Supporting Information for

Palladium(0)-catalyzed cyclopropanation of benzyl bromides via C(sp^3)-H bond activation

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Table of Contens

1 General information 2

2 Substrates Preparation 2

2.1 General Procedure for the Preparation of Benzyl Bromides: 2

2.2 The Synthesis of Endo-Norbornenesuccinimides (2a, 2b): 3

3 $Pd(OAc)_2$-Catalyzed Cyclopropanation of Benzyl Bromides and Norbornene Derivants and DFT Calculations 3

3.1 General Procedures for the Cyclopropanation 3

3.2 DFT Calculations on the origin of the selectivity between the C(sp^3)-H and C(sp^2)-H activation 4

3.3 Experimental Characterization of Products 30

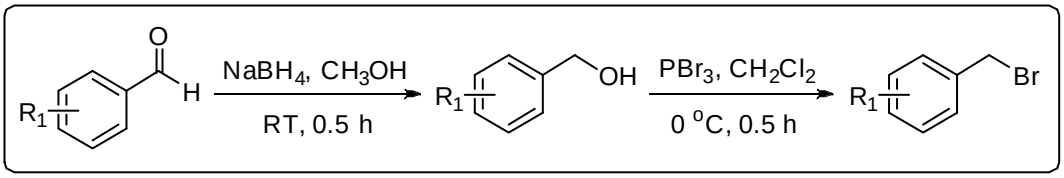
4 Copies for ^{1}H NMR and ^{13}C NMR 40

1 General information

Experimental: All cyclopropanation([2+1] cycloaddition) reactions were carried out under an inert atmosphere of nitrogen in standard Schlenk tube. All solvents were dried by standard methods before use. All reactions were monitored by TLC with silica gel-coated plates. NMR spectra were recorded on Bruker Avance 400 (400 MHz for ^{1}H; 100 MHz for ^{13}C) instruments. Chemical shifts were reported in parts per million (ppm) down field from TMS with the solvent resonance as the internal standard (for $CDCl_3$, ^{1}H NMR: 7.26 ppm, ^{13}C NMR: 77.16 ppm). Coupling constants (*J*) were reported in Hz. Mass spectra (EI, 70 eV) were recorded on an Agilent 5975 instrument. High resolution mass spectra (HRMS) were recorded on Waters Micromass GCT instrument. All commercially available reagents were used as received.

2 Substrates Preparation

2.1 General Procedure for the Preparation of Benzyl Bromides[1]:



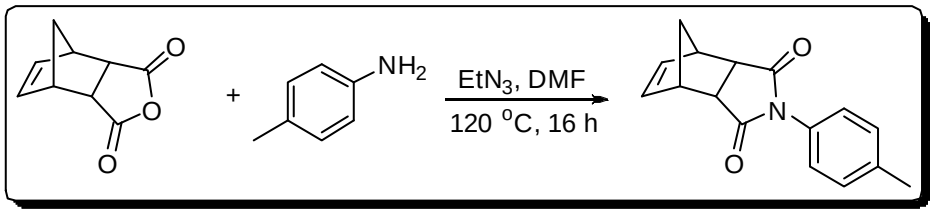
To a solution of benzaldehydes (10 mmol) dissolved in methanol (50 mL) was added sodium borohydride (20 mmol) at room temperature, and the mixture was stirred at the same temperature for 30 min and concentrated under reduced pressure. The residue was diluted with methylene chloride (500 mL) and washed with water, and dried over anhydrous Na_2SO_4, and concentrated under reduced pressure to give the corresponding crude phenylmethanols (85% yield) which were used directly without further purification.

To a solution of phenylmethanols (5 mmol) dissolved in methylene chloride (50 mL)

1. L. Feng, K. Lv, M. Liu, S. Wang, J. Zhao, X. You, S. Li, J. Cao, H. Guo, *Eur. J. Med. Chem.*, **55**, (2012) 125.

in an ice-water bath was added phosphorus tribromide (5.5 mmol), and the mixture was stirred at the same temperature for 30 min. The mixture was washed with cool water, dried over anhydrous Na_2SO_4 and concentrated under reduced pressure to yield (bromomethyl)benzenes as offwhite solids or light yellow oils (80% yield).

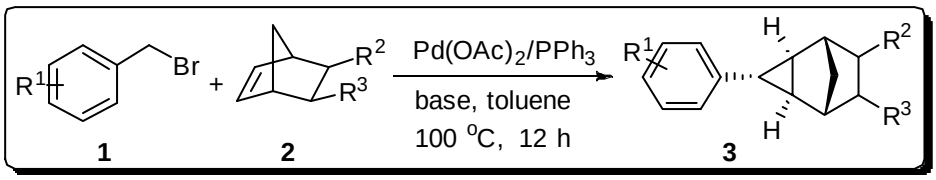
2.2 The Synthesis of Endo-Norbornenesuccinimides (2a, 2b)[2]:



Triethylamine (6.6 mmol, 0.92 mL) and the desired anhydride (6 mmol) were added to a solution of 4-toluidine (6 mmol) in 5 mL of *N*, *N*-dimethylformamide (DMF). The solution was heated for 16 h at 120 °C. After it returned to room temperature, the resulting mixture was treated with water and extracted with ethyl ether and washed with 1 N HCl (20 mL). The combined organic layers were washed with brine, dried over magnesium sulfate and concentrated *in vacuo*. The residue was purified by chromatography on a column of silica gel with PE/EA=3/1 to afford the pure products as white solid (86% yield). **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 7.25 (d, *J* = 8.0 Hz, 2H), 7.03 (d, *J* = 8.0 Hz, 2H), 6.28 (s, 2H), 3.52 (s, 2H), 3.43-3.44 (m, 2H), 2.38 (s, 3H), 1.80 (d, *J* = 8.8 Hz, 1H), 1.62 (d, *J* = 8.8 Hz, 1H).

3 Pd(OAc)$_2$-Catalyzed Cyclopropanation of Benzyl Bromides and Norbornene Derivants and DFT Calculations

3.1 General Procedures for the Cyclopropanation



2. M. Lanier, D. Schade, E. Willems, M. Tsuda, S. Spiering, J. Kalisiak, M. Mercola, J. R. Cashman, *J. Med. Chem.* **55**, (2012) 697.

To a flame-dried Teflon-screw-capped tube equipped with a magnetic stir bar, bromide **1** (0.55 mmol, 1.2 equiv.), norbornene derivative **2** (0.5 mmol, 1.0 equiv.), $Pd(OAc)_2$ (11.22 mg, 0.05 mmol, 10 mol%), PPh_3 (28.85 mg, 0.11 mmol, 22 mol%), K_2CO_3 (34.05 mg, 0.25 mmol, 0.5 equiv.) and toluene (2.0 mL) were added sequentially under nitrogen. The tube was sealed with a Teflon lined cap, the reaction mixture was stirred at 100 ^oC or 120 ^oC for 12 h. After completion of the reaction, the resulting mixture was cooled down to room temperature, diluted with CH_2Cl_2 (10 mL), filtered through a short pad of silica gel and washed with EtOAc (30 mL). The filtrate was concentrated under vacuum and the residue was purified by silica gel column chromatography to afford the product **3**.

3.2 **DFT Calculations on the origin of the selectivity between the C(sp^3)-H and C(sp^2)-H activation**

COMPUTATIONAL DETAILS

All calculations were performed with the Gaussian 09 program.[3] Geometry optimizations and frequency calculations were performed with B3LYP[4] functional using LANL2DZ[5] basis set for Pd and Br combined with 6-31G(d)[6] basis set for all the other atoms. Single point energy calculations were also performed to further refine the results with M06-2x[7] functional using def2-TZVP[8] basis set for Pd and Bras obtained from the EMSL Basis Set Library[9], combined with 6-311+G(d,p)[10] basis set

3. Gaussian 09, Revision B.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. ontgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2010.
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for all the remaining atoms, as well as the solvent of toluene using the CPCM[11] model. Imaginary frequency in frequency calculations were used to confirm whether the geometries were intermediates or transition states. For transition states, the intrinsic reaction coordination (IRC)[12] calculations were performed to determine the reactants and products.

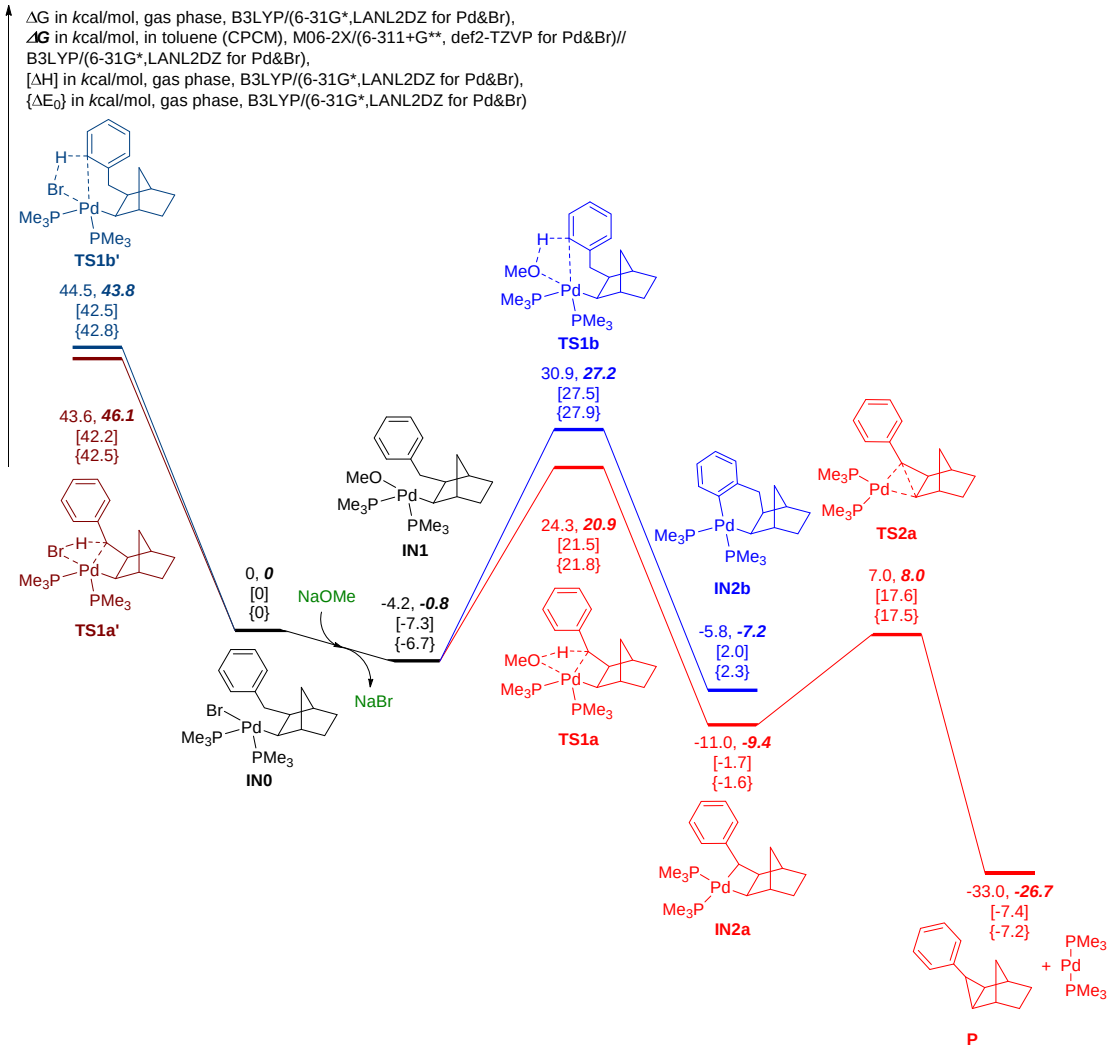


Figure 1. Comparison of the energy profiles of the selectivity between the C(sp^3)-H activation at the benzyl and C(sp^2)-H activation on the phenyl.

ORIGIN OF SELECTIVITY

To further understand the origin of the selectivity between the C(sp^3)-H at the benzyl

11. a) A. Klamt, G. Schu¨u¨rmann, *J. Chem. Soc., PerkinTrans.* **2**(1993) 799; b) Andzelm, J.; Ko¨lmel, C.; Klamt, A. *J. Chem.Phys.* **103(**1995) 9312-9320; c) Barone, V.; Cossi, M. *J. Phys. Chem. A* **102 (**1998) 1995-2001; d) Cossi, M.; Rega,N.; Scalmani, G.; Barone, V. *J. Comput. Chem.* **24** (2003) 669-681.
12. a) K. Fukui, *Acc. Chem. Res.*, **14** (1981) 363-368; b) H. P. Hratchian and H. B. Schlegel, *J. Chem. Phys.*, **120** (2004), 9918-9924; c) H. P. Hratchian and H. B. Schlegel, *J. Chem. Theory and Comput.*, **1** (2005) 61-69.

and C(sp^2)-H on the phenyl, we performed some DFT calculations on the deprotonation process with some simplification, namely replacement of PPh_3 with PMe_3. As we proposed above, we firstly start with **IN0** to conduct the calculation. As shown in **Figure 1, IN0** could either directly undergo deprotonation or undergo ligand exchange with the external base, namely NaOMe in our calculation. But it is unlikely to be directly deprotonated under the given reaction conditions because of the rather high energy barrier. This might be due to the lack of proton affinity as well as the large radius of bromine. Thus, after ligand exchange with NaOMe, **IN1** is formed, releasing NaBr. This process is slightly exothermic. The deprotonation process of **IN1** is much easier than that of **IN0**, as we expected, since the higher proton affinity of OMe. We located both **TS1a** and **TS1b** for C(sp^3)-H and C(sp^2)-H respectively. To our delight, the C(sp^3)-H showed much higher reactivity with a difference of more than 6 *k*cal/mol, which is in good accord with the experimental outcome. In addition, **IN2a** is more stable than **IN2b**, despite the rigid of 4-membered ring. These might be the results of both different degree of interaction and distortion. As shown in **Figure 2, TS1a** showed a much stronger interaction between OMe and H than **TS1b**, which contributes mostly to the interactions within the TSs, because the noted Pd-C and C-H are both lengthened to lead to weak interactions. Moreover, the reactive orbital of in OMe are more compliant with C(sp^3)-H than with C(sp^2)-H since they are sp^3 to most extend. In the perspective of distortion, **TS1a** showed no obvious distortion while in **TS1b** the phenyl must rotate in order to undergo deprotonation. The newly formed 6-membered ring from **TS1b** is locked in a boat conformation, making **IN2b** less stable. All these lead to the preference of C(sp^3)-H at the benzyl over C(sp^2)-H on the phenyl. Afterwards, the deprotonated intermediate **IN2a** would undergo normal reductive elimination (R. E.) to form the final product **P** and the active catalyst PdL_2. The activation energy for this process is rather small relative to the deprotonation process, which might be explicable by the tendency to releasing the tension of the 4-membered ring in **IN2a**. And thus, the final step has little impact on the selectivity between C(sp^3)-H and C(sp^2)-H.

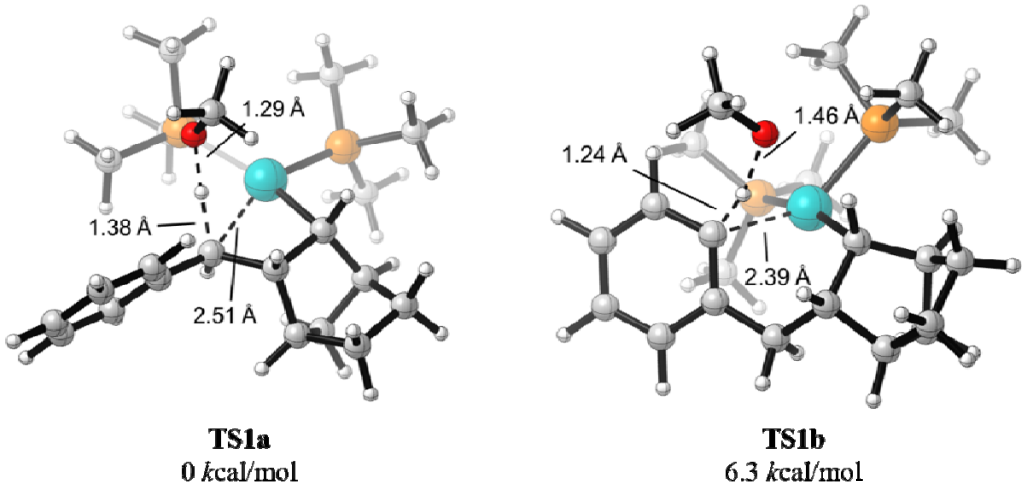


Figure 2. Optimized geometries of the transition states (**TS1a** and **TS1b**) with bond lengths in Å.

Table 1. Calculated energy values

Species	ZPE [a,b]	H_{298} [a,c]	G_{298} [a,d]	E'[e,f]	G'_{298} [e,f]
IN0	-1605.399137	-1605.367072	-1605.463715	-4167.846226	-4167.401582
IN1	-1707.25095	-1707.217932	-1707.314846	-1708.693409	-1708.206953
TS1a	-1707.205552	-1707.172108	-1707.269447	-1708.650924	-1708.172337
TS1b	-1707.195804	-1707.162601	-1707.259009	-1708.642871	-1708.16234
TS1a'	-1605.331472	-1605.29979	-1605.394241	-4167.766743	-4167.328042
TS1b'	-1605.330881	-1605.299311	-1605.392751	-4167.771139	-4167.331777
IN2a	-1591.582175	-1591.552565	-1591.642216	-1592.976491	-1592.541893
IN2b	-1591.575859	-1591.546599	-1591.633932	-1592.976121	-1592.538328
TS2a	-1591.551749	-1591.521873	-1591.613521	-1592.945043	-1592.514215
P	-542.811911	-542.800368	-542.850744	-542.9892421	-542.7636171
$Pd(PMe_3)_2$	-1048.779125	-1048.761222	-1048.826652	-1049.988177	-1049.805884
NaOMe	-277.378893	-277.373277	-277.405833	-277.4050428	-277.3923278
NaBr	-175.537718	-175.533985	-175.561368	-2736.565321	-2736.588303
MeOH	-115.660732	-115.656497	-115.683452	-115.7074269	-115.6786749

[a] With B3LYP functional; 6-31G(d) for C,H,O,N and LANL2DZ for Pd and Br

[b] Sum of electronic and zero-point energies

[c] Sum of electronic and thermal enthalpies

[d] Sum of electronic and thermal free energies

[e] Electronic energies

[f] With M06-2X functional; 6-311+G(d,p) for C,H,O,N and def2-TZVP for Pd and Br; solvation with CPCM in toluene

Cartesian coordinates

IN0

C	-0.55662	-0.56392	1.458485
C	-0.73982	-2.05007	1.871251
C	-2.81271	-1.41605	1.216458
C	-1.956	-0.16507	0.873253
H	-0.36219	0.007563	2.367598
H	-2.35309	0.710183	1.408703
C	-1.83108	-2.56458	0.911047
H	-2.22102	-3.54744	1.20422
H	-1.50194	-2.61443	-0.12679
C	-1.53655	-2.02504	3.205899
H	-1.59277	-3.03505	3.631183
H	-1.07563	-1.38027	3.964097
C	-2.9492	-1.52405	2.756581
H	-3.72943	-2.24538	3.025321
H	-3.22569	-0.56641	3.21454
H	0.1799	-2.63406	1.9137
H	-3.77074	-1.43723	0.688718
C	-1.97579	0.187139	-0.63784
H	-1.24688	0.992396	-0.80474
H	-1.61188	-0.66594	-1.21868
C	-3.33263	0.626367	-1.15007

C	-4.10988	-0.21176	-1.962
C	-3.85165	1.888476	-0.82175
C	-5.36416	0.192256	-2.42565
H	-3.72333	-1.19075	-2.23583
C	-5.10344	2.29839	-1.28085
H	-3.26321	2.561851	-0.20033
C	-5.86671	1.44902	-2.08582
H	-5.94667	-0.47576	-3.05524
H	-5.4823	3.282243	-1.01456
H	-6.84145	1.766279	-2.44707
Pd	1.16043	-0.06328	0.277161
Br	1.172034	-2.39036	-0.93758
P	1.16403	2.050936	1.251529
P	3.238074	0.27762	-1.16249
C	4.327745	1.792084	-1.21168
H	4.792209	1.968876	-0.23635
H	5.128518	1.66224	-1.94911
H	3.753567	2.682539	-1.48679
C	2.871323	0.09287	-2.96624
H	3.792864	0.080174	-3.55992
H	2.318513	-0.83755	-3.11364
H	2.243745	0.926491	-3.29935
C	4.519727	-1.01893	-0.85026
H	5.333243	-0.95795	-1.58255
H	4.933166	-0.88747	0.155478
H	4.041592	-1.9995	-0.90289
C	1.005561	3.437894	0.035096
H	1.767316	3.353031	-0.74314
H	0.024418	3.380735	-0.44644

H	1.104142	4.412095	0.5277
C	-0.10299	2.556379	2.502722
H	-0.03591	1.924744	3.392882
H	0.062079	3.598709	2.797392
H	-1.10892	2.456145	2.088114
C	2.713768	2.471196	2.173852
H	2.681693	3.498509	2.55504
H	2.824224	1.781975	3.01693
H	3.585785	2.357821	1.52693

IN1

C	0.346371	1.302856	0.891285
C	0.428696	2.82454	0.60247
C	2.553297	2.125305	0.280609
C	1.794015	0.796863	0.549508
H	0.1458	1.1649	1.958406
H	2.214468	0.287347	1.424076
C	1.496997	2.929414	-0.50689
H	1.804145	3.962072	-0.71724
H	1.208313	2.451333	-1.44806
C	1.193897	3.470996	1.790333
H	1.163083	4.566256	1.717446
H	0.762359	3.195191	2.758841
C	2.648909	2.935461	1.595624
H	3.36435	3.760328	1.496982
H	2.98536	2.312811	2.432093
H	-0.52305	3.325522	0.407875
H	3.517229	1.9791	-0.2159
C	1.918056	-0.19621	-0.6386

H	1.18317	-0.98686	-0.47226
H	1.659518	0.306765	-1.57902
C	3.290926	-0.82515	-0.75224
C	4.225589	-0.41234	-1.71146
C	3.657369	-1.85632	0.128059
C	5.490211	-1.00232	-1.78742
H	3.957154	0.376459	-2.41154
C	4.917938	-2.44847	0.056581
H	2.932346	-2.19458	0.865332
C	5.84174	-2.02188	-0.90199
H	6.198568	-0.66676	-2.54127
H	5.179303	-3.24812	0.745716
H	6.823922	-2.48413	-0.96044
Pd	-1.16672	-0.05494	0.272701
P	-2.42998	1.470541	-0.92922
P	-2.46396	-2.19252	-0.01812
C	-3.08444	-2.85317	1.59414
H	-3.92014	-2.24215	1.95181
H	-3.42102	-3.89205	1.49647
H	-2.27456	-2.79888	2.323179
C	-1.24845	-3.47798	-0.54725
H	-1.65808	-4.48932	-0.44031
H	-0.96665	-3.31653	-1.59317
H	-0.36737	-3.35253	0.086158
C	-3.9116	-2.61225	-1.11849
H	-4.15145	-3.6804	-1.0547
H	-4.79897	-2.04254	-0.8241
H	-3.68064	-2.37104	-2.16097
C	-3.34563	2.661506	0.15521

H	-3.98786	2.094816	0.836752
H	-2.64728	3.245277	0.759739
H	-3.96607	3.344148	-0.43728
C	-1.68231	2.572202	-2.21692
H	-1.23473	1.953672	-3.00151
H	-2.45051	3.212952	-2.66542
H	-0.8991	3.198806	-1.78889
C	-3.83866	0.77837	-1.91321
H	-4.39281	1.580579	-2.41404
H	-3.46152	0.08384	-2.66927
H	-4.5208	0.233195	-1.25638
O	-0.12532	-1.47524	1.418254
C	-0.00054	-1.32657	2.794607
H	0.597569	-2.16322	3.200162
H	0.520461	-0.40103	3.107119
H	-0.96826	-1.33548	3.339502

TS1a

C	-0.24906	1.811883	0.501245
C	-0.60659	3.001073	-0.4104
C	1.629361	2.779945	-0.70949
C	1.28742	1.638775	0.285247
H	-0.53983	1.960937	1.546861
H	1.817199	1.791946	1.234313
C	0.364925	2.819268	-1.5976
H	0.353932	3.66588	-2.29549
H	0.192289	1.896112	-2.16095
C	-0.02672	4.283755	0.254973
H	-0.41428	5.181495	-0.24314

H	-0.29803	4.357219	1.314466
C	1.514232	4.131084	0.034605
H	1.906212	4.95164	-0.57789
H	2.076009	4.13096	0.975463
H	-1.66338	3.10541	-0.67266
H	2.581428	2.630906	-1.2272
C	1.573305	0.208177	-0.21538
H	1.128746	-0.67144	0.744929
H	1.19852	0.099711	-1.24475
C	3.016485	-0.20405	-0.22852
C	3.59563	-0.77759	-1.37685
C	3.843592	-0.06316	0.903634
C	4.929029	-1.18632	-1.39922
H	2.986451	-0.89232	-2.27196
C	5.179993	-0.46061	0.880769
H	3.432319	0.356273	1.817618
C	5.734282	-1.02735	-0.26951
H	5.342436	-1.62119	-2.30675
H	5.79061	-0.33414	1.77213
H	6.774995	-1.34044	-0.28441
Pd	-0.89688	-0.13139	0.047519
P	-3.09172	0.508041	0.043122
P	-1.07843	-2.57585	-0.43977
C	-1.63712	-3.61094	0.984675
H	-2.67691	-3.38669	1.242774
H	-1.54686	-4.68191	0.768135
H	-0.99228	-3.34255	1.825097
C	0.582097	-3.29171	-0.8036
H	0.525778	-4.37738	-0.94685

H	1.005143	-2.83032	-1.70096
H	1.221777	-3.05099	0.049317
C	-2.08964	-3.24452	-1.85169
H	-1.98156	-4.33157	-1.94529
H	-3.15204	-3.0144	-1.71722
H	-1.75947	-2.77952	-2.78678
C	-3.58282	1.81668	1.254149
H	-3.36114	1.464757	2.266486
H	-3.01572	2.733536	1.081703
H	-4.65391	2.036433	1.1777
C	-3.77762	1.134963	-1.55722
H	-3.70963	0.344418	-2.311
H	-4.82551	1.439492	-1.45085
H	-3.18948	1.987383	-1.90794
C	-4.31235	-0.8144	0.478559
H	-5.33514	-0.41973	0.477196
H	-4.25143	-1.63798	-0.23763
H	-4.08415	-1.20662	1.474209
O	0.698959	-1.45272	1.675008
C	1.026579	-1.0608	2.972677
H	1.993422	-1.48252	3.308173
H	1.104773	0.039482	3.089201
H	0.265323	-1.39458	3.701379

TS1b

C	1.811893	-0.47713	0.063559
C	2.954975	0.068786	-0.8239
C	3.040039	-2.15516	-1.19381
C	1.820164	-2.01319	-0.23503

H	1.946658	-0.29269	1.128904
H	2.001465	-2.55059	0.705088
C	2.928929	-0.87246	-2.04415
H	3.779286	-0.72994	-2.72258
H	2.001896	-0.80406	-2.6243
C	4.297224	-0.34904	-0.15637
H	5.141912	0.151868	-0.64684
H	4.330131	-0.08654	0.906156
C	4.339098	-1.89107	-0.39748
H	5.219481	-2.17628	-0.98524
H	4.370044	-2.46425	0.53544
H	2.907483	1.135874	-1.05477
H	3.047124	-3.10182	-1.74476
C	0.576969	-2.65533	-0.88121
H	0.415318	-2.20651	-1.87225
H	0.810248	-3.71172	-1.0768
C	-0.71927	-2.58389	-0.09921
C	-1.71468	-3.53554	-0.39448
C	-0.9763	-1.57972	0.860041
C	-2.95442	-3.50754	0.237961
H	-1.51024	-4.30698	-1.13544
C	-2.25179	-1.56781	1.477993
C	-3.22867	-2.51359	1.187872
H	-3.70215	-4.26077	0.000356
H	-2.43611	-0.8079	2.233645
H	-4.18672	-2.49882	1.702997
Pd	-0.10738	0.377926	-0.20974
P	0.760078	2.466086	0.401899
P	-2.34311	1.060322	-1.06122

C	-2.38198	2.546309	-2.17594
H	-1.60565	2.444932	-2.94118
H	-3.35456	2.661823	-2.66867
H	-2.17371	3.455345	-1.60188
C	-3.81965	1.374765	0.014507
H	-4.71139	1.599708	-0.58242
H	-4.00893	0.485959	0.622154
H	-3.62203	2.213281	0.689464
C	-2.99033	-0.25131	-2.19831
H	-3.94593	0.041334	-2.64961
H	-2.2635	-0.43511	-2.99642
H	-3.12313	-1.18117	-1.63792
C	-0.54914	3.298626	1.406168
H	-1.42999	3.526218	0.799314
H	-0.82977	2.596329	2.19715
H	-0.17567	4.226821	1.854462
C	2.115947	2.378553	1.641166
H	3.054397	2.063526	1.179439
H	2.259879	3.351259	2.125117
H	1.793178	1.62244	2.370926
C	1.29876	3.787935	-0.78246
H	1.603206	4.699134	-0.25407
H	2.143219	3.426352	-1.3777
H	0.480166	4.030487	-1.46764
H	-0.2045	-0.95536	1.598991
O	0.337039	-0.11176	2.657199
C	0.071633	-0.56874	3.935362
H	-0.61556	-1.4451	3.947529
H	0.979519	-0.89927	4.48615

H	-0.41294	0.194774	4.583375

TS1a'

C	-0.67489	1.874992	0.439095
C	-1.39169	3.012053	-0.31065
C	0.803364	3.394675	-0.7564
C	0.823662	2.122773	0.127967
H	-0.91007	1.817586	1.50495
H	1.413114	2.282976	1.037761
C	-0.50596	3.208405	-1.5606
H	-0.77568	4.098226	-2.14285
H	-0.50203	2.342633	-2.2311
C	-1.08865	4.324472	0.471381
H	-1.72105	5.143988	0.107118
H	-1.28007	4.216916	1.544815
C	0.421934	4.587583	0.153171
H	0.552412	5.538273	-0.37664
H	1.040672	4.629998	1.056211
H	-2.46005	2.870114	-0.5
H	1.715534	3.547598	-1.3417
C	1.261767	0.834019	-0.56763
H	0.721251	-0.30447	0.796555
H	0.94072	0.836753	-1.61521
C	2.69277	0.424284	-0.51912
C	3.326586	0.000573	-1.70476
C	3.482205	0.510193	0.64299
C	4.680391	-0.33002	-1.73253
H	2.745718	-0.0487	-2.62461
C	4.837417	0.181189	0.616324

H	3.028527	0.812891	1.57989
C	5.445376	-0.24284	-0.56719
H	5.139476	-0.64617	-2.66627
H	5.419951	0.251957	1.531425
H	6.501634	-0.49836	-0.58237
Pd	-0.75232	-0.14274	-0.21143
Br	0.901691	-1.08678	2.504998
P	-3.12794	-0.19395	-0.02021
P	-0.31848	-2.50766	-0.8866
C	-0.91444	-3.82798	0.266176
H	-2.00636	-3.84571	0.308887
H	-0.55686	-4.81524	-0.04891
H	-0.52805	-3.60255	1.264882
C	1.467561	-2.95482	-1.00848
H	1.587783	-4.01182	-1.27323
H	1.972344	-2.33395	-1.75198
H	1.938433	-2.76472	-0.03969
C	-0.97357	-3.08287	-2.52621
H	-0.68943	-4.12064	-2.73612
H	-2.06608	-3.00776	-2.54432
H	-0.57908	-2.44139	-3.32106
C	-3.77791	0.768355	1.416727
H	-3.34561	0.362438	2.336555
H	-3.47677	1.815307	1.335769
H	-4.87079	0.709813	1.472982
C	-4.07873	0.485625	-1.45709
H	-3.8916	-0.13543	-2.33898
H	-5.1559	0.500473	-1.25402
H	-3.74246	1.500944	-1.6827

C	-3.99119	-1.81319	0.238318
H	-5.07059	-1.6649	0.359108
H	-3.82325	-2.47491	-0.61706
H	-3.59809	-2.29963	1.135723

TS1b'

C	1.780042	-0.49742	-0.11416
C	2.898373	0.231344	-0.91449
C	3.193468	-1.92878	-1.48385
C	1.918248	-1.97667	-0.59371
H	1.965727	-0.4239	0.959312
H	2.071803	-2.63748	0.26933
C	3.009146	-0.58426	-2.21605
H	3.875407	-0.30309	-2.82794
H	2.110869	-0.53587	-2.84001
C	4.250489	-0.12685	-0.23478
H	5.064586	0.476995	-0.65672
H	4.234544	0.049849	0.845854
C	4.425705	-1.63675	-0.59529
H	5.355606	-1.80624	-1.15041
H	4.452218	-2.28156	0.289936
H	2.762057	1.305043	-1.05588
H	3.308943	-2.81481	-2.11728
C	0.744631	-2.56125	-1.4076
H	0.590072	-1.94694	-2.30485
H	1.033377	-3.55905	-1.76442
C	-0.55459	-2.65639	-0.65246
C	-1.29397	-3.84907	-0.71324
C	-1.05892	-1.55134	0.063934

C	-2.53438	-3.96753	-0.09018
H	-0.89126	-4.69357	-1.26952
C	-2.31921	-1.69644	0.685737
C	-3.05172	-2.88017	0.618062
H	-3.08795	-4.90139	-0.14929
H	-2.70466	-0.88093	1.292685
H	-4.00718	-2.96057	1.131184
Pd	-0.17283	0.379148	-0.27009
P	0.697377	2.574976	0.293941
P	-2.36938	1.182859	-1.17993
C	-2.28991	2.698637	-2.2531
H	-1.50525	2.569374	-3.00565
H	-3.24286	2.877906	-2.76432
H	-2.04599	3.582029	-1.65496
C	-3.8615	1.561512	-0.14243
H	-4.71375	1.862636	-0.76291
H	-4.13975	0.674547	0.433136
H	-3.63352	2.365686	0.563966
C	-3.06112	-0.03769	-2.38889
H	-3.98038	0.337442	-2.85389
H	-2.32144	-0.23501	-3.17153
H	-3.26865	-0.97907	-1.87408
C	-0.5892	3.494834	1.260863
H	-1.45626	3.727902	0.63592
H	-0.91889	2.858495	2.08789
H	-0.18688	4.430427	1.666175
C	2.070789	2.561187	1.532184
H	2.994559	2.187074	1.085667
H	2.246748	3.568935	1.92563

H	1.786728	1.892109	2.350343
C	1.265374	3.866742	-0.91348
H	1.57655	4.784101	-0.40014
H	2.109889	3.48511	-1.49564
H	0.456673	4.107639	-1.61019
H	-0.33441	-0.86539	1.395433
Br	-0.06221	-0.56882	3.080822

IN2a

C	-1.18613	1.57895	0.431037
C	-2.32869	2.099289	-0.46156
C	-0.52966	3.303584	-1.13755
C	0.045927	2.39585	-0.02636
H	-1.40353	1.624571	1.503322
H	0.509935	3.004778	0.762525
C	-1.59905	2.397206	-1.7911
H	-2.22568	2.934384	-2.51483
H	-1.19063	1.500068	-2.2669
C	-2.67022	3.540476	0.013321
H	-3.59176	3.902425	-0.46133
H	-2.82227	3.589941	1.097781
C	-1.4264	4.367613	-0.4571
H	-1.71884	5.144135	-1.17402
H	-0.91347	4.867192	0.372715
H	-3.20792	1.449754	-0.54076
H	0.229429	3.721729	-1.8082
C	0.988624	1.274516	-0.5056
H	1.149745	1.300373	-1.58803
C	2.268409	1.106256	0.224295

C	3.484492	0.939822	-0.47305
C	2.346924	1.131191	1.635551
C	4.70162	0.78421	0.193263
H	3.47325	0.961618	-1.56119
C	3.561029	0.983873	2.302026
H	1.433148	1.252014	2.211261
C	4.750578	0.801109	1.588403
H	5.616669	0.663611	-0.38278
H	3.579802	1.007097	3.389551
H	5.696244	0.683376	2.110704
Pd	-0.4011	-0.31111	-0.05986
P	-2.28243	-1.53677	0.831064
P	0.956109	-2.15606	-0.95881
C	0.193857	-3.79199	-1.41475
H	-0.62405	-3.63119	-2.12532
H	0.927427	-4.46734	-1.87136
H	-0.21789	-4.27958	-0.52573
C	2.384983	-2.70475	0.085092
H	2.983989	-3.47485	-0.4158
H	3.01813	-1.84003	0.303113
H	2.013958	-3.1038	1.034784
C	1.798148	-1.74984	-2.55892
H	2.417865	-2.58226	-2.9129
H	1.046325	-1.51482	-3.31928
H	2.430615	-0.87015	-2.41923
C	-3.36141	-0.57699	1.991696
H	-2.77386	-0.26824	2.862122
H	-3.72518	0.327153	1.496718
H	-4.21751	-1.17097	2.332556

C	-3.5383	-2.17545	-0.37861
H	-3.06622	-2.89285	-1.05741
H	-4.38221	-2.6637	0.123427
H	-3.91522	-1.34185	-0.97964
C	-1.96907	-3.04841	1.865904
H	-2.89879	-3.45868	2.277664
H	-1.47985	-3.82253	1.267689
H	-1.30025	-2.78713	2.692358

IN2b

C	1.796875	0.181024	-0.40734
C	2.743316	-0.85866	0.260561
C	3.539644	1.09294	1.056693
C	2.34295	1.538009	0.172786
H	1.9172	0.159747	-1.49628
H	2.702415	2.178585	-0.64498
C	3.02673	-0.2376	1.641545
H	3.789031	-0.77992	2.215949
H	2.127412	-0.13085	2.257525
C	4.142895	-0.75182	-0.4076
H	4.788242	-1.58577	-0.10028
H	4.079543	-0.77311	-1.50157
C	4.685487	0.608079	0.138757
H	5.610334	0.463486	0.710112
H	4.903579	1.328892	-0.65729
H	2.371745	-1.88417	0.289433
H	3.849397	1.853999	1.781453
C	1.332282	2.386447	0.975071
H	0.9737	1.807518	1.837242

H	1.839835	3.277197	1.370989
C	0.17757	2.782093	0.093714
C	-0.09222	4.127167	-0.19491
C	-0.57422	1.764704	-0.5153
C	-1.09216	4.481608	-1.10361
H	0.493111	4.905754	0.292396
C	-1.56232	2.133941	-1.44288
C	-1.82055	3.478347	-1.7423
H	-1.29017	5.529215	-1.3179
H	-2.14222	1.367068	-1.95447
H	-2.58604	3.735533	-2.472
Pd	-0.28595	-0.2386	-0.1288
P	-0.08573	-2.65984	-0.5853
P	-2.56303	-0.30205	0.832502
C	-2.88808	-1.64792	2.074217
H	-2.10131	-1.63153	2.835725
H	-3.85853	-1.51989	2.56817
H	-2.8696	-2.63019	1.591842
C	-4.11072	-0.37108	-0.19313
H	-5.01251	-0.33154	0.429368
H	-4.11924	0.479905	-0.88063
H	-4.12876	-1.29041	-0.78705
C	-2.89407	1.191869	1.873503
H	-3.87164	1.131097	2.366269
H	-2.11197	1.280776	2.633894
H	-2.85181	2.084522	1.244734
C	-1.6536	-3.36816	-1.2904
H	-2.44137	-3.39084	-0.53148
H	-1.99511	-2.73531	-2.11574

H	-1.50125	-4.38723	-1.66475
C	1.067562	-3.06052	-1.98403
H	2.096218	-2.80503	-1.72004
H	1.018102	-4.12327	-2.24901
H	0.785652	-2.46191	-2.85605
C	0.35022	-3.97362	0.656899
H	0.356905	-4.97475	0.209418
H	1.336902	-3.76963	1.083792
H	-0.37821	-3.9553	1.474366

TS2a

C	-1.92734	-0.41841	0.405703
C	-2.46407	-1.68405	-0.27185
C	-3.67833	0.000491	-1.19268
C	-2.75349	0.701006	-0.18324
H	-1.7986	-0.42134	1.483683
H	-3.26218	1.39718	0.488492
C	-2.81583	-1.18304	-1.68923
H	-3.40203	-1.91173	-2.26152
H	-1.9398	-0.8993	-2.27714
C	-3.89234	-1.90474	0.315304
H	-4.27567	-2.89166	0.028508
H	-3.89963	-1.8598	1.410113
C	-4.73089	-0.7537	-0.33985
H	-5.5294	-1.15585	-0.97397
H	-5.20263	-0.10057	0.403026
H	-1.81467	-2.56031	-0.21522
H	-4.10007	0.654043	-1.96359
C	-1.37355	1.089183	-0.61478

Pd	0.378527	-0.43773	-0.0662
P	1.290344	-1.40127	1.915979
P	1.894199	-0.41482	-1.91551
C	2.658425	-2.05445	-2.35841
H	1.869027	-2.76415	-2.62744
H	3.364036	-1.97403	-3.19511
H	3.184075	-2.45656	-1.48645
C	3.432001	0.62312	-1.75079
H	4.072481	0.566562	-2.64022
H	3.148808	1.666241	-1.57699
H	4.003628	0.28584	-0.87965
C	1.344809	0.11999	-3.61934
H	2.152112	0.057369	-4.36035
H	0.514932	-0.51466	-3.9493
H	0.982467	1.153244	-3.58583
C	2.416387	-0.22931	2.82139
H	3.244254	0.052789	2.163028
H	1.864741	0.683342	3.067856
H	2.823225	-0.66648	3.742204
C	0.181607	-1.92841	3.321918
H	-0.47585	-2.73799	2.986419
H	0.747358	-2.27403	4.196479
H	-0.45134	-1.0871	3.625218
C	2.389084	-2.90377	1.831502
H	2.788102	-3.1869	2.814112
H	1.824123	-3.74829	1.422585
H	3.226253	-2.70232	1.154592
C	-0.6812	2.212211	0.059406
C	0.217626	3.013522	-0.6753

C	-0.92338	2.573934	1.400323
C	0.848233	4.113817	-0.10024
H	0.408415	2.767294	-1.71715
C	-0.28468	3.671408	1.978008
H	-1.61372	1.987957	2.000223
C	0.606411	4.448796	1.235452
H	1.527209	4.716554	-0.6989
H	-0.49153	3.923544	3.015495
H	1.098646	5.305998	1.686566
H	-1.18402	1.026464	-1.68151

P

C	0.930845	-0.76179	-0.23389
C	2.324891	-1.1369	0.282372
C	2.324922	1.13658	0.283468
C	0.93087	0.762015	-0.23316
H	0.532153	-1.3142	-1.08187
H	0.532199	1.315246	-1.08061
C	2.654867	-0.00064	1.27568
H	3.711144	-0.00079	1.567764
H	2.055225	-0.00107	2.18925
C	3.302889	-0.7845	-0.87513
H	4.304576	-1.18081	-0.67215
H	2.973075	-1.20373	-1.83193
C	3.302919	0.785266	-0.87437
H	4.304621	1.181337	-0.671
H	2.973131	1.205438	-1.83076
H	2.428107	-2.15681	0.665725
H	2.428168	2.156115	0.667805

C	-0.04369	-0.00028	0.639492
H	0.124764	-0.00082	1.715613
C	-1.50228	-0.0001	0.276007
C	-2.20509	1.203942	0.126906
C	-2.20534	-1.20401	0.126964
C	-3.57067	1.206582	-0.16215
H	-1.67224	2.145086	0.238687
C	-3.57092	-1.20638	-0.16208
H	-1.67268	-2.14526	0.238778
C	-4.25868	0.00017	-0.30819
H	-4.09682	2.151147	-0.27551
H	-4.09727	-2.15084	-0.27539
H	-5.32139	0.000275	-0.53602

$Pd(PMe_{3)2}$

Pd	-3E-06	0.004664	-0.01432
P	-2.31619	-0.00071	0.001036
P	2.316188	-0.0007	0.00102
C	3.171576	-1.38833	-0.88935
H	2.876481	-1.38024	-1.94334
H	4.264156	-1.30963	-0.82205
H	2.854582	-2.34427	-0.46077
C	3.179517	1.468856	-0.73775
H	4.271489	1.377479	-0.68036
H	2.884276	1.574925	-1.78643
H	2.868272	2.375615	-0.20979
C	3.146431	-0.09088	1.660059
H	2.828511	-1.00228	2.176081
H	4.240419	-0.09004	1.57446

H	2.834466	0.763735	2.268572
C	-3.17156	-1.38881	-0.88866
H	-4.26414	-1.3101	-0.82138
H	-2.87649	-1.38122	-1.94267
H	-2.85454	-2.34454	-0.45964
C	-3.1795	1.468458	-0.73852
H	-2.88424	1.573951	-1.78726
H	-4.27147	1.37713	-0.6811
H	-2.86825	2.3755	-0.21105
C	-3.14645	-0.08998	1.660114
H	-2.83446	0.764941	2.268181
H	-4.24044	-0.08915	1.574513
H	-2.82856	-1.00112	2.176616

NaOMe

Na	1.660314	-0.00025	0.000016
O	-0.27096	0.000856	-4.8E-05
C	-1.64014	-0.00036	0.000019
H	-2.08574	1.017578	-0.08194
H	-2.08452	-0.58076	-0.84072
H	-2.08465	-0.43878	0.922747

NaBr

Br	0	0	0.607751
Na	0	0	-1.93375

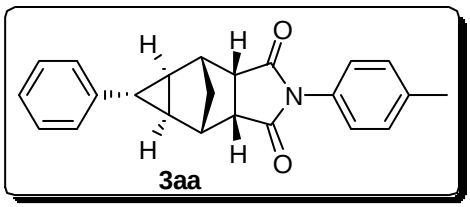
MeOH

O	0.748584	0.122507	0.000003
C	-0.66189	-0.01969	0.000002

H	-1.07986	0.990833	-0.00087
H	-1.03666	-0.54449	-0.89287
H	-1.0368	-0.54301	0.893688
H	1.13596	-0.76527	0.000015

3.3 Experimental Characterization of Products

***N*-(4-methylphenyl)-3-*exo*-phenyltricyclo[3.2.1.0^{2,4}]octane-6,7-*endo*-dicarboximide (3aa):** The title compound was prepared according to the general procedure and purified by flash column chromatography on silica gel with a gradient eluent of petroleum ether/EtOAc (10/1→3/1) to give white solid, 156.1 mg, 91 % yield. **Mp:** 257-259 ^{o}C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.30 (d, *J* = 8.0 Hz, 2H), 7.16-7.21 (t, *J* = 7.6 Hz, 2H), 7.15 (d, *J* = 7.6 Hz, 2H), 6.98 (d, *J* = 7.6 Hz, 2H), 3.29 (s, 2H), 3.12 (s, 2H), 2.39 (s, 3H), 2.10 (s, 1H), 1.61 (d, *J* = 11.2 Hz, 1H), 1.33 (s, 2H), 1.20 (d, *J* = 11.2 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 177.6, 141.2, 139.5, 130.7, 130.0, 129.1, 127.0, 126.8, 126.7, 49.9, 40.1, 32.5, 23.0, 21.9, 18.0; **HRMS (EI)** calcd. for $C_{23}H_{21}NO_2$ [M^+]: 343.1572, found: 343.1569. The configuration was confirmed by X-ray analysis (Figure S1) and undoubtedly determined that methylenecyclopropane moiety was formed



3aa

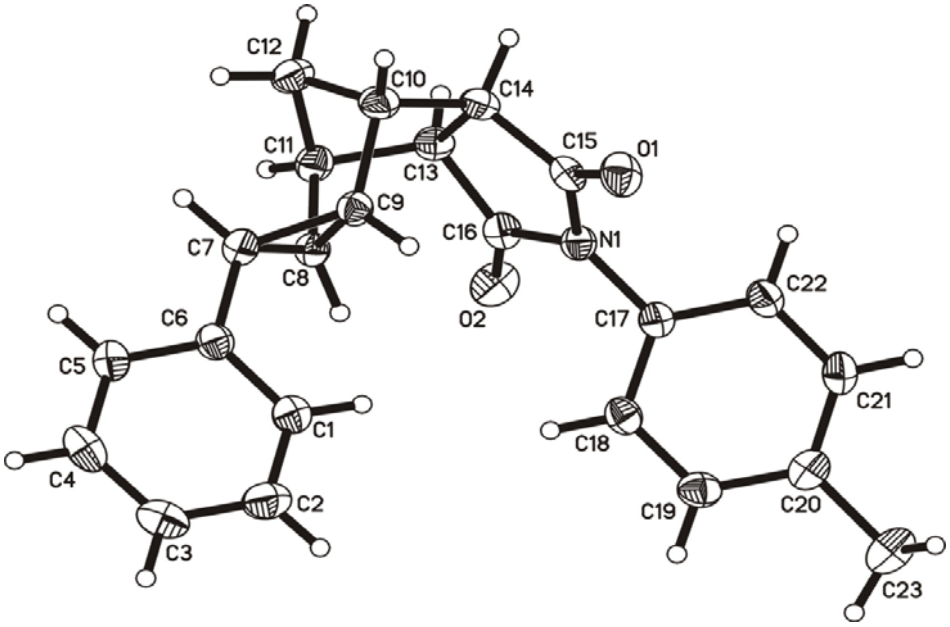
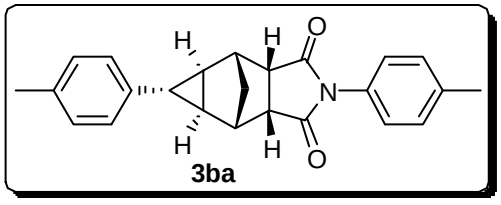


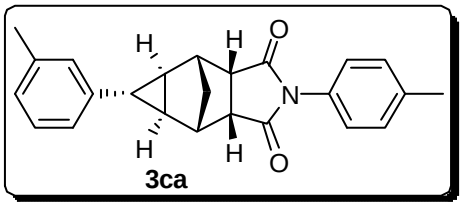
Figure S1. ORTEP drawing of product **3aa**

***N*-(4-methylphenyl)-3-*exo*-(4-methylphenyl)tricyclo[3.2.1.0^{2,4}]octane-6,7-*endo*-dic**



arboximide (3ba): The title compound was prepared according to the general procedure and purified by flash column chromatography on silica gel with a gradient eluent of petroleum ether/EtOAc (10/1→3/1) to give white solid, 169.7 mg, 95 % yield. **Mp:** 195-197 ^{o}C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.29 (d, *J* = 7.6 Hz, 2H), 7.14 (d, *J* = 8.0 Hz, 2H), 7.03 (d, *J* = 8.0 Hz, 2H), 6.87 (d, *J* = 8.0 Hz, 2H), 3.26 (s, 2H), 3.10 (s, 2H), 2.38 (s, 3H), 2.80 (s, 3H), 2.07 (s, 1H), 1.58 (d, *J* = 11.6 Hz, 1H), 1.28 (s, 2H), 1.18 (d, *J* = 12.4 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 177.6, 139.5, 138.0, 136.3, 135.3, 130.6, 129.8, 127.0, 126.7, 50.0, 40.1, 32.5, 22.8, 21.9, 21.6, 17.6; **HRMS (EI)** calcd. for $C_{24}H_{23}NO_2$ [M^+]: 357.1729, found: 357.1726.

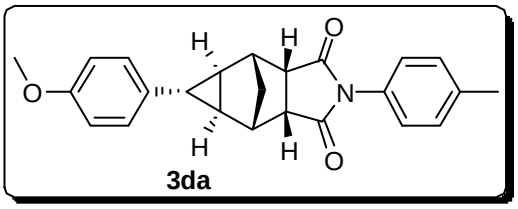
***N*-(4-methylphenyl)-3-*exo*-(3-methylphenyl)tricyclo[3.2.1.0^{2,4}]octane-6,7-*endo*-dic**



arboximide (3ca): The title compound was prepared according to the general procedure and purified by flash column chromatography on silica gel with a gradient eluent of petroleum ether/EtOAc (10/1→3/1) to give white solid, 166.0 mg, 93 % yield. **Mp:** 200-203 ^{o}C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.29 (d, *J* = 7.6 Hz, 2H), 7.08-7.16 (m, 3H), 6.96 (d, *J*

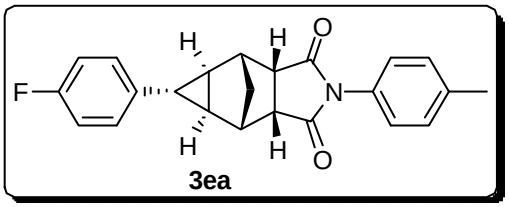
= 6.8 Hz, 1H), 6.78 (d, *J* = 7.2 Hz, 2H), 3.26 (s, 2H), 3.10 (s, 2H), 2.38 (s, 3H), 2.27 (s, 3H), 2.06 (s, 1H), 1.57 (d, *J* = 11.2 Hz, 1H), 1.30 (s, 2H), 1.18 (d, *J* = 11.2 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 177.7, 141.2, 139.5, 138.6, 135.3, 130.6, 129.0, 127.5, 127.1, 127.1, 123.9, 50.0, 40.1, 32.5, 23.1, 22.1, 21.9, 17.9; **HRMS (EI)** calcd. for $C_{24}H_{23}NO_2$ [M^+]: 357.1729, found: 357.1727.

***N*-(4-methylphenyl)-3-*exo*-(4-methoxyphenyl)tricyclo[3.2.1.0^{2,4}]octane-6,7-*endo*-dicarboximide (3da):** The title compound was prepared according to the general procedure and purified by flash column chromatography on silica gel with a gradient eluent of petroleum ether/EtOAc (10/1→3/1) to give white solid, 153.0 mg, 82 % yield. **Mp:** 189-192 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.29 (d, *J* = 7.2 Hz, 2H), 7.13 (d, *J* = 8.0 Hz, 2H), 6.91 (d, *J* = 8.4 Hz, 2H), 6.77 (d, *J* = 8.4 Hz, 2H), 3.76 (s, 3H), 3.27 (s, 2H), 3.10 (s, 2H), 2.38 (s, 3H), 2.06 (s, 1H), 1.57 (d, *J* = 11.6 Hz, 1H), 1.25 (s, 2H), 1.17 (d, *J* = 11.2 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 177.7, 158.7, 139.4, 130.6, 130.2, 127.9, 127.1, 127.0, 114.5, 55.9, 50.0, 40.1, 32.5, 22.5, 21.9, 17.3; **HRMS (EI)** calcd. for $C_{24}H_{23}NO_3$ [M^+]: 373.1678, found: 373.1680.



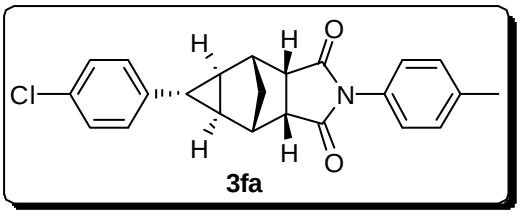
3da

***N*-(4-methylphenyl)-3-*exo*-(4-fluorophenyl)tricyclo[3.2.1.0^{2,4}]octane-6,7-*endo*-dicarboximide (3ea):** The title compound was prepared according to the general procedure and purified by flash column chromatography on silica gel with a gradient eluent of petroleum ether/EtOAc (10/1→3/1) to give white solid, 155.3 mg, 86 % yield. **Mp:** 232-235 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.31 (d, *J* = 7.6 Hz, 2H), 7.14 (d, *J* = 8.0 Hz, 2H), 6.94 (d, *J* = 8.4 Hz, 4H), 3.30 (s, 2H), 3.14 (s, 2H), 2.41 (s, 3H), 2.11 (s, 1H), 1.59 (d, *J* = 11.2 Hz, 1H), 1.29 (s, 2H), 1.22 (d, *J* = 11.2 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 177.5, 162.0 (d, $J_{C\text{-}F}$ = 242.0 Hz), 139.5, 136.7 (d, $J_{C\text{-}F}$ = 3.4 Hz), 130.6, 130.0, 128.3 (d, $J_{C\text{-}F}$ = 7.7 Hz), 126.9, 115.9 (d, $J_{C\text{-}F}$ = 21.5 Hz), 49.9, 40.1, 32.5, 22.8, 21.9, 17.3; **HRMS (EI)** calcd. for $C_{23}H_{20}FNO_2$ [M^+]: 361.1478, found: 361.1480.



3ea

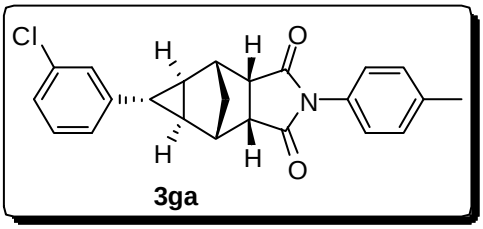
***N*-(4-methylphenyl)-3-*exo*-(4-chlorophenyl)tricyclo[3.2.1.0^{2,4}]octane-6,7-*endo*-dic**



3fa

arboximide (3fa): The title compound was prepared according to the general procedure and purified by flash column chromatography on silica gel with a gradient eluent of petroleum ether/EtOAc (10/1→3/1) to give white solid, 156.5 mg, 83 % yield. **Mp:** 226-229 ^{o}C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.29 (d, *J* = 8.4 Hz, 2H), 7.19 (d, *J* = 8.4 Hz, 2H), 7.12 (d, *J* = 8.4 Hz, 2H), 6.90 (d, *J* = 8.4 Hz, 2H), 3.28 (s, 2H), 3.11 (s, 2H), 2.39 (s, 3H), 2.07 (s, 1H), 1.56 (d, *J* = 11.6 Hz, 1H), 1.28 (s, 2H), 1.20 (d, *J* = 10.4 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 176.8, 139.1, 138.9, 131.7, 130.0, 129.3, 128.5, 127.5, 126.3, 49.2, 39.4, 31.8, 22.4, 21.3, 16.9; **HRMS (EI)** calcd. for $C_{23}H_{20}ClNO_2$ [M^+]: 377.1183, found: 377.1181.

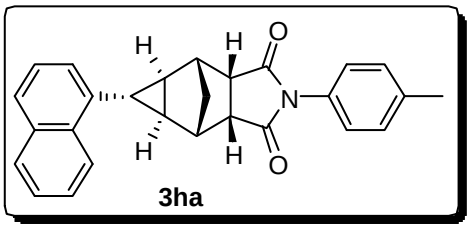
***N*-(4-methylphenyl)-3-*exo*-(3-chlorophenyl)tricyclo[3.2.1.0^{2,4}]octane-6,7-*endo*-dic**



3ga

arboximide (3ga): The title compound was prepared according to the general procedure and purified by flash column chromatography on silica gel with a gradient eluent of petroleum ether/EtOAc (10/1→3/1) to give white solid, 147.1 mg, 78 % yield. **Mp:** 227-230 ^{o}C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.33 (d, *J* = 7.6 Hz, 2H), 7.16 (d, *J* = 6.8 Hz, 4H), 6.98 (s, 1H), 6.89 (s, 1H), 3.31 (s, 2H), 3.14 (s, 2H), 2.41(s, 3H), 2.09 (s, 1H), 1.58 (d, *J* = 10.8 Hz, 1H), 1.33 (s, 2H), 1.22 (d, *J* = 10.4 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 177.5, 143.5, 139.6, 134.9, 130.7, 130.3, 129.9, 127.0, 126.9, 125.0, 49.8, 40.1, 32.5, 23.3, 21.9, 17.7; **HRMS (EI)** calcd. for $C_{23}H_{20}ClNO_2$ [M^+]: 377.1183, found: 377.1180.

***N*-(4-methylphenyl)-3-*exo*-(1-naphthalenyl)tricyclo[3.2.1.0^{2,4}]octane-6,7-*endo*-dic**

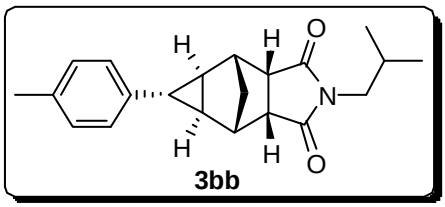


3ha

arboximide (3ha): The title compound was prepared according to the general procedure and purified by flash column chromatography on silica gel with a gradient eluent of petroleum

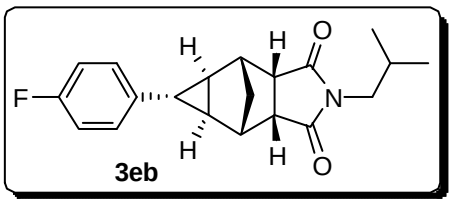
ether/EtOAc (10/1→3/1) to give white solid, 167.1 mg, 85 % yield. **Mp:** 246-249 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.19 (d, *J* = 8.0 Hz, 1H), 7.84 (d, *J* = 7.6 Hz, 1H), 7.71 (d, *J* = 8.4 Hz, 1H), 7.47-7.55 (m, 2H), 7.34 (t, *J* = 8.0 Hz, 1H), 7.23 (d, *J* = 7.2 Hz, 1H), 7.17 (d, *J* = 8.0 Hz, 2H), 6.98 (d, *J* = 8.0 Hz, 2H), 3.32 (s, 2H), 3.27 (s, 2H), 2.52 (s, 1H), 2.31 (s, 3H), 1.73 (d, *J* = 11.2 Hz, 1H), 1.48 (s, 2H), 1.31 (d, *J* = 11.2 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 177.0, 138.7, 135.5, 133.6, 133.0, 129.8, 129.2, 128.6, 127.2, 126.4, 126.0, 125.8, 125.5, 124.7, 124.0, 49.4, 39.4, 32.2, 21.2, 19.8, 15.3; **HRMS (EI)** calcd. for $C_{27}H_{23}NO_2$ [M^+]: 393.1729, found: 393.1731.

***N*-isobutyl-3-*exo*-(4-methylphenyl)tricyclo[3.2.1.0^{2,4}]octane-6,7-*endo*-dicarboximide (3bb):** The title compound was prepared according to the general procedure and purified by flash column chromatography on silica gel with a gradient eluent of petroleum ether/EtOAc (10/1→3/1) to give light yellow sticky oil, 145.4 mg, 90 % yield. **Mp:** 137-139 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.03 (d, *J* = 8.0 Hz, 2H), 6.87 (d, *J* = 8.0 Hz, 2H), 3.34 (d, *J* = 6.8 Hz, 2H), 3.13 (s, 2H), 3.02 (s, 2H), 2.29 (s, 3H), 2.00-2,10 (m, 2H), 1.56 (d, *J* = 11.6 Hz, 1H), 1.15 (s, 2H), 1.13 (s, 1H), 0.94 (d, *J* = 6.8 Hz, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 178.6, 138.0, 136.2, 129.6, 126.9, 49.9, 46.8, 39.5, 32.6, 28.1, 22.4, 21.6, 21.1, 17.7; **HRMS (EI)** calcd. for $C_{21}H_{25}NO_2$ [M^+]: 323.1885, found: 323.1886.



3bb

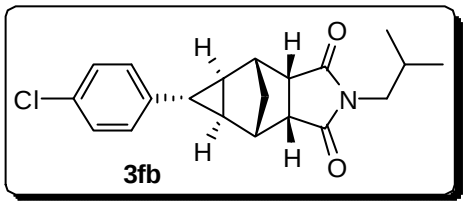
***N*-isobutyl-3-*exo*-(4-fluorophenyl)tricyclo[3.2.1.0^{2,4}]octane-6,7-*endo*-dicarboximide (3eb):** The title compound was prepared according to the general procedure and purified by flash column chromatography on silica gel with a gradient eluent of petroleum ether/EtOAc (10/1→3/1) to give light yellow sticky oil, 134.1 mg, 82 % yield. **Mp:** 124-127 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.87-6.95 (m, 4H), 3.33 (d, *J* = 7.2 Hz, 2H), 3.12 (s, 2H), 3.01 (s, 2H), 2.98-2,08 (m, 2H), 1.53 (d, *J* = 11.2 Hz, 1H), 1.16 (s, 1H), 1.13 (d, *J* = 2.0 Hz, 2H), 0.91 (d, *J* = 6.8 Hz, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 177.9, 161.3 (d, $J_{C\text{-}F}$ = 242.8 Hz), 136.0 (d, $J_{C\text{-}F}$ = 2.7 Hz), 127.9 (d, $J_{C\text{-}F}$ = 8.4 Hz), 115.1 (d, $J_{C\text{-}F}$ = 21.1 Hz), 49.2, 46.2, 38.8, 31.9, 27.4, 21.8, 20.4, 16.8; **HRMS (EI)** calcd. for



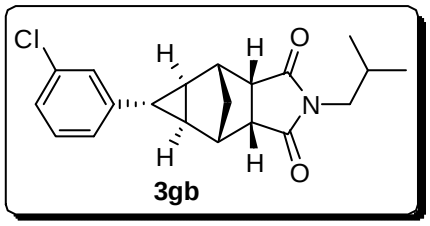
3eb

$C_{20}H_{22}FNO_2$ [M^+]: 327.1635, found: 327.1638.

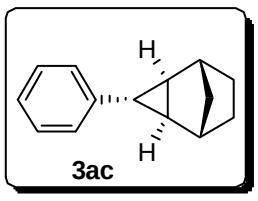
***N*-isobutyl-3-*exo*-(4-chlorophenyl)tricyclo[3.2.1.0^{2,4}]octane-6,7-*endo*-dicarboximide (3fb):** The title compound was prepared according to the general procedure and purified by flash column chromatography on silica gel with a gradient eluent of petroleum ether/EtOAc (10/1→3/1) to give light yellow solid, 132.1 mg, 77 % yield. **Mp:** 155-158 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.17 (d, *J* = 8.0 Hz, 2H), 6.89 (d, *J* = 7.6 Hz, 2H), 3.33 (d, *J* = 7.2 Hz, 2H), 3.13 (s, 2H), 3.01 (s, 2H), 2.00-2,08 (m, 2H), 1.53 (d, *J* = 11.2 Hz, 1H), 1.16 (s, 1H), 1.13 (s, 2H), 0.91 (d, *J* = 6.8 Hz, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 177.8, 139.0, 131.7, 128.4, 127.7, 49.2, 46.2, 38.8, 31.9, 27.4, 22.1, 20.4, 16.9; **HRMS (EI)** calcd. for $C_{20}H_{22}ClNO_2$ [M^+]: 343.1339, found: 343.1337.



***N*-isobutyl-3-*exo*-(3-chlorophenyl)tricyclo[3.2.1.0^{2,4}]octane-6,7-*endo*-dicarboximide (3gb):** The title compound was prepared according to the general procedure and purified by flash column chromatography on silica gel with a gradient eluent of petroleum ether/EtOAc (10/1→3/1) to give light yellow sticky oil, 127.0 mg, 74 % yield. **Mp:** 110-113 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.11-7.14 (m, 2H), 6.91 (s, 1H), 6.86 (d, *J* = 6.0 Hz, 1H), 3.34 (d, *J* = 7.2 Hz, 2H), 3.13 (s, 2H), 3.02 (s, 2H), 2.00-2,10 (m, 2H), 1.52 (d, *J* = 11.2 Hz, 1H), 1.16 (s, 2H), 1.13 (s, 1H), 0.94 (d, *J* = 6.8 Hz, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 177.8, 142.7, 134.2, 129.5, 126.3, 126.1, 124.7, 49.2, 46.3, 38.8, 31.9, 27.5, 22.4, 20.5, 17.2; **HRMS (EI)** calcd. for $C_{20}H_{22}ClNO_2$ [M^+]: 343.1339, found: 343.1337.

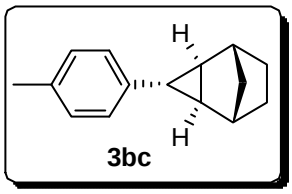


3-*exo*-phenyltricyclo[3.2.1.0^{2,4}]octane (3ac): The title compound was prepared according to the general procedure and purified by flash column chromatography on silica gel with a eluent of petroleum ether/EtOAc (100/1) to give light yellow sticky oil, 81.9 mg, 89 % yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.19 (t, *J* = 8.0 Hz, 2H), 7.09-7.12 (m, 1H), 7.01 (d, *J* = 6.8 Hz, 2H), 2.41 (s, 2H), 1.81 (t, *J* = 2.8 Hz, 1H),



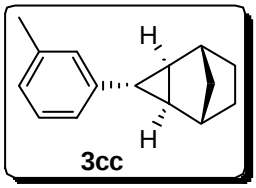
1.46-1.51 (m, 2H), 1.30-1.35 (m, 2H), 1.16-1.20 (m, 1H), 1.02 (d, *J* = 2.4 Hz, 2H), 0.74 (d, *J* = 10.4 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 143.2, 128.2, 125.9, 125.1, 36.5, 29.5, 28.8, 27.8, 18.4; **HRMS (EI)** calcd. for $C_{14}H_{16}$ [M^+]: 184.1252, found: 184.1250.

3-*exo*-(4-methylphenyl)tricyclo[3.2.1.0^{2,4}]octane (3bc): The title compound was



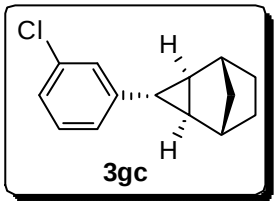
prepared according to the general procedure and purified by flash column chromatography on silica gel with a eluent of petroleum ether to give light yellow sticky oil, 91.1 mg, 92 % yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.01 (d, *J* = 8.4 Hz, 2H), 6.91 (dd, *J* = 2.0 Hz, *J* = 8.4 Hz, 2H), 2.39 (s, 2H), 2.27 (s, 3H), 1.78 (t, *J* = 2.4 Hz, 1H), 1.47-1.50 (m, 2H), 1.30-1.34 (m, 2H), 1.16 (dd, *J* = 2.0 Hz, *J* = 10.4 Hz, 1H), 0.98 (s, 2H) 0.72 (d, *J* = 10.4 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 140.1, 134.6, 128.9, 125.8, 36.4, 29.5, 28.8, 27.5, 21.0, 18.0; **HRMS (EI)** calcd. for $C_{15}H_{18}$ [M^+]: 198.1409, found: 198.1412.

3-*exo*-(3-methylphenyl)tricyclo[3.2.1.0^{2,4}]octane (3cc): The title compound was



prepared according to the general procedure and purified by flash column chromatography on silica gel with a eluent of petroleum ether to give light yellow sticky oil, 89.2 mg, 90 % yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.09 (t, *J* = 7.2 Hz, 1H), 6.91 (d, *J* = 7.6 Hz, 1H), 6.82 (d, *J* = 9.2 Hz, 2H), 2.40 (s, 2H), 2.29 (s, 3H), 1.78 (t, *J* = 2.8 Hz, 1H), 1.47-1.50 (m, 2H), 1.31-1.34 (m, 2H), 1.15-1.19 (m, 1H), 1.01 (d, *J* = 2.8 Hz, 2H), 0.73 (d, *J* = 10.8 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 143.2, 137.7, 128.1, 126.7, 125.9, 122.9, 36.4, 29.5, 28.8, 27.7, 21.5, 18.3; **HRMS (EI)** calcd. for $C_{15}H_{18}$ [M^+]: 198.1409, found: 198.1411.

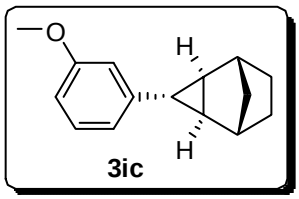
3-*exo*-(3-chlorophenyl)tricyclo[3.2.1.0^{2,4}]octane (3gc): The title compound was



prepared according to the general procedure and purified by flash column chromatography on silica gel with a eluent of petroleum ether to give light yellow sticky oil, 93.8 mg, 86 % yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.05-7.13 (m, 2H), 6.97 (t, *J* = 2.0 Hz, 1H), 6.88-6.91 (m, 1H), 2.41 (s, 2H), 1.78 (t, *J* = 2.8 Hz, 1H), 1.47-1.51

(m, 2H), 1.29-1.34 (m, 2H), 1.12-1.16 (m, 1H), 1.01 (d, *J* = 2.4 Hz, 2H), 0.74 (d, *J* = 10.8 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 145.5, 134.0, 129.3, 125.9, 125.2, 124.3, 36.4, 29.3, 28.7, 28.0, 18.2; **HRMS (EI)** calcd. for $C_{14}H_{15}Cl$ [M^+]: 218.0862, found: 218.0859.

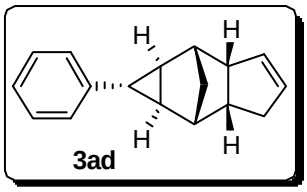
3-*exo*-(4-methoxyphenyl)tricyclo[3.2.1.0^{2,4}]octane (3ic): The title compound was



3ic

prepared according to the general procedure and purified by flash column chromatography on silica gel with a eluent of petroleum ether to give light yellow sticky oil, 99.6 mg, 93 % yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.12 (t, *J* = 8.0 Hz, 1H), 6.61-6.67 (m, 2H), 6.56 (d, *J* = 2.0 Hz, 1H), 3.76 (s, 3H), 2.40 (s, 2H), 1.79 (t, *J* = 2.8 Hz, 1H), 1.47-1.50 (m, 2H), 1.30-1.34 (m, 2H), 1.14-1.18 (m, 1H), 1.01 (d, *J* = 2.8 Hz, 2H), 0.73 (d, *J* = 10.8 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 159.5, 145.0, 129.0, 118.4, 111.7, 110.5, 55.1, 36.4, 29.4, 28.7, 27.7, 18.4; **HRMS (EI)** calcd. for $C_{15}H_{18}O$ [M^+]: 214.1358, found: 214.1360.

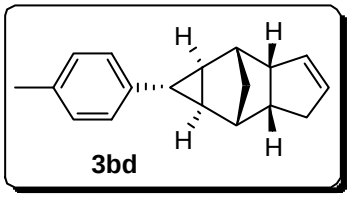
(1^a*R*,2*R*,2^a*R*,5^a*R*,6*S*,6^a*S*)-1-phenyl-1,1^a,2,2^a,3,5^a,6,6^a-octahydro-2,6-methanocyclop



3ad

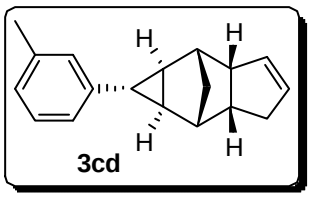
ropa[*f*]indene (3ad): The title compound was prepared according to the general procedure and purified by flash column chromatography on silica gel with a eluent of petroleum ether to give light yellow solid, 99.9 mg, 90 % yield. **Mp:** 94-99 ^{o}C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.18 (t, *J* = 7.6 Hz, 2H), 7.00 (t, *J* = 7.6 Hz, 1H), 6.99 (d, *J* = 7.2 Hz, 2H), 5.76 (dd, *J* = 2.0 Hz, *J* = 5.6 Hz, 1H), 5.58 (dd, *J* = 2.4 Hz, *J* = 5.6 Hz, 1H), 3.10-3.14 (m, 1H), 2.54-2.60 (m, 1H), 2.49-2.50 (m, 1H), 2.34-2.42 (m, 2H), 2.20-2.28 (m, 1H), 1.91 (t, *J* = 2.8 Hz, 1H), 1.30 (d, *J* = 10.8 Hz, 1H), 1.12-1.13 (m, 1H), 0.96 (d, *J* = 10.4 Hz, 1H), 0.86-0.89 (m, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 143.6, 132.3, 131.0, 128.2, 126.0, 125.2, 54.8, 43.2, 40.1, 38.7, 31.8, 31.6, 25.4, 22.5, 17.6; **HRMS (EI)** calcd. for $C_{17}H_{18}$ [M^+]: 222.1409, found: 222.1411.

(1^a*R*,2*R*,2^a*R*,5^a*R*,6*S*,6^a*S*)-1-(4-methylphenyl)-1,1^a,2,2^a,3,5^a,6,6^a-octahydro-2,6-met



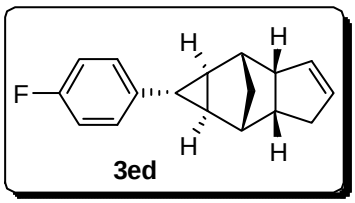
hanocyclopropa[*f*]indene (3bd): The title compound was prepared according to the general procedure and purified by flash column chromatography on silica gel with a eluent of petroleum ether to give light yellow solid, 109.8 mg, 93 % yield. **Mp:** 84-87 ^{o}C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.01 (d, *J* = 7.6 Hz, 2H), 6.90 (d, *J* = 7.6 Hz, 2H), 5.76 (d, *J* = 4.8 Hz, 1H), 5.59 (d, *J* = 1.2 Hz, 1H), 3.11-3.13 (m, 1H), 2.55-2.60 (m, 1H), 2.50 (s, 1H), 2.37 (s, 2H), 2.27 (s, 3H), 2.20-2.31 (m, 1H), 1.89 (s, 1H), 1.30 (d, *J* = 10.8 Hz, 1H), 1.09 (d, *J* = 6.8 Hz, 1H), 0.96 (d, *J* = 10.8 Hz, 1H), 0.84 (d, *J* = 6.8 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 140.4, 134.6, 132.3, 130.9, 128.8, 126.0, 54.8, 43.2, 40.1, 38.7, 31.7, 31.6, 24.9, 22.1, 21.0, 17.2; **HRMS (EI)** calcd. for $C_{18}H_{20}$ [M^+]: 236.1565, found: 236.1567.

(1^a*R*,2*R*,2^a*R*,5^a*R*,6*S*,6^a*S*)-1-(3-methylphenyl)-1,1^a,2,2^a,3,5^a,6,6^a-octahydro-2,6-met



hanocyclopropa[*f*]indene (3cd): The title compound was prepared according to the general procedure and purified by flash column chromatography on silica gel with a eluent of petroleum ether to give light yellow solid, 107.4 mg, 91 % yield. **Mp:** 70-73 ^{o}C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.08 (t, *J* = 7.6 Hz, 1H), 6.90 (t, *J* = 7.6 Hz, 1H), 6.80 (d, *J* = 8.0 Hz, 2H), 5.76 (dd, *J* = 2.0 Hz, *J* = 6.0 Hz, 1H), 5.58 (dd, *J* = 2.4 Hz, *J* = 5.2 Hz, 1H), 3.10-3.13 (m, 1H), 2.53-2.60 (m, 1H), 2.48-2.49 (m, 1H), 2.37-2.39 (m, 2H), 2.32-2.34 (m, 1H), 2.28 (s, 3H), 1.88 (t, *J* = 2.4 Hz, 1H), 1.29 (d, *J* = 10.4 Hz, 1H), 1.10-1.12 (m, 1H), 0.95 (d, *J* = 10.8 Hz, 1H), 0.85-0.88 (m, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 143.5, 137.6, 132.4, 131.0, 128.1, 127.0, 126.0, 123.0, 54.8, 43.2, 40.1, 38.7, 31.8, 31.6, 25.1, 22.3, 21.5, 17.5; **HRMS (EI)** calcd. for $C_{18}H_{20}$ [M^+]: 236.1565, found: 236.1568.

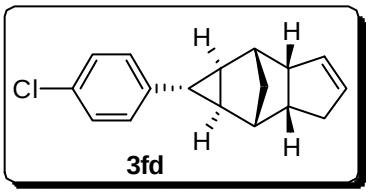
(1^a*R*,2*R*,2^a*R*,5^a*R*,6*S*,6^a*S*)-1-(4-fluorophenyl)-1,1^a,2,2^a,3,5^a,6,6^a-octahydro-2,6-meth



anocyclopropa[*f*]indene (3ed): The title compound was prepared according to the general procedure and purified by flash column chromatography on silica gel

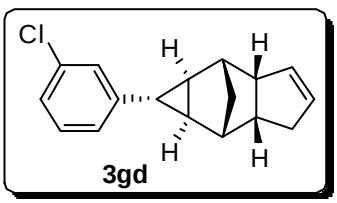
with a eluent of petroleum ether to give light yellow solid, 103.3 mg, 86 % yield. **Mp:** 77-81 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.92-6.96 (m, 2H), 6.86-6.91 (m, 2H), 5.75 (dd, *J* = 2.0 Hz, *J* = 5.6 Hz, 1H), 5.58 (dd, *J* = 2.4 Hz, *J* = 5.6 Hz, 1H), 3.10-3.14 (m, 1H), 2.54-2.60 (m, 1H), 2.49-2.50 (m, 1H), 2.35-2.41 (m, 2H), 2.20-2.28 (m, 1H), 1.90 (t, *J* = 2.8 Hz, 1H), 1.28 (d, *J* = 10.4 Hz, 1H), 1.05-1.07 (m, 1H), 0.98 (d, *J* = 10.8 Hz, 1H), 0.80-0.83 (m, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 161.0 (d, J_{C-F} = 240.9 Hz), 139.0 (d, J_{C-F} = 3.1 Hz), 132.3, 130.9, 127.3 (d, J_{C-F} = 7.0 Hz), 114.8 (d, J_{C-F} = 20.5 Hz), 54.7, 43.1, 40.0, 38.6, 31.7, 31.6, 25.2, 22.3, 16.9; **HRMS (EI)** calcd. for $C_{17}H_{17}F$ [M^+]: 240.1314, found: 240.1311.

(1^a*R*,2*R*,2^a*R*,5^a*R*,6*S*,6^a*S*)-1-(4-chlorophenyl)-1,1^a,2,2^a,3,5^a,6,6^a-octahydro-2,6-meth



anocyclopropa[*f*]indene (3fd): The title compound was prepared according to the general procedure and purified by flash column chromatography on silica gel with a eluent of petroleum ether to give light yellow solid, 117.8 mg, 92 % yield. **Mp:** 92-95 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.14 (d, *J* = 8.4 Hz, 2H), 6.91 (d, *J* = 8.4 Hz, 2H), 5.75 (dd, *J* = 2.0 Hz, *J* = 5.6 Hz, 1H), 5.58 (dd, *J* = 2.4 Hz, *J* = 5.6 Hz, 1H), 3.11-3.13 (m, 1H), 2.55-2.60 (m, 1H), 2.49 (d, *J* = 2.8 Hz, 1H), 2.34-2.39 (m, 2H), 2.25-2.28 (m, 1H), 1.87 (t, *J* = 2.4 Hz, 1H), 1.27 (d, *J* = 10.4 Hz, 1H), 1.05-1.07 (m, 1H), 0.97 (d, *J* = 10.4 Hz, 1H), 0.80-0.83 (m, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 142.1, 132.4, 130.9, 129.1, 128.2, 127.3, 54.7, 43.1, 40.1, 38.7, 31.7, 31.6, 25.5, 22.7, 17.1; **HRMS (EI)** calcd. for $C_{17}H_{17}Cl$ [M^+]: 256.1019, found: 256.1017.

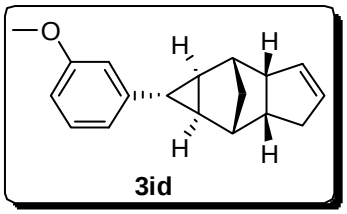
(1^a*R*,2*R*,2^a*R*,5^a*R*,6*S*,6^a*S*)-1-(3-chlorophenyl)-1,1^a,2,2^a,3,5^a,6,6^a-octahydro-2,6-meth



anocyclopropa[*f*]indene (3gd): The title compound was prepared according to the general procedure and purified by flash column chromatography on silica gel with a eluent of petroleum ether to give light yellow solid, 116.5 mg, 91 % yield. **Mp:** 101-103 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.04-7.12 (m, 2H), 7.04 (t, *J* = 1.6 Hz, 1H), 6.86-6.89 (m, 1H), 5.77 (dd, *J* = 2.0 Hz, *J* = 5.6 Hz, 1H), 5.58 (dd, *J* = 2.4 Hz, *J* = 5.6 Hz, 1H), 3.10-3.15 (m, 1H), 2.55-2.61 (m, 1H), 2.49-2.51 (m,

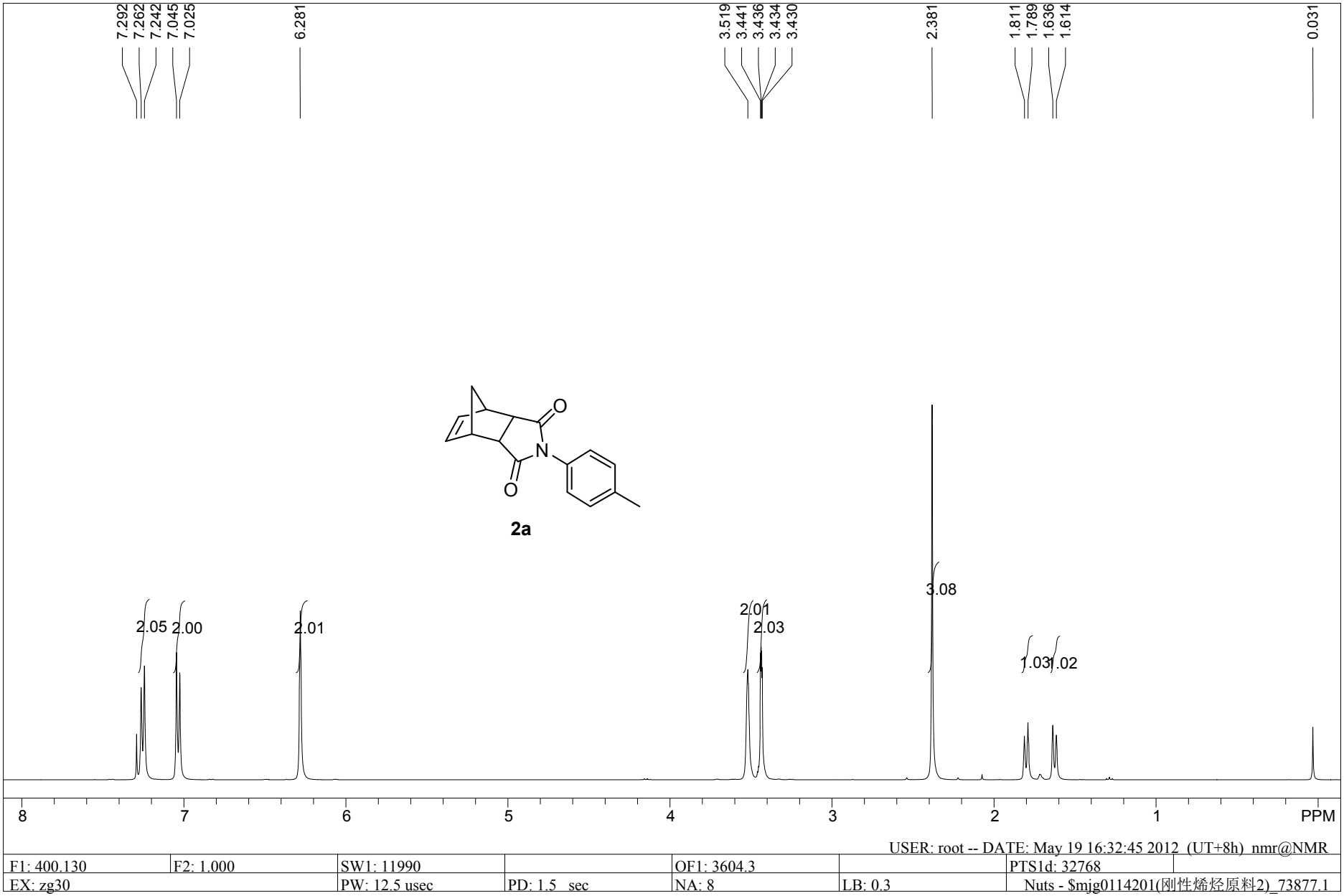
1H), 2.34-2.41 (m, 2H), 2.21-2.29 (m, 1H), 1.88 (t, *J* = 2.8 Hz, 1H), 1.26 (d, *J* = 10.4 Hz, 1H), 1.10-1.13 (m, 1H), 0.97 (d, *J* = 10.4 Hz, 1H), 0.85-0.88 (m, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 145.9, 134.0, 132.4, 130.8, 129.3, 126.0, 125.3, 124.4, 54.7, 43.1, 40.1, 38.7, 31.6, 31.6, 25.6, 22.7, 17.4; **HRMS (EI)** calcd. for $C_{17}H_{17}Cl$ [M^+]: 256.1019, found: 256.1016.

(1^a*R*,2*R*,2^a*R*,5^a*R*,6*S*,6^a*S*)-1-(4-methoxyphenyl)-1,1^a,2,2^a,3,5^a,6,6^a-octahydro-2,6-methanocyclopropa[*f*]indene (3id): The title compound was prepared according to the general procedure and purified by flash column chromatography on silica gel with a eluent of petroleum ether to give light yellow solid, 118.5 mg, 94 % yield. **Mp:** 102-105 ^{o}C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.11 (t, *J* = 8.0 Hz, 1H), 6.60-6.65 (m, 2H), 6.56 (d, *J* = 2.0 Hz, 1H), 5.75 (dd, *J* = 2.0 Hz, *J* = 5.6 Hz, 1H), 5.58 (dd, *J* = 2.8 Hz, *J* = 5.2 Hz, 1H), 3.75 (s, 3H), 3.10-3.13 (m, 1H), 2.55-2.59 (m, 1H), 2.49-2.50 (m, 1H), 2.34-2.41 (m, 2H), 2.24-2.27 (m, 1H), 1.89 (t, *J* = 2.8 Hz, 1H), 1.28 (d, *J* = 10.8 Hz, 1H), 1.13 (d, *J* = 6.0 Hz, 1H), 0.96 (d, *J* = 10.8 Hz, 1H), 0.88 (d, *J* = 4.4 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 159.5, 145.4, 132.3, 130.9, 129.1, 118.6, 112.2, 110.1, 55.2, 54.8, 43.2, 40.1, 38.7, 31.7, 31.6, 25.4, 22.5, 17.7; **HRMS (EI)** calcd. for $C_{18}H_{20}O$ [M^+]: 252.1514, found: 252.1517.



3id

4 Copies for ^{1}H NMR and ^{13}C NMR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O
N
O
2a
2.05
2.00
2.01
2.01
2.03
3.08
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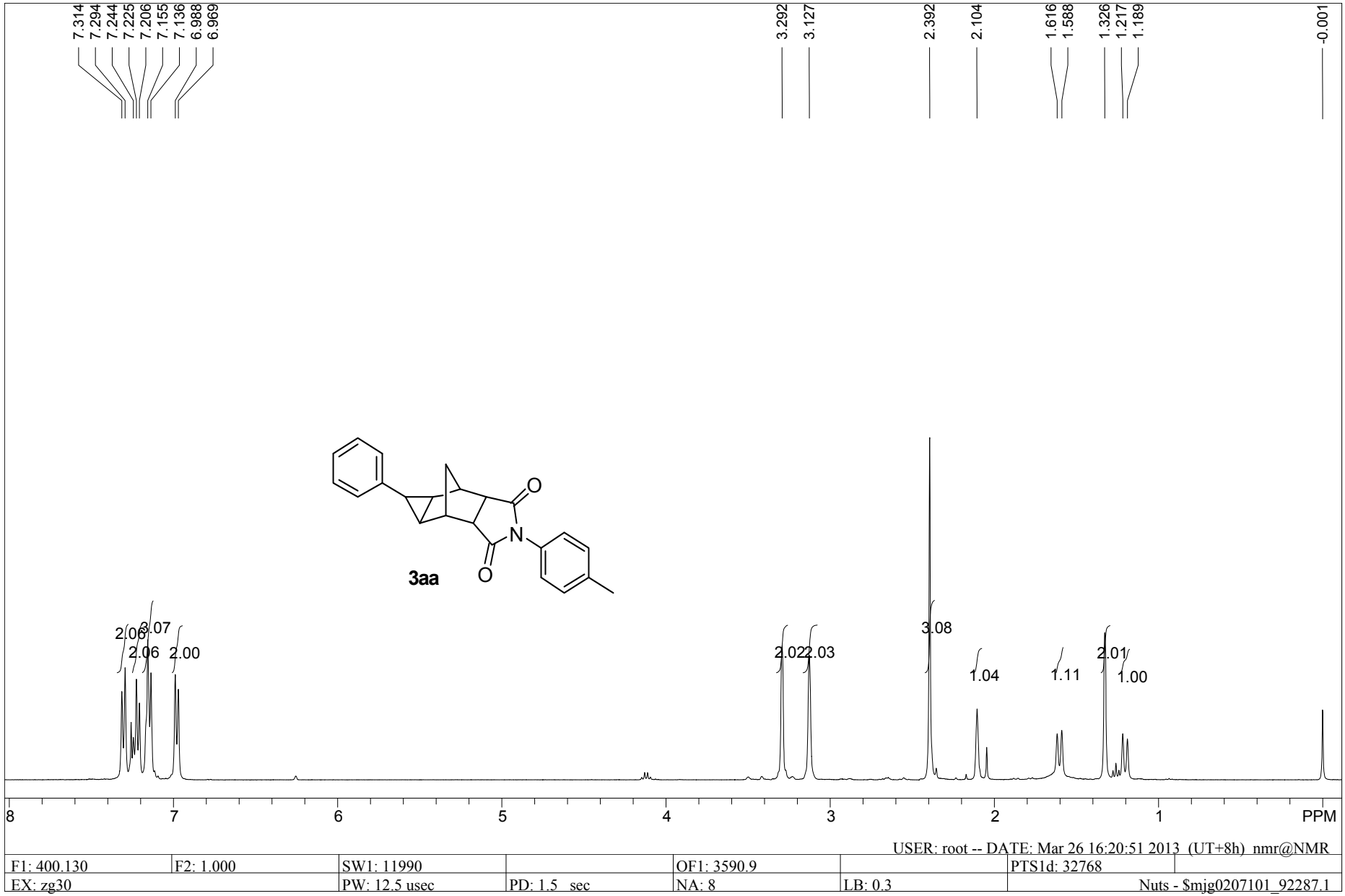
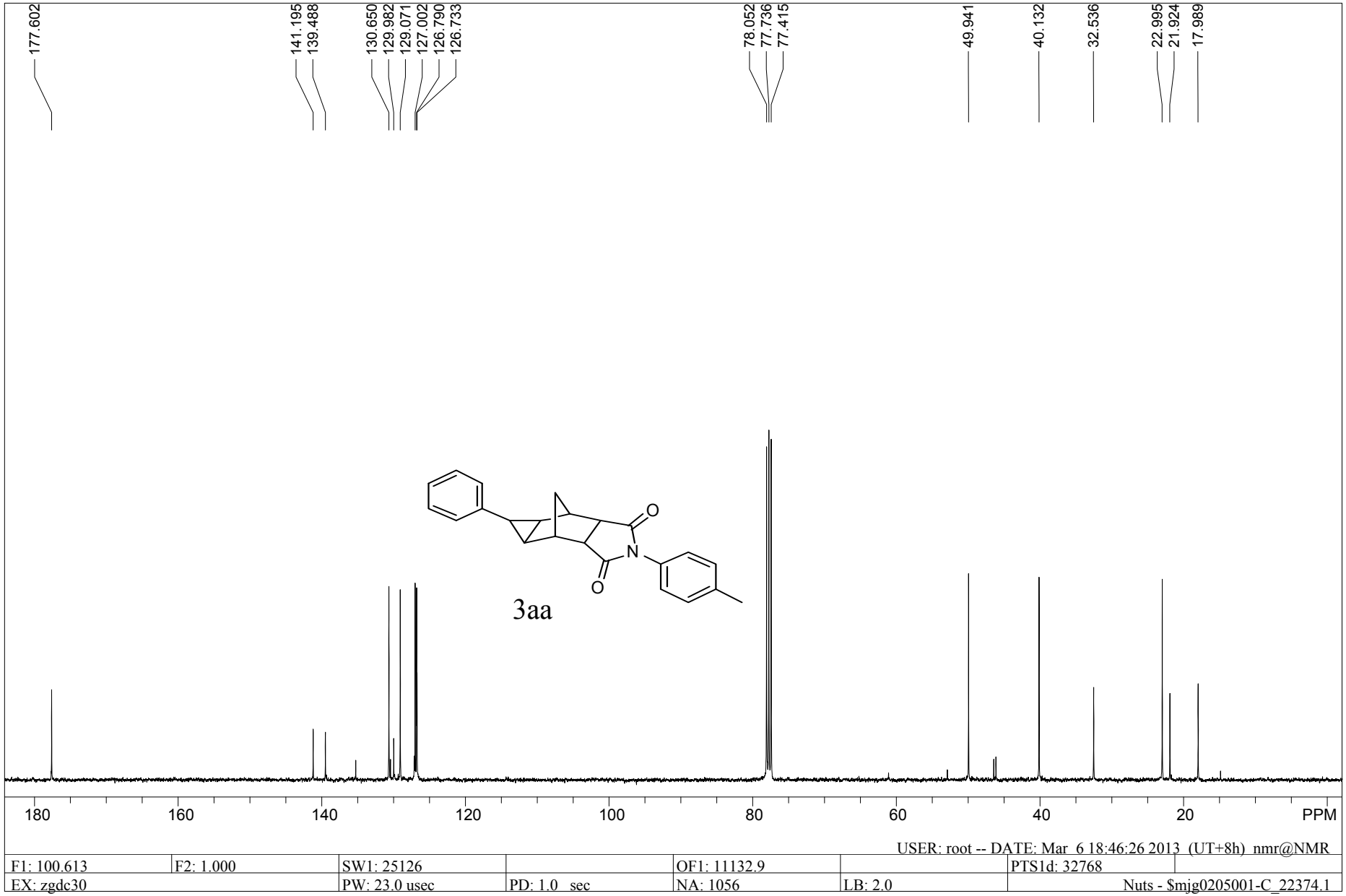
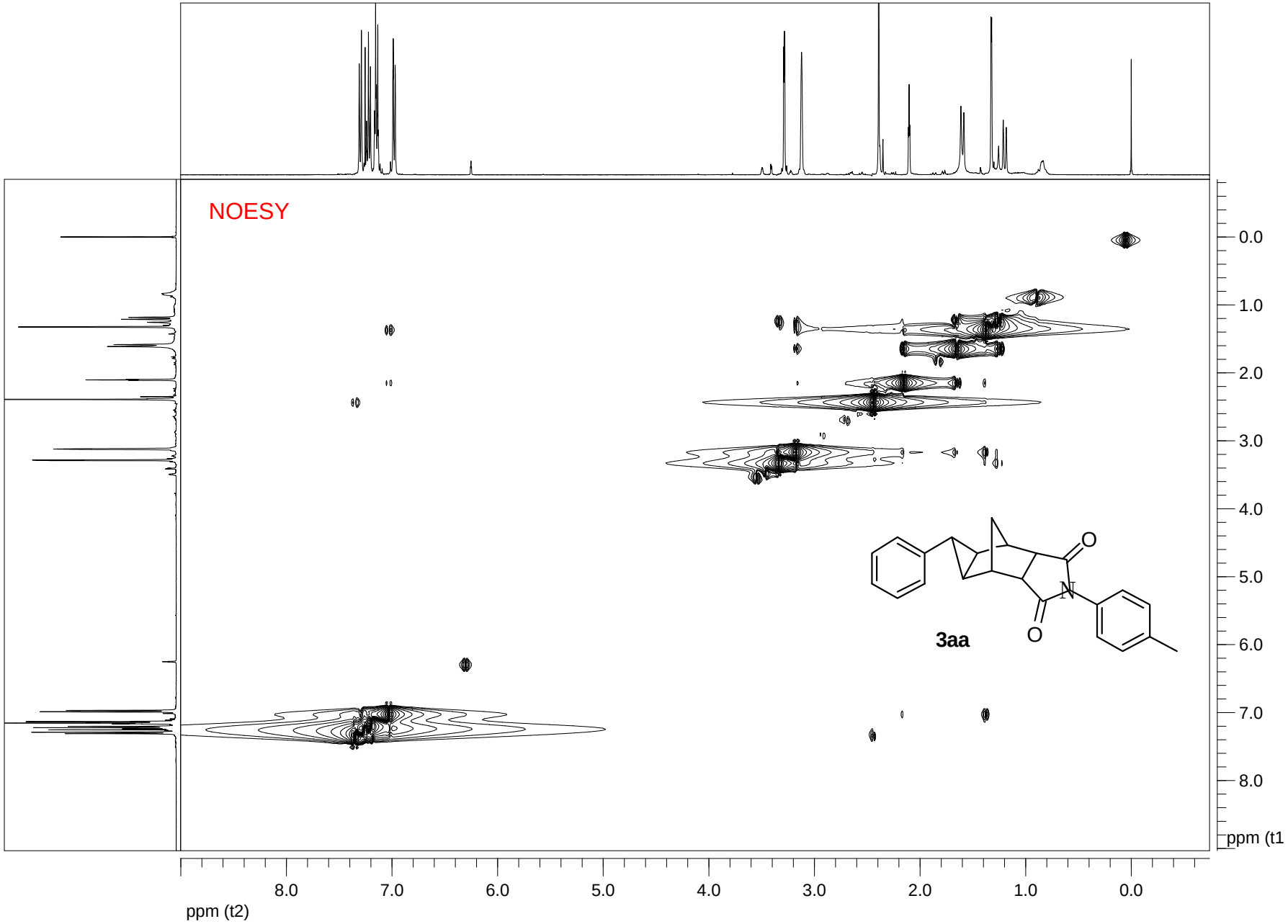
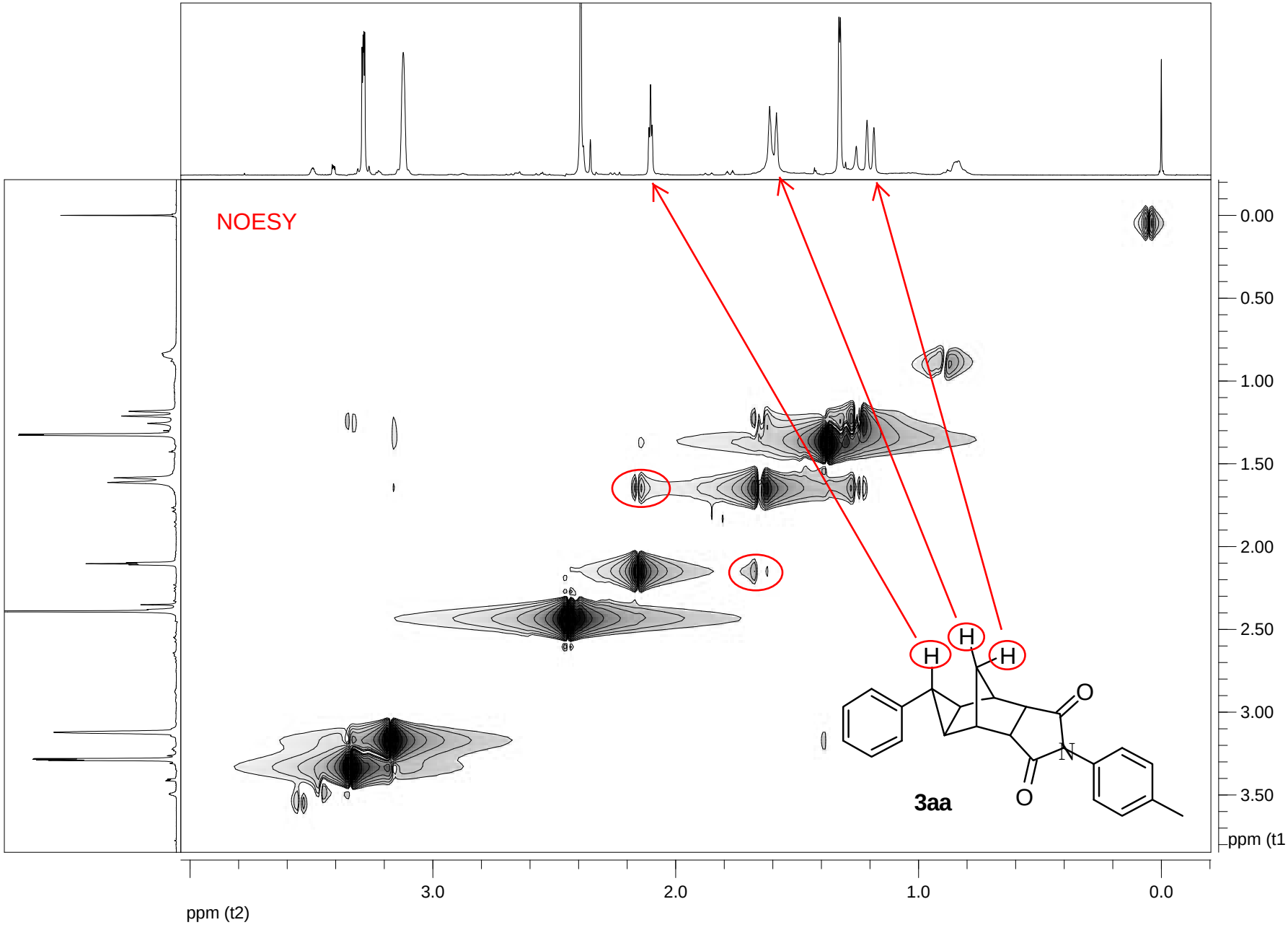
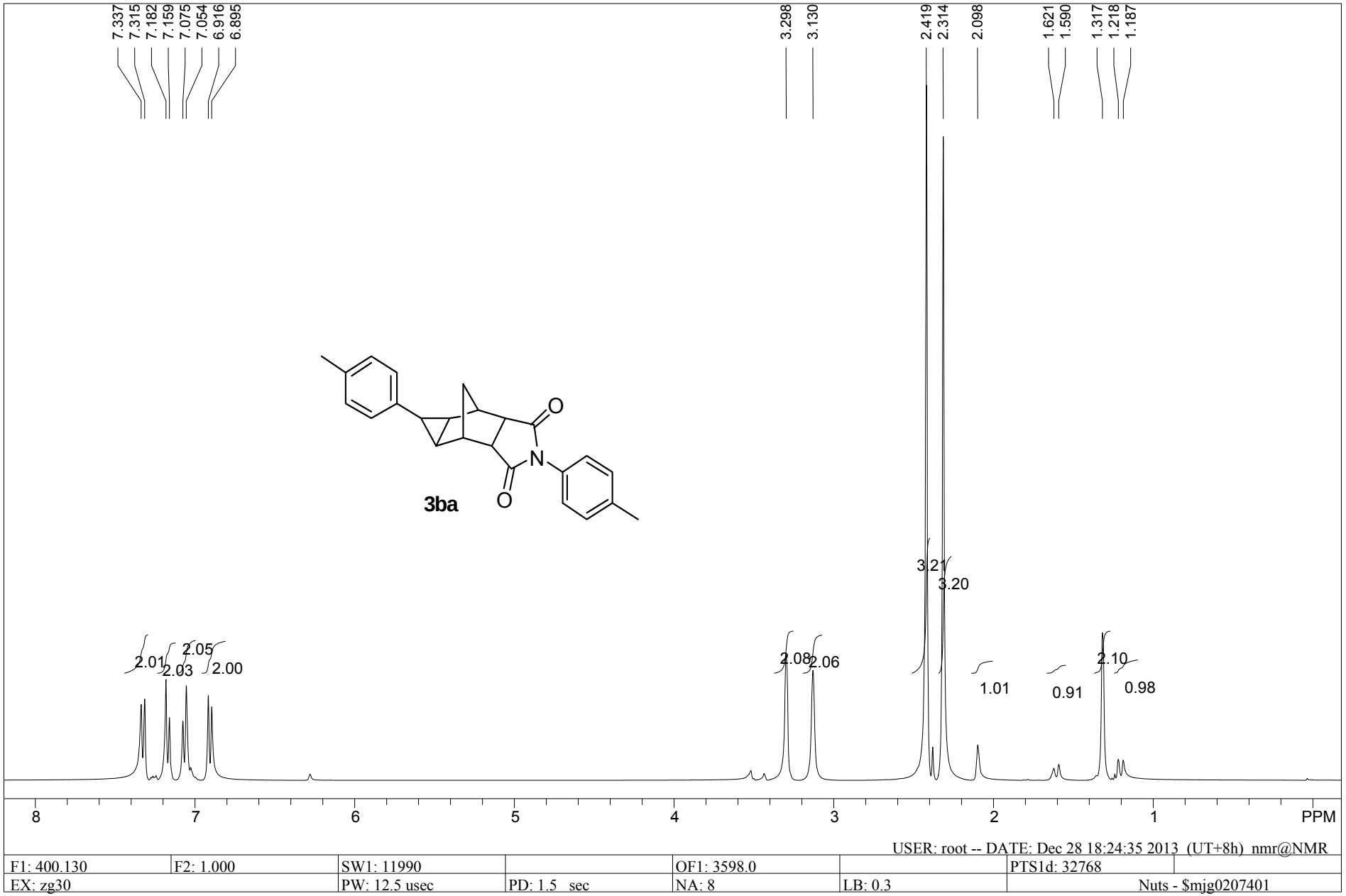
EX: zg30
PW: 12.5 usec
PD: 1.5 sec
NA: 8
LB: 0.3
Nuts - $mjg0114201(刚性烯烃原料2)_73877.1

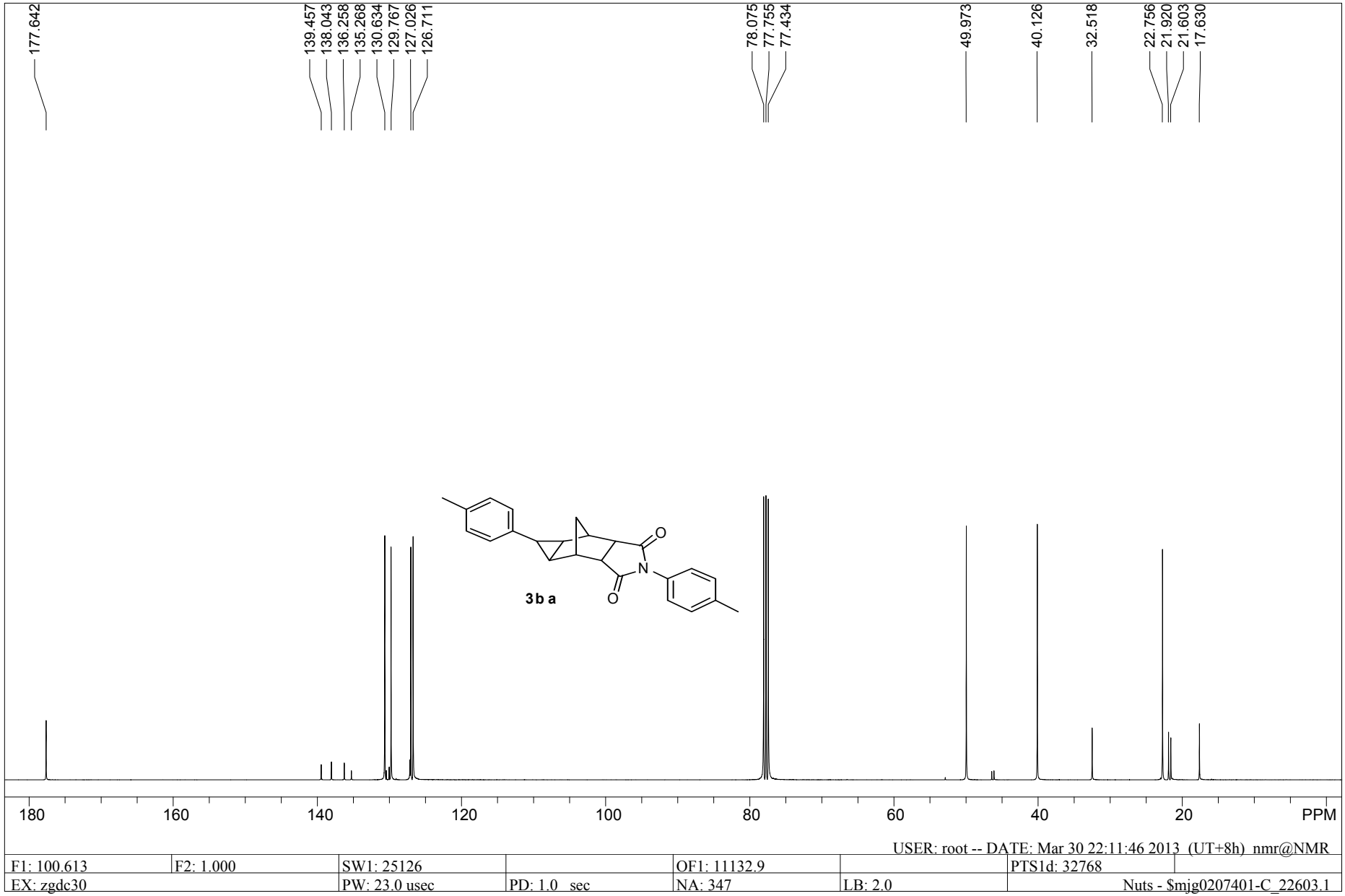

7.314
7.294
7.244
7.225
7.206
7.155
7.136
6.988
6.969
3.292
3.127
2.392
2.104
1.616
1.588
1.326
1.217
1.189
-0.001
O
N
O
3aa
2.06
3.07
2.06
2.00
2.02
2.03
3.08
1.04
1.11
2.01
1.00
8
7
6
5
4
3
2
1
PPM
USER: root -- DATE: Mar 26 16:20:51 2013 (UT+8h) nmr@NMR
F1: 400.130
F2: 1.000
SW1: 11990
OF1: 3590.9
PTS1d: 32768
EX: zg30
PW: 12.5 usec
PD: 1.5 sec
NA: 8
LB: 0.3
Nuts - $mjg0207101_92287.1

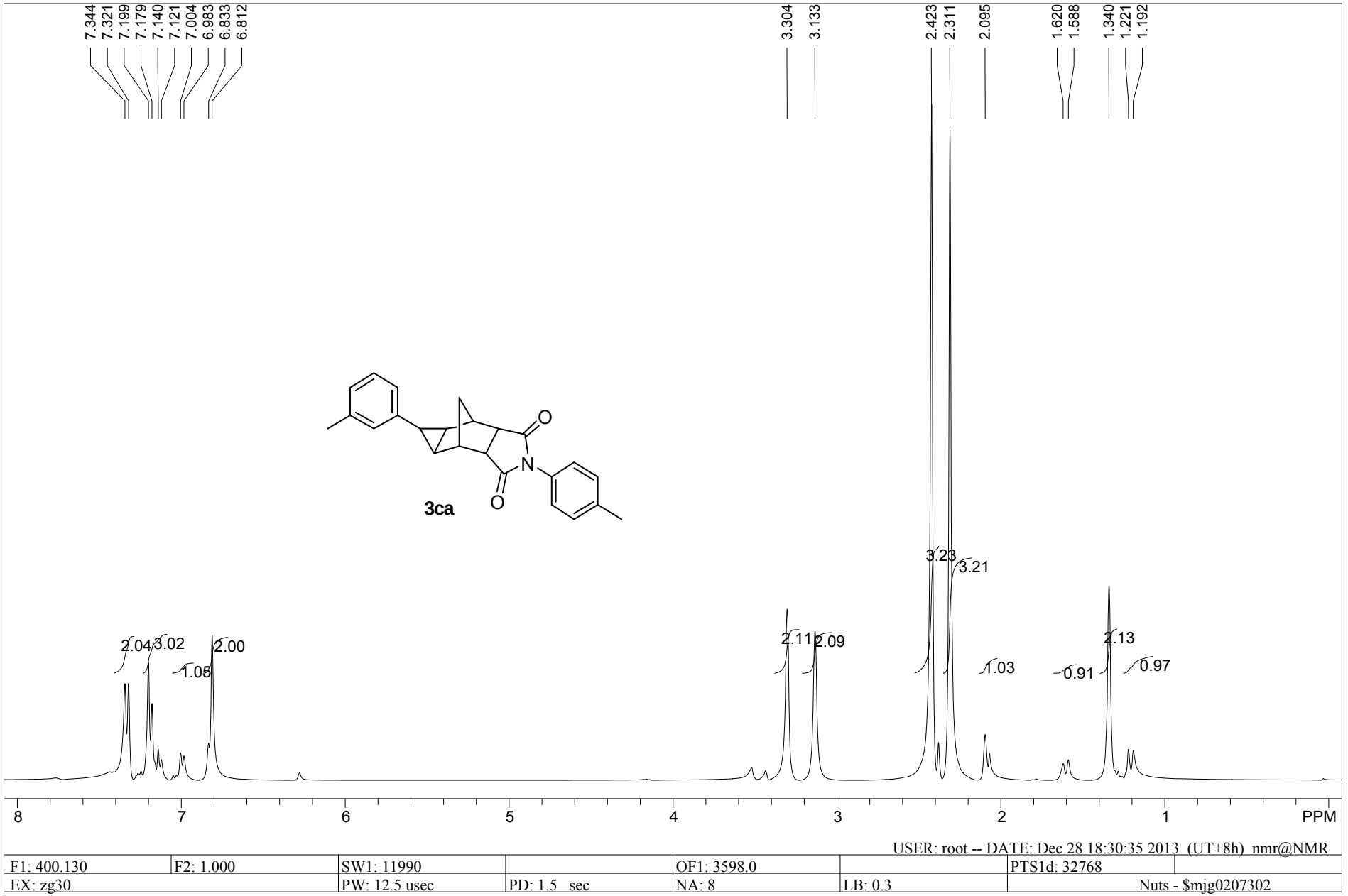

177.602
141.195
139.488
130.650
129.982
129.071
127.002
126.790
126.733
78.052
77.736
77.415
49.941
40.132
32.536
22.995
21.924
17.989
O
N
O
3aa
180
160
140
120
100
80
60
40
20
PPM
USER: root -- DATE: Mar 6 18:46:26 2013 (UT+8h) nmr@NMR
F1: 100.613
F2: 1.000
SW1: 25126
OF1: 11132.9
PTS1d: 32768
EX: zgdc30
PW: 23.0 usec
PD: 1.0 sec
NA: 1056
LB: 2.0
Nuts - $mjg0205001-C_22374.1

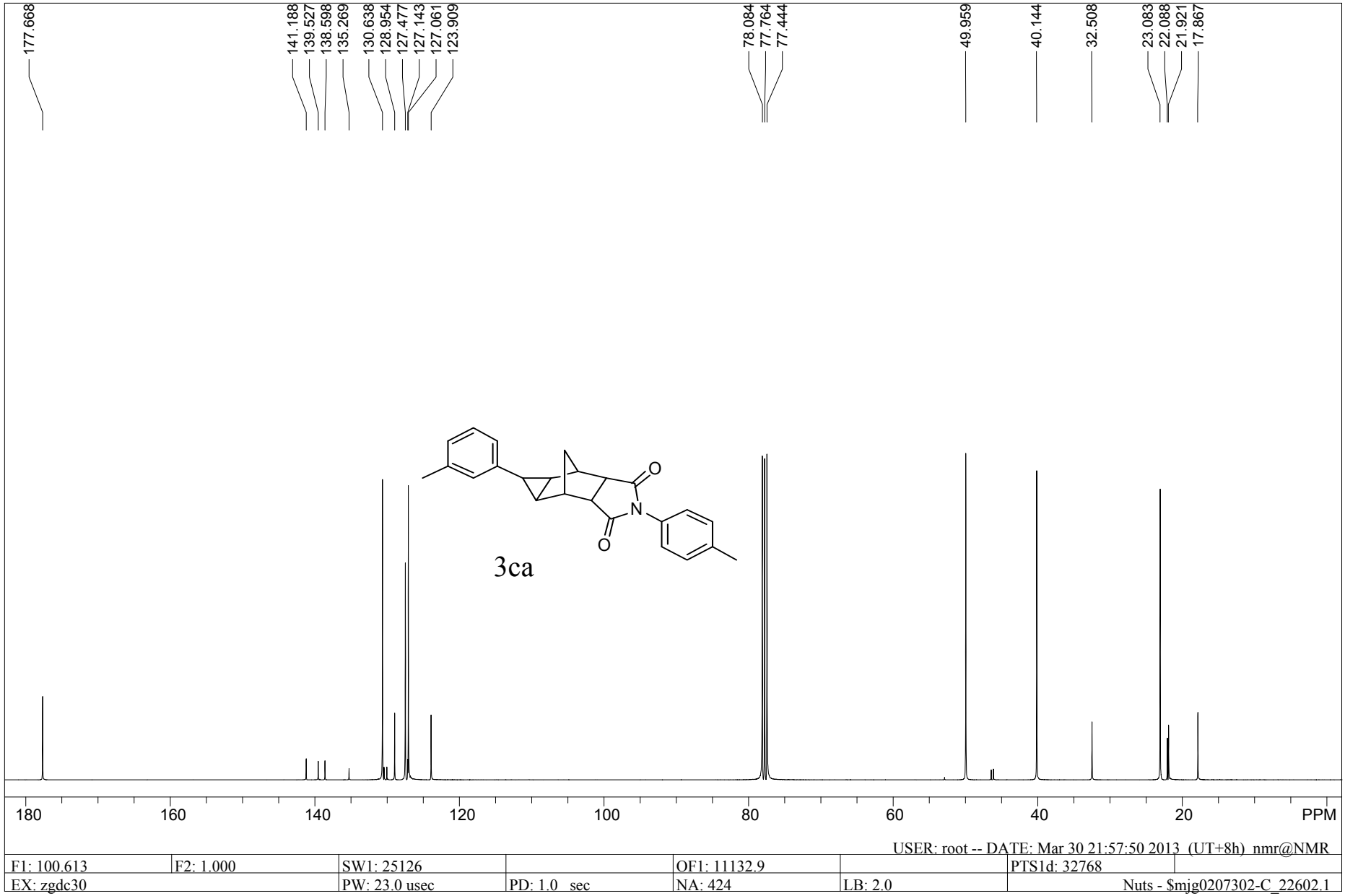


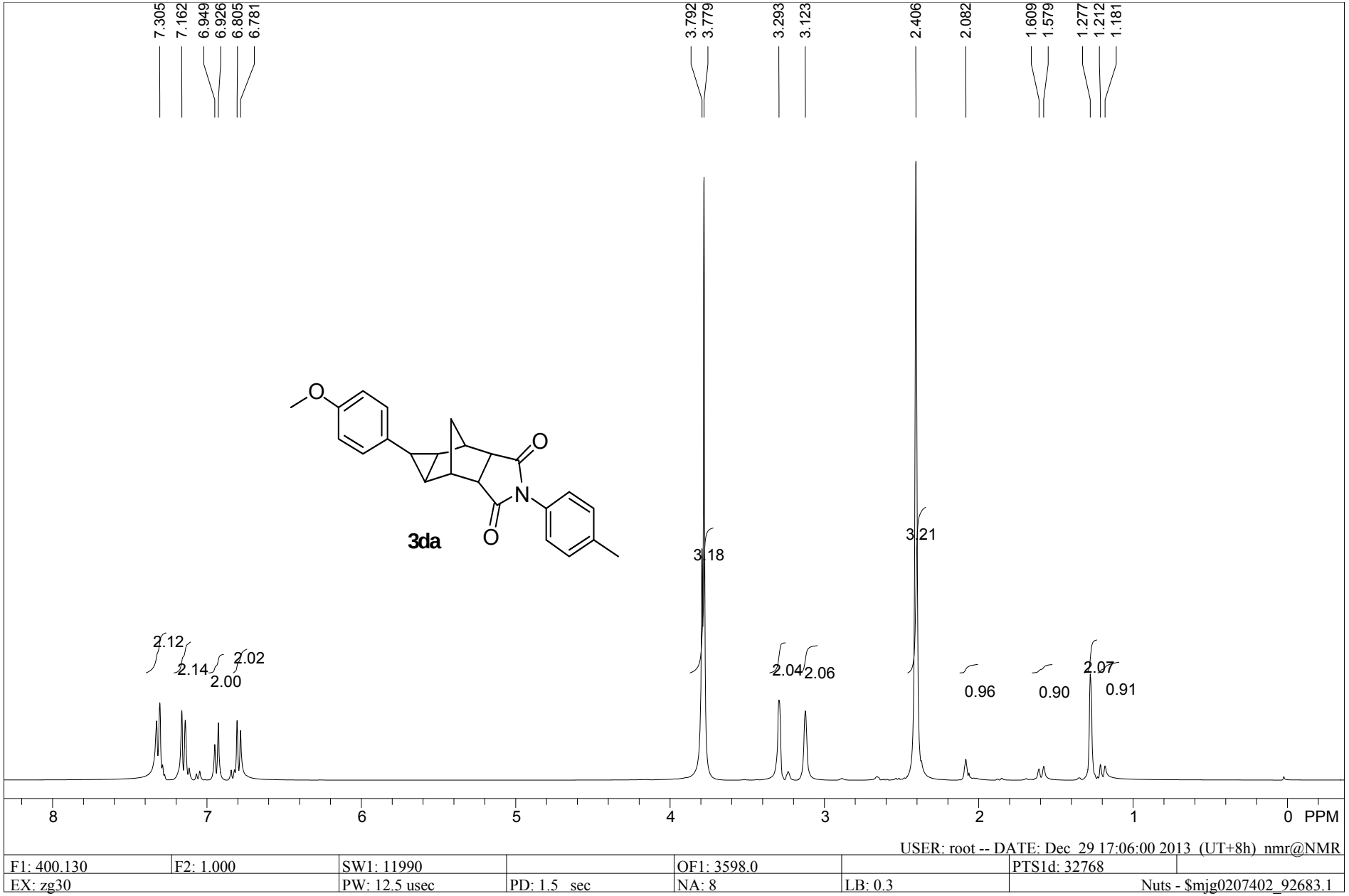


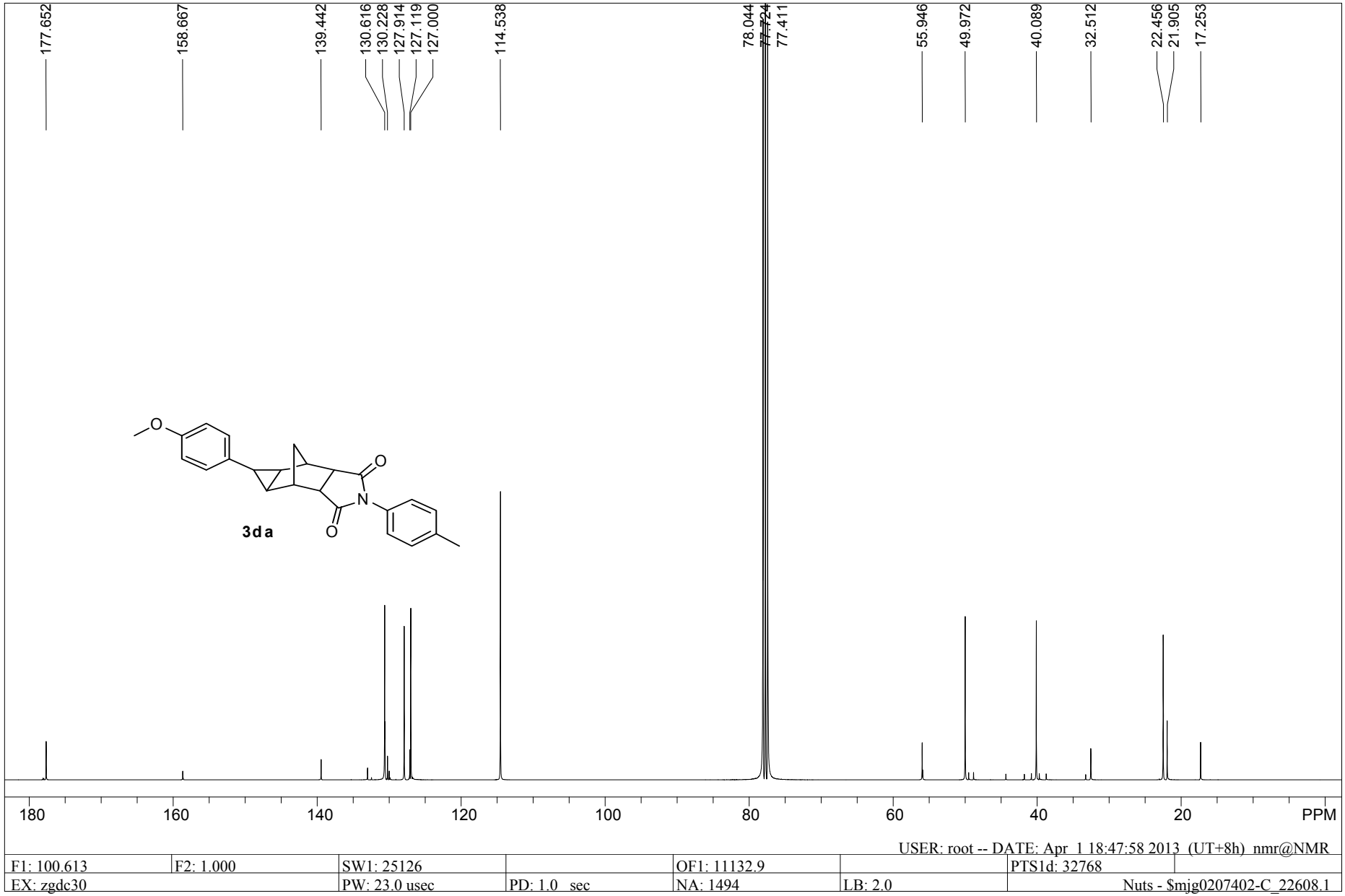

7.337
7.315
7.182
7.159
7.075
7.054
6.916
6.895
3.298
3.130
2.419
2.314
2.098
1.621
1.590
1.317
1.218
1.187
3ba
O
N
O
2.01
2.03
2.05
2.00
2.08
2.06
3.21
3.20
1.01
0.91
2.10
0.98
8
7
6
5
4
3
2
1
PPM
USER: root -- DATE: Dec 28 18:24:35 2013 (UT+8h) nmr@NMR
F1: 400.130
F2: 1.000
SW1: 11990
OF1: 3598.0
PTS1d: 32768
EX: zg30
PW: 12.5 usec
PD: 1.5 sec
NA: 8
LB: 0.3
Nuts - $mjg0207401

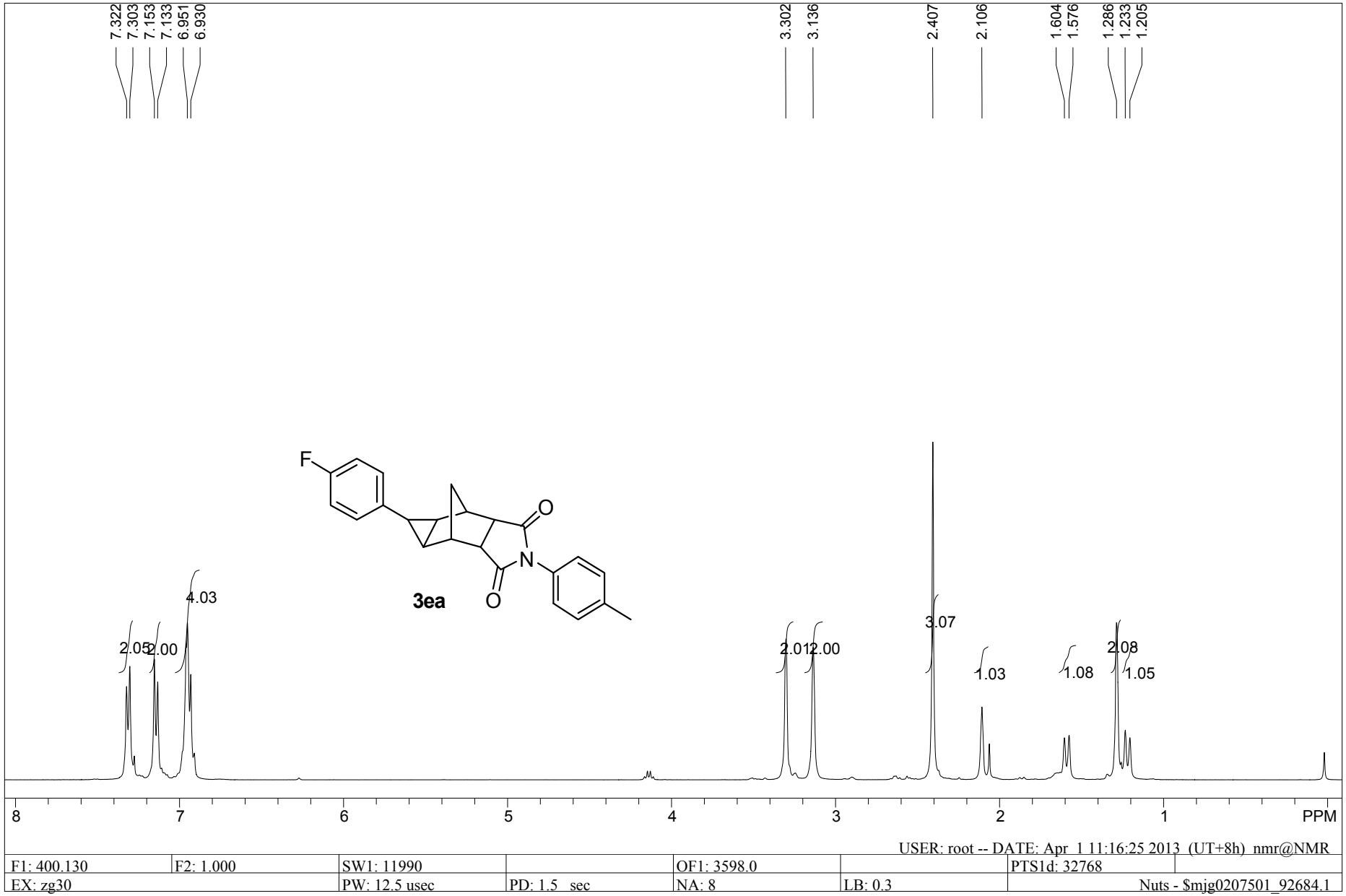

177.642
139.457
138.043
136.258
135.268
130.634
129.767
127.026
126.711
78.075
77.755
77.434
49.973
40.126
32.518
22.756
21.920
21.603
17.630
O
N
O
3b a
180
160
140
120
100
80
60
40
20
PPM
USER: root -- DATE: Mar 30 22:11:46 2013 (UT+8h) nmr@NMR
F1: 100.613
F2: 1.000
SW1: 25126
OF1: 11132.9
PTS1d: 32768
EX: zgdc30
PW: 23.0 usec
PD: 1.0 sec
NA: 347
LB: 2.0
Nuts - $mjg0207401-C_22603.1

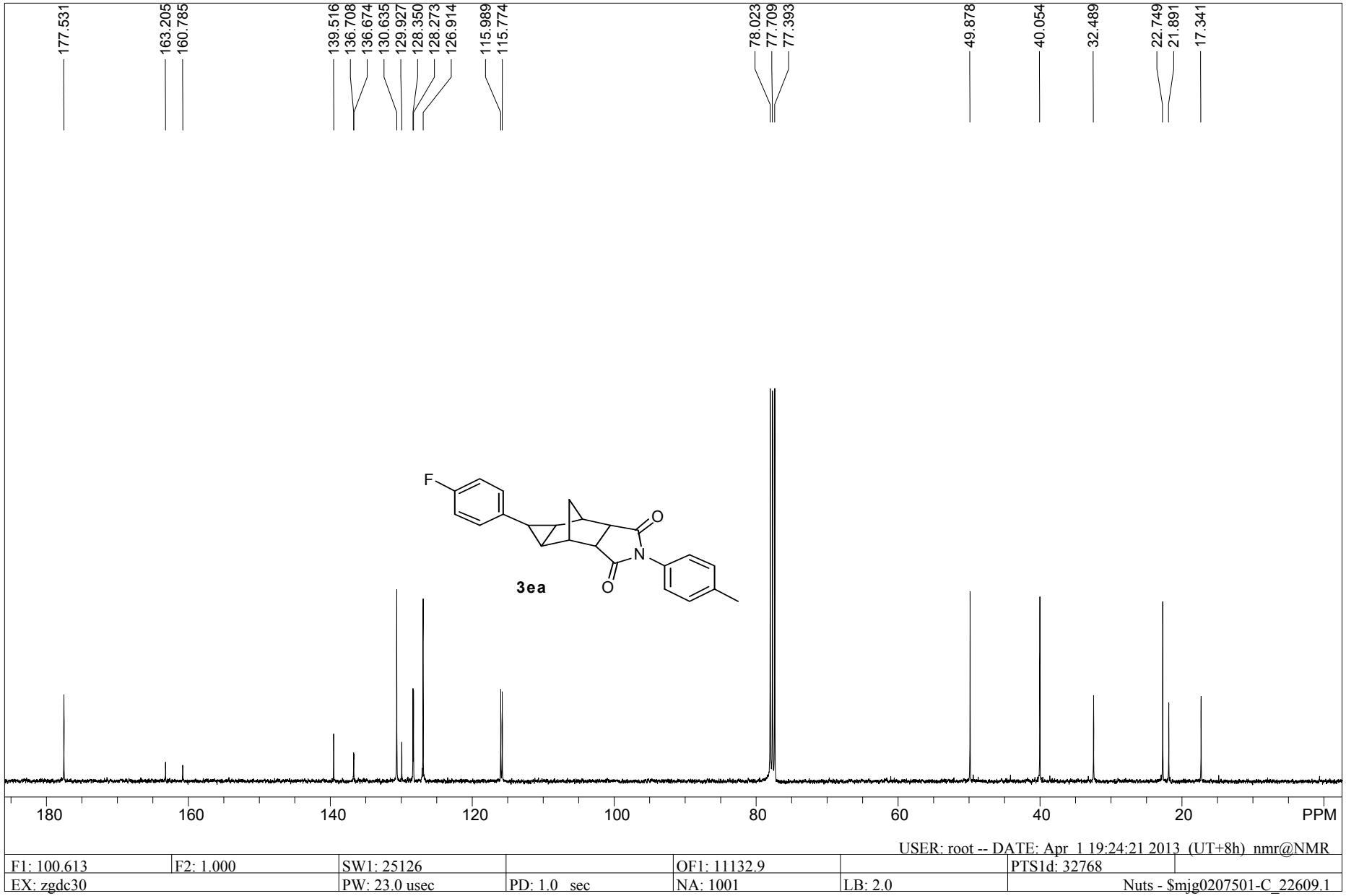

7.344
7.321
7.199
7.179
7.140
7.121
7.004
6.983
6.833
6.812
3.304
3.133
2.423
2.311
2.095
1.620
1.588
1.340
1.221
1.192
O
N
O
3ca
2.04
3.02
1.05
2.00
2.11
2.09
3.23
3.21
1.03
0.91
2.13
0.97
8
7
6
5
4
3
2
1
PPM
USER: root -- DATE: Dec 28 18:30:35 2013 (UT+8h) nmr@NMR
F1: 400.130
F2: 1.000
SW1: 11990
OF1: 3598.0
PTS1d: 32768
EX: zg30
PW: 12.5 usec
PD: 1.5 sec
NA: 8
LB: 0.3
Nuts - $mjg0207302

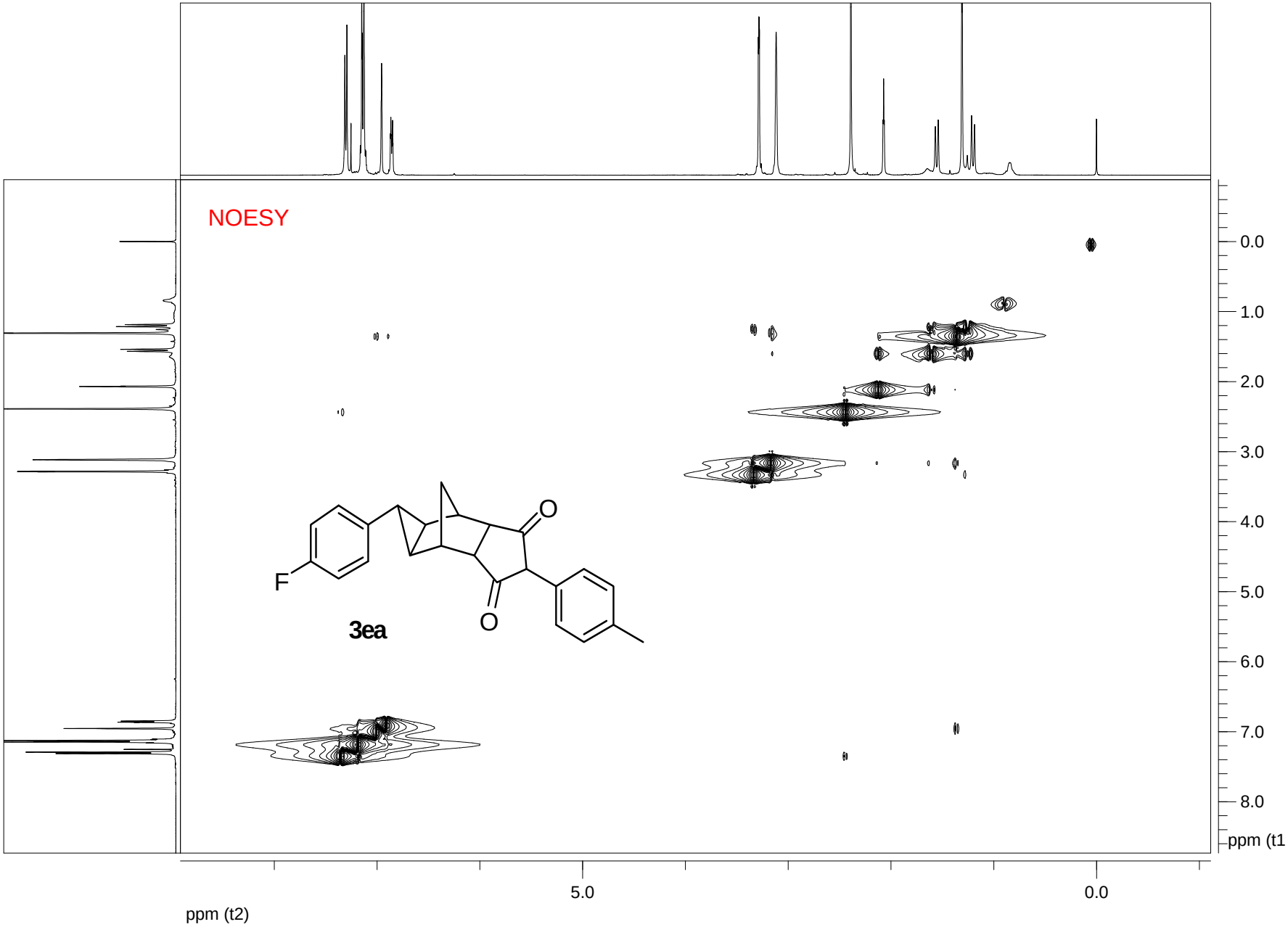

177.668
141.188
139.527
138.598
135.269
130.638
128.954
127.477
127.143
127.061
123.909
78.084
77.764
77.444
49.959
40.144
32.508
23.083
22.088
21.921
17.867
O
N
O
3ca
180
160
140
120
100
80
60
40
20
PPM
USER: root -- DATE: Mar 30 21:57:50 2013 (UT+8h) nmr@NMR
F1: 100.613
F2: 1.000
SW1: 25126
OF1: 11132.9
PTS1d: 32768
EX: zgdc30
PW: 23.0 usec
PD: 1.0 sec
NA: 424
LB: 2.0
Nuts - $mjg0207302-C_22602.1

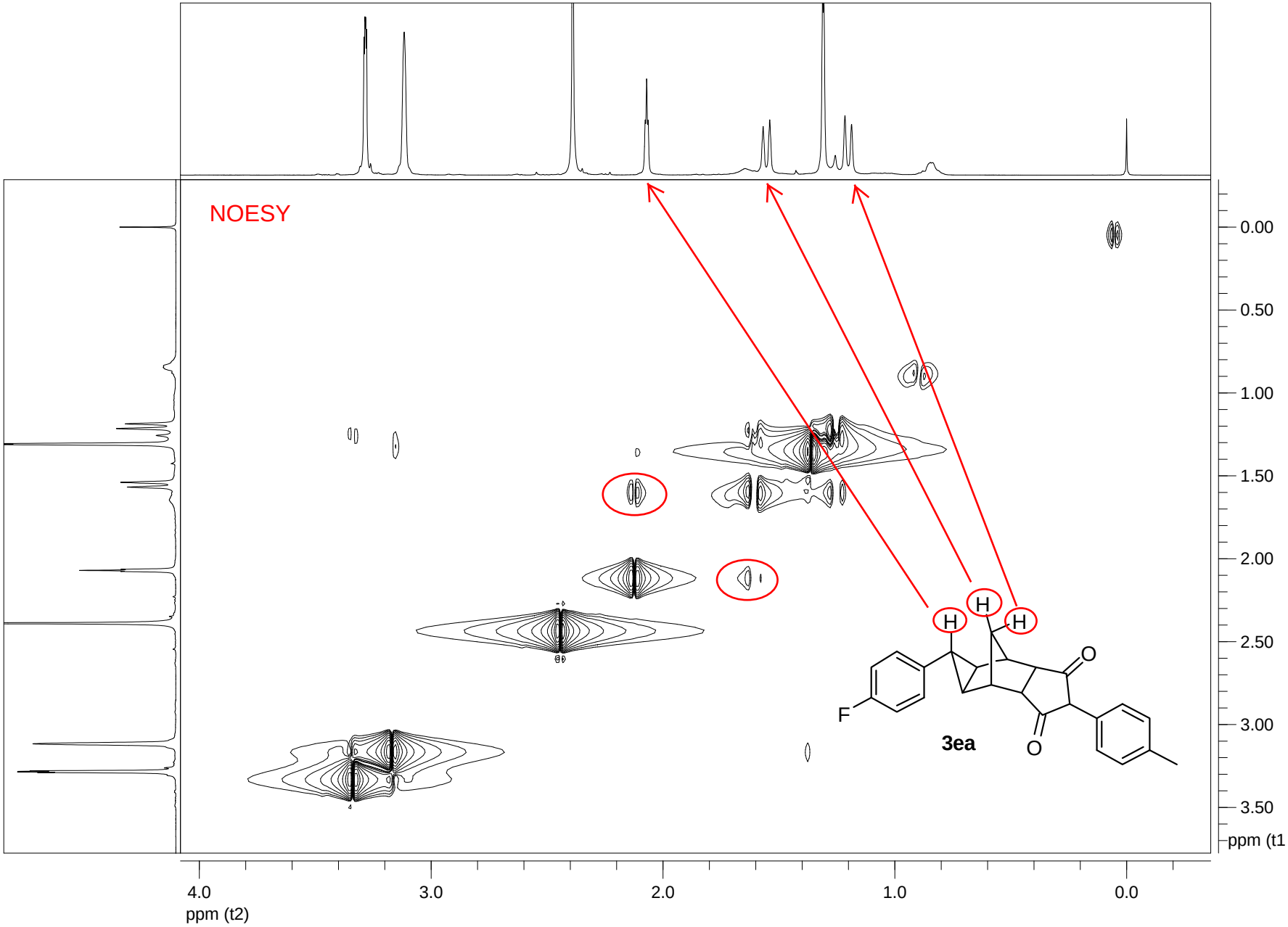

7.305
7.162
6.949
6.926
6.805
6.781
3.792
3.779
3.293
3.123
2.406
2.082
1.609
1.579
1.277
1.212
1.181
O
O
N
O
3da
3.18
3.21
2.12
2.14
2.00
2.02
2.04
2.06
0.96
0.90
2.07
0.91
8
7
6
5
4
3
2
1
0 PPM
USER: root -- DATE: Dec 29 17:06:00 2013 (UT+8h) nmr@NMR
F1: 400.130
F2: 1.000
SW1: 11990
OF1: 3598.0
PTS1d: 32768
EX: zg30
PW: 12.5 usec
PD: 1.5 sec
NA: 8
LB: 0.3
Nuts - $mjg0207402_92683.1

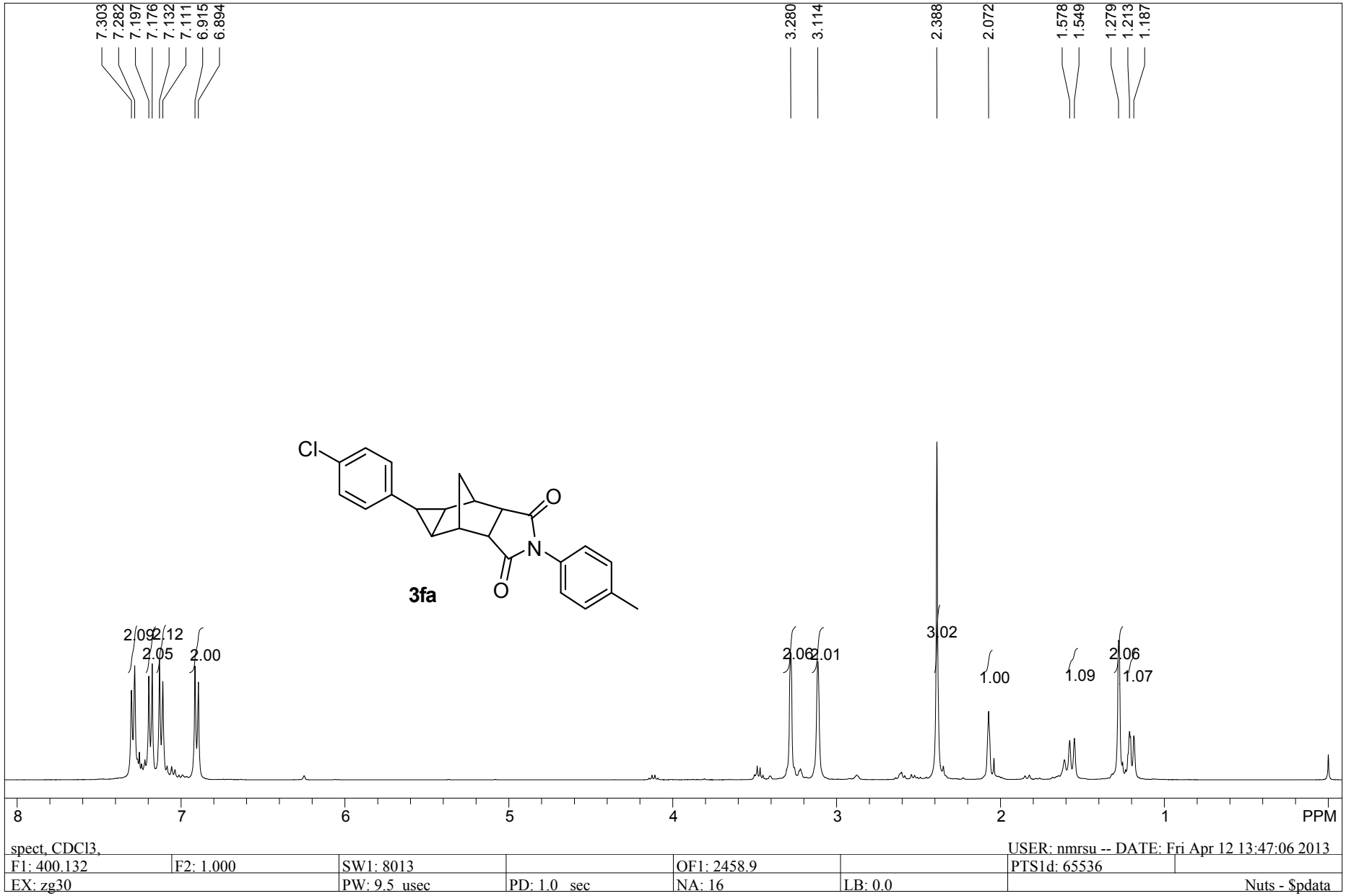

177.652
158.667
139.442
130.616
130.228
127.914
127.119
127.000
114.538
78.044
77.724
77.411
55.946
49.972
40.089
32.512
22.456
21.905
17.253
O
O
N
O
O
3da
180
160
140
120
100
80
60
40
20
PPM
USER: root -- DATE: Apr 1 18:47:58 2013 (UT+8h) nmr@NMR
F1: 100.613
F2: 1.000
SW1: 25126
OF1: 11132.9
PTS1d: 32768
EX: zgdc30
PW: 23.0 usec
PD: 1.0 sec
NA: 1494
LB: 2.0
Nuts - $mjg0207402-C_22608.1

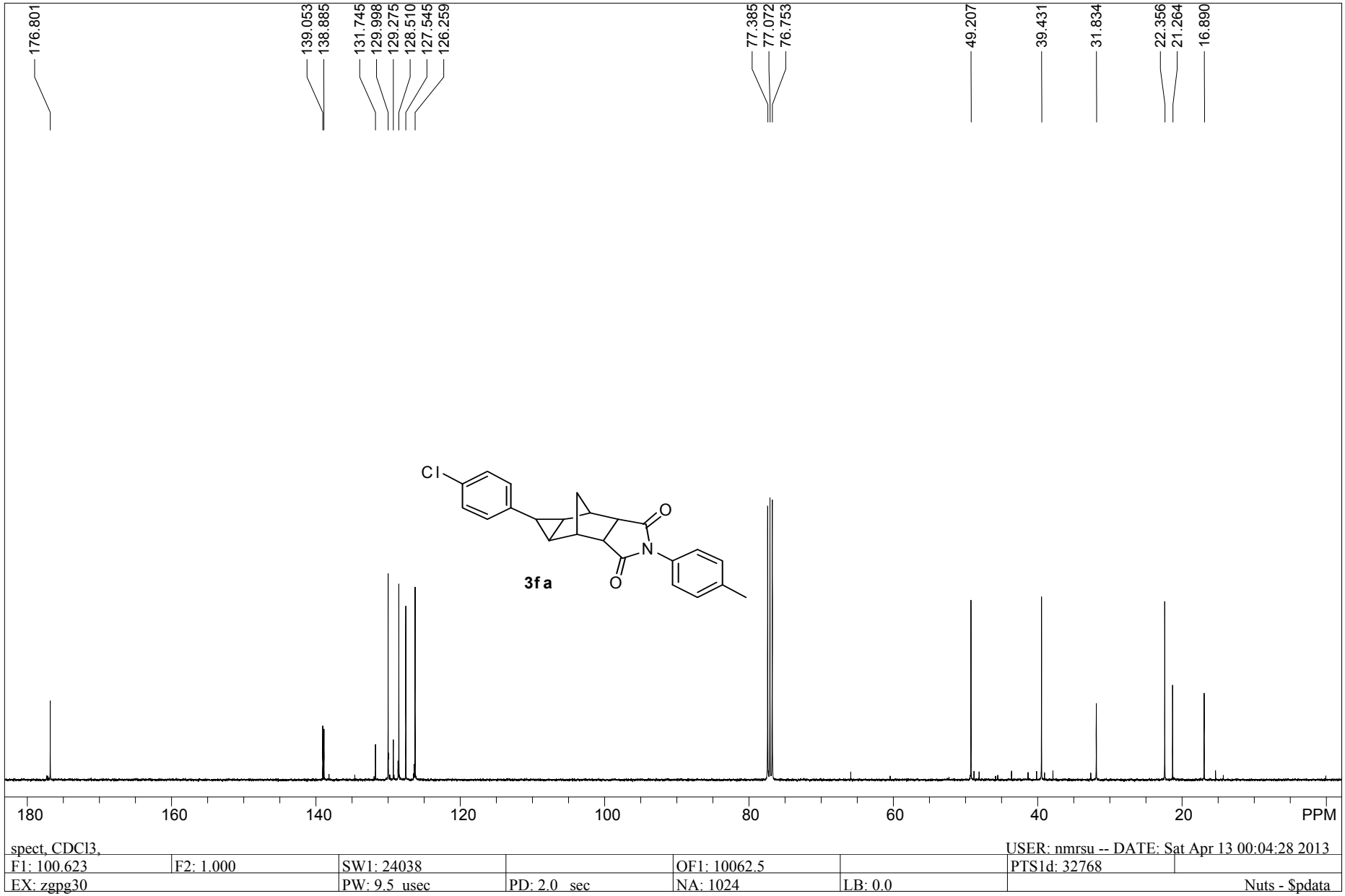

7.322
7.303
7.153
7.133
6.951
6.930
3.302
3.136
2.407
2.106
1.604
1.576
1.286
1.233
1.205
F
O
N
O
3ea
4.03
2.05
2.00
2.01
2.00
3.07
1.03
1.08
2.08
1.05
8
7
6
5
4
3
2
1
PPM
USER: root -- DATE: Apr 1 11:16:25 2013 (UT+8h) nmr@NMR
F1: 400.130
F2: 1.000
SW1: 11990
OF1: 3598.0
PTS1d: 32768
EX: zg30
PW: 12.5 usec
PD: 1.5 sec
NA: 8
LB: 0.3
Nuts - $mjg0207501_92684.1


177.531
163.205
160.785
139.516
136.708
136.674
130.635
129.927
128.350
128.273
126.914
115.989
115.774
78.023
77.709
77.393
49.878
40.054
32.489
22.749
21.891
17.341
F
O
N
O
3ea
180
160
140
120
100
80
60
40
20
PPM
USER: root -- DATE: Apr 1 19:24:21 2013 (UT+8h) nmr@NMR
F1: 100.613
F2: 1.000
SW1: 25126
OF1: 11132.9
PTS1d: 32768
EX: zgdc30
PW: 23.0 usec
PD: 1.0 sec
NA: 1001
LB: 2.0
Nuts - $mjg0207501-C_22609.1


NOESY
F
O
O
3ea
0.0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
ppm (t1
5.0
0.0
ppm (t2)

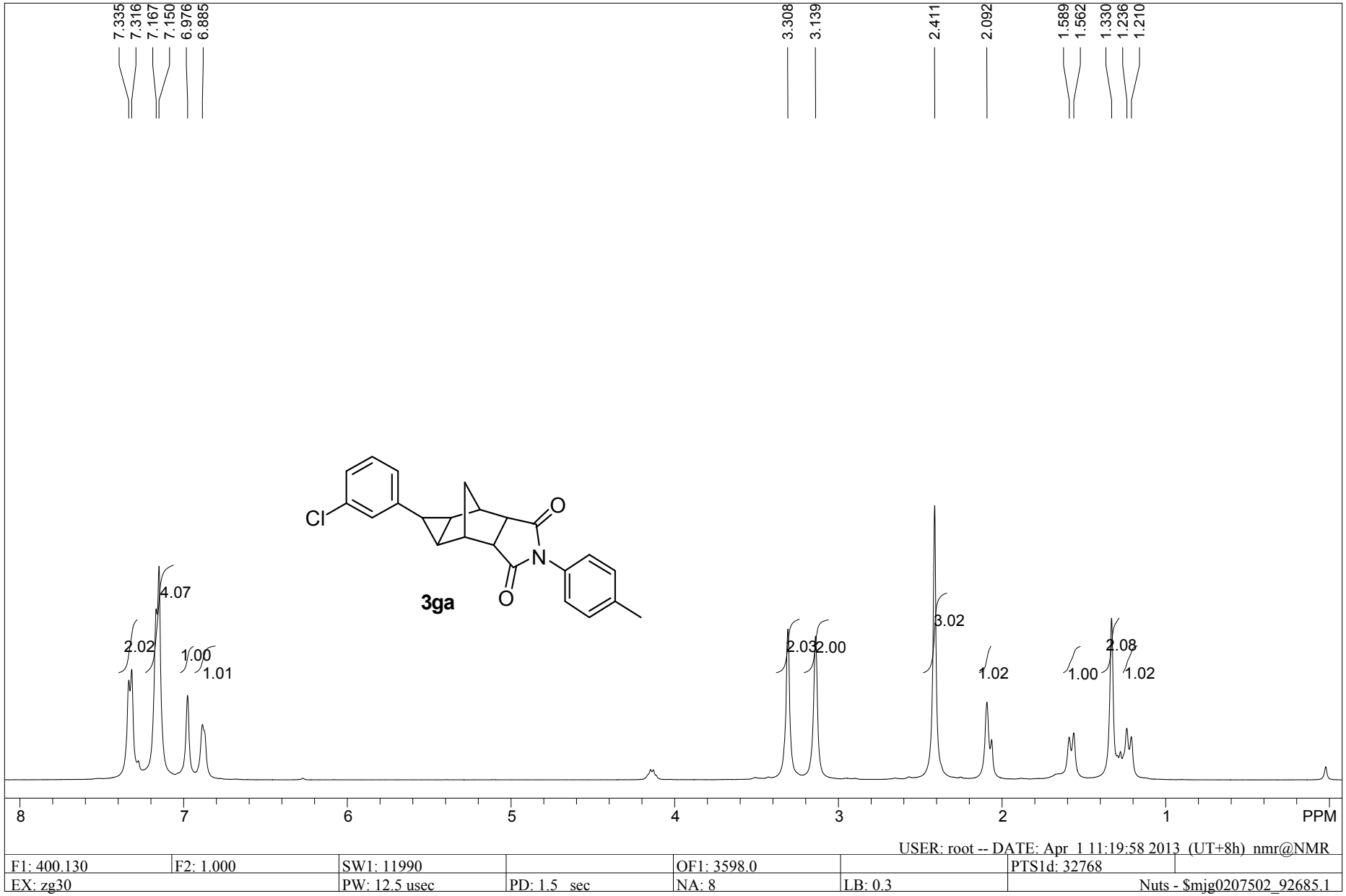


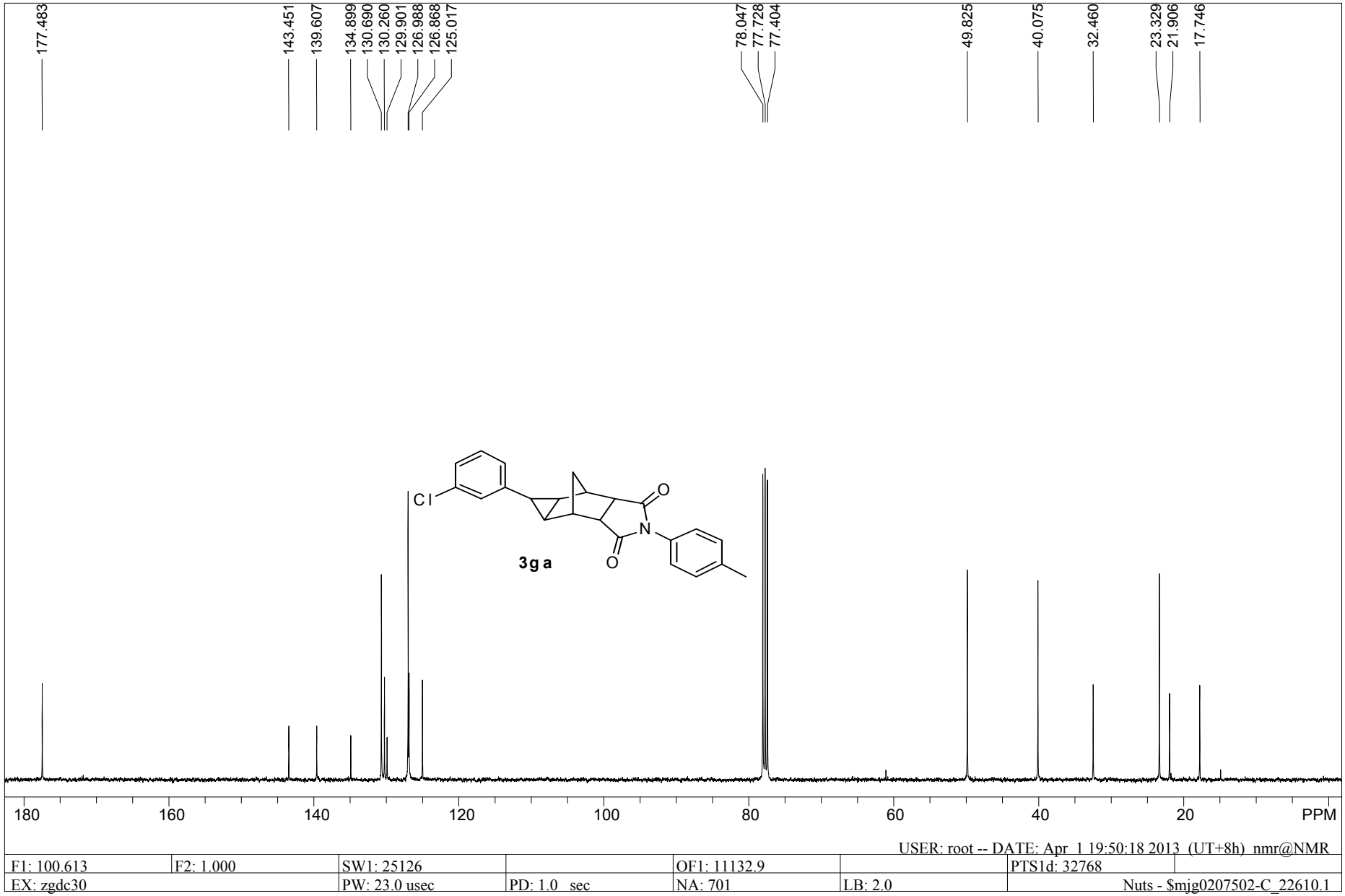

7.303
7.282
7.197
7.176
7.132
7.111
6.915
6.894
3.280
3.114
2.388
2.072
1.578
1.549
1.279
1.213
1.187
Cl
O
N
O
3fa
2.09
2.12
2.05
2.00
2.06
2.01
3.02
1.00
1.09
2.06
1.07
8
7
6
5
4
3
2
1
PPM
spect, CDCl3,
USER: nmrsu -- DATE: Fri Apr 12 13:47:06 2013
F1: 400.132
F2: 1.000
SW1: 8013
OF1: 2458.9
PTS1d: 65536
EX: zg30
PW: 9.5 usec
PD: 1.0 sec
NA: 16
LB: 0.0
Nuts - $pdata

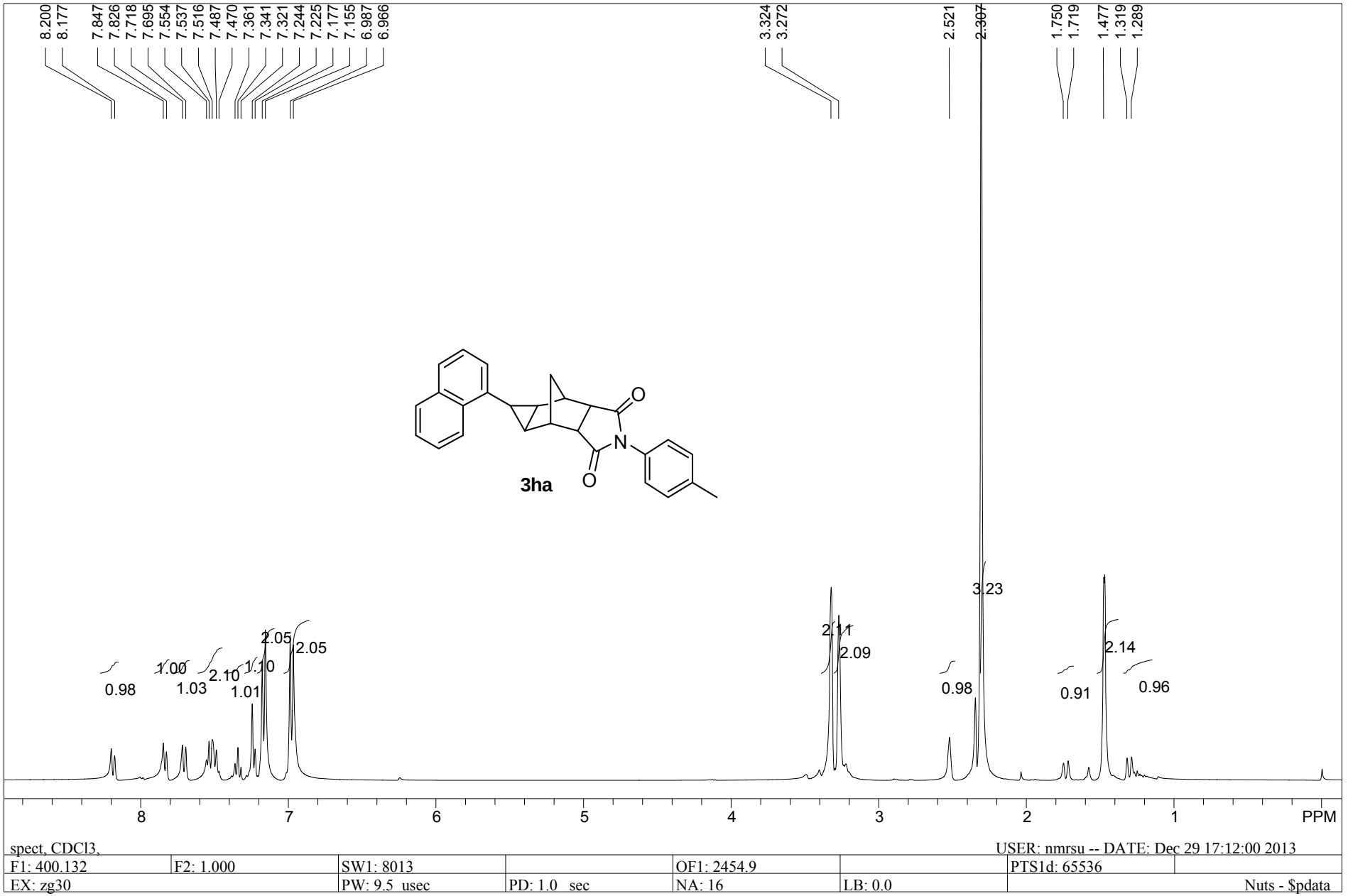


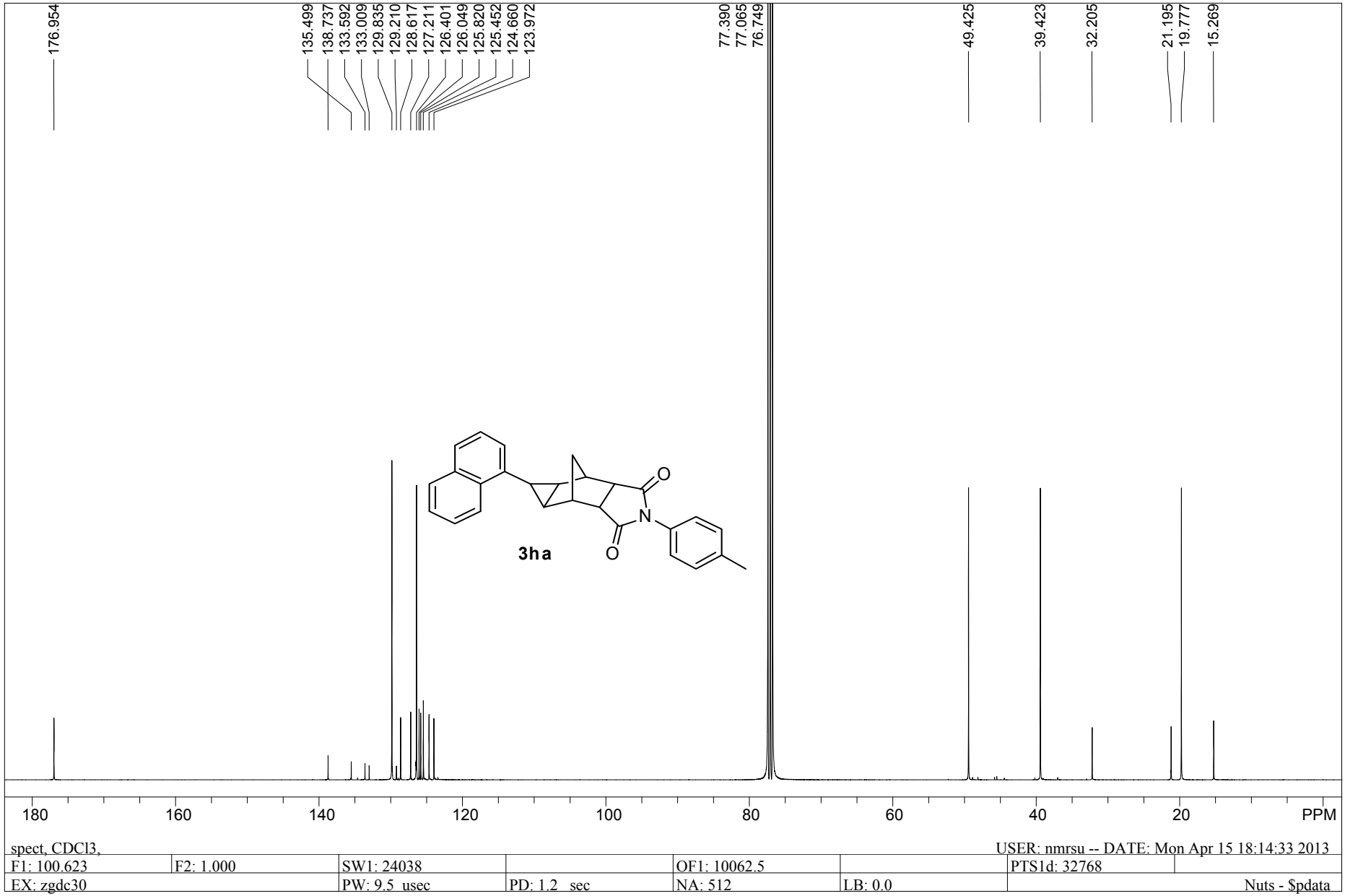
spect, CDCl3, USER: nmrsu -- DATE: Sat Apr 13 00:04:28 2013

F1: 100.623	F2: 1.000	SW1: 24038		OF1: 10062.5		PTS1d: 32768	
EX: zgpg30		PW: 9.5 usec	PD: 2.0 sec	NA: 1024	LB: 0.0		Nuts - $pdata


7.335
7.316
7.167
7.150
6.976
6.885
3.308
3.139
2.411
2.092
1.589
1.562
1.330
1.236
1.210
Cl
O
N
O
3ga
4.07
2.02
1.00
1.01
2.03
2.00
3.02
1.02
1.00
2.08
1.02
8
7
6
5
4
3
2
1
PPM
USER: root -- DATE: Apr 1 11:19:58 2013 (UT+8h) nmr@NMR
F1: 400.130
F2: 1.000
SW1: 11990
OF1: 3598.0
PTS1d: 32768
EX: zg30
PW: 12.5 usec
PD: 1.5 sec
NA: 8
LB: 0.3
Nuts - $mjg0207502_92685.1

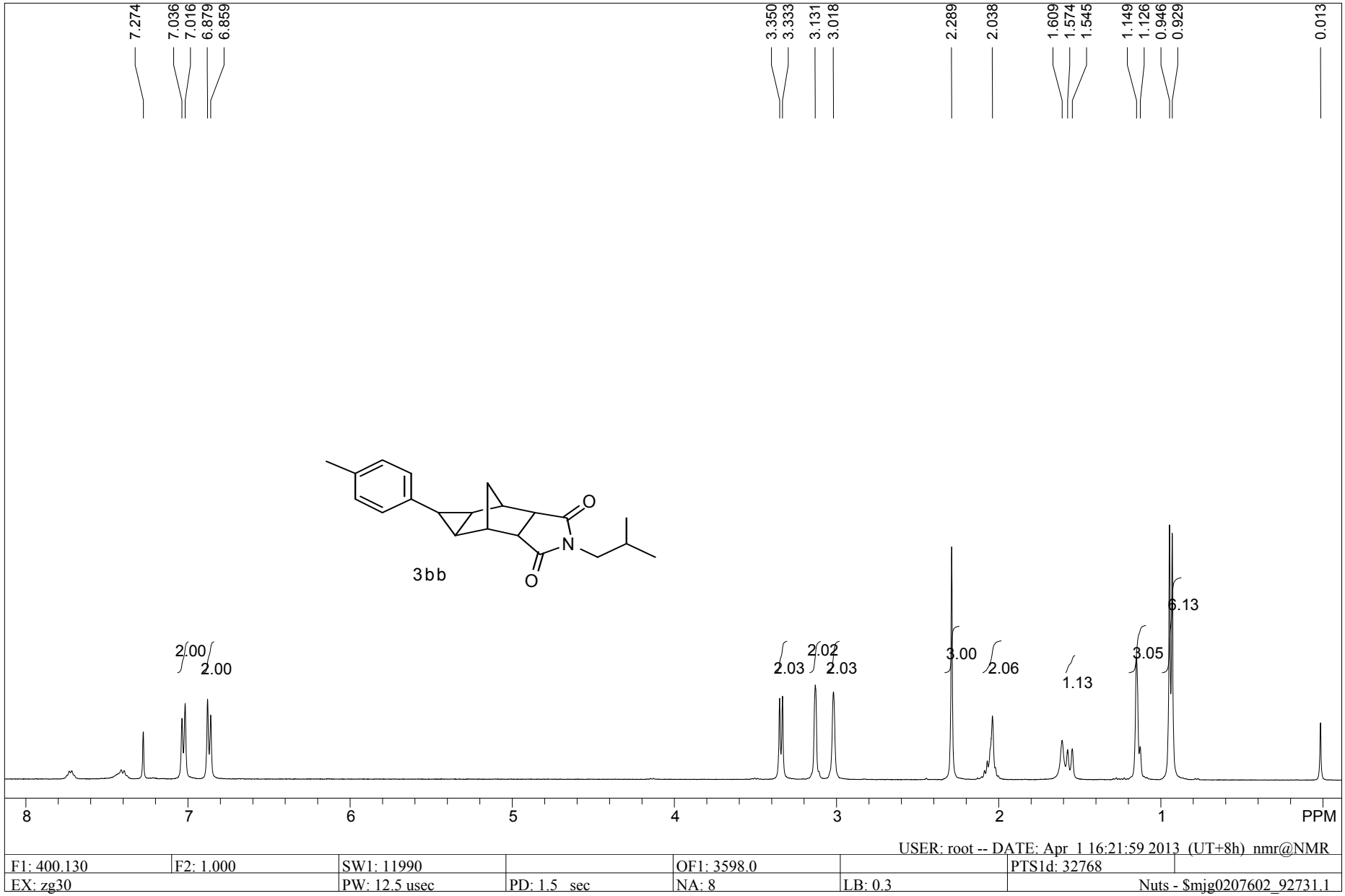

177.483
143.451
139.607
134.899
130.690
130.260
129.901
126.988
126.868
125.017
78.047
77.728
77.404
49.825
40.075
32.460
23.329
21.906
17.746
Cl
O
N
O
3g a
180
160
140
120
100
80
60
40
20
PPM
USER: root -- DATE: Apr 1 19:50:18 2013 (UT+8h) nmr@NMR
F1: 100.613
F2: 1.000
SW1: 25126
OF1: 11132.9
PTS1d: 32768
EX: zgdc30
PW: 23.0 usec
PD: 1.0 sec
NA: 701
LB: 2.0
Nuts - $mjg0207502-C_22610.1

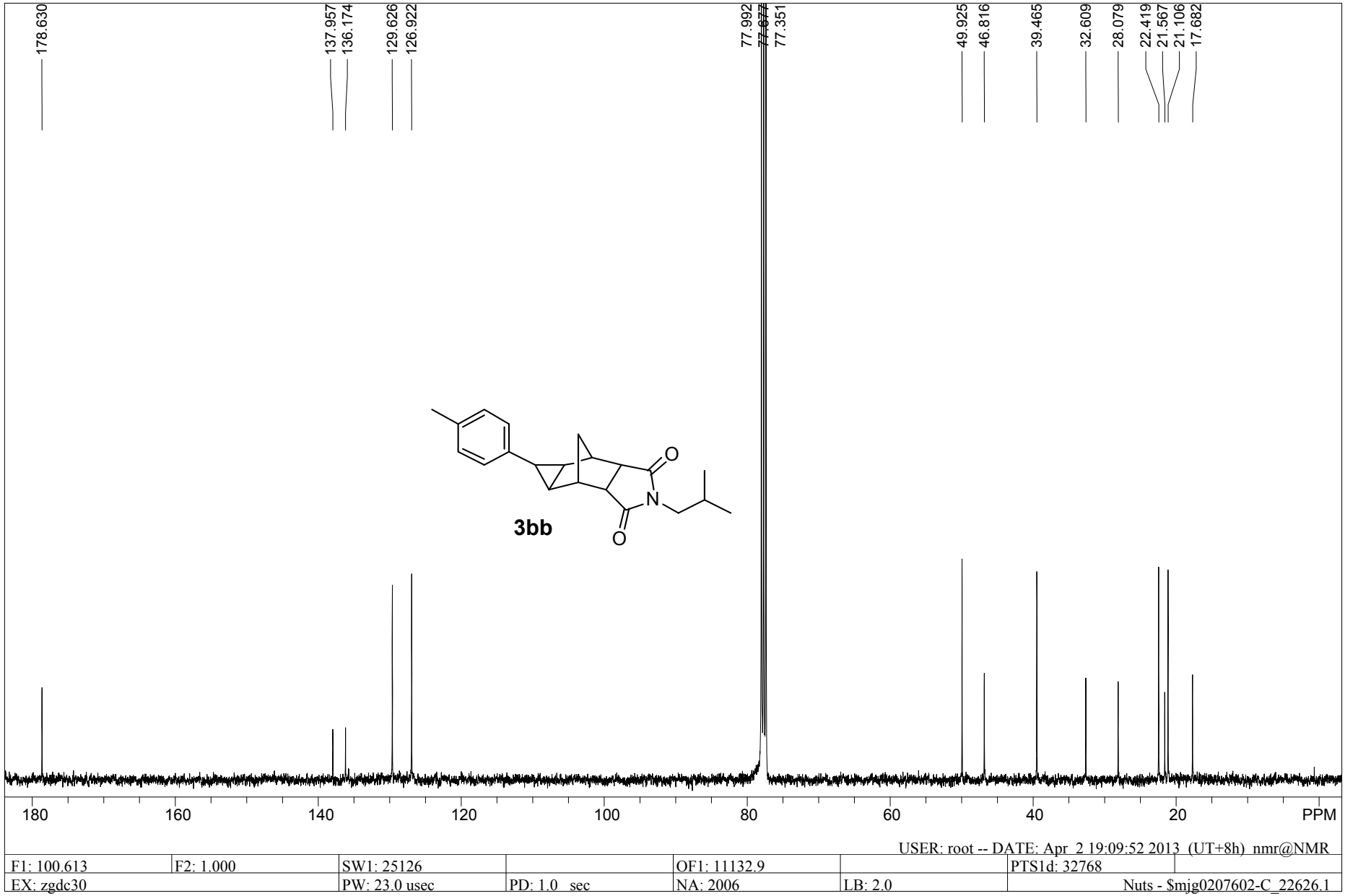


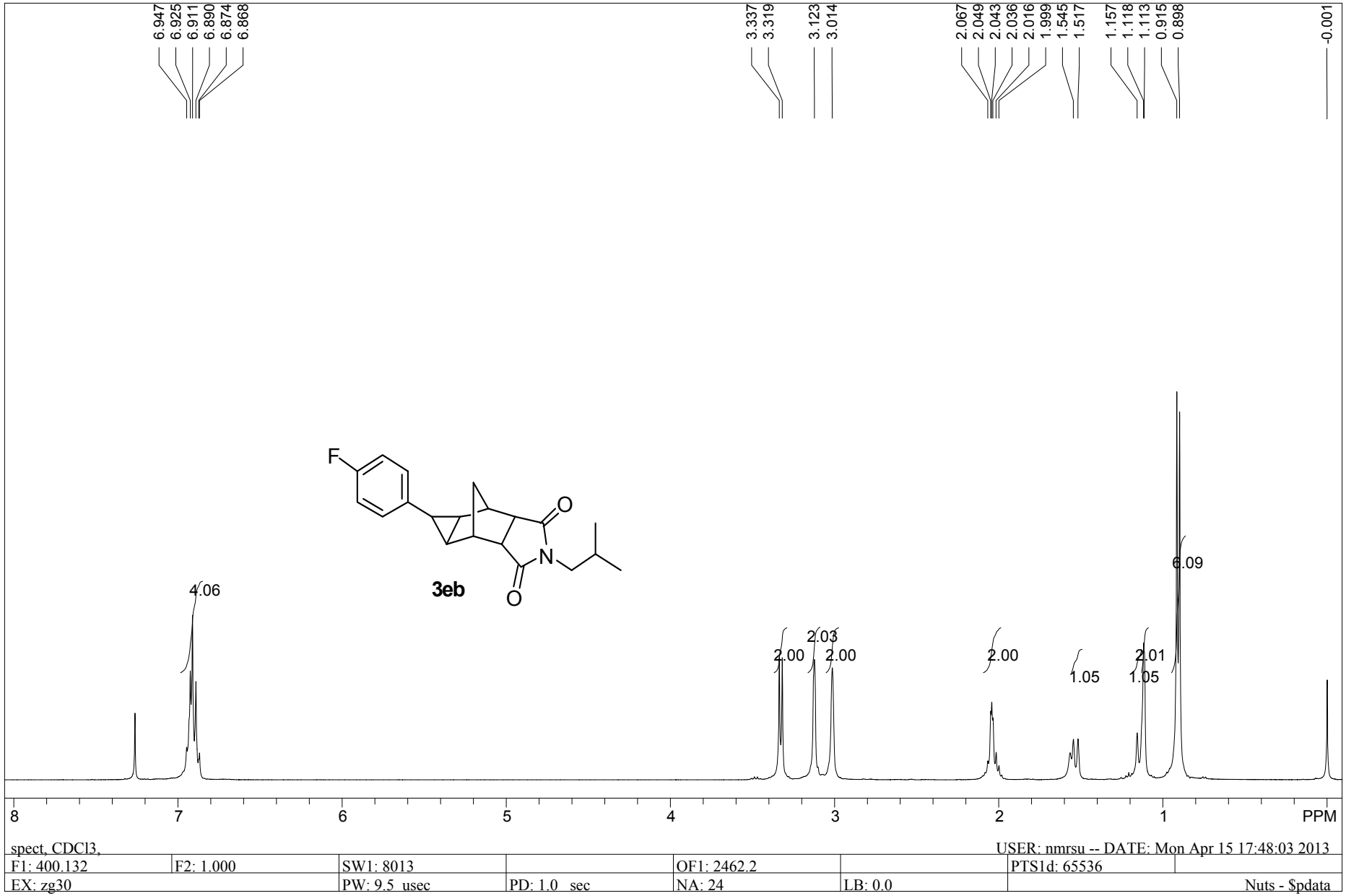


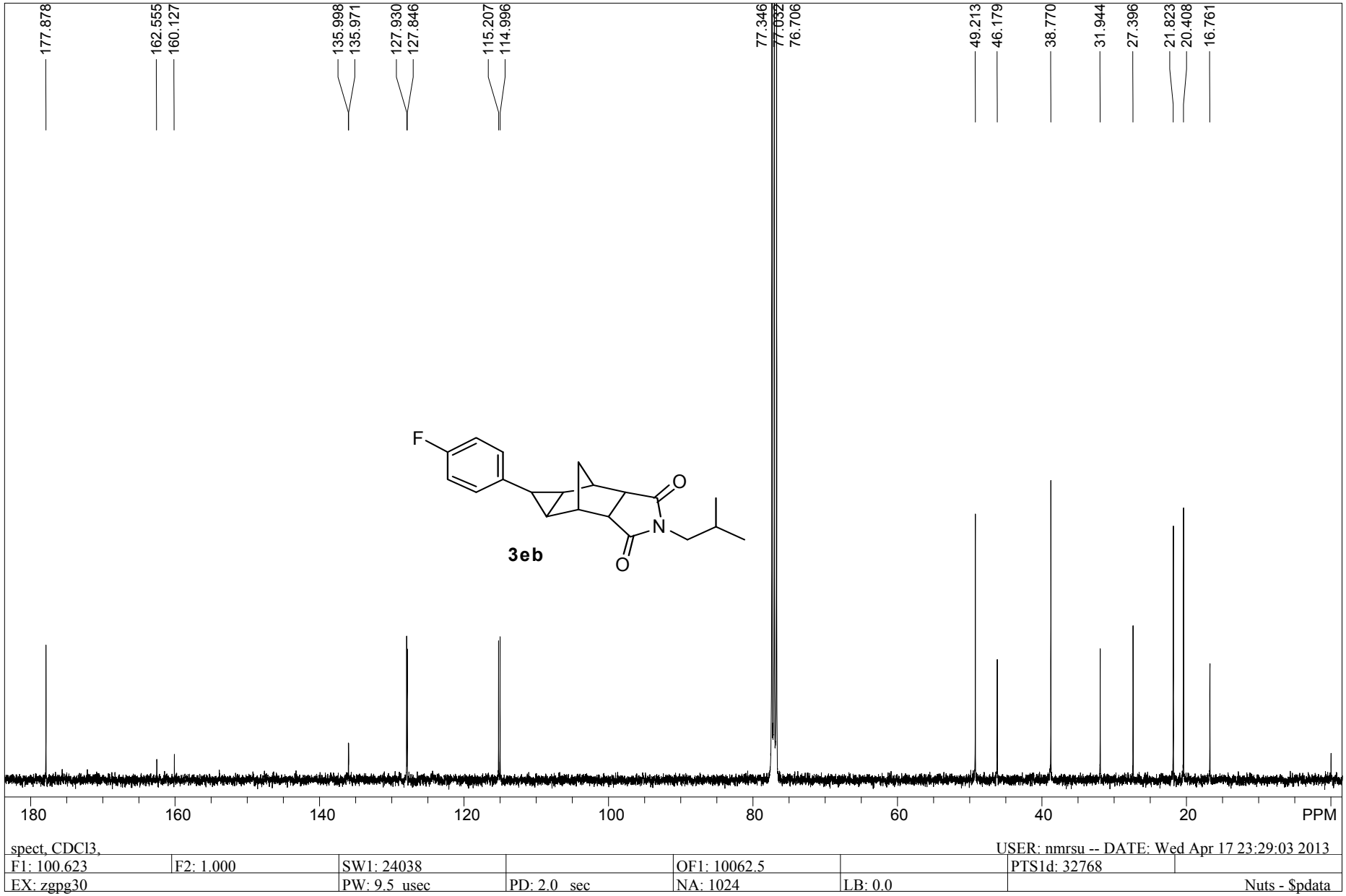
spect, CDCl3, USER: nmrsu -- DATE: Mon Apr 15 18:14:33 2013

F1: 100.623	F2: 1.000	SW1: 24038		OF1: 10062.5		PTS1d: 32768	
EX: zgdc30		PW: 9.5 usec	PD: 1.2 sec	NA: 512	LB: 0.0		Nuts - $pdata


7.274
7.036
7.016
6.879
6.859
3.350
3.333
3.131
3.018
2.289
2.038
1.609
1.574
1.545
1.149
1.126
0.946
0.929
0.013
O
N
O
3bb
2.00
2.00
2.03
2.02
2.03
3.00
2.06
1.13
3.05
6.13
8
7
6
5
4
3
2
1
PPM
USER: root -- DATE: Apr 1 16:21:59 2013 (UT+8h) nmr@NMR
F1: 400.130
F2: 1.000
SW1: 11990
OF1: 3598.0
PTS1d: 32768
EX: zg30
PW: 12.5 usec
PD: 1.5 sec
NA: 8
LB: 0.3
Nuts - $mjg0207602_92731.1

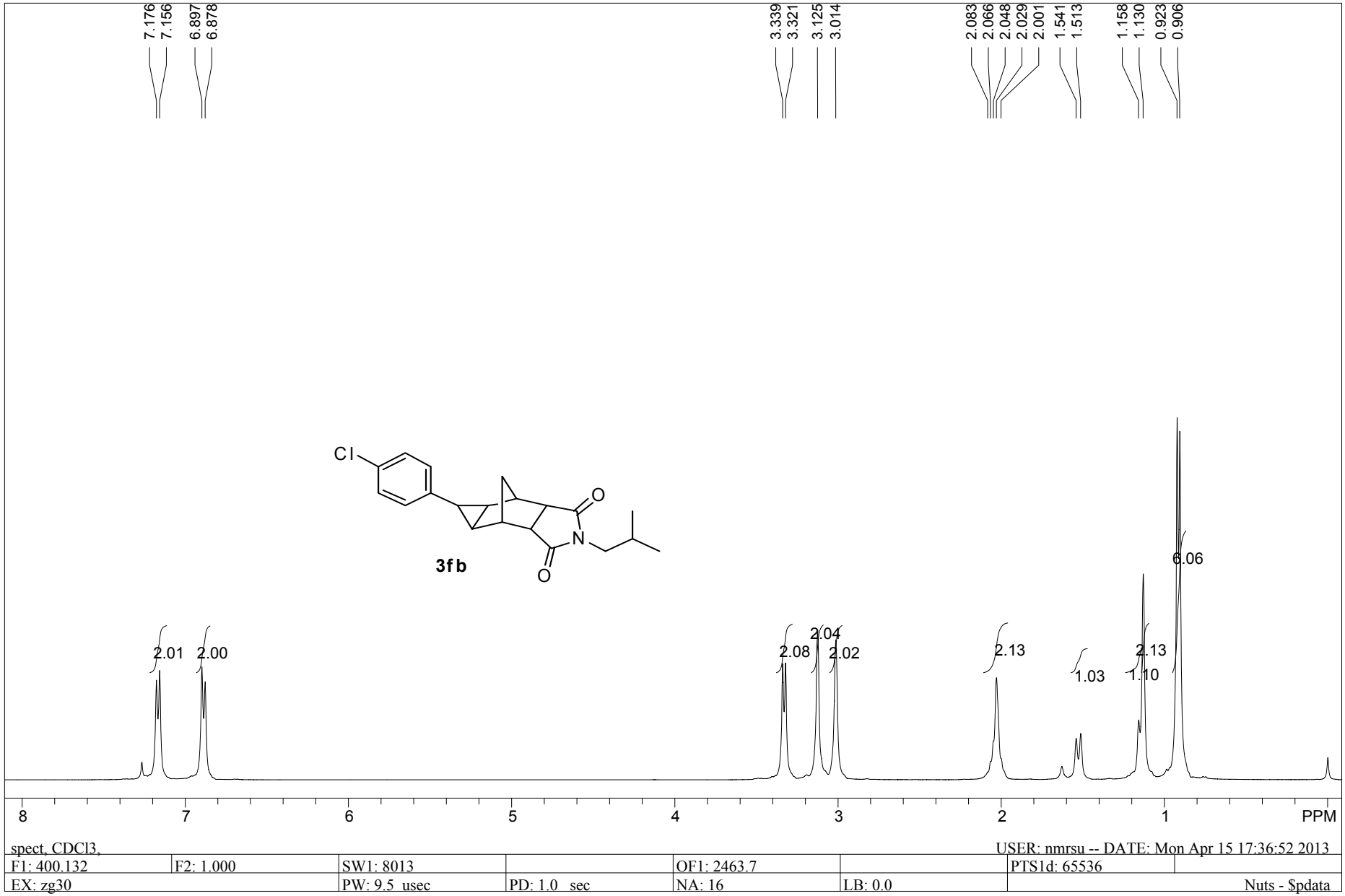

178.630
137.957
136.174
129.626
126.922
77.992
77.351
49.925
46.816
39.465
32.609
28.079
22.419
21.567
21.106
17.682
O
N
O
3bb
180
160
140
120
100
80
60
40
20
PPM
USER: root -- DATE: Apr 2 19:09:52 2013 (UT+8h) nmr@NMR
F1: 100.613
F2: 1.000
SW1: 25126
OF1: 11132.9
PTS1d: 32768
EX: zgdc30
PW: 23.0 usec
PD: 1.0 sec
NA: 2006
LB: 2.0
Nuts - $mjg0207602-C_22626.1

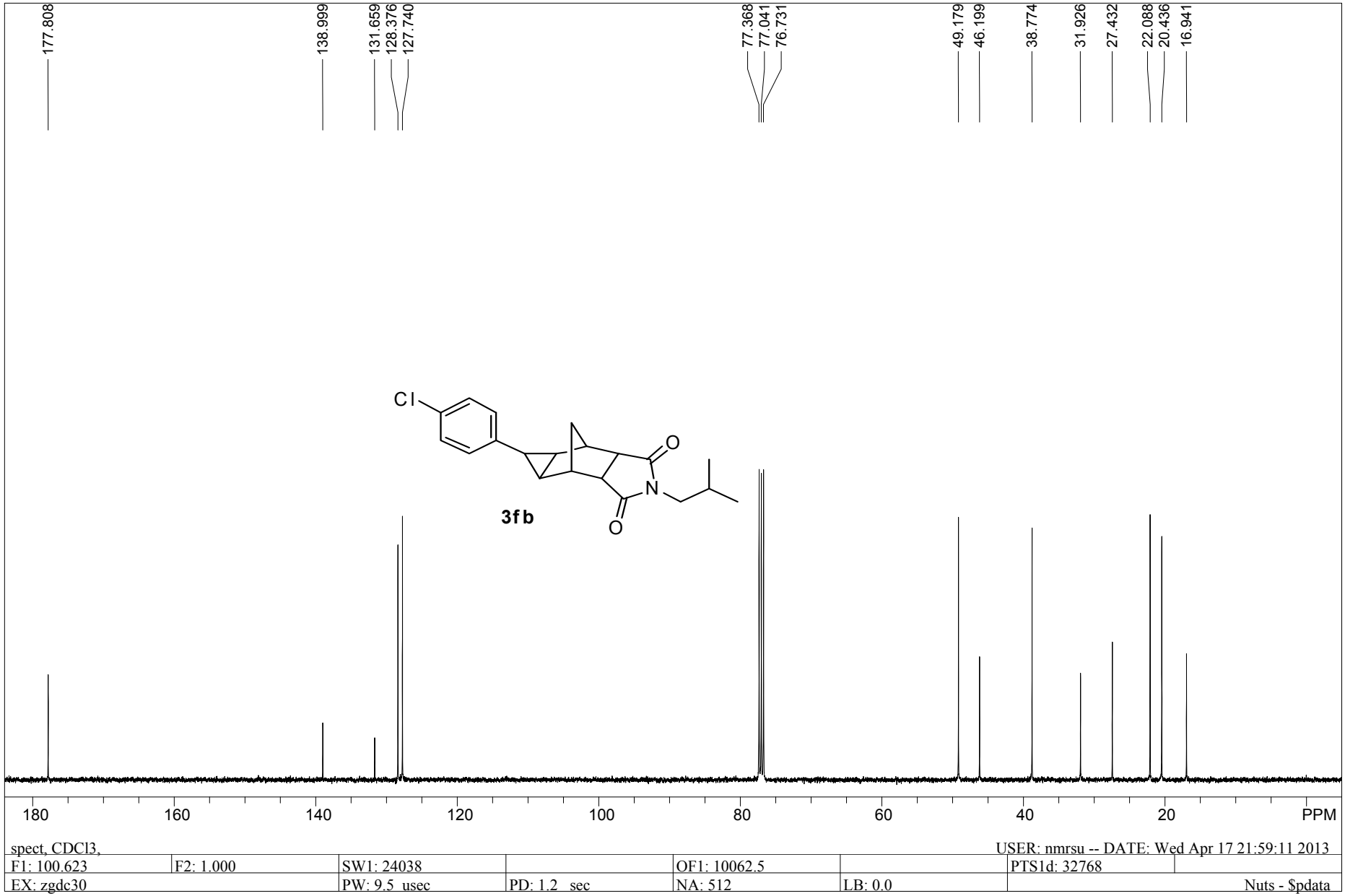

6.947
6.925
6.911
6.890
6.874
6.868
3.337
3.319
3.123
3.014
2.067
2.049
2.043
2.036
2.016
1.999
1.545
1.517
1.157
1.118
1.113
0.915
0.898
-0.001
F
O
N
O
3eb
4.06
2.00
2.03
2.00
2.00
1.05
2.01
1.05
6.09
8
7
6
5
4
3
2
1
PPM
spect, CDCl3,
USER: nmrsu -- DATE: Mon Apr 15 17:48:03 2013
F1: 400.132
F2: 1.000
SW1: 8013
OF1: 2462.2
PTS1d: 65536
EX: zg30
PW: 9.5 usec
PD: 1.0 sec
NA: 24
LB: 0.0
Nuts - $pdata

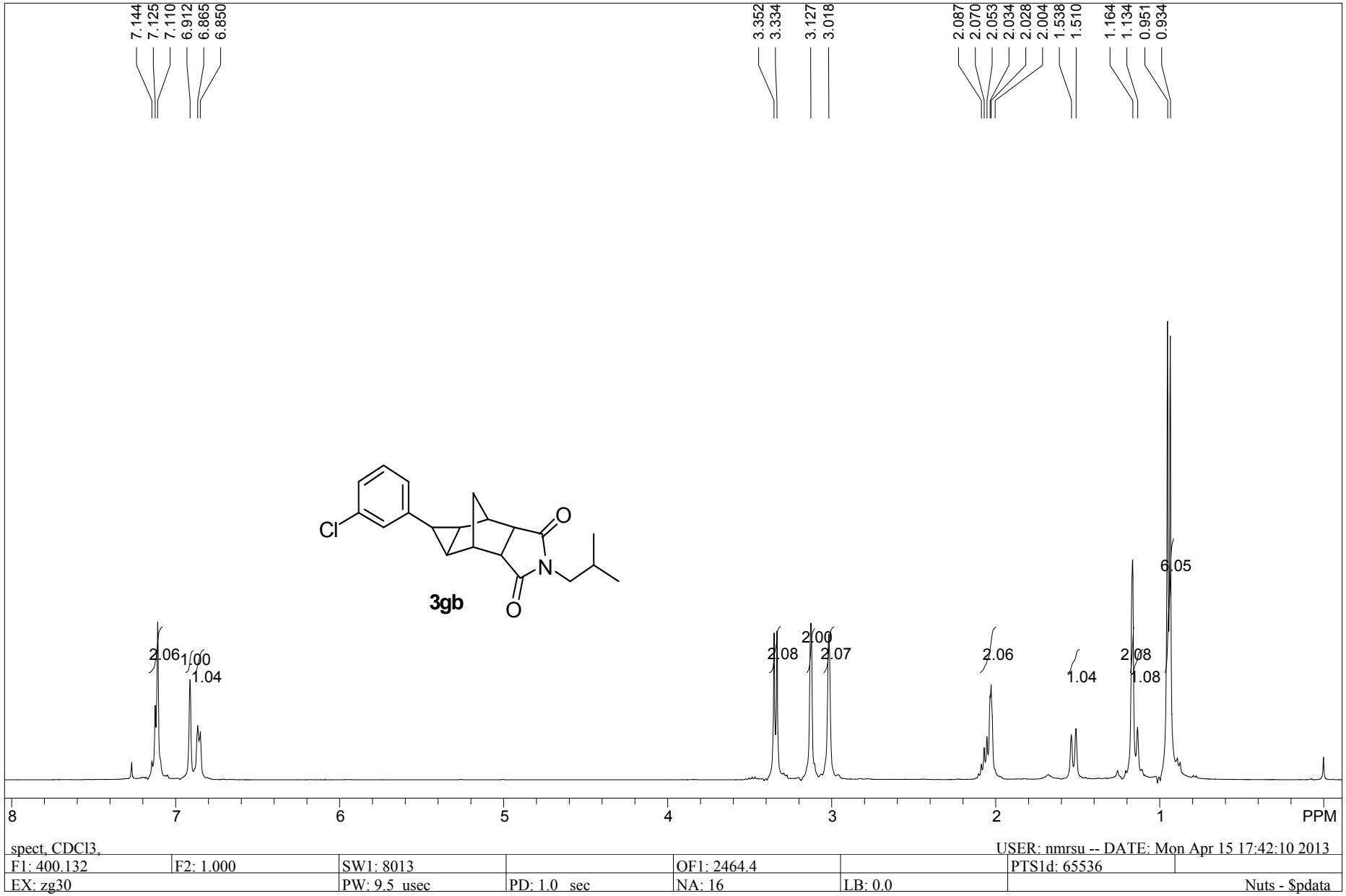


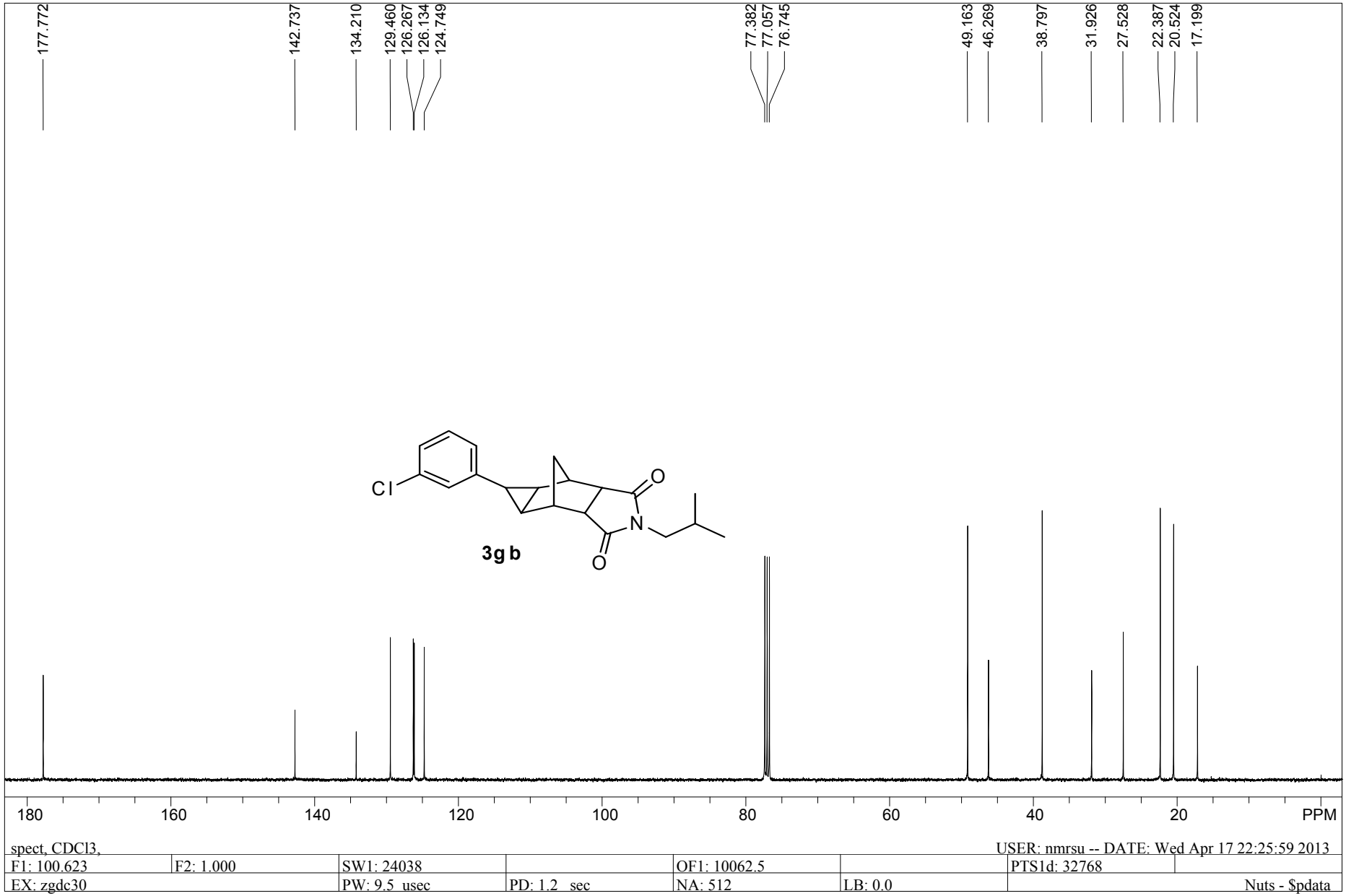
spect, CDCl3, USER: nmrsu -- DATE: Wed Apr 17 23:29:03 2013

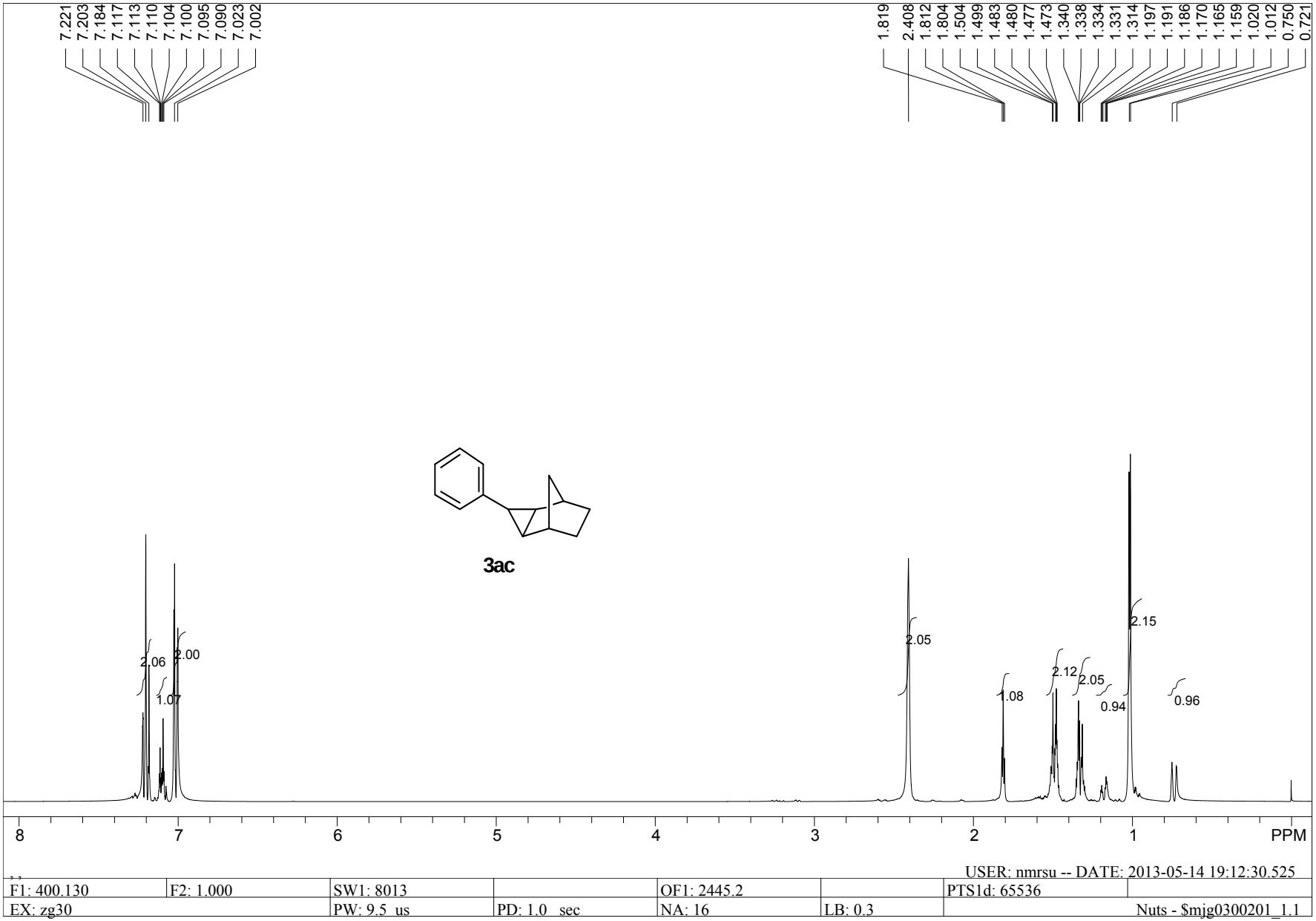
F1: 100.623	F2: 1.000	SW1: 24038		OF1: 10062.5		PTS1d: 32768	
EX: zgpg30		PW: 9.5 usec	PD: 2.0 sec	NA: 1024	LB: 0.0		Nuts - $pdata

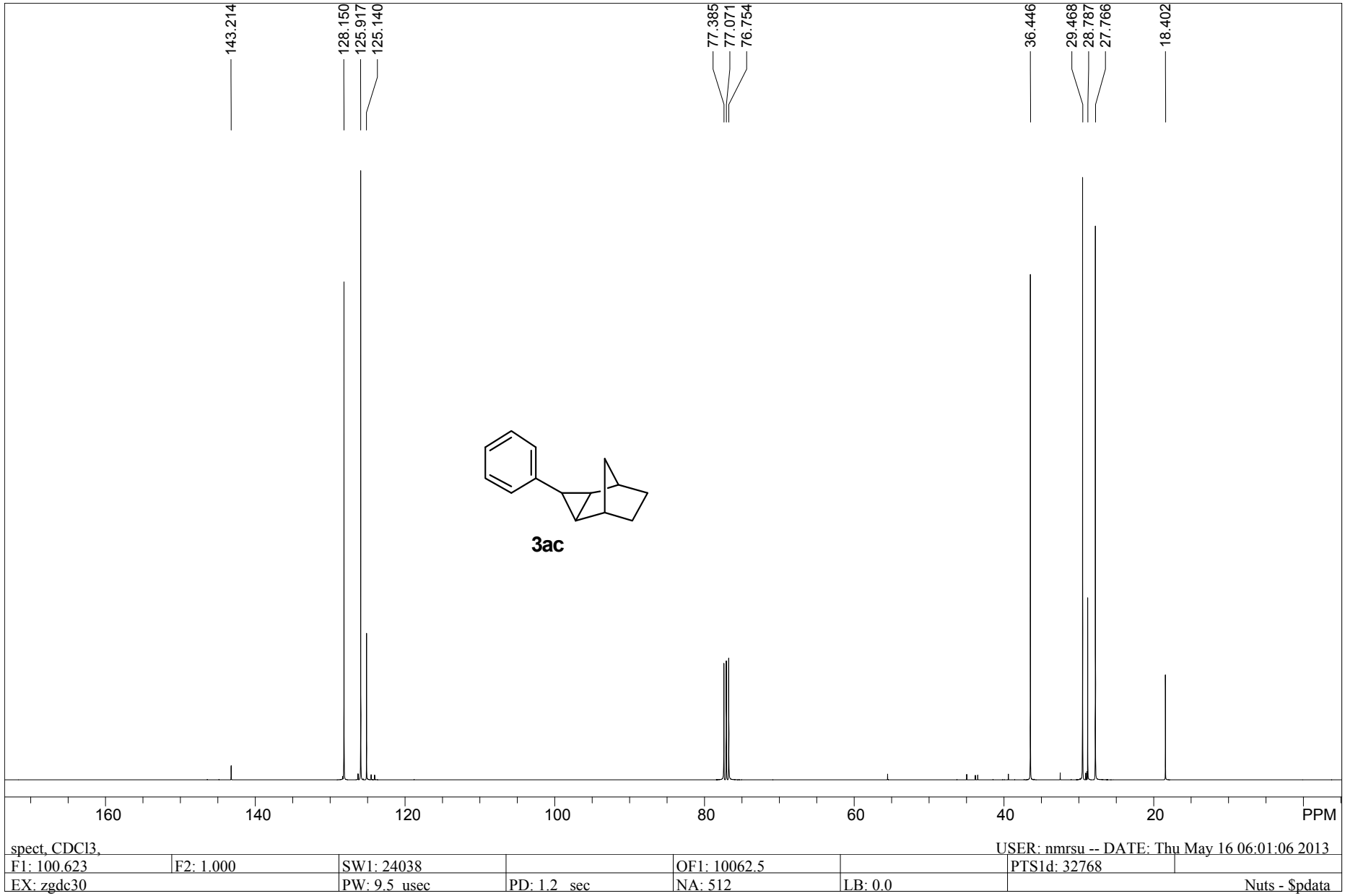

7.176
7.156
6.897
6.878
3.339
3.321
3.125
3.014
2.083
2.066
2.048
2.029
2.001
1.541
1.513
1.158
1.130
0.923
0.906
Cl
O
N
O
3fb
2.01
2.00
2.08
2.04
2.02
2.13
1.03
2.13
1.10
6.06
8
7
6
5
4
3
2
1
PPM
spect, CDCl3,
USER: nmrsu -- DATE: Mon Apr 15 17:36:52 2013
F1: 400.132
F2: 1.000
SW1: 8013
OF1: 2463.7
PTS1d: 65536
EX: zg30
PW: 9.5 usec
PD: 1.0 sec
NA: 16
LB: 0.0
Nuts - $pdata


177.808
138.999
131.659
128.376
127.740
77.368
77.041
76.731
49.179
46.199
38.774
31.926
27.432
22.088
20.436
16.941
Cl
O
N
O
3fb
180
160
140
120
100
80
60
40
20
PPM
spect, CDCl3,
USER: nmrsu -- DATE: Wed Apr 17 21:59:11 2013
F1: 100.623
F2: 1.000
SW1: 24038
OF1: 10062.5
PTS1d: 32768
EX: zgdc30
PW: 9.5 usec
PD: 1.2 sec
NA: 512
LB: 0.0
Nuts - $pdata


7.144
7.125
7.110
6.912
6.865
6.850
3.352
3.334
3.127
3.018
2.087
2.070
2.053
2.034
2.028
2.004
1.538
1.510
1.164
1.134
0.951
0.934
Cl
O
N
O
3gb
2.06
1.00
1.04
2.08
2.00
2.07
2.06
1.04
2.08
1.08
6.05
8
7
6
5
4
3
2
1
PPM
spect, CDCl3,
USER: nmrsu -- DATE: Mon Apr 15 17:42:10 2013
F1: 400.132
F2: 1.000
SW1: 8013
OF1: 2464.4
PTS1d: 65536
EX: zg30
PW: 9.5 usec
PD: 1.0 sec
NA: 16
LB: 0.0
Nuts - $pdata

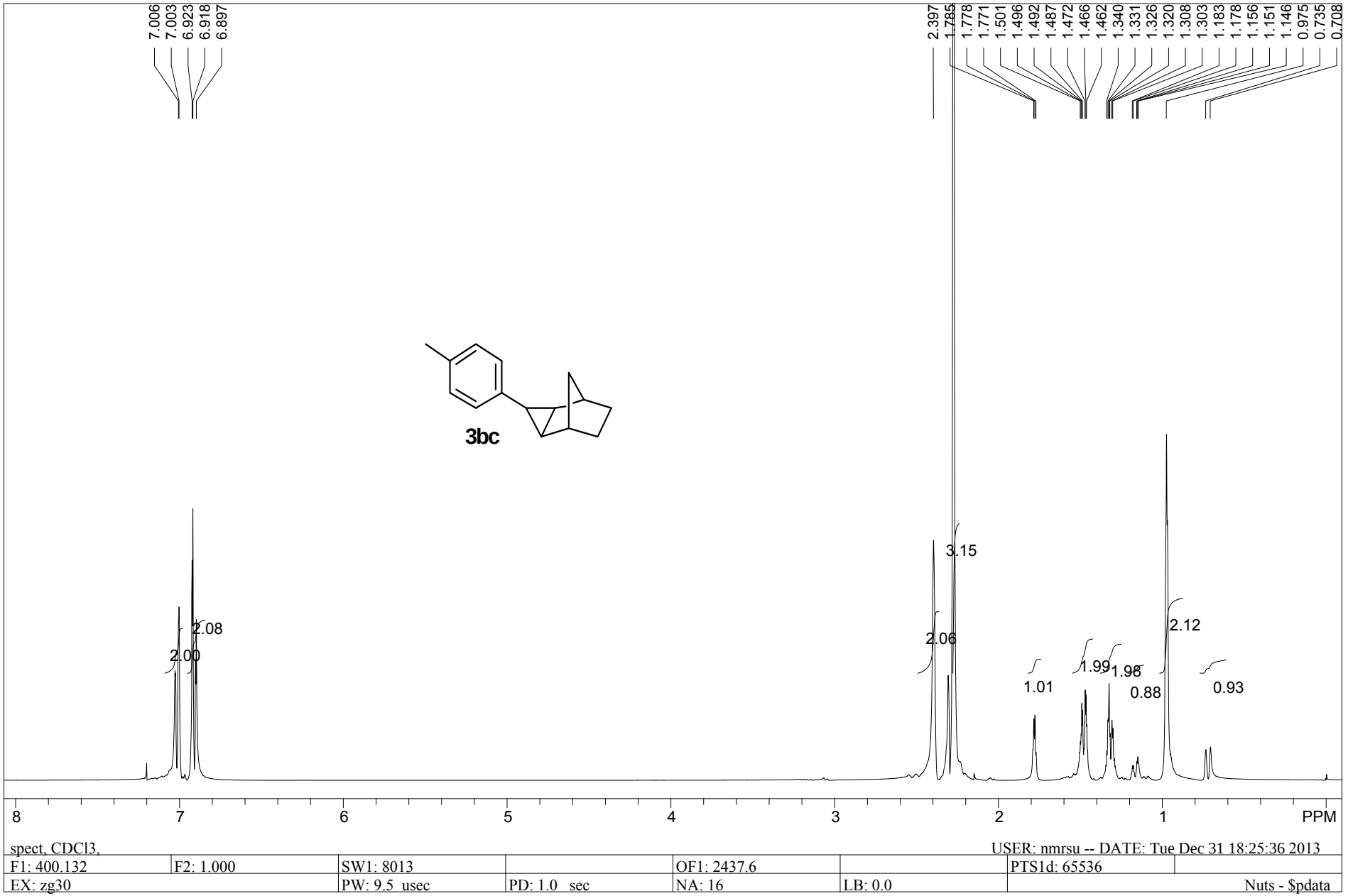

177.772
142.737
134.210
129.460
126.267
126.134
124.749
77.382
77.057
76.745
49.163
46.269
38.797
31.926
27.528
22.387
20.524
17.199
Cl
O
N
O
3g b
180
160
140
120
100
80
60
40
20
PPM
spect, CDCl3,
USER: nmrsu -- DATE: Wed Apr 17 22:25:59 2013
F1: 100.623
F2: 1.000
SW1: 24038
OF1: 10062.5
PTS1d: 32768
EX: zgdc30
PW: 9.5 usec
PD: 1.2 sec
NA: 512
LB: 0.0
Nuts - $pdata

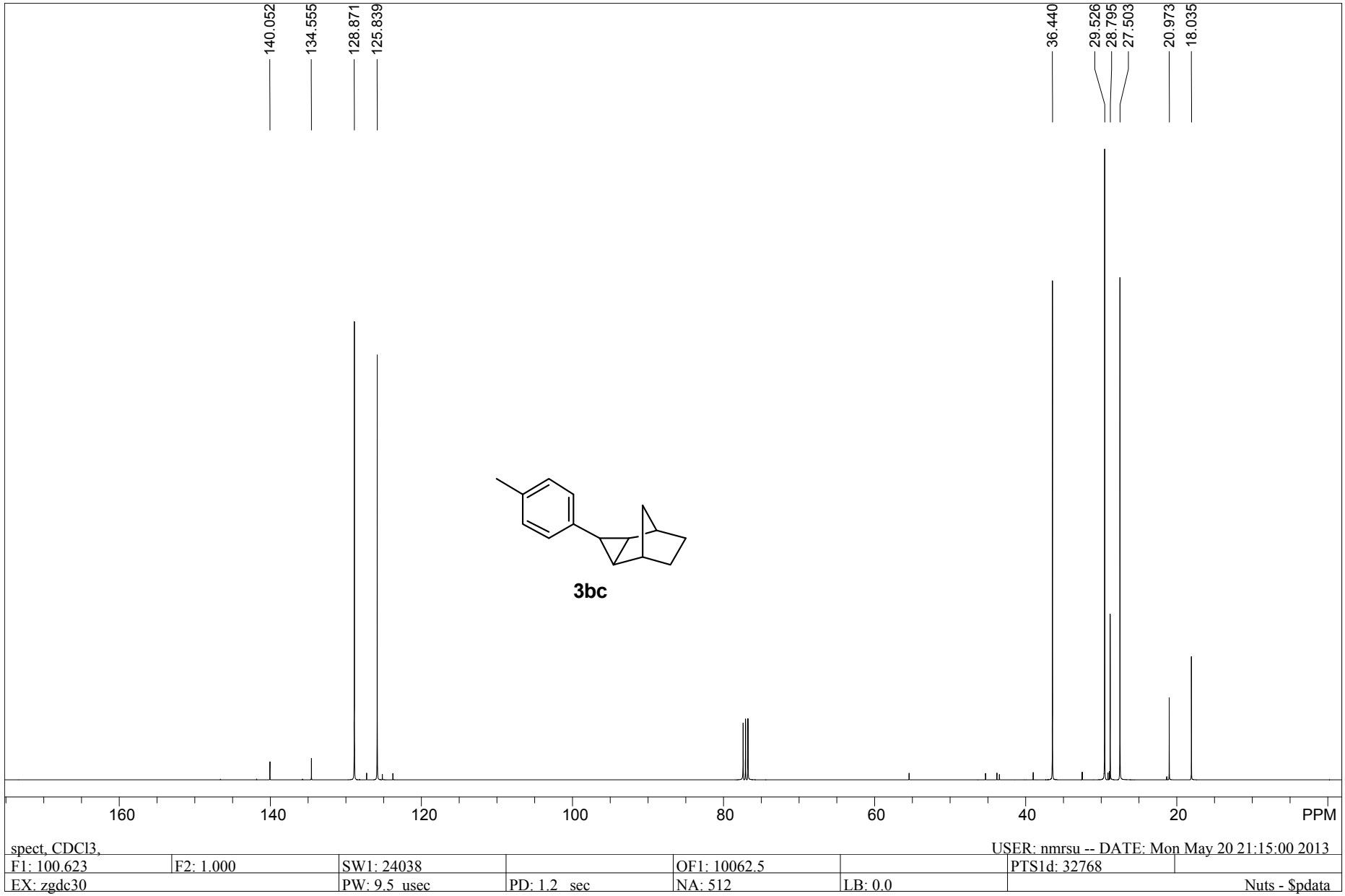

7.221
7.203
7.184
7.117
7.113
7.110
7.104
7.100
7.095
7.090
7.023
7.002
1.819
2.408
1.812
1.804
1.504
1.499
1.483
1.480
1.477
1.473
1.340
1.338
1.334
1.331
1.314
1.197
1.191
1.186
1.170
1.165
1.159
1.020
1.012
0.750
0.721
3ac
2.06
2.00
1.07
2.05
1.08
2.12
2.05
0.94
2.15
0.96
8
7
6
5
4
3
2
1
PPM
USER: nmrsu -- DATE: 2013-05-14 19:12:30.525
F1: 400.130
F2: 1.000
SW1: 8013
OF1: 2445.2
PTS1d: 65536
EX: zg30
PW: 9.5 us
PD: 1.0 sec
NA: 16
LB: 0.3
Nuts - $mjg0300201_1.1



spect, CDCl3, USER: nmrsu -- DATE: Thu May 16 06:01:06 2013

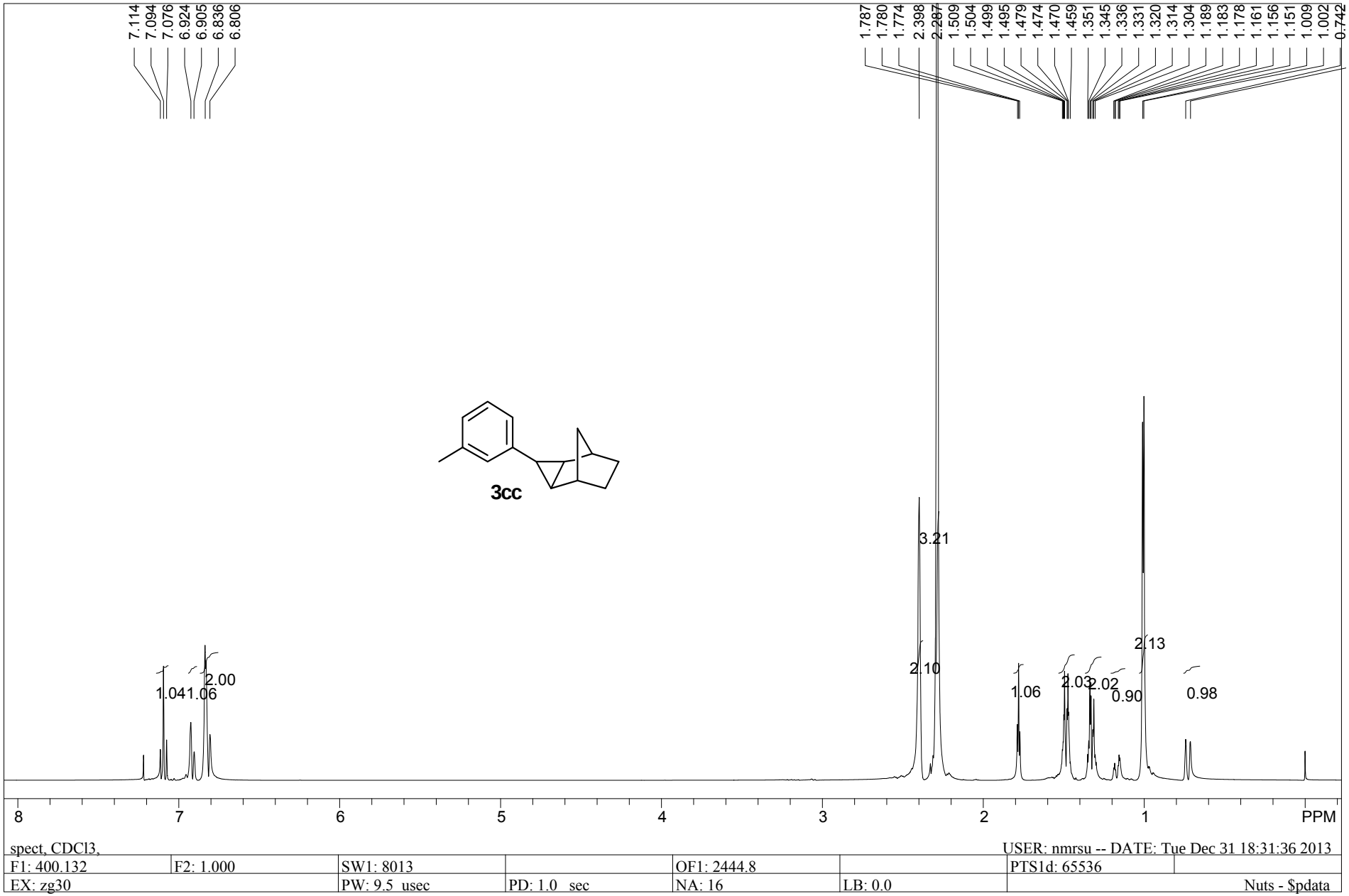
F1: 100.623	F2: 1.000	SW1: 24038		OF1: 10062.5		PTS1d: 32768	
EX: zgdc30		PW: 9.5 usec	PD: 1.2 sec	NA: 512	LB: 0.0		Nuts - $pdata

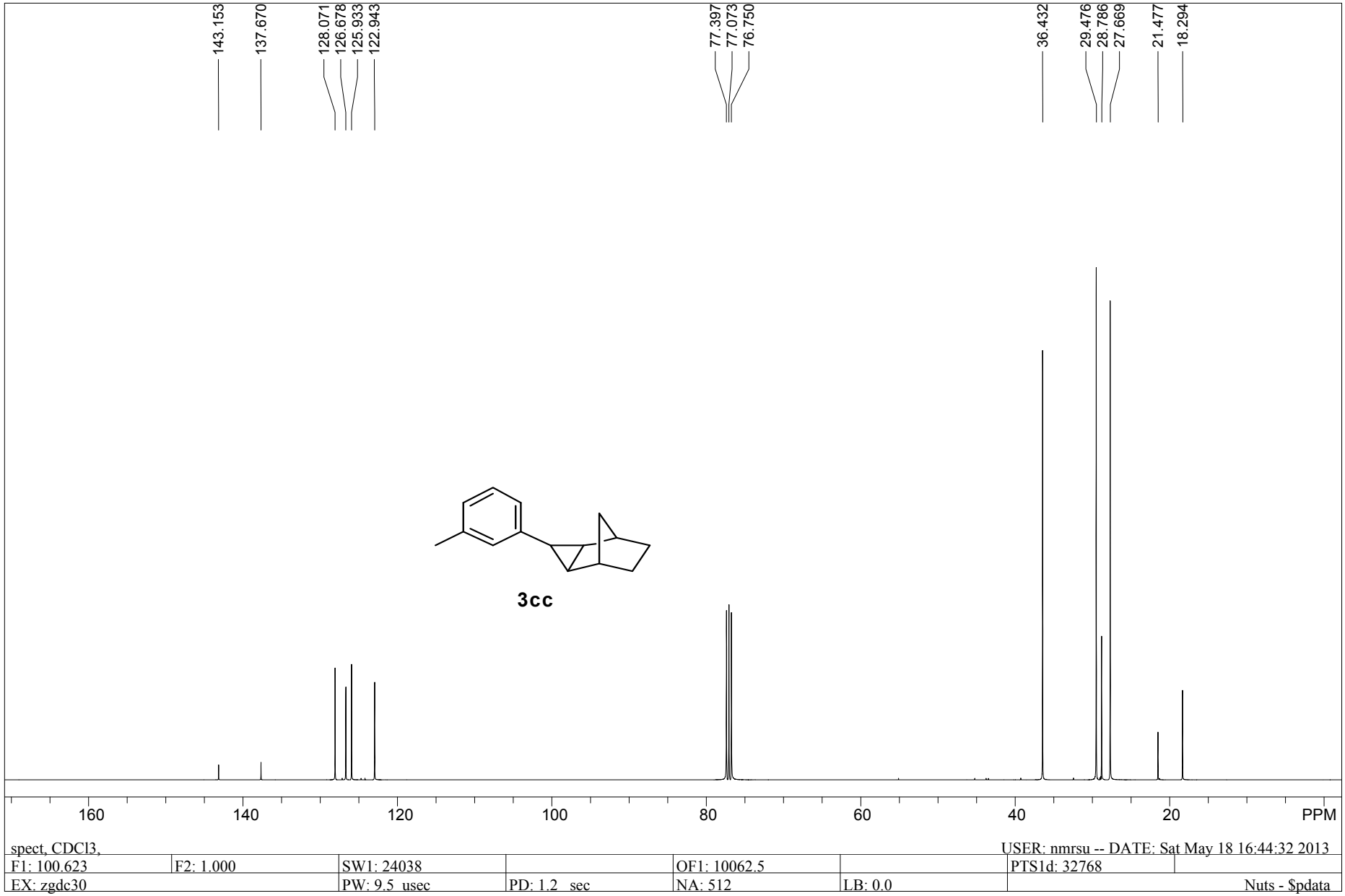

7.006
7.003
6.923
6.918
6.897
2.397
1.785
1.778
1.771
1.501
1.496
1.492
1.487
1.472
1.466
1.462
1.340
1.331
1.326
1.320
1.308
1.303
1.183
1.178
1.156
1.151
1.146
0.975
0.735
0.708
3bc
3.15
2.08
2.00
2.06
2.12
1.99
1.98
1.01
0.88
0.93
8
7
6
5
4
3
2
1
PPM
spect, CDCl3,
USER: nmrsu -- DATE: Tue Dec 31 18:25:36 2013
F1: 400.132
F2: 1.000
SW1: 8013
OF1: 2437.6
PTS1d: 65536
EX: zg30
PW: 9.5 usec
PD: 1.0 sec
NA: 16
LB: 0.0
Nuts - $pdata

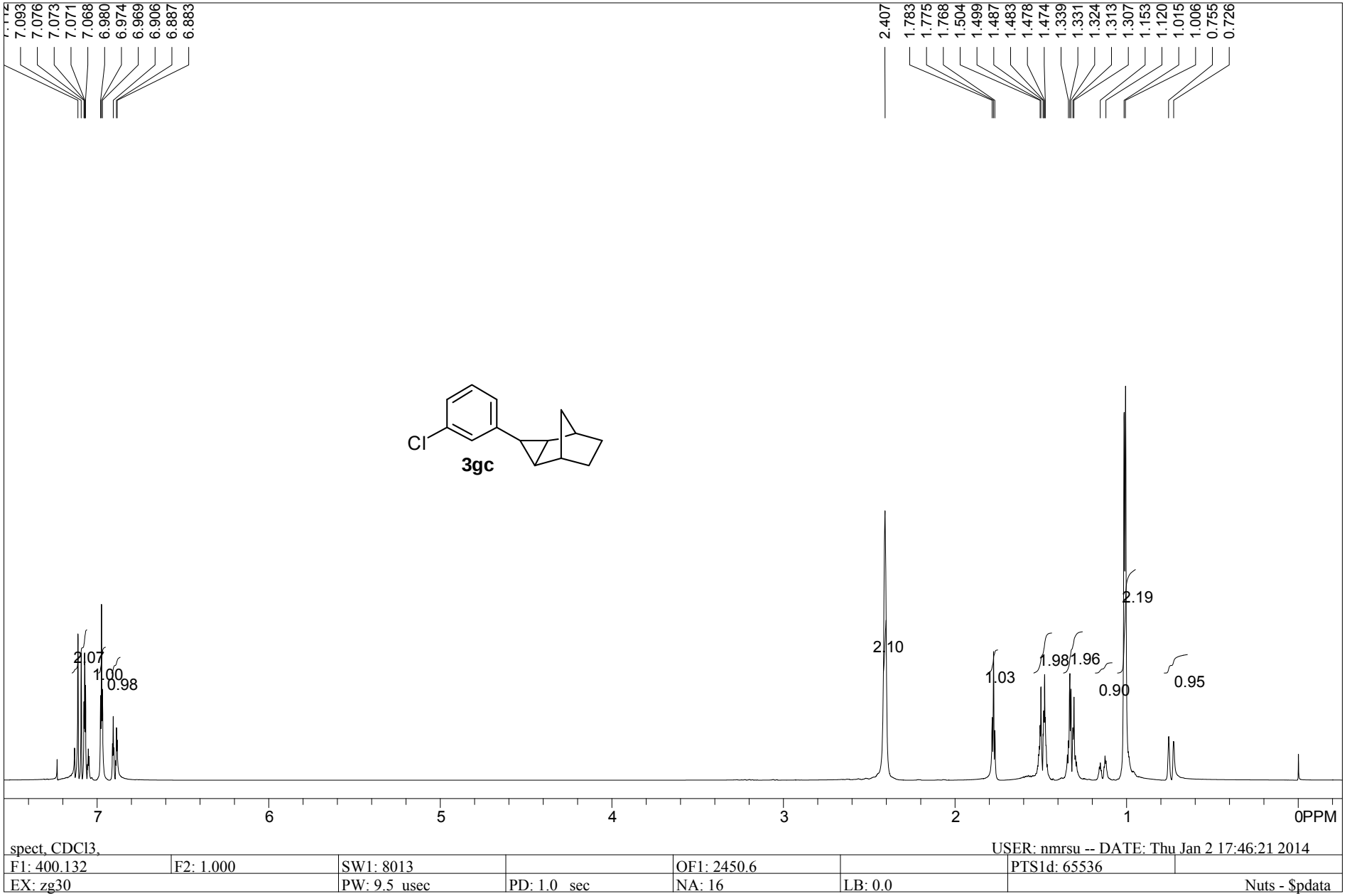


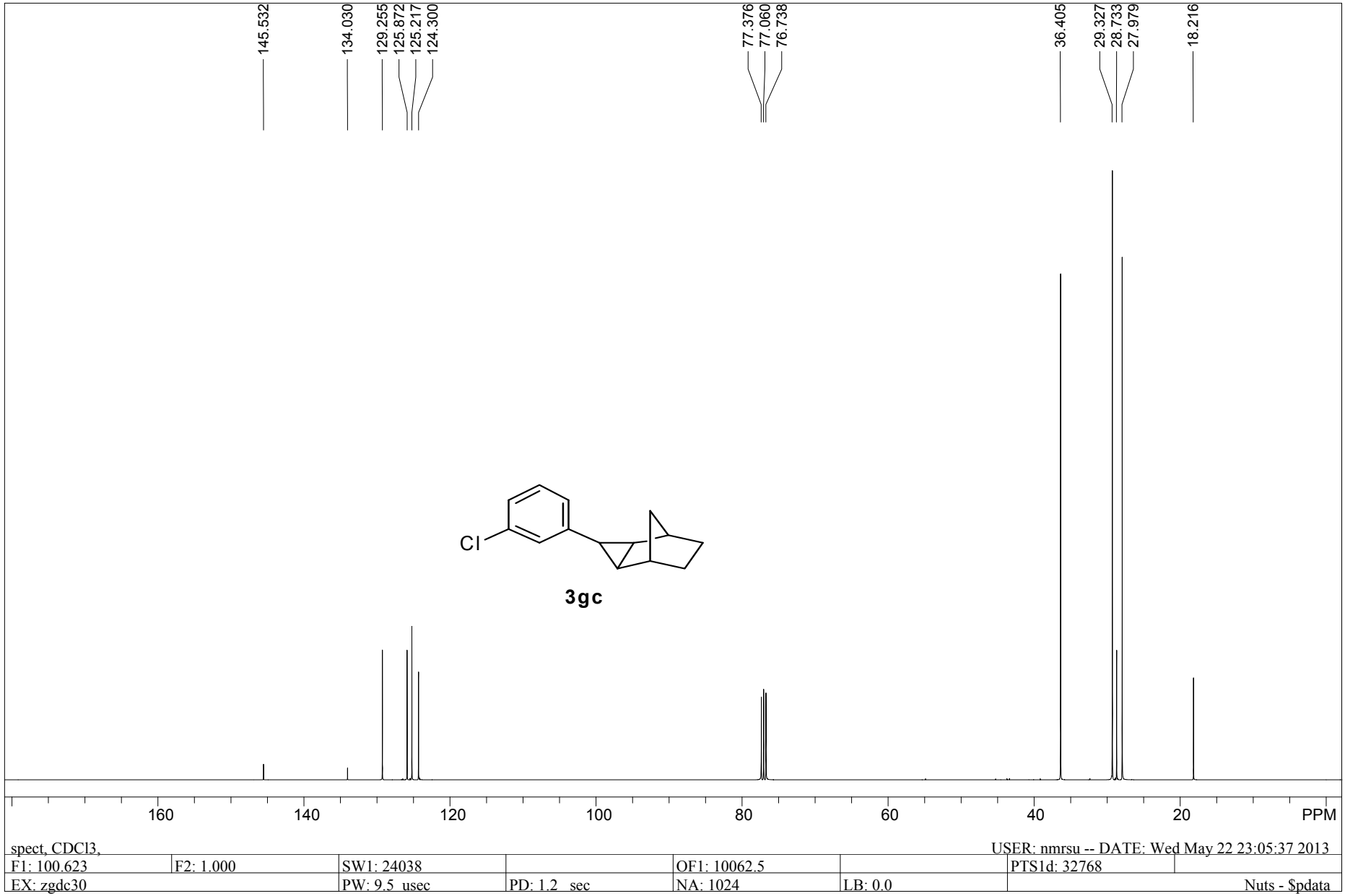
spect, CDCl3, USER: nmrsu -- DATE: Mon May 20 21:15:00 2013

F1: 100.623	F2: 1.000	SW1: 24038		OF1: 10062.5		PTS1d: 32768	
EX: zgdc30		PW: 9.5 usec	PD: 1.2 sec	NA: 512	LB: 0.0		Nuts - $pdata


7.114
7.094
7.076
6.924
6.905
6.836
6.806
1.787
1.780
1.774
2.398
2.287
1.509
1.504
1.499
1.495
1.479
1.474
1.470
1.459
1.351
1.345
1.336
1.331
1.320
1.314
1.304
1.189
1.183
1.178
1.161
1.156
1.151
1.009
1.002
0.742
3cc
3.21
2.10
2.13
2.00
1.04
1.06
1.06
2.03
2.02
0.90
0.98
8
7
6
5
4
3
2
1
PPM
spect, CDCl3,
USER: nmrsu -- DATE: Tue Dec 31 18:31:36 2013
F1: 400.132
F2: 1.000
SW1: 8013
OF1: 2444.8
PTS1d: 65536
EX: zg30
PW: 9.5 usec
PD: 1.0 sec
NA: 16
LB: 0.0
Nuts - $pdata

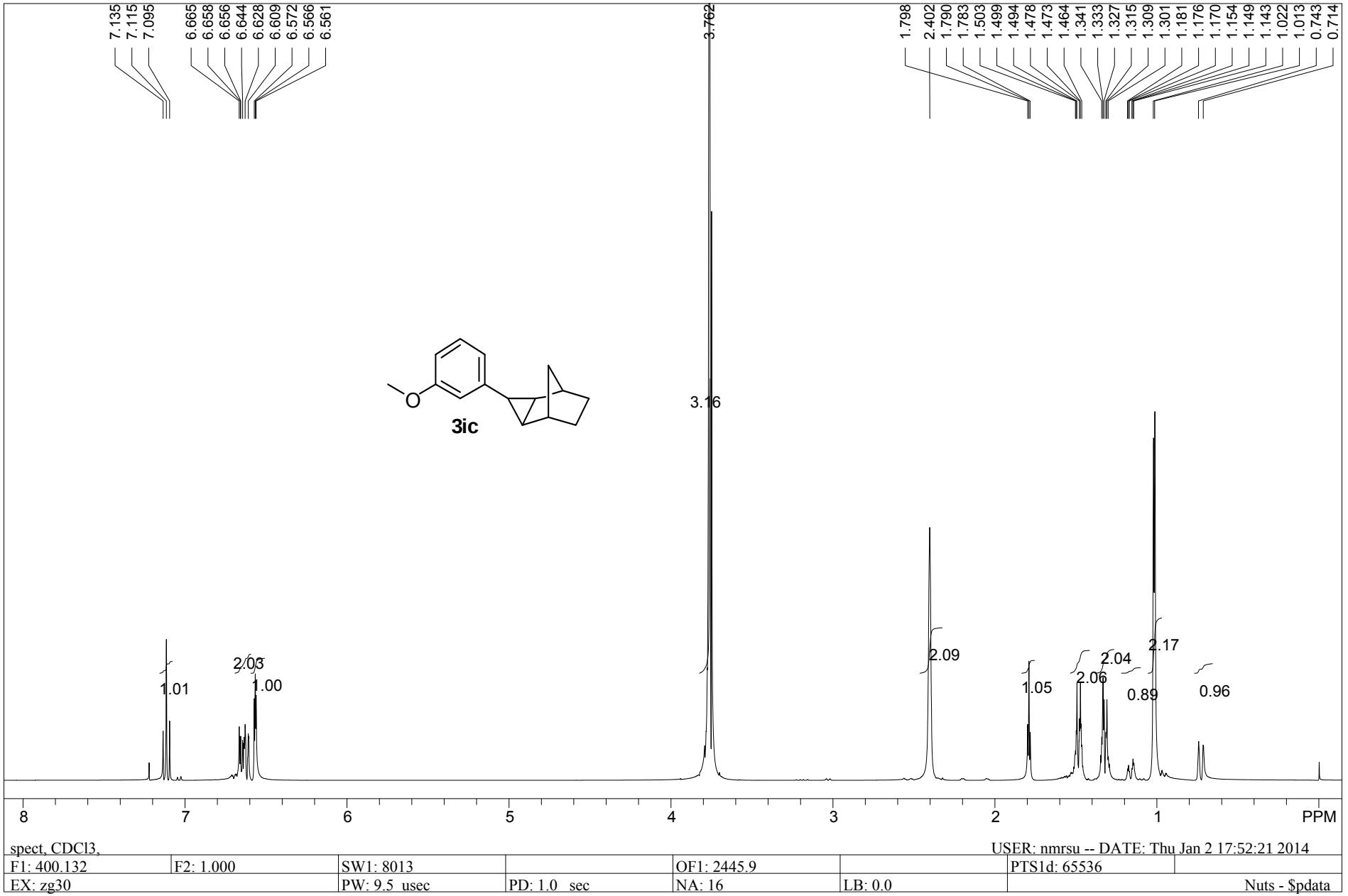

143.153
137.670
128.071
126.678
125.933
122.943
77.397
77.073
76.750
36.432
29.476
28.786
27.669
21.477
18.294
3cc
160
140
120
100
80
60
40
20
PPM
spect, CDCl3,
USER: nmrsu -- DATE: Sat May 18 16:44:32 2013
F1: 100.623
F2: 1.000
SW1: 24038
OF1: 10062.5
PTS1d: 32768
EX: zgdc30
PW: 9.5 usec
PD: 1.2 sec
NA: 512
LB: 0.0
Nuts - $pdata

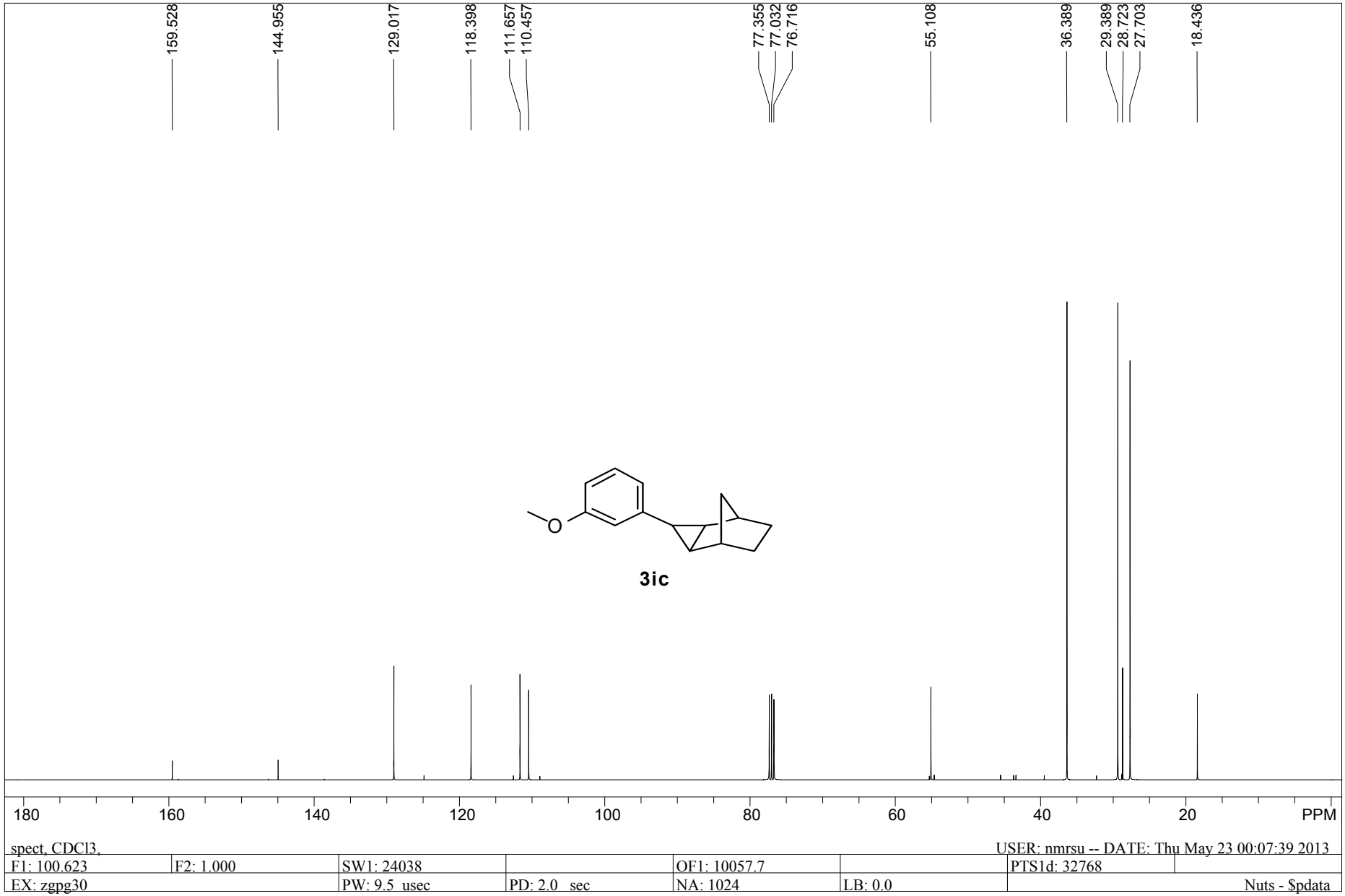

7.093
7.076
7.073
7.071
7.068
6.980
6.974
6.969
6.906
6.887
6.883
2.407
1.783
1.775
1.768
1.504
1.499
1.487
1.483
1.478
1.474
1.339
1.331
1.324
1.313
1.307
1.153
1.120
1.015
1.006
0.755
0.726
Cl
3gc
2.07
1.00
0.98
2.10
1.03
1.98
1.96
0.90
2.19
0.95
7
6
5
4
3
2
1
0PPM
spect, CDCl3,
USER: nmrsu -- DATE: Thu Jan 2 17:46:21 2014
F1: 400.132
F2: 1.000
SW1: 8013
OF1: 2450.6
PTS1d: 65536
EX: zg30
PW: 9.5 usec
PD: 1.0 sec
NA: 16
LB: 0.0
Nuts - $pdata

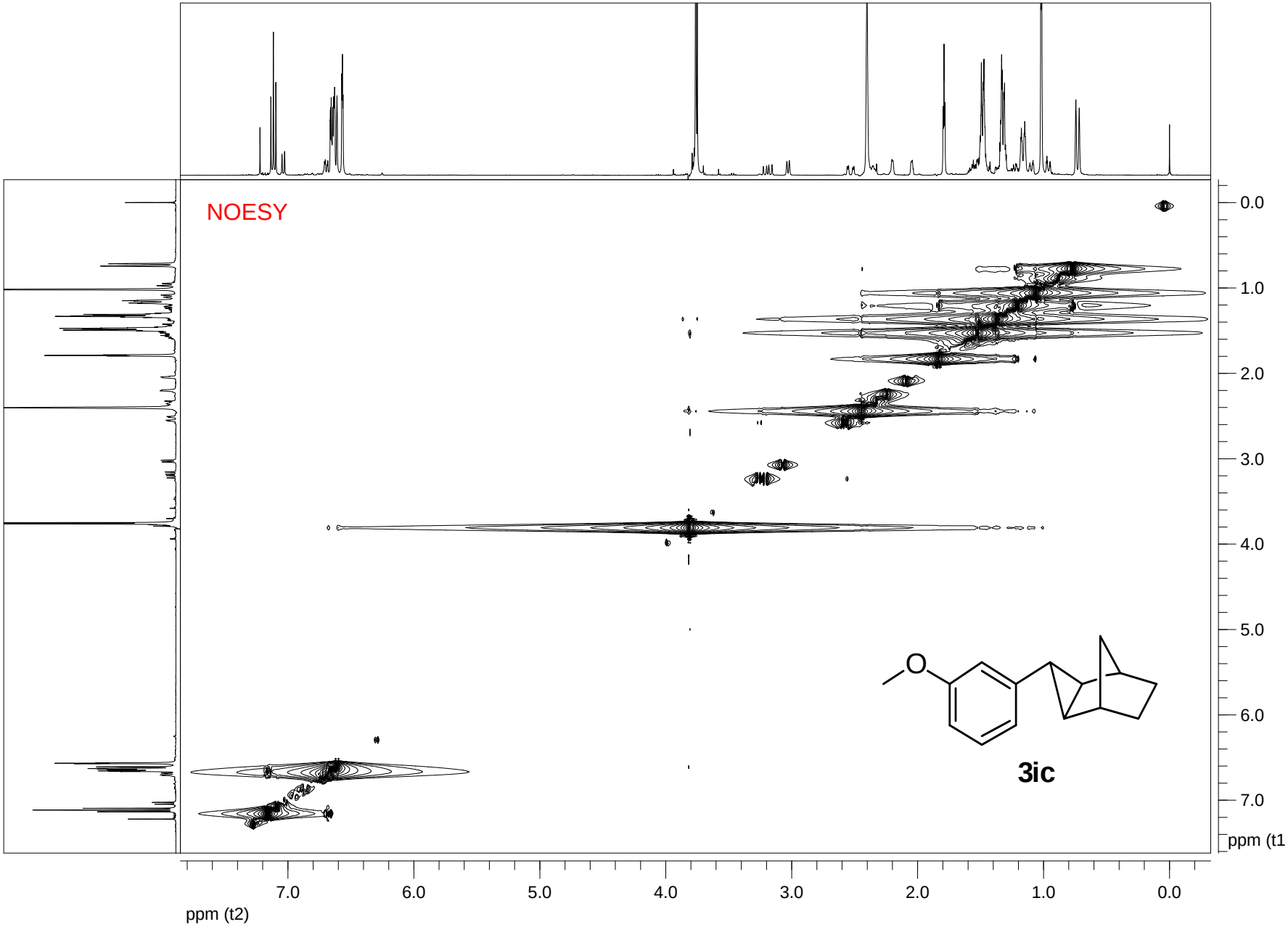


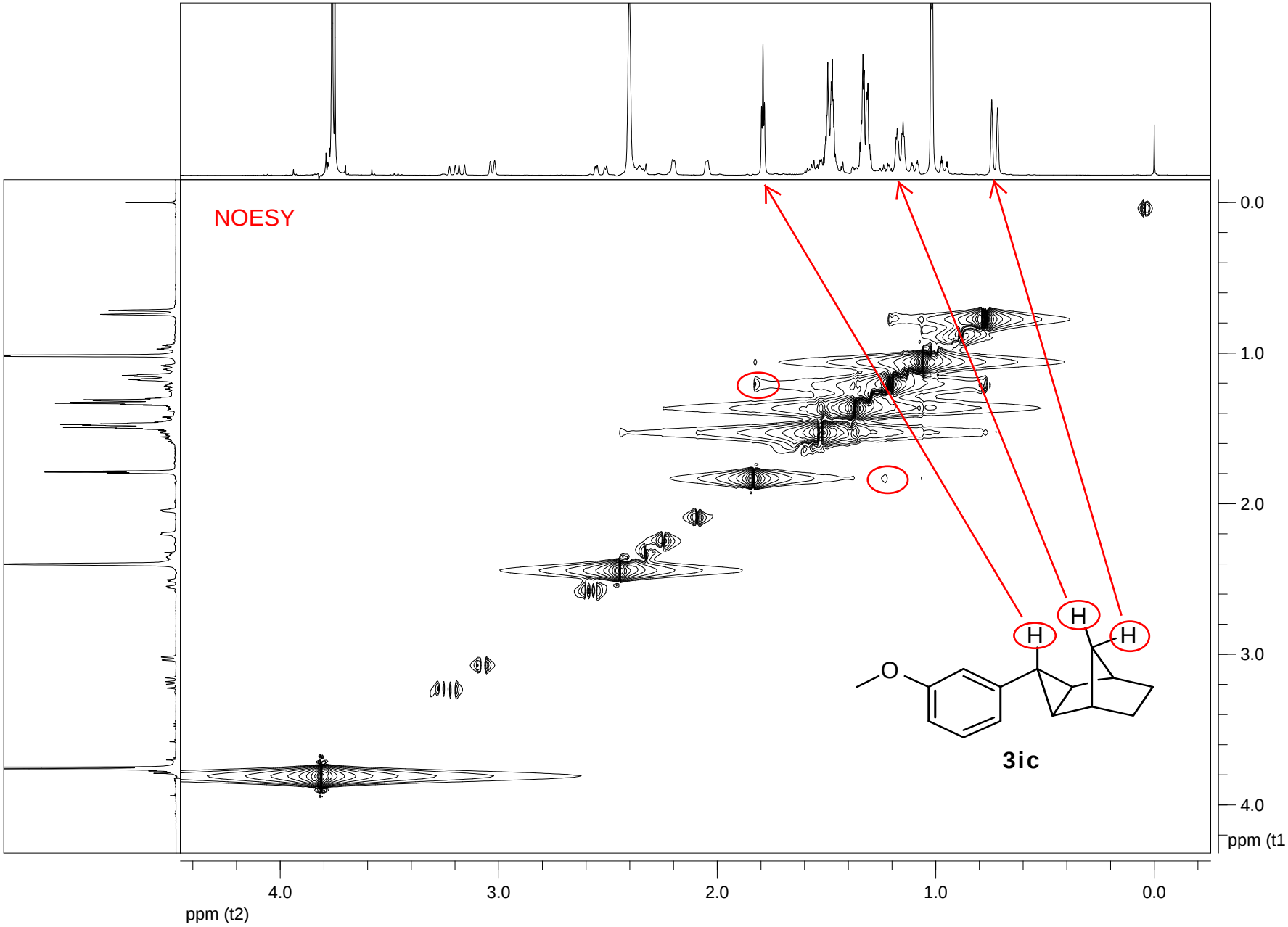
spect, CDCl3, USER: nmrsu -- DATE: Wed May 22 23:05:37 2013

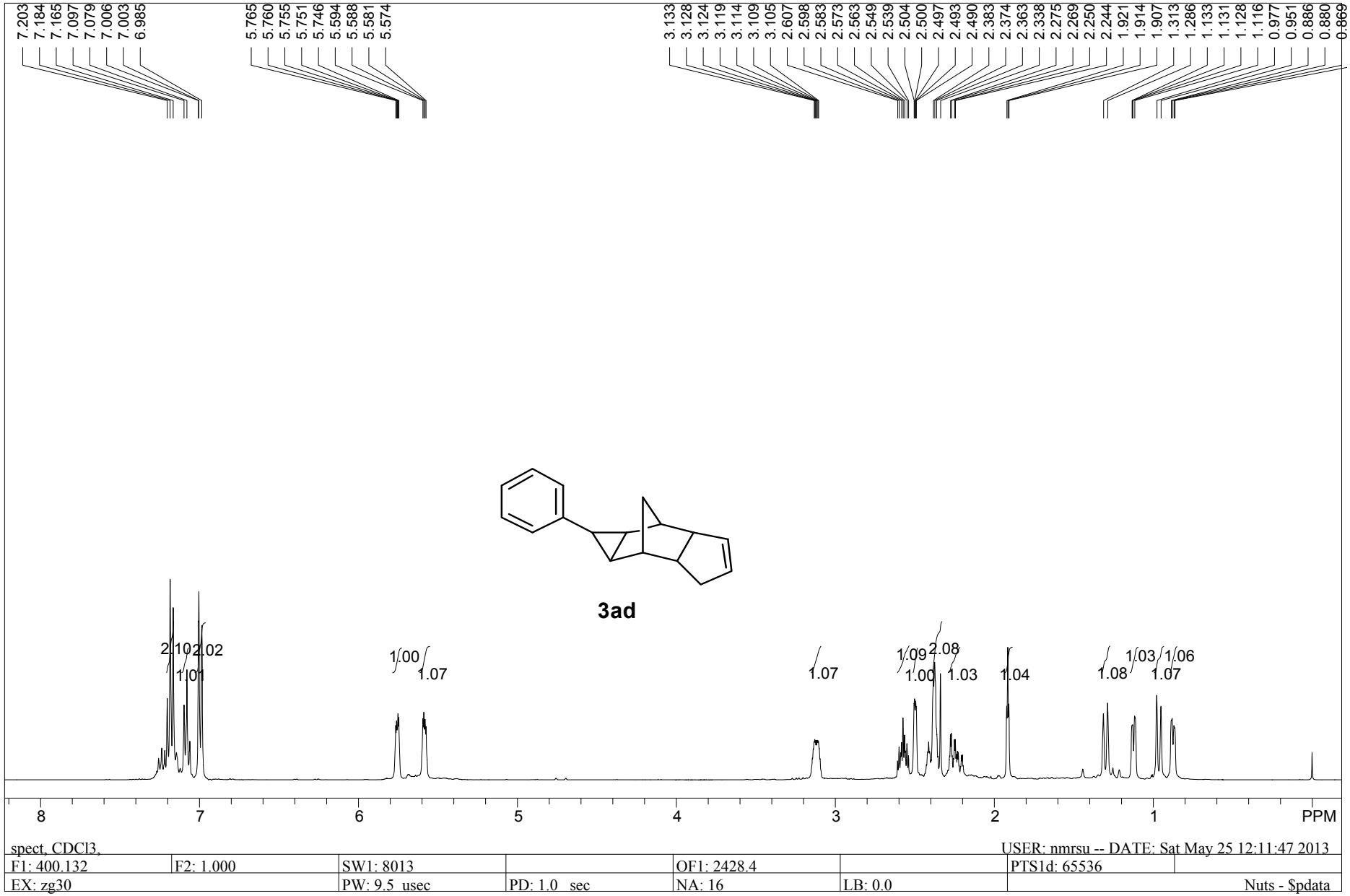
F1: 100.623	F2: 1.000	SW1: 24038		OF1: 10062.5		PTS1d: 32768	
EX: zgdc30		PW: 9.5 usec	PD: 1.2 sec	NA: 1024	LB: 0.0		Nuts - $pdata

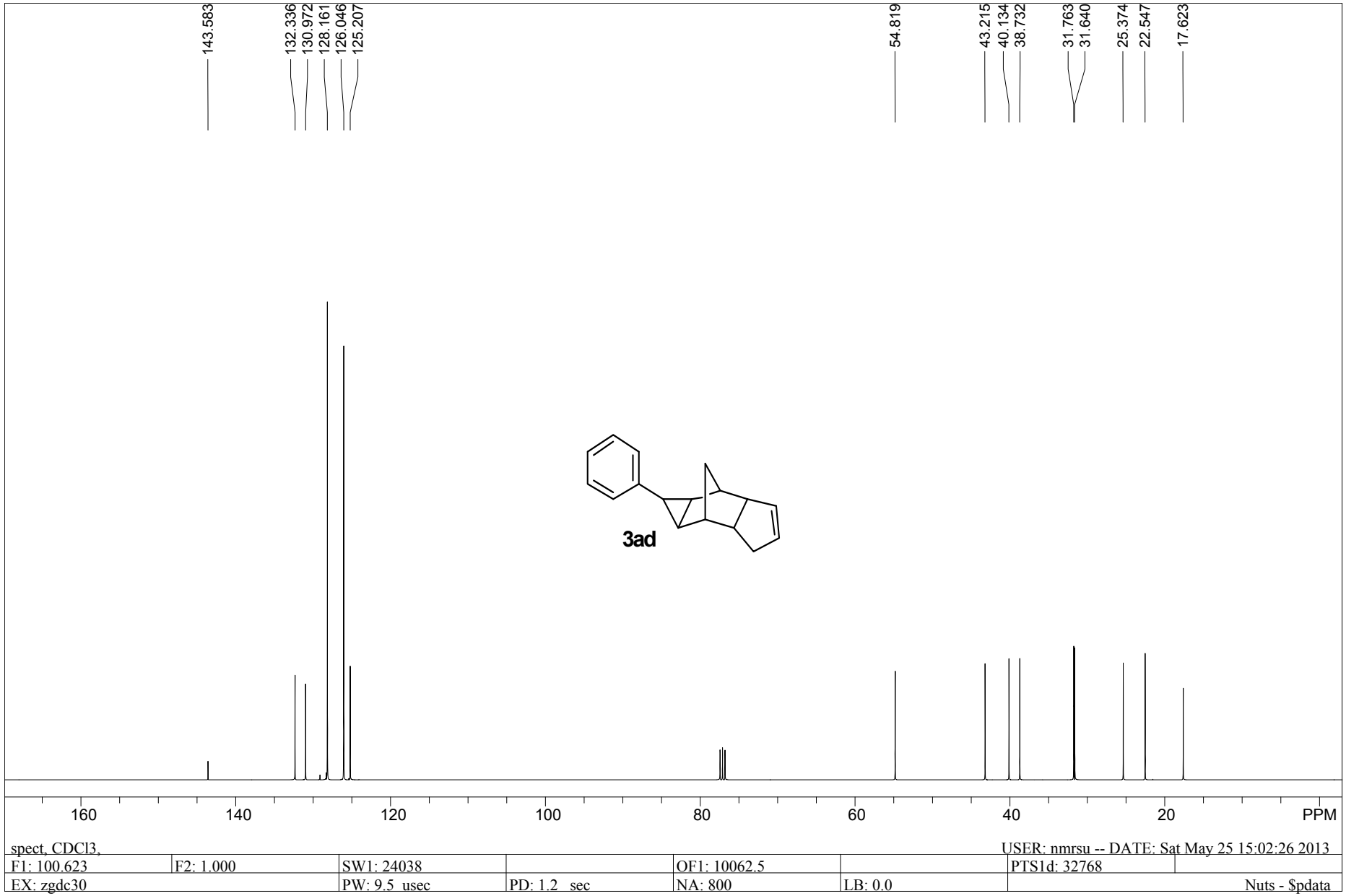

7.135
7.115
7.095
6.665
6.658
6.656
6.644
6.628
6.609
6.572
6.566
6.561
3.762
1.798
2.402
1.790
1.783
1.503
1.499
1.494
1.478
1.473
1.464
1.341
1.333
1.327
1.315
1.309
1.301
1.181
1.176
1.170
1.154
1.149
1.143
1.022
1.013
0.743
0.714
O
3ic
3.16
1.01
2.03
1.00
2.09
1.05
2.06
2.04
0.89
2.17
0.96
8
7
6
5
4
3
2
1
PPM
spect, CDCl3,
USER: nmrsu -- DATE: Thu Jan 2 17:52:21 2014
F1: 400.132
F2: 1.000
SW1: 8013
OF1: 2445.9
PTS1d: 65536
EX: zg30
PW: 9.5 usec
PD: 1.0 sec
NA: 16
LB: 0.0
Nuts - $pdata


159.528
144.955
129.017
118.398
111.657
110.457
77.355
77.032
76.716
55.108
36.389
29.389
28.723
27.703
18.436
O
3ic
180
160
140
120
100
80
60
40
20
PPM
spect, CDCl3,
USER: nmrsu -- DATE: Thu May 23 00:07:39 2013
F1: 100.623
F2: 1.000
SW1: 24038
OF1: 10057.7
PTS1d: 32768
EX: zgpg30
PW: 9.5 usec
PD: 2.0 sec
NA: 1024
LB: 0.0
Nuts - $pdata



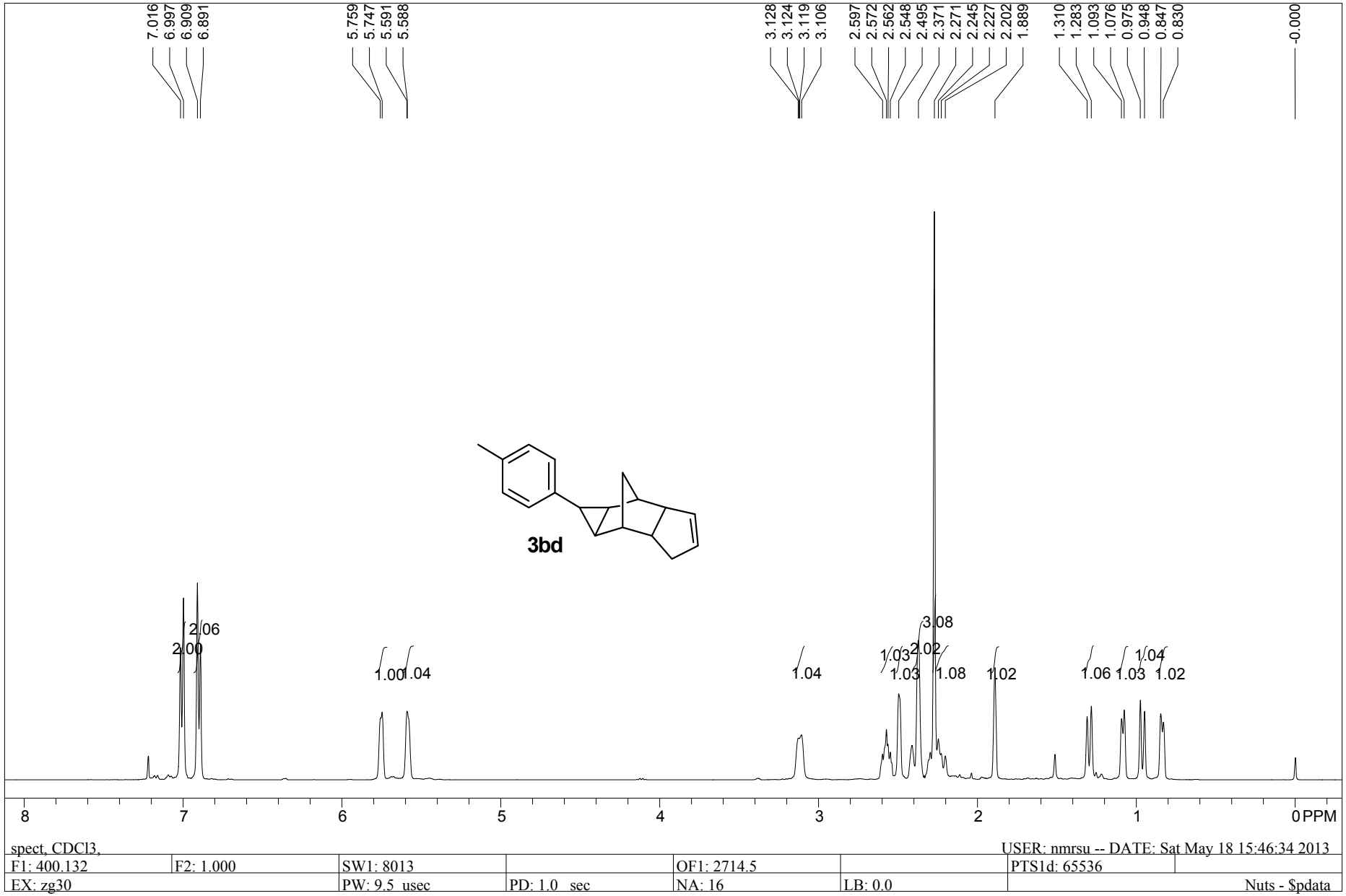


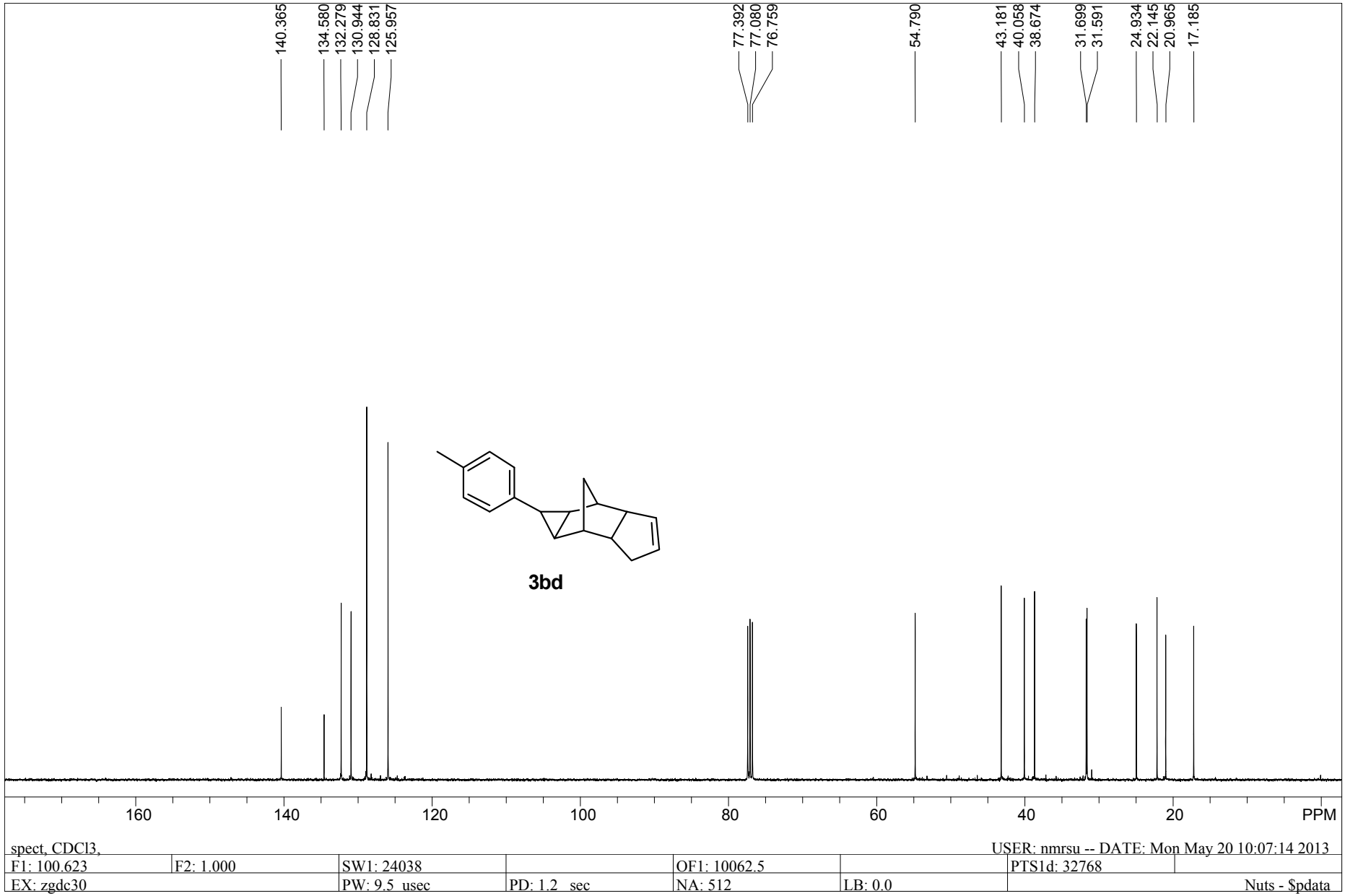

7.203
7.184
7.165
7.097
7.079
7.006
7.003
6.985
5.765
5.760
5.755
5.751
5.746
5.594
5.588
5.581
5.574
3.133
3.128
3.124
3.119
3.114
3.109
3.105
2.607
2.598
2.583
2.573
2.563
2.549
2.539
2.504
2.500
2.497
2.493
2.490
2.383
2.374
2.363
2.338
2.275
2.269
2.250
2.244
1.921
1.914
1.907
1.313
1.286
1.133
1.131
1.128
1.116
0.977
0.951
0.886
0.880
0.869
3ad
2.10
2.02
1.01
1.00
1.07
1.07
1.09
2.08
1.00
1.03
1.04
1.08
1.03
1.06
1.07
8
7
6
5
4
3
2
1
PPM
spect, CDCl3,
USER: nmrsu -- DATE: Sat May 25 12:11:47 2013
F1: 400.132
F2: 1.000
SW1: 8013
OF1: 2428.4
PTS1d: 65536
EX: zg30
PW: 9.5 usec
PD: 1.0 sec
NA: 16
LB: 0.0
Nuts - $pdata

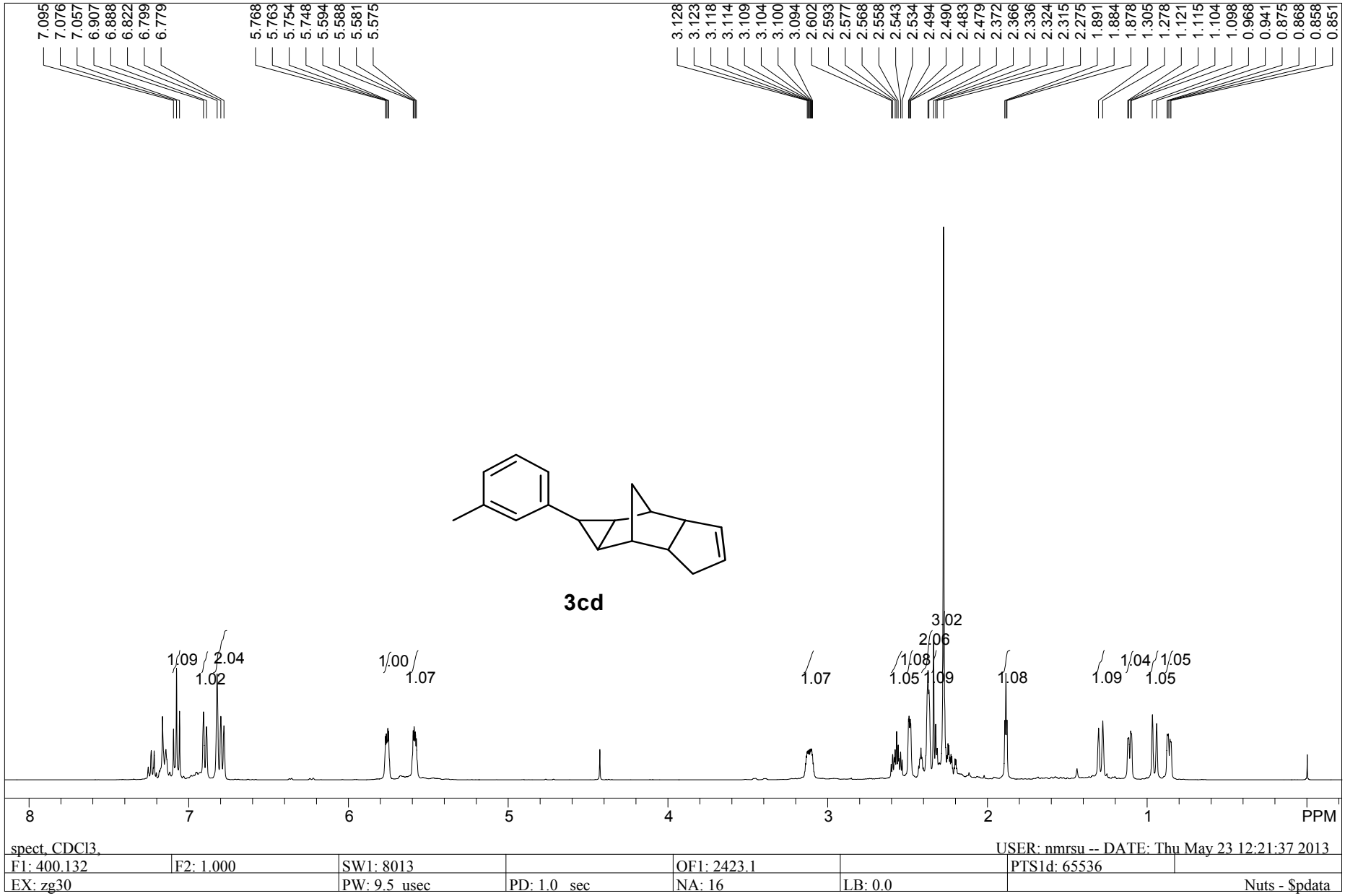


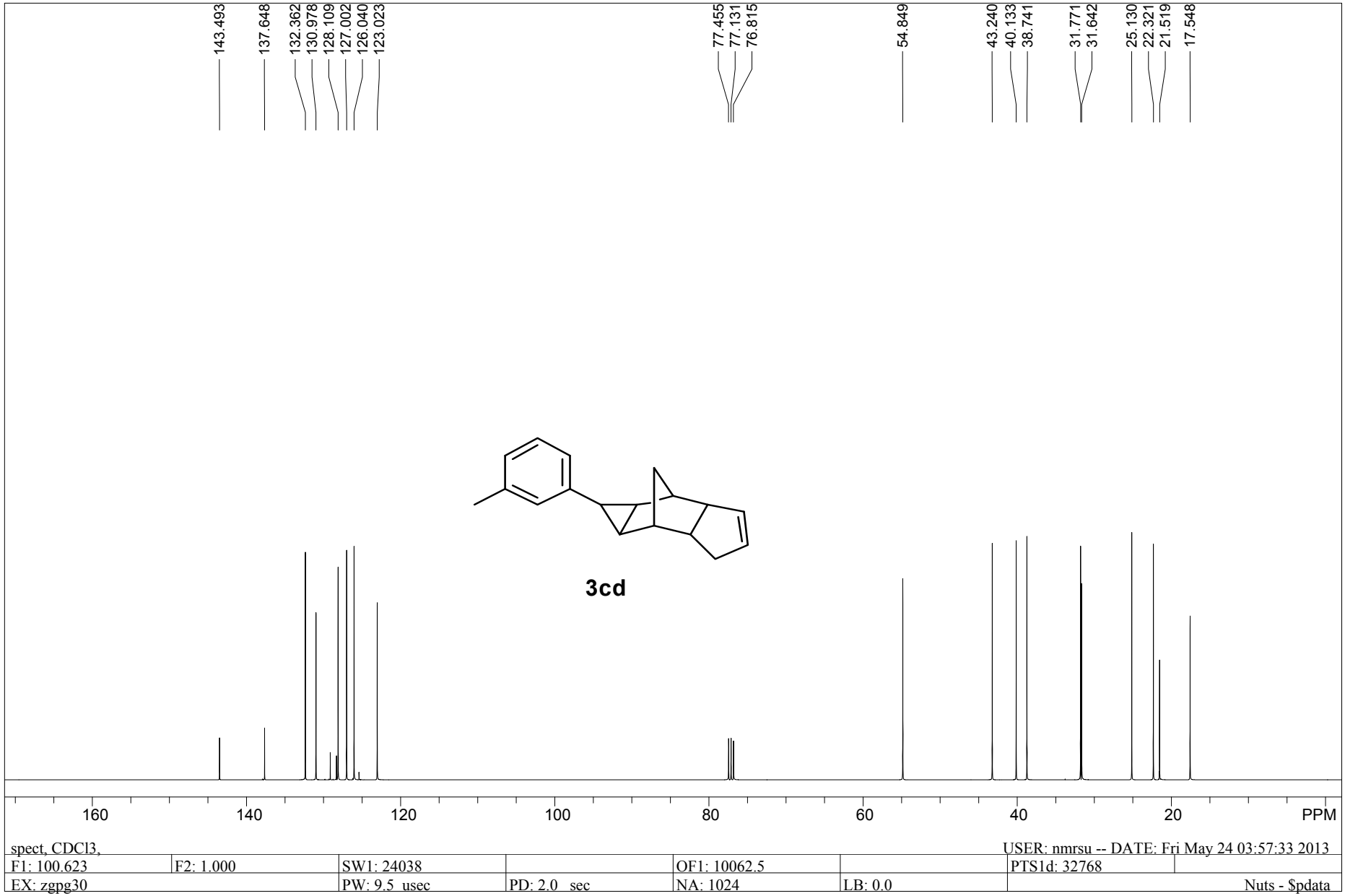
spect, CDCl3, USER: nmrsu -- DATE: Sat May 25 15:02:26 2013

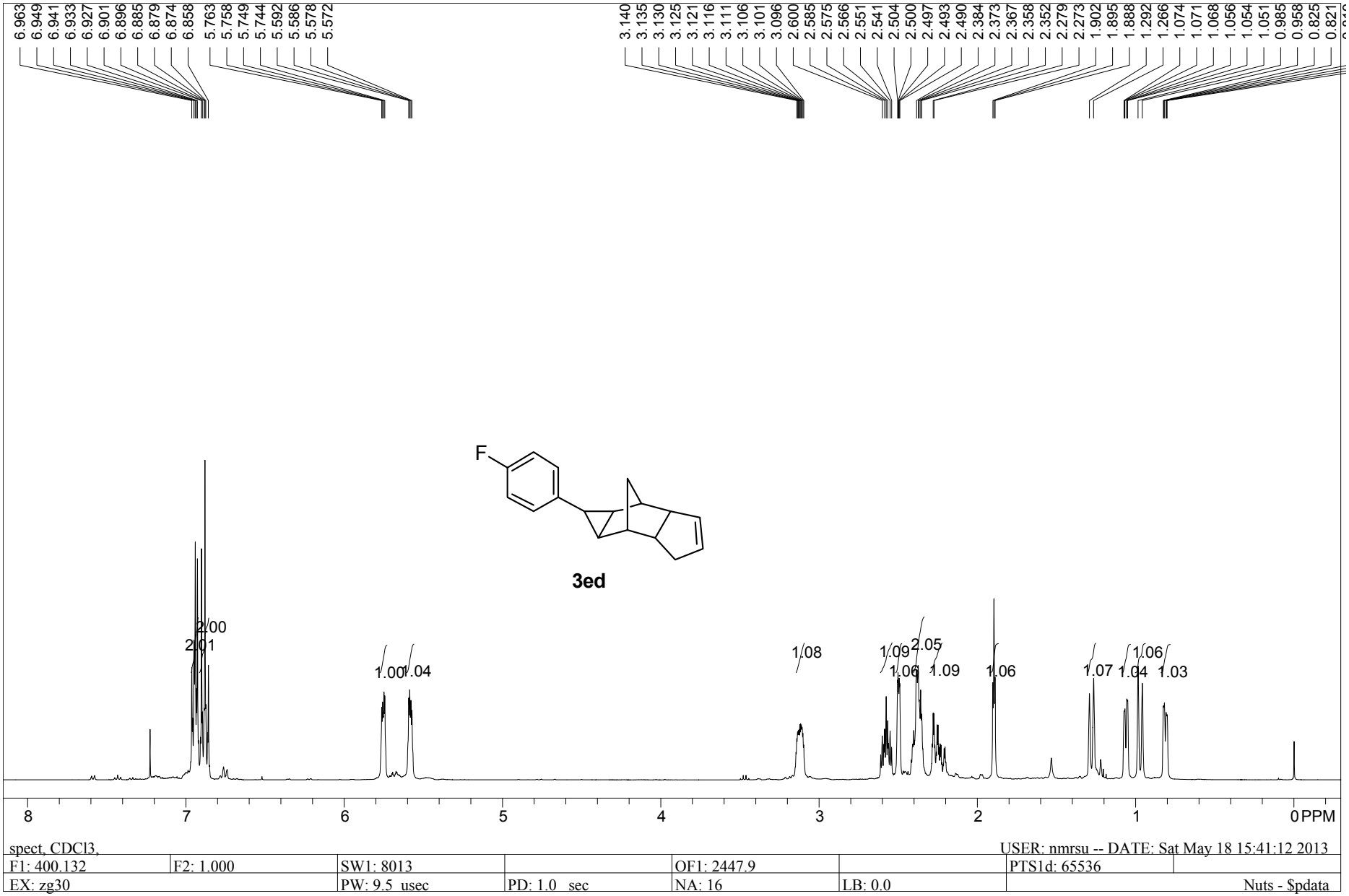
F1: 100.623	F2: 1.000	SW1: 24038		OF1: 10062.5		PTS1d: 32768	
EX: zgdc30		PW: 9.5 usec	PD: 1.2 sec	NA: 800	LB: 0.0		Nuts - $pdata

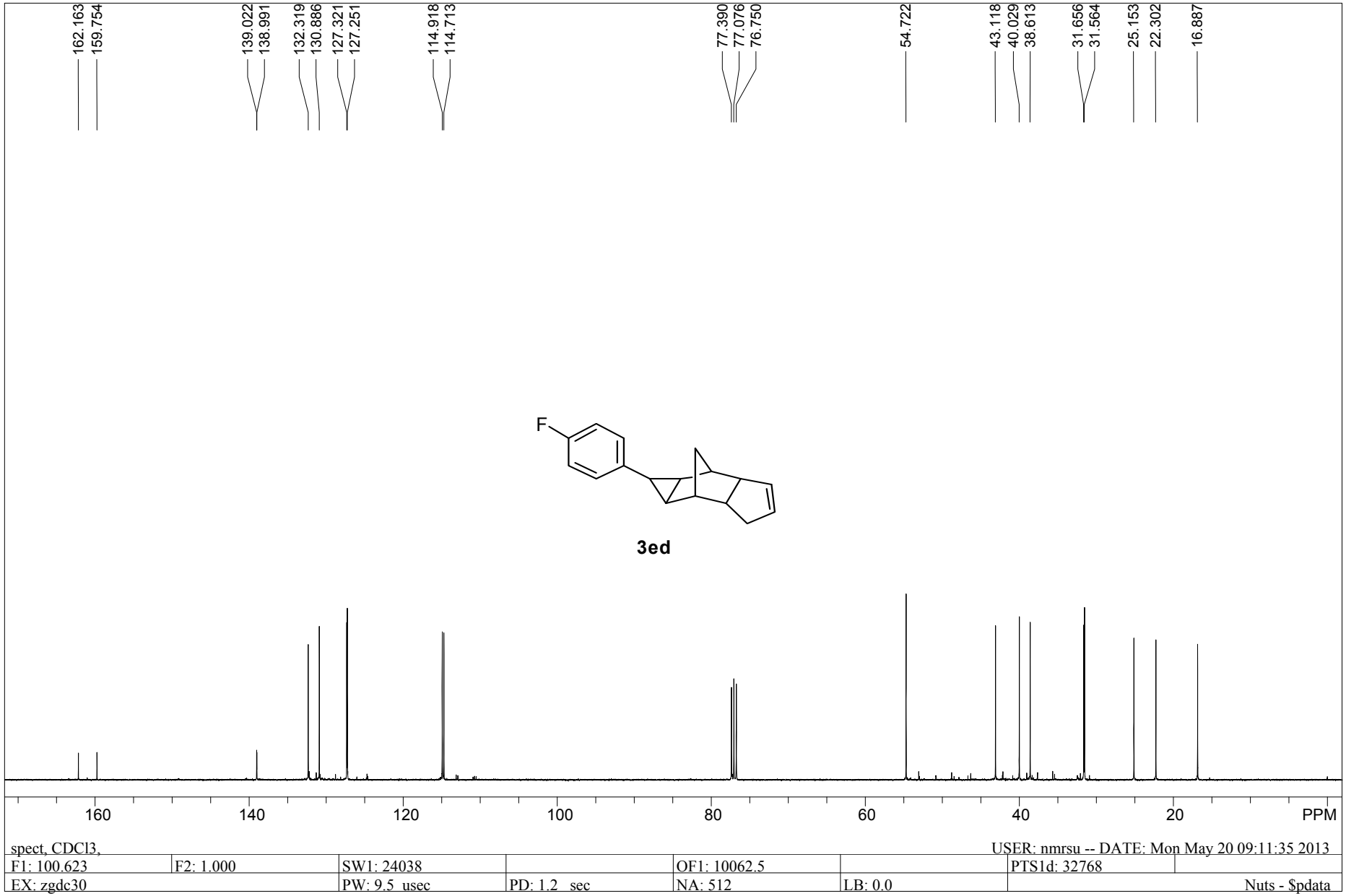

7.016
6.997
6.909
6.891
5.759
5.747
5.591
5.588
3.128
3.124
3.119
3.106
2.597
2.572
2.562
2.548
2.495
2.371
2.271
2.245
2.227
2.202
1.889
1.310
1.283
1.093
1.076
0.975
0.948
0.847
0.830
-0.000
3bd
2.06
2.00
1.00
1.04
1.04
3.08
1.03
2.02
1.03
1.08
1.02
1.06
1.04
1.03
1.02
8
7
6
5
4
3
2
1
0 PPM
spect, CDCl3,
USER: nmrsu -- DATE: Sat May 18 15:46:34 2013
F1: 400.132
F2: 1.000
SW1: 8013
OF1: 2714.5
PTS1d: 65536
EX: zg30
PW: 9.5 usec
PD: 1.0 sec
NA: 16
LB: 0.0
Nuts - $pdata


140.365
134.580
132.279
130.944
128.831
125.957
77.392
77.080
76.759
54.790
43.181
40.058
38.674
31.699
31.591
24.934
22.145
20.965
17.185
3bd
160
140
120
100
80
60
40
20
PPM
spect, CDCl3,
USER: nmrsu -- DATE: Mon May 20 10:07:14 2013
F1: 100.623
F2: 1.000
SW1: 24038
OF1: 10062.5
PTS1d: 32768
EX: zgdc30
PW: 9.5 usec
PD: 1.2 sec
NA: 512
LB: 0.0
Nuts - $pdata


7.095
7.076
7.057
6.907
6.888
6.822
6.799
6.779
5.768
5.763
5.754
5.748
5.594
5.588
5.581
5.575
3.128
3.123
3.118
3.114
3.109
3.104
3.100
3.094
2.602
2.593
2.577
2.568
2.558
2.543
2.534
2.494
2.490
2.483
2.479
2.372
2.366
2.336
2.324
2.315
2.275
1.891
1.884
1.878
1.305
1.278
1.121
1.115
1.104
1.098
0.968
0.941
0.875
0.868
0.858
0.851
3cd
1.09
2.04
1.02
1.00
1.07
1.07
3.02
2.06
1.08
1.05
1.09
1.08
1.09
1.04
1.05
1.05
8
7
6
5
4
3
2
1
PPM
spect, CDCl3,
USER: nmrsu -- DATE: Thu May 23 12:21:37 2013
F1: 400.132
F2: 1.000
SW1: 8013
OF1: 2423.1
PTS1d: 65536
EX: zg30
PW: 9.5 usec
PD: 1.0 sec
NA: 16
LB: 0.0
Nuts - $pdata


143.493
137.648
132.362
130.978
128.109
127.002
126.040
123.023
77.455
77.131
76.815
54.849
43.240
40.133
38.741
31.771
31.642
25.130
22.321
21.519
17.548
3cd
160
140
120
100
80
60
40
20
PPM
spect, CDCl3,
USER: nmrsu -- DATE: Fri May 24 03:57:33 2013
F1: 100.623
F2: 1.000
SW1: 24038
OF1: 10062.5
PTS1d: 32768
EX: zgpg30
PW: 9.5 usec
PD: 2.0 sec
NA: 1024
LB: 0.0
Nuts - $pdata

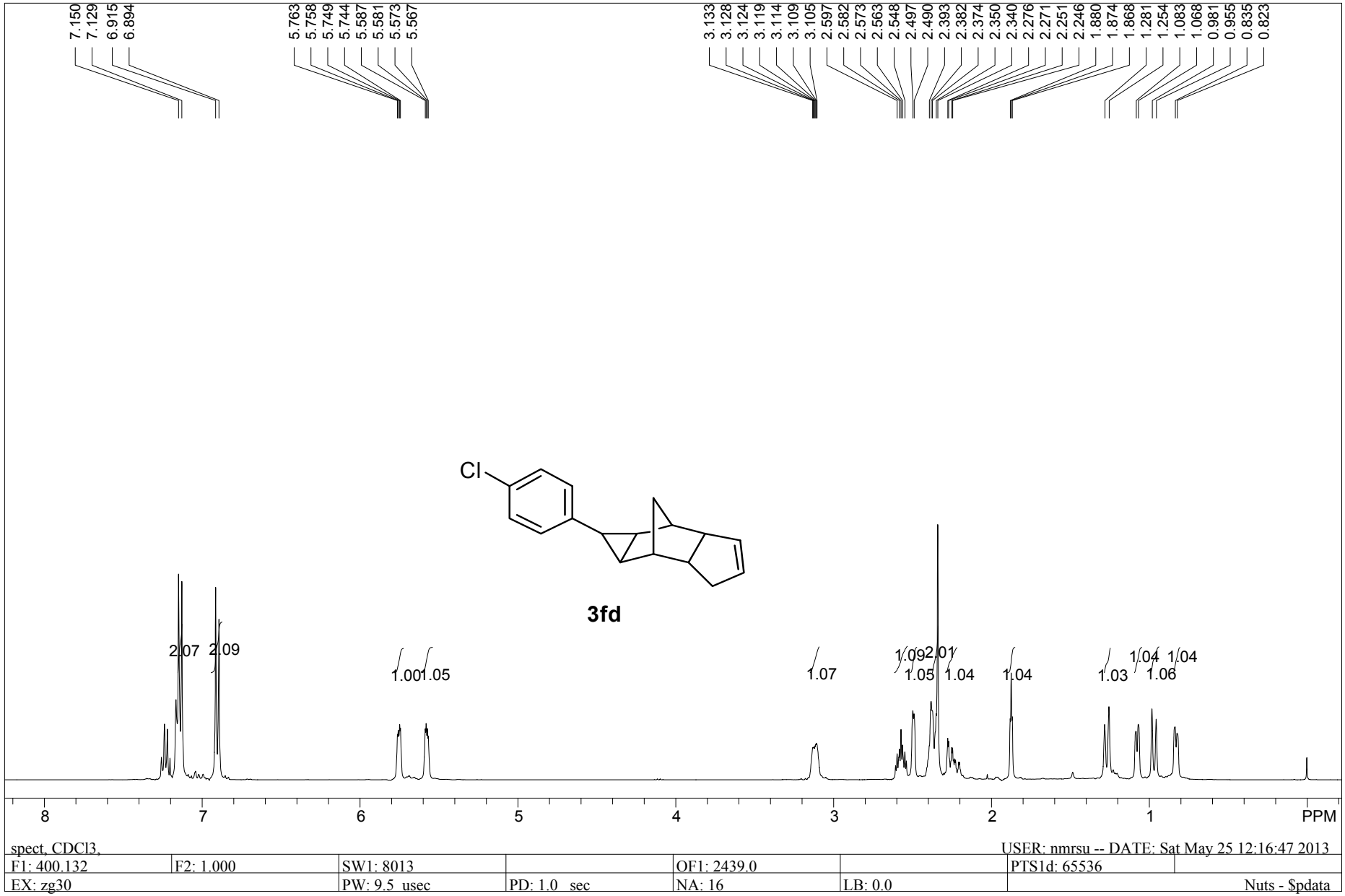

6.963
6.949
6.941
6.933
6.927
6.901
6.896
6.885
6.879
6.874
6.858
5.763
5.758
5.749
5.744
5.592
5.586
5.578
5.572
3.140
3.135
3.130
3.125
3.121
3.116
3.111
3.106
3.101
3.096
2.600
2.585
2.575
2.566
2.551
2.541
2.504
2.500
2.497
2.493
2.490
2.384
2.373
2.367
2.358
2.352
2.279
2.273
1.902
1.895
1.888
1.292
1.266
1.074
1.071
1.068
1.056
1.054
1.051
0.985
0.958
0.825
0.821
F
3ed
2.00
2.01
1.00
1.04
1.08
1.09
2.05
1.06
1.09
1.06
1.07
1.04
1.06
1.03
8
7
6
5
4
3
2
1
0 PPM
spect, CDCl3,
USER: nmrsu -- DATE: Sat May 18 15:41:12 2013
F1: 400.132
F2: 1.000
SW1: 8013
OF1: 2447.9
PTS1d: 65536
EX: zg30
PW: 9.5 usec
PD: 1.0 sec
NA: 16
LB: 0.0
Nuts - $pdata

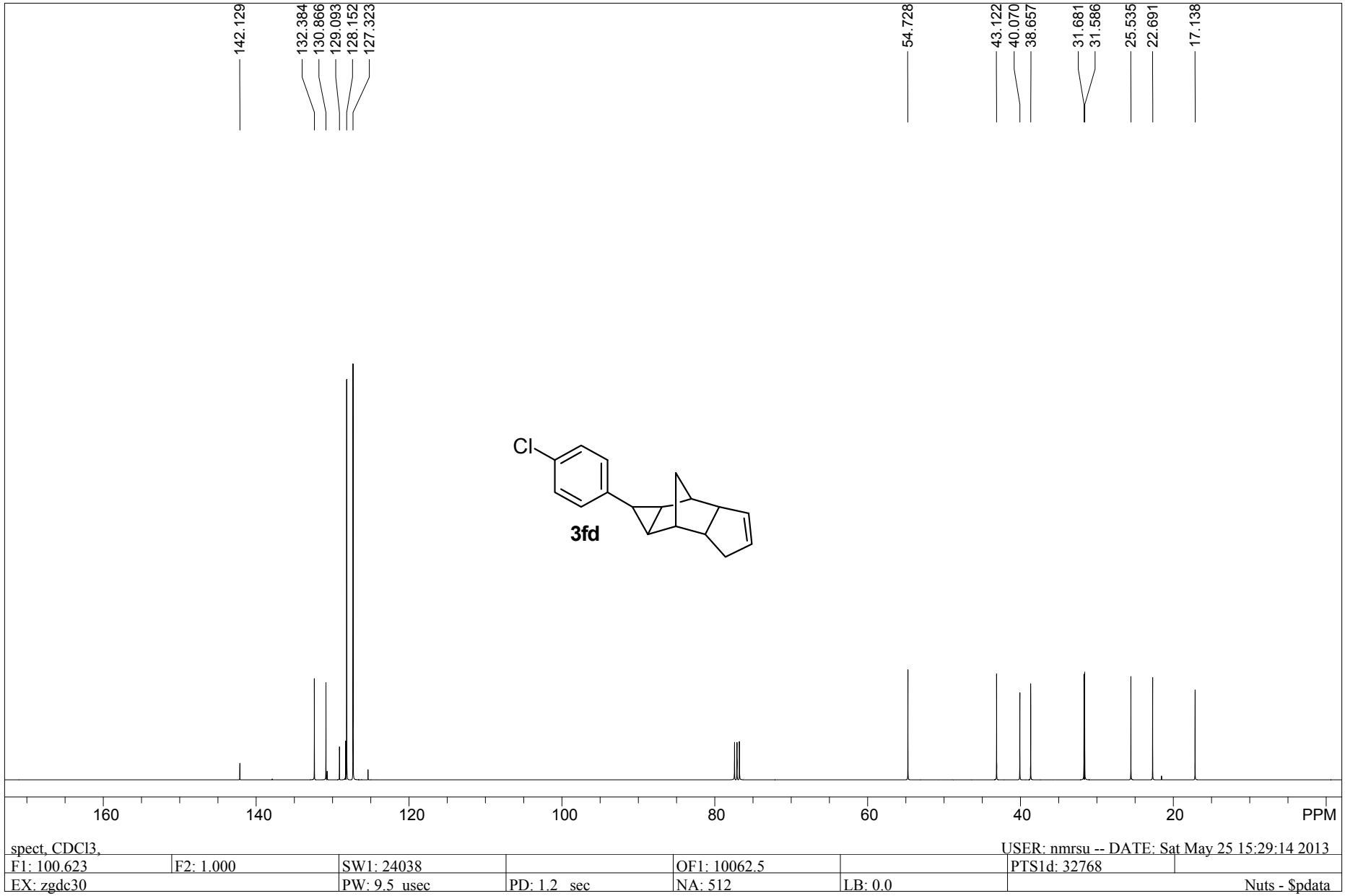


3ed

spect, CDCl3, USER: nmrsu -- DATE: Mon May 20 09:11:35 2013

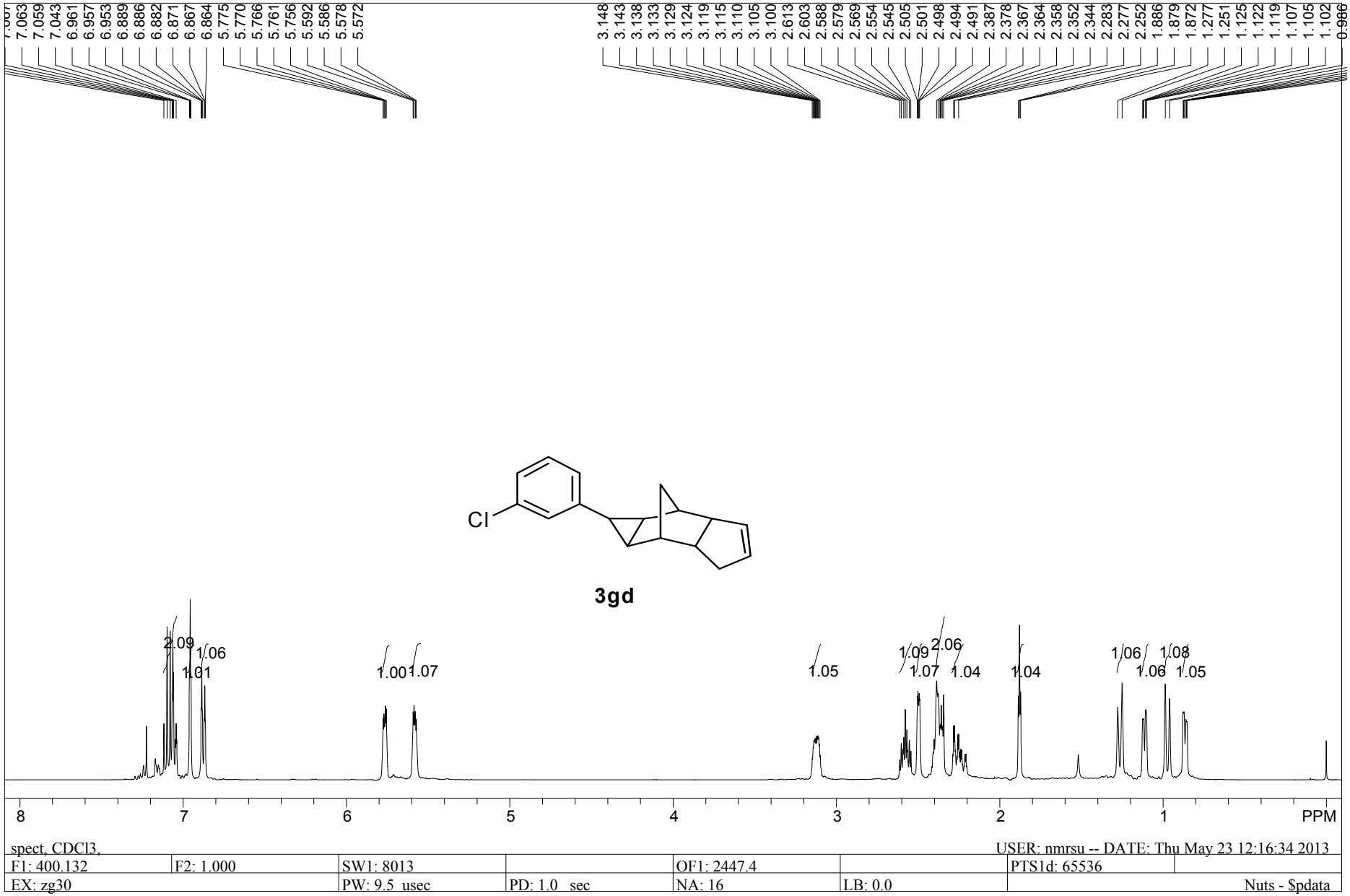
F1: 100.623	F2: 1.000	SW1: 24038		OF1: 10062.5		PTS1d: 32768	
EX: zgdc30		PW: 9.5 usec	PD: 1.2 sec	NA: 512	LB: 0.0		Nuts - $pdata

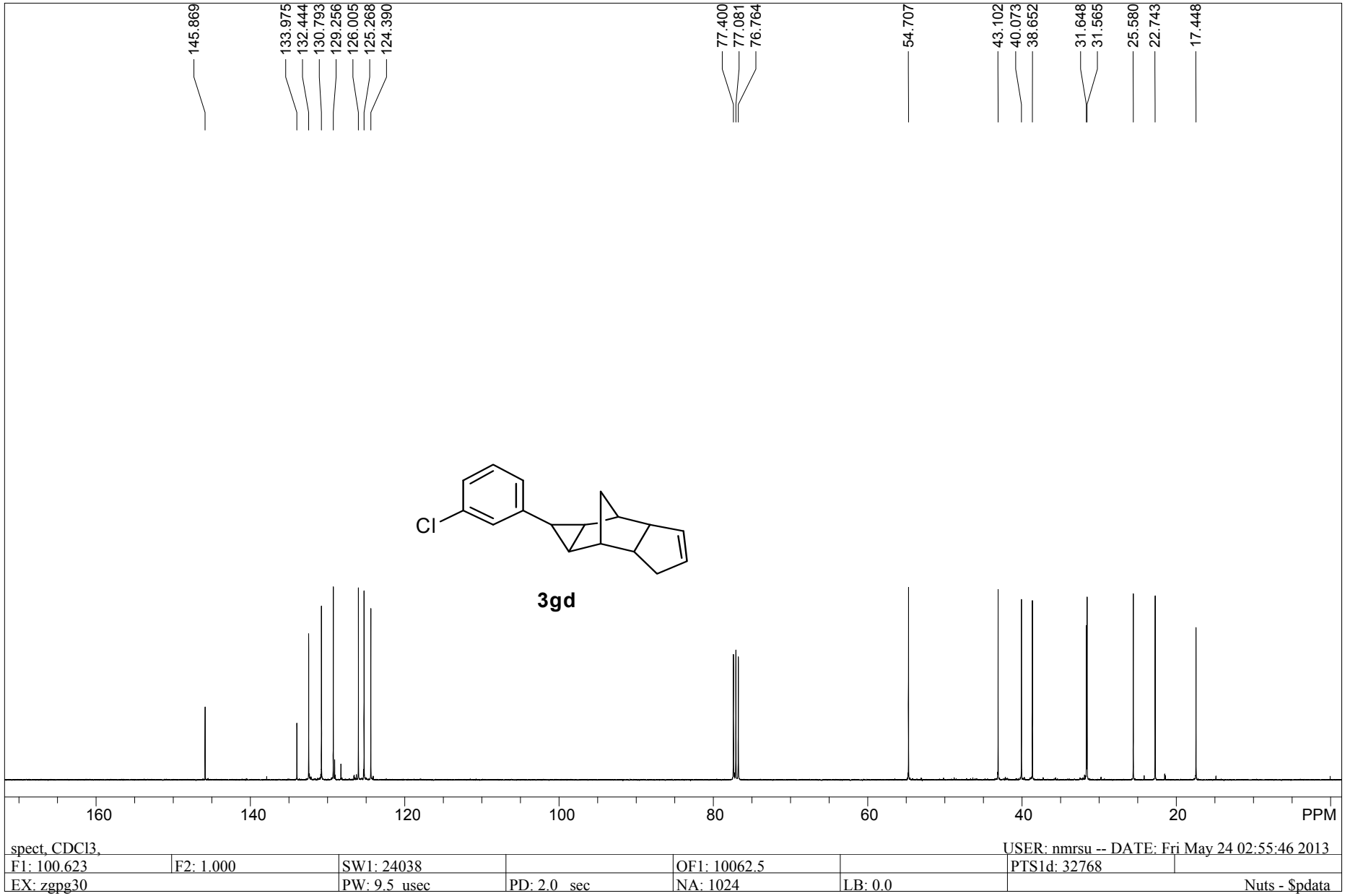

7.150
7.129
6.915
6.894
5.763
5.758
5.749
5.744
5.587
5.581
5.573
5.567
3.133
3.128
3.124
3.119
3.114
3.109
3.105
2.597
2.582
2.573
2.563
2.548
2.497
2.490
2.393
2.382
2.374
2.350
2.340
2.276
2.271
2.251
2.246
1.880
1.874
1.868
1.281
1.254
1.083
1.068
0.981
0.955
0.835
0.823
Cl
3fd
2.07
2.09
1.00
1.05
1.07
1.09
2.01
1.05
1.04
1.04
1.03
1.04
1.04
1.06
8
7
6
5
4
3
2
1
PPM
spect, CDCl3,
USER: nmrsu -- DATE: Sat May 25 12:16:47 2013
F1: 400.132
F2: 1.000
SW1: 8013
OF1: 2439.0
PTS1d: 65536
EX: zg30
PW: 9.5 usec
PD: 1.0 sec
NA: 16
LB: 0.0
Nuts - $pdata

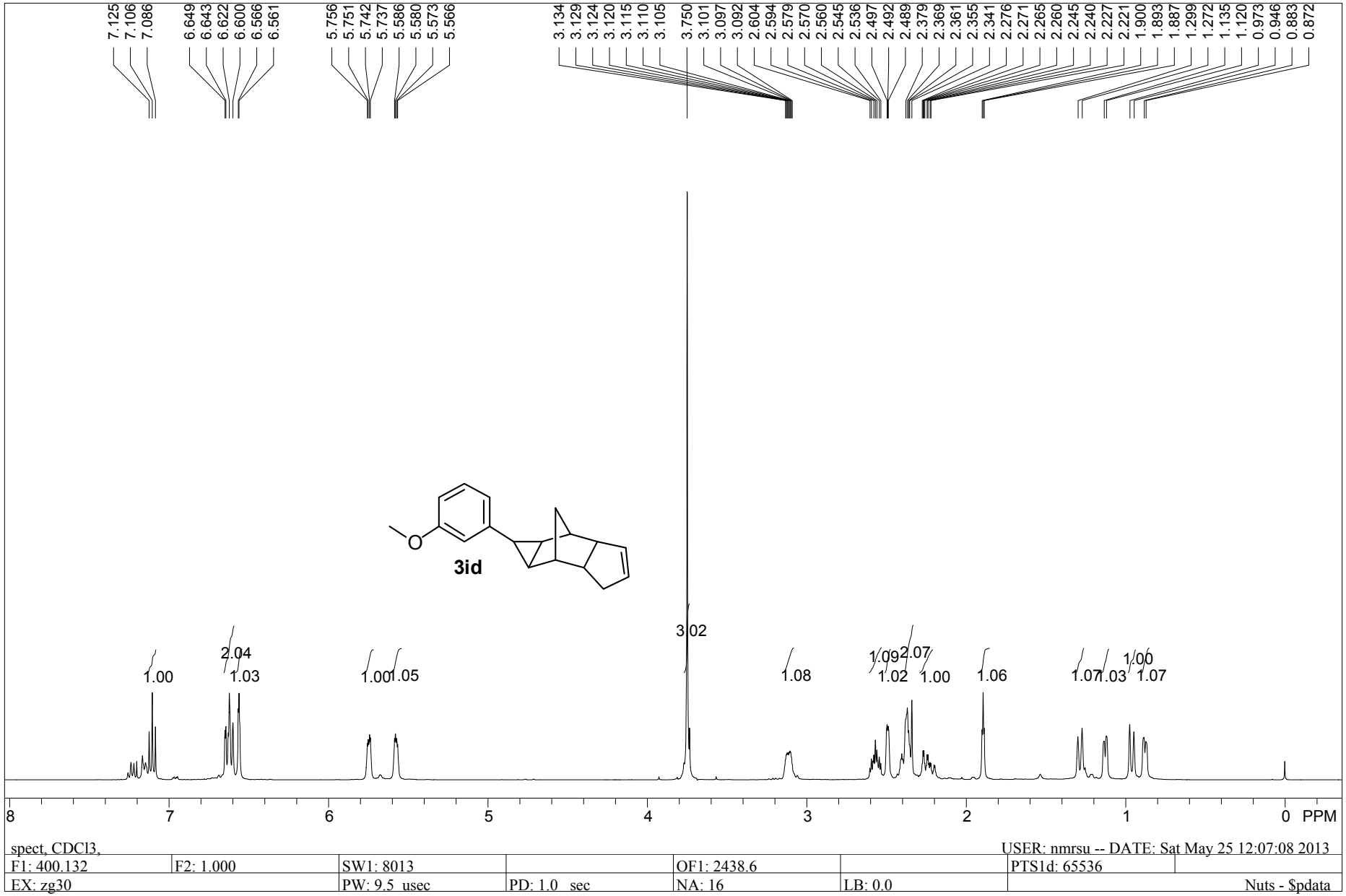


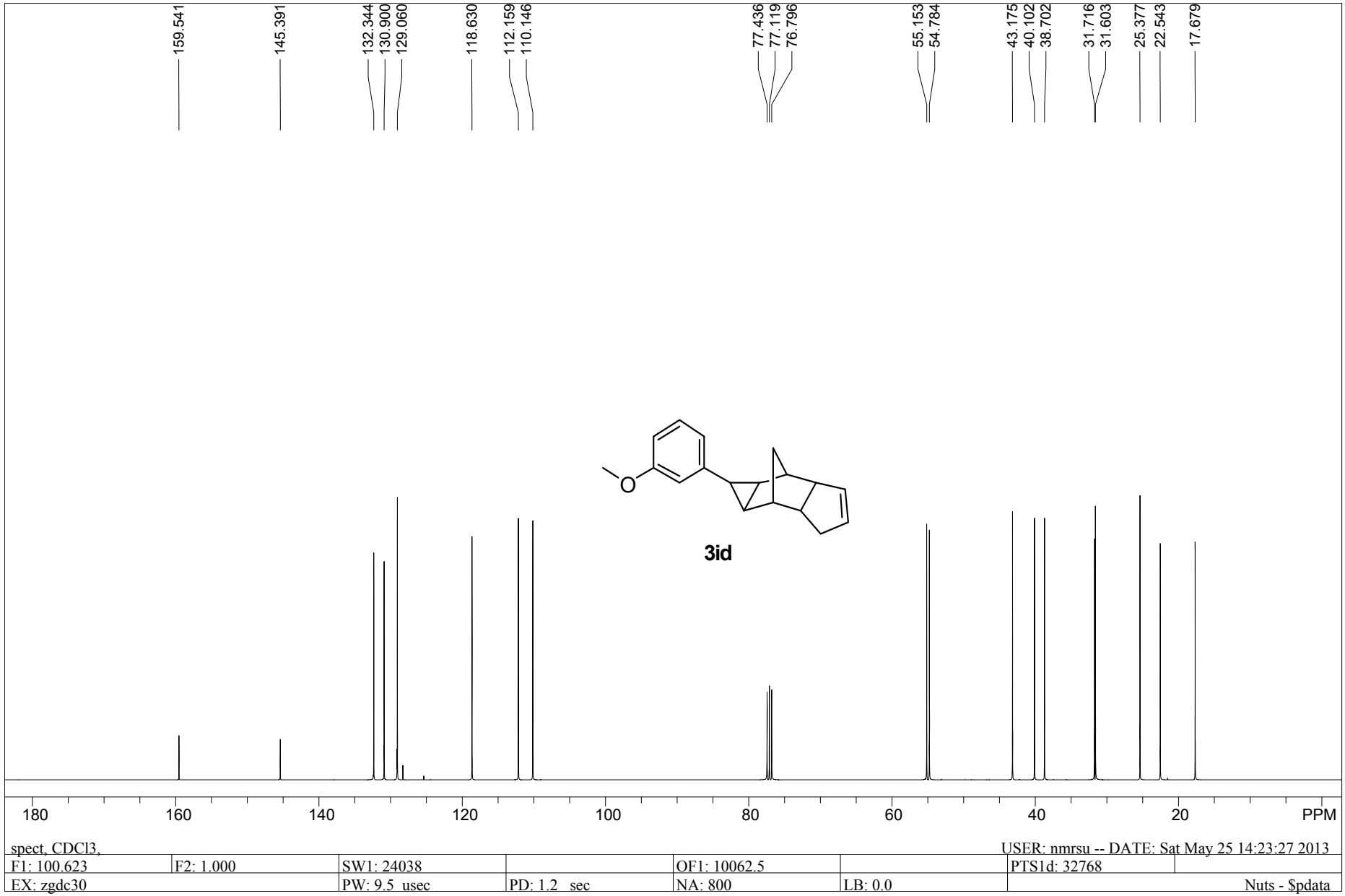
spect, CDCl3, USER: nmrsu -- DATE: Sat May 25 15:29:14 2013

F1: 100.623	F2: 1.000	SW1: 24038		OF1: 10062.5		PTS1d: 32768	
EX: zgdc30		PW: 9.5 usec	PD: 1.2 sec	NA: 512	LB: 0.0		Nuts - $pdata


7.063
7.059
7.043
6.961
6.957
6.953
6.889
6.886
6.882
6.871
6.867
6.864
5.775
5.770
5.766
5.761
5.756
5.592
5.586
5.578
5.572
3.148
3.143
3.138
3.133
3.129
3.124
3.119
3.115
3.110
3.105
3.100
2.613
2.603
2.588
2.579
2.569
2.554
2.545
2.505
2.501
2.498
2.494
2.491
2.387
2.378
2.367
2.364
2.358
2.352
2.344
2.283
2.277
2.252
1.886
1.879
1.872
1.277
1.251
1.125
1.122
1.119
1.107
1.105
1.102
0.986
Cl
3gd
2.09
1.06
1.01
1.00
1.07
1.05
1.09
2.06
1.07
1.04
1.04
1.06
1.08
1.06
1.05
8
7
6
5
4
3
2
1
PPM
spect, CDCl3,
USER: nmrsu -- DATE: Thu May 23 12:16:34 2013
F1: 400.132
F2: 1.000
SW1: 8013
OF1: 2447.4
PTS1d: 65536
EX: zg30
PW: 9.5 usec
PD: 1.0 sec
NA: 16
LB: 0.0
Nuts - $pdata


145.869
133.975
132.444
130.793
129.256
126.005
125.268
124.390
77.400
77.081
76.764
54.707
43.102
40.073
38.652
31.648
31.565
25.580
22.743
17.448
Cl
3gd
160
140
120
100
80
60
40
20
PPM
spect, CDCl3,
USER: nmrsu -- DATE: Fri May 24 02:55:46 2013
F1: 100.623
F2: 1.000
SW1: 24038
OF1: 10062.5
PTS1d: 32768
EX: zgpg30
PW: 9.5 usec
PD: 2.0 sec
NA: 1024
LB: 0.0
Nuts - $pdata


7.125
7.106
7.086
6.649
6.643
6.622
6.600
6.566
6.561
5.756
5.751
5.742
5.737
5.586
5.580
5.573
5.566
3.134
3.129
3.124
3.120
3.115
3.110
3.105
3.750
3.101
3.097
3.092
2.604
2.594
2.579
2.570
2.560
2.545
2.536
2.497
2.492
2.489
2.379
2.369
2.361
2.355
2.341
2.276
2.271
2.265
2.260
2.245
2.240
2.227
2.221
1.900
1.893
1.887
1.299
1.272
1.135
1.120
0.973
0.946
0.883
0.872
O
3id
1.00
2.04
1.03
1.00
1.05
3.02
1.08
1.09
2.07
1.02
1.00
1.06
1.07
1.03
1.00
1.07
8
7
6
5
4
3
2
1
0
PPM
spect, CDCl3,
USER: nmrsu -- DATE: Sat May 25 12:07:08 2013
F1: 400.132
F2: 1.000
SW1: 8013
OF1: 2438.6
PTS1d: 65536
EX: zg30
PW: 9.5 usec
PD: 1.0 sec
NA: 16
LB: 0.0
Nuts - $pdata



spect, CDCl3, USER: nmrsu -- DATE: Sat May 25 14:23:27 2013

F1: 100.623	F2: 1.000	SW1: 24038		OF1: 10062.5		PTS1d: 32768	
EX: zgdc30		PW: 9.5 usec	PD: 1.2 sec	NA: 800	LB: 0.0		Nuts - $pdata