

Supporting Information

**Rh Catalyzed C–H Activation and Oxidative Olefination without Chelate Assistance:
On the Reactivity of Bromoarenes**

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General Information

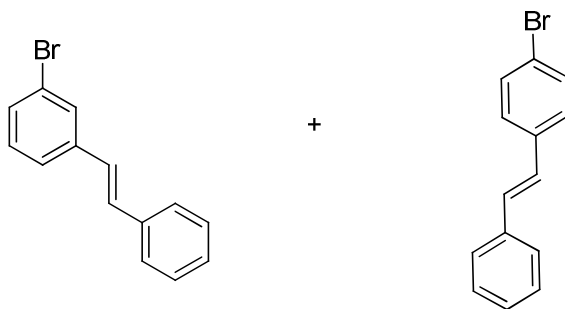
All reactions were carried out in dried reaction vessels with Teflon screw caps under argon. NMR-spectra were recorded on a Bruker ARX-300, AV-300, AV-400 MHz or on a Varian Associated, Varian 600 unity plus. Chemical shifts (δ) are quoted in ppm downfield of tetramethylsilane. Coupling constants (J) are quoted in Hz. All the solvents used for purifications were distilled. Flash chromatography was performed on Merck silica gel (40-63 mesh) by standard technique. GC-MS spectra were recorded on an Agilent Technologies 7890A GC-system with an Agilent 5975C VL MSD or an Agilent 5975 inert Mass Selective Detector (EI) and a HP-5MS column (0.25 mm x 30 m, film: 0.25 μ m). The major signals are quoted in m/z with the relative intensity in parentheses. The method used starts with the injection temperature T_0 . After holding this temperature for 3 min, the column is heated to temperature T_1 (ramp) and this temperature is held for an additional time t . Method: 50_40: T_0 = 50 $^{\circ}$ C, T_1 = 320 $^{\circ}$ C, ramp = 40 $^{\circ}$ C/min; t = 4 min.

1. Catalysis

Unless otherwise specified, the substrates (1 mmol scale), $[\text{RhCp}^*\text{Cl}_2]_2$ (0.025 mmol), AgSbF_6 (0.1 mmol), $\text{Cu}(\text{OAc})_2$ (2.2 mmol), pivalic acid (1.1 mmol) and 5 mL bromoarene were united under argon. The reactor was then closed and exposed to 140 $^{\circ}$ C for 21 h (magnetic stirring set to approx. 1000 turns/min). The reactor was then cooled to r.t. and the crude mixture (typically greenish slurry) was filtered through a short plug of SiO_2 with EtOAc.

After controlling conversion by GC-MS, the products were purified by SiO_2 column chromatography. The products were then analyzed by NMR and GC-MS mass spectrometry. ^{13}C and ^1H peak attributions were determined by ^1H - ^{13}C GHSQC, ^1H - ^{13}C GHMBC, ^1H - ^1H GCOSY and NOE-experiments. The isomeric ratios are reported in the same order as in the main text (Scheme 1).

2. Product purification and characterization



Chemical Formula: $\text{C}_{14}\text{H}_{11}\text{Br}$

Exact Mass: 258,0044

Molecular Weight: 259,1411

m/z : 258.0044 (100.0%), 260.0024 (97.3%), 259.0078 (15.1%), 261.0057 (14.7%), 260.0111 (1.1%), 262.0091 (1.0%)

Elemental Analysis: C, 64.89; H, 4.28; Br, 30.83

(3a) (*E*)-1-bromo-3-styrylbenzene and (3b) (*E*)-1-bromo-4-styrylbenzene. From bromobenzene and styrene. Product purified by SiO₂ gel column chromatography (height 340 mm, width 35 mm) in pentane/CH₂Cl₂ = 8/2. 65.9% isolated yield (white solid).

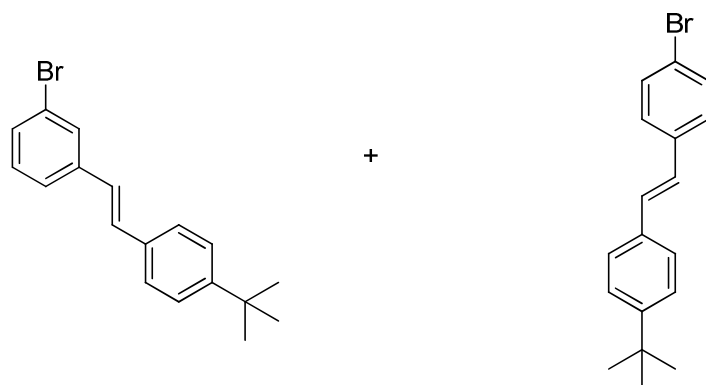
Both isomers are reported together (ratio: 14:7:ε:1 as determined by NMR). Traces of minor isomers (*R*_t = 8.77 min, 8.84 min,) and traces of dehalogenated product (*R*_t = 8.53 min) could be detected by GC-MS.

¹H NMR (300.1 MHz, CDCl₃) δ (ppm): 7.55 (dd, *J* ~ *J* ~ 1.8 Hz, 1H, CH), 7.43-7.07 (m, aromatic region), 6.99 (d, *J*_{trans} = 16.4 Hz, olefinic proton, major isomer), 6.98 (d, *J*_{trans} = 16.5 Hz, CH, minor isomer), 6.90 (d, *J*_{trans} = 16.5 Hz, olefinic proton, minor isomer), 6.89 (d, *J*_{trans} = 16.4 Hz, olefinic proton, major isomer).

¹³C{¹H} NMR (75.5 MHz, CDCl₃) δ (ppm): 139.61 (s, C_{quat}, major), 137.04 (s, C_{quat}, minor), 136.87 (s, C_{quat}, major), 136.36 (s, C_{quat}, minor), 131.88 (s, CH), 130.49 (s, CH), 130.26 (s, CH), 130.24 (s, CH), 129.50 (s, CH), 129.34 (s, CH), 128.86 (s, CH), 128.79 (s, CH), 128.16 (s, CH), 128.09 (s, CH), 128.01 (s, CH), 127.48 (s, CH), 127.17 (s, CH), 126.78 (s, CH), 126.68 (s, CH), 125.29 (s, CH), 123.00 (s, C_{quat}-Br, major), 121.41 (s, C_{quat}-Br, minor).

GC-MS: *R*_t (50_40): 9.34 min (major isomer), 9.38 min (minor isomer); EI: 261 (5), 260 (32), 259 (6), 258 (33), 180 (10), 179 (64), 178 (100), 177 (13), 176 (17), 152 (15), 151 (10), 89 (34), 88 (15), 77 (8), 76 (29), 75 (10), 63 (10), 51 (10), 50 (7).

ATR-FTIR (cm⁻¹): 3081 (olefinic C-H), 3059 (olefinic C-H), 3023 (olefinic C-H), 1585, 1554, 1494, 1470, 1449, 1424, 1073, 1007, 992, 965, 894, 880, 814, 750, 694, 682.



Chemical Formula: C₁₈H₁₉Br

Exact Mass: 314.0670

Molecular Weight: 315.2475

m/z: 314.0670 (100.0%), 316.0650 (97.3%), 315.0704 (19.5%), 317.0683 (18.9%), 316.0737 (1.8%), 318.0717 (1.7%)

Elemental Analysis: C, 68.58; H, 6.07; Br, 25.35

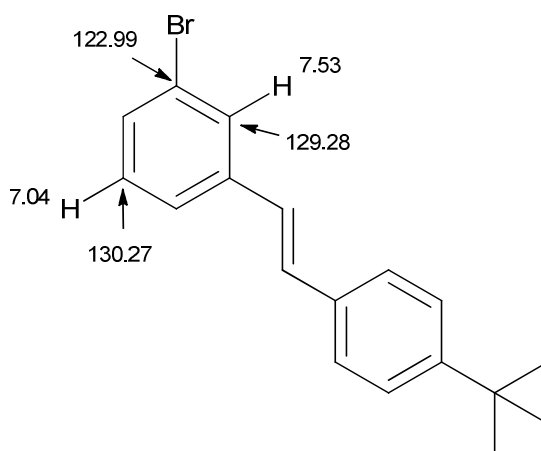
(3b) (*E*)-1-bromo-3-(4-(tert-butyl)styryl)benzene and (4b) (*E*)-1-bromo-4-(4-(tert-butyl)styryl)benzene. From bromobenzene and 4-tert-butylstyrene. Product purified by SiO₂ gel column chromatography (height 290 mm, width 35 mm) in pentane/CH₂Cl₂ = 8/2. 65.6% (21 h reaction time) or 68.7% (48 h reaction time) isolated yield (yellow solid).

Both isomers are reported together (ratio: 25:10:ε:1 as determined by NMR). Traces of minor isomers (*R*_t = 9.54 min, 9.59 min, 10.12 min) and traces of dehalogenated product (*R*_t = 9.48 min) could be detected by GC-MS.

^1H NMR (400.1 MHz, CDCl_3) δ (ppm): 7.52 (dd, $J \sim J \sim 1.7$ Hz, 1H, CH), 7.33-7.19 (m, aromatic region), 7.04 (dd, $J \sim J \sim 8.0$ Hz), 6.95 (d, $J_{\text{trans}} = 16.3$ Hz, olefinic proton, major isomer), 6.94 (d, $J_{\text{trans}} = 16.3$ Hz, olefinic proton, minor isomer), 6.85 (d, $J_{\text{trans}} = 16.3$ Hz, olefinic proton, minor isomer), 6.84 (d, $J_{\text{trans}} = 16.3$ Hz, olefinic proton, major isomer), 1.21 (broad m, *t*Bu-groups).

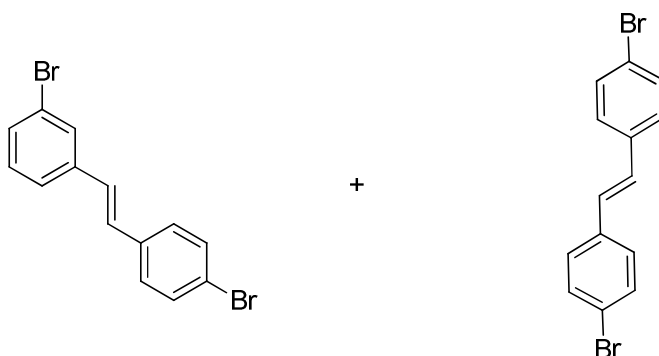
$^{13}\text{C}\{^1\text{H}\}$ NMR (100.6 MHz, CDCl_3) δ (ppm): 151.33 (s, C_{quat} , major), 151.17 (s, C_{quat} , minor), 139.84 (s, C_{quat} , major), 136.57 (s, C_{quat} , minor), 134.27 (s, C_{quat} , minor), 134.11 (s, C_{quat} , major), 131.83 (s, CH), 130.27 (s, CH), 130.22 (s, CH), 130.06 (s, CH), 129.33 (s, CH), 129.24 (s, CH), 127.99 (s, CH), 126.70 (s, CH), 126.55 (s, CH), 126.45 (s, CH), 126.39 (s, CH), 125.79 (s, CH), 125.78 (s, CH), 125.18 (s, CH), 122.99 (s, $\text{C}_{\text{quat}}\text{-Br}$), 121.16 (s, $\text{C}_{\text{quat}}\text{-Br}$), 34.77 (s, $\text{C}_{\text{quat}}\text{-}t\text{Bu-group}$, major), 34.75 (s, $\text{C}_{\text{quat}}\text{-}t\text{Bu-group}$, minor), 31.40 (s, both *t*Bu-group).

Major isomer



GC-MS: R_t (50_40): 10.23 min (major isomer), 10.25 min (minor isomer); EI: 317 (8), 316 (43), 315 (9), 314 (42), 302 (18), 301 (98), 300 (19), 299 (100), 220 (8), 205 (10), 203 (12), 202 (13), 191 (14), 189 (9), 179 (16), 178 (31), 176 (9), 165 (12), 152 (7), 128 (7), 115 (9), 102 (9), 101 (11), 96 (20), 95 (14), 91 (7), 89 (8), 77 (7), 76 (7), 57 (8), 41 (14).

ATR-FTIR (cm^{-1}): 3028 (olefinic C-H), 2961 (olefinic C-H), 2903 (olefinic C-H), 2867 (olefinic C-H), 1585, 1510, 1472, 1363, 1269, 1109, 1071, 964, 821, 685, 668.



Chemical Formula: $C_{14}H_{10}Br_2$

Exact Mass: 335,9149

Molecular Weight: 338,0372

m/z : 337.9129 (100.0%), 335.9149 (51.4%), 339.9108 (48.6%), 338.9162 (15.1%), 336.9183 (7.8%), 340.9142 (7.4%), 339.9196 (1.1%)

Elemental Analysis: C, 49.74; H, 2.98; Br, 47.28

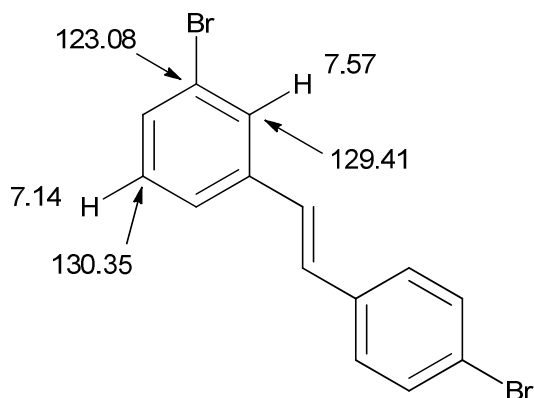
(3c) (*E*)-1-bromo-3-(4-bromostyryl)benzene and (4c) (*E*)-1-bromo-4-(4-bromostyryl)benzene. From bromobenzene and 4-bromostyrene. Product purified by SiO_2 gel column chromatography (height 370 mm, width 35 mm) in pentane/ CH_2Cl_2 = 8/2. 75.9% isolated yield (light yellow solid).

Both isomers are reported together (ratio: 11:6:ε:1 as determined by NMR). Traces of minor isomers (R_t = 9.57 min, 9.64 min, 10.05 min) and traces of dehalogenated product (R_t = 9.39 min) could be detected by GC-MS.

1H NMR (400.1 MHz, $CDCl_3$) δ (ppm): 7.57 (dd, $J \sim J \sim 1.8$ Hz, 1H, CH), 7.43-7.26 (m, aromatic region), 7.14 (dd, $J \sim J \sim 7.9$ Hz, 1H, CH), 6.94 (d, $J_{trans} = 16.4$ Hz, olefinic proton of major), 6.92 (s, olefinic proton of minor), 6.90 (d, $J_{trans} = 16.4$ Hz, olefinic proton of major).

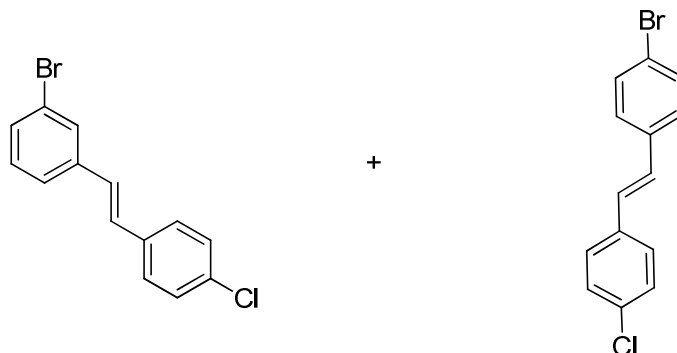
$^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$) δ (ppm): 139.26 (s, C_{quat}), 136.02 (s, C_{quat}), 135.85 (s, C_{quat}), 132.00 (s, CH), 131.99 (s, CH), 130.80 (s, CH), 130.35 (s, CH), 129.41 (s, CH), 128.99 (s, CH), 128.24 (s, CH), 128.23 (s, CH), 128.14 (s, CH), 127.92 (s, CH), 125.38 (s, CH), 123.08 (s, $C_{quat-Br}$), 121.96 (s, $C_{quat-Br}$), 121.77 (s, $C_{quat-Br}$).

Major isomer



GC-MS: R_t (50_40): 10.17 min (major isomer), 10.21 min (minor isomer) ; EI: 341 (5), 340 (30), 339 (10), 338 (62), 337 (5), 336 (32), 179 (16), 178 (100), 177 (14), 176 (23), 152 (10), 151 (10), 89 (22), 88 (20), 76 (14), 75 (10).

ATR-FTIR (cm^{-1}): 3049 (olefinic C-H), 3015 (olefinic C-H), 1581, 1555, 1486, 1410, 1074, 1007, 993, 970, 953, 876, 858, 834, 813, 787, 709, 694, 683, 658.



Chemical Formula: $\text{C}_{14}\text{H}_{10}\text{BrCl}$

Exact Mass: 291,9654

Molecular Weight: 293,5862

m/z : 291.9654 (100.0%), 293.9634 (97.3%), 293.9625 (32.0%), 295.9604 (31.1%), 292.9688 (15.1%), 294.9667 (14.7%), 294.9658 (4.8%), 296.9638 (4.7%), 293.9722 (1.1%), 295.9701 (1.0%)

Elemental Analysis: C, 57.27; H, 3.43; Br, 27.22; Cl, 12.08

(3d) (*E*)-1-bromo-3-(4-chlorostyryl)benzene and (4d) (*E*)-1-bromo-4-(4-chlorostyryl)benzene. From bromobenzene and 4-chlorostyrene. Product purified by SiO_2 gel column chromatography (height 310 mm, width 35 mm) in pentane/ CH_2Cl_2 = 8/2. 62.1% isolated yield (light yellow powder).

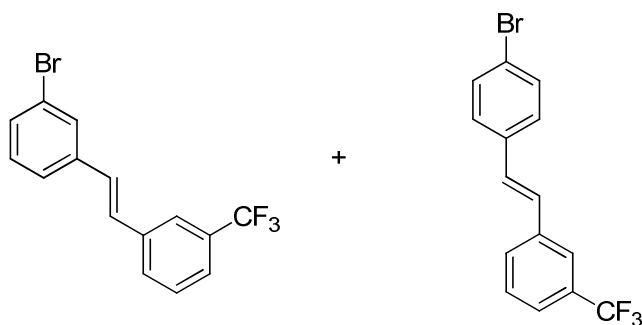
Both isomers are reported together (ratio: 13:6:ε:1 as determined by NMR). Traces of minor isomers (R_t = 9.38 min, 9.77 min,) and traces of dehalogenated product (R_t = 9.10 min) could be detected by GC-MS.

^1H NMR (300.1 MHz, CDCl_3) δ (ppm): 7.57 (dd, $J \sim J \sim 1.8$ Hz, 1H, CH), 7.38-7.17 (m, aromatic region), 7.15-7.20 (m, olefinic region), 7.11 (dd, $J \sim J \sim 7.9$ Hz, 1H, CH), 6.93 (d, J_{trans} = 16.6 Hz, olefinic proton, major), 6.92 (d, J_{trans} = 16.4 Hz, olefinic proton, minor), 6.86 (d, J_{trans} = 16.4 Hz, olefinic proton, minor), 6.85 (d, J_{trans} = 16.6 Hz, olefinic proton, major).

$^{13}\text{C}\{^1\text{H}\}$ NMR (75.5 MHz, CDCl_3) δ (ppm): 139.24 (s, C_{quat} , major), 136.00 (s, C_{quat} , minor), 135.54 (s, C_{quat} , minor), 135.37 (s, C_{quat} , major), 133.74 (s, C_{quat} , major), 133.56 (s, C_{quat} , minor), 131.94 (s, CH), 130.73 (s, CH), 130.31 (s, CH), 129.36 (s, CH), 129.03 (s, CH), 129.01 (s, CH), 128.88 (s, CH), 128.14 (s, CH), 128.10 (s, CH), 128.07 (s, CH), 127.91 (s, CH), 127.81 (s, CH), 127.76 (s, CH), 125.34 (s, CH), 123.04 (s, $\text{C}_{\text{quat}}\text{-Br}$, major), 121.70 (s, $\text{C}_{\text{quat}}\text{-Br}$, minor).

GC-MS: R_t (50_40): 9.89 min (major isomer), 9.92 min (minor isomer); EI: 296 (10), 294 (39), 292 (39), 212 (10), 179 (16), 178 (100), 177 (18), 176 (26), 152 (8), 151 (10), 88 (37), 76 (13), 75 (14), 63 (7), 51 (7).

ATR-FTIR (cm^{-1}): 3052 (olefinic C-H), 3016 (olefinic C-H), 1588, 1557, 1489, 1408, 1094, 1072, 1010, 993, 970, 876, 858, 817, 787, 704, 683, 666.



Chemical Formula: $C_{15}H_{10}BrF_3$

Exact Mass: 325.9918

Molecular Weight: 327.1391

m/z: 325.9918 (100.0%), 327.9898 (97.3%), 326.9952 (16.2%), 328.9931 (15.8%), 327.9985 (1.2%), 329.9965 (1.2%)

Elemental Analysis: C, 55.07; H, 3.08; Br, 24.43; F, 17.42

(3e) (*E*)-1-bromo-3-(3-(trifluoromethyl)styryl)benzene and (4e) (*E*)-1-(4-bromostyryl)-3-(trifluoromethyl)benzene. From bromobenzene and 1-(trifluoromethyl)-3-vinylbenzene. Product purified by SiO_2 gel column chromatography (height 330 mm, width 35 mm) in pentane/ CH_2Cl_2 (8:2). 74.8% isolated yield (light yellow oil).

Both isomers are reported together (ratio: 18:8:2:1 as determined by NMR). Traces of minor isomers (R_t = 8.62 min, 8.69 min, 9.10 min) and traces of dehalogenated product (R_t = 8.42 min) could be detected by GC-MS.

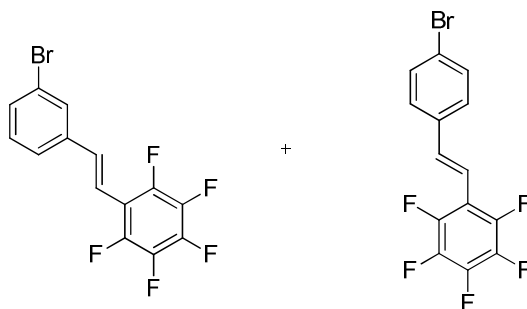
1H NMR (400.1 MHz, $CDCl_3$) δ (ppm): 7.61 (broad m, aromatic proton), 7.54 (t, J = 1.9 Hz), 7.50 (broad dm, J = 7.7 Hz), 7.41-7.21 (aromatic area), 7.10 (dd, $J \sim J \sim 7.8$ Hz, and possibly another signal underneath), 7.01-6.89 (olefinic area), 6.95 (d, J = 16.4 Hz, olefinic proton), 6.90 (d, J = 16.4 Hz, corresponding olefinic proton).

$^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$) δ (ppm): 138.76 (s, C_{quat} , major), 137.67 (s, C_{quat} , minor), 137.49 (s, C_{quat} , major), 135.54 (s, C_{quat} , minor), 131.85 (s, CH), 131.10 (q, C_{quat} , J = 32.2 Hz, C- CF_3 of major), 131.09 (q, C_{quat} , J = 32.2 Hz, C- CF_3 of minor), 130.89 (s, CH), 130.21 (s, CH), 129.65 (q, CH major, J = 1.2 Hz), 129.57 (q, CH minor, J = 1.2 Hz), 129.36 (s, CH), 129.15 (s, CH), 129.13 (s, CH), 128.81 (s, CH), 128.44 (s, CH), 128.09 (s, CH), 127.71 (s, CH), 126.66 (s, CH), 125.33 (s, CH), 126.60 (q, CH major, J = 3.8 Hz), 124.24 (q, CH minor, J = 3.8 Hz), 124.08 (q, C_{quat} , J = 272.4 Hz, CF_3 of minor), 124.04 (q, C_{quat} , J = 272.4 Hz, CF_3 of major), 123.15 (q, CH major, J = 3.8 Hz), 123.05 (q, CH minor, J = 3.8 Hz), 122.93 (s, C_{quat} , C-Br of major), 121.92 (s, C_{quat} , C-Br of minor).

$^{19}F\{^1H\}$ NMR (282.4 MHz, $CDCl_3$) δ (ppm): -62.69 (s, minor), -62.70 (s, major).

GC-MS: R_t (50_40): 9.23 min (major isomer), 9.27 min (minor isomer) ; EI: 329 (16), 328 (98), 327 (17), 326 (100), 247 (13), 246 (30), 245 (7), 227 (32), 225 (8), 207 (12), 179 (14), 178 (92), 177 (9), 176 (14), 152 (9), 151 (9), 75 (8).

ATR-FTIR (cm^{-1}): 3059 (olefinic C-H), 3041 (olefinic C-H), 1591, 1336, 1324, 1250, 1217, 1154, 1109, 1093, 1071, 956, 895, 879, 794, 773, 691, 697, 661.



Chemical Formula: C₁₄H₆BrF₅

Exact Mass: 347.9573

Molecular Weight: 349.0935

m/z: 347.9573 (100.0%), 349.9553 (97.3%), 348.9607 (15.1%), 350.9586 (14.7%), 349.9640 (1.1%), 351.9620 (1.0%)

Elemental Analysis: C, 48.17; H, 1.73; Br, 22.89; F, 27.21

(3f) (E)-1-(3-bromostyryl)-2,3,4,5,6-pentafluorobenzene and (4f) (E)-1-(4-bromostyryl)-2,3,4,5,6-pentafluorobenzene. From bromobenzene and 1,2,3,4,5-pentafluoro-6-vinylbenzene. Product purified by SiO₂ gel column chromatography (height 340 mm, width 35 mm) in pentane/CH₂Cl₂.(8:2). 52.5% isolated yield (white solid).

Both isomers are reported together (ratio: 57:23:4:1 as determined by NMR). Traces of a minor isomer (*R*_t = 8.87 min) and traces of dehalogenated product (*R*_t = 8.13 min) could be detected by GC-MS.

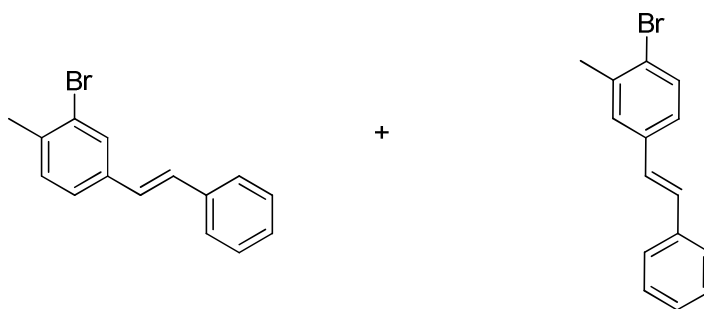
¹H NMR (400.1 MHz, CDCl₃) δ (ppm): 7.55 (t, *J* = 1.9 Hz, 1H of major), 7.40 (AA' part of a AA'BB' 4 spin system, 7.419, 7.413, 7.408, 7.397, 7.392, 7.386, 2H of minor), 7.35 (ddd, ³*J*_{ortho} ~ 7.9 Hz, *J* = 1.9 Hz, *J* = 1.0 Hz, 1H of major), 7.33 (dm, ³*J*_{ortho} ~ 7.9 Hz, 1H of major), 7.26 (BB' part of a AA'BB' 4 spin system, 7.289, 7.282, 7.277, overlapped, 7.261, overlapped, 2H of minor), 7.25 (broad d, *J*_{trans} = 16.8 Hz, olefinic proton of minor), 7.23 (broad d, *J*_{trans} = 16.8 Hz, olefinic proton of major), 7.15 (dd, ³*J*_{ortho} ~ ³*J*_{ortho} ~ 7.9 Hz, 1H of major), 6.85 (d, *J*_{trans} = 16.8 Hz, olefinic proton of major), 6.85 (d, *J*_{trans} = 16.8 Hz, olefinic proton of minor).

¹³C{¹H} NMR (100.6 MHz, CDCl₃) δ (ppm): 146.09 (m, C_{quat}), 143.60 (m, C_{quat}), 141.26 (m, C_{quat}), 138.89 (m, C_{quat}), 138.52 (s, C_{quat}, probably major), 135.77 (td, *J* = 8.3 Hz, *J* = 2.5 Hz, CH of minor), 135.45 (td, *J* = 8.6 Hz, *J* = 2.5 Hz, CH of major), 135.33 (s, C_{quat}, probably minor), 131.98 (s, CH), 131.72 (s, CH), 130.28 (s, CH), 129.61 (s, CH), 128.26 (s, CH), 125.46 (s, CH), 123.03 (s, C_{quat}, major), 122.96 (s, C_{quat}, minor), 114.07 (q, *J* = 2.5 Hz, CH of major), 113.30 (q, *J* = 2.5 Hz, CH of major), 111.87 (m, C_{quat}). The three missing C_{quat} are probably overlapped in broad multiplet areas.

¹⁹F{¹H} NMR (282.4 MHz, CDCl₃) δ (ppm): -142.40 (second ordered m, 2F of major), -142.58 (second ordered m, 2F of minor), -155.59 (tt, *J*_{ortho} = 20.8 Hz, *J*_{meta} = 1.2 Hz, 1F of major), -155.90 (~tt, *J*_{ortho} = 20.8 Hz, *J*_{meta} = 1.1 Hz, 1F of minor), -162.52 to -162.81 (overlapped second ordered multiplets, 2F and major and of minor).

GC-MS: *R*_t (50_40): 8.95 min (major isomer), 8.99 min (minor isomer) ; EI: 351 (14), 350 (94), 349 (15), 348 (96), 330 (17), 328 (18), 270 (8), 269 (50), 268 (24), 251 (8), 250 (53), 249 (10), 248 (13), 230 (8), 229 (10), 220 (14), 219, (100), 217 (7), 199 (10), 192 (8), 134 (13), 109 (27), 77 (10), 75 (9), 51 (9), 50 (7).

ATR-FTIR (cm⁻¹): 1519, 1491, 1419, 1131, 999, 959, 890, 813, 784, 681.



Chemical Formula: $C_{15}H_{13}Br$

Exact Mass: 272,0201

Molecular Weight: 273,1677

m/z: 272.0201 (100.0%), 274.0180 (97.3%), 273.0234 (16.2%), 275.0214 (15.8%), 274.0268 (1.2%), 276.0247 (1.2%)

Elemental Analysis: C, 65.95; H, 4.80; Br, 29.25

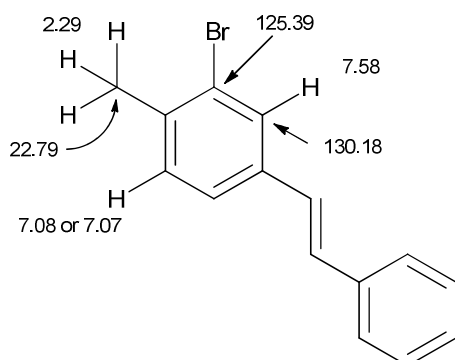
(3g) (E)-2-bromo-1-methyl-4-styrylbenzene and (4g) (E)-1-bromo-2-methyl-4-styrylbenzene. From 2-bromotoluene and styrene. Product purified by SiO_2 gel column chromatography (height 300 mm, width 35 mm) in pentane/ CH_2Cl_2 = 8/2. 52.3% isolated yield (off white solid).

Both isomers are reported together (ratio: 19:11:0:1 as determined by NMR). Traces of a third minor isomer (R_t = 9.06 min) could be detected by GC-MS.

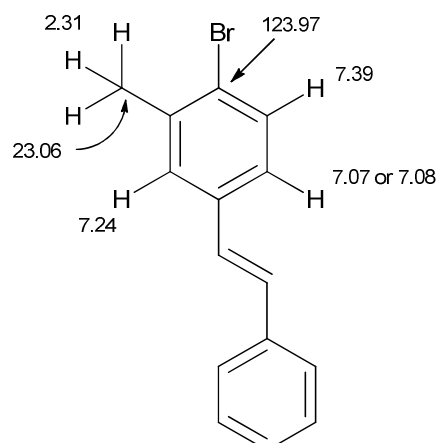
1H NMR (300.1 MHz, $CDCl_3$) δ (ppm): 7.58 (d, J = 1.7 Hz, 1H, CH), 7.40- 7.37 (m, aromatic region), 7.27-7.12 (m, aromatic region), 7.08 (broad d, J ~ 7.8 Hz, 2H, 2xCH), 6.98 (d, J_{trans} = 16.4 Hz, olefinic proton, minor isomer), 6.95 (d, J_{trans} = 16.4 Hz, olefinic proton, major isomer), 6.89 (d, J_{trans} = 16.4 Hz, olefinic proton, minor isomer), 6.87 (d, J_{trans} = 16.4 Hz, olefinic proton, major isomer), 2.31 (s, CH_3 , minor isomer), 2.29 (s, 3H, CH_3 , major isomer).

$^{13}C\{^1H\}$ NMR (75.5 MHz, $CDCl_3$) δ (ppm): 138.10 (s, C_{quat}), 137.18 (s, C_{quat}), 137.12 (s, C_{quat}), 137.10 (s, C_{quat}), 137.02 (s, C_{quat}), 136.65 (s, C_{quat}), 132.65 (s, CH), 131.02 (s, CH), 130.18 (s, CH), 129.25 (s, CH), 129.24 (s, CH), 128.95 (s, CH), 128.84 (s, CH), 128.83 (s, CH), 127.92 (s, CH), 127.91 (s, CH), 127.67 (s, CH), 127.09 (s, CH), 126.66 (s, CH), 126.64 (s, CH), 125.47 (s, CH), 125.39 (s, $C_{quat}-Br$), 125.37 (s, CH), 123.97 (s, $C_{quat}-Br$), 23.06 (s, CH_3 , minor isomer), 22.79 (s, CH_3 , major isomer).

Major isomer

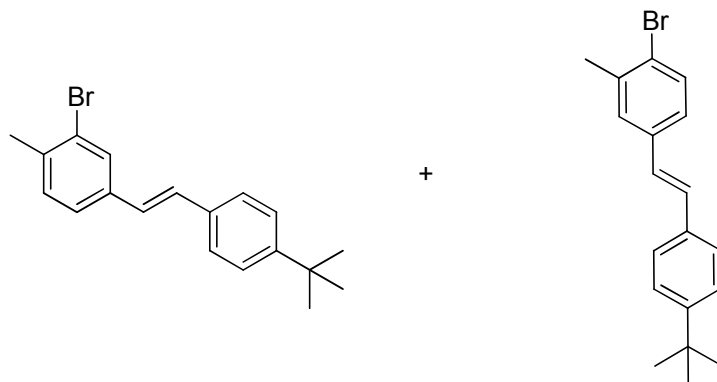


Minor isomer



GC-MS: R_t (50_40): 9.66 min (major isomers); EI: 275 (10), 274 (61), 273 (11), 272 (62), 193 (16), 192 (28), 191 (21), 190 (9), 189 (17), 179 (16), 178 (100), 177 (7), 165 (17), 152 (9), 115 (11), 96 (8), 95 (15), 94 (13), 89 (12), 83 (10), 82 (10), 63 (7).

ATR-FTIR (cm^{-1}): 3055 (olefinic C-H), 3026 (olefinic C-H), 2916 (olefinic C-H), 2852 (olefinic C-H), 1493, 1477, 1448, 1376, 1154, 1025, 995, 966, 895, 814, 752, 698, 689.



Chemical Formula: $\text{C}_{19}\text{H}_{21}\text{Br}$

Exact Mass: 328.0827

Molecular Weight: 329.2740

m/z : 328.0827 (100.0%), 330.0806 (97.3%), 329.0860 (20.5%), 331.0840 (20.0%), 330.0894 (2.0%), 332.0873 (1.9%)

Elemental Analysis: C, 69.30; H, 6.43; Br, 24.27

(3h) (*E*)-2-bromo-4-(4-(*tert*-butyl)styryl)-1-methylbenzene and (4h) (*E*)-1-bromo-4-(4-(*tert*-butyl)styryl)-2-methylbenzene. From 2-bromotoluene and 4-*tert*-butylstyrene. Product purified by SiO_2 gel column chromatography (height 300 mm, width 35 mm) in pentane/ CH_2Cl_2 = 8/2. 47.4% isolated yield (yellow oil).

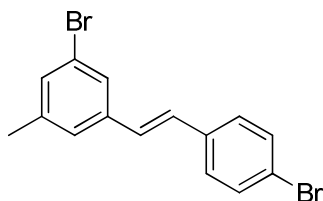
Both isomers are reported together (ratio: 15:9:0:1 as determined by NMR). Traces of a third minor isomer (R_t = 9.79 min) could be detected by GC-MS.

^1H NMR (300.1 MHz, CDCl_3) δ (ppm): 7.57 (d, J = 1.7 Hz, 1H, CH), 7.38-7.18 (m, aromatic region), 7.06 (broad d, 2H, 2xCH), 6.97 (d, J_{trans} = 16.3 Hz, olefinic proton, minor isomer), 6.94 (d, J_{trans} = 16.3 Hz, olefinic proton, major isomer), 6.85 (d, J_{trans} = 16.3 Hz, olefinic proton, minor isomer), 6.84 (d, J_{trans} = 16.3 Hz, olefinic proton, major isomer), 2.29 (s, CH_3 , minor isomer), 2.27 (s, CH_3 , major isomer), 1.23 (m, *t*Bu-groups).

$^{13}\text{C}\{^1\text{H}\}$ NMR (75.5 MHz, CDCl_3) δ (ppm): 151.09 (C_{quat}), 151.07 (C_{quat}), 138.04 (C_{quat}), 137.25 (C_{quat}), 136.86 (C_{quat}), 134.41 (C_{quat}), 134.33 (C_{quat}), 132.62 (CH), 131.00 (CH), 130.08 (CH), 129.06 (CH), 128.86 (CH), 126.89 (CH), 126.42 (CH), 126.41 (CH), 126.31 (CH), 125.79 (CH), 125.77 (CH), 125.38 (CH), 125.29 (CH), 123.74 ($\text{C}_{\text{quat}}\text{-Br}$), 34.76 ($\text{C}_{\text{quat}}\text{-}t\text{Bu}$ -groups), 31.41 (CH_3 , *t*Bu-groups), 23.07 (CH_3 , minor isomer), 22.79 (CH_3 , major isomer). One C_{quat} , one $\text{C}_{\text{quat}}\text{-Br}$ and one CH are overlapped.

GC-MS: R_t (50_40): 10.54 min (major isomers); EI: 331 (11), 330 (51), 329 (11), 328 (52), 316 (20), 315 (98), 314 (20), 313 (100), 234 (9), 219 (8), 204 (7), 203 (10), 202 (10), 192 (9), 191 (14), 189 (12), 179 (7), 178 (15), 165 (7), 143 (8), 142 (8), 115 (11), 103 (19), 102 (11), 101 (8), 89 (9), 41 (7).

ATR-FTIR (cm^{-1}): 2961 (olefinic C-H), 2867 (olefinic C-H), 1600, 1511, 1363, 1269, 962, 823, 630.



Chemical Formula: $\text{C}_{15}\text{H}_{12}\text{Br}_2$

Exact Mass: 349,9306

Molecular Weight: 352,0638

m/z : 351.9285 (100.0%), 349.9306 (51.4%), 353.9265 (48.6%), 352.9319 (16.2%), 350.9339 (8.3%), 354.9298 (7.9%), 353.9352 (1.2%)

Elemental Analysis: C, 51.17; H, 3.44; Br, 45.39

(3i) (*E*)-1-bromo-3-(4-bromostyryl)-5-methylbenzene. From 3-bromotoluene and 4-bromostyrene. Product purified by SiO_2 gel column chromatography (height 300 mm, width 35 mm) in pentane/ CH_2Cl_2 = 8/2. 39.0% isolated yield (off white solid) after 21 hours reaction time.

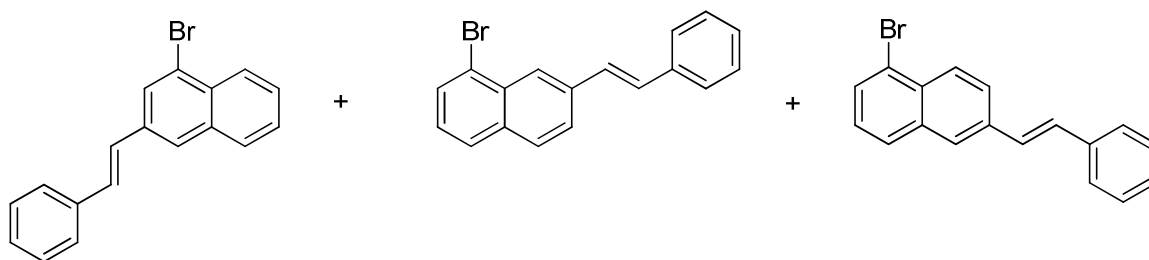
Traces of a minor isomer (R_t = 9.74 min) and traces of dehalogenated product (R_t = 9.65 min) could be detected by GC-MS. Molar ratio as determined by NMR: (1: ϵ :0).

^1H NMR (300.1 MHz, CDCl_3) δ (ppm): 7.36 (AA' half of AA'BB' 4 spin system, 7.383, 7.375, 7.369, 7.352, 7.347, 7.339), 7.33 (broad s, CH), 7.21 (BB' half of AA'BB' 4 spin system, 7.236, 7.229, 7.223, 7.206, 7.200, 7.193), 7.11 (broad s, CH), 7.07 (broad s, CH), 6.88 (d, J_{trans} = 16.5 Hz, olefinic proton), 6.81 (d, J_{trans} = 16.5 Hz, olefinic proton), 2.22 (s, 3H, CH_3).

$^{13}\text{C}\{^1\text{H}\}$ NMR (75.5 MHz, CDCl_3) δ (ppm): 140.40 (C_{quat}), 138.91 (C_{quat}), 135.88 (C_{quat}), 131.93 (CH), 131.43 (CH), 128.64 (CH), 128.15 (CH), 128.00 (CH), 126.50 (CH), 126.21 (CH), 122.80 (s, $\text{C}_{quat}\text{-Br}$), 121.80 (s, $\text{C}_{quat}\text{-Br}$), 21.26 (s, CH_3).

GC-MS: R_t (50_40): 10.43 min; EI: 355 (8), 354 (48), 353 (16), 352 (99), 351 (9), 350 (51), 258 (8), 256 (9), 193 (17), 192 (100), 191 (60), 190 (19), 189 (34), 176 (13), 165 (19), 152 (7), 115 (9), 96 (27), 95 (29), 82 (14), 75 (7), 63 (9).

ATR-FTIR (cm^{-1}): 3022 (olefinic C-H), 2950 (olefinic C-H), 2916 (olefinic C-H), 2856 (olefinic C-H), 1485, 1073, 1007, 956, 834, 816, 800, 688, 671.



Chemical Formula: $C_{18}H_{13}Br$

Exact Mass: 308.0201

Molecular Weight: 309.1998

m/z : 308.0201 (100.0%), 310.0180 (97.3%), 309.0234 (19.5%), 311.0214 (18.9%),
310.0268 (1.8%), 312.0247 (1.7%)

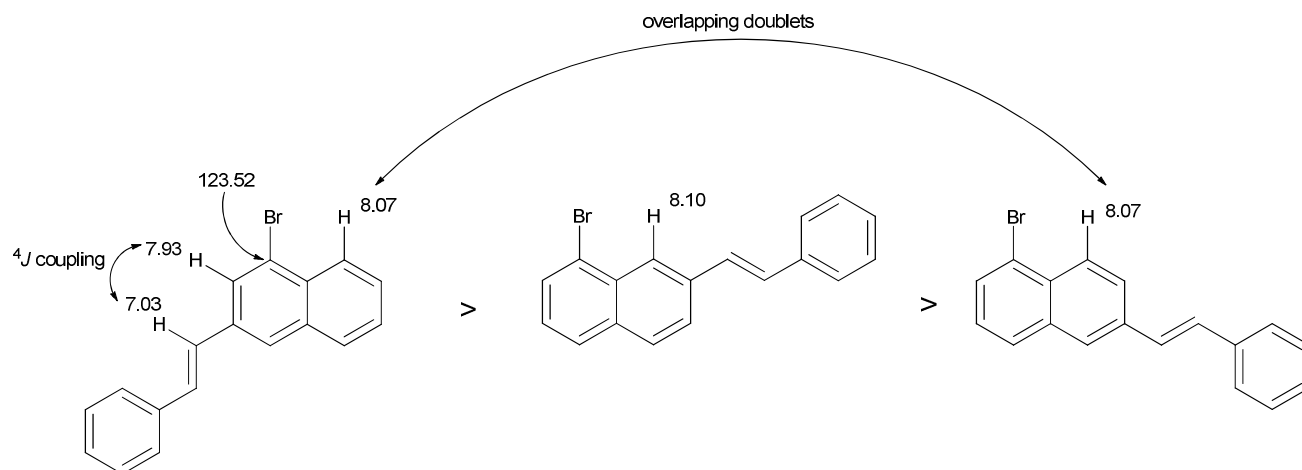
Elemental Analysis: C, 69.92; H, 4.24; Br, 25.84

(7j) (*E*)-1-bromo-3-styrylnaphthalene, (8j) (*E*)-1-bromo-7-styrylnaphthalene and (9j) (*E*)-1-bromo-6-styrylnaphthalene. From 1-bromonaphthalene and styrene. Product purified by SiO_2 gel column chromatography (height 300 mm, width 35 mm) in pentane, then pentane/ CH_2Cl_2 = 8/2. 36.5% isolated yield (off white solid).

All three isomers are reported together (ratio: 10:7:6:ε:1 as determined by NMR). Traces of minor isomers (R_t = 10.14 min, 10.22 min, 10.27 min, 10.31 min) and traces of two dehalogenated products (R_t = 9.42 min, 9.99 min) could be detected by GC-MS.

1H NMR (400.1 MHz, $CDCl_3$) δ (ppm): 8.10 (s, 1H, CH), 8.07 (broad d, $J \sim 8.8$ Hz), 8.07 (broad d, $J \sim 7.8$ Hz), 7.93 (d, $J = 1.6$ Hz, 1H, CH), 7.70-7.11 (aromatic region), 7.08 (d, $J_{trans} = 16.4$ Hz, 1H, olefinic proton), 7.03 (d, $J_{trans} = 16.4$ Hz, 1H, olefinic proton).

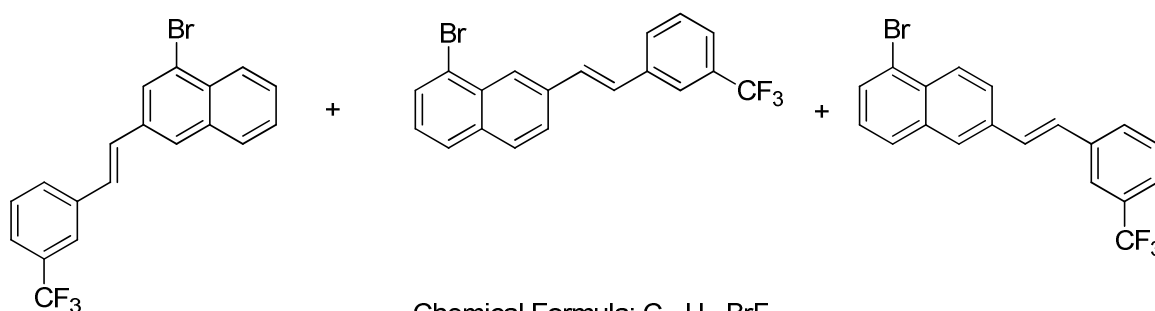
$^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$) δ (ppm): 137.22 (s, C_{quat}), 137.18 (s, C_{quat}), 137.02 (s, C_{quat}), 136.47 (s, C_{quat}), 135.79 (s, C_{quat}), 135.63 (s, C_{quat}), 135.05 (s, C_{quat}), 134.77 (s, C_{quat}), 134.28 (s, C_{quat}), 132.40 (s, C_{quat}), 131.59 (s, C_{quat}), 131.51 (s, C_{quat}), 130.50 (s, CH), 130.09 (s, CH), 130.08 (s, CH), 130.03 (s, CH), 129.89 (s, CH), 128.89 (s, CH), 128.88 (s, CH), 128.87 (s, CH), 128.58 (s, CH), 128.51 (s, CH), 128.12 (s, CH), 128.06 (s, CH), 128.05 (s, CH), 128.03 (s, CH), 127.80 (s, CH), 127.62 (s, CH), 127.51 (s, CH), 127.34 (s, CH), 127.28 (s, CH), 127.19 (s, CH), 126.81 (s, CH), 126.79 (s, CH), 126.78 (s, CH), 126.77 (s, CH), 126.56 (s, CH), 126.23 (s, CH), 125.94 (s, CH), 125.11 (s, CH), 124.32 (s, CH), 123.52 (s, $C_{quat}-Br$), 122.98 (s, $C_{quat}-Br$), 122.84 (s, $C_{quat}-Br$). The four missing CH are probably overlapped.



The species at the left side is the only one which shows a long range (GHMBC) correlation between the C_{quat}-Br and the olefinic proton.

GC-MS: R_t (50_40): 10.22 min (minor isomer), 10.26 min (minor isomer), 10.31 min (minor isomer), 10.98 (major isomer), 11.05 (major isomer); EI: 311 (12), 310 (64), 309 (15), 308 (62), 230 (11), 229 (59), 228 (100), 227 (26), 226 (41), 2020 (16), 114 (32), 113 (27), 101 (17), 100 (7).

ATR-FTIR (cm⁻¹): 3055 (olefinic C-H), 3025 (olefinic C-H), 1591, 1494, 1447, 1360, 1260, 1200, 961, 909, 876, 820, 740, 687, 658.



Chemical Formula: C₁₉H₁₂BrF₃

Exact Mass: 376.0074

Molecular Weight: 377.1978

m/z: 376.0074 (100.0%), 378.0054 (97.3%), 377.0108 (20.5%), 379.0088 (20.0%), 378.0142 (2.0%), 380.0121 (1.9%)

Elemental Analysis: C, 60.50; H, 3.21; Br, 21.18; F, 15.11

(7k) (E)-1-bromo-3-(3-(trifluoromethyl)styryl)naphthalene, (8k) (E)-1-bromo-7-(3-(trifluoromethyl)styryl)naphthalene and (9k) (E)-1-bromo-6-(3-(trifluoromethyl)styryl)naphthalene. From 1-bromonaphthalene and 3-(trifluoromethyl)-styrene. Product purified by SiO₂ gel column chromatography (height 300 mm, width 35 mm) in pentane, then pentane/CH₂Cl₂ = 8/2. 34.4% isolated yield (yellow sticky oil).

All isomers are reported together (ratio: 18:15:9:ε:1 as determined by NMR). Traces of minor isomers (R_t = 10.00 min, 10.02 min, 10.07 min, 10.47 min) and traces of dehalogenated product (R_t = 9.82 min) could be detected by GC-MS.

¹H NMR (300.1 MHz, CDCl₃) δ (ppm): 8.07-8.02 (m, aromatic region), 7.86 (d, *J* = 1.7 Hz, 1H, CH), 7.69-7.29 (m, aromatic region), 7.20-7.06 (m, aromatic region), 7.02 (d, *J*_{trans} = 16.3 Hz, olefinic proton), 6.96 (d, *J*_{trans} = 16.3 Hz, olefinic proton).

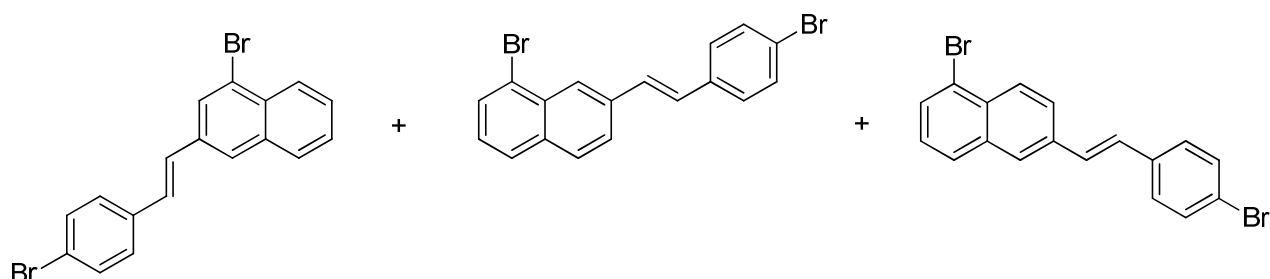
¹³C{¹H} NMR (75.5 MHz, CDCl₃) δ (ppm): 137.95 (s, C_{quat}), 137.92 (s, C_{quat}), 137.74 (s, C_{quat}), 135.72 (s, C_{quat}), 135.05 (s, C_{quat}), 134.92 (s, C_{quat}), 134.85 (s, C_{quat}), 134.63 (s, C_{quat}), 134.46 (s, C_{quat}), 132.29 (s, C_{quat}), 131.78 (s, C_{quat}), 131.70 (s, C_{quat}), 131.23 (q, C_{quat}, ²*J* = 32.2 Hz), 131.22 (q, C_{quat}, ²*J* = 32.2 Hz), 130.60 (s, CH), 130.29 (s, CH), 130.17 (s, CH), 129.79-129.74 (m, CH area), 129.76 (s, CH), 129.74 (s, CH), 129.30 (s, CH), 129.27 (s, CH), 129.26 (s, CH), 129.05 (s, CH), 129.01 (s, CH), 128.60 (s, CH), 128.32 (s, CH), 128.28 (s, CH), 128.14 (s, CH), 127.79 (s, CH), 127.74 (s, CH), 127.64 (s, CH), 127.38 (s, CH), 127.32 (s, CH), 127.28 (s, CH), 127.19 (s, CH), 127.08 (s, CH), 126.90 (s, CH), 126.51 (s, CH), 126.43 (s, CH), 124.87 (s, CH), 124.53-124.29 (m, CHs of the major isomers coupling with CF₃-group), 124.28 (q, ¹*J* = 272.2 Hz, CF₃), 124.26 (q, ¹*J* = 272.2 Hz, CF₃), 124.14 (s, CH), 123.63 (s, C_{quat}-Br, major isomer), 123.35-123.16 (m, CHs of the major isomers coupling with

CF₃-group), 123.05 (s, C_{quat}-Br, major isomer), 122.83 (s, C_{quat}-Br, major isomer). The missing lines are overlapped.

¹⁹F{¹H} NMR (282.4 MHz, CDCl₃) δ (ppm): -62.69 (CF₃, major isomer), -62.67 (CF₃, other major isomer), -62.66 (CF₃, other major isomer). Much smaller peaks of minor isomers could be observed.

GC-MS: R_t (50_40): 9.99 min (minor isomer), 10.02 min (minor isomer), 10.07 min (minor isomer), 10.47 min (minor isomer), 10.72 min (major isomer), 10.76 min (major isomer), 10.83 min (major isomer); EI: 379 (20), 378 (97), 377 (21), 376 (100), 297 (13), 296 (33), 277 (8), 275 (8), 257 (10), 229 (14), 228 (72), 227 (18), 152 (7), 151 (8), 139 (14), 138 (7), 127 (7), 114 (8), 113 (17).

ATR-FTIR (cm⁻¹): 3040, 2928, 1328, 1163, 1120, 1096, 1074, 957, 695, 663, 632.



Chemical Formula: C₁₈H₁₂Br₂

Exact Mass: 385.9306

Molecular Weight: 388.0959

m/z: 387.9285 (100.0%), 385.9306 (51.4%), 389.9265 (48.6%), 388.9319 (19.5%), 386.9339 (10.0%), 390.9298 (9.5%), 389.9352 (1.8%)

Elemental Analysis: C, 55.71; H, 3.12; Br, 41.18

(7I) (*E*)-1-bromo-3-(4-bromostyryl)naphthalene, (8I) (*E*)-1-bromo-7-(4-bromostyryl)naphthalene and (9I) (*E*)-1-bromo-6-(4-bromostyryl)naphthalene. From 1-bromonaphthalene and 4-bromostyrene. Product purified by SiO₂ gel column chromatography (height 300 mm, width 35 mm) in pentane, then pentane/CH₂Cl₂ = 8/2. 57.1% isolated yield (yellow sticky oil).

All isomers are reported together. Minor isomers (R_t = 11.07 min, 11.12 min, 11.20 min) and traces of three dehalogenated products (R_t = 10.16 min, 10.87 min, 10.98 min) could be detected by GC-MS.

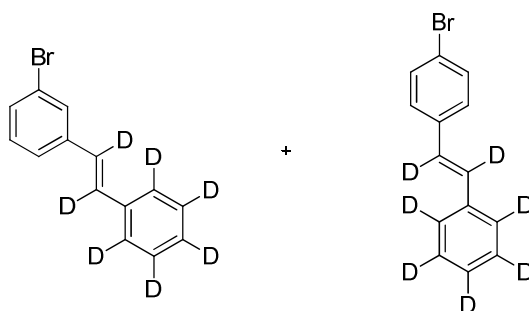
¹H NMR (400.1 MHz, CDCl₃) δ (ppm): 8.06-8.03 (m, aromatic region), 7.86 (d, *J* = 1.6 Hz, 1H, CH), 7.74-7.56 (m, aromatic region), 7.44-7.10 (m, aromatic region), 7.07-6.88 (m, olefinic region), 7.04 (d, *J* = 16.8 Hz, olefinic proton), 7.00 (d, *J* = 16.8 Hz, olefinic proton), 6.98 (d, *J* = 16.4 Hz, olefinic proton), 6.96 (d, *J* = 16.4 Hz, olefinic proton), 6.90 (d, *J* = 16.4 Hz, olefinic proton).

¹³C{¹H} NMR (100.6 MHz, CDCl₃) δ (ppm): 136.11 (s, C_{quat}), 136.06 (s, C_{quat}), 136.03 (s, C_{quat}), 135.89 (s, C_{quat}), 135.36 (s, C_{quat}), 135.18 (s, C_{quat}), 134.95 (s, C_{quat}), 134.67 (s, C_{quat}), 134.33 (s, C_{quat}), 132.32 (s, C_{quat}), 131.95 (s, CH), 131.93 (s, CH), 131.92 (s, CH), 131.64 (s, C_{quat}), 131.57 (s, C_{quat}), 130.55 (s, CH), 130.02 (s, CH), 129.22 (s, CH), 128.94 (s, CH), 128.69 (s, CH), 128.67 (s, CH), 128.62 (s, CH), 128.52 (s, CH), 128.23 (s, CH), 128.18 (s, CH), 128.15 (s, CH), 128.06 (s, CH), 127.96 (s, CH), 127.78 (s, CH), 127.67 (s, CH), 127.48 (s, CH), 127.33 (s, CH), 127.17 (s, CH), 126.99 (s, CH), 126.84 (s, CH), 126.75 (s, CH), 126.36 (s, CH), 126.12 (s, CH), 124.92 (s, CH), 124.16 (s, CH), 123.57 (s, C_{quat}-Br), 122.99

(s, C_{quat}-Br), 122.83 (s, C_{quat}-Br), 121.83 (s, C_{quat}-Br), 121.75 (s, C_{quat}-Br), 121.73 (s, C_{quat}-Br). (Only the main visible lines are given).

GC-MS: R_t (50_40): 11.07 min (minor isomer), 11.12 min (minor isomer), 11.20 min (minor isomer), 12.30 min (major isomer), 12.35 min (major isomer), 12.46 min (major isomer); EI: 391 (7), 390 (40), 389 (16), 388 (81), 387 (8), 386 (42), 229 (19), 228 (100), 227 (37), 226 (57), 225 (8), 224 (9), 207 (8), 114 (36), 113 (49), 112 (10), 101 (16), 100 (9).

ATR-FTIR (cm⁻¹): 3053 (olefinic C-H), 3023 (olefinic C-H), 1485, 1072, 1007, 960, 854, 844, 818, 764, 741, 660, 631.



Chemical Formula: C₁₄H₄D₇Br

Exact Mass: 265.0484

Molecular Weight: 266.1843

m/z: 265.0484 (100.0%), 267.0463 (97.3%), 266.0517 (15.1%), 268.0497 (14.7%), 267.0551 (1.1%), 269.0530 (1.0%)

Elemental Analysis: C, 63.17; H, 6.81; Br, 30.02

(3m) (E)-1-(2-(3-bromophenyl)-1,2-dideutero vinyl)-2,3,4,5,6-pentadeutero benzene and (4m) (E)-1-(2-(4-bromophenyl)-1,2-dideutero vinyl)-2,3,4,5,6-pentadeutero benzene. From bromobenzene and styrene-d₈. Product purified by SiO₂ gel column chromatography (height 370 mm, width 35 mm) in pentane/CH₂Cl₂ (8:2). 54.3% isolated yield (white solid).

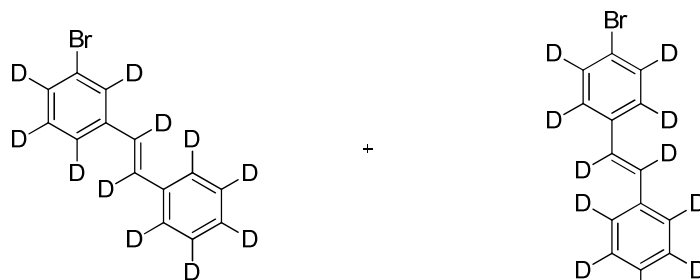
Both isomers are reported together (ratio: 2.1:1 as determined by NMR). Traces of minor isomers (R_t = 8.62 min, 8.69 min, 9.10 min) and traces of dehalogenated product (R_t = 8.42 min) could be detected by GC-MS.

¹H NMR (300.1 MHz, CDCl₃) δ (ppm): 7.54 (t, *J* = 1.8 Hz, 1H of major), 7.42-7.21 (aromatic area), 7.35 (AA' half of AA'BB' 4 spin system, 7.375, 7.367, 7.360, 7.345, 7.338, 7.330, 2H of minor), 7.23 (BB' half of AA'BB' 4 spin system, first three lines overlapped, 7.225, 7.218, 7.211, 2H of minor), 7.08 (dd, ³*J*_{ortho} ~ ³*J*_{ortho} ~ 7.9 Hz, 1H of major).

¹³C{¹H} NMR (75.5 MHz, CDCl₃) δ (ppm): 139.38 (s, C_{quat}), 136.46 (s, C_{quat}), 136.12 (s, C_{quat}), 131.71 (s, CH), 130.30 (s, CH), 130.10 (s, CH), 129.15 (s, CH), 127.89 (s, CH), 125.10 (s, CH), 122.84 (s, C_{quat}, C-Br of major), 121.22 (s, C_{quat}, C-Br of minor). One C_{quat} is overlapped.

GC-MS: R_t (50_40): 9.23 min (major isomer), 9.27 min (minor isomer) ; EI: 268 (13), 267 (79), 266 (25), 265 (82), 264 (14), 187 (14), 186 (91), 185 (92), 184 (100), 183 (25), 182 (16), 181 (14), 158 (9), 157 (14), 156 (13), 155 (9), 93 (28), 92 (30), 91 (9), 90 (11), 79 (29), 54 (8).

ATR-FTIR (cm⁻¹): 2288 (olefinic C-D), 2271 (olefinic C-D), 2225 (olefinic C-D), 1581, 1485, 1398, 1379, 1072, 1005, 834, 825, 797, 783, 717, 649.



Chemical Formula: C₁₄D₁₁Br

Exact Mass: 269.0735

Molecular Weight: 270.2089

m/z: 269.0735 (100.0%), 271.0714 (97.3%), 270.0768 (15.1%), 272.0748 (14.7%), 271.0802 (1.1%), 273.0781 (1.0%)

Elemental Analysis: C, 62.23; H, 8.20; Br, 29.57

(3n) (E)-1-bromo-3-(1,2-dideutero-2-(pentadeuterophenyl)vinyl)-2,4,5,6-tetradeuterobenzene and (4n) (E)-1-bromo-4-(1,2-dideutero-2-(pentadeuterophenyl)vinyl)-2,3,5,6-tetradeuterobenzene. From bromobenzene-d₅ and styrene-d₈. Product purified by SiO₂ gel column chromatography (height 340 mm, width 35 mm) in pentane/CH₂Cl₂ (8:2). 54.3% isolated yield (white solid).

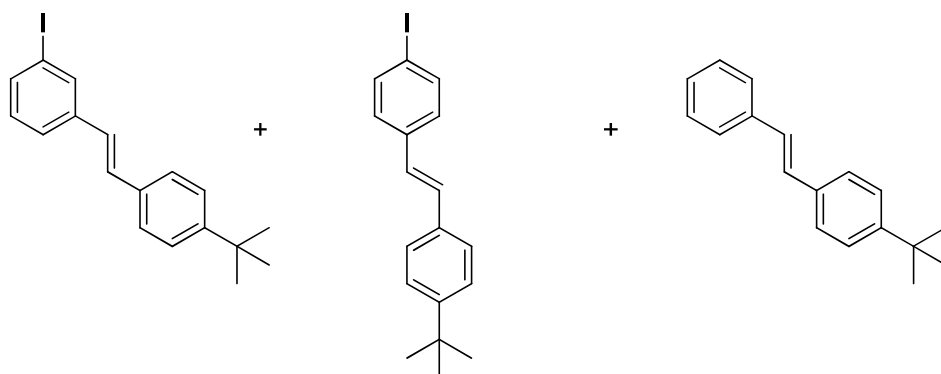
Both isomers are reported together (ratio: 1.9:1 as determined by NMR). ¹³C{¹H} NMR is measured for 5324 scans (instead of 1024), with a relaxation time of 6 sec. (instead of 2).

Traces of minor isomers (R_t = 8.75 min, 8.82 min, 9.23 min) and traces of dehalogenated product (R_t = 8.50 min) could be detected by GC-MS.

¹³C{¹H} NMR (100.6 MHz, CDCl₃) δ (ppm): 139.25 (s), 136.67 (s), 136.50 (s), 136.01 (s), 131.33 (t, ¹J = 25.3 Hz), 130.17-125.65 (dense aromatic area), 128.20 (large t, ¹J = 24.3 Hz), 124.71 (t, ¹J = 24.3 Hz), 122.63 (s, C-Br of major), 121.01 (s, C-Br of major).

GC-MS: R_t (50_40): 9.33 min (major isomer), 9.36 min (minor isomer) ; EI: 272 (9), 271 (60), 270 (10), 269 (64), 268 (14), 191 (8), 190 (54), 189 (27), 188 (100), 187 (22), 186 (12), 184 (14), 160 (15), 158 (10), 95 (12), 94 (27), 92 (10), 80 (23), 66 (9), 54 (9).

ATR-FTIR (cm⁻¹): 2286 (olefinic C-D), 2233 (olefinic C-D), 2216 (olefinic C-D), 1553, 1391, 1369, 1326, 1314, 1198, 1021, 1011, 945, 840, 825, 783, 771, 764, 744, 733, 718, 682.



Chemical Formula: C₁₈H₁₉I
 Exact Mass: 362,0531
 Molecular Weight: 362,2479
 m/z: 362.0531 (100.0%), 363.0565 (19.5%),
 364.0599 (1.8%)
 Elemental Analysis: C, 59.68; H, 5.29; I, 35.03

Chemical Formula: C₁₈H₂₀
 Exact Mass: 236,1565
 Molecular Weight: 236,3514
 m/z: 236.1565 (100.0%), 237.1599 (19.5%),
 238.1632 (1.8%)
 Elemental Analysis: C, 91.47; H, 8.53

(3o) (E)-1-(4-(tert-butyl)styryl)-3-iodobenzene, (4o) (E)-1-(4-(tert-butyl)styryl)-4-iodobenzene and (5o) (E)-1-(tert-butyl)-4-styrylbenzene. From iodobenzene and 4-tert-butylstyrene. Product purified by SiO₂ gel column chromatography (height 310 mm, width 35 mm) in pentane/CH₂Cl₂ = 8/2. 55% isolated yield, that is a mixture of 0.29 mmol of **3o/4o** and 0.26 mmol of **5o** (orange solid).

All products are reported together (ratio 2.3:1:2.9 as determined by NMR).

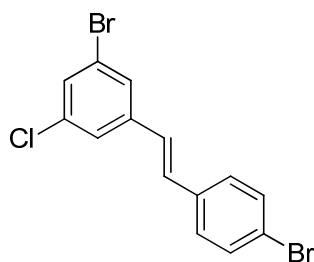
¹H NMR (300.1 MHz, CDCl₃) δ (ppm): 7.74 (dd, *J* = *J* = 1.6 Hz, 1H, CH), 7.54-7.52 (m, aromatic proton), 7.45- 7.20 (m, aromatic region), 7.15-7.06 (m, aromatic region), 7.01 (d, *J*_{trans} = 16.4 Hz, olefinic proton), 6.97 (d, *J*_{trans} = 16.4 Hz, olefinic proton), 6.95 (d, *J*_{trans} = 16.0 Hz, olefinic proton), 6.93 (d, *J*_{trans} = 16.0 Hz, olefinic proton), 6.84 (d, *J*_{trans} = 16.4 Hz, olefinic proton), 6.81 (d, *J*_{trans} = 16.4 Hz, olefinic proton), 1.23-1.22 (m, *t*Bu-groups).

¹³C{¹H} NMR (75.5 MHz, CDCl₃) δ (ppm): 151.30 (s, C_{quat}), 151.20 (s, C_{quat}), 150.84 (s, C_{quat}), 139.90 (s, C_{quat}), 137.78 (s, CH), 137.62 (s, C_{quat}), 137.14 (s, C_{quat}), 136.23 (s, CH), 135.26 (s, CH), 134.65 (s, C_{quat}), 134.23 (s, C_{quat}), 134.12 (s, C_{quat}), 130.38 (s, CH), 129.92 (s, CH), 129.41 (s, CH), 128.76 (s, CH), 128.59 (s, CH), 128.24 (s, CH), 128.02 (s, CH), 127.52 (s, CH), 126.79 (s, CH), 126.54 (s, CH), 126.47 (s, CH), 126.38 (s, CH), 126.27 (s, CH), 125.79 (s, CH), 125.76 (s, CH), 125.72 (s, CH), 94.96 (s, C_{quat}-I), 92.62 (s, C_{quat}-I), 34.77 (s, C_{quat}-*t*Bu-group), 34.73 (s, C_{quat}-*t*Bu-group), 31.43 (s, *t*Bu-group), 31.41 (s, *t*Bu-group). One C_{quat} and two CH lines are overlapped.

GC-MS: R_t (50_40): 9.49 min (deiodinated product); EI: 236 (46), 222 (19), 221 (100), 178 (14), 91 (15).

GC-MS: R_t (50_40): 11.07 min (iodinated product, major isomer), 11.14 min (iodinated product, minor isomer); EI: 363 (12), 362 (66), 348 (18), 347 (100), 178 (14).

ATR-FTIR (cm⁻¹): 2960 (olefinic C-H), 2867 (olefinic C-H), 1507, 1466, 1363, 1269, 1109, 962, 819, 781, 754, 690.



Chemical Formula: C₁₄H₉Br₂Cl

Exact Mass: 369,8760

Molecular Weight: 372,4823

m/z: 371.8739 (100.0%), 369.8760 (51.4%), 373.8719 (48.6%), 373.8710 (32.0%), 371.8730 (16.4%), 375.8689 (15.5%), 372.8773 (15.1%), 370.8793 (7.8%), 374.8752 (7.4%), 374.8743 (4.8%), 372.8764 (2.5%), 376.8723 (2.4%), 373.8806 (1.1%)

Elemental Analysis: C, 45.14; H, 2.44; Br, 42.90; Cl, 9.52

(3q) (E)-1-bromo-3-(4-bromostyryl)-5-chlorobenzene. From 1-bromo-3-chlorobenzene and 4-bromostyrene. Product purified by SiO₂ gel column chromatography (height 300 mm, width 35 mm) in pentane. 24.6% isolated yield (white solid).

Traces of a minor isomer (*R*_t = 9.91 min) could be detected by GC-MS. Molar ratio as determined by NMR: (20:ε:1).

¹H NMR (300.1 MHz, CDCl₃) δ (ppm): 7.40-7.21 (m, aromatic region), 6.89 (d, *J*_{trans} = 16.2 Hz, olefinic proton), 6.78 (d, *J*_{trans} = 16.2 Hz, olefinic proton).

¹³C{¹H} NMR (75.5 MHz, CDCl₃) δ (ppm): 140.34 (s, C_{quat}), 135.49 (s, C_{quat}), 135.28 (s, C_{quat}), 132.05 (s, CH), 130.30 (s, CH), 130.25 (s, CH), 128.31 (s, CH), 127.77 (s, CH), 126.48 (s, CH), 125.31 (s, CH), 123.16 (s, C_{quat}-Br), 122.41 (s, C_{quat}-Br).

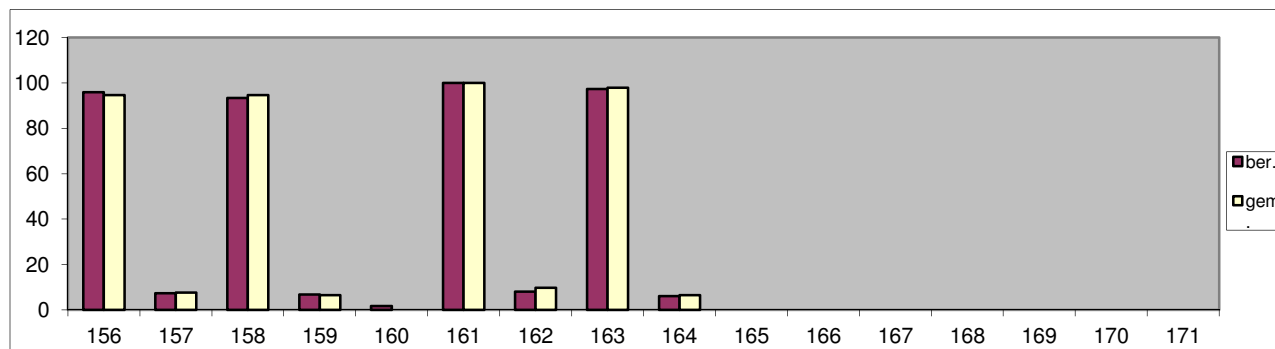
GC-MS: *R*_t (50_40): 10.61 min (major isomer); EI: 376 (11), 375 (8), 374 (52), 373 (11), 372 (74), 370 (34), 258 (13), 256 (14), 214 (33), 213 (16), 212 (100), 177 (21), 176 (58), 175 (8), 151 (13), 150 (10), 107 (11), 106 (30), 88 (48), 87 (12), 75 (18), 74 (9), 63 (7), 50 (8).

ATR-FTIR (cm⁻¹): 3107 (olefinic C-H), 3070 (olefinic C-H), 3024 (olefinic C-H), 2922 (olefinic C-H), 2851 (olefinic C-H), 1581, 1553, 1485, 1417, 1106, 1073, 1006, 963, 928, 843, 805, 771, 703, 687, 665.

3. H/D Scrambling experiment (Eq. 4 of manuscript)

2.5 mL bromobenzene and 2.5 mL bromobenzene-d₅ were engaged using the general procedure without the olefin coupling partner. The crude reaction mixture was analyzed by GC-MS to determine the deuteration grade.

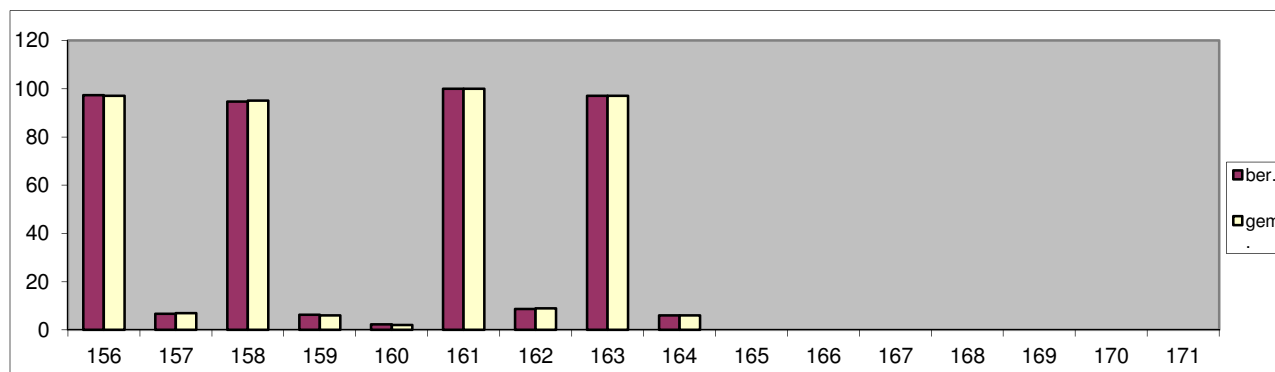
Obtained results:



Degree of deuteration of bromobenzene	D ₀	D ₁	D ₂	D ₃	D ₄	D ₅
Amount	0,96	0,01	0,00	0,00	0,02	1,00
Fraction %	48,37	0,43	0,00	0,00	0,79	50,40

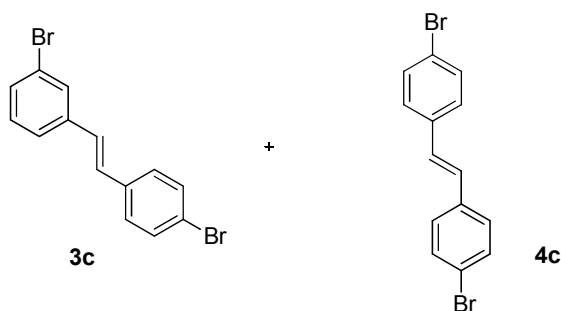
As control experiment the deuteration grade of a 1:1 mixture of the starting materials bromobenzene and bromobenzene-d₅ was analyzed by GC-MS.

Obtained results:



Degree of deuteration of bromobenzene	D ₀	D ₁	D ₂	D ₃	D ₄	D ₅
Amount	0,97	0,00	0,00	0,00	0,02	1,00
Fraction %	48,69	0,21	0,08	0,00	1,10	49,93

4. Kinetic isotope effect measurement (Eq. 5)



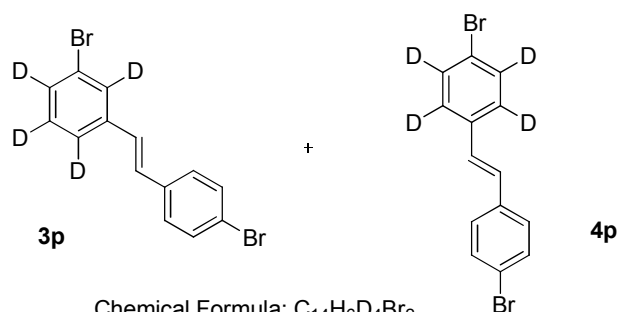
Chemical Formula: C₁₄H₁₀Br₂

Exact Mass: 335.9149

Molecular Weight: 338.0372

m/z: 337.9129 (100.0%), 335.9149 (51.4%), 339.9108 (48.6%), 338.9162 (15.1%), 336.9183 (7.8%), 340.9142 (7.4%), 339.9196 (1.1%)

Elemental Analysis: C, 49.74; H, 2.98; Br, 47.28



Chemical Formula: C₁₄H₆D₄Br₂

Exact Mass: 339.9400

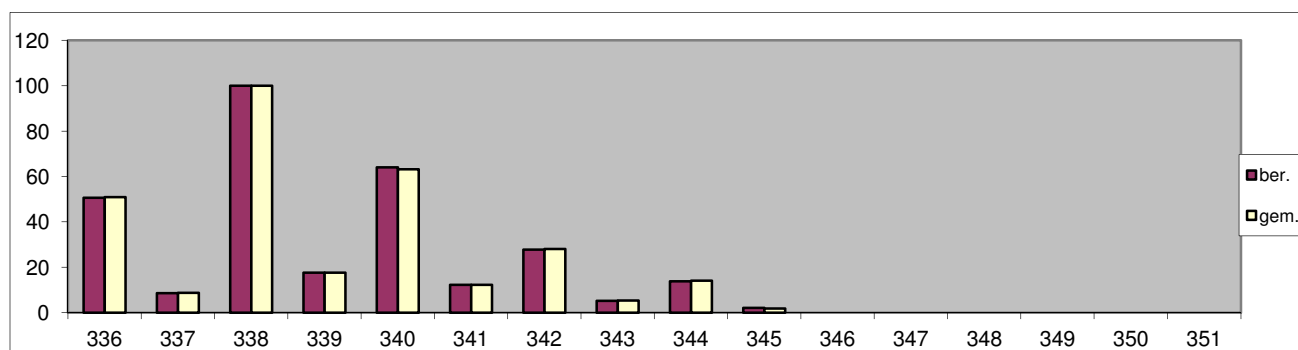
Molecular Weight: 342.0618

m/z: 341.9380 (100.0%), 339.9400 (51.4%), 343.9359 (48.6%), 342.9413 (15.1%), 340.9434 (7.8%), 344.9393 (7.4%), 343.9447 (1.1%)

Elemental Analysis: C, 49.16; H, 4.12; Br, 46.72

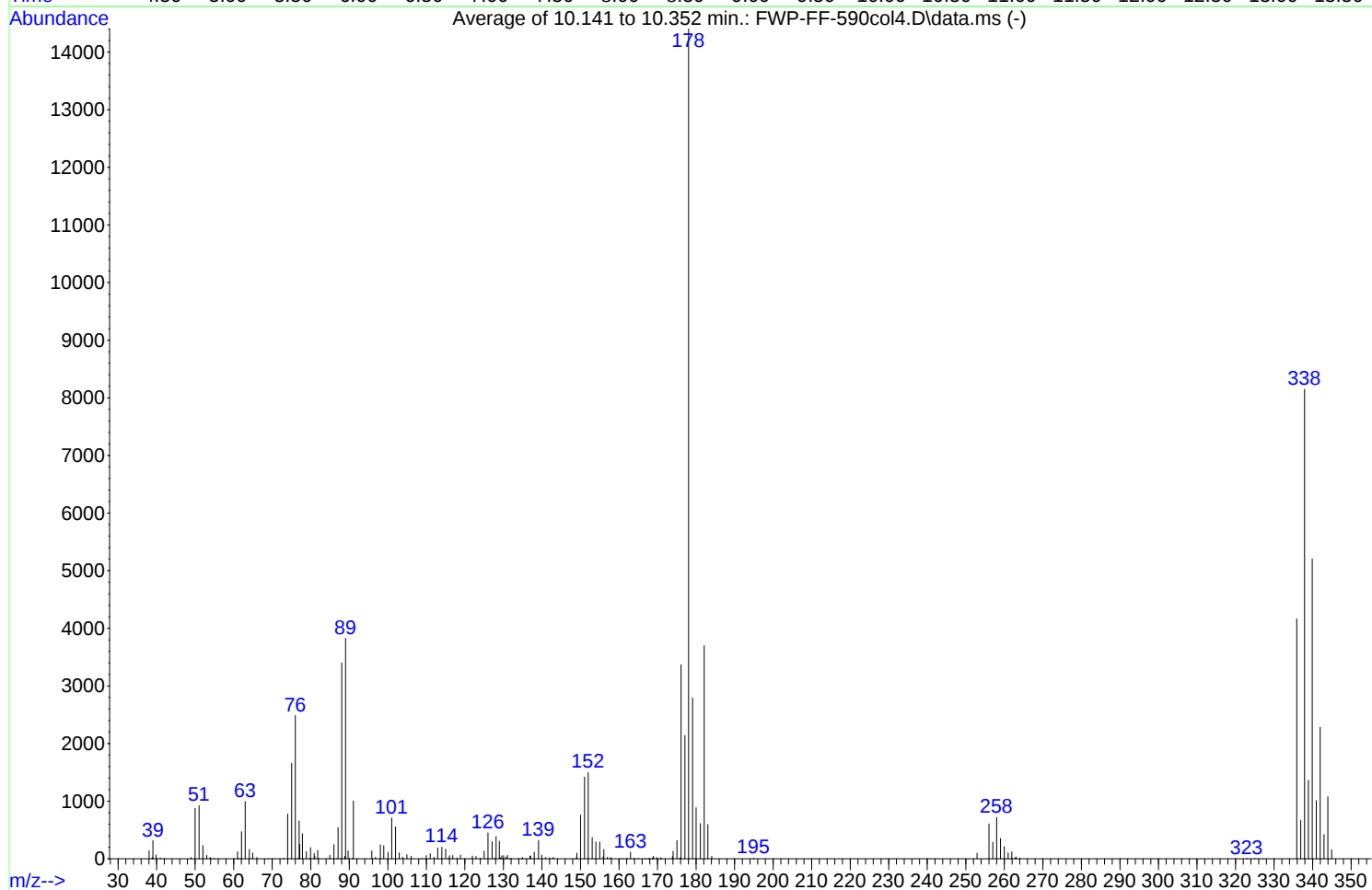
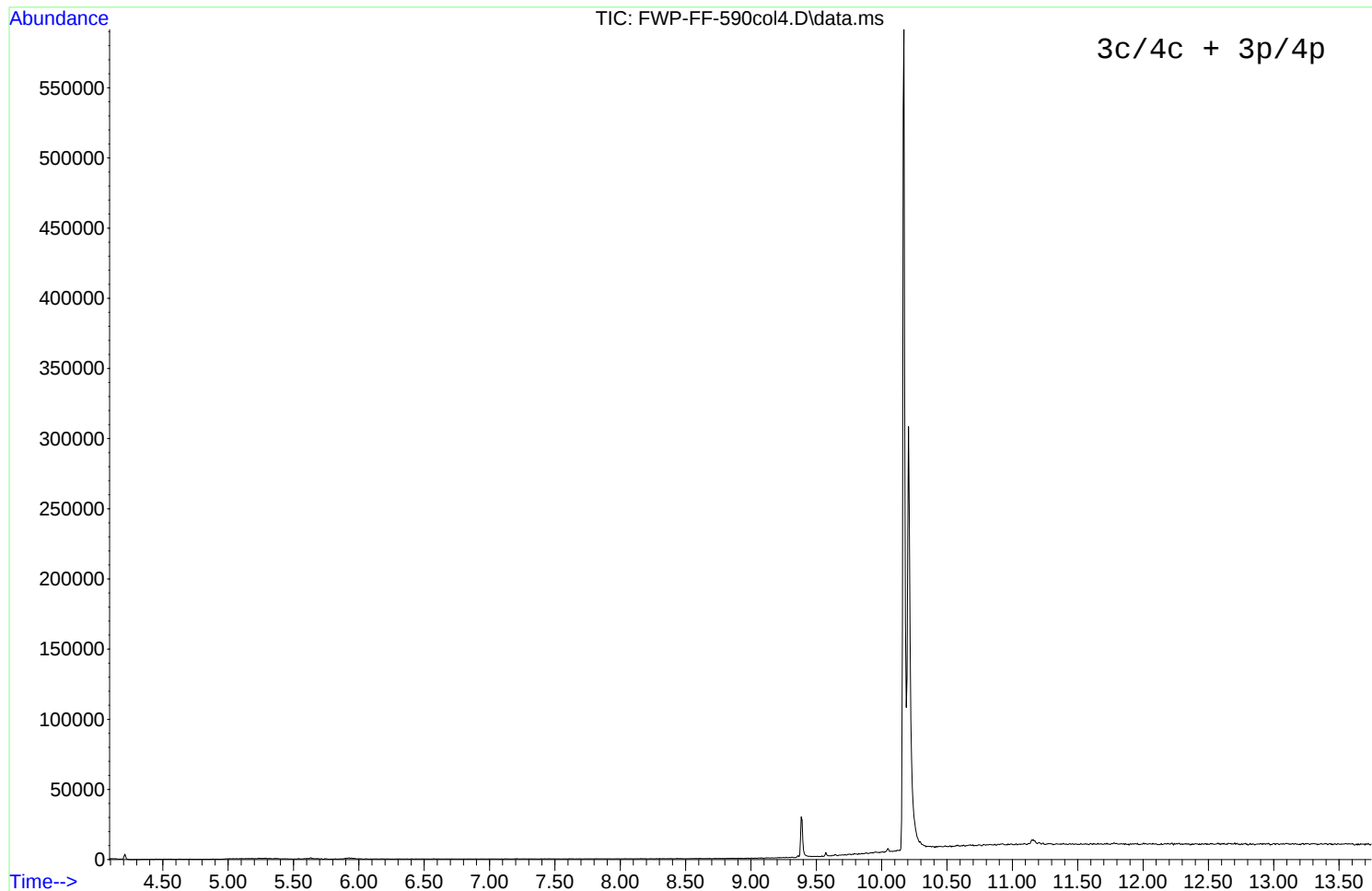
Using the general procedure 4-bromostyrene was reacted with 2.5 mL bromobenzene and 2.5 mL bromobenzene-d₅. The mixture of products was analyzed by GC-MS to determine the deuteration grade.

Obtained results:

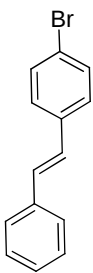


Degree of deuteration in 3c/4c/3p/4p	D ₀	D ₁	D ₂	D ₃	D ₄	D ₅
Amount	1,00	0,01	0,00	0,02	0,27	0,00
Fraction %	76,59	0,93	0,00	1,49	20,99	0,00

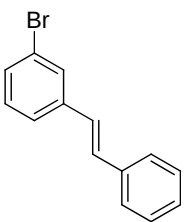
$$k_H/k_D = (76.59 + 0.93) / (20.99 + 1.49) = 77.52 / 22.48 = 3.45$$



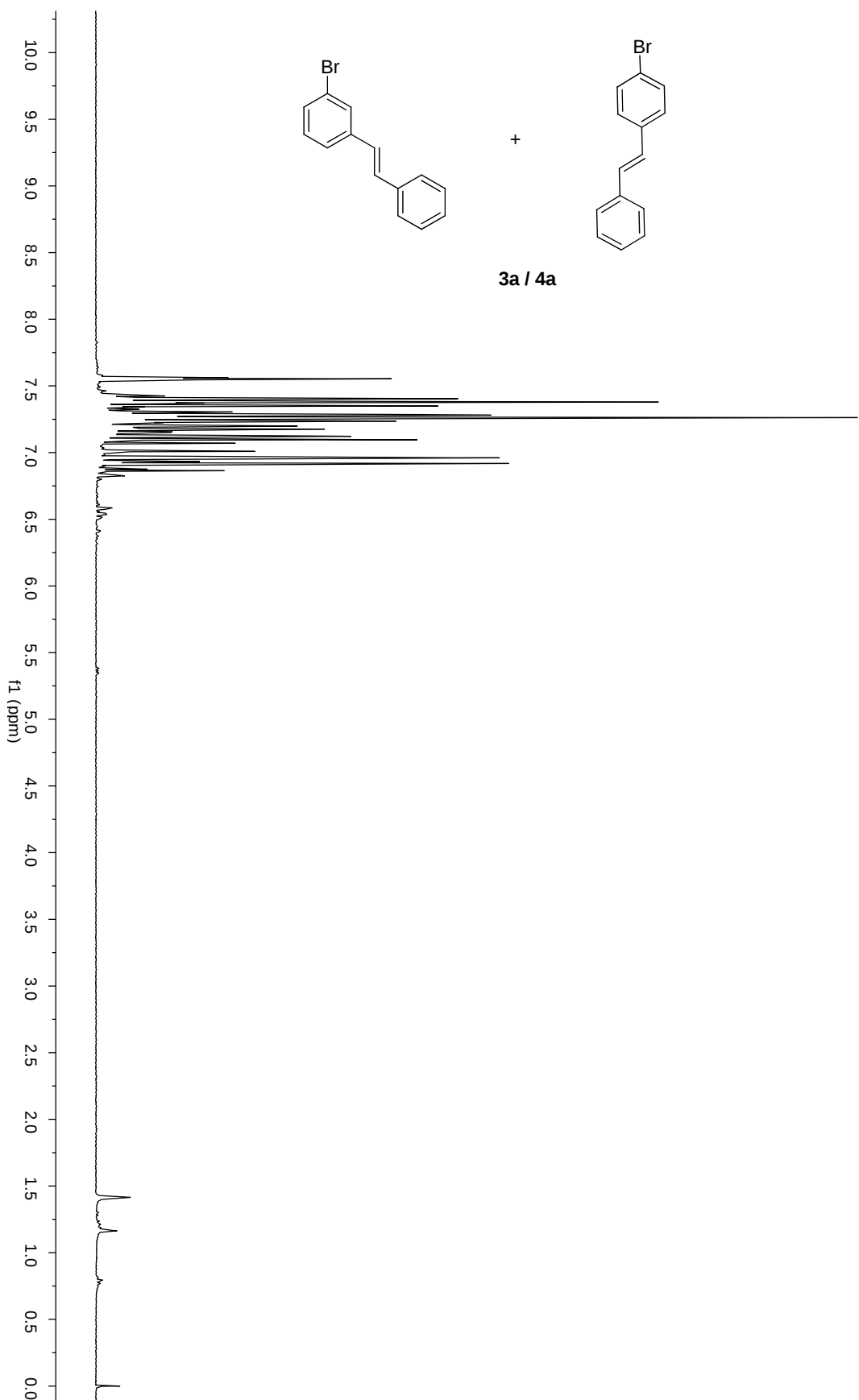
Jul14-2011
glo patureau fwp ff 565 b
proton CDC13 /opt/topspin av1.36



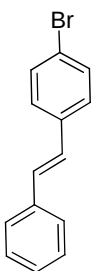
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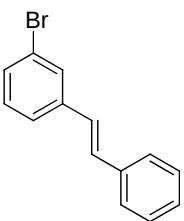
3a / 4a



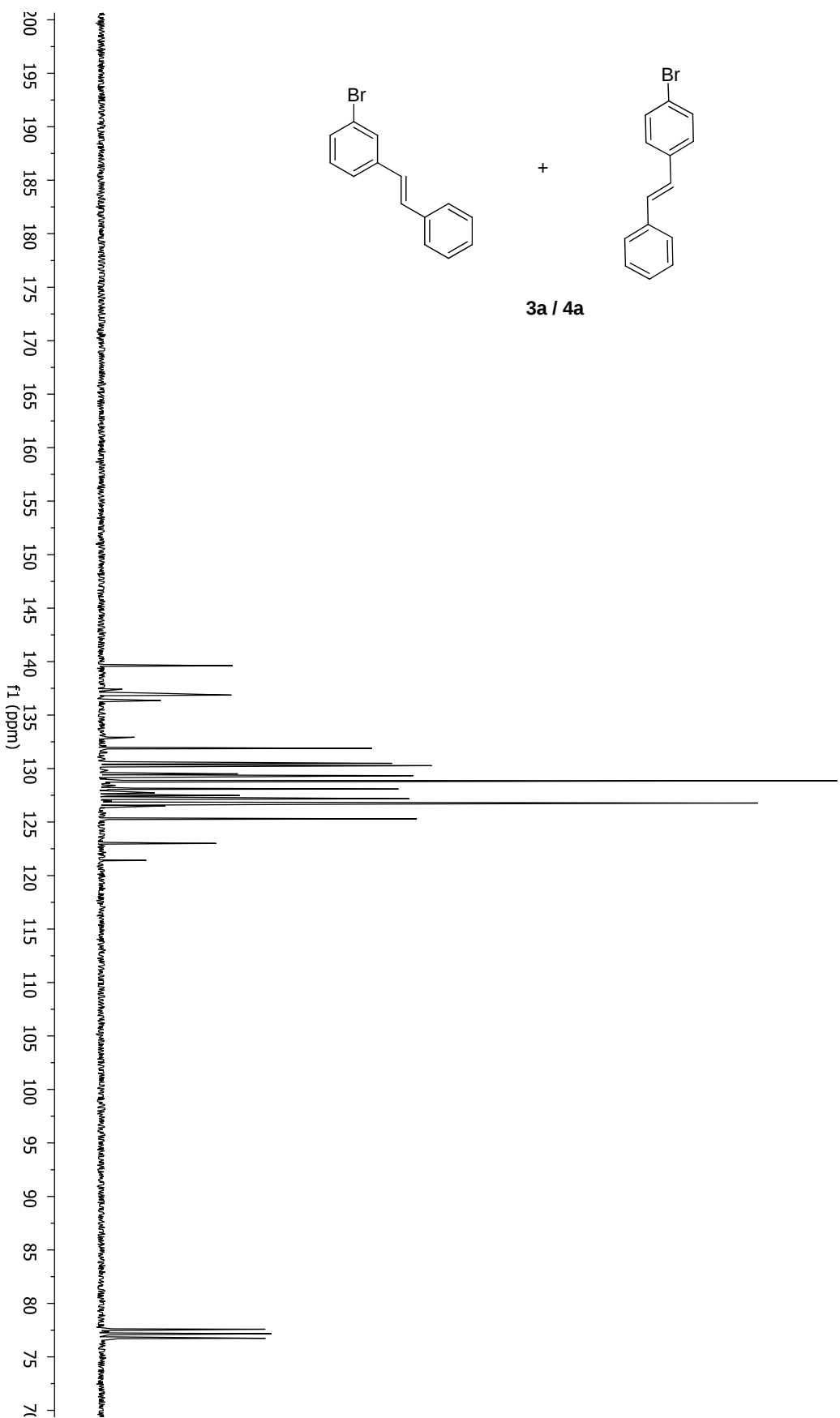
Jul14-2011
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carbon CDCl3 /opt/topspin av1 36

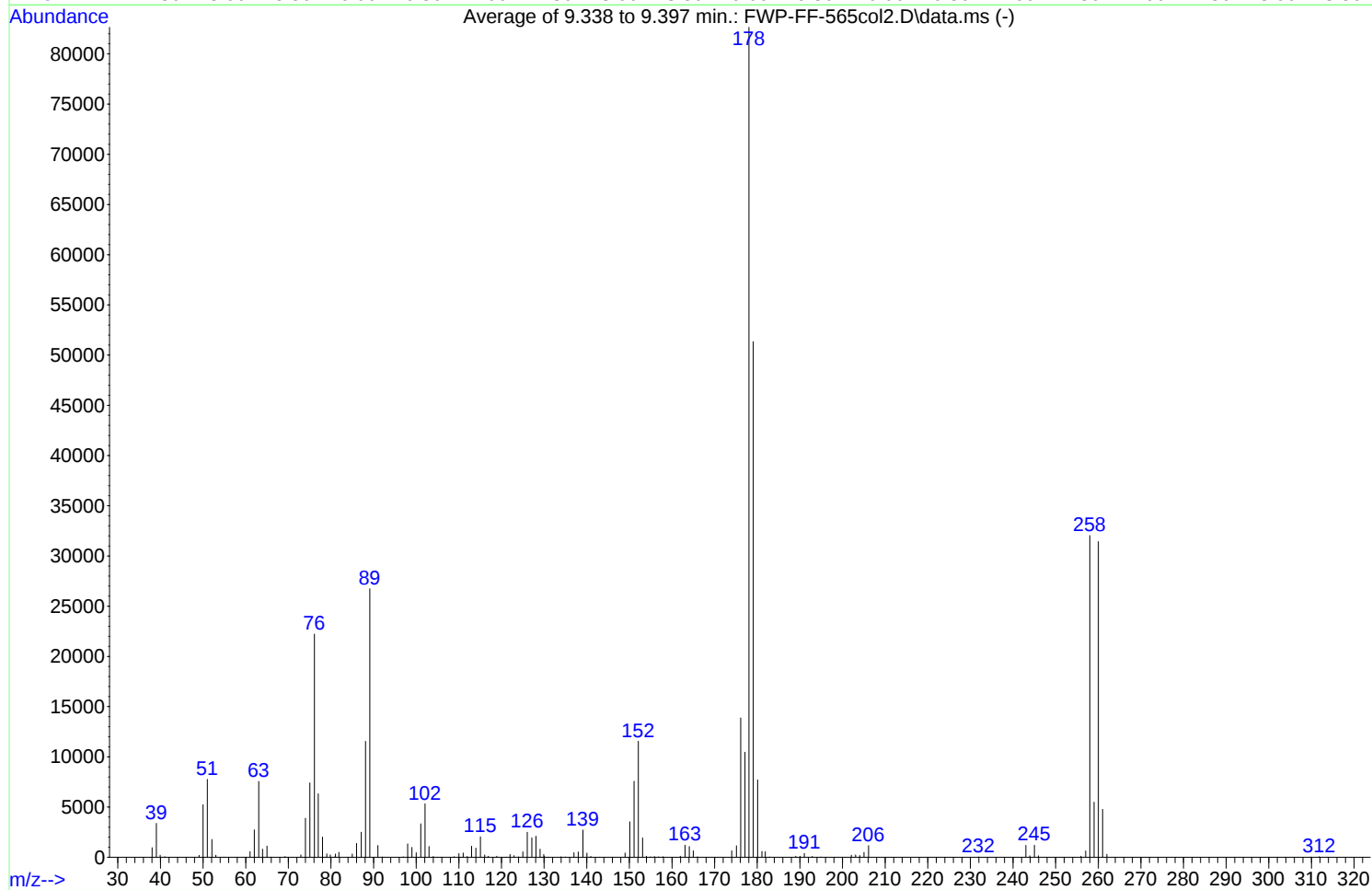
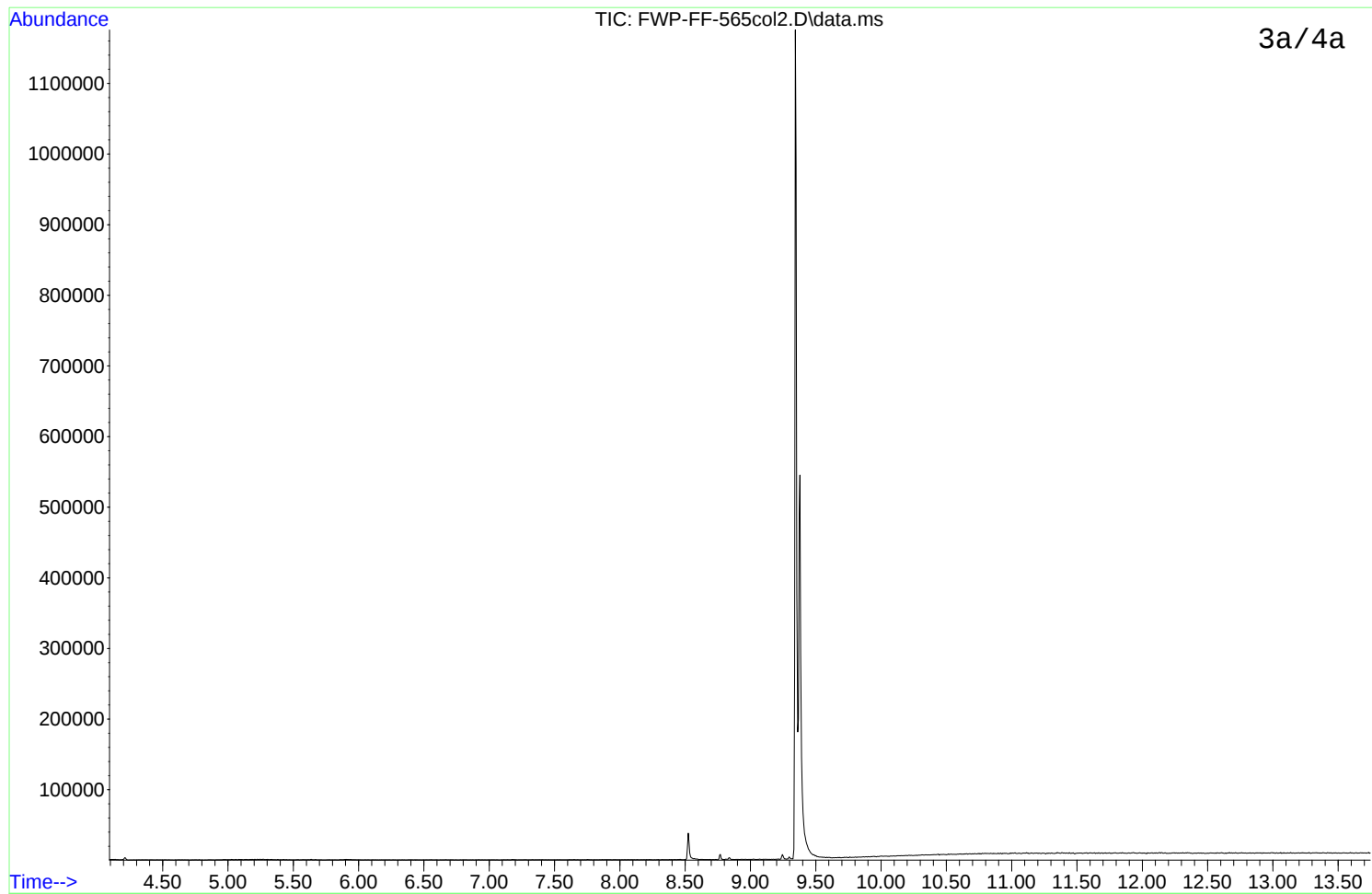


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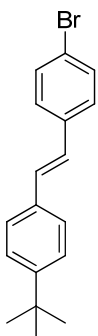


3a / 4a

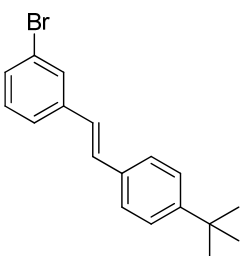




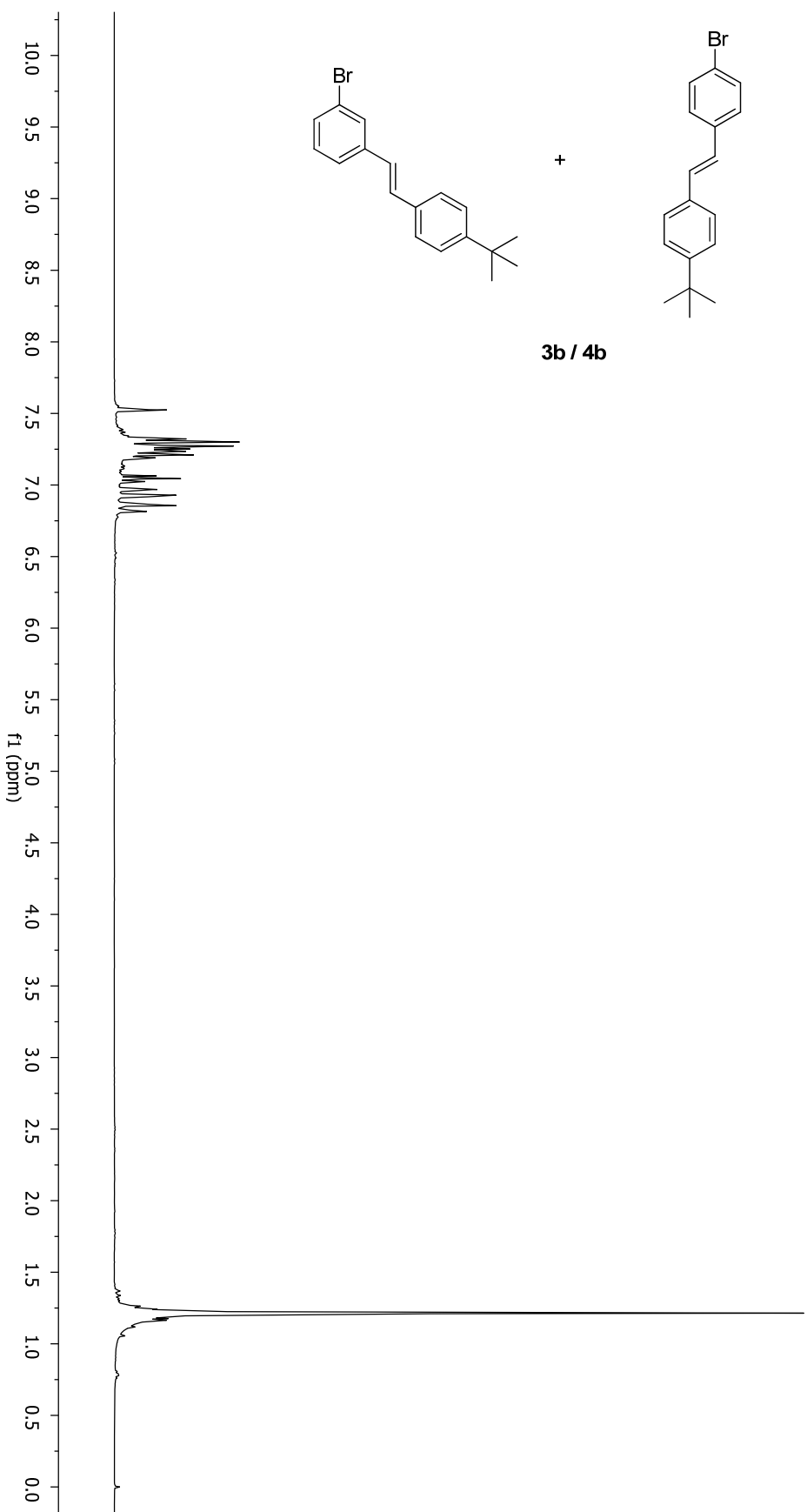
Jun24-2011
glo patureau fwp 553
proton CDCl3 /opt/topspin av1 47



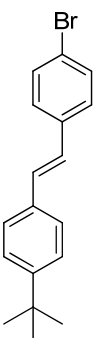
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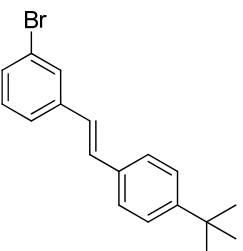
3b / 4b



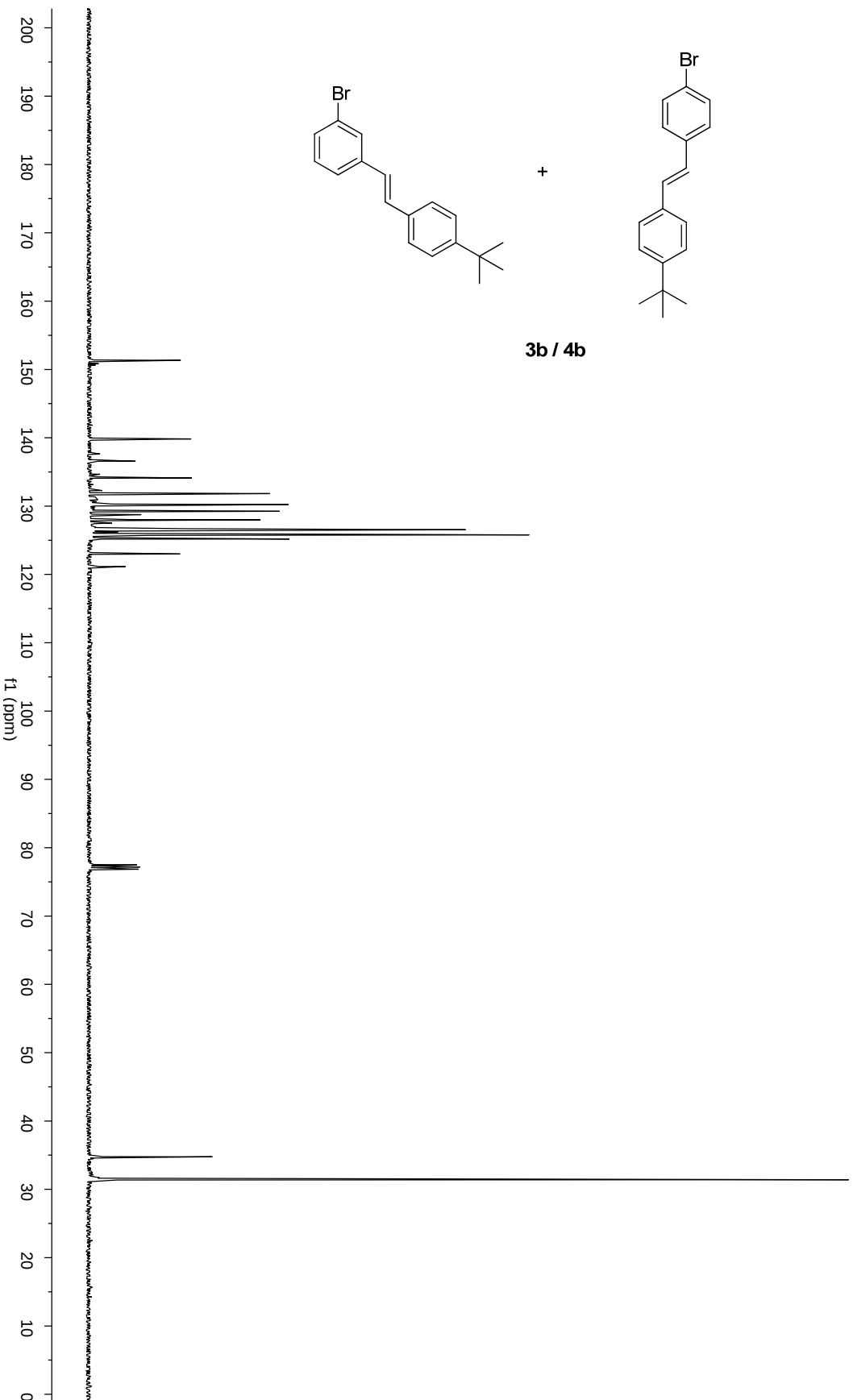
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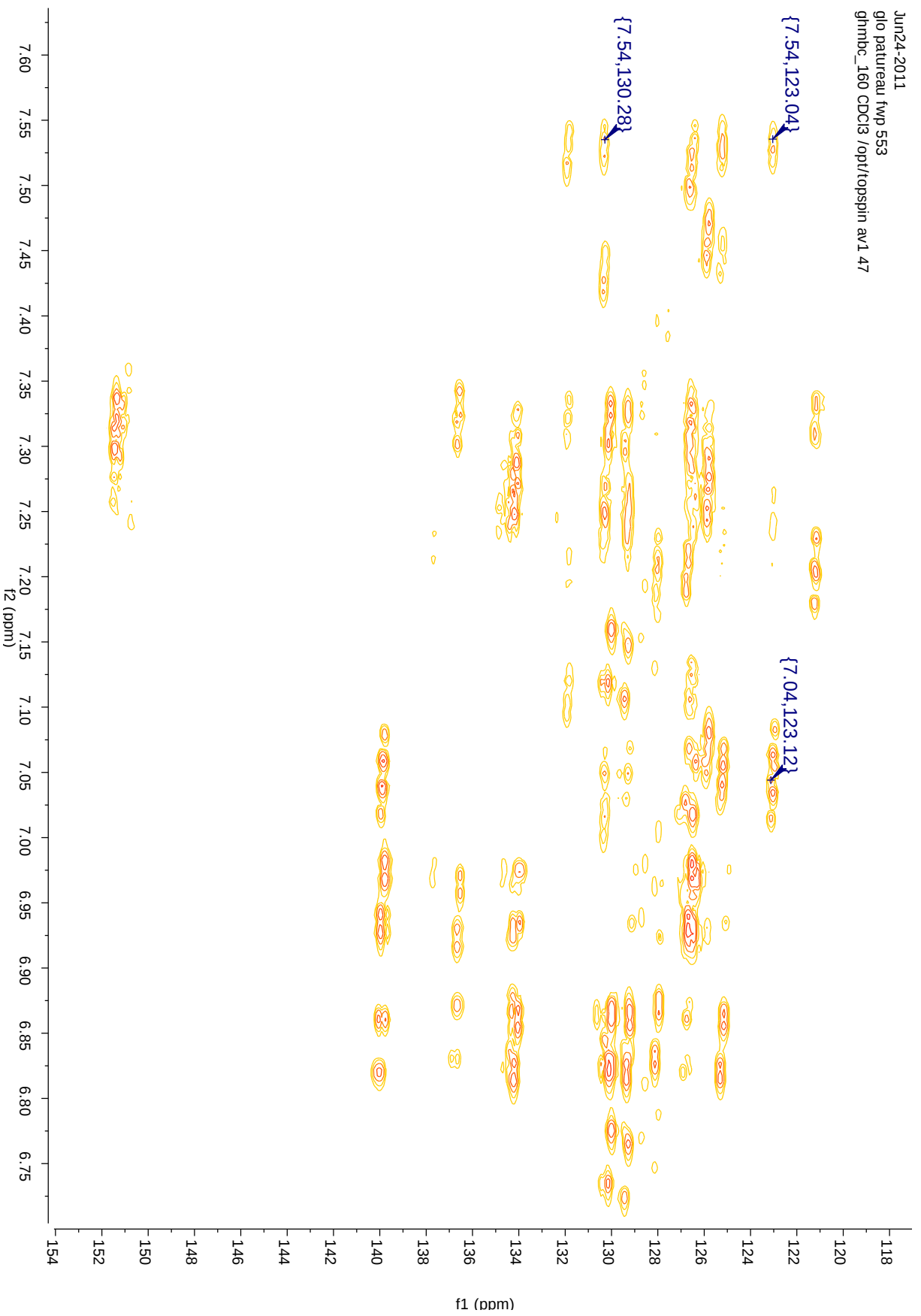
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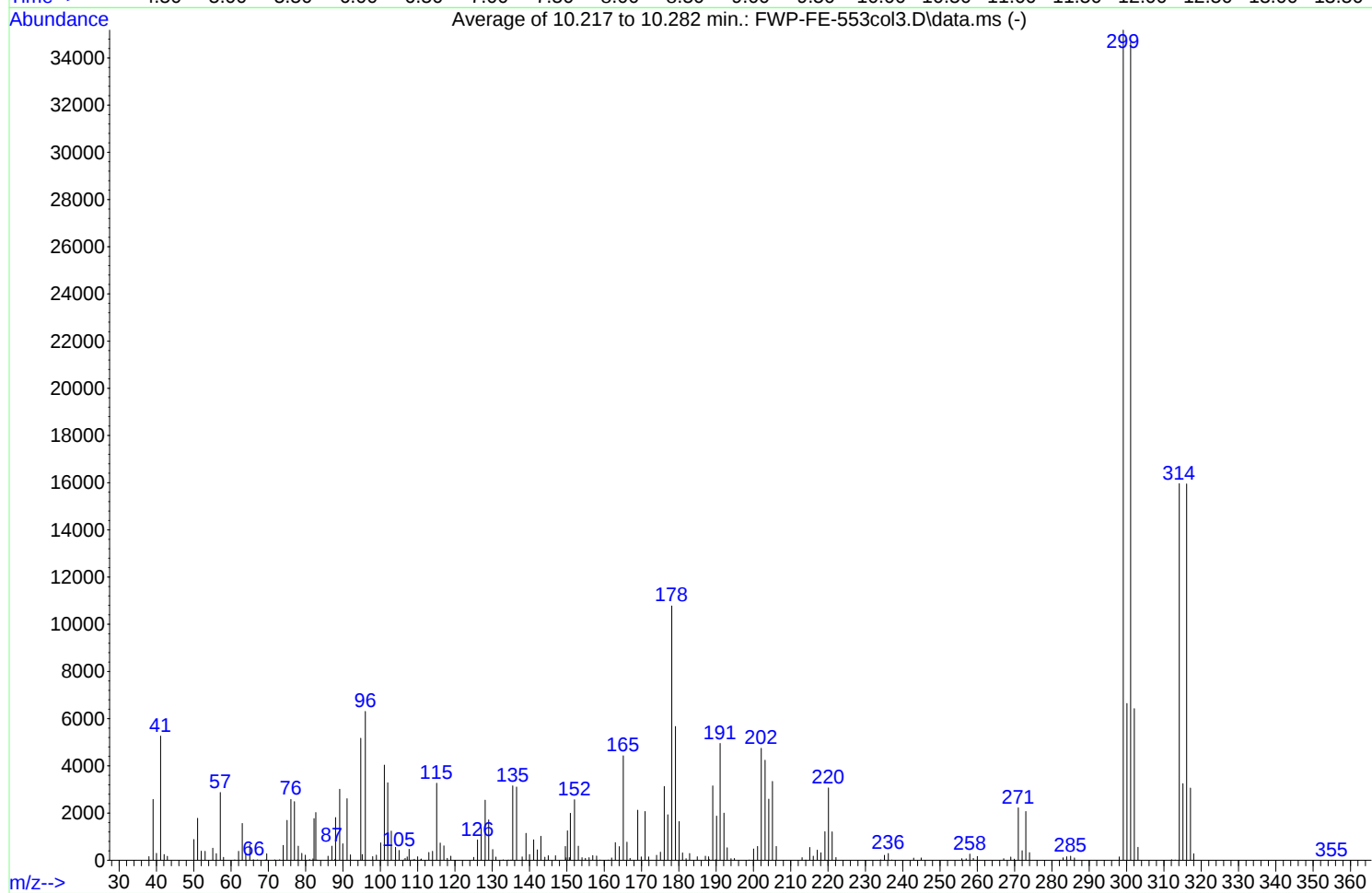
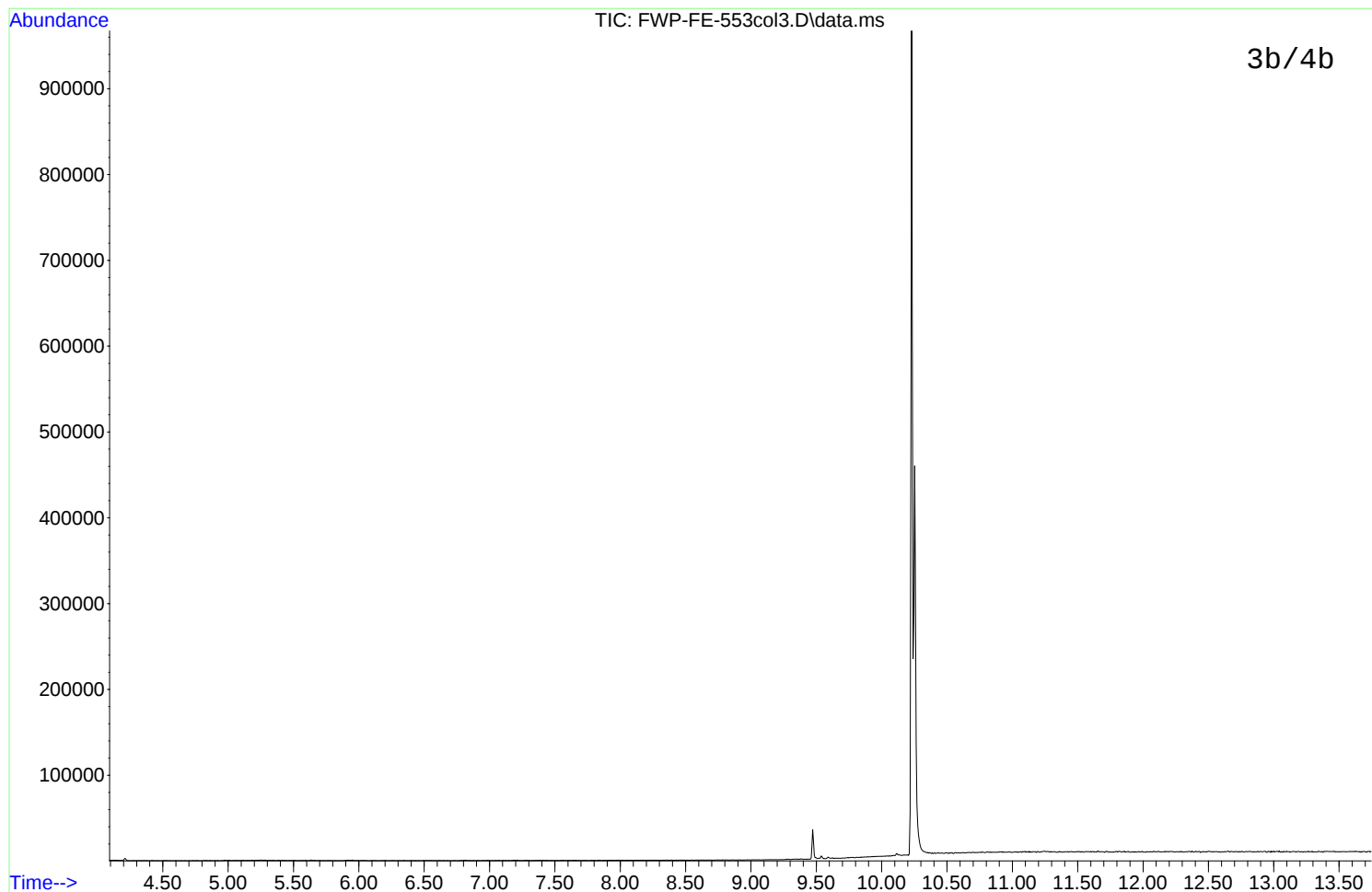


3b / 4b

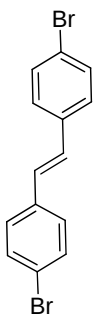


Jun24-2011
glo patureau fwp 553
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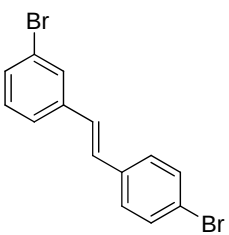




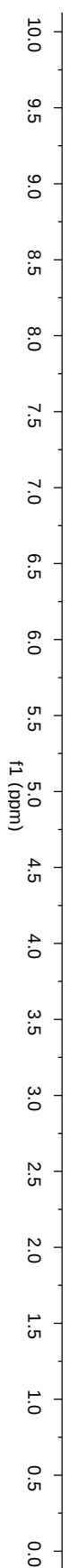
Jul19-2011
glo patureau fwp 577
proton CDC13 /opt/topspin av1 51



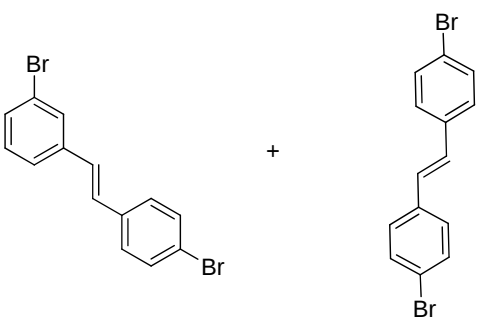
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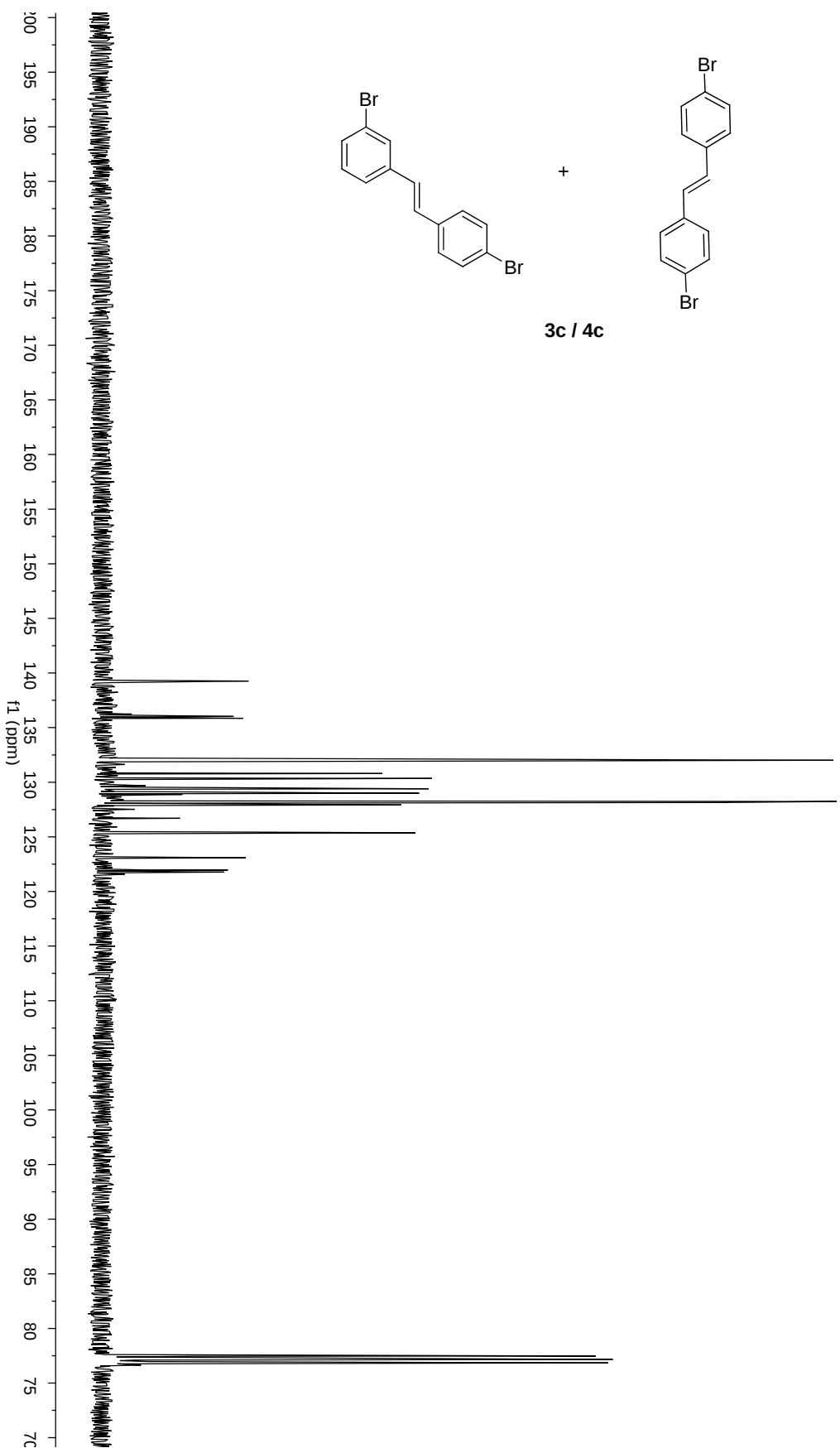
3c / 4c



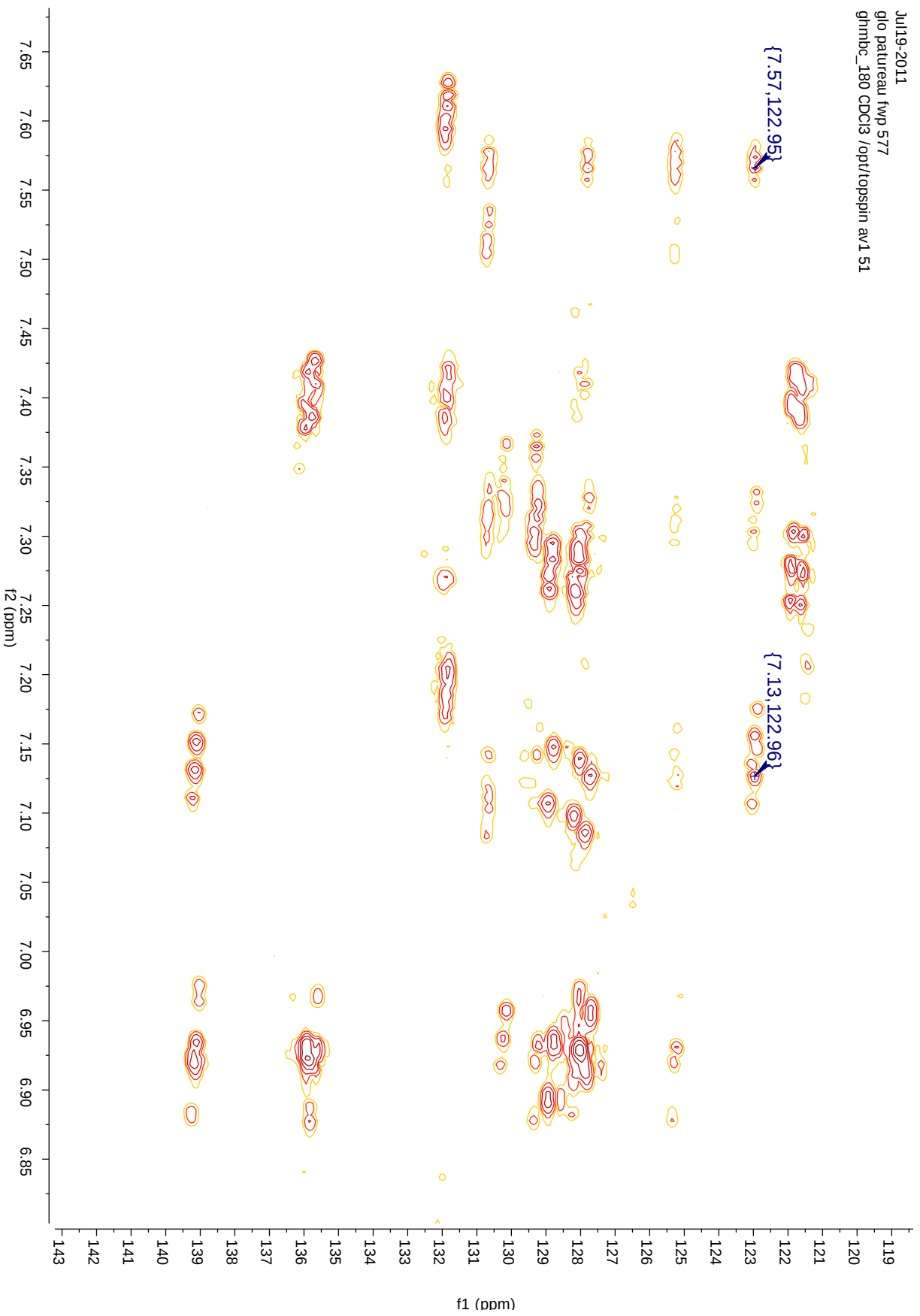
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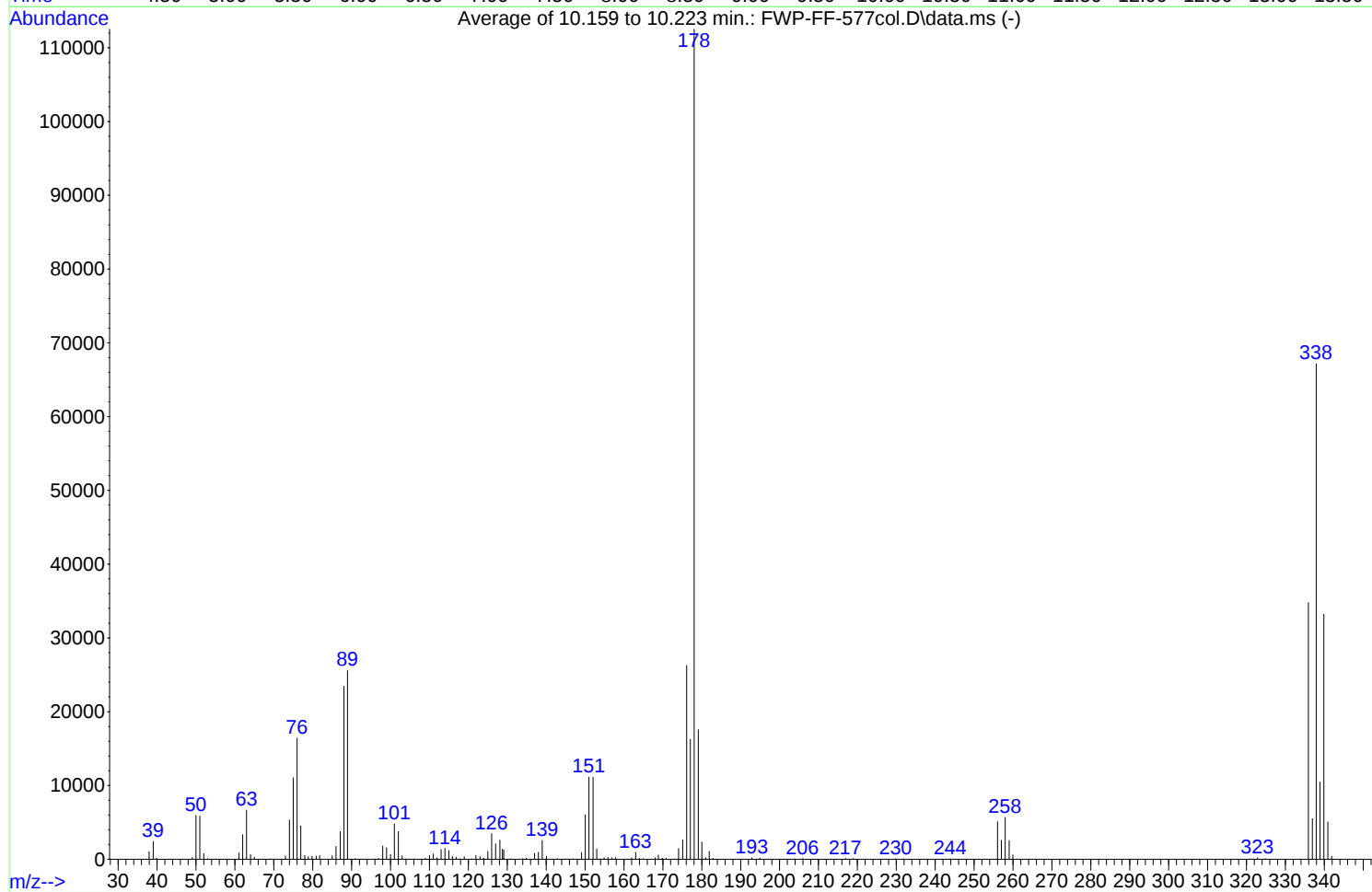
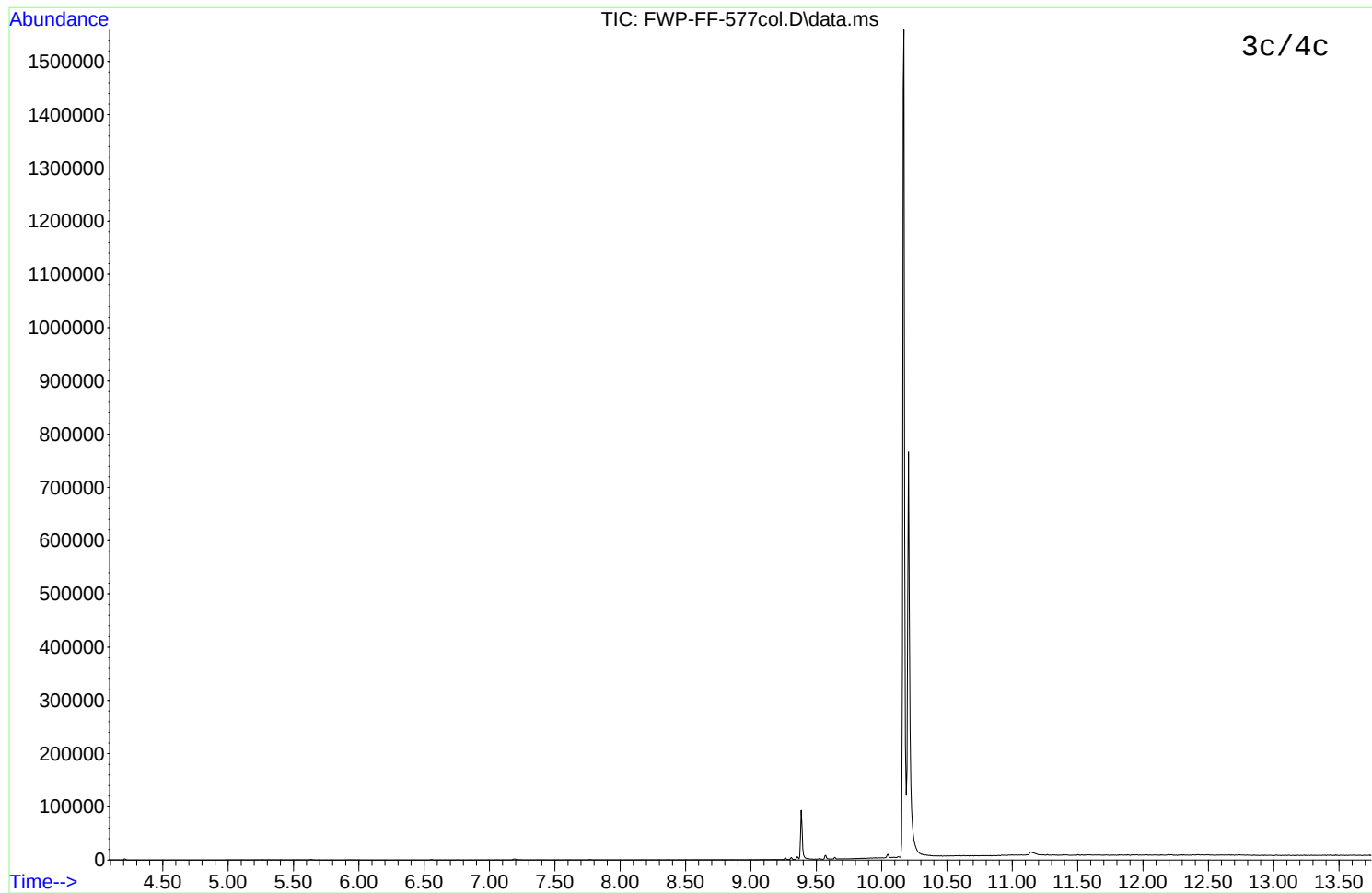


3c / 4c

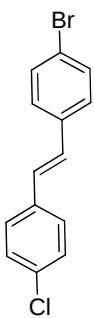


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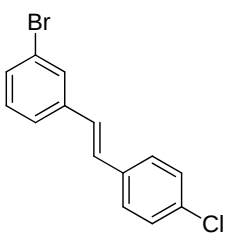




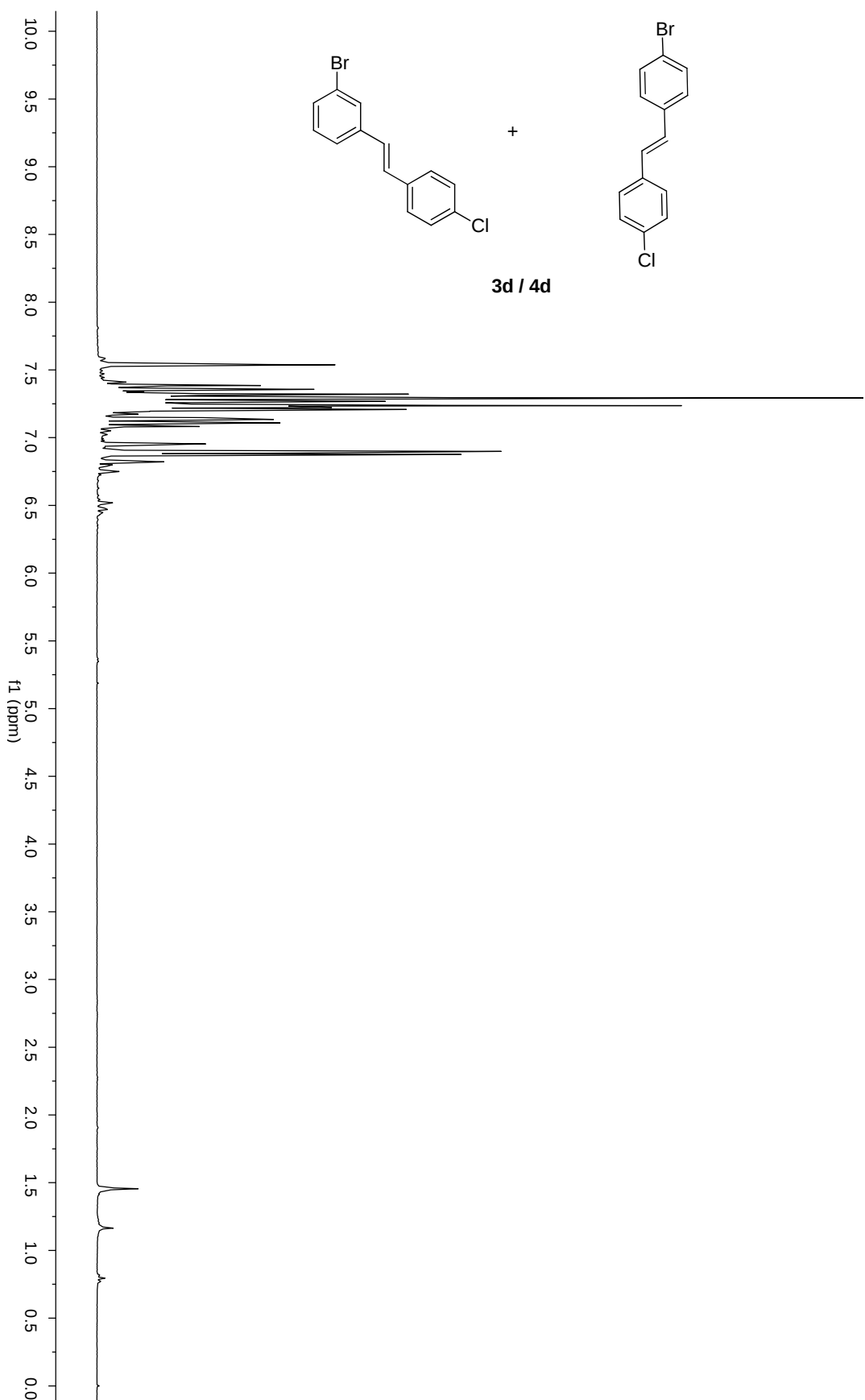
Jul13-2011
glo patureau fwp ff 570
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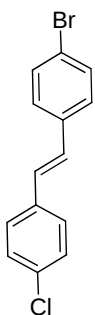
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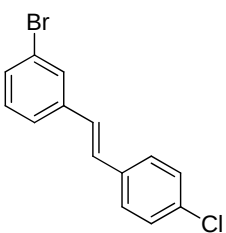
3d / 4d



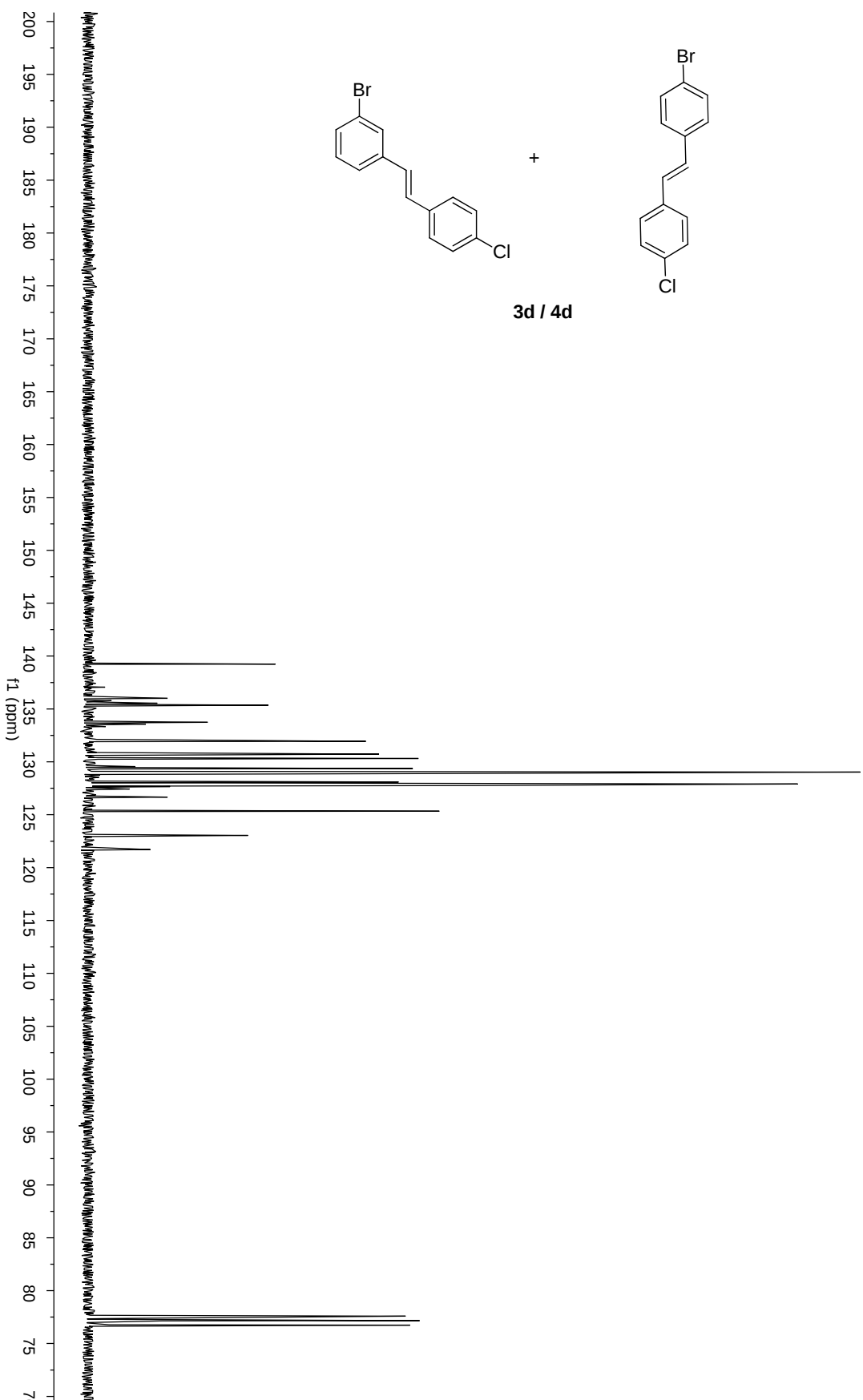
Jul13-2011
glo patureau fwp ff 570
carbon CDC13 /opt/topspin av1 7

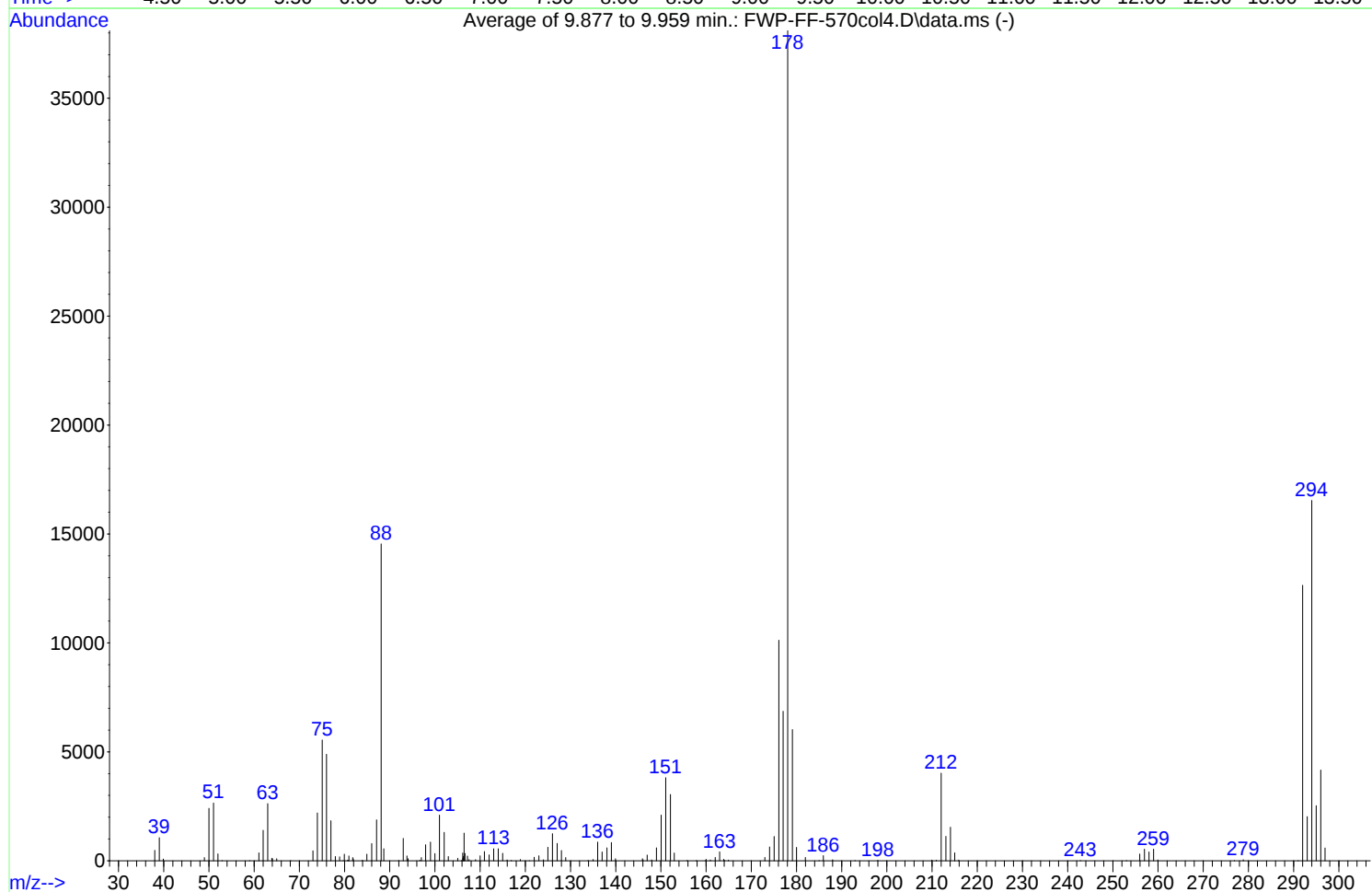
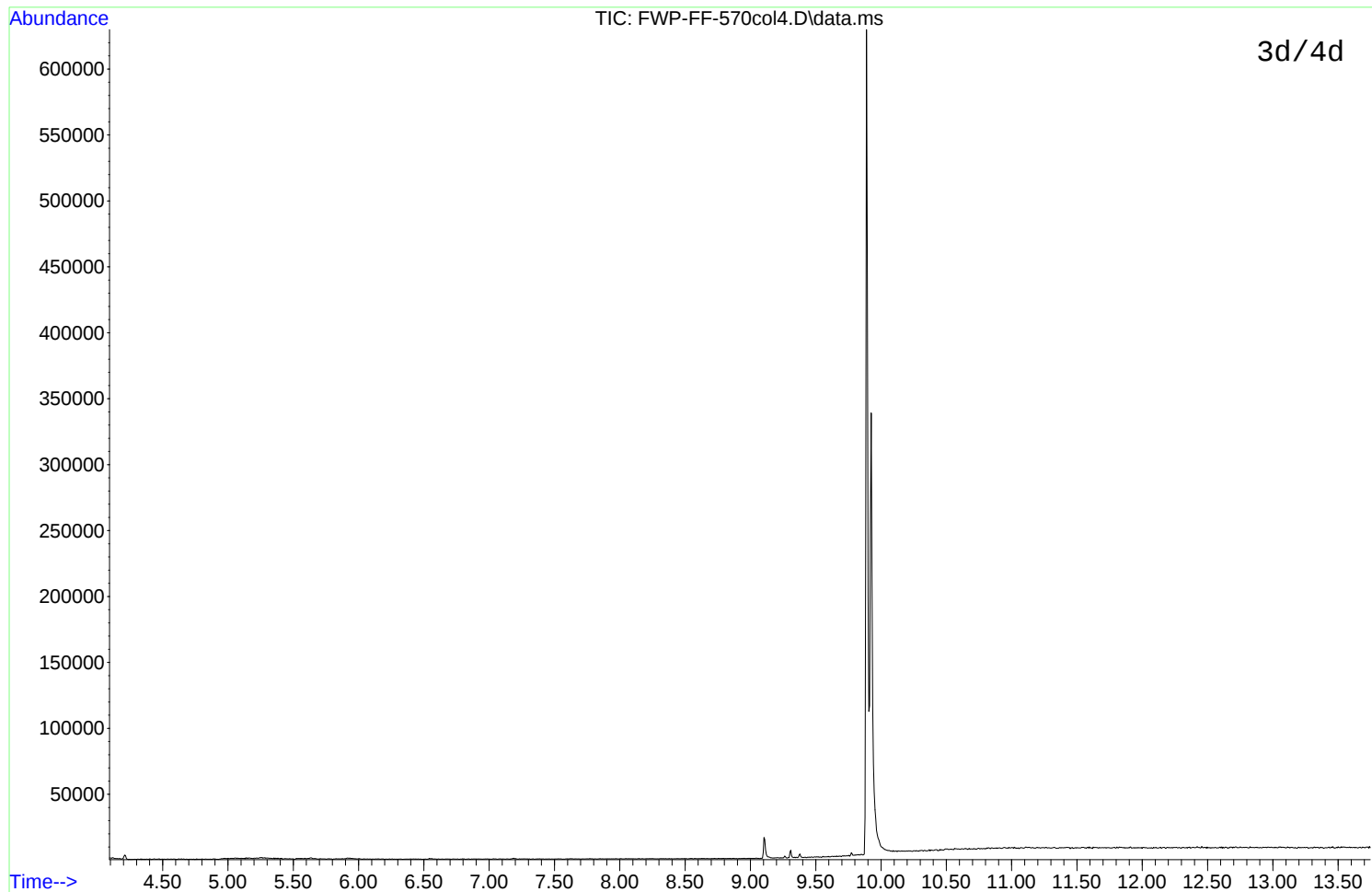


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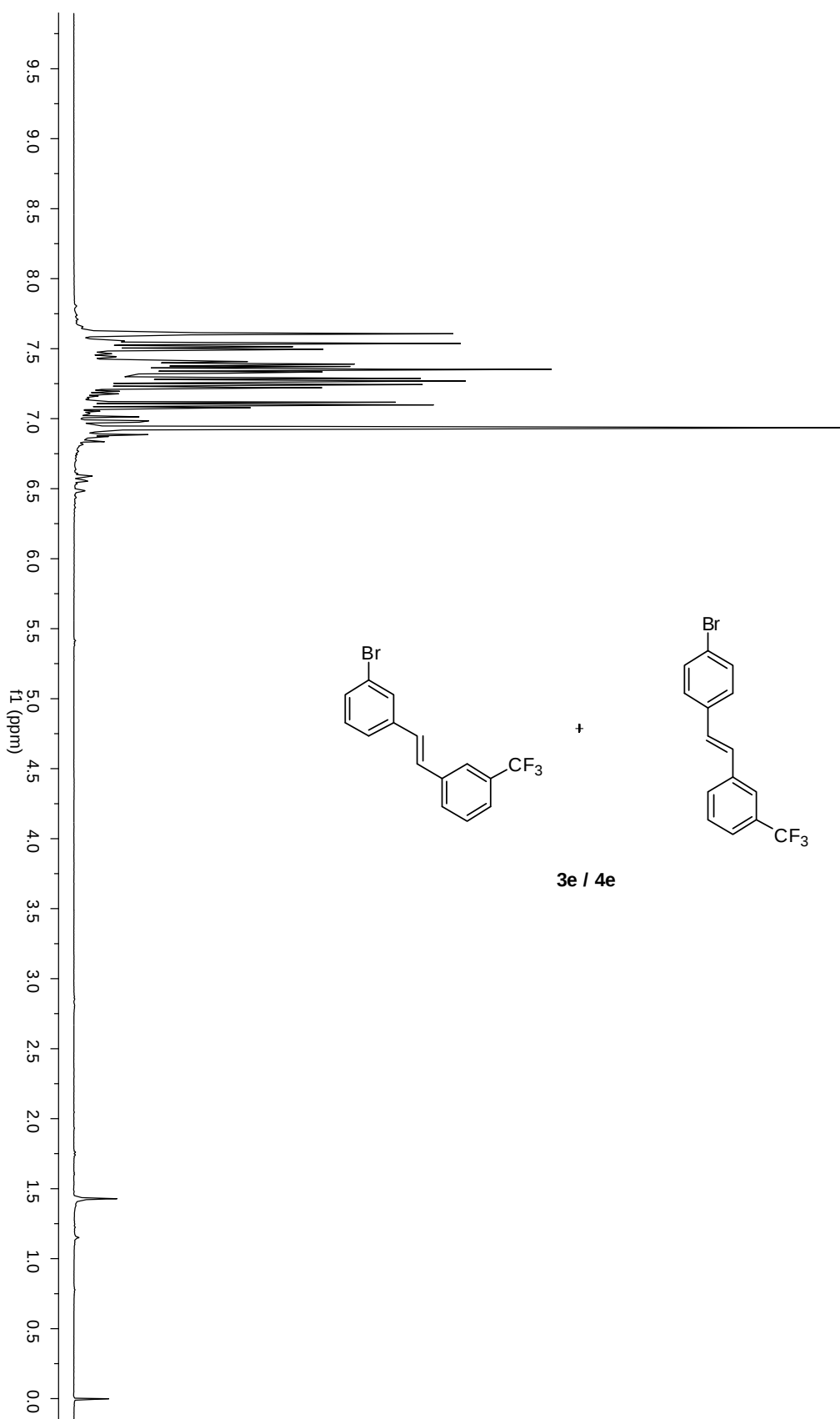


3d / 4d

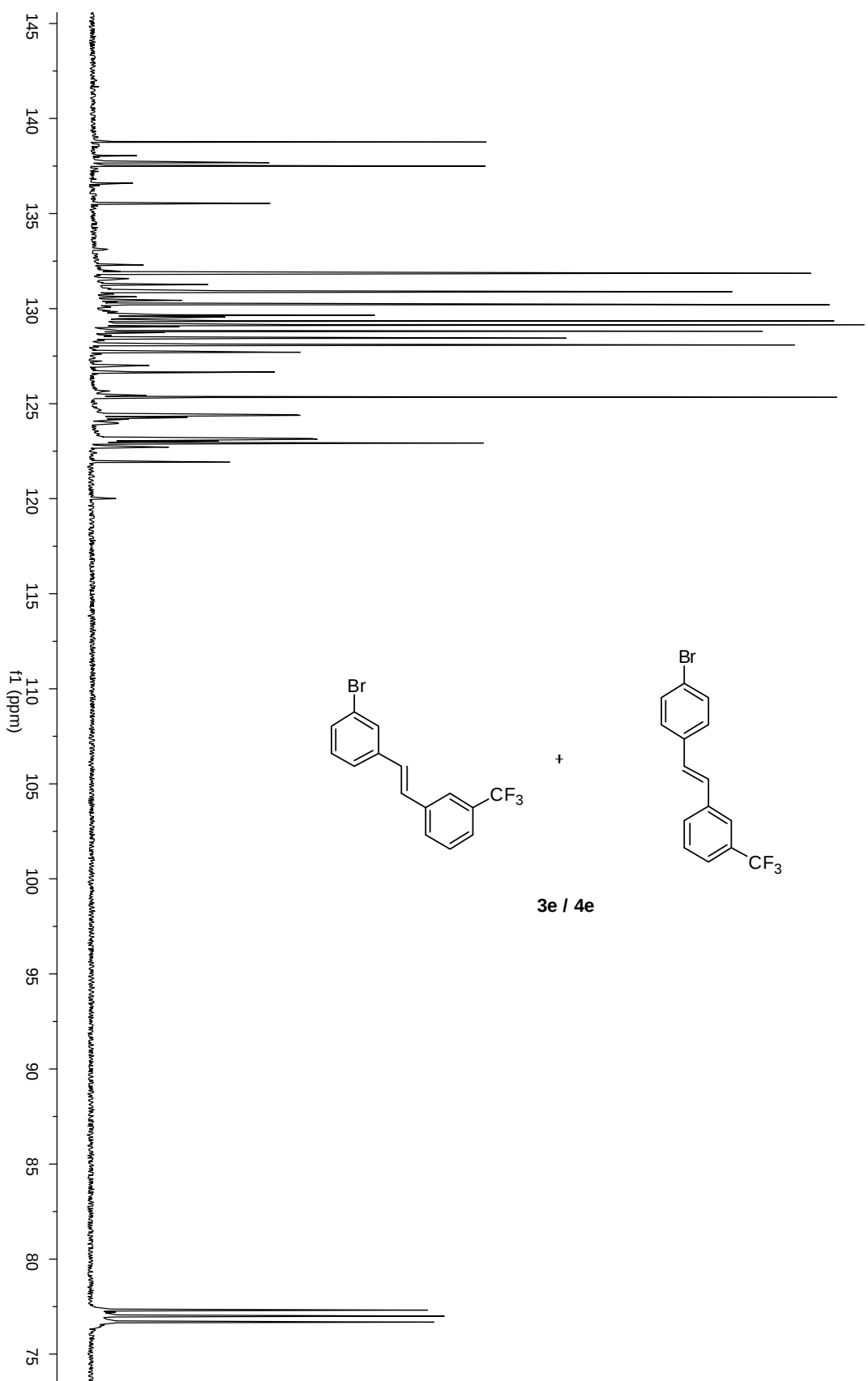




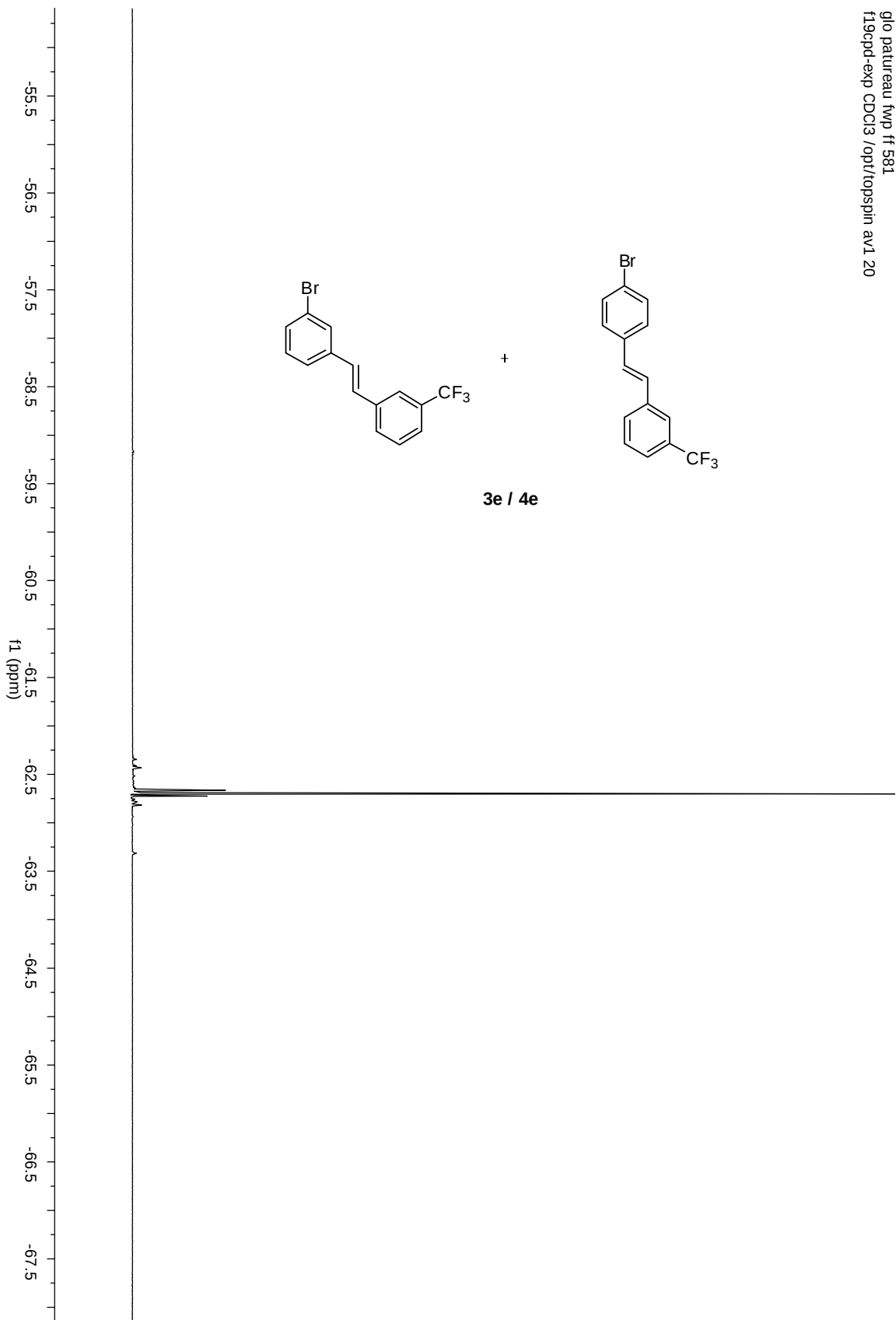
Jul29-2011
glo patureau fwp 581
proton CDCl3 /opt/topspin av1.51

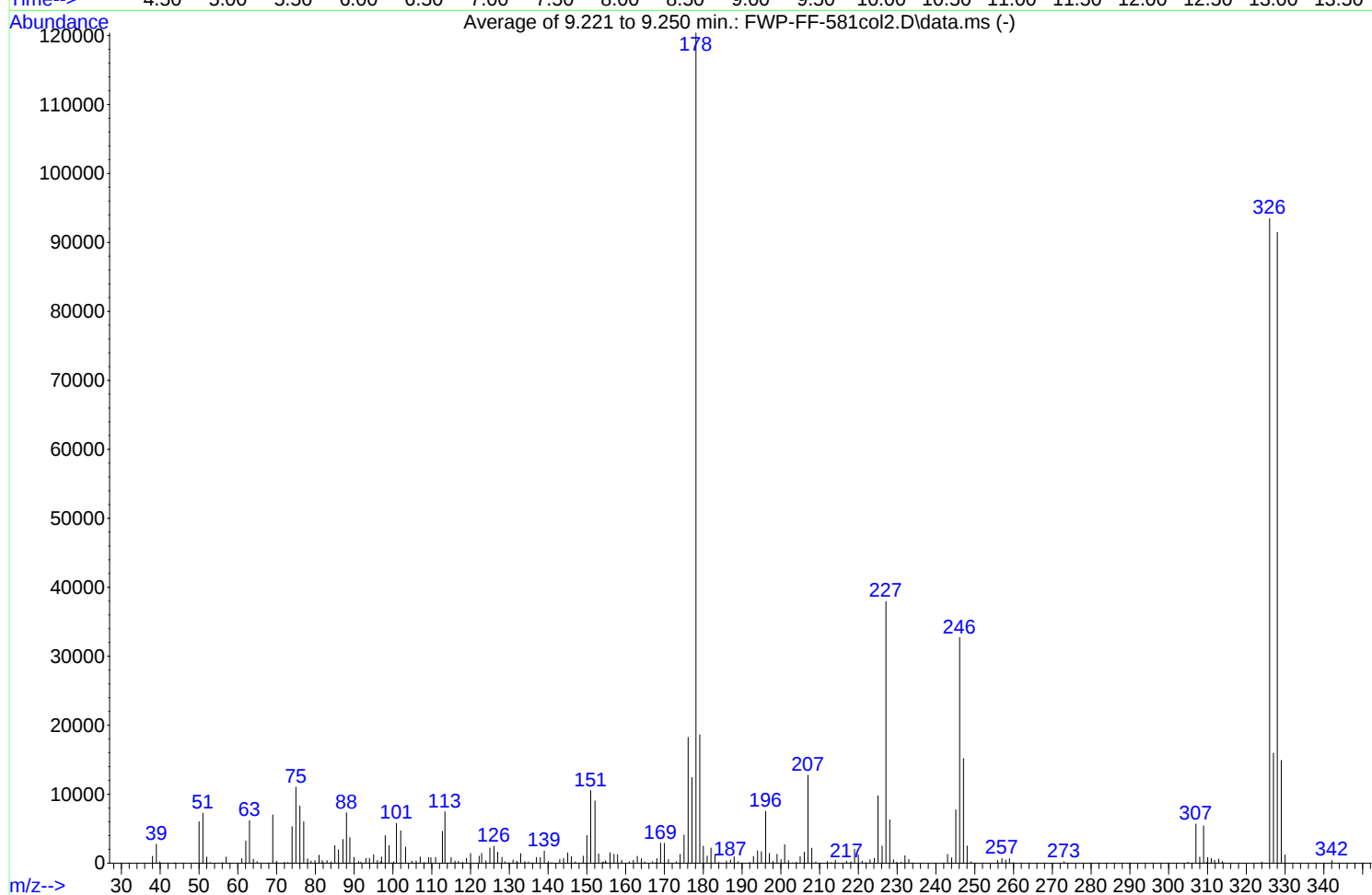
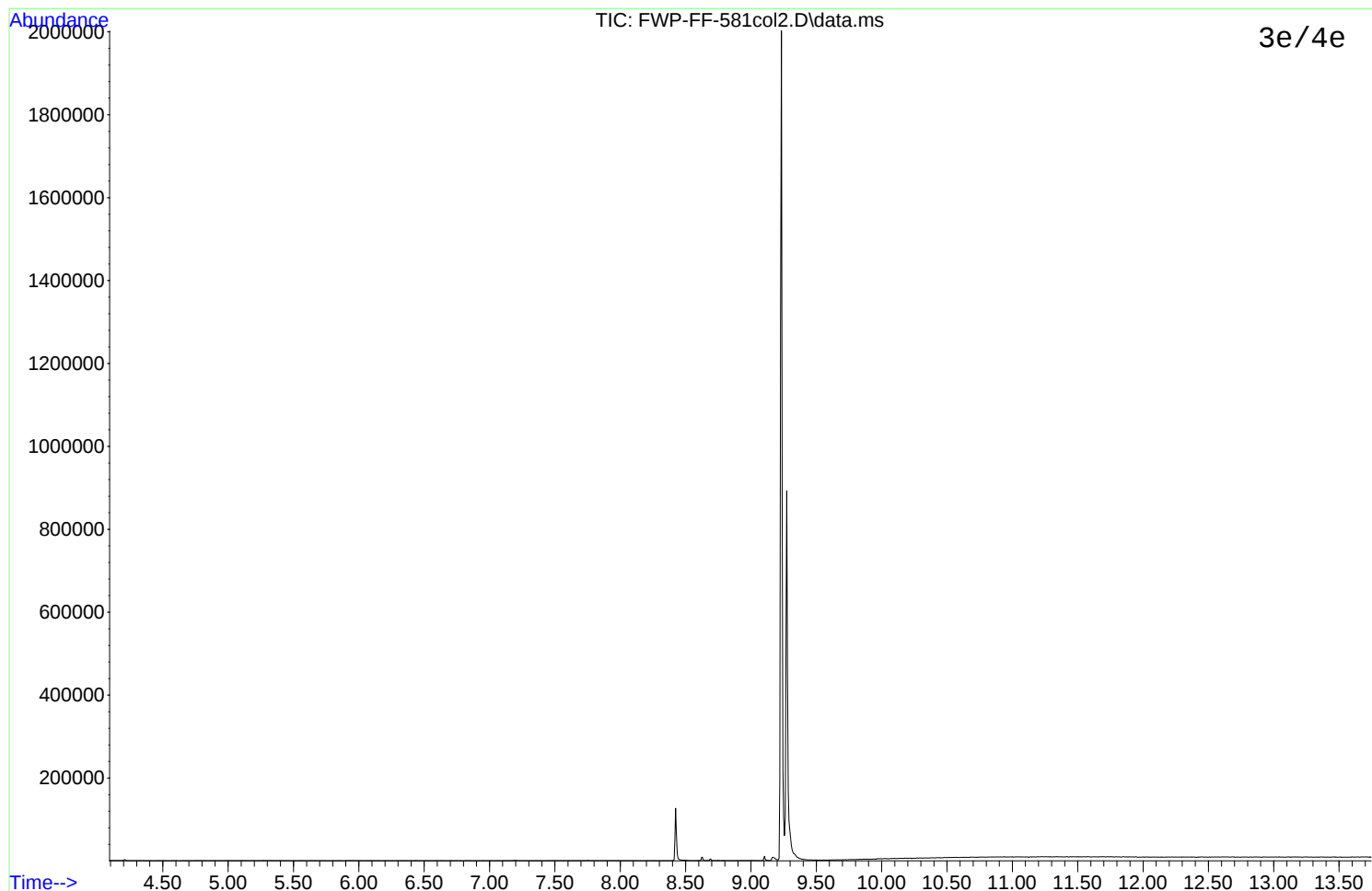


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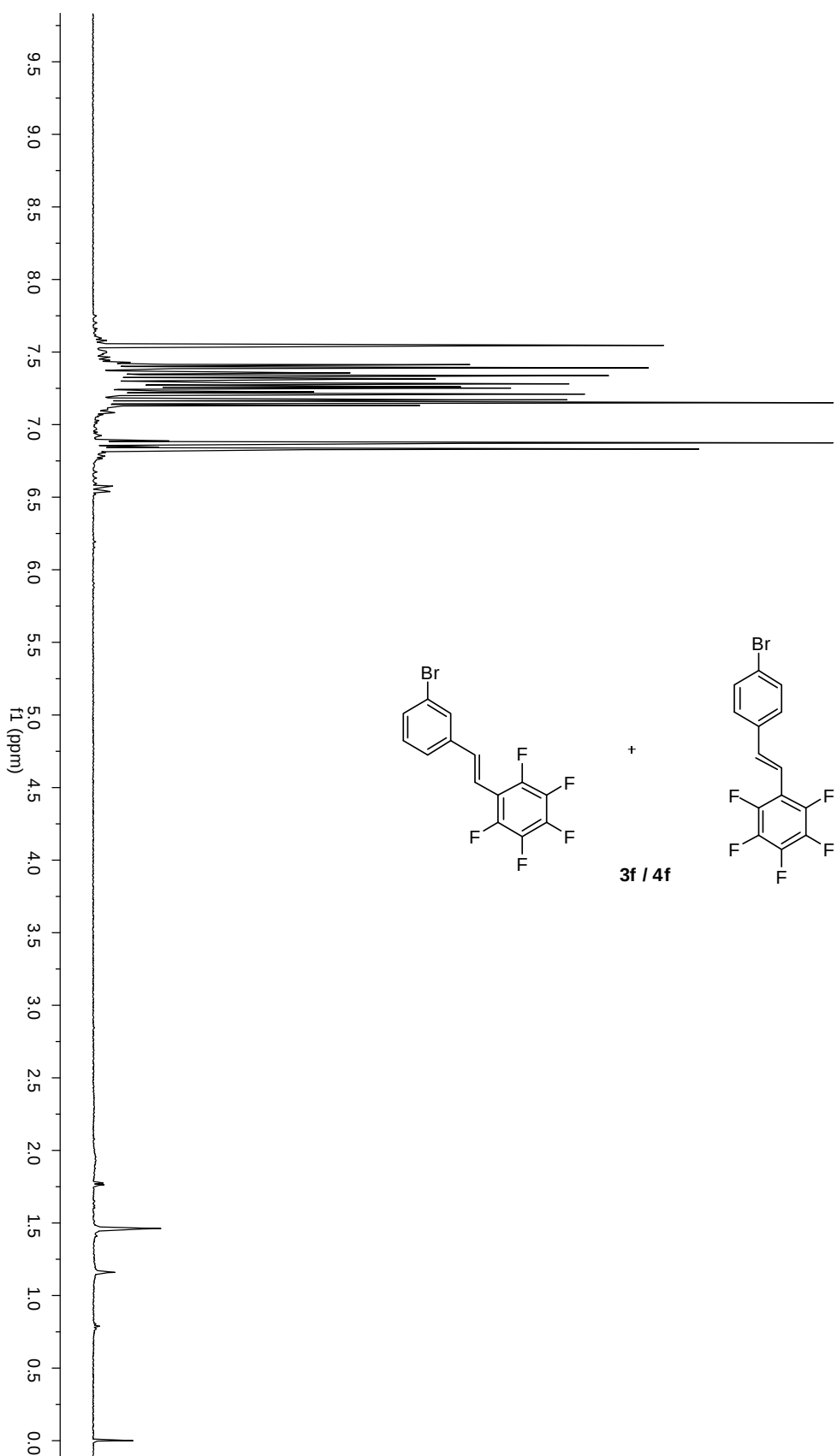


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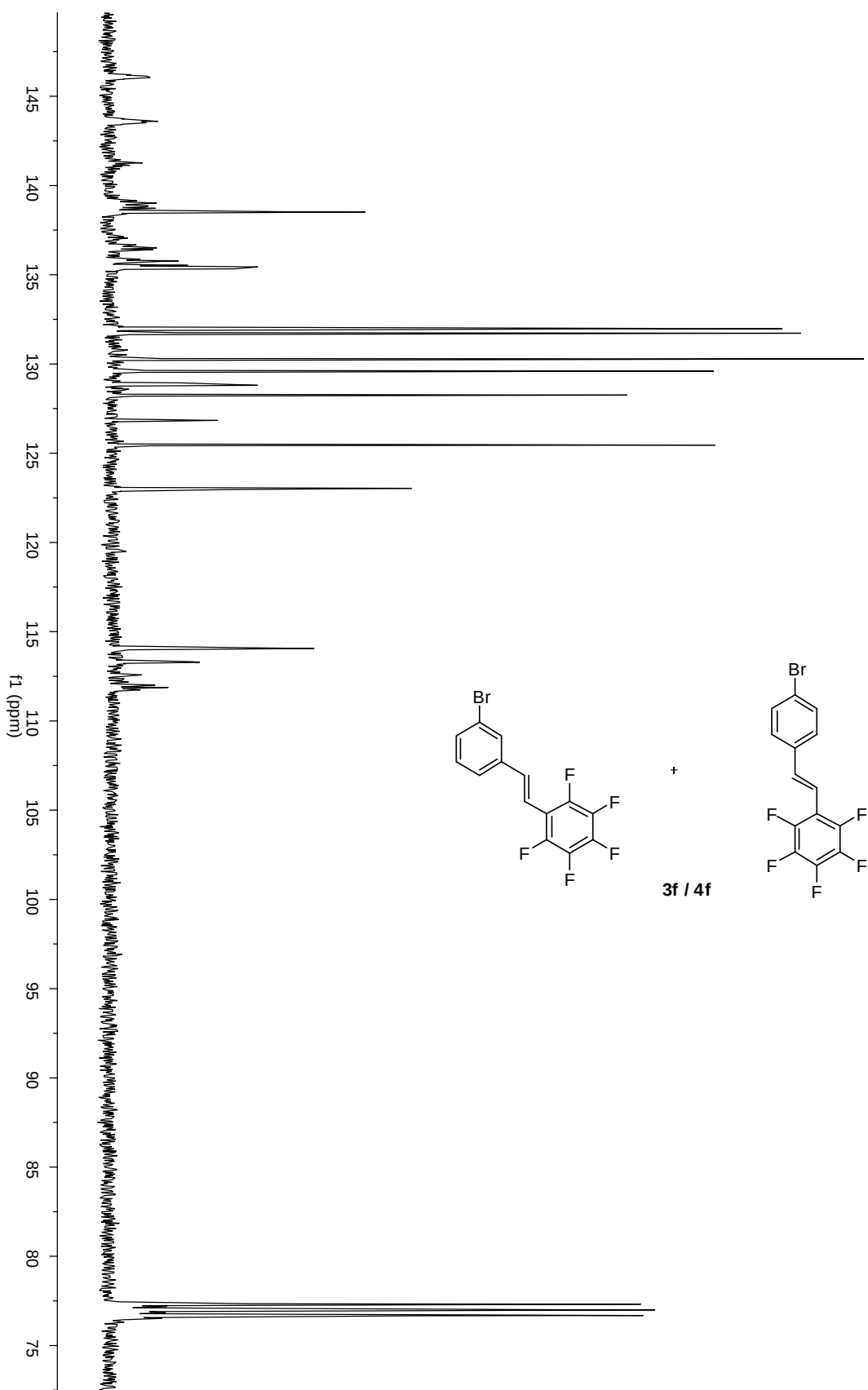




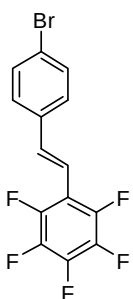
Jul25-2011
glo patureau fwp 580
proton CDCl3 /opt/topspin av1.3



Jul25-2011
glo patureau fwp 580
carbon CDCl3 /opt/topspin av1.3

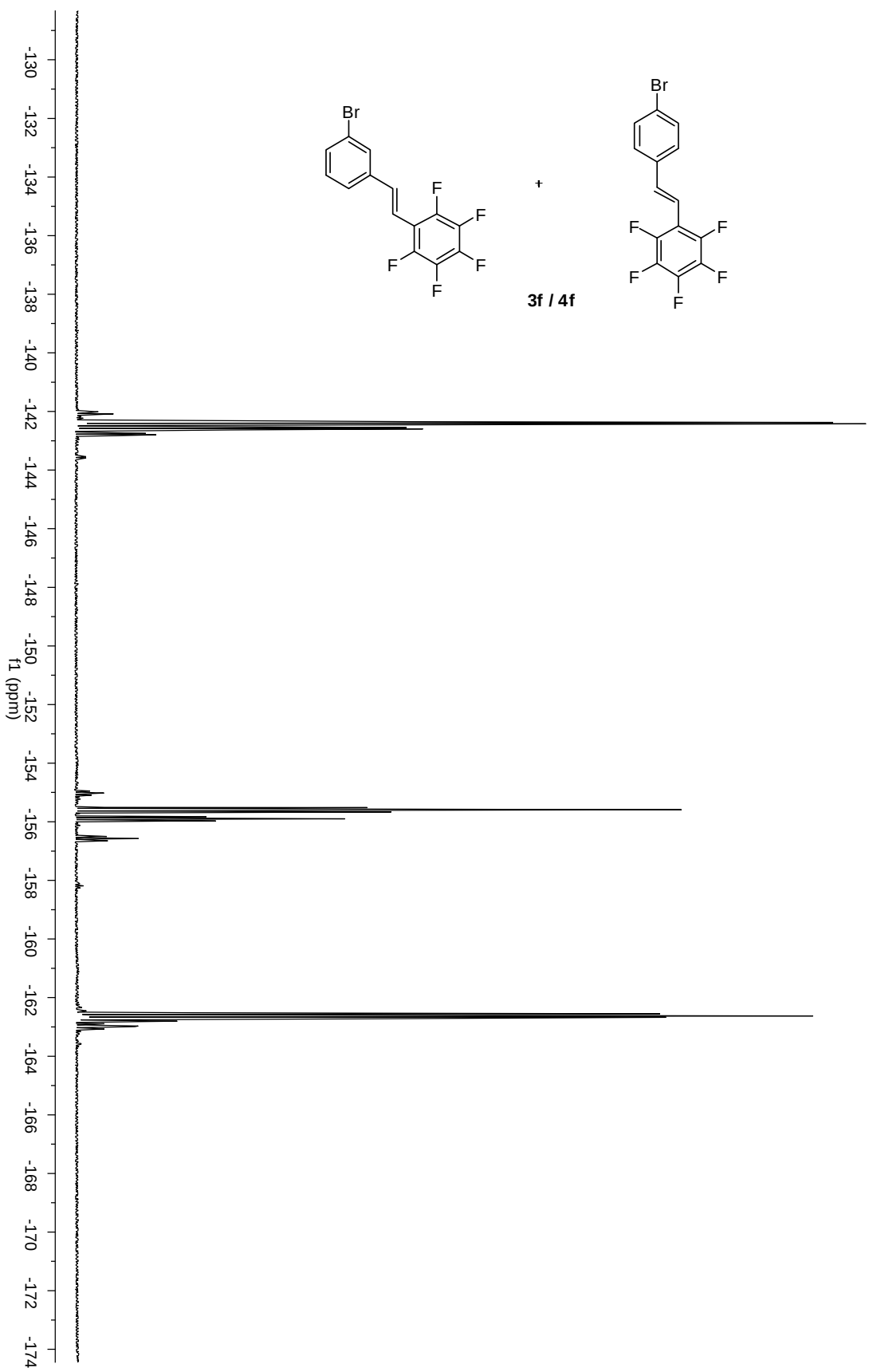
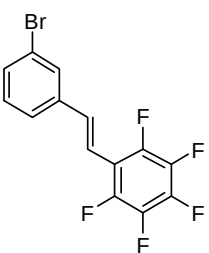


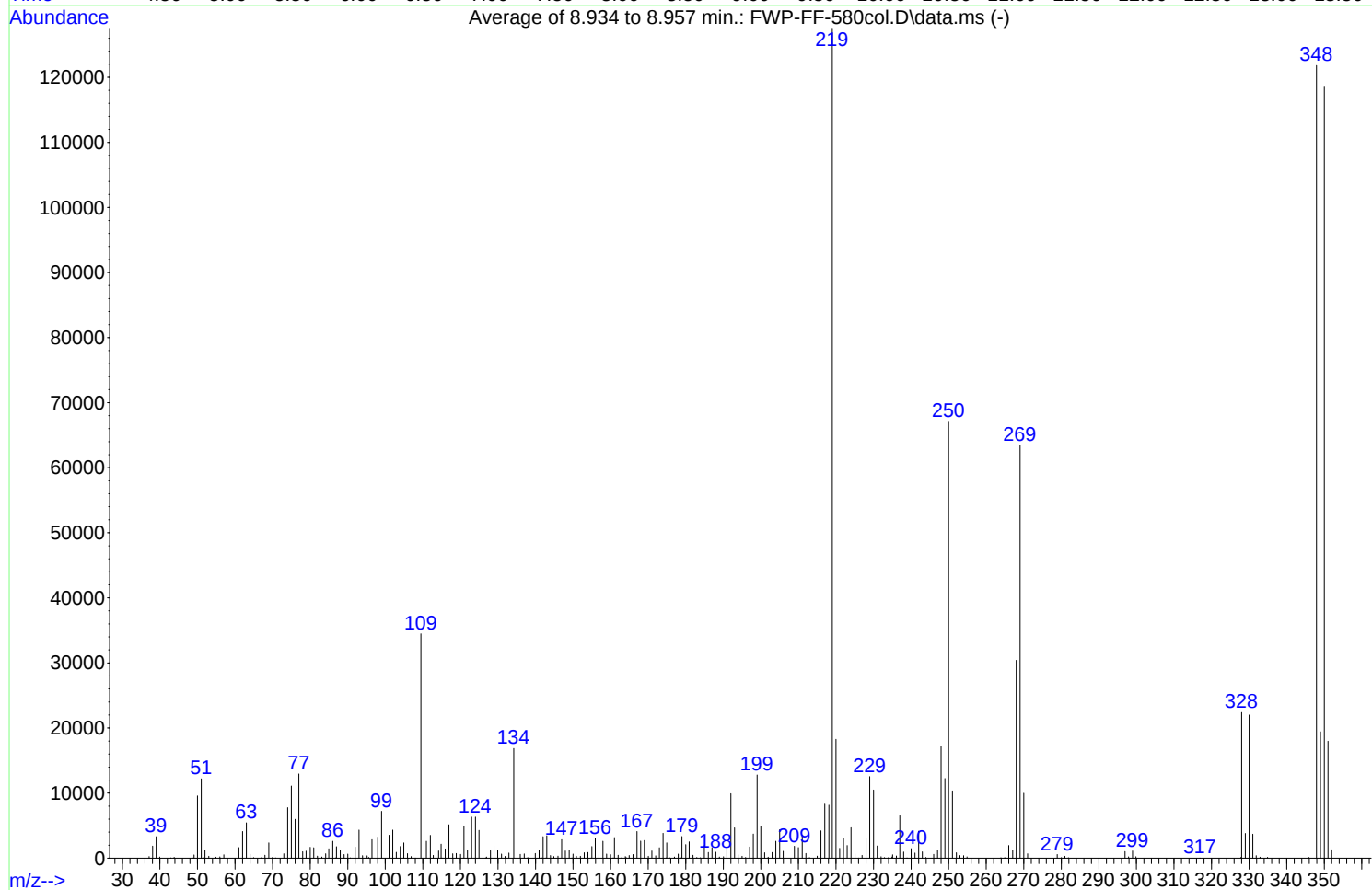
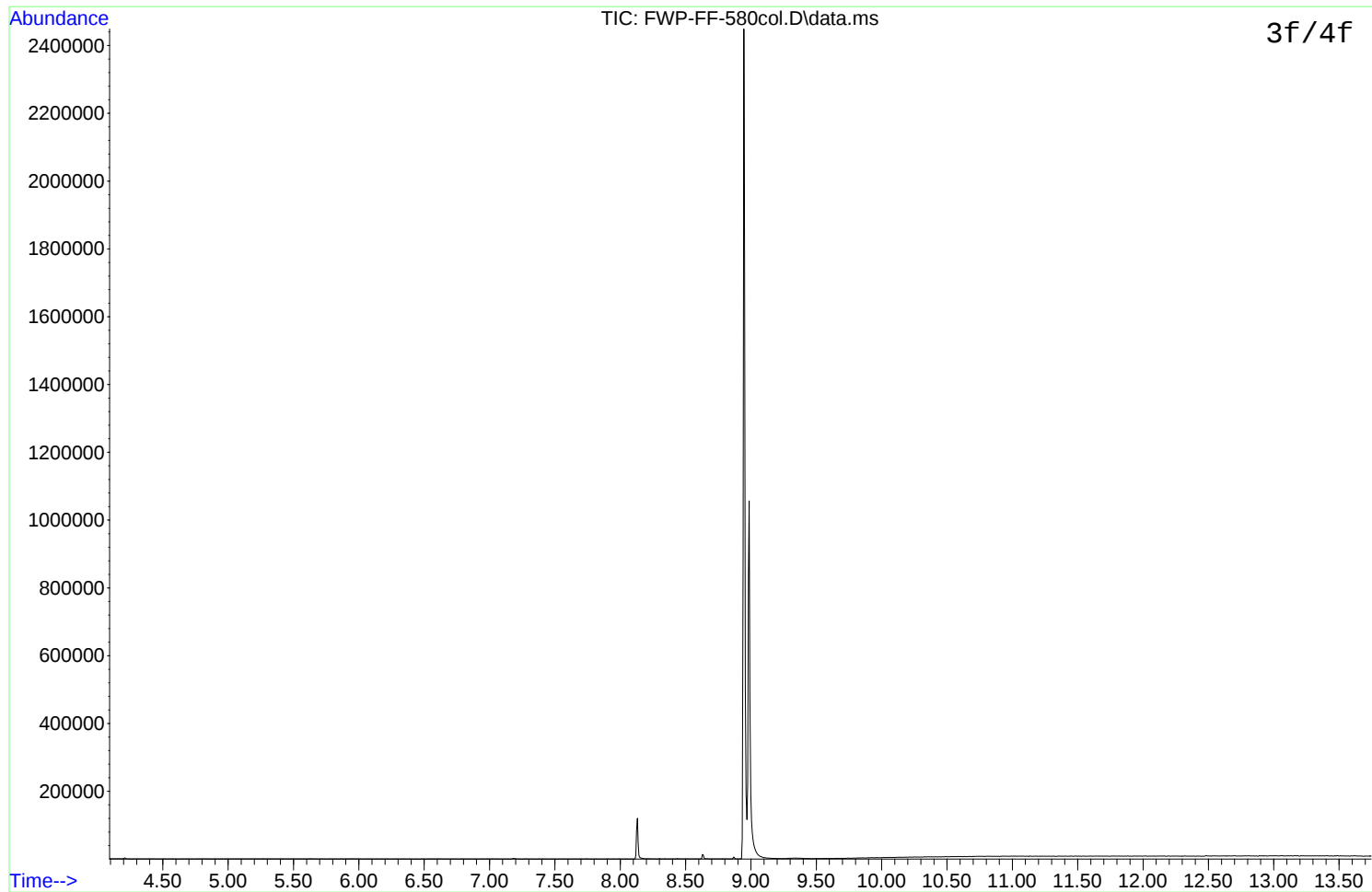
Jul21-2011
glo patureau twp ff 580
f19cpd-exp CDC13 /opt/topspin av1 33



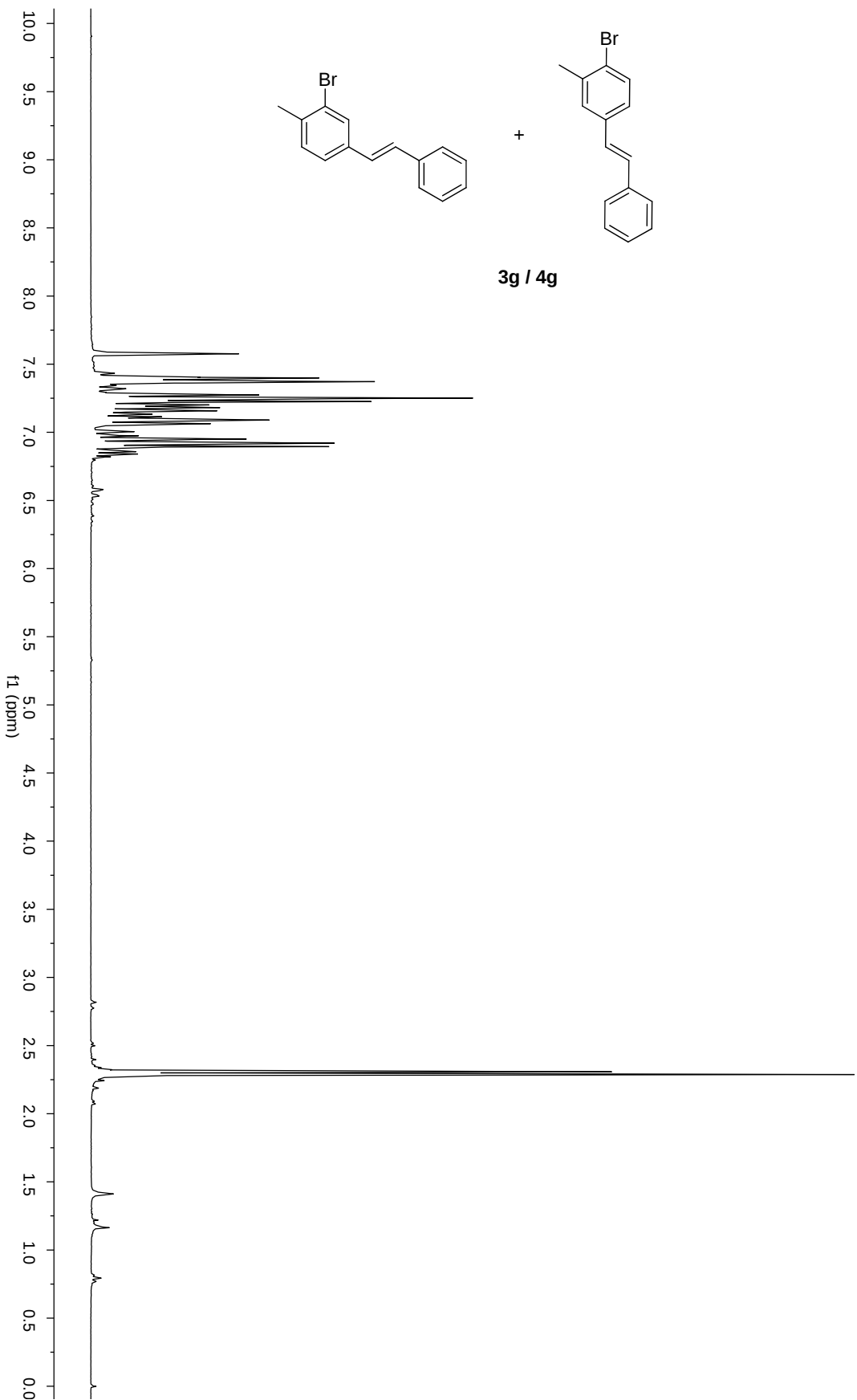
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3f / 4f

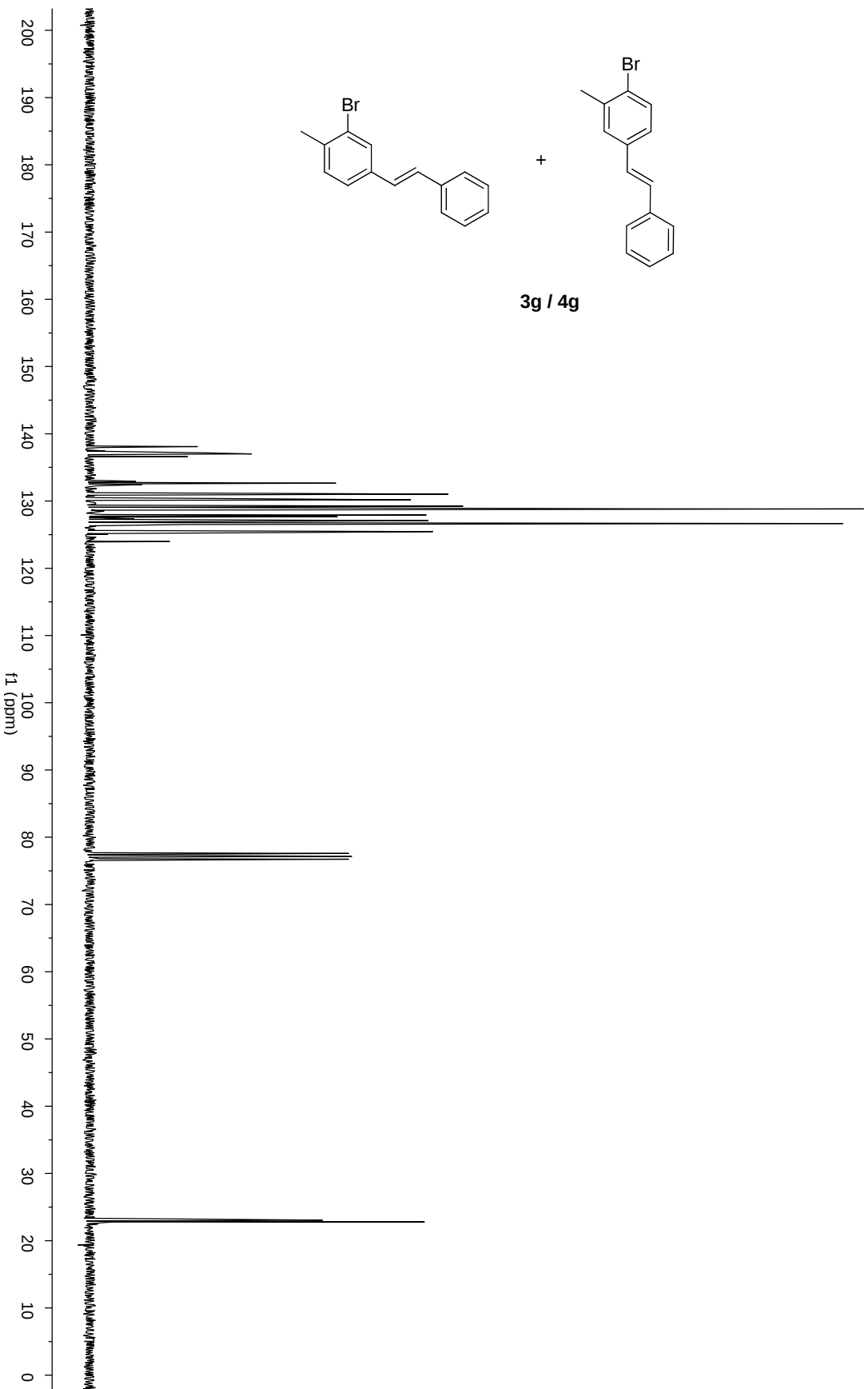
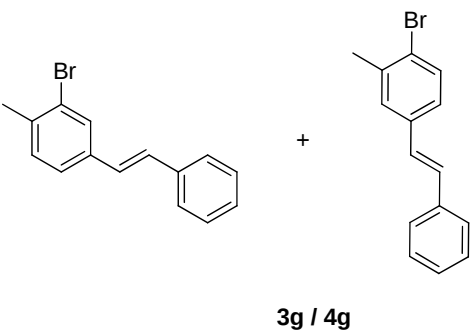




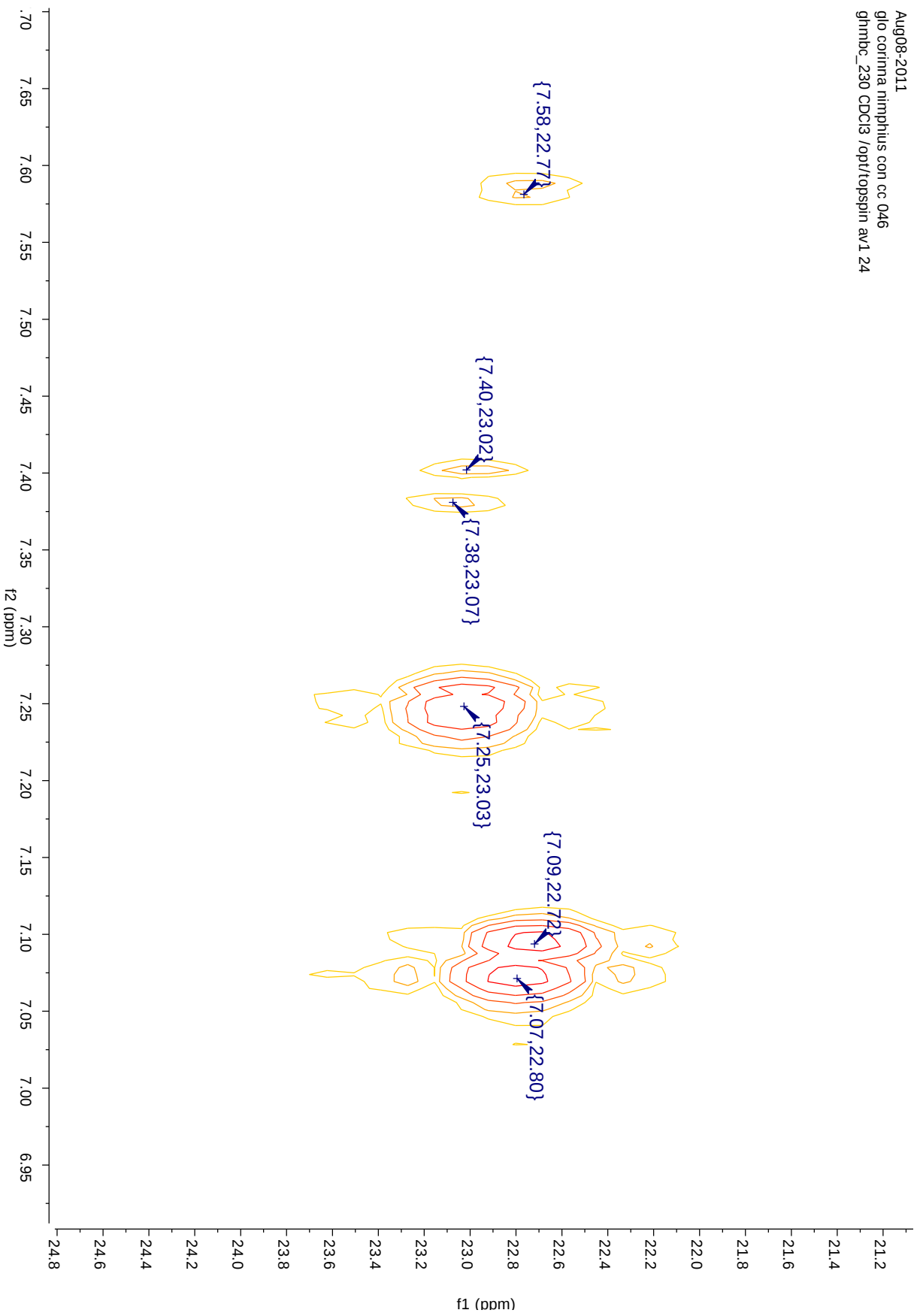
Aug05-2011
glo nimphius con cc 046
proton CDC13 /opt/topspin av1.43



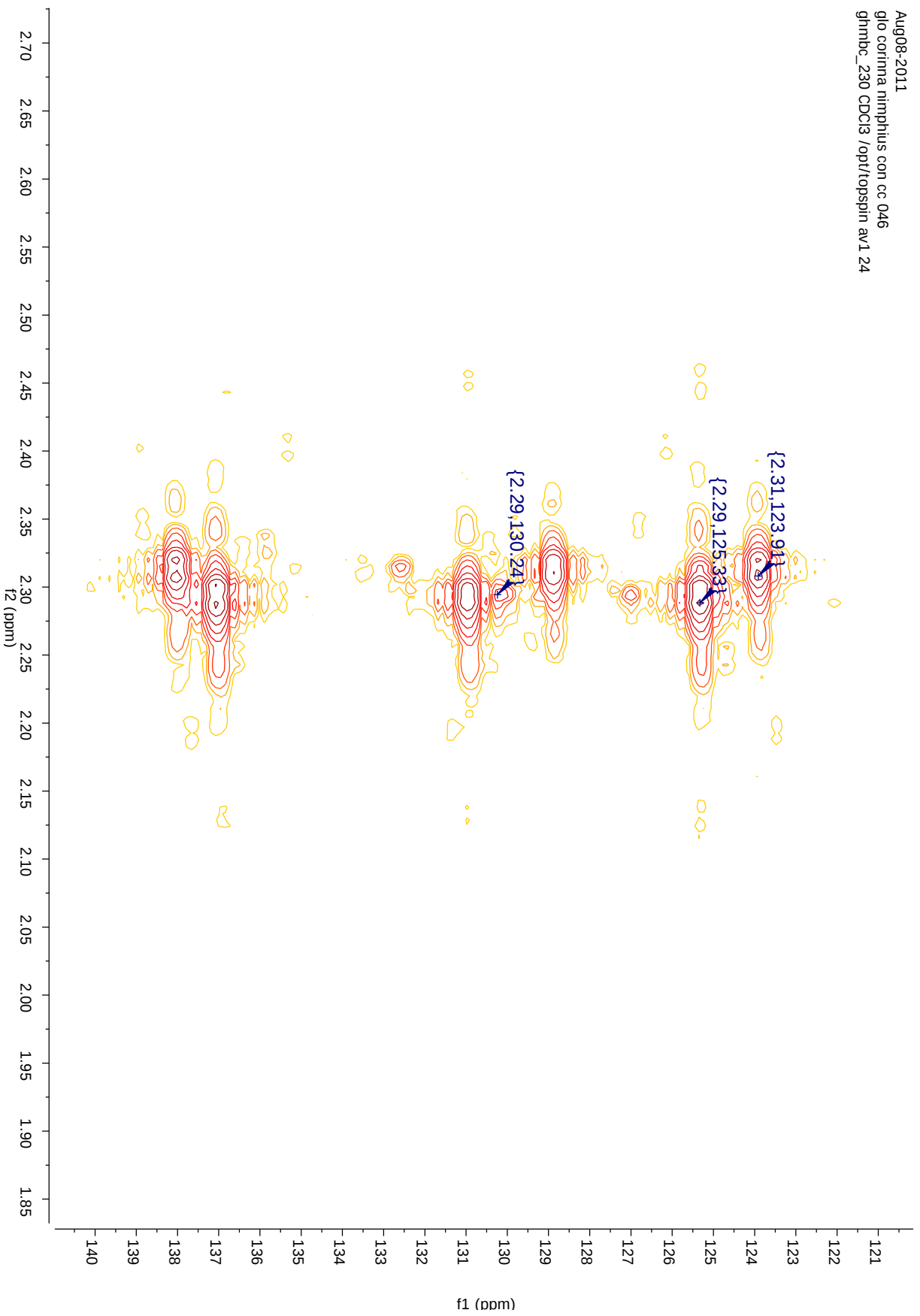
Aug05-2011
gio nimphius con cc 046
carbon CDCl3 /opt/topspin av1.43



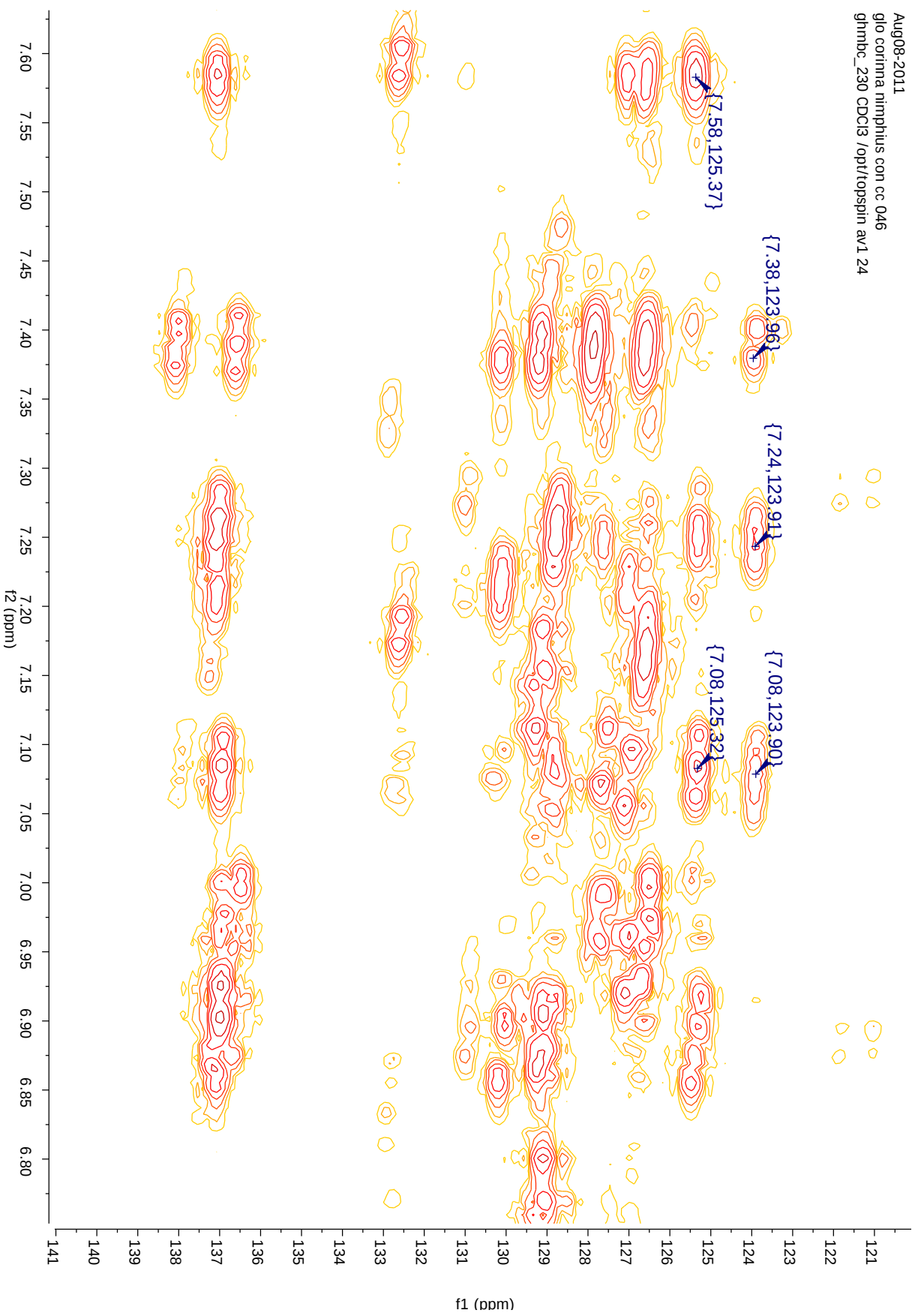
Aug08-2011
glo corinna nimphus con cc 046
ghmbc_230 CDC13 /opt/topspin av1 24

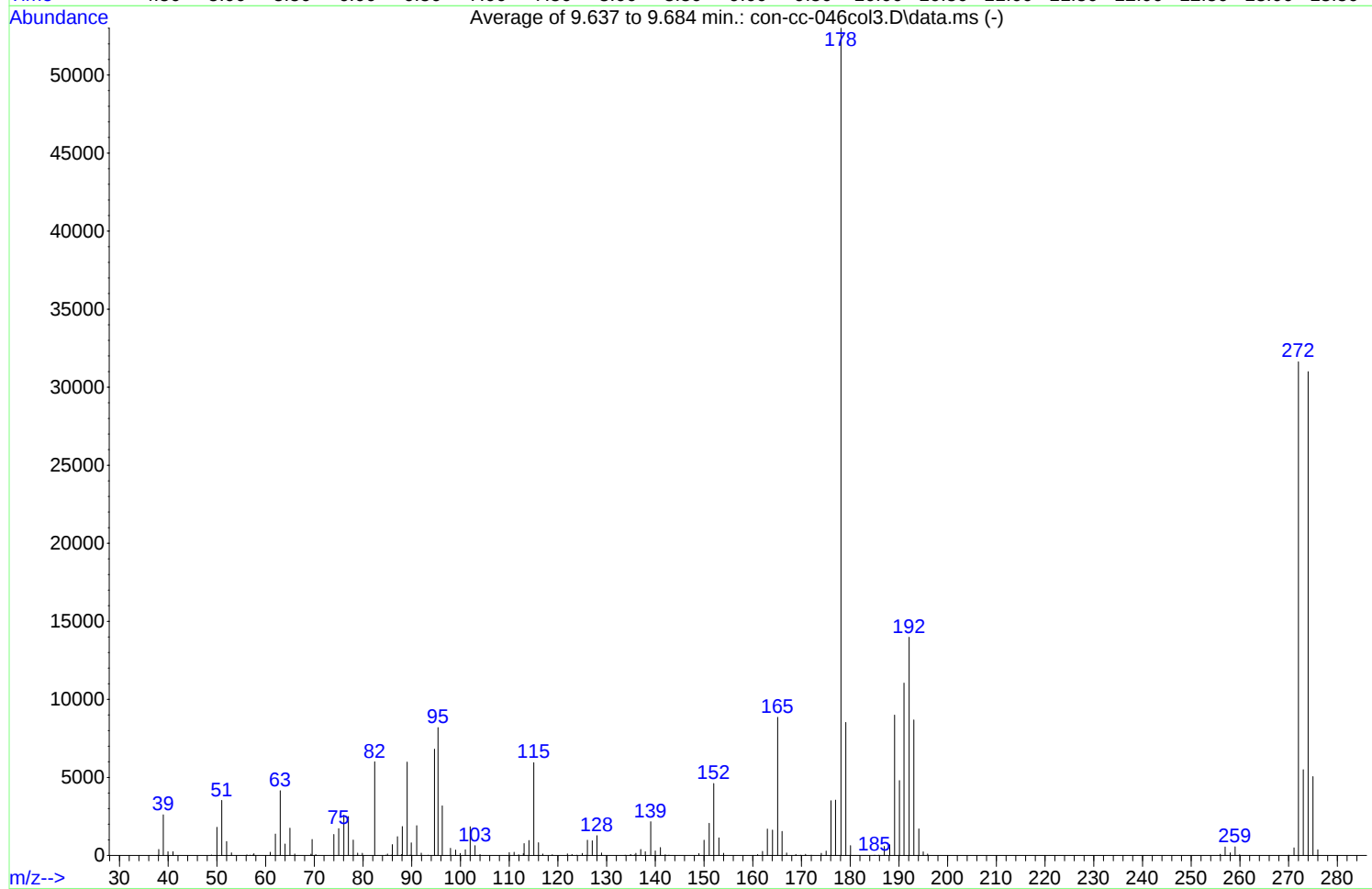
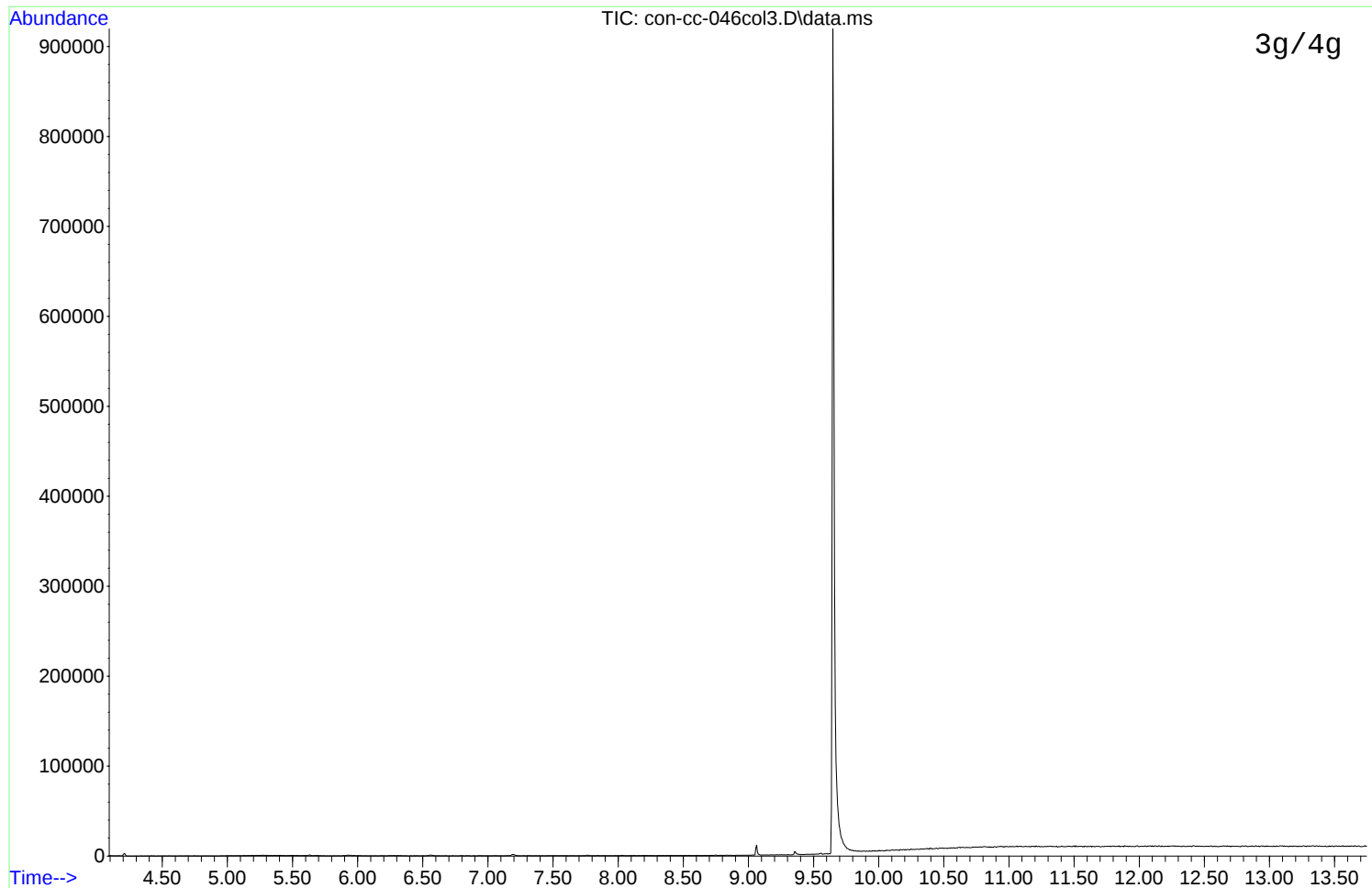


Aug08-2011
gio corinna nimphus con cc 046
ghmbc_230 CDC13 /opt/topspin av1 24

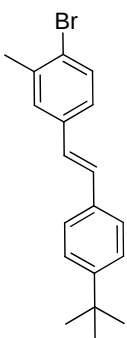


Aug08-2011
glo corinna nimphus con cc 046
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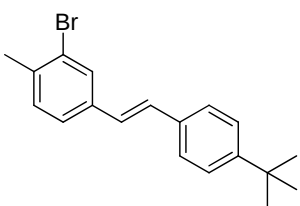




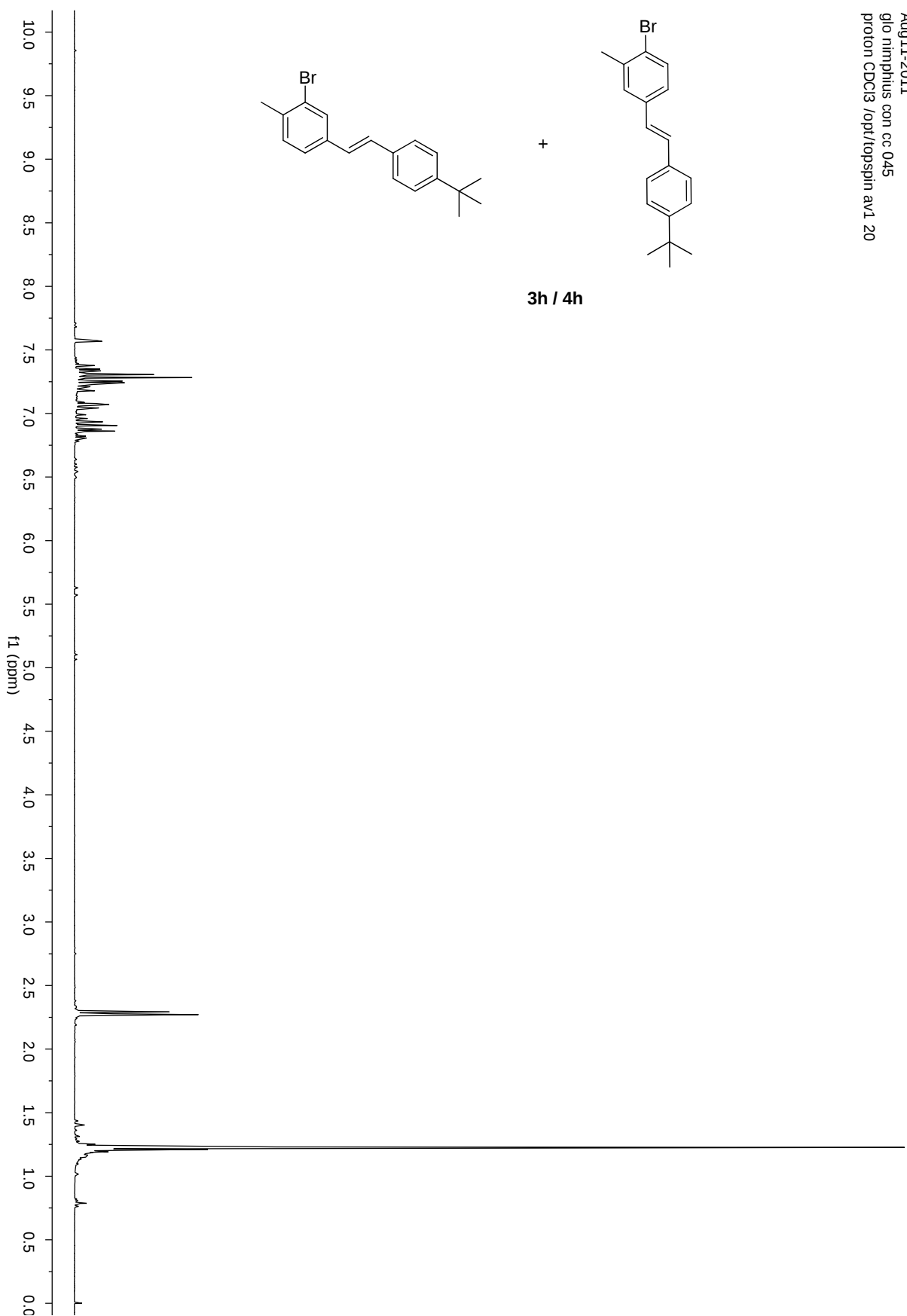
Aug11-2011
glo nimphius con cc 045
proton CDC13 /opt/topspin av1.20



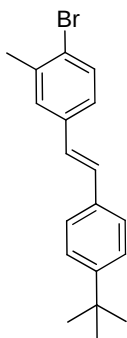
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3h / 4h

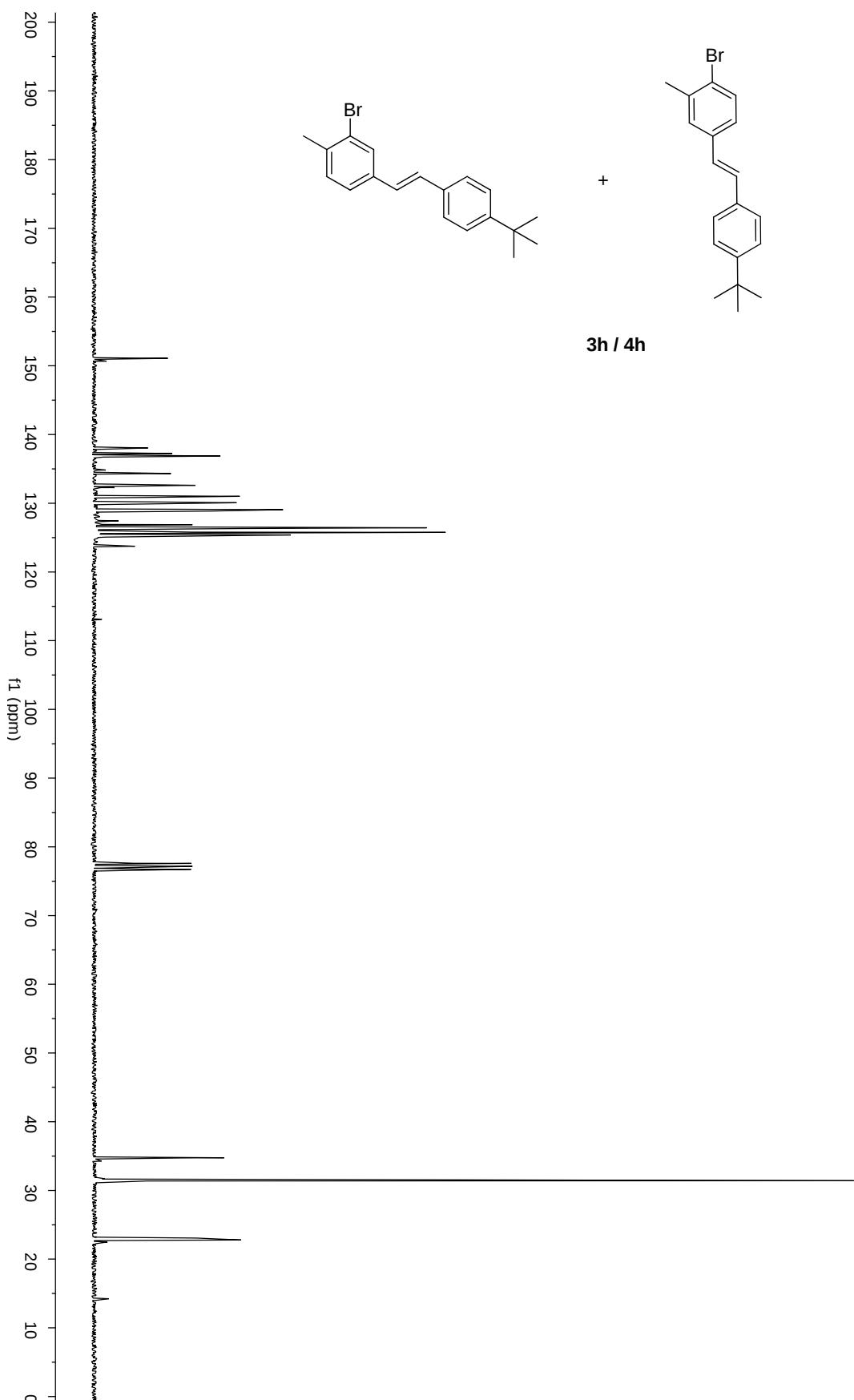
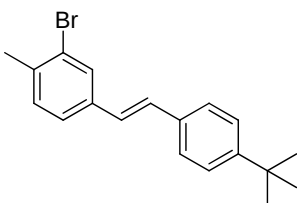


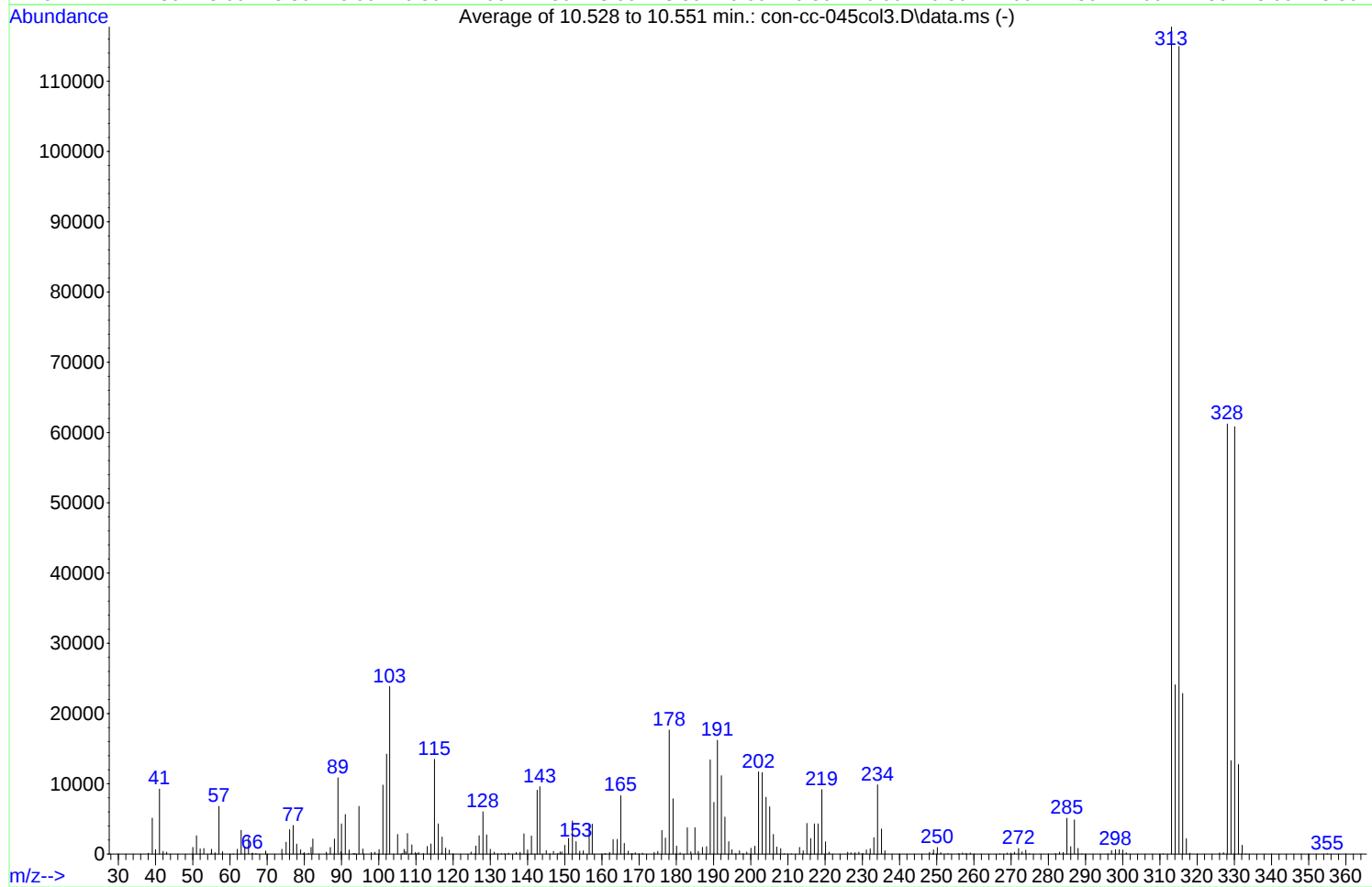
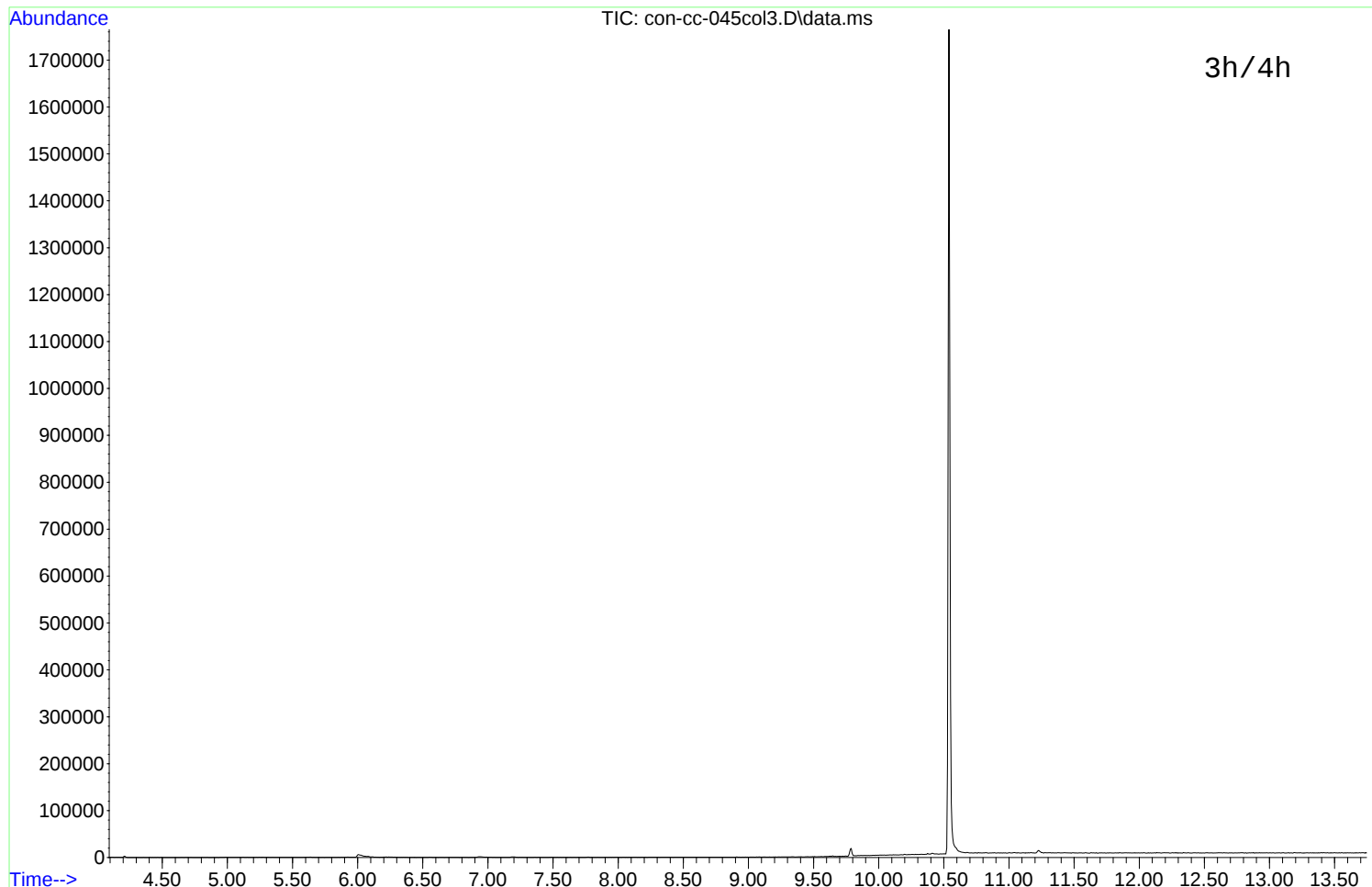
Aug11-2011
gio nimphius con cc 045
carbon CDCl3 /opt/topspin av1.20



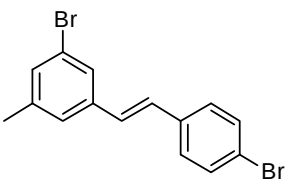
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3h / 4h

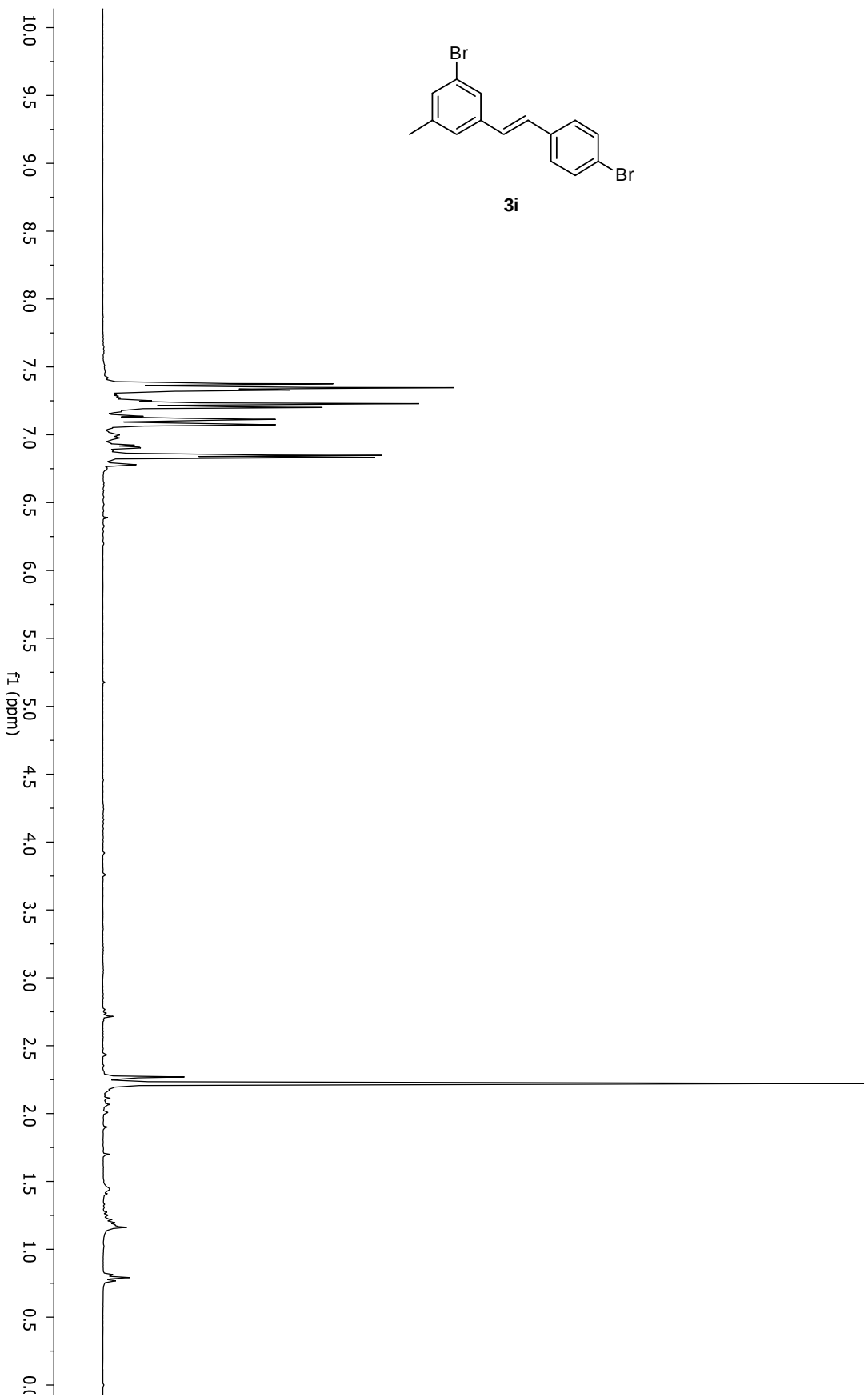




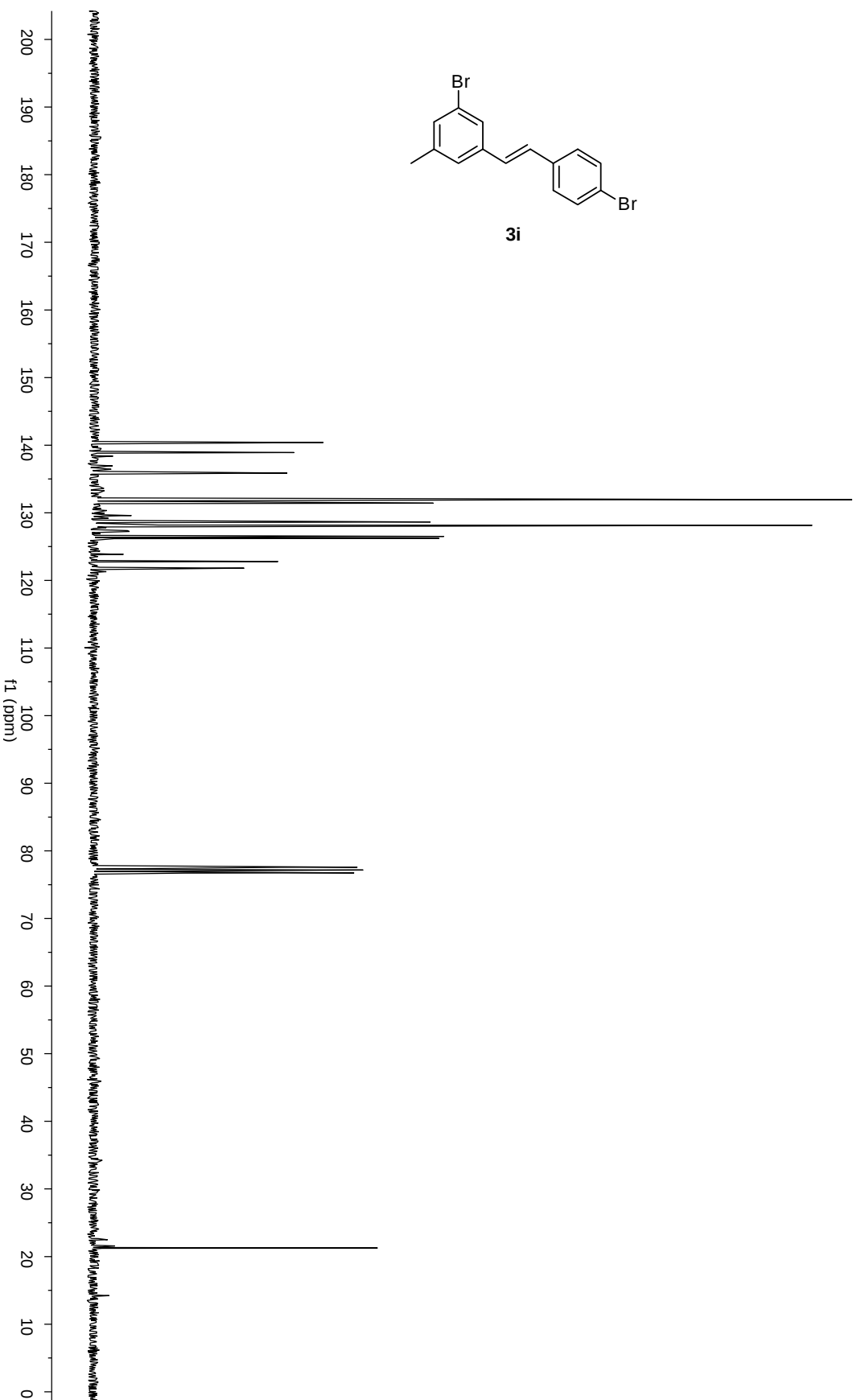
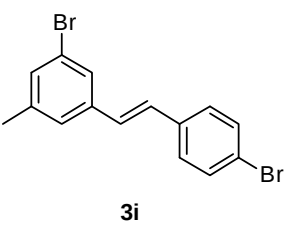
Jul25-2011
glo nimphius con cc 043 2 f1
proton CDCl3 /opt/topspin av1 31

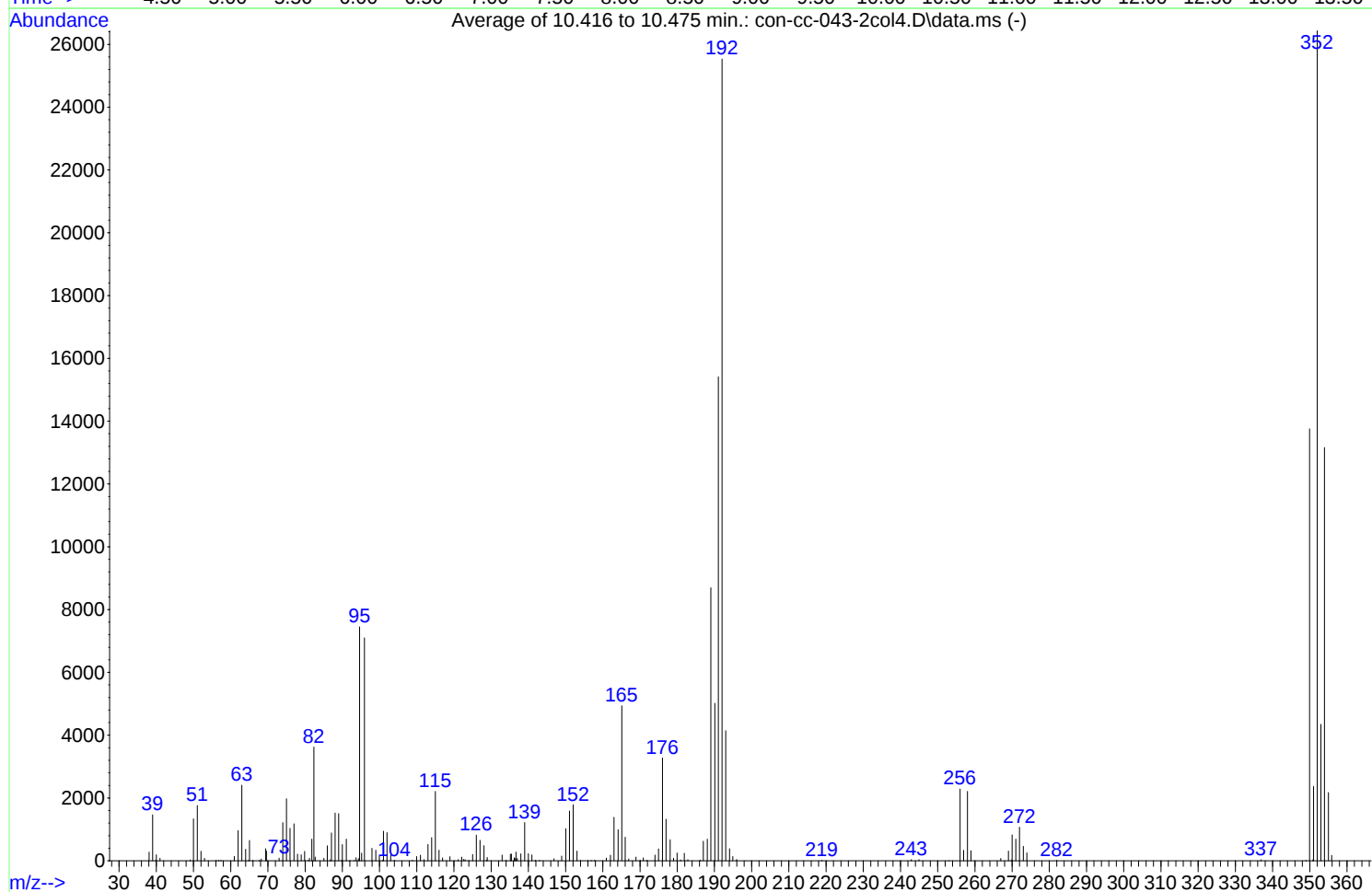
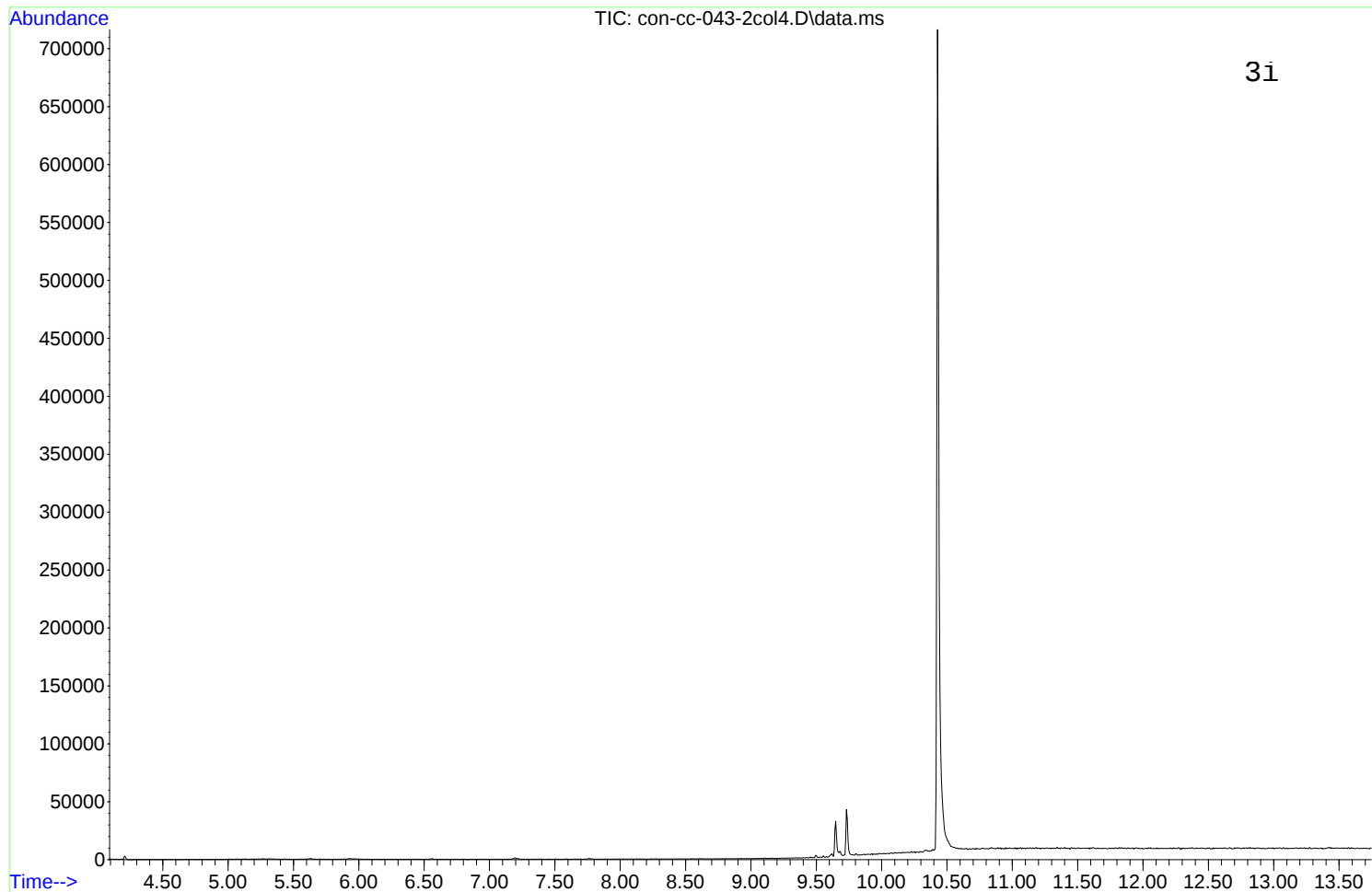


3i

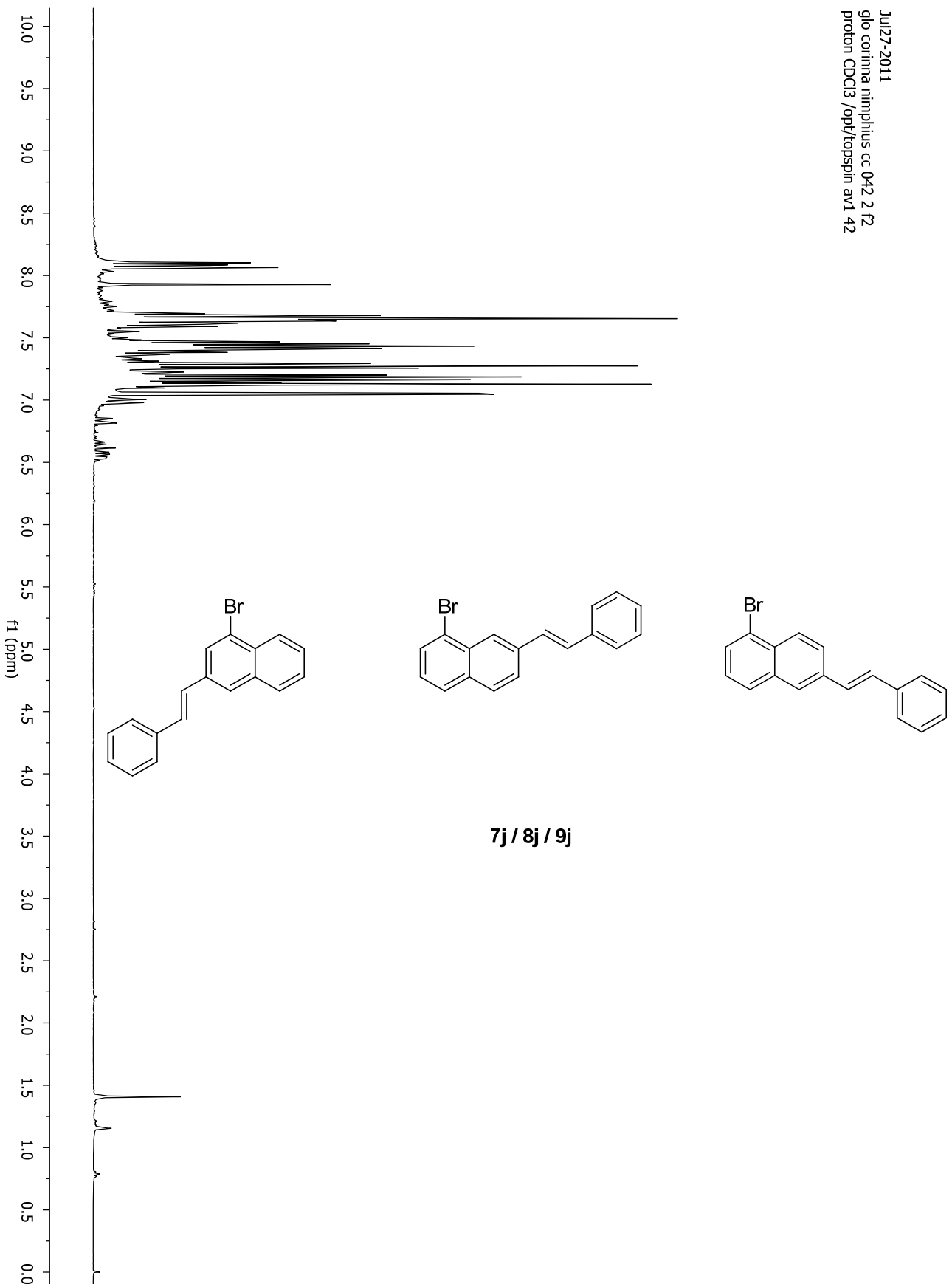


Jul25-2011
glo nimphius con cc 043 2 f1
carbon CDCl3 /opt/topspin av1 31

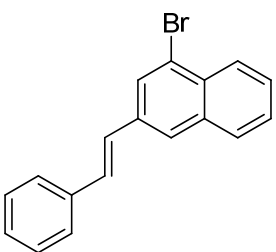
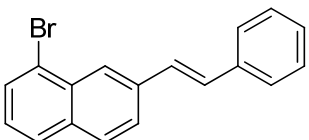
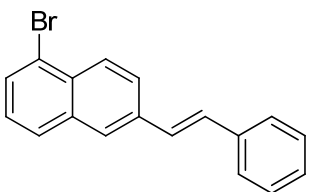




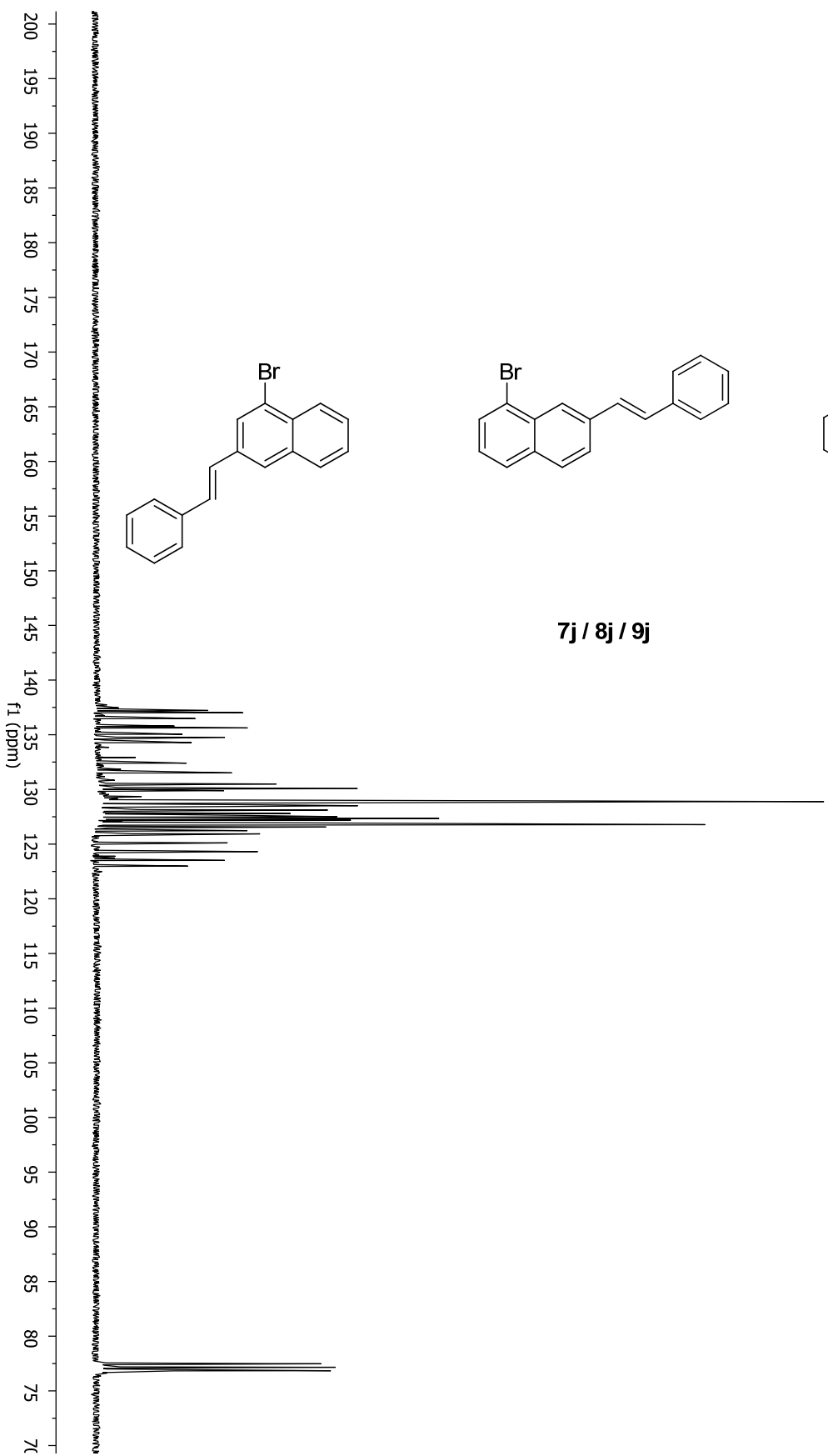
Jul27-2011
glo corinna nimphius cc 042 2 f2
proton CDCl3 /opt/topspin av1 42



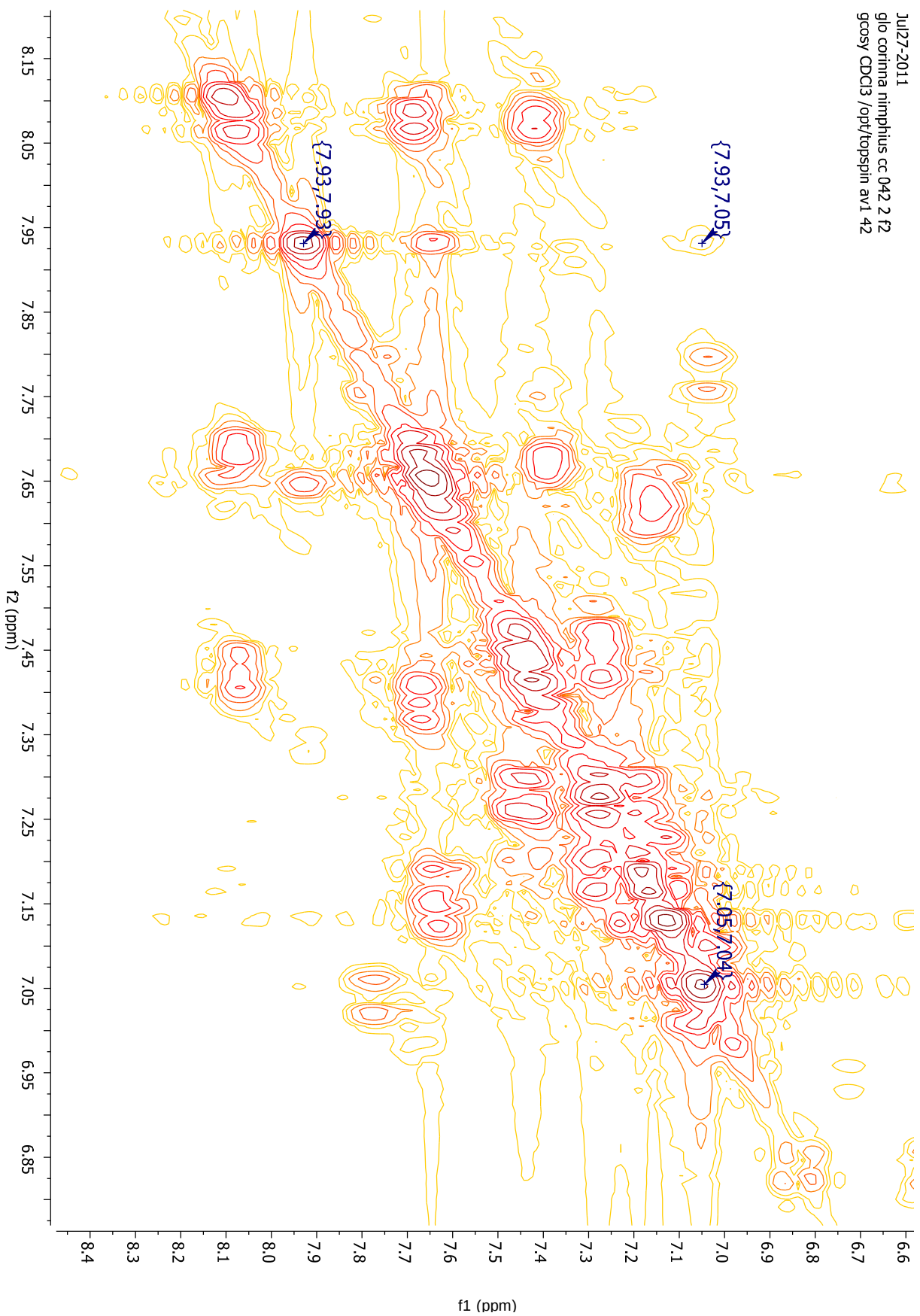
Jul27-2011
glo corinna nimphus cc 042.2 f2
carbon_5120 CDCI3 /opt/topspin av1 42



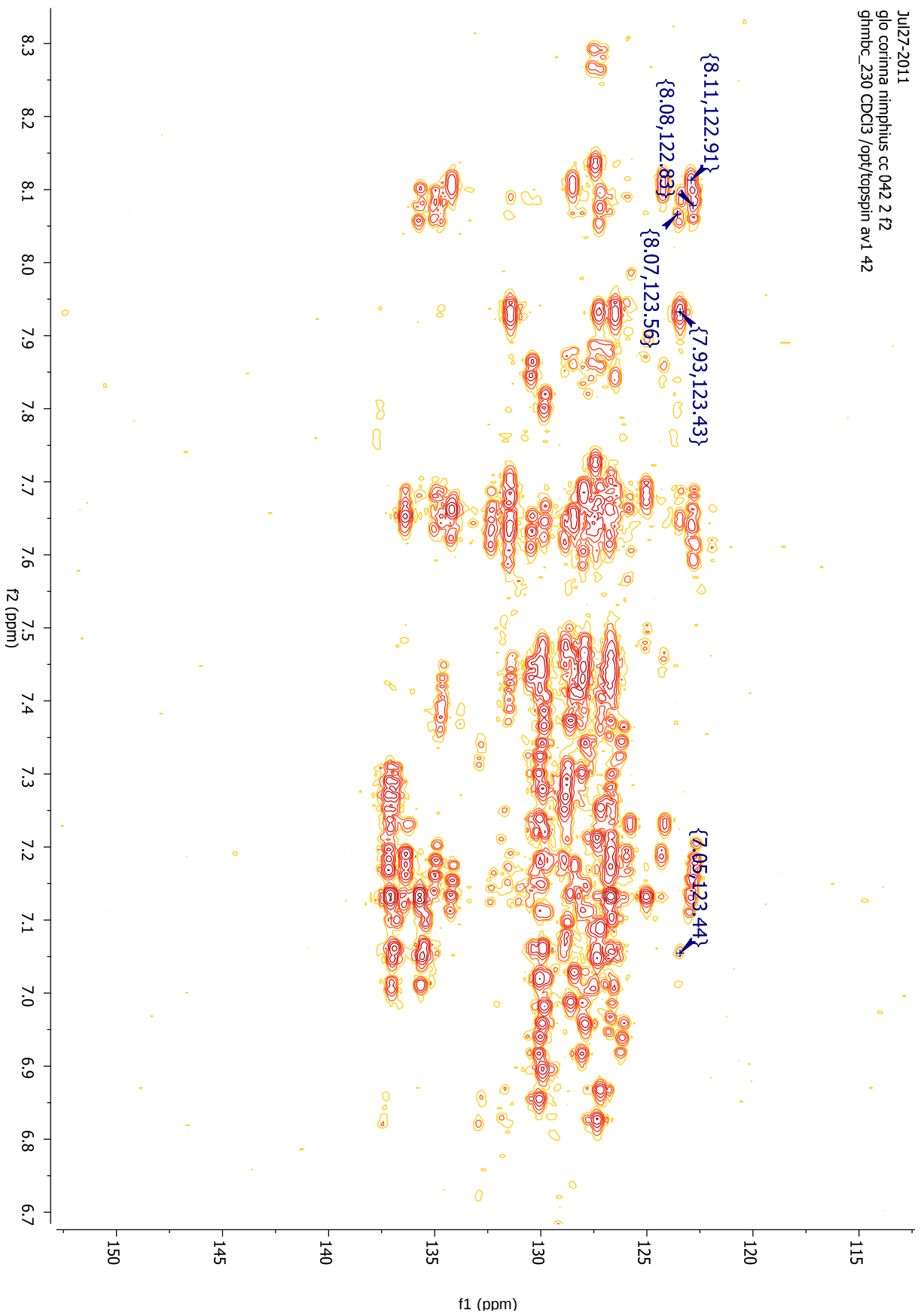
7j / 8j / 9j

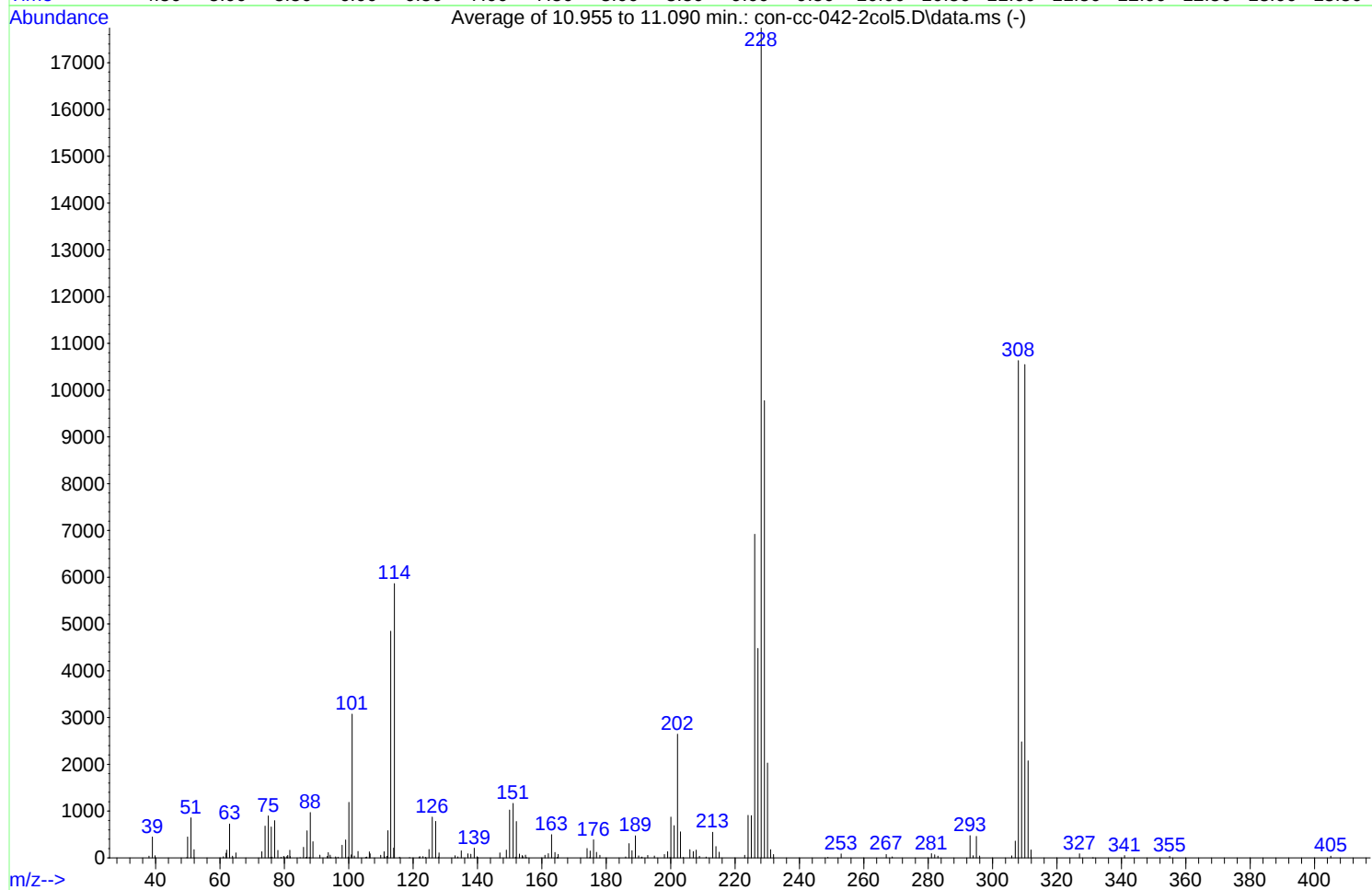
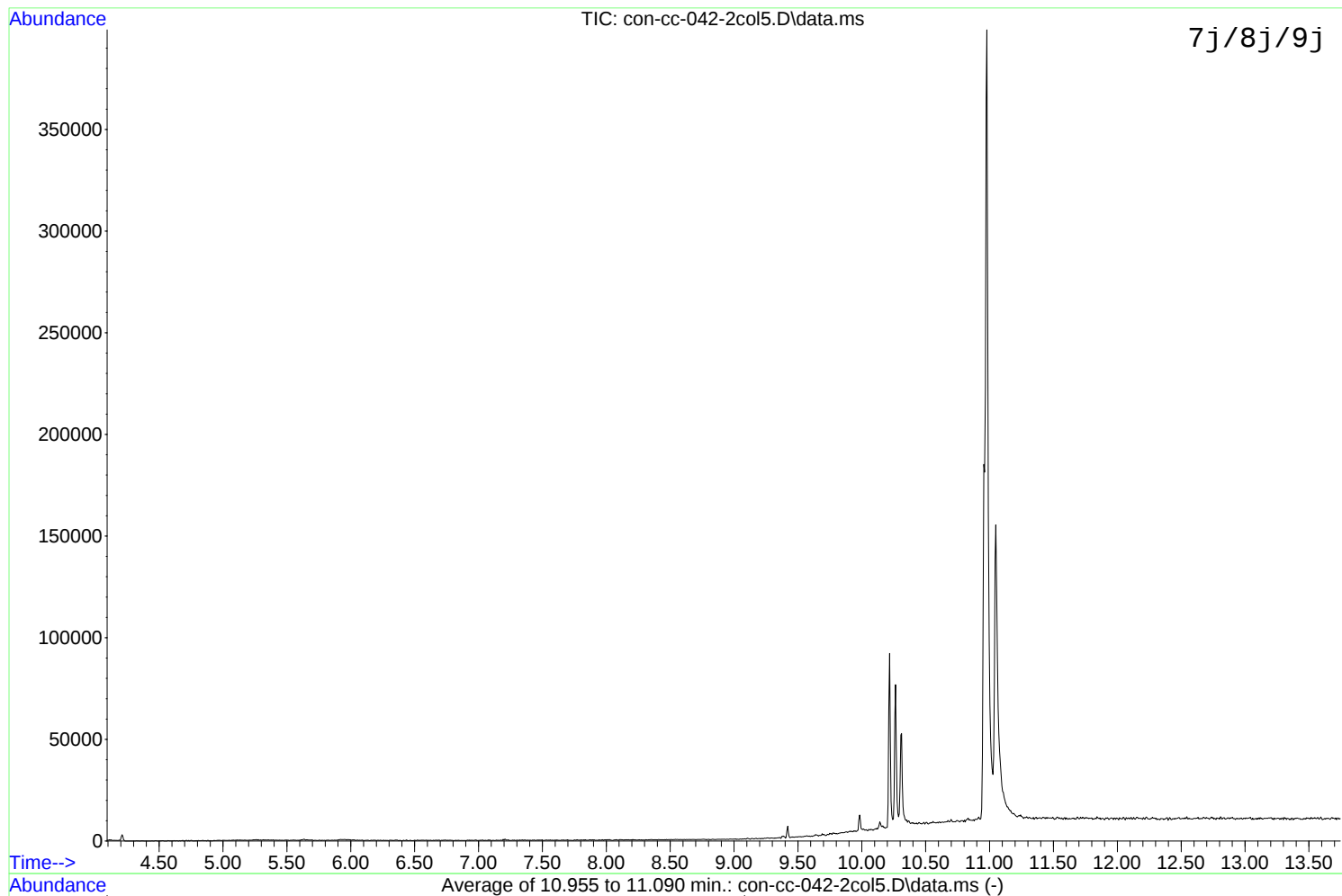


Jul27-2011
glo corinna nimphus cc 042 2 f2
gcosy CDC13 /opt/topspin av1 42

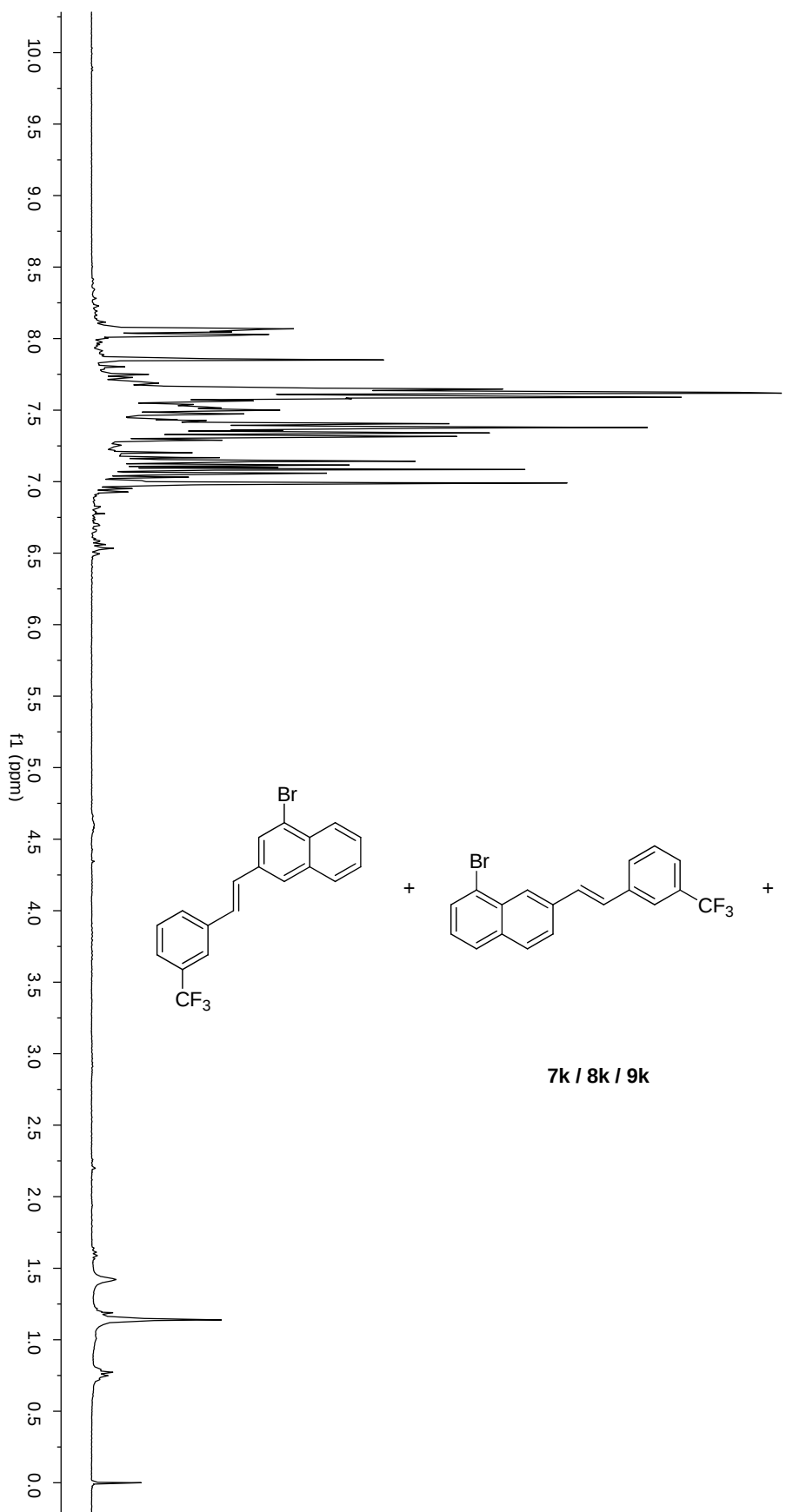


Jul27-2011
glo corinna nimphus cc 042 2 f2
gimbc_230 CDC3 /opt/topspin av1 42

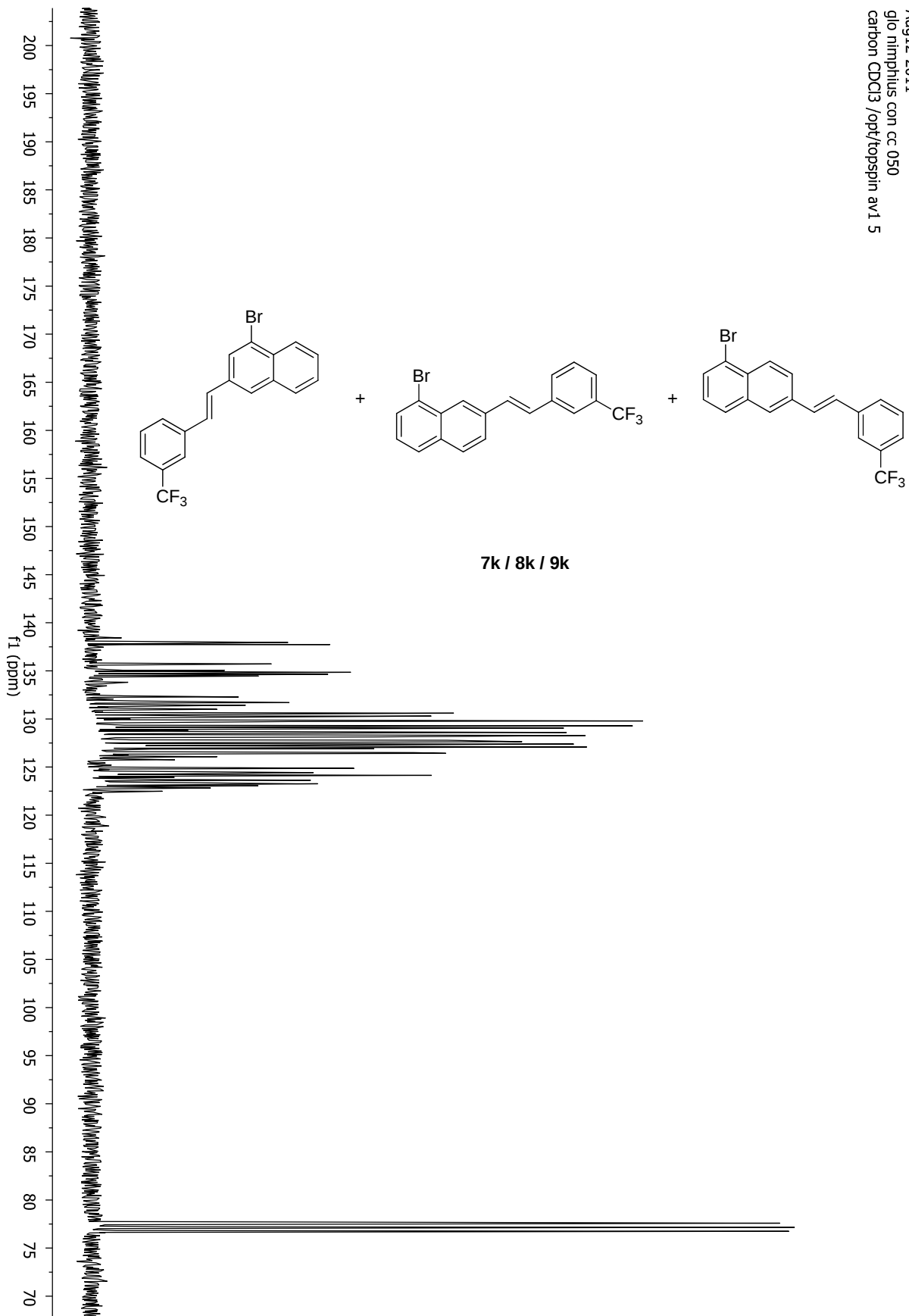




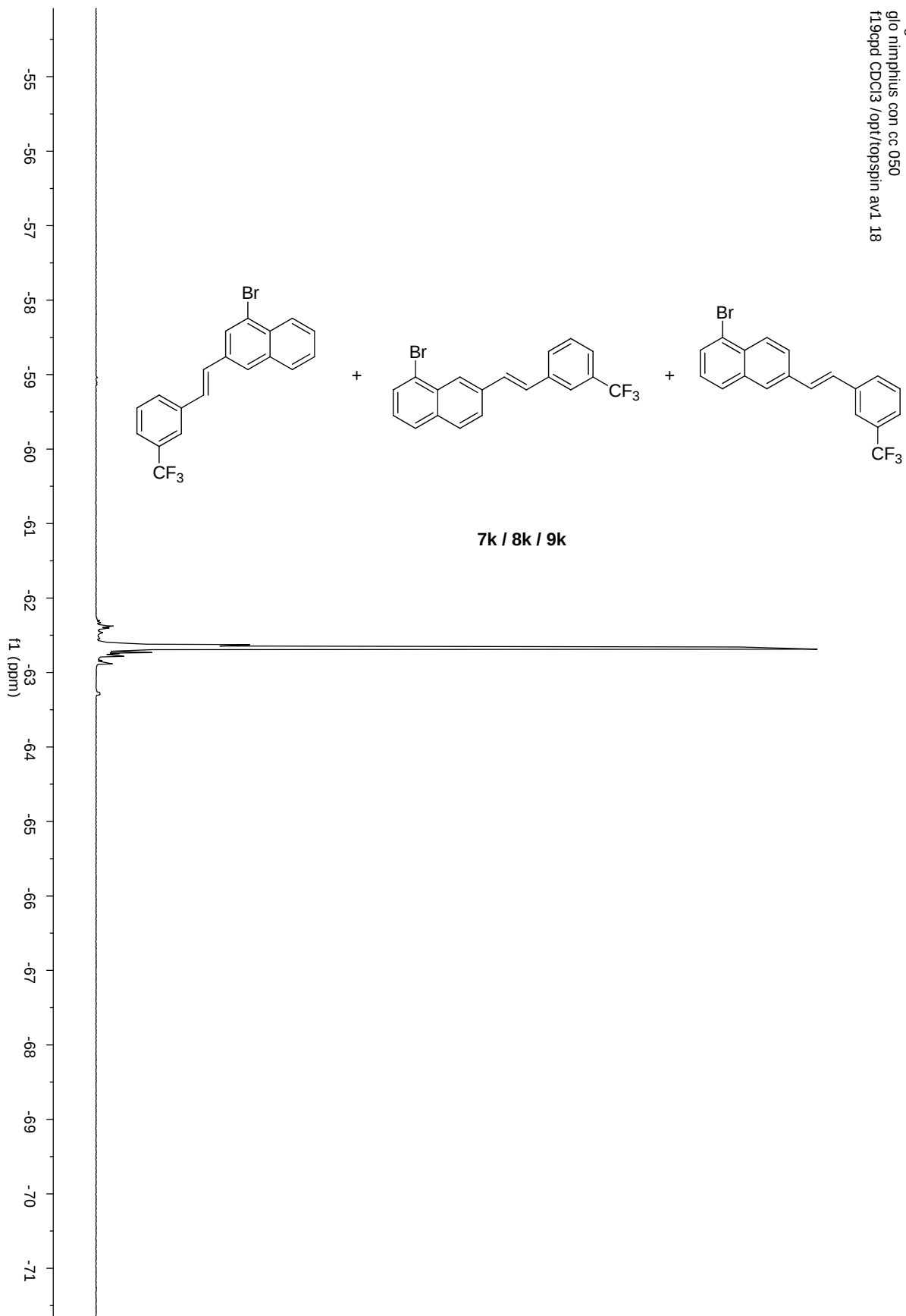
Aug12-2011
glo nimphus con cc 050
proton CDCl3 /opt/topspin av1.5

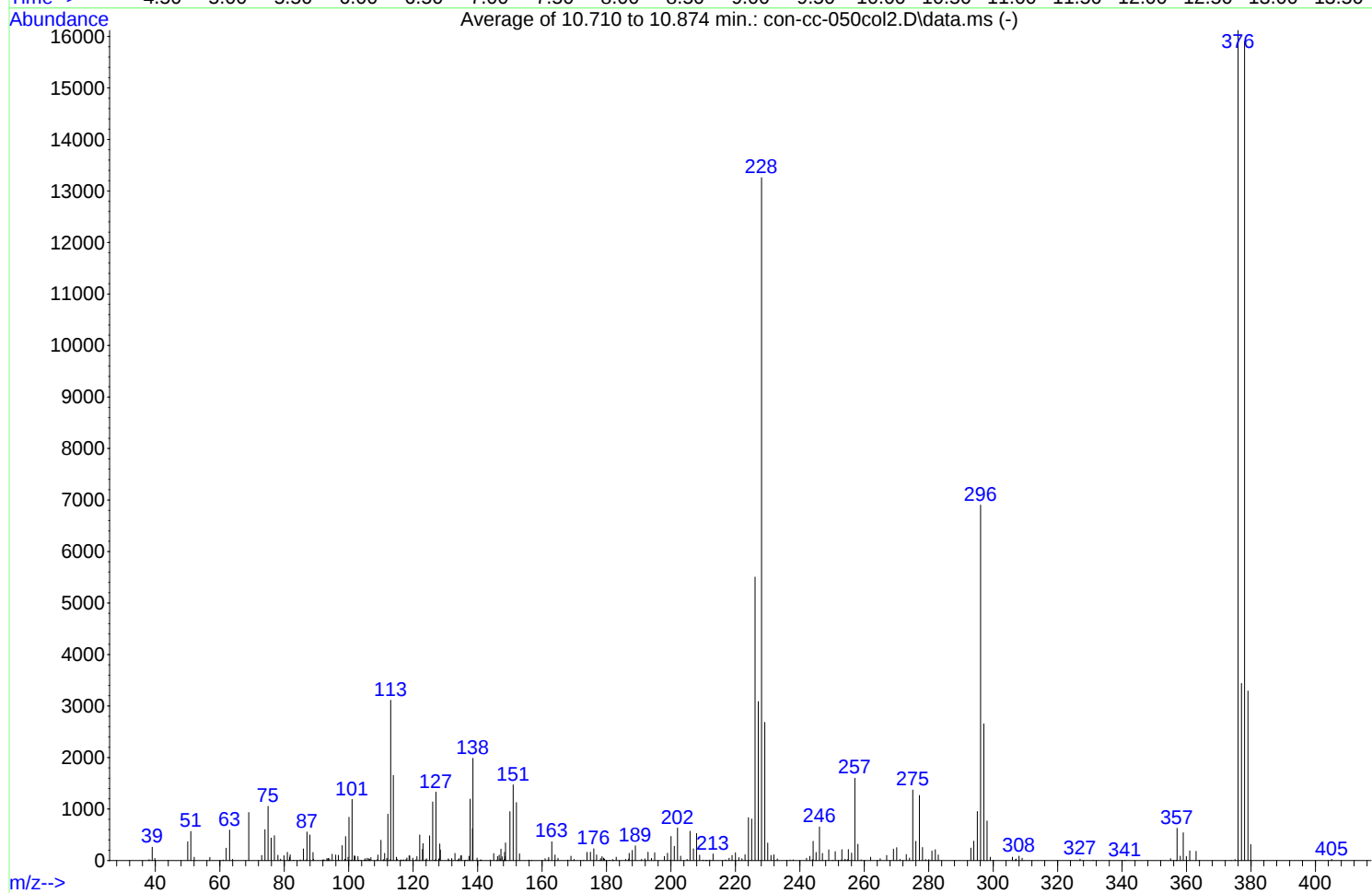
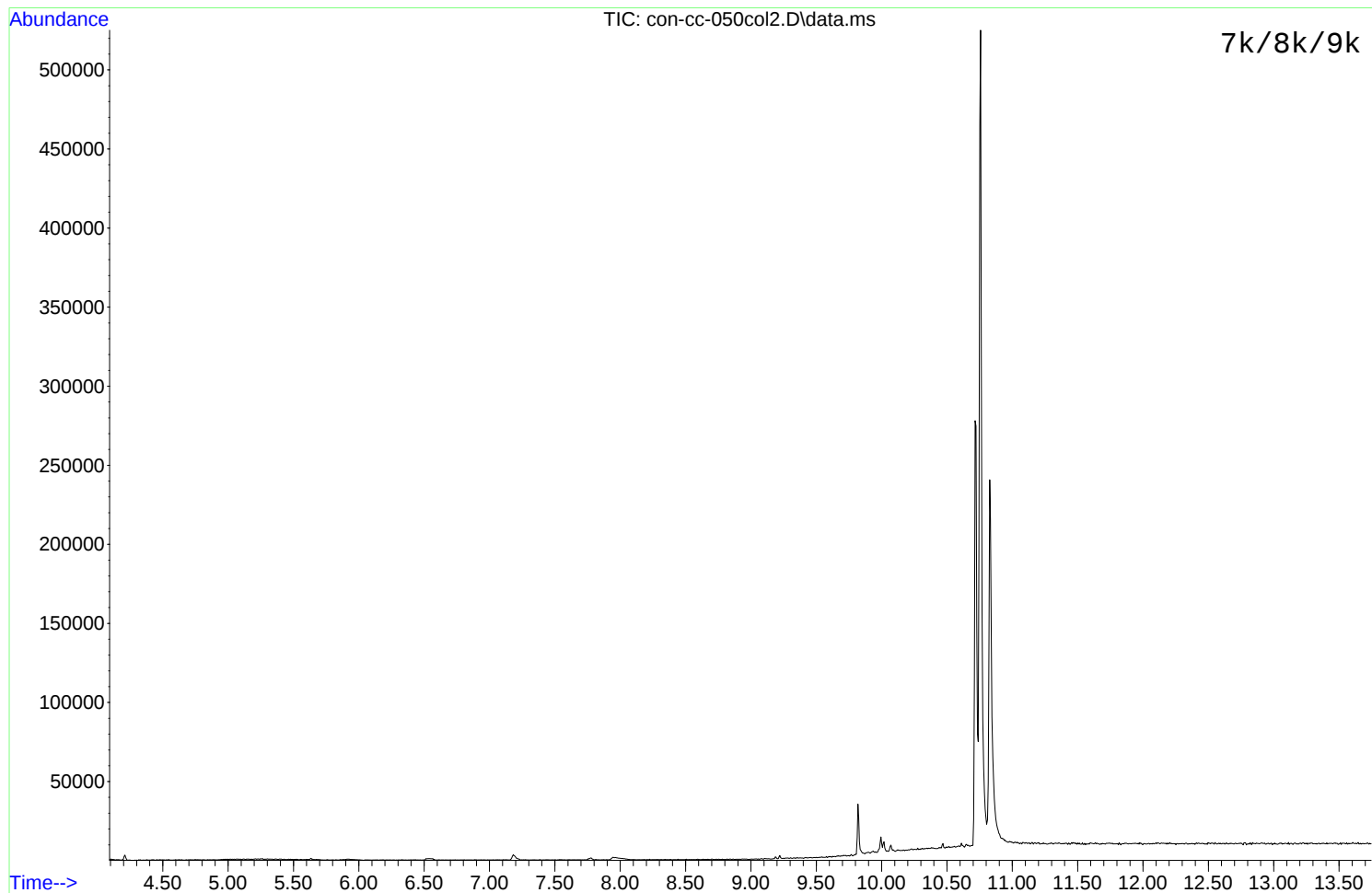


Aug12-2011
glo nimphius con cc 050
carbon CDCl3 /opt/topspin av1 5

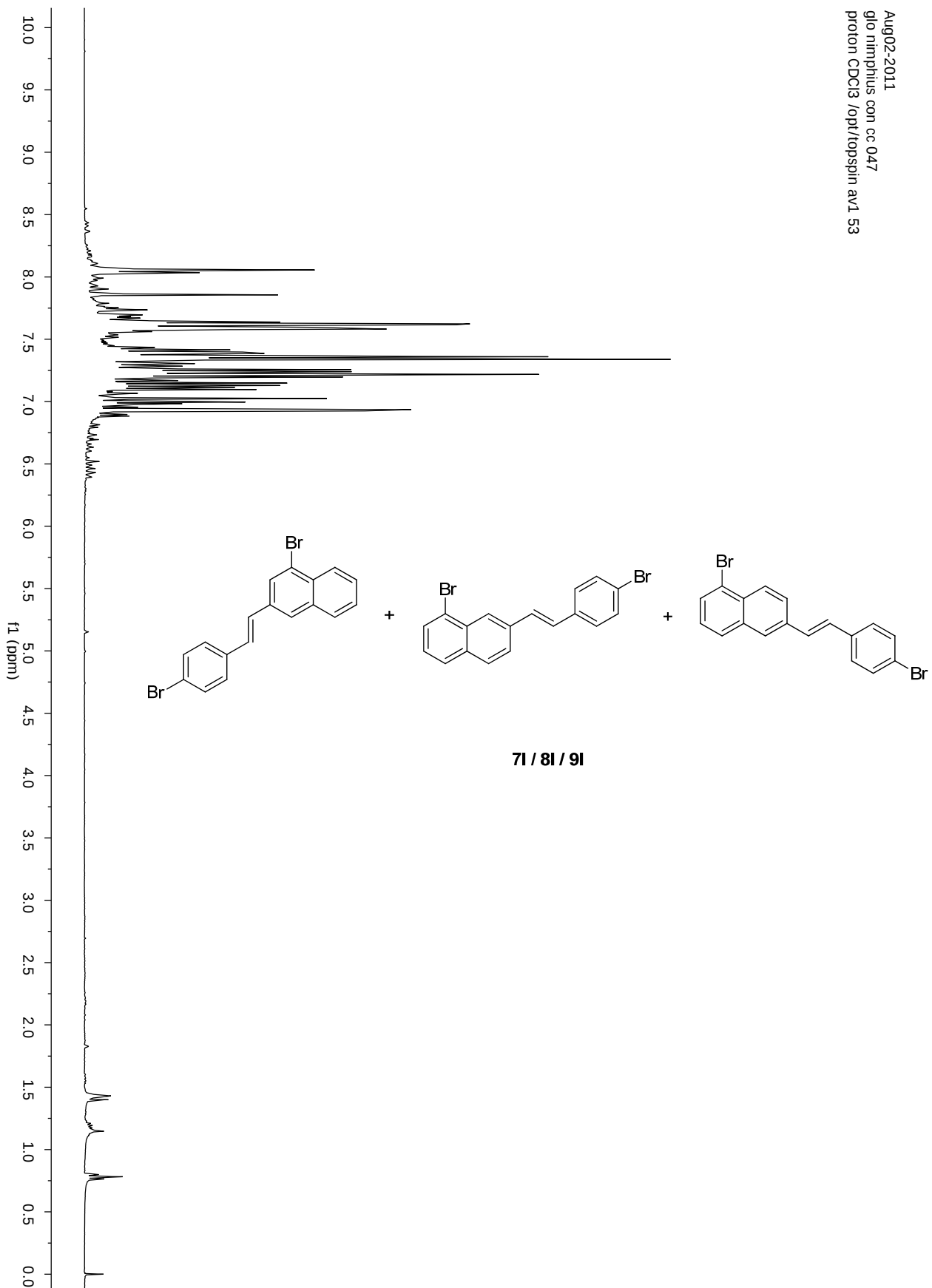


Aug09-2011
glo nimphius con cc 050
f19cpd CDCl3 /opt/topspin av1.18

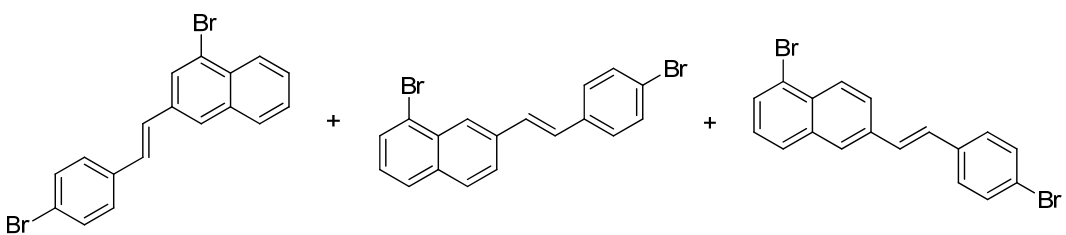




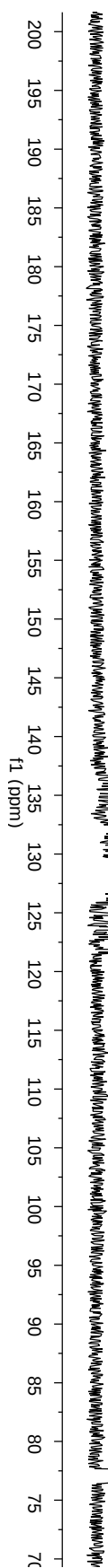
Aug02-2011
glo nimphius con cc 047
proton CDCl3 /opt/topspin av1.53

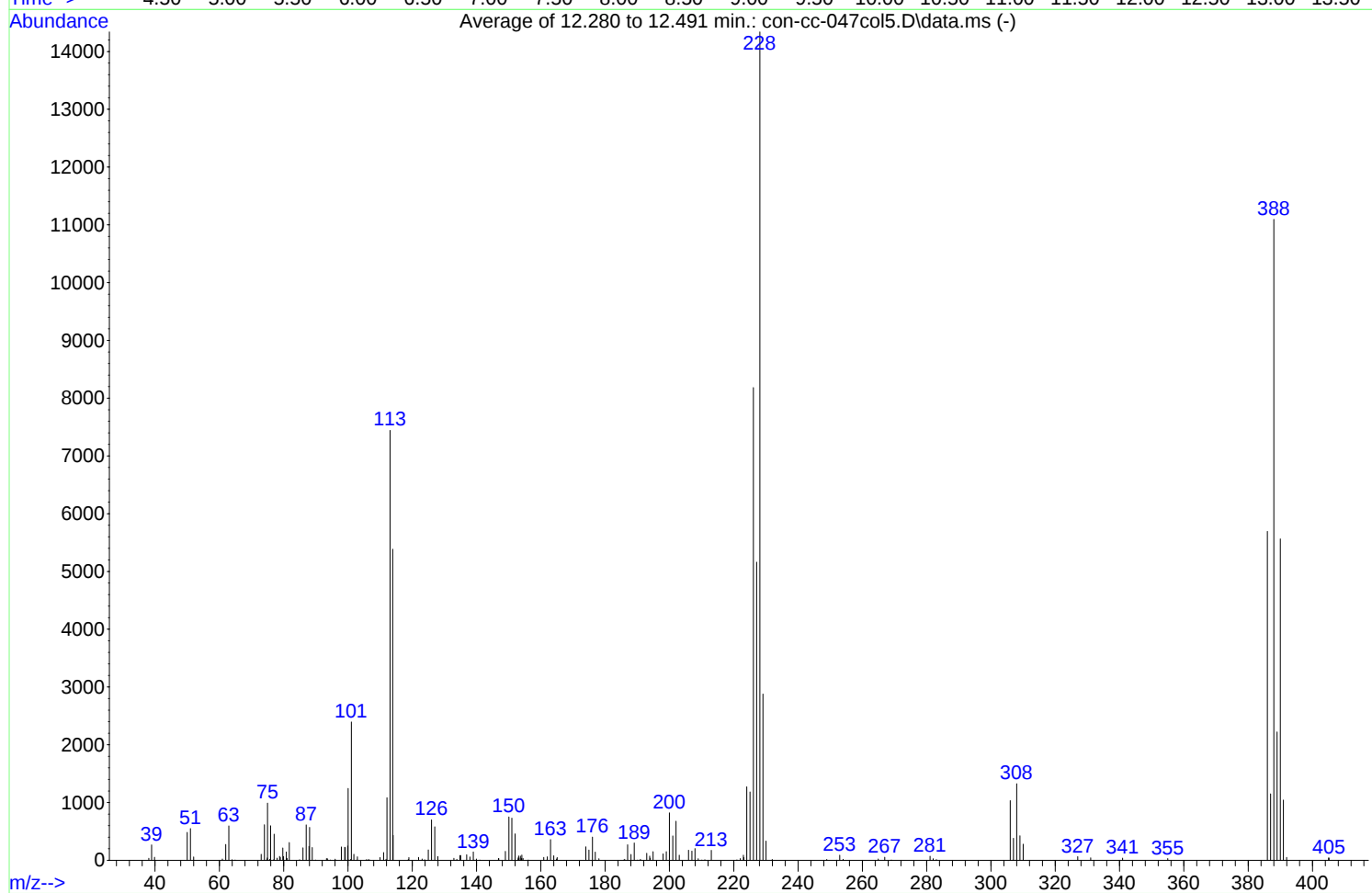
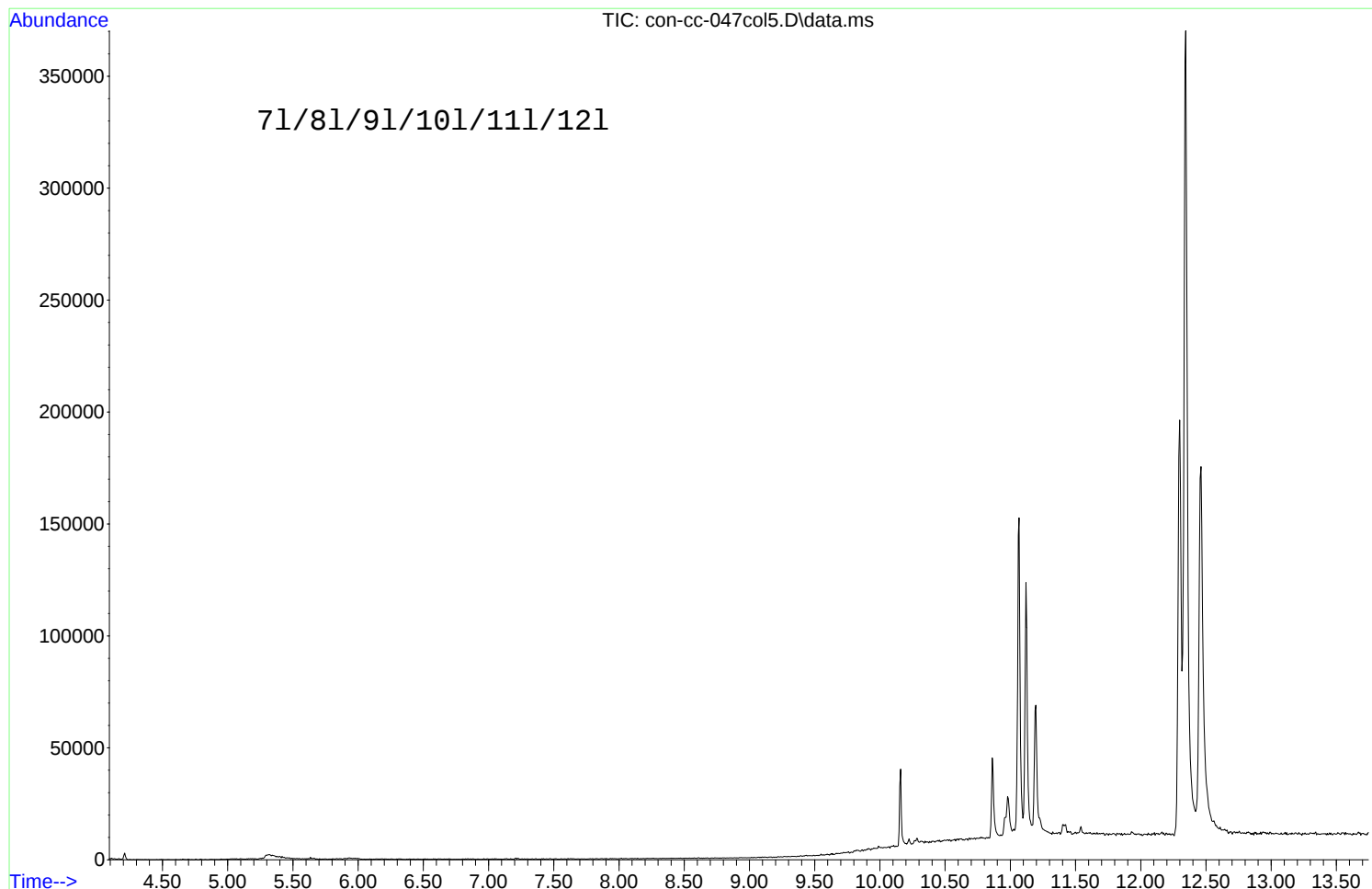


Aug02-2011
gio nimphius con cc 047
carbon CDCl3 /opt/topspin av1.53

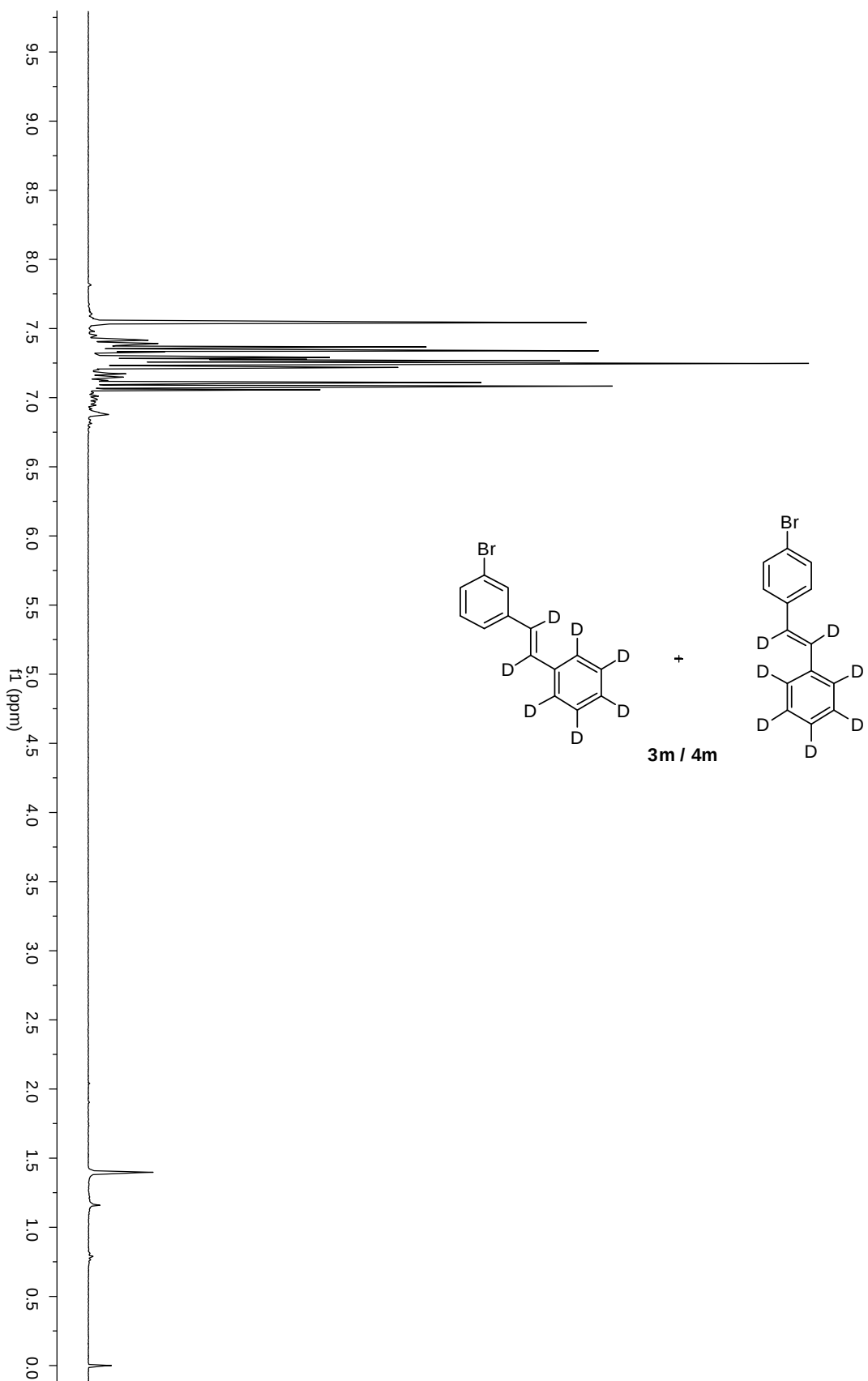


71 / 81 / 91

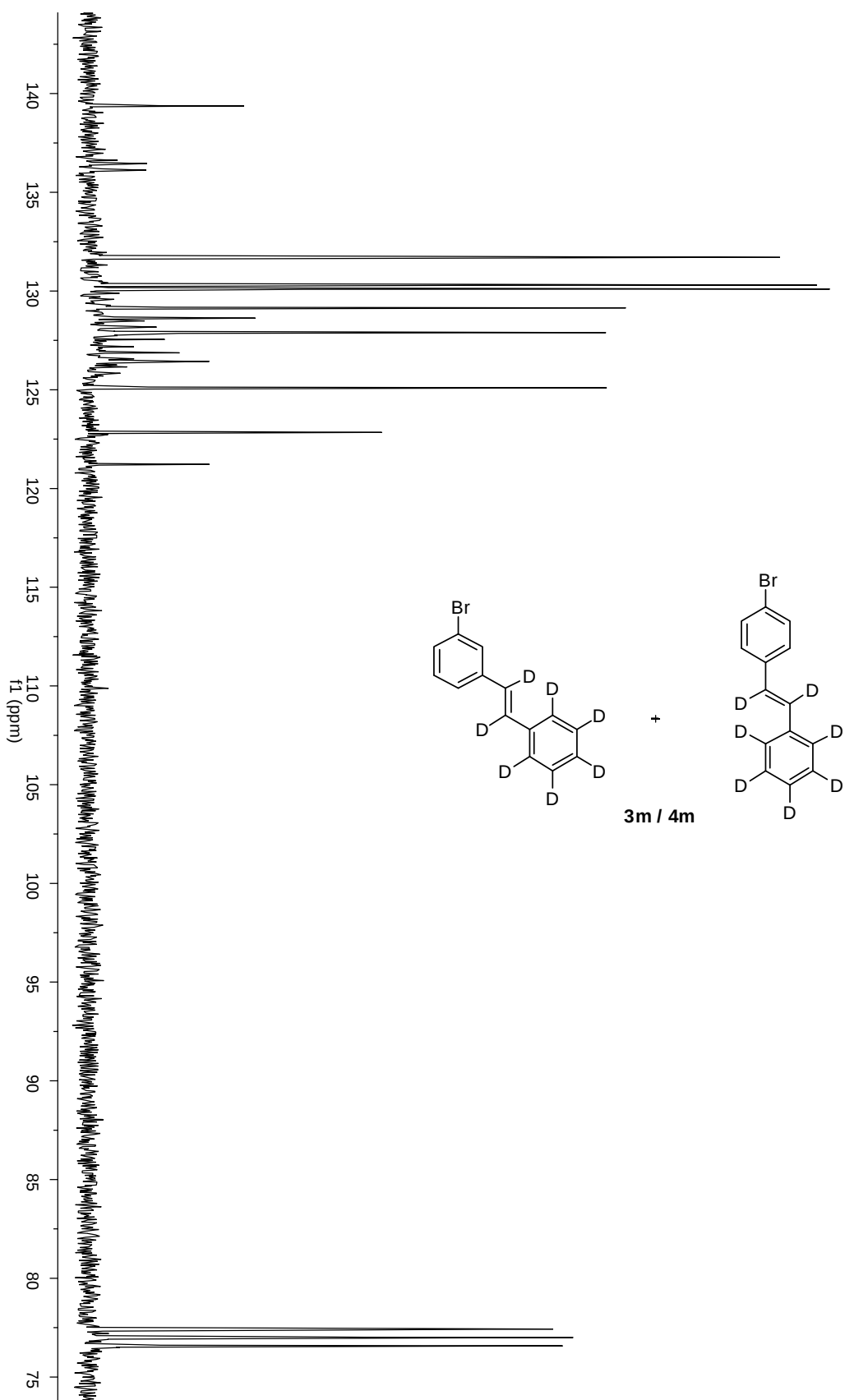


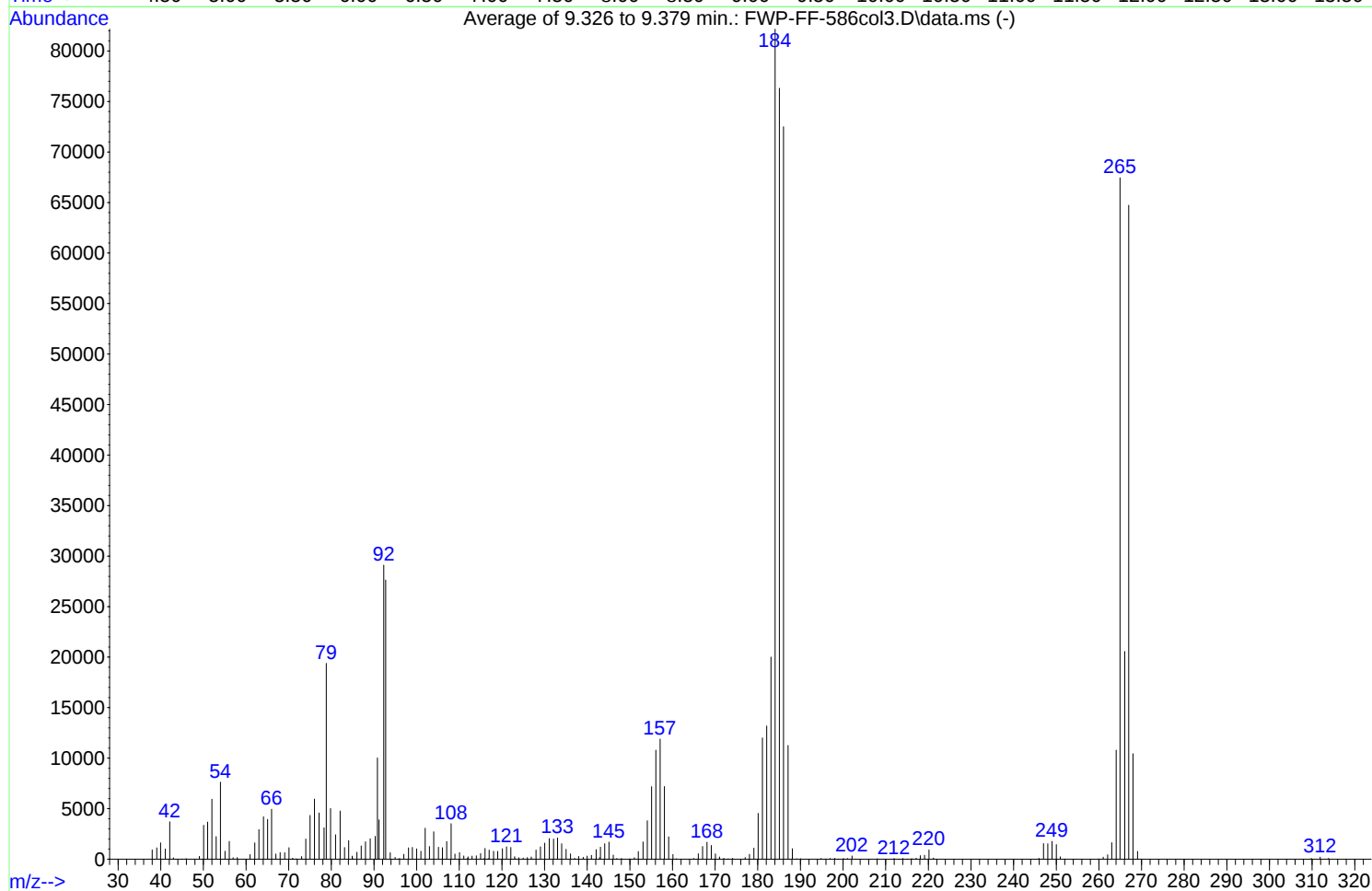
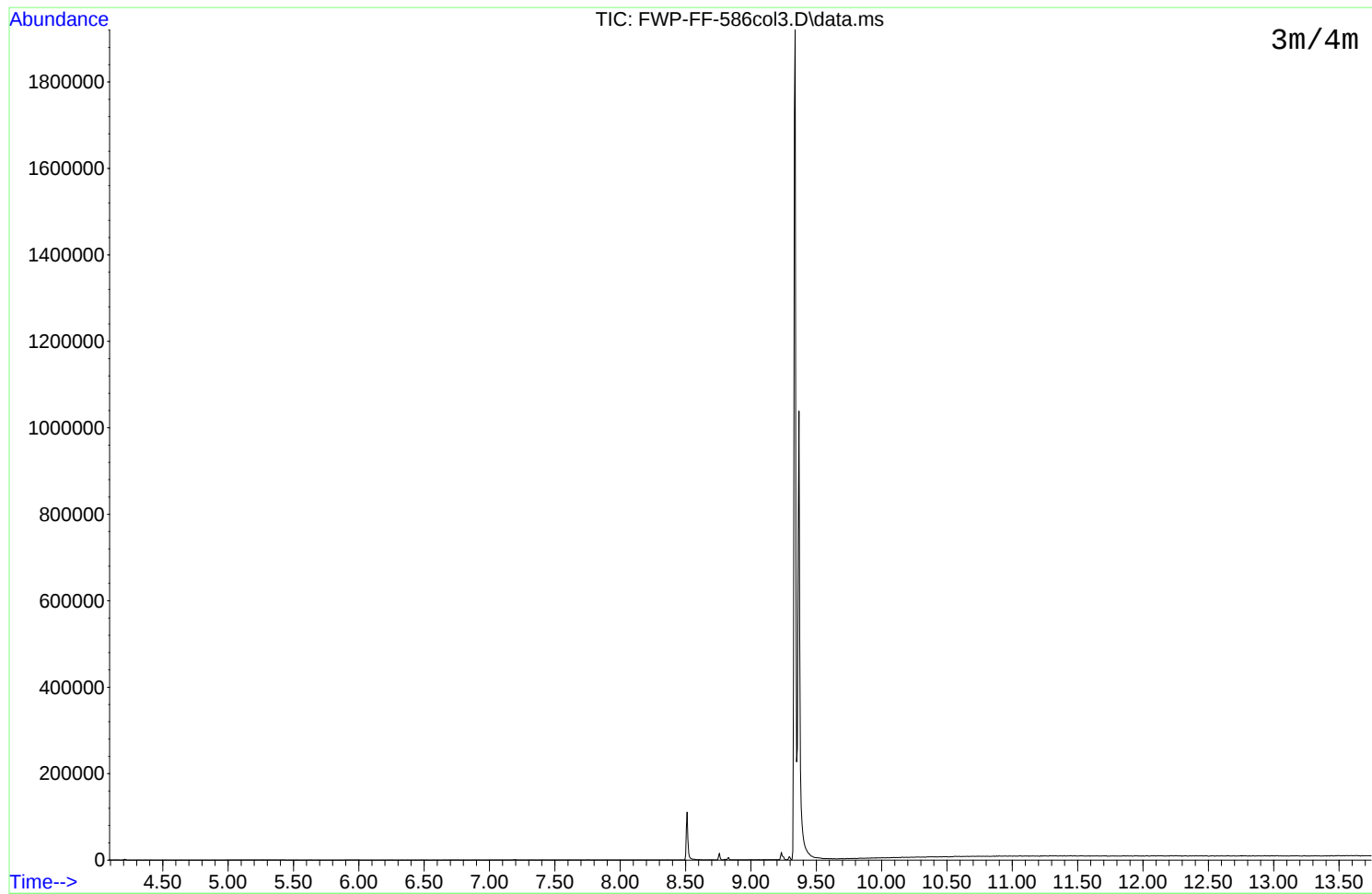


Aug03-2011
glo patureau twp ff 586
proton CDCl3 /opt/topspin av1.17

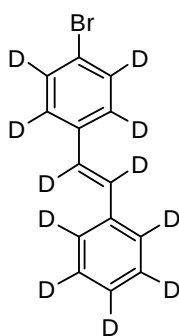


Aug03-2011
glo patureau fwp ff 586
carbon CDCl3 /opt/lospspin av1.17



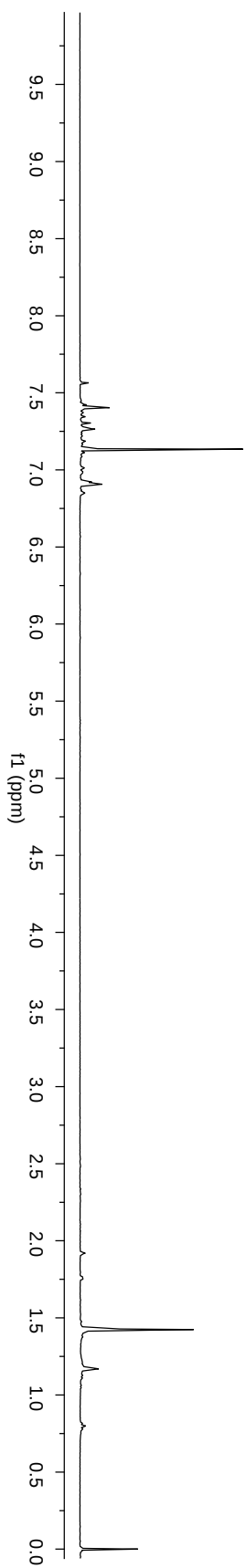
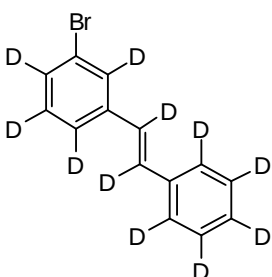


Aug01-2011
glo patureau fwp ff 584
proton CDCl3 /opt/topspin av1.24

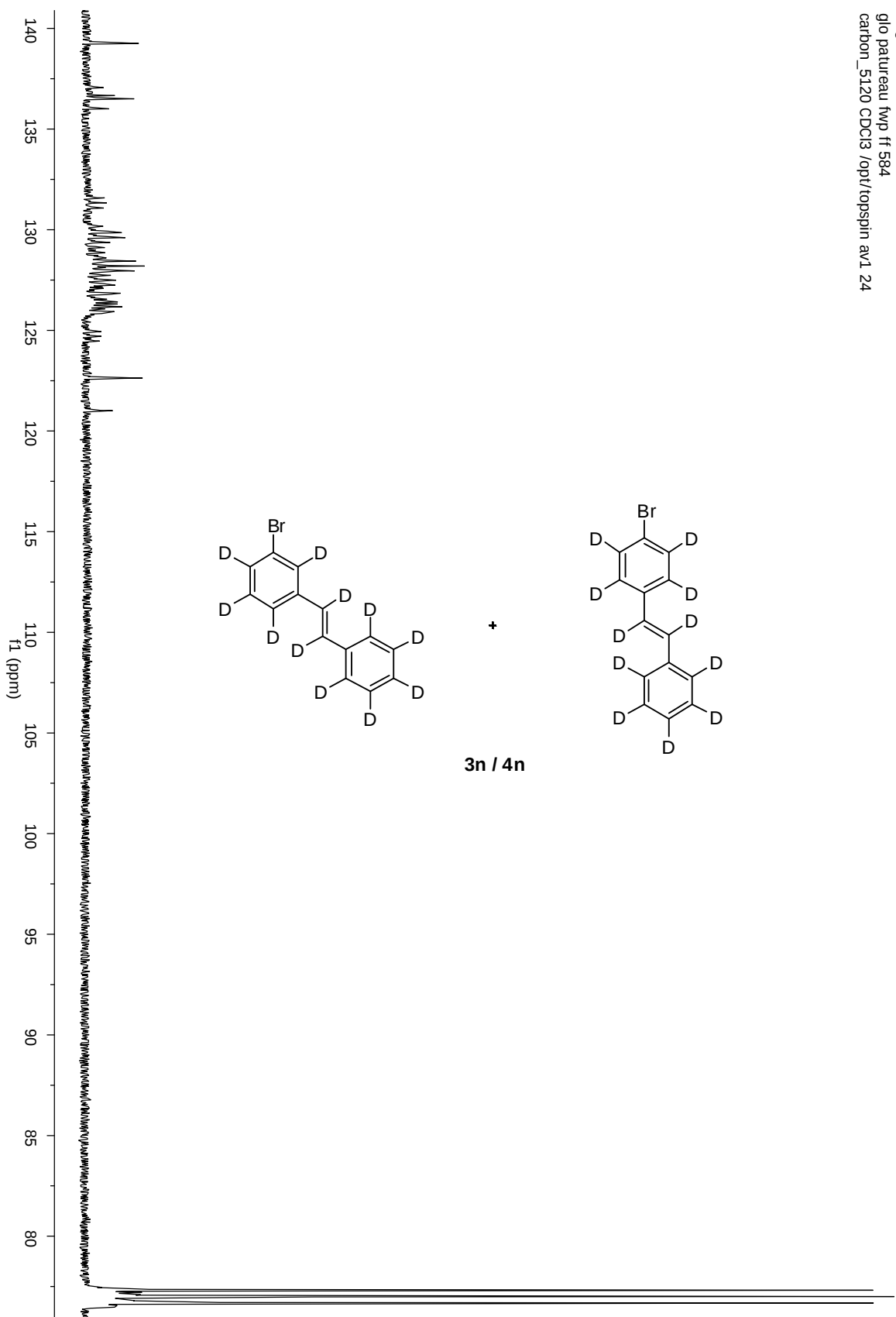


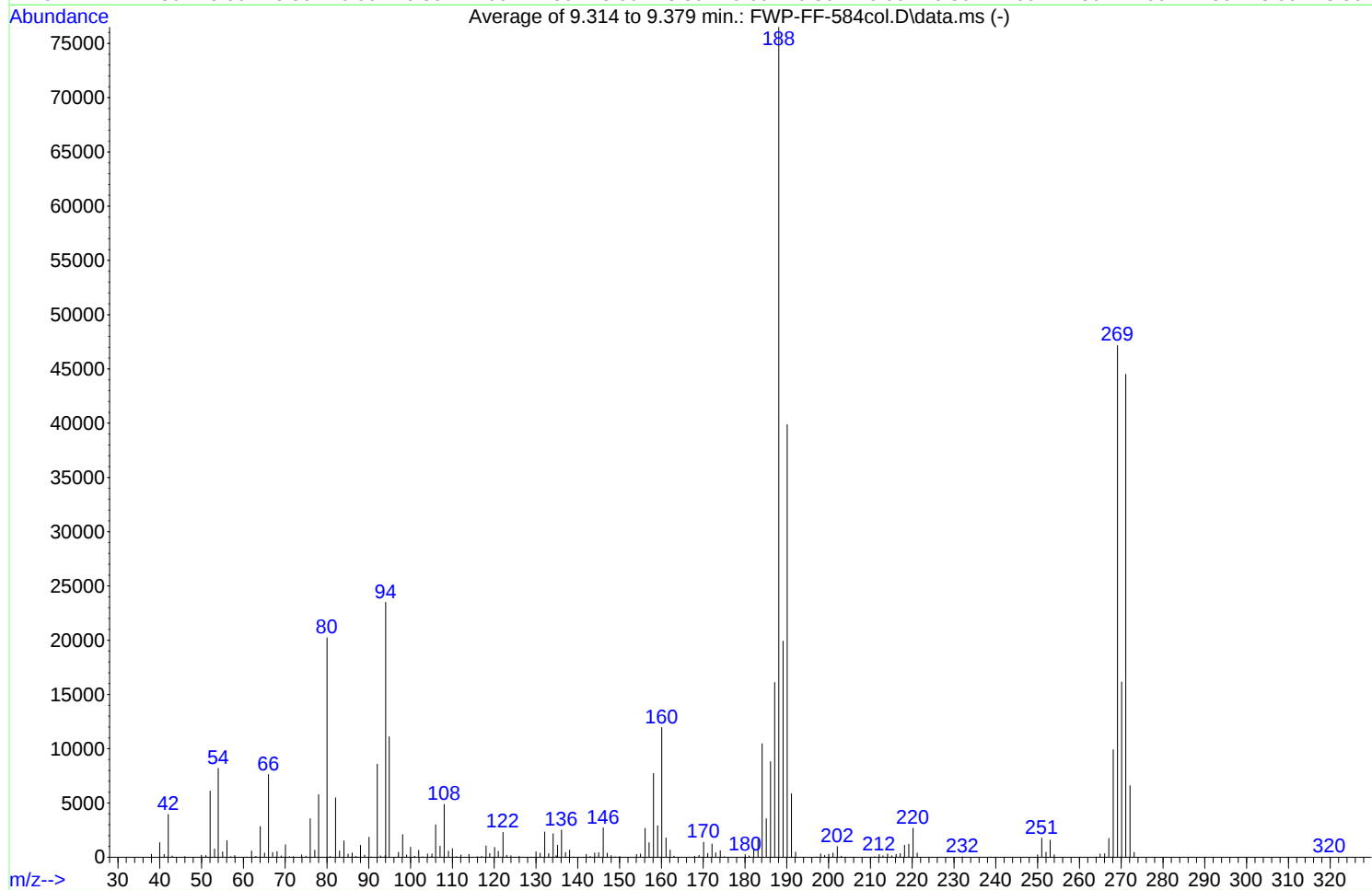
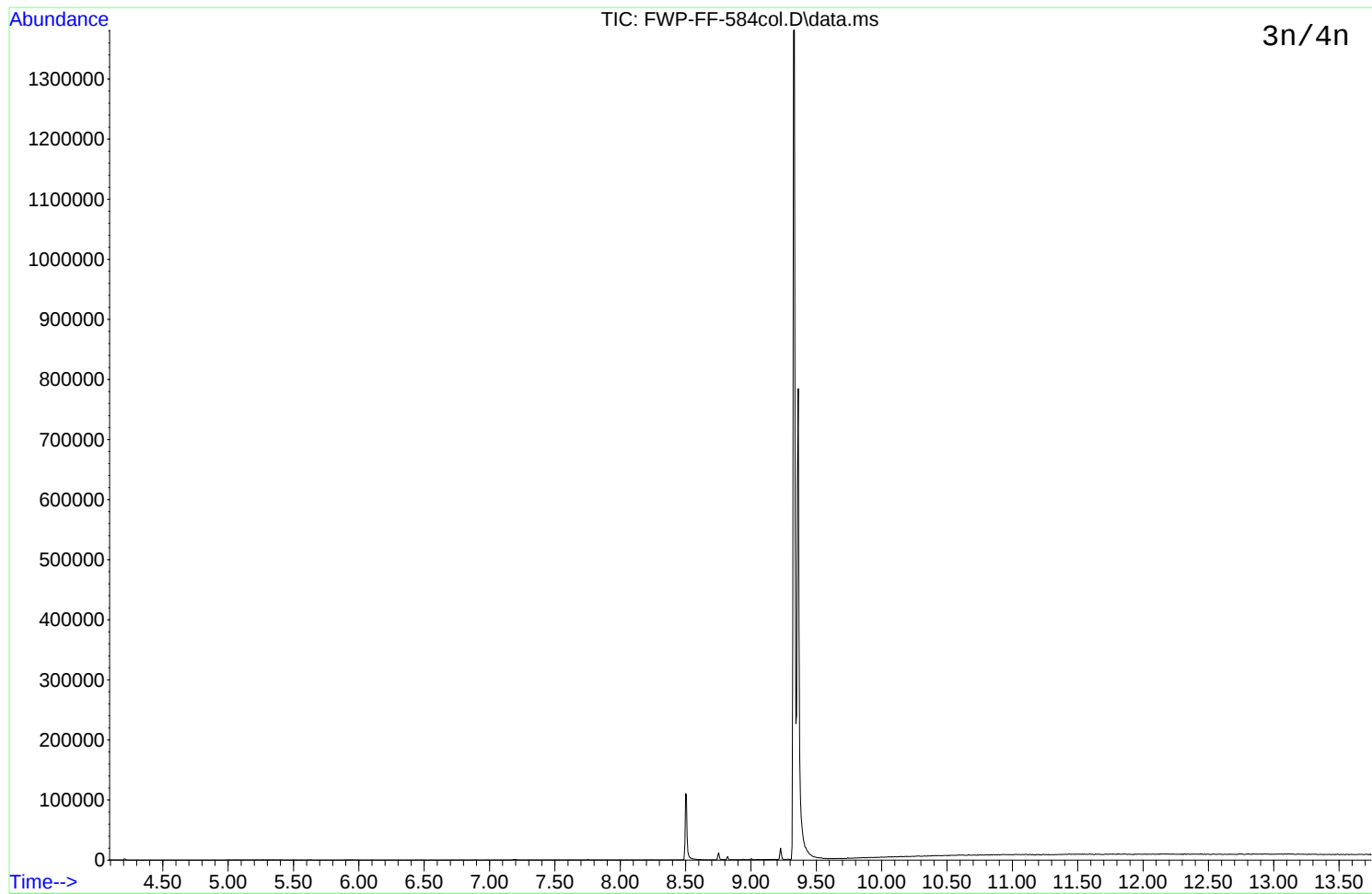
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3n / 4n

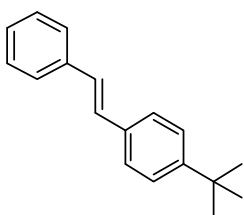


Aug01-2011
glo patureau twp ft 584
carbon_5120 CDCl3 /opt/topspin av1 24

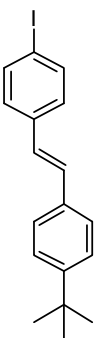




Sep21-2011
glo nimphius con cc 081
proton CDC13 /opt/topspin av1.1

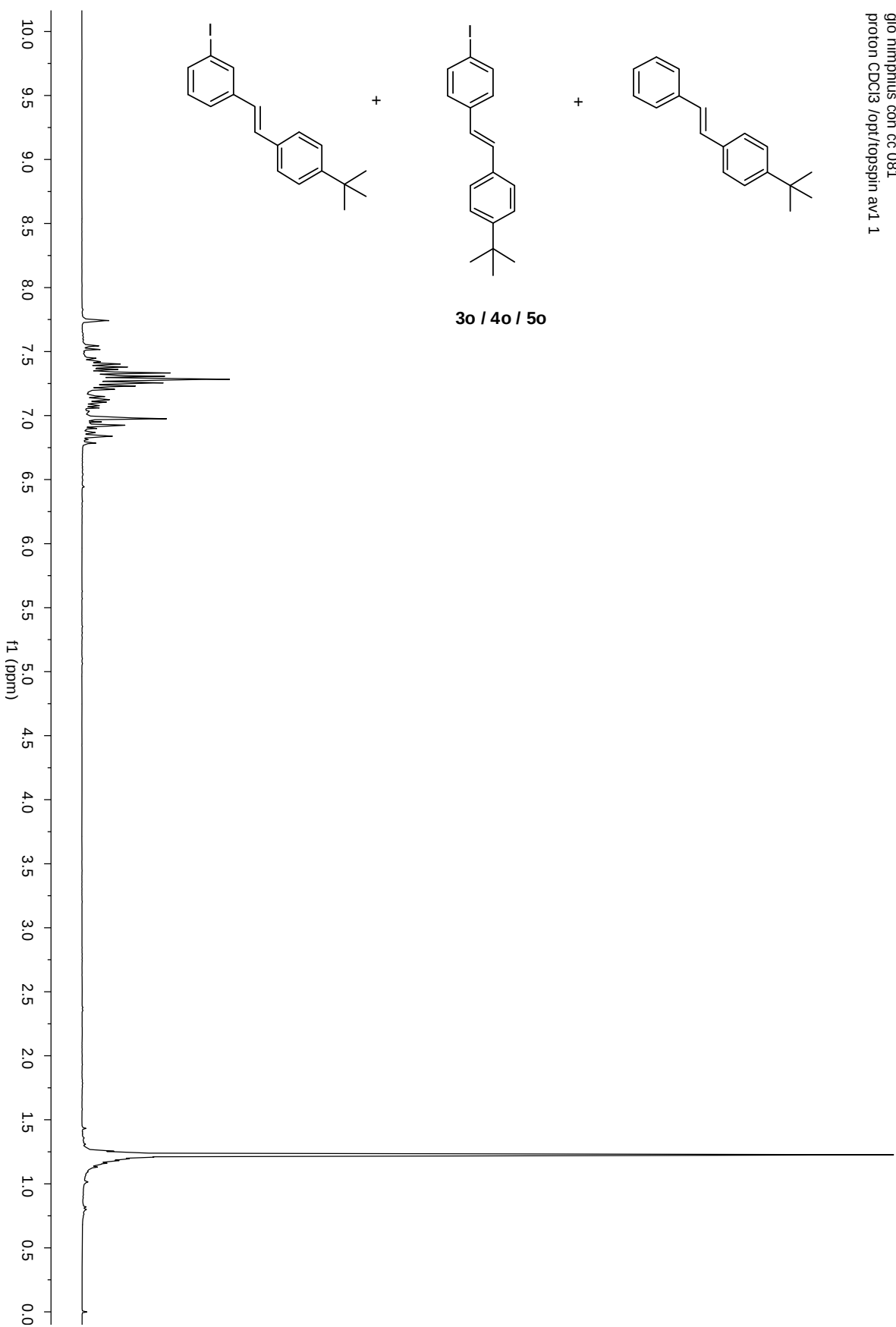
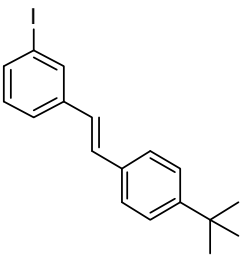


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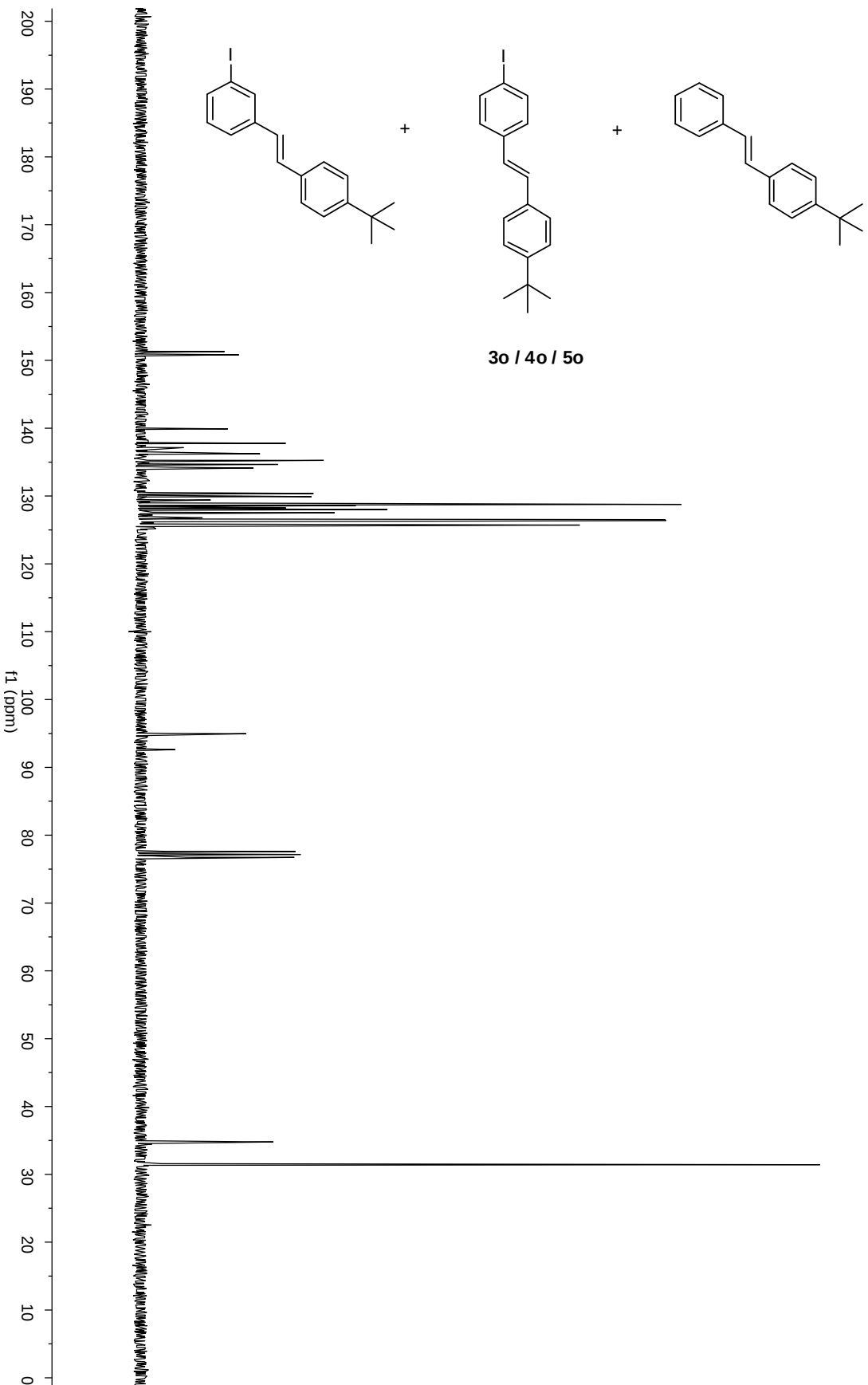


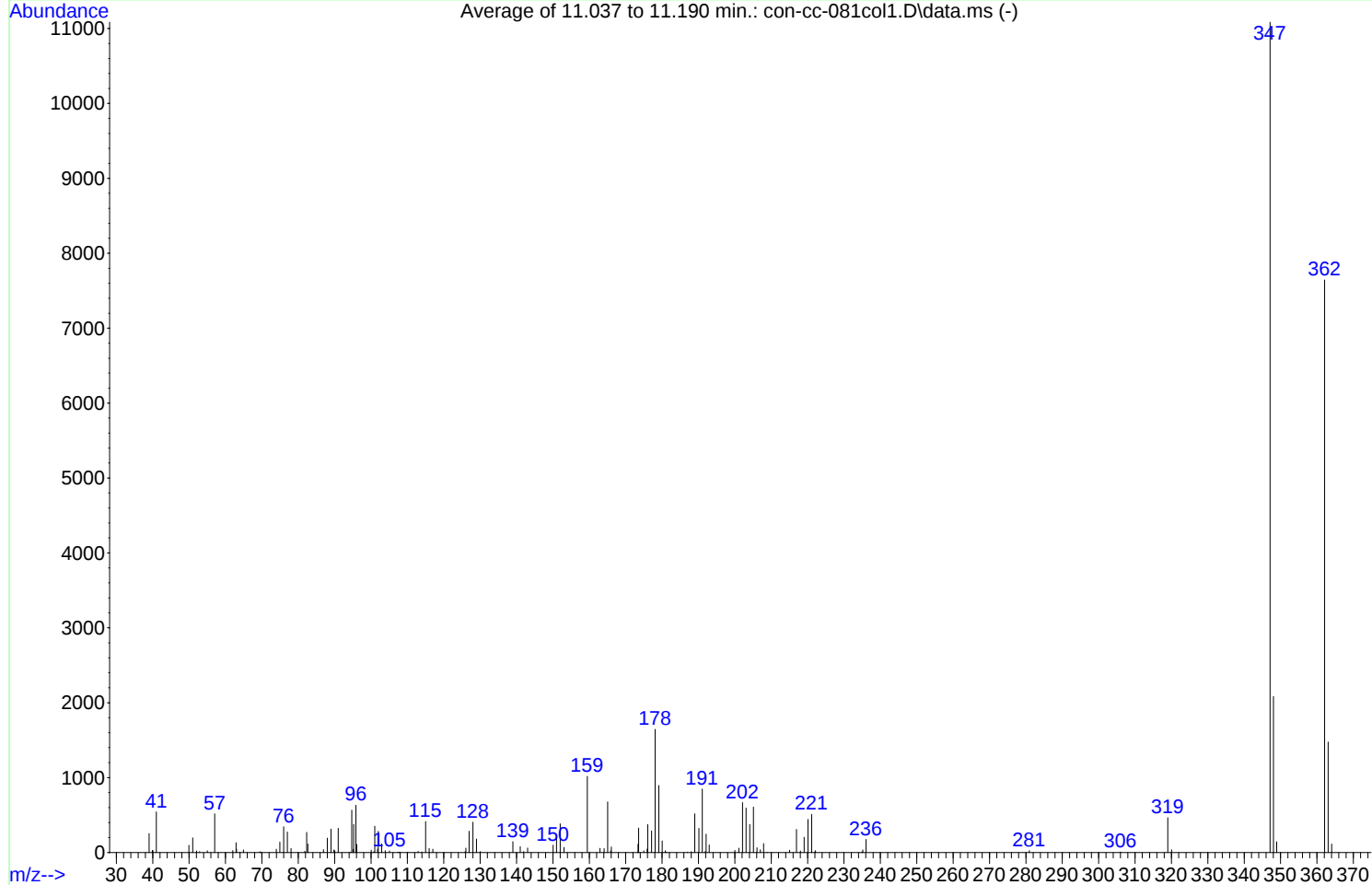
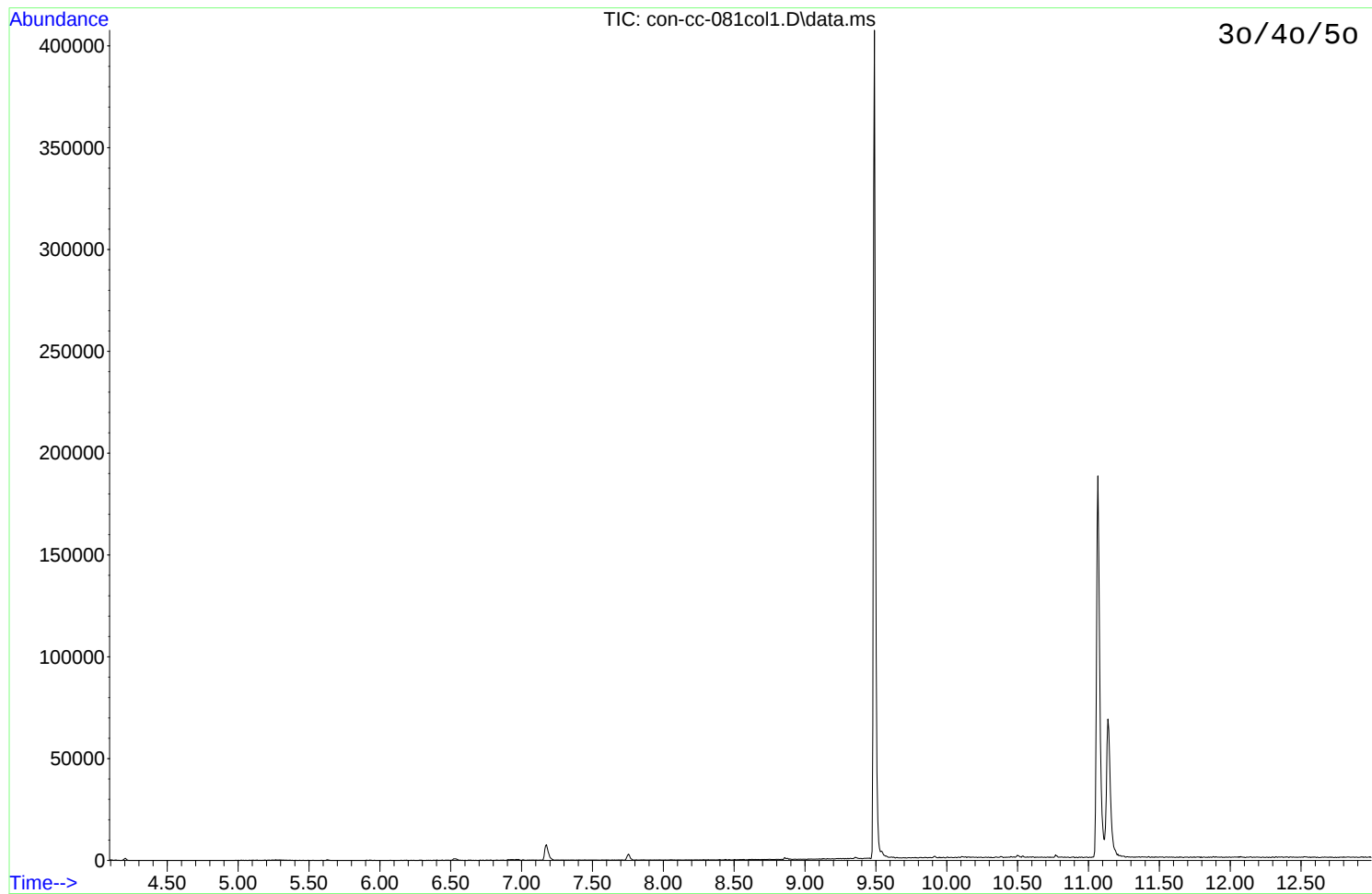
30 / 40 / 50

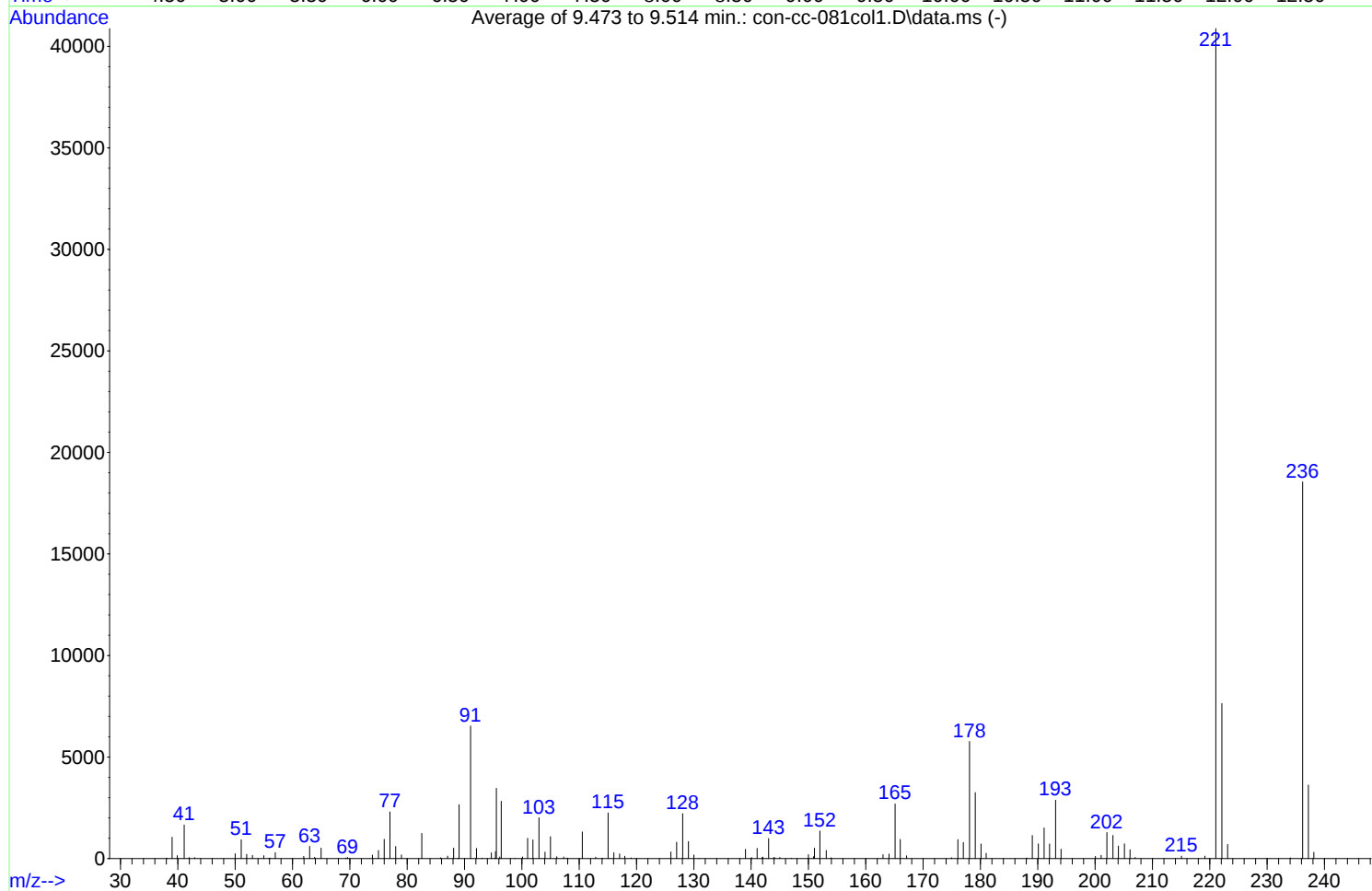
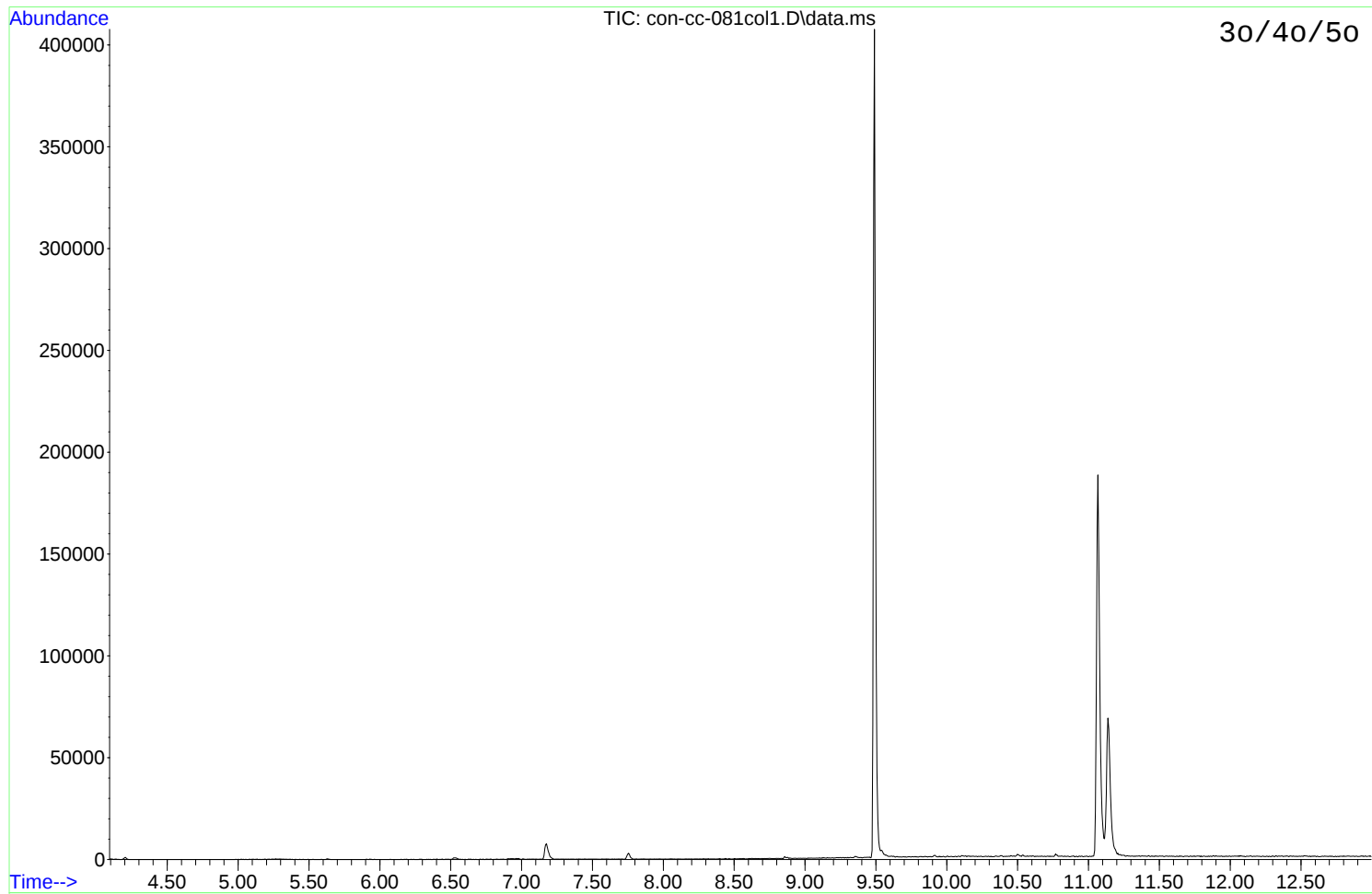
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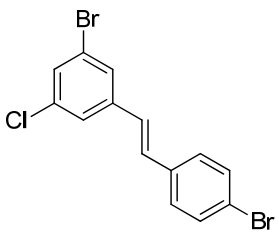
Sep21-2011
glo nimphus con cc 081
carbon CDCl3 /opt/topspin av1.1



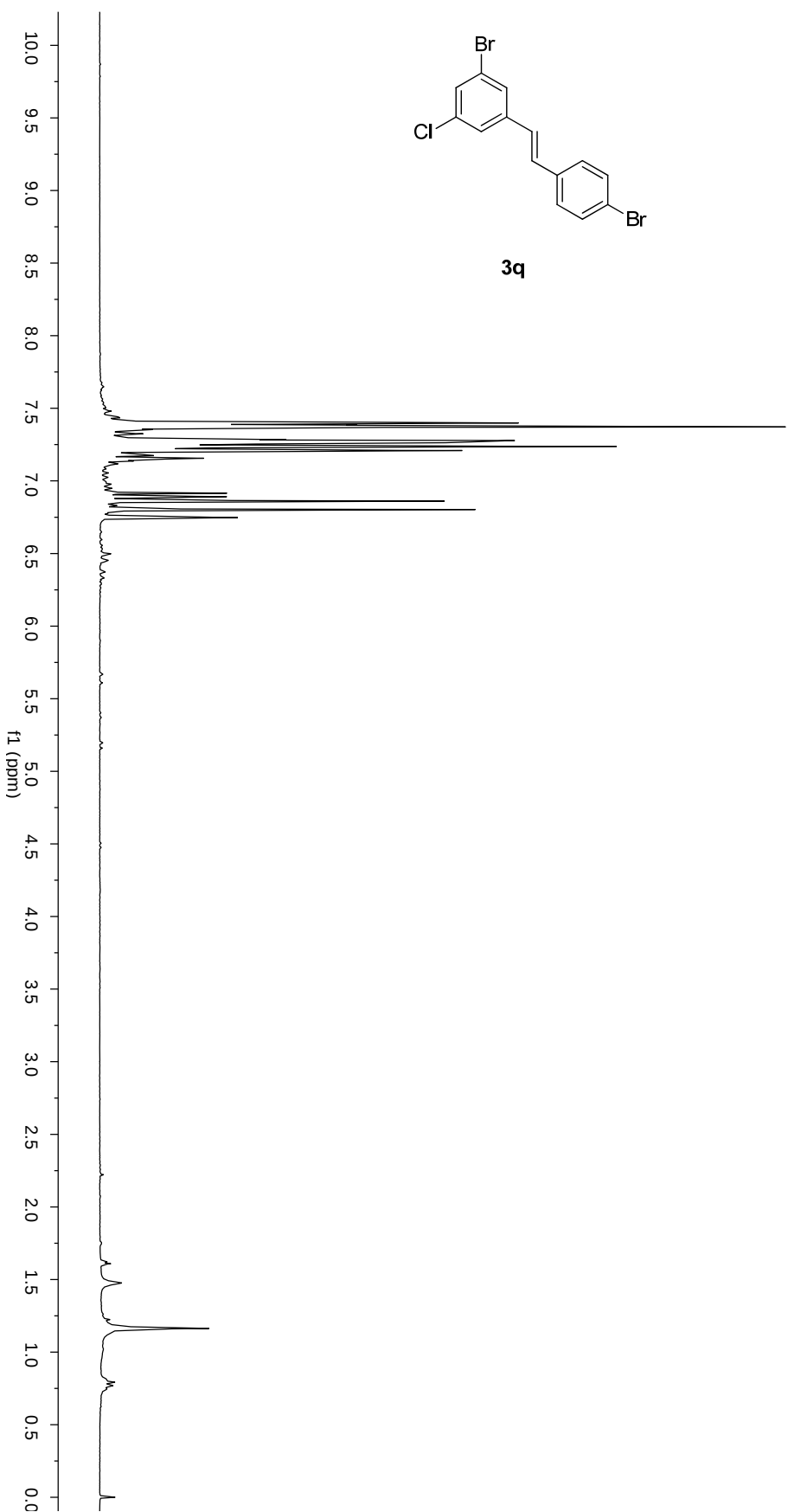




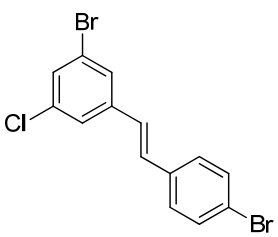
Aug12-2011
glo nimphius con cc 051
proton CDC13 /opt/topspin av1.6



3q



Aug12-2011
gio nimphius con cc 051
carbon CDCl3 /opt/topspin av1.6



3q

