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Supporting Information

Catalytic Enantioselective Trifluoromethylthiolation of Oxindoles using Shelf-Stable N-(Trifluoromethylthio)phthalimide and a Cinchona Alkaloid Catalyst

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Table of Contents

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General Methods. Unless otherwise noted, all commercially available compounds were used as provided without further purification. Solvents for chromatography were technical grade and distilled prior to use. Dry dichloromethane, chloroform and chlorobenzene used in reactions were obtained by distilling over calcium hydride and were stored over activated molecular sieves (4 Å). Diethyl ether, toluene and *o*-xylene used in reactions were obtained by distilling over sodium-benzophenone ketyl. Analytical thin-layer chromatography (TLC) was performed on Macherey-Nagel silica gel 60 aluminium plates with F-254 indicator, visualised by UV irradiation. Column chromatography was performed using MN silica gel (particle size 0.040-0.063 mm). ^{1}H-NMR, ^{13}C-NMR, and ^{19}F-NMR spectra were recorded on a vnmrs-400 or vnmrs-600 spectrometer in $CDCl_3$ with residual proton signal of the deuterated solvents as the internal reference (δH = 7.26 ppm and δC = 77 ppm for $CDCl_3$ or δH = 0.00 ppm for TMS). Data are reported in the following order: chemical shift (δ) in ppm; multiplicities are indicated s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), dd (doublet of doublet), tt (triplet of triplet), dt (doublet of triplet), td (triplet of doublet); coupling constants (*J*) are in Hertz (Hz). IR spectra were recorded on a Jasco FT/IR-420 spectrometer and are reported in terms of frequency of absorption (cm^{-1}). (MS-EI, 70 eV) were conducted on Finnigan SSQ 7000 mass spectrometer. (MS-ESI) were conducted on ThermoFinnigan LCQ Deca XP plus. Melting points were recorded on a Büchi 560 Melting Point Apparatus. Optical rotations were measured on a Perkin Elmer 241 polarimeter. The enantiomeric excesses were determined by Supercritical Fluid Chromatography (SFC) analysis and HPLC ananlysis using a chiral stationary phase column (column, Daicel Co. Chiralpak IA or (S,S)-Whelk-01 columns. The chiral SFC methods and HPLC methods were calibrated with the corresponding racemic mixtures. Chemical yields refer to pure isolated substances. The yields and enantiomeric excesses are given in the corresponding tables.

The oxindoles **5a,**[1] **5b-l**,[2] and **5m-r**[3] were synthesized according to the literature procedures.

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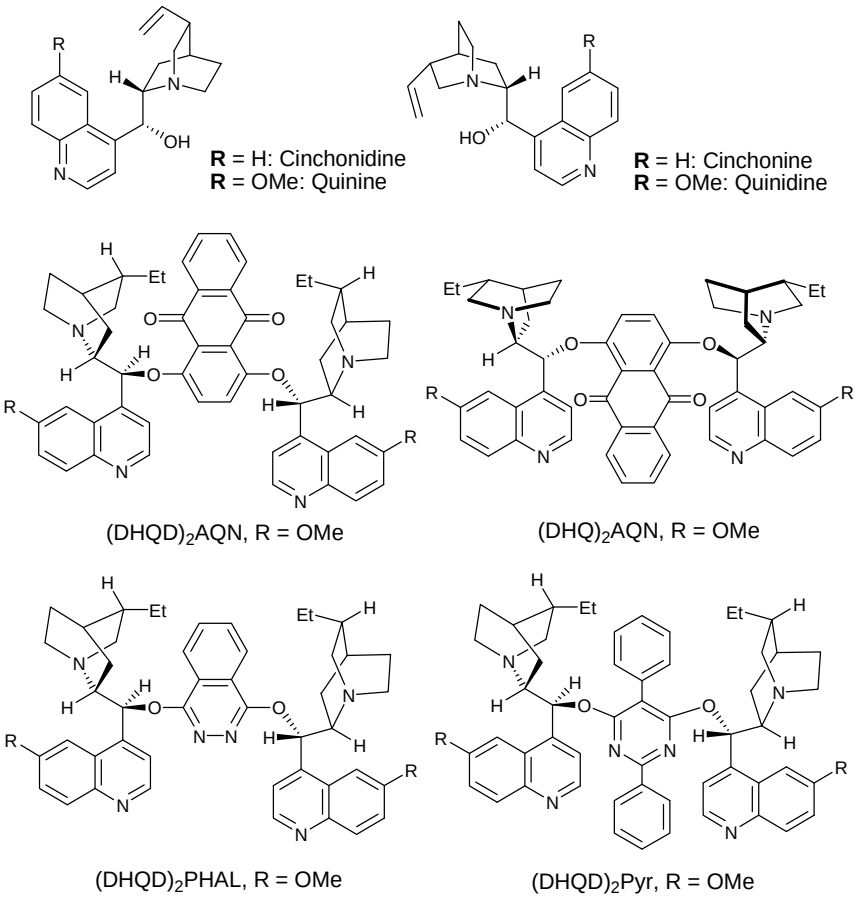
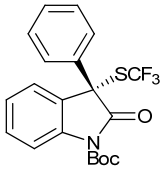
General procedure for enantioselective trifluoromethanesulfenylation:

In a screwcapped reaction tube, a mixture of oxindole **5a** (0.1 mmol, 1.0 equiv) and $(DHQD)_2Pyr$ (10 mol%) was dissolved in toluene (0.5 mL) and *N*-(trifluoromethylthio)phthalimide **1** (0.12 mmol, 1.2 equiv) was added at –10°C. The resulting solution was stirred at –10°C until being completed (TLC monitoring). The crude reaction mixture was directly charged on silica gel and purified by column chromatography (SiO_2, *n*-hexane/Et_2O, 94:6) to afford the desired product **6a**.

Figure 1. Structure of the catalysts evaluated in this study.

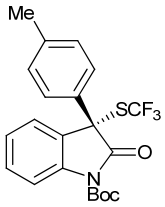


(*S*)-*tert*-Butyl 3-phenyl-3-(trifluoromethanesulfenyl)-2-oxoindoline-1-carboxylate



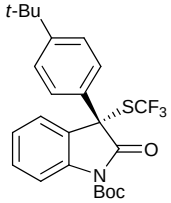
Isolated as a colorless oil, $[\alpha]_D^{RT}$ = +66.5 (*c*=1.62 in $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.97 (d, *J* = 8.3 Hz, 1H), 7.57 (dd, *J* = 7.6, 1.0 Hz, 1H), 7.55–7.49 (m, 2H), 7.46 (td, *J* = 7.9, 1.4 Hz, 1H), 7.40–7.30 (m, 4H), 1.62 (s, 9H); ^{13}C NMR (151 MHz, $CDCl_3$): δ = 172.3, 148.9, 139.2, 134.0, 130.4, 129.4, 129.1, 128.5 (q, *J* = 310.8 Hz, SCF_3), 127.7, 126.9, 126.0, 124.8, 115.7, 85.0, 59.5, 28.0; ^{19}F NMR (564 MHz, $CDCl_3$): δ = –38.8 (s, SCF_3); IR (ATR): $\tilde{\nu}$ =2984, 2935, 2429, 2262, 1778, 1604, 1474, 1340, 1294, 1253, 1117, 1029, 934, 840, 756, 697, 605, 541, 468 cm^{-1}; MS (ESI): m/z (%) = 432 ([M+Na]$^+$, 3), 327 (10), 313 (15), 180 (46), 166 (34) 148 (23); The enantiomeric excess was determined by chiral SFC using a (S,S) Whelk-01 column, 2% MeOH/CO_2, 4 mL min^{-1}, 231 nm; major enantiomer: t_R = 5.22 min, minor enantiomer: t_R = 7.20 min (92% ee).

(*S*)-*tert*-Butyl 3-*p*-tolyl-3-(trifluoromethanesulfenyl)-2-oxoindoline-1-carboxylate



Isolated as a colorless oil, $[\alpha]_D^{RT}$ = +55.3 (*c*=1.70 in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.96 (d, *J* = 8.2 Hz, 1H), 7.56 (dd, *J* = 7.6, 1.0 Hz, 1H), 7.48–7.42 (m, 1H), 7.42–7.35 (m, 2H), 7.32 (td, *J* = 7.6, 1.0 Hz, 1H), 7.16 (d, *J* = 8.1 Hz, 2H), 2.32 (s, 3H), 1.61 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 172.4, 148.9, 139.6, 139.2, 131.0, 130.3, 129.8, 128.5 (q, *J* = 310.9 Hz, SCF_3), 127.6, 126.9, 126.2, 124.7, 115.6, 85.0, 59.3, 28.0, 21.0; ^{19}F NMR (376 MHz, $CDCl_3$): δ = –38.9 (s, SCF_3); IR (ATR): $\tilde{\nu}$ =2982, 2323, 2098, 1774, 1738, 1605, 1469, 1339, 1289, 1249, 1111, 1026, 837, 749 cm^{-1}; MS (EI) *m/z* (%) = 423 ([M]$^+$, 4), 323 (13), 322 (17), 223 (17), 222 (100), 57 (27); HPLC conditions: IA column, *n*-hexane/2-propanol = 99/1, flow rate = 1.0 mL min^{-1}, minor enantiomer: t_R = 6.10 min; major enantiomer: t_R = 9.80 min (95% ee).

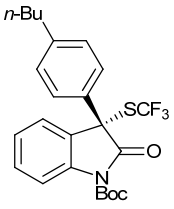
(*S*)-*tert*-Butyl 3-(4-*tert*-butylphenyl)-3-(trifluoromethanesulfenyl)-2-oxoindoline-1 -carboxylate



Isolated as a colorless oil, $[\alpha]_D^{RT}$ = +43.4 (*c*=2.02 in $CHCl_3$);^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.95 (d, *J* = 8.2 Hz, 1H), 7.57 (dd, *J* = 7.6, 1.1 Hz, 1H), 7.47–7.41 (m, 3H), 7.39–7.35 (m, 2H), 7.32 (td, *J* = 7.6, 1.0 Hz, 1H), 1.61 (s,

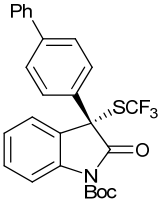
9H), 1.28 (s, 9H); ^{13}C NMR (151 MHz, $CDCl_3$): δ = 172.5, 152.6, 148.9, 139.2, 130.9, 130.3, 128.6 (q, J = 311.0 Hz, SCF_3), 127.4, 126.9, 126.2, 126.1, 124.7, 115.6, 85.0, 59.3, 34.6, 31.1, 28.0; ^{19}F NMR (564 MHz, $CDCl_3$): δ = –38.9 (s, SCF_3); IR (ATR): $\tilde{\nu}$ =2970, 2318, 1772, 1736, 1606, 1471, 1342, 1289, 1251, 1114, 1022, 938, 830, 750, 679 cm^{-1}; MS (ESI): m/z (%) = 488 ([M+Na]$^+$, 94), 483 (23), 411 (13), 410 (62), 388 (24), 366 (29), 264 (45), 191 (11); The enantiomeric excess was determined by chiral SFC using a (S,S) Whelk-01 column, 2% $MeOH/CO_2$, 4 mL min^{-1}, 231 nm; major enantiomer: t_R = 4.73 min, minor enantiomer: t_R = 9.58 min (94% ee).

(*S*)-*tert*-Butyl 3-(4-butylphenyl)-3-(trifluoromethanesulfenyl)-2-oxoindoline-1-Carboxylate



Isolated as a colorless oil, $[\alpha]_D^{RT}$ = +45.6 (c=1.77 in $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.96 (d, J = 8.3 Hz, 1H), 7.57 (dd, J = 7.6, 1.1 Hz, 1H), 7.45 (ddd, J = 8.3, 7.7, 1.4 Hz, 1H), 7.42–7.39 (m, 2H), 7.32 (td, J = 7.6, 1.0 Hz, 1H), 7.18–7.14 (m, 2H), 2.60–2.55 (m, 2H), 1.62 (s, 9H), 1.59–1.53 (m, 2H), 1.37–1.29 (m, 2H), 0.91 (dd, J = 8.5, 6.3 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$): δ = 172.5, 148.9, 144.5, 139.2, 131.1, 130.3, 129.2, 128.6 (q, J = 311.0 Hz, SCF_3), 127.6, 126.9, 126.2, 124.7, 115.6, 85.0, 59.4, 35.2, 33.3, 28.0, 22.3, 13.9; ^{19}F NMR (564 MHz, $CDCl_3$): δ = –38.9 (s, SCF_3); IR (ATR): $\tilde{\nu}$ = 2938, 2866, 2170, 1768, 1734, 1602, 1467, 1372, 1332, 1284, 1250, 1103, 1022, 868, 829, 753, 673 cm^{-1}; MS (ESI): *m/z* (%) = 488 ([M+Na]$^+$, 20), 410 (15), 366 (4), 181 (12), 180 (92), 166 (14), 148 (29), 134 (11); The enantiomeric excess was determined by chiral SFC using a (S,S) Whelk-01 column, 2% $MeOH/CO_2$, 4 mL min^{-1}, 231 nm; major enantiomer: t_R = 6.04 min, minor enantiomer: t_R = 11.39 min (94% ee).

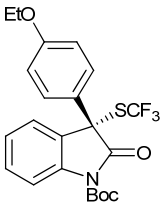
(*S*)-*tert*-Butyl 3-(biphenyl-4-yl)-3-(trifluoromethanesulfenyl)-2-oxoindoline-1 -carboxylate



Isolated as a colorless oil, $[\alpha]_D^{RT}$ = +43.1 (c=1.93 in $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.99 (d, J = 8.4 Hz, 1H), 7.61 (dd, J = 7.7, 1.1 Hz, 1H), 7.60–7.56 (m, 4H), 7.56–7.53 (m, 2H), 7.48 (ddd, J = 8.2, 7.7, 1.4 Hz, 1H),

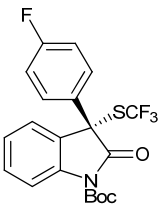
7.46–7.42 (m, 2H), 7.39–7.33 (m, 2H), 1.63 (s, 9H); ^{13}C NMR (151 MHz, $CDCl_3$): δ 172.3, 148.9, 142.3, 139.9, 139.3, 132.8, 130.4, 128.9, 128.5 (q, J = 310.9 Hz, SCF_3), 128.1, 127.8, 127.8, 127.1, 126.9, 126.0, 124.9, 115.7, 85.1, 59.4, 28.0; ^{19}F NMR (564 MHz, $CDCl_3$): δ = –38.8 (s, SCF_3); IR (ATR): $\tilde{\nu}$ = 2983, 2288, 2062, 1970, 1775, 1737, 1604, 1474, 1339, 1289, 1250, 1108, 1017, 906, 832, 747, 697 cm^{-1}; MS (ESI): *m/z* (%) = 508 ([M+Na]$^+$, 55), 430 (22), 408 (13), 386 (6), 284 (20), 191 (16); The enantiomeric excess was determined by chiral SFC using a (S,S) Whelk-01 column, 5% MeOH/CO_2, 4 mL min^{-1}, 231 nm; major enantiomer: t_R = 8.14 min, minor enantiomer: t_R = 16.08 min (91% ee).

(*S*)-*tert*-Butyl 3-(4-ethoxyphenyl)-3-(trifluoromethanesulfenyl)-2-oxoindoline-1 -carboxylate



Isolated as a colorless oil, $[\alpha]_D^{RT}$ = +39.8 (*c*=1.48 in $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.95 = (d, J = 8.2 Hz, 1H), 7.57 (dd, J = 7.6, 1.1 Hz, 1H), 7.47–7.41 (m, 3H), 7.32 (td, J = 7.6, 1.0 Hz, 1H), 6.88–6.83 (m, 2H), 4.00 (q, J = 7.0 Hz, 2H), 1.61 (s, 9H), 1.39 (t, J = 7.0 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$): δ = 172.6, 159.7, 149.0, 139.2, 130.3, 129.1, 128.5 (q, J = 311.3 Hz, SCF_3), 126.9, 126.2, 125.2, 124.7, 115.7, 114.9, 85.0, 63.6, 59.0, 28.0, 14.7; ^{19}F NMR (564 MHz, $CDCl_3$): δ = –39.1 (s, SCF_3); IR (ATR): $\tilde{\nu}$ = 2983, 2263, 1775, 1738, 1605, 1472, 1340, 1292, 1250, 1107, 1040, 920, 828, 750 cm^{-1}; MS (ESI): *m/z* (%) = 476 ([M+Na]$^+$, 16), 398 (4), 181 (11), 180 (89), 166 (27), 148 (35); The enantiomeric excess was determined by chiral SFC using a (S,S) Whelk-01 column, 5% MeOH/CO_2, 4 mL min^{-1}, 231 nm; major enantiomer: t_R = 4.76 min, minor enantiomer: t_R = 9.00 min (94% ee).

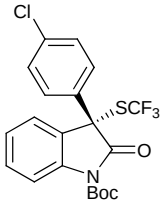
(*S*)-*tert*-Butyl 3-(4-fluorophenyl)-3-(trifluoromethanesulfenyl)-2-oxoindoline-1 -carboxylate



Isolated as a colorless oil, $[\alpha]_D^{RT}$ = +80.5 (*c*=1.53 in $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.97 (d, J = 8.2 Hz, 1H), 7.56 (dd, J = 7.6, 1.0 Hz, 1H), 7.54–7.50 (m, 2H), 7.47 (ddd, J = 8.2, 7.7, 1.4 Hz, 1H), 7.34 (td, J = 7.6, 1.0 Hz, 1H), 7.08–7.02 (m, 2H), 1.62 (s, 9H); ^{13}C NMR (151 MHz, $CDCl_3$): δ =

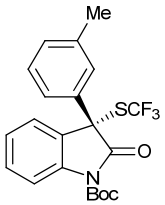
172.2, 163.2 (d, J = 250.7 Hz), 148.8, 139.2, 130.6, 129.9 (d, J = 8.5 Hz), 129.7 (d, J = 2.7 Hz), 128.4 (q, J = 311.1 Hz, SCF_3), 126.8, 125.8, 124.9, 116.1 (d, J = 21.9 Hz), 115.8, 85.2, 58.8, 28.0; ^{19}F NMR (564 MHz, $CDCl_3$): δ = –38.9 (s, SCF_3), –111.5–111.6 (m, F); IR (ATR): $\tilde{\nu}$ = 2984, 2292, 1739, 1603, 1470, 1339, 1290, 1244, 1106, 1020, 936, 826, 752 cm^{-1}; MS (ESI): *m/z* (%) = 450 ($[M+Na]^+$, 31), 348 (3), 181 (13), 180 (100), 166 (16), 148 (35); The enantiomeric excess was determined by chiral SFC using a (S,S) Whelk-01 column, 2% $MeOH/CO_2$, 4 mL min^{-1}, 231 nm; major enantiomer: t_R = 3.44 min, minor enantiomer: t_R = 5.55 min (92% ee).

(*S*)-*tert*-Butyl 3-(4-chlorophenyl)-3-(trifluoromethanesulfenyl)-2-oxoindoline-1-carboxylate



Isolated as a colorless oil, $[\alpha]_D^{RT}$ = +70.7 (*c*=1.57 in $CHCl_3$); ^1H NMR (600 MHz, $CDCl_3$): δ = 7.97 (d, J = 8.2 Hz, 1H), 7.54 (dd, J = 7.6, 1.1 Hz, 1H), 7.50–7.44 (m, 3H), 7.36–7.30 (m, 3H), 1.62 (s, 9H); ^{13}C NMR (151 MHz, $CDCl_3$): δ = 172.0, 148.8, 139.2, 135.8, 132.5, 130.6, 129.3, 129.2, 128.4 (q, J = 311.2 Hz, SCF_3), 126.8, 125.6, 125.0, 115.8, 85.3, 58.9, 28.0; ^{19}F NMR (564 MHz, $CDCl_3$): δ = –38.8 (s, SCF_3); IR (ATR): $\tilde{\nu}$ = 2983, 2171, 1773, 1739, 1603, 1476, 1339, 1290, 1250, 1103, 1016, 825, 752 cm^{-1}; MS (ESI): *m/z* (%) = 468 ($[M+Na]^+$+2, 35), 466 ($[M+Na]^+$, 100), 390 (25), 388 (64), 368 (9), 366 (27), 344 (10), 244 (10), 242 (33), 208 (14), 191 (16); The enantiomeric excess was determined by chiral SFC using a (S,S) Whelk-01 column, 2% $MeOH/CO_2$, 4 mL min^{-1}, 231 nm; major enantiomer: t_R = 5.17 min, minor enantiomer: t_R = 9.28 min (84% ee).

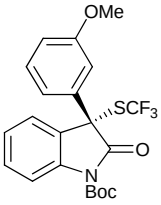
(*S*)-*tert*-Butyl 3-*m*-tolyl-3-(trifluoromethanesulfenyl)-2-oxoindoline-1-carboxylate



Isolated as a white solid, mp: 93–95 °C, $[\alpha]_D^{RT}$ = +63.7 (*c*=1.68 in $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ = 7.96 (d, J = 8.2 Hz, 1H), 7.55 (dd, J = 7.6, 1.1 Hz, 1H), 7.48–7.42 (m, 1H), 7.36–7.29 (m, 2H), 7.24 (dt, J = 10.7, 6.4 Hz, 2H), 7.18–7.14 (m, 1H), 2.33 (s, 3H), 1.62 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 172.4, 148.9, 139.2, 139.1, 134.0, 130.3, 130.2, 128.9, 128.6 (q, J = 311.0 Hz, SCF_3), 128.2, 126.9, 126.2, 124.8, 124.7, 115.6, 85.0, 59.5, 28.0, 21.5; ^{19}F NMR (376 MHz, $CDCl_3$): δ –38.9 (s, SCF_3);

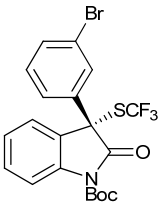
IR (ATR): $\tilde{\nu}$ = 2982, 2931, 2326, 2092, 1776, 1738, 1602, 1471, 1338, 1289, 1250, 1111, 1033, 841, 748, 693 cm^{-1}; MS (ESI): *m/z* (%) = 446 ($[M+Na]^+$, 25), 369 (14), 368 (72), 346 (13), 324 (26), 222 (50) ; HPLC conditions: IA column, *n*-hexane/2-propanol = 99/1, flow rate = 1.0 mL min^{-1}, minor enantiomer: t_R = 5.99 min; major enantiomer: t_R = 8.77 min (92% ee).

(*S*)-*tert*-Butyl 3-(3-methoxyphenyl)-3-(trifluoromethanesulfenyl)-2-oxoindoline-1-carboxylate



Isolated as a white solid, mp: 71–73 °C, $[\alpha]_D^{RT}$ = +61.7 (*c*=1.69 in $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ = 7.96 (d, *J* = 8.2 Hz, 1H), 7.56 (dd, *J* = 7.6, 1.1 Hz, 1H), 7.45 (td, *J* = 8.0, 1.4 Hz, 1H), 7.32 (td, *J* = 7.6, 1.0 Hz, 1H), 7.26 (dd, *J* = 8.6, 7.6 Hz, 1H), 7.09 (t, *J* = 2.2, 1H), 7.05 (ddd, *J* = 7.9, 1.9, 0.8 Hz, 1H), 6.89 (ddd, *J* = 8.3, 2.5, 0.8 Hz, 1H), 3.78 (s, 3H), 1.62 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 172.2, 160.0, 148.9, 139.2, 135.5, 130.4, 130.0, 128.5 (q, *J* = 310.8 Hz, SCF_3), 126.9, 126.0, 124.8, 119.8, 115.7, 114.8, 113.7, 85.0, 59.4, 55.3, 28.0; ^{19}F NMR (564 MHz, $CDCl_3$): δ = –38.9 (s, SCF_3); IR (ATR): $\tilde{\nu}$ = 2982, 2844, 2344, 2110, 2011, 1792, 1730, 1597, 1469, 1369, 1250, 1109, 1045, 939, 841, 763, 687 cm^{-1}; MS (ESI): *m/z* (%) = 462 ($[M+Na]^+$, 14), 457 ($[M+H_2O]^+$, 5), 385 (5), 384 (27), 340 (14), 238 (11); HPLC conditions: IA column, *n*-hexane/2-propanol = 99/1, flow rate = 1.0 mL min^{-1}, minor enantiomer: t_R = 10.26 min; major enantiomer: t_R = 12.90 min (90% ee).

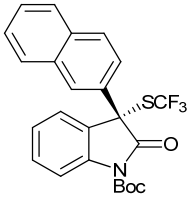
(*S*)-*tert*-Butyl 3-(3-bromophenyl)-3-(trifluoromethanesulfenyl)-2-oxoindoline-1-carboxylate



Isolated as a white solid, mp: 111–113 °C, $[\alpha]_D^{RT}$ = +51.4 (*c*=1.50 in $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ = 7.98 (d, *J* = 8.3 Hz, 1H), 7.62 (t, *J* = 1.9 Hz, 1H), 7.54 (dd, *J* = 7.6, 1.0 Hz, 1H), 7.52–7.45 (m, 3H), 7.34 (td, *J* = 7.6, 1.0 Hz, 1H), 7.25 (t, *J* = 8.0 Hz, 1H), 1.62 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 171.8, 148.7, 139.2, 136.2, 132.6, 130.7, 130.5, 128.4 (q, *J* = 311.0 Hz, SCF_3), 126.8, 126.5, 125.3, 125.1, 123.2, 115.9, 85.3, 58.9, 28.0; ^{19}F NMR (376 MHz, $CDCl_3$): δ = –38.7 (s, SCF_3); IR (ATR): $\tilde{\nu}$ = 2983, 2289, 2103, 1774, 1739, 1600, 1470, 1338, 1289, 1250, 1105, 1024, 939, 841, 753,

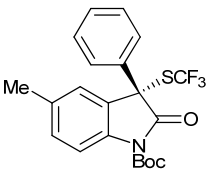
681 cm^{-1}; MS (ESI): *m/z* (%) = 512 ($[M+Na]^+$+2, 30), 510 ($[M+Na]^+$, 28), 507 ($[M+H_2O]^+$+2, 18), 505 ($[M+H_2O]^+$, 18), 435 (14), 434 (79), 433 (13), 432 (78), 390 (15), 388 (15), 288 (19), 286 (19); HPLC conditions: IA column, *n*-hexane/2-propanol = 99/1, flow rate = 1.0 mL min^{-1}, minor enantiomer: t_R = 5.38 min; major enantiomer: t_R = 7.53 min (88% ee).

(*S*)-*tert*-Butyl 3-(naphthalen-2-yl)-3-(trifluoromethanesulfenyl)-2-oxoindoline-1-carboxylate



Isolated as a colorless oil, $[\alpha]_D^{RT}$ = +30.3 (*c*=1.91 in $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ = 8.01 (d, *J* = 8.2 Hz, 1H), 7.88–7.76 (m, 4H), 7.73 (dd, *J* = 8.8, 2.0 Hz, 1H), 7.64 (dd, *J* = 7.6, 1.1 Hz, 1H), 7.56–7.45 (m, 3H), 7.37 (td, *J* = 7.6, 1.0 Hz, 1H), 1.61 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 172.3, 148.9, 139.3, 133.2, 132.9, 130.5, 130.1, 129.2, 128.6 (q, *J* = 311.0 Hz, SCF_3), 128.5, 127.6, 127.5, 127.3, 127.0, 126.8, 126.1, 124.9, 124.4, 115.8, 85.1, 59.8, 28.0; ^{19}F NMR (376 MHz, $CDCl_3$): δ = –38.6 (s, SCF_3); IR (ATR): $\tilde{\nu}$ = 2983, 2309, 1738, 1602, 1470, 1339, 1288, 1249, 1106, 1025, 905, 820, 747, 677 cm^{-1}; MS (EI) *m/z* (%) = 459 ($[M]^+$, 5), 359 (11), 358 (30), 259 (21), 258 (100), 230 (6), 229 (4), 57 (23), 45 (11); HPLC conditions: IA column, *n*-hexane/2-propanol = 99/1, flow rate = 1 mL min^{-1}, minor enantiomer: t_R = 9.49 min; major enantiomer: t_R = 27.82 min (88% ee).

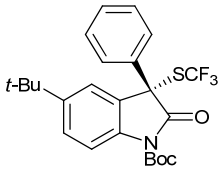
(*S*)-*tert*-Butyl 5-methyl-3-phenyl-3-(trifluoromethanesulfenyl)-2-oxoindoline-1-carboxylate



Isolated as a colorless oil, $[\alpha]_D^{RT}$ = +76.8 (*c*=1.60 in $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ = 7.83 (d, *J* = 8.4 Hz, 1H), 7.55–7.48 (m, 2H), 7.40–7.32 (m, 4H), 7.25 (d, *J* = 8.0, 1H), 2.42 (s, 3H), 1.61 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 172.5, 149.0, 136.9, 134.6, 134.2, 131.0, 129.3, 129.1, 128.6 (q, *J* = 310.9 Hz, SCF_3), 127.7, 127.2, 126.0, 115.5, 84.9, 59.7, 28.0, 21.1; ^{19}F NMR (376 MHz, $CDCl_3$): δ = –38.9 (s, SCF_3); IR (ATR): $\tilde{\nu}$ = 2981, 2328, 2104, 1773, 1738, 1603, 1468, 1340, 1292, 1249, 1142, 1096, 845, 751 cm^{-1}; MS (ESI): *m/z* (%) = 446 ($[M+Na]^+$, 22), 441 ($[M+H_2O]^+$, 10), 369 (5), 368 (29), 346 (10), 324 (8), 222 (10); HPLC conditions: IA column,

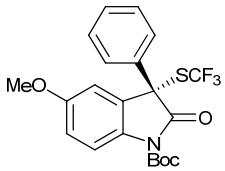
n-hexane/2-propanol = 99/1, flow rate = 1.0 mL min^{-1}, minor enantiomer: t_R = 6.21 min; major enantiomer: t_R = 9.76 min (94% ee).

(*S*)-*tert*-Butyl 5-*tert*-butyl-3-phenyl-3-(trifluoromethanesulfenyl)-2-oxoindoline-1 -carboxylate



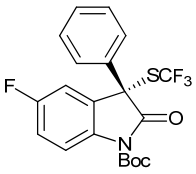
Isolated as a colorless oil, $[\alpha]_D^{RT}$ = +61.0 (*c*=1.21 in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.85 (d, *J* = 8.7 Hz, 1H), 7.58 (d, *J* = 2.0 Hz, 1H), 7.54–7.49 (m, 2H), 7.47 (dd, *J* = 8.6, 2.1 Hz, 1H), 7.39–7.34 (m, 3H), 1.61 (s, 9H), 1.36 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 172.8, 148.9, 148.1, 136.8, 134.3, 129.3, 129.1, 128.6 (q, *J* = 310.7 Hz, SCF_3), 127.7, 127.1, 125.3, 124.2, 115.2, 84.8, 59.9, 34.7, 31.3, 28.0; ^{19}F NMR (376 MHz, $CDCl_3$): δ = –38.9 (s, SCF_3); IR (ATR): $\tilde{\nu}$ = 2967, 2290, 1777, 1739, 1601, 1489, 1369, 1334, 1303, 1252, 1148, 1031, 925, 836, 757, 699, 576, 465 cm^{-1}; MS (ESI): *m/z* (%) = 488 ([M+Na]$^+$, 15), 411 (14), 410 (63), 366 (15), 309 (27), 264 (26), 254 (12); The enantiomeric excess was determined by chiral SFC using a (S,S) Whelk-01 column, 2% MeOH/CO_2, 2 mL min^{-1}, 231 nm; major enantiomer: t_R = 5.72 min, minor enantiomer: t_R = 9.21 min (92% ee).

(*S*)-*tert*-Butyl 5-methoxy-3-phenyl-3-(trifluoromethanesulfenyl)-2-oxoindoline-1 -carboxylate



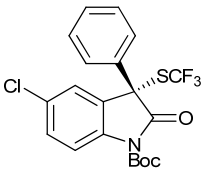
Isolated as a colorless oil, $[\alpha]_D^{RT}$ = +71.2 (*c*=1.00 in $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.89 (d, *J* = 9.0 Hz, 1H), 7.55–7.48 (m, 2H), 7.36 (dd, *J* = 5.2, 2.0 Hz, 3H), 7.10 (d, *J* = 2.6 Hz, 1H), 6.99 (dd, *J* = 9.0, 2.7 Hz, 1H), 3.85 (s, 3H), 1.61 (s, 9H); ^{13}C NMR (151 MHz, $CDCl_3$): δ = 172.4, 157.0, 149.0, 134.1, 132.6, 129.4, 129.1, 128.5 (q, *J* = 311.0 Hz, SCF_3), 127.7, 127.3, 116.8, 115.8, 112.4, 84.8, 59.8, 55.8, 28.0; ^{19}F NMR (282 MHz, $CDCl_3$): δ –38.8 (s, SCF_3); IR (ATR): $\tilde{\nu}$ = 2980, 2841, 2424, 2288, 1775, 1736, 1602, 1488, 1334, 1280, 1152, 1036, 840, 756, 607, 567, 466 cm^{-1}; MS (ESI): *m/z* (%) = 462 ([M+Na]$^+$, 18), 385 (6), 384 (37), 362 (7), 340 (14), 238 (12); HPLC conditions: IA column, *n*-hexane/2-propanol = 99/1, flow rate = 1.0 mL min^{-1}, minor enantiomer: t_R = 9.09 min; major enantiomer: t_R = 14.18 min (94% ee).

(*S*)-*tert*-Butyl 5-fluoro-3-phenyl-3-(trifluoromethanesulfenyl)-2-oxoindoline-1-carboxylate



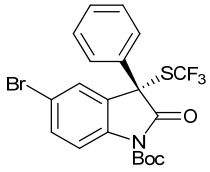
Isolated as a colorless oil, $[\alpha]_D^{RT}$ = +59.2 (*c*=1.43 in $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ = 7.98 (dd, *J* = 9.0, 4.5 Hz, 1H), 7.53–7.47 (m, 2H), 7.42–7.35 (m, 3H), 7.29 (dd, *J* = 7.6, 2.7 Hz, 1H), 7.17 (td, *J* = 8.9, 2.7 Hz, 1H), 1.61 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 171.9, 159.9 (d, *J* = 245.1 Hz), 148.9, 135.2 (d, *J* = 2.4 Hz), 133.5, 129.6, 129.3, 128.4 (q, *J* = 311.0 Hz, SCF_3), 128.0 (d, *J* = 8.3 Hz), 127.5, 117.3 (d, *J* = 22.9 Hz), 117.3 (d, *J* = 7.8 Hz), 114.0 (d, *J* = 25.1 Hz), 85.3, 59.4, 28.0; ^{19}F NMR (564 MHz, $CDCl_3$): δ = –38.8 (s, SCF_3), –116.42–116.48 (m, F); IR (ATR): $\tilde{\nu}$ = 2982, 2931, 2263, 1774, 1737, 1597, 1488, 1330, 1253, 1110, 1033, 910, 826, 729 cm^{-1}; MS (ESI): *m/z* (%) = 450 ($[M+Na]^+$, 17), 445 ($[M+H_2O]^+$, 12), 410 (7), 373 (10), 372 (56), 350 (6), 209 (22), 226 (12); HPLC conditions: IA column, *n*-hexane/2-propanol = 99/1, flow rate = 1.0 mL min^{-1}, minor enantiomer: t_R = 5.23 min; major enantiomer: t_R = 8.95 min (90% ee).

(*S*)-*tert*-Butyl 5-chloro-3-phenyl-3-(trifluoromethanesulfenyl)-2-oxoindoline-1-carboxylate



Isolated as a colorless oil, $[\alpha]_D^{RT}$ = +75.0 (*c*=1.50 in $CHCl_3$); ^1H NMR (600 MHz, $CDCl_3$): δ = 7.94 (d, *J* = 8.8 Hz, 1H), 7.54 (d, *J* = 2.2 Hz, 1H), 7.53–7.47 (m, 2H), 7.43 (dd, *J* = 8.8, 2.3 Hz, 1H), 7.42–7.35 (m, 3H), 1.61 (s, 9H); ^{13}C NMR (151 MHz, $CDCl_3$): δ = 171.6, 148.7, 137.7, 133.4, 130.5, 130.4, 129.7, 129.3, 128.4 (q, *J* = 311.1 Hz, SCF_3), 128.0, 127.5, 126.8, 117.0, 85.5, 59.2, 28.0; ^{19}F NMR (282 MHz, $CDCl_3$): δ = –38.7 (s, SCF_3); IR (ATR): $\tilde{\nu}$ = 3460, 2984, 2934, 2271, 1780, 1740, 1595, 1474, 1372, 1331, 1290, 1256, 1150, 1028, 959, 863, 830, 757, 700, 553, 471 cm^{-1}; MS (ESI): *m/z* (%) = 468 ($[M+Na]^+$+2, 14), 466 ($[M+Na]^+$, 38), 463 ($[M+H_2O]^+$+2, 11), 461 ($[M+H_2O]^+$, 33), 391 (6), 390 (37), 389 (17), 388 (100), 368 (4), 366 (13), 344 (7), 244 (8), 242 (25); HPLC conditions: IA column, *n*-hexane/2-propanol = 99/1, flow rate = 1.0 mL min^{-1}, minor enantiomer: t_R = 4.90 min; major enantiomer: t_R = 8.08 min (86% ee).

(*S*)-*tert*-Butyl 5-bromo-3-phenyl-3-(trifluoromethanesulfenyl)-2-oxoindoline-1 -carboxylate



Isolated as a colorless oil, $[\alpha]_D^{RT}$ = +76.3 (*c*=1.97 in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.89 (d, *J* = 8.8 Hz, 1H), 7.68 (d, *J* = 2.1 Hz, 1H), 7.58 (dd, *J* = 8.8, 2.1 Hz, 1H), 7.53–7.46 (m, 2H), 7.43–7.35 (m, 3H), 1.61 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 171.5, 148.7, 138.3, 133.4, 129.6, 129.3, 128.4 (q, *J* = 311.1 Hz, SCF_3), 128.3, 127.5, 117.8, 117.4, 85.5, 59.1, 28.0; ^{19}F NMR (376 MHz, $CDCl_3$): δ = –38.7 (s, SCF_3); IR (ATR): $\tilde{\nu}$ = 3460, 2984, 2934, 2268, 1778, 1739, 1599, 1471, 1371, 1331, 1291, 1255, 1149, 1114, 1025, 951, 863, 829, 758, 693, 613, 541, 468 cm^{-1}; MS (ESI): *m/z* (%) = 512 ($[M+Na]^+$+2, 11), 510 ($[M+Na]^+$, 12), 507 ($[M+H_2O]^+$+2, 16), 505 ($[M+H_2O]^+$, 17), 435 (16), 434 (91), 433 (15), 432 (89), 427 (36), 355 (17), 354 (100), 288 (10), 286 (10); The enantiomeric excess was determined by chiral SFC using a (S,S) Whelk-01 column, 2% $MeOH/CO_2$, 4 mL min^{-1}, 231 nm; major enantiomer: t_R = 5.08 min, minor enantiomer: t_R = 7.06 min (85% ee).

X-Ray Crystallographic Analysis of 7k:

Suitable crystals for single crystal analysis were obtained by recrystallization from a DCM/hexane mixture and slow evaporation of the solvent at ambient temperature. Intensity data were collected at 100 K with a *Bruker APEX* area detector equipped with an *Incoatec microsource* (Mo-K_α, λ = 0.71073 Å, multilayer optics). Temperature was controlled with an *Oxford Cryostream 700* instrument. Intensities were processed with *SAINT+*[4] and corrected for absorption by multi-scan methods using *SADABS*[5].

The crystal structure of **6k** was solved by direct methods (SHELXS-97)[6] and refined by full matrix least squares procedures based on F^2 as implemented in SHELXL-13[6]. Non-hydrogen atoms were assigned anisotropic displacement parameters and hydrogen atoms were placed in idealized positions. The crystal data and refinement results are summarized in Table 1.

After the assignment of the well ordered electron density maxima, residual density close to

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C3 indicated minor positional disorder of the bromine atom. The introduction of a split model with two alternative bromine positions converged with a 90/10 ration.

Table 1: Crystal data and refinement results of **6k**

Parameter	6K
Empirical formula	$C_{20}H_{17}BrF_3NO_3S$
M/g mol^{-1}	488.32
Crystal dimensions/mm	0.09 x 0.09 x 0.12
Crystal shape	Plate
Crystal color	Colorless
Crystal system	Orthorhombic
Space group (no.)	$P2_12_12_1$
a/Å	9.7850(8)
b/Å	14.3183(11)
c/Å	14.4323(11)
α/°	90
β/°	90
γ/°	90
V/Å^3	2022.0(3)
Z	4
μ(Mo K$_\alpha$)/mm^{-1}	2.185
Total reflections	29388
Unique reflections	5385
Flack parameter	0.020(4)
Variables refined	275
R_{int}	0.0536
wR_2 (all reflections)	0.0653
R_1 (all/obs.)	0.0335/0.0301
GOF on F^2	1.073
Diff. peak/hole [e/ Å^{-3}]	0.361/-0.216

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3. S. -W. Duan, J. An, J. -R. Chen and W. -J. Xiao, *Org. Lett.*, 2011, **13**, 2290.
4. SAINT, *Bruker AXS, Program for Reduction of Data collected on Bruker CCD Area Detector Diffractometer V.6.02*, Bruker AXS Inc., Madison, WI, USA, 1999.
5. SADABS, *Program for Empirical Absorption Correction of Area Detector Data V 2004/1*, Bruker AXS Inc., Madison, WI, USA, 2004.
6. (*a*) G. M. Sheldrick, *SHELXL-13 Program for Crystal Structure Refinement*, Universität Göttingen, 2013; (*b*) G. Sheldrick, *Acta Crystallogr., Sect. A* 2008, **64**, 112.

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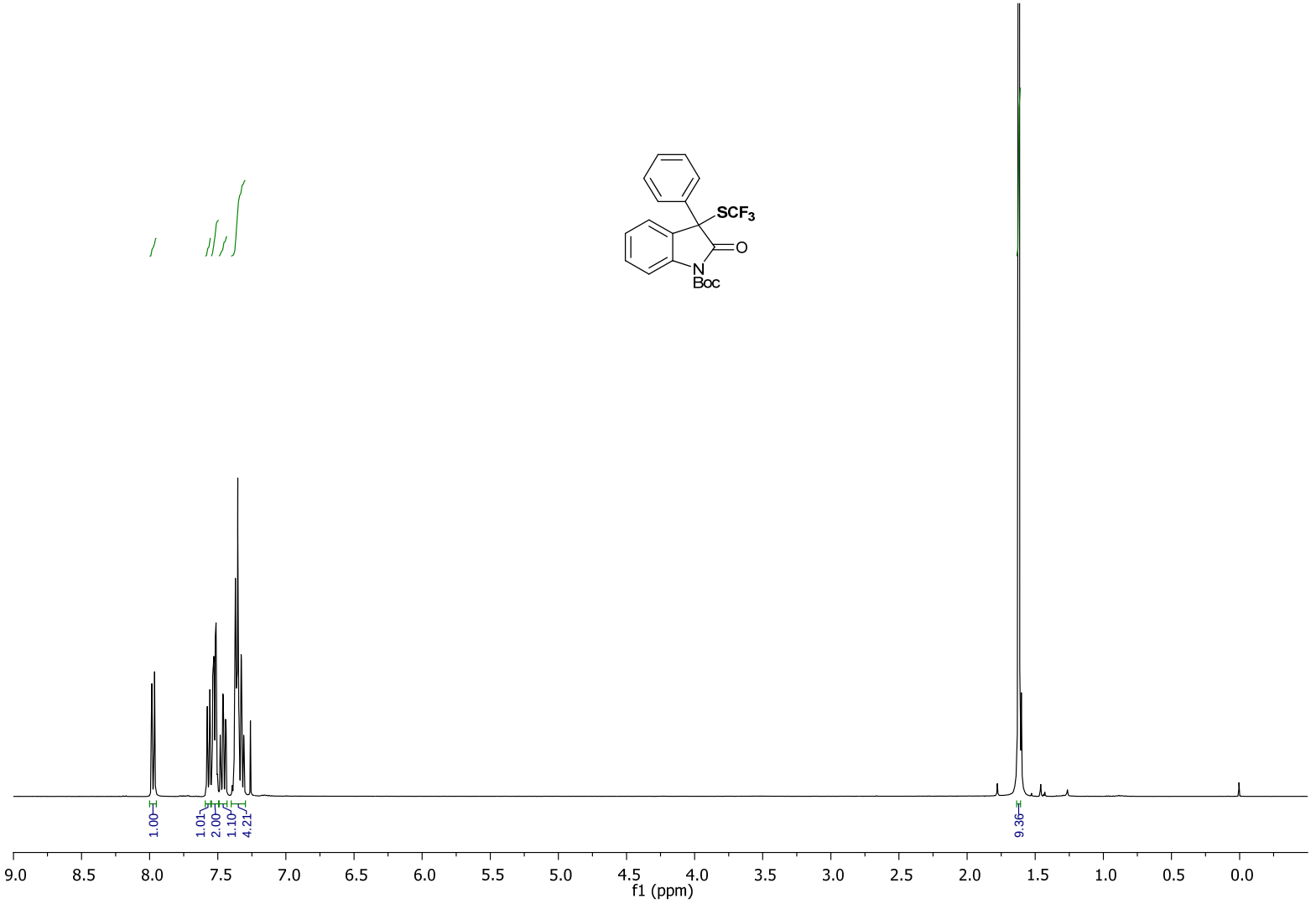

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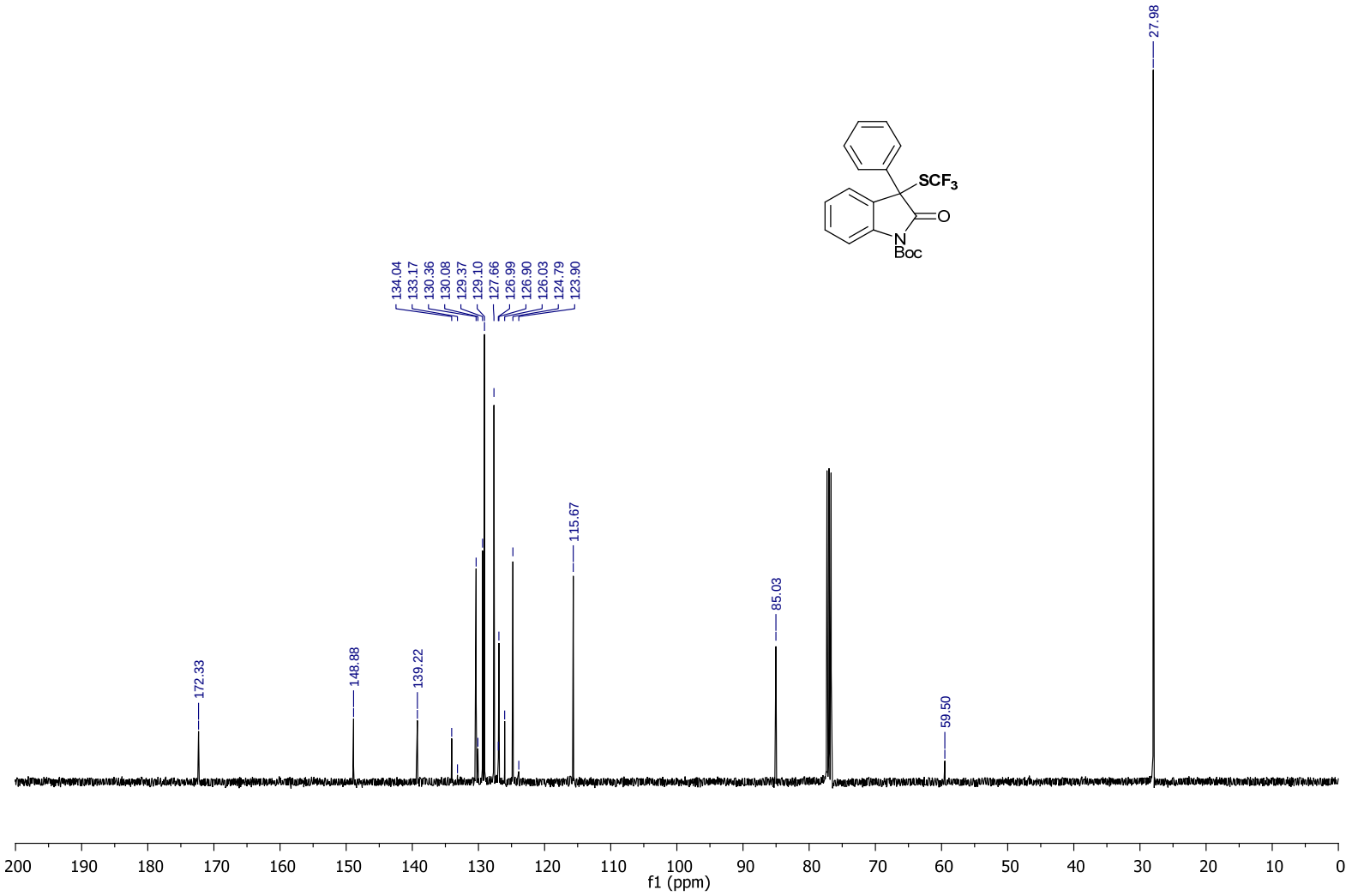

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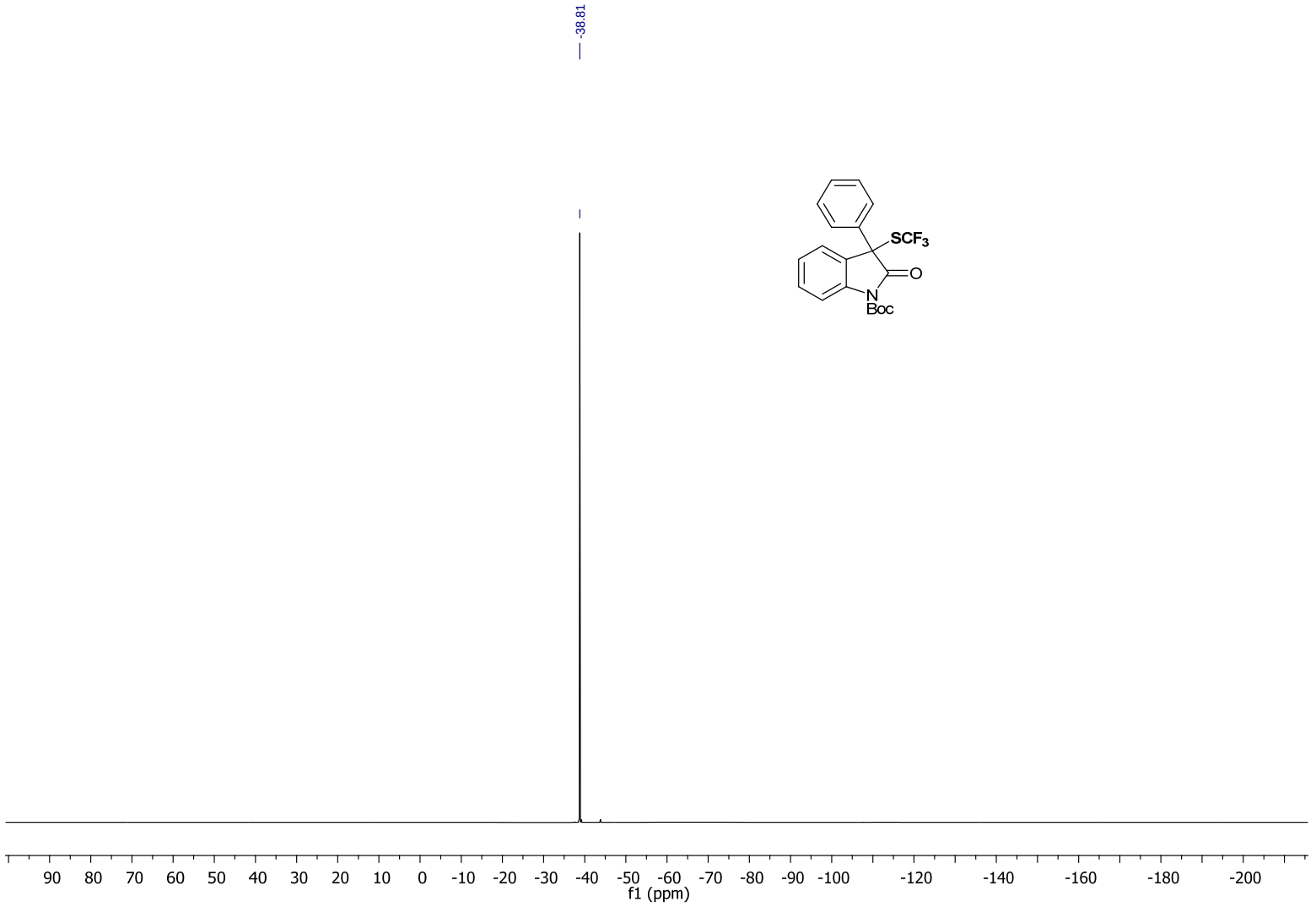

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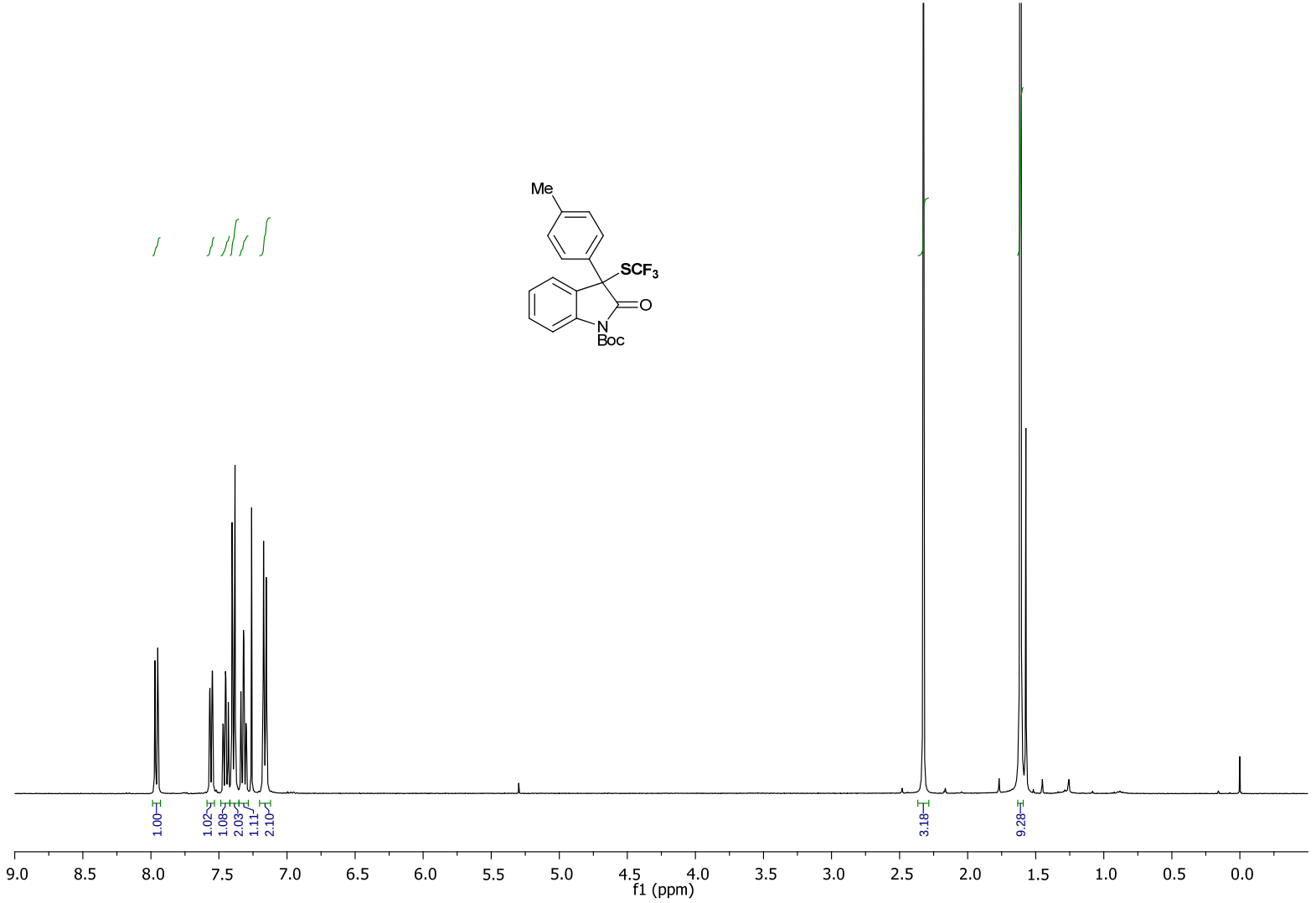

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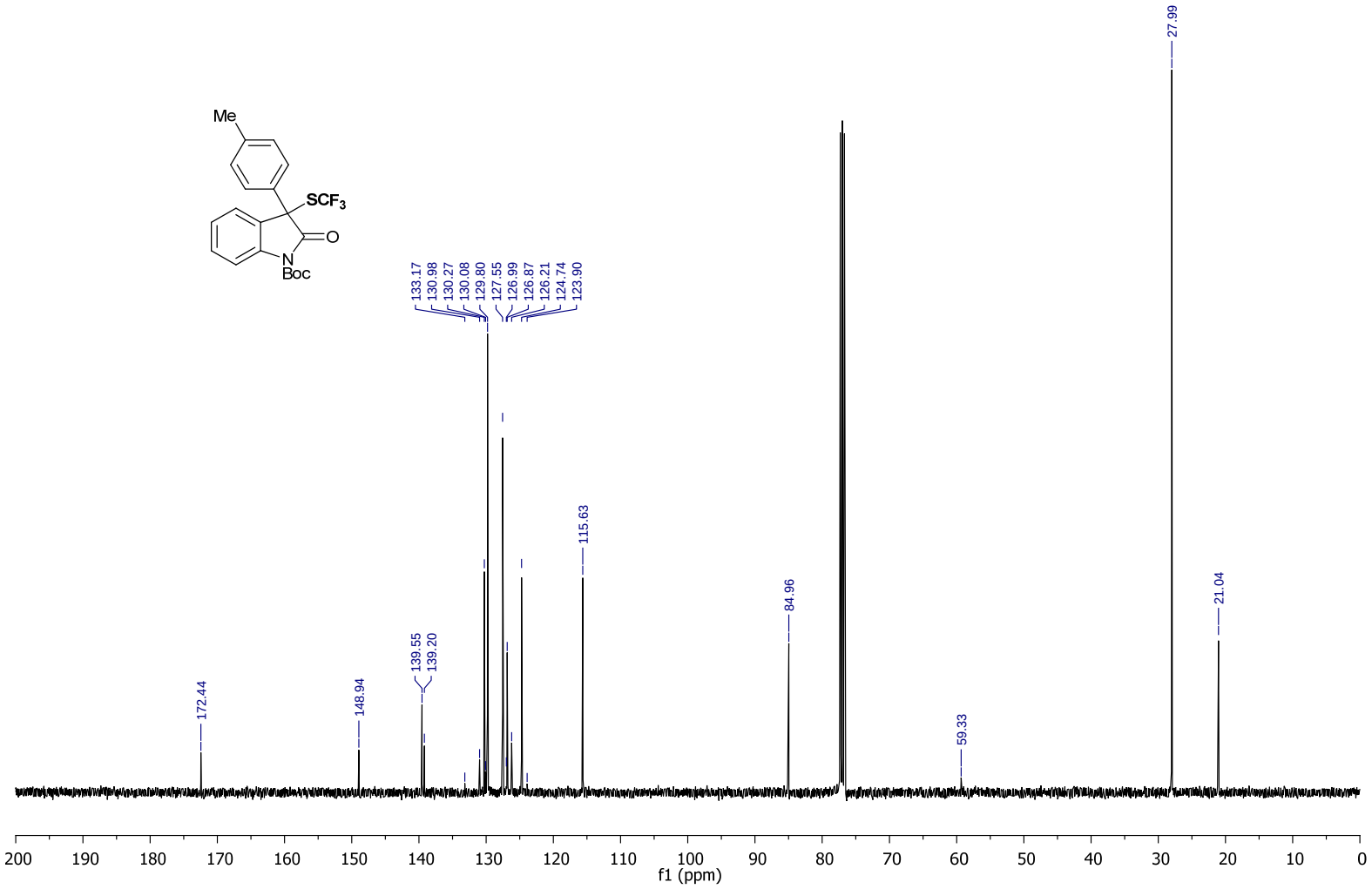

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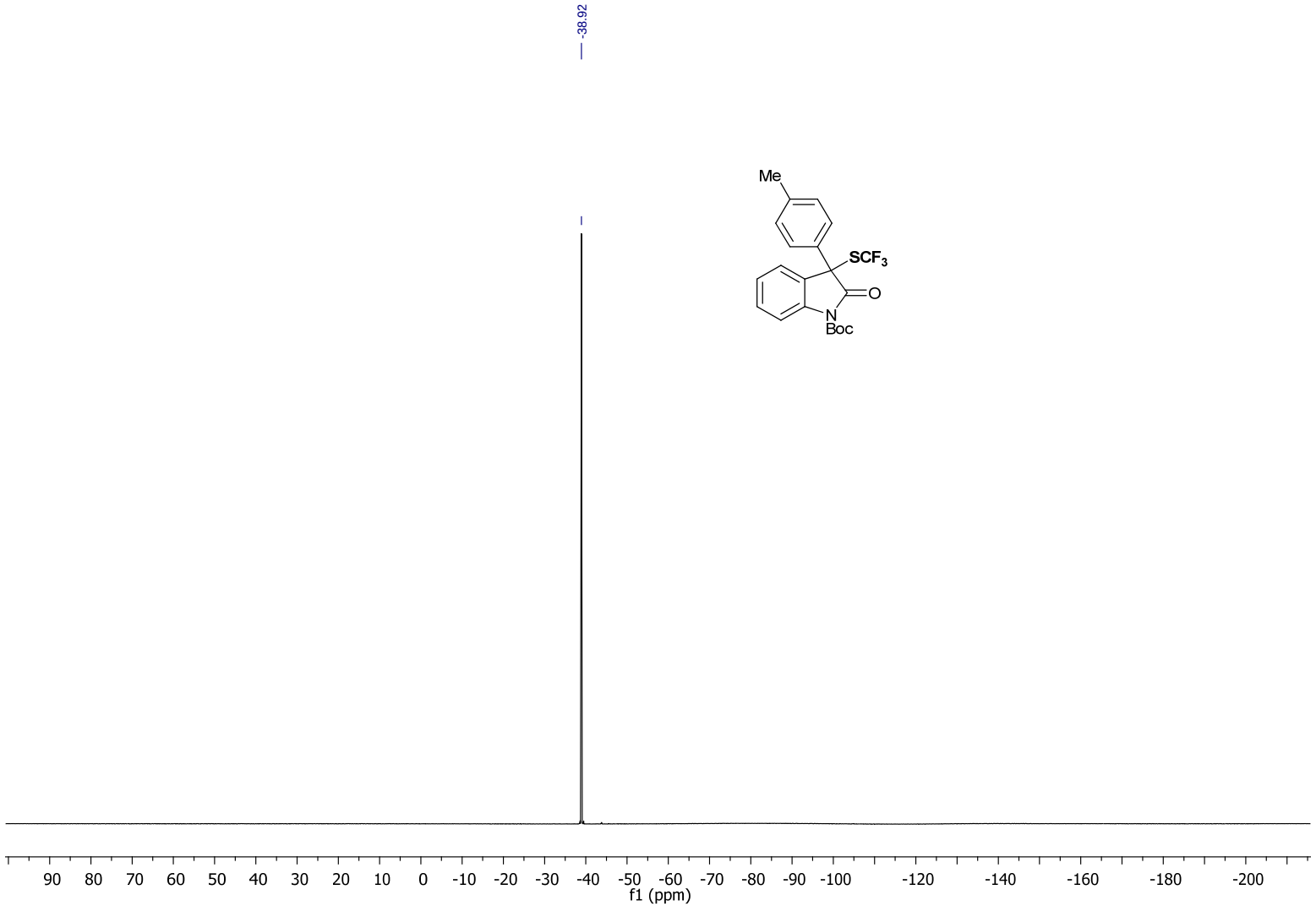

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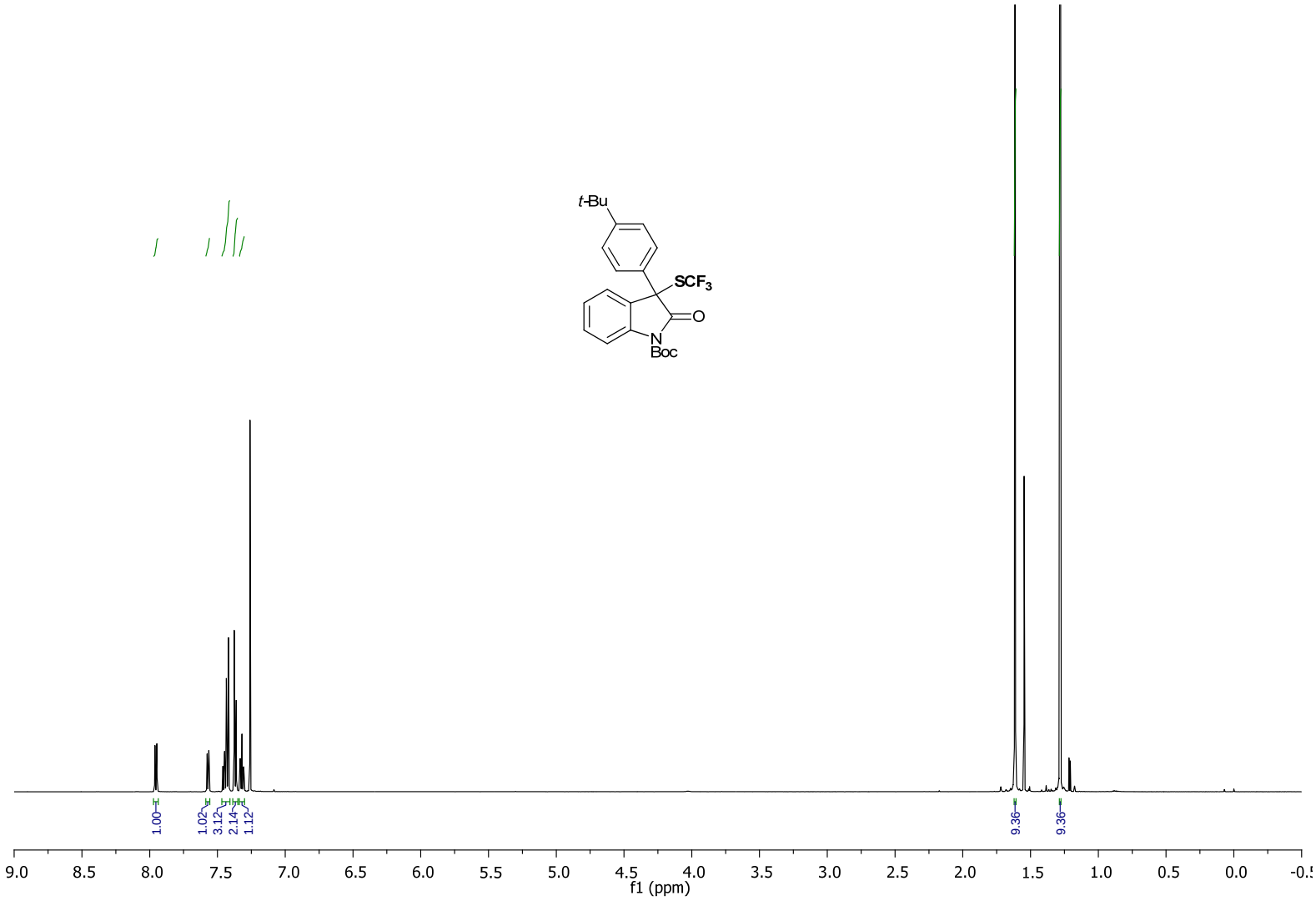

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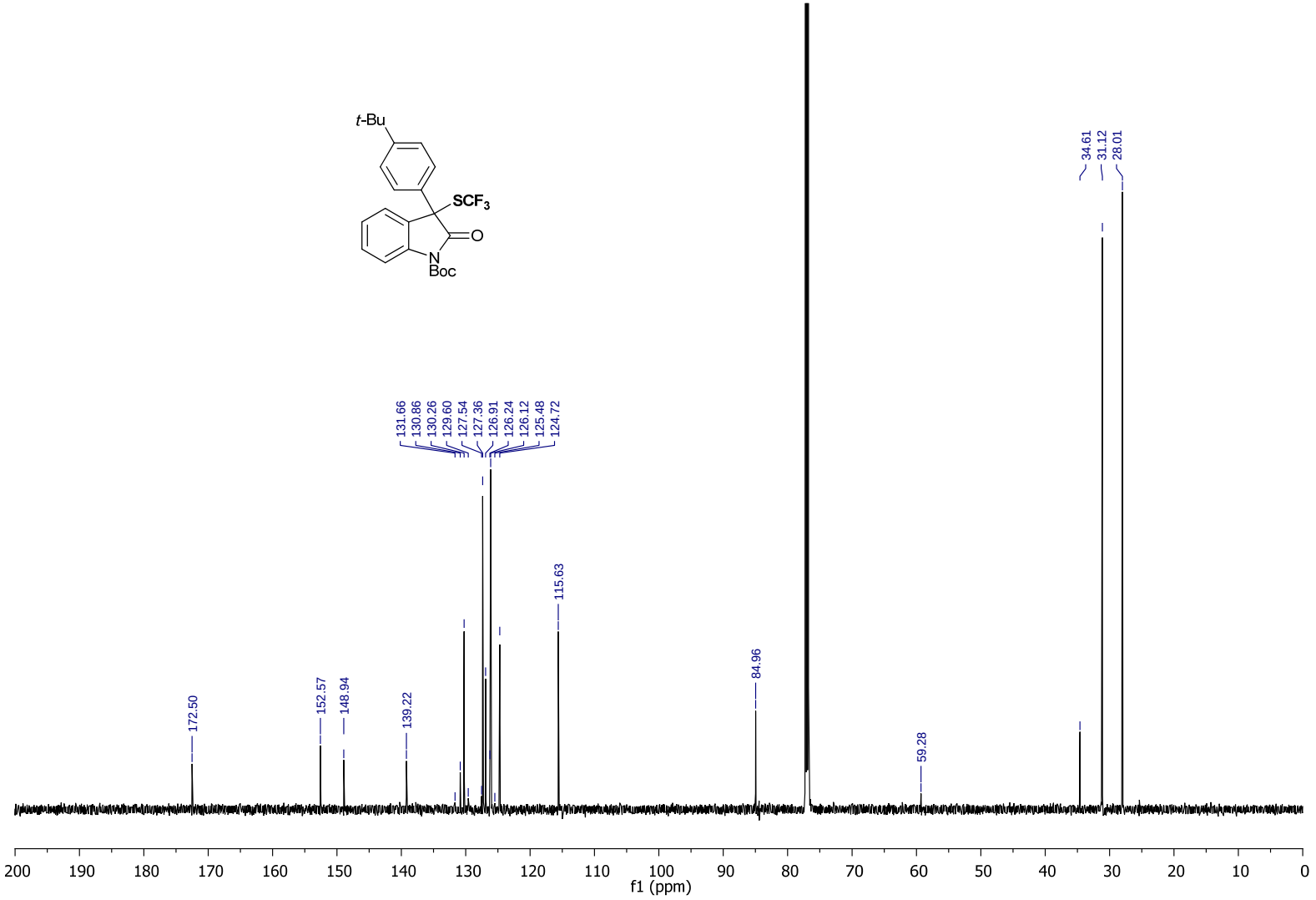

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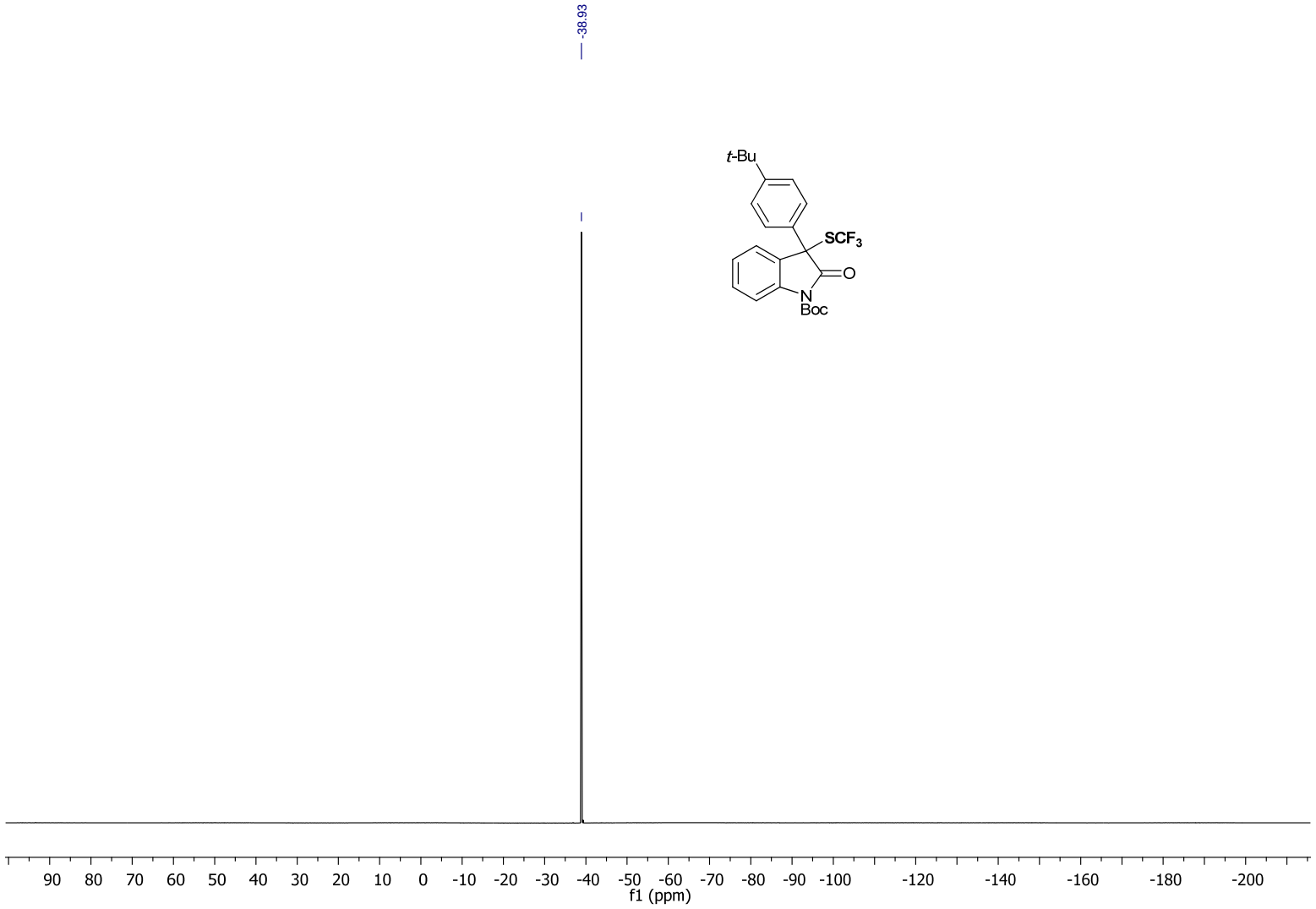

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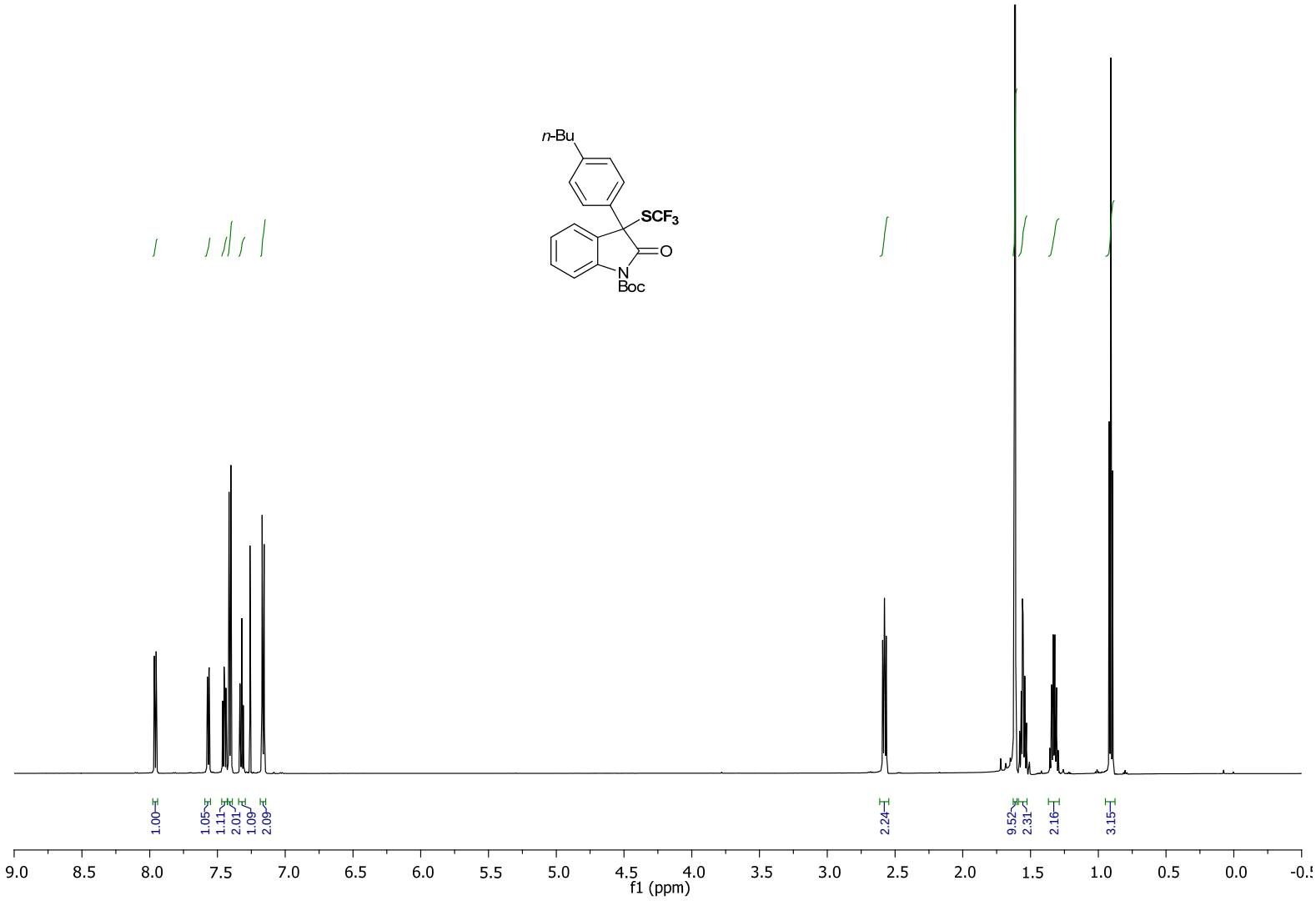

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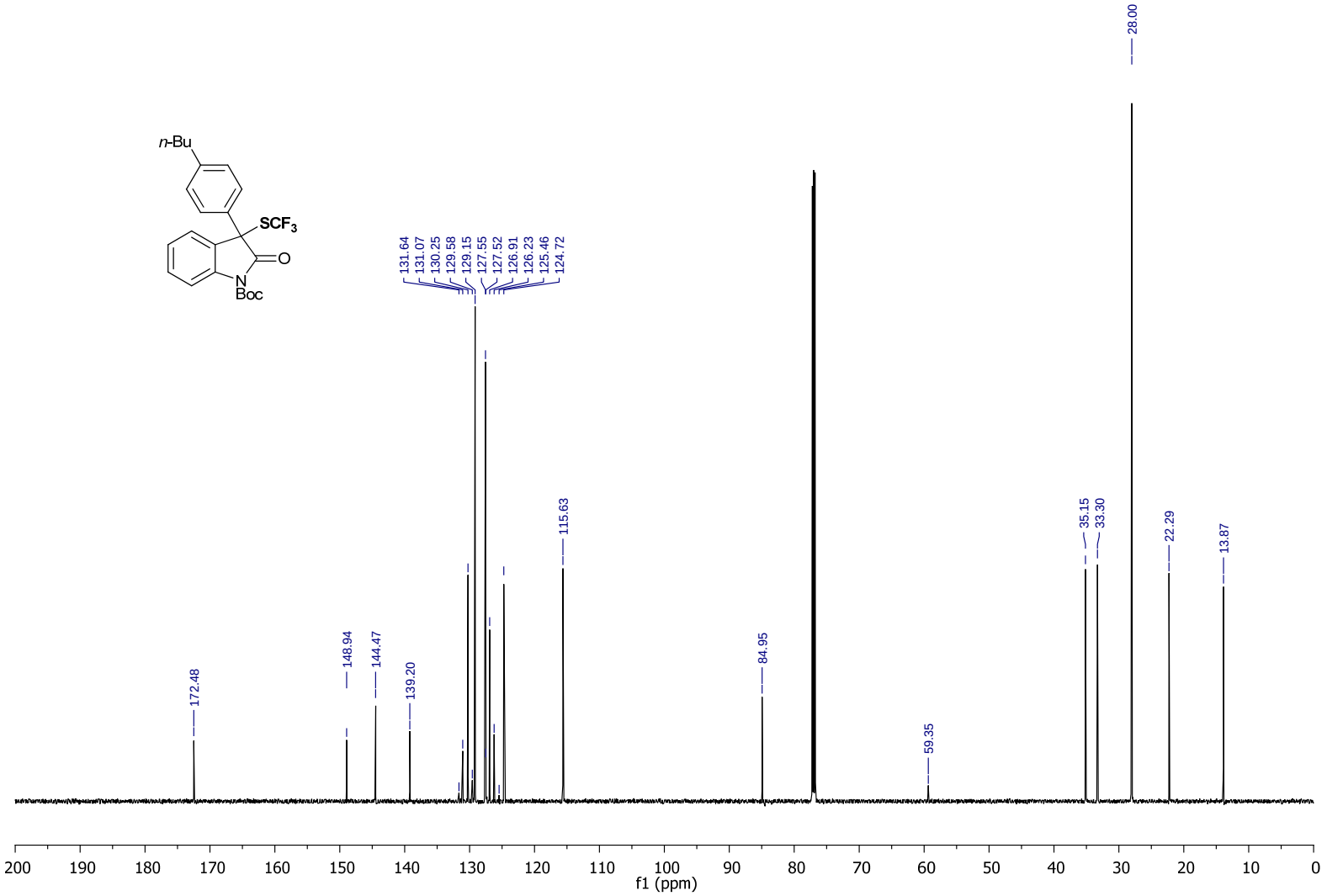

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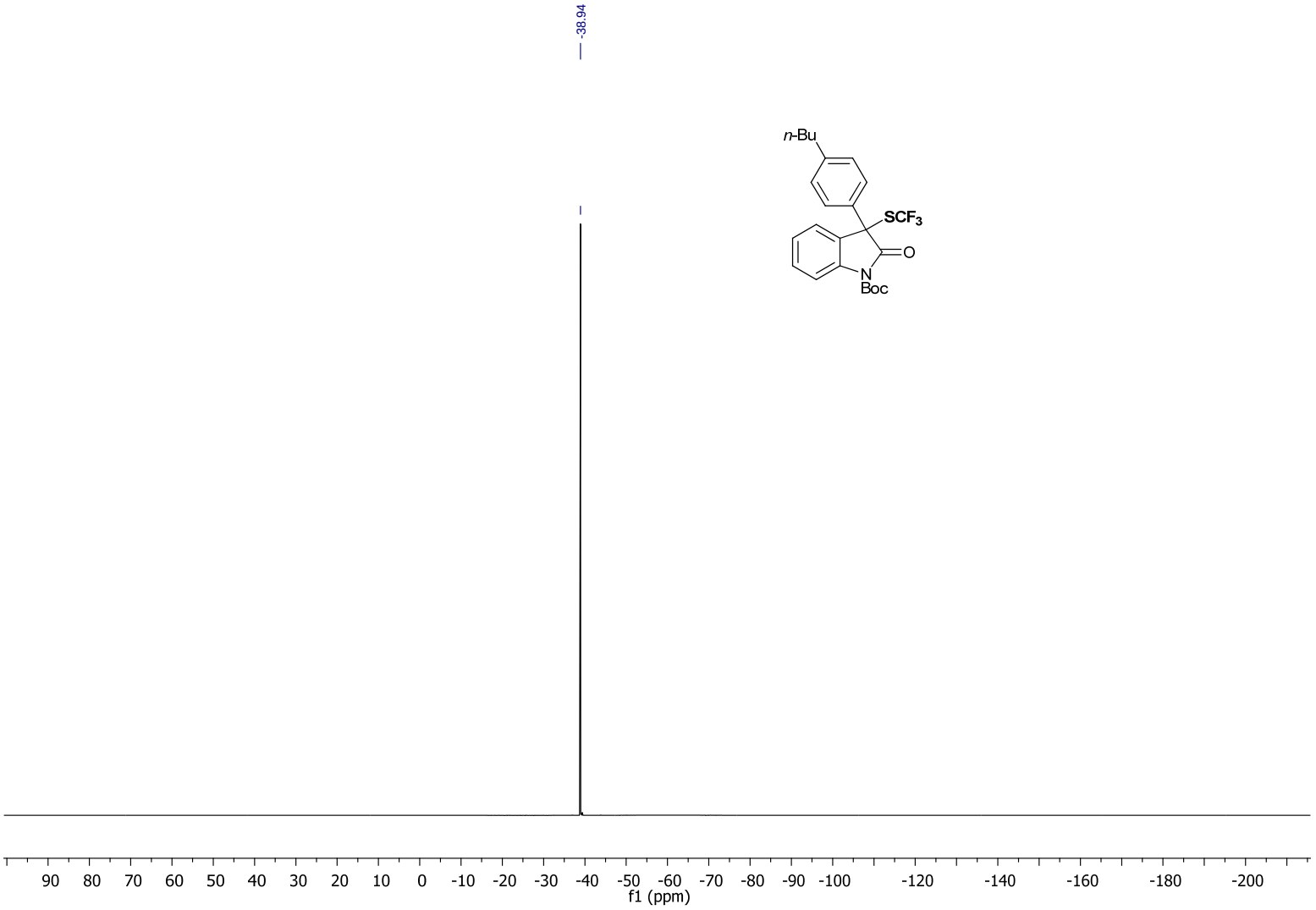

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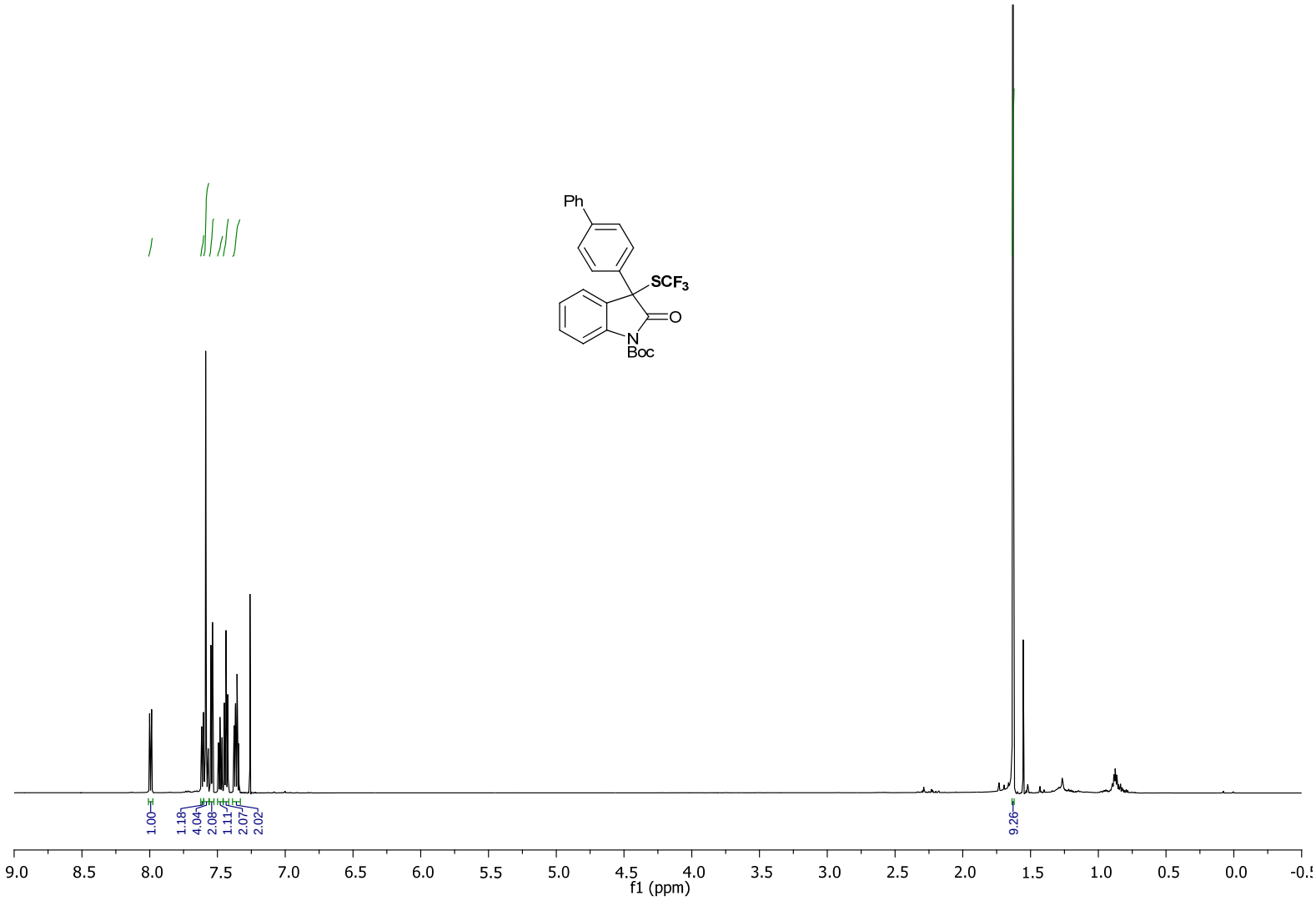

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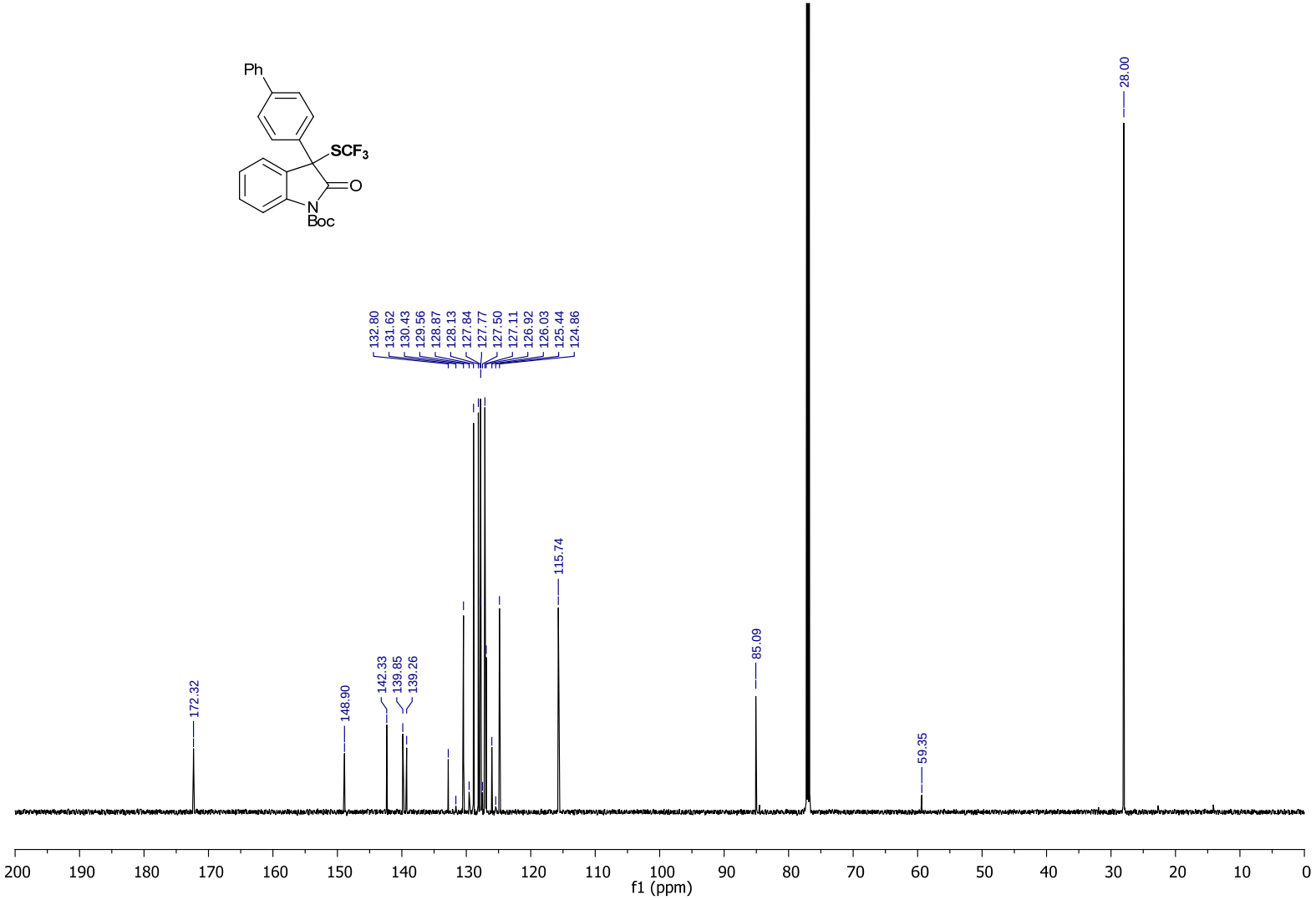

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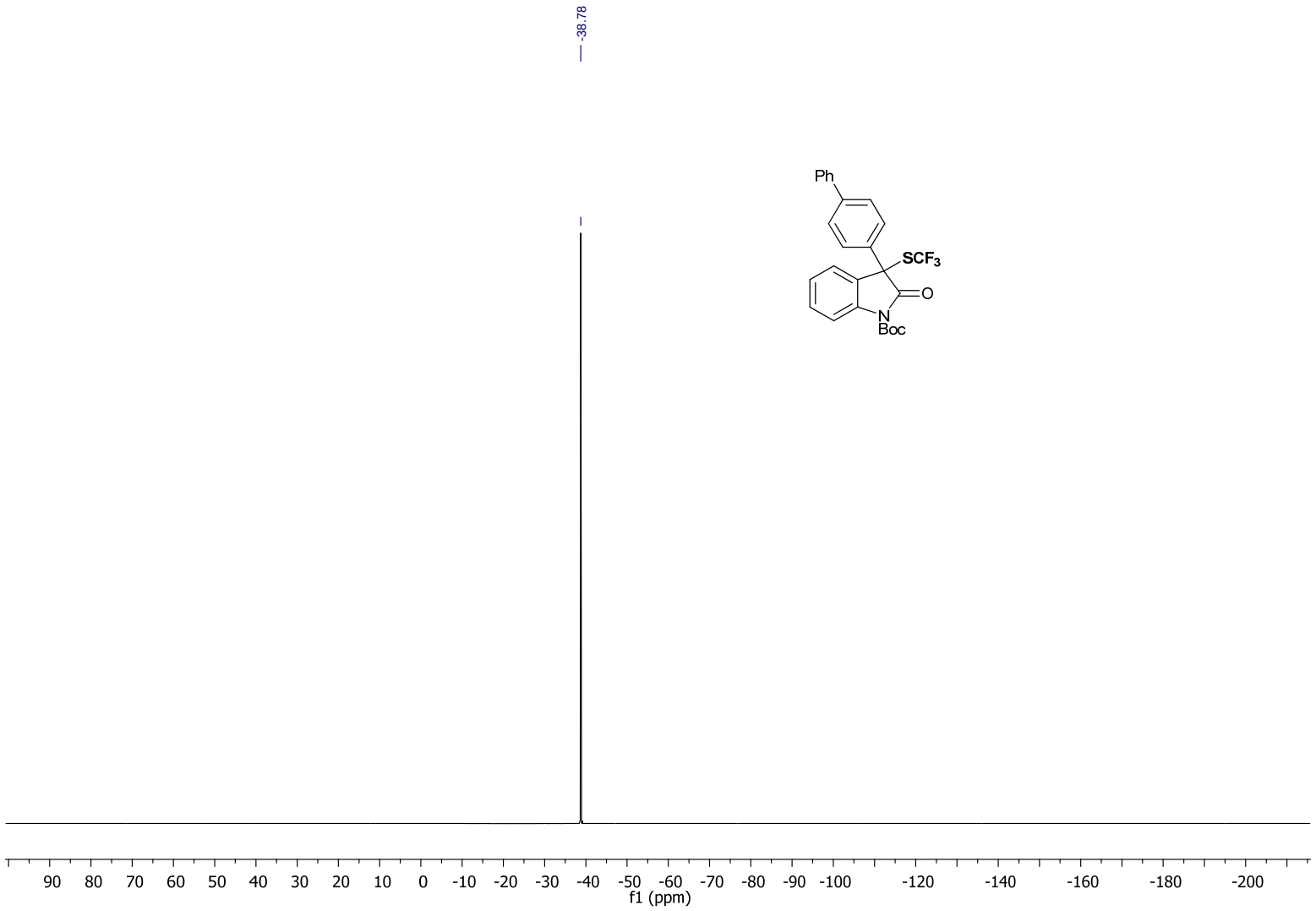

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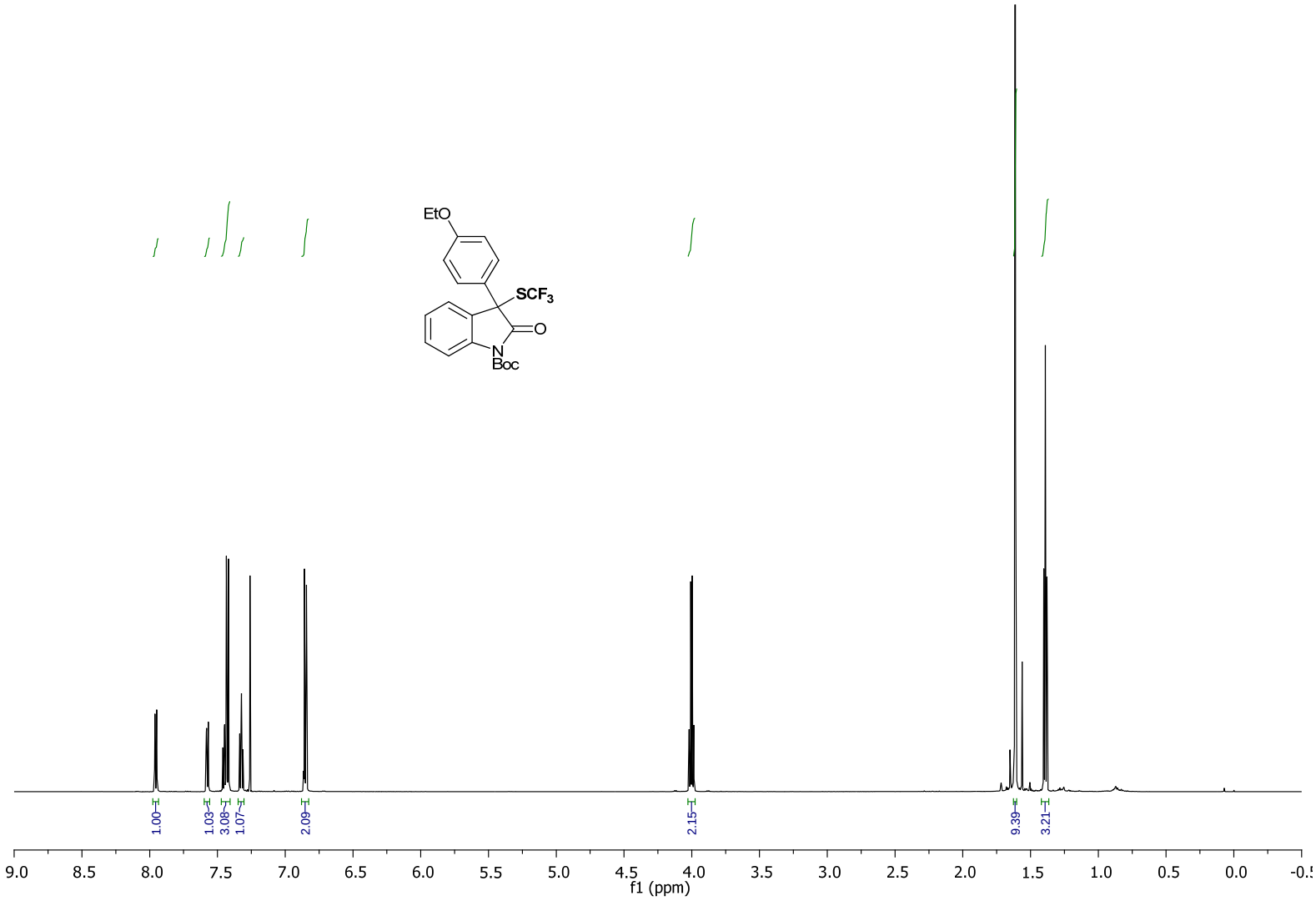

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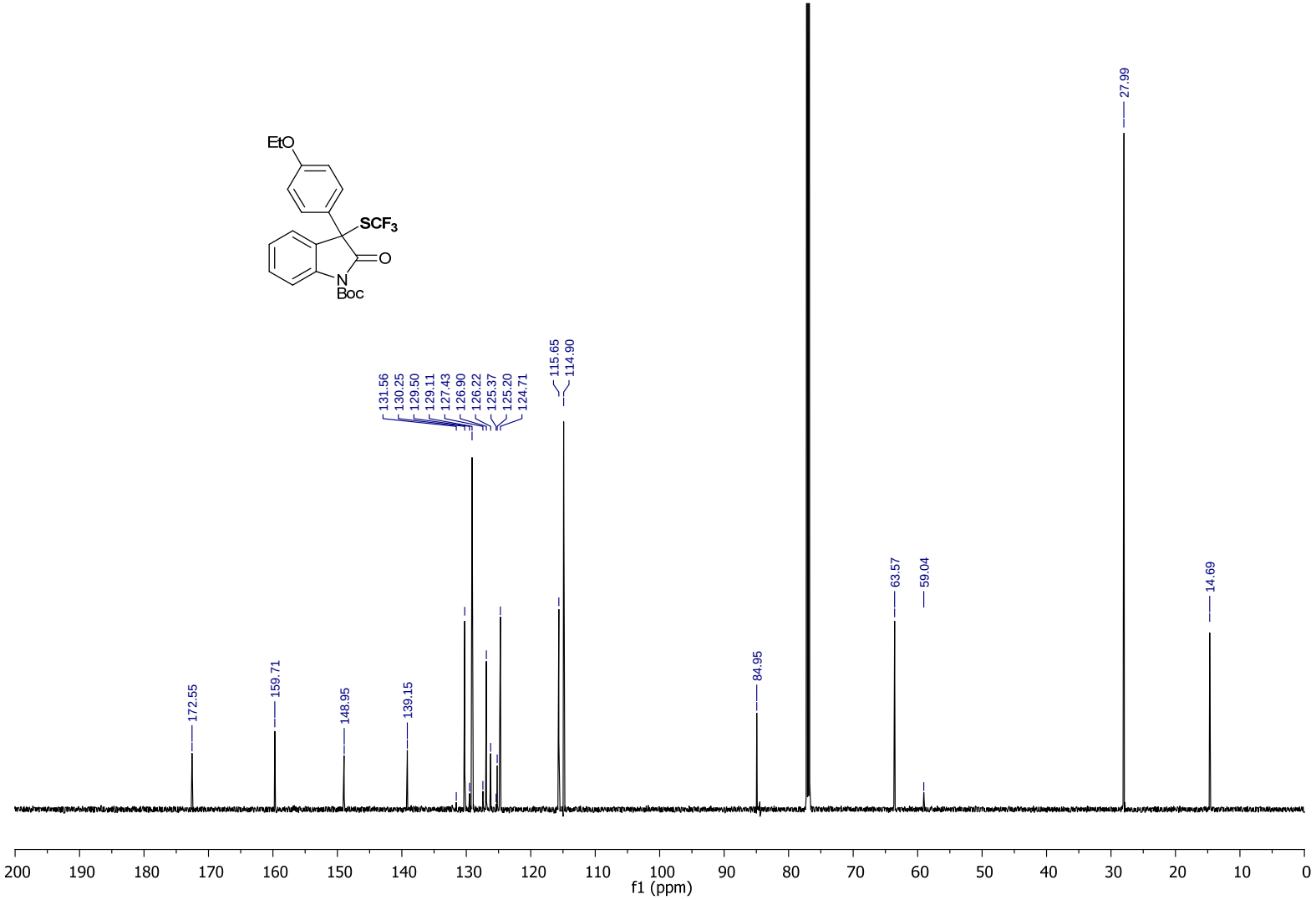

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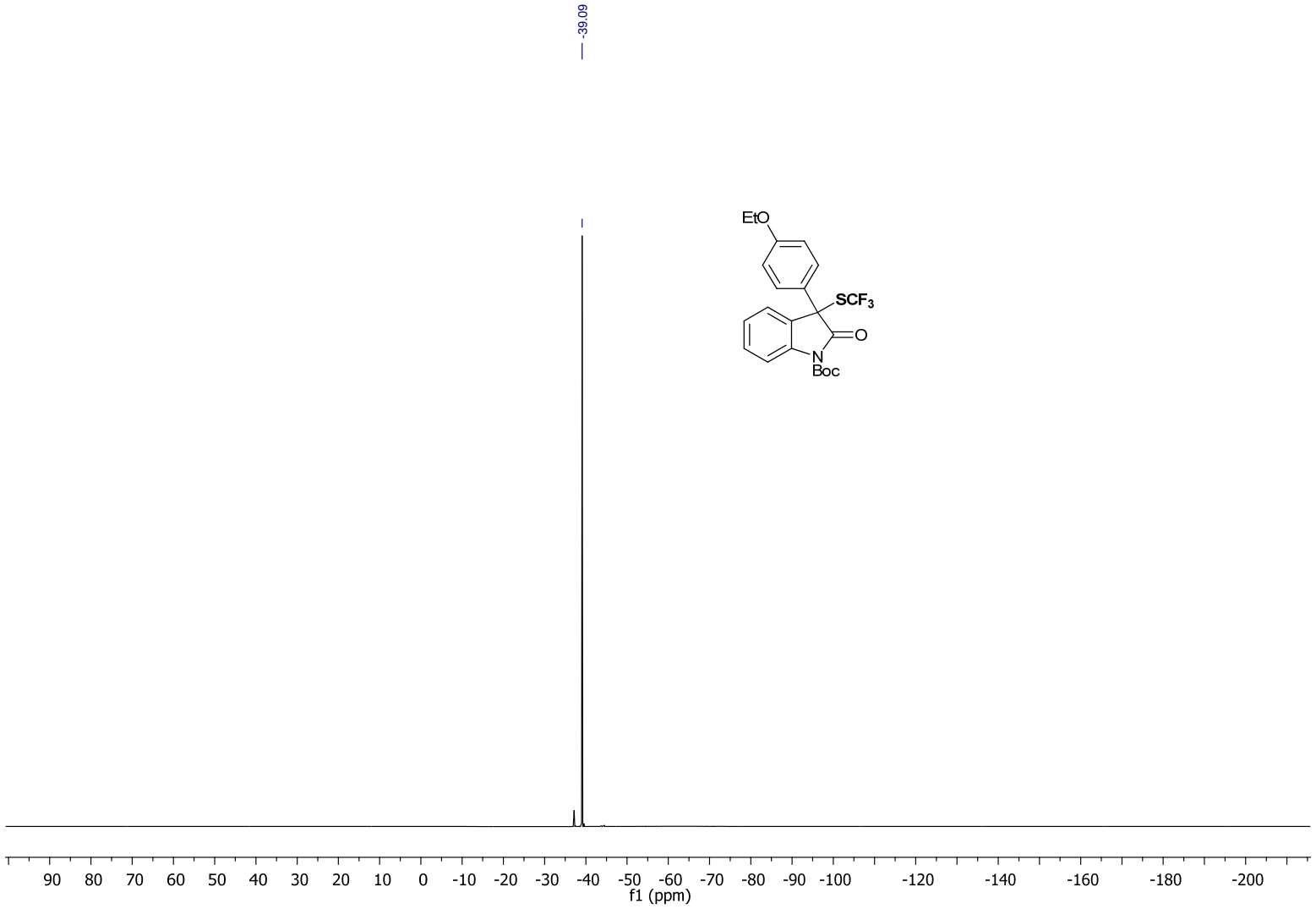

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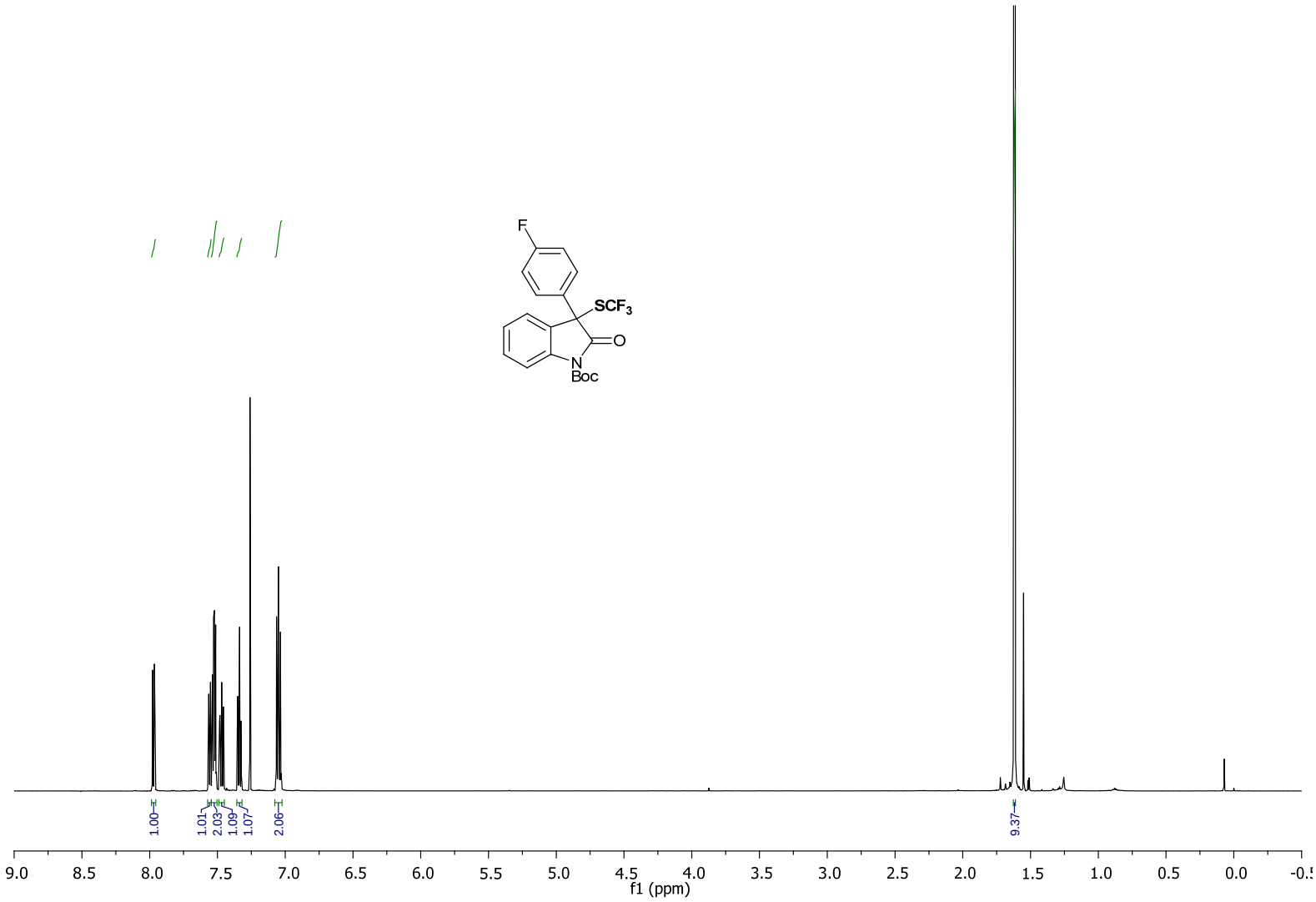

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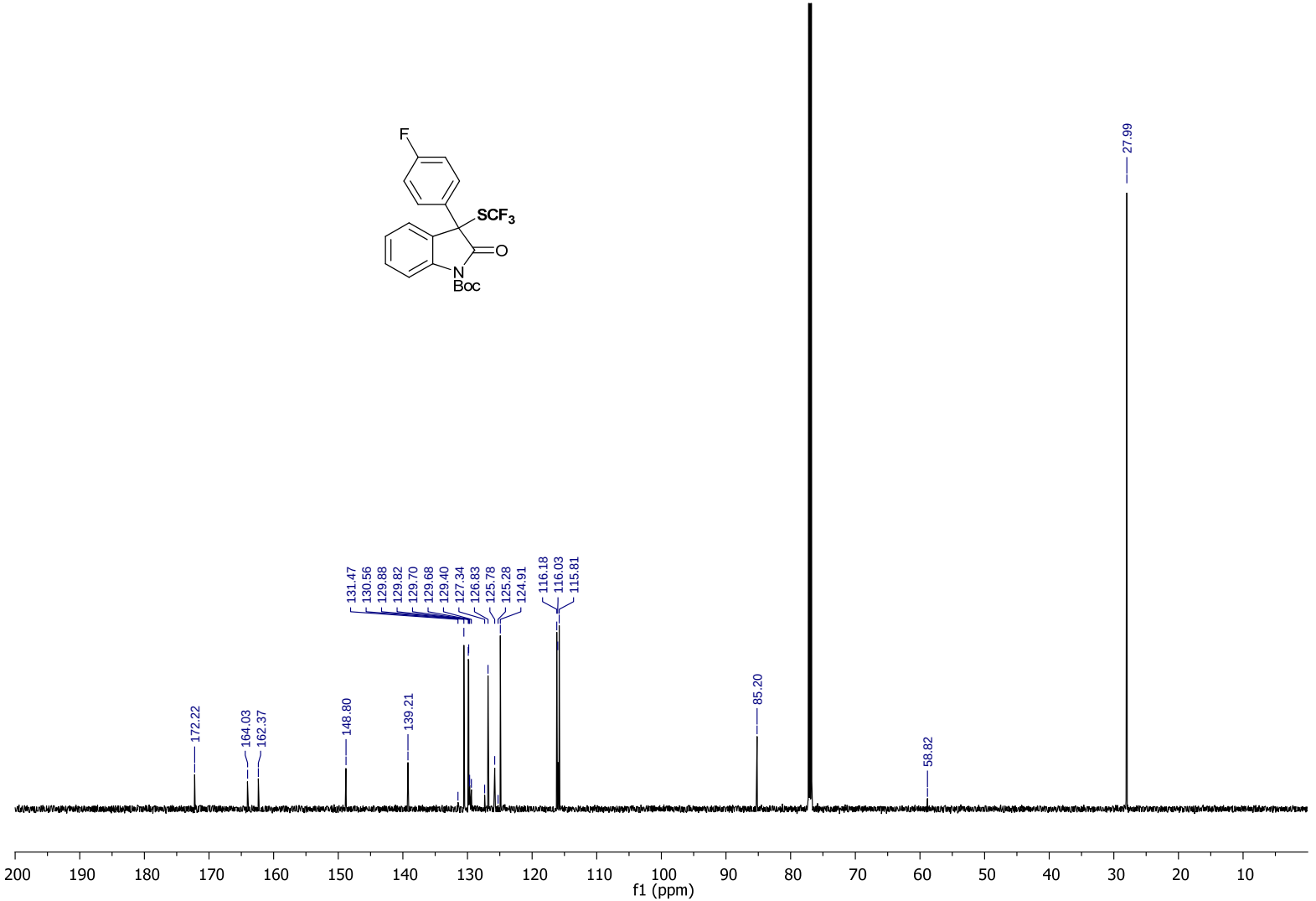

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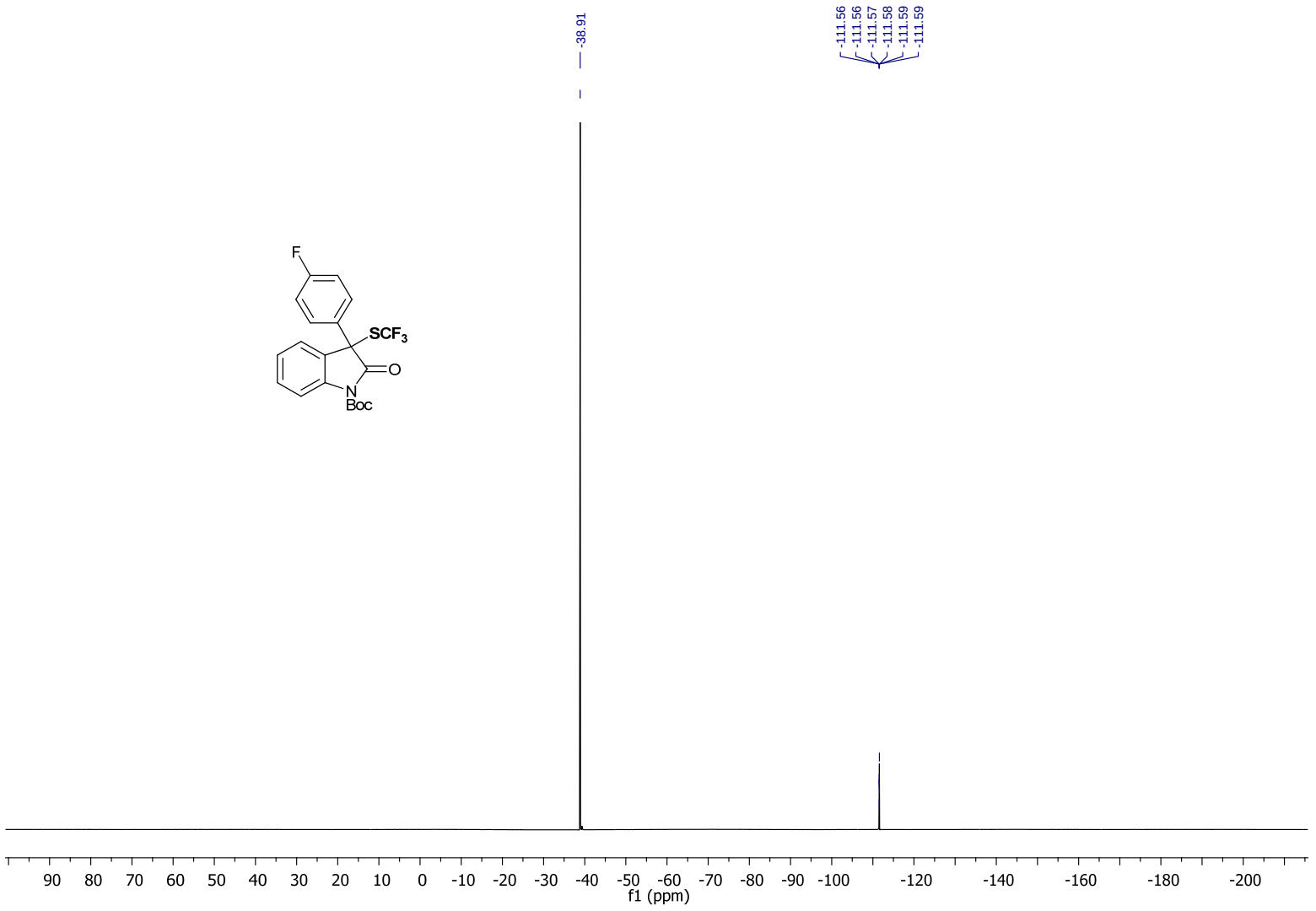

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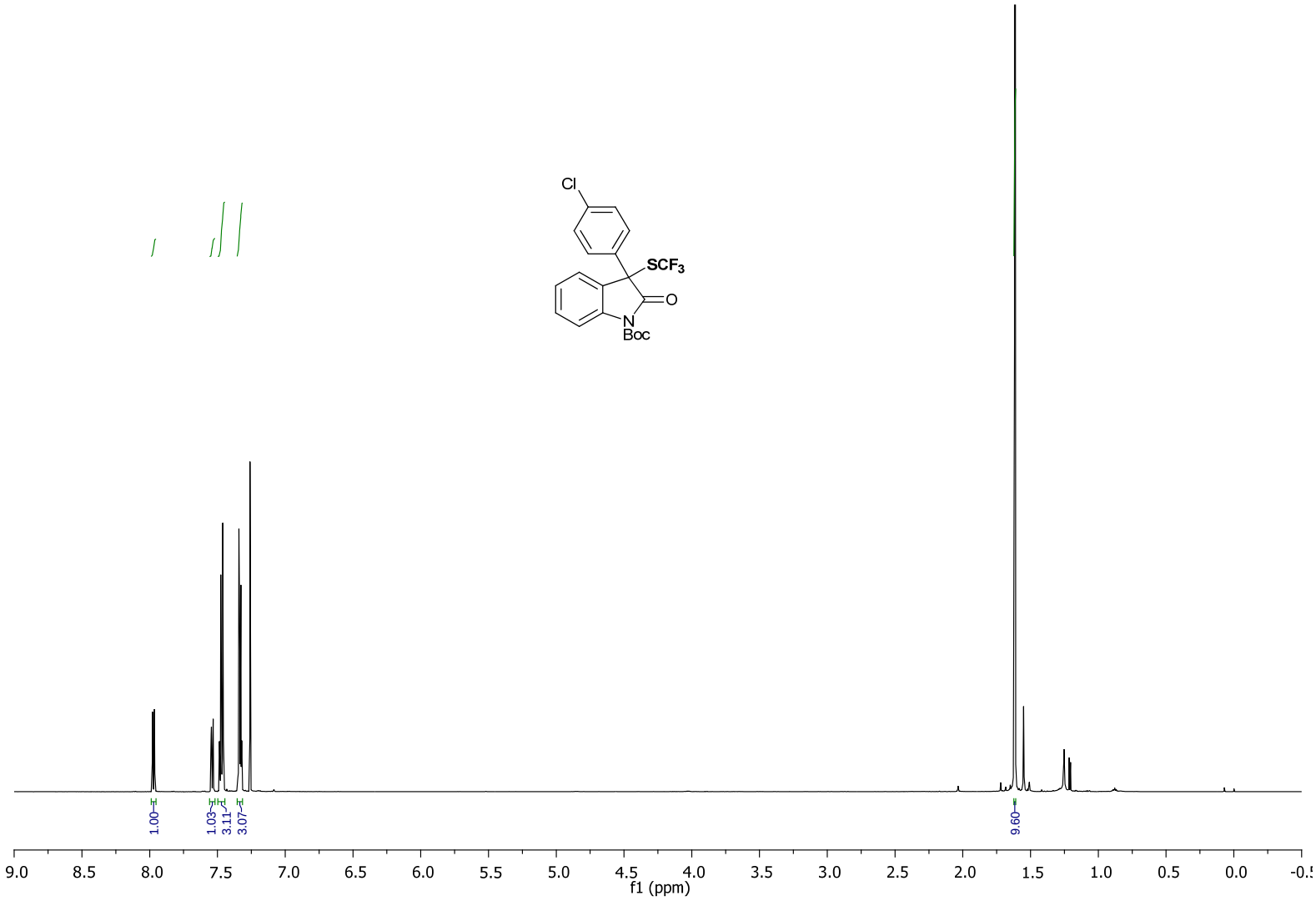

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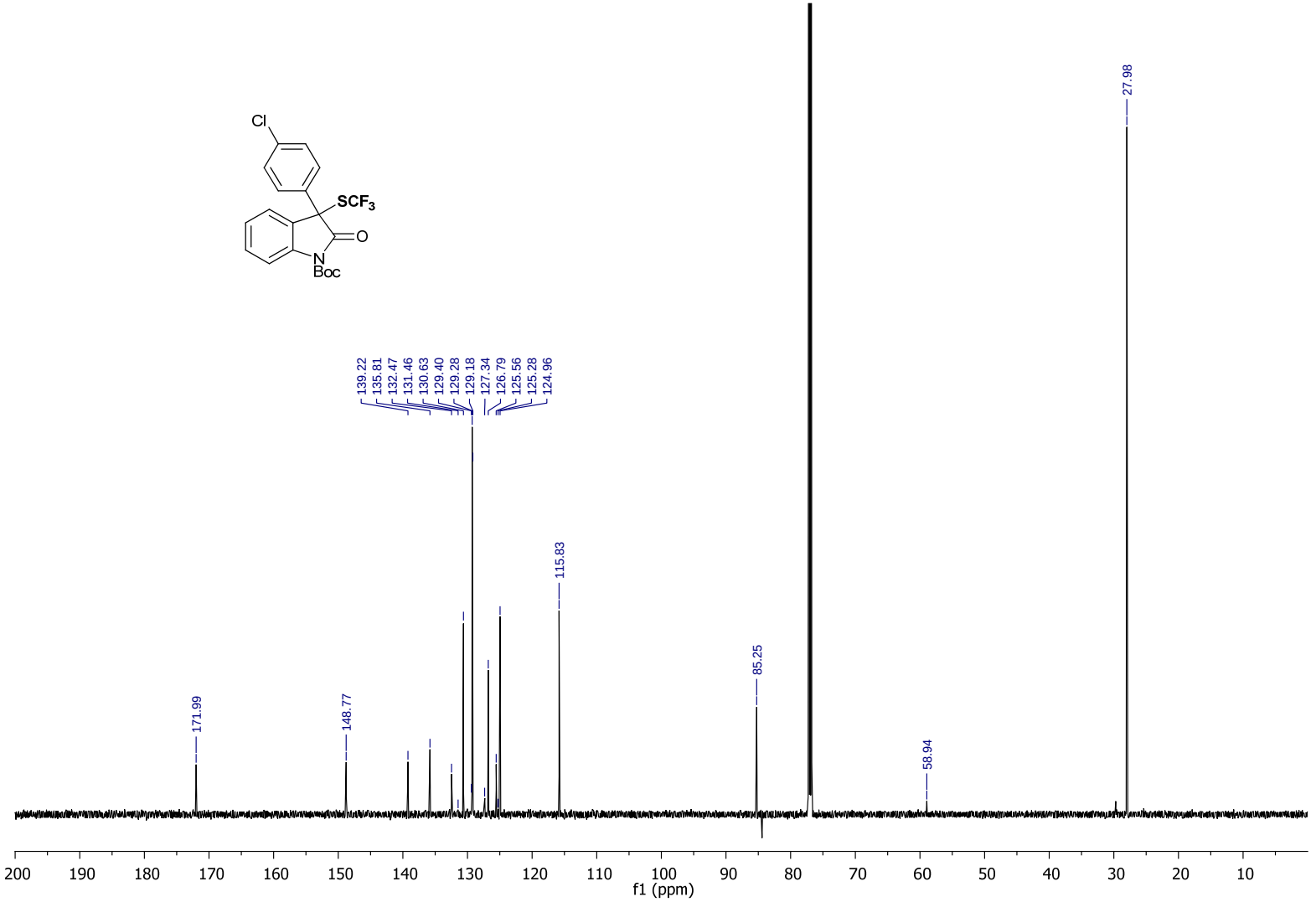

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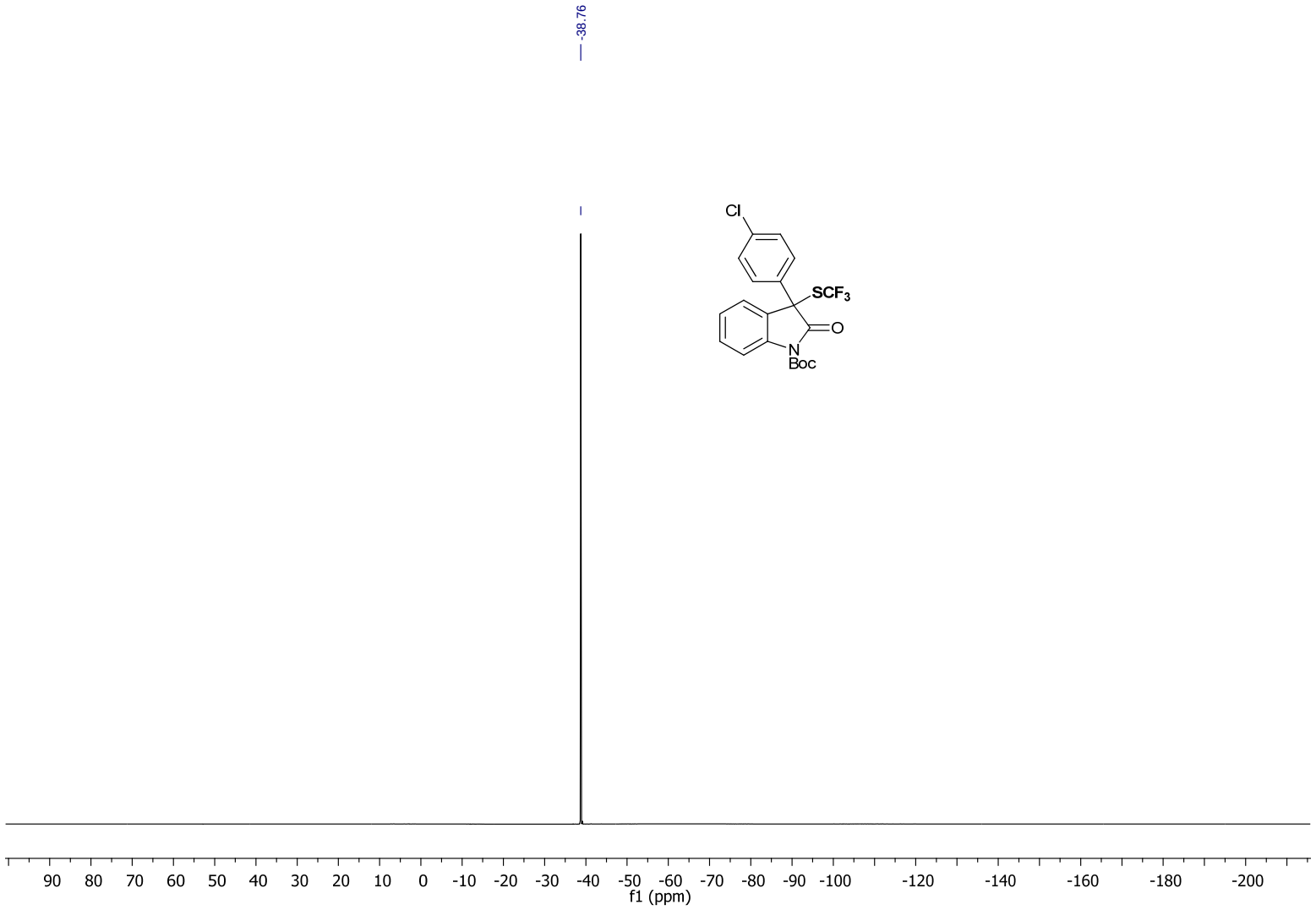

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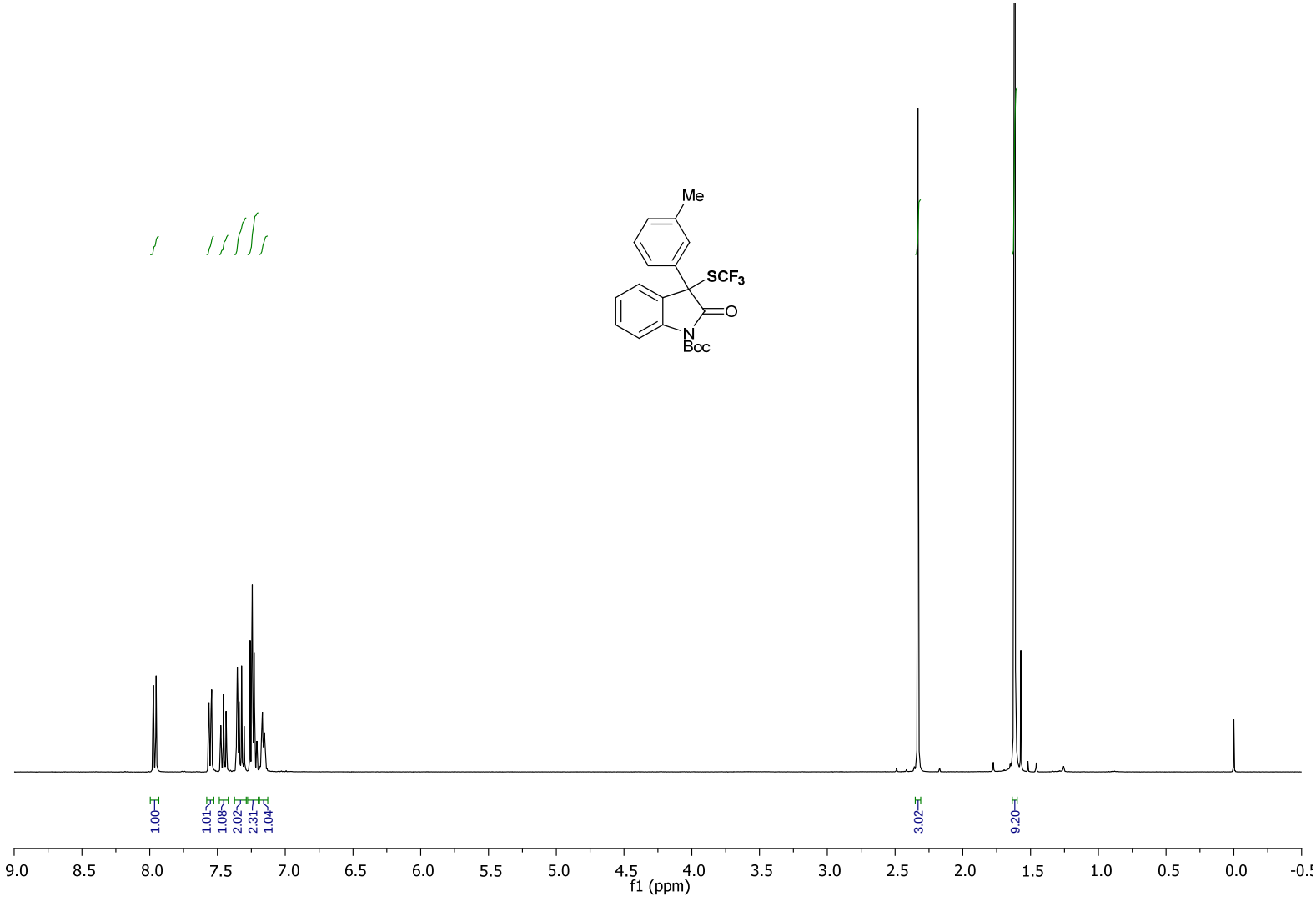

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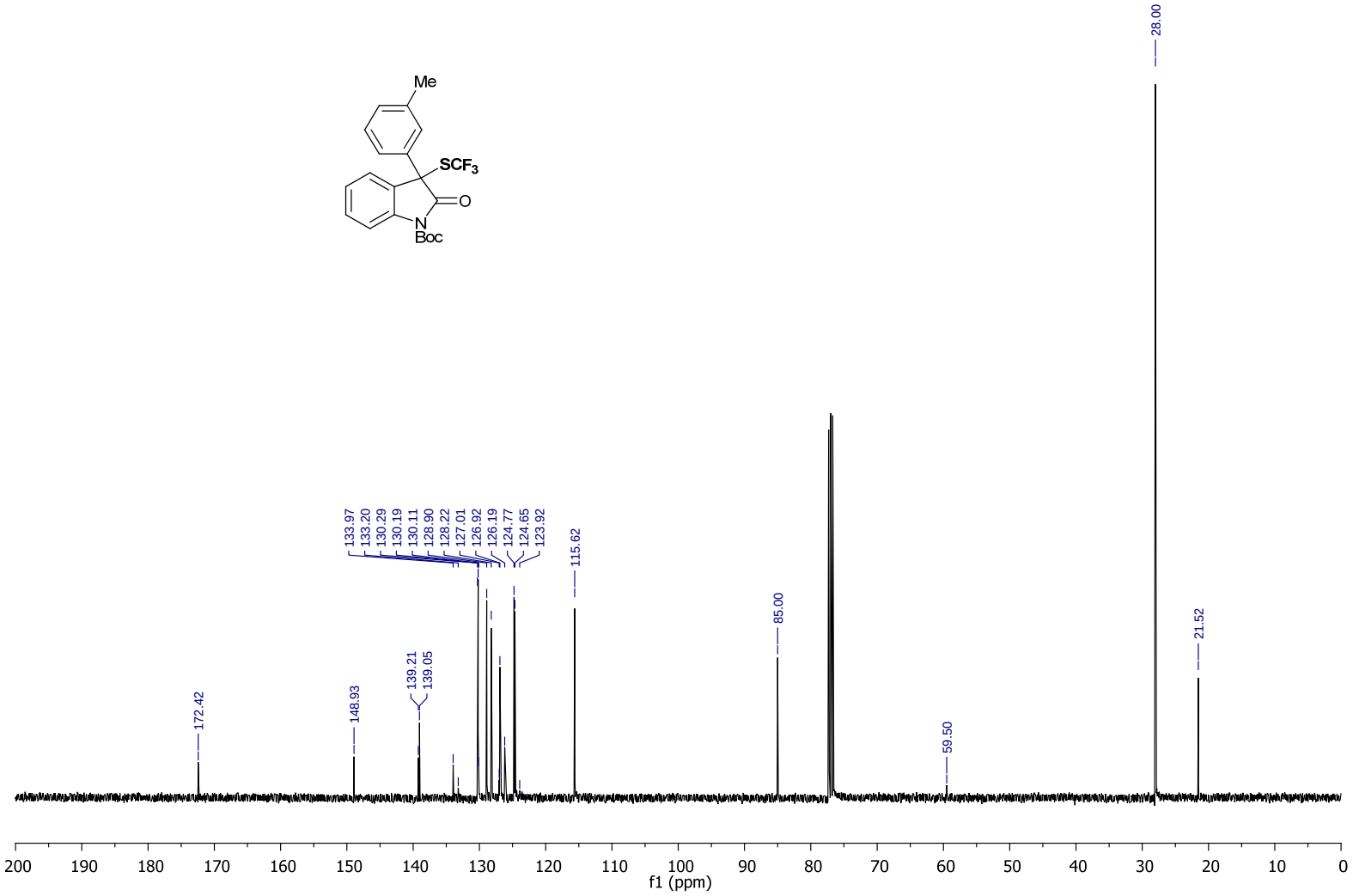

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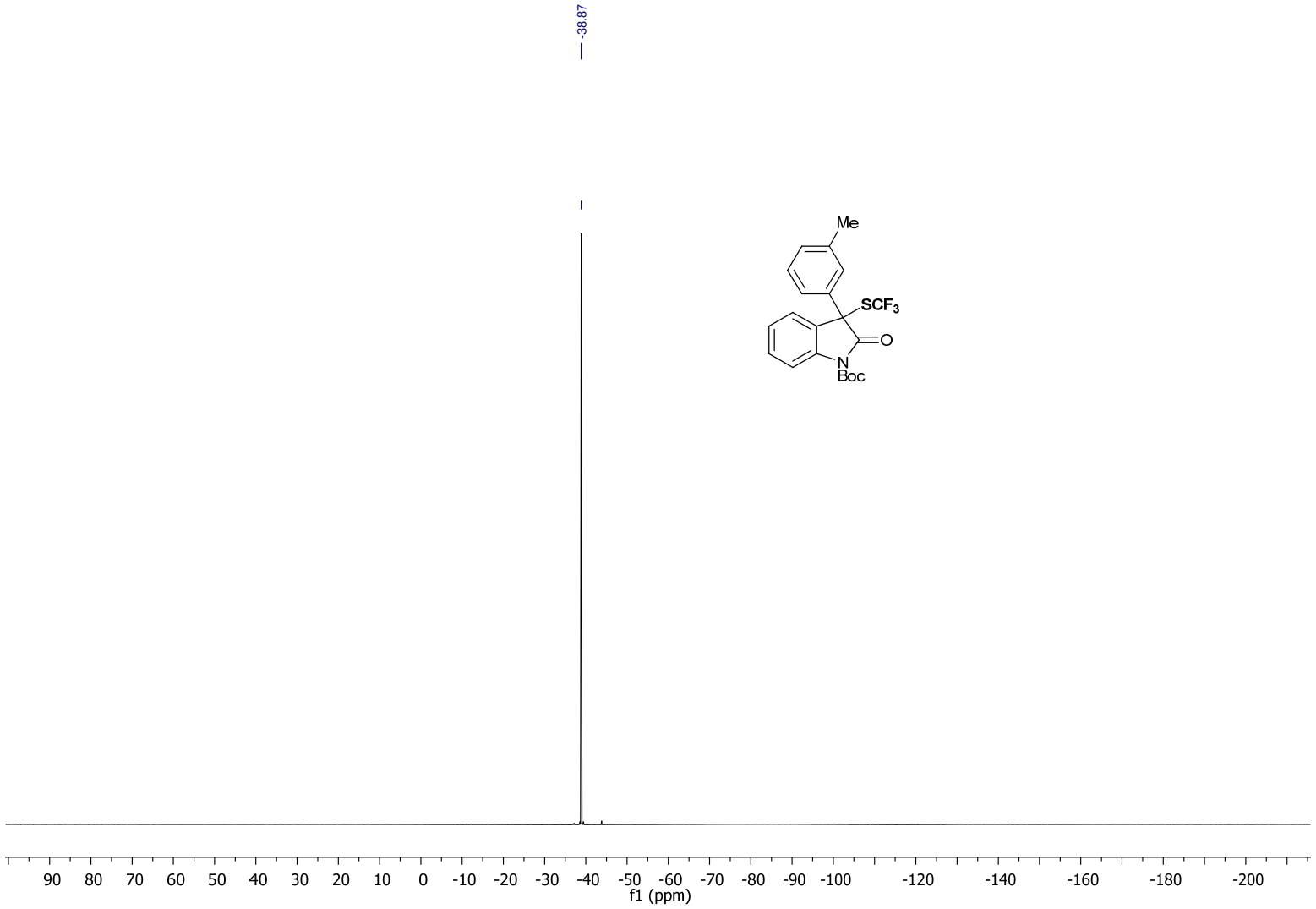

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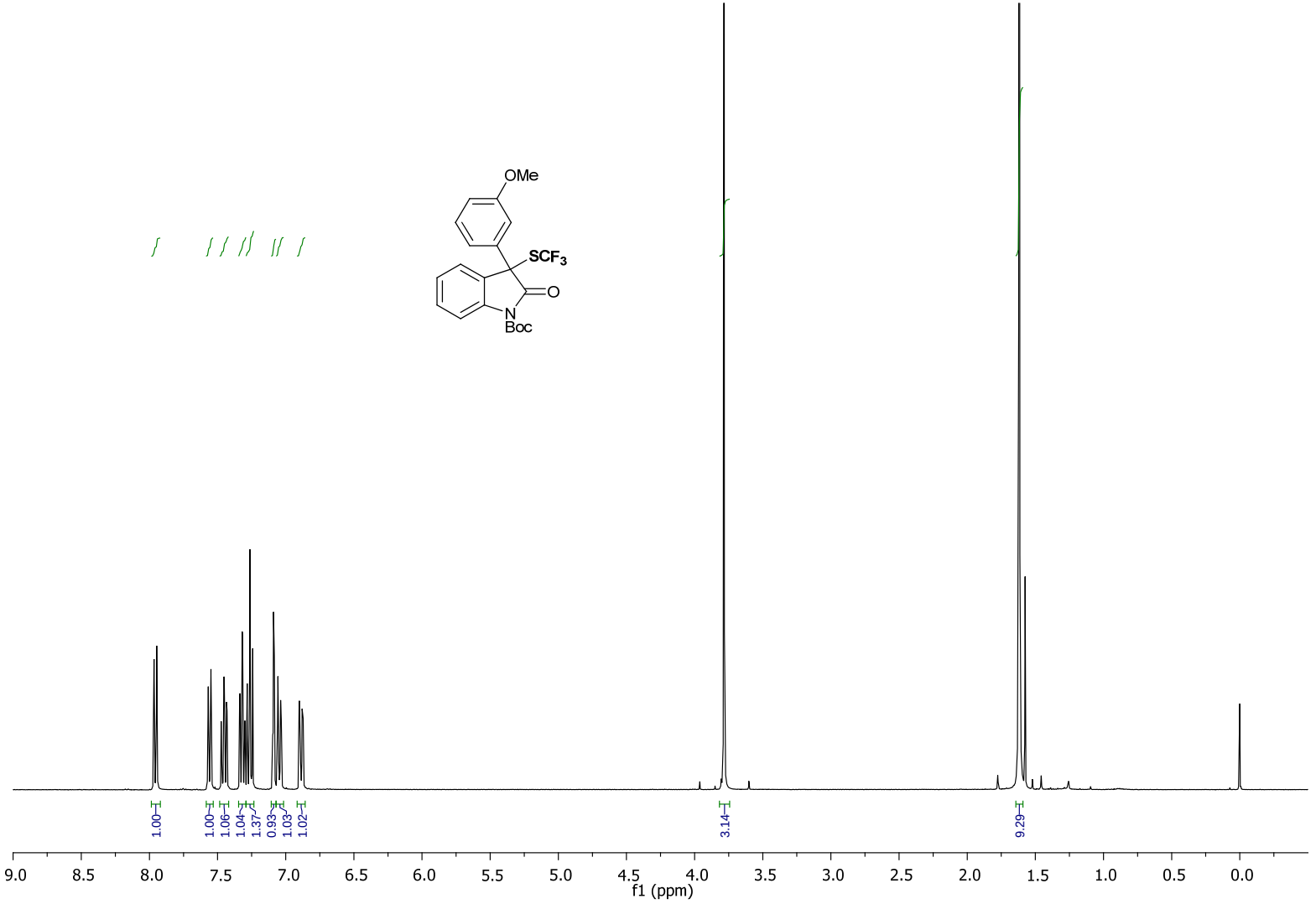

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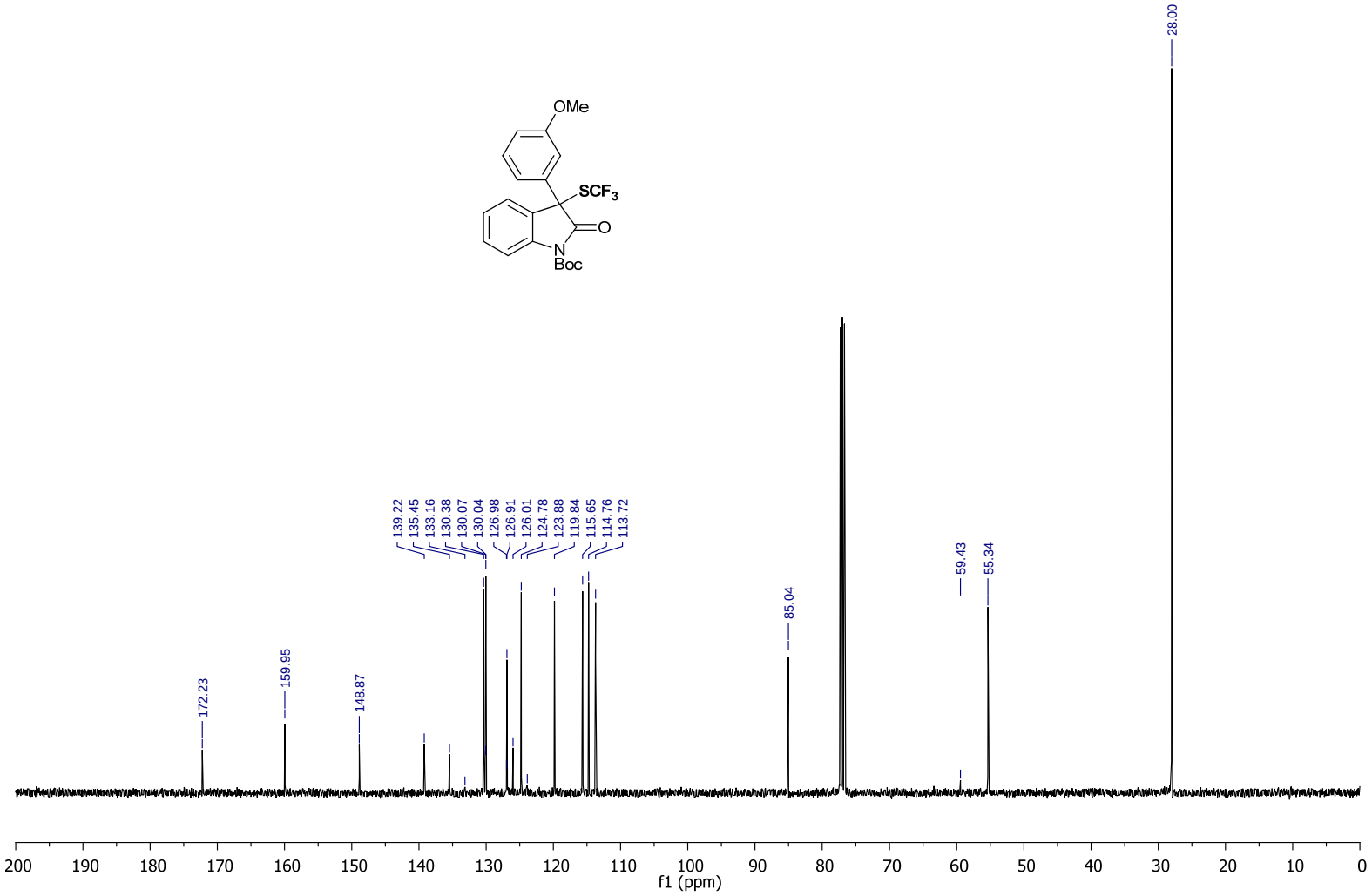

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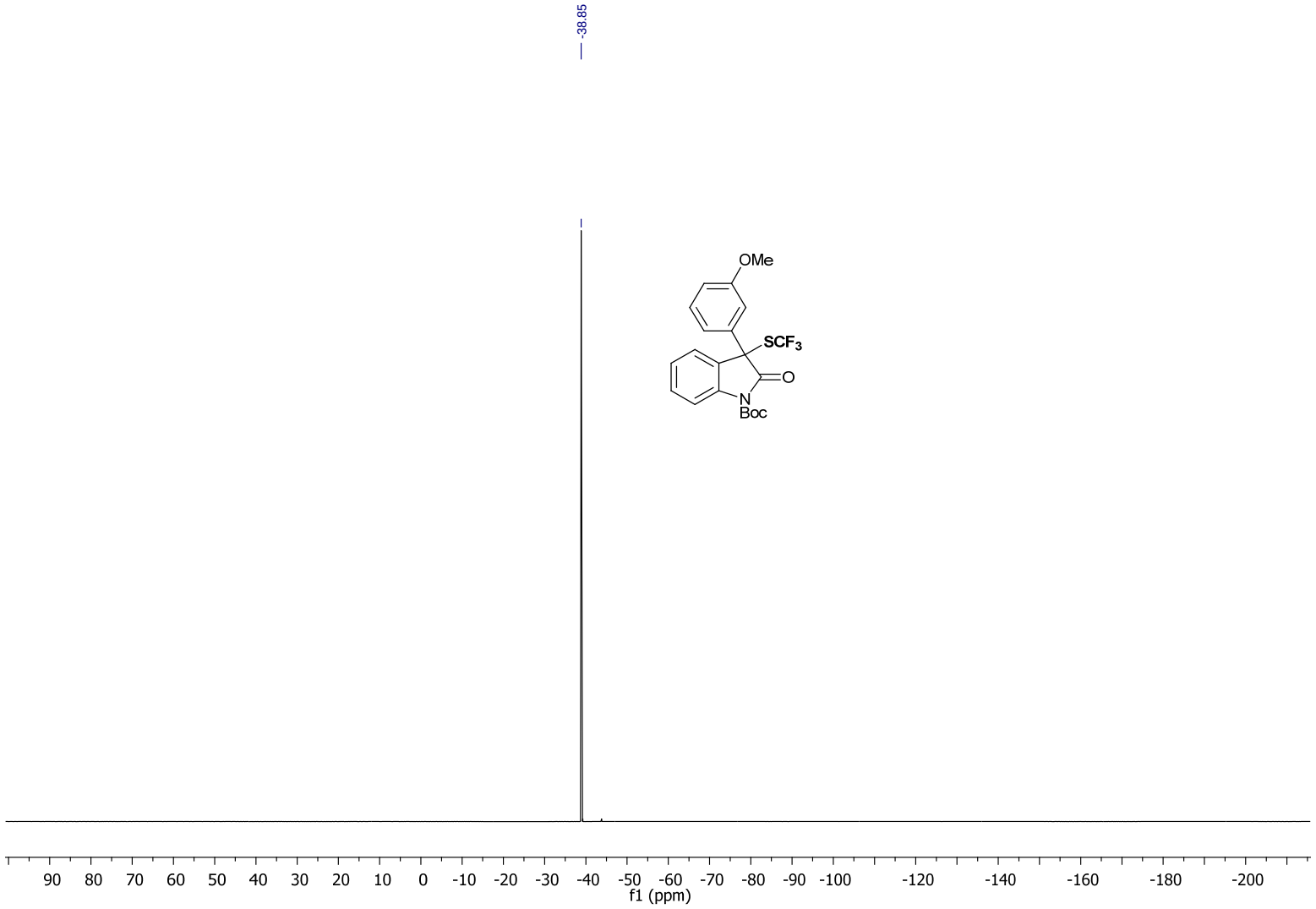

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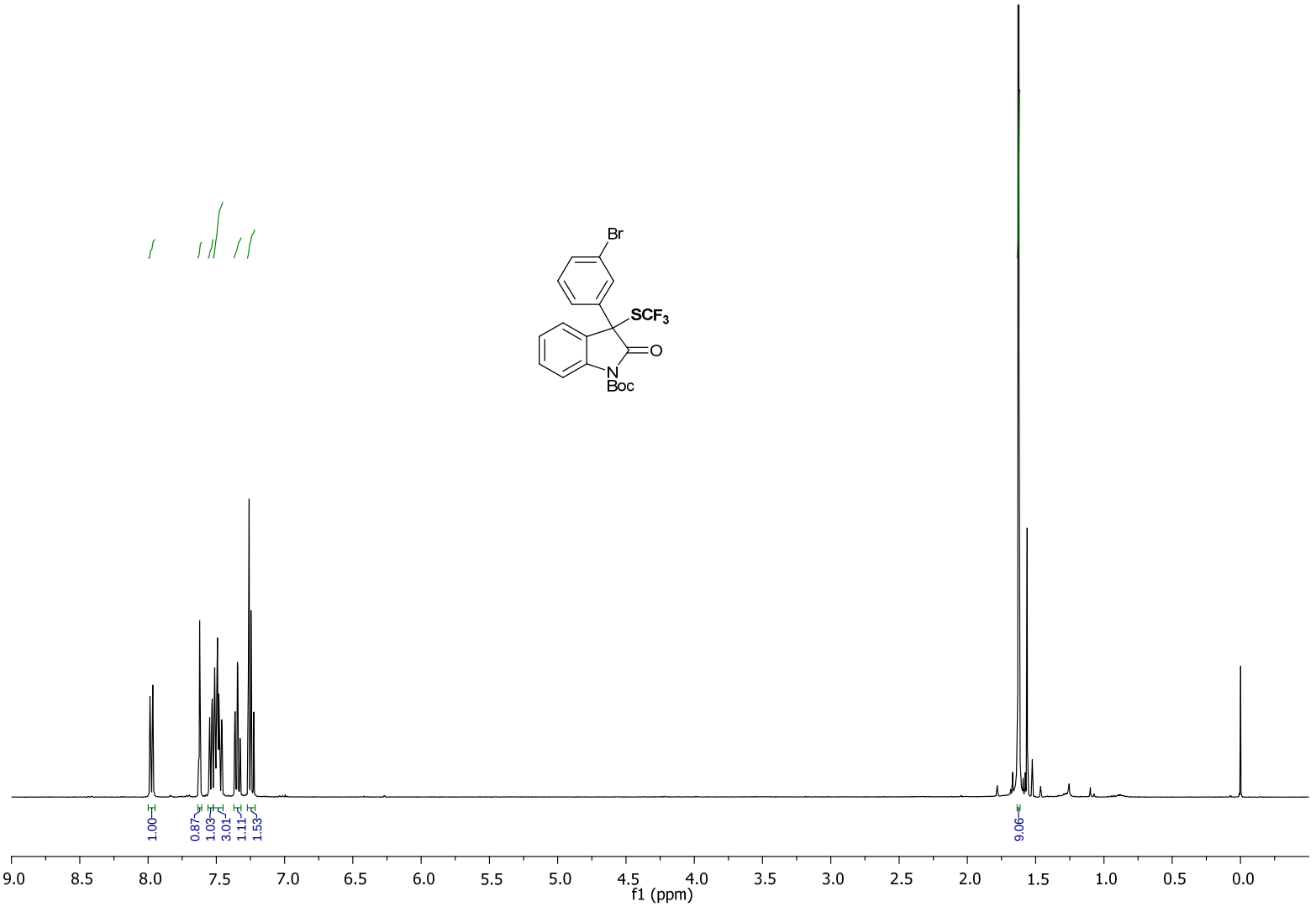

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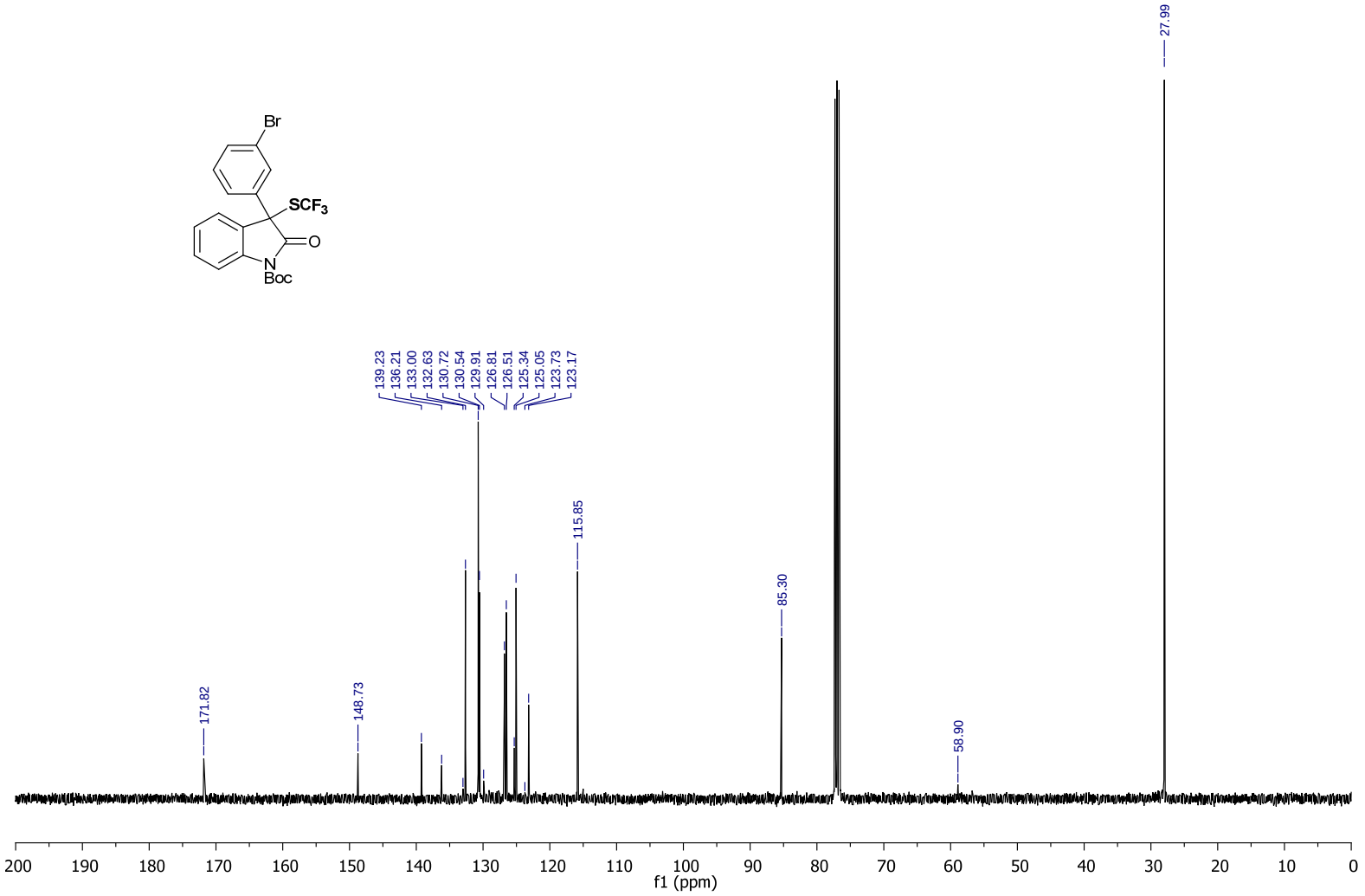

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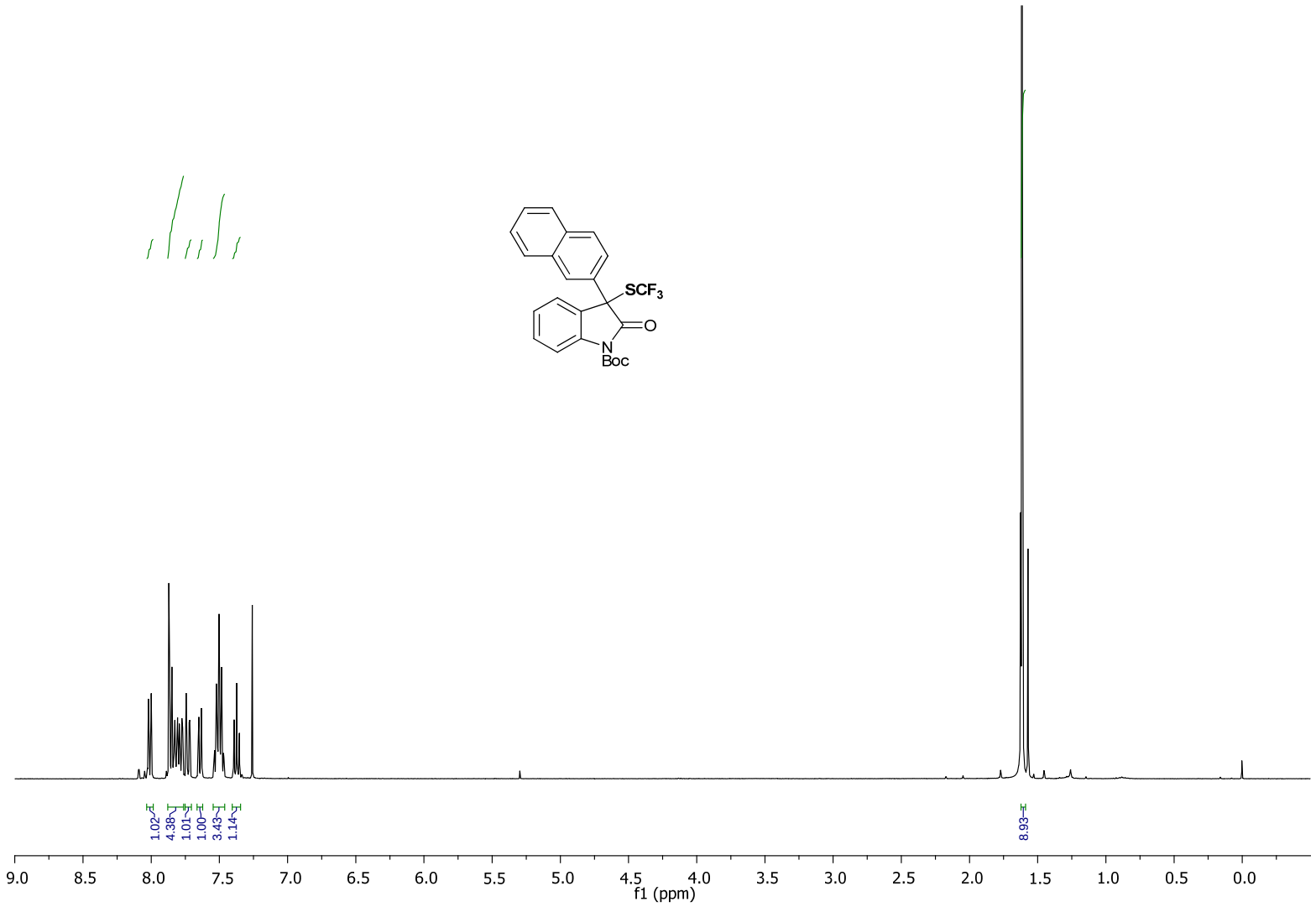

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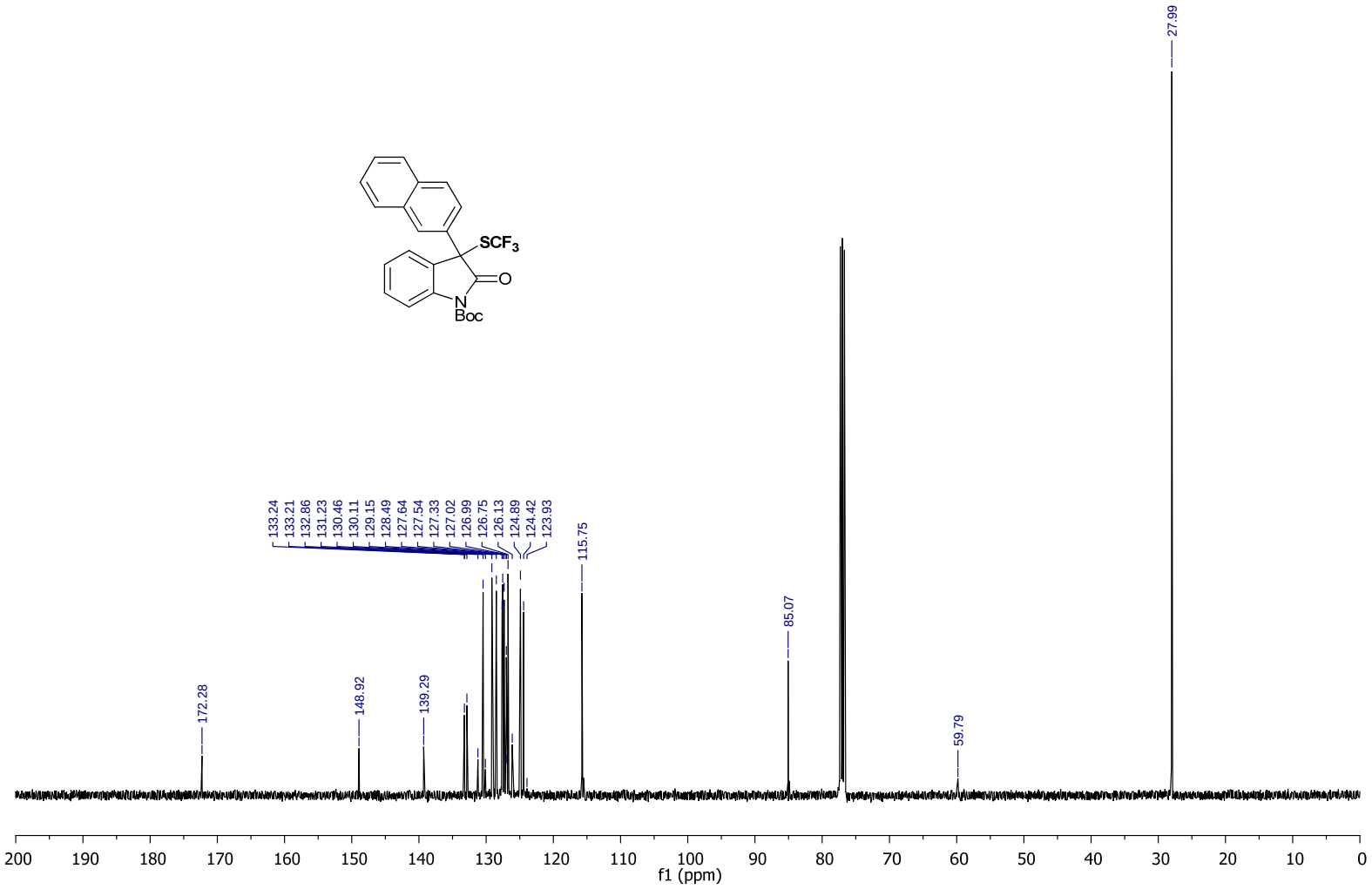

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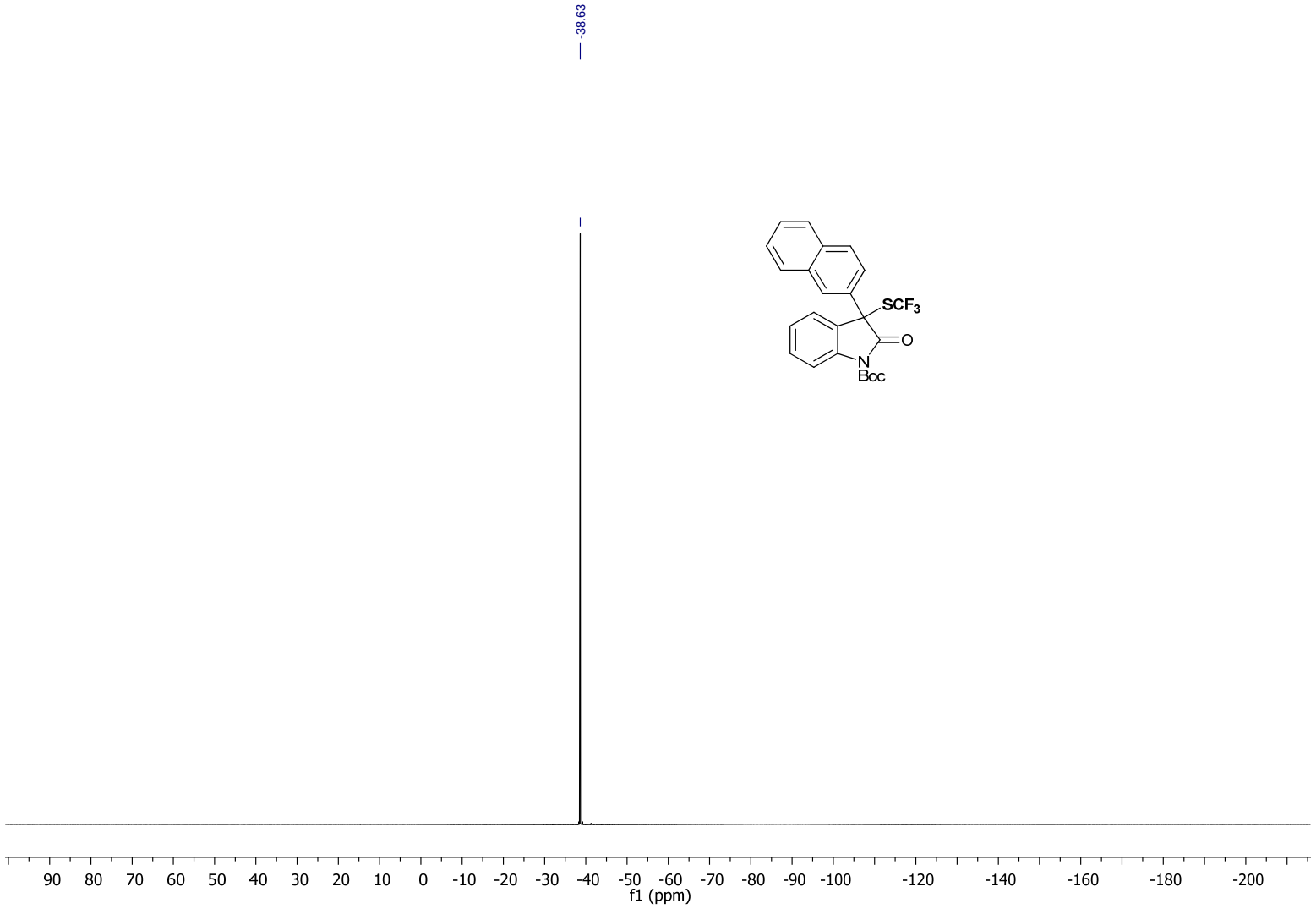

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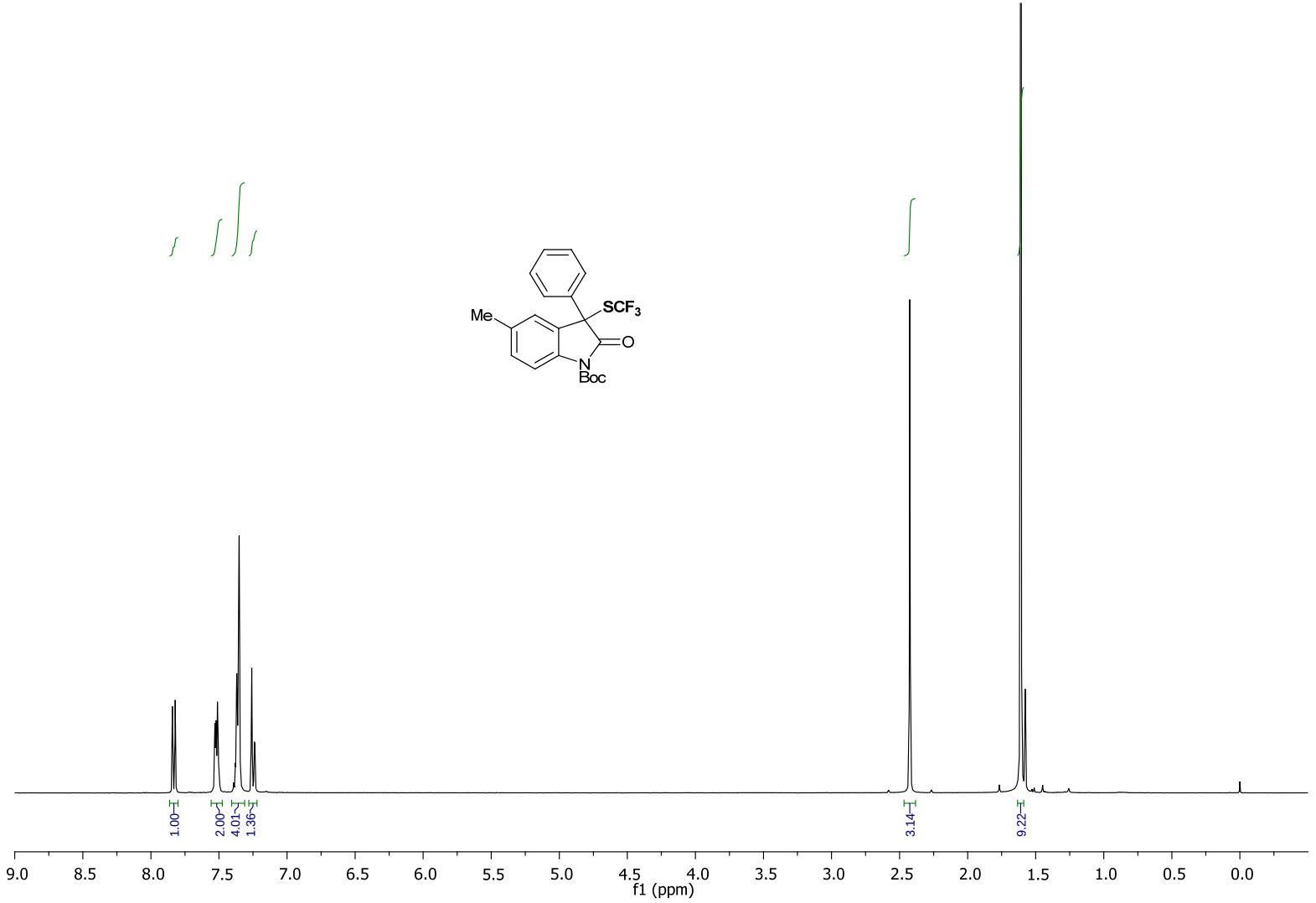

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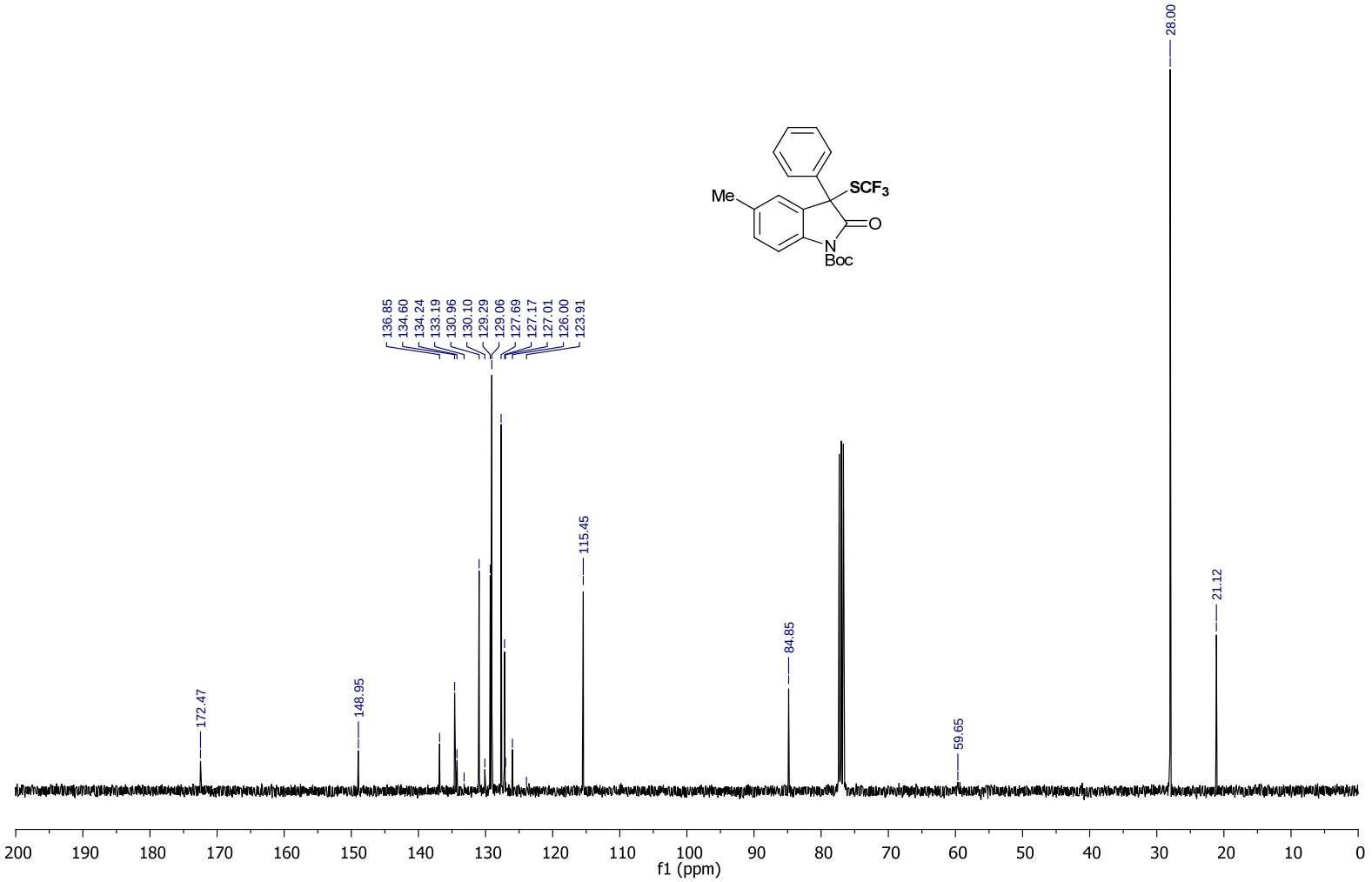

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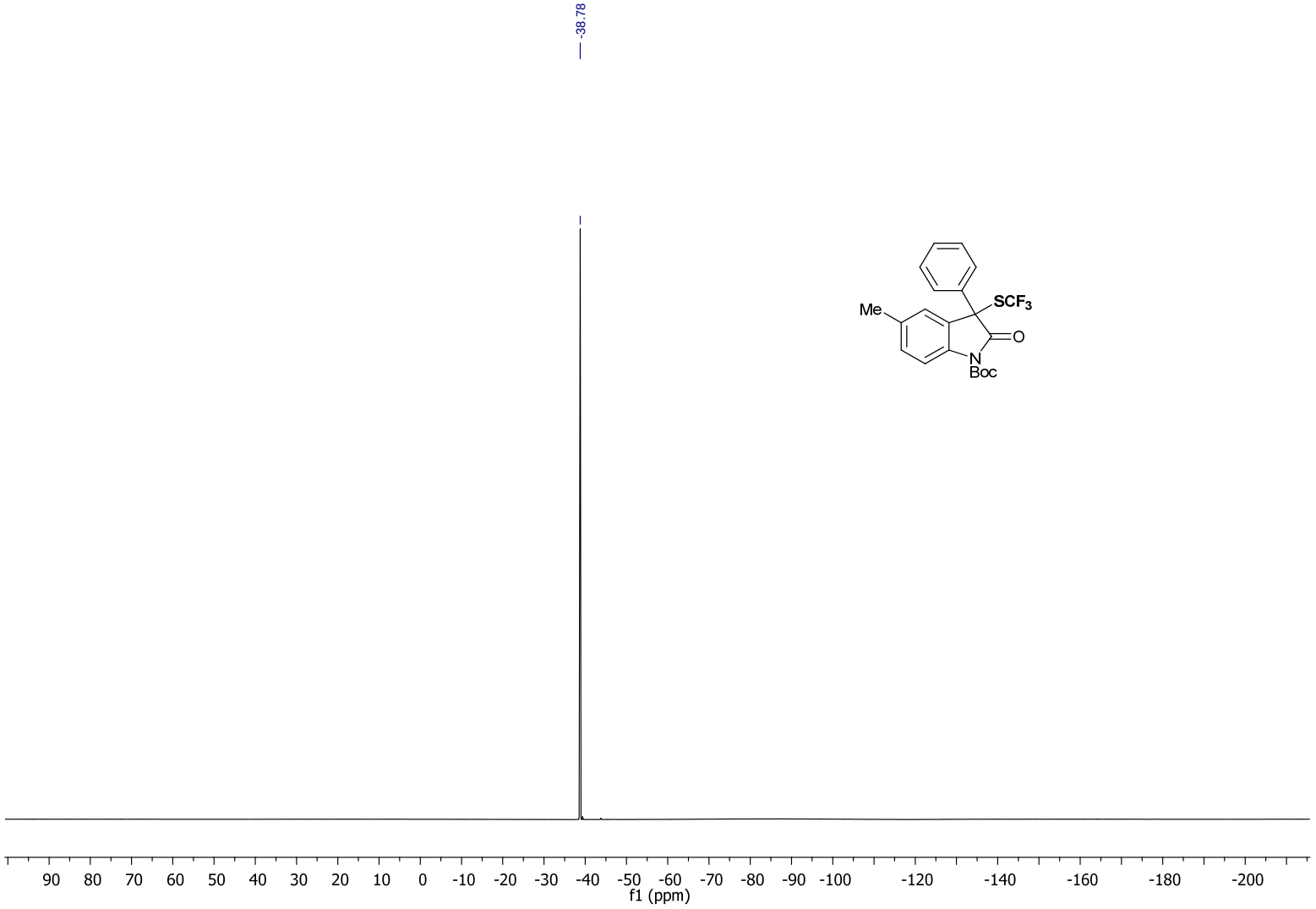

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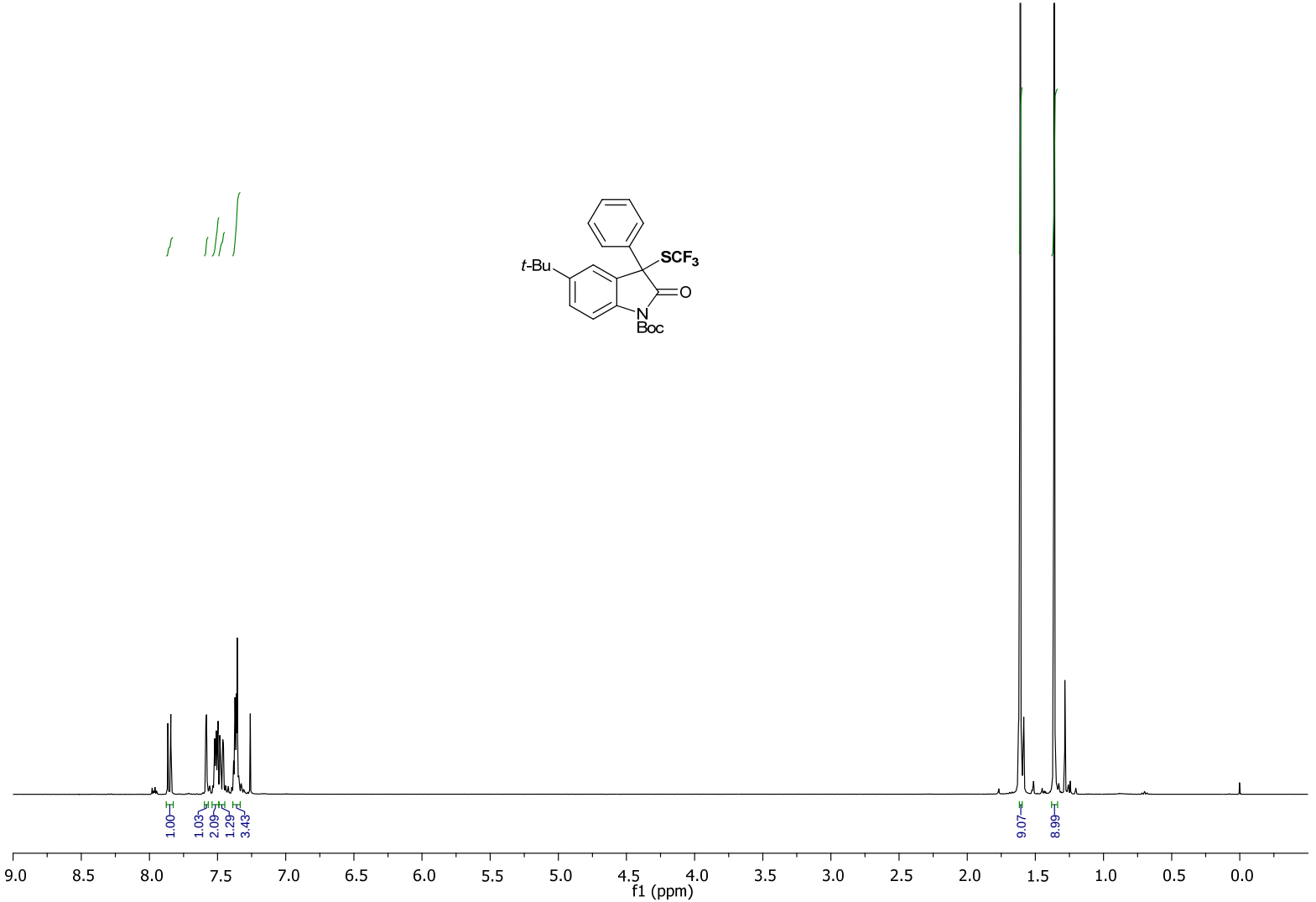

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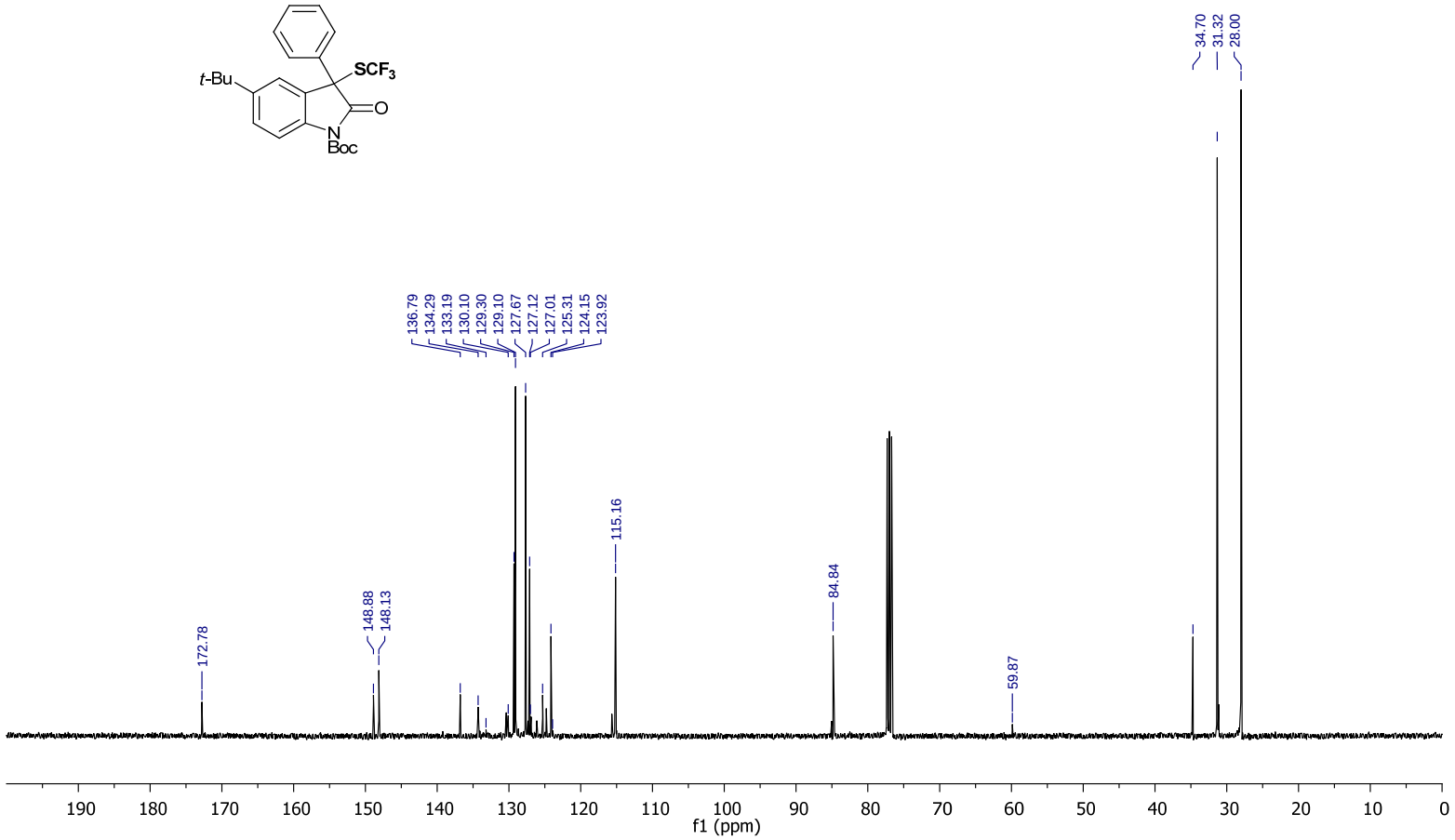

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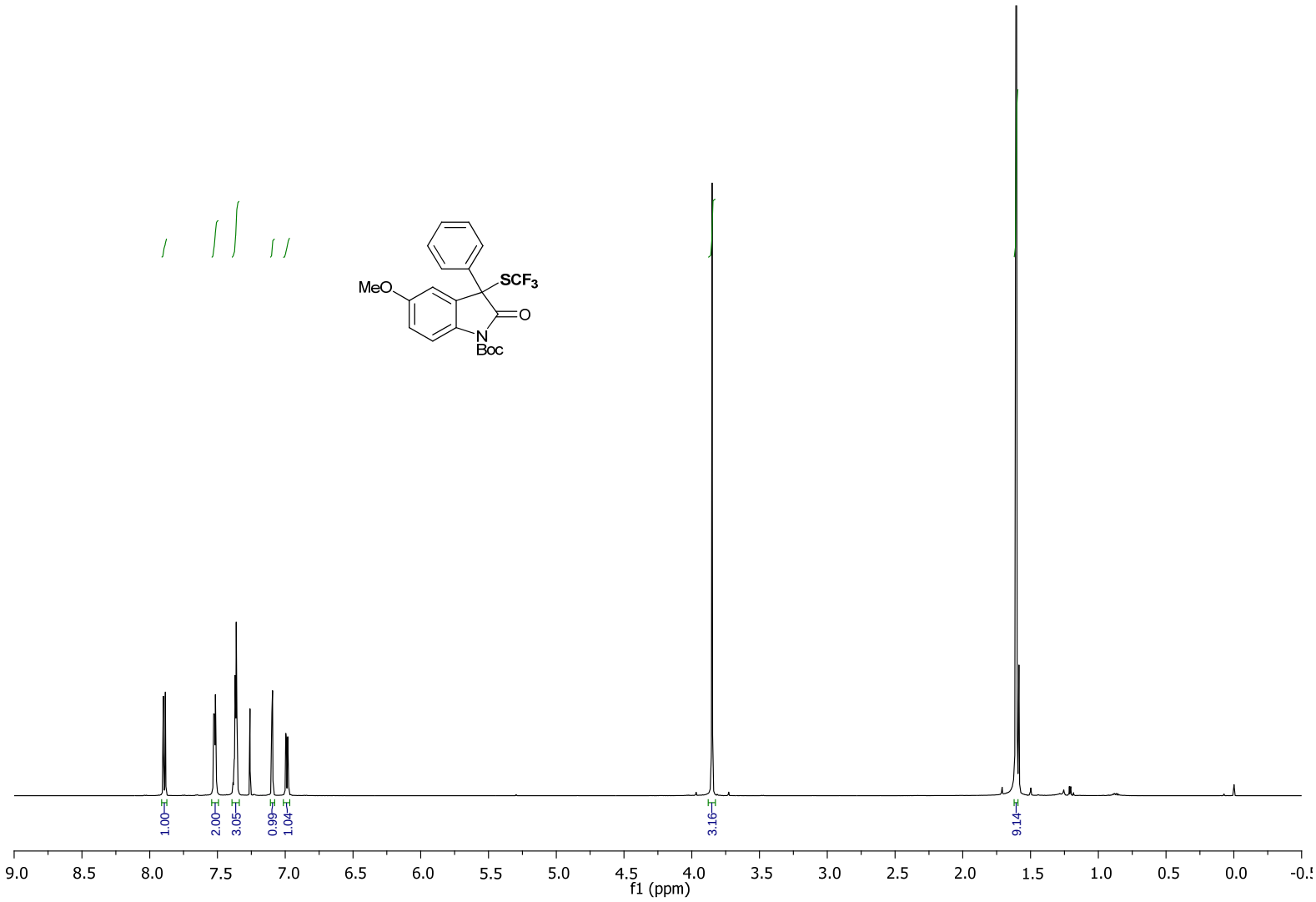

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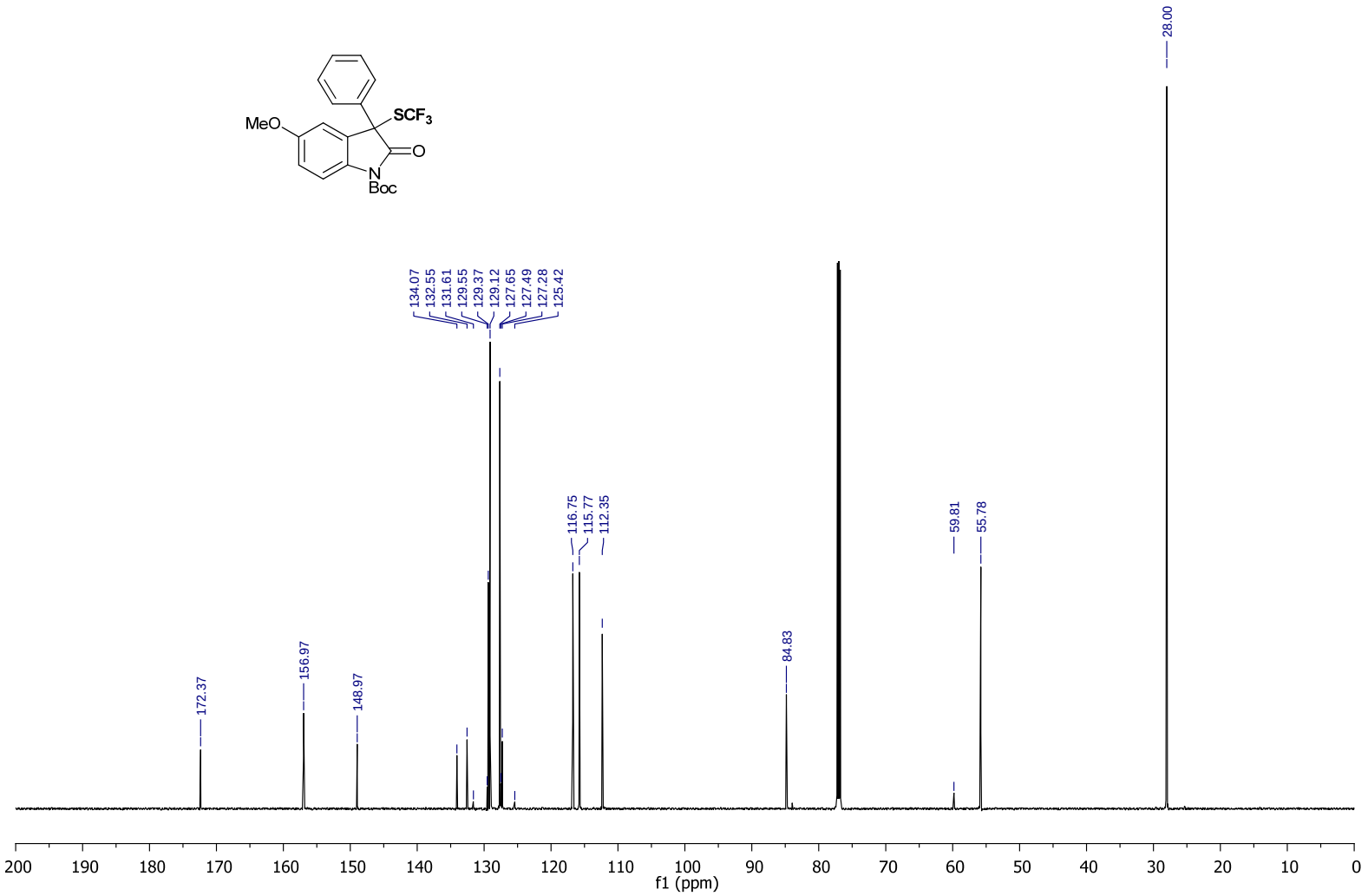

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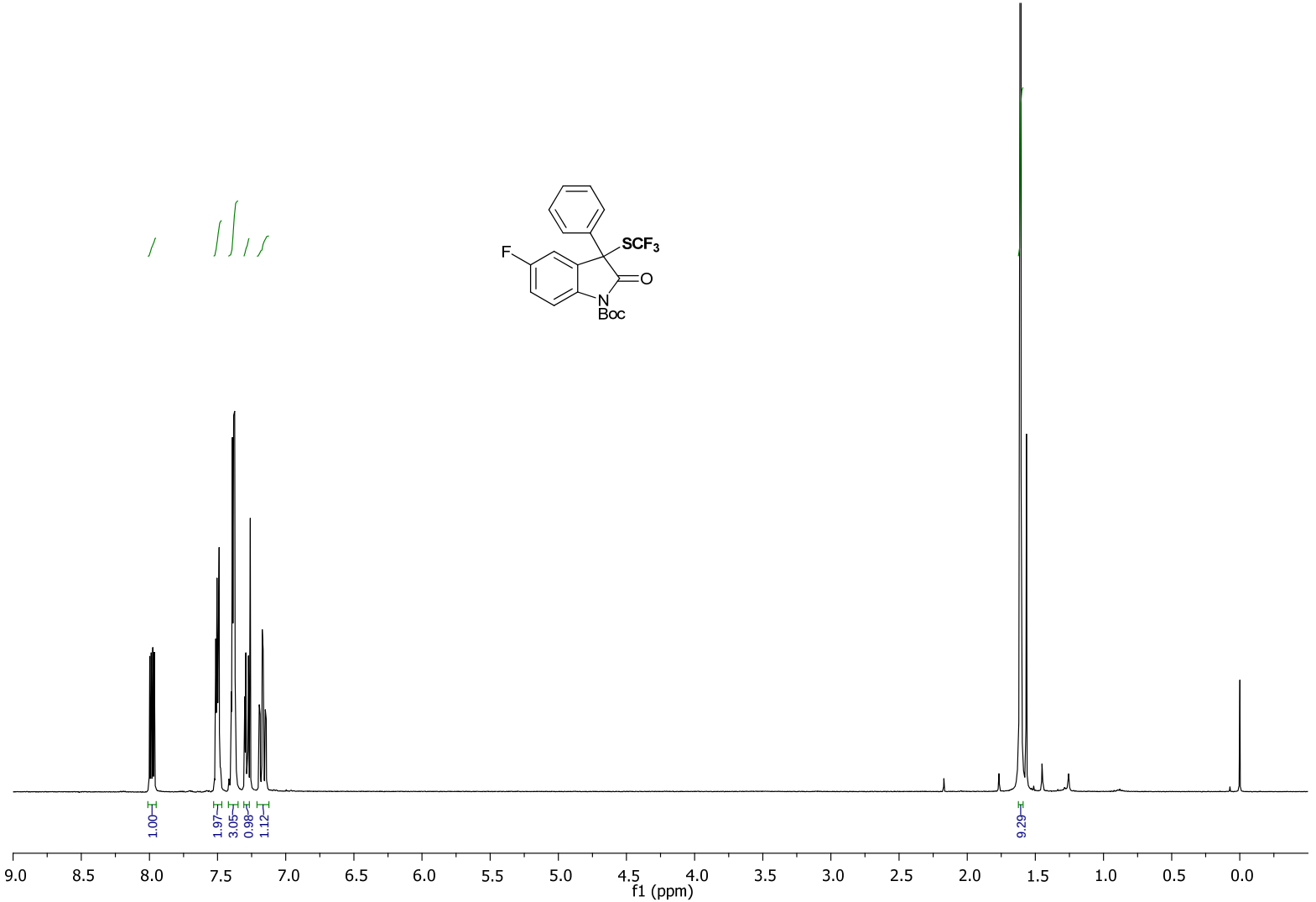

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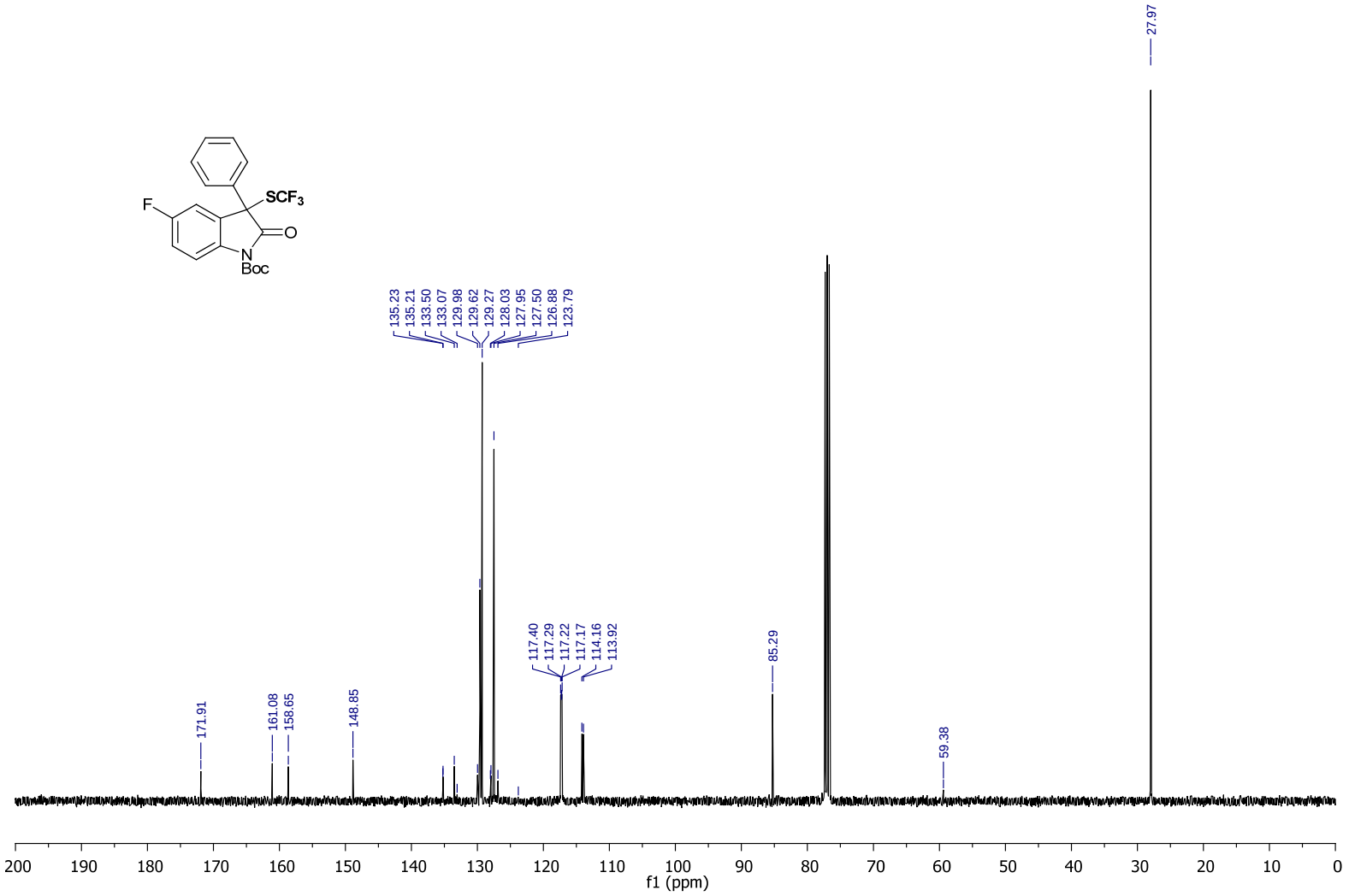

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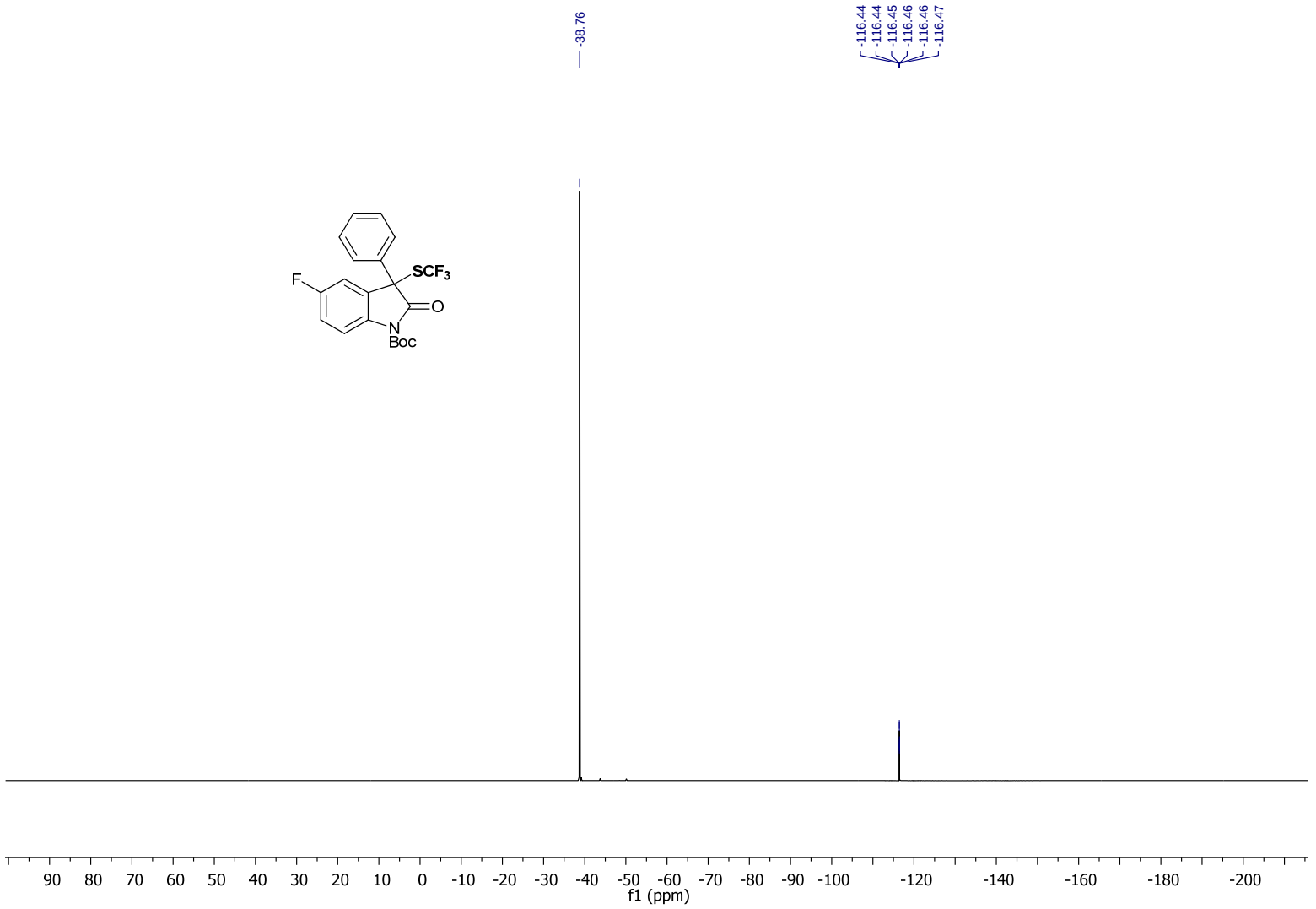

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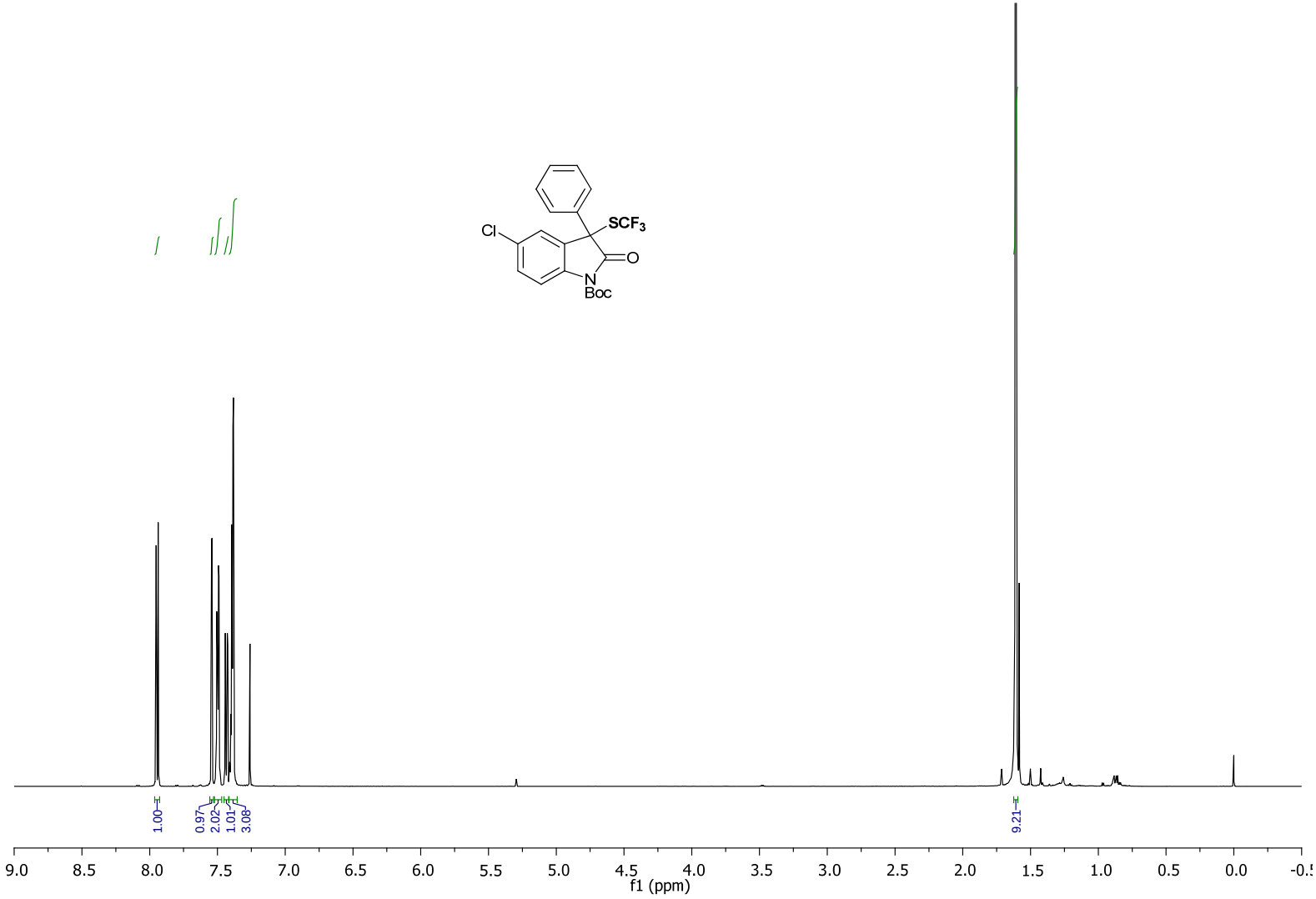

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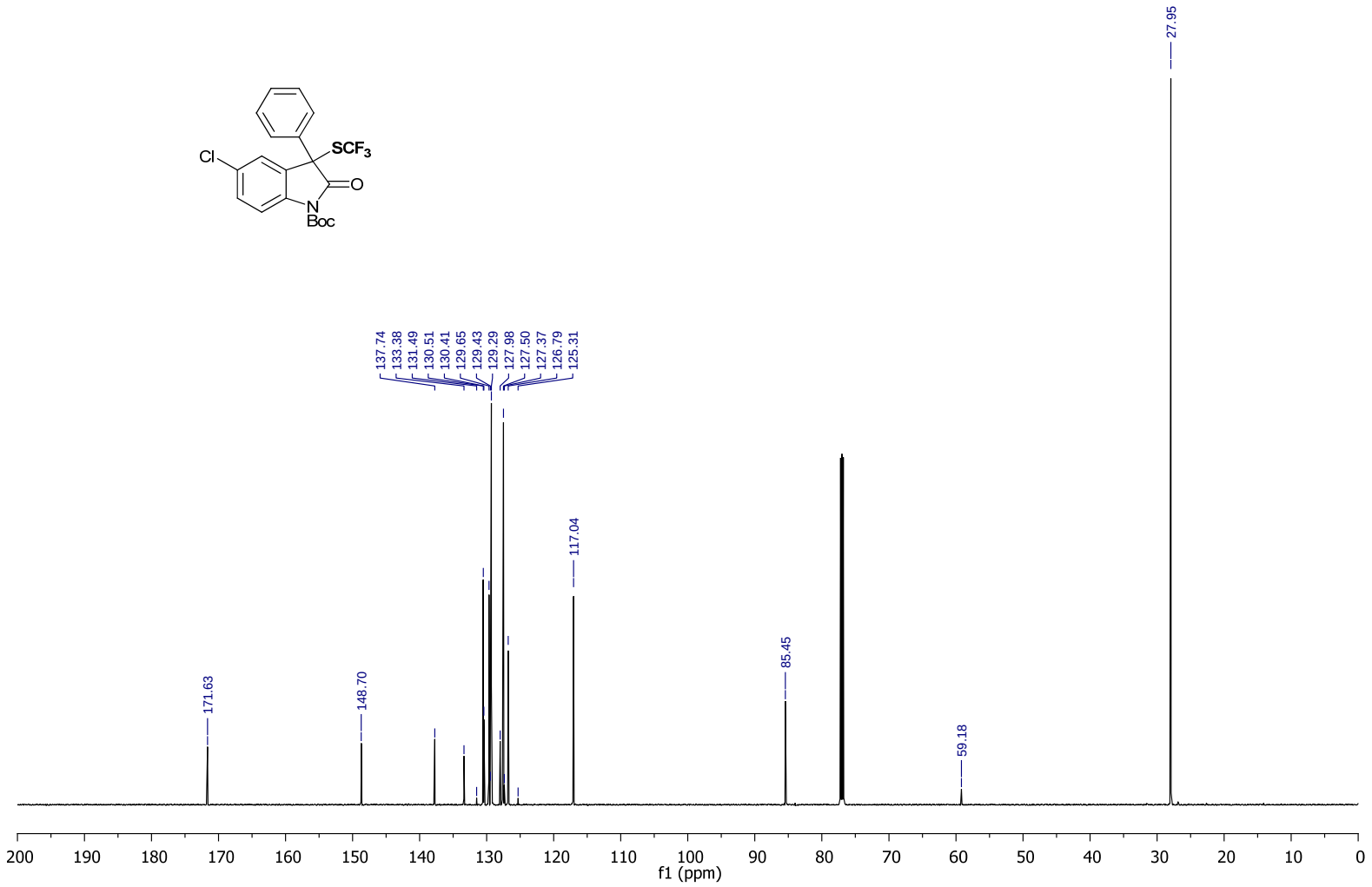

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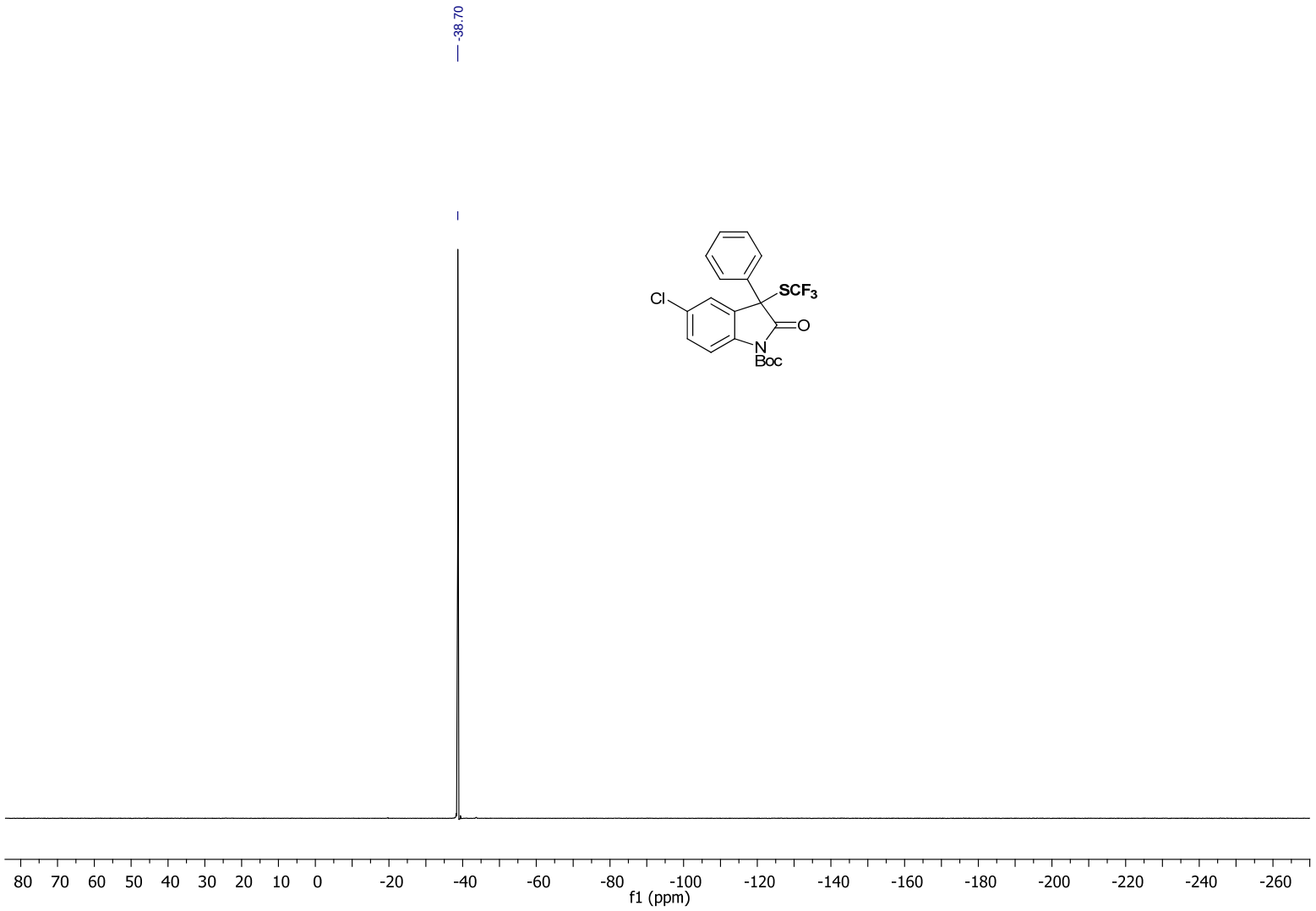

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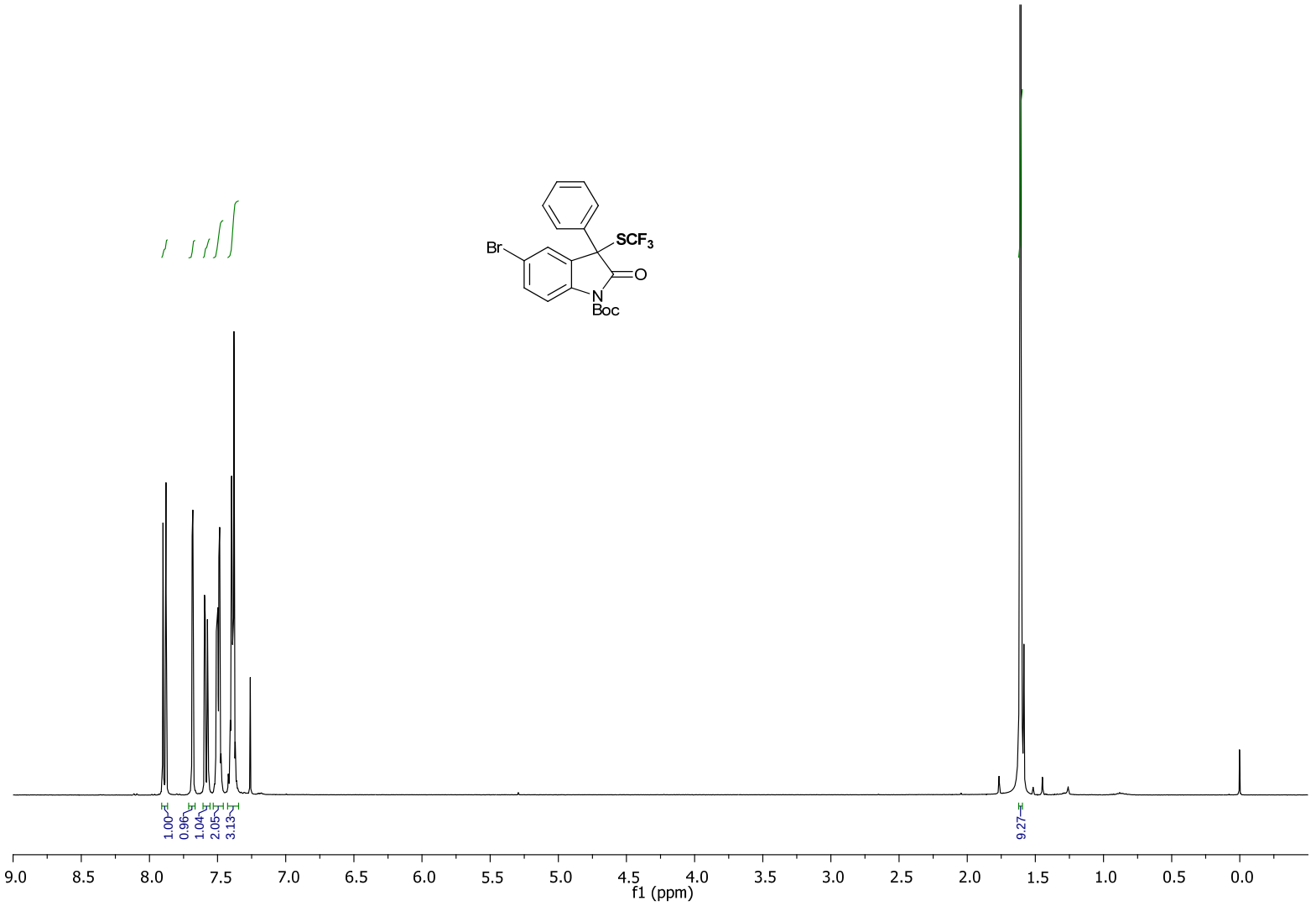

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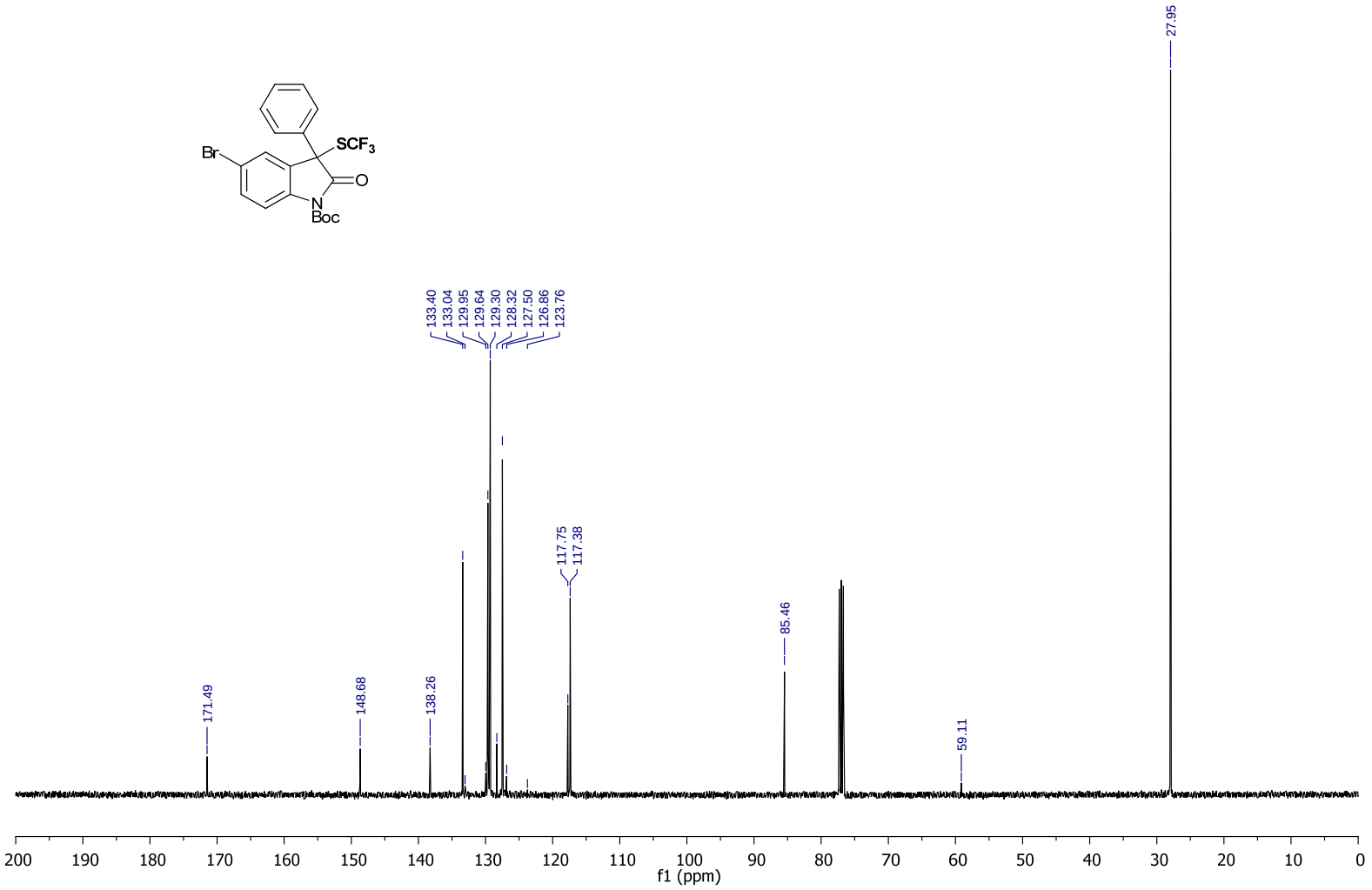

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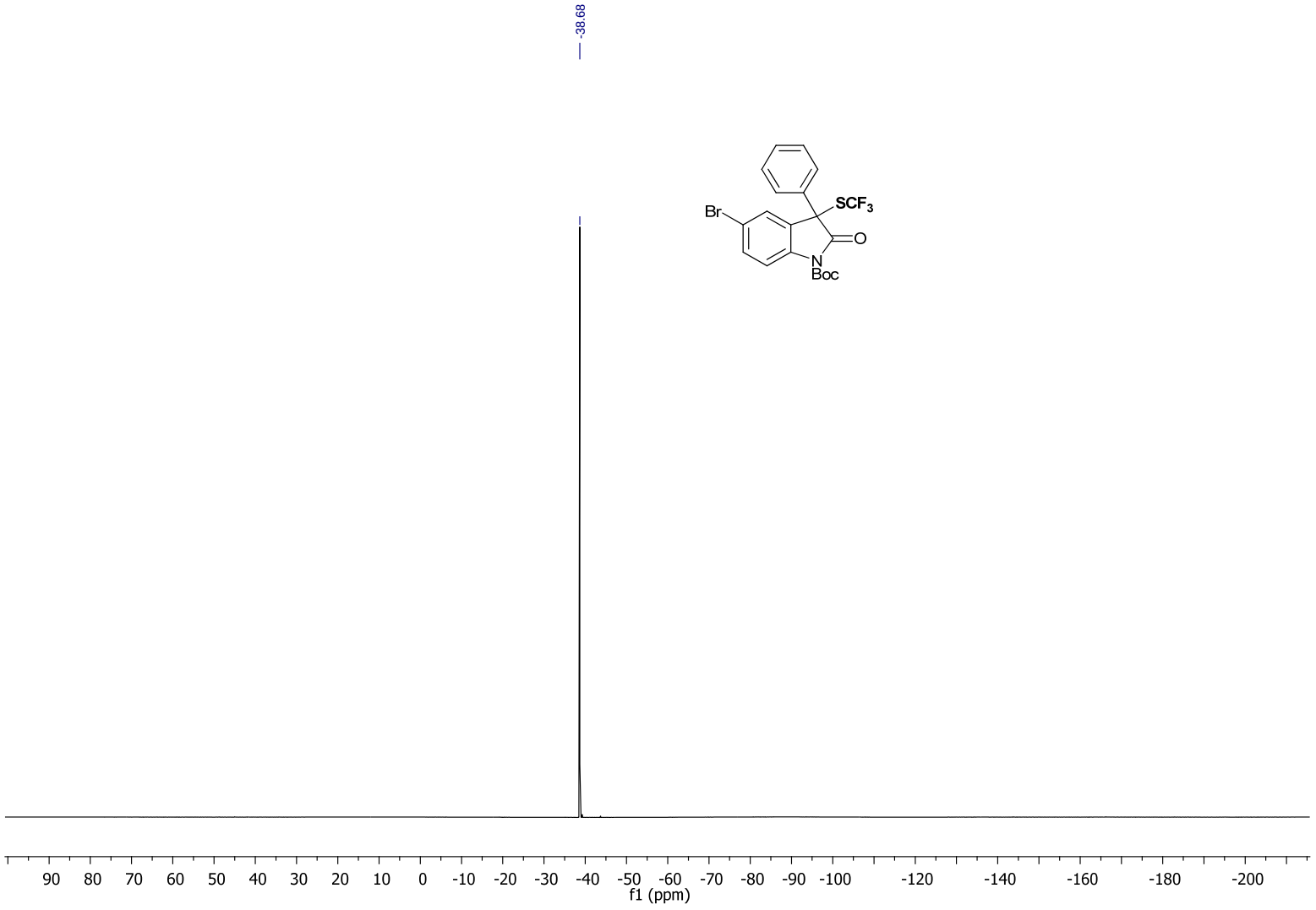

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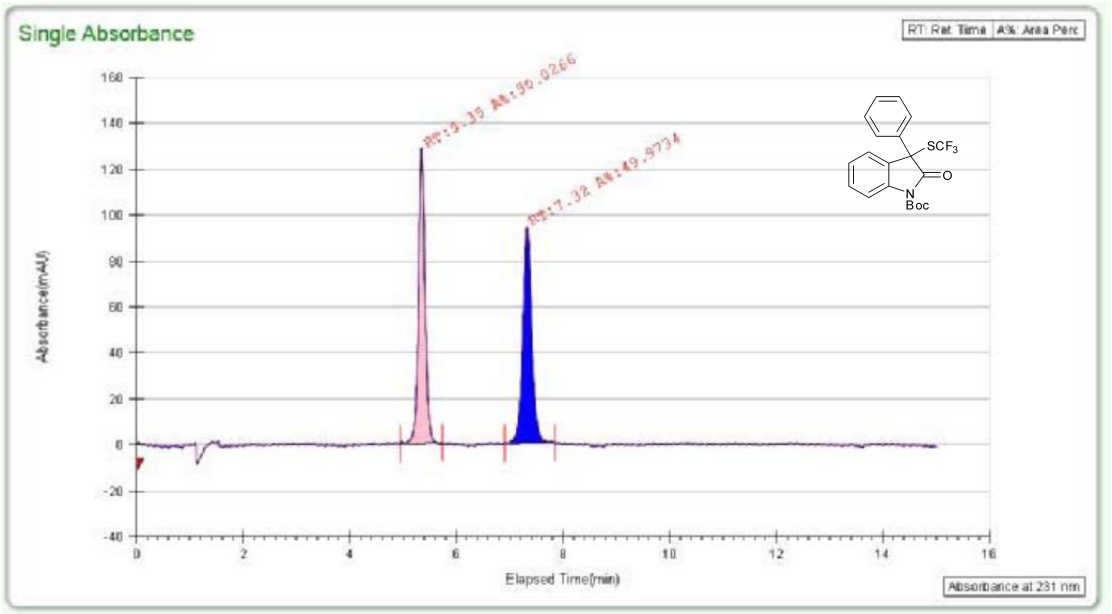

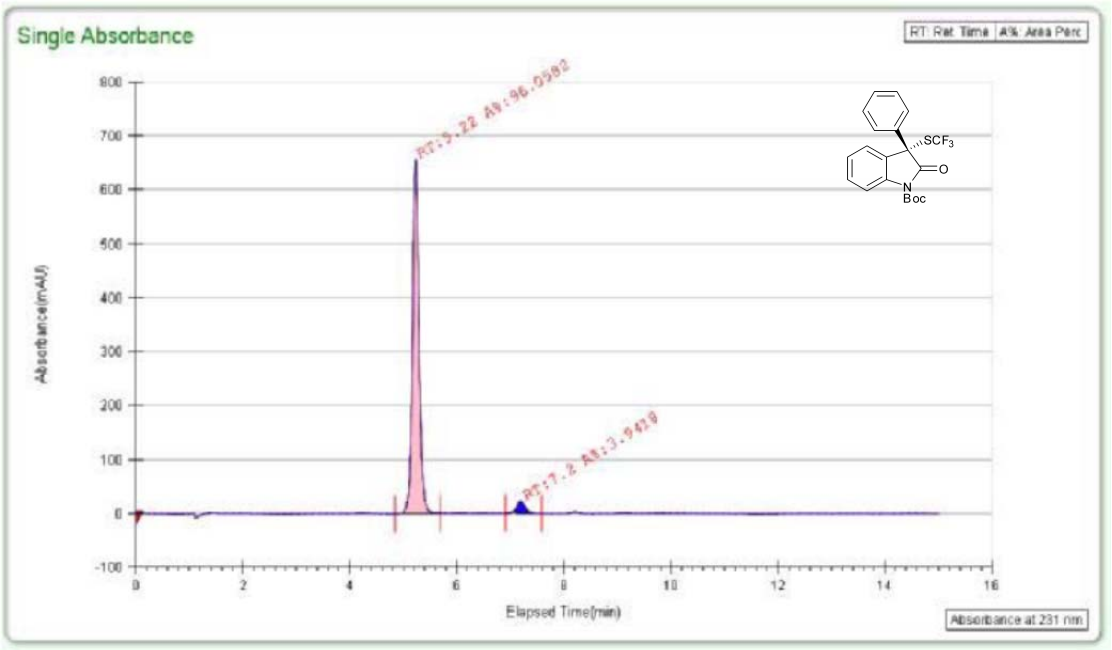

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1	96.0582	5555.0719	5.22	4.8446	5.6962
2	3.9418	227.957	7.2	6.9095	7.5828

Chromatogram : XL380Ra_IA_991_flow1_40999913

Data file: XL380Ra_IA_991_flow1_40999913.DATA
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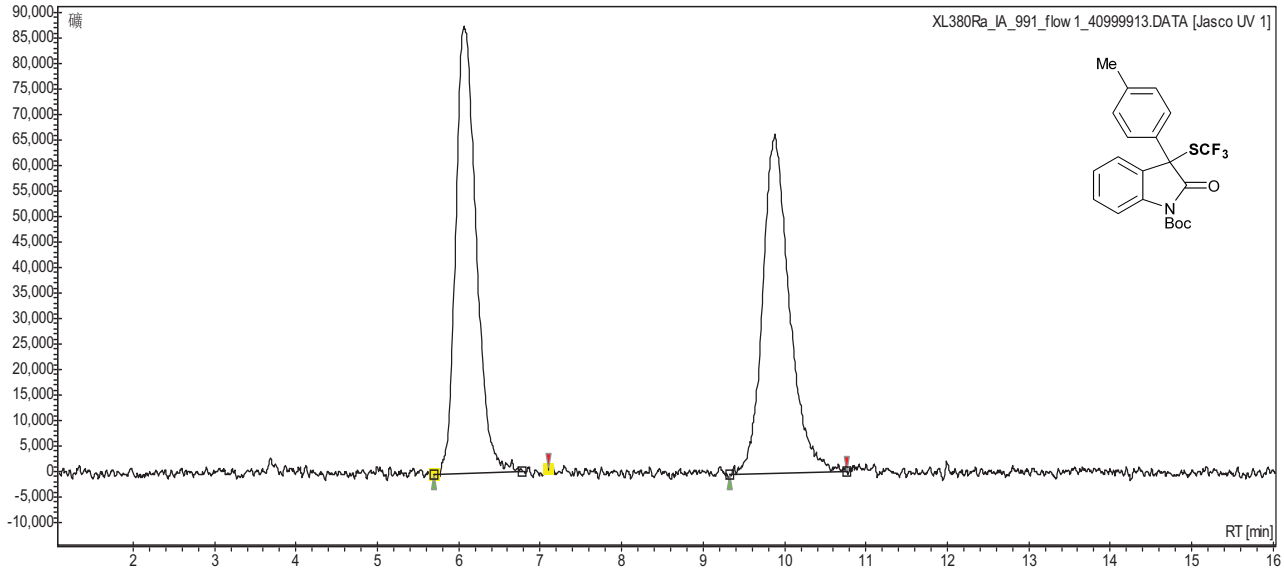
Date: 2013/8/13 2:13:58



XL380Ra_IA_991_flow1_40999913.DATA [Jasco UV 1]

Index	Start	Time	End	Area %
	[Min]	[Min]	[Min]	[%]
1	5.702	6.067	7.107	50.015
2	9.331	9.883	10.765	49.985
Total				100.000

Chromatogram : XL380_IA_991_flow1_40999914

Data file: XL380_IA_991_flow1_40999914.DATA
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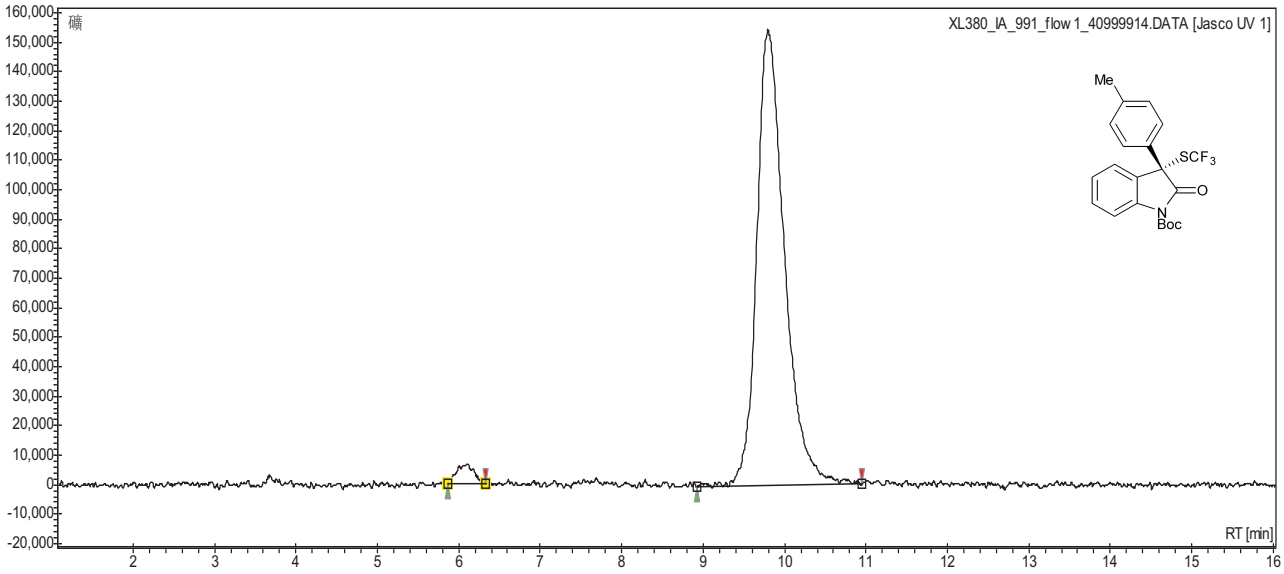

XL380_IA_991_flow1_40999914.DATA [Jasco UV 1]

Index	Start	Time	End	Area %
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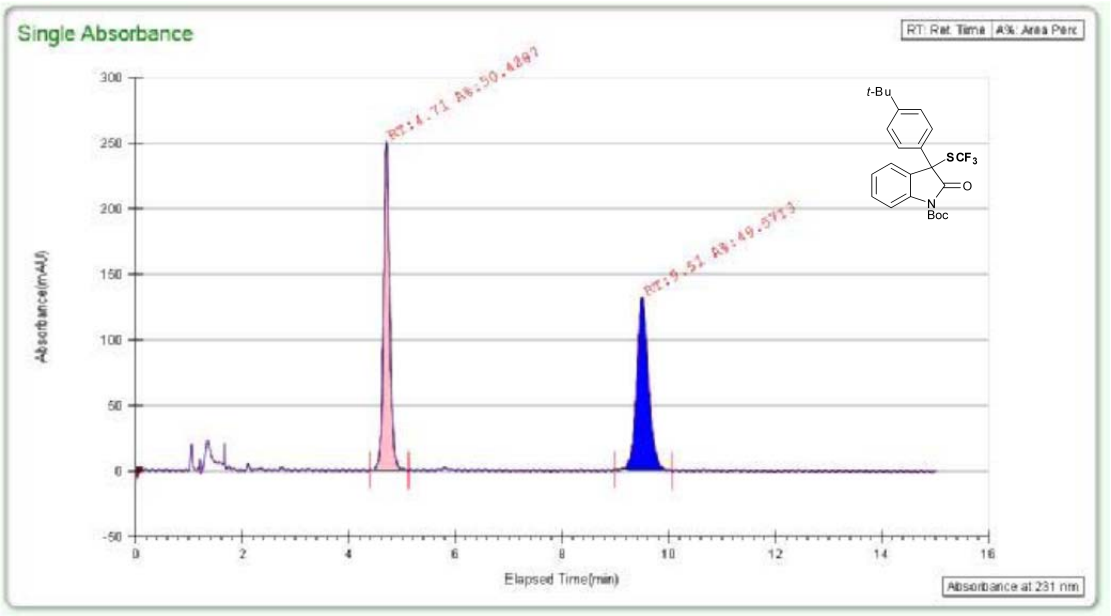
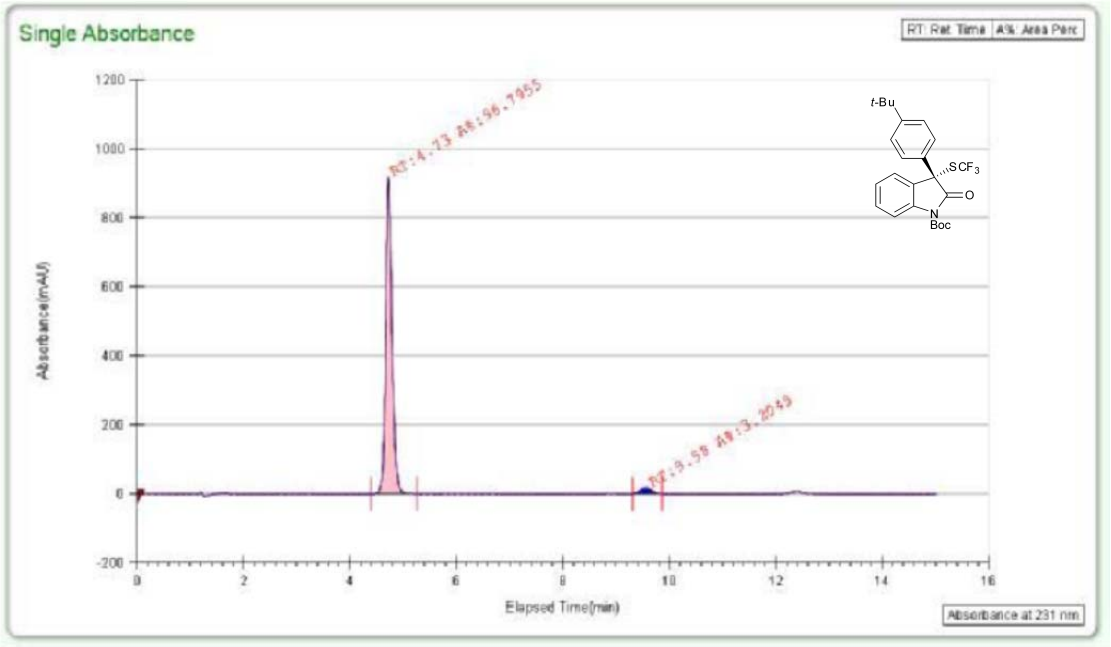
1	8.926	9.800	10.950	97.369
Total				100.000





Peak Info					
Number	Area %	Area	RT (min)	St. (min)	End (min)
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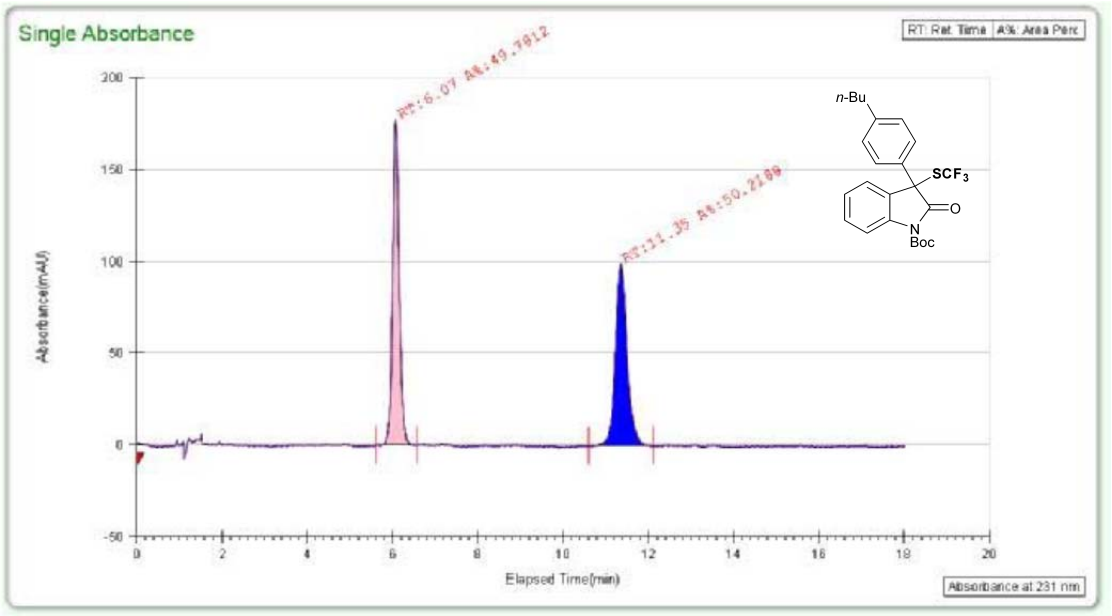

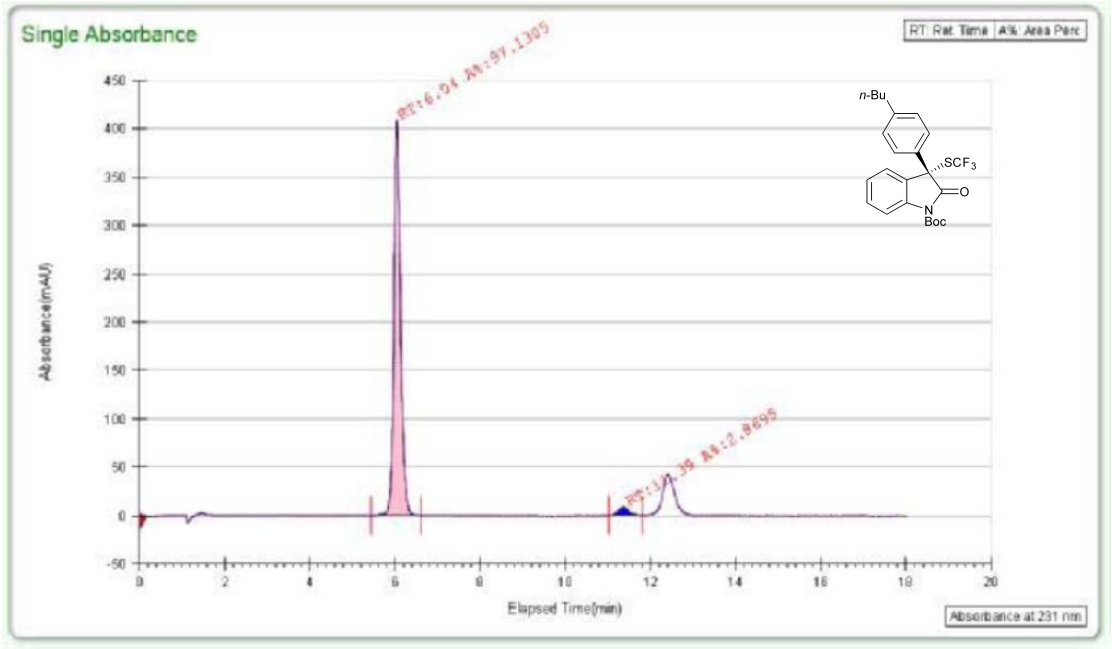

Peak Info

Number	Area %	Area	RT (min)	St. (min)	End (min)
1	97.1305	4327.0845	6.04	5.4346	6.5995
2	2.8695	127.8331	11.39	11.0184	11.8102

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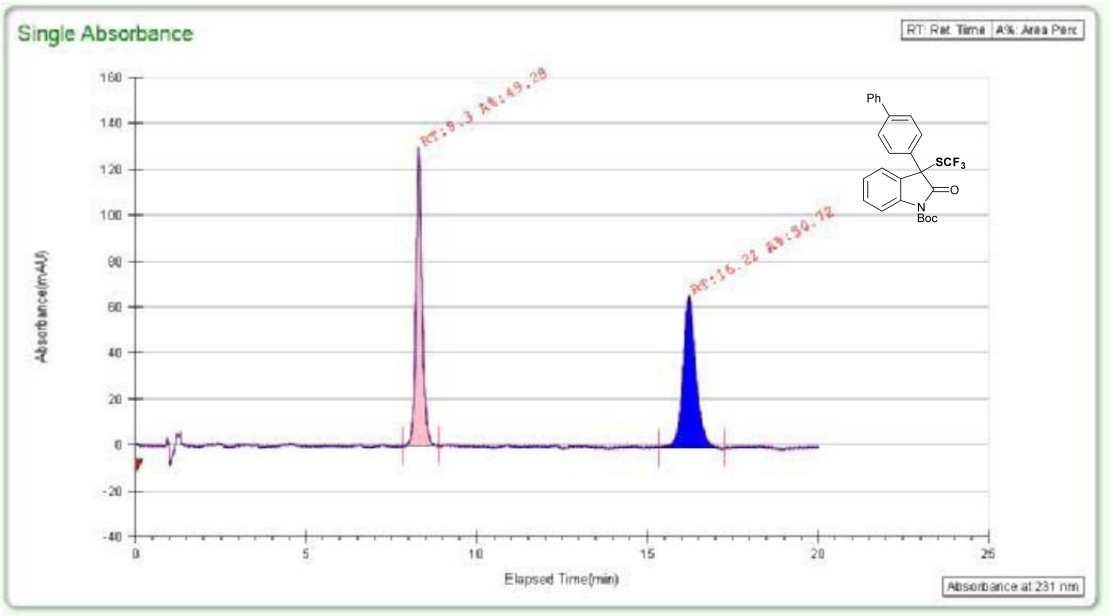

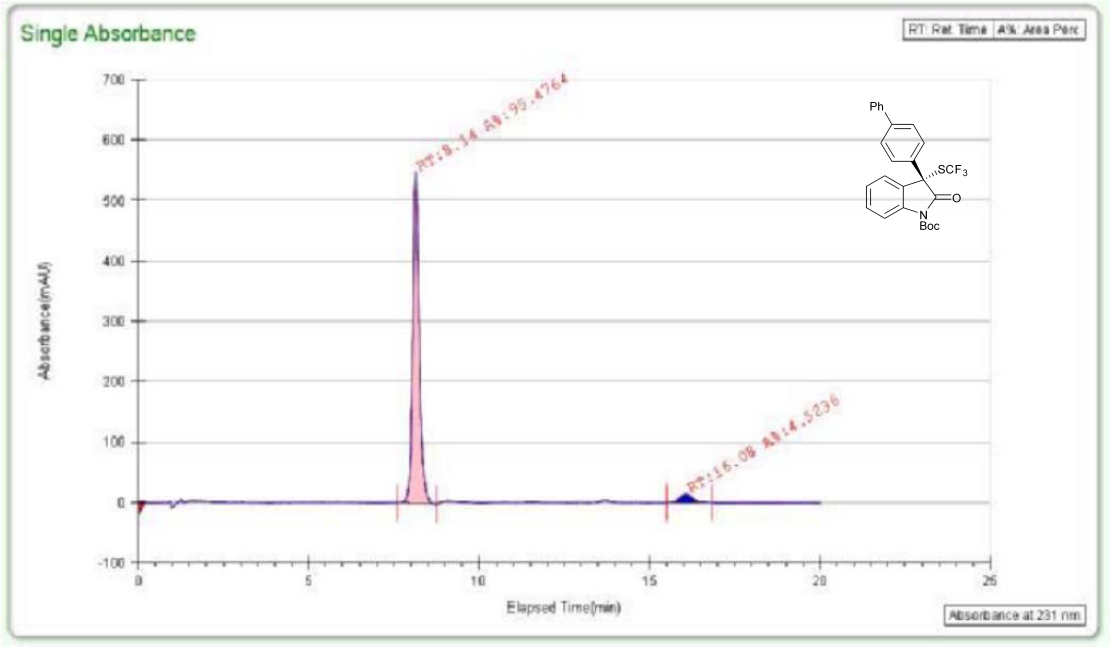

Peak Info

Number	Area %	Area	RT (min)	St. (min)	End (min)
1	95.4764	7319.7238	8.14	7.5994	8.7462
2	4.5236	346.804	16.08	15.5093	16.8413

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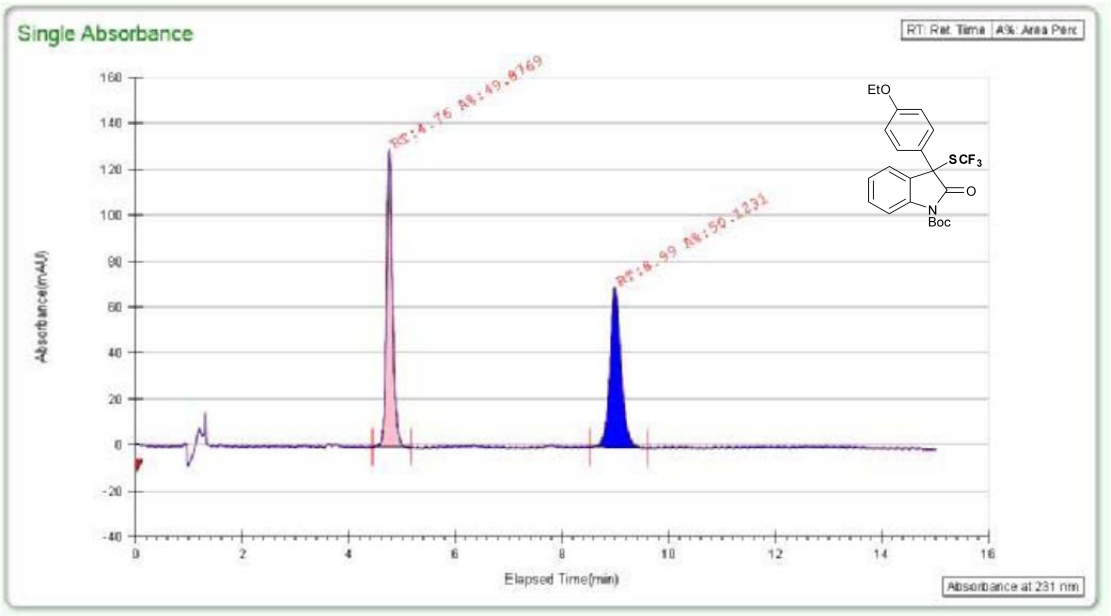

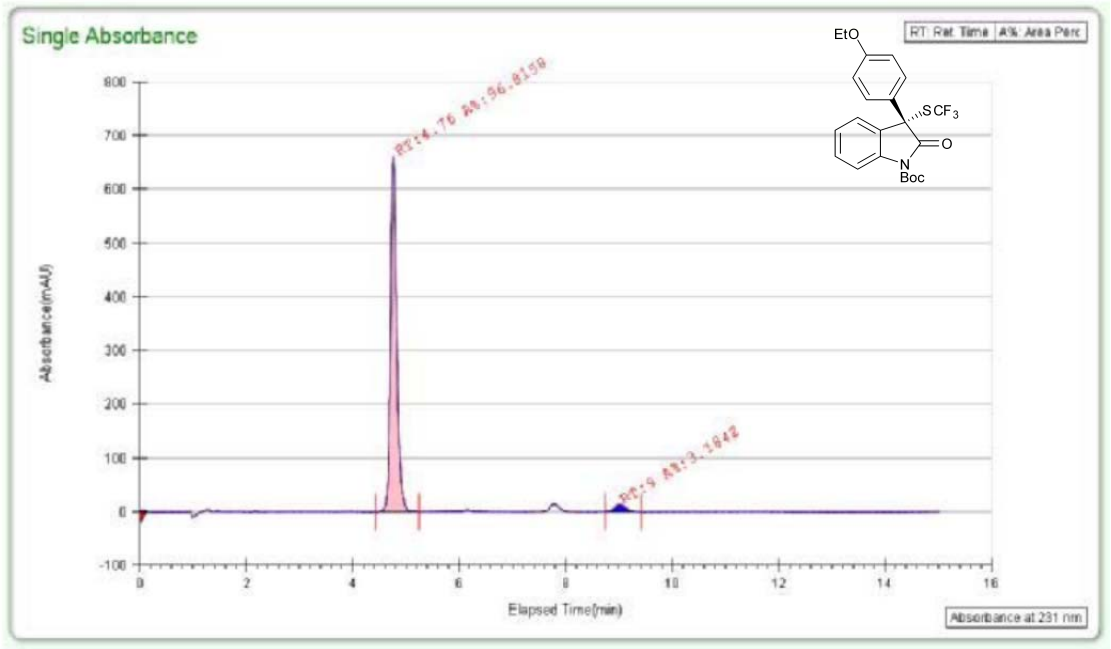

Peak Info					
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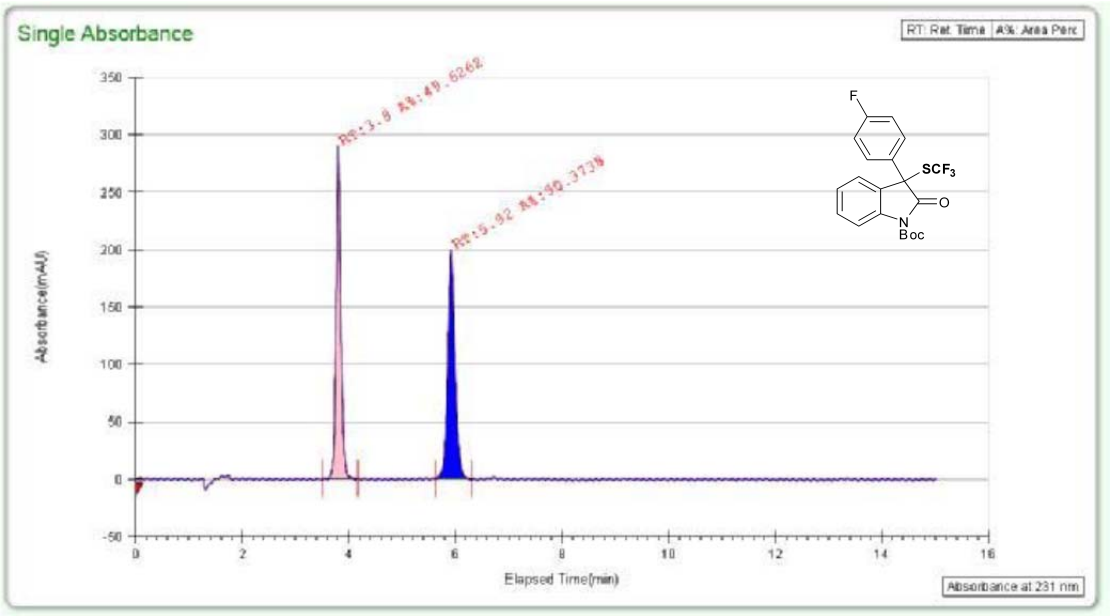
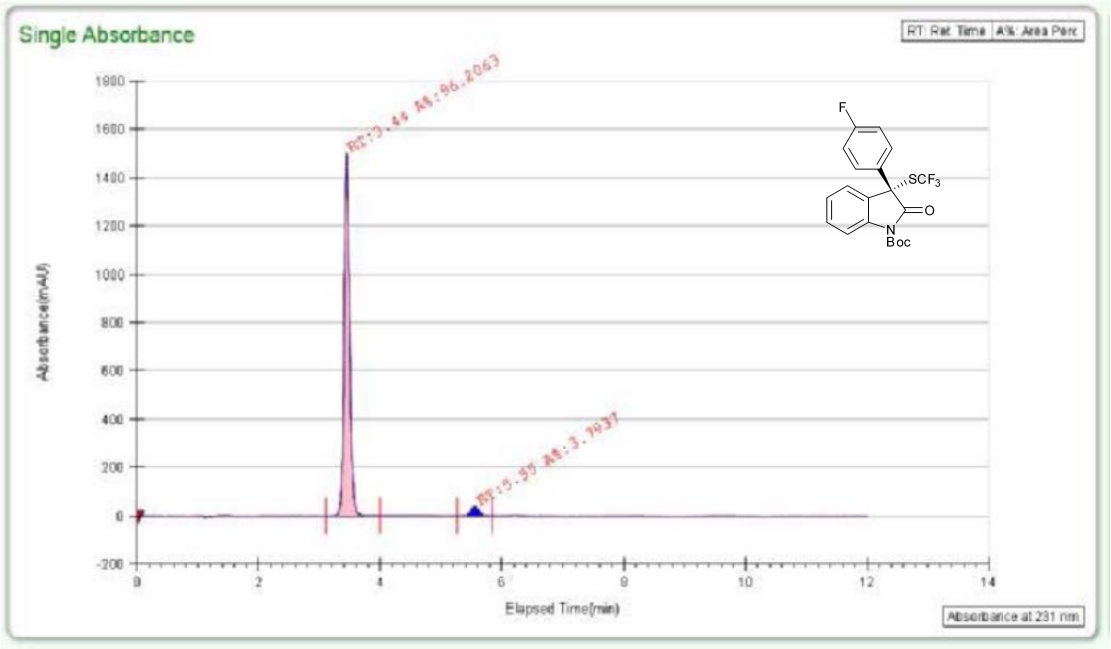
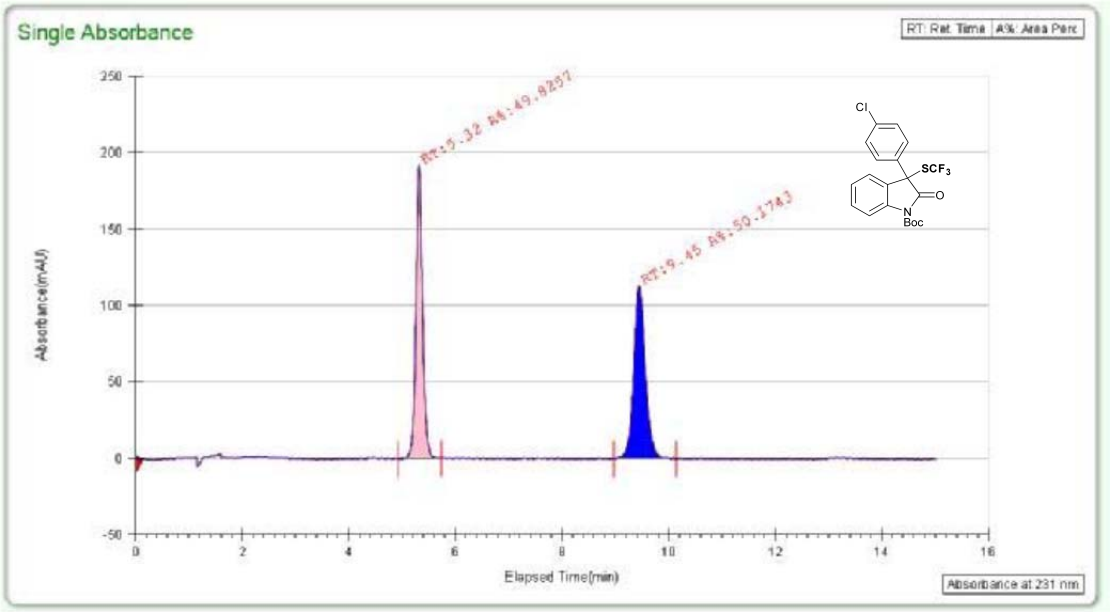
1	96.8158	5214.6745	4.76	4.428	5.2396
2	3.1842	171.5056	9	8.7346	9.4081

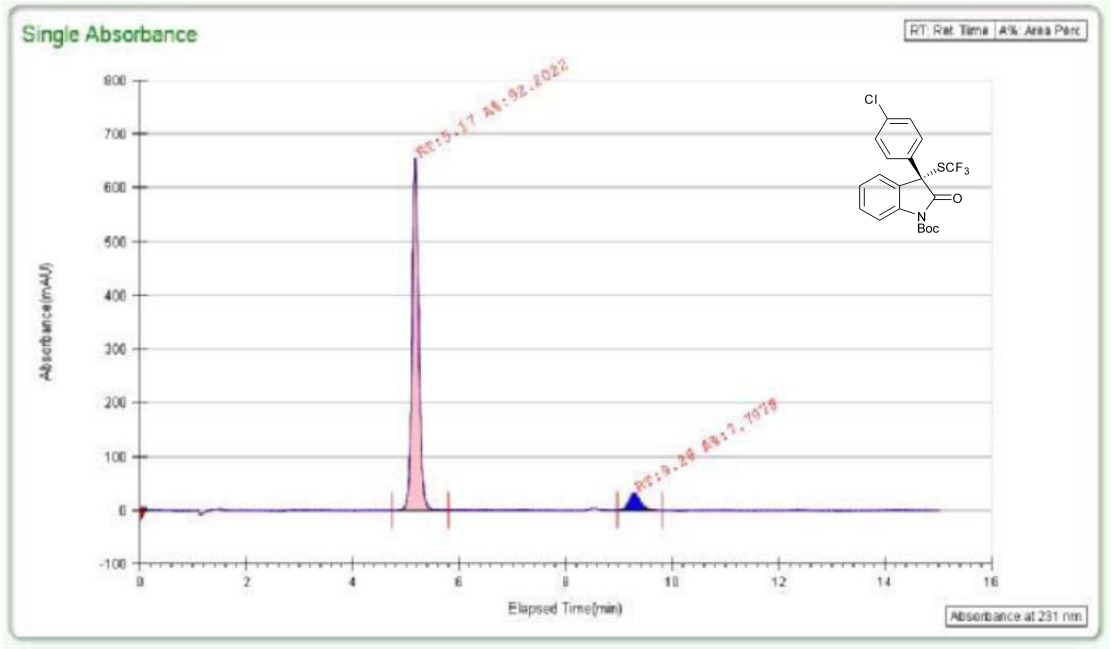




Peak Info

Number	Area %	Area	RT (min)	St. (min)	End (min)
1	96.2063	9083.2178	3.44	3.1098	3.9947
2	3.7937	358.1768	5.55	5.2646	5.8346



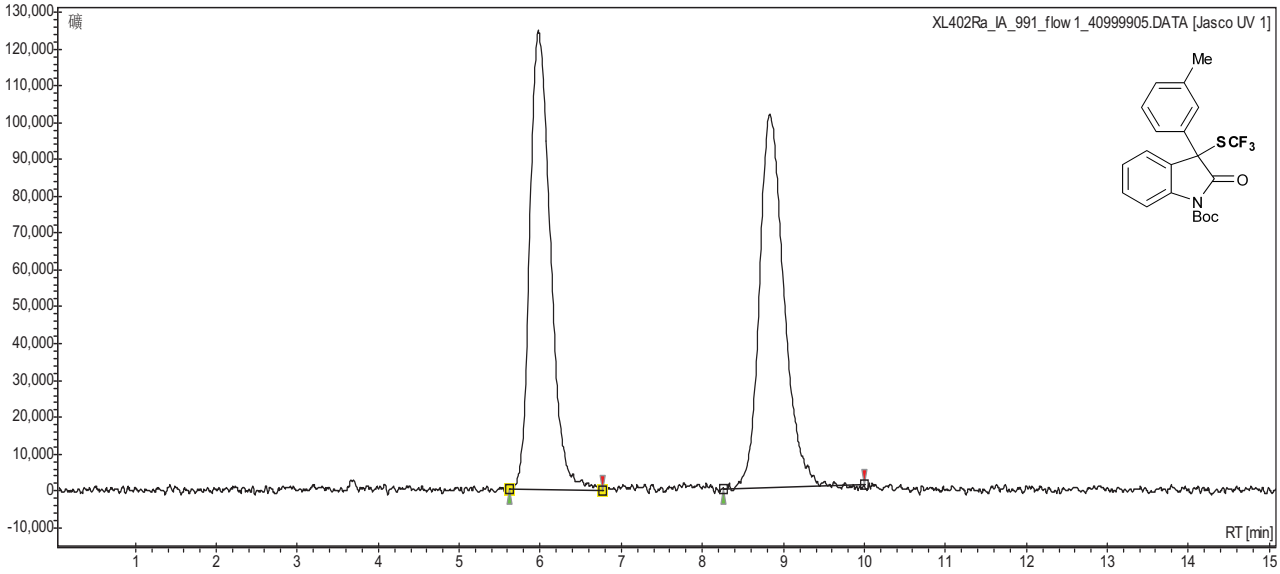


Peak Info

Number	Area %	Area	RT (min)	St. (min)	End (min)
1	92.2022	5577.1574	5.17	4.7447	5.7962
2	7.7978	471.6772	9.28	8.973	9.8048

Chromatogram : XL402Ra_IA_991_flow1_40999905

Data file: XL402Ra_IA_991_flow1_40999905.DATA
Method: HPLC1_IA_991_flow1_acq_40
Date: 2013/8/12 20:43:55

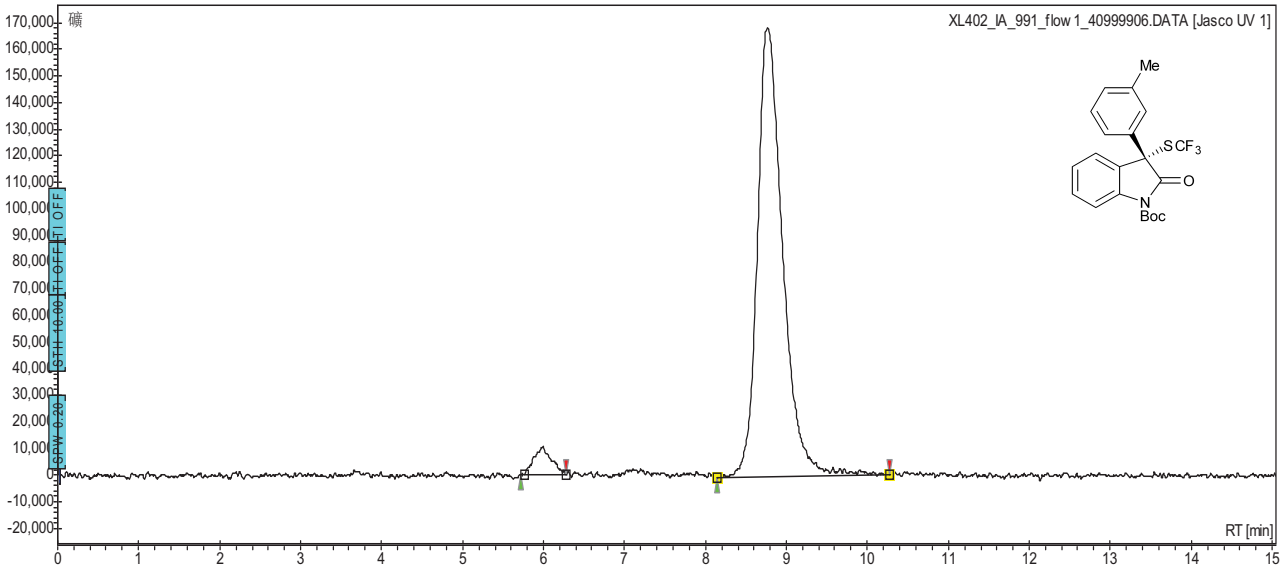


XL402Ra_IA_991_flow1_40999905.DATA [Jasco UV 1]

Index	Start	Time	End	Area %
	[Min]	[Min]	[Min]	[%]
1	5.620	5.975	6.777	50.911
2	8.264	8.842	10.000	49.089
Total				100.000

Chromatogram : XL402_IA_991_flow1_40999906

Data file: XL402_IA_991_flow1_40999906.DATA
Method: HPLC1_IA_991_flow1_acq_40
Date: 2013/8/12 21:26:34

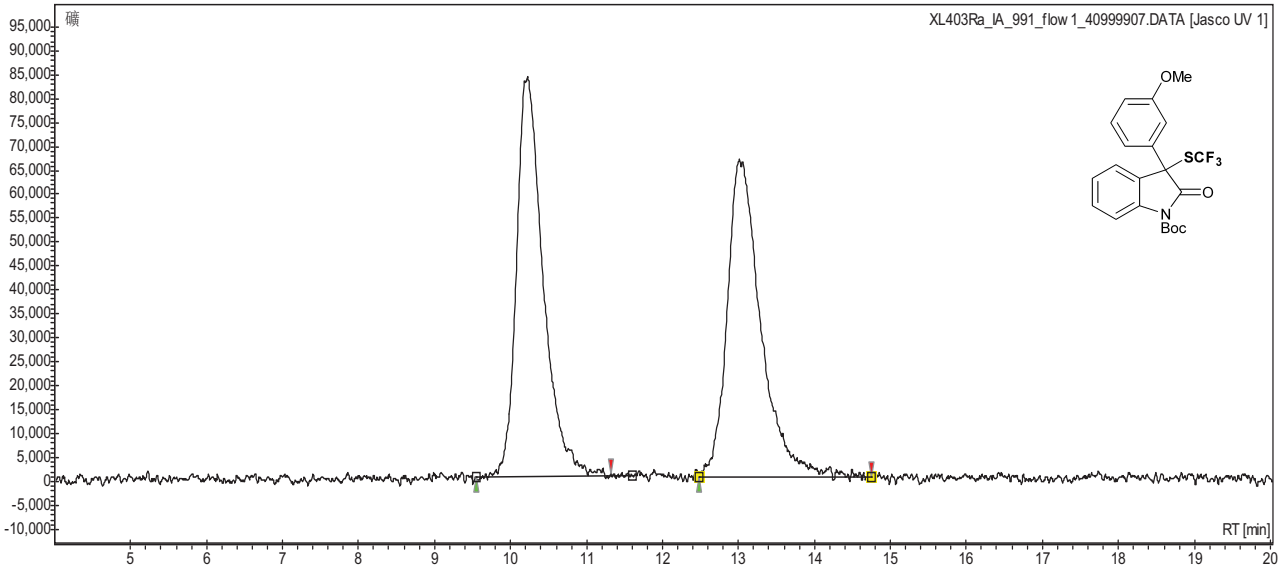


XL402_IA_991_flow1_40999906.DATA [Jasco UV 1]

Index	Start	Time	End	Area %
	[Min]	[Min]	[Min]	[%]
2	5.724	5.992	6.278	4.031
1	8.140	8.767	10.279	95.969
Total				100.000

Chromatogram : XL403Ra_IA_991_flow1_40999907

Data file: XL403Ra_IA_991_flow1_40999907.DATA
Method: HPLC1_IA_991_flow1_acq_40
Date: 2013/8/12 22:06:10

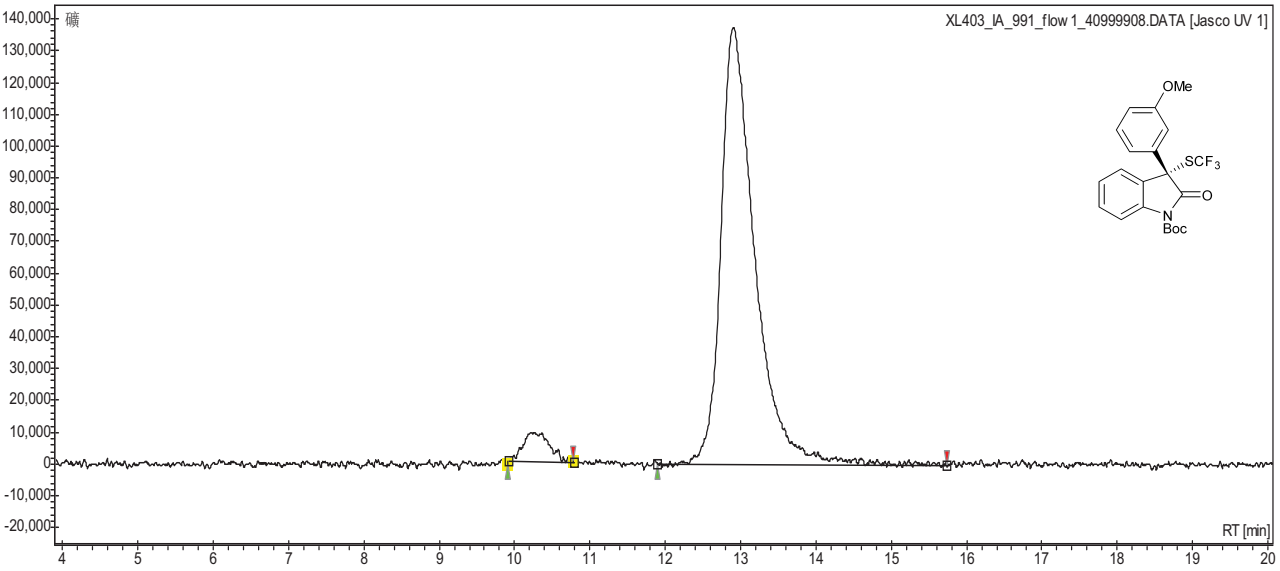


XL403Ra_IA_991_flow1_40999907.DATA [Jasco UV 1]

Index	Start	Time	End	Area %
	[Min]	[Min]	[Min]	[%]
1	9.545	10.225	11.322	49.933
2	12.479	13.008	14.752	50.067
Total				100.000

Chromatogram : XL403_IA_991_flow1_40999908

Data file: XL403_IA_991_flow1_40999908.DATA
Method: HPLC1_IA_991_flow1_acq_40
Date: 2013/8/12 22:48:48

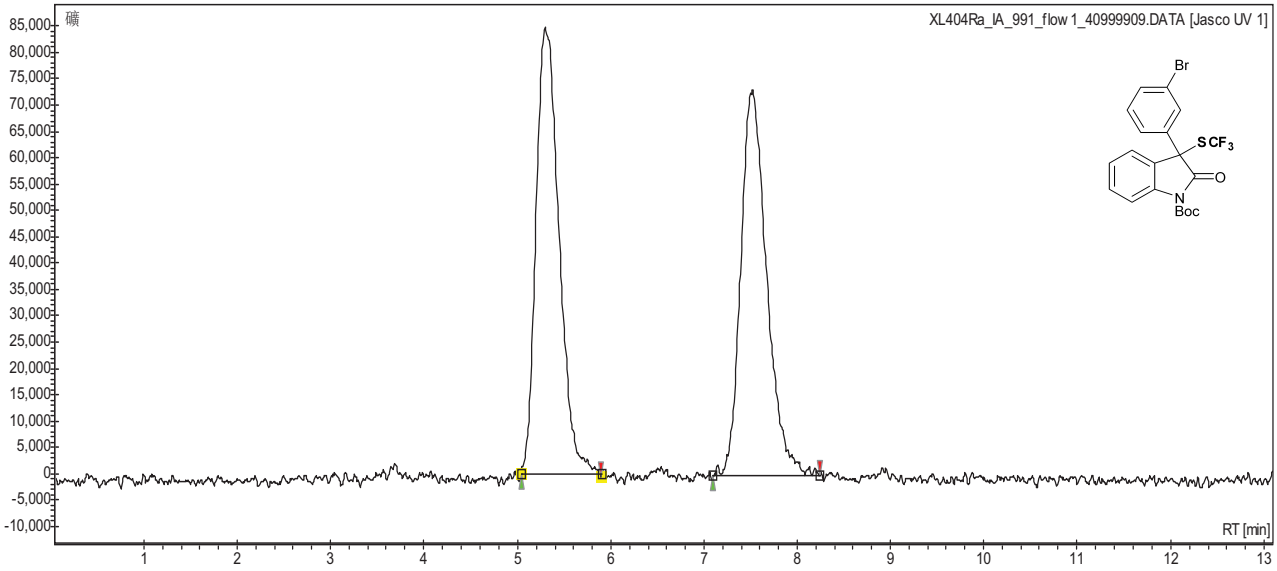


XL403_IA_991_flow1_40999908.DATA [Jasco UV 1]

Index	Start	Time	End	Area %
	[Min]	[Min]	[Min]	[%]
2	9.917	10.258	10.772	5.069
1	11.902	12.900	15.734	94.931
Total				100.000

Chromatogram : XL404Ra_IA_991_flow1_40999909

Data file: XL404Ra_IA_991_flow1_40999909.DATA
Method: HPLC1_IA_991_flow1_acq_40
Date: 2013/8/12 23:23:24

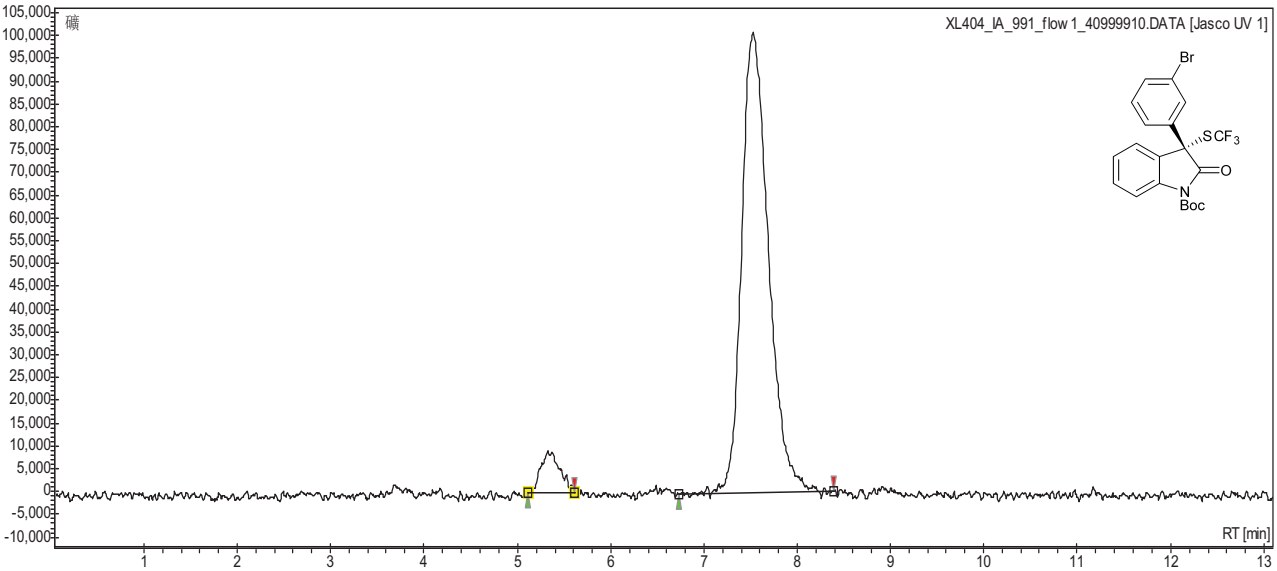


XL404Ra_IA_991_flow1_40999909.DATA [Jasco UV 1]

Index	Start	Time	End	Area %
	[Min]	[Min]	[Min]	[%]
1	5.043	5.300	5.895	50.506
2	7.102	7.517	8.237	49.494
Total				100.000

Chromatogram : XL404_IA_991_flow1_40999910

Data file: XL404_IA_991_flow1_40999910.DATA
Method: HPLC1_IA_991_flow1_acq_40
Date: 2013/8/13 0:06:03

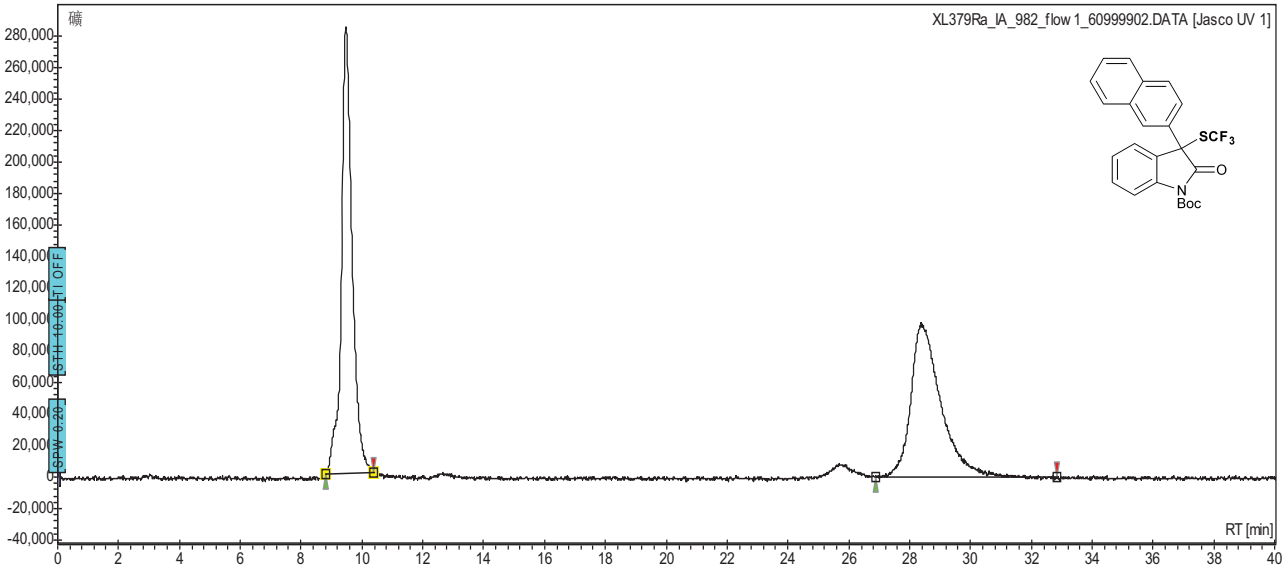


XL404_IA_991_flow1_40999910.DATA [Jasco UV 1]

Index	Start	Time	End	Area %
	[Min]	[Min]	[Min]	[%]
2	5.120	5.375	5.615	6.182
1	6.735	7.525	8.394	93.818
Total				100.000

Chromatogram : XL379Ra_IA_982_flow1_60999902

Data file: XL379Ra_IA_982_flow1_60999902.DATA
Method: HPLC1_IA_982_flow1_acq_60
Date: 2013/8/12 18:06:00

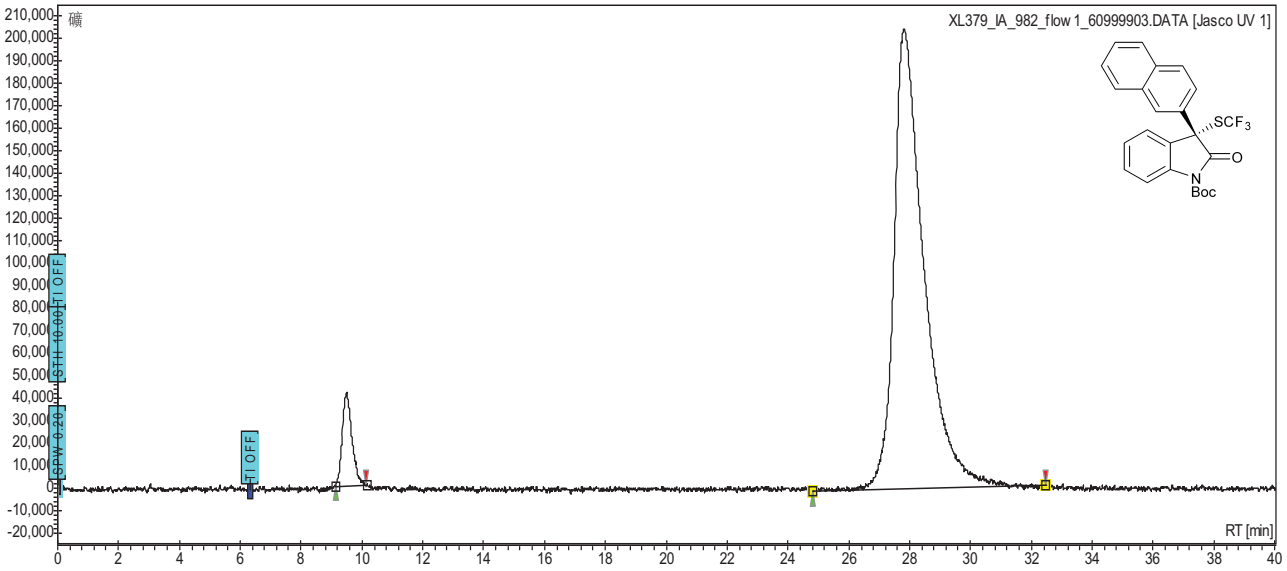


XL379Ra_IA_982_flow1_60999902.DATA [Jasco UV 1]

Index	Start	Time	End	Area %
	[Min]	[Min]	[Min]	[%]
1	8.831	9.467	10.403	51.479
2	26.901	28.375	32.851	48.521
Total				100.000

Chromatogram : XL379_IA_982_flow1_60999903

Data file: XL379_IA_982_flow1_60999903.DATA
Method: HPLC1_IA_982_flow1_acq_60
Date: 2013/8/12 19:08:39

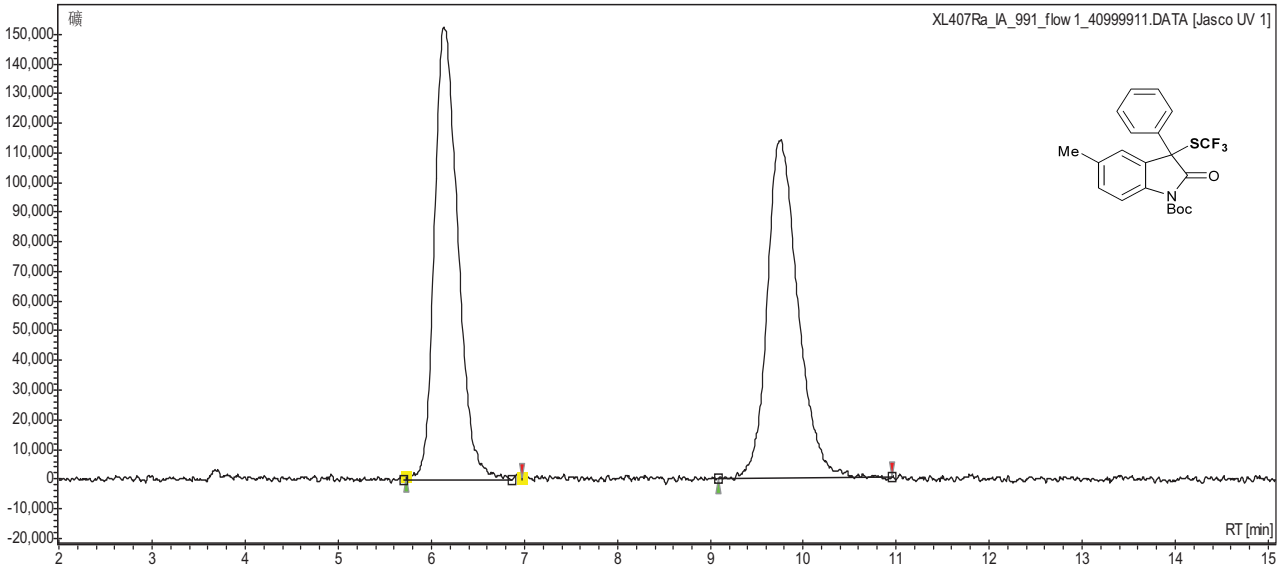


XL379_IA_982_flow1_60999903.DATA [Jasco UV 1]

Index	Start	Time	End	Area %
	[Min]	[Min]	[Min]	[%]
1	9.153	9.492	10.150	6.198
2	24.819	27.817	32.479	93.802
Total				100.000

Chromatogram : XL407Ra_IA_991_flow1_40999911

Data file: XL407Ra_IA_991_flow1_40999911.DATA
Method: HPLC1_IA_991_flow1_acq_40
Date: 2013/8/13 0:48:42

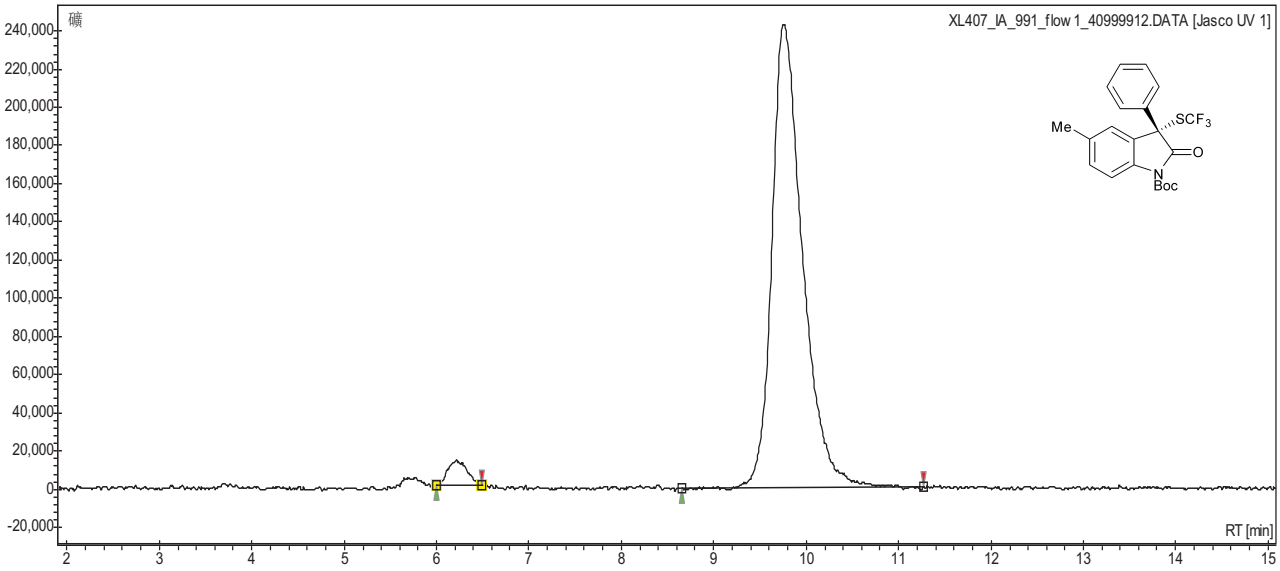


XL407Ra_IA_991_flow1_40999911.DATA [Jasco UV 1]

Index	Start	Time	End	Area %
	[Min]	[Min]	[Min]	[%]
1	5.731	6.133	6.983	50.708
2	9.091	9.758	10.950	49.292
Total				100.000

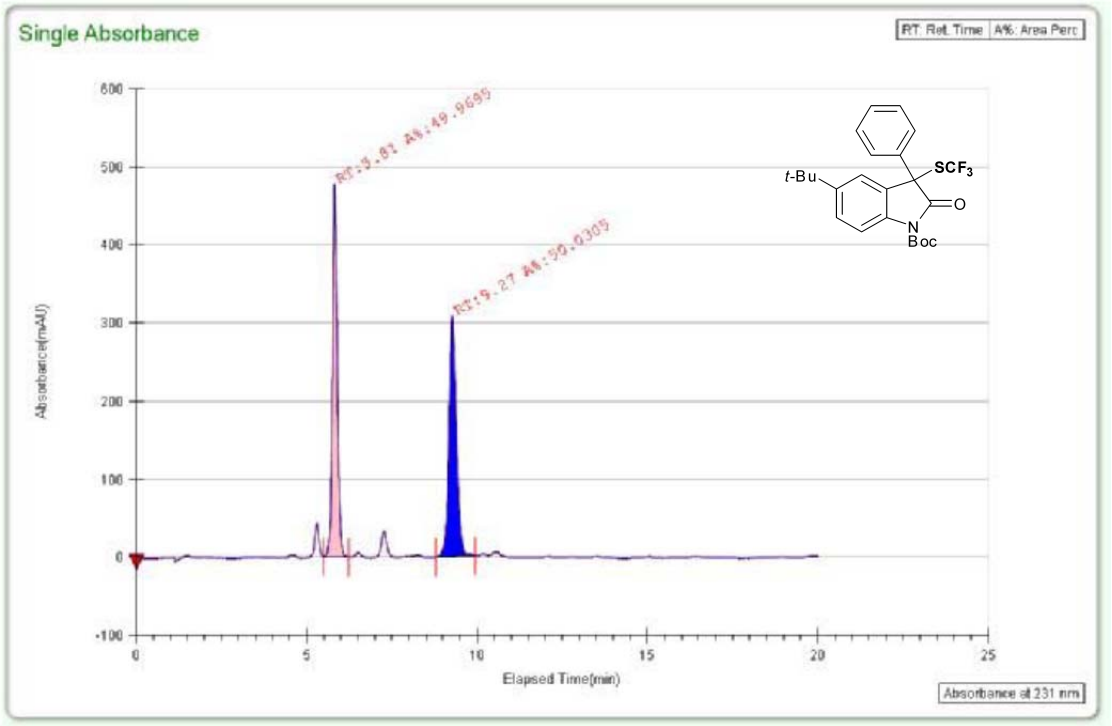
Chromatogram : XL407_IA_991_flow1_40999912

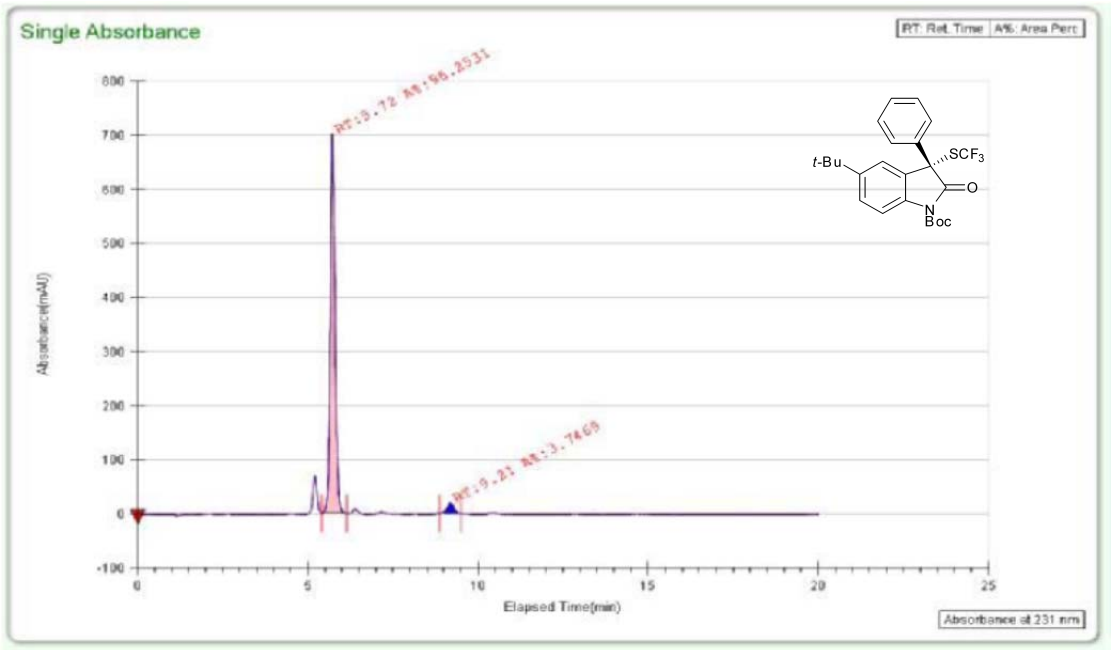
Data file: XL407_IA_991_flow1_40999912.DATA
Method: HPLC1_IA_991_flow1_acq_40
Date: 2013/8/13 1:31:20



XL407_IA_991_flow1_40999912.DATA [Jasco UV 1]

Index	Start	Time	End	Area %
	[Min]	[Min]	[Min]	[%]
2	6.005	6.208	6.486	3.166
1	8.657	9.758	11.268	96.834
Total				100.000



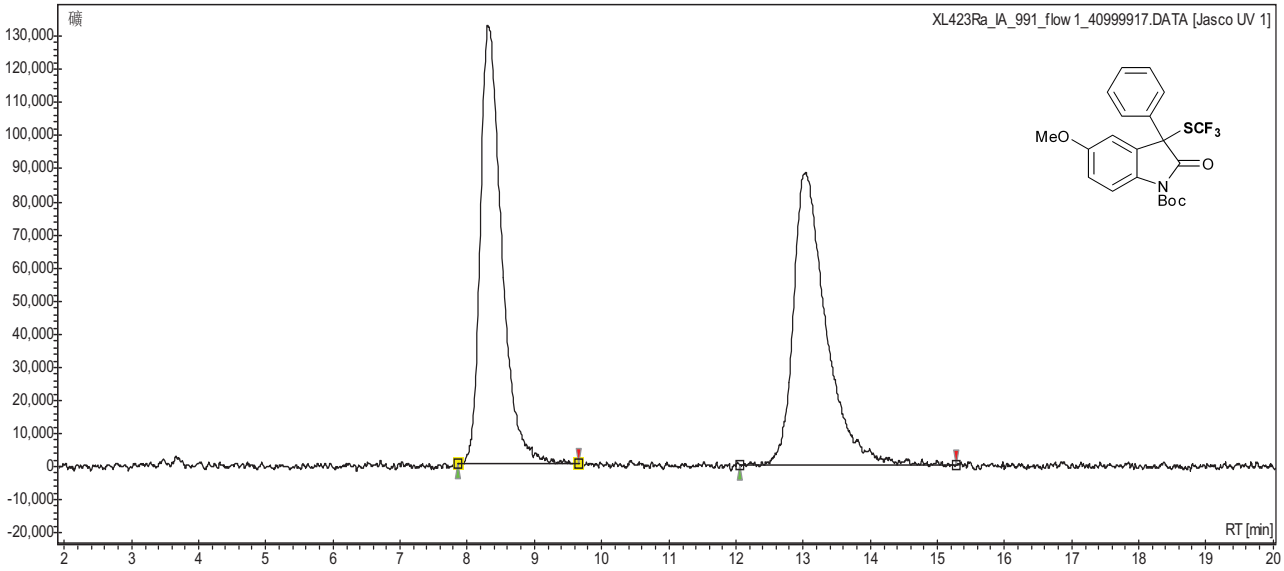


Peak Info

Number	Area %	Area	RT (min)	St. (min)	End (min)
1	96.2531	6623.7255	5.72	5.3979	6.1512
2	3.7469	257.8481	9.21	8.8713	9.5064

Chromatogram : XL423Ra_IA_991_flow1_40999917

Data file: XL423Ra_IA_991_flow1_40999917.DATA
Method: HPLC1_IA_991_flow1_acq_40
Date: 2013/8/13 5:04:28

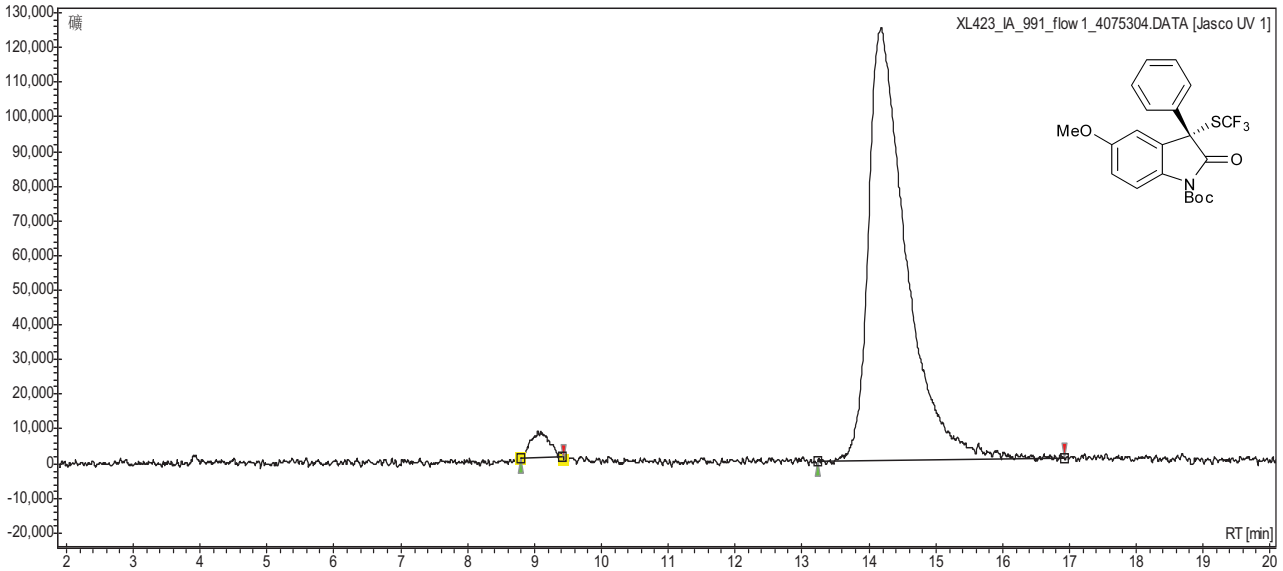


XL423Ra_IA_991_flow1_40999917.DATA [Jasco UV 1]

Index	Start	Time	End	Area %
	[Min]	[Min]	[Min]	[%]
1	7.863	8.308	9.657	49.539
2	12.066	13.042	15.289	50.461
Total				100.000

Chromatogram : XL423_IA_991_flow1_4075304

Data file: XL423_IA_991_flow1_4075304.DATA
Method: HPLC1_IA_991_flow1_acq_40
Date: 2013/8/15 21:49:15

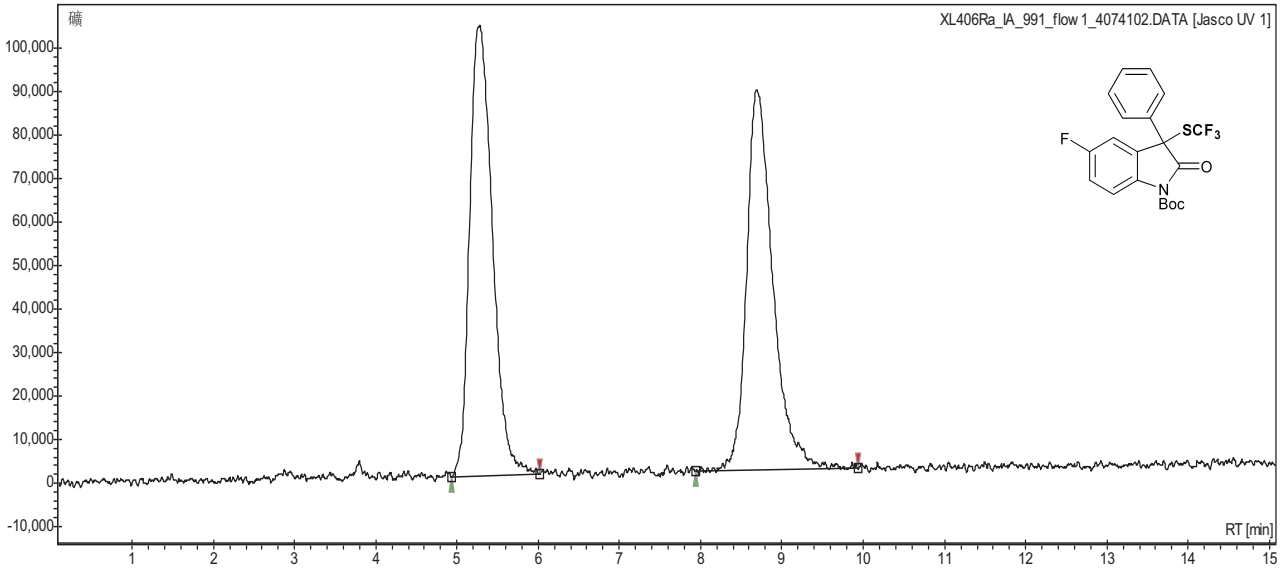


XL423_IA_991_flow1_4075304.DATA [Jasco UV 1]

Index	Start	Time	End	Area %
	[Min]	[Min]	[Min]	[%]
1	8.793	9.092	9.431	2.937
2	13.238	14.183	16.922	97.063
Total				100.000

Chromatogram : XL406Ra_IA_991_flow1_4074102

Data file: XL406Ra_IA_991_flow1_4074102.DATA
Method: HPLC1_IA_991_flow1_acq_40
Date: 2013/8/14 10:04:16

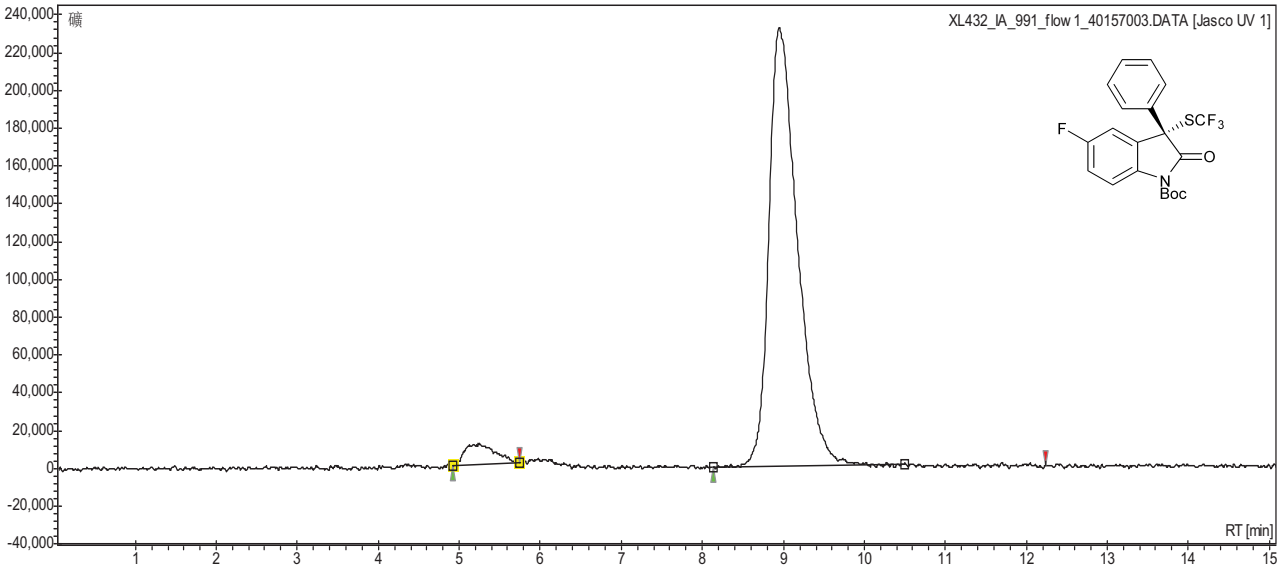


XL406Ra_IA_991_flow1_4074102.DATA [Jasco UV 1]

Index	Start	Time	End	Area %
	[Min]	[Min]	[Min]	[%]
1	4.927	5.267	6.019	50.600
2	7.932	8.692	9.932	49.400
Total				100.000

Chromatogram : XL432_IA_991_flow1_40157003

Data file: XL432_IA_991_flow1_40157003.DATA
Method: HPLC1_IA_991_flow1_acq_40
Date: 2013/8/18 23:06:55

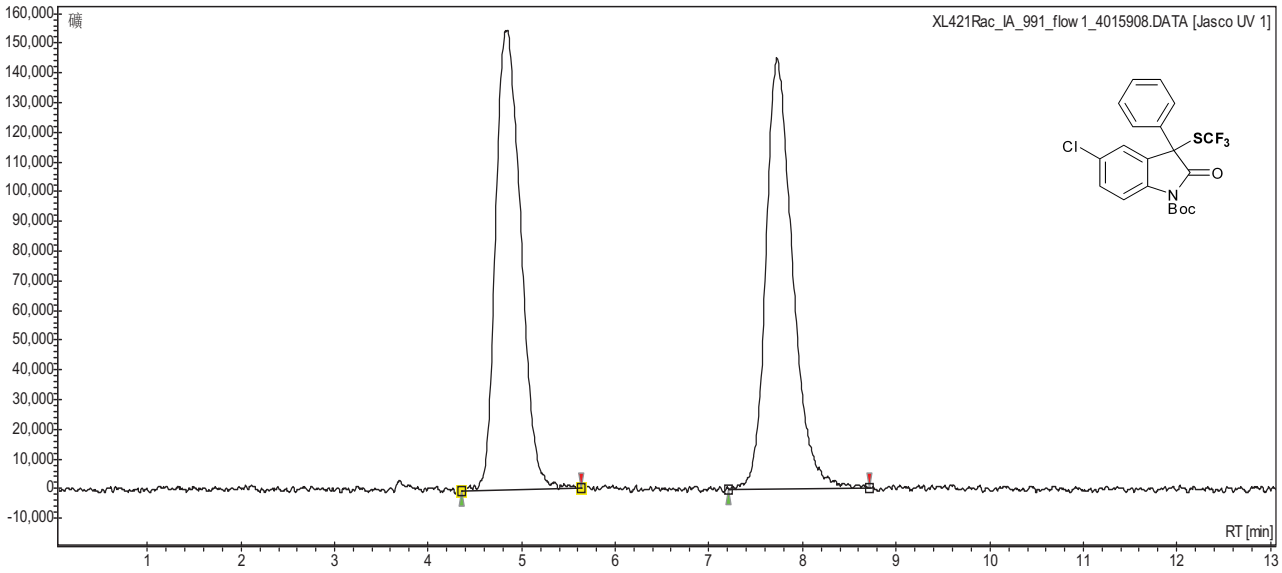


XL432_IA_991_flow1_40157003.DATA [Jasco UV 1]

Index	Start	Time	End	Area %
	[Min]	[Min]	[Min]	[%]
2	4.914	5.225	5.750	5.119
1	8.140	8.950	12.231	94.881
Total				100.000

Chromatogram : XL421Rac_IA_991_flow1_4015908

Data file: XL421Rac_IA_991_flow1_4015908.DATA
Method: HPLC1_IA_991_flow1_acq_40
Date: 2013/8/15 1:04:20

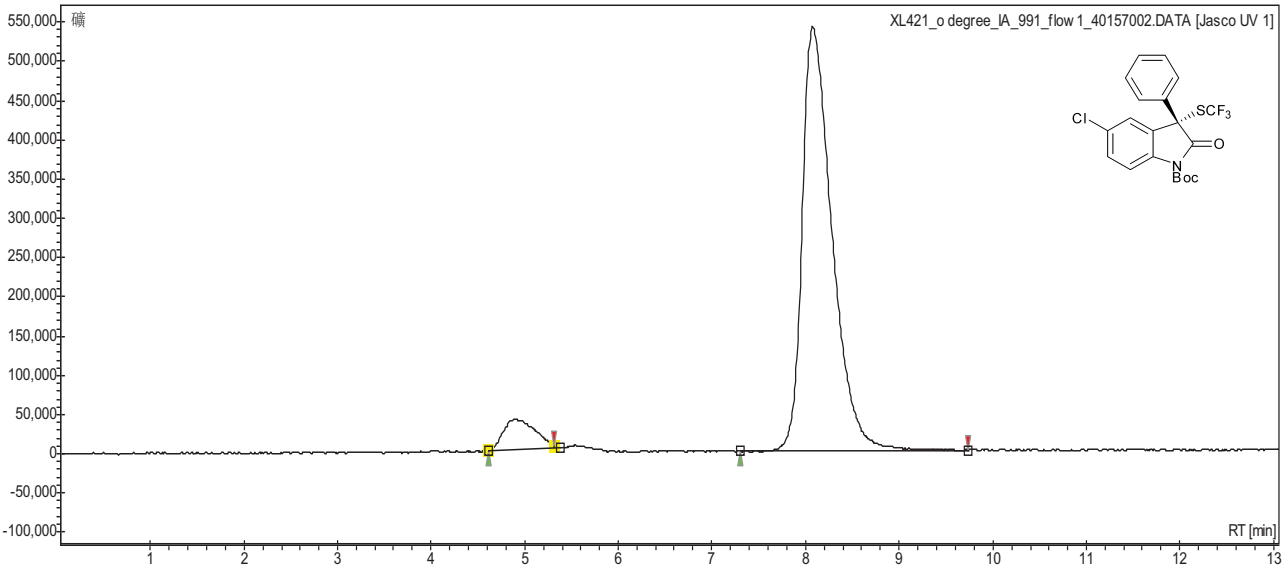


XL421Rac_IA_991_flow1_4015908.DATA [Jasco UV 1]

Index	Start	Time	End	Area %
	[Min]	[Min]	[Min]	[%]
1	4.362	4.842	5.633	50.202
2	7.215	7.725	8.721	49.798
Total				100.000

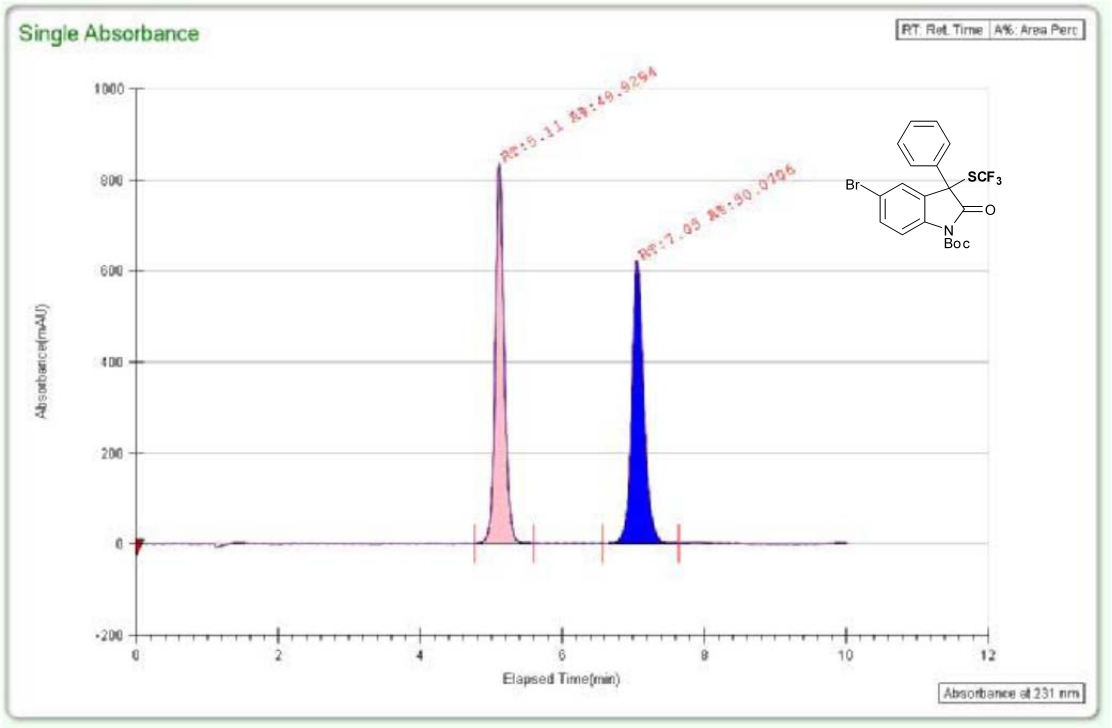
Chromatogram : XL421_o degree_IA_991_flow1_40157002

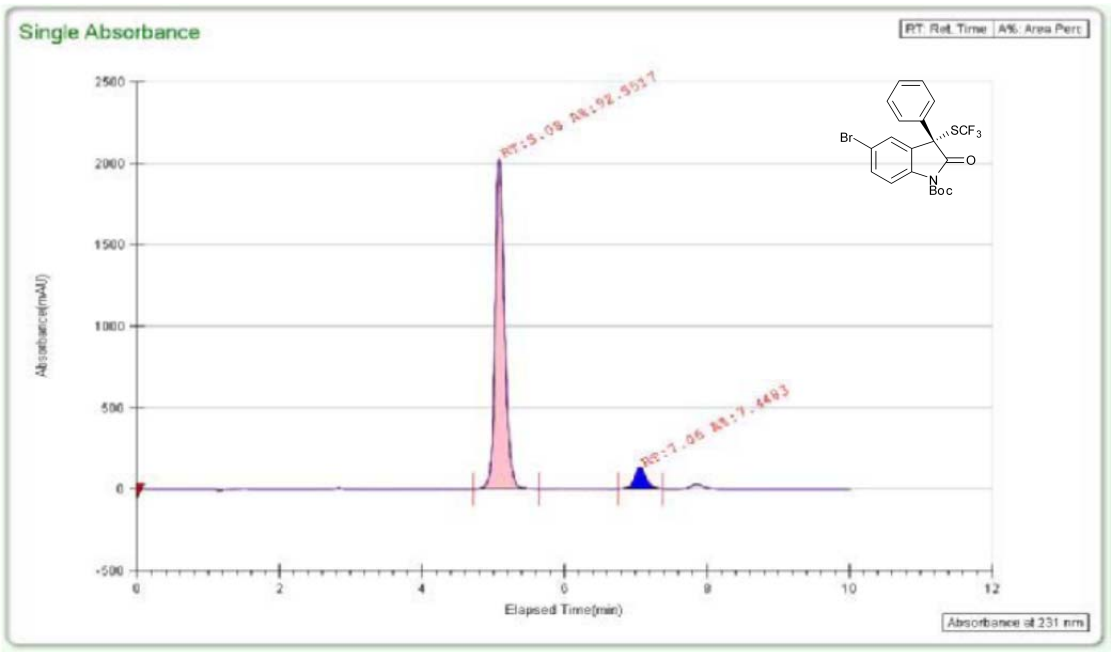
Data file: XL421_o degree_IA_991_flow1_40157002.DATA
Method: HPLC1_IA_991_flow1_acq_40
Date: 2013/8/18 22:24:16



XL421_o degree_IA_991_flow1_40157002.DATA [Jasco UV 1]

Index	Start	Time	End	Area %
	[Min]	[Min]	[Min]	[%]
2	4.614	4.900	5.319	6.947
1	7.298	8.075	9.736	93.053
Total				100.000





Peak Info

Number	Area %	Area	RT (min)	St. (min)	End (min)
1	92.5517	18419.7121	5.08	4.7133	5.6465
2	7.4483	1482.3594	7.06	6.7514	7.3781