Supporting Information

Visible-light-mediated radical oxydifluoromethylation of olefinic amides for the synthesis of CF_2H-containing heterocycles

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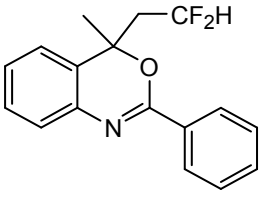
General: Solvents were purified or dried in a standard manner. Reactions were monitored by TLC on silica gel plates (GF254), and the analytical thin-layer chromatography (TLC) was performed on precoated, glass-backed silica gel plates. ^{1}H NMR, ^{13}C NMR and $^{19}F\{^{1}H\}$ NMR spectra were recorded on a 500 MHz NMR spectrometers with TMS as an internal standard. Chemical shifts (δ) are reported in ppm downfield from tetramethylsilane. Abbreviations for signal couplings are: s, singlet; d, doublet; t, triplet; m, multiplet. HRMS analyses was recorded on Waters Q-TOF Global mass spectrometer. All of olefinic amides **1** and *N*-allylamides **4** were synthesized according to the literature.[1]

General experimental details

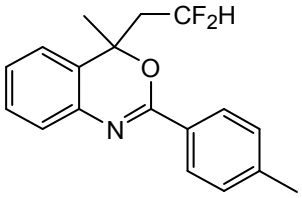
To a mixture of olefinic amides **1** (0.20 mmol), 2-((difluoromethyl)sulfonyl) benzo[d]thiazole (0.24 mmol) and Na_2CO_3 (0.24 mmol) in 2.0 mL of CH_3CN was added *fac*-Ir(ppy)$_3$ (0.004 mmol, 2.0 mol%) under N_2 atmosphere. The solution was stirred at room temperature under 5 W blue LED irradiation for 10 h. Then the reaction mixture was diluted by adding EtOAc and brine. The aqueous layer was extracted with EtOAc The combined organic layer was dried over $MgSO_4$, filtered and concentrated. The residue was purified by flash column chromatography (petroleum ether/ethyl acetate 25:1 as the eluant) on silica gel to give the desired benzoxazine **3**.



4-(2,2-difluoroethyl)-4-methyl-2-phenyl-4H-benzo[d][1,3]oxazine (**3a**):

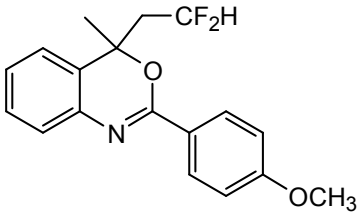
^{1}H NMR (500 MHz, $CDCl_3$): δ 8.18 (d, J = 7.1 Hz, 2H), 7.56-7.53 (m, 1H), 7.51-7.48 (m, 2H), 7.40-7.36 (m, 2H), 7.29-7.25 (m, 1H), 7.15 (d, J = 7.4 Hz, 1H), 6.05 (tdd, J = 55.8 Hz, J = 5.2 Hz, J = 4.0 Hz, 1H), 2.71-2.49 (m, 2H), 1.83 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 155.8, 138.4, 132.5, 131.6, 129.2, 128.5, 128.4, 127.9, 127.0, 125.7,

122.6, 115.0 (t, J = 238.0 Hz), 77.5 (t, J = 5.8 Hz), 45.0(t, J = 21.0 Hz), 27.5. ^{19}F NMR (470 MHz, $CDCl_3$): δ -112.2 (d, J = 291.0 Hz, 1F), -113.0 (d, J = 291.0 Hz, 1F). HRMS (ESI): calcd for $[M+H]^+$ $C_{17}H_{16}F_2NO$: 288.1195, found: 288.1197.

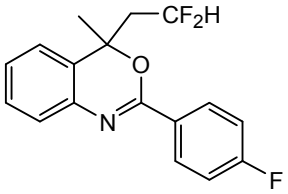


4-(2,2-difluoroethyl)-4-methyl-2-p-tolyl-4H-benzo[d][1,3]oxazine (**3b**):

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.06 (d, J = 8.2 Hz, 2H), 7.36 (dd, J = 5.1 Hz, J = 1.2 Hz, 2H), 7.29 (d, J = 8.1 Hz, 2H), 7.26-7.23 (m, 1H), 7.14 (d, J = 7.6 Hz, 1H), 6.04 (tdd, J = 55.9 Hz, J = 5.1 Hz, J = 4.1 Hz, 1H), 2.69-2.48 (m, 2H), 2.45 (s, 3H), 1.82 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 156.0, 142.1, 138.6, 129.7, 129.2, 129.1, 128.5, 127.8, 126.7, 125.5, 122.6, 114.9 (t, J = 238.0 Hz), 77.4 (t, J = 5.5 Hz), 44.9 (t, J = 21.3 Hz), 27.3, 21.6. ^{19}F NMR (470 MHz, $CDCl_3$): δ -112.2 (d, J = 291.0 Hz, 1F), -113.0 (d, J = 290.0 Hz, 1F). HRMS (ESI): calcd for $[M+H]^+$ $C_{18}H_{18}F_2NO$: 302.1351, found: 302.1354.

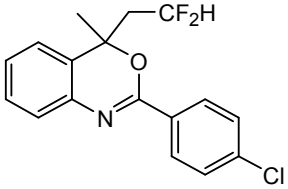


4-(2,2-difluoroethyl)-2-(4-methoxyphenyl)-4-methyl-4H-benzo[d][1,3]oxazine (**3c**): ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.11 (d, J = 8.9 Hz, 2H), 7.36-7.34 (m, 2H), 7.25-7.21 (m, 1H), 7.13 (d, J = 7.4 Hz, 1H), 6.98 (d, J = 8.9 Hz, 2H), 6.03 (tdd, J = 55.8 Hz, J = 5.0 Hz, J = 4.1 Hz, 1H), 3.89 (s, 3H), 2.68-2.46 (m, 2H), 1.81 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 162.5, 155.8, 138.7, 129.7, 129.2, 128.4, 126.5, 125.4, 124.9, 122.5, 115.0 (t, J = 238.0 Hz), 113.7, 77.3 (t), 55.4, 44.8 (t, J = 21.2 Hz), 27.2. ^{19}F NMR (470 MHz, $CDCl_3$): δ -112.2 (d, J = 291.0 Hz, 1F), -113.0 (d, J = 290.0 Hz, 1F). HRMS (ESI): calcd for $[M+H]^+$ $C_{18}H_{18}F_2NO_2$: 318.1300, found: 318.1297.



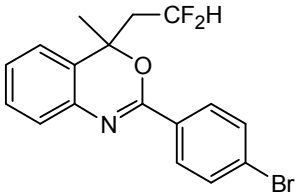
4-(2,2-difluoroethyl)-2-(4-fluorophenyl)-4-methyl-4H-benzo[d][1,3]oxazine (**3d**):

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.17 (dd, J = 8.8 Hz, J = 5.5 Hz, 2H), 7.39-7.34 (m, 2H), 7.28-7.24 (m, 1H), 7.18-7.14 (m, 3H), 6.01 (tt, J = 55.7 Hz, J = 4.3 Hz, 1H), 2.69-2.47 (m, 2H), 1.83 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 165.0 (d, J = 250.8 Hz), 154.9, 138.3, 130.1 (d, J = 8.7 Hz), 129.3, 128.6, 128.3, 127.0, 125.6, 122.6, 115.9 (t, J = 238.0 Hz), 115.4 (d, J = 21.8 Hz), 77.7 (t, J = 5.9 Hz), 45.0 (t, J = 21.2 Hz), 27.5. ^{19}F NMR (470 MHz, $CDCl_3$): δ -118.1 (s, 1F), -112.3 (d, J = 290.9 Hz, 1F), -113.0 (d, J = 290.6 Hz, 1F). HRMS (ESI): calcd for $[M+H]^+$ $C_{17}H_{15}F_3NO$: 306.1100, found: 306.1105.



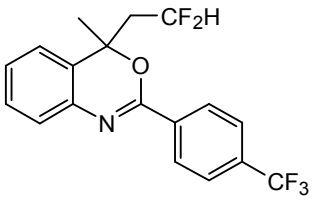
2-(4-chlorophenyl)-4-(2,2-difluoroethyl)-4-methyl-4H-benzo[d][1,3]oxazine (**3e**):

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.10 (d, J = 8.6 Hz, 2H), 7.45 (d, J = 8.7 Hz, 2H), 7.39-7.34 (m, 2H), 7.29-7.25 (m, 1H), 7.14 (d, J = 7.9 Hz, 1H), 6.12-5.88 (m, 1H), 2.68-2.46 (m, 2H), 1.82 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 154.9, 138.2, 137.8, 131.0, 129.3, 129.2, 128.6, 128.3, 127.2, 125.7, 122.7, 114.9 (t, J = 237.8 Hz),77.8 (t, J = 5.9 Hz), 45.0 (t, J = 21.1 Hz), 27.5. ^{19}F NMR (470 MHz, $CDCl_3$): δ -112.3 (d, J = 291.0 Hz, 1F), -112.9 (d, J = 290.8 Hz, 1F). HRMS (ESI): calcd for $[M+H]^+$ $C_{17}H_{15}ClF_2NO$: 322.0805, found: 322.0804.



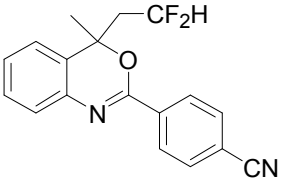
2-(4-bromophenyl)-4-(2,2-difluoroethyl)-4-methyl-4H-benzo[d][1,3]oxazine (**3f**):

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.02 (d, J = 8.6 Hz, 2H), 7.60 (d, J = 8.6 Hz, 2H), 7.39-7.34 (m, 2H), 7.29-7.25 (m, 1H), 7.14 (d, J = 7.3 Hz, 1H), 5.99 (tt, J = 55.2 Hz, J = 4.9 Hz, 1H), 2.67-2.46 (m, 2H), 1.82 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 155.0, 138.1, 131.6, 131.4, 129.4, 129.3, 128.3, 127.2, 126.4, 125.7, 122.7, 114.9 (t, J = 238.1 Hz), 77.8 (t, J = 5.7 Hz), 45.0 (t, J = 21.2 Hz), 27.5. ^{19}F NMR (470 MHz, $CDCl_3$): δ -112.3 (d, J = 290.9 Hz, 1F), -113.0 (d, J = 291.0 Hz, 1F). HRMS (ESI): calcd for $[M+H]^+$ $C_{17}H_{15}BrF_2NO$: 366.0300, found: 366.0304.



4-(2,2-difluoroethyl)-2-(4-(trifluoromethyl)phenyl)-4-methyl-4H-benzo[d][1,3] oxazine (**3g**):

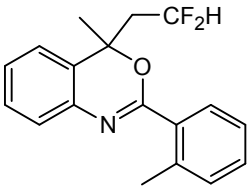
^{1}H NMR (500 MHz, $CDCl_3$): δ 8.24 (d, J = 8.2 Hz, 2H), 7.69 (d, J = 8.3 Hz, 2H), 7.35-7.34 (m, 2H), 7.27-7.24 (m, 1H), 7.12 (d, J = 7.6 Hz, 1H), 5.96 (tdd, J = 55.6 Hz, J = 5.0 Hz, J = 4.3 Hz, 1H), 2.65-2.44 (m, 2H), 1.81 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 154.4, 138.0, 135.8, 133.0 (q, J = 32.4 Hz), 129.4, 128.3, 128.1, 127.6, 126.0, 125.3 (q, J = 3.5 Hz), 123.9 (q, J = 270.9 Hz), 122.7, 114.8 (t, J = 237.9 Hz), 78.0 (t, J = 5.7 Hz), 45.1 (t, J = 21.3 Hz), 27.6. ^{19}F NMR (470 MHz, $CDCl_3$): δ -62.8 (s, 3F), -112.70 (s, 1F), -112.72 (s, 1F). HRMS (ESI): calcd for $[M+H]^+$ $C_{18}H_{15}F_5NO$: 356.1069, found: 356.1075.



4-(4-(2,2-difluoroethyl)-4-methyl-4H-benzo[d][1,3]oxazin-2-yl)benzonitrile (**3h**):

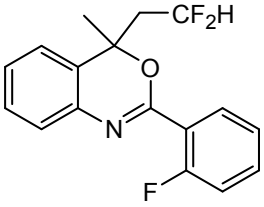
^{1}H NMR (500 MHz, $CDCl_3$): δ 8.26 (d, J = 8.6 Hz, 1H), 7.76 (d, J = 8.6 Hz, 1H), 7.40-7.35 (m, 2H), 7.30 (td, J = 7.6 Hz, J = 1.9 Hz, 1H), 7.16 (d, J = 7.9 Hz, 1H), 5.98 (tdd, J = 55.7 Hz, J = 5.0 Hz, J = 4.3 Hz, 1H), 2.68-2.47 (m, 2H), 1.84 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 153.9, 137.8, 136.6, 132.1, 129.4, 128.24, 128.16, 127.9,

126.1, 122.8, 118.4, 114.8 (t, J = 238.1 Hz), 114.7, 78.2 (t, J = 6.1 Hz), 45.2 (t, J = 21.3 Hz), 27.8. ^{19}F NMR (470 MHz, $CDCl_3$): δ -112.7 (s, 2F). HRMS (ESI): calcd for $[M+H]^+$ $C_{18}H_{15}F_2N_2O$: 313.1147, found: 313.1152.



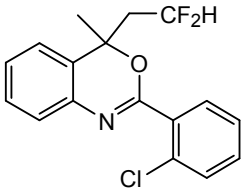
4-(2,2-difluoroethyl)-4-methyl-2-o-tolyl-4H-benzo[d][1,3]oxazine (**3i**):

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.80 (d, J = 7.9 Hz, 1H), 7.40-7.33 (m, 3H), 7.31-7.26 (m, 3H), 7.14 (d, J = 7.8 Hz, 1H), 5.99 (tdd, J = 55.9 Hz, J = 5.1 Hz, J = 4.1 Hz, 1H), 2.74-2.54 (m, 2H), 2.67 (s, 3H), 1.82 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 157.5, 138.3, 138.2, 132.4, 131.5, 130.5, 129.4, 129.2, 127.8, 127.1, 125.8, 125.7, 122.6, 115.0 (t, J = 237.6 Hz), 77.9 (t, J = 6.1 Hz), 45.1 (t, J = 21.2 Hz), 28.0, 21.6. ^{19}F NMR (470 MHz, $CDCl_3$): δ -112.3 (d, J = 290.9 Hz, 1F), -113.0 (d, J = 290.3 Hz, 1F). HRMS (ESI): calcd for $[M+H]^+$ $C_{18}H_{18}F_2NO$: 302.1351, found: 302.1350.



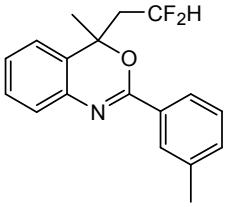
4-(2,2-difluoroethyl)-2-(2-fluorophenyl)-4-methyl-4H-benzo[d][1,3]oxazine (**3j**):

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.97 (td, J = 8.9 Hz, J = 1.8 Hz, 1H), 7.48-7.43 (m, 1H), 7.34-7.31 (m, 2H), 7.26-7.20 (m, 2H), 7.15-7.10 (m, 2H), 6.06 (tdd, J = 56.0 Hz, J = 5.5 Hz, J = 3.5 Hz, 1H), 2.69-2.48 (m, 2H), 1.79 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 161.5 (d, J = 255.4 Hz), 154.6 (d, J = 2.9 Hz), 138.0, 132.9 (d, J = 8.8 Hz), 131.1, 129.2, 128.5, 127.4, 125.8, 124.1 (d, J = 3.6 Hz), 122.6, 121.1 (d, J = 9.7 Hz), 116.8 (d, J = 22.1 Hz), 115.0 (t, J = 237.4 Hz), 78.1 (dd, J = 7.9 Hz, J = 4.5 Hz), 44.9 (t, J = 21.5 Hz), 27.3. ^{19}F NMR (470 MHz, $CDCl_3$): δ -111.4 (s, 1F), -112.1 (d, J = 290.9 Hz, 1F), -113.2 (d, J = 290.8 Hz, 1F). HRMS (ESI): calcd for $[M+H]^+$ $C_{17}H_{15}F_3NO$: 306.1100, found: 306.1103.



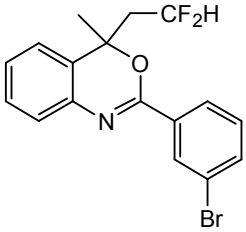
2-(2-chlorophenyl)-4-(2,2-difluoroethyl)-4-methyl-4H-benzo[d][1,3]oxazine (**3k**):

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.75 (dd, J = 7.6 Hz, J = 1.7 Hz, 1H), 7.45 (dd, J = 8.0 Hz, J = 1.2 Hz, 1H), 7.39 (td, J = 7.4 Hz, J = 1.8 Hz, 1H), 7.35-7.30 (m, 3H), 7.28-7.25 (m, 1H), 7.11 (d, J = 7.8 Hz, 1H), 6.03 (tdd, J = 55.9 Hz, J = 5.3 Hz, J = 3.9 Hz, 1H), 2.73-2.54 (m, 2H), 1.81 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 156.3, 137.8, 133.1, 132.5, 131.4, 131.2, 130.7, 129.2, 127.9, 127.5, 126.8, 125.8, 122.7, 115.0 (t, J = 237.6 Hz), 78.9 (t, J = 5.3 Hz), 45.2 (t, J = 21.6 Hz), 28.2. ^{19}F NMR (470 MHz, $CDCl_3$): δ -112.4 (d, J = 290.9 Hz, 1F), -113.2 (d, J = 290.5 Hz, 1F). HRMS (ESI): calcd for $[M+H]^+$ $C_{17}H_{15}ClF_2NO$: 322.0805, found: 322.0891.



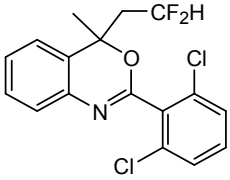
4-(2,2-difluoroethyl)-4-methyl-2-m-tolyl-4H-benzo[d][1,3]oxazine (**3l**):

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.99 (s, 1H), 7.94 (d, J = 7.1 Hz, 1H), 7.39-7.34 (m, 4H), 7.27-7.24 (m, 1H), 7.14 (d, J = 7.6 Hz, 1H), 6.03 (tt, J = 55.8 Hz, J = 5.1 Hz, 1H), 2.69-2.49 (m, 2H), 2.46 (s, 3H), 1.83 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 156.0, 138.5, 138.1, 132.4, 132.3, 129.2, 128.5, 128.4, 128.2, 126.9, 125.6, 125.0, 122.6, 114.9 (t, J = 238.0 Hz), 77.5 (t, J = 5.8 Hz) , 44.9 (t, J = 21.3 Hz), 27.4, 21.4. ^{19}F NMR (470 MHz, $CDCl_3$): δ -112.3 (d, J = 290.8 Hz, 1F), -113.0 (d, J = 290.8 Hz, 1F). HRMS (ESI): calcd for $[M+H]^+$ $C_{18}H_{18}F_2NO$: 302.1351, found: 302.1352.

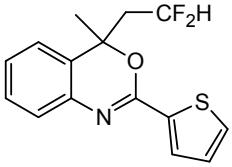


2-(3-bromophenyl)-4-(2,2-difluoroethyl)-4-methyl-4H-benzo[d][1,3]oxazine (**3m**):

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.26 (s, 1H), 8.05 (d, J = 7.9 Hz, 1H), 7.62 (dd, J = 7.9 Hz, J = 0.6 Hz, 1H), 7.35-7.29 (m, 3H), 7.25-7.22 (m, 1H), 7.11 (d, J = 7.6 Hz, 1H), 5.96 (tt, J = 60.5 Hz, J = 4.8 Hz, 1H), 2.64-2.44 (m, 2H), 1.79 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 154.4, 138.0, 134.5, 134.4, 130.8, 129.9, 129.3, 128.2, 127.4, 126.4, 125.8, 122.7, 122.5, 114.9 (t, J = 238.1 Hz), 77.9 (t, J = 6.1 Hz), 45.0 (t, J = 21.5 Hz), 27.6. ^{19}F NMR (470 MHz, $CDCl_3$): δ -112.3 (d, J = 291.0 Hz, 1F), -113.0 (d, J = 291.1 Hz, 1F). HRMS (ESI): calcd for $[M+H]^+$ $C_{17}H_{15}BrF_2NO$: 366.0300, found: 366.0303.



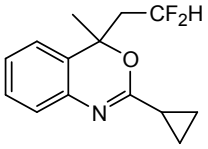
2-(2,6-dichlorophenyl)-4-(2,2-difluoroethyl)-4-methyl-4H-benzo[d][1,3]oxazine (**3n**): ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.40 (d, J = 1.2 Hz, 1H), 7.38 (s, 1H), 7.37-7.35 (m, 1H), 7.34-7.32 (m, 2H), 7.31-7.29 (m, 1H), 7.14 (d, J = 7.4 Hz, 1H), 6.10 (tt, J = 55.9 Hz, J = 4.1 Hz, 1H), 2.85-2.75 (m, 1H), 2.59-2.49 (m, 1H), 1.85 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 153.6, 136.8, 134.1, 132.9, 131.0, 129.3, 128.1, 127.9, 127.7, 126.0, 123.1, 114.8 (t, J = 237.7 Hz), 79.5 (t, J = 5.4 Hz) , 45.7 (t, J = 21.4 Hz), 29.1. ^{19}F NMR (470 MHz, $CDCl_3$): δ -112.4 (d, J = 290.8 Hz, 1F), -113.7 (d, J = 289.7 Hz, 1F). HRMS (ESI): calcd for $[M+H]^+$ $C_{17}H_{14}Cl_2F_2NO$: 356.0415, found: 356.0417.



4-(2,2-difluoroethyl)-4-methyl-2-(thiophen-2-yl)-4H-benzo[d][1,3]oxazine (**3o**):

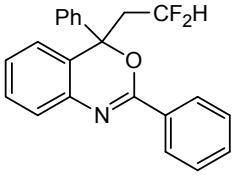
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.75 (dd, J = 3.7 Hz, J = 1.2 Hz, 1H), 7.53 (dd, J = 5.0 Hz, J = 1.2 Hz, 1H), 7.37-7.31 (m, 2H), 7.25-7.22 (m, 1H), 7.15-7.12 (m, 2H), 6.04 (tdd, J = 55.8 Hz, J = 5.2 Hz, J = 4.0 Hz, 1H), 2.69-2.44 (m, 2H), 1.82 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 152.5, 138.3, 136.8, 130.5, 123.0, 129.2, 128.5, 127.8, 126.8, 125.4, 122.6, 114.8 (t, J = 237.7 Hz), 77.9 (dd, J = 6.6 Hz, J = 5.2 Hz), 44.8 (t, J = 21.2 Hz), 27.1. ^{19}F NMR (470 MHz, $CDCl_3$): δ -112.2 (d, J = 290.9 Hz, 1F), -

113.1 (d, J = 290.9 Hz, 1F). HRMS (ESI): calcd for $[M+H]^+$ $C_{15}H_{14}F_2NOS$: 294.0759, found: 294.0764.



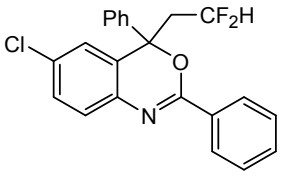
2-cyclopropyl-4-(2,2-difluoroethyl)-4-methyl-4H-benzo[d][1,3]oxazine (**3p**):

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.27-7.23 (m, 1H), 7.15-7.11 (m, 2H), 7.00 (d, J = 7.6 Hz, 1H), 5.95-5.71 (m, 1H), 2.51-2.32 (m, 2H), 1.71-1.66 (m, 1H), 1.62 (s, 3H), 1.04-1.02 (m, 2H), 0.87-0.83 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 162.4, 138.2, 129.1, 127.7, 126.1, 124.4, 122.5, 114.9 (t, J = 237.9 Hz), 77.1 (t), 44.9 (t, J = 21.2 Hz), 27.6, 14.6, 6.8, 6.7. ^{19}F NMR (470 MHz, $CDCl_3$): δ -112.2 (d, J = 290.5 Hz, 1F), -112.9 (d, J = 291.0 Hz, 1F). HRMS (ESI): calcd for $[M+H]^+$ $C_{14}H_{16}F_2NO$: 252.1195, found: 252.1191.



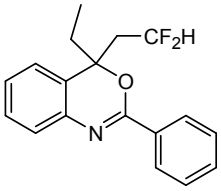
4-(2,2-difluoroethyl)-2,4-diphenyl-4H-benzo[d][1,3]oxazine (**3r**):

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.27 (dd, J = 8.1 Hz, 2H), 7.57-7.49 (m, 3H), 7.44-7.37 (m, 4H), 7.34-7.26 (m, 5H), 6.09 (tt, J = 55.7 Hz, J = 4.3 Hz, 1H), 3.06 (td, J = 15.1 Hz, J = 4.2 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 155.9, 142.0, 139.2, 132.1, 131.7, 129.5, 128.6, 128.4, 128.3, 127.9, 126.7, 126.5, 125.9, 125.5, 124.4, 115.2 (t, J = 238.7 Hz), 80.9 (t, J = 6.4 Hz), 44.9 (t, J = 22.2 Hz). ^{19}F NMR (470 MHz, $CDCl_3$): δ -111.0 (d, J = 289.1 Hz, 1F), -112.0 (d, J = 289.1 Hz, 1F). HRMS (ESI): calcd for $[M+H]^+$ $C_{22}H_{18}BrF_2NO$: 350.1351, found: 350.1356.



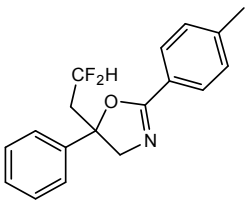
6-chloro-4-(2,2-difluoroethyl)-2,4-diphenyl-4H-benzo[d][1,3]oxazine (**3s**):

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.26 (d, J = 7.7 Hz, 2H), 7.59-7.56 (m, 1H), 7.53-7.50 (m, 2H), 7.39-7.36 (m, 5H), 7.35-7.32 (m, 2H), 7.23 (d, J = 1.6 Hz, 1H), 6.08 (tt, J = 59.9 Hz, J = 4.3 Hz, 1H), 3.06-2.99 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 156.1, 141.2, 137.8, 131.9, 131.8, 131.7, 129.7, 128.8, 128.7, 128.5, 128.2, 128.0, 127.2, 125.4, 124.5, 115.0 (t, J = 238.7 Hz), 80.7 (t, J = 5.6 Hz), 44.7 (t, J = 22.4 Hz). ^{19}F NMR (470 MHz, $CDCl_3$): δ -111.1 (d, J = 289.6 Hz, 1F), -112.2 (d, J = 290.8 Hz, 1F). HRMS (ESI): calcd for $[M+H]^+$ $C_{22}H_{17}ClF_2NO$: 384.0961, found: 384.0967.



4-ethyl-4-(2,2-difluoroethyl)-2-phenyl-4H-benzo[d][1,3]oxazine (**3t**):

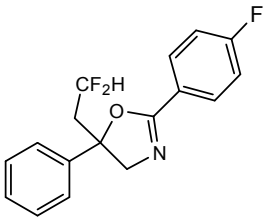
^{1}H NMR (500 MHz, $CDCl_3$): δ 8.18 (d, J = 8.2 Hz, 2H), 7.56-7.48 (m, 3H), 7.38-7.34 (m, 2H), 7.27-7.23 (m, 1H), 7.08 (d, J = 7.5 Hz, 1H), 5.98 (tt, J = 60.4 Hz, J = 4.5 Hz, 1H), 2.61 (td, J = 15.9 Hz, J = 4.5 Hz, 2H), 2.16-2.07 (m, 2H), 0.95 (t, J = 7.4 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 156.0, 139.2, 132.5, 131.5, 129.1, 128.3, 127.8, 126.8, 125.8, 125.7, 123.3, 115.2 (t, J = 237.9 Hz), 80.8 (t, J = 5.8 Hz), 44.6 (t, J = 21.1 Hz), 34.1, 7.7. ^{19}F NMR (470 MHz, $CDCl_3$): δ -112.4 (s, 2F). HRMS (ESI): calcd for $[M+H]^+$ $C_{18}H_{18}F_2NO$: 302.1351, found: 302.1350.



5-(2,2-difluoroethyl)-4,5-dihydro-5-phenyl-2-p-tolyloxazole (**5a**):

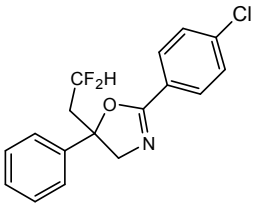
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.96 (d, J = 8.1 Hz, 2H), 7.43-7.42 (m, 4H), 7.39-7.32 (m, 1H), 7.29 (d, J = 8.3 Hz, 2H), 5.83 (tt, J = 55.7 Hz, J = 4.7 Hz, 1H), 4.33 (d, J = 14.7 Hz, 1H), 4.19 (d, J = 14.8 Hz, 1H), 2.68-2.61 (m, 2H), 2.45 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 163.0, 142.9, 142.2, 129.2, 128.9, 128.2, 128.0, 124.6, 124.3, 115.0 (t, J = 238.2 Hz), 85.4 (t, J = 5.9 Hz), 68.0, 45.3 (t, J = 21.5 Hz), 21.6. ^{19}F NMR

(470 MHz, $CDCl_3$): δ -113.11 (s, 1F), -113.13 (s, 1F). HRMS (ESI): calcd for $[M+H]^+$ $C_{18}H_{18}F_2NO$: 302.1351, found: 302.1352.



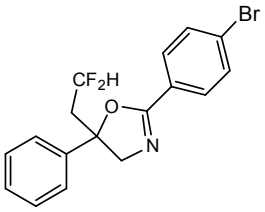
5-(2,2-difluoroethyl)-2-(4-fluorophenyl)-4,5-dihydro-5-phenyloxazole (**5b**):

^1H NMR (500 MHz, $CDCl_3$): δ 8.04 (dd, J = 8.8 Hz, J = 5.4 Hz, 2H), 7.42-7.37 (m, 4H), 7.34-7.31 (m, 1H), 7.14 (t, J = 8.6 Hz, 2H), 5.78 (tt, J = 55.7 Hz, J = 4.7 Hz, 1H), 4.31 (d, J = 14.8 Hz, 1H), 4.19 (d, J = 14.8 Hz, 1H), 2.65-2.58 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 164.9 (d, J = 250.9 Hz), 161.9, 142.7, 130.5 (d, J = 8.7 Hz), 129.0, 128.0, 124.3, 123.7 (d, J = 3.3 Hz), 115.7 (d, J = 22.1 Hz), 115.0 (t, J = 238.3 Hz), 85.8 (t, J = 5.6 Hz), 68.1, 45.3 (t, J = 21.2 Hz). ^{19}F NMR (470 MHz, $CDCl_3$): δ -107.5 (s, 1F), -113.19 (s, 1F), -113.20 (s, 1F). HRMS (ESI): calcd for $[M+H]^+$ $C_{17}H_{15}F_3NO$: 306.1100, found: 306.1104.



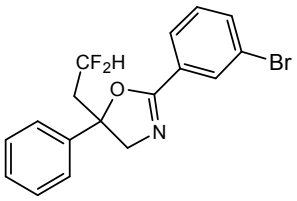
2-(4-chlorophenyl)-5-(2,2-difluoroethyl)-4,5-dihydro-5-phenyloxazole (**5c**):

^1H NMR (500 MHz, $CDCl_3$): δ 7.99 (d, J = 8.6 Hz, 2H), 7.47-7.43 (m, 3H), 7.42-7.39 (m, 3H), 7.37-7.34 (m, 1H), 5.80 (tt, J = 55.7 Hz, J = 4.7 Hz, 1H), 4.34 (d, J = 14.9 Hz, 1H), 4.21 (d, J = 14.9 Hz, 1H), 2.68-2.61 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 162.0, 142.6, 138.0, 129.6, 129.0, 128.9, 128.1, 125.9, 124.3, 114.9 (t, J = 238.4 Hz), 85.8 (t, J = 5.6 Hz), 68.1, 45.2 (t, J = 21.4 Hz). ^{19}F NMR (470 MHz, $CDCl_3$): δ -113.22 (s, 1F), -113.23 (s, 1F). HRMS (ESI): calcd for $[M+H]^+$ $C_{17}H_{15}ClF_2NO$: 322.0805, found: 322.0809.



2-(4-bromophenyl)-5-(2,2-difluoroethyl)-4,5-dihydro-5-phenyloxazole (**5d**):

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.89 (d, J = 8.5 Hz, 2H), 7.59 (d, J = 8.6 Hz, 2H), 7.42-7.36 (m, 4H), 7.34-7.31 (m, 1H), 5.77 (tt, J = 55.7 Hz, J = 4.7 Hz, 1H), 4.31 (d, J = 15.0 Hz, 1H), 4.18 (d, J = 14.9 Hz, 1H), 2.65-2.58 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 162.1, 142.6, 131.8, 129.8, 129.0, 128.1, 126.4, 126.3, 124.3, 114.9 (t, J = 238.4 Hz), 85.8 (t, J = 5.8 Hz), 68.1, 45.2 (t, J = 21.4 Hz). ^{19}F NMR (470 MHz, $CDCl_3$): δ -113.21 (s, 1F), -113.22 (s, 1F). HRMS (ESI): calcd for $[M+H]^+$ $C_{17}H_{15}BrF_2NO$: 366.0300, found: 366.0306.



2-(3-bromophenyl)-5-(2,2-difluoroethyl)-4,5-dihydro-5-phenyloxazole (**5e**): ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.20 (d, J = 1.6 Hz, 1H), 7.99 (d, J = 7.8 Hz, 1H), 7.68 (d, J = 8.1 Hz, 1H), 7.45-7.40 (m, 4H), 7.38-7.35 (m, 2H), 5.81 (tt, J = 55.7 Hz, J = 4.6 Hz, 1H), 4.36 (d, J = 15.0 Hz, 1H), 4.23 (d, J = 14.9 Hz, 1H), 2.68-2.61 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 161.5, 142.6, 134.7, 131.2, 130.1, 129.4, 129.0, 128.1, 126.8, 124.3, 122.6, 114.9 (t, J = 238.4 Hz), 86.0 (t, J = 5.8 Hz), 68.0, 45.3 (t, J = 21.5 Hz). ^{19}F NMR (470 MHz, $CDCl_3$): δ -113.24 (s, 1F), -113.25 (s, 1F). HRMS (ESI): calcd for $[M+H]^+$ $C_{17}H_{15}BrF_2NO$: 366.0300, found: 366.0304.

References:

(1) (a) Y.-M. Wang, J. Wu, C. Hoong, V. Rauniyar, F. D. Toste, *J. Am. Chem. Soc.* **2012**, *134*, 12928. (b) Q.-H. Deng, J.-R. Chen, Q. Wei, Q.-Q. Zhao, L.-Q. Lu and W.-J. Xiao, *Chem. Commun.,* 2015, **51**, 3537; (c) H. Yang, X.-H. Duan, J.-F. Zhao and L.-N. Guo, *Org. Lett.,* 2015, **17**, 1998

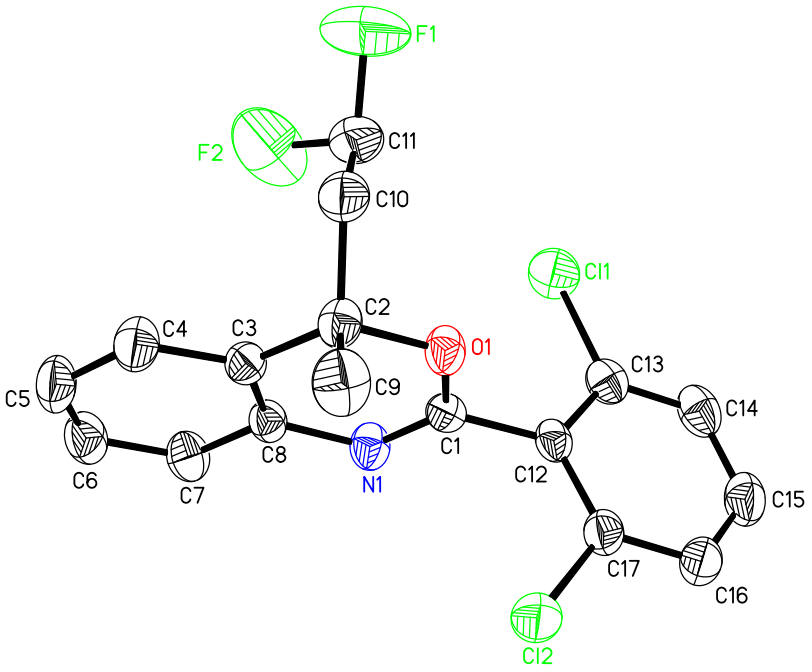
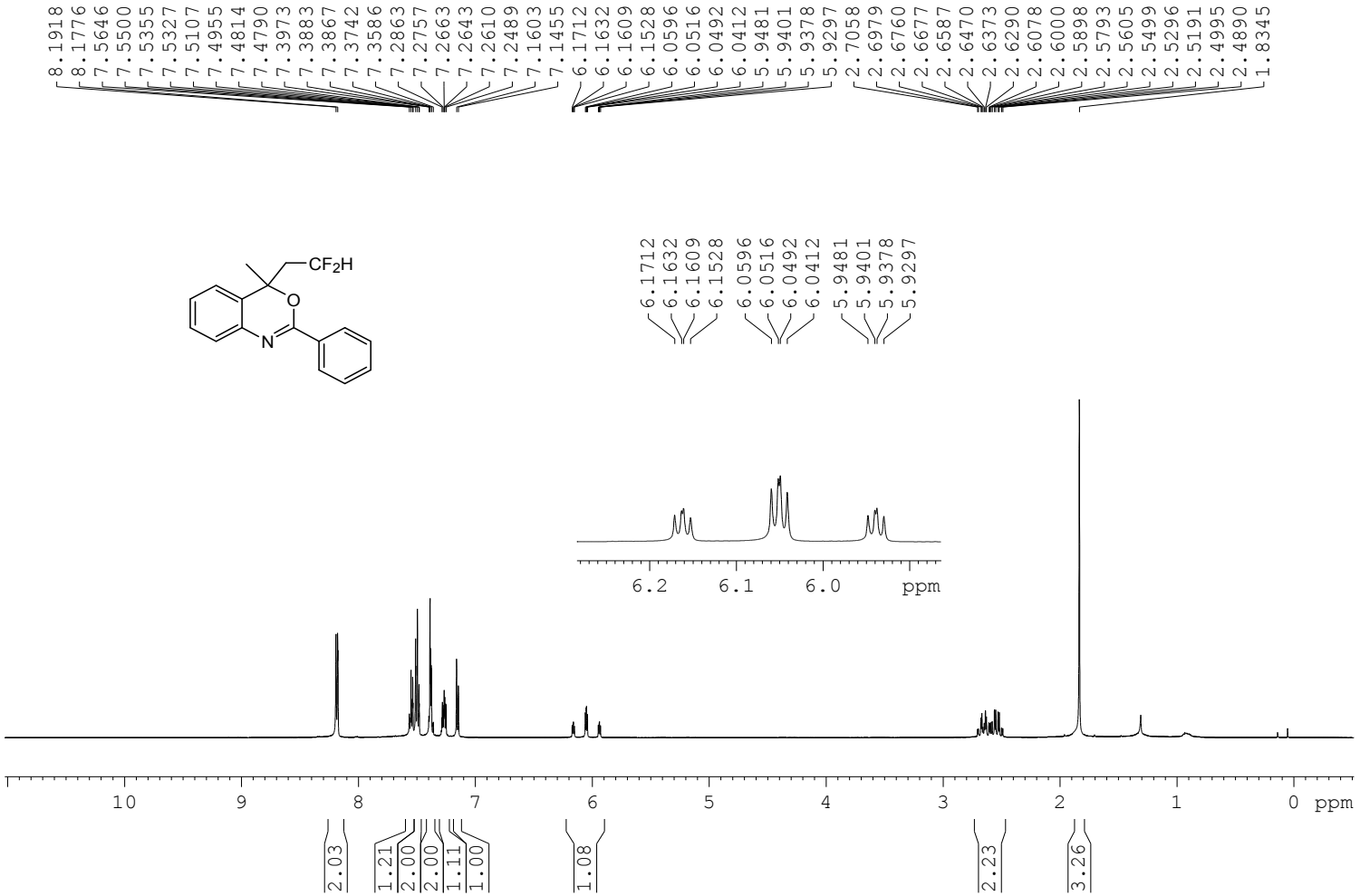


Figure 1 The ORTEP drawing of **3n** (Thermal ellipsoids are set at 30% probability level)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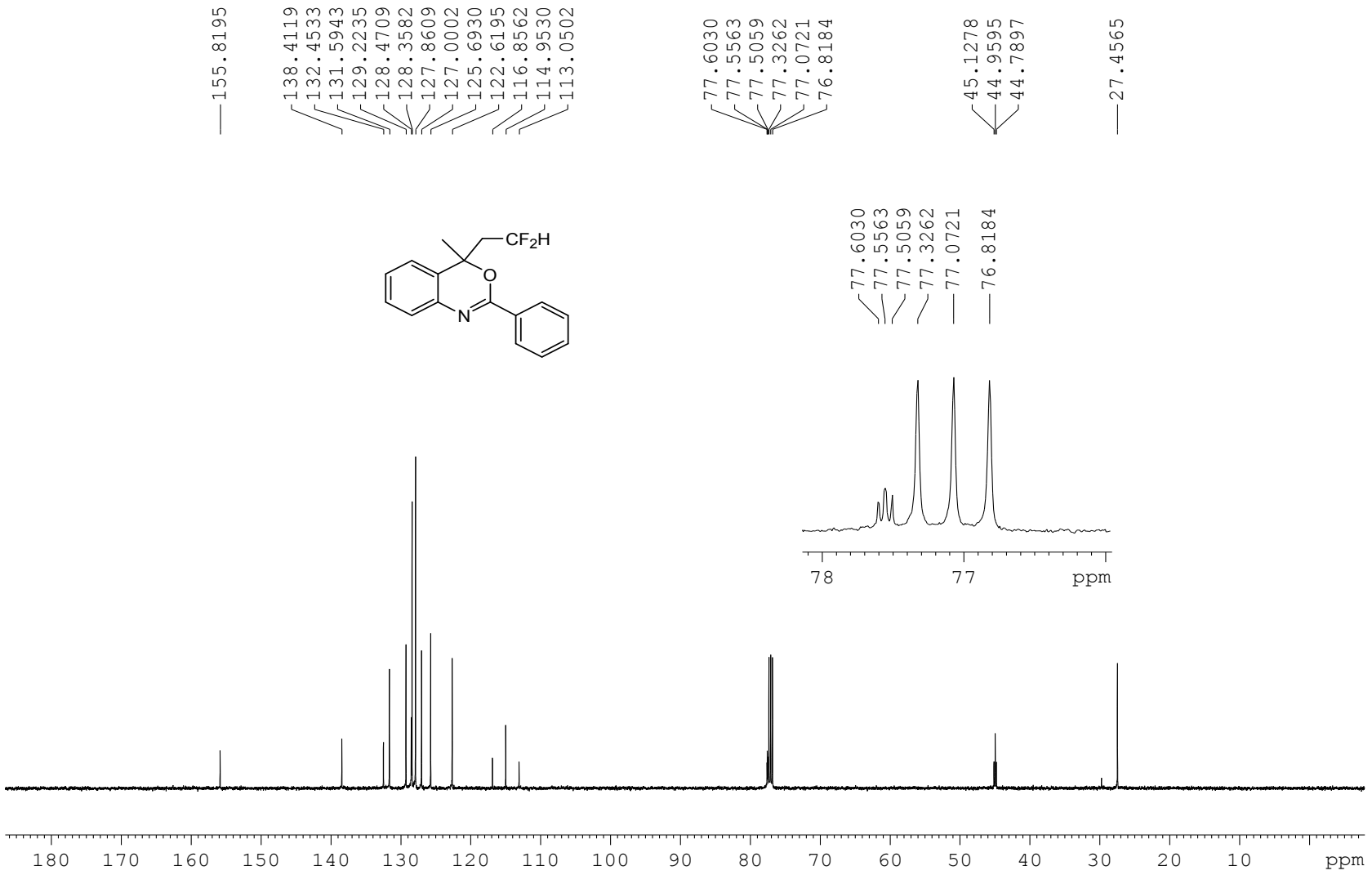
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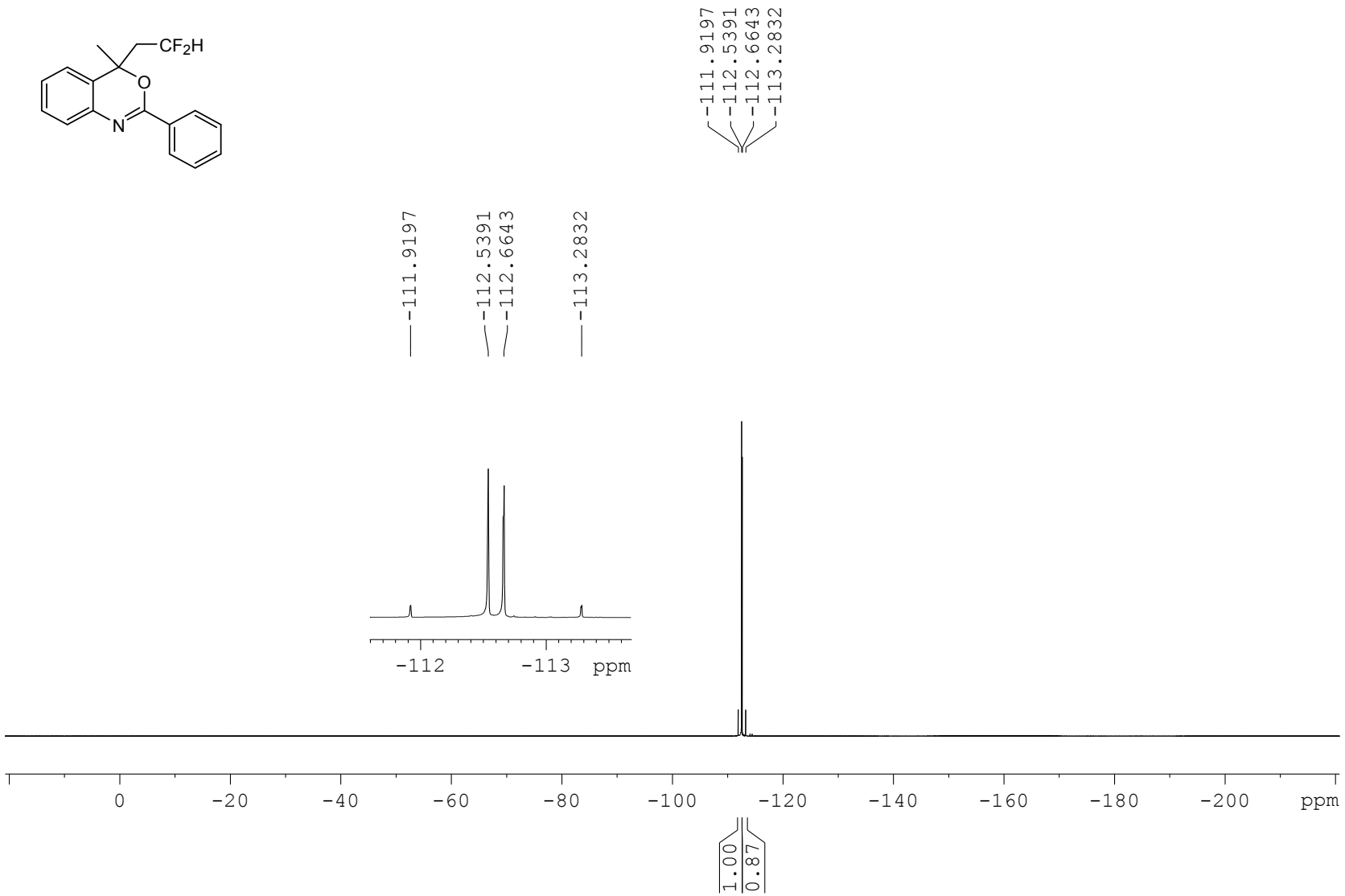
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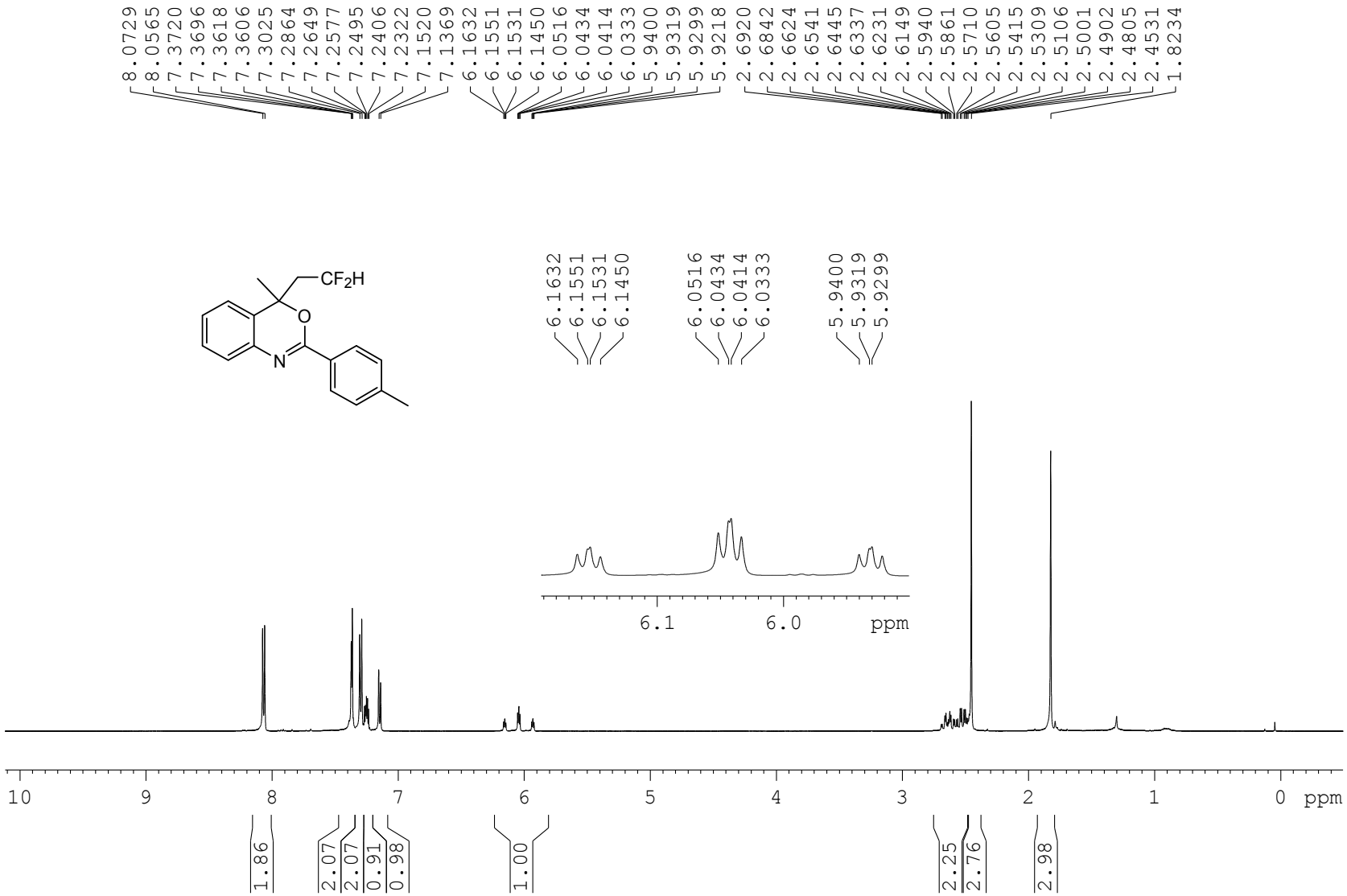
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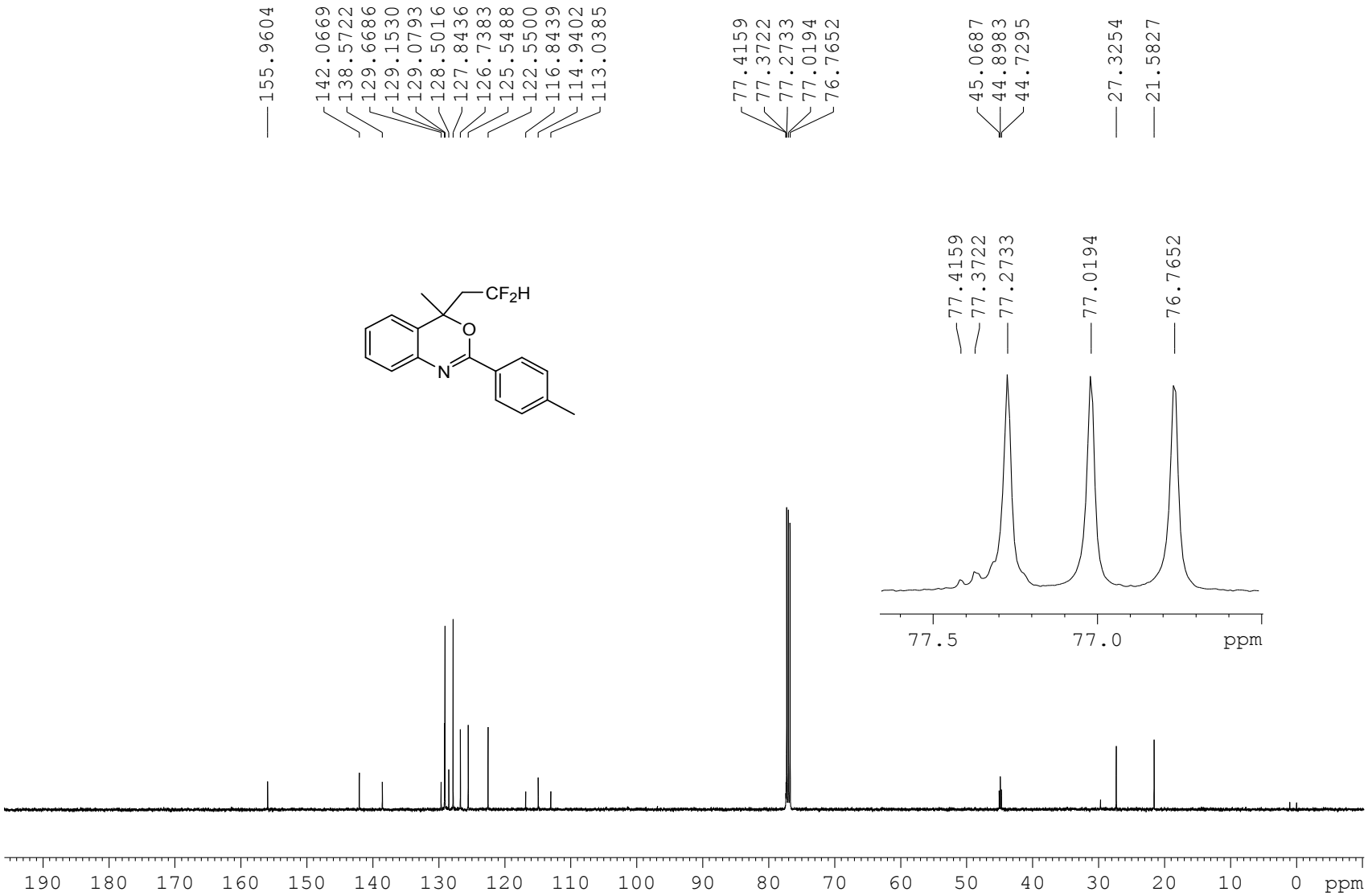
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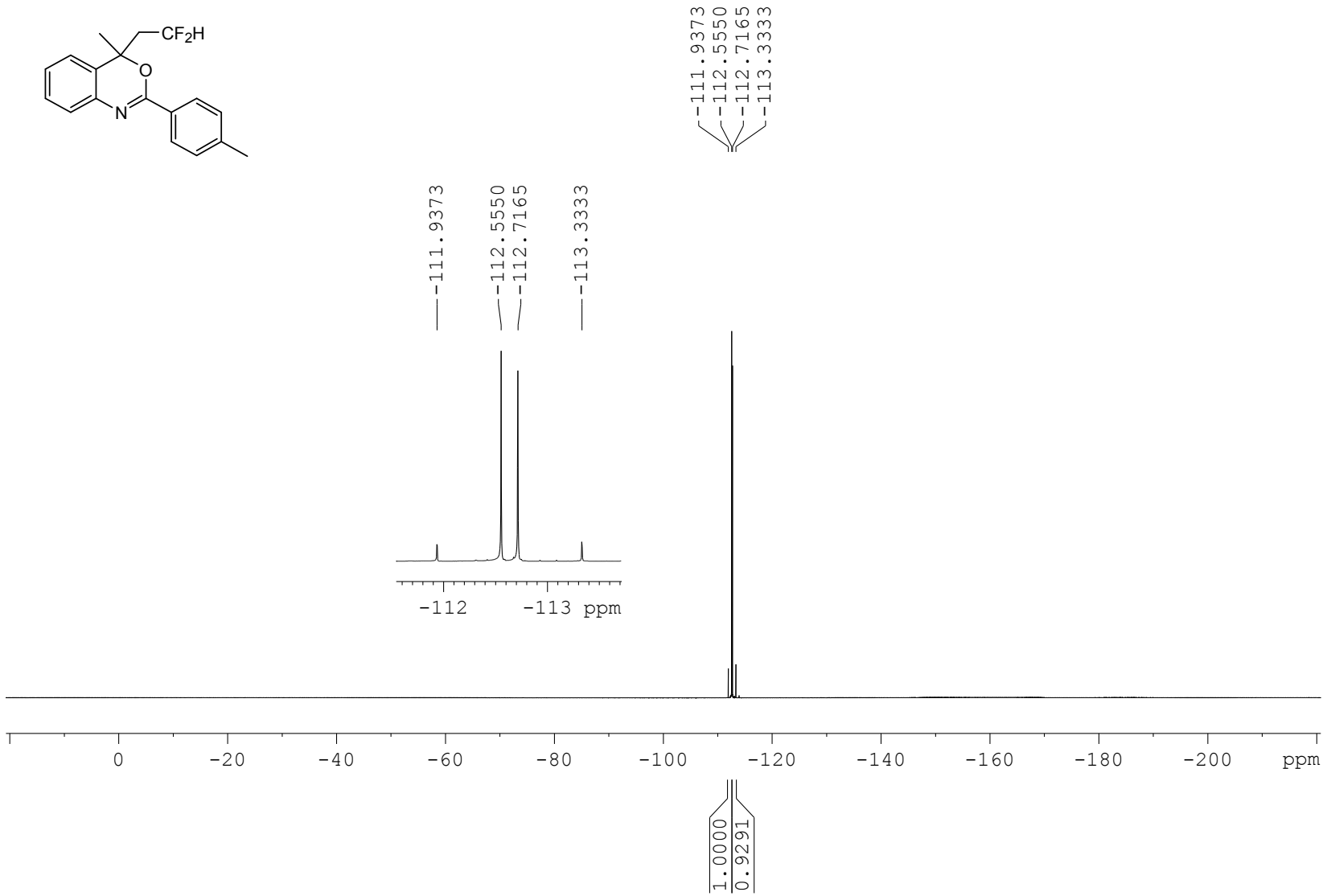
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-160
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-200
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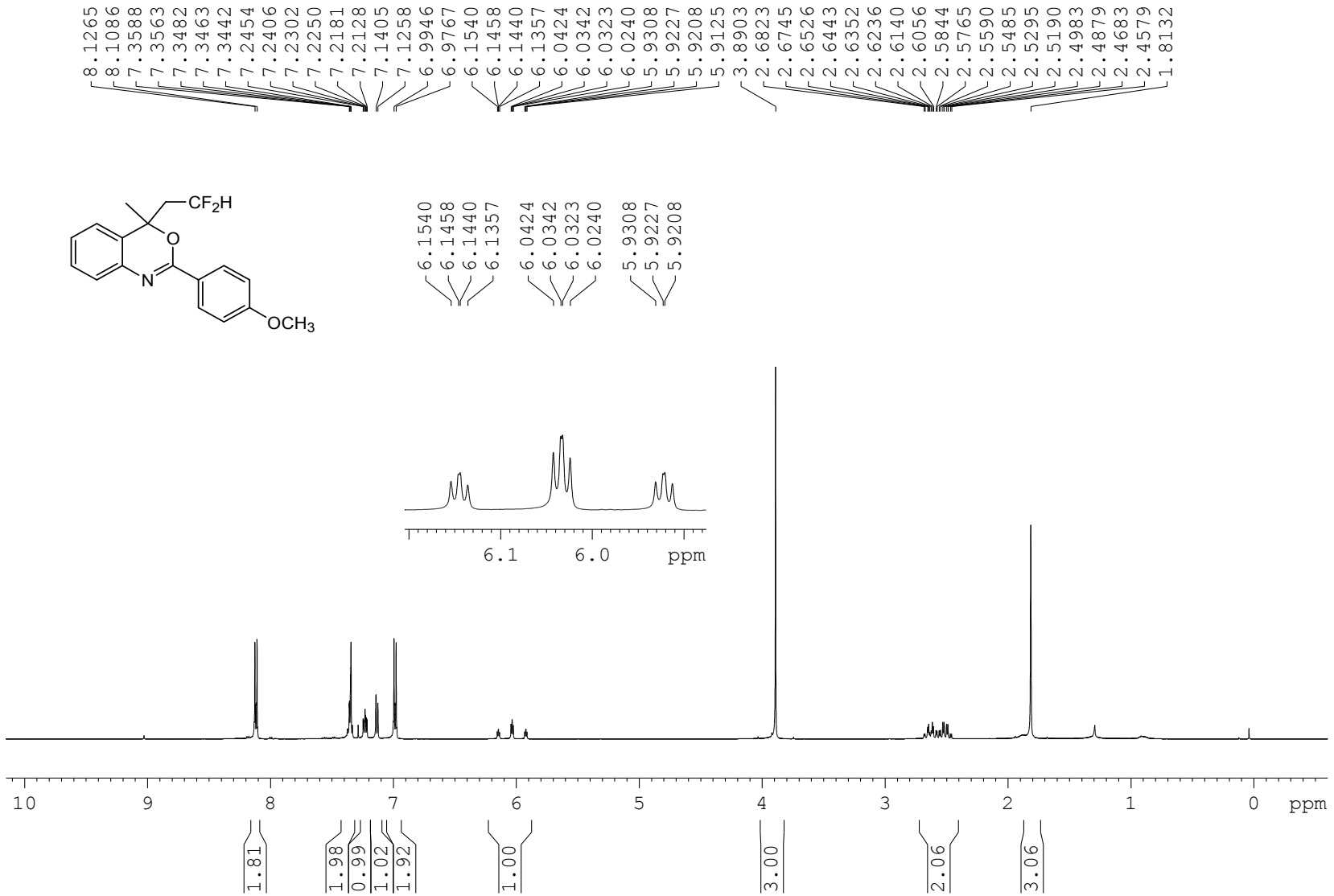
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7.3442
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7.2250
7.2181
7.2128
7.1405
7.1258
6.9946
6.9767
6.1540
6.1458
6.1440
6.1357
6.0424
6.0342
6.0323
6.0240
5.9308
5.9227
5.9208
5.9125
3.8903
2.6823
2.6745
2.6526
2.6443
2.6352
2.6236
2.6140
2.6056
2.5844
2.5765
2.5590
2.5485
2.5295
2.5190
2.4983
2.4879
2.4683
2.4579
1.8132
CF2H
O
N
OCH3
6.1540
6.1458
6.1440
6.1357
6.0424
6.0342
6.0323
6.0240
5.9308
5.9227
5.9208
6.1
6.0
ppm
10
9
8
7
6
5
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ppm
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1.92
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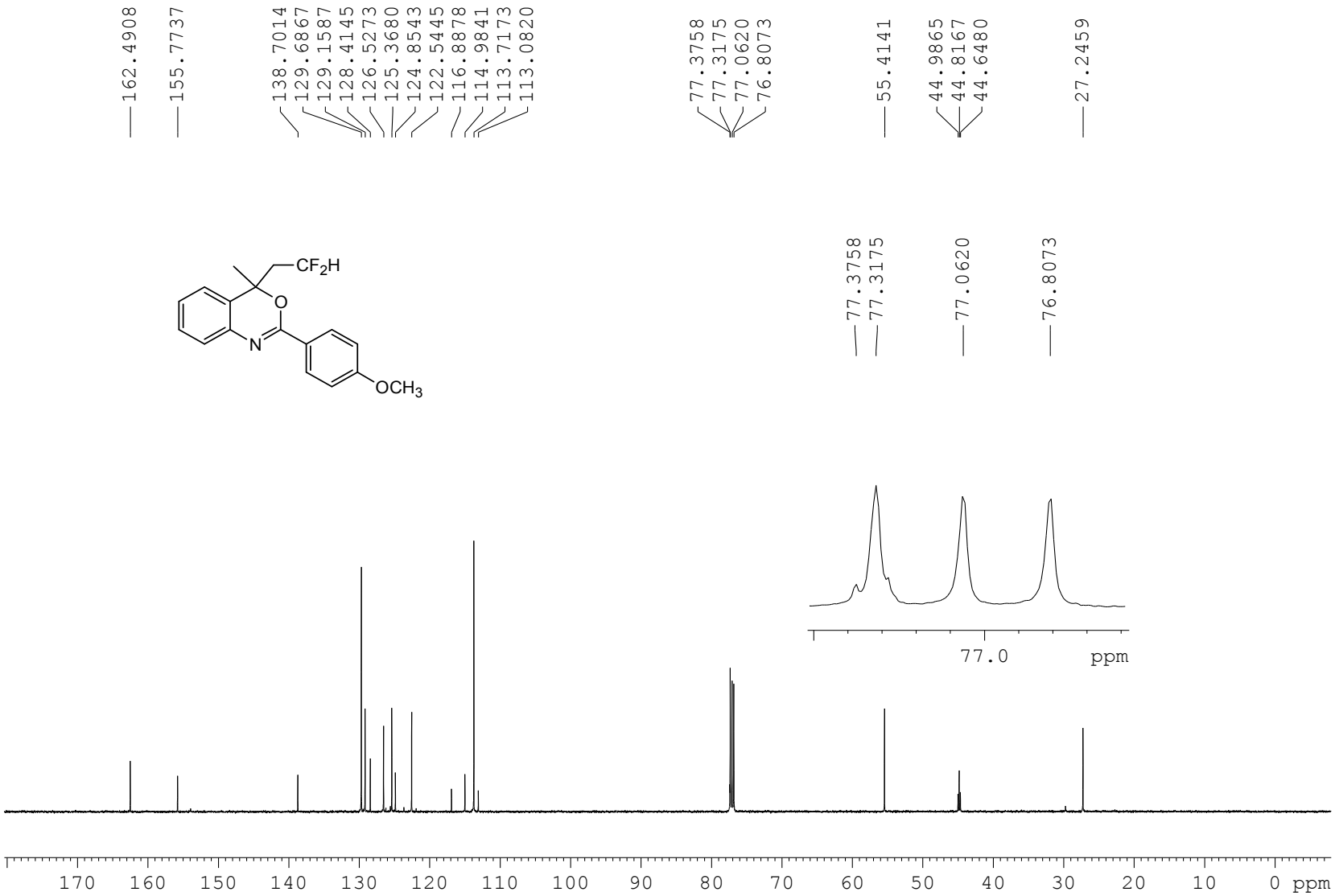
2.06
3.06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116.8878
114.9841
113.7173
113.0820
77.3758
77.3175
77.0620
76.8073
55.4141
44.9865
44.8167
44.6480
27.2459
CF2H
O
N
OCH3
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150
140
130
120
110
100
90
80
70
60
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40
30
20
10
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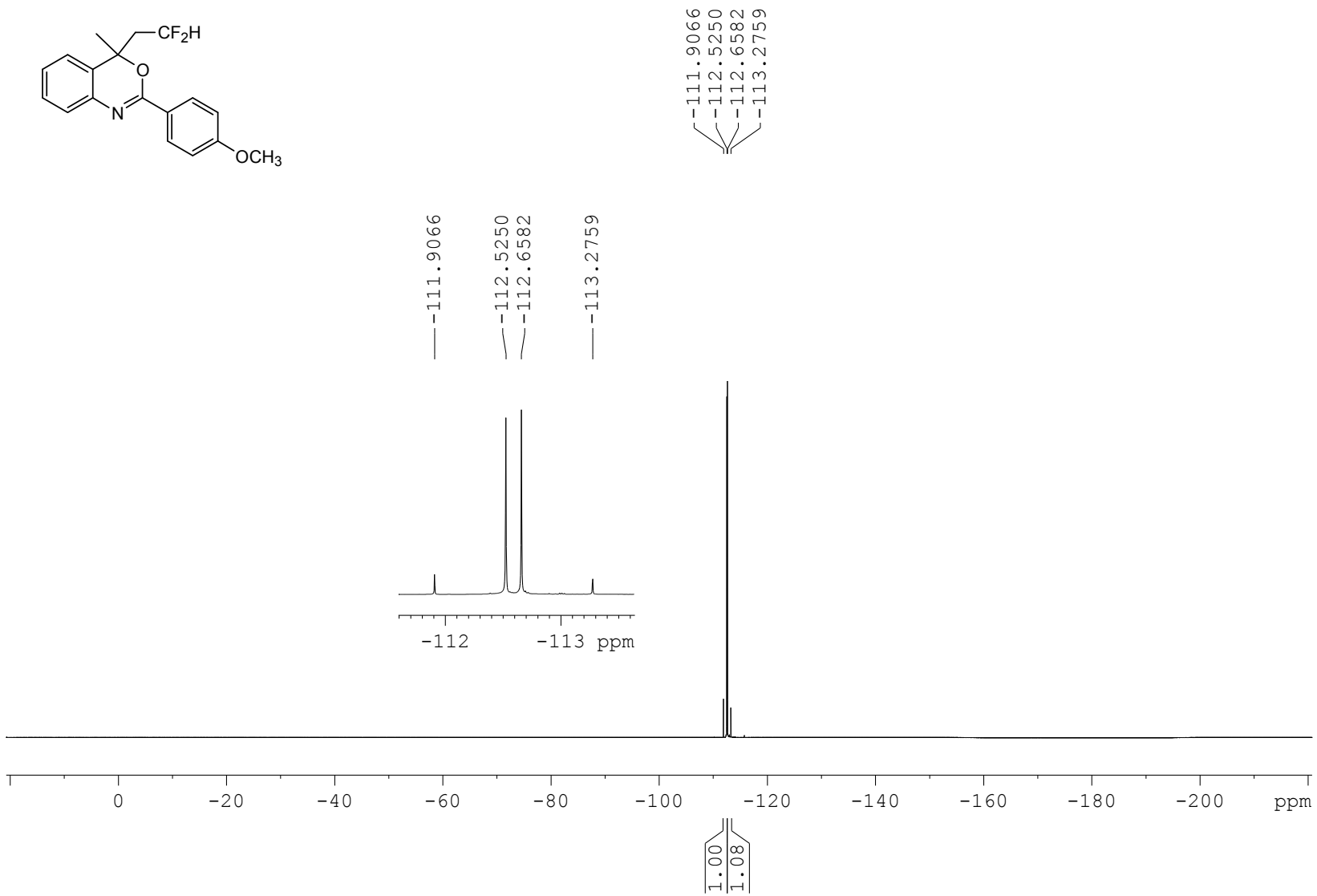
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N
OCH3
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-113.2759
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-113.2759
-112
-113 ppm
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-160
-180
-200
ppm
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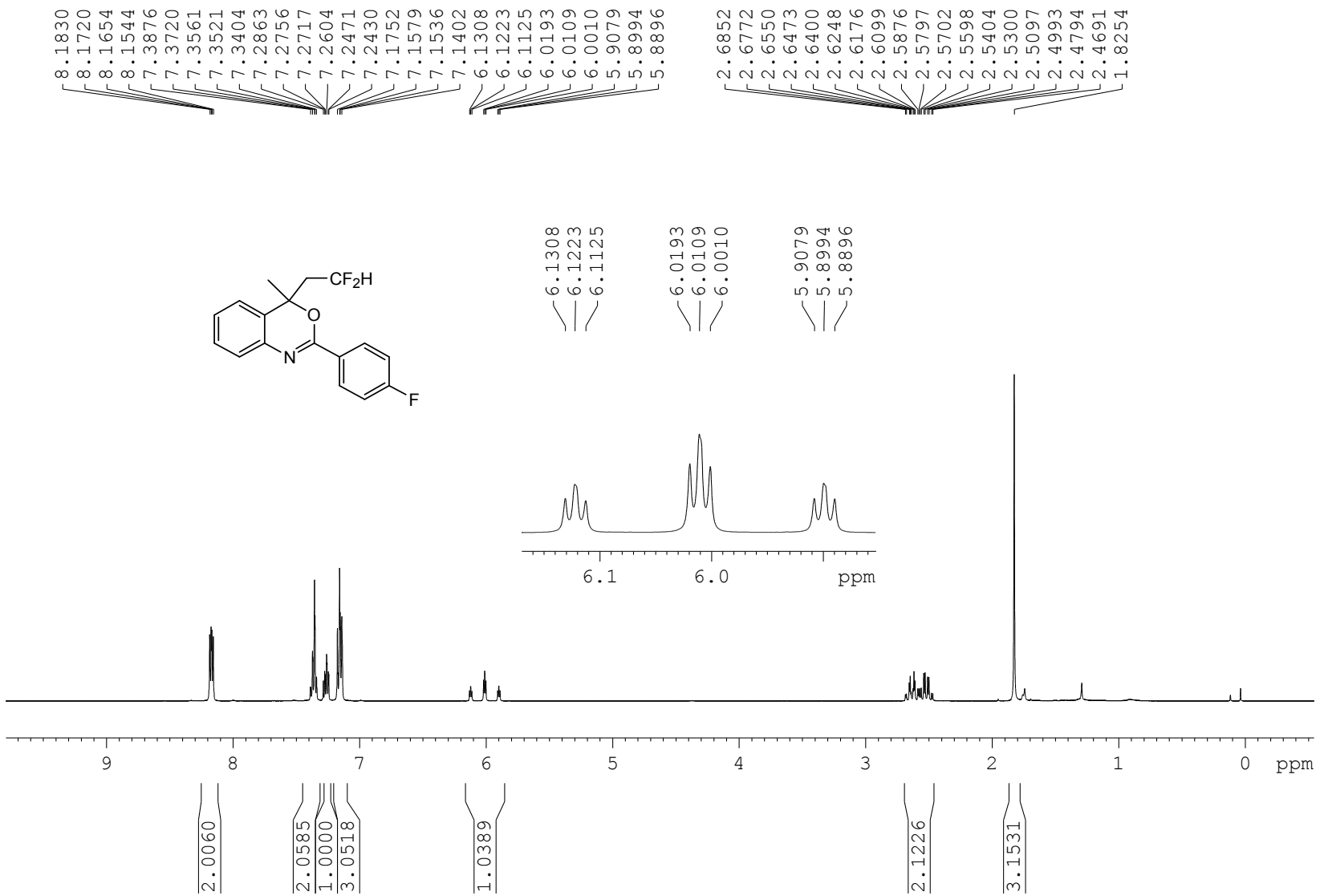
1.08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7.2863
7.2756
7.2717
7.2604
7.2471
7.2430
7.1752
7.1579
7.1536
7.1402
6.1308
6.1223
6.1125
6.0193
6.0109
6.0010
5.9079
5.8994
5.8896
2.6852
2.6772
2.6550
2.6473
2.6400
2.6248
2.6176
2.6099
2.5876
2.5797
2.5702
2.5598
2.5404
2.5300
2.5097
2.4993
2.4794
2.4691
1.8254
CF2H
O
N
F
6.1
6.0
ppm
9
8
7
6
5
4
3
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1
0
ppm
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3.0518
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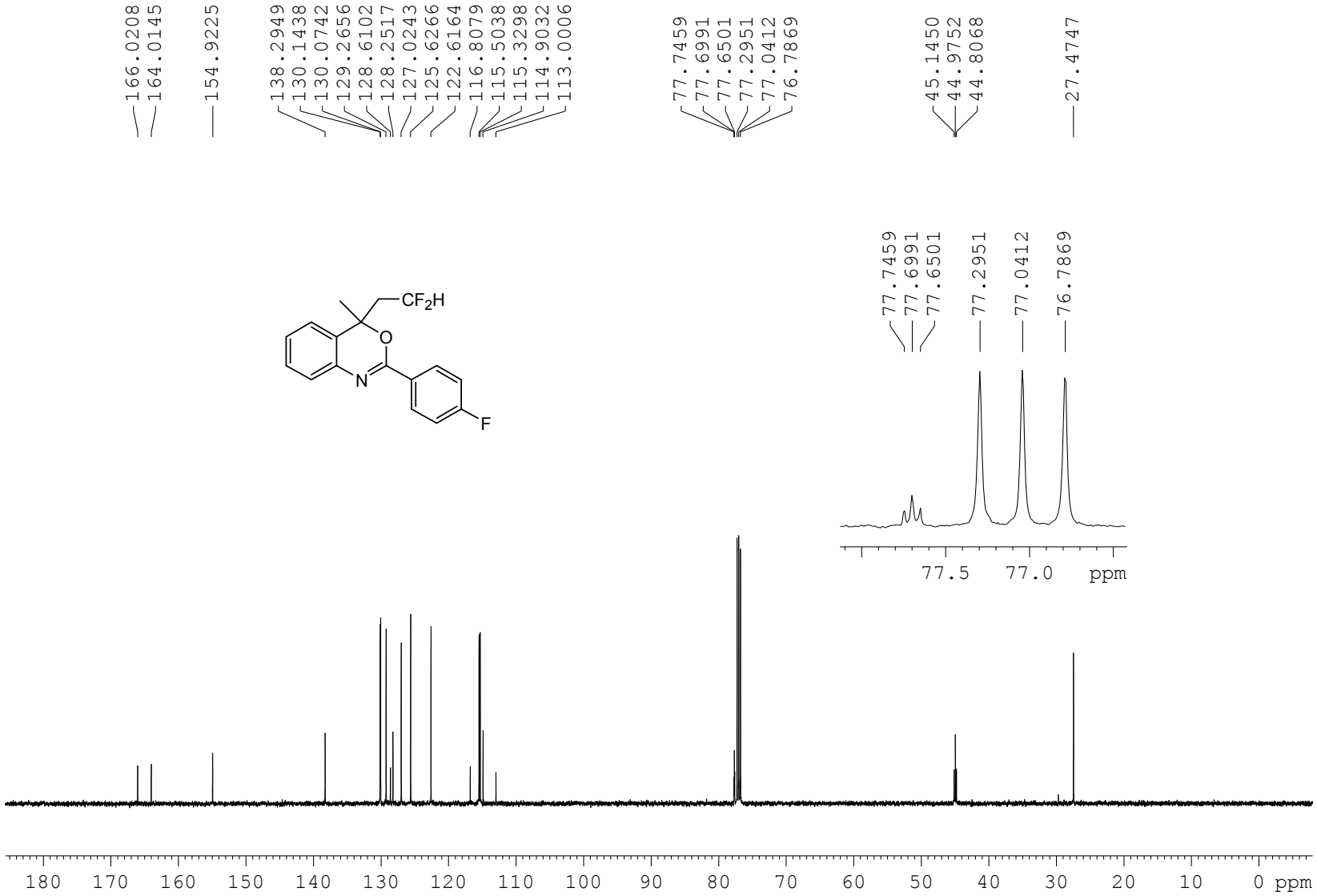
3.1531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122.6164
116.8079
115.5038
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114.9032
113.0006
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77.6501
77.2951
77.0412
76.7869
45.1450
44.9752
44.8068
27.4747
CF2H
O
N
F
77.5
77.0
ppm
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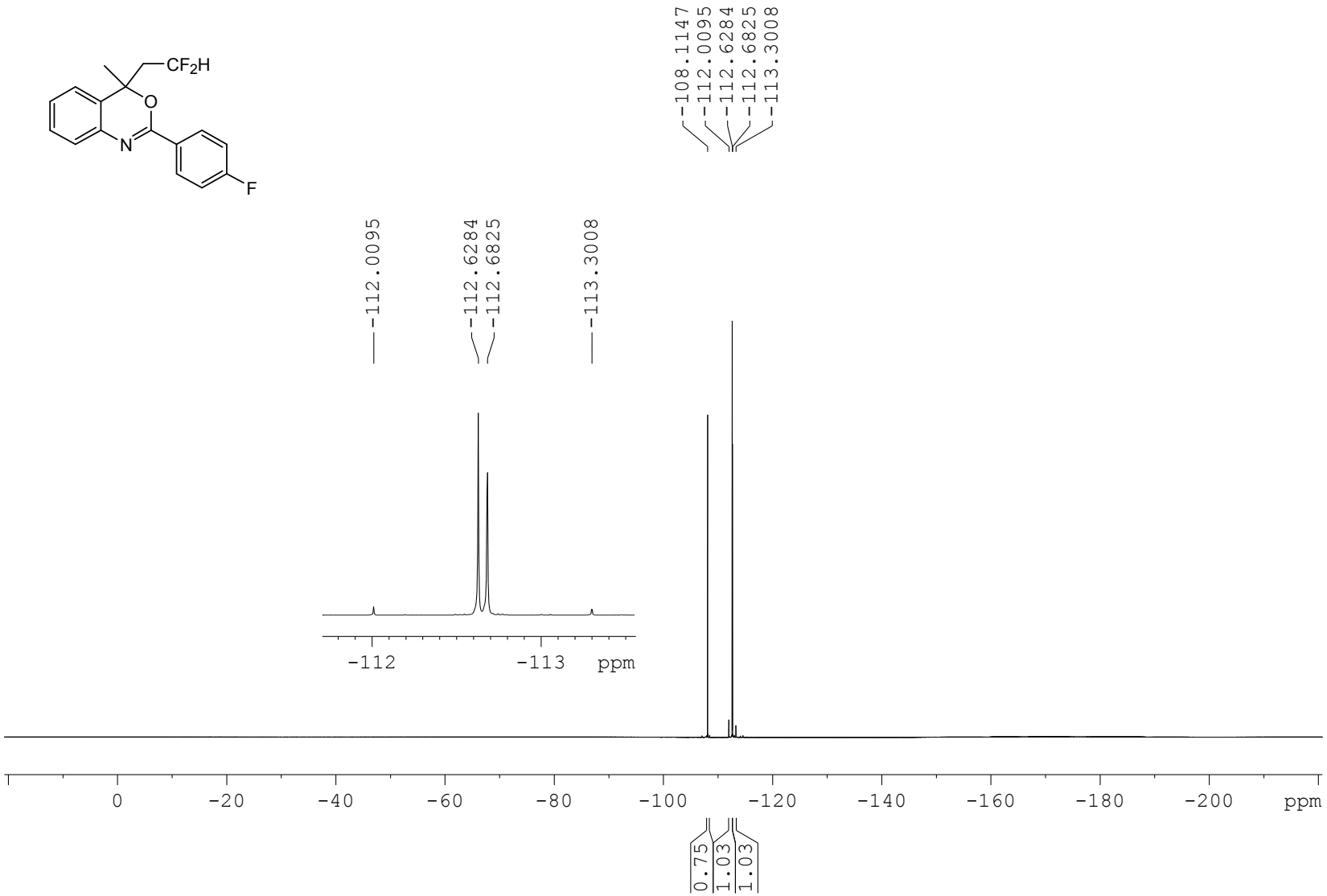
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0 ppm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N
F
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-112.0095
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-112.6825
-113.3008
-112
-113
ppm
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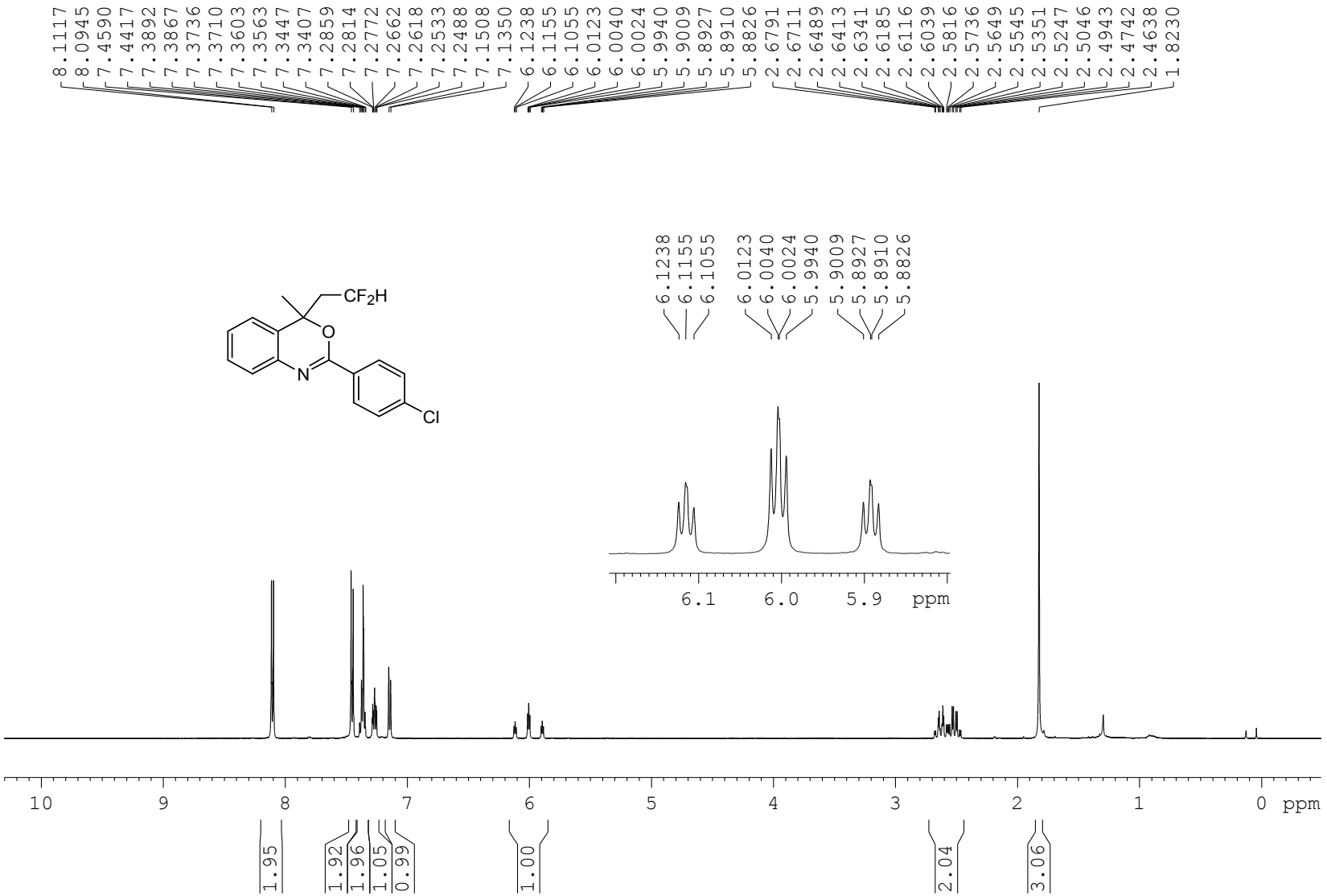
-60
-80
-100
-120
-140
-160
-180
-200
ppm
0.75
1.03
1.03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7.3892
7.3867
7.3736
7.3710
7.3603
7.3563
7.3447
7.3407
7.2859
7.2814
7.2772
7.2662
7.2618
7.2533
7.2488
7.1508
7.1350
6.1238
6.1155
6.1055
6.0123
6.0040
6.0024
5.9940
5.9009
5.8927
5.8910
5.8826
2.6791
2.6711
2.6489
2.6413
2.6341
2.6185
2.6116
2.6039
2.5816
2.5736
2.5649
2.5545
2.5351
2.5247
2.5046
2.4943
2.4742
2.4638
1.8230
CF2H
O
N
Cl
6.1
6.0
5.9
ppm
10
9
8
7
6
5
4
3
2
1
0
ppm
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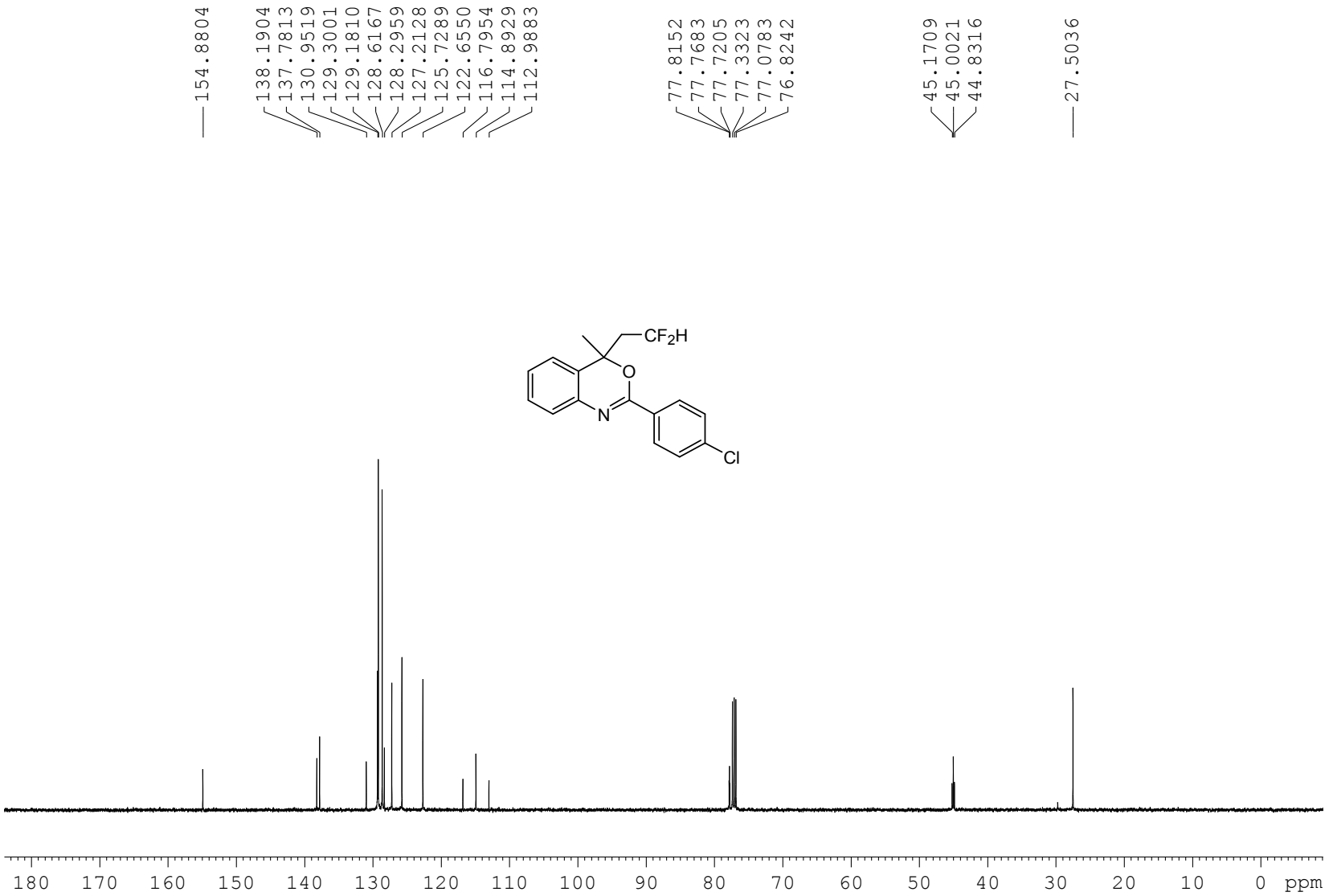
1.92
1.96
1.05
0.99
1.00
2.04
3.06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122.6550
116.7954
114.8929
112.9883
77.8152
77.7683
77.7205
77.3323
77.0783
76.8242
45.1709
45.0021
44.8316
27.5036
CF2H
O
N
Cl
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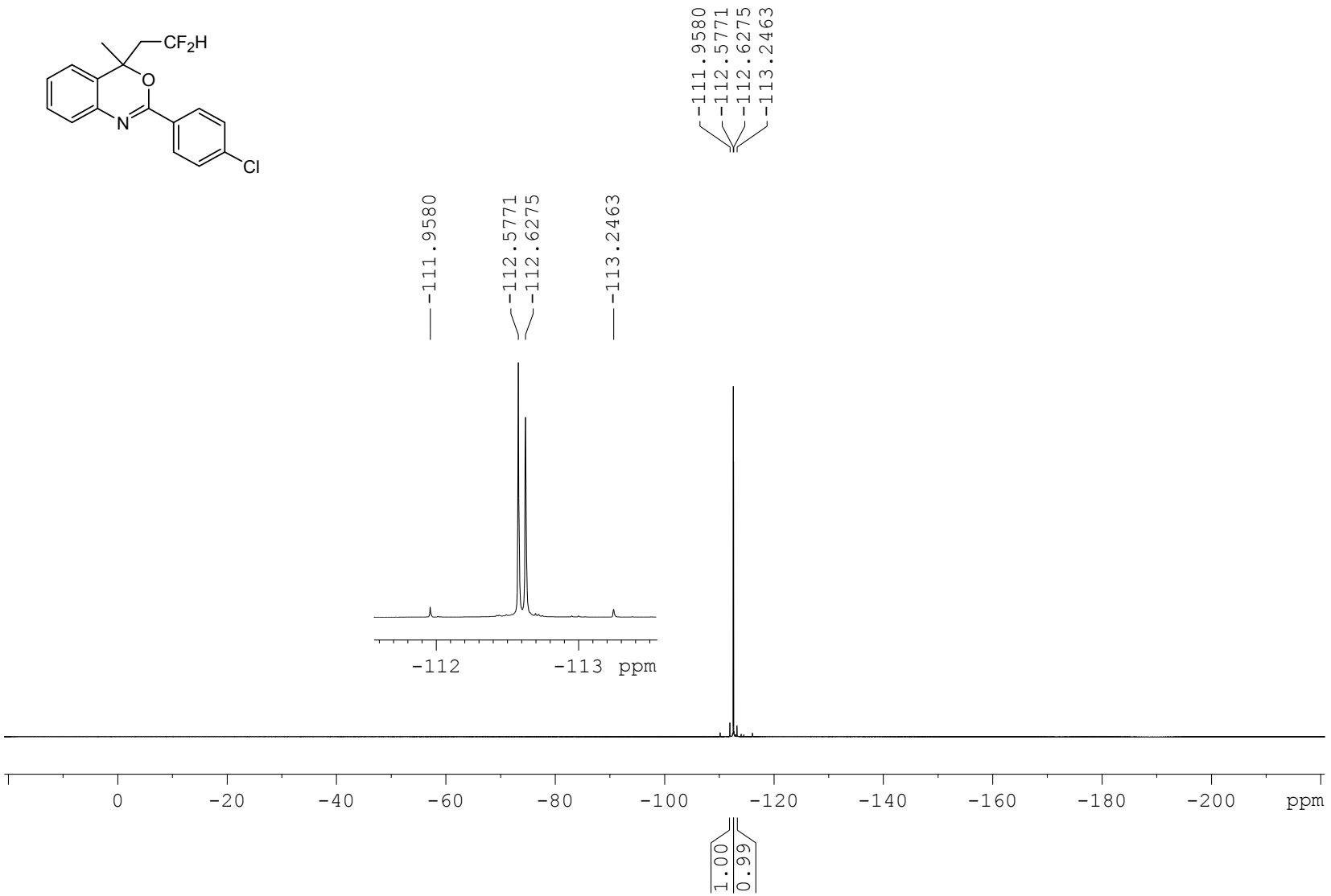
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm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O
N
Cl
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-113.2463
-111.9580
-112.5771
-112.6275
-113.2463
-112
-113 ppm
0
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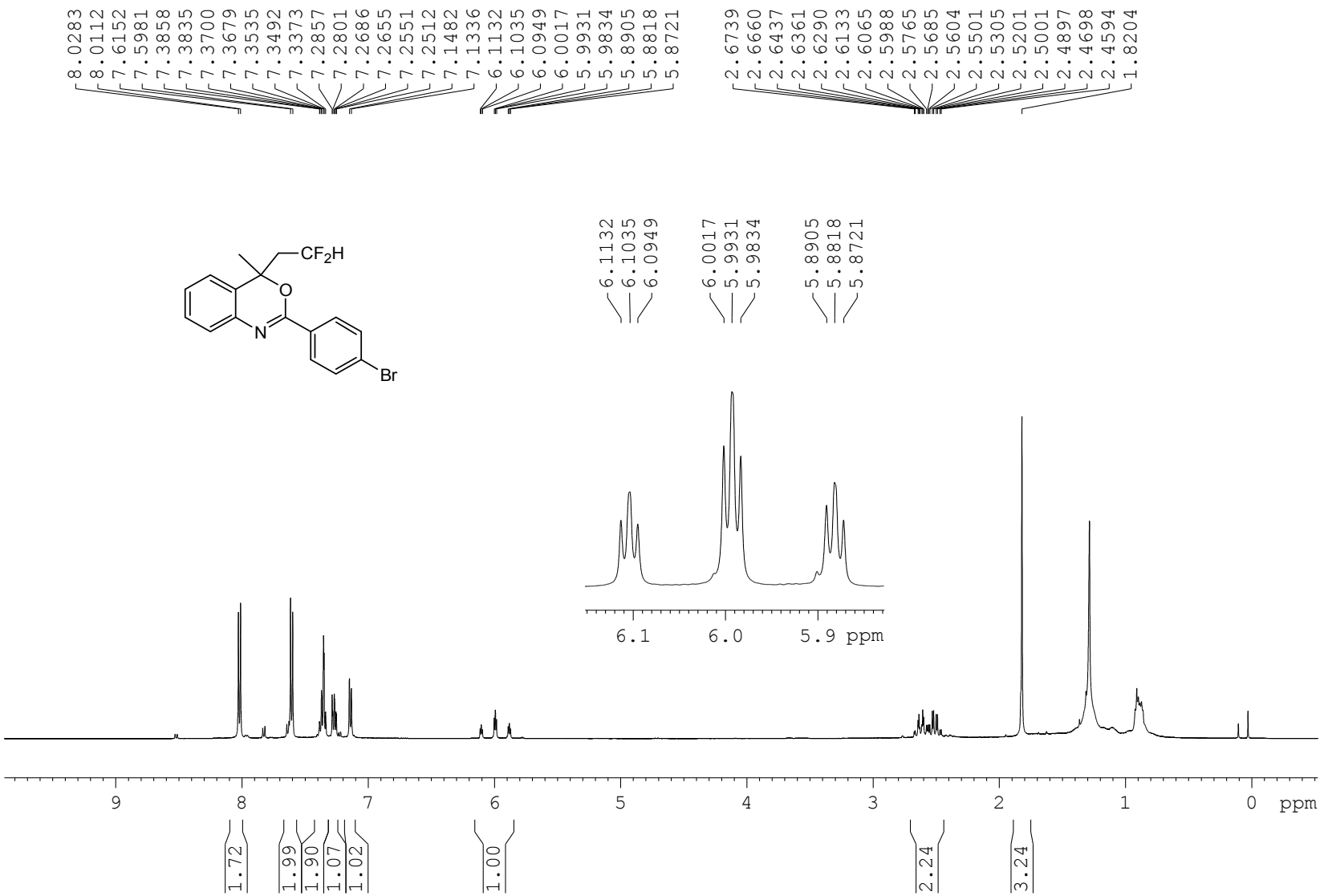
-40
-60
-80
-100
-120
-140
-160
-180
-200
ppm
1.00
0.99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7.3700
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7.3492
7.3373
7.2857
7.2801
7.2686
7.2655
7.2551
7.2512
7.1482
7.1336
6.1132
6.1035
6.0949
6.0017
5.9931
5.9834
5.8905
5.8818
5.8721
2.6739
2.6660
2.6437
2.6361
2.6290
2.6133
2.6065
2.5988
2.5765
2.5685
2.5604
2.5501
2.5305
2.5201
2.5001
2.4897
2.4698
2.4594
1.8204
CF2H
O
N
Br
6.1 6.0 5.9 ppm
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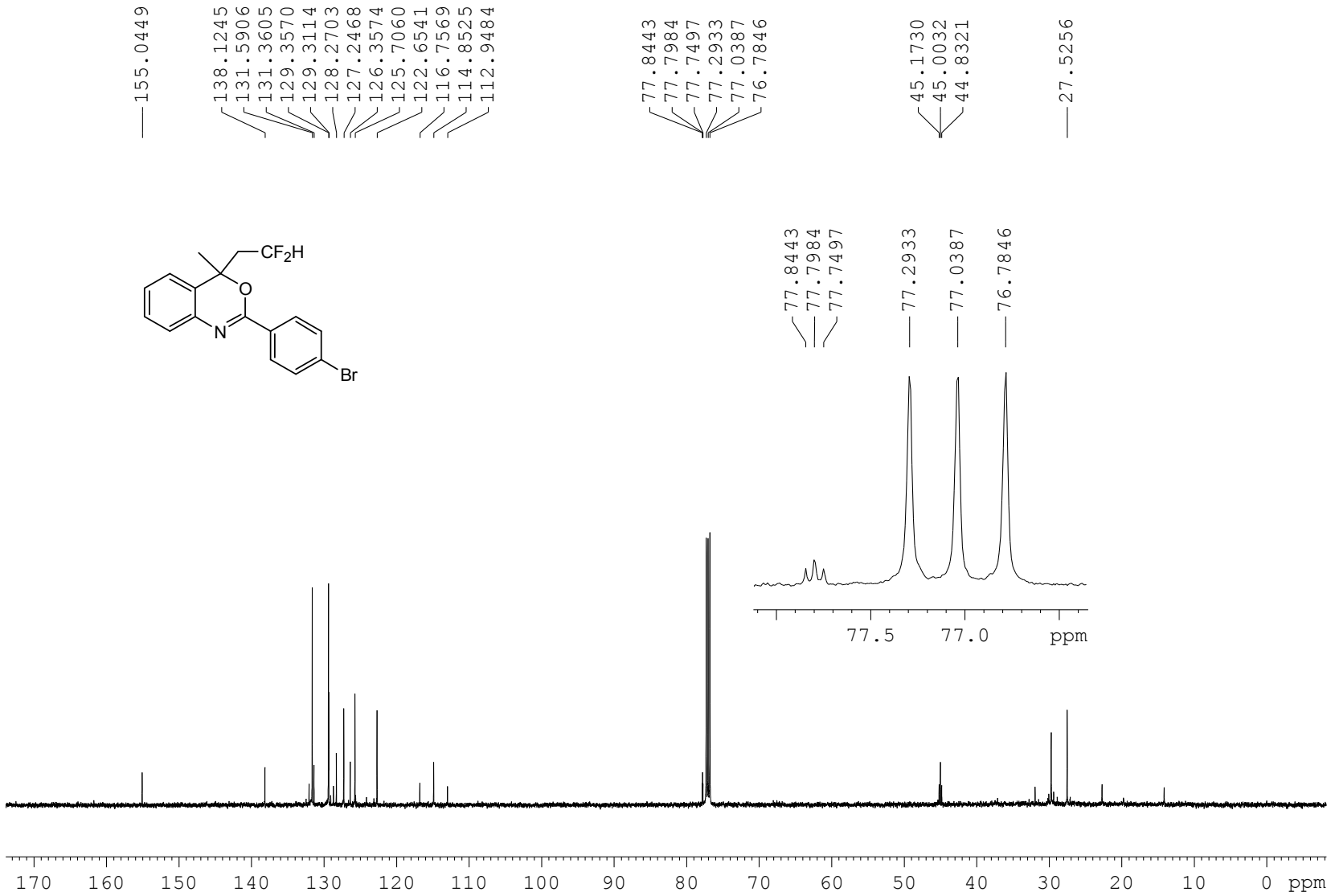
1.99
1.90
1.07
1.02
1.00
2.24
3.24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127.2468
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125.7060
122.6541
116.7569
114.8525
112.9484
77.8443
77.7984
77.7497
77.2933
77.0387
76.7846
45.1730
45.0032
44.8321
27.5256
CF2H
O
N
Br
77.5
77.0
ppm
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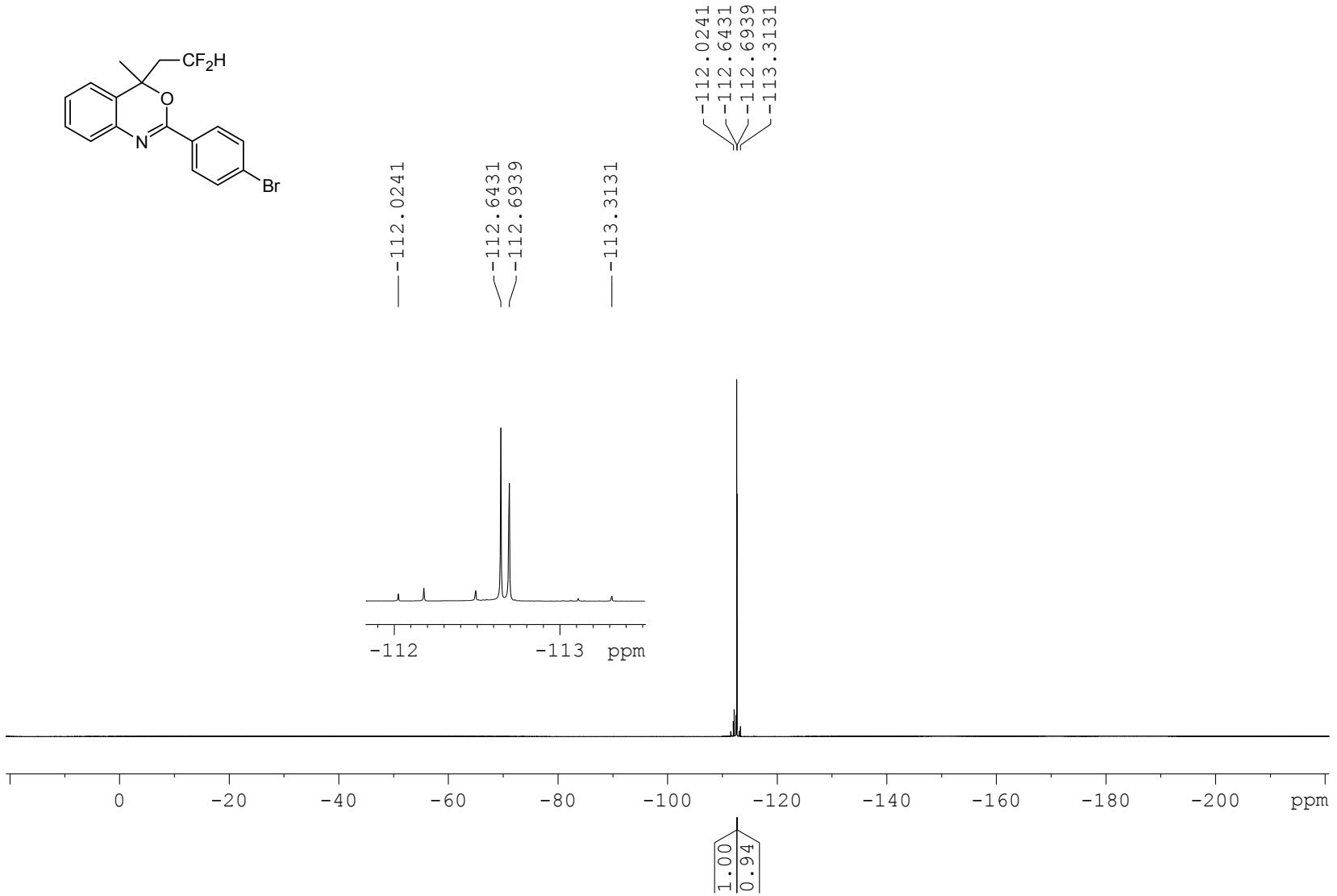
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm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O
N
Br
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-112.6431
-112.6939
-113.3131
-112.0241
-112.6431
-112.6939
-113.3131
-112
-113
ppm
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-40
-60
-80
-100
-120
-140
-160
-180
-200
ppm
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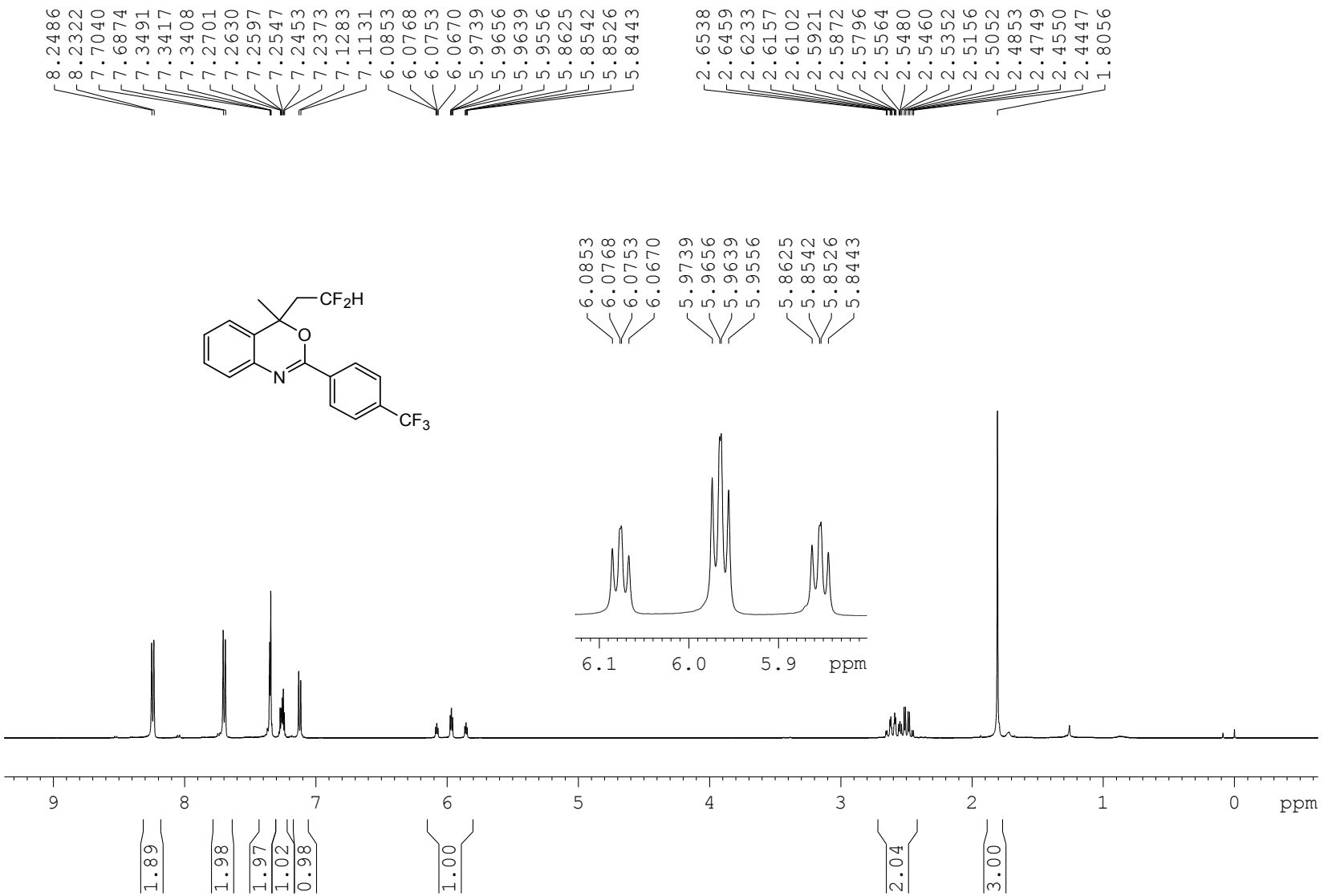
0.94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7.3408
7.2701
7.2630
7.2597
7.2547
7.2453
7.2373
7.1283
7.1131
6.0853
6.0768
6.0753
6.0670
5.9739
5.9656
5.9639
5.9556
5.8625
5.8542
5.8526
5.8443
2.6538
2.6459
2.6233
2.6157
2.6102
2.5921
2.5872
2.5796
2.5564
2.5480
2.5460
2.5352
2.5156
2.5052
2.4853
2.4749
2.4550
2.4447
1.8056
CF2H
O
N
CF3
6.1
6.0
5.9
ppm
9
8
7
6
5
4
3
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1
0
ppm
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1.02
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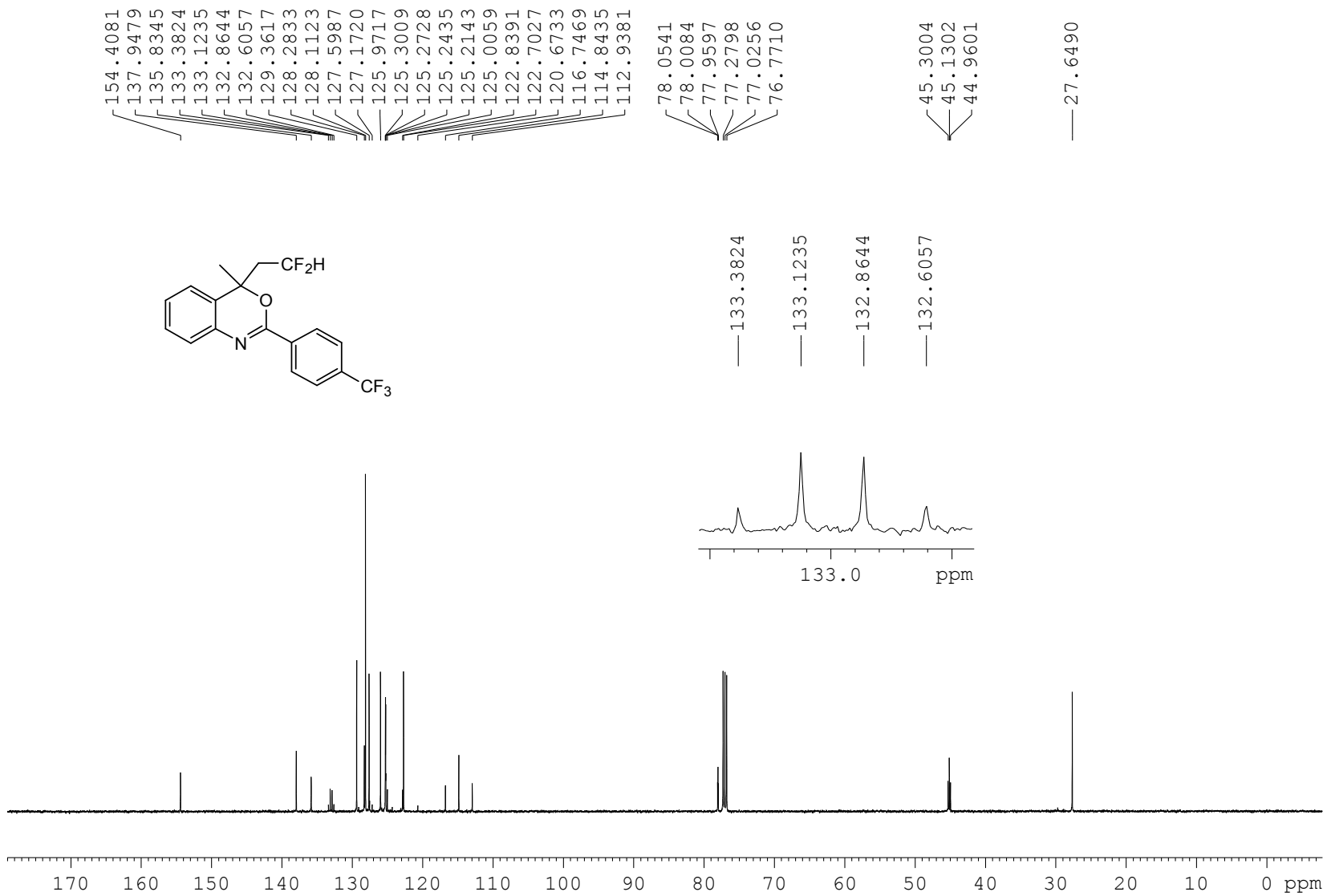
2.04
3.00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127.1720
125.9717
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125.2728
125.2435
125.2143
125.0059
122.8391
122.7027
120.6733
116.7469
114.8435
112.9381
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78.0084
77.9597
77.2798
77.0256
76.7710
45.3004
45.1302
44.9601
27.6490
CF2H
O
N
CF3
133.3824
133.1235
132.8644
132.6057
133.0
ppm
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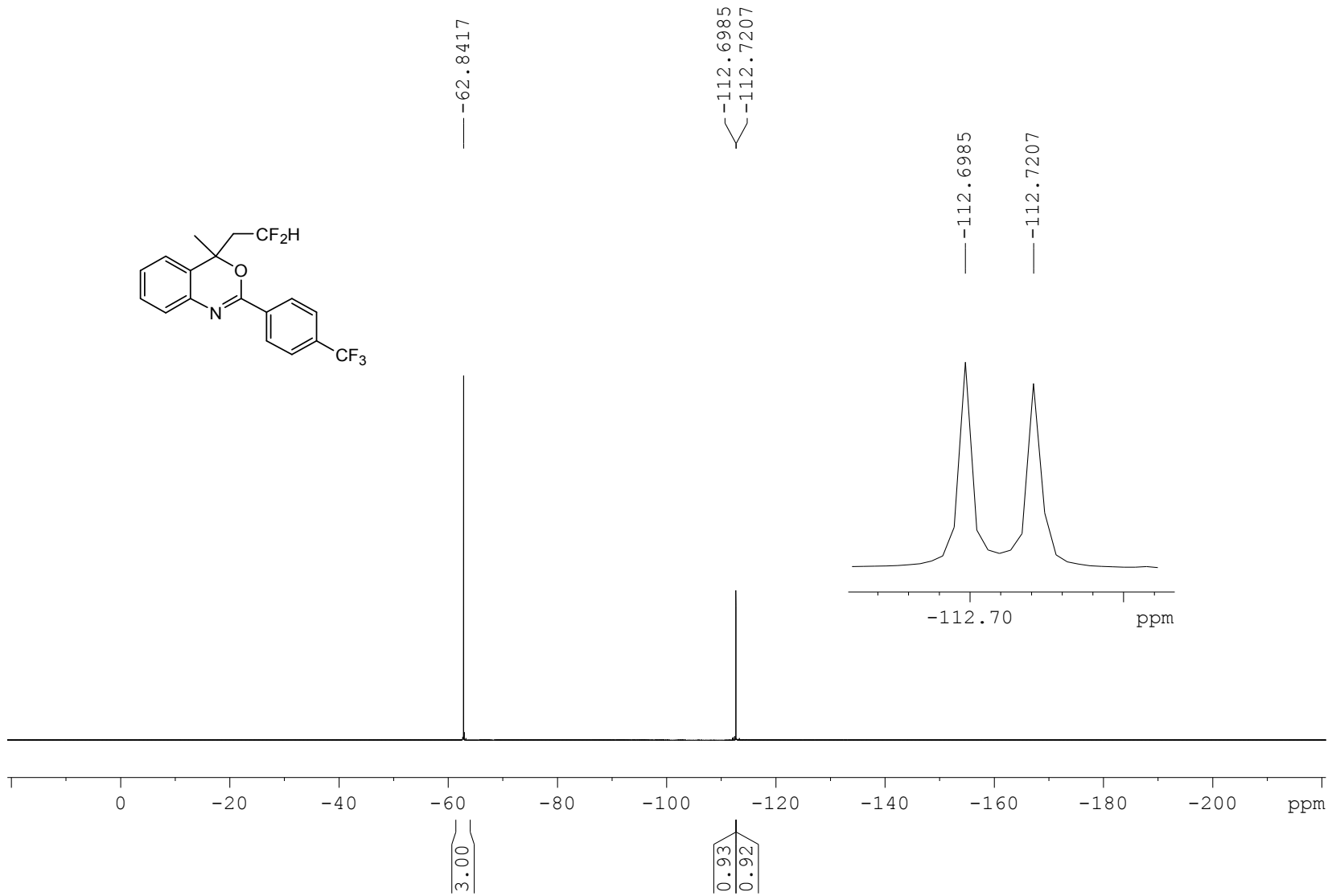
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0 ppm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-112.7207
CF2H
O
N
CF3
-112.70
ppm
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-60
-80
-100
-120
-140
-160
-180
-200
ppm
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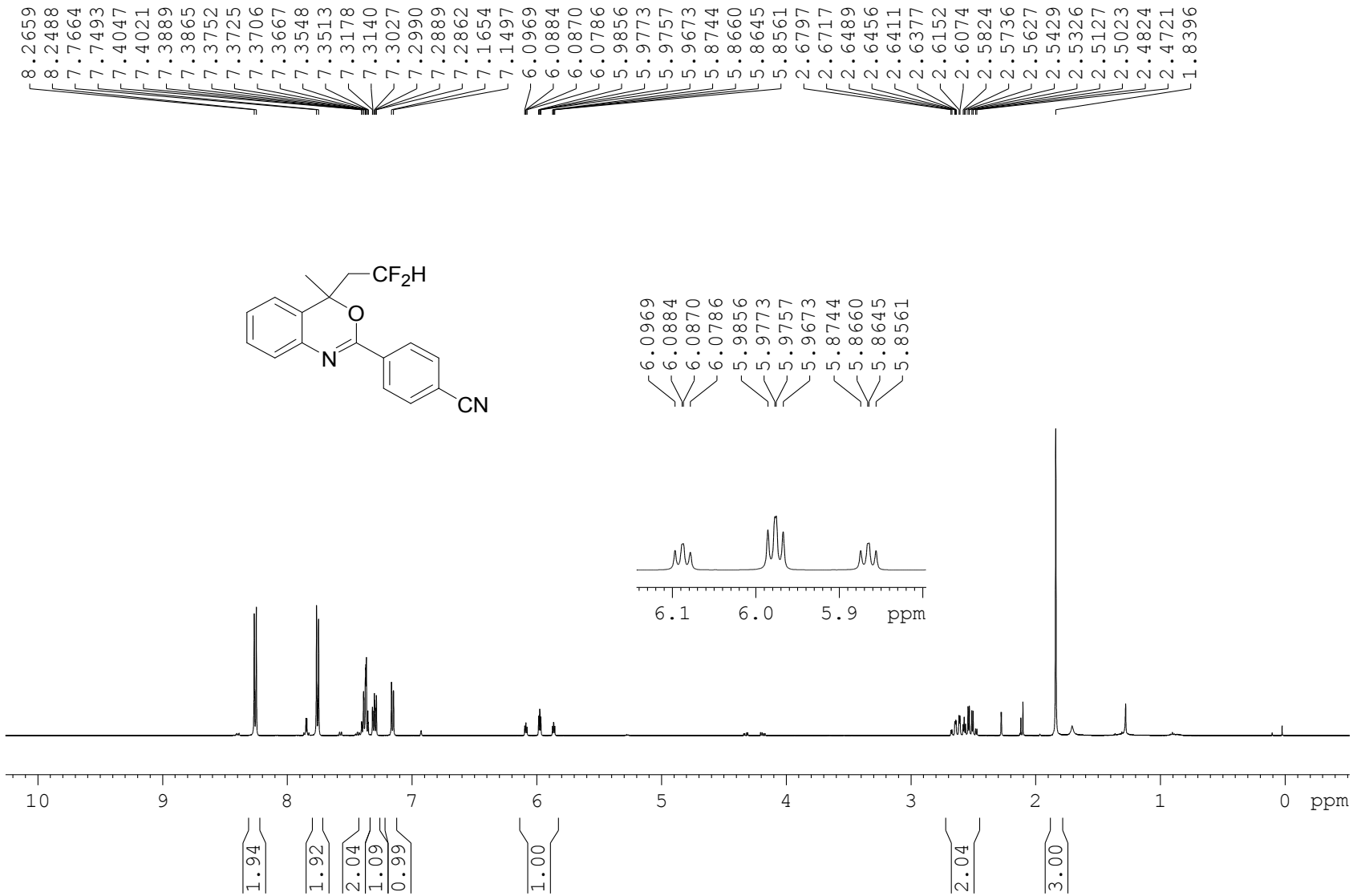
0.92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7.3865
7.3752
7.3725
7.3706
7.3667
7.3548
7.3513
7.3178
7.3140
7.3027
7.2990
7.2889
7.2862
7.1654
7.1497
6.0969
6.0884
6.0870
6.0786
5.9856
5.9773
5.9757
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5.8660
5.8645
5.8561
2.6797
2.6717
2.6489
2.6456
2.6411
2.6377
2.6152
2.6074
2.5824
2.5736
2.5627
2.5429
2.5326
2.5127
2.5023
2.4824
2.4721
1.8396
CF2H
O
N
CN
6.1
6.0
5.9
ppm
10
9
8
7
6
5
4
3
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1
0
ppm
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1.92
2.04
1.09
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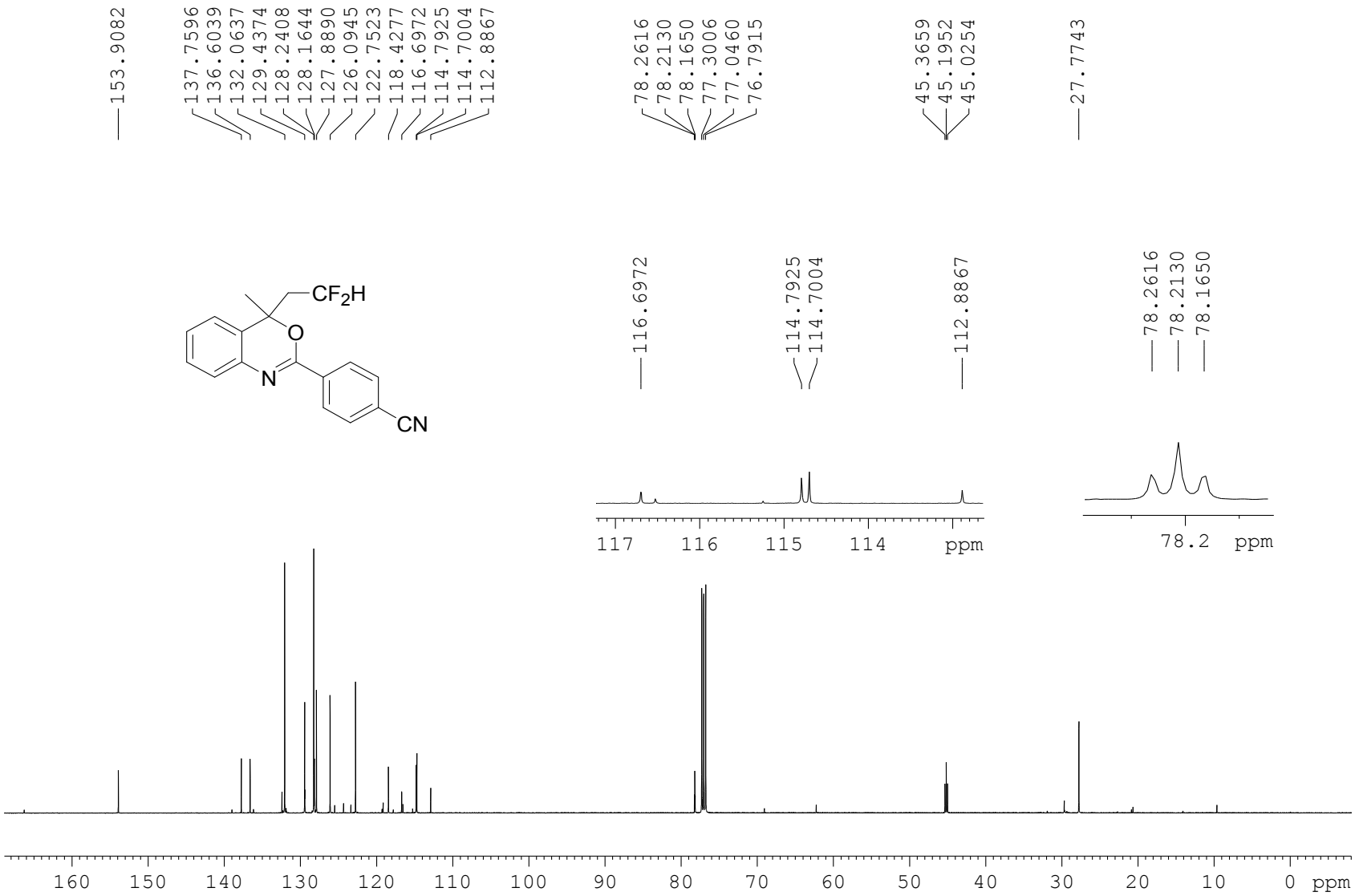
1.00
2.04
3.00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128.1644
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126.0945
122.7523
118.4277
116.6972
114.7925
114.7004
112.8867
78.2616
78.2130
78.1650
77.3006
77.0460
76.7915
45.3659
45.1952
45.0254
27.7743
CF2H
O
N
CN
117
116
115
114
ppm
78.2
ppm
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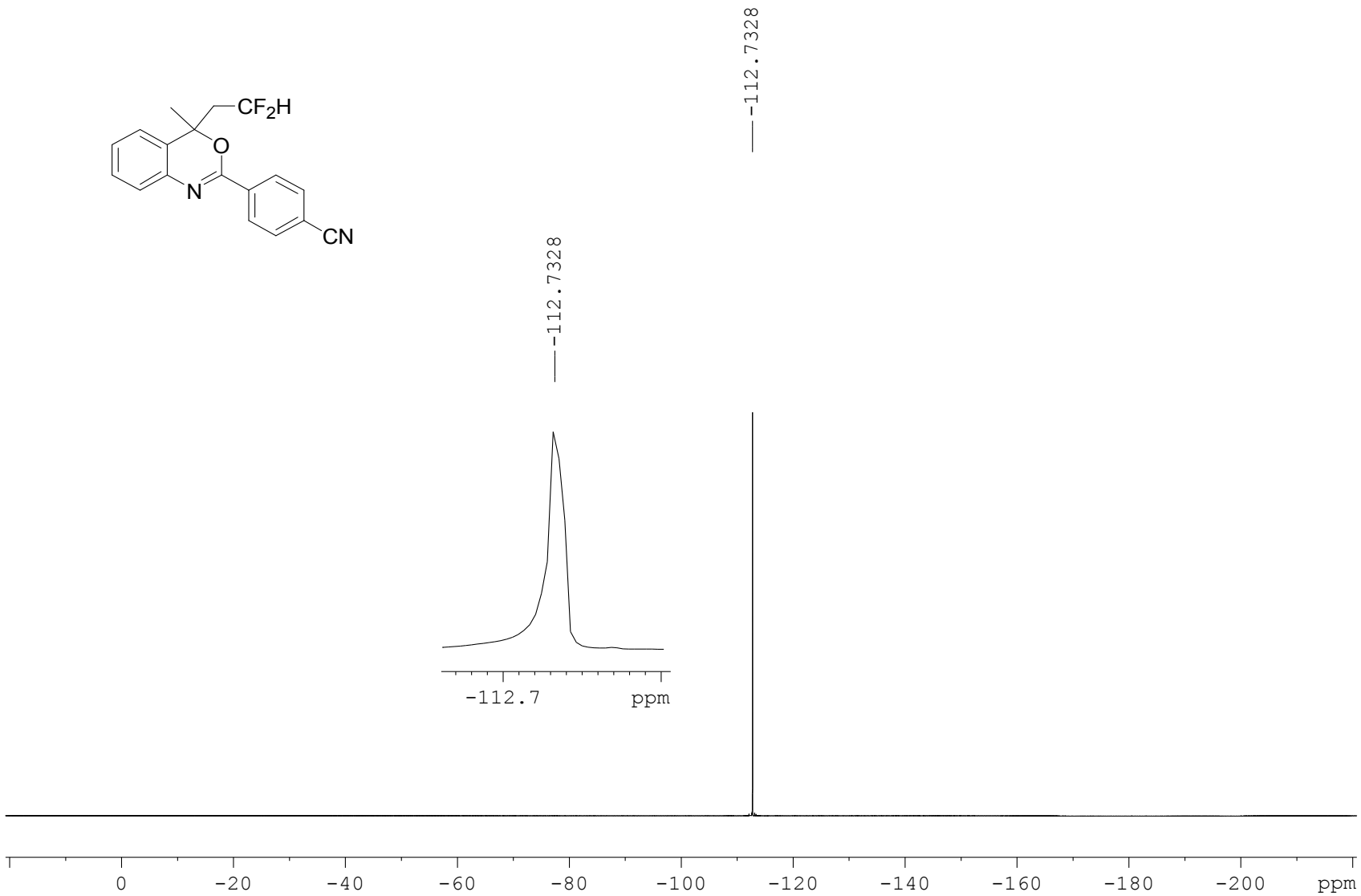
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm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O
N
CN
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ppm
0
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-60
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-100
-120
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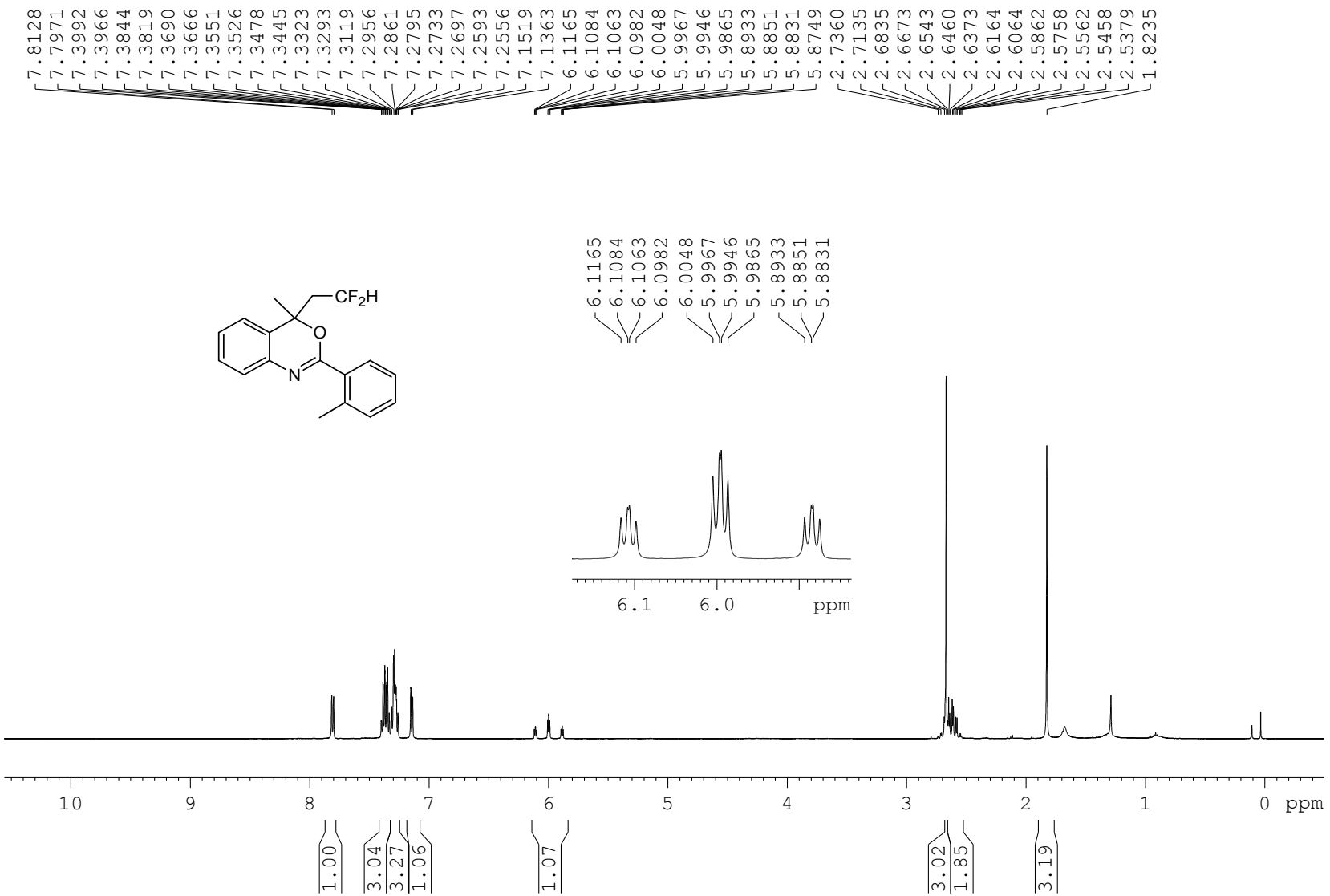
-160
-180
-200
ppm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7.3551
7.3526
7.3478
7.3445
7.3323
7.3293
7.3119
7.2956
7.2861
7.2795
7.2733
7.2697
7.2593
7.2556
7.1519
7.1363
6.1165
6.1084
6.1063
6.0982
6.0048
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5.9946
5.9865
5.8933
5.8851
5.8831
5.8749
2.7360
2.7135
2.6835
2.6673
2.6543
2.6460
2.6373
2.6164
2.6064
2.5862
2.5758
2.5562
2.5458
2.5379
1.8235
CF2H
O
N
6.1
6.0
ppm
10
9
8
7
6
5
4
3
2
1
0 ppm
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3.27
1.06
1.07
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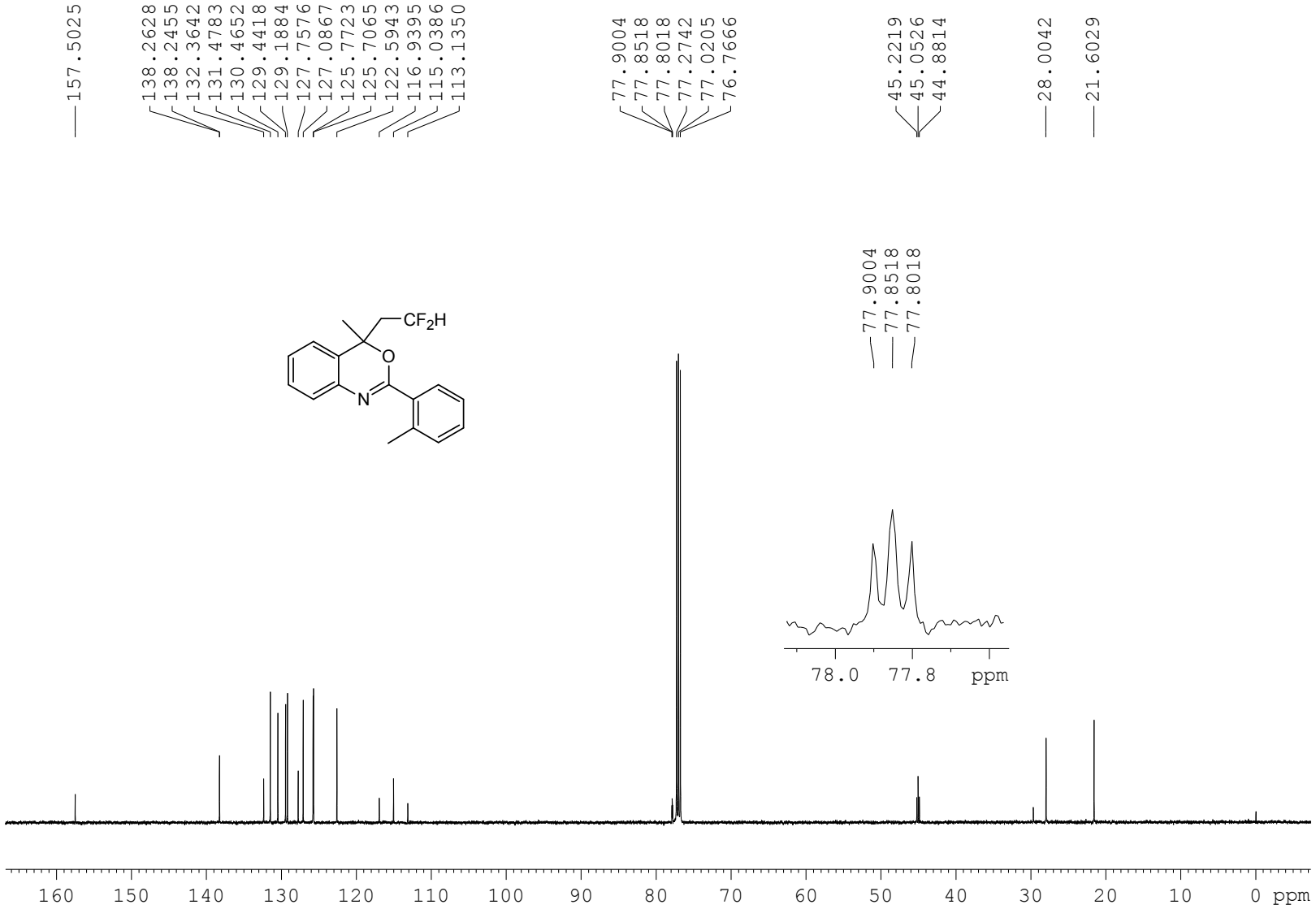
3.19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125.7723
125.7065
122.5943
116.9395
115.0386
113.1350
77.9004
77.8518
77.8018
77.2742
77.0205
76.7666
45.2219
45.0526
44.8814
28.0042
21.6029
CF2H
O
N
78.0
77.8
ppm
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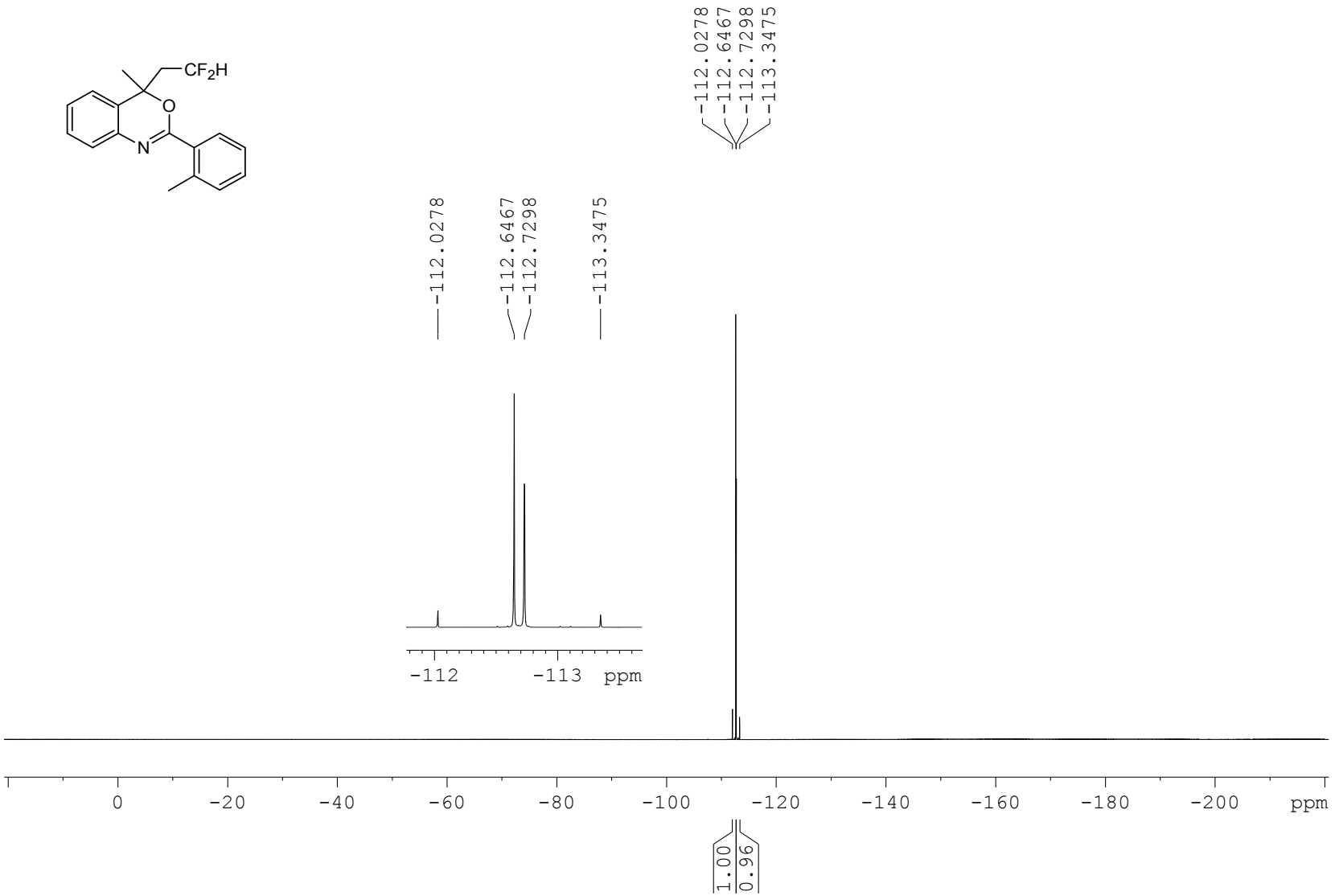
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0 ppm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O
N
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-112
-113
ppm
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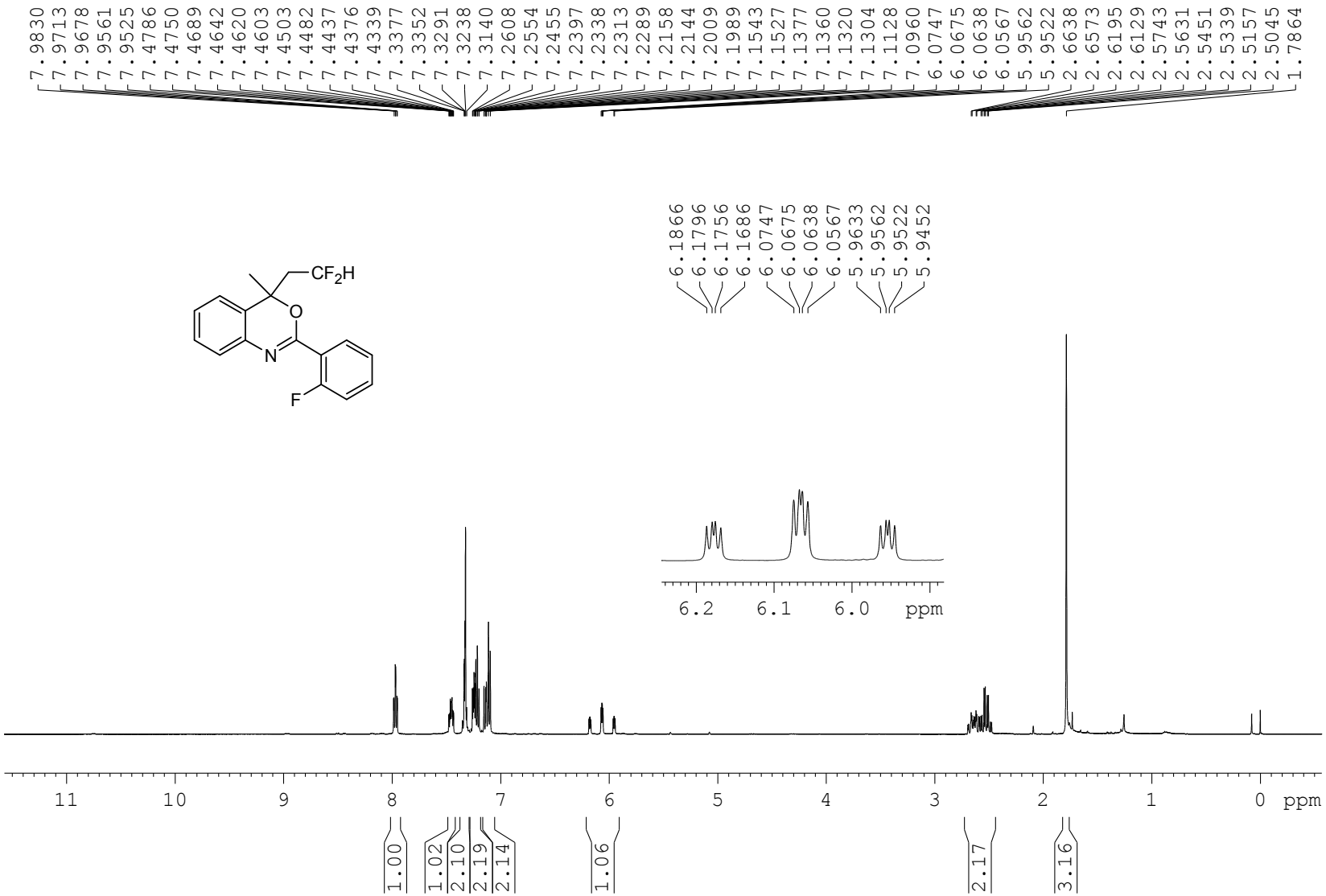
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7.3377
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7.3238
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7.2397
7.2338
7.2313
7.2289
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7.2144
7.2009
7.1989
7.1543
7.1527
7.1377
7.1360
7.1320
7.1304
7.1128
7.0960
6.0747
6.0675
6.0638
6.0567
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5.9522
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2.5631
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2.5339
2.5157
2.5045
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6.0675
6.0638
6.0567
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5.9562
5.9522
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CF2H
O
N
F
6.2
6.1
6.0
ppm
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10
9
8
7
6
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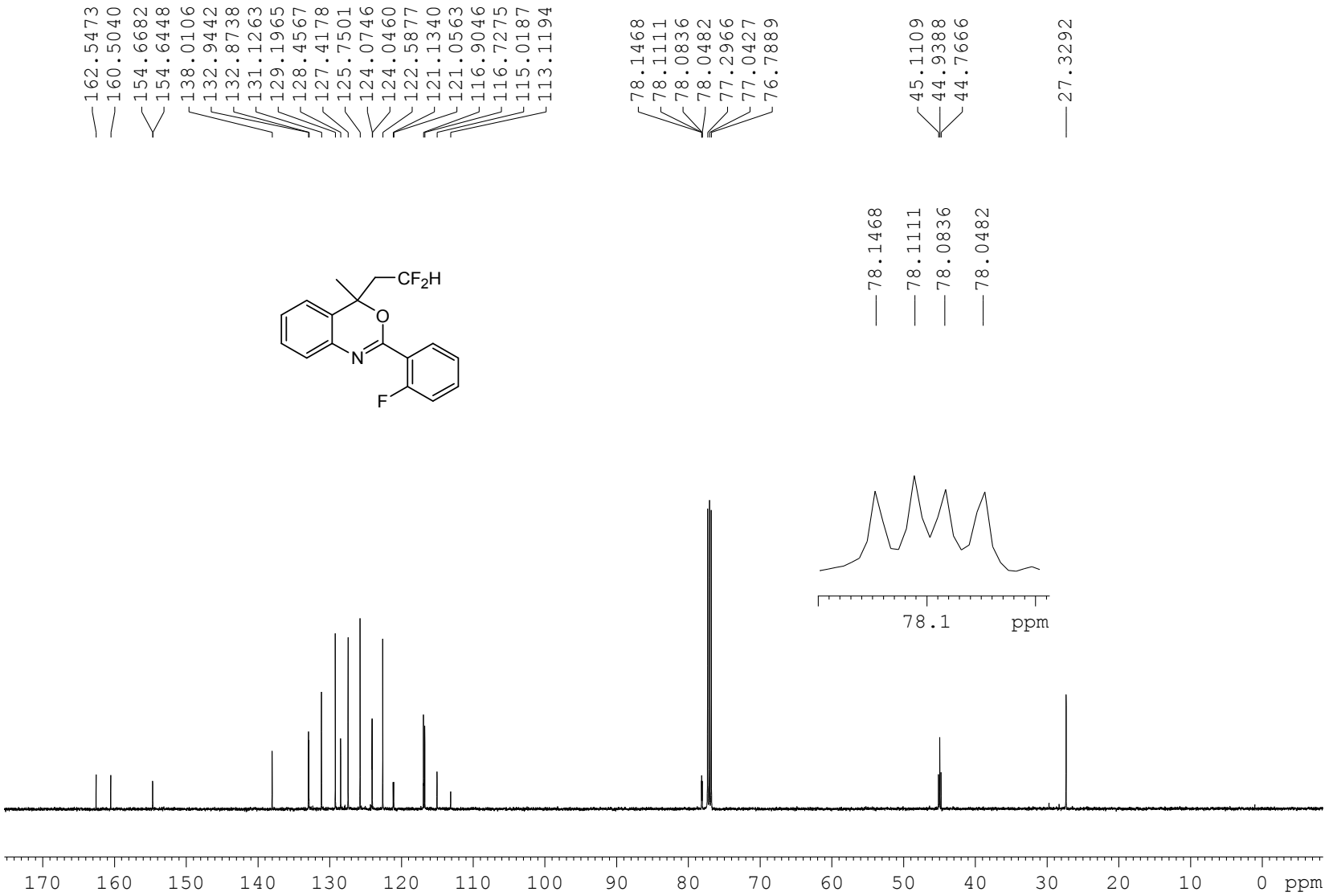
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O
N
F
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78.1111
78.0836
78.0482
78.1
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140
130
120
110
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60
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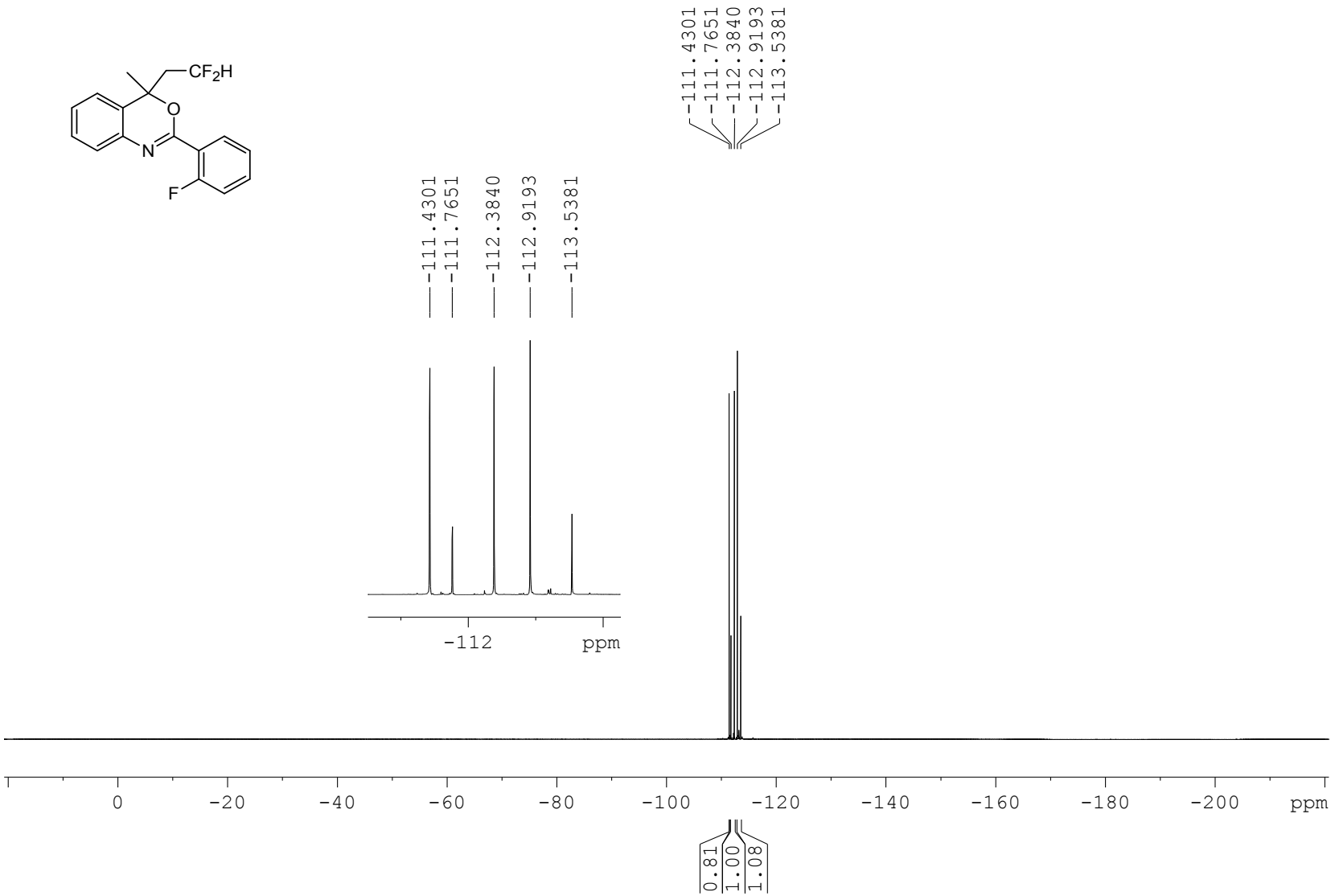
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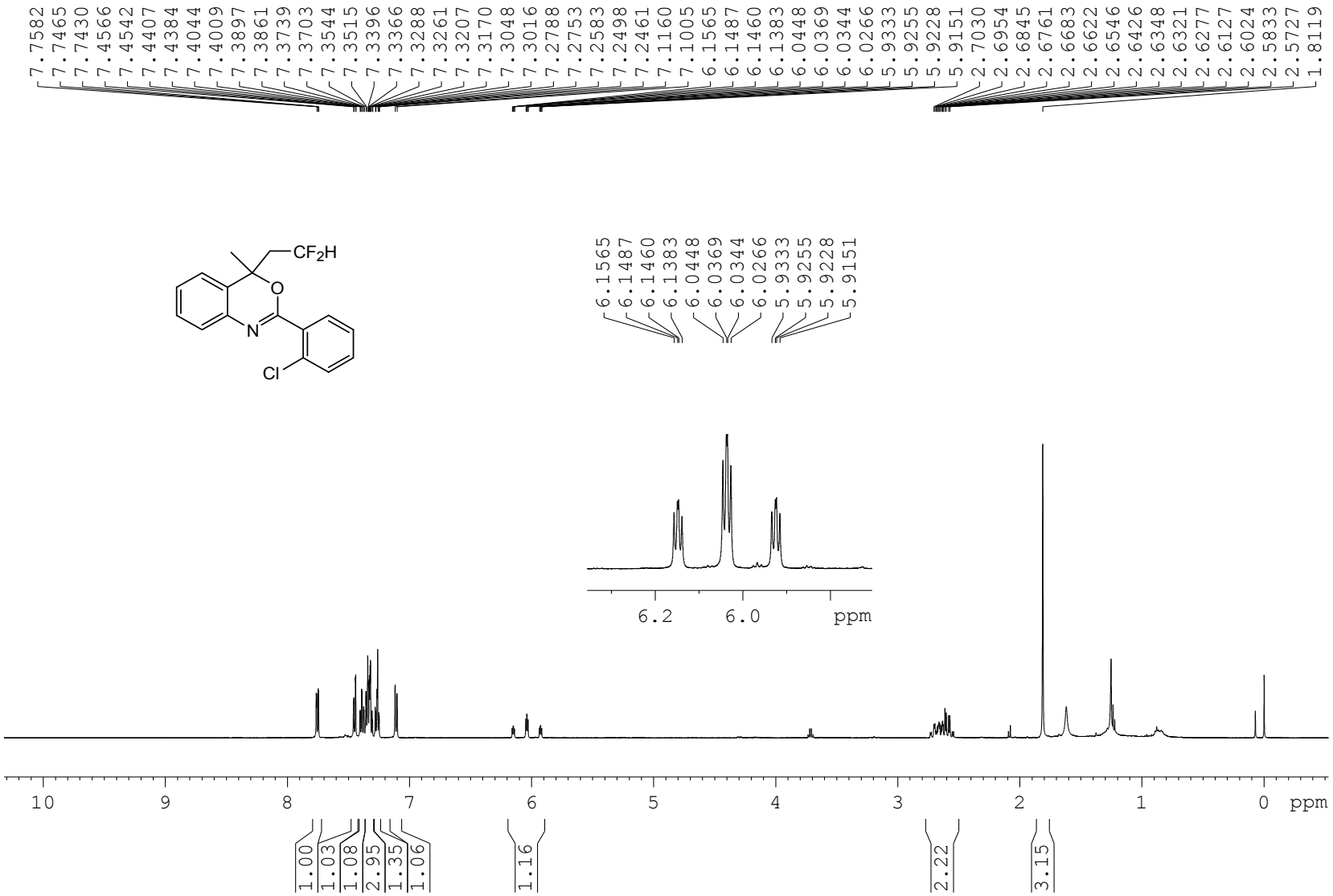
1.08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7.3861
7.3739
7.3703
7.3544
7.3515
7.3396
7.3366
7.3288
7.3261
7.3207
7.3170
7.3048
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7.2788
7.2753
7.2583
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7.2461
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6.1565
6.1487
6.1460
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6.0448
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6.0344
6.0266
5.9333
5.9255
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2.6845
2.6761
2.6683
2.6622
2.6546
2.6426
2.6348
2.6321
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CF2H
O
N
Cl
6.2
6.0
ppm
10
9
8
7
6
5
4
3
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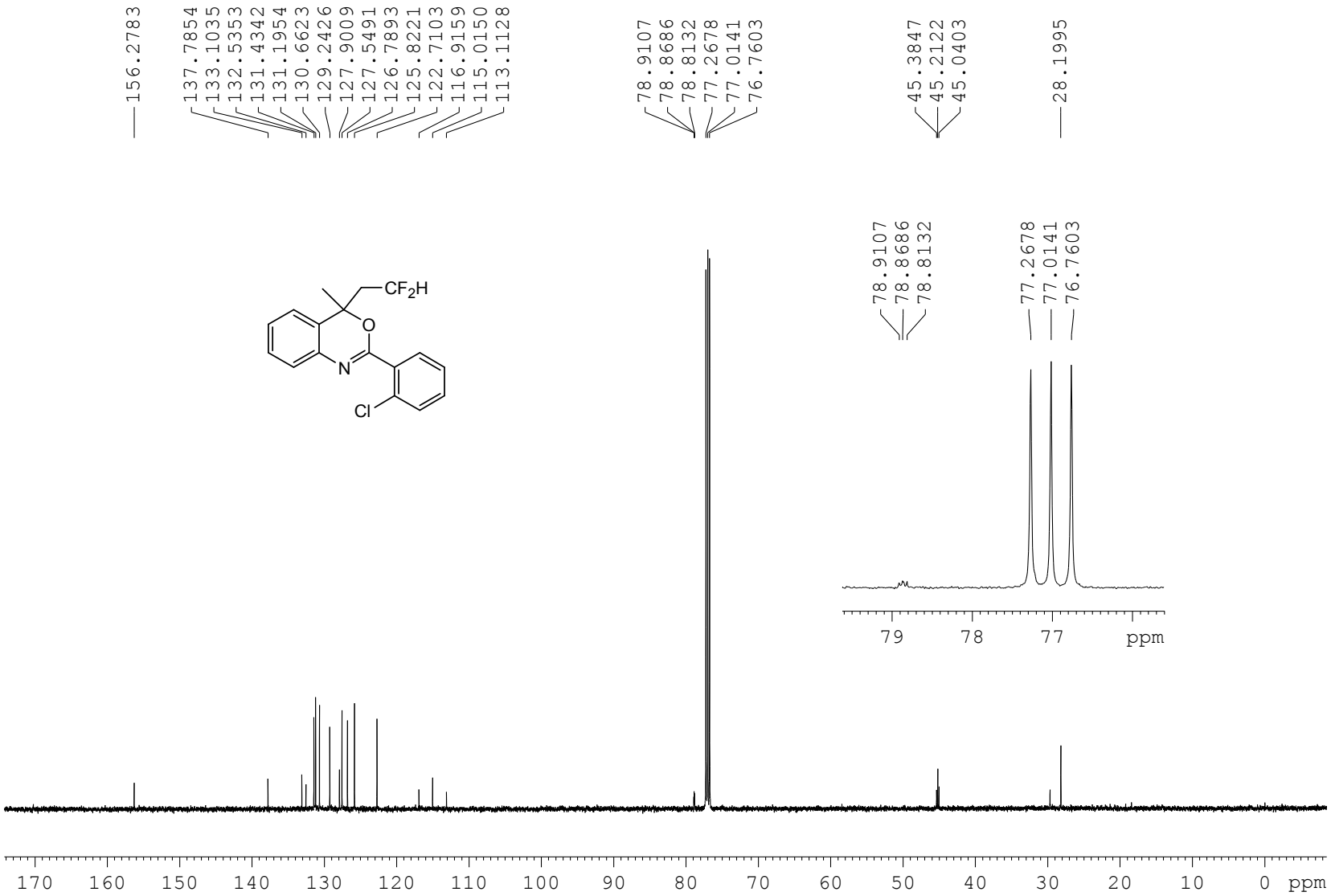
ppm
1.00
1.03
1.08
2.95
1.35
1.06
1.16
2.22
3.15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126.7893
125.8221
122.7103
116.9159
115.0150
113.1128
78.9107
78.8686
78.8132
77.2678
77.0141
76.7603
45.3847
45.2122
45.0403
28.1995
CF2H
O
N
Cl
78.9107
78.8686
78.8132
77.2678
77.0141
76.7603
79
78
77
ppm
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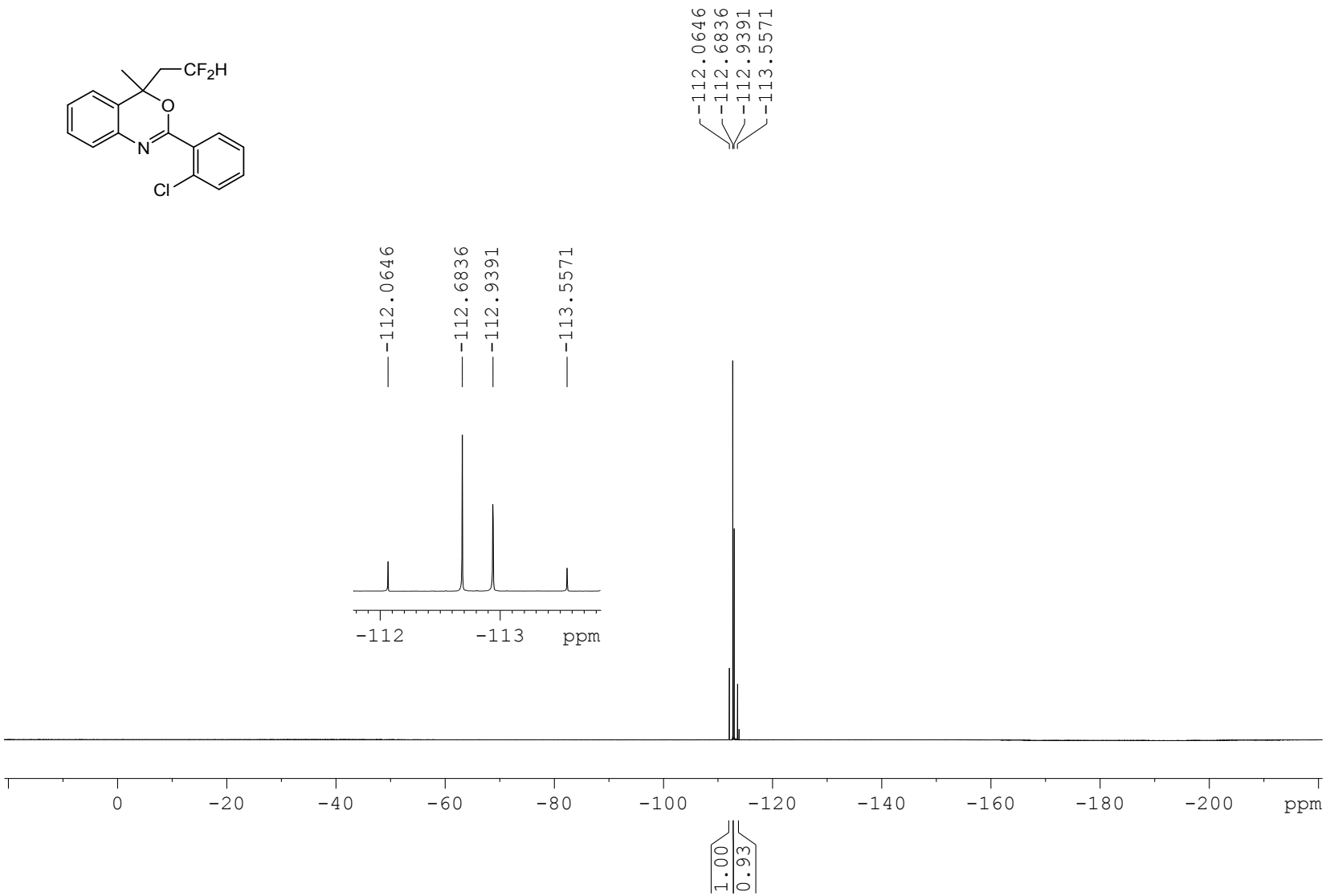
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm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-112
-113
ppm
0
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-40
-60
-80
-100
-120
-140
-160
-180
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ppm
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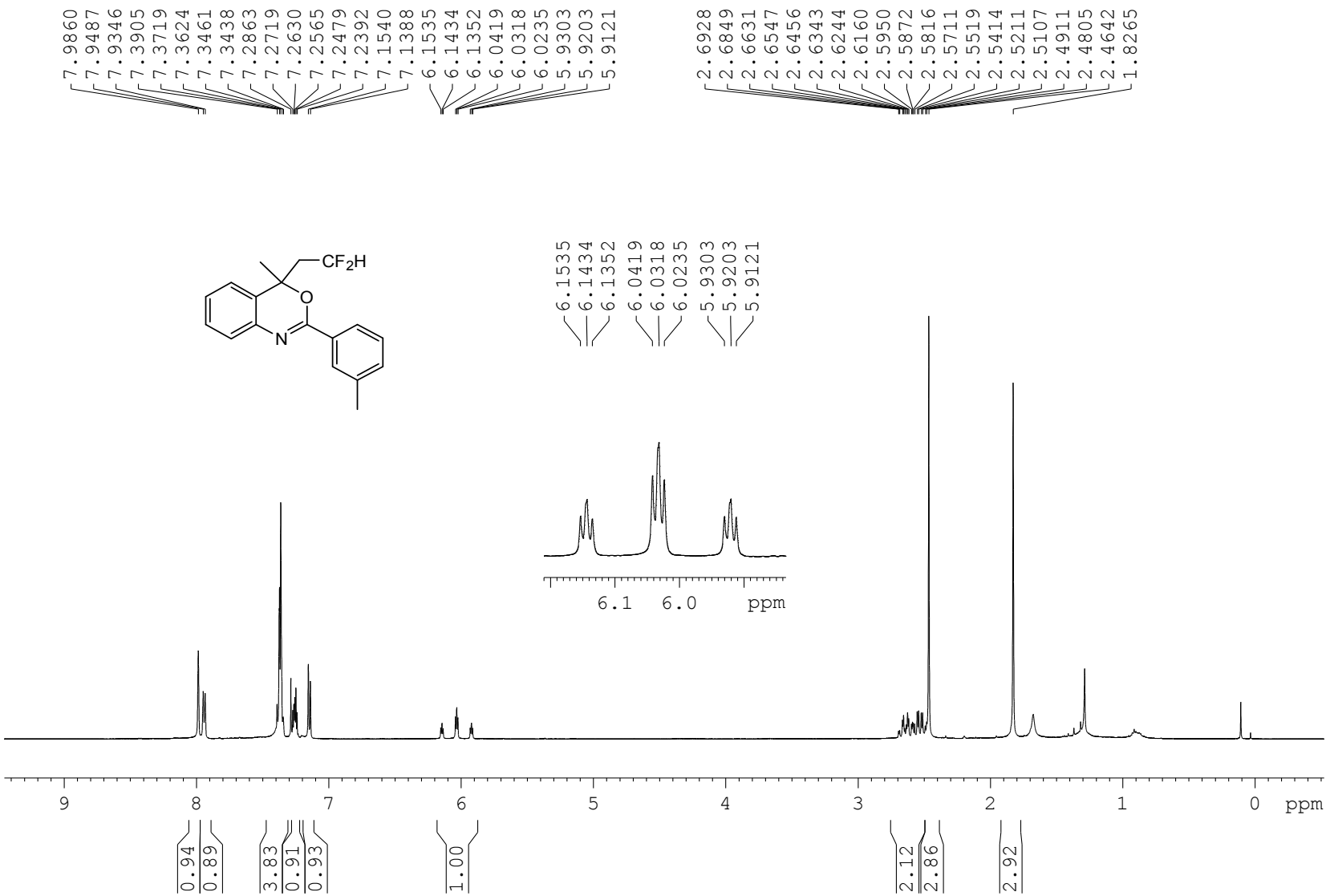
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7.2565
7.2479
7.2392
7.1540
7.1388
6.1535
6.1434
6.1352
6.0419
6.0318
6.0235
5.9303
5.9203
5.9121
2.6928
2.6849
2.6631
2.6547
2.6456
2.6343
2.6244
2.6160
2.5950
2.5872
2.5816
2.5711
2.5519
2.5414
2.5211
2.5107
2.4911
2.4805
2.4642
1.8265
CF2H
O
N
6.1 6.0 ppm
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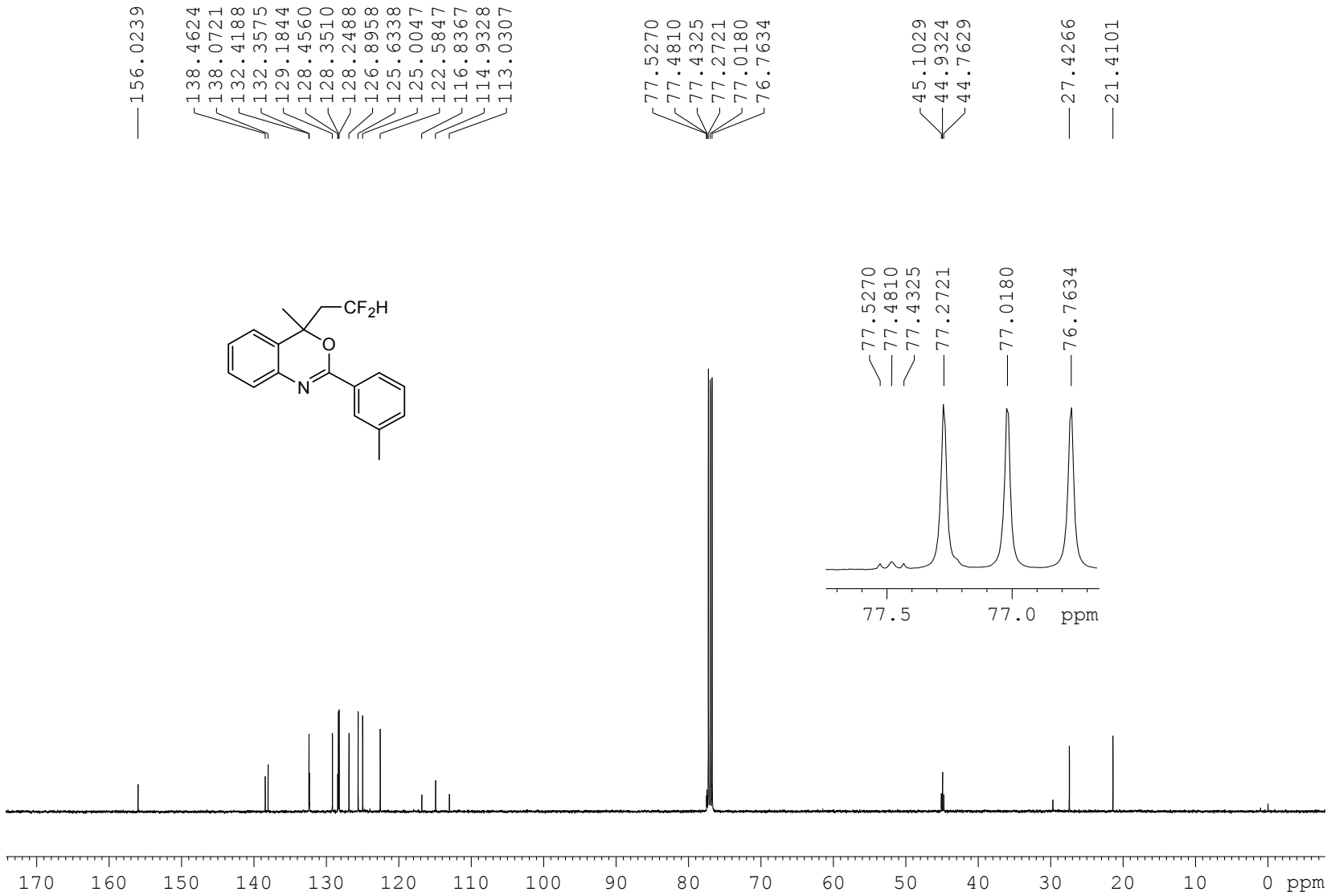
0.91
0.93
1.00
2.12
2.86
2.92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125.0047
122.5847
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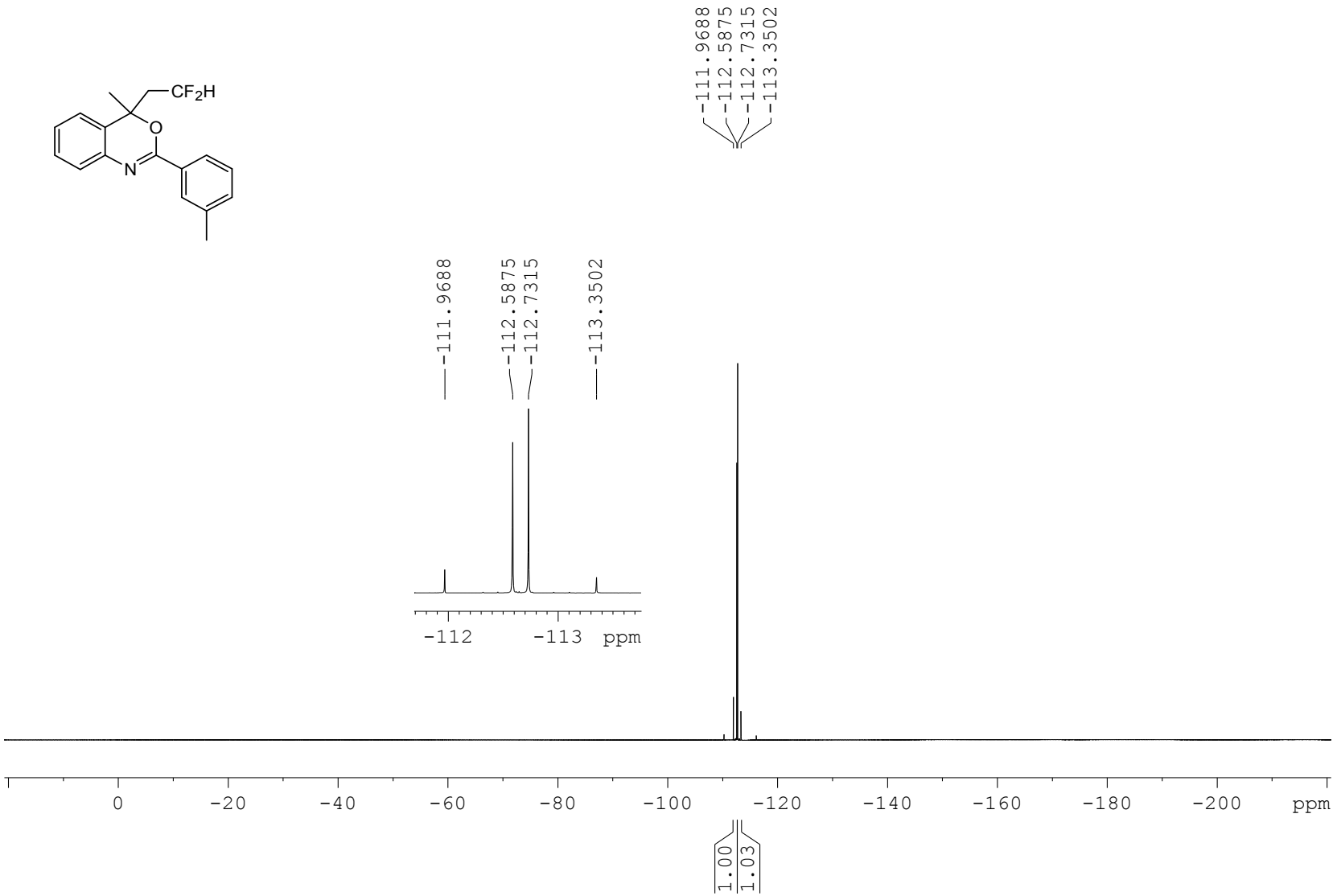
114.9328
113.0307
77.5270
77.4810
77.4325
77.2721
77.0180
76.7634
45.1029
44.9324
44.7629
27.4266
21.4101
CF2H
O
N
77.5
77.0
ppm
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0 ppm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O
N
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-111.9688
-112.5875
-112.7315
-113.3502
-112
-113
ppm
0
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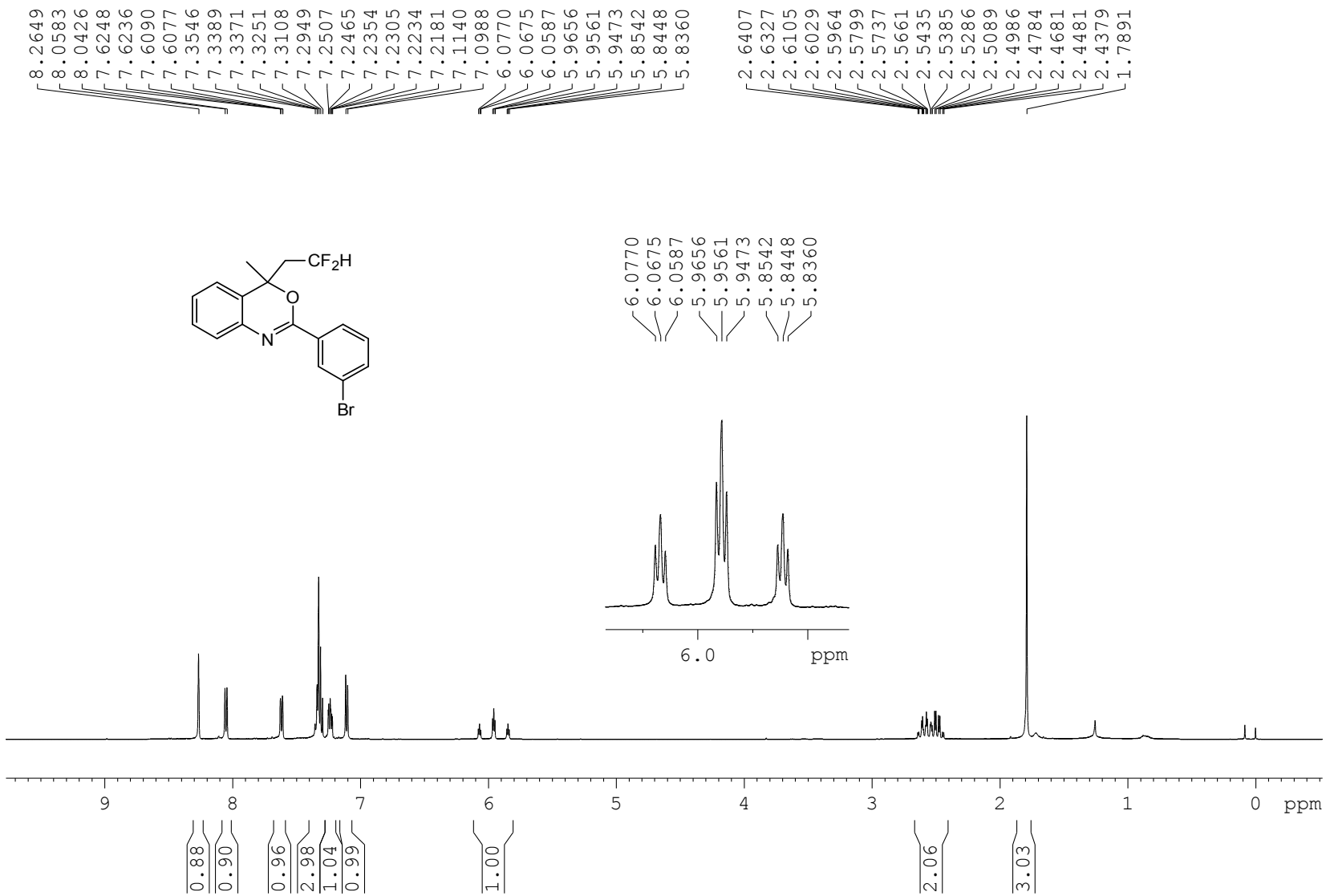
-40
-60
-80
-100
-120
-140
-160
-180
-200
ppm
1.00
1.03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7.3371
7.3251
7.3108
7.2949
7.2507
7.2465
7.2354
7.2305
7.2234
7.2181
7.1140
7.0988
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5.8448
5.8360
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2.6327
2.6105
2.6029
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2.5737
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2.4986
2.4784
2.4681
2.4481
2.4379
1.7891
CF2H
O
N
Br
6.0
ppm
9
8
7
6
5
4
3
2
1
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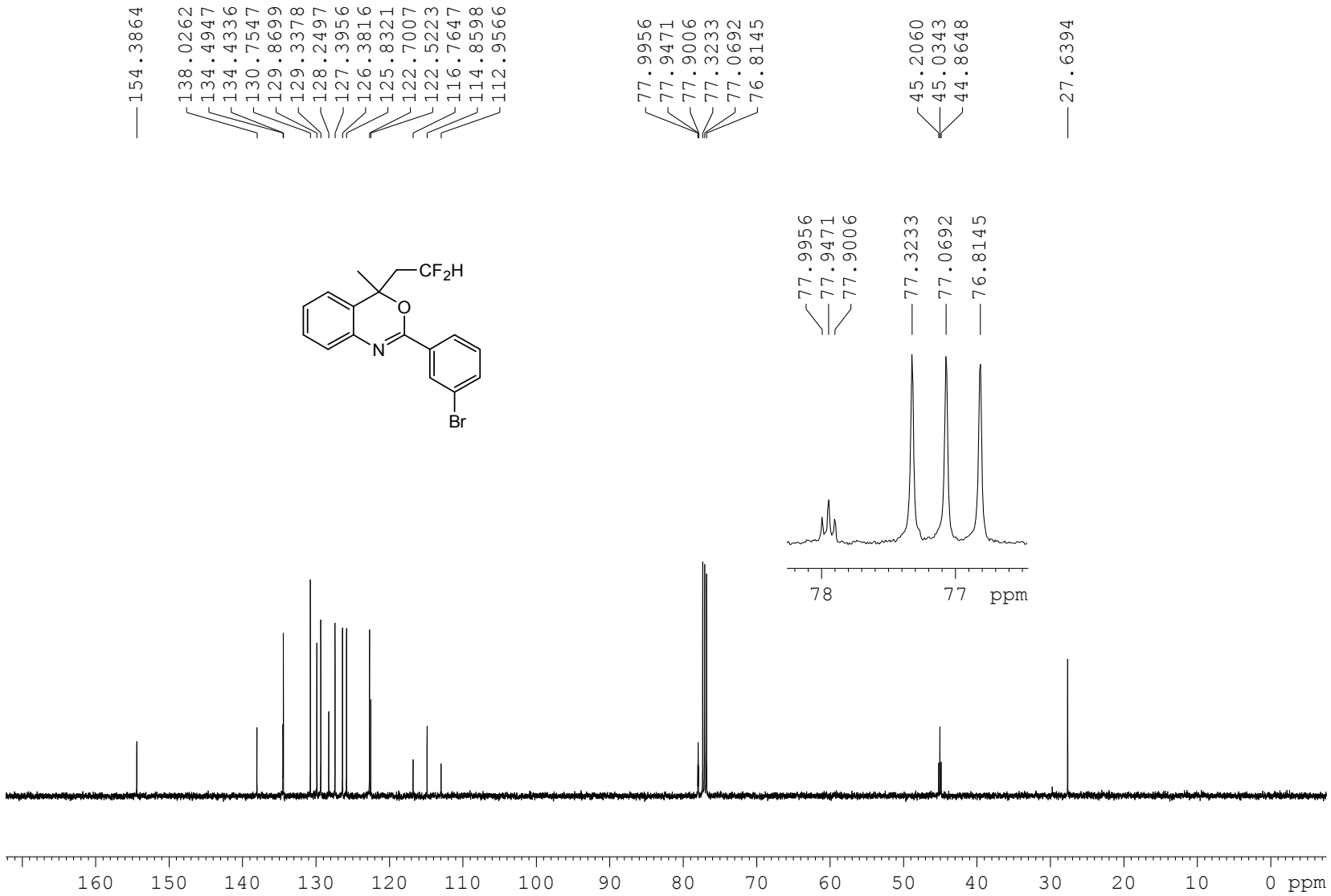
ppm
0.88
0.90
0.96
2.98
1.04
0.99
1.00
2.06
3.03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125.8321
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122.5223
116.7647
114.8598
112.9566
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77.9471
77.9006
77.3233
77.0692
76.8145
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45.0343
44.8648
27.6394
CF2H
O
N
Br
78
77
ppm
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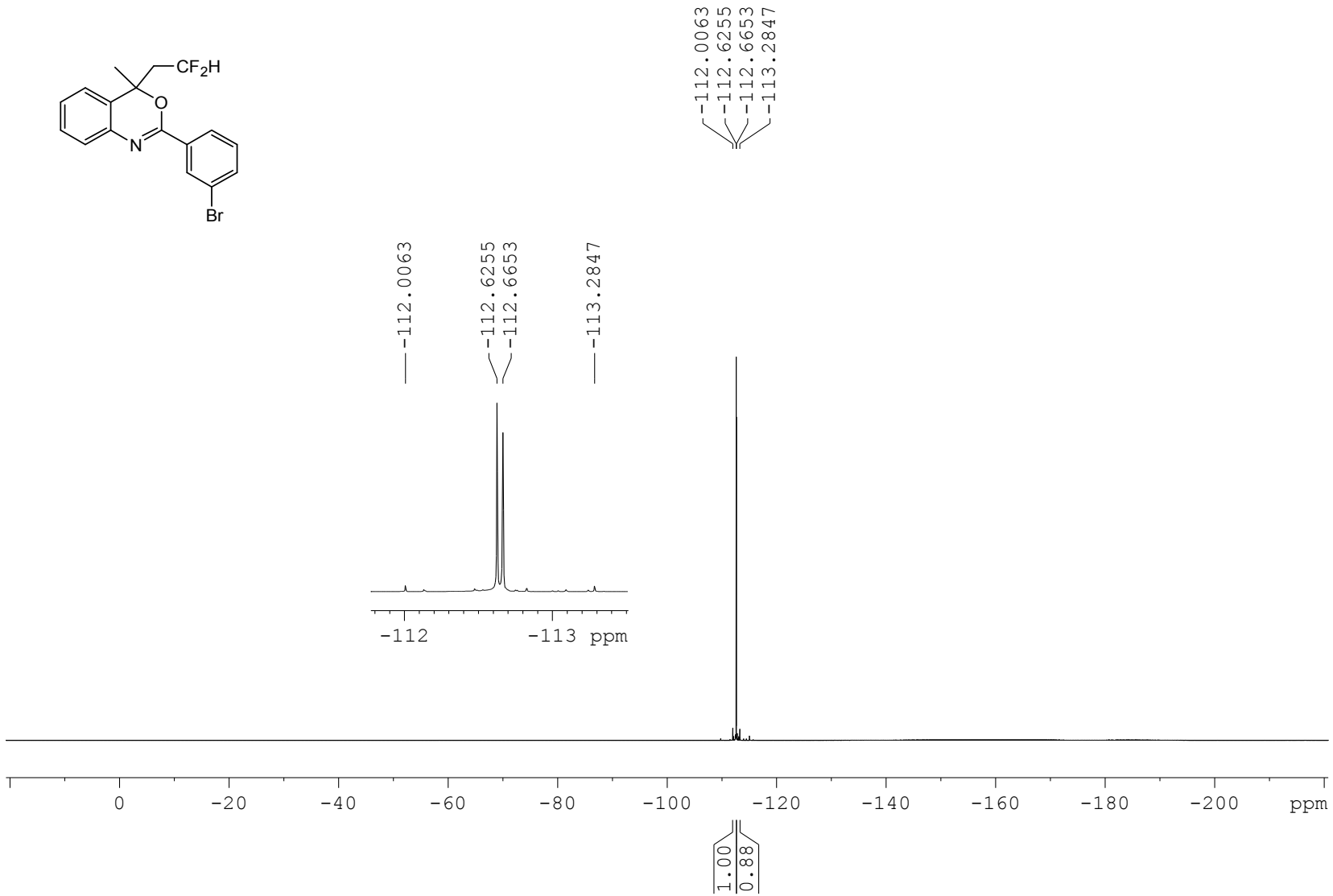
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0 ppm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N
Br
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-113.2847
-112.0063
-112.6255
-112.6653
-113.2847
-112
-113 ppm
0
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-40
-60
-80
-100
-120
-140
-160
-180
-200
ppm
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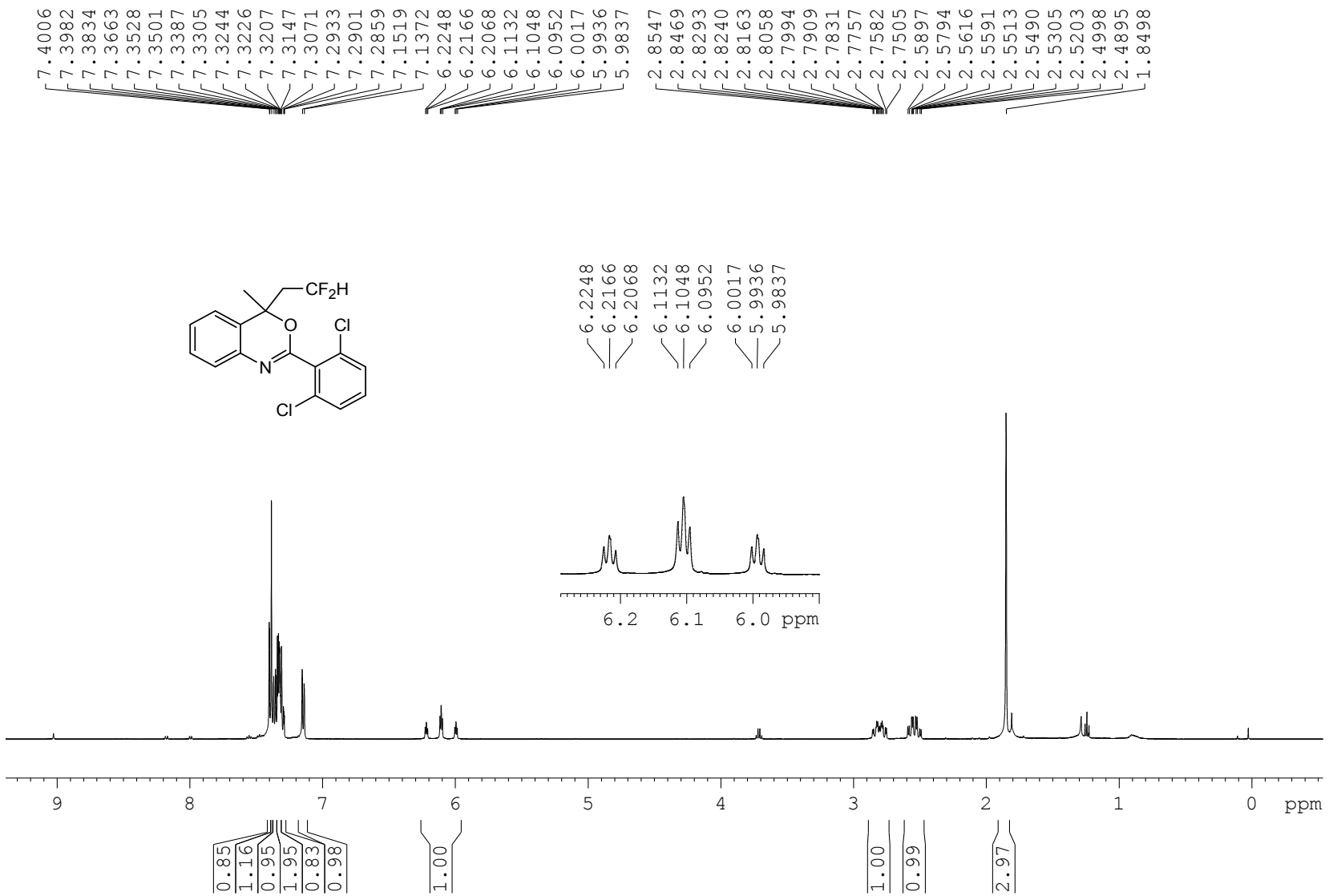
0.88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7.3244
7.3226
7.3207
7.3147
7.3071
7.2933
7.2901
7.2859
7.1519
7.1372
6.2248
6.2166
6.2068
6.1132
6.1048
6.0952
6.0017
5.9936
5.9837
2.8547
2.8469
2.8293
2.8240
2.8163
2.8058
2.7994
2.7909
2.7831
2.7757
2.7582
2.7505
2.5897
2.5794
2.5616
2.5591
2.5513
2.5490
2.5305
2.5203
2.4998
2.4895
1.8498
CF2H
O
Cl
N
Cl
6.2 6.1 6.0 ppm
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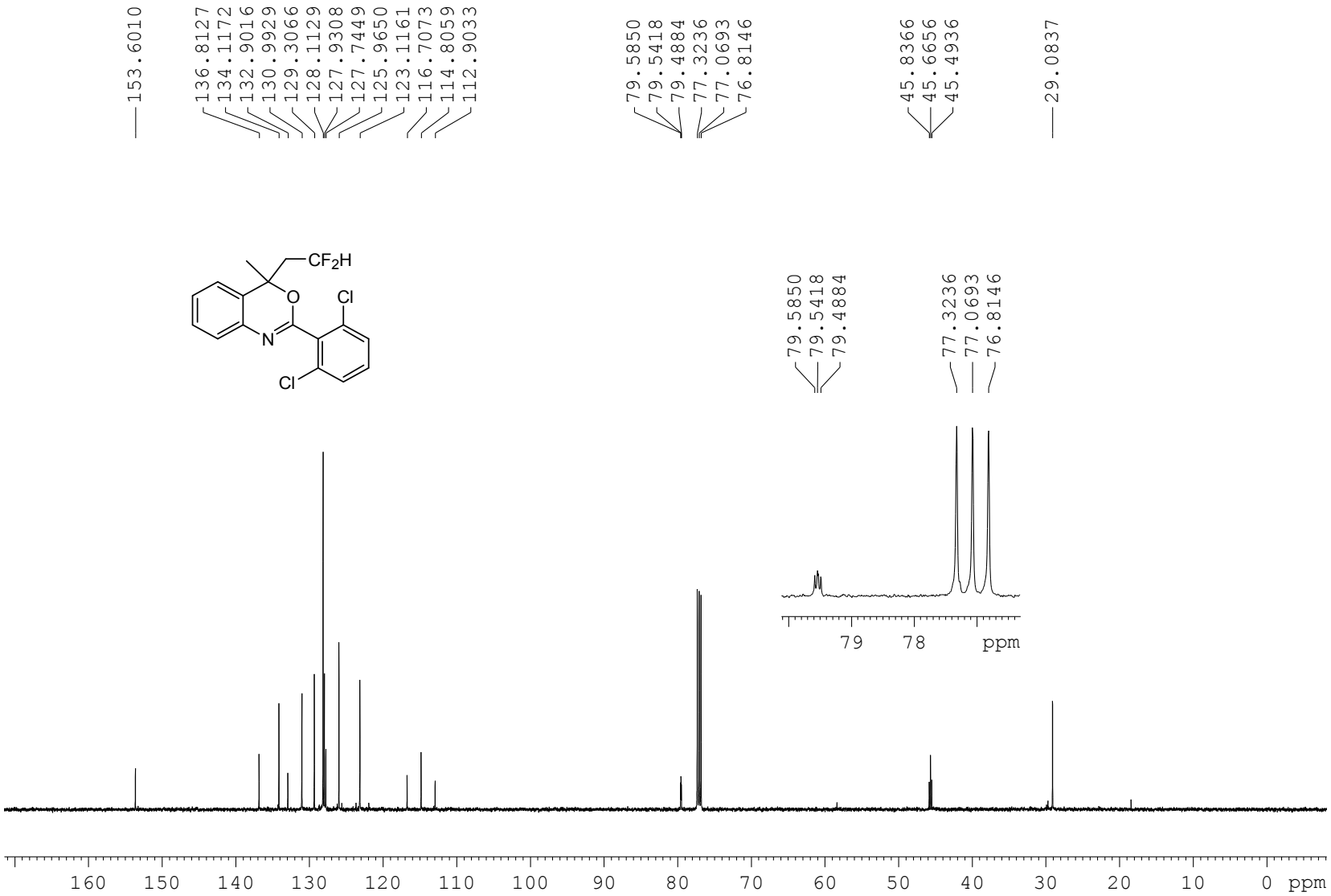
0.95
1.95
0.83
0.98
1.00
1.00
0.99
2.97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123.1161
116.7073
114.8059
112.9033
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79.5418
79.4884
77.3236
77.0693
76.8146
45.8366
45.6656
45.4936
29.0837
CF2H
O
N
Cl
Cl
79.5850
79.5418
79.4884
77.3236
77.0693
76.8146
79
78
ppm
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150
140
130
120
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80
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60
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20
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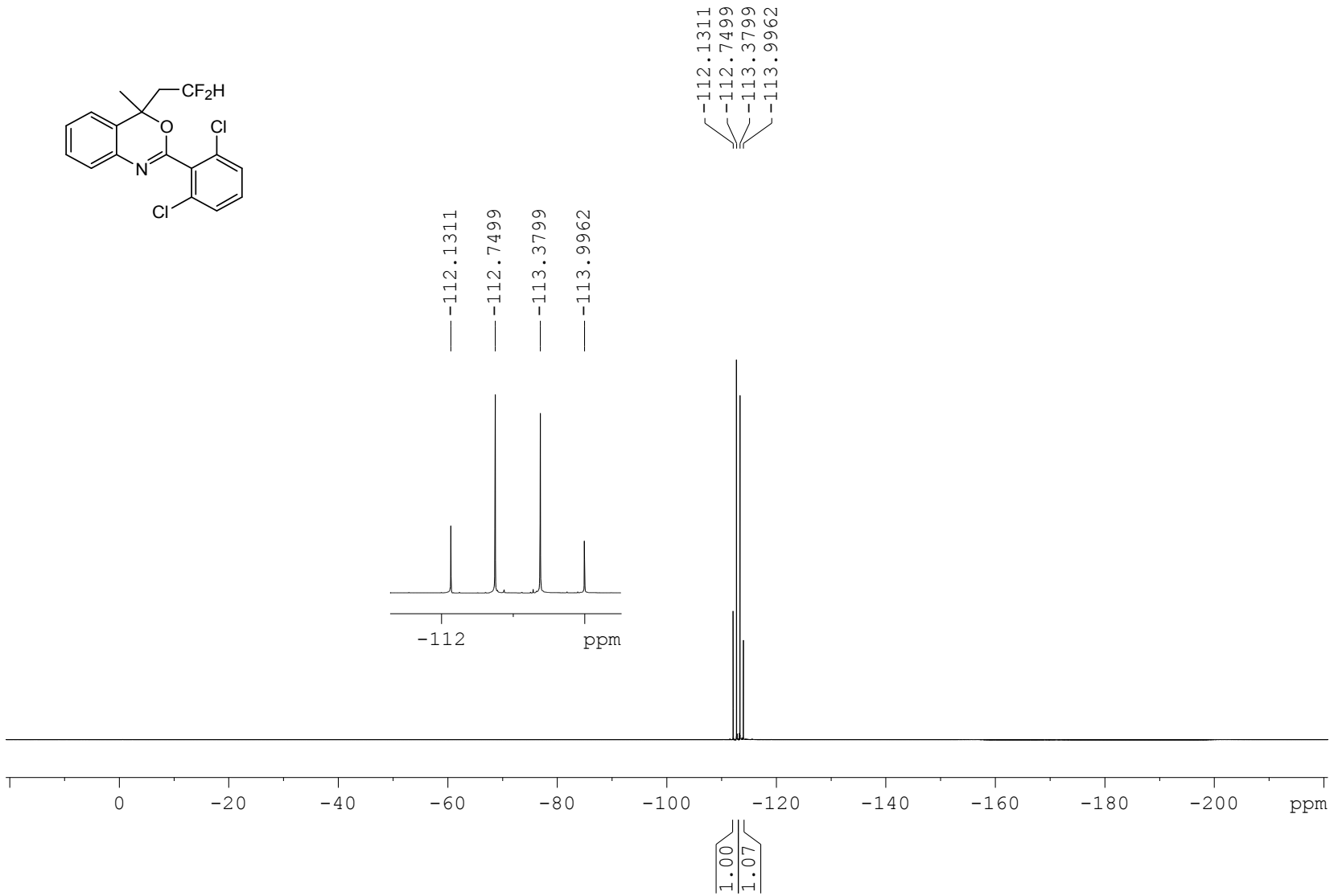
0
ppm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O
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N
Cl
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ppm
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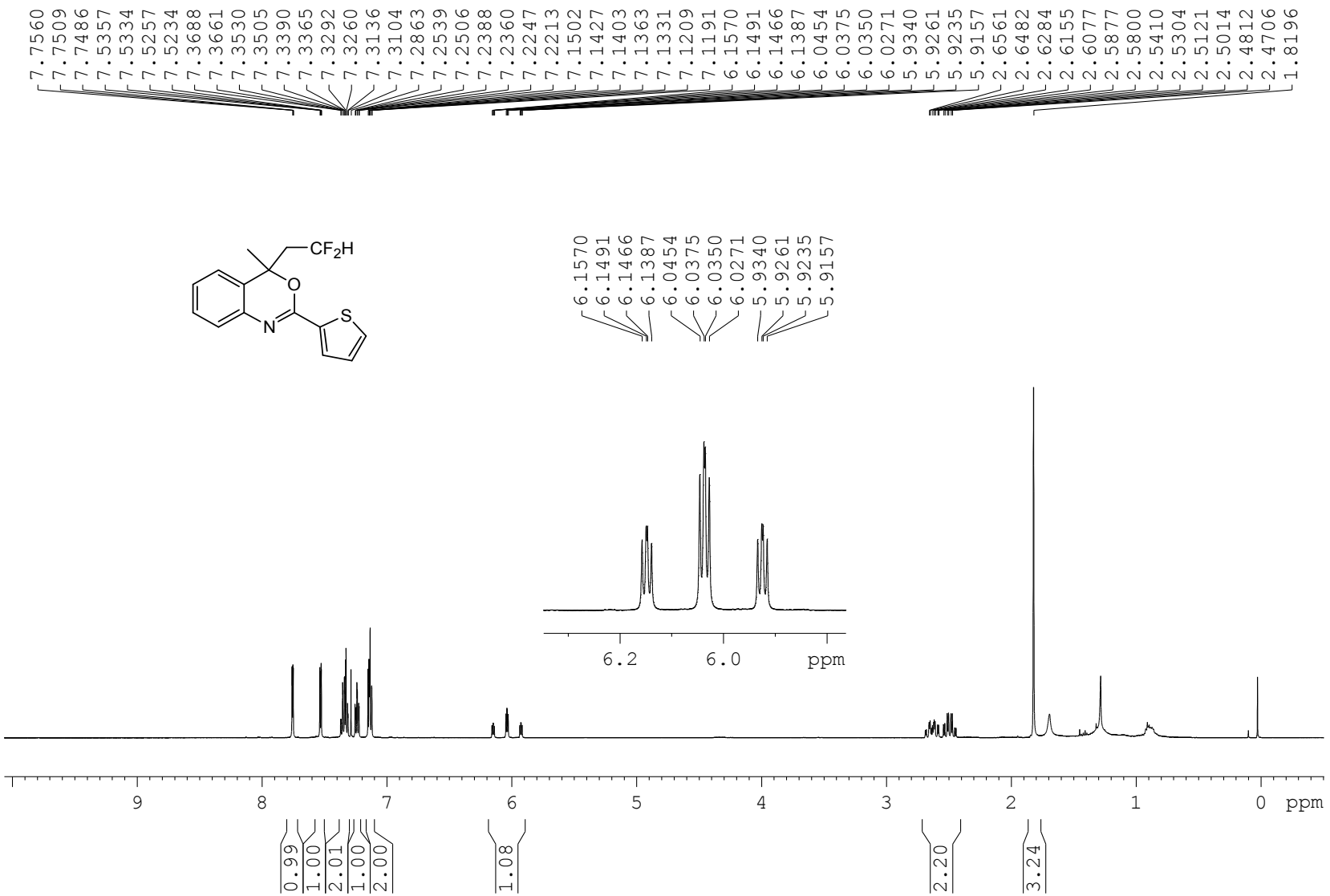
1.07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7.3365
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7.2539
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7.2388
7.2360
7.2247
7.2213
7.1502
7.1427
7.1403
7.1363
7.1331
7.1209
7.1191
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6.1491
6.1466
6.1387
6.0454
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2.5800
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2.5121
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CF2H
O
N
S
6.2
6.0
ppm
9
8
7
6
5
4
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1
0
ppm
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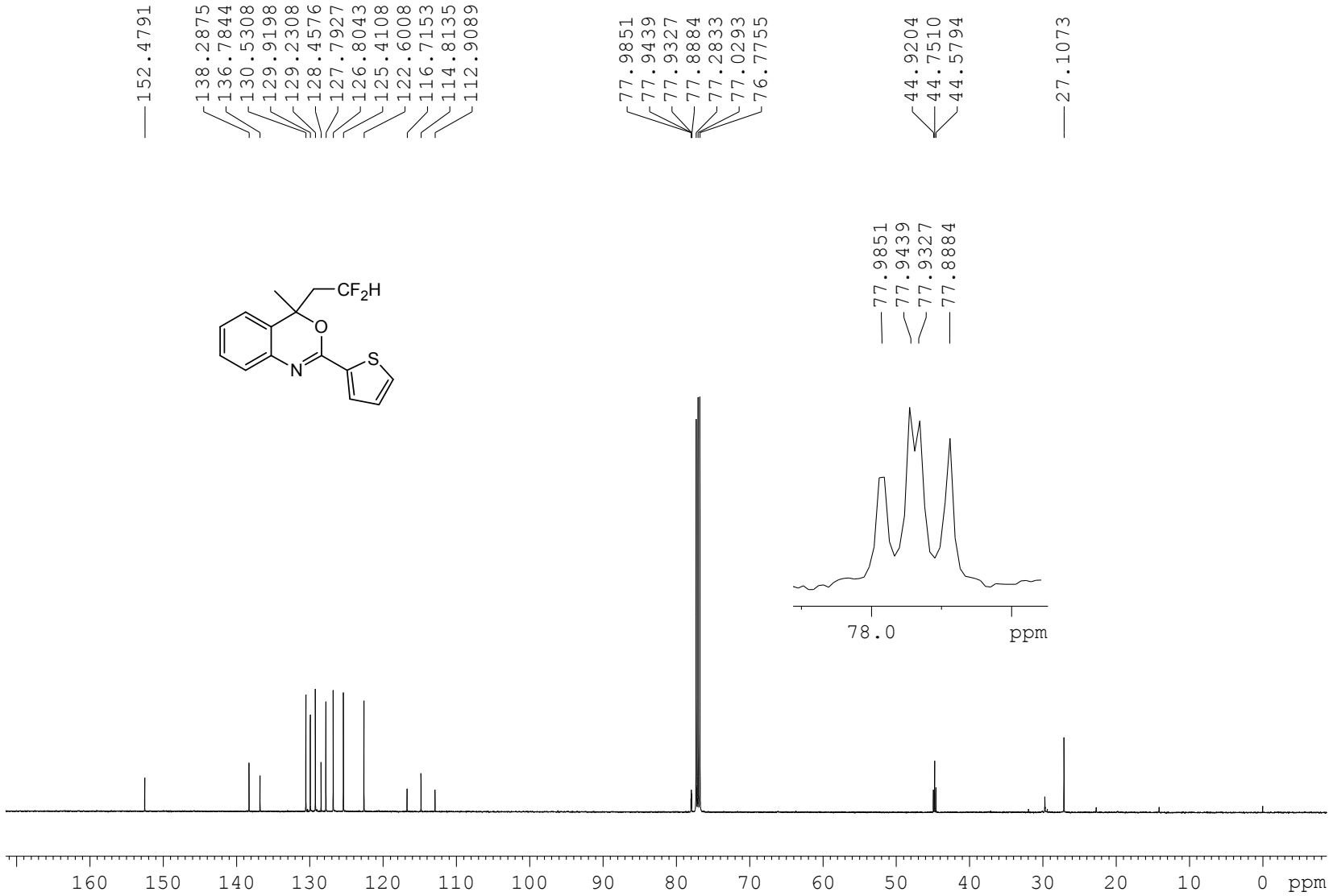
1.00
2.00
1.08
2.20
3.24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116.7153
114.8135
112.9089
77.9851
77.9439
77.9327
77.8884
77.2833
77.0293
76.7755
44.9204
44.7510
44.5794
27.1073
CF2H
O
N
S
77.9851
77.9439
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77.8884
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140
130
120
110
100
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80
70
60
50
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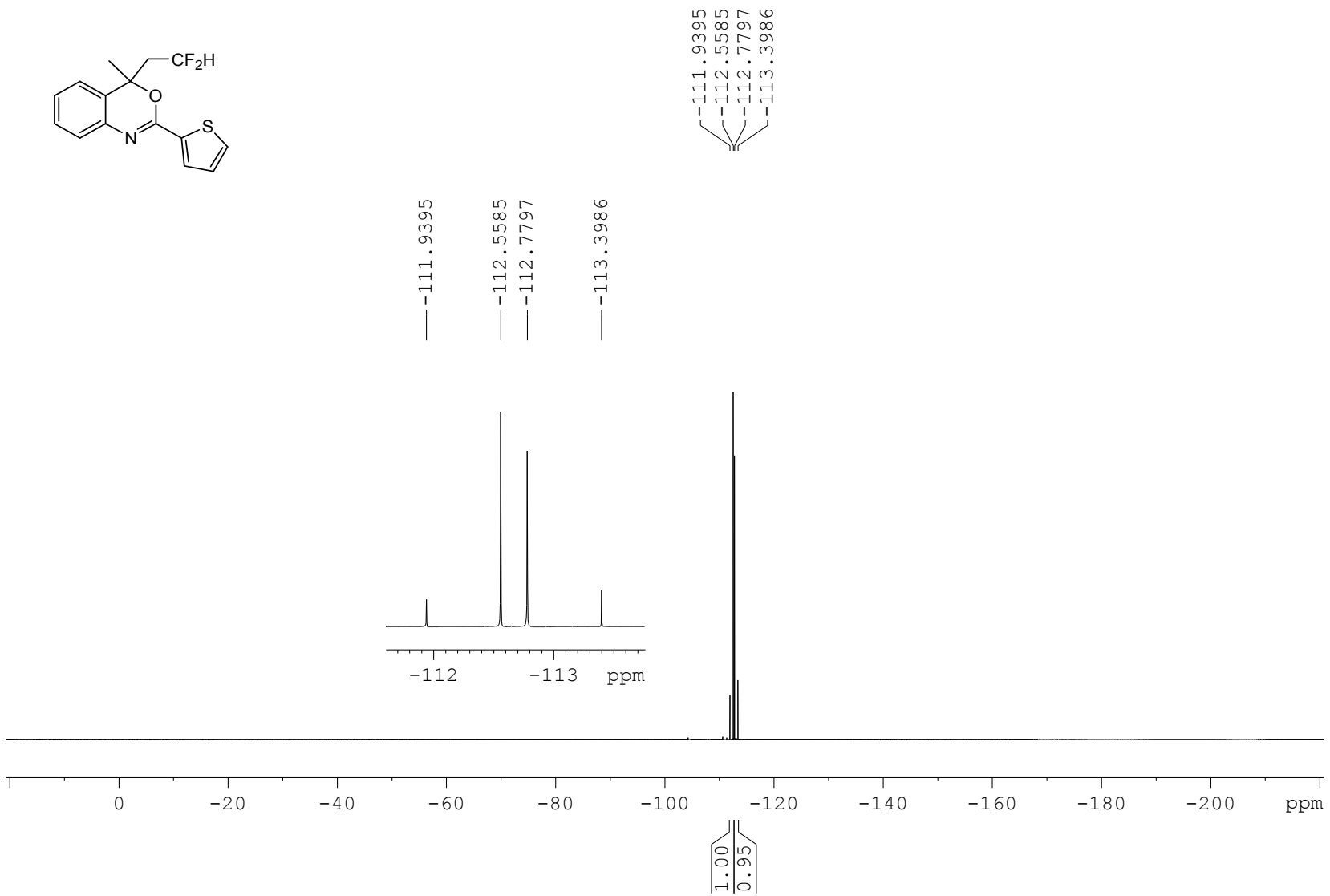
30
20
10
0
ppm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S
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-113.3986
-112
-113
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-60
-80
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-160
-180
-200
ppm
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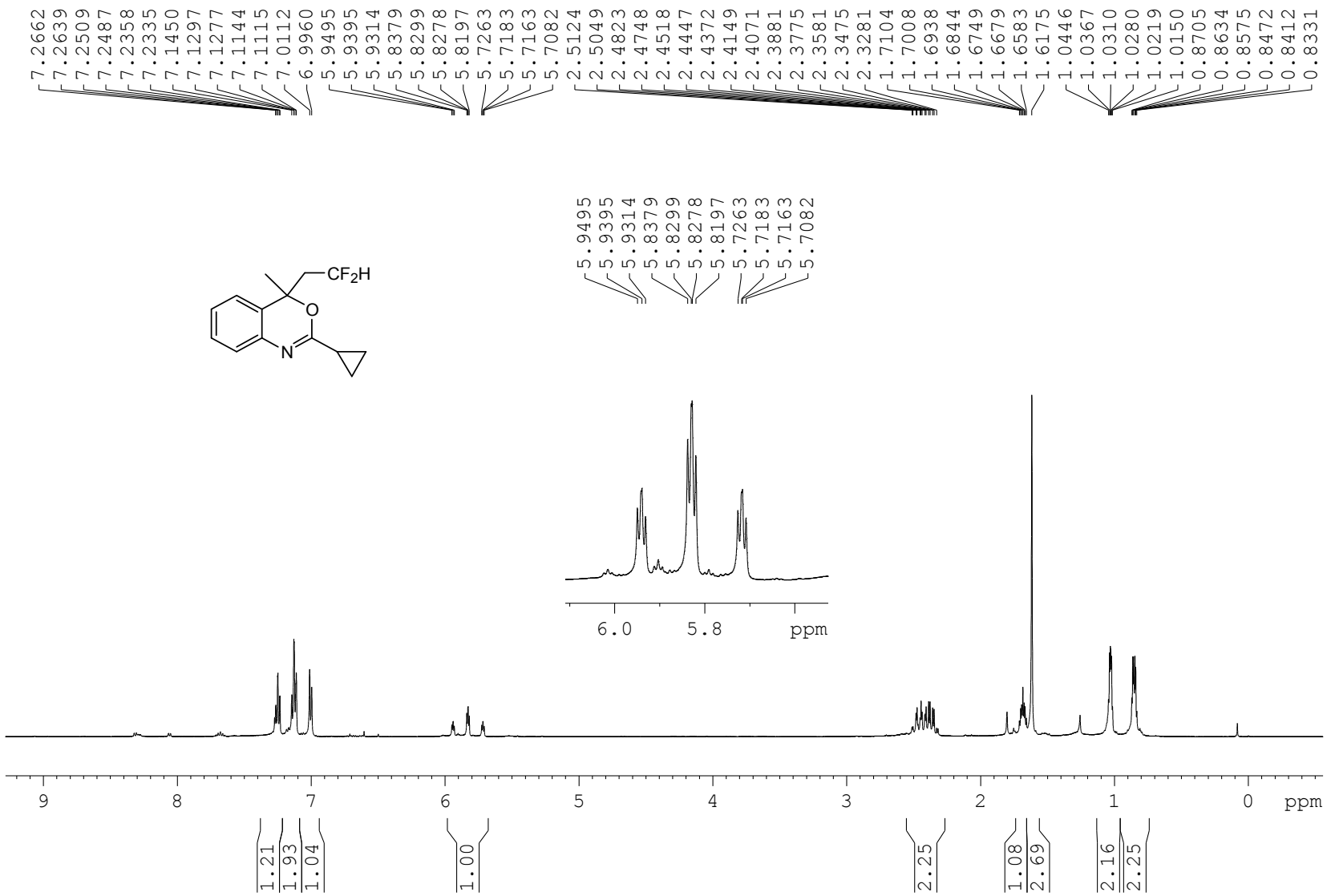
0.95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7.2358
7.2335
7.1450
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7.1277
7.1144
7.1115
7.0112
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5.8278
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5.7183
5.7163
5.7082
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2.4823
2.4748
2.4518
2.4447
2.4372
2.4149
2.4071
2.3881
2.3775
2.3581
2.3475
2.3281
1.7104
1.7008
1.6938
1.6844
1.6749
1.6679
1.6583
1.6175
1.0446
1.0367
1.0310
1.0280
1.0219
1.0150
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0.8412
0.8331
CF2H
O
N
6.0
5.8
ppm
9
8
7
6
5
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ppm
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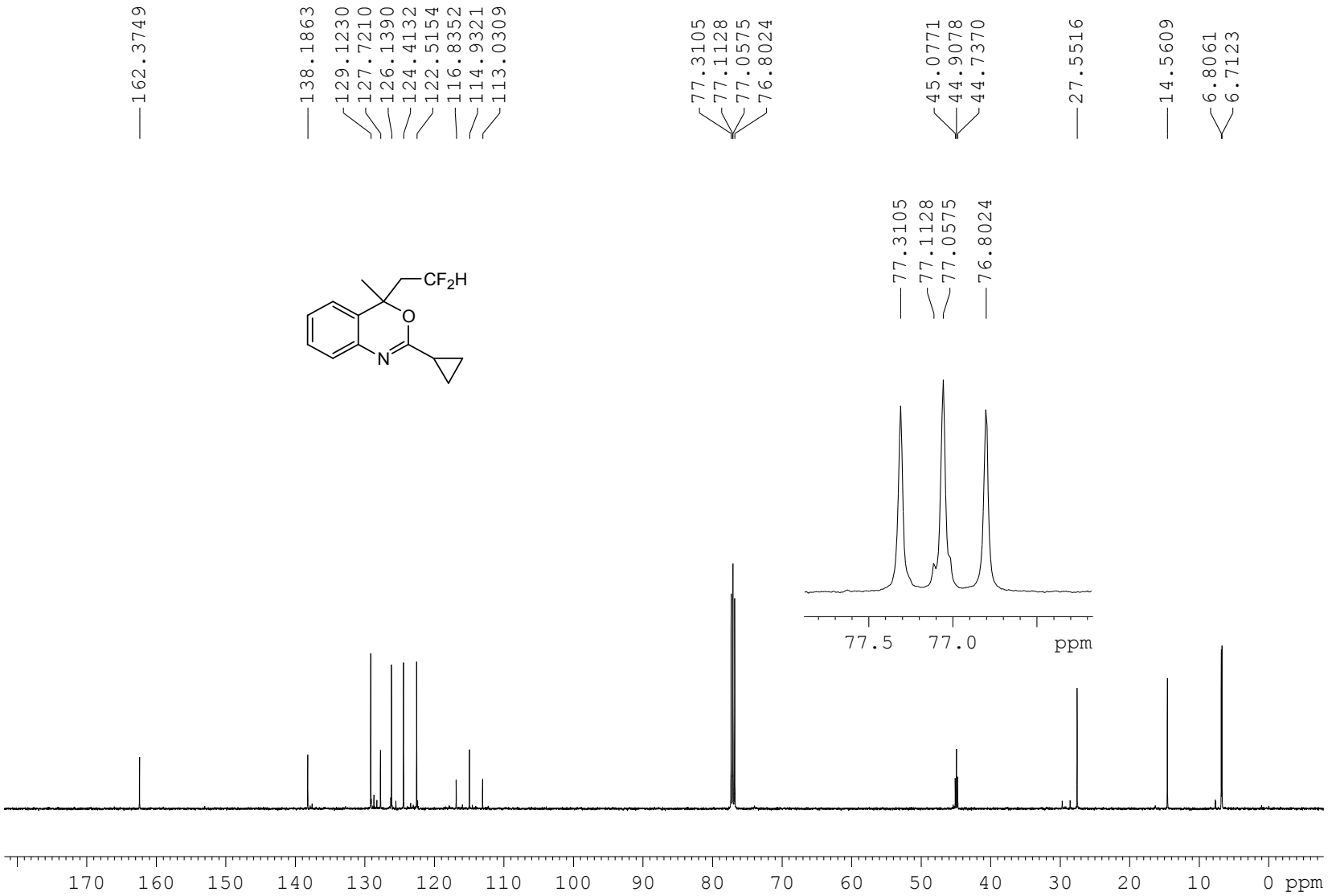
2.25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77.1128
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6.7123
CF2H
O
N
77.5
77.0
ppm
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110
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70
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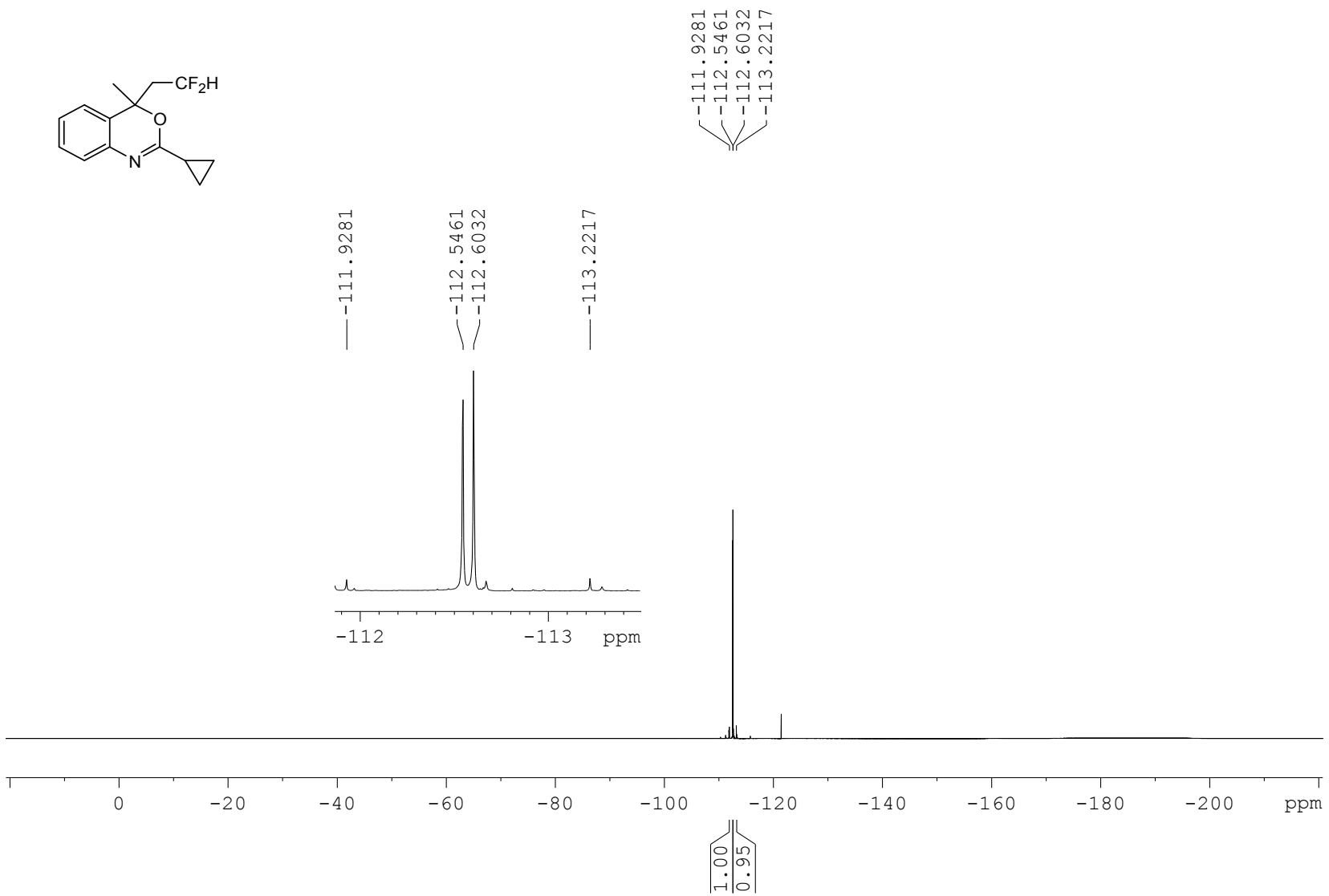
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-112.6032
-113.2217
-111.9281
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-112
-113
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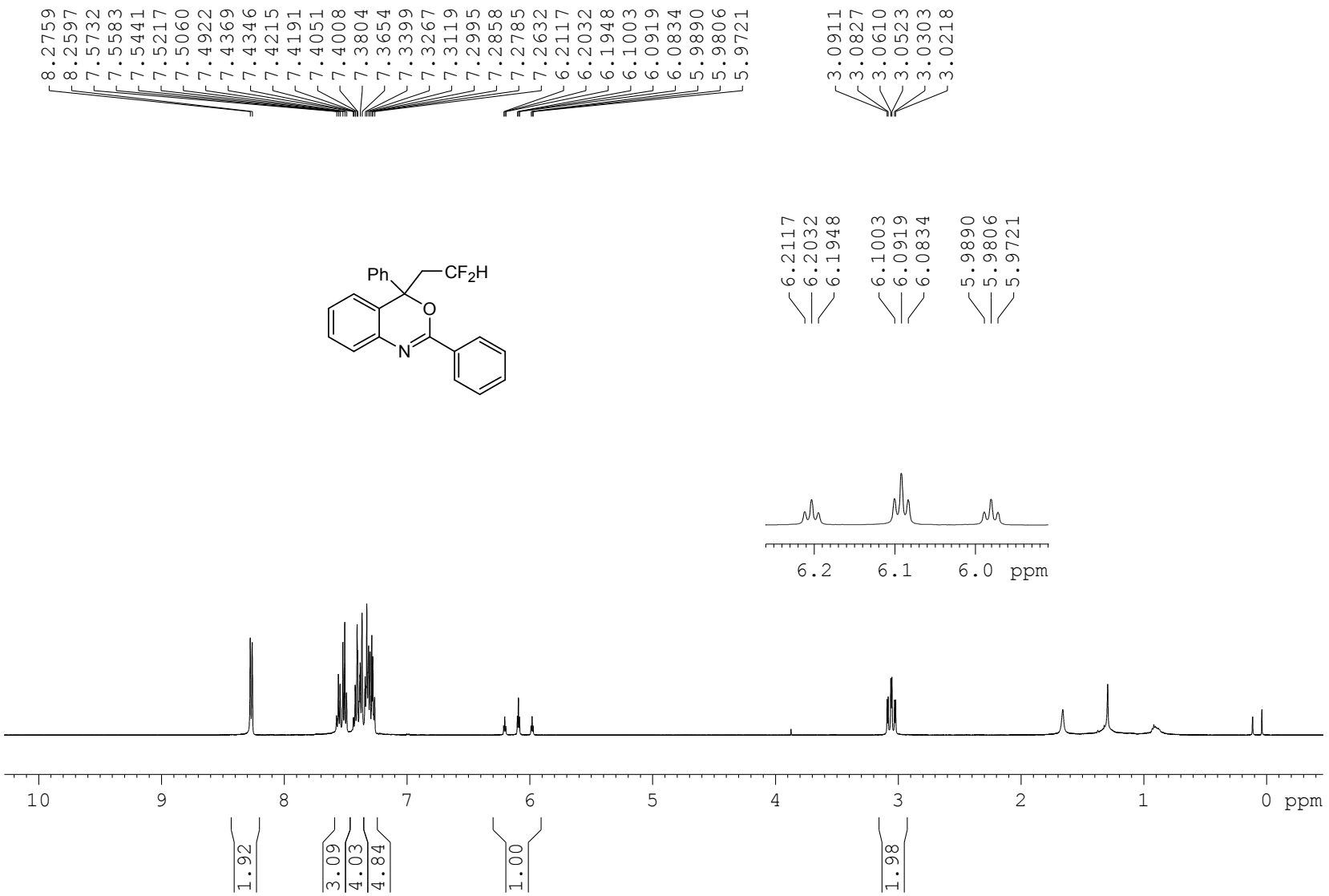
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7.5217
7.5060
7.4922
7.4369
7.4346
7.4215
7.4191
7.4051
7.4008
7.3804
7.3654
7.3399
7.3267
7.3119
7.2995
7.2858
7.2785
7.2632
6.2117
6.2032
6.1948
6.1003
6.0919
6.0834
5.9890
5.9806
5.9721
3.0911
3.0827
3.0610
3.0523
3.0303
3.0218
Ph
CF2H
O
N
6.2
6.1
6.0 ppm
10
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5
4
3
2
1
0 ppm
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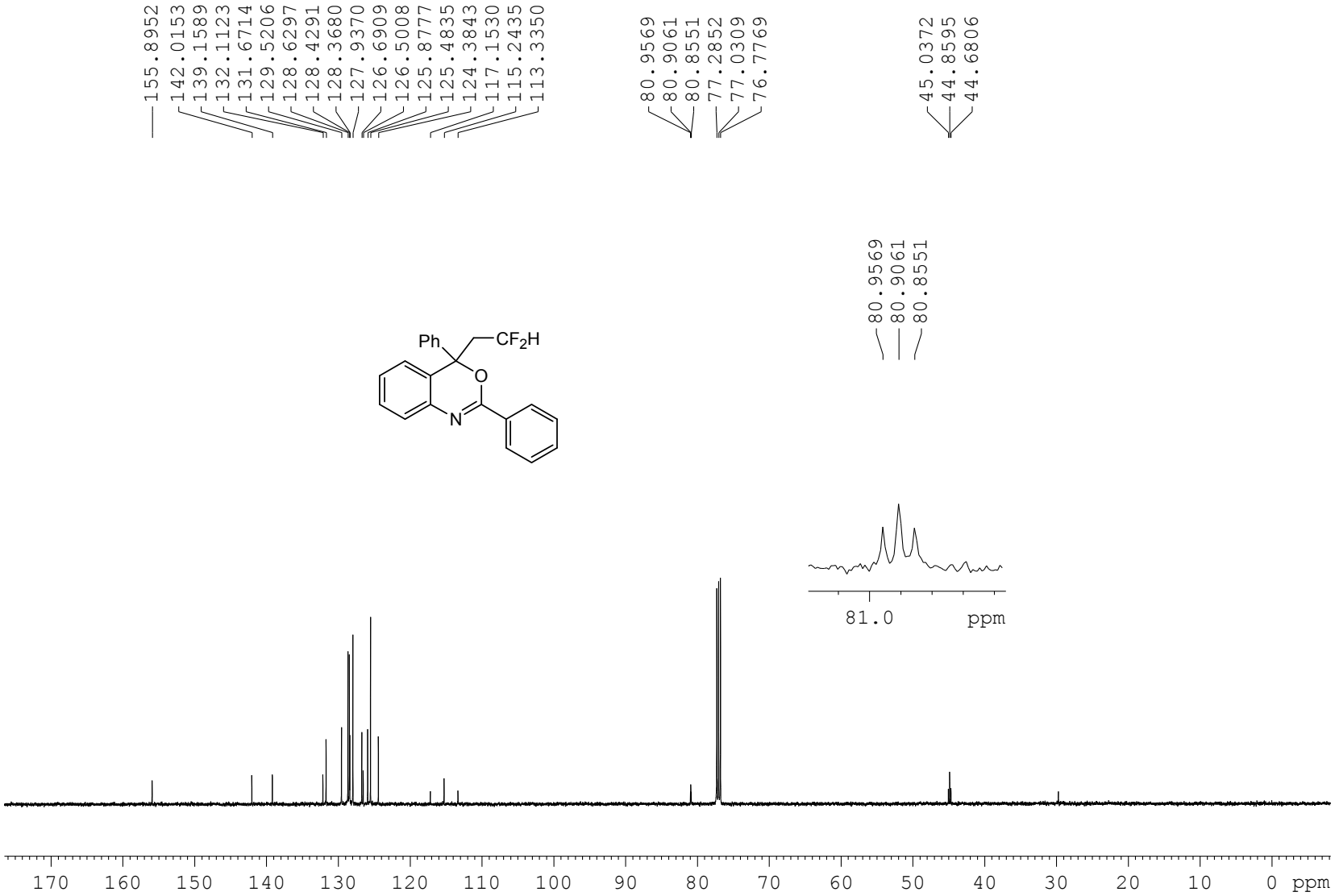
3.09
4.03
4.84
1.00
1.98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128.3680
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126.6909
126.5008
125.8777
125.4835
124.3843
117.1530
115.2435
113.3350
80.9569
80.9061
80.8551
77.2852
77.0309
76.7769
45.0372
44.8595
44.6806
Ph
CF2H
O
N
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ppm
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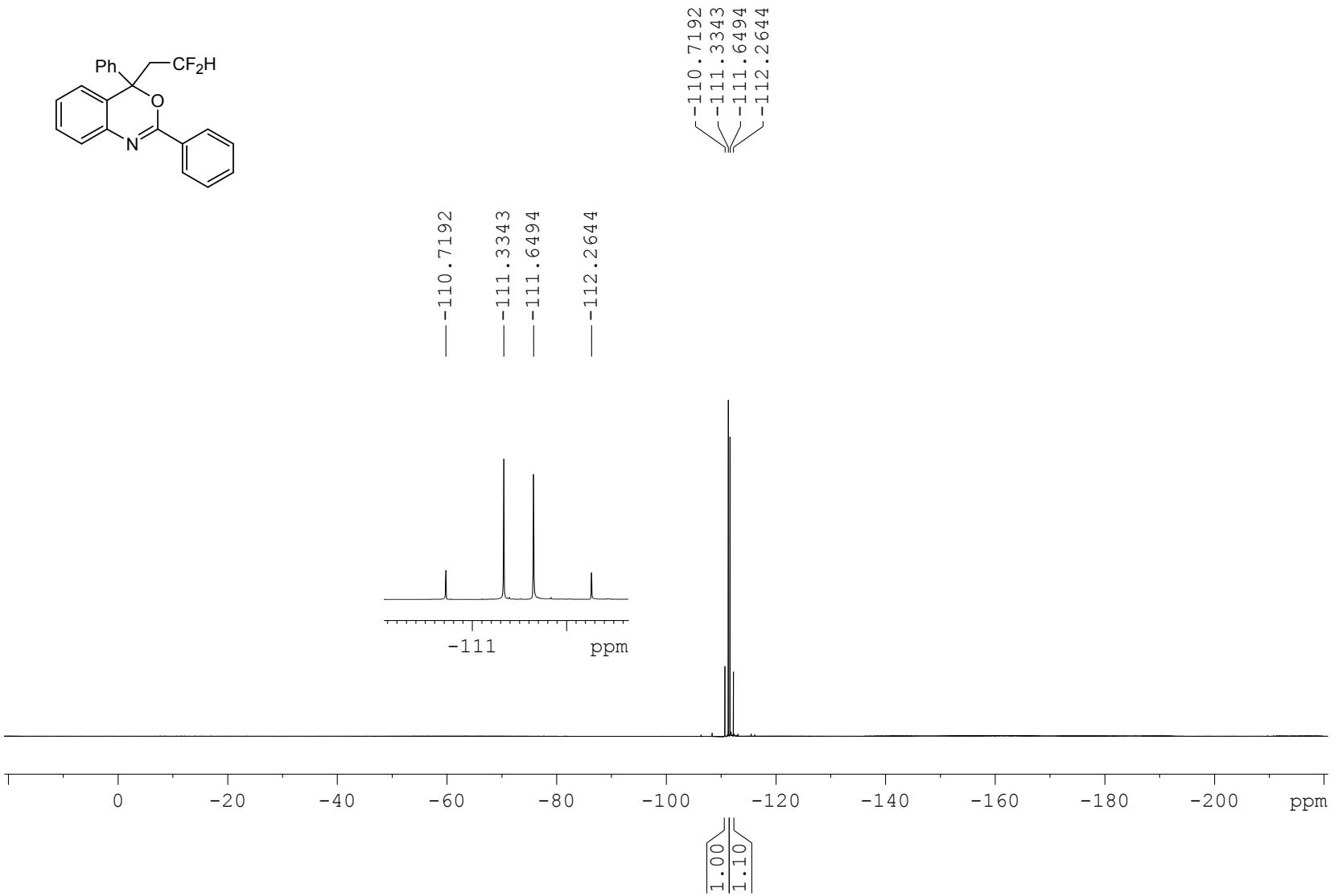
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0 ppm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-112.2644
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-160
-180
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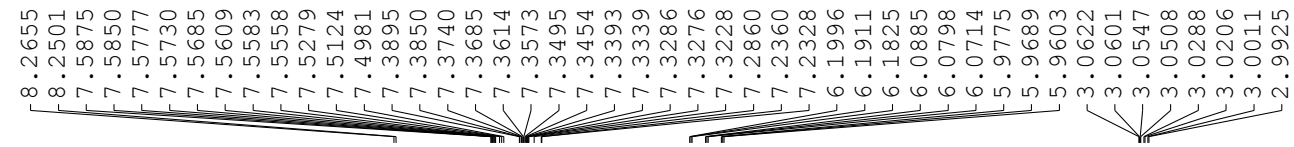
ppm
1.00
1.10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8.2501
7.5875
7.5850
7.5777
7.5730
7.5685
7.5609
7.5583
7.5558
7.5279
7.5124
7.4981
7.3895
7.3850
7.3740
7.3685
7.3614
7.3573
7.3495
7.3454
7.3393
7.3339
7.3286
7.3276
7.3228
7.2860
7.2360
7.2328
7.1996
7.1911
7.1825
7.0885
7.0798
7.0714
5.9775
5.9689
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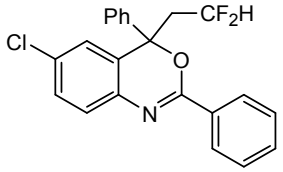
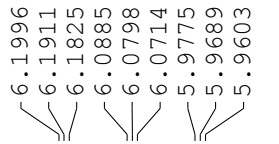
3.0622
3.0601
3.0547
3.0508
3.0288
3.0206
3.0011
2.9925


Ph
CF2H
Cl
O
N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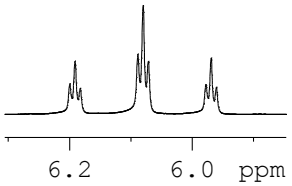
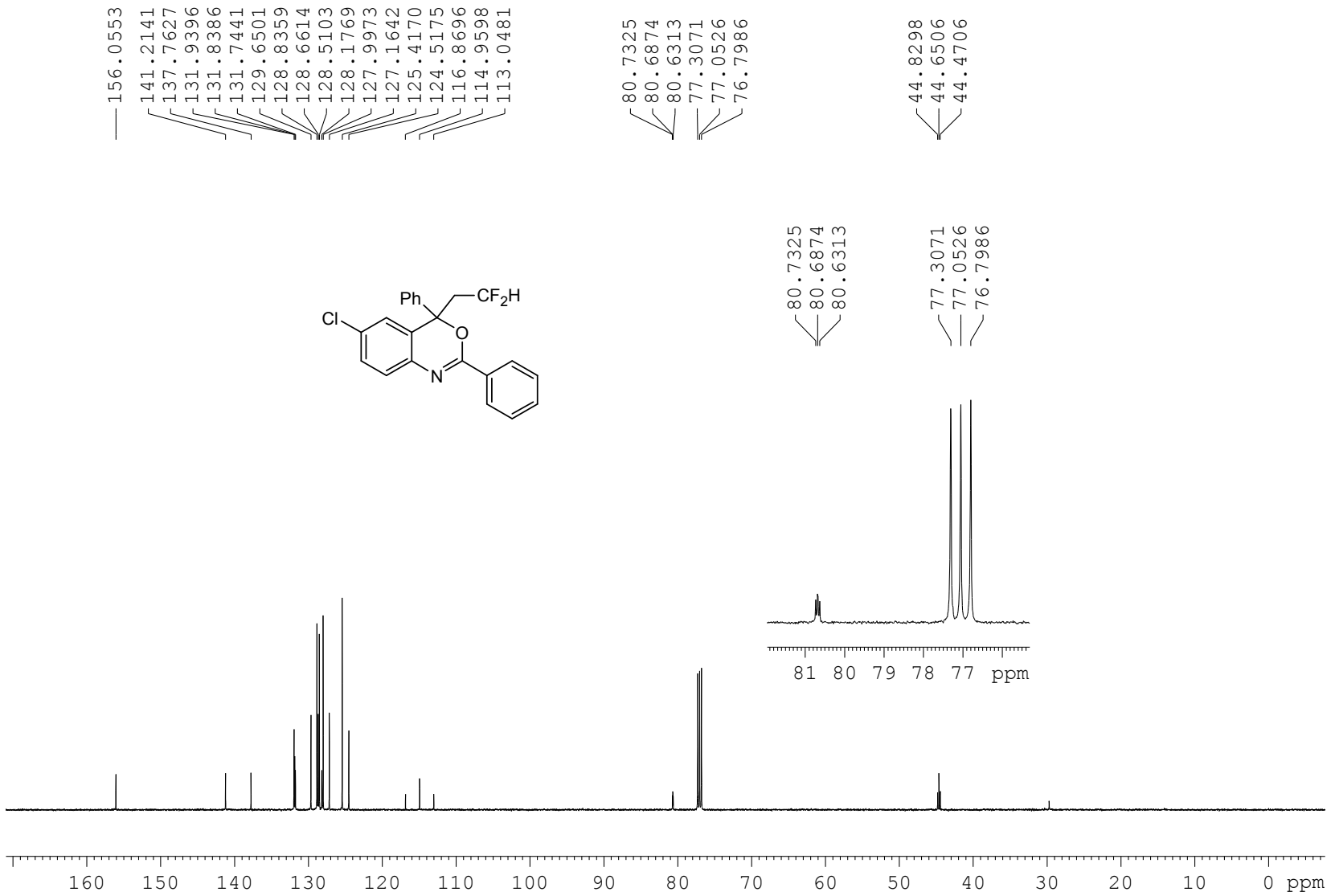
6.1911
6.1825
6.0885
6.0798
6.0714
5.9775
5.9689
5.9603


6.2
6.0
ppm

10
9
8
7
6
5
4
3
2
1
0
ppm
2.01
1.16
2.02
4.80
2.27
1.00
1.04
2.10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137.7627
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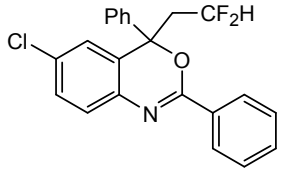
131.8386
131.7441
129.6501
128.8359
128.6614
128.5103
128.1769
127.9973
127.1642
125.4170
124.5175
116.8696
114.9598
113.0481
80.7325
80.6874
80.6313
77.3071
77.0526
76.7986
44.8298
44.6506
44.4706
Ph
CF2H
Cl
O
N
80.7325
80.6874
80.6313
77.3071
77.0526
76.7986
81 80 79 78 77 ppm
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


Ph
CF2H
Cl
O
N

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-111.3852
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-110.7690
-111.3852
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-112.4676
-111
-112
ppm
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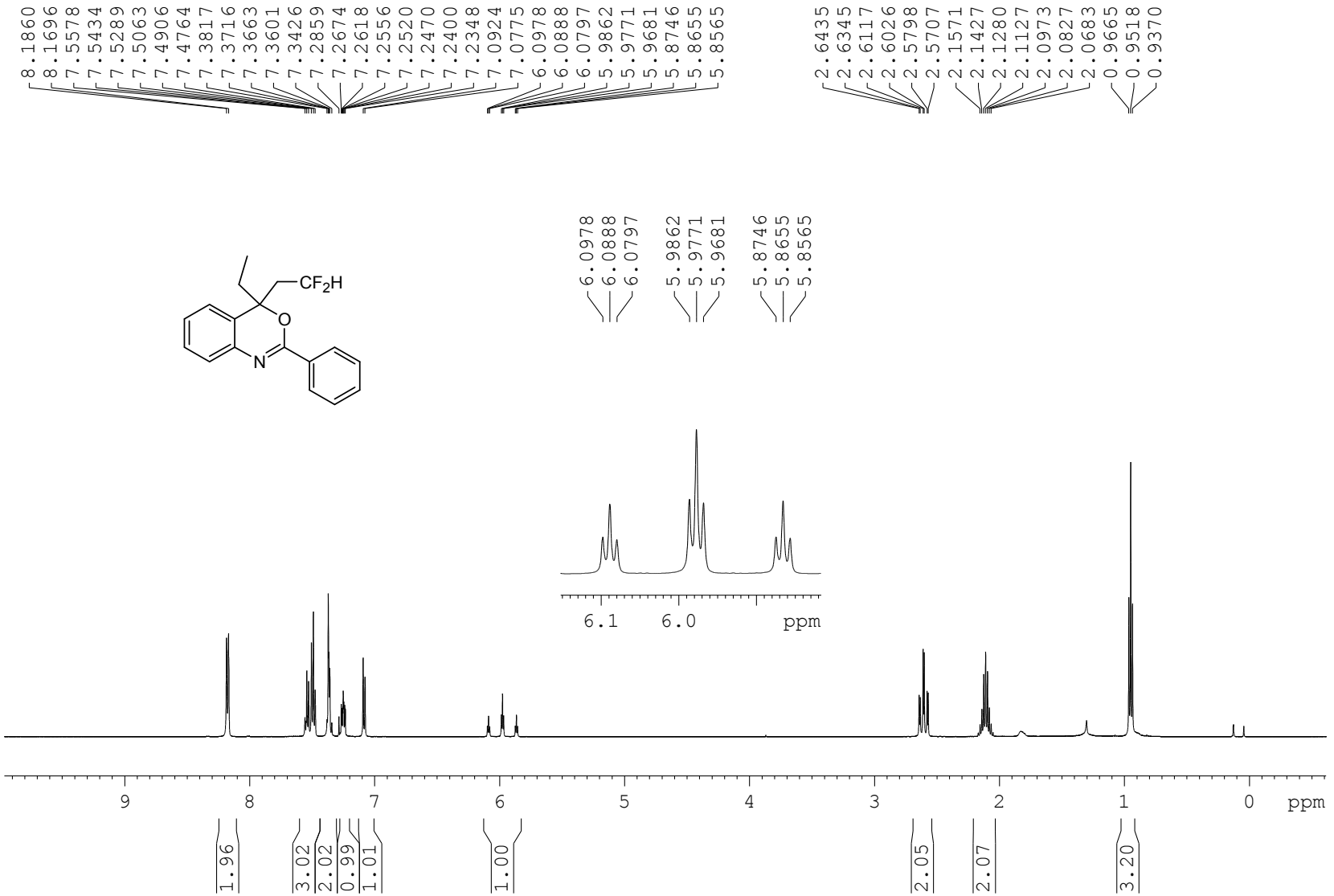
-80
-100
-120
-140
-160
-180
-200
ppm
1.00
1.02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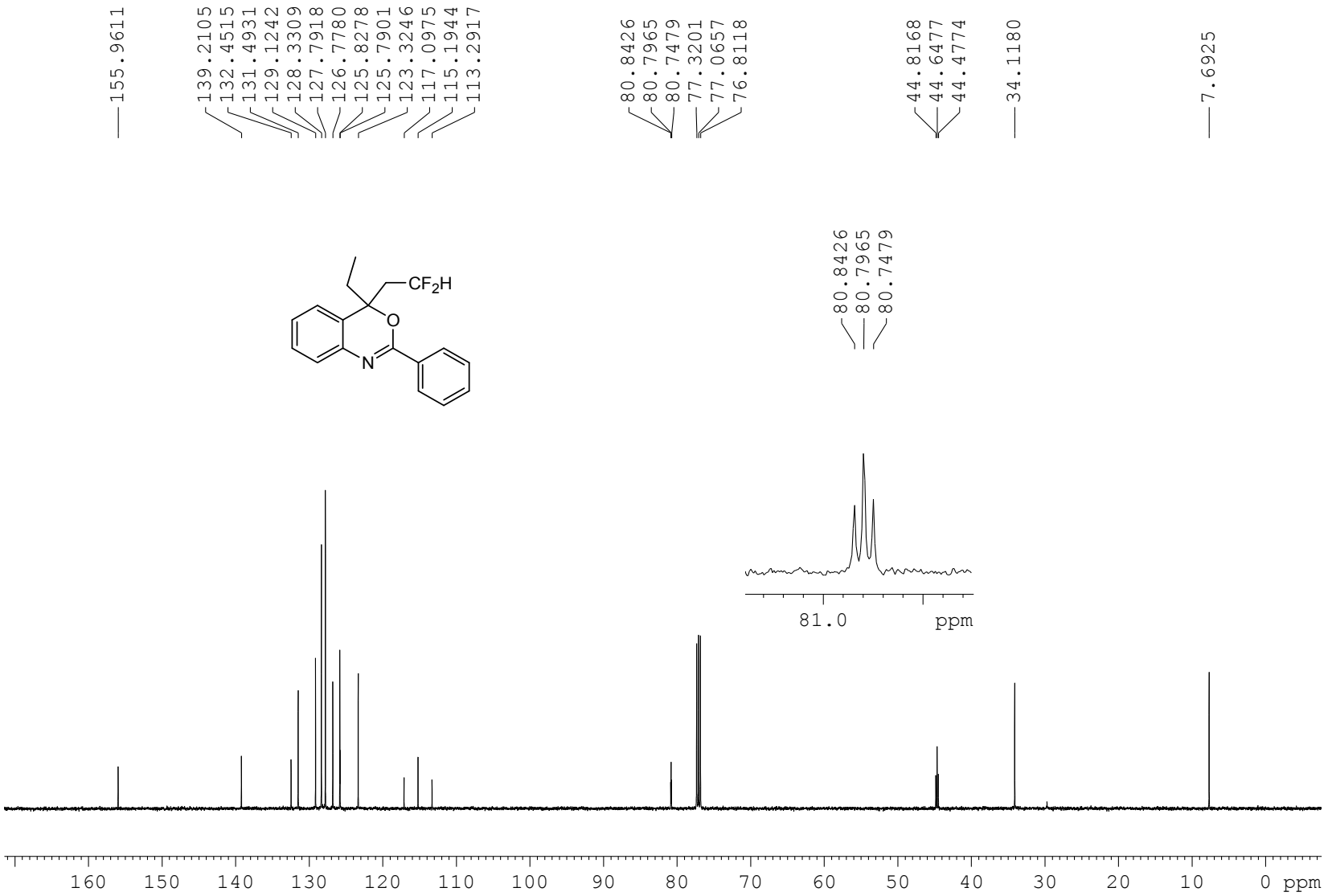
7.5434
7.5289
7.5063
7.4906
7.4764
7.3817
7.3716
7.3663
7.3601
7.3426
7.2859
7.2674
7.2618
7.2556
7.2520
7.2470
7.2400
7.2348
7.0924
7.0775
6.0978
6.0888
6.0797
5.9862
5.9771
5.9681
5.8746
5.8655
5.8565
2.6435
2.6345
2.6117
2.6026
2.5798
2.5707
2.1571
2.1427
2.1280
2.1127
2.0973
2.0827
2.0683
0.9665
0.9518
0.9370
CF2H
O
N
6.1
6.0
ppm
9
8
7
6
5
4
3
2
1
0
ppm
1.96
3.02
2.02
0.99
1.01
1.00
2.05
2.07
3.20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131.4931
129.1242
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127.7918
126.7780
125.8278
125.7901
123.3246
117.0975
115.1944
113.2917
80.8426
80.7965
80.7479
77.3201
77.0657
76.8118
44.8168
44.6477
44.4774
34.1180
7.6925
CF2H
O
N
81.0
ppm
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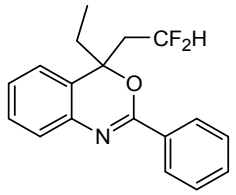
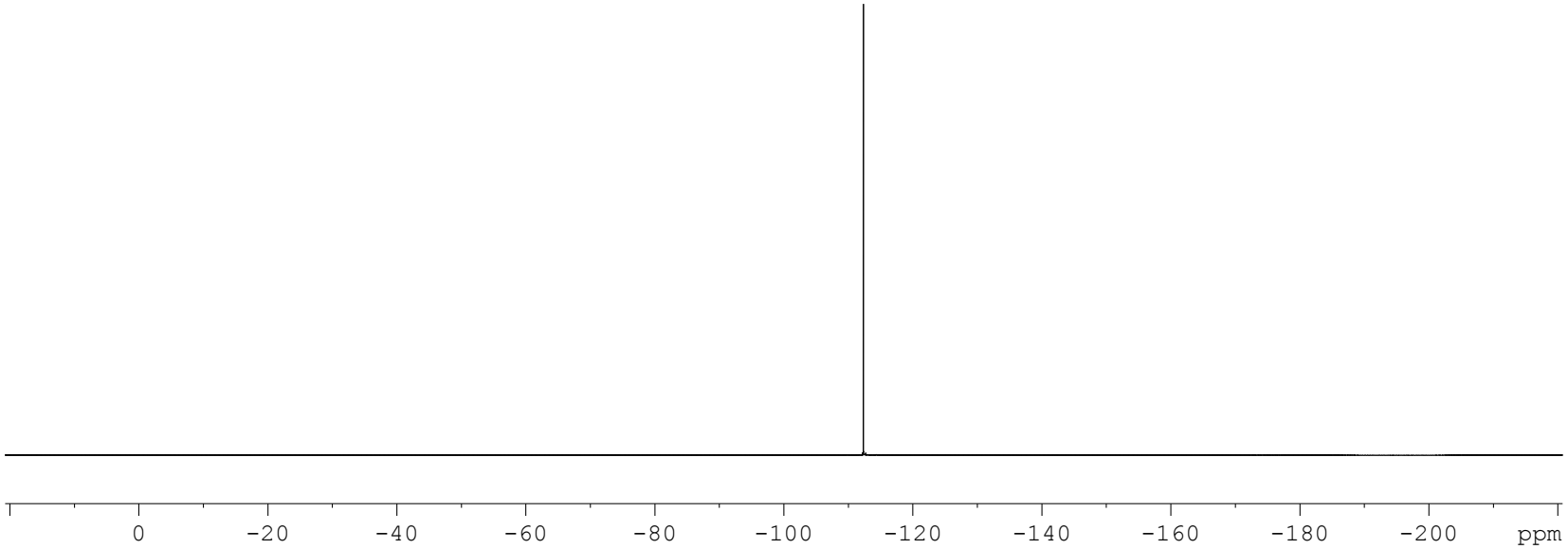
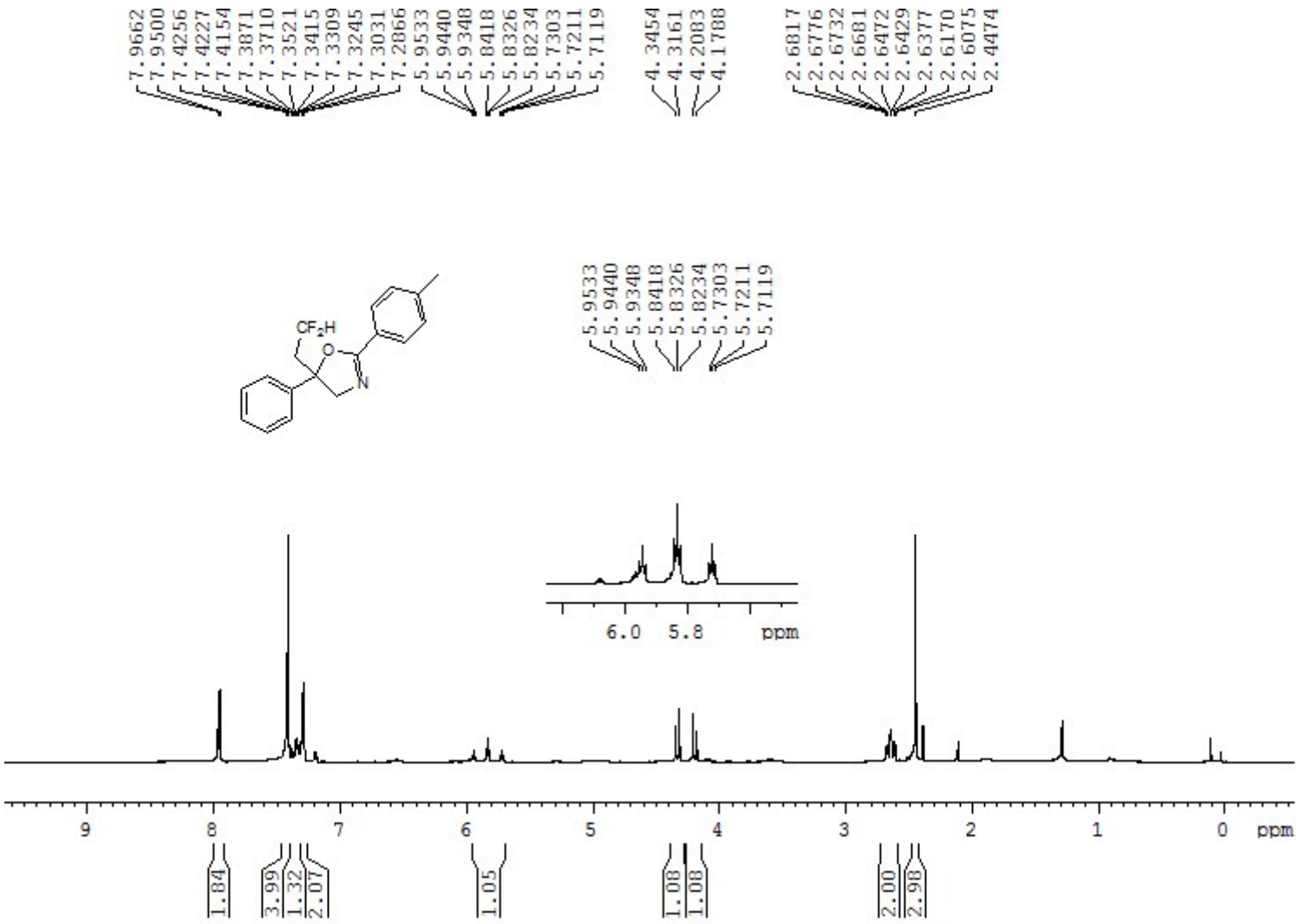
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0 ppm



-112.3502

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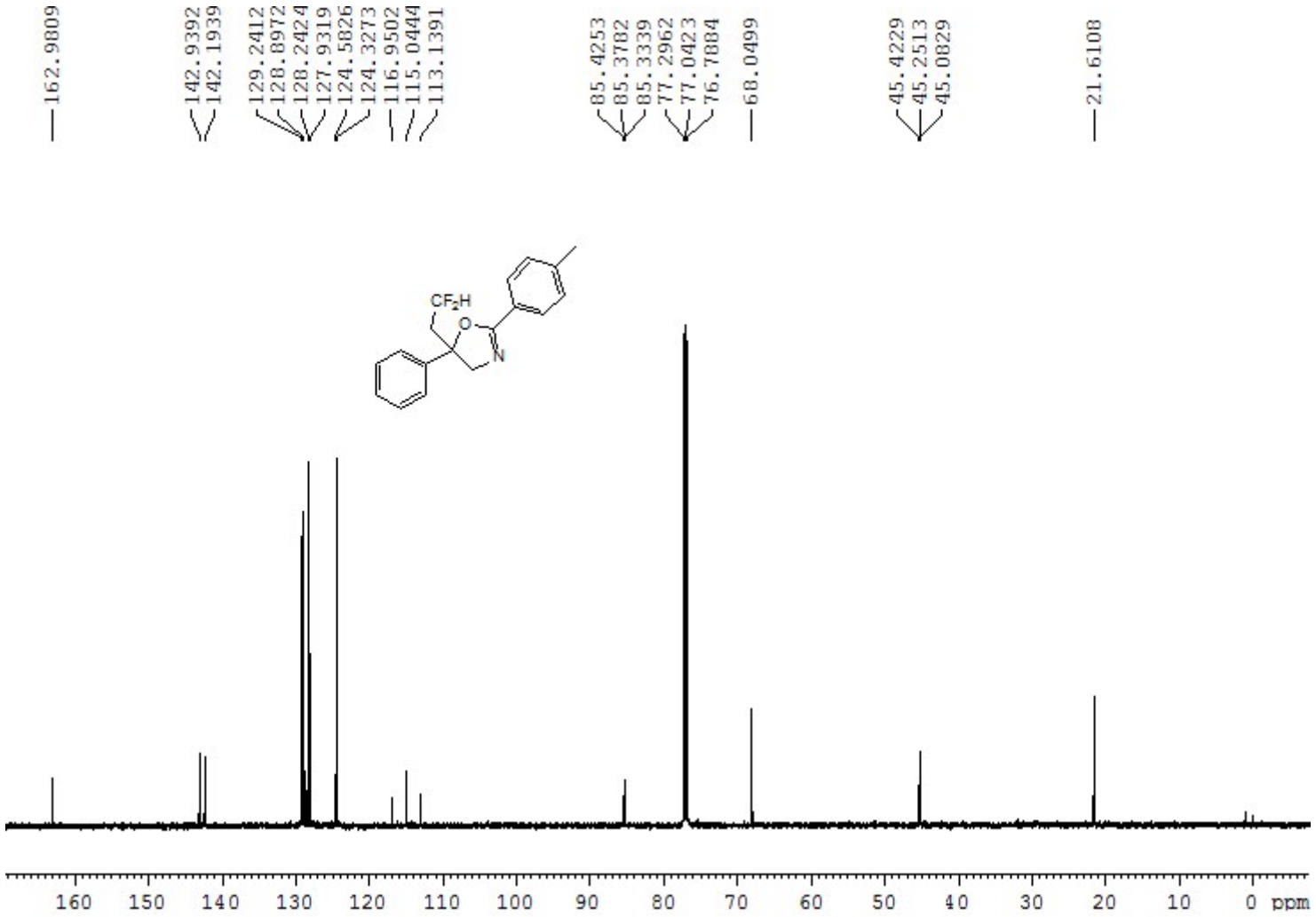
7.4154
7.3871
7.3710
7.3521
7.3415
7.3309
7.3245
7.3031
7.2866
5.9533
5.9440
5.9348
5.8418
5.8326
5.8234
5.7303
5.7211
5.7119
4.3454
4.3161
4.2083
4.1788
2.6817
2.6776
2.6732
2.6681
2.6472
2.6429
2.6377
2.6170
2.6075
2.4474
CF2H
O
N
6.0
5.8
ppm
9
8
7
6
5
4
3
2
1
0
ppm
1.84
3.99
1.32
2.07
1.05
1.08
1.08
2.00
2.98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127.9319
124.5826
124.3273
116.9502
115.0444
113.1391
85.4253
85.3782
85.3339
77.2962
77.0423
76.7884
68.0499
45.4229
45.2513
45.0829
21.6108
CF2H
O
N
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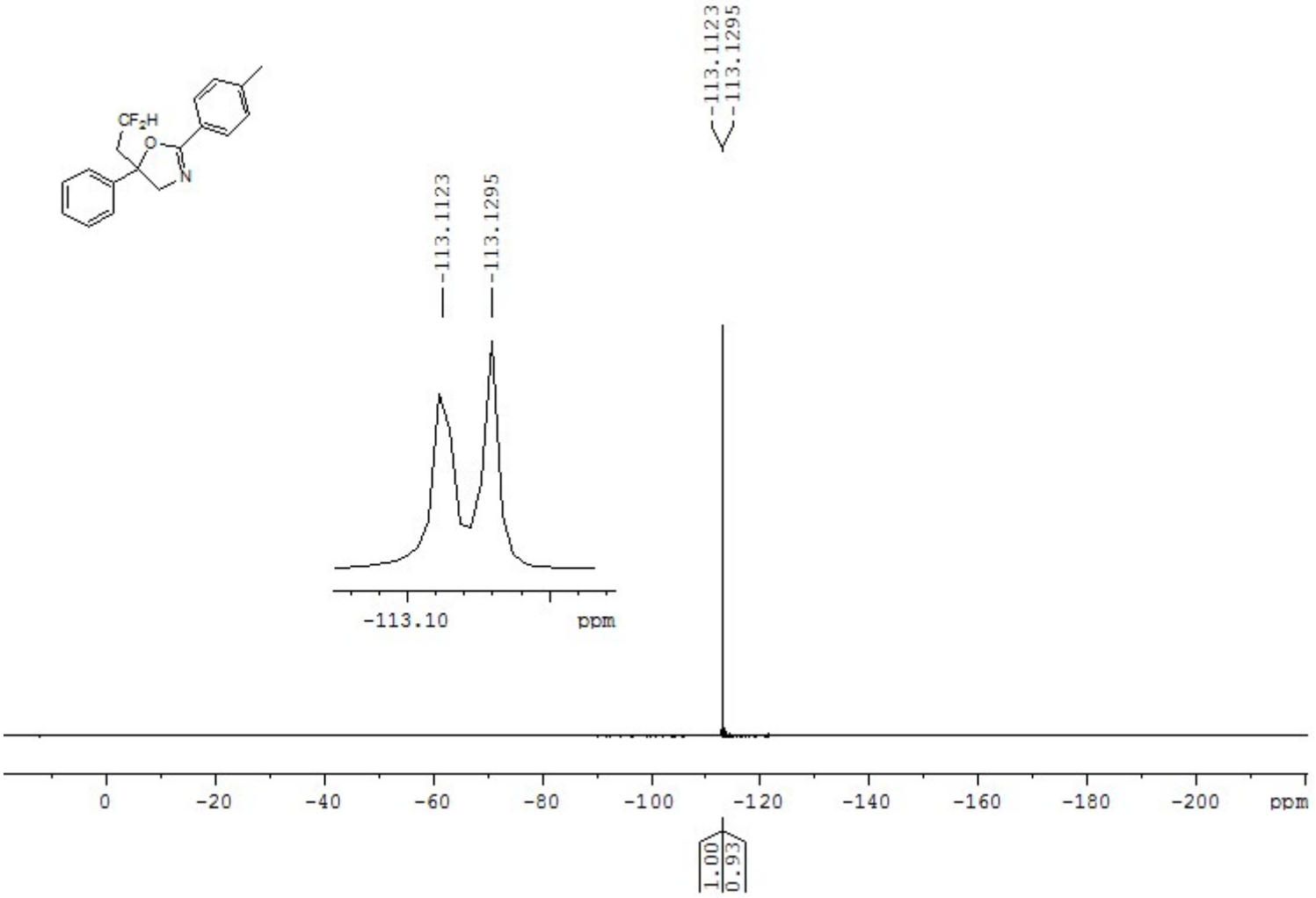
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0 ppm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O
N
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-113.1295
-113.1123
-113.1295
-113.10
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-80
-100
-120
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-160
-180
-200
ppm
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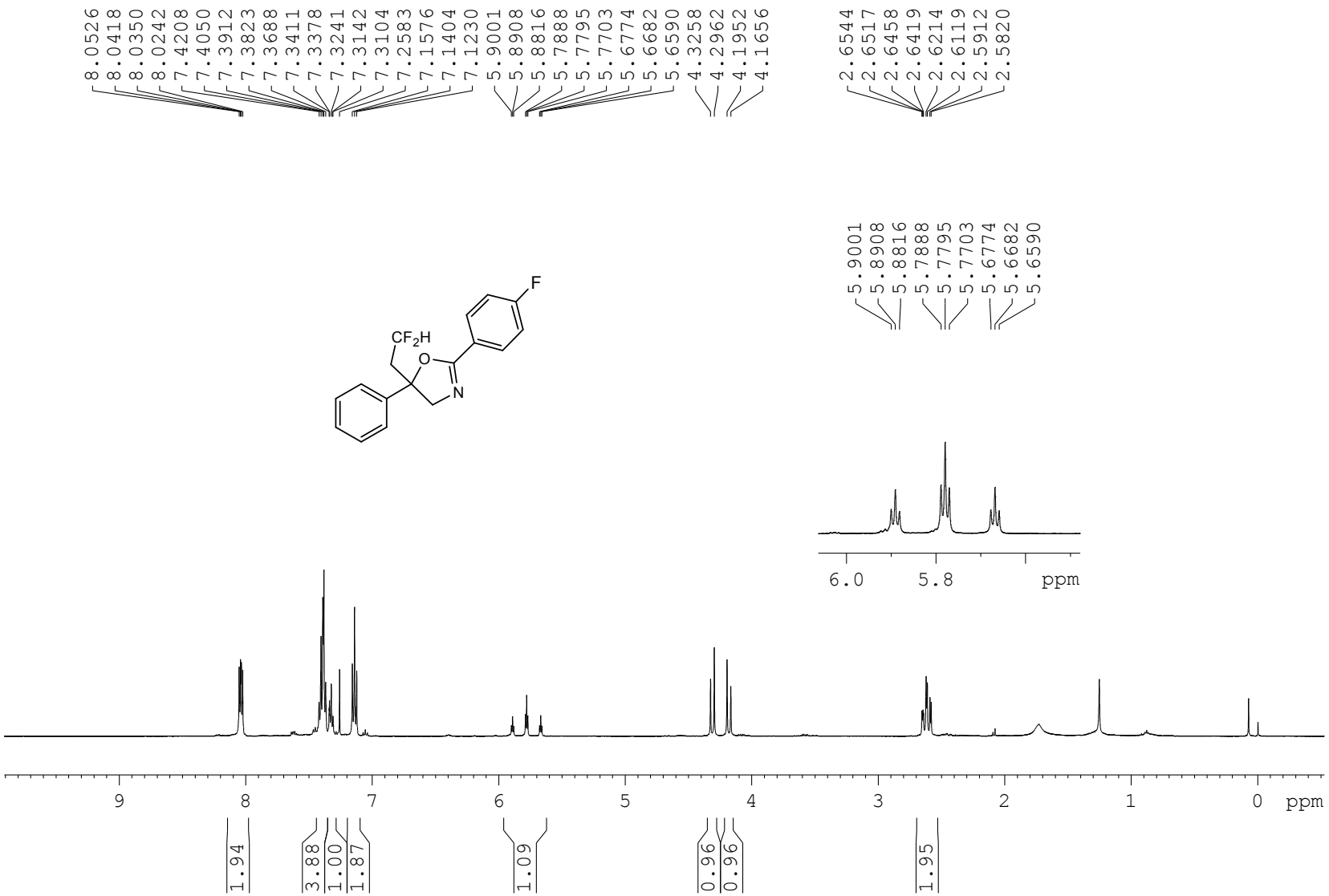
0.93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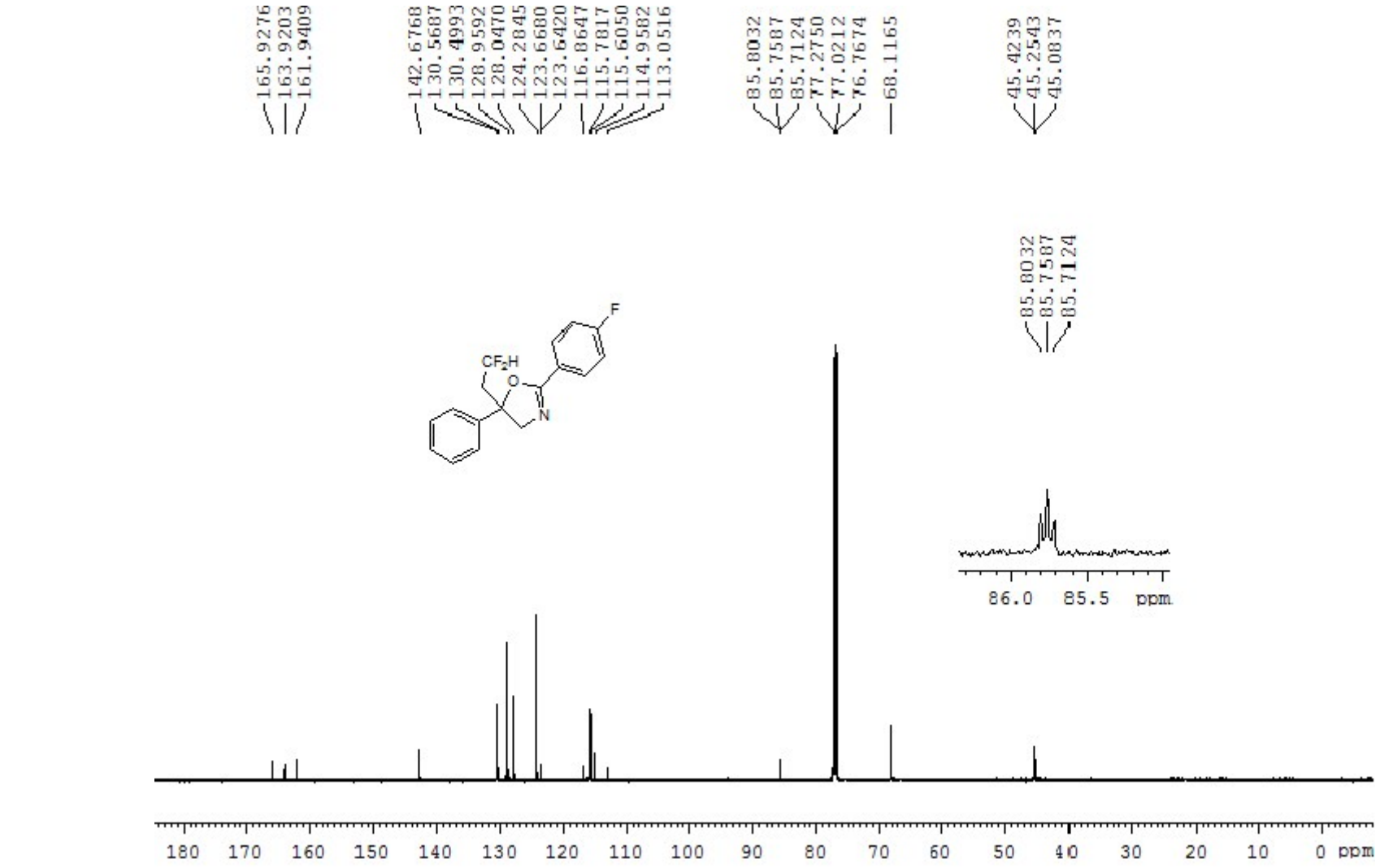
8.0418
8.0350
8.0242
7.4208
7.4050
7.3912
7.3823
7.3688
7.3411
7.3378
7.3241
7.3142
7.3104
7.2583
7.1576
7.1404
7.1230
5.9001
5.8908
5.8816
5.7888
5.7795
5.7703
5.6774
5.6682
5.6590
4.3258
4.2962
4.1952
4.1656
2.6544
2.6517
2.6458
2.6419
2.6214
2.6119
2.5912
2.5820
F
CF2H
O
N
6.0
5.8
ppm
9
8
7
6
5
4
3
2
1
0
ppm
1.94
3.88
1.00
1.87
1.09
0.96
0.96
1.95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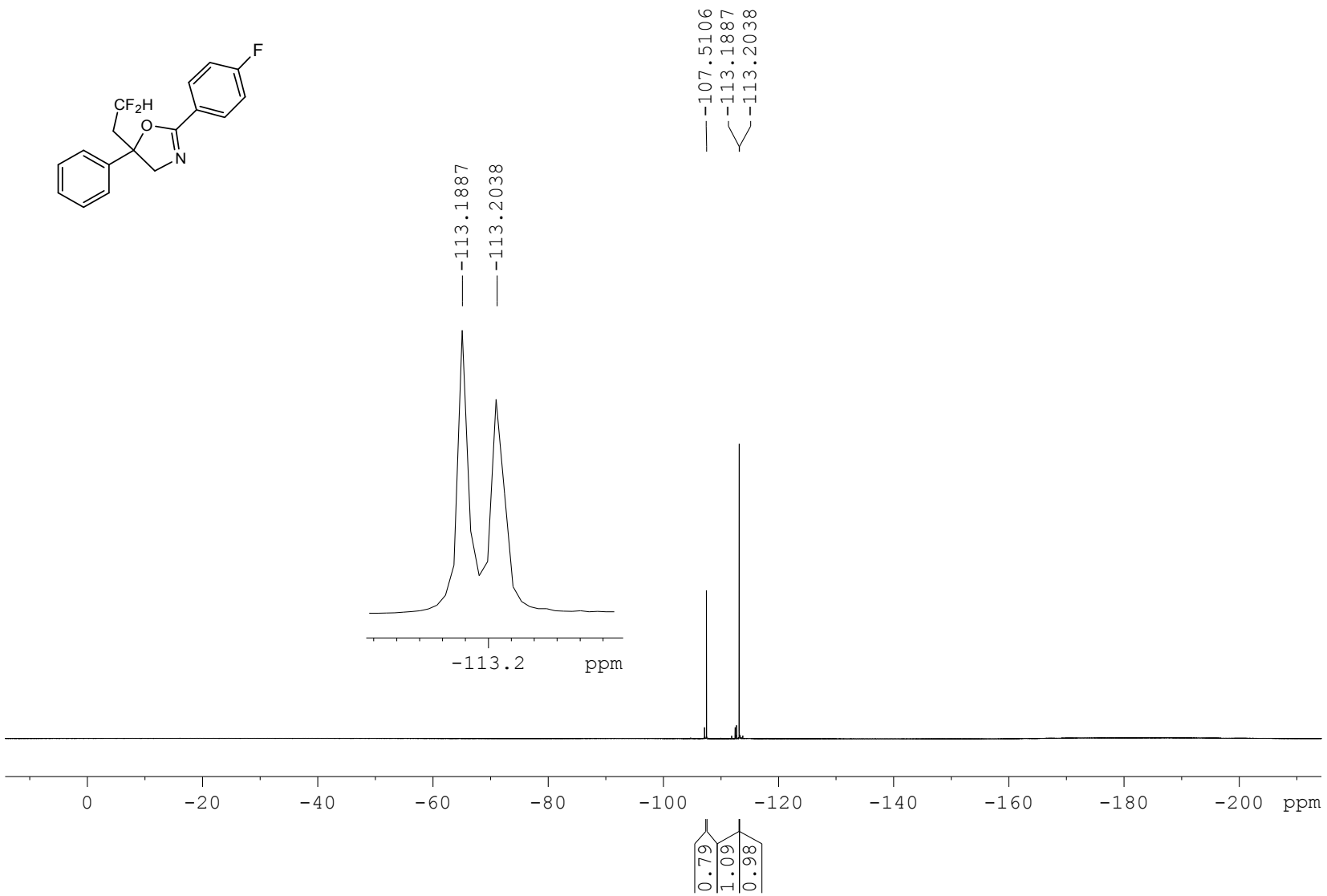
130.4993
128.9592
128.0470
124.2845
123.6680
123.6420
116.8647
115.7817
115.6050
114.9582
113.0516
85.8032
85.7587
85.7124
77.2750
77.0212
76.7674
68.1165
45.4239
45.2543
45.0837
F
CF2H
O
N
86.0
85.5
ppm
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0 ppm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O
N
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-113.1887
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-113.2
ppm
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-60
-80
-100
-120
-140
-160
-180
-200
ppm
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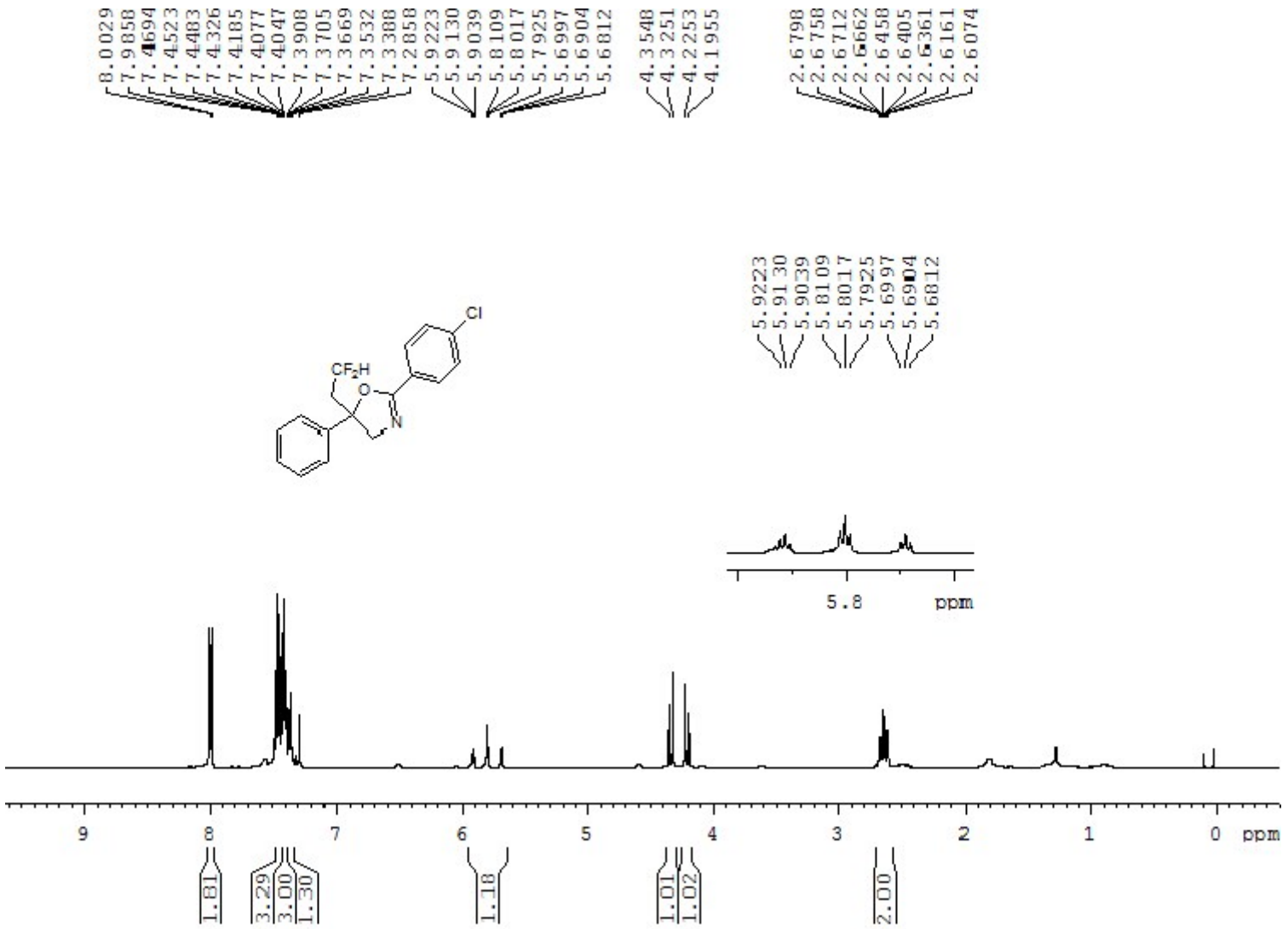
1.09
0.98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7.4483
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7.4185
7.4077
7.4047
7.3908
7.3705
7.3669
7.3532
7.3388
7.2858
5.9223
5.9130
5.9039
5.8109
5.8017
5.7925
5.6997
5.6904
5.6812
4.3548
4.3251
4.2253
4.1955
2.6798
2.6758
2.6712
2.6662
2.6458
2.6405
2.6361
2.6161
2.6074
CF2H
O
N
Cl
5.8
ppm
9
8
7
6
5
4
3
2
1
0
ppm
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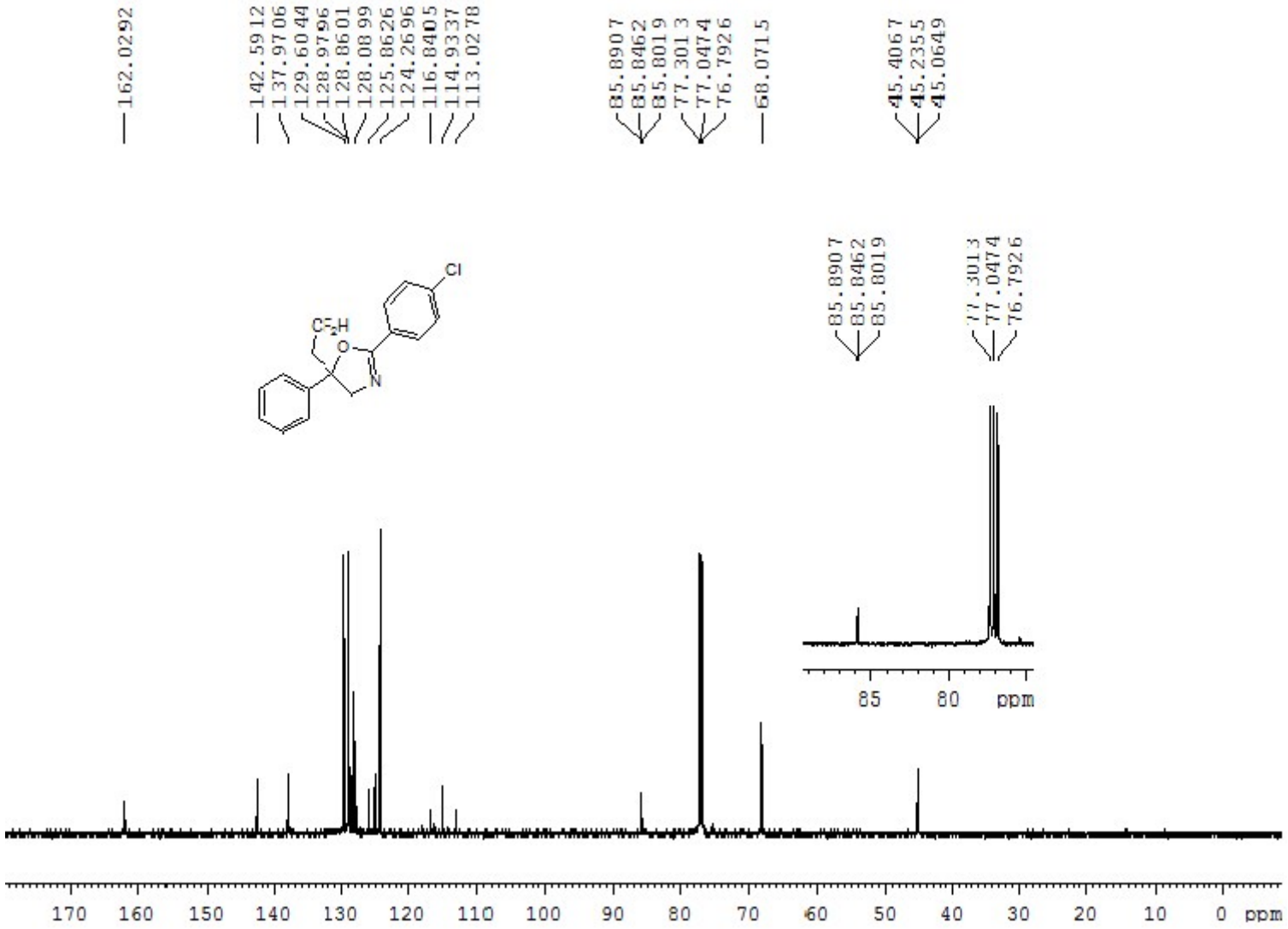
3.29
3.00
1.30
1.18
1.01
1.02
2.00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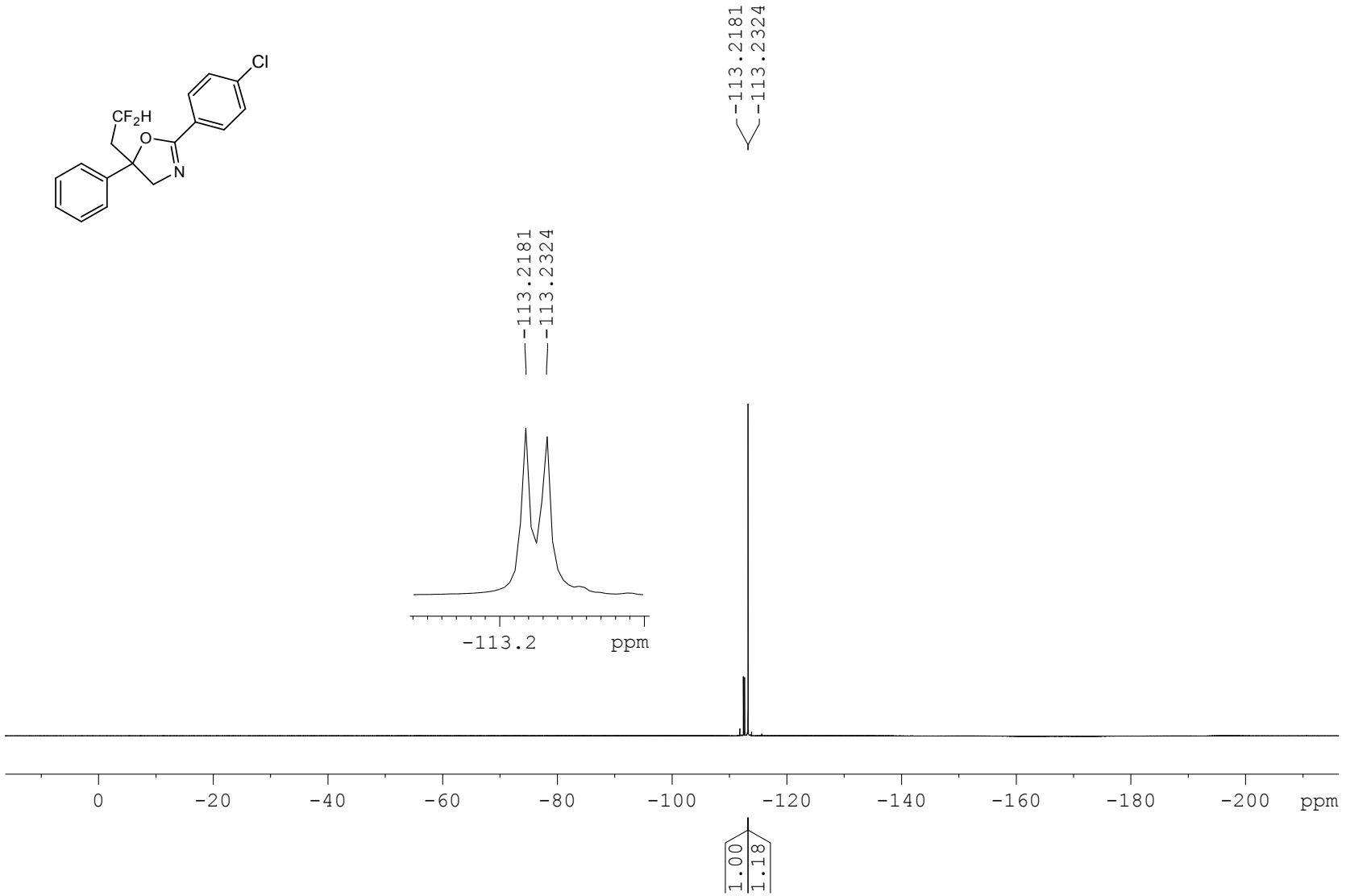
128.0899
125.8626
124.2696
116.8405
114.9337
113.0278
85.8907
85.8462
85.8019
77.3013
77.0474
76.7926
68.0715
45.4067
45.2355
45.0649
Cl
O
N
85
80
ppm
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


Cl
CF2H
O
N
-113.2181
-113.2324
-113.2181
-113.2324
-113.2
ppm
0
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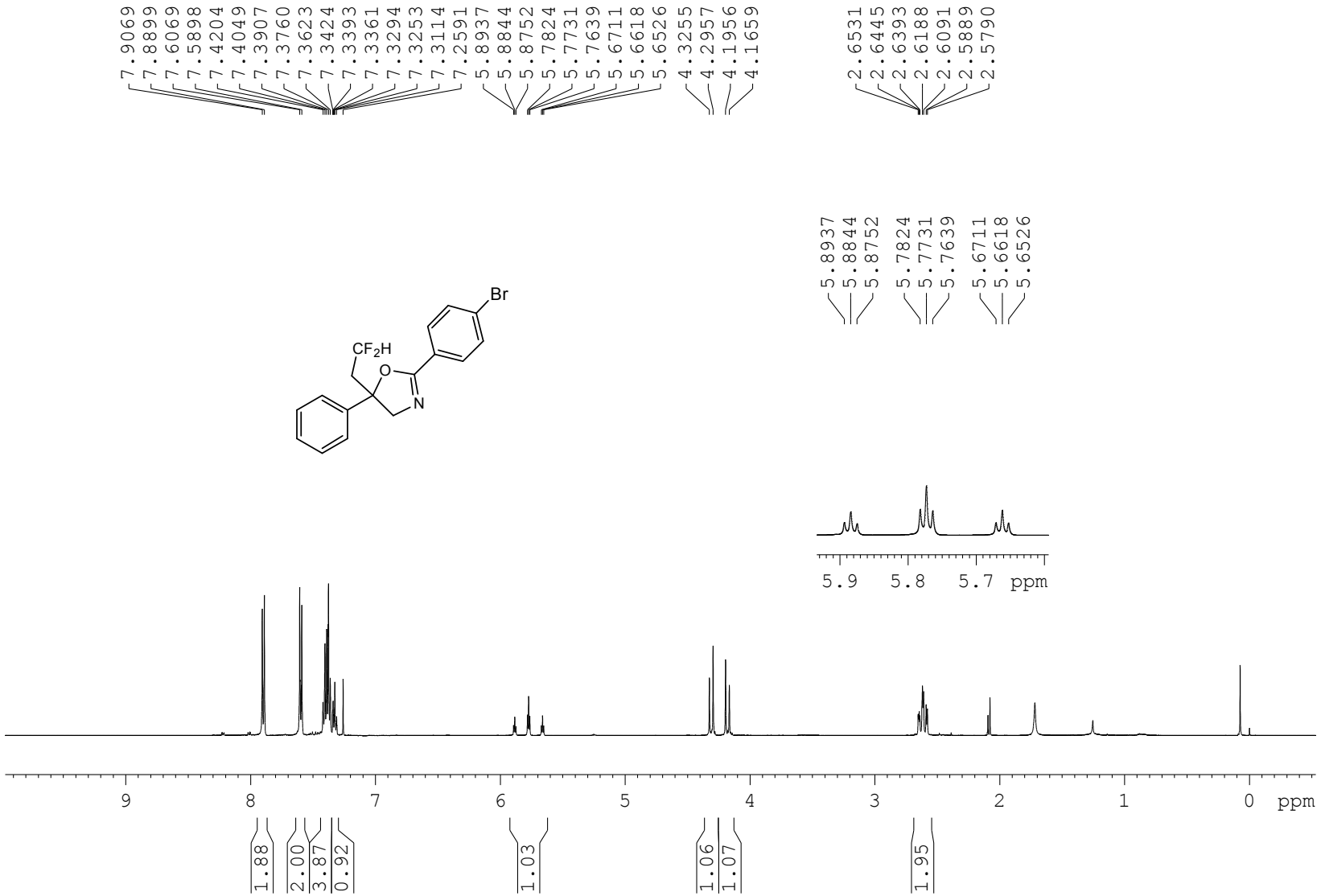
-40
-60
-80
-100
-120
-140
-160
-180
-200
ppm
1.00
1.18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7.5898
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7.3907
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7.3623
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7.3393
7.3361
7.3294
7.3253
7.3114
7.2591
5.8937
5.8844
5.8752
5.7824
5.7731
5.7639
5.6711
5.6618
5.6526
4.3255
4.2957
4.1956
4.1659
2.6531
2.6445
2.6393
2.6188
2.6091
2.5889
2.5790
Br
CF2H
O
N
5.9
5.8
5.7
ppm
9
8
7
6
5
4
3
2
1
0
ppm
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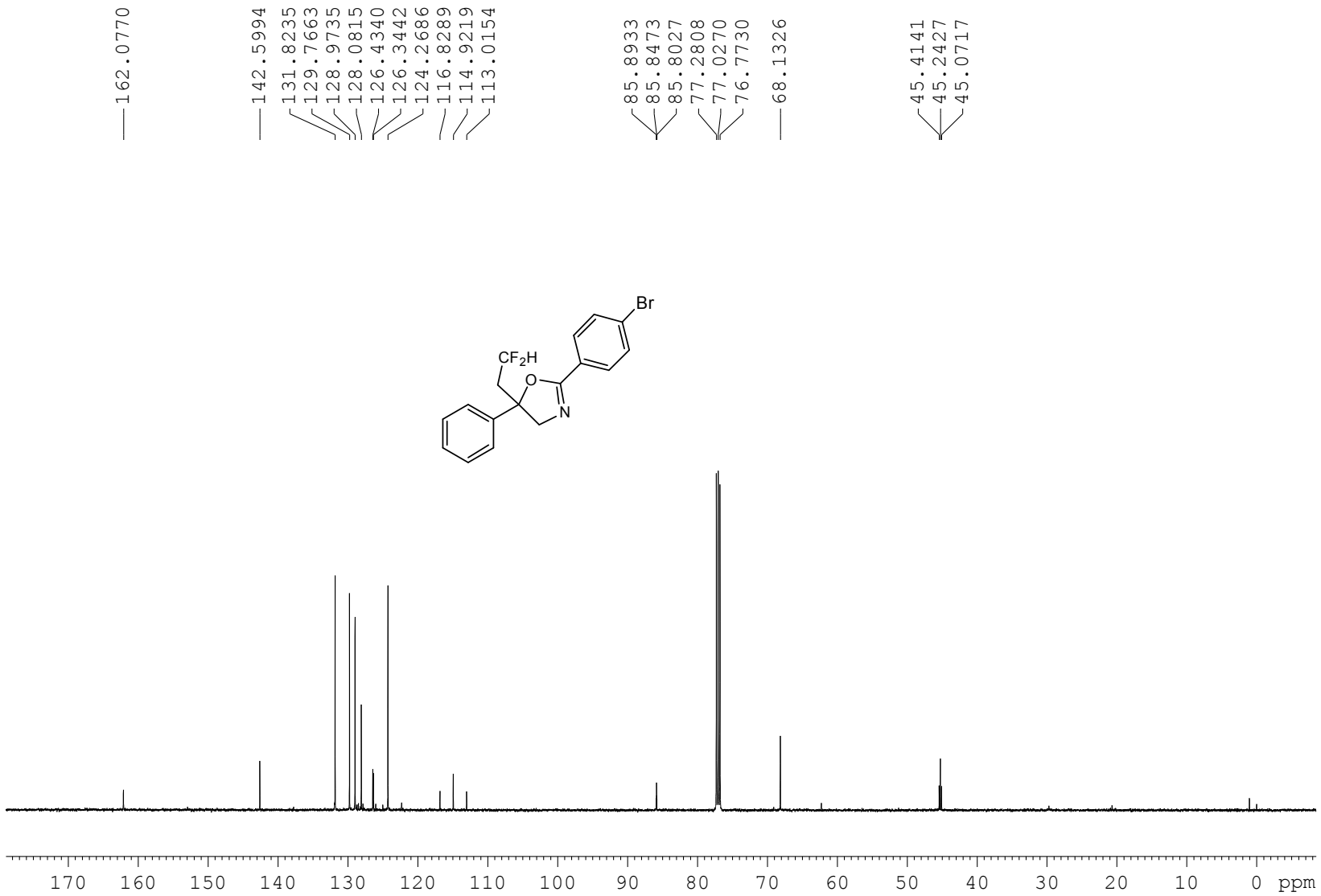
2.00
3.87
0.92
1.03
1.06
1.07
1.95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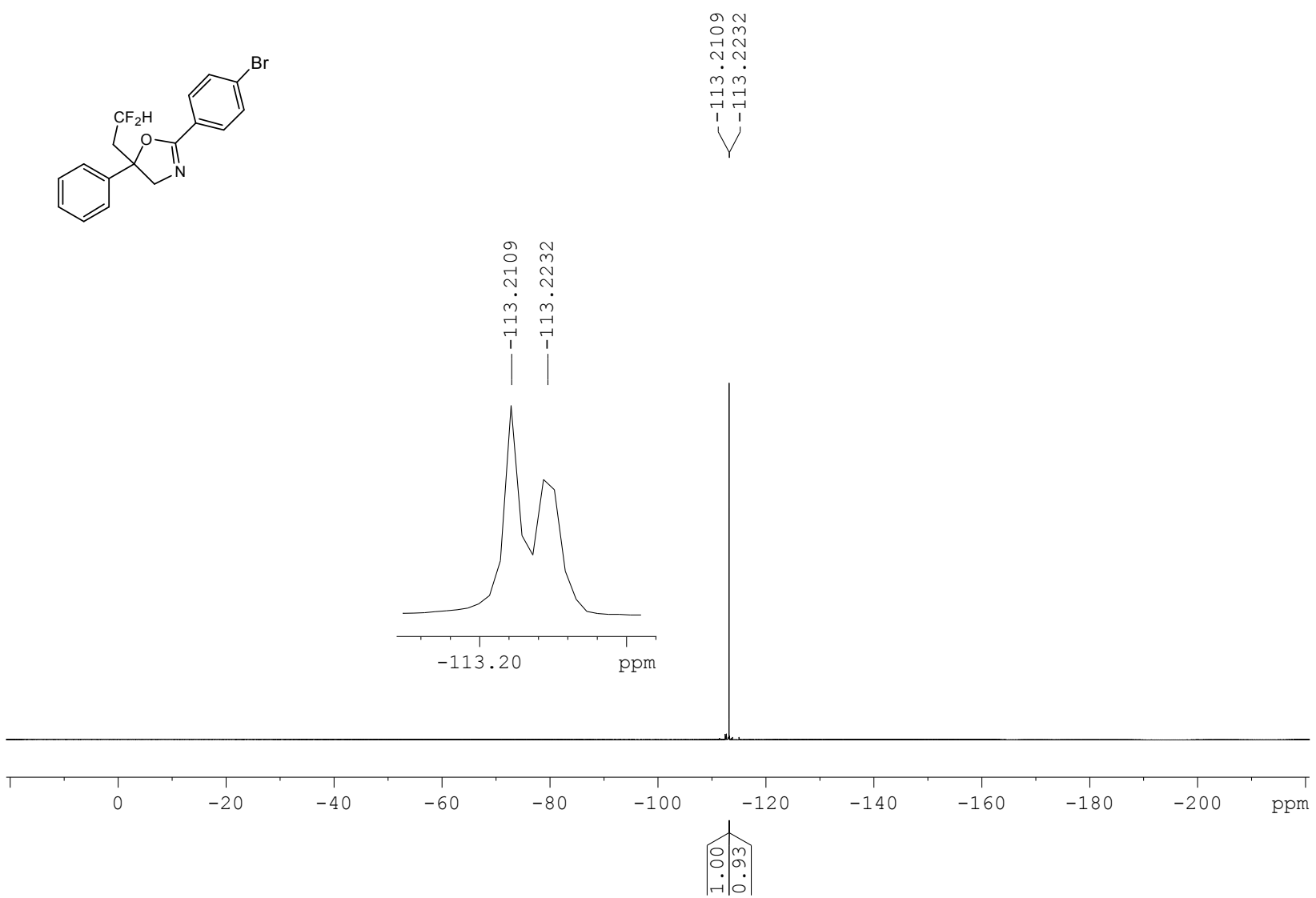
126.3442
124.2686
116.8289
114.9219
113.0154
85.8933
85.8473
85.8027
77.2808
77.0270
76.7730
68.1326
45.4141
45.2427
45.0717
Br
CF2H
O
N
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


Br
CF2H
O
N
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-113.2232
-113.2109
-113.2232
-113.20
ppm
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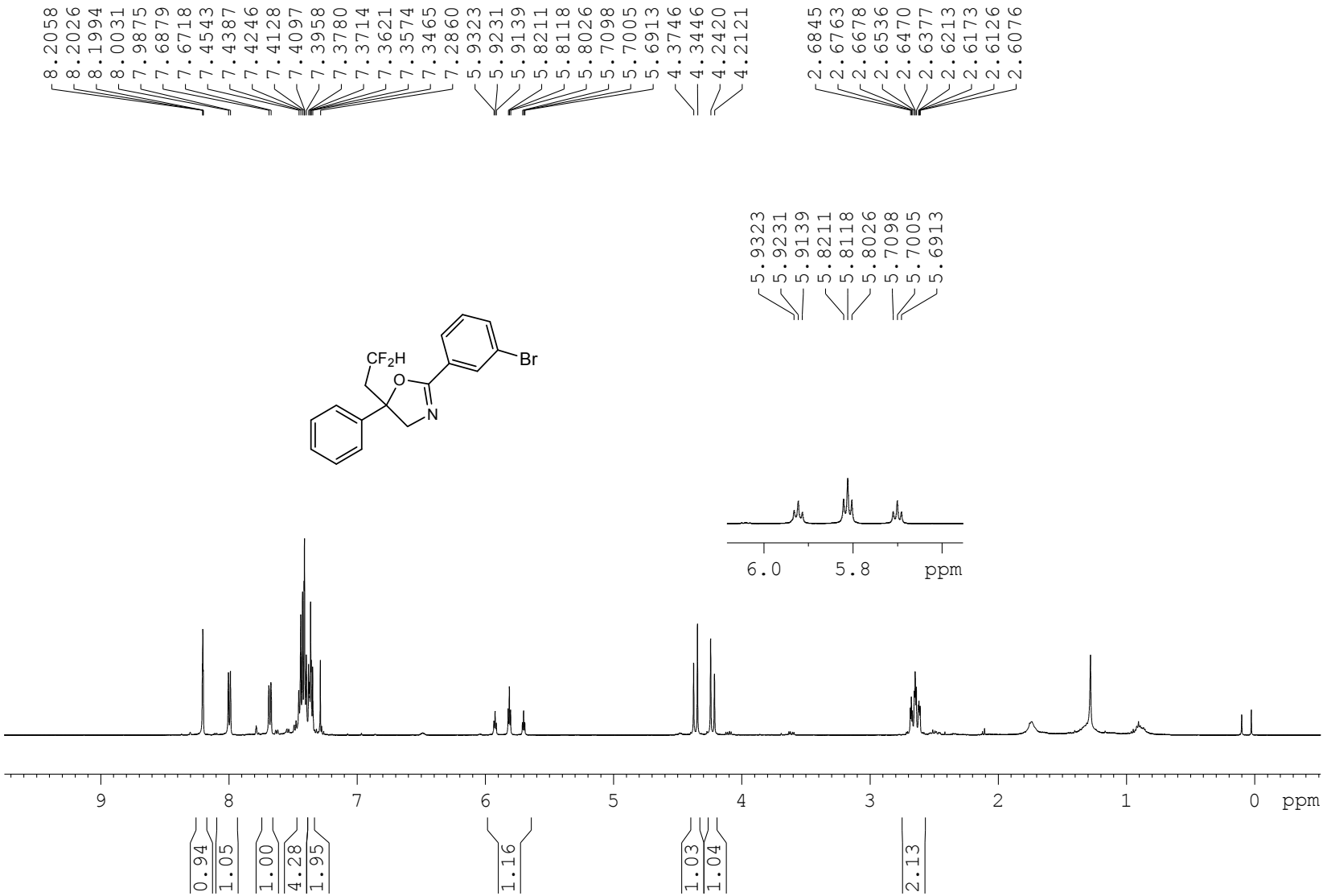
-40
-60
-80
-100
-120
-140
-160
-180
-200
ppm
1.00
0.93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8.2026
8.1994
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7.4128
7.4097
7.3958
7.3780
7.3714
7.3621
7.3574
7.3465
7.2860
5.9323
5.9231
5.9139
5.8211
5.8118
5.8026
5.7098
5.7005
5.6913
4.3746
4.3446
4.2420
4.2121
2.6845
2.6763
2.6678
2.6536
2.6470
2.6377
2.6213
2.6173
2.6126
2.6076
CF2H
O
N
Br
6.0
5.8
ppm
9
8
7
6
5
4
3
2
1
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ppm
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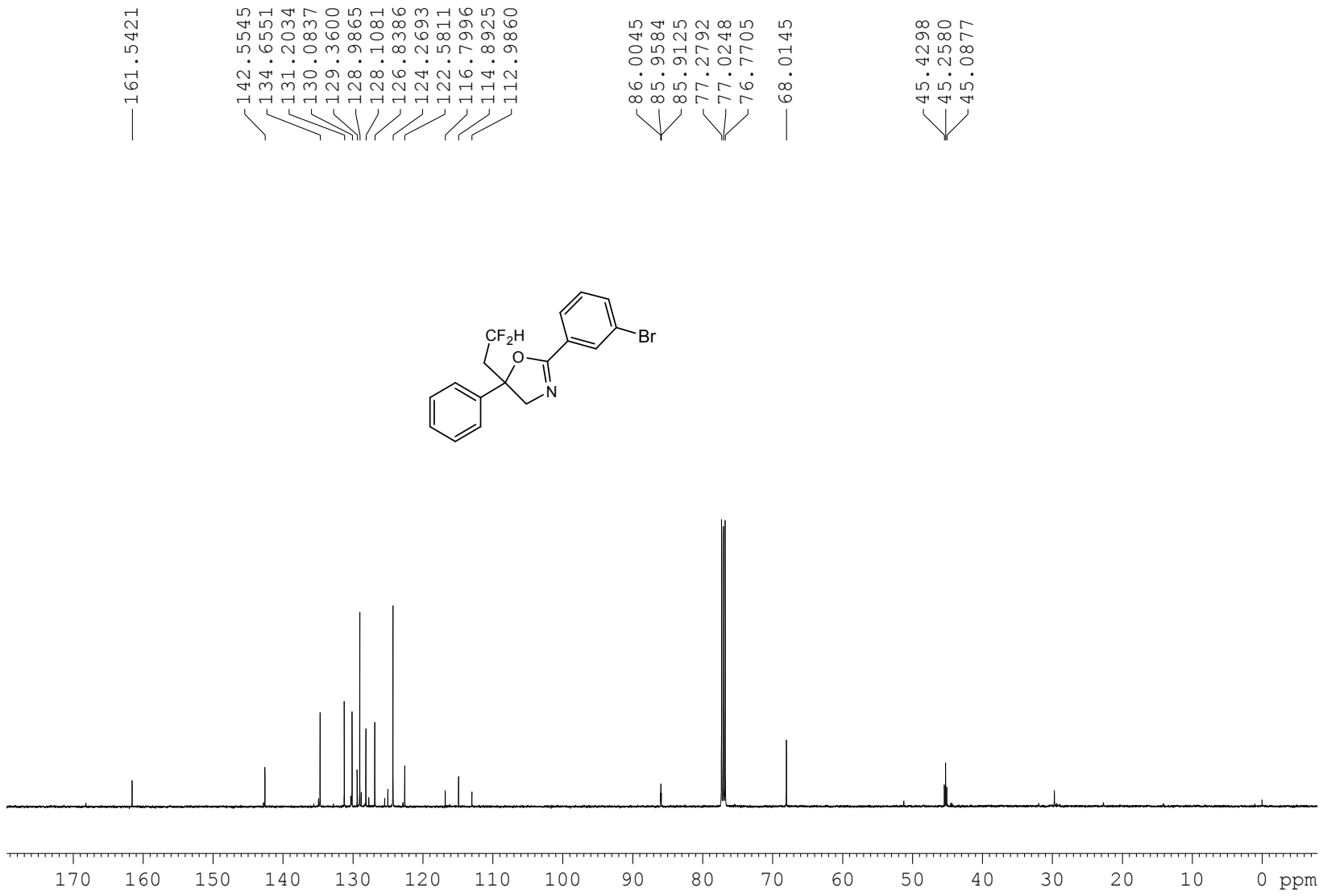
1.05
1.00
4.28
1.95
1.16
1.03
1.04
2.13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142.5545
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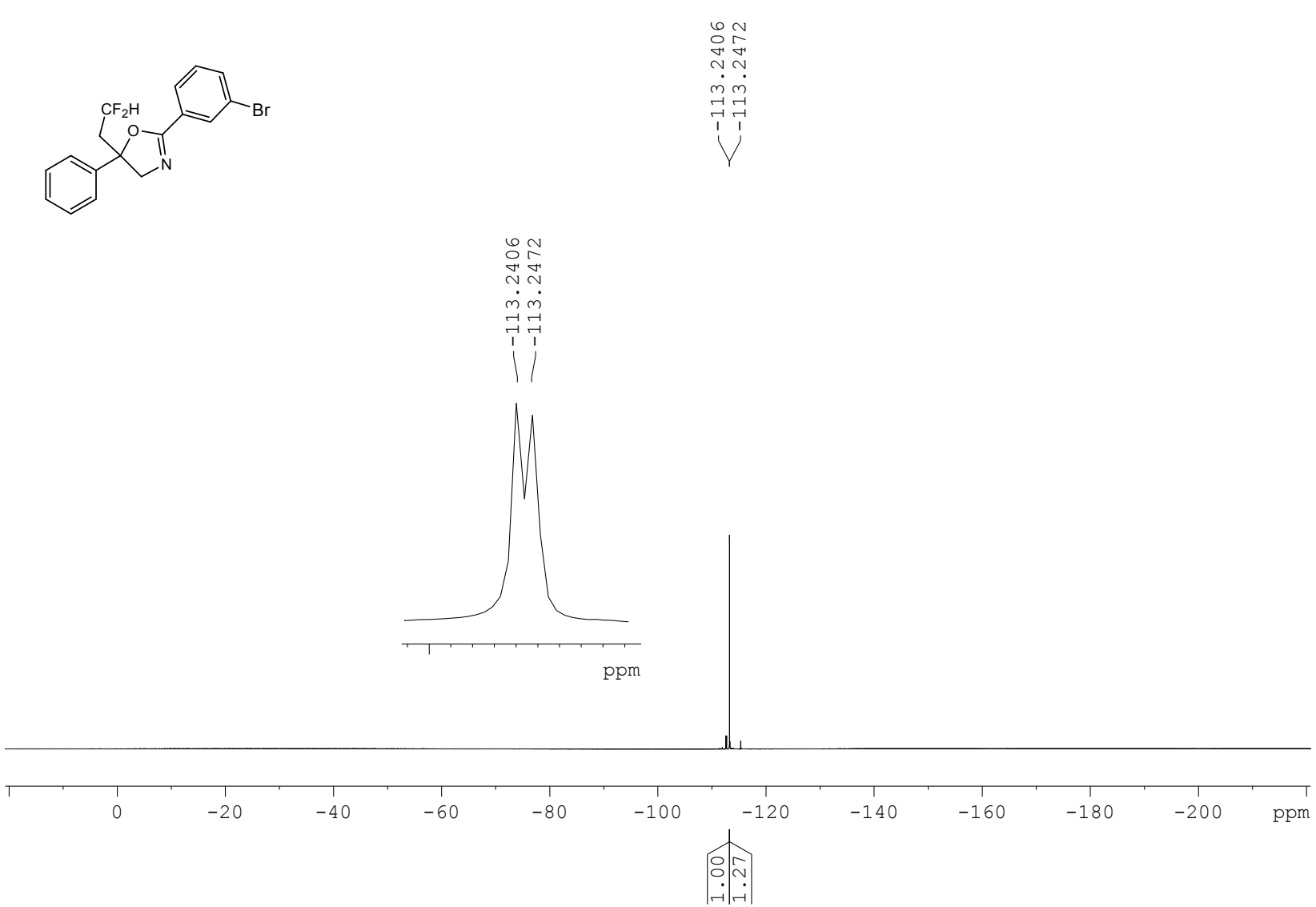
126.8386
124.2693
122.5811
116.7996
114.8925
112.9860
86.0045
85.9584
85.9125
77.2792
77.0248
76.7705
68.0145
45.4298
45.2580
45.0877
CF2H
O
N
Br
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0 ppm


CF2H
O
N
Br
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-113.2472
-113.2406
-113.2472
ppm
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-40
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-80
-100
-120
-140
-160
-180
-200
ppm
1.00
1.27