquisition Time (sec): (F1) 3.9715
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 Pulse Program: zgpg30
 Temperature: 298.7
 Number of Scans: 16
 Acq. Date: Thu Jul 18 06:59:29 AM



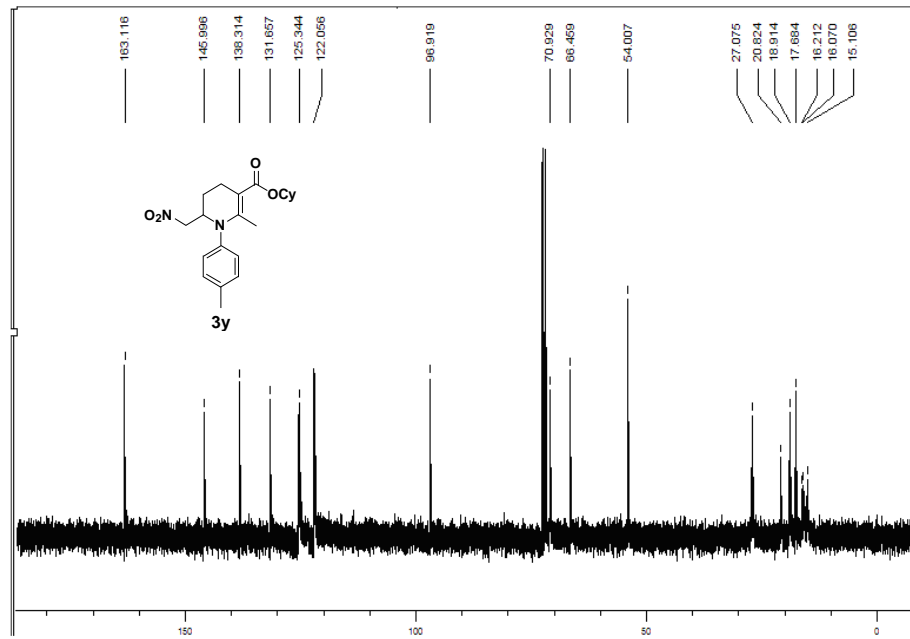
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 Temperature: 298.8
 Number of Scans: 300
 Acq. Date: Thu Jul 18 07:19:12 AM



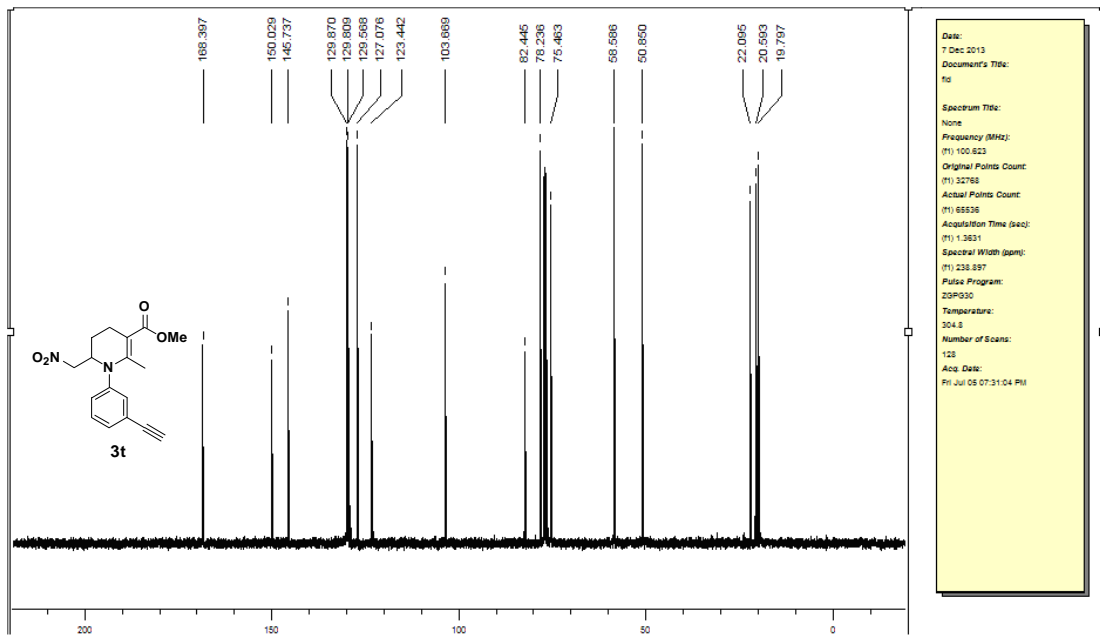
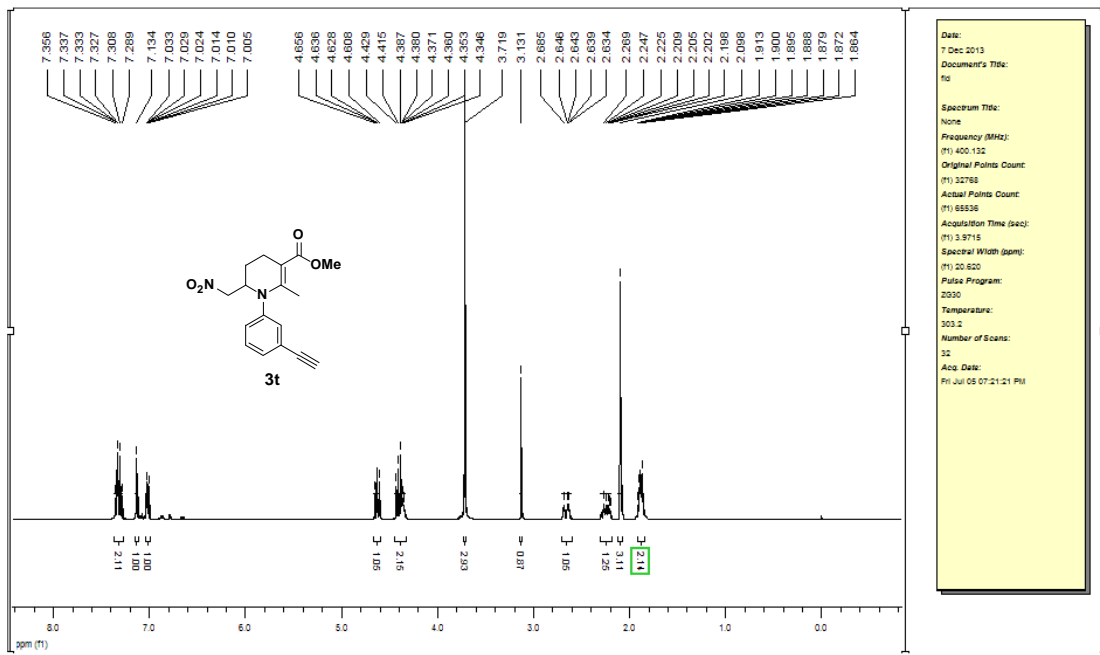


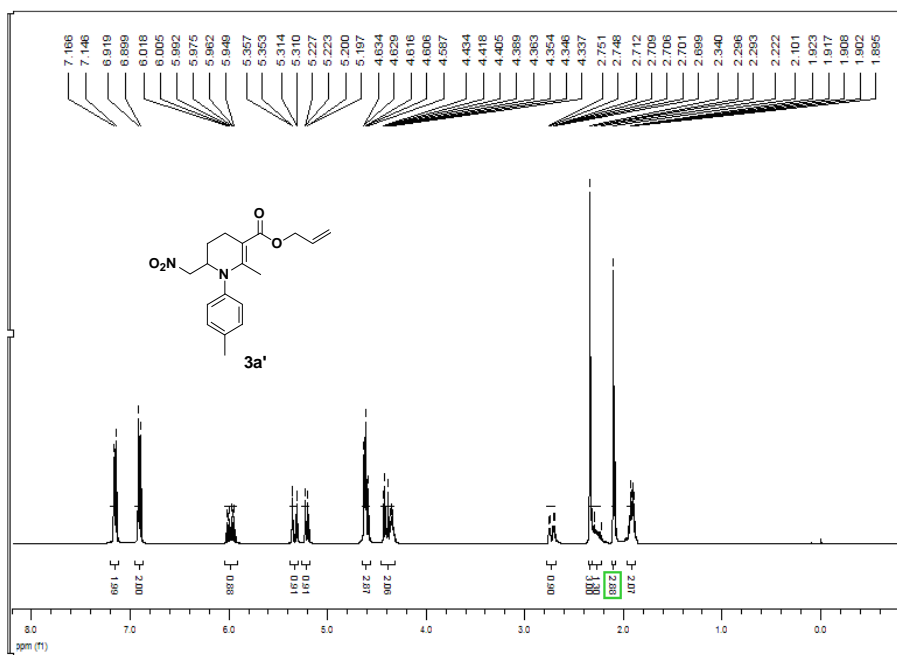


Date: 7 Dec 2013
 Document's Title: fo
 Spectrum Title: new experiment
 Frequency (MHz): (f1) 399.794
 Original Points Count: (f1) 16384
 Actual Points Count: (f1) 52768
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 Spectral Width (ppm): (f1) 16.034
 Pulse Program: s2oul
 Temperature: 35
 Number of Scans: 16
 Acq. Date: Jul 29 2013

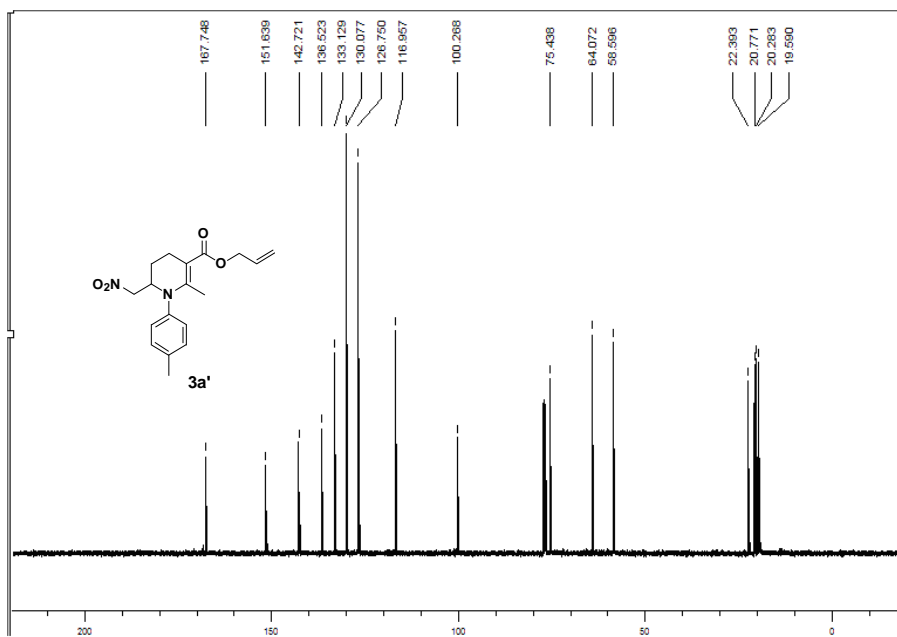


Date: 7 Dec 2013
 Document's Title: fo
 Spectrum Title: new experiment
 Frequency (MHz): (f1) 100.629
 Original Points Count: (f1) 32768
 Actual Points Count: (f1) 65536
 Acquisition Time (sec): (f1) 1.2245
 Spectral Width (ppm): (f1) 263.734
 Pulse Program: s2oul
 Temperature: 35
 Number of Scans: 64
 Acq. Date: Jul 29 2013

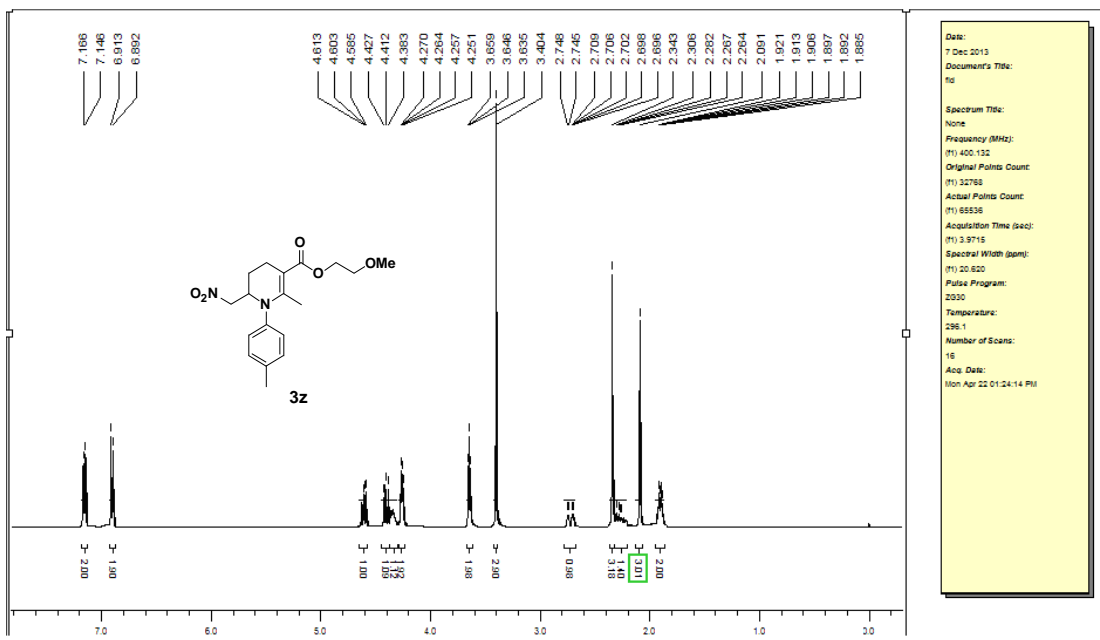




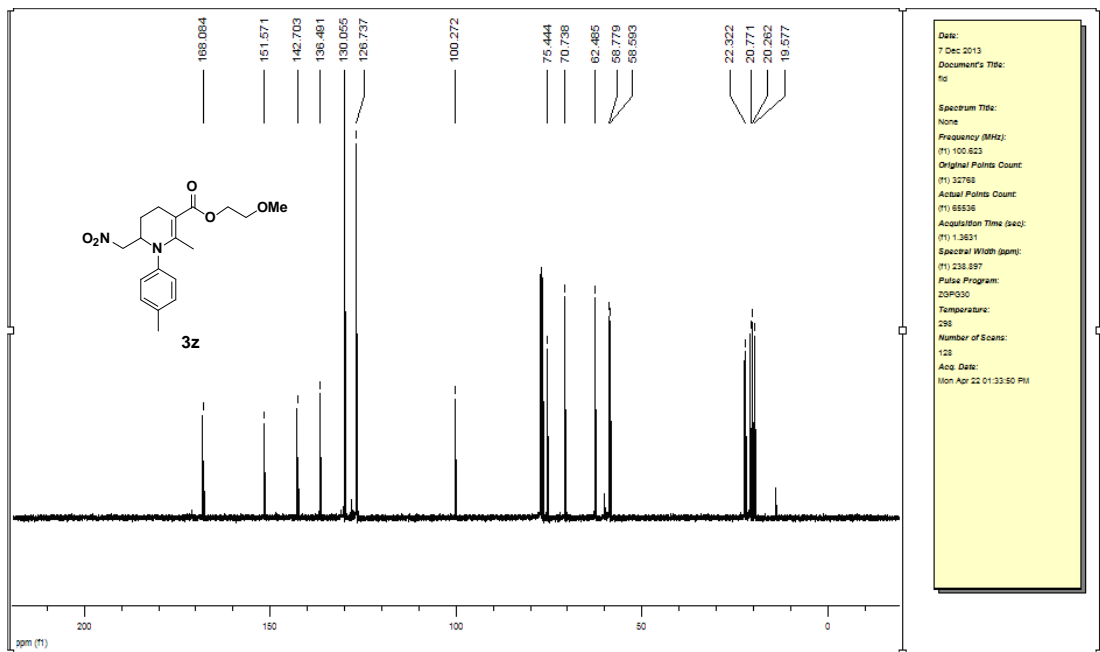
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 Actual Points Count: (f1) 32768
 Acquisition Time (sec): (f1) 3.9715
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 Pulse Program: 2D30
 Temperature: 297.3
 Number of Scans: 32
 Acq. Date: Mon Jul 15 09:48:57 AM



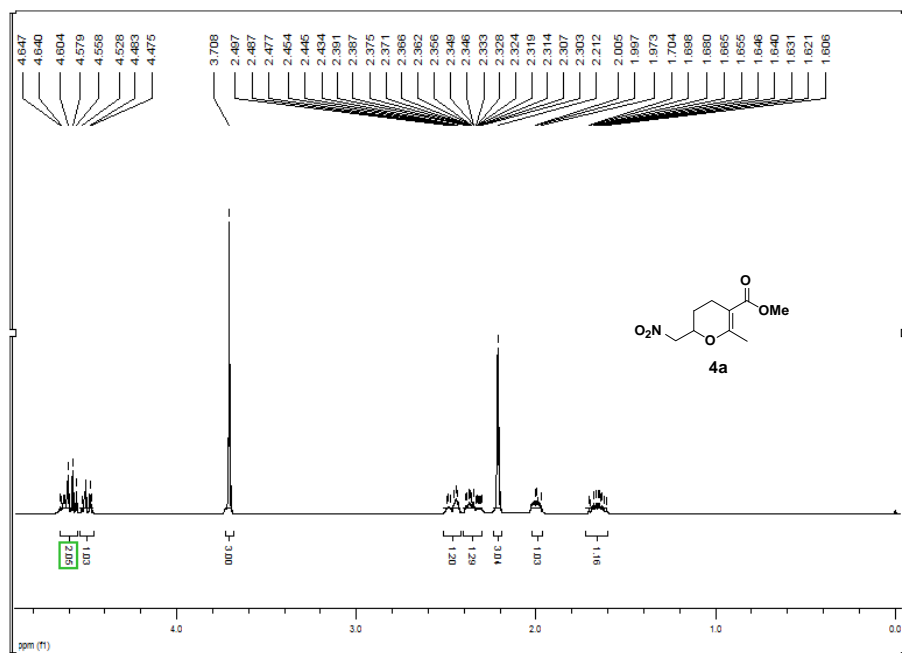
Date: 7 Dec 2013
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 Actual Points Count: (f1) 32768
 Acquisition Time (sec): (f1) 1.3631
 Spectral Width (ppm): (f1) 238.897
 Pulse Program: 2DPO20
 Temperature: 297.3
 Number of Scans: 128
 Acq. Date: Mon Jul 15 09:56:41 AM



Date: 7 Dec 2013
 Documents Title: fo
 Spectrum Title: None
 Frequency (MHz): (F1) 400.132
 Original Points Count: (F1) 32768
 Actual Points Count: (F1) 65536
 Acquisition Time (sec): (F1) 3.9716
 Spectral Width (ppm): (F1) 20.620
 Pulse Program: z300
 Temperature: 296.1
 Number of Scans: 16
 Acq. Date: Mon Apr 22 01:24:14 PM

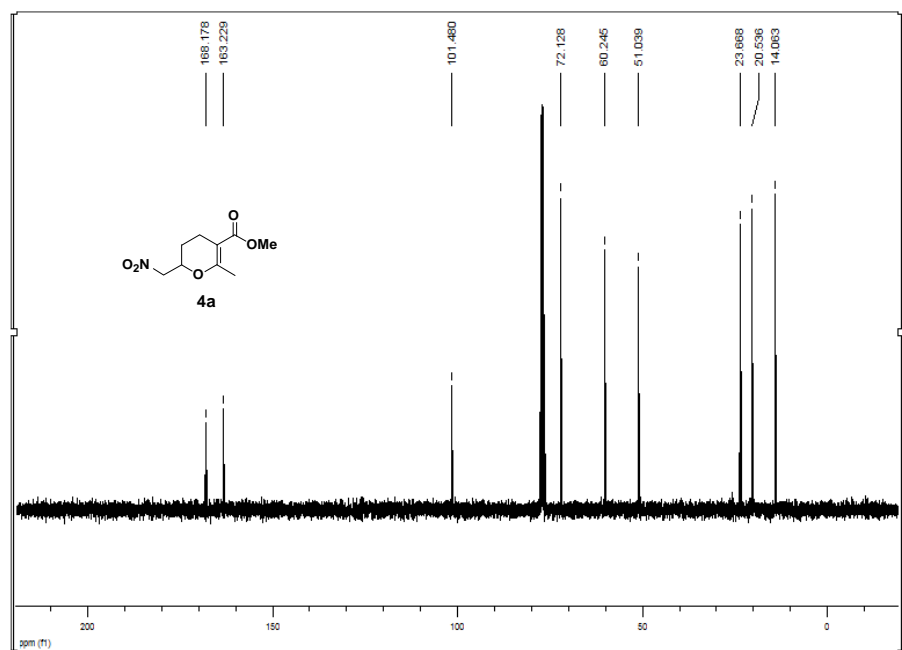


Date: 7 Dec 2013
 Documents Title: fo
 Spectrum Title: None
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 Actual Points Count: (F1) 65536
 Acquisition Time (sec): (F1) 1.3631
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 Pulse Program: z0P030
 Temperature: 298
 Number of Scans: 128
 Acq. Date: Mon Apr 22 01:33:50 PM



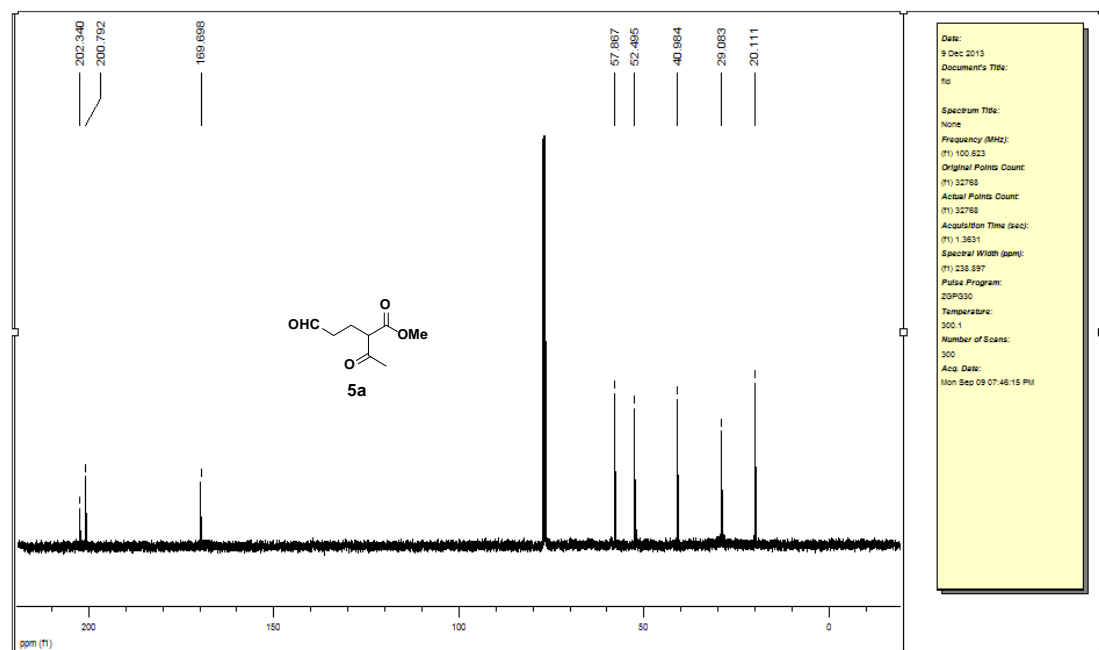
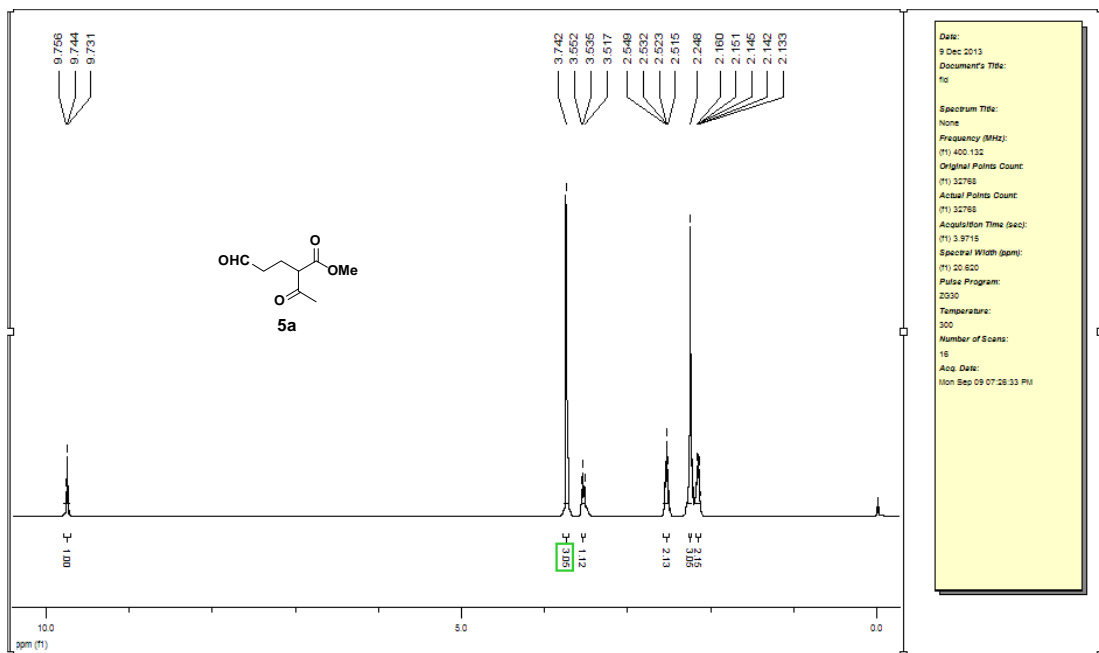
Date: 16 Dec 2013
 Document's Title: 4a

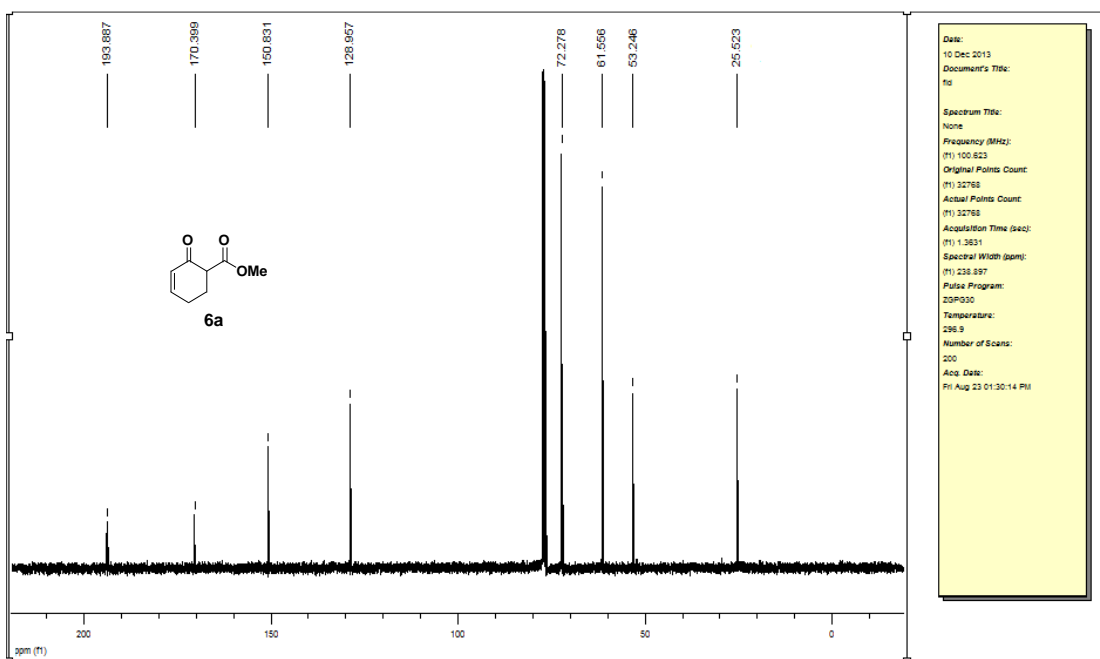
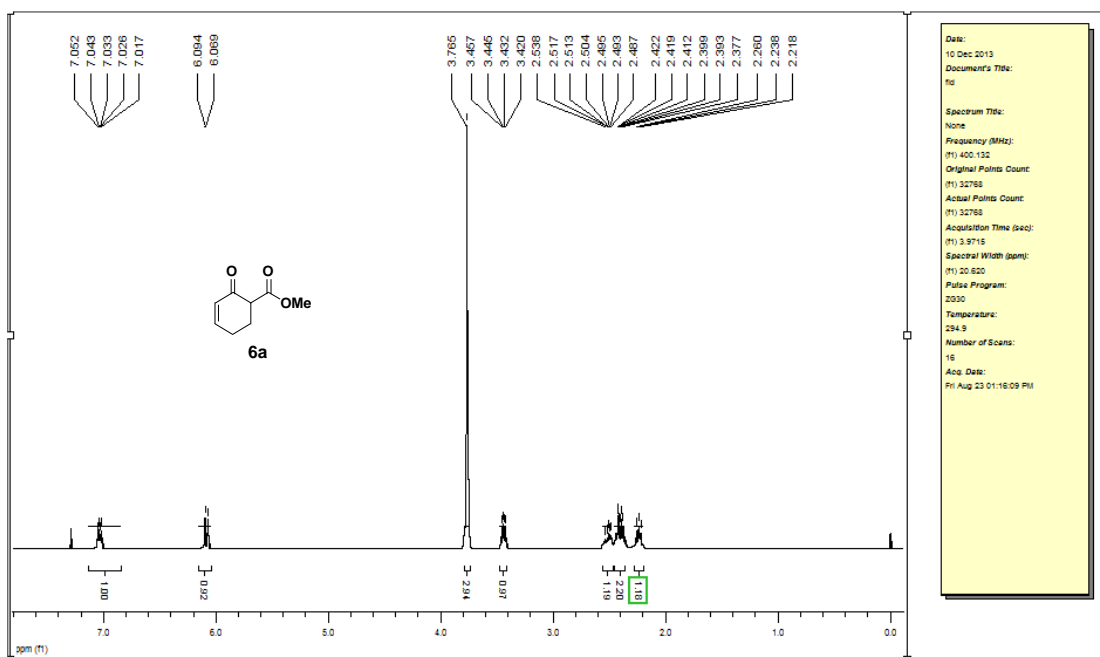
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 Actual Points Count: (f1) 32768
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 Pulse Program: 2050
 Temperature: 303.2
 Number of Scans: 16
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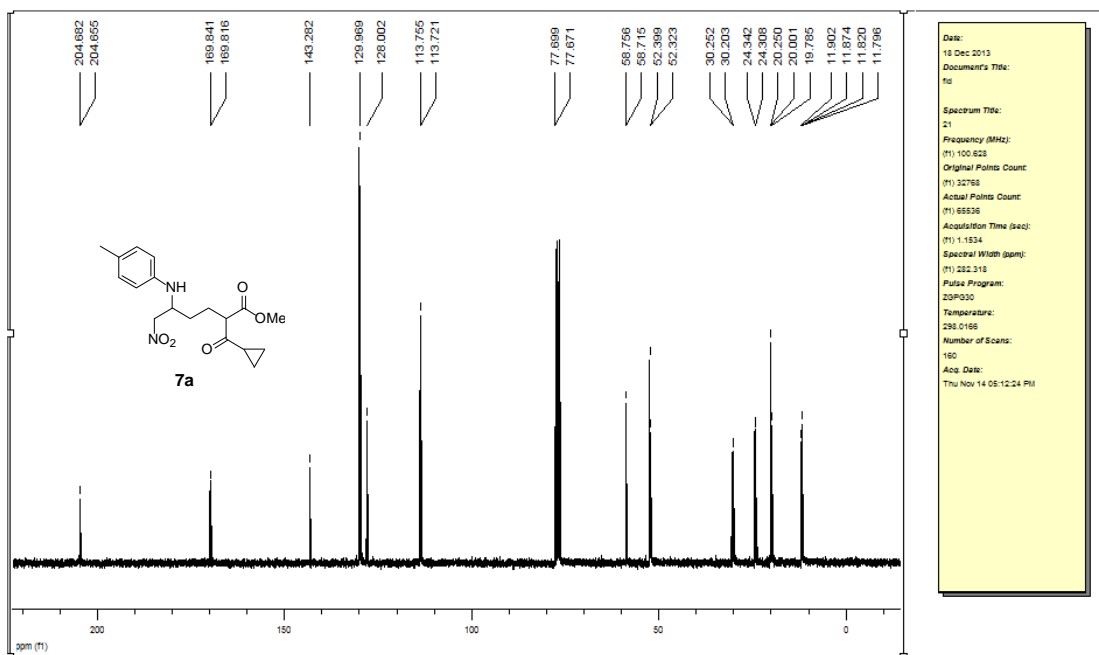
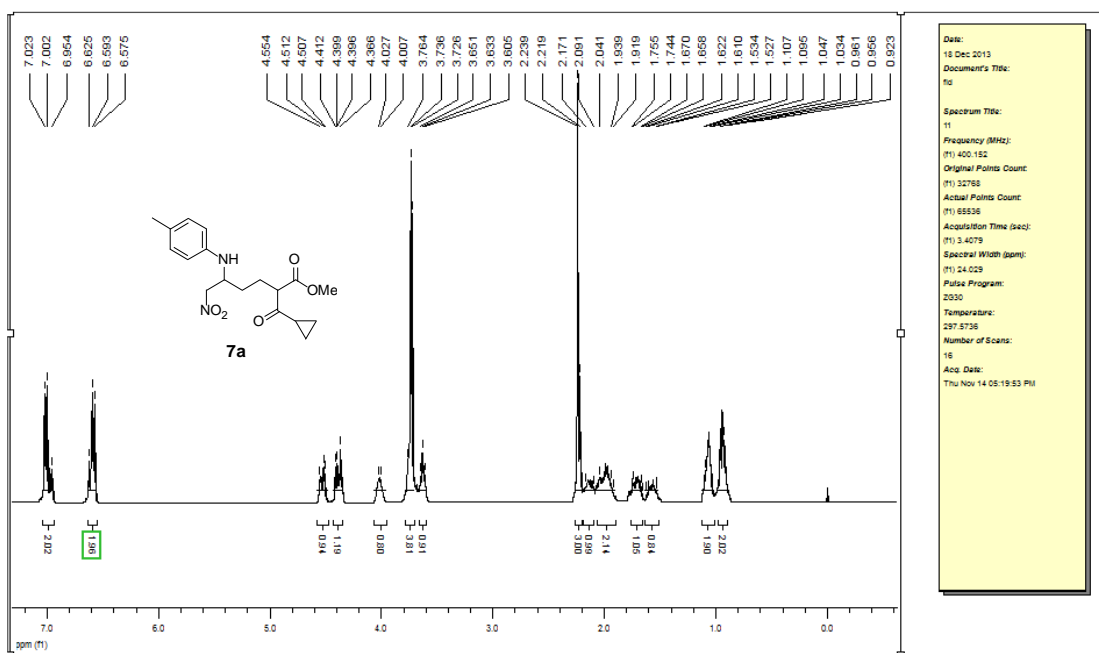


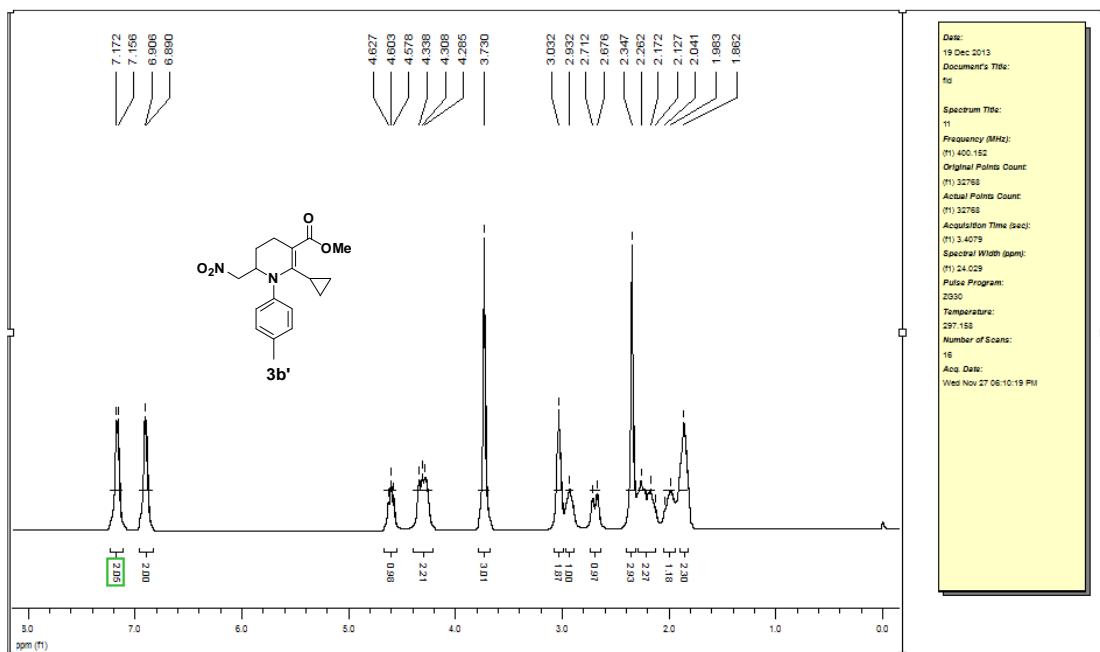
Date: 16 Dec 2013
 Document's Title: 4a

Spectrum Title: None
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 Actual Points Count: (f1) 32768
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 Spectral Width (ppm): (f1) 238.897
 Pulse Program: 20M930
 Temperature: 304.3
 Number of Scans: 64
 Acq. Date: Fri Jul 05 05:47:43 PM

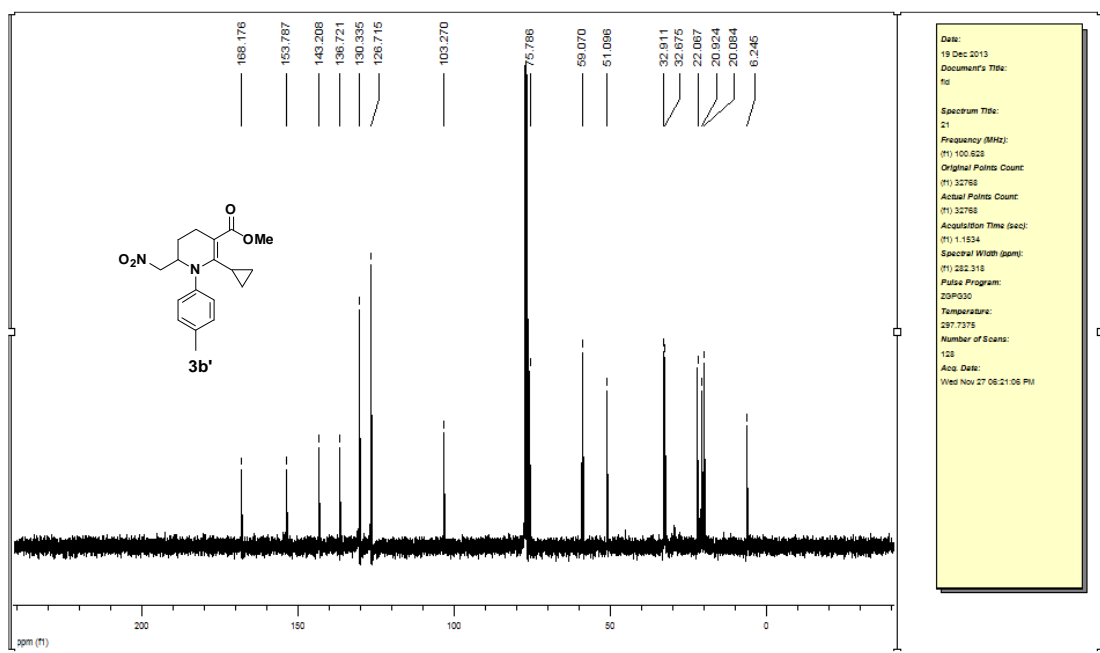




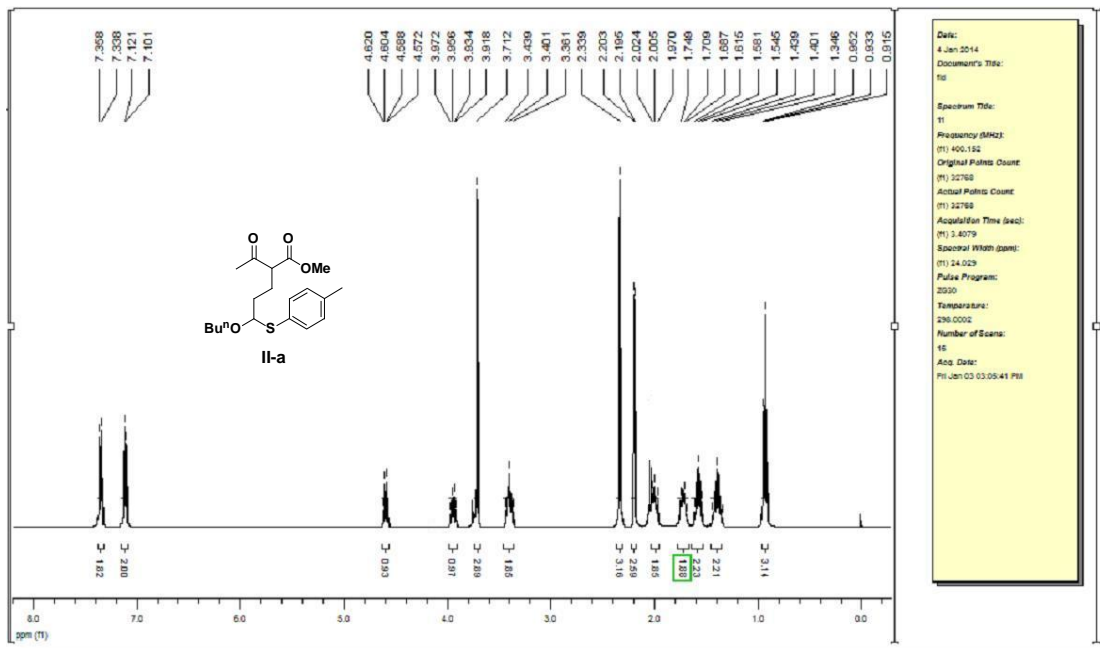




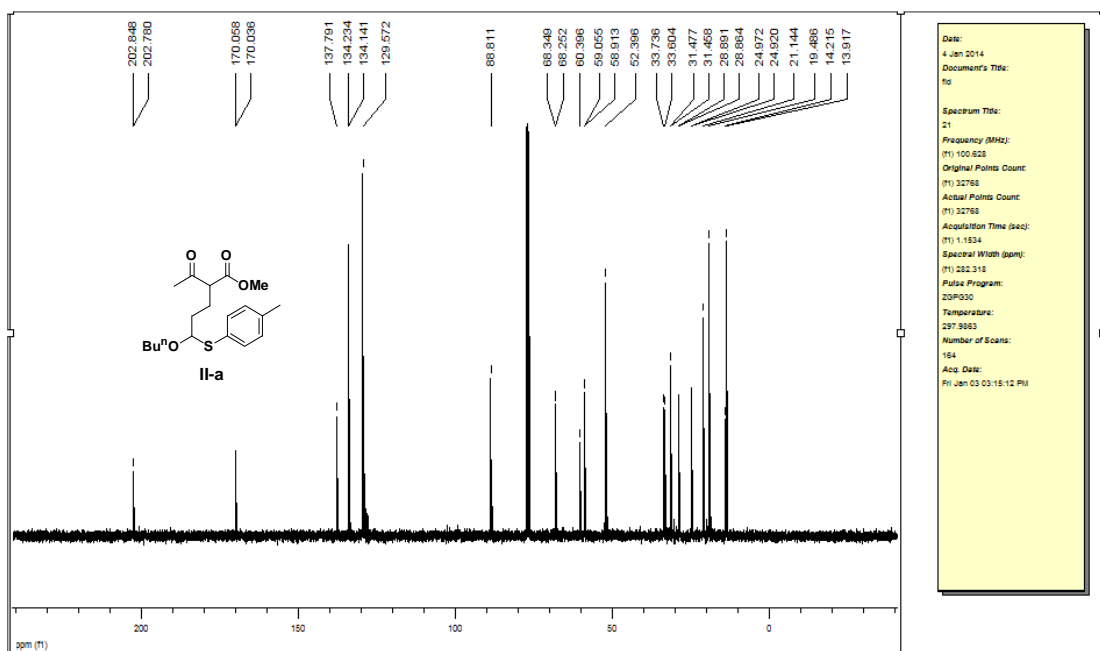
Date: 19 Dec 2013
 Document's Title: fd
 Spectrum Title: 11
 Frequency (MHz): (F1) 400.152
 Original Points Count: (F1) 32768
 Actual Points Count: (F1) 32768
 Acquisition Time (sec): (F1) 3.4079
 Spectral Width (ppm): (F1) 24.029
 Pulse Program: ZD30
 Temperature: 297.155
 Number of Scans: 16
 Acq. Date: Wed Nov 27 08:10:19 PM



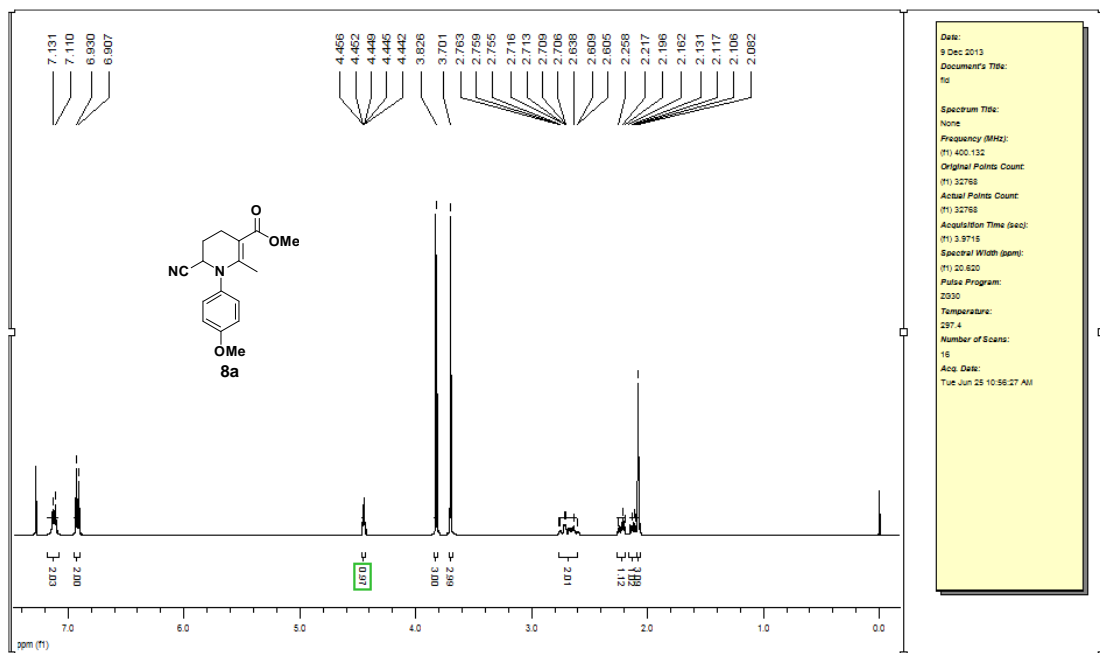
Date: 19 Dec 2013
 Document's Title: fd
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 Original Points Count: (F1) 32768
 Actual Points Count: (F1) 32768
 Acquisition Time (sec): (F1) 1.1534
 Spectral Width (ppm): (F1) 232.318
 Pulse Program: ZDQ30
 Temperature: 297.375
 Number of Scans: 128
 Acq. Date: Wed Nov 27 08:21:08 PM



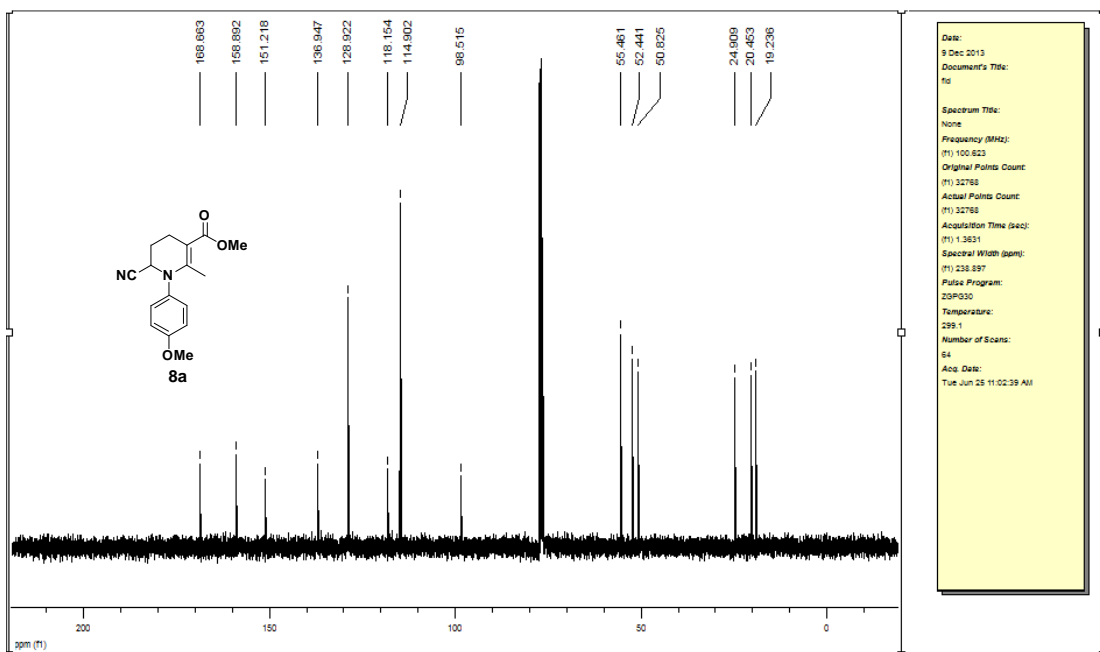
Date: 4 Jan 2014
 Document's Title: fo
 Spectrum Title: 11
 Frequency (MHz): (F1) 400.152
 Original Points Count: (F1) 32768
 Actual Points Count: (F1) 32768
 Acquisition Time (sec): (F1) 3.4079
 Spectral Width (ppm): (F1) 24.029
 Pulse Program: 2D30
 Temperature: 295.0000
 Number of Scans: 16
 Acq. Date: Fri Jan 03 03:05:41 PM



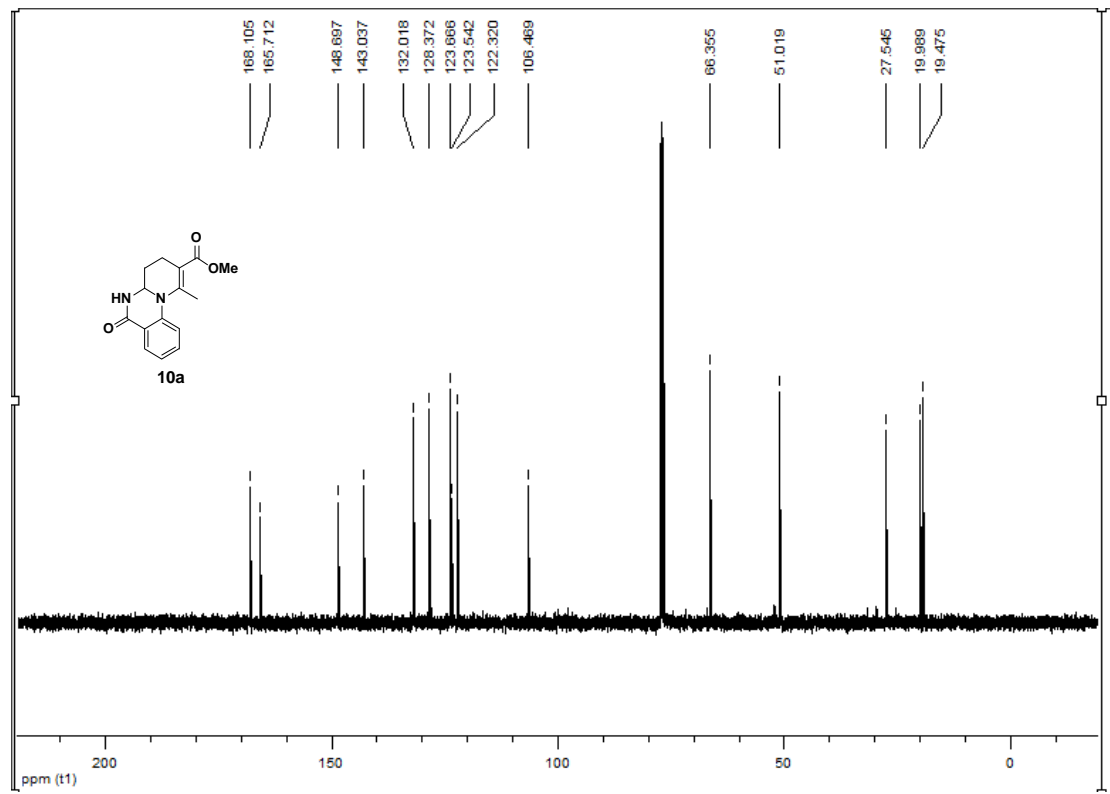
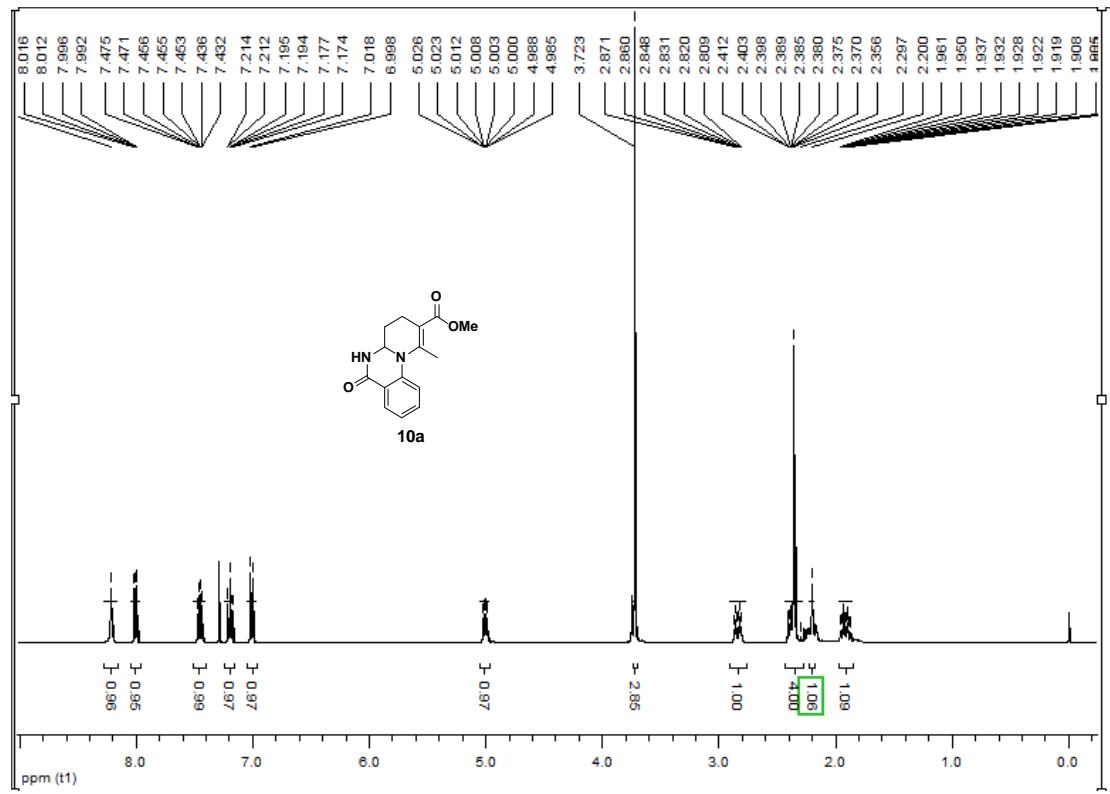
Date: 4 Jan 2014
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 Original Points Count: (F1) 32768
 Actual Points Count: (F1) 32768
 Acquisition Time (sec): (F1) 1.1534
 Spectral Width (ppm): (F1) 282.318
 Pulse Program: 2DPO30
 Temperature: 297.9583
 Number of Scans: 184
 Acq. Date: Fri Jan 03 03:15:12 PM

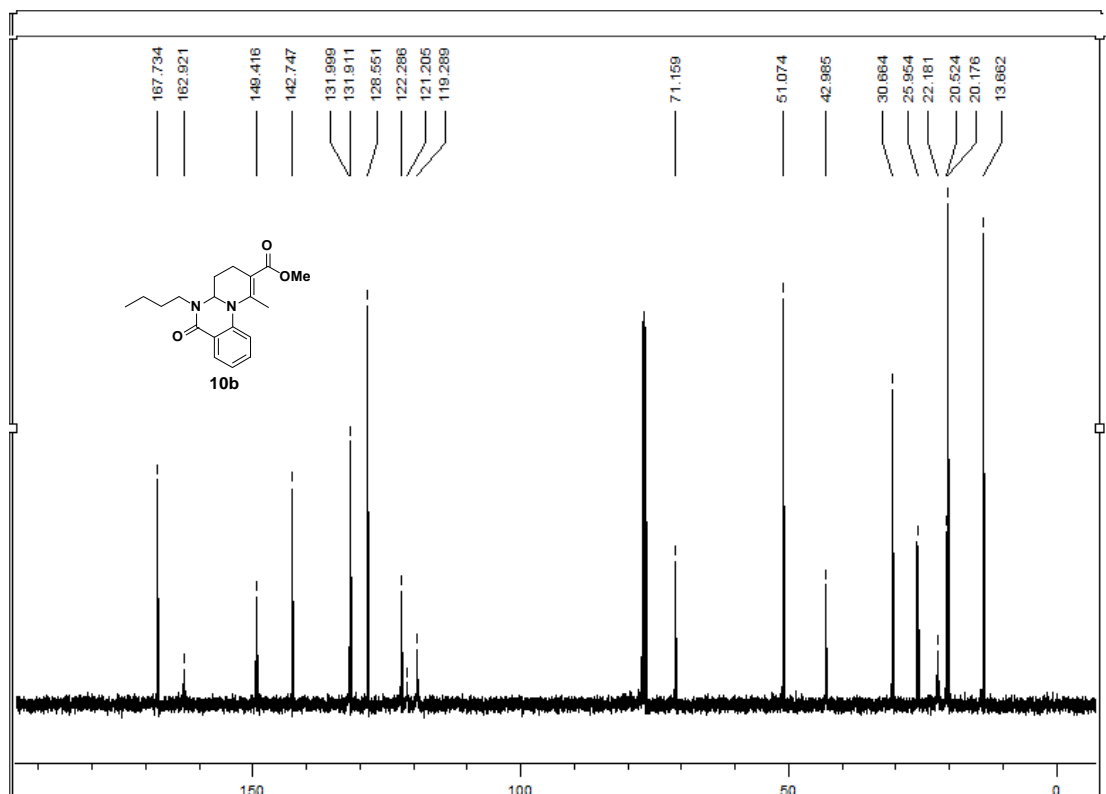
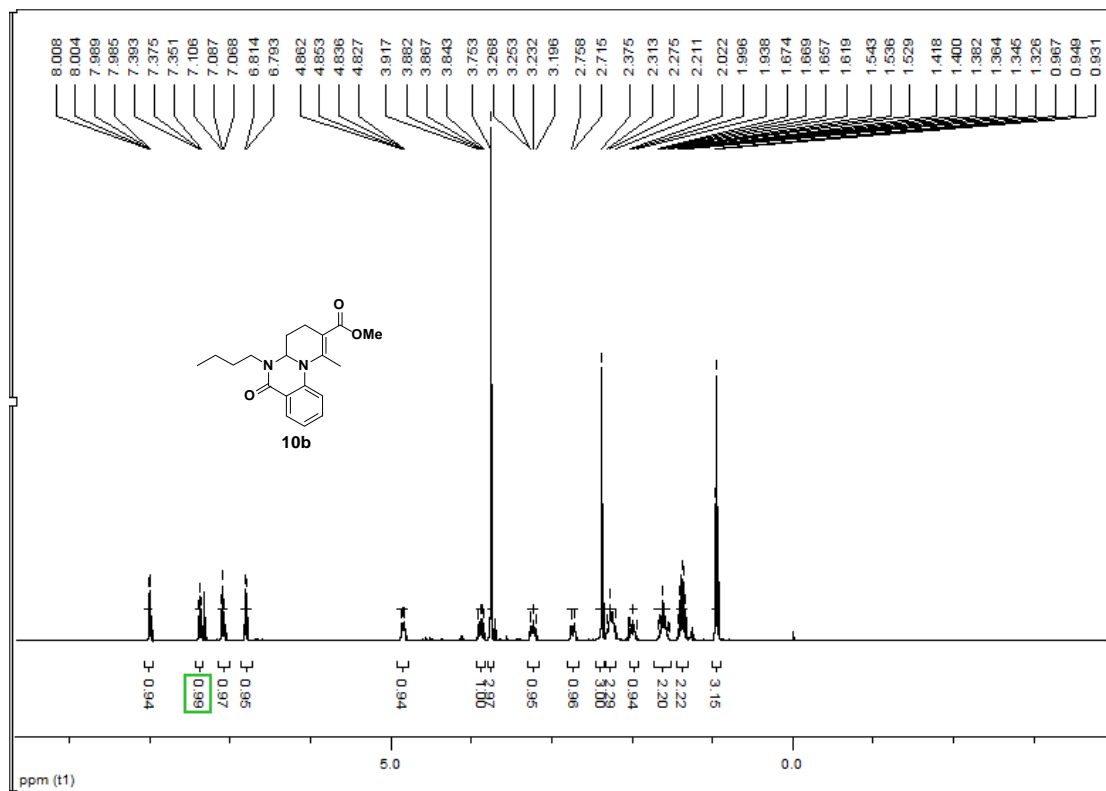


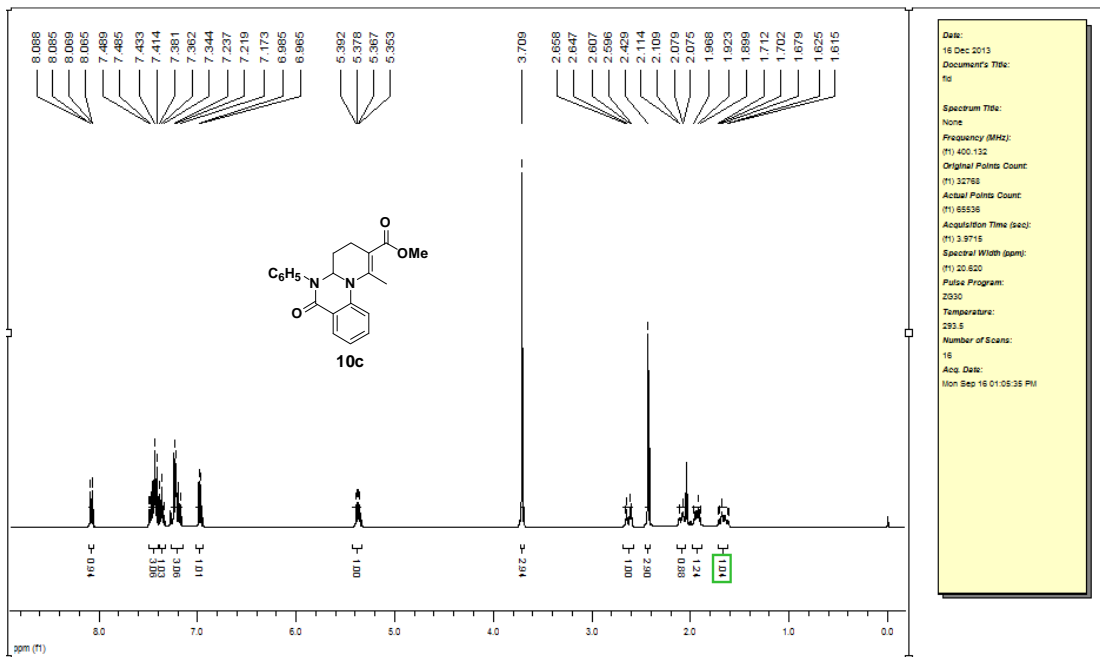
Date: 9 Dec 2013
 Document's Title: fd
 Spectrum Title: None
 Frequency (MHz): (f1) 400.152
 Original Points Count: (f1) 32768
 Actual Points Count: (f1) 32768
 Acquisition Time (sec): (f1) 3.9715
 Spectral Width (ppm): (f1) 20.620
 Pulse Program: zgpg30
 Temperature: 293.0
 Number of Scans: 16
 Acq. Date: Tue Jun 25 10:56:27 AM



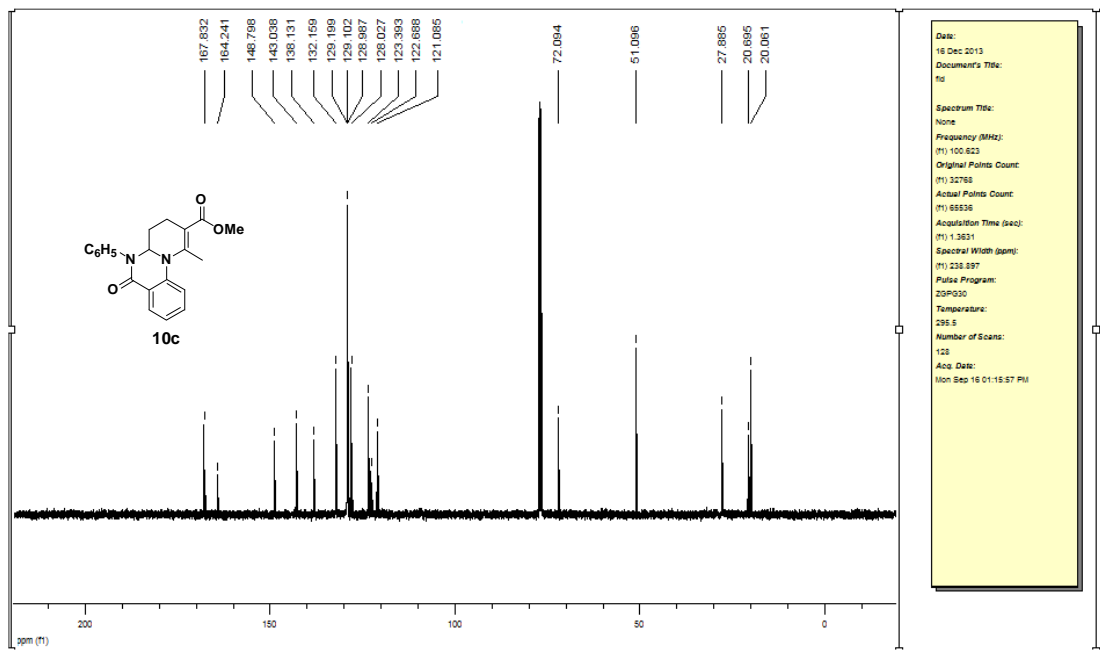
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 Original Points Count: (f1) 32768
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 Acquisition Time (sec): (f1) 1.3631
 Spectral Width (ppm): (f1) 238.897
 Pulse Program: zgpg30
 Temperature: 299.1
 Number of Scans: 64
 Acq. Date: Tue Jun 25 11:02:39 AM



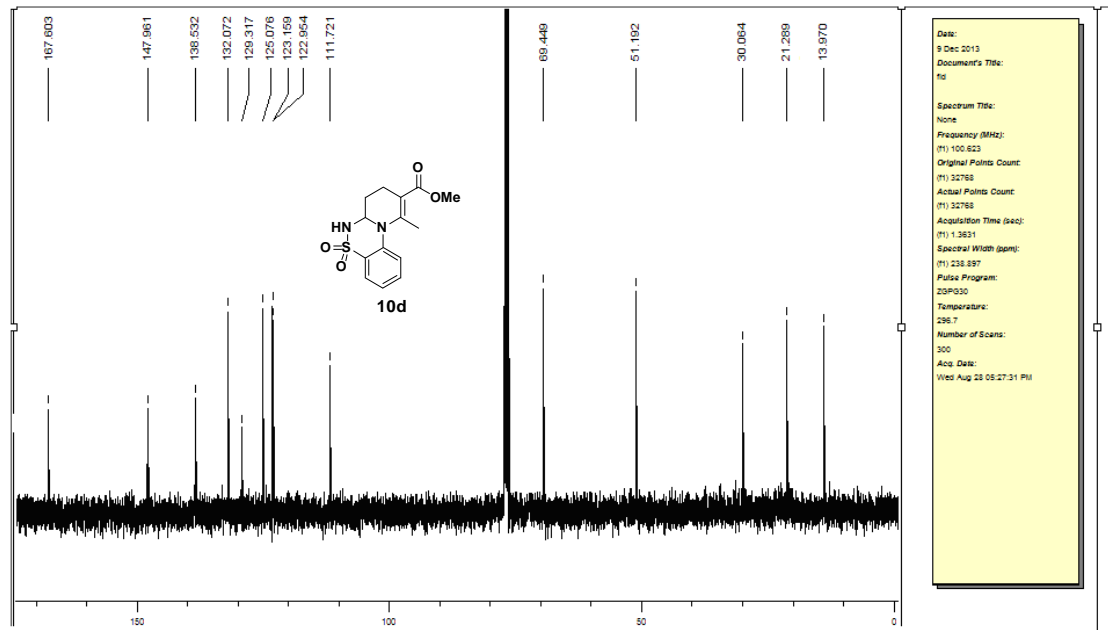
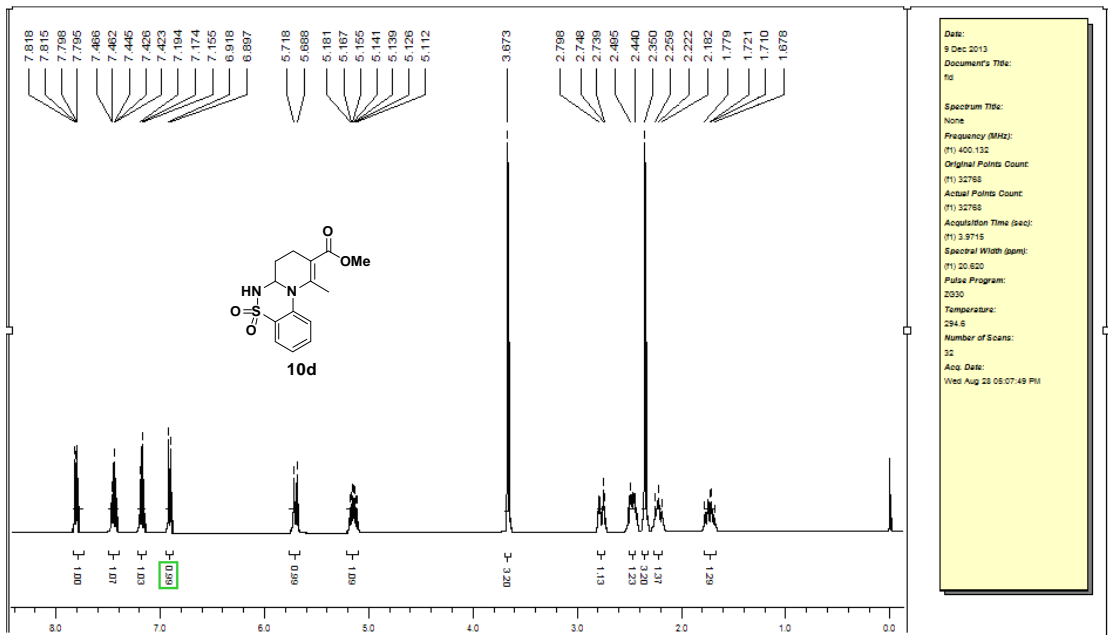


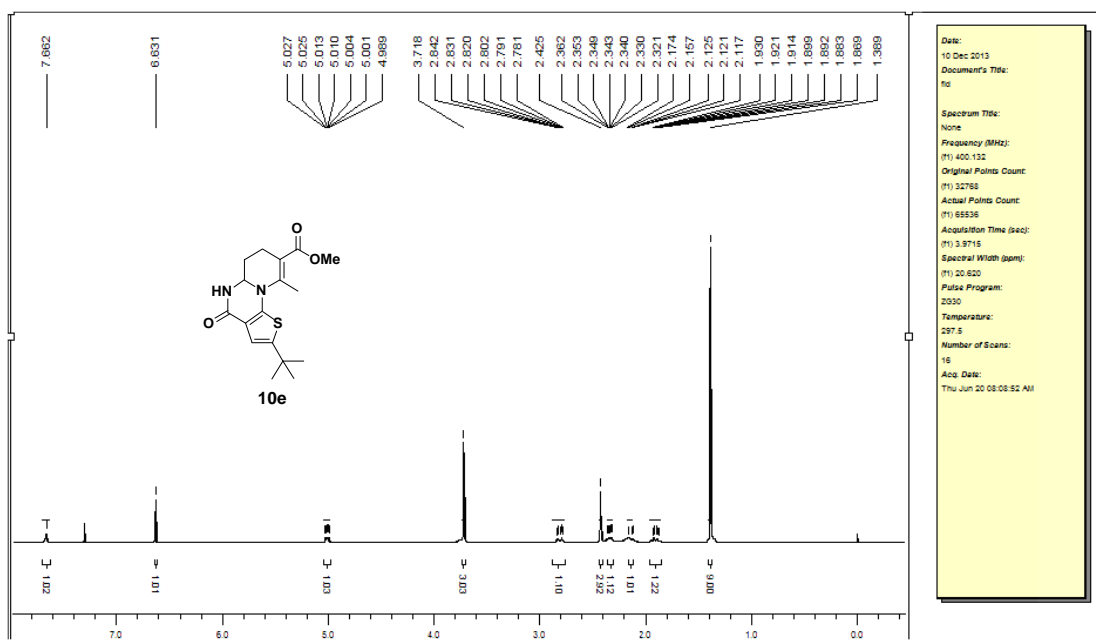


Date: 16 Dec 2013
 Document's Title: fd
 Spectrum Title: None
 Frequency (MHz): (f1) 400.132
 Original Points Count: (f1) 32768
 Actual Points Count: (f1) 65536
 Acquisition Time (sec): (f1) 3.9715
 Spectral Width (ppm): (f1) 20.620
 Pulse Program: 2D30
 Temperature: 293.5
 Number of Scans: 16
 Acq. Date: Mon Sep 16 01:05:35 PM

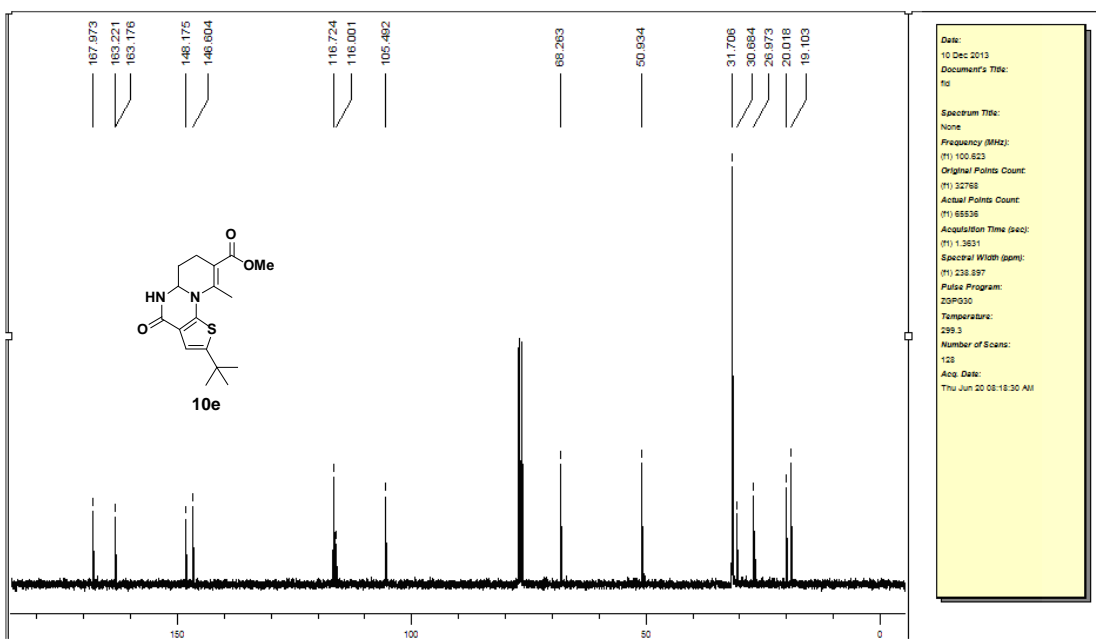


Date: 16 Dec 2013
 Document's Title: fd
 Spectrum Title: None
 Frequency (MHz): (f1) 100.623
 Original Points Count: (f1) 32768
 Actual Points Count: (f1) 65536
 Acquisition Time (sec): (f1) 1.3831
 Spectral Width (ppm): (f1) 236.897
 Pulse Program: 2D30
 Temperature: 293.5
 Number of Scans: 128
 Acq. Date: Mon Sep 16 01:15:57 PM

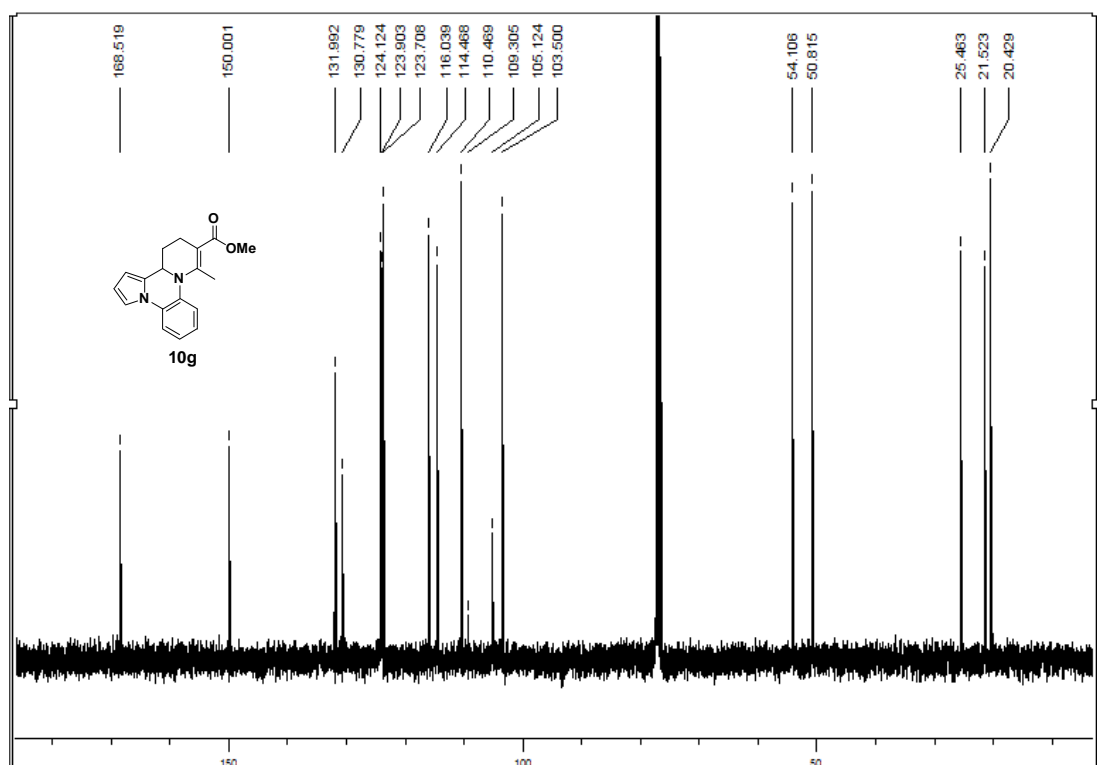
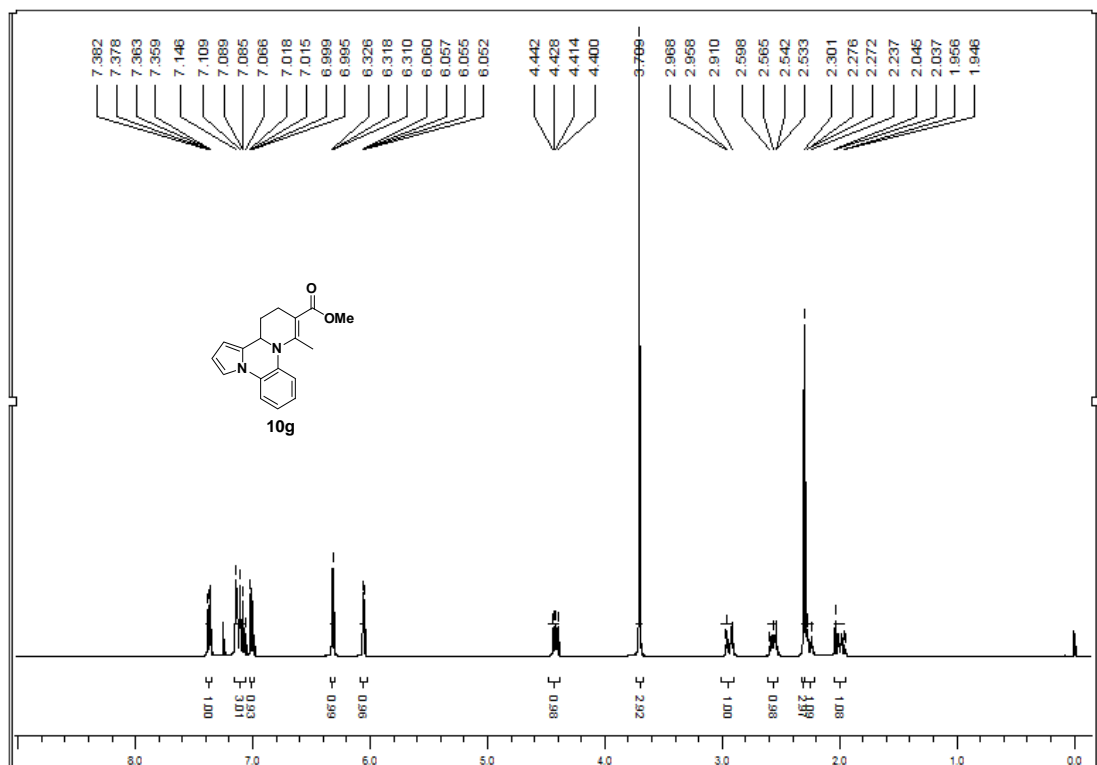


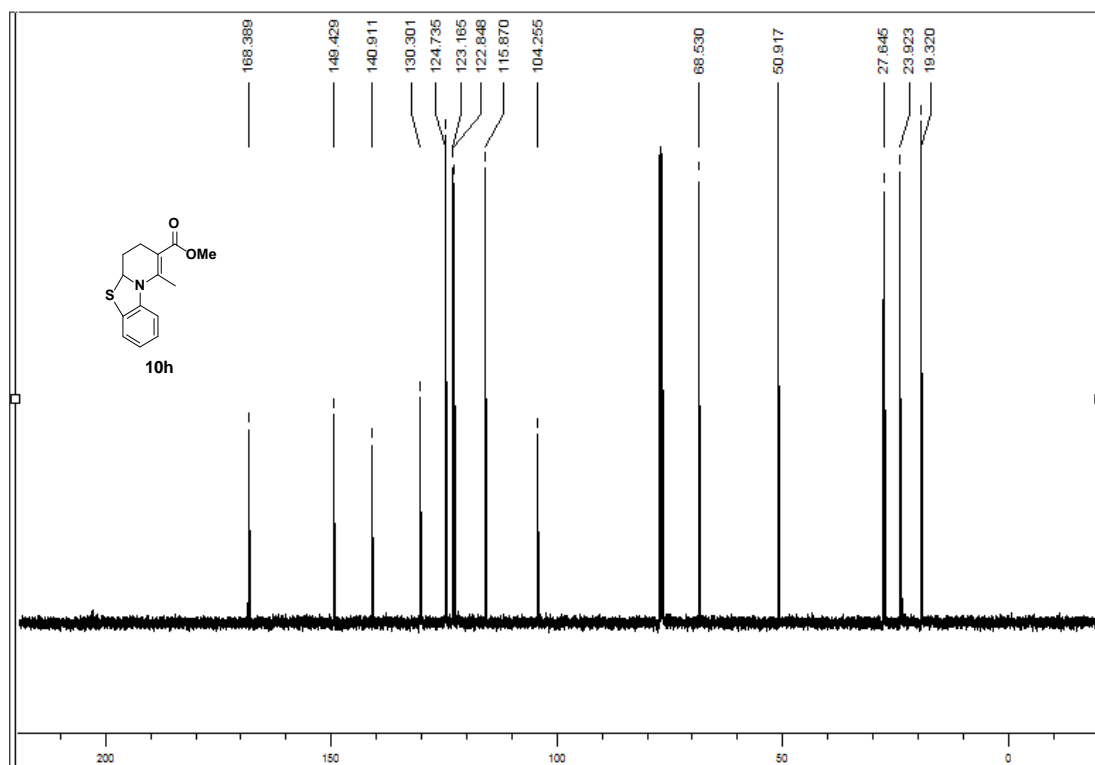
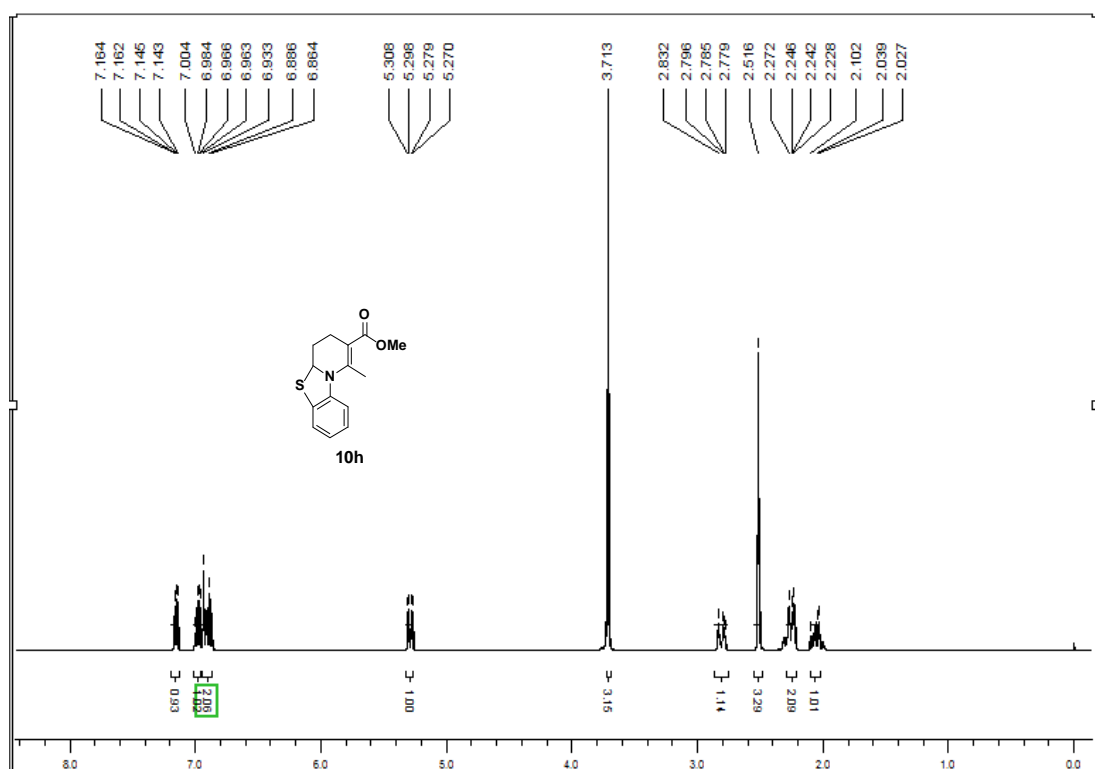


Date: 10 Dec 2013
 Document's Title: fo
 Spectrum Title: None
 Frequency (MHz): (F1) 400.132
 Original Points Count: (F1) 32768
 Actual Points Count: (F1) 65536
 Acquisition Time (sec): (F1) 3.9716
 Spectral Width (ppm): (F1) 20.620
 Pulse Program: zgpg30
 Temperature: 297.5
 Number of Scans: 16
 Acq. Date: Thu Jun 20 08:52 AM



Date: 10 Dec 2013
 Document's Title: fo
 Spectrum Title: None
 Frequency (MHz): (F1) 100.623
 Original Points Count: (F1) 32768
 Actual Points Count: (F1) 65536
 Acquisition Time (sec): (F1) 1.3631
 Spectral Width (ppm): (F1) 236.897
 Pulse Program: zgpg30
 Temperature: 299.3
 Number of Scans: 128
 Acq. Date: Thu Jun 20 08:18:30 AM





References

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- [3] R. Noeel, C. Vanucci-Bacque, M. –C. Fargeau-Bellassoued, G. Lhomme, *J. Org. Chem.* **2005**, *70*, 9044-9047.
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