Electronic Supplementary Material (ESI) for Chemical Communications

Rh(III)-Catalyzed Dehydrogenative Alkylation of (Hetero)Arenes with Allylic Alcohols

(Supporting Information)

Zhuangzhi Shi, Mélissa Boultadakis-Arapinis and Frank Glorius*

Westfälische Wilhelms-Universität Münster, Organisch-Chemisches Institut,

Corrensstrasse 40, 48149 Münster, Germany

E-mail: glorius@uni-muenster.de

CONTENTS:

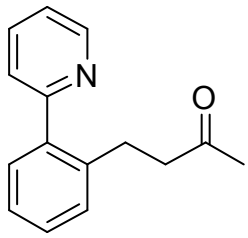
1. General Information.

All reactions were carried out in flame-dried reaction vessels with Teflon screw caps under argon. All new compounds were fully characterized. NMR-spectra were recorded on a Bruker ARX-300, AV-300, AV-400 MHz or on a Varian Associated, Varian 600 unity plus. ESI mass spectra were recorded on a Bruker Daltonics MicroTof.

Unless otherwise noted, chemicals obtained from commercial suppliers were used without further purification. $[Cp^*RhCl_2]_2$, hept-1-en-3-ol (**2c)**, 1-phenylprop-2-en-1-ol (**2d)**, crotyl alcohol (**2e)** were purchased from Sigma-Aldrich. $AgSbF_6$, $Cu(OAc)_2$, but-3-en-2-ol (**2a)**, allyl alcohol (**2b)**, crotyl alcohol (**2e)** were purchased from Alfa Aesar. The preparation of the starting materials **2b-2g** were described in a previously reported communication[1] and other materials were readily usable from our stockings.

2. Experimental Procedures and Characterization of Products

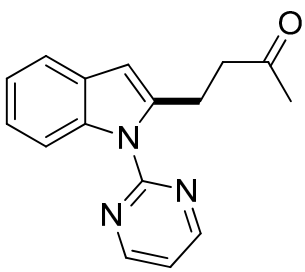
4-(2-(Pyridin-2-yl)phenyl)butan-2-one (3aa)



3aa

Typical procedure : To a 10 mL Schlenk tube was added $[Cp^*RhCl_2]_2$ (3.1 mg, 2.5 mol %), $AgSbF_6$ (6.8 mg, 10 mol %) and $Cu(OAc)_2$ (76 mg, 2.1 eq) and the tube was purged with Ar for three times, followed by addition of **1a** (29.0 μL, 0.20 mmol), **2a** (35.0 μL, 0.40 mmol) and 1,4-dioxane (1.0 mL). The formed mixture was stirred at 60 ºC under Ar for 18 h as monitored by TLC. The solution was then cooled to rt, and 1, 4-dioxane was removed under vaccum directly. The crude product was checked by ^{1}H NMR as a mixture of *mono*-and *di*-substituted products (the ratio is 6: 1). Then the mixture was purified by column chromatography on silica gel (eluent: petroleum ether / ethyl acetate = 2 : 1) to afford 33.0 mg (76%) of two products. **3aa** is the main product: ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.59 (d, *J* = 4.3 Hz, 1H), 7.69 (td, *J* = 7.7, 1.7 Hz, 1H), 7.33 (d, *J* = 7.8 Hz, 1H), 7.31 – 7.14 (m, 5H), 2.96 – 2.81 (m, 2H), 2.68 – 2.55 (m, 2H), 1.97 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 208.29, 159.80, 148.90, 140.12, 139.03, 136.54, 129.87, 129.77, 128.55, 126.28, 124.04, 121.85, 45.38, 29.80, 27.37; HRMS m/z (ESI) calcd for $C_{15}H_{15}NONa$ $(M + Na)^+$ 248.1051, found 248.1048.

4-(1-(Pyrimidin-2-yl)-1*H*-indol-2-yl)butan-2-one (3ba)

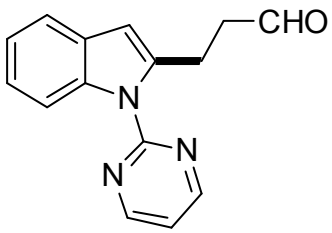


3ba

The reaction of **1b** (39.0 mg, 0.20 mmol), **2a** (35.0 μL, 0.40 mmol), $[Cp^*RhCl_2]_2$ (3.1 mg, 2.5 mol %), $AgSbF_6$ (6.8 mg, 10 mol %) and $Cu(OAc)_2$ (76.0 mg, 2.1 eq), in 1, 4-dioxane (1.0 mL) under Ar afforded 48.5 mg (92%) of **3ba**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.78 (d, *J* = 4.8 Hz, 2H), 8.45 – 8.21 (m, 1H), 7.59 – 7.46 (m, 1H), 7.32 – 7.07 (m, 3H), 6.46 (d, *J* = 0.8 Hz, 1H), 3.54 – 3.37 (m, 2H), 3.02 – 2.80 (m, 2H), 2.17 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 207.93, 158.15, 140.48, 136.85, 129.16, 122.73, 121.89, 119.73,

117.05, 114.05, 106.01, 43.46, 29.97, 23.72; HRMS m/z (ESI) calcd for $C_{21}H_{17}N_3ONa$ $(M + Na)^+$ 350.1268, found 350.1264.

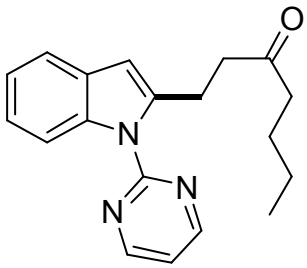
3-(1-(Pyrimidin-2-yl)-1*H*-indol-2-yl)propanal (3bb)



3bb

The reaction of **1b** (39.0 mg, 0.20 mmol), **2b** (27.0 μL, 0.40 mmol), $[Cp^*RhCl_2]_2$ (3.1 mg, 2.5 mol %), $AgSbF_6$ (6.8 mg, 10 mol %) and $Cu(OAc)_2$ (76.0 mg, 2.1 eq), in 1, 4-dioxane (1.0 mL) under Ar afforded 33.5 mg (76%) of **3bb**: ^1H NMR (300 MHz, $CDCl_3$) δ 9.83 (t, J = 1.4 Hz, 1H), 8.78 (d, J = 4.8 Hz, 2H), 8.41 – 8.30 (m, 1H), 7.56 – 7.51 (m, 1H), 7.30 – 7.11 (m, 3H), 6.47 (d, J = 0.7 Hz, 1H), 3.50 (t, J = 7.2 Hz, 2H), 2.91 (td, J = 7.5, 1.4 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 201.27, 158.12, 158.05, 139.82, 136.88, 129.08, 122.91, 122.01, 119.80, 117.05, 114.22, 106.38, 43.47, 22.39; HRMS m/z (ESI) calcd for $C_{15}H_{13}N_3ONa$ $(M + Na)^+$ 274.0956, found 274.0951.

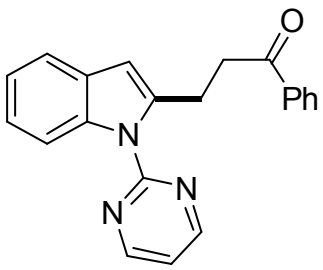
1-(1-(Pyrimidin-2-yl)-1*H*-indol-2-yl)heptan-3-one (3bc)



3bc

The reaction of **1b** (39.0 mg, 0.20 mmol), **2c** (55.0 μL, 0.40 mmol), $[Cp^*RhCl_2]_2$ (3.1 mg, 2.5 mol %), $AgSbF_6$ (6.8 mg, 10 mol %) and $Cu(OAc)_2$ (76.0 mg, 2.1 eq), in 1, 4-dioxane (1.0 mL) under Ar afforded 53.0 mg (86%) of **3bc**: ^1H NMR (300 MHz, $CDCl_3$) δ 8.78 (d, J = 4.8 Hz, 2H), 8.37 – 8.24 (m, 1H), 7.57 – 7.46 (m, 1H), 7.26 – 7.11 (m, 3H), 6.45 (d, J = 0.8 Hz, 1H), 3.49 – 3.33 (m, 2H), 2.87 (dd, J = 8.6, 6.7 Hz, 2H), 2.42 (t, J = 7.4 Hz, 2H), 1.62 – 1.51 (m, 2H), 1.37 – 1.24 (m, 2H), 0.89 (t, J = 7.3 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 210.33, 158.16, 140.70, 136.88, 129.21, 122.71, 121.89, 119.73, 117.04, 114.04, 106.01, 42.61, 42.52, 25.98, 23.73, 22.33, 13.84; HRMS m/z (ESI) calcd for $C_{19}H_{21}N_3ONa$ $(M + Na)^+$ 330.1582, found 330.1577.

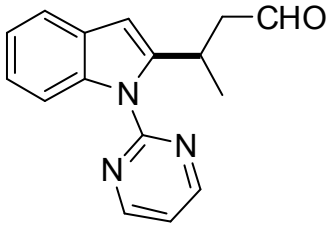
1-Phenyl-3-(1-(pyrimidin-2-yl)-1*H*-indol-2-yl)propan-1-one (3bd)



3bd

The reaction of **1b** (39.0 mg, 0.20 mmol), **2d** (53.0 μL, 0.40 mmol), $[Cp^*RhCl_2]_2$ (3.1 mg, 2.5 mol %), $AgSbF_6$ (6.8 mg, 10 mol %) and $Cu(OAc)_2$ (76.0 mg, 2.1 eq), in 1, 4-dioxane (1.0 mL) under Ar afforded 53.0 mg (81%) of **3bd**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.77 (d, *J* = 4.8 Hz, 2H), 8.37 – 8.30 (m, 1H), 8.04 – 7.94 (m, 2H), 7.62 – 7.51 (m, 2H), 7.51 – 7.42 (m, 2H), 7.29 – 7.09 (m, 3H), 6.54 (d, *J* = 0.6 Hz, 1H), 3.65 – 3.56 (m, 2H), 3.48 (ddd, *J* = 8.4, 6.0, 1.8 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 199.23, 158.17, 158.11, 140.80, 136.85, 136.82, 133.03, 129.21, 128.56, 128.02, 122.71, 121.89, 119.72, 117.02, 114.10, 106.16, 38.80, 24.11; HRMS m/z (ESI) calcd for $C_{21}H_{17}N_3ONa$ $(M + Na)^+$ 350.1269, found 350.1264.

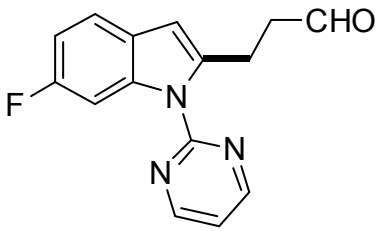
3-(1-(Pyrimidin-2-yl)-1*H*-indol-2-yl)butanal (3be)



3be

The reaction of **1b** (78.0 mg, 0.40 mmol), **2e** (crotyl alcohol (mixture of *cis* and *trans*), 64.0 μL, 0.80 mmol), $[Cp^*RhCl_2]_2$ (6.2 mg, 2.5 mol %), $AgSbF_6$ (13.6 mg, 10 mol %) and $Cu(OAc)_2$ (152.0 mg, 2.1 eq), in 1, 4-dioxane (2.0 mL) under Ar afforded 40.0 mg (38%) of **3be**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.68 (t, *J* = 1.9 Hz, 1H), 8.70 (d, *J* = 4.8 Hz, 2H), 8.20 – 8.06 (m, 1H), 7.49 – 7.43 (m, 1H), 7.22 – 7.02 (m, 3H), 6.46 (s, 1H), 4.32 (dq, *J* = 14.2, 7.0 Hz, 1H), 2.89 (ddd, *J* = 16.9, 5.1, 1.6 Hz, 1H), 2.55 (ddd, *J* = 16.9, 8.3, 2.2 Hz, 1H), 1.27 (d, *J* = 6.9 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 201.78, 158.24, 158.01, 145.29, 136.86, 128.94, 122.94, 121.93, 119.93, 117.34, 113.74, 104.30, 51.24, 27.01, 20.94; HRMS m/z (ESI) calcd for $C_{16}H_{15}N_3ONa$ $(M + Na)^+$ 288.1113, found 288.1107.

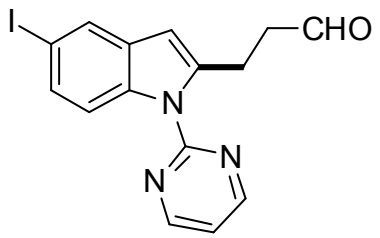
3-(6-Fluoro-1-(pyrimidin-2-yl)-1*H*-indol-2-yl)propanal (3cb)



3cb

The reaction of **1c** (42.6 mg, 0.20 mmol), **2b** (27.0 μL, 0.40 mmol), $[Cp^*RhCl_2]_2$ (3.1 mg, 2.5 mol %), $AgSbF_6$ (6.8 mg, 10 mol %) and $Cu(OAc)_2$ (76.0 mg, 2.1 eq), in 1, 4-dioxane (1.0 mL) under Ar afforded 41.0 mg (76%) of **3cb**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.84 (t, *J* = 1.4 Hz, 1H), 8.78 (d, *J* = 4.8 Hz, 2H), 8.13 (dd, *J* = 11.2, 2.4 Hz, 1H), 7.42 (dd, *J* = 8.5, 5.6 Hz, 1H), 7.17 (t, *J* = 4.8 Hz, 1H), 6.95 (ddd, *J* = 9.2, 8.6, 2.4 Hz, 1H), 6.43 (d, *J* = 0.8 Hz, 1H), 3.50 (t, *J* = 7.4 Hz, 2H), 2.90 (ddd, *J* = 8.4, 6.9, 1.4 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 201.48, 160.22 (d, *J* = 236.2 Hz), 158.16, 157.95, 140.34 (d, *J* = 3.8 Hz), 136.92 (d, *J* = 12.8 Hz), 125.40, 120.16 (d, *J* = 9.8 Hz), 117.22, 110.20 (d, *J* = 24.0 Hz), 106.19, 101.81 (d, *J* = 28.5 Hz), 43.45, 22.55; HRMS m/z (ESI) calcd for $C_{15}H_{12}FN_3ONa$ $(M + Na)^+$ 292.0862, found 292.0857.

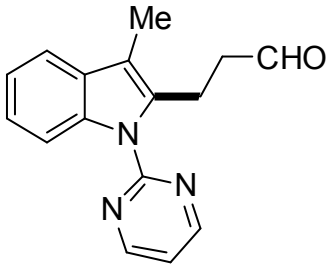
3-(5-Iodo-1-(pyrimidin-2-yl)-1*H*-indol-2-yl)propanal (3db)



3db

The reaction of **1d** (64.2 mg, 0.20 mmol), **2b** (27.0 μL, 0.40 mmol), $[Cp^*RhCl_2]_2$ (3.1 mg, 2.5 mol %), $AgSbF_6$ (6.8 mg, 10 mol %) and $Cu(OAc)_2$ (76.0 mg, 2.1 eq), in 1, 4-dioxane (1.0 mL) under Ar afforded 47.0 mg (62%) of **3db**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.84 (t, *J* = 1.3 Hz, 1H), 8.77 (d, *J* = 4.8 Hz, 2H), 8.10 (d, *J* = 8.8 Hz, 1H), 7.84 (d, *J* = 1.7 Hz, 1H), 7.48 (dd, *J* = 8.8, 1.8 Hz, 1H), 7.17 (t, *J* = 4.8 Hz, 1H), 6.38 (d, *J* = 0.7 Hz, 1H), 3.48 (t, *J* = 7.2 Hz, 2H), 2.90 (td, *J* = 7.5, 1.3 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 201.22, 158.19, 157.81, 140.88, 136.13, 131.50, 131.20, 128.53, 117.36, 116.38, 105.31, 85.79, 43.39, 22.33; HRMS m/z (ESI) calcd for $C_{15}H_{12}N_3ONa$ $(M + Na)^+$ 399.9923, found 399.9917.

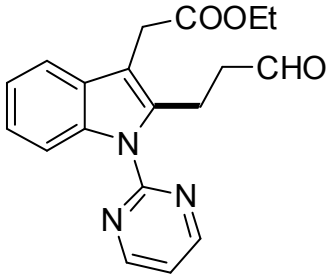
3-(3-Methyl-1-(pyrimidin-2-yl)-1*H*-indol-2-yl)propanal (3eb)



3eb

The reaction of **1e** (41.8 mg, 0.20 mmol), **2b** (27.0 μL, 0.40 mmol), $[Cp^*RhCl_2]_2$ (3.1 mg, 2.5 mol %), $AgSbF_6$ (6.8 mg, 10 mol %) and $Cu(OAc)_2$ (76.0 mg, 2.1 eq), in 1, 4-dioxane (1.0 mL) under Ar afforded 39.3 mg (74%) of **3eb**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.73 (t, *J* = 1.3 Hz, 1H), 8.65 (d, *J* = 4.8 Hz, 2H), 8.36 – 8.20 (m, 1H), 7.55 – 7.35 (m, 1H), 7.31 – 7.08 (m, 2H), 7.02 (t, *J* = 4.8 Hz, 1H), 3.52 – 3.27 (m, 2H), 2.77 (ddd, *J* = 8.6, 6.9, 1.3 Hz, 2H), 2.22 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 201.69, 158.05, 136.04, 134.89, 130.31, 123.10, 121.71, 117.99, 116.62, 114.19, 113.68, 44.22, 19.46, 8.76; HRMS m/z (ESI) calcd for $C_{16}H_{15}N_3ONa$ $(M + Na)^+$ 288.1113, found 288.1107.

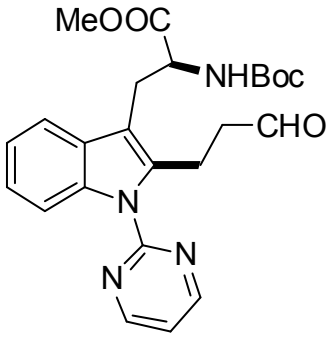
Ethyl 2-(2-(3-oxopropyl)-1-(pyrimidin-2-yl)-1*H*-indol-3-yl)acetate (3fb)



3fb

The reaction of **1f** (56.2 mg, 0.20 mmol), **2b** (27.0 μL, 0.40 mmol), $[Cp^*RhCl_2]_2$ (3.1 mg, 2.5 mol %), $AgSbF_6$ (6.8 mg, 10 mol %) and $Cu(OAc)_2$ (76.0 mg, 2.1 eq), in 1, 4-dioxane (1.0 mL) under Ar afforded 53.6 mg (80%) of **3fb**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.82 (s, 1H), 8.76 (d, *J* = 4.8 Hz, 2H), 8.36 – 8.27 (m, 1H), 7.64 – 7.55 (m, 1H), 7.25 (ddd, *J* = 7.1, 4.4, 1.6 Hz, 2H), 7.15 (t, *J* = 4.8 Hz, 1H), 4.14 (q, *J* = 7.1 Hz, 2H), 3.77 (s, 2H), 3.52 – 3.41 (m, 2H), 2.95 (td, *J* = 7.6, 0.9 Hz, 2H), 1.24 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 201.37, 171.30, 158.16, 157.95, 137.04, 136.05, 129.25, 123.34, 122.05, 118.27, 117.09, 114.21, 111.08, 60.95, 44.43, 30.64, 19.27, 14.18; HRMS m/z (ESI) calcd for $C_{19}H_{19}N_3O_3Na$ $(M + Na)^+$ 360.1324, found 360.1319.

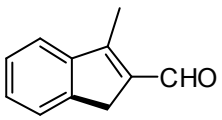
Methyl 2-((tert-butoxycarbonyl)amino)-3-(2-(3-oxopropyl)-1-(pyrimidin-2-yl) -1-indol-3-yl)propanoate (3gb)



3gb

The reaction of **1g** (198.0 mg, 0.50 mmol), **2b** (68.0 μL, 1.0 mmol), $[Cp^*RhCl_2]_2$ (8.3 mg, 2.5 mol %), $AgSbF_6$ (17.0 mg, 10 mol %) and $Cu(OAc)_2$ (190.0 mg, 2.1 eq), in 1, 4-dioxane (2.5 mL) under Ar afforded 156.0 mg (70%) of **3gb**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.72 (s, 1H), 8.77 (d, *J* = 4.8 Hz, 2H), 8.28 (d, *J* = 7.9 Hz, 1H), 7.51 (d, *J* = 8.1 Hz, 1H), 7.26 – 7.15 (m, 3H), 5.12 (d, *J* = 8.1 Hz, 1H), 4.63 (dd, *J* = 14.2, 6.2 Hz, 1H), 3.65 (s, 3H), 3.42 (t, *J* = 7.4 Hz, 2H), 3.28 (d, *J* = 6.3 Hz, 2H), 2.78 (t, *J* = 7.4 Hz, 2H), 1.40 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 172.64, 158.18, 157.84, 155.01, 137.10, 136.23, 129.51, 123.34, 122.01, 118.21, 117.14, 114.08, 112.47, 79.92, 53.81, 52.35, 44.24, 28.24, 27.62, 18.94. HRMS m/z (ESI) calcd for $C_{24}H_{28}N_4O_5Na$ $(M + Na)^+$ 475.1957, found 475.1952.

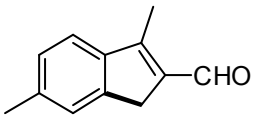
3-Methyl-1*H*-indene-2-carbaldehyde (4hb) [2]



4hb

Typical procedure : To a 10 mL Schlenk tube was added $[Cp^*RhCl_2]_2$ (3.1 mg, 2.5 mol %), $AgSbF_6$ (6.8 mg, 10 mol %) and $Cu(OAc)_2$ (76.0g, 2.1 eq) and the tube was purged with Ar for three times, followed by addition of **1h** (24.0 μL, 0.20 mmol), **2b** (27.0 μL, 0.40 mmol) and 1,4-dioxane (1.0 mL). The formed mixture was stirred at 120 ºC under Ar for 36 h as monitored by TLC. The solution was then cooled to rt, and 1, 4-dioxane was removed under vaccum directly. Then the mixture was purified by column chromatography on silica gel (eluent: petroleum ether / ethyl acetate = 20 : 1) to afford 18.6 mg (60%) of **4hb**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 10.24 (s, 1H), 7.62-7.56 (m, 1H), 7.56 – 7.51 (m, 1H), 7.46 – 7.35 (m, 2H), 3.63 (d, *J* = 2.2 Hz, 2H), 2.56 (t, *J* = 2.3 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 187.10, 155.89, 144.71, 144.32, 139.50, 129.09, 126.89, 124.57, 121.65, 35.71, 10.80; HRMS m/z (ESI) calcd for $C_{11}H_{10}ONa$ $(M + Na)^+$ 181.0629, found 181.0624.

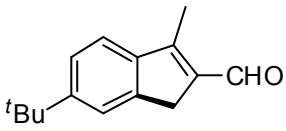
3, 6-Dimethyl-1*H*-indene-2-carbaldehyde (4hb)



4ib

The reaction of **1i** (27.0 μL, 0.20 mmol), **2b** (27.0 μL, 0.40 mmol), $[Cp^*RhCl_2]_2$ (3.1 mg, 2.5 mol %), $AgSbF_6$ (6.8 mg, 10 mol %) and $Cu(OAc)_2$ (76.0 mg, 2.1 eq), in 1, 4-dioxane (1.0 mL) under Ar afforded 24.0 mg (70%) of **4ib**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 10.19 (s, 1H), 7.47 (d, J = 7.8 Hz, 1H), 7.35 (d, J = 0.6 Hz, 1H), 7.21 (d, J = 7.8 Hz, 1H), 3.59 (d, J = 2.2 Hz, 2H), 2.54 (t, J = 2.3 Hz, 3H), 2.44 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 187.01, 156.25, 144.71, 142.19, 139.64, 138.77, 127.84, 125.34, 121.42, 35.43, 21.81, 10.84; HRMS m/z (ESI) calcd for $C_{12}H_{12}ONa$ $(M + Na)^+$ 195.0786, found 195.0780.

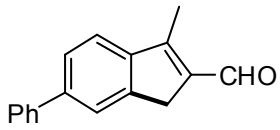
6-(*tert*-Butyl)-3-methyl-1*H*-indene-2-carbaldehyde (4jb)



4jb

The reaction of **1j** (37.0 μL, 0.20 mmol), **2b** (27.0 μL, 0.40 mmol), $[Cp^*RhCl_2]_2$ (3.1 mg, 2.5 mol %), $AgSbF_6$ (6.8 mg, 10 mol %) and $Cu(OAc)_2$ (76.0 mg, 2.1 eq), in 1, 4-dioxane (1.0 mL) under Ar afforded 28.6 mg (67%) of **4jb**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.20 (s, 1H), 7.58 (dd, J = 1.7, 0.8 Hz, 1H), 7.52 (dd, J = 8.1, 0.6 Hz, 1H), 7.45 (dd, J = 8.1, 1.8 Hz, 1H), 3.63 (d, J = 2.2 Hz, 2H), 2.55 (t, J = 2.3 Hz, 3H), 1.37 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 186.99, 156.16, 153.03, 144.49, 142.19, 139.12, 124.23, 121.58, 121.25, 35.71, 35.12, 31.44, 10.83; HRMS m/z (ESI) calcd for $C_{15}H_{18}ONa$ $(M + Na)^+$ 237.1255, found 237.1250.

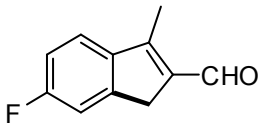
3-Methyl-6-phenyl-1*H*-indene-2-carbaldehyde (4kb)



4kb

The reaction of **1k** (40.0 mg, 0.20 mmol), **2b** (27.0 μL, 0.40 mmol), $[Cp^*RhCl_2]_2$ (3.1 mg, 2.5 mol %), $AgSbF_6$ (6.8 mg, 10 mol %) and $Cu(OAc)_2$ (76.0 mg, 2.1 eq), in 1, 4-dioxane (1.0 mL) under Ar afforded 33.2 mg (71%) of **4kb**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.24 (s, 1H), 7.76 (s, 1H), 7.68 – 7.61 (m, 4H), 7.50 – 7.44 (m, 2H), 7.38 (ddd, J = 7.3, 3.9, 1.2 Hz, 1H), 3.70 (d, J = 2.2 Hz, 2H), 2.59 (t, J = 2.3 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 186.94, 155.69, 145.04, 143.89, 142.34, 140.86, 139.68, 128.85, 127.61, 127.27, 126.17, 123.32, 121.95, 35.81, 10.88; HRMS m/z (ESI) calcd for $C_{17}H_{14}ONa$ $(M + Na)^+$ 257.0942, found 257.0937.

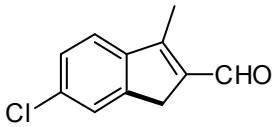
6-Fluoro-3-methyl-1*H*-indene-2-carbaldehyde (4lb)



4lb

The reaction of **1l** (25.0 μL, 0.20 mmol), **2b** (27.0 μL, 0.40 mmol), $[Cp^*RhCl_2]_2$ (3.1 mg, 2.5 mol %), $AgSbF_6$ (6.8 mg, 10 mol %) and $Cu(OAc)_2$ (76.0 mg, 2.1 eq), in 1, 4-dioxane (1.0 mL) under Ar afforded 18.0 mg (51%) of **4lb**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 10.18 (s, 1H), 7.52 (dd, *J* = 8.4, 5.1 Hz, 1H), 7.26 – 7.19 (m, 1H), 7.10 (td, *J* = 9.1, 2.4 Hz, 1H), 3.62 (d, *J* = 2.2 Hz, 2H), 2.55 (t, *J* = 2.3 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 186.70, 163.92 (d, *J* = 247.5 Hz), 155.13, 146.73 (d, *J* = 9.0 Hz), 140.74 (d, *J* = 2.2 Hz), 139.34 (d, *J* = 3.8 Hz), 122.87 (d, *J* = 9.0 Hz), 114.44 (d, *J* = 23.2 Hz), 112.14 (d, *J* = 23.2 Hz), 35.84 (d, *J* = 2.2 Hz), 10.89; HRMS m/z (ESI) calcd for $C_{11}H_9FONa$ $(M + Na)^+$ 199.0535, found 199.0530.

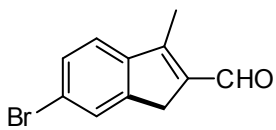
6-Chloro-3-methyl-1*H*-indene-2-carbaldehyde (4mb)



4mb

The reaction of **1m** (26.0 μL, 0.20 mmol), **2b** (27.0 μL, 0.40 mmol), $[Cp^*RhCl_2]_2$ (3.1 mg, 2.5 mol %), $AgSbF_6$ (6.8 mg, 10 mol %) and $Cu(OAc)_2$ (76.0 mg, 2.1 eq), in 1, 4-dioxane (1.0 mL) under Ar afforded 24.0 mg (64%) of **4mb**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 10.21 (s, 1H), 7.55 – 7.45 (m, 2H), 7.37 (dd, *J* = 8.2, 1.9 Hz, 1H), 3.61 (d, *J* = 2.2 Hz, 2H), 2.54 (t, *J* = 2.3 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 186.90, 154.75, 145.79, 143.23, 139.61, 135.26, 127.37, 124.99, 122.52, 35.66, 10.82; HRMS m/z (ESI) calcd for $C_{11}H_9ClONa$ $(M + Na)^+$ 215.0240, found 215.0234.

6-Bromo-3-methyl-1*H*-indene-2-carbaldehyde (4nb)

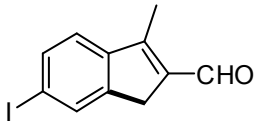


4nb

The reaction of **1n** (39.6 mg, 0.20 mmol), **2b** (27.0 μL, 0.40 mmol), $[Cp^*RhCl_2]_2$ (3.1 mg, 2.5 mol %), $AgSbF_6$ (6.8 mg, 10 mol %) and $Cu(OAc)_2$ (76.0 mg, 2.1 eq), in 1, 4-dioxane (1.0 mL) under Ar afforded 30.0 mg (64%) of **4nb**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 10.22 (s, 1H), 7.68 (s, 1H), 7.53 (d, *J* = 8.2 Hz, 1H), 7.43 (d, *J* = 8.2 Hz, 1H), 3.61 (d, *J* = 1.8 Hz, 2H), 2.54 (t, *J* = 2.2 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 186.93, 154.77,

146.04, 143.66, 139.54, 130.23, 127.93, 123.57, 122.84, 35.68, 10.78; HRMS m/z (ESI) calcd for $C_{11}H_9BrONa$ $(M + Na)^+$ 258.9734, found 258.9729.

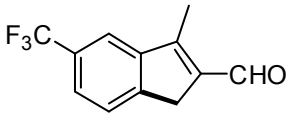
6-Iodo-3-methyl-1*H*-indene-2-carbaldehyde (4ob)



4ob

The reaction of **1l** (49.2 mg, 0.20 mmol), **2b** (27.0 μL, 0.40 mmol), $[Cp^*RhCl_2]_2$ (3.1 mg, 2.5 mol %), $AgSbF_6$ (6.8 mg, 10 mol %) and $Cu(OAc)_2$ (76.0 mg, 2.1 eq), in 1, 4-dioxane (1.0 mL) under Ar afforded 35.0 mg (62%) of **4ob**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 10.23 (s, 1H), 7.89 (d, J = 0.8 Hz, 1H), 7.83 – 7.72 (m, 1H), 7.31 (d, J = 8.1 Hz, 1H), 3.58 (d, J = 2.2 Hz, 2H), 2.53 (t, J = 2.3 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 186.96, 154.90, 146.12, 144.23, 139.31, 136.07, 133.80, 123.08, 95.42, 35.54, 10.73; HRMS m/z (ESI) calcd for $C_{11}H_9IONa$ $(M + Na)^+$ 306.9596, found 306.9590.

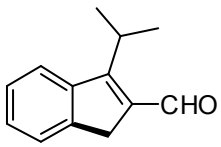
3-Methyl-5-(trifluoromethyl)-1*H*-indene-2-carbaldehyde (4pb)



4pb

The reaction of **1p** (31.0 μL, 0.20 mmol), **2b** (27.0 μL, 0.40 mmol), $[Cp^*RhCl_2]_2$ (3.1 mg, 2.5 mol %), $AgSbF_6$ (6.8 mg, 10 mol %) and $Cu(OAc)_2$ (76.0 mg, 2.1 eq), in 1, 4-dioxane (1.0 mL) under Ar afforded 13.0 mg (29%) of **4pb**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 10.27 (s, 1H), 7.81 (s, 1H), 7.76 – 7.58 (m, 2H), 3.70 (d, J = 1.6 Hz, 2H), 2.60 (t, J = 2.3 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 187.03, 154.26, 147.61, 145.28, 140.71, 125.70 (q, J = 3.8 Hz), 124.92, 122.26 (q, J = 270.8 Hz), 118.52 (q, J = 4.0 Hz), 35.96, 10.80; HRMS m/z (ESI) calcd for $C_{12}H_9F_3ONa$ $(M + Na)^+$ 249.0503, found 249.0498.

3-Isopropyl-1*H*-indene-2-carbaldehyde (4qb)

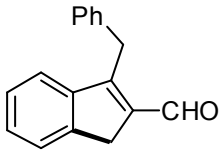


4qb

The reaction of **1q** (30.0 μL,, 0.20 mmol), **2b** (27.0 μL, 0.40 mmol), $[Cp^*RhCl_2]_2$ (3.1 mg, 2.5 mol %), $AgSbF_6$ (6.8 mg, 10 mol %) and $Cu(OAc)_2$ (76.0 mg, 2.1 eq), in 1, 4-dioxane (1.0 mL) under Ar afforded 26.0 mg (70%) of **4qb**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 10.32 (s, 1H), 7.94 – 7.68 (m, 1H), 7.54 (dd, J = 6.6, 1.2 Hz, 1H), 7.46 – 7.31 (m, 2H), 3.82 (dq, J = 14.2, 7.1 Hz, 1H), 3.63 (s, 2H), 1.52 (d, J = 7.1 Hz, 6H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 187.23, 165.32, 145.29, 142.74, 128.54, 126.52, 124.92, 124.01, 35.94, 27.02, 22.18; HRMS m/z (ESI) calcd for $C_{13}H_{14}ONa$ $(M + Na)^+$ 209.0942, found 209.0937.

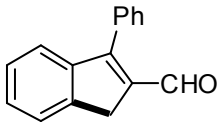
3-Benzyl-1*H*-indene-2-carbaldehyde (4rb)



4rb

The reaction of **1r** (39.2 mg, 0.20 mmol), **2b** (27.0 μL, 0.40 mmol), $[Cp^*RhCl_2]_2$ (3.1 mg, 2.5 mol %), $AgSbF_6$ (6.8 mg, 10 mol %) and $Cu(OAc)_2$ (76.0 mg, 2.1 eq), in 1, 4-dioxane (1.0 mL) under Ar afforded 25.0 mg (53%) of **4rb**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 10.27 (s, 1H), 7.53 (d, J = 7.4 Hz, 1H), 7.46 (d, J = 7.5 Hz, 1H), 7.36 (t, J = 7.4 Hz, 1H), 7.32 – 7.21 (m, 6H), 4.39 (s, 2H), 3.72 (s, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 187.32, 157.24, 144.61, 143.80, 140.58, 137.65, 128.98, 128.82, 128.37, 126.90, 126.79, 124.67, 122.72, 35.96, 31.34; HRMS m/z (ESI) calcd for $C_{17}H_{14}ONa$ $(M + Na)^+$ 257.0942, found 257.0937.

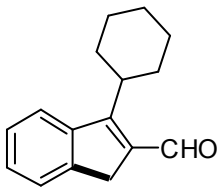
3-Phenyl-1*H*-indene-2-carbaldehyde (4sb)



4sb

The reaction of **1s** (36.4 mg, 0.20 mmol), **2b** (27.0 μL, 0.40 mmol), $[Cp^*RhCl_2]_2$ (3.1 mg, 2.5 mol %), $AgSbF_6$ (6.8 mg, 10 mol %) and $Cu(OAc)_2$ (76.0 mg, 2.1 eq), in 1, 4-dioxane (1.0 mL) under Ar afforded 24.0 mg (56%) of **4sb**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.93 (s, 1H), 7.62 (d, J = 7.4 Hz, 1H), 7.58 – 7.49 (m, 6H), 7.49 – 7.35 (m, 2H), 3.82 (s, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 189.32, 158.98, 144.41, 143.70, 140.49, 132.00, 129.60, 129.29, 129.11, 128.71, 127.03, 124.87, 123.35, 35.99; HRMS m/z (ESI) calcd for $C_{16}H_{12}ONa$ $(M + Na)^+$ 243.0786, found 243.0780.

3-Cyclohexyl-1*H*-indene-2-carbaldehyde (4tb)

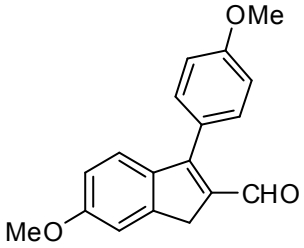


4tb

The reaction of **1t** (38.0 mg, 0.20 mmol), **2b** (27.0 μL, 0.40 mmol), $[Cp^*RhCl_2]_2$ (3.1 mg, 2.5 mol %), $AgSbF_6$ (6.8 mg, 10 mol %) and $Cu(OAc)_2$ (76.0 mg, 2.1 eq), in 1, 4-dioxane (1.0 mL) under Ar

afforded 32.0 mg (71%) of **4tb**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.34 (s, 1H), 7.79 (dd, *J* = 6.0, 2.4 Hz, 1H), 7.60 – 7.51 (m, 1H), 7.42 – 7.33 (m, 2H), 3.63 (s, 2H), 3.45-3.30 (m, 1H), 2.12 – 1.73 (m, 8H), 1.46 – 1.37 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 187.41, 164.20, 145.24, 143.21, 139.09, 128.49, 126.47, 124.86, 124.06, 38.11, 36.01, 32.24, 26.66, 26.01; HRMS m/z (ESI) calcd for $C_{16}H_{18}ONa$ $(M + Na)^+$ 249.1255, found 249.1250.

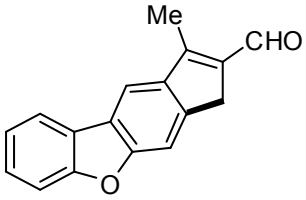
5-Methoxy-3-(4-methoxyphenyl)-1*H*-indene-2-carbaldehyde (4ub)



4ub

The reaction of **1u** (48.4 mg, 0.20 mmol), **2b** (27.0 μL, 0.40 mmol), $[Cp^*RhCl_2]_2$ (3.1 mg, 2.5 mol %), $AgSbF_6$ (6.8 mg, 10 mol %) and $Cu(OAc)_2$ (76.0 mg, 2.1 eq), in 1, 4-dioxane (1.0 mL) under Ar afforded 35.5 mg (63%) of **4ub**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.83 (s, 1H), 7.58 – 7.39 (m, 3H), 7.14 (d, *J* = 2.2 Hz, 1H), 7.09 – 7.02 (m, 2H), 6.92 (dd, *J* = 8.5, 2.3 Hz, 1H), 3.90 (s, 3H), 3.88 (s, 3H), 3.76 (s, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 188.84, 161.30, 160.50, 159.06, 147.04, 138.18, 136.74, 130.97, 124.51, 124.36, 114.16, 113.80, 110.06, 55.59, 55.38, 35.89; HRMS m/z (ESI) calcd for $C_{18}H_{16}O_3Na$ $(M + Na)^+$ 303.0997, found 303.0992.

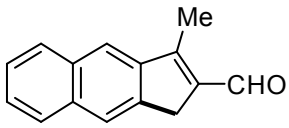
1-Methyl-3*H*-indeno[5,6-b]benzofuran-2-carbaldehyde (4vb)



4vb

The reaction of **1v** (42.0 mg, 0.20 mmol), **2b** (27.0 μL, 0.40 mmol), $[Cp^*RhCl_2]_2$ (3.1 mg, 2.5 mol %), $AgSbF_6$ (6.8 mg, 10 mol %) and $Cu(OAc)_2$ (76.0 mg, 2.1 eq), in 1, 4-dioxane (1.0 mL) under Ar afforded 34.0 mg (68%) of **4vb**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 10.21 (s, 1H), 8.07 (s, 1H), 7.99 (dd, *J* = 7.6, 0.5 Hz, 1H), 7.67 (s, 1H), 7.58 (d, *J* = 8.2 Hz, 1H), 7.52 – 7.44 (m, 1H), 7.42 – 7.34 (m, 1H), 3.73 (s, 2H), 2.65 (t, *J* = 2.1 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 186.66, 157.61, 156.60, 155.78, 144.41, 140.20, 139.07, 127.28, 123.94, 123.76, 122.94, 120.48, 113.41, 111.83, 108.27, 35.66, 11.01; HRMS m/z (ESI) calcd for $C_{17}H_{12}O_2Na$ $(M + Na)^+$ 271.0735, found 271.0730.

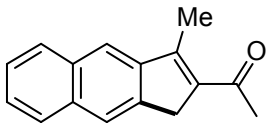
3-Methyl-1*H*-cyclopenta[*b*]naphthalene-2-carbaldehyde (4wb)



4wb

The reaction of **1w** (34.0 mg, 0.20 mmol), **2b** (27.0 μL, 0.40 mmol), $[Cp^*RhCl_2]_2$ (3.1 mg, 2.5 mol %), $AgSbF_6$ (6.8 mg, 10 mol %) and $Cu(OAc)_2$ (76.0 mg, 2.1 eq), in 1, 4-dioxane (1.0 mL) under Ar afforded 32.0 mg (77%) of **4wb**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 10.30 (s, 1H), 8.01 (s, 1H), 7.90 (m, 3H), 7.58 – 7.44 (m, 2H), 3.73 (s, 2H), 2.63 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 187.45, 155.28, 143.74, 140.43, 140.38, 134.12, 132.60, 128.57, 127.89, 126.57, 125.66, 122.98, 120.89, 34.79, 10.78; HRMS m/z (ESI) calcd for $C_{15}H_{12}ONa$ $(M + Na)^+$ 231.0786, found 231.0780.

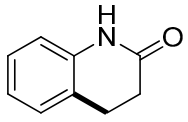
1-(3-Methyl-1*H*-cyclopenta[*b*]naphthalen-2-yl)ethanone (4wa)



4wa

The reaction of **1w** (34.0 mg, 0.20 mmol), **2a** (35.0 μL, 0.40 mmol), $[Cp^*RhCl_2]_2$ (3.1 mg, 2.5 mol %), $AgSbF_6$ (6.8 mg, 10 mol %) and $Cu(OAc)_2$ (76.0 mg, 2.1 eq), in 1, 4-dioxane (1.0 mL) under Ar afforded 25.0 mg (60%) of **4wa**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 – 7.90 (m, 2H), 7.86 (d, J = 8.6 Hz, 2H), 7.57 – 7.43 (m, 2H), 3.80 (dd, J = 2.3, 1.0 Hz, 2H), 2.63 (t, J = 2.3 Hz, 3H), 2.49 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.18, 149.44, 144.48, 139.92, 138.73, 133.65, 132.73, 128.47, 127.78, 126.08, 125.49, 122.43, 120.62, 38.29, 30.47, 13.04; HRMS m/z (ESI) calcd for $C_{16}H_{14}ONa$ $(M + Na)^+$ 245.0942, found 245.0937.

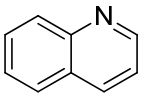
3,4-Dihydroquinolin-2(1*H*)-one (5xb) [3]



5xb

The reaction of **1x** (54.0 mg, 0.40 mmol), **2b** (82.0 μL, 1.60 mmol), $[Cp^*RhCl_2]_2$ (6.2 mg, 2.5 mol %), $AgSbF_6$ (13.7 mg, 10 mol %) and $Cu(OAc)_2$ (291.0 mg, 4.0 eq), in 1,4-dioxane (2.0 mL) under Ar afforded 24.0 mg (41%) of **5xb**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.07 (br s, 1H), 7.23-7.13 (m, 2H), 6.99 (td, J = 7.5, 1.1 Hz, 1H), 6.84 (d, J = 7.8 Hz, 1H), 2.98 (t, J = 7.9 Hz, 2H), 2.66 (dd, J = 7.9, 7.2 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 172.13, 137.23, 127.88, 127.48, 123.58, 123.04, 115.48, 30.70, 25.29; HRMS m/z (ESI) calcd for C_9H_9NONa $(M + Na)^+$ 170.0576, found 170.0579.

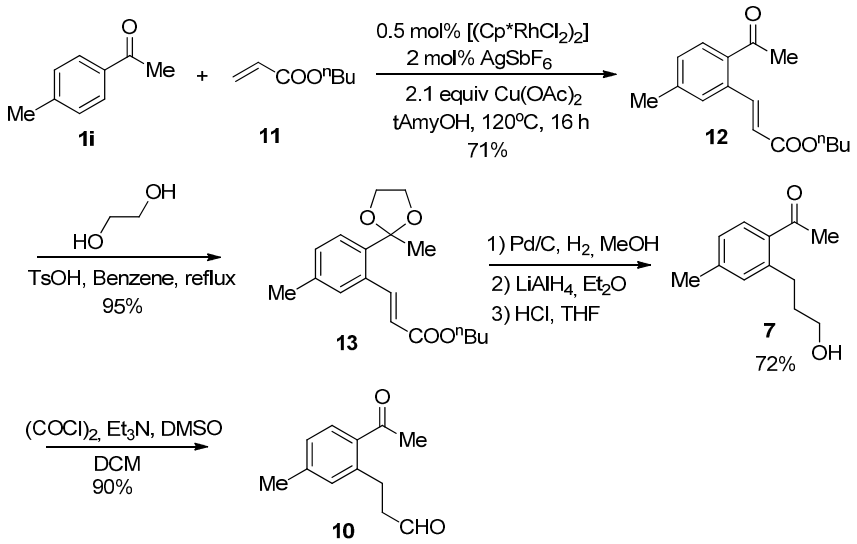
Quinoline (6xb)[4]



6xb

The reaction of **1x** (54.0 mg, 0.40 mmol), **2b** (82.0 μL, 1.60 mmol), $[Cp^*RhCl_2]_2$ (6.2 mg, 2.5 mol %), $AgSbF_6$ (13.7 mg, 10 mol %) and AgOAc (267.0 mg, 4.0 eq), in 1,4-dioxane (2.0 mL) under Ar afforded quinoline **6xb** as a major product (38% NMR yield, a sample of which could be obtained in a pure form for characterization) and just traces of **1y**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.94 (d, *J* = 2.4 Hz, 1H), 8.19 (d, *J* = 8.2 Hz, 1H), 8.14 (d, *J* = 8.5 Hz, 1H), 7.84 (d, *J* = 8.2 Hz, 1H), 7.79-7.70 (m, 1H), 7.61-7.52 (m, 1H), 7.43 (dd, *J* = 8.2, 4.2 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 150.17, 148.03, 136.32, 129.60, 129.28, 127.81, 126.65, 121.12; HRMS m/z (ESI) calcd for C_9H_7NH $(M + H)^+$ 130.0651, found 130.0644.

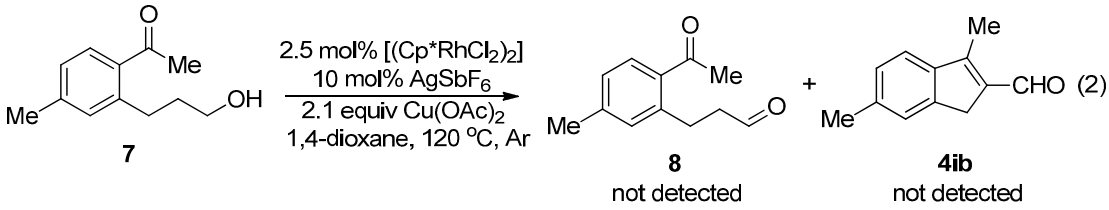
According to the following route[5], compounds **7** and **10** were synthesized.



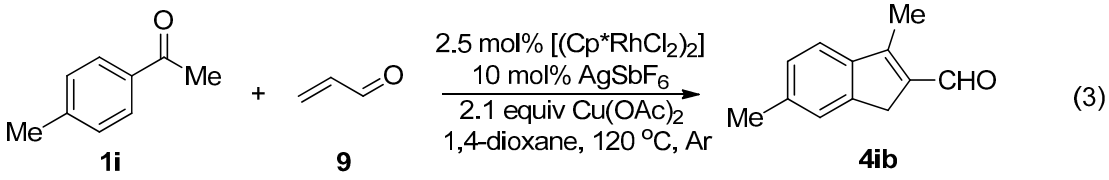
7: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.62 (d, *J* = 7.8 Hz, 1H), 7.08 (d, *J* = 7.8 Hz, 2H), 3.58 (t, *J* = 5.9 Hz, 2H), 2.92 (t, *J* = 7.3 Hz, 2H), 2.58 (s, 3H), 2.36 (s, 3H), 1.87 (ddd, *J* = 13.0, 7.2, 6.1 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 202.31, 142.48, 134.73, 132.28, 130.07, 126.58, 61.39, 34.52, 29.66, 29.40.

10: ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.81 (t, *J* = 1.4 Hz, 1H), 7.68 (d, *J* = 7.8 Hz, 1H), 7.11 (d, *J* = 10.4 Hz, 2H), 3.15 (t, *J* = 7.5 Hz, 2H), 2.77 (td, *J* = 7.5, 1.3 Hz, 2H), 2.58

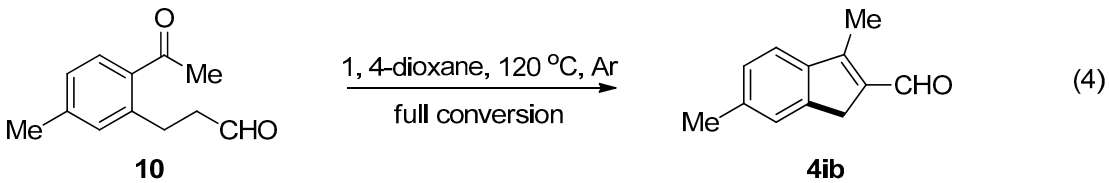
(s, 3H), 2.36 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 202.06, 200.75, 142.75, 141.55, 134.08, 132.51, 130.57, 127.08, 45.58, 29.29, 27.29, 21.39.



To a 10 mL Schlenk tube was added compound **7** (38.4 mg, 0.2 mmol), $[Cp^*RhCl_2]_2$ (3.1 mg, 2.5 mol %), $AgSbF_6$ (6.8 mg, 10 mol %) and $Cu(OAc)_2$ (76.0 mg, 2.1 eq), in 1,4-dioxane (1.0 mL) at 120 ºC under Ar for 12 h. The solution was then cooled to rt, and the solvent was removed under vaccum directly. Detected by GC-MS, there were no products **8** and **4ib** formed.



To a 10 mL Schlenk tube was added compound **1i** (27.0 μL, 0.20 mmol), **9** (27.0 μL, 0.40 mmol), $[Cp^*RhCl_2]_2$ (3.1 mg, 2.5 mol %), $AgSbF_6$ (6.8 mg, 10 mol %) and $Cu(OAc)_2$ (76.0 mg, 2.1 eq), in 1,4-dioxane (1.0 mL) under Ar at 120 ºC for 36 h. The solution was then cooled to rt, and 1, 4-dioxane was removed under vaccum directly. Then the mixture was purified by column chromatography on silica gel (eluent: petroleum ether / ethyl acetate = 20 : 1) to afford 10.0 mg (28%) of **4ib**.



To a 10 mL Schlenk tube was added compound **10** (38.0 mg, 0.20 mmol) in 1,4-dioxane (1.0 mL) at 120 ºC under Ar for 12 h. The solution was then cooled to rt, and the solvent was removed under vaccum directly. Detected by GC-MS, product **4ib** was formed in full conversion.

3. References

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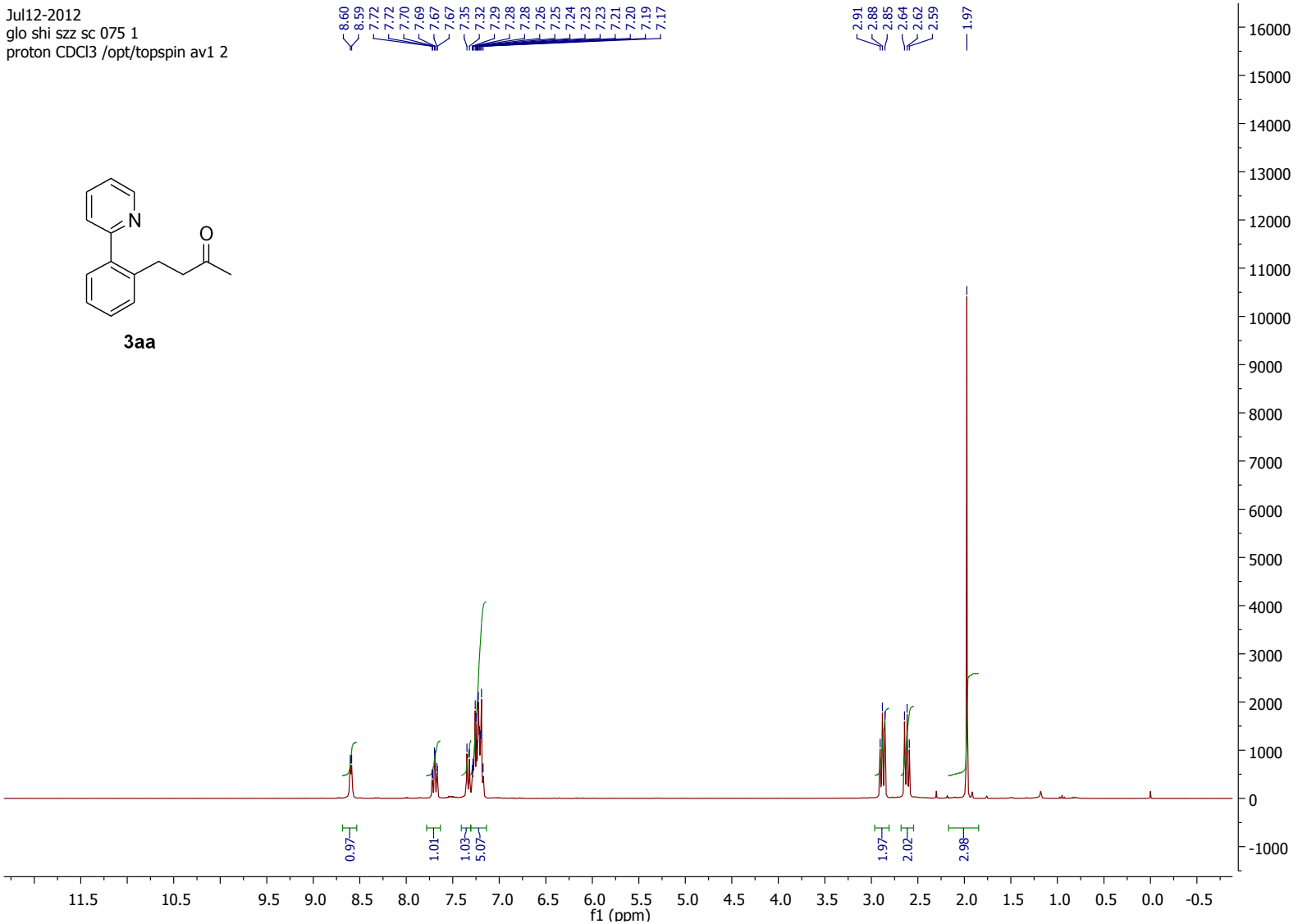
4. J. Chen, Y. Zhang, L. Yang, X. Zhang, J. Liu, L.Li, H. Zhang, Tetrahedron **2007**, *63*, 4266.

5. F. W. Patureau, T. Besset, F. Glorius, *Angew. Chem. Int. Ed*. **2011**, *50*, 1064.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7.67
7.35
7.32
7.29
7.28
7.28
7.26
7.25
7.24
7.23
7.23
7.21
7.20
7.19
7.17
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2.88
2.85
2.64
2.62
2.59
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O
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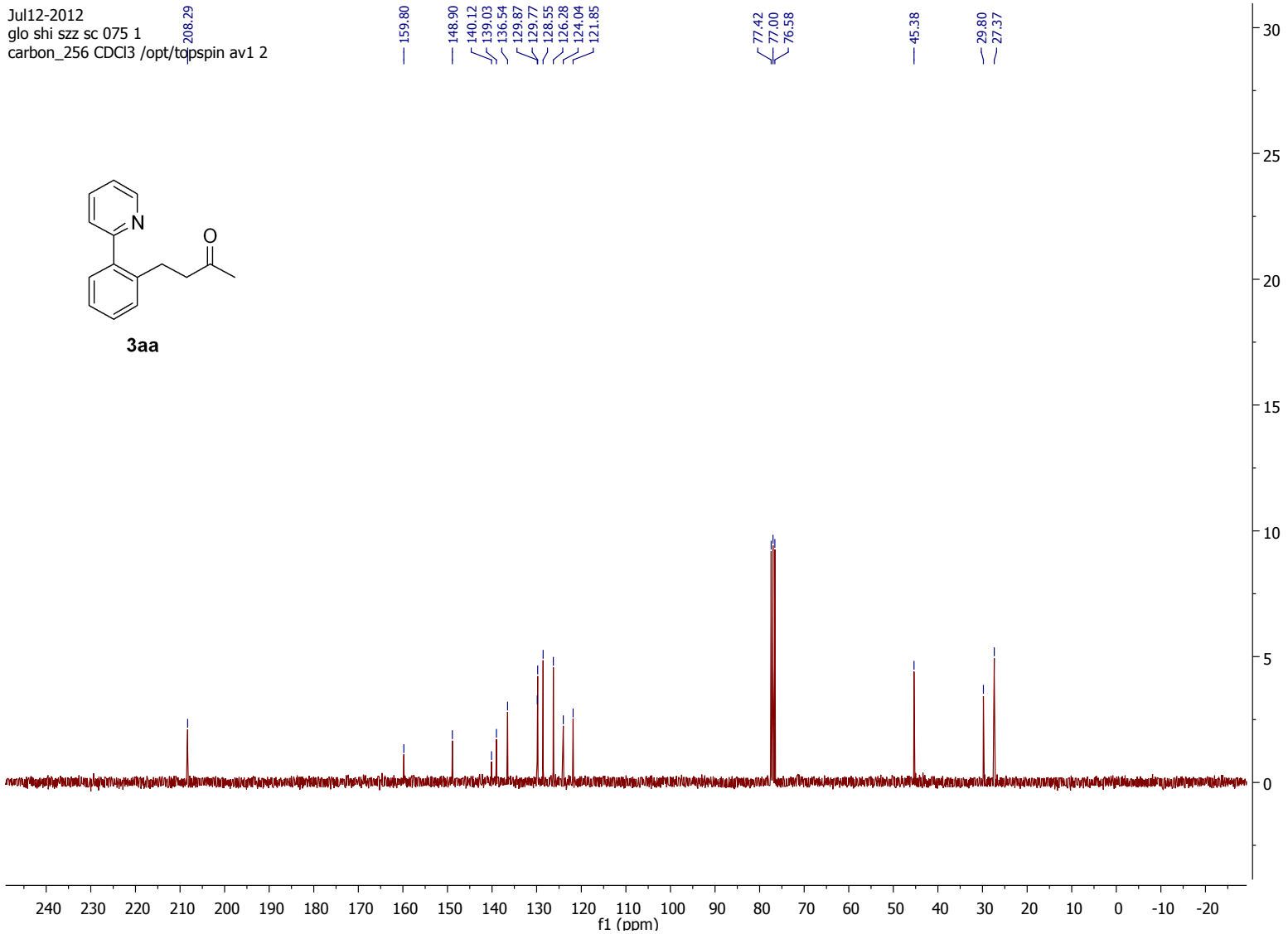
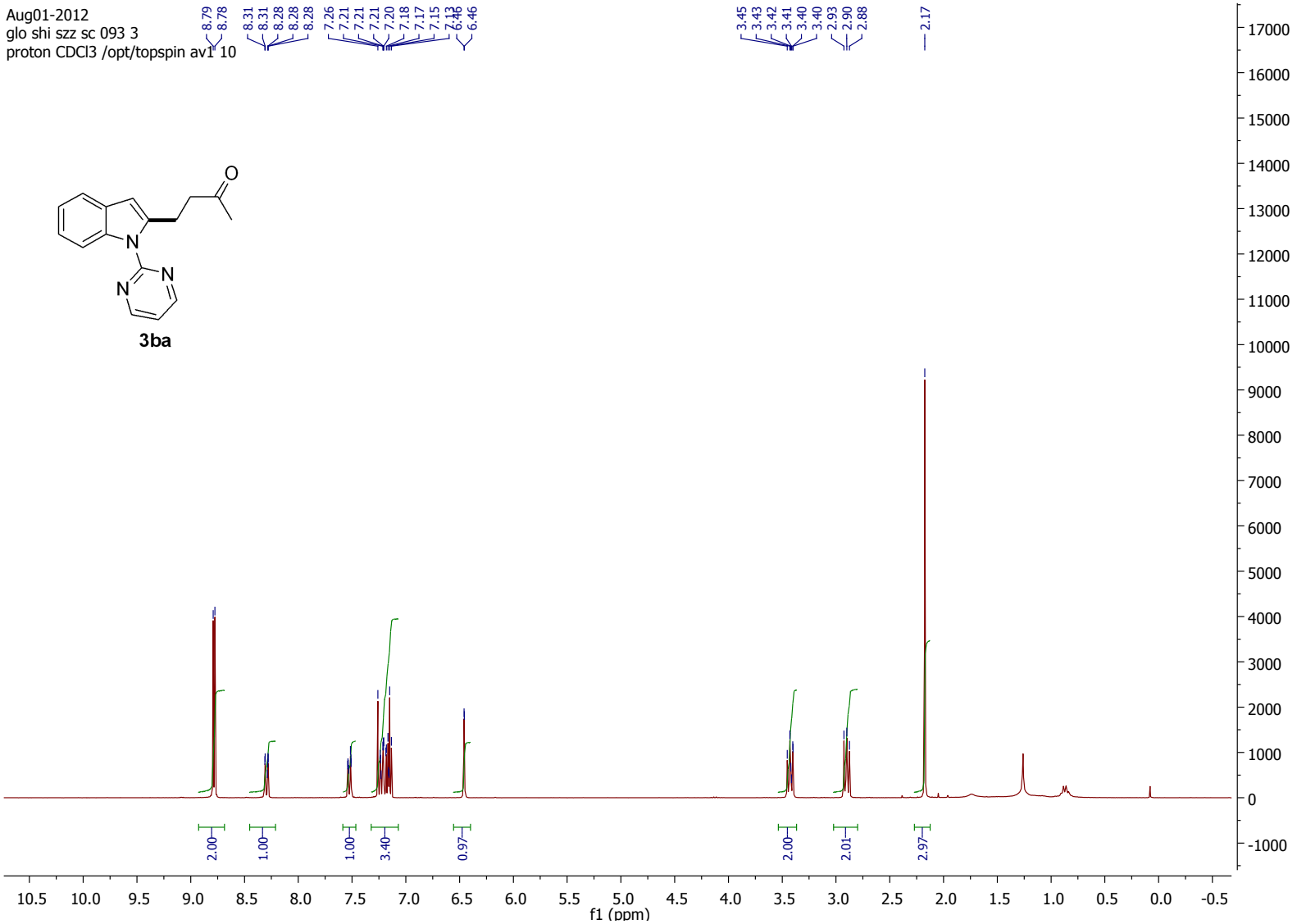
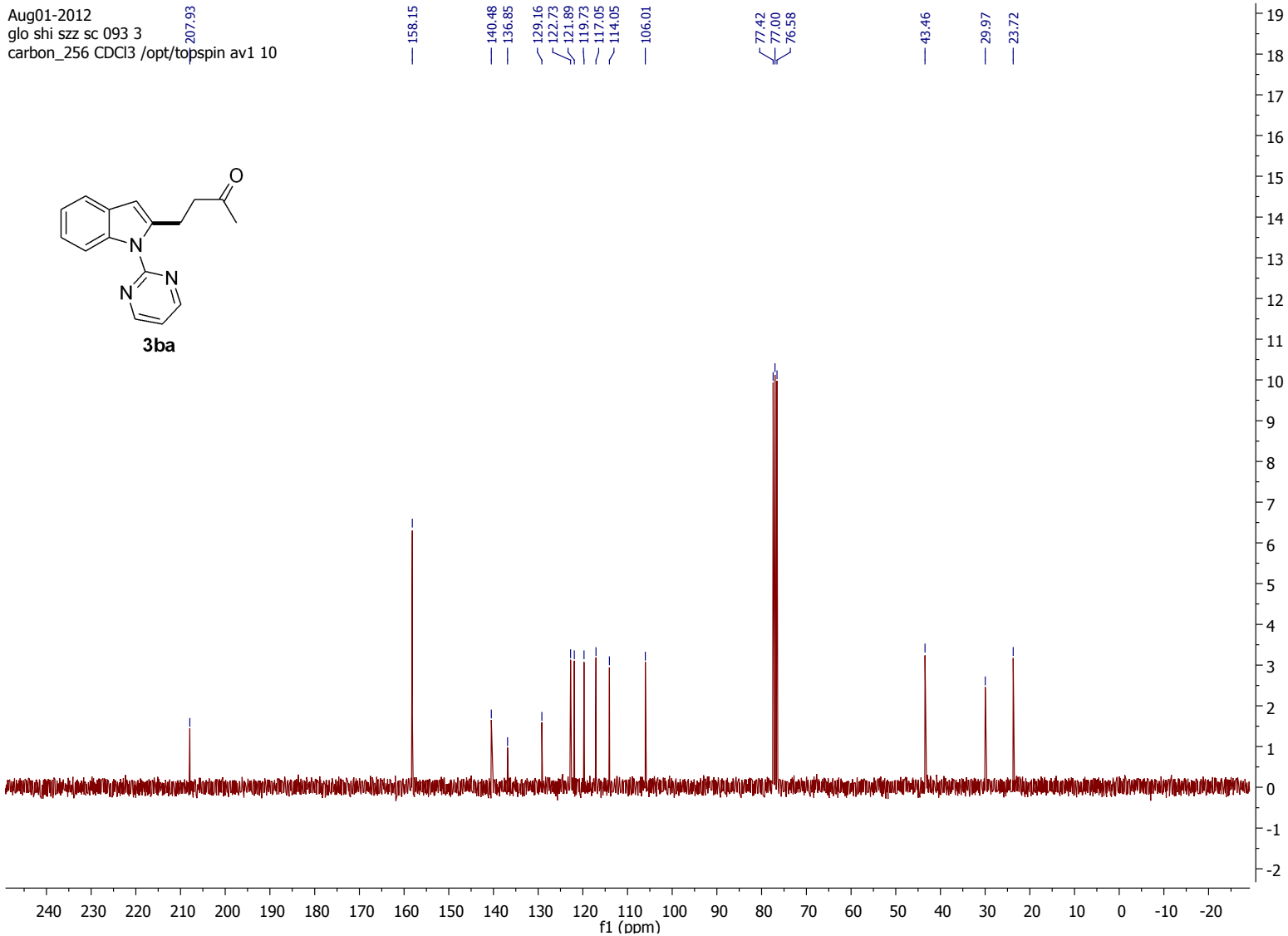
1.01
1.03
5.07
1.97
2.02
2.98
f1 (ppm)



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119.73
117.05
114.05
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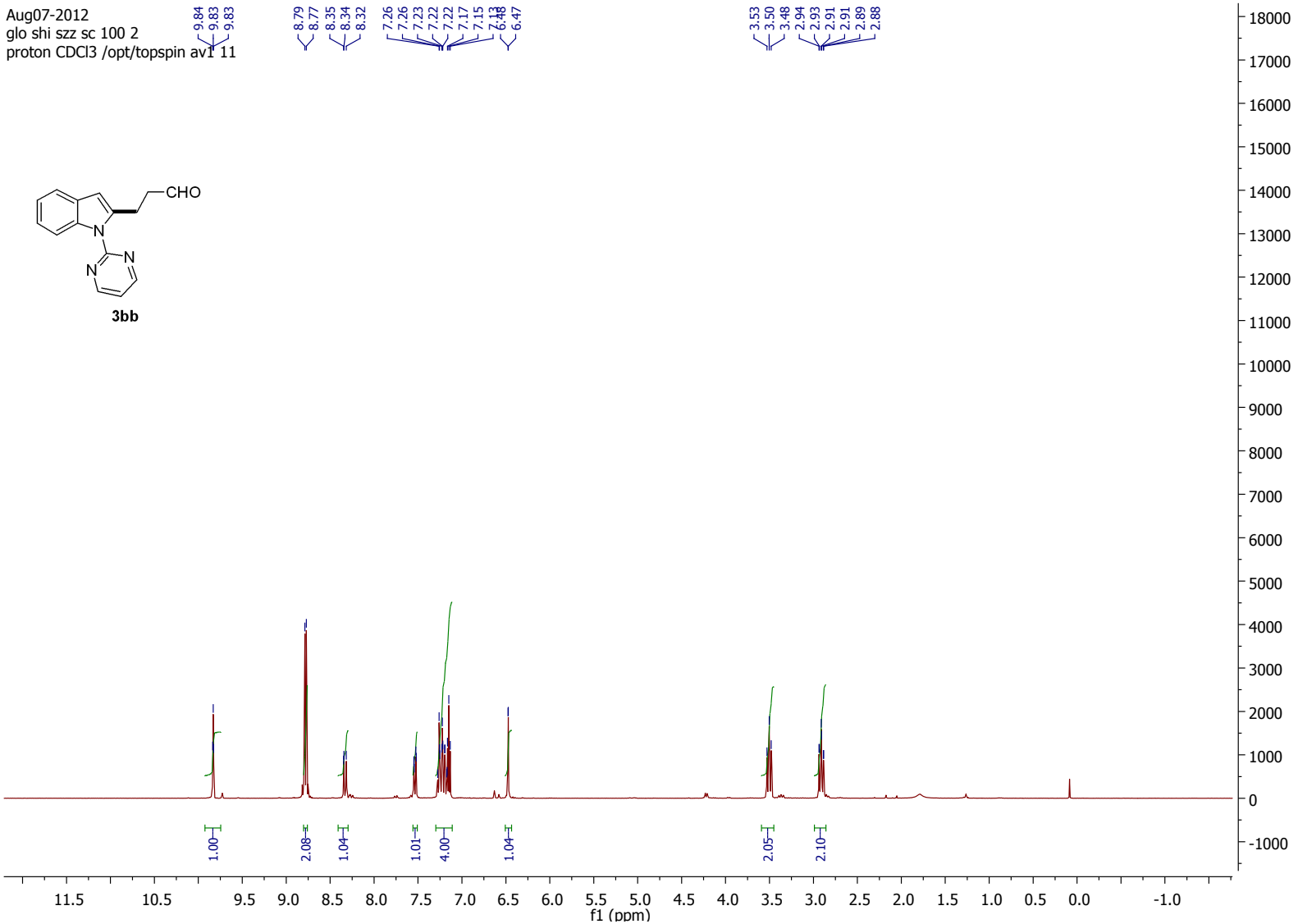
N
N
3ba
f1 (ppm)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7.26
7.23
7.22
7.22
7.17
7.15
7.13
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6.47
3.53
3.50
3.48
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2.93
2.91
2.91
2.89
2.88
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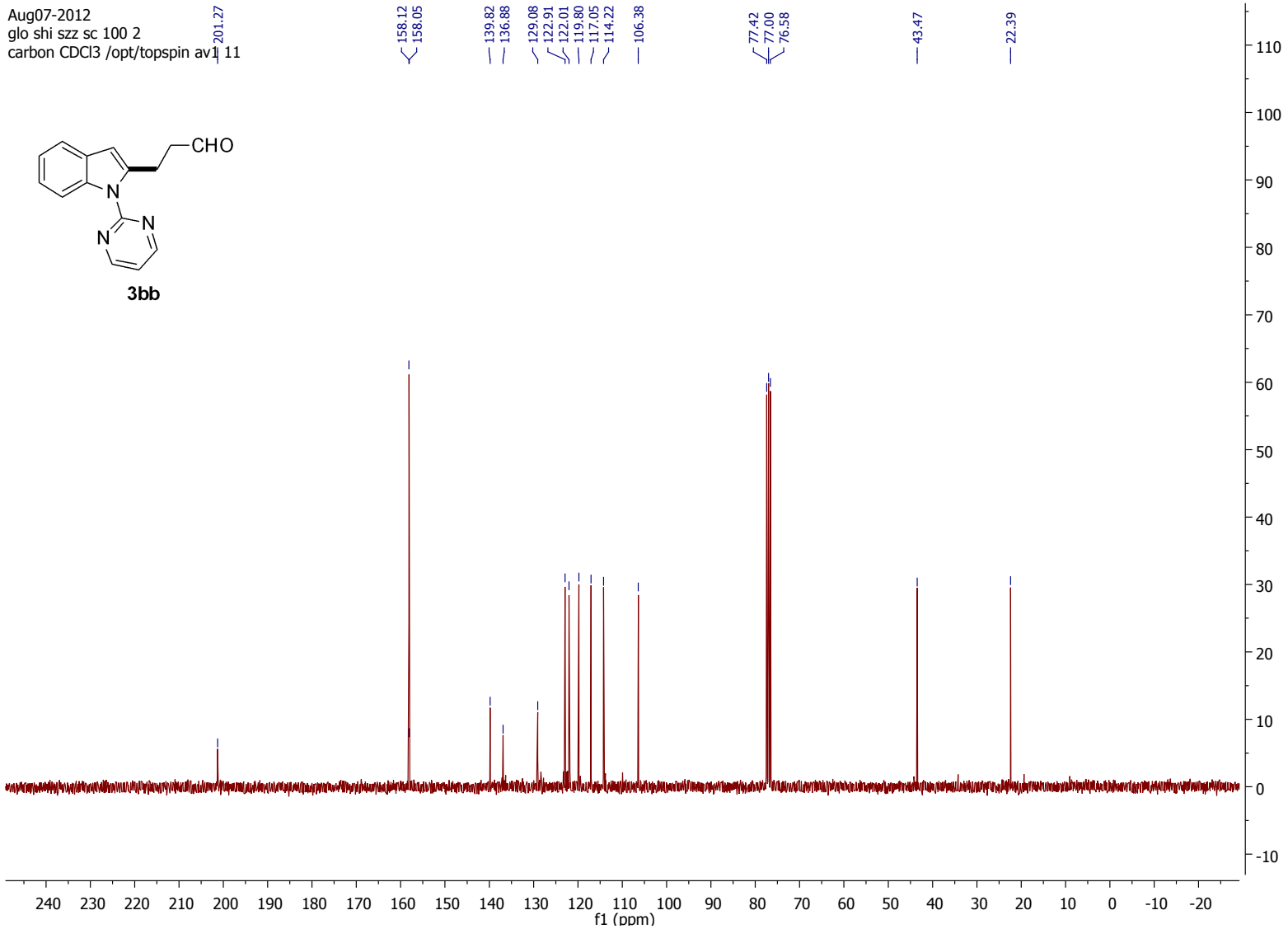
f1 (ppm)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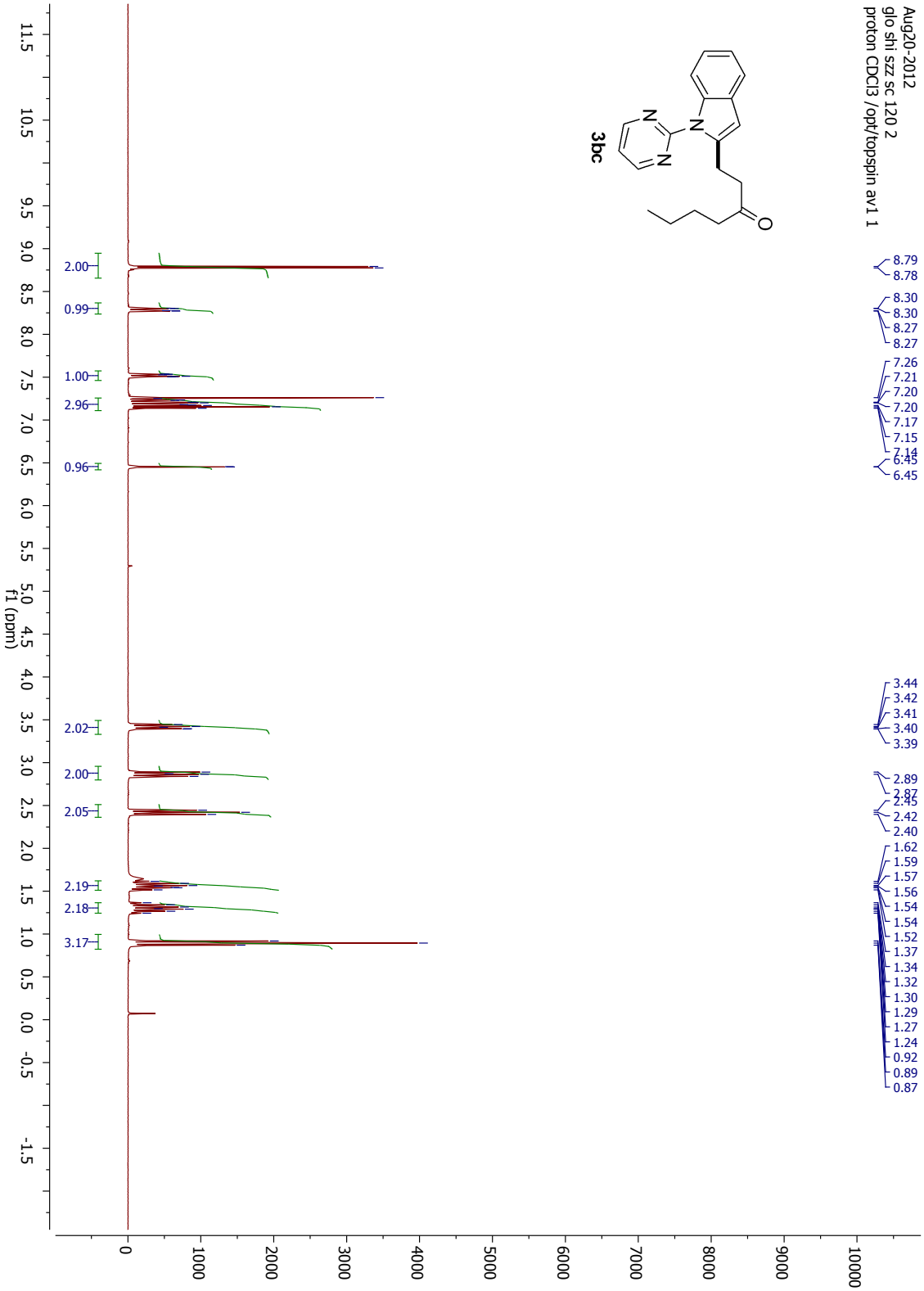
N
3bb
f1 (ppm)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9.0
8.5
8.0
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7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
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-1.5
2.00
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1.00
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0.96
2.02
2.00
2.05
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7.20
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7.14
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1.32
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4000
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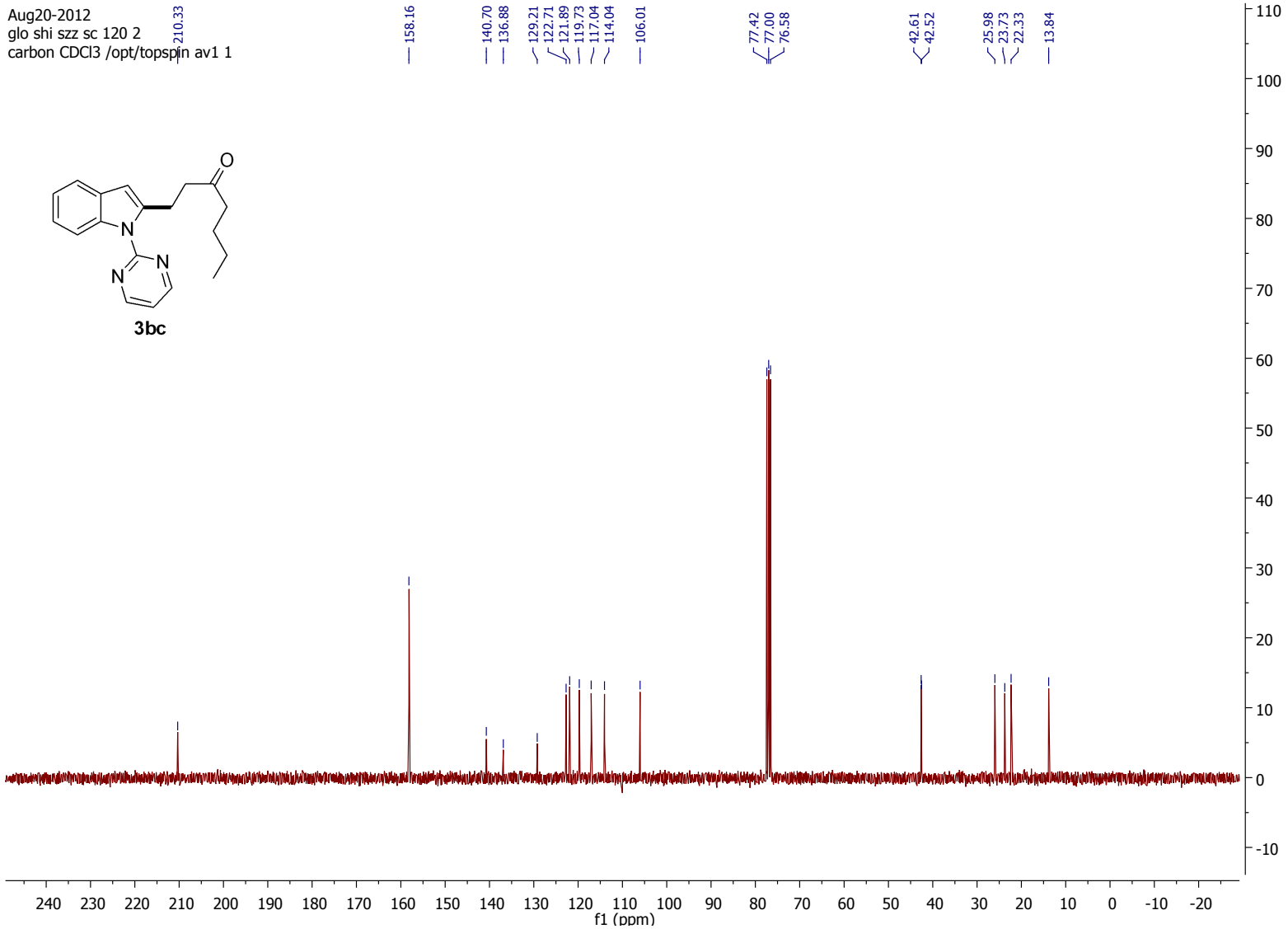
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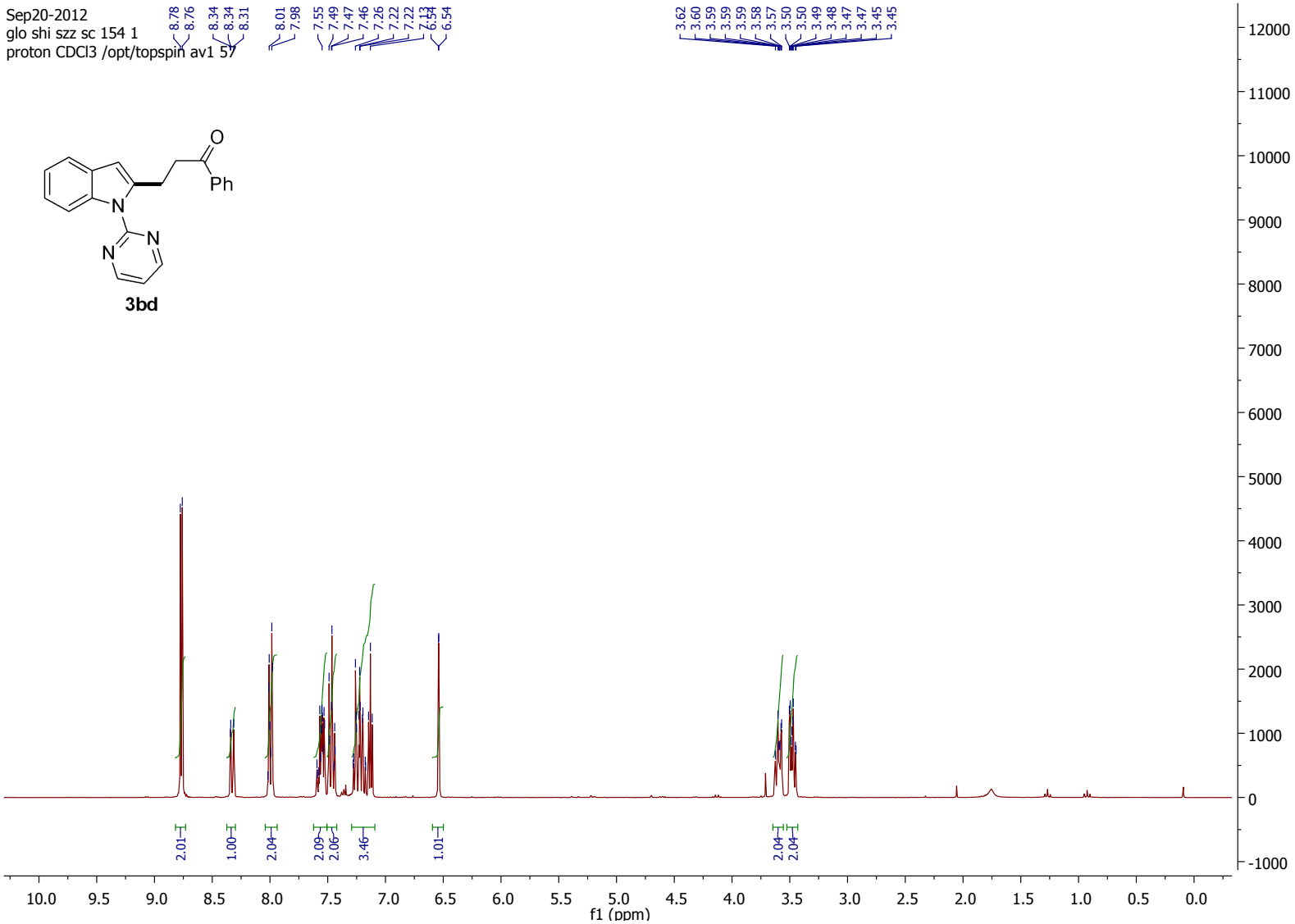
f1 (ppm)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3.47
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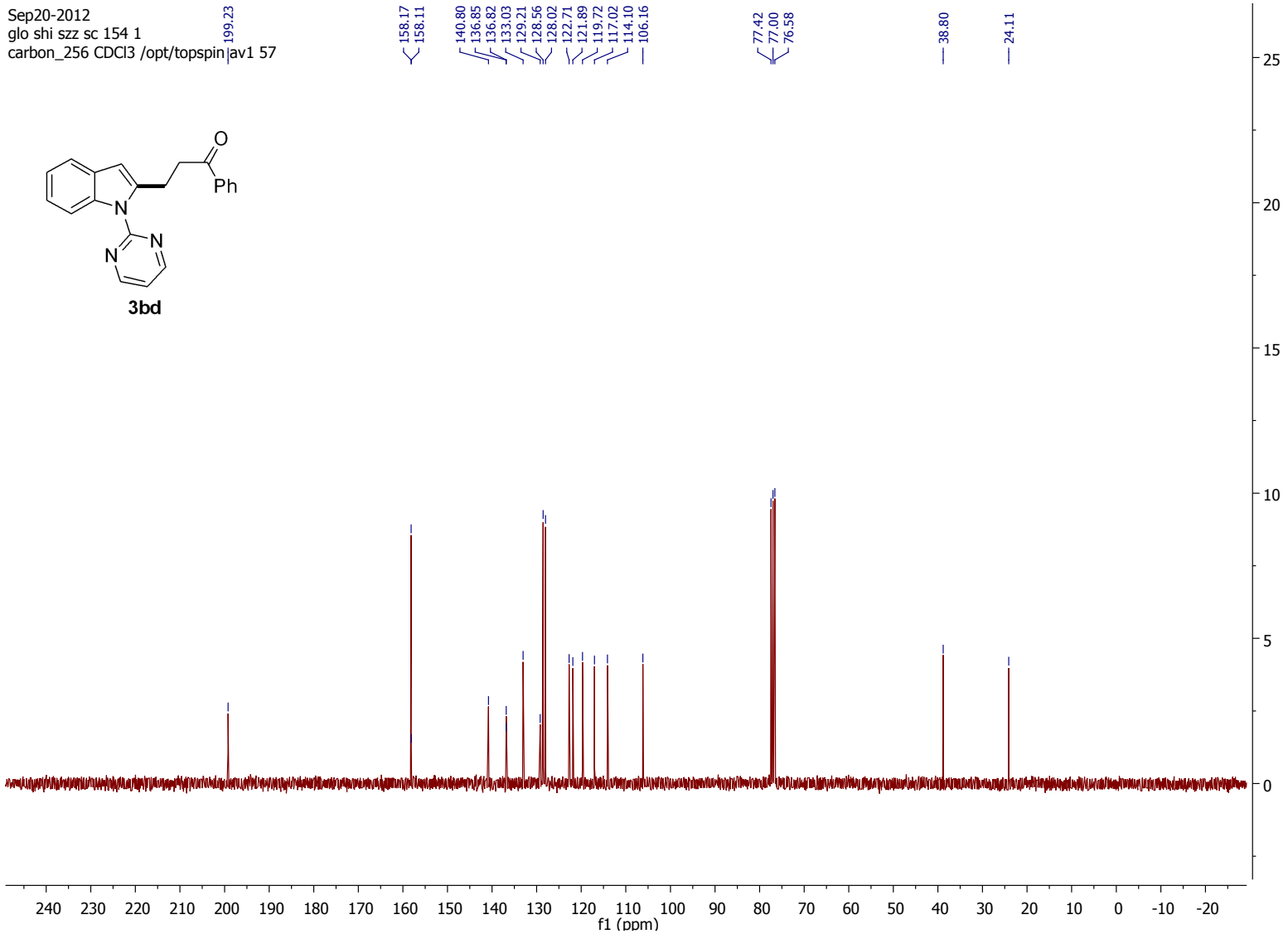
f1 (ppm)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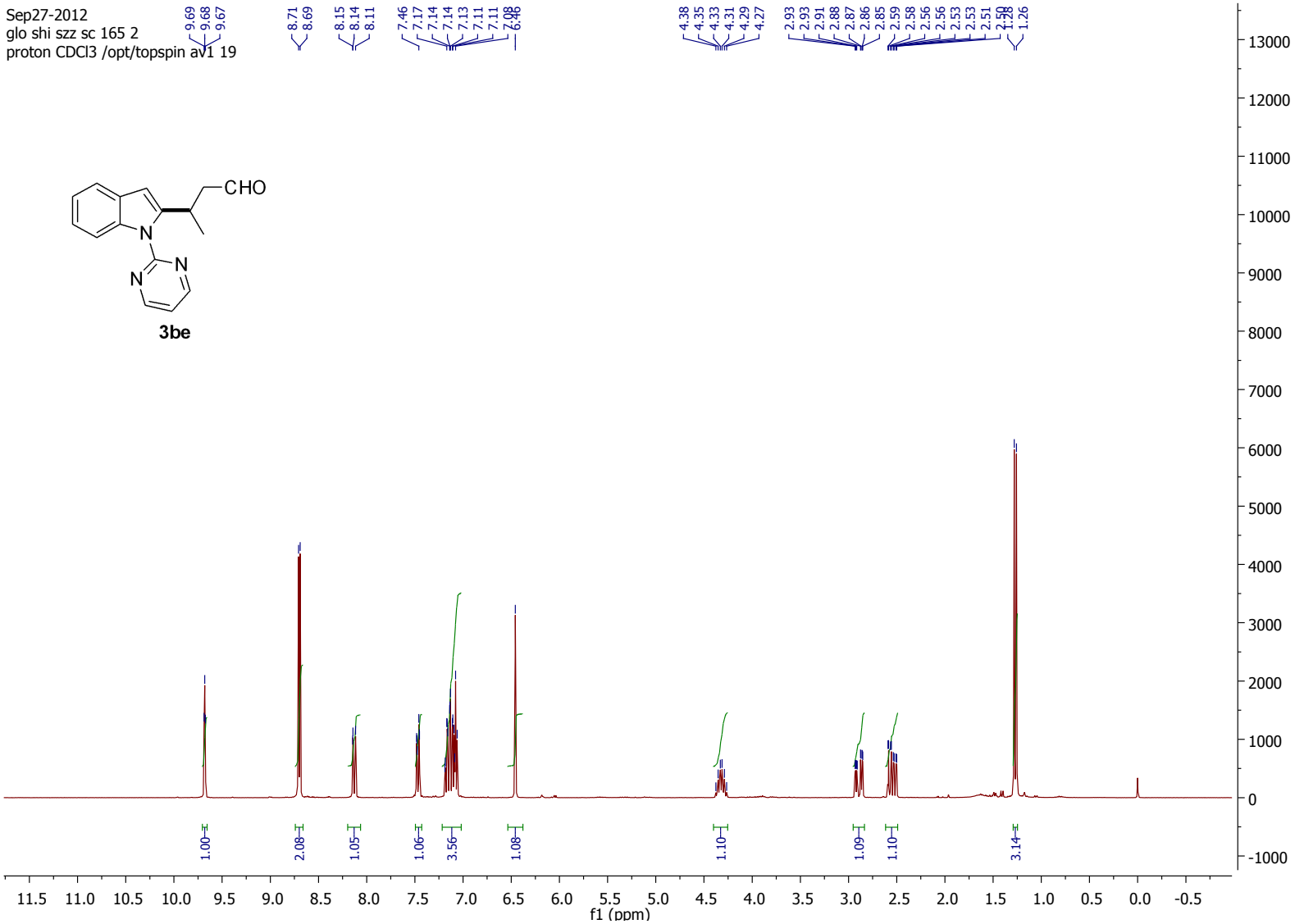
f1 (ppm)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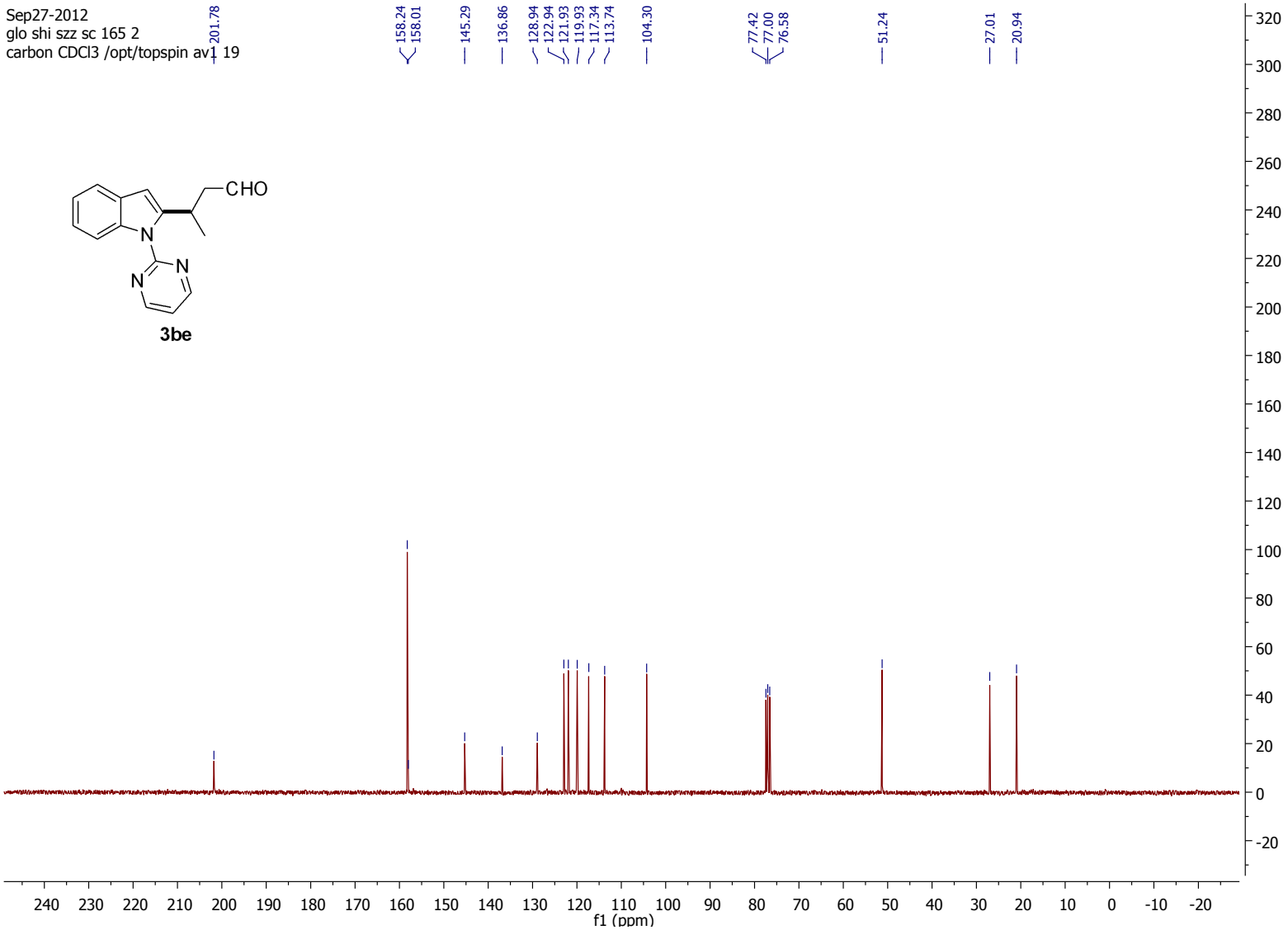
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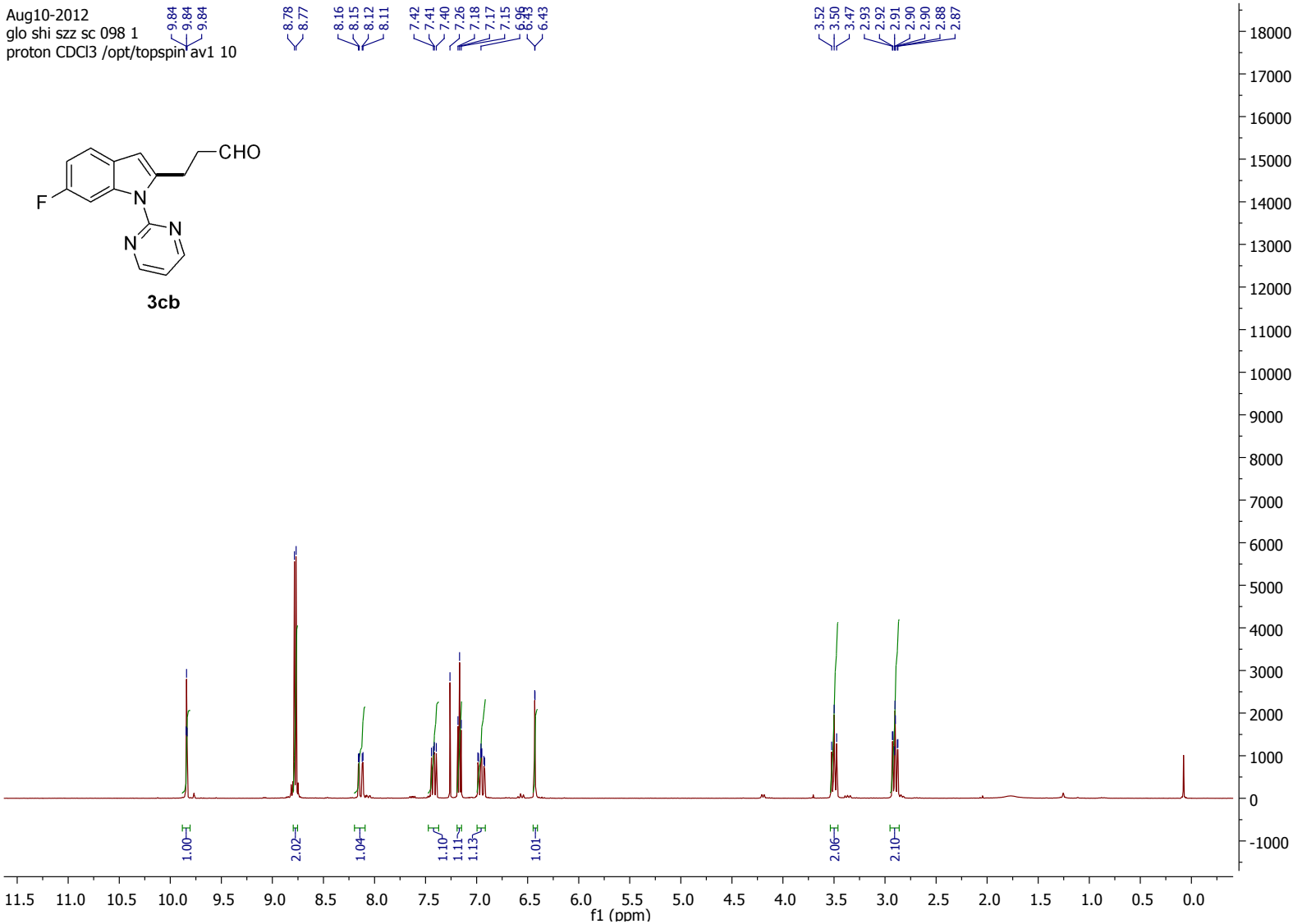

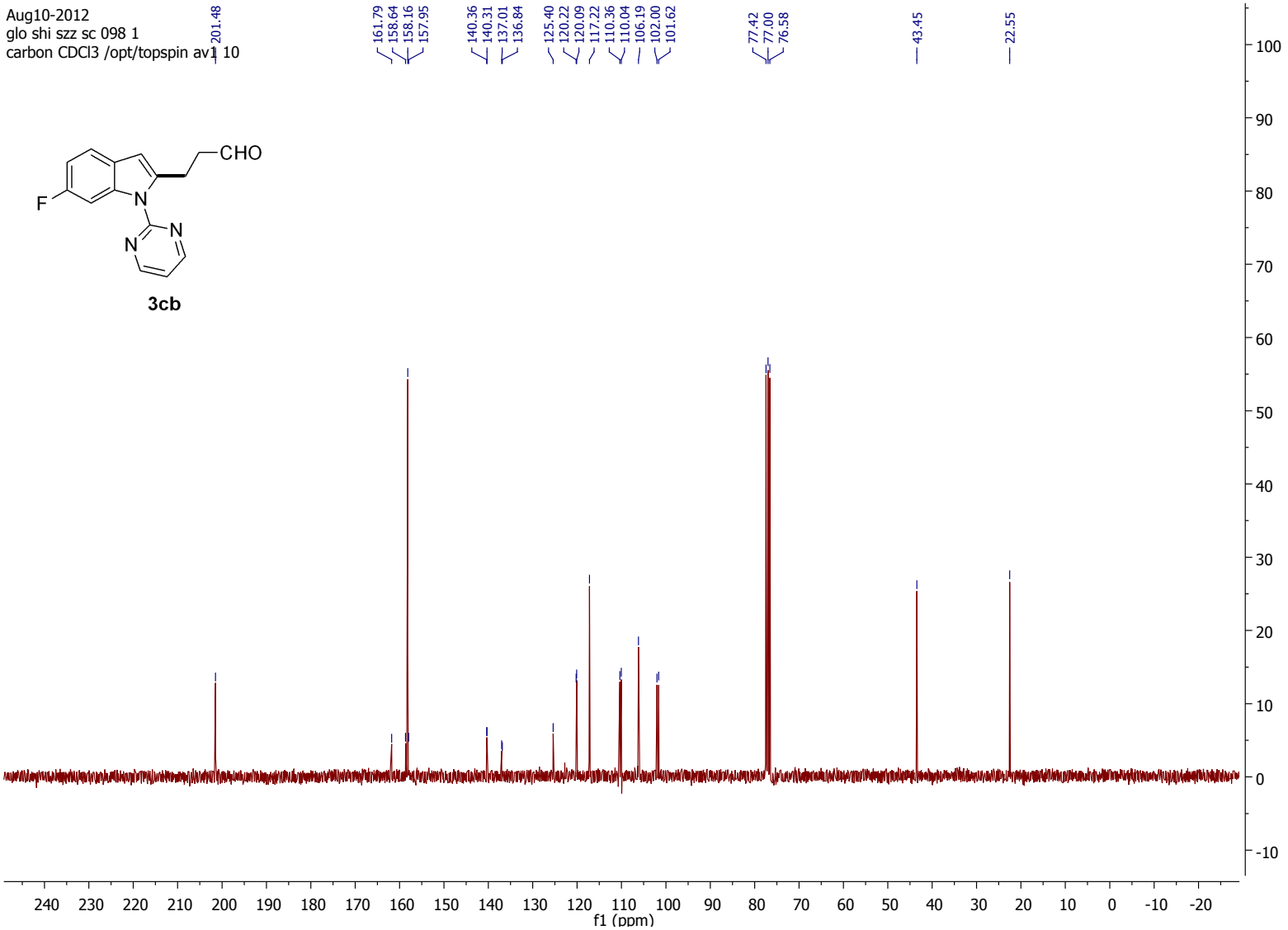
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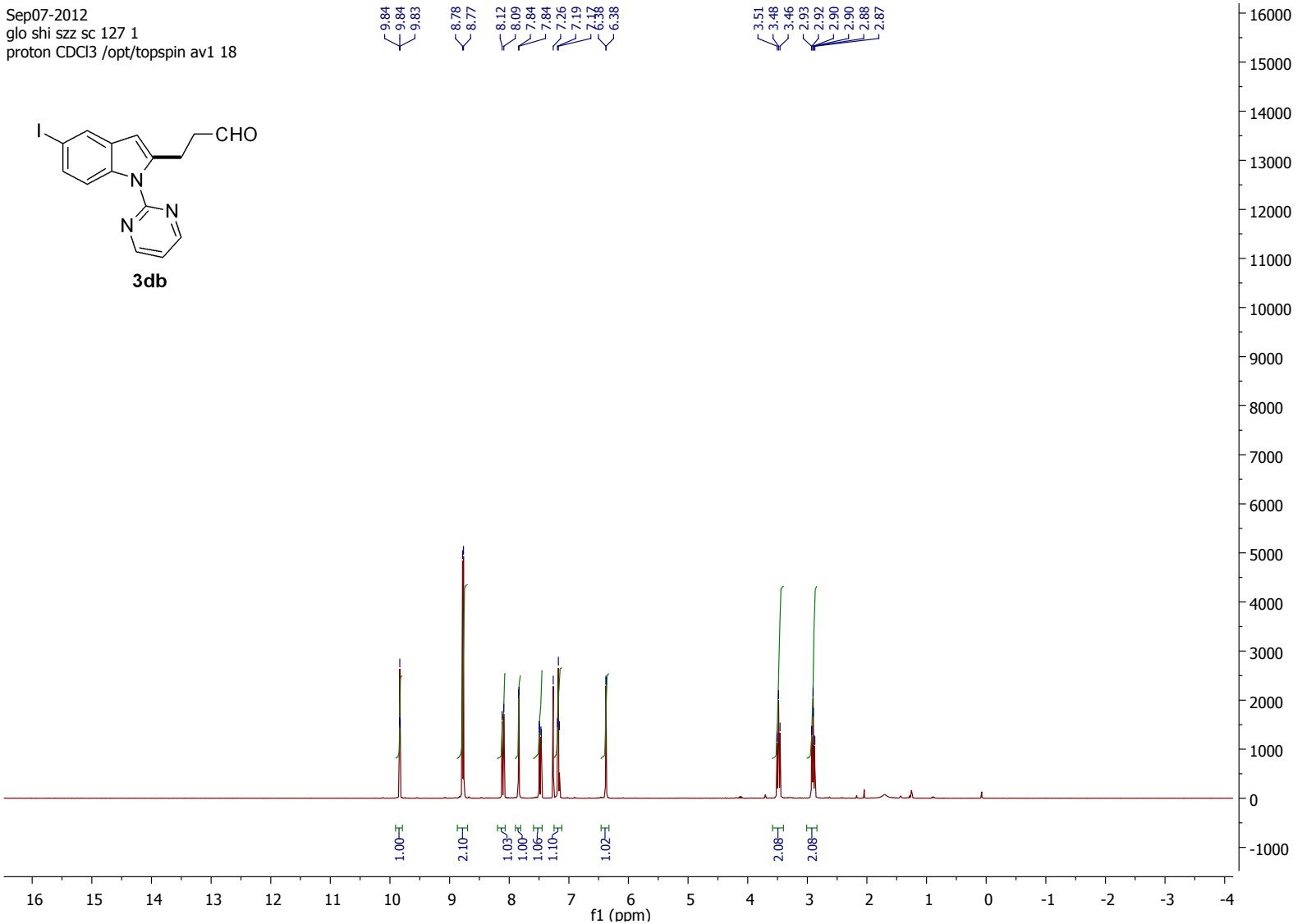
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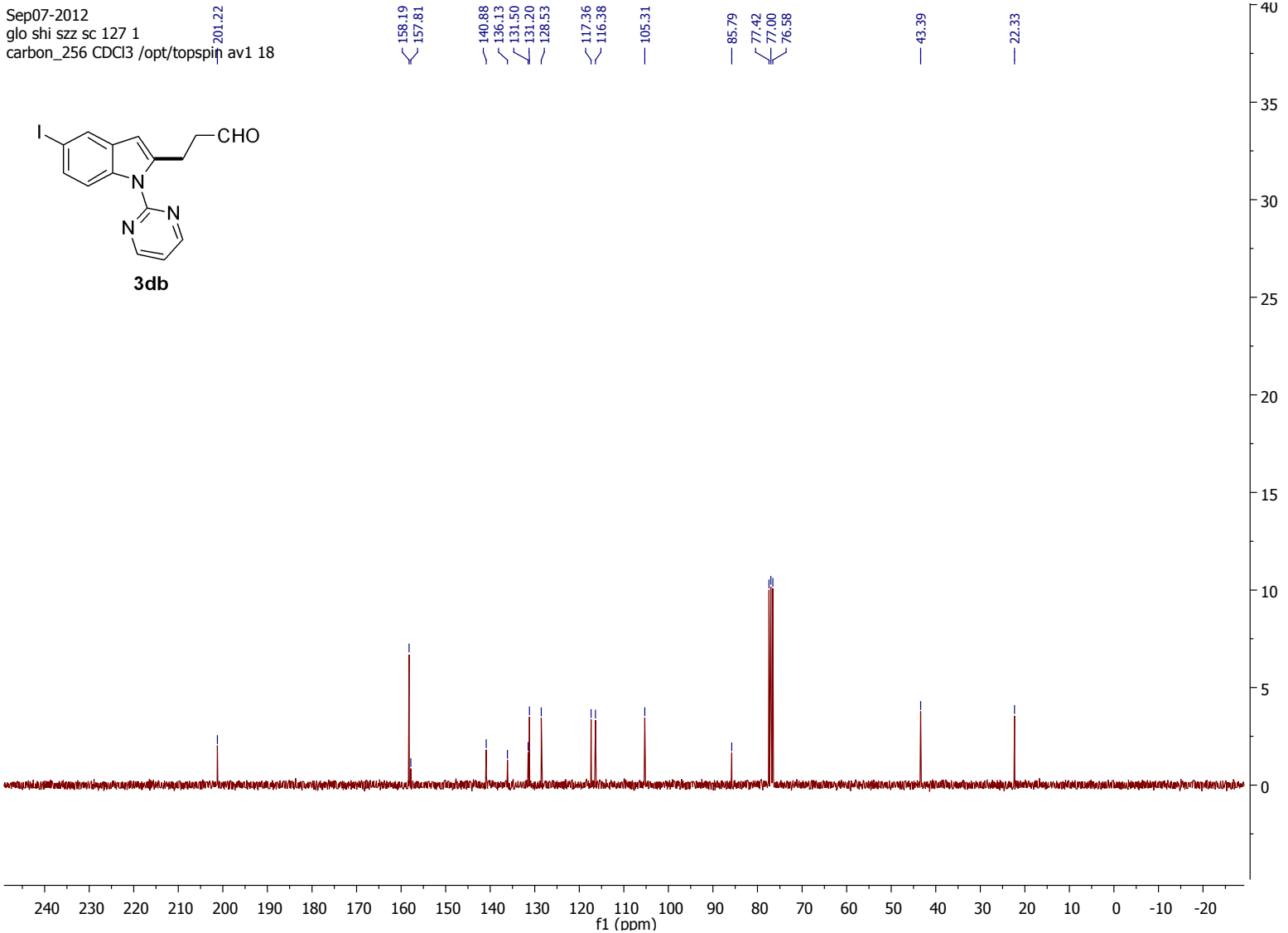
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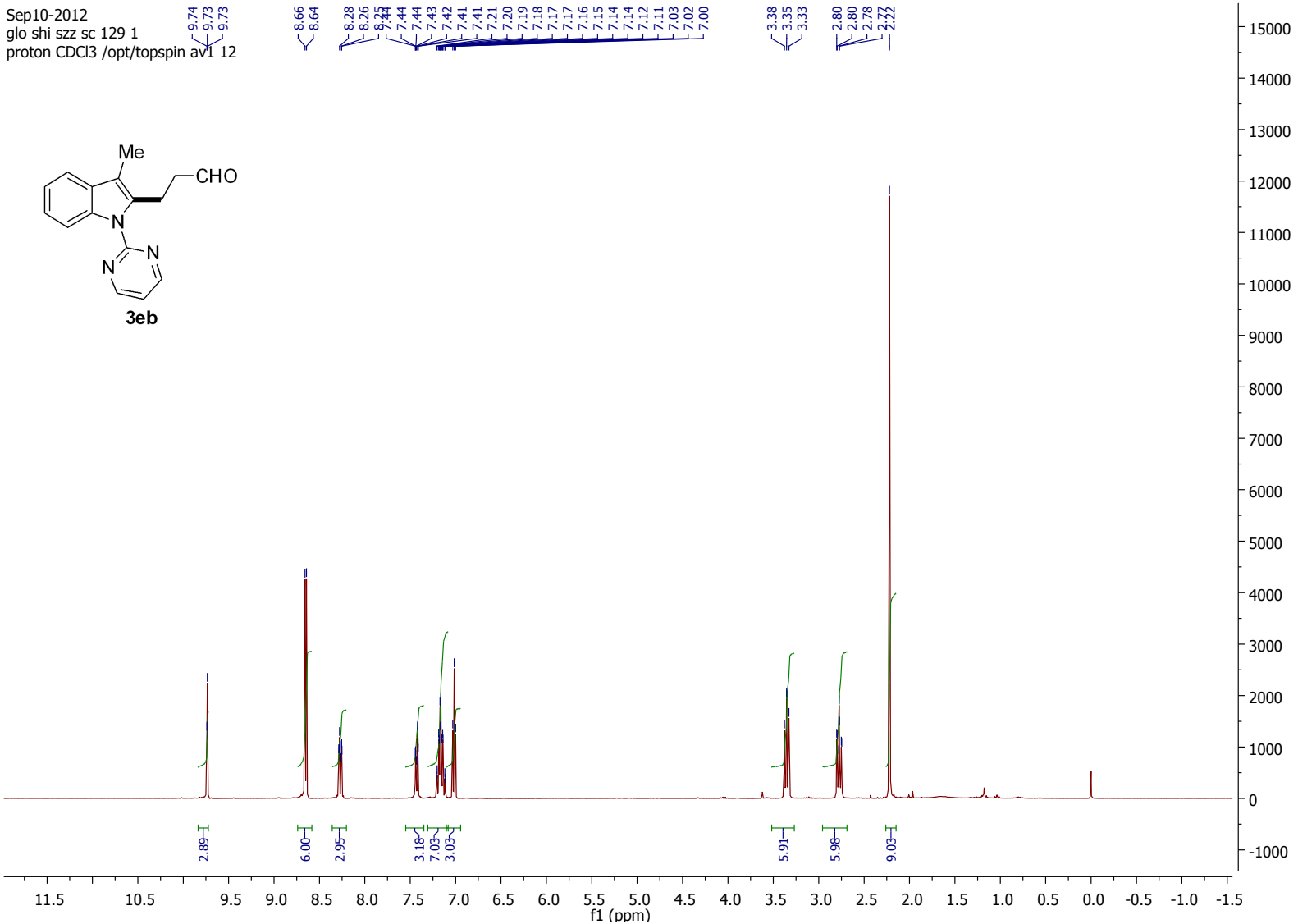
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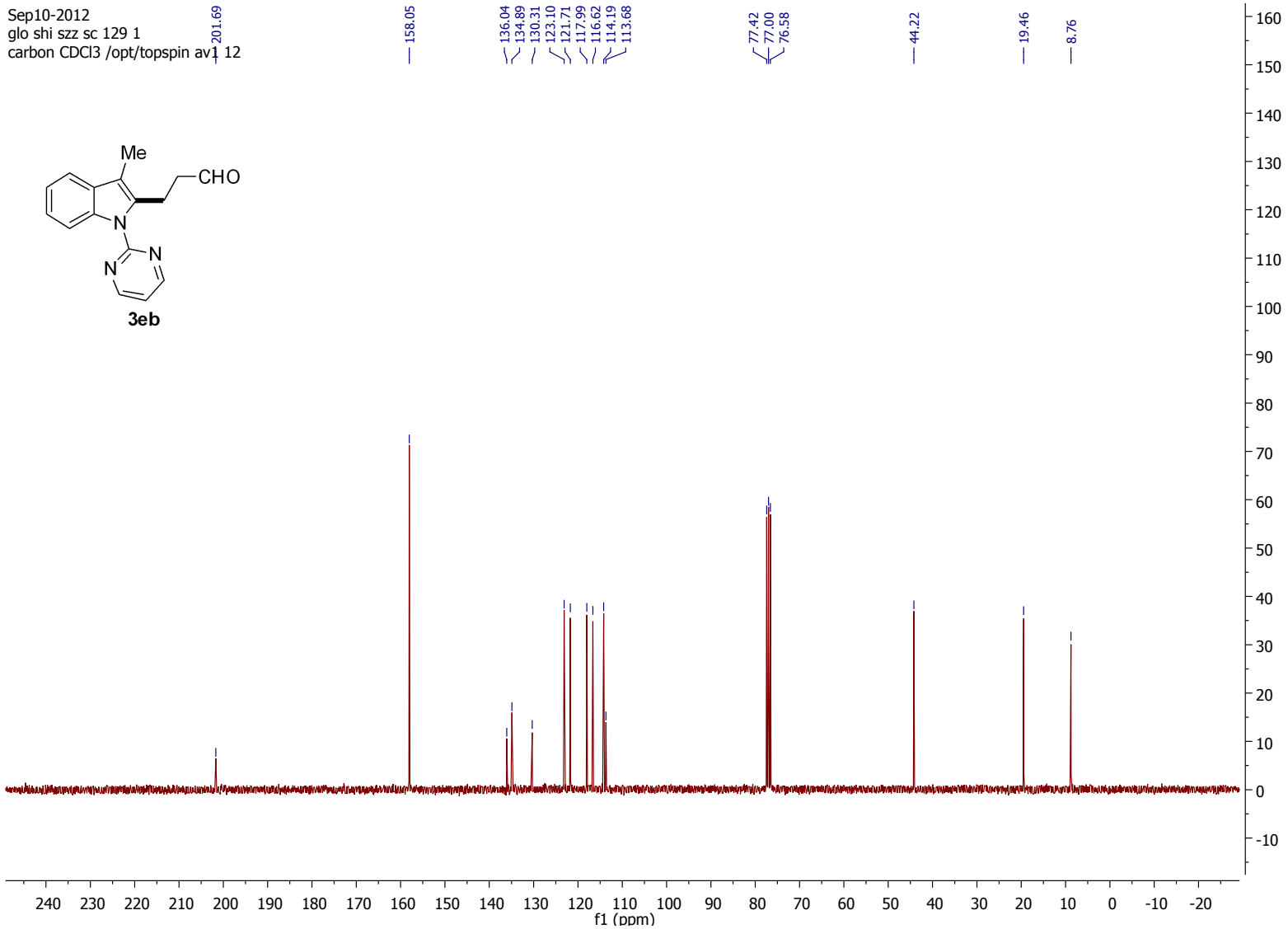
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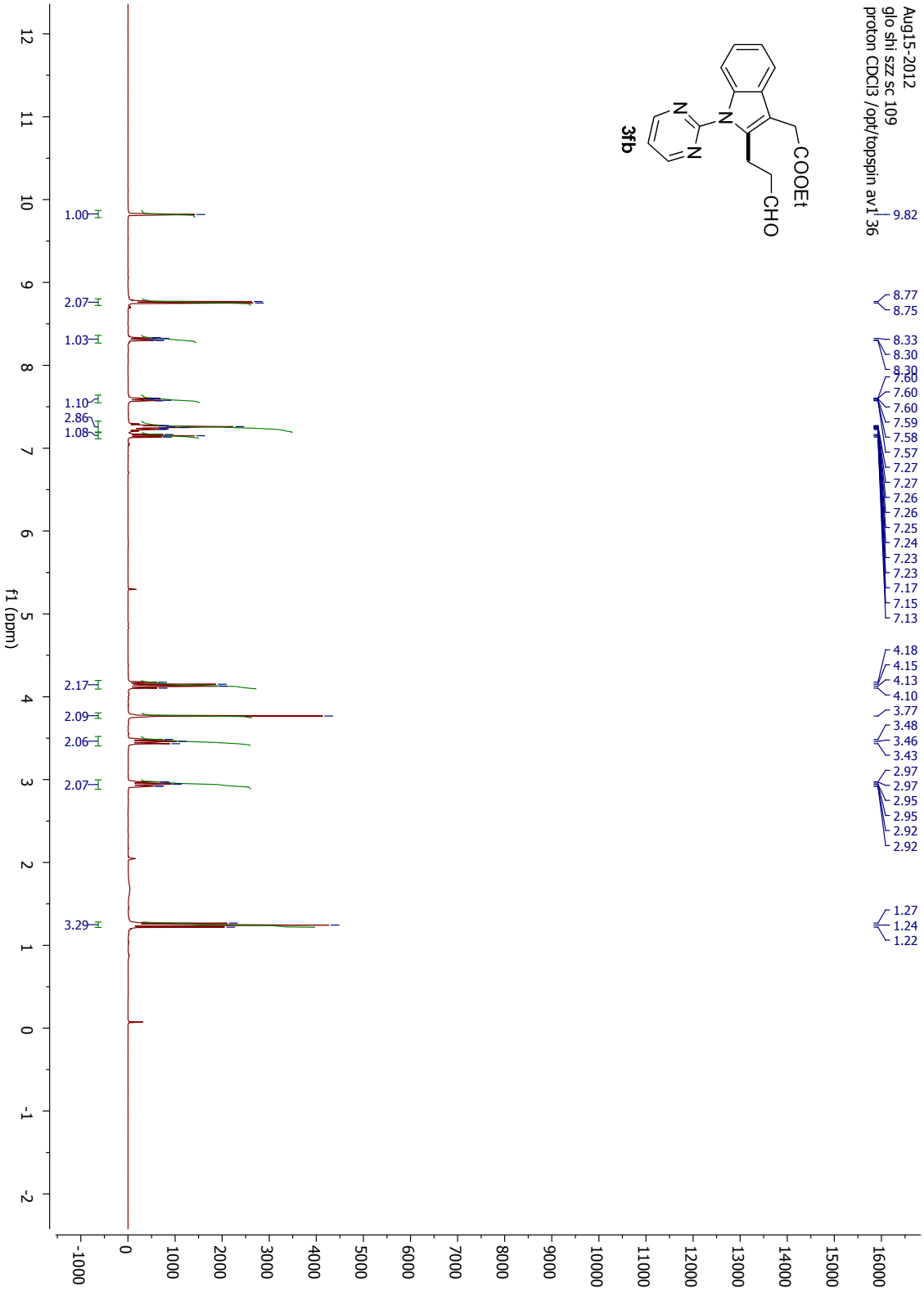
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8.33
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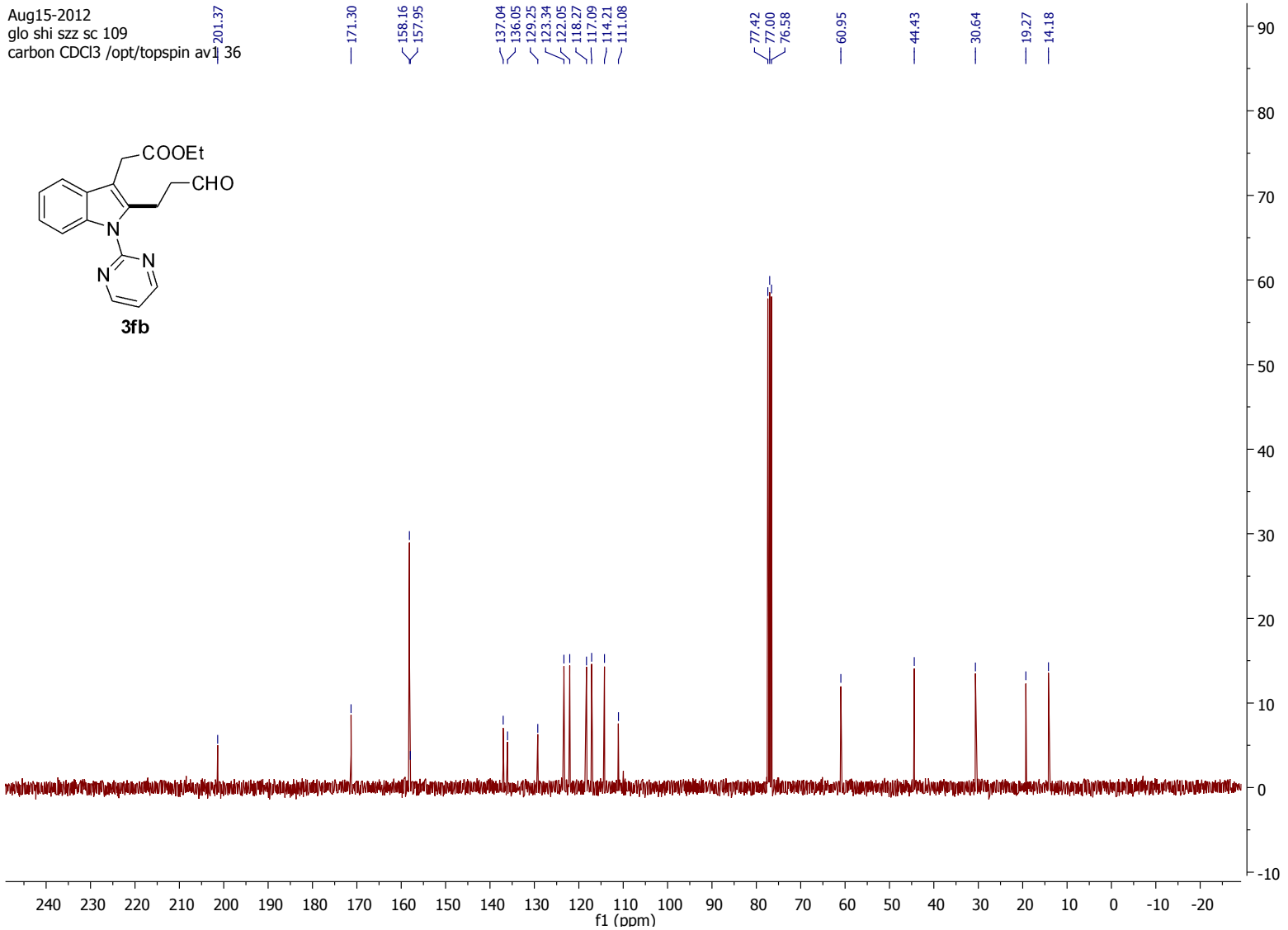
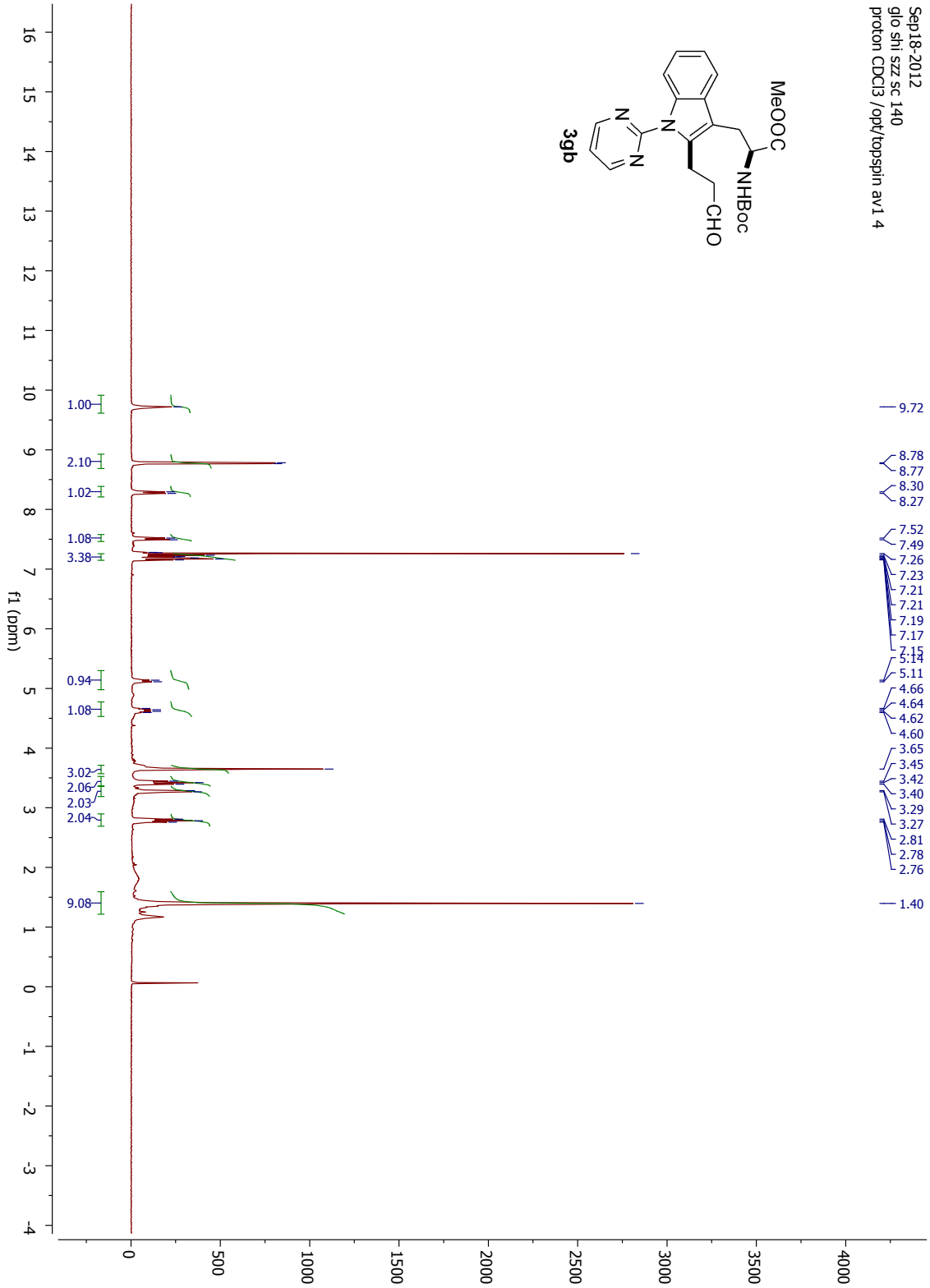
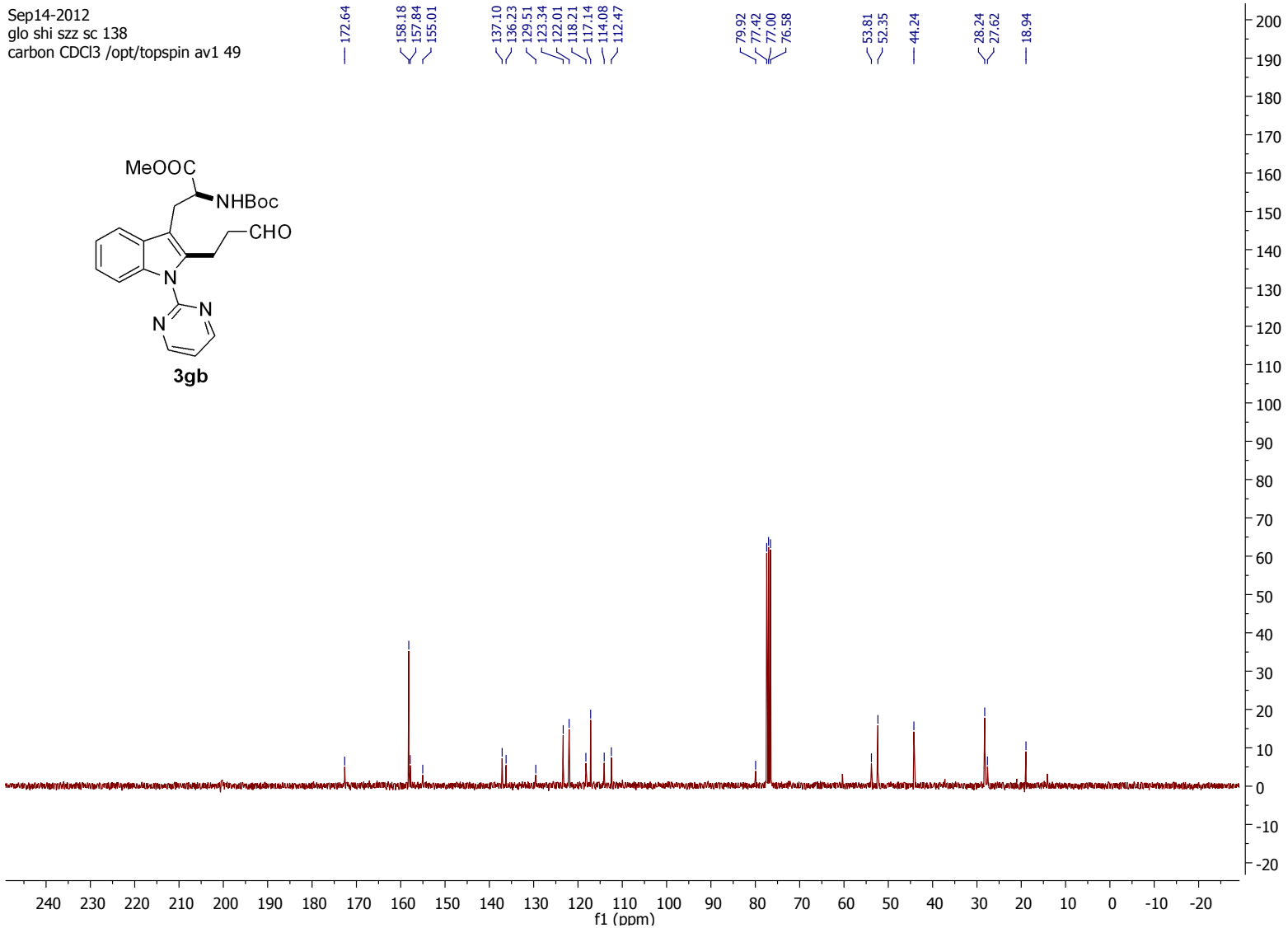
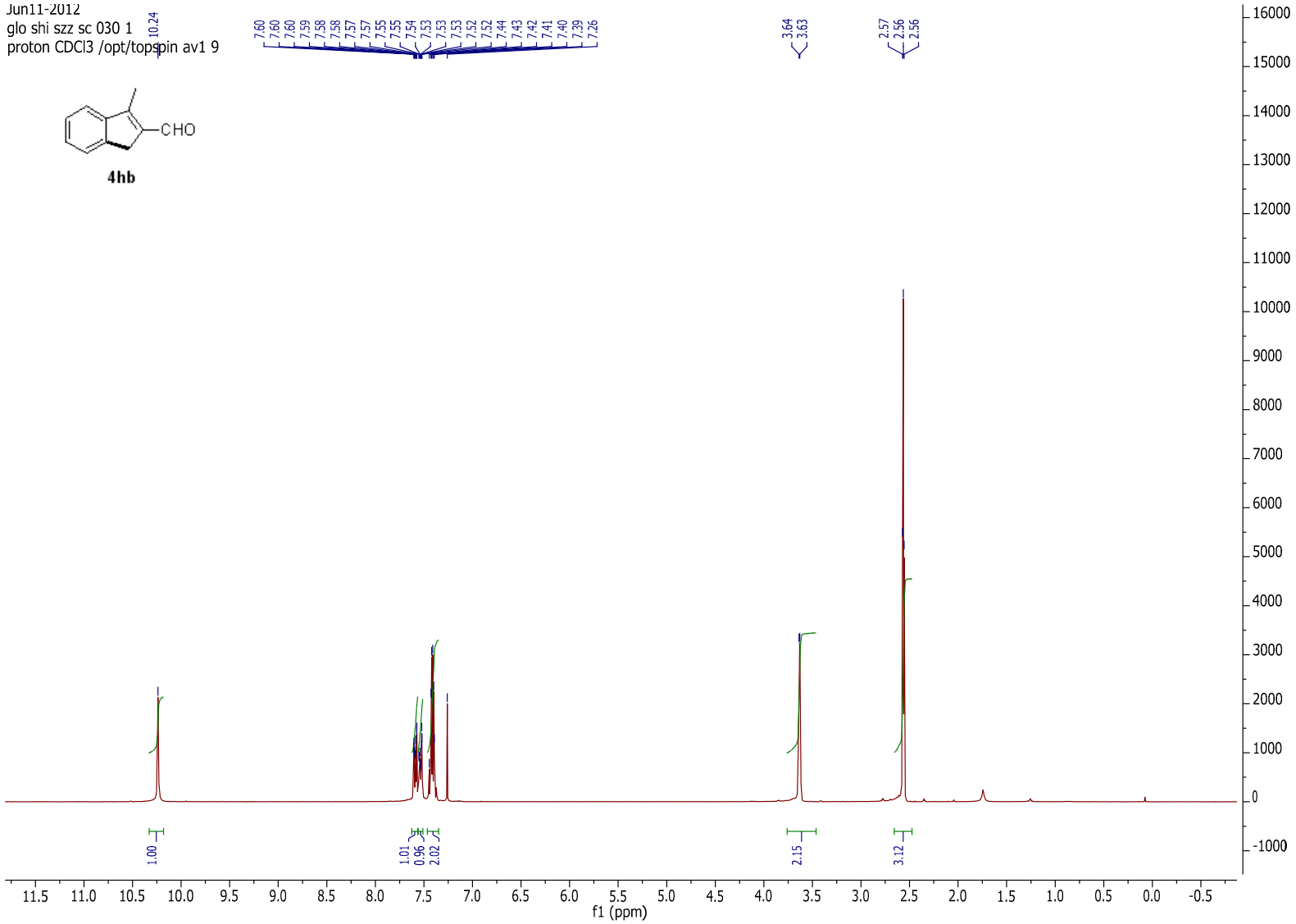
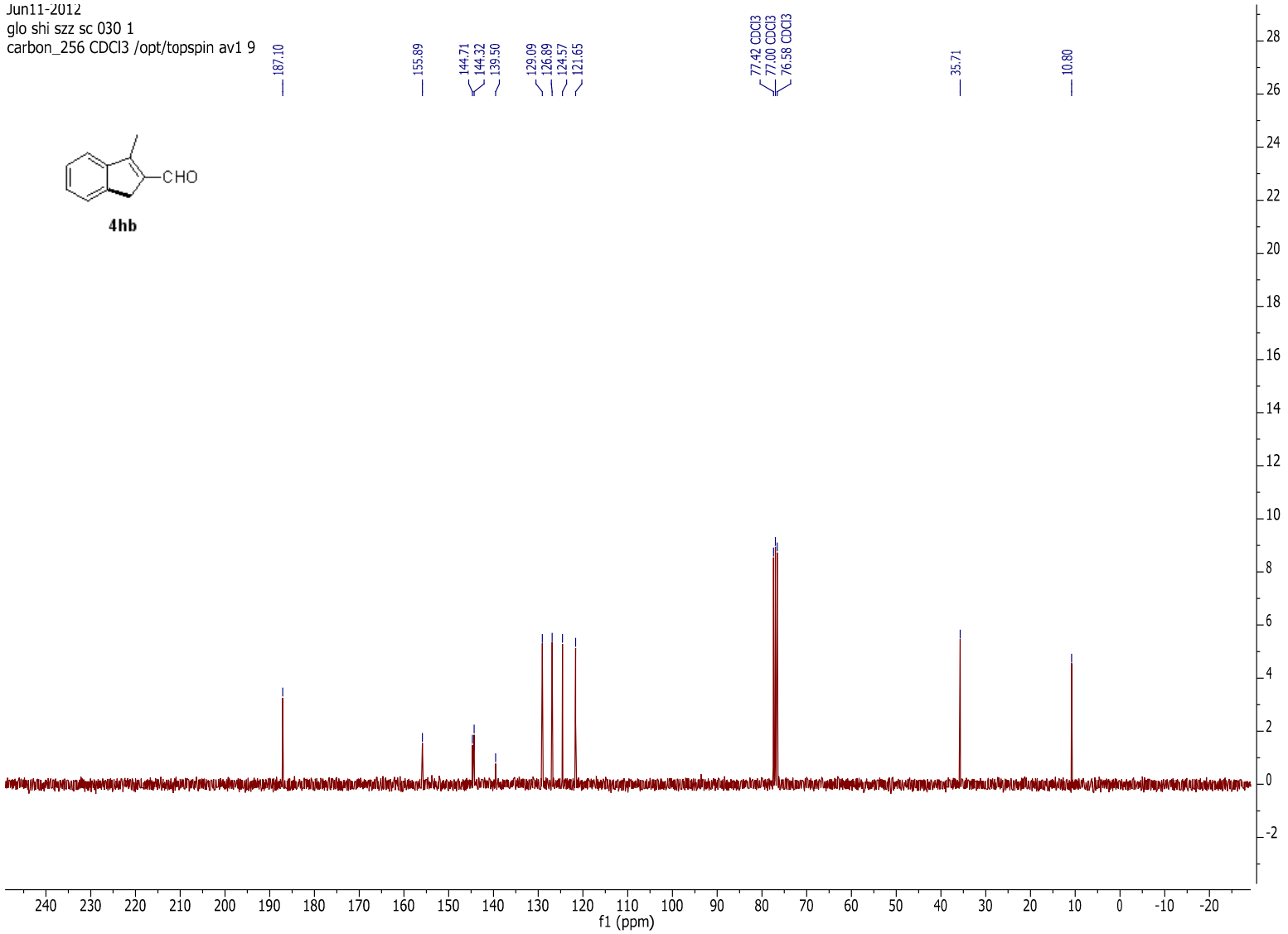
1.22

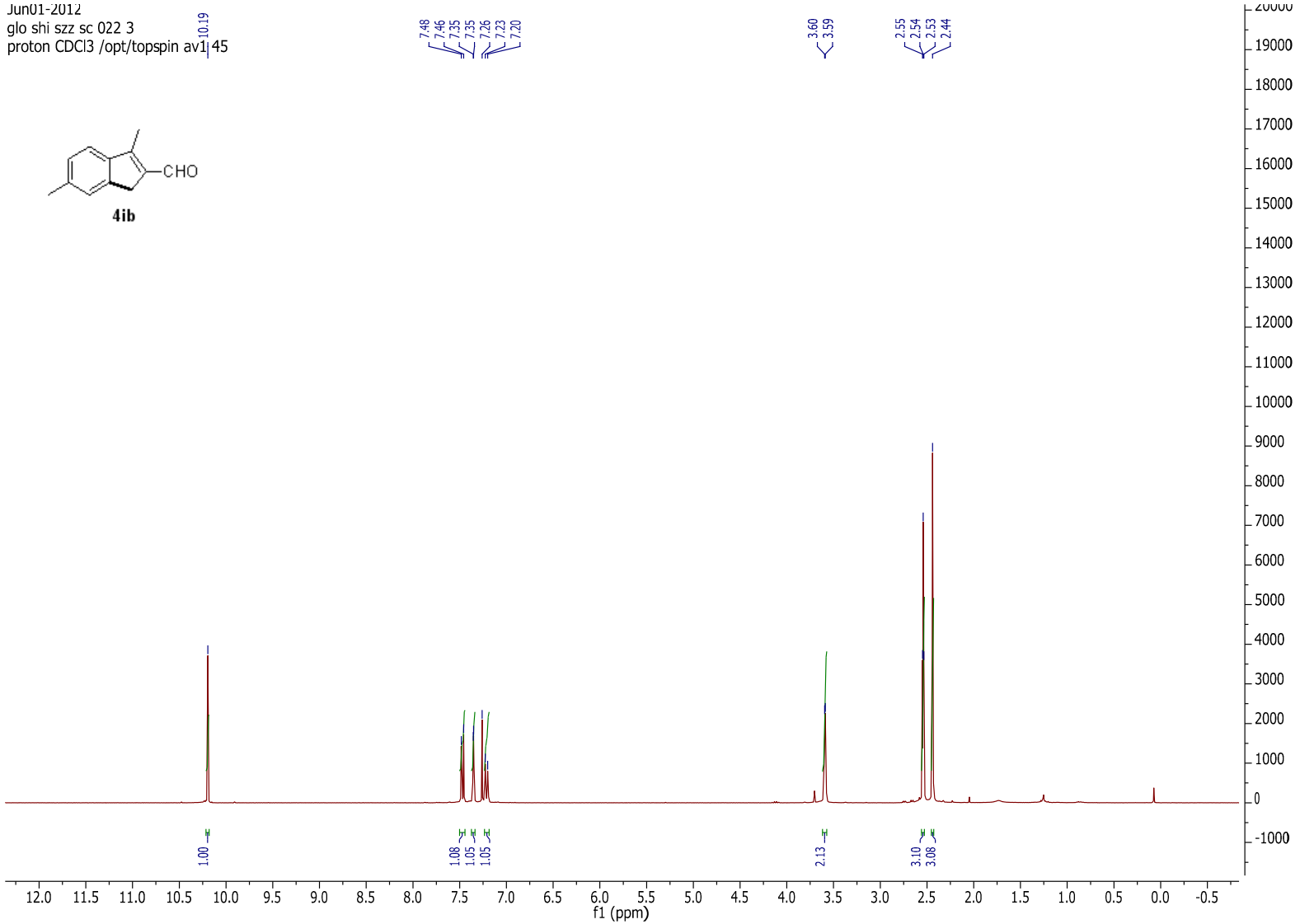


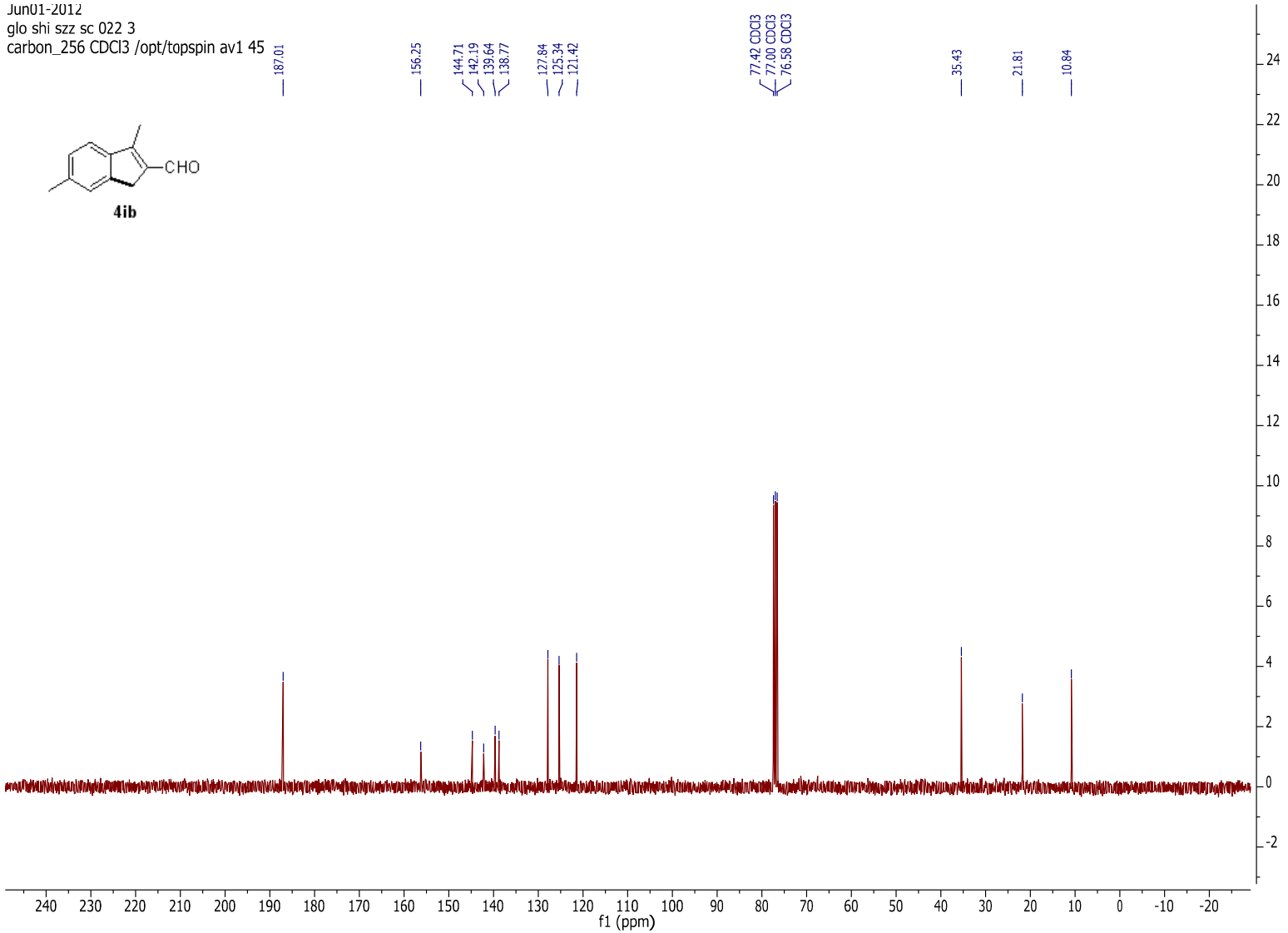

Sep18-2012
glo shi szz sc 140
proton CDCl3 /opt/topspin av1 4
3gb
MeOOC
NHBoc
CHO
f1 (ppm)
1.00
2.10
1.02
1.08
3.38
0.94
1.08
3.02
2.06
2.03
2.04
9.08
9.72
8.78
8.77
8.30
8.27
7.52
7.49
7.26
7.23
7.21
7.21
7.19
7.17
7.15
5.14
5.11
4.66
4.64
4.62
4.60
3.65
3.45
3.42
3.40
3.29
3.27
2.81
2.78
2.76
1.40

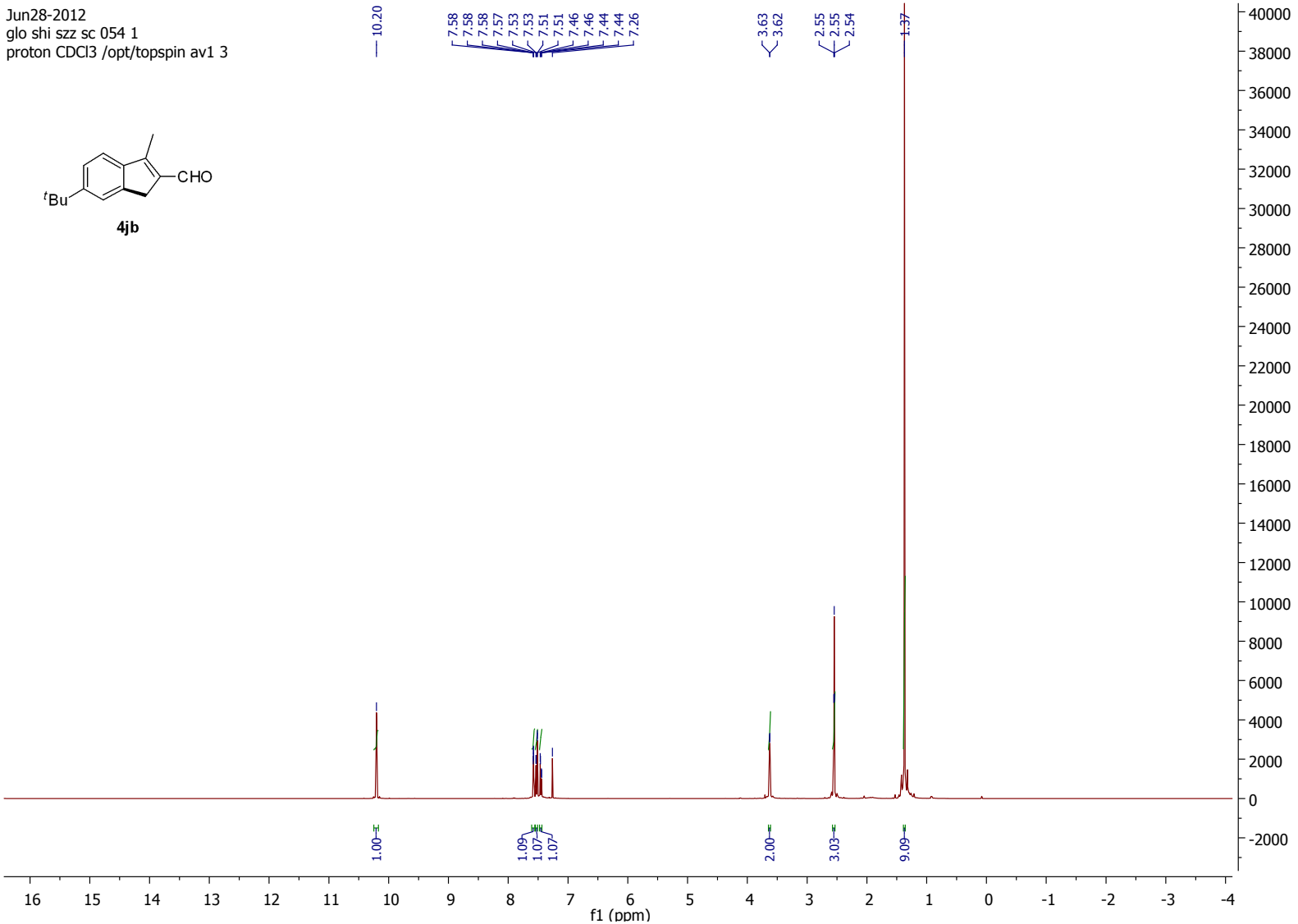


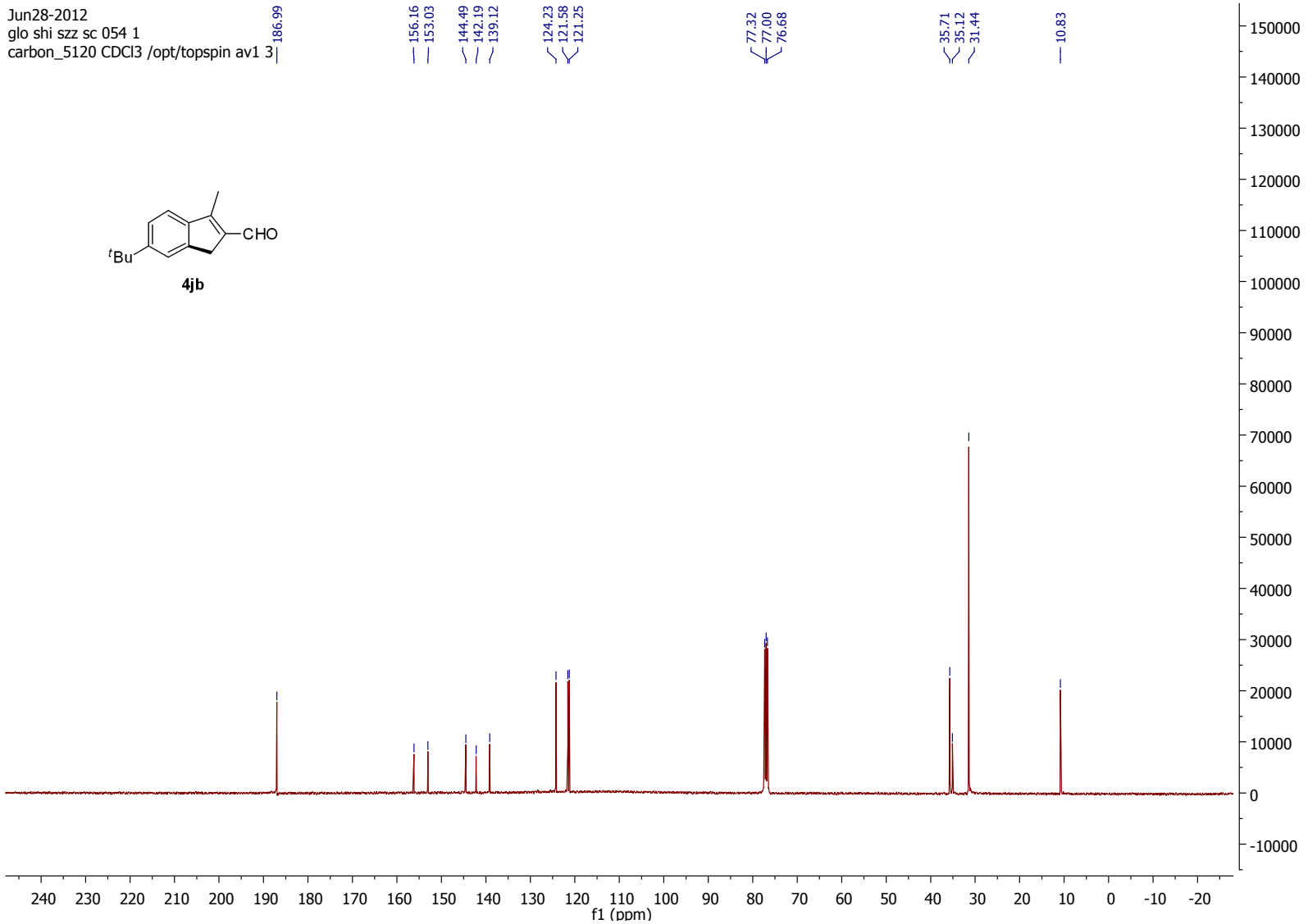

Jun11-2012
glo shi szz sc 030 1
proton CDCl3 /opt/topspin av1 9
CHO
4hb
f1 (ppm)

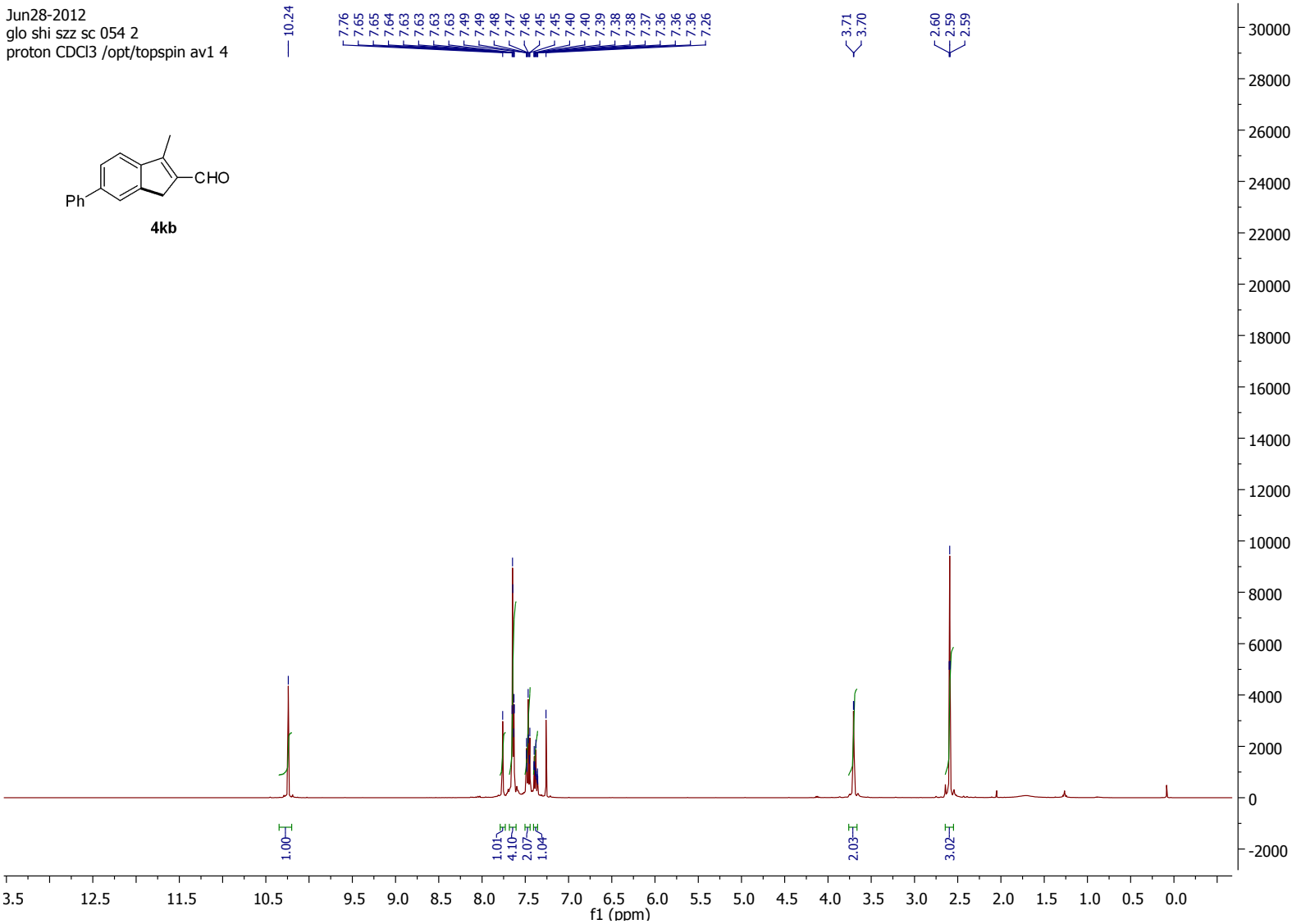

Jun11-2012
glo shi szz sc 030 1
carbon_256 CDCl3 /opt/topspin av1 9
187.10
155.89
144.71
144.32
139.50
129.09
126.89
124.57
121.65
77.42 CDCl3
77.00 CDCl3
76.58 CDCl3
35.71
10.80
CHO
4hb
f1 (ppm)

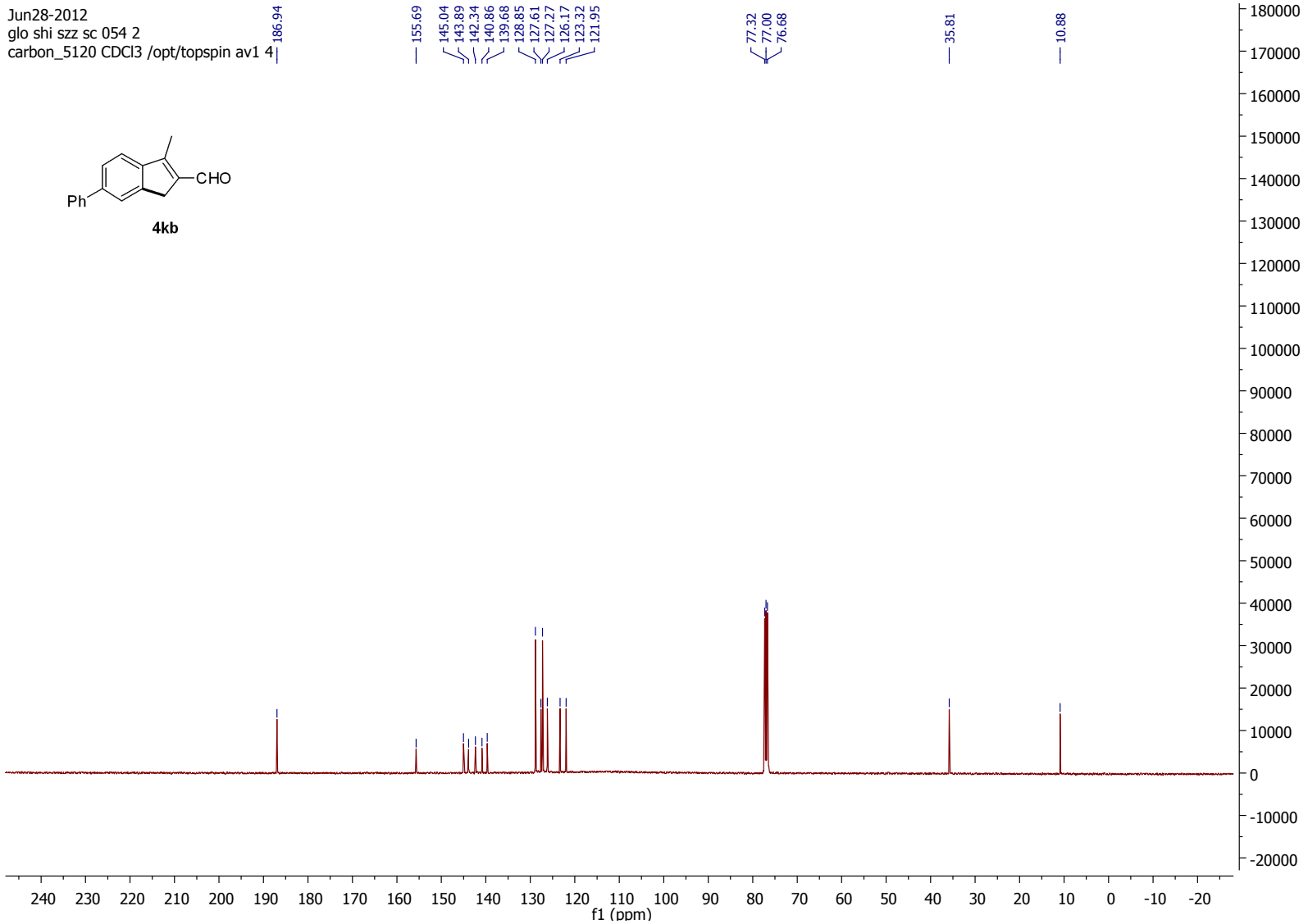

Jun01-2012
glo shi szz sc 022 3
proton CDCl3 /opt/topspin av1 45
10.19
7.48
7.46
7.35
7.35
7.26
7.23
7.20
3.60
3.59
2.55
2.54
2.53
2.44
CHO
4ib
1.00
1.08
1.05
1.05
2.13
3.10
3.08
f1 (ppm)

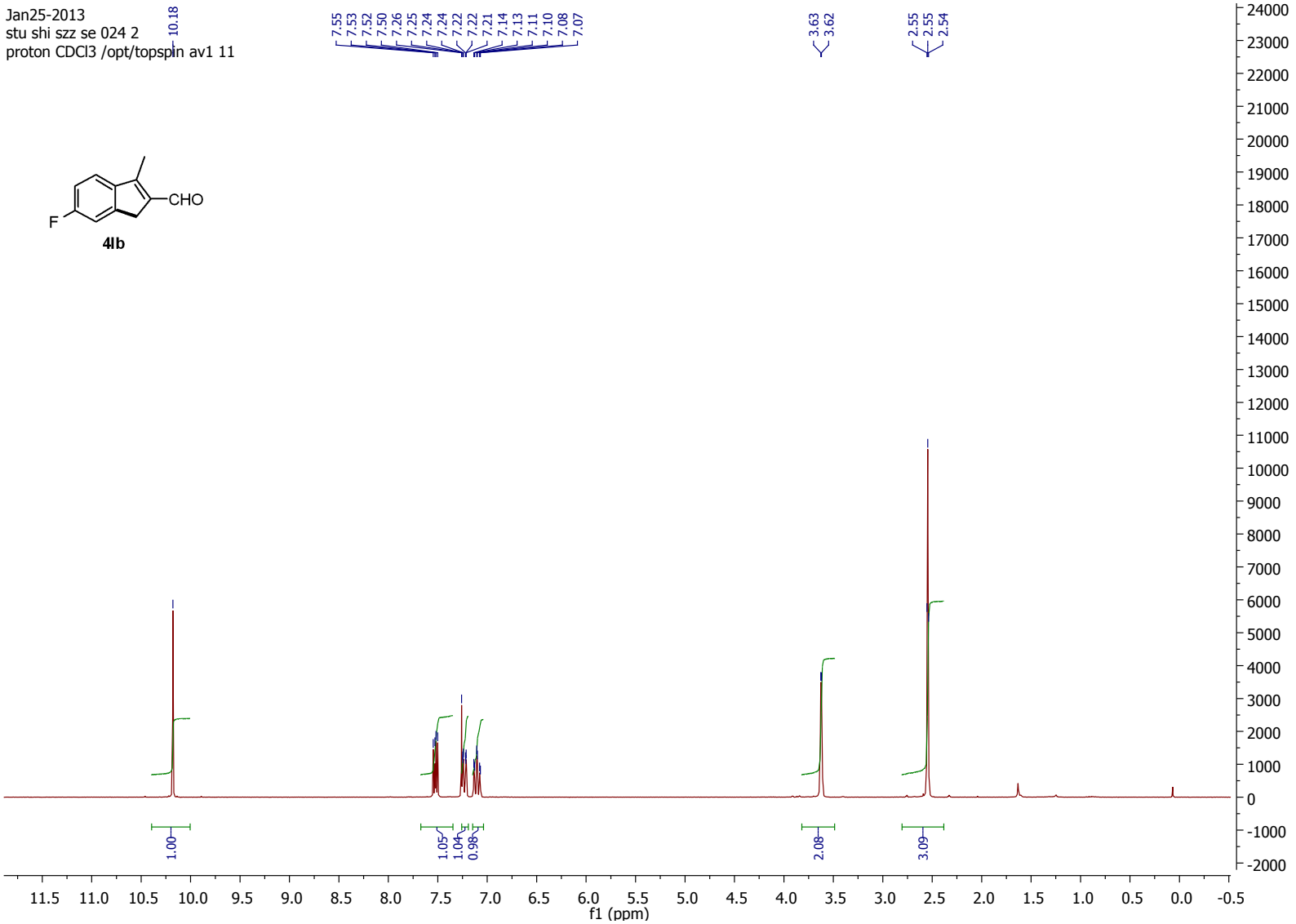


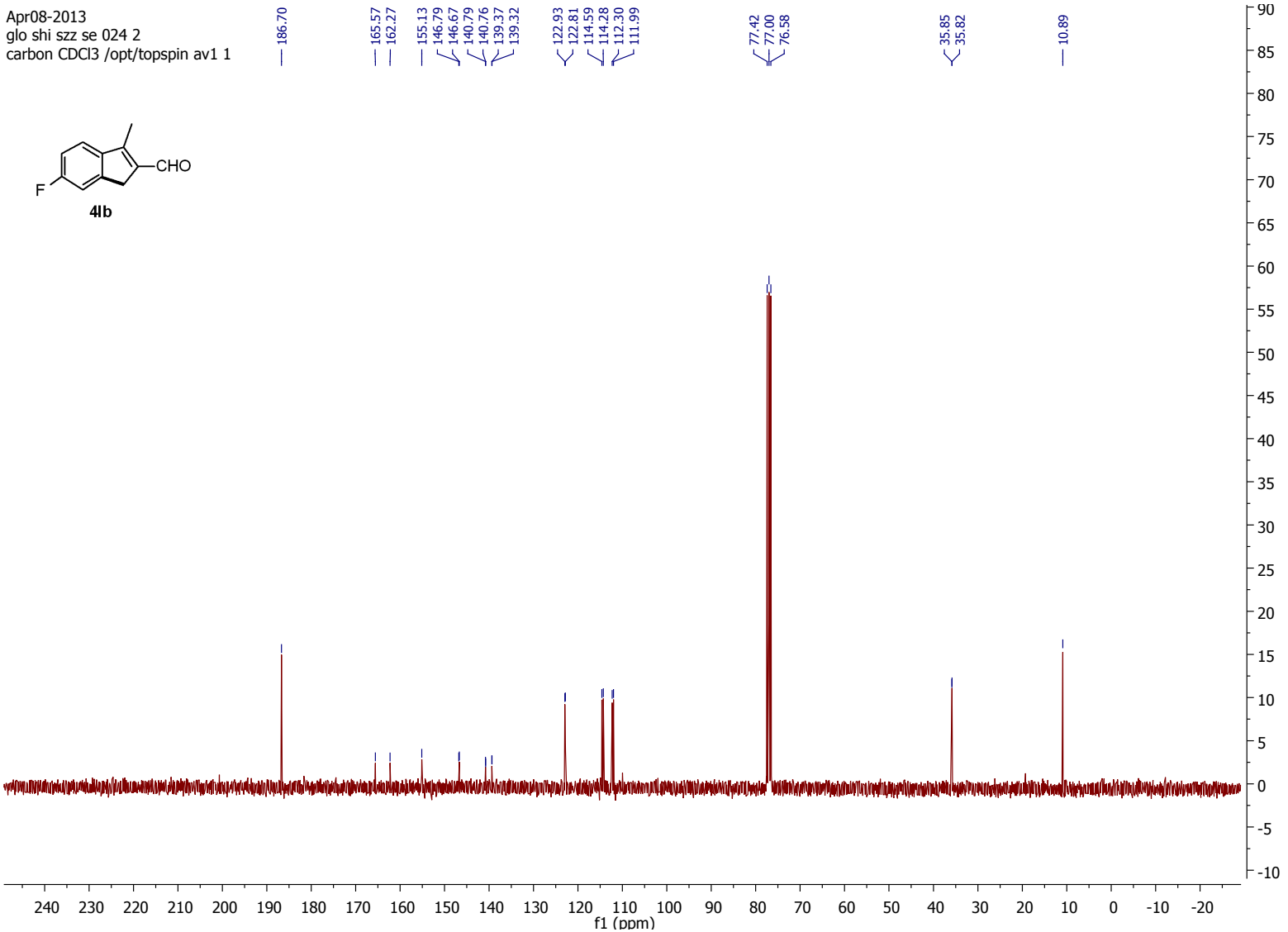

Jun28-2012
glo shi szz sc 054 1
proton CDCl3 /opt/topspin av1 3
CHO
tBu
4jb
10.20
7.58
7.58
7.58
7.57
7.53
7.53
7.51
7.51
7.46
7.46
7.44
7.44
7.26
3.63
3.62
2.55
2.55
2.54
1.37
1.00
1.09
1.07
1.07
2.00
3.03
9.09
f1 (ppm)

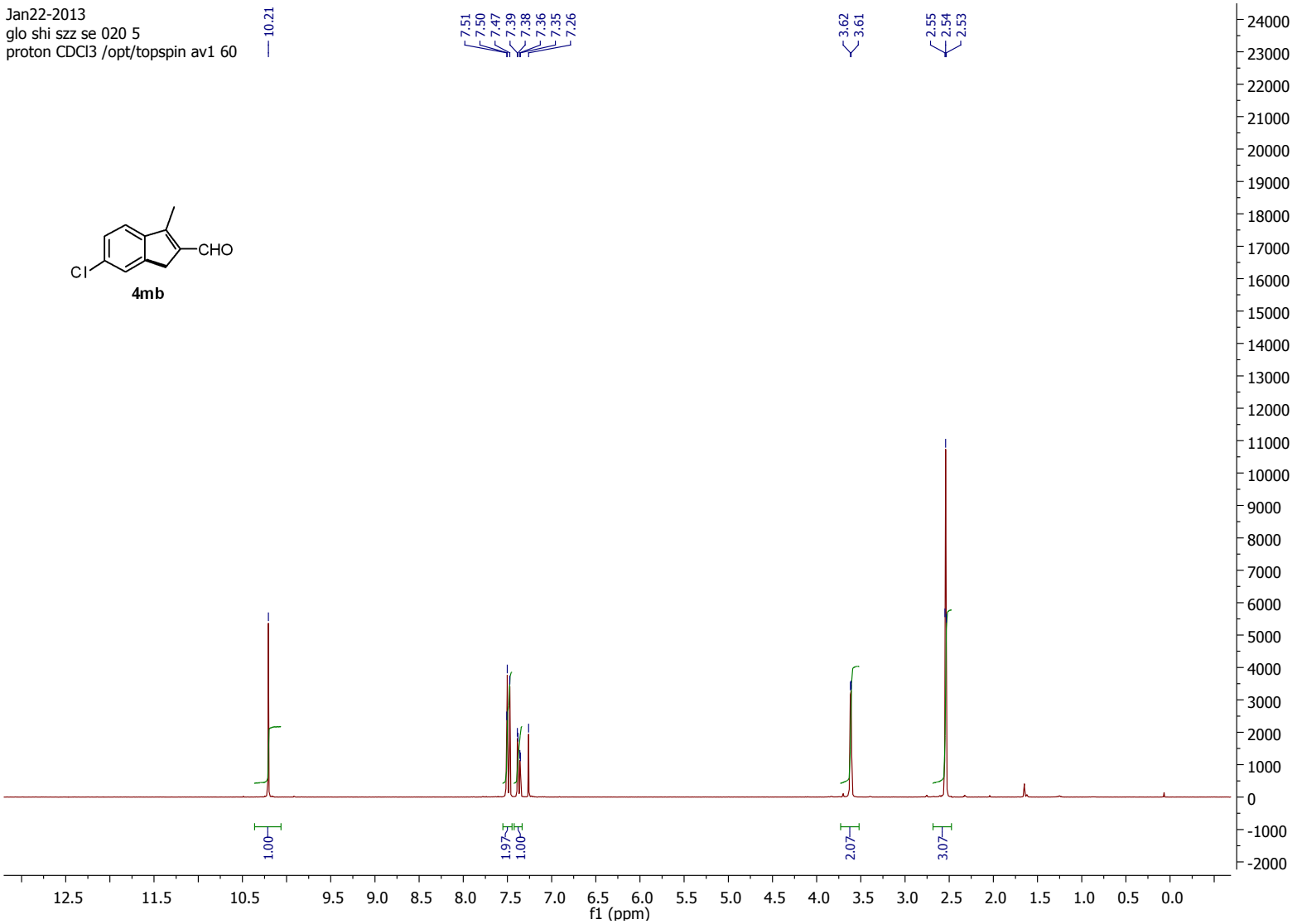

Jun28-2012
glo shi szz sc 054 1
carbon_5120 CDCl3 /opt/topspin av1 3
186.99
156.16
153.03
144.49
142.19
139.12
124.23
121.58
121.25
77.32
77.00
76.68
35.71
35.12
31.44
10.83
CHO
tBu
4jb
f1 (ppm)

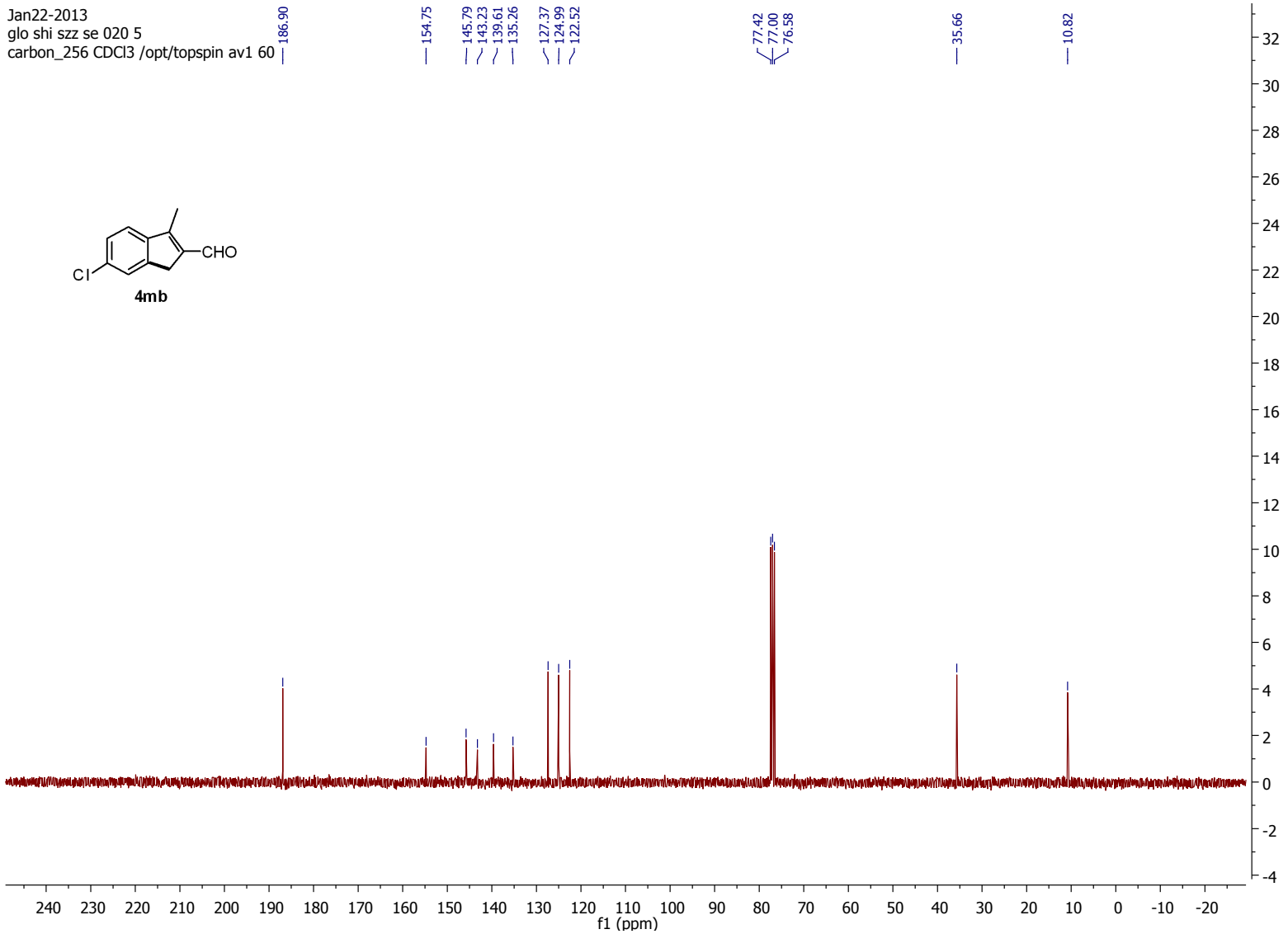


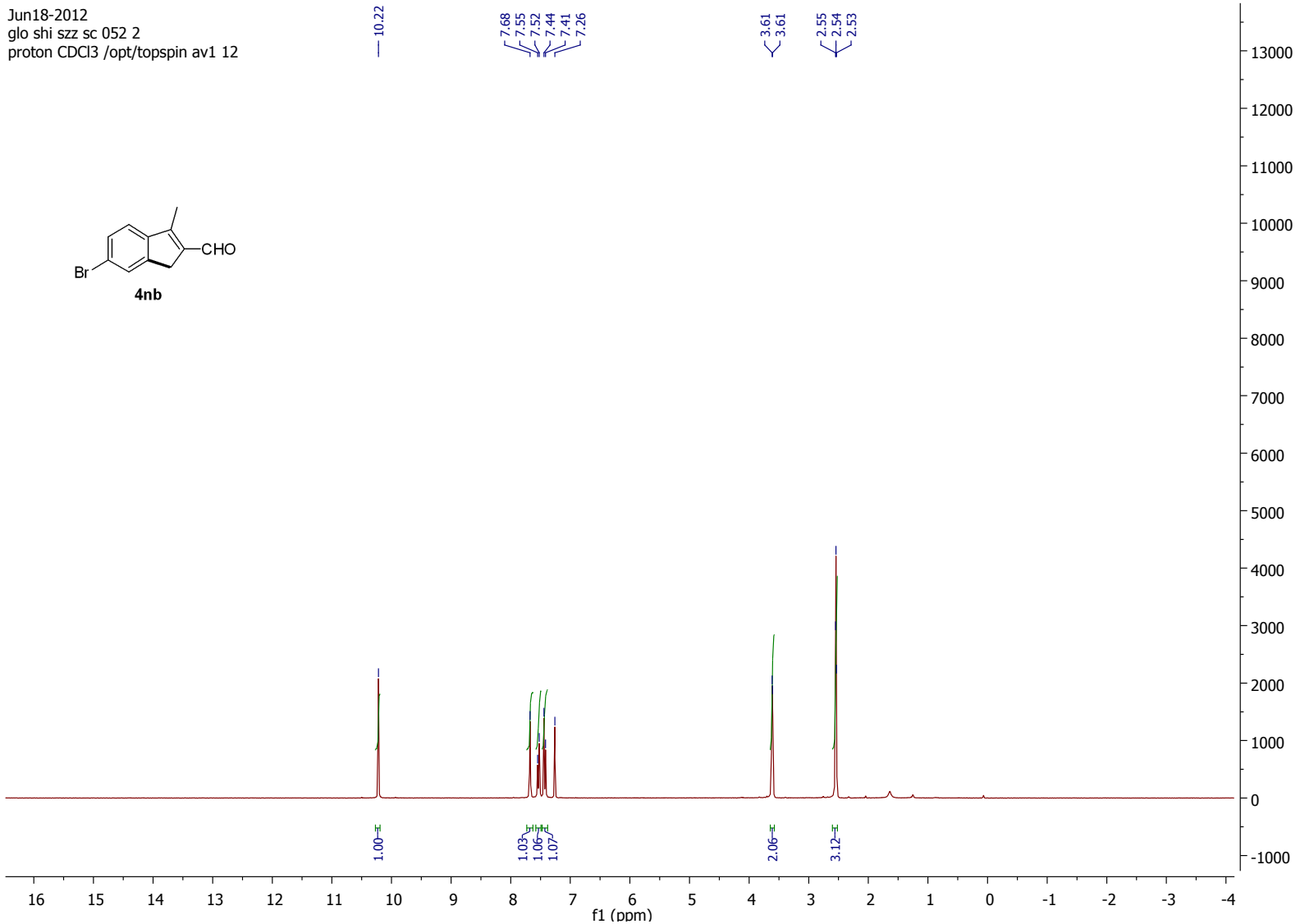

Jun28-2012
glo shi szz sc 054 2
carbon_5120 CDCl3 /opt/topspin av1 4
186.94
155.69
145.04
143.89
142.34
140.86
139.68
128.85
127.61
127.27
126.17
123.32
121.95
77.32
77.00
76.68
35.81
10.88
CHO
Ph
4kb
f1 (ppm)

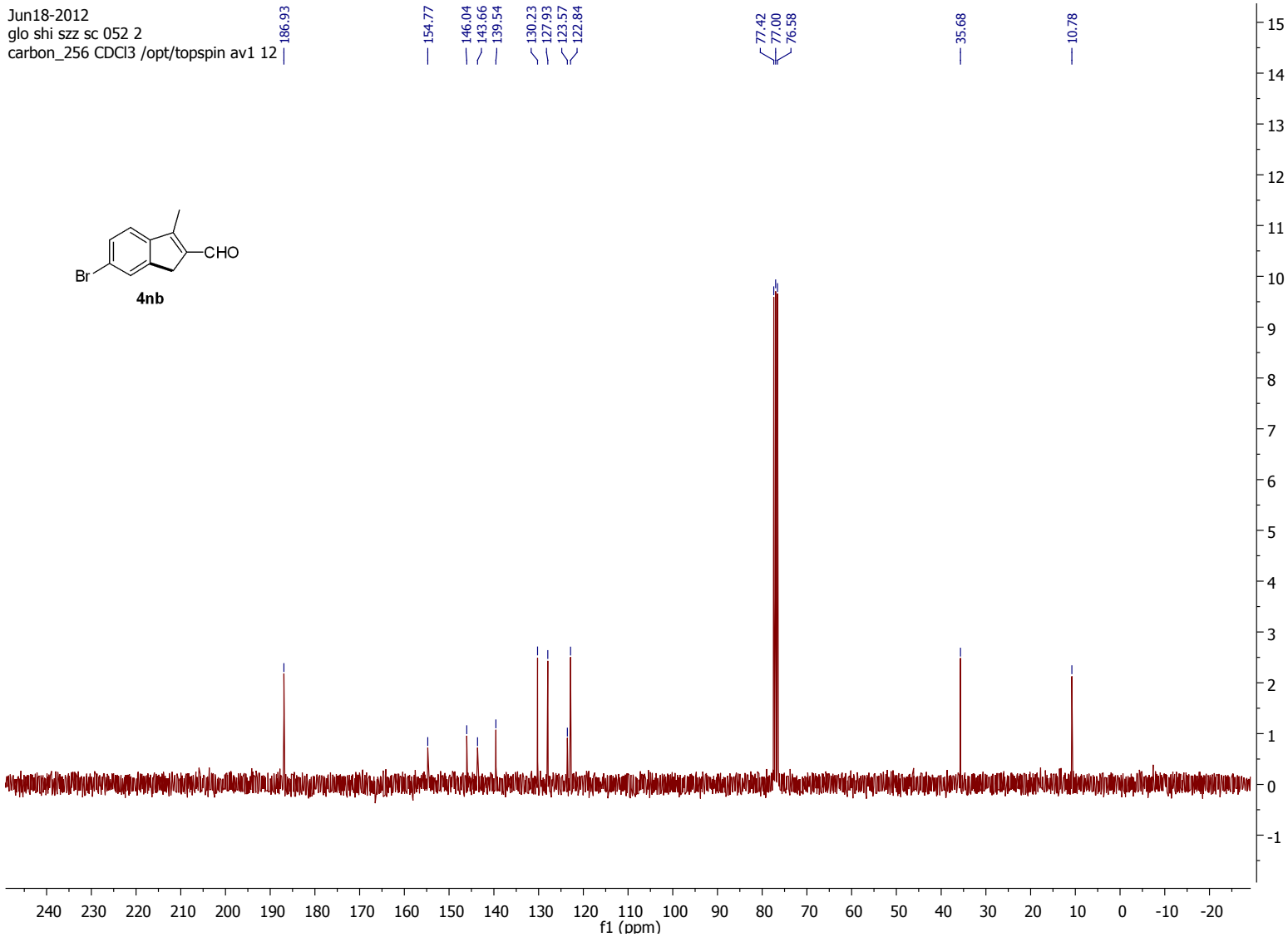


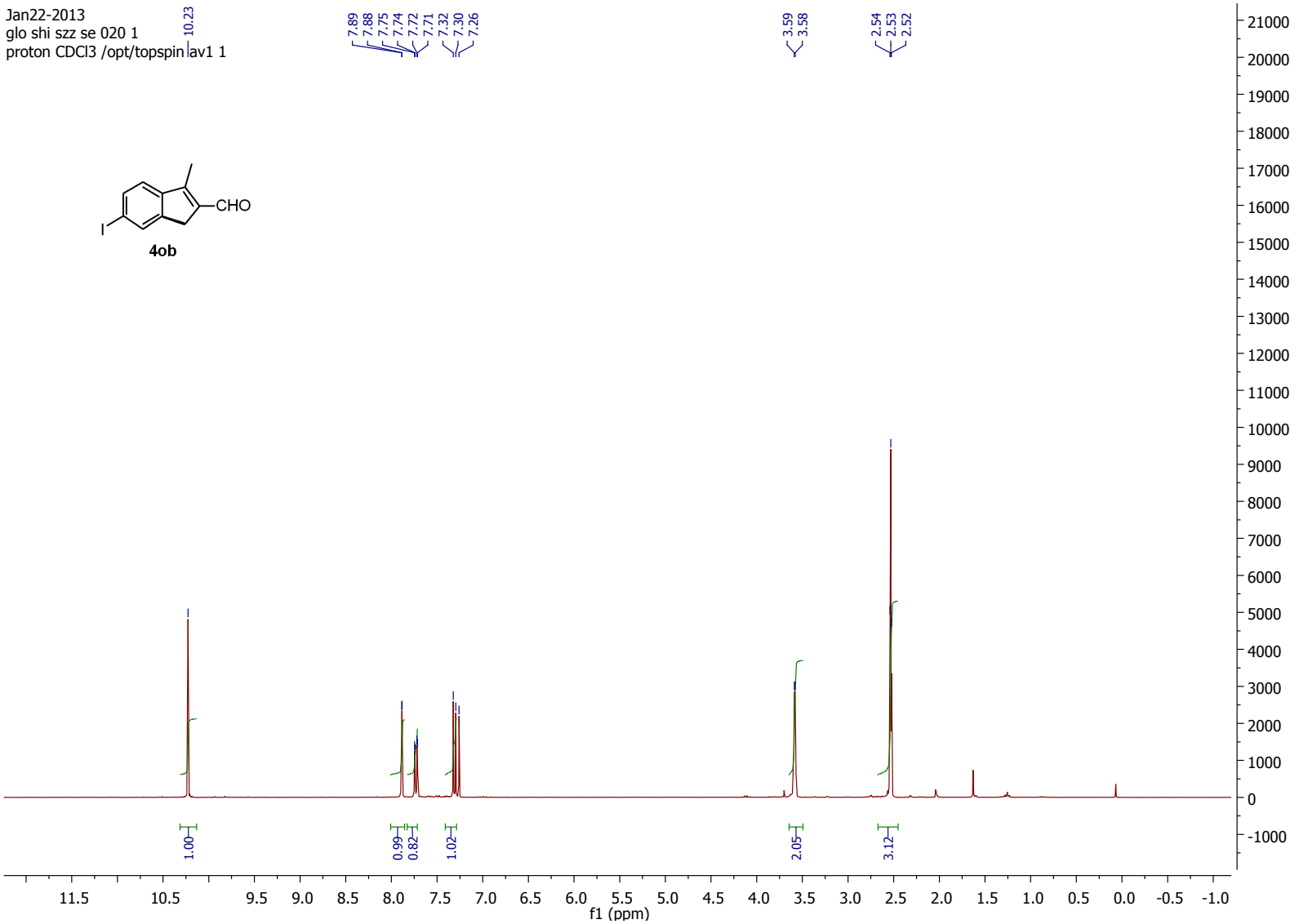


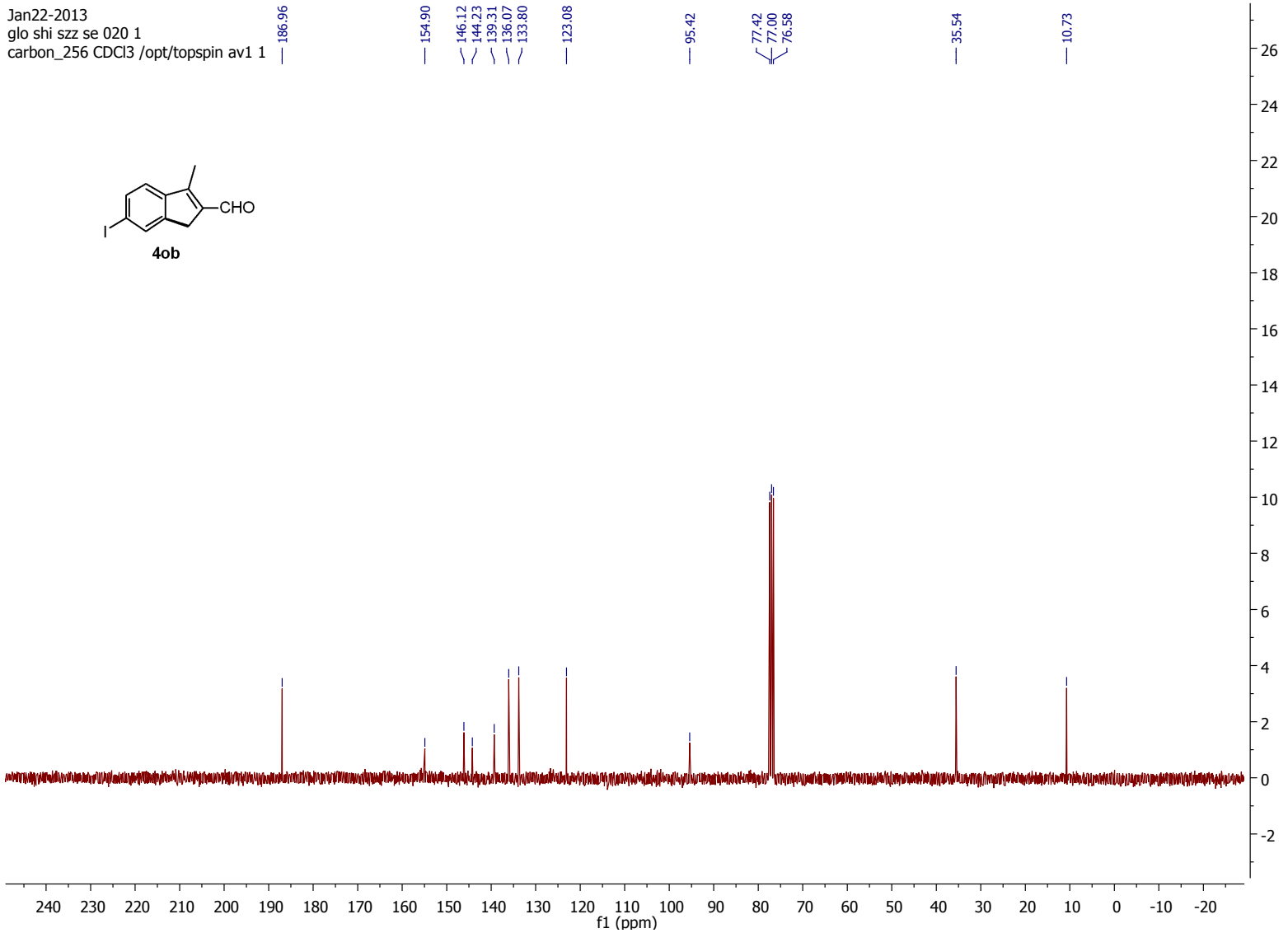


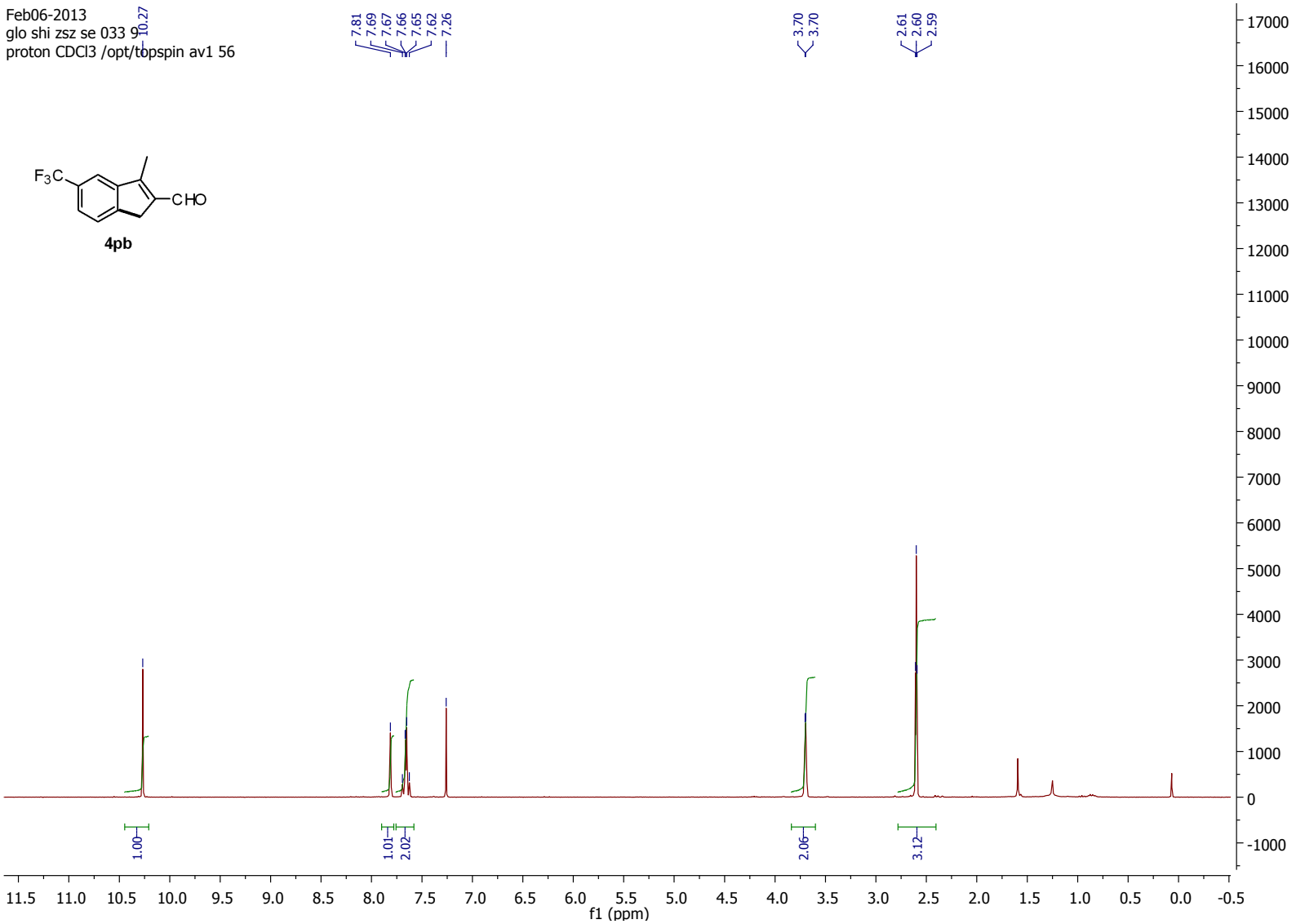

Jan22-2013
glo shi szz se 020 5
carbon_256 CDCl3 /opt/topspin av1 60
186.90
154.75
145.79
143.23
139.61
135.26
127.37
124.99
122.52
77.42
77.00
76.58
35.66
10.82
CHO
Cl
4mb
f1 (ppm)

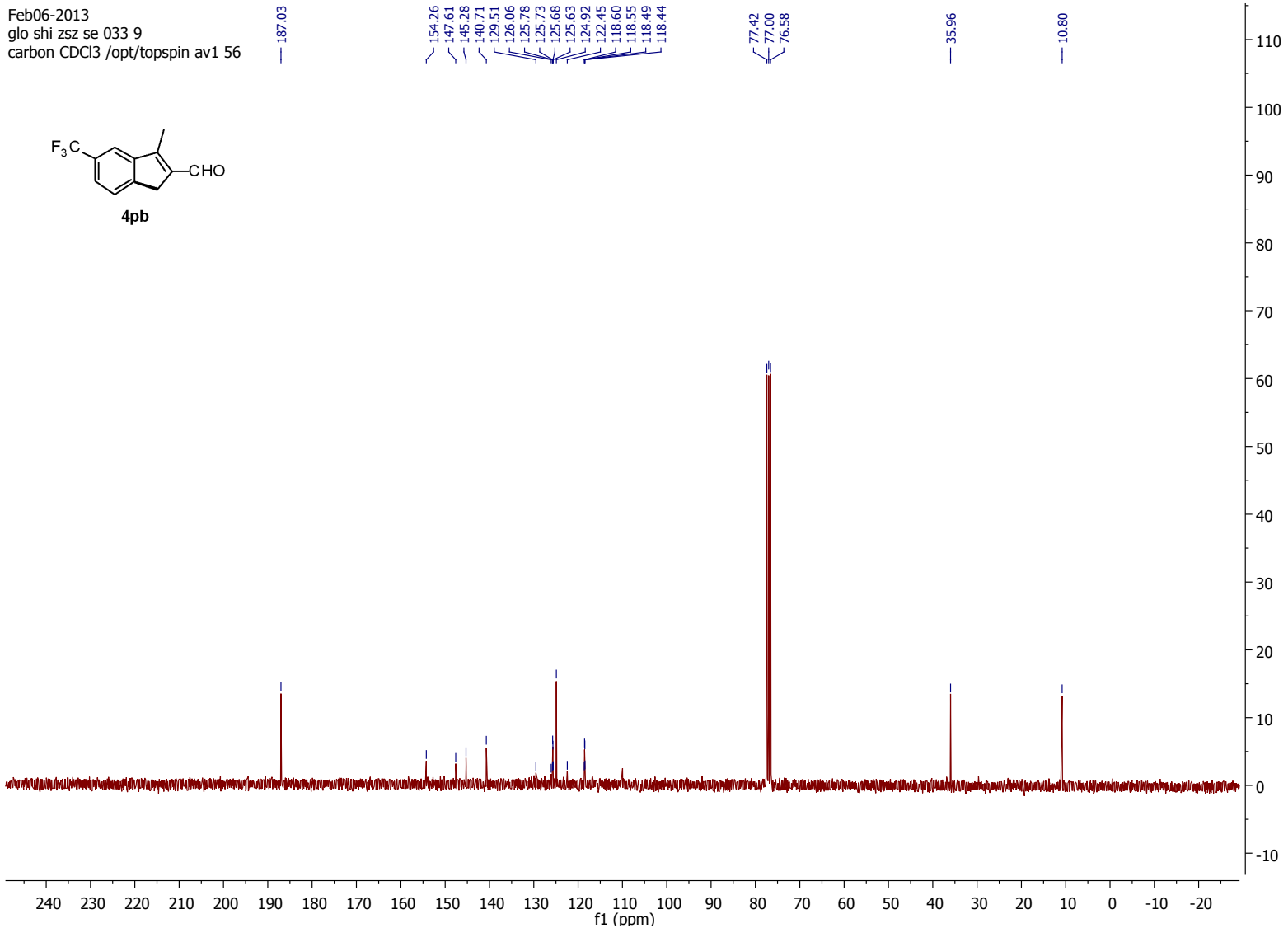


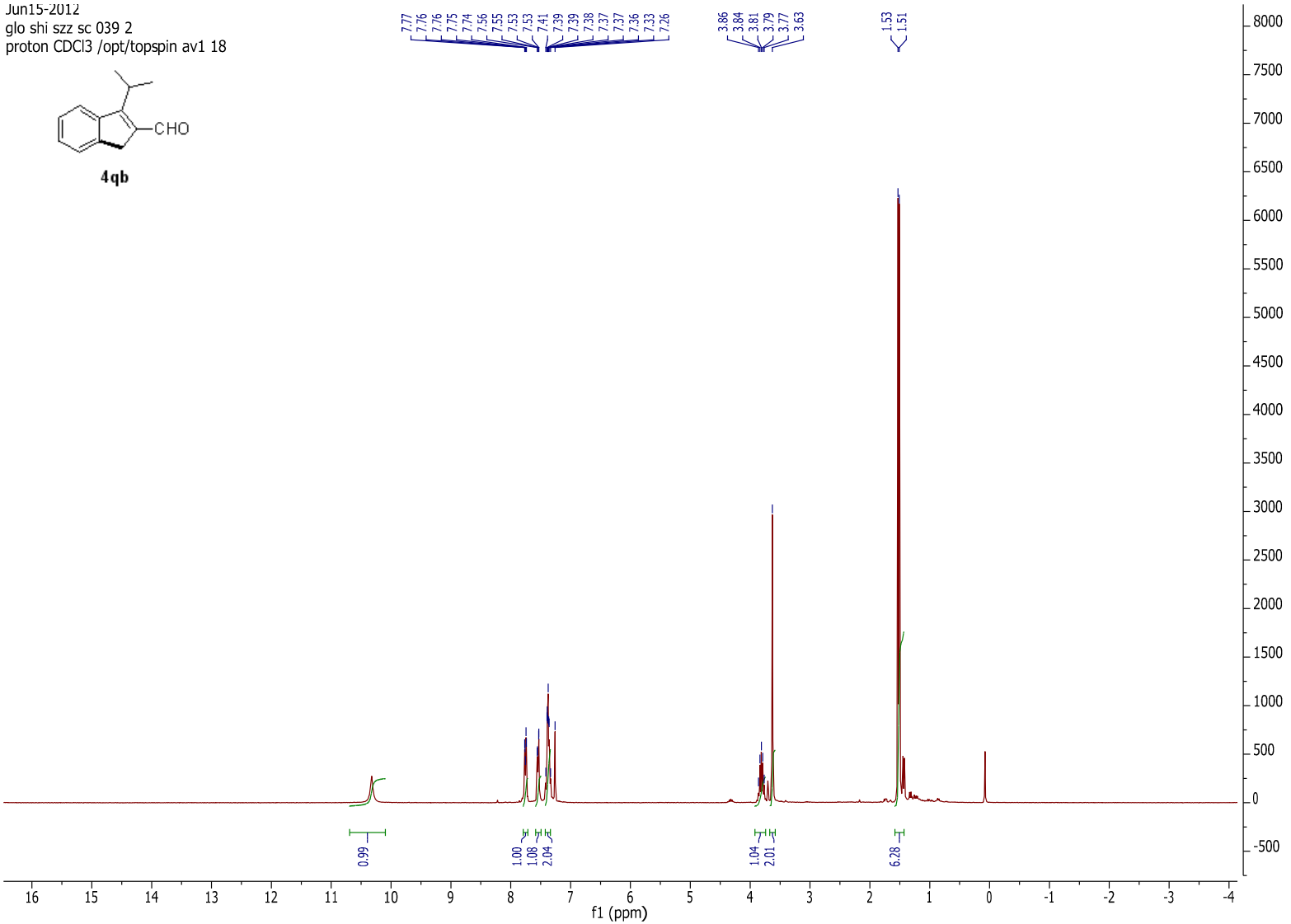


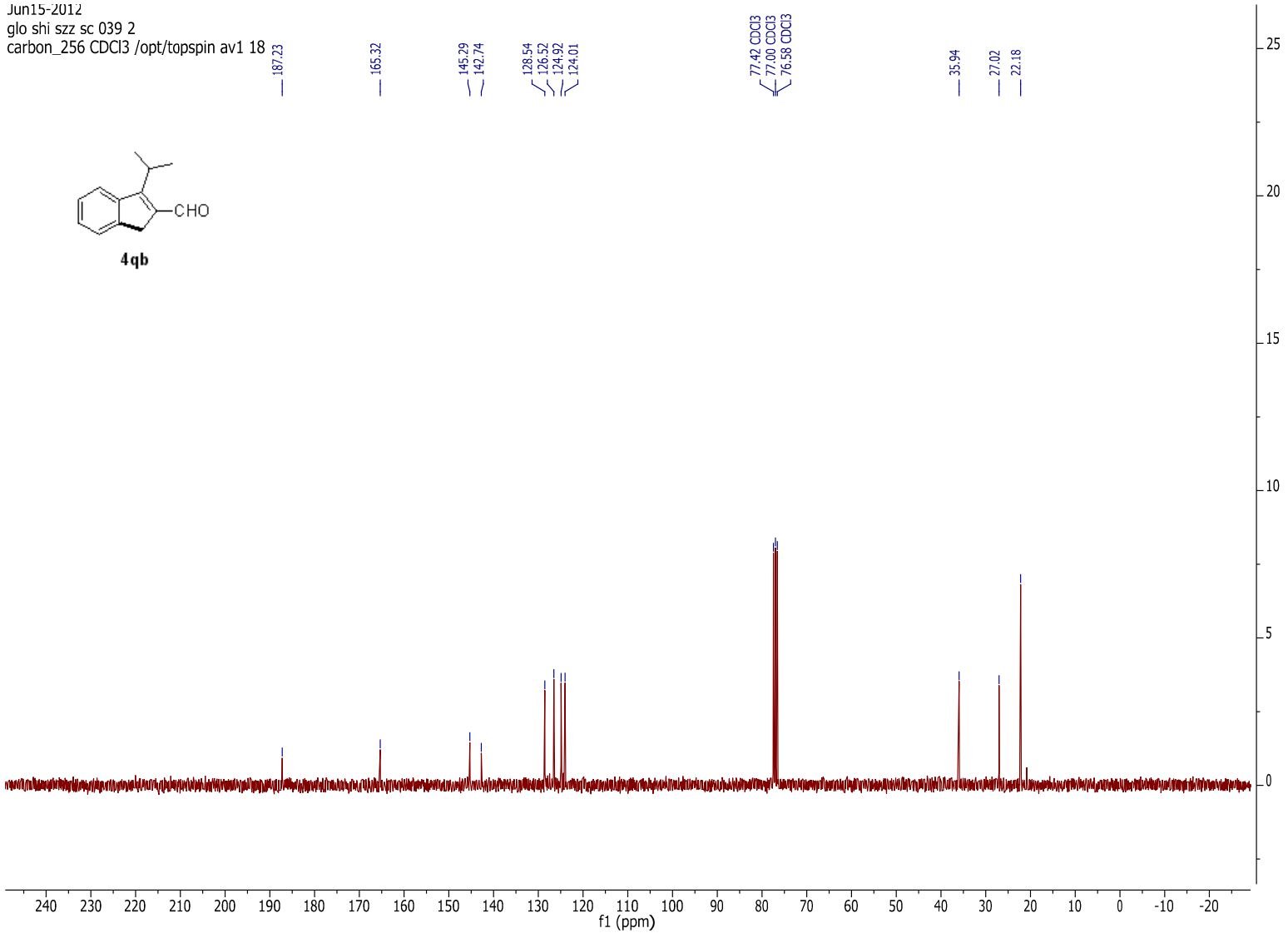

Jan22-2013
glo shi szz se 020 1
proton CDCl3 /opt/topspin av1 1
10.23
7.89
7.88
7.75
7.74
7.72
7.71
7.32
7.30
7.26
3.59
3.58
2.54
2.53
2.52
CHO
I
4ob
1.00
0.99
0.82
1.02
2.05
3.12
f1 (ppm)

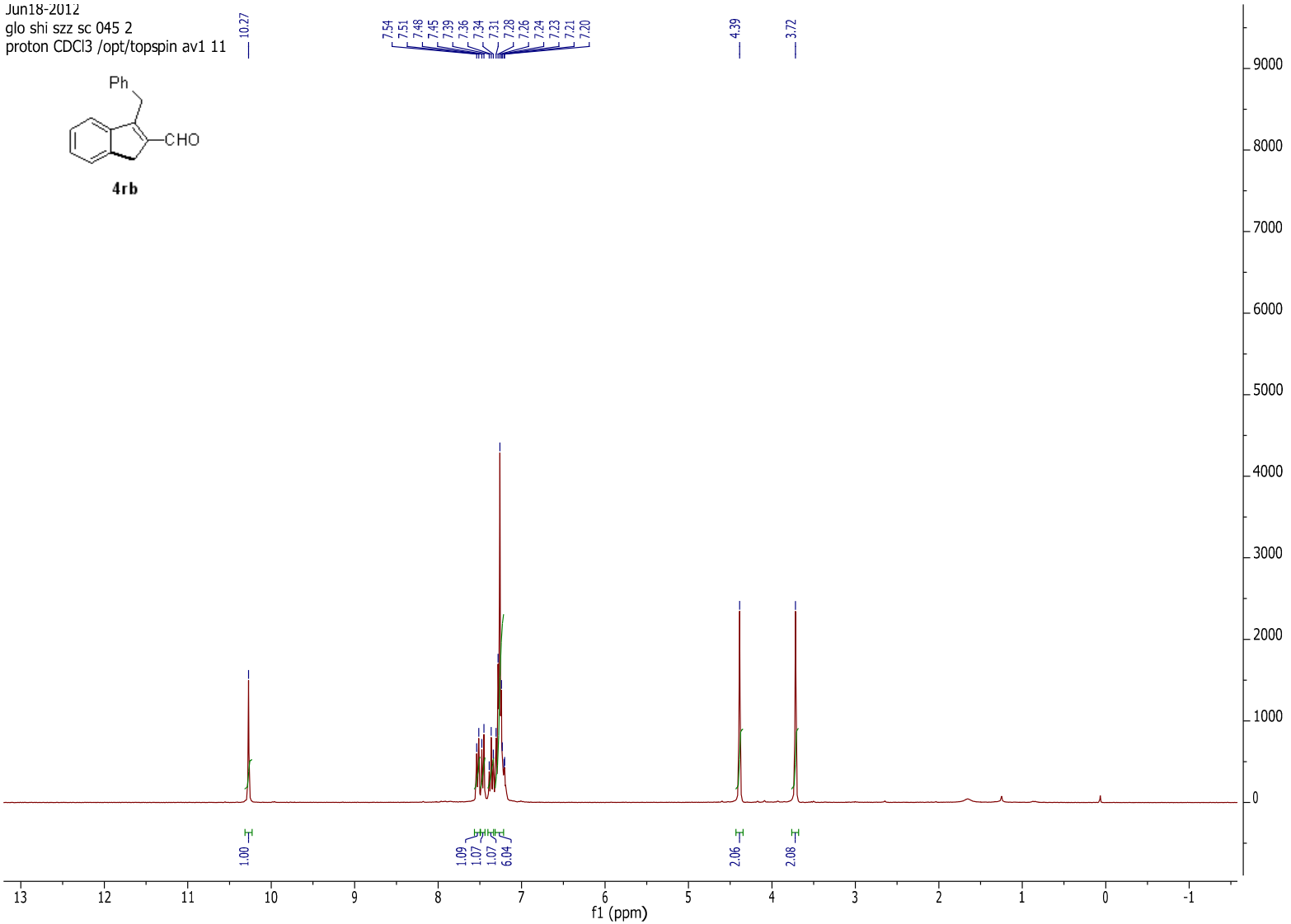

Jan22-2013
glo shi szz se 020 1
carbon_256 CDCl3 /opt/topspin av1 1
186.96
154.90
146.12
144.23
139.31
136.07
133.80
123.08
95.42
77.42
77.00
76.58
35.54
10.73
CHO
I
4ob
f1 (ppm)

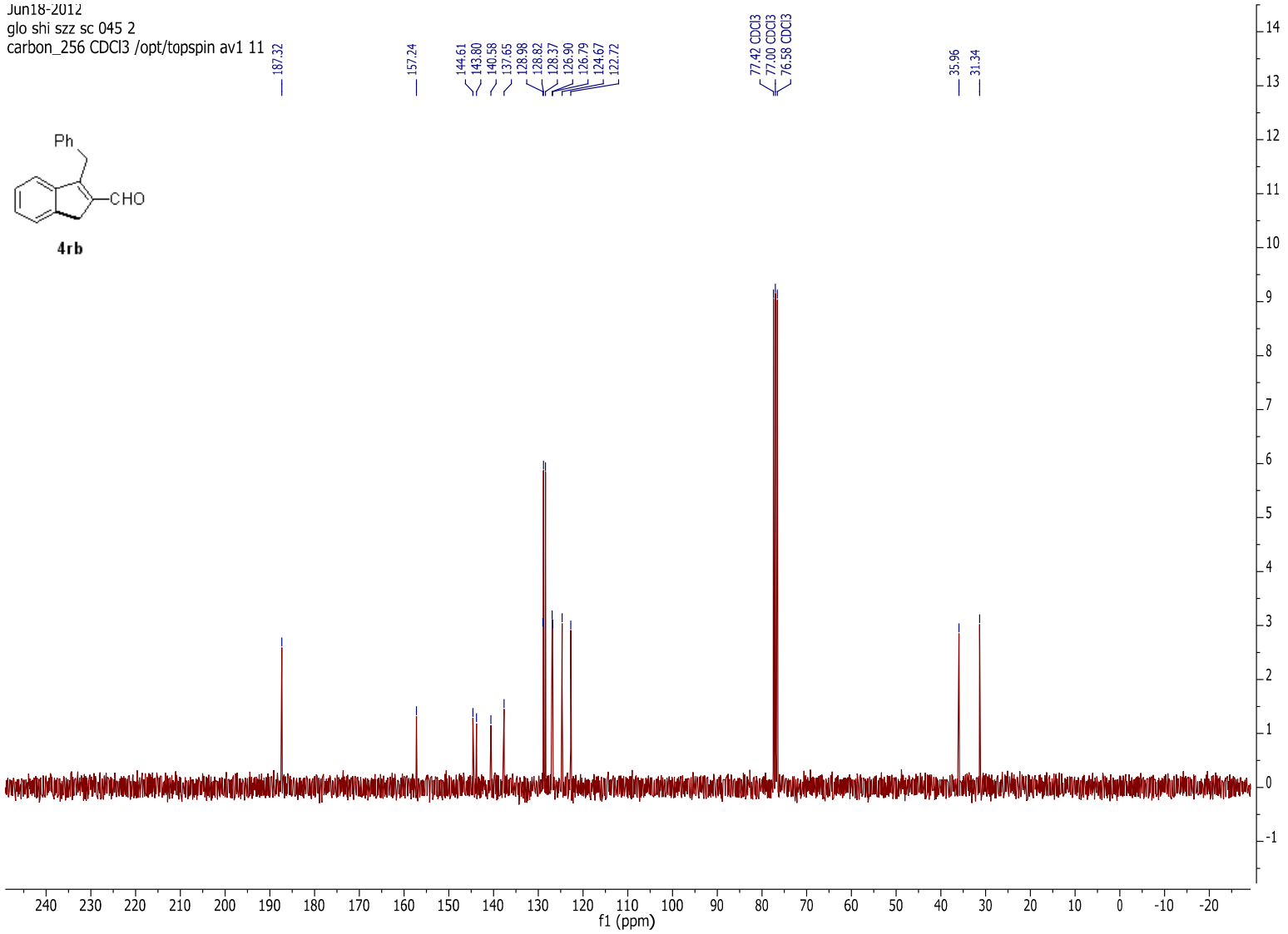

Feb06-2013
glo shi zsz se 033 9
proton CDCl3 /opt/topspin av1 56
10.27
7.81
7.69
7.67
7.66
7.65
7.62
7.26
3.70
3.70
2.61
2.60
2.59
F3C
CHO
4pb
1.00
1.01
2.02
2.06
3.12
f1 (ppm)

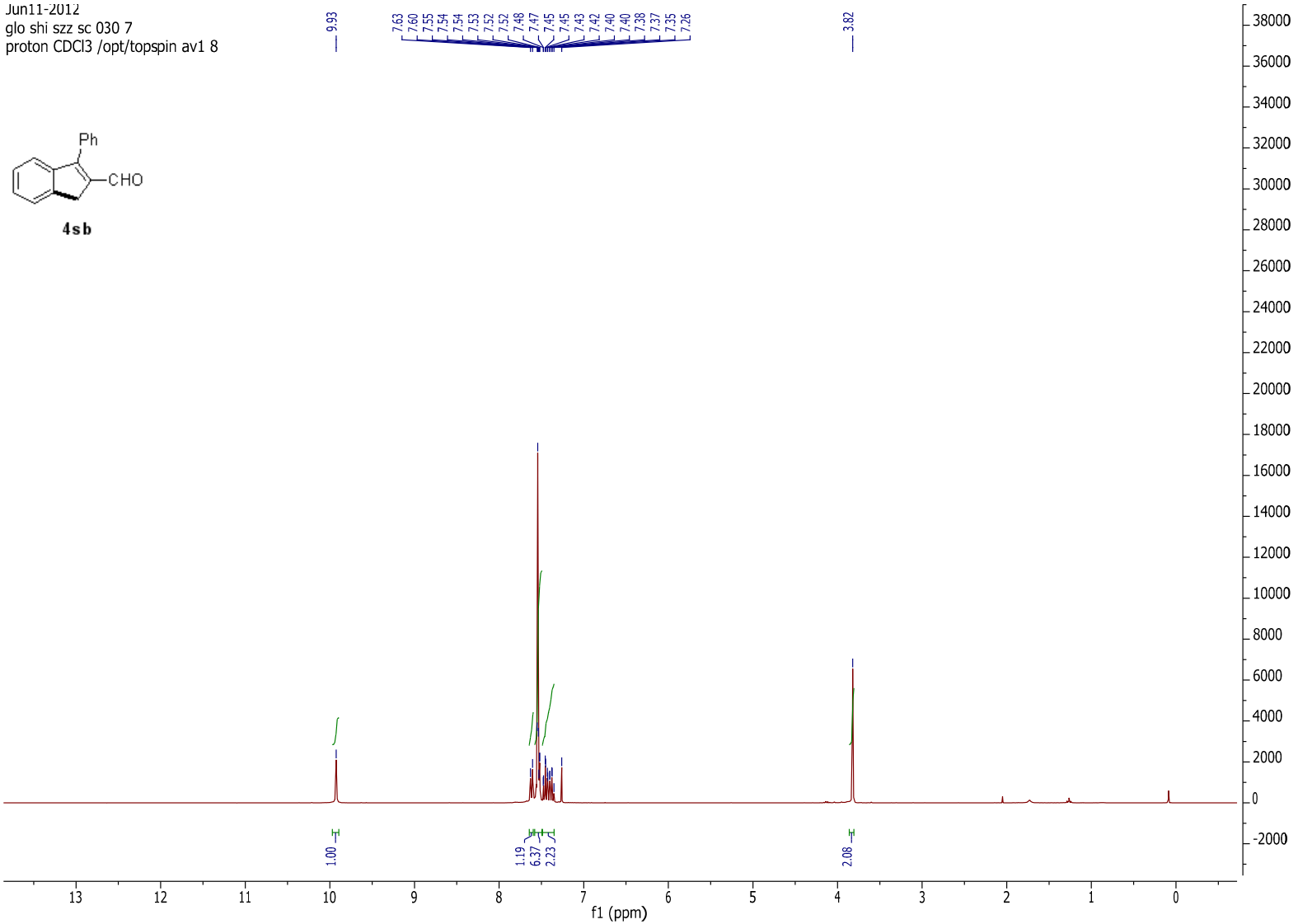


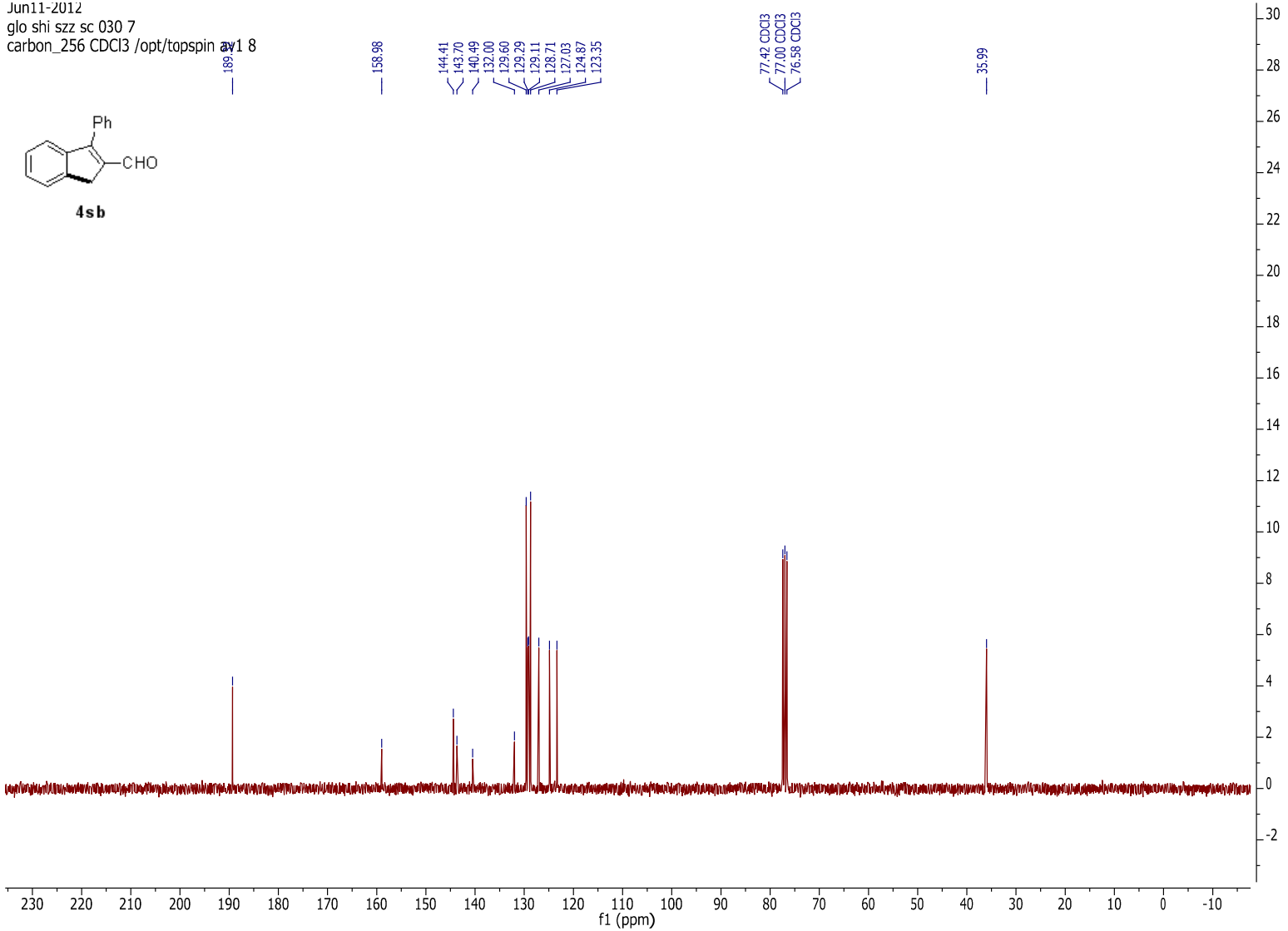

Jun15-2012
glo shi szz sc 039 2
proton CDCl3 /opt/topspin av1 18
CHO
4qb
7.77
7.76
7.76
7.75
7.74
7.56
7.55
7.53
7.53
7.41
7.39
7.39
7.38
7.37
7.37
7.36
7.33
7.26
3.86
3.84
3.81
3.79
3.77
3.63
1.53
1.51
0.99
1.00
1.08
2.04
1.04
2.01
6.28
f1 (ppm)

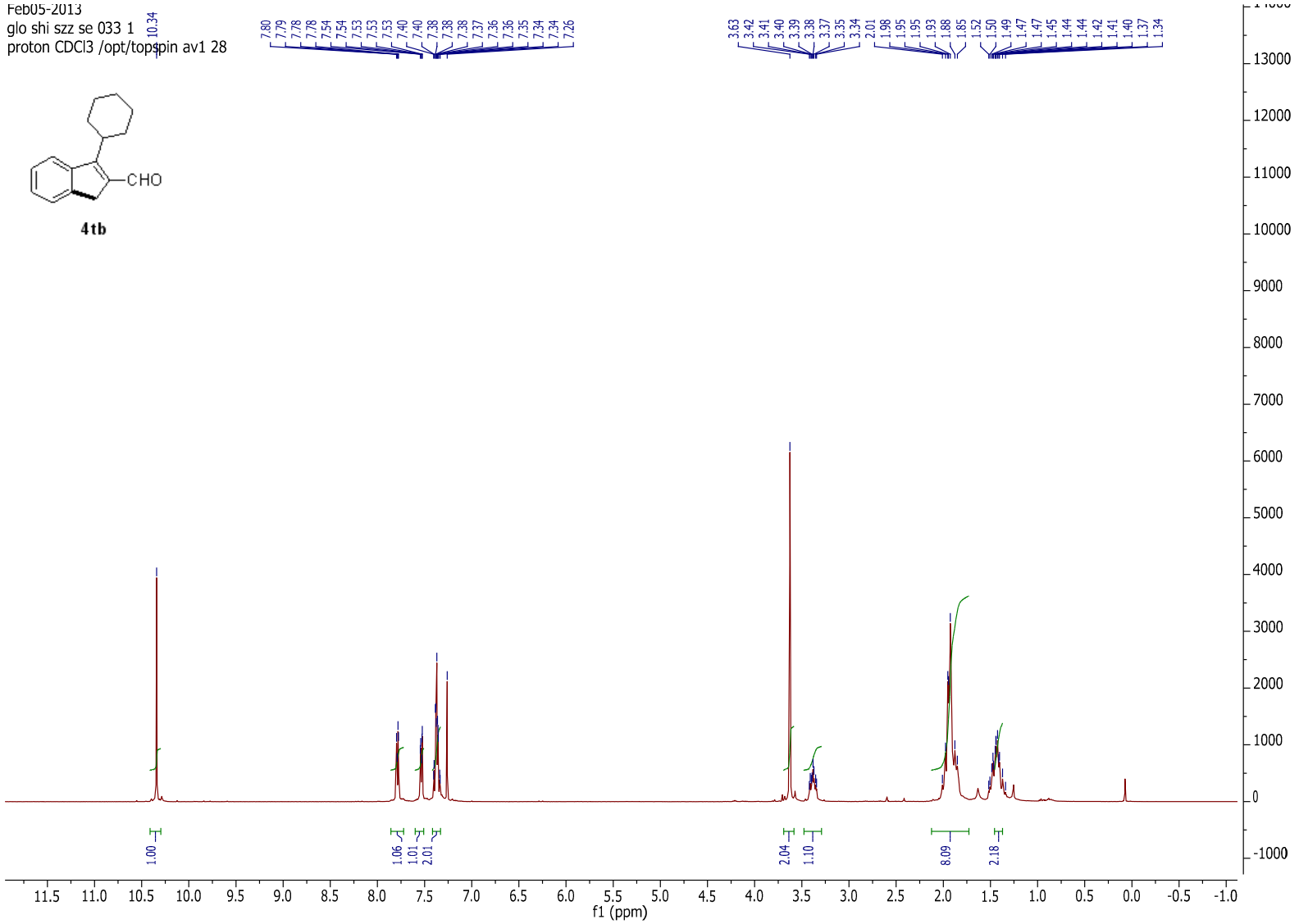

Jun15-2012
glo shi szz sc 039 2
carbon_256 CDCl3 /opt/topspin av1 18
187.23
165.32
145.29
142.74
128.54
126.52
124.92
124.01
77.42 CDCl3
77.00 CDCl3
76.58 CDCl3
35.94
27.02
22.18
CHO
4qb
f1 (ppm)

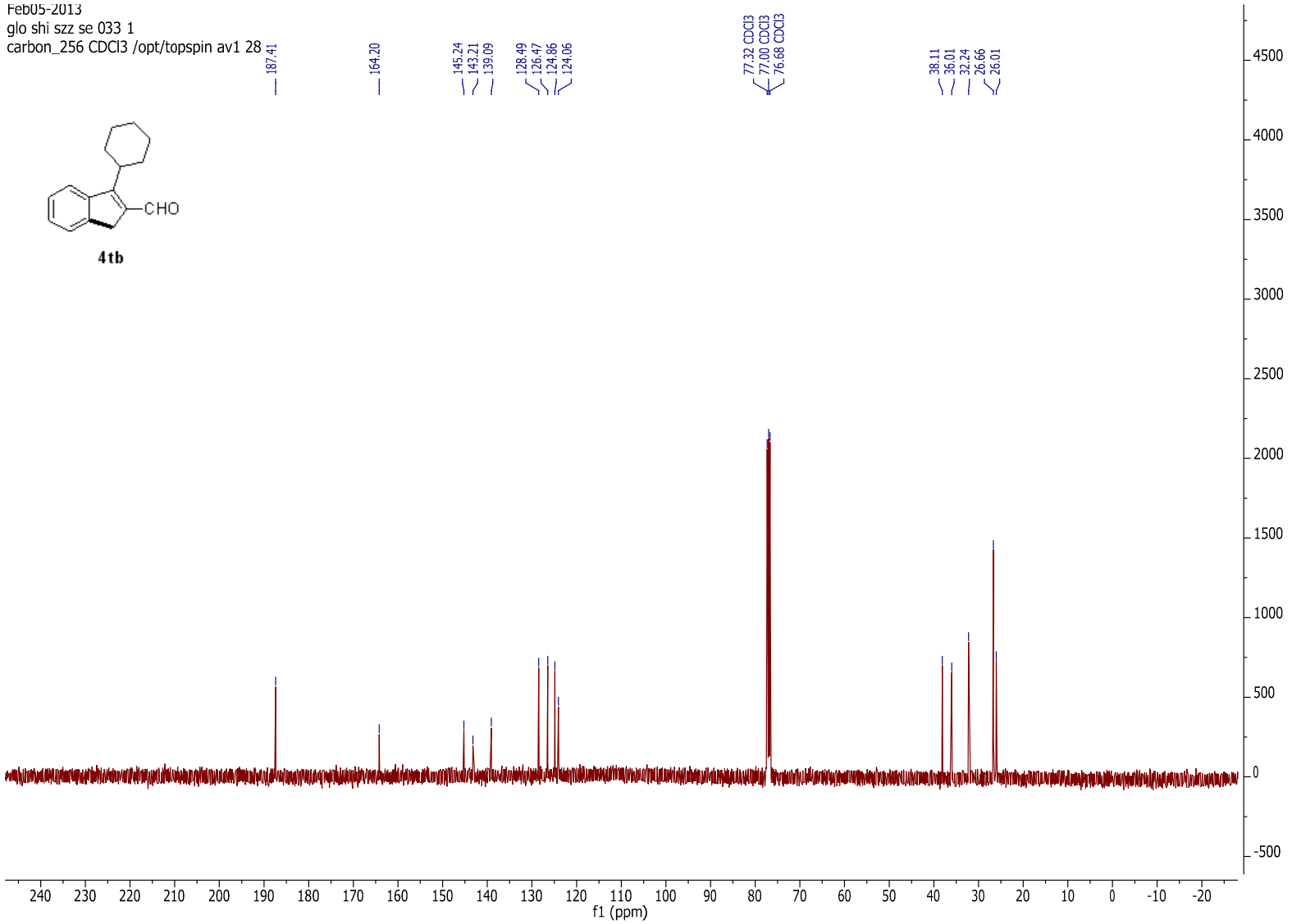

Jun18-2012
glo shi szz sc 045 2
proton CDCl3 /opt/topspin av1 11
Ph
CHO
4rb
10.27
7.54
7.51
7.48
7.45
7.39
7.36
7.34
7.31
7.28
7.26
7.24
7.23
7.21
7.20
4.39
3.72
1.00
1.09
1.07
1.07
6.04
2.06
2.08
f1 (ppm)

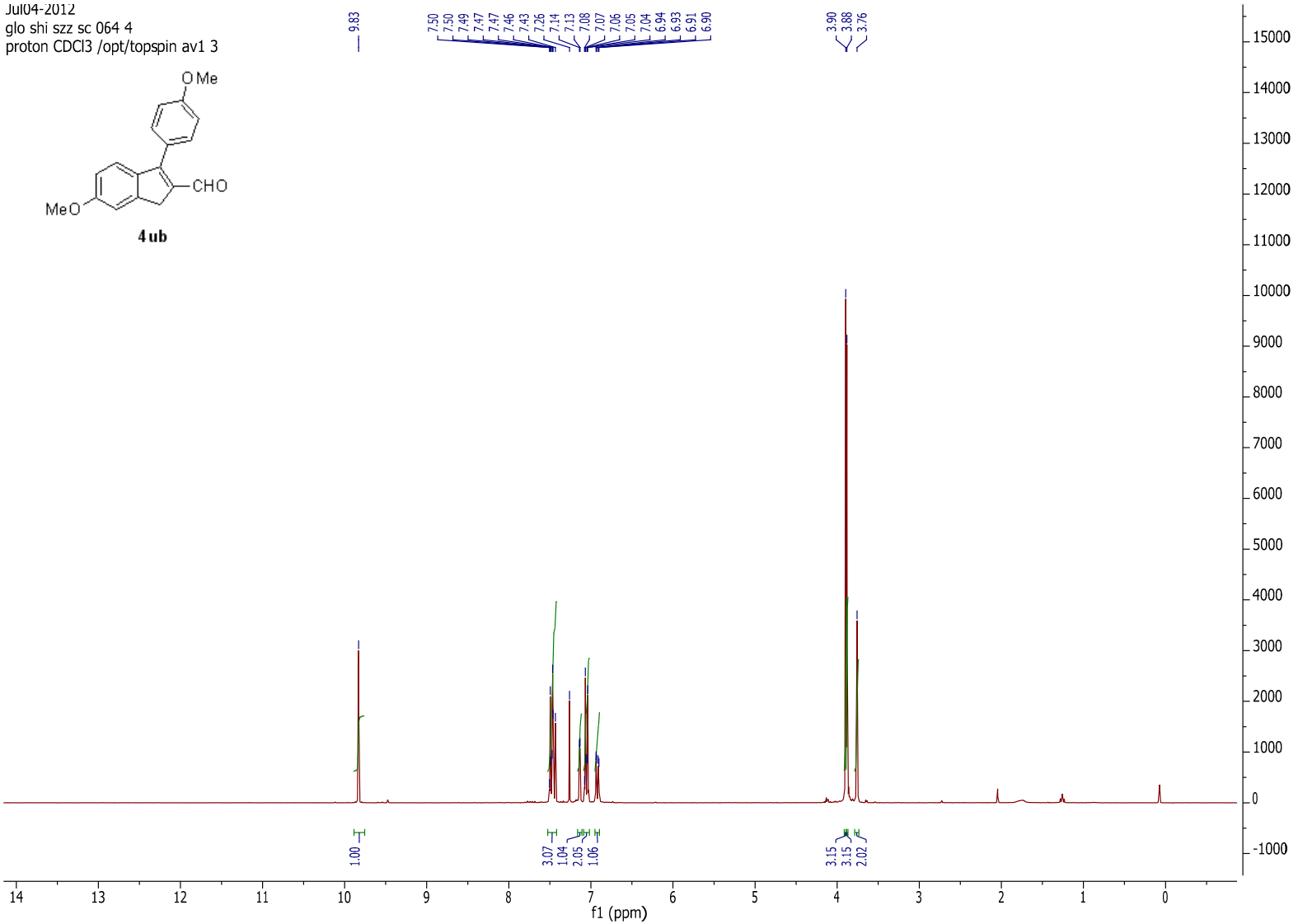



Jun11-2012
glo shi szz sc 030 7
proton CDCl3 /opt/topspin av1 8
9.93
7.63
7.60
7.55
7.54
7.54
7.53
7.52
7.52
7.48
7.47
7.45
7.45
7.43
7.42
7.40
7.40
7.38
7.37
7.35
7.26
3.82
Ph
CHO
4sb
1.00
1.19
6.37
2.23
2.08
f1 (ppm)


Jun11-2012
glo shi szz sc 030 7
carbon_256 CDCl3 /opt/topspin av1 8
189.41
158.98
144.41
143.70
140.49
132.00
129.60
129.29
129.11
128.71
127.03
124.87
123.35
77.42 CDCl3
77.00 CDCl3
76.58 CDCl3
35.99
Ph
CHO
4sb
f1 (ppm)




Feb05-2013
glo shi szz se 033 1
carbon_256 CDCl3 /opt/topspin av1 28
187.41
164.20
145.24
143.21
139.09
128.49
126.47
124.86
124.06
77.32 CDCl3
77.00 CDCl3
76.68 CDCl3
38.11
36.01
32.24
26.66
26.01
CHO
4tb
f1 (ppm)


Jul04-2012
glo shi szz sc 064 4
proton CDCl3 /opt/topspin av1 3
O Me
CHO
MeO
4 ub
9.83
7.50
7.50
7.49
7.47
7.47
7.46
7.43
7.26
7.14
7.13
7.08
7.07
7.06
7.05
7.04
6.94
6.93
6.91
6.90
3.90
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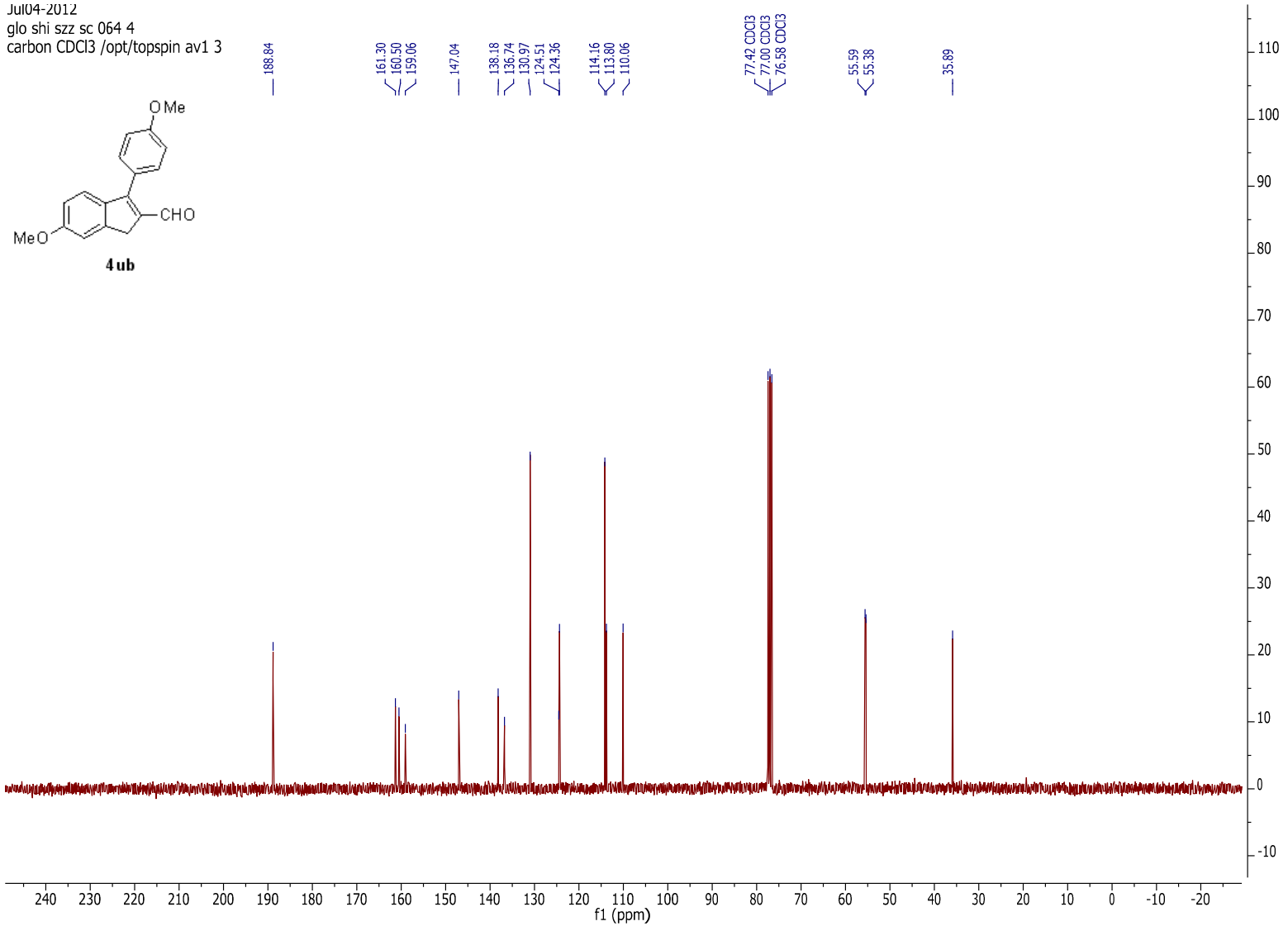
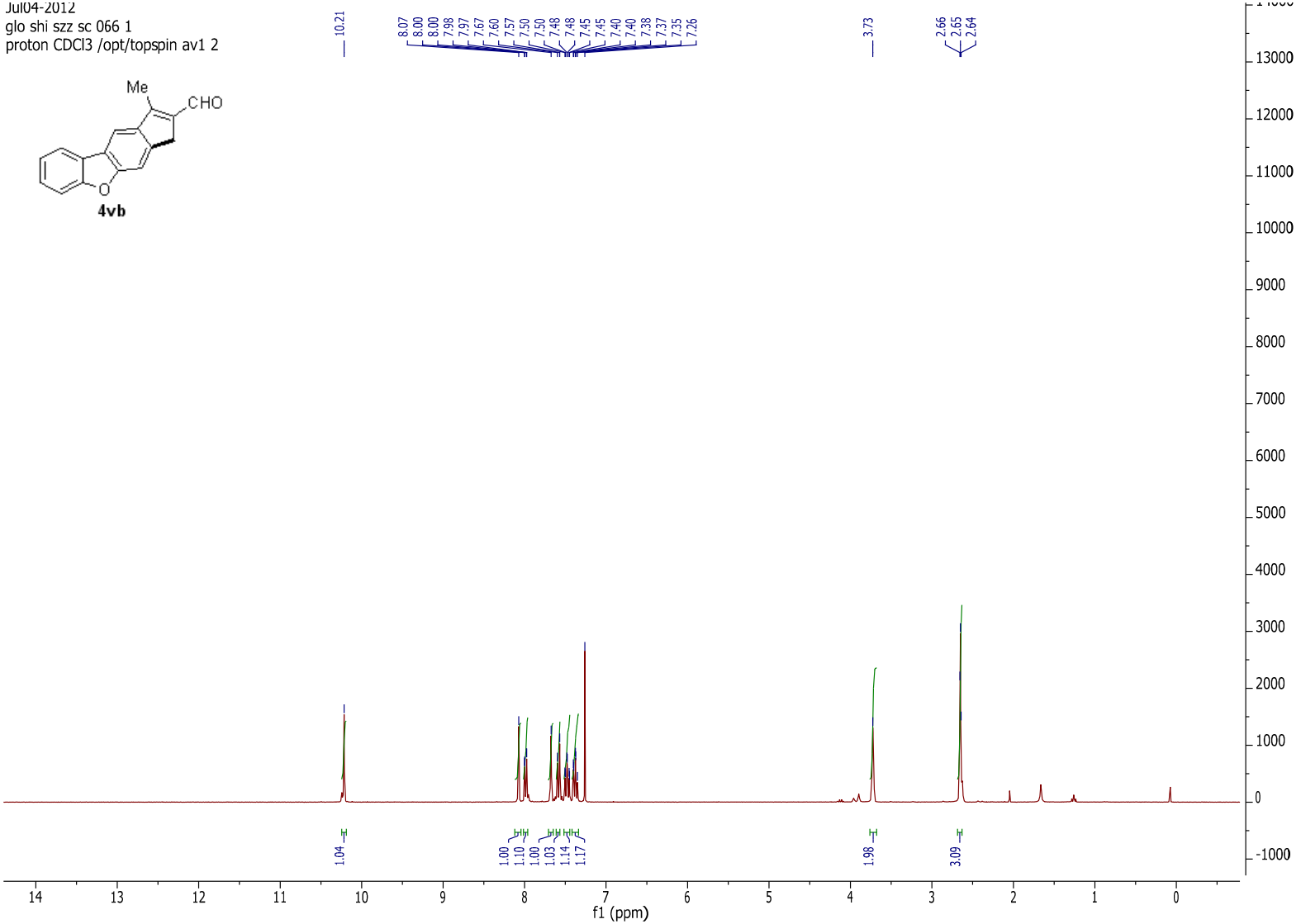
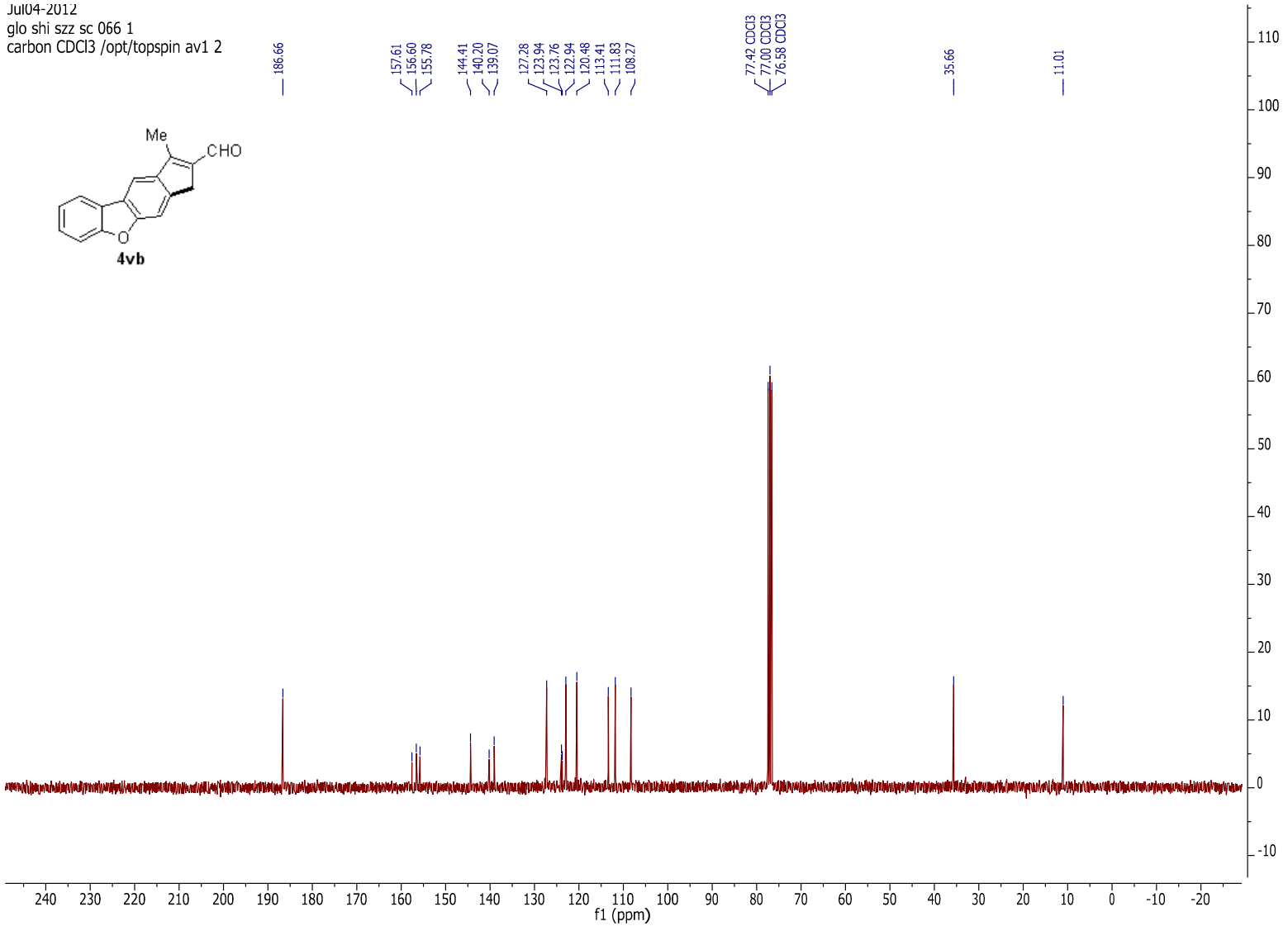
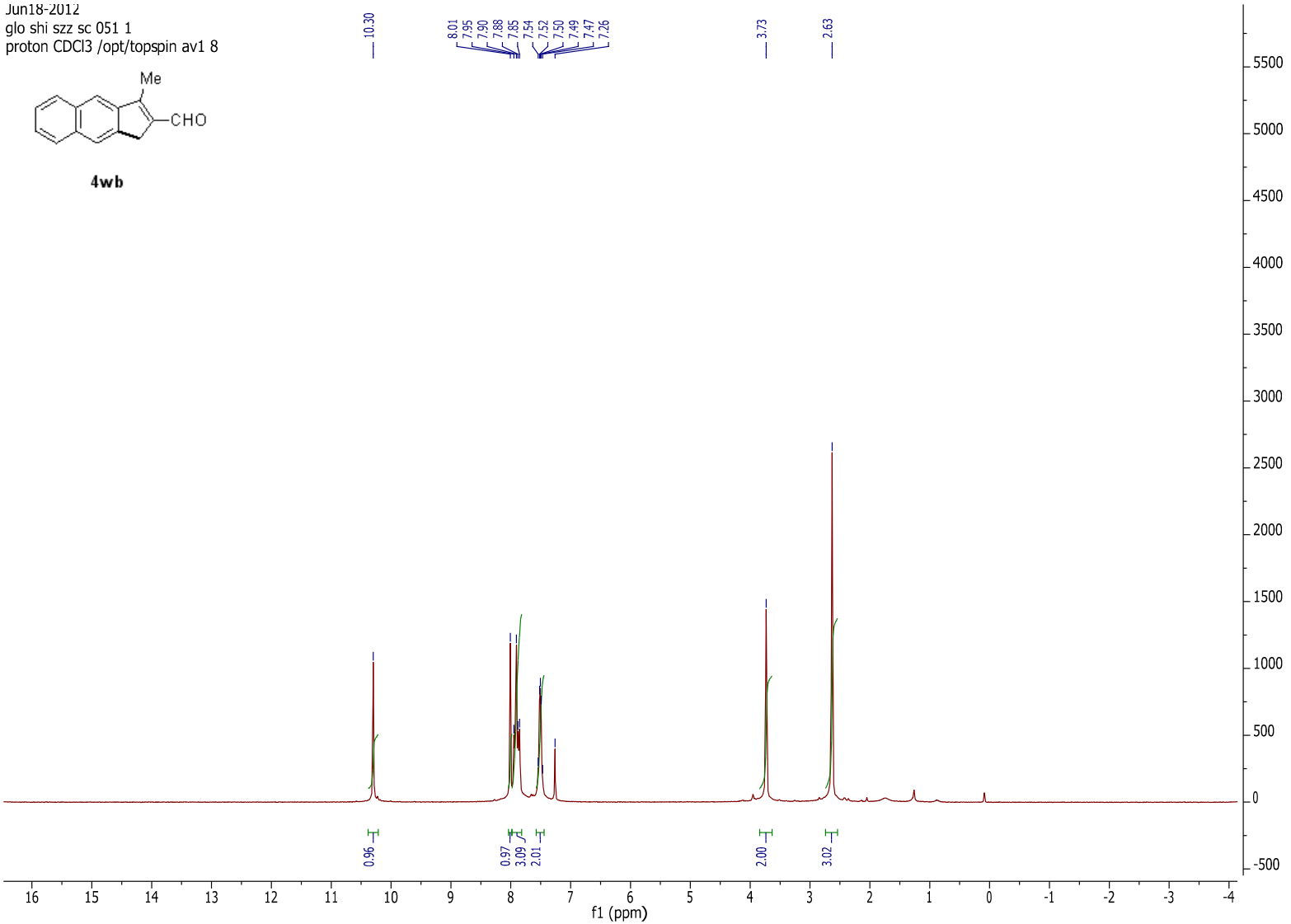
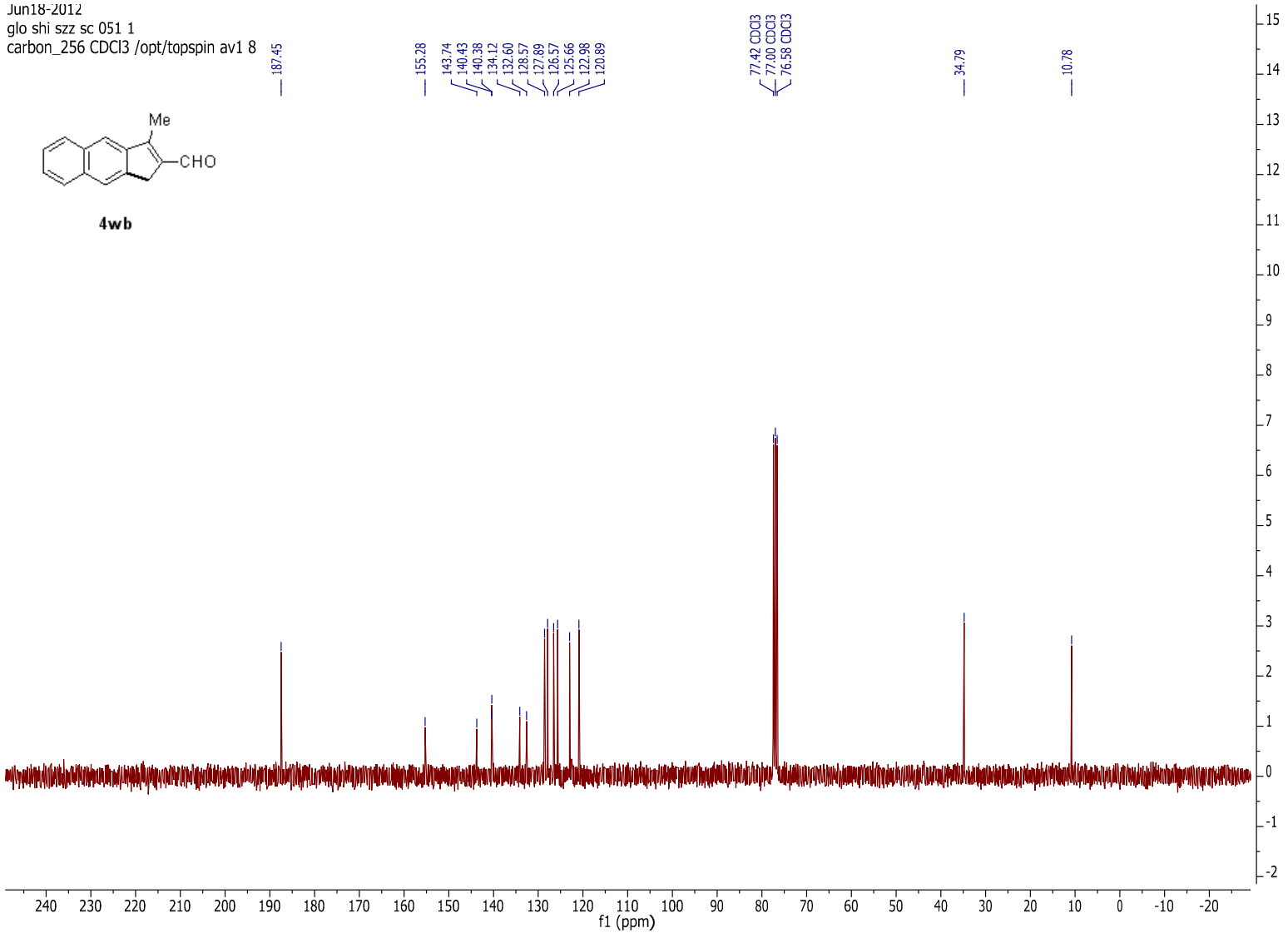
3.07
1.04
2.05
1.06
3.15
3.15
2.02
f1 (ppm)

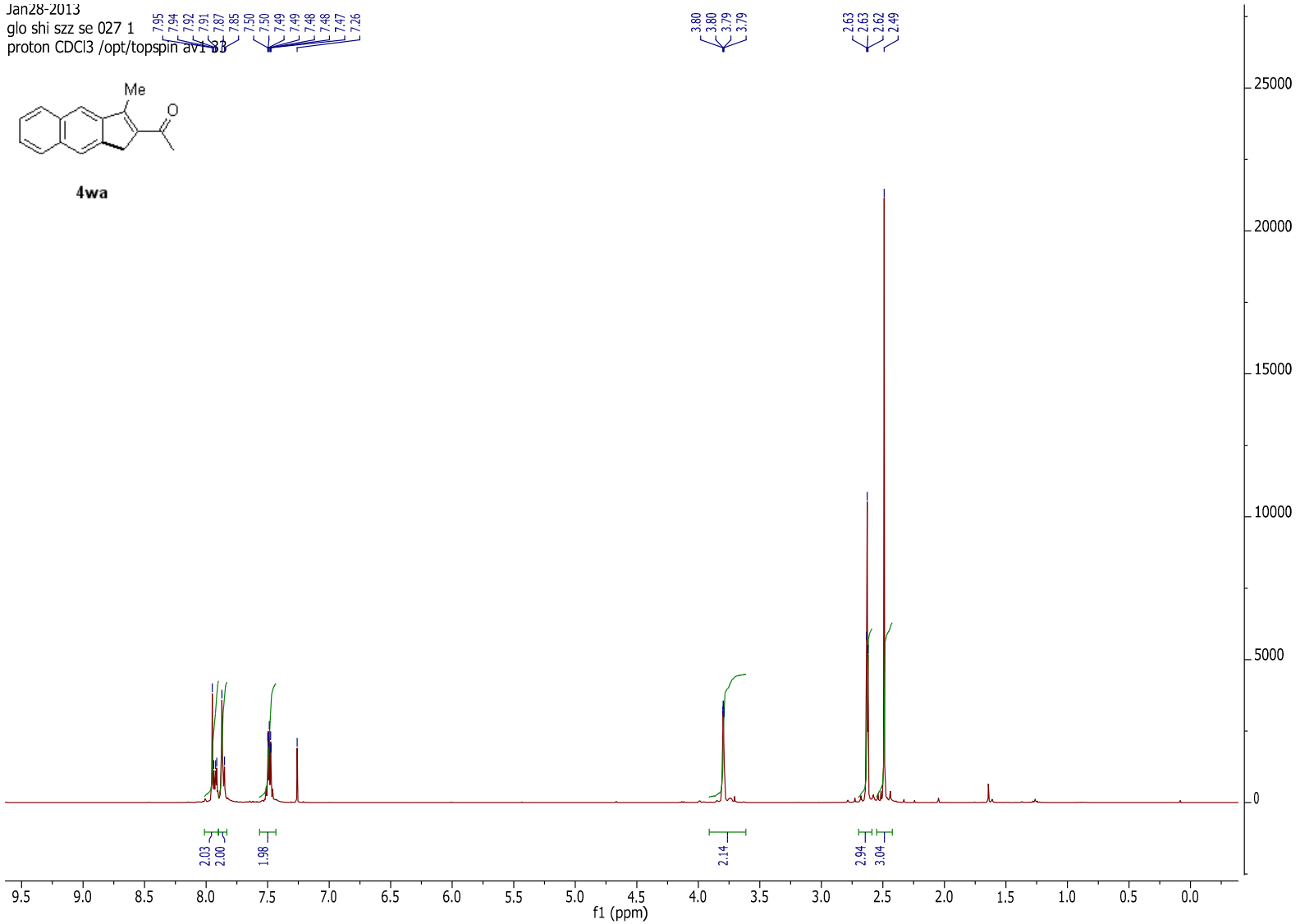

Jul04-2012
glo shi szz sc 064 4
carbon CDCl3 /opt/topspin av1 3
188.84
161.30
160.50
159.06
147.04
138.18
136.74
130.97
124.51
124.36
114.16
113.80
110.06
77.42 CDCl3
77.00 CDCl3
76.58 CDCl3
55.59
55.38
35.89
O Me
CHO
MeO
4ub
f1 (ppm)

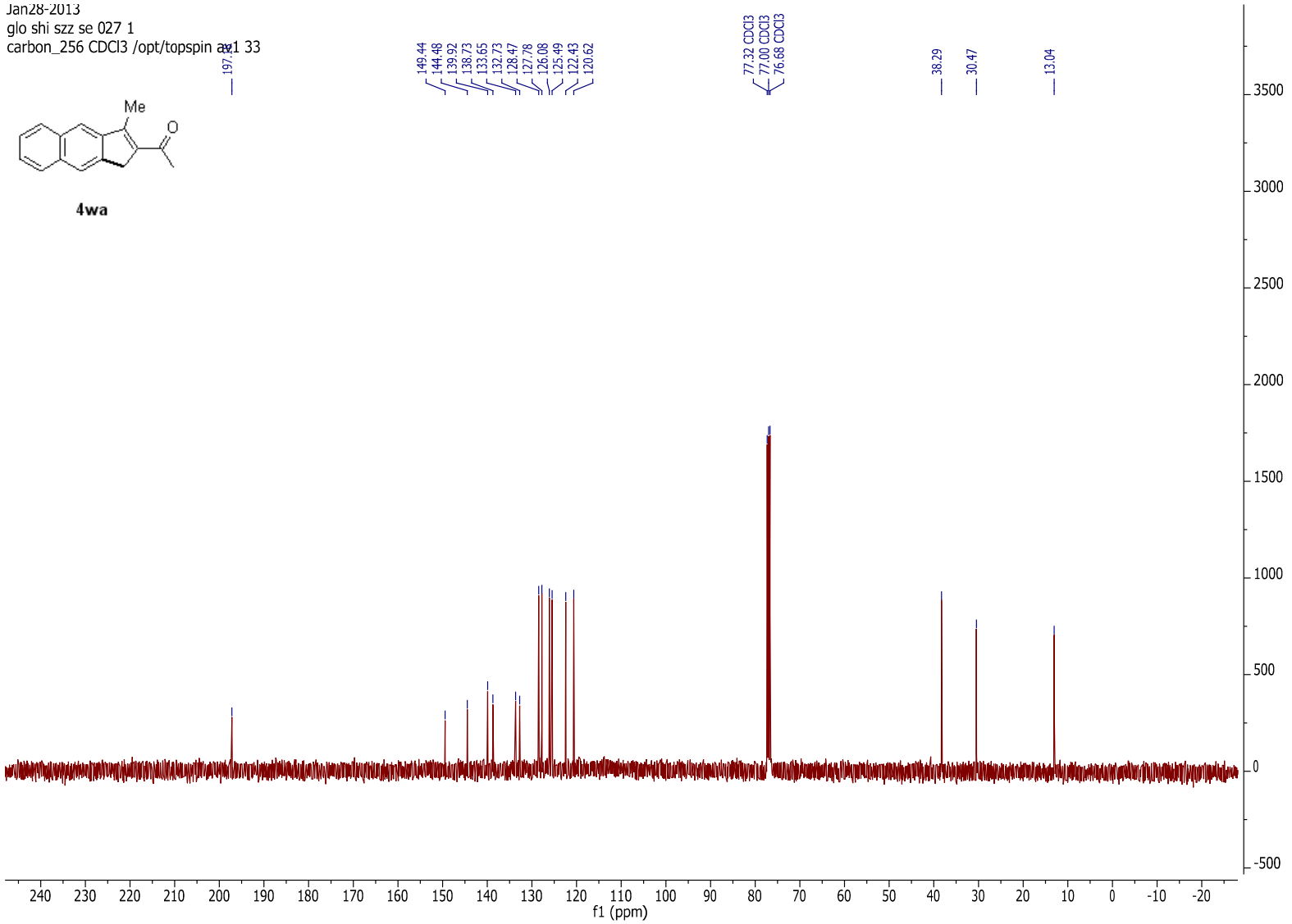

Jul04-2012
glo shi szz sc 066 1
proton CDCl3 /opt/topspin av1 2
Me
CHO
O
4vb
10.21
8.07
8.00
8.00
7.98
7.97
7.67
7.60
7.57
7.50
7.50
7.48
7.48
7.45
7.45
7.40
7.40
7.38
7.37
7.35
7.26
3.73
2.66
2.65
2.64
1.04
1.00
1.10
1.00
1.03
1.14
1.17
1.98
3.09
f1 (ppm)

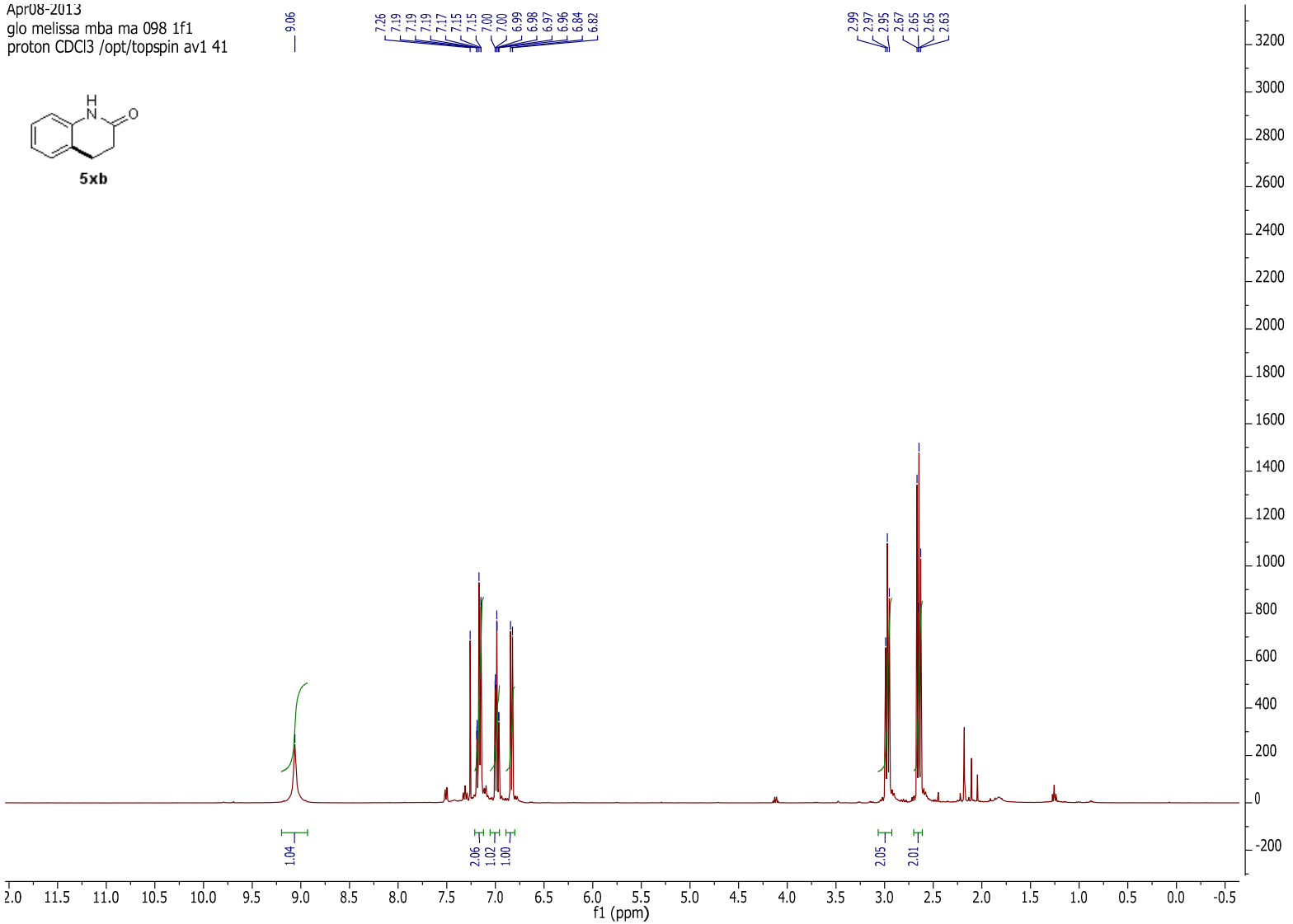

Jul04-2012
glo shi szz sc 066 1
carbon CDCl3 /opt/topspin av1 2
186.66
157.61
156.60
155.78
144.41
140.20
139.07
127.28
123.94
123.76
122.94
120.48
113.41
111.83
108.27
77.42 CDCl3
77.00 CDCl3
76.58 CDCl3
35.66
11.01
Me
CHO
O
4vb
f1 (ppm)

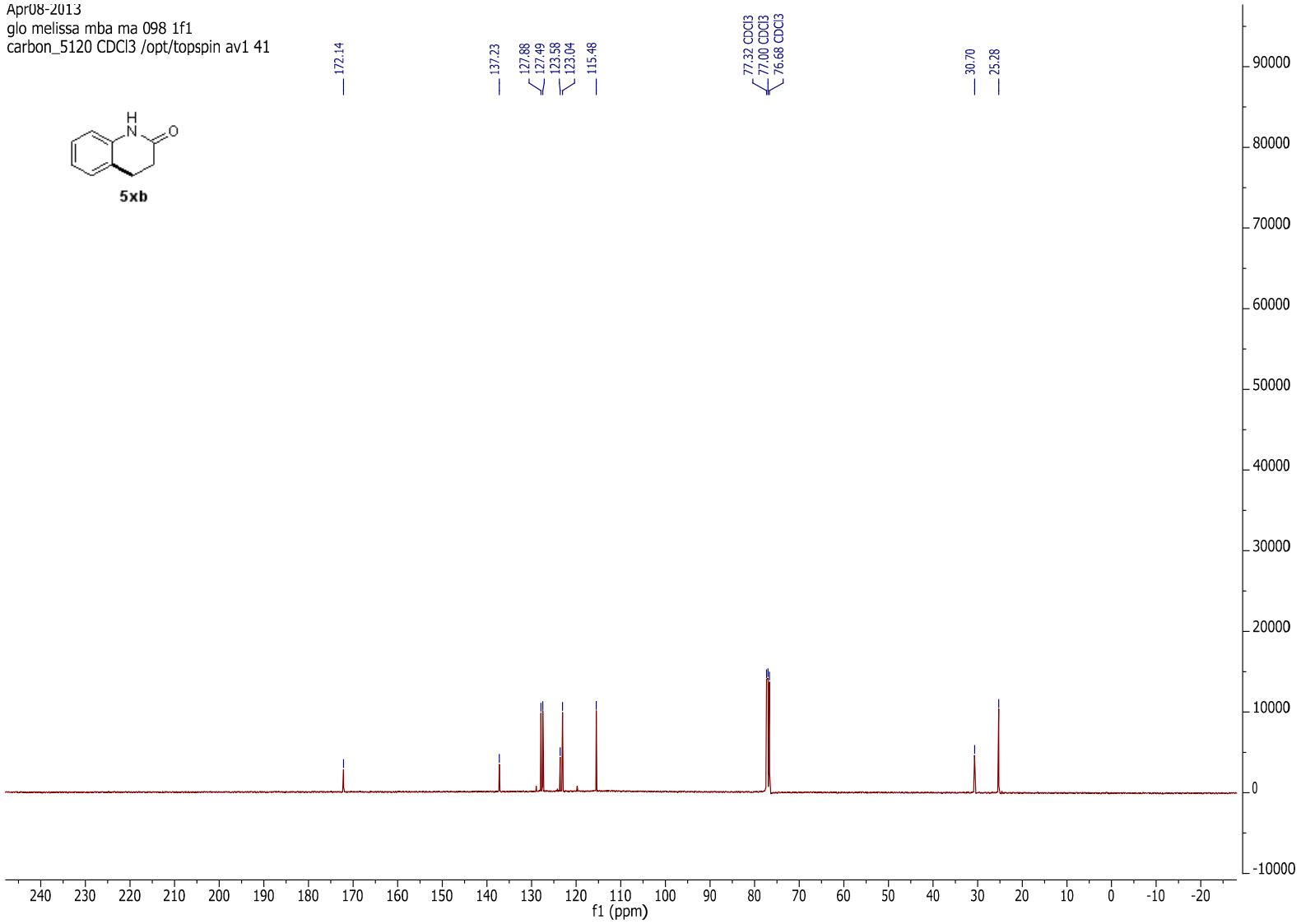

Jun18-2012
glo shi szz sc 051 1
proton CDCl3 /opt/topspin av1 8
Me
CHO
4wb
10.30
8.01
7.95
7.90
7.88
7.85
7.54
7.52
7.50
7.49
7.47
7.26
3.73
2.63
0.96
0.97
3.09
2.01
2.00
3.02
f1 (ppm)

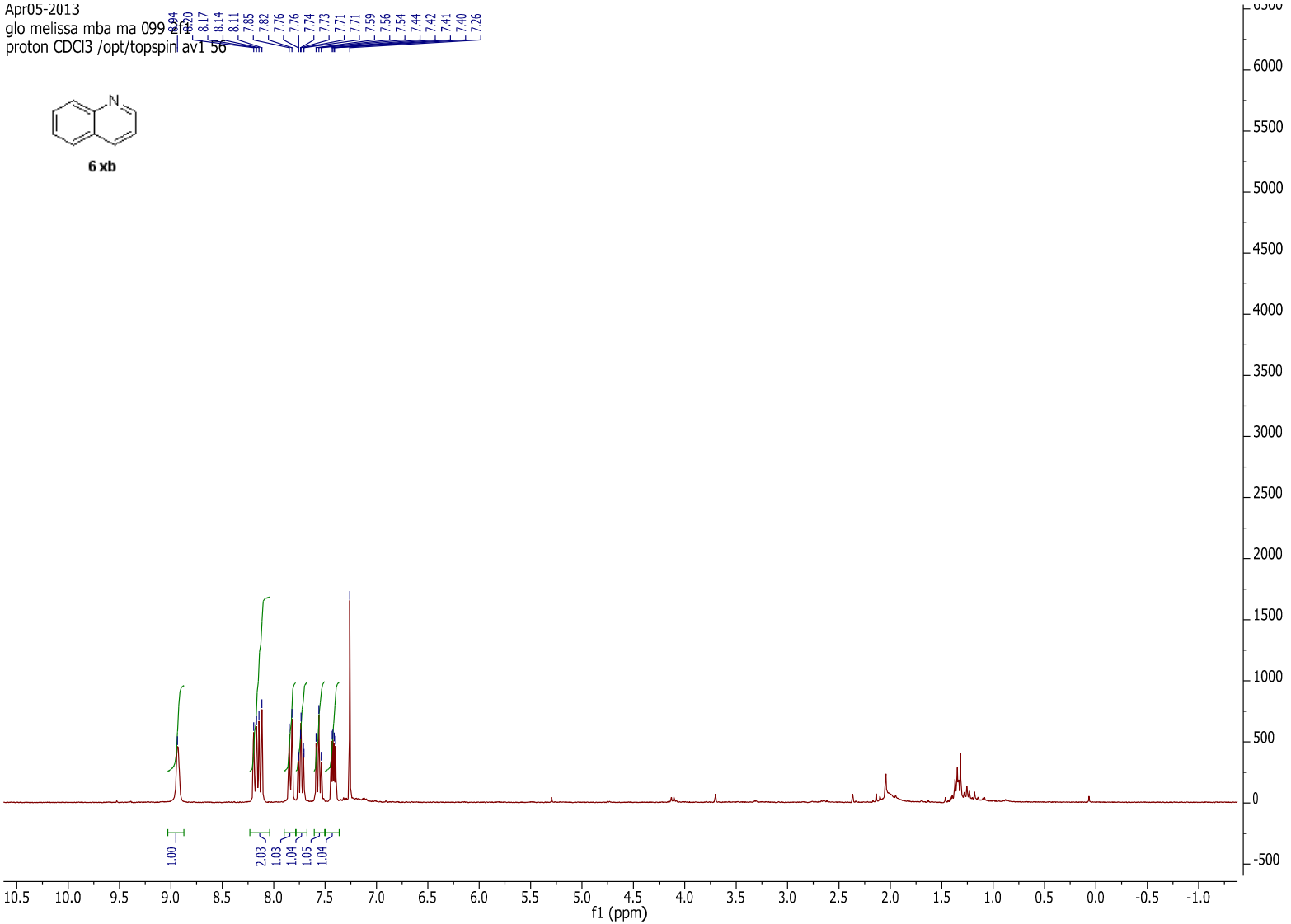

Jun18-2012
glo shi szz sc 051 1
carbon_256 CDCl3 /opt/topspin av1 8
187.45
155.28
143.74
140.43
140.38
134.12
132.60
128.57
127.89
126.57
125.66
122.98
120.89
77.42 CDCl3
77.00 CDCl3
76.58 CDCl3
34.79
10.78
Me
CHO
4wb
f1 (ppm)

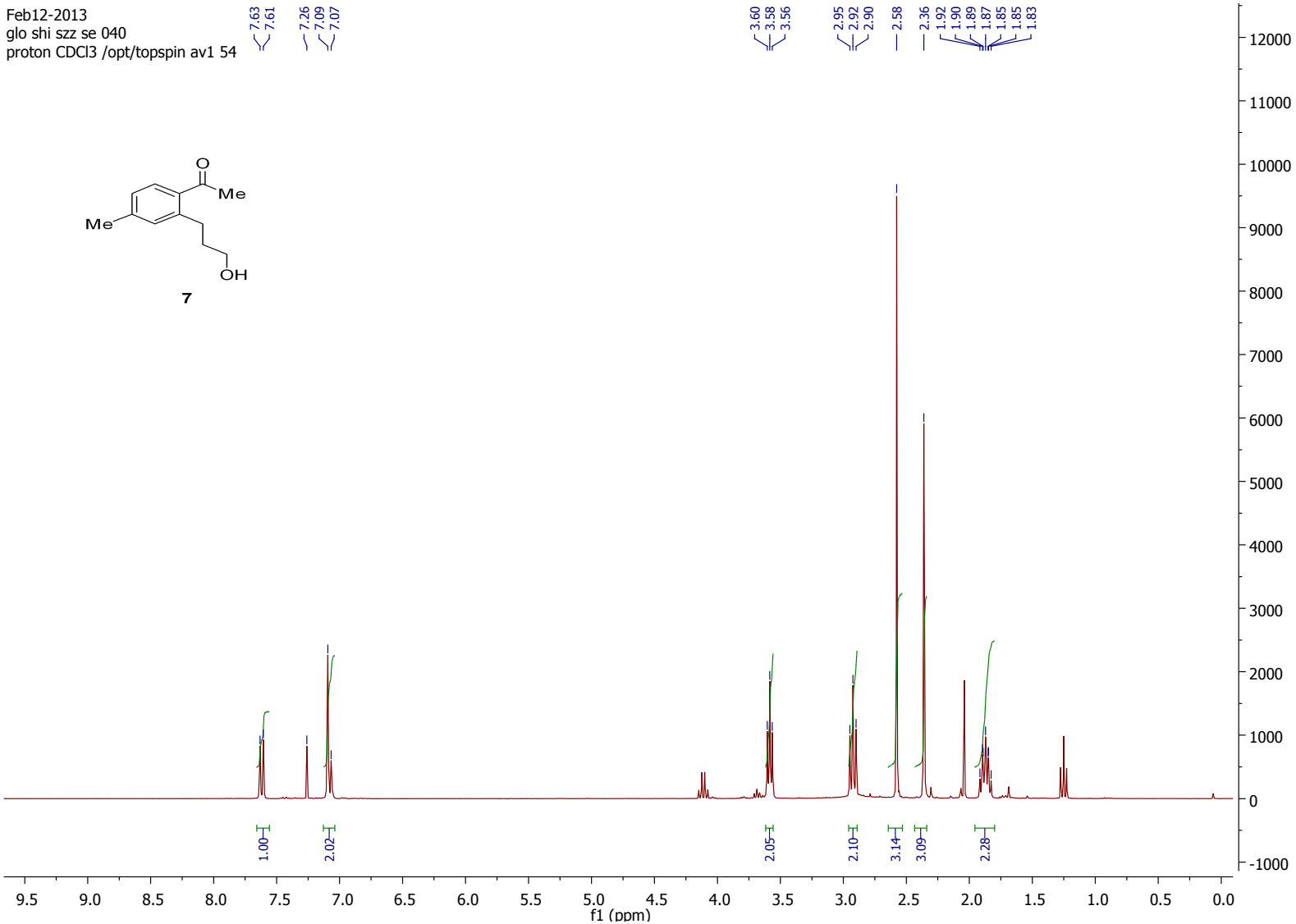

Jan28-2013
glo shi szz se 027 1
proton CDCl3 /opt/topspin av1 33
7.95
7.94
7.92
7.91
7.87
7.85
7.50
7.50
7.49
7.49
7.48
7.48
7.47
7.26
3.80
3.80
3.79
3.79
2.63
2.63
2.62
2.49
Me
O
4wa
25000
20000
15000
10000
5000
0
2.03
2.00
1.98
2.14
2.94
3.04
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

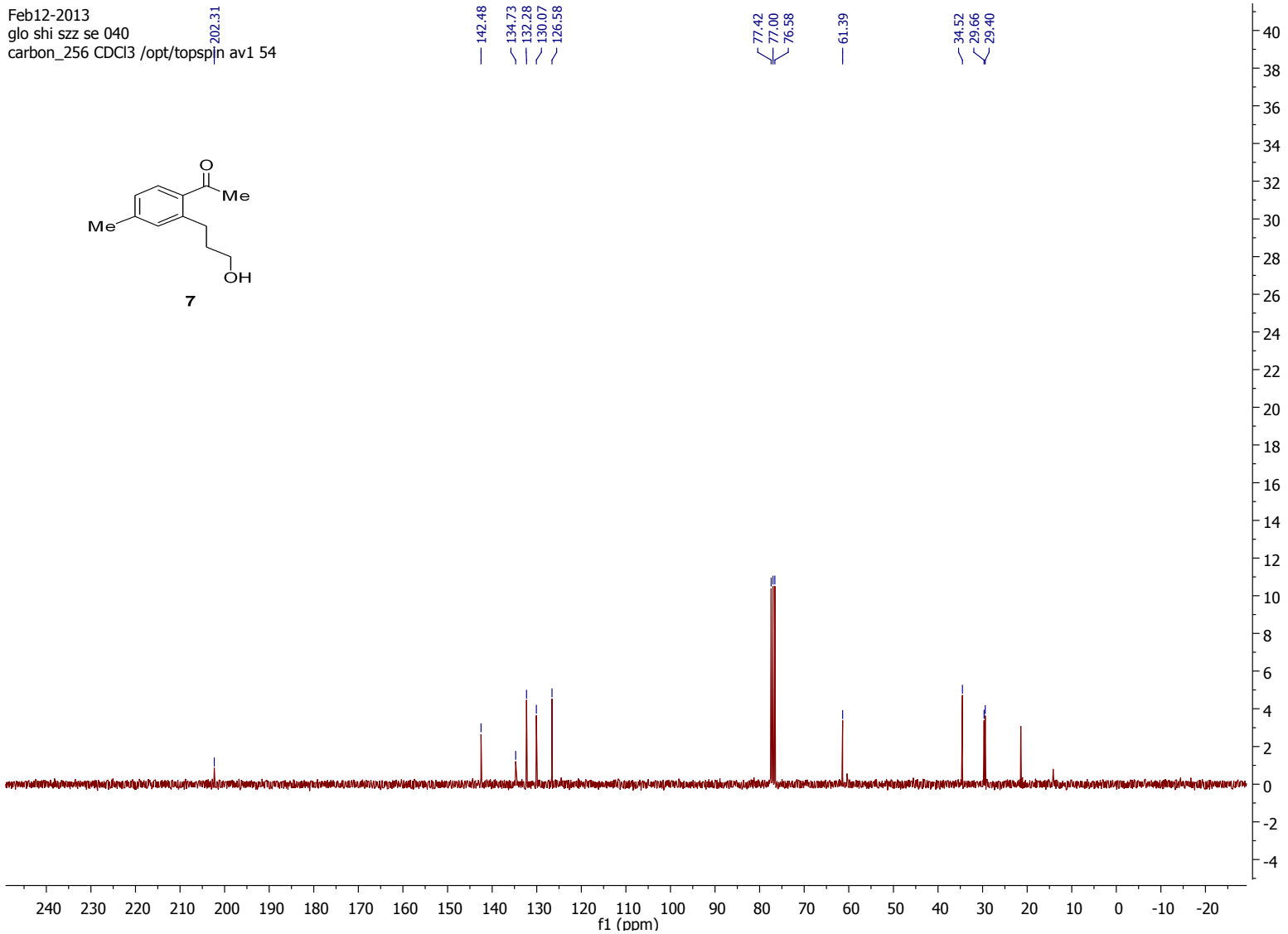

Jan28-2013
glo shi szz se 027 1
carbon_256 CDCl3 /opt/topspin a
197.21
149.44
144.48
139.92
138.73
133.65
132.73
128.47
127.78
126.08
125.49
122.43
120.62
77.32 CDCl3
77.00 CDCl3
76.68 CDCl3
38.29
30.47
13.04
Me
O
4wa
f1 (ppm)

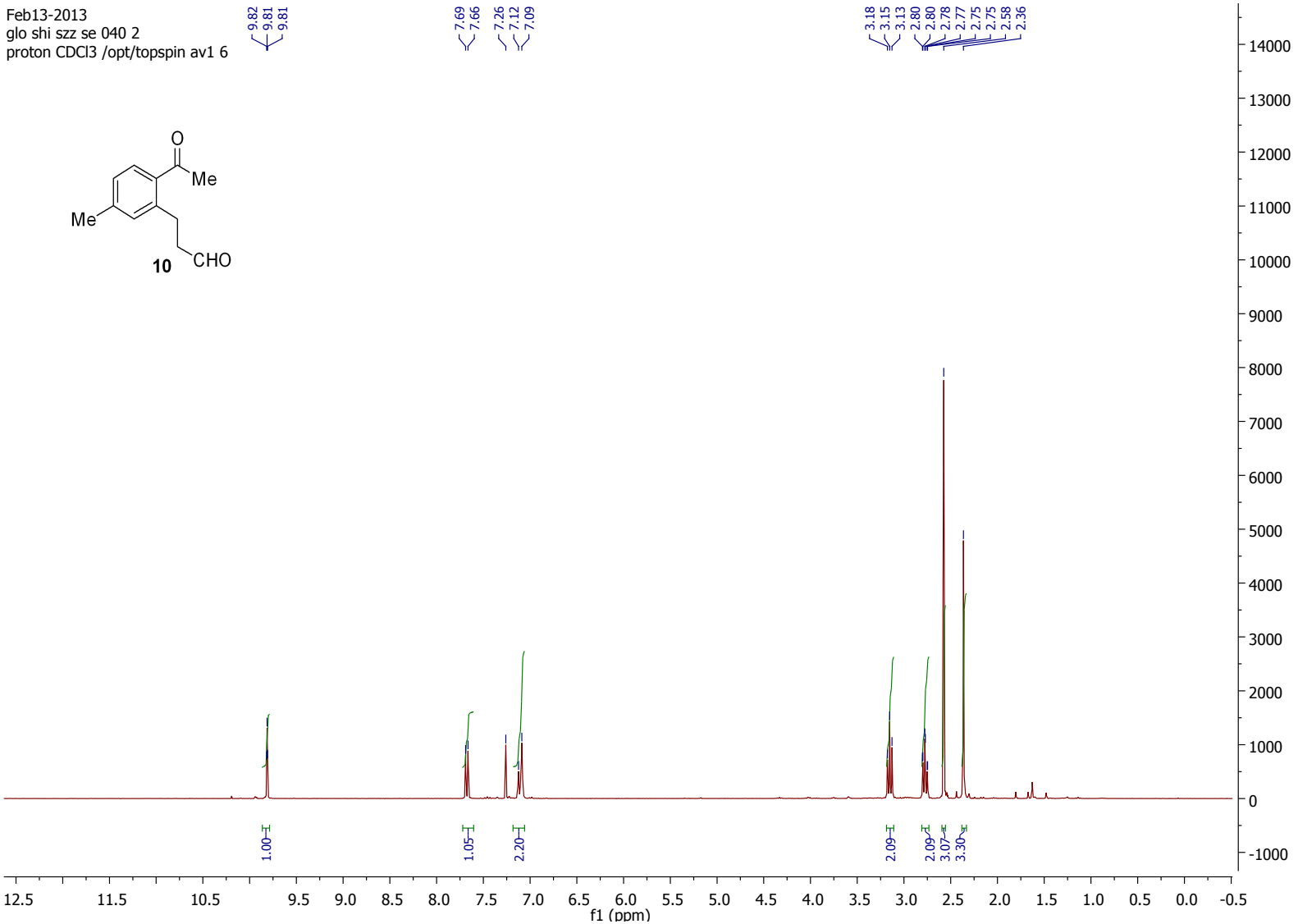


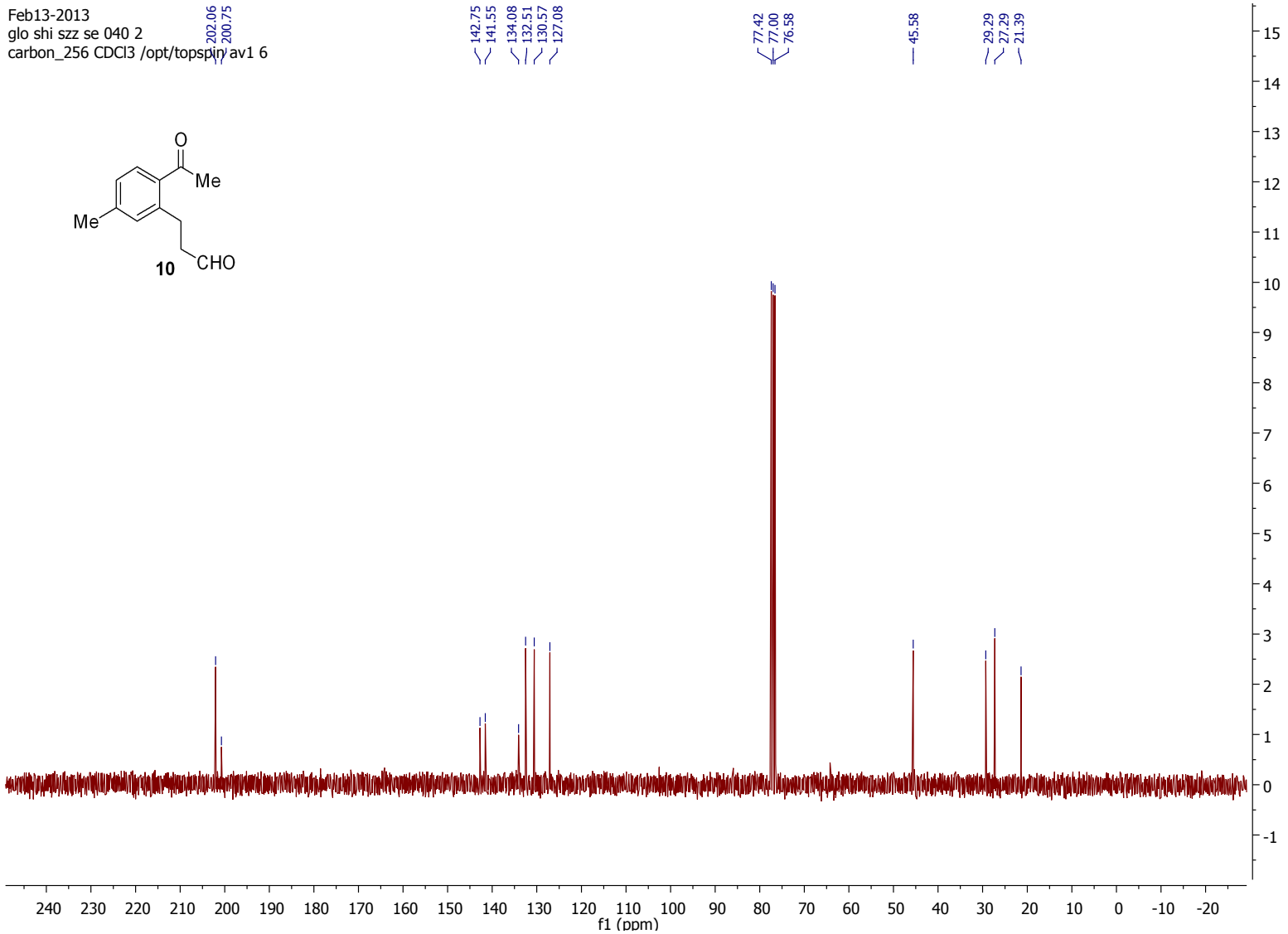

Apr08-2013
glo melissa mba ma 098 1f1
carbon_5120 CDCl3 /opt/topspin av1 41
172.14
137.23
127.88
127.49
123.58
123.04
115.48
77.32 CDCl3
77.00 CDCl3
76.68 CDCl3
30.70
25.28
5xb
f1 (ppm)


Apr05-2013
glo melissa mba ma 099 ef2
proton CDCl3 /opt/topspin av1 56
9.04
8.20
8.17
8.14
8.11
7.85
7.82
7.76
7.76
7.74
7.73
7.71
7.71
7.59
7.56
7.54
7.44
7.42
7.41
7.40
7.26
N
6 xb
1.00
2.03
1.03
1.04
1.05
1.04
f1 (ppm)




Feb12-2013
glo shi szz se 040
carbon_256 CDCl3 /opt/topspin av1 54
202.31
142.48
134.73
132.28
130.07
126.58
77.42
77.00
76.58
61.39
34.52
29.66
29.40
O
Me
Me
OH
7
f1 (ppm)


Feb13-2013
glo shi szz se 040 2
proton CDCl3 /opt/topspin av1 6
9.82
9.81
9.81
7.69
7.66
7.26
7.12
7.09
3.18
3.15
3.13
2.80
2.80
2.78
2.77
2.75
2.75
2.58
2.36
O
Me
Me
CHO
10
1.00
1.05
2.20
2.09
2.09
3.07
3.30
f1 (ppm)


Feb13-2013
glo shi szz se 040 2
carbon_256 CDCl3 /opt/topspin/ av1 6
202.06
200.75
142.75
141.55
134.08
132.51
130.57
127.08
77.42
77.00
76.58
45.58
29.29
27.29
21.39
O
Me
Me
CHO
10
f1 (ppm)