# Synthesis of Fluorenones via Quaternary Ammonium Salt-Promoted Intramolecular Dehydrogenative Arylation of Aldehydes

## (Supporting Information)

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**CONTENTS:**

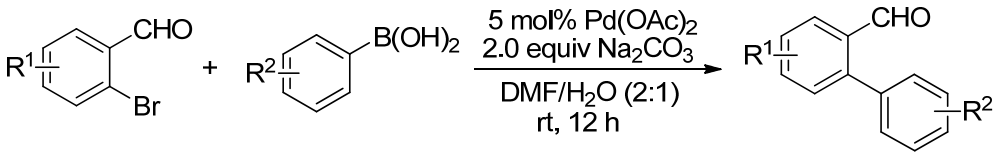
# 1. General Information.

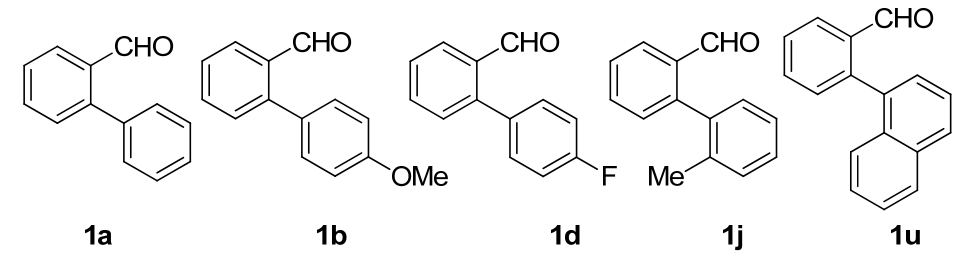
All reactions were carried out in flame-dried reaction vessels with Teflon screw caps under argon. All new compounds were fully characterized. NMR-spectra were recorded on a Bruker ARX-300, AV-300, AV-400 MHz or on a Varian Associated, Varian 600 unity plus. ESI mass spectra were recorded on a Bruker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

Unless otherwise noted, materials obtained from commercial suppliers were used without further purification. TEAB was purchased from TCI. Biarylcarboxaldehydes **1a-1w** were prepared according to method A[1], B[2], C[3]. Starting materials **3**[4] and **5**[5] were prepared according to reported procedures.

## 2. General procedure for synthesis of the biarylcarboxaldehydes.

### Method A:[1]

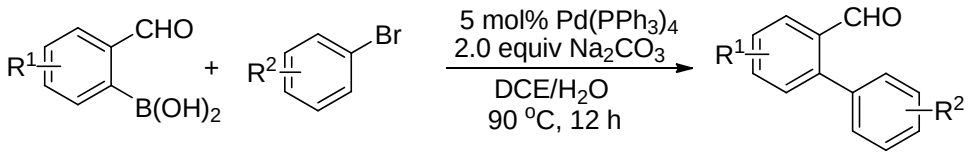


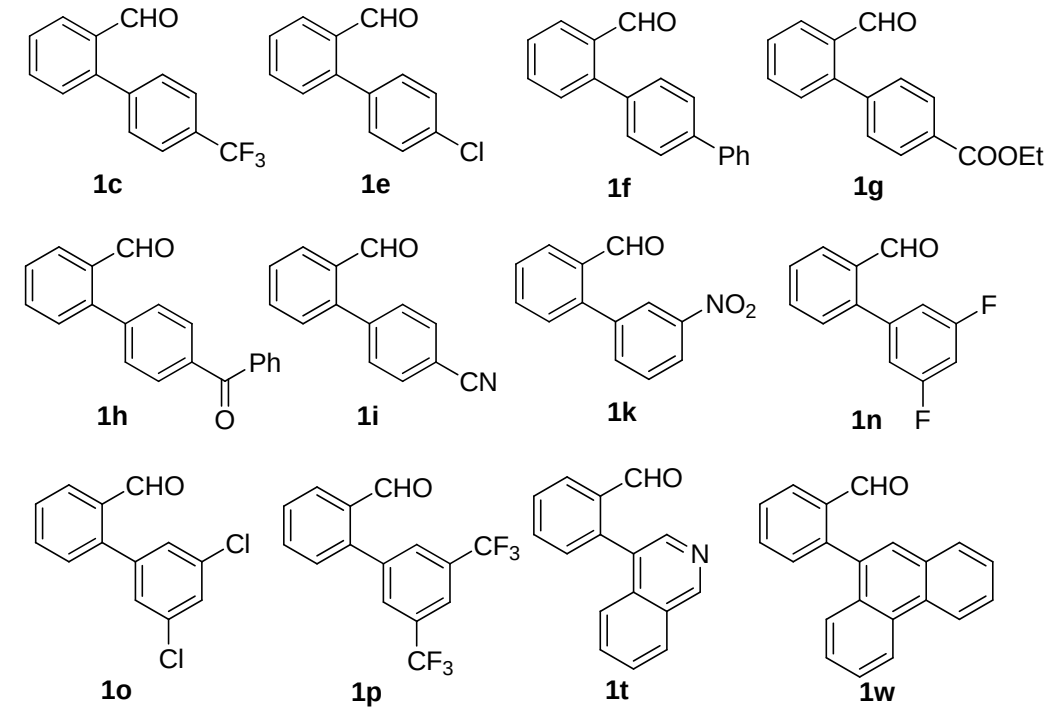




**1a** **1b** **1d** **1j** **1u**

Representative Procedure for Method A. Synthesis of **1a**: To 80 mL of a 2:1 DMF/$H_2O$ solution containing 2-bromobenzaldehyde (7.36 g, 40 mmol, 1.0 equiv), and $Na_2CO_3$ (4.24 g, 40 mmol, 1.0 equiv) were added phenylboronic acid (4.88 g, 40 mmol, 1.0 equiv) and the reaction mixture was stirred for 2 min. $Pd(OAc)_2$ (448 mg, 2 mmol, 0.05 equiv) was then added and the flask was flushed with Ar, sealed and allowed to stir at 25 $^oC$ for 12 h. The reaction mixture was extracted with ethyl ether (2 x 10 mL). The combined ether layers were dried over anhydrous $Na_2SO_4$ and concentrated under vacuum to yield the crude product, which was purified by flash chromatography on silica gel using ethyl acetate/*n*-penta = 1 : 30 as eluent affording **1a** 6.4g (88%). **1b**, **1d**, **1j** and **1u** were also produced according to this method.

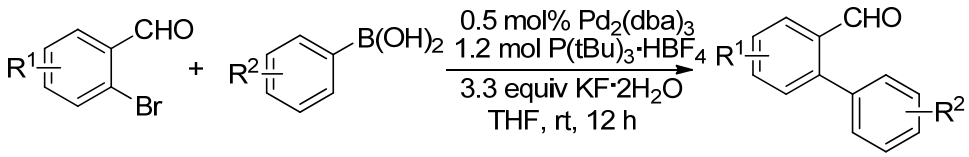
## Method B:[2]

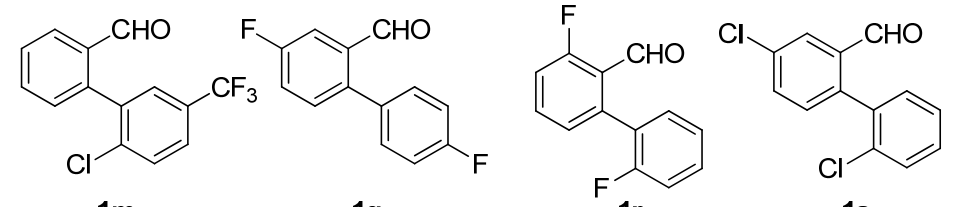



Representative Procedure for Method B. Synthesis of **1c**: To a solution of 2-formylbenzeneboronic acid (225 mg, 1.5 mmol, 1.5 equiv), 1-bromo-4-(trifluoromethyl)benzene (281 μL, 1.0 mmol, 1.0 equiv) and $Pd(PPh_3)_4$ (86 mg, 0.05 mmol, 0.05 equiv) in DME (6 mL) under Ar, followed by a solution of $Na_2CO_3$ (10%, l mL). The resulting heterogeneous mixture is refluxed 12h, before it is diluted with diethyl ether (30 ml). The organic layer is separated, washed with brine, dried over $Na_2SO_4$, and evaporated. Chromatographic purification of the crude product (*n*-penta/ethyl acetate = 40/1) affords the **1c** as a solid (225 mg, 90%). **1e**, **1f**, **1g, 1h**, **1i**, **1k, 1n**, **1o**, **1p, 1t** and **1w** were also produced according to this method.

## Method C:[3]



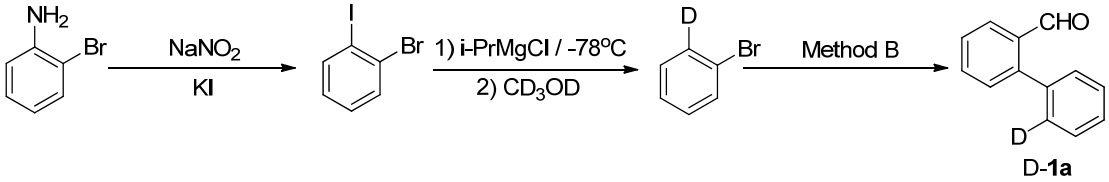




**1m** **1q** **1r** **1s**

Representative Procedure for Method C. Synthesis of **1m**: 2-formylbenzeneboronic acid (165.0 mg, 1.1 mmol, 1.1 equiv), $KF{\cdot}2H_2O$ (310.0 mg, 3.3 mmol, 3.3 equiv), $Pd_2(dba)_3$ (8.0 mg, 0.005 mmol, 0.005 equiv) and $[HP(t\text{-}Bu)_3]BF_4$ (3.5 mg, 0.012 mmol, 0.012 equiv) were added to a 25-mL vial that contained a stir bar. The vial was purged with argon for 3 min, and then it was sealed with a septum cap. THF (2.0 mL) and the 2-bromo-1-chloro-4-(trifluoromethyl)-benzene (150 μL, 1.0 mmol, 1.0 equiv) were added, and the reaction mixture was stirred at rt for 12 h. Next, the mixture was concentrated, and the residue was purified by flash chromatography on silica gel (*n*-penta/ethyl acetate = 40/1) affords the **1m** as a solid (270 mg, 95%). **1q, 1r** and **1s** were also produced arrording to this method, which were difficult to be produced according to method A and B.

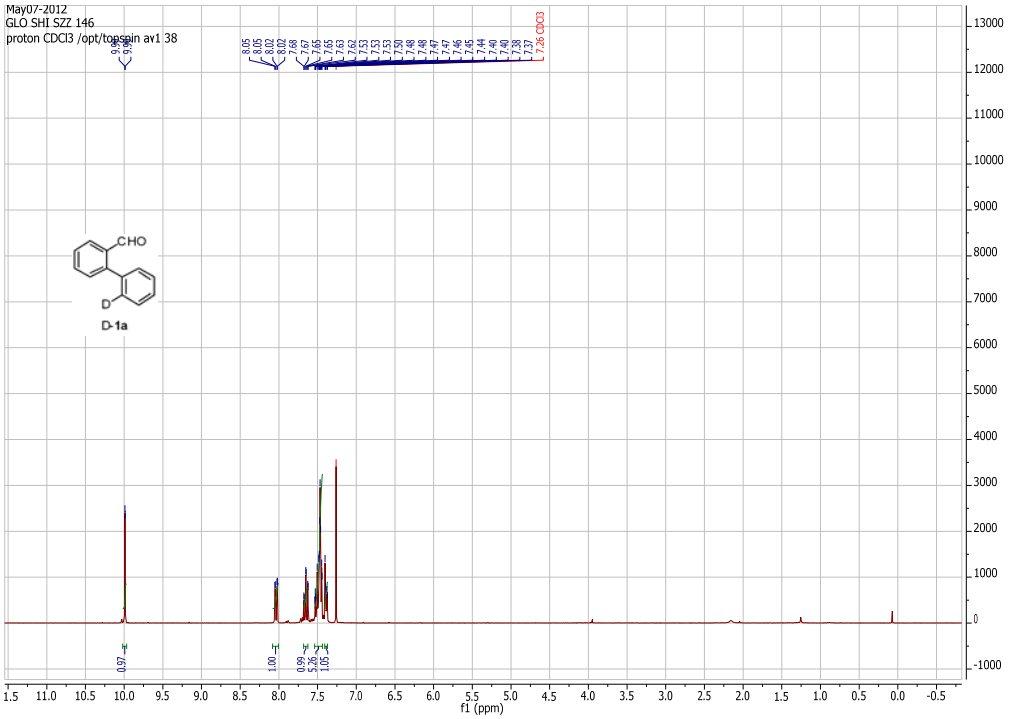
# 3. Mechanistic Studies

## Synthesis of compound D-1a

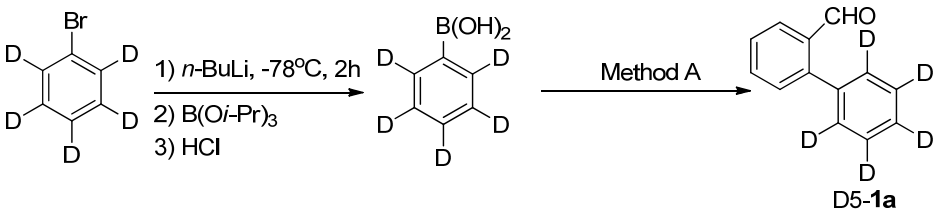



2-Deuterio bromobenzene was prepared following a procedure by Cheng et al.[6]

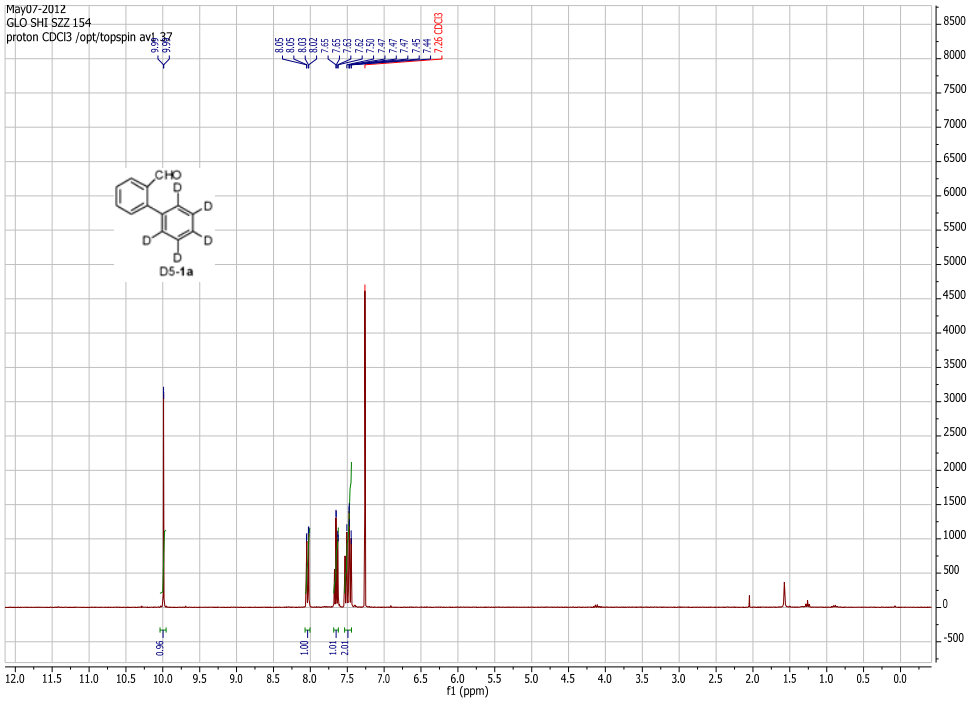
To a solution of 2-formylbenzeneboronic acid (225 mg, 1.5 mmol, 1.5 equiv), 2-deuterio bromobenzene (106 μL, 1.0 mmol, 1.0 equiv) and $Pd(PPh_3)_4$ (87 mg, 0.05 mmol, 0.05 equiv) in DME (6 mL) under Ar, followed by a solution of $Na_2CO_3$ (10%, l mL). The resulting heterogeneous mixture is refluxed 12h, before it is diluted with diethyl ether (30 ml). The organic layer is separated, washed with brine, dried over $Na_2SO_4$, and evaporated. Chromatographic purification of the crude product (*n*-penta/ethyl acetate = 30/1) affords the aldehyde D-**1a** as a colorless oil (0.15 g, 85%). The deuterium content of D-**1a** was observed to be more than 94% in $^1H$ NMR.



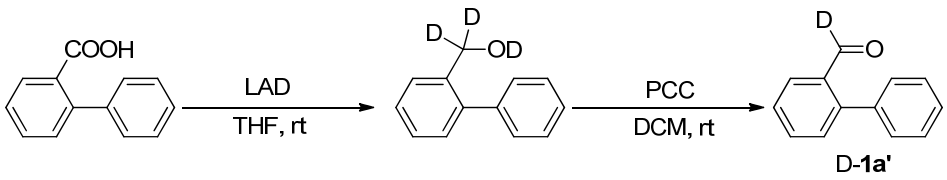
**Synthesis of compound D5-1a**




(D5-phenyl)boronic acid was prepared following a procedure by Cheng et al.[6] To 5 mL of a 2:1 DMF/$H_2O$ solution containing 2.0 mmol of 2-bromobenzaldehyde and 2.0 mmol of $Na_2CO_3$ were added 2.2 mmol of (D5-phenyl)boronic acid and the reaction mixture was stirred for 2 min. $Pd(OAc)_2$ (5 mol %) was then added and the flask was flushed with Ar, sealed and allowed to stir at 25 °C for 12 h. The reaction mixture was extracted with ethyl ether (2 x 10 mL). The combined ether layers were dried over anhydrous $Na_2SO_4$ and concentrated under vacuum to yield the crude product. Chromatographic purification of the crude product (*n*-penta/ethyl acetate = 30/1) affords the aldehyde D5-**1a** as a colorless oil (0.37 g, 80%). The deuterium content of D5-**1a** was observed to be more than 98% in $^1$H NMR.

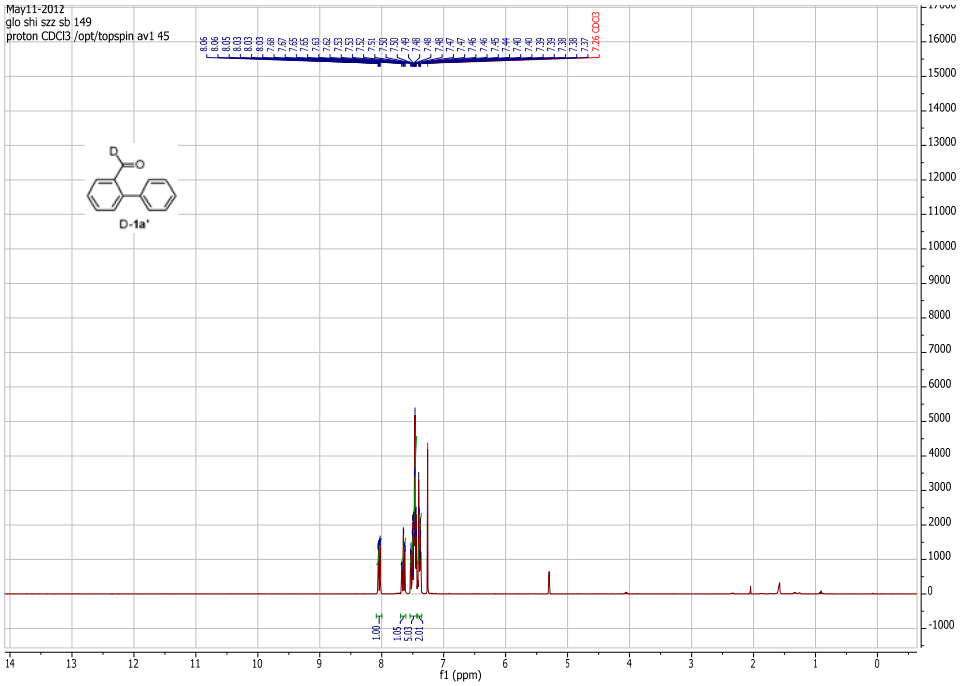


**Synthesis of compound D-1a'**:

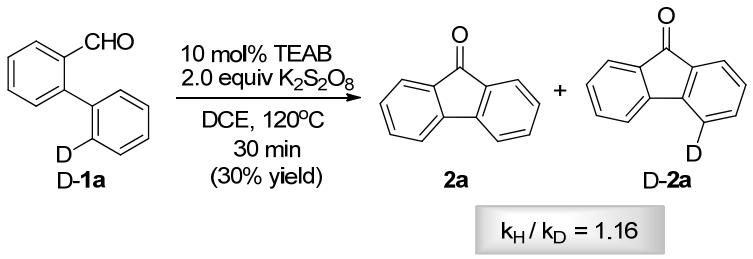



Following a modified procedure by Dong,[7] a suspension of lithium aluminum deuteride (168 mg, 4 mmol, 2.0 eq.) in 8 mL THF was cooled to 0 °C and a solution of 2-phenylbenzoic acid (396 mg, 2 mmol, 1.0 eq.) in 4 mL THF was added dropwise. The reaction was warmed to rt, stirred for 1 h and then quenched with EtOAc. 1 M HCl (30 mL) was added and the resulting mixture was extracted with EtOAc (3 x 10 mL). The combined organic layers were dried over $Na_2SO_4$ and then concentrated to give the crude deuterium alcohol product without further purifuction.

To a solution of Celite 860 mg, PCC (860 mg, 4.0 mmol, 2.0 equiv) in DCM (12 mL) under Ar at 0°C over a period of 15 min. solution of the above deuterium alcohol product (2 mmol) in 3 mL DCM was added dropwise over 10 min and the reaction was allowed to warm up to room temperature over night. Chromatographic purification of the crude product (*n*-penta/ethyl acetate = 30/1) affords the aldehyde D-**1a'** as a colorless oil (0.26 g, 71%). The deuterium content of D-**1a'** was observed to be more than 99% in $^1$H NMR.

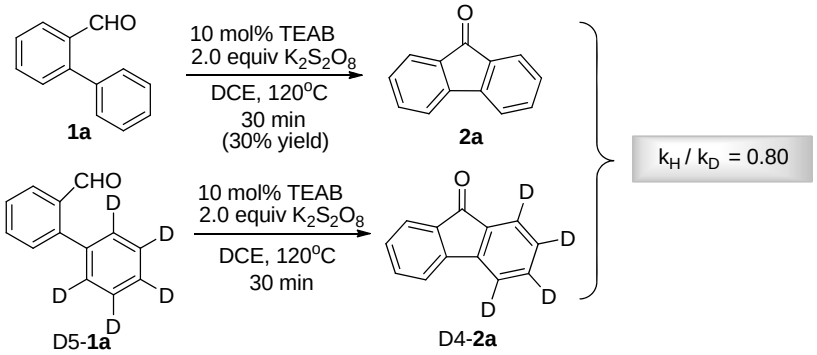


**Intramolecular Kinetic Isotope Effect of D-1a:**




To a 10 mL Schlenk tube was added TEAB (4.2 mg, 10 mol %), $K_2S_2O_8$ (108 mg, 2.0 equiv) and the tube was purged with Ar for three times, followed by addition of D-**1a** (36.6 mg, 0.20 mmol ) and DCE (1.0 mL). The formed mixture was stirred at 120 ºC under Ar for 30 min. At the end of the reaction, the mixture was diluted with EA (10 mL). The solvent was concentrated and the residue was purified on a silica gel column using EtOAc/*n*-Penta as eluent to afford product mixture **2a** + D-**2a** in 30% yield. The intramolecular kinetic isotopic effect $k_H/k_D$ = 1.16 was determined by HRMS.

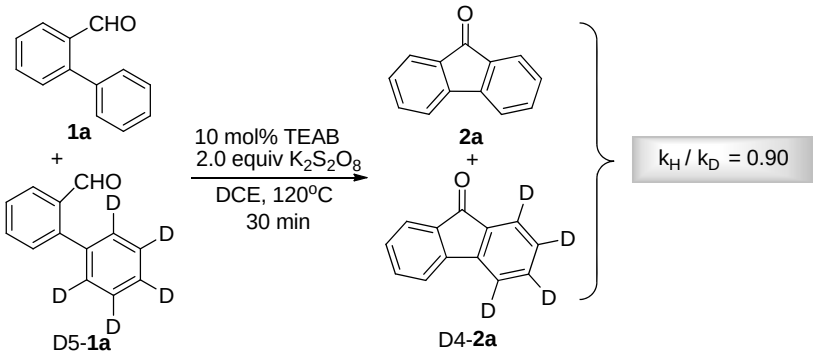
**The Kinetic Isotope Effect of Intermolecular Parallel Experiments Between 1a and D5-1a:**




To two 10 mL Schlenk tubes, were added TEAB (4.2 mg, 10 mol %), $K_2S_2O_8$ (108 mg, 2.0 equiv) and the tubes were purged with Ar for three times, separately. One tube was added **1a** (36.4 mg, 0.20 mmol ) + DCE (1.0 mL) and another one was added D5-**1a** (37.4 mg, 0.20 mmol ) + DCE (1.0 mL). Then they were stirred at 120 ºC under Ar for 30 min. At the end of the reaction, the mixtures of these two tubes were combined, then diluted with EA (20 mL). The solvent was concentrated and the residue was purified on a silica gel column using EtOAc/*n*-Penta as eluent to afford

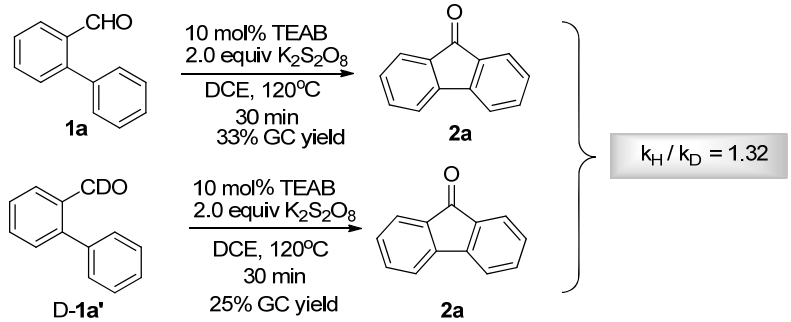
product mixture **2a** + D4-**2a**. The intermolecular kinetic isotopic effect $k_H/k_D$ = 0.80 was determined by HRMS.

**The Kinetic Isotope Effect of Intermolecular Competition Experiments Between 1a and D5-1a:**




To a 10 mL Schlenk tube was added TEAB (8.4 mg, 10 mol %), $K_2S_2O_8$ (216 mg, 4.0 equiv) and the tube was purged with Ar for three times, followed by addition of **1a** (36.4 mg, 0.20 mmol) and D5-**1a** (37.4 mg, 0.20 mmol) and DCE (2.0 mL). The formed mixture was stirred at 120 ºC under Ar for 30 min. At the end of the reaction, the mixture was diluted with EA (10 mL). The solvent was concentrated and the residue was purified on a silica gel column using EtOAc/*n*-Penta as eluent to afford product mixture **2a** + D4-**2a**. The intramolecular kinetic isotopic effect $k_H/k_D$ = 0.90 was determined by HRMS.

**The Kinetic Isotope Effect of Intermolecular Parallel Experiments Between 1a and D-1a':**

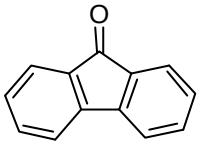



To two 10 mL Schlenk tubes, were added TEAB (8.4 mg, 10 mol %), $K_2S_2O_8$ (216 mg, 2.0 equiv) and the tubes were purged with Ar for three times, separately. One tube was added **1a** (72.8 mg, 0.40 mmol) + DCE (2.0 mL) and another one was added D-**1a'** (73.2 mg, 0.40 mmol) + DCE (2.0 mL). Then they were stirred at 120 ºC

under Ar for 30 min. At the end of the reaction, diphenyl ether 40 μL were added separately to two tubes as a standard compound. The intermolecular kinetic isotopic effect $k_H/k_D$ = 1.32 was determined by GC.

## 4. Experimental Procedures and Characterization of Products

### 9*H*-fluoren-9-one (2a)

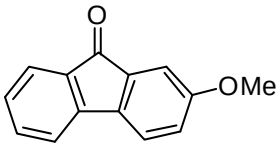


**2a**

**Typical procedure:** To a 10 mL Schlenk tube was added TEAB (4.2 mg, 10 mol %), $K_2S_2O_8$ (108 mg, 2.0 equiv) and the tube was purged with Ar for three times, followed by addition of **1a** (32.0 μL, 0.20 mmol) and DCE (1.0 mL). The formed mixture was stirred at 120 ºC under Ar for 36 h. The solution was then cooled to rt, and DCE was removed under vaccum directly. The crude product was purified by column chromatography on silica gel (eluent: *n*-penta / ethyl acetate = 30 : 1) to afford 25.0 mg (68%) of **2a**. $^1$H NMR (300 MHz, $CDCl_3$) δ 7.66 (dt, *J* = 7.3, 0.9 Hz, 1H), 7.57 – 7.43 (m, 2H), 7.34 – 7.26 (m, 1H). $^{13}$C NMR (75 MHz, $CDCl_3$) δ 193.91, 144.40, 134.66, 134.12, 129.05, 124.30, 120.28. HRMS m/z (ESI) calcd for $C_{13}H_8ONa$ $(M + Na)^+$ 203.0473, found 203.0467.

Gram scale synthesis of **2a** : To a 100 mL Schlenk tube was added TEAB (0.21 g, 10 mol %), $K_2S_2O_8$ (5.4 g, 2.0 equiv) and the tube was purged with Ar for three times, followed by addition of **1a** (1.82 g, 10 mmol ) and DCE (50 mL). The formed mixture was stirred at 120 ºC under Ar for 36 h. The solution was then cooled to rt, and DCE was removed under vaccum directly. The crude product was purified by column chromatography on silica gel (eluent: *n*-penta / ethyl acetate = 30 : 1) to afford 1.17 g (65%) of **2a**.

### 2-Methoxy-9*H*-fluoren-9-one (2b)

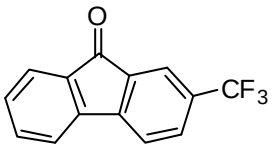


**2b**

The reaction of **1b** (42.4 mg, 0.20 mmol), TEAB (4.2 mg, 10 mol %), $K_2S_2O_8$ (108.0 mg, 2.0 equiv) in DCE (1.0 mL) under Ar afforded 16.8 mg (40%) of **2b**: $^1$H NMR (300 MHz, $CDCl_3$) δ 7.63 – 7.56 (m, 1H), 7.48 – 7.35 (m, 3H), 7.26 – 7.13 (m, 2H), 6.97 (dd, *J* = 8.2, 2.5 Hz, 1H), 3.85 (s, 3H). $^{13}$C NMR (75 MHz, $CDCl_3$) δ 193.85, 160.78, 144.84, 136.95, 135.85, 134.83, 134.25, 127.84, 124.29, 121.31,

120.25, 119.54, 109.32, 55.70. HRMS m/z (ESI) calcd for $C_{14}H_{10}O_2Na$ $(M + Na)^+$ 233.0578, found 233.0573.

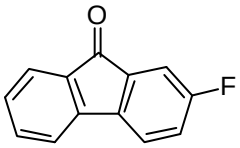
**2-(Trifluoromethyl)-9*H*-fluoren-9-one (2c)**



**2c**

The reaction of **1c** (50.0 mg, 0.20 mmol), TEAB (4.2 mg, 10 mol %), $K_2S_2O_8$ (108.0 mg, 2.0 equiv) in DCE (1.0 mL) under Ar afforded 37.5 mg (76%) of **2c**: $^1$H NMR (300 MHz, $CDCl_3$) δ 7.93 – 7.87 (m, 1H), 7.78 – 7.70 (m, 2H), 7.66 – 7.53 (m, 3H), 7.38 (td, *J* = 7.3, 1.4 Hz, 1H). $^{13}$C NMR (75 MHz, $CDCl_3$) δ 192.16, 147.40, 143.03, 135.12, 134.46, 134.28, 131.62 (q, *J* = 4.0 Hz), 130.22, 124.76, 123.64 (q, *J* = 270.8 Hz), 121.26 (q, *J* = 3.8 Hz), 121.10, 120.48. HRMS m/z (ESI) calcd for $C_{14}H_7F_3ONa$ $(M + Na)^+$ 271.0347, found 271.0341.

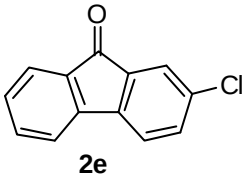
**2-Fluoro-9*H*-fluoren-9-one (2d)**



**2d**

The reaction of **1d** (40.0 mg, 0.20 mmol), TEAB (4.2 mg, 10 mol %), $K_2S_2O_8$ (108.0 mg, 2.0 equiv) in DCE (1.0 mL) under Ar afforded 29.0 mg (73%) of **2d**: $^1$H NMR (400 MHz, $CDCl_3$) δ 7.65 (d, *J* = 7.3 Hz, 1H), 7.54 – 7.45 (m, 3H), 7.33 (dd, *J* = 7.3, 2.4 Hz, 1H), 7.31 – 7.26 (m, 1H), 7.20 – 7.13 (m, 1H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 192.49, 163.52 (d, *J* = 251.5 Hz), 143.90, 140.15, 136.29 (d, *J* = 7.1 Hz) , 135.03, 134.31, 128.73, 124.60, 121.59 (d, *J* = 8.1 Hz), 120.84 (d, *J* = 24.2 Hz), 120.11, 111.94 (d, *J* = 23.2 Hz). HRMS m/z (ESI) calcd for $C_{13}H_7FONa$ $(M + Na)^+$ 221.0379, found 221.0373.

**2-Chloro-9*H*-fluoren-9-one (2e).**

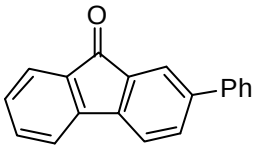


**2e**

The reaction of **1e** (43.2 mg, 0.20 mmol), TEAB (4.2 mg, 10 mol %), $K_2S_2O_8$ (108.0 mg, 2.0 equiv) in DCE (1.0 mL) under Ar afforded 34.8 mg (81%) of **2e**: $^1$H NMR (400 MHz, $CDCl_3$) δ 7.65 (dt, *J* = 7.4, 0.8 Hz, 1H), 7.60 (t, *J* = 1.2 Hz, 1H), 7.53 – 7.47 (m, 2H), 7.44 (d, *J* = 1.2 Hz, 2H), 7.31 (ddd, *J* = 7.4, 5.1, 3.4 Hz, 1H). $^{13}$C NMR

(101 MHz, $CDCl_3$) δ 192.44, 143.63, 142.53, 135.61, 135.05, 135.01, 134.15, 133.90, 129.27, 124.65, 124.60, 121.35, 120.40. HRMS m/z (ESI) calcd for $C_{13}H_7ClONa$ $(M + Na)^+$ 237.0083, found 237.0078.

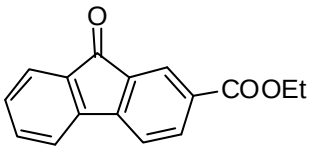
**2-Phenyl-9*H*-fluoren-9-one (2f)**



**2f**

The reaction of **1f** (51.6 mg, 0.20 mmol), TEAB (4.2 mg, 10 mol %), $K_2S_2O_8$ (108.0 mg, 2.0 equiv) in DCE (1.0 mL) under Ar afforded 34.0 mg (66%) of **2f**: $^1H$ NMR (400 MHz, $CDCl_3$) δ 7.91 (d, $J$ = 1.7 Hz, 1H), 7.76 – 7.66 (m, 2H), 7.66 – 7.43 (m, 7H), 7.41 – 7.36 (m, 1H), 7.30 (td, $J$ = 7.3, 1.2 Hz, 1H). $^{13}C$ NMR (101 MHz, $CDCl_3$) δ 193.82, 144.27, 143.20, 142.28, 139.82, 134.87, 134.79, 134.45, 133.18, 129.00, 128.92, 127.90, 126.78, 124.39, 122.97, 120.67, 120.37. HRMS m/z (ESI) calcd for $C_{19}H_{12}ONa$ $(M + Na)^+$ 279.0786, found 279.0780.

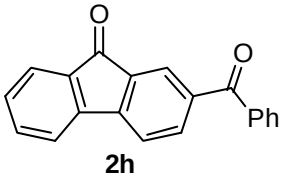
**Ethyl 9-oxo-9*H*-fluorene-2-carboxylate (2g)**



**2g**

The reaction of **1g** (50.8 mg, 0.20 mmol), TEAB (4.2 mg, 10 mol %), $K_2S_2O_8$ (108.0 mg, 2.0 equiv) in DCE (1.0 mL) under Ar afforded 32.1 mg (64%) of **2g**: $^1H$ NMR (300 MHz, $CDCl_3$) δ 8.30 (d, $J$ = 1.0 Hz, 1H), 8.21 (dd, $J$ = 7.8, 1.6 Hz, 1H), 7.70 (d, $J$ = 7.3 Hz, 1H), 7.59 (d, $J$ = 7.8 Hz, 2H), 7.54 (td, $J$ = 7.4, 1.1 Hz, 1H), 7.38 (dd, $J$ = 7.3, 1.2 Hz, 1H), 4.39 (q, $J$ = 7.1 Hz, 2H), 1.41 (t, $J$ = 7.1 Hz, 3H). $^{13}C$ NMR (75 MHz, $CDCl_3$) δ 192.74, 165.52, 148.23, 143.32, 136.30, 134.93, 134.72, 134.12, 131.35, 130.08, 125.25, 124.57, 121.14, 120.12, 61.35, 14.30. HRMS m/z (ESI) calcd for $C_{16}H_{12}O_3Na$ $(M + Na)^+$ 275.0684, found 275.0679.

**2-Benzoyl-9*H*-fluoren-9-one (2h)**

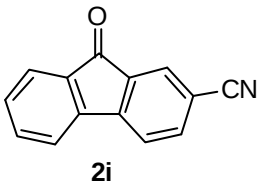


**2h**

The reaction of **1h** (57.2 mg, 0.20 mmol), TEAB (4.2 mg, 10 mol %), $K_2S_2O_8$ (108.0 mg, 2.0 equiv) in DCE (1.0 mL) under Ar afforded 34.5 mg (61%) of **2h**: $^1H$ NMR (400 MHz,

$CDCl_3$) δ 8.09 – 8.02 (m, 2H), 7.82 – 7.77 (m, 2H), 7.72 (dt, *J* = 7.4, 0.9 Hz, 1H), 7.68 – 7.49 (m, 6H), 7.39 (td, *J* = 7.4, 1.0 Hz, 1H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 195.23, 192.68, 147.91, 143.31, 138.36, 137.13, 136.73, 135.01, 134.78, 133.89, 132.72, 130.16, 129.82, 128.51, 125.80, 124.63, 121.21, 120.29. HRMS m/z (ESI) calcd for $C_{20}H_{12}O_2Na$ $(M + Na)^+$ 307.0735, found 307.0730.

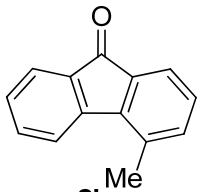
**2-Cyano-9*H*-fluoren-9-one (2i)**



**2i**

The reaction of **1i** (41.4 mg, 0.20 mmol), TEAB (4.2 mg, 10 mol %), $K_2S_2O_8$ (108.0 mg, 2.0 equiv) in DCE (1.0 mL) under Ar afforded 24.2 mg (59%) of **2i**: $^1$H NMR (300 MHz, $CDCl_3$) δ 7.90 (dd, *J* = 1.4, 0.6 Hz, 1H), 7.80 (dd, *J* = 7.7, 1.5 Hz, 1H), 7.76 – 7.71 (m, 1H), 7.68 – 7.55 (m, 3H), 7.42 (td, *J* = 7.2, 1.6 Hz, 1H). $^{13}$C NMR (75 MHz, $CDCl_3$) δ 191.36, 148.00, 142.67, 138.49, 135.34, 134.48, 134.12, 130.79, 127.47, 124.95, 121.47, 120.90, 118.09, 112.59. HRMS m/z (ESI) calcd for $C_{14}H_7NONa$ $(M + Na)^+$ 228.0425, found 228.0420.

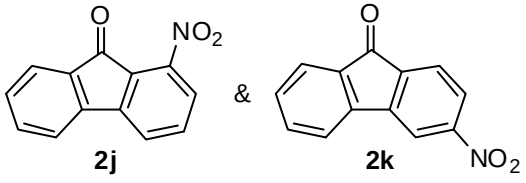
**4-Methyl-9*H*-fluoren-9-one (2j)**



**2j**

The reaction of **1j** (39.2 mg, 0.20 mmol), TEAB (4.2 mg, 10 mol %), $K_2S_2O_8$ (108.0 mg, 2.0 equiv) in DCE (1.0 mL) under Ar afforded 21.0 mg (54%) of **2j**: $^1$H NMR (300 MHz, $CDCl_3$) δ 7.68 (d, *J* = 7.3 Hz, 1H), 7.62 (d, *J* = 7.6 Hz, 1H), 7.57 – 7.45 (m, 2H), 7.33 – 7.24 (m, 2H), 7.18 (t, *J* = 7.4 Hz, 1H), 2.59 (s, 3H). $^{13}$C NMR (75 MHz, $CDCl_3$) δ 194.24, 145.28, 142.13, 137.37, 134.61, 134.48, 134.41, 133.59, 128.74, 128.37, 124.24, 123.33, 121.93, 20.22. HRMS m/z (ESI) calcd for $C_{14}H_{10}ONa$ $(M + Na)^+$ 217.0629, found 217.0624.

**1-Nitro-9*H*-fluoren-9-one (2j) & 3-Nitro-9*H*-fluoren-9-one (2k)**

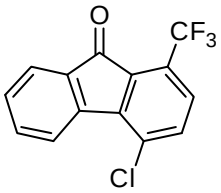


**2j** **2k**

The reaction of **1j** (41.4 mg, 0.20 mmol), TEAB (4.2 mg, 10 mol %), $K_2S_2O_8$

(108.0 mg, 2.0 equiv) in DCE (1.0 mL) under Ar afforded 15.0 mg (36%) of **2j** and 12.5 mg of **2k** (28%), which can be separated easily by column chromatography. **2j**: $^{1}$H NMR (300 MHz, $CDCl_3$) δ 7.79 – 7.52 (m, 6H), 7.39 (ddd, *J* = 7.3, 6.8, 1.8 Hz, 1H). $^{13}$C NMR (75 MHz, $CDCl_3$) δ 187.47, 152.73, 146.26, 142.10, 135.53, 135.26, 133.30, 130.48, 125.25, 124.93, 123.63, 123.10, 120.75. HRMS m/z (ESI) calcd for $C_{13}H_7NO_3Na$ $(M + Na)^+$ 248.0324, found 248.0318. **2k**: $^{1}$H NMR (300 MHz, $CDCl_3$) δ 8.34 (d, *J* = 1.6 Hz, 1H), 8.19 (dd, *J* = 8.0, 1.9 Hz, 1H), 7.81 (d, *J* = 8.0 Hz, 1H), 7.75 (d, *J* = 7.4 Hz, 1H), 7.69 – 7.57 (m, 2H), 7.42 (td, *J* = 7.3, 1.3 Hz, 1H). $^{13}$C NMR (75 MHz, $CDCl_3$) δ 188.64, 152.10, 145.69, 142.44, 138.34, 135.70, 134.07, 130.51, 125.01, 124.77, 124.71, 121.22, 115.33. HRMS m/z (ESI) calcd for $C_{13}H_7NO_3Na$ $(M + Na)^+$ 248.0324, found 248.0318.

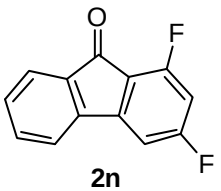
**4-Chloro-1-(trifluoromethyl)-9*H*-fluoren-9-one (2m)**



**2m**

The reaction of **1m** (56.8 mg, 0.20 mmol), TEAB (4.2 mg, 10 mol %), $K_2S_2O_8$ (108.0 mg, 2.0 equiv) in DCE (1.0 mL) under Ar afforded 31.0 mg (55%) of **2m**. $^{1}$H NMR (300 MHz, $CDCl_3$) δ 8.24 (d, *J* = 7.7 Hz, 1H), 7.74 (d, *J* = 7.4 Hz, 1H), 7.61 – 7.48 (m, 3H), 7.41 (td, *J* = 7.5, 0.9 Hz, 1H). $^{13}$C NMR (75 MHz, $CDCl_3$) δ 190.84, 142.59, 141.64, 135.90, 135.19, 133.28, 130.29, 126.90 (q, *J* = 5.8 Hz), 126.30 (q, *J* = 35.2 Hz), 124.89, 124.26, 122.14 (q, *J* = 272.2 Hz), 109.99. HRMS m/z (ESI) calcd for $C_{16}H_6ClF_3ONa$ $(M + Na)^+$ 304.9957, found 304.9951.

**1, 3-Difluoro-9H-fluoren-9-one (2n)**

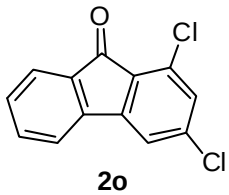


**2n**

The reaction of **1n** (43.6 mg, 0.20 mmol), TEAB (4.2 mg, 10 mol %), $K_2S_2O_8$ (108.0 mg, 2.0 equiv) in DCE (1.0 mL) under Ar afforded 30.2 mg (70%) of **2n**. $^{1}$H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, *J* = 7.4 Hz, 1H), 7.56 – 7.50 (m, 2H), 7.41 – 7.35 (m, 1H), 7.06 (dd, *J* = 7.6, 1.9 Hz, 1H), 6.66 (td, *J* = 9.1, 2.0 Hz, 1H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 188.60, 167.91 (dd, *J* = 260.6, 11.1 Hz), 159.88 (dd, *J* = 266.6, 14.1 Hz), 148.34 (q, *J* = 5.7 Hz), 141.95, 134.64, 134.43, 130.41, 124.46, 120.81, 116.54

(dd, $J$ = 13.1, 3.5 Hz), 105.03 (dd, $J$ = 24.2, 2.5 Hz), 104.66. HRMS m/z (ESI) calcd for $C_{13}H_6F_2ONa$ $(M + Na)^+$ 239.0284, found 239.0279.

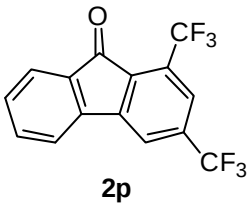
**1, 3-Dichloro-9*H*-fluoren-9-one (2o)**



**2o**

The reaction of **1o** (50.0 mg, 0.20 mmol), TEAB (4.2 mg, 10 mol %), $K_2S_2O_8$ (108.0 mg, 2.0 equiv) in DCE (1.0 mL) under Ar afforded 42.7 mg (86%) of **2o**. $^1$H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, $J$ = 7.4 Hz, 1H), 7.60 – 7.52 (m, 2H), 7.42 (ddd, $J$ = 14.0, 6.2, 1.7 Hz, 2H), 7.28 (d, $J$ = 14.2 Hz, 1H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 189.51, 147.59, 141.37, 141.03, 134.82, 134.15, 133.32, 130.34, 127.91, 124.66, 120.64, 119.49. HRMS m/z (ESI) calcd for $C_{13}H_6Cl_2ONa$ $(M + Na)^+$ 270.9693, found 270.9688.

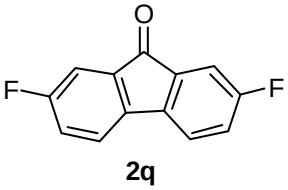
**1, 3-Bis(trifluoromethyl)-9*H*-fluoren-9-one (2p)**



**2p**

The reaction of **1p** (63.6 mg, 0.20 mmol), TEAB (4.2 mg, 10 mol %), $K_2S_2O_8$ (108.0 mg, 2.0 equiv) in DCE (1.0 mL) under Ar afforded 59.0 mg (92%) of **2p**. $^1$H NMR (400 MHz, $CDCl_3$) δ 7.95 (s, 1H), 7.81 (s, 1H), 7.74 (d, $J$ = 7.4 Hz, 1H), 7.66 – 7.56 (m, 2H), 7.43 (td, $J$ = 7.3, 1.3 Hz, 1H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 188.41, 147.31, 141.62, 136.16 (q, J = 33.7 Hz), 135.55, 133.55, 133.23, 130.92, 128.58 (q, $J$ = 36.0 Hz), 125.28, 123.30 (q, $J$ = 3.0 Hz), 122.80 (q, $J$ = 274.4 Hz), 121.75 (q, $J$ = 275.4 Hz), 120.81, 120.30 (q, $J$ = 3.3 Hz). HRMS m/z (ESI) calcd for $C_{15}H_6F_6ONa$ $(M + Na)^+$ 339.0211, found 339.0215.

**2, 7-Difluoro-9*H*-fluoren-9-one (2q)**

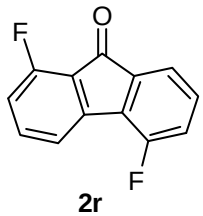


**2q**

The reaction of **1q** (43.6 mg, 0.20 mmol), TEAB (4.2 mg, 10 mol %), $K_2S_2O_8$ (108.0 mg, 2.0 equiv) in DCE (1.0 mL) under Ar afforded 23.8 mg (55%) of **2q**. $^1$H NMR (300 MHz, $CDCl_3$) δ 7.43 (dd, $J$ = 8.2, 4.3 Hz, 2H), 7.33 (dd, $J$ = 7.2, 2.4 Hz, 2H), 7.16 (td, $J$ = 8.8, 2.5 Hz, 2H). $^{13}$C NMR (75 MHz, $CDCl_3$) δ 191.09, 163.26 (dd, $J$ = 248.2, 1.1 Hz), 139.68-139.61 (m) 136.46-136.32 (m), 121.34, 121.24

(d, $J$ = 30.0 Hz), 112.25 (d, $J$ = 24.0 Hz). HRMS m/z (ESI) calcd for $C_{13}H_6F_2ONa$ $(M + Na)^+$ 239.0284, found 239.0279.

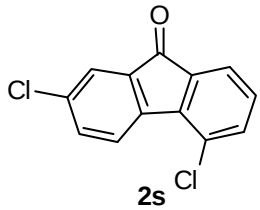
**1, 5-Difluoro-9*H*-fluoren-9-one (2r)**



**2r**

The reaction of **1r** (43.6 mg, 0.20 mmol), TEAB (4.2 mg, 10 mol %), $K_2S_2O_8$ (108.0 mg, 2.0 equiv) in DCE (1.0 mL) under Ar afforded 27.0 mg (63%) of **2r**. $^1$H NMR (300 MHz, $CDCl_3$) δ 7.51 (m, 3H), 7.32 (m, 1H), 7.25 – 7.17 (m, 1H), 7.03-6.92 (m, 1H). $^{13}$C NMR (75 MHz, $CDCl_3$) δ 188.88, 159.29 (d, $J$ = 262.5 Hz), 157.79 (d, $J$ = 253.5 Hz), 143.18 (q, $J$ = 2.0 Hz), 137.58 (d, $J$ = 8.2 Hz), 136.41 (d, $J$ = 3.0 Hz), 131.44 (d, $J$ = 6.8 Hz), 122.58 (d, $J$ = 3.0 Hz), 120.41 (d, $J$ = 3.0 Hz), 120.23 (q, $J$ = 2.8 Hz), 117.68 (d, $J$ = 21.0 Hz). HRMS m/z (ESI) calcd for $C_{13}H_6F_2ONa$ $(M + Na)^+$ 239.0284, found 239.0279.

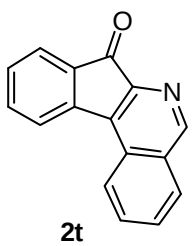
**2, 5-Dichloro-9*H*-fluoren-9-one (2s)**



**2s**

The reaction of **1s** (50.0 mg, 0.20 mmol), TEAB (4.2 mg, 10 mol %), $K_2S_2O_8$ (108.0 mg, 2.0 equiv) in DCE (1.0 mL) under Ar afforded 25.5 mg (51%) of **2s**. $^1$H NMR (300 MHz, $CDCl_3$) δ 8.09 (d, $J$ = 8.1 Hz, 1H), 7.65 (d, $J$ = 1.8 Hz, 1H), 7.59 (dd, $J$ = 7.2, 1.0 Hz, 1H), 7.53 – 7.42 (m, 2H), 7.25 (dd, $J$ = 8.1, 7.3 Hz, 1H). $^{13}$C NMR (75 MHz, $CDCl_3$) δ 191.16, 141.22, 139.98, 136.44, 136.07, 135.63, 135.52, 134.40, 130.23, 129.60, 125.04, 124.72, 122.85. HRMS m/z (ESI) calcd for $C_{13}H_6Cl_2ONa$ $(M + Na)^+$ 270.9693, found 270.9688.

**7*H*-Indeno[2,1-*c*]isoquinolin-7-one (2t)**

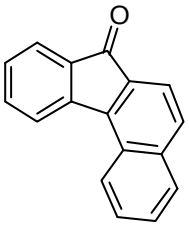


**2t**

The reaction of **1t** (46.6 mg, 0.20 mmol), TEAB (4.2 mg, 10 mol %), $K_2S_2O_8$ (108.0 mg, 2.0 equiv) in DCE (1.0 mL) under Ar afforded 16.0 mg (35%) of **2t**. $^1$H NMR (400 MHz, $CDCl_3$) δ 9.16 (s, 1H), 8.41 (d, $J$ = 8.4 Hz, 1H), 8.05 (d, $J$ = 8.2 Hz, 1H), 7.95 (d,

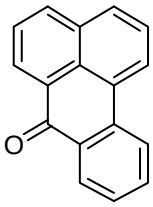
*J* = 7.5 Hz, 1H), 7.86 (ddd, *J* = 8.3, 7.0, 1.2 Hz, 1H), 7.77 – 7.71 (m, 2H), 7.56 (td, *J* = 7.6, 1.2 Hz, 1H), 7.40 – 7.34 (m, 1H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 193.00, 153.98, 146.26, 142.21, 136.88, 134.90, 132.58, 132.04, 131.06, 129.66, 129.56, 129.40, 124.40, 123.96, 123.59. HRMS m/z (ESI) calcd for $C_{16}H_9NONa$ $(M + Na)^+$ 254.0582, found 254.0576.

**7*H*-Benzo[*c*]fluoren-7-one (2u) & 7*H*-Benzo[*de*]anthracen-7-one (2v)**



**2u**

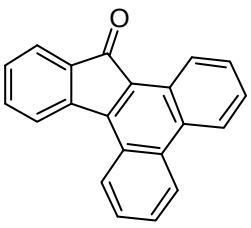
&



**2v**

The reaction of **1u** (46.4 mg, 0.20 mmol), TEAB (4.2 mg, 10 mol %), $K_2S_2O_8$ (108.0 mg, 2.0 equiv) in DCE (1.0 mL) under Ar afforded 26.7 mg (58%) of **2s** afforded 13.0 mg (29%) of **2u** and 13.7 mg of **2v** (29%), which can be separated easily by column chromatography. **2u**: $^1$H NMR (400 MHz, $CDCl_3$) δ 8.48 (d, *J* = 8.2 Hz, 1H), 8.01 (d, *J* = 7.6 Hz, 1H), 7.88 (d, *J* = 7.9 Hz, 1H), 7.76 (q, *J* = 8.2 Hz, 2H), 7.71 – 7.66 (m, 1H), 7.65 – 7.56 (m, 2H), 7.52 (td, *J* = 7.6, 1.3 Hz, 1H), 7.31 (t, *J* = 7.4 Hz, 1H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 194.45, 144.99, 142.85, 138.01, 134.52, 134.45, 131.82, 129.90, 129.63, 128.82, 128.70, 128.26, 127.73, 124.80, 124.03, 123.34, 119.86. HRMS m/z (ESI) calcd for $C_{17}H_{10}ONa$ $(M + Na)^+$ 253.0629, found 2530622. **2v**: $^1$H NMR (300 MHz, $CDCl_3$) δ 8.78 (dd, *J* = 7.3, 1.3 Hz, 1H), 8.52 (dd, *J* = 7.9, 1.2 Hz, 1H), 8.48 (d, *J* = 6.8 Hz, 1H), 8.36 (d, *J* = 8.1 Hz, 1H), 8.23 (dd, *J* = 8.1, 1.1 Hz, 1H), 8.02 (d, *J* = 8.2 Hz, 1H), 7.82 – 7.67 (m, 3H), 7.56 (td, *J* = 7.7, 1.1 Hz, 1H). $^{13}$C NMR (75 MHz, $CDCl_3$) δ 183.89, 136.19, 135.14, 134.64, 133.37, 132.99, 131.14, 130.21, 129.82, 128.30, 128.14, 126.61, 126.56, 124.16, 123.05. HRMS m/z (ESI) calcd for $C_{17}H_{10}ONa$ $(M + Na)^+$ 253.0629, found 2530624.

**13*H*-Indeno[1,2-*l*]phenanthren-13-one (2w)**

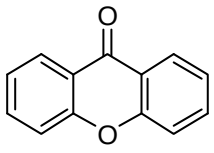


**2w**

The reaction of **1w** (56.4 mg, 0.20 mmol), TEAB (4.2 mg, 10 mol %), $K_2S_2O_8$ (108.0 mg, 2.0 equiv) in DCE (1.0 mL) under Ar afforded 34.7 mg (62%) of **2w**. $^1$H NMR (400 MHz, $CDCl_3$) δ 9.28 – 9.21 (m, 1H), 8.76 – 8.71 (m, 1H), 8.67 – 8.59 (m, 2H),

8.05 (d, *J* = 7.6 Hz, 1H), 7.81 – 7.62 (m, 5H), 7.50 (td, *J* = 7.6, 1.3 Hz, 1H), 7.35 – 7.30 (m, 1H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 195.92, 144.69, 143.85, 134.62, 134.36, 133.97, 131.00, 129.23, 128.87, 128.41, 127.62, 127.40, 127.21, 126.08, 125.73, 125.28, 123.91, 123.52, 123.34, 122.65. HRMS m/z (ESI) calcd for $C_{21}H_{12}ONa$ $(M + Na)^+$ 303.0786, found 303.0780.

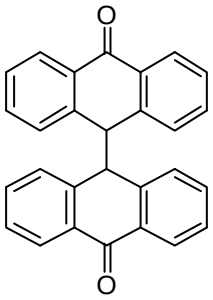
**9*H*-Xanthen-9-one (3)**



**4**

The reaction of **3** (39.6 mg, 0.20 mmol), TEAB (4.2 mg, 10 mol %), $K_2S_2O_8$ (108.0 mg, 2.0 equiv) in DCE (1.0 mL) under Ar afforded 20.2 mg (52%) of **4**. $^1$H NMR (400 MHz, $CDCl_3$) δ 8.35 (dd, *J* = 8.0, 1.6 Hz, 2H), 7.73 (ddd, *J* = 8.7, 7.1, 1.7 Hz, 2H), 7.57 – 7.48 (m, 2H), 7.39 (ddd, *J* = 8.0, 7.3, 1.0 Hz, 2H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 156.17, 134.81, 126.73, 123.90, 121.85, 117.97. HRMS m/z (ESI) calcd for $C_{13}H_8O_2Na$ $(M + Na)^+$ 219.0422, found 219.0420.

**[9, 9'-Bianthracene]-10, 10'(9*H*, 9'*H*)-dione (6)**



**6**

The reaction of **5** (39.2 mg, 0.20 mmol), TEAB (4.2 mg, 10 mol %), $K_2S_2O_8$ (108.0 mg, 2.0 equiv) in DCE (1.0 mL) under Ar afforded 19.5 mg (51%) of **6**. $^1$H NMR (300 MHz, $CDCl_3$) δ 8.01 – 7.88 (m, 4H), 7.46 – 7.36 (m, 8H), 6.86 (dt, *J* = 5.3, 3.2 Hz, 4H), 4.77 (s, 2H). $^{13}$C NMR (75 MHz, $CDCl_3$) δ 182.96, 139.81, 133.72, 132.13, 128.45, 127.88, 126.59, 54.30. HRMS m/z (ESI) calcd for $C_{28}H_{18}O_2Na$ $(M + Na)^+$ 409.1204, found 409.1201.

## 5. References

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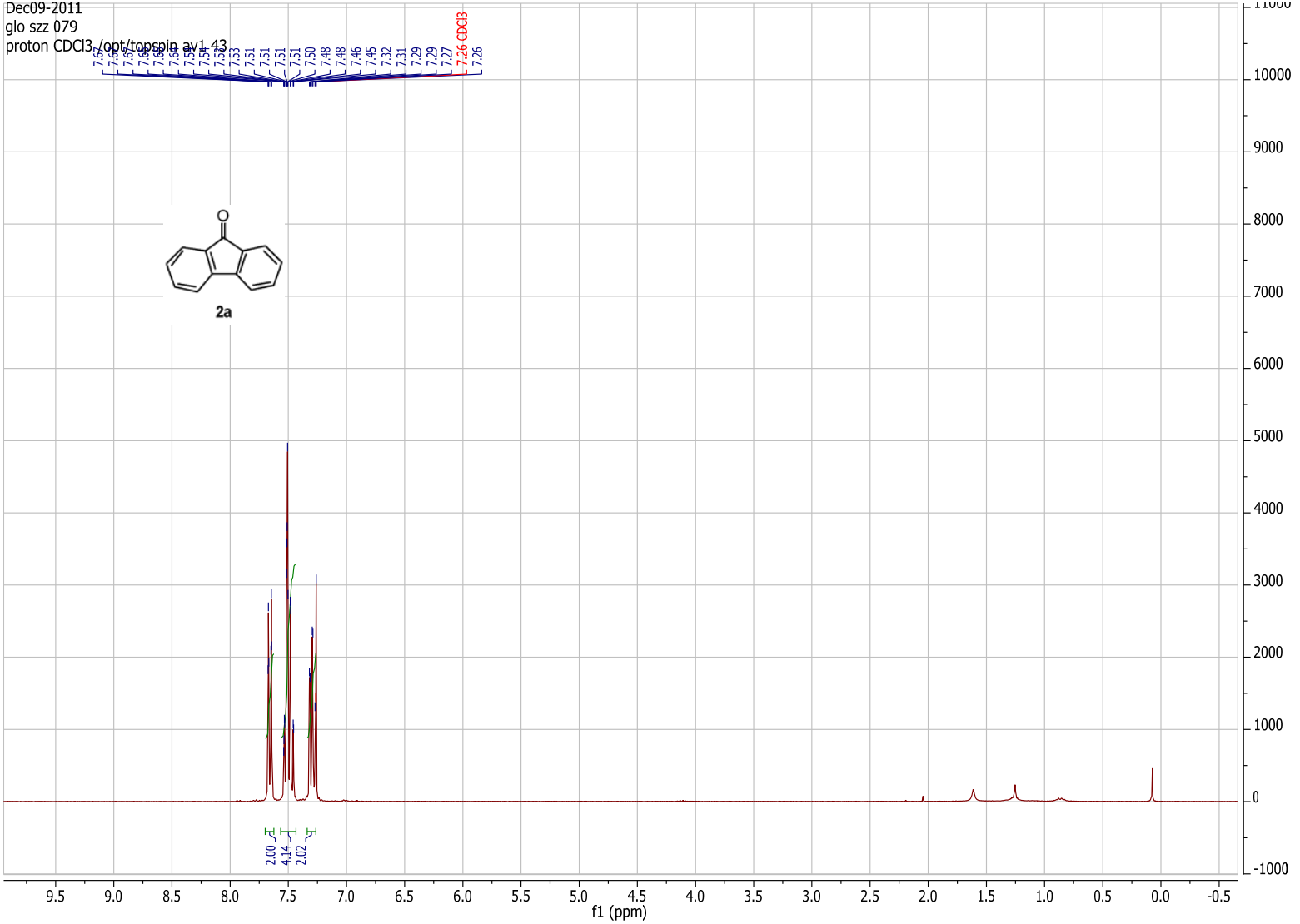

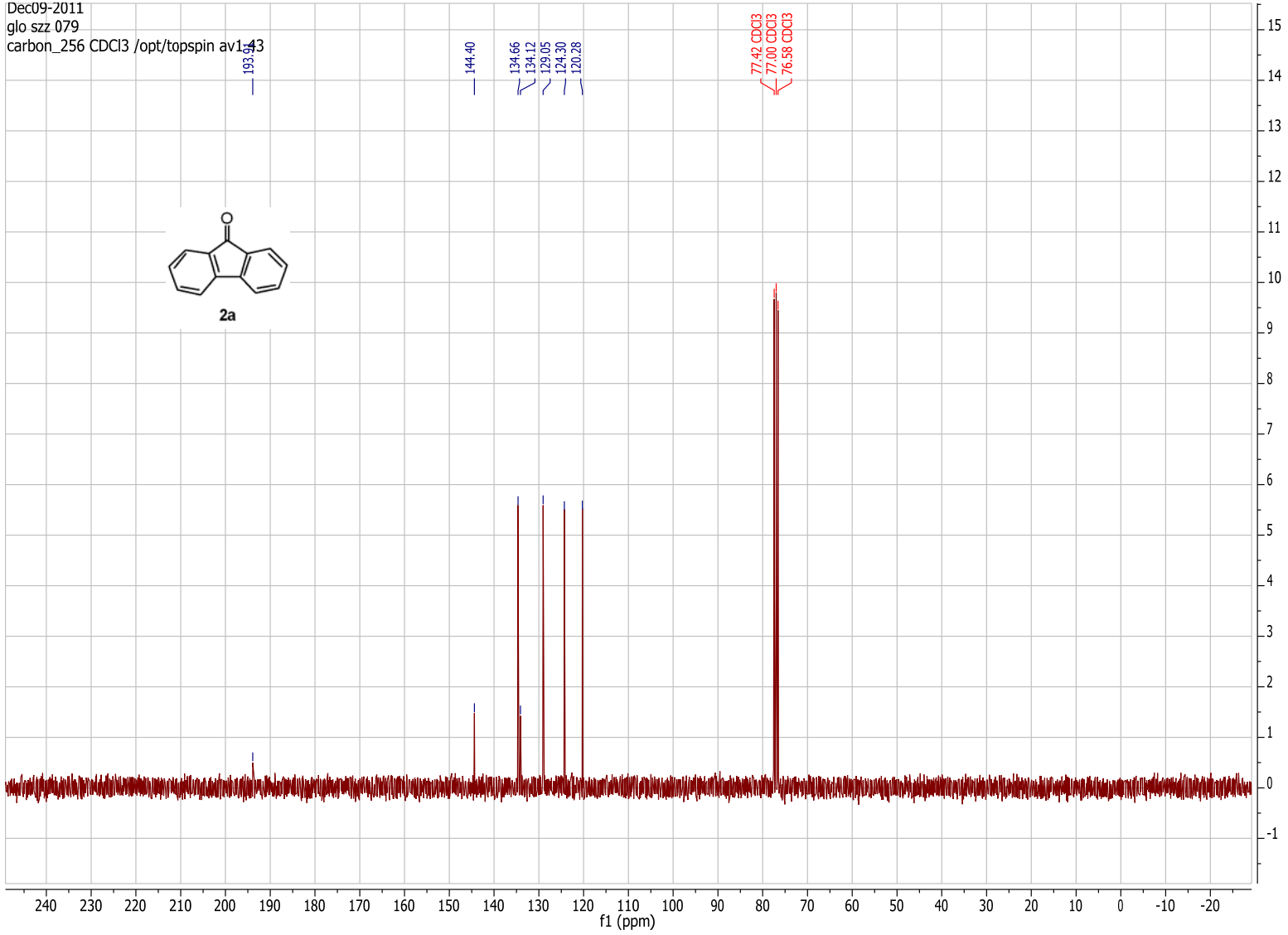

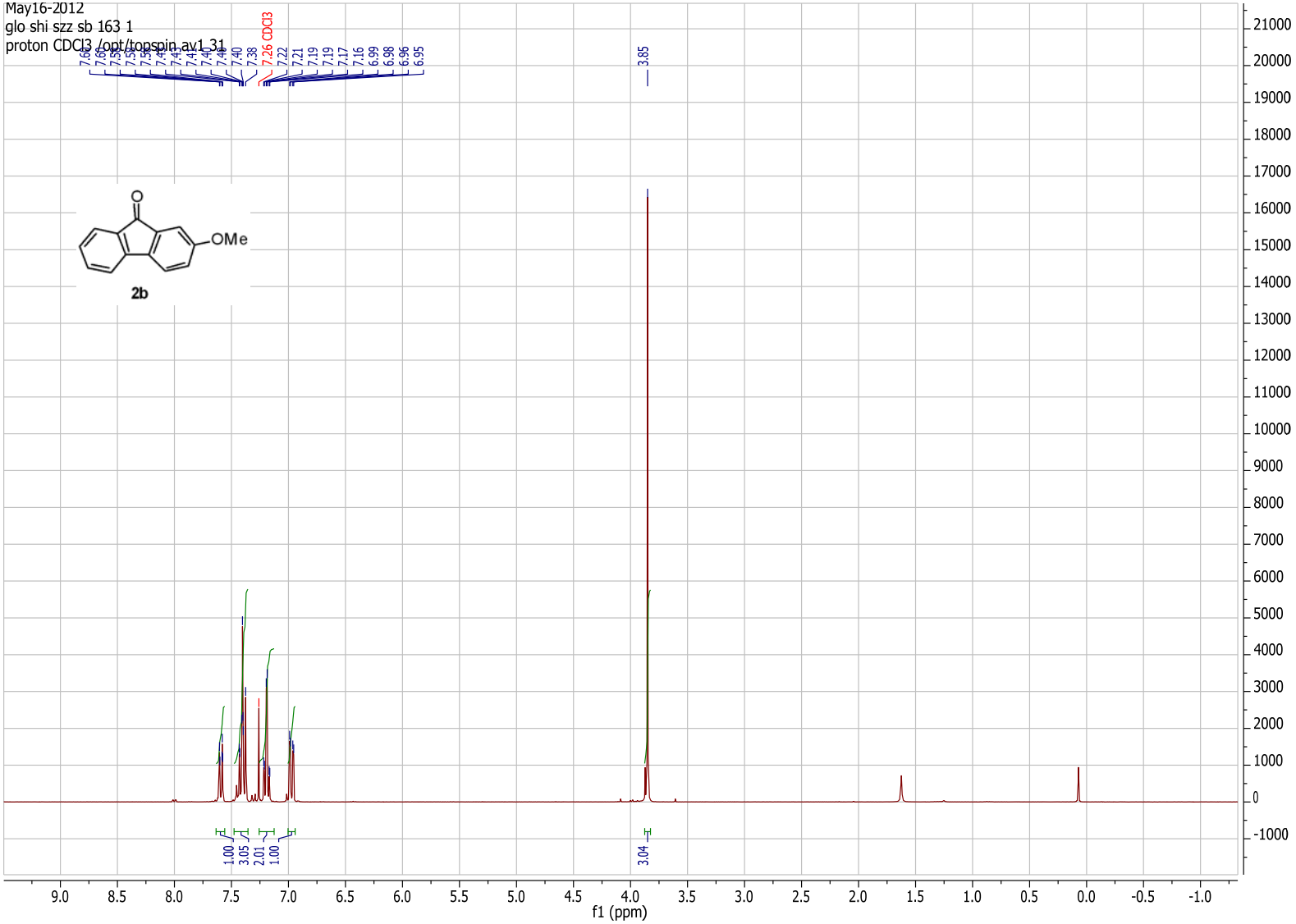

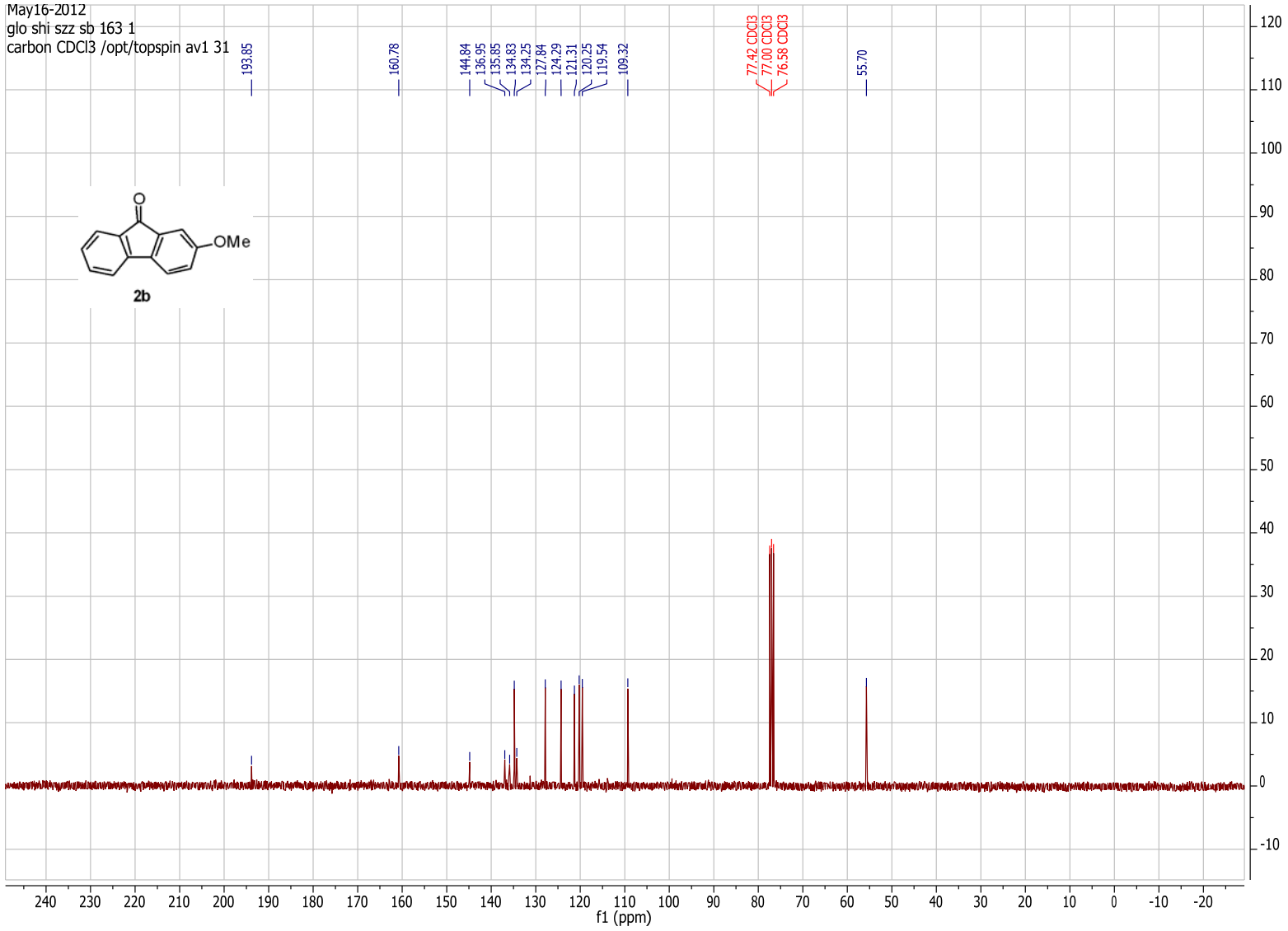

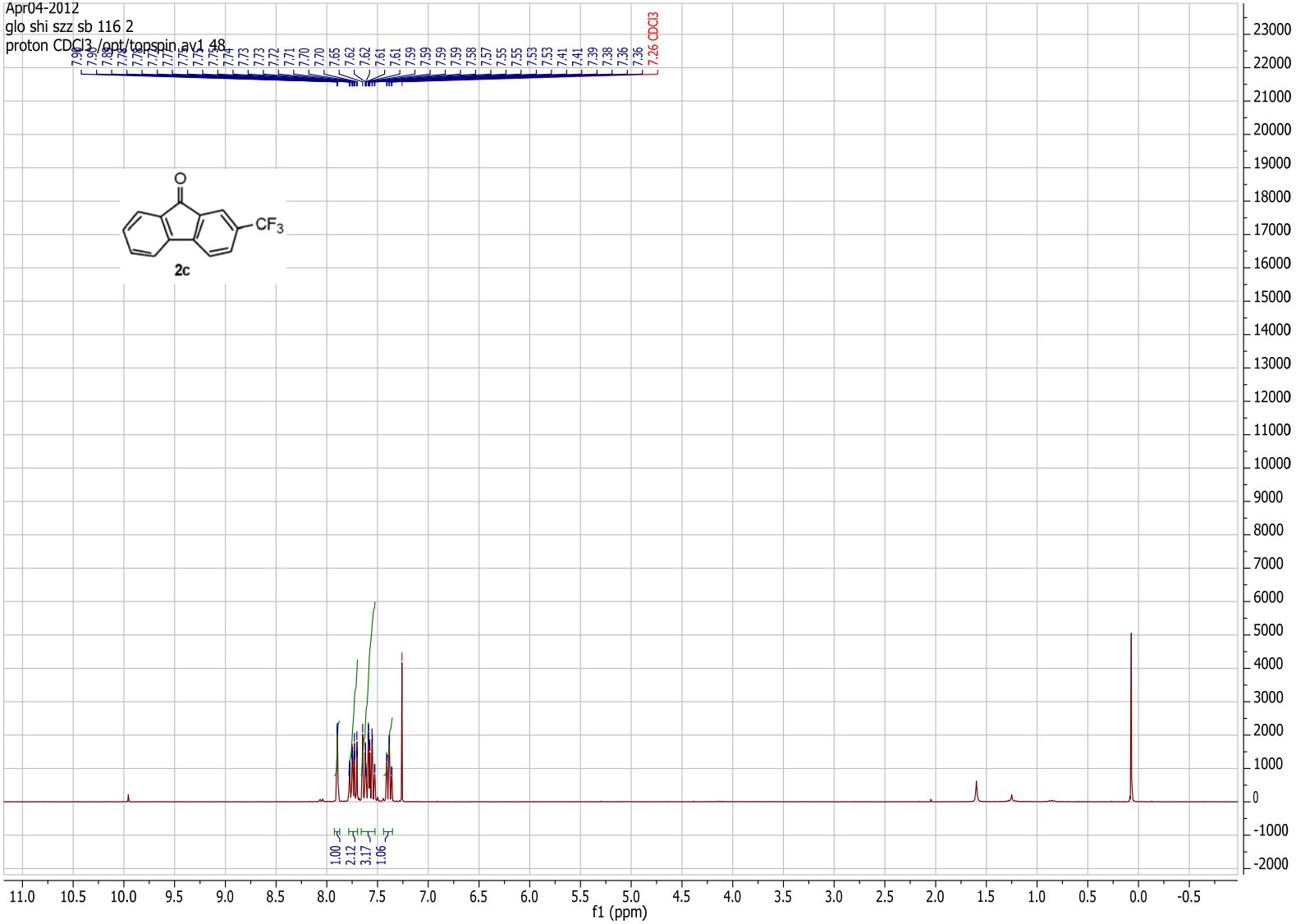

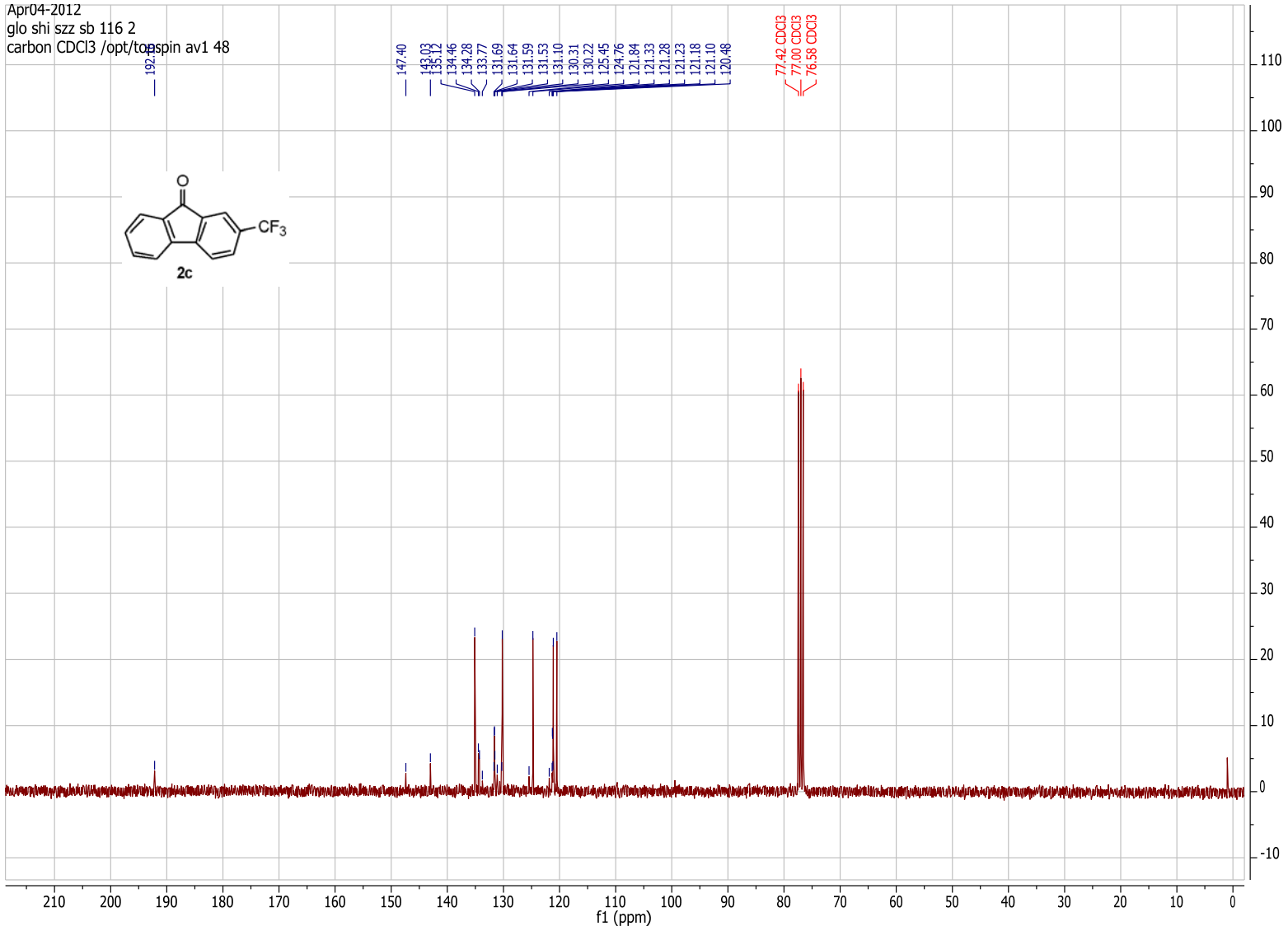

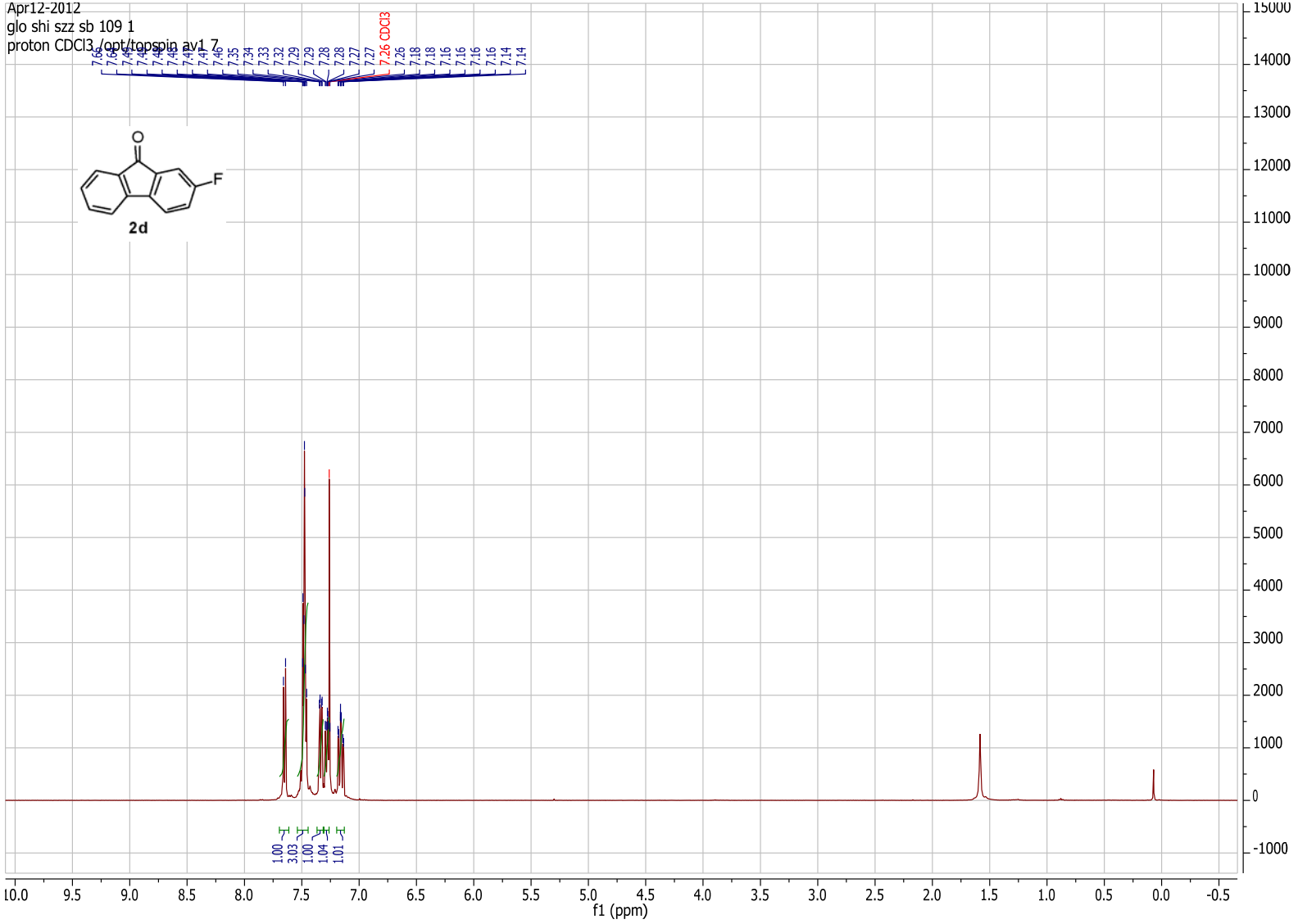
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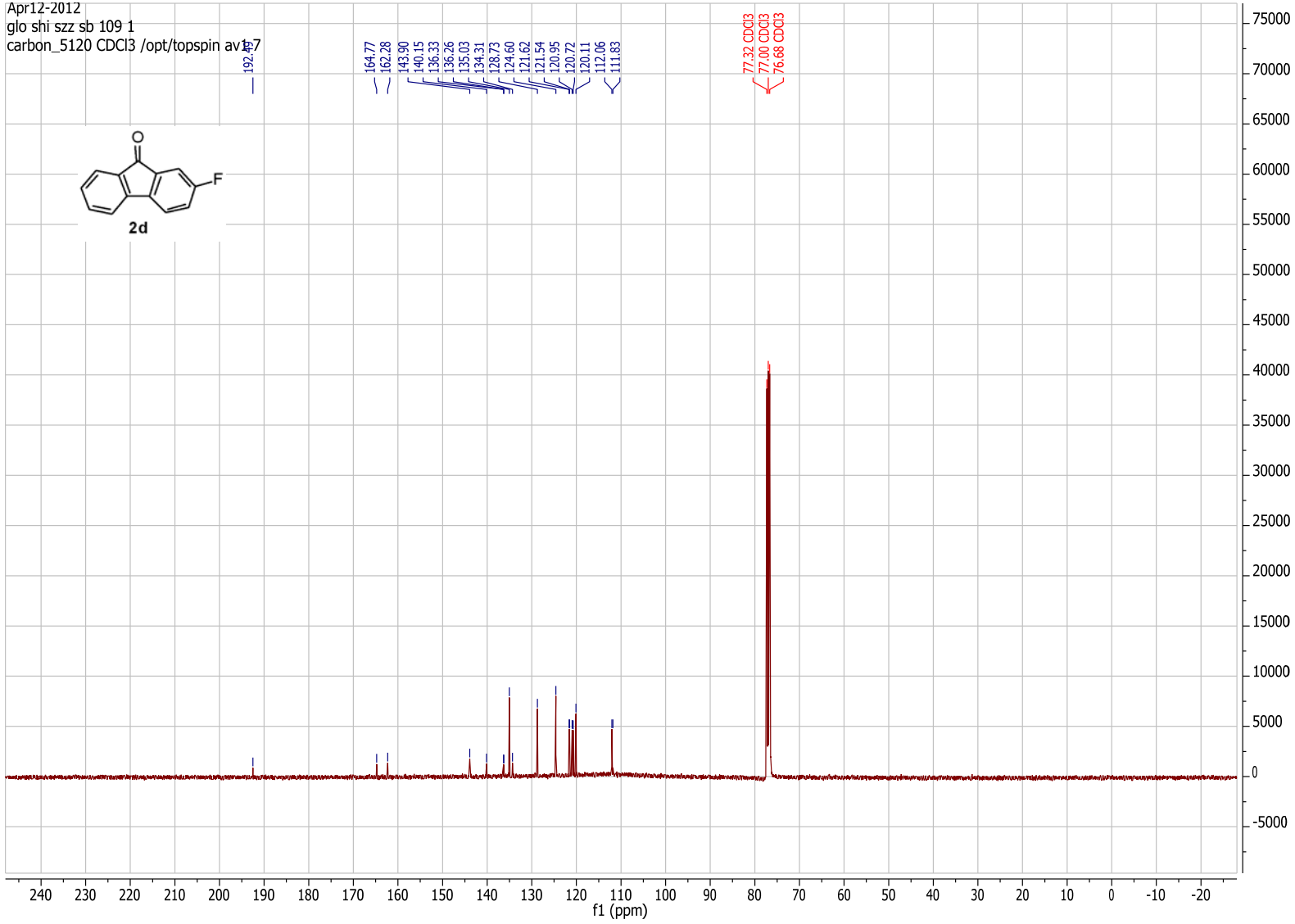

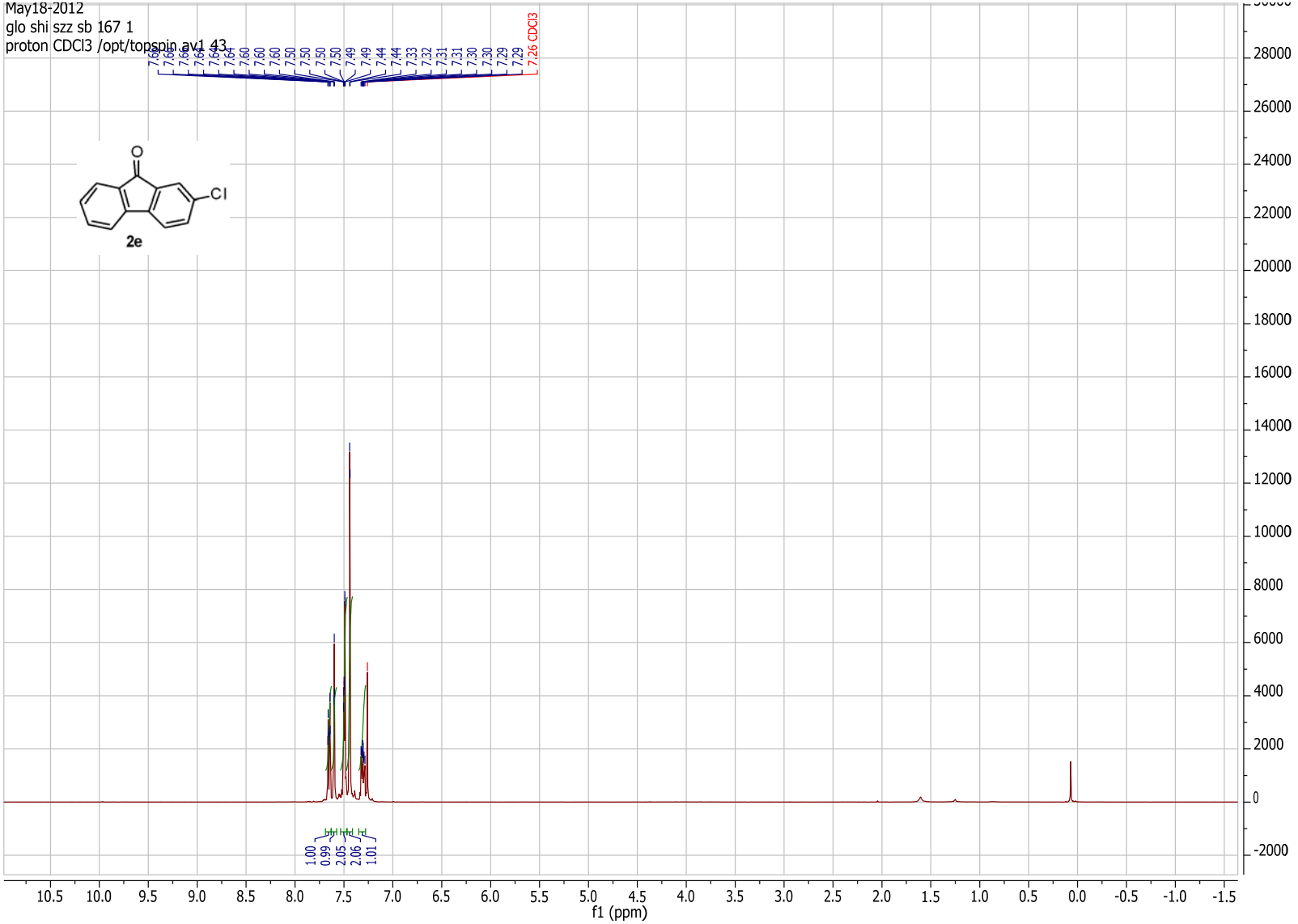

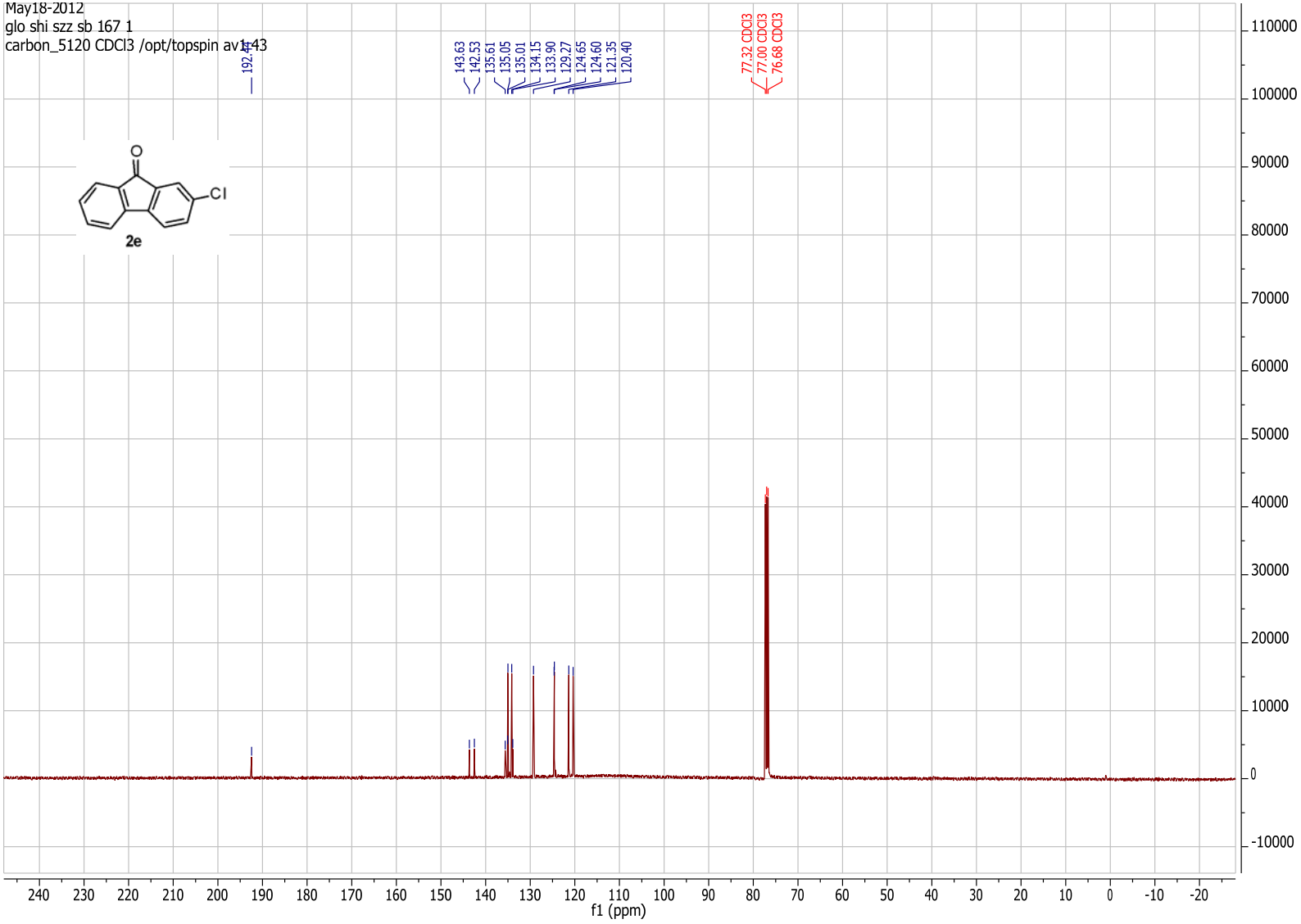

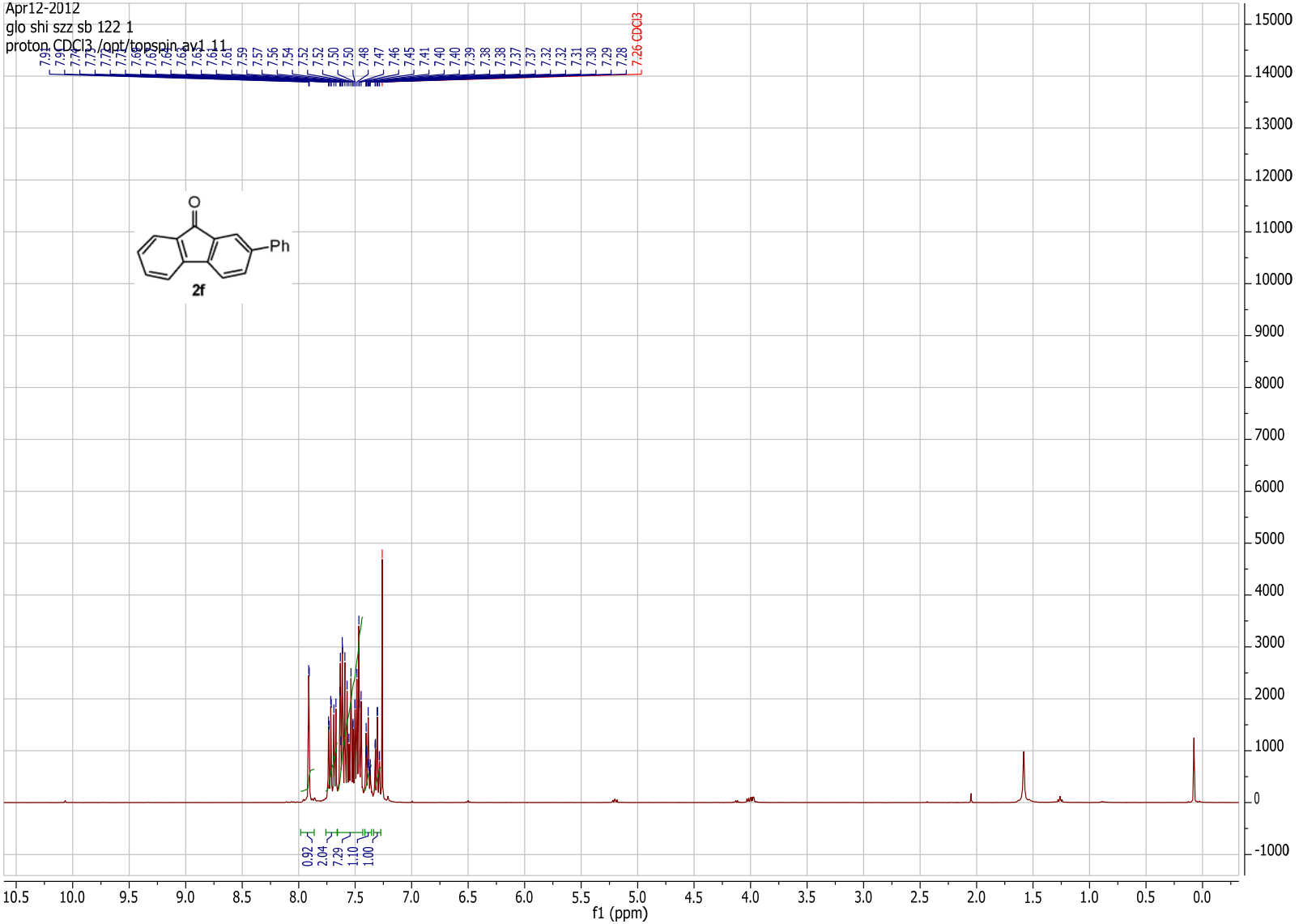

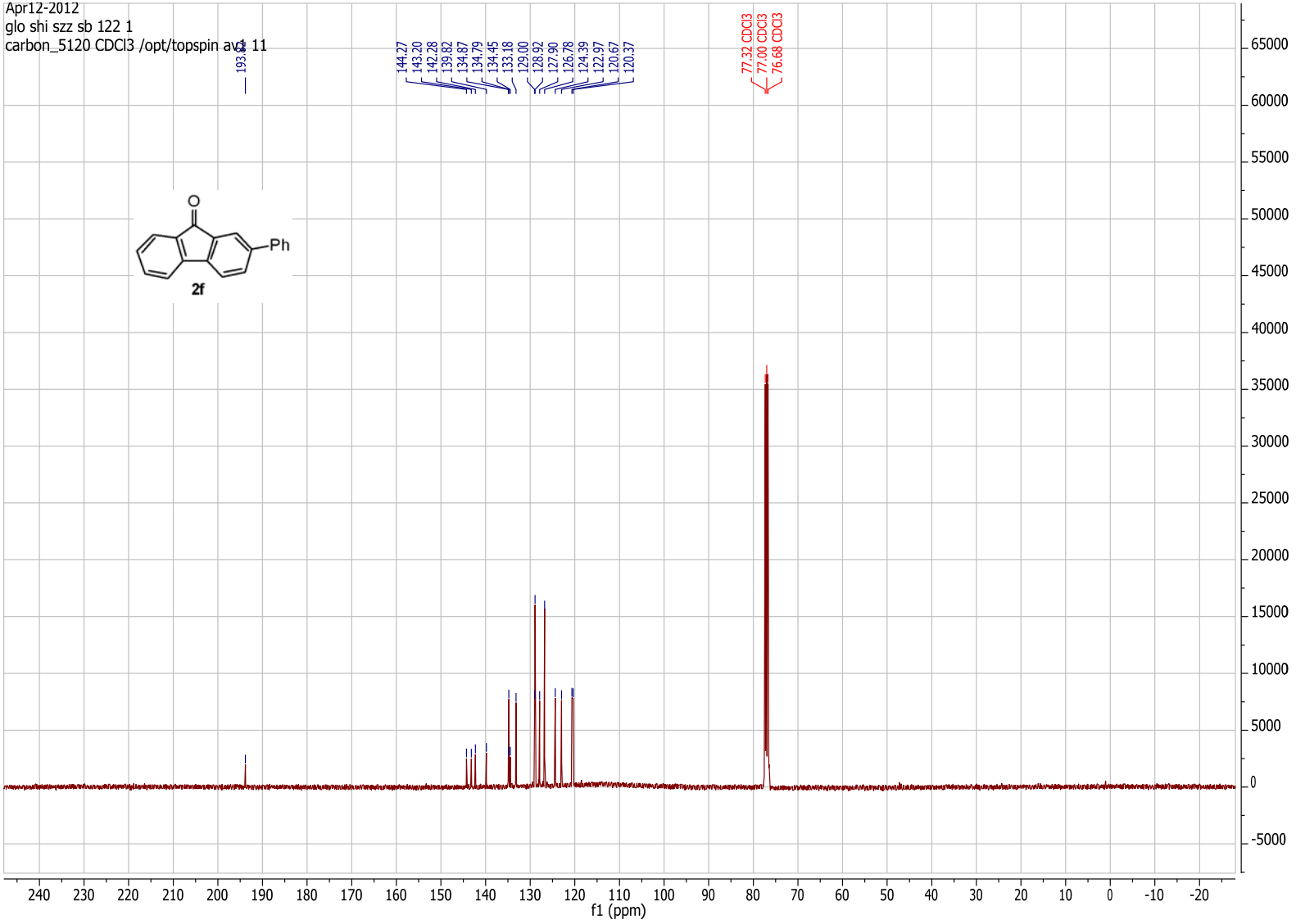

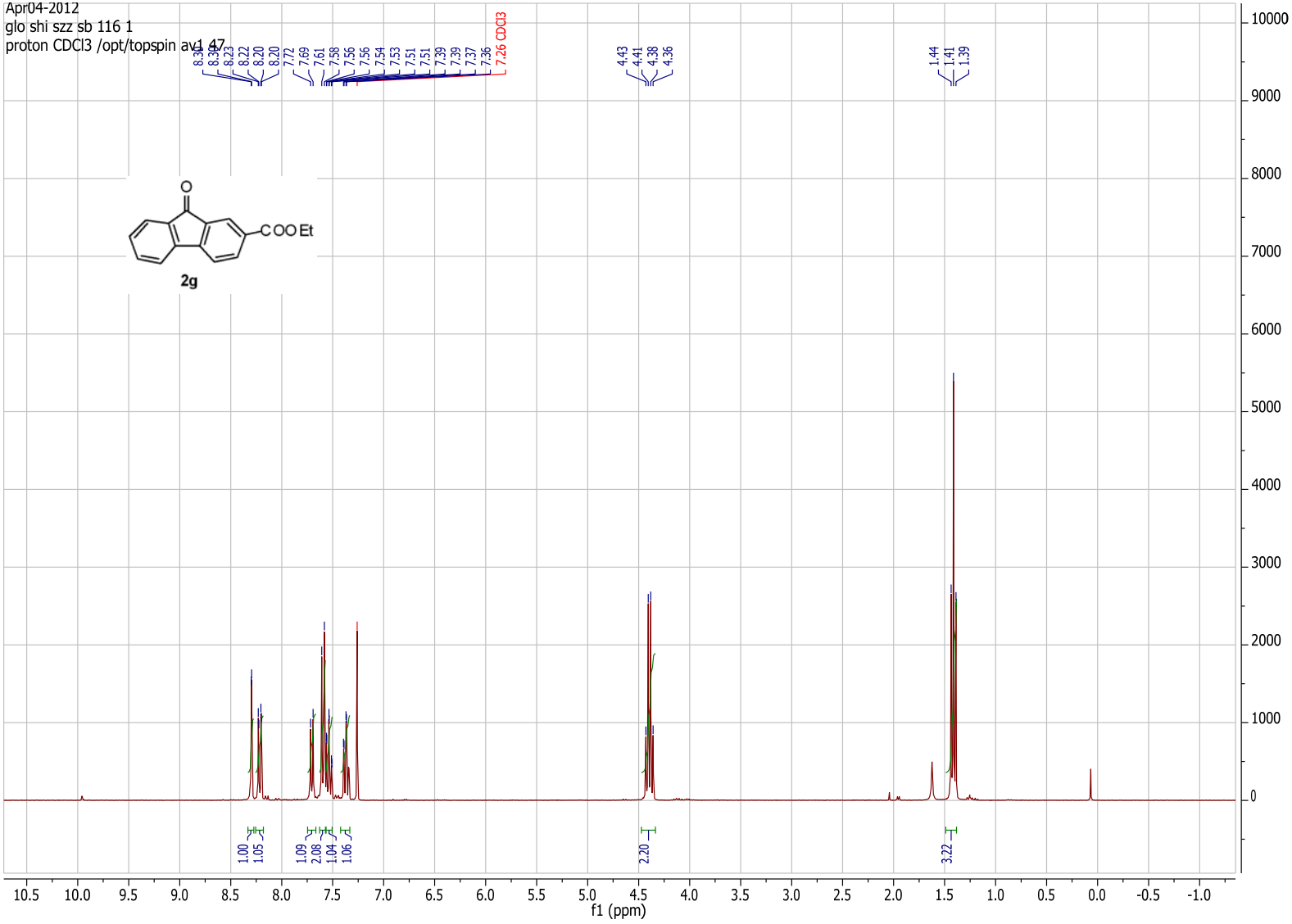

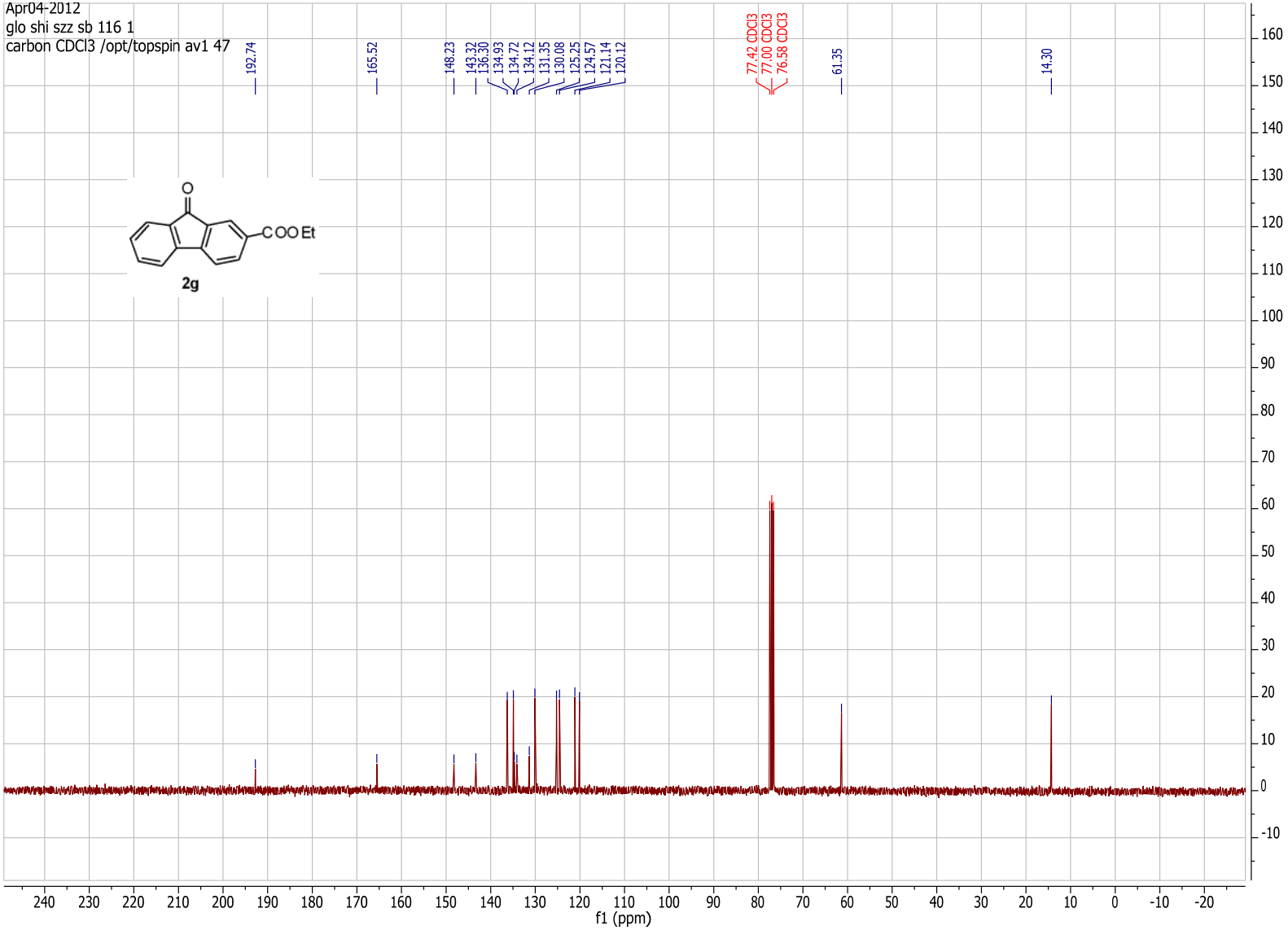

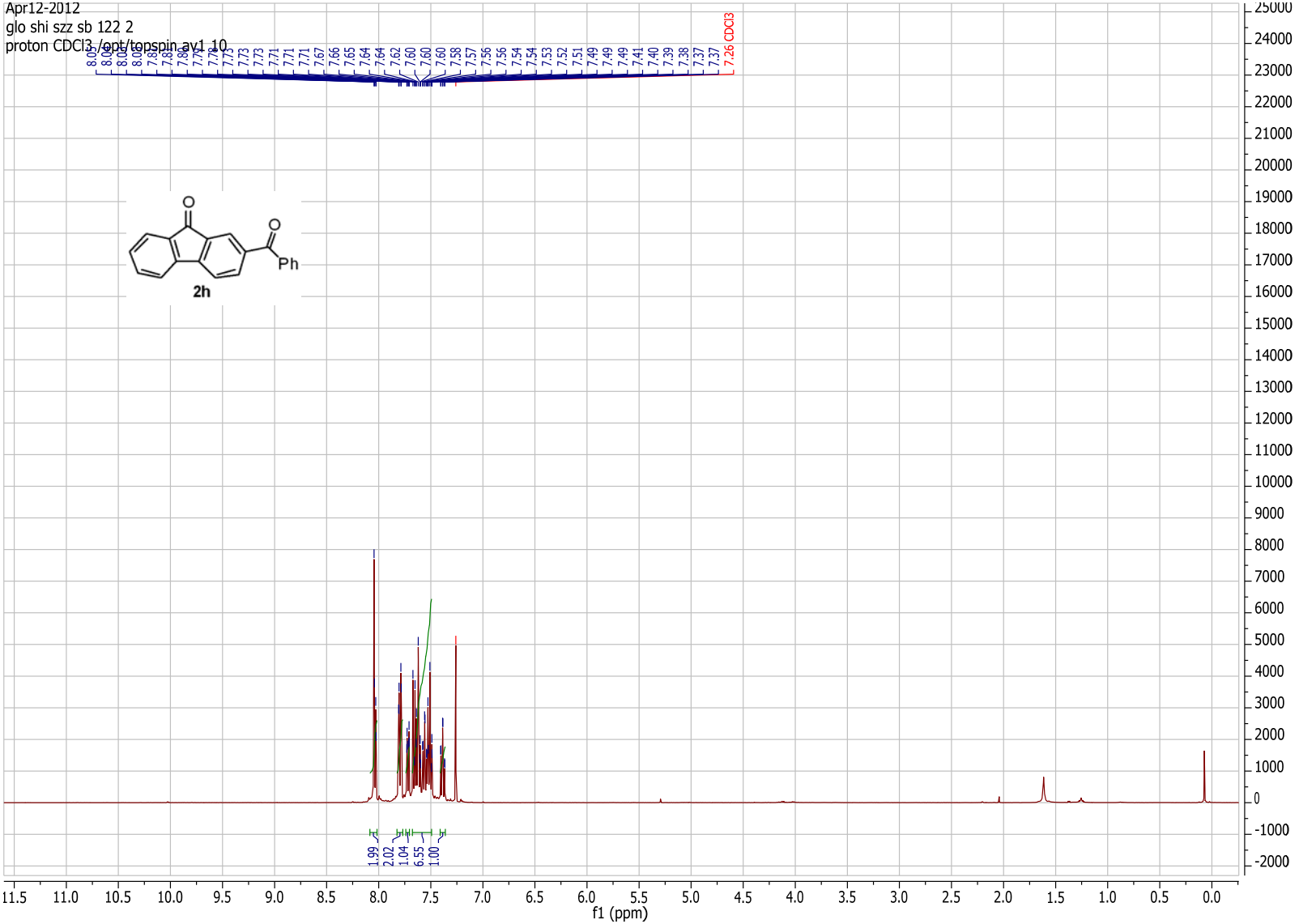

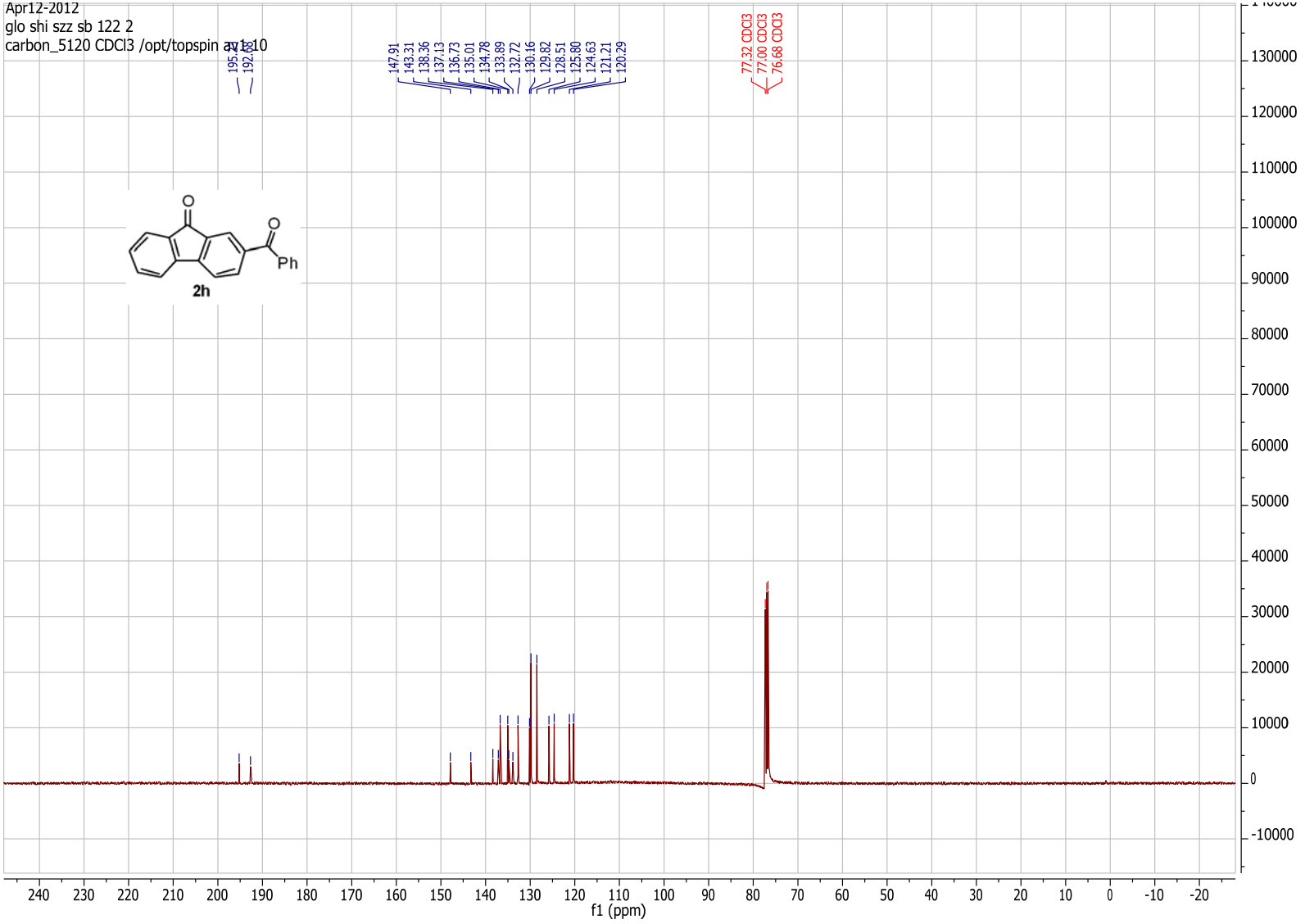

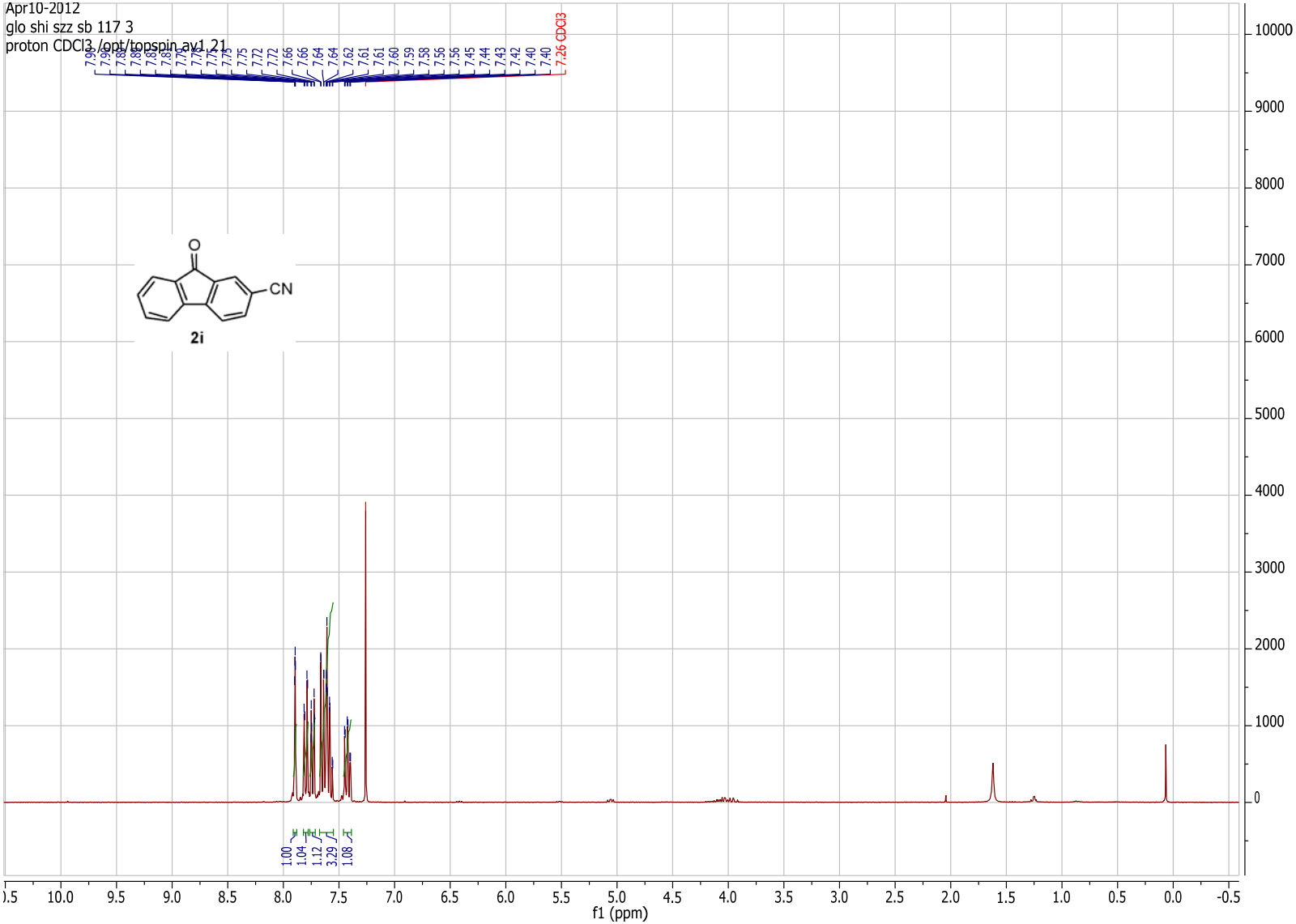

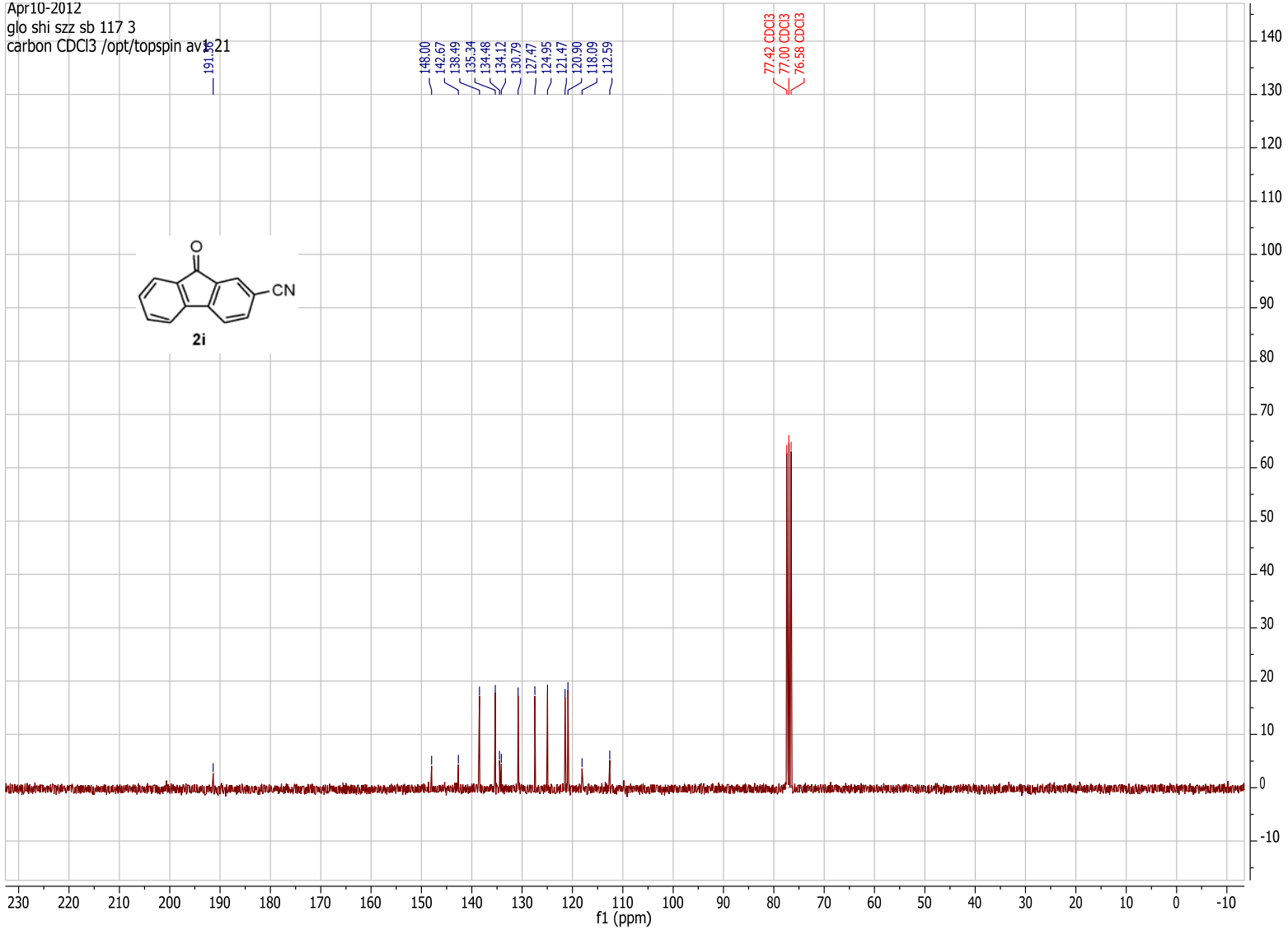

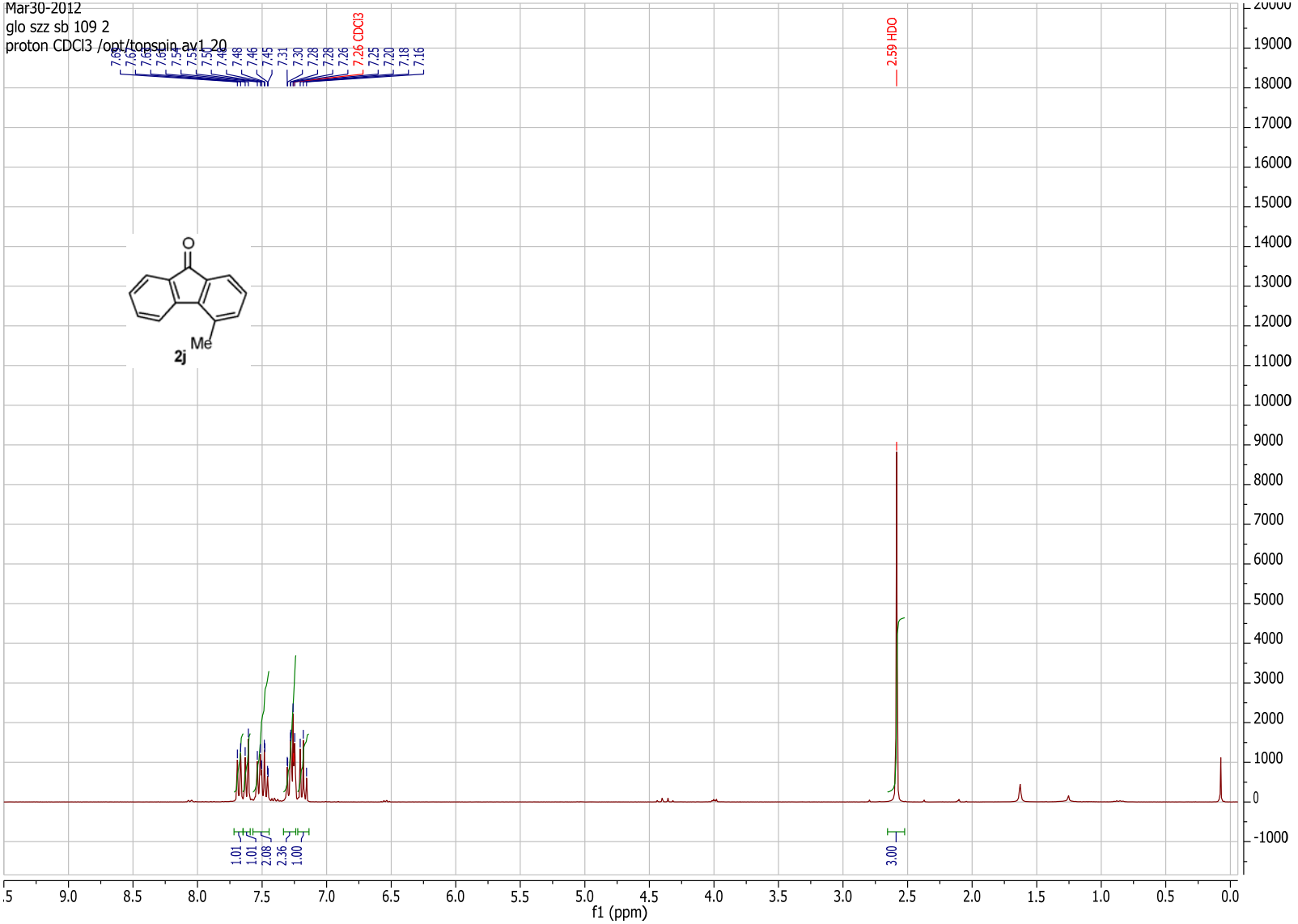

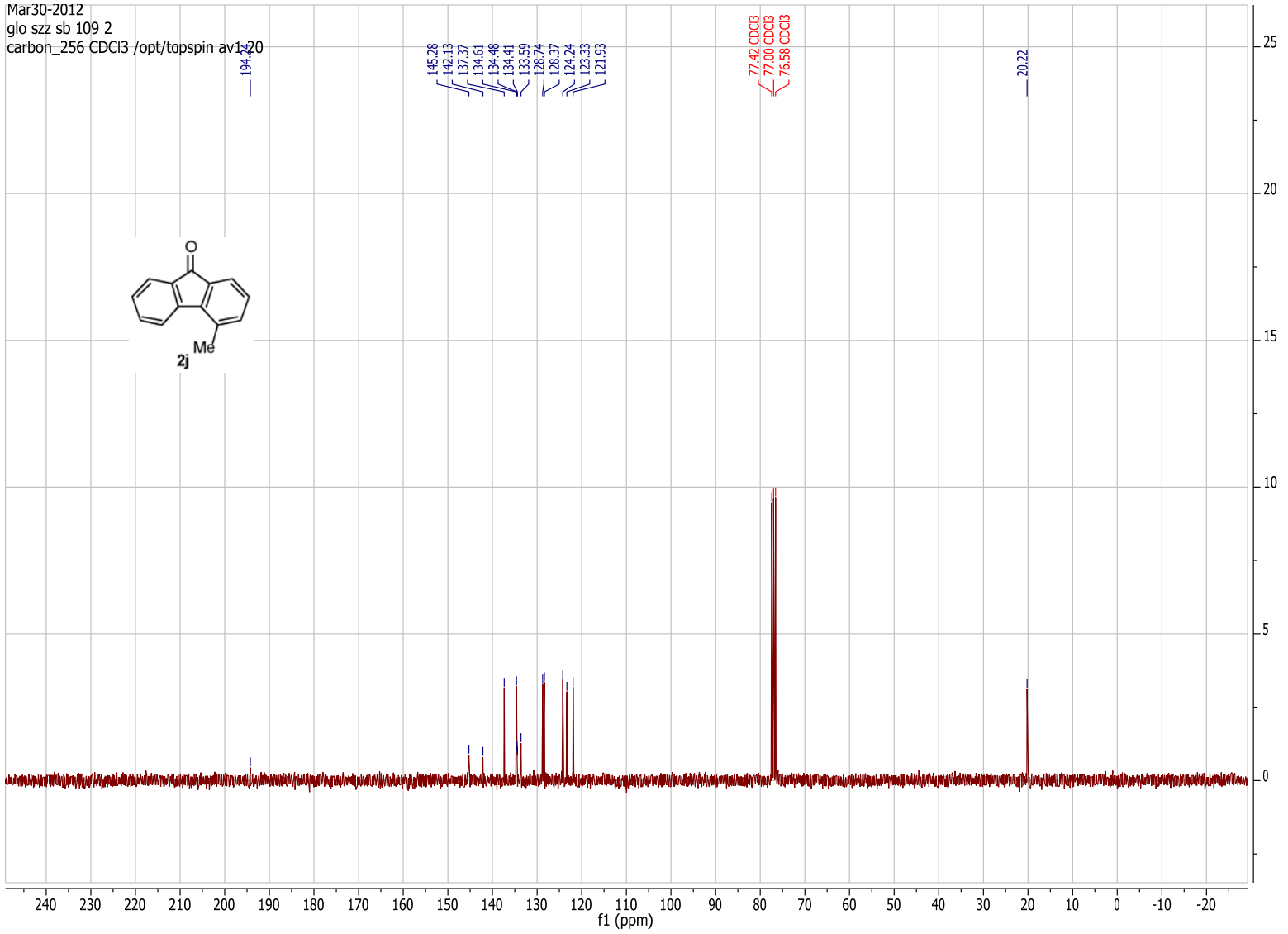

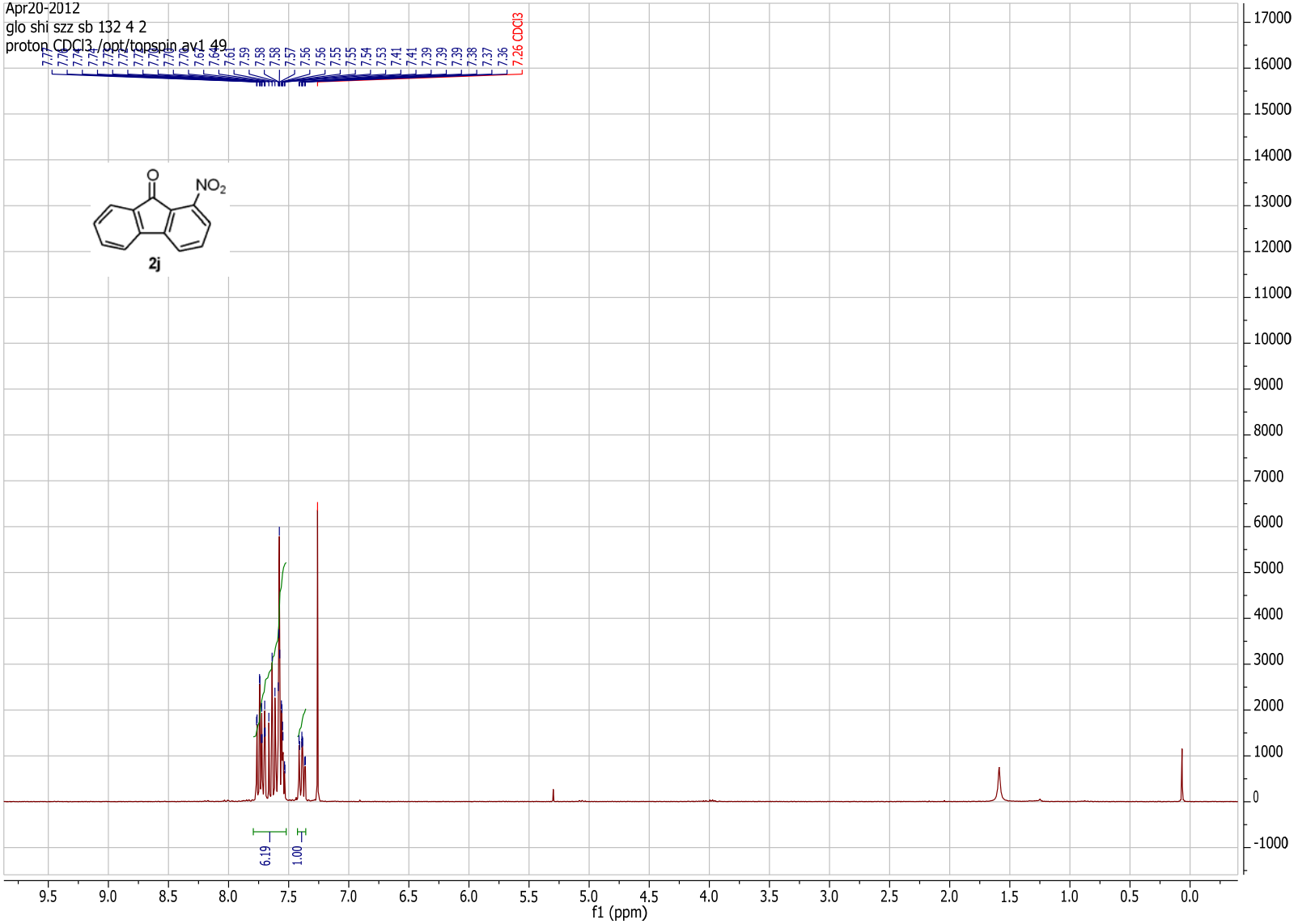

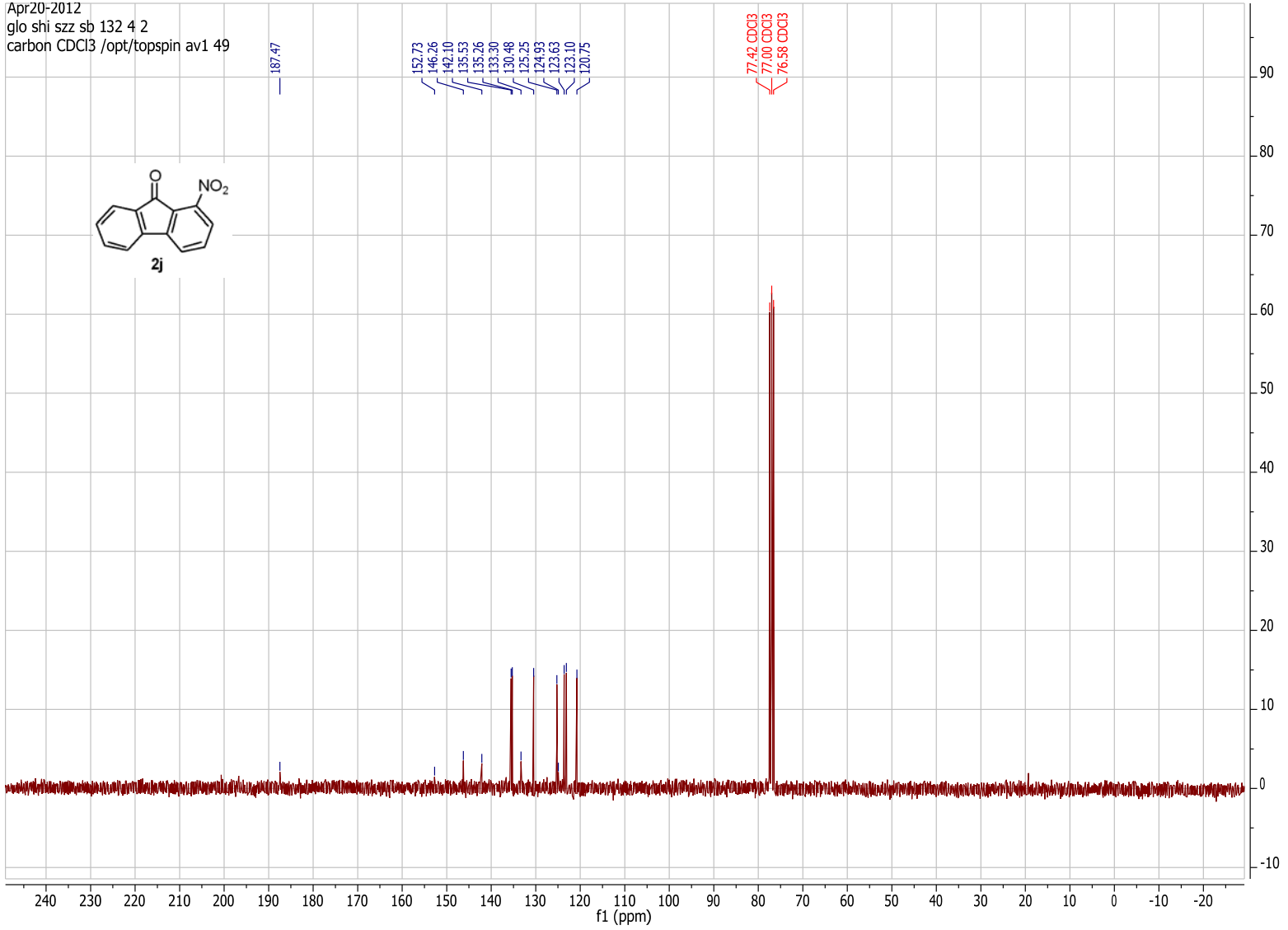

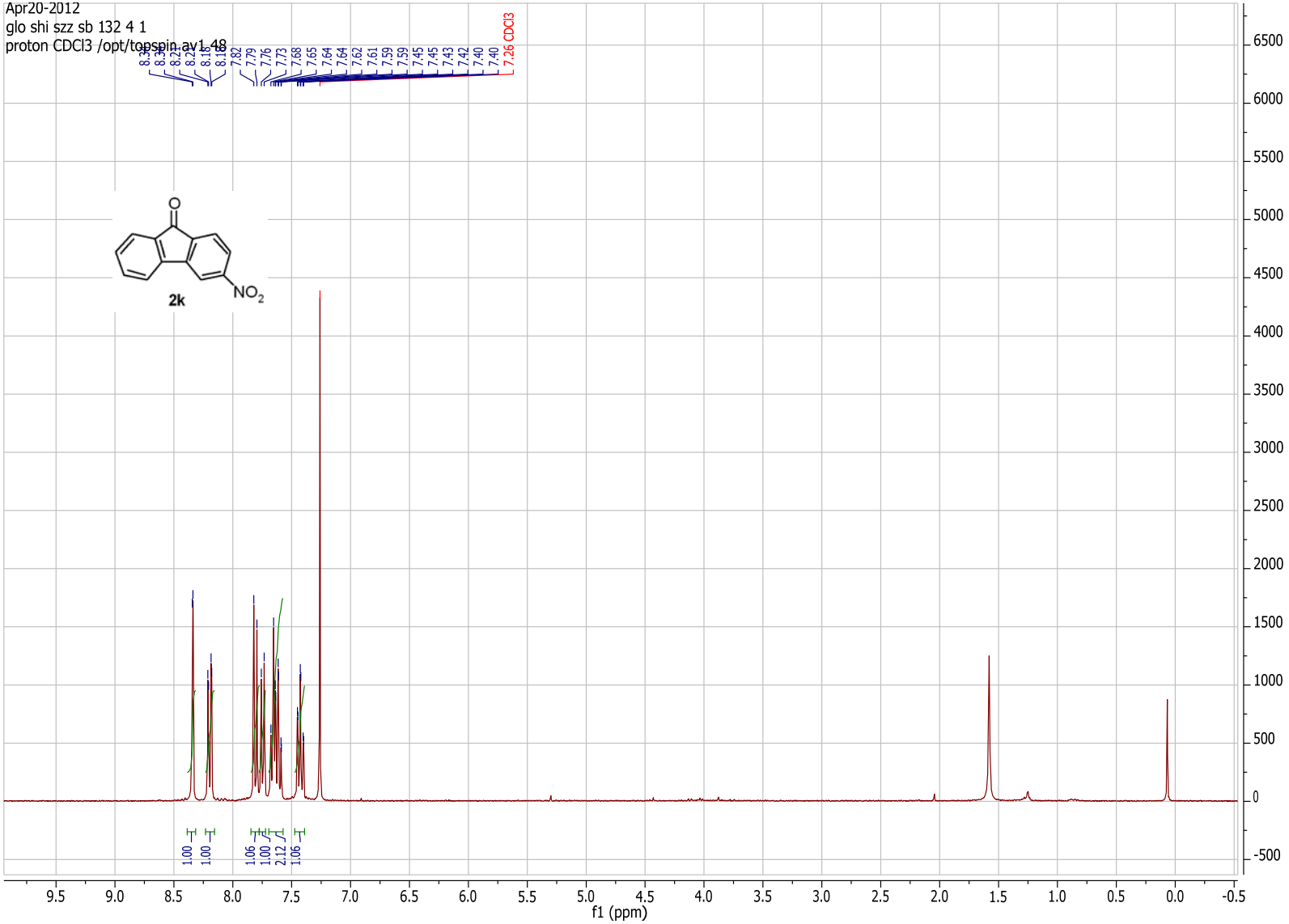

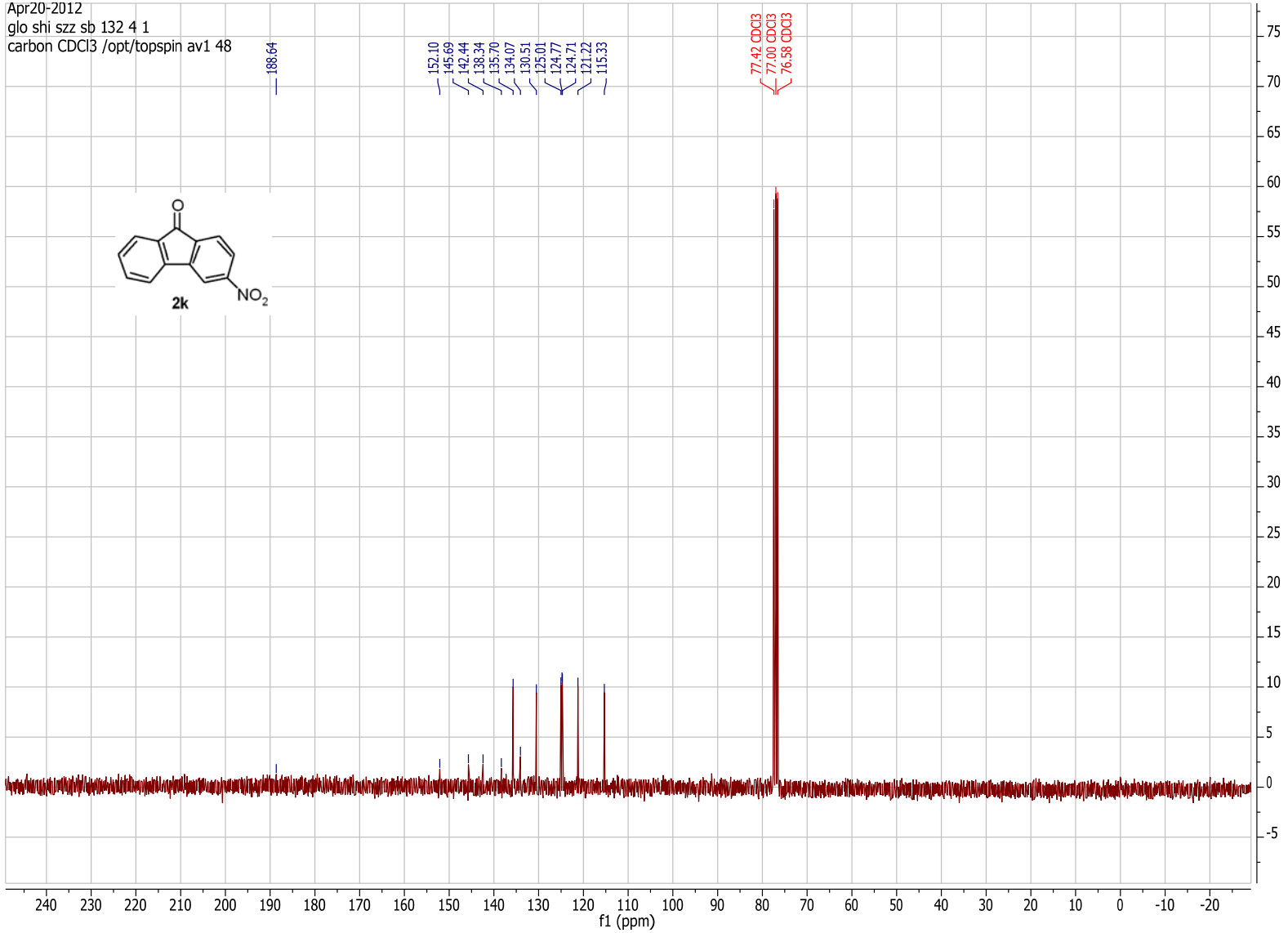

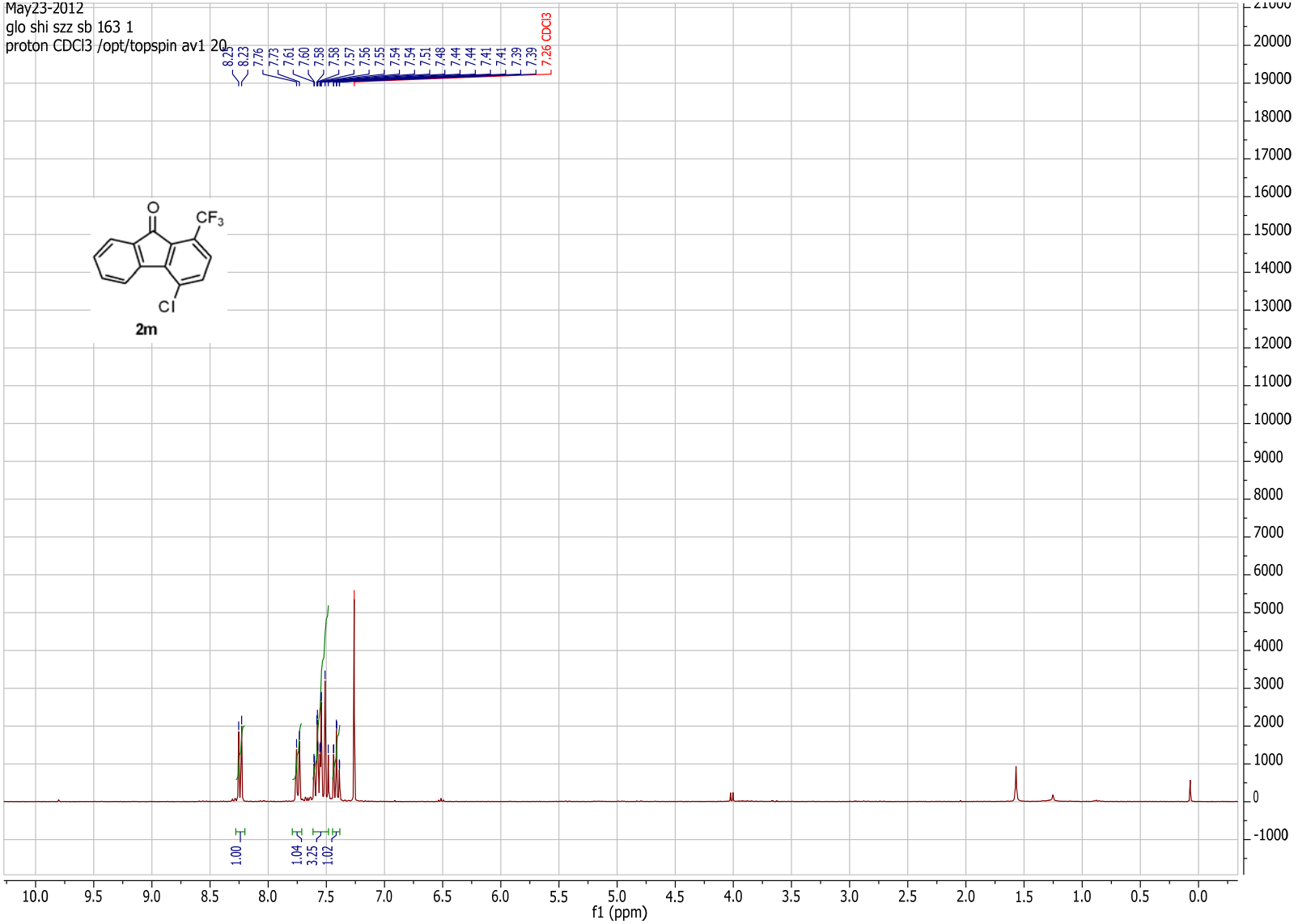

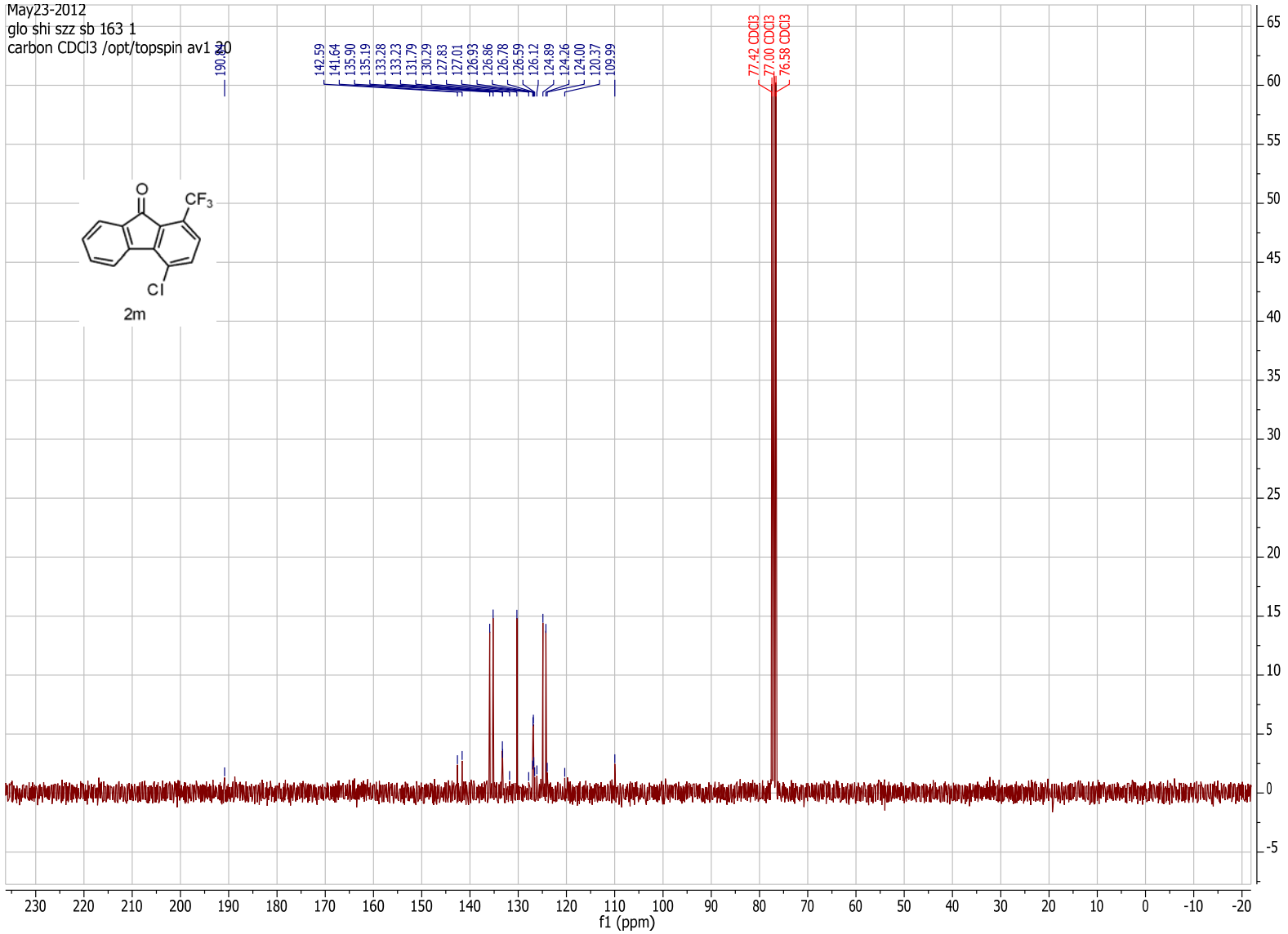

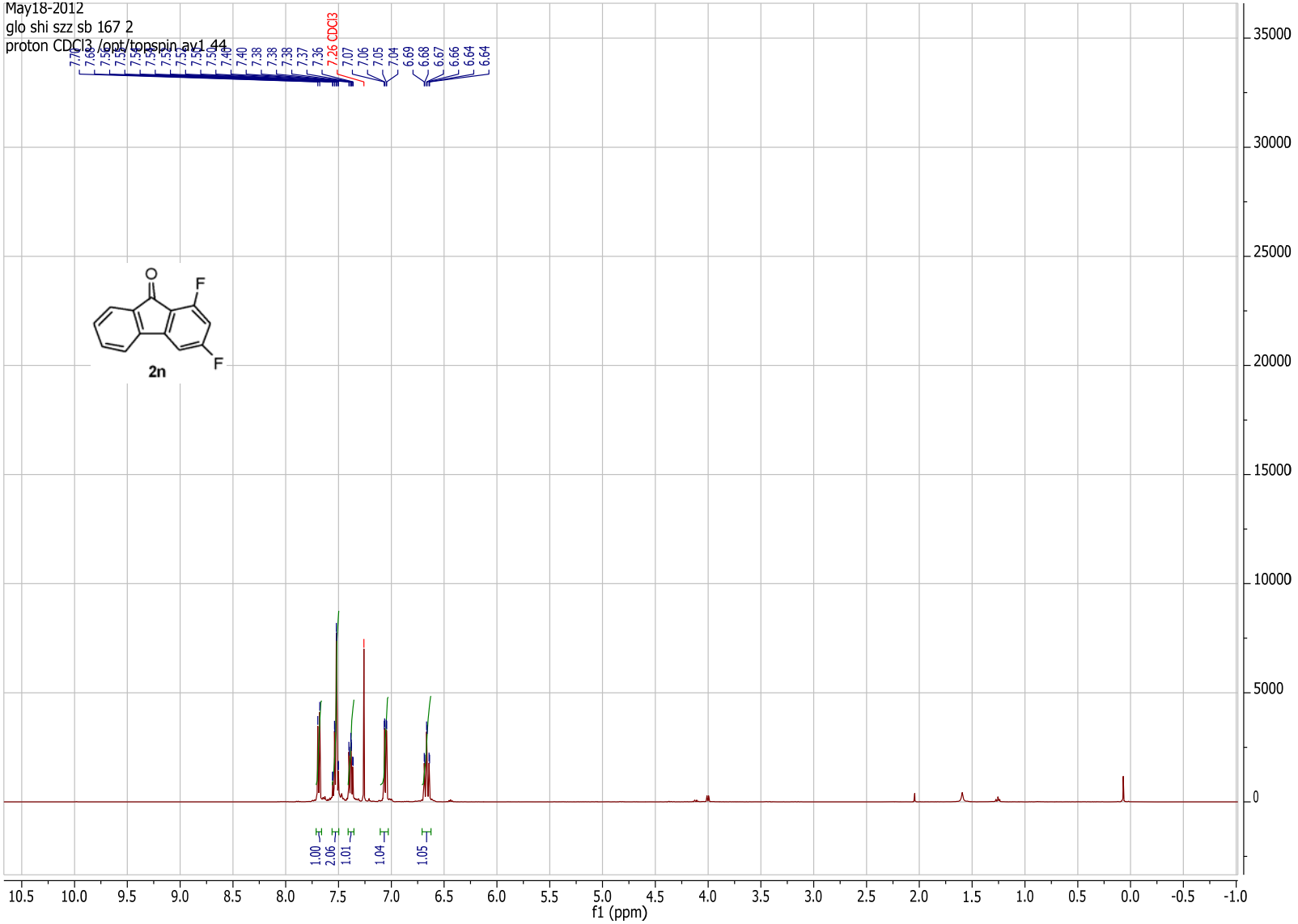

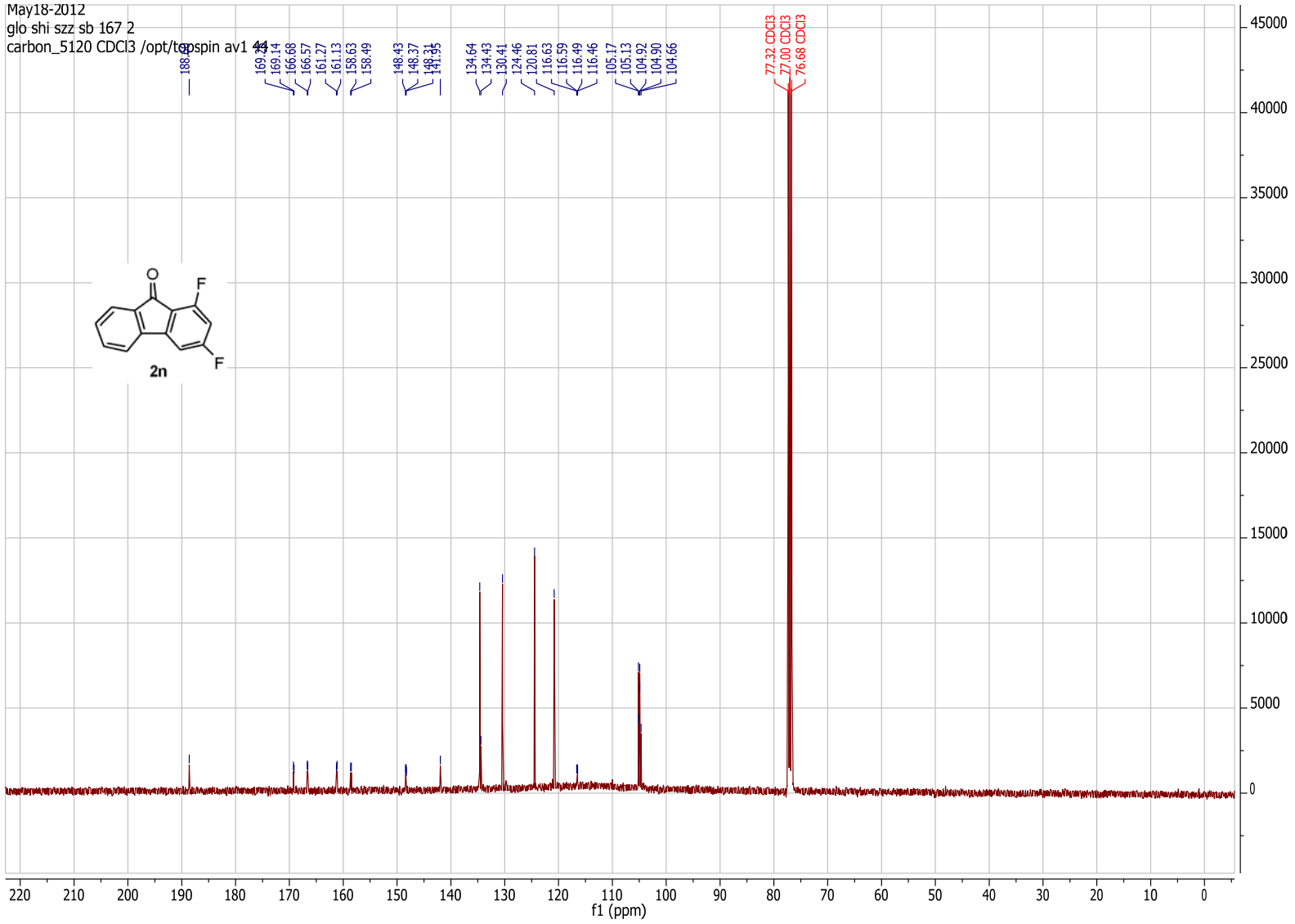

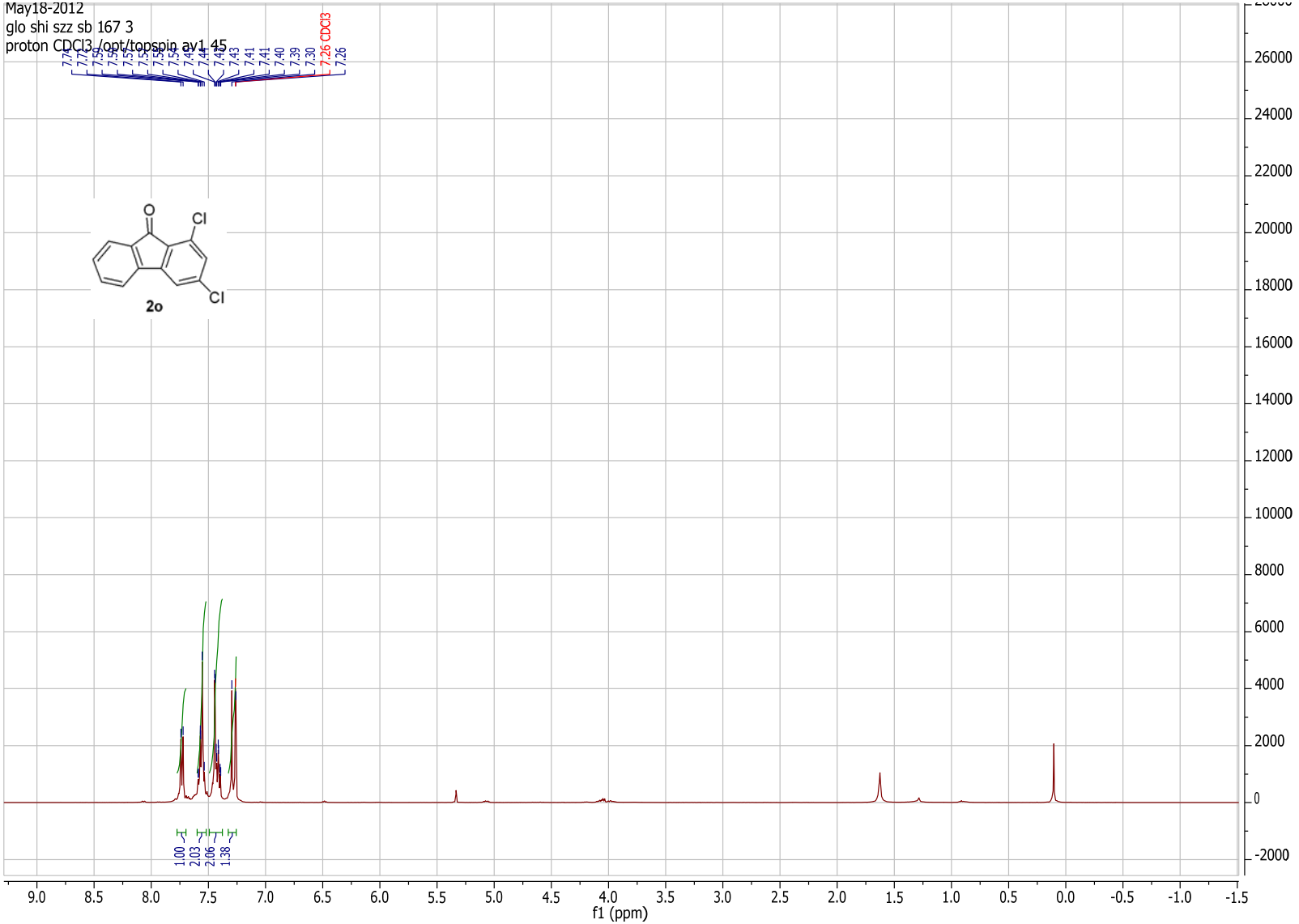

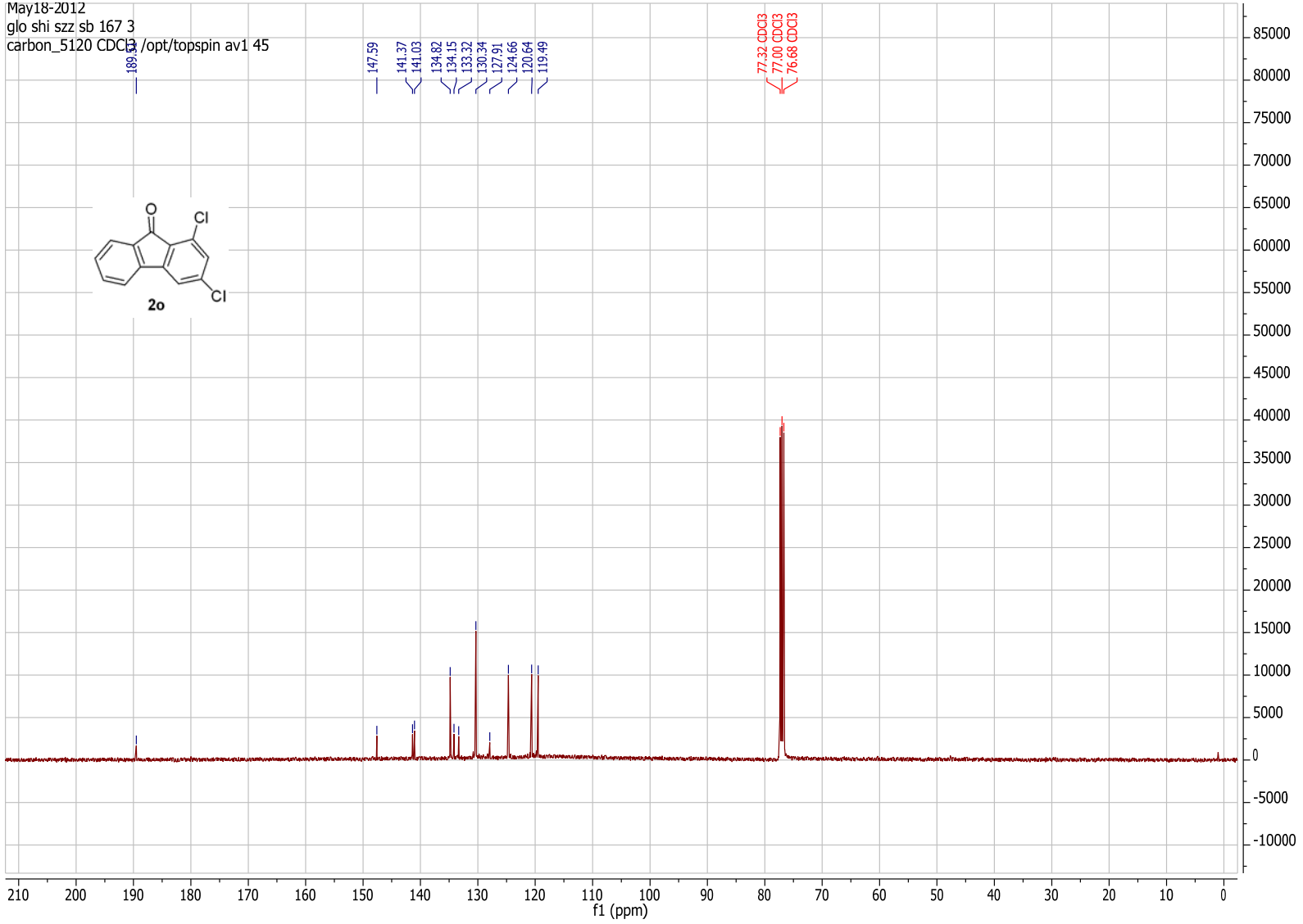

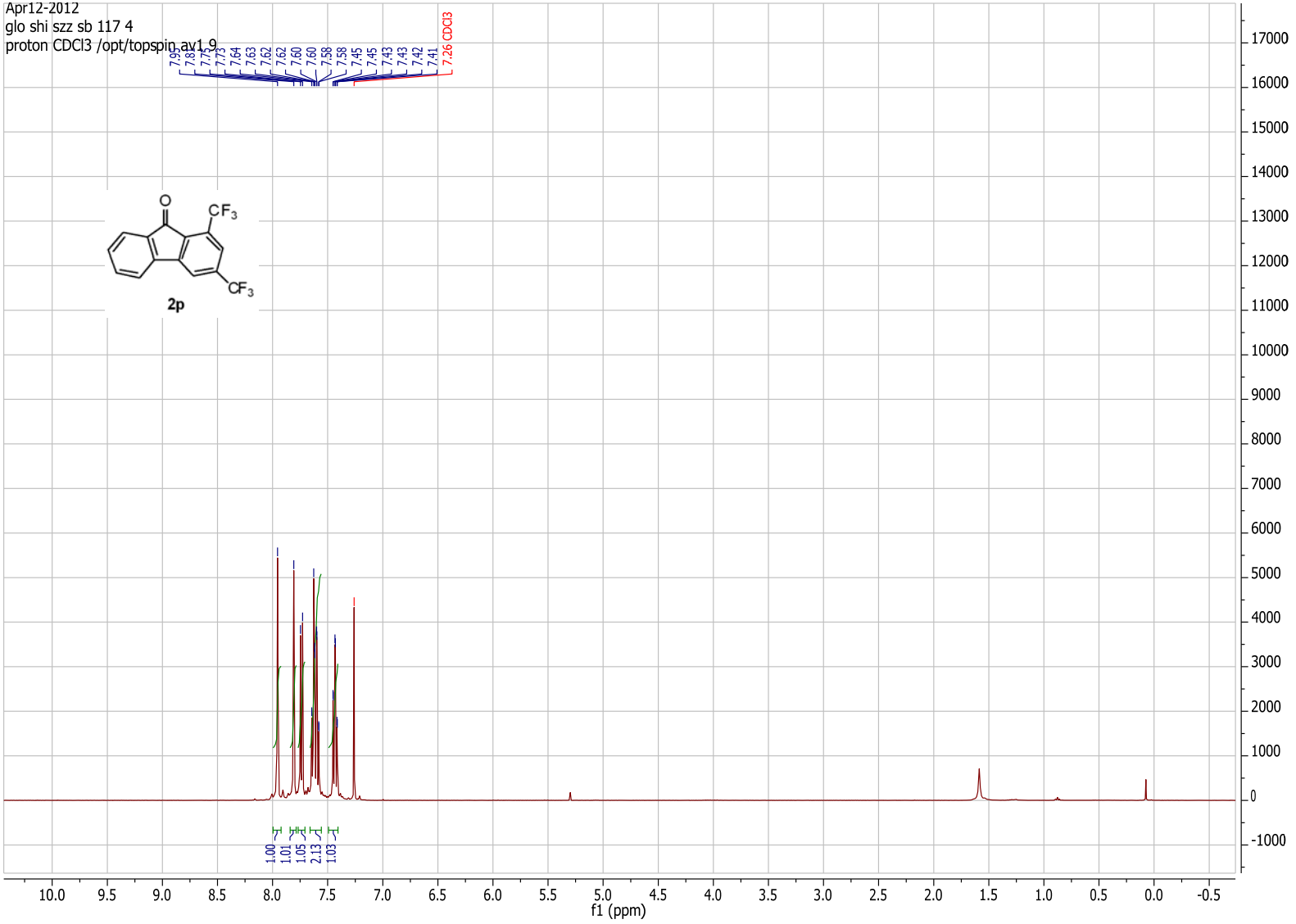

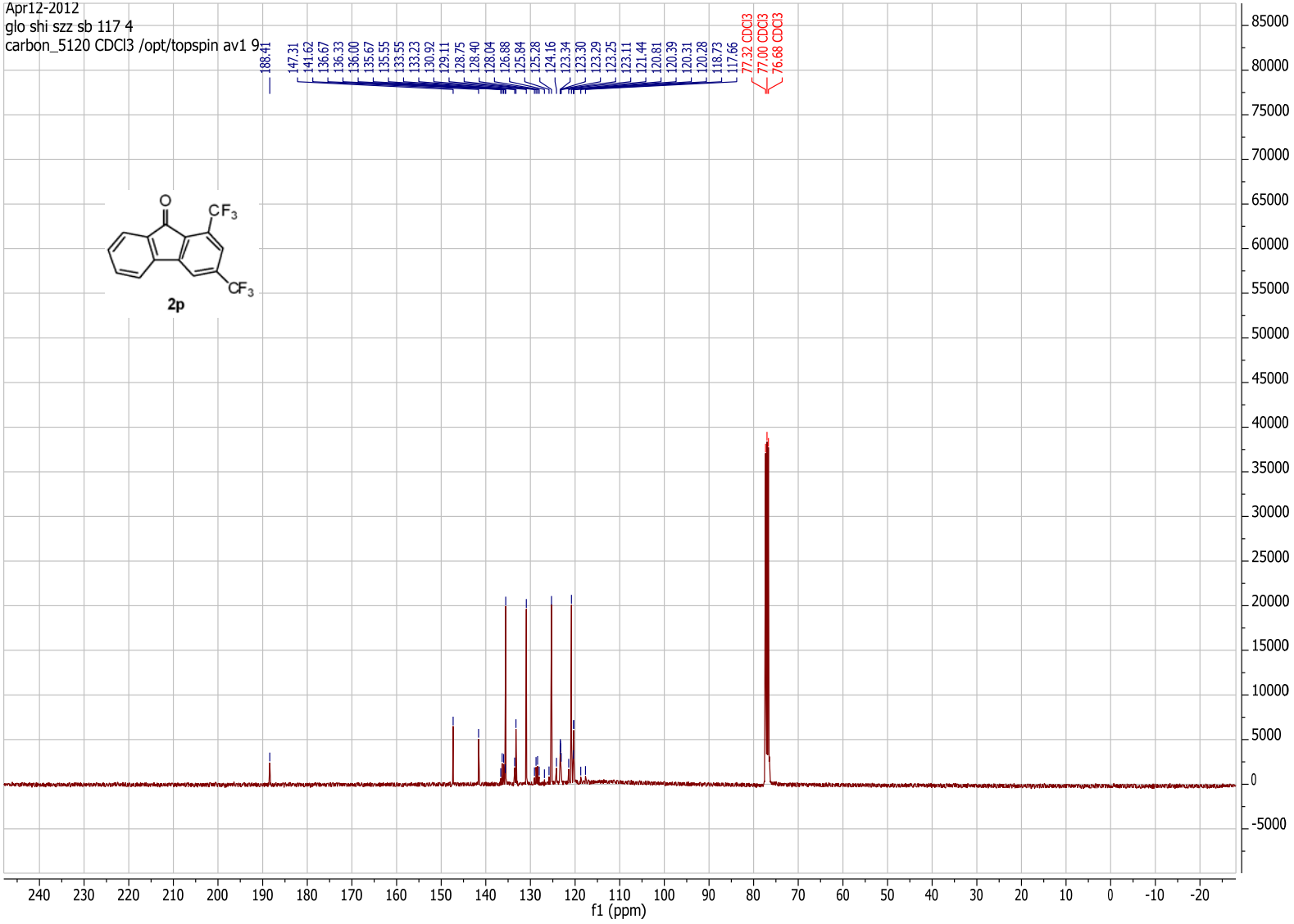

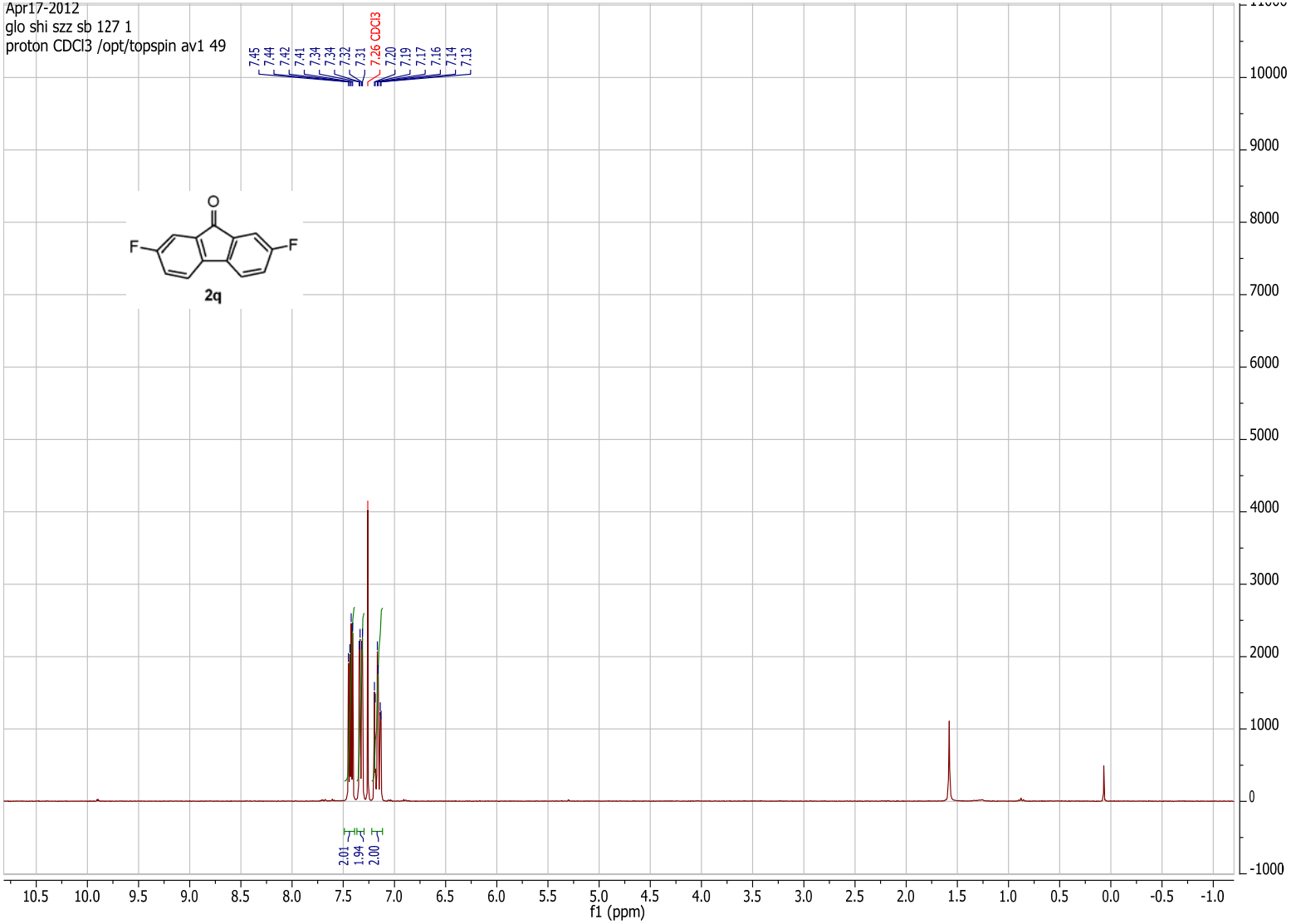

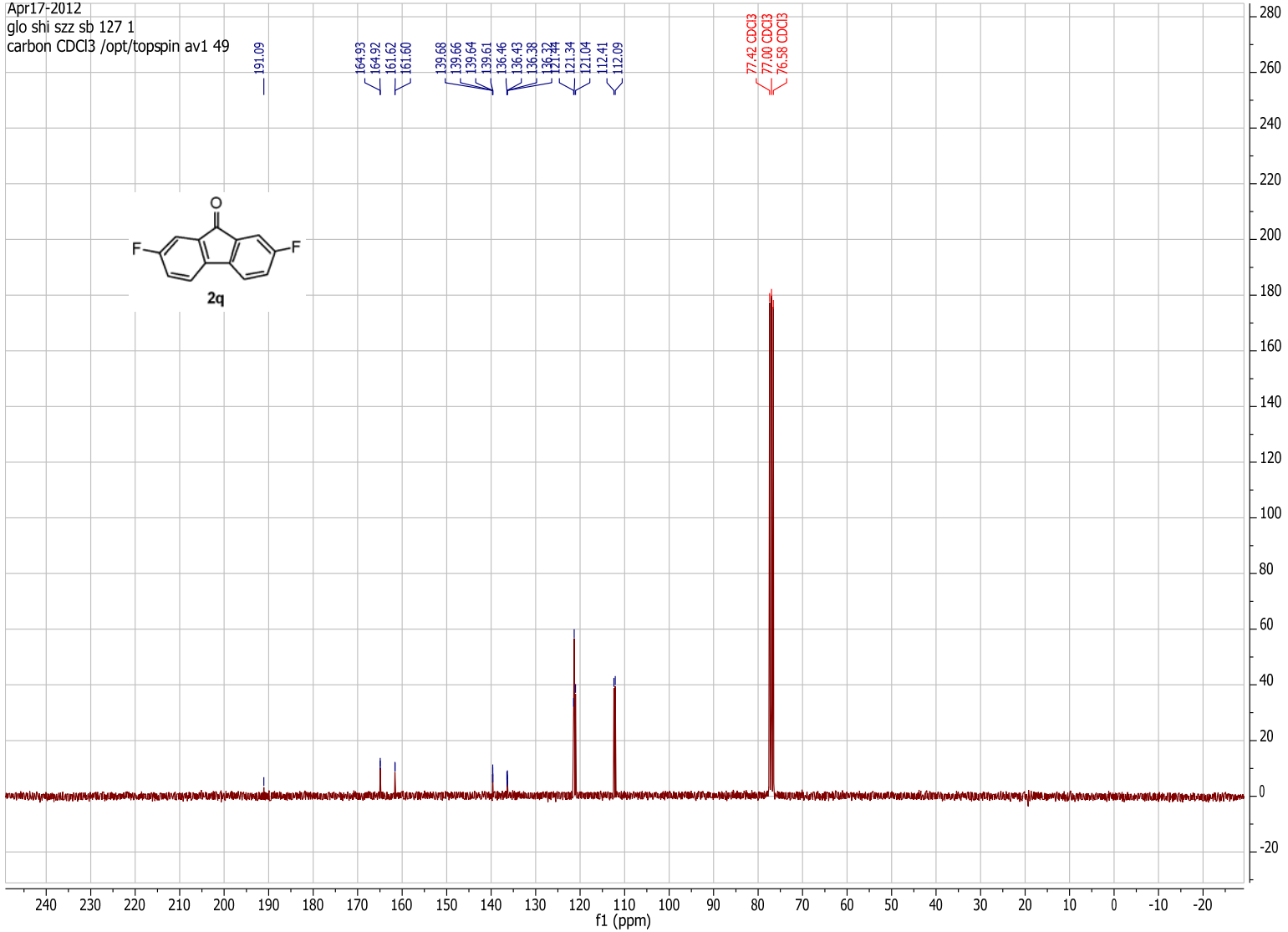

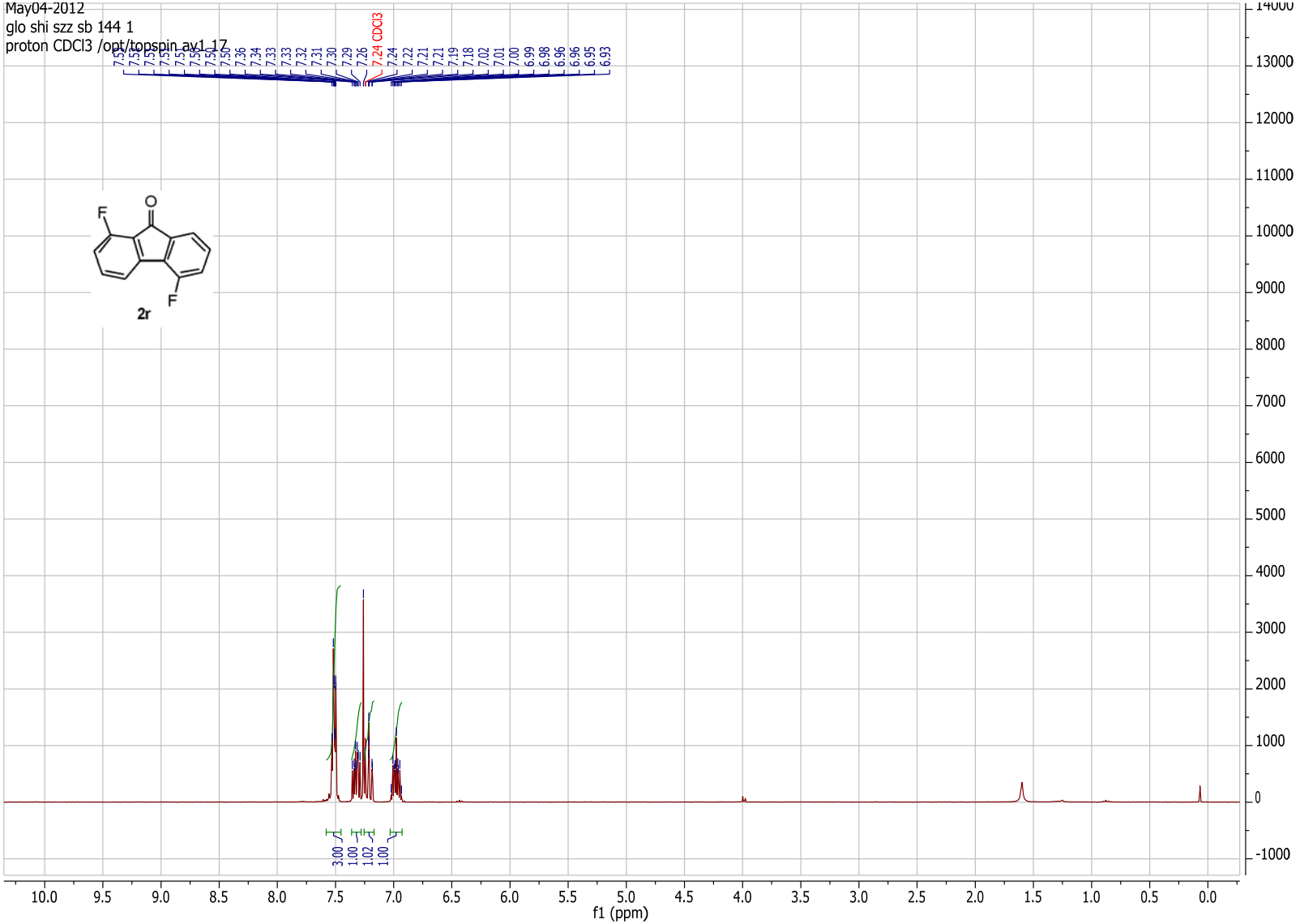

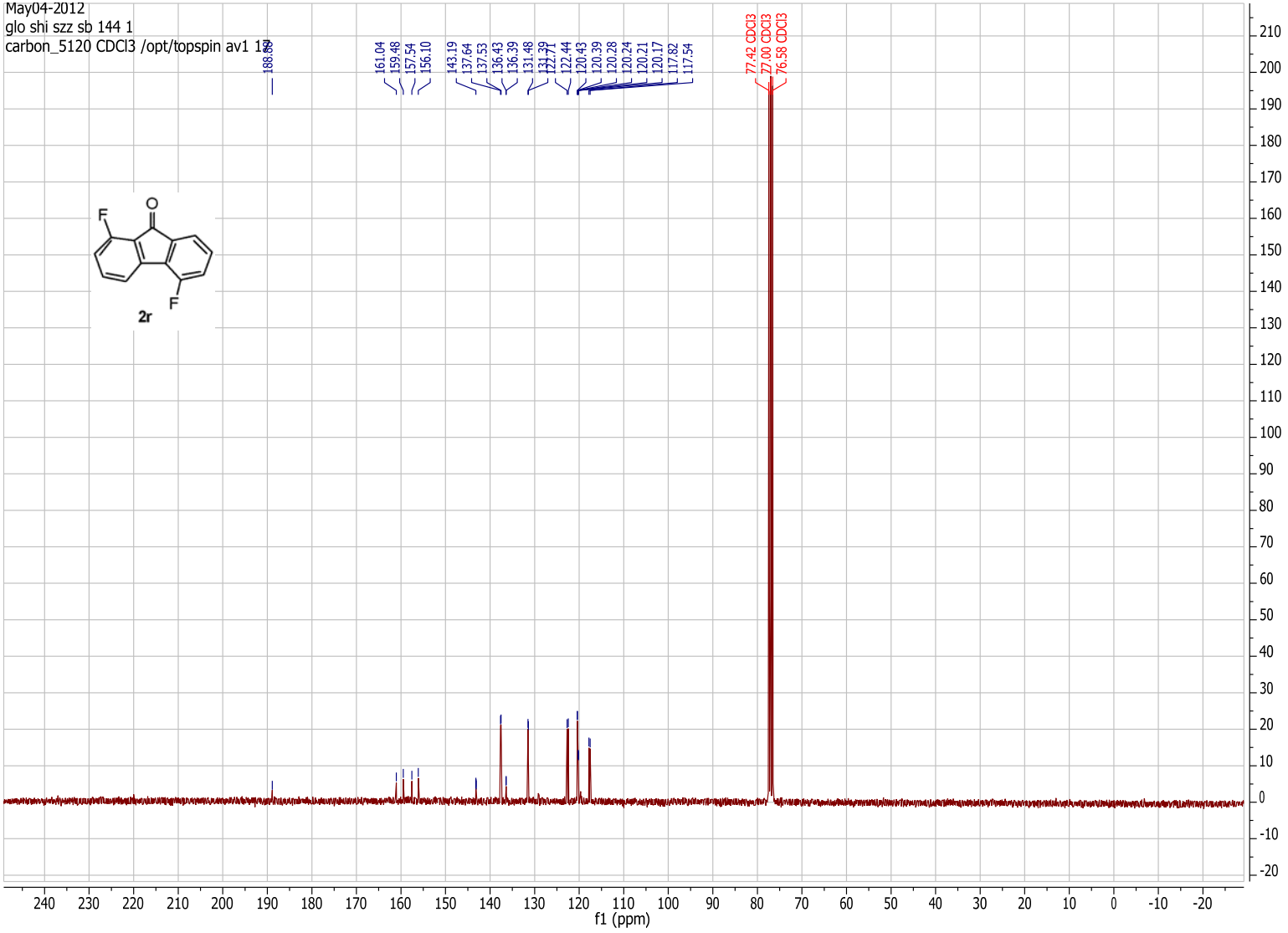
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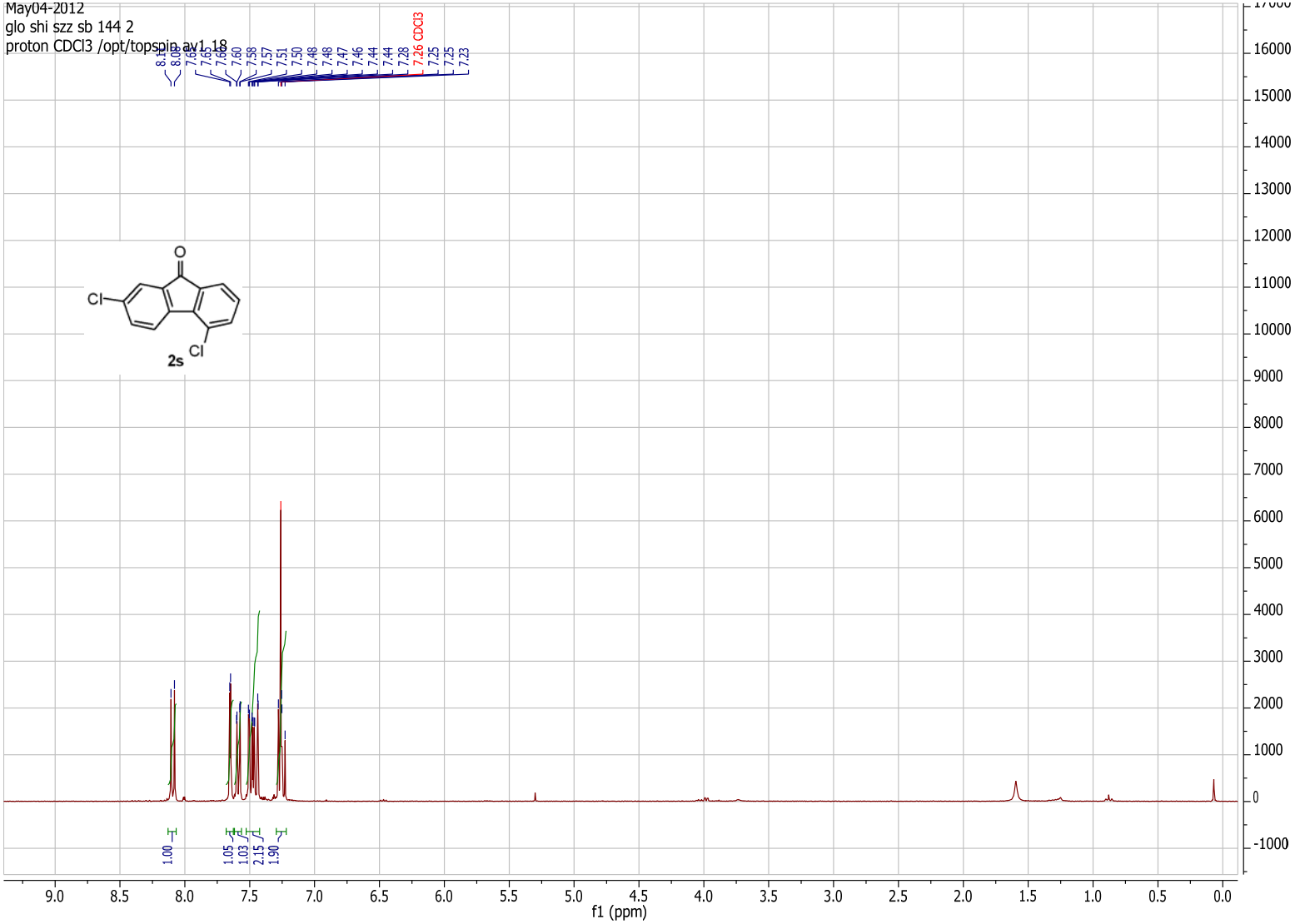

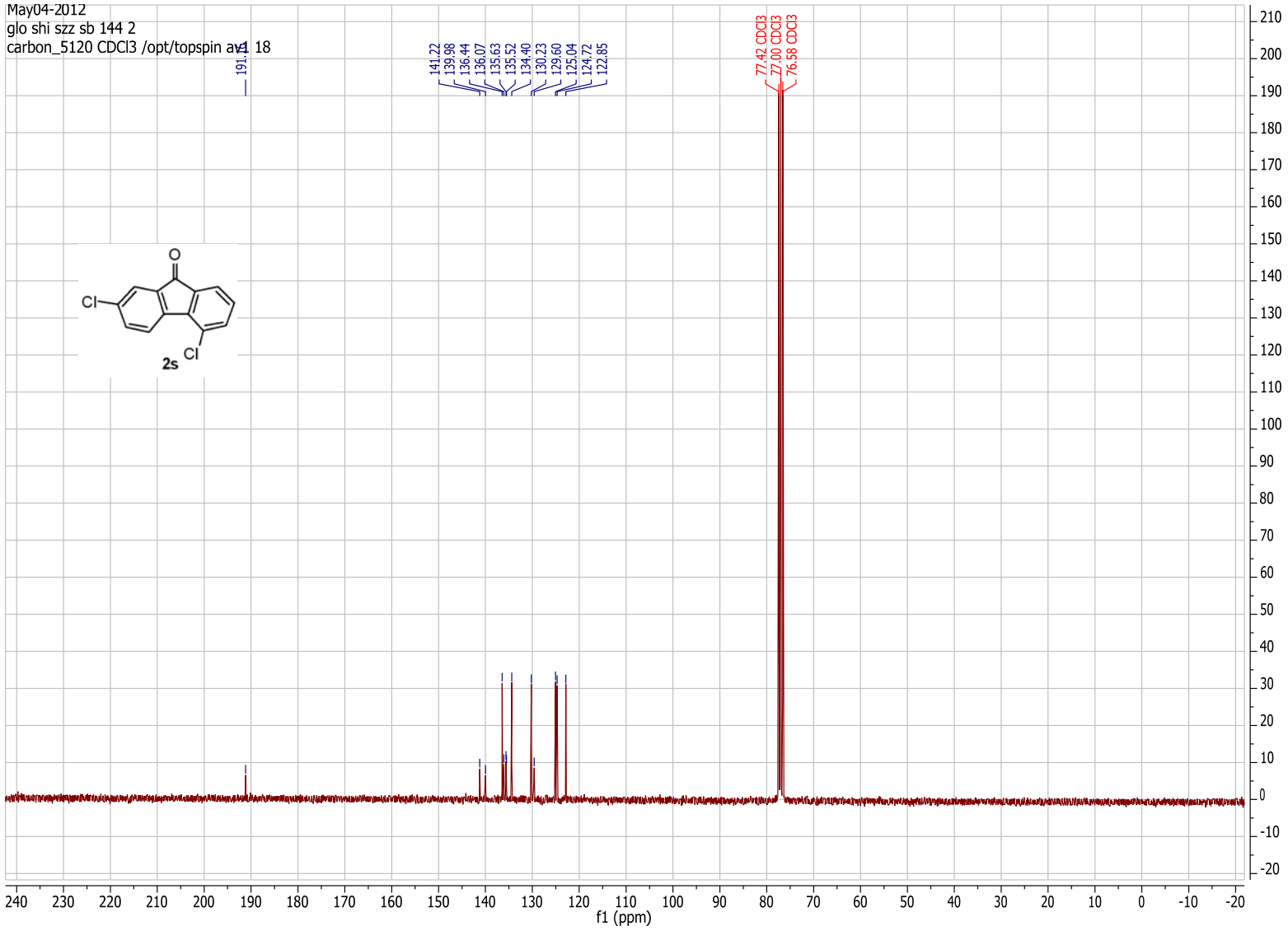

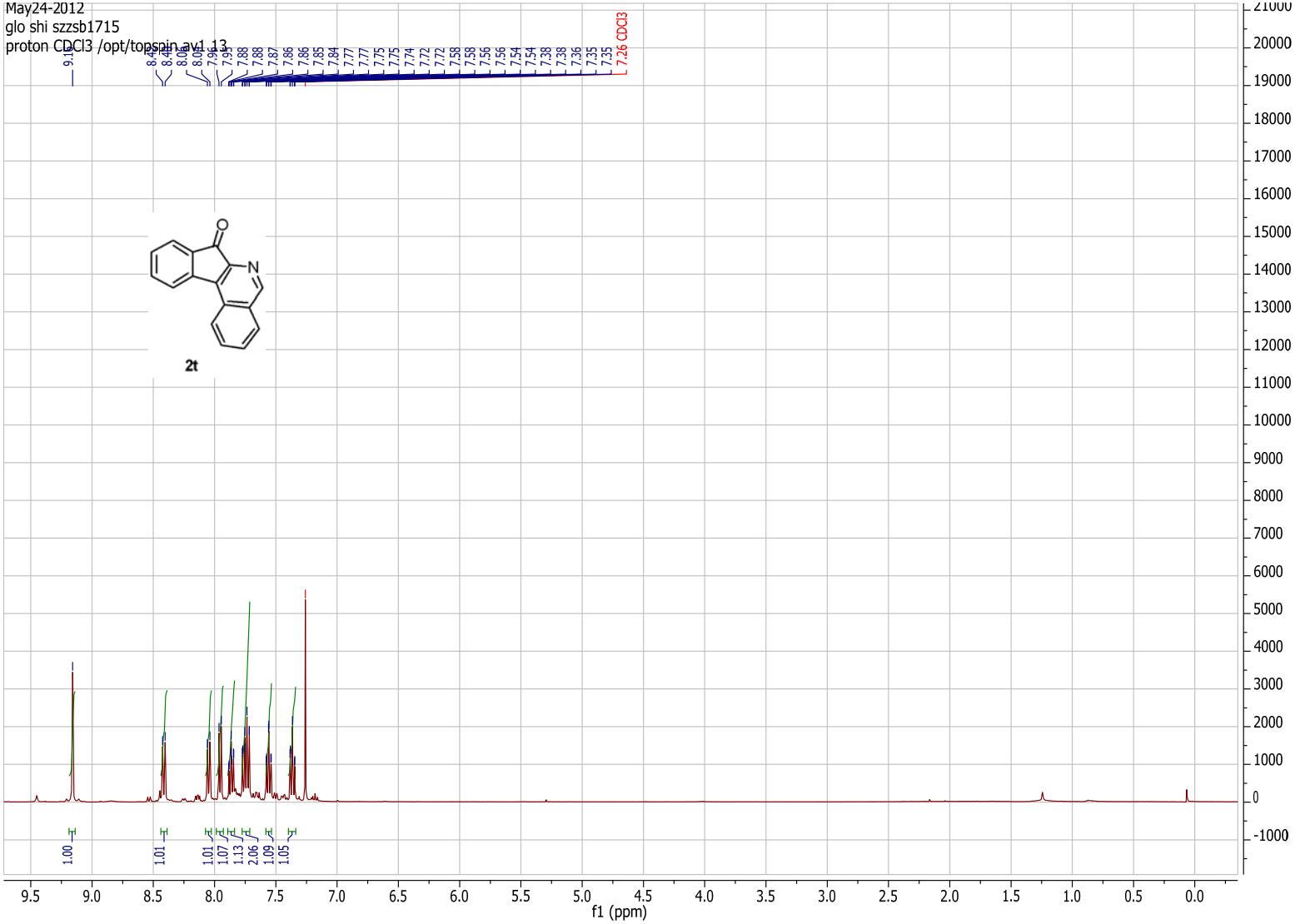

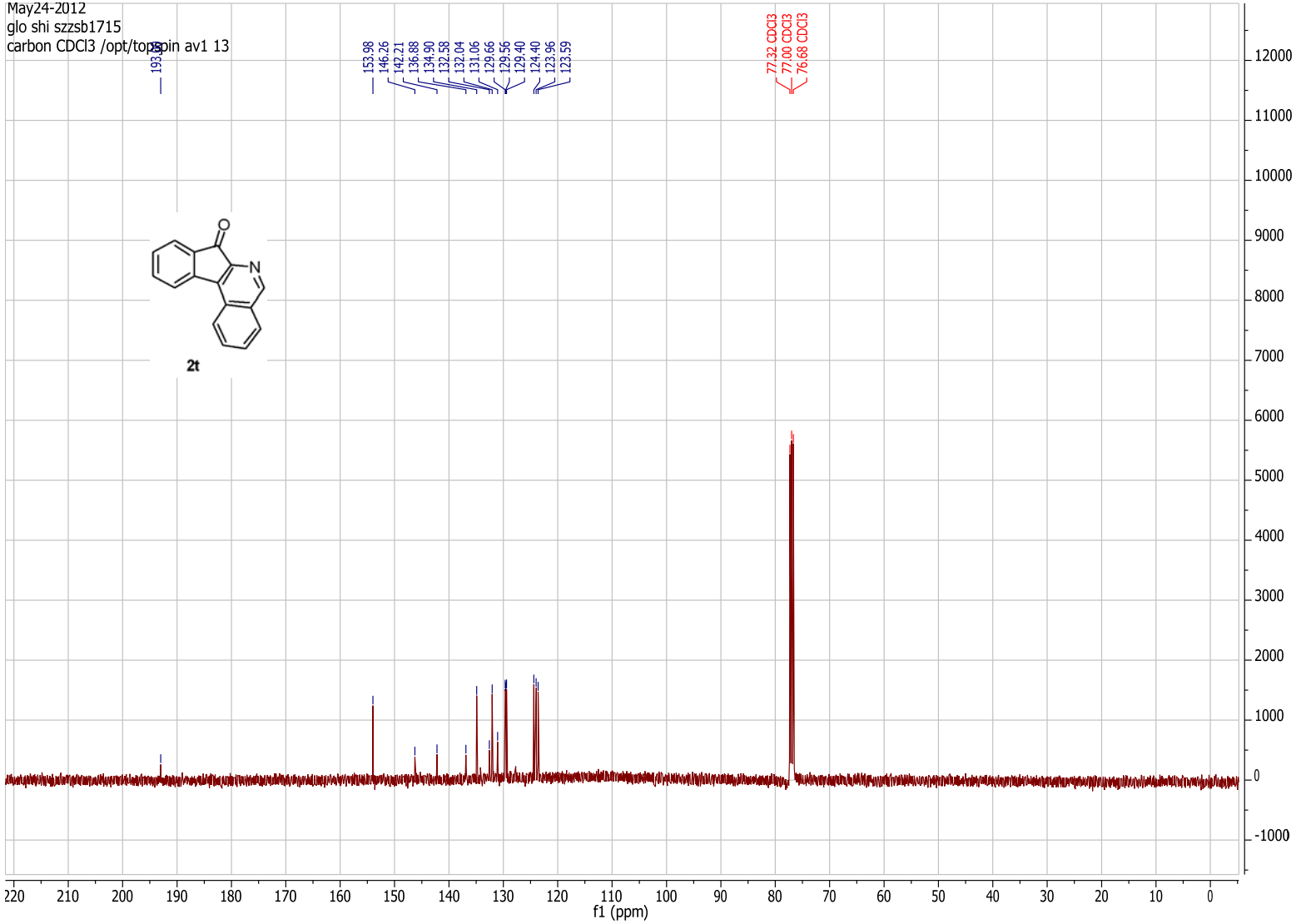
May24-2012
glo shi szzsb1715
carbon CDCl3 /opt/topspin av1 13
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153.98
146.26
142.21
136.88
134.90
132.58
132.04
131.06
129.66
129.56
129.40
124.40
123.96
123.59
77.32 CDCl3
77.00 CDCl3
76.68 CDCl3
2t
f1 (ppm)