Electronic Supplementary Material (ESI) for ChemComm.

Highly enantioselective aza-Henry reaction with isatin *N*-Boc ketimines

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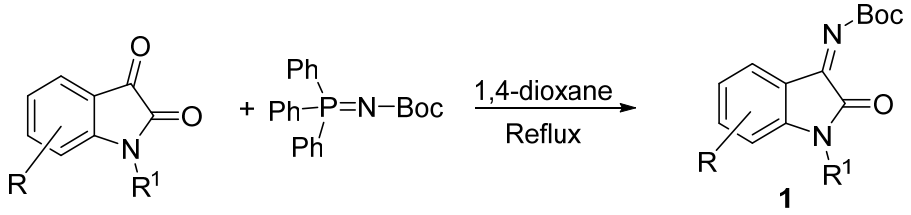
SUPPORTING INFORMATION

Table of Contents:

General Experimental Methods

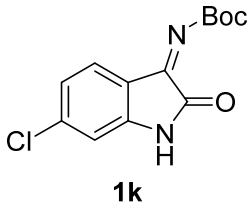
Commercial reagents were used as purchased. Commercial anhydrous 1,4-dioxane (Aldrich Cat. 29630-9) was used for isatin *N*-Boc ketimines synthesis. THF was freshly destilled from Na-benzophenone. Diisopropyl amine was dried and stored over CaH_2. All reactions were carried out in glassware oven-dried overnight at 120 °C. Reactions were monitored by TLC analysis using Merck Silica Gel 60 F-254 thin layer plates. Flash column chromatography was performed on Merck silica gel 60, 0.040-0.063 mm. NMR spectra were recorded in the deuterated solvents as stated, using residual non-deuterated solvent as internal standard. Specific optical rotations were measured using sodium light (D line 589 nm). Mass spectra (ESI) were recorded on a mass spectrometer equipped with an electrospray source with a capillary voltage of 3.3 kV. Chiral HPLC analyses were performed in a chromatograph equipped with a UV diode-array detector using chiral stationary phase columns from Daicel. 1-Methyl isatin, 1-benzyl isatin, 1-methoxymethyl isatin and 1-benzyloxycarbonyl isatin were prepared from isatin according to reported procedures.[1]

Synthesis of *N*-*tert*-butoxycarbonyl ketimines 1.



The isatin (1.0-3.0 mmol) and *tert*-butoxycarbonylaminotriphenylphosphine[2] (1.3 mmol/mmol isatin) were placed in a round-bottom flask equipped with a condenser under nitrogen atmosphere. Anhydrous 1,4-dioxane (1 mL/mmol isatin) was injected and the mixture was heated at reflux temperature until the reaction was complete (10-24 h). The solvents were evaporated under reduced pressure and the crude was purified by flash chromatography affording ketimines **1**. Ketimines **1** were recrystallyzed from hexane-EtOAc or hexane-CH_2Cl_2 when necessary. NMR data for compounds **1a-j, 1m** coincided with those reported in the literature.[3]

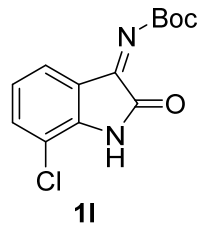
***tert*-Butyl (6-chloro-2-oxoindolin-3-ylidene)carbamate (1k)**



1k

Obtained in 63% yield as a yellow solid, mp ºC; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.64 (br s, 1H), 7.54 (d, *J* = 8.4 Hz, 1H), 7.04 (dd, *J* = 8.1, 1.8 Hz, 1H), 6.91 (s, 1H), 1.60 (s, 9H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 160.5 (C), 146.9 (CH), 141.6 (C), 136.9 (C), 125.5 (C), 123.7 (CH), 112.3 (CH), 111.7 (C), 84.0 (C), 28.0 (CH_3); MS(ESI) *m/z*: 303.0510 $(M+Na)^+$, $C_{13}H_{13}ClN_2NaO_3$ required 303.0507.

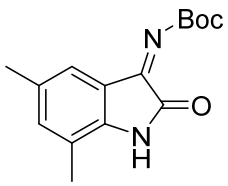
***tert*-Butyl (7-chloro-2-oxoindolin-3-ylidene)carbamate (1l)**



1l

Obtained in 96% yield as a yellow solid, mp ºC; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.04 (br s, 1H), 7.56 (d, *J* = 7.8 Hz, 1H), 7.44 (dd, *J* = 8.1, 0.9 Hz, 1H), 7.06 (t, *J* = 7.8 Hz, 1H), 1.61 (s, 9H); ^{13}C NMR (DMSO, 75 MHz) δ 159.5 (C), 158.1 (C), 153.7 (C), 144.7 (CH), 135.4 (CH), 123.9 (CH), 122.5 (C), 121.0 (C), 115.7 (C), 82.6 (C), 27.6 (CH_3); MS(ESI) *m/z*: 303.0507 $(M+Na)^+$, $C_{13}H_{13}ClN_2NaO_3$ required 303.0507.

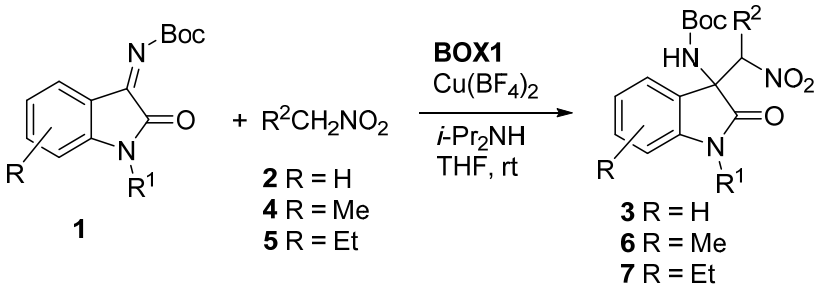
***tert*-butyl (*Z*)-(5,7-dimethyl-2-oxoindolin-3-ylidene)carbamate (1n)**



1n

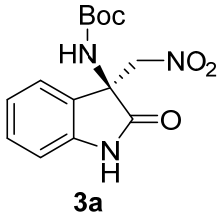
Obtained in 65% yield as a yellow solid, mp ºC; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 9.25 (br s, 1H), 7.27 (s, 1H), 7.06 (s, 1H), 2.27 (s, 3H), 2.21 (s, 3H), 1.61 (s, 9H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 142.2 (CH), 137.6 (C), 137.5 (C), 133.0 (CH), 122.5 (C), 97.7 (C), 83.2 (C), 28.0 (CH_3), 20.8 (CH_3), 15.7 (CH_3); MS(ESI) *m/z*: 297.1212 $(M+Na)^+$, $C_{15}H_{18}N_2NaO_3$ required 297.1210.

General procedure for the enantioselective aza-Henry reaction



Copper (II) tetrafluoroborate hydrate (5.9 mg, 0.025 mmol) contained in a Schlenck tube was dried under vacuum and the tube was filled with nitrogen. A solution of ligand **BOX1** (8.4 mg, 0.025 mmol) and nitroalkane (9.2 eq) in THF (0.25 mL) was added via syringe. After stirring for 1 h, a solution of ketimine **1** (0.25 mmol) and diisopropylamine (4.5 μL, 0.032 mmol) in THF (0.38 mL) was added. The reaction was stirred at room temperature until completion (monitored by TLC). The solvent was removed under reduced pressure, and the residue chromatographed on silica gel eluting with hexane/EtOAc mixtures to give compounds **3 (6,7)**.

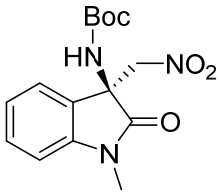
***tert*-Butyl (*S*)-(3-(nitromethyl)-2-oxoindolin-3-yl)carbamate (3a)**



Purified by column chromatography eluting with hexane/EtOAc 60:40, (60 mg, 99% yield). The *ee* (99.6%) was determined by HPLC analysis, Chiralpak AD-H, hexane/*i*-PrOH 80:20, 1 mL/min, major enantiomer (*S*) t_r = 12.5 min, minor enantiomer (*R*) t_r = 14.5 min.

White solid; mp 179-181 °C (hexane-EtOAc); $[\alpha]_D^{20}$ +16.3 (*c* 0.9, CH_2Cl_2, 99.6% *ee*); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.04 (s, 1H), 7.31 (m, 2H), 7.07 (td, *J* = 7.8, 0.9 Hz, 1H), 6.91 (dd, *J* = 8.4, 0.9 Hz, 1H), 6.13 (s, 1H), 4.86 (d, *J* = 12.3 Hz, 1H), 4.60 (d, *J* = 12.3 Hz, 1H), 1.35 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 174.3 (C), 153.8 (C), 140.4 (C), 130.4 (CH), 126.2 (C), 124.1 (CH), 123.4 (CH), 110.9 (CH), 81.6 (C), 78.0 (CH_2), 60.2 (C), 28.1 (CH_3); MS(ESI) *m/z*: 330.1059 $(M+Na)^+$, $C_{14}H_{17}N_3NaO_5$ required 330.1060.

***tert*-Butyl (*S*)-(1-methyl-3-(nitromethyl)-2-oxoindolin-3-yl)carbamate (3b)**

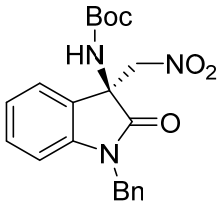


3b

Purified by column chromatography eluting with hexane/EtOAc 70:30 (62.4 mg, 82% yield). The *ee* (99.8%) was determined by HPLC analysis, Chiralcel OD-H, hexane/*i*-PrOH 80:20, 1 mL/min, major enantiomer (*S*) t_r = 8.4 min, minor enantiomer (*R*) t_r = 10.8 min.

Yellow solid; mp 140-142 °C (hexane-EtOAc); $[\alpha]_D^{20}$ +17.0 (*c* 0.9, CH_2Cl_2, 99.8% *ee*); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.42 (m, 1H), 7.36 (dd, *J* = 7.8, 1.2 Hz, 1H), 7.09 (td, *J* = 7.5, 0.9 Hz, 1H), 6.90 (d, *J* = 7.8 Hz, 1H), 5.98 (s, 1H), 4.92 (d, *J* = 12.3 Hz, 1H), 4.59 (d, *J* = 12.3 Hz, 1H), 3.27 (s, 3H), 1.31 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 172.7 (C), 153.7 (C), 143.3 (C), 130.4 (CH), 125.8 (C), 124.3 (CH), 123.4 (CH), 108.9 (CH), 81.2 (C), 77.8 (CH_2), 59.8 (C), 28.0 (CH_3), 26.8 (CH_3); MS(ESI) *m/z*: 344.1217 $(M+Na)^+$, $C_{15}H_{19}N_3NaO_5$ required 344.1217.

***tert*-Butyl (*S*)-(1-benzyl-3-(nitromethyl)-2-oxoindolin-3-yl)carbamate (3c)**

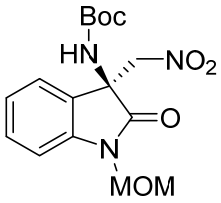


3c

Purified by column chromatography eluting with hexane/EtOAc 80:20 (76.3 mg, 79% yield). The *ee* (99.9%) was determined by HPLC analysis, Chiralcel OD-H, hexane/*i*-PrOH 95:05, 1 mL/min, major enantiomer (*S*) t_r = 17.8 min, minor enantiomer (*R*) t_r = 21.0 min.

Yellow solid; mp 154-156 °C (hexane-EtOAc); $[\alpha]_D^{20}$ +30.2 (*c* 1.0, CH_2Cl_2, 99.9% *ee*); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.44 (d, *J* = 7.2 Hz, 1H), 7.39-7.27 (m, 6H), 7.24 (dd, *J* = 7.8, 1.2 Hz, 1H), 7.05 (td, *J* = 7.5, 0.9 Hz, 1H), 6.77 (d, *J* = 8.1 Hz, 1H), 5.98 (s, 1H), 5.06 (d, *J* = 15.6 Hz, 1H), 4.98 (d, *J* = 12.3 Hz, 1H), 4.87 (d, *J* = 15.9 Hz, 1H) 4.66 (d, *J* = 12.3 Hz, 1H), 1.36 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 172.9 (C), 153.8 (C), 142.5 (C), 135.0 (C), 130.3 (CH), 128.9 (2CH), 127.9 (CH), 127.3 (2CH), 125.8 (C), 124.5 (C), 123.4 (CH), 109.9 (CH), 81.3 (C), 77.8 (CH_2), 59.9 (C), 44.5 (CH_2), 28.1 (CH_3); MS(ESI) *m/z*: 420.1531 $(M+Na)^+$, $C_{21}H_{23}N_3NaO_5$ required 420.1530.

***tert*-Butyl (*S*)-(1-(methoxymethyl)-3-(nitromethyl)-2-oxoindolin-3-yl)carbamate (3d)**

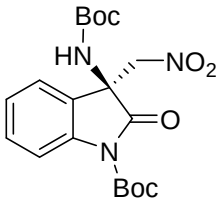


3d

Purified by column chromatography eluting with hexane/EtOAc 70:30 (85.8 mg, 84% yield). The *ee* (99.9%) was determined by HPLC analysis, Chiralcel OD-H, hexane/*i*-PrOH 95:05, 1 mL/min, major enantiomer (*S*) t_r = 16.5 min, minor enantiomer (*R*) t_r = 20.0 min.

Yellow solid; mp 152-154 °C (hexane-EtOAc); $[\alpha]_D^{20}$ -1.2 (*c* 1.0, CH_2Cl_2, 99.9% *ee*); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.43-7.35 (m, 2H), 7.20-7.09 (m, 2H), 5.97 (s, 1H), 5.21 (d, *J* = 10.8 Hz, 1H), 5.14 (d, *J* = 11.1 Hz, 1H), 4.92 (d, *J* = 12.3 Hz, 1H), 4.64 (d, *J* = 12.6 Hz, 1H), 3.42 (s, 3H), 1.34 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 173.4 (C), 153.7 (C), 141.7 (C), 130.5 (CH), 125.4 (C), 124.3 (CH), 123.9 (CH), 110.4 (CH), 81.4 (C), 77.9 (CH_2), 72.1 (CH_2), 60.1 (C), 56.7 (CH_3), 28.1 (CH_3); MS(ESI) *m/z*: 374.1325 $(M+Na)^+$, $C_{16}H_{21}N_3NaO_6$ required 374.1323.

***tert*-Butyl (*S*)-3-((tert-butoxycarbonyl)amino)-3-(nitromethyl)-2-oxoindoline-1-carboxylate (3e)**

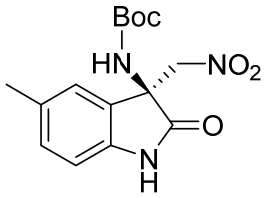


3e

Purified by column chromatography eluting with hexane/EtOAc 60:40 (78.8 mg, 91% yield). The *ee* (99.9%) was determined by HPLC analysis, Chiralpak AD-H, hexane/*i*-PrOH 80:20, 1 mL/min, major enantiomer (*S*) t_r = 13.9 min, minor enantiomer (*R*) t_r = 18.8 min.

White solid; mp 139-141 °C (hexane-EtOAc); $[\alpha]_D^{20}$ +3.9 (*c* 1.4, CH_2Cl_2, 99.9% *ee*); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.89 (ddd, *J* = 8.4, 0.9, 0.6 Hz, 1H), 7.40 (td, *J* = 9.0, 1.5 Hz, 1H), 7.32 (dd, *J* = 7.5, 0.9 Hz, 1H), 7.18 (td, *J* = 7.5, 0.9 Hz, 1H), 6.17 (s, 1H), 4.86 (d, *J* = 12.6 Hz, 1H), 4.62 (d, *J* = 12.6 Hz, 1H), 1.64 (s, 9H), 1.27 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 171.1 (C), 153.4 (C), 148.5 (C), 139.5 (C), 130.6 (CH), 125.1 (C), 124.9 (CH), 123.4 (CH), 115.6 (CH), 85.2 (C), 81.8 (C), 78.1 (CH_2), 60.1 (C), 28.0 (CH_3), 27.9 (CH_3); MS(ESI) *m/z*: 430.1587 $(M+Na)^+$, $C_{19}H_{25}N_3NaO_7$ required 430.1585.

***tert*-Butyl (*S*)-(5-methyl-3-(nitromethyl)-2-oxoindolin-3-yl)carbamate (3f)**

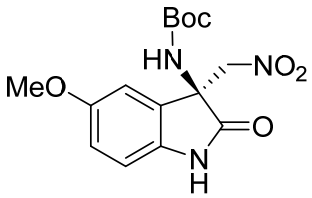


3f

Purified by column chromatography eluting with hexane/EtOAc 70:30 (75.2 mg, 94% yield). The *ee* (96.3%) was determined by HPLC analysis, Chiralpak AD-H, hexane/*i*-PrOH 80:20, 1 mL/min, major enantiomer (*S*) t_r = 10.4 min, minor enantiomer (*R*) t_r = 13.8 min.

Yellow solid; mp 115-117 °C (hexane-EtOAc); $[\alpha]_D^{20}$ +31 (*c* 0.9, CH_2Cl_2, 96.3% *ee*); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.25 (s, 1H), 7.11 (d, *J* = 2.0 Hz, 1H), 7.09 (dd, *J* = 8.1, 2.0 Hz, 1H), 6.78 (d, *J* = 8.1 Hz, 1H), 6.14 (s, 1H), 4.85 (d, *J* = 12.6 Hz, 1H), 4.59 (d, *J* = 12.3 Hz, 1H), 2.30 (s, 3H), 1.35 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 174.3 (C), 153.8 (C), 137.8 (C), 133.1 (CH), 130.8 (CH), 126.3 (C), 124.8 (CH), 110.5 (CH), 81.5 (C), 78.0 (CH_2), 60.2 (C), 28.1 (CH_3), 21.1 (CH_3); MS(ESI) *m/z*: 344.1216 $(M+Na)^+$, $C_{15}H_{19}N_3NaO_5$ required 344.1217.

***tert*-Butyl (*S*)-(5-methoxy-3-(nitromethyl)-2-oxoindolin-3-yl)carbamate (3g)**

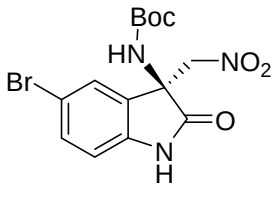


3g

Purified by column chromatography eluting with hexane/EtOAc 70:30 (82.2 mg, 97% yield). The *ee* (97.7%) was determined by HPLC analysis, Chiralpak AD-H, hexane/*i*-PrOH 80:20, 1 mL/min, major enantiomer (*S*) t_r = 13.3 min, minor enantiomer (*R*) t_r = 19.6 min.

Yellow solid; mp 141-143 °C (hexane-EtOAc); $[\alpha]_D^{20}$ +31.5 (*c* 0.9, CH_2Cl_2, 97.7.0% *ee*); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.33 (br s, 1H), 6.93 (s, 1H), 6.84-6.77 (m, 2H), 6.15 (s, 1H), 4.87 (d, *J* = 12.3 Hz, 1H), 4.61 (d, *J* = 12.3 Hz, 1H), 3.76 (s, 3H), 1.36 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 174.2 (C), 156.2 (C), 153.8 (C), 133.9 (CH), 127.5 (C), 115.2 (CH), 111.3 (CH), 111.1 (C), 81.4 (C), 77.9 (CH_2), 60.5 (C), 55.8 (CH_3), 28.1 (CH_3); MS(ESI) *m/z*: 360.1164 $(M+Na)^+$, $C_{15}H_{19}N_3NaO_6$ required 360.1166.

***tert*-Butyl (*S*)-(5-bromo-3-(nitromethyl)-2-oxoindolin-3-yl)carbamate (3h)**

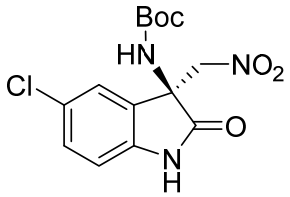


3h

Purified by column chromatography eluting with hexane/EtOAc 70:30 (91.6 mg, 95% yield). The *ee* (81.3%) was determined by HPLC analysis, Chiralpak AD-H, hexane/*i*-PrOH 810:20, 1 mL/min, major enantiomer (*S*) t_r = 9.6 min, minor enantiomer (*R*) t_r = 10.9 min.

Yellow solid; mp 146-150 °C (hexane-EtOAc); $[\alpha]_D^{20}$ +42.1 (*c* 1.0, MeOH, 81.3% *ee*); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.94 (br s, 1H), 7.47-7.43 (m, 2H), 6.79 (dd, *J* = 8.1, 0.6 Hz, 1H), 6.09 (s, 1H), 4.85 (d, *J* = 12.7 Hz, 1H), 4.59 (d, *J* = 12.7 Hz, 1H), 1.38 (s, 9H); ^{13}C NMR (75 MHz, CD_3OD) δ 176.8 (C), 162.1 (C), 155.7 (C), 142.9 (C), 134.0 (CH), 130.9 (C), 128.1 (CH), 115.9 (C), 113.2 (CH), 82.1 (C), 78.4 (CH_2), 61.6 (C), 28.4. (CH_3); MS(ESI) *m/z*: 408.0163 $(M+Na)^+$, $C_{14}H_{16}BrN_3NaO_5$ required 408.0166.

tert-Butyl (*S*)-(5-chloro-3-(nitromethyl)-2-oxoindolin-3-yl)carbamate (3i)

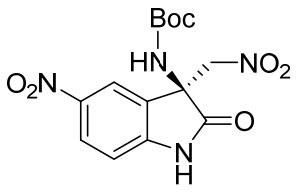


3i

Purified by column chromatography eluting with hexane/EtOAc 70:30 (74.4 mg, 87% yield). The *ee* (97.5%) was determined by HPLC analysis, Chiralpak AD-H, hexane/*i*-PrOH 80:20, 1 mL/min, major enantiomer (*S*) t_r = 10.0 min, minor enantiomer (*R*) t_r = 11.1 min.

White solid; mp 194-196 °C (hexane-EtOAc); $[\alpha]_D^{20}$ +40.8 (*c* 1.0, CH_2Cl_2, 97.5% *ee*); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.25 (s, 1H), 7.32 (d, *J* = 2.1 Hz, 1H), 7.28 (dd, *J* = 8.1, 2.1 Hz, 1H), 6.83 (d, *J* = 8.1 Hz, 1H), 6.14 (s, 1H), 4.85 (d, *J* = 12.8 Hz, 1H), 4.59 (d, *J* = 12.8 Hz, 1H), 1.38 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 173.7 (C), 153.8 (C), 138.9 (C), 130.5 (CH), 128.9 (C), 127.8 (C), 124.7 (CH), 111.9 (CH), 82.0 (C), 77.6 (CH_2), 60.1 (C), 28.1 (CH_3); MS(ESI) *m/z*: 364.0669 $(M+Na)^+$, $C_{14}H_{16}ClN_3NaO_5$ required 364.0671.

tert-Butyl (*S*)-(5-nitro-3-(nitromethyl)-2-oxoindolin-3-yl)carbamate (3j)

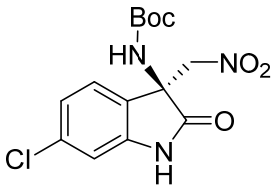


3j

Purified by column chromatography eluting with hexane/EtOAc 70:30 (75.2 mg, 94% yield). The *ee* (6.6%) was determined by HPLC analysis, Chiralpak AD-H, hexane/*i*-PrOH 80:20, 1 mL/min, major enantiomer (*S*) t_r = 16.7 min, minor enantiomer (*R*) t_r = 18.1 min.

Yellow solid; mp 167-169 °C (hexane-EtOAc); ^{1}H NMR (300 MHz, CD_3OD) δ 8.30-8.25 (m, 2H), 7.07 (dd, *J* = 8.4, 0.3 Hz, 1H), 5.04 (d, *J* = 13.2 Hz, 1H), 4.98 (d, *J* = 13.2 Hz, 1H), 1.32 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 177.3 (C), 150.1 (C), 144.6 (C), 129.7 (C), 128.0 (CH), 120.9 (CH), 111.4 (CH), 78.2 (CH_2), 61.3 (C), 54.8 (C), 28.4 (CH_3); MS(ESI) *m/z*: 375.0909 $(M+Na)^+$, $C_{14}H_{16}N_4NaO_7$ required 375.0911.

***tert*-Butyl (*S*)-(6-chloro-3-(nitromethyl)-2-oxoindolin-3-yl)carbamate (3k)**

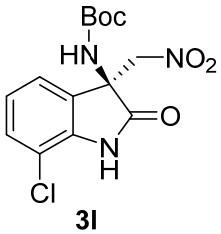


3k

Purified by column chromatography eluting with hexane/EtOAc 70:30 (78.3 mg, 92% yield). The *ee* (96.2%) was determined by HPLC analysis, Chiralpak AD-H, hexane/*i*-PrOH 90:10, 1 mL/min, major enantiomer (*S*) t_r = 16.6 min, minor enantiomer (*R*) t_r = 23.6 min.

Yellow oil; $[\alpha]_D^{20}$ -11.4 (*c* 1.0, CH_2Cl_2, 96.2% *ee*); ^{1}H NMR (300 MHz, $CDCl_3$+CD_3OD) δ 10.3 (s, 1H), 7.20 (d, *J* = 8.1 Hz 1H), 6.92-6.85 (m, 2H), 6.24 (br s, 1H), 4.83 (d, *J* = 12.5 Hz, 1H), 4.58 (d, *J* = 12.5 Hz, 1H), 1.26 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$+CD_3OD) δ 174.3 (C), 159.8 (C), 142.9 (C), 135.6 (C), 125.1 (CH), 122.3 (CH), 111.3 (CH), 80.9 (C), 59.6 (C), 27.9 (CH_3); MS(ESI) *m/z*: 364.0674 $(M+Na)^+$, $C_{14}H_{16}ClN_3NaO_5$ required 364.0671.

***tert*-Butyl (*S*)-(7-chloro-3-(nitromethyl)-2-oxoindolin-3-yl)carbamate (3l)**

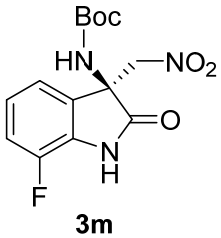


3l

Purified by column chromatography eluting with hexane/EtOAc 70:30 (121.0 mg, 94% yield). The *ee* (98.1%) was determined by HPLC analysis, Chiralpak AD-H, hexane/*i*-PrOH 80:20, 1 mL/min, major enantiomer (*S*) t_r = 11.1 min, minor enantiomer (*R*) t_r = 19.1 min.

White solid; mp 172-175 °C (hexane-EtOAc); $[\alpha]_D^{20}$ -31.9 (*c* 1.0, CH_2Cl_2, 98.1% *ee*); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.14 (br s, 1H), 7.32 (dd, *J* = 8.4, 1.2 Hz, 1H), 7.23 (d, *J* = 6.9 Hz, 1H), 7.03 (t, *J* = 7.8 Hz, 1H), 6.14 (s, 1H), 4.89 (d, *J* = 12.6 Hz, 1H), 4.60 (d, *J* = 12.6 Hz, 1H), 1.34 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 173.2 (C), 153.6 (C), 148.5 (C), 138.1 (C), 130.3 (CH), 124.3 (CH), 122.5 (CH), 116.0 (C), 81.8 (C), 77.7 (CH_2), 61.0 (C), 28.0 (CH_3); MS(ESI) *m/z*: 364.0673 $(M+Na)^+$, $C_{14}H_{16}ClN_3NaO_5$ required 364.0671.

***tert*-Butyl (*S*)-(7-fluoro-3-(nitromethyl)-2-oxoindolin-3-yl)carbamate (3m)**

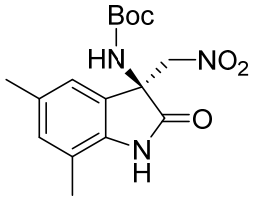


3m

Purified by column chromatography eluting with hexane/EtOAc 70:30 (70.2 mg, 86% yield). The *ee* (93.1%) was determined by HPLC analysis, Chiralpak AD-H, hexane/*i*-PrOH 80:20, 1 mL/min, major enantiomer (*S*) t_r = 10.7 min, minor enantiomer (*R*) t_r = 15.9 min.

Yellow solid; mp 166-170 °C (hexane-EtOAc); $[\alpha]_D^{20}$ +3.3 (*c* 1.1, CH_2Cl_2, 93.1% *ee*); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.43 (s, 1H), 7.14-7.00 (m, 3H), 6.20 (s, 1H), 4.91 (d, *J* = 12.6 Hz, 1H), 4.61 (d, *J* = 12.6 Hz, 1H), 1.34 (s, 9H); ^{13}C NMR (75 MHz, CD_3OD) δ 176.8 (C), 155.6 (C), 148.7 (d, *J* = 242.3 Hz, C), 131.1 (d, *J* = 26.4 Hz, C), 124.4 (d, *J* = 5.9 Hz, CH), 120.6 (d, *J* = 3.4 Hz, CH), 118.0 (d, *J* = 17.5 Hz, C), 115.1 (d, *J* = 2.6 Hz, C), 82.0 (C), 78.7 (CH_2), 61.8 (C), 28.3 (CH_3); ^{19}F NMR (282 MHz, CD_3OD) δ -136.2 (s, 1F); MS(ESI) *m/z*: 348.0963 $(M+Na)^+$, $C_{14}H_{16}FN_3NaO_5$ required 348.0966.

***tert*-Butyl (*S*)-(5,7-dimethyl-3-(nitromethyl)-2-oxoindolin-3-yl)carbamate (3n)**

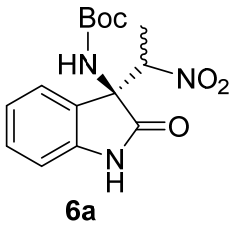


3n

Purified by column chromatography eluting with hexane/EtOAc 70:30 (112.7 mg, 89% yield). The *ee* (98.7%) was determined by HPLC analysis, Chiralpak AD-H, hexane/*i*-PrOH 80:20, 1 mL/min, major enantiomer (*S*) t_r = 9.0 min, minor enantiomer (*R*) t_r = 13.9 min.

White solid; mp 189-193 °C (hexane-EtOAc); $[\alpha]_D^{20}$ +17.4 (*c* 1.0, CH_2Cl_2, 98.7% *ee*); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.76 (br s, 1H), 6.95 (s, 1H), 6.93 (s, 1H), 6.17 (s, 1H), 4.83 (d, *J* = 12.3 Hz, 1H), 4.61 (d, *J* = 12.3 Hz, 1H), 2.27 (s, 3H), 2.19 (s, 3H), 1.33 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 174.8 (C), 153.8 (C), 136.5 (C), 133.0 (CH), 132.3 (CH), 126.1 (C), 122.0 (C), 119.8 (C), 81.4 (C), 78.1 (CH_2), 60.7 (C), 28.0 (CH_3), 21.0 (CH_3), 16.2 (CH_3); MS(ESI) *m/z*: 358.1375 $(M+Na)^+$, $C_{16}H_{21}N_3NaO_5$ required 358.1373.

***tert*-Butyl (*S*)-3-(1-nitroethyl)-2-oxoindolin-3-yl)carbamate (6a)**



6a

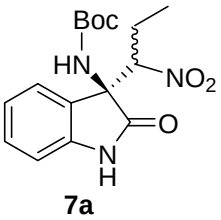
Purified by column chromatography eluting with hexane/EtOAc 70:30 (55.8 mg, 68% yield). Diastereomer ratio 91:09. The *ee* (99.8% major diastereomer, 99.1% minor diastereomer) was determined by HPLC analysis, Chiralpak AD-H, hexane/*i*-PrOH 80:20, 1 mL/min, Major diastereomer: major enantiomer (3*S*) t_r = 9.2 min, minor enantiomer (3*R*) t_r = 15.5 min; Minor diastereomer: major enantiomer (3*S*) t_r = 7.8 min, minor enantiomer (3*R*) t_r = 10.9 min.

White solid; mp 159-162 °C (hexane-CH_2Cl_2); $[\alpha]_D^{20}$ +39.2 (*c* 0.9, CH_2Cl_2) for the diastereomer mixture. Major diastereomer: ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.53 (s, 1H), 7.23 (td, *J* = 7.8, 1.2 Hz, 1H), 7.10 (dd, *J* = 7.5, 0.9 Hz, 1H), 7.03 (td, *J* = 7.5, 0.9 Hz, 1H), 6.81 (d, *J* = 7.8 Hz, 1H), 6.26 (s, 1H), 4.72 (q, *J* = 6.9 Hz, 1H), 1.76 (d, *J* = 6.9

Hz, 3H), 1.32 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 174.0 (C), 154.1 (C), 140.4 (C), 130.2 (CH), 126.7 (C), 123.3 (CH), 123.1 (CH), 110.7 (CH), 85.5 (CH), 81.4 (C), 62.1 (C), 28.0 (CH_3), 13.0 (CH_3); MS(ESI) *m/z*: 344.1215 $(M+Na)^+$, $C_{15}H_{19}N_3NaO_5$ required 344.1217.

Minor diastereomer: ^{1}H NMR (300 MHz, $CDCl_3$, representative peaks taken from the diastereomer mixture) δ 6.30 (s, 1H), 4.96 (q, *J* = 6.9 Hz, 1H).

tert-Butyl (*S*)-(3-(1-nitropropyl)-2-oxoindolin-3-yl)carbamate (7a)



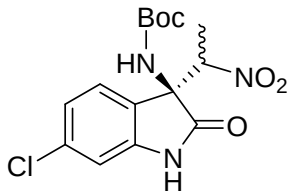
7a

Purified by column chromatography eluting with hexane/EtOAc 70:30 (62.7 mg, 75% yield). Diastereomer ratio 91:9. The *ee* (99.6% major diastereomer, 98.0% minor diastereomer) was determined by HPLC analysis, Chiralpak AD-H, hexane/*i*-PrOH 90:10, 1 mL/min, Major diastereomer: major enantiomer (3*S*) t_r = 14.1 min, minor enantiomer (3*R*) t_r = 21.3 min; Minor diastereomer: major enantiomer (3*S*) t_r = 15.4 min, minor enantiomer (3*R*) t_r = 25.8 min.

White solid; mp 170-172 °C (hexane- CH_2Cl_2); $[\alpha]_D^{20}$ +18.2 (*c* 1.1, CH_2Cl_2) for the diastereomer mixture. Major diastereomer: ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.25 (s, 1H), 7.23 (td, *J* = 7.5, 1.5 Hz, 1H), 7.07-6.98 (m, 2H), 6.79 (d, *J* = 7.8 Hz, 1H), 6.25 (s, 1H), 4.41 (dd, *J* = 12.0, 2.7 Hz, 1H), 2.57-2.43 (m, 1H), 2.23-2.12 (m, 1H), 1.32 (s, 9H), 0.96 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 174.0 (C), 154.0 (C), 140.2 (C), 130.1 (CH), 124.8 (C), 123.3 (CH), 122.9 (CH), 110.6 (CH), 92.8 (CH), 81.4 (C), 61.9 (C), 28.1 (CH_3), 20.3 (CH_2), 10.5 (CH_3); MS(ESI) *m/z*: 358.1376 $(M+Na)^+$, $C_{16}H_{21}N_3NaO_5$ required 358.1373.

Minor diastereomer: ^{1}H NMR (300 MHz, $CDCl_3$, representative peaks taken from the diastereomer mixture) δ 5.98 (s, 1H), 4,76 (dd, *J* = 10.7, 3.4 Hz, 1H), 1.88-1.68 (m, 2H), 0.90 (t, *J* = 7.2 Hz, 3H).

***tert*-Butyl (*S*)-(6-chloro-3-(1-nitroethyl)-2-oxoindolin-3-yl)carbamate (6k)**



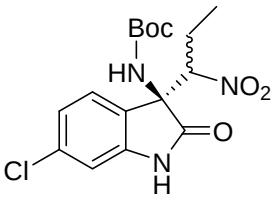
6k

Purified by column chromatography eluting with hexane/EtOAc 70:30 (88.3 mg, 95% yield). Diastereomer ratio 60:40 The *ee* (91.7% major diastereomer, 88.8% minor diastereomer) was determined by HPLC analysis, Chiralpak AD-H, hexane/*i*-PrOH 80:20, 1 mL/min, Major diastereomer: major enantiomer (3*S*) t_r = 7.3 min, minor enantiomer (3*R*) t_r = 11.0 min; Minor diastereomer: major enantiomer (3*S*) t_r = 6.5 min, minor enantiomer (3*R*) t_r = 9.1 min.

The major diasteromer could be obtained in 91:9 dr after crystallyzation from CH_2Cl_2. Yellow solid; mp 182 °C(dec.) (hexane-DCM); $[\alpha]_D^{20}$ +17.1 (*c* 1.0, CH_2Cl_2) for the 91:9 dr mixture; Major diastereomer: ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.64 (s, 1H), 6.99 (d, *J* = 1.2 Hz, 2H), 6.73 (s, 1H), 6.31 (s, 1H), 4.65 (q, *J* = 6.9 Hz, 1H), 1.79 (d, *J* = 6.9 Hz, 3H), 1.37 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 173.5 (C), 154.2 (C), 141.6 (C), 136.0 (C), 125.5 (C), 123.9 (CH), 123.3 (CH), 111.5 (CH), 85.4 (CH), 81.8 (C), 61.7 (C), 28.1 (CH_3), 13.0 (CH_3); MS(ESI) *m/z*: 378.0829 $(M+Na)^+$, $C_{15}H_{18}ClN_3NaO_5$ required 378.0827.

Minor diastereomer: ^{1}H NMR (300 MHz, $CDCl_3$, representative peaks taken from the diastereomer mixture) δ 8.60 (s, 1H), 7.01 (d, *J* = 1.5 Hz, 1H), 6.78 (s, 1H), 6.35 (s, 1H), 4.94 (q, *J* = 6.6 Hz, 1H).

***tert*-Butyl (*S*)-(6-chloro-3-(1-nitropropyl)-2-oxoindolin-3-yl)carbamate (7k)**



7k

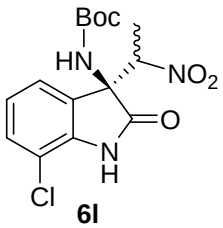
Purified by column chromatography eluting with hexane/EtOAc 70:30 (80.9 mg, 91% yield). Diastereomer ratio 85:15. The *ee* (87.8% major diastereomer, 78.8% minor diastereomer) was determined by HPLC analysis, Chiralpak AD-H, hexane/*i*-PrOH 80:20, 1 mL/min, Major diastereomer: major enantiomer (*S*) t_r = 6.3 min, minor enantiomer (*R*) t_r = 8.6 min; Minor diastereomer: major enantiomer (*S*) t_r = 7.3 min, minor enantiomer (*R*) t_r = 9.6 min.

White solid; mp 196 °C (dec.)(hexane-CH_2Cl_2); $[\alpha]_D^{20}$ -6.8 (*c* 1.2, CH_2Cl_2) for the diastereomer mixture; Major diastereomer: ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.41 (s, 1H), 7.20-6.93 (m, 2H), 6.73 (s, 1H), 6.28 (s, 1H), 4.36 (dd, *J* = 12.0, 2.7 Hz, 1H), 2.58-2.43 (m, 1H), 2.27-2.10 (m, 1H), 1.36 (s, 9H), 0.96 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 173.6 (C), 154.2 (C), 141.5 (C), 136.0 (C), 125.6 (C), 123.7 (CH), 123.3

(CH), 111.4 (CH), 92.7 (CH), 81.8 (C), 61.6 (C), 28.1 (CH_3), 20.3 (CH_2), 10.4 (CH_3); MS(ESI) *m/z*: 392.0982 $(M+Na)^+$, $C_{16}H_{20}ClN_3NaO_5$ required 392.0984.

Minor diastereomer: ^{1}H NMR (300 MHz, $CDCl_3$, representative peaks taken from the diastereomer mixture) δ 8.35 (s, 1H), 5.96 (s, 1H), 4,73 (dd, *J* = 11.4, 3.0 Hz, 1H), 0.90 (t, *J* = 7.5 Hz, 3H).

***tert*-Butyl (*S*)-(7-chloro-3-(1-nitroethyl)-2-oxoindolin-3-yl)carbamate (6l)**



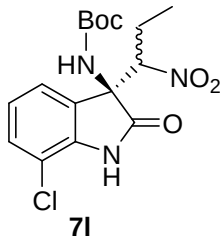
6l

Purified by column chromatography eluting with hexane/EtOAc 70:30 (78.1 mg, 91% yield). Diastereomer ratio 76:24. The *ee* (98.9% mayor diastereomer, 99.9% minor diastereomer) was determined by HPLC analysis, Chiralpak AD-H, hexane/*i*-PrOH 80:20, 1 mL/min, Major diastereomer: major enantiomer (*S*) t_r = 9.31 min, minor enantiomer (*R*) t_r = 29.7 min; Minor diastereomer: major enantiomer (*S*) t_r = 8.6, minor enantiomer (*R*) t_r = 14.2 min.

White solid; mp 170-172 °C (hexane-DCM); $[\alpha]_D^{20}$ -22 (*c* 1.1, MeOH) for the diastereomeric mixture. Major diastereomer: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.97 (s, 1H), 7.27-7.20 (m, 1H), 6.97-6.93 (m, 2H), 6.19 (s, 1H), 4.62 (q, *J* = 6.9 Hz, 1H), 1.73 (d, *J* = 6.9 Hz, 3H), 1.24 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 173.8 (C), 153.9 (C), 137.9 (C), 130.1 (CH), 124.3 (CH), 121.5 (CH), 115.8 (C), 85.3 (CH), 81.7 (C), 63.0 (C), 28.0 (CH_3), 13.0 (CH_3); MS(ESI) *m/z*: 378.0826 $(M+Na)^+$, $C_{15}H_{18}ClN_3NaO_5$ required 378.0827.

Minor diastereomer: ^{1}H NMR (300 MHz, $CDCl_3$, representative peaks taken from the diastereomer mixture) δ 8.01 (s, 1H), 6.16 (s, 1H), 4.90 (q, *J* = 6.6 Hz, 1H), 1.31 (d, *J* = 6.9 Hz, 3H).

***tert*-Butyl (*S*)-(7-chloro-3-(1-nitropropyl)-2-oxoindolin-3-yl)carbamate (7l)**



7l

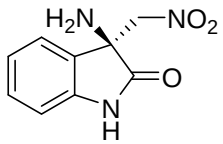
Purified by column chromatography eluting with hexane/EtOAc 70:30 (66.7 mg, 89% yield). Diastereomer ratio 88:12. The *ee* (99.8% mayor diastereomer, 99.8% minor diastereomer) was determined by HPLC analysis, Chiralpak AD-H, hexane/*i*-PrOH 80:20, 1 mL/min, Major diastereomer: major enantiomer (*S*) t_r = 8.7 min, minor enantiomer (*R*) t_r = 15.1 min; Minor diastereomer: major enantiomer (*S*) t_r = 9.4 min, minor enantiomer (*R*) t_r = 16.0 min.

The major diastereomer was obtained pure after crystallyzation from hexane-CH_2Cl_2: White solid; mp 214-216 °C (hexane-DCM); $[\alpha]_D^{20}$ -12.7 (*c* 0.9, MeOH, 100% *ee*) for the pure major diastereomer; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.86 (br s, 1H), 7.29 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.00 (t, *J* = 7.5 Hz, 1H), 6.95 (dd, *J* = 7.8, 1.5 Hz, 1H), 6.23 (s, 1H), 4.39 (dd, *J* = 12, 2.7 Hz, 1H), 2.50 (m, 1H), 2.20 (m, 1H), 1.31 (s, 9H), 0.97 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 173.2 (C), 153.7 (C), 137.6 (C), 130.1 (CH), 124.3 (CH), 121.3 (CH), 120.1 (C), 115.7 (C), 92.5 (CH), 90.3 (C), 62.9 (C), 28.0 (CH_3), 20.2 (CH_2), 10.5 (CH_3); MS(ESI) *m/z*: 392.0984 $(M+Na)^+$, $C_{16}H_{20}ClN_3NaO_5$ required 392.0984.

Minor diastereomer: ^{1}H NMR (300 MHz, $CDCl_3$, representative peaks taken from the diastereomer mixture) δ 8.06 (s, 1H), 5.93 (s, 1H), 4.75 (dd, *J* = 11.1, 3.3 Hz, 1H), 0.91 (t, *J* = 7.2 Hz, 3H).

Transformations of nitroamine 3a

Deprotection of the Boc moiety.[4] (*S*)-3-amino-3-(nitromethyl)indolin-2-one (8)

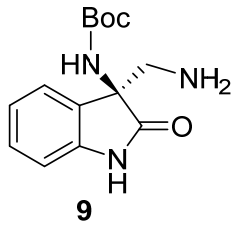


8

Trifluoroacetic acid (1.1 mL) was added dropwise to a stirred solution of compound **3a** (101.0 mg, 0.33 mmol, 96% ee) in CH_2Cl_2 (5 mL) at 0 ºC and stirred during 2 hours at room temperarure. The reaction was concentrated, diluted with CH_2Cl_2 (15 mL), washed with $NaHCO_3$, dried over $MgSO_4$ and concentrated under reduced pressure to give 65.5 mg (96%) of compound **8**: The *ee* (95.6%) was determined by HPLC analysis, Chiralpak AD-H, hexane/*i*-PrOH 80:20, 1 mL/min, major enantiomer (*S*) t_r = 14.9 min, minor enantiomer (*R*) t_r = 12.8 min. $[\alpha]_D^{20}$ +53.9 (*c* 0.8, MeOH, 95% *ee*); ^{1}H NMR (300 MHz, CD_3CN) δ 8.69 (br s, 1H), 7.37 (dq, *J* = 7.5, 0.6 Hz, 1H), 7.29 (td, *J* = 7.5, 1.5 Hz, 1H), 7.05 (td, *J* = 7.8, 0.9 Hz, 1H), 6.94 (ddd, *J* = 7.5, 0.9, 0.6 Hz, 1H), 4.89 (d, *J* = 12.9 Hz, 1H), 4.83 (d, *J* = 12.9 Hz, 1H); ^{13}C NMR (75 MHz, CD_3CN) δ 178.9 (C), 142.9 (C), 131.0 (CH), 129.7 (C), 125.0 (CH), 123.4 (CH), 111.3 (CH), 80.5 (CH_2), 60.4 (C); MS(ESI) *m/z*: 230.0538 $(M+Na)^+$, $C_9H_9N_3NaO_3$ required 230.0536.

Synthesis of diamines 9 and 10

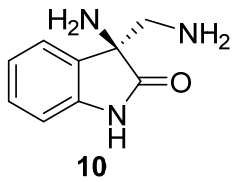
***tert*-Butyl (*S*)-(3-(aminomethyl)-2-oxoindolin-3-yl)carbamate (9)**



9

To a solution of compound **3a** (100.0 mg, 0.33 mmol) in methanol (2.4 mL) at 0 ºC was added $NiCl_2$ (44 mg, 0.34 mmol) followed by $NaBH_4$ (61.7 mg, 1.63 mmol) and the mixture was stirred for 30 min.[5] Then, saturated aqueous NH_4Cl (10 mL) was added and the mixture extracted with ethyl acetate (4×30 mL), washed with brine (15 mL), dried over $MgSO_4$ and concentrated under reduced pressure. The crude was filtered through a short pad of silica gel eluting with CH_2Cl_2:MeOH:Et_3N (90:10:1) and concentrated under reduced pressure to give 90.0 mg (99%) of compound **5a**: The *ee* (95.8%) was determined by HPLC analysis, Chiralpak AY-H, hexane/*i*-PrOH 80:20, 1 mL/min, major enantiomer (*S*) t_r = 8.6 min, minor enantiomer (*R*) t_r = 17.1 min. $[\alpha]_D^{20}$ +35.8 (*c* 1.0, MeOH, 95.8% *ee*); ^{1}H NMR (300 MHz, CD_3OD) δ 7.30-7.23 (m, 2H), 7.06 (t, *J* = 7.5 Hz, 1H), 6.92 (dt, *J* = 7.8, 0.9 Hz, 1H), 3.03 (d, *J* = 13.8 Hz, 1H), 2.85 (d, *J* = 13.5 Hz, 1H), 1.29(br s, 9H); ^{13}C NMR (75 MHz, CD_3OD) δ 180.1 (C), 156.5 (C), 142.8 (C), 129.9 (CH), 127.8 (C), 123.7 (CH), 123.6 (CH), 111.3 (CH), 81.3 (C), 63.7 (C), 48.9 (CH_2), 28.4 (CH_3); MS(ESI) *m/z*: 300.1315 $(M+Na)^+$, $C_{14}H_{19}N_3NaO_3$ required 300.1319

(*S*)-3-amino-3-(aminomethyl)indolin-2-one (10)

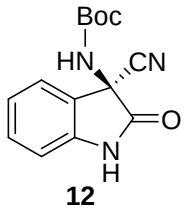


10

A 1M solution of HCl in diethyl ether (6.2 mL, 6.2 mmol) was added dropwise to a solution of compound **9** (85 mg, 0.31 mmol) in methanol at 0 ºC. The reaction was stirred overnight at room temperature and concentrated under reduced pressure. The mixture was dissolved with ethyl acetate (2 mL), basified with 1 M aqueous NaOH (2 mL), extracted with EtOAc (4×30 mL), dried over $MgSO_4$ and concentrated under reduced pressure to give 35.5 mg (65%) of diamine **10**: $[\alpha]_D^{20}$ +53.2 (*c* 0.6, MeOH); ^{1}H NMR (300 MHz, CD_3OD) δ 7.39 (dq, *J* = 7.5, 0.6 Hz, 1H), 7.27 (td, *J* = 7.5, 1.5 Hz, 1H), 7.07 (td, *J* = 7.5, 1.2 Hz, 1H), 6.93 (dt, *J* = 7.8, 0.6 Hz, 1H), 2.94 (d, *J* = 13.2 Hz, 1H), 2.89 (d, *J* = 13.2 Hz, 1H); ^{13}C NMR (75 MHz, CD_3OD) δ 182.8 (C), 143.1 (C), 132.2 (C), 130.4 (CH), 124.9 (CH), 123.7 (CH), 111.3 (CH), 62.9 (C), 49.9 (CH_2); MS(ESI) *m/z*: 200.0792 $(M+Na)^+$, $C_{14}H_{19}N_3NaO_3$ required 200.0794.

Synthesis of nitrile 12 and ester 13

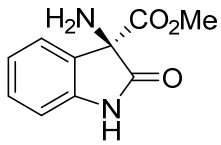
***tert*-Butyl (*S*)-(3-cyano-2-oxoindolin-3-yl)carbamate (12)**



12

Compound **3a** (70 mg, 0.23 mmol) was added to a solution of $SnCl_2 \cdot 2H_2O$ (102.9 mg, 0.46 mmol), thiophenol (140 μL, 1.37 mmol) and triethylamine (190 μL, 1.37 mmol) in absolute EtOH (1.2 mL) at room temperature. After 20 min, the reaction mixture was poured into 1M aqueous HCl (5 mL) and CH_2Cl_2 (6 mL) at 0 °C. The layers were separated and the aqueous layer was extracted con CH_2Cl_2 (3 x 20 mL). The organic layer was washed with aqueous $NaHCO_3$ (3 mL), brine (3 mL) and dried over $MgSO_4$. After removal of the solvent, the residue was chromatographed through a short plug of silica gel eluting with hexane EtOAc 6:4 to remove the excess of thiophenol and then with EtOAc. The EtOAc fraction was concentrated under reduced pressure to give 50.1 mg (75%) of a estereoismeric mixture of oximes **11**. To the solution of oximes 11 in THF (1.8 mL) at 0 °C under nitrogen atmosphere was added triethylamine (119 μL, 119 mmol) and $SOCl_2$ (25 μL, 0.34 mmol). After 45 min, water (4 ml) was added and the mixture extracted with EtOAc (2 x 30 mL), washed with brine (3 mL), dried over $MgSO_4$ and concentrated under reduced pressure. Column chromatography eluting with hexane/EtOAc 6:4 gave 39.6 mg (84%) of compound **12**: The *ee* (94.8%) was determined by HPLC analysis, Chiralpak IC, hexane/*i*-PrOH 90:10, 1 mL/min, major enantiomer (*S*) t_r = 17.3 min, minor enantiomer (*R*) t_r = 21.0 min. $[\alpha]_D^{20}$ -21.6 (*c* 1.3, MeOH, 94.8% *ee*), $[\alpha]_D^{20}$ -53.0 (*c* 0.6, $CHCl_3$, 94.8% *ee*), Lit.[6] $[\alpha]_D^{20}$ +55 (*c* 1.0, $CHCl_3$, 91% *ee*, for the *R*-enantiomer); ^{1}H NMR (300 MHz, CD_3OD) δ 7.50 (d, *J* = 7.2 Hz, 1H), 7.37 (td, *J* = 7.8, 1.2 Hz, 1H), 7.13 (td, *J* = 8.7, 0.9 Hz, 1H), 6.97 (ddd, *J* = 7.8, 1.2, 0.9 Hz, 1H), 1.33 (s, 9H); ^{13}C NMR (75 MHz, CD_3OD) δ 171.8 (C), 155.7 (C), 143.1 (C), 132.3 (CH), 127.5 (C), 125.4 (C), 124.6 (CH), 116.2 (C), 112.1(CH), 82.5 (C), 28.4 (CH_3); MS(ESI) *m/z*: 296.1009 $(M+Na)^+$, $C_{14}H_{15}N_3NaO_3$ required 296.1006.

Methyl (*R*)-3-amino-2-oxoindoline-3-carboxylate (13)



13

Dry HCl was bubbled through a solution of compound **12** (36 mg, 0.13 mmol) in anhydrous methanol (3.0 ml) at 0 °C for 3 + 2 min.[7] The mixture was stirred for 24 h at room temperature. Saturated aqueous $NaHCO_3$ (5 mL) was added. MeOH was removed under reduced pressure and the aqueous layer was extracted with CH_2Cl_2 (2x30 mL) and dried

with $MgSO_4$. Removal of the solvents under reduced pressure gave 17.0 mg (61%) of ester **13**: The *ee* (92%) was determined by HPLC analysis, Chiralpak AD-H, hexane/*i*-PrOH 80:20, 1 mL/min, major enantiomer (*R*) t_r = 12.5 min, minor enantiomer (*S*) t_r = 11.5 min. $[\alpha]_D^{20}$ +113.4 (*c* 1.3, MeOH, 92% *ee*), Lit[7] $[\alpha]_D^{20}$ -114 (for the *S*-enantiomer); ^{1}H NMR (300 MHz, CD_3OD) δ 7.33-7.27 (m, 2H), 7.04 (td, J = 7.5, 0.9, 1H), 6.94 /td, J = 8.1, 0.6, 1H), 3.67 (s, 3H); ^{13}C NMR (75 MHz, CD_3OD) δ 178.3 (C), 171.7 (C), 143.9 (C), 131.2 (CH), 130.8 (C), 124.8 (CH), 123.9 (CH), 111.5 (CH), 66.9 (C), 53.6 (CH_3); MS(ESI) *m/z*: 229.0586 $(M+Na)^+$, $C_{10}H_{10}N_2NaO_3$ required 229.0584.

Notes and references

1. (a) H. Jie, J. Li, X. Jia, *Synlett* 2012, **23**, 2274. (b) D. J. Vyas, R. Frohlich, M. Oestreich, *J. Org. Chem*. 2010, **75**, 6720.

2. P. Cali, M. Begtrup, *Synthesis* 2002, 63.

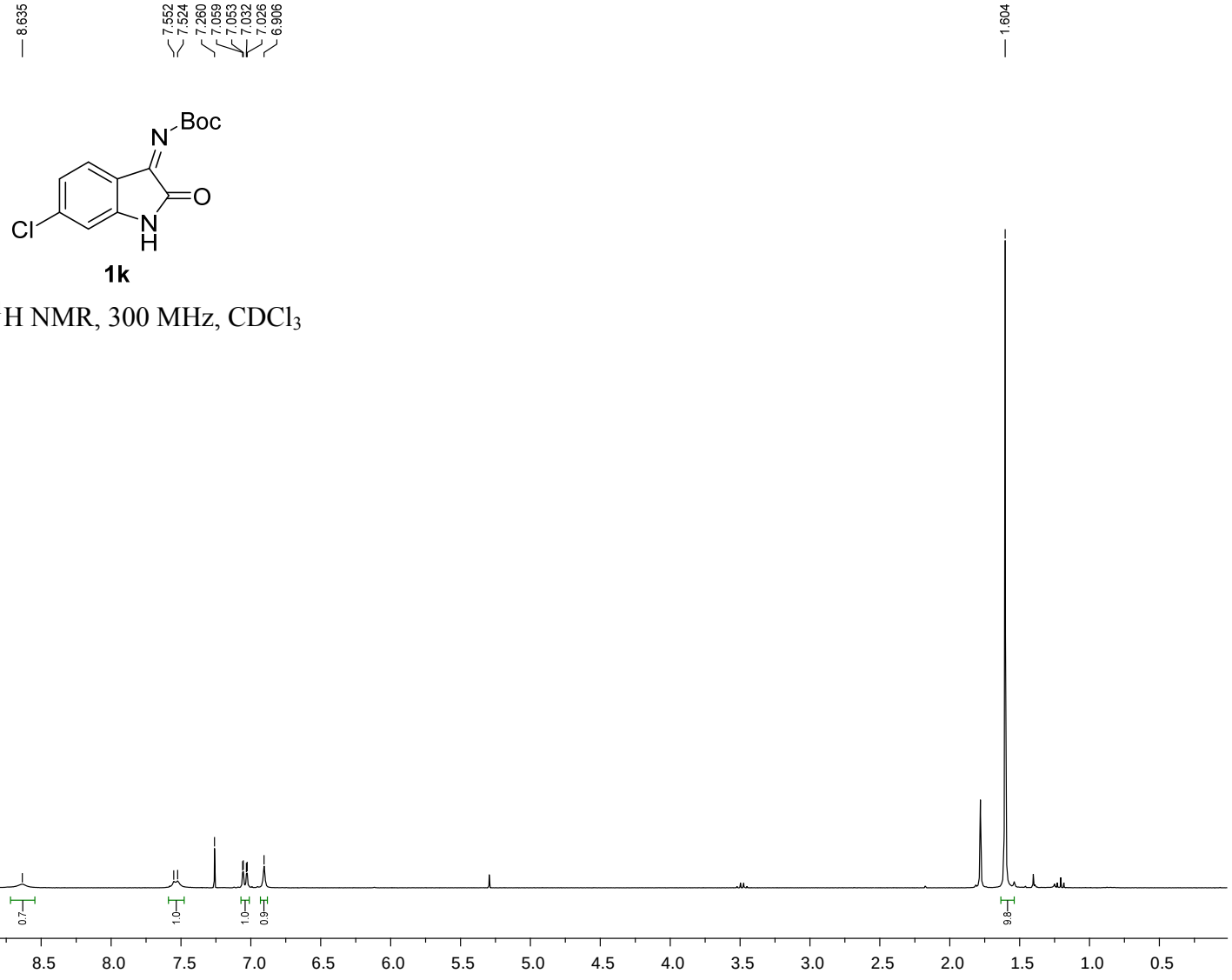
3. (a) W. Yan, D. Wang, J. Feng, P. Li, D. Zhao, R. Wang, *Org. Lett*. 2012, **14**, 2512.
(b) M. G. Sankar, M. Garcia-Castro, Y. Wang, K. Kumar, *Asian J. Org. Chem.* 2013, **2**, 646.

4. Chen X.; Chen H.; Ji X.; Jiang H.; Yao Z.; Liu H.; *Org. Lett*. 2013, 15, 1846.

5. Wei Y.; He W.; Liu Y.; Liu P.; Zhang S.; *Org. Lett*. 2012, 14, 704-707.

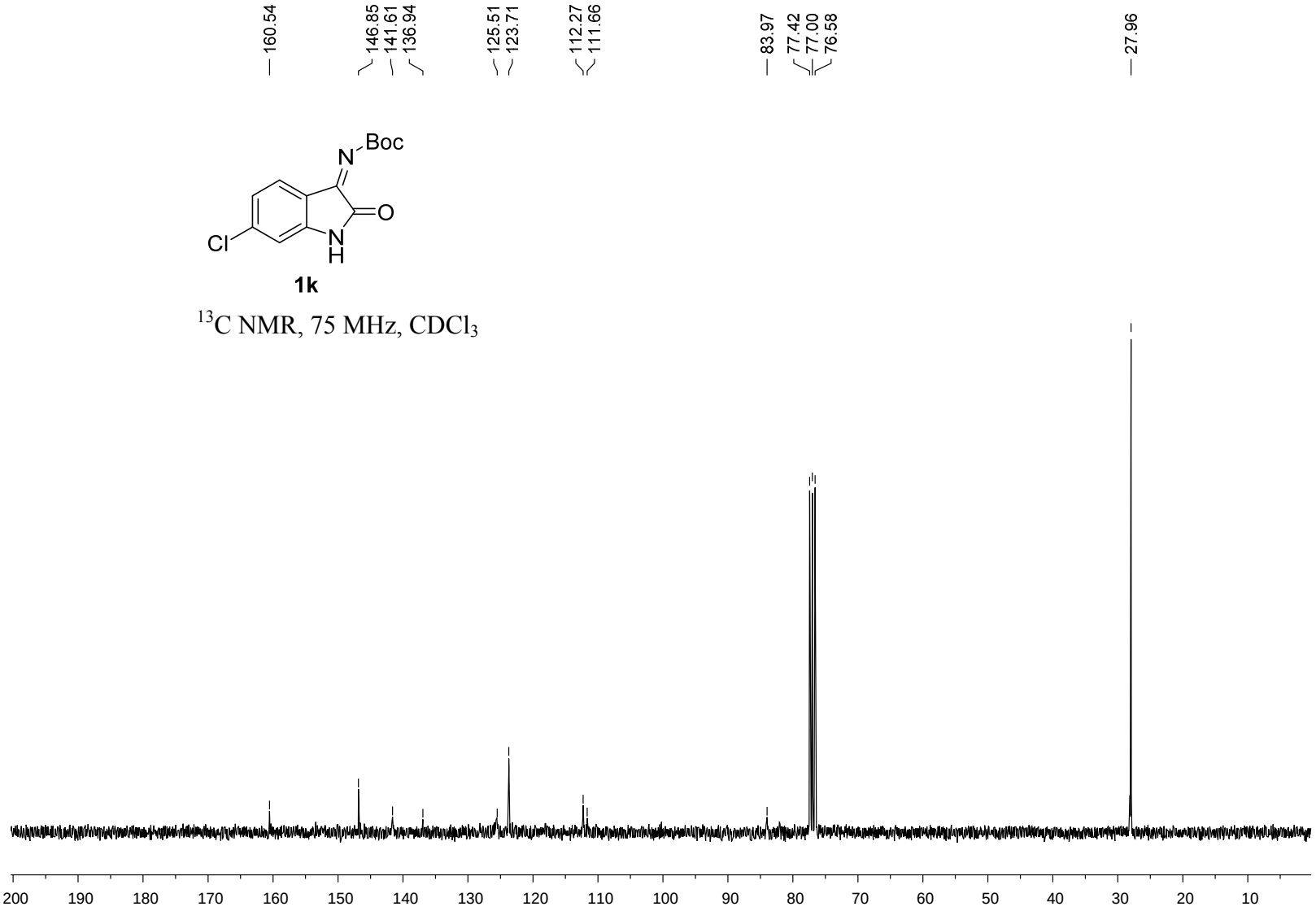
6. D. Wang, J. Liang, J. Feng, K. Wang, Q.Sun, L. Zhao, D. Li, W. Yan, R.Wang, *Adv. Synth. Catal.* 2013, **355**, 548

7. When we carried out the reaction bubbling HCl for 15 min the *ee* of compound **13** decreased to 81%.



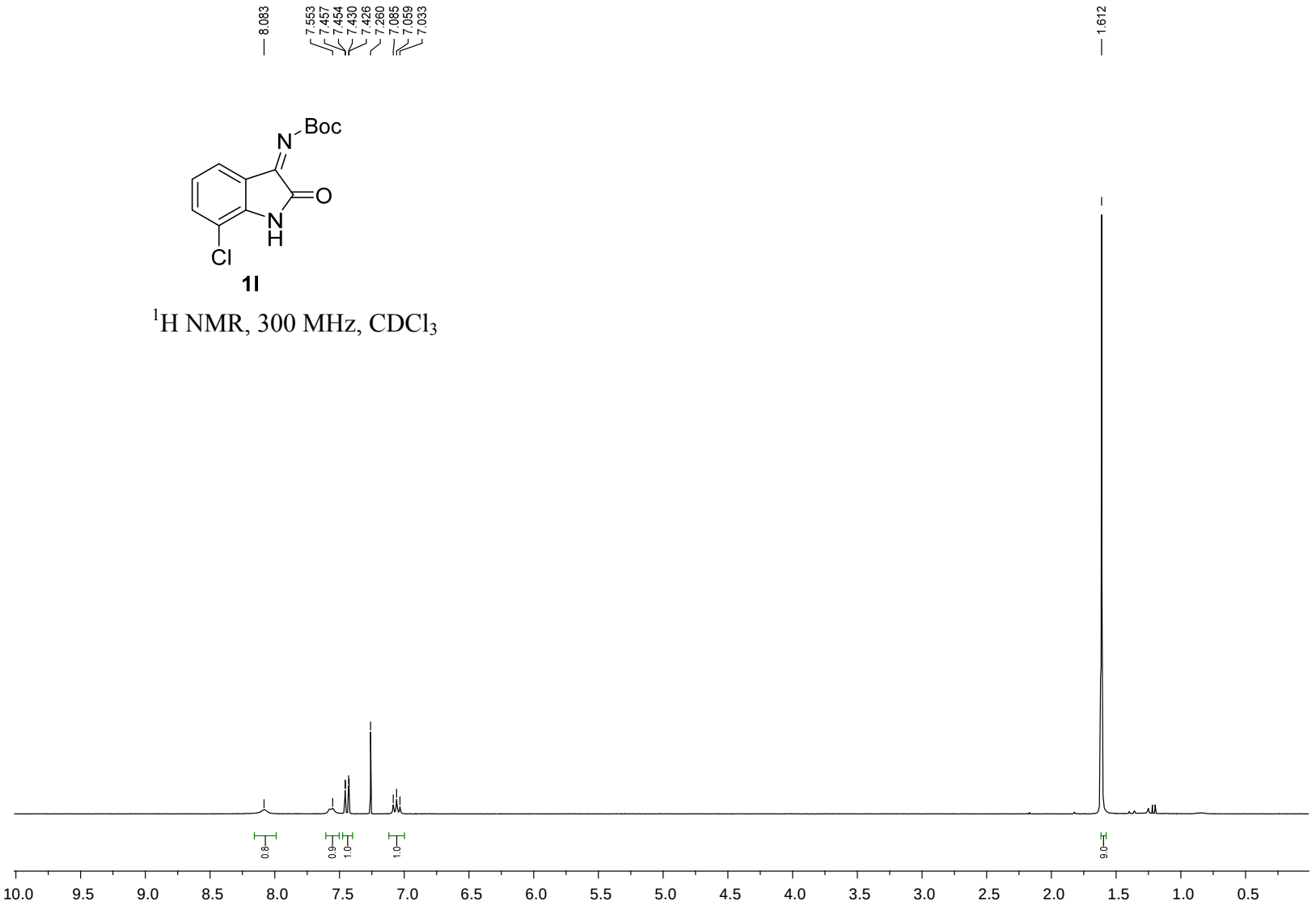
1k

^{1}H NMR, 300 MHz, $CDCl_3$



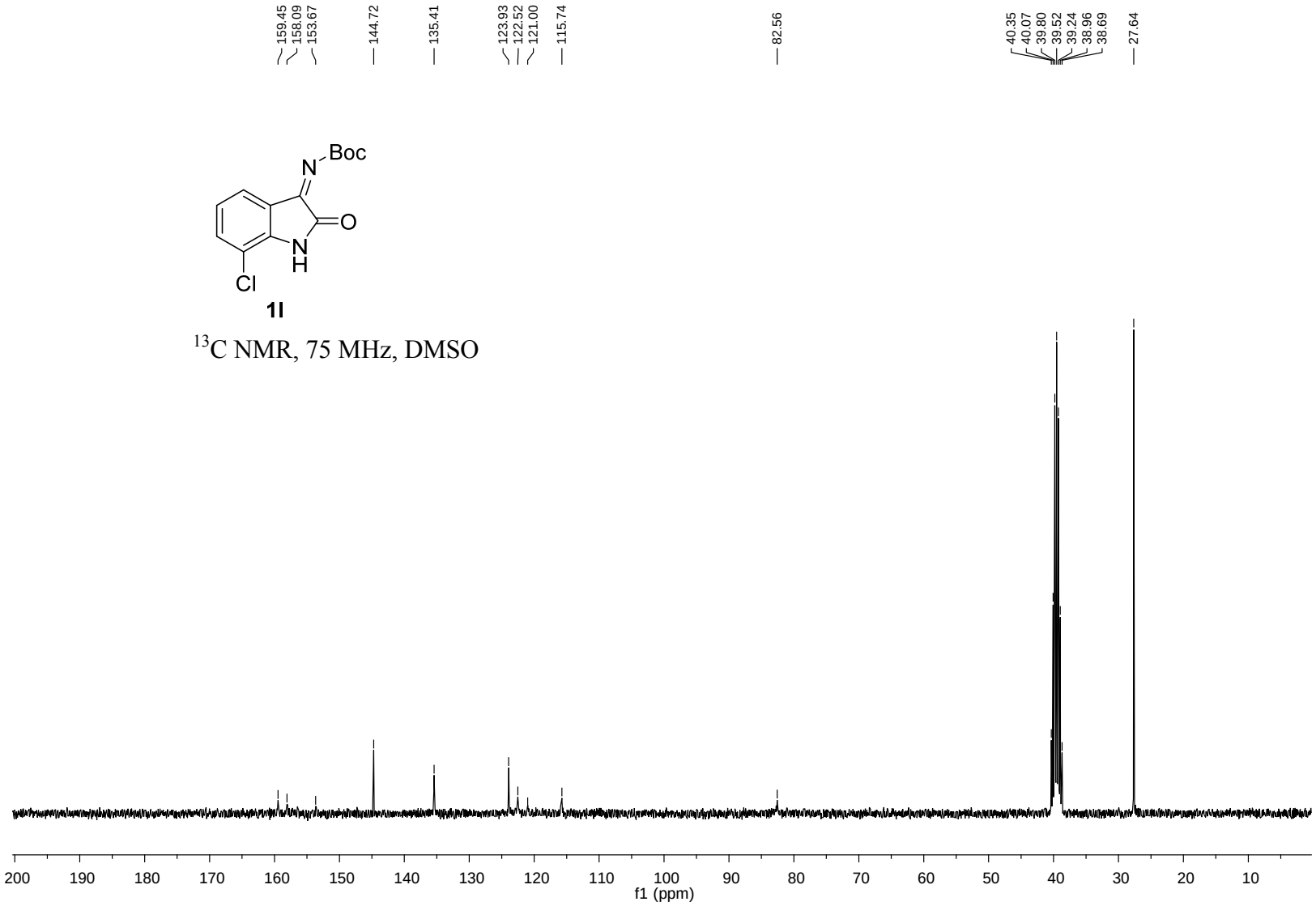
1k

^{13}C NMR, 75 MHz, $CDCl_3$



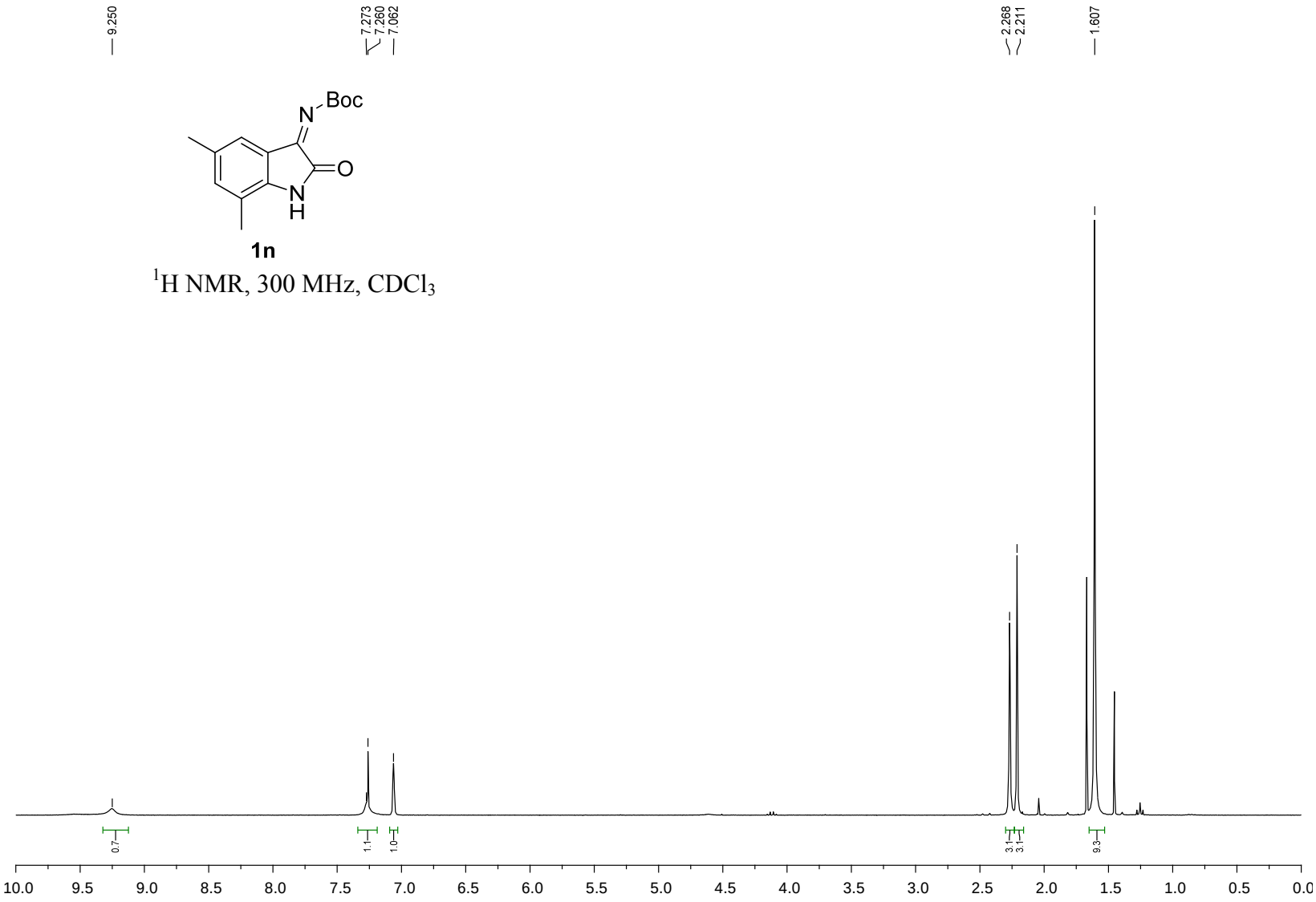
1l

^{1}H NMR, 300 MHz, $CDCl_3$



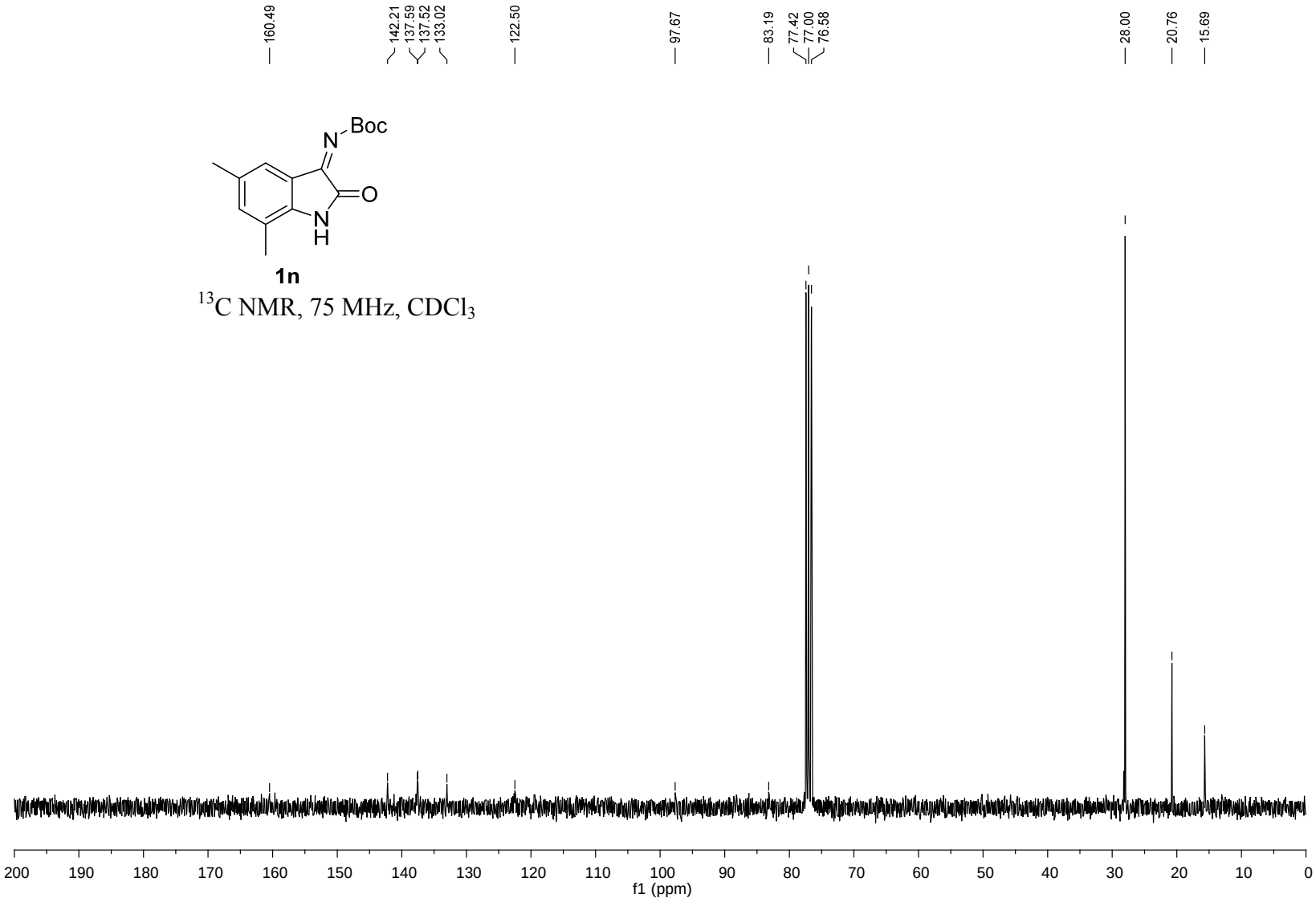
1l

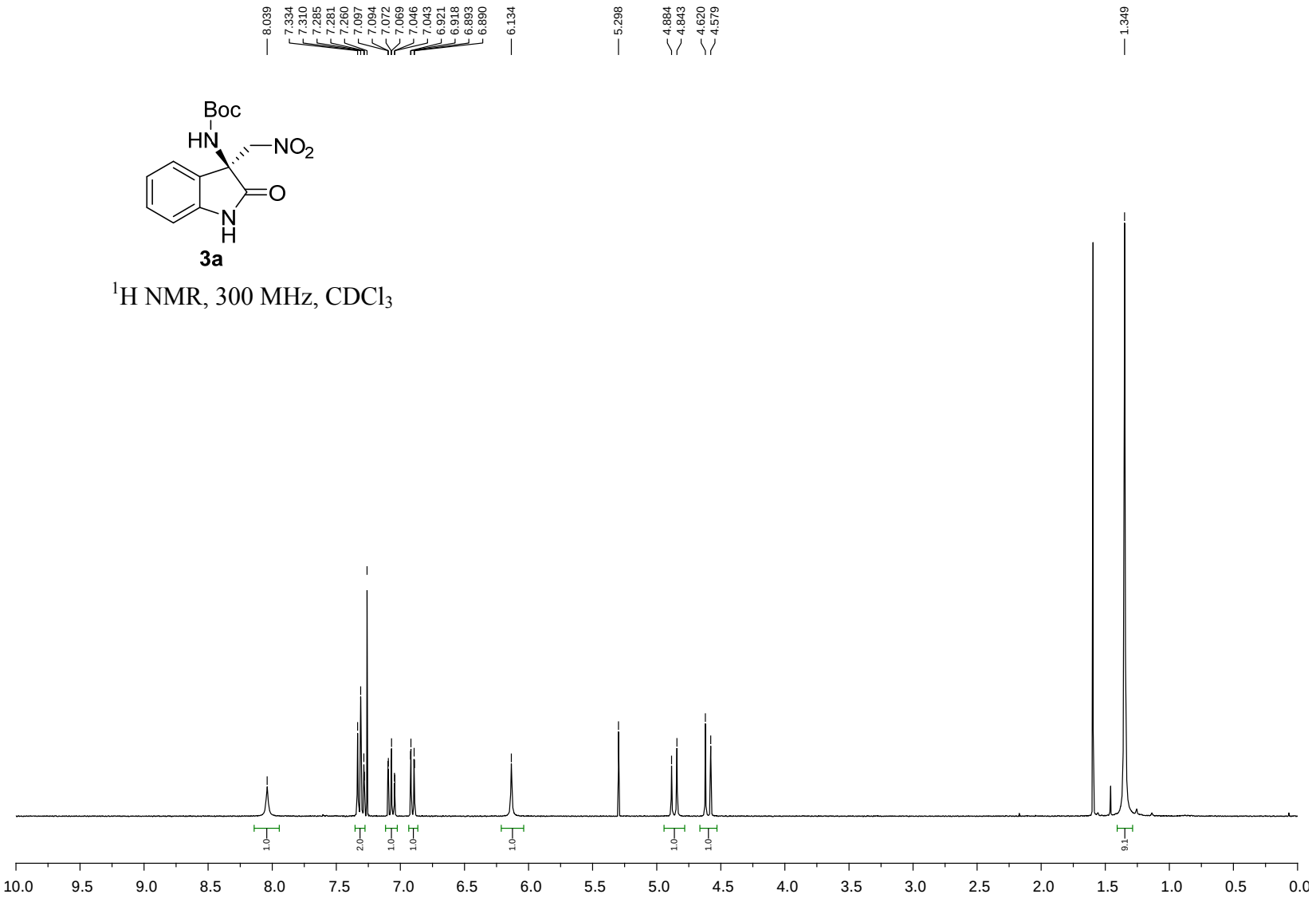
^{13}C NMR, 75 MHz, DMSO



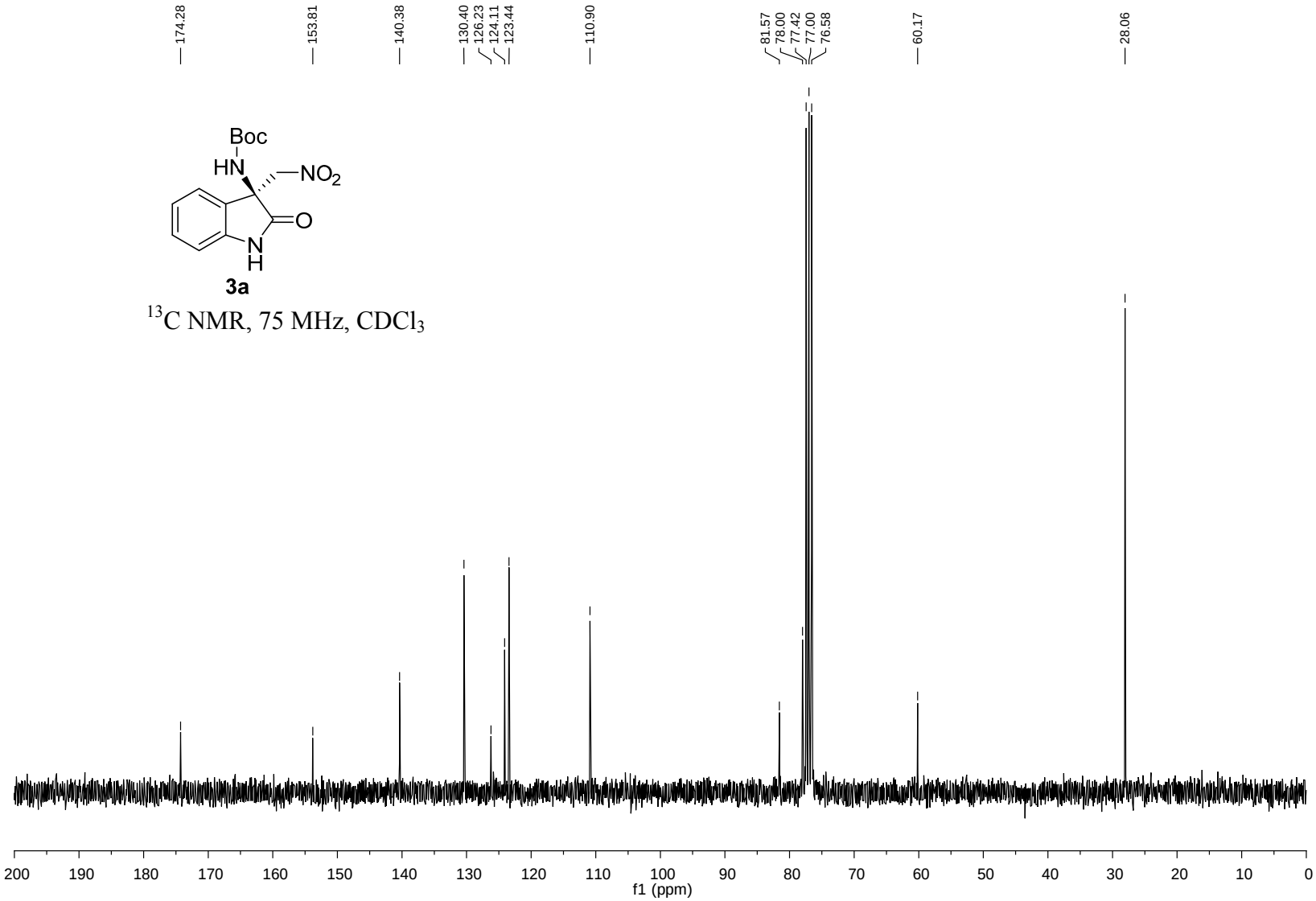
1n

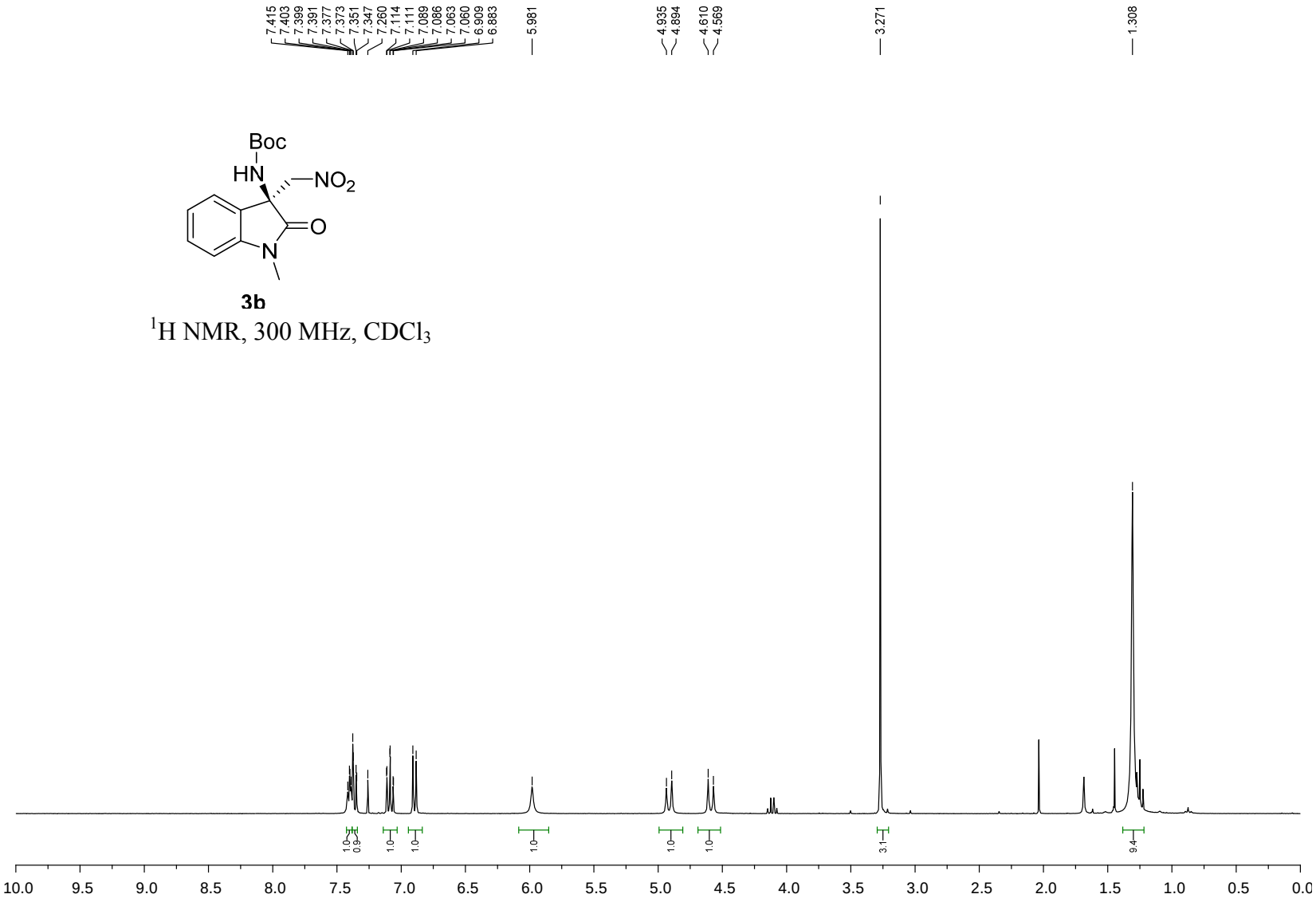
^{1}H NMR, 300 MHz, $CDCl_3$


160.49
142.21
137.59
137.52
133.02
122.50
97.67
83.19
77.42
77.00
76.58
28.00
20.76
15.69
N
Boc
O
N
H
1n
13C NMR, 75 MHz, CDCl3
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



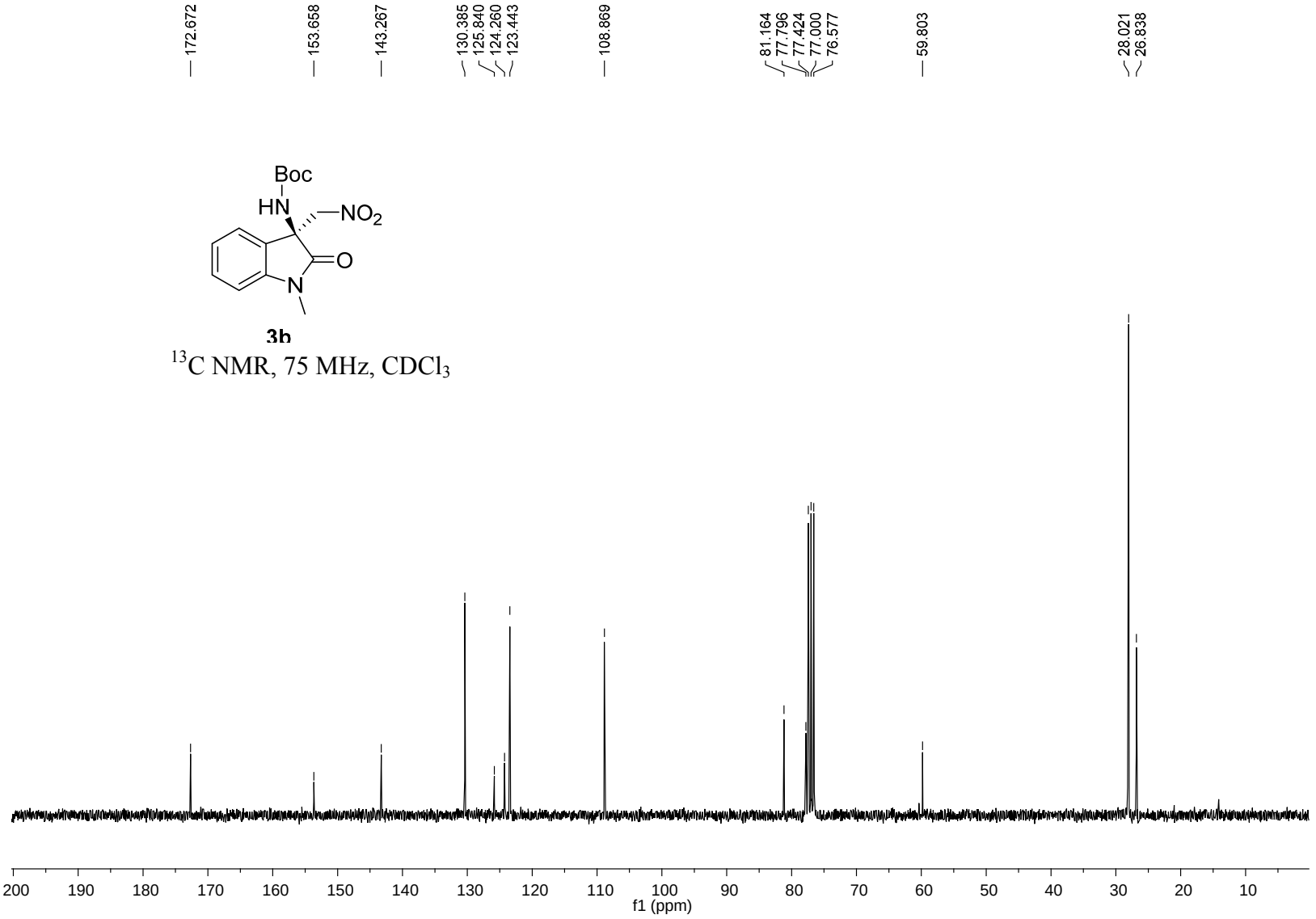
^{1}H NMR, 300 MHz, $CDCl_3$


174.28
153.81
140.38
130.40
126.23
124.11
123.44
110.90
81.57
78.00
77.42
77.00
76.58
60.17
28.06
Boc
HN
NO2
O
N
H
3a
13C NMR, 75 MHz, CDCl3
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



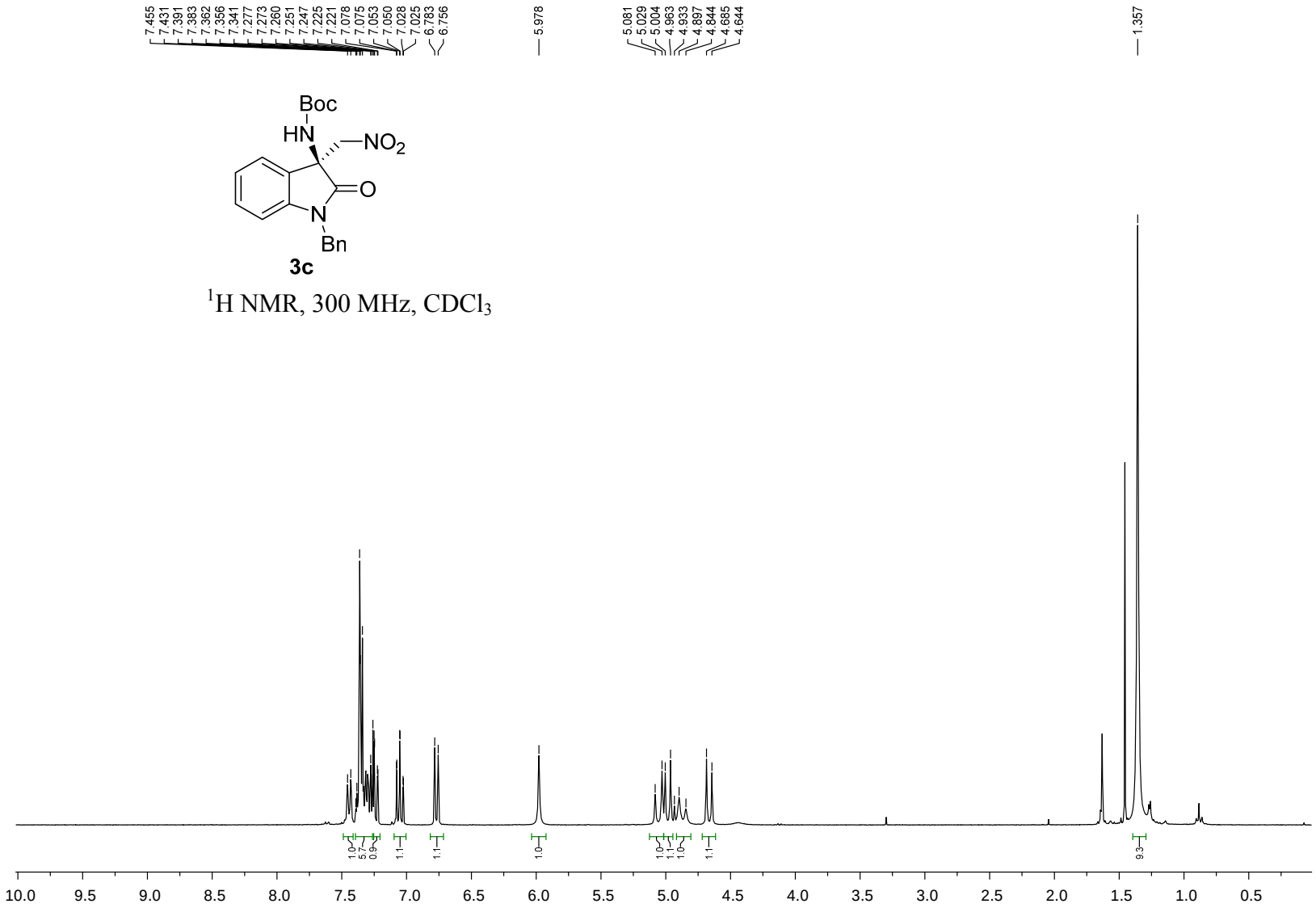
3b

^{1}H NMR, 300 MHz, $CDCl_3$

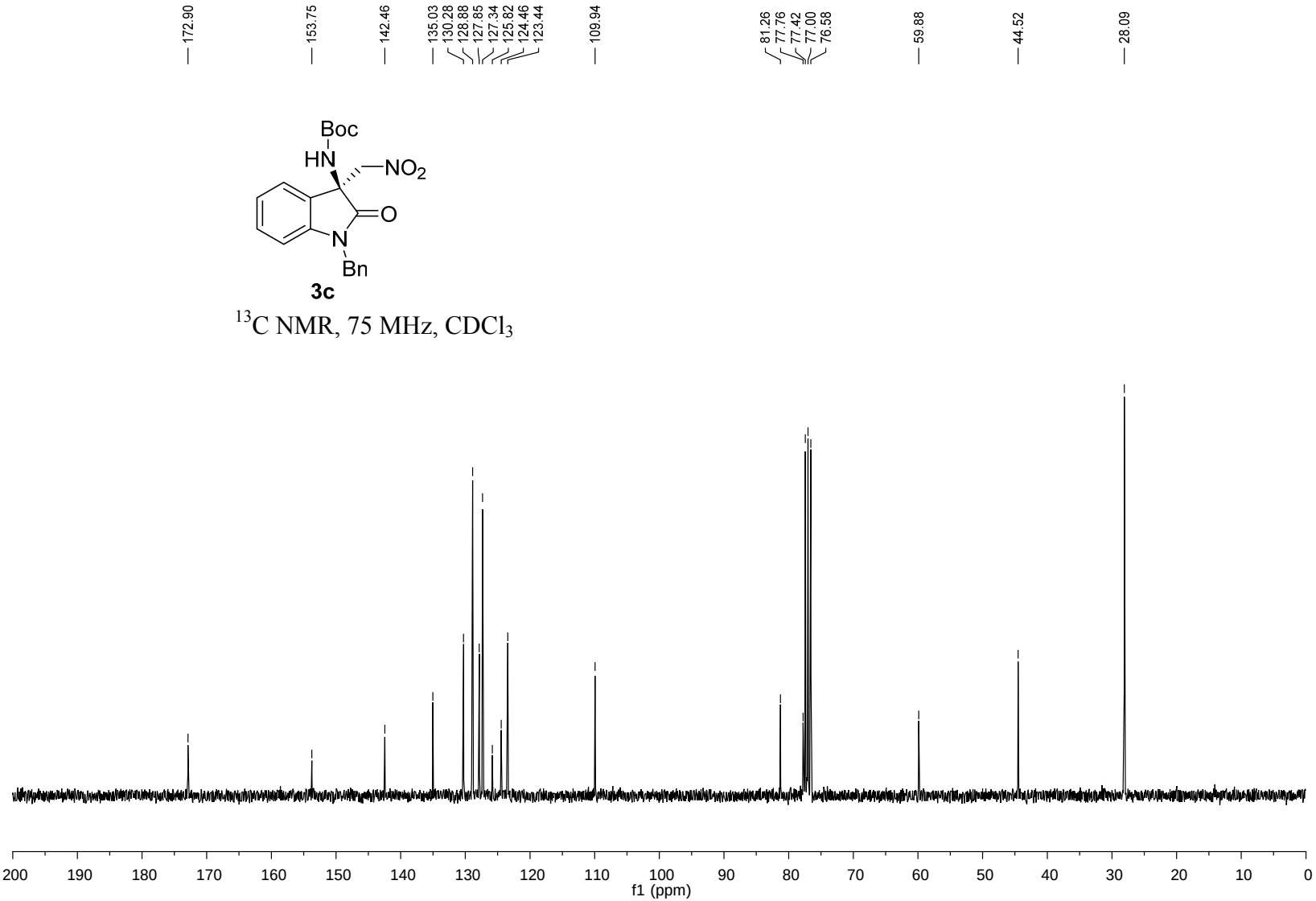


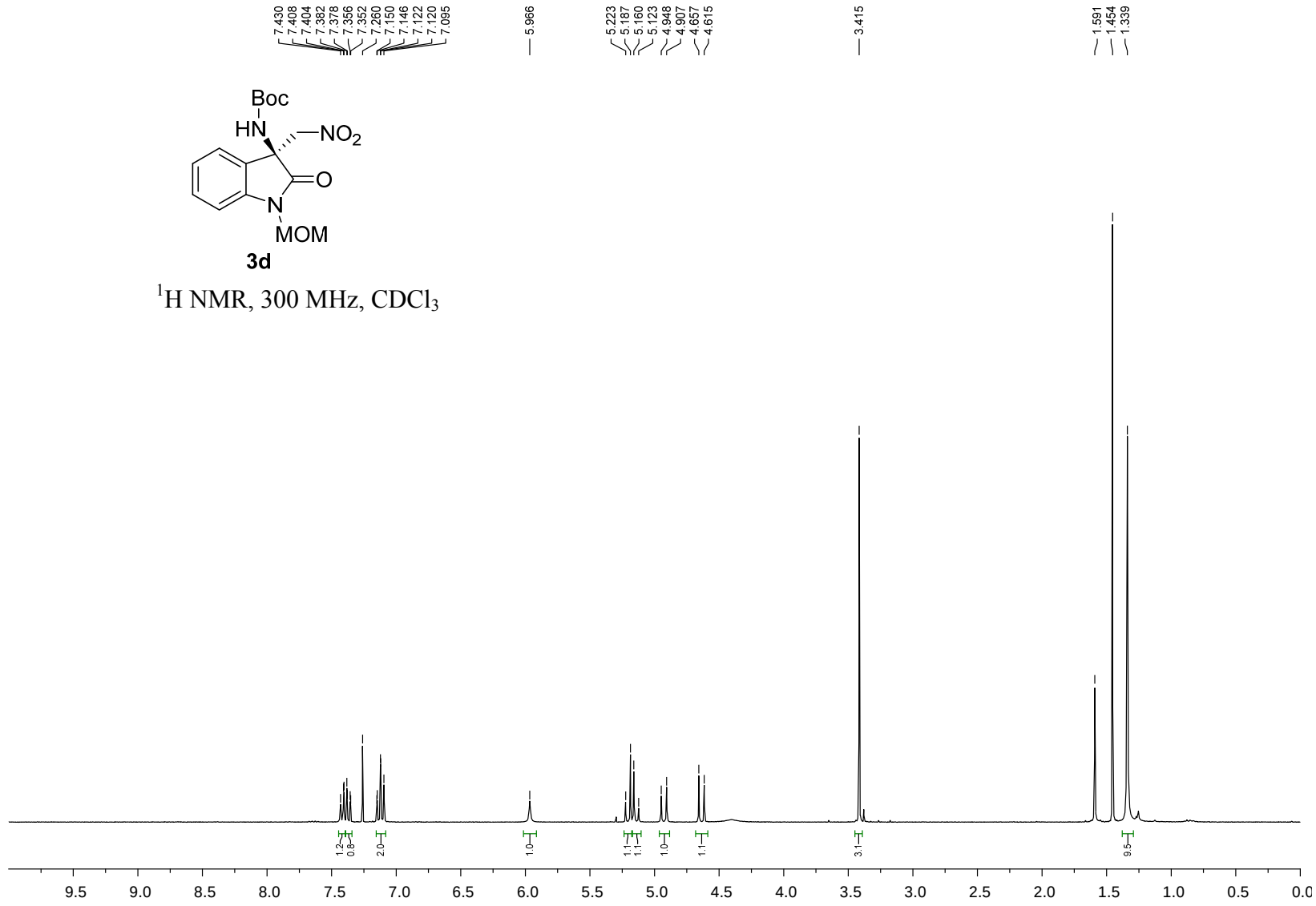
3h

^{13}C NMR, 75 MHz, $CDCl_3$

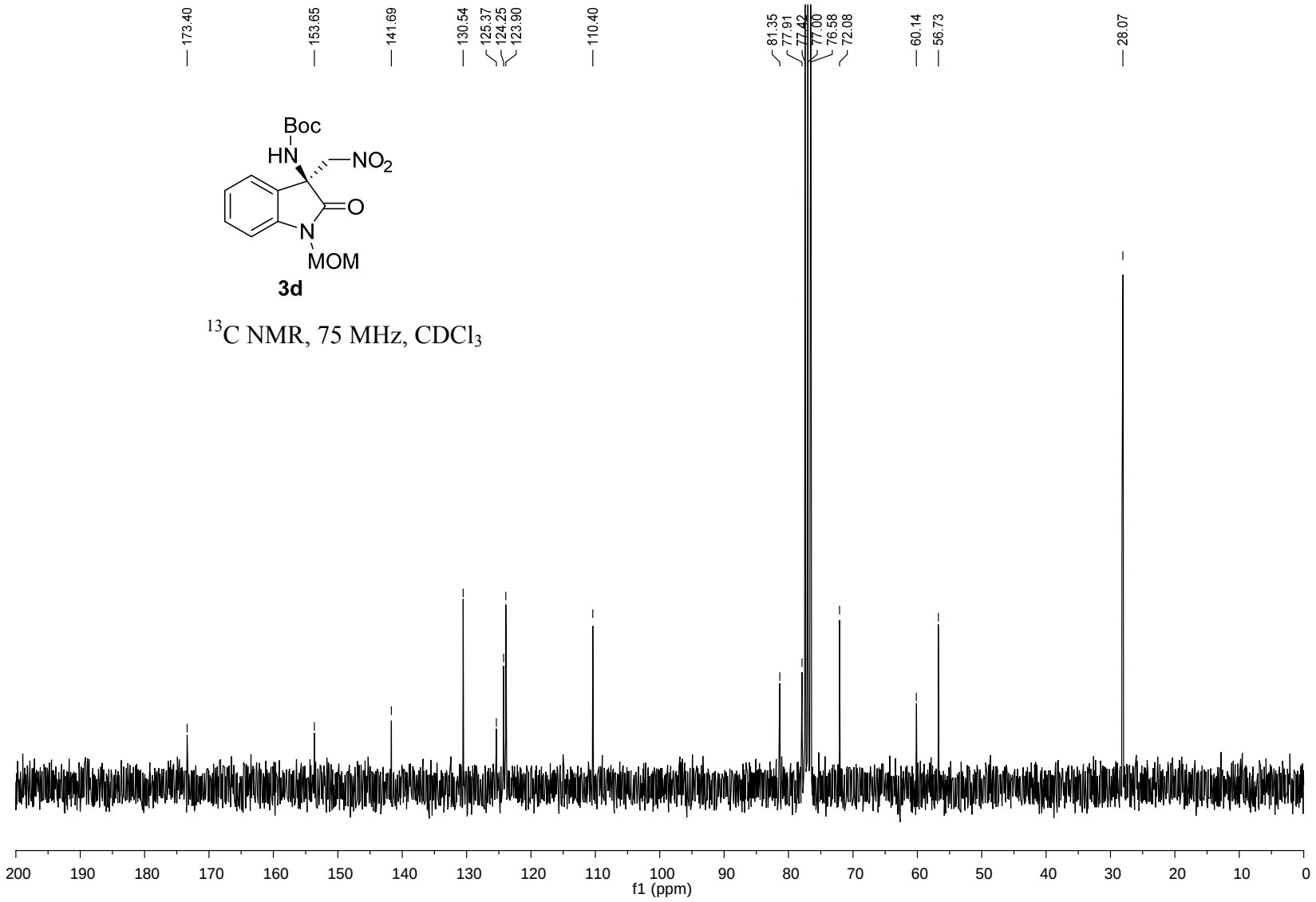


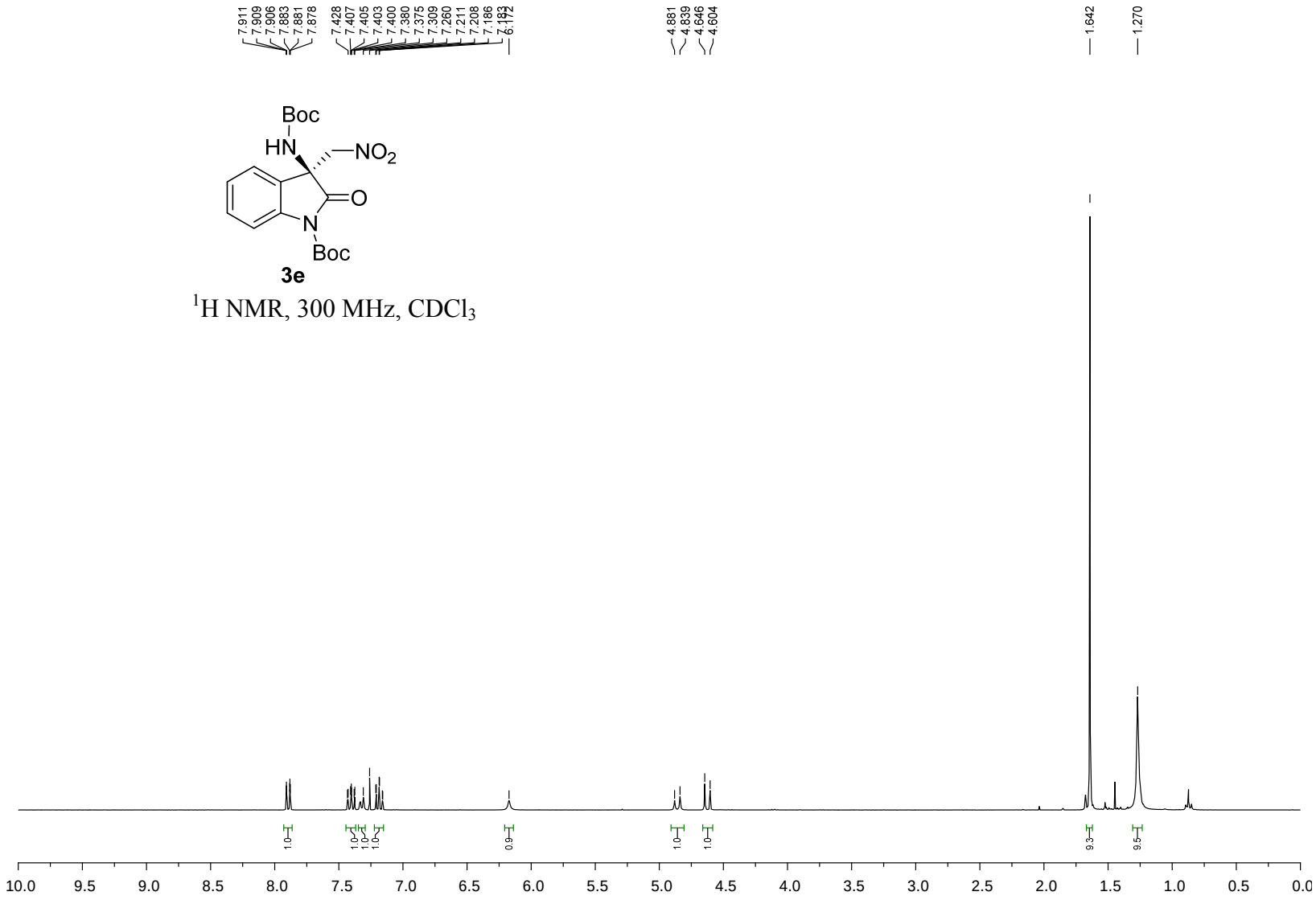
^{1}H NMR, 300 MHz, $CDCl_3$


172.90
153.75
142.46
135.03
130.28
128.88
127.85
127.34
125.82
124.46
123.44
109.94
81.26
77.76
77.42
77.00
76.58
59.88
44.52
28.09
Boc
HN
NO2
O
N
Bn
3c
13C NMR, 75 MHz, CDCl3
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



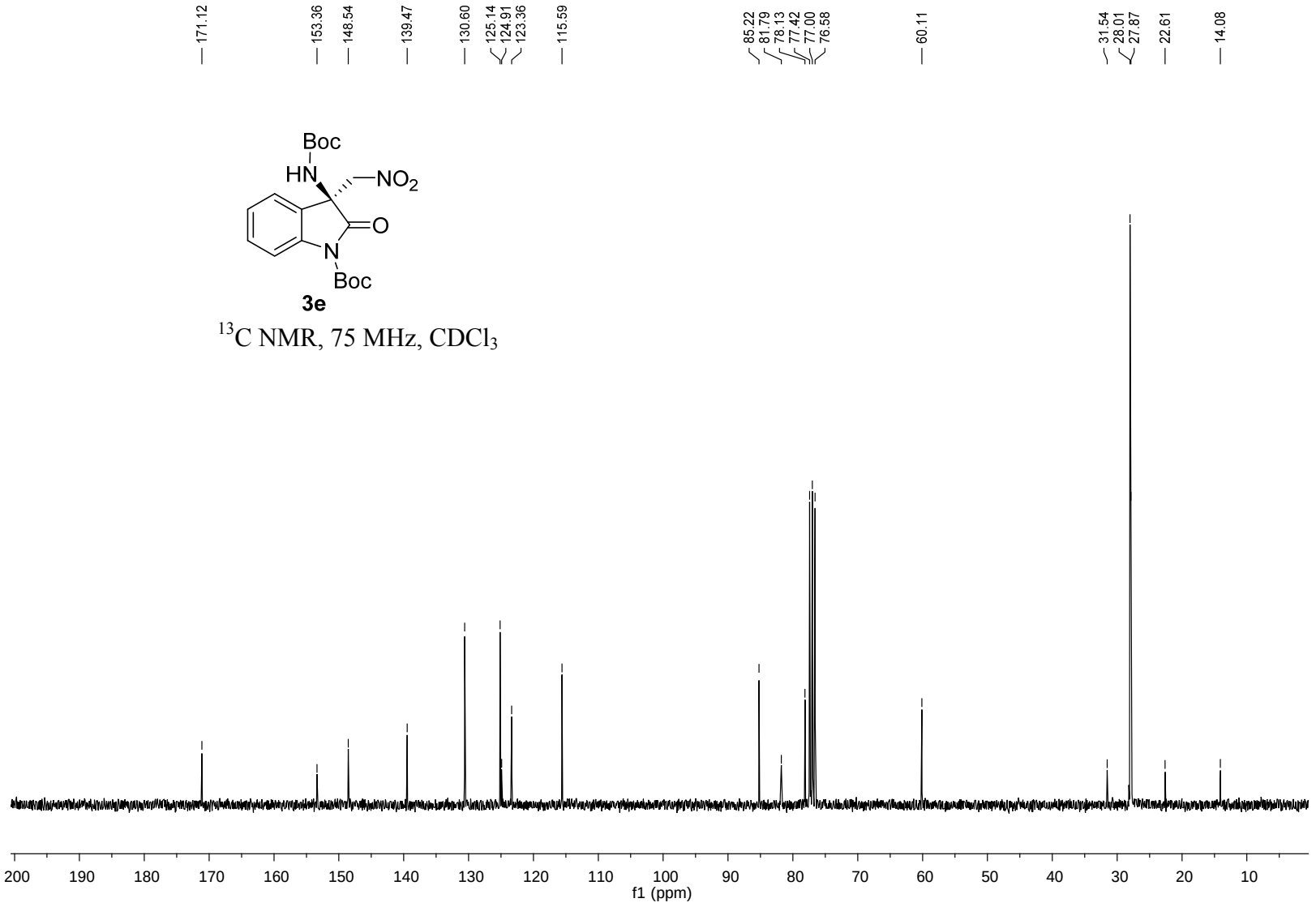
^{1}H NMR, 300 MHz, $CDCl_3$


173.40
153.65
141.69
130.54
125.37
124.25
123.90
110.40
81.35
77.91
77.42
77.00
76.58
72.08
60.14
56.73
28.07
Boc
HN
NO2
O
N
MOM
3d
13C NMR, 75 MHz, CDCl3
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

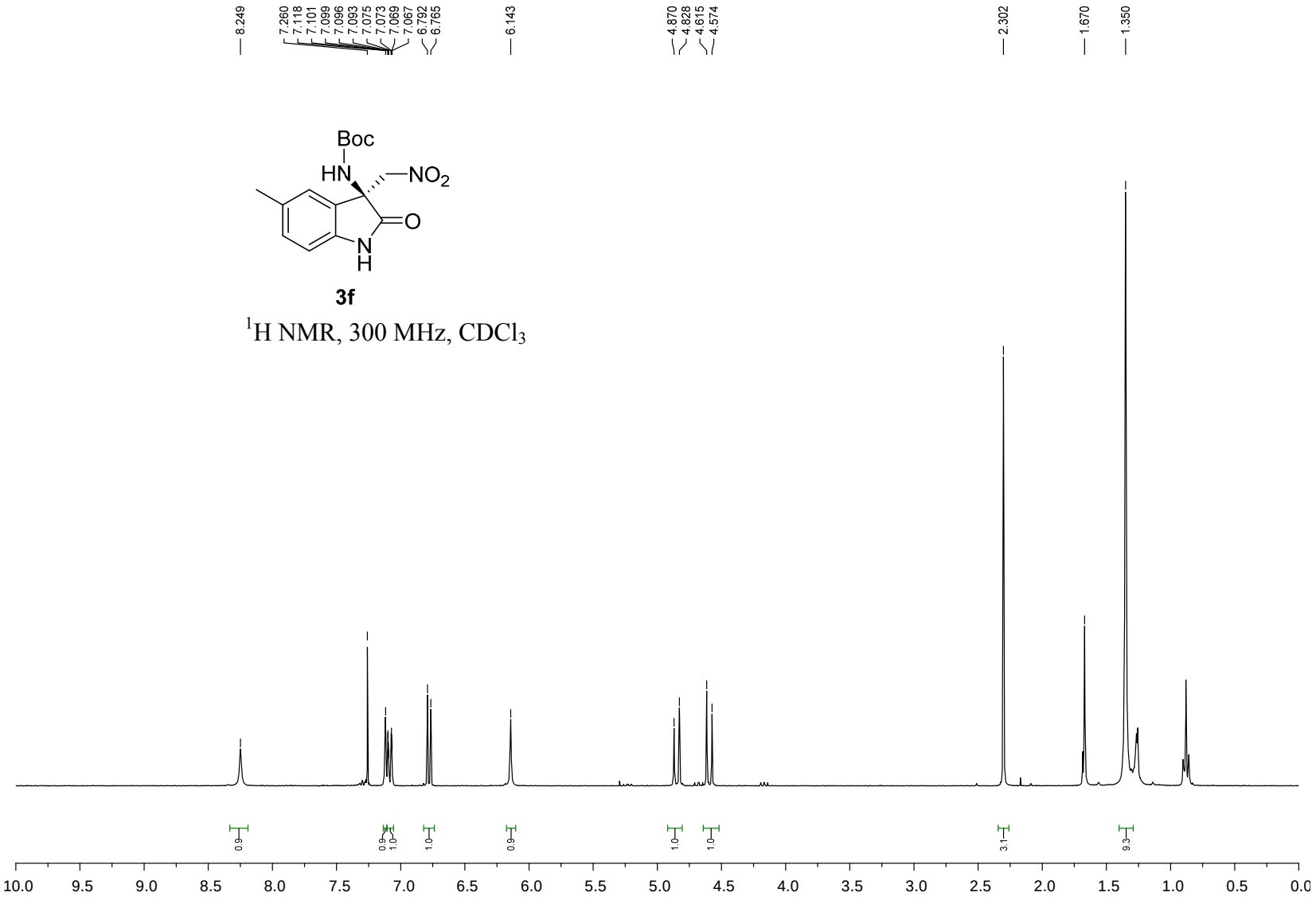


3e

^{1}H NMR, 300 MHz, $CDCl_3$

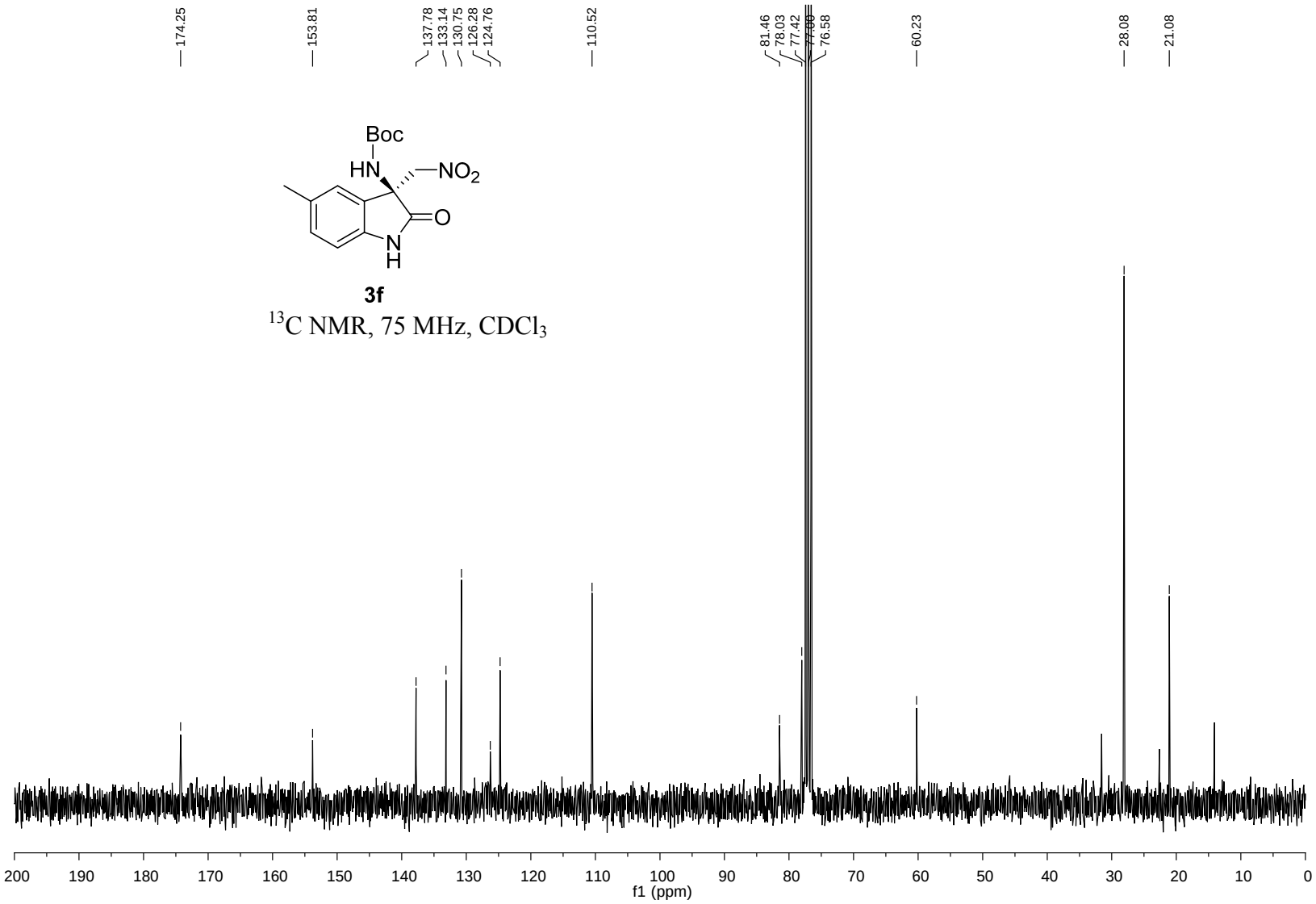


^{13}C NMR, 75 MHz, $CDCl_3$



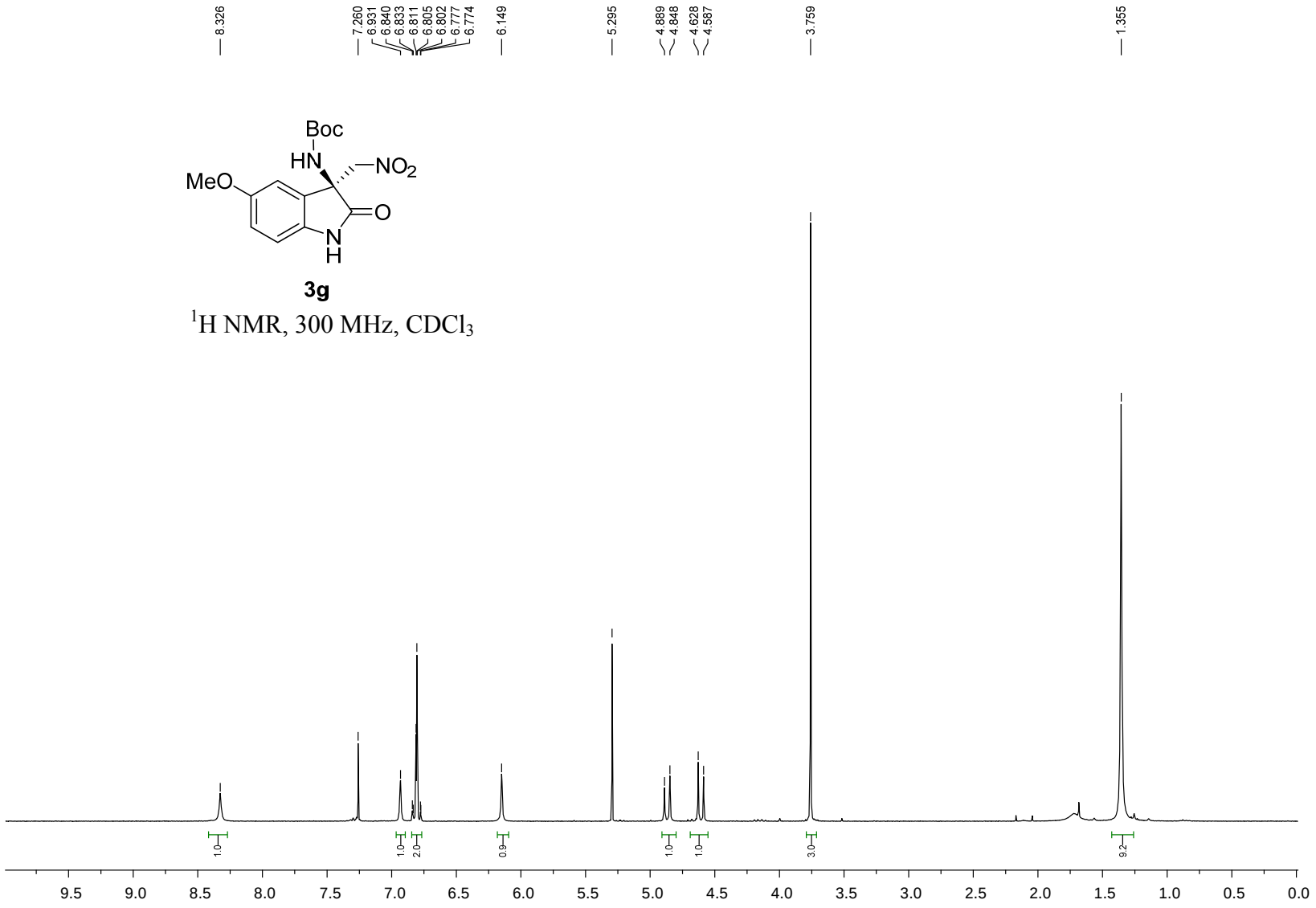
3f

^{1}H NMR, 300 MHz, $CDCl_3$



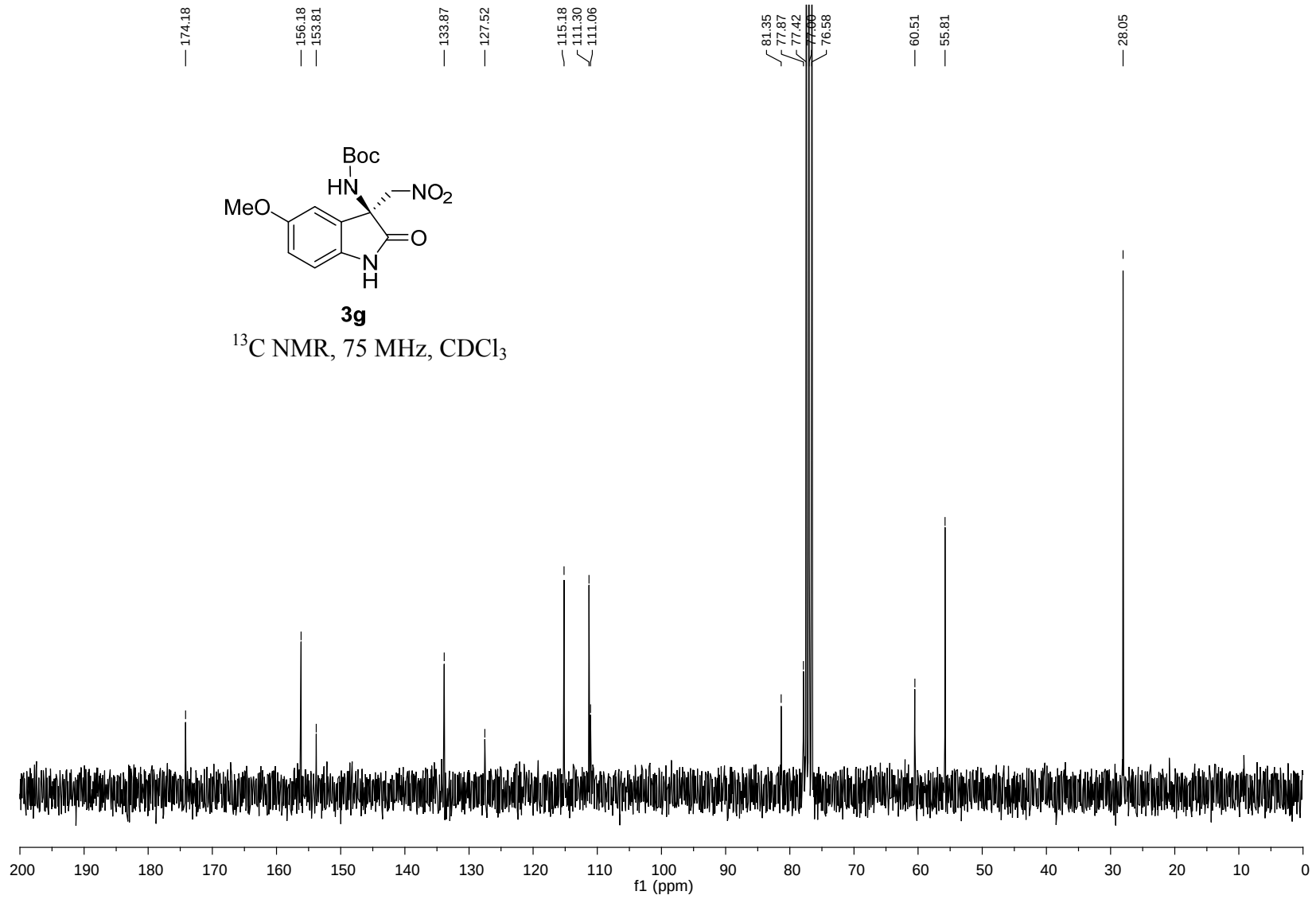
3f

^{13}C NMR, 75 MHz, $CDCl_3$



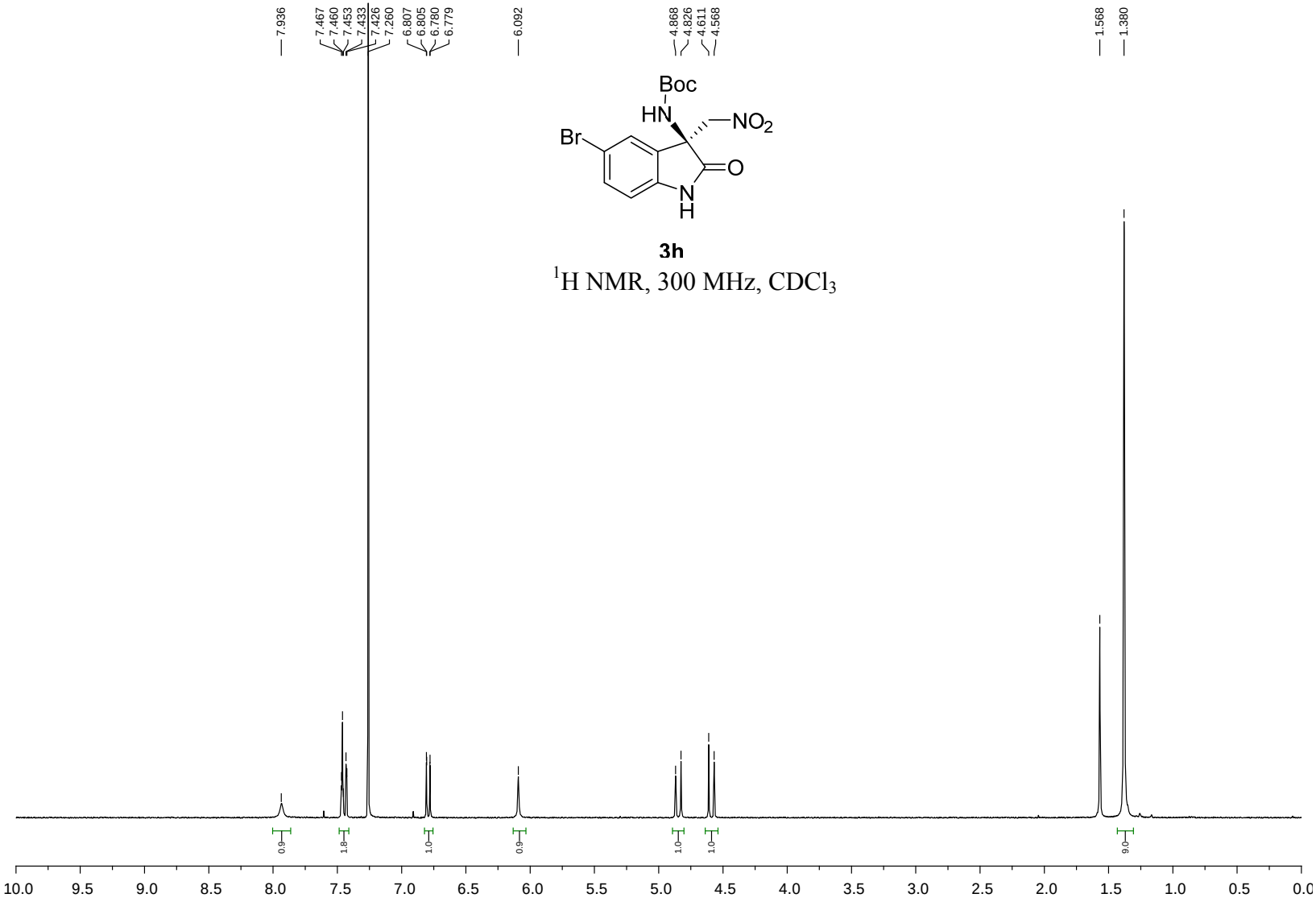
3g

^{1}H NMR, 300 MHz, $CDCl_3$



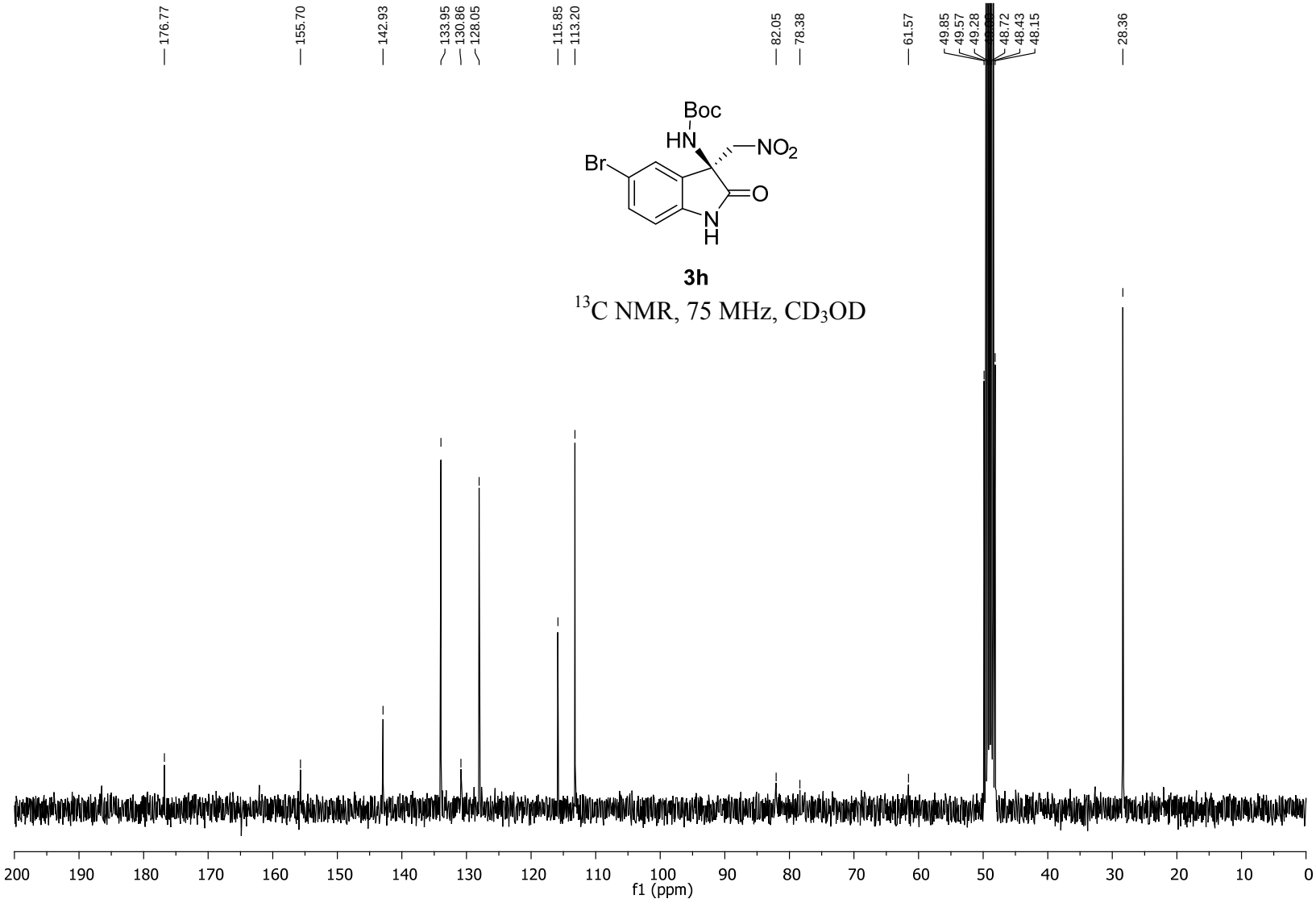
3g

^{13}C NMR, 75 MHz, $CDCl_3$



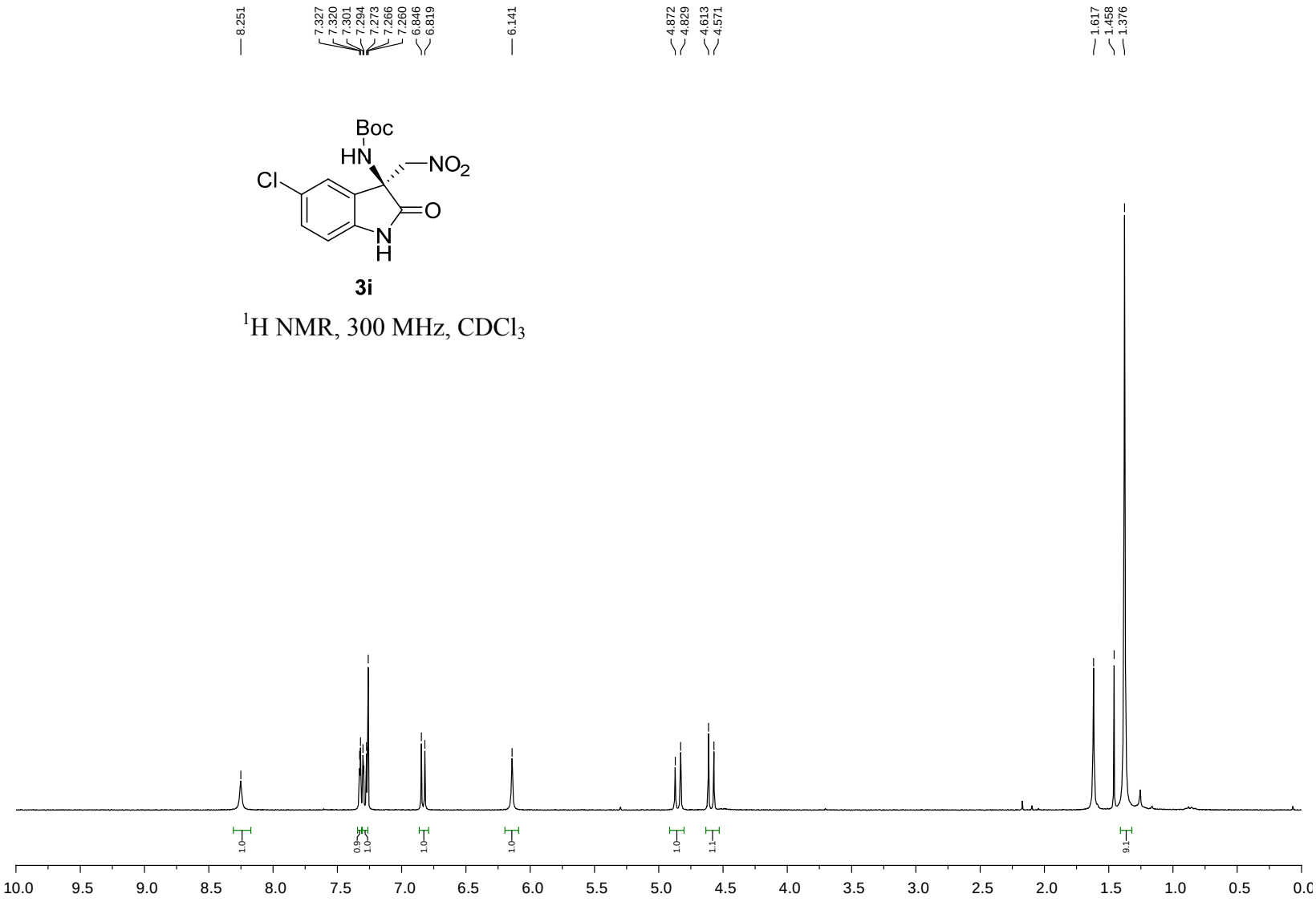
3h

^{1}H NMR, 300 MHz, $CDCl_3$



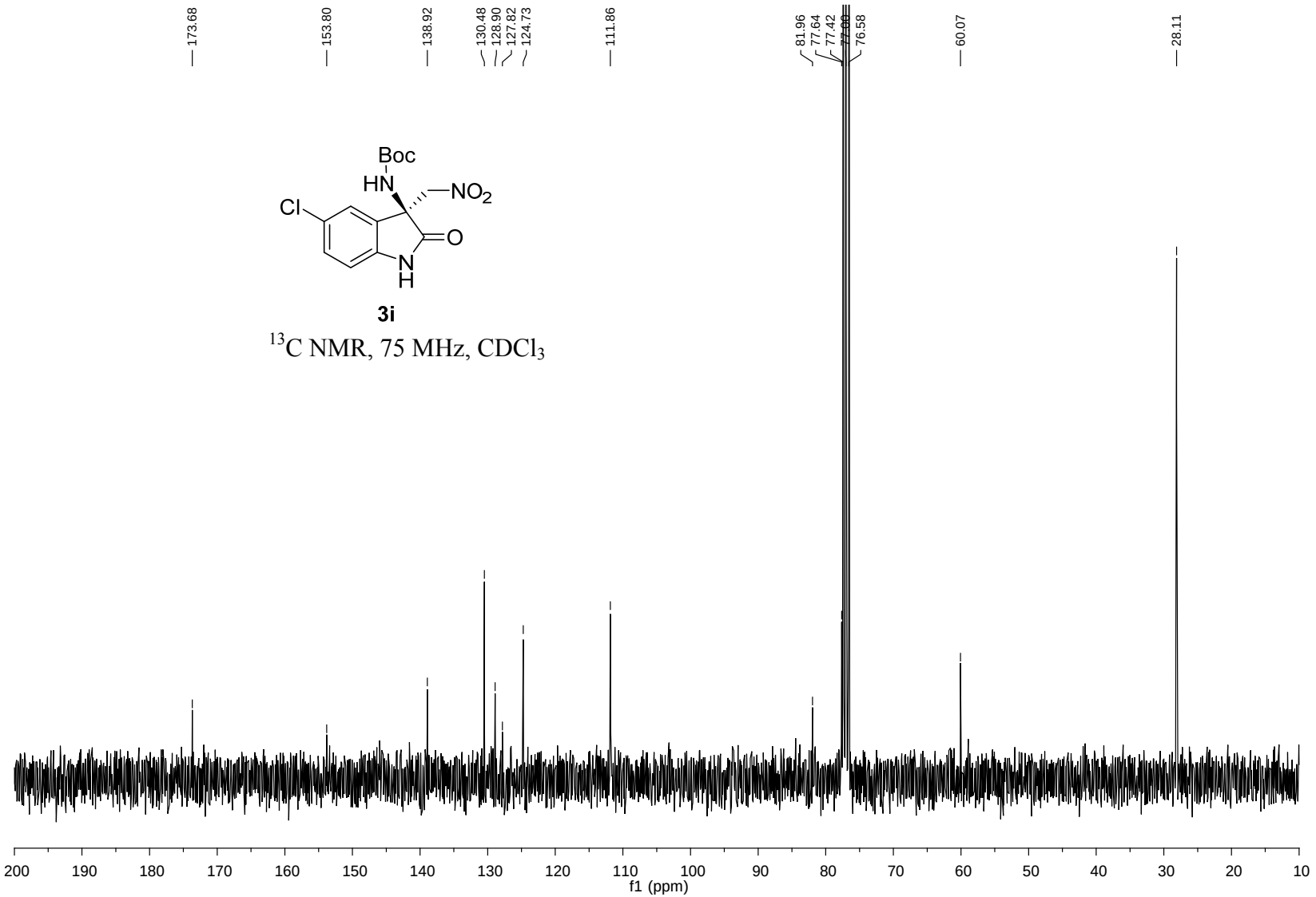
3h

^{13}C NMR, 75 MHz, CD_3OD



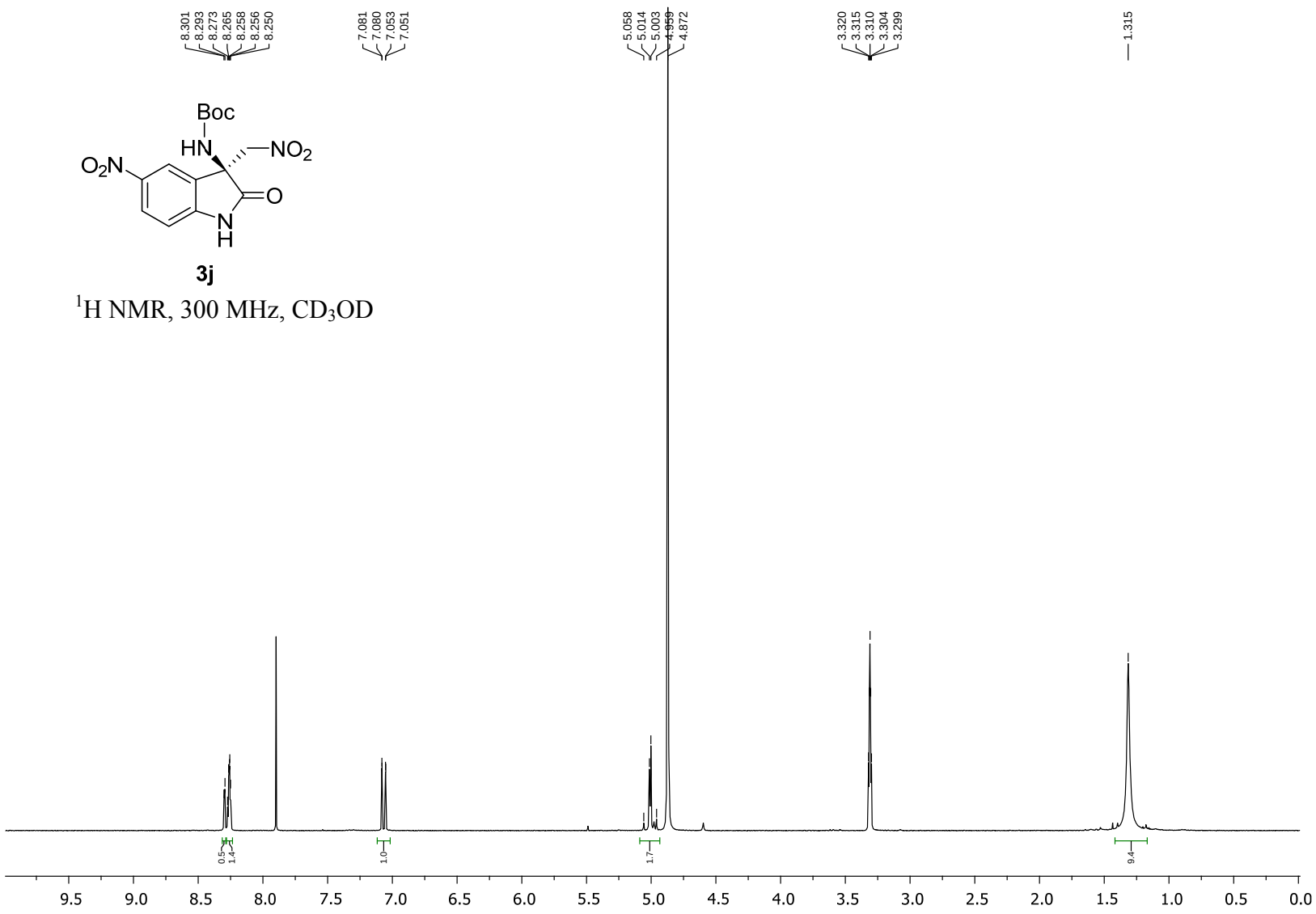
3i

^{1}H NMR, 300 MHz, $CDCl_3$



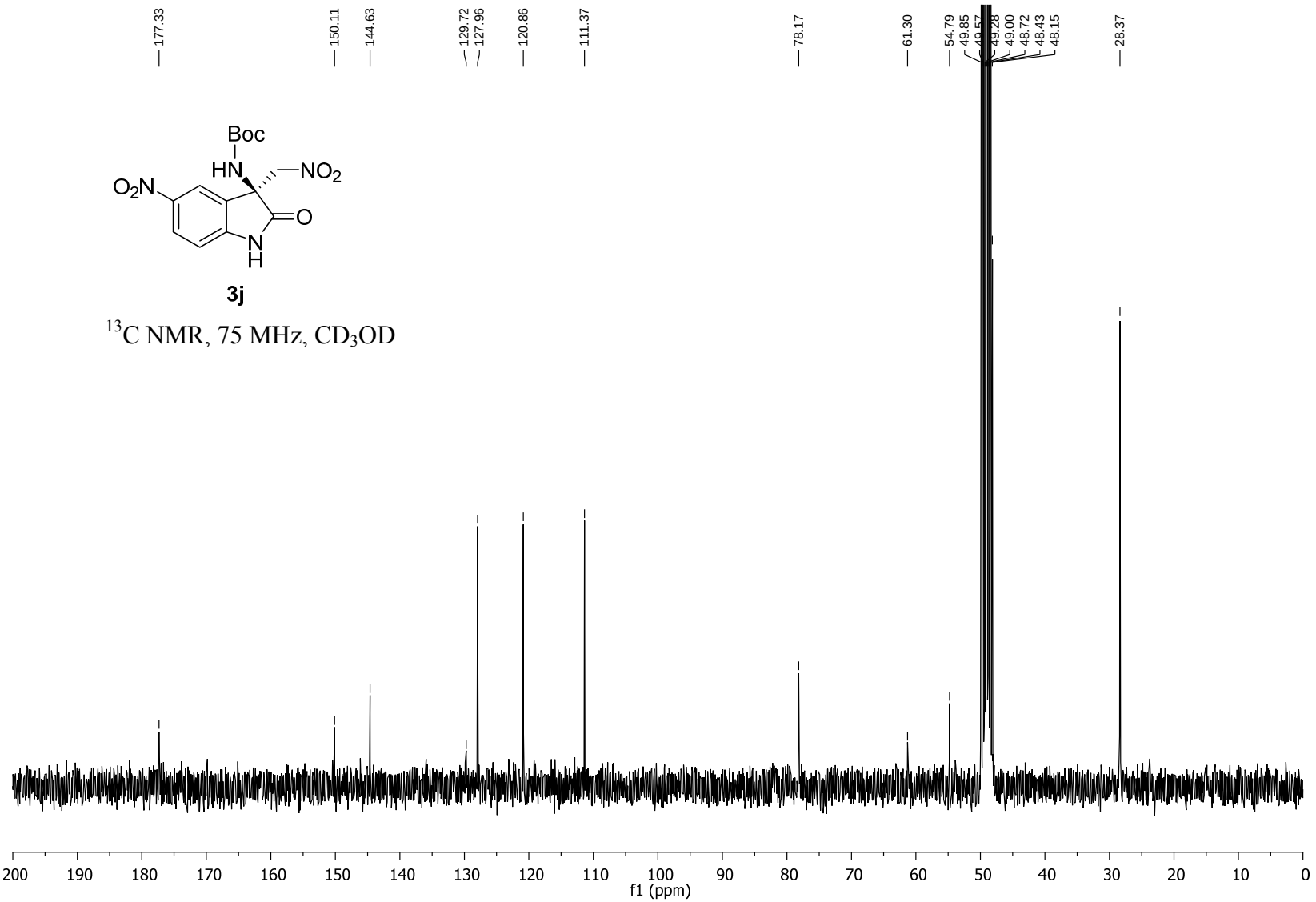
3i

^{13}C NMR, 75 MHz, $CDCl_3$



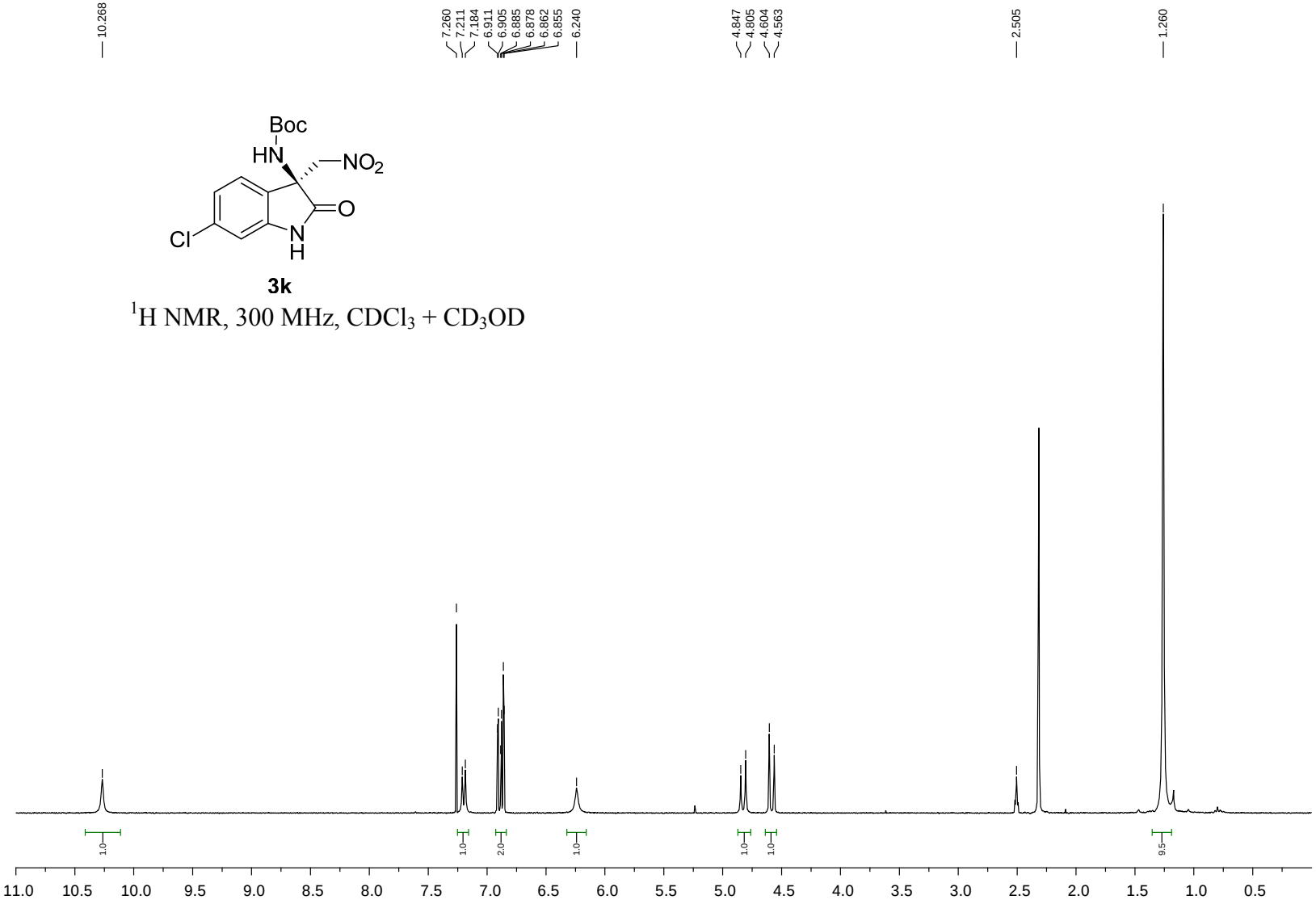
3j

^{1}H NMR, 300 MHz, CD_3OD



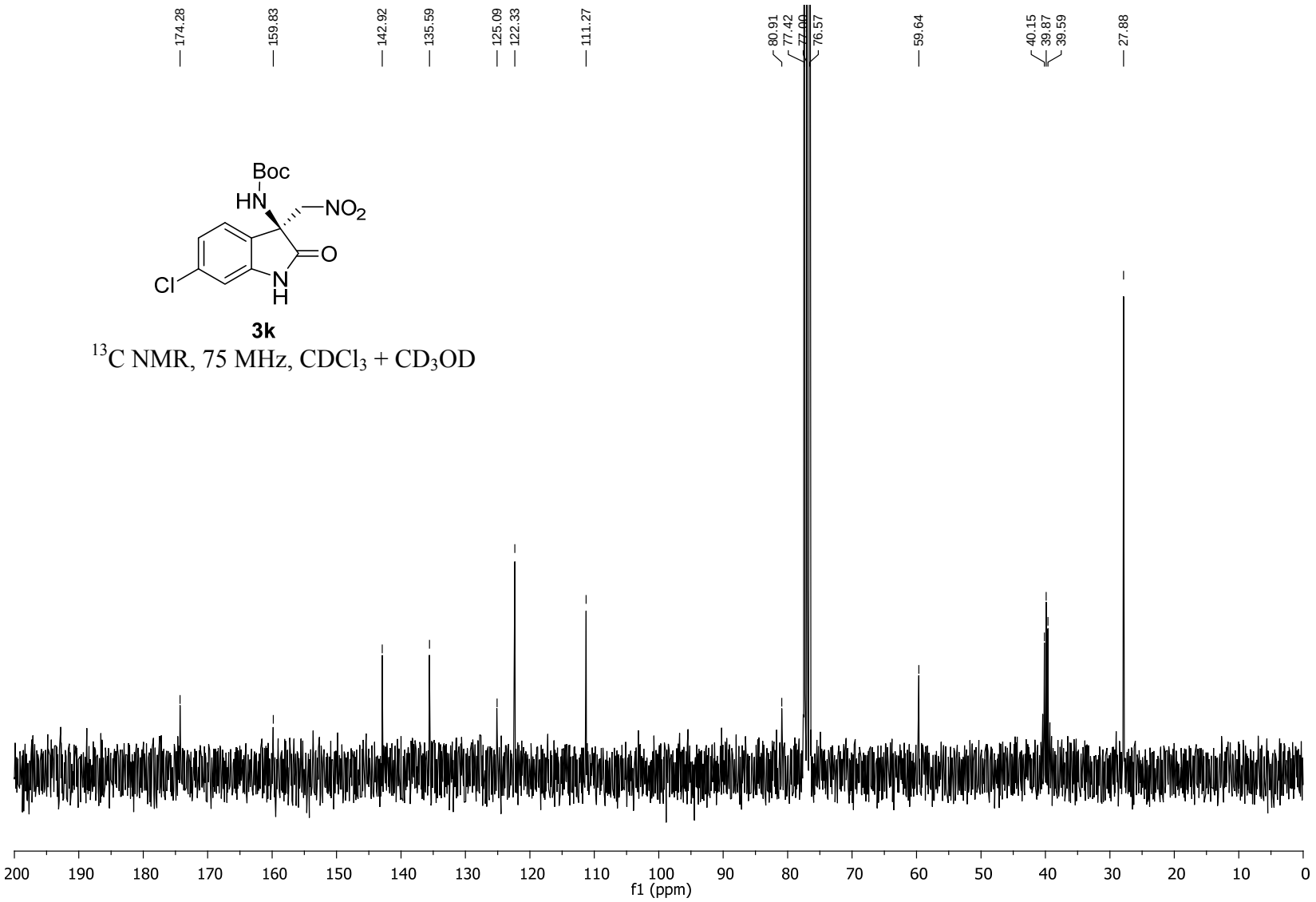
3j

^{13}C NMR, 75 MHz, CD_3OD



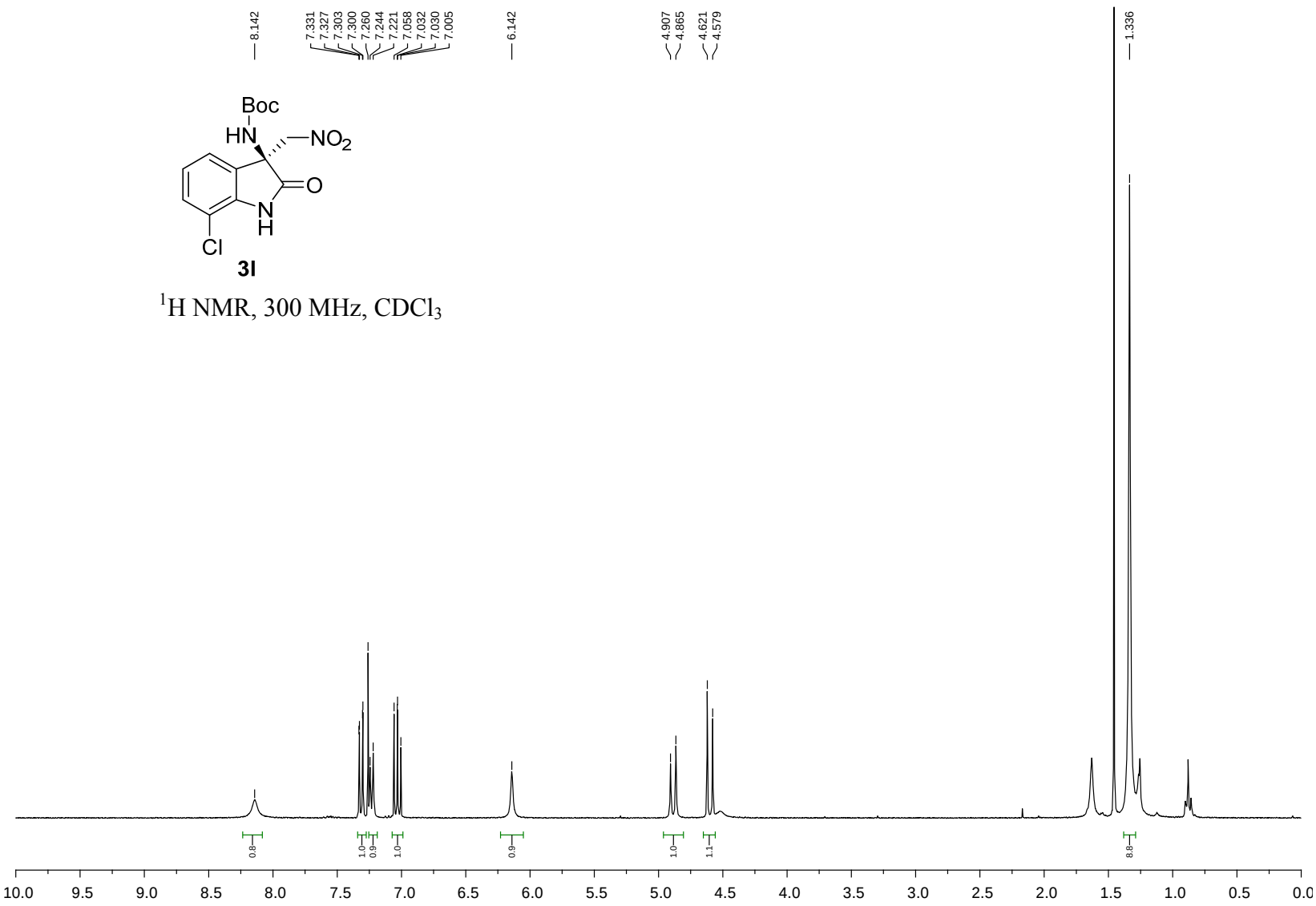
3k

^{1}H NMR, 300 MHz, $CDCl_3$ + CD_3OD

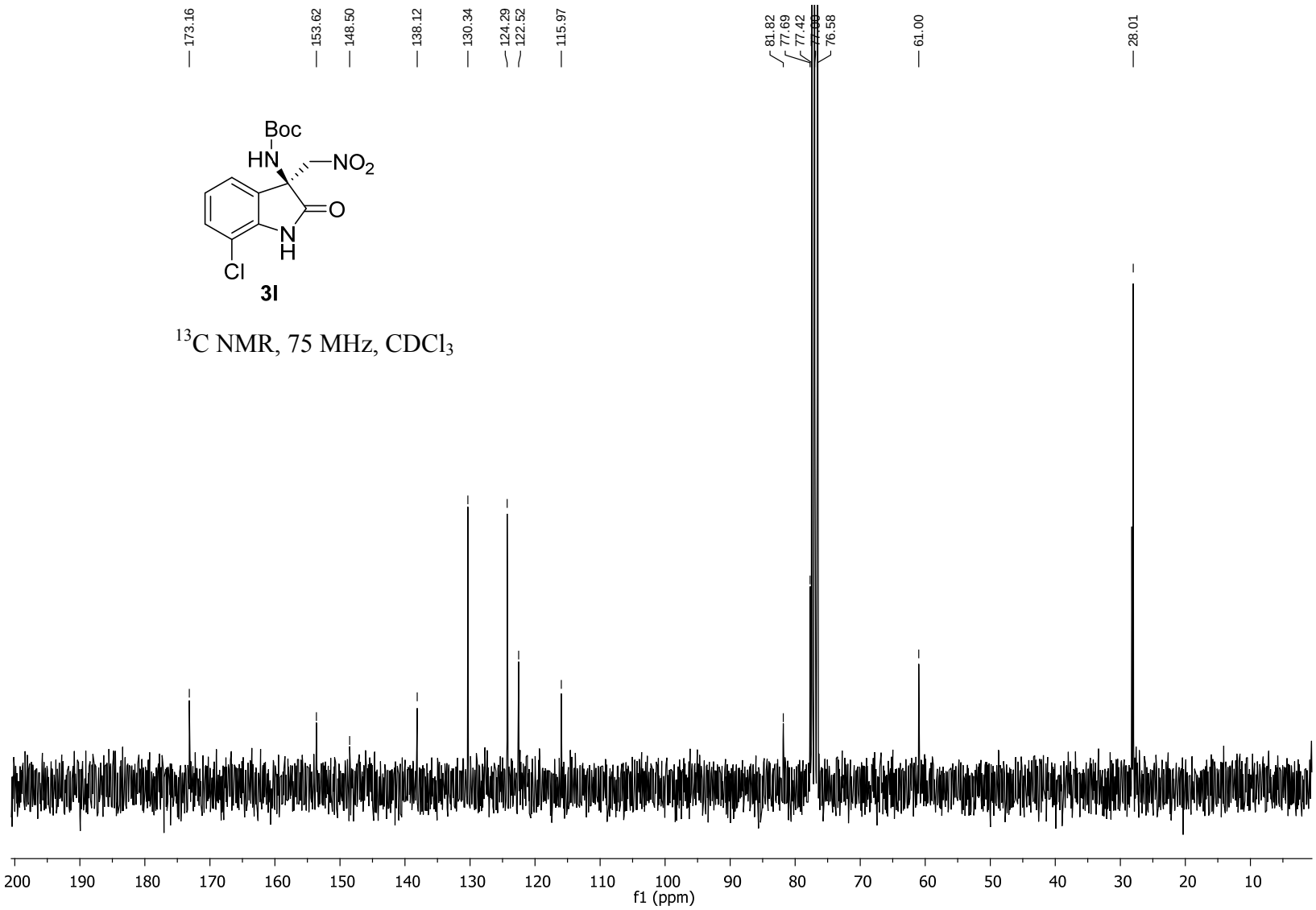


3k

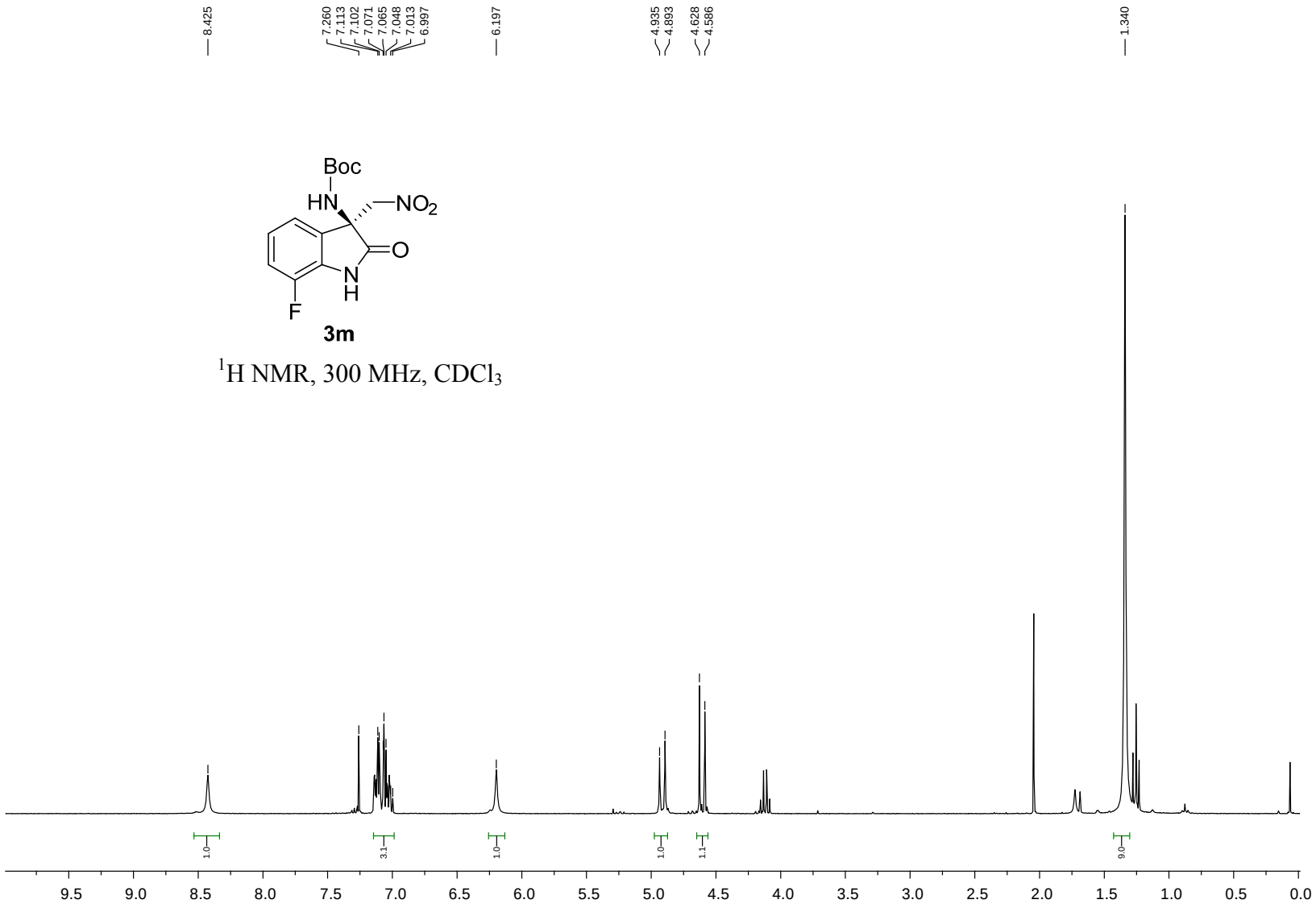
^{13}C NMR, 75 MHz, $CDCl_3$ + CD_3OD



^{1}H NMR, 300 MHz, $CDCl_3$

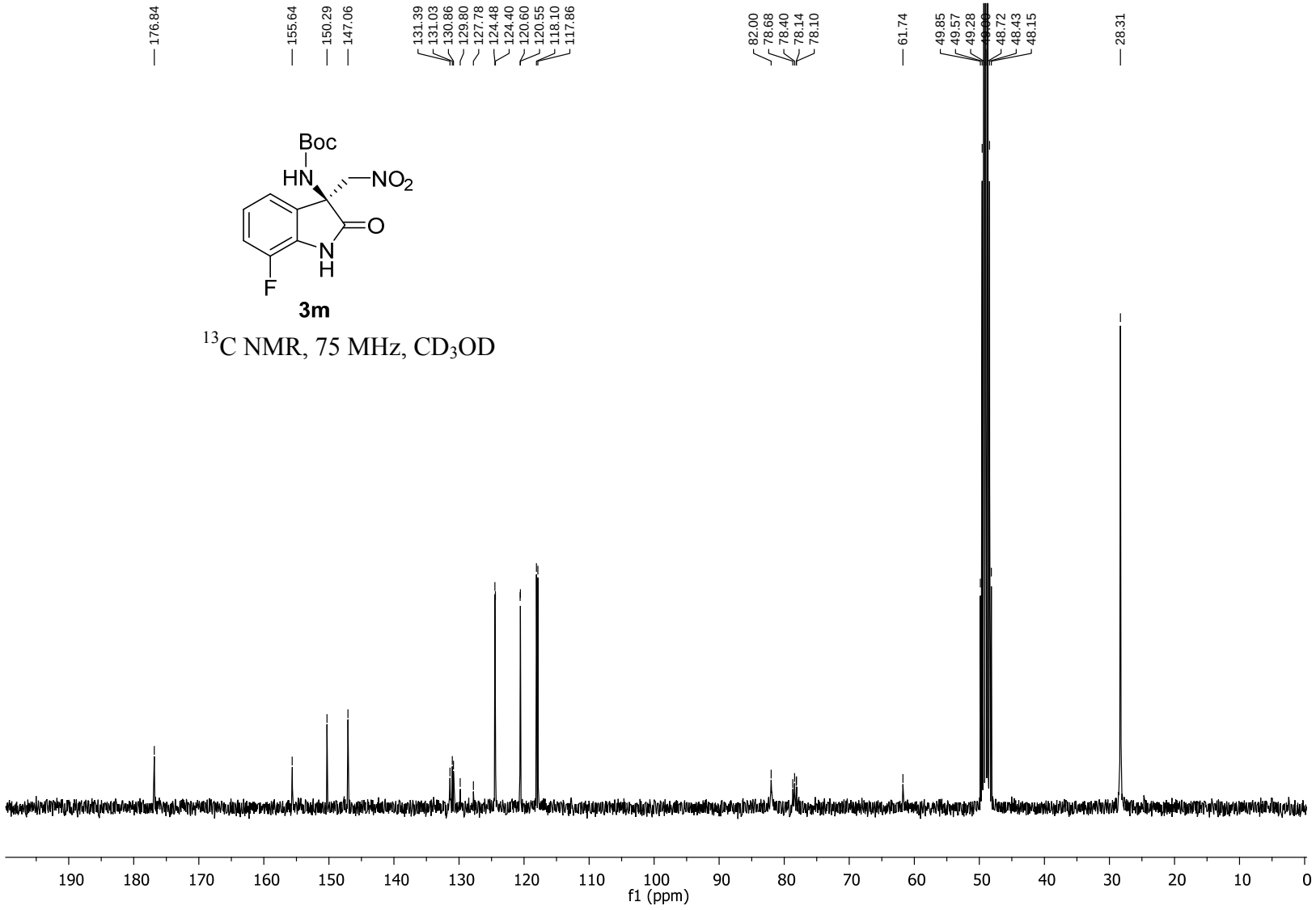


^{13}C NMR, 75 MHz, $CDCl_3$



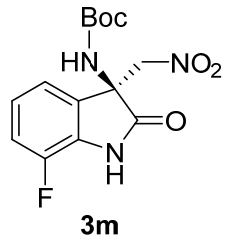
3m

^{1}H NMR, 300 MHz, $CDCl_3$



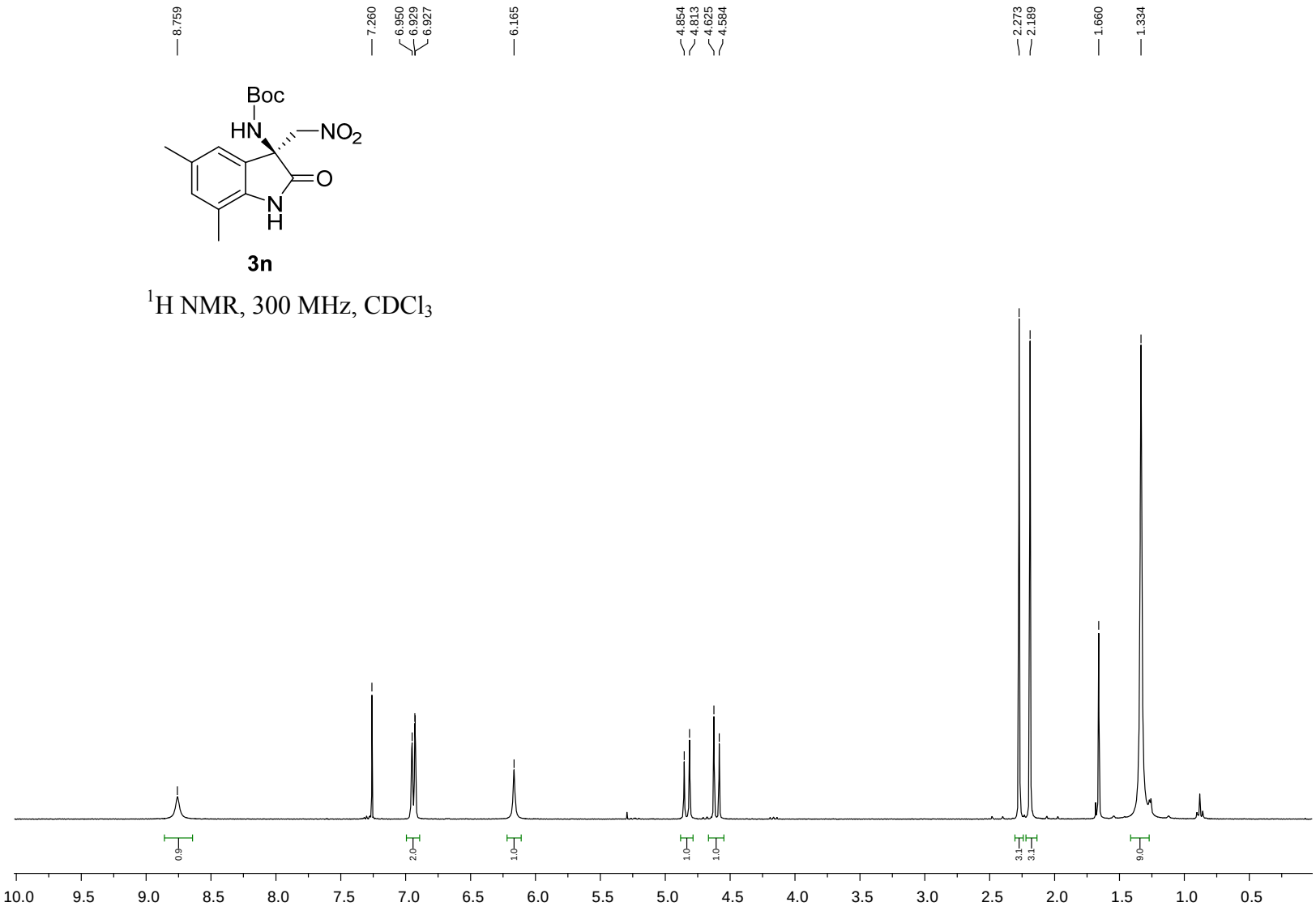
3m

^{13}C NMR, 75 MHz, CD_3OD



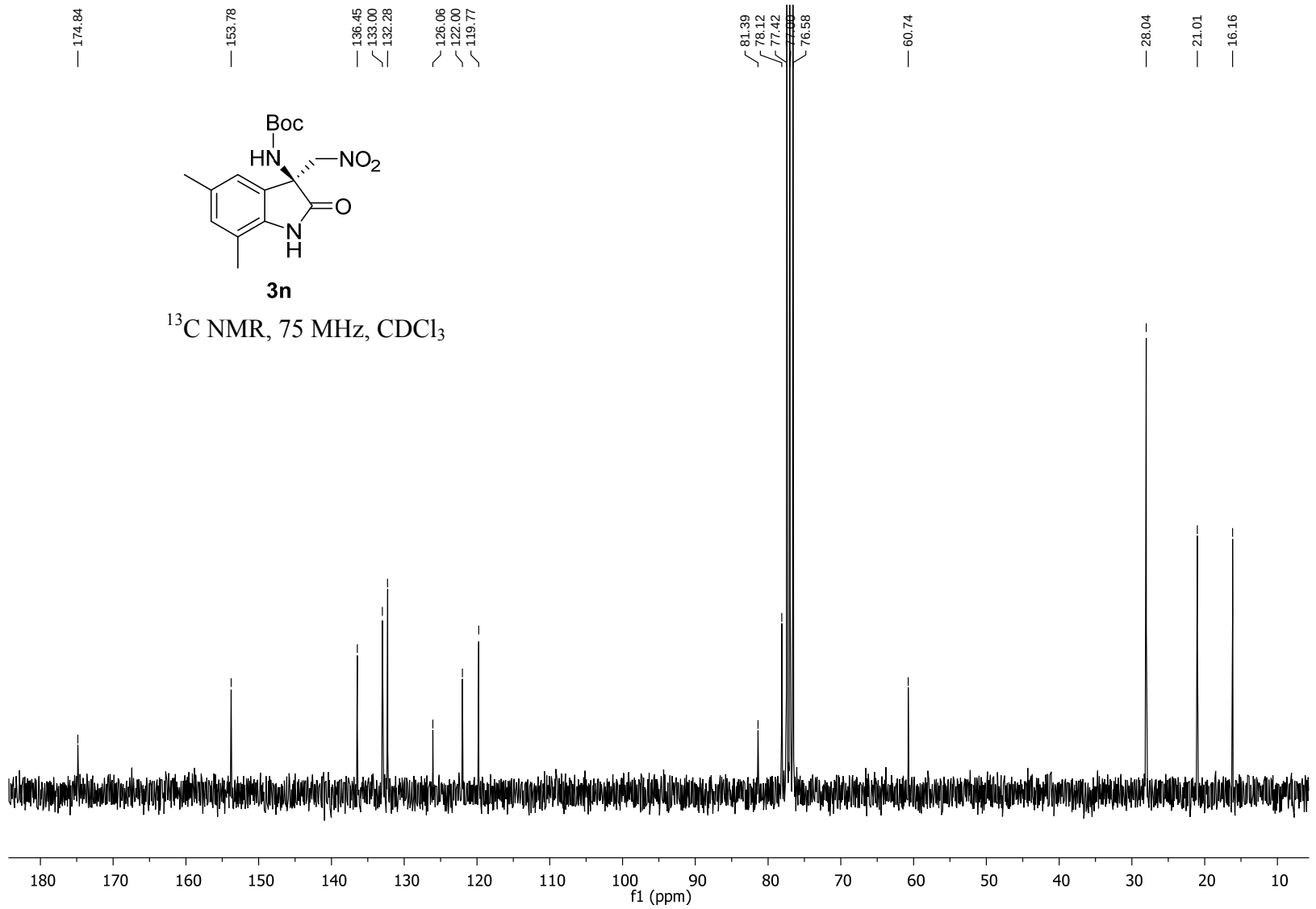
3m

^{19}F NMR, 282 MHz, CD_3OD



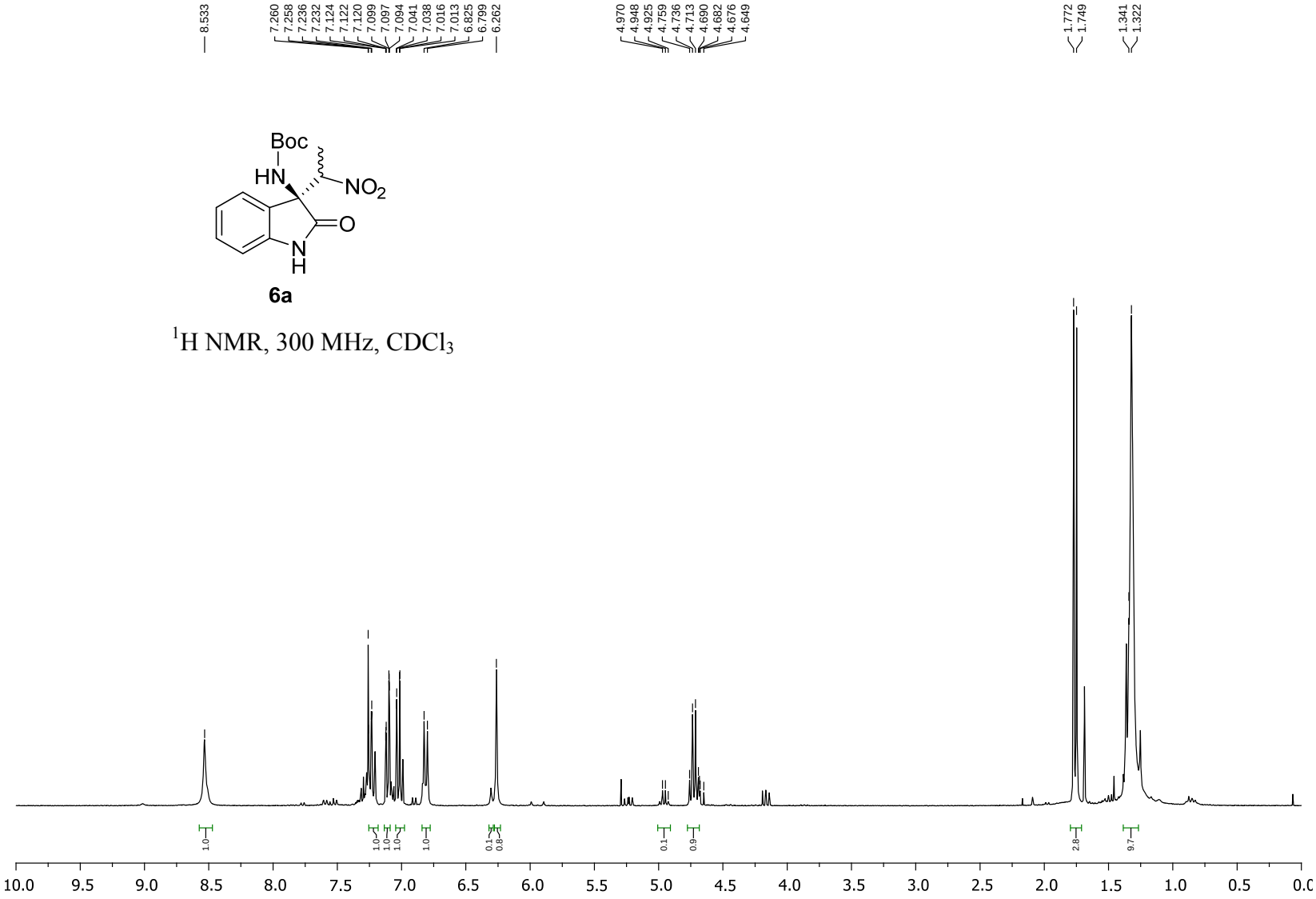
3n

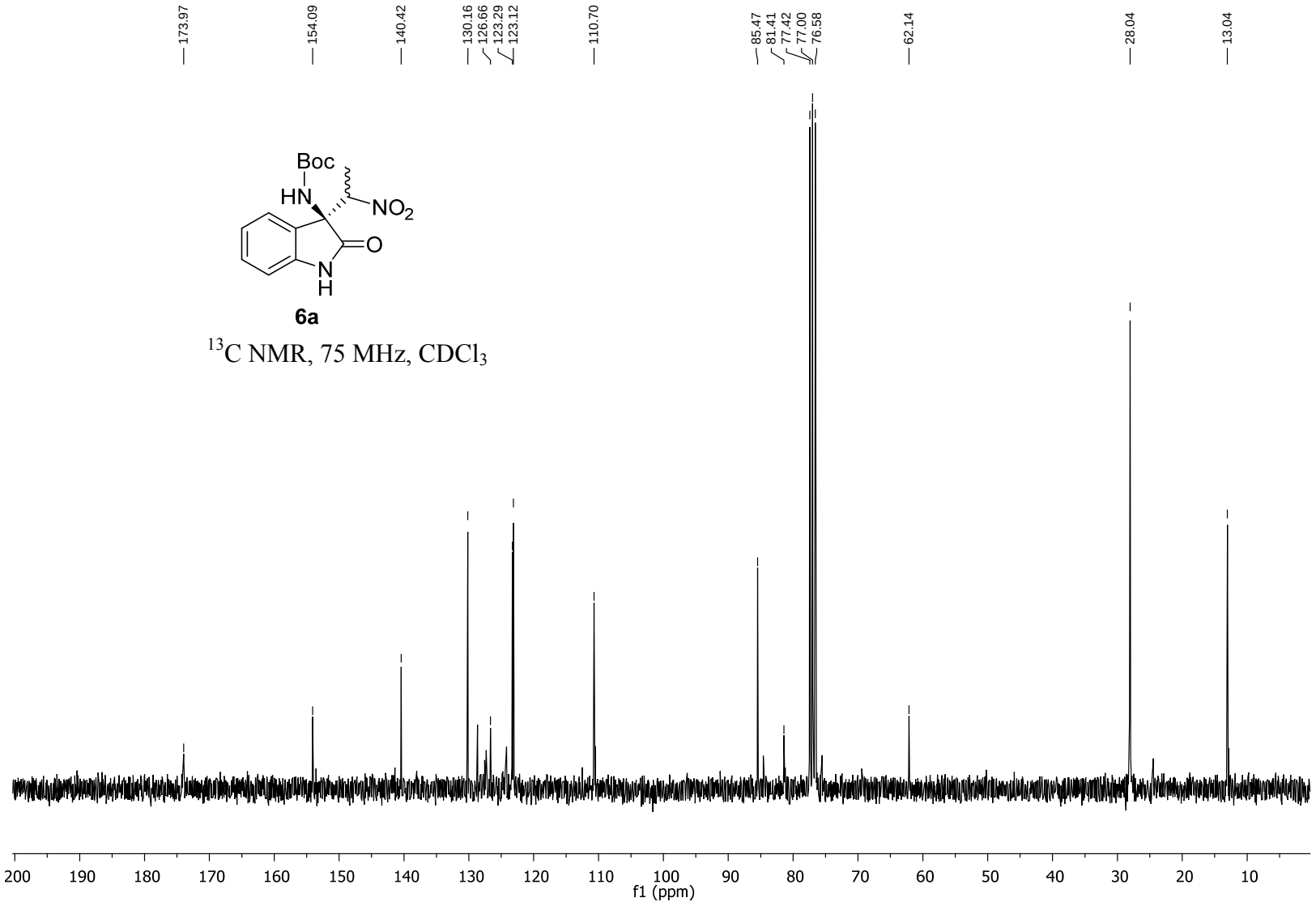
^{1}H NMR, 300 MHz, $CDCl_3$

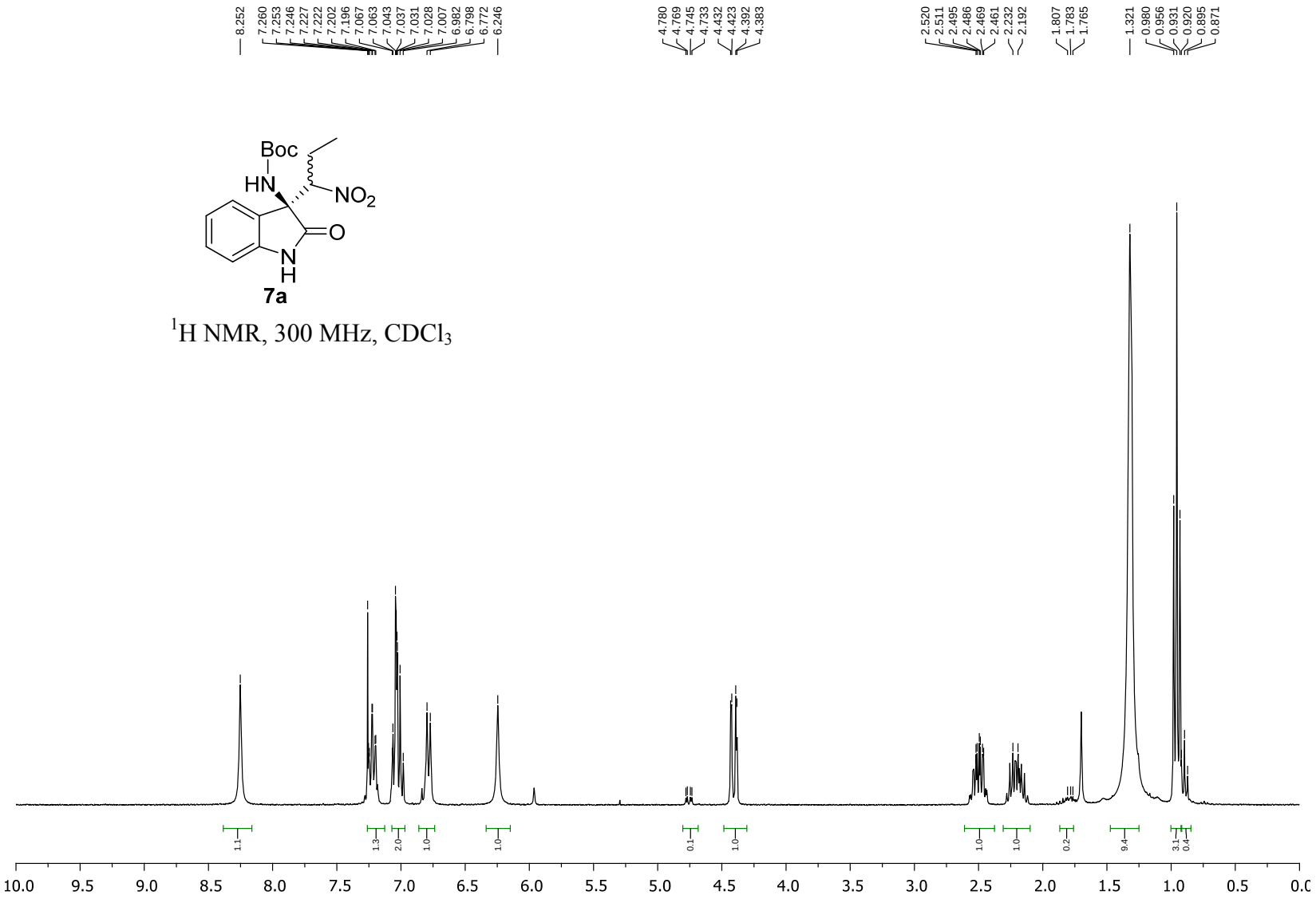


3n

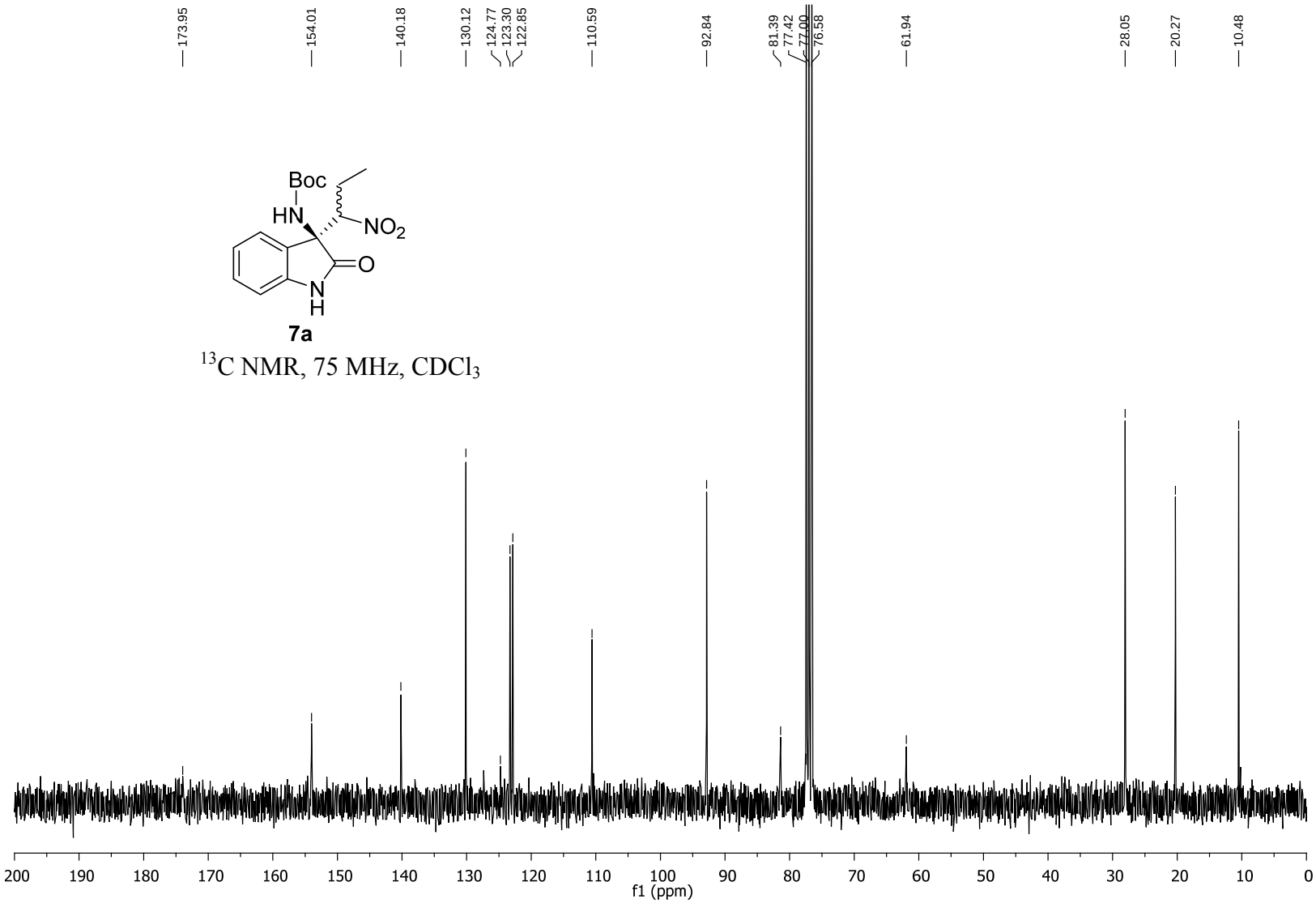
^{13}C NMR, 75 MHz, $CDCl_3$


8.533
7.260
7.258
7.236
7.232
7.124
7.122
7.120
7.099
7.097
7.094
7.041
7.038
7.016
7.013
6.825
6.799
6.262
4.970
4.948
4.925
4.759
4.736
4.713
4.690
4.682
4.676
4.649
1.772
1.749
1.341
1.322
Boc
HN
NO2
O
N
H
6a
1H NMR, 300 MHz, CDCl3
1.0
1.0
1.0
1.0
1.0
0.1
0.8
0.1
0.9
2.8
9.7
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0


173.97
154.09
140.42
130.16
126.66
123.29
123.12
110.70
85.47
81.41
77.42
77.00
76.58
62.14
28.04
13.04
Boc
HN
NO2
O
N
H
6a
13C NMR, 75 MHz, CDCl3
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

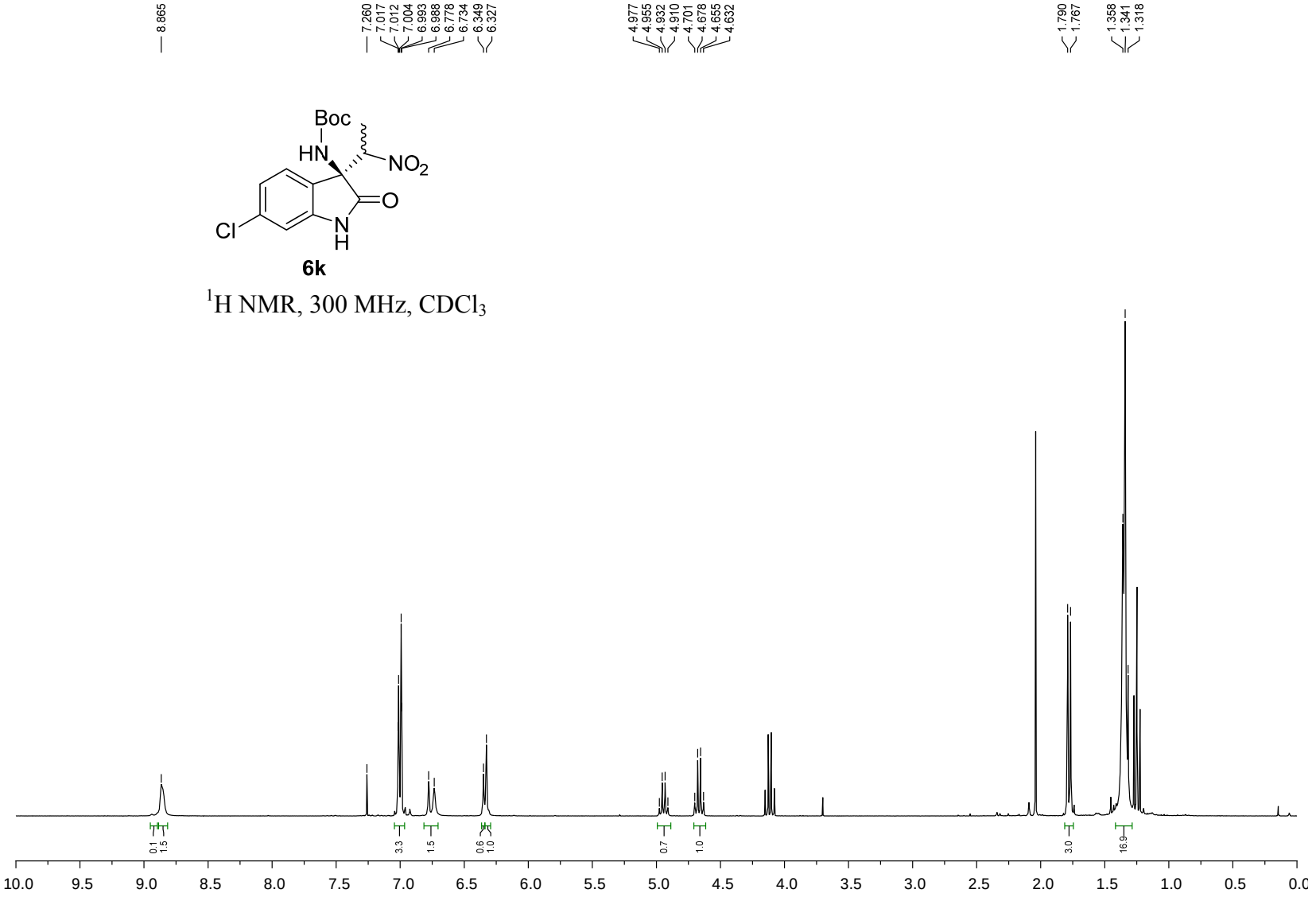


^{1}H NMR, 300 MHz, $CDCl_3$



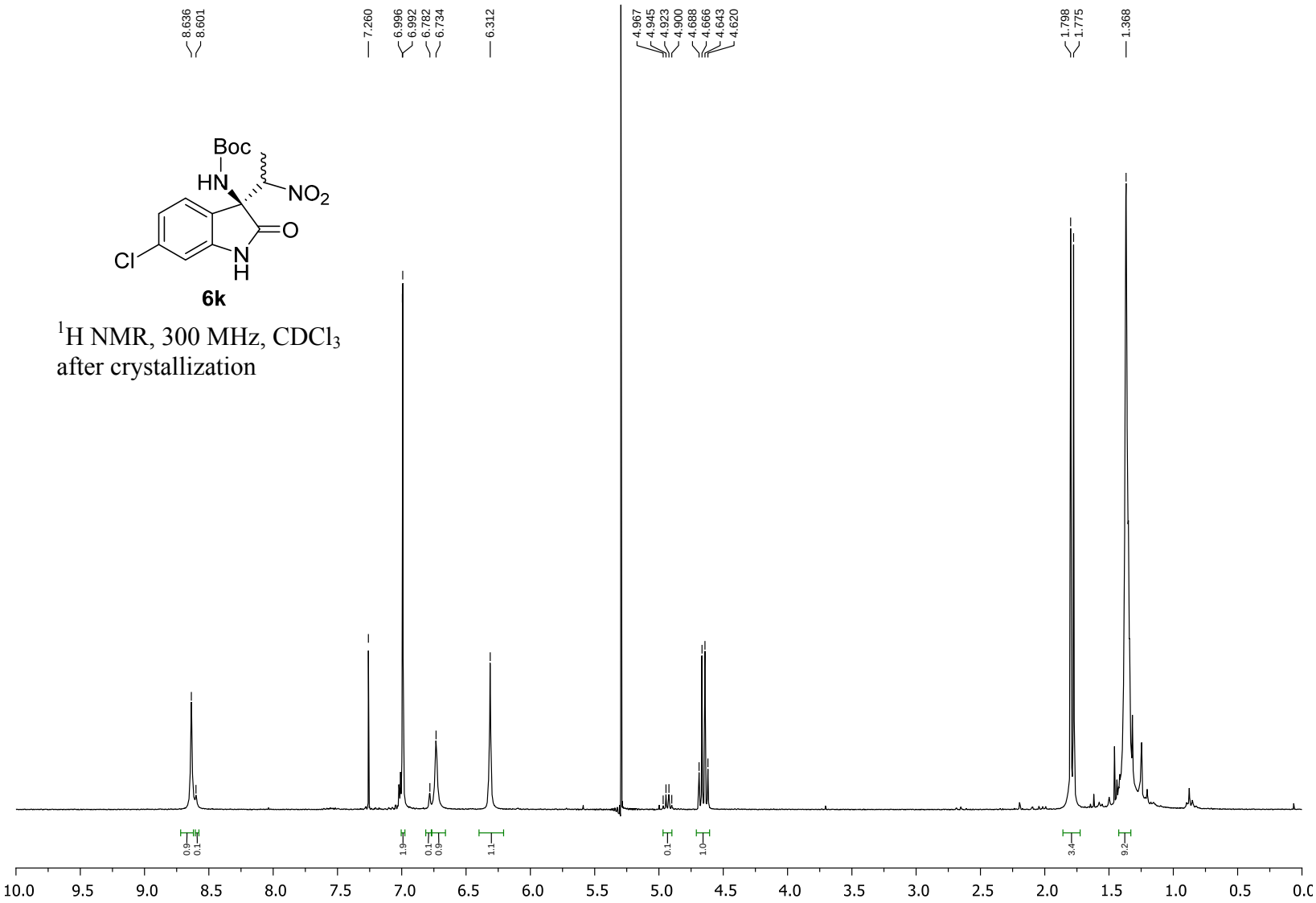
7a

^{13}C NMR, 75 MHz, $CDCl_3$

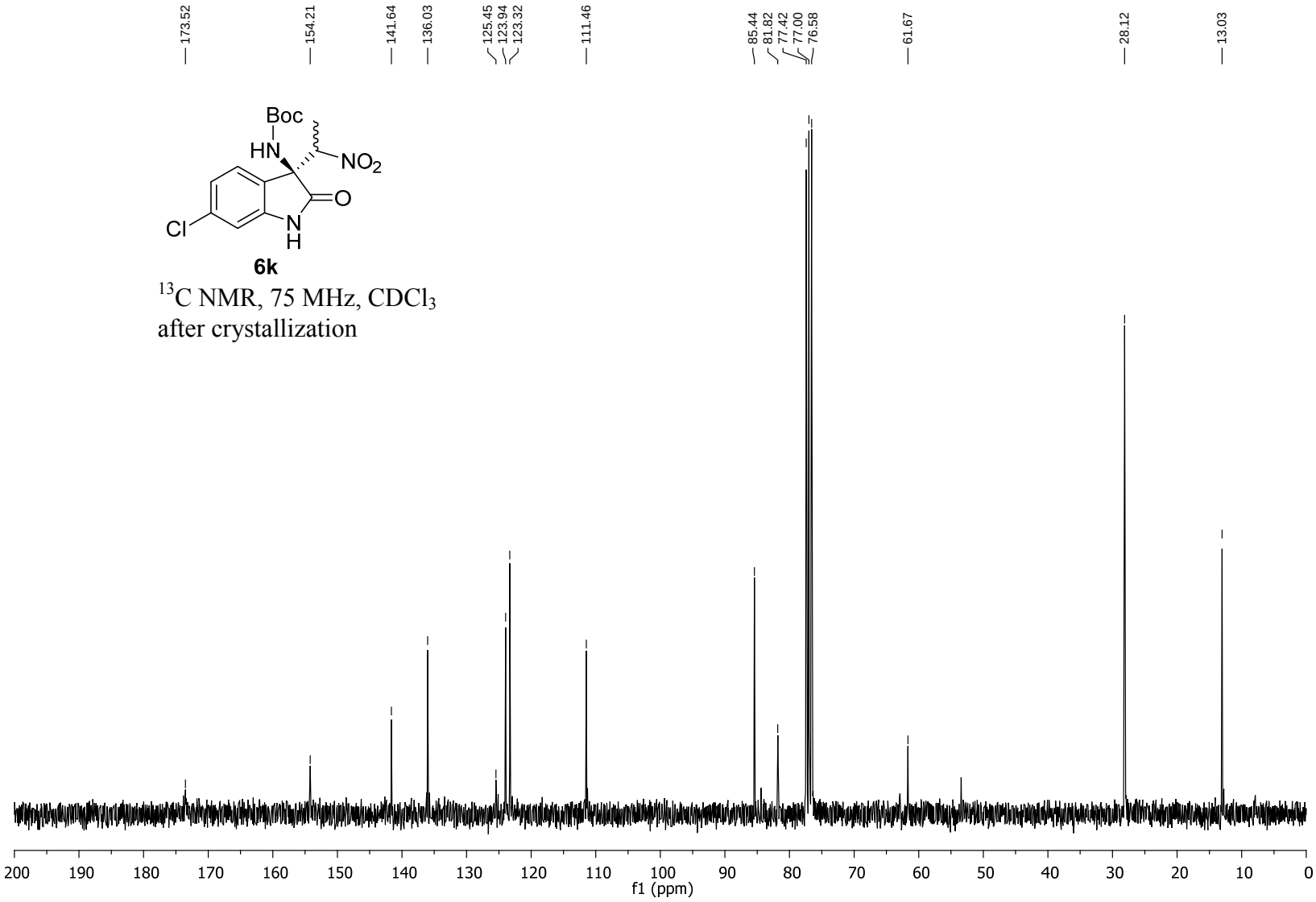


6k

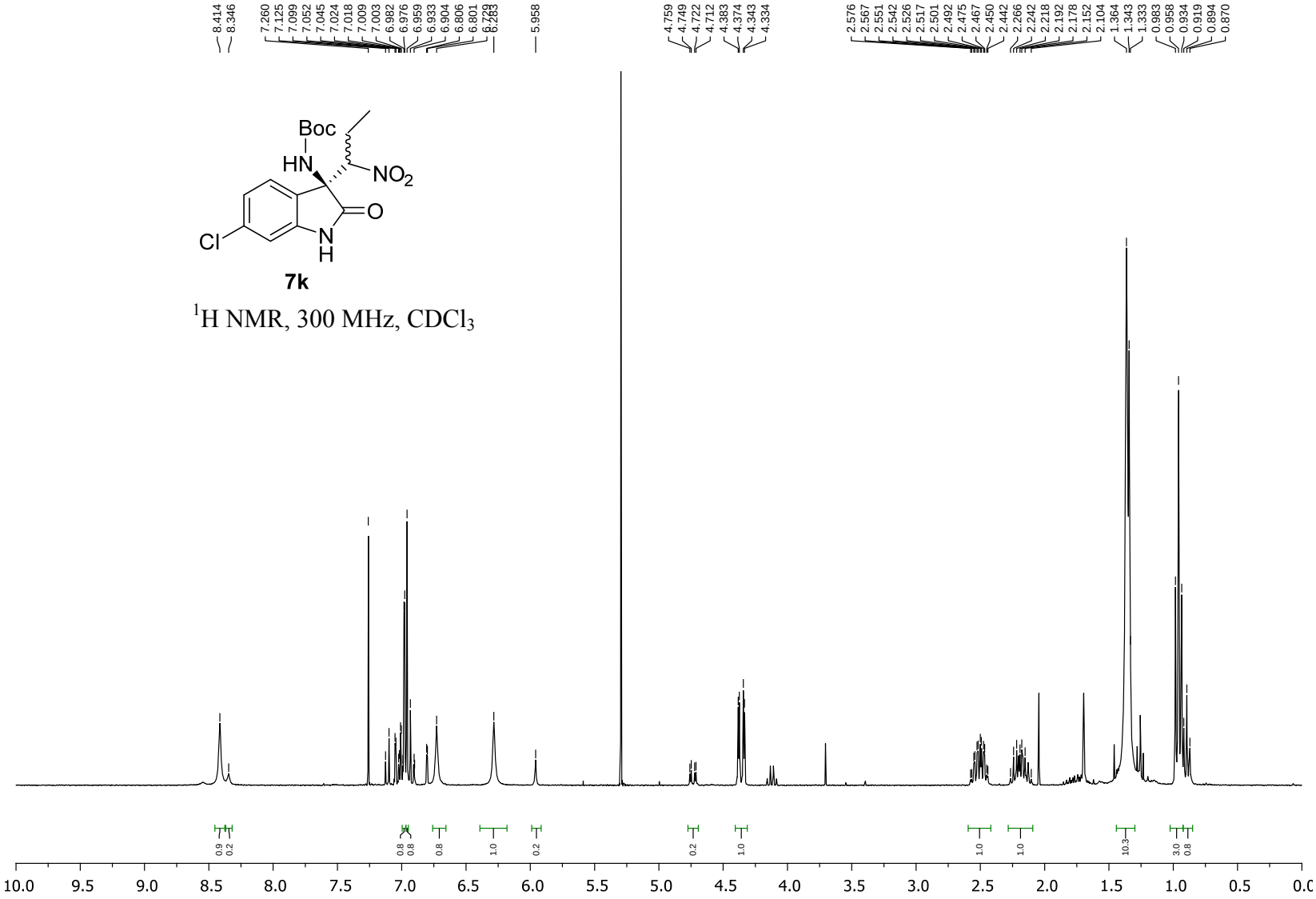
^{1}H NMR, 300 MHz, $CDCl_3$

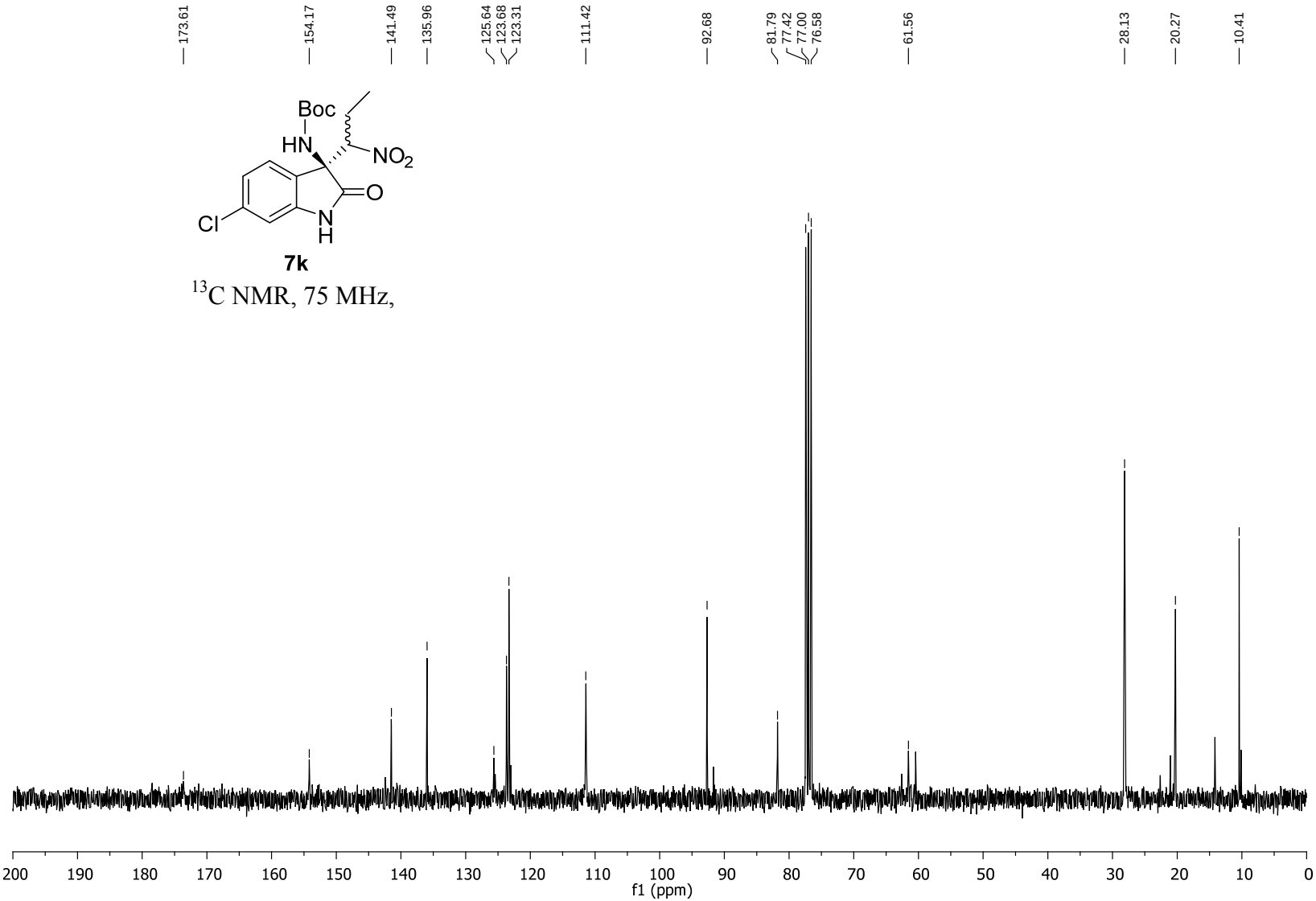


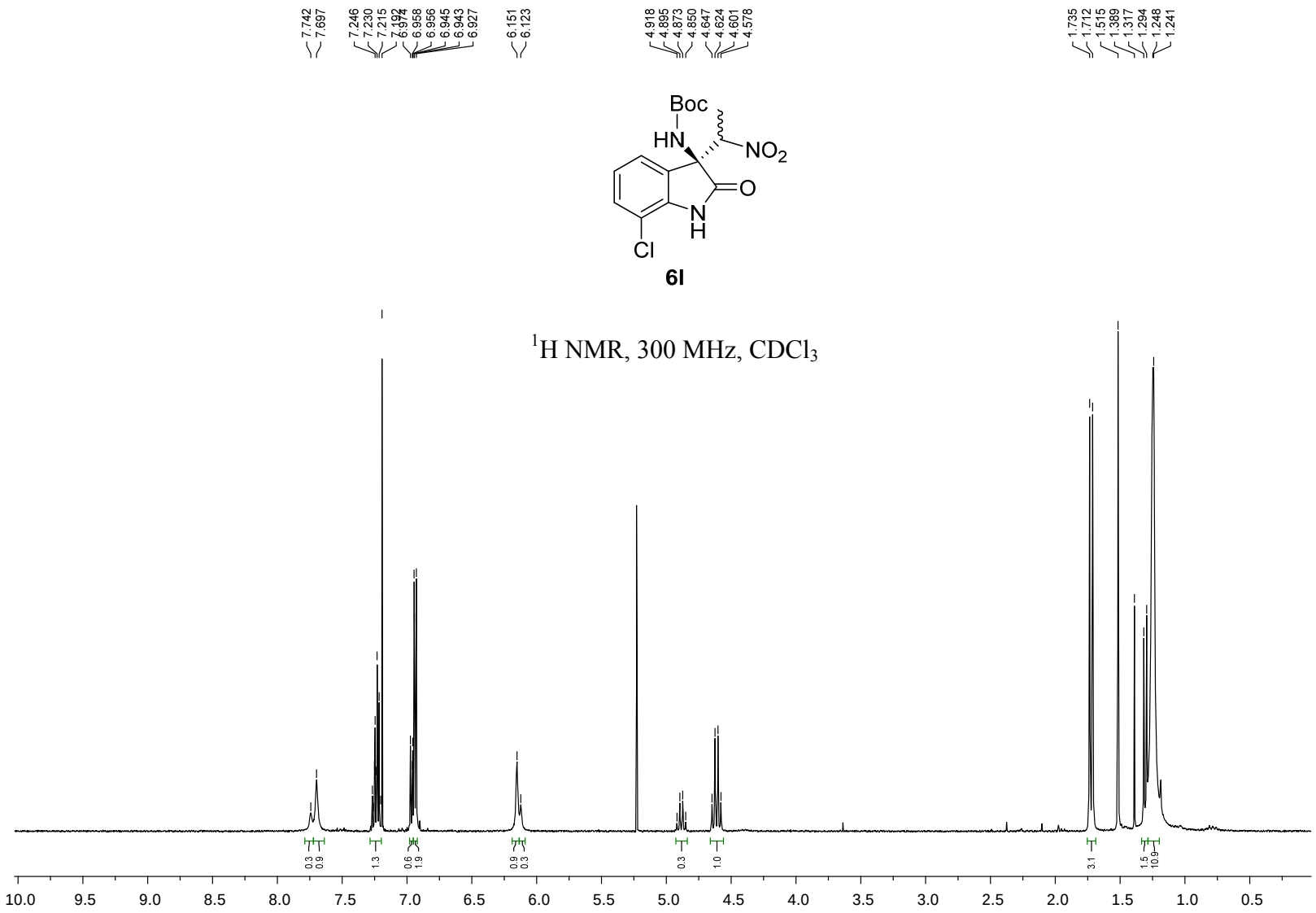
^{1}H NMR, 300 MHz, $CDCl_3$
after crystallization



^{13}C NMR, 75 MHz, $CDCl_3$
after crystallization

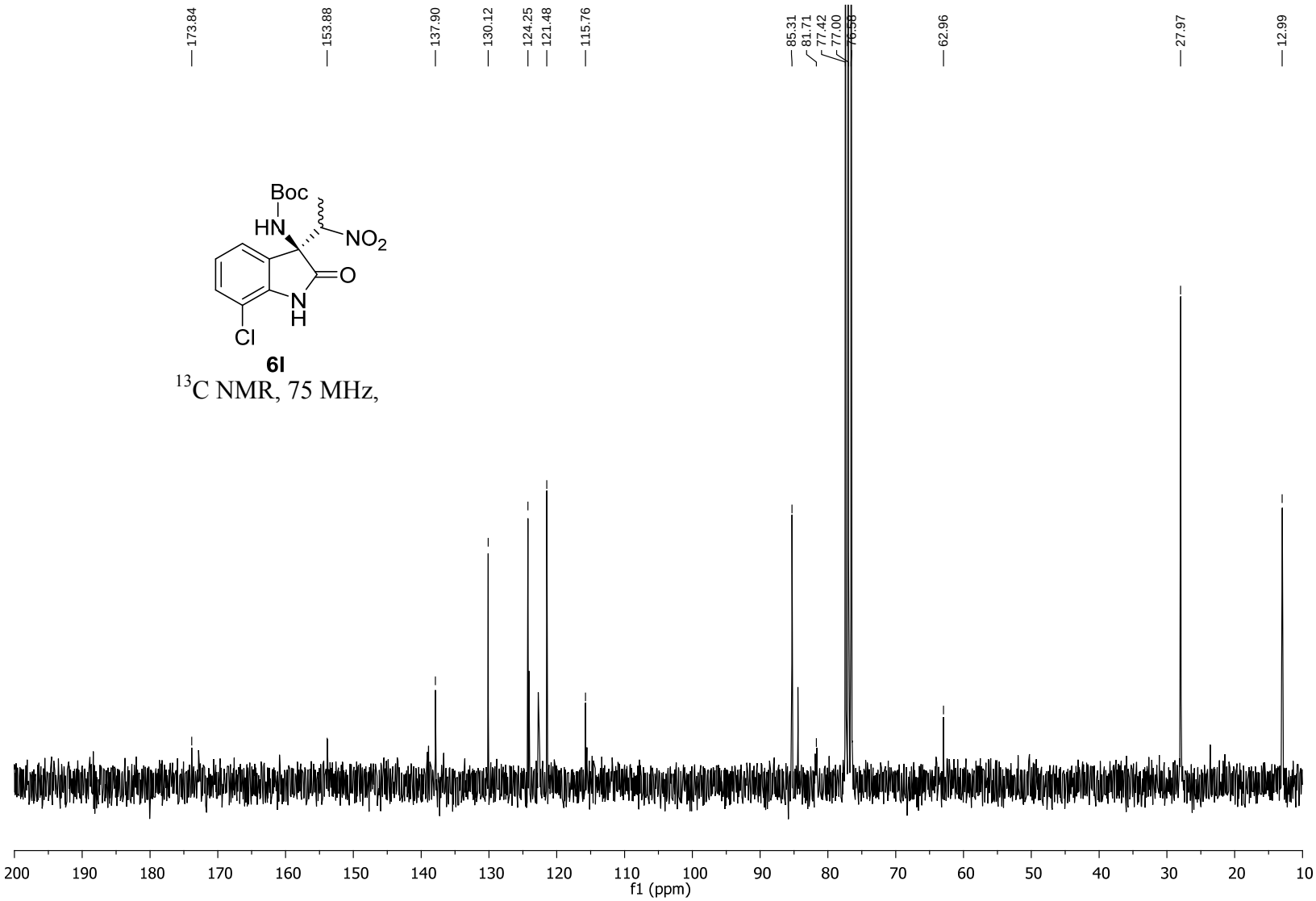

8.414
8.346
7.260
7.125
7.099
7.052
7.045
7.024
7.018
7.009
7.003
6.982
6.976
6.959
6.933
6.904
6.806
6.801
6.729
6.283
5.958
4.759
4.749
4.722
4.712
4.383
4.374
4.343
4.334
2.576
2.567
2.551
2.542
2.526
2.517
2.501
2.492
2.475
2.467
2.450
2.442
2.266
2.242
2.218
2.192
2.178
2.152
2.104
1.364
1.343
1.333
0.983
0.958
0.934
0.919
0.894
0.870
Boc
HN
NO2
O
Cl
N
H
7k
1H NMR, 300 MHz, CDCl3
0.9
0.2
0.8
0.8
0.8
1.0
0.2
0.2
1.0
1.0
1.0
10.3
3.0
0.8
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5


173.61
154.17
141.49
135.96
125.64
123.68
123.31
111.42
92.68
81.79
77.42
77.00
76.58
61.56
28.13
20.27
10.41
Boc
HN
NO2
O
Cl
N
H
7k
13C NMR, 75 MHz,
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



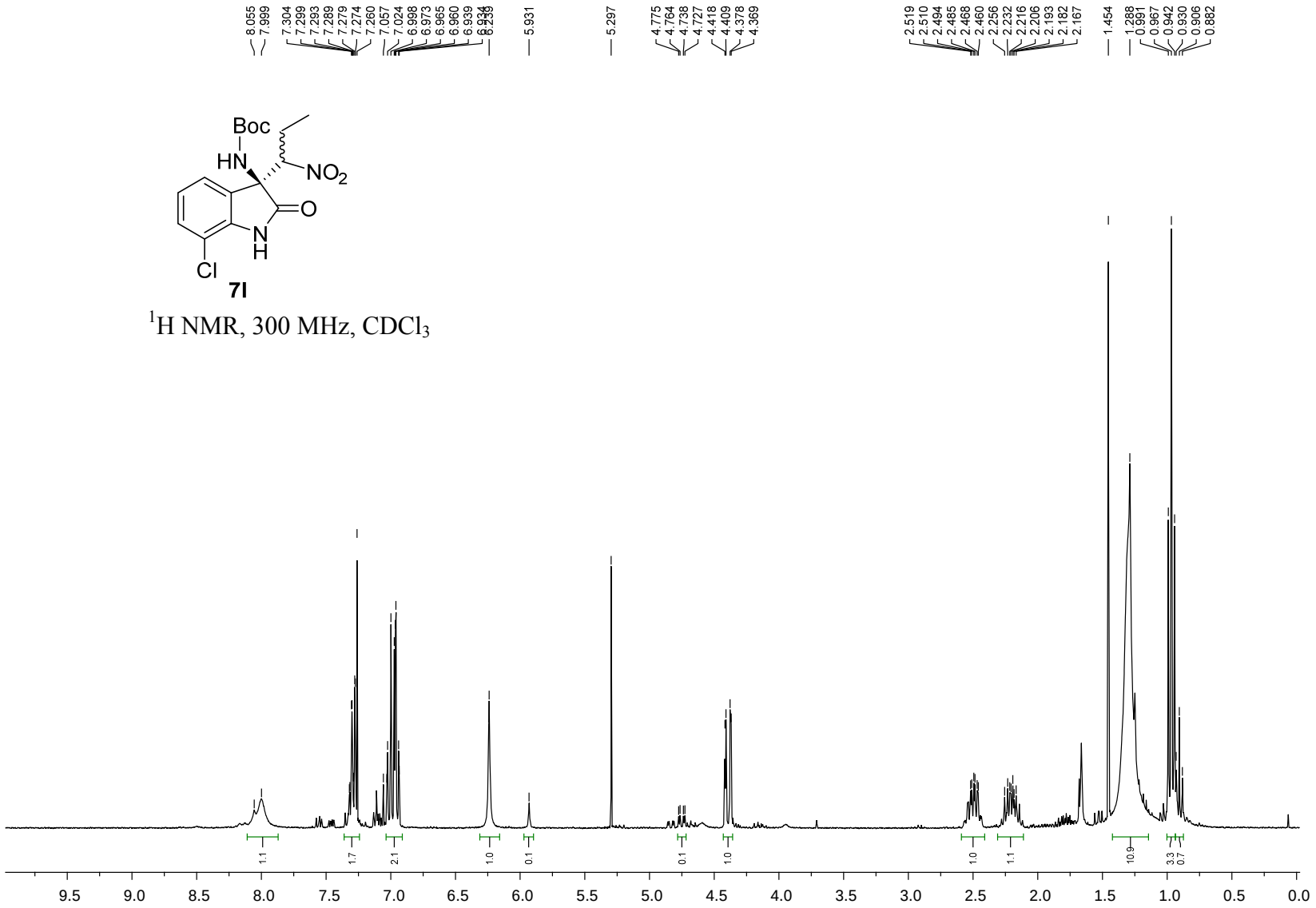
6l

^{1}H NMR, 300 MHz, $CDCl_3$



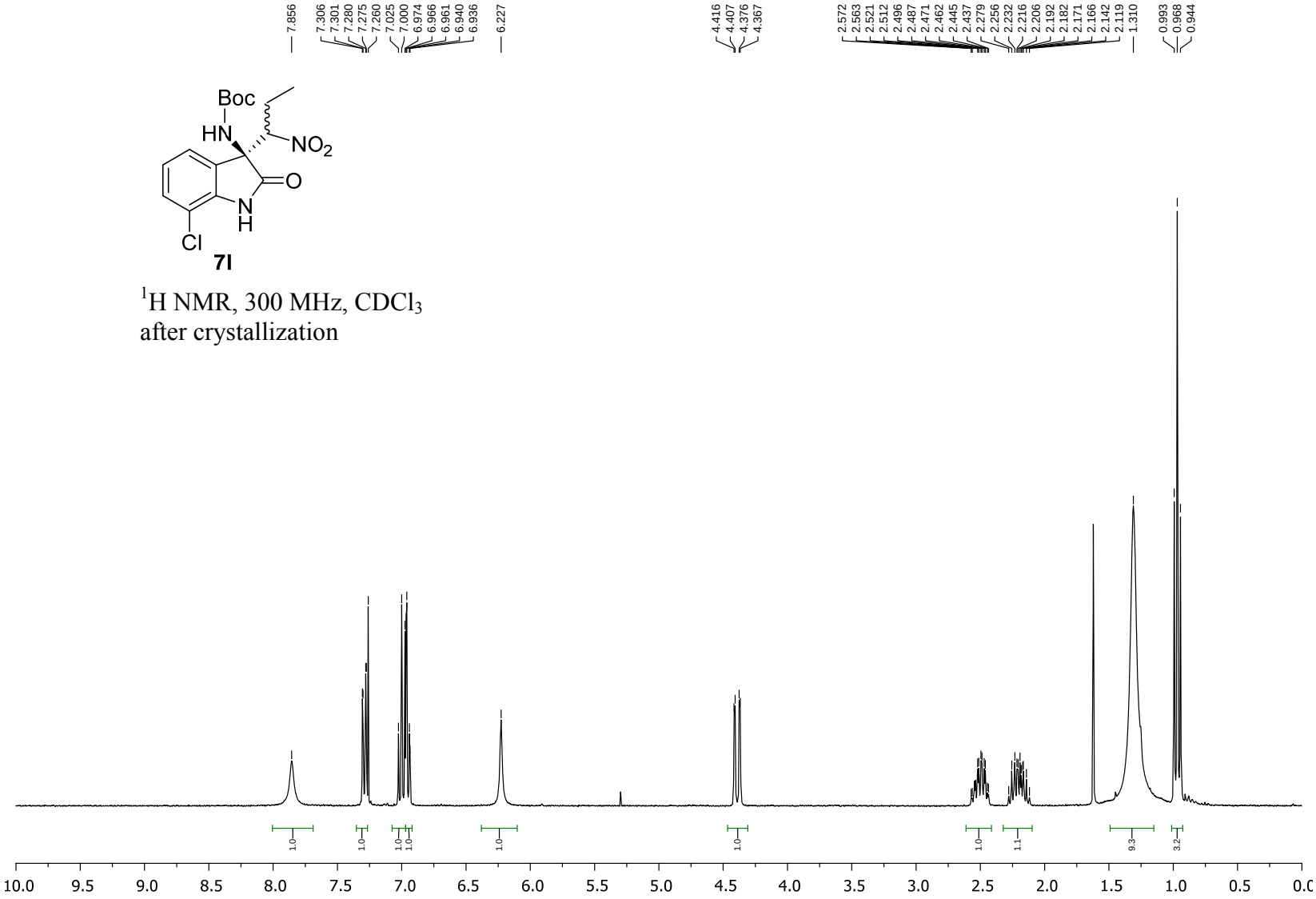
6l

^{13}C NMR, 75 MHz,

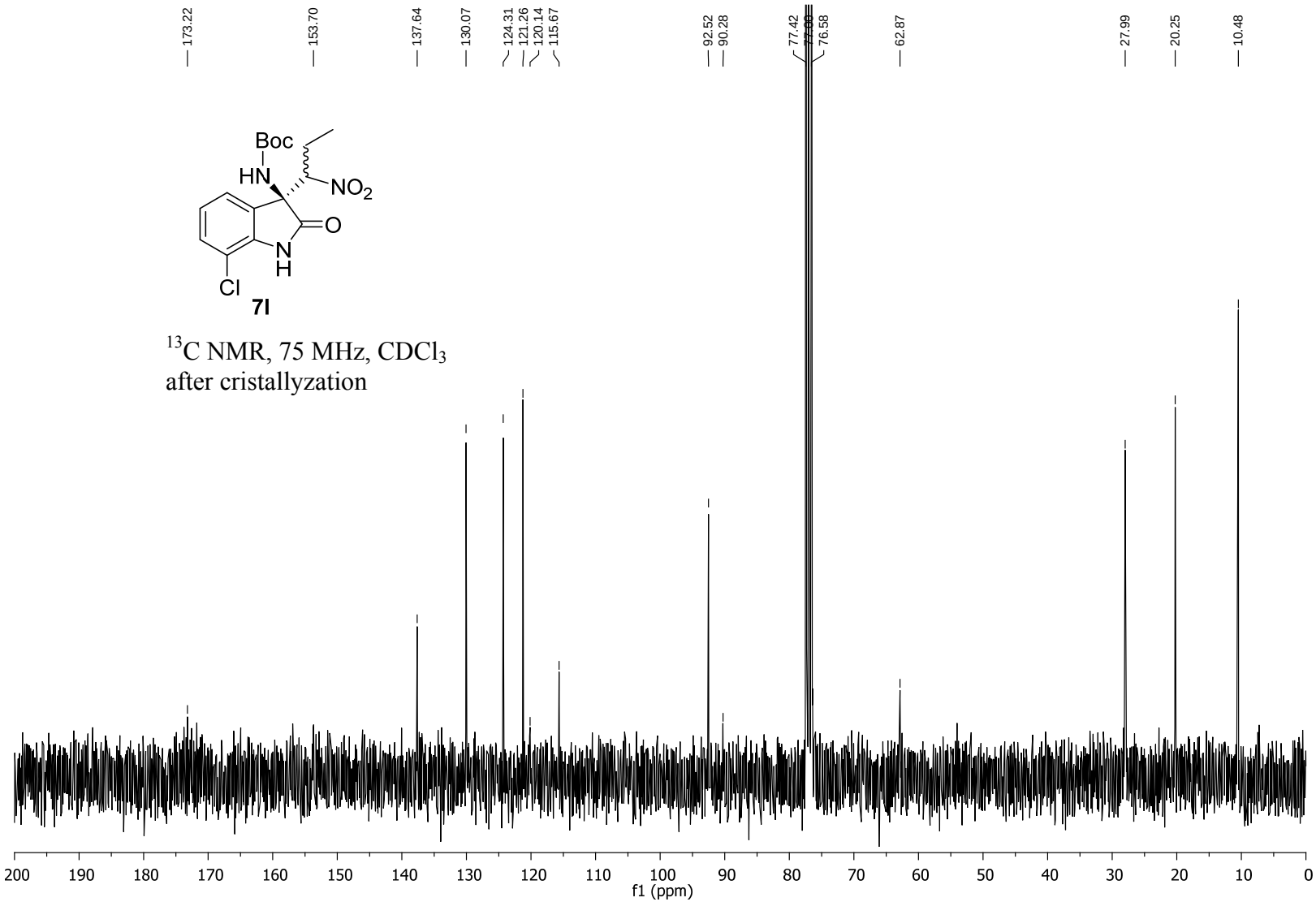


7l

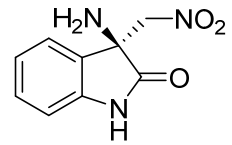
^{1}H NMR, 300 MHz, $CDCl_3$



^{1}H NMR, 300 MHz, $CDCl_3$
after crystallization

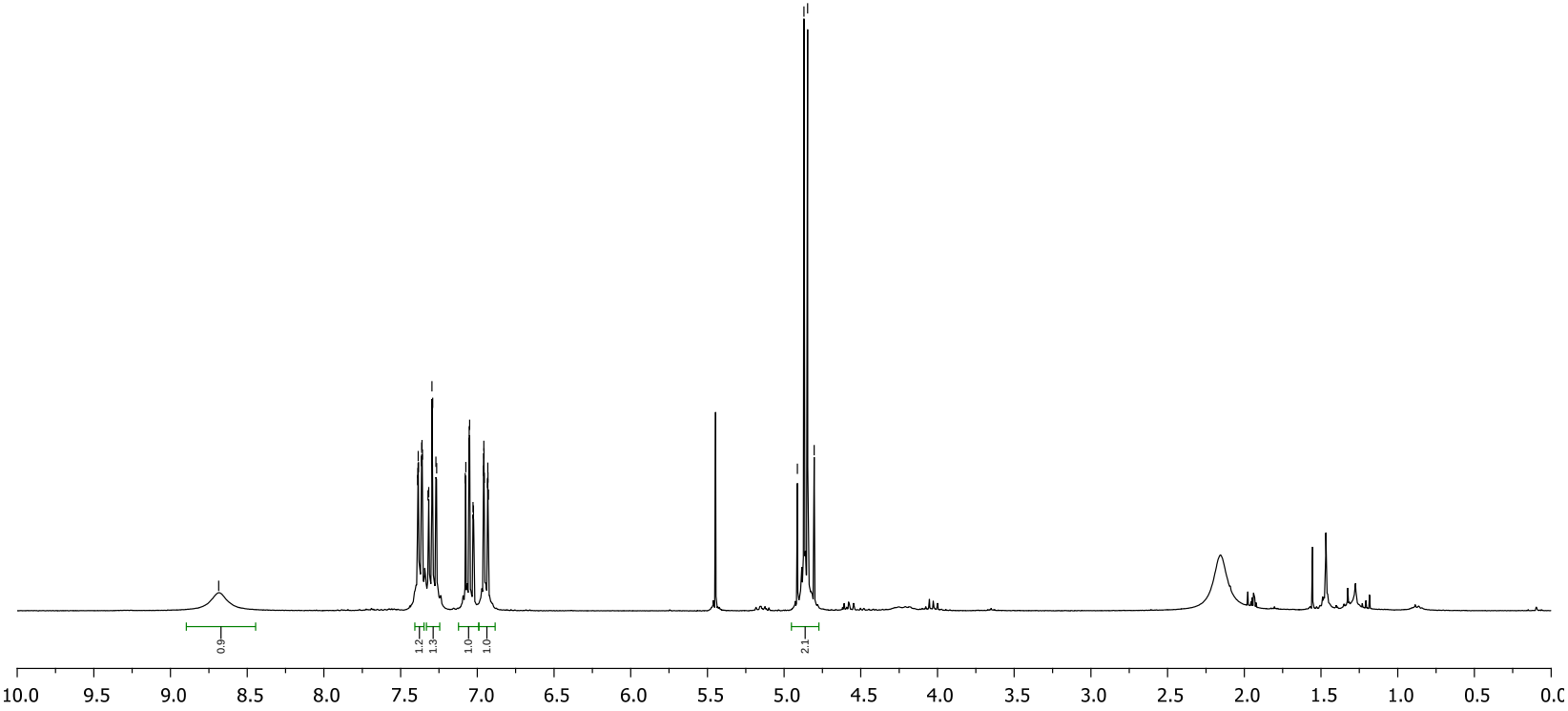


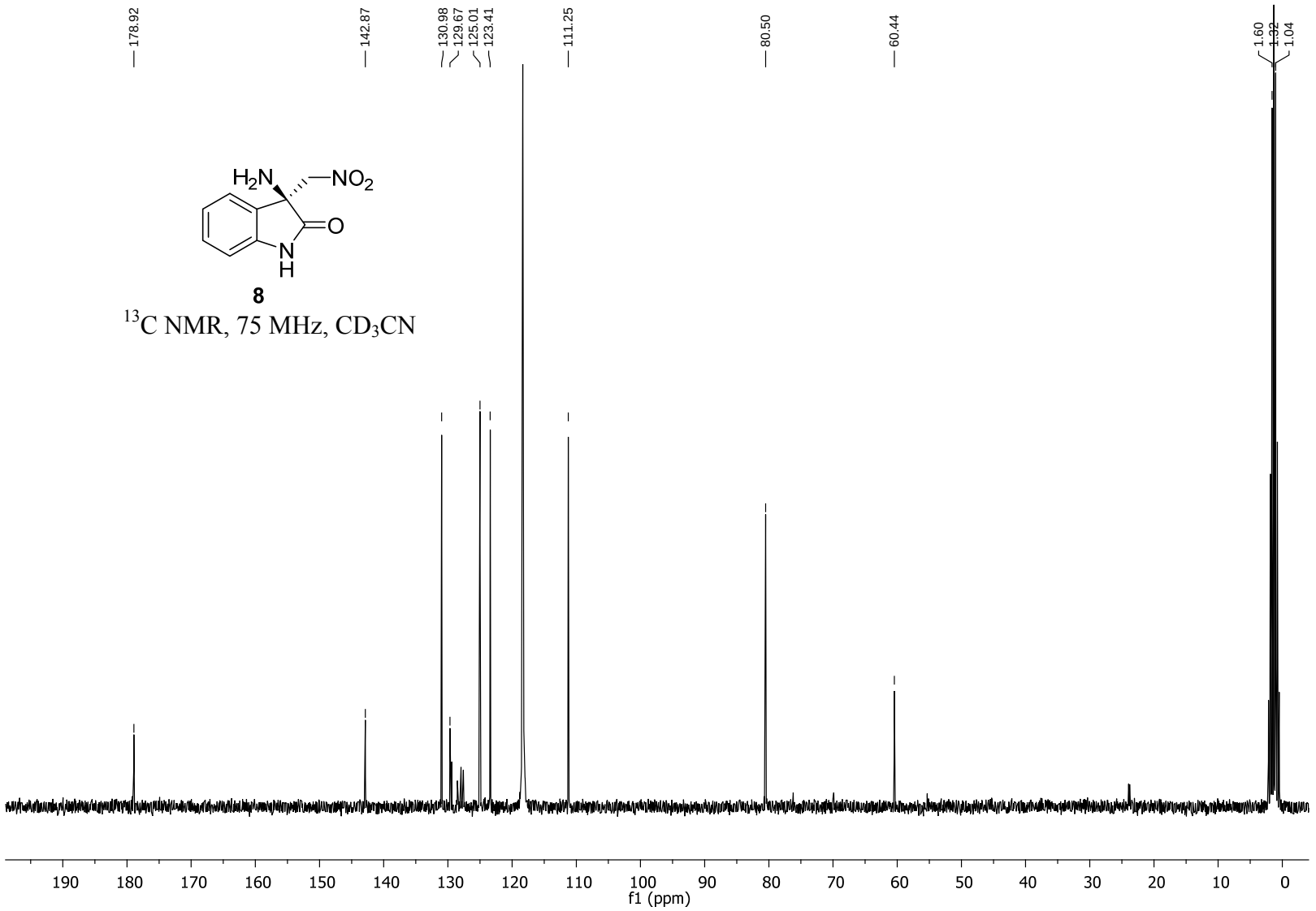
^{13}C NMR, 75 MHz, $CDCl_3$
after cristallyzation

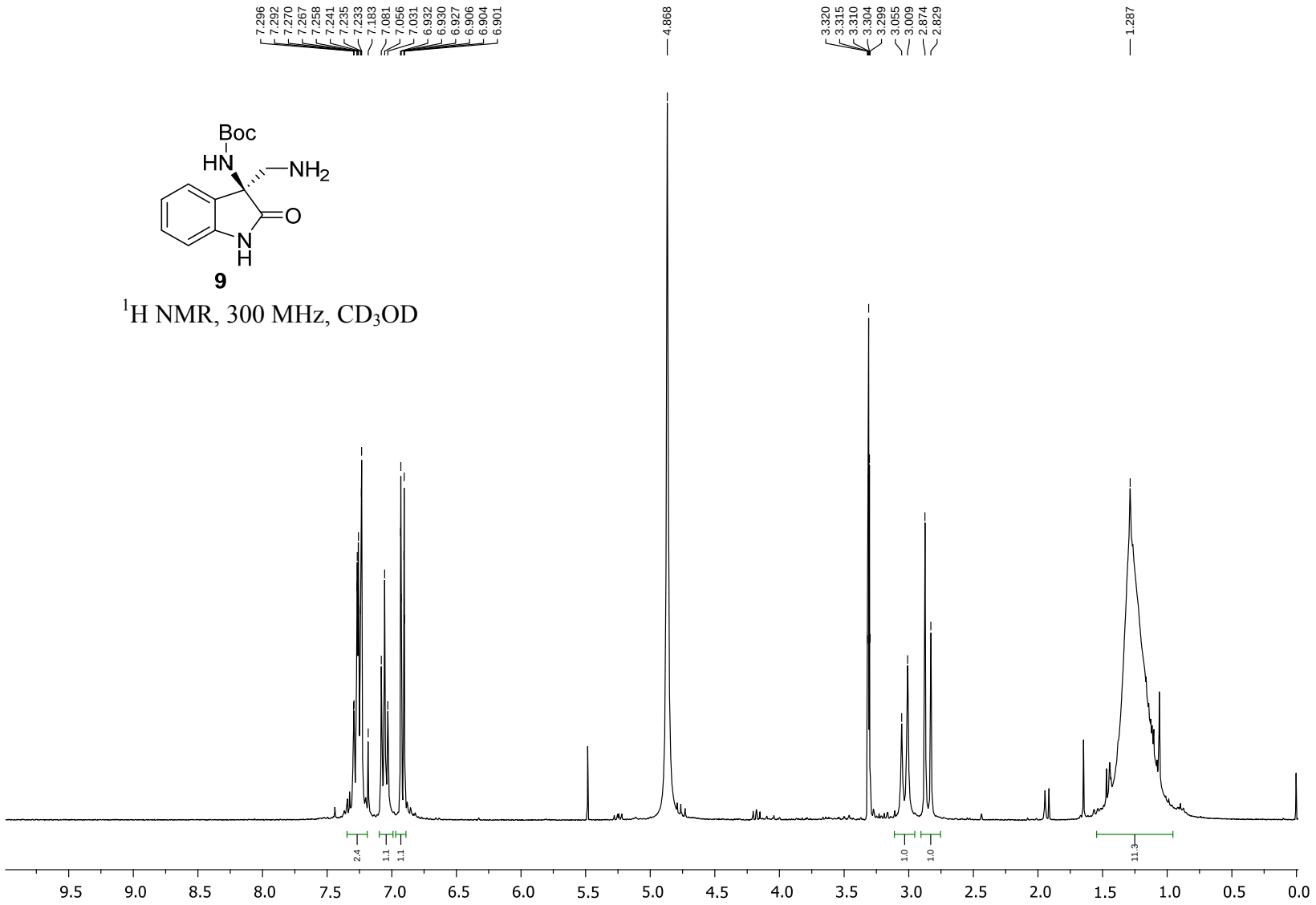


8

^{1}H NMR, 300 MHz, CD_3CN

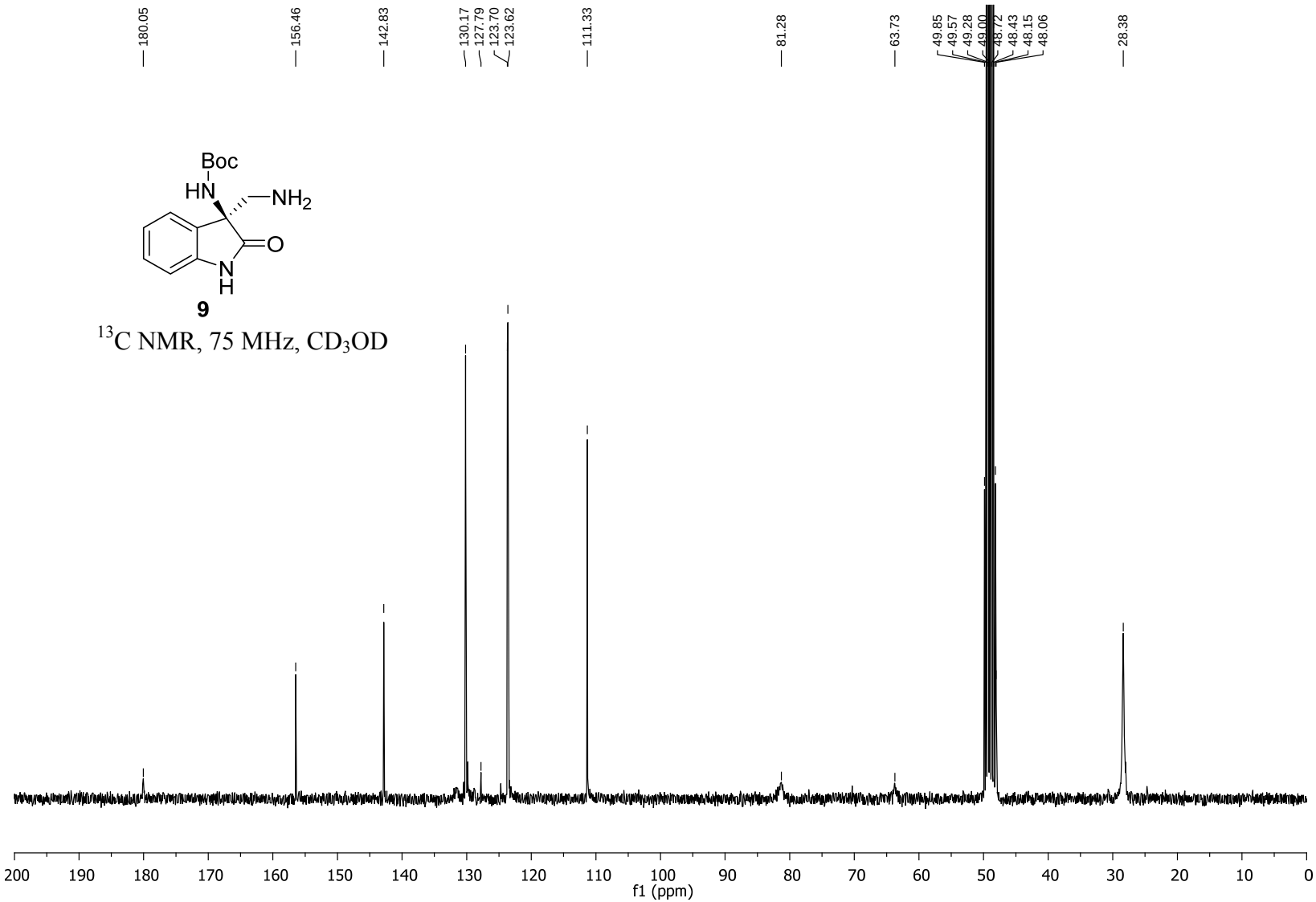


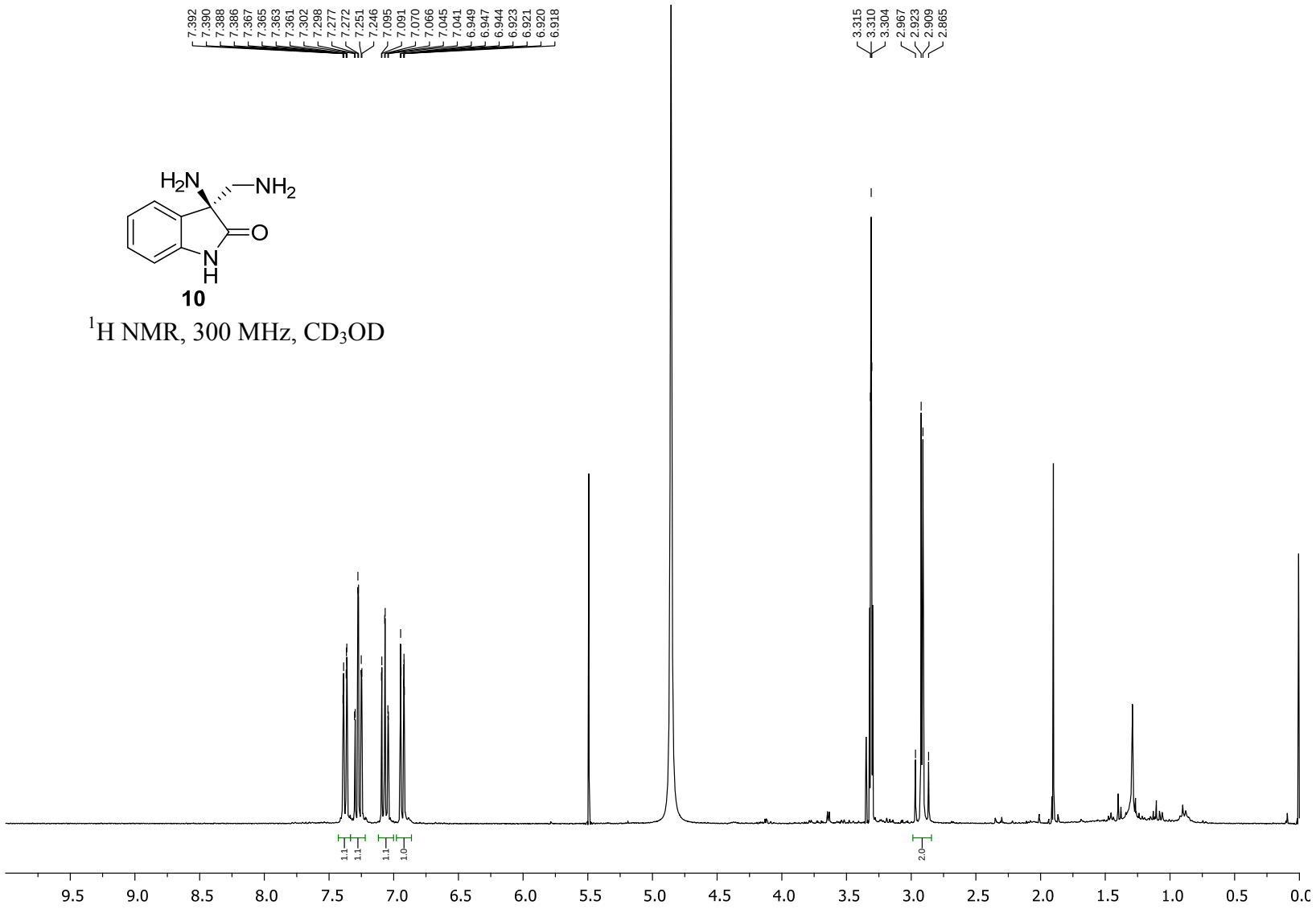

178.92
142.87
130.98
129.67
125.01
123.41
111.25
80.50
60.44
1.60
1.32
1.04
H2N
NO2
O
N
H
8
13C NMR, 75 MHz, CD3CN
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



9

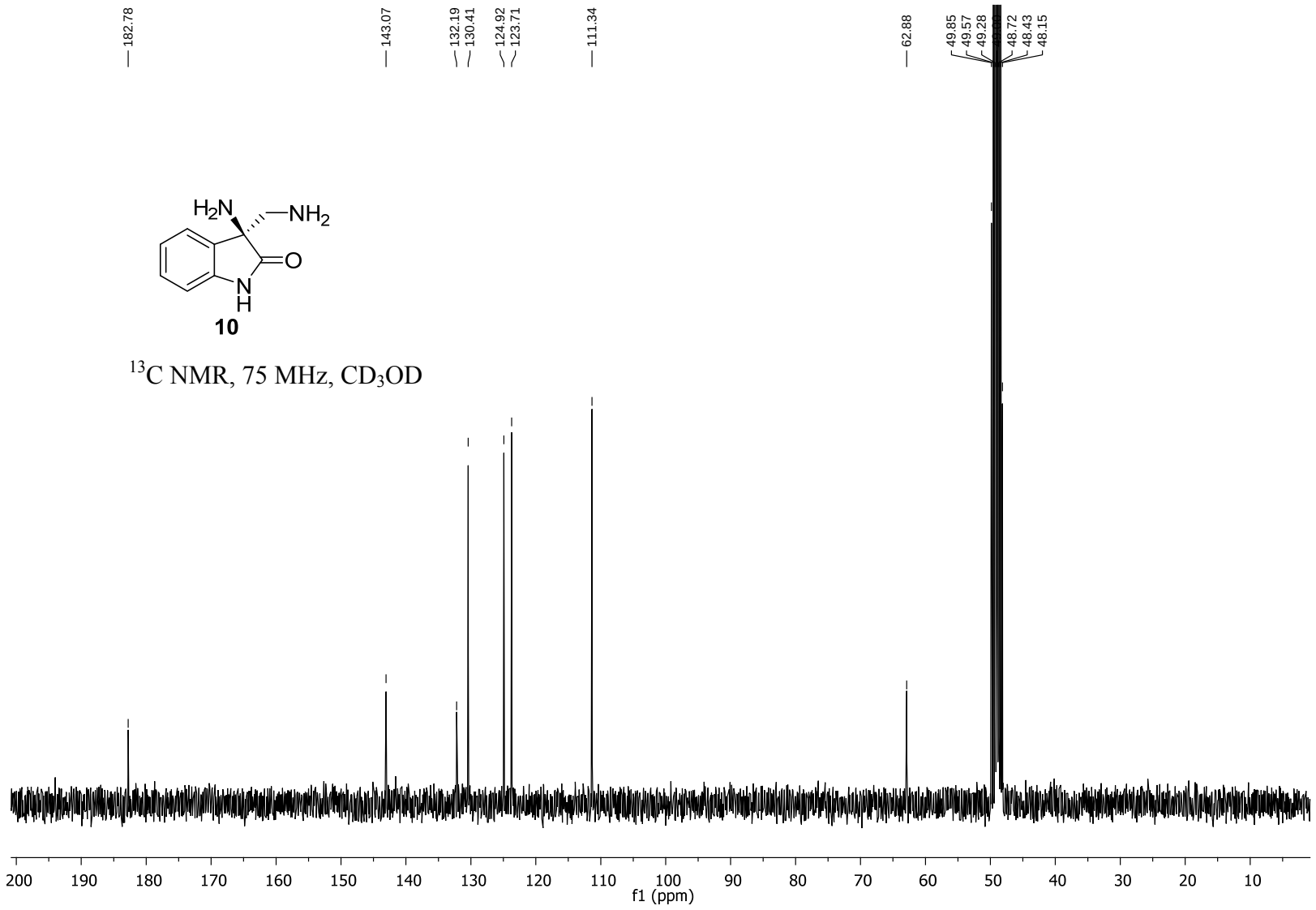
^{1}H NMR, 300 MHz, CD_3OD

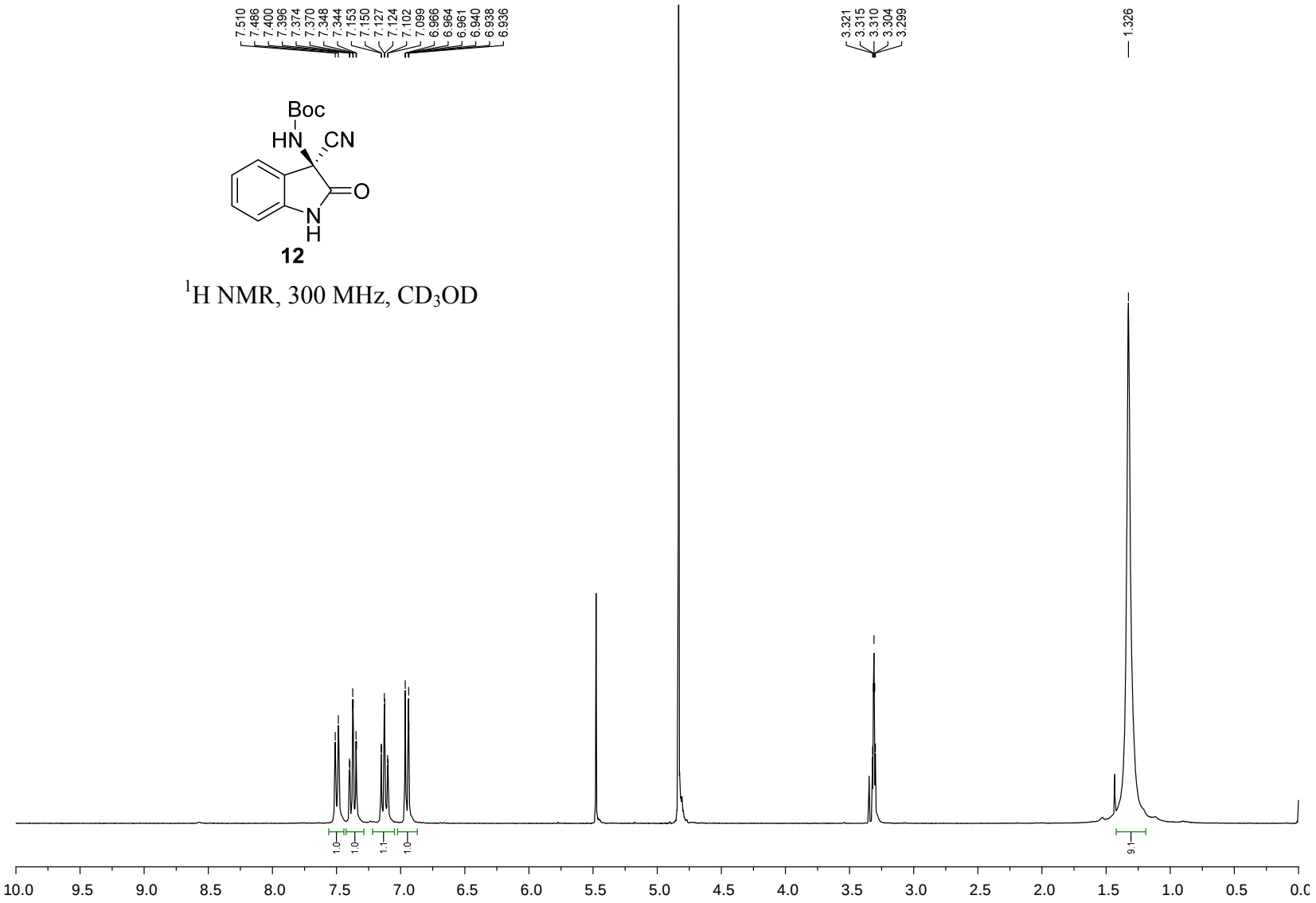

180.05
156.46
142.83
130.17
127.79
123.70
123.62
111.33
81.28
63.73
49.85
49.57
49.28
49.00
48.72
48.43
48.15
48.06
28.38
Boc
HN
NH2
O
N
H
9
13C NMR, 75 MHz, CD3OD
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



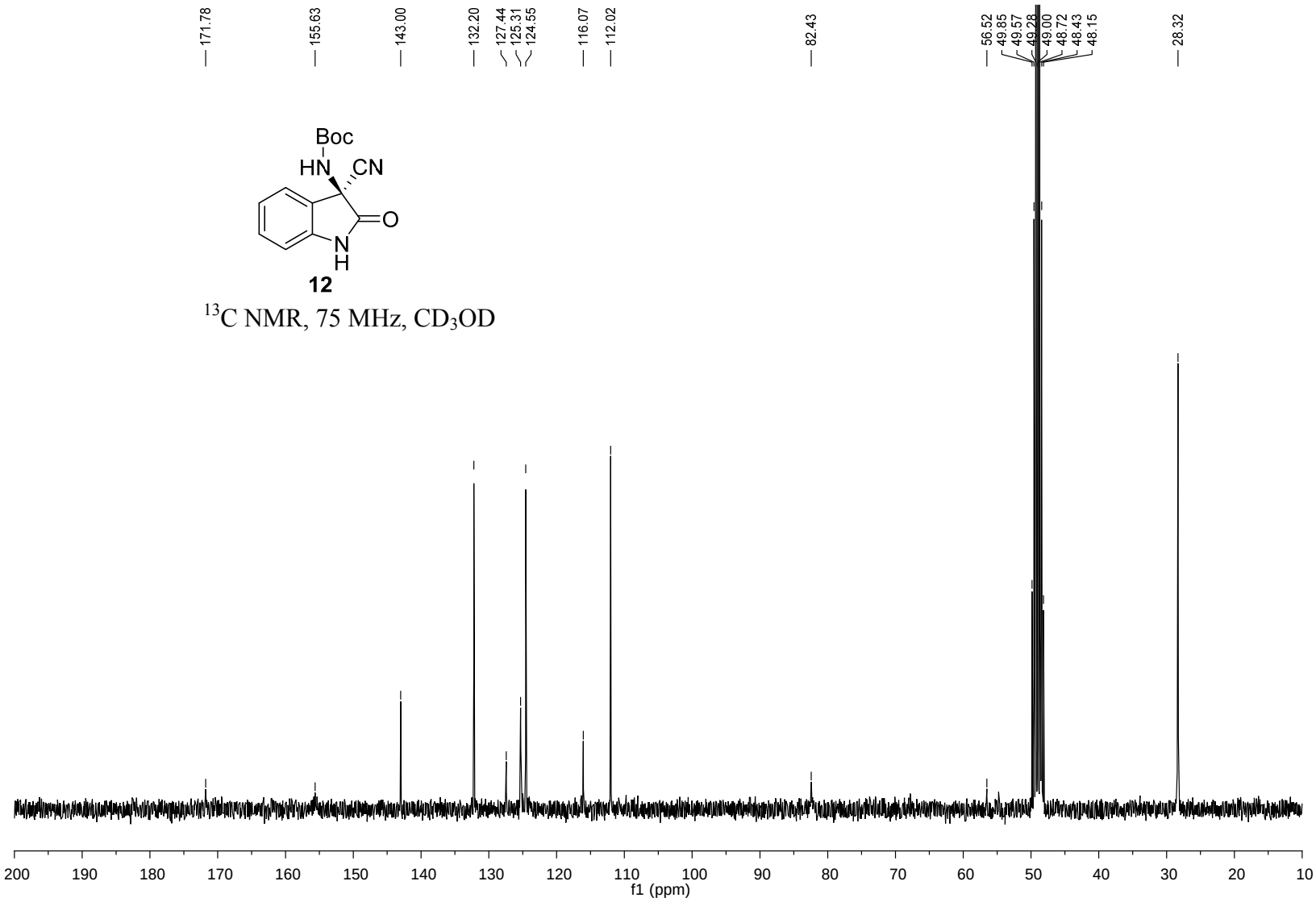
10

^{1}H NMR, 300 MHz, CD_3OD

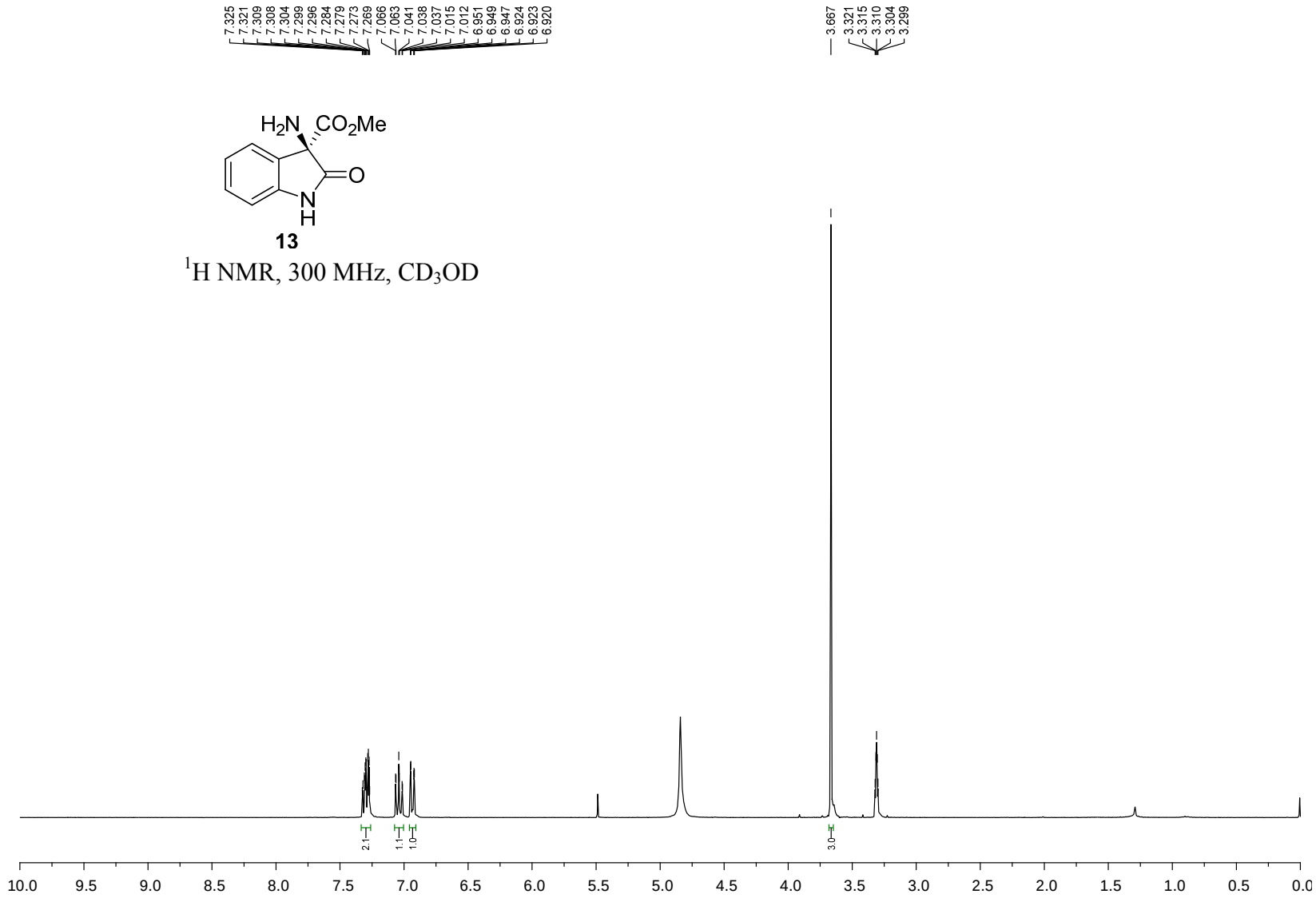

182.78
143.07
132.19
130.41
124.92
123.71
111.34
62.88
49.85
49.57
49.28
48.72
48.43
48.15
H2N
NH2
O
N
H
10
13C NMR, 75 MHz, CD3OD
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)



^{1}H NMR, 300 MHz, CD_3OD

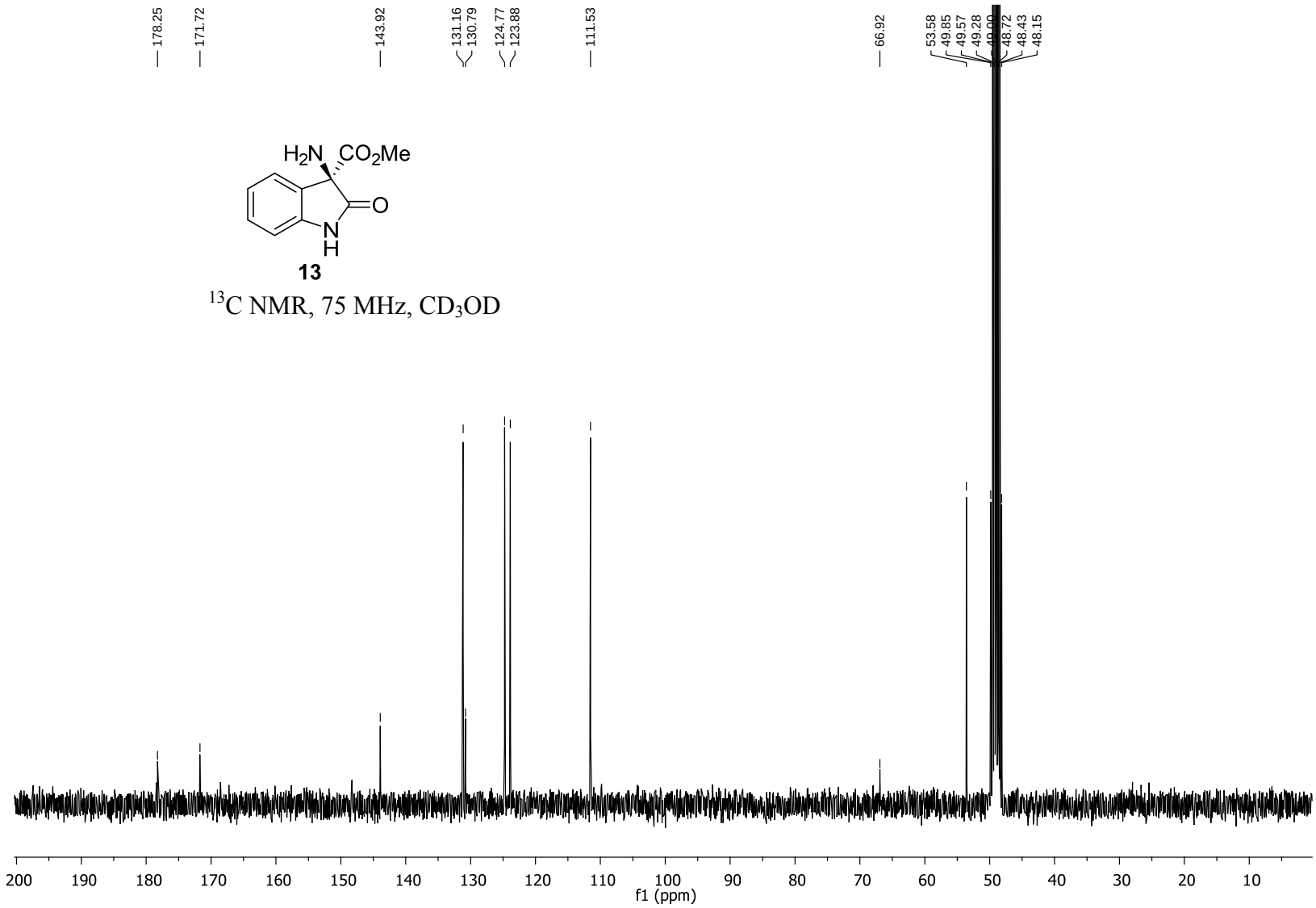


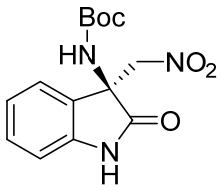
^{13}C NMR, 75 MHz, CD_3OD



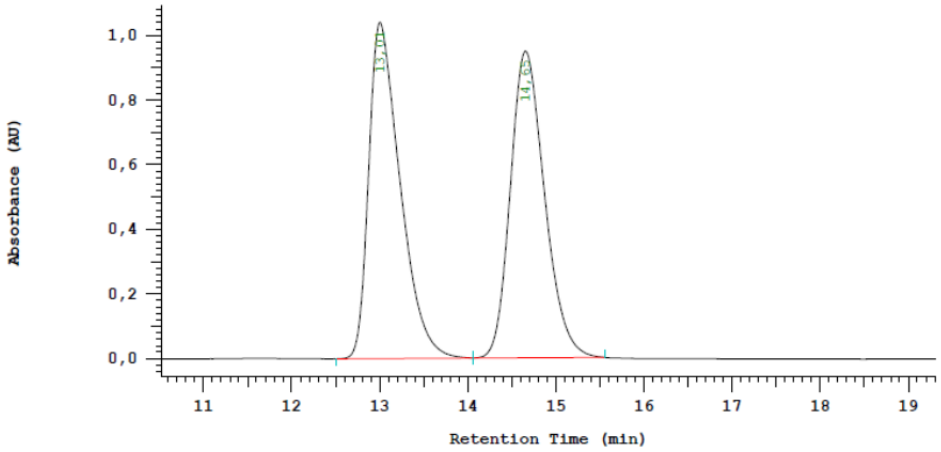
13

^{1}H NMR, 300 MHz, CD_3OD

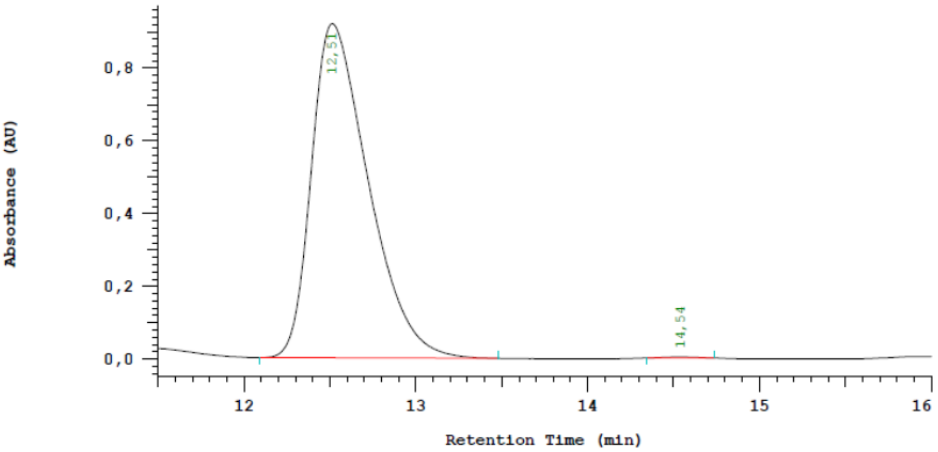

178.25
171.72
143.92
131.16
130.79
124.77
123.88
111.53
66.92
53.58
49.85
49.57
49.28
48.72
48.43
48.15
H2N
CO2Me
O
N
H
13
13C NMR, 75 MHz, CD3OD
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)



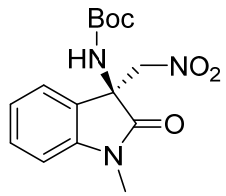
3a



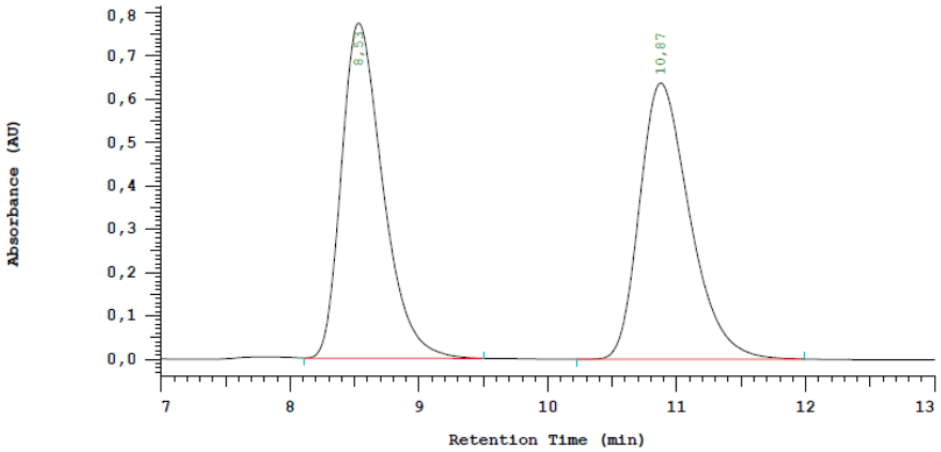
No.	RT	Area	Area %
1	13,01	12867494	50,162
2	14,65	12784535	49,838
		25652029	100,000



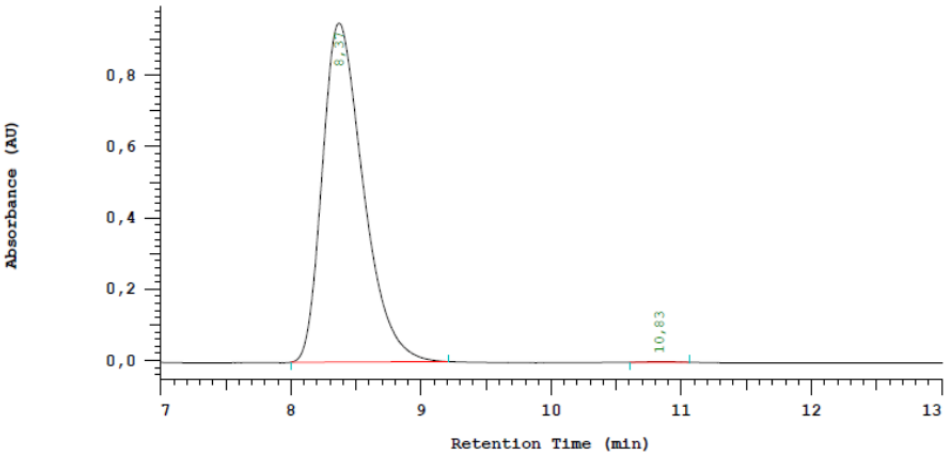
No.	RT	Area	Area %
1	12,51	10581300	99,819
2	14,54	19183	0,181
		10600483	100,000



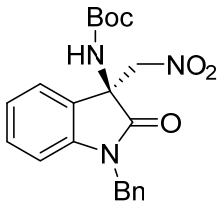
3b



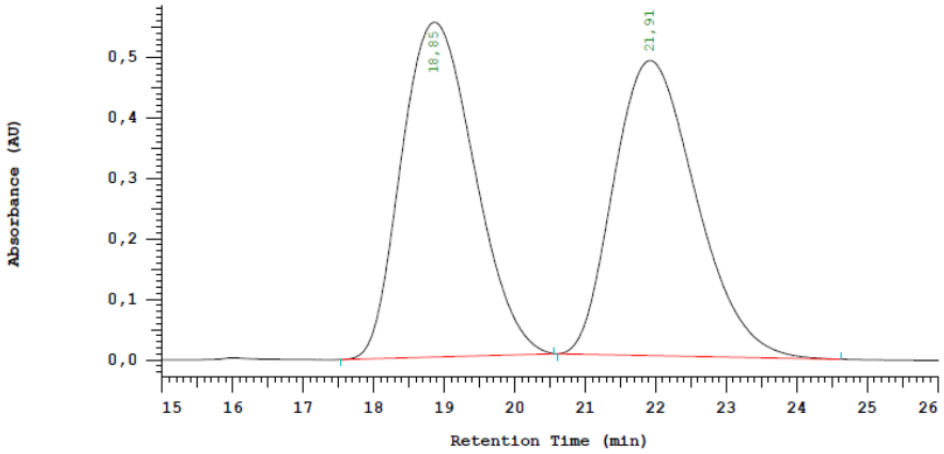
No.	RT	Area	Area %
1	8,53	8619237	50,076
2	10,87	8593203	49,924
		17212440	100,000



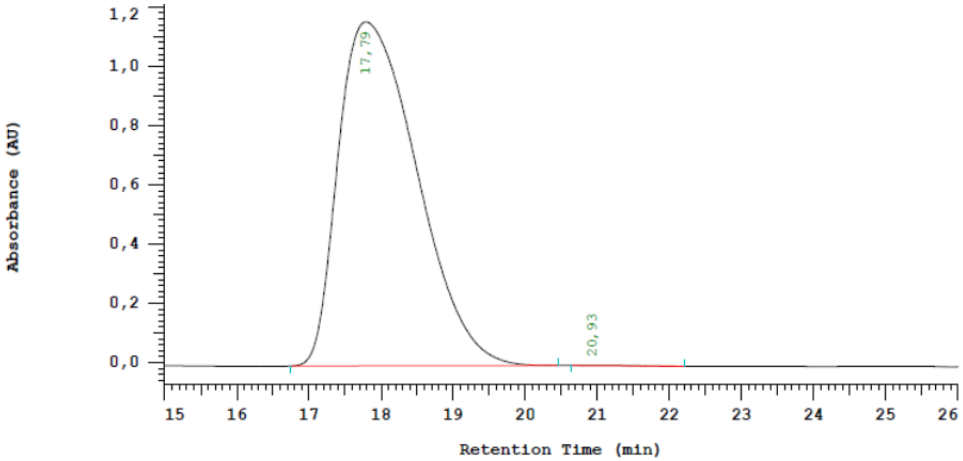
No.	RT	Area	Area %
1	8,37	10379298	99,895
2	10,83	10859	0,105
		10390157	100,000



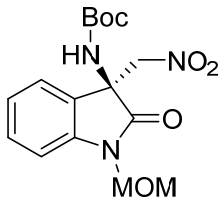
3c



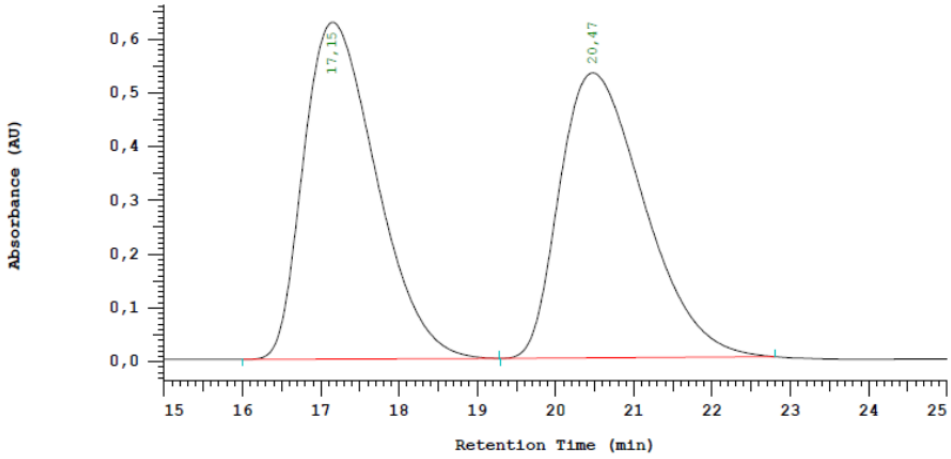
No.	RT	Area	Area %
1	18,85	19903152	50,169
2	21,91	19769376	49,831
		39672528	100,000



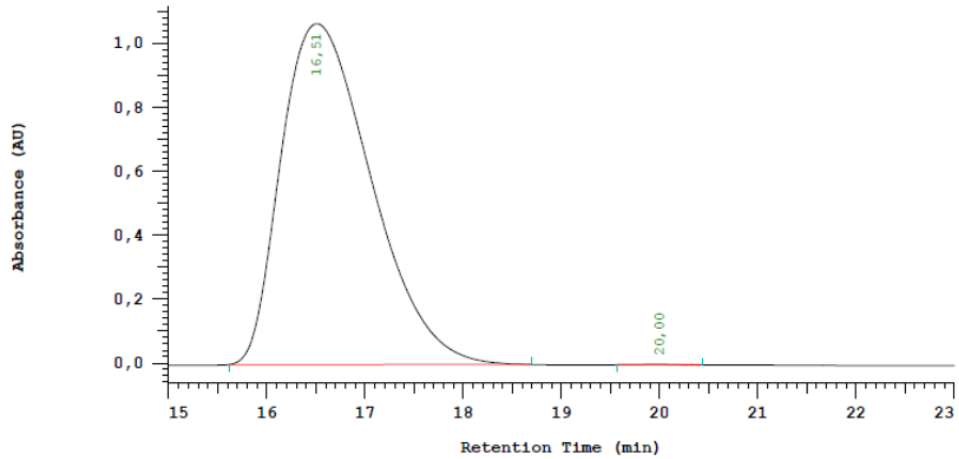
No.	RT	Area	Area %
1	17,79	44062803	99,940
2	20,93	26478	0,060
		44089281	100,000



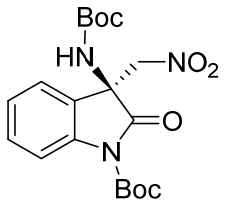
3d



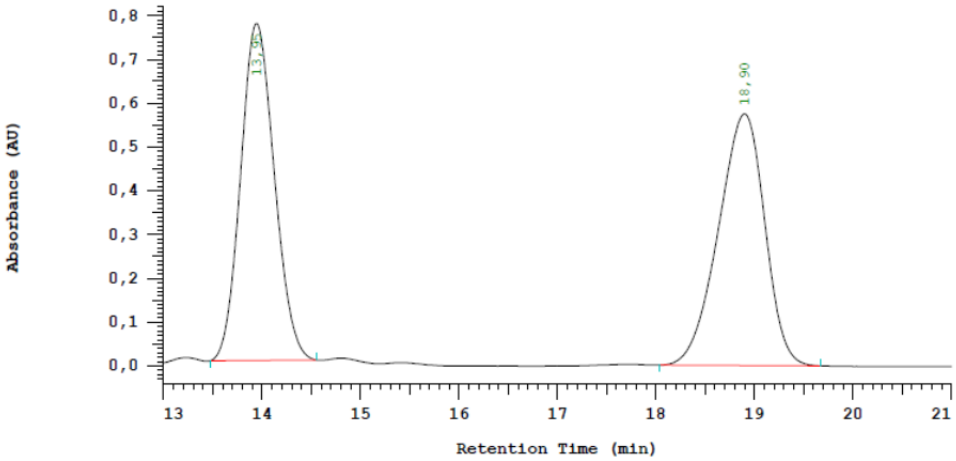
No.	RT	Area	Area %
1	17,15	20196947	50,355
2	20,47	19911790	49,645
		40108737	100,000



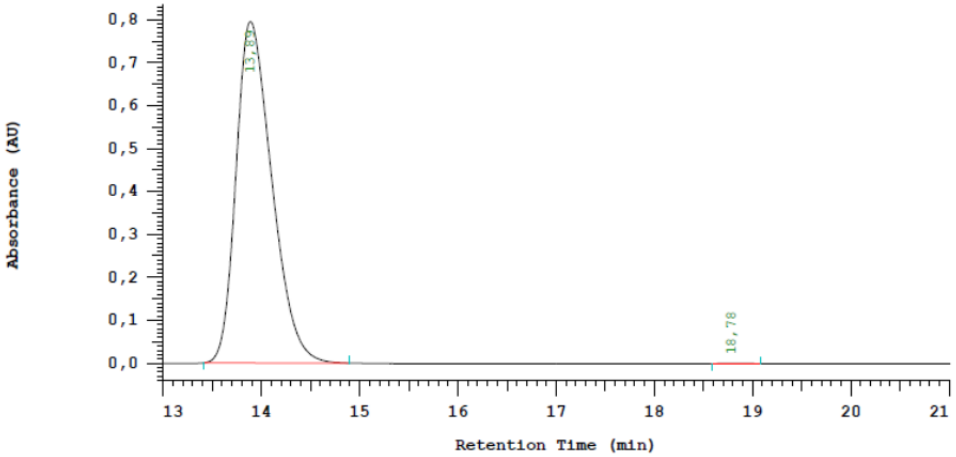
No.	RT	Area	Area %
1	16,51	34046969	99,958
2	20,00	14192	0,042
		34061161	100,000



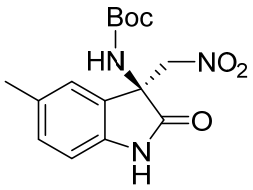
3e



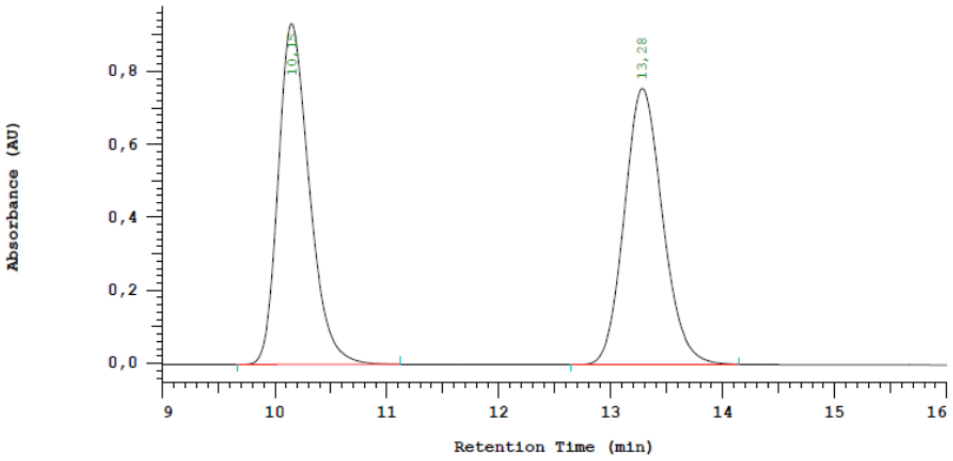
No.	RT	Area	Area %
1	13,95	9142905	49,341
2	18,90	9387131	50,659
		18530036	100,000



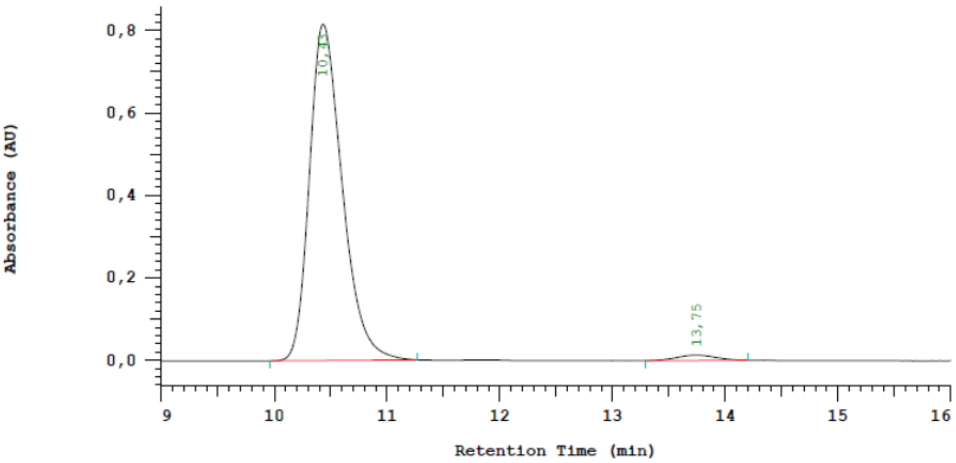
No.	RT	Area	Area %
1	13,89	10069129	99,937
2	18,78	6323	0,063
		10075452	100,000



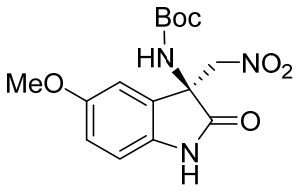
3f



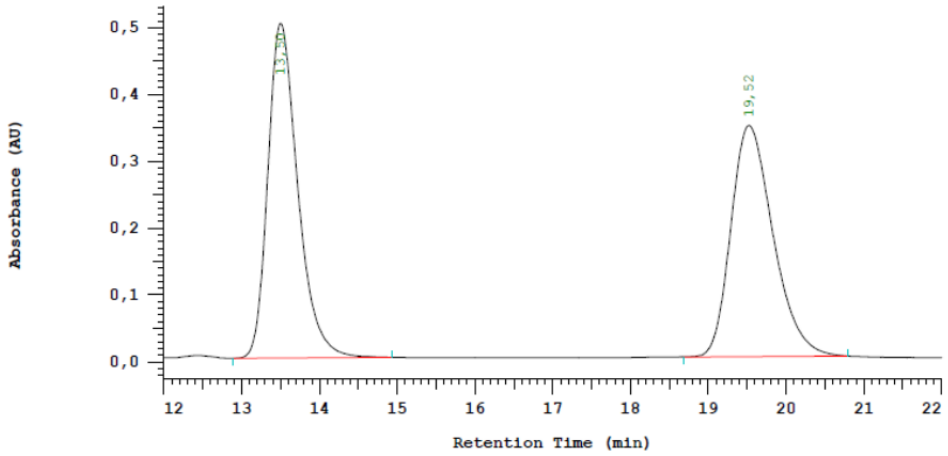
No.	RT	Area	Area %
1	10,15	9017338	50,074
2	13,28	8990774	49,926
		18008112	100,000



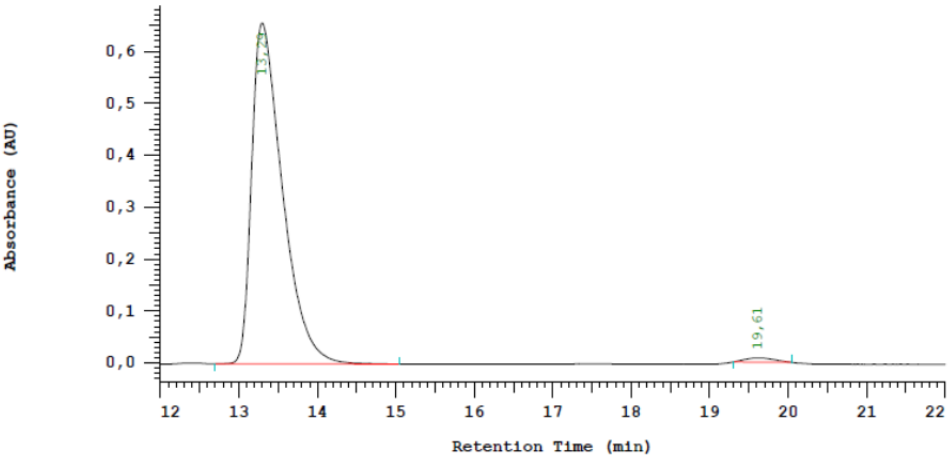
No.	RT	Area	Area %
1	10,43	8240385	98,138
2	13,75	156365	1,862
		8396750	100,000



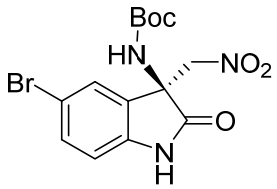
3g



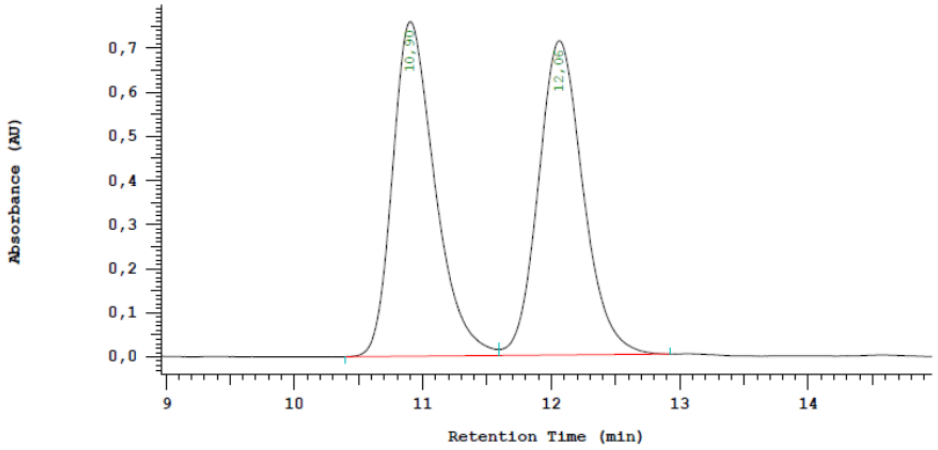
No.	RT	Area	Area %
1	13,50	6693464	50,697
2	19,52	6509455	49,303
		13202919	100,000



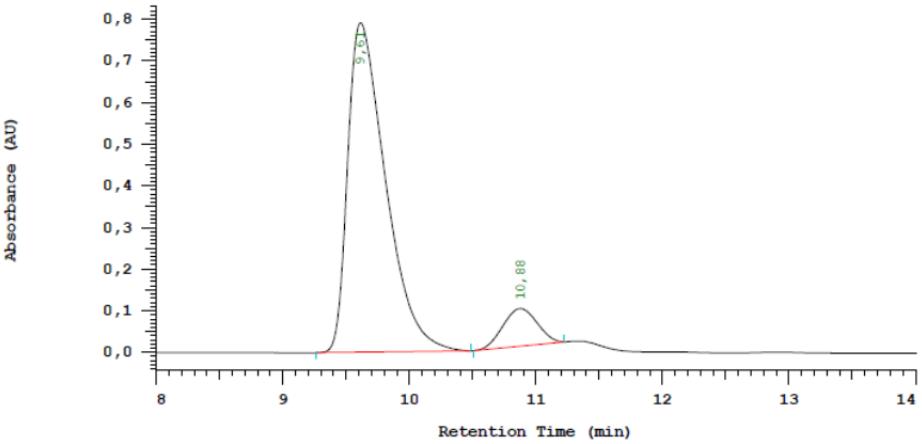
No.	RT	Area	Area %
1	13,29	8918647	98,829
2	19,61	105668	1,171
		9024315	100,000



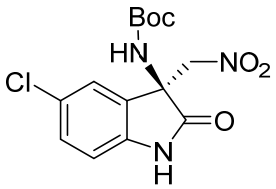
3h



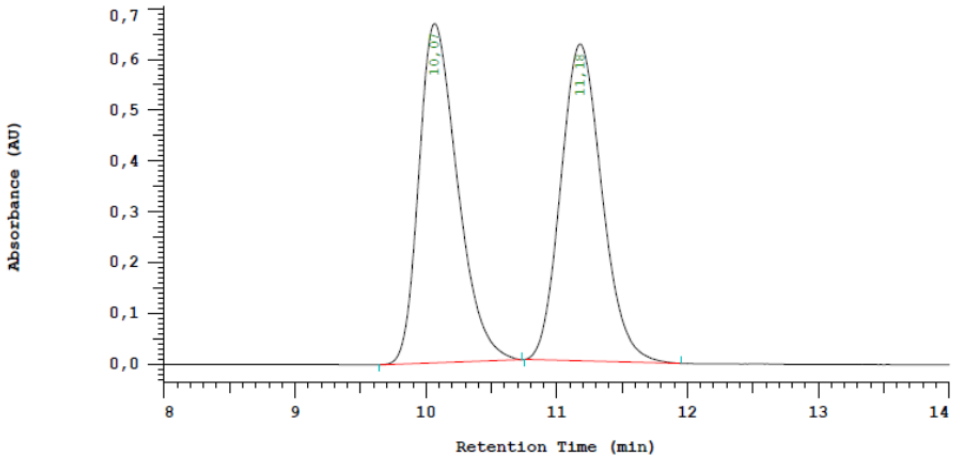
No.	RT	Area	Area %
1	10,90	8667669	50,121
2	12,06	8625720	49,879
		17293389	100,000



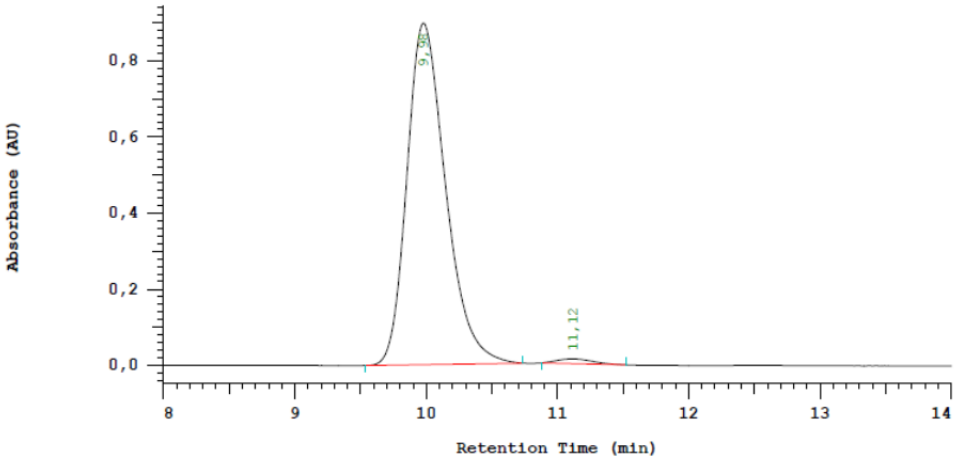
No.	RT	Area	Area %
1	9,61	8211008	90,665
2	10,88	845461	9,335
		9056469	100,000



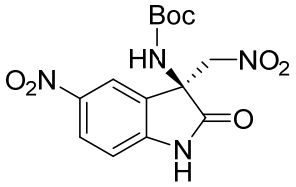
3i



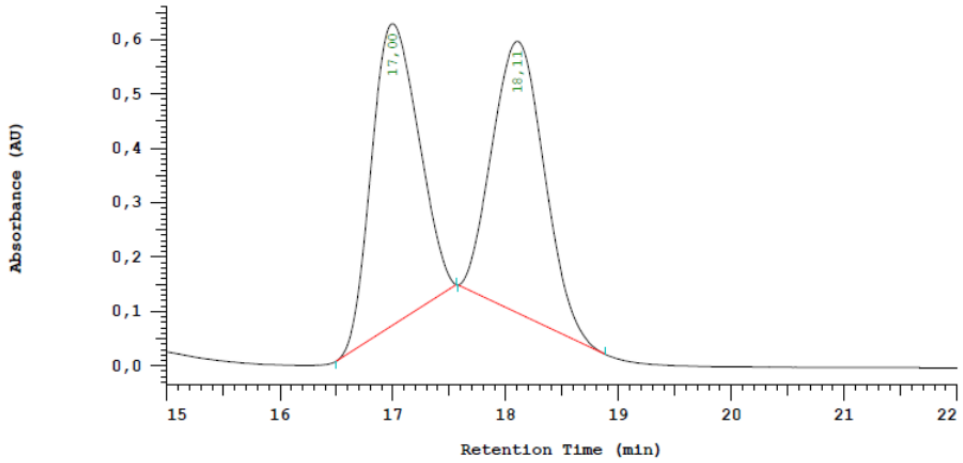
No.	RT	Area	Area %
1	10,07	6830474	50,035
2	11,18	6821033	49,965
		13651507	100,000



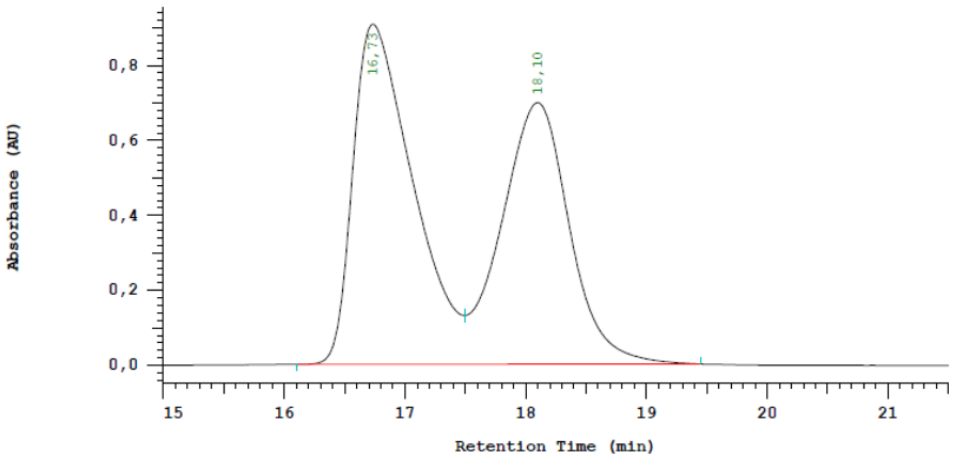
No.	RT	Area	Area %
1	9,98	9192478	98,750
2	11,12	116391	1,250
		9308869	100,000



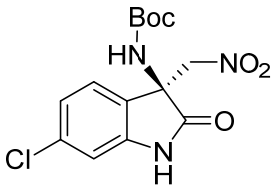
3j



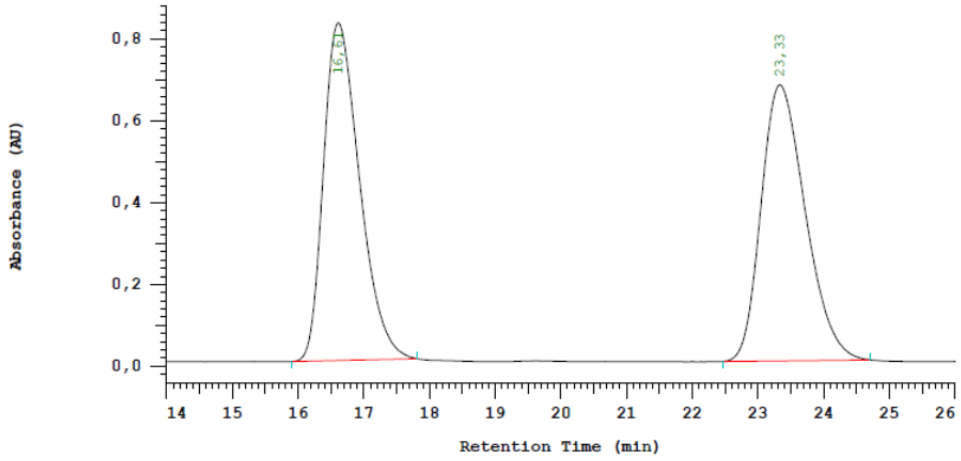
No.	RT	Area	Area %
1	17,00	7982237	49,860
2	18,11	8026920	50,140
		16009157	100,000



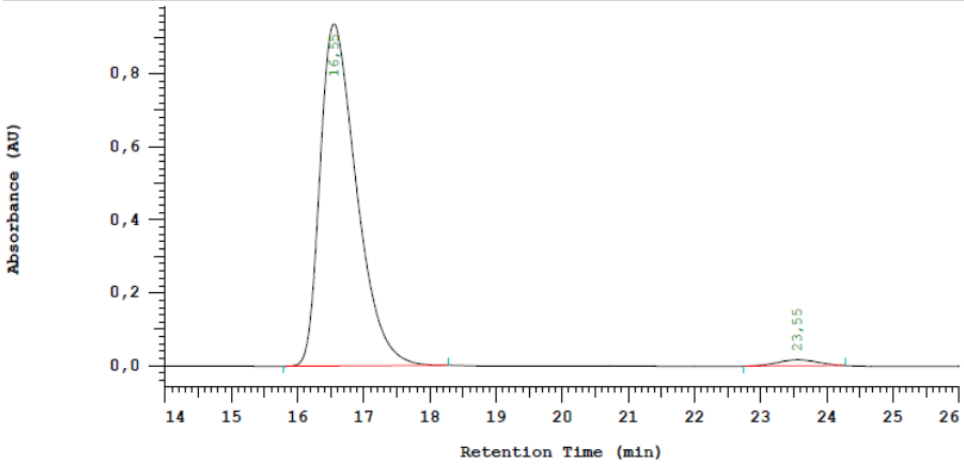
No.	RT	Area	Area %
1	16,73	15608905	53,316
2	18,10	13667102	46,684
		29276007	100,000



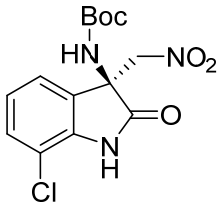
3k



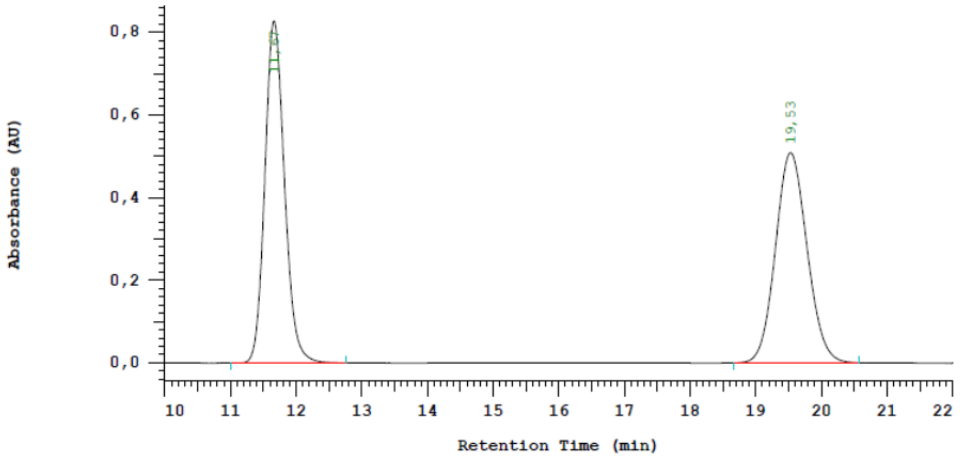
No.	RT	Area	Area %
1	16,61	15743883	50,021
2	23,33	15730854	49,979
		31474737	100,000



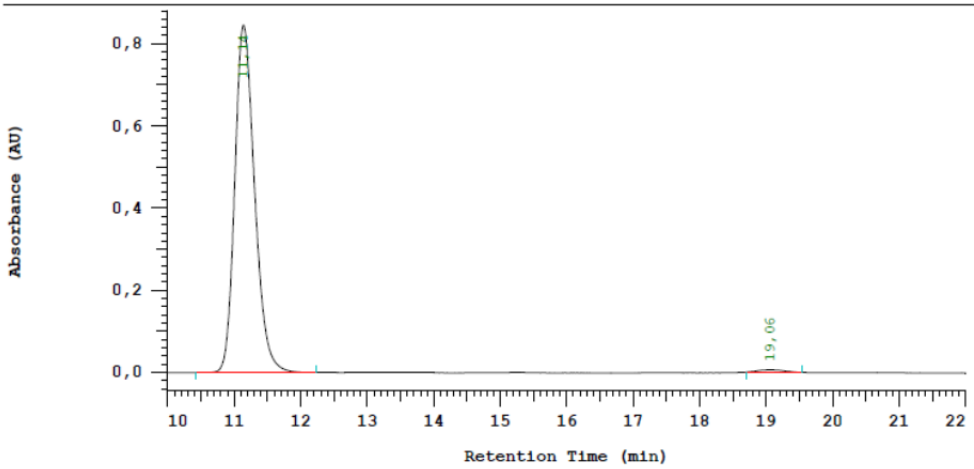
No.	RT	Area	Area %
1	16,55	17902590	98,080
2	23,55	350547	1,920
		18253137	100,000



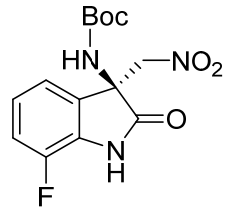
3l



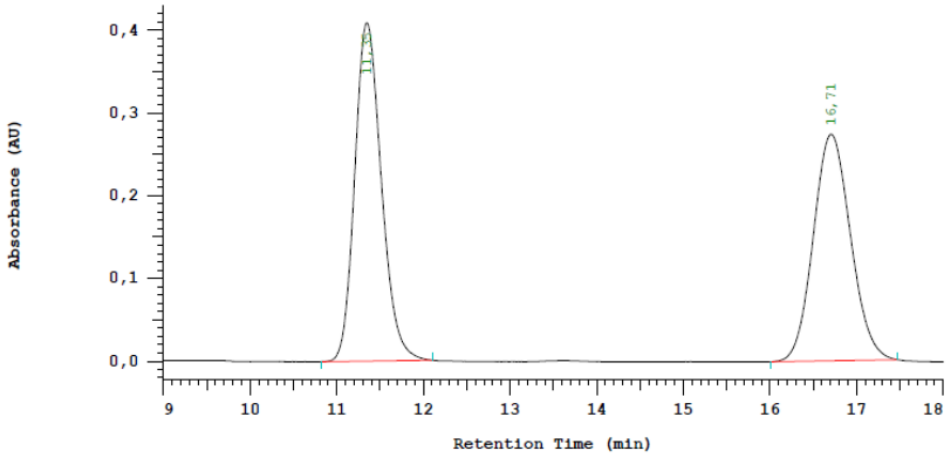
No.	RT	Area	Area %
1	11,67	8558211	50,223
2	19,53	8482315	49,777
		17040526	100,000



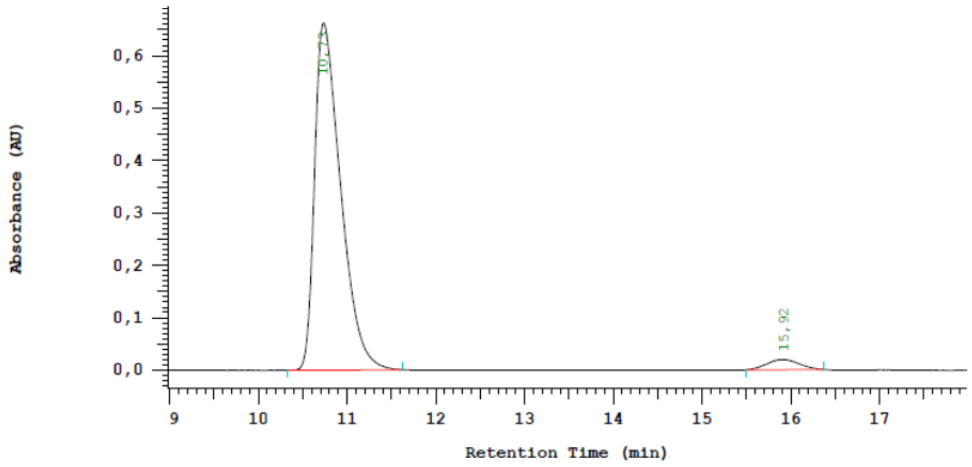
No.	RT	Area	Area %
1	11,14	8780284	99,030
2	19,06	85966	0,970
		8866250	100,000



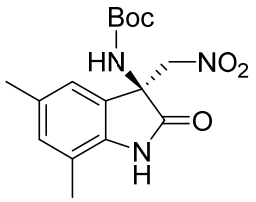
3m



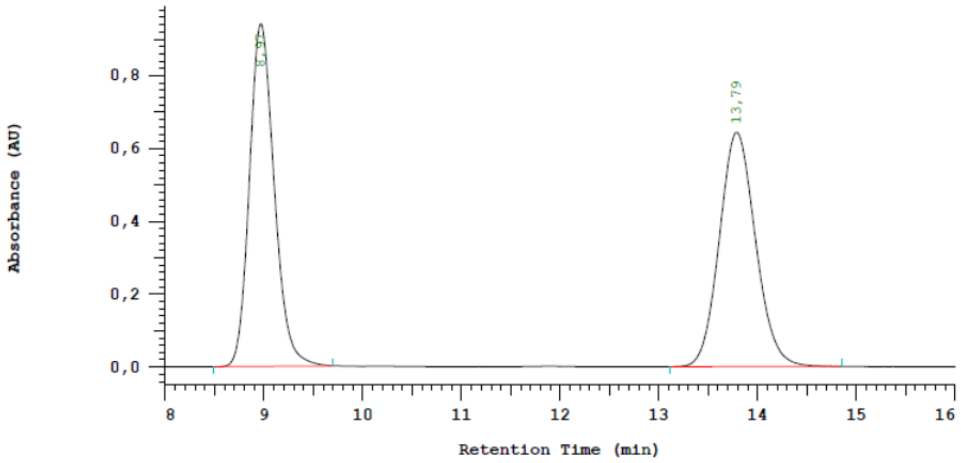
No.	RT	Area	Area %
1	11,35	4365515	51,691
2	16,71	4079968	48,309
		8445483	100,000



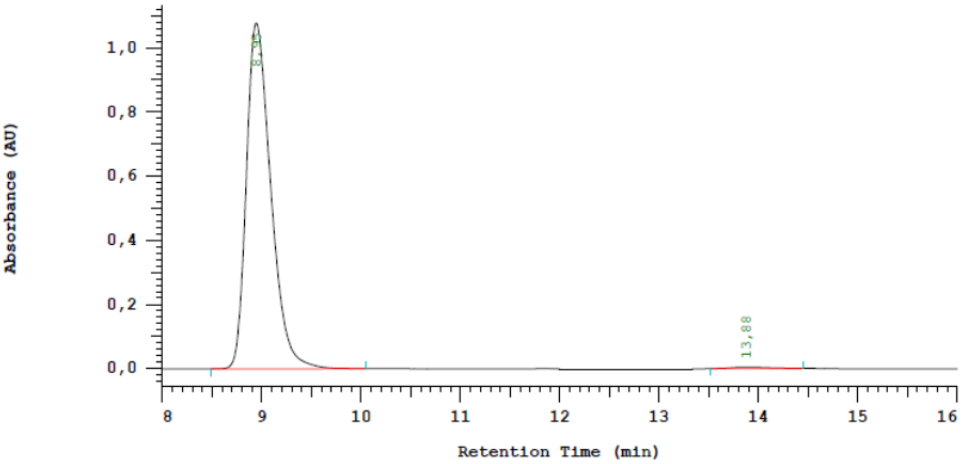
No.	RT	Area	Area %
1	10,73	6753701	96,571
2	15,92	239836	3,429
		6993537	100,000



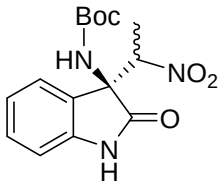
3n



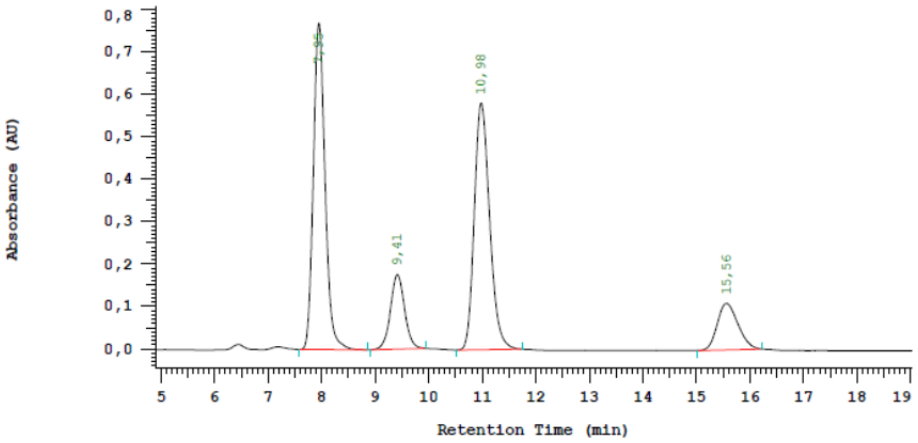
No.	RT	Area	Area %
1	8,97	8202350	50,038
2	13,79	8189796	49,962
		16392146	100,000



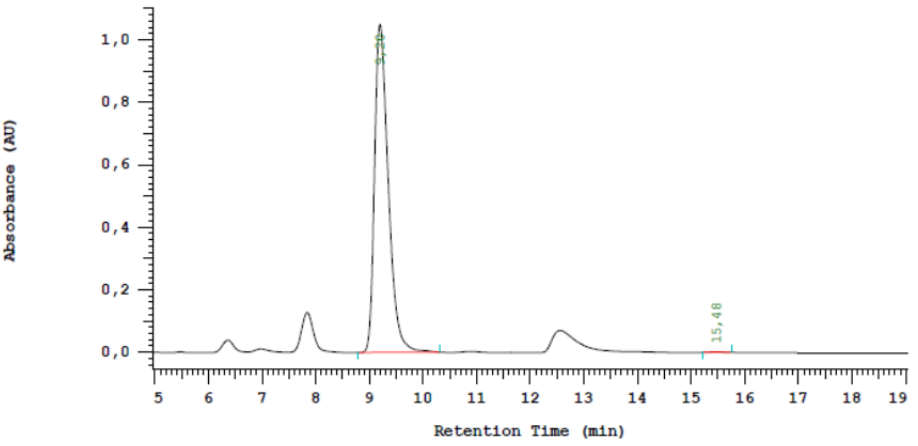
No.	RT	Area	Area %
1	8,95	9216366	99,365
2	13,88	58889	0,635
		9275255	100,000



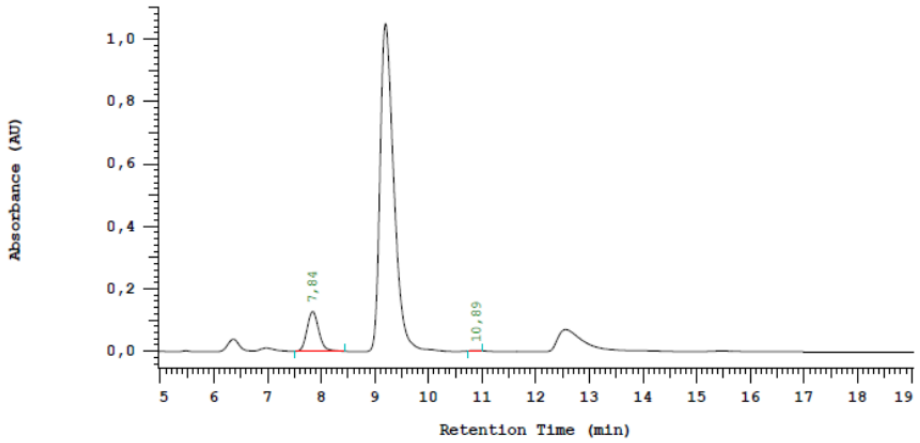
6a



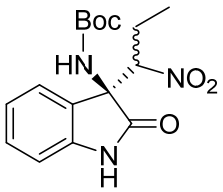
No.	RT	Area	Area %
1	7,95	5871660	39,809
2	9,41	1614931	10,949
3	10,98	5792594	39,273
4	15,56	1470269	9,968
		14749454	100,000



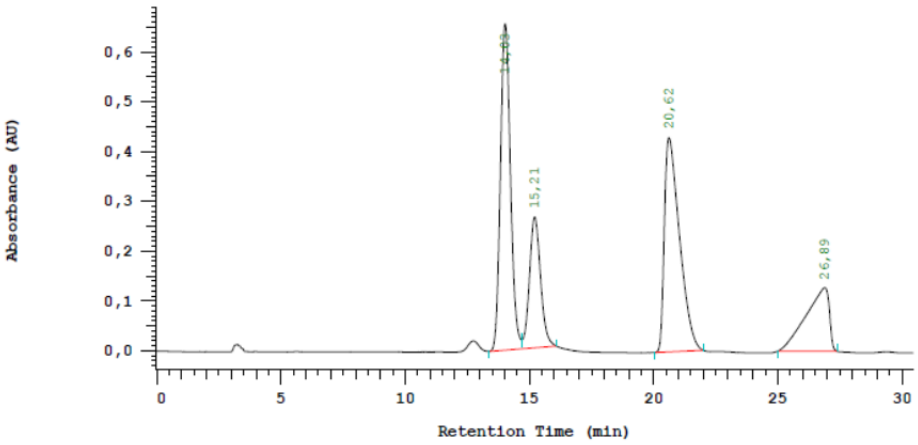
No.	RT	Area	Area %
1	9,20	9329764	99,903
2	15,48	9013	0,097
		9338777	100,000



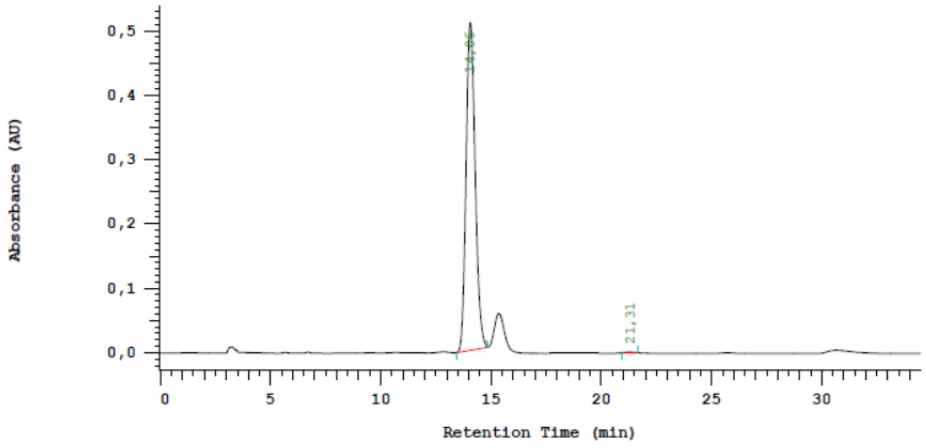
No.	RT	Area	Area %
1	7,84	971006	99,528
2	10,89	4608	0,472
		975614	100,000



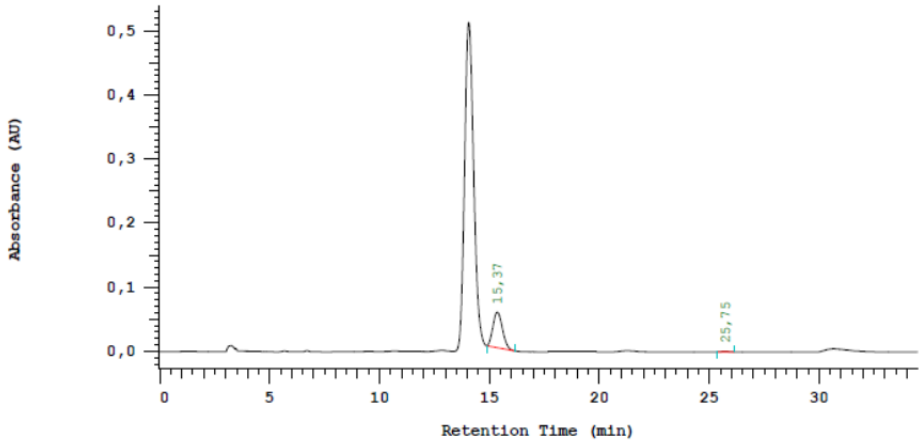
7a



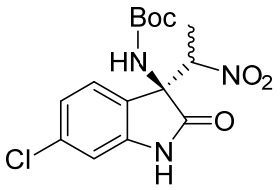
No.	RT	Area	Area %
1	14,03	9085546	34,386
2	15,21	4094374	15,496
3	20,62	9056690	34,276
4	26,89	4185997	15,842
		26422607	100,000



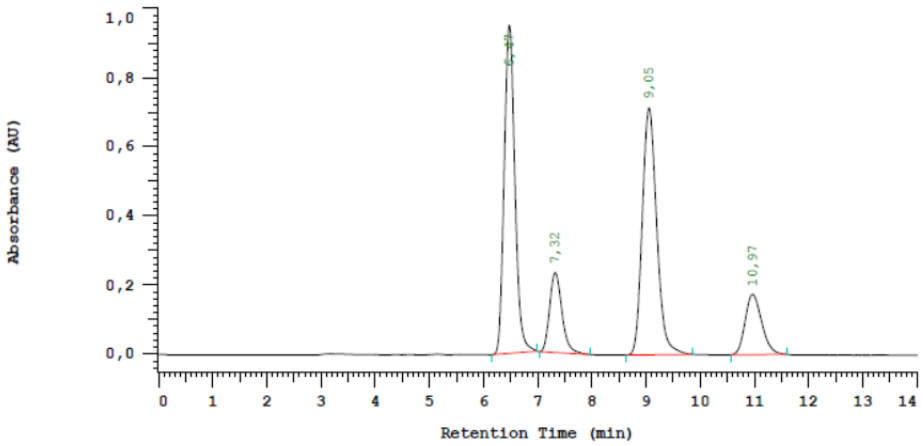
No.	RT	Area	Area %
1	14,06	7212816	99,804
2	21,31	14150	0,196
		7226966	100,000



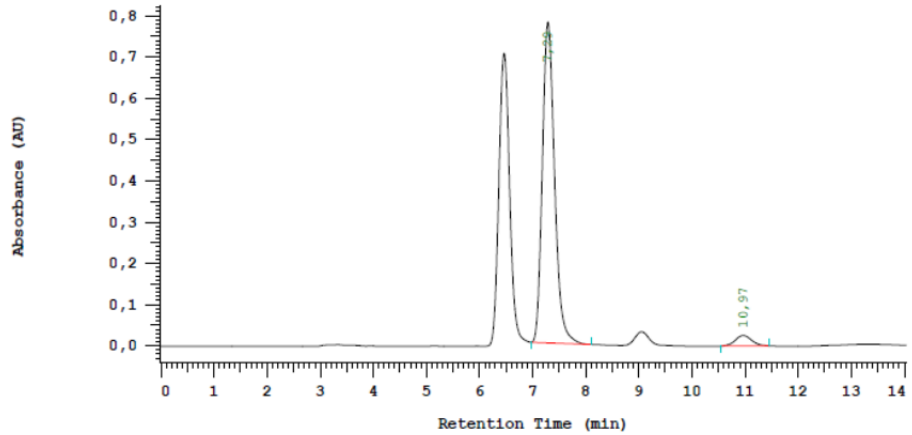
No.	RT	Area	Area %
1	15,37	836580	99,003
2	25,75	8420	0,997
		845000	100,000



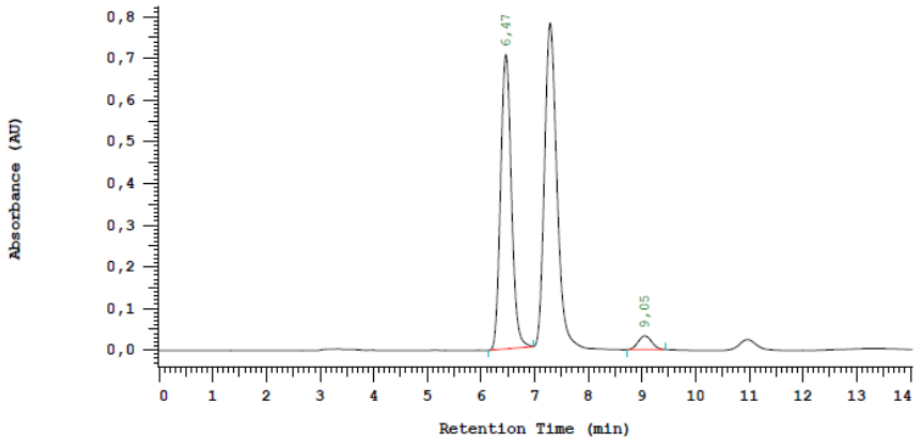
6k



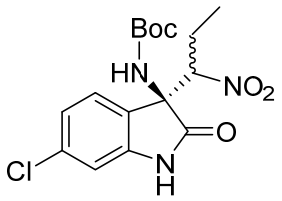
No.	RT	Area	Area %
1	6,47	6495834	38,737
2	7,32	1827124	10,896
3	9,05	6593635	39,320
4	10,97	1852431	11,047
		16769024	100,000



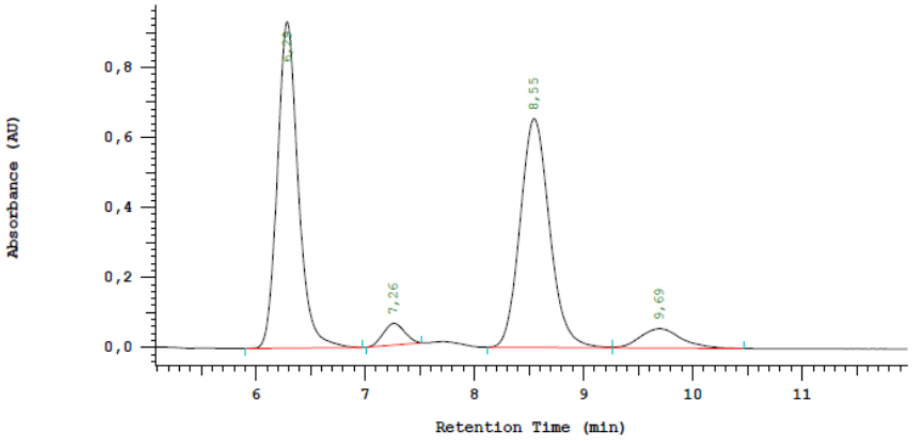
No.	RT	Area	Area %
1	7,29	6183790	95,835
2	10,97	268776	4,165
		6452566	100,000



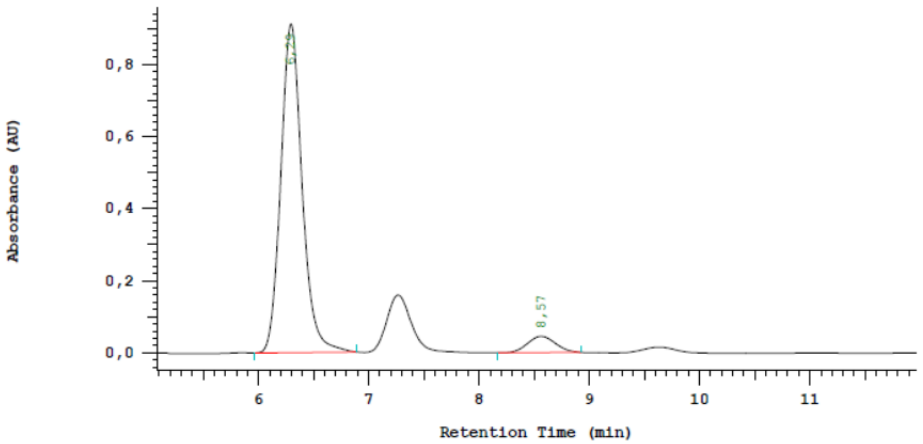
No.	RT	Area	Area %
1	6,47	4932579	94,419
2	9,05	291547	5,581
		5224126	100,000



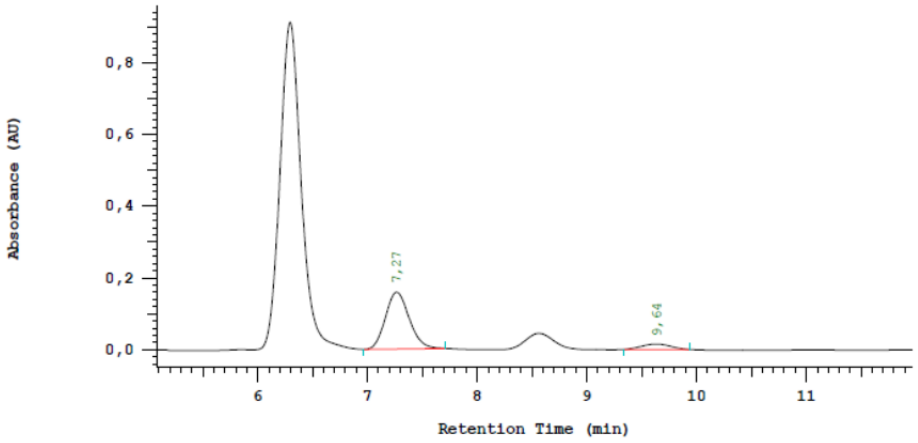
7k



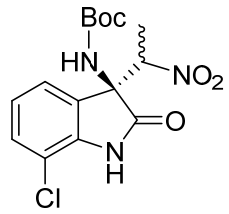
No.	RT	Area	Area %
1	6,29	6192657	46,019
2	7,26	417839	3,105
3	8,55	6124110	45,509
4	9,69	722238	5,367
		13456844	100,000



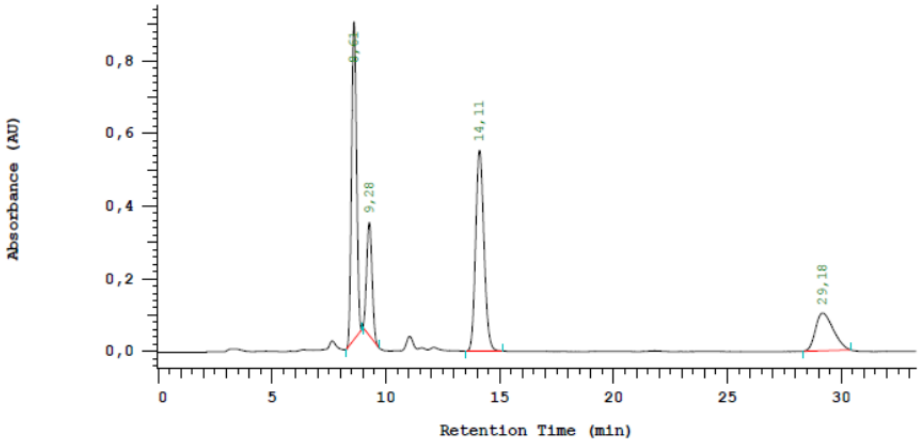
No.	RT	Area	Area %
1	6,29	6130985	93,922
2	8,57	396783	6,078
		6527768	100,000



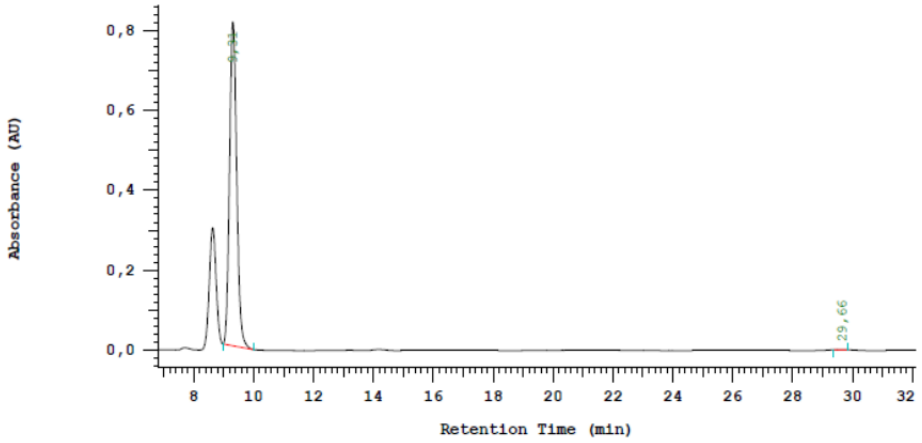
No.	RT	Area	Area %
1	7,27	1192955	89,386
2	9,64	141656	10,614
		1334611	100,000



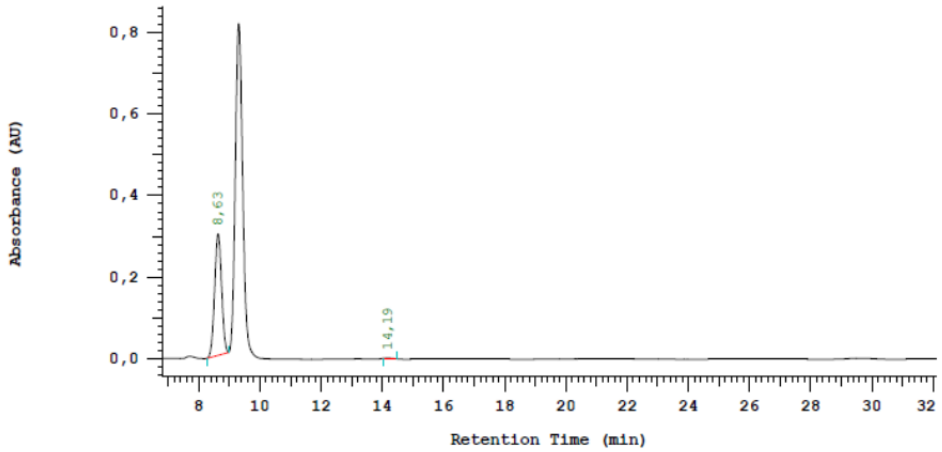
6l



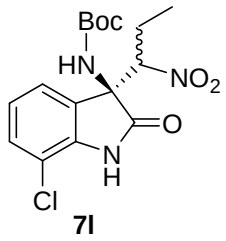
No.	RT	Area	Area %
1	8,61	6501619	34,503
2	9,28	2567359	13,625
3	14,11	6987628	37,083
4	29,18	2786799	14,789
		18843405	100,000



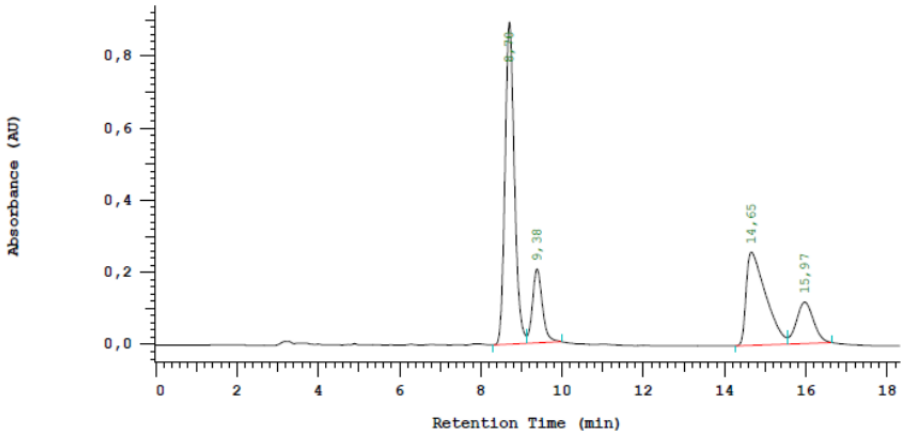
No.	RT	Area	Area %
1	9,31	6687116	99,934
2	29,66	4392	0,066
		6691508	100,000



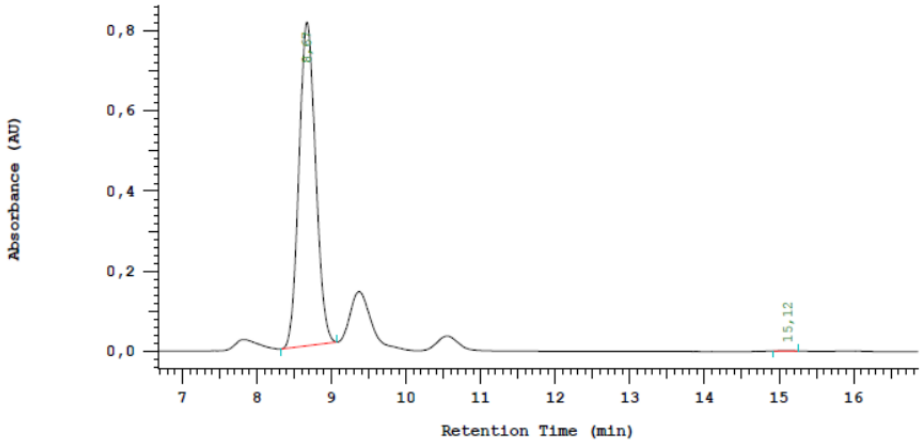
No.	RT	Area	Area %
1	8,63	2328697	99,470
2	14,19	12399	0,530
		2341096	100,000



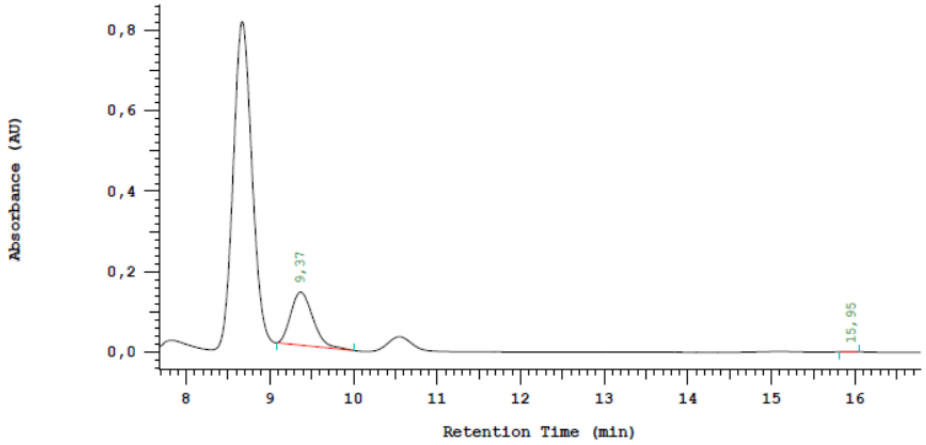
7l



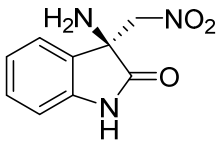
No.	RT	Area	Area %
1	8,70	7142709	48,182
2	9,38	1725965	11,643
3	14,65	4286676	28,916
4	15,97	1669156	11,259
		14824506	100,000



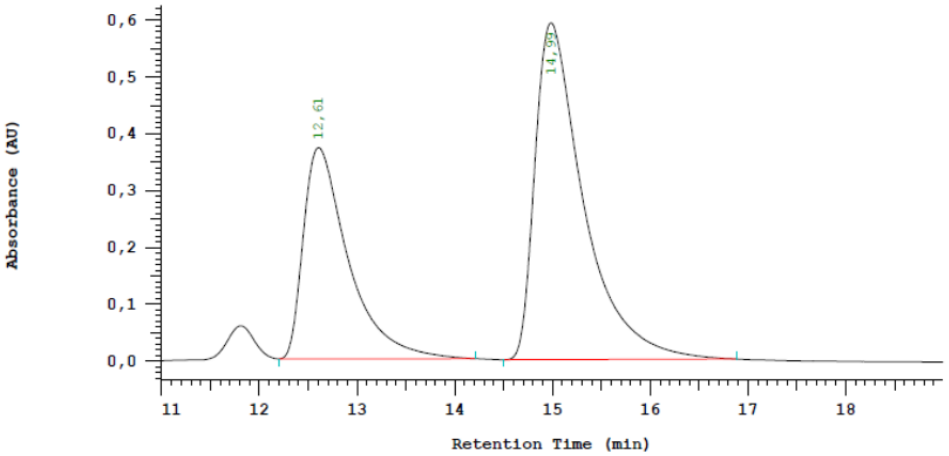
No.	RT	Area	Area %
1	8,67	6243861	99,917
2	15,12	5158	0,083
		6249019	100,000



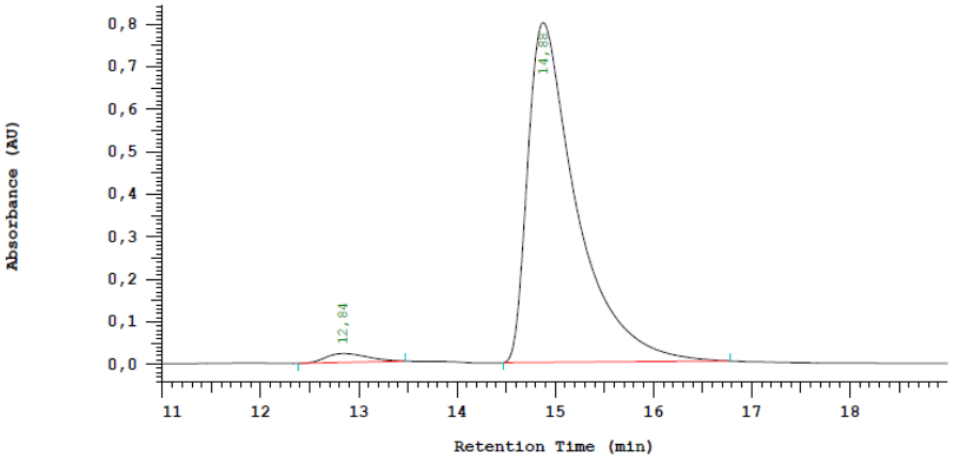
No.	RT	Area	Area %
1	9,37	1214954	99,910
2	15,95	1095	0,090
		1216049	100,000



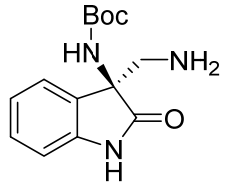
8



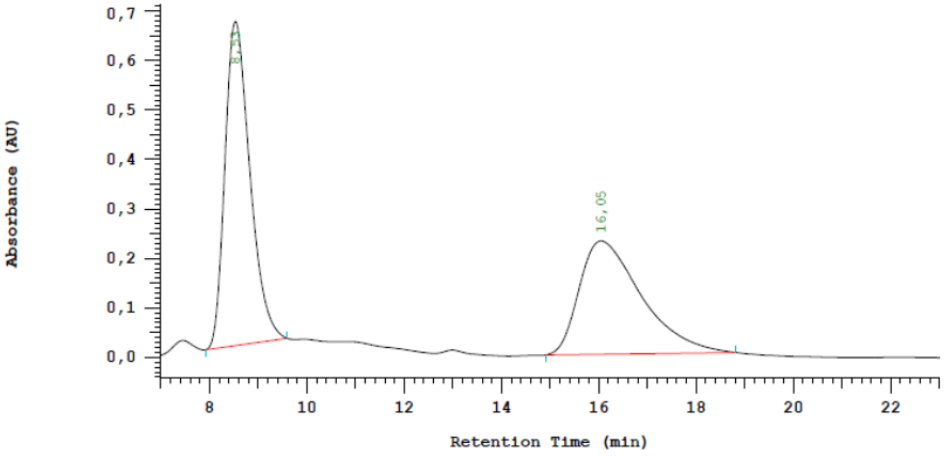
No.	RT	Area	Area %
1	12,61	5944486	36,755
2	14,99	10228991	63,245
		16173477	100,000



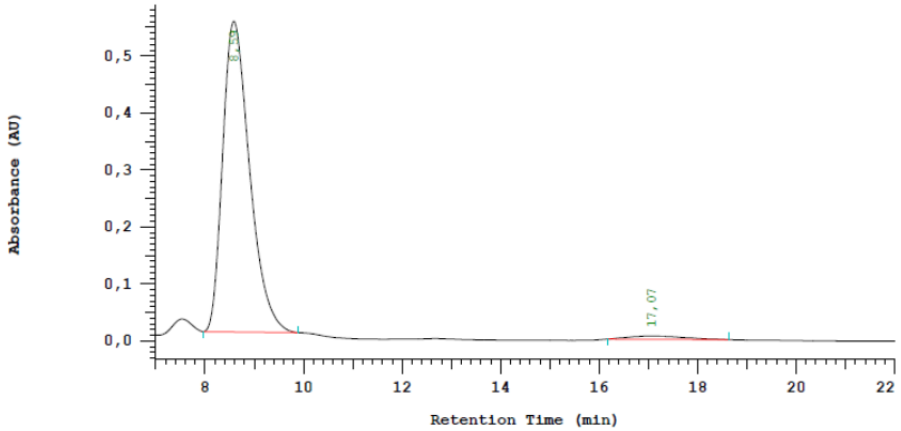
No.	RT	Area	Area %
1	12,84	306491	2,176
2	14,88	13780825	97,824
		14087316	100,000



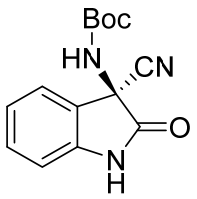
9



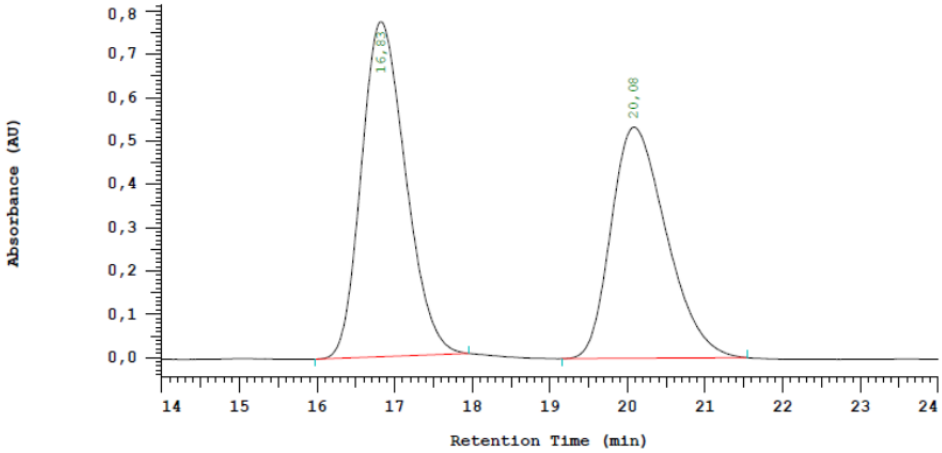
No.	RT	Area	Area %
1	8,53	11689984	53,547
2	16,05	10141208	46,453
		21831192	100,000



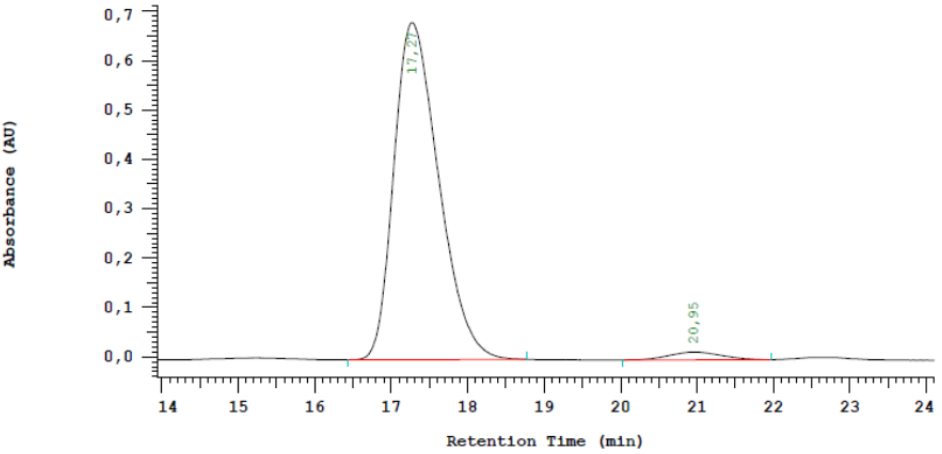
No.	RT	Area	Area %
1	8,59	10366628	97,844
2	17,07	228476	2,156
		10595104	100,000



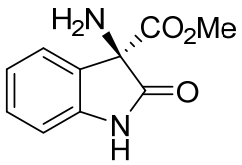
12



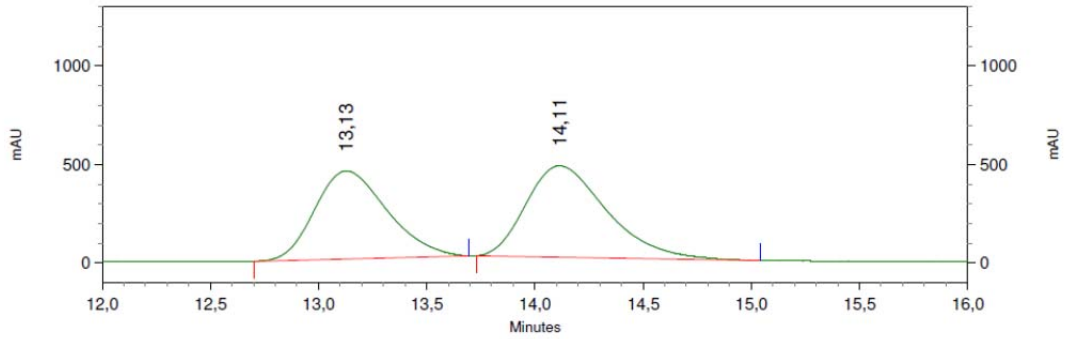
No.	RT	Area	Area %
1	16,83	15301796	53,653
2	20,08	13218218	46,347
		28520014	100,000



No.	RT	Area	Area %
1	17,27	13886897	97,396
2	20,95	371345	2,604
		14258242	100,000

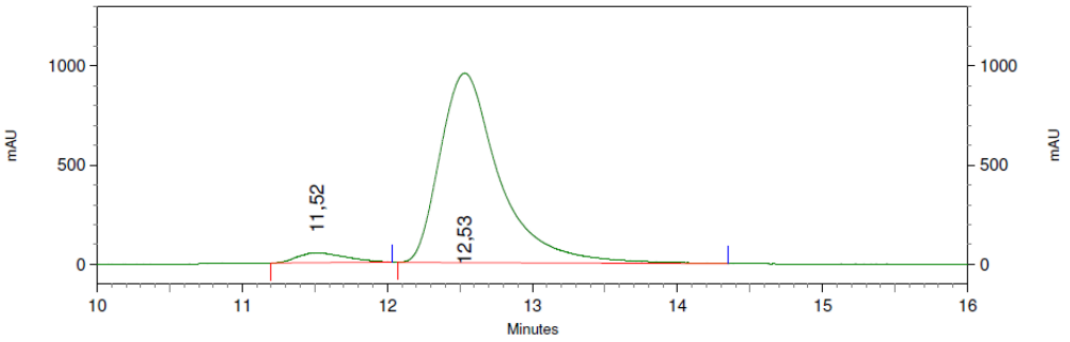


13



1: 211 nm, 4 nm Results

Retention Time	Area	Area Percent
13,13	41518833	46,345
14,11	48066914	53,655



1: 265 nm, 4 nm Results

Retention Time	Area	Area Percent
11,52	4648003	4,112
12,53	108397210	95,888