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***Supporting information***

# Palladacycle-Catalyzed Cascade Reaction of Bicyclic Alkenes with Alkynyl Imines: Synthesis of Polycyclic *5H*-Benzo[*b*]azepines

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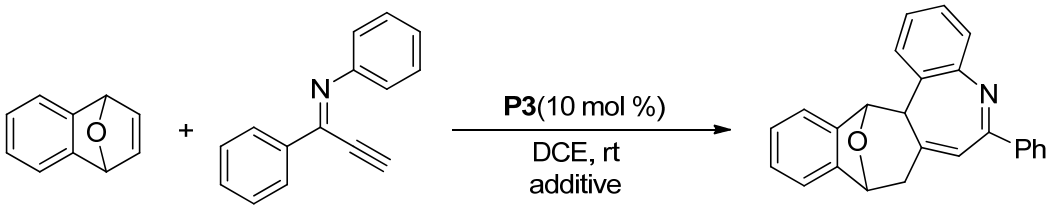
## 1. General Methods

Commercially available reagents were used without further purification. Solvents were purified prior to use according to the standard methods. Unless otherwise noted, all reactions were carried out under an atmosphere of argon and flame-dried glassware with standard vacuum-line techniques. Column chromatography was carried out on silica gel (300–400 mesh) using a forced flow of eluent.

NMR spectra are recorded at room temperature on 400 MHz Varian-400 、 Aglient-400 or 300 MHz Bruker AM-300 NMR spectrometers. The chemical shifts for $^1$H NMR are reported in ppm from tetramethylsilane (TMS) with the solvent resonance as the internal standard (7.26 ppm for $CHCl_3$). Data are reported as follows: chemical shift, integration, coupling constants (Hz), and, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, sep = septet, bs = broad singlet, m = multiplet). Chemical shifts are reported in ppm from tetramethylsilane with the solvent resonance as the internal standard ($CDCl_3$: 77.16 ppm). HRMS data were obtained on Bruker APEXIII mass spectrometer and MS data were performed on HP 5989A mass spectrometer with or without internal standard. Melting point was measured on XT-4 micro-melting point apparatus.

## 2. Evaluation of acid additive for the reaction of oxabicyclic alkene 1a with alkynyl imine 2a[a]



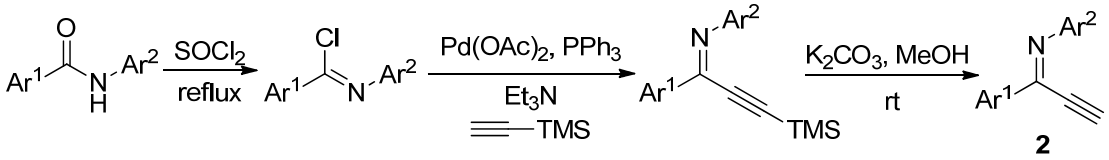

**1a** **2a** **3a**

| entry | Additive (equiv) | solvent | yield (%)[b] |
|---|---|---|---|
| 1 | $CH_3COOH$ (0.5) | $ClCH_2CH_2Cl$ | 40 |
| 2 | $C_6H_5COOH$ (0.5) | $ClCH_2CH_2Cl$ | 37 |
| 3 | *p*-$FC_6H_4CO_2H$ (0.5) | $ClCH_2CH_2Cl$ | 62 |
| 4 | *p*-$ClC_6H_4CO_2H$ (0.5) | $ClCH_2CH_2Cl$ | 54 |
| 5 | *p*-$BrC_6H_4CO_2H$ (0.5) | $ClCH_2CH_2Cl$ | 72 |

| | | | |
|---|---|---|---|
| 6 | 2-$BrC_6H_4CO_2H$ (0.5) | $ClCH_2CH_2Cl$ | 34 |
| 7 | *p*-$IC_6H_4CO_2H$ (0.5) | $ClCH_2CH_2Cl$ | 62 |
| 8 | *p*-$MeOC_6H_4CO_2H$(0.5) | $ClCH_2CH_2Cl$ | 60 |
| 9 | *p*-$HOC_6H_4CO_2H$(0.5) | $ClCH_2CH_2Cl$ | 37 |
| 10 | 1,3,4-$F_3C_6H_2CO_2H$(0.5) | $ClCH_2CH_2Cl$ | 40 |
| 11 | 2-$NO_2C_6H_4CO_2H$ (0.5) | $ClCH_2CH_2Cl$ | 29 |
| 12 | -- | $ClCH_2CH_2Cl$ | 51 |
| 13 | $Et_3N$ (0.5) | $ClCH_2CH_2Cl$ | -- |
| 14 | $Cs_2CO_3$ (0.5) | $ClCH_2CH_2Cl$ | -- |

[a]Reaction conditions: **1a** (0.2 mmol), **2a** (0.1 mmol), $ClCH_2CH_2Cl$ (2.0 mL). [b]Isolated yields. [c]$^1H$ NMR yields using mesitylene as internal standard.

## 3. General procedure for the preparation of alkynyl imine[1]

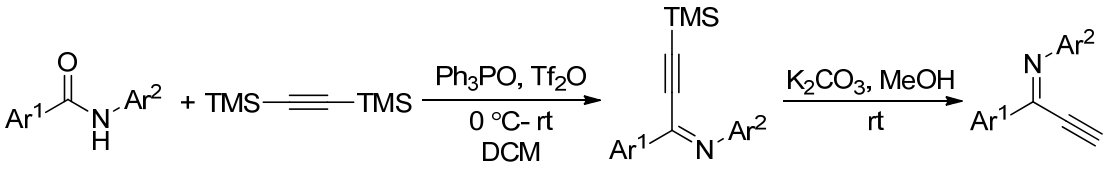



**Method A**: Amide (10.16 mmol) and thionyl chloride (16.38 g, 10.0 mL) were stirred at 65 °C for 2 h, and the excess of thionylchloride was then removed by distillation. The crude product was then heated with hexane, filtered, and the filtrate evaporated, to give the imidoyl chloride, in almost quantitative yield. The imidoyl chloride was used in subsequent reactions without further purification.

A solution of above imidoyl chloride (0.010 mol) in 25 mL of deaerated triethylamine was treated with 1.05 g of ethynyltrimethylsilane, with 0.01 g of palladium(II) acetate, and then with 0.02 g of triphenyl-phosphine. The mixture was slowly heated to 80 °C and kept at 80 °C for 2 h. After cooling, diluting with an equal volume of ether, and filtering. The filtrate was concentrated and eluted through a short column of silica gel with hexane. The eluate was concentrated and distilled to yield a viscous yellow oil which was identified as trimethylsilyl substituted alkynyl imine.

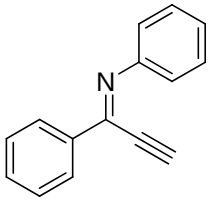
To a solution of above trimethylsilyl substituted alkynyl imine (5.42 mmol) in 10 mL

of anhydrous methanol was added 100 mg of anhydrous potassium carbonate. Immediately an exothermic reaction took place, and a copious crystalline precipitate was formed. The mixture was filtered and the crystalline pale yellow solid **2** was washed with cold methanol.



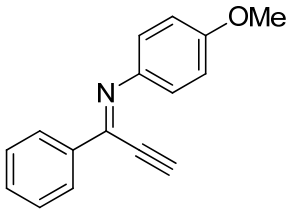

**Method B**: To a solution of triphenylphosphine oxide (0.83 g, 3 mmol) in dry $CH_2Cl_2$ (7 mL) was added trifluoromethanesulfonic anhydride (0.25 mL, 1.5 mmol) was added slowly at 0 $^oC$. The reaction mixture was stirred for 10 min at 0 $^oC$. The amide (solid, 1 mmol) and a solution of alkynes (1.2 mmol) in dry $CH_2Cl_2$ (2 mL) were successively added at this temperature. The reaction temperature was then allowed to warm to room temperature, and the reaction progress was monitored by TLC. The reaction was quenched with 10% aqueous $NaHCO_3$ solution. The aqueous layer was extracted with $CH_2Cl_2$, and the combined organic layers were dried over $Na_2SO_4$, filtered, and concentrated. The crude products were purified by flash chromatography on silica gel.

To a solution of above trimethylsilyl substituted alkynyl imine (5.42 mmol) in 10 mL of anhydrous methanol was added 100 mg of anhydrous potassium carbonate. Immediately an exothermic reaction took place, and a copious crystalline precipitate was formed. The mixture was filtered and the crystalline pale yellow solid **2** was washed with cold methanol.

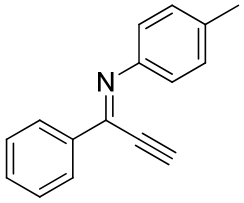



**2a**,[2] method **A**, yield: 52%. $^1H$ NMR ($CDCl_3$, 400 MHz): δ 3.15 (1H, s), 6.97 (2H, d, $J$ = 7.6 Hz), 7.04 (1H, t, $J$ = 7.6 Hz), 7.25 (2H, t, $J$ = 7.6 Hz), 7.34 (3H, m), 8.06-8.08 (2H, m). $^{13}C$ NMR ($CDCl_3$, 100 MHz): δ 76.4, 85.8, 120.4, 125.1, 128.2, 128.5, 128.7,

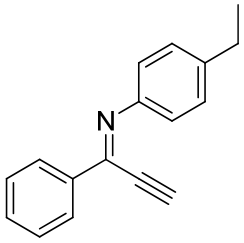
131.5, 136.8, 149.1, 151.3.




**2b**,[2] method **A**, yield: 69%. $^{1}$H NMR ($CDCl_3$, 400 MHz): δ 3.27 (1H, s), 3.72 (3H, s), 6.82-7.37 (7H, m), 8.08-8.10 (2H, m). $^{13}$C NMR ($CDCl_3$, 100 MHz): δ 55.5, 77.0, 85.4, 113.9, 122.7, 128.0, 128.5, 131.1, 137.2, 144.0, 147.6, 157.6.

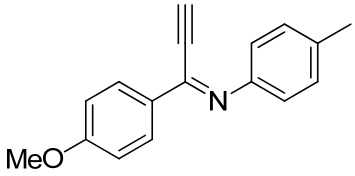



**2c**,[2] method **B**, yield: 50%. $^{1}$H NMR ($CDCl_3$, 400 MHz): δ 2.36 (3H, s), 3.32 (1H, s), 7.04-7.06 (2H, m), 7.18-7.20 (2H, m), 7.45-7.47 (3H, m), 8.17-8.20 (2H, m). $^{13}$C NMR ($CDCl_3$, 100 MHz): δ 17.2, 72.7, 81.5, 116.7, 124.2, 124.5, 125.4, 127.3, 130.9, 133.0, 144.55, 144.63.

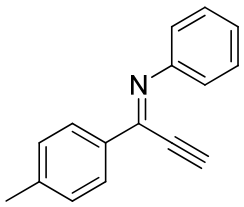



**2d**, method **B**, yield: 13%. dark brown solid, Mp: 57-59$^{o}$C, $^{1}$H NMR ($CDCl_3$, 400 MHz): δ 1.26 (3H, td, $J$ = 7.6, 1.6 Hz), 2.67 (2H, q, $J$ = 7.6 Hz), 3.34 (1H, t, $J$ = 0.8 Hz), 7.07-7.09 (2H, m), 7.20-7.25 (2H, m), 7.45-7.49 (3H, m), 8.17-8.20 (2H, m). $^{13}$C NMR ($CDCl_3$, 100 MHz): δ 15.7, 28.6, 76.7, 85.5, 120.8, 128.15, 128.18, 128.5, 131.3, 137.1, 141.4, 148.5, 148.7. MS (EI) m/z (rel): 233 ($M^{+}$,63), 218 (95), 205 (23), 204 (100), 89 (20), 77 (33), 63 (15), 51 (18). IR (KBr, film): 3181, 2961, 2089, 1586, 1564, 1494, 1268, 1209, 1037, 1031, 844, 749, 688, 674 cm$^{-1}$. HRMS for $C_{17}H_{15}N$:

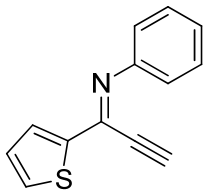
Calc. 233.1204; Found. 233.1203.



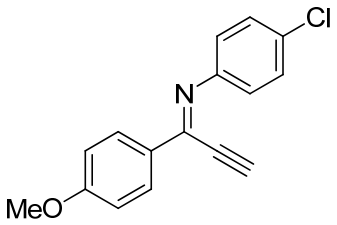

**2e**, method **B**, yield: 71%. white solid, Mp: 90-92 $^{o}$C, $^{1}$H NMR ($CDCl_3$, 400 MHz): δ 2.38 (3H, s), 3.31 (1H, s), 3.88 (3H, s), 6.96-6.98 (2H, m), 7.03-7.05 (2H, m), 7.18-7.20 (2H, m), 8.14-8.16 (2H, m). $^{13}$C NMR ($CDCl_3$, 100 MHz): δ 21.1, 55.5, 76.7, 85.2, 113.8, 120.7, 129.3, 129.9, 130.0, 134.5, 147.9, 148.8, 162.2. MS (EI) m/z (rel): 249 ($M^+$, 82), 248 (42), 234 (100), 206 (28), 205 (28), 191 (36), 91 (43), 65 (35). IR (KBr, film): 3254, 2093, 1603, 1544, 1504, 1310, 1254, 1165, 1018, 830, 798, 679 $cm^{-1}$. HRMS for $C_{17}H_{15}NO$: Calc. 249.1154; Found. 249.1151.



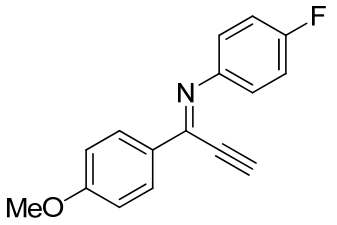

**2f**,[2] method **A**, yield: 70%. $^{1}$H NMR ($CDCl_3$, 400 MHz): δ 2.43 (3H, s), 3.30 (1H, s), 7.10-7.12 (2H, m), 7.17-7.20 (1H, m), 7.28 (2H, d, *J* = 8.0 Hz), 7.38-7.42 (2H, m), 8.10 (2H, d, *J* = 8.4 Hz); $^{13}$C NMR ($CDCl_3$, 100 MHz): δ 21.6 76.5, 85.5, 120.5, 124.9, 128.2, 128.7, 129.2, 134.3, 142.0, 149.1, 151.4



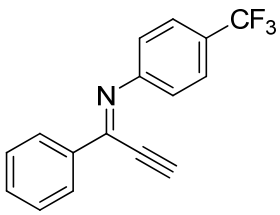

**2g**,[2] method **A**, yield: 20%. $^{1}$H NMR ($CDCl_3$, 400 MHz): δ 3.28 (1H, s), 7.11-7.21 (4H, m), 7.38 (2H, t, *J* = 7.6 Hz), 7.50 (1H, d, *J* = 4.8 Hz), 7.75 (1H, d, *J* = 4.0 Hz); $^{13}$C NMR ($CDCl_3$, 100 MHz): δ 75.8, 84.2, 121.1, 125.4, 127.8, 128.7, 130.8, 131.7, 143.2, 144.3, 150.2.




**2h**, method **B**, yield: 53%. dark red solid, Mp: 58-60 $^{o}$C, $^{1}$H NMR ($CDCl_3$, 400 MHz): δ 3.32 (1H, s), 3.86 (3H, s), 6.94-7.02 (4H, m), 7.31-7.33 (2H, m), 8.11-8.13 (2H, m). $^{13}$C NMR ($CDCl_3$, 100 MHz): δ 55.6, 76.3, 86.0, 113.9, 122.1, 128.8, , 129.5, 130.0, 130.1, 149.0, 150.0, 162.6. MS (EI) m/z (rel): 269 ($M^+$, 91), 268 (43), 234 (100), 219 (47), 191 (93), 111 (67), 75 (83), 63 (37). IR (KBr, film): 3173, 2089, 1605, 1578, 1556, 1507, 1315, 1262, 1167, 1021, 840, 738, 670 cm$^{-1}$. HRMS for $C_{16}H_{12}NOCl$: Calc. 269.0607; Found. 269.0605.



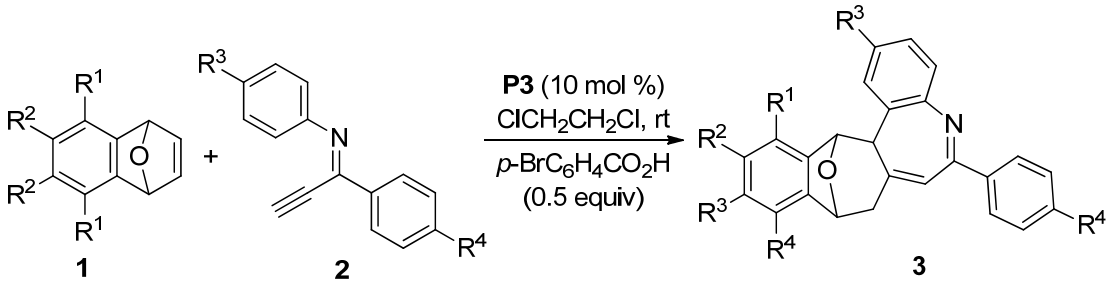

**2i**, method **B**, yield: 59%. pale yellow solid, Mp: 127-129 $^{o}$C, $^{1}$H NMR (400 MHz, $CDCl_3$): δ 3.34 (1H, s), 3.88 (3H,s), 6.98 (2H, d, $J$ = 9.2 Hz), 7.08-7.10 (4H, m), 8.15 (2H, d, $J$ = 8.8 Hz). $^{13}$C NMR ($CDCl_3$, 100 MHz): δ 55.5, 76.4, 85.7, 113.8, 115.4 (d, $J$ = 22.3 Hz), 122.3 (d, $J$ = 8.2 Hz), 129.7, 130.0, 147.4 (d, $J$ = 3.6 Hz), 148.7 (d, $J$ = 1.5 Hz), 160.3 (d, $J$ = 241.7 Hz), 162.4. $^{19}$F NMR (376MHz, $CDCl_3$): δ -118.62 (1F, s). MS (EI) m/z (rel): 253 ($M^+$,100), 252 (72), 238 (44), 210 (42), 209 (54), 146 (20), 95 (62), 7 (41). IR (KBr, film): 3186, 2086, 1603, 1553, 1496, 1314, 1114, 1022, 841, 757, 736 cm$^{-1}$. HRMS for $C_{16}H_{12}NOF$: Calc. 253.0903 ; Found. 253.0901.



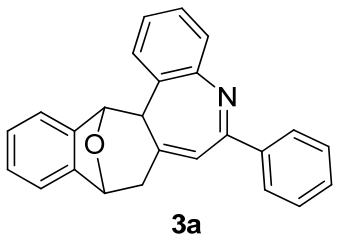

**2g**, method **B**, yield: 72%. dark yellow solid, Mp: 100-103 $^{o}$C, $^{1}$H NMR (400 MHz,

$CDCl_3$): δ 3.38 (1H, s), 7.14 (2H, d, *J* = 8.0 Hz), 7.48-7.57 (3H, m), 7.66 (2H, d, *J* = 8.0 Hz), 8.19-8.20 (2H, m). $^{13}C$ NMR ($CDCl_3$, 100 MHz): δ 75.9, 86.9, 120.5, 123.0 (q, *J* = 269.9 Hz), 126.1 (q, *J* = 3.7 Hz), 126.6, 128.4, 128.7, 132.0, 136.3, 150.5 (1C, m), 154.5 (1C, m). $^{19}F$ NMR (376 MHz, $CDCl_3$): δ -61.94 (3F, s). MS (EI) m/z (rel): 273 ($M^+$, 64), 272 (74), 204 (100), 196 (19), 145 (62), 95 (23), 75 (22), 51 (22). IR (KBr, film): 3367, 3183, 2090, 1567, 1446, 1314, 1277, 1172, 1119, 1104, 1066, 853, 734, 691 $cm^{-1}$. HRMS for $C_{16}H_{10}NF_3$: Calc. 273.0765 ; Found. 273.0766.

## 4. General Procedure for Palladacycle P3-Catalyzed Reaction of Bicyclic Alkenes 1 with Imines 2[a]



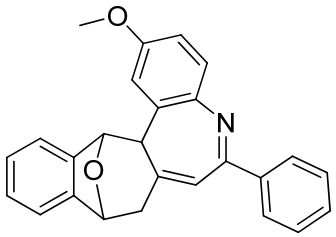

To a flame dried Schlenk tube was added sequentially catalyst **P3** (0.02 mmol, 10mol%), *p*-$BrC_6H_4COOH$ (0.1 mmol, 0.5 equiv.), and 1 mL $CH_2ClCH_2Cl$ (DCE). The resulting mixture was allowed to stir for 10 min, and then a solution of bicycle alkene **1** (0.26 mmol, 1.3 equiv) and *N*-(1-arylpropinylidene)anilines **2** (0.2 mmol) in 1 mL DCE was added slowly. The reaction was allowed to stir until the disappearance of imine **2** as monitored by TLC. The reaction mixture was concentrated in vacuum. Then the residue was purified by silica gel chromatography with ethyl acetate/petroleum ether (1/15) as the eluent to afford **3**.




**3a**

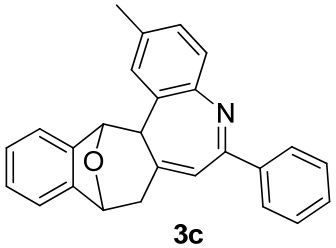
white solid, yield: 72%, Mp: 169-171 °C，$^1H$ NMR ($CDCl_3$, 400 MHz): δ 2.58 (1H, d, *J* = 16.8 Hz), 2.65 (1H, s), 3.16-3.22 (1H, m), 5.43 (1H, d, *J* = 4.8 Hz), 5.82 (1H, s), 5.97 (1H, s), 7.17 (1H, d, *J* = 6.8 Hz), 7.25 (1H, td, *J* = 7.2, 1.2 Hz), 7.32 (1H, td, *J* =

7.2, 1.2 Hz), 7.36-7.46 (5H, m), 7.55 (1H, dd, *J* = 7.6, 1.6 Hz), 7.81 (1H, dd, *J* = 7.6, 1.2 Hz), 7.86-7.89 (2H, m). $^{13}$C NMR ($CDCl_3$, 100 MHz): δ 35.5, 45.2, 77.5, 78.3, 119.3, 120.7, 120.8, 124.3, 126.1, 126.8, 127.3, 127.8, 128.0, 128.4, 130.2, 132.4, 139.8, 143.9, 144.1, 144.8, 146.8, 162.2. MS (EI) m/z (rel): 349 ($M^+$, 93), 348 (27), 320 (48), 231 (100), 230 (92), 193 (30), 131 (28), 77 (25). IR (KBr, film): 2947, 2928, 1629, 1534, 1365, 1037, 948, 762, 749, 728, 688cm$^{-1}$. HRMS for $C_{25}H_{19}NO$: Calc. 349.1467; Found. 349.1470.




**3b**

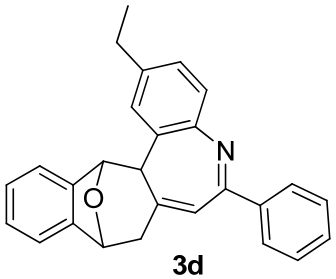
yellow-white solid, yield: 56%, Mp: 70-73 °C, $^1$H NMR ($CDCl_3$, 400 MHz): δ 2.56 (1H, d, *J* = 16.8 Hz), 2.59 (1H, s), 3.14-3.19 (1H, m), 3.91 (3H, s), 5.41 (1H, d, *J* = 4.8 Hz), 5.78 (1H, s), 5.94 (1H, s), 6.96 (1H, dd, *J* = 8.8, 3.2 Hz), 7.16 (1H, d, *J* = 7.6 Hz), 7.22-7.37 (7H, m), 7.47 (1H, d, *J* = 8.8 Hz), 7.82-7.85 (2H, m). $^{13}$C NMR ($CDCl_3$, 100 MHz): δ 35.5, 45.3, 55.7, 77.4, 78.2, 108.9, 113.0, 119.4, 120.7, 120.8, 127.6, 127.8, 127.9, 128.4, 129.9, 133.1, 140.1, 141.0, 143.2, 143.9, 144.2, 159.7, 160.5. MS (ESI) m/z (rel): 380 ($M^+$+H). IR (KBr, film): 2951, 1604, 1501, 1481, 1461, 1274, 1243, 1048, 1033, 946, 773, 748, 693, 663 cm$^{-1}$. HRMS for $C_{26}H_{21}NO_2$: Calc. 379.1572; Found. 379.1574.




**3c**

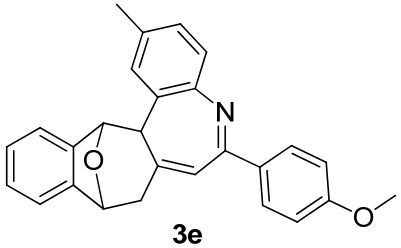
pale-yellow solid, yield: 57%, Mp: 83-85 °C, $^1$H NMR ($CDCl_3$, 400 MHz): δ 2.49 (3H, s), 2.57 (1H, d, *J* = 16.8 Hz), 2.61 (1H, s), 3.17-3.23 (1H, m), 5.43 (1H, d, *J* = 4.8 Hz),

5.81 (1H, s), 5.56 (1H, d, *J* = 0.8 Hz), 7.16 (1H, d, *J* = 7.2 Hz), 7.20-7.39 (7H, m), 7.44 (1H, d, *J* = 8.0 Hz), 7.60 (1H, s), 7.84-7.86 (2H, m). $^{13}$C NMR ($CDCl_3$, 100 MHz): δ 21.5, 35.5, 45.2, 77.4, 78.3, 119.4, 120.7, 120.8, 124.6, 126.1, 127.69, 127.74, 127.88, 127.9, 128.4, 130.0, 132.1, 137.4, 140.0, 144.0, 144.1, 144.4, 144.6, 161.6. MS (EI) m/z (rel): 363 ($M^+$, 100), 364 (30), 348 (33), 334 (38), 245 (36), 244 (35), 231 (23), 215 (30). IR (KBr, film): 2920, 1621, 1478, 1460, 1360, 1177, 1041, 981, 944, 827, 747, 689, 662 $cm^{-1}$. HRMS for $C_{26}H_{21}NO$: Calc. 363.1623; Found. 363.1624.



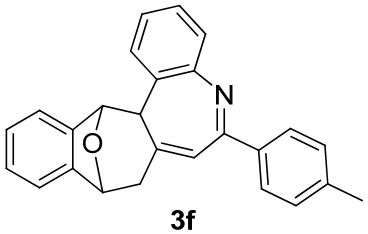

**3d**

pale-yellow liquid, yield: 57%, $^1$H NMR ($CDCl_3$, 400 MHz): δ 1.32 (3H, t, *J* = 7.2 Hz), 2.54 (1H, d, *J* = 16.8 Hz), 2.59 (1H, s), 2.74-2.80 (2H, m), 3.14-3.20 (1H, m), 5.41 (1H, d, *J* = 4.8 Hz), 5.80 (1H, s), 5.94 (1H, s), 7.13 (1H, d, *J* = 7.2 Hz), 7.22 (2H, t, *J* = 5.6 Hz), 7.28 (1H, t, *J* = 7.2 Hz), 7.33-7.36 (4H, m), 7.46 (1H, d, *J* = 8.0 Hz), 7.60 (1H, s), 7.82-7.85 (2H, m). $^{13}$C NMR ($CDCl_3$, 100 MHz): δ 16.0, 28.9, 35.5, 45.3, 77.4, 78.3, 119.4, 120.67, 120.74, 123.5, 126.2, 126.4, 127.7, 127.9, 128.4, 130.0, 132.1, 140.0, 143.7, 144.0, 144.1, 144.3, 144.8, 161.5. MS (ESI) m/z (rel):378 $[M+H]^+$. IR (KBr, film): 2960, 2927, 1631, 1537, 1446, 1116, 1043, 1009, 946, 929, 846, 832, 745, 690, 662 $cm^{-1}$. HRMS for $C_{27}H_{24}NO$: Calc. 378.1852; Found. 378.1851 $[M+H]^+$



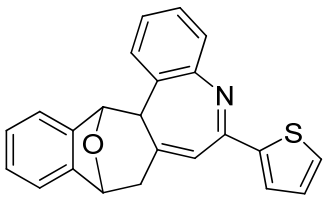

**3e**

white solid, yield: 51%, Mp: 184-186 °C，$^1$H NMR ($CDCl_3$, 400 MHz): δ 2.48 (3H, s), 2.55 (1H, d, *J* = 16.8 Hz), 2.63 (1H, s), 3.17-3.22 (1H, m), 3.82 (3H, s), 5.42 (1H, d, *J* = 4.8 Hz), 5.80 (1H, s), 5.92 (1H, s), 6.87-6.90 (2H, m), 7.16 (1H, d, *J* = 7.2 Hz), 7.19 (1H, dd, *J* = 8.0, 1.6 Hz), 7.24 (1H, td, *J* = 7.2, 1.2 Hz), 7.30 (1H, td, *J* = 7.2, 0.8 Hz), 7.36 (1H, d, *J* = 6.8 Hz), 7.41 (1H, d, *J* = 8.0 Hz), 7.59 (1H, s), 7.80-7.83 (2H, m). $^{13}$C NMR ($CDCl_3$, 100 MHz): δ 21.5, 35.5, 45.2, 55.5, 77.5, 78.4, 113.7, 119.3, 120.7, 120.8, 124.6, 126.0, 127.66, 127.7, 127.9, 129.4, 132.1, 132.8, 136.9, 144.0, 144.1, 144.2, 144.8, 161.0, 161.3. MS (EI) m/z (rel): 393 ($M^+$, 5), 81(100), 43 (90), 75 (47), 79 (43), 41 (35), 57 (35), 183 (34), 185 (33). IR (KBr, film): 2968, 2917, 1633,1509, 1245, 1177, 1041, 1015, 864, 747 $cm^{-1}$. HRMS for $C_{27}H_{23}NO_2$: Calc. 393.1729; Found. 393.1726.



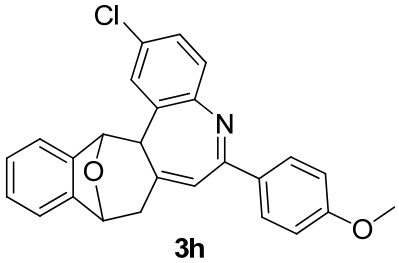

**3f**

slight yellow solid, yield: 61%, Mp: 180-182 °C, $^1$H NMR ($CDCl_3$, 400 MHz): δ 2.37 (3H, s), 2.56 (1H, d, *J* = 17.2 Hz), 2.65 (1H, s), 3.16-3.21 (1H, m), 5.43 (1H, d, *J* = 4.8 Hz), 5.81 (1H, s), 5.95 (1H, s), 7.15-7.26 (4H, m), 7.31 (1H, t, *J* = 7.2 Hz), 7.35-7.44 (3H, m), 7.52 (1H, d, *J* = 7.2 Hz), 7.78 (3H, t, *J* = 8.0 Hz). $^{13}$C NMR ($CDCl_3$, 100 MHz): δ 21.5, 35.4, 45.2, 77.5, 78.3, 119.3, 120.7, 120.8, 124.2, 126.0, 126.7, 127.0, 127.7, 127.90, 127.93, 129.1, 132.5, 137.1, 140.5, 144.0, 144.1, 144.5, 146.9, 162.1. MS (EI) m/z (rel): 363 ($M^+$, 33), 245 (100), 244 (61), 230 (44), 207 (22), 173 (19), 118 (19), 246 (19). IR (KBr, film): 2959, 2922, 2853, 1631, 1606, 1537, 1446, 1259, 1085, 1009, 803, 746, 624 $cm^{-1}$. HRMS (ESI) for $C_{26}H_{22}NO$: Calc. 364.1696; Found. 364.1698 $[M+H]^+$.



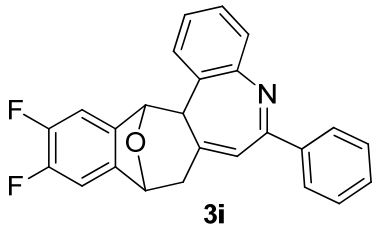

**3g**

slight yellow solid, yield: 45%, Mp: 233-235 $^{o}$C, $^{1}$H NMR ($CDCl_3$, 400 MHz): δ 2.55 (1H, d, *J* = 17.2 Hz), 2.72 (1H, s), 3.15-3.20 (1H, m), 5.41 (1H, d, *J* = 4.8 Hz), 5.79 (1H, s), 6.04 (1H, s), 6.99-7.01 (1H, m), 7.17 (1H, d, *J* = 7.2 Hz), 7.22-7.43 (7H, m), 7.48 (1H, dd, *J* = 7.2, 1.2 Hz), 7.76 (1H, d, *J* = 7.2 Hz). $^{13}$C NMR ($CDCl_3$, 100 MHz): δ 35.5, 45.2, 77.5, 78.3, 118.3, 120.7, 120.9, 124.3, 126.2, 126.9, 127.3, 127.7, 127.8, 128.0, 128.3, 129.8, 132.0, 143.9, 144.1, 145.2, 146.6, 147.3, 156.9. MS (EI) m/z (rel): 355 ($M^+$, 32), 237 (100), 236 (67), 173 (27), 84 (20), 238 (20), 77 (19), 128 (17). IR (KBr, film): 2928, 1628, 1473, 1428, 1154, 978, 824, 752, 710 cm$^{-1}$. HRMS (ESI) for $C_{23}H_{18}NOS$: Calc. 356.1104; Found. 356.1106 $[M+H]^+$.



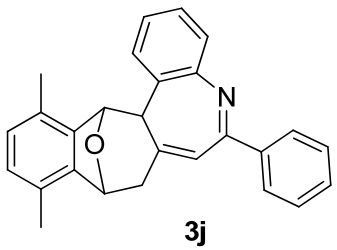

**3h**

white solid, yield: 31%, Mp: 210-213 $^{o}$C, $^{1}$H NMR ($CDCl_3$, 400 MHz): δ 2.55 (1H, d, *J* = 17.2 Hz), 2.61 (1H, s), 3.15-3.21 (1H, m), 3.82 (3H, s), 5.42 (1H, d, *J* = 4.8 Hz), 5.73 (1H, s), 5.92 (1H, s), 6.87-6.89 (2H, m), 7.15 (1H, d, *J* = 7.2 Hz), 7.23 (1H, td, *J* = 7.2, 1.2 Hz), 7.28-7.36 (3H, m), 7.40 (1H, d, *J* = 8.4 Hz), 7.77-7.81 (3H, m). $^{13}$C NMR ($CDCl_3$, 100 MHz): δ 35.4, 45.0, 55.5, 77.4, 78.0, 113.8, 119.4, 120.7, 120.8, 124.3, 126.9, 127.2, 127.9, 128.0, 129.6, 132.3, 132.7, 133.6, 143.6, 144.1, 144.2, 145.6, 161.6, 161.9. MS (EI) m/z (rel): 413 ($M^+$, 64), 295 (100), 294 (33), 297 (32), 414 (28), 296 (26), 264 (22), 415 (22). IR (KBr, film): 2928, 1601, 1460, 1442, 1414, 1255, 1212, 1165, 1017, 832, 748, 726, 655 cm$^{-1}$. HRMS for $C_{26}H_{20}NO_2Cl$: Calc. 413.1183; Found. 413.1182.



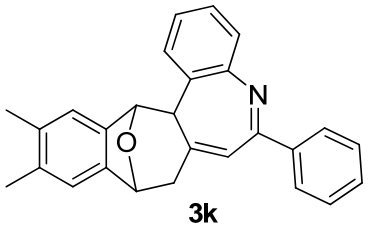

**3i**

pale-yellow solid, yield: 41%, Mp: 86-88 °C, $^{1}$H NMR ($CDCl_3$, 400 MHz): δ 2.54 (1H, d, *J* = 17.2 Hz), 2.58 (1H, s), 3.13-3.19 (1H, m), 5.36 (1H, d, *J* = 4.8 Hz), 5.75 (1H, s), 6.00 (1H, s), 6.96-7.00 (1H, m), 7.15-7.19 (1H, m), 7.38-7.45 (5H, m), 7.53-7.55 (1H, m), 7.72-7.74 (1H, m), 7.89-7.92 (2H, m). $^{13}$C NMR ($CDCl_3$, 100 MHz): δ 35.1, 44.9, 78.06, 78.08, 110.3 (d, *J* = 2.6 Hz), 110.5 (d, *J* = 3.0 Hz), 119.6, 124.0, 126.2, 126.9, 127.3, 127.9, 128.5, 130.4, 131.8, 139.6, 139.9 (q, *J* = 3.0 Hz), 140.1 (q, *J* = 3.0 Hz), 143.4, 146.8, 148.8 (1C, m), 151.2 (1C, m), 162.0. $^{19}$F NMR ($CDCl_3$, 376 MHz): δ -137.92-(-137.82) (1F, m), -137.53-(-137.43) (1F, m). MS (EI) m/z (rel): 385 ($M^+$, 22), 151 (100), 231 (72), 230 (54), 152 (46), 107 (32), 154 (31), 101 (27). IR (KBr, film): 2924, 1731, 1488, 1473, 1355, 1209, 1070, 1010, 873, 760, 733, 690, 658, 645cm$^{-1}$. HRMS for $C_{25}H_{17}NOF_2$: Calc. 385.1278; Found. 385.1274.



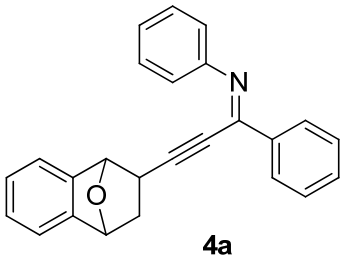

**3j**

pale-yellow solid, yield: 64%, Mp: 92-96 °C, $^{1}$H NMR ($CDCl_3$, 400 MHz): δ 2.11 (3H, s), 2.35 (3H, s), 2.57 (1H, d, *J* = 17.2 Hz), 2.60 (1H, s), 3.15-3.20 (1H, s), 5.43 (1H, d, *J* = 4.8 Hz), 5.84 (1H, s), 6.01 (1H, s), 6.93 (1H, d, *J* = 8.0 Hz), 7.00 (1H, d, *J* = 7.2 Hz), 7.38-7.47 (5H, m), 7.55 (1H, d, *J* = 7.6 Hz), 7.83 (1H, d, *J* = 8.0 Hz), 7.91-7.93 (2H, m). $^{13}$C NMR ($CDCl_3$, 100 MHz): δ 17.9, 18.2, 34.1, 43.7, 76.7, 77.6, 119.3, 124.4, 126.1, 126.8, 127.3, 127.8, 127.9, 128.0, 128.4, 129.1, 129.4, 130.2, 132.4, 139.9, 142.1, 142.4, 145.2, 147.0, 162.1. MS (EI) m/z (rel): 377 ($M^+$, 20), 231 (100), 230 (67), 81 (38), 159 (28), 146 (19), 232 (17), 43 (16). IR (KBr, film): 2922, 1630, 1535, 1472, 1445, 1268,1214, 1060, 1038, 840, 805, 758, 742, 686 cm$^{-1}$. HRMS for $C_{27}H_{23}NO$: Calc. 377.1780 ; Found. 377.1775.



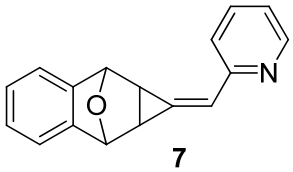
**3k**

pale-yellow solid, yield: 59%, Mp: 99-102 $^{o}$C, $^{1}$H NMR ($CDCl_3$, 400 MHz): δ 2.24 (3H, s), 2.32 (3H, s), 2.54(1H, d, *J* = 16.8 Hz), 2.62 (1H, s), 3.13-3.19 (1H, m), 5.35 (1H, d, *J* = 7.2 Hz), 5.74 (1H, s), 5.99 (1H, s), 6,92 (1H, s), 7.12 (1H, s), 7.36-7.45 (5H, m), 7.54 (1H, dd, *J* = 7.6, 1.6Hz), 7.80 (1H, dd, *J* = 7.6, 0.8 Hz), 7.90-7.93 (2H, m). $^{13}$C NMR ($CDCl_3$, 100 MHz): δ 20.1, 20.2, 35.6, 45.3, 77.3, 78.1, 119.2, 121.8, 121.9, 124.3, 126.0, 126.7, 127.2, 128.0, 128.4, 130.2, 132.6, 135.9, 136.1, 139.9, 141.6, 141.8, 145.3, 146.9, 162.1. MS (EI) m/z (rel): 377 ($M^+$, 100), 348 (76), 362 (67), 230 (31), 215 (30), 378 (30), 349 (26), 217 (22). IR (KBr, film): 2921, 1629, 1537, 1447, 1043, 976, 942, 761, 727, 695 cm$^{-1}$. HRMS for $C_{27}H_{23}NO$: Calc. 377.1780; Found. 377.1783.



**4a**

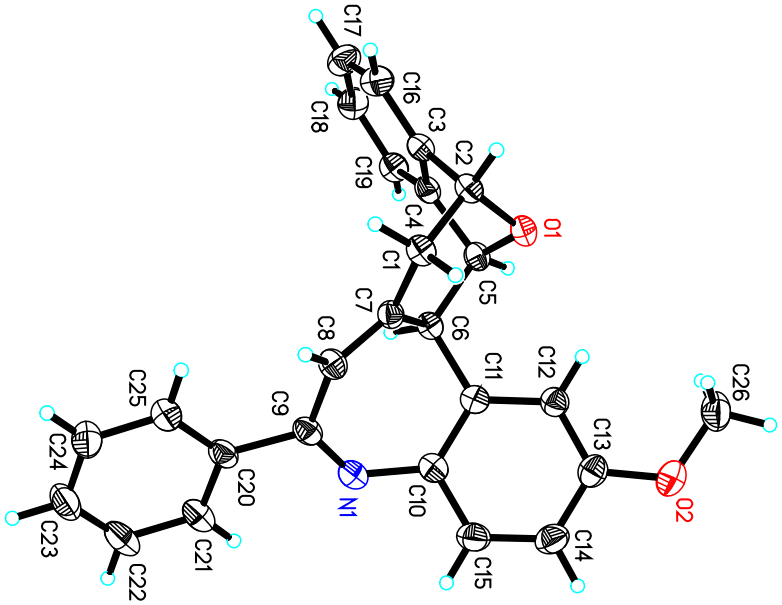
pale-yellow solid, Mp: 98-100 $^{o}$C, $^{1}$H NMR ($CDCl_3$, 400 MHz): δ 1.70 (1H, dd, *J* = 8.4, 12.0 Hz), 1.95 (1H, tt, *J* = 4.4, 11.6 Hz), 2.46 (1H, q, *J* = 4.0 Hz), 5.15 (1H, s), 5.34 (1H, d, *J* = 4.8 Hz), 7.03-7.13 (7H, m), 7.28-7.39 (5H, m), 8.10-8.13 (2H, m). $^{13}$C NMR ($CDCl_3$, 100 MHz): δ 32.4, 36.4, 75.7, 79.1, 83.8, 102.0, 119.2, 119.4, 120.9, 124.7, 127.0, 127.4, 128.2, 128.4, 131.1, 137.4, 143.9, 145.3, 150.2, 151.8. MS (EI) m/z (rel): 349 ($M^+$, 44), 207 (100), 231 (67), 230 (64), 73 (56), 77 (32), 193 (28), 320 (27). IR (KBr, film): 2203, 1587, 1565, 1447, 1321, 1274, 1215, 978, 945, 834, 773, 691, 672 cm$^{-1}$. HRMS for $C_{25}H_{19}NO$: Calc. 349.1467 ; Found. 349.1471.

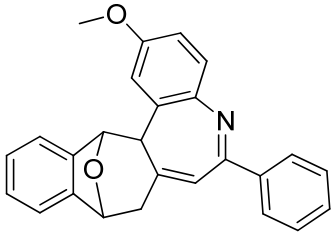



**7**

brown solid, Mp: 56-58$^0$C, $^1$H NMR ($CD_3OD$, 400 MHz): δ 2.01 (1H, d, *J* = 7.2 Hz), 2.25 (1H, dd, *J* = 7.2, 1.2 Hz), 5.48 (1H, s), 5.61 (1H, s), 6.83 (1H, s), 7.17-7.21 (2H, m), 7.25-7.28 (1H, m), 7.38-7.44 (2H, m),7.84(1H, td, *J* = 7.6, 2.0 Hz), 7.93(1H, d, *J*=8.0Hz), 8.45(1H, d, *J*=4.8Hz). $^{13}$C NMR ($CD_3OD$, 100 MHz): δ 25.7, 26.8, 80.6, 81.1, 120.46, 120.5, 120.9, 122.1, 123.2, 127.3, 127.4, 138.3, 140.0, 147.8, 148.1, 149.4, 157.0. IR (KBr, film): 3048, 3009, 1743, 1584, 1562, 1468, 1431, 1207, 1190, 1146, 981, 879, 791, 755, 669cm$^{-1}$. MS (ESI) found: m/z 248 $[M+H]^+$; HRMS (ESI) for $C_{17}H_{14}NO$ $[M+H]^+$ calcd. 248.1070; found: 248.1069.

## 5. ORTEP drawing, crystal data, and atomic coordinates of compound 3b




**3b**

Table 1. Crystal data and structure refinement for cd212154.

| | |
|---|---|
| Identification code | cd212154 |
| Empirical formula | C26 H21 N O2 |
| Formula weight | 379.44 |
| Temperature | 293(2) K |
| Wavelength | 0.71073 A |
| Crystal system, space group | Triclinic, P-1 |
| Unit cell dimensions | a = 9.7339(16) A alpha = 69.234(3) deg.<br>b = 10.1445(16) A beta = 70.764(4) deg.<br>c = 11.2108(17) A gamma = 78.702(4) deg. |
| Volume | 973.4(3) A^3 |
| Z, Calculated density | 2, 1.295 Mg/m^3 |
| Absorption coefficient | 0.082 mm^-1 |
| F(000) | 400 |
| Crystal size | 0.265 x 0.211 x 0.153 mm |
| Theta range for data collection | 2.03 to 26.00 deg. |
| Limiting indices | -11<=h<=10, -12<=k<=9, -13<=l<=12 |
| Reflections collected / unique | 5912 / 3809 [R(int) = 0.0320] |
| Completeness to theta = 26.00 | 99.8 % |
| Absorption correction | Empirical |
| Max. and min. transmission | 1.00000 and 0.50856 |
| Refinement method | Full-matrix least-squares on F^2 |
| Data / restraints / parameters | 3809 / 0 / 263 |

| | |
|---|---|
| Goodness-of-fit on F^2 | 1.053 |
| Final R indices [I>2sigma(I)] | R1 = 0.0493, wR2 = 0.1318 |
| R indices (all data) | R1 = 0.0612, wR2 = 0.1430 |
| Largest diff. peak and hole | 0.242 and -0.223 e.A^-3 |

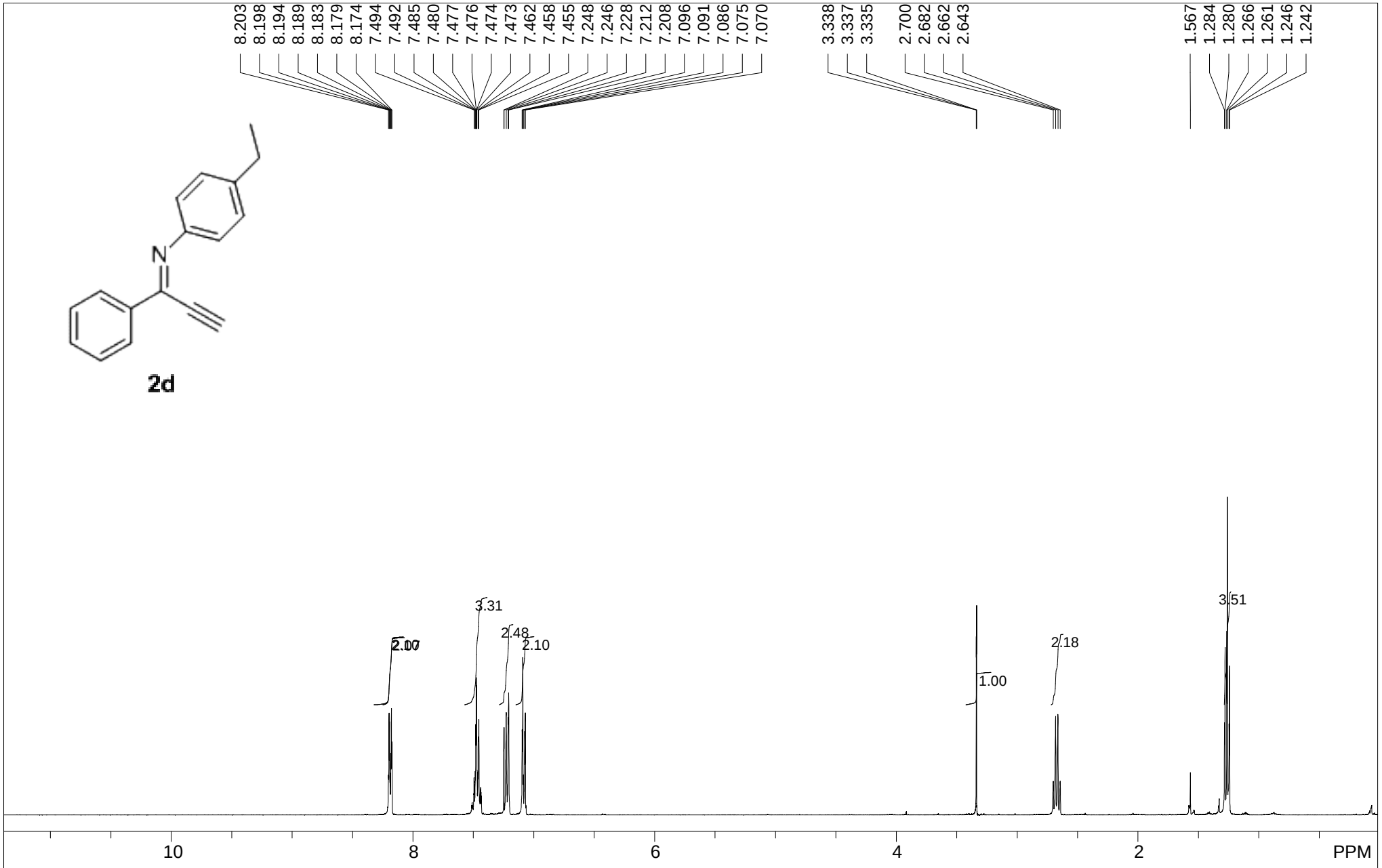
Table 2. Atomic coordinates ( x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for cd212154.
U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

| | x | y | z | U(eq) |
|---|---|---|---|---|
| N(1) | 3964(2) | 2018(2) | 1472(1) | 45(1) |
| O(1) | 759(1) | 3226(1) | 5732(1) | 43(1) |
| O(2) | -2021(1) | 1598(2) | 3481(1) | 65(1) |
| C(1) | 2428(2) | 4840(2) | 4072(2) | 41(1) |
| C(2) | 1678(2) | 4275(2) | 5553(2) | 41(1) |
| C(3) | 2724(2) | 3424(2) | 6342(2) | 40(1) |
| C(4) | 2768(2) | 2031(2) | 6410(1) | 39(1) |
| C(5) | 1766(2) | 1997(2) | 5646(2) | 40(1) |
| C(6) | 2592(2) | 2199(2) | 4176(1) | 37(1) |
| C(7) | 3115(2) | 3667(2) | 3471(1) | 37(1) |
| C(8) | 4094(2) | 3929(2) | 2279(2) | 41(1) |
| C(9) | 4693(2) | 2927(2) | 1525(2) | 41(1) |
| C(10) | 2466(2) | 1891(2) | 2106(2) | 43(1) |
| C(11) | 1712(2) | 2007(2) | 3370(2) | 40(1) |
| C(12) | 202(2) | 1915(2) | 3846(2) | 43(1) |
| C(13) | -542(2) | 1684(2) | 3094(2) | 49(1) |
| C(14) | 213(2) | 1487(2) | 1875(2) | 57(1) |
| C(15) | 1693(2) | 1576(2) | 1402(2) | 54(1) |
| C(16) | 3541(2) | 3803(2) | 6943(2) | 51(1) |
| C(17) | 4385(2) | 2740(2) | 7646(2) | 57(1) |
| C(18) | 4423(2) | 1357(2) | 7717(2) | 54(1) |
| C(19) | 3615(2) | 975(2) | 7094(2) | 46(1) |
| C(20) | 6223(2) | 3041(2) | 643(2) | 45(1) |
| C(21) | 6837(2) | 2137(2) | -120(2) | 55(1) |
| C(22) | 8234(2) | 2263(2) | -968(2) | 67(1) |
| C(23) | 9043(2) | 3291(3) | -1089(2) | 69(1) |
| C(24) | 8454(2) | 4203(3) | -356(2) | 68(1) |
| C(25) | 7065(2) | 4066(2) | 514(2) | 58(1) |
| C(26) | -2851(2) | 1833(2) | 4691(2) | 69(1) |

## 6. Reference

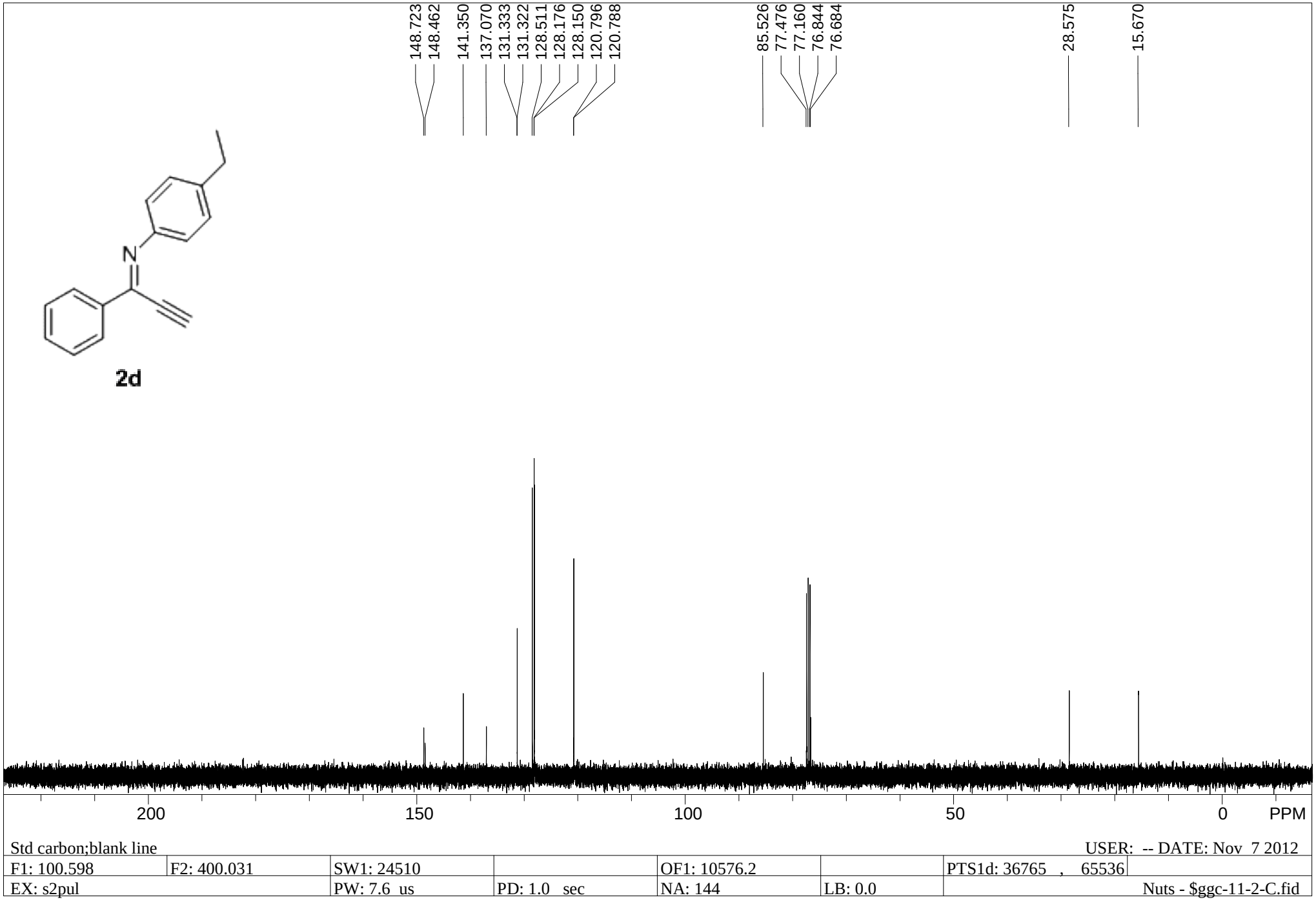
1. K. Sangu, K. Fuchibe and T. Akiyama, *Org. Lett*. 2004, **6**, 353.

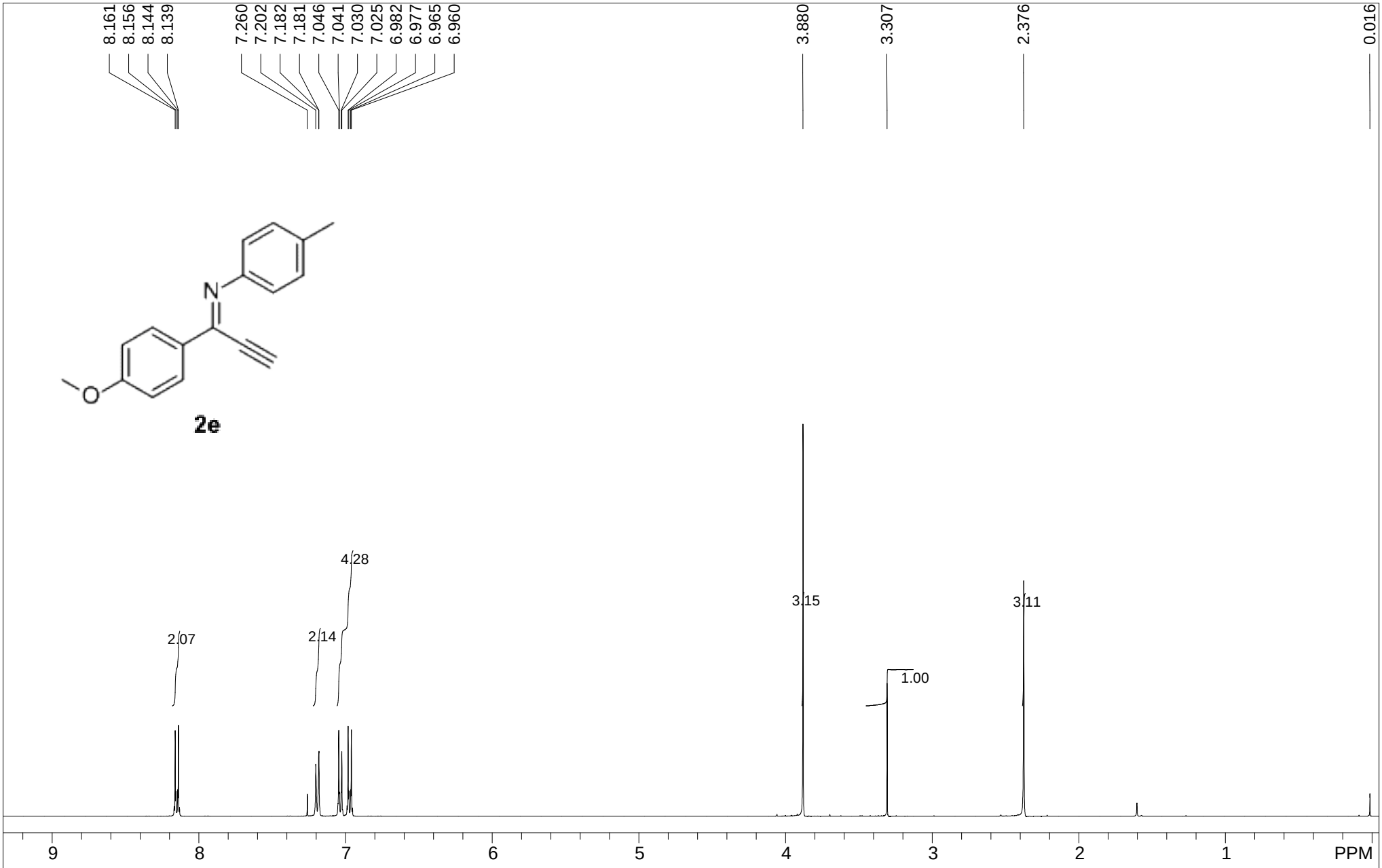
2. G. -L. Cheng and X.-L. Cui, *Org. Lett*. 2013, **15**, 1480.




Std proton;blank line USER: -- DATE: Nov 7 2012

| | | | | | | |
|---|---|---|---|---|---|---|
| F1: 400.032 | F2: 100.597 | SW1: 7225 | | OF1: 2801.7 | | PTS1d: 21676 , 32768 |
| EX: s2pul | | PW: 10.5 us | PD: 1.0 sec | NA: 8 | LB: 0.0 | Nuts - $ggc-11-2h.fid |

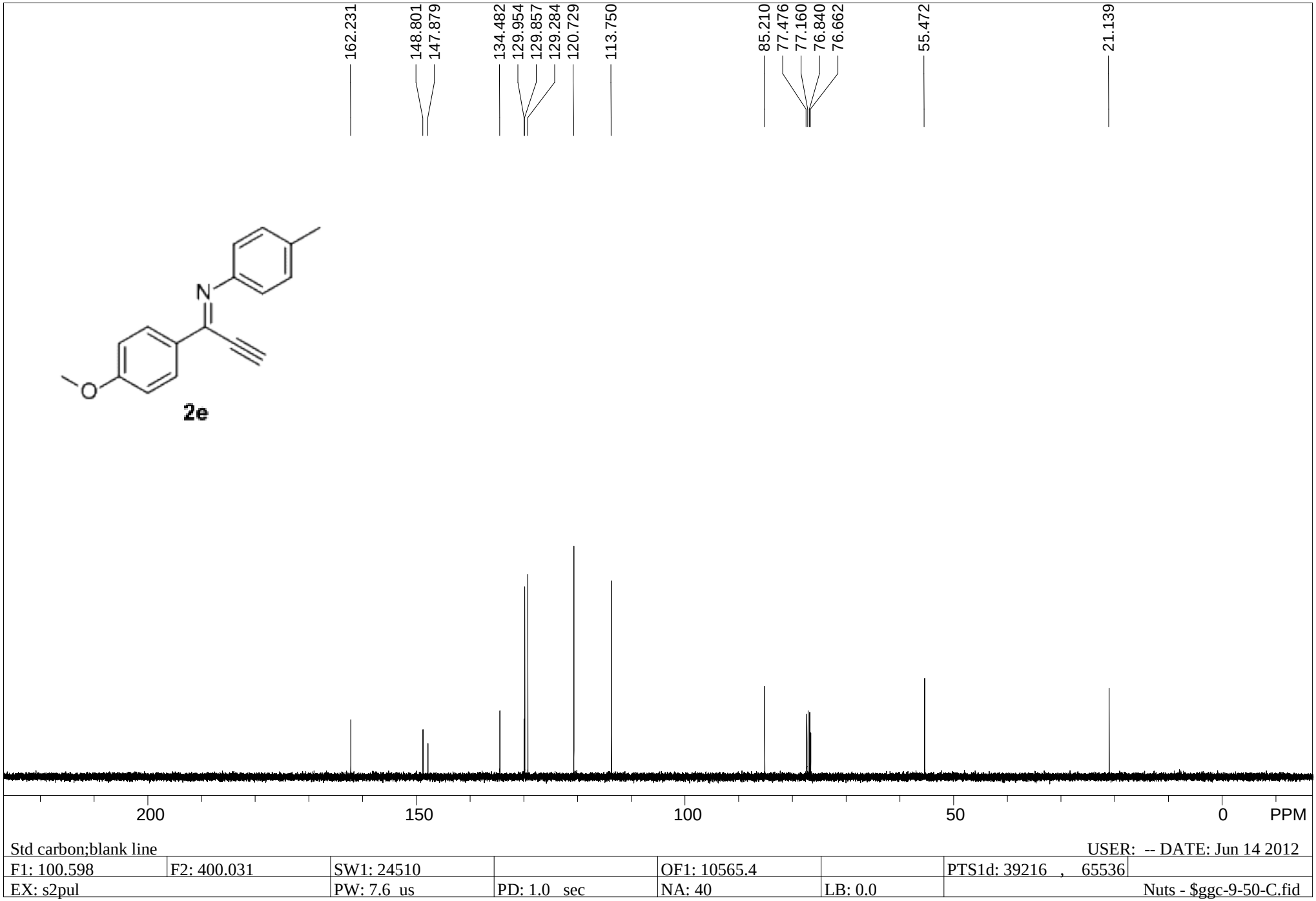

148.723
148.462
141.350
137.070
131.333
131.322
128.511
128.176
128.150
120.796
120.788
85.526
77.476
77.160
76.844
76.684
28.575
15.670
N
2d
200
150
100
50
0
PPM
Std carbon;blank line
USER: -- DATE: Nov 7 2012
F1: 100.598
F2: 400.031
SW1: 24510
OF1: 10576.2
PTS1d: 36765 , 65536
EX: s2pul
PW: 7.6 us
PD: 1.0 sec
NA: 144
LB: 0.0
Nuts - $ggc-11-2-C.fid

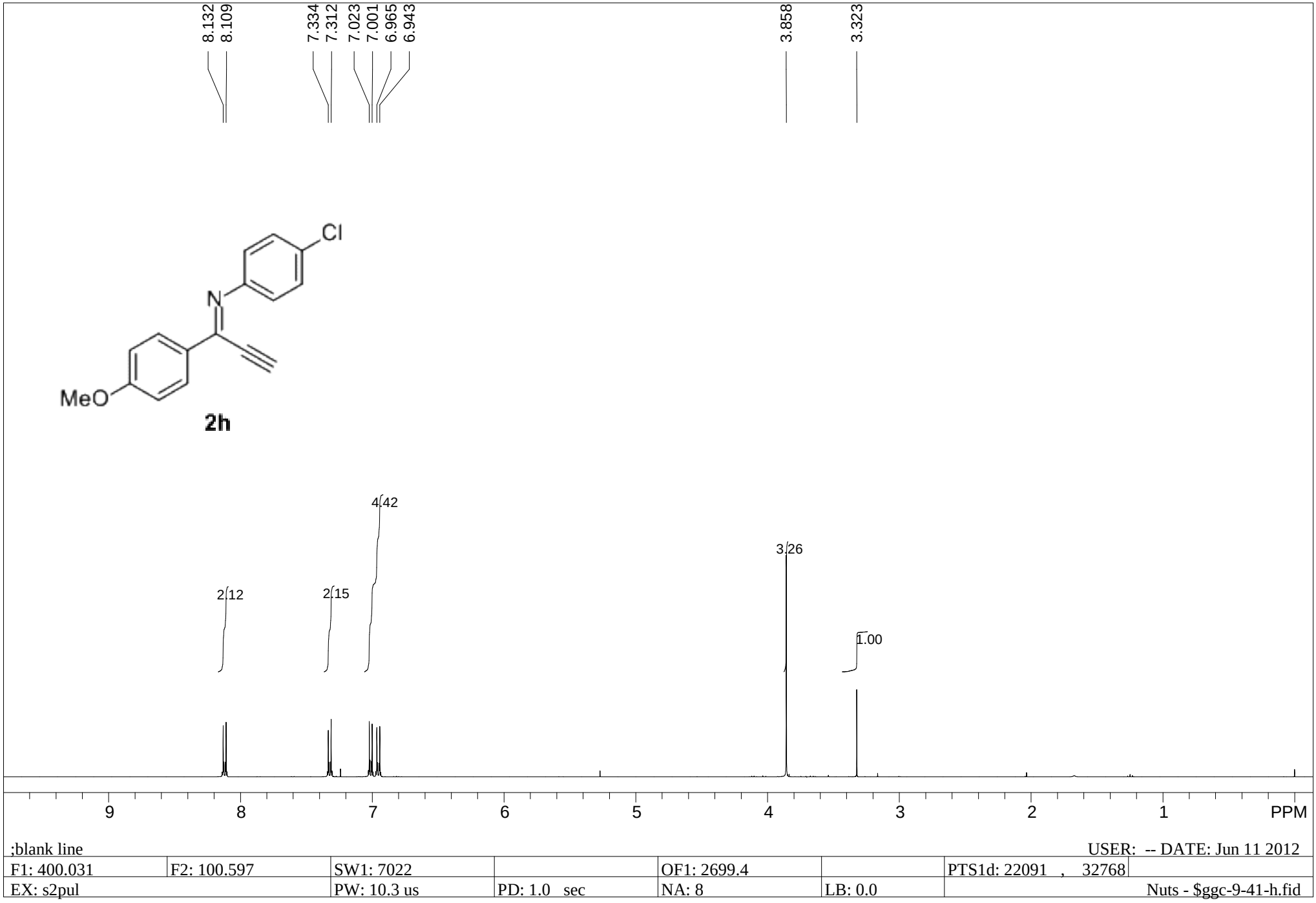



18871-66-4;blank line;blank line;blank line

USER: -- DATE: Mar 2 2013

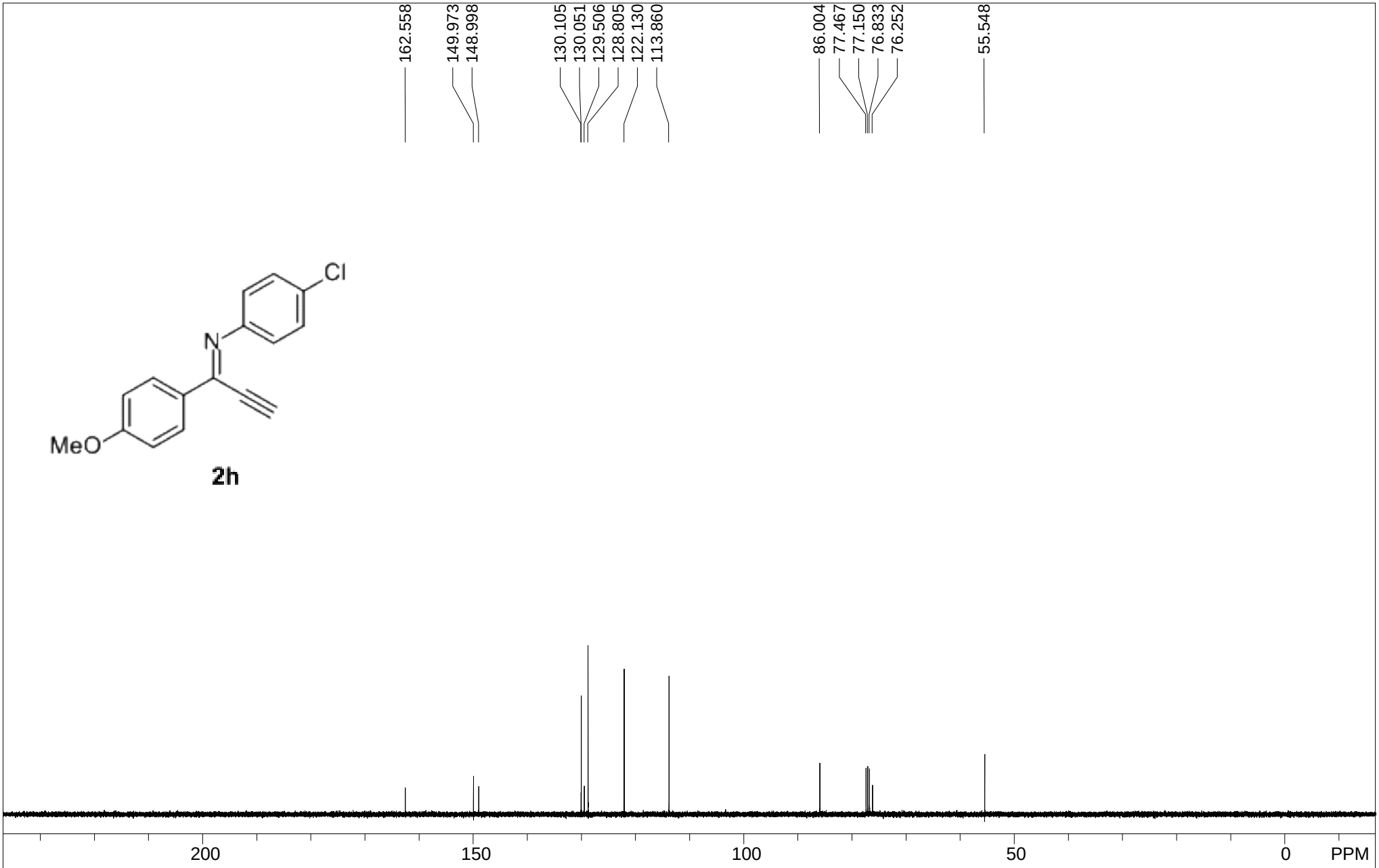
| | | | | | | |
|---|---|---|---|---|---|---|
| F1: 400.032 | F2: 100.597 | SW1: 7225 | | OF1: 2804.9 | | PTS1d: 21677 , 32768 |
| EX: s2pul | | PW: 10.1 us | PD: 1.0 sec | NA: 8 | LB: 0.0 | Nuts - $ggc-9-50--hhh.fid |

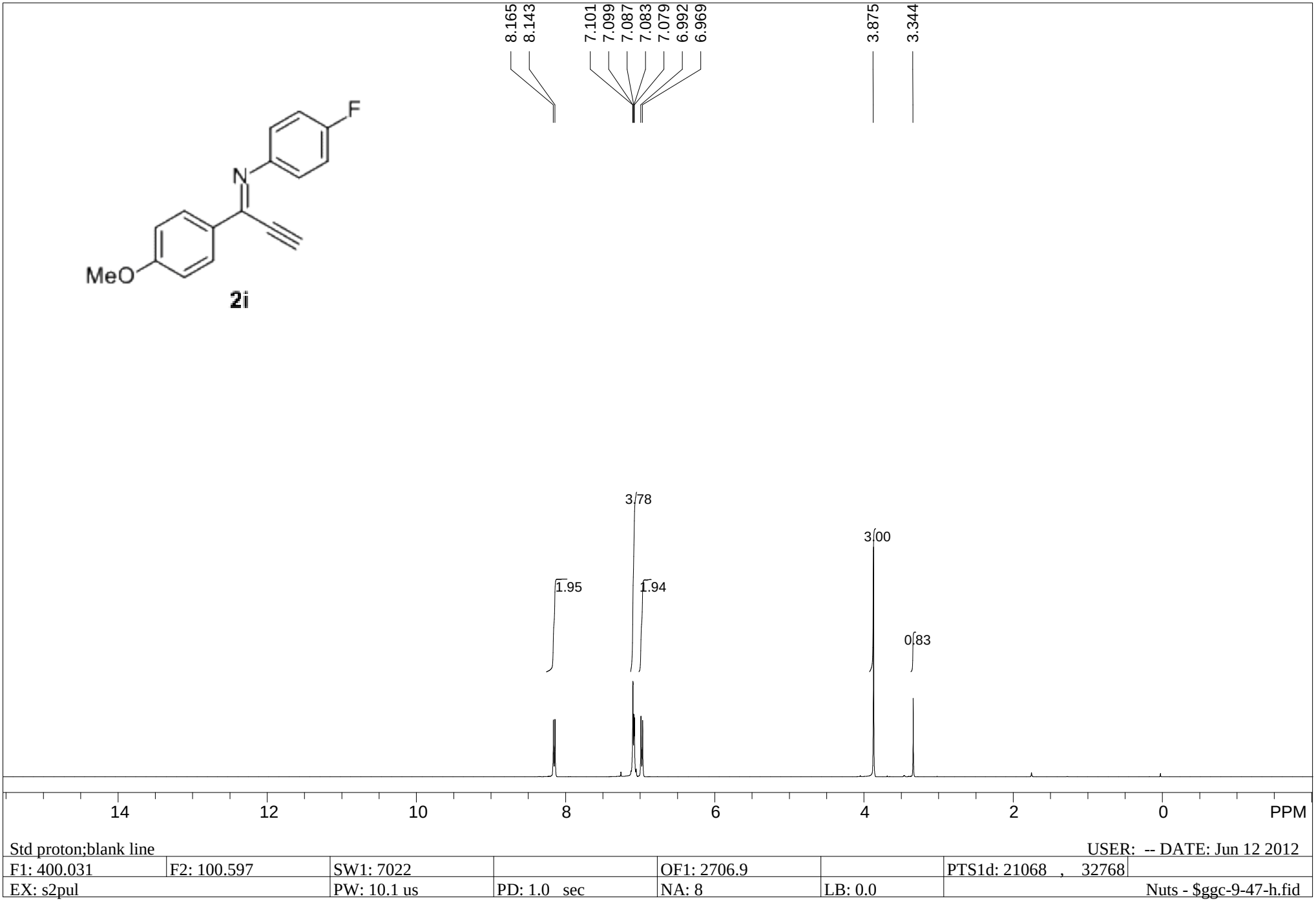

162.231
148.801
147.879
134.482
129.954
129.857
129.284
120.729
113.750
85.210
77.476
77.160
76.840
76.662
55.472
21.139
N
O
2e
200
150
100
50
0
PPM
Std carbon;blank line
USER: -- DATE: Jun 14 2012
F1: 100.598
F2: 400.031
SW1: 24510
OF1: 10565.4
PTS1d: 39216 , 65536
EX: s2pul
PW: 7.6 us
PD: 1.0 sec
NA: 40
LB: 0.0
Nuts - $ggc-9-50-C.fid

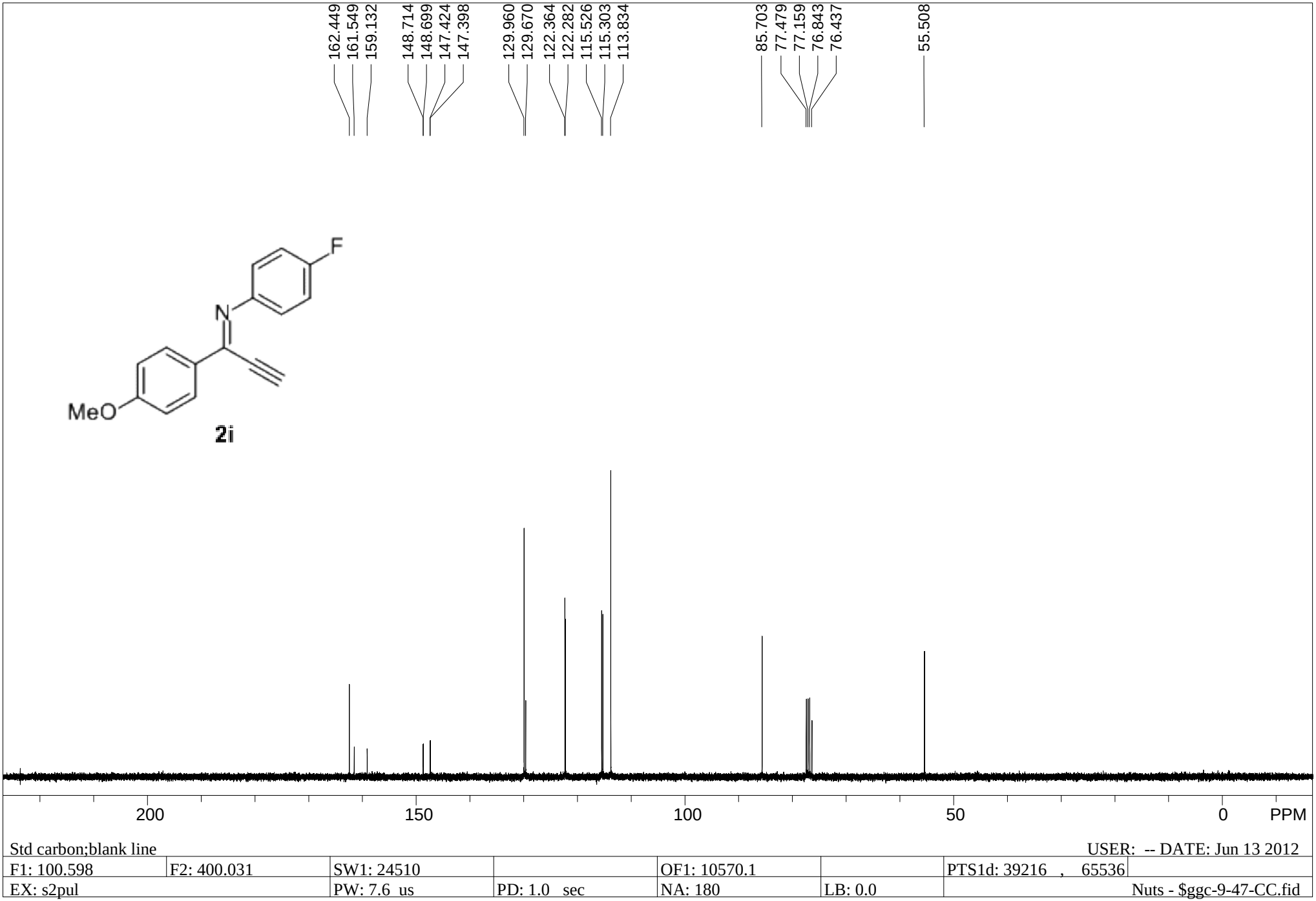



;blank line USER: -- DATE: Jun 11 2012

| | | | | | | |
|---|---|---|---|---|---|---|
| F1: 400.031 | F2: 100.597 | SW1: 7022 | | OF1: 2699.4 | | PTS1d: 22091 , 32768 |
| EX: s2pul | | PW: 10.3 us | PD: 1.0 sec | NA: 8 | LB: 0.0 | Nuts - $ggc-9-41-h.fid |

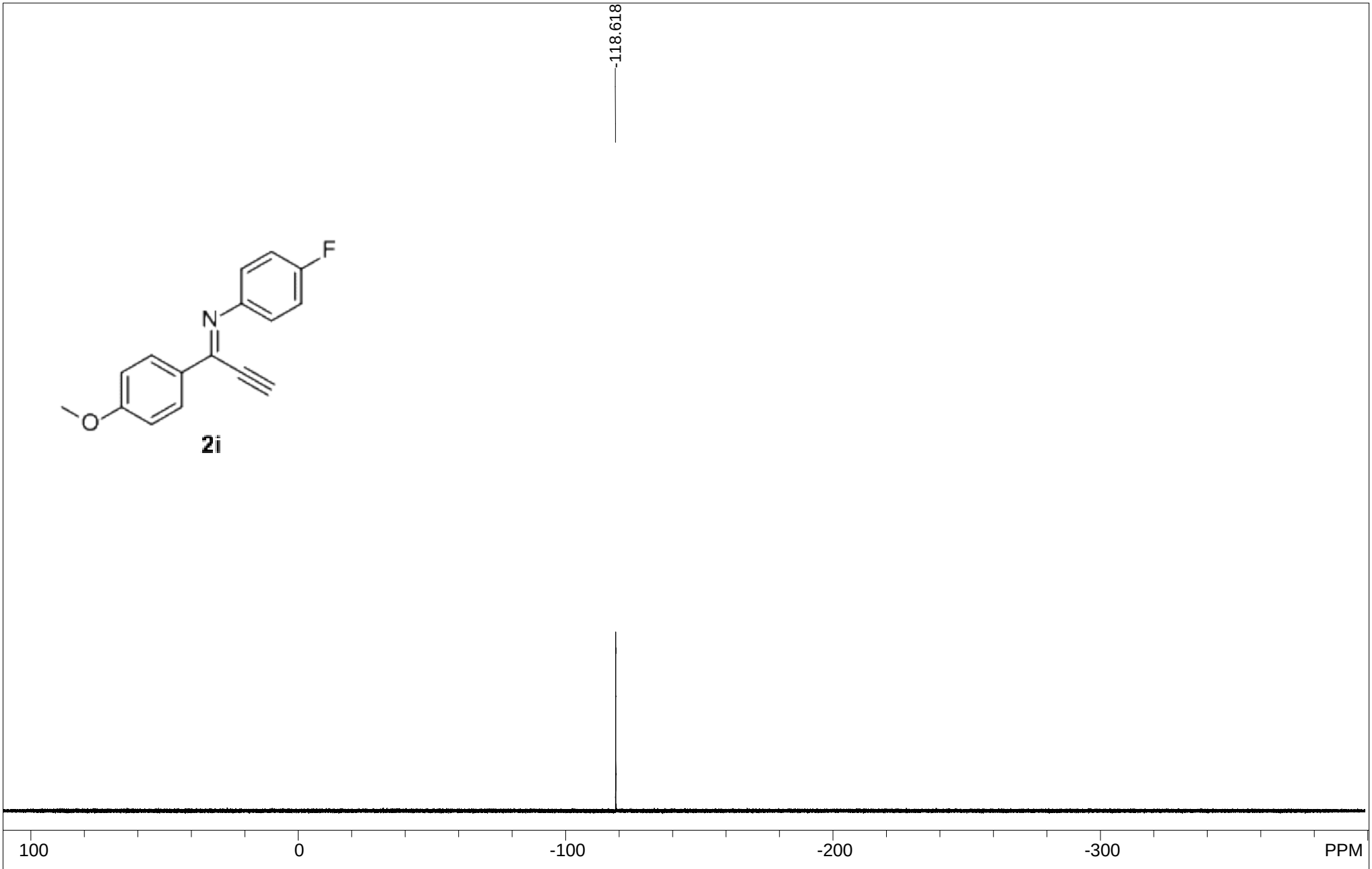

162.558
149.973
148.998
130.105
130.051
129.506
128.805
122.130
113.860
86.004
77.467
77.150
76.833
76.252
55.548
Cl
N
MeO
2h
200
150
100
50
0
PPM
Std carbon;blank line
USER: -- DATE: Jun 11 2012
F1: 100.598
F2: 400.031
SW1: 25510
OF1: 11074.3
PTS1d: 40816 , 65536
EX: s2pul
PW: 7.6 us
PD: 1.0 sec
NA: 48
LB: 0.0
Nuts - $ggc-9-41-C.fid


8.165
8.143
7.101
7.099
7.087
7.083
7.079
6.992
6.969
3.875
3.344
F
N
MeO
2i
3.78
3.00
1.95
1.94
0.83
14
12
10
8
6
4
2
0
PPM
Std proton;blank line
USER: -- DATE: Jun 12 2012
F1: 400.031
F2: 100.597
SW1: 7022
OF1: 2706.9
PTS1d: 21068 , 32768
EX: s2pul
PW: 10.1 us
PD: 1.0 sec
NA: 8
LB: 0.0
Nuts - $ggc-9-47-h.fid



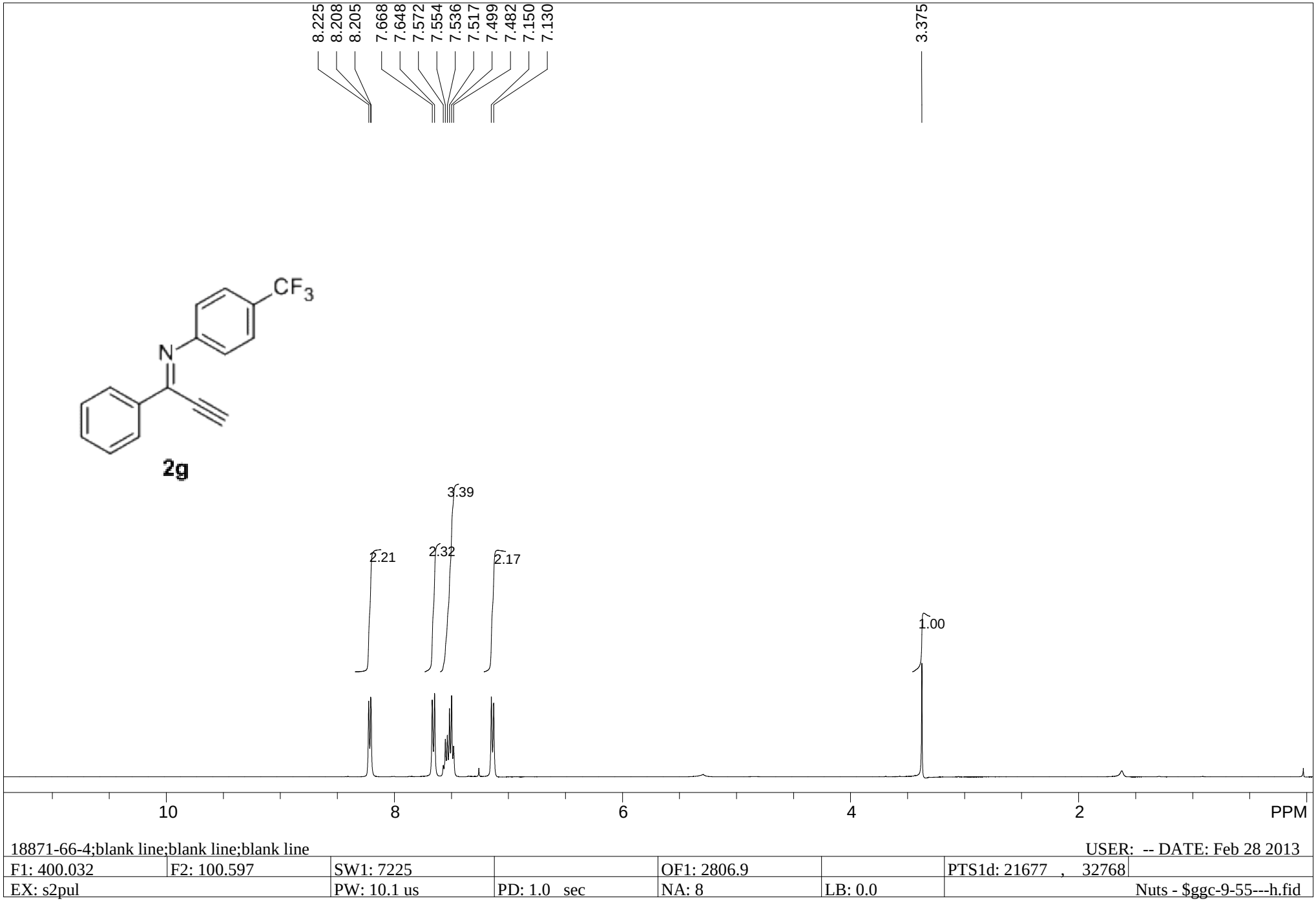

Std carbon;blank line USER: -- DATE: Jun 13 2012

| | | | | | | |
|---|---|---|---|---|---|---|
| F1: 100.598 | F2: 400.031 | SW1: 24510 | | OF1: 10570.1 | | PTS1d: 39216 , 65536 |
| EX: s2pul | | PW: 7.6 us | PD: 1.0 sec | NA: 180 | LB: 0.0 | Nuts - $ggc-9-47-CC.fid |



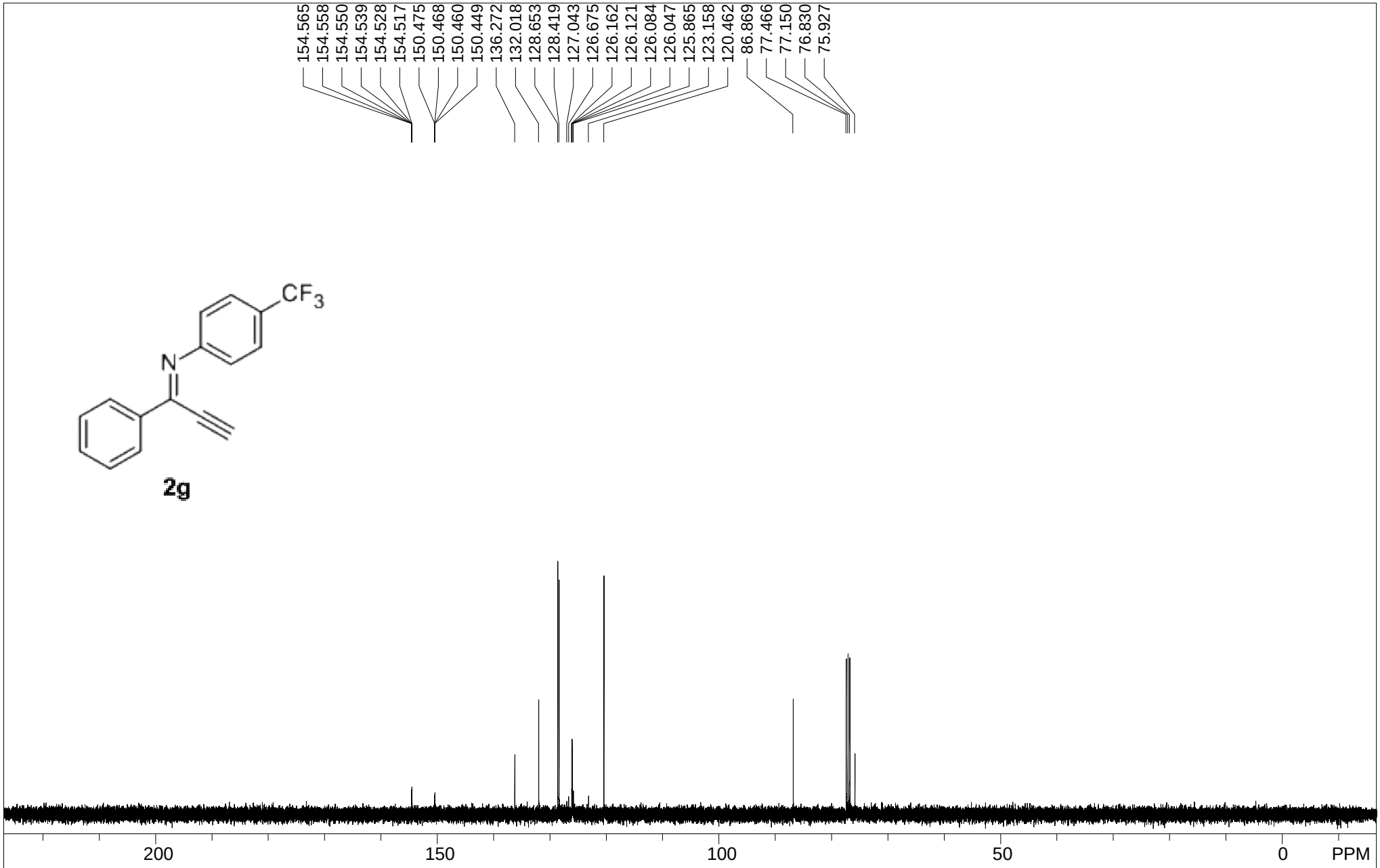

Std Fluorine USER: -- DATE: Mar 2 2013

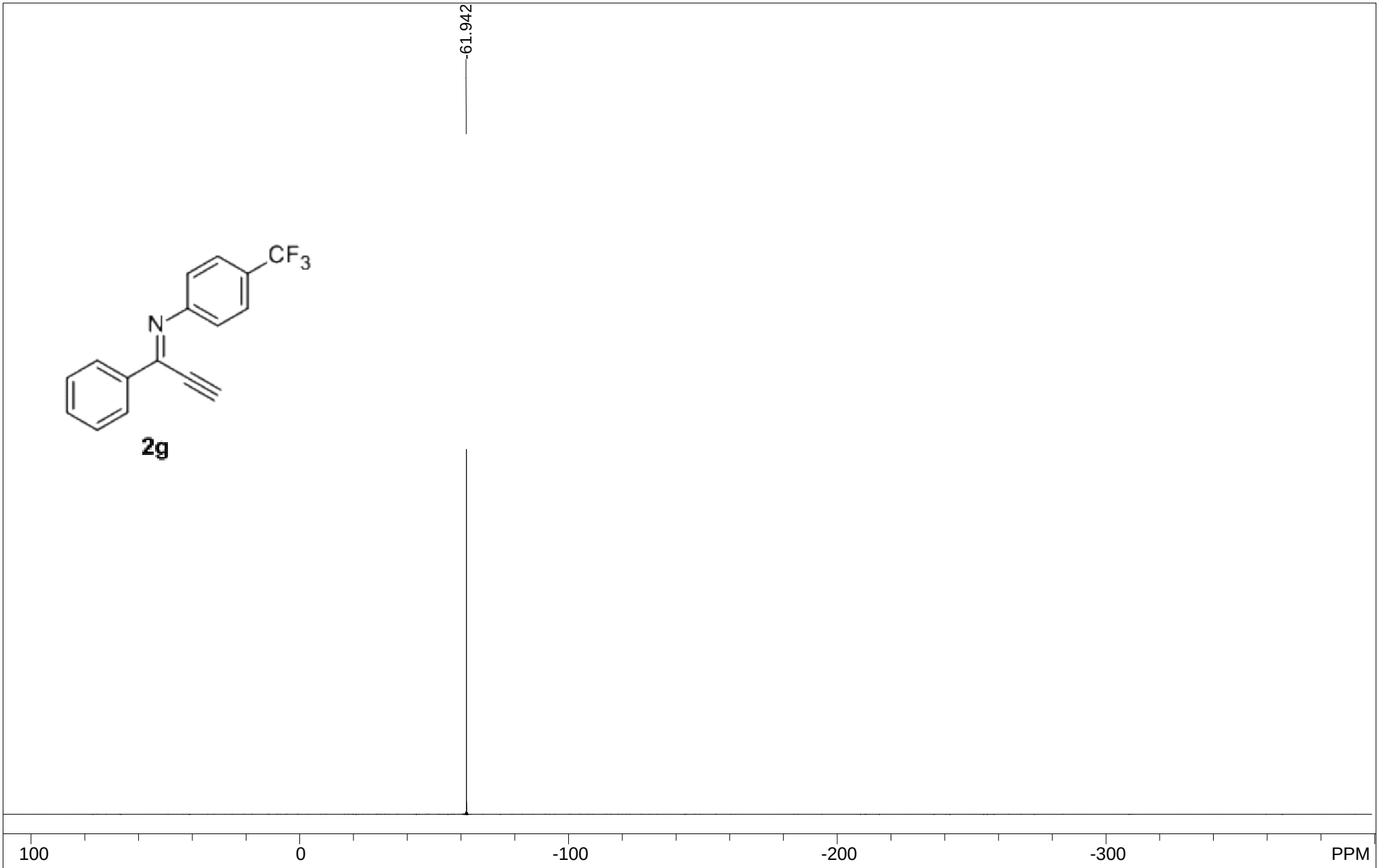
| | | | | | | |
|---|---|---|---|---|---|---|
| F1: 376.349 | F2: 100.597 | SW1: 192308 | | OF1: -54578.5 | | PTS1d: 192308 , 262144 |
| EX: s2pul | | PW: 6.1 us | PD: 3.0 sec | NA: 16 | LB: 0.0 | Nuts - $ggc-9-47--f.fid |




18871-66-4;blank line;blank line;blank line USER: -- DATE: Feb 28 2013

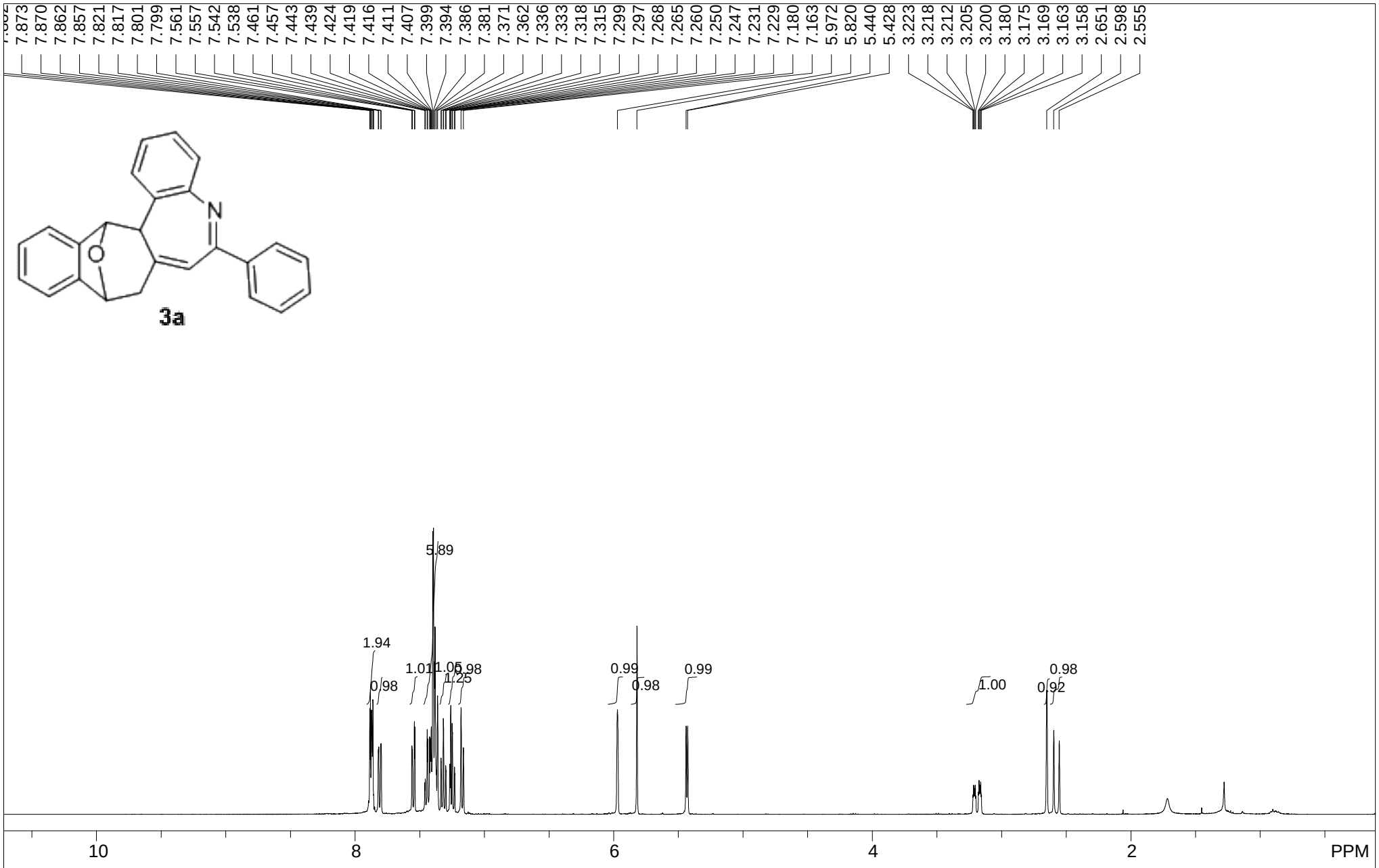
| | | | | | | |
|---|---|---|---|---|---|---|
| F1: 400.032 | F2: 100.597 | SW1: 7225 | | OF1: 2806.9 | | PTS1d: 21677 , 32768 |
| EX: s2pul | | PW: 10.1 us | PD: 1.0 sec | NA: 8 | LB: 0.0 | Nuts - $ggc-9-55---h.fid |


154.565
154.558
154.550
154.539
154.528
154.517
150.475
150.468
150.460
150.449
136.272
132.018
128.653
128.419
127.043
126.675
126.162
126.121
126.084
126.047
125.865
123.158
120.462
86.869
77.466
77.150
76.830
75.927
CF3
N
2g
200
150
100
50
0
PPM
2010573-21-23-1
USER: -- DATE: Feb 28 2013
F1: 100.598
F2: 400.031
SW1: 24510
OF1: 10576.7
PTS1d: 44118 , 65536
EX: s2pul
PW: 7.6 us
PD: 1.0 sec
NA: 80
LB: 0.0
Nuts - $ggc-9-55---C.fid




Std Fluorine USER: -- DATE: Feb 28 2013

| | | | | | | |
|---|---|---|---|---|---|---|
| F1: 376.349 | F2: 100.597 | SW1: 192308 | | OF1: -54578.5 | | PTS1d: 192308 , 262144 |
| EX: s2pul | | PW: 6.1 us | PD: 3.0 sec | NA: 4 | LB: 0.0 | Nuts - $ggc-9-55---f.fid |

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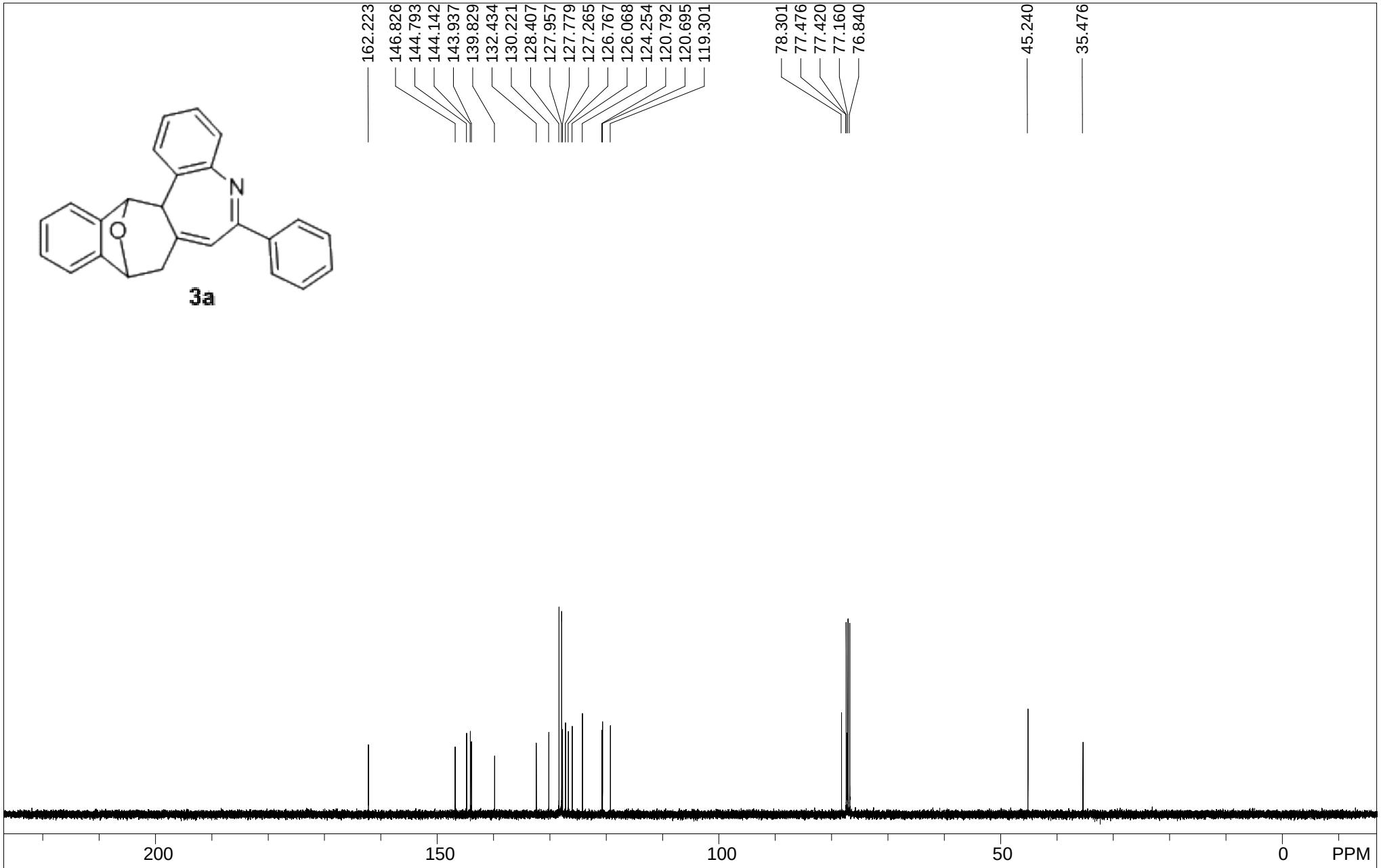
USER: -- DATE: Apr 29 2012

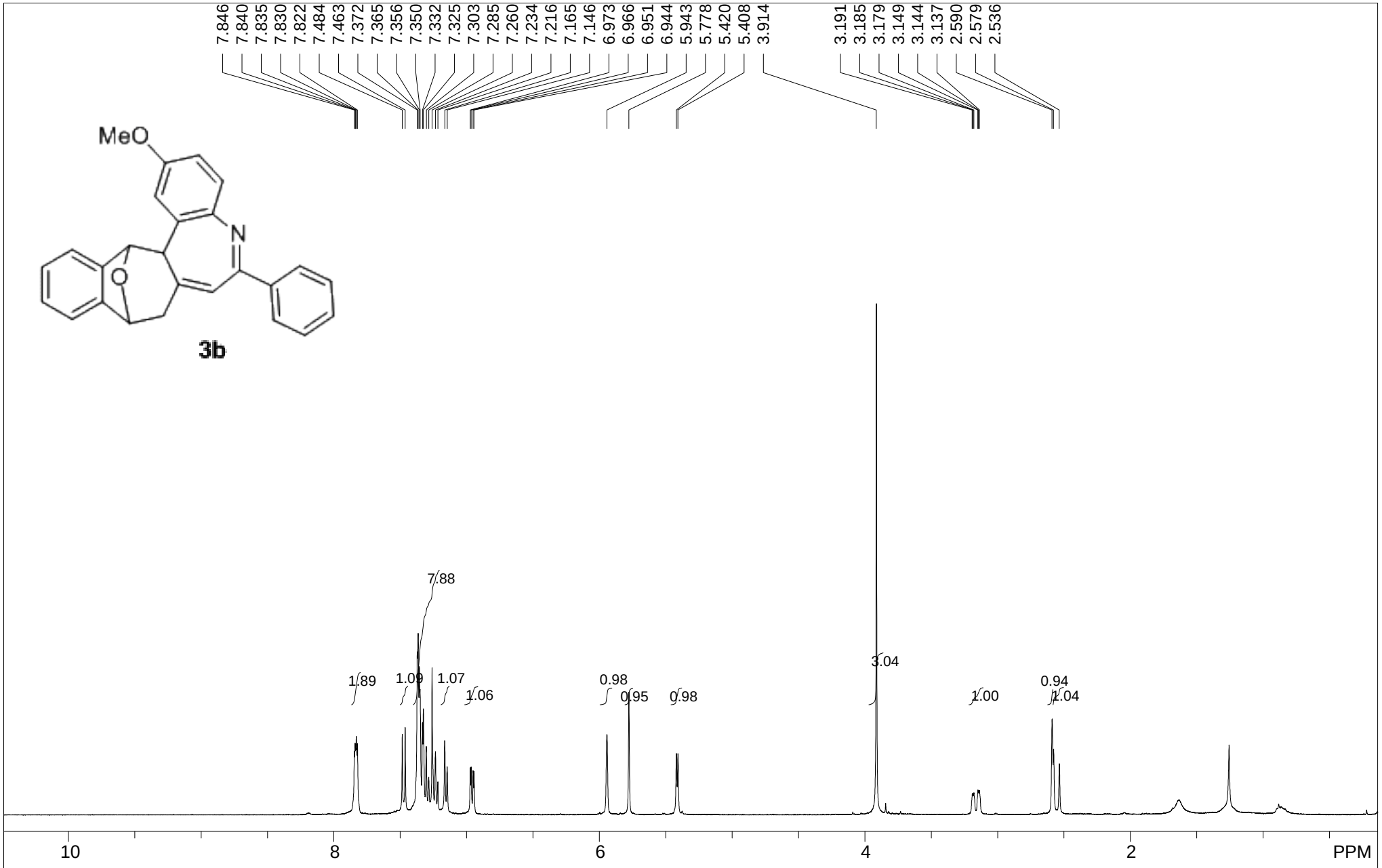
| | | | | | | |
|---|---|---|---|---|---|---|
| F1: 400.031 | F2: 100.597 | SW1: 6410 | | OF1: 2407.4 | | PTS1d: 19231 , 32768 |
| EX: s2pul | | PW: 10.3 us | PD: 2.0 sec | NA: 24 | LB: 0.0 | Nuts - $ggc-8-86b---h.fid |

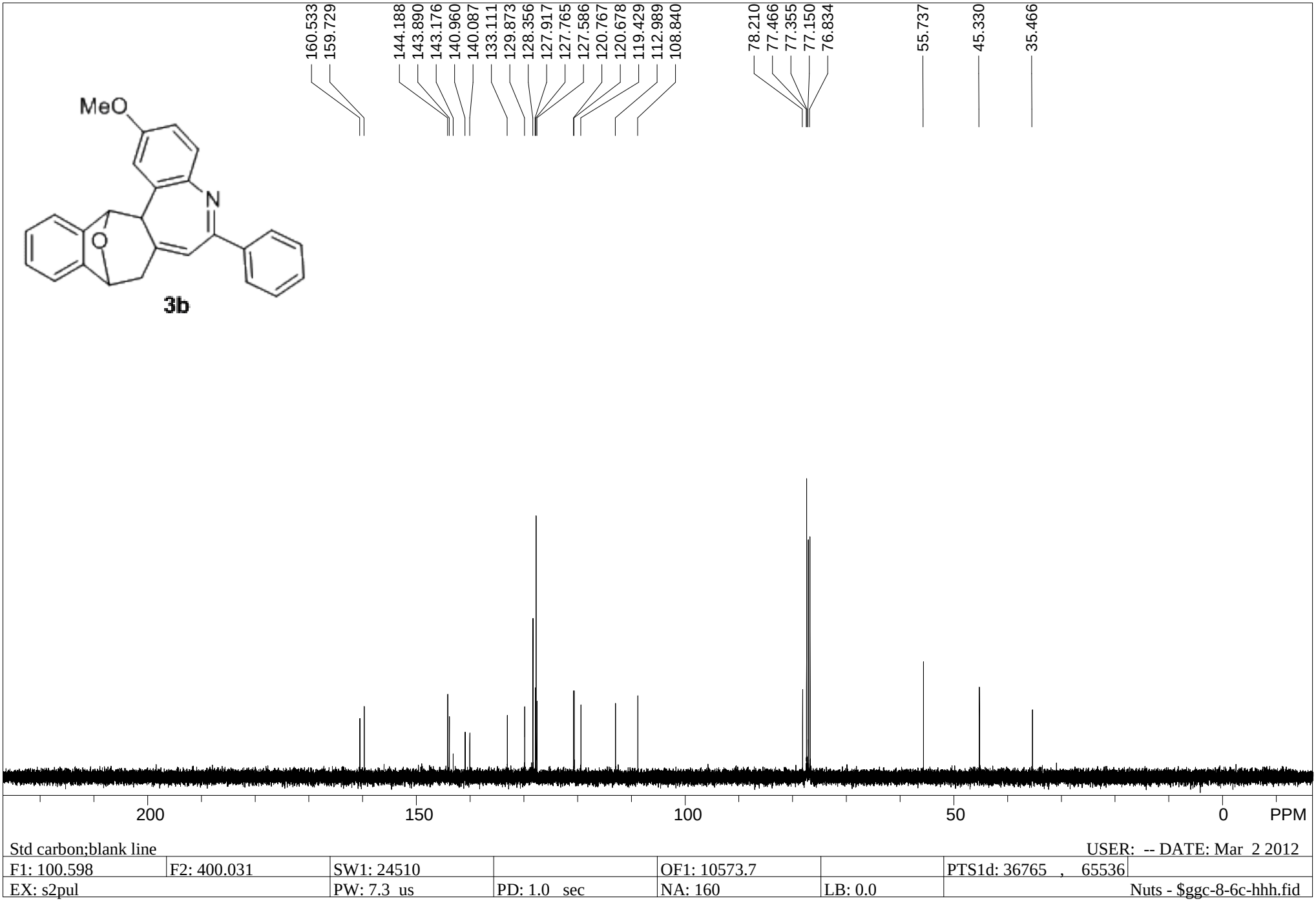


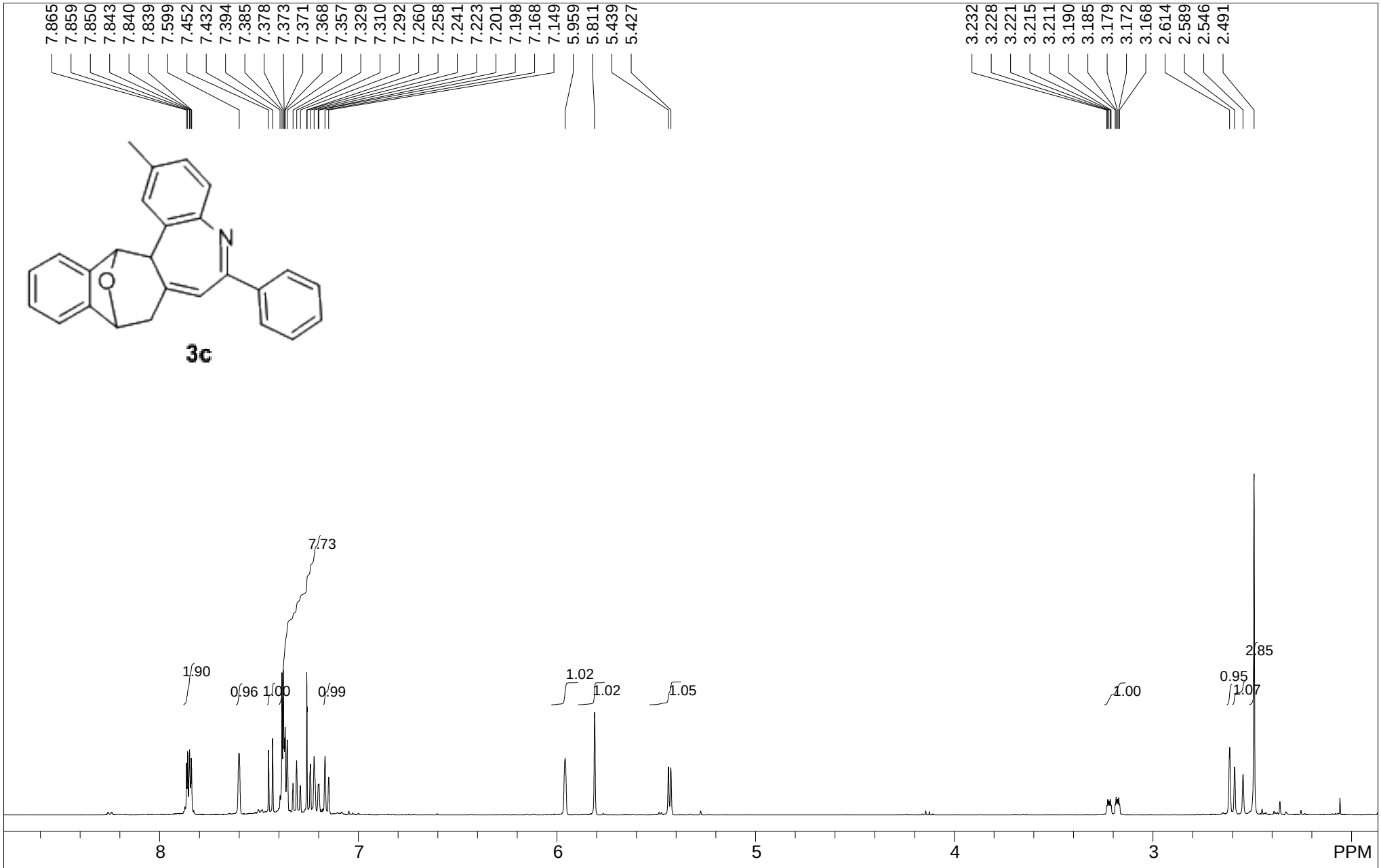

Std carbon;blank line

USER: -- DATE: Apr 29 2012

| | | | | | | |
|---|---|---|---|---|---|---|
| F1: 100.598 | F2: 400.031 | SW1: 24510 | | OF1: 10573.2 | | PTS1d: 39216 , 65536 |
| EX: s2pul | | PW: 7.3 us | PD: 1.0 sec | NA: 400 | LB: 0.0 | Nuts - $ggc-8-86b---C-5.fid |


7.846
7.840
7.835
7.830
7.822
7.484
7.463
7.372
7.365
7.356
7.350
7.332
7.325
7.303
7.285
7.260
7.234
7.216
7.165
7.146
6.973
6.966
6.951
6.944
5.943
5.778
5.420
5.408
3.914
3.191
3.185
3.179
3.149
3.144
3.137
2.590
2.579
2.536
MeO
N
O
3b
7.88
1.89
1.09
1.07
1.06
0.98
0.95
0.98
3.04
1.00
0.94
1.04
10
8
6
4
2
PPM
Std proton;blank line
USER: -- DATE: Apr 20 2012
F1: 400.032
F2: 100.597
SW1: 7143
OF1: 2767.2
PTS1d: 21429 , 32768
EX: s2pul
PW: 10.3 us
PD: 1.0 sec
NA: 28
LB: 0.0
Nuts - $ggc-8-6----hhh.fid


160.533
159.729
144.188
143.890
143.176
140.960
140.087
133.111
129.873
128.356
127.917
127.765
127.586
120.767
120.678
119.429
112.989
108.840
78.210
77.466
77.355
77.150
76.834
55.737
45.330
35.466
MeO
N
O
3b
200
150
100
50
0
PPM
Std carbon;blank line
USER: -- DATE: Mar 2 2012
F1: 100.598
F2: 400.031
SW1: 24510
OF1: 10573.7
PTS1d: 36765 , 65536
EX: s2pul
PW: 7.3 us
PD: 1.0 sec
NA: 160
LB: 0.0
Nuts - $ggc-8-6c-hhh.fid

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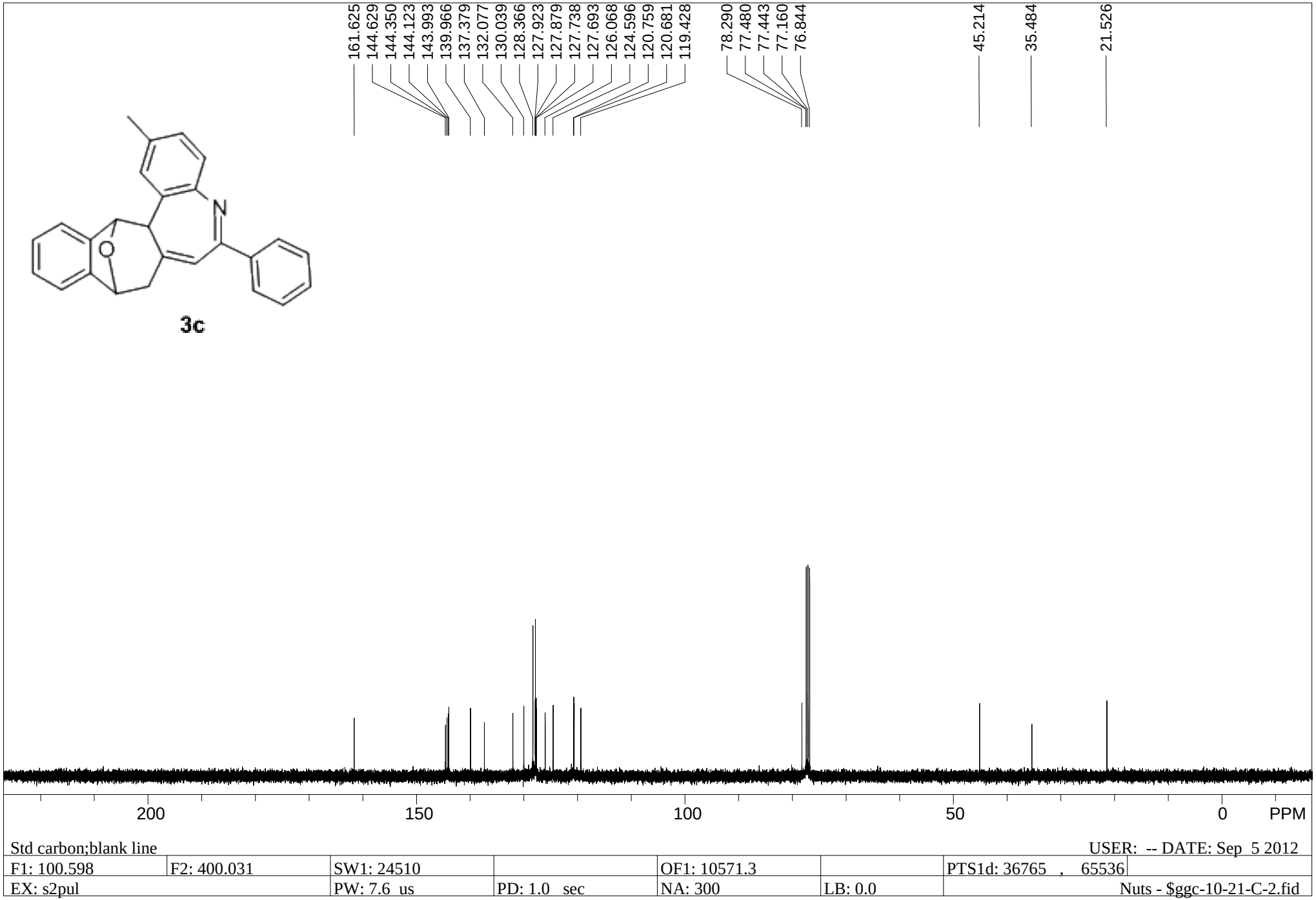
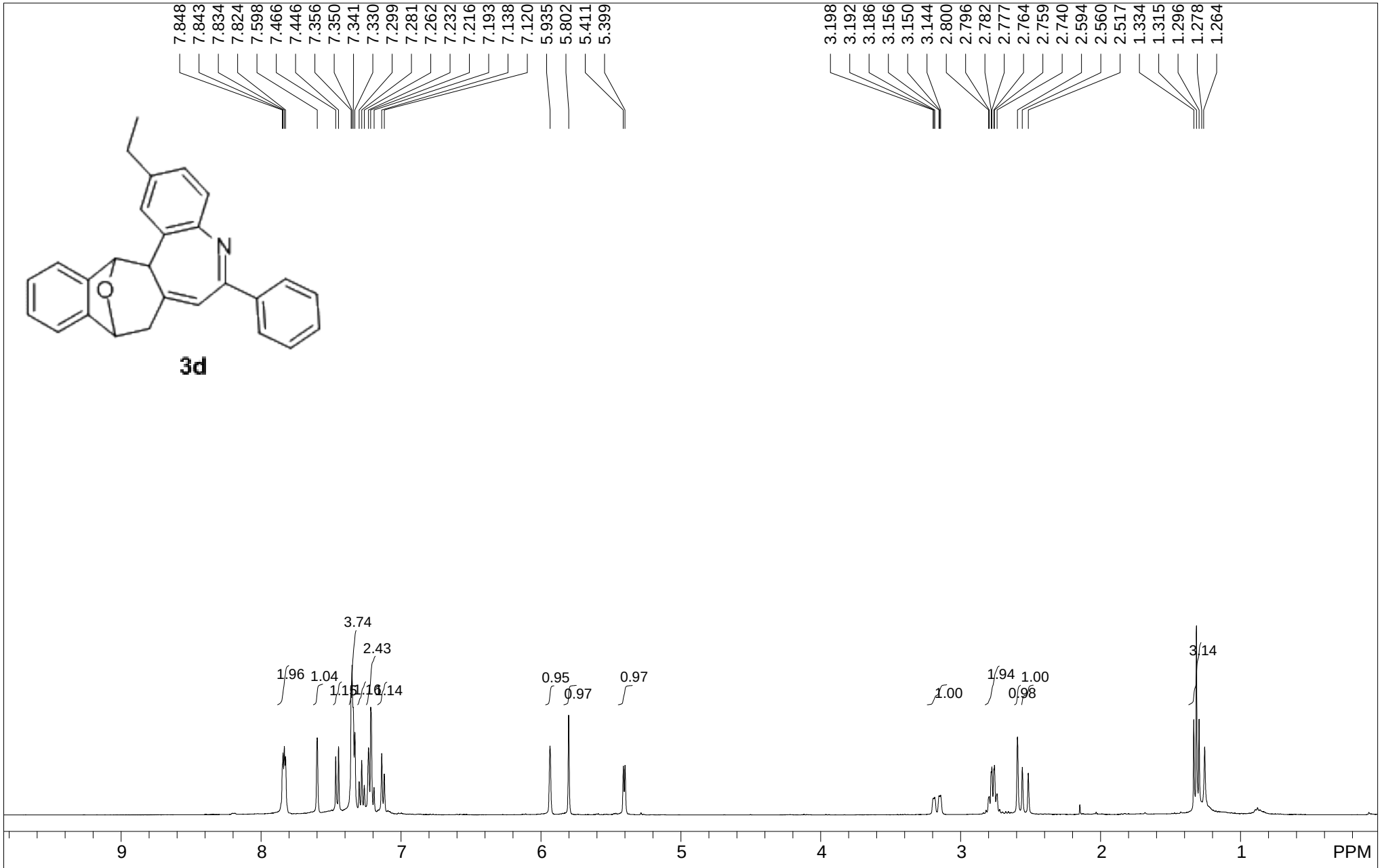
USER: -- DATE: Sep 7 2012

| | | | | | | |
|---|---|---|---|---|---|---|
| F1: 400.031 | F2: 100.597 | SW1: 7022 | | OF1: 2707.0 | | PTS1d: 21068 , 32768 |
| EX: s2pul | | PW: 10.1 us | PD: 1.0 sec | NA: 12 | LB: 0.0 | Nuts - $ggc-10-21-h-3.fid |


161.625
144.629
144.350
144.123
143.993
139.966
137.379
132.077
130.039
128.366
127.923
127.879
127.738
127.693
126.068
124.596
120.759
120.681
119.428
78.290
77.480
77.443
77.160
76.844
45.214
35.484
21.526
O
N
3c
200
150
100
50
0
PPM
Std carbon;blank line
USER: -- DATE: Sep 5 2012
F1: 100.598
F2: 400.031
SW1: 24510
OF1: 10571.3
PTS1d: 36765 , 65536
EX: s2pul
PW: 7.6 us
PD: 1.0 sec
NA: 300
LB: 0.0
Nuts - $ggc-10-21-C-2.fid

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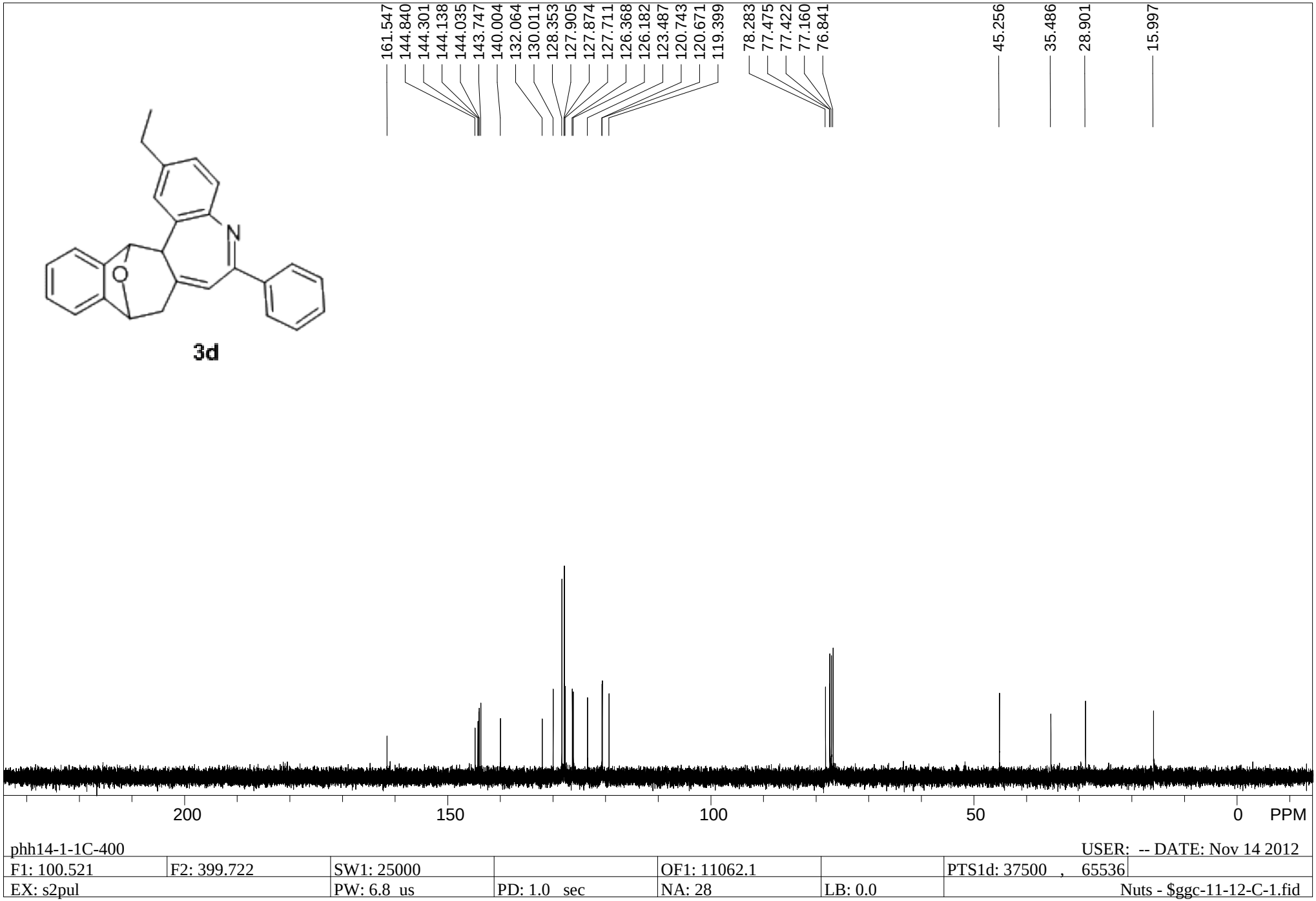
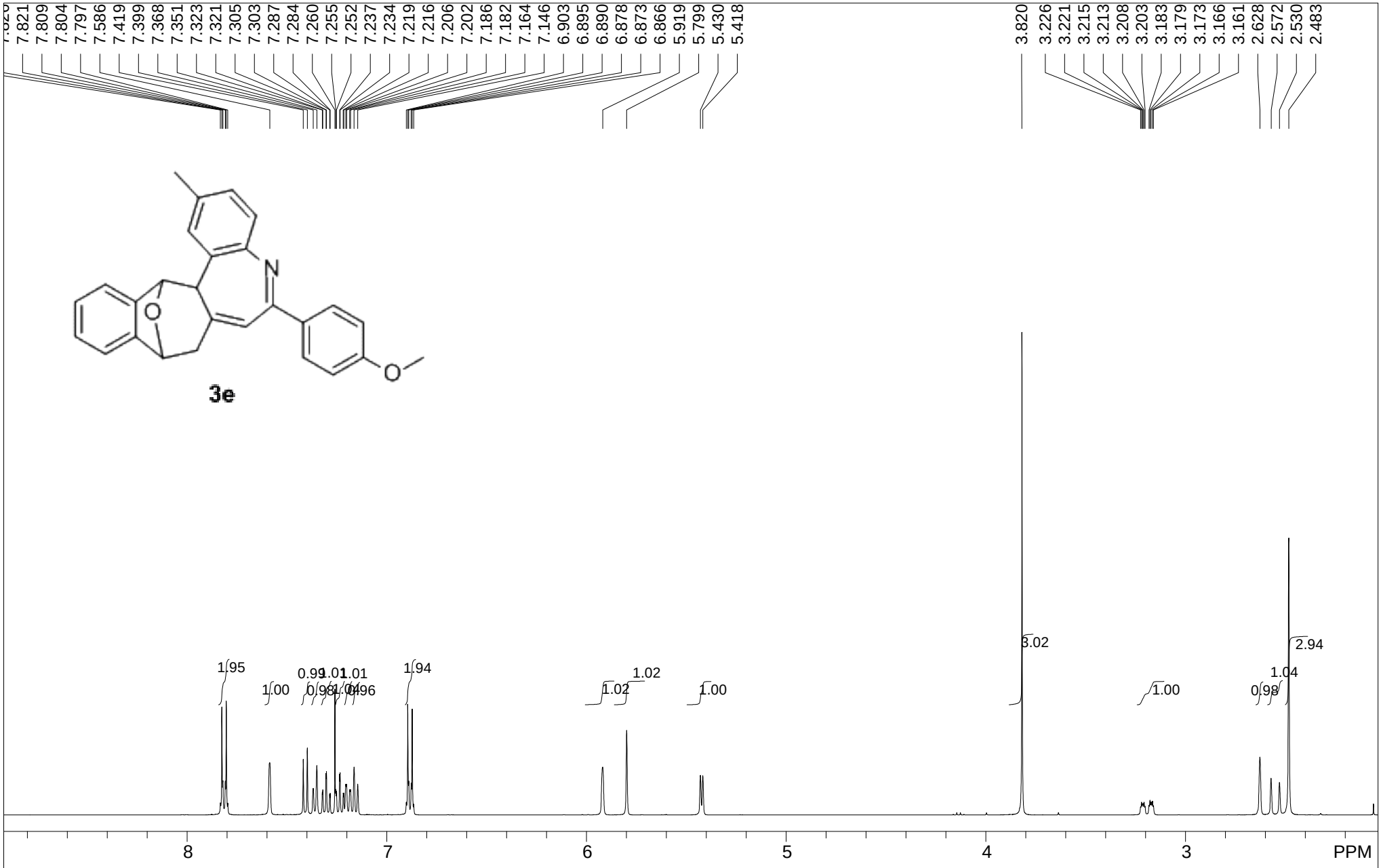
| | | | | | | |
|---|---|---|---|---|---|---|
| F1: 399.723 | F2: 100.519 | SW1: 7184 | | OF1: 2781.3 | | PTS1d: 21552 , 32768 |
| EX: s2pul | | PW: 7.8 us | PD: 1.0 sec | NA: 16 | LB: 0.0 | Nuts - $ggc-11-12-h-.fid |

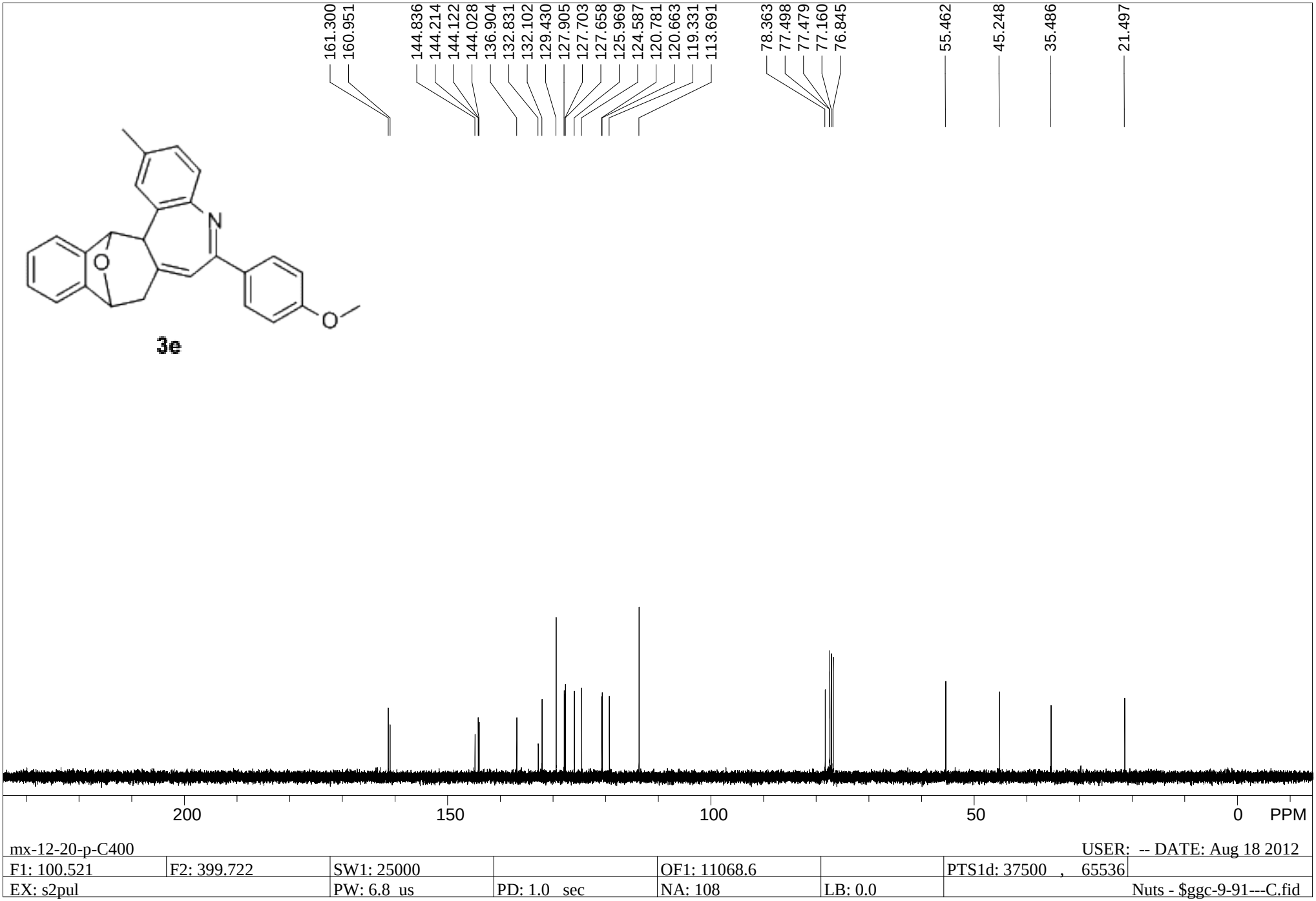


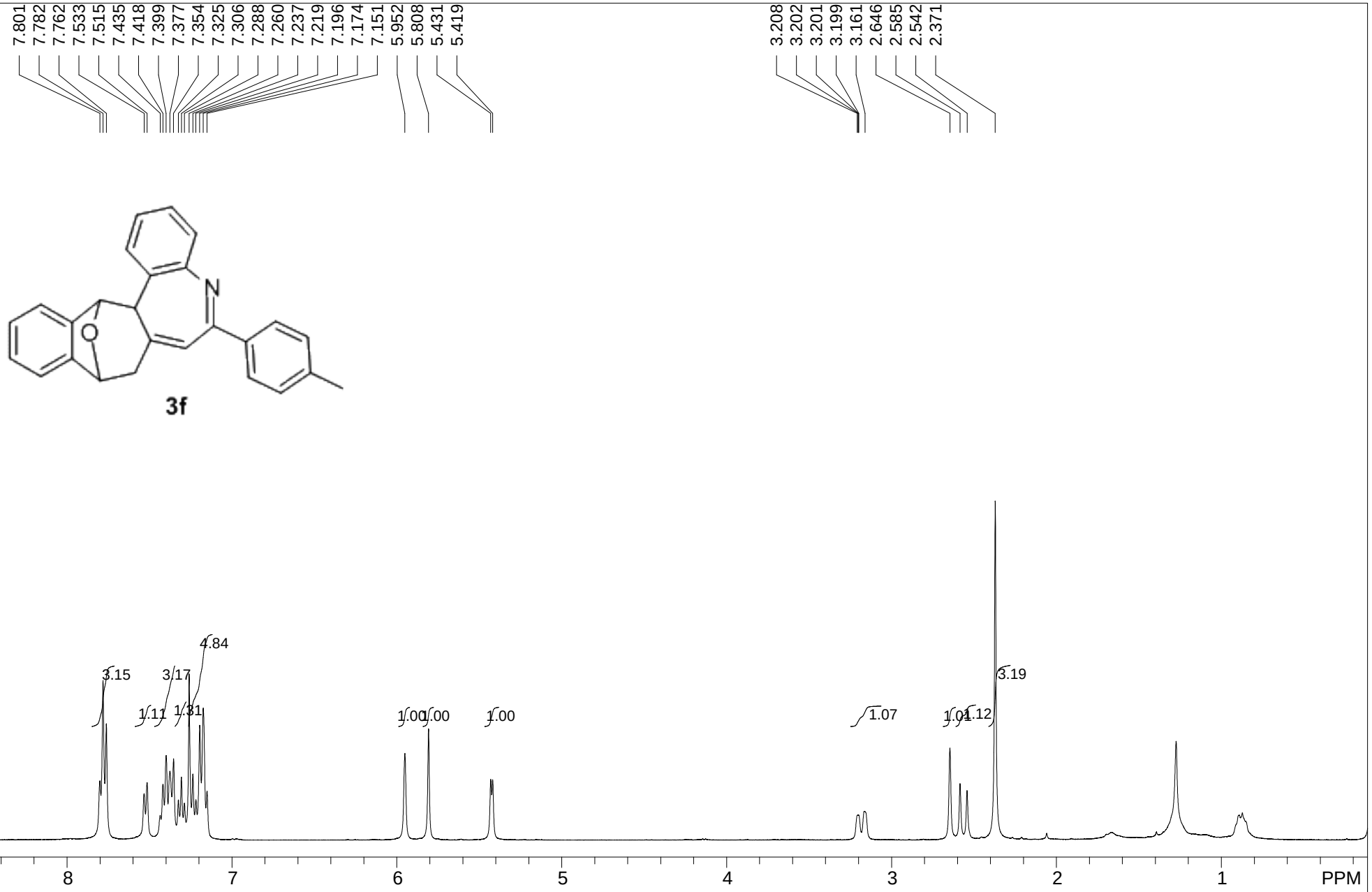

phh14-1-1C-400 USER: -- DATE: Nov 14 2012

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| F1: 100.521 | F2: 399.722 | SW1: 25000 | | OF1: 11062.1 | | PTS1d: 37500 , 65536 | |
| EX: s2pul | | PW: 6.8 us | PD: 1.0 sec | NA: 28 | LB: 0.0 | Nuts - $ggc-11-12-C-1.fid | |




| | | | | | | | |
|---|---|---|---|---|---|---|---|
| mx-12-20-p-h | | | | | | USER: -- DATE: Aug 18 2012 | |
| F1: 399.723 | F2: 100.519 | SW1: 6793 | | OF1: 3366.5 | | PTS1d: 20380 , 32768 | |
| EX: s2pul | | PW: 7.0 us | PD: 1.0 sec | NA: 24 | LB: 0.0 | | Nuts - $ggc-9-91-h4.fid |


161.300
160.951
144.836
144.214
144.122
144.028
136.904
132.831
132.102
129.430
127.905
127.703
127.658
125.969
124.587
120.781
120.663
119.331
113.691
78.363
77.498
77.479
77.160
76.845
55.462
45.248
35.486
21.497
N
O
O
3e
200
150
100
50
0
PPM
mx-12-20-p-C400
USER: -- DATE: Aug 18 2012
F1: 100.521
F2: 399.722
SW1: 25000
OF1: 11068.6
PTS1d: 37500 , 65536
EX: s2pul
PW: 6.8 us
PD: 1.0 sec
NA: 108
LB: 0.0
Nuts - $ggc-9-91---C.fid

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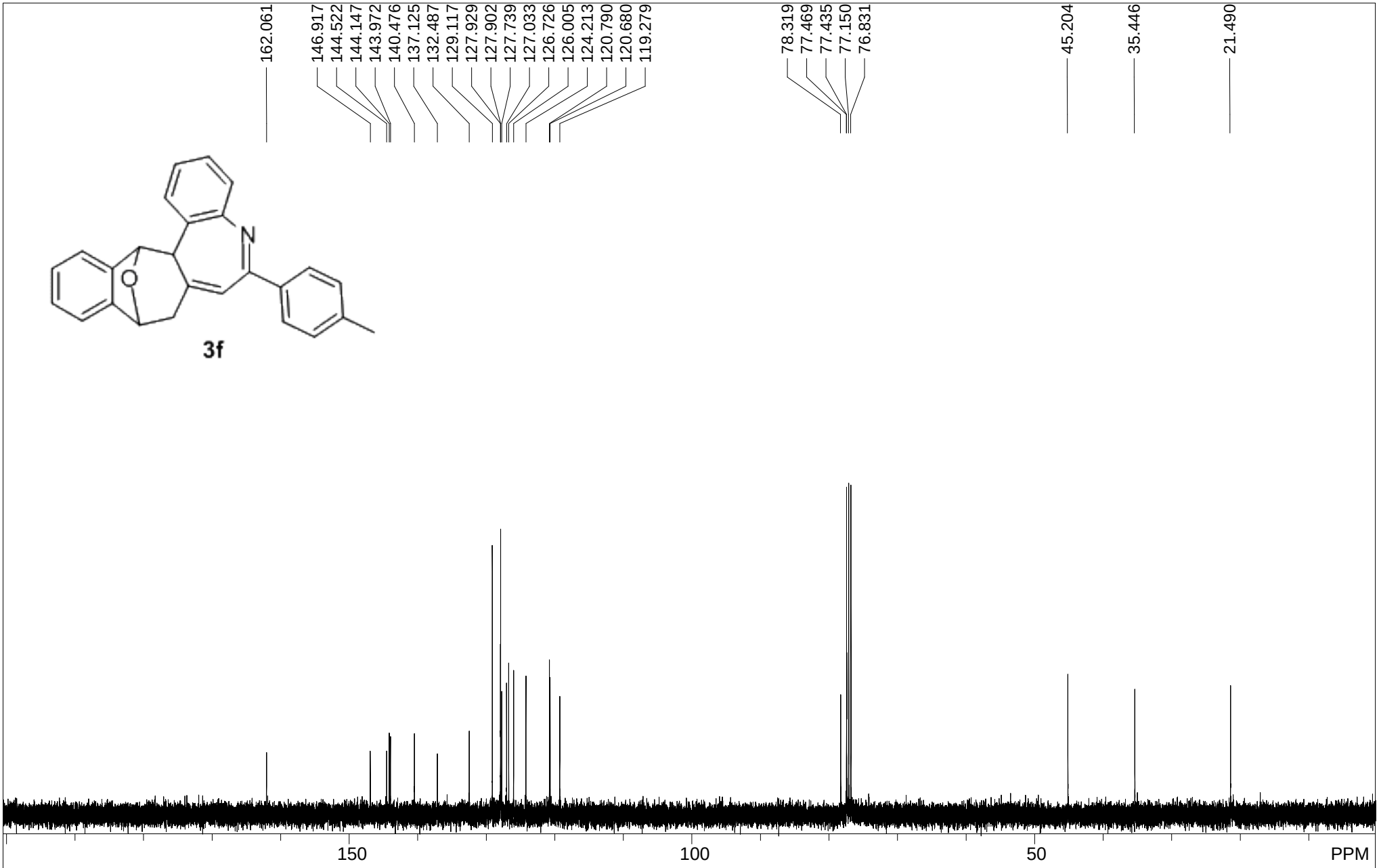
| | | | | | | |
|---|---|---|---|---|---|---|
| F1: 399.723 | F2: 100.519 | SW1: 7184 | | OF1: 2798.5 | | PTS1d: 21552 , 32768 |
| EX: s2pul | | PW: 6.3 us | PD: 1.0 sec | NA: 8 | LB: 0.0 | Nuts - $ggc-16-14--4-h.fid |

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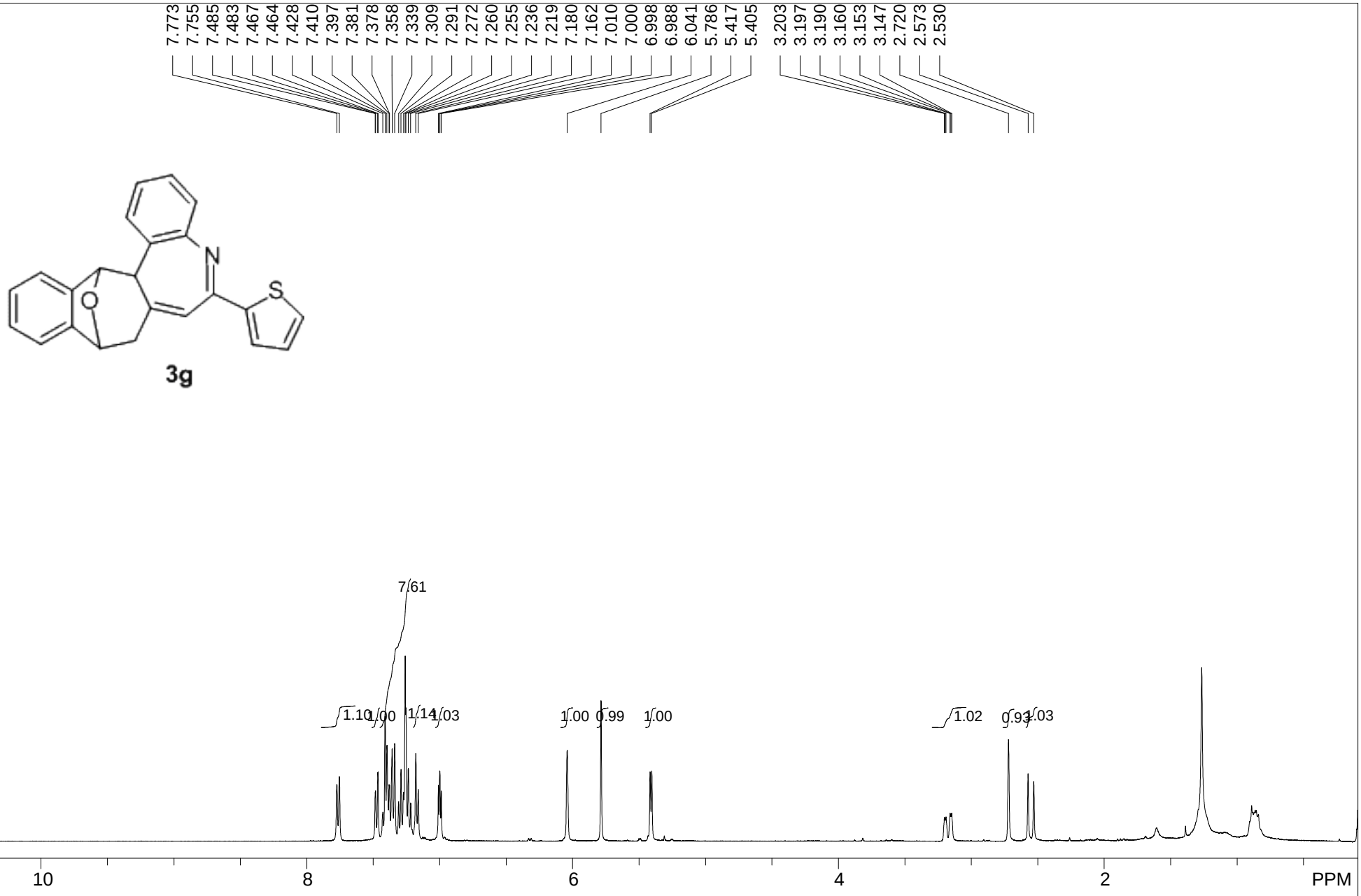
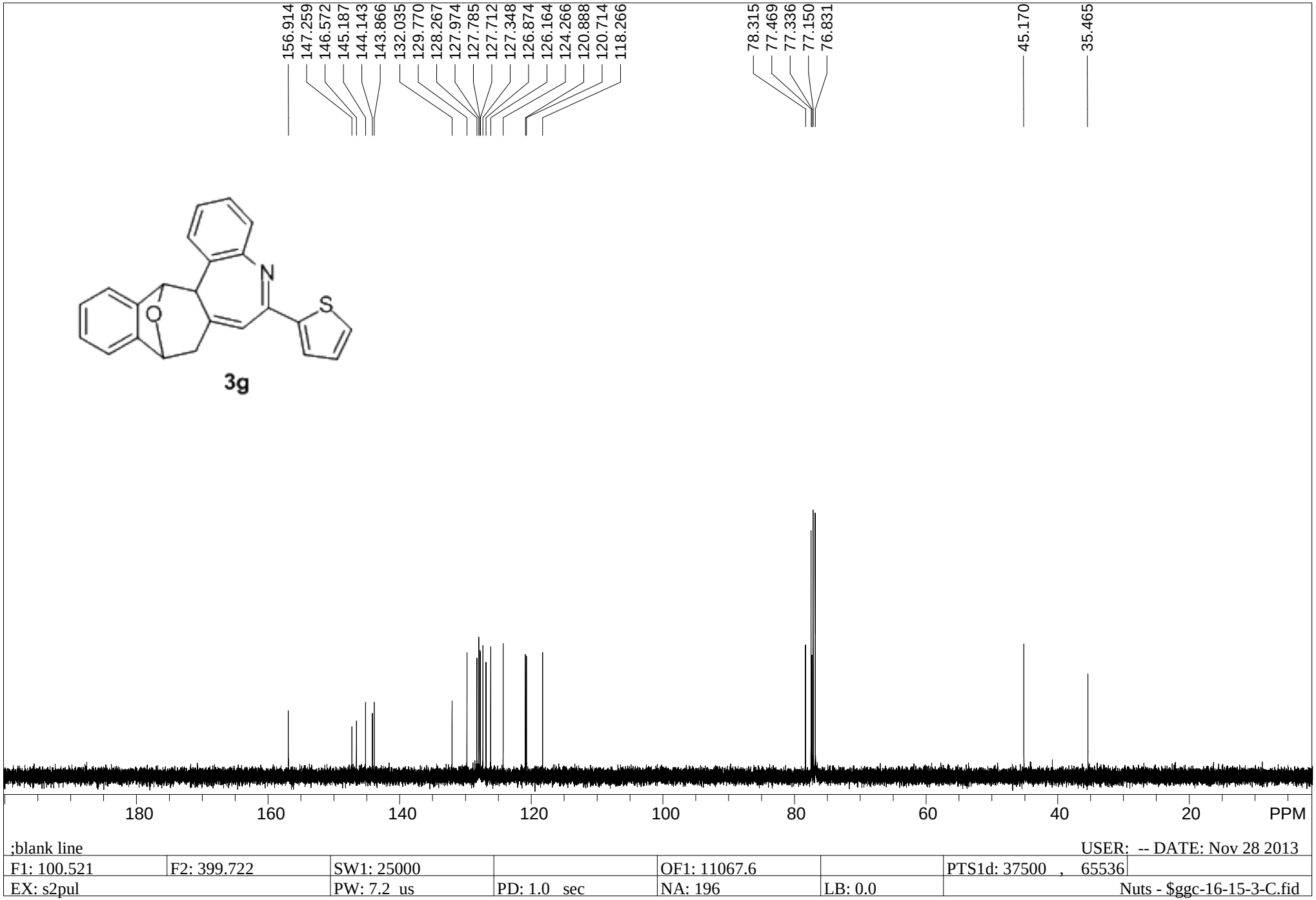
USER: -- DATE: Nov 28 2013

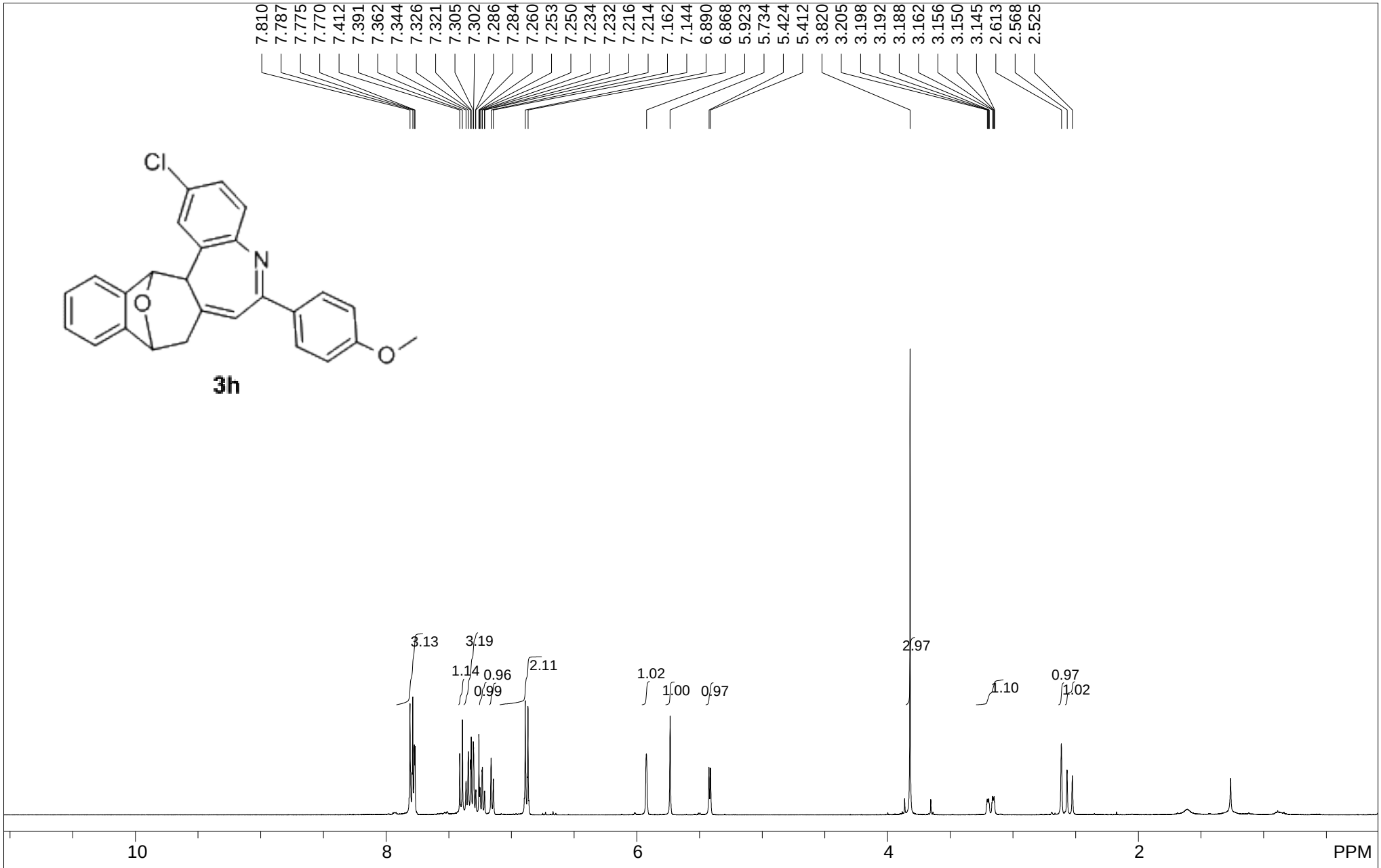
| | | | | | | | |
|---|---|---|---|---|---|---|---|
| F1: 100.521 | F2: 399.722 | SW1: 25000 | | OF1: 11066.9 | | PTS1d: 37500 , 65536 | |
| EX: s2pul | | PW: 7.2 us | PD: 1.0 sec | NA: 240 | LB: 0.0 | | Nuts - $ggc-16-14-3-C.fid |

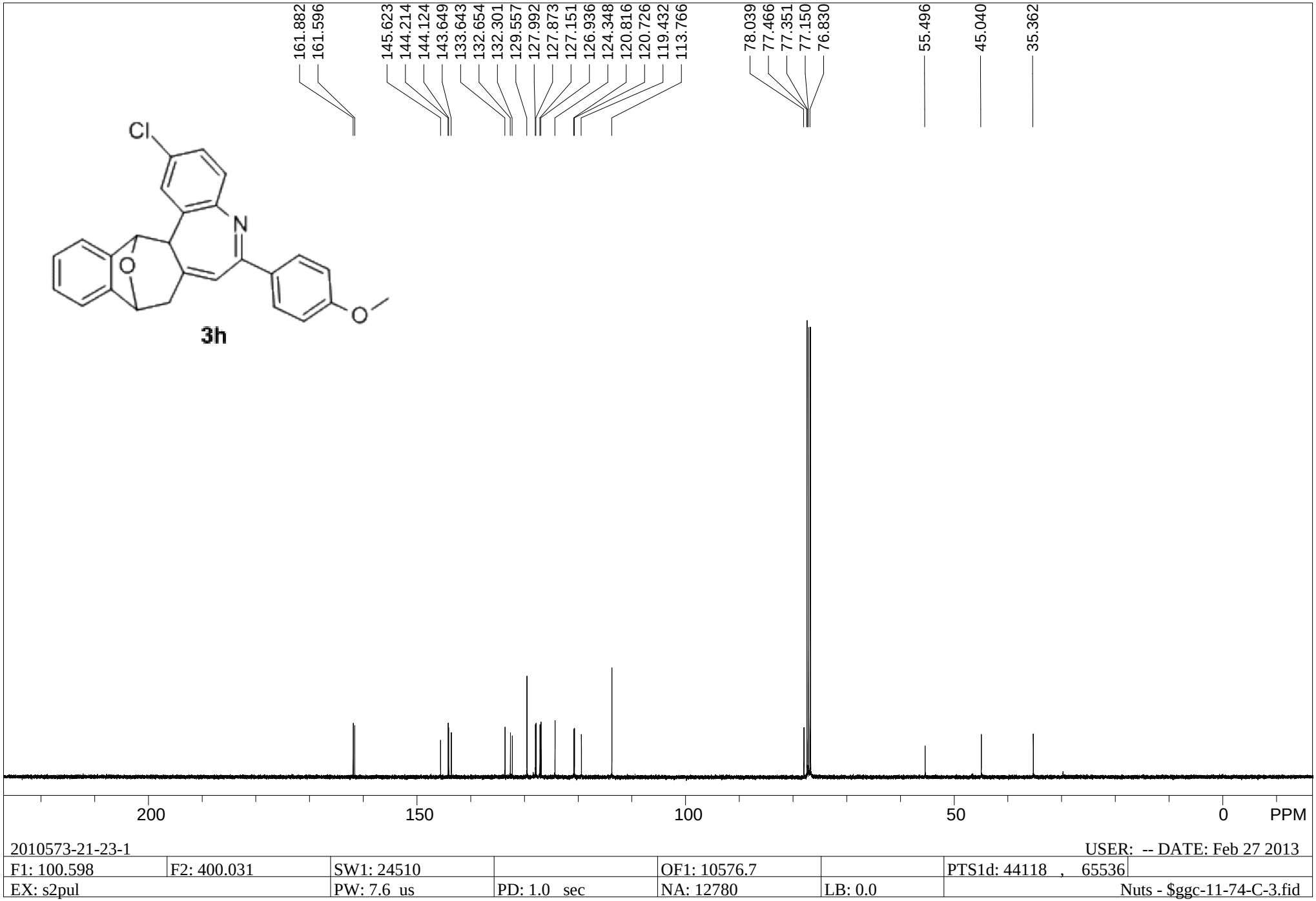


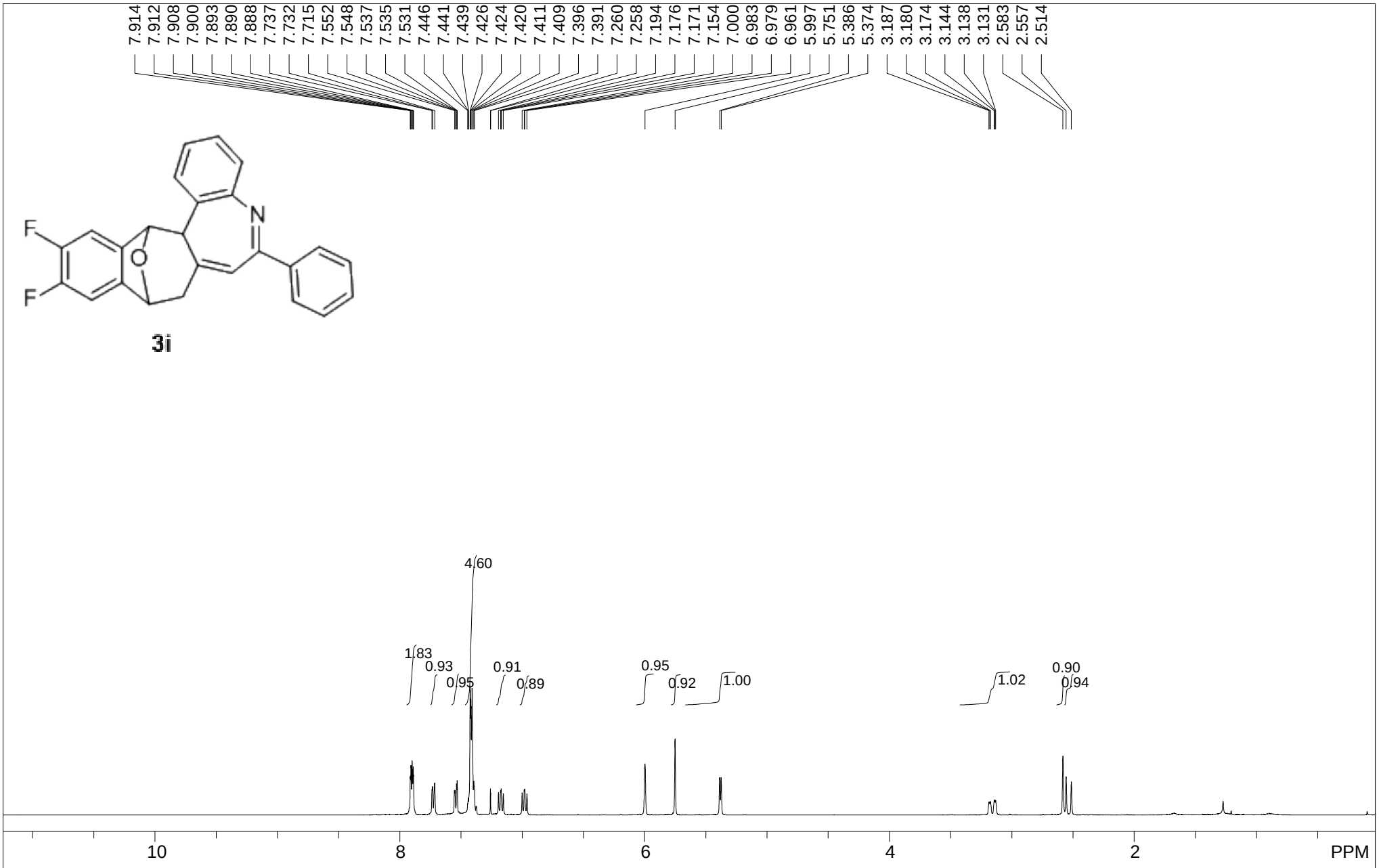

;blank line USER: -- DATE: Nov 28 2013

| | | | | | | |
|---|---|---|---|---|---|---|
| F1: 399.723 | F2: 100.519 | SW1: 7184 | | OF1: 2798.4 | | PTS1d: 21552 , 32768 |
| EX: s2pul | | PW: 6.3 us | PD: 1.0 sec | NA: 12 | LB: 0.0 | Nuts - $ggc-16-15---4-h.fid |


156.914
147.259
146.572
145.187
144.143
143.866
132.035
129.770
128.267
127.974
127.785
127.712
127.348
126.874
126.164
124.266
120.888
120.714
118.266
78.315
77.469
77.336
77.150
76.831
45.170
35.465
N
O
S
3g
180
160
140
120
100
80
60
40
20
PPM
;blank line
USER: -- DATE: Nov 28 2013
F1: 100.521
F2: 399.722
SW1: 25000
OF1: 11067.6
PTS1d: 37500 , 65536
EX: s2pul
PW: 7.2 us
PD: 1.0 sec
NA: 196
LB: 0.0
Nuts - $ggc-16-15-3-C.fid

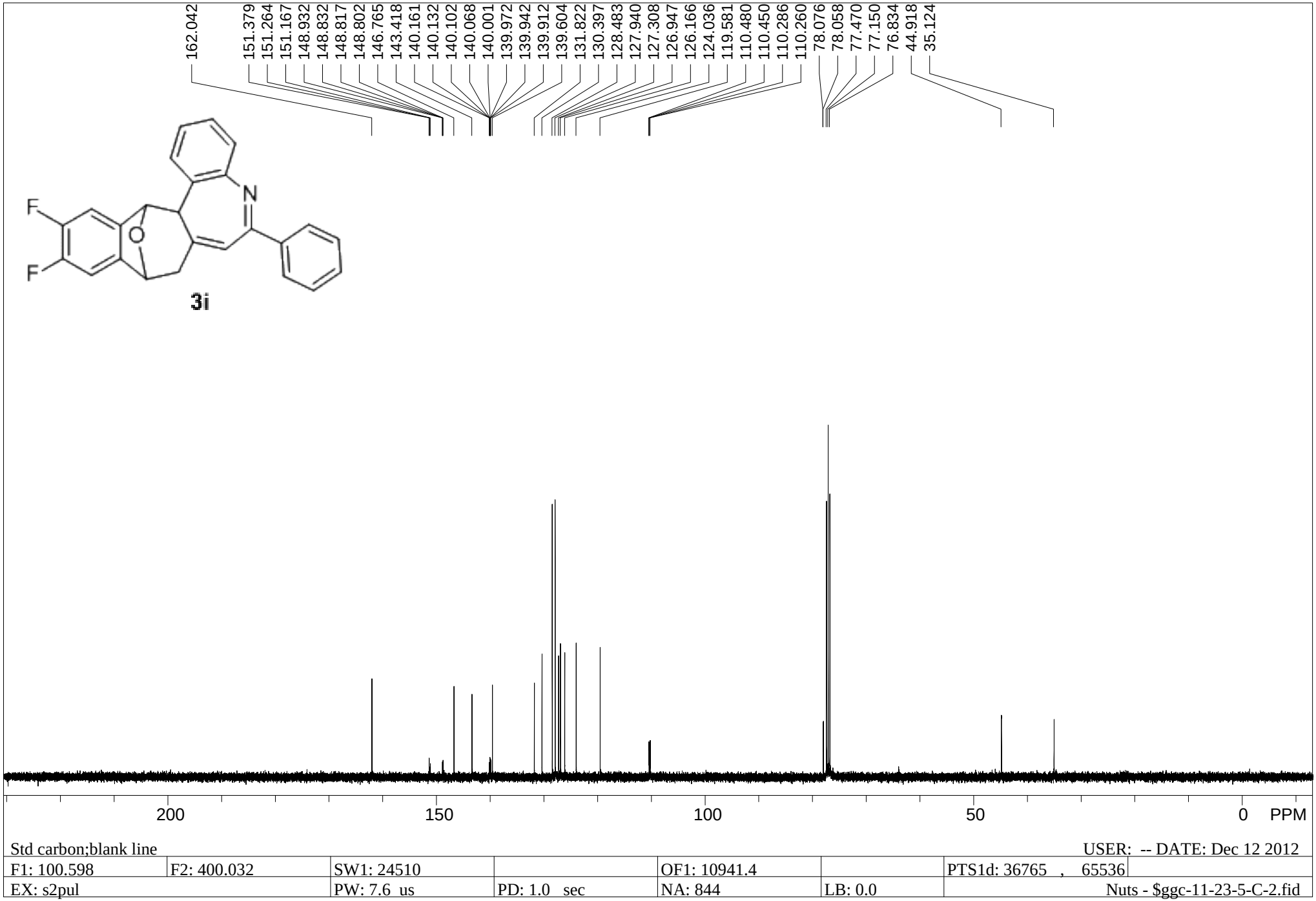

7.810
7.787
7.775
7.770
7.412
7.391
7.362
7.344
7.326
7.321
7.305
7.302
7.286
7.284
7.260
7.253
7.250
7.234
7.232
7.216
7.214
7.162
7.144
6.890
6.868
5.923
5.734
5.424
5.412
3.820
3.205
3.198
3.192
3.188
3.162
3.156
3.150
3.145
2.613
2.568
2.525
Cl
N
O
O
3h
3.13
3.19
1.14
0.96
0.99
2.11
1.02
1.00
0.97
2.97
1.10
0.97
1.02
10
8
6
4
2
PPM
18871-66-4;blank line;blank line;blank line
USER: -- DATE: Feb 27 2013
F1: 400.032
F2: 100.597
SW1: 7225
OF1: 2806.7
PTS1d: 21677 , 32768
EX: s2pul
PW: 10.1 us
PD: 1.0 sec
NA: 12
LB: 0.0
Nuts - $ggc-11-74--h.fid


161.882
161.596
145.623
144.214
144.124
143.649
133.643
132.654
132.301
129.557
127.992
127.873
127.151
126.936
124.348
120.816
120.726
119.432
113.766
78.039
77.466
77.351
77.150
76.830
55.496
45.040
35.362
Cl
N
O
O
3h
200
150
100
50
0
PPM
2010573-21-23-1
USER: -- DATE: Feb 27 2013
F1: 100.598
F2: 400.031
SW1: 24510
OF1: 10576.7
PTS1d: 44118 , 65536
EX: s2pul
PW: 7.6 us
PD: 1.0 sec
NA: 12780
LB: 0.0
Nuts - $ggc-11-74-C-3.fid



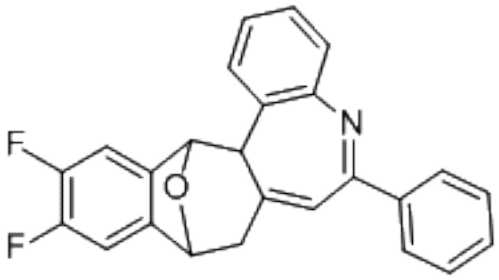

pP3239-1;blank line USER: -- DATE: Dec 12 2012

| | | | | | | |
|---|---|---|---|---|---|---|
| F1: 400.032 | F2: 100.597 | SW1: 7225 | | OF1: 2806.9 | | PTS1d: 21676 , 32768 |
| EX: s2pul | | PW: 10.5 us | PD: 1.0 sec | NA: 8 | LB: 0.0 | Nuts - $ggc-11-23-5-h.fid |




Std carbon;blank line USER: -- DATE: Dec 12 2012

| | | | | | | |
|---|---|---|---|---|---|---|
| F1: 100.598 | F2: 400.032 | SW1: 24510 | | OF1: 10941.4 | | PTS1d: 36765 , 65536 |
| EX: s2pul | | PW: 7.6 us | PD: 1.0 sec | NA: 844 | LB: 0.0 | Nuts - $ggc-11-23-5-C-2.fid |

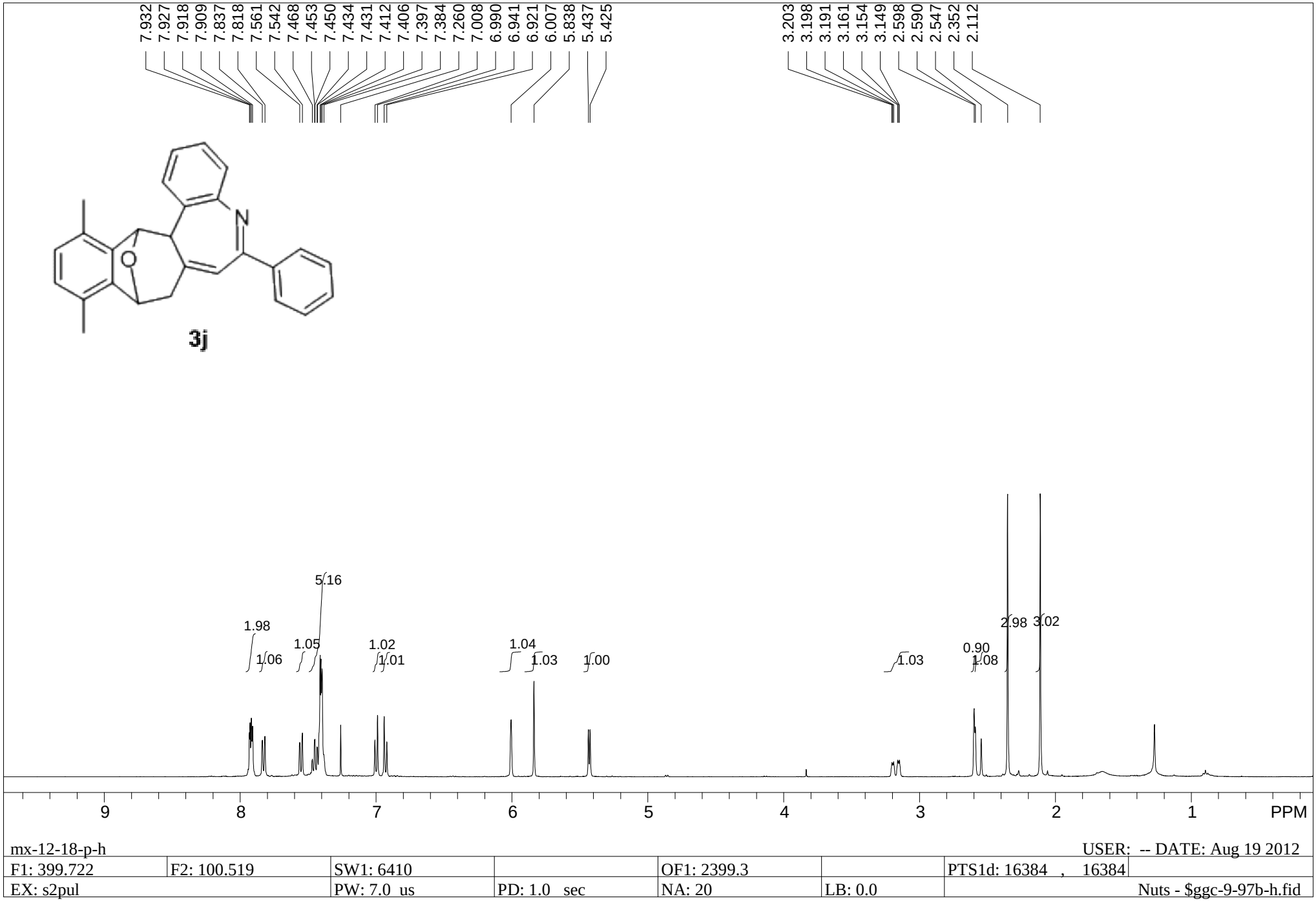


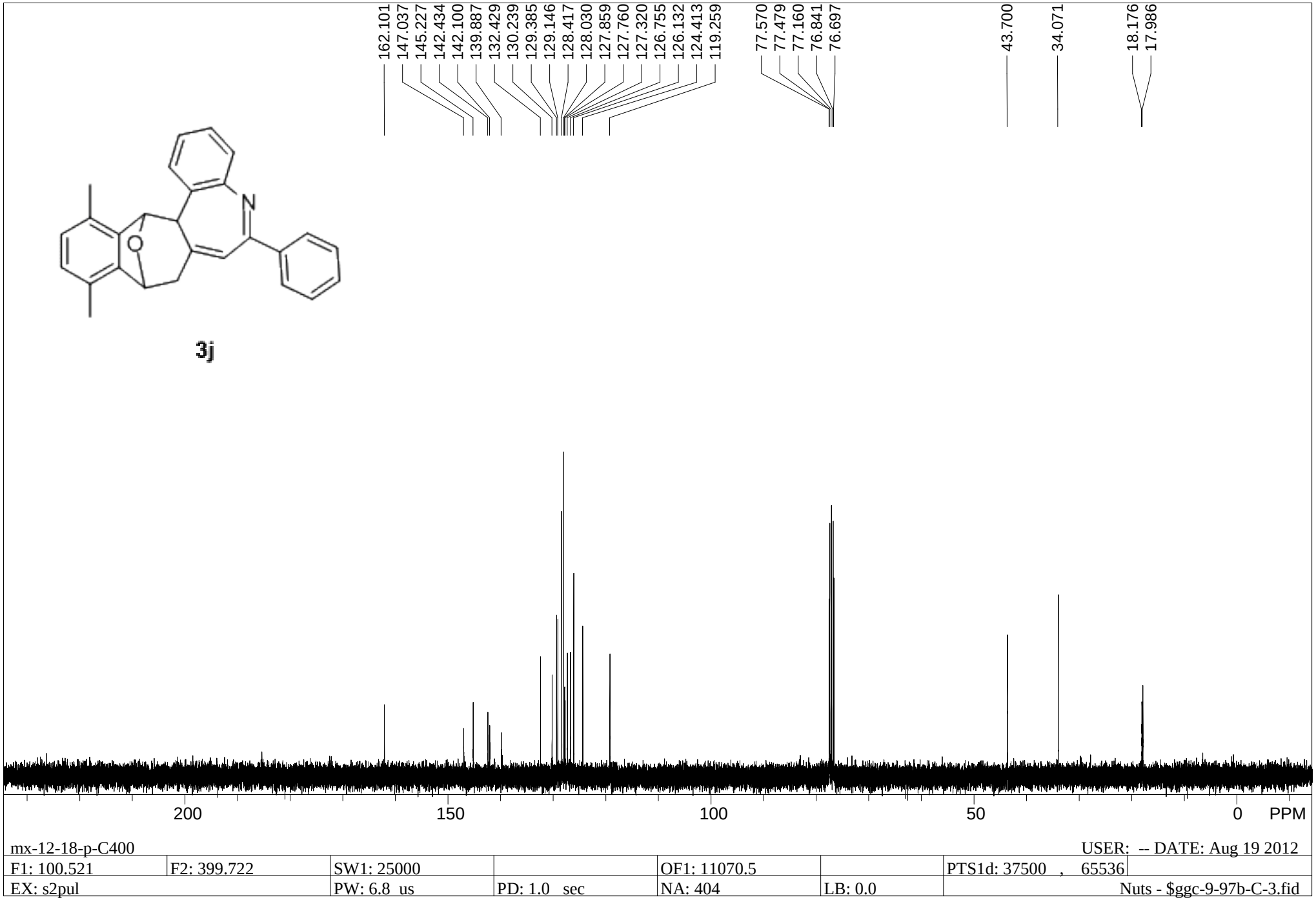

**3i**

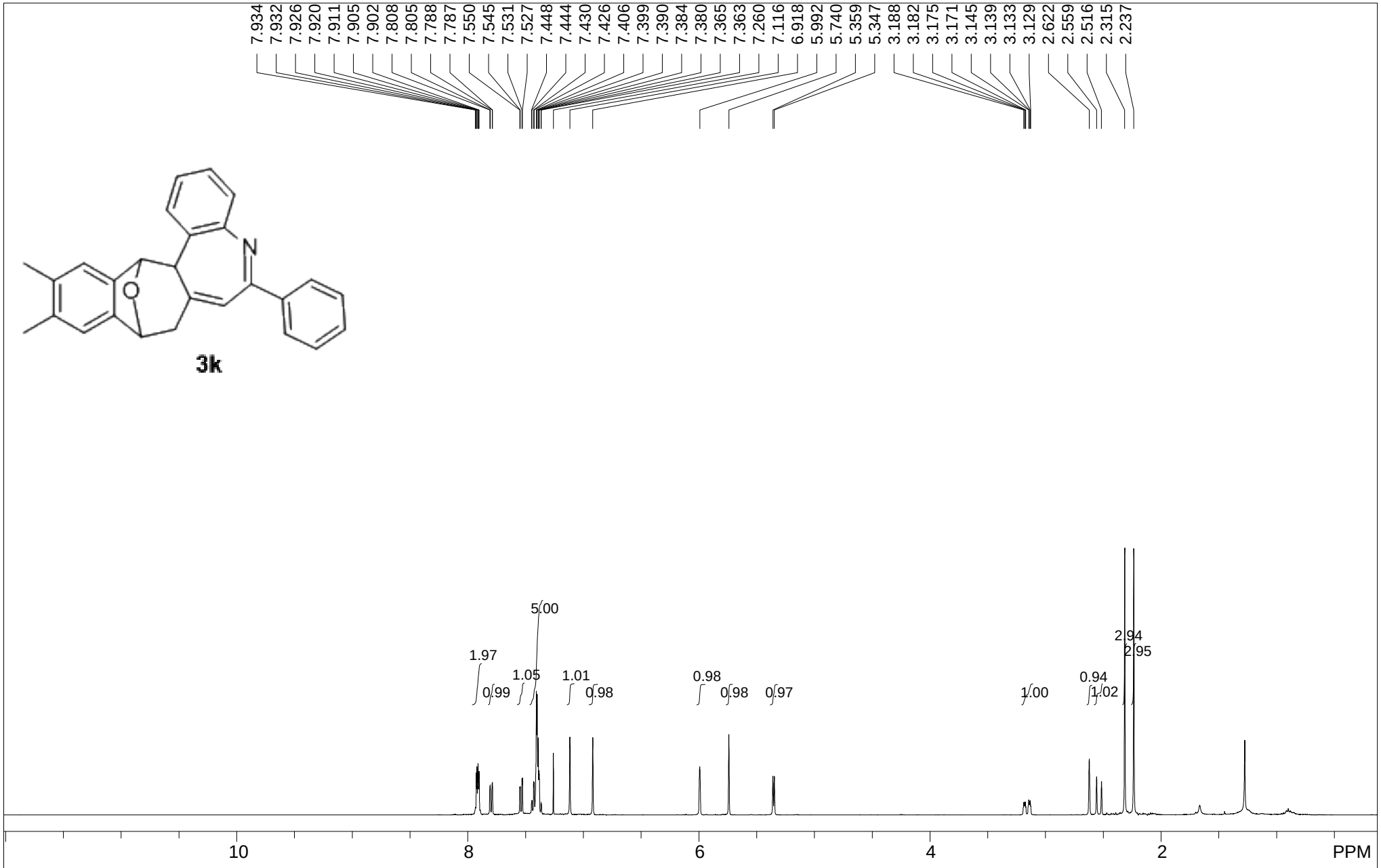


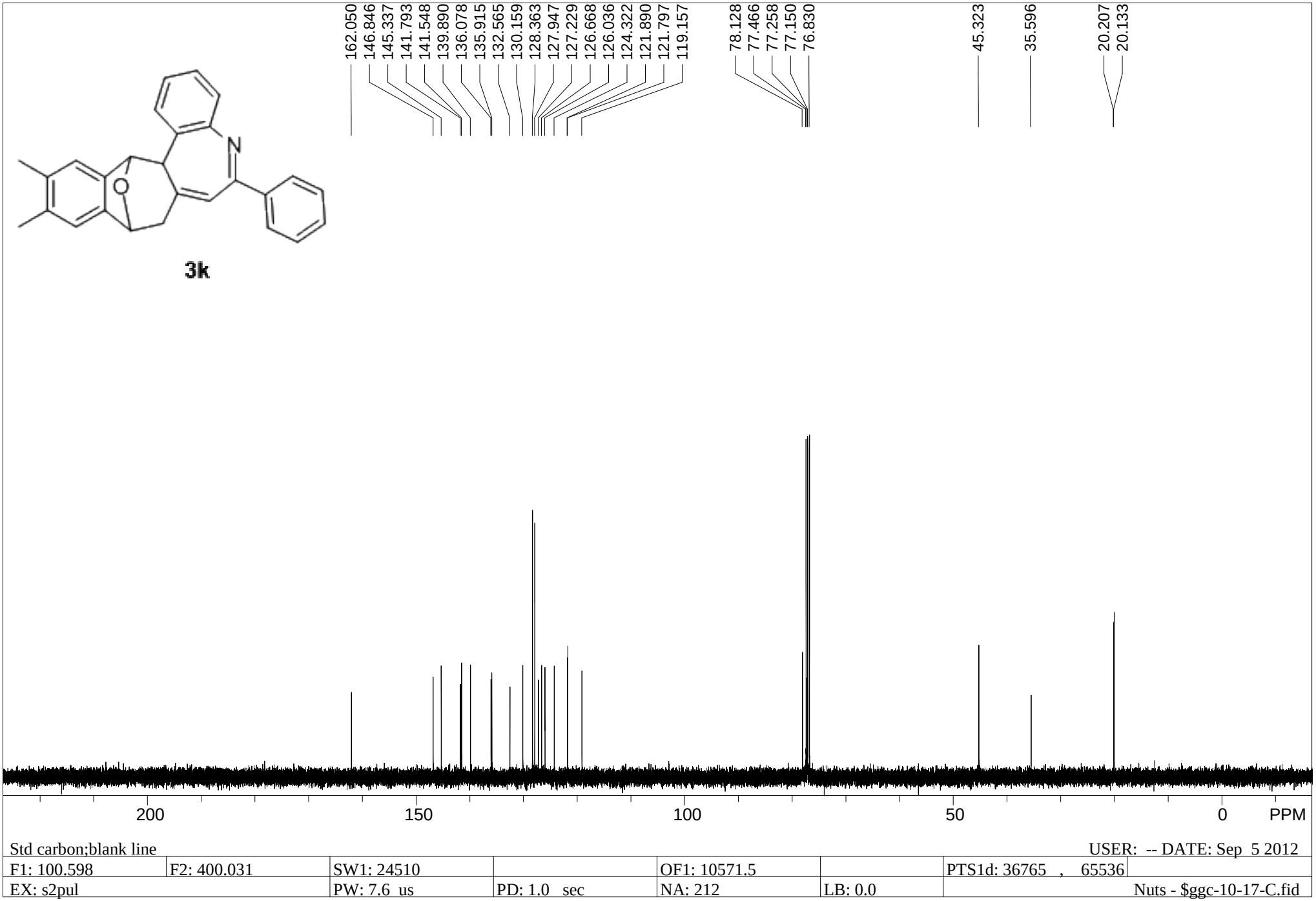

STANDARD PROTON PARAMETERS USER: -- DATE: Nov 24 2012

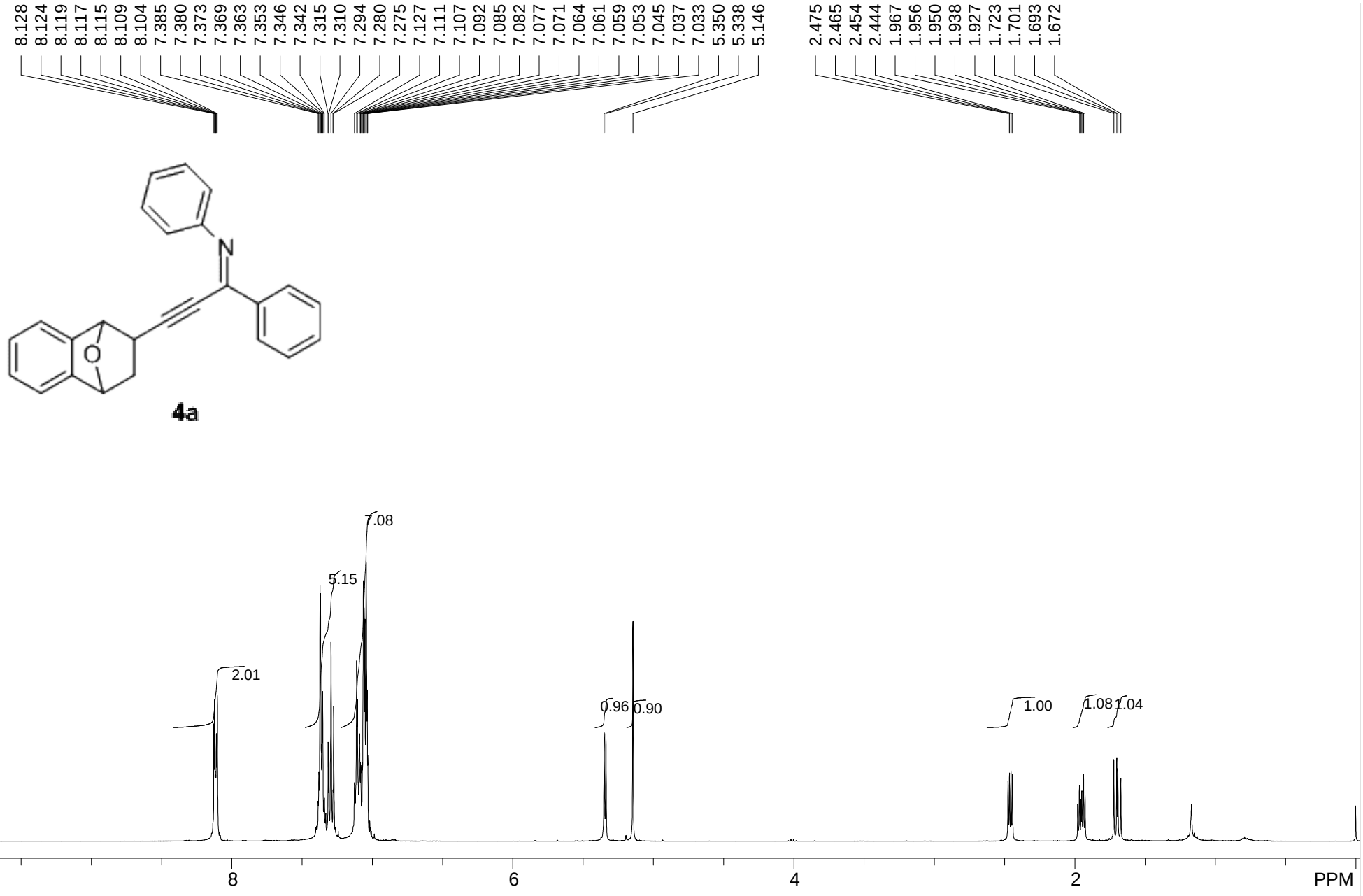
| | | | | | | |
|---|---|---|---|---|---|---|
| F1: 376.074 | F2: 100.519 | SW1: 147059 | | OF1: -38589.2 | | PTS1d: 147059 , 262144 |
| EX: s2pul | | PW: 5.9 us | PD: 3.0 sec | NA: 8 | LB: 0.0 | Nuts - $ggc-11-23-f.fid |


7.932
7.927
7.918
7.909
7.837
7.818
7.561
7.542
7.468
7.453
7.450
7.434
7.431
7.412
7.406
7.397
7.384
7.260
7.008
6.990
6.941
6.921
6.007
5.838
5.437
5.425
3.203
3.198
3.191
3.161
3.154
3.149
2.598
2.590
2.547
2.352
2.112
N
O
3j
1.98
1.06
1.05
5.16
1.02
1.01
1.04
1.03
1.00
1.03
0.90
1.08
2.98
3.02
9
8
7
6
5
4
3
2
1
PPM
mx-12-18-p-h
USER: -- DATE: Aug 19 2012
F1: 399.722
F2: 100.519
SW1: 6410
OF1: 2399.3
PTS1d: 16384 , 16384
EX: s2pul
PW: 7.0 us
PD: 1.0 sec
NA: 20
LB: 0.0
Nuts - $ggc-9-97b-h.fid


162.101
147.037
145.227
142.434
142.100
139.887
132.429
130.239
129.385
129.146
128.417
128.030
127.859
127.760
127.320
126.755
126.132
124.413
119.259
77.570
77.479
77.160
76.841
76.697
43.700
34.071
18.176
17.986
N
O
3j
200
150
100
50
0
PPM
mx-12-18-p-C400
USER: -- DATE: Aug 19 2012
F1: 100.521
F2: 399.722
SW1: 25000
OF1: 11070.5
PTS1d: 37500 , 65536
EX: s2pul
PW: 6.8 us
PD: 1.0 sec
NA: 404
LB: 0.0
Nuts - $ggc-9-97b-C-3.fid


7.934
7.932
7.926
7.920
7.911
7.905
7.902
7.808
7.805
7.788
7.787
7.550
7.545
7.531
7.527
7.448
7.444
7.430
7.426
7.406
7.399
7.390
7.384
7.380
7.365
7.363
7.260
7.116
6.918
5.992
5.740
5.359
5.347
3.188
3.182
3.175
3.171
3.145
3.139
3.133
3.129
2.622
2.559
2.516
2.315
2.237
O
N
3k
1.97
0.99
1.05
5.00
1.01
0.98
0.98
0.98
0.97
1.00
0.94
1.02
2.94
2.95
10
8
6
4
2
PPM
p3439-3;blank line
USER: -- DATE: Sep 8 2012
F1: 400.032
F2: 100.597
SW1: 7396
OF1: 2807.1
PTS1d: 22189 , 32768
EX: s2pul
PW: 10.1 us
PD: 1.0 sec
NA: 16
LB: 0.0
Nuts - $ggc-10-17-h.fid


162.050
146.846
145.337
141.793
141.548
139.890
136.078
135.915
132.565
130.159
128.363
127.947
127.229
126.668
126.036
124.322
121.890
121.797
119.157
78.128
77.466
77.258
77.150
76.830
45.323
35.596
20.207
20.133
N
O
3k
200
150
100
50
0
PPM
Std carbon;blank line
USER: -- DATE: Sep 5 2012
F1: 100.598
F2: 400.031
SW1: 24510
OF1: 10571.5
PTS1d: 36765 , 65536
EX: s2pul
PW: 7.6 us
PD: 1.0 sec
NA: 212
LB: 0.0
Nuts - $ggc-10-17-C.fid

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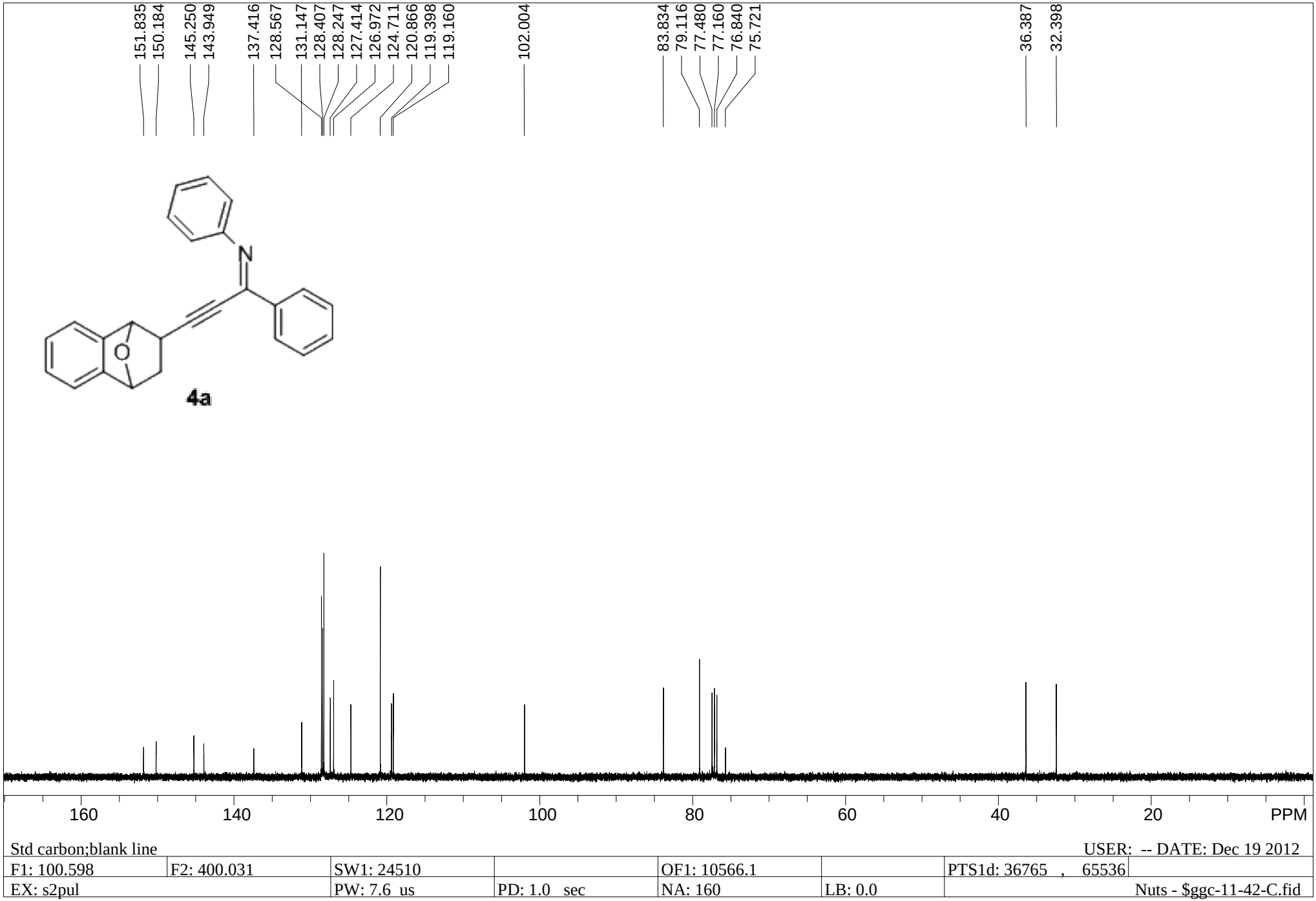
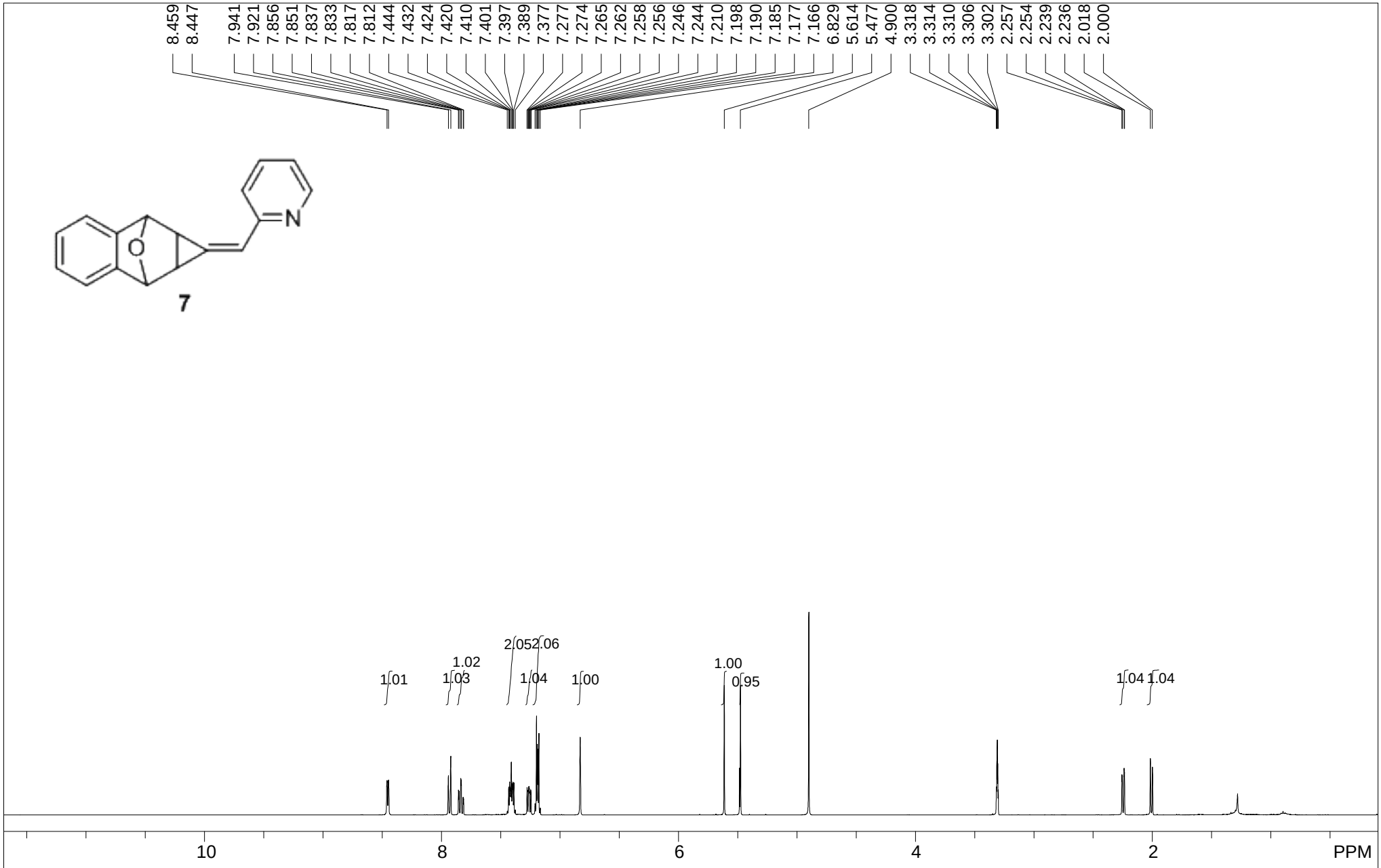
USER: -- DATE: Dec 19 2012

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| F1: 400.032 | F2: 100.597 | SW1: 7225 | | OF1: 2747.9 | | PTS1d: 21676 , 32768 | |
| EX: s2pul | | PW: 10.5 us | PD: 1.0 sec | NA: 12 | LB: 0.0 | | Nuts - $ggc-11-42-h.fid |




Std carbon;blank line USER: -- DATE: Dec 19 2012

| | | | | | | |
|---|---|---|---|---|---|---|
| F1: 100.598 | F2: 400.031 | SW1: 24510 | | OF1: 10566.1 | | PTS1d: 36765 , 65536 |
| EX: s2pul | | PW: 7.6 us | PD: 1.0 sec | NA: 160 | LB: 0.0 | Nuts - $ggc-11-42-C.fid |

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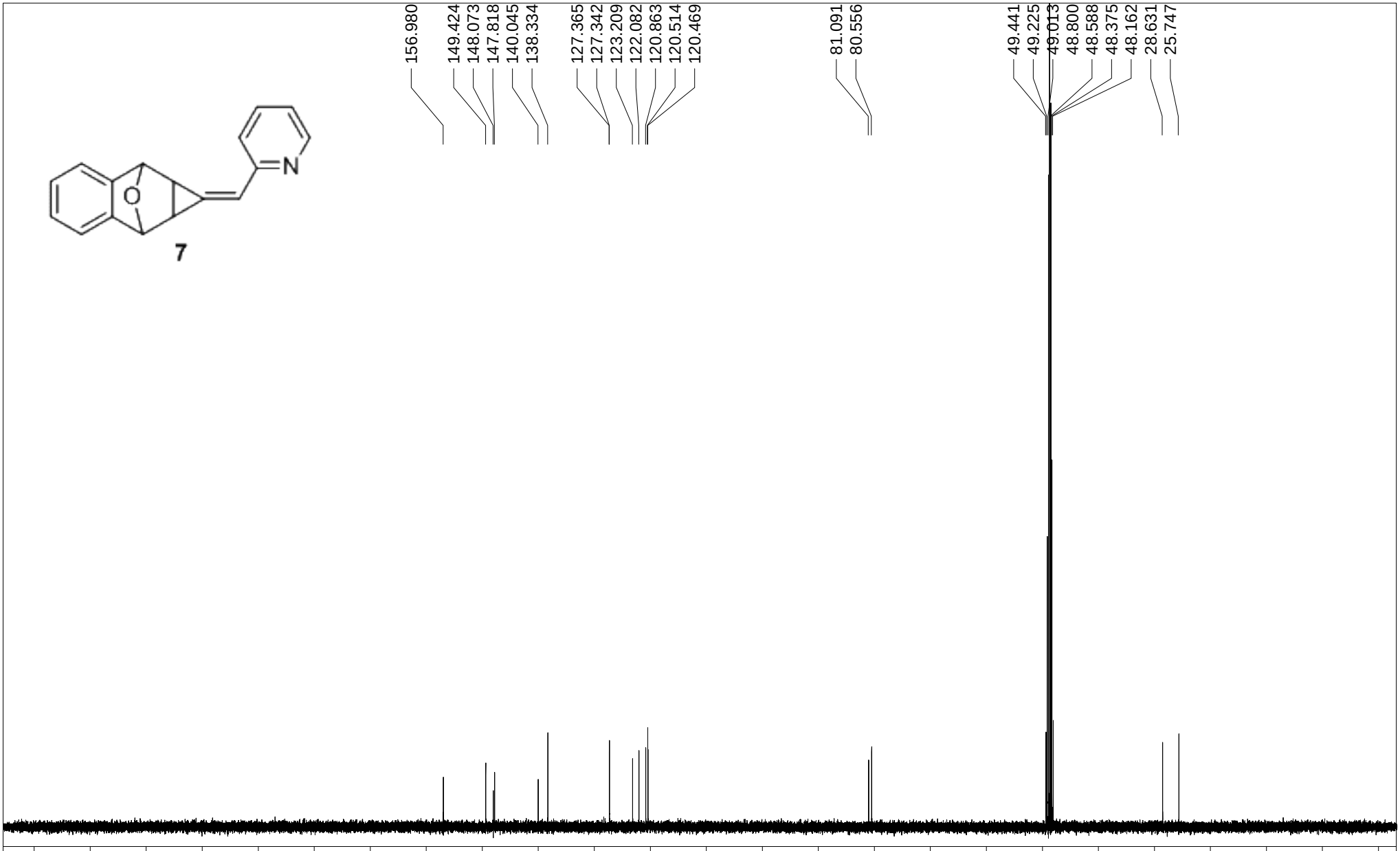
| | | | | | | |
|---|---|---|---|---|---|---|
| F1: 399.724 | F2: 100.520 | SW1: 7184 | | OF1: 2800.4 | | PTS1d: 21552 , 32768 |
| EX: s2pul | | PW: 6.3 us | PD: 1.0 sec | NA: 20 | LB: 0.0 | Nuts - $ggc-15-78-3-h.fid |




;blank line USER: -- DATE: Nov 5 2013

| | | | | | | |
|---|---|---|---|---|---|---|
| F1: 100.521 | F2: 399.724 | SW1: 25000 | | OF1: 11177.3 | | PTS1d: 37500 , 65536 |
| EX: s2pul | | PW: 7.2 us | PD: 1.0 sec | NA: 184 | LB: 0.0 | Nuts - $ggc-15-78-3-C.fid |