Electronic Supplementary Material (ESI) for Chemical Science.

A General Approach to 2,2-Disubstituted Indoxyls: Total Synthesis of Brevianamide A and Trigonoliimine C

Fan Xu, Myles W. Smith*

Department of Biochemistry, UT Southwestern

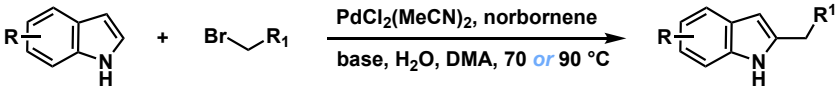
*myles.smith@utsouthwestern.edu

1. General Information

All reactions were carried out under an argon atmosphere with dry solvents under anhydrous conditions, unless otherwise stated. Dry methylene chloride (CH_2Cl_2), tetrahydrofuran (THF), diethyl ether (Et_2O), and toluene (PhMe) were obtained by passing commercially available pre-dried, oxygen-free formulations through activated alumina columns; acetonitrile (MeCN), *N,N*-dimethylformamide (DMF), and ethanol (EtOH) were purchased in anhydrous form from Sigma–Aldrich, Acros, or Fisher and used as received; 2,2,2-trifluoroethanol (TFE), 1,1,1,3,3,3-hexafluoroisopropanol (HFIP), and acetic acid (AcOH) were purchased from Oakwood and used as received; triethylamine (NEt_3) was purchased from Fisher and used as received. Yields refer to chromatographically and spectroscopically (^1H and ^{13}C NMR) homogeneous materials, unless otherwise stated. Reagents were purchased at the highest commercial quality and used without further purification, unless otherwise stated. Reactions were magnetically stirred and monitored by thin-layer chromatography (TLC) carried out on 0.25 mm E. Merck silica gel plates (60 F_{254}) using UV light and an aqueous solution of cerium ammonium sulfate and ammonium molybdate and heat as visualizing agents. Preparative TLC was carried out on 0.25 mm E. Merck silica gel plates (60 F_{254}). SiliCycle silica gel (60 Å, academic grade, particle size 40–63 μm) was used for flash column chromatography. NMR spectra were recorded on Varian MR400, Bruker AN400 and AN600 instruments and calibrated using residual undeuterated solvent as an internal reference. The following abbreviations are used to explain multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, p = pentet, h = hextet, m = multiplet, br = broad, app = apparent. Low-resolution mass spectroscopic data were acquired on an AB Sciex QTRAP-4500 LC/MS. High-resolution mass spectrometric data were acquired on Shimadzu 9030 qTOF mass spectrometer in positive ion mode. HPLC analyses were performed on an Agilent 1200 Series system using a CHIRALCEL OD-H column. Optical rotation data were recorded on a Rudolph Research Analytical Autopol® IV Polarimeter.

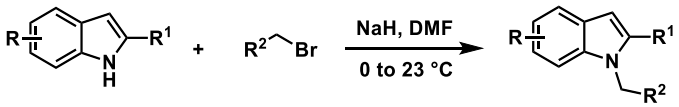
2. General Procedures

(i) General Procedure A for Indole C-2 Alkylation:



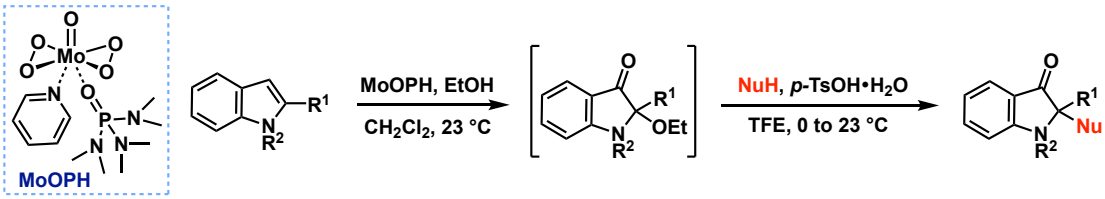
Using a slightly modified literature procedure,[1] a flask equipped with a magnetic stir bar and a rubber septum was charged with indole substrate (1.0 equiv), norbornene (2.0 equiv), the base [K_2CO_3 (2.0 equiv), $KHCO_3$ (3.0 equiv), or K_2HPO_4 (3.0 equiv) as indicated], and $PdCl_2(MeCN)_2$ (0.1 equiv). The flask was evacuated and backfilled with argon three times. DMA (0.3–0.5 M in substrate) and H_2O (2.5 equiv) were added to the flask sequentially, and the reaction vessel evacuated briefly and backfilled with argon three further times. The alkyl bromide (2.0 equiv) was then added via syringe, and the reaction mixture was placed in an oil bath preheated to 70 °C or 90 °C, as indicated. The reaction was stirred at this temperature overnight until completion or no further progress (TLC or ^{1}H NMR). The reaction mixture was then cooled to 23 °C and passed through a pad of celite, washing with ethyl acetate (~30 mL). The filtrate was washed with brine twice, dried over Na_2SO_4, filtered, and concentrated in vacuo. The resulting crude product was chromatographed on silica gel to give the C2-alkylated indole.

(ii) General Procedure B for Indole N-Alkylation:



To a solution of indole substrate (1.0 equiv) in DMF (0.1 M) was added NaH (1.2 equiv) at 0 °C. The reaction mixture was stirred at 0 °C for 30 min and then alkyl bromide (1.2 equiv) was added. The reaction mixture was stirred at 0 °C and warm to 23 °C slowly until full conversion of the indole. The reaction was quenched with brine and extracted with ethyl acetate (2 × 10 mL). The combined organic layers were washed with brine, dried over Na_2SO_4, filtered, and concentrated under vacuum. The resulting crude product was chromatographed on silica gel to give the desired product.

(iii) General Procedure C for Indoxyl Synthesis:

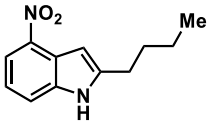


Step 1: To a solution of indole substrate (0.1 mmol) in CH_2Cl_2 (2.0 mL) and EtOH (2.0 mL) was added MoOPH (2.0 equiv) under argon. The flask was covered with aluminum foil and stirred at 23 °C overnight. Upon completion of the reaction (TLC), the reaction mixture was transferred to a separatory funnel containing saturated aq. $NaHCO_3$ (20 mL) and extracted with

CH_2Cl_2 (10 mL). The aqueous layer was re-extracted with CH_2Cl_2 (2 × 10 mL). The combined organic layers were washed with brine, dried over Na_2SO_4, filtered, and concentrated under vacuum. The crude material was used in the next step directly.

Step 2: The crude material obtained in the previous step was dissolved in TFE (2.0 mL) and then the nucleophile (3.0 equiv or 5.0 equiv) was added. The resulting solution was cooled to 0 °C. A solution of *p*-TsOH•H_2O in TFE (10 mg/mL, 190 μL, 0.1 equiv) was added to the solution slowly. The solution was stirred at 0 °C and warm to 23 °C gradually. Upon completion of the reaction (typically 1–2 h; TLC), the reaction mixture was transferred to a separatory funnel containing saturated aq. $NaHCO_3$ (20 mL) and extracted with CH_2Cl_2 (10 mL). The aqueous layer was re-extracted with CH_2Cl_2 (2 × 10 mL). The combined organic layers were washed with brine, dried over Na_2SO_4, filtered, and concentrated under vacuum. The resulting crude product was chromatographed on silica gel to give the desired product.

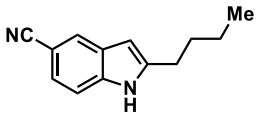
3. Preparation and Characterization of Indole Substrates



S1

Indole S1: Prepared from 4-nitroindole according to General Procedure A with 1-bromobutane and K_2HPO_4 as base in 77% yield.

Physical properties: yellow solid;
R_f = 0.15 (silica gel, 10% EtOAc/hexanes);
MS (ESI): calcd for $C_{12}H_{15}N_2O_2$ $[M + H]^+$ 219.1, found 219.1;
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.33 (br s, 1H), 8.10 (d, *J* = 8.1 Hz, 0H), 7.60 (d, *J* = 7.2 Hz, 1H), 7.17 (t, *J* = 8.0 Hz, 1H), 7.04–7.03 (m, 1H), 2.85 (t, *J* = 7.7 Hz, 2H), 1.77 (p, *J* = 7.6 Hz, 2H), 1.44 (h, *J* = 7.4 Hz, 2H), 0.97 (t, *J* = 7.4 Hz, 3H).
^{13}C NMR (151 MHz, $CDCl_3$): δ 145.8, 139.5, 138.2, 123.6, 119.9, 117.6, 117.2, 100.7, 31.1, 28.2, 22.5, 14.0.

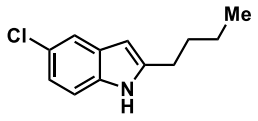


S2

Indole S2: Prepared from 5-cyanoindole according to General Procedure A with 1-bromobutane and $KHCO_3$ as base in 48% yield.

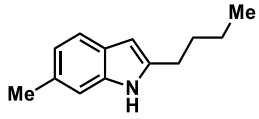
Physical properties: light yellow solid;
R_f = 0.18 (silica gel, 10% EtOAc/hexanes);
MS (ESI): calcd for $C_{13}H_{15}N_2$ $[M + H]^+$ 119.1, found 119.1;
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.25 (br s, 1H), 7.85 (s, 1H), 7.41–7.30 (m, 2H), 6.31 (s, 1H), 2.78 (t, *J* = 7.7 Hz, 2H), 1.72 (p, *J* = 7.6 Hz, 2H), 1.42 (h, *J* = 7.4 Hz, 2H), 0.96 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 142.8, 137.8, 128.8, 125.2, 124.2, 121.3, 111.2, 102.4, 100.2, 31.1, 27.9, 22.5, 13.9.



S3

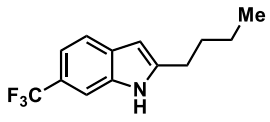
Indole S3: Prepared from 5-chloroindole according to General Procedure A with 1-bromobutane and $KHCO_3$ as base in 58% yield. ^{1}H NMR data matches those previously reported.[2]



S4

Indole S4: Prepared from 6-methylindole according to General Procedure A with 1-bromobutane and K_2CO_3 as base in 18% yield.

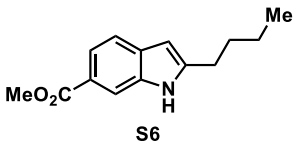
Physical properties: light yellow solid;
R_f = 0.41 (silica gel, 10% EtOAc/hexanes);
MS (ESI): calcd for $C_{13}H_{18}N$ $[M + H]^+$ 188.1, found 188.1;
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.72 (br s, 1H), 7.40 (d, *J* = 8.0 Hz, 1H), 7.09 (s, 1H), 6.90 (d, *J* = 7.9 Hz, 1H), 6.36–6.03 (m, 1H), 2.73 (t, *J* = 7.6 Hz, 2H), 2.44 (s, 3H), 1.69 (p, *J* = 7.6 Hz, 2H), 1.41 (h, *J* = 7.4 Hz, 2H), 0.95 (t, *J* = 7.3 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$): δ 139.4, 136.4, 130.7, 126.7, 121.3, 119.5, 110.5, 99.3, 31.4, 28.1, 22.5, 21.8, 14.0.



S5

Indole S5: Prepared from 6-(trifluoromethyl)indole according to General Procedure A with 1-bromobutane and K_2CO_3 as base in 17% yield.

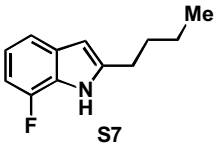
Physical properties: light yellow solid;
R_f = 0.38 (silica gel, 10% EtOAc/hexanes);
MS (ESI): calcd for $C_{13}H_{15}F_3N$ $[M + H]^+$ 242.1, found 242.1;
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.06 (br s, 1H), 7.62–7.53 (m, 2H), 7.32 (d, *J* = 8.3 Hz, 1H), 6.31 (d, *J* = 2.2 Hz, 1H), 2.79 (t, *J* = 7.6 Hz, 2H), 1.73 (p, *J* = 7.6 Hz, 2H), 1.43 (h, *J* = 7.3 Hz, 2H), 0.97 (t, *J* = 7.4 Hz, 3H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 143.1, 134.8, 131.4, 125.5 (q, *J* = 271.4 Hz), 123.1 (q, *J* = 31.7 Hz), 120.0, 116.5 (q, *J* = 3.5 Hz), 107.8 (q, *J* = 4.4 Hz), 100.0, 31.2, 28.1, 22.5, 14.0.
^{19}F NMR (565 MHz, $CDCl_3$): δ -60.3.



S6

Indole S6: Prepared from methyl indole-6-carboxylate according to General Procedure A with 1-bromobutane and $KHCO_3$ as base in 39% yield.

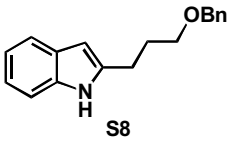
Physical properties: light yellow solid;
R_f = 0.2 (silica gel, 10% EtOAc/hexanes);
MS (ESI): calcd for $C_{14}H_{18}NO_2$ $[M + H]^+$ 232.1, found 232.0;
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.23 (br s, 1H), 8.07 (s, 1H), 7.77 (dd, *J* = 8.3, 1.5 Hz, 1H), 7.53 (d, *J* = 8.3 Hz, 1H), 6.29 (dd, *J* = 2.1, 1.0 Hz, 1H), 3.93 (s, 3H), 2.79 (t, *J* = 7.7 Hz, 2H), 1.73 (p, *J* = 7.5 Hz, 2H), 1.43 (h, *J* = 7.3 Hz, 2H), 0.96 (t, *J* = 7.4 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$): δ 168.9, 144.5, 135.3, 133.0, 122.1, 120.7, 119.2, 112.9, 99.9, 52.0, 31.1, 28.1, 22.5, 13.9.



S7

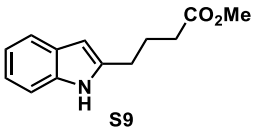
Indole S7: Prepared from 7-fluoroindole according to General Procedure A with 1-bromobutane and K_2CO_3 as base in 17% yield.

Physical properties: light yellow oil;
R_f = 0.44 (silica gel, 10% EtOAc/hexanes);
MS (ESI): calcd for $C_{12}H_{15}FN$ $[M + H]^+$ 199.1, found 199.2;
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.03 (br s, 1H), 7.28 (d, *J* = 7.9 Hz, 1H), 7.00–6.94 (m, 1H), 6.85–6.80 (m, 1H), 6.27 (t, *J* = 2.7 Hz, 1H), 2.77 (t, *J* = 7.7 Hz, 2H), 1.72 (p, *J* = 7.6 Hz, 2H), 1.43 (h, *J* = 7.4 Hz, 2H), 0.96 (t, *J* = 7.4 Hz, 2H).
^{13}C NMR (151 MHz, $CDCl_3$): δ 149.2 (d, $J_{C\text{-}F}$ = 242.4 Hz), 140.9, 132.6 (d, $J_{C\text{-}F}$ = 5.3 Hz), 124.0 (d, $J_{C\text{-}F}$ = 12.7 Hz), 119.9 (d, $J_{C\text{-}F}$ = 6.3 Hz), 115.6 (d, $J_{C\text{-}F}$ = 3.2 Hz), 106.0 (d, $J_{C\text{-}F}$ = 15.9 Hz), 100.4 (d, $J_{C\text{-}F}$ = 2.5 Hz), 31.4, 28.0, 22.5, 14.0.
^{19}F NMR (376 MHz, $CDCl_3$): δ -136.0.



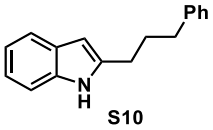
S8

Indole S8: Prepared from indole according to General Procedure A with benzyl 3-bromopropyl ether and K_2CO_3 as base in 25% yield. ^{1}H NMR data matches those previously reported.[3]



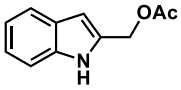
S9

Indole S9: Prepared from indole according to General Procedure A with methyl 4-bromobutanoate and K_2CO_3 as base in 42% yield. ^{1}H NMR data matches those previously reported.[2]



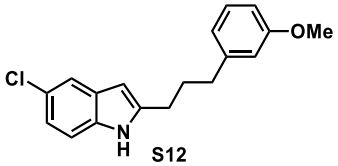
S10

Indole S10: Prepared from indole according to General Procedure A with 1-bromo-3-phenylpropane and K_2CO_3 as base in 65% yield. ^{1}H NMR data matches those previously reported.[4]



S11

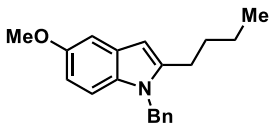
Indole S11: Prepared according to a literature procedure.[5] ^{1}H NMR data matches those previously reported.



S12

Indole S12: Prepared from 5-chloroindole according to General Procedure A with 1-(3-bromopropyl)-3-methoxybenzene[6] and K_2CO_3 as base in 33% yield.

Physical properties: light yellow oil;
R_f = 0.18 (silica gel, 10% EtOAc/hexanes);
MS (ESI): calcd for $C_{18}H_{19}ClNO$ $[M + H]^+$ 300.1, found 300.1;
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.83 (br s, 1H), 7.50 (d, *J* = 2.0 Hz, 1H), 7.25 (t, *J* = 7.8 Hz, 1H), 7.17 (d, *J* = 8.6 Hz, 1H), 7.08 (dd, *J* = 8.5, 2.0 Hz, 1H), 6.85–6.71 (m, 3H), 6.21 (dd, *J* = 2.2, 1.0 Hz, 1H), 3.82 (s, 3H), 2.75 (t, *J* = 7.8 Hz, 2H), 2.69 (t, *J* = 7.5 Hz, 2H), 2.05 (p, *J* = 7.6 Hz, 2H). **^{13}C NMR** (151 MHz, $CDCl_3$): δ 159.8, 143.4, 141.1, 134.3, 130.0, 129.5, 125.3, 121.3, 121.0, 119.3, 114.5, 111.4, 111.3, 99.6, 55.3, 35.4, 30.5, 27.7.

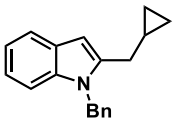


S13

Indole S13: Prepared according to General Procedure B with benzyl bromide in 61% yield.

Physical properties: colorless oil;
R_f = 0.48 (silica gel, 10% EtOAc/hexanes);
MS (ESI): calcd for $C_{20}H_{24}NO$ $[M + H]^+$ 294.2, found 294.2;

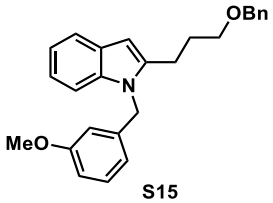
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.30–7.22 (m, 3H), 7.09–7.02 (m, 2H), 6.76 (dd, *J* = 8.8, 2.5 Hz, 1H), 6.29 (s, 1H), 5.29 (s, 2H), 3.85 (s, 3H), 2.66 (t, *J* = 7.7 Hz, 2H), 1.67 (p, *J* = 7.5 Hz, 2H), 1.41 (h, *J* = 7.4 Hz, 2H), 0.92 (t, *J* = 7.4 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$): δ 154.2, 142.2, 138.2, 132.5, 128.9, 128.4, 127.3, 126.0, 110.6, 110.1, 102.2, 99.2, 56.0, 46.6, 30.8, 26.6, 22.6, 14.0.



S14

Indole S14: Prepared according to General Procedure B with benzyl bromide in 82% yield.

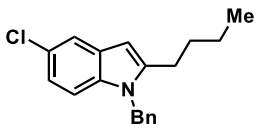
Physical properties: light yellow oil;
R_f = 0.58 (silica gel, 10% EtOAc/hexanes);
MS (ESI): calcd for $C_{19}H_{20}N$ $[M + H]^+$ 262.2, found 262.2;
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.64–7.57 (m, 1H), 7.31–7.17 (m, 4H), 7.14–7.06 (m, 2H), 7.00–6.92 (m, 2H), 6.53 (d, *J* = 1.1 Hz, 1H), 5.33 (s, 2H), 2.60 (d, *J* = 6.7 Hz, 2H), 1.17–0.99 (m, 1H), 0.70–0.55 (m, 2H), 0.31–0.13 (m, 2H).
^{13}C NMR (101 MHz, $CDCl_3$): δ 141.1, 138.1, 137.3, 128.9, 128.3, 127.3, 126.0, 121.0, 120.0, 119.6, 109.4, 100.0, 46.6, 31.7, 9.7, 5.0.



S15

Indole S15: Prepared from **S8** according to General Procedure B with 3-methoxybenzyl bromide in 40% yield.

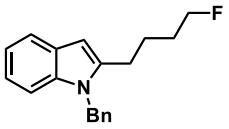
Physical properties: yellow oil;
R_f = 0.42 (silica gel, 10% EtOAc/hexanes);
MS (ESI): calcd for $C_{26}H_{28}NO_2$ $[M + H]^+$ 385.2, found 385.2;
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.59–7.54 (m, 1H), 7.37–7.28 (m, 5H), 7.22–7.04 (m, 4H), 6.75 (dd, *J* = 8.5, 2.8 Hz, 1H), 6.55–6.46 (m, 2H), 6.33 (s, 1H), 5.30 (s, 2H), 4.48 (s, 2H), 3.69 (s, 3H), 3.54 (t, *J* = 6.2 Hz, 2H), 2.80 (t, *J* = 7.6 Hz, 2H), 2.07–1.92 (m, 2H).
^{13}C NMR (151 MHz, $CDCl_3$): δ 160.1, 140.8, 139.8, 138.6, 137.3, 129.9, 128.5, 128.2, 127.8, 127.7, 121.0, 120.0, 119.6, 118.3, 112.4, 112.0, 109.4, 99.7, 73.1, 69.5, 55.3, 46.4, 28.8, 23.4.



S16

Indole S16: Prepared from **S3** according to General Procedure B with benzyl bromide in 35% yield.

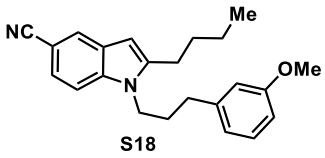
Physical properties: colorless oil;
R_f = 0.65 (silica gel, 10% EtOAc/hexanes);
MS (ESI): calcd for $C_{19}H_{21}ClN$ $[M + H]^+$ 298.1, found 298.1;
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.52 (d, *J* = 1.9 Hz, 1H), 7.30–7.22 (m, 3H), 7.11–7.00 (m, 2H), 6.97–6.89 (m, 2H), 6.29 (d, *J* = 1.1 Hz, 1H), 5.29 (s, 2H), 2.65 (t, *J* = 7.7 Hz, 2H), 1.72–1.60 (m, 2H), 1.45–1.34 (m, 2H), 0.91 (t, *J* = 7.3 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$): δ 142.9, 137.5, 135.6, 128.8, 128.4, 128.2, 127.4, 125.8, 121.0, 119.2, 110.3, 99.1, 46.6, 30.4, 26.5, 22.5, 13.8.



S17

Indole S17: Prepared according to General Procedure B with benzyl bromide in 87% yield.

Physical properties: light yellow oil;
R_f = 0.52 (silica gel, 10% EtOAc/hexanes);
MS (ESI): calcd for $C_{19}H_{21}FN$ $[M + H]^+$ 282.2, found 282.2;
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.55–7.45 (m, 1H), 7.20–7.08 (m, 4H), 7.03–6.99 (m, 2H), 6.92–6.84 (m, 2H), 6.28 (d, *J* = 1.0 Hz, 1H), 5.24 (s, 2H), 4.42–4.35 (m, 1H), 4.28 (t, *J* = 5.8 Hz, 1H), 2.67–2.59 (m, 2H), 1.78–1.60 (m, 4H).
^{13}C NMR (101 MHz, $CDCl_3$): δ 140.6, 138.0, 137.4, 128.9, 128.2, 127.4, 126.0, 121.1, 120.0, 119.7, 109.4, 99.8, 83.9 (d, $J_{C\text{-}F}$ = 164.9 Hz), 46.5, 30.1 (d, $J_{C\text{-}F}$ = 19.7 Hz), 26.4, 24.3 (d, $J_{C\text{-}F}$ = 4.9 Hz).
^{19}F NMR (376 MHz, $CDCl_3$): δ -218.6.

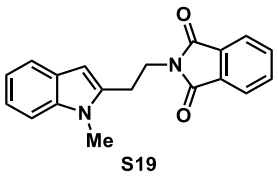


S18

Indole S18: Prepared from **S2** according to General Procedure B with 1-(3-bromopropyl)-3-methoxybenzene[6] in 72% yield.

Physical properties: colorless oil;
R_f = 0.22 (silica gel, 10% EtOAc/hexanes);
MS (ESI): calcd for $C_{23}H_{27}N_2O$ $[M + H]^+$ 347.2, found 347.1;
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.76 (d, *J* = 1.0 Hz, 1H), 7.26 (dd, *J* = 8.5, 1.6 Hz, 1H), 7.20–7.12 (m, 1H), 7.12–7.08 (m, 1H), 6.72–6.68 (m, 2H), 6.64 (t, *J* = 2.1 Hz, 1H), 6.23 (d, *J* = 1.0 Hz, 1H), 4.04–3.95 (m, 2H), 3.72 (s, 3H), 2.66–2.51 (m, 4H), 1.99 (p, *J* = 7.5 Hz, 2H), 1.70–1.56 (m, 2H), 1.36 (h, *J* = 7.4 Hz, 2H), 0.89 (t, *J* = 7.4 Hz, 3H).

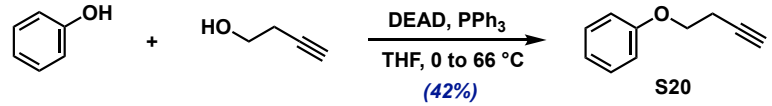
^{13}C NMR (151 MHz, $CDCl_3$): δ 159.9, 143.8, 142.2, 138.3, 129.8, 128.0, 125.2, 123.7, 121.3, 120.7, 114.4, 111.5, 109.8, 102.1, 99.9, 55.3, 42.8, 33.1, 31.3, 30.5, 26.5, 22.7, 14.0.



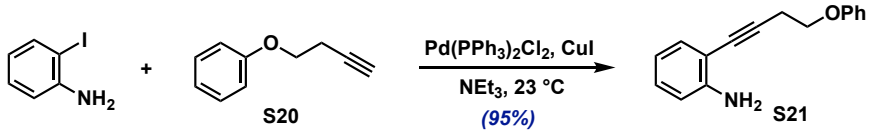
S19

Indole S19: Prepared from **23** according to General Procedure B with iodomethane in 70% yield.

Physical properties: grey solid;
R_f = 0.14 (silica gel, 10% EtOAc/hexanes);
MS (ESI): calcd for $C_{19}H_{17}N_2O_2$ $[M + H]^+$ 305.1, found 305.1;
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.85 (dd, *J* = 5.4, 3.0 Hz, 2H), 7.72 (dd, *J* = 5.5, 3.1 Hz, 2H), 7.52 (d, *J* = 7.8 Hz, 1H), 7.29 (d, *J* = 8.1 Hz, 1H), 7.18 (t, *J* = 7.0 Hz, 1H), 7.07 (t, *J* = 7.4 Hz, 1H), 6.36 (s, 1H), 4.03 (t, *J* = 7.8 Hz, 2H), 3.79 (s, 3H), 3.18 (t, *J* = 7.8 Hz, 2H).
^{13}C NMR (151 MHz, $CDCl_3$): δ 168.3, 137.7, 136.5, 134.2, 132.2, 127.8, 123.5, 121.2, 120.2, 119.5, 109.1, 100.3, 37.1, 29.7, 26.1.



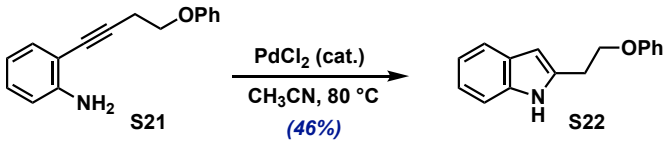
Alkyne S20: To a solution of phenol (1.4 g, 14.9 mmol, 1.0 equiv), PPh_3 (3.9 g, 14.9 mmol, 1.0 equiv) and but-3-yn-1-ol (1.4 mL, 18.5 mmol, 1.2 equiv) in THF (30 mL) was added DEAD (40% in toluene, 6.8 mL, 1.0 equiv) at 0 ºC. The mixture was stirred at reflux until completion and cooled to room temperature. The reaction mixture was concentrated, and the residue chromatographed on silica gel with hexanes/EtOAc (60:1) as the eluent to afford the desired alkyne (915 mg, 42%) mixed with small amount of phenol. ^{1}H NMR data were consistent with literature.[7]



Aniline S21: A flask equipped with a magnetic stir bar and a rubber septum was charged with 2-iodoaniline (984 mg, 4.50 mmol, 1.0 equiv), **S20** (915 mg, 5.0 mmol, 1.1 equiv), $PdCl_2(PPh_3)_2$ (70.1 mg, 0.1 mmol, 0.02 equiv), and CuI (44.0 mg, 0.23 mmol, 0.05 equiv). The flask was evacuated and backfilled with argon three times, and degassed Et_3N (10 mL) was added to the flask. The reaction was stirred at 23 °C until completion (5 h). The reaction mixture was transferred to a separatory funnel containing brine (20 mL) and extracted with CH_2Cl_2 (20 mL). The aqueous layer was re-extracted with CH_2Cl_2 (2 × 10 mL). The combined organic layers were washed with brine, dried over Na_2SO_4, filtered, and concentrated under vacuum. The resulting crude product was chromatographed on silica gel using

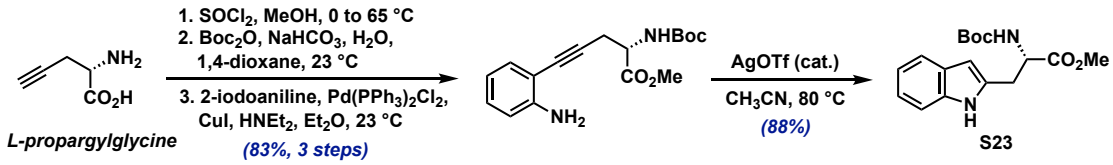
EtOAc/hexanes to give the desired product **S21** as a yellow oil (1.0 g, 95%).

Physical properties: yellow oil;
R_f = 0.27 (silica gel, 10% EtOAc/hexanes);
MS (ESI): calcd for $C_{16}H_{16}NO$ $[M + H]^+$ 238.1, found 238.1;
^{1}H NMR (600 MHz, $CDCl_3$): δ 7.33–7.28 (m, 2H), 7.25 (dd, *J* = 7.8, 1.8 Hz, 1H), 7.09 (ddd, *J* = 8.9, 7.4, 1.6 Hz, 1H), 6.97 (tt, *J* = 7.4, 1.1 Hz, 1H), 6.95–6.93 (m, 2H), 6.72–6.58 (m, 2H), 4.19 (t, *J* = 6.9 Hz, 4H), 2.96 (t, *J* = 6.9 Hz, 2H).
^{13}C NMR (151 MHz, $CDCl_3$): δ 158.6, 148.1, 132.1, 129.7, 129.4, 121.2, 117.9, 114.8, 114.3, 108.3, 91.5, 78.8, 66.3, 20.9.



Indole S22: To a solution of **S21** (1.0 g, 4.2 mmol, 1.0 equiv) in CH_3CN (12 mL) was added $PdCl_2$ (38.4 mg, 0.22 mmol, 0.05 equiv) at 23 ºC. The reaction was warmed to 80 ºC and stirred at this temperature until completion (2 h). After cooling to room temperature, the reaction mixture was concentrated and the residue chromatographed on silica gel using EtOAc/hexanes to give the desired product **S22** as a white solid (460 mg, 46%).

Physical properties: white solid;
R_f = 0.28 (silica gel, 10% EtOAc/hexanes);
MS (ESI): calcd for $C_{16}H_{16}NO$ $[M + H]^+$ 238.1, found 238.1;
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.35 (br s, 1H), 7.60 (d, *J* = 7.8 Hz, 1H), 7.42–7.31 (m, 3H), 7.18 (td, *J* = 8.1, 7.6, 1.4 Hz, 1H), 7.12 (td, *J* = 7.4, 1.2 Hz, 1H), 7.07–6.97 (m, 3H), 6.36 (d, *J* = 1.2 Hz, 1H), 4.29 (t, *J* = 6.0 Hz, 2H), 3.26 (t, *J* = 6.0 Hz, 2H).
^{13}C NMR (101 MHz, $CDCl_3$): δ 158.6, 136.8, 136.2, 129.8, 128.6, 121.5, 121.4, 120.1, 119.8, 114.8, 110.7, 100.5, 67.8, 28.5.

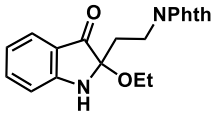


Indole S23: S23 was prepared according to the reported procedure from L-propargylglycine.[8] ^{1}H NMR data were consistent with the literature.

4. Preparation and Characterization of Indoxyl Products

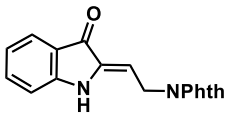
Indoxyl 24: To a solution of **23** (1.0 g, 3.4 mmol) in CH_2Cl_2 (50 mL) and EtOH (50 mL) was added MoOPH (2.9 g, 6.8 mmol, 2.0 equiv) under argon. The flask was covered with aluminum foil and stirred at 23 °C overnight. Upon completion of the reaction (TLC), the reaction mixture was transferred to a separatory funnel containing saturated aq. $NaHCO_3$ (50 mL) and extracted

with CH_2Cl_2 (50 mL). The aqueous layer was re-extracted with CH_2Cl_2 (2 × 20 mL). The combined organic layers were washed with brine, dried over Na_2SO_4, filtered, and concentrated under vacuum. The crude material was chromatographed rapidly on triethylamine-deactivated silica gel with EtOAc/hexanes to give 2-ethoxyindoxyl **24**.



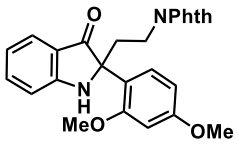
24

Physical properties: yellow solid;
R_f = 0.38 (silica gel, 30% EtOAc/hexanes);
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.83 (dd, *J* = 5.4, 3.1 Hz, 1H), 7.70 (dd, *J* = 5.5, 3.0 Hz, 1H), 7.51 (d, *J* = 7.7 Hz, 0H), 7.45 (ddd, *J* = 8.4, 7.2, 1.4 Hz, 1H), 6.84 (d, *J* = 8.1 Hz, 0H), 6.78 – 6.73 (m, 1H), 5.69 (s, 1H), 4.04 (ddd, *J* = 14.4, 10.4, 4.9 Hz, 1H), 3.88 (ddd, *J* = 14.5, 5.8, 4.0 Hz, 1H), 3.34–3.24 (m, 1H), 3.12–3.01 (m, 1H), 2.42 (ddd, *J* = 14.5, 10.4, 5.8 Hz, 1H), 1.75–1.64 (m, 1H), 0.68 (t, *J* = 7.0 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$): δ 200.2, 168.8, 159.7, 138.5, 134.1, 132.4, 125.0, 123.3, 119.2, 119.0, 111.8, 91.1, 58.9, 33.5, 33.1, 14.9.



26

Elimination Product 26:
Physical properties: yellow solid;
R_f = 0.40 (silica gel, 30% EtOAc/hexanes);
^{1}H NMR (400 MHz, DMSO-d_6): δ 9.74 (s, 1H), 7.90–7.85 (m, 2H), 7.84–7.81 (m, 2H), 7.57–7.46 (m, 2H), 7.02 (d, *J* = 8.4 Hz, 1H), 6.84 (t, *J* = 7.4 Hz, 1H), 5.69 (t, *J* = 6.9 Hz, 1H), 4.50 (d, *J* = 7.0 Hz, 2H).
^{13}C NMR (151 MHz, DMSO-d_6): δ 185.9, 168.1, 154.6, 137.6, 137.4, 134.9, 132.3, 124.8, 123.6, 120.6, 119.7, 112.3, 107.2, 35.0.

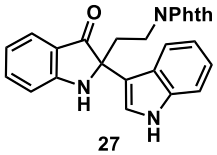


25

Indoxyl 25: Prepared from **24** (0.1 mmol) according to General Procedure C (step 2) with 1,3-dimethoxybenzene (5.0 equiv) in 95% yield.

Physical properties: yellow solid;
R_f = 0.13 (silica gel, 30% EtOAc/hexanes);
MS (ESI): calcd for $C_{26}H_{23}N_2O_5$ $[M + H]^+$ 443.1601, found 443.1627;

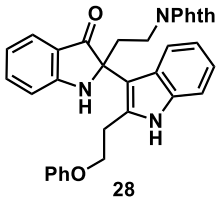
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.75 (dd, *J* = 5.4, 3.1 Hz, 2H), 7.65 (dd, *J* = 5.5, 3.1 Hz, 2H), 7.54 (d, *J* = 7.6 Hz, 1H), 7.46–7.35 (m, 2H), 6.80 (d, *J* = 8.3 Hz, 1H), 6.72 (t, *J* = 7.4 Hz, 1H), 6.46 (d, *J* = 2.5 Hz, 1H), 6.37 (dd, *J* = 8.7, 2.5 Hz, 1H), 3.86 (s, 3H), 3.79–3.70 (m, 1H), 3.74 (s, 3H), 3.69–3.60 (m, 1H), 2.56–2.49 (m, 2H).
^{13}C NMR (101 MHz, $CDCl_3$): δ 201.6, 168.1, 160.5, 160.4, 158.9, 137.4, 133.8, 132.3, 128.2, 124.8, 123.1, 120.6, 119.1, 118.5, 112.4, 104.1, 100.1, 69.6, 55.7, 55.5, 35.2, 33.8.



27

Indoxyl 27: Prepared from **24** (0.1 mmol) according to General Procedure C (step 2) with indole (3.0 equiv) in 88% yield.

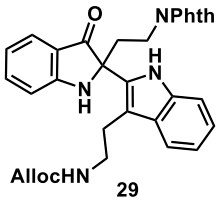
Physical properties: yellow solid;
R_f = 0.32 (silica gel, 50% EtOAc/hexanes);
MS (ESI): calcd for $C_{26}H_{19}N_3NaO_3$ $[M + Na]^+$ 444.1319, found 444.1339;
^{1}H NMR (400 MHz, DMSO-d_6): δ 11.07 (d, *J* = 2.6 Hz, 1H), 8.00 (s, 1H), 7.80 (s, 4H), 7.53 (ddd, *J* = 8.4, 7.0, 1.4 Hz, 1H), 7.42–7.35 (m, 3H), 7.31 (d, *J* = 8.1 Hz, 1H), 7.05–6.98 (m, 2H), 6.86 (ddd, *J* = 8.1, 7.0, 1.1 Hz, 1H), 6.72 (ddd, *J* = 7.7, 7.0, 0.9 Hz, 1H), 3.71–3.57 (m, 2H), 2.59–2.52 (m, 1H), 2.45–2.35 (m, 1H).
^{13}C NMR (101 MHz, DMSO-d_6): δ 206.9, 172.9, 166.4, 143.0, 142.0, 139.4, 136.8, 129.9, 129.5, 128.5, 128.1, 126.5, 125.3, 123.9, 123.2, 122.6, 117.7, 117.2, 116.9, 72.6, 39.4, 38.7.



28

Indoxyl 28: Prepared from **24** (0.1 mmol) according to General Procedure C (step 2) with **S22** (3.0 equiv) in 88% yield.

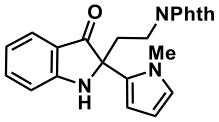
Physical properties: yellow foam;
R_f = 0.17 (silica gel, 30% EtOAc/hexanes);
MS (ESI): calcd for $C_{34}H_{27}N_3NaO_4$ $[M + Na]^+$ 564.1894, found 564,1910;
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.41 (br s, 1H), 7.91 (d, *J* = 8.1 Hz, 1H), 7.58–7.51 (m, 5H), 7.47 (ddd, *J* = 8.3, 7.1, 1.3 Hz, 1H), 7.32–7.24 (m, 2H), 7.05–6.88 (m, 7H), 6.78 (t, *J* = 7.4 Hz, 1H), 6.12 (s, 1H), 4.25–4.15 (m, 2H), 3.97 (ddd, *J* = 14.0, 8.4, 6.9 Hz, 1H), 3.82 (ddd, *J* = 14.1, 7.6, 4.4 Hz, 1H), 3.55 (ddd, *J* = 15.9, 7.1, 4.2 Hz, 1H), 3.32 (ddd, *J* = 15.8, 6.5, 4.1 Hz, 1H), 3.15 (dt, *J* = 14.1, 8.0 Hz, 1H), 2.29 (ddd, *J* = 14.2, 7.0, 4.4 Hz, 1H).
^{13}C NMR (101 MHz, $CDCl_3$): δ 201.7, 168.3, 159.8, 158.3, 137.7, 135.4, 133.9, 133.7, 131.6, 129.7, 126.3, 125.6, 122.8, 121.6, 121.5, 121.4, 119.8, 119.7, 118.9, 114.8, 112.1, 110.5, 108.3, 69.2, 67.9, 35.1, 34.0, 28.0.



29

Indoxyl 29: Prepared from **24** (0.1 mmol) according to General Procedure C (step 2) with *N*-Alloc tryptamine (3.0 equiv) in 77% yield.

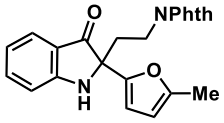
Physical properties: yellow foam;
R_f = 0.15 (silica gel, 33% EtOAc/hexanes);
MS (ESI): calcd for $C_{32}H_{28}N_4NaO_5$ $[M + Na]^+$ 571.1952, found 571.1942;
^{1}H NMR (400 MHz, $CDCl_3$): δ 9.11 (br s, 1H), 7.64 (dd, *J* = 5.5, 3.1 Hz, 2H), 7.55 (dd, *J* = 5.5, 3.1 Hz, 2H), 7.52–7.44 (m, 2H), 7.35 (d, *J* = 7.9 Hz, 1H), 7.23 (d, *J* = 8.1 Hz, 1H), 7.16 (s, 1H), 7.06 (t, *J* = 8.2 Hz, 2H), 6.95 (t, *J* = 7.5 Hz, 1H), 6.75 (t, *J* = 7.4 Hz, 1H), 5.94 (ddt, *J* = 16.3, 10.8, 5.6 Hz, 1H), 5.33 (dq, *J* = 17.2, 1.6 Hz, 1H), 5.28–5.21 (m, 2H), 4.67–4.57 (m, 2H), 3.82 (t, *J* = 7.0 Hz, 2H), 3.41–3.19 (m, 2H), 3.16–2.98 (m, 2H), 2.67 (dt, *J* = 14.2, 7.2 Hz, 1H), 2.42 (dt, *J* = 13.9, 6.7 Hz, 1H).
^{13}C NMR (101 MHz, $CDCl_3$): δ 201.0, 168.2, 161.2, 157.2, 138.4, 135.4, 133.9, 133.0, 131.7, 130.3, 128.7, 125.3, 123.1, 122.3, 119.5, 118.9, 118.2, 118.0, 117.8, 112.7, 111.2, 109.7, 67.8, 65.8, 42.5, 36.9, 33.7, 25.3.



30

Indoxyl 30: Prepared from **24** (0.1 mmol) according to General Procedure C (step 2) with 1-methylpyrrole (3.0 equiv) in 78% yield.

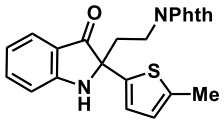
Physical properties: yellow solid;
R_f = 0.15 (silica gel, 33% EtOAc/hexanes);
MS (ESI): calcd for $C_{23}H_{20}N_3O_3$ $[M + H]^+$ 386.1499, found 386.1497;
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.72 (dd, *J* = 5.5, 3.1 Hz, 2H), 7.64 (dd, *J* = 5.5, 3.1 Hz, 2H), 7.50 (d, *J* = 7.2 Hz, 1H), 7.43 (ddd, *J* = 8.4, 7.1, 1.4 Hz, 1H), 6.92 (d, *J* = 8.2 Hz, 1H), 6.74 (t, *J* = 7.2 Hz, 1H), 6.39 (t, *J* = 2.1 Hz, 1H), 6.04 (t, *J* = 2.5 Hz, 1H), 5.96 (dd, *J* = 2.7, 1.8 Hz, 1H), 5.57 (br s, 1H), 4.00 (ddd, *J* = 14.1, 9.8, 5.8 Hz, 1H), 3.80 (ddd, *J* = 14.2, 6.4, 4.1 Hz, 1H), 3.18 (s, 3H), 2.66 (ddd, *J* = 14.2, 9.8, 6.4 Hz, 1H), 1.96 (ddd, *J* = 14.1, 5.7, 4.1 Hz, 1H).
^{13}C NMR (101 MHz, $CDCl_3$): δ 201.5, 168.6, 160.4, 137.2, 133.7, 132.1, 125.8, 122.9, 122.3, 121.6, 118.9, 118.7, 118.5, 112.0, 106.3, 67.3, 35.9, 34.4, 34.2.



31

Indoxyl 31: Prepared from **24** (0.1 mmol) according to General Procedure C (step 2) with 2-methylfuran (3.0 equiv) in 82% yield.

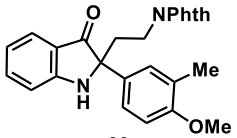
Physical properties: yellow solid;
R_f = 0.30 (silica gel, 33% EtOAc/hexanes);
MS (ESI): calcd for $C_{23}H_{19}N_2O_4$ $[M + H]^+$ 387.1339, found 387.1340;
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.72 (dd, *J* = 5.5, 3.1 Hz, 2H), 7.65 (dd, *J* = 5.5, 3.1 Hz, 2H), 7.52 (d, *J* = 7.7 Hz, 1H), 7.45 (t, *J* = 7.7 Hz, 1H), 6.95 (d, *J* = 8.3 Hz, 1H), 6.79 (t, *J* = 7.4 Hz, 1H), 5.99 (d, *J* = 3.2 Hz, 1H), 5.59 (br s, 1H), 5.47 (s, 1H), 3.97 (ddd, *J* = 14.9, 9.6, 5.8 Hz, 1H), 3.85–3.77 (m, 1H), 2.87 (ddd, *J* = 15.3, 9.6, 6.4 Hz, 1H), 2.04 (dt, *J* = 14.4, 5.2 Hz, 1H), 1.95 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$): δ 198.6, 168.3, 160.6, 152.7, 148.5, 137.6, 133.9, 132.0, 125.7, 123.0, 119.4, 118.9, 112.5, 107.2, 106.5, 67.3, 34.0, 33.0, 13.4.



32

Indoxyl 32: Prepared from **24** (0.1 mmol) according to General Procedure C (step 2) with 2-methylthiophene (3.0 equiv) in 81% yield.

Physical properties: yellow solid;
R_f = 0.24 (silica gel, 30% EtOAc/hexanes);
MS (ESI): calcd for $C_{23}H_{18}N_2NaO_3S$ $[M + Na]^+$ 425.0930, found 425.0942;
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.71 (dd, *J* = 5.4, 3.1 Hz, 2H), 7.64 (dd, *J* = 5.5, 3.1 Hz, 2H), 7.51 (d, *J* = 7.7 Hz, 1H), 7.46 (ddd, *J* = 8.3, 7.0, 1.4 Hz, 1H), 6.96 (d, *J* = 8.2 Hz, 1H), 6.79 (t, *J* = 7.4 Hz, 1H), 6.71 (d, *J* = 3.5 Hz, 1H), 6.23 (dd, *J* = 3.5, 1.4 Hz, 1H), 5.86 (br s, 1H), 3.97 (ddd, *J* = 15.0, 9.6, 5.7 Hz, 1H), 3.81 (ddd, *J* = 14.3, 6.4, 4.2 Hz, 1H), 2.72 (ddd, *J* = 14.3, 9.6, 6.4 Hz, 1H), 2.11–2.02 (m, 1H), 2.07 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$): δ 199.2, 168.5, 160.0, 139.5, 139.4, 137.7, 133.9, 132.0, 125.9, 125.3, 123.8, 123.1, 119.4, 118.0, 112.1, 68.9, 35.5, 33.9, 15.0.

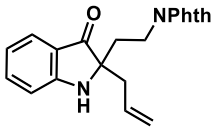


33

Indoxyl 33: Prepared from **24** (0.1 mmol) according to General Procedure C (step 2) with 2-methylanisole (5.0 equiv) in 31% yield.

Physical properties: yellow solid;
R_f = 0.21 (silica gel, 30% EtOAc/hexanes);
MS (ESI): calcd for $C_{26}H_{23}N_2O_4$ $[M + H]^+$ 427.1652, found 427.1678;
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.66–7.55 (m, 4H), 7.50–7.44 (m, 2H), 7.20–7.06 (m, 2H), 7.02 (d, *J* = 8.3 Hz, 1H), 6.76 (t, *J* = 7.4 Hz, 1H), 6.36 (d, *J* = 8.5 Hz, 1H), 5.89 (br s, 1H), 4.00 (ddd,

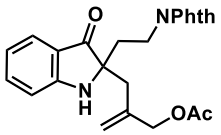
J = 14.4, 11.0, 5.0 Hz, 1H), 3.78 (ddd, *J* = 14.4, 5.9, 3.3 Hz, 1H), 3.46 (s, 3H), 2.96 (ddd, *J* = 14.5, 11.1, 5.9 Hz, 1H), 1.93 (s, 3H), 1.96–1.88 (m, 1H).
^{13}C NMR (101 MHz, $CDCl_3$): δ 200.7, 168.5, 160.1, 156.9, 137.6, 133.6, 131.8, 128.4, 127.7, 126.7, 125.9, 123.7, 122.8, 118.9, 118.3, 111.9, 109.8, 69.5, 55.1, 34.2, 34.0, 16.3.



34

Indoxyl 34: Prepared from **24** (0.1 mmol) according to General Procedure C (step 2) with allyltrimethylsilane (5.0 equiv) in 93% yield.

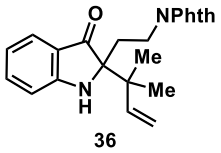
Physical properties: light yellow solid;
R_f = 0.25 (silica gel, 30% EtOAc/hexanes);
MS (ESI): calcd for $C_{21}H_{19}N_2O_3$ $[M + H]^+$ 347.1390, found 347.1384;
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.76 (dd, *J* = 5.5, 3.1 Hz, 2H), 7.67 (dd, *J* = 5.5, 3.1 Hz, 2H), 7.49 (d, *J* = 7.7 Hz, 1H), 7.41 (ddd, *J* = 8.4, 7.0, 1.4 Hz, 1H), 6.84 (d, *J* = 8.2 Hz, 1H), 6.78 (td, *J* = 7.4, 6.9, 0.8 Hz, 1H), 5.67 (ddt, *J* = 17.3, 10.1, 7.3 Hz, 1H), 5.17–5.02 (m, 2H), 4.85 (s, 1H), 3.62 (t, *J* = 7.4 Hz, 2H), 2.46 (dd, *J* = 13.8, 7.3 Hz, 1H), 2.38 (dd, *J* = 13.8, 7.4 Hz, 1H), 2.26 (dt, *J* = 13.8, 7.8 Hz, 1H), 2.05 (dt, *J* = 13.9, 7.0 Hz, 1H).
^{13}C NMR (101 MHz, $CDCl_3$): δ 203.0, 168.1, 160.7, 137.5, 134.0, 132.1, 131.6, 124.7, 123.3, 121.0, 120.0, 119.1, 112.7, 68.0, 42.0, 34.4, 33.3.



35

Indoxyl 35: Prepared from **24** (0.1 mmol) according to General Procedure C (step 2) with 2-[(acetoxymethyl)allyl]trimethylsilane (5.0 equiv) in 75% yield.

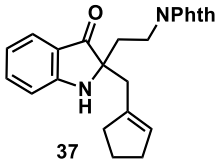
Physical properties: yellow solid;
R_f = 0.37 (silica gel, 50% EtOAc/hexanes);
MS (ESI): calcd for $C_{24}H_{23}N_2O_5$ $[M + H]^+$ 419.1601, found 419.1622;
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.76 (dd, *J* = 5.5, 3.1 Hz, 2H), 7.67 (m, *J* = 5.5, 3.1 Hz, 2H), 7.46 (d, *J* = 7.8 Hz, 1H), 7.42 (t, *J* = 7.7 Hz, 1H), 6.85 (d, *J* = 8.2 Hz, 1H), 6.75 (t, *J* = 7.4 Hz, 1H), 5.35 (br s, 1H), 5.08 (s, 1H), 5.03 (s, 1H), 4.52 (d, *J* = 13.5 Hz, 1H), 4.35 (d, *J* = 13.5 Hz, 1H), 3.70–3.46 (m, 2H), 2.48 (d, *J* = 13.9 Hz, 1H), 2.43 (d, *J* = 13.9 Hz, 1H), 2.27 (ddd, *J* = 13.7, 8.9, 7.0 Hz, 1H), 2.08 (s, 3H), 2.10–1.98 (m, 1H).
^{13}C NMR (101 MHz, $CDCl_3$): δ 202.9, 170.9, 168.0, 160.7, 138.6, 137.6, 134.0, 132.1, 124.8, 123.3, 120.8, 119.0, 118.5, 112.5, 68.2, 67.4, 40.4, 35.1, 33.1, 21.0.



36

Indoxyl 36: Prepared from **24** (0.1 mmol) according to General Procedure C (step 2) with tributyl(3-methyl-2-butenyl)tin (5.0 equiv) in 75% yield.

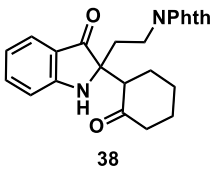
Physical properties: yellow solid;
R_f = 0.37 (silica gel, 25% EtOAc/hexanes);
MS (ESI): calcd for $C_{23}H_{23}N_2O_3$ $[M + H]^+$ 375.1703, found 375.1692;
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.80–7.71 (m, 2H), 7.70–7.63 (m, 2H), 7.46 (d, *J* = 7.8 Hz, 1H), 7.40 (t, *J* = 7.6 Hz, 1H), 6.86 (d, *J* = 8.2 Hz, 1H), 6.73 (td, *J* = 7.4, 2.1 Hz, 1H), 6.03 (ddd, *J* = 17.4, 10.8, 2.1 Hz, 1H), 5.19 –5.02 (m, 2H), 4.85 (s, 1H), 3.52–3.36 (m, 2H), 2.57–2.45 (m, 1H), 2.03–1.93 (m, 1H), 1.15 (s, 3H), 0.95 (s, 3H).
^{13}C NMR (151 MHz, $CDCl_3$): δ 202.8, 168.1, 161.1, 143.3, 137.3, 134.0, 132.1, 124.3, 123.3, 122.3, 118.7, 114.7, 111.8, 71.6, 43.6, 33.5, 31.6, 21.5, 21.2.



37

Indoxyl 37: Prepared from **24** (0.1 mmol) according to General Procedure C (step 2) with methylenecyclopentane (5.0 equiv) in 84% yield.

Physical properties: yellow solid;
R_f = 0.35 (silica gel, 33% EtOAc/hexanes);
MS (ESI): calcd for $C_{24}H_{23}N_2O_3$ $[M + H]^+$ 387.1703, found 387.1697;
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (dd, *J* = 5.4, 3.1 Hz, 2H), 7.67 (dd, *J* = 5.5, 3.0 Hz, 2H), 7.48 (d, *J* = 7.8 Hz, 1H), 7.40 (t, *J* = 7.7 Hz, 1H), 6.83 (d, *J* = 8.2 Hz, 1H), 6.76 (t, *J* = 7.4 Hz, 1H), 5.44 (s, 1H), 4.82 (s, 1H), 3.60 (t, *J* = 7.5 Hz, 2H), 2.55 (d, *J* = 14.1 Hz, 1H), 2.44 (d, *J* = 14.1 Hz, 1H), 2.27 (dt, *J* = 13.6, 7.9 Hz, 1H), 2.22–1.97 (m, 5H), 1.76–1.59 (m, 2H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 203.5, 168.1, 160.8, 138.8, 137.3, 134.0, 132.2, 130.1, 124.7, 123.3, 121.1, 119.1, 112.7, 68.3, 39.1, 36.8, 35.0, 33.4, 32.5, 24.1.

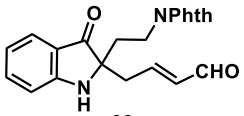


38

Indoxyl 38: Prepared from **24** (0.1 mmol) according to General Procedure C (step 2) with 1-(trimethylsiloxy)cyclohexene (5.0 equiv) in 95% yield (dr = 1.2:1).

Physical properties: yellow solid;

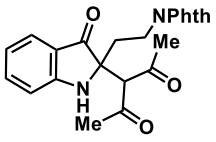
R_f = 0.18 (silica gel, 33% EtOAc/hexanes);
MS (ESI): calcd for $C_{24}H_{23}N_2O_4$ $[M + H]^+$ 403.1652, found 403.1654;
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.77–7.68 (m, 2H), 7.68–7.60 (m, 2H), 7.47–7.32 (m, 2H), 6.84 (d, *J* = 8.2 Hz, 0.55H), 6.80 (d, *J* = 8.2 Hz, 0.45H), 6.69 (t, *J* = 7.3 Hz, 0.47H), 6.65 (t, *J* = 7.4 Hz, 0.53H), 5.67 (br s, 1H), 3.69–3.39 (m, 2H), 2.97 (dd, *J* = 12.8, 4.9 Hz, 0.55H), 2.72–2.63 (m, 0.45H), 2.50 (dd, *J* = 12.3, 5.4 Hz, 0.45H), 2.44–2.28 (m, 3H), 2.27–2.15 (m, 1H), 2.10–1.99 (m, 1H), 1.96–1.89 (m, 0.45H), 1.84–1.76 (m, 0.55H), 1.72–1.49 (m, 3H), 1.35–1.25 (m, 1H).
^{13}C NMR (101 MHz, $CDCl_3$): δ 213.2, 211.3, 203.2, 201.9, 167.92, 167.88, 161.4, 159.8, 137.8, 137.3, 133.9, 133.8, 132.1, 124.6, 124.2, 123.2, 120.4, 119.9, 118.4, 118.1, 112.1, 111.7, 69.0, 67.5, 56.7, 55.4, 43.8, 43.0, 34.4, 33.3, 33.0, 30.7, 29.6, 29.1, 27.4, 27.1, 25.2, 25.1. [**Note:** 2 carbon signals are missing due to signal overlap]



39

Indoxyl 39: Prepared from **24** (0.1 mmol) according to General Procedure C (step 2) with 1-(trimethylsiloxy)-1,3-butadiene (5.0 equiv) in 62% yield.

Physical properties: brown oil;
R_f = 0.22 (silica gel, 50% EtOAc/hexanes);
MS (ESI): calcd for $C_{22}H_{19}N_2O_4$ $[M + H]^+$ 375.1339, found 375.1355;
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.36 (d, *J* = 7.8 Hz, 1H), 7.79 (dd, *J* = 5.5, 3.1 Hz, 2H), 7.70 (dd, *J* = 5.5, 3.0 Hz, 2H), 7.52 (d, *J* = 7.6 Hz, 1H), 7.45 (ddd, *J* = 8.4, 7.1, 1.3 Hz, 1H), 6.87 (d, *J* = 8.3 Hz, 1H), 6.81 (ddd, 7.9, 7.1, 0.8 Hz, 1H), 6.64 (dt, *J* = 15.3, 7.5 Hz, 1H), 6.13 (ddt, *J* = 15.6, 7.8, 1.3 Hz, 1H), 5.00 (s, 1H), 3.73–3.56 (m, 2H), 2.85–2.63 (m, 2H), 2.30 (ddd, *J* = 13.9, 8.5, 7.0 Hz, 1H), 2.07 (ddd, *J* = 13.9, 8.3, 5.5 Hz, 1H).
^{13}C NMR (101 MHz, $CDCl_3$): δ 201.9, 193.5, 168.1, 160.5, 150.4, 138.0, 136.5, 134.2, 132.0, 124.9, 123.4, 120.4, 119.6, 112.7, 67.7, 40.6, 35.0, 33.0.



40

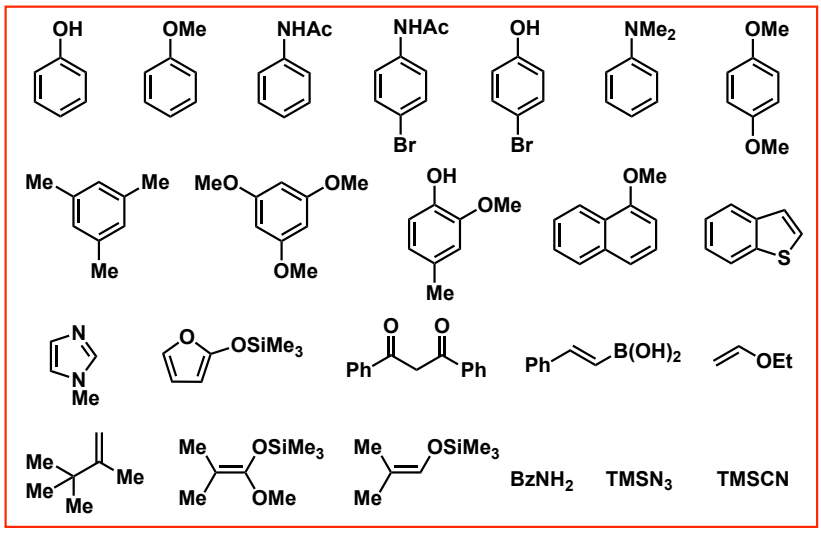
Indoxyl 40: Prepared from **24** (0.1 mmol) according to General Procedure C (step 2) with acetylacetone (5.0 equiv) in 41% yield.

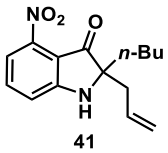
Physical properties: yellow oil;
R_f = 0.25 (silica gel, 50% EtOAc/hexanes);
MS (ESI): calcd for $C_{23}H_{20}N_2NaO_5$ $[M + Na]^+$ 427.1264, found 427.1279;
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.74 (dd, *J* = 5.5, 3.1 Hz, 2H), 7.66 (dd, *J* = 5.5, 3.1 Hz, 2H), 7.44 (ddd, *J* = 8.4, 6.9, 1.3 Hz, 1H), 7.37 (d, *J* = 7.8 Hz, 1H), 6.88 (d, *J* = 8.3 Hz, 1H), 6.72 (t,

J = 7.4 Hz, 1H), 6.06 (s, 1H), 4.38 (s, 1H), 3.67–3.45 (m, 2H), 2.41–2.32 (m, 1H), 2.25 (s, 3H), 2.19–2.11 (m, 1H), 2.08 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 202.9, 201.2, 199.8, 167.9, 161.6, 138.5, 134.0, 132.1, 124.4, 123.3, 120.0, 119.2, 112.8, 69.8, 69.2, 34.1, 32.8, 32.5, 32.1.

Table S1: Unsuccessful nucleophiles.





41

Indoxyl 41: Prepared from **S1** (0.1 mmol) according to General Procedure C (using 5 equiv MoOPH in the first step) with allyltrimethylsilane (5.0 equiv) in 77% yield (2 steps). A larger scale reaction with 4.0 mmol of **S1** yielded **41** in 70% yield (2 steps).

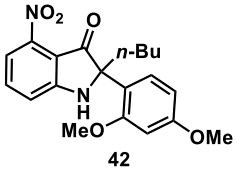
Physical properties: yellow solid;

R_f = 0.35 (silica gel, 30% EtOAc/hexanes);

MS (ESI): calcd for $C_{15}H_{19}N_2O_3$ $[M + H]^+$ 275.1390, found 275.1400;

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.49 (t, J = 8.0 Hz, 1H), 7.14 (d, J = 7.6 Hz, 1H), 7.09 (d, J = 8.4 Hz, 1H), 5.66 (ddt, J = 17.3, 10.1, 7.3 Hz, 1H), 5.17 (br s, 1H), 5.14–5.03 (m, 2H), 2.51–2.36 (m, 2H), 1.82 (ddd, J = 13.5, 11.2, 4.6 Hz, 1H), 1.74–1.61 (m, 1H), 1.30–1.18 (m, 3H), 1.14–1.02 (m, 1H), 0.82 (t, J = 7.1 Hz, 3H).

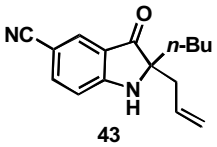
^{13}C NMR (101 MHz, $CDCl_3$): δ 198.5, 161.2, 146.1, 136.9, 131.6, 120.0, 116.9, 113.3, 111.8, 70.7, 41.9, 36.7, 25.4, 23.0, 14.0.



42

Indoxyl 42: Prepared from **S1** (0.1 mmol) according to General Procedure C (using 5 equiv MoOPH in the first step) with 1,3-dimethoxybenzene (5.0 equiv) in 65% yield (2 steps). A larger scale reaction with 4.0 mmol of **S1** yielded **42** in 58% yield (2 steps).

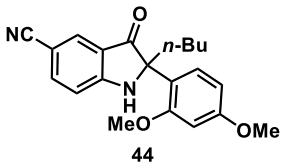
Physical properties: yellow solid;
R_f = 0.25 (silica gel, 30% EtOAc/hexanes);
MS (ESI): calcd for $C_{20}H_{22}N_2NaO_5$ $[M + Na]^+$ 393.1421, found 393.1434;
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.43 (t, *J* = 8.0 Hz, 1H), 7.38 (d, *J* = 8.6 Hz, 1H), 7.06 (d, *J* = 7.6 Hz, 1H), 7.00 (d, *J* = 8.4 Hz, 1H), 6.49 (d, *J* = 2.5 Hz, 1H), 6.44 (dd, *J* = 8.7, 2.5 Hz, 1H), 6.19 (br s, 1H), 3.82 (s, 3H), 3.77 (s, 3H), 2.20–1.98 (m, 2H), 1.35–1.19 (m, 3H), 1.11–0.99 (m, 1H), 0.82 (t, *J* = 7.1 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$): δ 197.0, 160.63, 160.59, 158.6, 146.4, 136.5, 128.0, 119.5, 116.5, 112.6, 111.7, 104.1, 100.2, 71.8, 55.7, 55.6, 37.6, 25.7, 23.0, 14.0.



43

Indoxyl 43: Prepared from **S2** (0.1 mmol) according to General Procedure C with allyltrimethylsilane (5.0 equiv) in 72% yield (2 steps).

Physical properties: light yellow oil;
R_f = 0.40 (silica gel, 30% EtOAc/hexanes);
MS (ESI): calcd for $C_{16}H_{19}N_2O$ $[M + H]^+$ 255.1492, found 255.1498;
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.85 (d, *J* = 0.8 Hz, 1H), 7.60 (dd, *J* = 8.6, 1.7 Hz, 1H), 6.87 (d, *J* = 8.6 Hz, 1H), 5.62 (ddt, *J* = 17.3, 10.1, 7.3 Hz, 1H), 5.24 (br s, 1H), 5.17–5.03 (m, 2H), 2.49–2.30 (m, 2H), 1.88–1.76 (m, 1H), 1.72–1.61 (m, 1H), 1.33–1.14 (m, 3H), 1.08–0.93 (m, 1H), 0.82 (t, *J* = 7.1 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$): δ 202.2, 161.3, 139.8, 131.3, 130.0, 121.1, 120.2, 119.3, 112.3, 101.0, 70.8, 41.6, 36.4, 25.4, 23.0, 14.0.

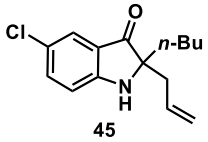


44

Indoxyl 44: Prepared from **S2** (0.1 mmol) according to General Procedure C with 1,3-dimethoxybenzene (5.0 equiv) in 54% yield (2 steps).

Physical properties: yellow oil;
R_f = 0.28 (silica gel, 30% EtOAc/hexanes);
MS (ESI): calcd for $C_{21}H_{23}N_2O_3$ $[M + H]^+$ 351.1703, found 351.1719;
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.90 (s, 1H), 7.56 (dd, *J* = 8.6, 1.8 Hz, 1H), 7.36 (d, *J* = 8.6 Hz, 1H), 6.81 (d, *J* = 8.6 Hz, 1H), 6.49 (d, *J* = 2.5 Hz, 1H), 6.43 (dd, *J* = 8.6, 2.5 Hz, 1H), 6.37 (br

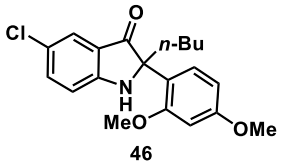
s, 1H), 3.81 (s, 3H), 3.78 (s, 3H), 2.19–2.10 (m, 1H), 2.07–1.99 (m, 1H), 1.31–1.18 (m, 3H), 1.05–0.92 (m, 1H), 0.81 (t, J = 7.1 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$): δ 200.9, 160.8, 160.7, 158.6, 139.6, 130.0, 127.7, 121.1, 119.5, 119.0, 112.0, 104.2, 100.2, 100.1, 71.7, 55.7, 55.6, 37.6, 25.6, 23.0, 14.0.



45

Indoxyl 45: Prepared from **S3** (0.1 mmol) according to General Procedure C with allyltrimethylsilane (5.0 equiv) in 70% yield (2 steps).

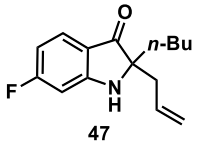
Physical properties: light yellow oil;
R_f = 0.45 (silica gel, 17% EtOAc/hexanes);
MS (ESI): calcd for $C_{15}H_{19}ClNO$ $[M + H]^+$ 264.1150, found 264.1146;
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.52 (d, J = 2.2 Hz, 1H), 7.36 (dd, J = 8.7, 2.3 Hz, 1H), 6.80 (d, J = 8.7 Hz, 1H), 5.64 (ddt, J = 17.3, 10.1, 7.3 Hz, 1H), 5.14–5.00 (m, 2H), 4.62 (br s, 1H), 2.46–2.31 (m, 2H), 1.85–1.73 (m, 1H), 1.63 (td, J = 13.1, 3.5 Hz, 1H), 1.29–1.12 (m, 3H), 1.10–0.93 (m, 1H), 0.81 (t, J = 7.0 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$): δ 203.5, 159.0, 137.2, 132.0, 124.0, 123.9, 122.5, 119.6, 113.5, 70.6, 41.9, 36.6, 25.5, 23.1, 14.0.



46

Indoxyl 46: Prepared from **S3** (0.1 mmol) according to General Procedure C with 1,3-dimethoxybenzene (5.0 equiv) in 40% yield (2 steps).

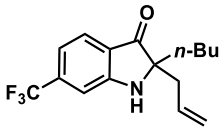
Physical properties: light yellow oil;
R_f = 0.73 (silica gel, 50% EtOAc/hexanes);
MS (ESI): calcd for $C_{20}H_{23}ClNO_3$ $[M + H]^+$ 360.1361, found 360.1379;
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.58 (d, J = 2.2 Hz, 1H), 7.38 (d, J = 8.6 Hz, 1H), 7.33 (dd, J = 8.7, 2.3 Hz, 1H), 6.75 (d, J = 8.6 Hz, 1H), 6.49 (d, J = 2.5 Hz, 1H), 6.42 (dd, J = 8.6, 2.5 Hz, 1H), 5.84 (br s, 1H), 3.81 (s, 3H), 3.77 (s, 3H), 2.18–2.08 (m, 1H), 2.05–1.95 (m, 1H), 1.36–1.17 (m, 3H), 1.07–0.94 (m, 1H), 0.82 (t, J = 7.2 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$): δ 202.1, 160.5, 158.7, 158.6, 137.0, 127.8, 123.9, 123.2, 122.3, 120.1, 113.2, 104.1, 100.1, 71.9, 55.61, 55.55, 37.7, 25.7, 23.1, 14.1.



47

Indoxyl 47: Prepared from 2-*n*-butyl-6-fluoroindole[1] (0.1 mmol) according to General Procedure C with allyltrimethylsilane (5.0 equiv) in 56% yield (2 steps).

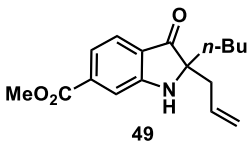
Physical properties: yellow oil;
R_f = 0.57 (silica gel, 17% EtOAc/hexanes);
MS (ESI): calcd for $C_{15}H_{19}FNO$ $[M + H]^+$ 248.1445, found 248.1443;
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.56 (dd, *J* = 9.1, 6.0 Hz, 1H), 6.54–6.44 (m, 2H), 5.65 (ddt, *J* = 17.3, 10.1, 7.3 Hz, 1H), 5.18–4.95 (m, 2H), 4.73 (br s, 1H), 2.46–2.31 (m, 2H), 1.83–1.74 (m, 1H), 1.63 (ddd, *J* = 13.4, 12.1, 3.5 Hz, 1H), 1.31–1.15 (m, 3H), 1.11–0.96 (m, 1H), 0.82 (t, *J* = 7.0 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$): δ 202.5, 169.6 (d, $J_{C\text{-}F}$ = 255.0 Hz), 162.0 (d, $J_{C\text{-}F}$ = 14.1 Hz), 132.1, 126.9 (d, $J_{C\text{-}F}$ = 12.4 Hz), 119.6, 118.0, 107.5 (d, $J_{C\text{-}F}$ = 24.7 Hz), 98.4 (d, $J_{C\text{-}F}$ = 25.7 Hz), 70.5, 41.9, 36.5, 25.4, 23.1, 14.0.
^{19}F NMR (376 MHz, $CDCl_3$): δ -100.0.



48

Indoxyl 48: Prepared from **S5** (0.1 mmol) according to General Procedure C with allyltrimethylsilane (5.0 equiv) in 74% yield (2 steps).

Physical properties: yellow oil;
R_f = 0.75 (silica gel, 30% EtOAc/hexanes);
MS (ESI): calcd for $C_{16}H_{19}F_3NO$ $[M + H]^+$ 298.1413, found 298.1422;
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.66 (d, *J* = 8.0 Hz, 1H), 7.10 (s, 1H), 7.01 (d, *J* = 8.1 Hz, 1H), 5.65 (ddt, *J* = 17.3, 10.1, 7.3 Hz, 1H), 5.17–5.01 (m, 2H), 4.79 (br s, 1H), 2.49–2.31 (m, 2H), 1.87–1.76 (m, 1H), 1.71–1.62 (m, 1H), 1.29–1.17 (m, 3H), 1.09–0.94 (m, 1H), 0.82 (t, *J* = 7.1 Hz, 3H).
^{13}C NMR (151 MHz, $CDCl_3$): δ 204.0, 159.7, 138.3 (q, *J* = 32.0 Hz), 131.8, 125.4, 123.7 (q, *J* = 276.8 Hz), 123.6, 119.9, 115.2 (q, *J* = 3.4 Hz), 109.3 (q, *J* = 4.2 Hz), 70.5, 41.9, 36.6, 25.4, 23.0, 14.0.
^{19}F NMR (376 MHz, $CDCl_3$): δ -63.6.

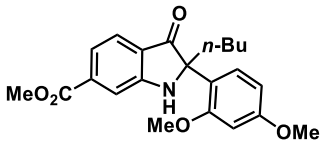


49

Indoxyl 49: Prepared from **S6** (0.1 mmol) according to General Procedure C with allyltrimethylsilane (5.0 equiv) in 63% yield (2 steps).

Physical properties: yellow oil;
R_f = 0.58 (silica gel, 30% EtOAc/hexanes);
MS (ESI): calcd for $C_{17}H_{22}NO_3$ $[M + H]^+$ 288.1594, found 288.1588;

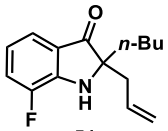
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.61 (d, *J* = 8.0 Hz, 1H), 7.52 (s, 1H), 7.42 (d, *J* = 8.0 Hz, 1H), 5.64 (ddt, *J* = 17.2, 10.1, 7.3 Hz, 1H), 5.09 (d, *J* = 17.0, 1H), 5.04 (d, *J* = 10.0, 1H), 4.71 (br s, 1H), 3.92 (s, 3H), 2.53–2.26 (m, 2H), 1.88–1.74 (m, 1H), 1.67 (dd, *J* = 12.8, 3.4 Hz, 1H), 1.30–1.15 (m, 3H), 1.08–0.92 (m, 1H), 0.81 (t, *J* = 6.9 Hz, 3H).
^{13}C NMR (151 MHz, $CDCl_3$): δ 204.5, 166.7, 160.1, 137.8, 132.0, 124.5, 124.3, 119.7, 119.4, 113.6, 70.5, 52.7, 42.0, 36.7, 25.5, 23.1, 14.0.



50

Indoxyl 50: Prepared from **S6** (0.1 mmol) according to General Procedure C with 1,3-dimethoxybenzene (5.0 equiv) in 42% yield (2 steps).

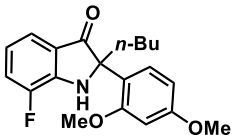
Physical properties: yellow oil;
R_f = 0.38 (silica gel, 30% EtOAc/hexanes);
MS (ESI): calcd for $C_{22}H_{26}NO_5$ $[M + H]^+$ 384.1805, found 384.1820;
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.67 (d, *J* = 8.0 Hz, 0H), 7.48 (s, 1H), 7.38 (d, *J* = 8.4 Hz, 2H), 6.48 (d, *J* = 2.5 Hz, 1H), 6.42 (dd, *J* = 8.6, 2.5 Hz, 1H), 5.90 (br s, 1H), 3.91 (s, 3H), 3.78 (s, 3H), 3.77 (s, 3H), 2.20–2.09 (m, 1H), 2.08–1.98 (m, 1H), 1.35–1.18 (m, 3H), 1.07–0.94 (m, 1H), 0.81 (t, *J* = 7.1 Hz, 3H).
^{13}C NMR (151 MHz, $CDCl_3$): δ 203.3, 166.9, 160.4, 159.7, 158.7, 137.6, 127.8, 124.4, 124.3, 120.1, 118.7, 113.3, 104.0, 100.1, 71.6, 55.58, 55.55, 52.6, 37.8, 25.7, 23.1, 14.1.



51

Indoxyl 51: Prepared from **S7** (0.1 mmol) according to General Procedure C with allyltrimethylsilane (5.0 equiv) in 63% yield (2 steps).

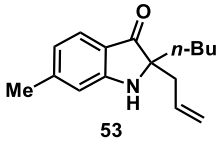
Physical properties: yellow oil;
R_f = 0.74 (silica gel, 30% EtOAc/hexanes);
MS (ESI): calcd for $C_{15}H_{19}FNO$ $[M + H]^+$ 248.1445, found 248.1457;
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.37 (d, *J* = 7.7 Hz, 1H), 7.18 (dd, *J* = 10.6, 7.8 Hz, 1H), 6.73 (td, *J* = 7.8, 4.1 Hz, 1H), 5.66 (ddt, *J* = 17.3, 10.1, 7.3 Hz, 1H), 5.25–5.04 (m, 2H), 4.63 (br s, 1H), 2.53–2.32 (m, 2H), 1.83–1.76 (m, 1H), 1.67 (ddd, *J* = 13.9, 12.2, 3.7 Hz, 1H), 1.33–1.18 (m, 3H), 1.10–0.97 (m, 1H), 0.82 (t, *J* = 7.0 Hz, 3H).
^{13}C NMR (151 MHz, $CDCl_3$): δ 203.8 (d, $J_{C\text{-}F}$ = 3.7 Hz), 149.8 (d, $J_{C\text{-}F}$ = 257.8 Hz), 149.0 (d, $J_{C\text{-}F}$ = 27.8 Hz), 131.9, 124.6 (d, $J_{C\text{-}F}$ = 4.4 Hz), 121.8 (d, $J_{C\text{-}F}$ = 15.9 Hz), 120.1 (d, $J_{C\text{-}F}$ = 3.9 Hz), 119.7, 118.7 (d, $J_{C\text{-}F}$ = 4.7 Hz), 70.5, 41.9, 36.6, 25.4, 23.1, 14.0.
^{19}F NMR (565 MHz, $CDCl_3$): δ -136.5.



52

Indoxyl 52: Prepared from **S7** (0.1 mmol) according to General Procedure C with 1,3-dimethoxybenzene (5.0 equiv) in 56% yield (2 steps).

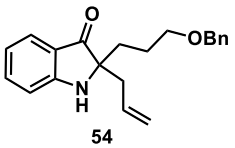
Physical properties: yellow oil;
R_f = 0.62 (silica gel, 30% EtOAc/hexanes);
MS (ESI): calcd for $C_{20}H_{23}FNO_3$ $[M + H]^+$ 344.1656, found 344.1678;
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.43 (d, *J* = 7.7 Hz, 1H), 7.39 (d, *J* = 8.6 Hz, 1H), 7.14 (dd, *J* = 10.7, 7.8 Hz, 1H), 6.68 (td, *J* = 7.8, 4.0 Hz, 1H), 6.50 (d, *J* = 2.5 Hz, 1H), 6.42 (dd, *J* = 8.6, 2.5 Hz, 1H), 5.91 (br s, 1H), 3.82 (s, 3H), 3.78 (s, 3H), 2.18 (td, *J* = 13.0, 3.9 Hz, 1H), 2.07–1.98 (m, 1H), 1.42–1.15 (m, 3H), 1.08–0.95 (m, 1H), 0.82 (t, *J* = 7.2 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$): δ 202.5 (d, *J* = 3.5 Hz), 160.5, 158.8, 149.8 (d, *J* = 216.9 Hz), 148.7 (d, *J* = 42.1 Hz), 127.8, 124.5 (d, *J* = 4.9 Hz), 121.5 (d, *J* = 16.2 Hz), 120.03 (d, *J* = 4.1 Hz), 119.99, 117.9 (d, *J* = 4.7 Hz), 104.0, 100.1, 71.8, 55.6, 55.5, 37.8, 25.7, 23.1, 14.1.
^{19}F NMR (376 MHz, $CDCl_3$): δ -137.2.



53

Indoxyl 53: Prepared from **S4** (0.1 mmol) according to General Procedure C with allyltrimethylsilane (5.0 equiv) in 41% yield (2 steps).

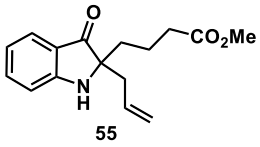
Physical properties: light yellow oil;
R_f = 0.73 (silica gel, 33% EtOAc/hexanes);
MS (ESI): calcd for $C_{16}H_{22}NO$ $[M + H]^+$ 244.1696, found 244.1700;
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.46 (d, *J* = 7.9 Hz, 1H), 6.65 (s, 1H), 6.62 (d, *J* = 8.0 Hz, 1H), 5.67 (ddt, *J* = 17.3, 10.1, 7.3 Hz, 1H), 5.15–4.97 (m, 2H), 4.50 (br s, 1H), 2.38 (t, *J* = 6.9 Hz, 2H), 2.34 (s, 3H), 1.84–1.72 (m, 1H), 1.69–1.55 (m, 1H), 1.29–1.15 (m, 3H), 1.13–0.97 (m, 1H), 0.81 (t, *J* = 7.0 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$): δ 203.9, 161.2, 148.9, 132.6, 124.4, 120.6, 119.4, 119.2, 112.4, 69.8, 42.0, 36.6, 25.5, 23.1, 22.6, 14.0.



54

Indoxyl 54: Prepared from **S8** (0.1 mmol) according to General Procedure C with allyltrimethylsilane (5.0 equiv) in 56% yield (2 steps).

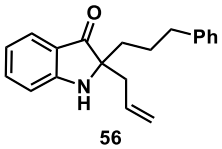
Physical properties: light yellow foam;
R_f = 0.54 (silica gel, 30% EtOAc/hexanes);
MS (ESI): calcd for $C_{21}H_{24}NO_2$ $[M + H]^+$ 322.1802, found 322.1795;
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.56 (d, *J* = 7.8 Hz, 1H), 7.41 (ddd, *J* = 8.4, 7.0, 1.4 Hz, 1H), 7.38–7.23 (m, 5H), 6.83–6.74 (m, 2H), 5.67 (ddt, *J* = 17.3, 10.1, 7.3 Hz, 1H), 5.28–4.94 (m, 2H), 4.71 (br s, 1H), 4.45 (AB q, *J* = 18.5, 11.9 Hz, 2H), 3.67–3.27 (m, 2H), 2.49–2.27 (m, 2H), 1.94–1.74 (m, 2H), 1.62–1.49 (m, 1H), 1.47–1.35 (m, 1H).
^{13}C NMR (101 MHz, $CDCl_3$): δ 204.5, 160.8, 138.5, 137.3, 132.3, 128.5, 127.8, 127.7, 124.6, 121.4, 119.4, 118.8, 112.4, 73.1, 70.3, 69.3, 41.9, 33.4, 23.8.



55

Indoxyl 55: Prepared from **S9** (0.1 mmol) according to General Procedure C with allyltrimethylsilane (5.0 equiv) in 60% yield (2 steps).

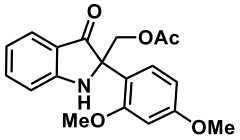
Physical properties: light yellow oil;
R_f = 0.40 (silica gel, 33% EtOAc/hexanes);
MS (ESI): calcd for $C_{16}H_{20}NO_3$ $[M + H]^+$ 274.1438, found 274.1433;
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.57 (d, *J* = 8.2 Hz, 1H), 7.43 (ddd, *J* = 8.3, 7.1, 1.4 Hz, 1H), 6.85 (d, *J* = 8.2 Hz, 1H), 6.82–6.76 (m, 1H), 5.66 (ddt, *J* = 17.3, 10.1, 7.3 Hz, 1H), 5.18–4.94 (m, 2H), 4.66 (br s, 1H), 3.62 (s, 3H), 2.45–2.32 (m, 2H), 2.30–2.17 (m, 2H), 1.81 (ddd, *J* = 13.4, 11.9, 4.9 Hz, 1H), 1.70 (dd, *J* = 12.1, 4.2 Hz, 1H), 1.66–1.56 (m, 1H), 1.45–1.30 (m, 1H).
^{13}C NMR (101 MHz, $CDCl_3$): δ 204.2, 173.8, 160.8, 137.4, 132.1, 124.7, 121.4, 119.6, 118.9, 112.5, 69.3, 51.7, 41.9, 35.9, 33.9, 18.9.



56

Indoxyl 56: Prepared from **S10** (0.1 mmol) according to General Procedure C with allyltrimethylsilane (5.0 equiv) in 52% yield (2 steps).

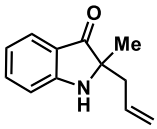
Physical properties: yellow oil;
R_f = 0.62 (silica gel, 30% EtOAc/hexanes);
MS (ESI): calcd for $C_{20}H_{22}NO$ $[M + H]^+$ 292.1696, found 292.1670;
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.57 (d, *J* = 7.8 Hz, 1H), 7.42 (ddd, *J* = 8.4, 7.0, 1.4 Hz, 1H), 7.23 (d, *J* = 7.6 Hz, 2H), 7.18–7.13 (m, 1H), 7.12–7.08 (m, 2H), 6.82 (d, *J* = 8.2 Hz, 1H), 6.78 (t, *J* = 7.4 Hz, 1H), 5.65 (ddt, *J* = 17.3, 10.1, 7.3 Hz, 1H), 5.18–4.97 (m, 2H), 4.53 (br s, 1H), 2.62–2.46 (m, 2H), 2.45–2.32 (m, 2H), 1.87 (ddd, *J* = 13.5, 12.0, 4.8 Hz, 1H), 1.74–1.65 (m, 1H), 1.64–1.50 (m, 1H), 1.49–1.34 (m, 1H).
^{13}C NMR (101 MHz, $CDCl_3$): δ 204.4, 160.7, 142.0, 137.3, 132.2, 128.5, 128.4, 126.0, 124.7, 121.5, 119.5, 118.9, 112.4, 69.5, 42.0, 36.4, 36.2, 25.3.



57

Indoxyl 57: Prepared from **S11** (0.1 mmol) according to General Procedure C with 1,3-dimethoxybenzene (5.0 equiv) in 32% yield (2 steps).

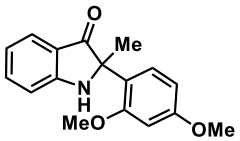
Physical properties: light yellow oil;
R_f = 0.21 (silica gel, 30% EtOAc/hexanes);
MS (ESI): calcd for $C_{19}H_{20}NO_5$ $[M + H]^+$ 342.1336, found 342.1334;
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.66 (d, *J* = 7.7 Hz, 1H), 7.46–7.36 (m, 2H), 6.82 (d, *J* = 8.2 Hz, 1H), 6.78 (t, *J* = 7.5 Hz, 1H), 6.50 (d, *J* = 2.5 Hz, 1H), 6.43 (dd, *J* = 8.7, 2.5 Hz, 1H), 5.90 (br s, 1H), 5.05 (d, *J* = 10.8 Hz, 1H), 4.22 (d, *J* = 10.8 Hz, 1H), 3.88 (s, 3H), 3.77 (s, 3H), 1.86 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$): δ 200.5, 171.2, 161.1, 160.7, 159.2, 137.5, 128.7, 124.8, 120.9, 118.6, 115.8, 112.2, 104.3, 100.0, 70.2, 66.1, 55.7, 55.6, 20.9.



58

Indoxyl 58: Prepared from 2-methylindole (0.1 mmol) according to General Procedure C with allyltrimethylsilane (5.0 equiv) in 96% yield (2 steps).

Physical properties: yellow oil;
R_f = 0.52 (silica gel, 30% EtOAc/hexanes);
MS (ESI): calcd for $C_{12}H_{14}NO$ $[M + H]^+$ 188.1070, found 188.1077;
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.60 (d, *J* = 7.7 Hz, 1H), 7.44 (ddd, *J* = 8.3, 7.1, 1.4 Hz, 1H), 6.90–6.70 (m, 2H), 5.72 (ddt, *J* = 17.3, 10.1, 7.3 Hz, 1H), 5.26–4.99 (m, 2H), 4.66 (br s, 1H), 2.41 (dd, *J* = 13.7, 7.2 Hz, 1H), 2.34 (dd, *J* = 13.8, 7.5 Hz, 1H), 1.31 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$): δ 204.6, 160.1, 137.3, 132.5, 125.0, 120.4, 119.5, 119.0, 112.6, 66.4, 42.1, 22.5.

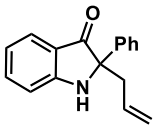


59

Indoxyl 59: Prepared from 2-methylindole (0.1 mmol) according to General Procedure C with 1,3-dimethoxybenzene (5.0 equiv) in 37% yield (2 steps).

Physical properties: light yellow solid;

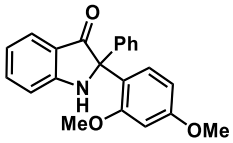
R_f = 0.39 (silica gel, 30% EtOAc/hexanes);
MS (ESI): calcd for $C_{17}H_{18}NO_3$ $[M + H]^+$ 284.1281, found 284.1279;
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.68 (d, *J* = 8.0 Hz, 1H), 7.42 (ddd, *J* = 8.4, 7.1, 1.4 Hz, 1H), 7.37 (d, *J* = 8.5 Hz, 1H), 6.83–6.76 (m, 2H), 6.51–6.40 (m, 2H), 5.47 (br s, 1H), 3.78 (s, 3H), 3.71 (s, 3H), 1.64 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$): δ 203.9, 160.7, 159.4, 158.8, 137.0, 127.9, 125.0, 120.9, 120.5, 118.5, 112.3, 104.0, 100.0, 67.3, 55.56, 55.55, 23.7.



60

Indoxyl 60: Prepared from 2-phenylindole (0.1 mmol) according to General Procedure C with allyltrimethylsilane (5.0 equiv) in 65% yield (2 steps).

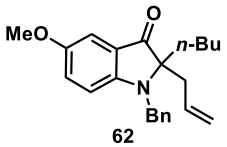
Physical properties: yellow solid;
R_f = 0.68 (silica gel, 30% EtOAc/hexanes);
MS (ESI): calcd for $C_{17}H_{16}NO$ $[M + H]^+$ 250.1226, found 250.1223;
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.56–7.52 (m, 2H), 7.49 (d, *J* = 7.8 Hz, 1H), 7.40 (ddd, *J* = 8.4, 7.1, 1.4 Hz, 1H), 7.31–7.24 (m, 2H), 7.22–7.17 (m, 1H), 6.88 (d, *J* = 8.2 Hz, 1H), 6.81–6.71 (m, 1H), 5.50 (dddd, *J* = 17.0, 10.1, 8.4, 5.9 Hz, 1H), 5.15–4.94 (m, 3H), 2.97 (ddt, *J* = 14.0, 5.9, 1.4 Hz, 1H), 2.56 (dd, *J* = 14.0, 8.4 Hz, 1H).
^{13}C NMR (151 MHz, $CDCl_3$): δ 201.2, 160.4, 138.6, 137.5, 132.7, 128.8, 127.8, 126.0, 125.6, 119.9, 119.7, 119.4, 112.4, 70.8, 42.9.



61

Indoxyl 61: Prepared from 2-phenylindole (0.1 mmol) according to General Procedure C with 1,3-dimethoxybenzene (5.0 equiv) in 34% yield (2 steps).

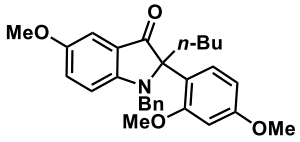
Physical properties: yellow solid;
R_f = 0.31 (silica gel, 20% EtOAc/hexanes);
MS (ESI): calcd for $C_{22}H_{20}NO_3$ $[M + H]^+$ 346.1, found 346.1;
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.61 (d, *J* = 7.7 Hz, 1H), 7.47–7.40 (m, 2H), 7.38–7.32 (m, 2H), 7.28–7.18 (m, 3H), 6.89 (d, *J* = 8.3 Hz, 1H), 6.78 (t, *J* = 7.0 Hz, 1H), 6.51–6.44 (m, 2H), 6.10 (br s, 1H), 3.80 (s, 3H), 3.57 (s, 3H).
^{13}C NMR (151 MHz, $CDCl_3$): δ 200.1, 160.8, 160.2, 159.2, 140.7, 137.5, 129.2, 128.2, 127.3, 126.2, 125.6, 121.2, 119.3, 118.7, 111.8, 103.8, 100.7, 73.2, 55.8, 55.6.



62

Indoxyl 62: Prepared from **S13** (0.1 mmol) according to General Procedure C with allyltrimethylsilane (5.0 equiv) in 50% yield (2 steps).

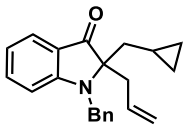
Physical properties: yellow oil;
R_f = 0.69 (silica gel, 30% EtOAc/hexanes);
MS (ESI): calcd for $C_{23}H_{28}NO_2$ $[M + H]^+$ 350.2115, found 350.2129;
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.37–7.27 (m, 5H), 7.09–7.04 (m, 2H), 6.60–6.54 (m, 1H), 5.42 (ddt, *J* = 17.1, 10.1, 7.1 Hz, 1H), 5.00 (dd, *J* = 17.0, 1.7 Hz, 1H), 4.91 (d, *J* = 10.1 Hz, 1H), 4.56 (d, *J* = 16.6 Hz, 1H), 4.49 (d, *J* = 16.7 Hz, 1H), 3.76 (s, 3H), 2.56 (dd, *J* = 14.3, 6.8 Hz, 1H), 2.47 (dd, *J* = 14.4, 7.5 Hz, 1H), 1.94–1.73 (m, 1H), 1.70–1.55 (m, 1H), 1.19–0.99 (m, 2H), 0.99–0.87 (m, 2H), 0.72 (t, *J* = 7.3 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$): δ 203.5, 157.7, 152.2, 138.5, 132.2, 128.8, 128.1, 127.5, 127.2, 120.6, 118.9, 110.5, 104.5, 75.0, 55.9, 47.1, 41.3, 35.9, 25.5, 22.9, 13.9.



63

Indoxyl 63: Prepared from **S13** (0.1 mmol) according to General Procedure C with 1,3-dimethoxybenzene (5.0 equiv) in 37% yield (2 steps).

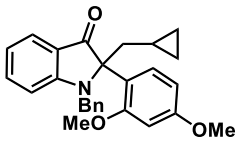
Physical properties: light yellow oil;
R_f = 0.34 (silica gel, 30% EtOAc/hexanes);
MS (ESI): calcd for $C_{28}H_{32}NO_4$ $[M + H]^+$ 446.2326, found 446.2350;
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36 (d, *J* = 8.6 Hz, 1H), 7.24–7.17 (m, 3H), 7.15 (d, *J* = 2.8 Hz, 1H), 7.11–7.05 (m, 2H), 7.03 (dd, *J* = 8.9, 2.7 Hz, 1H), 6.55–6.43 (m, 2H), 6.34 (d, *J* = 2.5 Hz, 1H), 4.28 (d, *J* = 16.1 Hz, 1H), 4.12 (d, *J* = 16.1 Hz, 1H), 3.79 (s, 3H), 3.78 (s, 3H), 3.39 (s, 3H), 2.21–2.01 (m, 2H), 1.25–1.02 (m, 4H), 0.80 (t, *J* = 7.2 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$): δ 204.6, 161.0, 158.6, 156.3, 151.7, 139.0, 129.7, 128.5, 127.2, 127.1, 126.3, 122.2, 120.4, 109.9, 104.8, 104.4, 99.5, 73.7, 56.0, 55.5, 55.3, 47.5, 34.9, 24.9, 23.2, 14.0.



64

Indoxyl 64: Prepared from **S14** (0.1 mmol) according to General Procedure C with allyltrimethylsilane (5.0 equiv) in 78% yield (2 steps).

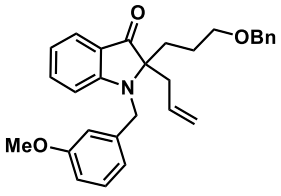
Physical properties: yellow oil;
R_f = 0.72 (silica gel, 30% EtOAc/hexanes);
MS (ESI): calcd for $C_{22}H_{24}NO$ $[M + H]^+$ 318.1852, found 318.1847;
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.63 (d, *J* = 7.7 Hz, 1H), 7.44–7.19 (m, 6H), 6.72 (t, *J* = 7.4 Hz, 1H), 6.59 (d, *J* = 8.3 Hz, 1H), 5.55–5.34 (m, 1H), 4.96 (d, *J* = 17.0 Hz, 1H), 4.90 (d, *J* = 10.3 Hz, 1H), 4.61 (AB q, *J* = 22.3, 16.9 Hz, 2H), 2.57 (dd, *J* = 14.5, 6.8 Hz, 1H), 2.47 (dd, *J* = 14.4, 7.5 Hz, 1H), 2.04 (dd, *J* = 14.5, 4.5 Hz, 1H), 1.47 (dd, *J* = 14.5, 8.6 Hz, 1H), 0.46–0.34 (m, 1H), 0.33–0.24 (m, 1H), 0.21–0.11 (m, 1H), 0.10–0.02 (m, 1H), 0.01– -0.07 (m, 1H).
^{13}C NMR (101 MHz, $CDCl_3$): δ 203.7, 161.3, 138.1, 137.3, 132.0, 128.8, 127.4, 127.1, 124.4, 121.2, 119.0, 117.3, 109.3, 74.6, 47.2, 40.8, 40.6, 5.7, 5.5, 4.3.



65

Indoxyl 65: Prepared from **S14** (0.1 mmol) according to General Procedure C with 1,3-dimethoxybenzene (5.0 equiv) in 50% yield (2 steps).

Physical properties: yellow oil;
R_f = 0.53 (silica gel, 30% EtOAc/hexanes);
MS (ESI): calcd for $C_{27}H_{28}NO_3$ $[M + H]^+$ 414.2, found 414.2;
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.67 (dd, *J* = 7.5, 1.4 Hz, 1H), 7.36–7.25 (m, 2H), 7.22–7.14 (m, 3H), 7.10–7.00 (m, 2H), 6.70 (t, *J* = 7.4 Hz, 1H), 6.54 (d, *J* = 8.3 Hz, 1H), 6.44 (dd, *J* = 8.6, 2.5 Hz, 1H), 6.29 (d, *J* = 2.5 Hz, 1H), 4.31 (s, 2H), 3.76 (s, 3H), 3.39 (s, 3H), 2.50 (dd, *J* = 13.5, 4.8 Hz, 1H), 1.83 (dd, *J* = 13.5, 8.2 Hz, 1H), 0.52–0.39 (m, 1H), 0.35–0.25 (m, 1H), 0.20–0.07 (m, 2H), 0.07– -0.05 (m, 1H).
^{13}C NMR (101 MHz, $CDCl_3$): δ 204.5, 161.1, 159.9, 158.6, 138.6, 136.1, 129.4, 128.4, 127.1, 127.0, 123.7, 122.9, 120.3, 116.5, 108.6, 104.3, 99.6, 73.1, 55.5, 55.2, 47.3, 39.3, 6.1, 5.6, 4.5.



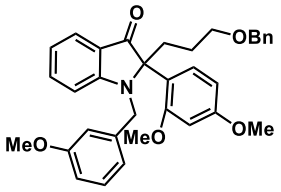
66

Indoxyl 66: Prepared from **S15** (0.1 mmol) according to General Procedure C with allyltrimethylsilane (5.0 equiv) in 66% yield (2 steps).

Physical properties: yellow oil;
R_f = 0.55 (silica gel, 30% EtOAc/hexanes);
MS (ESI): calcd for $C_{29}H_{31}NNaO_3$ $[M + Na]^+$ 464.2196, found 464.2208;
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.59 (d, *J* = 7.6 Hz, 1H), 7.37 (ddd, *J* = 8.5, 7.1, 1.4 Hz, 1H), 7.34–7.29 (m, 2H), 7.34–7.20 (m, 4H), 6.93 (d, *J* = 7.6 Hz, 1H), 6.88 (t, *J* = 2.0 Hz, 1H), 6.81

(dd, *J* = 8.2, 2.5 Hz, 1H), 6.72 (t, *J* = 7.4 Hz, 1H), 6.65 (d, *J* = 8.4 Hz, 1H), 5.44 (ddt, *J* = 17.1, 10.1, 7.1 Hz, 1H), 5.09–4.87 (m, 2H), 4.54 (AB q, *J* = 22.6, 16.7 Hz, 2H), 4.38 (AB q, *J* = 14.4, 11.9 Hz, 2H), 3.76 (s, 3H), 3.34–3.13 (m, 2H), 2.58 (dd, *J* = 14.4, 6.7 Hz, 1H), 2.49 (dd, *J* = 14.4, 7.5 Hz, 1H), 1.90 (ddd, *J* = 13.9, 11.0, 6.1 Hz, 1H), 1.79 (ddd, *J* = 14.0, 11.1, 4.9 Hz, 1H), 1.44–1.22 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 203.3, 161.5, 160.0, 139.8, 138.5, 137.6, 131.9, 129.9, 128.4, 127.7, 127.6, 124.4, 120.9, 119.5, 119.1, 117.5, 112.9, 112.7, 109.3, 74.0, 72.8, 70.0, 55.3, 46.9, 41.1, 32.5, 23.8.



67

Indoxyl 67: Prepared from **S15** (0.1 mmol) according to General Procedure C with 1,3-dimethoxybenzene (5.0 equiv) in 63% yield (2 steps).

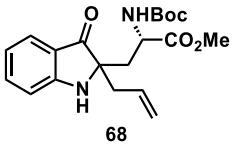
Physical properties: yellow oil;

R_f = 0.40 (silica gel, 33% EtOAc/hexanes);

MS (ESI): calcd for $C_{34}H_{35}NNaO_5$ $[M + Na]^+$ 560.2407, found 560.2396;

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.56 (d, *J* = 7.5 Hz, 1H), 7.33–7.16 (m, 7H), 7.03 (t, *J* = 7.9 Hz, 1H), 6.68–6.58 (m, 3H), 6.53–6.45 (m, 2H), 6.39 (dd, *J* = 8.7, 2.5 Hz, 1H), 6.25 (d, *J* = 2.5 Hz, 1H), 4.36 (AB q, *J* = 13.8, 12.3 Hz, 2H), 4.22 (d, *J* = 16.2 Hz, 1H), 4.10 (d, *J* = 16.2 Hz, 1H), 3.69 (s, 3H), 3.59 (s, 3H), 3.34–3.22 (m, 2H), 3.30 (s, 3H), 2.25–2.10 (m, 2H), 1.44–1.31 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 204.1, 161.1, 160.0, 159.8, 158.6, 140.3, 138.6, 136.5, 129.8, 129.5, 128.5, 127.7, 127.6, 123.7, 122.3, 120.1, 119.4, 116.8, 112.7, 112.6, 108.8, 104.5, 99.7, 72.9, 72.7, 70.3, 55.5, 55.3, 55.2, 47.1, 31.5, 23.3.



68

Indoxyl 68: Prepared from **S23** (0.1 mmol) according to General Procedure C with allyltrimethylsilane (5.0 equiv) in 67% yield (2 steps; dr = 1.3:1).

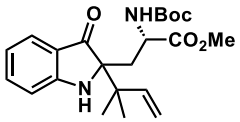
Physical properties: yellow oil;

R_f = 0.52 (silica gel, 50% EtOAc/hexanes);

MS (ESI): calcd for $C_{20}H_{26}N_2NaO_5$ $[M + Na]^+$ 397.1734, found 397.1756;

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.57 (d, *J* = 7.8, Hz, 0.57H), 7.56 (d, *J* = 7.7, Hz, 0.43H), 7.48–7.35 (m, 1H), 6.88–6.75 (m, 2H), 5.72–5.52 (m, 1H), 5.15–4.89 (m, 3.57H), 4.77 (d, *J* = 9.4 Hz, 0.43H), 4.52–4.43 (m, 0.43H), 4.35 (q, *J* = 6.4 Hz, 0.57H), 3.65 (s, 1.3H), 3.66 (s, 1.8H), 2.49–2.26 (m, 3H), 2.20–2.07 (m, 1H), 1.40 (s, 5.1H), 1.24 (s, 3.9H).

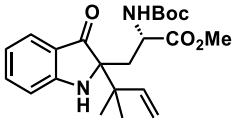
^{13}C NMR (151 MHz, $CDCl_3$): δ 203.9, 202.9, 173.2, 172.7, 160.4, 160.1, 156.1, 155.0, 137.28, 137.25, 131.5, 131.3, 124.7, 124.6, 121.1, 121.0, 120.3, 120.1, 119.3, 119.2, 112.82, 112.77, 80.2, 80.0, 67.4, 67.3, 52.6, 52.5, 51.1, 50.3, 42.2, 42.1, 38.7, 38.3, 28.4, 28.2.
Optical rotation: $[\alpha]^{27}_D$ = -6 (c = 0.5, $CHCl_3$).



69 *(major)*

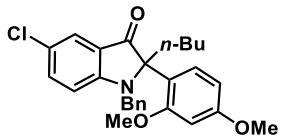
Indoxyl 69: Prepared from **S23** (1.0 mmol) according to General Procedure C with tributyl(3-methyl-2-butenyl)tin (5.0 equiv) in 65% yield (2 steps; dr = 1.4:1).

Physical properties: yellow foam;
R_f = 0.25 (silica gel, 30% EtOAc/hexanes);
MS (ESI): calcd for $C_{22}H_{31}N_2O_5$ $[M + H]^+$ 403.2227, found 403.2239;
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.54 (d, *J* = 7.7 Hz, 1H), 7.41 (td, *J* = 8.1, 7.7, 1.4 Hz, 1H), 6.87–6.71 (m, 2H), 6.02 (dd, *J* = 17.4, 10.8 Hz, 1H), 5.13 (dd, *J* = 10.8, 1.2 Hz, 1H), 5.06 (d, *J* = 17.4 Hz, 1H), 4.75 (d, *J* = =7.0 Hz, 1H), 4.72 (s, 1H), 4.12 (br s, 1H), 3.65 (s, 3H), 2.71 (dd, *J* = 14.8, 5.7 Hz, 1H), 2.35 (d, *J* = 13.7 Hz, 1H), 1.37 (s, 9H), 1.14 (s, 3H), 0.88 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$): δ 202.6, 172.7, 160.4, 154.6, 143.1, 136.9, 124.1, 122.9, 119.3, 114.9, 112.0, 79.9, 70.7, 52.3, 51.0, 43.9, 36.2, 28.4, 21.4, 20.9.
Optical rotation: $[\alpha]^{27}_D$ = -16 (c = 0.5, $CHCl_3$). [**Note:** optical rotation data obtained on a 1.4:1 mixture of diastereomers]



69 *(minor)*

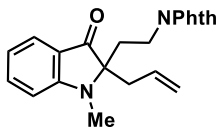
Physical properties: yellow foam;
R_f = 0.23 (silica gel, 30% EtOAc/hexanes);
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.51 (d, *J* = 7.7 Hz, 1H), 7.43–7.32 (m, 1H), 6.82 (d, *J* = 8.1 Hz, 1H), 6.74 (t, *J* = 7.4 Hz, 1H), 6.01 (dd, *J* = 17.4, 10.8 Hz, 1H), 5.15 (dd, *J* = 10.8, 1.2 Hz, 1H), 5.09 (dd, *J* = 17.4, 1.2 Hz, 1H), 4.79 (br s, 1H), 4.54 (d, *J* = 9.4 Hz, 1H), 4.33 (td, *J* = 9.2, 5.4 Hz, 1H), 3.62 (s, 3H), 2.43–2.21 (m, 2H), 1.17 (s, 9H), 1.14 (s, 3H), 0.90 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$): δ 204.1, 173.4, 160.9, 154.7, 143.0, 137.0, 124.1, 122.4, 118.8, 115.2, 111.8, 79.7, 70.5, 52.4, 50.6, 43.9, 35.7, 28.2, 21.3, 21.2.
Optical rotation: $[\alpha]^{27}_D$ = -16 (c = 0.5, $CHCl_3$). [**Note:** optical rotation data obtained on a 1.4:1 mixture of diastereomers]



70

Indoxyl 70: Prepared from **S16** (0.1 mmol) according to General Procedure C with 1,3-dimethoxybenzene (5.0 equiv) in 62% yield (2 steps).

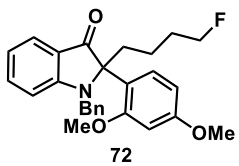
Physical properties: light yellow oil;
R_f = 0.64 (silica gel, 30% EtOAc/hexanes);
MS (ESI): calcd for $C_{27}H_{29}ClNO_3$ $[M + H]^+$ 450.1830, found 450.1817;
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.60 (d, *J* = 2.2 Hz, 1H), 7.35 (d, *J* = 8.6 Hz, 1H), 7.27 (dd, *J* = 8.5, 2.1 Hz, 1H), 7.23–7.17 (m, 3H), 7.12–6.99 (m, 2H), 6.59–6.44 (m, 2H), 6.34 (d, *J* = 2.5 Hz, 1H), 4.31 (d, *J* = 16.1 Hz, 1H), 4.15 (d, *J* = 16.1 Hz, 1H), 3.78 (s, 3H), 3.40 (s, 3H), 2.27–1.93 (m, 2H), 1.25–0.98 (m, 4H), 0.80 (t, *J* = 7.3 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$): δ 203.2, 161.2, 158.5, 158.3, 138.2, 136.1, 129.7, 128.6, 127.3, 127.2, 123.4, 123.1, 121.7, 119.8, 109.8, 104.5, 99.5, 73.7, 55.5, 55.2, 47.1, 34.8, 24.8, 23.2, 14.0.



71

Indoxyl 71: Prepared from **S19** (0.1 mmol) according to General Procedure C with allyltrimethylsilane (5.0 equiv) in 57% yield (2 steps).

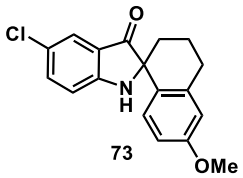
Physical properties: light yellow solid;
R_f = 0.24 (silica gel, 30% EtOAc/hexanes);
MS (ESI): calcd for $C_{22}H_{20}N_2NaO_3$ $[M + Na]^+$ 383.1366, found 383.1374;
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.77–7.72 (m, 2H), 7.69–7.63 (m, 2H), 7.50–7.39 (m, 2H), 6.73 (d, *J* = 8.9 Hz, 1H), 6.63 (t, *J* = 7.4 Hz, 1H), 5.41–5.25 (m, 1H), 5.03 (dd, *J* = 16.9, 1.7 Hz, 1H), 4.89 (dd, *J* = 10.1, 1.0 Hz, 1H), 3.45 (ddd, *J* = 13.6, 9.7, 6.9 Hz, 1H), 3.29 (ddd, *J* = 13.8, 9.9, 4.1 Hz, 1H), 3.08 (s, 3H), 2.56 (dd, *J* = 14.1, 6.7 Hz, 1H), 2.43 (dd, *J* = 14.1, 7.6 Hz, 1H), 2.36 (ddd, *J* = 13.8, 10.0, 7.0 Hz, 1H), 2.02 (ddd, *J* = 13.9, 9.7, 4.2 Hz, 1H).
^{13}C NMR (101 MHz, $CDCl_3$): δ 201.8, 167.9, 161.1, 137.9, 134.0, 132.1, 131.3, 124.5, 123.3, 120.0, 119.1, 116.9, 108.0, 71.5, 40.7, 33.1, 32.9, 27.5.



72

Indoxyl 72: Prepared from **S17** (0.1 mmol) according to General Procedure C with 1,3-dimethoxybenzene (5.0 equiv) in 63% yield (2 steps).

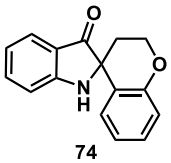
Physical properties: light yellow oil;
R_f = 0.43 (silica gel, 30% EtOAc/hexanes);
MS (ESI): calcd for $C_{27}H_{29}FNO_3$ $[M + H]^+$ 434.2126, found 434.2108;
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.64 (d, *J* = 7.7 Hz, 1H), 7.42–7.31 (m, 2H), 7.24–7.18 (m, 3H), 7.12–7.04 (m, 2H), 6.73 (t, *J* = 7.4 Hz, 1H), 6.64 (d, *J* = 8.3 Hz, 1H), 6.49 (dd, *J* = 8.6, 2.5 Hz, 1H), 6.33 (d, *J* = 2.5 Hz, 1H), 4.39–4.18 (m, 2H), 4.37 (d, *J* = 16.0 Hz, 1H), 4.13 (d, *J* = 16.1 Hz, 1H), 3.79 (s, 3H), 3.36 (s, 3H), 2.18 (td, *J* = 12.4, 5.1 Hz, 1H), 2.06 (td, *J* = 12.6, 4.1 Hz, 1H), 1.69–1.38 (m, 2H), 1.32–1.09 (m, 2H).
^{13}C NMR (101 MHz, $CDCl_3$): δ 204.3, 161.1, 160.3, 158.5, 138.7, 136.6, 129.7, 128.5, 127.3, 127.2, 123.8, 122.3, 119.9, 116.7, 108.6, 104.5, 99.5, 83.8 (d, $J_{C\text{-}F}$ = 164.7 Hz), 73.0, 55.5, 55.2, 47.1, 34.7, 30.7 (d, $J_{C\text{-}F}$ = 19.6 Hz), 18.7 (d, $J_{C\text{-}F}$ = 5.6 Hz).
^{19}F NMR (376 MHz, $CDCl_3$): δ -217.4.



73

Indoxyl 73: Prepared from **S12** (0.1 mmol) according to General Procedure C in 69% yield (2 steps).

Physical properties: yellow oil;
R_f = 0.45 (silica gel, 30% EtOAc/hexanes);
MS (ESI): calcd for $C_{18}H_{17}ClNO_2$ $[M + H]^+$ 314.0942, found 314.0955;
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.52 (d, *J* = 2.2 Hz, 1H), 7.34 (dd, *J* = 8.7, 2.2 Hz, 1H), 6.70 (dd, *J* = 11.0, 8.6 Hz, 2H), 6.62–6.50 (m, 2H), 4.97 (s, 1H), 3.68 (s, 3H), 2.88–2.68 (m, 2H), 2.26–2.13 (m, 1H), 2.07–1.95 (m, 1H), 1.85–1.66 (m, 2H).
^{13}C NMR (101 MHz, $CDCl_3$): δ 203.9, 159.3, 158.9, 139.7, 137.3, 127.7, 127.1, 124.6, 124.4, 121.1, 113.8, 113.56, 113.55, 68.8, 55.4, 34.1, 29.6, 19.4.

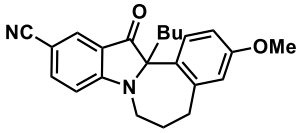


74

Indoxyl 74: Prepared from **S22** (0.1 mmol) according to General Procedure C in 70% yield (2 steps).

Physical properties: light green oil;
R_f = 0.53 (silica gel, 33% EtOAc/hexanes);
MS (ESI): calcd for $C_{16}H_{14}NO_2$ $[M + H]^+$ 252.1019, found 252.1022;

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.64 (d, *J* = 8.1 Hz, 1H), 7.51 (t, *J* = 7.7 Hz, 1H), 7.22–7.13 (m, 1H), 6.95–6.85 (m, 4H), 6.78 (t, *J* = 7.5 Hz, 1H), 5.04 (br s, 1H), 4.74 (ddd, *J* = 10.8, 7.3, 3.2 Hz, 1H), 4.21 (ddd, *J* = 11.4, 8.2, 3.0 Hz, 1H), 2.29 (ddd, *J* = 13.9, 8.2, 3.1 Hz, 1H), 2.04 (ddd, *J* = 13.8, 7.4, 3.0 Hz, 1H).
^{13}C NMR (101 MHz, $CDCl_3$): δ 203.3, 160.7, 155.7, 137.8, 129.9, 126.6, 125.5, 121.2, 121.1, 120.0, 119.9, 117.9, 112.6, 64.1, 62.7, 32.3

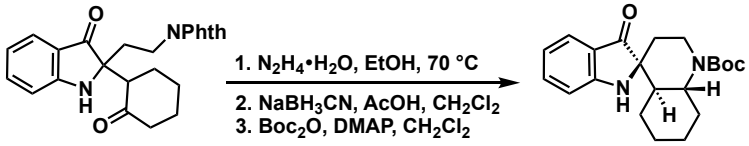


75

Indoxyl 75: Prepared from **S18** (0.1 mmol) according to General Procedure C in 58% yield (2 steps).

Physical properties: yellow oil;
R_f = 0.42 (silica gel, 30% EtOAc/hexanes);
MS (ESI): calcd for $C_{23}H_{25}N_2O_2$ $[M + H]^+$ 361.1911, found 361.1928;
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.87 (d, *J* = 1.7 Hz, 1H), 7.66 (dd, *J* = 8.7, 1.8 Hz, 1H), 7.61 (d, *J* = 8.9 Hz, 1H), 6.91 (d, *J* = 8.7 Hz, 1H), 6.83 (dd, *J* = 8.8, 2.8 Hz, 1H), 6.57 (d, *J* = 2.8 Hz, 1H), 3.91 (ddd, *J* = 14.9, 7.9, 3.6 Hz, 1H), 3.77 (s, 3H), 3.51 (ddd, *J* = 14.9, 8.9, 7.4 Hz, 1H), 2.58 (ddd, *J* = 14.5, 12.0, 4.6 Hz, 1H), 2.48 (dt, *J* = 14.6, 4.1 Hz, 1H), 2.38–2.24 (m, 2H), 2.07 (ddd, *J* = 13.9, 12.4, 4.3 Hz, 1H), 2.04–1.89 (m, 1H), 1.39–1.18 (m, 2H), 1.18–0.91 (m, 2H), 0.84 (t, *J* = 7.3 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$): δ 199.5, 161.4, 159.1, 140.2, 140.0, 130.7, 129.9, 127.8, 120.9, 119.5, 117.2, 112.3, 109.3, 99.5, 77.8, 55.4, 40.2, 38.7, 32.2, 25.71, 25.68, 22.8, 14.0.

5. Experimental Procedures for Synthetic Applications



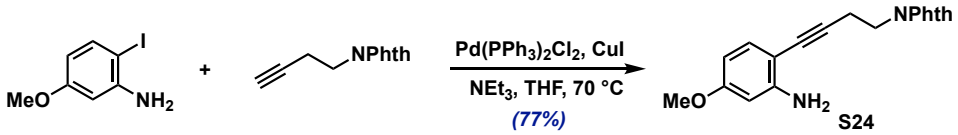
38 (dr = 1.2:1) (47%, 3 steps) 76 [X-ray]

Iboluteine core 76: *Step 1:* To a solution of **38** (12.0 mg, 0.03 mmol, 1.0 equiv) in EtOH (2.0 mL) was added NH_2NH_2•H_2O (45 µL, 0.90 mmol, 30.0 equiv) under argon. The reaction mixture was stirred at 70 °C for 2 h. The reaction mixture was transferred to a separatory funnel containing saturated aq. $NaHCO_3$ (10 mL) and extracted with CH_2Cl_2 (10 mL). The aqueous layer was re-extracted with CH_2Cl_2 (2 × 10 mL). The combined organic layers were washed with brine, dried over Na_2SO_4, filtered, and concentrated under vacuum.
Step 2: The crude material obtained in the previous step was dissolved in CH_2Cl_2 (2.0 mL) and then AcOH (20.5 mg in 1.0 mL CH_2Cl_2, 175 µL, 2.0 equiv) was added, followed by $NaBH_3CN$ (6.0 mg, 0.09 mmol, 3.0 equiv). The resulting solution was stirred at 23 °C overnight. The reaction mixture was transferred to a separatory funnel containing saturated aq. $NaHCO_3$ (10 mL) and extracted with CH_2Cl_2 (10 mL). The aqueous layer was re-extracted with CH_2Cl_2 (2 ×

10 mL). The combined organic layers were washed with brine, dried over Na_2SO_4, filtered, and concentrated under vacuum.

Step 3: The crude material obtained in the previous step was dissolved in CH_2Cl_2 (2.0 mL) and cooled to 0 °C. DMAP (7.7 mg in 0.77 mL CH_2Cl_2, 40 μL, 0.1 equiv) was added, followed by Boc_2O (9.0 mg, 0.039 mmol, 1.3 equiv). The reaction mixture was stirred at 23 °C overnight (17 h). The reaction mixture was transferred to a separatory funnel containing saturated aq. $NaHCO_3$ (10 mL) and extracted with CH_2Cl_2 (10 mL). The aqueous layer was re-extracted with CH_2Cl_2 (2 × 10 mL). The combined organic layers were washed with brine, dried over Na_2SO_4, filtered, and concentrated under vacuum. The resulting crude product was chromatographed on silica gel using hexane/ ethyl acetate to give the desired product **76** as a light yellow solid (5.2 mg, 47% in three steps).

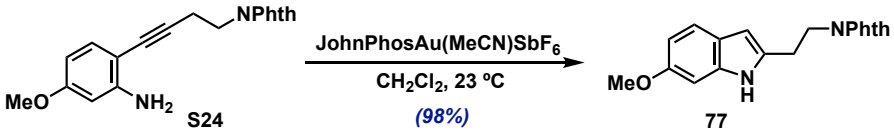
Physical properties: light yellow solid;
R_f = 0.41 (silica gel, 25% EtOAc/hexanes);
MS (ESI): calcd for $C_{21}H_{29}N_2O_3$ $[M + H]^+$ 357.2, found 357.2;
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.55 (d, *J* = 7.8 Hz, 1H), 7.43 (ddd, *J* = 8.4, 7.0, 1.4 Hz, 1H), 6.84 (d, *J* = 8.3 Hz, 1H), 6.79 (t, *J* = 7.4 Hz, 1H), 4.80 (s, 1H), 4.00 (dd, *J* = 14.2, 7.7 Hz, 1H), 3.54 (td, *J* = 10.9, 3.2 Hz, 1H), 3.23 (ddd, *J* = 14.1, 11.6, 5.9 Hz, 1H), 2.25–2.09 (m, 2H), 1.99 (td, *J* = 11.5, 2.9 Hz, 1H), 1.83–1.70 (m, 2H), 1.62–1.55 (m, 2H), 1.50 (s, 9H), 1.43–1.29 (m, 3H), 1.06–0.93 (m, 1H).
^{13}C NMR (101 MHz, $CDCl_3$): δ 205.5, 161.1, 155.1, 137.6, 124.5, 120.7, 118.9, 112.3, 80.0, 67.6, 56.2, 44.9, 36.7, 36.0, 31.3, 28.7, 26.0, 25.6, 25.4.



Alkynyl aniline S24: A flask equipped with a magnetic stir bar and a rubber septum was charged with 2-iodo-5-methoxyaniline (1.8 g, 7.39 mmol, 1.0 equiv), *N*-(3-butynyl)phthalimide (1.61 g, 8.13 mmol, 1.1 equiv), $PdCl_2(PPh_3)_2$ (103 mg, 0.15 mmol, 0.02 equiv), and CuI (56 mg, 0.29 mmol, 0.04 equiv). The flask was evacuated and backfilled with argon three times, and THF (10 mL) and Et_3N (10 mL) were added. The reaction was stirred at 70 °C until completion (5 h). The reaction mixture was transferred to a separatory funnel containing brine (20 mL) and extracted with EtOAc (30 mL). The aqueous layer was re-extracted with EtOAc (2 × 20 mL). The combined organic layers were washed with brine, dried over Na_2SO_4, filtered, and concentrated under vacuum. The resulting crude product was chromatographed on silica gel eluting with hexanes/CH_2Cl_2/EtOAc (5:5:2) to give the desired product **S24** as a yellow solid (1.82 g, 77%).

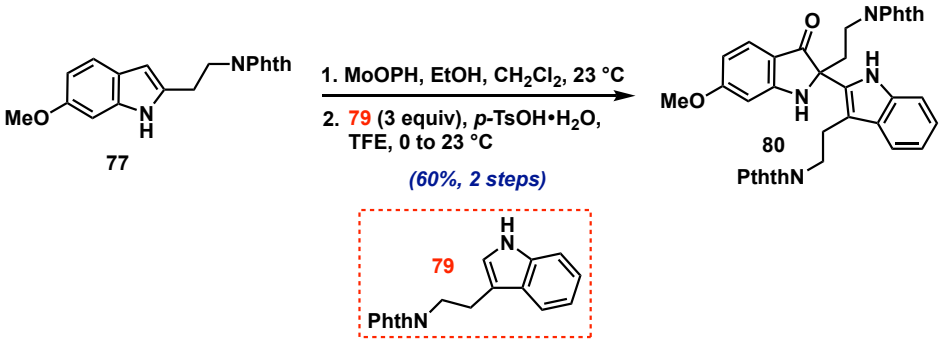
Physical properties: yellow solid;
R_f = 0.35 (silica gel, 33% EtOAc/hexanes);
MS (ESI): calcd for $C_{19}H_{16}N_2O_3$ $[M + H]^+$ 321.1, found 321.1;

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.84 (dd, *J* = 5.4, 3.0 Hz, 2H), 7.71 (dd, *J* = 5.5, 3.1 Hz, 2H), 7.07 (d, *J* = 8.2 Hz, 1H), 6.31–6.06 (m, 2H), 4.26 (br s, 2H), 3.97 (t, *J* = 6.7 Hz, 2H), 3.72 (s, 3H), 2.87 (t, *J* = 6.7 Hz, 2H).
^{13}C NMR (101 MHz, $CDCl_3$): δ 168.4, 160.8, 149.6, 134.2, 133.4, 132.1, 123.5, 104.2, 101.0, 99.5, 89.7, 79.0, 55.2, 37.2, 19.9.



2-alkylindole 77: A flask equipped with a magnetic stir bar and a rubber septum was charged with **S24** (340 mg, 1.06 mmol, 1.0 equiv). The flask was evacuated and backfilled with argon three times, and CH_2Cl_2 (20 mL) was added, followed by JohnPhosAu(CH_3CN)$SbPF_6$ (20.3 mg, 0.026 mmol, 0.025 equiv). The reaction was stirred at 23 °C overnight (~17 h), at which point the reaction mixture was transferred to a separatory funnel containing saturated aq. $NaHCO_3$ (20 mL) and extracted with CH_2Cl_2 (20 mL). The aqueous layer was re-extracted with CH_2Cl_2 (2 × 10 mL). The combined organic layers were washed with brine, dried over Na_2SO_4, filtered, and concentrated under vacuum. The resulting crude product was chromatographed on silica gel eluting with hexanes/CH_2Cl_2/EtOAc (5:5:2) to give the desired product **77** as a light yellow foam (335 mg, 98%).

Physical properties: yellow solid;
R_f = 0.37 (silica gel, 33% EtOAc/hexanes);
MS (ESI): calcd for $C_{19}H_{16}N_2O_3$ $[M + H]^+$ 321.1, found 321.1;
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.13 (br s, 1H), 7.82 (dd, *J* = 5.4, 3.1 Hz, 2H), 7.70 (dd, *J* = 5.5, 3.1 Hz, 2H), 7.36 (d, *J* = 8.6 Hz, 1H), 6.83 (d, *J* = 2.3 Hz, 1H), 6.73 (dd, *J* = 8.6, 2.3 Hz, 1H), 6.24 (d, *J* = 1.1 Hz, 1H), 4.03 (t, *J* = 7.4 Hz, 2H), 3.82 (s, 3H), 3.16 (t, *J* = 7.4 Hz, 2H).
^{13}C NMR (101 MHz, $CDCl_3$): δ 168.4, 156.2, 137.0, 134.2, 133.8, 132.1, 123.5, 123.0, 120.6, 109.6, 101.0, 94.6, 55.8, 37.3, 27.6.



Indoxyl 80: To a solution of indole substrate **77** (165 mg, 0.51 mmol, 1.0 equiv) in CH_2Cl_2 (12.0 mL) and EtOH (12.0 mL) was added MoOPH (446 mg, 1.03 mmol, 2.0 equiv) under argon. The flask was covered with aluminum foil and stirred at 23 °C overnight. Upon completion of the reaction (TLC), the reaction mixture was transferred to a separatory funnel containing saturated aq. $NaHCO_3$ (50 mL) and extracted with CH_2Cl_2 (20 mL). The aqueous

layer was re-extracted with CH_2Cl_2 (2 × 20 mL). The combined organic layers were washed with brine, dried over Na_2SO_4, filtered, and concentrated under vacuum. The crude material was used in the next step directly.

The crude material obtained above was dissolved in TFE (10.0 mL) and **79**[9] (437 mg, 1.51 mmol, 3.0 equiv) was added. The resulting solution was cooled to 0 °C and a solution of *p*-TsOH•H_2O in TFE (10 mg/mL, 0.95 mL, 0.1 equiv) was slowly added. The reaction was stirred at 0 °C and warm to 23 °C gradually. Upon completion of the reaction (typically 1–2 h; TLC), the reaction mixture was transferred to a separatory funnel containing saturated aq. $NaHCO_3$ (20 mL) and extracted with CH_2Cl_2 (10 mL). The aqueous layer was re-extracted with CH_2Cl_2 (2 × 10 mL). The combined organic layers were washed with brine, dried over Na_2SO_4, filtered, and concentrated under vacuum. The resulting crude product was chromatographed on silica gel eluting with hexanes/CH_2Cl_2/EtOAc (5:5:2) to give the desired product **80** as a yellow solid (206 mg, 60% in two steps) whose spectroscopic data matched those previously reported by Movassaghi (Tables S2 & S3).[10]

Physical properties: yellow solid;
R_f = 0.29 (silica gel, 50% EtOAc/hexanes);
MS (ESI): calcd for $C_{37}H_{29}N_4O_6$ $[M + H]^+$ 625.2082, found 625.2098;
^{1}H NMR (400 MHz, $CDCl_3$): δ 9.13 (s, 1H), 7.89 (dd, *J* = 5.4, 3.0 Hz, 2H), 7.75 (dd, *J* = 5.5, 3.0 Hz, 2H), 7.62 (dd, *J* = 5.4, 3.1 Hz, 2H), 7.53 (dd, *J* = 5.5, 3.1 Hz, 2H), 7.50 (d, *J* = 7.9 Hz, 1H), 7.43 (d, *J* = 8.7 Hz, 1H), 7.24 (d, *J* = 8.1 Hz, 1H), 7.06 (t, *J* = 6.9 Hz, 1H), 6.98 (t, *J* = 7.4 Hz, 1H), 6.81 (s, 1H), 6.66 (d, *J* = 2.1 Hz, 1H), 6.36 (dd, *J* = 8.7, 2.1 Hz, 1H), 3.94–3.73 (m, 4H), 3.89 (s, 3H), 3.12 (t, *J* = 8.7 Hz, 1H), 2.70 (dt, *J* = 14.8, 7.5 Hz, 1H), 2.46–2.35 (m, 1H).
^{13}C NMR (101 MHz, $CDCl_3$): δ 198.1, 168.72, 168.66, 168.2, 163.4, 135.4, 134.2, 133.9, 132.4, 131.7, 131.0, 128.5, 126.7, 123.5, 123.1, 122.4, 119.7, 118.1, 111.8, 111.2, 109.8, 108.7, 94.7, 68.2, 55.8, 38.9, 36.9, 33.7, 24.3.

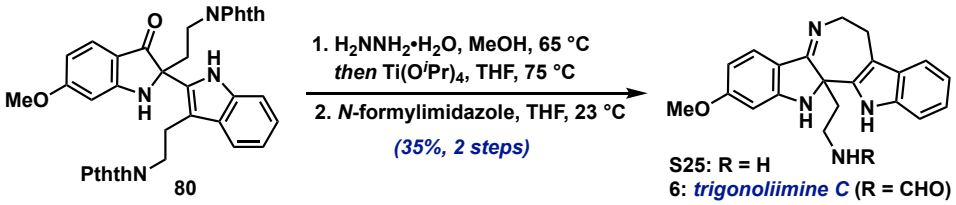
Table S2: Comparison of ^{1}H NMR shifts (δ) of Movassaghi's trigonoliimine C precursor **80** and our own synthetic **80** in $CDCl_3$.

80 (Movassaghi) (500 MHz)	**80** (Smith) (400 MHz)
9.10 (s, 1H)	9.13 (s, 1H)
7.87 (dd, *J* = 5.4, 3.0 Hz, 2H)	7.89 (dd, *J* = 5.4, 3.0 Hz, 2H)
7.73 (dd, *J* = 5.4, 3.0 Hz, 2H)	7.75 (dd, *J* = 5.5, 3.0 Hz, 2H)
7.61 (dd, *J* = 5.5, 3.0 Hz, 2H)	7.62 (dd, *J* = 5.4, 3.1 Hz, 2H)
7.52 (dd, *J* = 5.5, 3.0 Hz, 2H)	7.53 (dd, *J* = 5.5, 3.1 Hz, 2H)
7.49 (d, *J* = 7.9 Hz, 1H)	7.50 (d, *J* = 7.9 Hz, 1H)
7.42 (d, *J* = 8.7 Hz, 1H)	7.43 (d, *J* = 8.7 Hz, 1H)
7.22 (d, *J* = 8.1 Hz, 1H)	7.24 (d, *J* = 8.1 Hz, 1H)
7.05 (app t, *J* = 8.1 Hz, 1H)	7.06 (t, *J* = 6.9 Hz, 1H)
6.97 (app t, *J* = 7.9 Hz, 1H)	6.98 (t, *J* = 7.4 Hz, 1H)
6.78 (s, 1H)	6.81 (s, 1H)

6.64 (d, J = 2.1 Hz, 1H)	6.66 (d, J = 2.1 Hz, 1H)
6.34 (dd, J = 8.7, 2.1 Hz, 1H)	6.36 (dd, J = 8.7, 2.1 Hz, 1H)
3.91–3.73 (m, 4H)	3.94–3.73 (m, 4H)
3.87 (s, 3H)	3.89 (s, 3H)
3.11 (t, J = 8.7 Hz, 2H)	3.12 (t, J = 8.7 Hz, 1H)
2.70–2.64 (m, 1H)	2.70 (dt, J = 14.8, 7.5 Hz, 1H)
2.41–2.36 (m, 1H)	2.46–2.35 (m, 1H)

Table S3: Comparison of ^{13}C NMR shifts (δ) of Movassaghi's trigonoliimine C precursor **80** and our own synthetic **80** in $CDCl_3$.

80 (Movassaghi) (126 MHz)	**80** (Smith) (101 MHz)
198.2	198.1
168.8	168.72
168.7	168.66
168.3	168.2
163.4	163.4
135.5	135.4
134.3	134.2
134.0	133.9
132.4	132.4
131.7	131.7
131.1	131.0
128.6	128.5
126.8	126.7
123.5	123.5
123.2	123.1
122.5	122.4
119.8	119.7
118.1	118.1
111.9	111.8
111.2	111.2
109.9	109.8
108.7	108.7
94.8	94.7
68.2	68.2
55.9	55.8
39.0	38.9
37.0	36.9
33.7	33.7
24.4	24.3



Trigonoliimine C (6): *Step 1:* Hydrazine monohydrate (75 µL, 1.5 mmol, 15.0 equiv) was added via syringe to a solution of **80** (63.2 mg, 0.1 mmol, 1 equiv) in MeOH (3 mL) under an atmosphere of argon at 23 °C. The reaction vial was sealed and heated to 65 °C. After 2.5 h, the yellow homogeneous reaction mixture was allowed to cool to 23 °C and concentrated to result in a yellow solid. This solid was redissolved in THF (3 mL) and a solution of titanium isoproxide (0.26 mL, 0.2 mmol, 2.0 equiv) in THF was added via syringe, and the resulting mixture was warmed to 75 °C. After 2 h, the reaction mixture was concentrated under reduced pressure and the crude residue was purified by flash column chromatography using CH_2Cl_2/MeOH/NH_3•H_2O (100:5:0.2) as eluent to afford slightly impure imine **S25** as a yellow solid.

Step 2: **S25** was dissolved in THF (3 mL) and freshly prepared *N*-formylimidazole[11] (11 mg, 0.11 mmol, 1.1 equiv) in THF (1 mL) was added to the flask under argon at 23 °C. The resulting mixture was stirred at 23 °C for 1 h. The reaction mixture was transferred to a separatory funnel containing saturated aq. $NaHCO_3$ (10 mL) and extracted with CH_2Cl_2 (10 mL). The aqueous layer was re-extracted with CH_2Cl_2 (2 × 10 mL). The combined organic layers were washed with brine, dried over Na_2SO_4, filtered, and concentrated under vacuum. The resulting crude product was chromatographed on silica gel eluting with CH_2Cl_2/MeOH/ NH_3•H_2O (100:2:0.2) to give trigonoliimine C (**6**) as a yellow solid (13.1 mg, 35% over two steps).

Physical properties: light yellow solid;
R_f = 0.29 (silica gel, 10% MeOH/CH_2Cl_2 with 2 drops of NH_3•H_2O);
MS (ESI): calcd for $C_{22}H_{22}N_4NaO_2$ $[M + Na]^+$ 397.2, found 397.2;
^{1}H NMR (400 MHz, CD_3OD): δ 7.96 (s, 1H), 7.56 (d, *J* = 9.4 Hz, 1H), 7.44 (dt, J = 7.8, 1.0 Hz, 1H), 7.35 (dt, *J* = 8.2, 0.9 Hz, 1H), 7.13 (ddd, *J* = 8.2, 7.0, 1.2 Hz, 1H), 7.02 (ddd, *J* = 8.0, 7.0, 1.0 Hz, 1H), 6.46–6.39 (m, 2H), 4.48 (td, *J* = 13.3, 3.0 Hz, 1H), 3.99 (dt, *J* = 13.1, 3.6 Hz, 1H), 3.85 (s, 3H), 3.30–3.23 (m, 2H), 3.19 (dt, *J* = 16.9, 3.8 Hz, 1H), 3.06 (ddd, *J* = 17.0, 13.6, 3.8 Hz, 1H), 2.80 (ddd, *J* = 14.2, 9.9, 6.1 Hz, 1H), 2.51 (ddd, *J* = 14.2, 10.0, 5.4 Hz, 1H).
^{13}C NMR (151 MHz, CD_3OD): δ 175.6, 167.5, 163.9, 159.8, 136.9, 131.9, 129.8, 125.5, 123.0, 120.0, 118.8, 116.8, 111.8, 110.5, 108.9, 95.6, 68.7, 56.0, 47.8, 40.6, 35.1, 24.6.

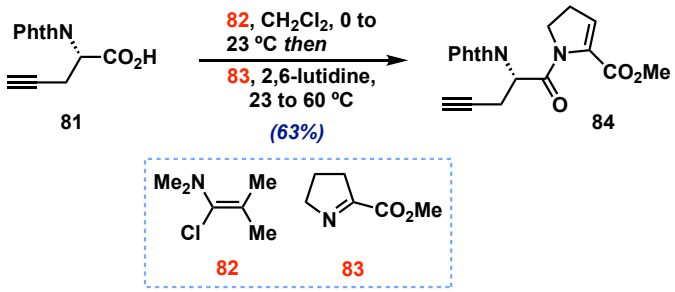
Table S4: Comparison of ^{1}H NMR shifts (δ) of Movassaghi's trigonoliimine C (**6**) and our own synthetic **6** in CD_3OD.

6 (Movassaghi) (500 MHz)	**6** (Smith) (400 MHz)
7.96 (s, 1H)	7.96 (s, 1H)
7.50 (d, *J* = 9.3 Hz, 1H)	7.56 (d, *J* = 9.4 Hz, 1H)
7.43 (dt, *J* = 7.9, 0.9 Hz, 1H)	7.44 (dt, *J* = 7.8, 1.0 Hz, 1H)

7.33 (dt, *J* = 8.1, 0.8 Hz, 1H)	7.35 (dt, *J* = 8.2, 0.9 Hz, 1H)
7.09 (ddd, *J* = 8.1, 7.0, 1.1 Hz, 1H)	7.13 (ddd, *J* = 8.2, 7.0, 1.2 Hz, 1H)
7.00 (ddd, *J* = 7.9, 7.0, 0.9 Hz, 1H)	7.02 (ddd, *J* = 8.0, 7.0, 1.0 Hz, 1H)
6.36 (d, *J* = 2.4 Hz, 1H) 6.36 (dd, *J* = 6.8, 2.2 Hz, 1H)	6.46–6.39 (m, 2H)
4.42 (td, *J* = 14.3, 2.7 Hz, 1H)	4.48 (td, *J* = 13.3, 3.0 Hz, 1H)
4.01 (dt, *J* = 12.4, 3.5 Hz, 1H)	3.99 (dt, *J* = 13.1, 3.6 Hz, 1H)
3.82 (s, 3H)	3.85 (s, 3H)
3.30–3.28 (m, 2H)	3.30–3.23 (m, 2H)
3.15 (dt, *J* = 16.7, 3.1 Hz, 1H)	3.19 (dt, *J* = 16.9, 3.8 Hz, 1H)
2.99 (ddd, *J* = 16.8, 13.5, 3.4 Hz, 1H)	3.06 (ddd, *J* = 17.0, 13.6, 3.8 Hz, 1H)
2.75 (ddd, *J* = 14.1, 10.2, 6.5 Hz, 1H)	2.80 (ddd, *J* = 14.2, 9.9, 6.1 Hz, 1H)
2.40 (ddd, *J* = 14.0, 8.9, 6.9 Hz, 1H)	2.51 (ddd, *J* = 14.2, 10.0, 5.4 Hz, 1H)

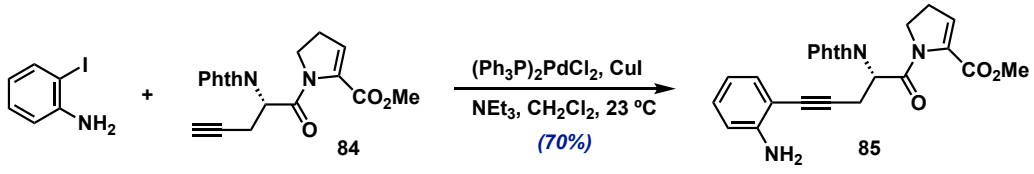
Table S5: Comparison of ^{13}C NMR shifts (δ) of Movassaghi's trigonoliimine C and our own synthetic **6** in CD_3OD.

6 (Movassaghi) (126 MHz)	**6** (Smith) (101 MHz)
175.6	175.6
167.3	167.5
164.0	163.9
159.6	159.8
137.1	136.9
132.3	131.9
130.0	129.8
125.6	125.5
123.1	123.0
120.1	120.0
119.0	118.8
117.4	116.8
111.9	111.8
110.6	110.5
108.7	108.9
95.9	95.6
68.7	68.7
56.1	56.0
48.1	47.8
40.8	40.6
35.3	35.1
24.7	24.6



Enamide 84: To a solution of **81**[12] (846 mg, 3.48 mmol, 1.0 equiv) in CH_2Cl_2 (25 mL) was added Ghosez reagent (**82**, 0.6 mL, 4.54 mmol, 1.3 equiv) dropwise at 0 °C. The reaction mixture was stirred at 0 °C and allowed to warm to 23 °C gradually (~2 h). A solution of **83**[13] (583 mg, 4.59 mmol, 1.3 equiv) and 2,6-lutidine (1.0 mL, 7.55 mmol, 2.6 equiv) in CH_2Cl_2 (6 mL) were then added to the solution slowly. After stirring at 23 °C for 2 h the flask was sealed and warm up to 60 °C overnight (~14 h). The reaction mixture was transferred to a separatory funnel containing 1 N aq. HCl (20 mL) and extracted with CH_2Cl_2 (20 mL). The aqueous layer was re-extracted with CH_2Cl_2 (2 × 10 mL). The combined organic layers were washed with brine, dried over Na_2SO_4, filtered, and concentrated under vacuum. The resulting crude product was chromatographed on silica gel with EtOAc/hexanes to give enamide **84** as light yellow solid (1.17 g, 63% corrected), containing 32% (w/w, 0.40 g) of *N*,*N*-dimethylisobutyramide. This impurity did not interfere in the subsequent Sonogashira coupling.

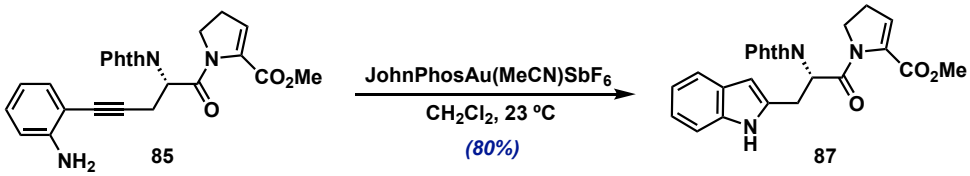
Physical properties: light yellow solid;
R_f = 0.36 (silica gel, 50% EtOAc/hexanes);
MS (ESI): calcd for $C_{19}H_{16}N_2O_5$ $[M + H]^+$ 353.1, found 353.1;
^{1}H NMR (600 MHz, $CDCl_3$): δ 7.88 (dd, *J* = 5.4, 3.1 Hz, 2H), 7.76 (dd, *J* = 5.5, 3.0 Hz, 2H), 6.02 (t, *J* = 3.1 Hz, 1H), 5.22 (dd, *J* = 10.2, 5.0 Hz, 1H), 4.16 (br s, 1H), 3.79 (s, 3H), 3.78–3.71 (m, 1H), 3.28–3.13 (m, 1H), 3.02 (ddd, *J* = 17.5, 5.0, 2.7 Hz, 1H), 2.74 (dtd, *J* = 17.7, 9.8, 2.5 Hz, 1H), 2.49 (ddt, *J* = 17.5, 10.4, 3.5 Hz, 1H), 1.87 (t, *J* = 2.7 Hz, 1H).
^{13}C NMR (151 MHz, $CDCl_3$): δ 167.1, 166.2, 161.3, 136.4, 134.6, 131.5, 123.9, 79.7, 71.1, 52.5, 51.3, 50.2, 29.3, 20.0. [**Note:** 1 carbon signal missing due to overlap]
Optical rotation: $[\alpha]^{26}_D$ = -102 (c = 0.5, $CHCl_3$).



Aniline 85: A flask equipped with a magnetic stir bar and a rubber septum was charged with 2-iodoaniline (729 mg, 3.33 mmol, 2.0 equiv), **84** (584 mg, 1.66 mmol, 1.0 equiv), $PdCl_2(PPh_3)_2$ (65 mg, 0.093 mmol, 0.05 equiv), and CuI (36.7 mg, 0.19 mmol, 0.1 equiv). The flask was evacuated and backfilled with argon three times, and degassed CH_2Cl_2 (10 mL) and Et_3N (10 mL) were added to the flask. The reaction was stirred at 23 °C until completion (6 h). The reaction mixture was then transferred to a separatory funnel containing brine (20 mL) and extracted with CH_2Cl_2 (20 mL). The aqueous layer was re-extracted with CH_2Cl_2 (2 × 10 mL). The combined organic layers were washed with brine, dried over Na_2SO_4, filtered, and

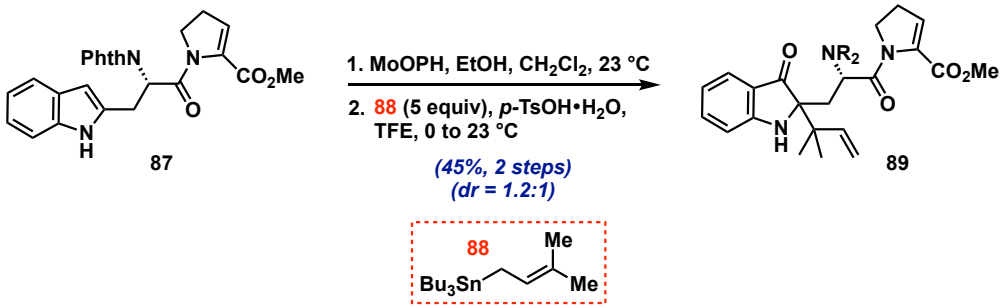
concentrated under vacuum. The resulting crude product was chromatographed on silica gel eluting with hexanes/CH_2Cl_2/EtOAc (5:5:2) to give aniline **85** as a light yellow foam (510 mg, 70%).

Physical properties: light yellow foam;
R_f = 0.10 (silica gel, 33% EtOAc/hexanes);
MS (ESI): calcd for $C_{25}H_{21}N_3O_5$ $[M + H]^+$ 444.2, found 444.2;
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.85 (dd, *J* = 5.5, 3.0 Hz, 2H), 7.73 (dd, *J* = 5.5, 3.1 Hz, 2H), 7.08–6.93 (m, 2H), 6.58 (d, *J* = 7.9 Hz, 1H), 6.54 (td, *J* = 7.5, 1.1 Hz, 1H), 6.02 (t, *J* = 3.0 Hz, 1H), 5.31 (dd, *J* = 9.1, 5.8 Hz, 1H), 4.28–4.09 (m, 3H), 3.84–3.74 (m, 1H), 3.80 (s, 3H), 3.45–3.24 (m, 2H), 2.81–2.66 (m, 1H), 2.50 (ddt, *J* = 17.6, 10.4, 3.5 Hz, 1H).
^{13}C NMR (151 MHz, $CDCl_3$): δ 167.2, 166.3, 161.3, 148.2, 136.3, 134.6, 134.5, 132.1, 131.4, 129.2, 123.8, 117.4, 114.2, 107.7, 90.3, 79.8, 52.4, 51.7, 50.3, 29.1, 21.3.
Optical rotation: $[\alpha]^{26}_D$ = -79 (c = 0.5, $CHCl_3$).



Indole 87: A flask equipped with a magnetic stir bar and a rubber septum was charged with **85** (410 mg, 0.93 mmol, 1.0 equiv). The flask was evacuated and backfilled with argon three times, and CH_2Cl_2 (10 mL) was added. JohnPhosAu(CH_3CN)SbF_6 (**86**, 42 mg, 0.05 mmol, 0.05 equiv) was then added and the reaction stirred at rt until completion (~3 h). The reaction mixture was transferred to a separatory funnel containing saturated aq. $NaHCO_3$ (20 mL) and extracted with CH_2Cl_2 (10 mL). The aqueous layer was re-extracted with CH_2Cl_2 (2 × 10 mL). The combined organic layers were washed with brine, dried over Na_2SO_4, filtered, and concentrated under vacuum. The resulting crude product was chromatographed on silica gel eluting with hexanes/CH_2Cl_2/EtOAc (5:5:2) to give indole **87** as a light yellow foam (328 mg, 80%).

Physical properties: light yellow foam;
R_f = 0.15 (silica gel, 33% EtOAc/hexanes);
MS (ESI): calcd for $C_{25}H_{21}N_3O_5$ $[M + H]^+$ 444.2, found 444.2;
^{1}H NMR (400 MHz, $CDCl_3$): δ 9.08 (br s, 1H), 7.77 (dd, *J* = 5.5, 3.1 Hz, 2H), 7.70 (dd, *J* = 5.5, 3.1 Hz, 2H), 7.41 (d, *J* = 7.8 Hz, 1H), 7.33 (d, *J* = 8.0 Hz, 1H), 7.10 (ddd, *J* = 8.2, 7.0, 1.2 Hz, 1H), 7.00 (t, *J* = 7.5 Hz, 1H), 6.17 (br s, 1H), 6.03 (t, *J* = 3.0 Hz, 1H), 5.32 (dd, *J* = 8.1, 4.6 Hz, 1H), 4.18 (br s, 1H), 3.90–3.63 (m, 2H), 3.79 (s, 3H), 3.42 (dd, *J* = 14.6, 4.6 Hz, 1H), 2.74–2.58 (m, 1H), 2.47 (ddt, *J* = 17.8, 10.3, 3.8 Hz, 1H).
^{13}C NMR (151 MHz, $CDCl_3$): δ 167.8, 166.9, 161.3, 136.3, 135.9, 134.4, 131.3, 128.2, 123.6, 123.5, 121.3, 119.7, 119.3, 119.2, 111.0, 101.8, 53.0, 52.4, 50.3, 28.9. [**Note:** 1 carbon signal missing due to overlap]
Optical rotation: $[\alpha]^{26}_D$ = -37 (c = 0.5, $CHCl_3$).



Prenyl Indoxyl 89: *Step 1:* To a solution of **87** (45.1 mg, 0.1 mmol) in CH_2Cl_2 (2.0 mL) and EtOH (2.0 mL) was added MoOPH (93 mg, 2.0 equiv) under argon. The flask was covered with aluminum foil and stirred at 23 °C overnight. Upon completion of the reaction (TLC), the reaction mixture was transferred to a separatory funnel containing saturated aq. $NaHCO_3$ (20 mL) and extracted with CH_2Cl_2 (10 mL). The aqueous layer was re-extracted with CH_2Cl_2 (2 × 10 mL). The combined organic layers were washed with brine, dried over Na_2SO_4, filtered, and concentrated under vacuum. The crude material was purified by rapid column chromatography on triethylamine-deactivated silica gel and used in the next step directly.

Step 2: The so-obtained material was dissolved in TFE (2.0 mL) and tributyl(3-methyl-2-butenyl)tin (**88**, 0.19 mL, 5.0 equiv) was added. The resulting solution was cooled to 0 °C and a solution of *p*-TsOH•H_2O in TFE (10 mg/mL, 190 µL, 0.1 equiv) was added slowly. The reaction mixture was stirred at 0 °C and allowed to warm to 23 °C gradually. Upon completion (typically 1–2 h; TLC), the reaction mixture was transferred to a separatory funnel containing saturated aq. $NaHCO_3$ (20 mL) and extracted with CH_2Cl_2 (10 mL). The aqueous layer was re-extracted with CH_2Cl_2 (2 × 10 mL). The combined organic layers were washed with brine, dried over Na_2SO_4, filtered, and concentrated under vacuum. The resulting crude product was chromatographed on silica gel to give indoxyl **89** (24 mg, 45%, dr = 1.2:1).

Physical properties: yellow foam;

R_f = 0.27 (silica gel, 50% EtOAc/hexanes);

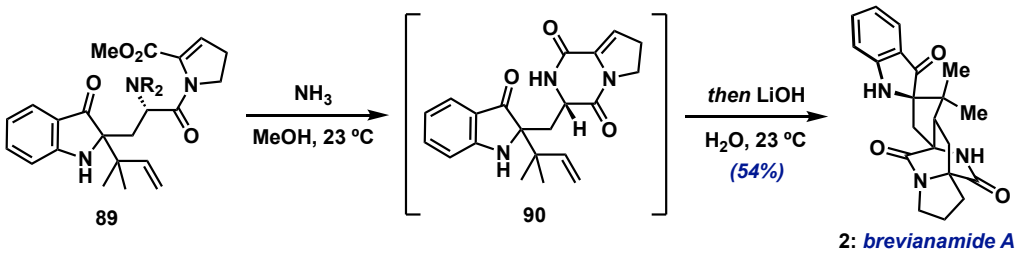
MS (ESI): calcd for $C_{30}H_{30}N_3O_6$ $[M + H]^+$ 528.2, found 528.3;

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.75–7.71 (m, 2H), 7.70–7.66 (m, 2H), 7.61 (br s, 4H), 7.44 (d, *J* = 7.8Hz, 1H), 7.41 (d, *J* = 7.7 Hz, 1H), 7.39 (t, *J* = 7.6 Hz, 1H), 6.95 (t, *J* = 7.7 Hz, 1H), 6.84 (d, *J* = 8.3 Hz, 1H), 6.70 (t, *J* = 7.4 Hz, 1H), 6.61 (t, *J* = 7.4 Hz, 1H), 6.15–6.02 (m, 3H), 5.95 (br s, 2H), 5.24 (s, 1H), 5.15–5.02 (m, 4H), 4.88 (d, *J* = 11.4 Hz, 1H), 4.72 (br s, 1H), 4.53 (dd, *J* = 8.8, 4.2 Hz, 1H), 4.15–4.00 (m, 1H), 3.98–3.89 (m, 1H), 3.81–3.67 (m, 5H), 3.78 (s, 3H), 3.40 (dd, *J* = 14.3, 9.0 Hz, 1H), 3.31 (t, *J* = 13.8 Hz, 1H), 2.71 (t, *J* = 8.4 Hz, 2H), 2.58 (dd, *J* = 15.0, 3.5 Hz, 1H), 2.47–2.39 (m, 3H), 1.14 (s, 3H), 1.13 (s, 3H), 0.99 (s, 3H), 0.98 (s, 3H).

[**Note:** Characterization data were acquired on a sample of ~1.1:1 dr. Because this close ratio made distinguishing major diastereomer peaks from minor ones difficult, each proton of the individual diastereomers was assigned an integral of 1H]

^{13}C NMR (151 MHz, $CDCl_3$): δ 203.3, 167.7, 167.2, 166.8, 162.0, 161.3, 160.9, 143.0, 142.9, 137.3, 136.9, 136.8, 136.5, 134.4, 134.3, 133.9, 131.6, 131.5, 124.4, 124.3, 123.6, 123.2, 122.0, 121.7, 118.6, 118.2, 114.7, 114.6, 111.7, 111.1, 71.9, 71.6, 52.51, 52.47, 50.2, 48.8, 48.5, 44.3, 43.8, 34.2, 29.8, 29.3, 29.1, 21.9, 21.7, 21.2, 21.1. [**Note:** 5 carbon signals missing due to overlap]

Optical rotation: $[\alpha]^{27}_{D}$ = -12 (c = 0.5, $CHCl_3$).



Brevianamide A (2): A flask equipped with a magnetic stir bar and a rubber septum was charged with **89** (15.1 mg, 0.029 mmol, 1.0 equiv). The flask was evacuated and backfilled with argon three times, followed by 7 N NH_3 in MeOH (1.0 mL) was added. The reaction was stirred at 23 °C until consumption of starting material (2 h), at which point the reaction mixture was concentrated in vacuo. Aqueous LiOH solution (1 M, 2 mL) was added to the crude residue, and the reaction mixture was stirred at 23 °C for 4 h. The reaction mixture was transferred to a separatory funnel containing saturated aq. NH_4Cl (10 mL) and extracted with CH_2Cl_2 (10 mL). The aqueous layer was re-extracted with CH_2Cl_2 (3 × 10 mL). The combined organic layers were washed with brine, dried over Na_2SO_4, filtered, and concentrated under vacuum. The resulting crude product was purified by PTLC using CH_2Cl_2/MeOH (10:1) to give brevianamide A (**2**) as a yellow solid (5.6 mg, 54% in two steps). The spectroscopic data of our synthetic sample matched those previously obtained by Lawrence (Tables S6 & S7).[13]

Physical properties: yellow solid;
R_f = 0.43 (silica gel, 10% MeOH/CH_2Cl_2);
MS (ESI): calcd for $C_{21}H_{24}N_3O_4$ $[M + H]^+$ 366.1812, found 366.1829;
^{1}H NMR (600 MHz, $CDCl_3$): δ 7.58 (dd, *J* = 7.8, 3.6 Hz, 1H), 7.44 (ddd, *J* = 8.3, 7.1, 1.3 Hz, 1H), 7.07–6.96 (m, 1H), 6.84–6.76 (m, 2H), 5.13 (s, 1H), 3.52–3.41 (m, 2H), 2.84–2.72 (m, 2H), 2.49–2.37 (m, 2H), 2.08–2.00 (m, 2H), 1.95–1.82 (m, 3H), 1.12 (s, 3H), 0.92 (s, 3H).
^{13}C NMR (151 MHz, $CDCl_3$): δ 202.2, 172.6, 169.9, 160.2, 137.8, 124.8, 121.1, 119.2, 112.1, 78.9, 69.5, 67.8, 55.7, 48.6, 44.1, 37.2, 29.2, 28.9, 25.1, 23.8, 19.6.
Optical rotation: $[\alpha]^{24}_{D}$ = +35 (c = 0.12, EtOH). [**Note:** this sample came from a batch of prenyl addition product **89** of 1.1:1 dr].

Table S6: Comparison of ^{1}H NMR shifts (δ) of Lawrence's synthetic brevianamide A (**2**) [13] and our own synthetic **2** in $CDCl_3$.

brevianamide A (Lawrence) (500 MHz)	brevianamide A (Smith) (600 MHz)
7.57 (dd, *J* = 7.7, 1.2 Hz, 1H)	7.58 (dd, *J* = 7.8, 3.6 Hz, 1H)
7.44 (ddd, *J* = 8.3, 7.1, 1.4 Hz, 1H)	7.44 (ddd, *J* = 8.3, 7.1, 1.3 Hz, 1H)
6.84–6.78 (m, 2H)	7.07–6.96 (m, 1H)
6.62 (br s, 1H)	6.84–6.76 (m, 2H)
4.98 (br s, 1H)	5.13 (s, 1H)
3.52–3.41 (m, 2H)	3.52–3.41 (m, 2H)

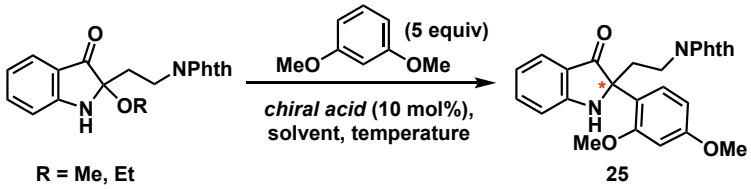
2.81–2.74 (m, 2H)	2.84–2.72 (m, 2H)
2.40 (ddd, *J* = 9.8, 7.3, 1.1 Hz, 1H)	2.49–2.37 (m, 2H)
2.35 (d, *J* = 15.6 Hz, 1H)	
2.04 (app pd, *J* = 6.8, 1.6 Hz, 2H)	2.08–2.00 (m, 2H)
1.96–1.81 (m, 3H)	1.95–1.82 (m, 3H)
1.12 (s, 3H)	1.12 (s, 3H)
0.93 (s, 3H)	0.92 (s, 3H)

Table S7: Comparison of ^{13}C NMR shifts (δ) of Lawrence's synthetic brevianamide A (**2**)[13] and our own synthetic **2** in $CDCl_3$.

brevianamide A (Lawrence) (126 MHz)	brevianamide A (Smith) (151 MHz)
202.2	202.2
172.4	172.6
169.8	169.9
160.2	160.2
137.8	137.8
124.8	124.8
121.2	121.1
119.3	119.2
112.1	112.1
78.9	78.9
69.5	69.5
67.8	67.8
55.7	55.7
48.4	48.6
44.1	44.1
37.4	37.2
29.2	29.2
29.0	28.9
25.1	25.1
24.1	23.8
19.9	19.6

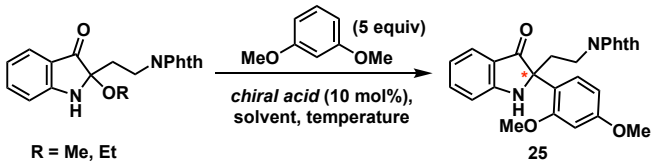
6. Preliminary Investigations toward Asymmetric Indoxyl Synthesis

General Procedure D for Asymmetric Screens:



To a solution of 2-alkoxyindoxyl (0.03 mmol) in 1.0 mL solvent was added 1,3-dimethoxybenzene (20 μL, 0.15 mmol, 5 equiv) under argon. The reaction mixture was cooled to 0 °C and a chiral acid (10 mol%) was added. The reaction was stirred at this temperature until completion (TLC), at which point the reaction mixture was transferred to a separatory funnel containing saturated aq. $NaHCO_3$ (10 mL) and extracted with CH_2Cl_2 (10 mL). The aqueous layer was re-extracted with CH_2Cl_2 (2 × 10 mL). The combined organic layers were washed with brine, dried over Na_2SO_4, filtered, and concentrated under vacuum. The resulting crude product was chromatographed on silica gel (0–35% EtOAc/hexanes gradient) to give indoxyl **25**. The enantiopurity was determined by HPLC (OD-H, hexane/*i*-PrOH = 75/25, 0.5 mL/min, t_R (major) = 36.01 min, t_R (minor) = 43.50 min).

Table S8: Screening Results for Asymmetric Synthesis of Indoxyl **25**.

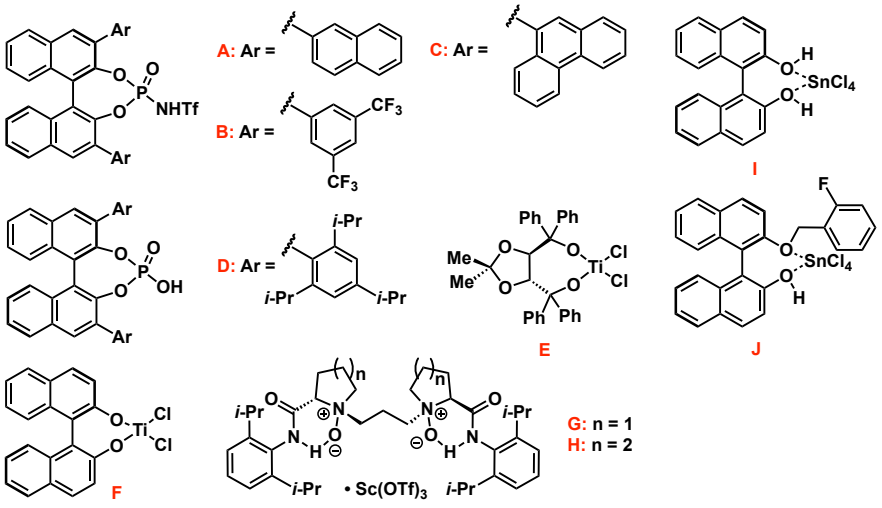


R = Me, Et

25

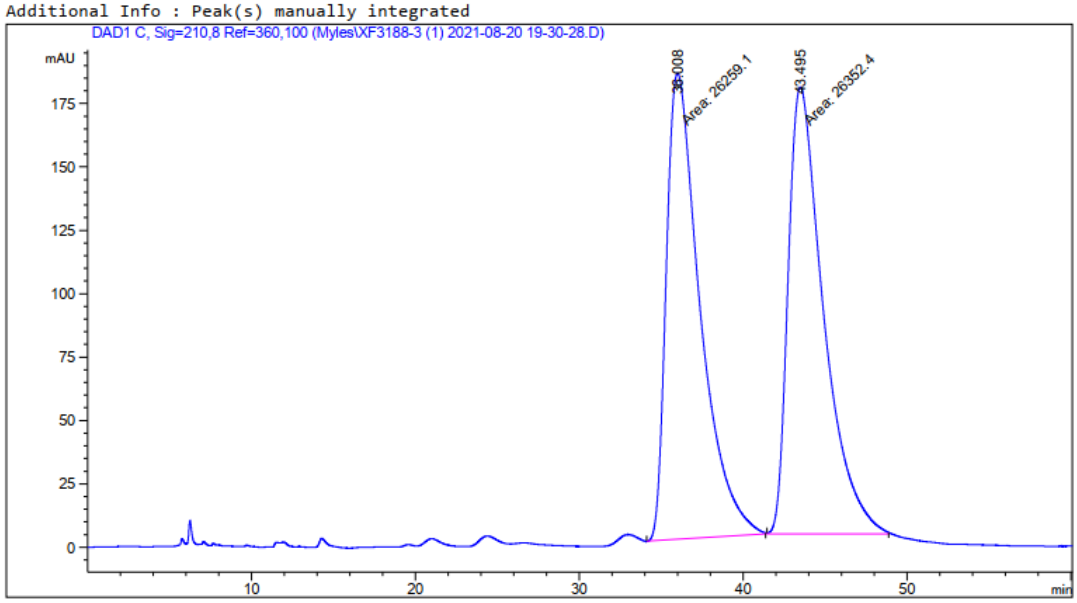
Entry	R	acid	solvent	temp. (°C)	yield (%)[b]	ee (%)[c]
1	Me	B	TFE	0	79	6
2	Me	B	6:1 CH_3CN/TFE	0	27	6
3	Me	B	6:1 CH_2Cl_2/TFE	0	45	8
4	Me	B	CH_2Cl_2	0	20	5.5
5	Me	A	TFE	0	84	15
6	Me	A	HFIP	0	72	18
7	Me	C	HFIP	0	64	18
8	Me	D	TFE	0	18	4
9[d]	Me	C	TFE	0	95	22
10[e]	Me	C	TFE	0	77	14
11	Me	I	CH_2Cl_2	0	32	3
12	Me	J	CH_2Cl_2	0	16	7
13	Me	I	TFE	0	52	0
14	Et	A	TFE	0	88	18
15	Et	B	TFE	0	69	6
16	Et	C	TFE	0	81	22
17	Et	C	4:1 CH_2Cl_2/TFE	0–23	72	23
18	Et	C	4:1 CH_3CN/TFE	0–23	26	25
19	Et	C	4:1 $PhCF_3$/TFE	0–23	69	23
20[f]	Et	C	TFE	0	0	n/a
21[g]	Et	C	TFE	0	95	24
22	Et	E	TFE	0	93	0
23	Et	F	TFE	0	98	0
24	Et	G	TFE	0	75	0
25	Et	H	TFE	0	73	0
26[h]	Et	C	TFE	0	92	25
27	Et	C	TFE	–20	0	n/a

[a]Reactions conducted on ~0.03 mmol of **24** in 1 mL solvent. [b]Isolated yield; [c]Enantioselectivity determined via HPLC analysis on a chiral stationary phase.[d]Indole (5 equiv) as nucleophile. [e]Allyltrimethylsilane (5 equiv) as nucleophile. [f]With 20 mg 4Å MS. [g]c = 0.1 M. [h]20 mol% chiral acid.



rac-**25** (OD-H, hexane/*i*-PrOH = 75/25, 0.5 mL/min)

Additional Info : Peak(s) manually integrated

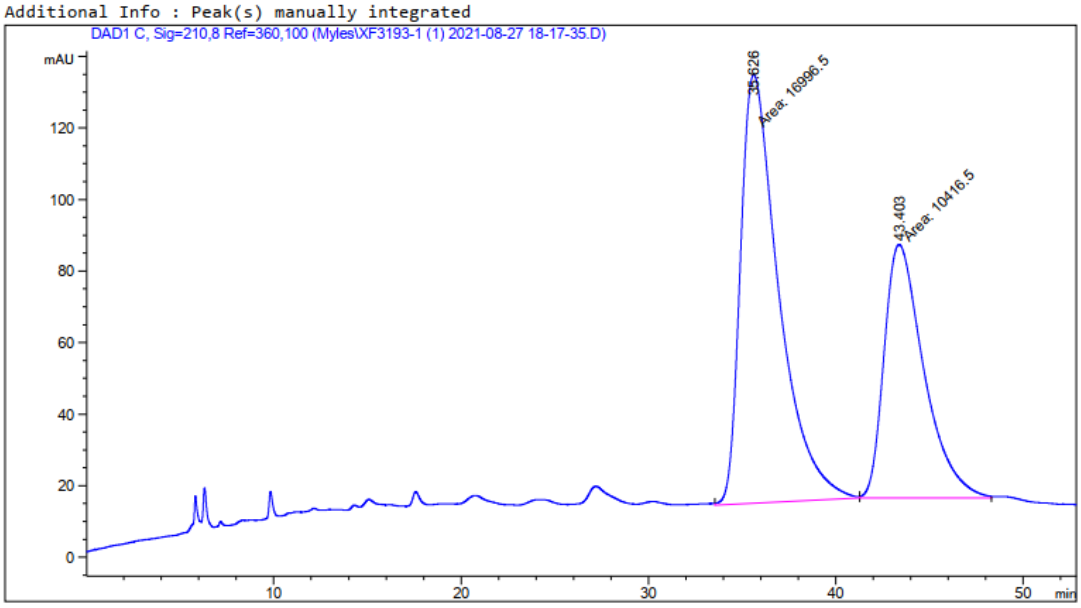


Signal 1: DAD1 C, Sig=210,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	36.008	MM	2.3823	2.62591e4	183.71150	49.9113
2	43.495	MM	2.4922	2.63524e4	176.23567	50.0887

Enantioenriched **25** (OD-H, hexane/*i*-PrOH = 75/25, 0.5 mL/min)

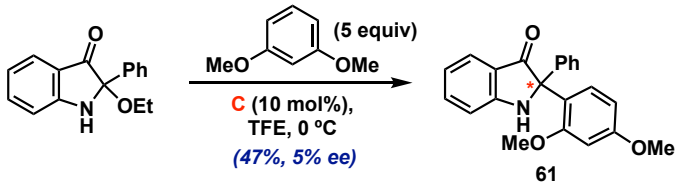
Additional Info : Peak(s) manually integrated



Signal 1: DAD1 C, Sig=210,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	35.626	MM	2.3652	1.69965e4	119.76664	62.0015
2	43.403	MM	2.4530	1.04165e4	70.77306	37.9985

Testing an alternate 2-alkoxyindoxyl substrate:

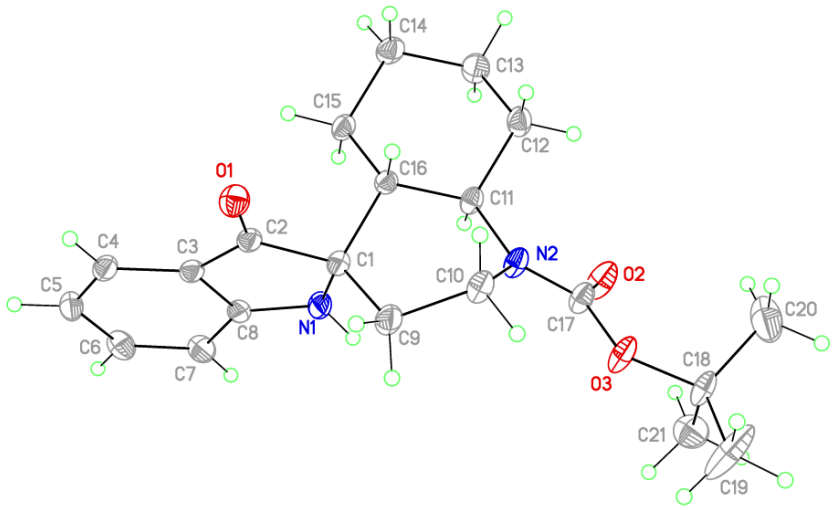


7. Details for Single Crystal X-ray Analysis of Indoxyl 76

X-ray Experimental for $C_{21}H_{28}N_2O_3$: Crystals grew as large, colorless prisms by slow evaporation from ethyl acetate. The data crystal was cut from a larger crystal and had approximate dimensions; 0.46 x 0.29 x 0.25 mm. The data were collected at -173 °C on a Nonius Kappa CCD diffractometer using a Bruker AXS Apex II detector and a graphite monochromator with MoKα radiation (λ = 0.71073Å). Reduced temperatures were maintained by use of an Oxford Cryosystems 700 low-temperature device. A total of 2220 frames of data were collected using ω-scans with a scan range of 0.6° and a counting time of 27 seconds per frame. Details of crystal data, data collection and structure refinement are listed in Table 1. Data reduction were performed using SAINT V8.40A.[14] The structure was solved by direct methods using SHELXT[15] and refined by full-matrix least-squares on F^2 with anisotropic displacement parameters for the non-H atoms using SHELXL-2018/3.[16] Structure analysis was aided by use of the programs PLATON[17] and OLEX2[18]. The hydrogen atoms bound to carbon atoms were calculated in idealized positions. The hydrogen atom bound to N1 was observed in a ΔF map and refined with an isotropic displacement parameter.

The function, $\Sigma w(|F_o|^2 - |F_c|^2)^2$, was minimized, where $w = 1/[(\sigma(F_o))^2 + (0.0464*P)^2 + (2.5859*P)]$ and $P = (|F_o|^2 + 2|F_c|^2)/3$. $R_w(F^2)$ refined to 0.108, with R(F) equal to 0.05413 and a goodness of fit, S, = 1.03. Definitions used for calculating R(F),$R_w(F^2)$ and the goodness of fit, S, are given below[19] The data were checked for secondary extinction but no correction was necessary. Neutral atom scattering factors and values used to calculate the linear absorption coefficient are from the International Tables for X-ray Crystallography (1992).[20] All figures were generated using SHELXTL/PC.[21] Tables of positional and thermal parameters, bond lengths and angles, torsion angles and figures are found elsewhere.

Figure 1. View of **76** showing the atom labeling scheme. Displacement ellipsoids are scaled to the 50% probability level.



8. References

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[19] $R_W(F^2) = \{\Sigma w(|F_o|^2 - |F_c|^2)^2/\Sigma w(|F_o|)^4\}^{1/2}$ where w is the weight given each reflection.
$R(F) = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|\}$ for reflections with $F_o > 4(\sigma(F_o))$.
$S = [\Sigma w(|F_o|^2 - |F_c|^2)^2/(n - p)]^{1/2}$, where n is the number of reflections and p is the number of refined parameters.

[20] International Tables for X-ray Crystallography (1992). Vol. C, Tables 4.2.6.8 and 6.1.1.4, A. J. C. Wilson, editor, Boston: Kluwer Academic Press.

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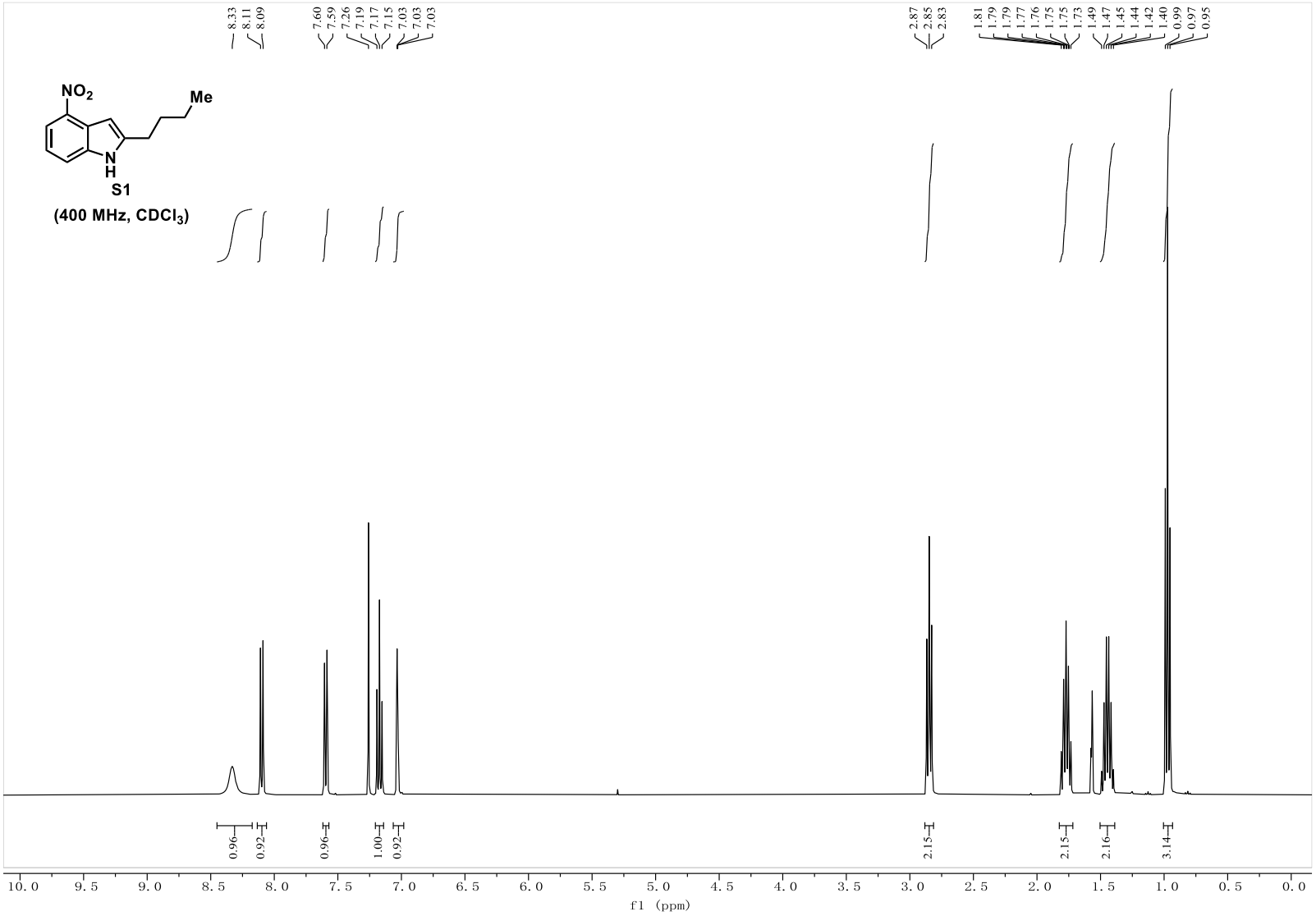
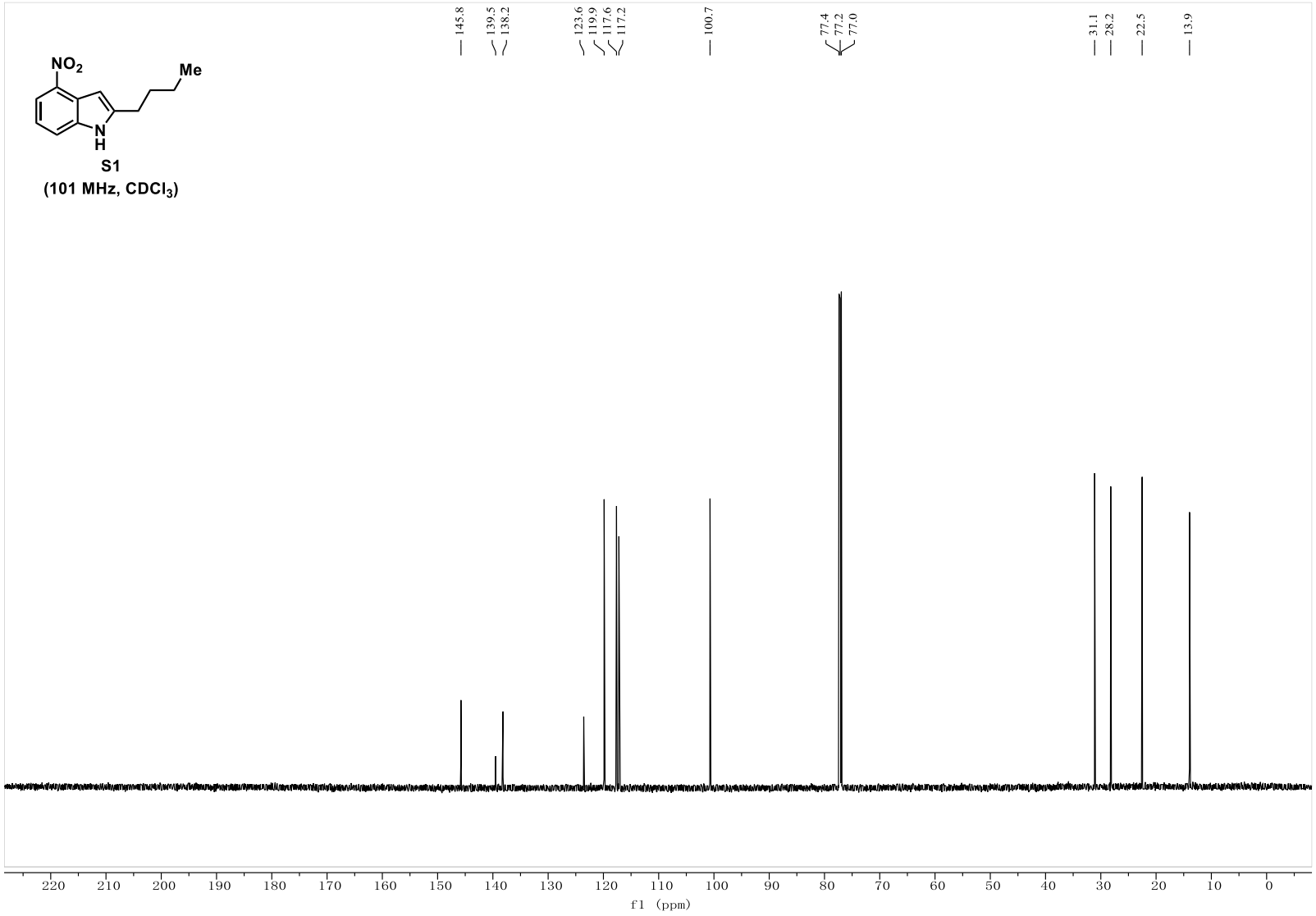
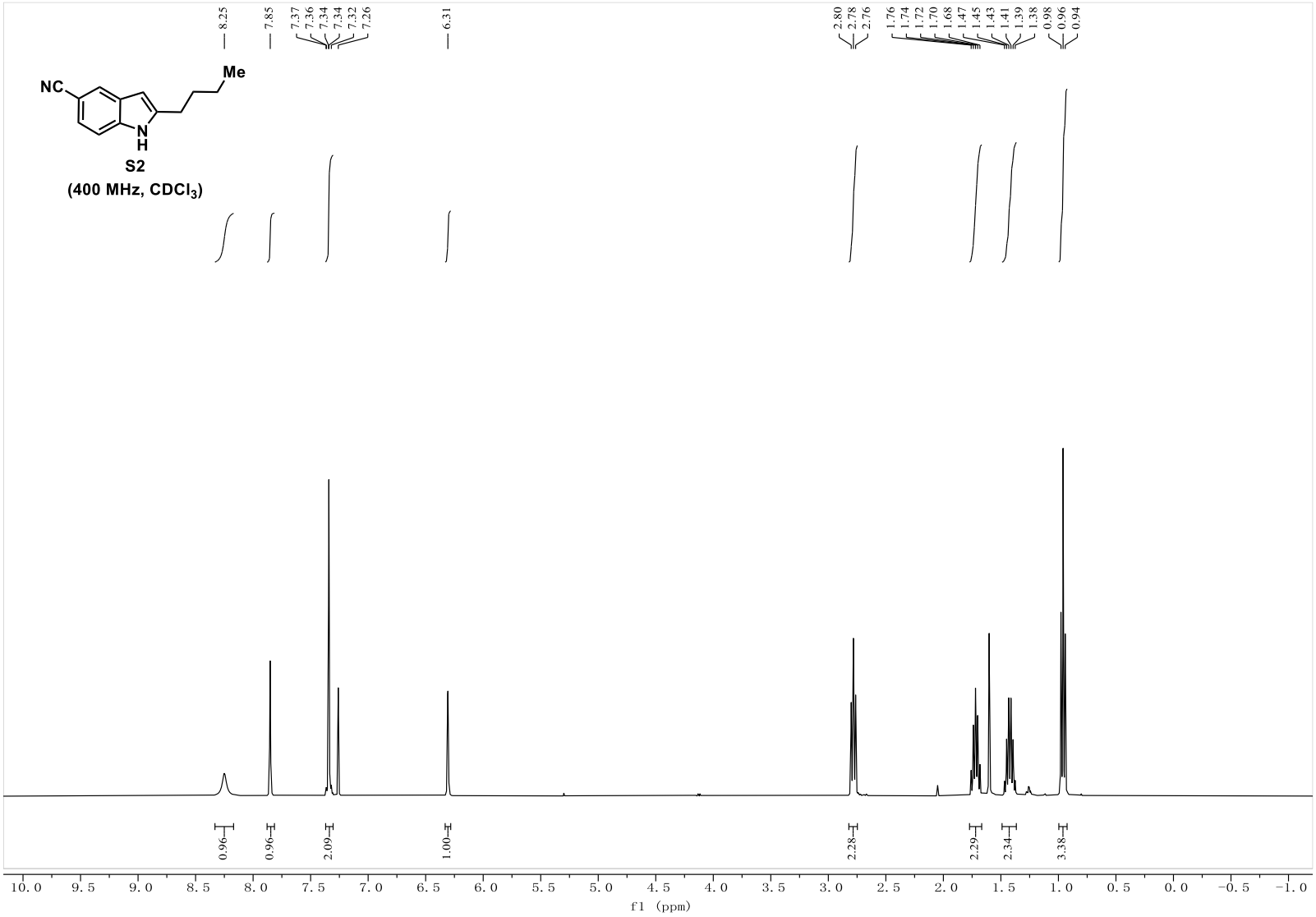
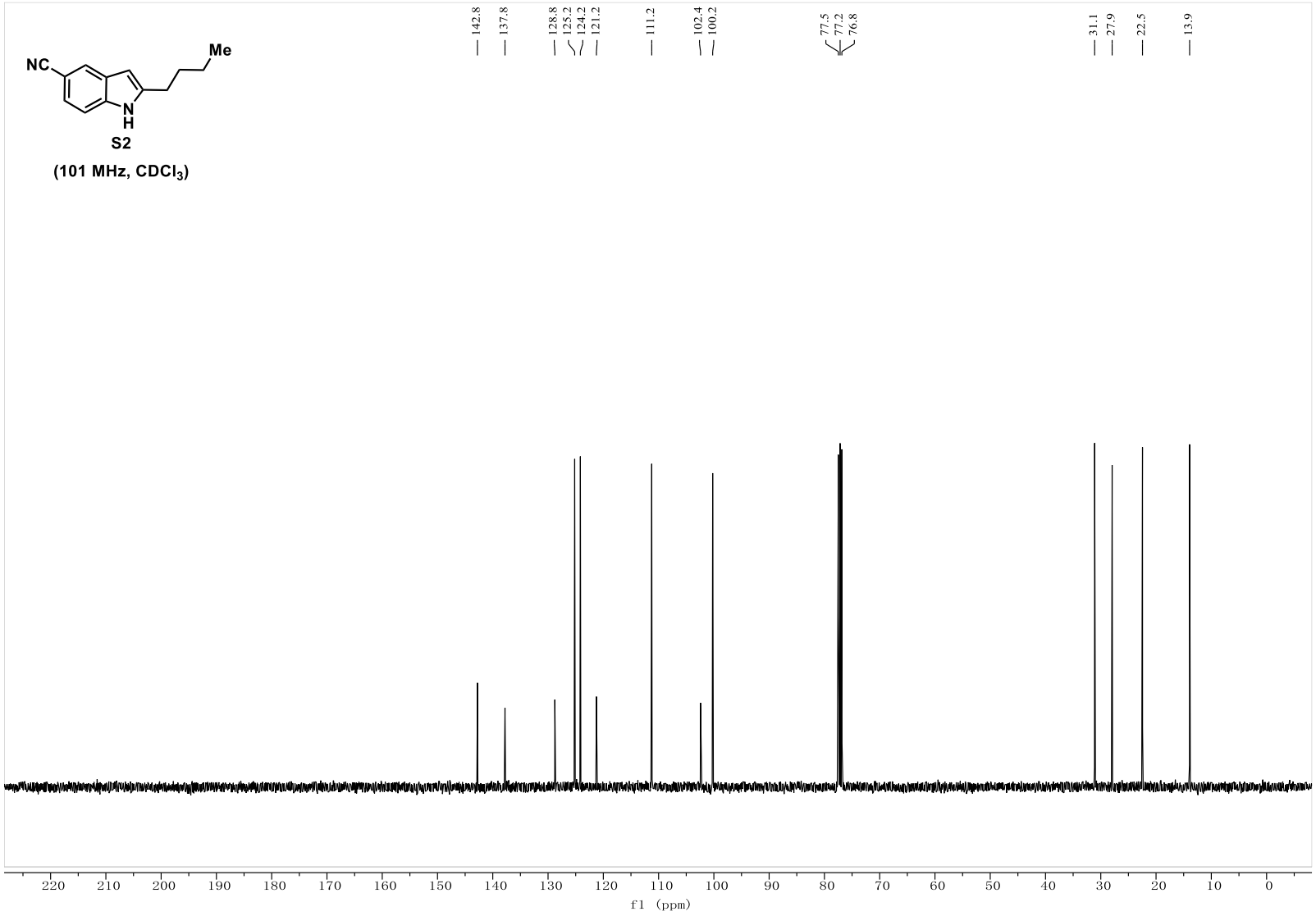
9. NMR Spectra




NO2
Me
N
H
S1
(101 MHz, CDCl3)
145.8
139.5
138.2
123.6
119.9
117.6
117.2
100.7
77.4
77.2
77.0
31.1
28.2
22.5
13.9
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


8.25
7.85
7.37
7.36
7.34
7.34
7.32
7.26
6.31
2.80
2.78
2.76
1.76
1.74
1.72
1.70
1.68
1.47
1.45
1.43
1.41
1.39
1.38
0.98
0.96
0.94
NC
Me
N
H
S2
(400 MHz, CDCl3)
0.96
0.96
2.09
1.00
2.28
2.29
2.34
3.38
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 −0.5 −1.0
f1 (ppm)


NC
Me
N
H
S2
(101 MHz, CDCl3)
142.8
137.8
128.8
125.2
124.2
121.2
111.2
102.4
100.2
77.5
77.2
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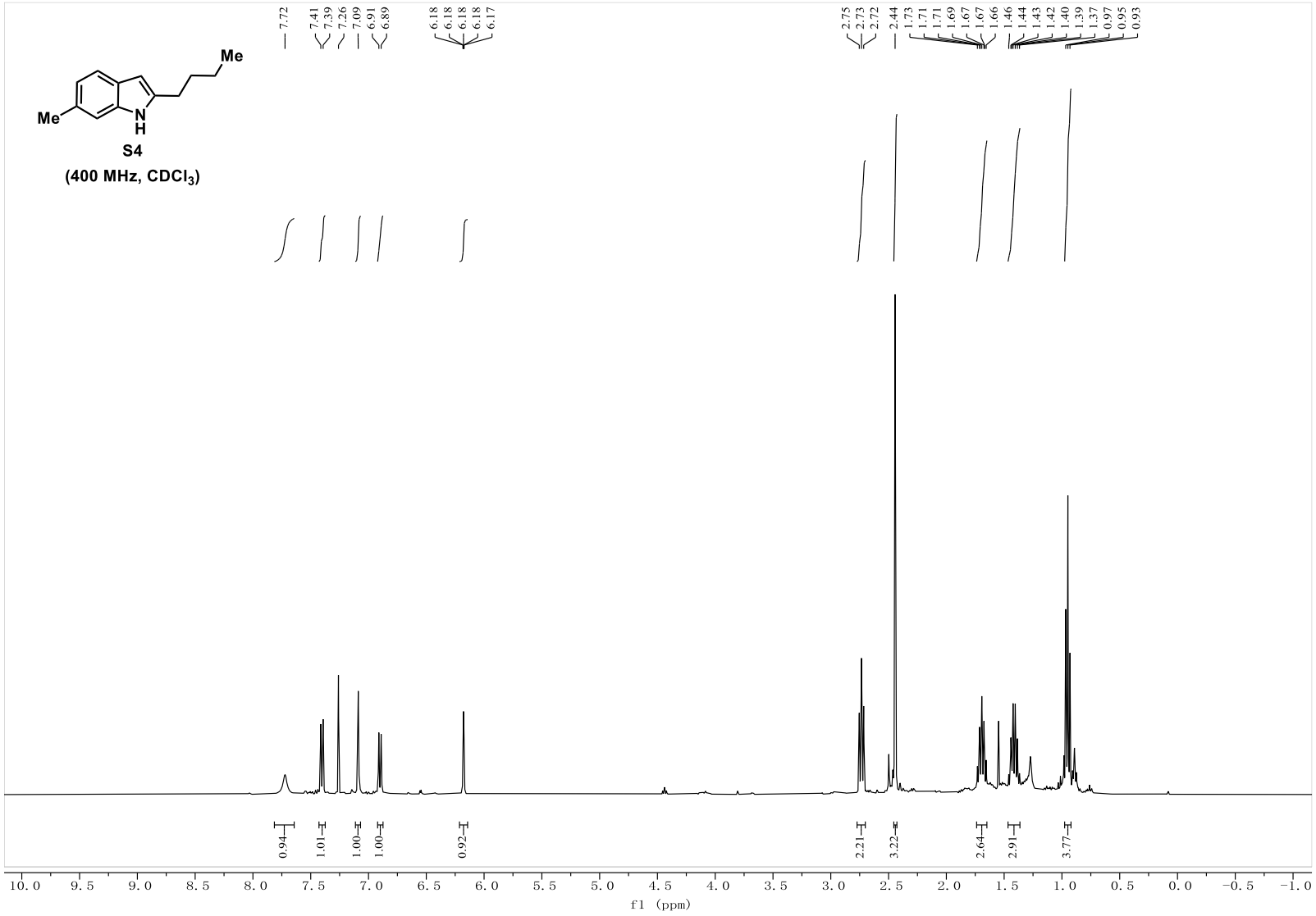
22.5
13.9
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


Me
Me
N
H
S4
(400 MHz, CDCl3)
7.72
7.41
7.39
7.26
7.09
6.91
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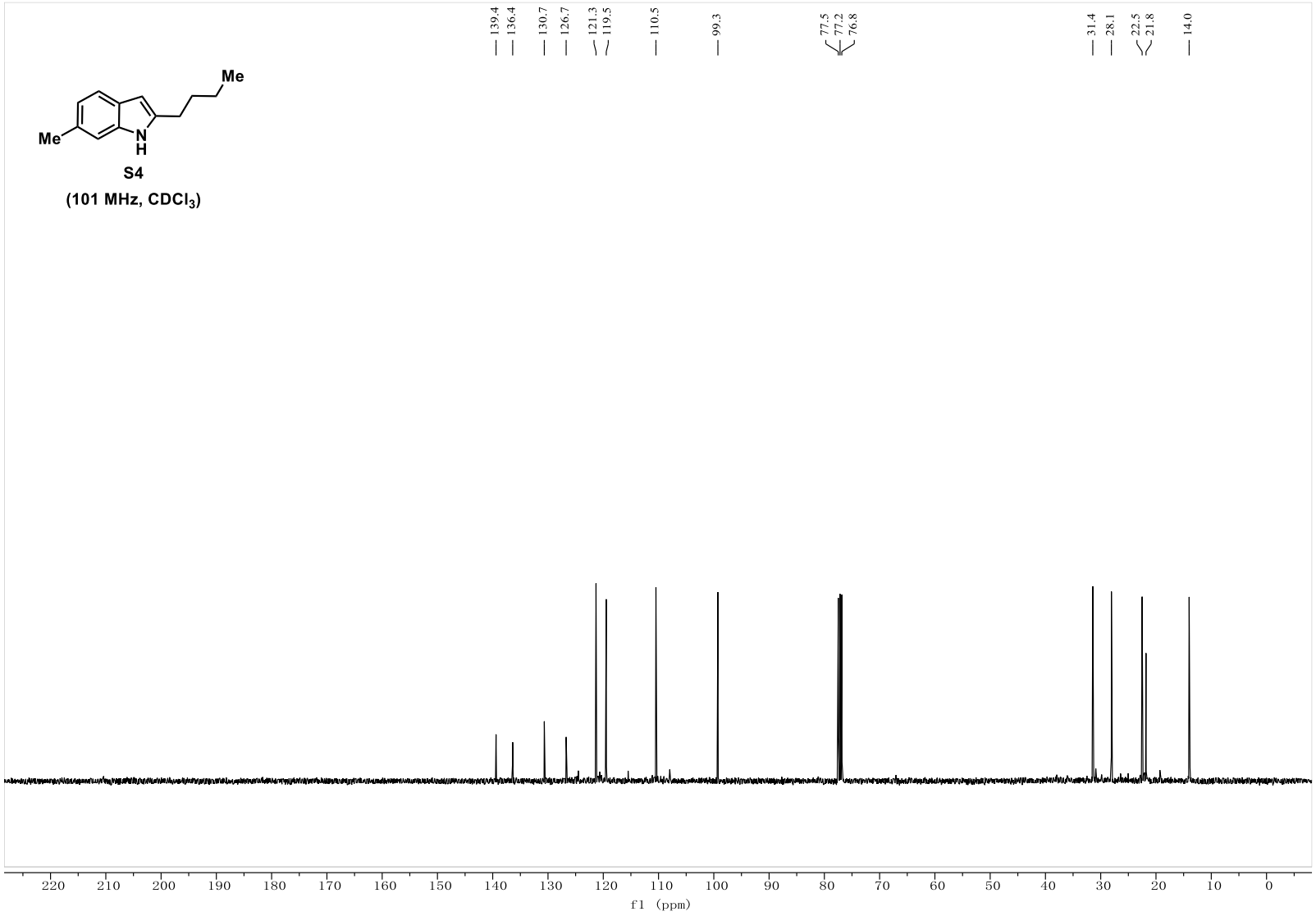
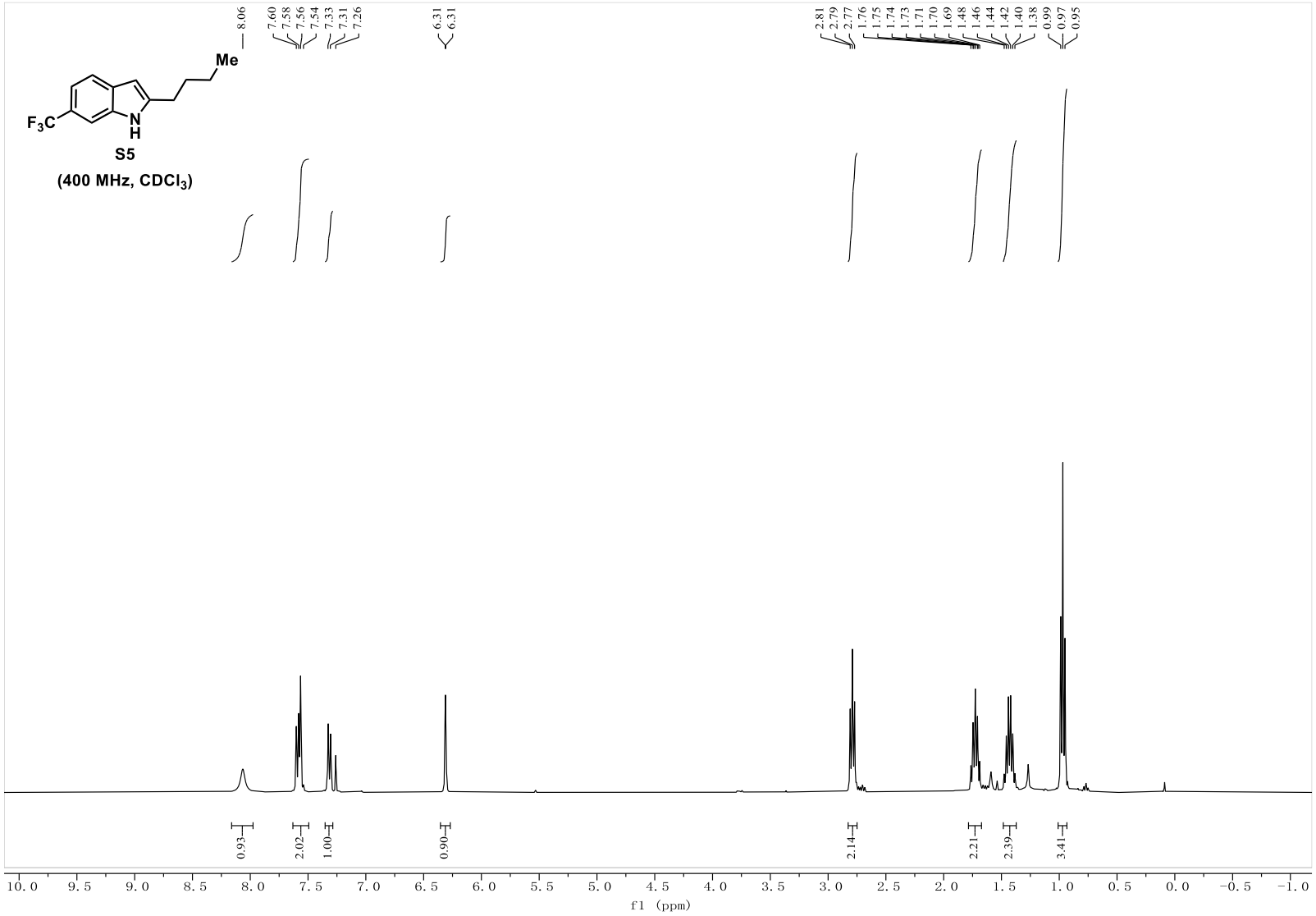
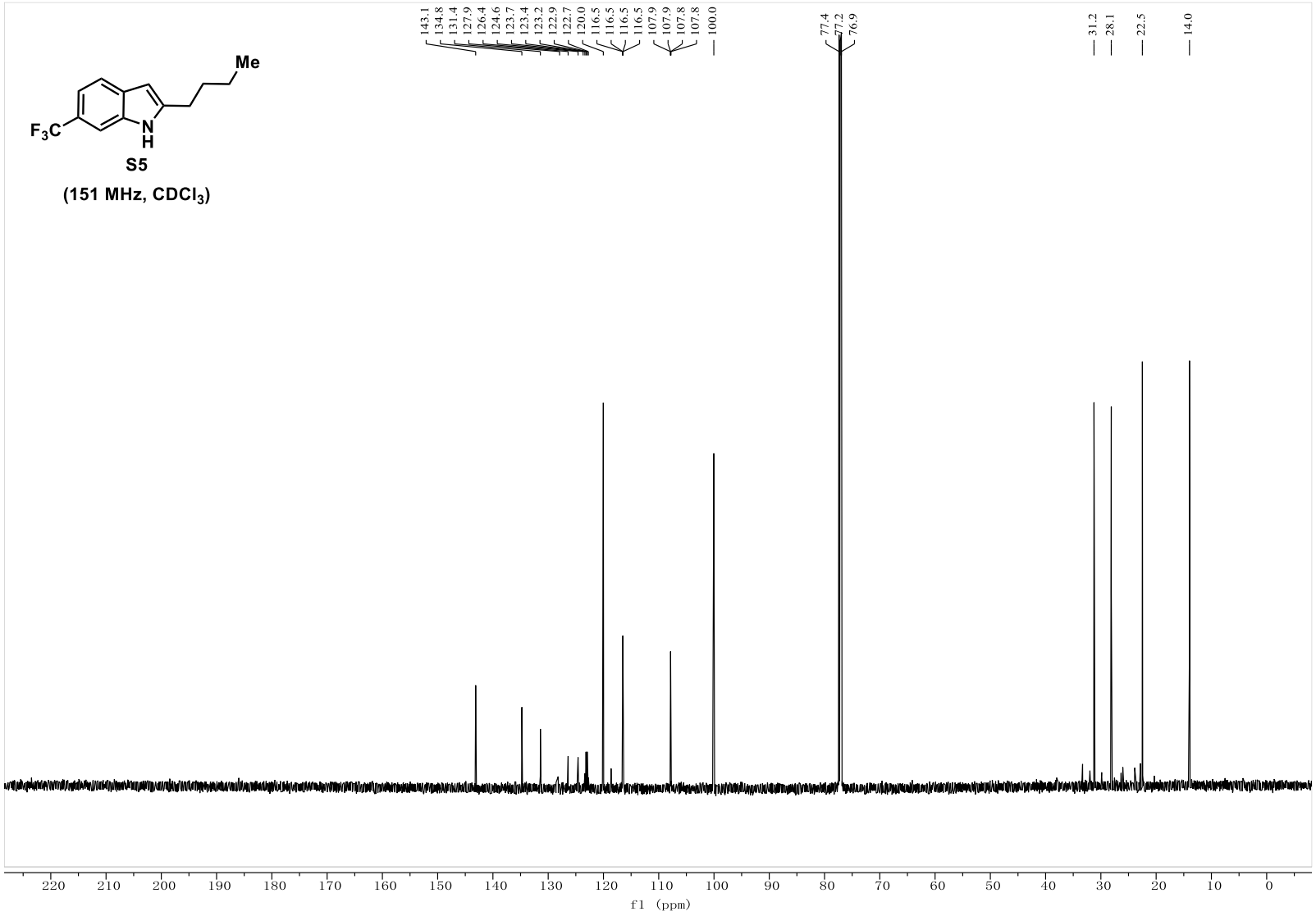
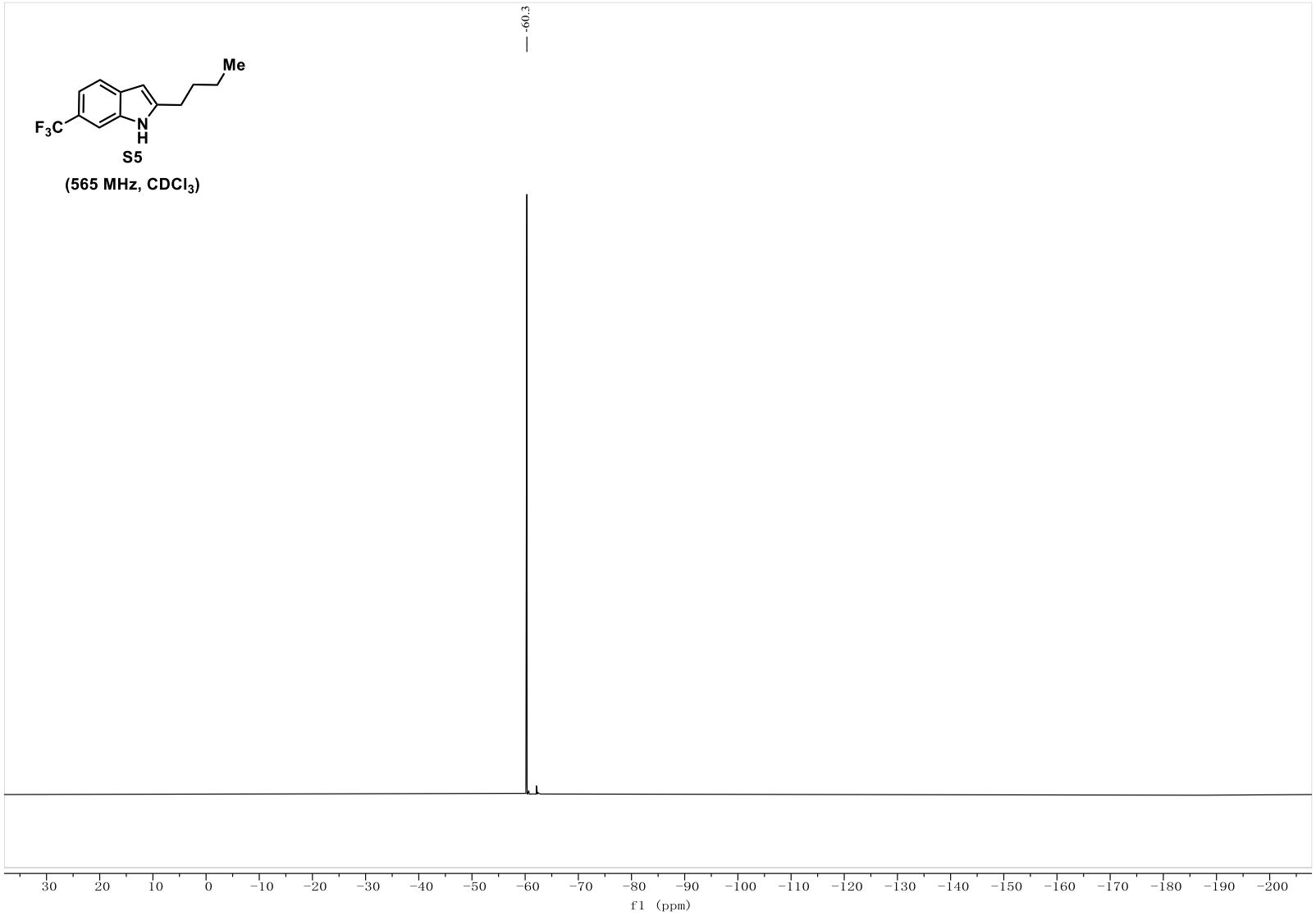
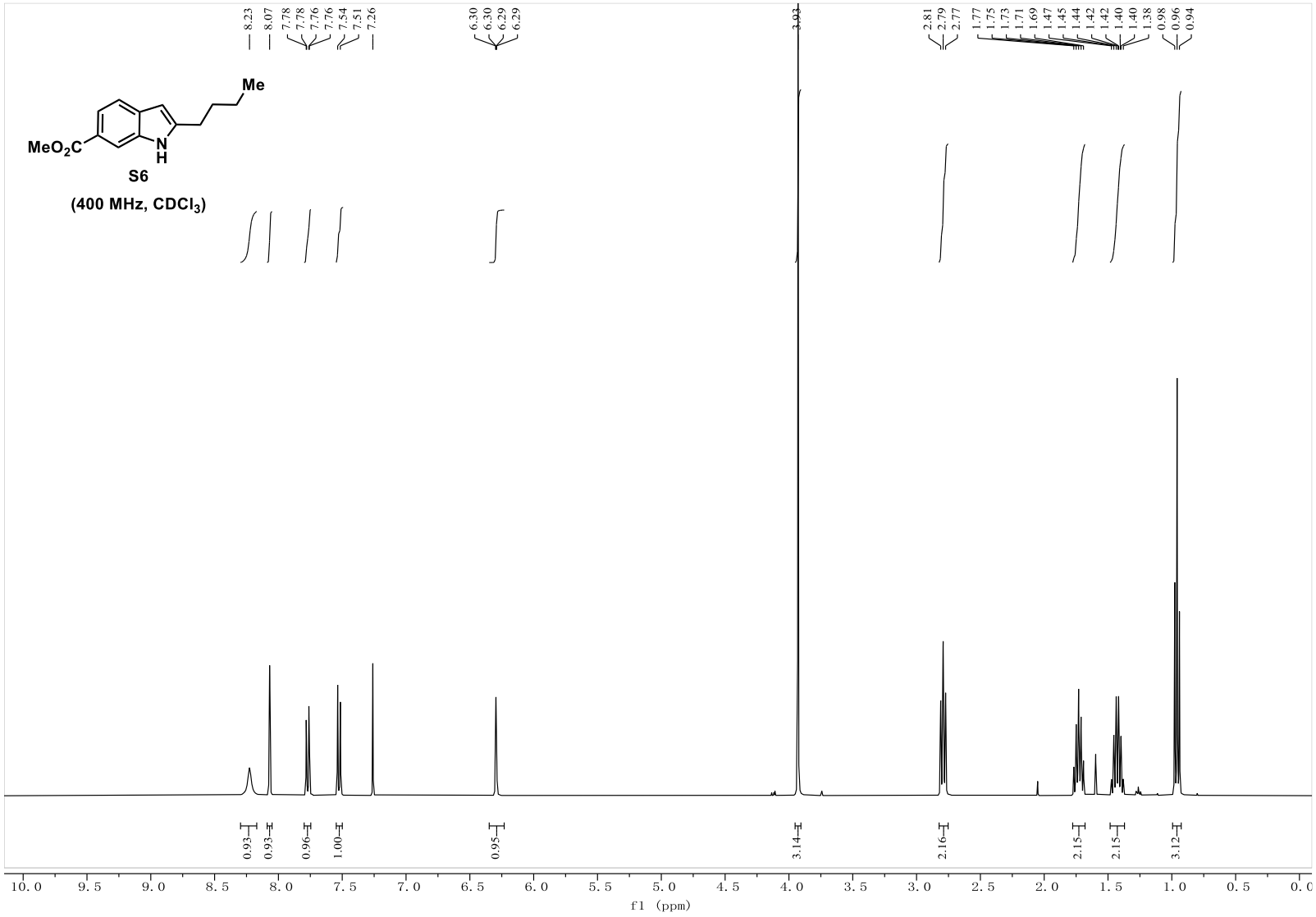
6.18
6.18
6.18
6.18
6.17
2.75
2.73
2.72
2.44
1.73
1.71
1.71
1.69
1.67
1.67
1.66
1.46
1.44
1.43
1.42
1.40
1.39
1.37
0.97
0.95
0.93
0.94
1.01
1.00
1.00
0.92
2.21
3.22
2.64
2.91
3.77
f1 (ppm)

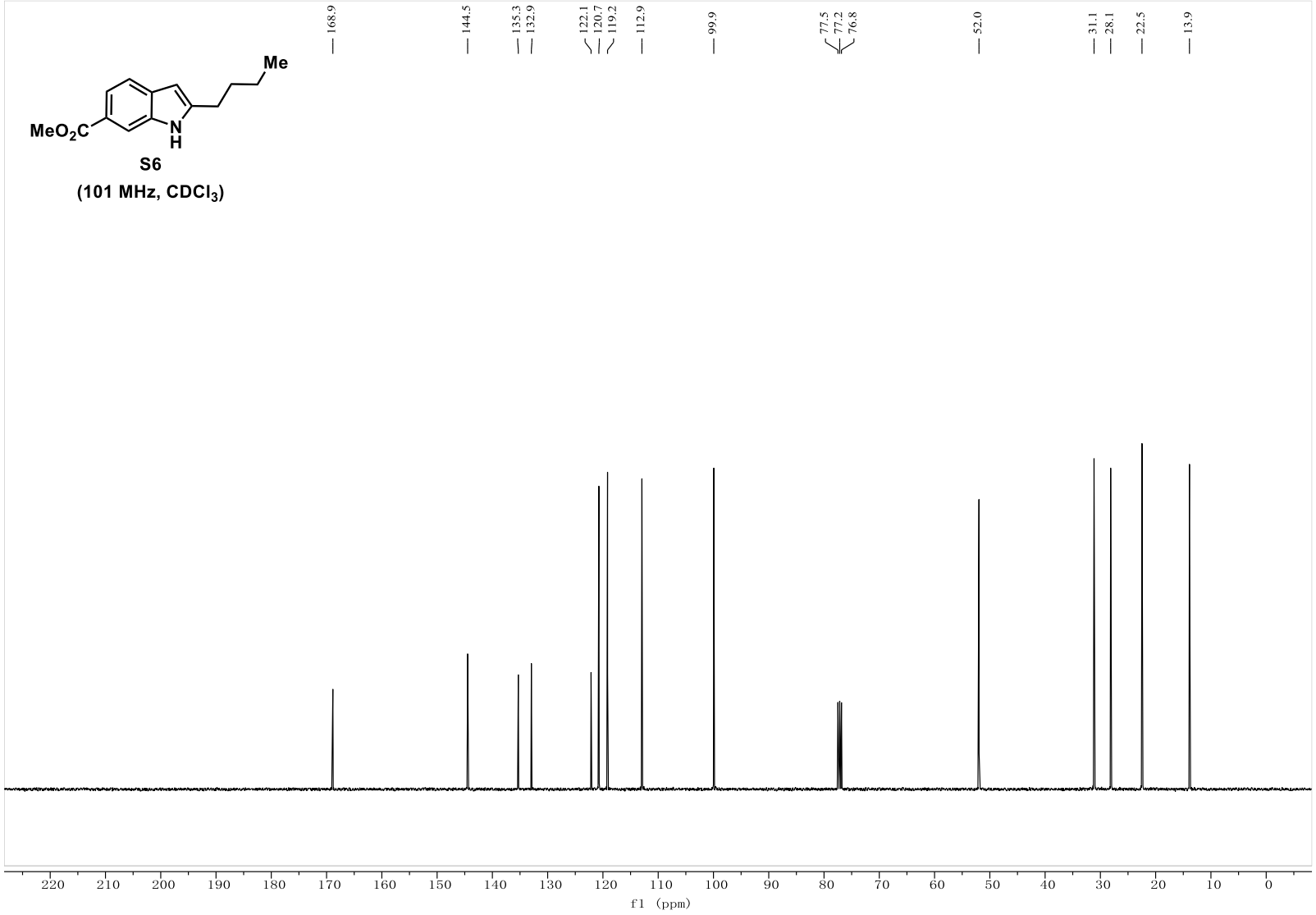

Me
Me
N
H
S4
(101 MHz, CDCl3)
139.4
136.4
130.7
126.7
121.3
119.5
110.5
99.3
77.5
77.2
76.8
31.4
28.1
22.5
21.8
14.0
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

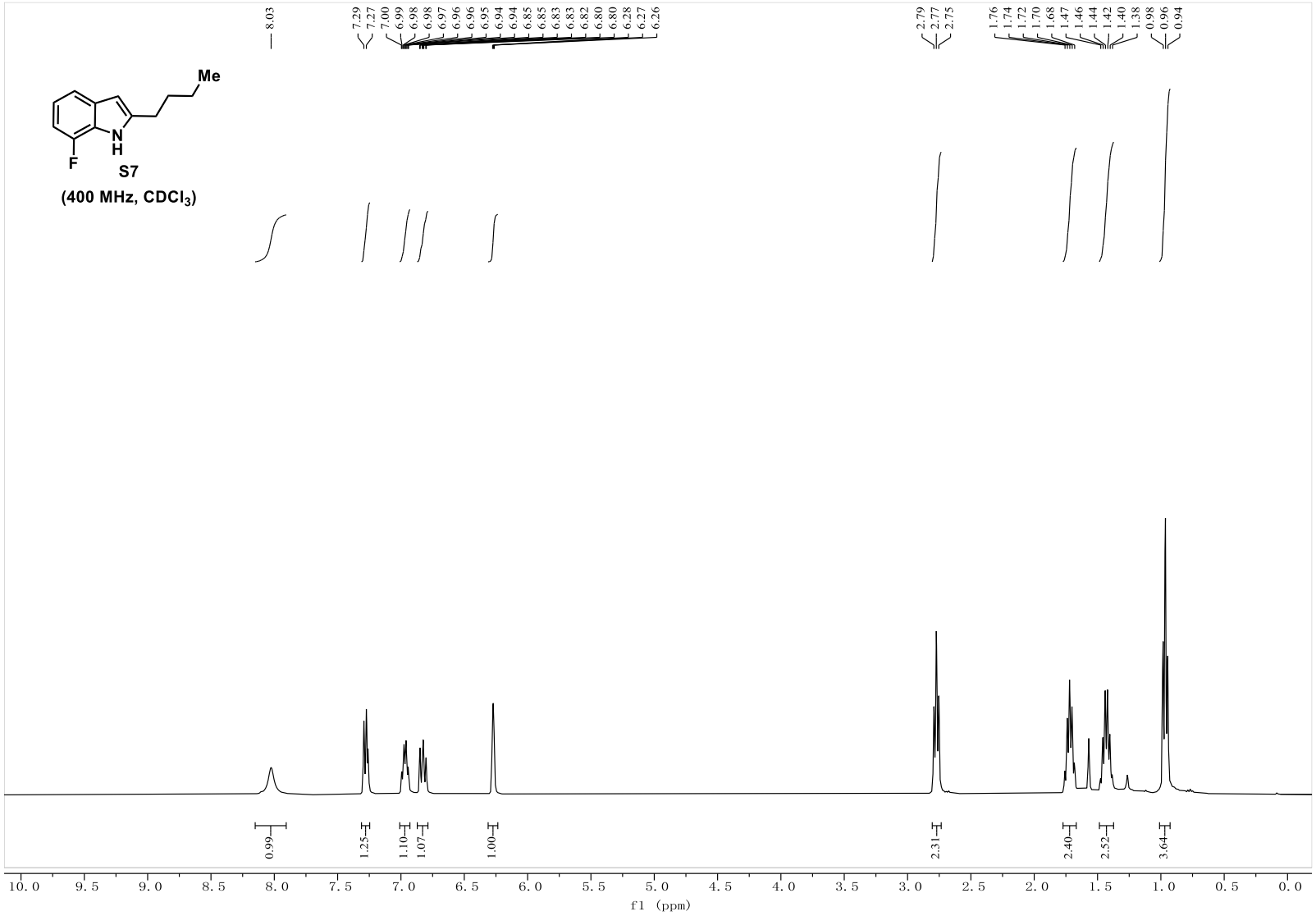

8.06
7.60
7.58
7.56
7.54
7.33
7.31
7.26
6.31
6.31
2.81
2.79
2.77
1.76
1.75
1.74
1.73
1.71
1.70
1.69
1.48
1.46
1.44
1.42
1.40
1.38
0.99
0.97
0.95
Me
F3C
N
H
S5
(400 MHz, CDCl3)
0.93
2.02
1.00
0.90
2.14
2.21
2.39
3.41
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5 −1.0
f1 (ppm)

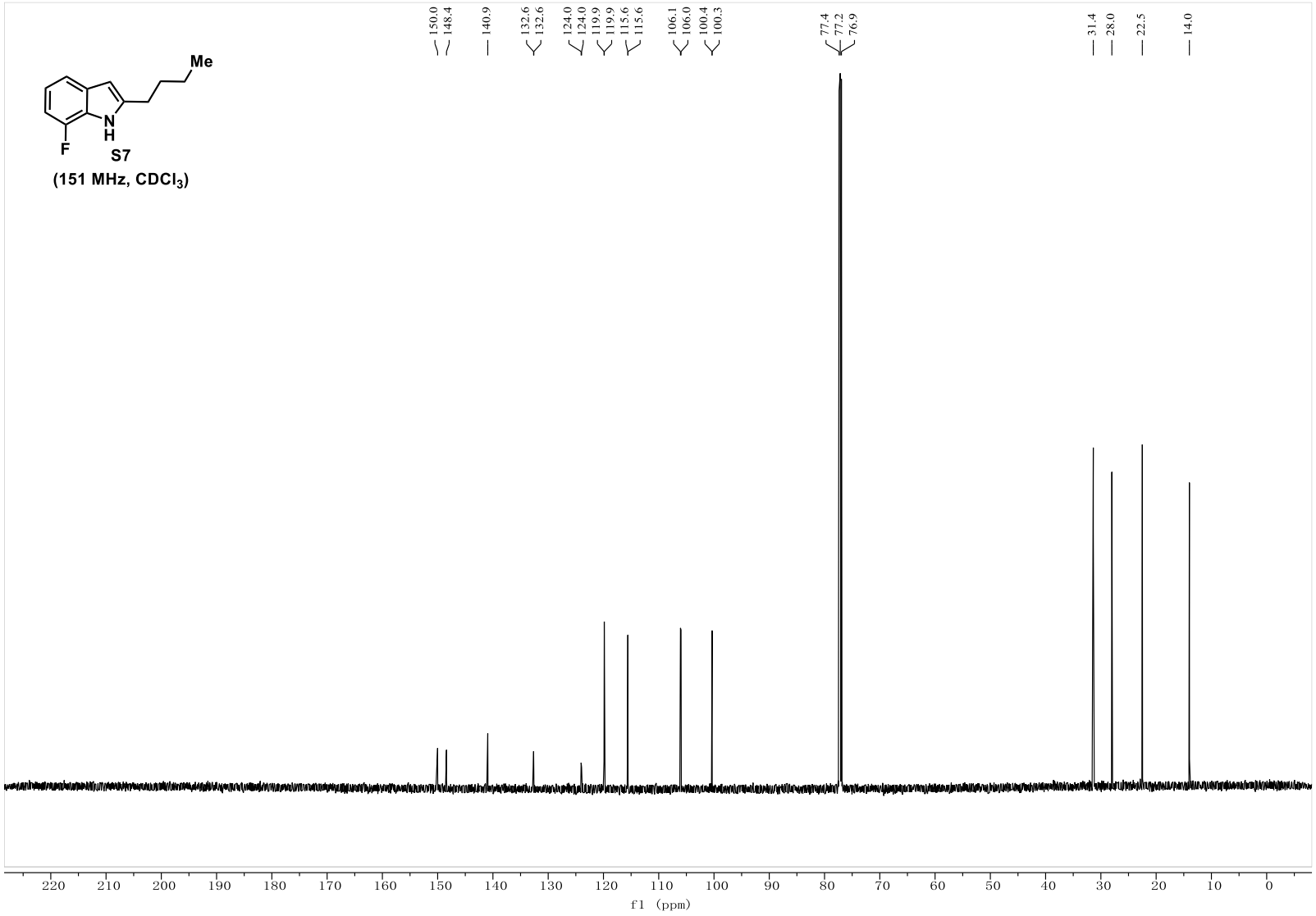

143.1
134.8
131.4
127.9
126.4
124.6
123.7
123.4
123.2
122.9
122.7
120.0
116.5
116.5
116.5
107.9
107.9
107.8
107.8
100.0
77.4
77.2
76.9
31.2
28.1
22.5
14.0
Me
F3C
N
H
S5
(151 MHz, CDCl3)
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

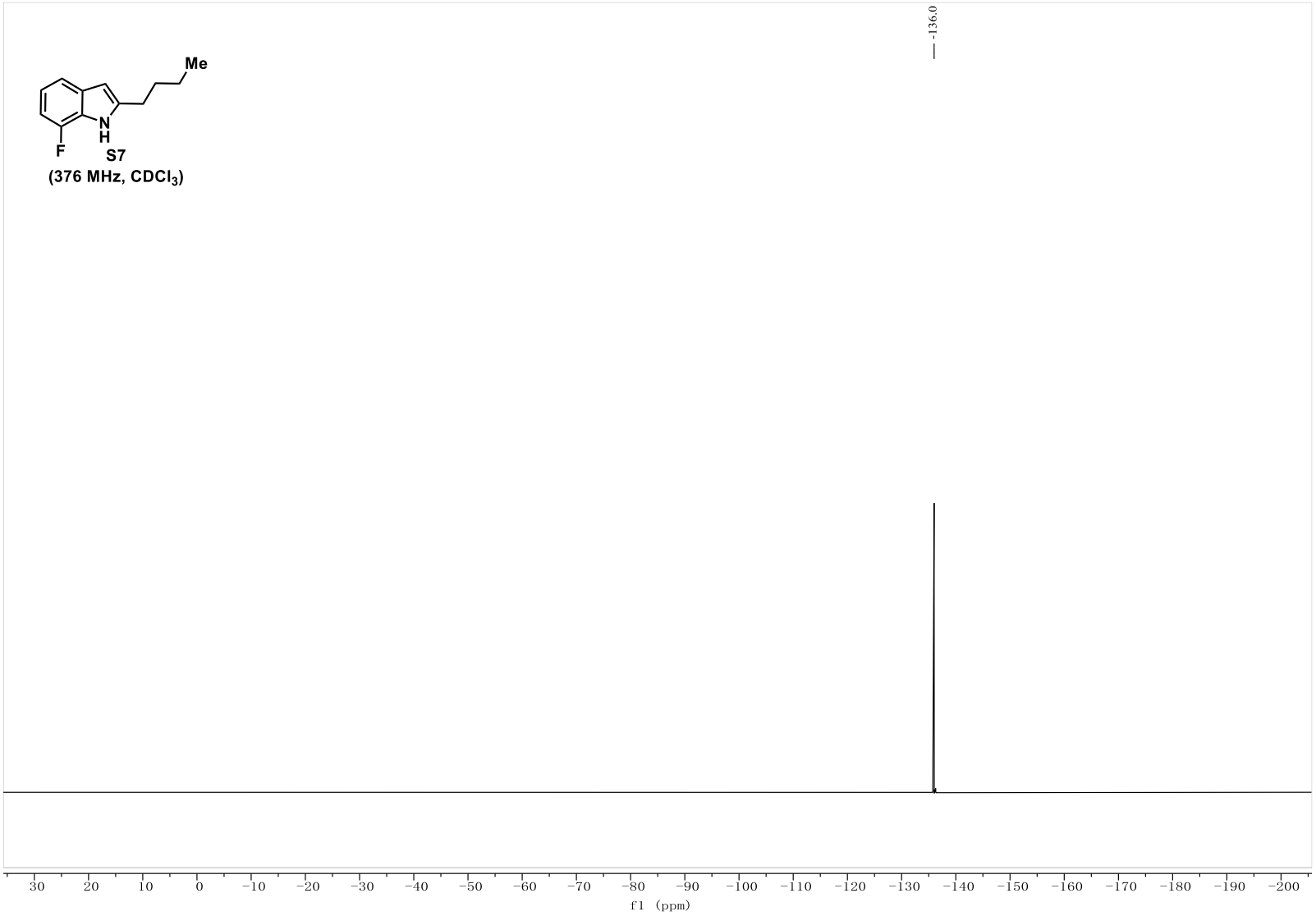

-60.3
Me
F3C
N
H
S5
(565 MHz, CDCl3)
30 20 10 0 −10 −20 −30 −40 −50 −60 −70 −80 −90 −100 −110 −120 −130 −140 −150 −160 −170 −180 −190 −200
f1 (ppm)

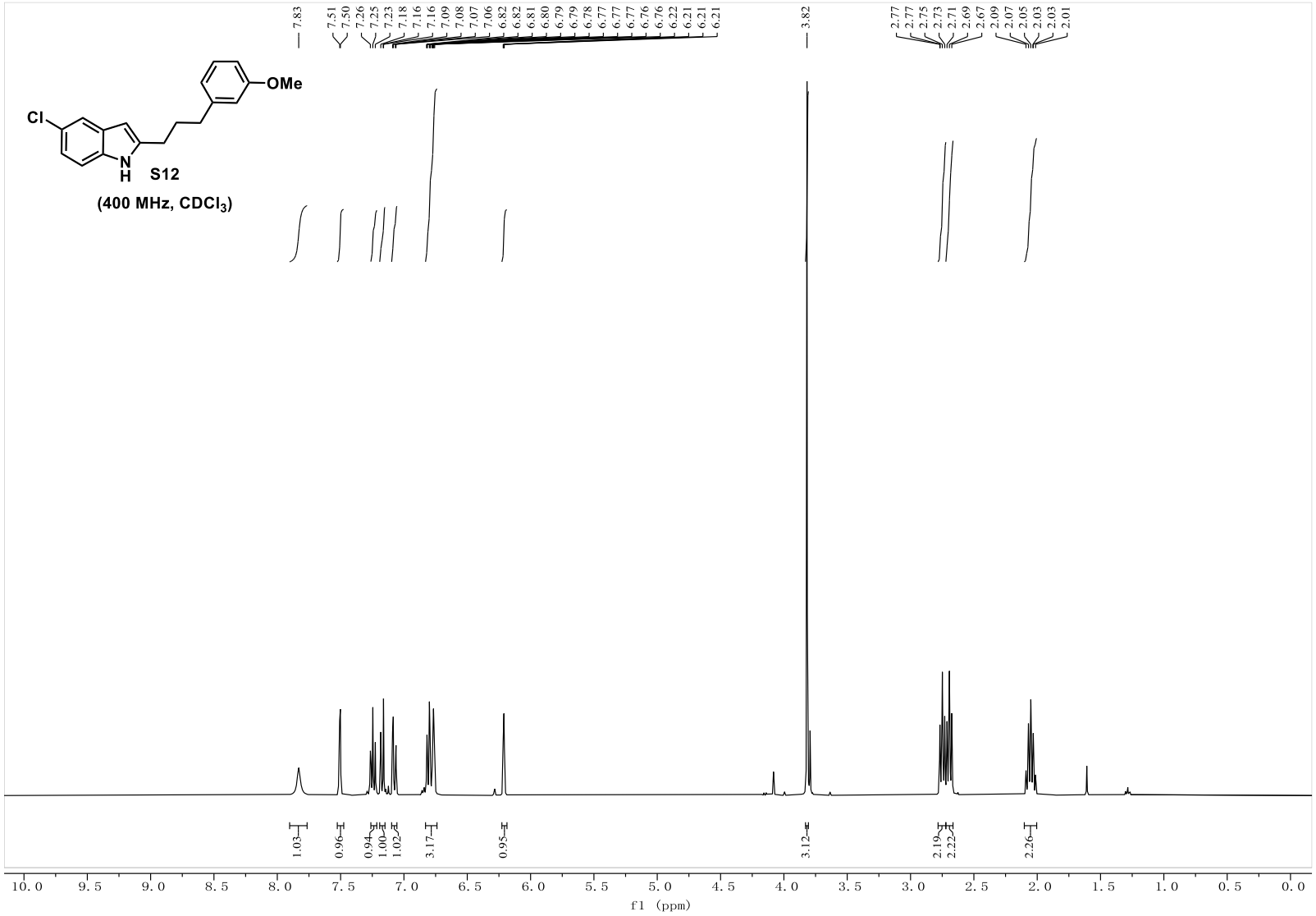

8.23
8.07
7.78
7.78
7.76
7.76
7.54
7.51
7.26
6.30
6.30
6.29
6.29
3.93
2.81
2.79
2.77
1.77
1.75
1.73
1.71
1.69
1.47
1.45
1.44
1.42
1.42
1.40
1.40
1.38
0.98
0.96
0.94
Me
MeO2C
N
H
S6
(400 MHz, CDCl3)
0.93
0.93
0.96
1.00
0.95
3.14
2.16
2.15
2.15
3.12
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

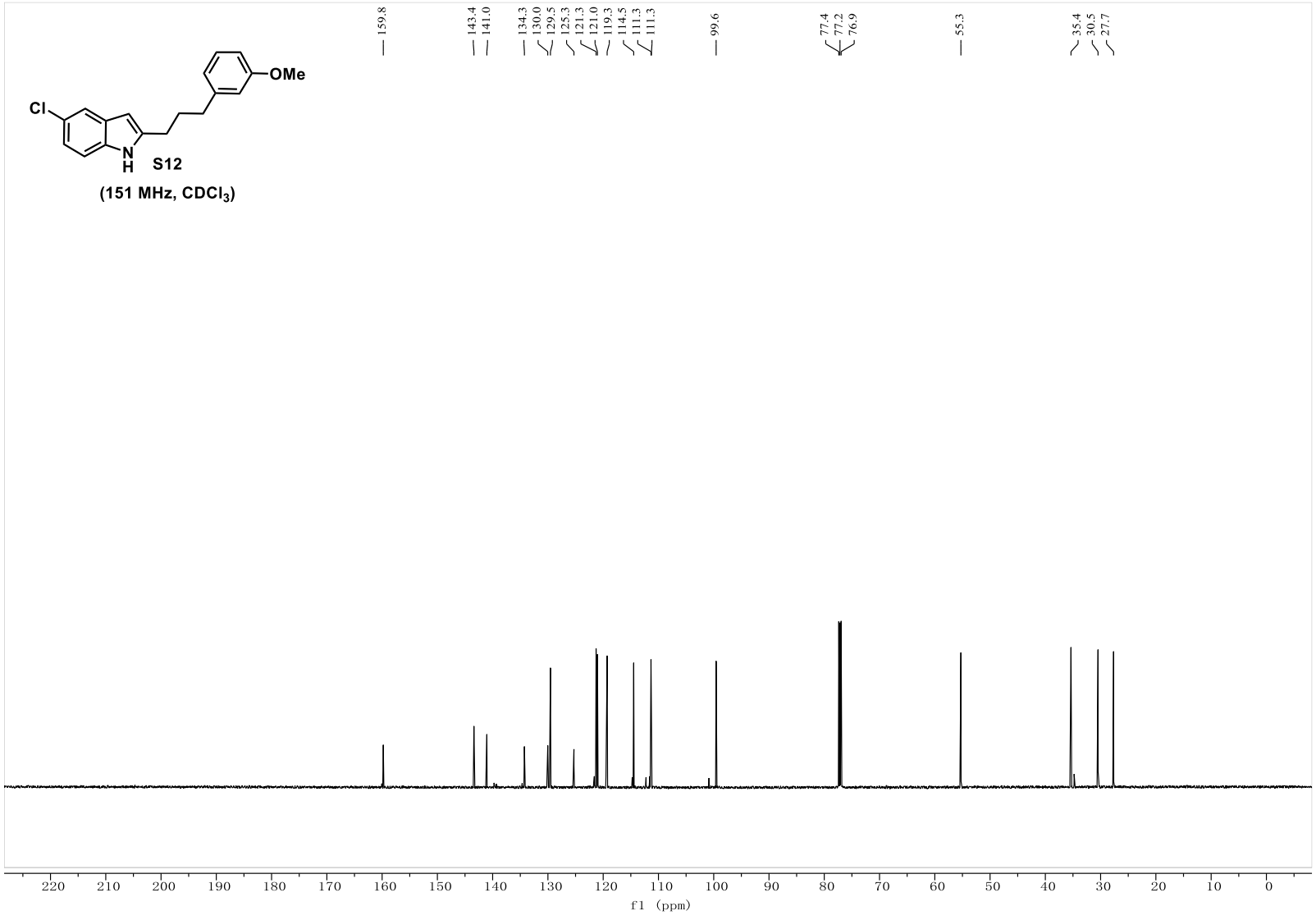

168.9
144.5
135.3
132.9
122.1
120.7
119.2
112.9
99.9
77.5
77.2
76.8
52.0
31.1
28.1
22.5
13.9
Me
MeO2C
N
H
S6
(101 MHz, CDCl3)
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

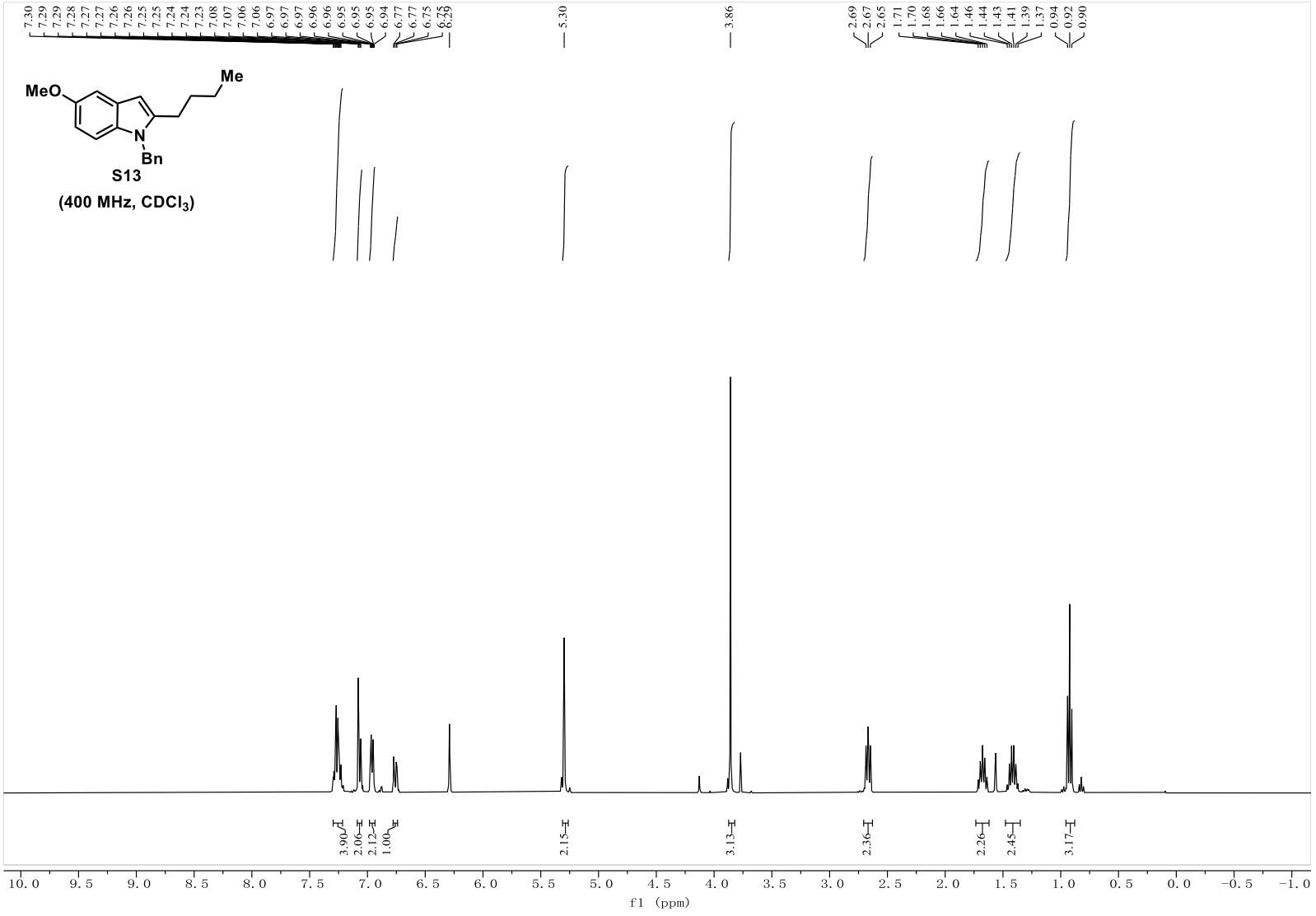

Me
N
H
F
S7
(400 MHz, CDCl3)
8.03
7.29
7.27
7.00
6.99
6.98
6.98
6.97
6.96
6.96
6.95
6.94
6.94
6.85
6.85
6.83
6.83
6.82
6.80
6.80
6.28
6.27
6.26
2.79
2.77
2.75
1.76
1.74
1.72
1.70
1.68
1.47
1.46
1.44
1.42
1.40
1.38
0.98
0.96
0.94
0.99
1.25
1.10
1.07
1.00
2.31
2.40
2.52
3.64
10.0
9.5
9.0
8.5
8.0
7.5
7.0
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
f1 (ppm)

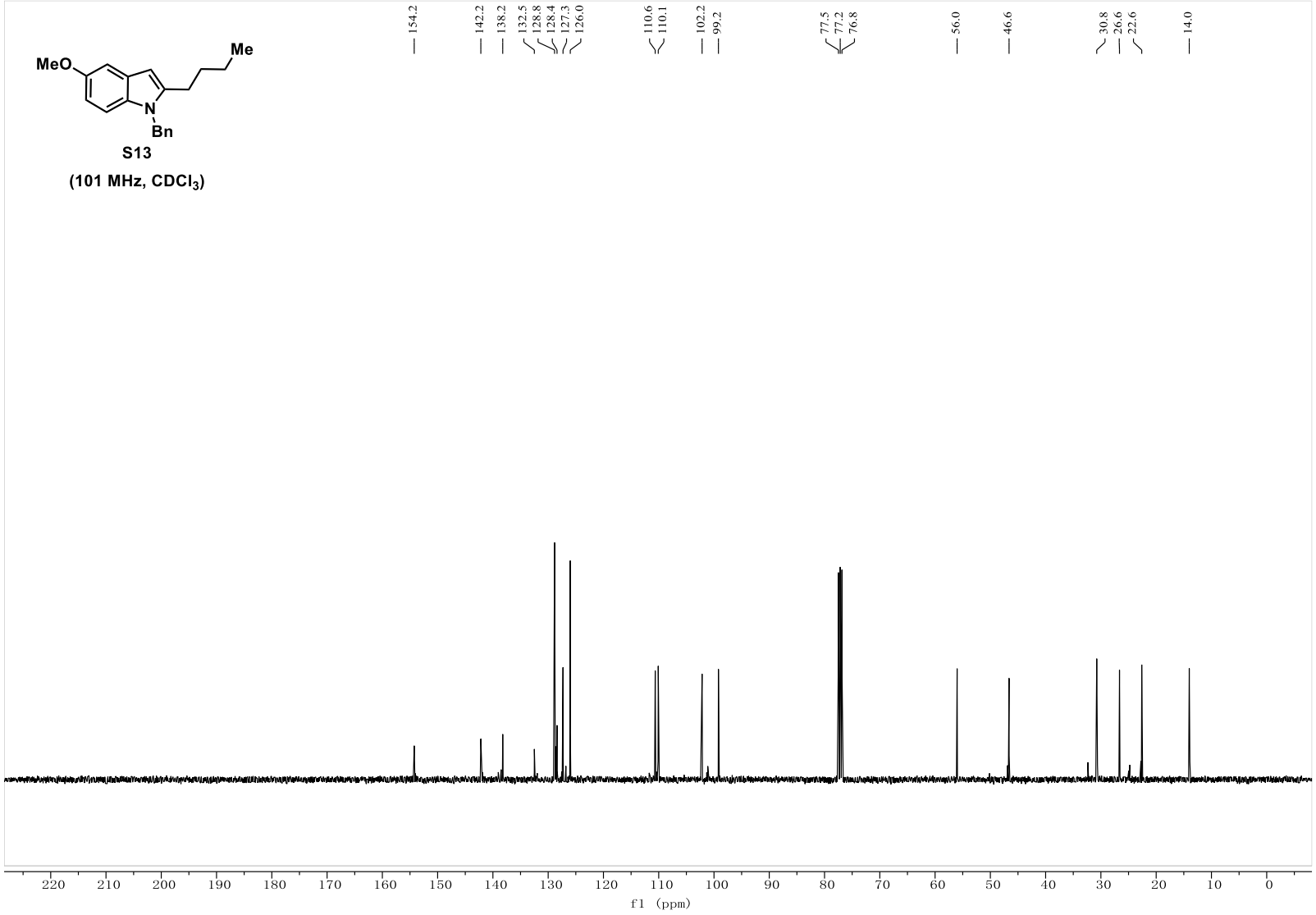

150.0
148.4
140.9
132.6
132.6
124.0
124.0
119.9
119.9
115.6
115.6
106.1
106.0
100.4
100.3
77.4
77.2
76.9
31.4
28.0
22.5
14.0
Me
N
H
F
S7
(151 MHz, CDCl3)
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

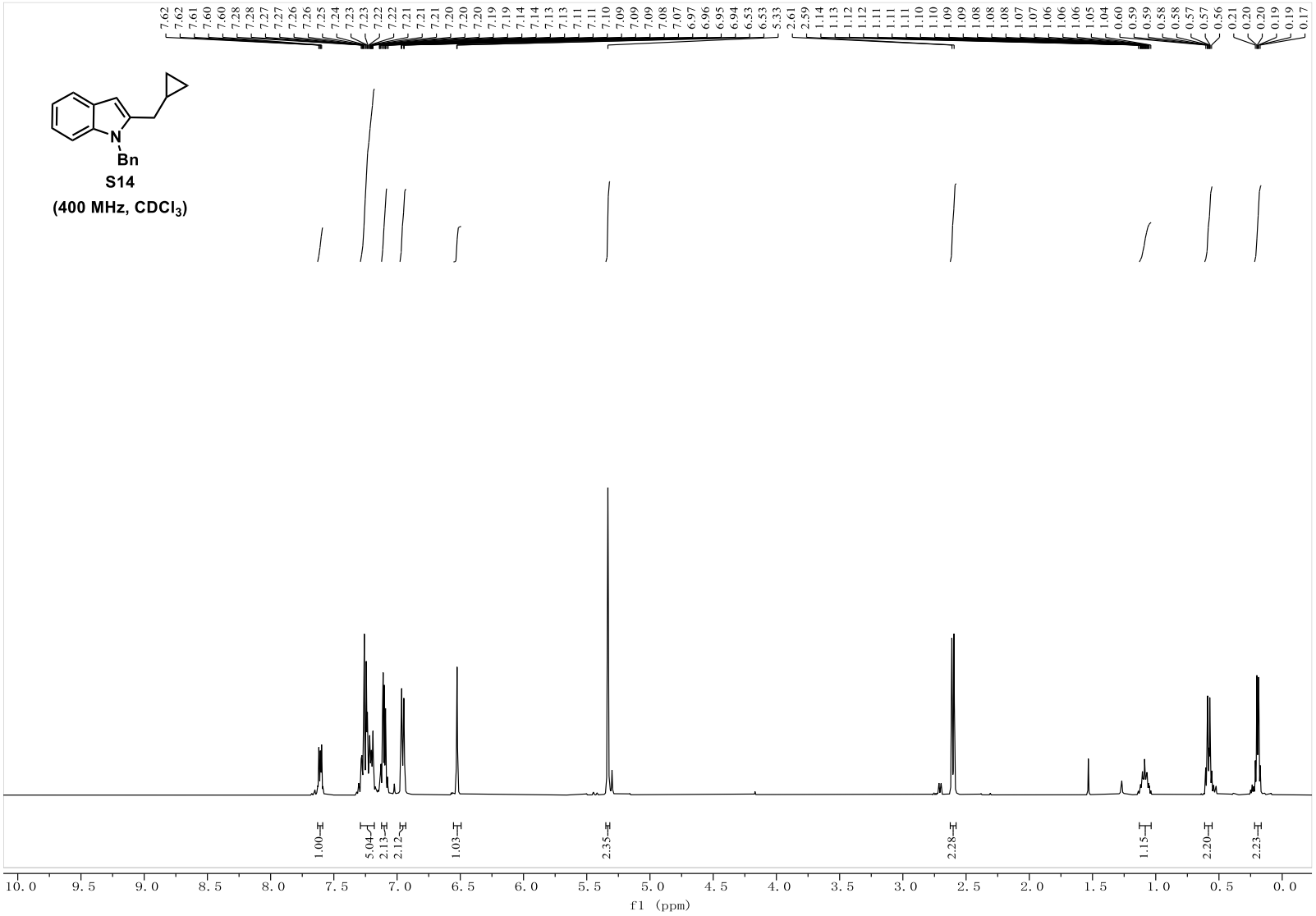

Me
N
H
F
S7
(376 MHz, CDCl3)
-136.0
30 20 10 0 −10 −20 −30 −40 −50 −60 −70 −80 −90 −100 −110 −120 −130 −140 −150 −160 −170 −180 −190 −200
f1 (ppm)

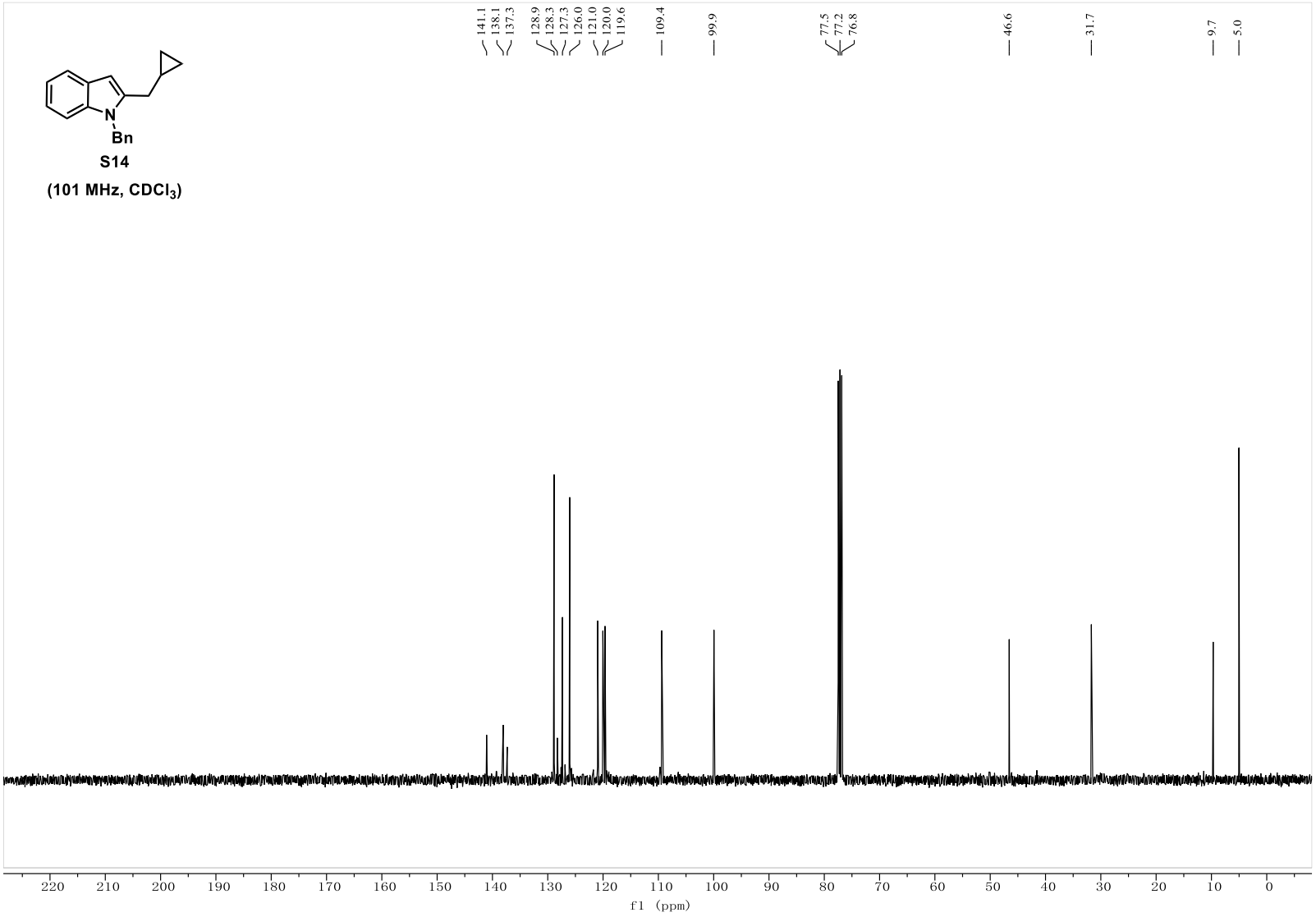

7.83
7.51
7.50
7.26
7.25
7.23
7.18
7.16
7.16
7.09
7.08
7.07
7.06
6.82
6.82
6.81
6.80
6.79
6.79
6.78
6.77
6.77
6.77
6.76
6.76
6.22
6.21
6.21
6.21
3.82
2.77
2.77
2.75
2.73
2.71
2.69
2.67
2.09
2.07
2.05
2.03
2.03
2.01
OMe
Cl
N
H
S12
(400 MHz, CDCl3)
1.03
0.96
0.94
1.00
1.02
3.17
0.95
3.12
2.19
2.22
2.26
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
f1 (ppm)

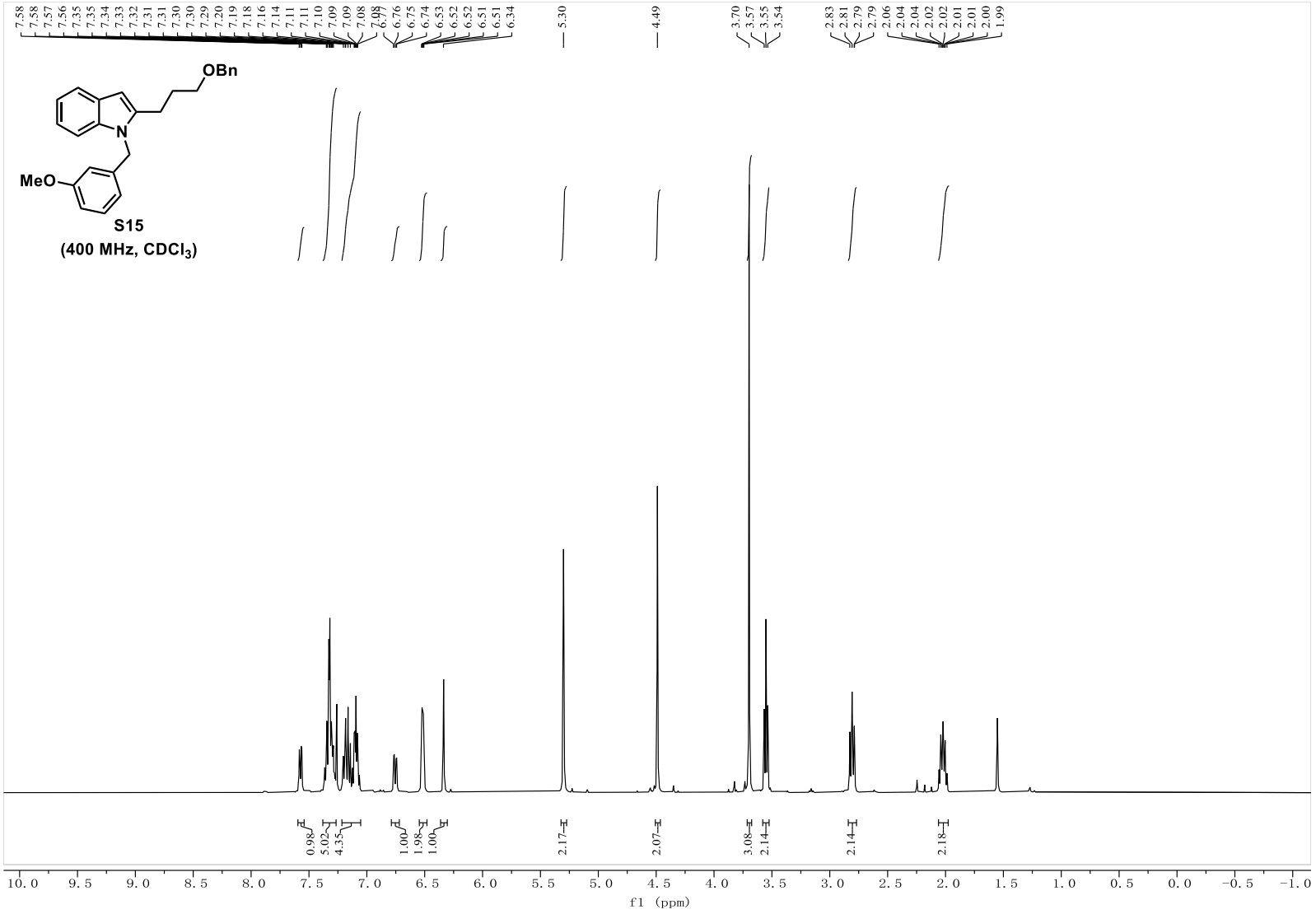

159.8
143.4
141.0
134.3
130.0
129.5
125.3
121.3
121.0
119.3
114.5
111.3
111.3
99.6
77.4
77.2
76.9
55.3
35.4
30.5
27.7
OMe
Cl
N
H
S12
(151 MHz, CDCl3)
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

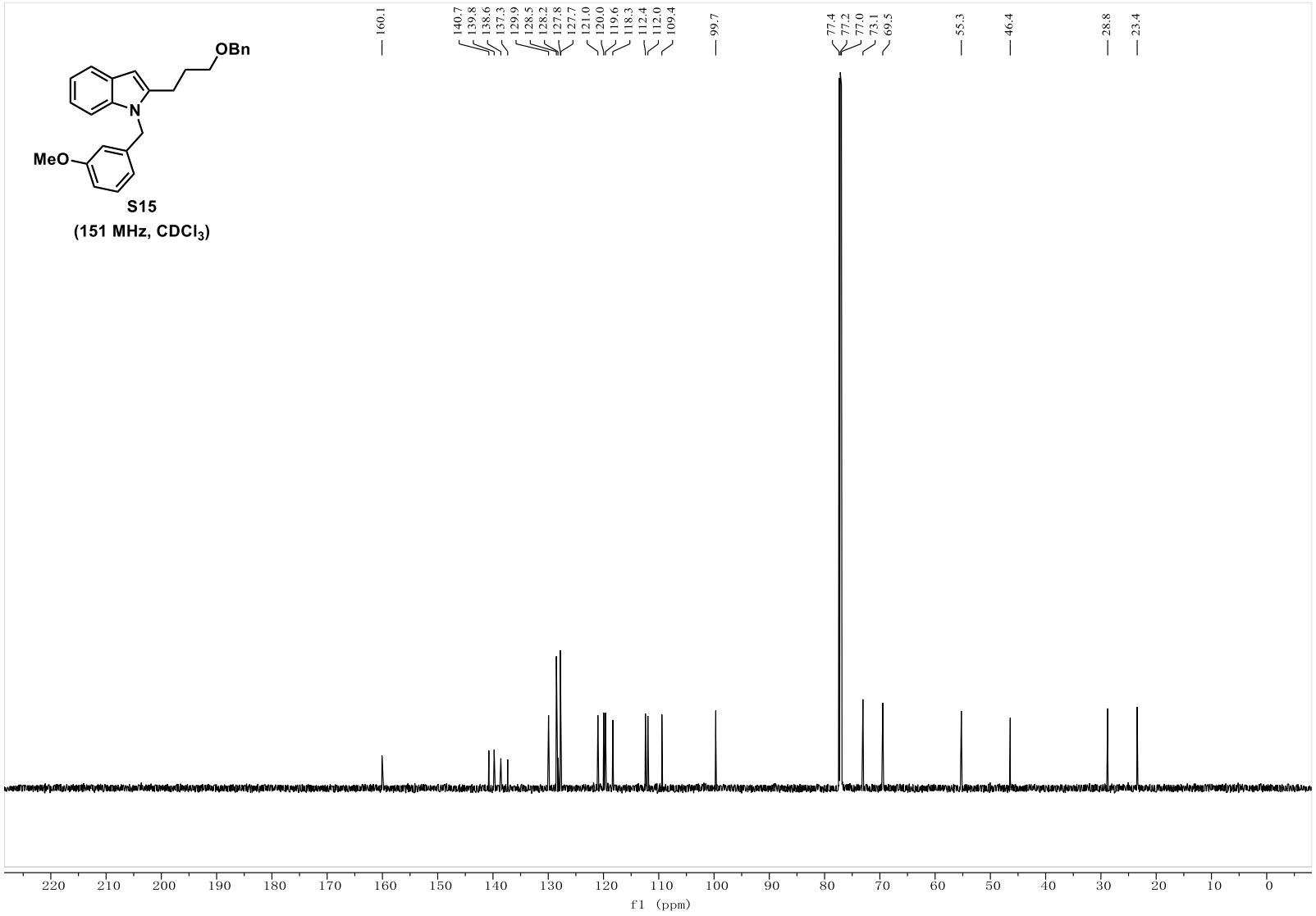

MeO
Me
N
Bn
S13
(400 MHz, CDCl3)
f1 (ppm)

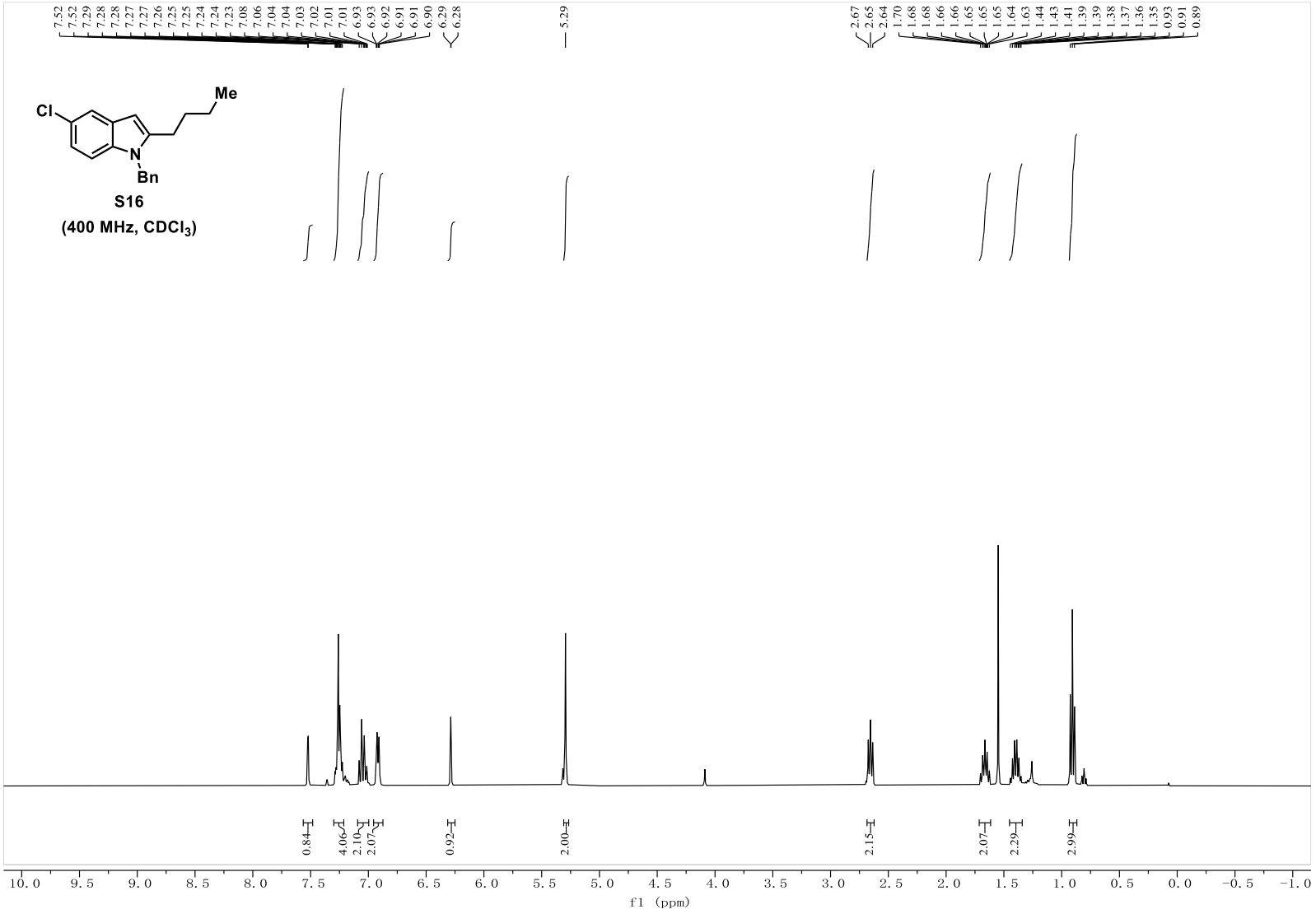

MeO
Me
N
Bn
S13
(101 MHz, CDCl3)
154.2
142.2
138.2
132.5
128.8
128.4
127.3
126.0
110.6
110.1
102.2
99.2
77.5
77.2
76.8
56.0
46.6
30.8
26.6
22.6
14.0
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

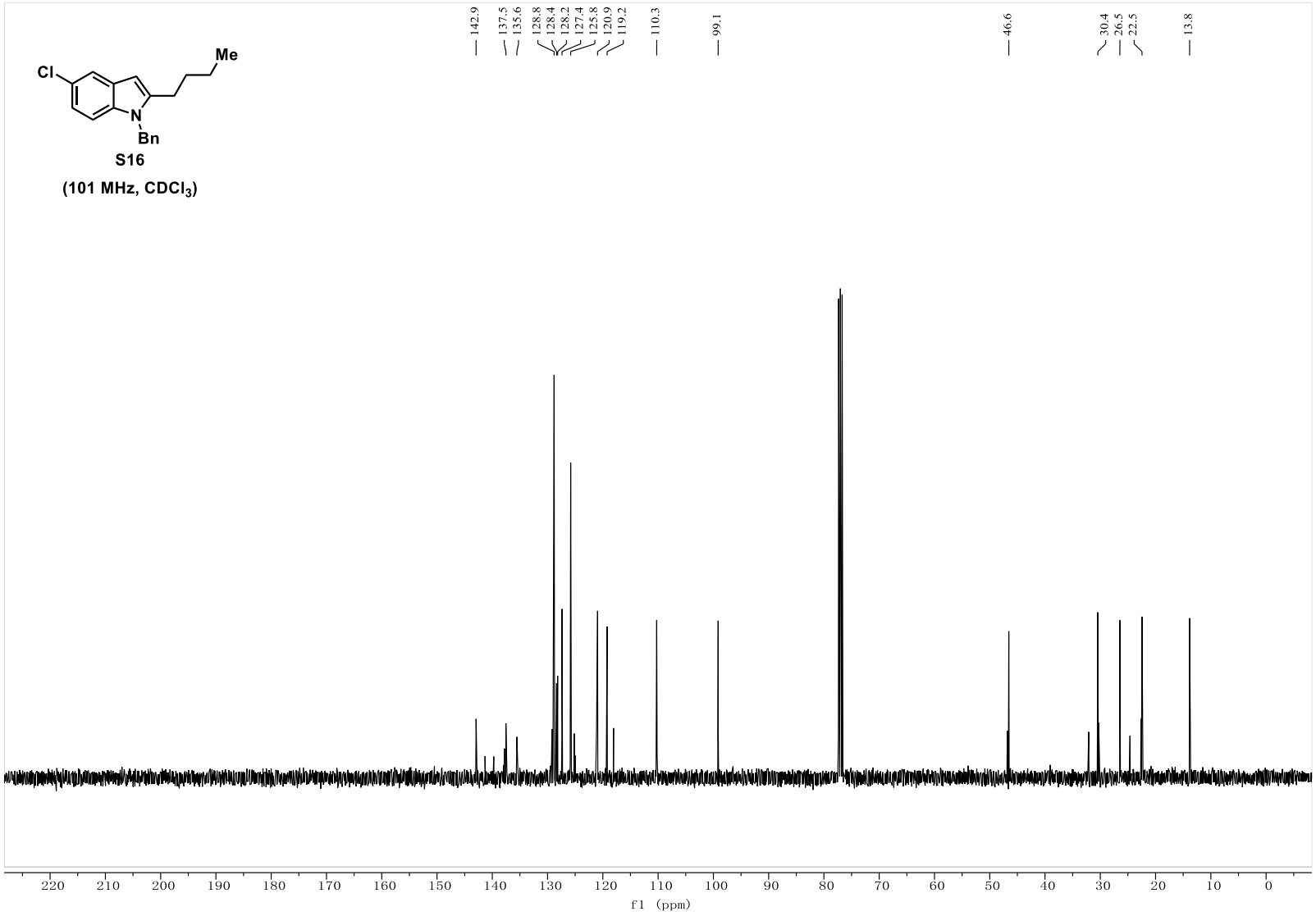

S14
(400 MHz, CDCl3)
f1 (ppm)

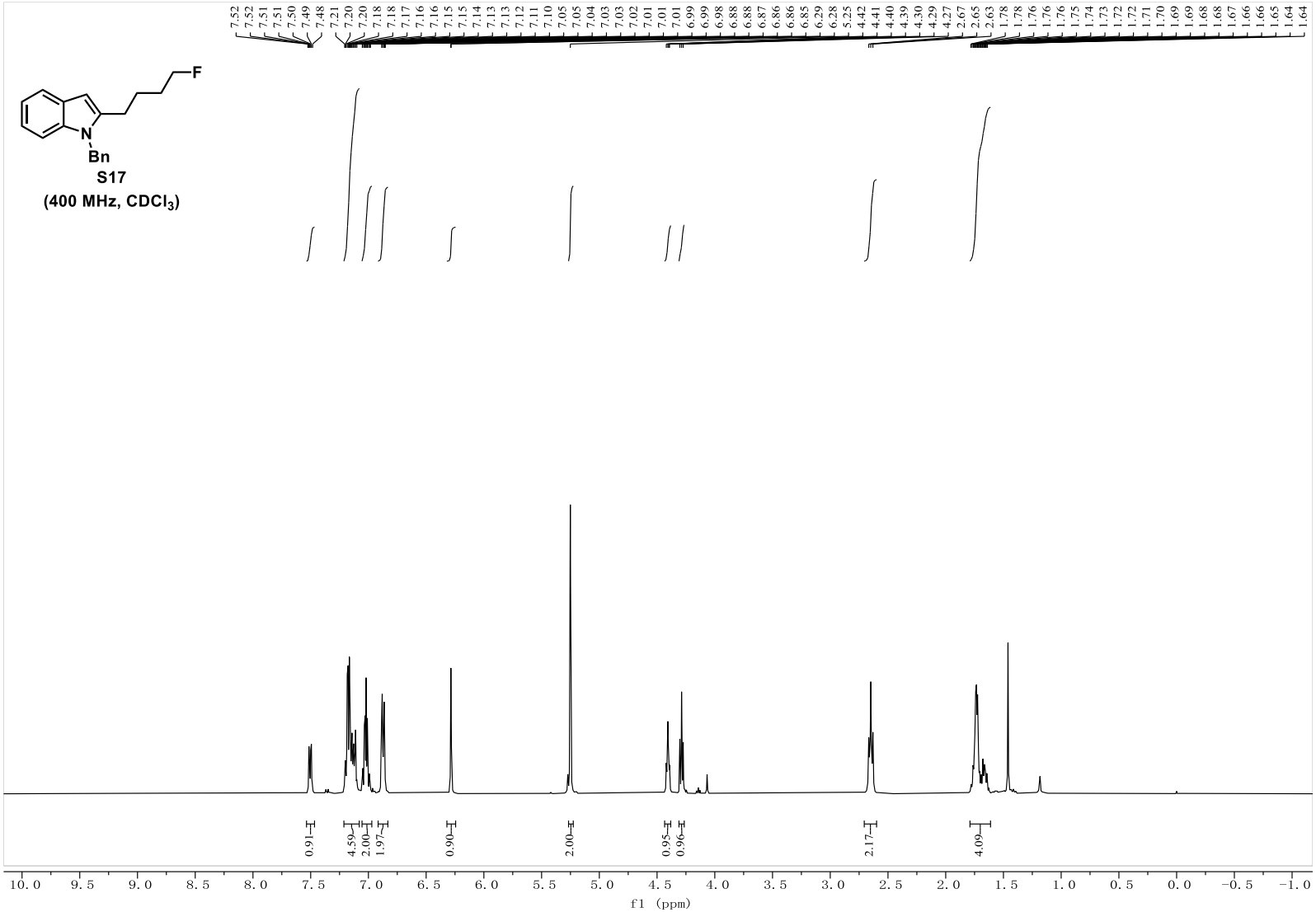

141.1
138.1
137.3
128.9
128.3
127.3
126.0
121.0
120.0
119.6
109.4
99.9
77.5
77.2
76.8
46.6
31.7
9.7
5.0
N
Bn
S14
(101 MHz, CDCl3)
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

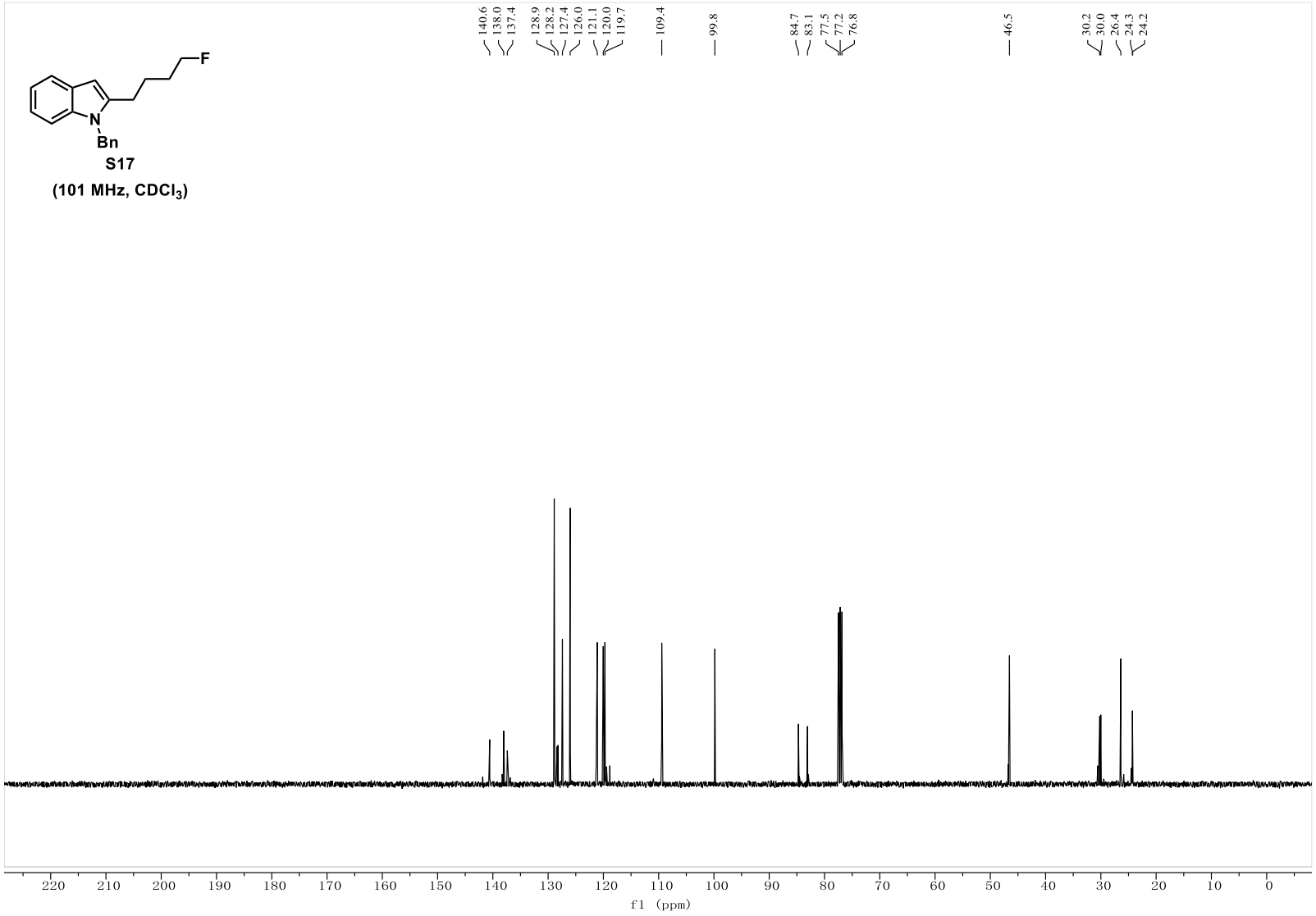

OBn
N
MeO
S15
(400 MHz, CDCl3)
f1 (ppm)

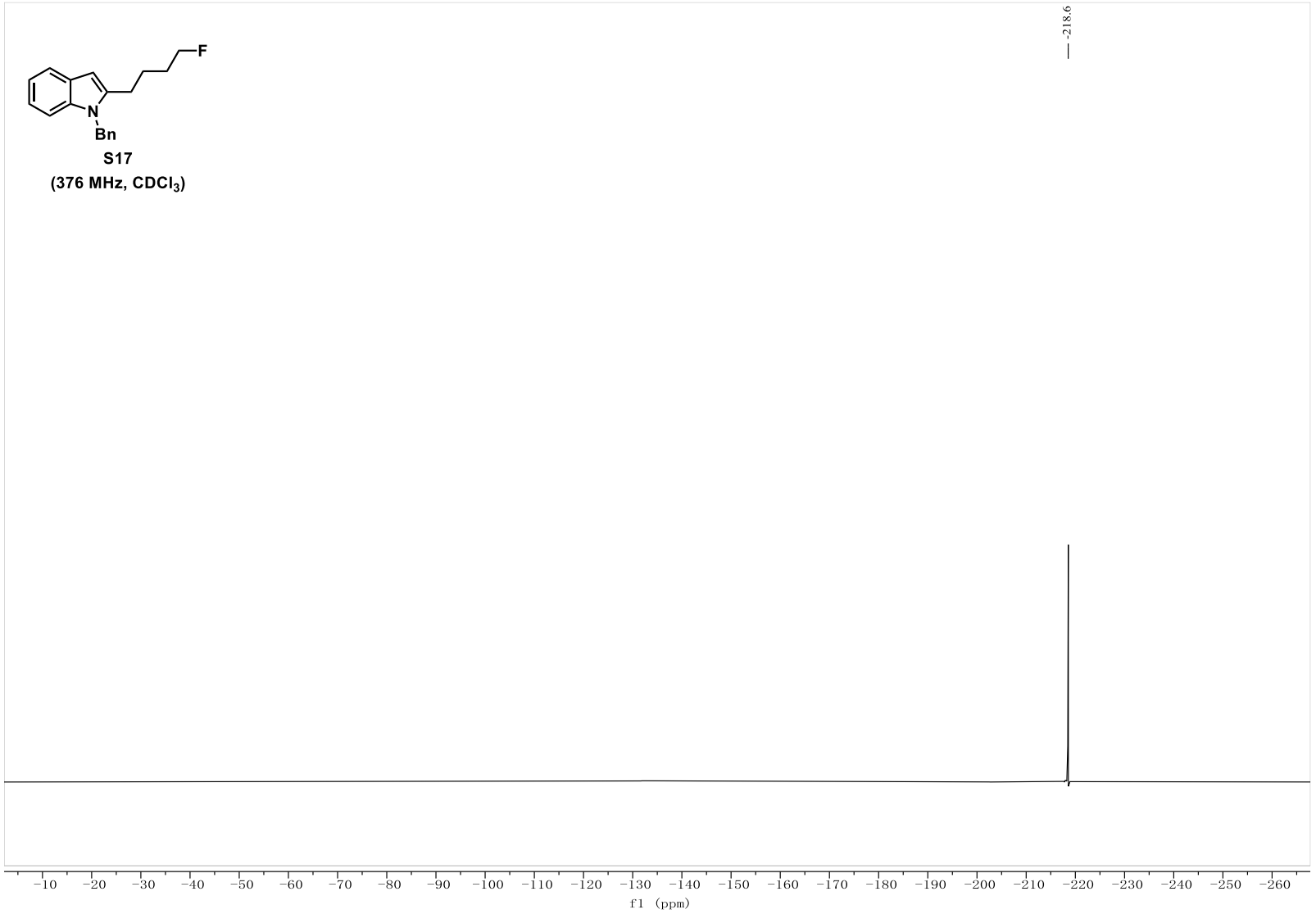

OBn
N
MeO
S15
(151 MHz, CDCl3)
160.1
140.7
139.8
138.6
137.3
129.9
128.5
128.2
127.8
127.7
121.0
120.0
119.6
118.3
112.4
112.0
109.4
99.7
77.4
77.2
77.0
73.1
69.5
55.3
46.4
28.8
23.4
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

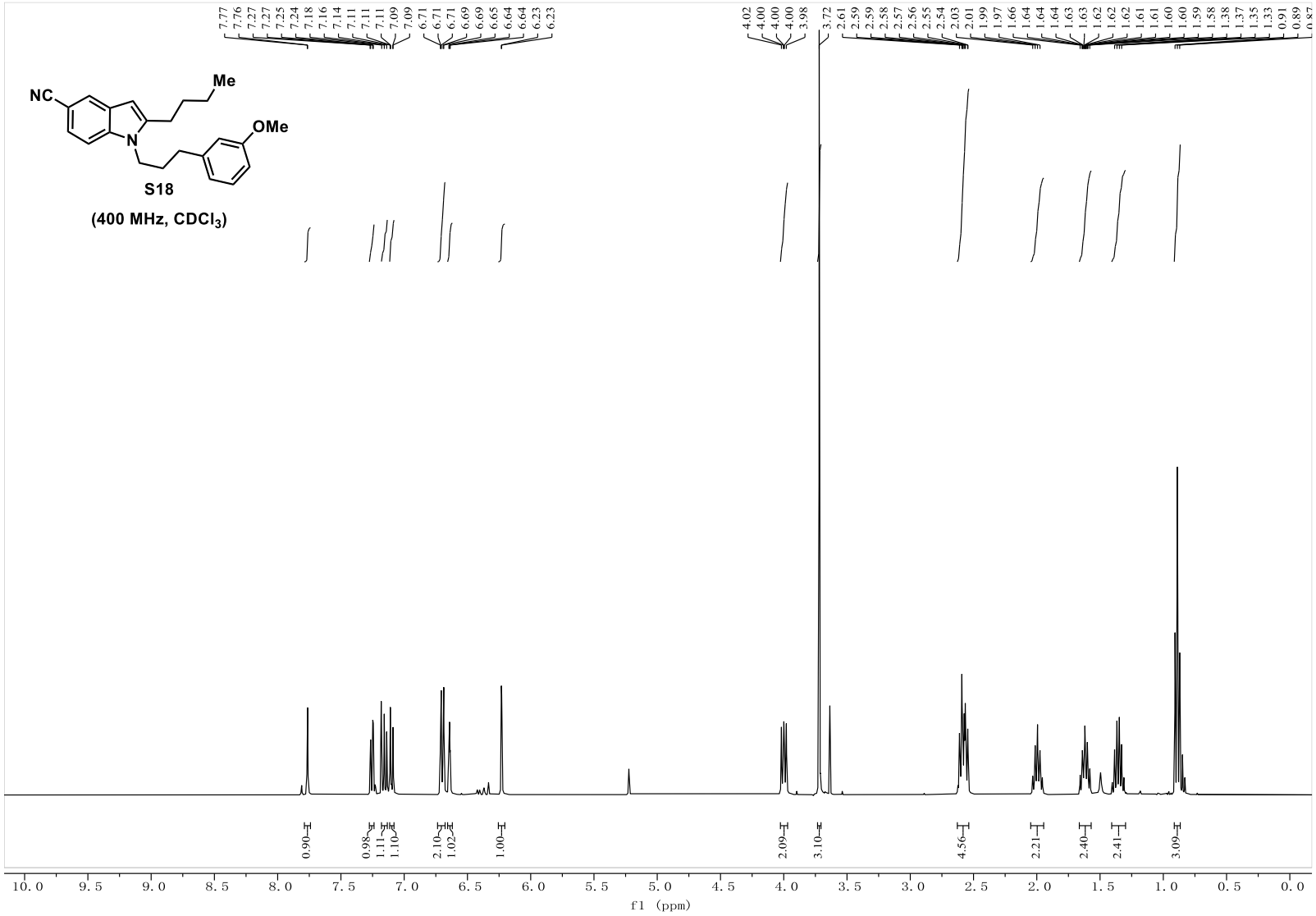

7.52
7.52
7.29
7.28
7.28
7.27
7.27
7.26
7.25
7.25
7.24
7.24
7.23
7.08
7.06
7.04
7.04
7.03
7.02
7.01
7.01
6.93
6.93
6.92
6.91
6.91
6.90
6.29
6.28
5.29
2.67
2.65
2.64
1.70
1.68
1.68
1.66
1.66
1.65
1.65
1.65
1.64
1.63
1.44
1.43
1.41
1.39
1.39
1.38
1.37
1.36
1.35
0.93
0.91
0.89
Cl
Me
N
Bn
S16
(400 MHz, CDCl3)
0.84
4.06
2.10
2.07
0.92
2.00
2.15
2.07
2.29
2.99
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
−0.5
−1.0
f1 (ppm)

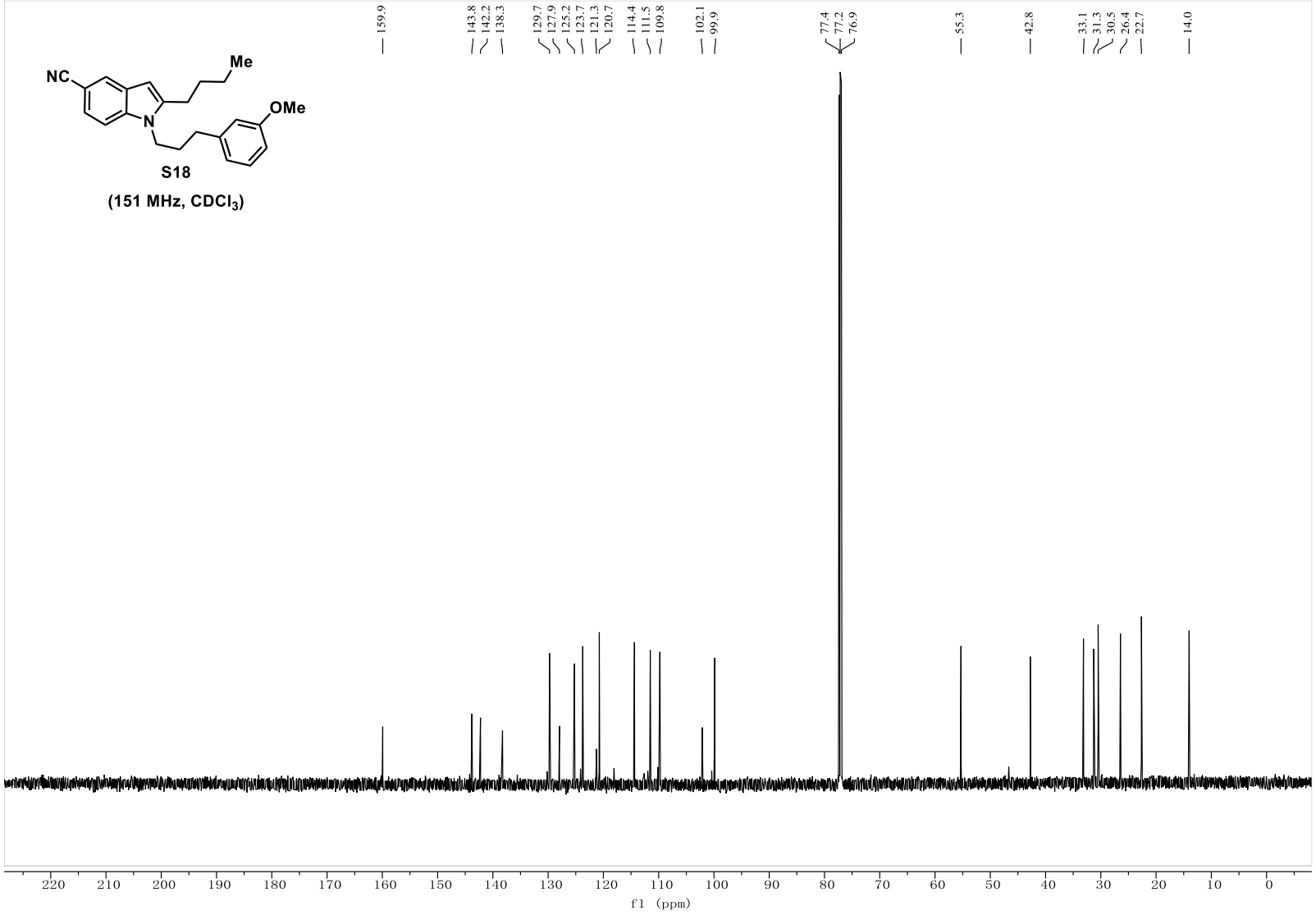

Cl
Me
N
Bn
S16
(101 MHz, CDCl3)
142.9
137.5
135.6
128.8
128.4
128.2
127.4
125.8
120.9
119.2
110.3
99.1
46.6
30.4
26.5
22.5
13.8
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

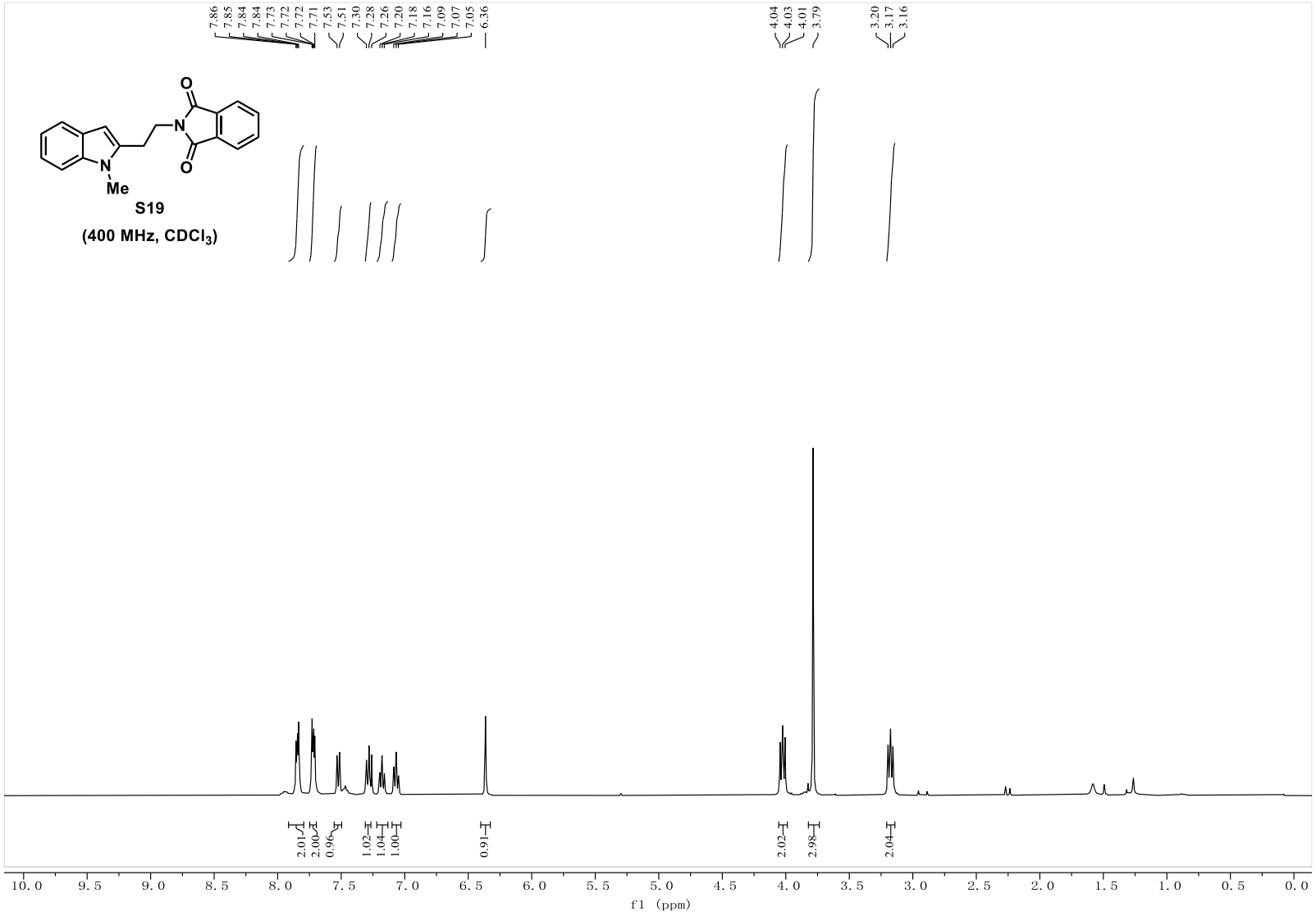

F
N
Bn
S17
(400 MHz, CDCl3)
7.52 7.52 7.51 7.51 7.50 7.49 7.48 7.21 7.20 7.20 7.18 7.18 7.17 7.16 7.16 7.15 7.15 7.14 7.13 7.13 7.12 7.11 7.10 7.05 7.05 7.04 7.03 7.03 7.02 7.01 7.01 7.01 6.99 6.99 6.98 6.88 6.88 6.87 6.86 6.86 6.86 6.85 6.29 6.28 5.25 4.42 4.41 4.40 4.39 4.30 4.29 4.27 2.67 2.65 2.63 1.78 1.78 1.76 1.76 1.76 1.75 1.74 1.73 1.72 1.72 1.71 1.70 1.69 1.69 1.68 1.68 1.67 1.66 1.66 1.65 1.64 1.64
0.91 4.59 2.00 1.97 0.90 2.00 0.95 0.96 2.17 4.09
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 −0.5 −1.0
f1 (ppm)

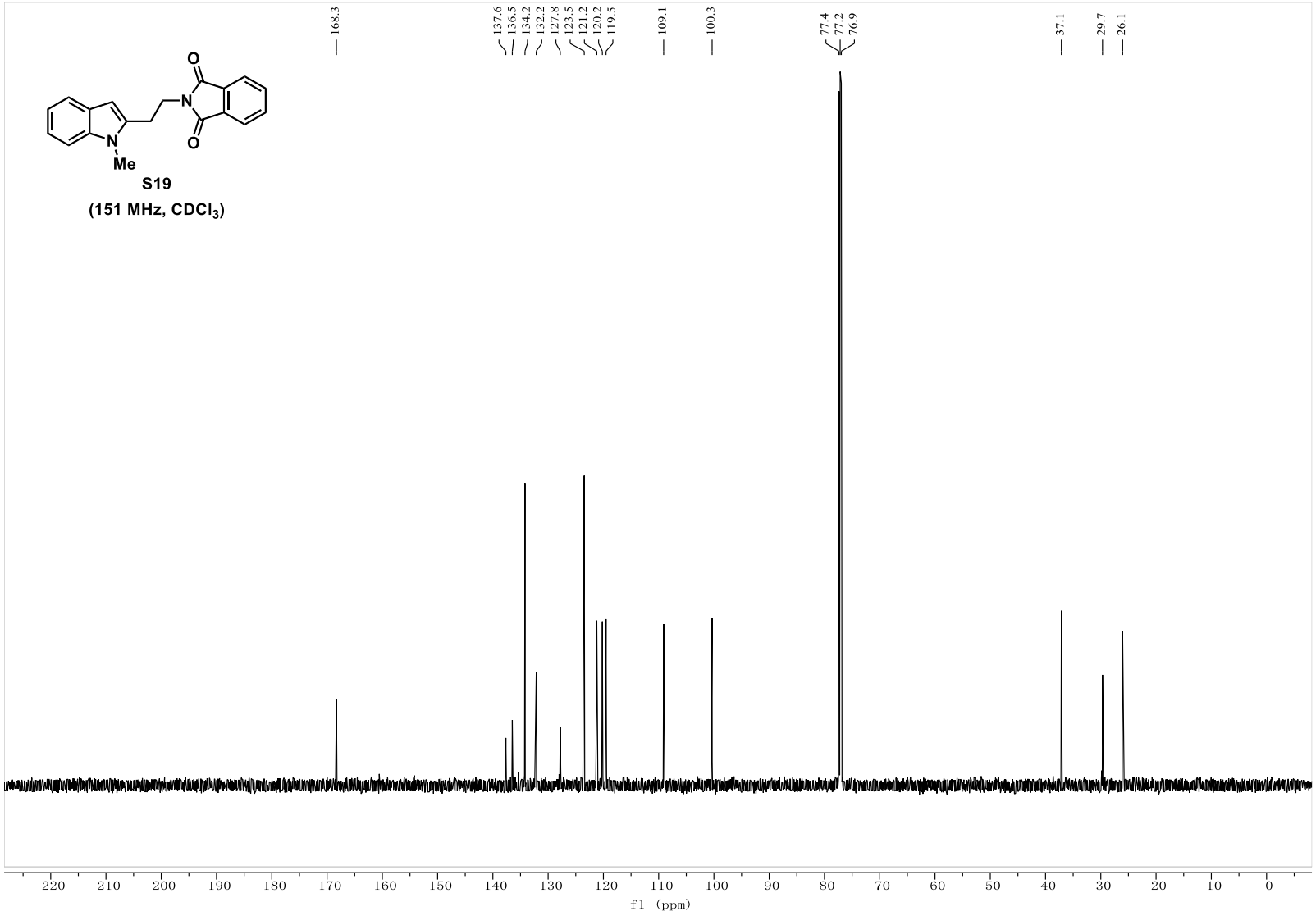

F
N
Bn
S17
(101 MHz, CDCl3)
140.6
138.0
137.4
128.9
128.2
127.4
126.0
121.1
120.0
119.7
109.4
99.8
84.7
83.1
77.5
77.2
76.8
46.5
30.2
30.0
26.4
24.3
24.2
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

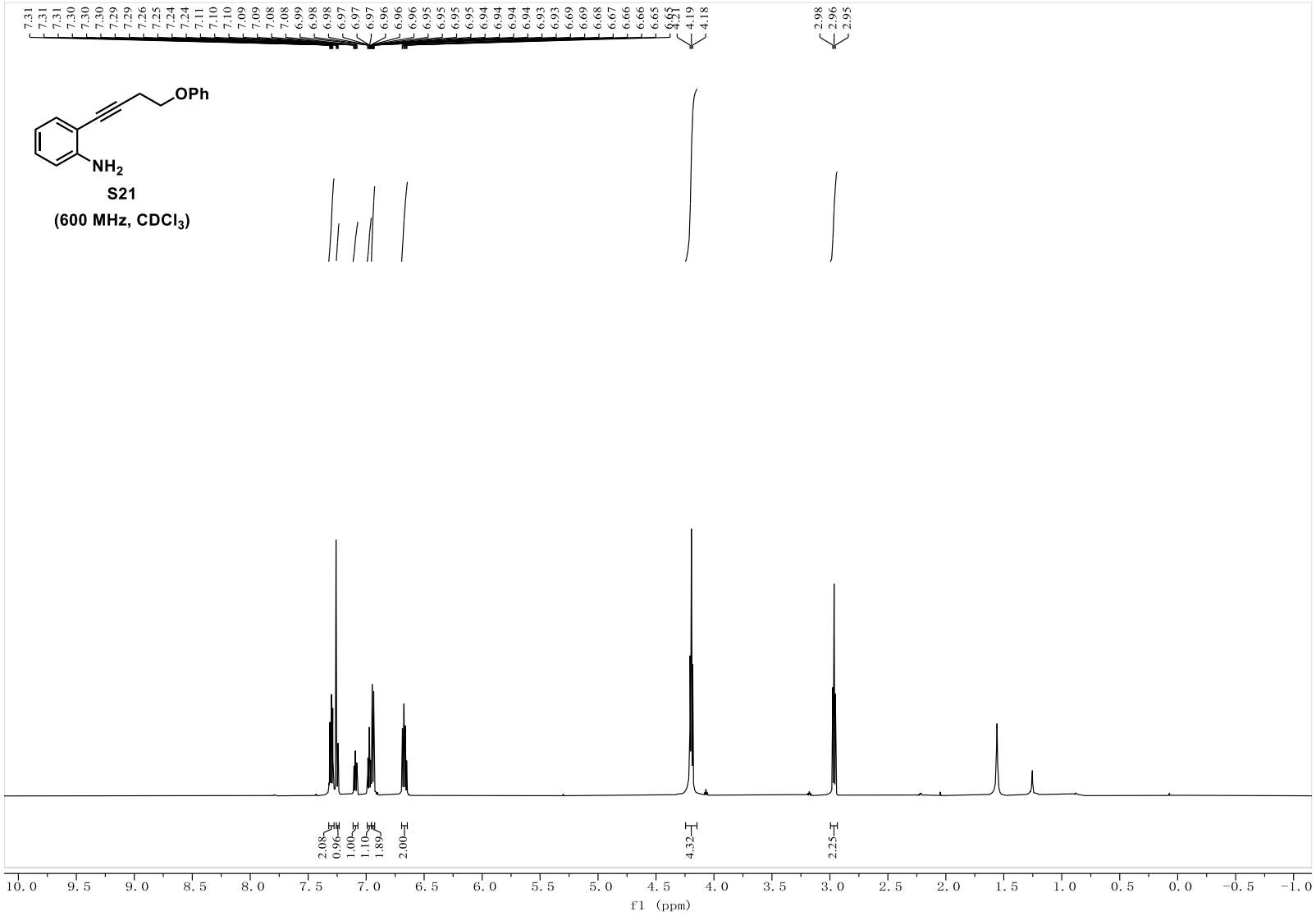

F
N
Bn
S17
(376 MHz, CDCl3)
-218.6
-10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 -230 -240 -250 -260
f1 (ppm)

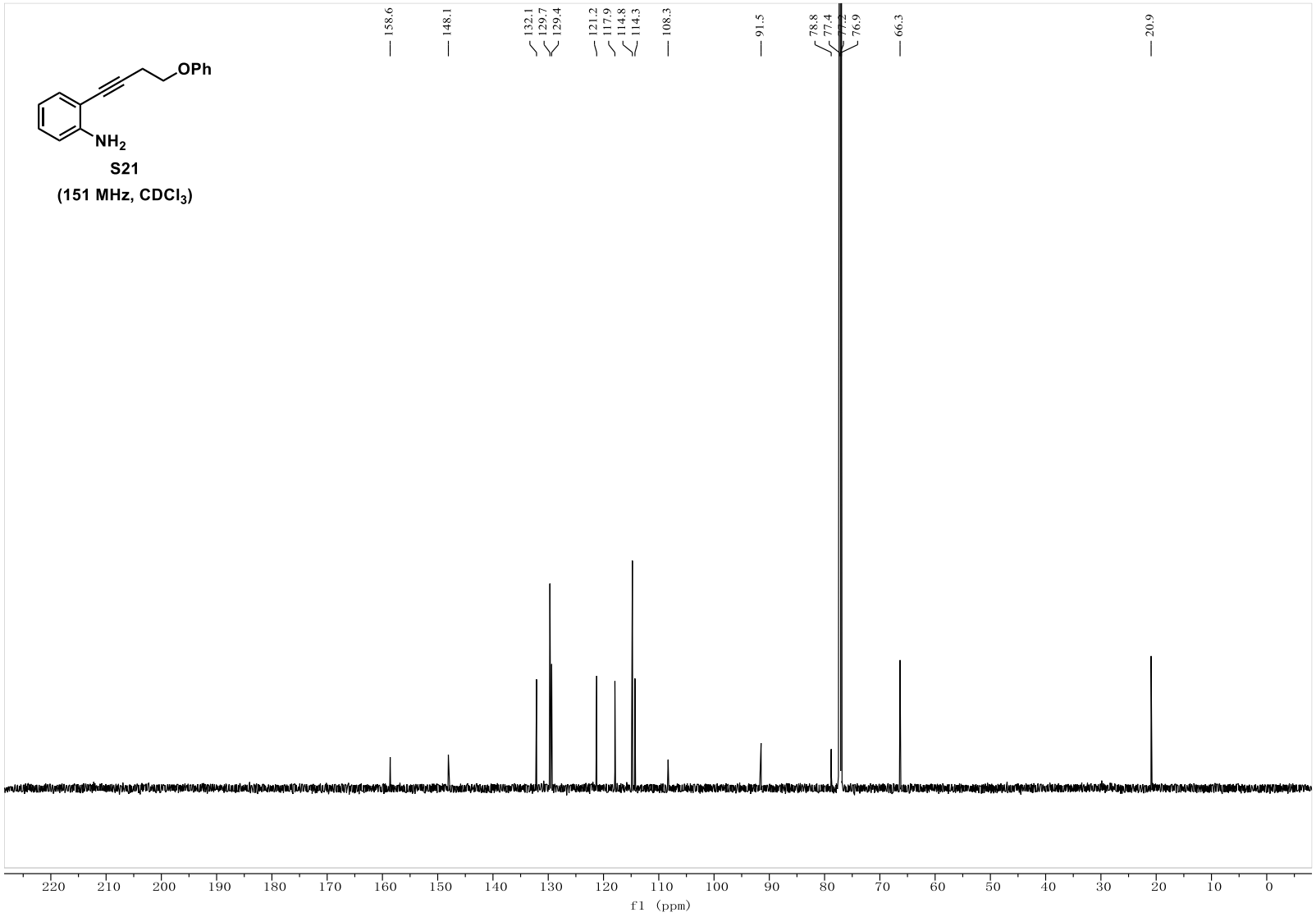

NC
Me
OMe
N
S18
(400 MHz, CDCl3)
7.77 7.76 7.27 7.27 7.25 7.24 7.18 7.16 7.14 7.11 7.11 7.11 7.09 7.09 6.71 6.71 6.69 6.69 6.65 6.64 6.64 6.23 6.23
4.02 4.00 4.00 4.00 3.98 3.72 2.61 2.59 2.59 2.58 2.57 2.56 2.55 2.54 2.03 2.01 1.99 1.97 1.66 1.64 1.64 1.64 1.63 1.63 1.62 1.62 1.62 1.61 1.61 1.60 1.60 1.59 1.58 1.38 1.37 1.35 1.33 0.91 0.89
0.90 0.98 1.11 1.10 2.10 1.02 1.00 2.09 3.10 4.56 2.21 2.40 2.41 3.09
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
f1 (ppm)

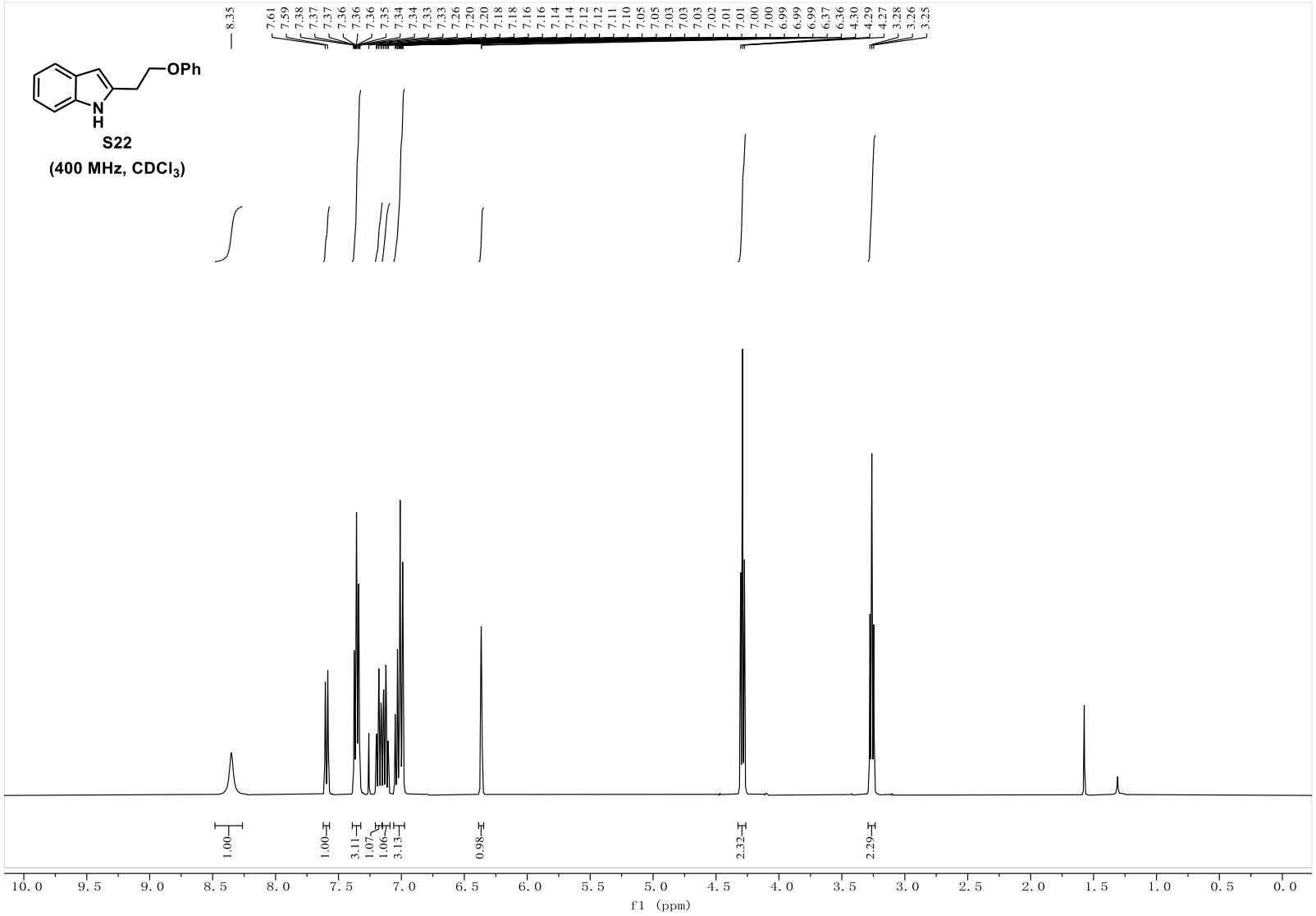

NC
Me
OMe
N
S18
(151 MHz, CDCl3)
159.9
143.8
142.2
138.3
129.7
127.9
125.2
123.7
121.3
120.7
114.4
111.5
109.8
102.1
99.9
77.4
77.2
76.9
55.3
42.8
33.1
31.3
30.5
26.4
22.7
14.0
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

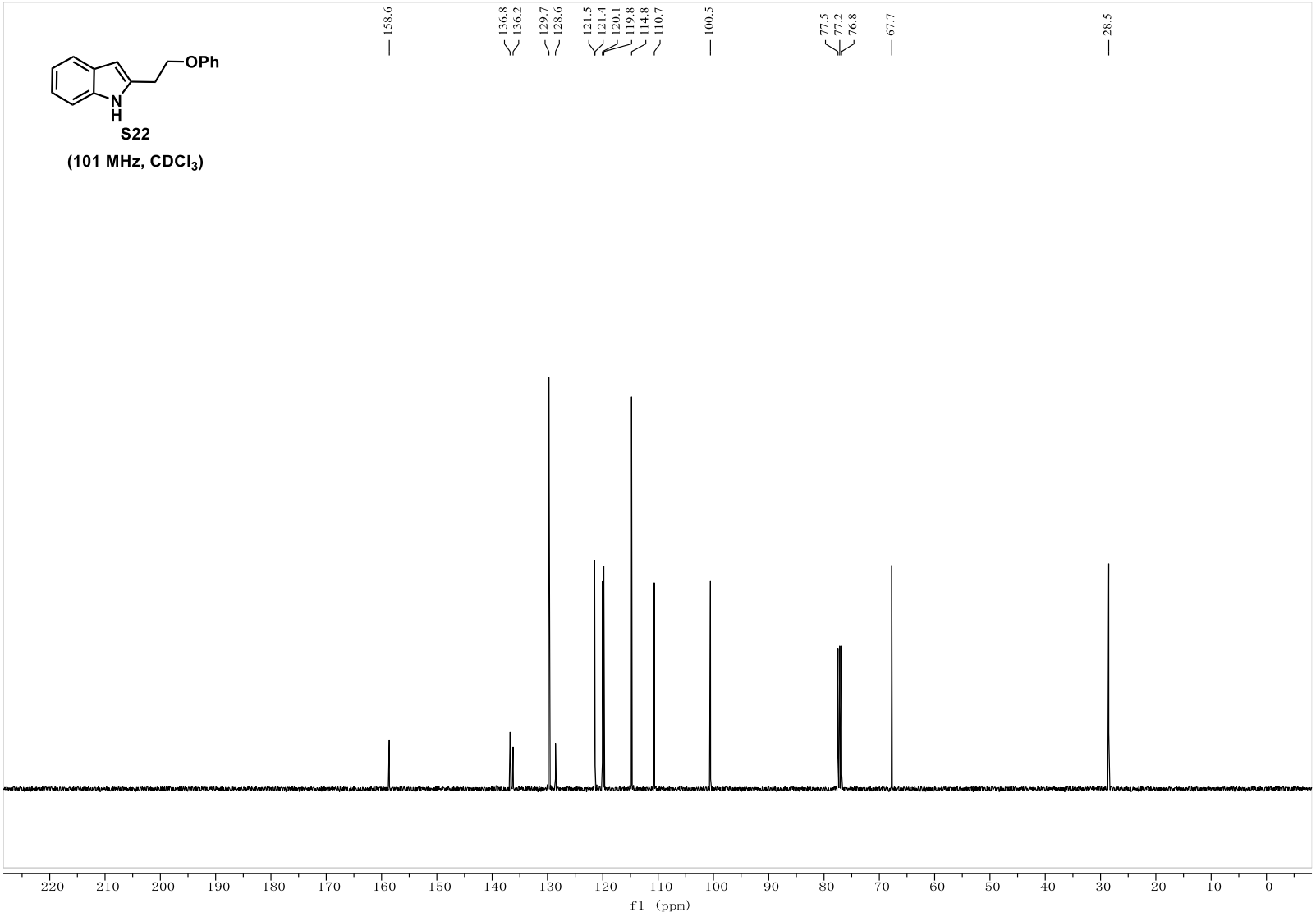

7.86
7.85
7.84
7.84
7.73
7.72
7.72
7.71
7.53
7.51
7.30
7.28
7.26
7.20
7.18
7.16
7.09
7.07
7.05
6.36
4.04
4.03
4.01
3.79
3.20
3.17
3.16
O
N
O
N
Me
O
S19
(400 MHz, CDCl3)
2.01
2.00
0.96
1.02
1.04
1.00
0.91
2.02
2.98
2.04
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

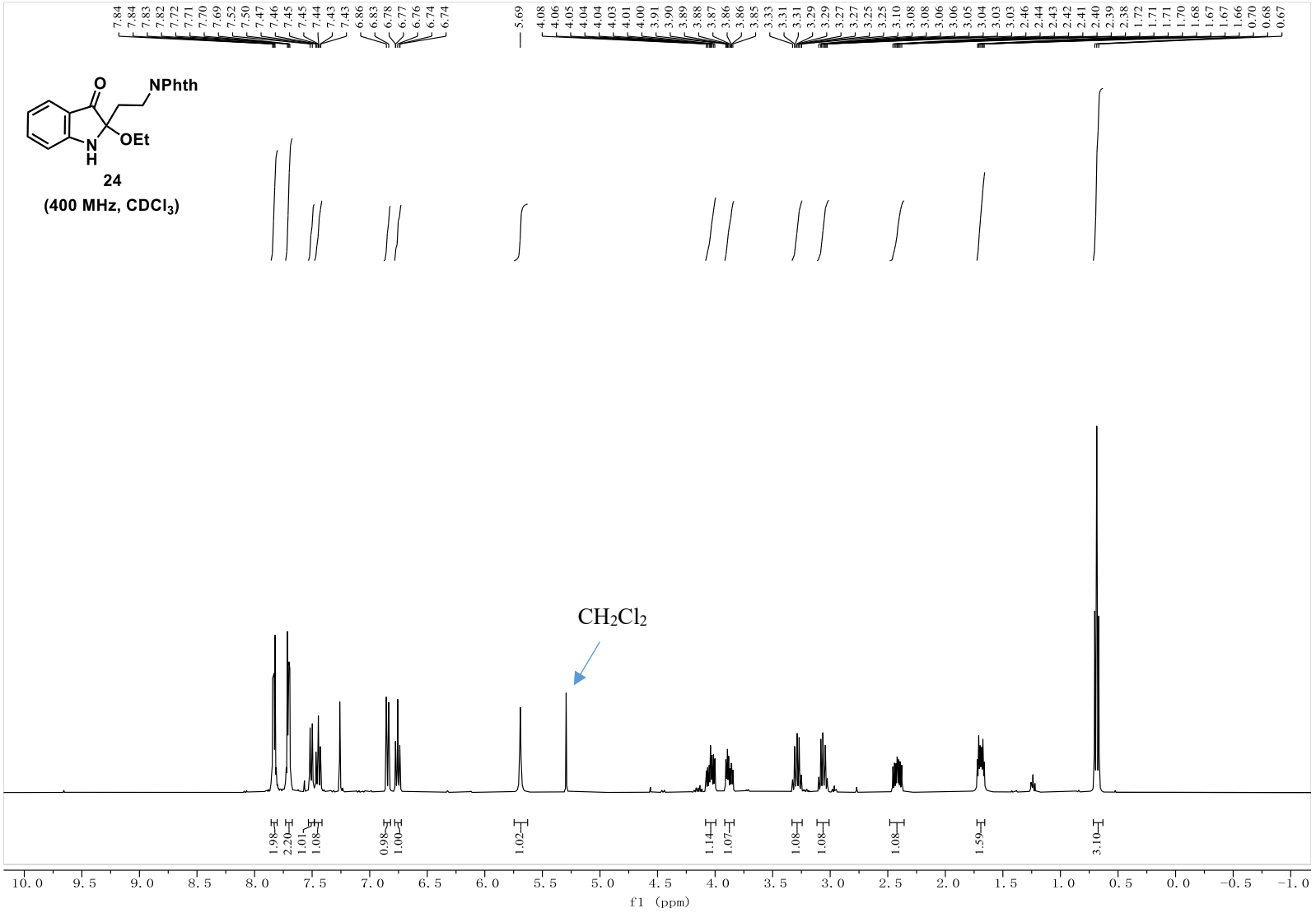

168.3
137.6
136.5
134.2
132.2
127.8
123.5
121.2
120.2
119.5
109.1
100.3
77.4
77.2
76.9
37.1
29.7
26.1
O
N
O
N
Me
S19
(151 MHz, CDCl3)
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

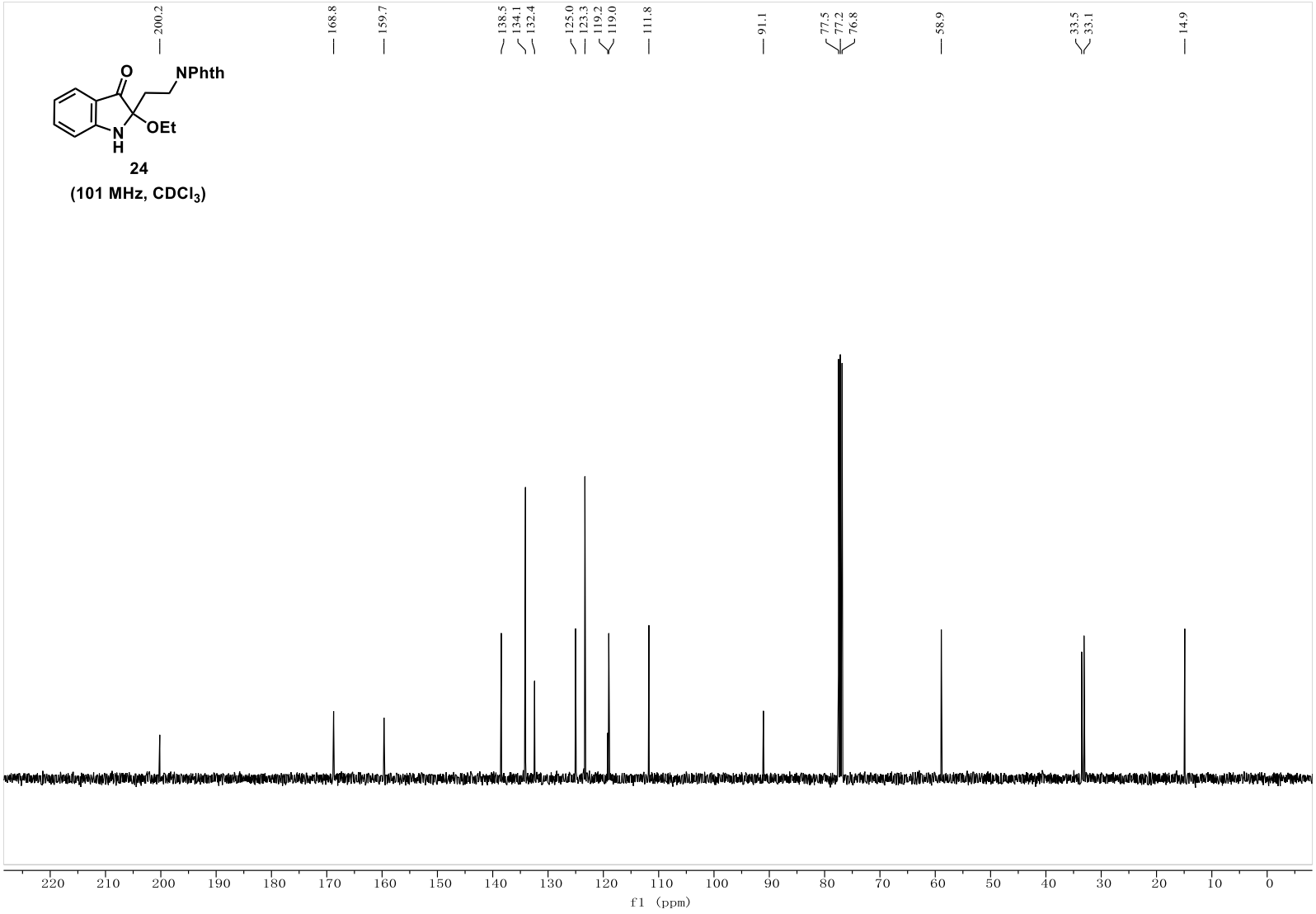

OPh
NH2
S21
(600 MHz, CDCl3)
f1 (ppm)

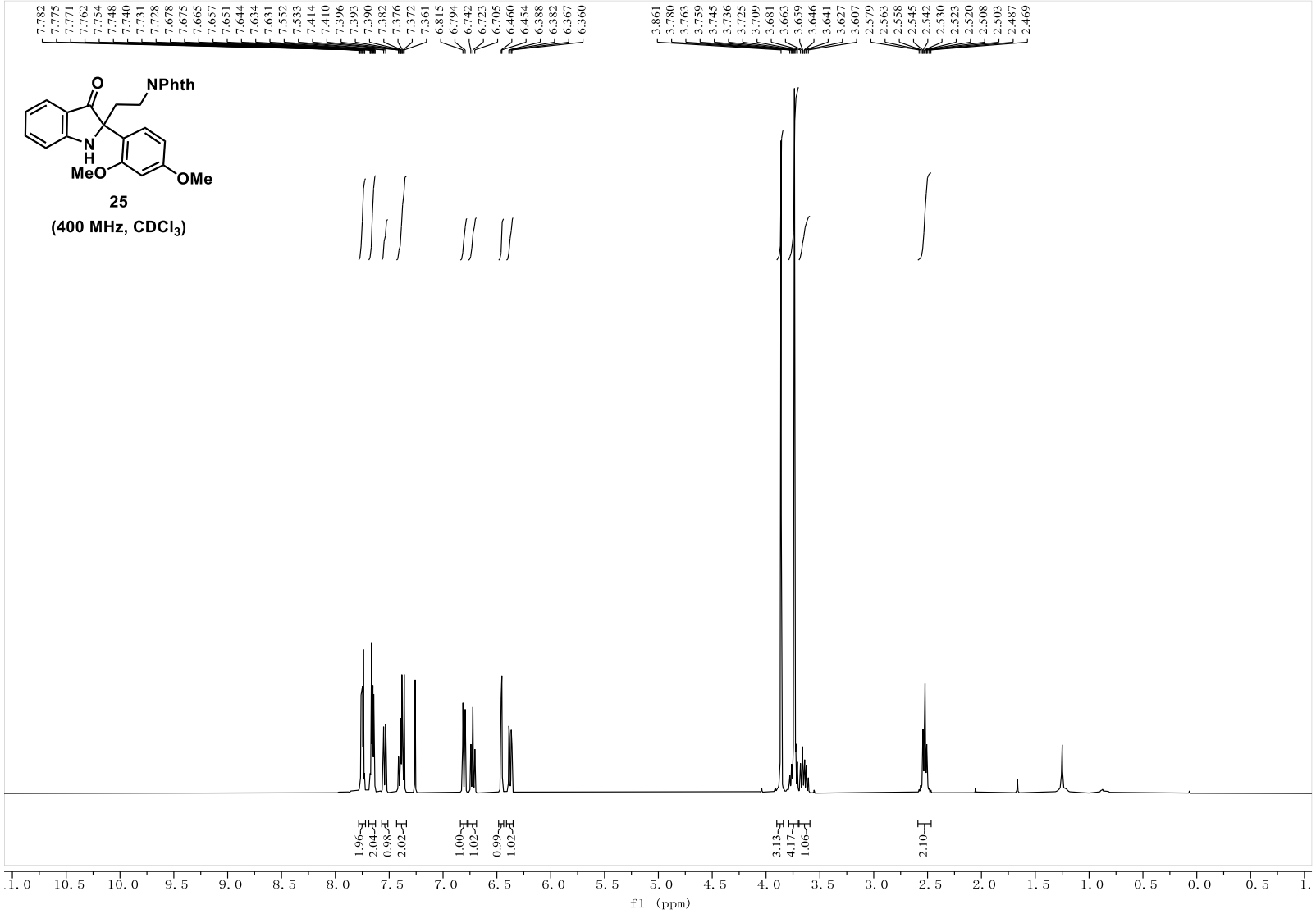

OPh
NH2
S21
(151 MHz, CDCl3)
158.6
148.1
132.1
129.7
129.4
121.2
117.9
114.8
114.3
108.3
91.5
78.8
77.4
77.2
76.9
66.3
20.9
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

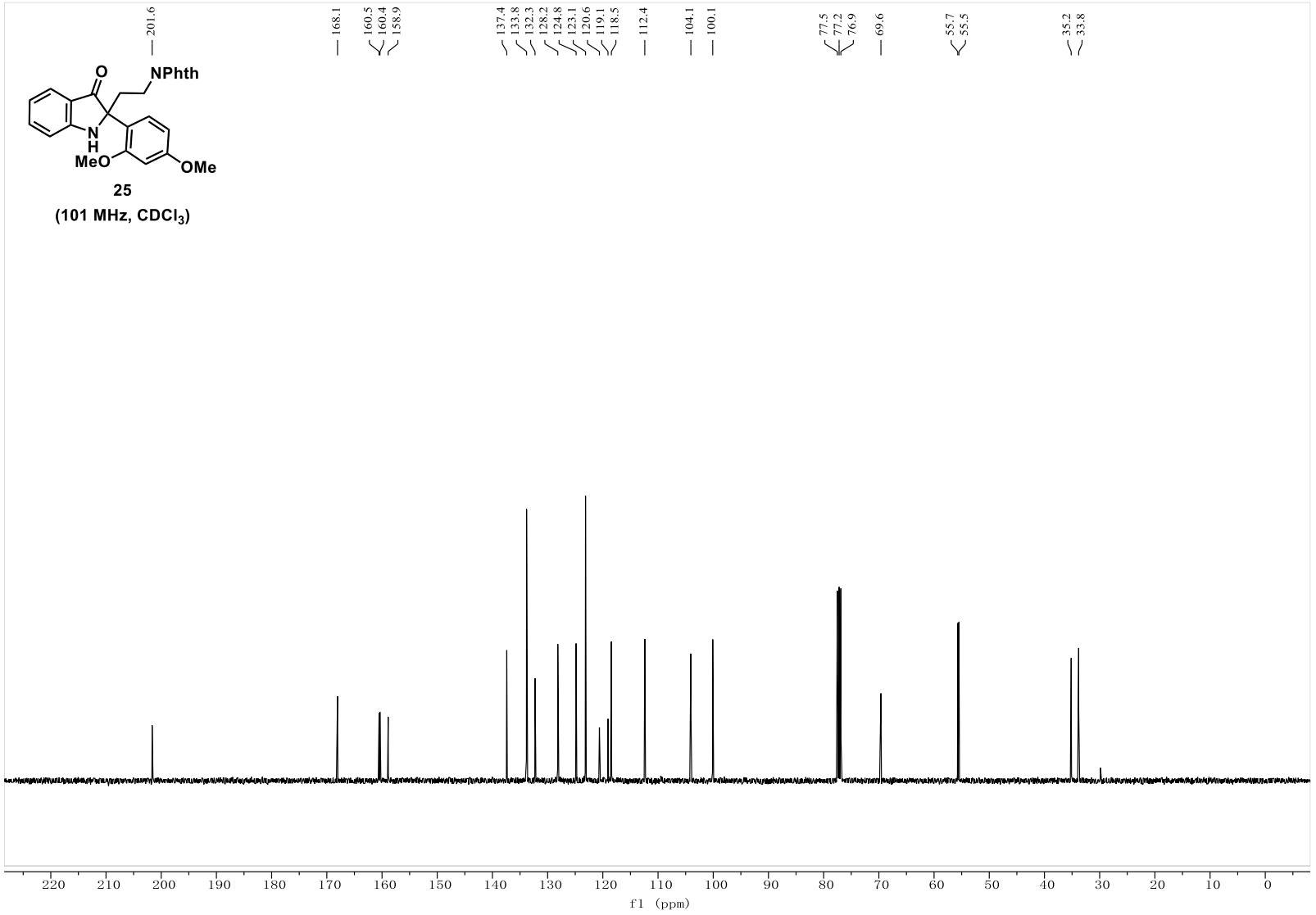

OPh
N
H
S22
(400 MHz, CDCl3)
8.35
7.61
7.59
7.38
7.37
7.37
7.36
7.36
7.36
7.35
7.34
7.34
7.33
7.33
7.26
7.20
7.20
7.18
7.18
7.16
7.16
7.14
7.14
7.12
7.12
7.11
7.10
7.05
7.05
7.03
7.03
7.03
7.02
7.01
7.01
7.00
7.00
6.99
6.99
6.99
6.37
6.36
4.30
4.29
4.27
3.28
3.26
3.25
1.00
1.00
3.11
1.07
1.06
3.13
0.98
2.32
2.29
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
f1 (ppm)

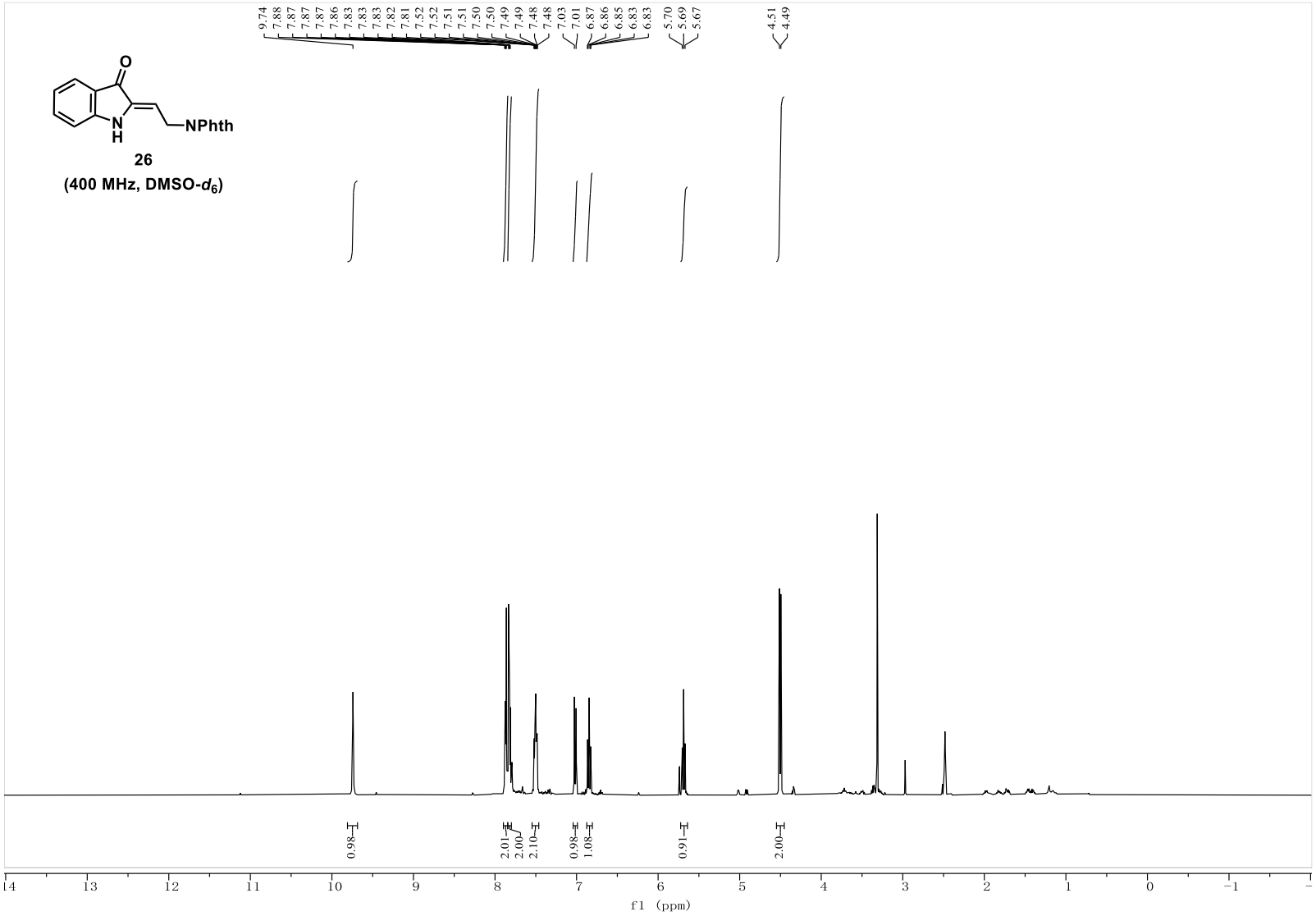

OPh
N
H
S22
(101 MHz, CDCl3)
158.6
136.8
136.2
129.7
128.6
121.5
121.4
120.1
119.8
114.8
110.7
100.5
77.5
77.2
76.8
67.7
28.5
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

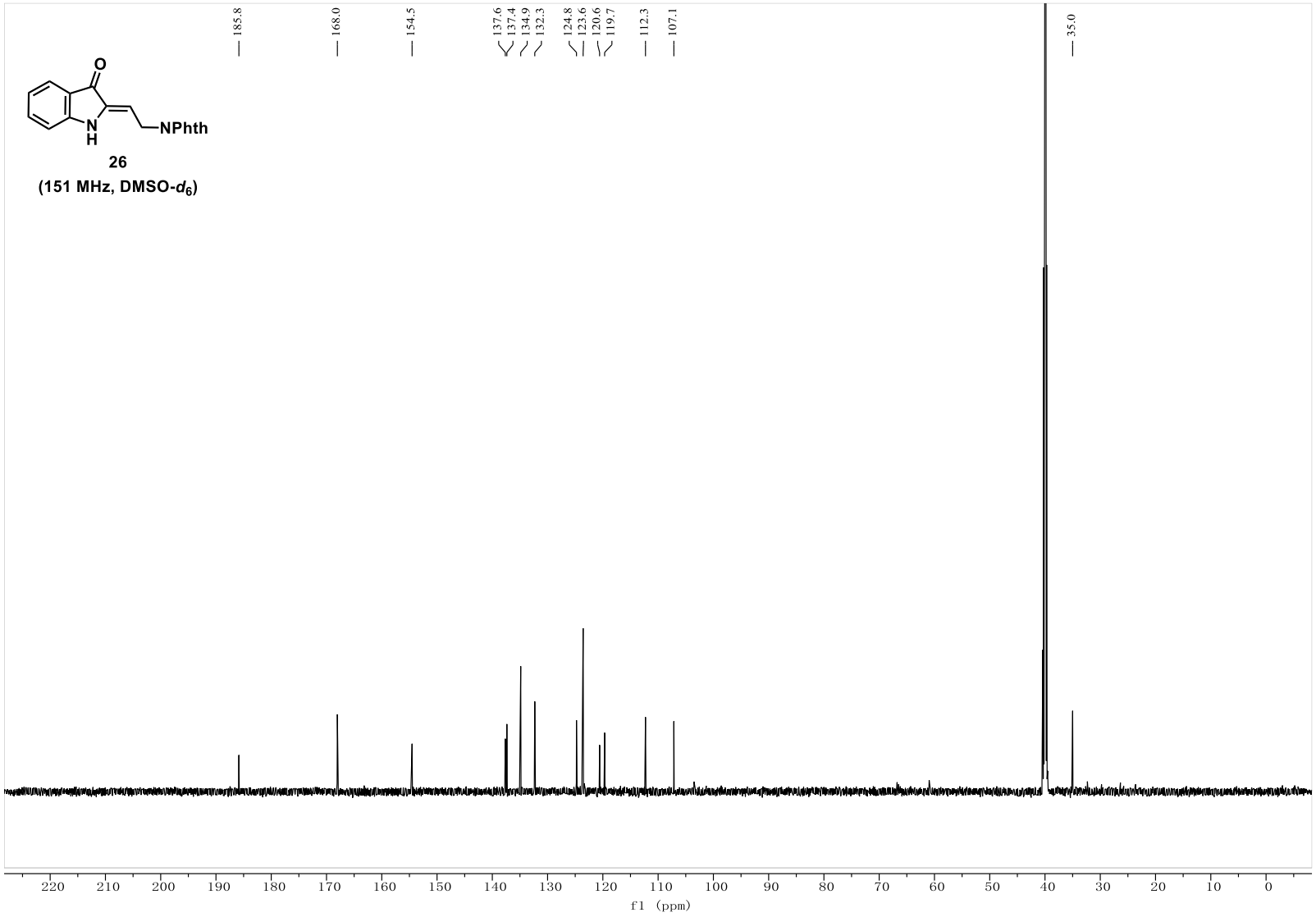

NPhth
O
OEt
N
H
24
(400 MHz, CDCl3)
CH2Cl2
f1 (ppm)

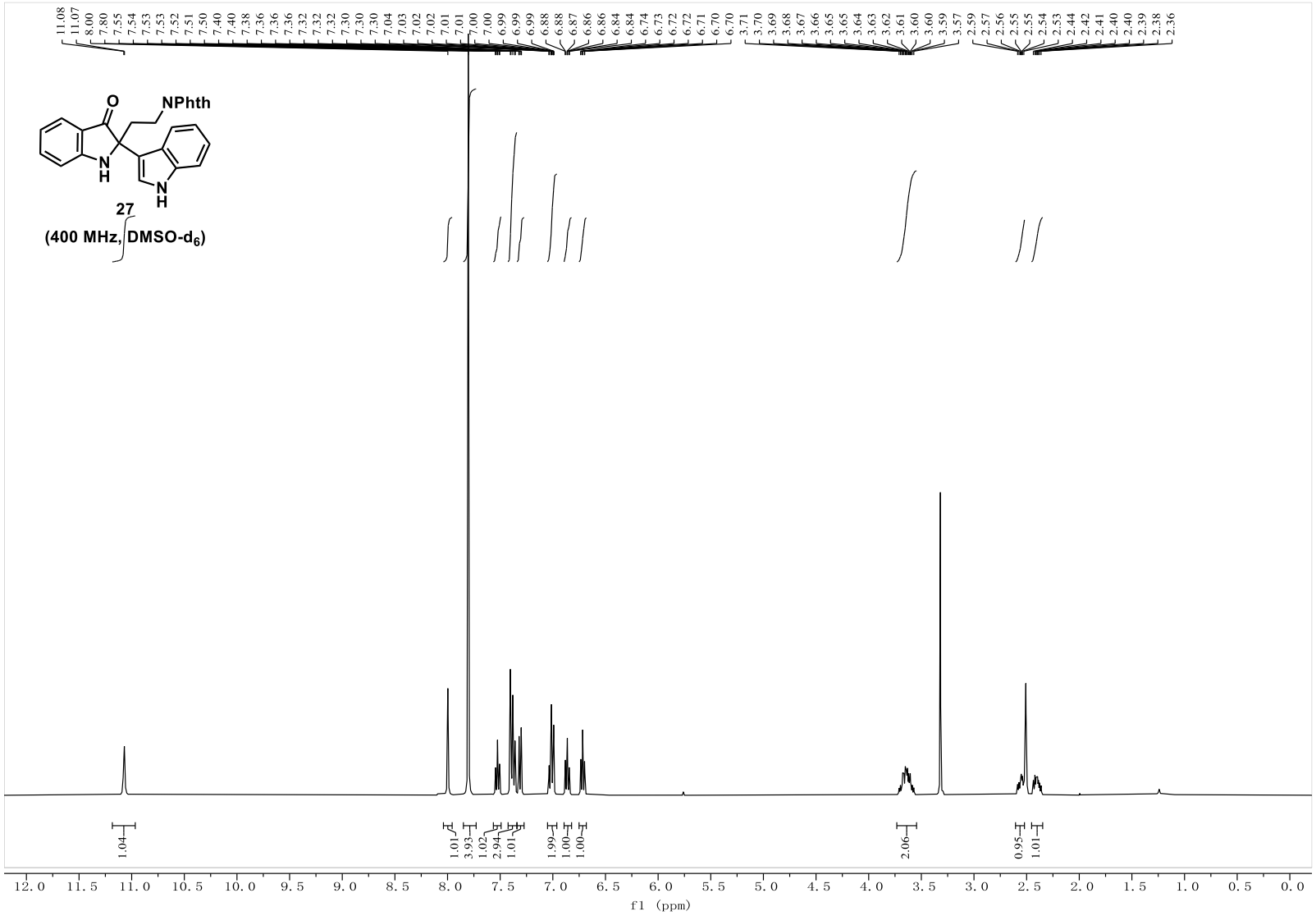

200.2
168.8
159.7
138.5
134.1
132.4
125.0
123.3
119.2
119.0
111.8
91.1
77.5
77.2
76.8
58.9
33.5
33.1
14.9
O
NPhth
OEt
N
H
24
(101 MHz, CDCl3)
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

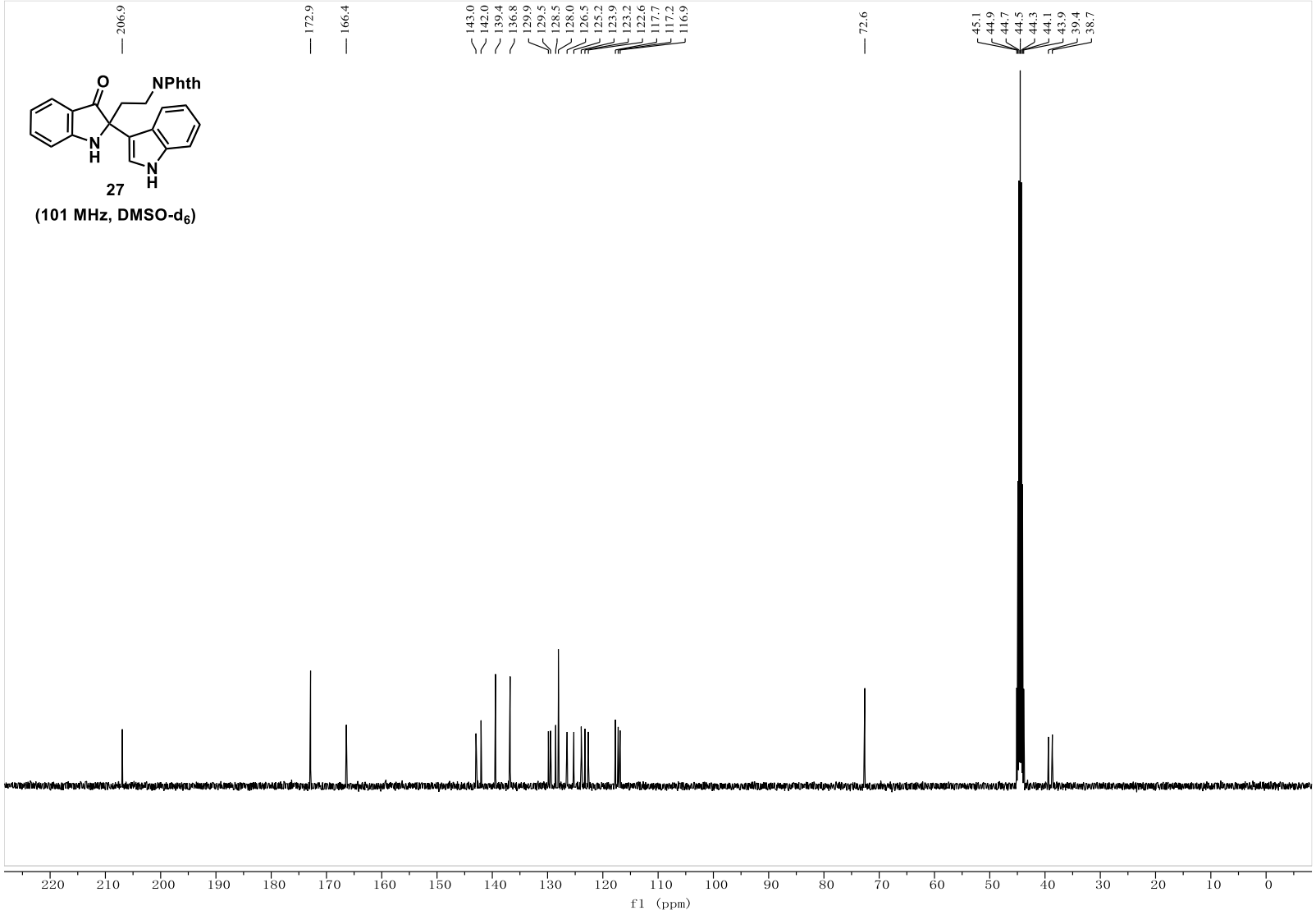

7.782
7.775
7.771
7.762
7.754
7.748
7.740
7.731
7.728
7.678
7.675
7.665
7.657
7.651
7.644
7.634
7.631
7.552
7.533
7.414
7.410
7.396
7.393
7.390
7.382
7.376
7.372
7.361
6.815
6.794
6.742
6.723
6.705
6.460
6.454
6.388
6.382
6.367
6.360
3.861
3.780
3.763
3.759
3.745
3.736
3.725
3.709
3.681
3.663
3.659
3.646
3.641
3.627
3.607
2.579
2.563
2.558
2.545
2.542
2.530
2.523
2.520
2.508
2.503
2.487
2.469
O
NPhth
N
H
MeO
OMe
25
(400 MHz, CDCl3)
1.96
2.04
0.98
2.02
1.00
1.02
0.99
1.02
3.13
4.17
1.06
2.10
f1 (ppm)

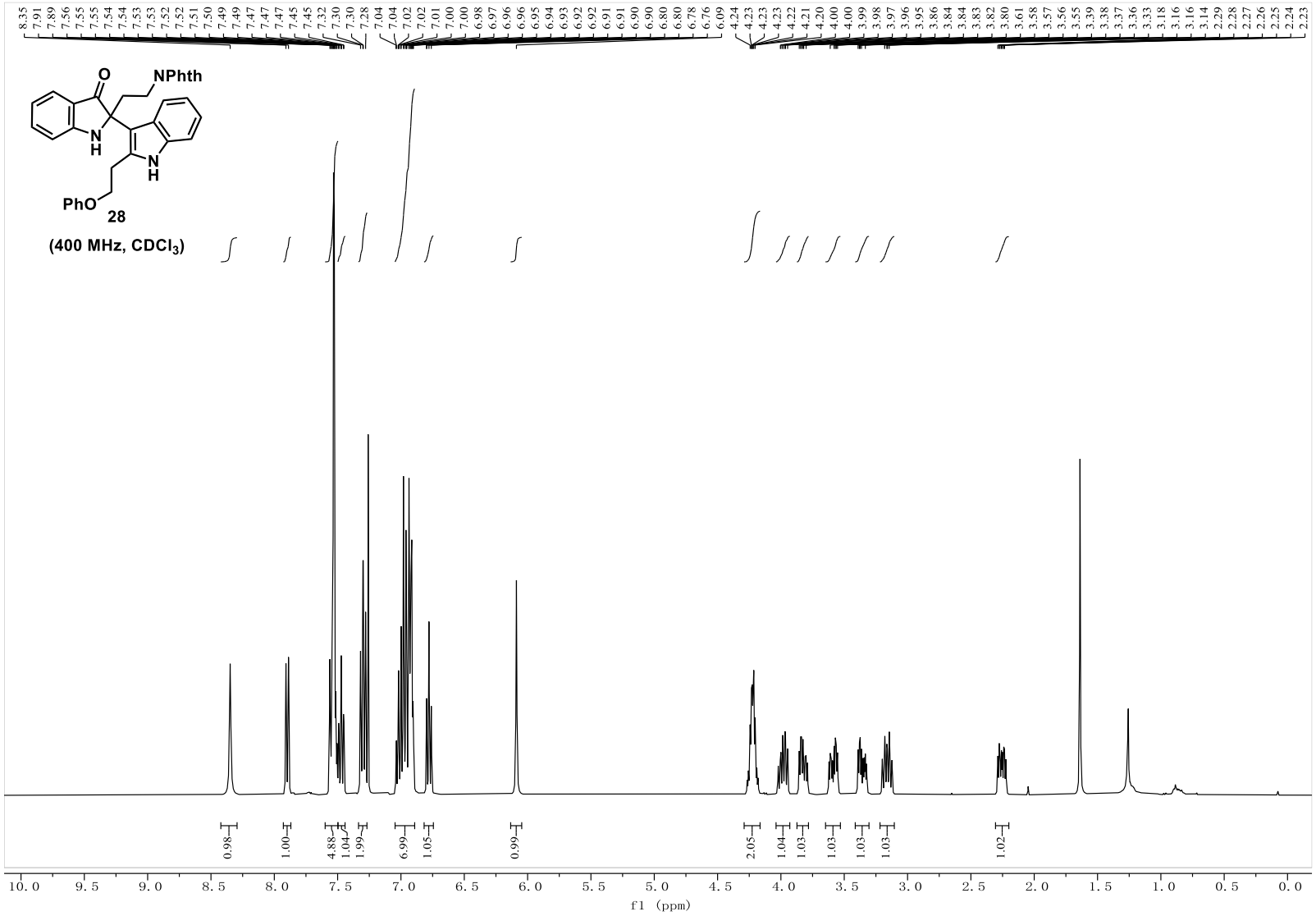

201.6
168.1
160.5
160.4
158.9
137.4
133.8
132.3
128.2
124.8
123.1
120.6
119.1
118.5
112.4
104.1
100.1
77.5
77.2
76.9
69.6
55.7
55.5
35.2
33.8
O
NPhth
N
H
MeO
OMe
25
(101 MHz, CDCl3)
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

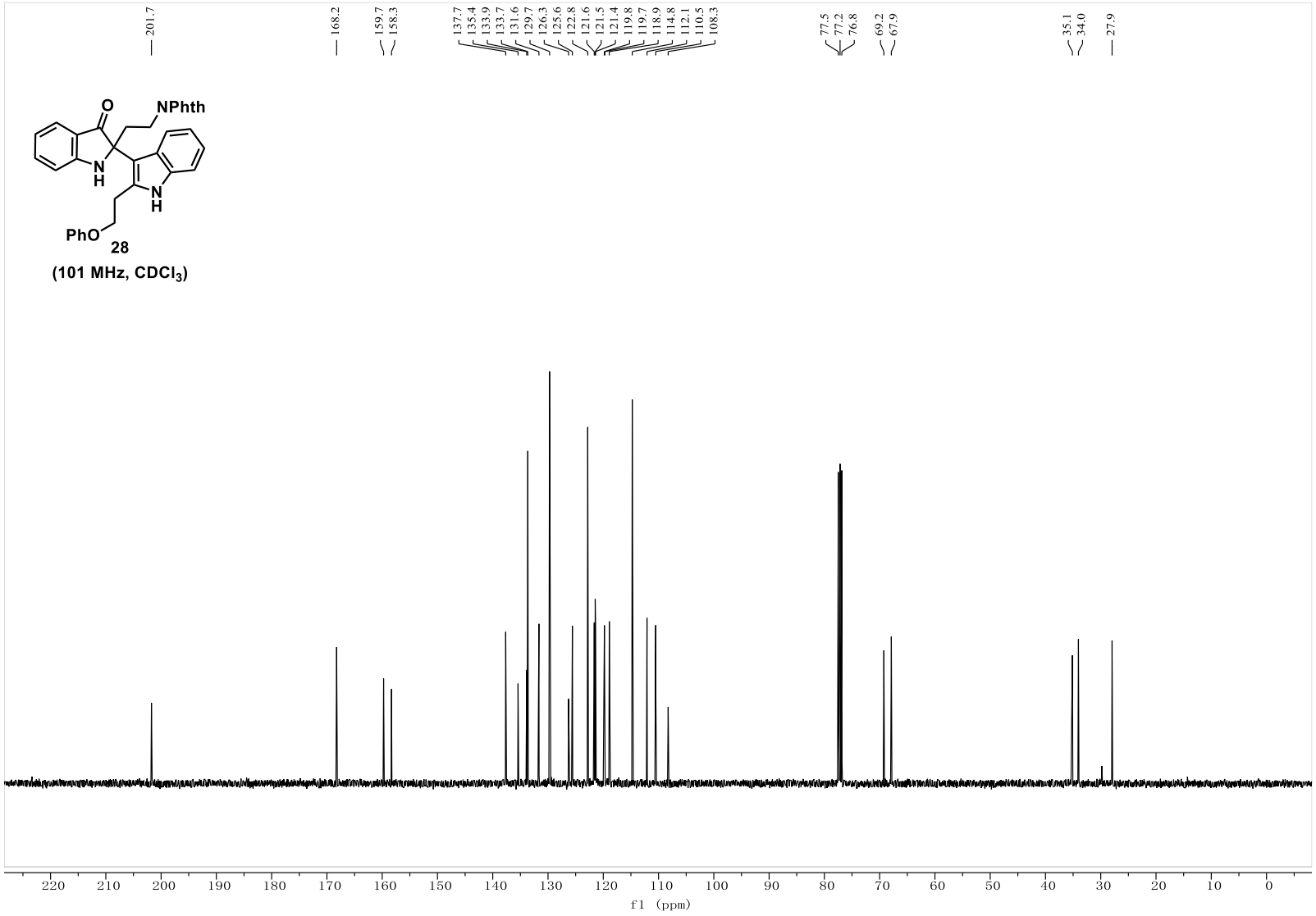

9.74
7.88
7.87
7.87
7.87
7.86
7.83
7.83
7.82
7.81
7.52
7.52
7.51
7.51
7.50
7.50
7.49
7.49
7.48
7.48
7.03
7.01
6.87
6.86
6.85
6.83
6.83
5.70
5.69
5.67
4.51
4.49
O
N
H
NPhth
26
(400 MHz, DMSO-d_6)
0.98
2.01
2.00
2.10
0.98
1.08
0.91
2.00
f1 (ppm)

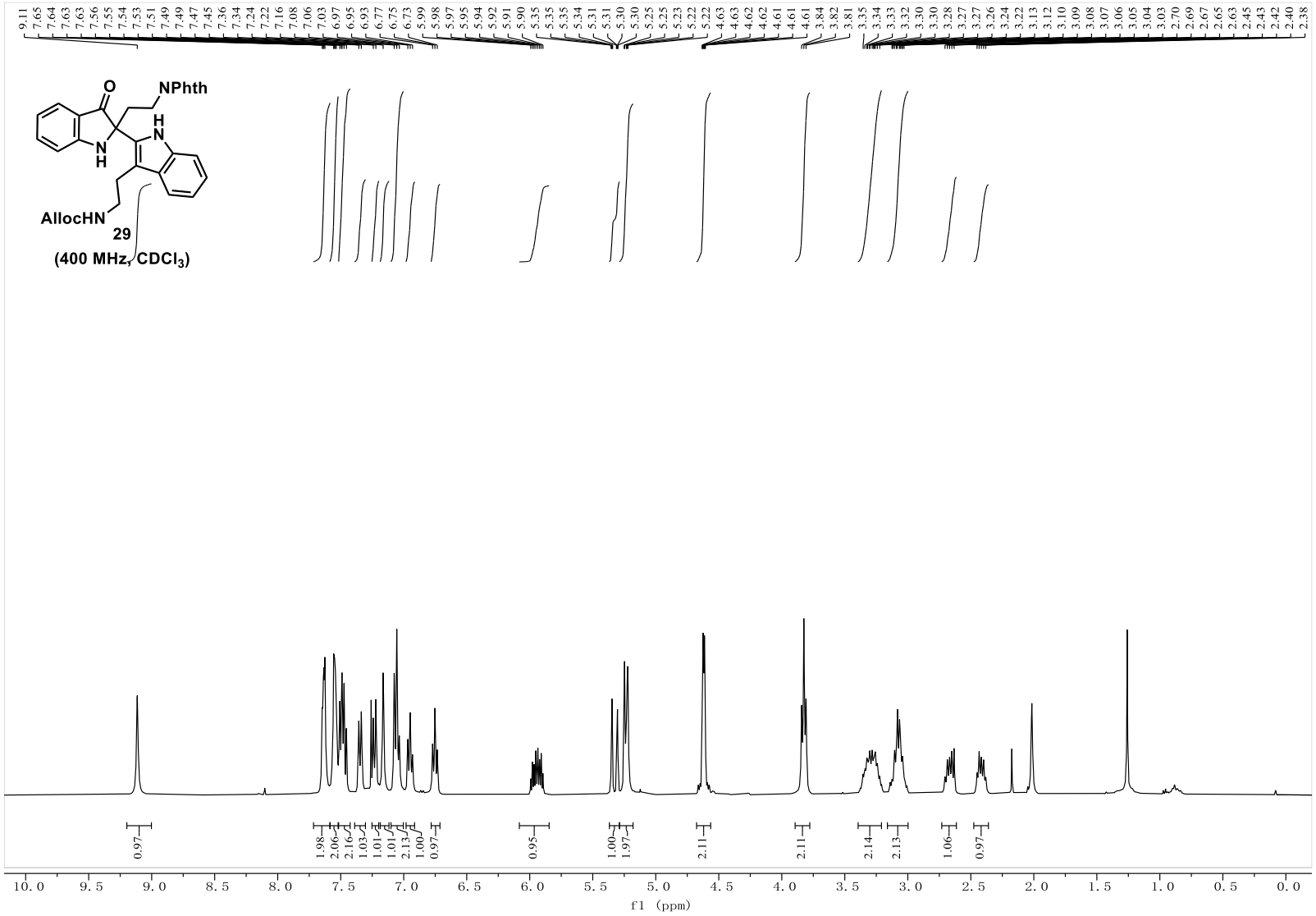

185.8
168.0
154.5
137.6
137.4
134.9
132.3
124.8
123.6
120.6
119.7
112.3
107.1
35.0
O
N
H
NPhth
26
(151 MHz, DMSO-d_6)
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

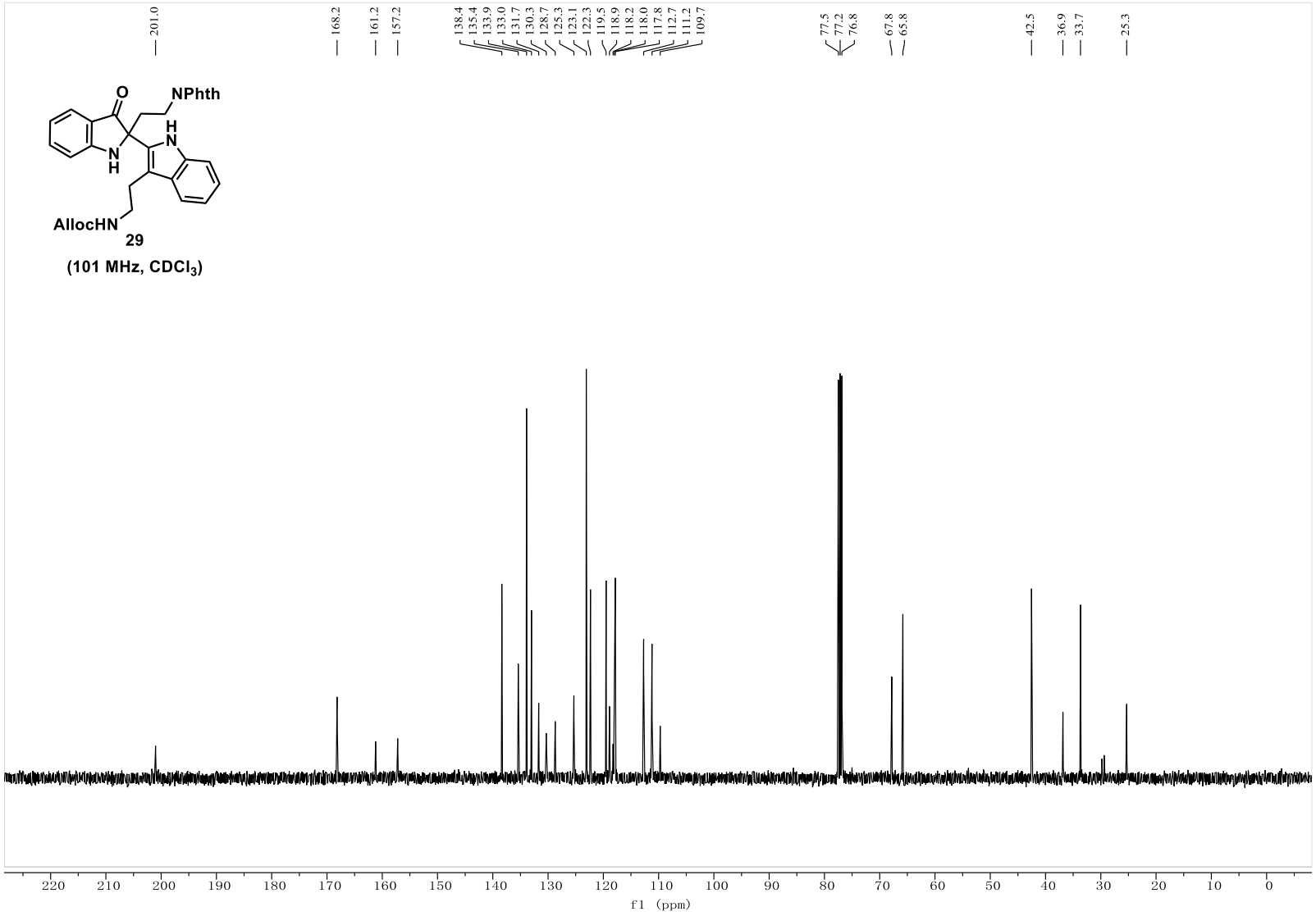

11.08
11.07
8.00
7.80
7.55
7.54
7.53
7.53
7.52
7.51
7.50
7.40
7.40
7.38
7.36
7.36
7.32
7.32
7.32
7.30
7.30
7.30
7.04
7.03
7.02
7.02
7.01
7.01
7.00
7.00
6.99
6.99
6.99
6.88
6.88
6.87
6.86
6.86
6.84
6.84
6.74
6.73
6.72
6.72
6.71
6.70
6.70
3.71
3.70
3.69
3.68
3.67
3.66
3.65
3.65
3.64
3.63
3.62
3.61
3.60
3.60
3.59
3.57
2.59
2.57
2.56
2.55
2.55
2.54
2.53
2.44
2.42
2.41
2.40
2.40
2.39
2.38
2.36
O
NPhth
N
H
N
H
27
(400 MHz, DMSO-d6)
1.04
1.01
3.93
1.02
2.94
1.01
1.99
1.00
1.00
2.06
0.95
1.01
12.0 11.5 11.0 10.5 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
f1 (ppm)

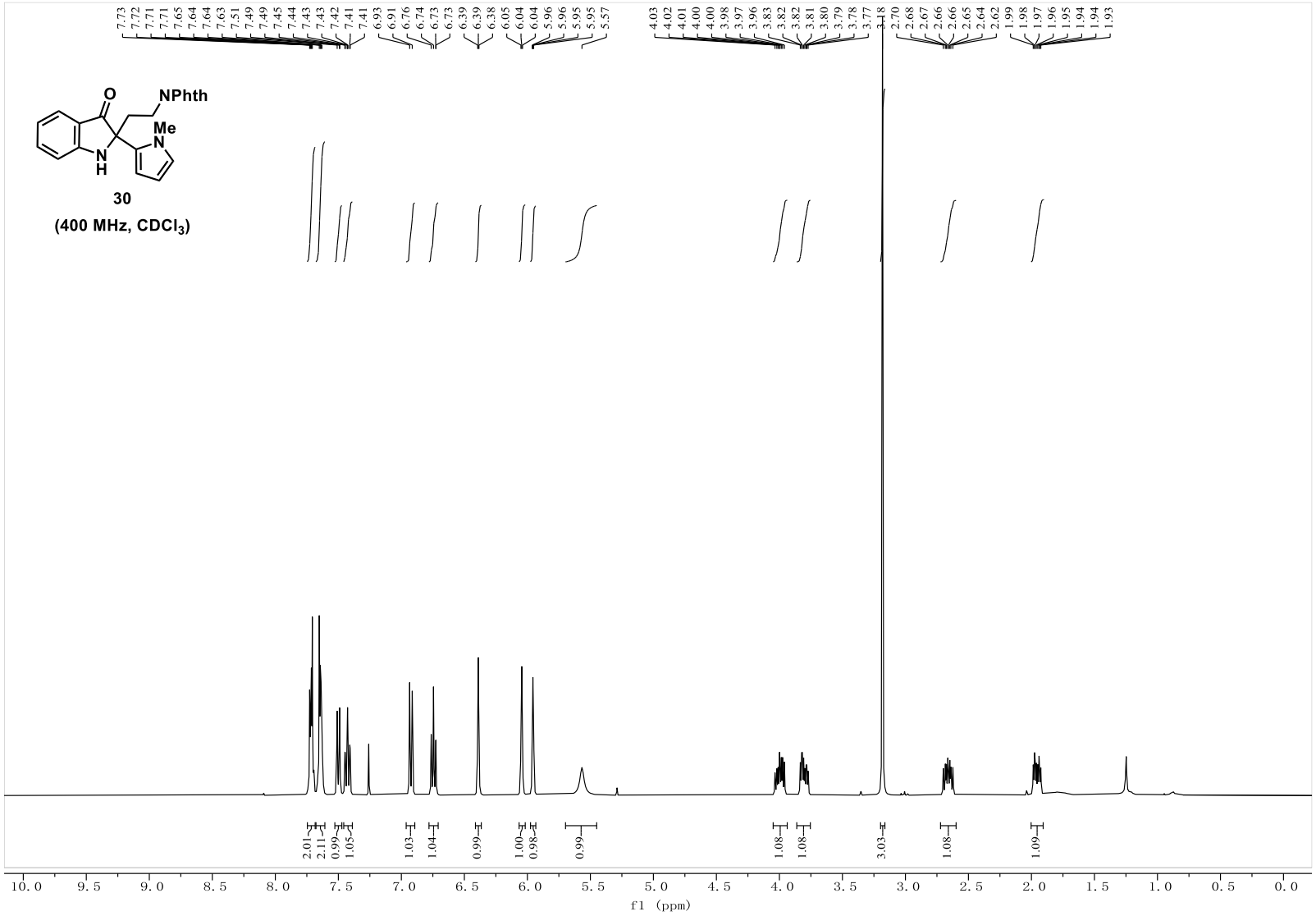

206.9
172.9
166.4
143.0
142.0
139.4
136.8
129.9
129.5
128.5
128.0
126.5
125.2
123.9
123.2
122.6
117.7
117.2
116.9
72.6
45.1
44.9
44.7
44.5
44.3
44.1
43.9
39.4
38.7
O
NPhth
N
H
N
H
27
(101 MHz, DMSO-d6)
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

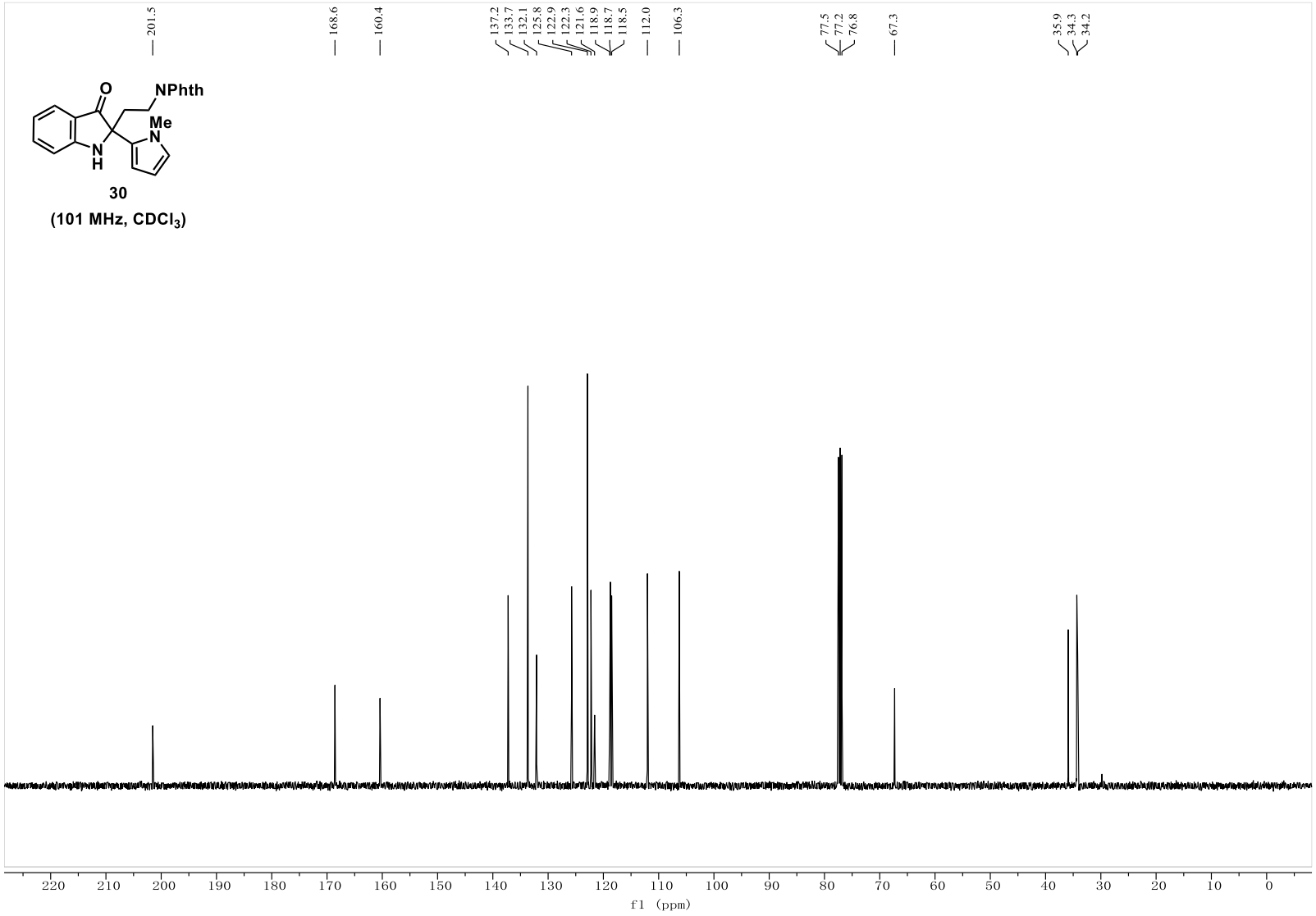

O
NPhth
N
H
N
H
PhO
28
(400 MHz, CDCl3)
f1 (ppm)

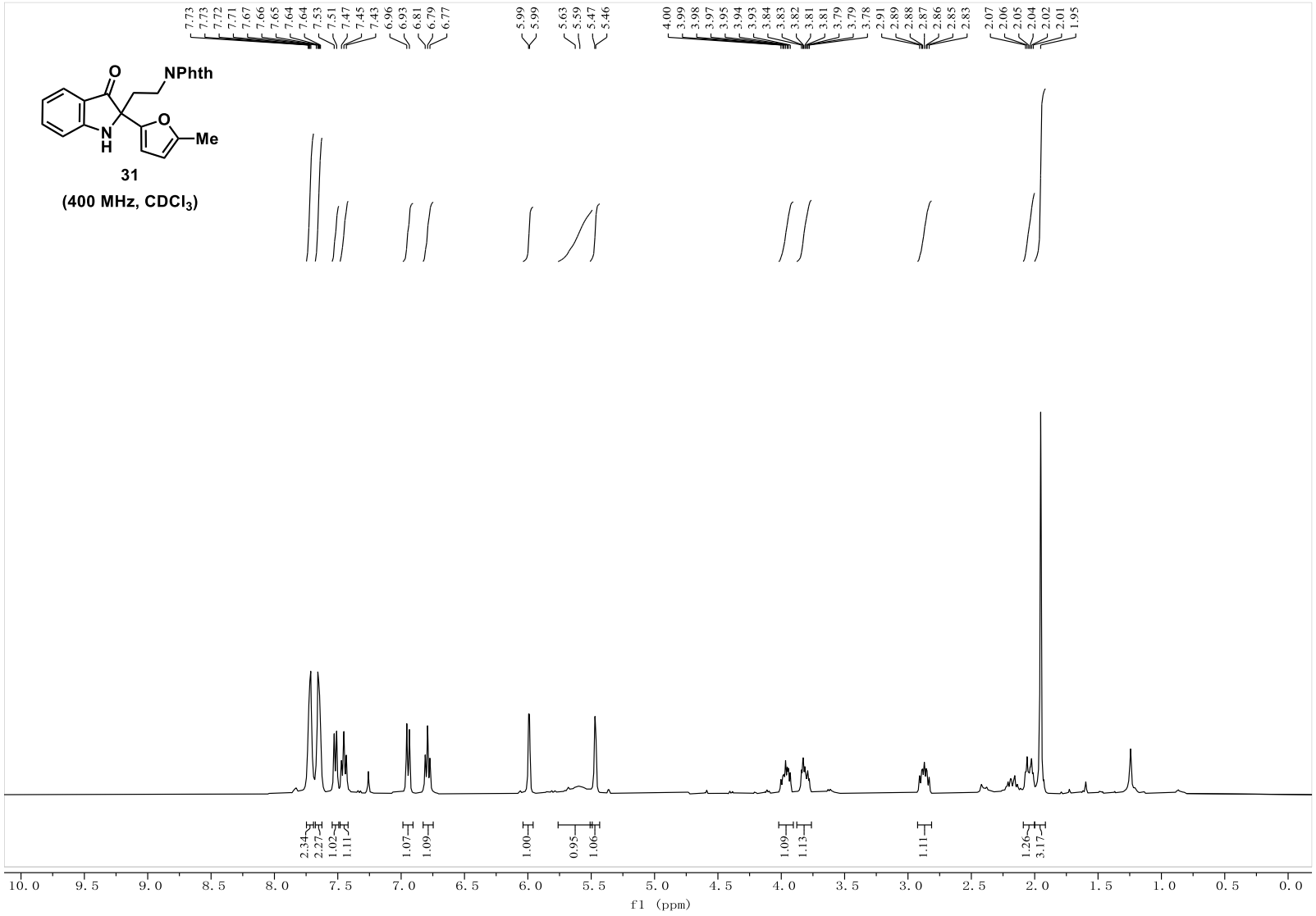

201.7
168.2
159.7
158.3
137.7
135.4
133.9
133.7
131.6
129.7
126.3
125.6
122.8
121.6
121.5
121.4
119.8
119.7
118.9
114.8
112.1
110.5
108.3
77.5
77.2
76.8
69.2
67.9
35.1
34.0
27.9
O
NPhth
N
H
N
H
PhO
28
(101 MHz, CDCl3)
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

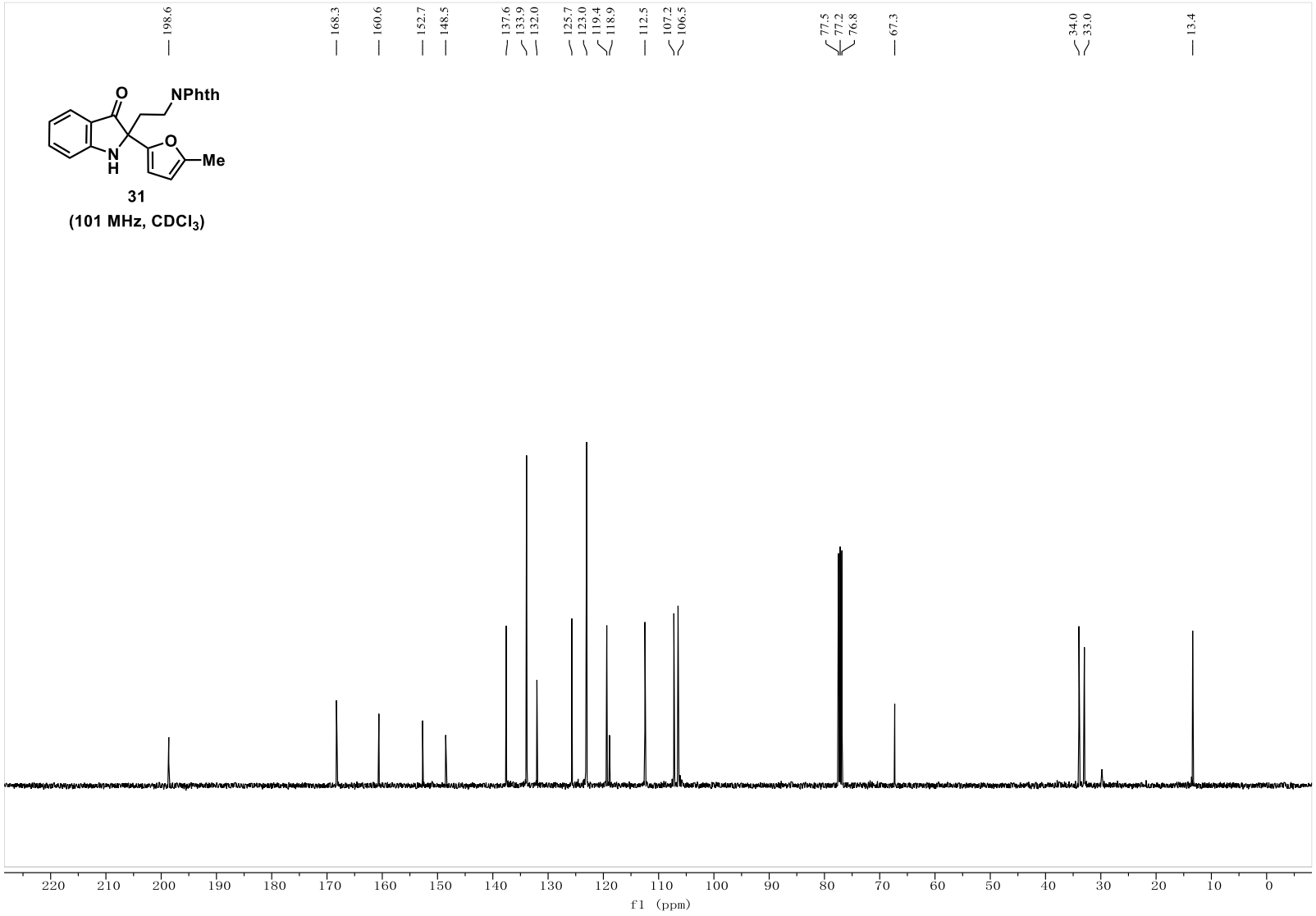

NPhth
AllocHN
29
(400 MHz, CDCl3)
f1 (ppm)

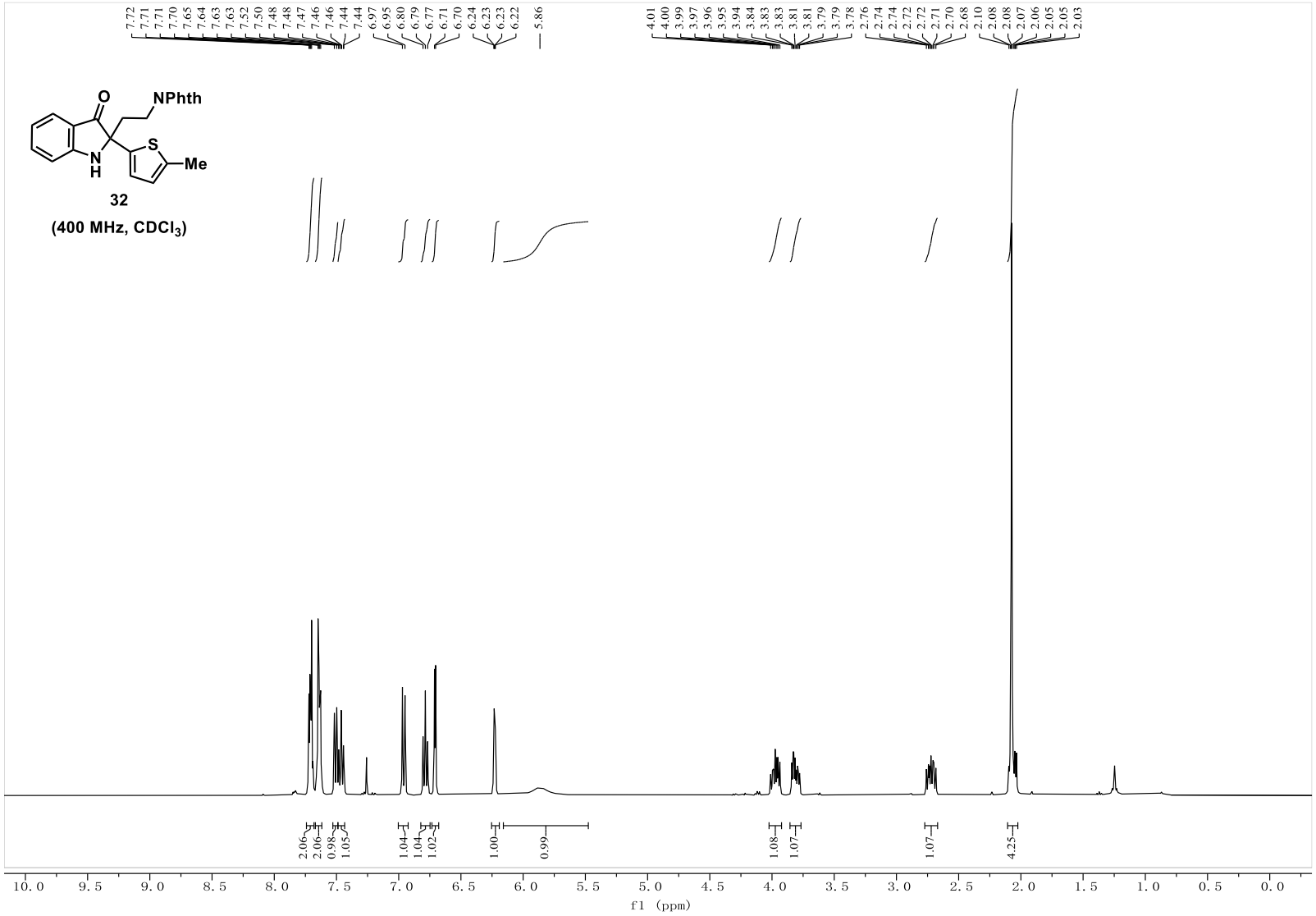

201.0
168.2
161.2
157.2
138.4
135.4
133.9
133.0
131.7
130.3
128.7
125.3
123.1
122.3
119.5
118.9
118.2
118.0
117.8
112.7
111.2
109.7
77.5
77.2
76.8
67.8
65.8
42.5
36.9
33.7
25.3
O
NPhth
H
N
N
H
AllocHN
29
(101 MHz, CDCl3)
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

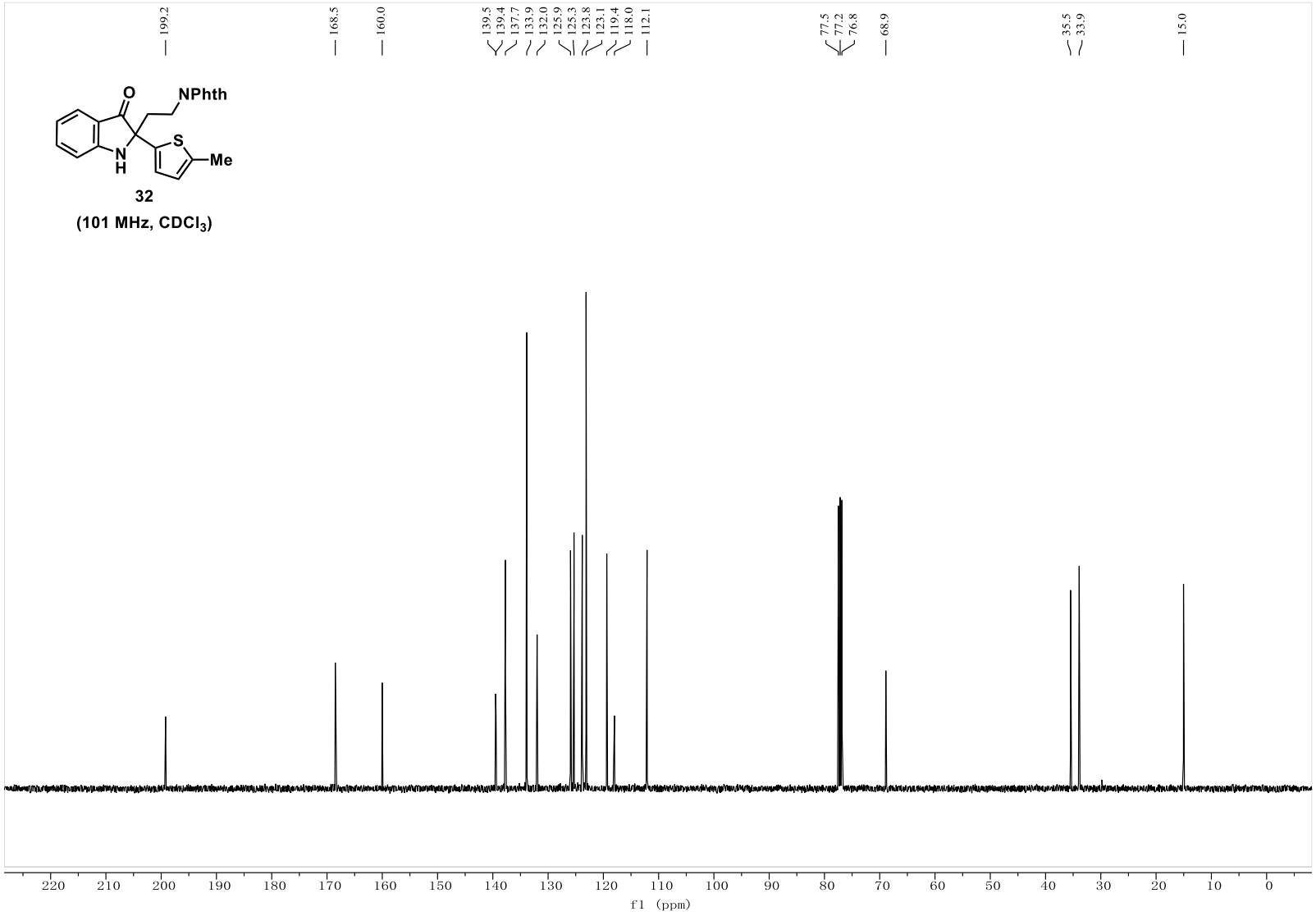

7.73 7.72 7.71 7.71 7.65 7.64 7.64 7.63 7.51 7.49 7.49 7.45 7.44 7.43 7.43 7.42 7.41 7.41
6.93 6.91 6.76 6.74 6.73 6.73 6.39 6.39 6.38 6.05 6.04 6.04 5.96 5.96 5.95 5.95 5.57
4.03 4.02 4.01 4.00 4.00 3.98 3.97 3.96 3.83 3.82 3.82 3.81 3.80 3.79 3.78 3.77 3.18
2.70 2.68 2.67 2.66 2.66 2.65 2.64 2.62 1.99 1.98 1.97 1.96 1.95 1.94 1.94 1.93
O
NPhth
Me
N
N
H
30
(400 MHz, CDCl3)
2.01 2.11 0.99 1.05 1.03 1.04 0.99 1.00 0.98 0.99 1.08 1.08 3.03 1.08 1.09
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
f1 (ppm)

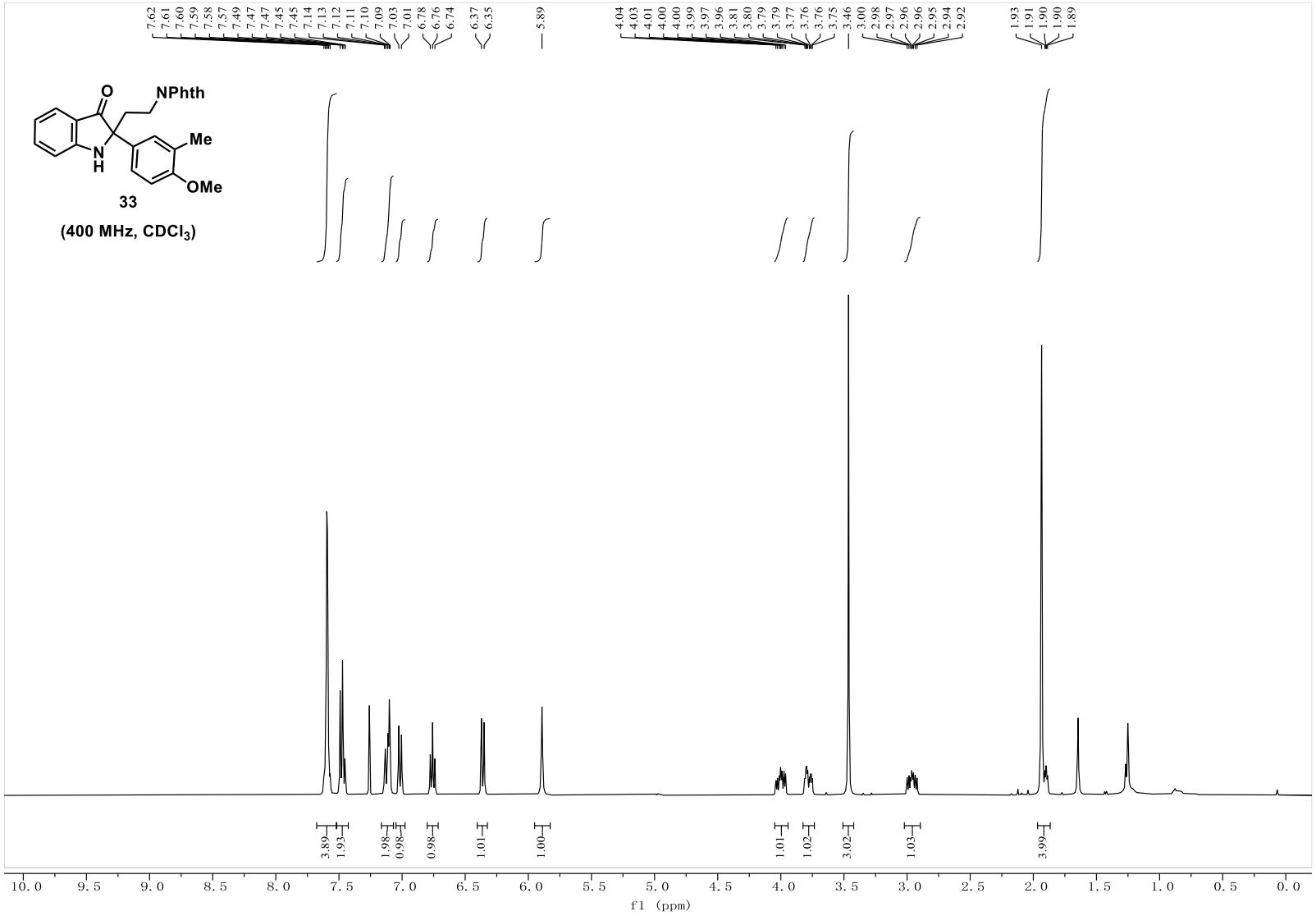

201.5
168.6
160.4
137.2
133.7
132.1
125.8
122.9
122.3
121.6
118.9
118.7
118.5
112.0
106.3
77.5
77.2
76.8
67.3
35.9
34.3
34.2
O
NPhth
Me
N
N
H
30
(101 MHz, CDCl3)
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

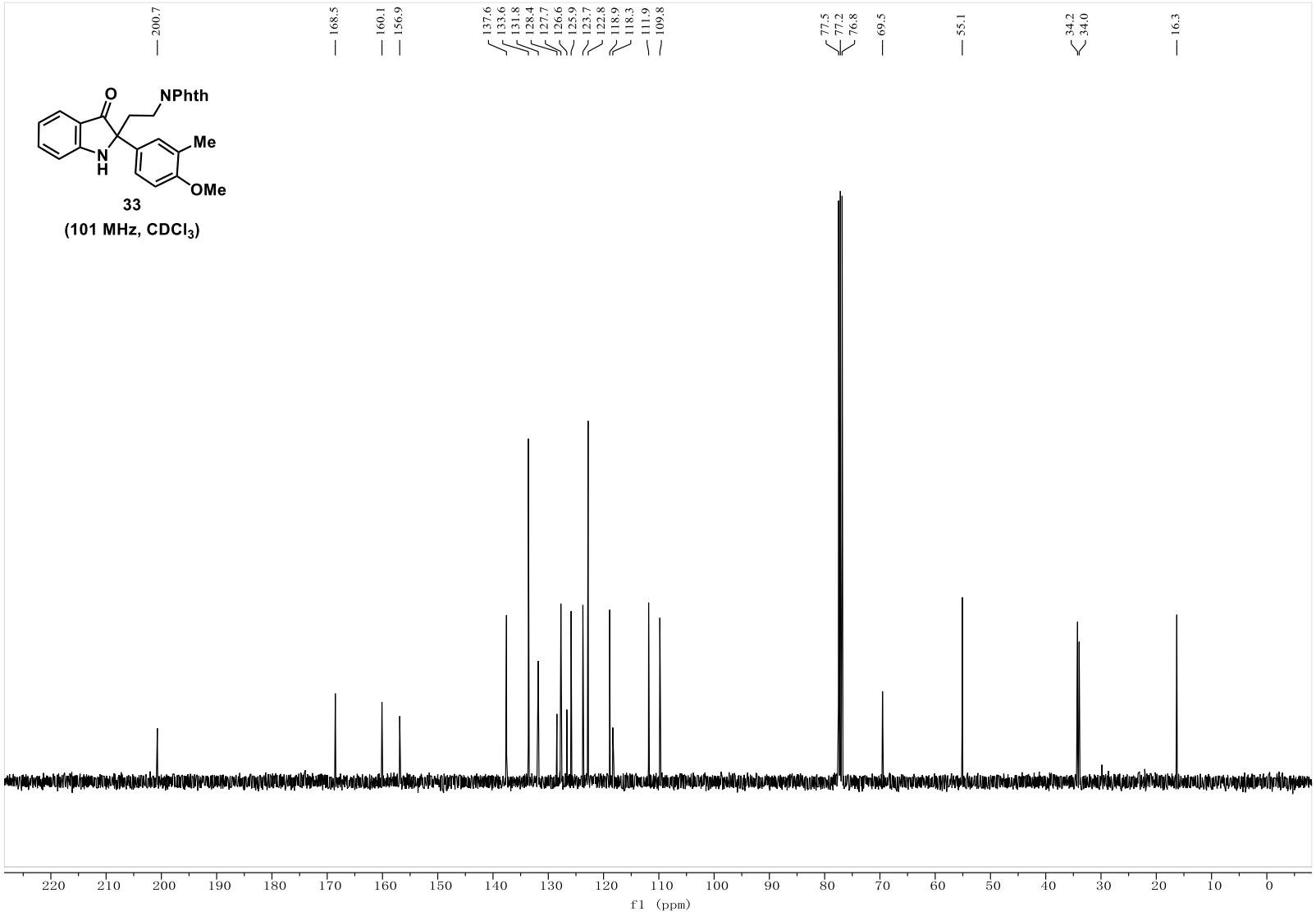

7.73
7.73
7.72
7.71
7.67
7.66
7.65
7.64
7.64
7.53
7.51
7.47
7.45
7.43
6.96
6.93
6.81
6.79
6.77
5.99
5.99
5.63
5.59
5.47
5.46
4.00
3.99
3.98
3.97
3.95
3.94
3.93
3.84
3.83
3.82
3.81
3.81
3.79
3.79
3.78
2.91
2.89
2.88
2.87
2.86
2.85
2.83
2.07
2.06
2.05
2.04
2.02
2.01
1.95
O
NPhth
O
N
H
Me
31
(400 MHz, CDCl3)
2.34
2.27
1.02
1.11
1.07
1.09
1.00
0.95
1.06
1.09
1.13
1.11
1.26
3.17
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
f1 (ppm)

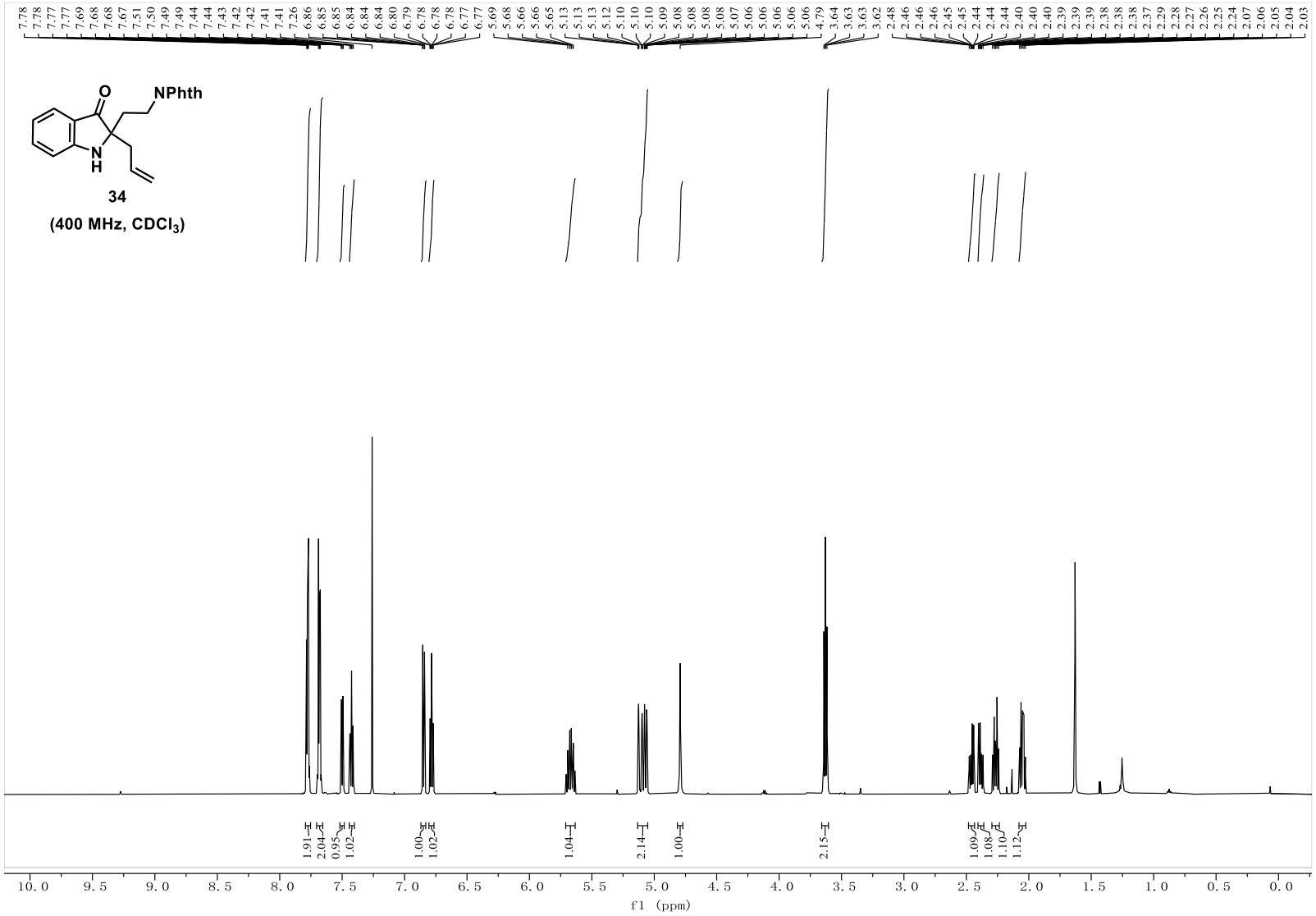

198.6
168.3
160.6
152.7
148.5
137.6
133.9
132.0
125.7
123.0
119.4
118.9
112.5
107.2
106.5
77.5
77.2
76.8
67.3
34.0
33.0
13.4
O
NPhth
O
N
H
Me
31
(101 MHz, CDCl3)
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

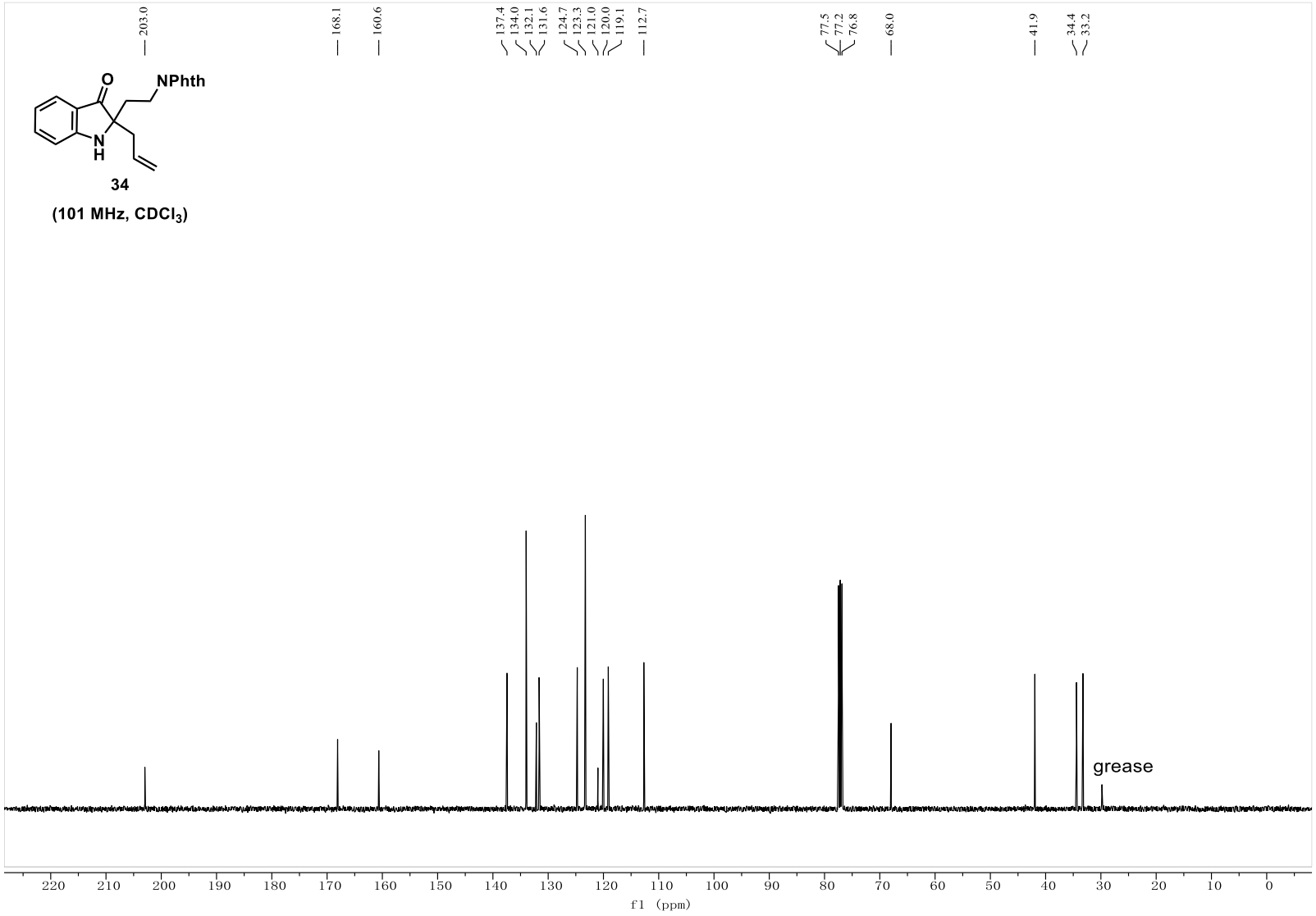

7.72 7.71 7.71 7.70 7.65 7.64 7.63 7.63 7.52 7.50 7.48 7.48 7.47 7.46 7.46 7.44 7.44
6.97 6.95 6.80 6.79 6.77 6.71 6.70 6.24 6.23 6.23 6.22 5.86
4.01 4.00 3.99 3.97 3.96 3.95 3.94 3.84 3.83 3.83 3.81 3.81 3.79 3.79 3.78
2.76 2.74 2.74 2.72 2.72 2.71 2.70 2.68 2.10 2.08 2.08 2.07 2.06 2.05 2.05 2.03
O
NPhth
S
N
H
Me
32
(400 MHz, CDCl3)
2.06 2.06 0.98 1.05 1.04 1.04 1.02 1.00 0.99 1.08 1.07 1.07 4.25
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
f1 (ppm)

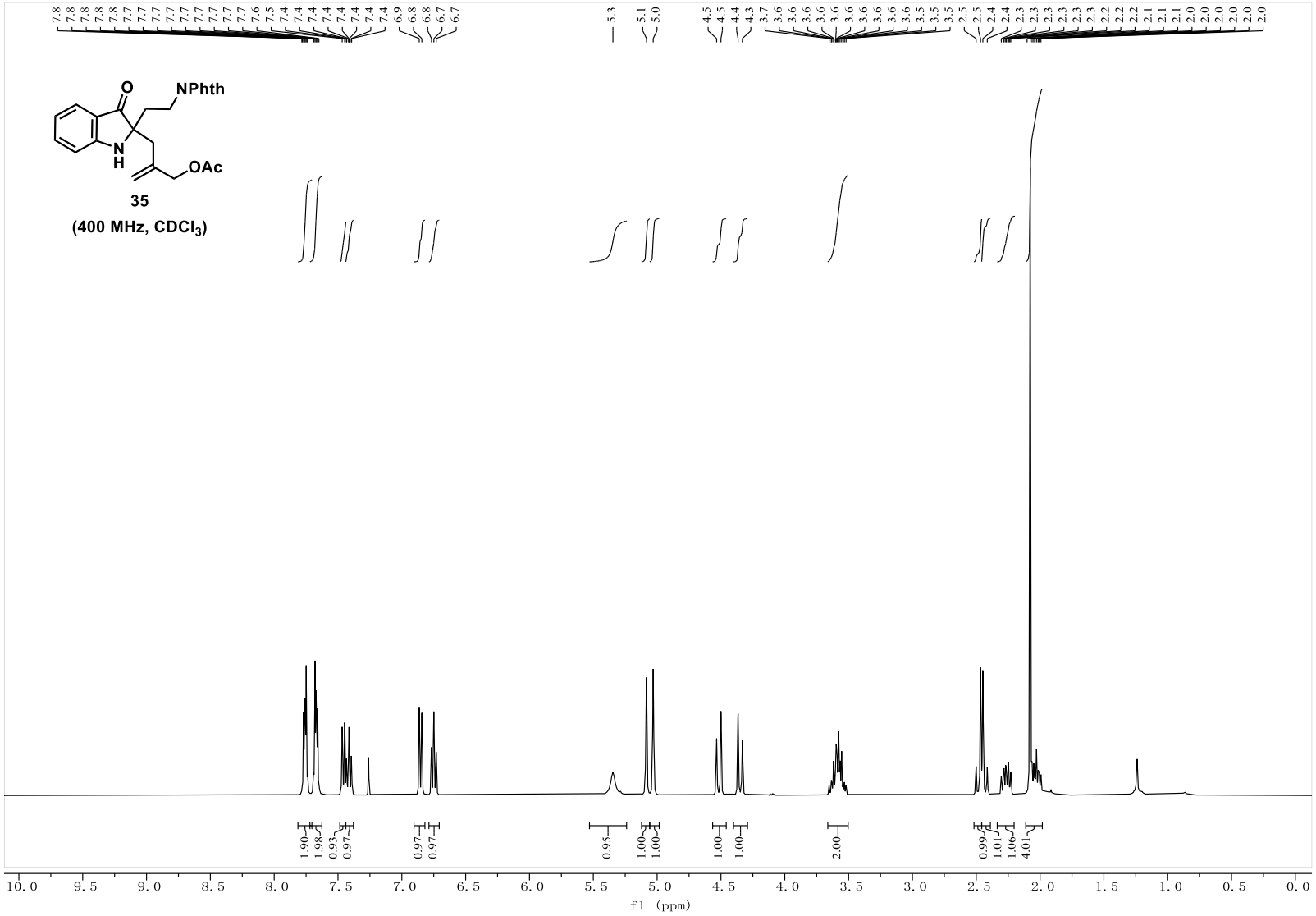

199.2
168.5
160.0
139.5
139.4
137.7
133.9
132.0
125.9
125.3
123.8
123.1
119.4
118.0
112.1
77.5
77.2
76.8
68.9
35.5
33.9
15.0
O
NPhth
N
H
S
Me
32
(101 MHz, CDCl3)
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

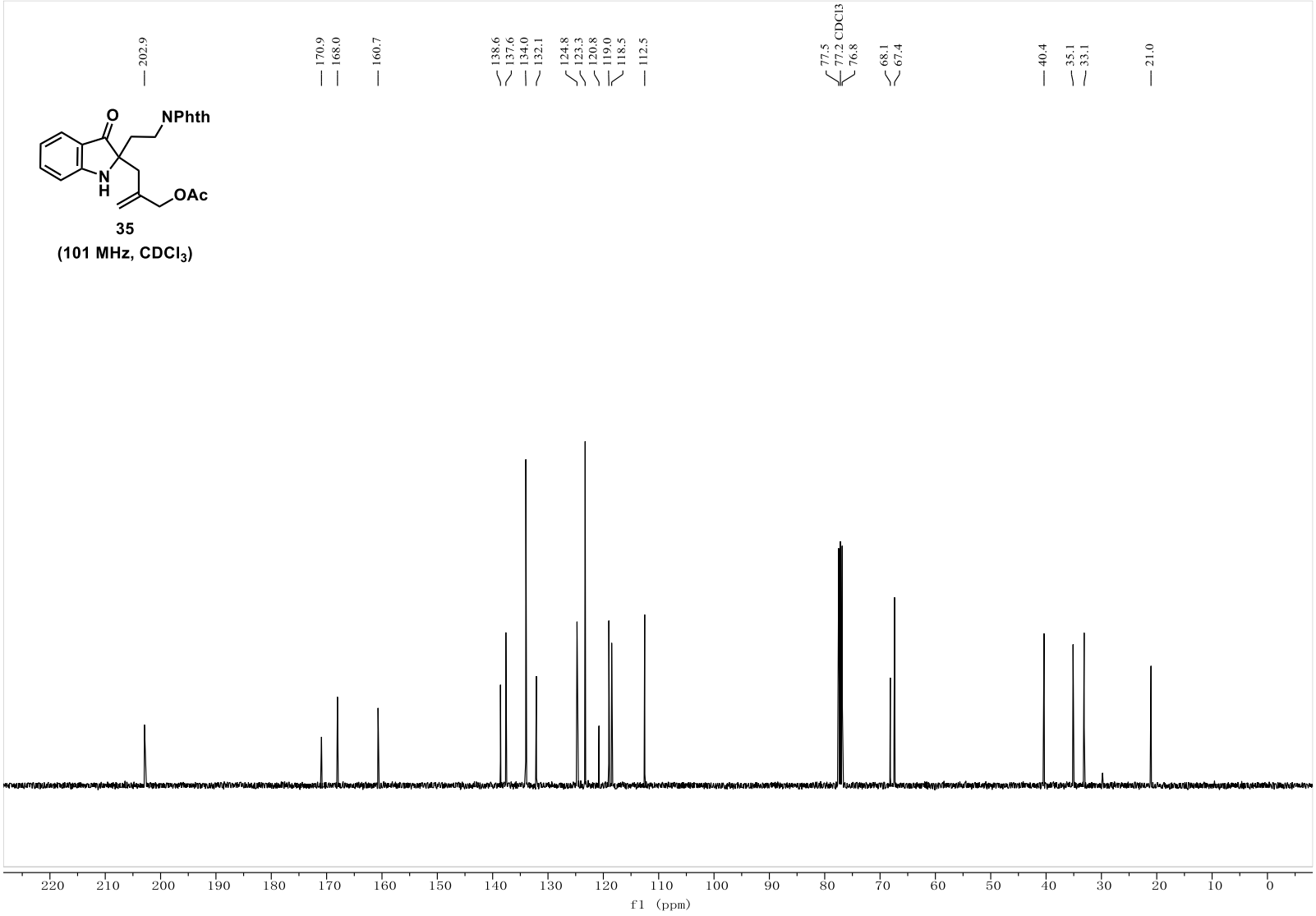

7.62
7.61
7.60
7.59
7.58
7.57
7.49
7.47
7.47
7.45
7.45
7.14
7.13
7.12
7.11
7.10
7.09
7.03
7.01
6.78
6.76
6.74
6.37
6.35
5.89
4.04
4.03
4.01
4.00
4.00
3.99
3.97
3.96
3.81
3.80
3.79
3.79
3.77
3.76
3.76
3.75
3.46
3.00
2.98
2.97
2.96
2.96
2.95
2.94
2.92
1.93
1.91
1.90
1.90
1.89
O
NPhth
Me
N
H
OMe
33
(400 MHz, CDCl3)
3.89
1.93
1.98
0.98
0.98
1.01
1.00
1.01
1.02
3.02
1.03
3.99
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
f1 (ppm)

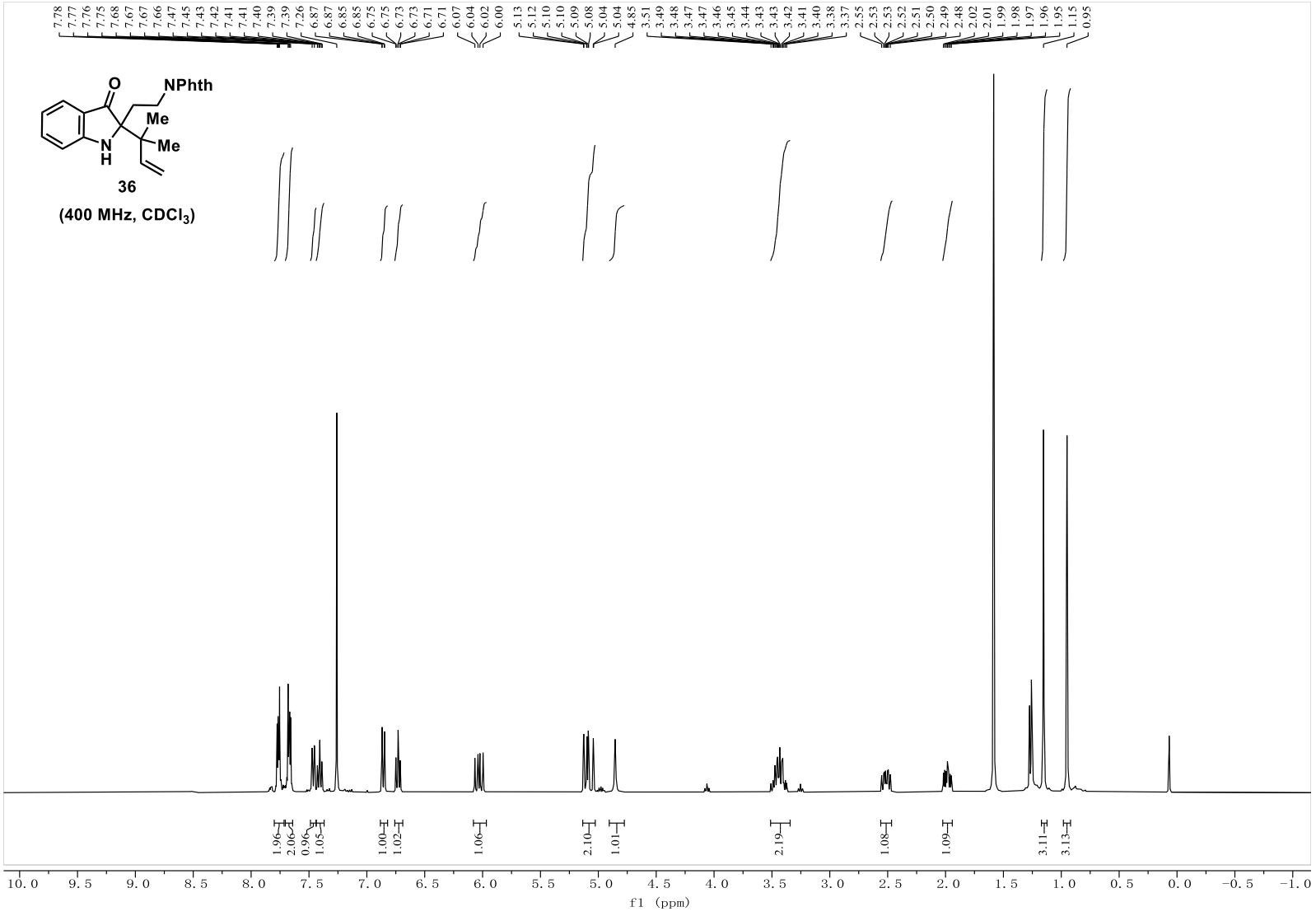

200.7
168.5
160.1
156.9
137.6
133.6
131.8
128.4
127.7
126.6
125.9
123.7
122.8
118.9
118.3
111.9
109.8
77.5
77.2
76.8
69.5
55.1
34.2
34.0
16.3
O
NPhth
Me
N
H
OMe
33
(101 MHz, CDCl3)
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

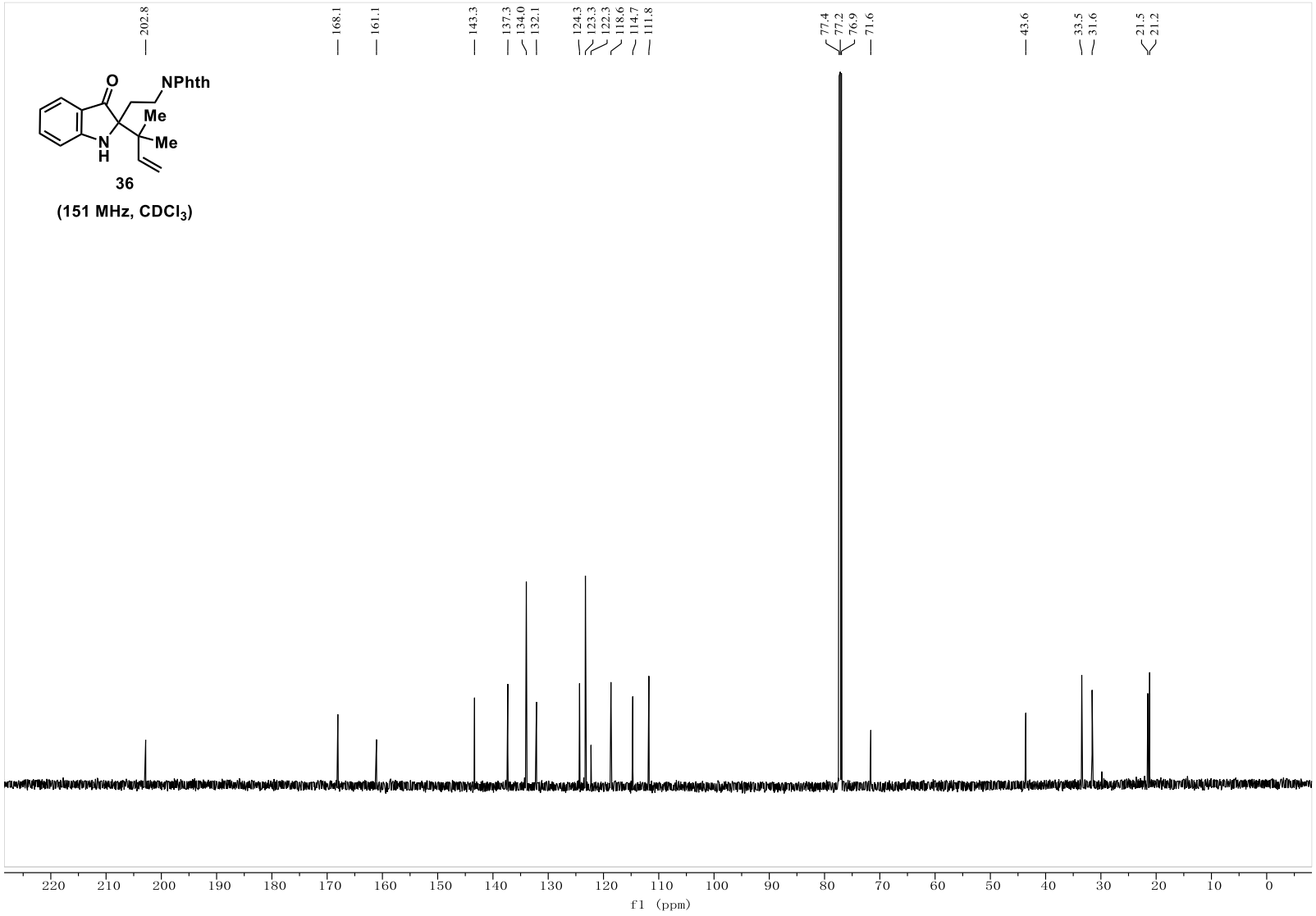

NPhth
O
N
H
34
(400 MHz, CDCl3)
f1 (ppm)

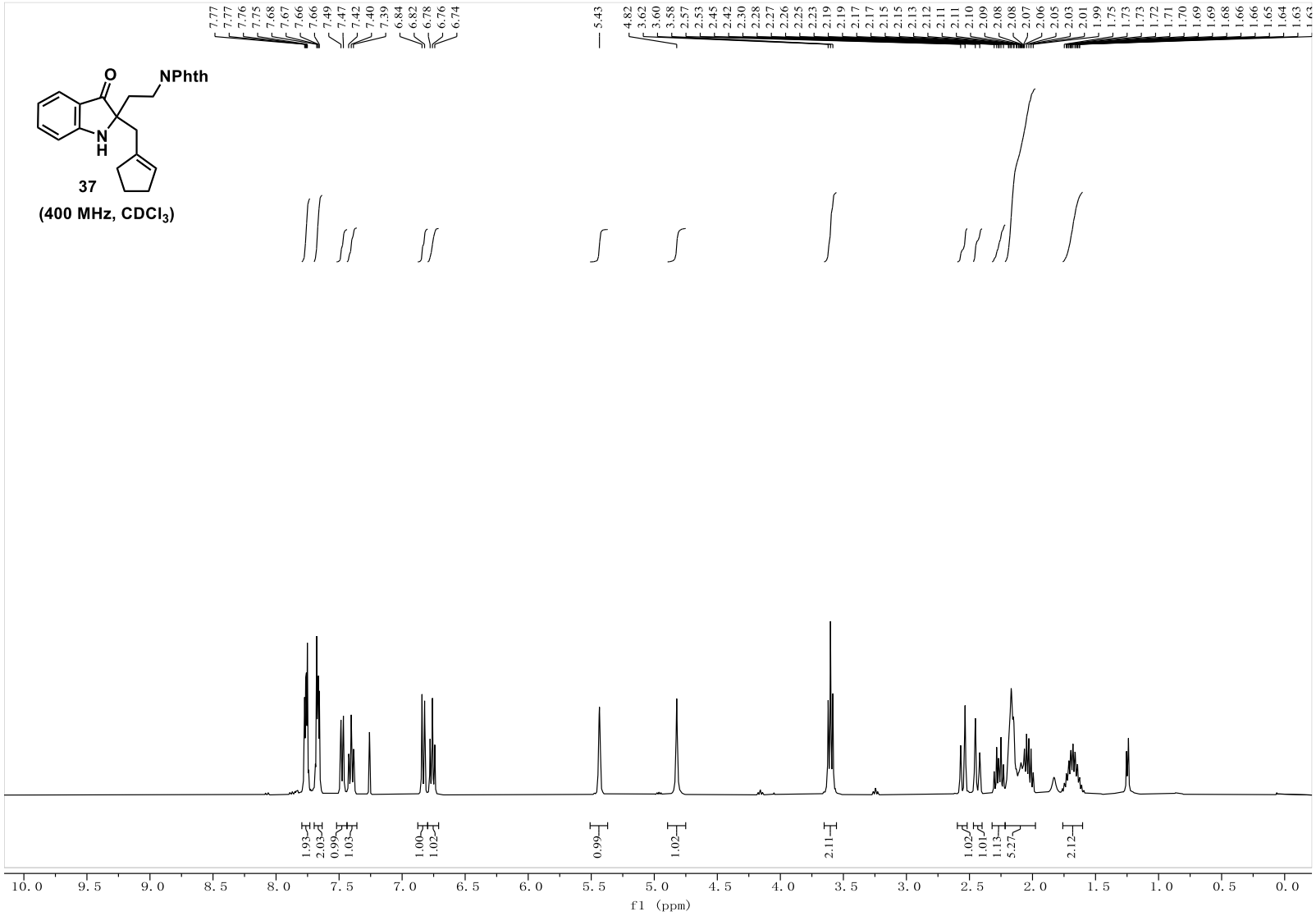

203.0
168.1
160.6
137.4
134.0
132.1
131.6
124.7
123.3
121.0
120.0
119.1
112.7
77.5
77.2
76.8
68.0
41.9
34.4
33.2
O
NPhth
N
H
34
(101 MHz, CDCl3)
grease
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

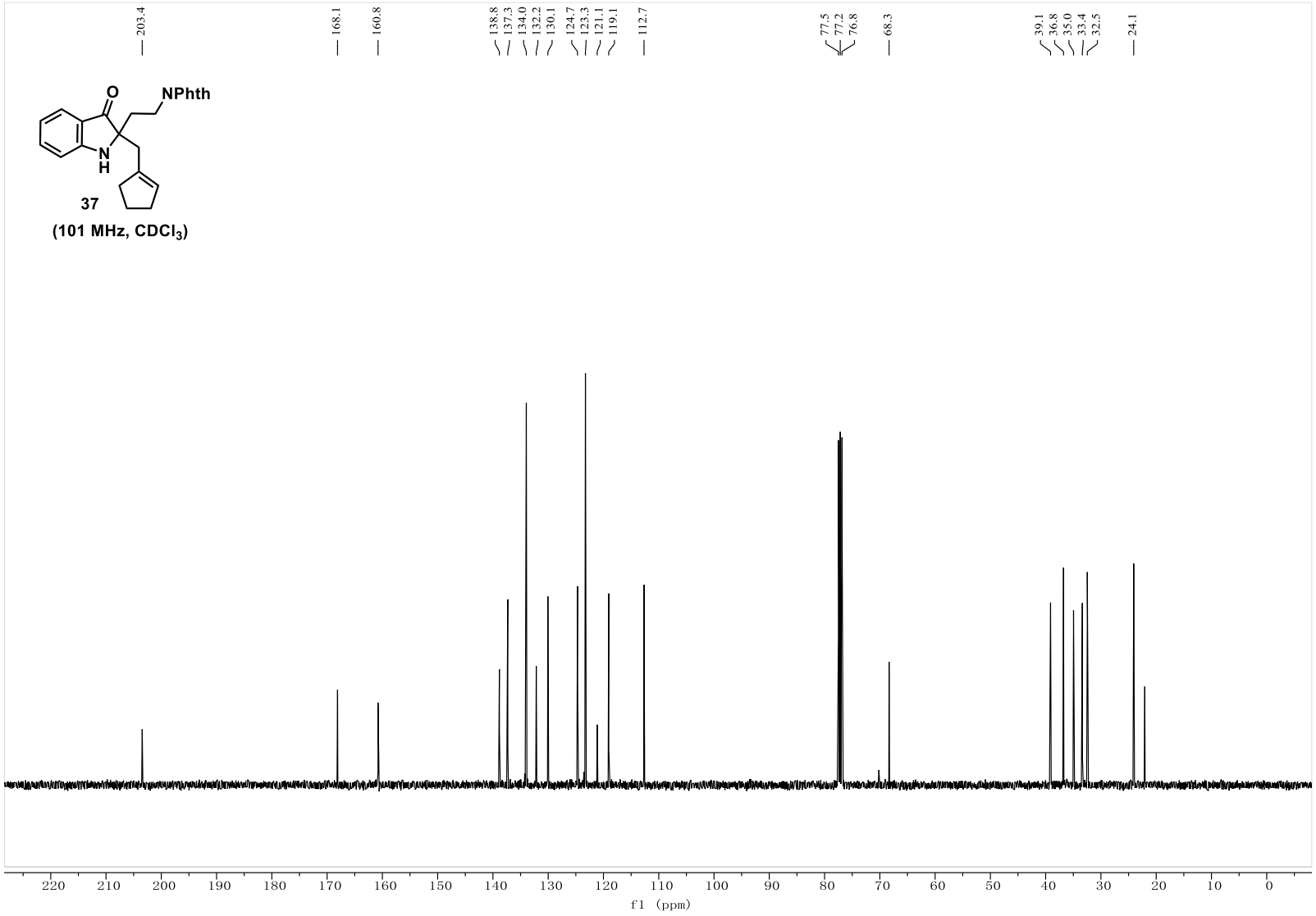

O
NPhth
N
H
OAc
35
(400 MHz, CDCl3)
f1 (ppm)

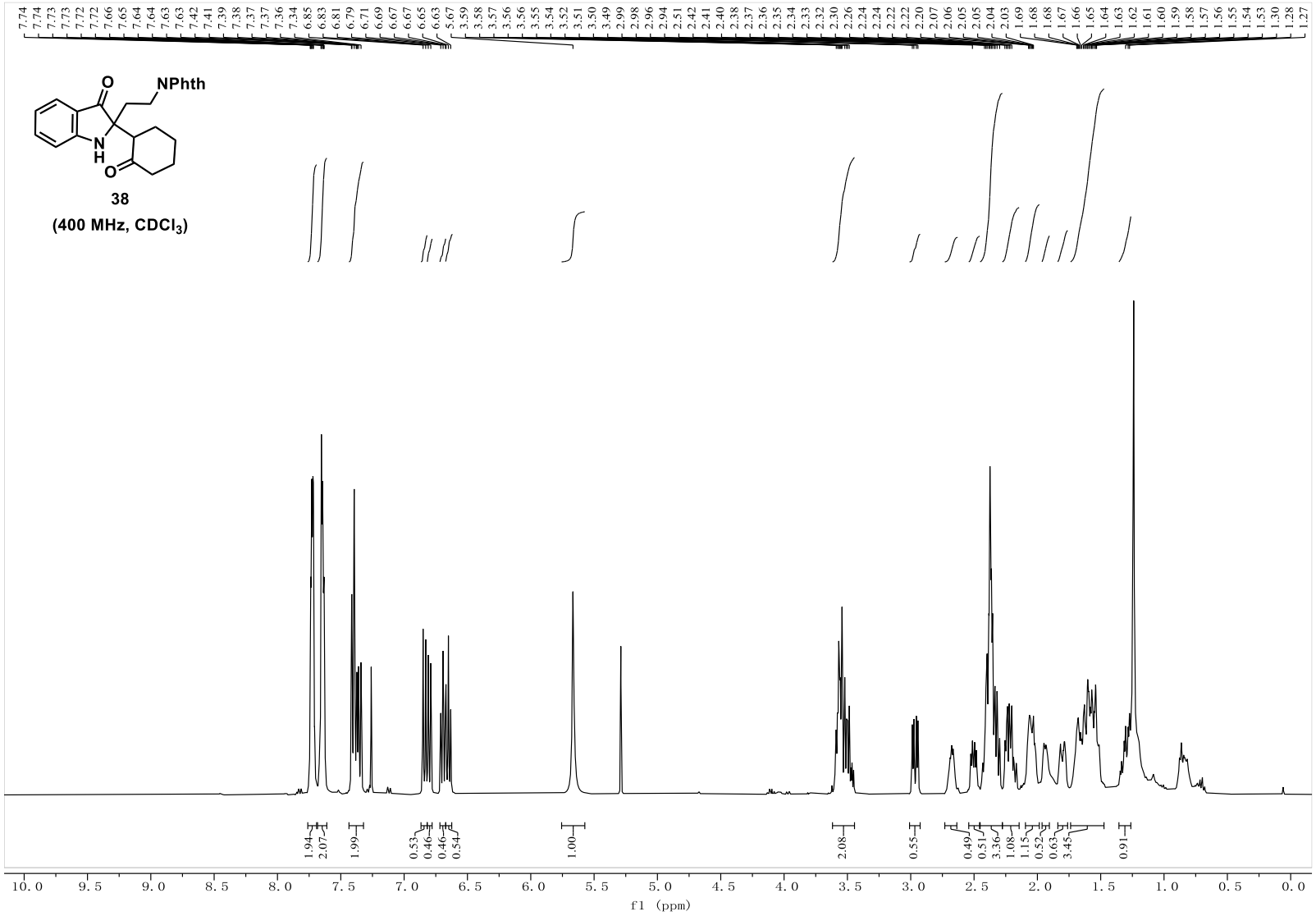

202.9
170.9
168.0
160.7
138.6
137.6
134.0
132.1
124.8
123.3
120.8
119.0
118.5
112.5
77.5
77.2 CDCl3
76.8
68.1
67.4
40.4
35.1
33.1
21.0
O
NPhth
N
H
OAc
35
(101 MHz, CDCl3)
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

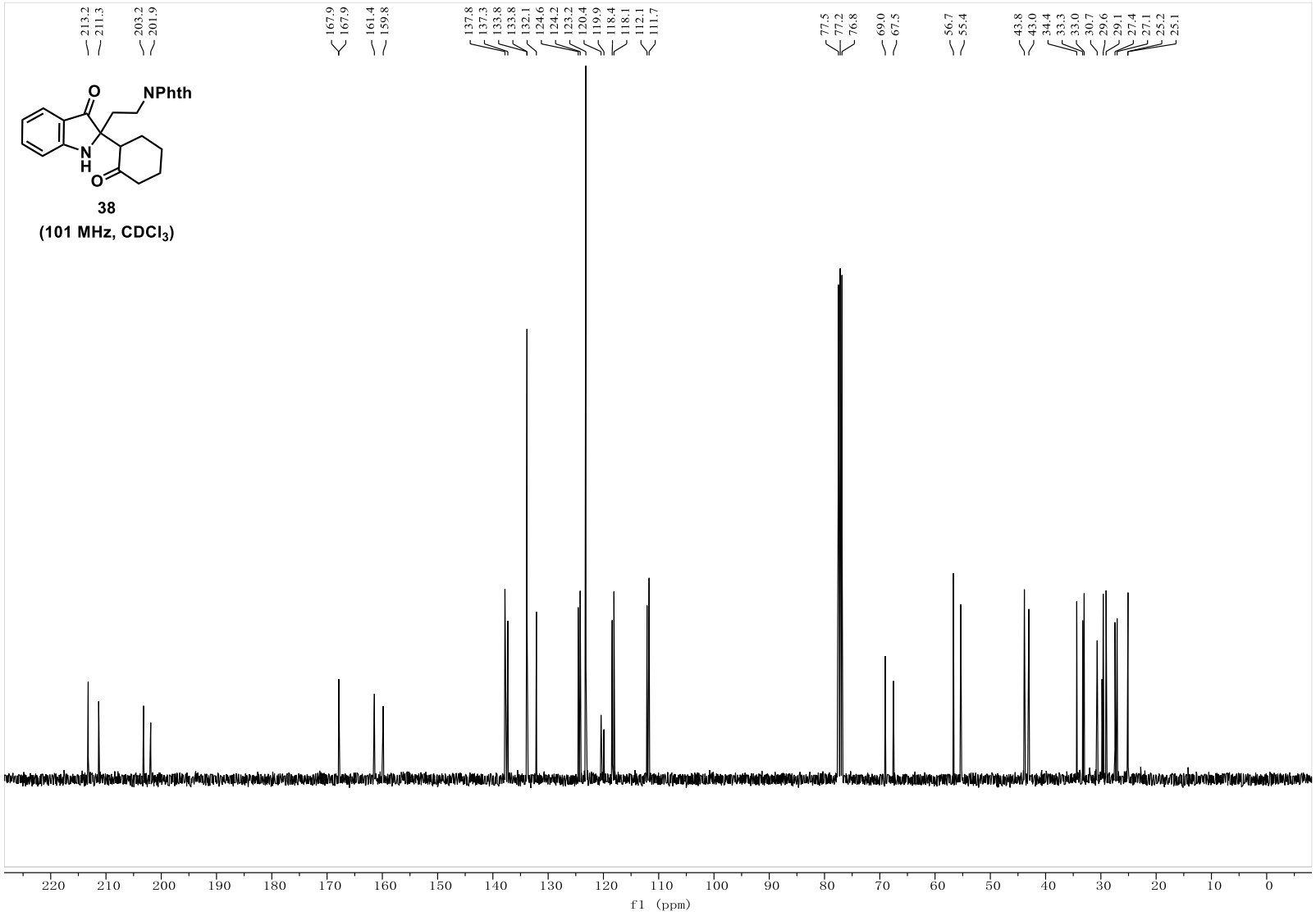

O
NPhth
Me
Me
N
H
36
(400 MHz, CDCl3)
f1 (ppm)

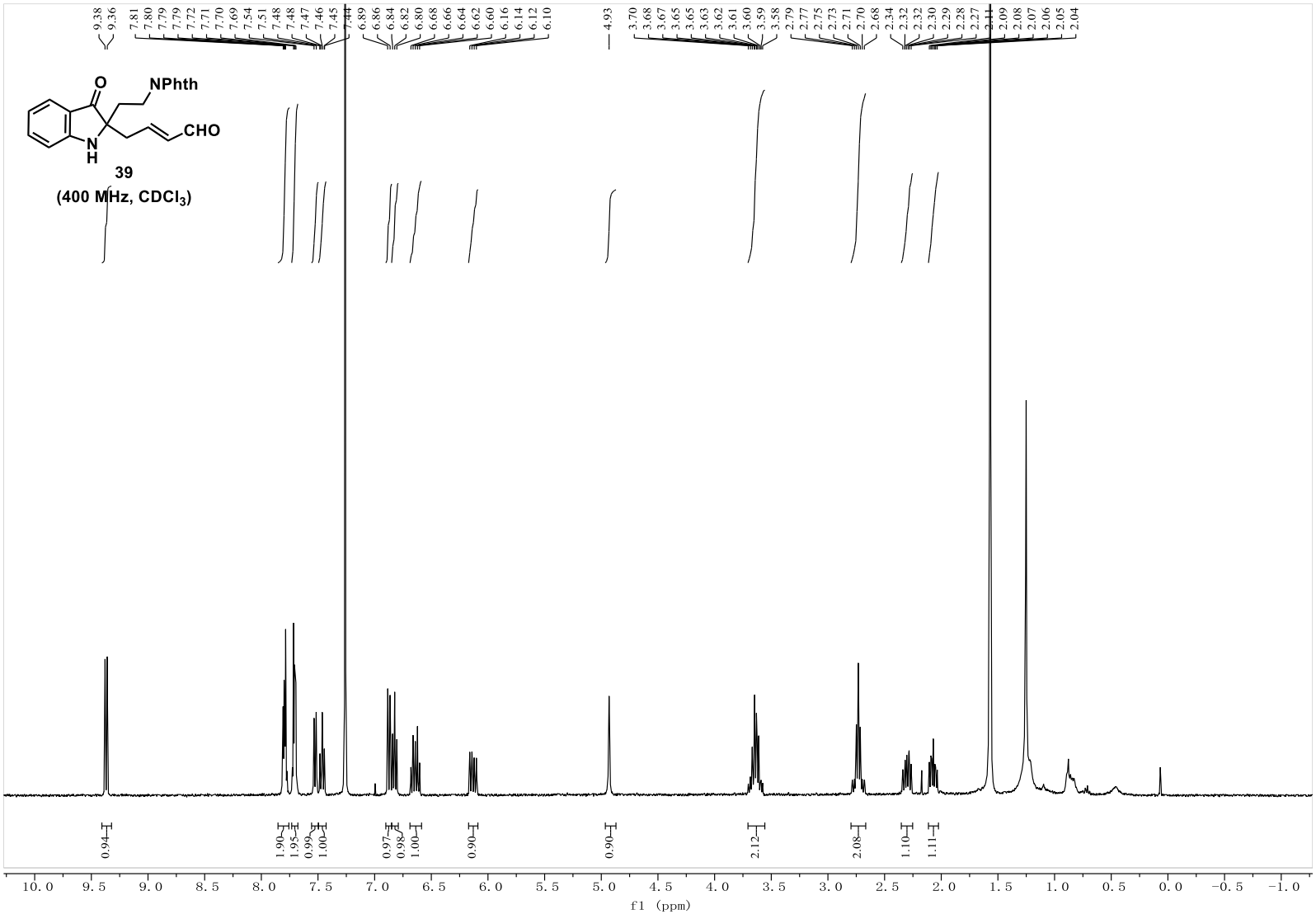

202.8
168.1
161.1
143.3
137.3
134.0
132.1
124.3
123.3
122.3
118.6
114.7
111.8
77.4
77.2
76.9
71.6
43.6
33.5
31.6
21.5
21.2
O
NPhth
Me
Me
N
H
36
(151 MHz, CDCl3)
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

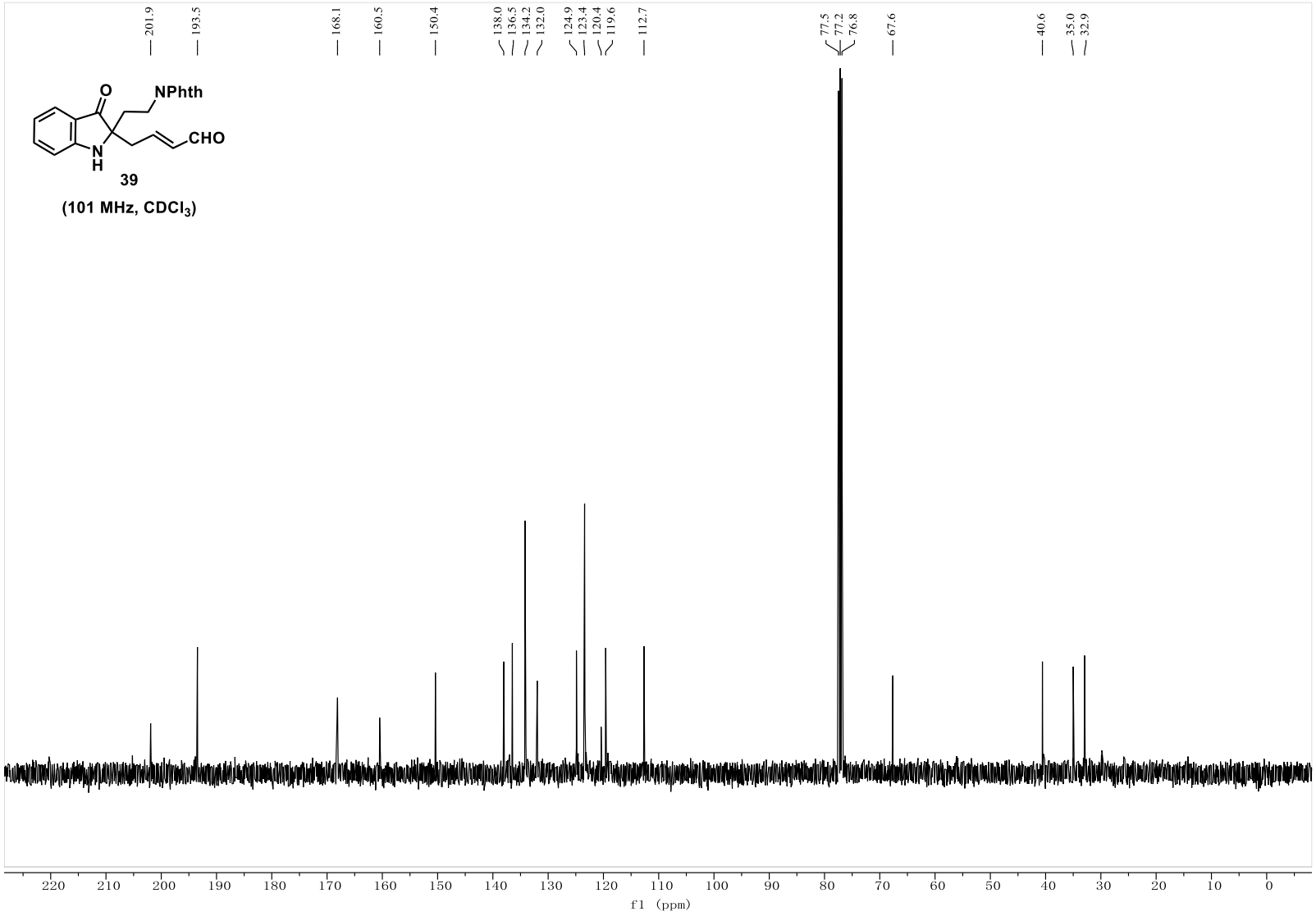

O
NPhth
N
H
37
(400 MHz, CDCl3)
f1 (ppm)

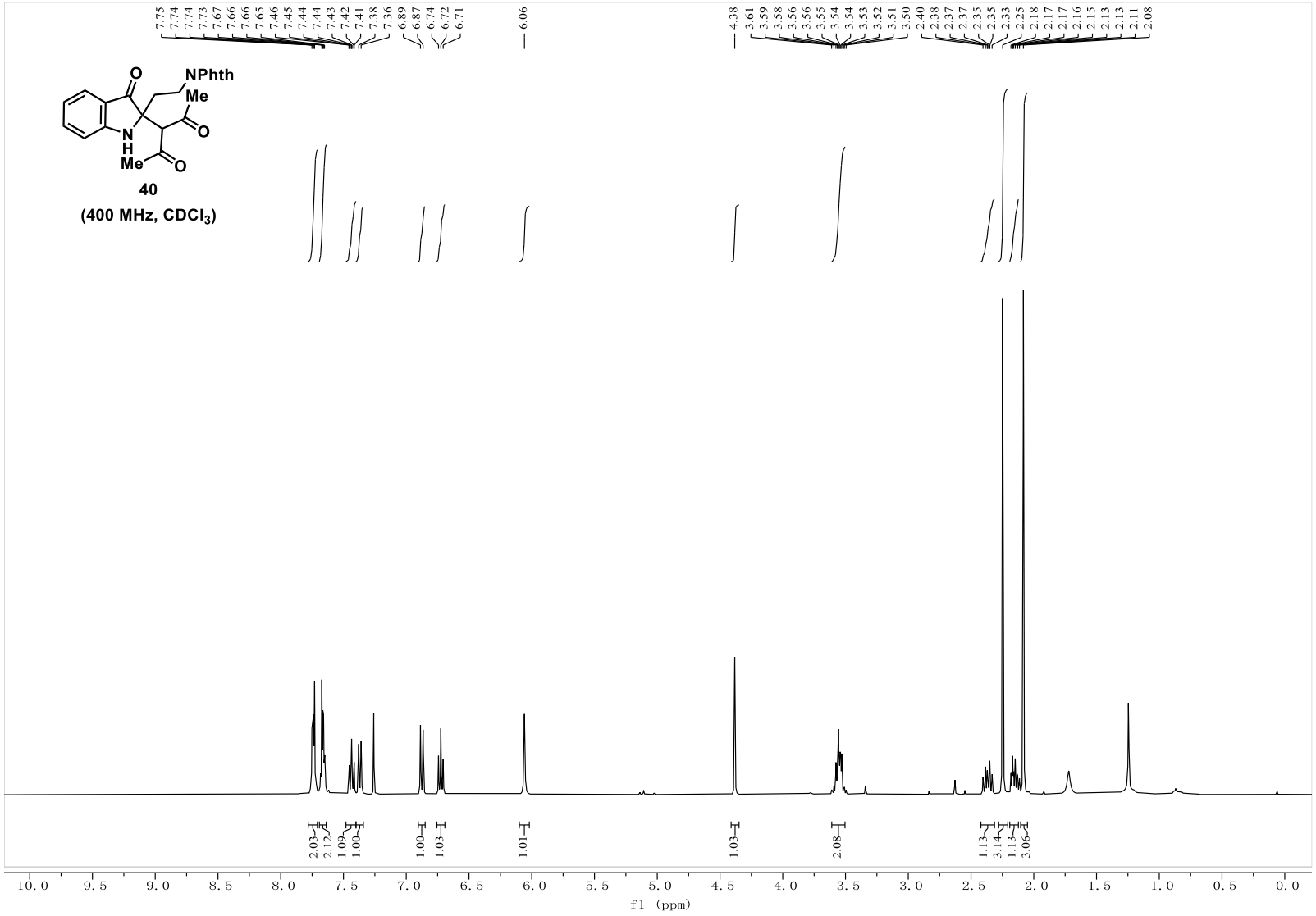

203.4
168.1
160.8
138.8
137.3
134.0
132.2
130.1
124.7
123.3
121.1
119.1
112.7
77.5
77.2
76.8
68.3
39.1
36.8
35.0
33.4
32.5
24.1
O
NPhth
N
H
37
(101 MHz, CDCl3)
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

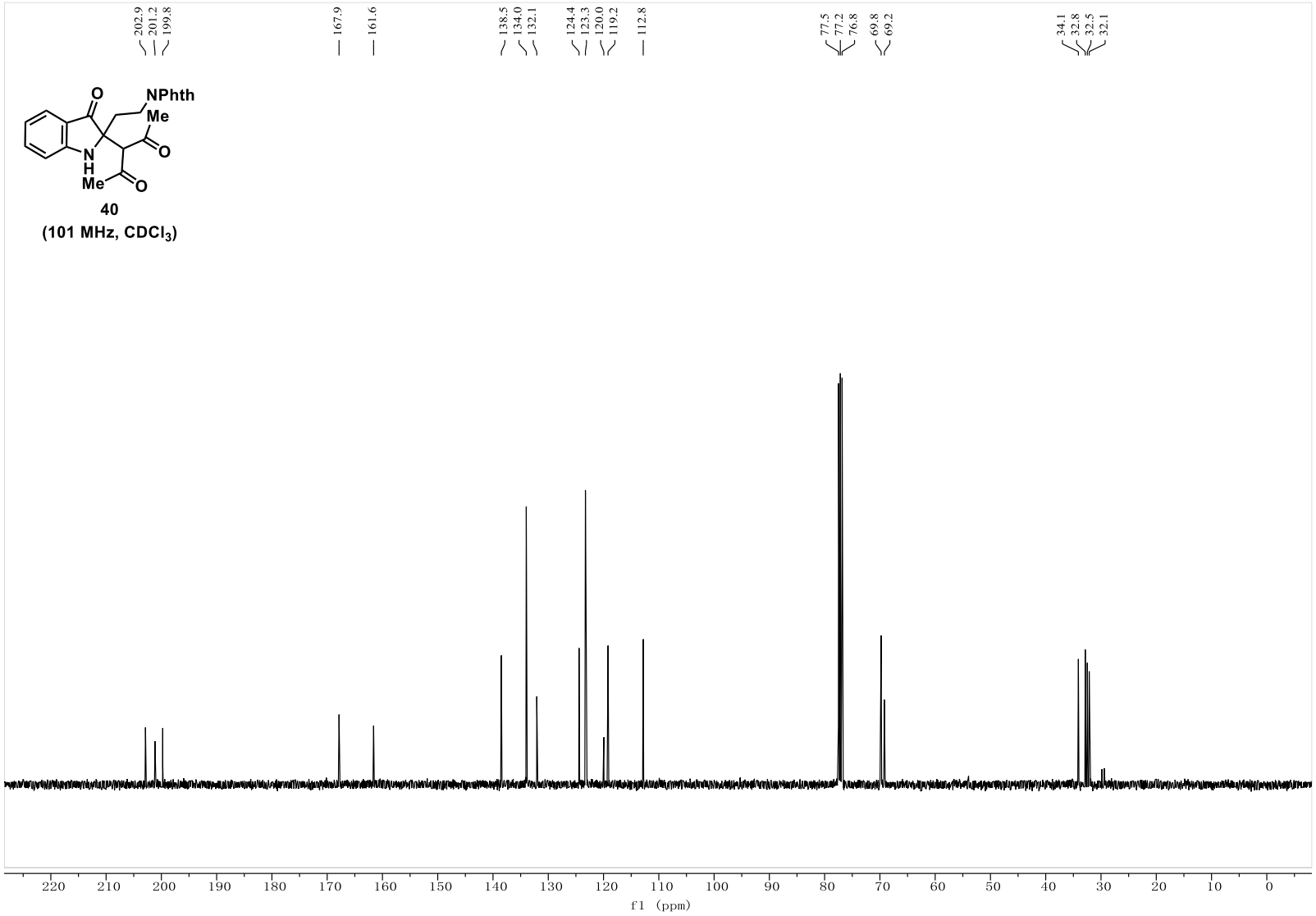

NPhth
O
N
H
O
38
(400 MHz, CDCl3)
f1 (ppm)

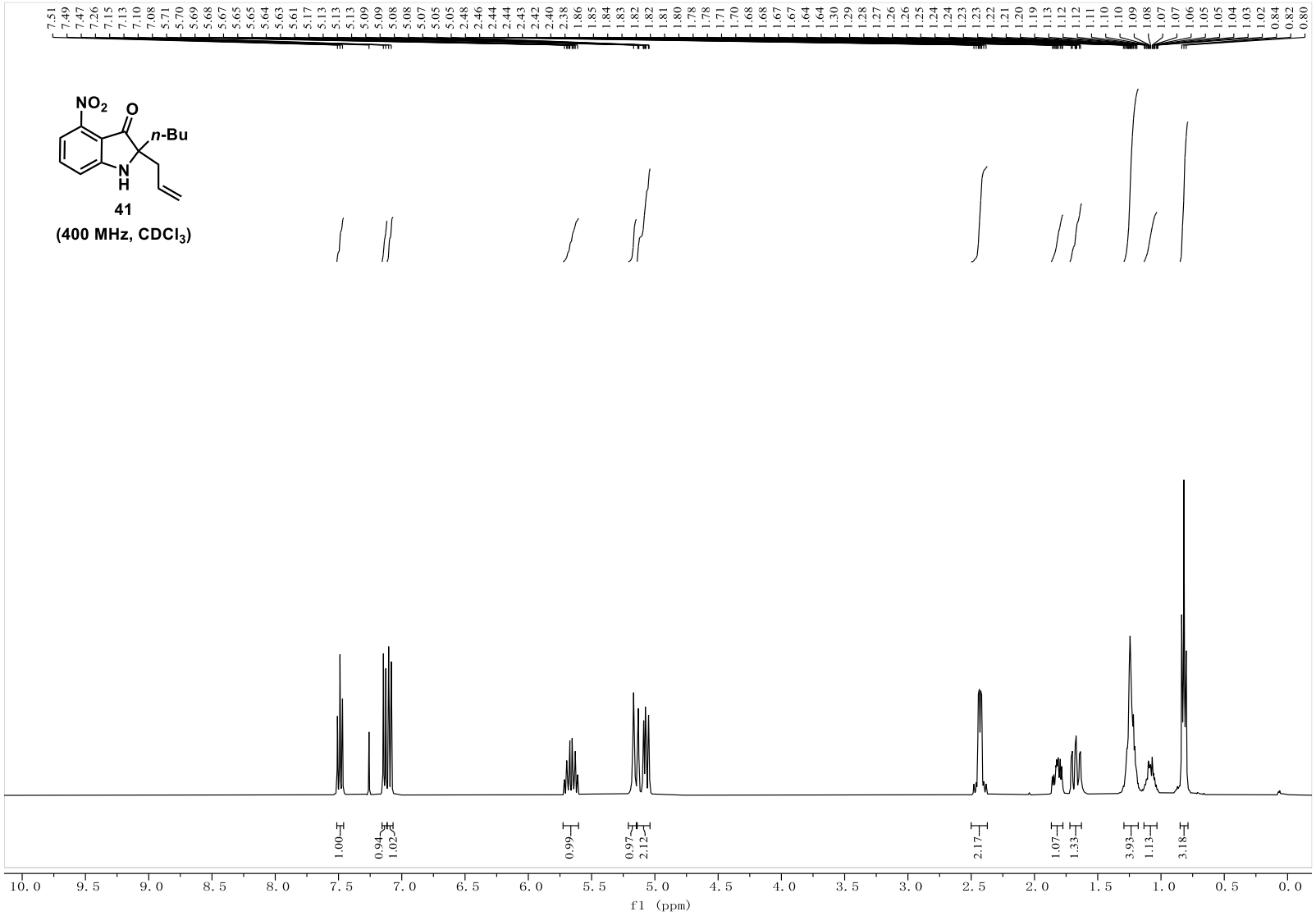

213.2
211.3
203.2
201.9
167.9
167.9
161.4
159.8
137.8
137.3
133.8
133.8
132.1
124.6
124.2
123.2
120.4
119.9
118.4
118.1
112.1
111.7
77.5
77.2
76.8
69.0
67.5
56.7
55.4
43.8
43.0
34.4
33.3
33.0
30.7
29.6
29.1
27.4
27.1
25.2
25.1
O
NPhth
N
H
O
38
(101 MHz, CDCl3)
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

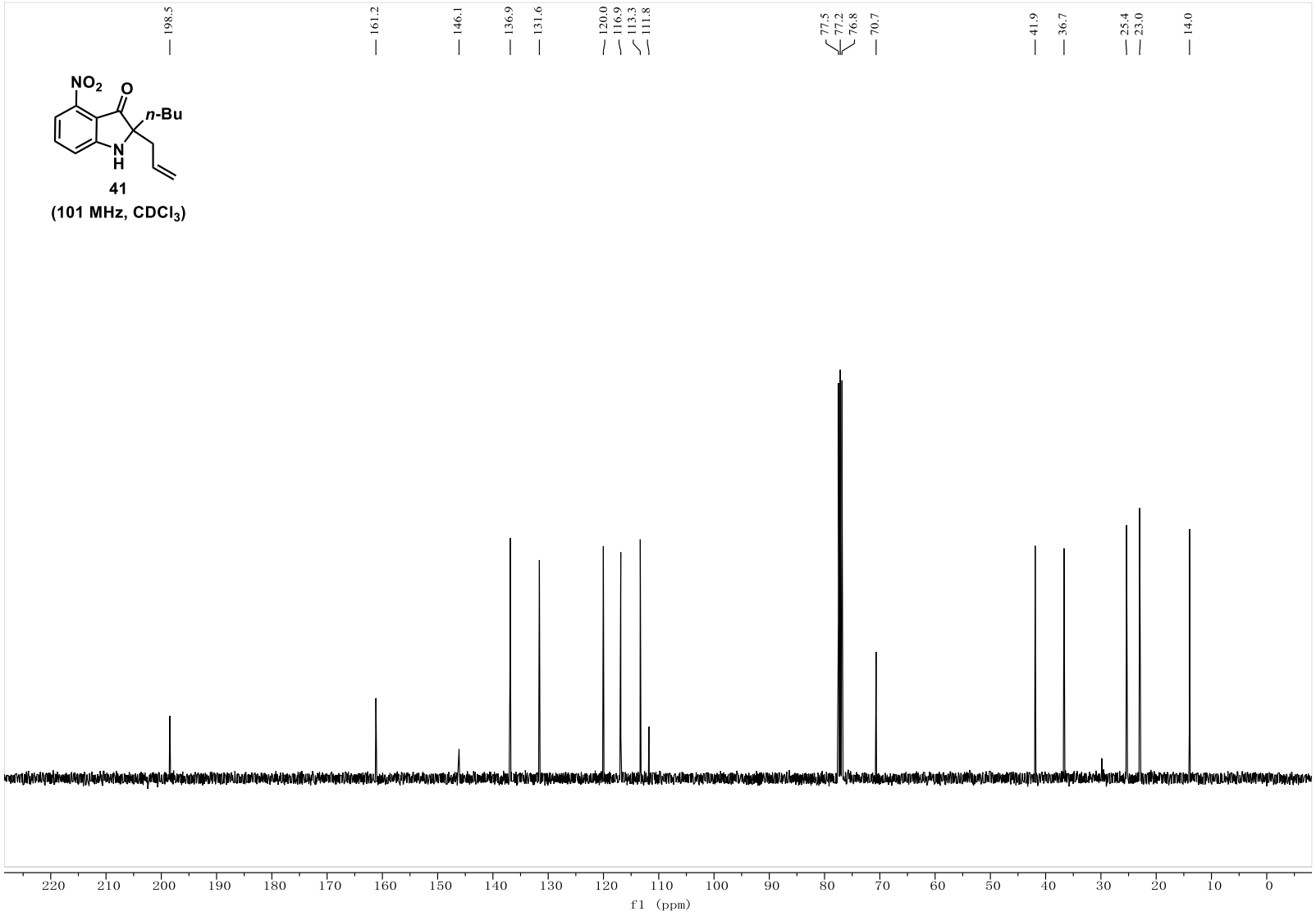

O
NPhth
CHO
N
H
39
(400 MHz, CDCl3)
f1 (ppm)

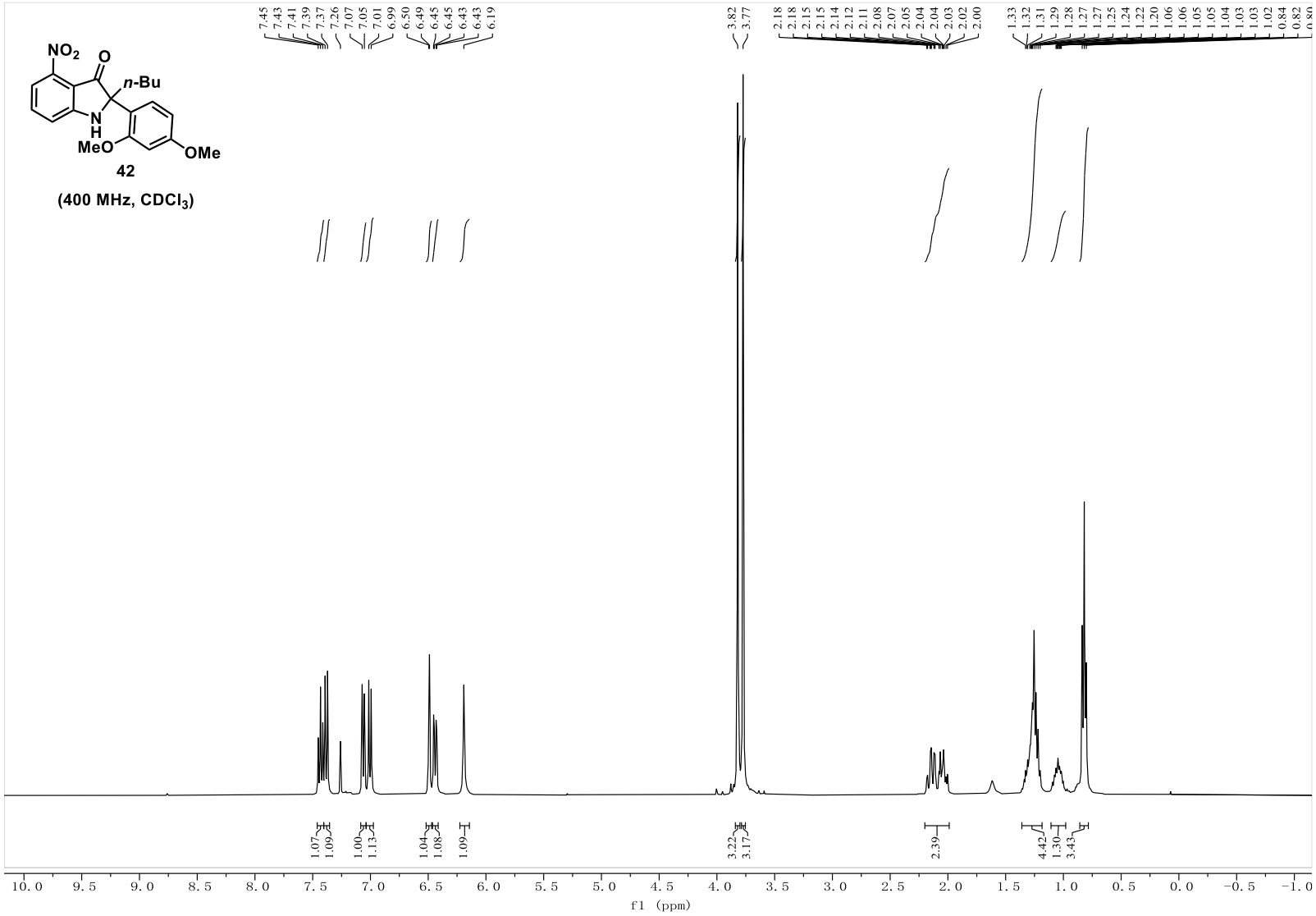

201.9
193.5
168.1
160.5
150.4
138.0
136.5
134.2
132.0
124.9
123.4
120.4
119.6
112.7
77.5
77.2
76.8
67.6
40.6
35.0
32.9
O
NPhth
CHO
N
H
39
(101 MHz, CDCl3)
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

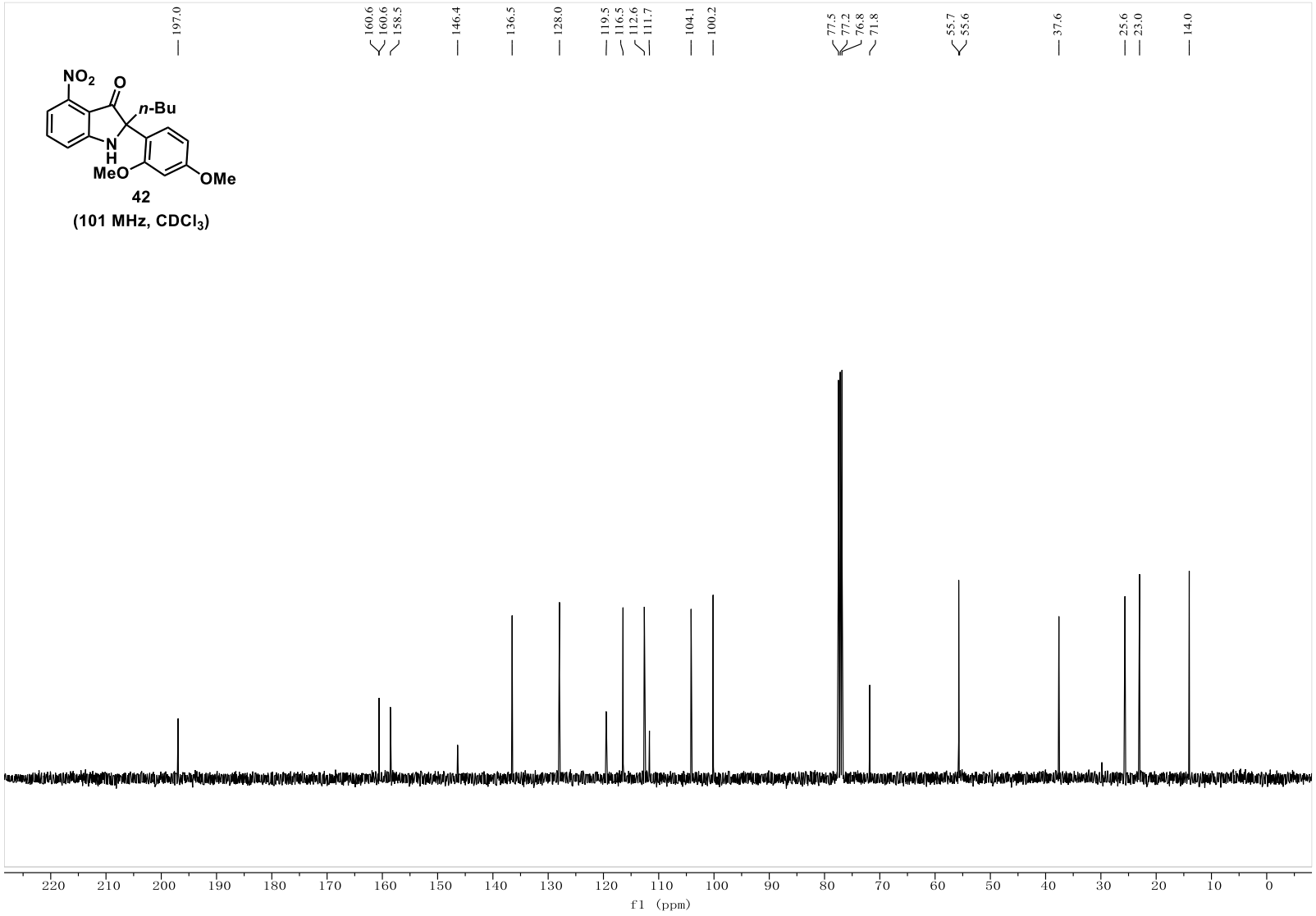

7.75 7.74 7.74 7.73 7.67 7.66 7.66 7.65 7.46 7.45 7.44 7.44 7.43 7.42 7.41 7.38 7.36 6.89 6.87 6.74 6.72 6.71 6.06
4.38 3.61 3.59 3.58 3.56 3.56 3.55 3.54 3.54 3.53 3.52 3.51 3.50 2.40 2.38 2.37 2.37 2.35 2.35 2.33 2.25 2.18 2.17 2.17 2.16 2.15 2.13 2.13 2.11 2.08
O
NPhth
Me
O
N
H
Me
O
40
(400 MHz, CDCl3)
2.03 2.12 1.09 1.00 1.00 1.03 1.01 1.03 2.08 1.13 3.14 1.13 3.06
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
f1 (ppm)

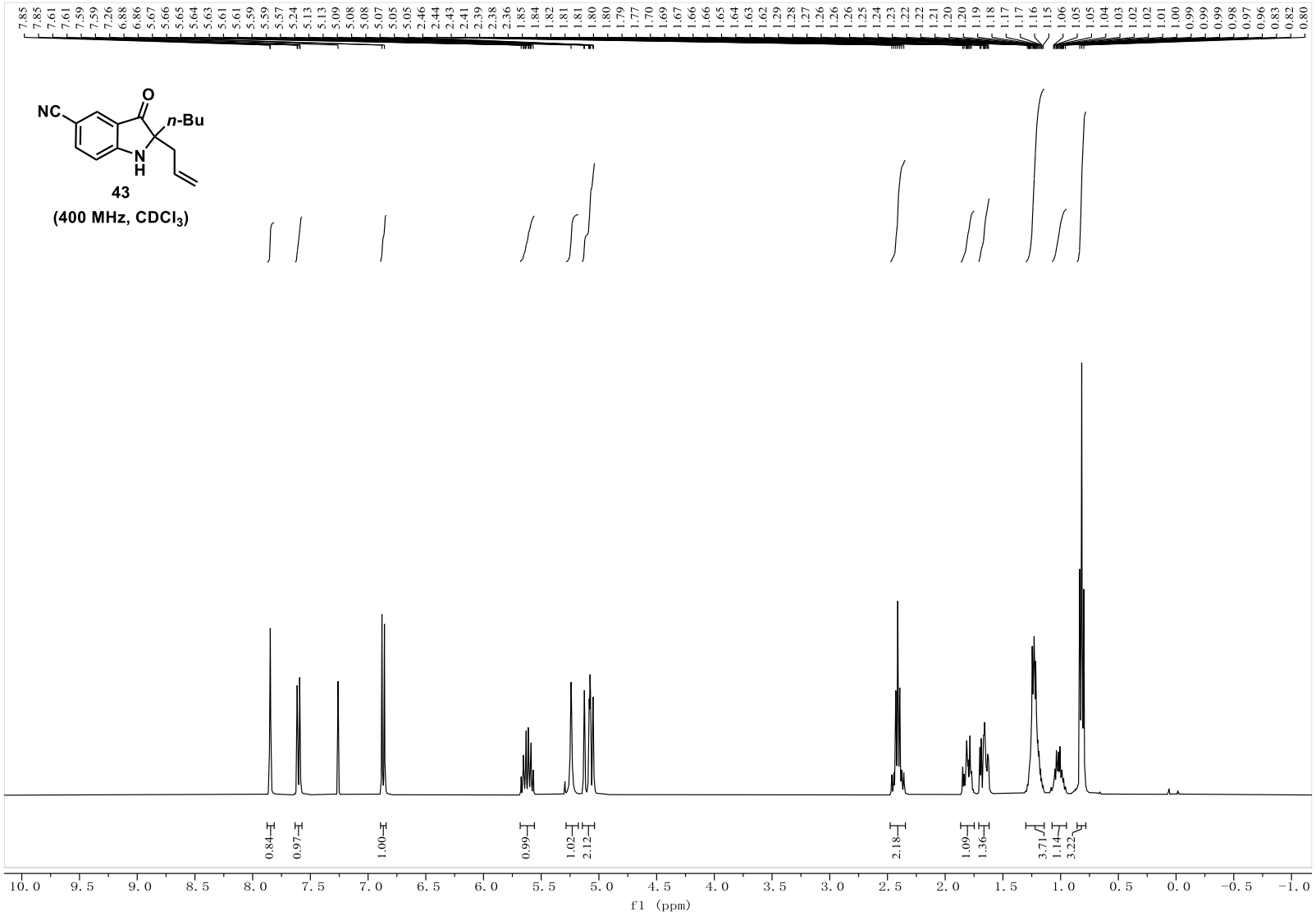

202.9
201.2
199.8
167.9
161.6
138.5
134.0
132.1
124.4
123.3
120.0
119.2
112.8
77.5
77.2
76.8
69.8
69.2
34.1
32.8
32.5
32.1
O
NPhth
Me
O
N
H
Me
O
40
(101 MHz, CDCl3)
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

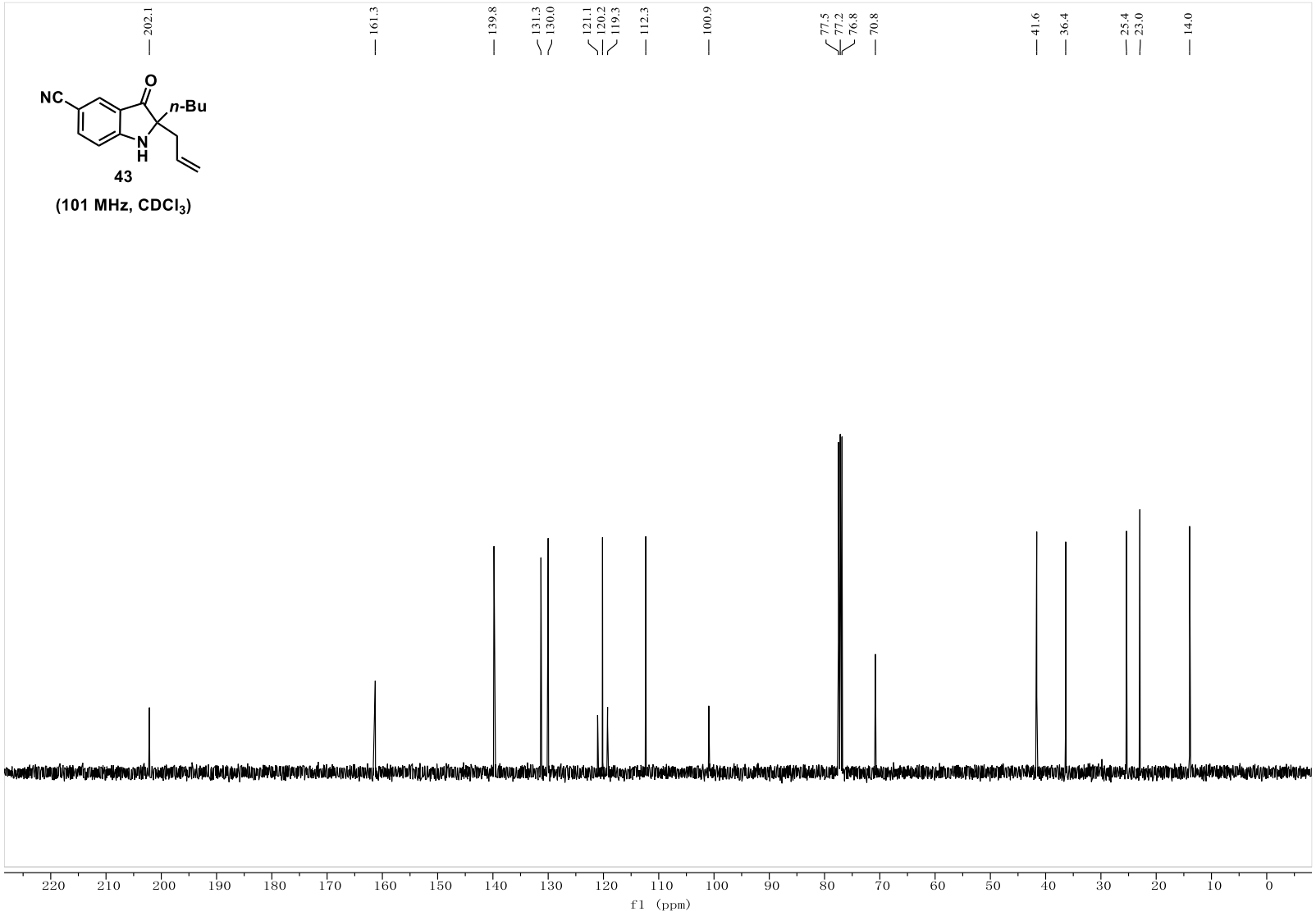

NO2
O
n-Bu
N
H
41
(400 MHz, CDCl3)
f1 (ppm)

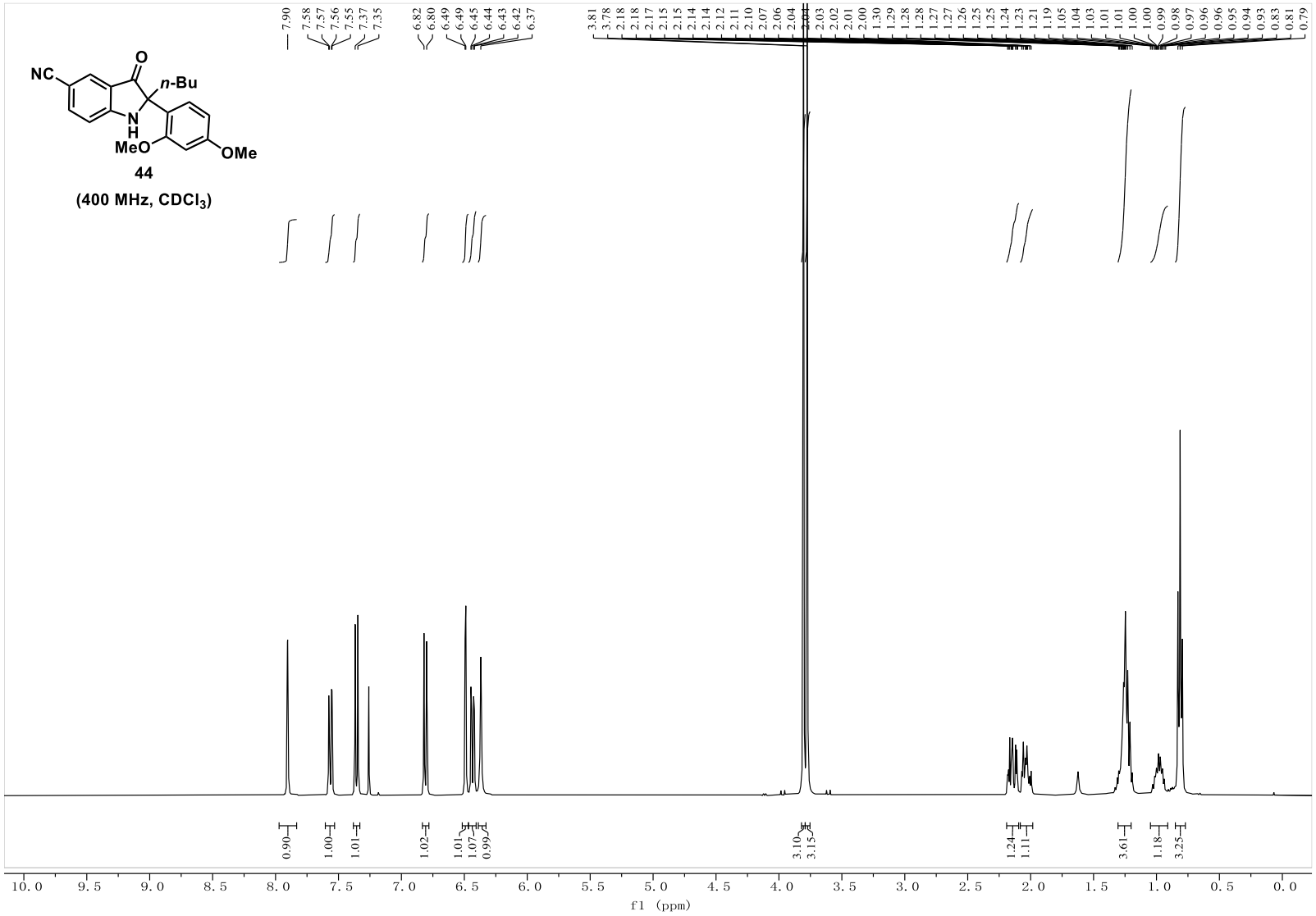

198.5
161.2
146.1
136.9
131.6
120.0
116.9
113.3
111.8
77.5
77.2
76.8
70.7
41.9
36.7
25.4
23.0
14.0
NO2
O
n-Bu
N
H
41
(101 MHz, CDCl3)
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

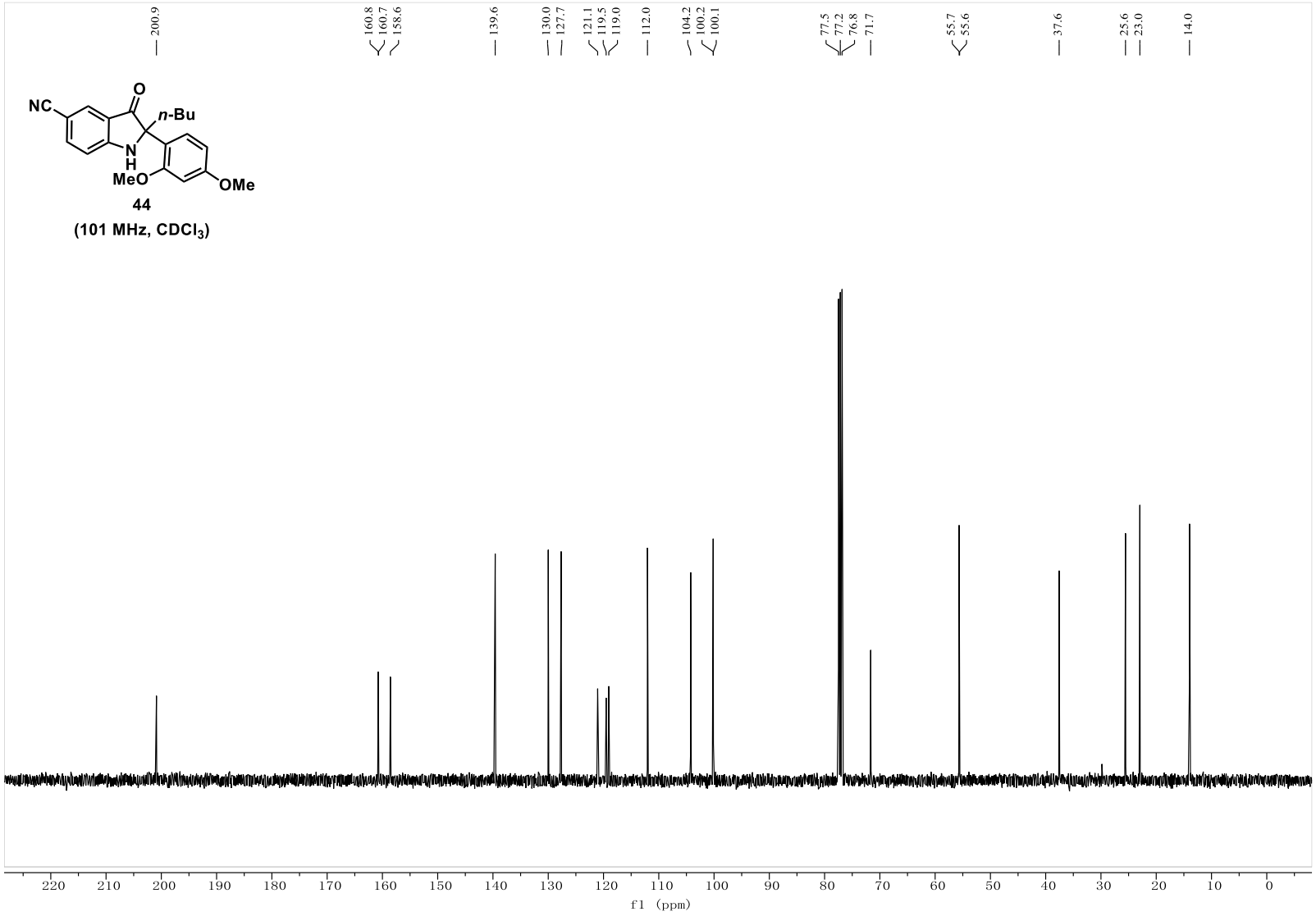

NO2
O
n-Bu
N
H
MeO
OMe
42
(400 MHz, CDCl3)
f1 (ppm)

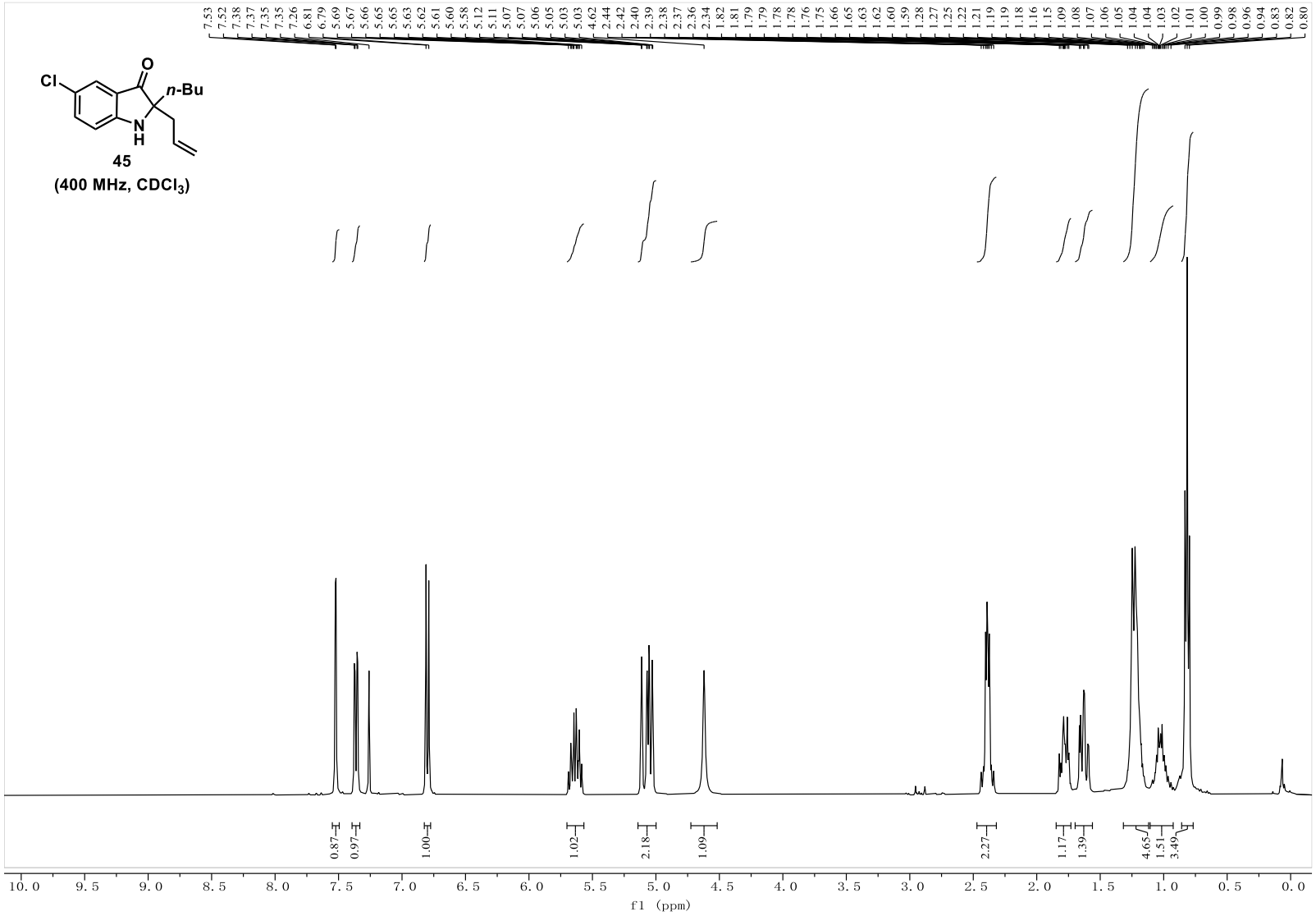

197.0
160.6
160.6
158.5
146.4
136.5
128.0
119.5
116.5
112.6
111.7
104.1
100.2
77.5
77.2
76.8
71.8
55.7
55.6
37.6
25.6
23.0
14.0
NO2
O
n-Bu
N
H
MeO
OMe
42
(101 MHz, CDCl3)
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

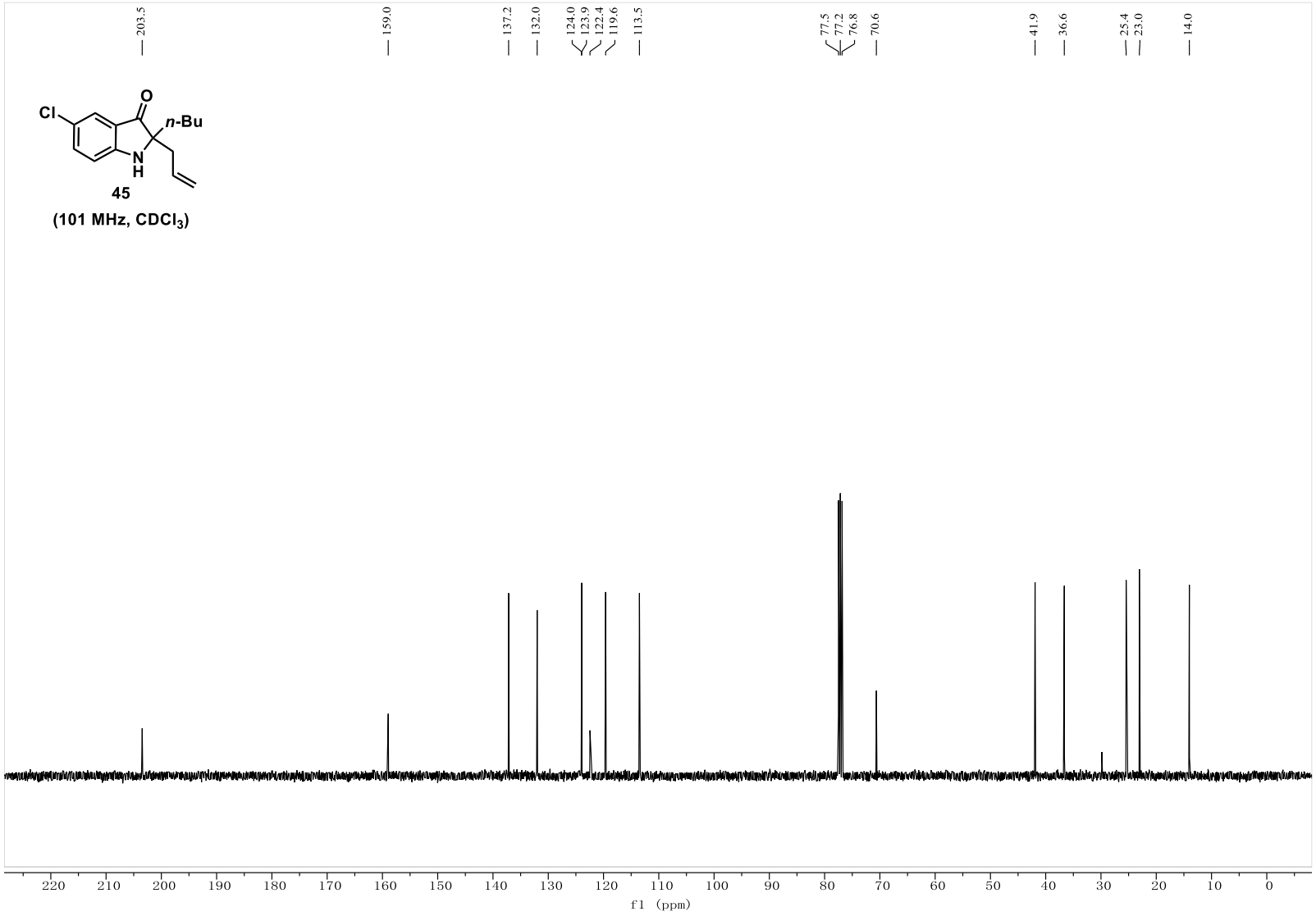

NC
O
n-Bu
N
H
43
(400 MHz, CDCl3)
f1 (ppm)

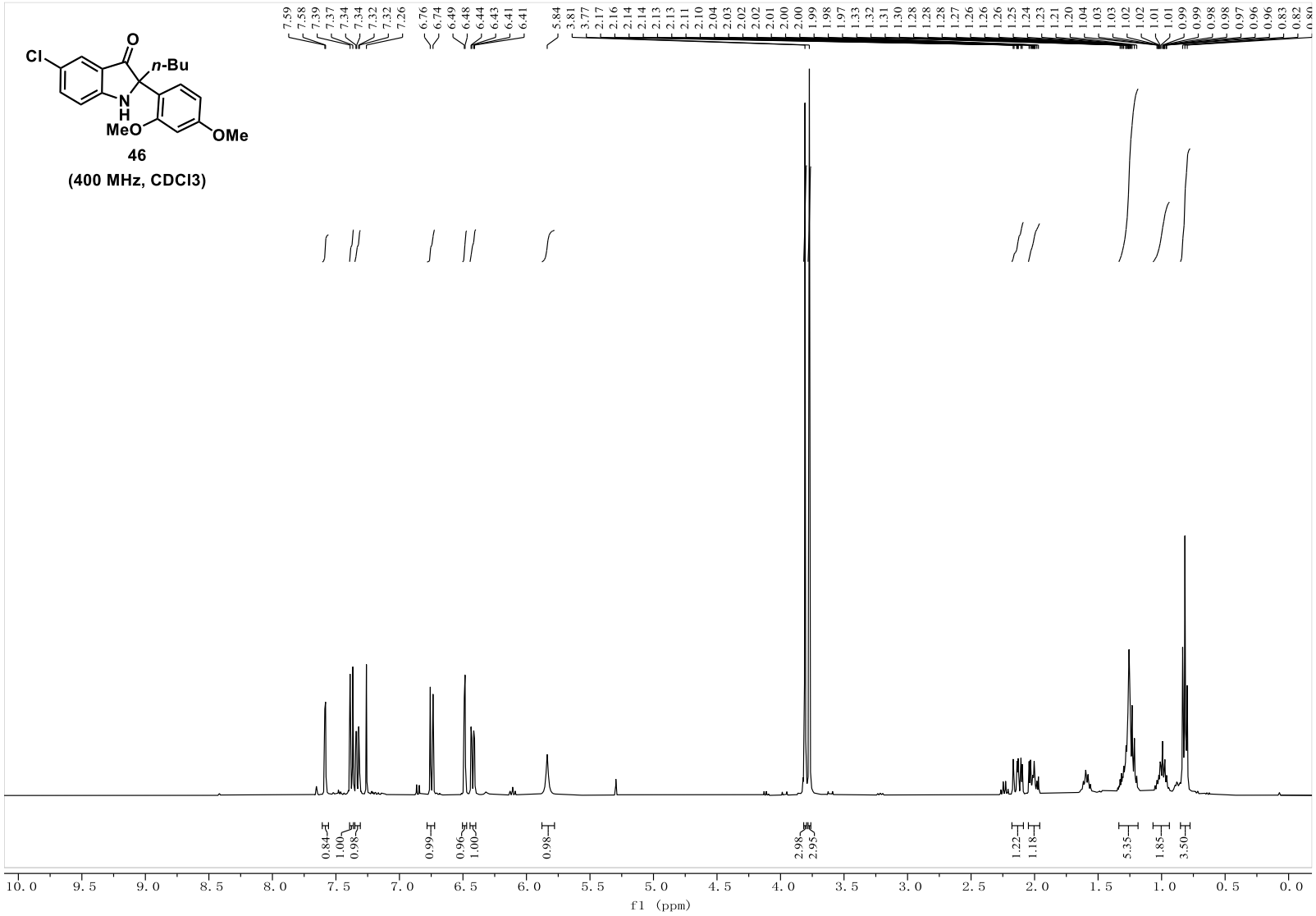

202.1
161.3
139.8
131.3
130.0
121.1
120.2
119.3
112.3
100.9
77.5
77.2
76.8
70.8
41.6
36.4
25.4
23.0
14.0
NC
O
n-Bu
N
H
43
(101 MHz, CDCl3)
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

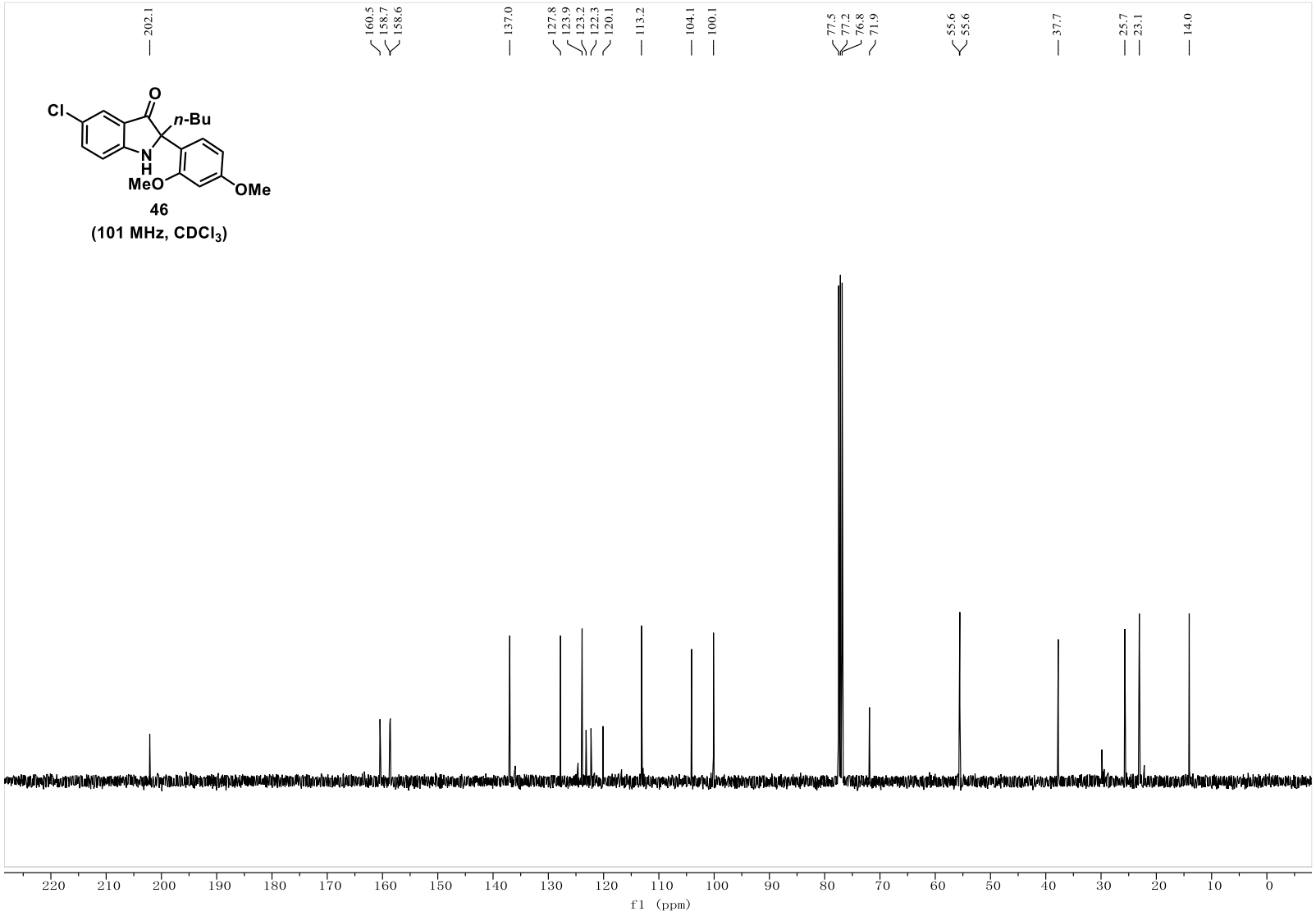

NC
O
n-Bu
N
H
MeO
OMe
44
(400 MHz, CDCl3)
f1 (ppm)

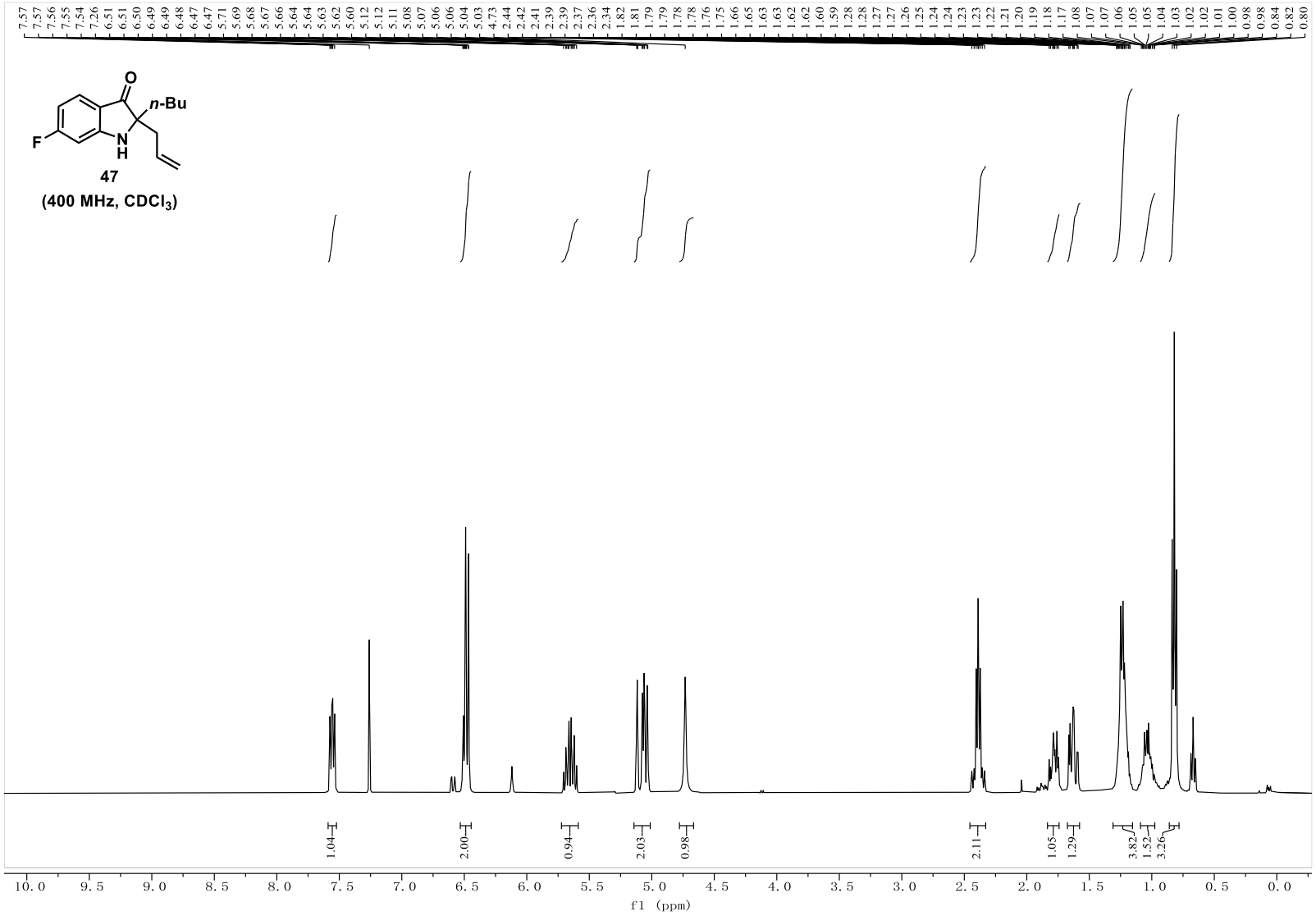

200.9
160.8
160.7
158.6
139.6
130.0
127.7
121.1
119.5
119.0
112.0
104.2
100.2
100.1
77.5
77.2
76.8
71.7
55.7
55.6
37.6
25.6
23.0
14.0
NC
O
n-Bu
N
H
MeO
OMe
44
(101 MHz, CDCl3)
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

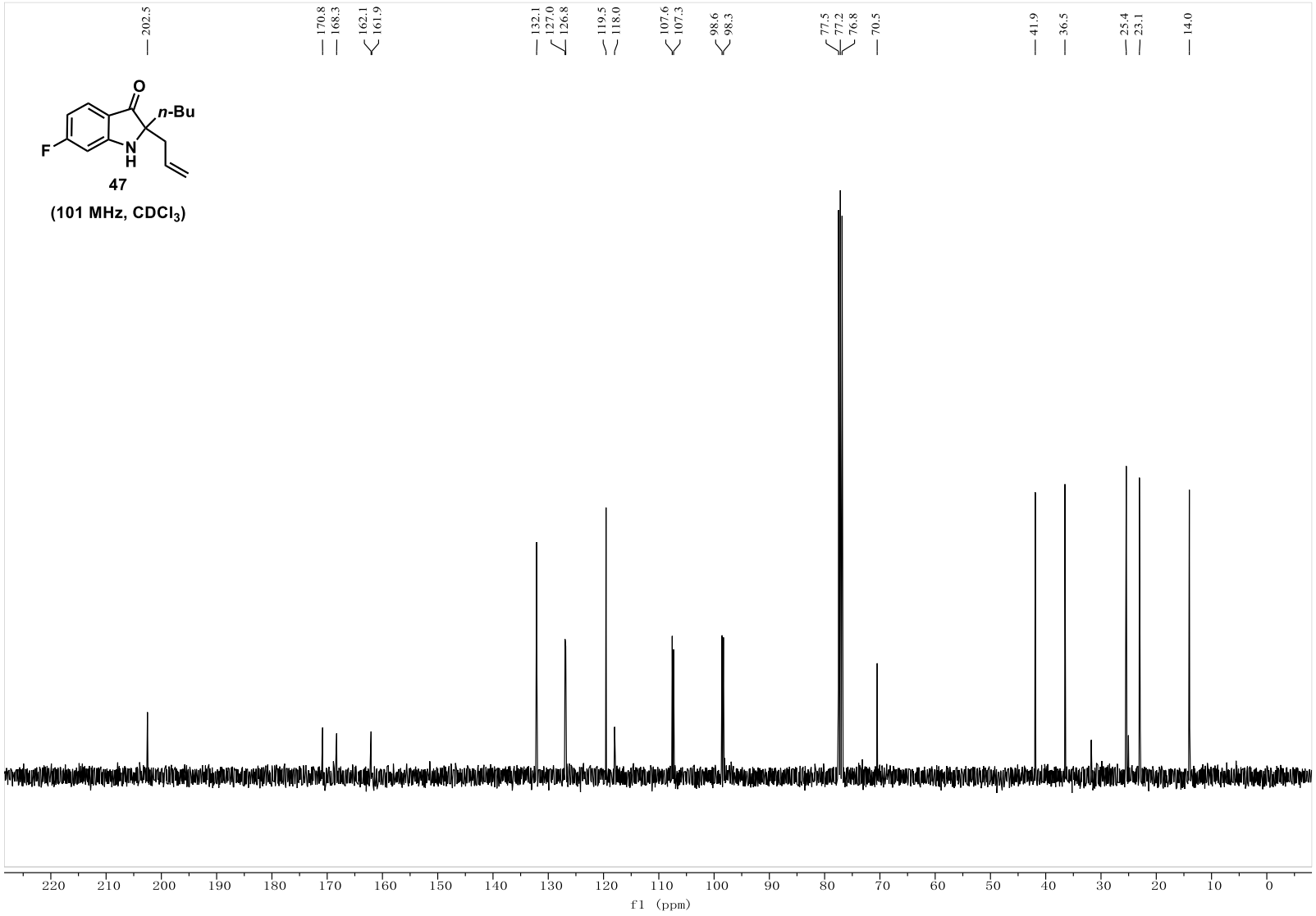

Cl
O
n-Bu
N
H
45
(400 MHz, CDCl3)
7.53 7.52 7.38 7.37 7.35 7.35 7.26 6.81 6.79 5.69 5.67 5.66 5.65 5.65 5.63 5.62 5.61 5.60 5.58 5.12 5.11 5.07 5.07 5.06 5.05 5.03 5.03 4.62 2.44 2.42 2.40 2.39 2.38 2.37 2.36 2.34 1.82 1.81 1.79 1.79 1.78 1.78 1.76 1.75 1.66 1.65 1.63 1.62 1.60 1.59 1.28 1.27 1.25 1.22 1.21 1.19 1.19 1.18 1.16 1.15 1.09 1.08 1.07 1.06 1.05 1.04 1.04 1.03 1.02 1.01 1.00 0.99 0.98 0.96 0.94 0.83 0.82 0.80
0.87 0.97 1.00 1.02 2.18 1.09 2.27 1.17 1.39 4.65 1.51 3.49
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
f1 (ppm)

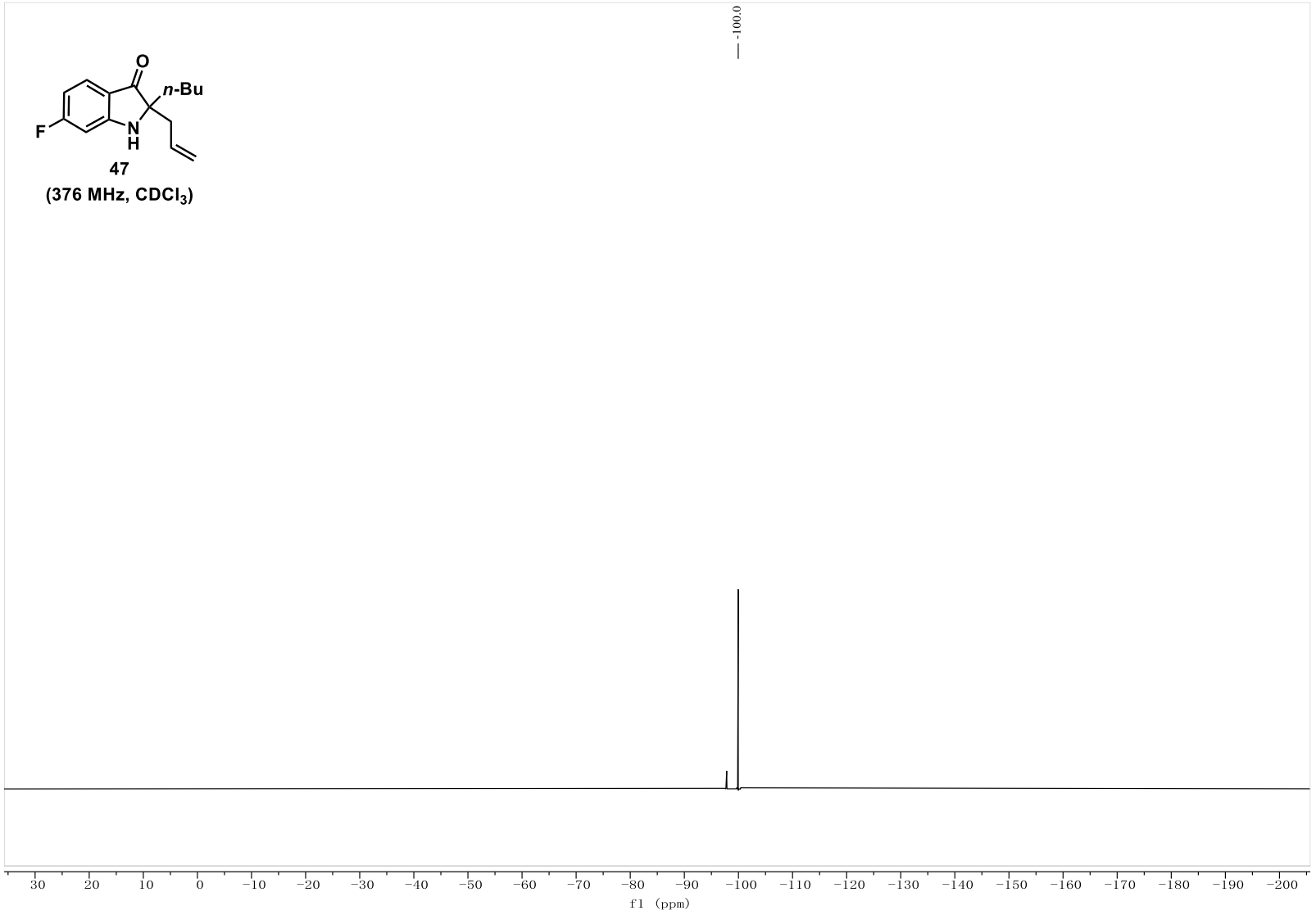

203.5
159.0
137.2
132.0
124.0
123.9
122.4
119.6
113.5
77.5
77.2
76.8
70.6
41.9
36.6
25.4
23.0
14.0
Cl
O
n-Bu
N
H
45
(101 MHz, CDCl3)
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

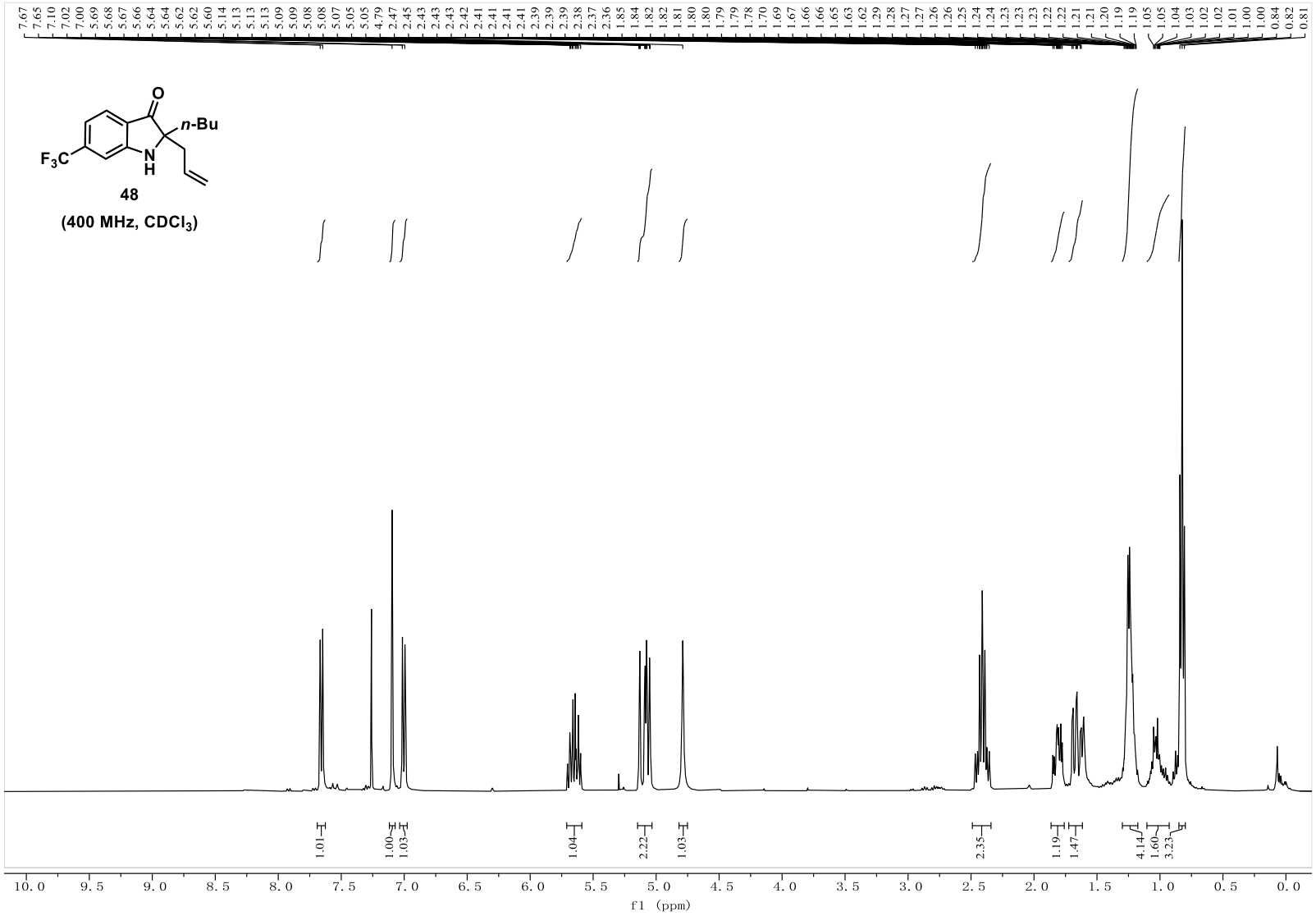

Cl
O
n-Bu
N
H
MeO
OMe
46
(400 MHz, CDCl3)
f1 (ppm)

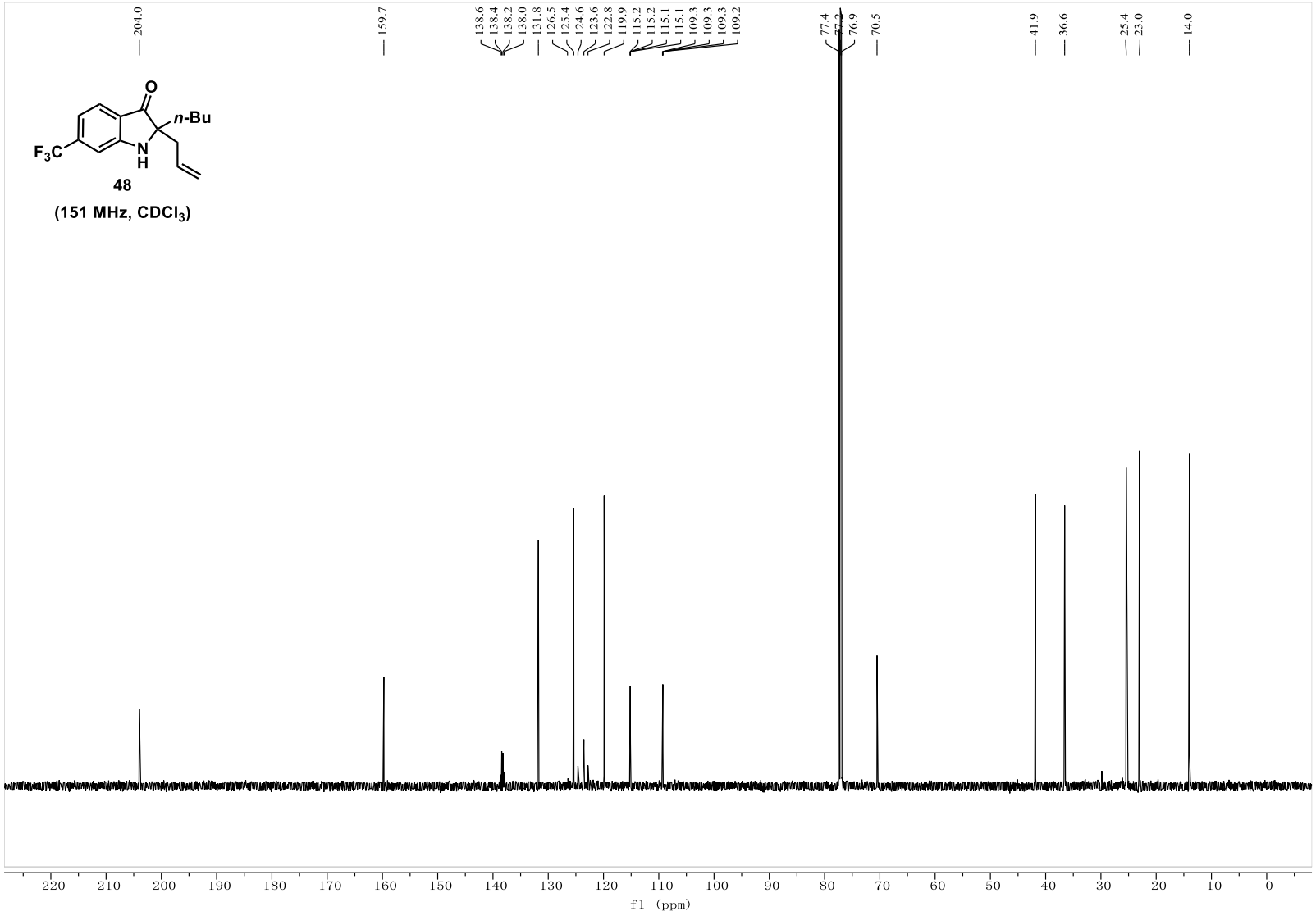

202.1
160.5
158.7
158.6
137.0
127.8
123.9
123.2
122.3
120.1
113.2
104.1
100.1
77.5
77.2
76.8
71.9
55.6
55.6
37.7
25.7
23.1
14.0
Cl
O
n-Bu
N
H
MeO
OMe
46
(101 MHz, CDCl3)
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

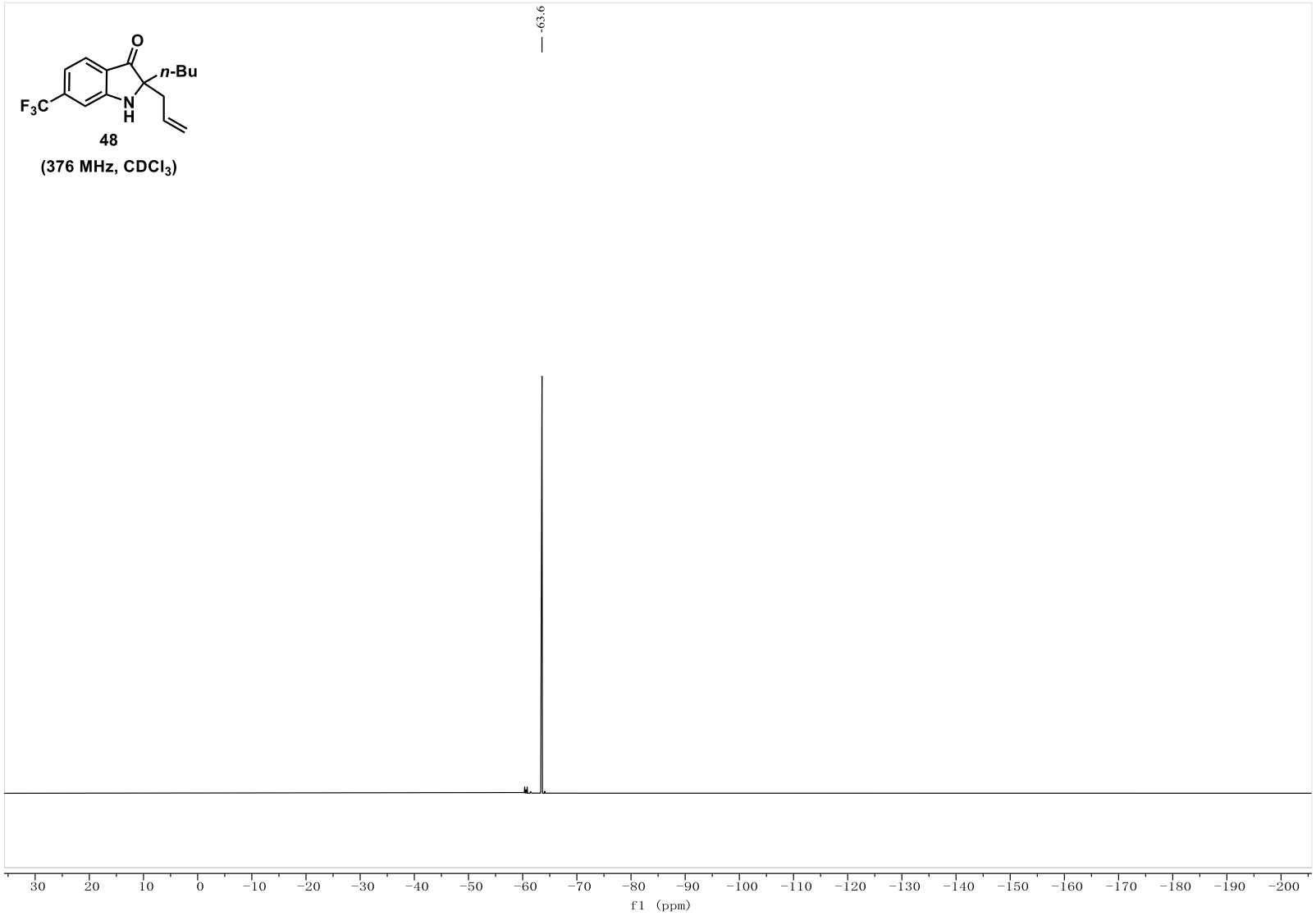

O
n-Bu
F
N
H
47
(400 MHz, CDCl3)
f1 (ppm)

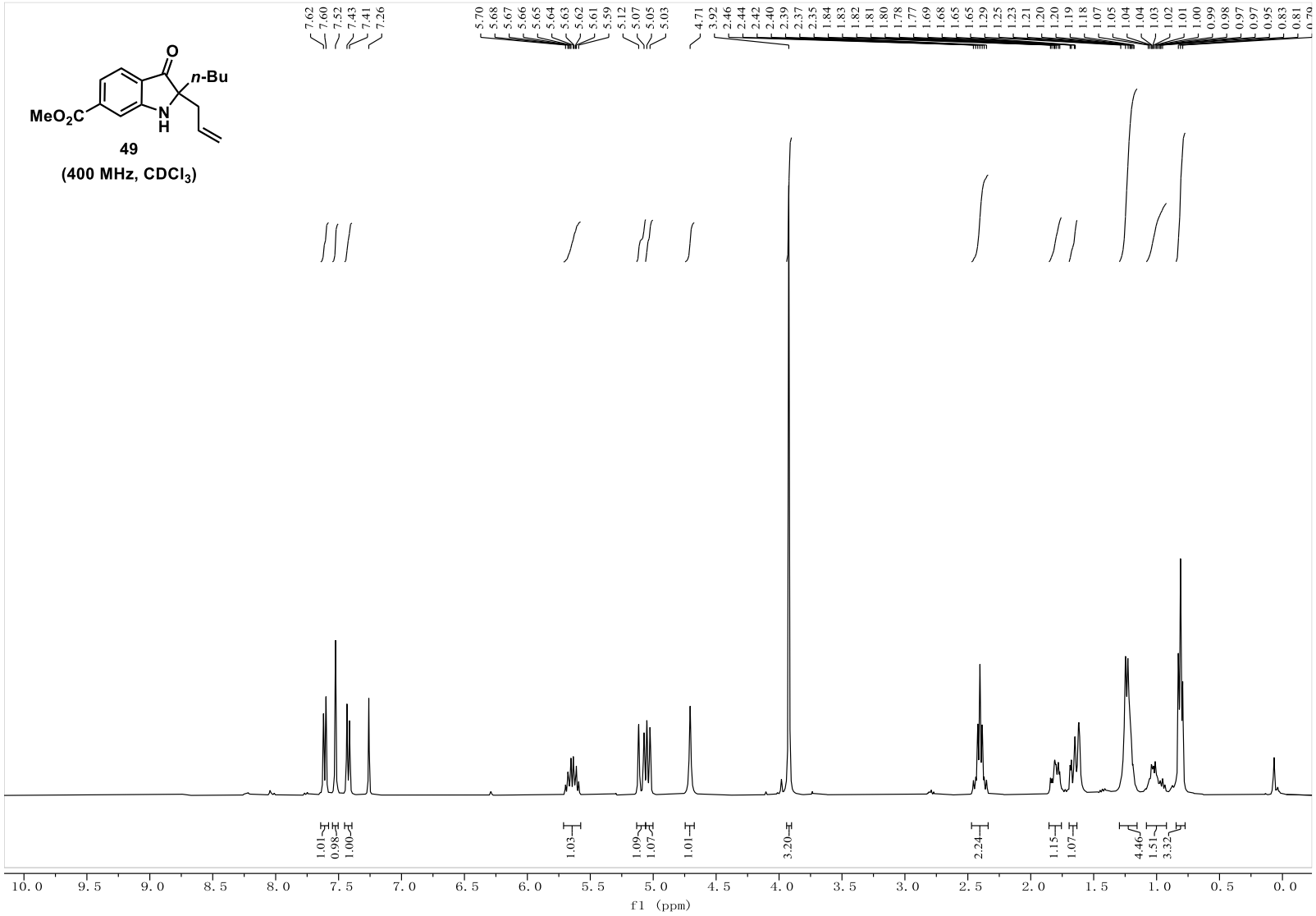

202.5
170.8
168.3
162.1
161.9
132.1
127.0
126.8
119.5
118.0
107.6
107.3
98.6
98.3
77.5
77.2
76.8
70.5
41.9
36.5
25.4
23.1
14.0
O
n-Bu
F
N
H
47
(101 MHz, CDCl3)
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

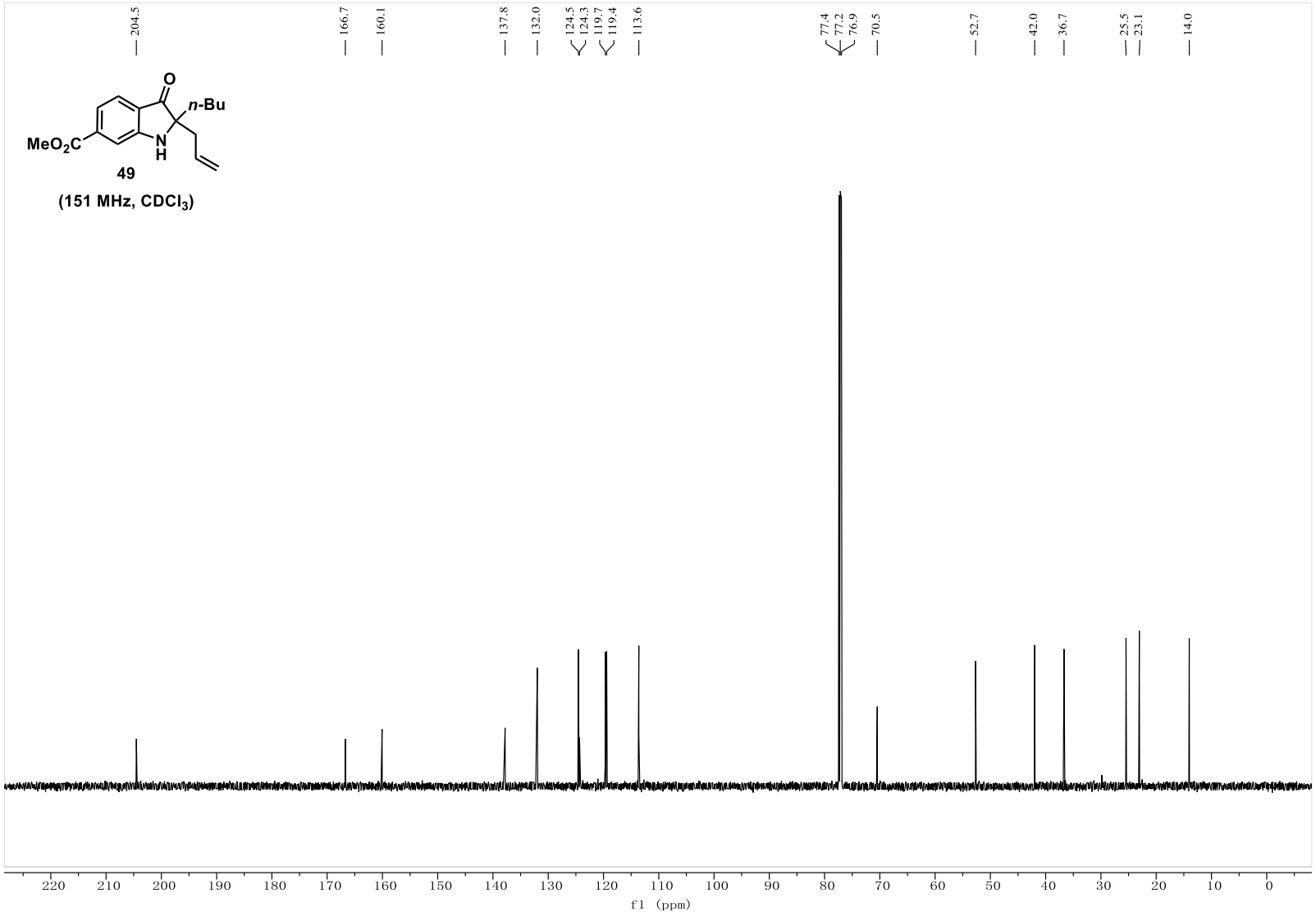

O
n-Bu
F
N
H
47
(376 MHz, CDCl3)
-100.0
30
20
10
0
−10
−20
−30
−40
−50
−60
−70
−80
−90
−100
−110
−120
−130
−140
−150
−160
−170
−180
−190
−200
f1 (ppm)

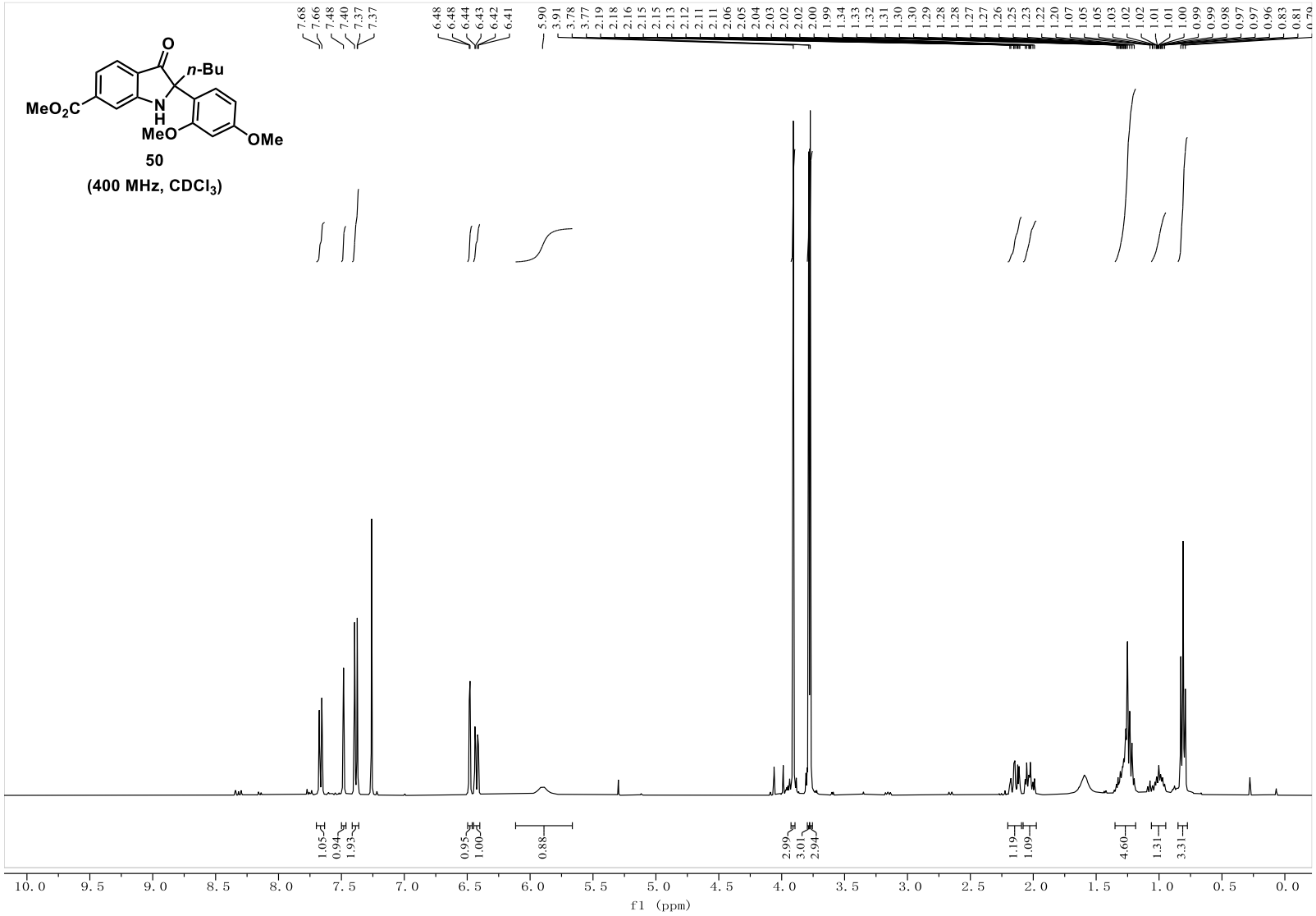

O
n-Bu
F3C
N
H
48
(400 MHz, CDCl3)
1.01
1.00
1.03
1.04
2.22
1.03
2.35
1.19
1.47
4.14
1.60
3.23
f1 (ppm)

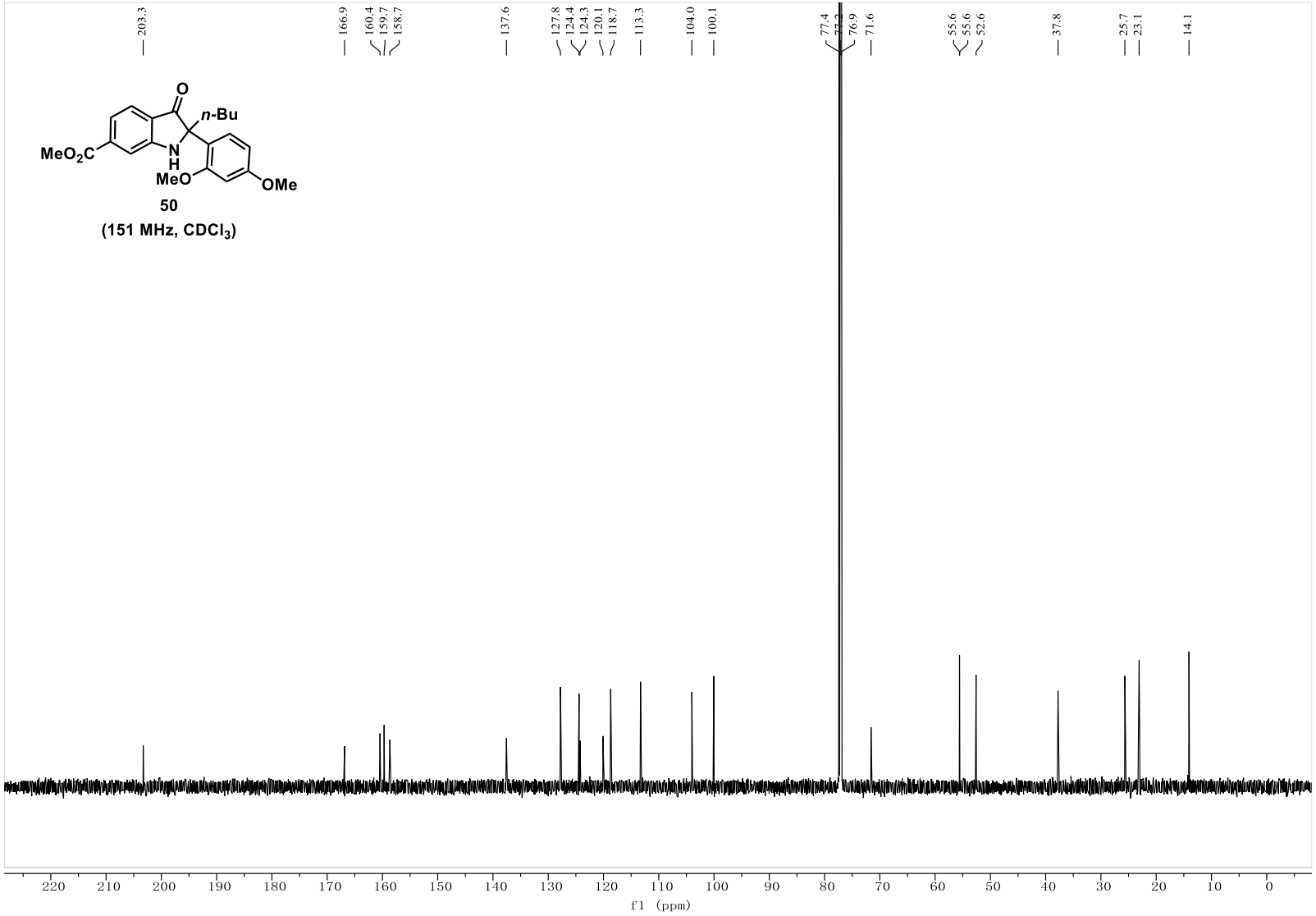

204.0
159.7
138.6
138.4
138.2
138.0
131.8
126.5
125.4
124.6
123.6
122.8
119.9
115.2
115.2
115.1
115.1
109.3
109.3
109.3
109.2
77.4
77.2
76.9
70.5
41.9
36.6
25.4
23.0
14.0
O
n-Bu
F3C
N
H
48
(151 MHz, CDCl3)
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

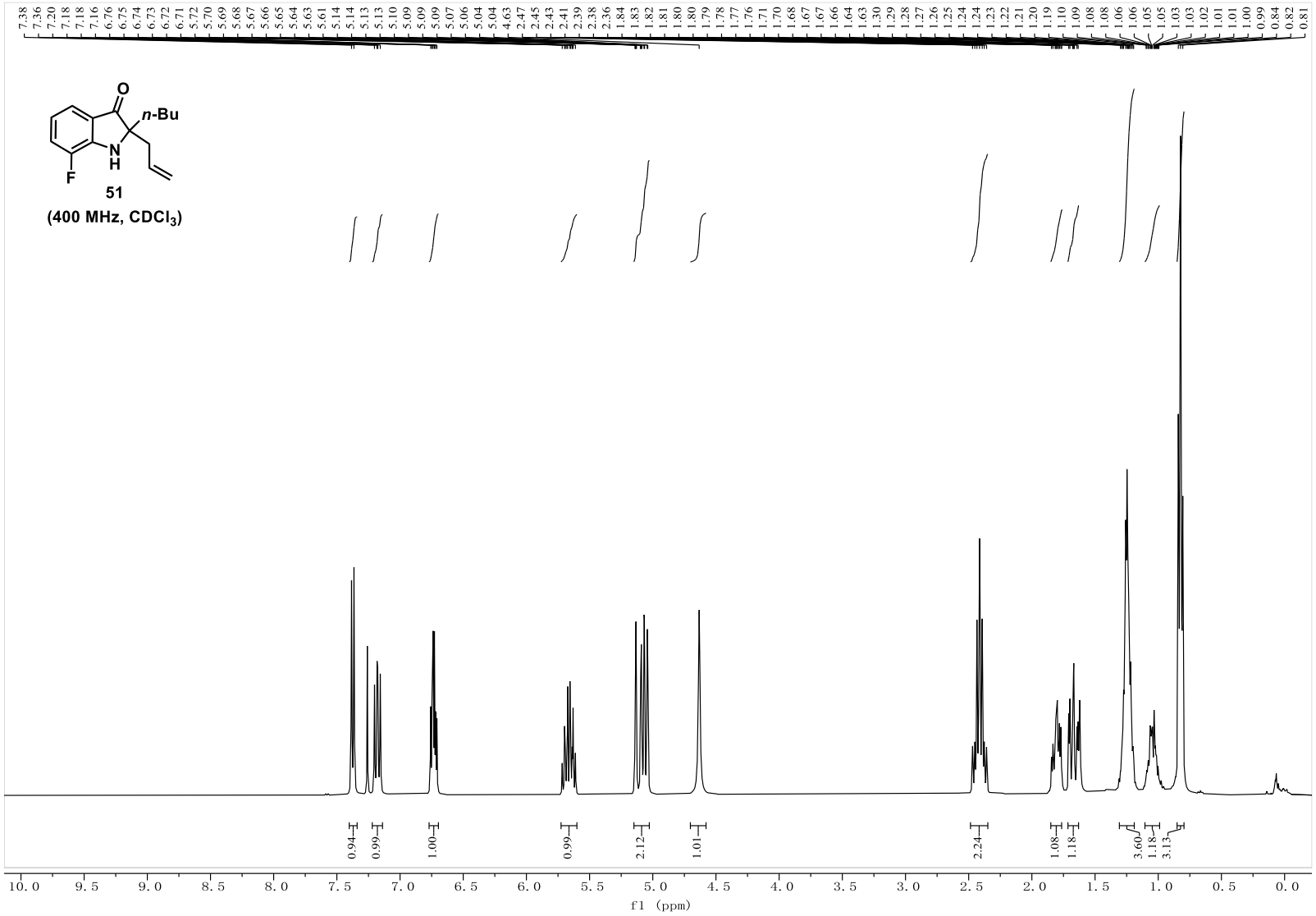

O
n-Bu
F3C
N
H
48
(376 MHz, CDCl3)
-63.6
30
20
10
0
−10
−20
−30
−40
−50
−60
−70
−80
−90
−100
−110
−120
−130
−140
−150
−160
−170
−180
−190
−200
f1 (ppm)

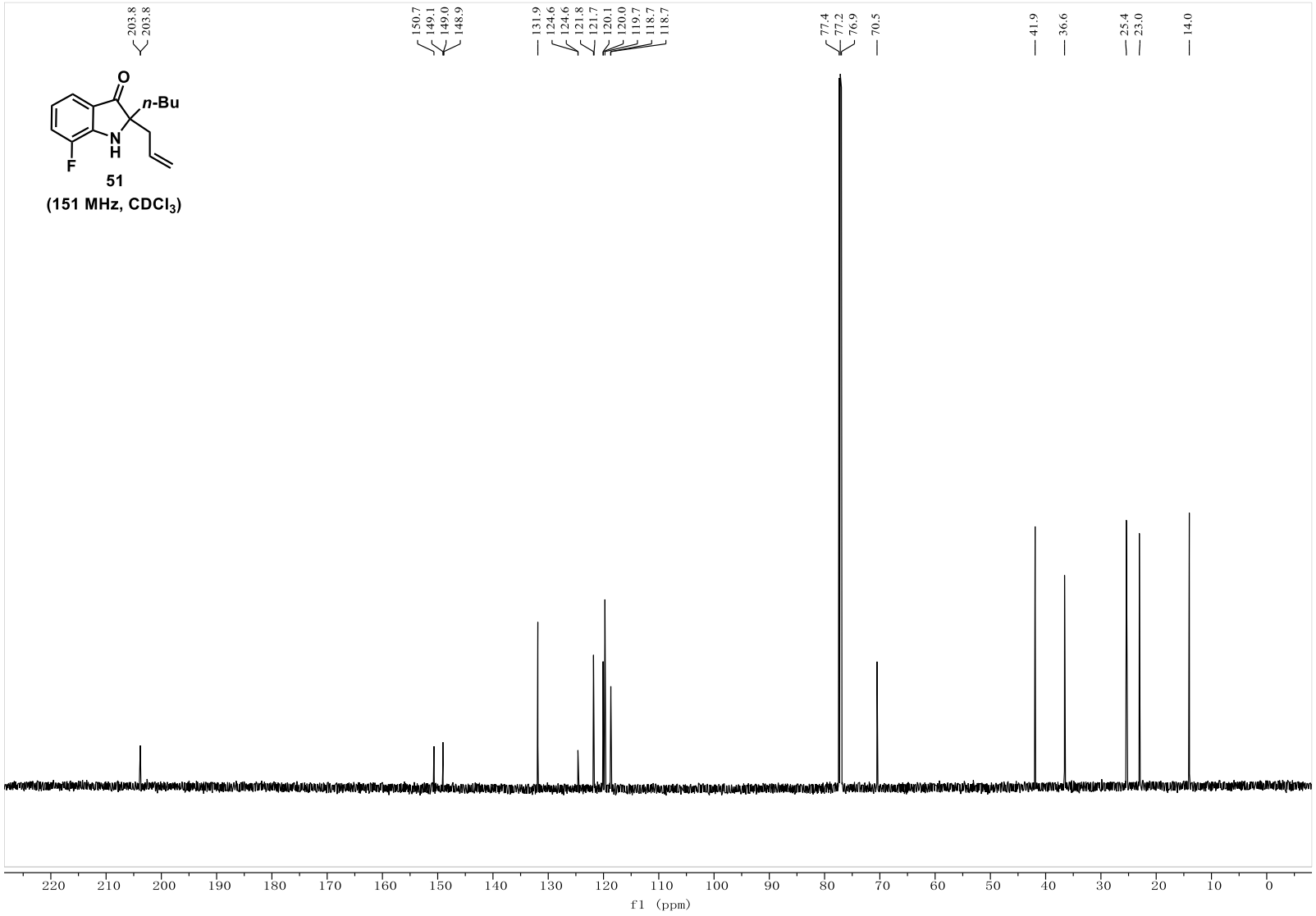

MeO2C
O
n-Bu
N
H
49
(400 MHz, CDCl3)
f1 (ppm)

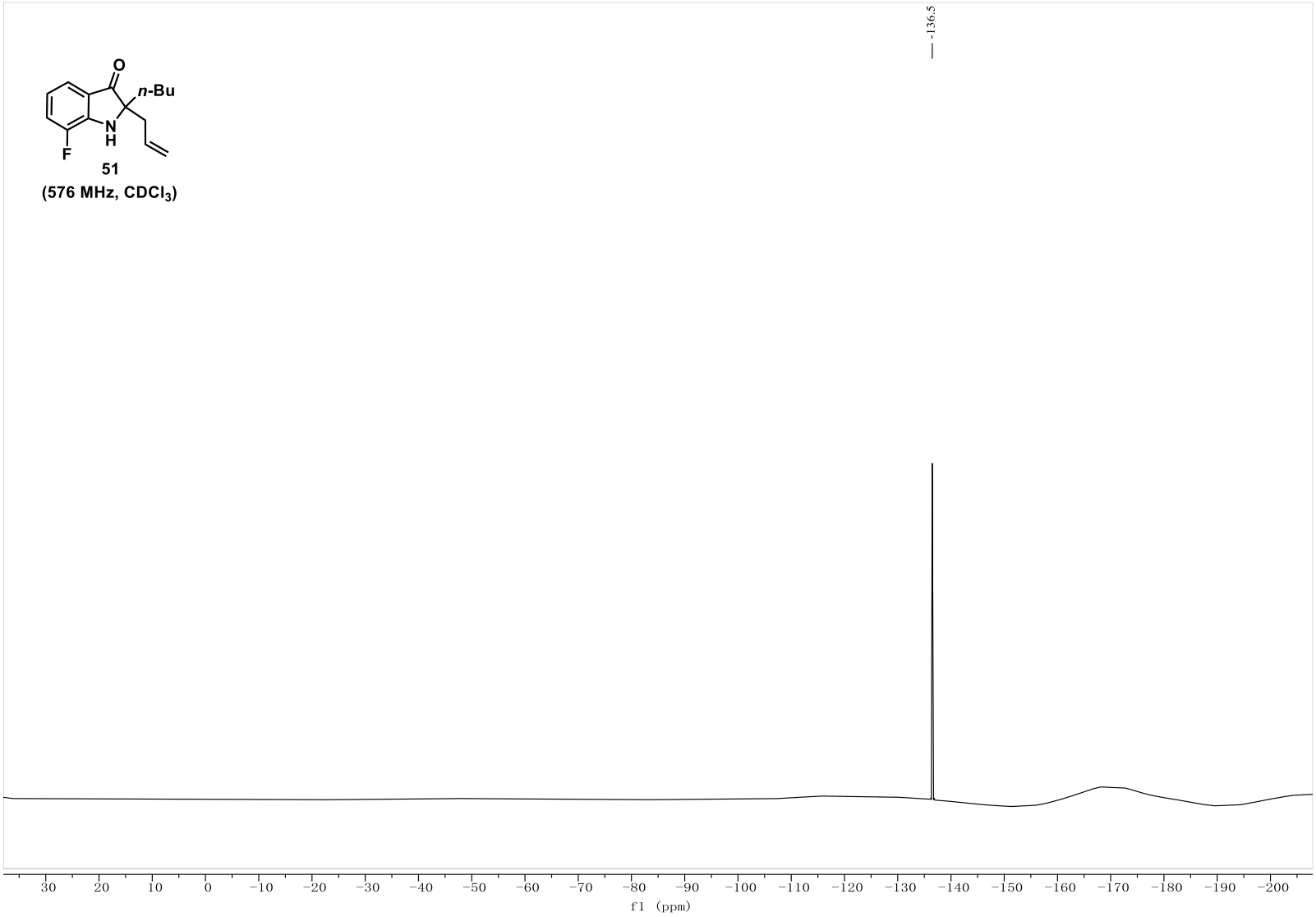

204.5
166.7
160.1
137.8
132.0
124.5
124.3
119.7
119.4
113.6
77.4
77.2
76.9
70.5
52.7
42.0
36.7
25.5
23.1
14.0
O
n-Bu
MeO2C
N
H
49
(151 MHz, CDCl3)
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

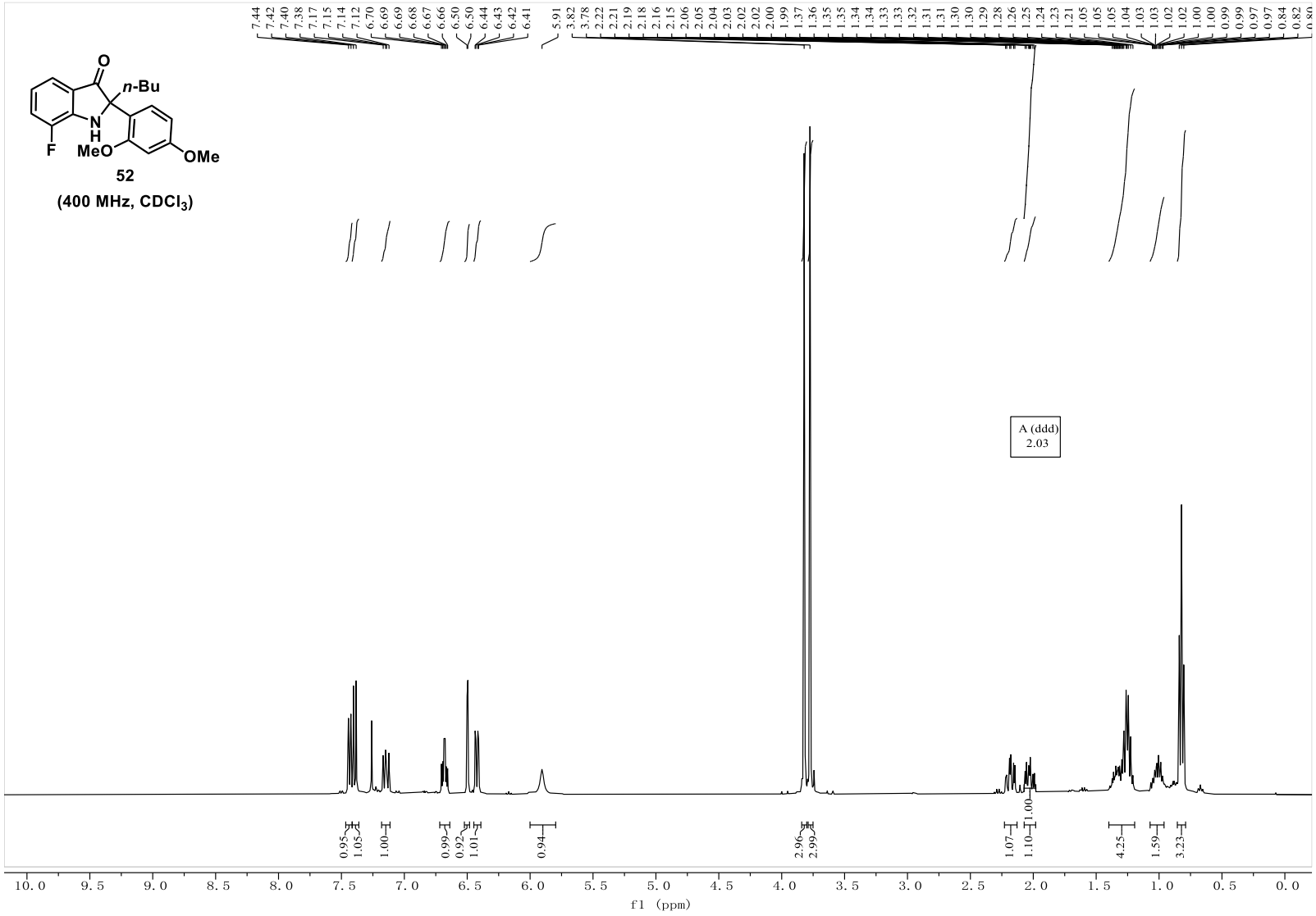

MeO2C
n-Bu
N
H
MeO
OMe
50
(400 MHz, CDCl3)
f1 (ppm)

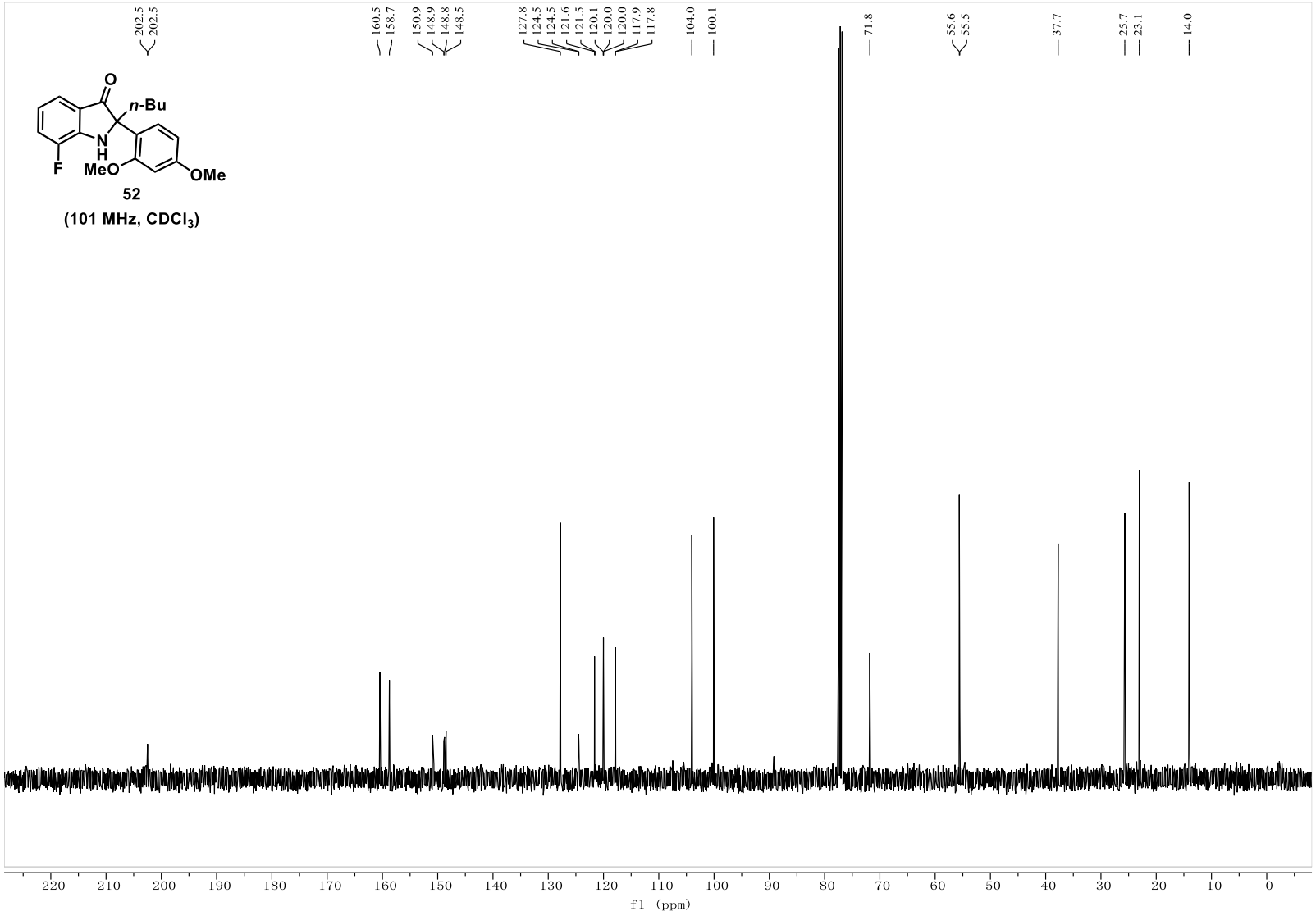

203.3
166.9
160.4
159.7
158.7
137.6
127.8
124.4
124.3
120.1
118.7
113.3
104.0
100.1
77.4
77.2
76.9
71.6
55.6
55.6
52.6
37.8
25.7
23.1
14.1
O
n-Bu
MeO2C
N
H
MeO
OMe
50
(151 MHz, CDCl3)
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

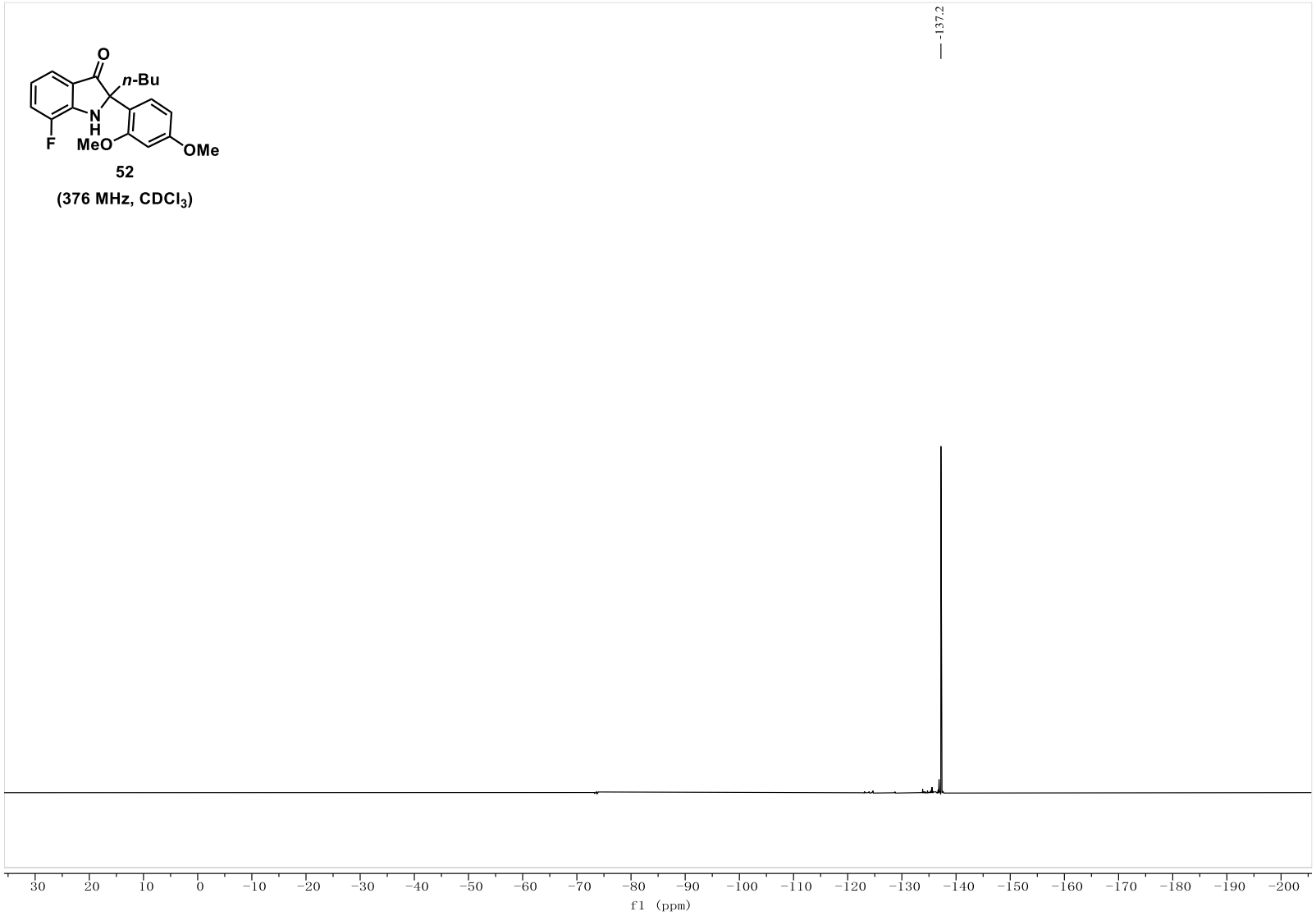

O
n-Bu
N
H
F
51
(400 MHz, CDCl3)
0.94
0.99
1.00
0.99
2.12
1.01
2.24
1.08
1.18
3.60
1.18
3.13
f1 (ppm)


203.8
203.8
150.7
149.1
149.0
148.9
131.9
124.6
124.6
121.8
121.7
120.1
120.0
119.7
118.7
118.7
77.4
77.2
76.9
70.5
41.9
36.6
25.4
23.0
14.0
O
n-Bu
N
H
F
51
(151 MHz, CDCl3)
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


O
n-Bu
N
H
F
51
(576 MHz, CDCl3)
-136.5
30 20 10 0 −10 −20 −30 −40 −50 −60 −70 −80 −90 −100 −110 −120 −130 −140 −150 −160 −170 −180 −190 −200
f1 (ppm)

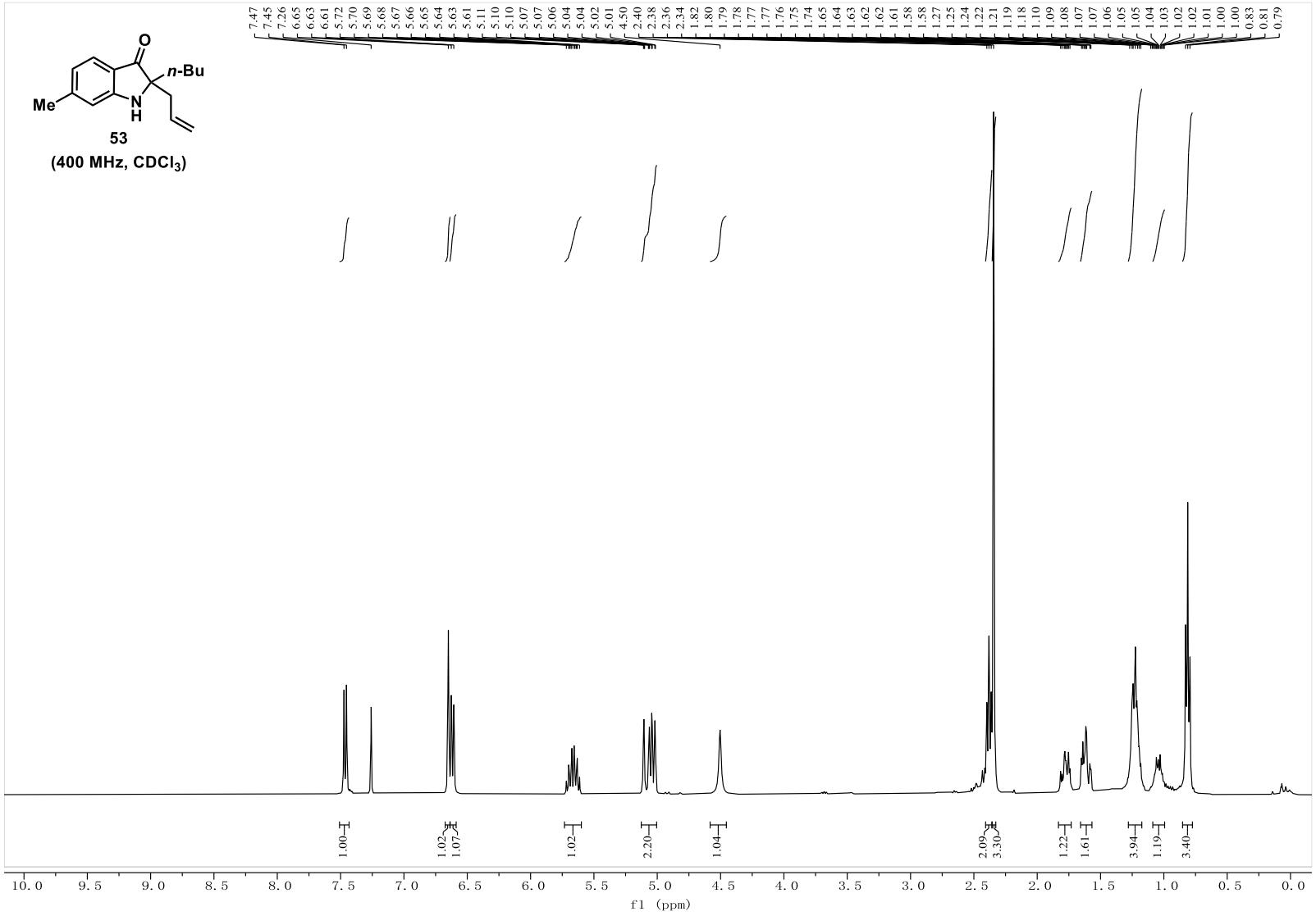

O
n-Bu
N
H
F
MeO
OMe
52
(400 MHz, CDCl3)
A (ddd)
2.03
f1 (ppm)

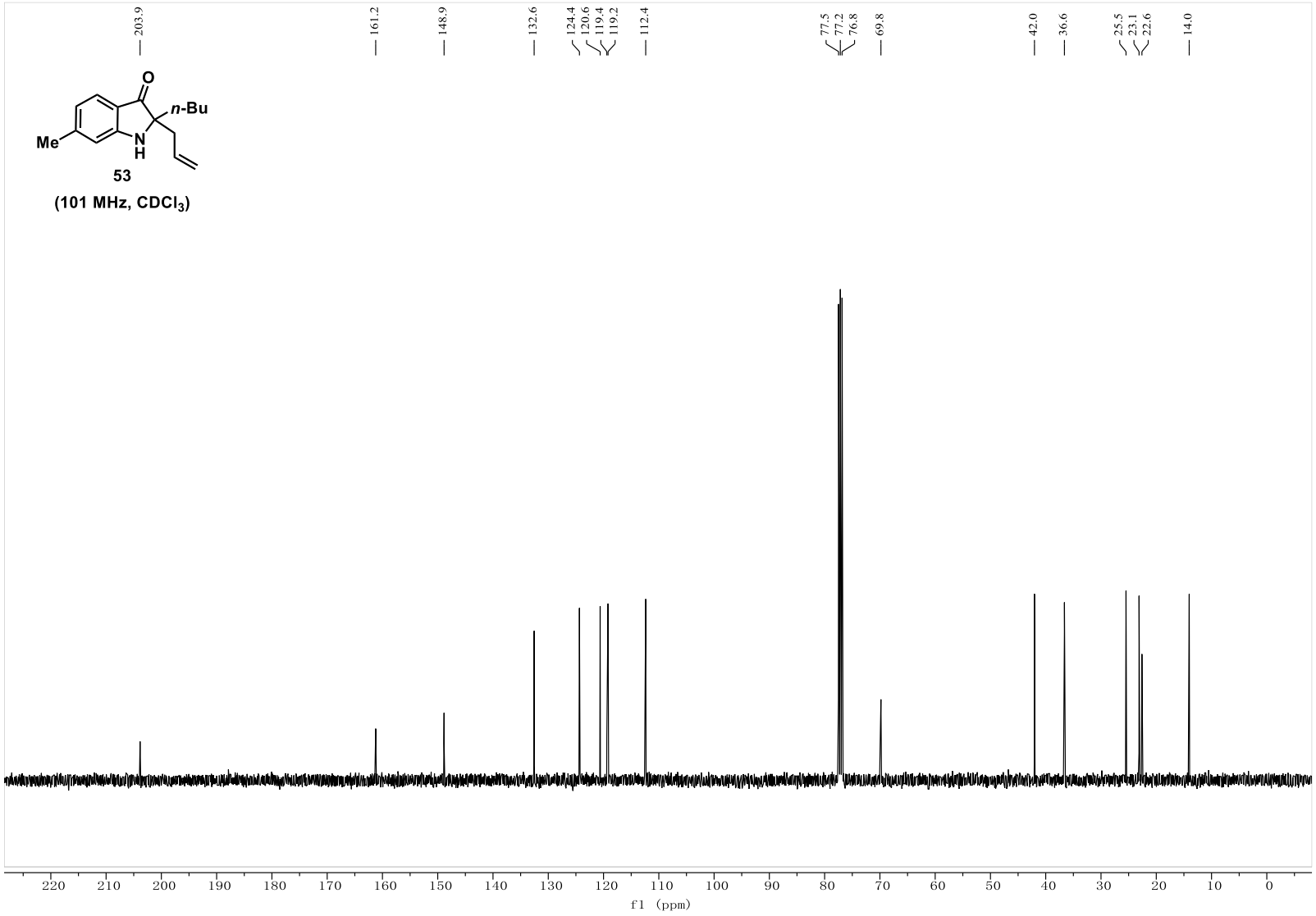

202.5
202.5
160.5
158.7
150.9
148.9
148.8
148.5
127.8
124.5
124.5
121.6
121.5
120.1
120.0
120.0
117.9
117.8
104.0
100.1
71.8
55.6
55.5
37.7
25.7
23.1
14.0
O
n-Bu
N
H
F
MeO
OMe
52
(101 MHz, CDCl3)
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

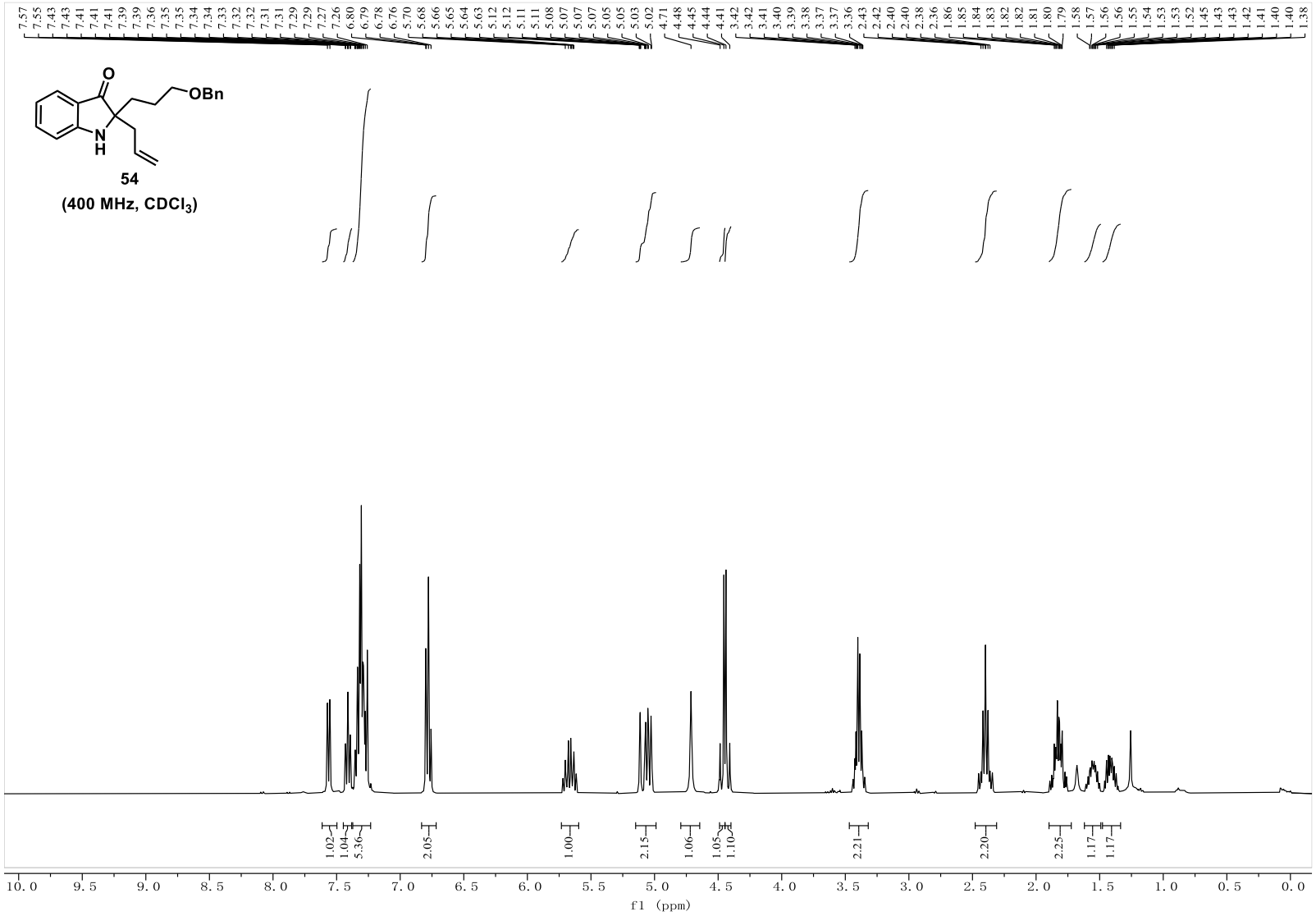


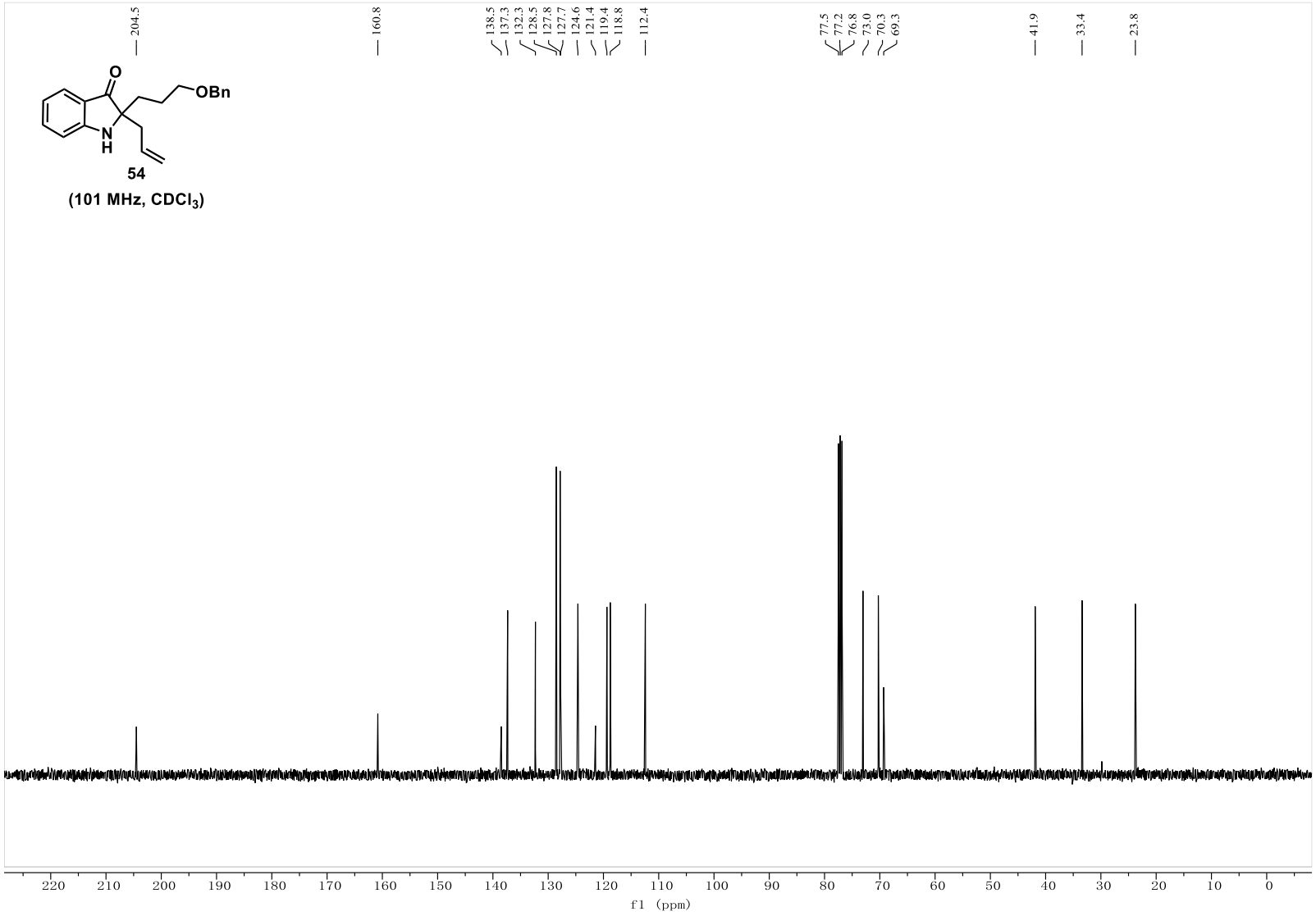
52

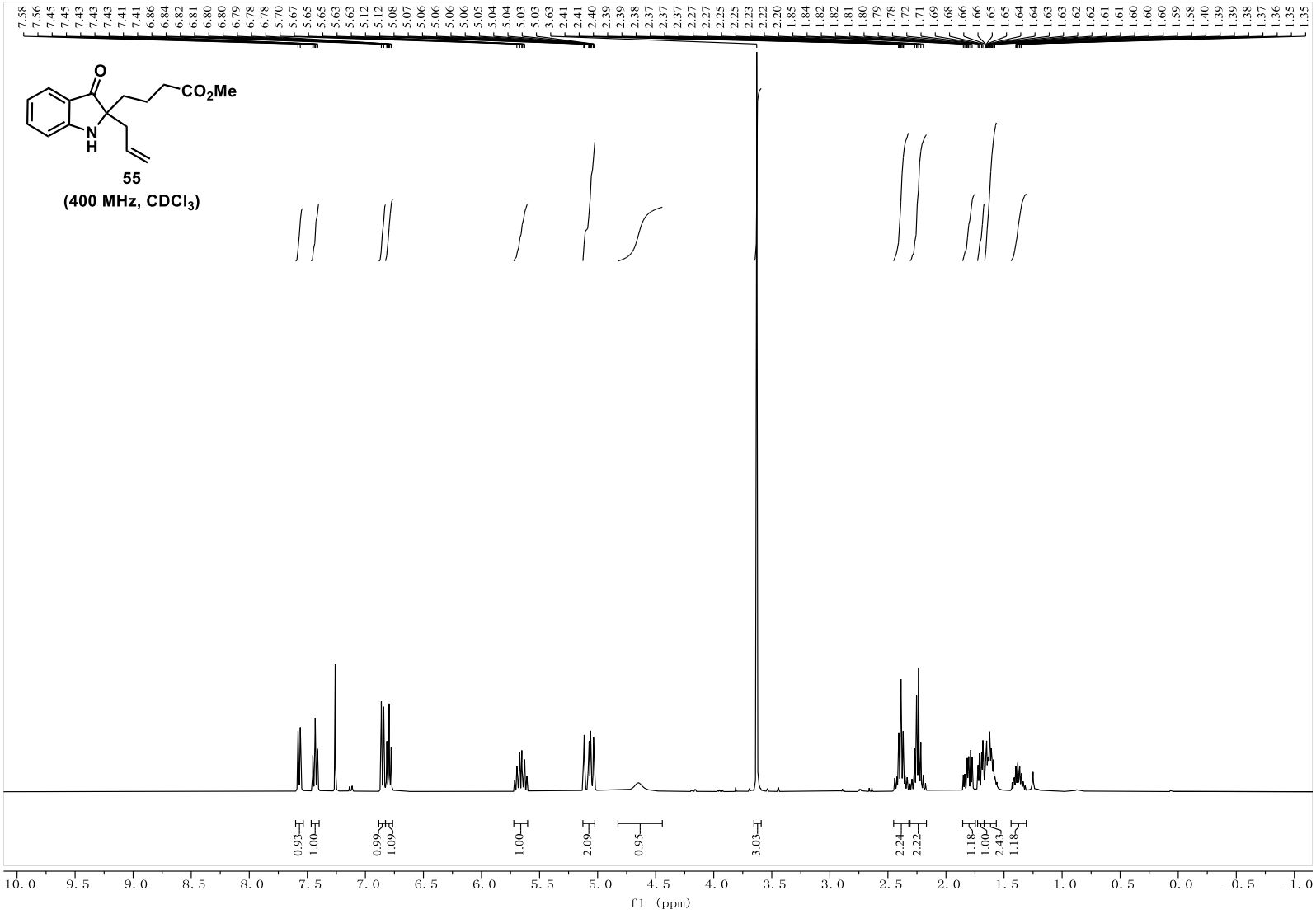
(376 MHz, $CDCl_3$)

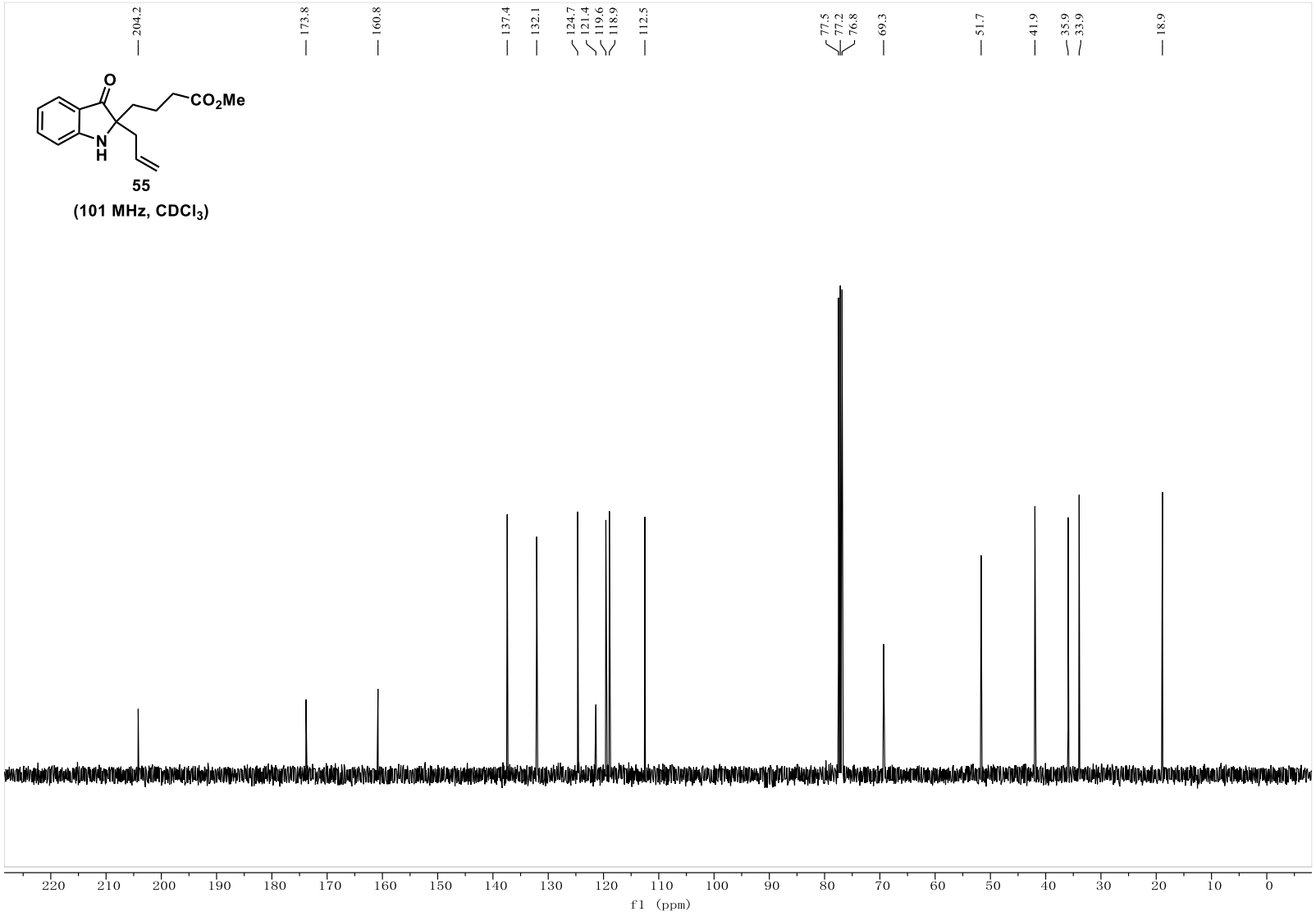

O
n-Bu
Me
N
H
53
(400 MHz, CDCl3)
7.47 7.45 7.26 6.65 6.63 6.61 5.72 5.70 5.69 5.68 5.67 5.66 5.65 5.64 5.63 5.61 5.11 5.10 5.10 5.07 5.07 5.06 5.04 5.04 5.02 5.01 4.50 2.40 2.38 2.36 2.34 1.82 1.80 1.79 1.78 1.77 1.77 1.76 1.75 1.74 1.65 1.64 1.63 1.62 1.62 1.61 1.58 1.58 1.27 1.25 1.24 1.22 1.21 1.19 1.18 1.10 1.09 1.08 1.07 1.07 1.06 1.05 1.05 1.04 1.03 1.02 1.02 1.01 1.00 1.00 0.83 0.81 0.79
1.00 1.02 1.07 1.02 2.20 1.04 2.09 3.30 1.22 1.61 3.94 1.19 3.40
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
f1 (ppm)

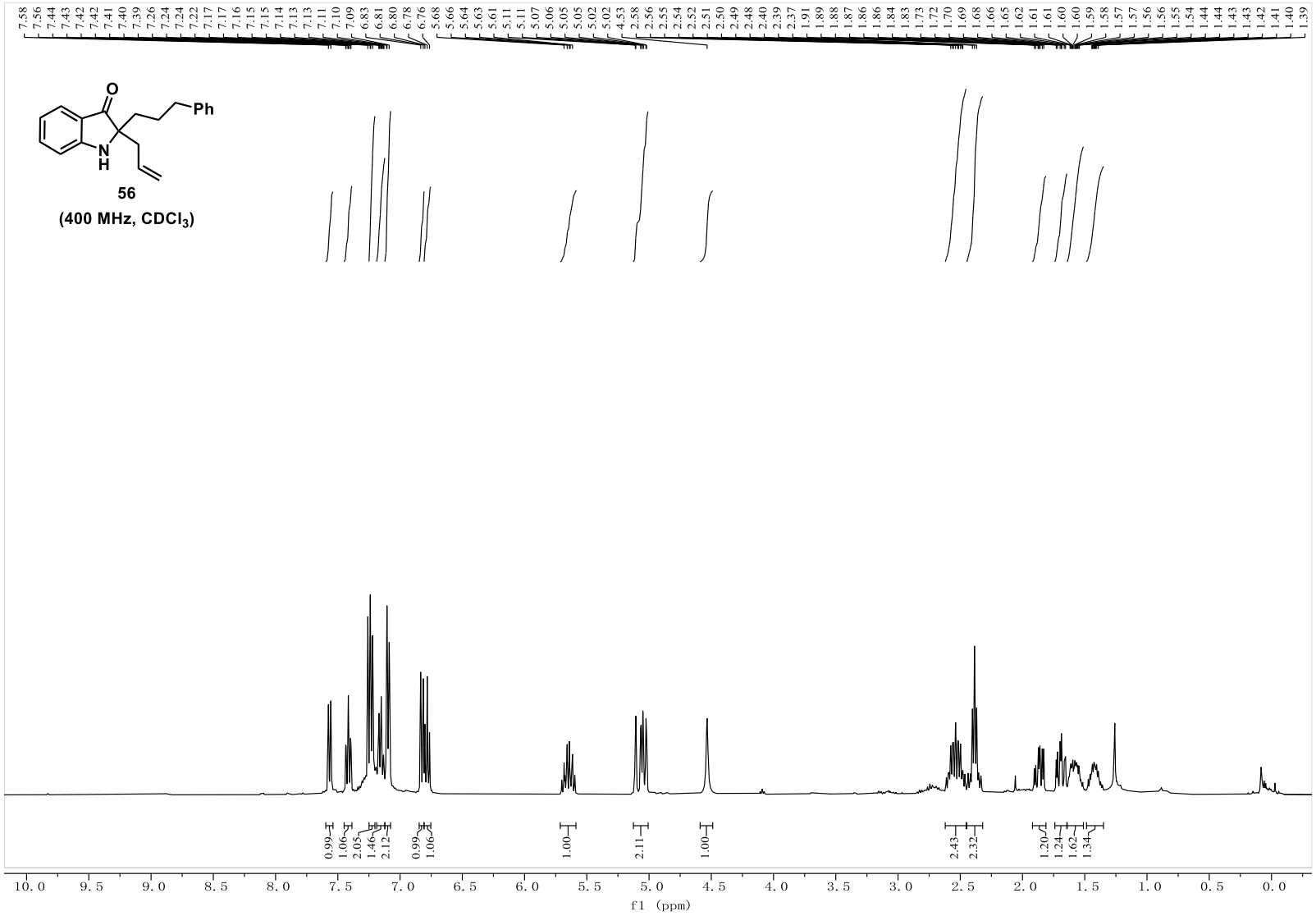

203.9
161.2
148.9
132.6
124.4
120.6
119.4
119.2
112.4
77.5
77.2
76.8
69.8
42.0
36.6
25.5
23.1
22.6
14.0
O
n-Bu
Me
N
H
53
(101 MHz, CDCl3)
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

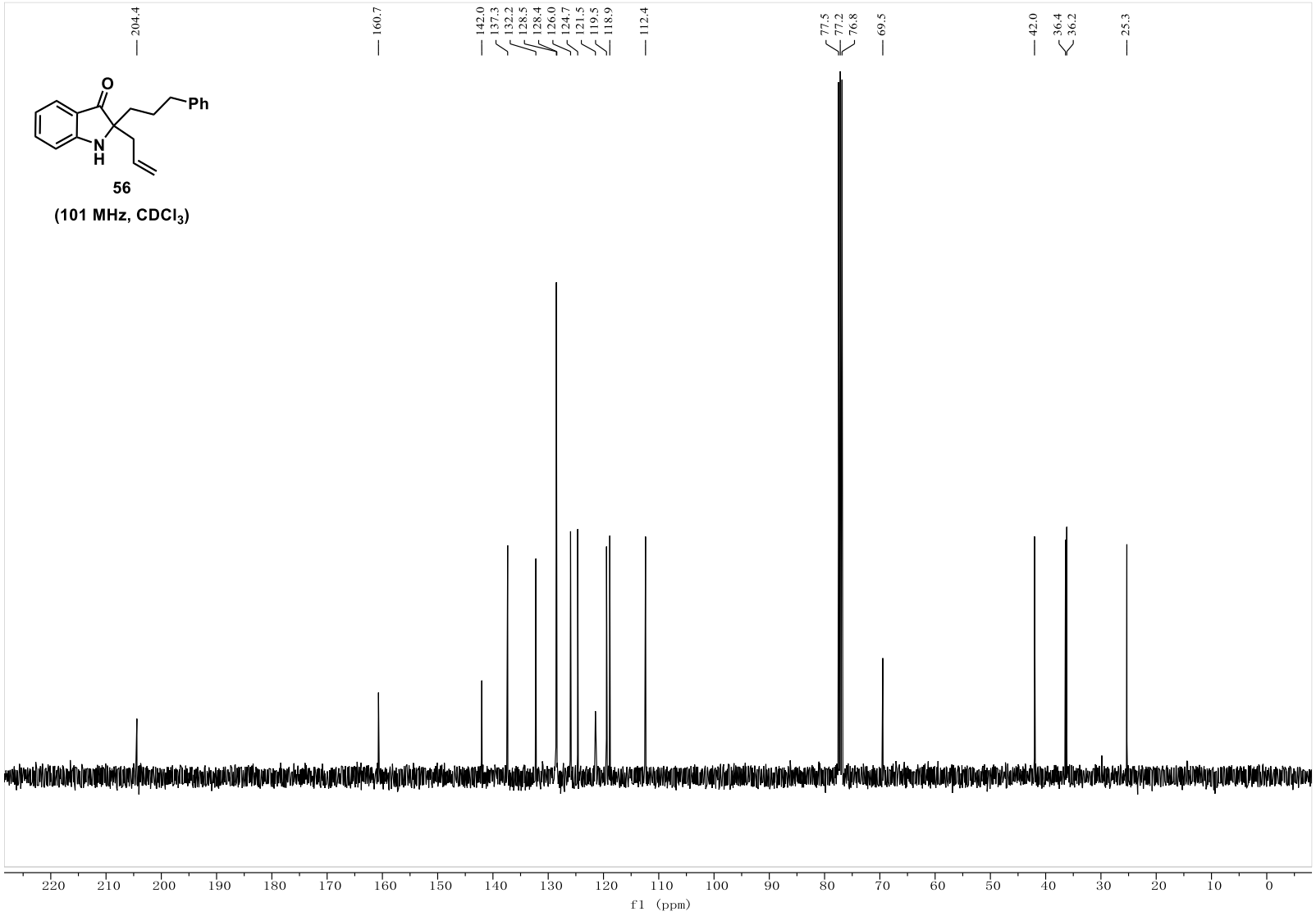

O
OBn
N
H
54
(400 MHz, CDCl3)
f1 (ppm)

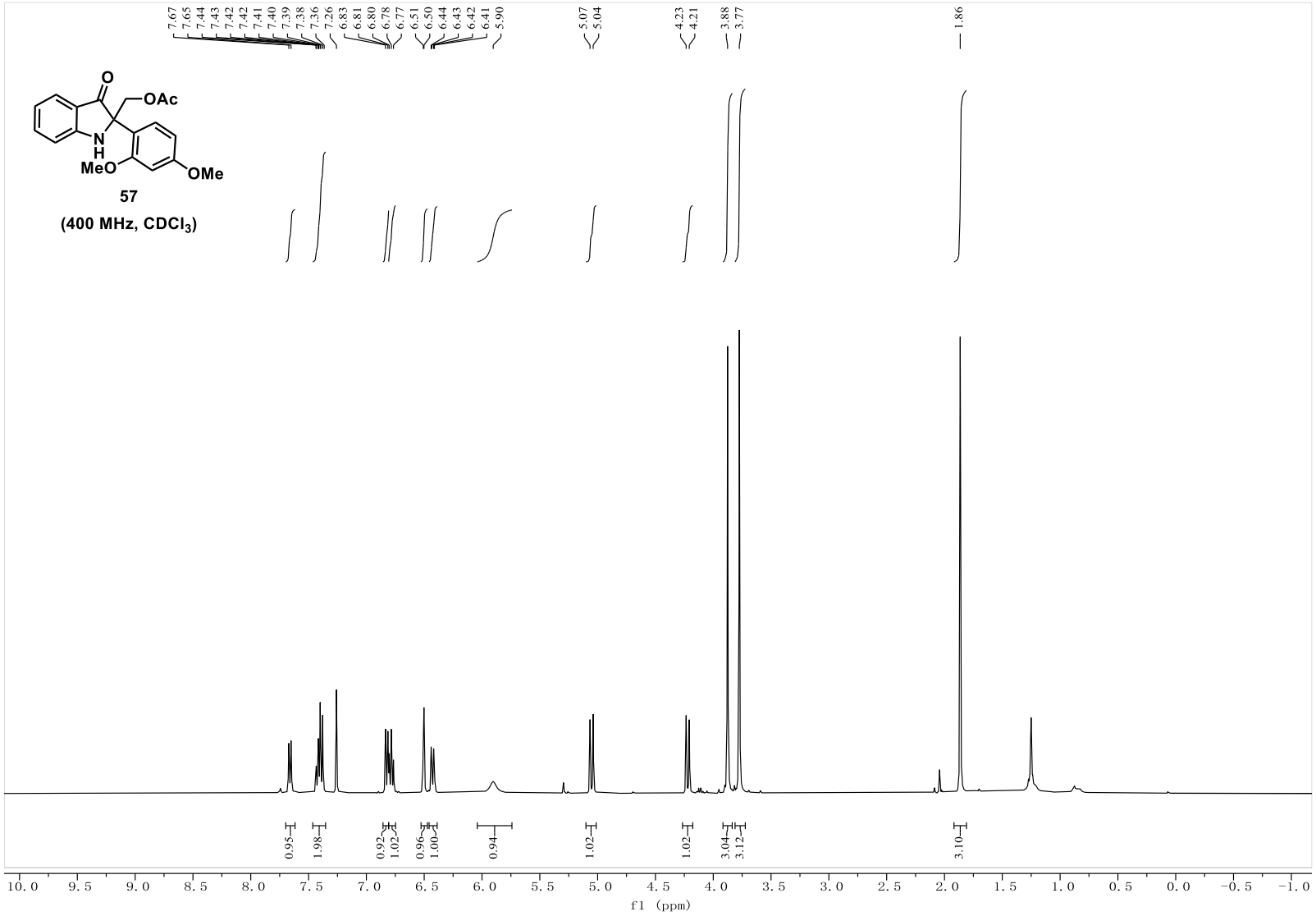

204.5
160.8
138.5
137.3
132.3
128.5
127.8
127.7
124.6
121.4
119.4
118.8
112.4
77.5
77.2
76.8
73.0
70.3
69.3
41.9
33.4
23.8
O
OBn
N
H
54
(101 MHz, CDCl3)
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

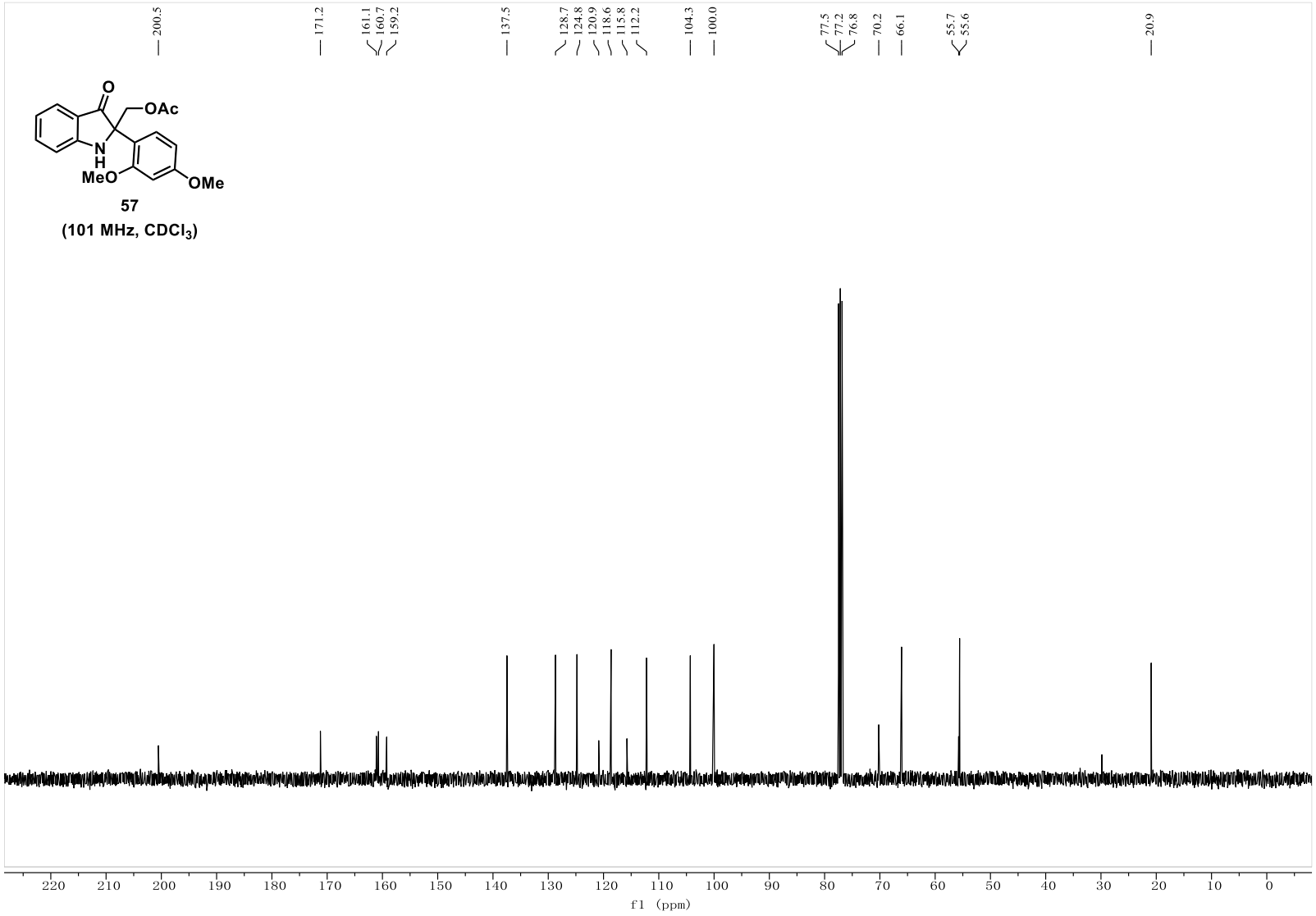

O
CO2Me
N
H
55
(400 MHz, CDCl3)
f1 (ppm)

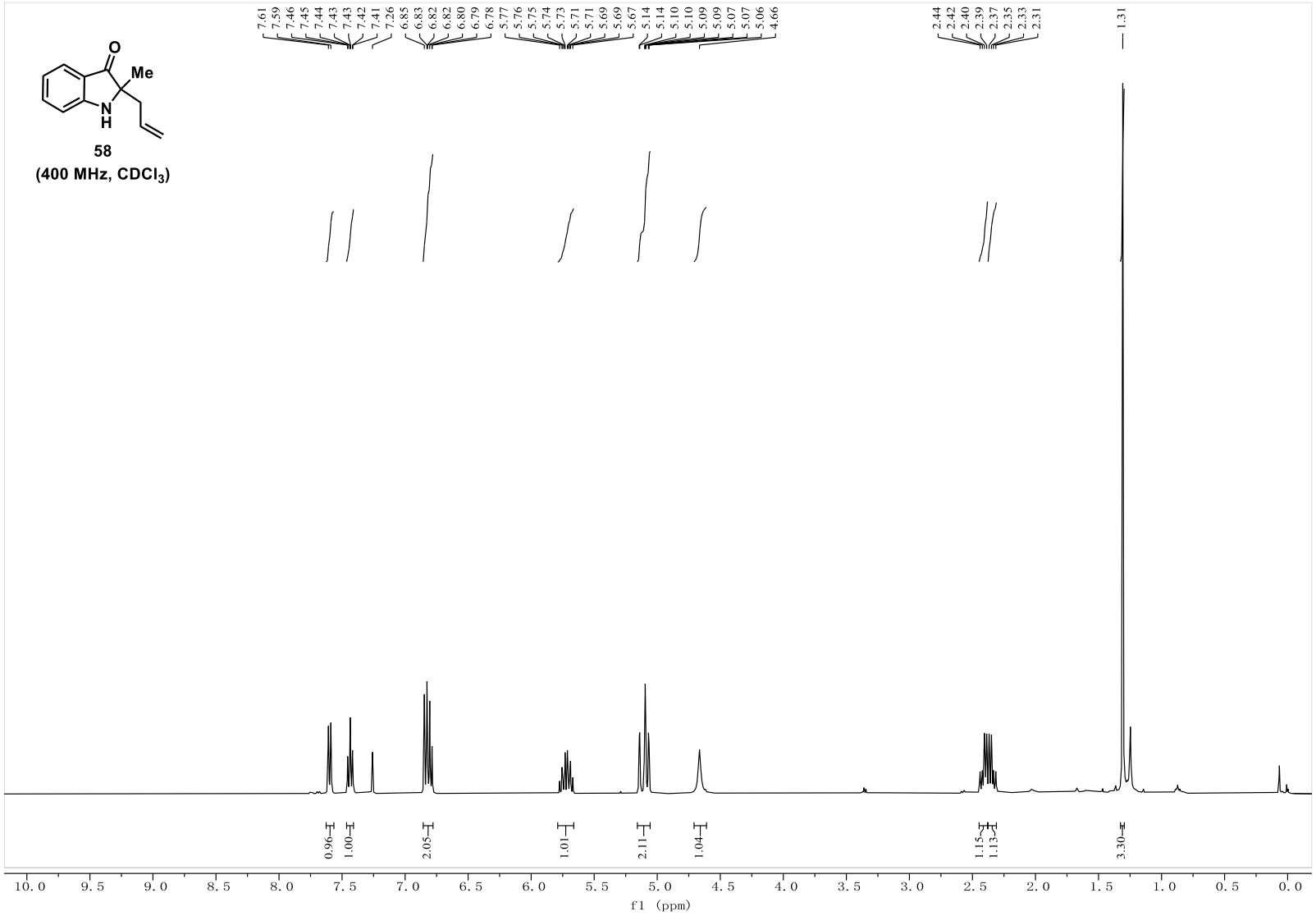

204.2
173.8
160.8
137.4
132.1
124.7
121.4
119.6
118.9
112.5
77.5
77.2
76.8
69.3
51.7
41.9
35.9
33.9
18.9
O
CO2Me
N
H
55
(101 MHz, CDCl3)
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

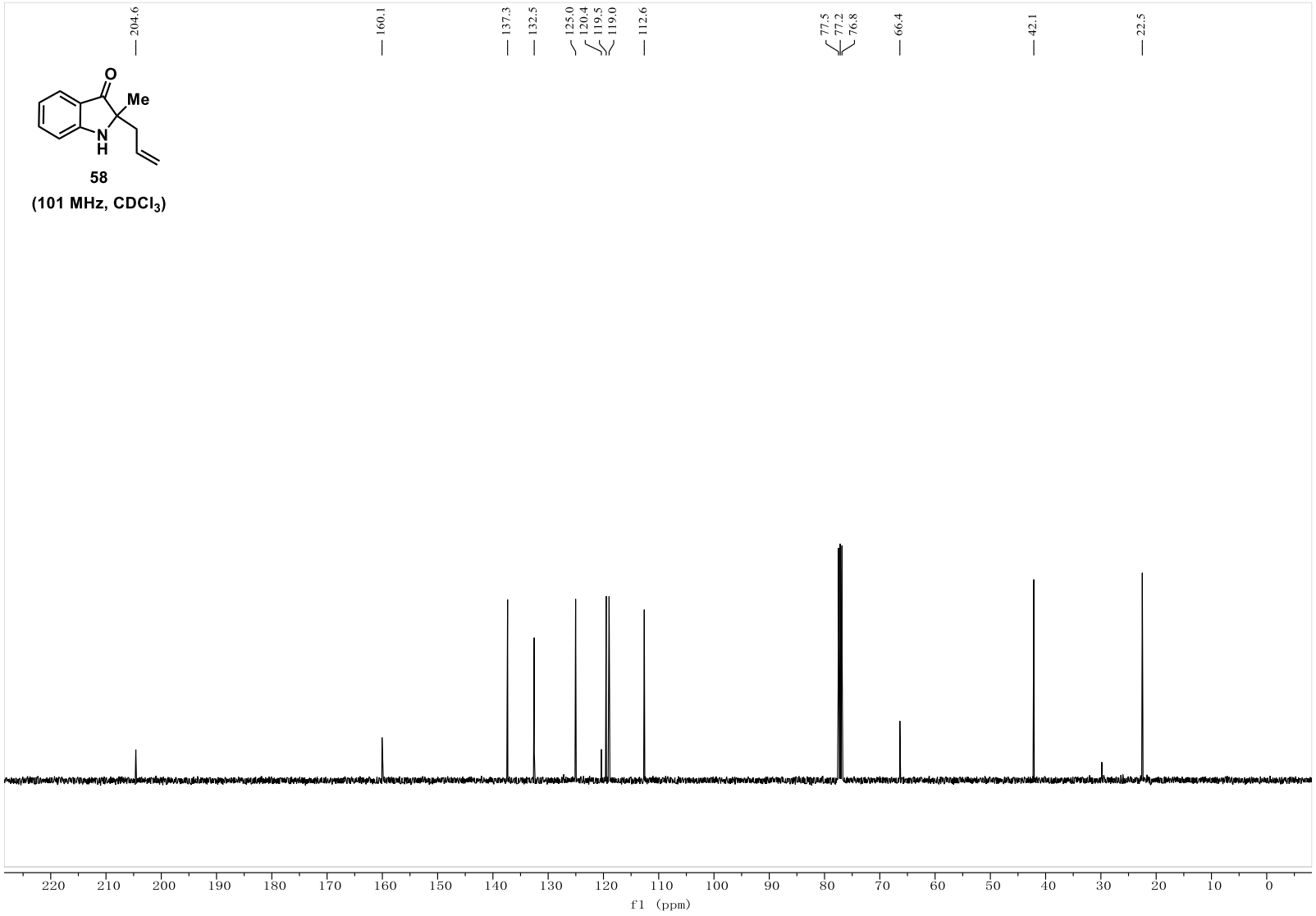

O
Ph
N
H
56
(400 MHz, CDCl3)
f1 (ppm)

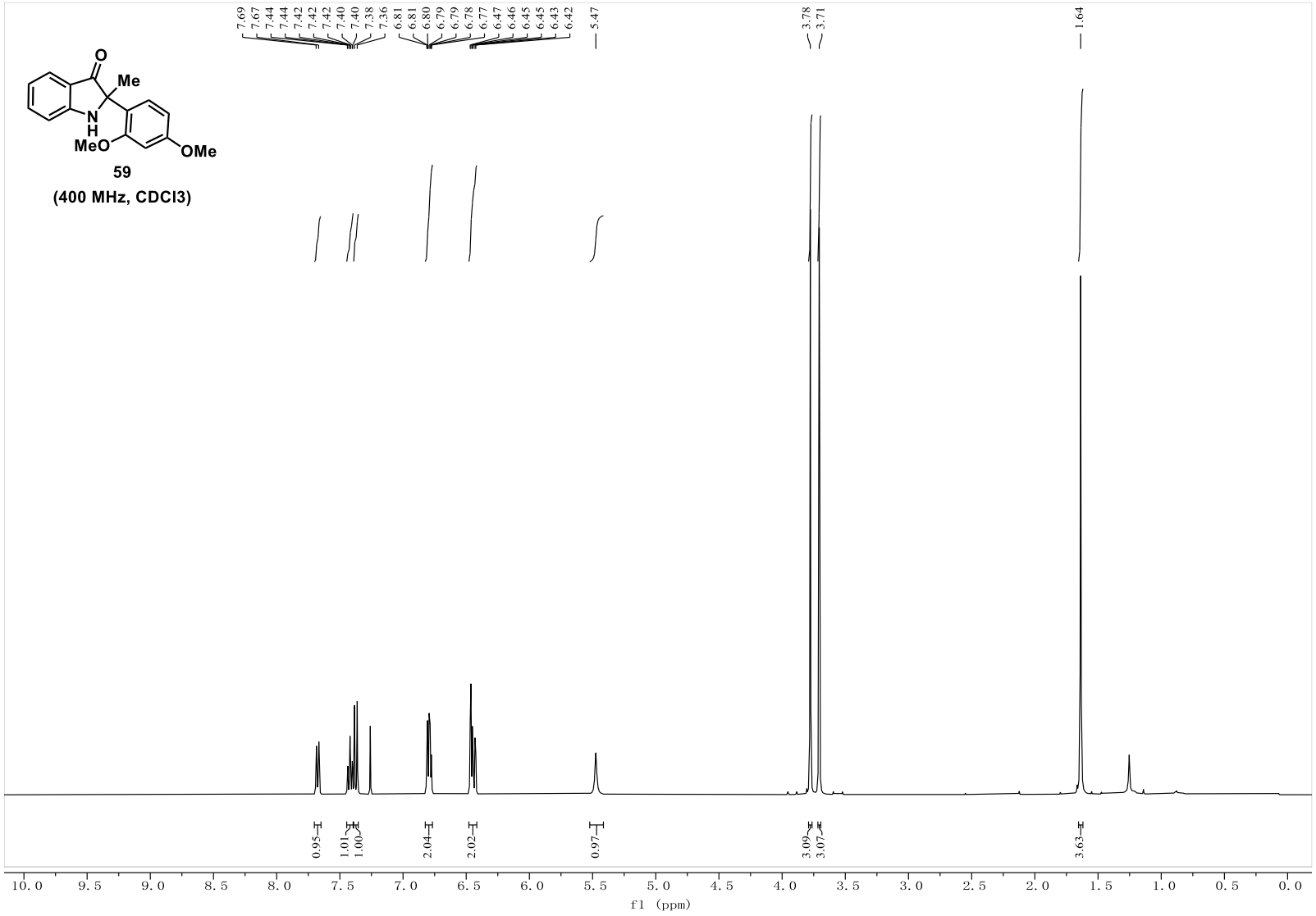

204.4
160.7
142.0
137.3
132.2
128.5
128.4
126.0
124.7
121.5
119.5
118.9
112.4
77.5
77.2
76.8
69.5
42.0
36.4
36.2
25.3
O
Ph
N
H
56
(101 MHz, CDCl3)
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

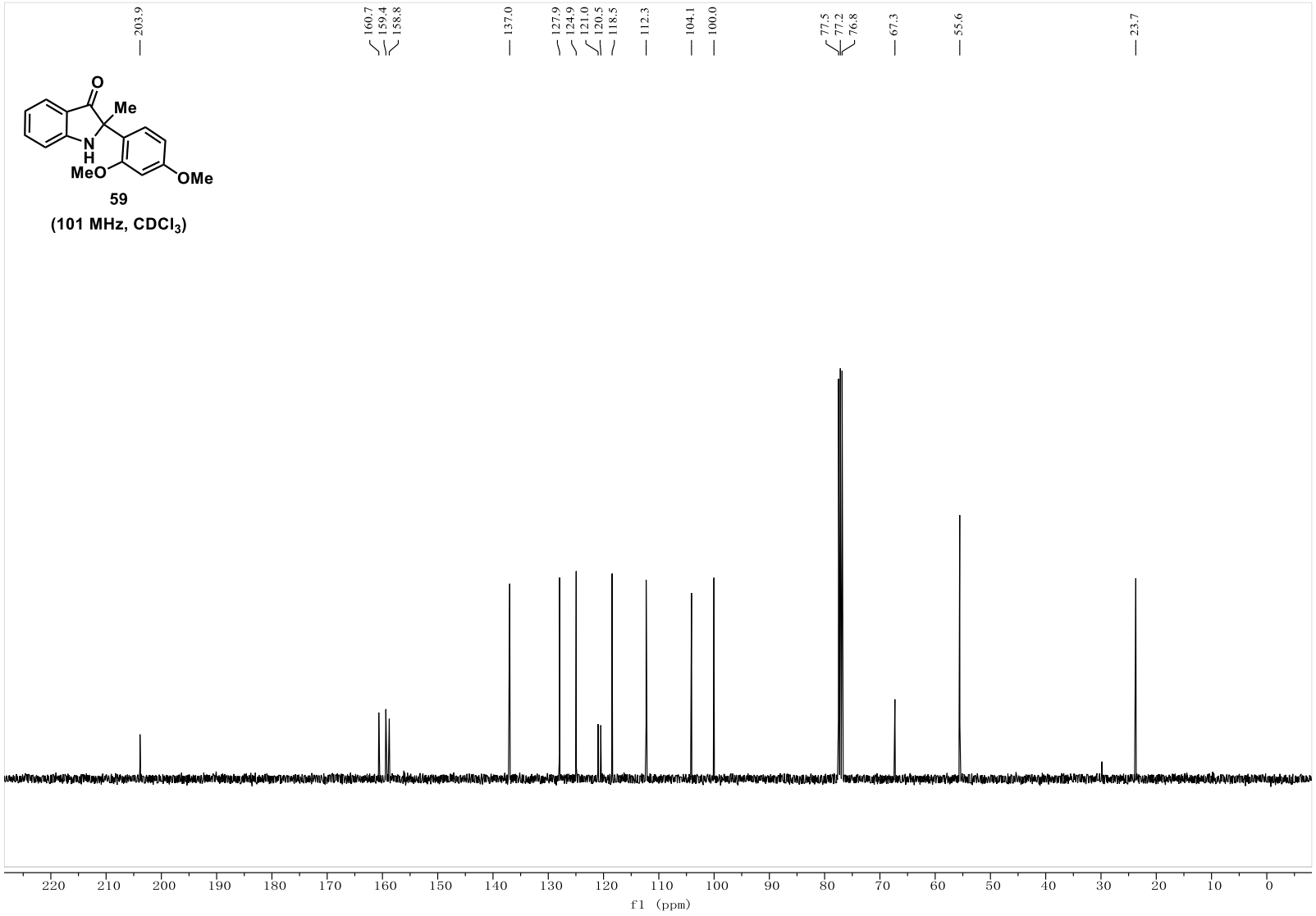

7.67
7.65
7.44
7.43
7.42
7.42
7.41
7.40
7.39
7.38
7.36
7.26
6.83
6.81
6.80
6.78
6.77
6.51
6.50
6.44
6.43
6.42
6.41
5.90
5.07
5.04
4.23
4.21
3.88
3.77
1.86
O
OAc
N
H
MeO
OMe
57
(400 MHz, CDCl3)
0.95
1.98
0.92
1.02
0.96
1.00
0.94
1.02
1.02
3.04
3.12
3.10
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5 −1.0
f1 (ppm)

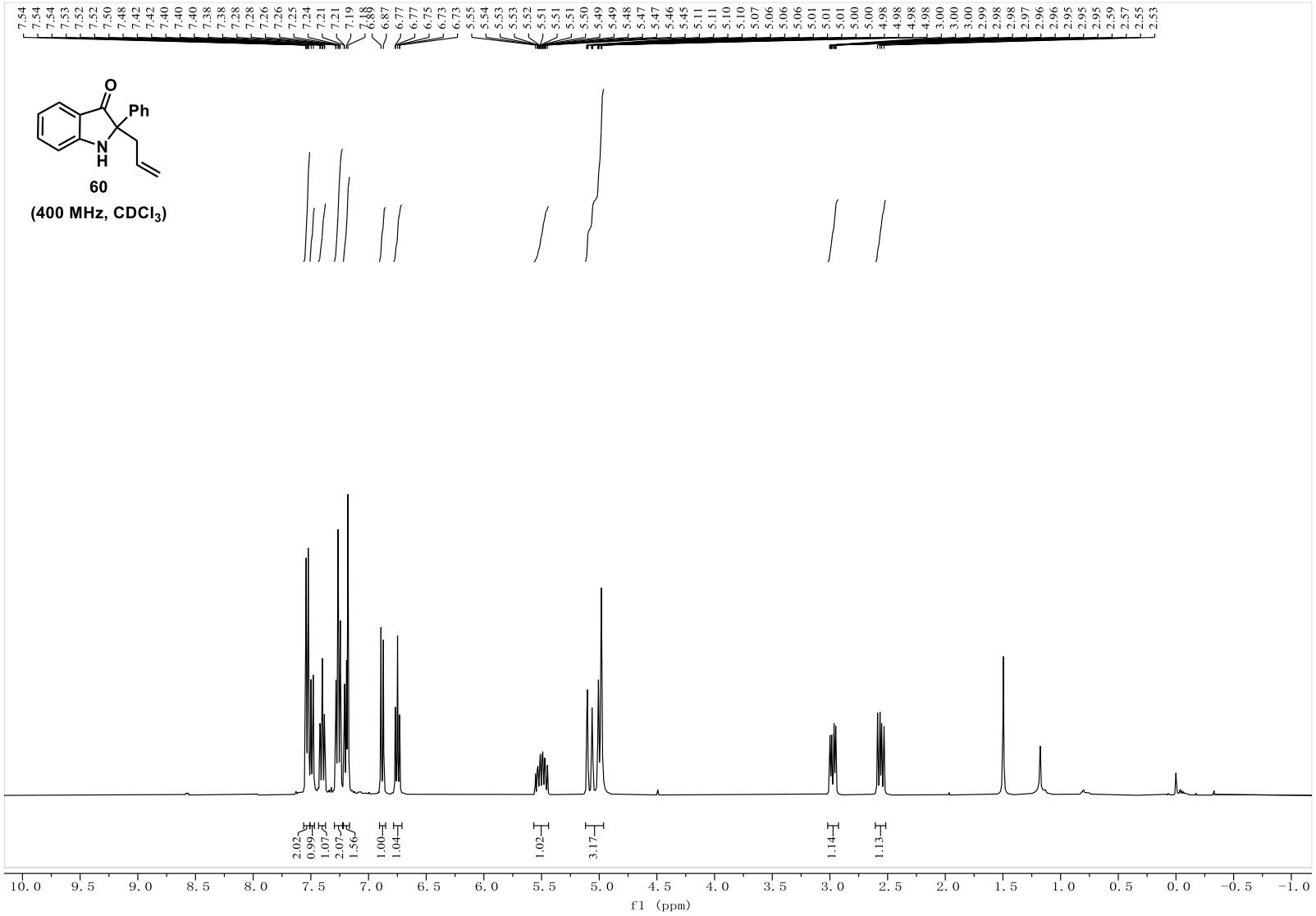

200.5
171.2
161.1
160.7
159.2
137.5
128.7
124.8
120.9
118.6
115.8
112.2
104.3
100.0
77.5
77.2
76.8
70.2
66.1
55.7
55.6
20.9
O
OAc
N
H
MeO
OMe
57
(101 MHz, CDCl3)
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

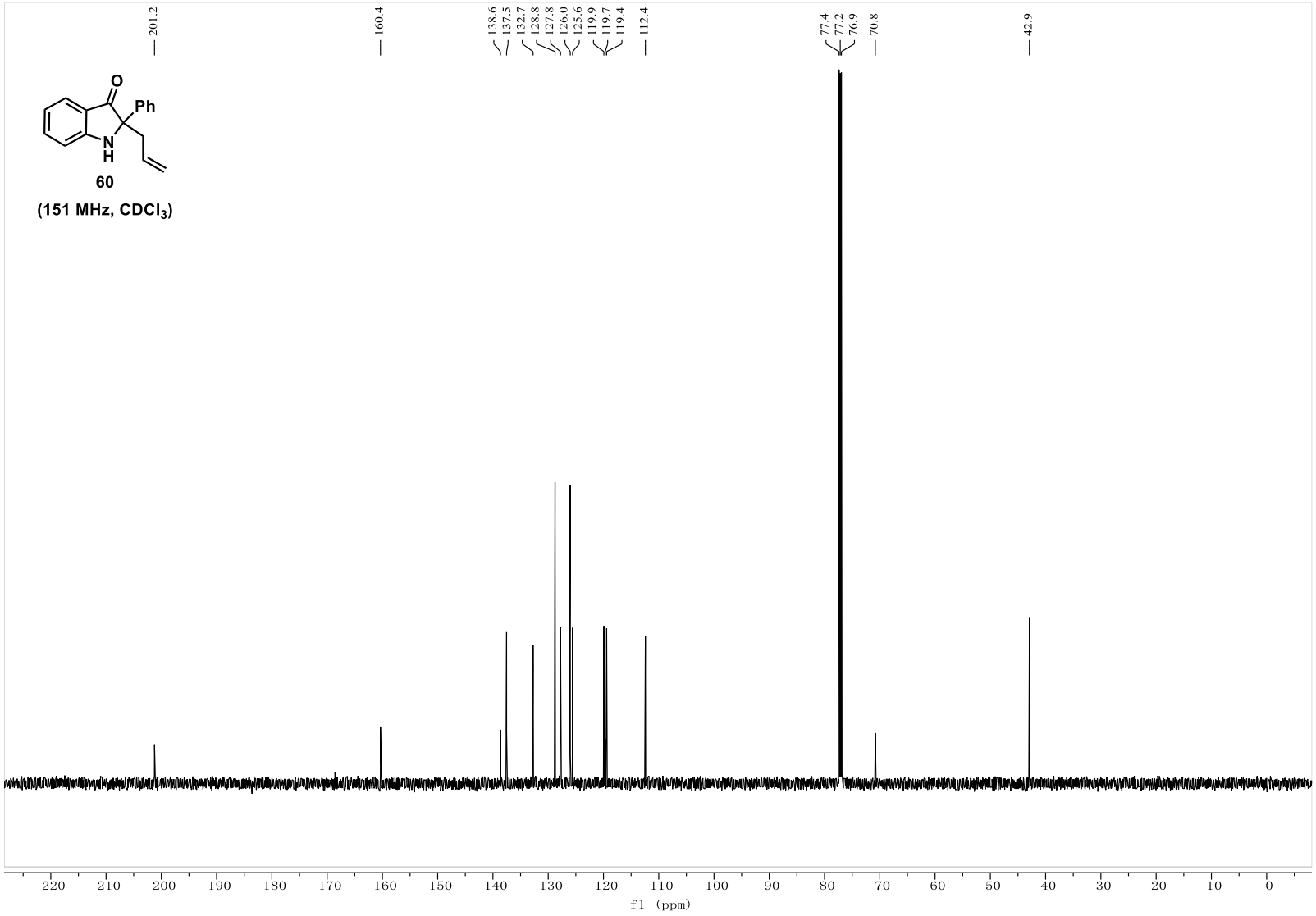

O
Me
N
H
58
(400 MHz, CDCl3)
7.61 7.59 7.46 7.45 7.44 7.43 7.43 7.42 7.41 7.26 6.85 6.83 6.82 6.82 6.80 6.79 6.78 5.77 5.76 5.75 5.74 5.73 5.71 5.71 5.69 5.69 5.67 5.14 5.14 5.10 5.10 5.09 5.09 5.07 5.07 5.06 4.66
2.44 2.42 2.40 2.39 2.37 2.35 2.33 2.31
1.31
0.96 1.00 2.05 1.01 2.11 1.04 1.15 1.13 3.30
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
f1 (ppm)

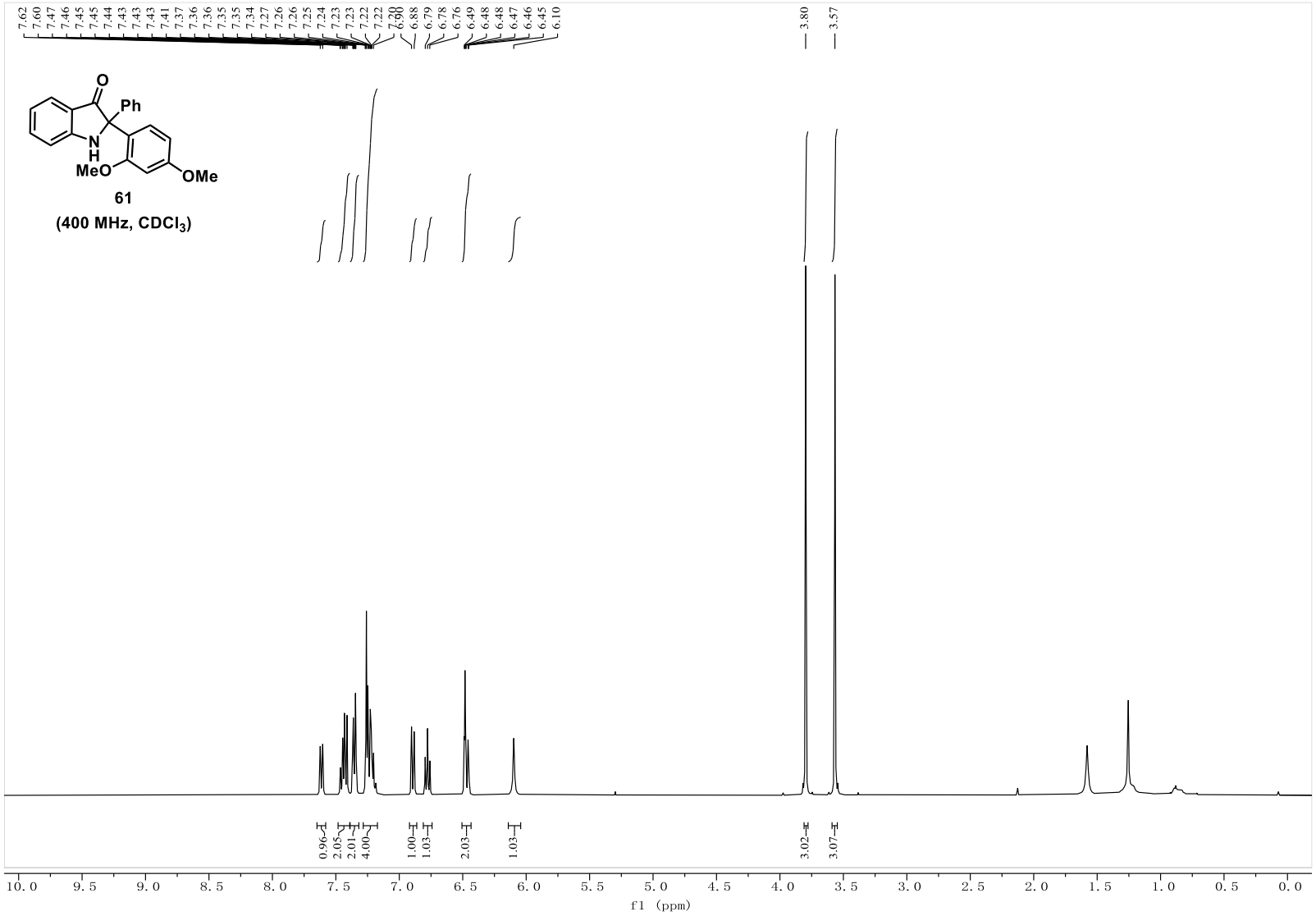

204.6
160.1
137.3
132.5
125.0
120.4
119.5
119.0
112.6
77.5
77.2
76.8
66.4
42.1
22.5
O
Me
N
H
58
(101 MHz, CDCl3)
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

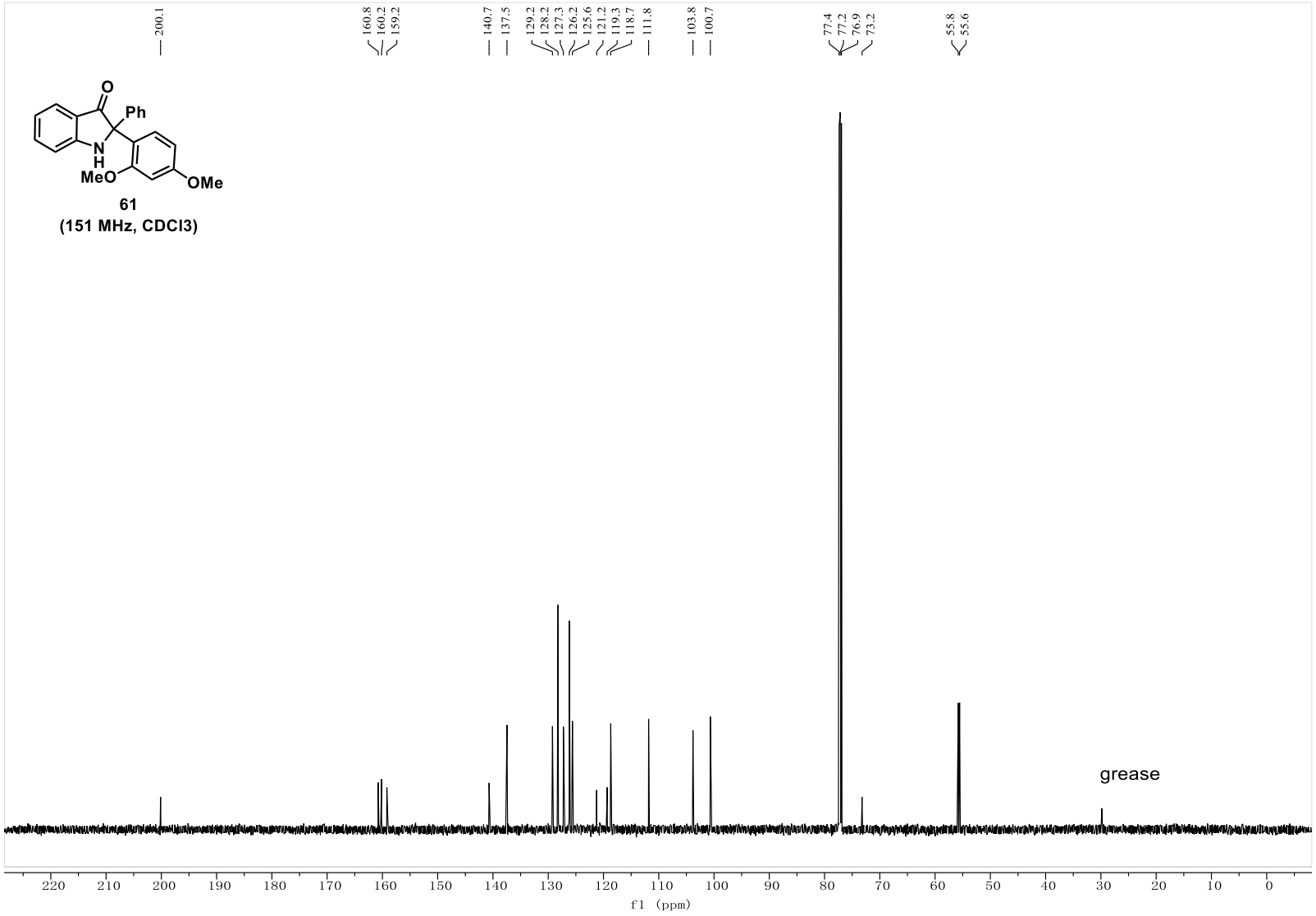

O
Me
N
H
MeO
OMe
59
(400 MHz, CDCl3)
7.69
7.67
7.44
7.44
7.42
7.42
7.42
7.40
7.40
7.38
7.36
6.81
6.81
6.80
6.79
6.79
6.78
6.77
6.47
6.46
6.45
6.45
6.43
6.42
5.47
3.78
3.71
1.64
0.95
1.01
1.00
2.04
2.02
0.97
3.09
3.07
3.63
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

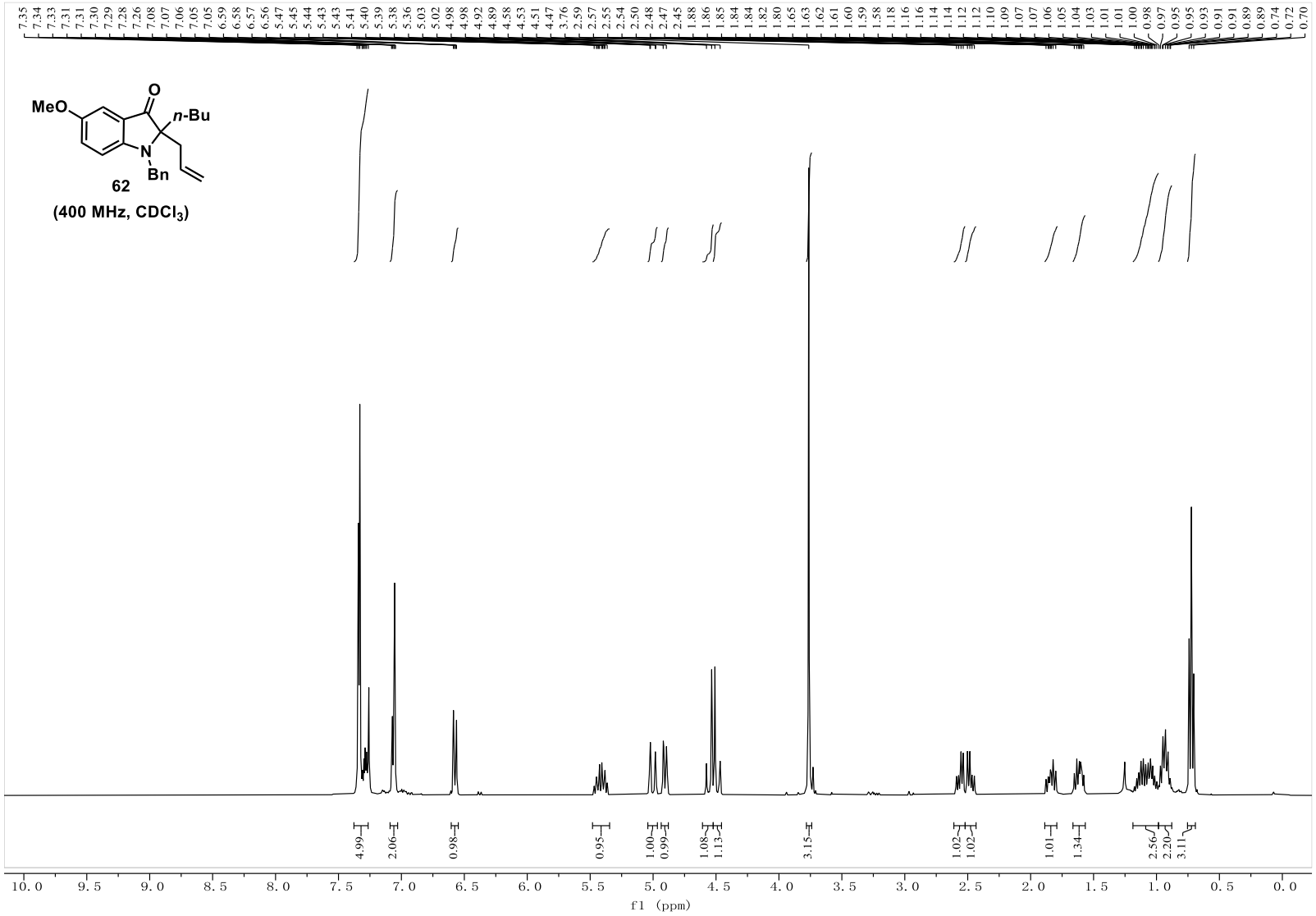

203.9
160.7
159.4
158.8
137.0
127.9
124.9
121.0
120.5
118.5
112.3
104.1
100.0
77.5
77.2
76.8
67.3
55.6
23.7
O
Me
N
H
MeO
OMe
59
(101 MHz, CDCl3)
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

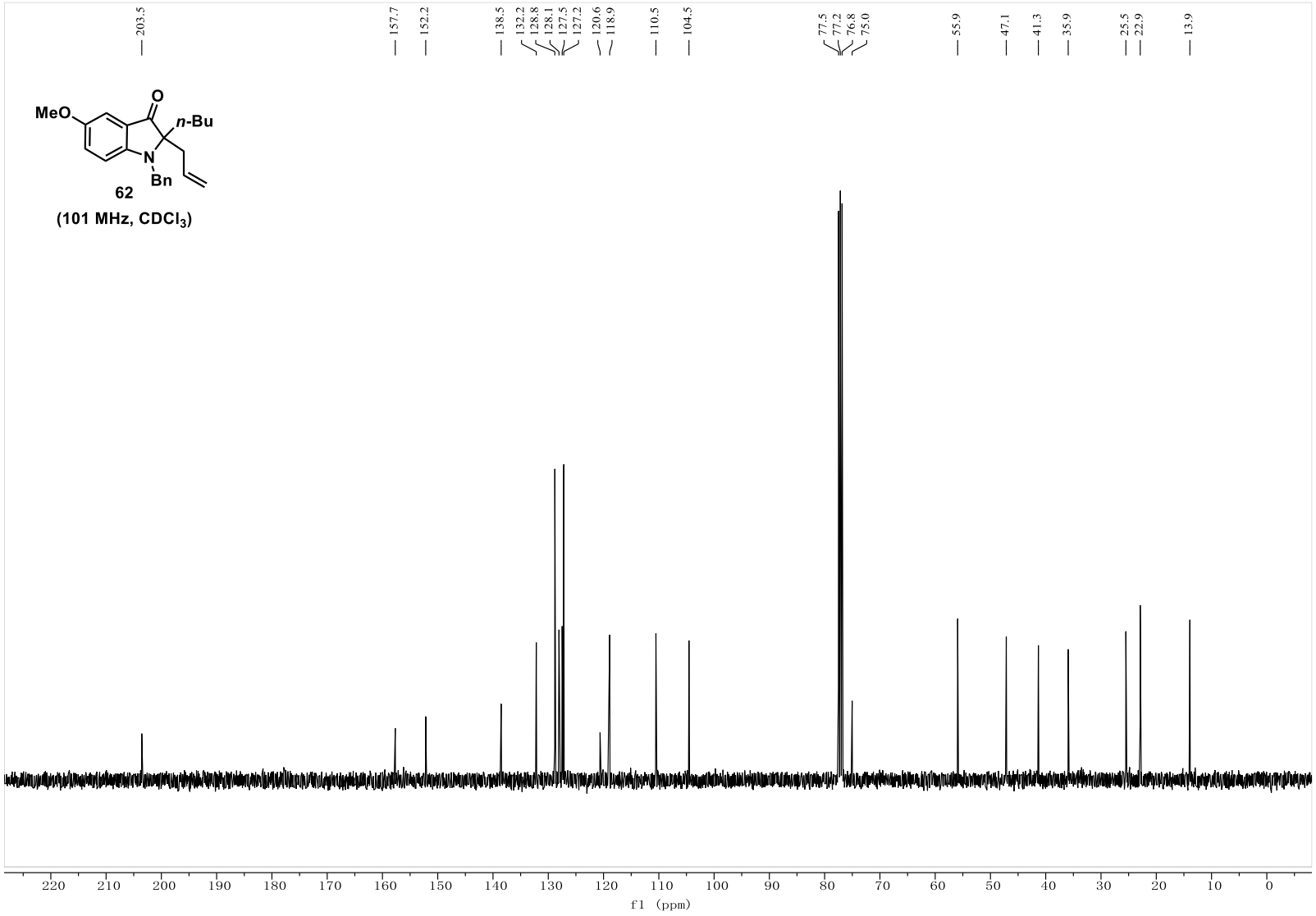

O
Ph
N
H
60
(400 MHz, CDCl3)
f1 (ppm)

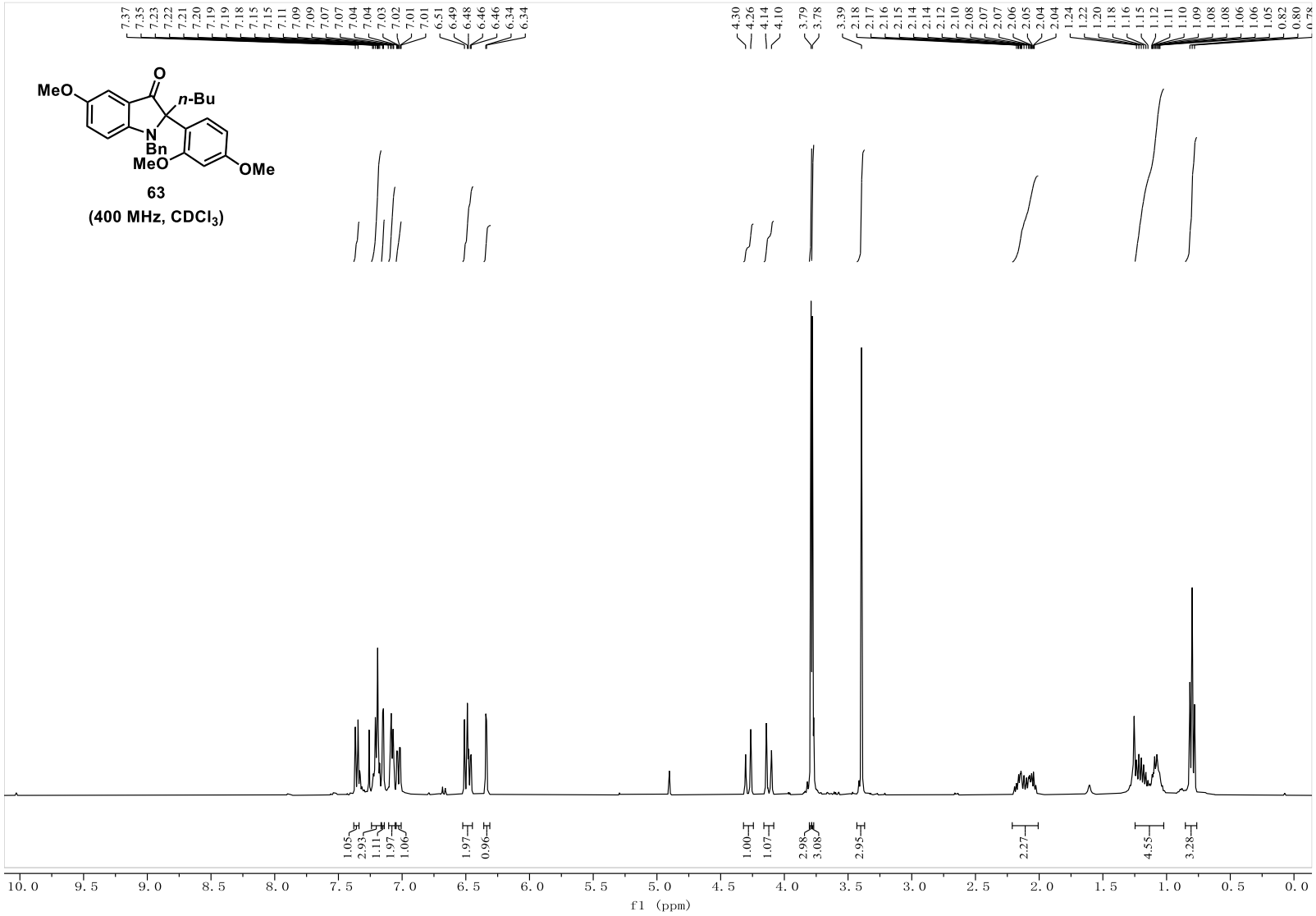

201.2
160.4
138.6
137.5
132.7
128.8
127.8
126.0
125.6
119.9
119.7
119.4
112.4
77.4
77.2
76.9
70.8
42.9
O
Ph
N
H
60
(151 MHz, CDCl3)
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

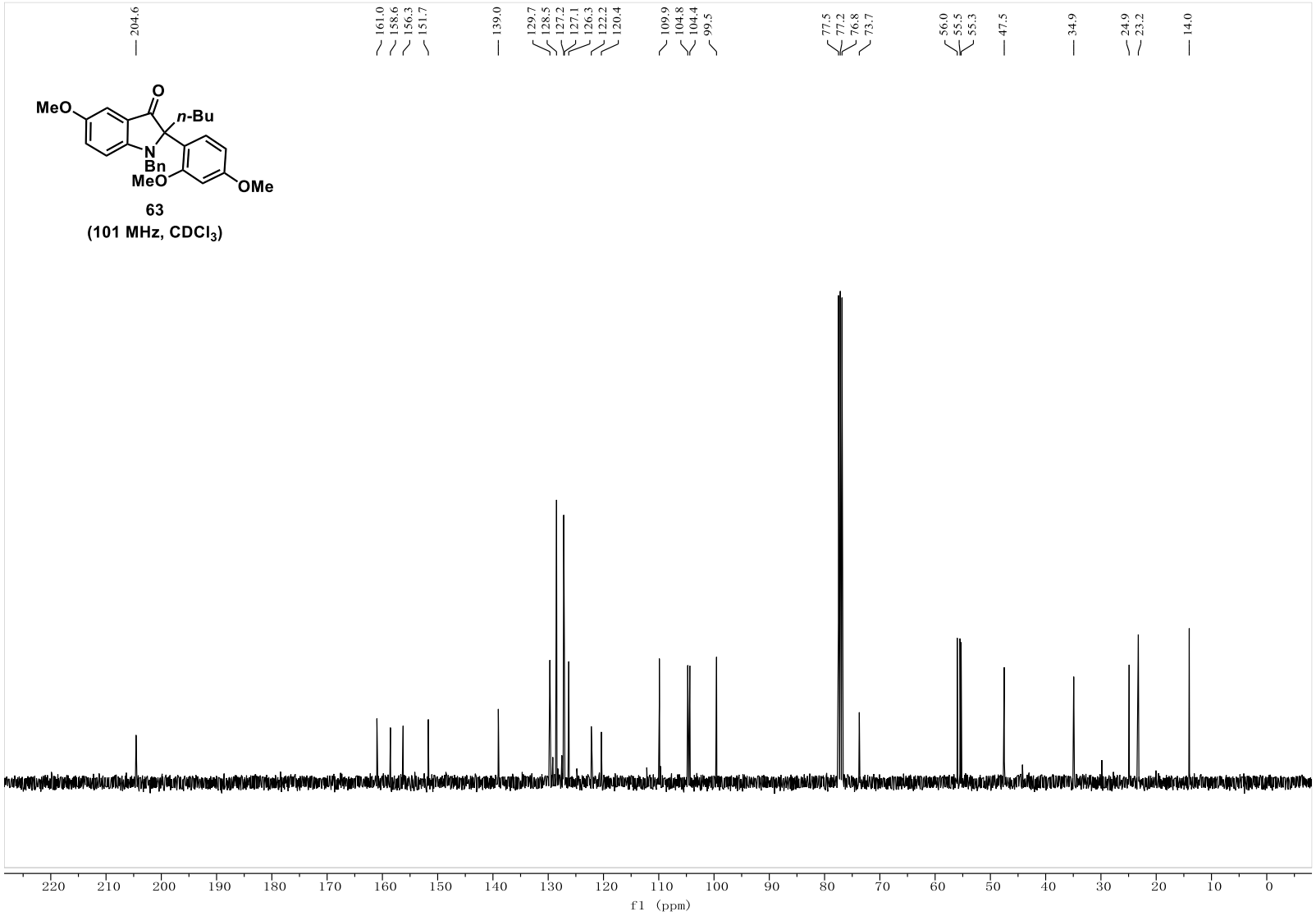

7.62
7.60
7.47
7.46
7.45
7.45
7.44
7.43
7.43
7.43
7.41
7.37
7.36
7.36
7.35
7.35
7.34
7.27
7.26
7.26
7.25
7.24
7.23
7.23
7.22
7.22
7.20
6.90
6.88
6.79
6.78
6.76
6.49
6.48
6.48
6.47
6.46
6.45
6.10
3.80
3.57
O
Ph
N
H
MeO
OMe
61
(400 MHz, CDCl3)
0.96
2.05
2.01
4.00
1.00
1.03
2.03
1.03
3.02
3.07
10.0
9.5
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
f1 (ppm)

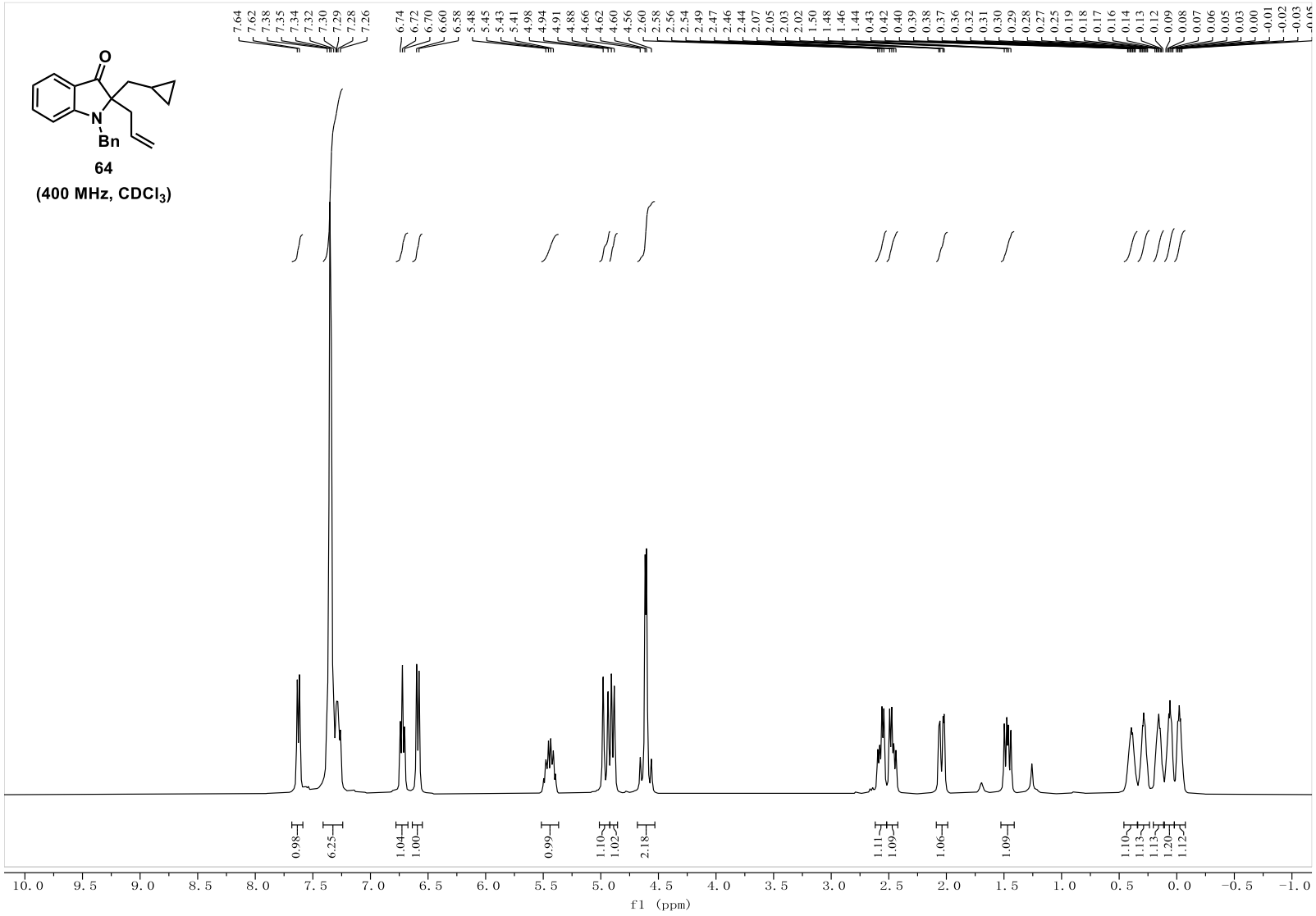

200.1
160.8
160.2
159.2
140.7
137.5
129.2
128.2
127.3
126.2
125.6
121.2
119.3
118.7
111.8
103.8
100.7
77.4
77.2
76.9
73.2
55.8
55.6
O
Ph
N
H
MeO
OMe
61
(151 MHz, CDCl3)
grease
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

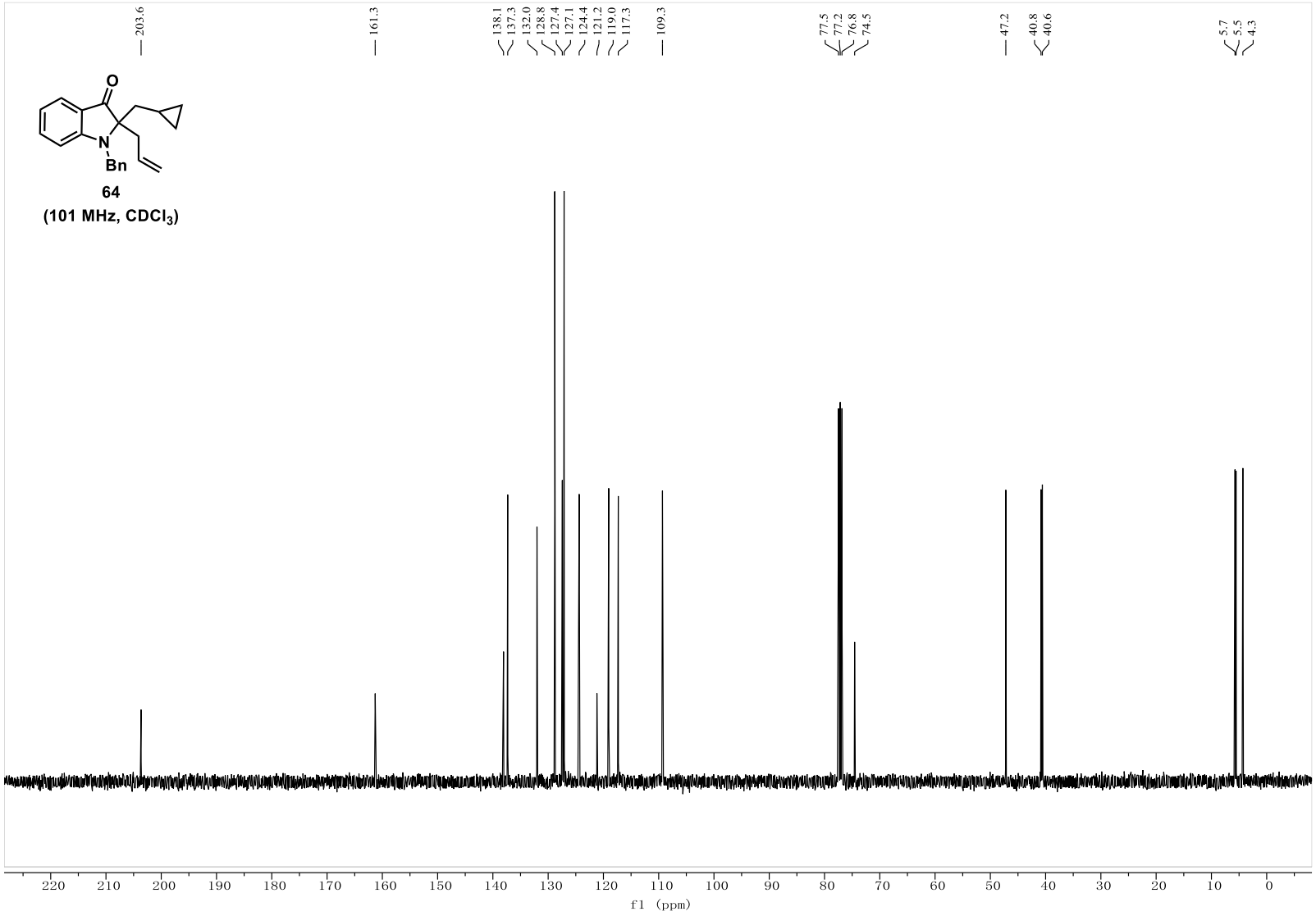

MeO
O
n-Bu
N
Bn
62
(400 MHz, CDCl3)
f1 (ppm)

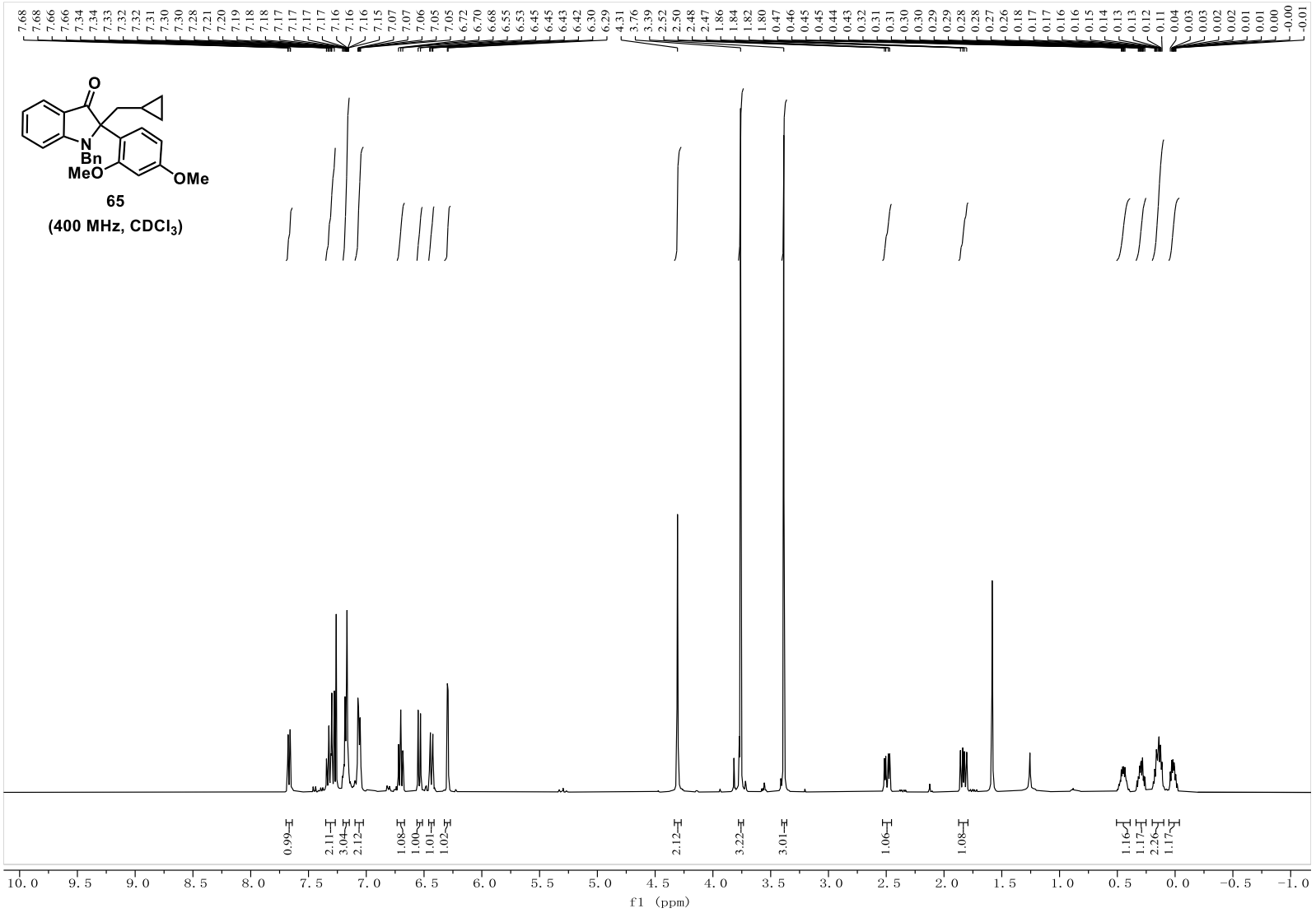

203.5
157.7
152.2
138.5
132.2
128.8
128.1
127.5
127.2
120.6
118.9
110.5
104.5
77.5
77.2
76.8
75.0
55.9
47.1
41.3
35.9
25.5
22.9
13.9
MeO
O
n-Bu
N
Bn
62
(101 MHz, CDCl3)
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

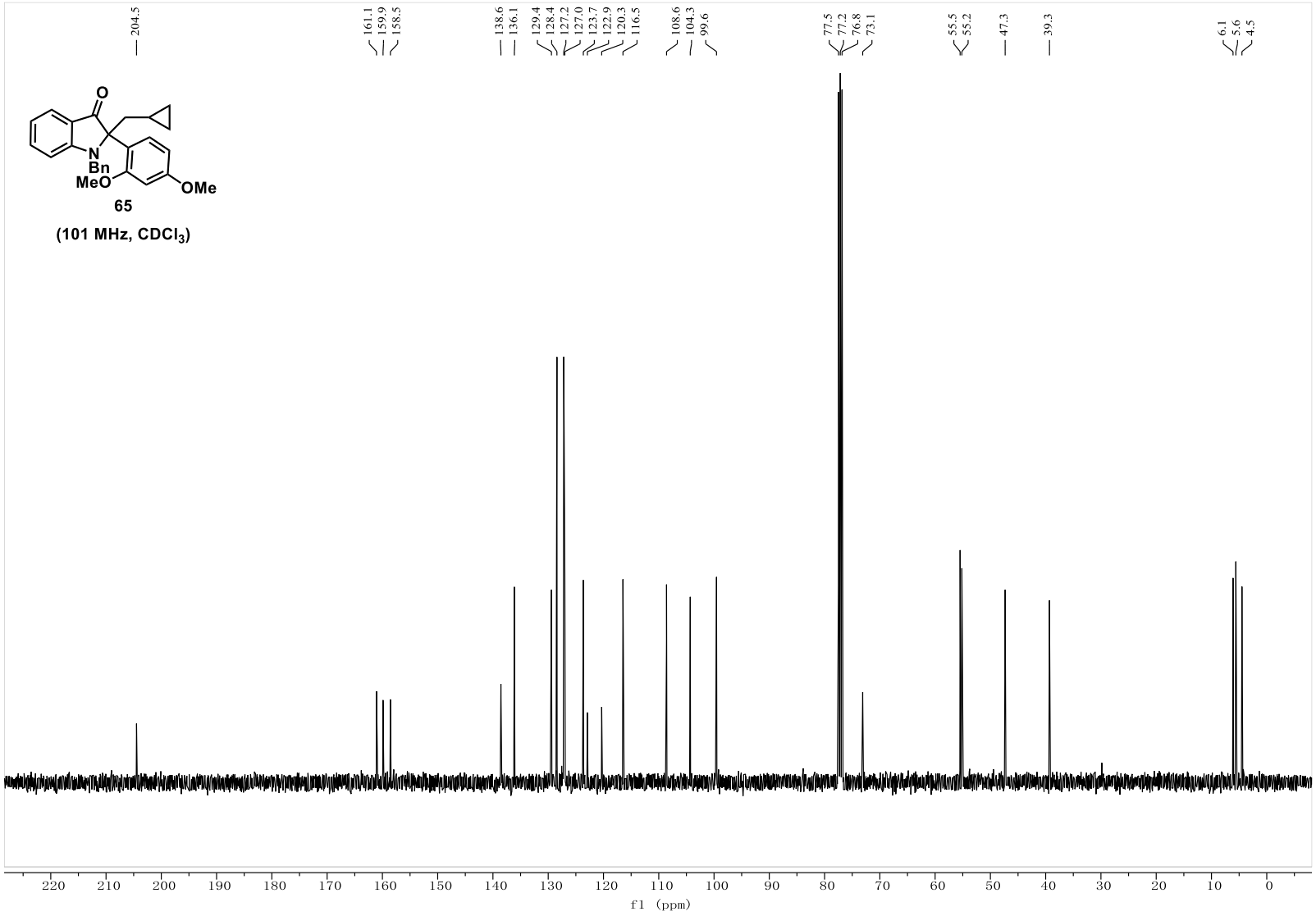

MeO
O
n-Bu
N
Bn
MeO
OMe
63
(400 MHz, CDCl3)
f1 (ppm)

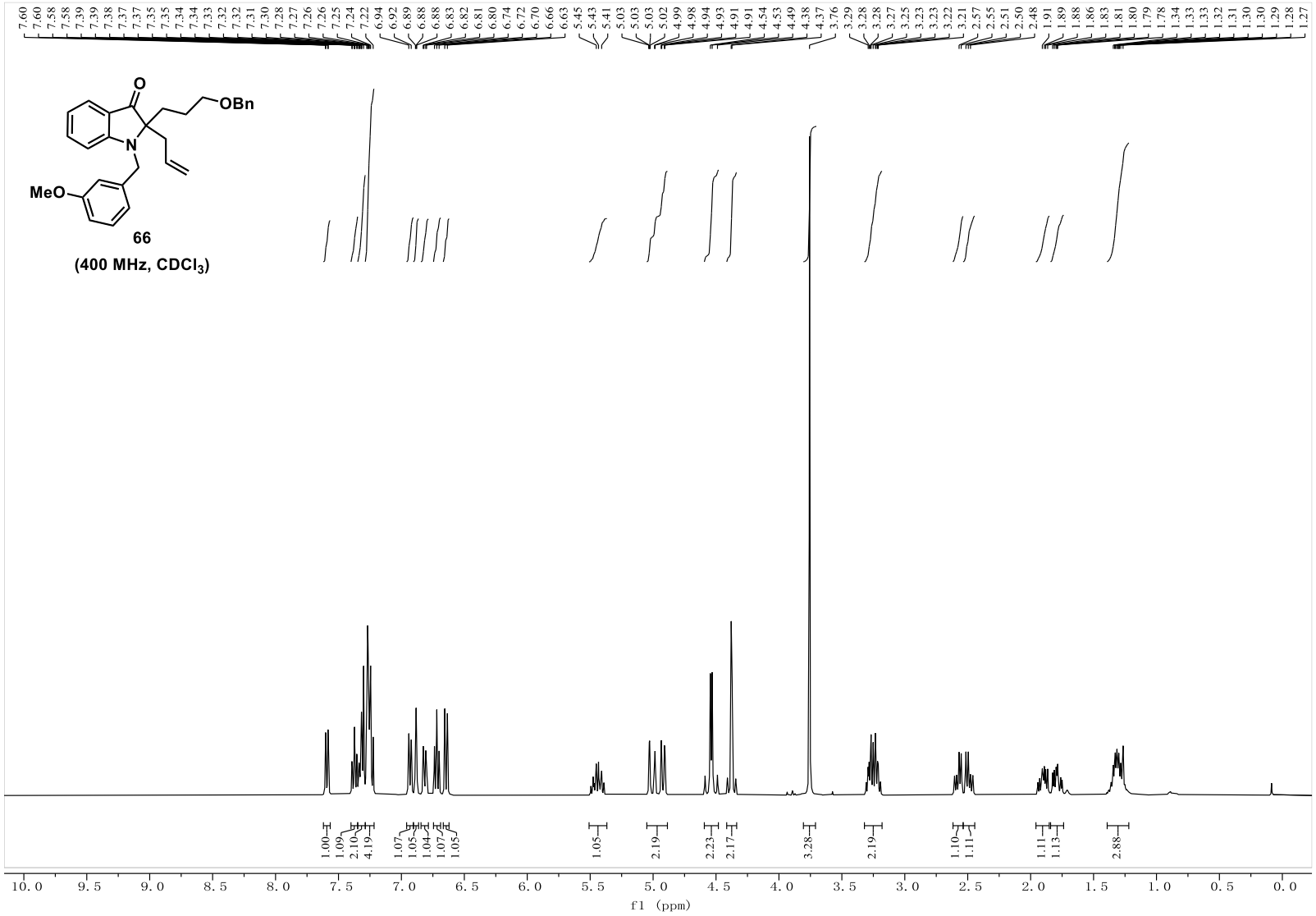

204.6
161.0
158.6
156.3
151.7
139.0
129.7
128.5
127.2
127.1
126.3
122.2
120.4
109.9
104.8
104.4
99.5
77.5
77.2
76.8
73.7
56.0
55.5
55.3
47.5
34.9
24.9
23.2
14.0
MeO
O
n-Bu
N
Bn
MeO
OMe
63
(101 MHz, CDCl3)
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

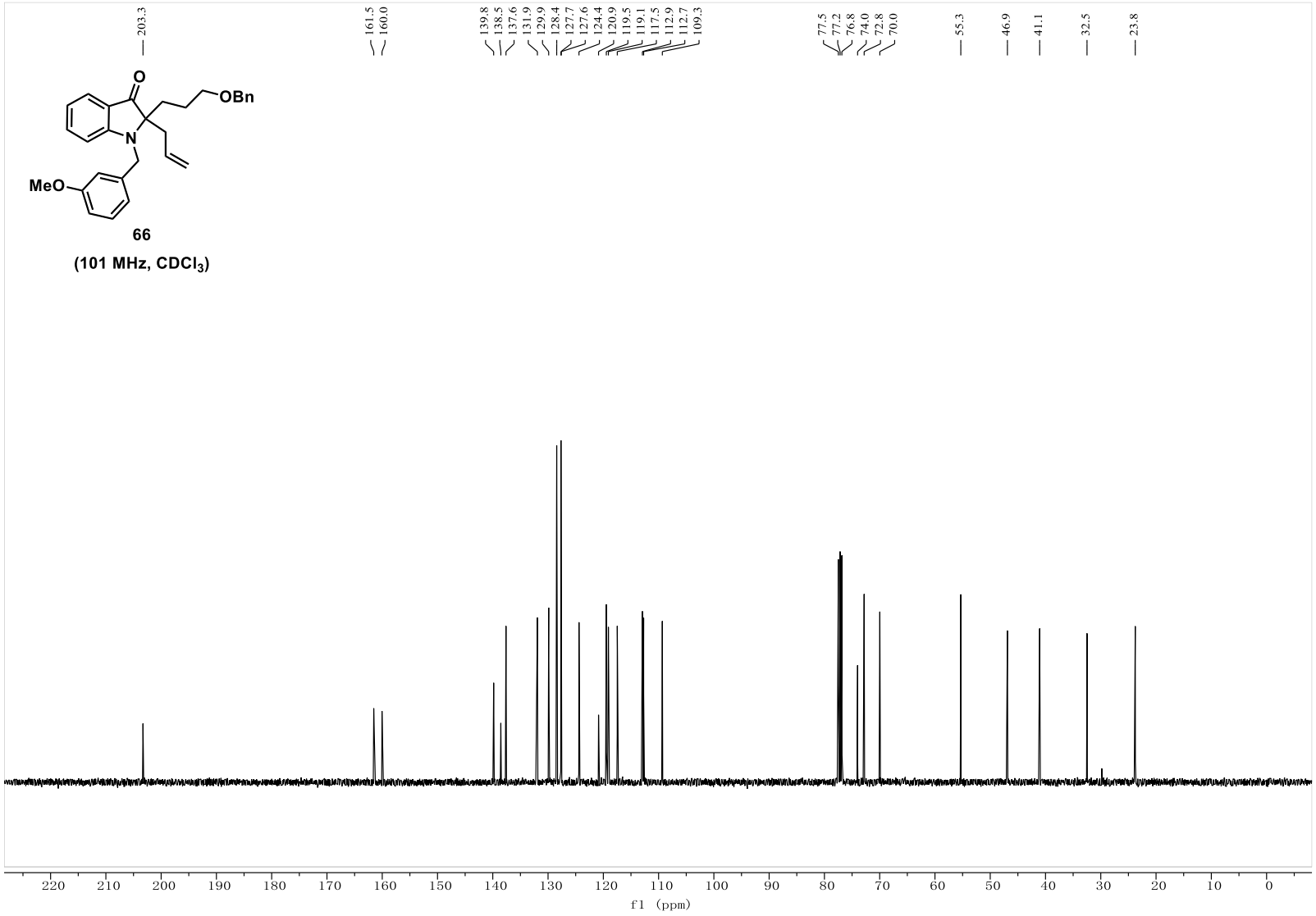

O
N
Bn
64
(400 MHz, CDCl3)
f1 (ppm)

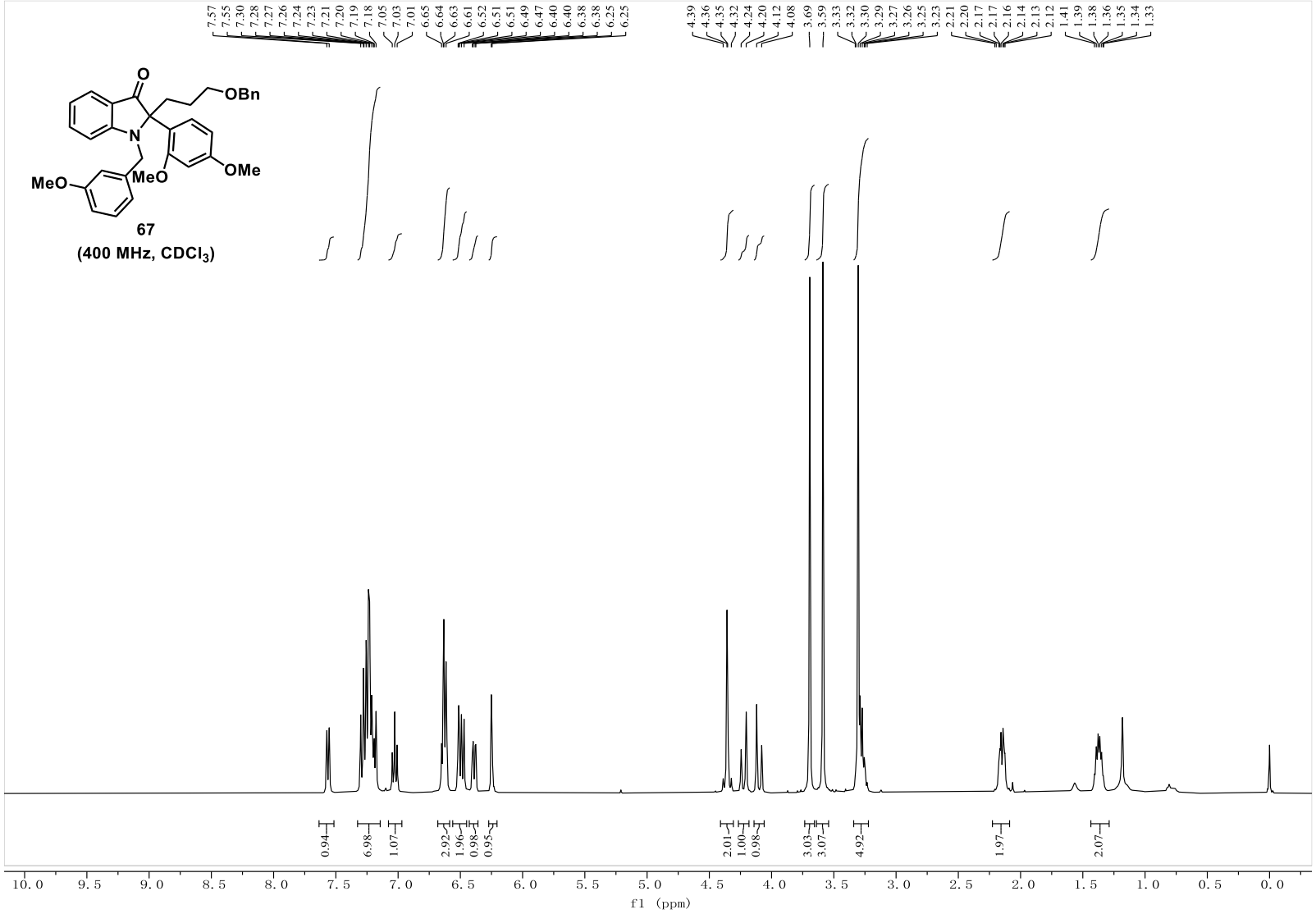

203.6
161.3
138.1
137.3
132.0
128.8
127.4
127.1
124.4
121.2
119.0
117.3
109.3
77.5
77.2
76.8
74.5
47.2
40.8
40.6
5.7
5.5
4.3
O
N
Bn
64
(101 MHz, CDCl3)
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

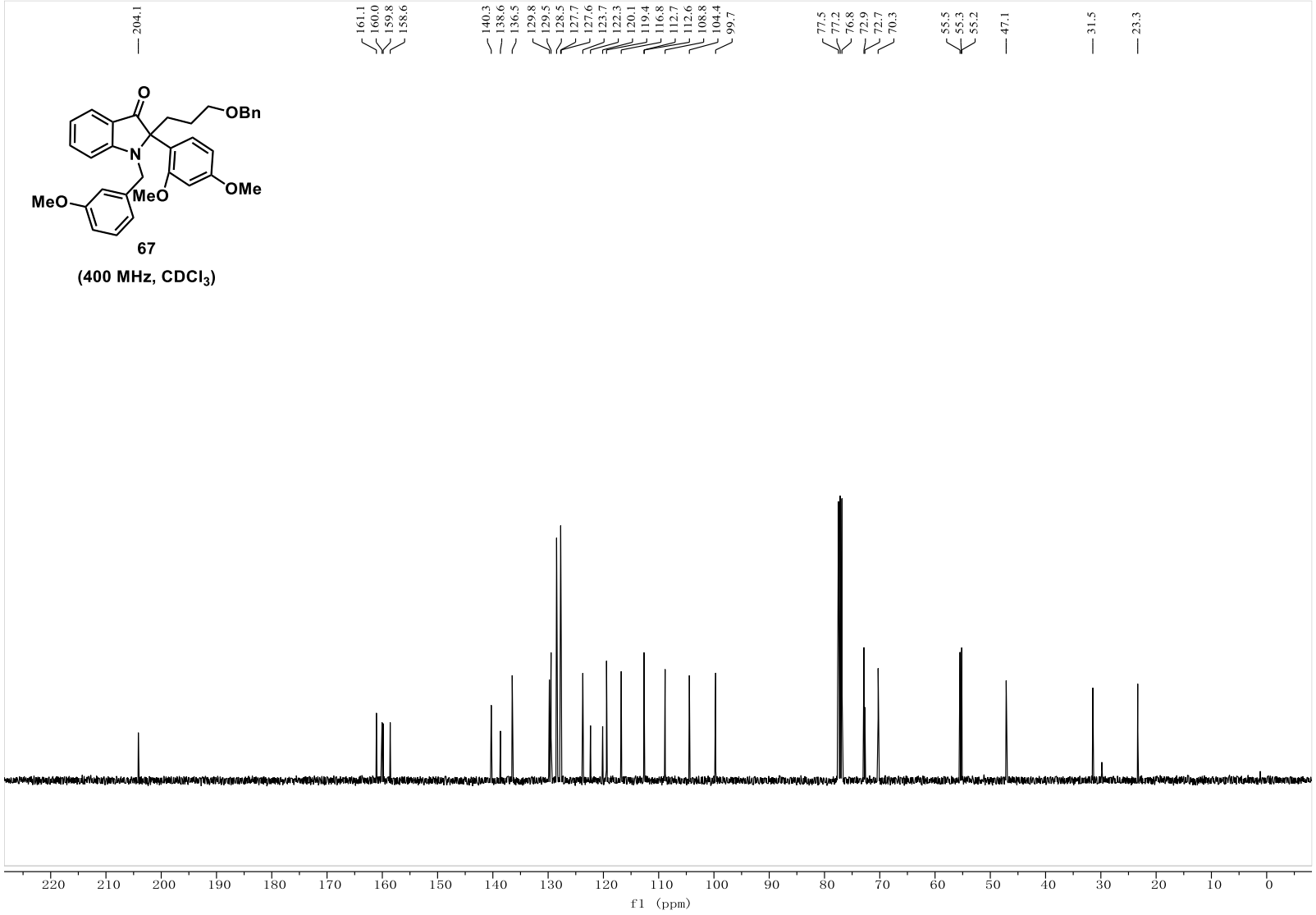

65
(400 MHz, CDCl3)
f1 (ppm)

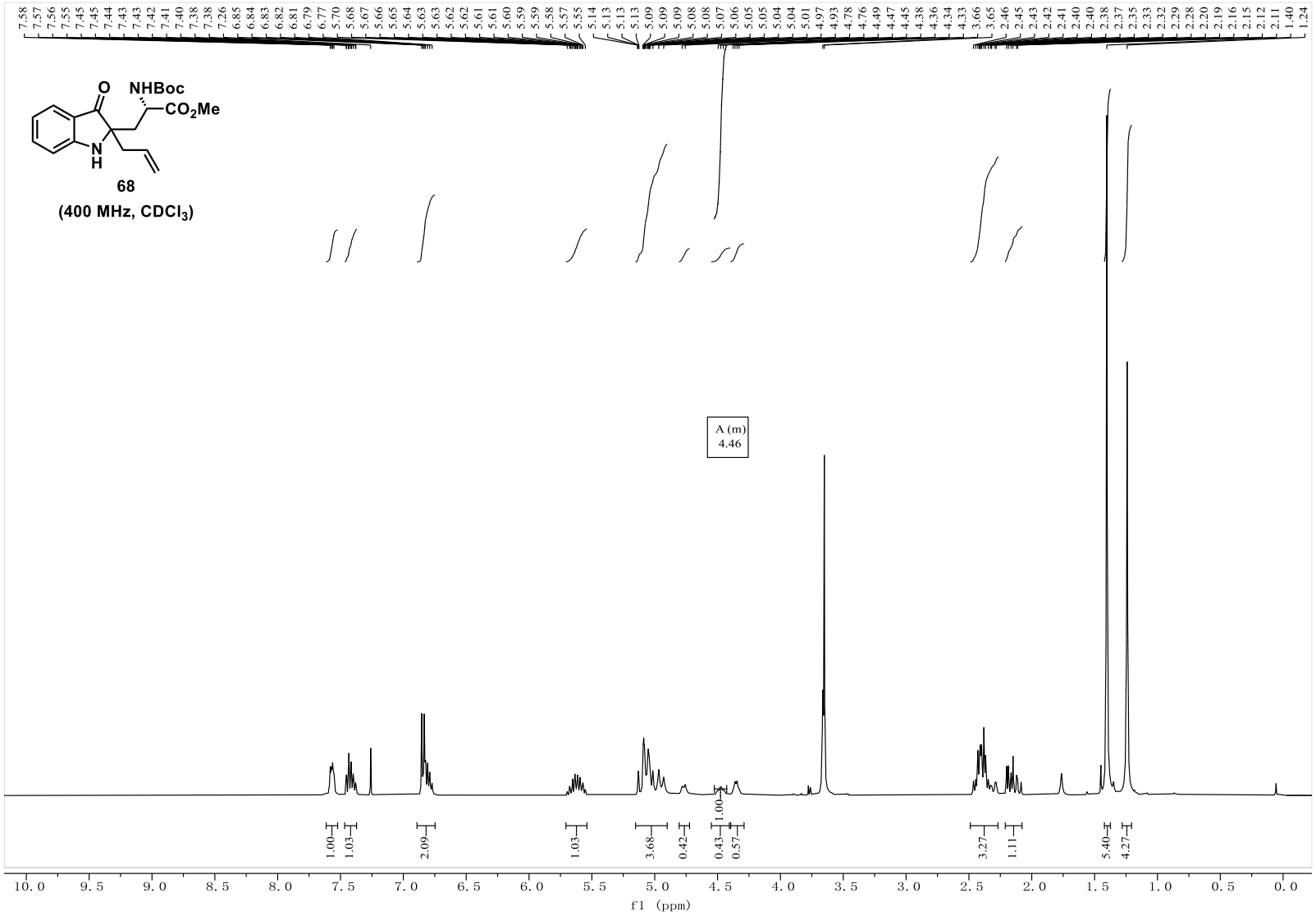

204.5
161.1
159.9
158.5
138.6
136.1
129.4
128.4
127.2
127.0
123.7
122.9
120.3
116.5
108.6
104.3
99.6
77.5
77.2
76.8
73.1
55.5
55.2
47.3
39.3
6.1
5.6
4.5
O
N
Bn
MeO
OMe
65
(101 MHz, CDCl3)
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

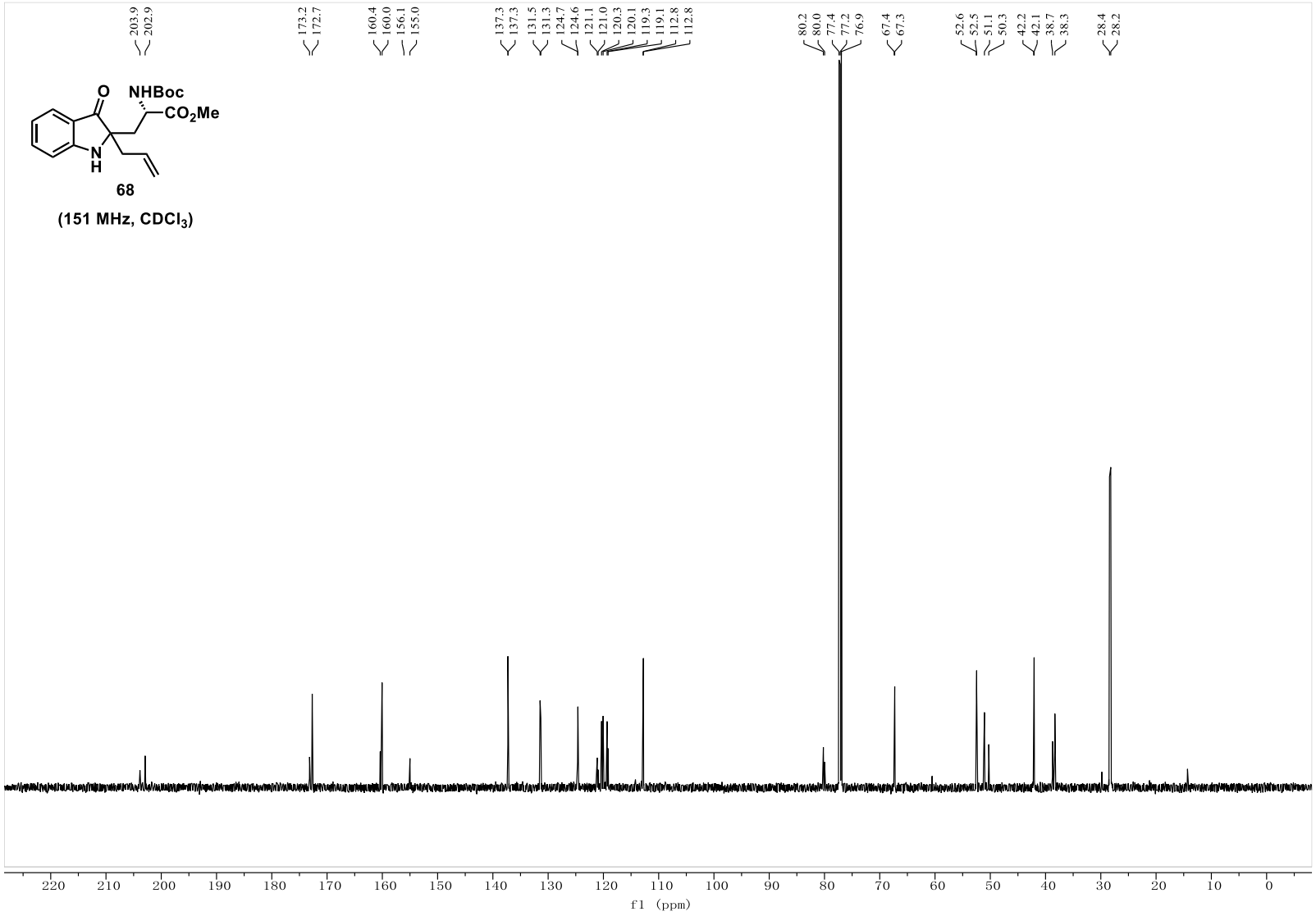

O
OBn
N
MeO
66
(400 MHz, CDCl3)
f1 (ppm)

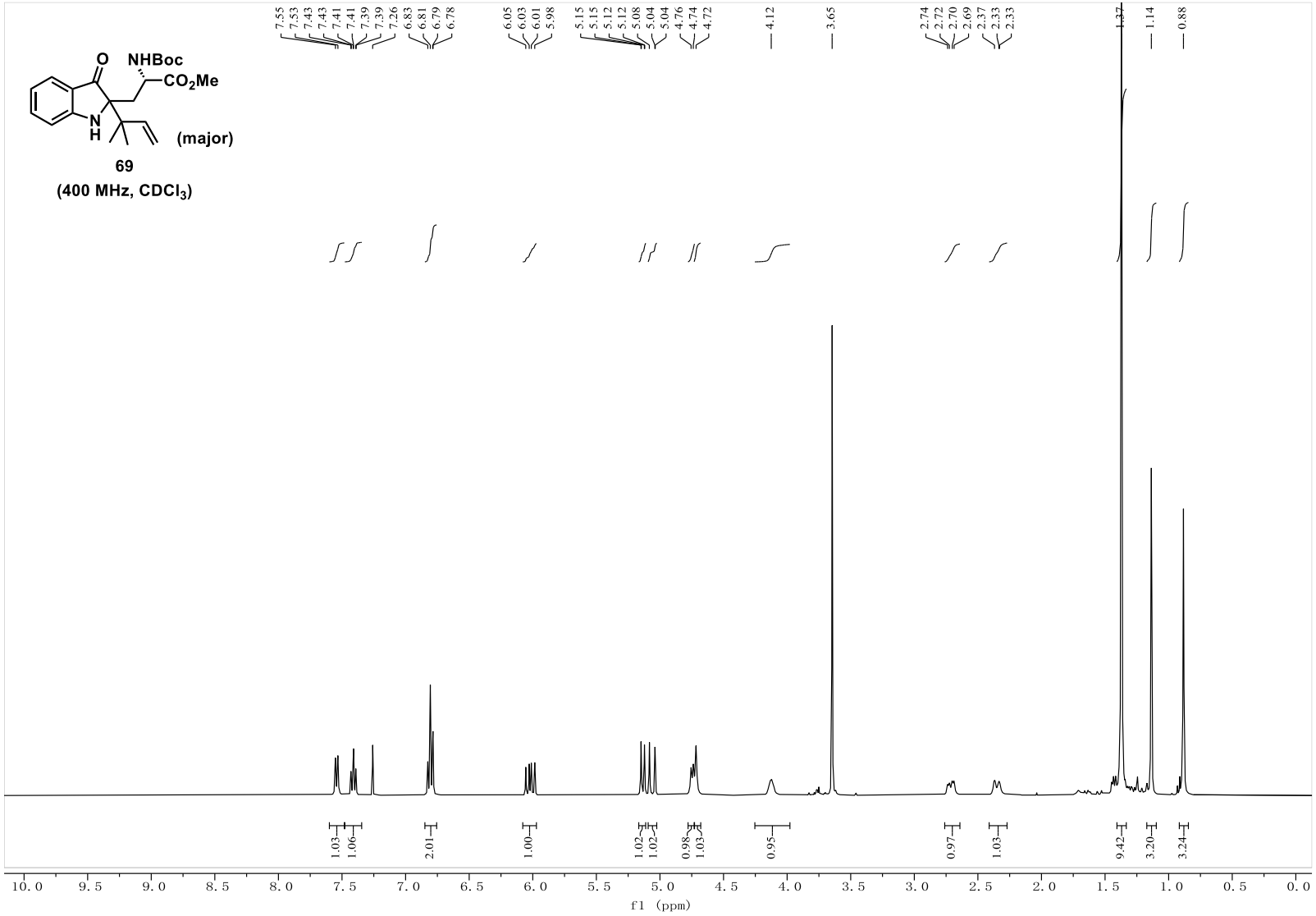

203.3
161.5
160.0
139.8
138.5
137.6
131.9
129.9
128.4
127.7
127.6
124.4
120.9
119.5
119.1
117.5
112.9
112.7
109.3
77.5
77.2
76.8
74.0
72.8
70.0
55.3
46.9
41.1
32.5
23.8
O
OBn
N
MeO
66
(101 MHz, CDCl3)
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

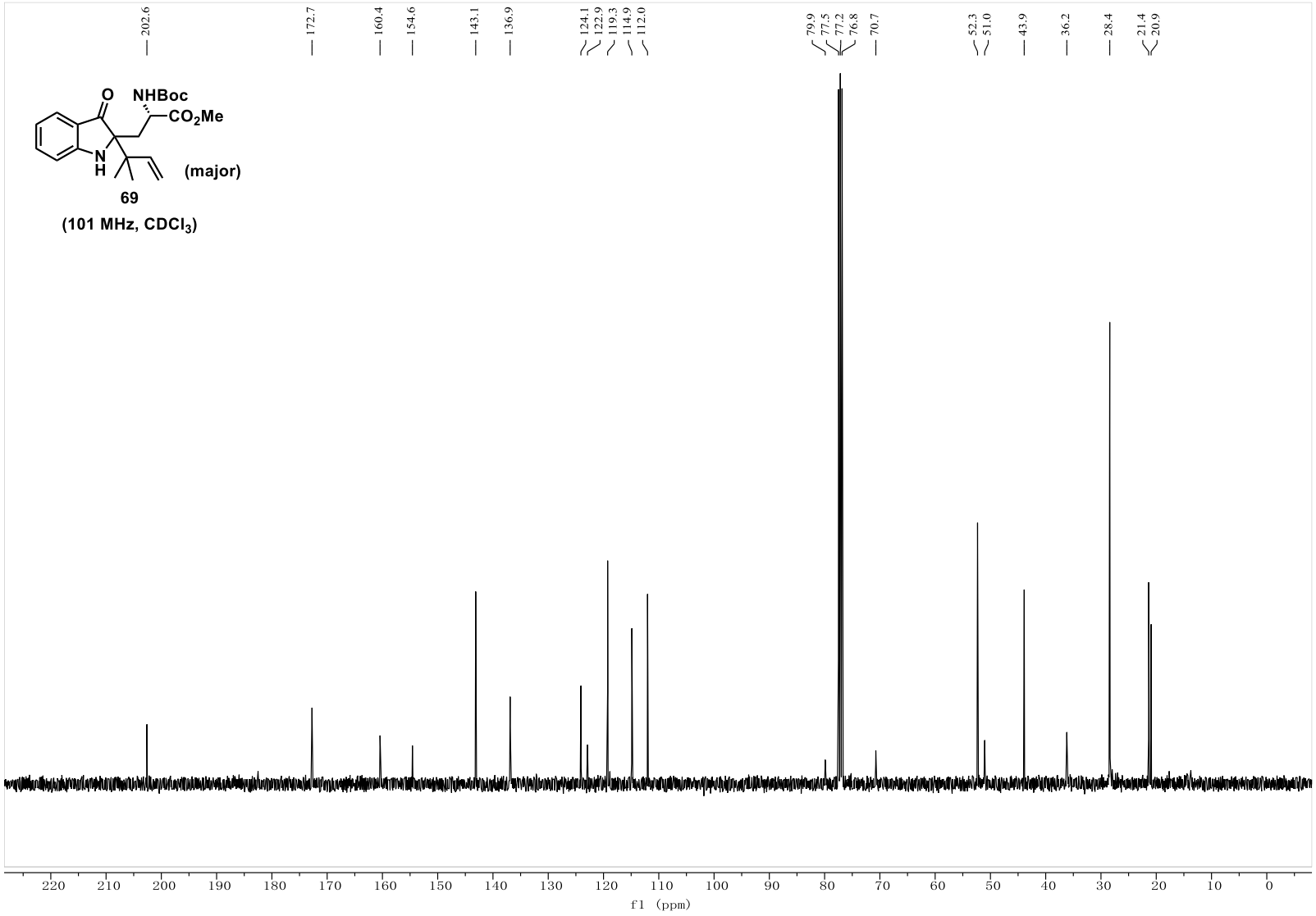

67
(400 MHz, CDCl3)
f1 (ppm)

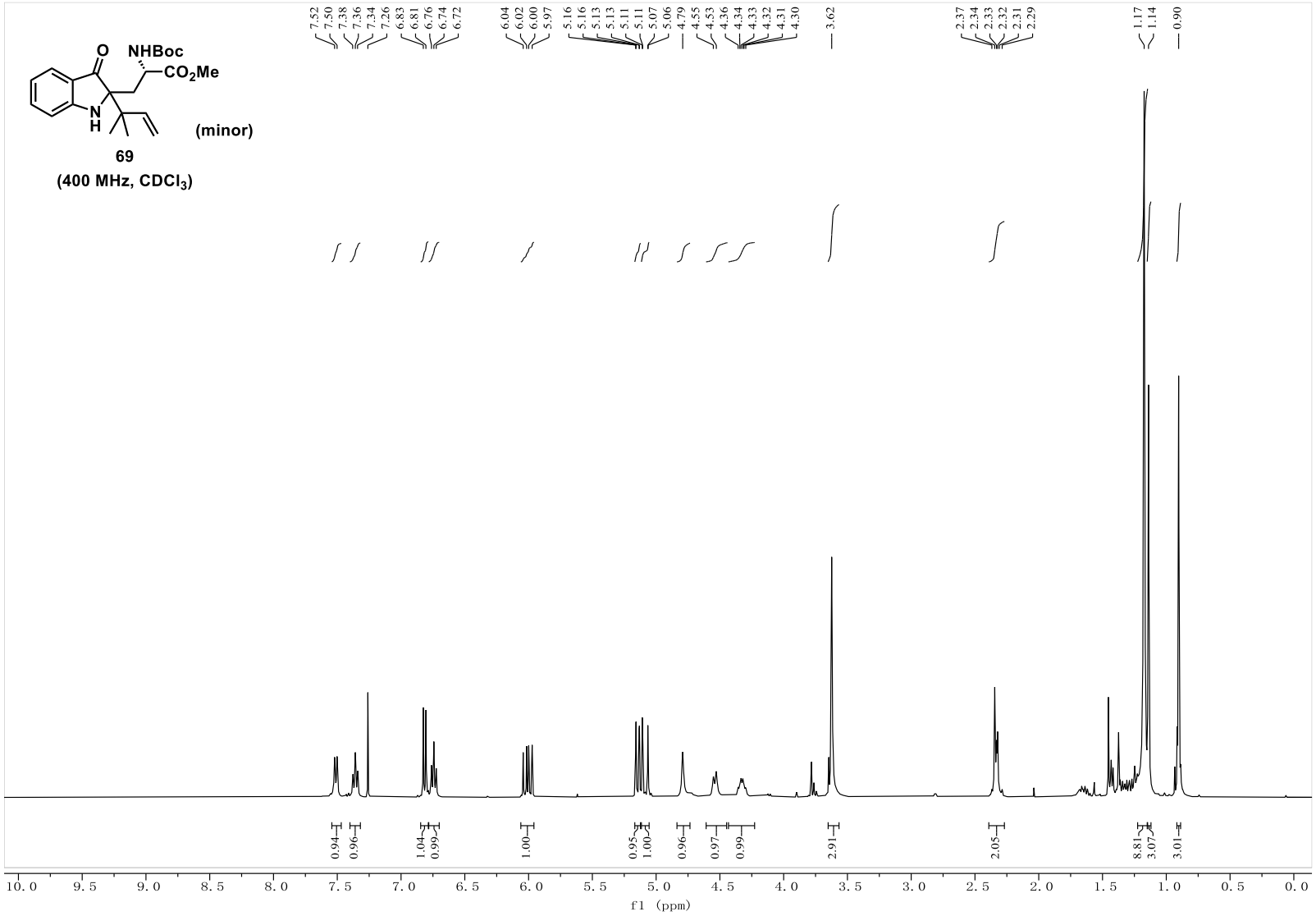

204.1
161.1
160.0
159.8
158.6
140.3
138.6
136.5
129.8
129.5
128.5
127.7
127.6
123.7
122.3
120.1
119.4
116.8
112.7
112.6
108.8
104.4
99.7
77.5
77.2
76.8
72.9
72.7
70.3
55.5
55.3
55.2
47.1
31.5
23.3
O
OBn
N
MeO
MeO
OMe
67
(400 MHz, CDCl3)
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

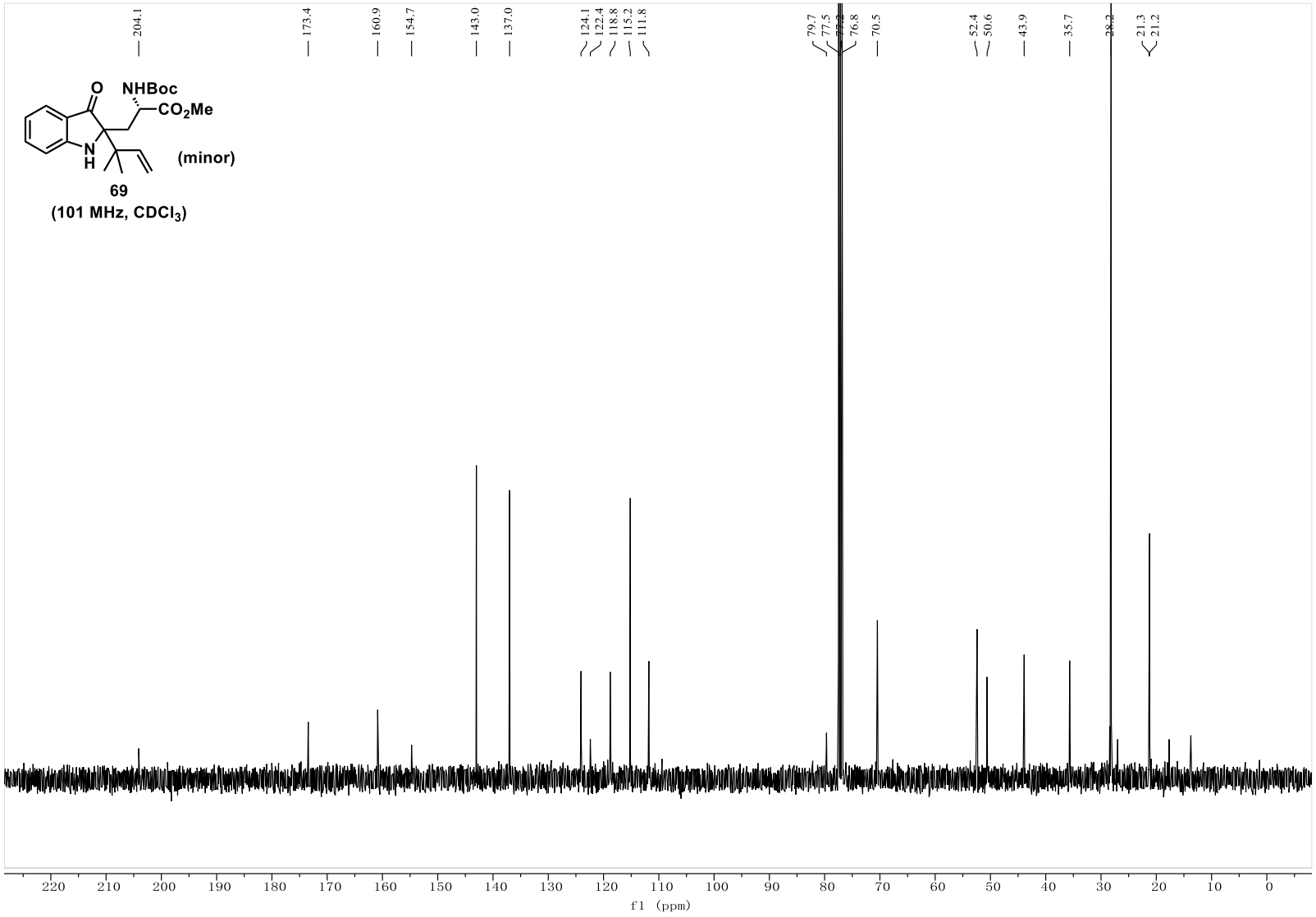

O
NHBoc
CO2Me
N
H
68
(400 MHz, CDCl3)
A (m)
4.46
f1 (ppm)

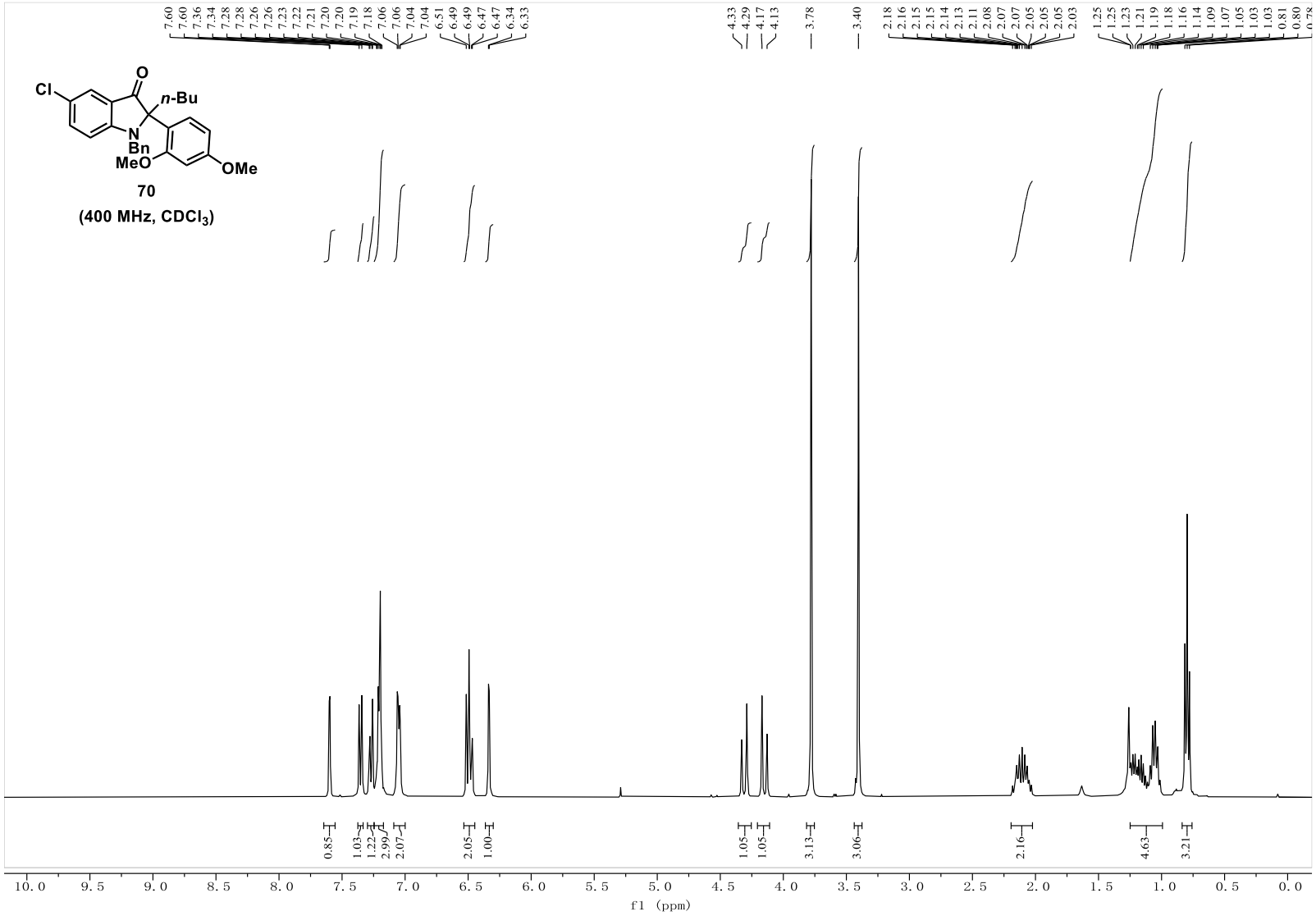

203.9
202.9
173.2
172.7
160.4
160.0
156.1
155.0
137.3
137.3
131.5
131.3
124.7
124.6
121.1
121.0
120.3
120.1
119.3
119.1
112.8
112.8
80.2
80.0
77.4
77.2
76.9
67.4
67.3
52.6
52.5
51.1
50.3
42.2
42.1
38.7
38.3
28.4
28.2
O
NHBoc
CO2Me
N
H
68
(151 MHz, CDCl3)
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

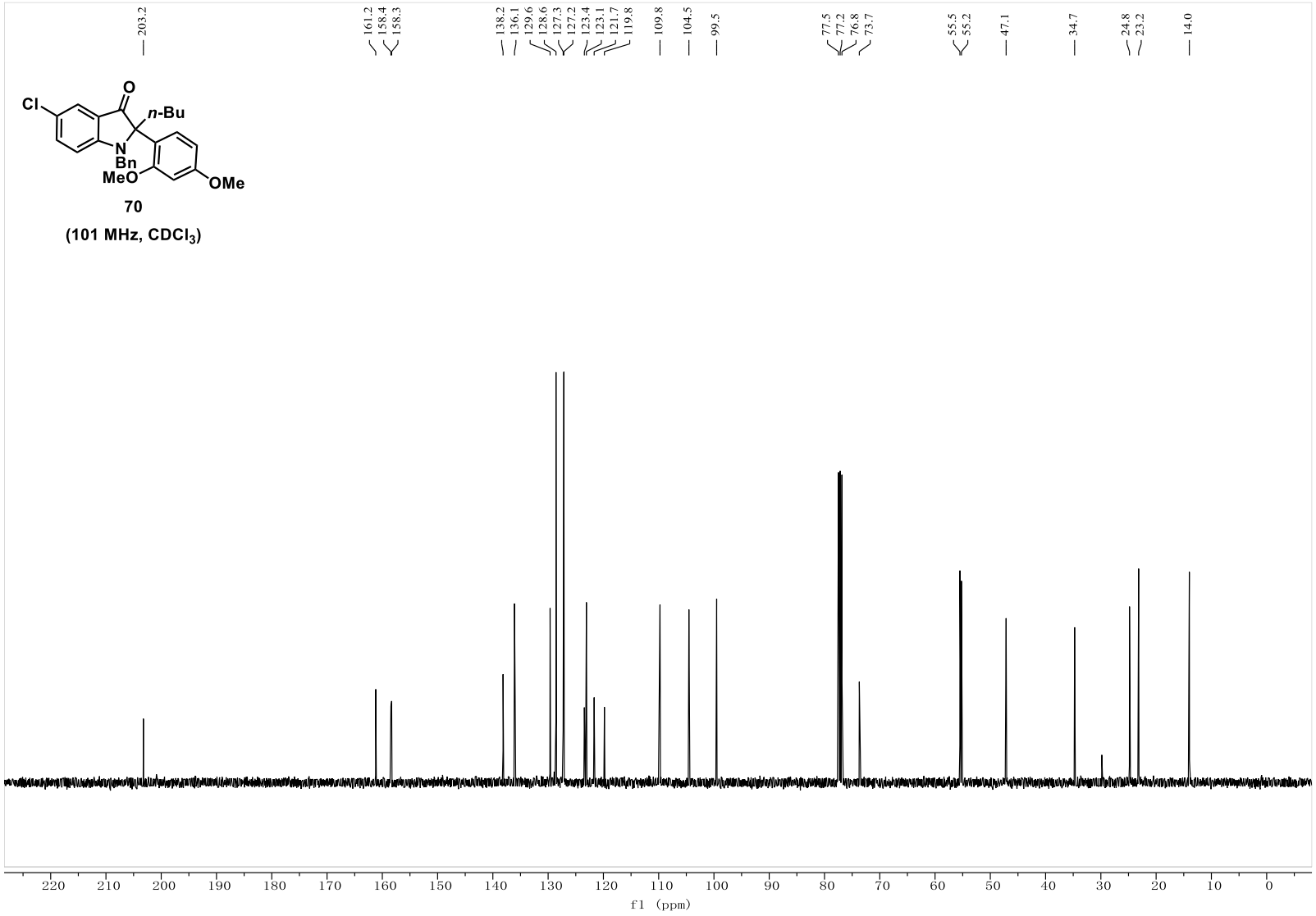

O
NHBoc
CO2Me
N
H
(major)
69
(400 MHz, CDCl3)
7.55
7.53
7.43
7.43
7.41
7.41
7.39
7.39
7.26
6.83
6.81
6.79
6.78
6.05
6.03
6.01
5.98
5.15
5.15
5.12
5.12
5.08
5.04
5.04
4.76
4.74
4.72
4.12
3.65
2.74
2.72
2.70
2.69
2.37
2.33
2.33
1.37
1.14
0.88
1.03
1.06
2.01
1.00
1.02
1.02
0.98
1.03
0.95
0.97
1.03
9.42
3.20
3.24
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
f1 (ppm)

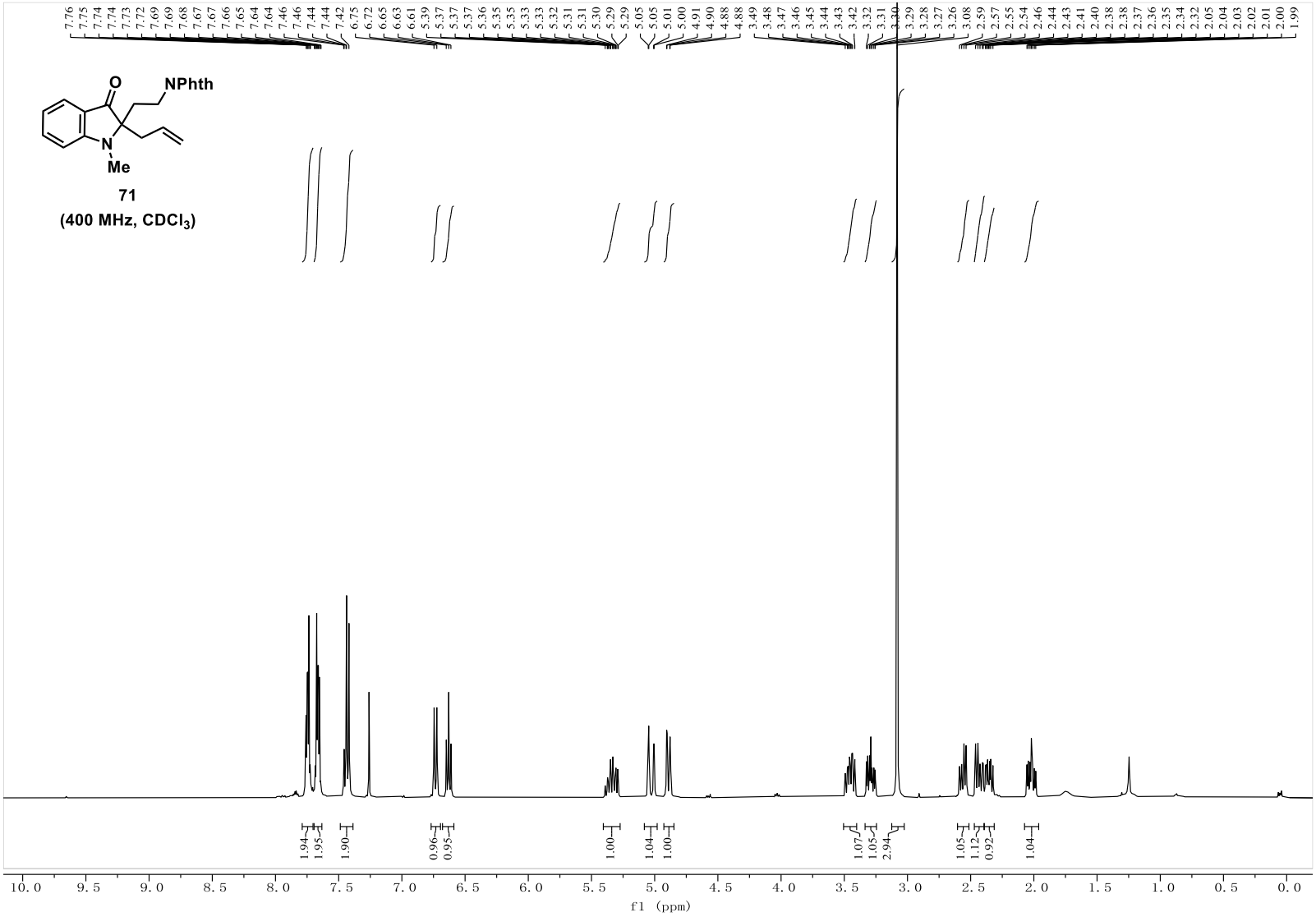

202.6
172.7
160.4
154.6
143.1
136.9
124.1
122.9
119.3
114.9
112.0
79.9
77.5
77.2
76.8
70.7
52.3
51.0
43.9
36.2
28.4
21.4
20.9
O
NHBoc
CO2Me
N
H
(major)
69
(101 MHz, CDCl3)
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

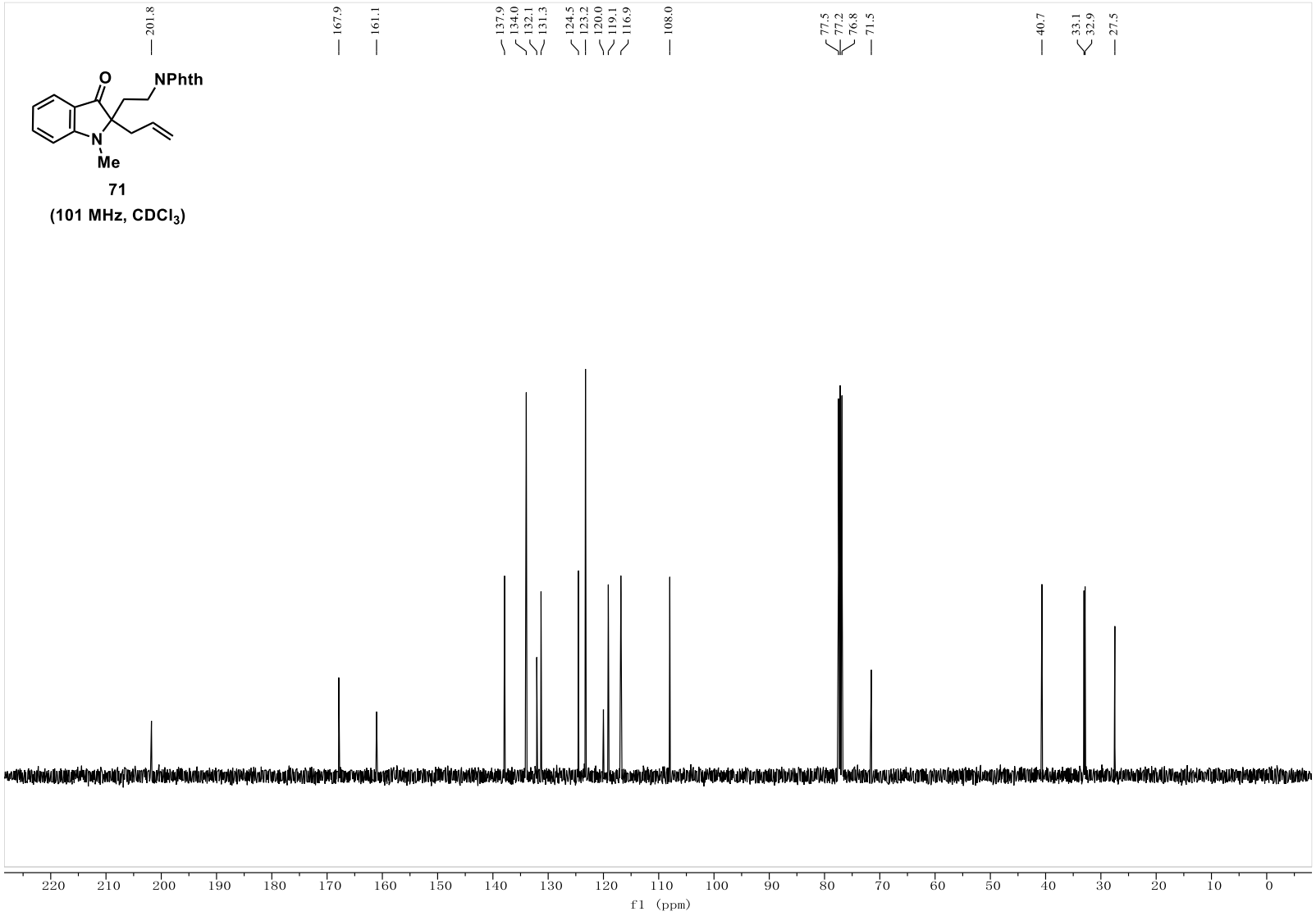

O
NHBoc
CO2Me
N
H
(minor)
69
(400 MHz, CDCl3)
7.52
7.50
7.38
7.36
7.34
7.26
6.83
6.81
6.76
6.74
6.72
6.04
6.02
6.00
5.97
5.16
5.16
5.13
5.13
5.11
5.11
5.07
5.06
4.79
4.55
4.53
4.36
4.34
4.33
4.32
4.31
4.30
3.62
2.37
2.34
2.33
2.32
2.31
2.29
1.17
1.14
0.90
0.94
0.96
1.04
0.99
1.00
0.95
1.00
0.96
0.97
0.99
2.91
2.05
8.81
3.07
3.01
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
f1 (ppm)

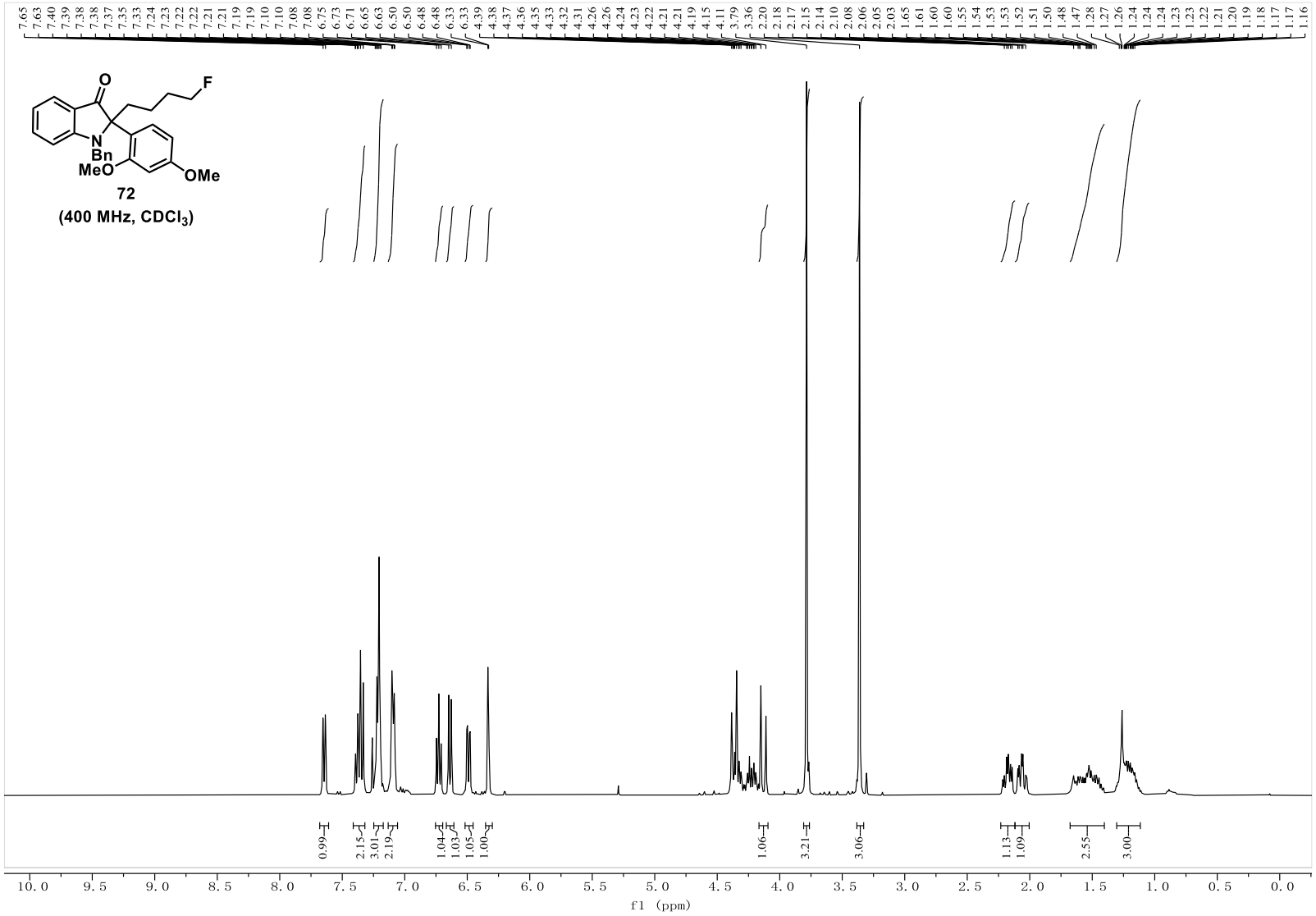

204.1
173.4
160.9
154.7
143.0
137.0
124.1
122.4
118.8
115.2
111.8
79.7
77.5
76.8
70.5
52.4
50.6
43.9
35.7
28.2
21.3
21.2
O
NHBoc
CO2Me
N
H
(minor)
69
(101 MHz, CDCl3)
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

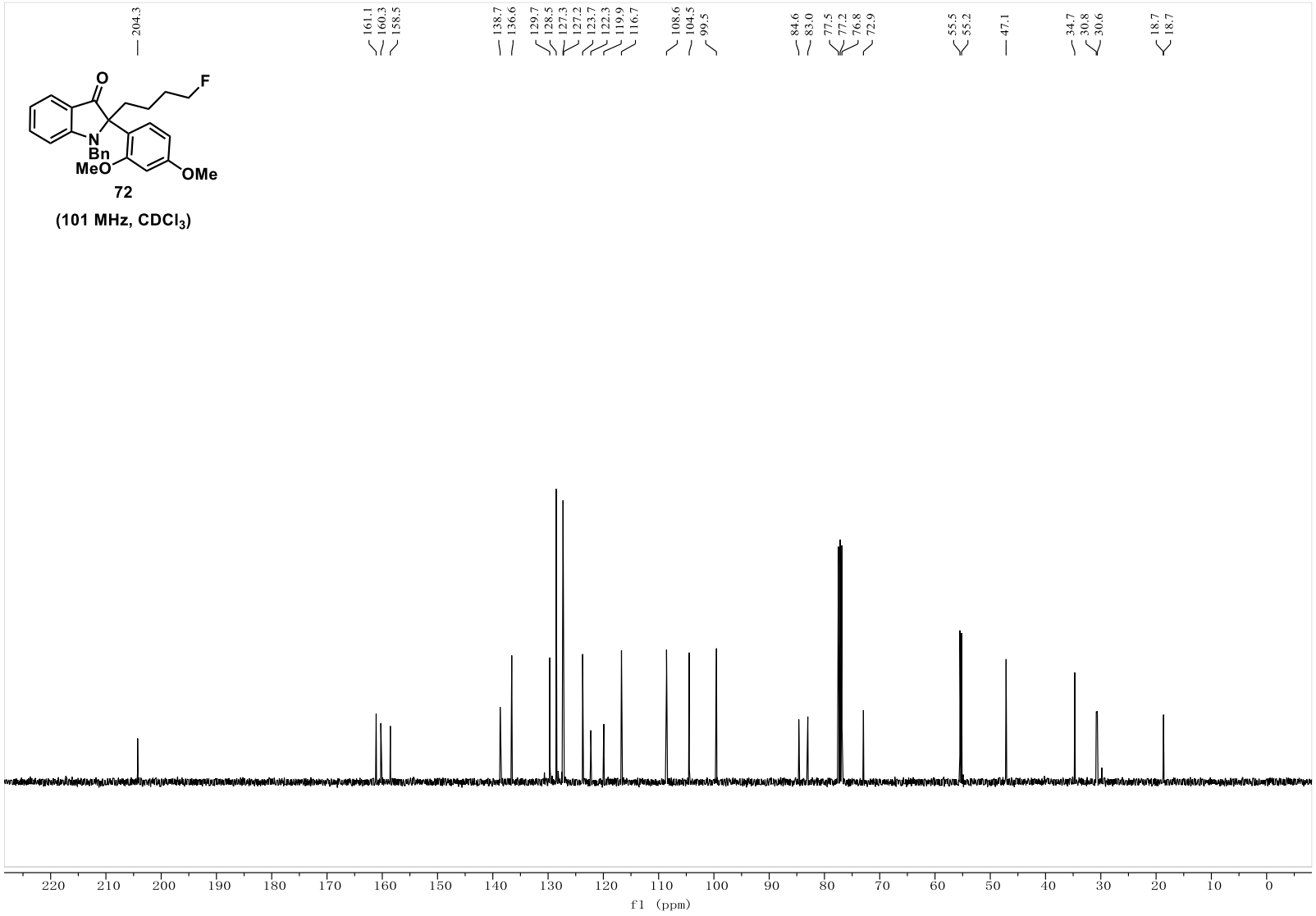

Cl
O
n-Bu
N
Bn
MeO
OMe
70
(400 MHz, CDCl3)
7.60 7.60 7.36 7.34 7.28 7.28 7.26 7.26 7.23 7.22 7.21 7.20 7.20 7.19 7.18 7.06 7.06 7.04 7.04 6.51 6.49 6.49 6.47 6.47 6.34 6.33
4.33 4.29 4.17 4.13 3.78 3.40 2.18 2.16 2.15 2.15 2.14 2.13 2.11 2.08 2.07 2.07 2.05 2.05 2.05 2.03 1.25 1.25 1.23 1.21 1.19 1.18 1.16 1.14 1.09 1.07 1.05 1.03 1.03 0.81 0.80
0.85 1.03 1.22 2.99 2.07 2.05 1.00 1.05 1.05 3.13 3.06 2.16 4.63 3.21
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
f1 (ppm)

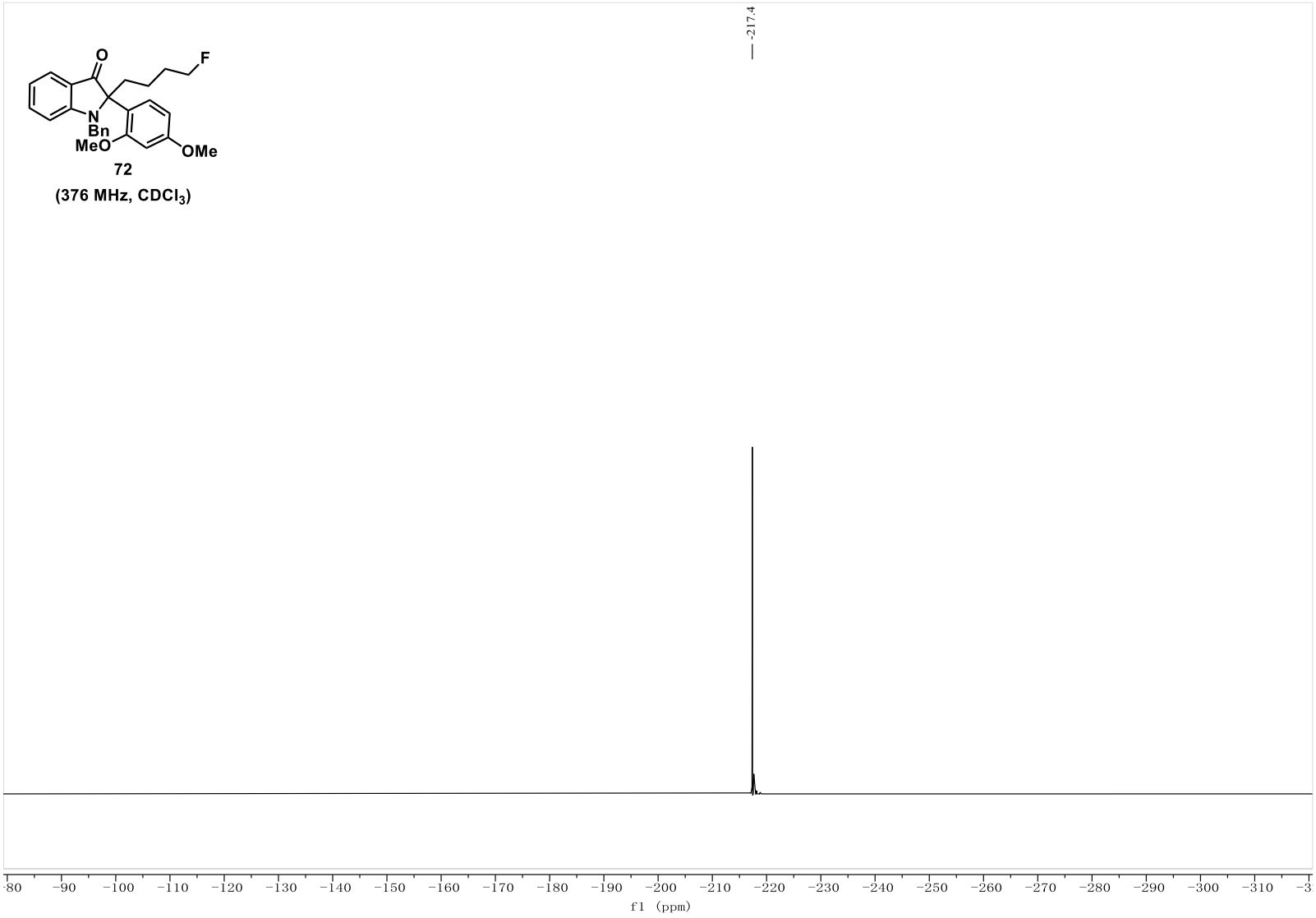

203.2
161.2
158.4
158.3
138.2
136.1
129.6
128.6
127.3
127.2
123.4
123.1
121.7
119.8
109.8
104.5
99.5
77.5
77.2
76.8
73.7
55.5
55.2
47.1
34.7
24.8
23.2
14.0
Cl
O
n-Bu
N
Bn
MeO
OMe
70
(101 MHz, CDCl3)
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

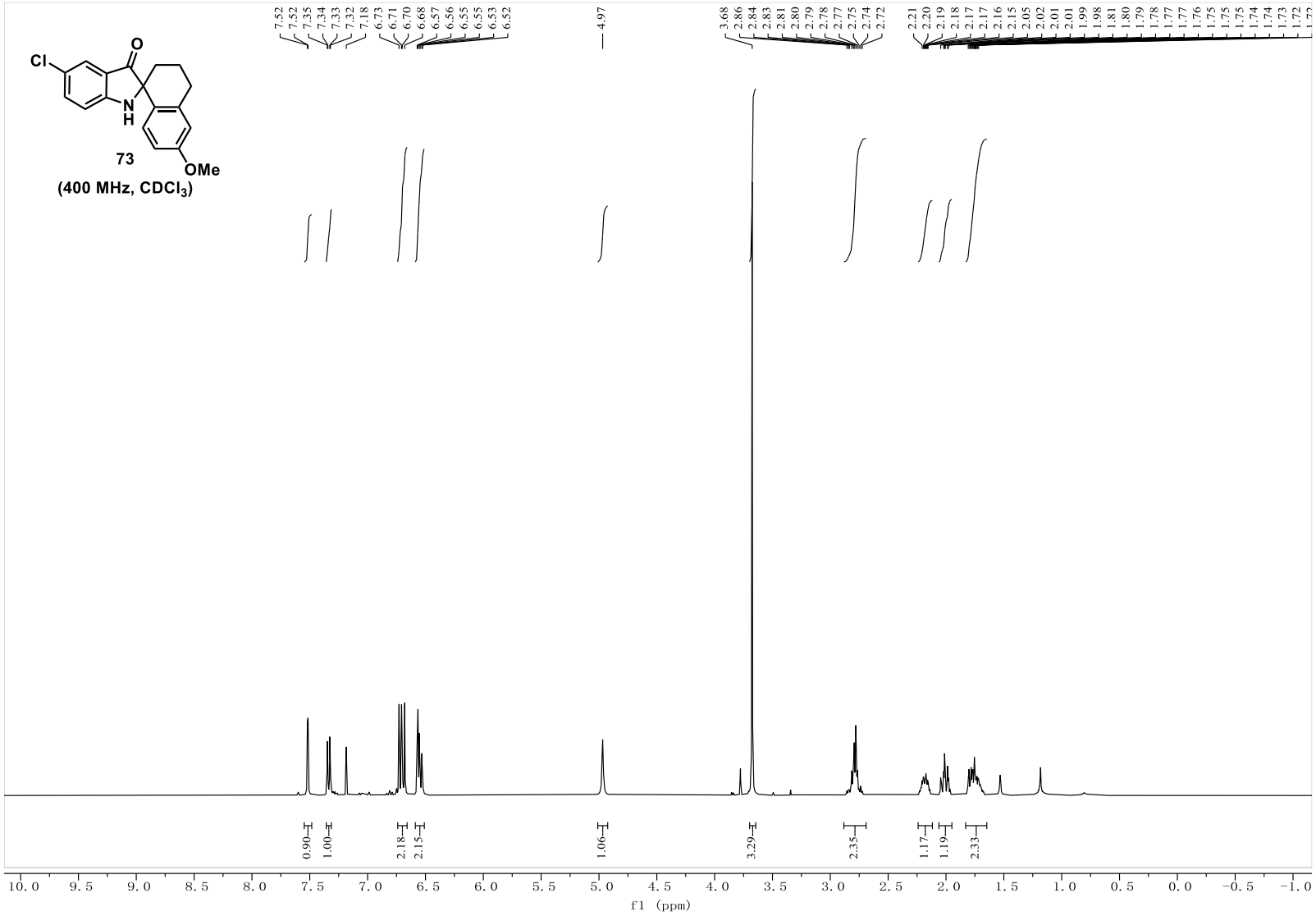

O
NPhth
N
Me
71
(400 MHz, CDCl3)
f1 (ppm)

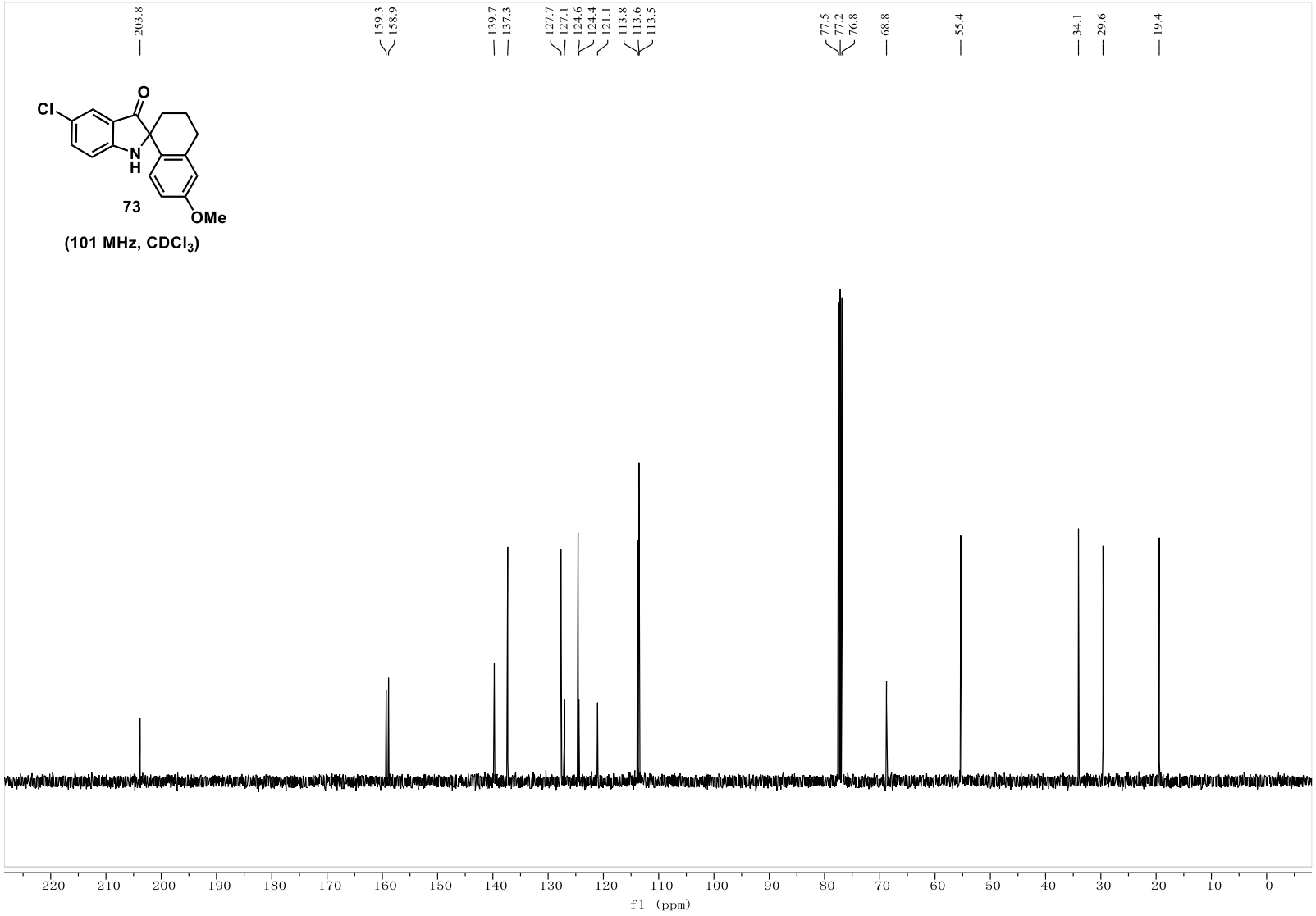

201.8
167.9
161.1
137.9
134.0
132.1
131.3
124.5
123.2
120.0
119.1
116.9
108.0
77.5
77.2
76.8
71.5
40.7
33.1
32.9
27.5
O
NPhth
N
Me
71
(101 MHz, CDCl3)
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

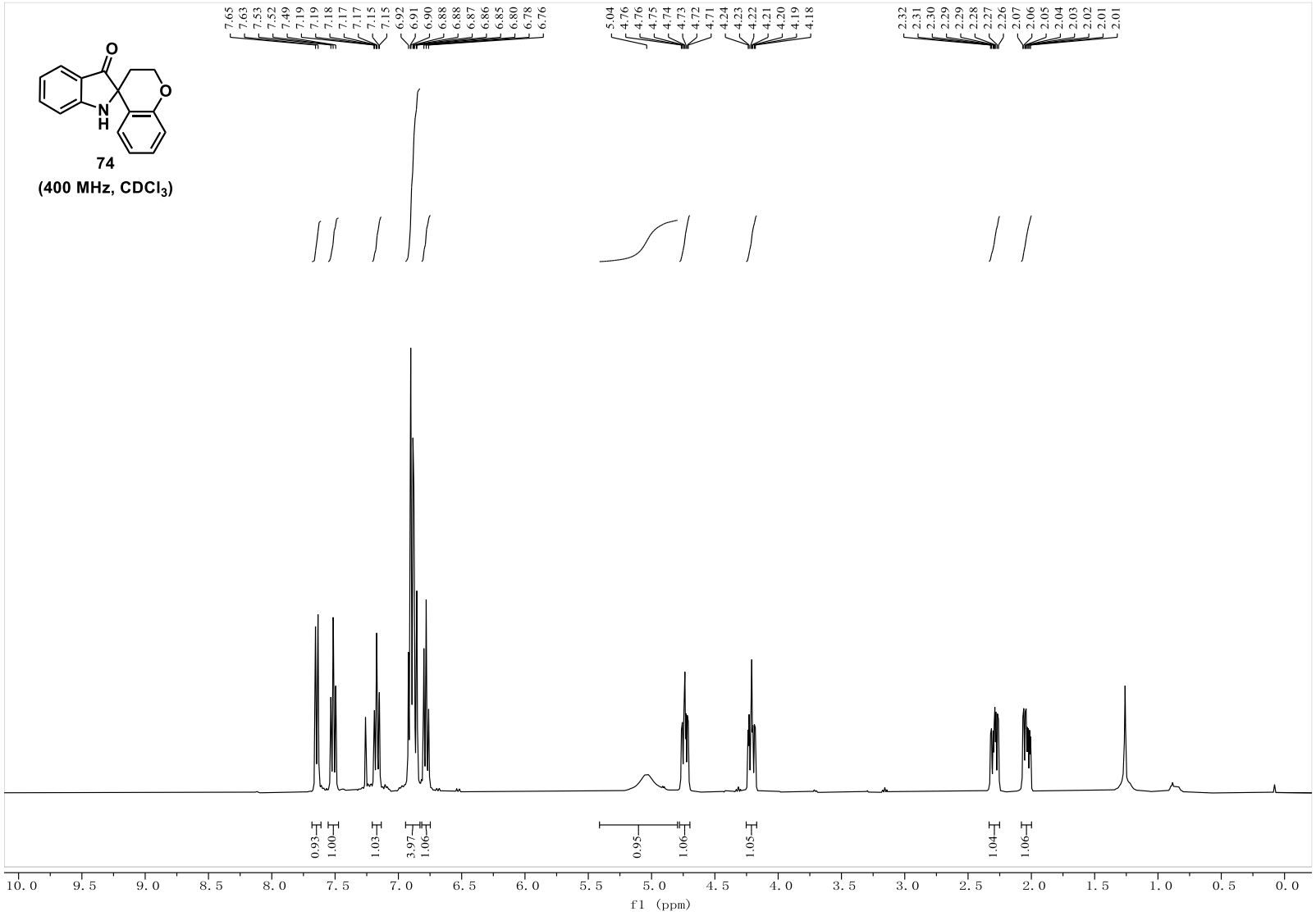

O
F
N
Bn
MeO
OMe
72
(400 MHz, CDCl3)
f1 (ppm)

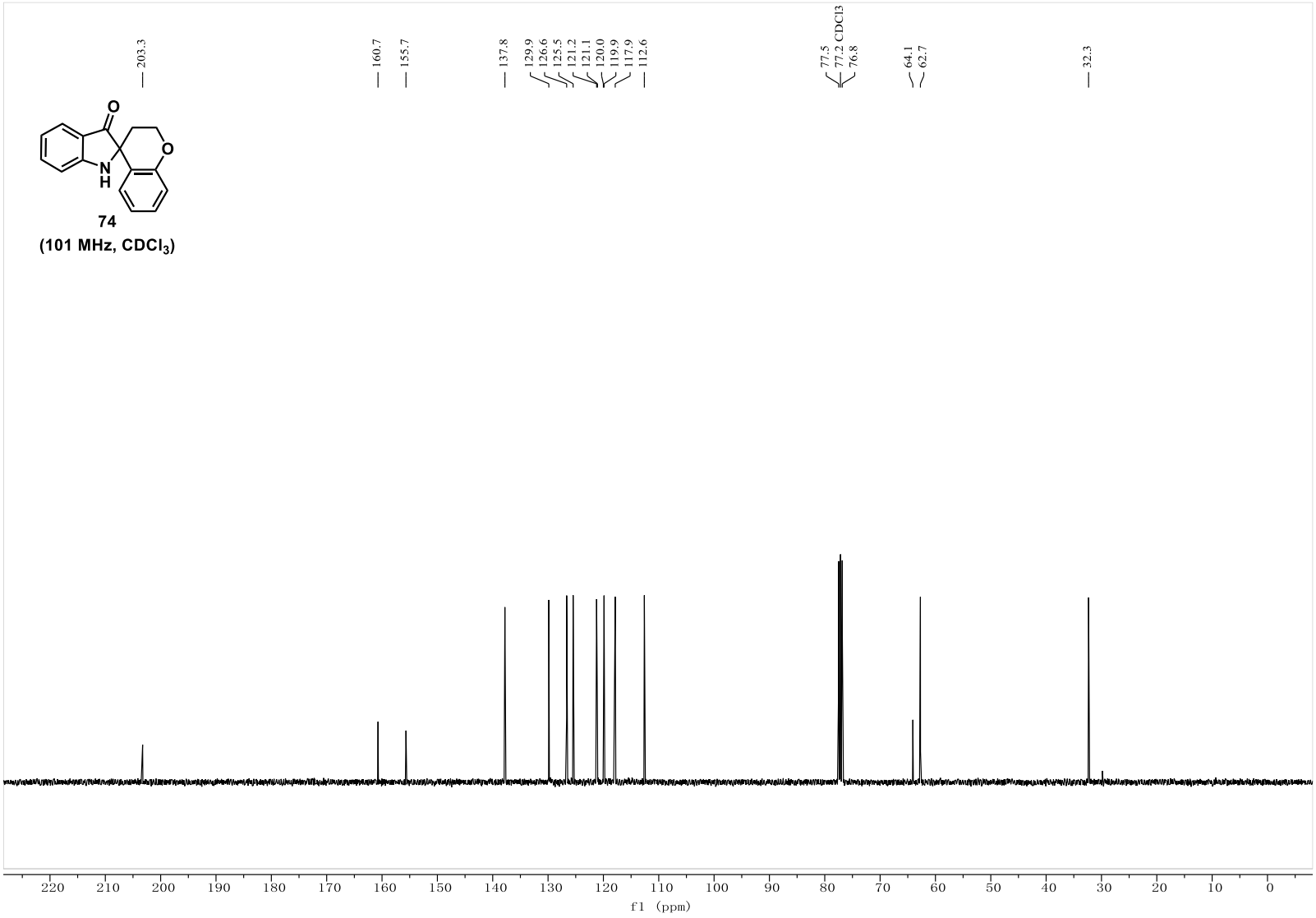

204.3
161.1
160.3
158.5
138.7
136.6
129.7
128.5
127.3
127.2
123.7
122.3
119.9
116.7
108.6
104.5
99.5
84.6
83.0
77.5
77.2
76.8
72.9
55.5
55.2
47.1
34.7
30.8
30.6
18.7
18.7
O
F
N
Bn
MeO
OMe
72
(101 MHz, CDCl3)
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

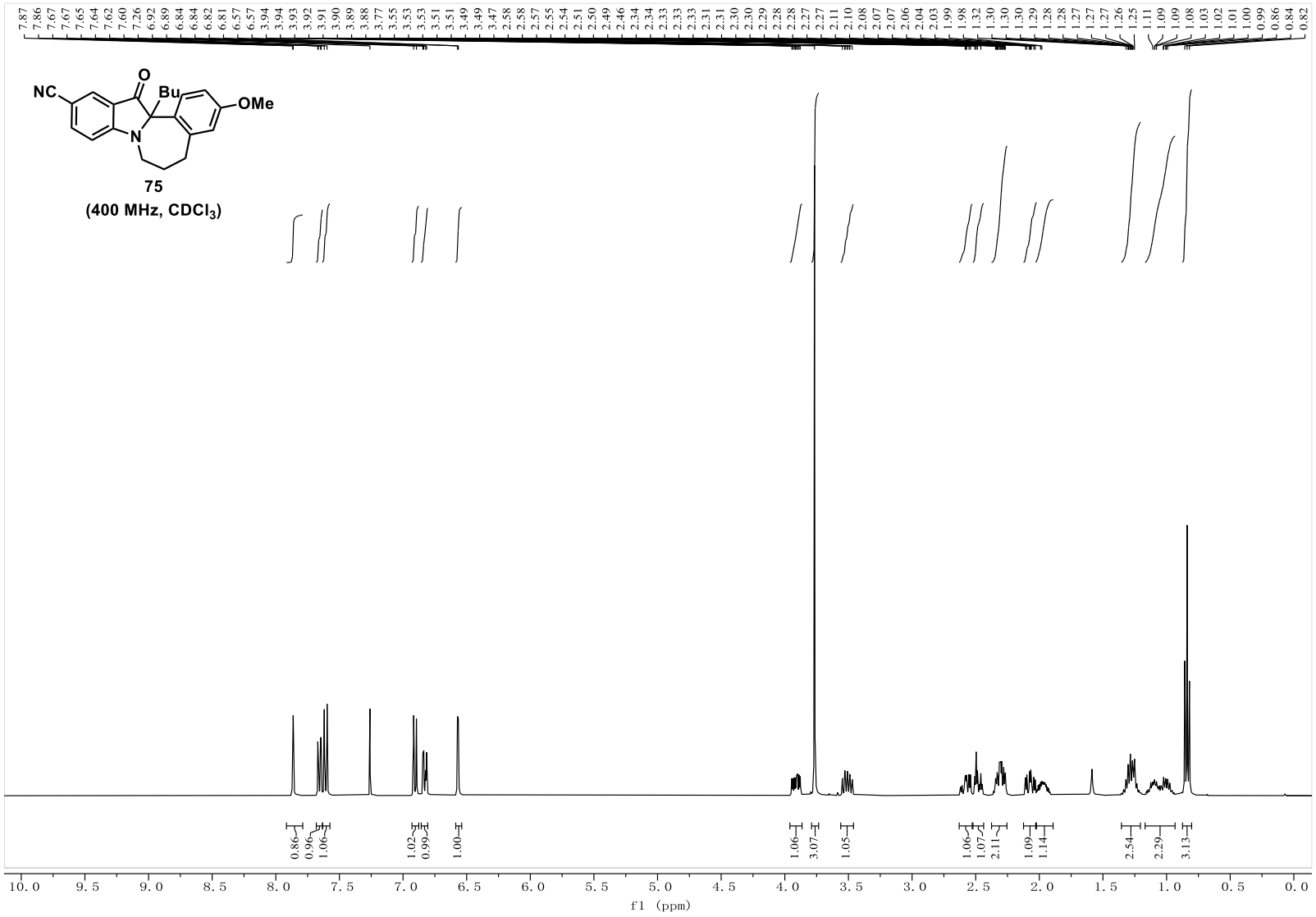

-217.4
O
F
N
Bn
MeO
OMe
72
(376 MHz, CDCl3)
-80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 -230 -240 -250 -260 -270 -280 -290 -300 -310
f1 (ppm)

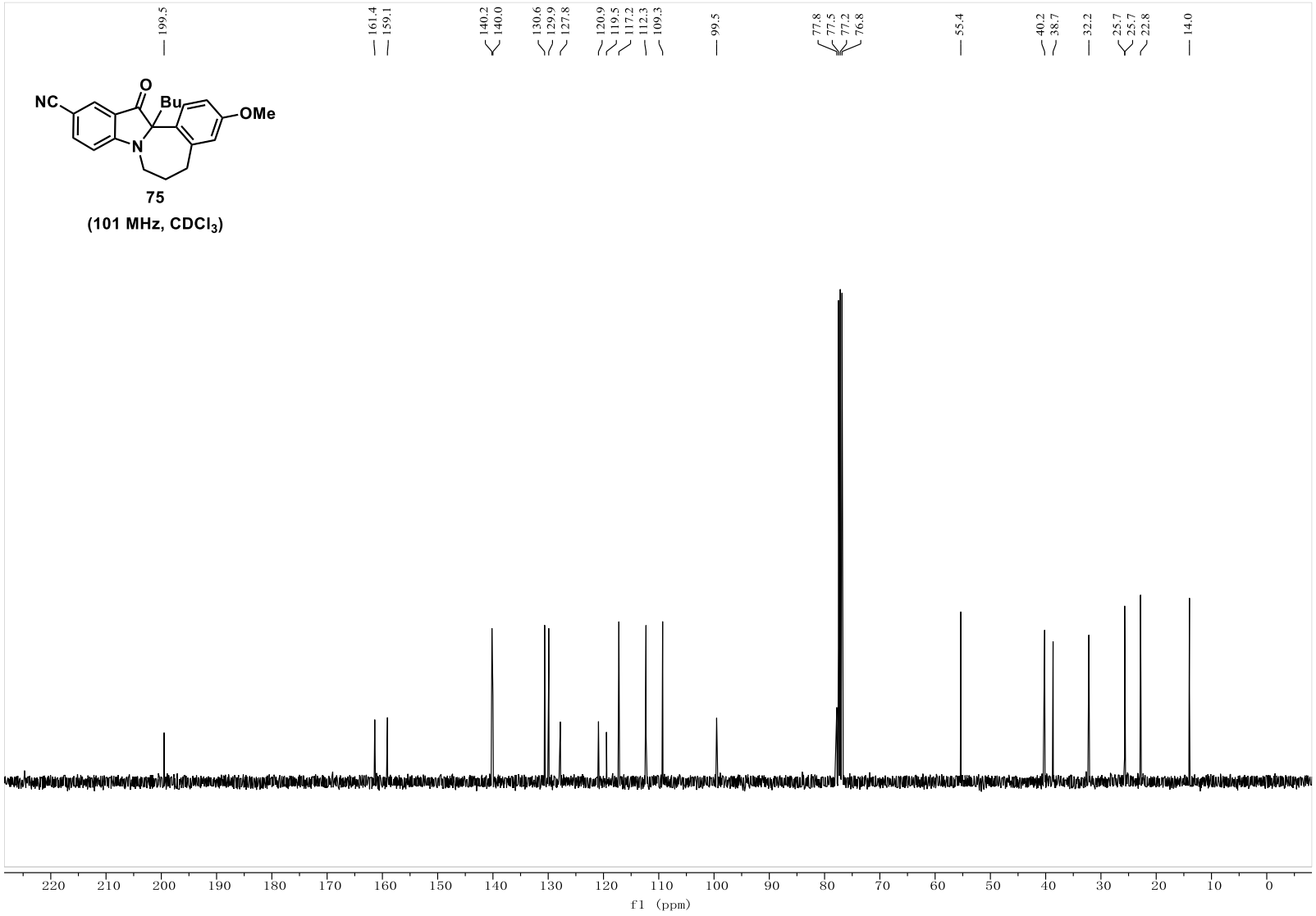

Cl
O
N
H
73
OMe
(400 MHz, CDCl3)
7.52
7.52
7.35
7.34
7.33
7.32
7.18
6.73
6.71
6.70
6.68
6.57
6.56
6.55
6.55
6.53
6.52
4.97
3.68
2.86
2.84
2.83
2.81
2.80
2.79
2.78
2.77
2.75
2.74
2.72
2.21
2.20
2.19
2.18
2.17
2.17
2.16
2.15
2.05
2.02
2.01
2.01
1.99
1.98
1.81
1.80
1.79
1.78
1.77
1.77
1.76
1.75
1.75
1.75
1.74
1.74
1.73
1.72
0.90
1.00
2.18
2.15
1.06
3.29
2.35
1.17
1.19
2.33
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
−0.5
−1.0
f1 (ppm)

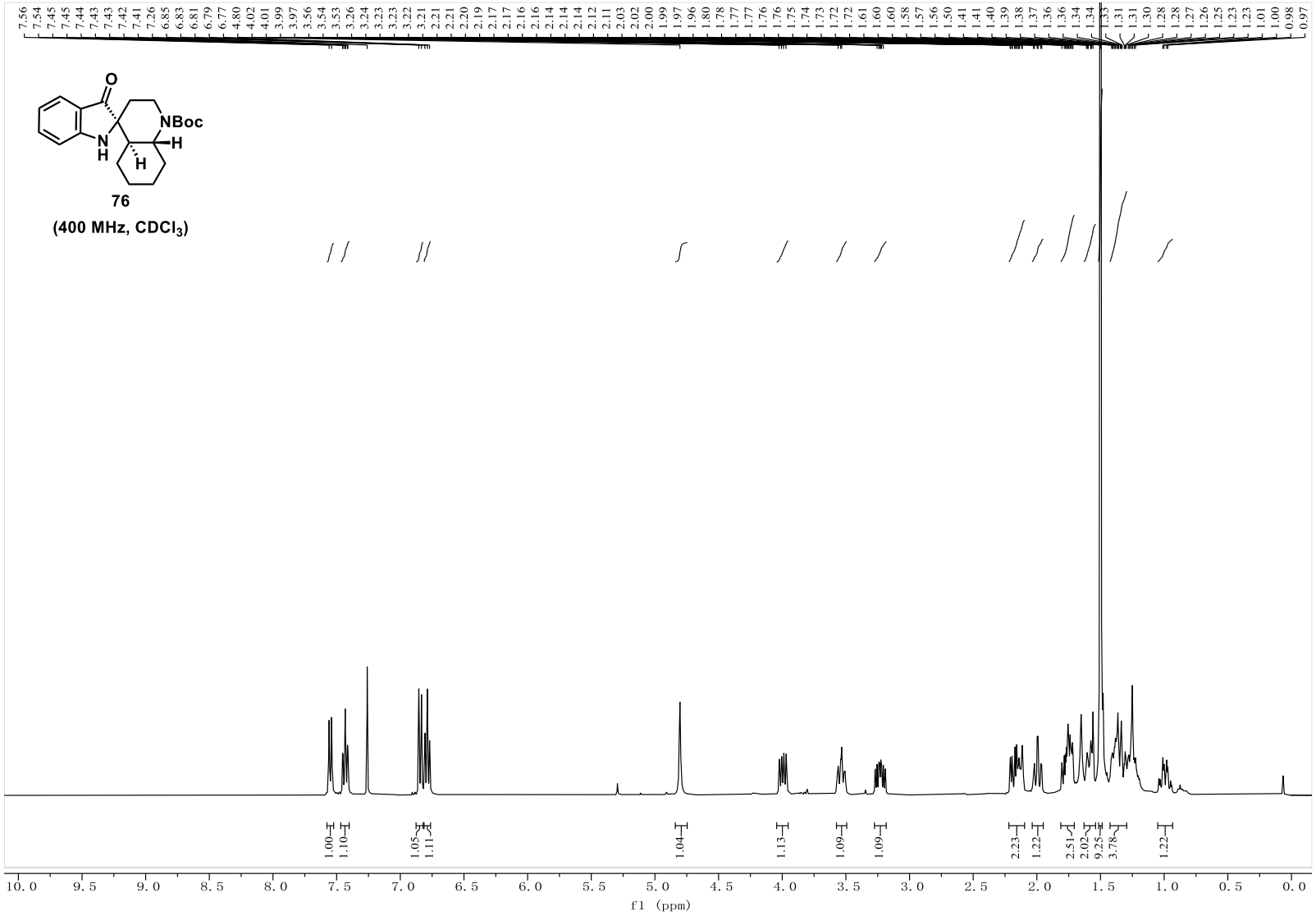

203.8
159.3
158.9
139.7
137.3
127.7
127.1
124.6
124.4
121.1
113.8
113.6
113.5
77.5
77.2
76.8
68.8
55.4
34.1
29.6
19.4
Cl
O
N
H
73
OMe
(101 MHz, CDCl3)
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

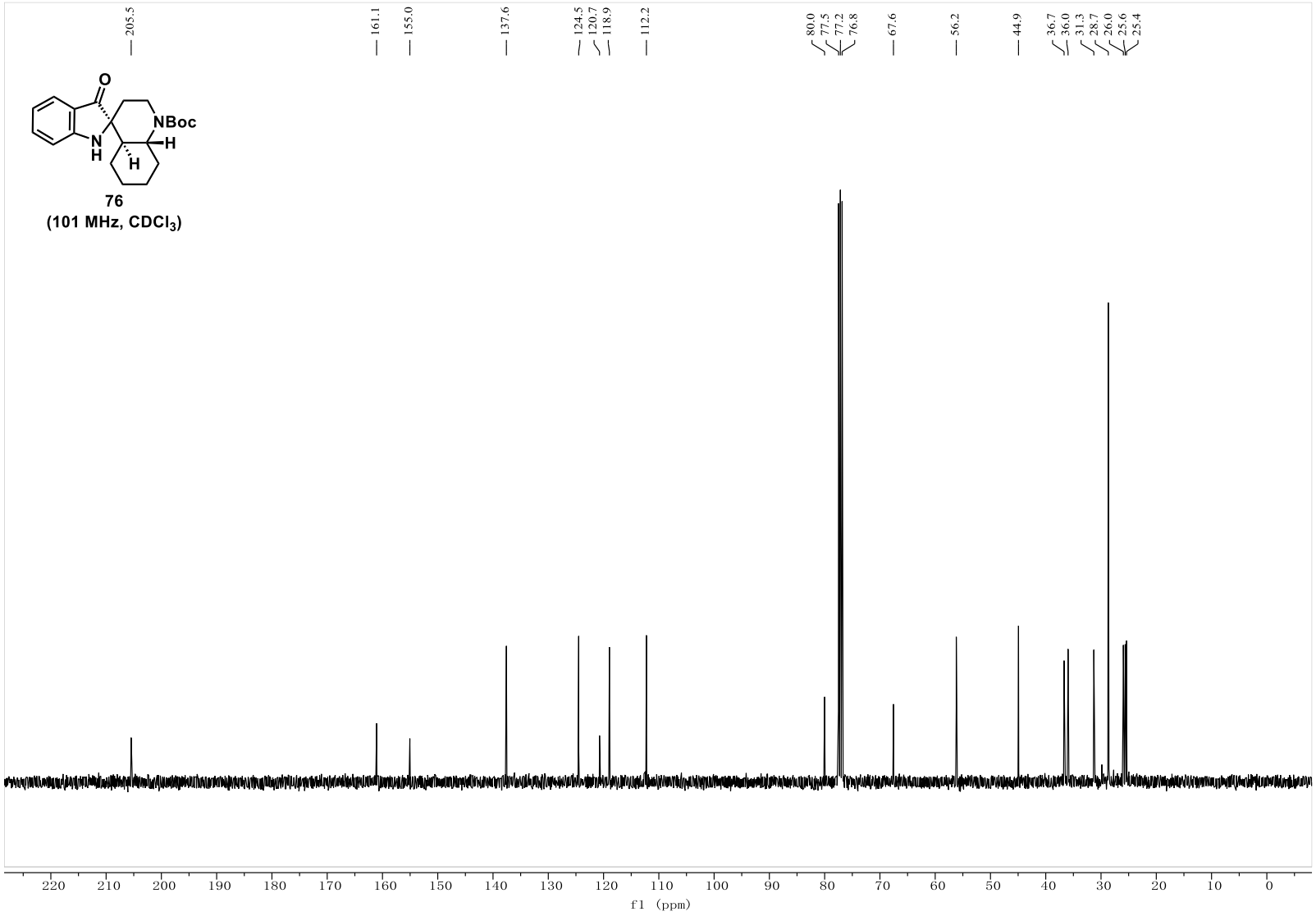

74
(400 MHz, CDCl3)
7.65 7.63 7.53 7.52 7.49 7.19 7.19 7.18 7.17 7.17 7.15 7.15 6.92 6.91 6.90 6.88 6.88 6.87 6.86 6.85 6.80 6.78 6.76
5.04 4.76 4.76 4.75 4.74 4.73 4.72 4.71 4.24 4.23 4.22 4.21 4.20 4.19 4.18
2.32 2.31 2.30 2.29 2.29 2.28 2.27 2.26 2.07 2.06 2.05 2.04 2.03 2.02 2.01 2.01
0.93 1.00 1.03 3.97 1.06 0.95 1.06 1.05 1.04 1.06
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
f1 (ppm)

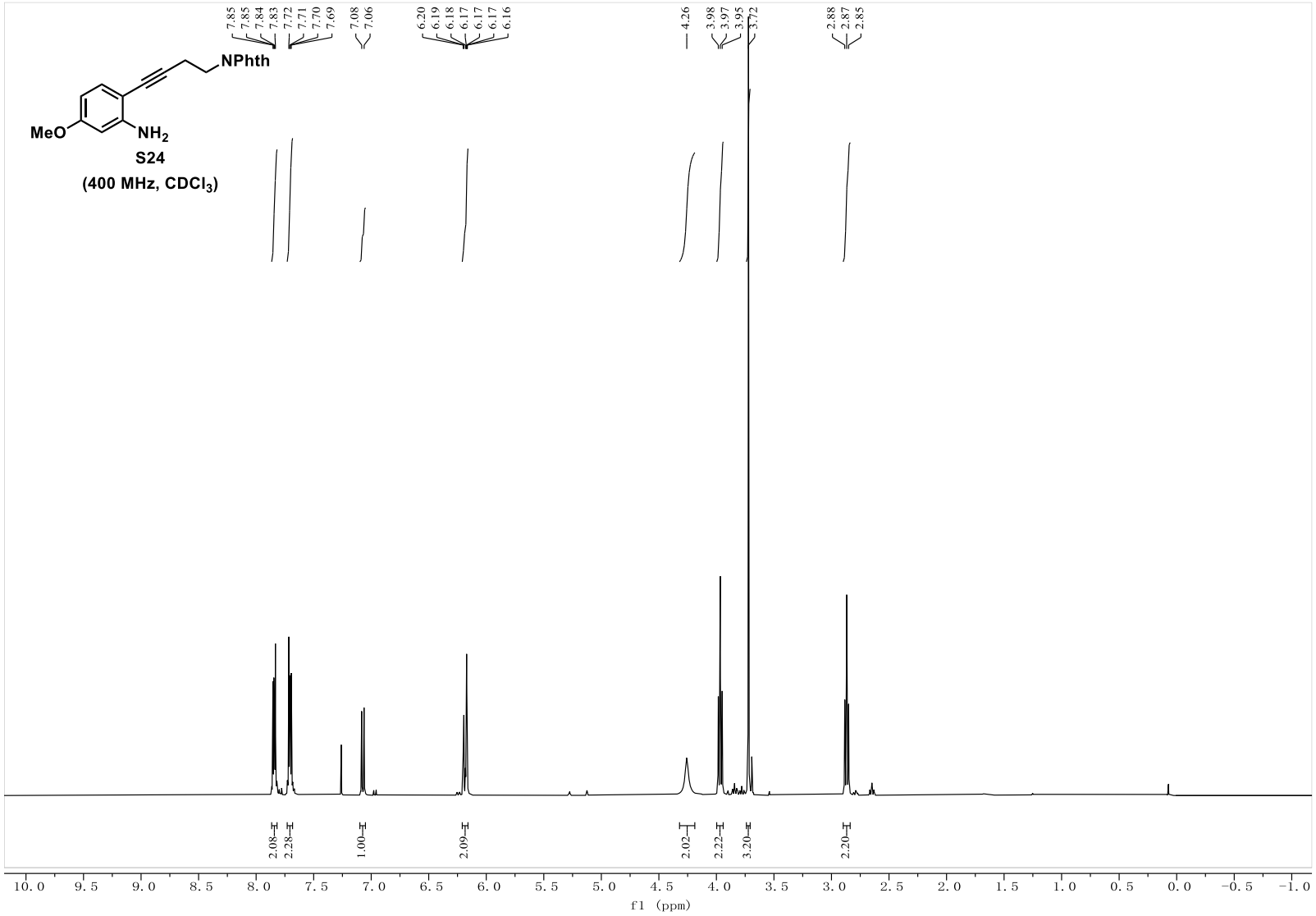

203.3
160.7
155.7
137.8
129.9
126.6
125.5
121.2
121.1
120.0
119.9
117.9
112.6
77.5
77.2 CDCl3
76.8
64.1
62.7
32.3
O
O
N
H
74
(101 MHz, CDCl3)
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

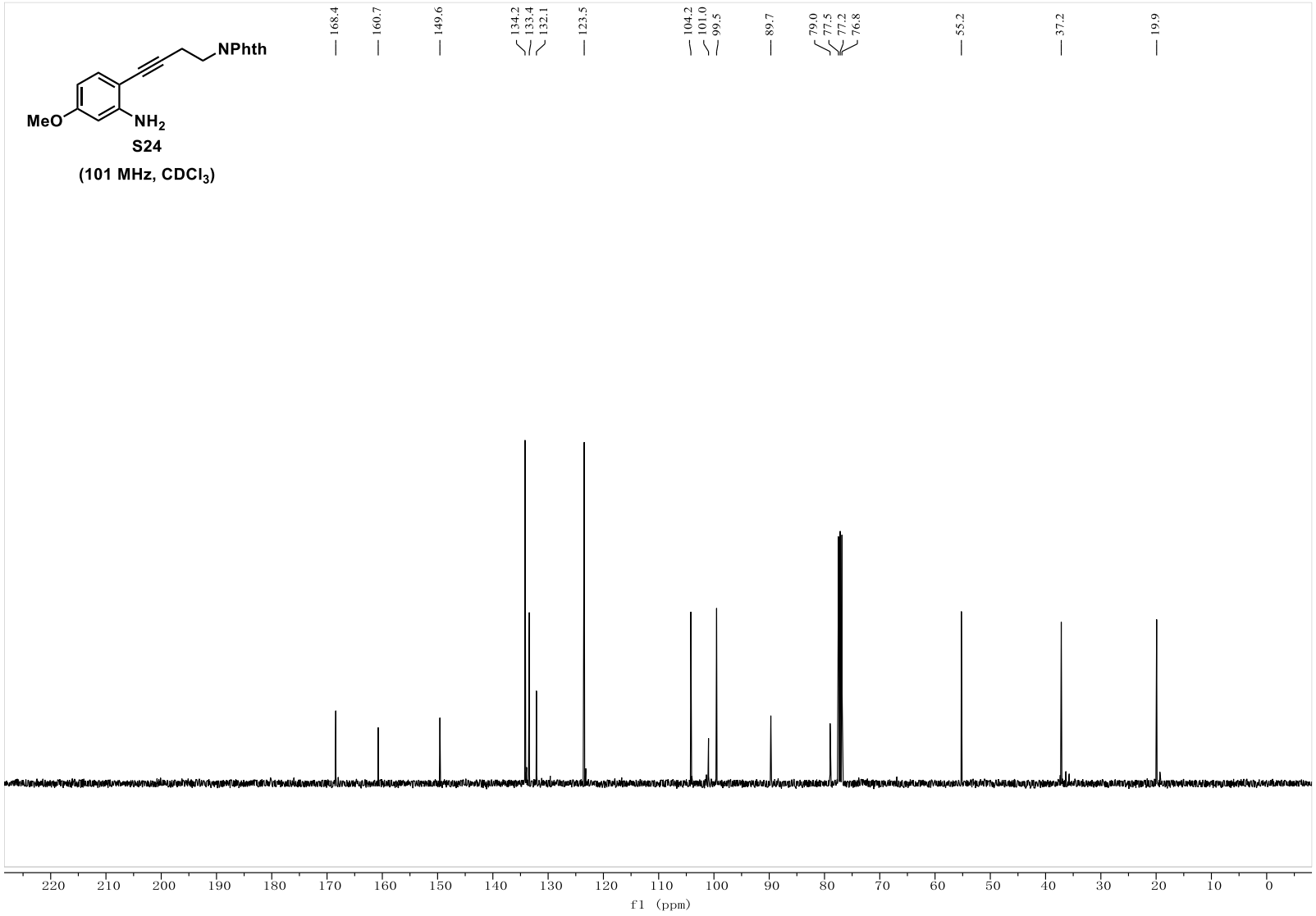

NC
O
Bu
OMe
N
75
(400 MHz, CDCl3)
f1 (ppm)

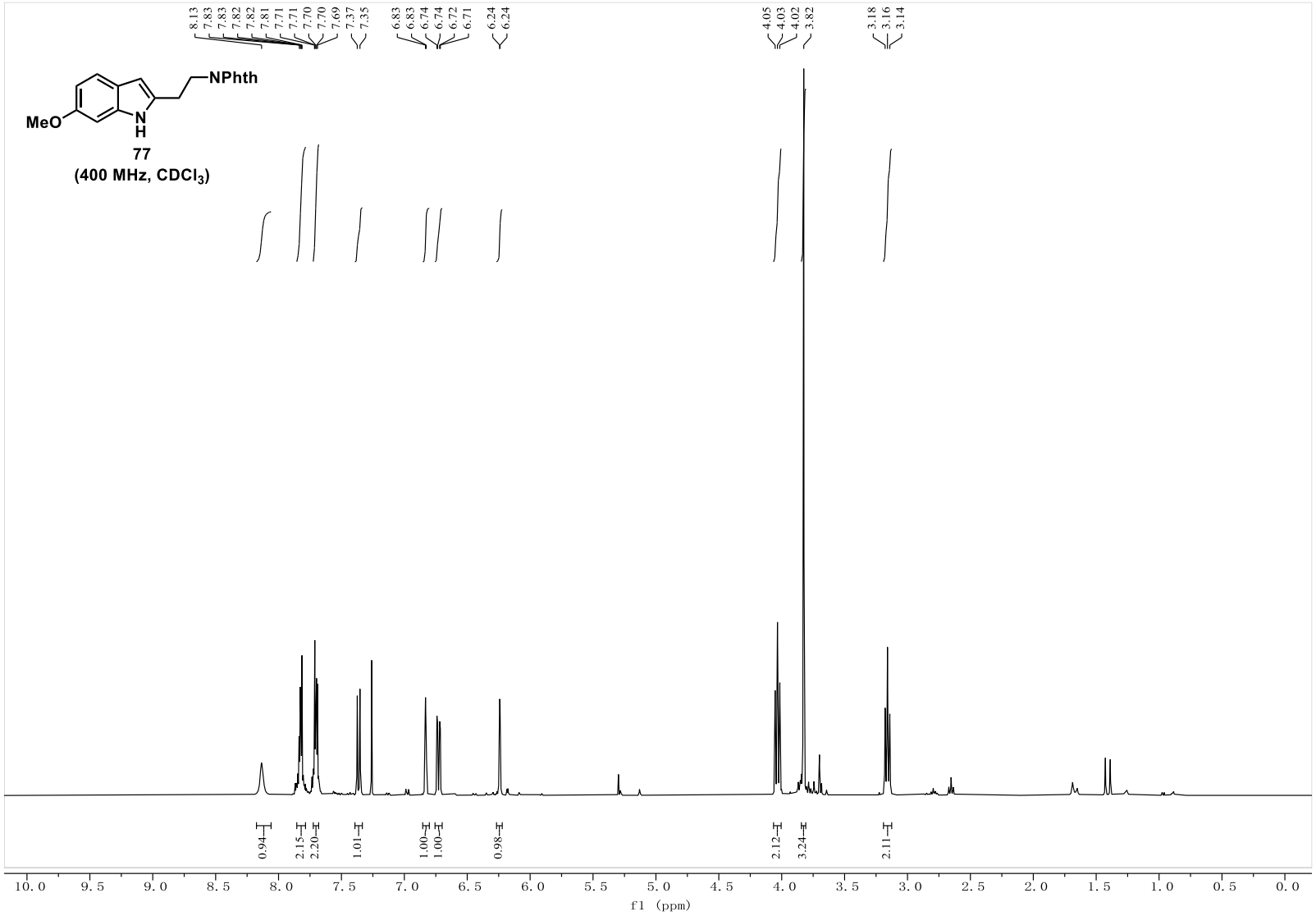

199.5
161.4
159.1
140.2
140.0
130.6
129.9
127.8
120.9
119.5
117.2
112.3
109.3
99.5
77.8
77.5
77.2
76.8
55.4
40.2
38.7
32.2
25.7
25.7
22.8
14.0
NC
O
Bu
OMe
N
75
(101 MHz, CDCl3)
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

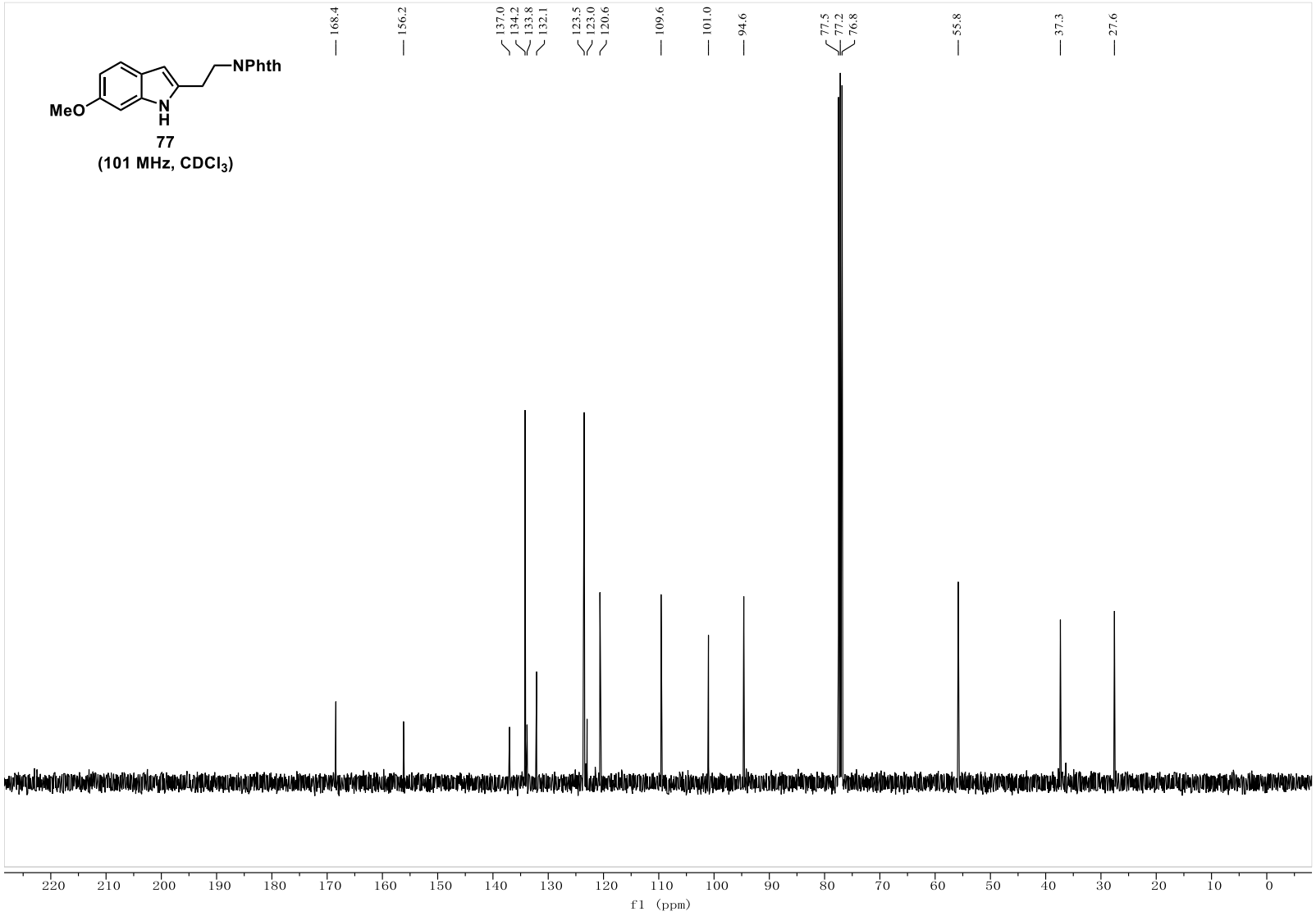

O
NBoc
N
H
H
H
76
(400 MHz, CDCl3)
7.56 7.54 7.45 7.45 7.44 7.43 7.43 7.42 7.41 7.26 6.85 6.83 6.81 6.79 6.77 4.80 4.02 4.01 3.99 3.97 3.56 3.54 3.53 3.26 3.24 3.23 3.23 3.22 3.21 2.21 2.21 2.20 2.19 2.17 2.17 2.16 2.16 2.14 2.14 2.14 2.12 2.11 2.03 2.02 2.00 1.99 1.97 1.96 1.80 1.78 1.77 1.77 1.76 1.76 1.75 1.74 1.73 1.72 1.72 1.61 1.60 1.60 1.58 1.57 1.56 1.50 1.41 1.41 1.40 1.39 1.38 1.37 1.36 1.36 1.34 1.34 1.33 1.31 1.31 1.30 1.28 1.28 1.27 1.26 1.25 1.23 1.23 1.01 1.00 0.98 0.97
1.00 1.10 1.05 1.11 1.04 1.13 1.09 1.09 2.23 1.22 2.51 2.02 9.25 3.78 1.22
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
f1 (ppm)

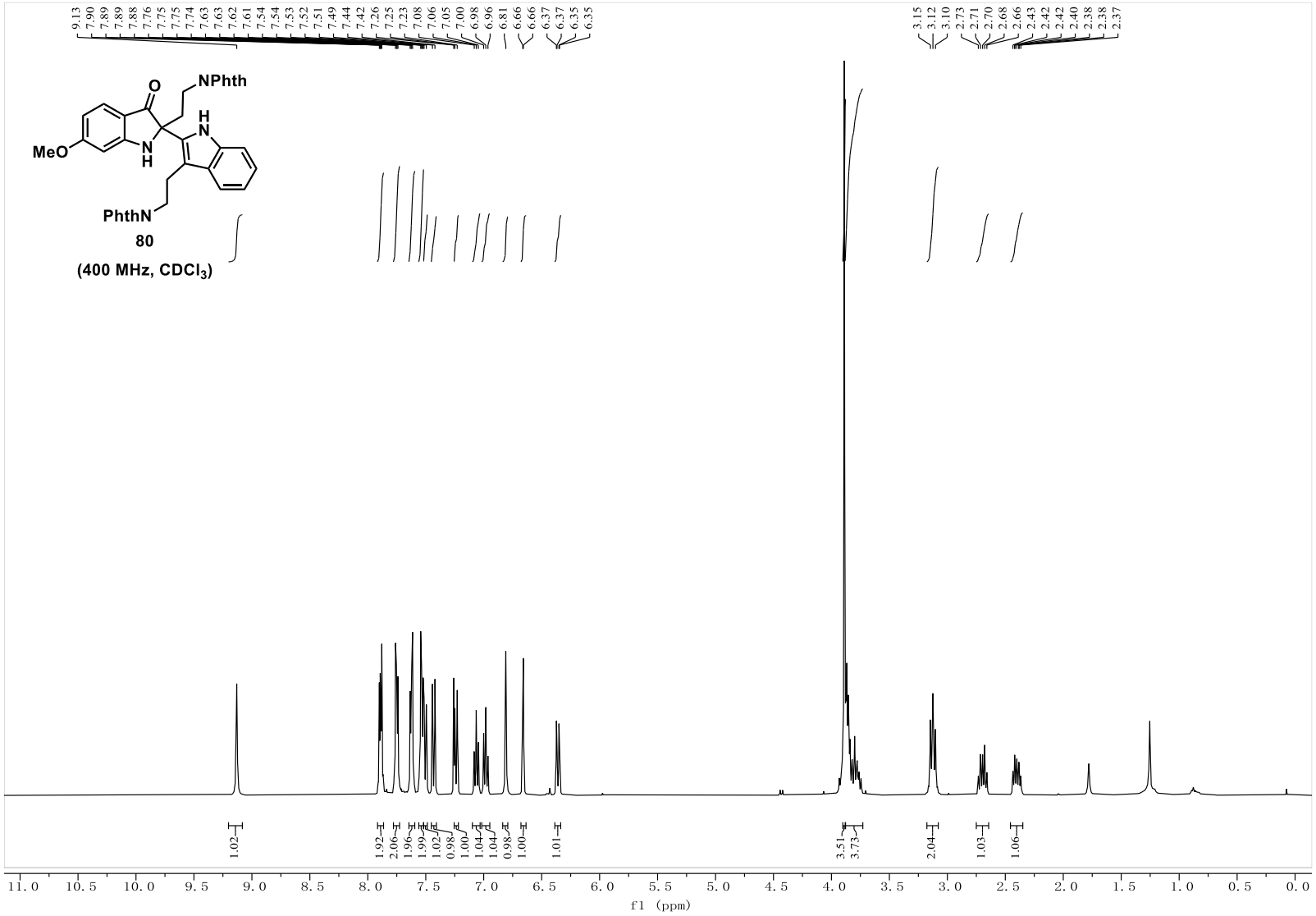

205.5
161.1
155.0
137.6
124.5
120.7
118.9
112.2
80.0
77.5
77.2
76.8
67.6
56.2
44.9
36.7
36.0
31.3
28.7
26.0
25.6
25.4
O
NBoc
N
H
H
H
76
(101 MHz, CDCl3)
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

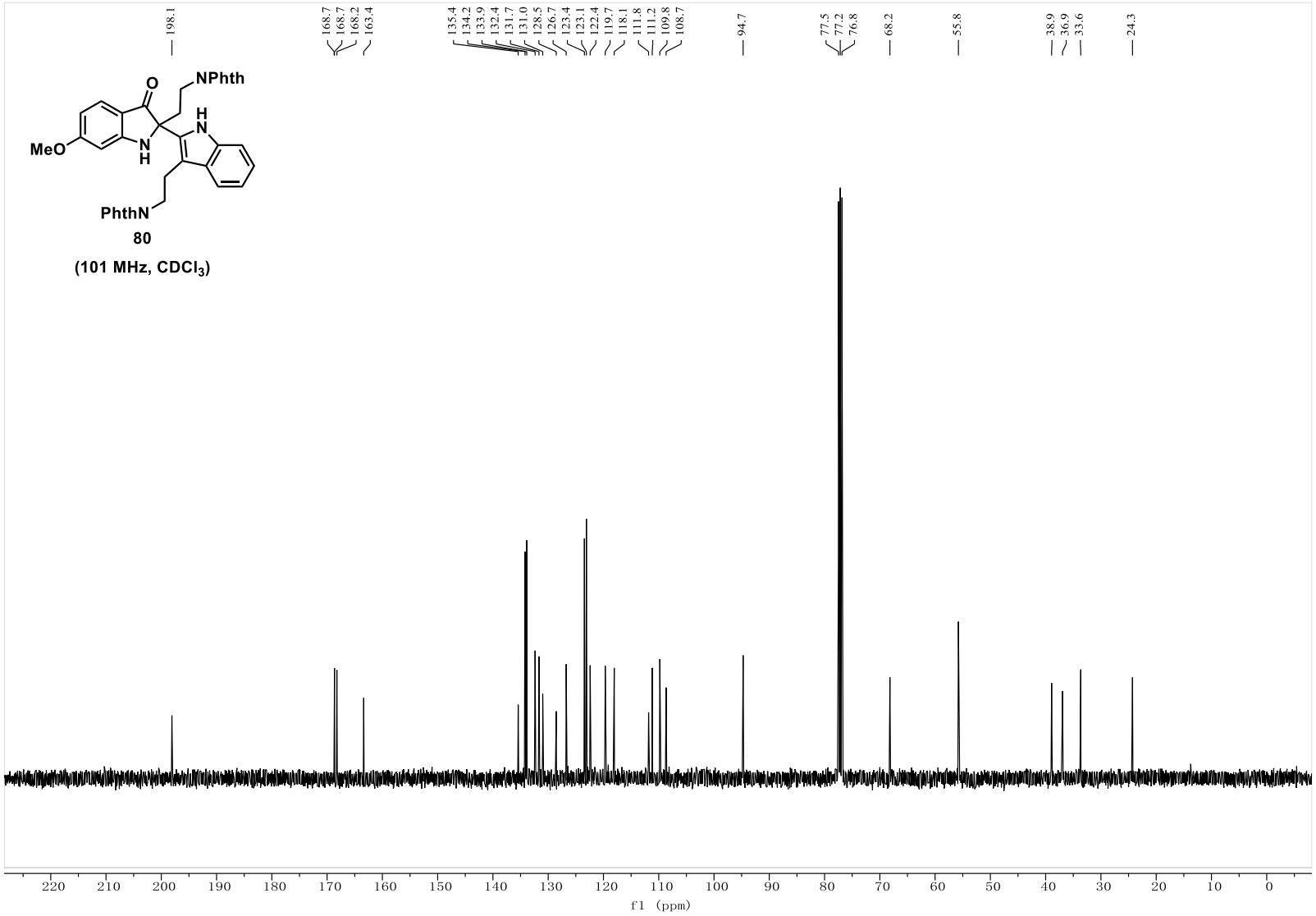

NPhth
MeO
NH2
S24
(400 MHz, CDCl3)
7.85
7.85
7.84
7.83
7.72
7.71
7.70
7.69
7.08
7.06
6.20
6.19
6.18
6.17
6.17
6.17
6.16
4.26
3.98
3.97
3.95
3.72
2.88
2.87
2.85
2.08
2.28
1.00
2.09
2.02
2.22
3.20
2.20
f1 (ppm)

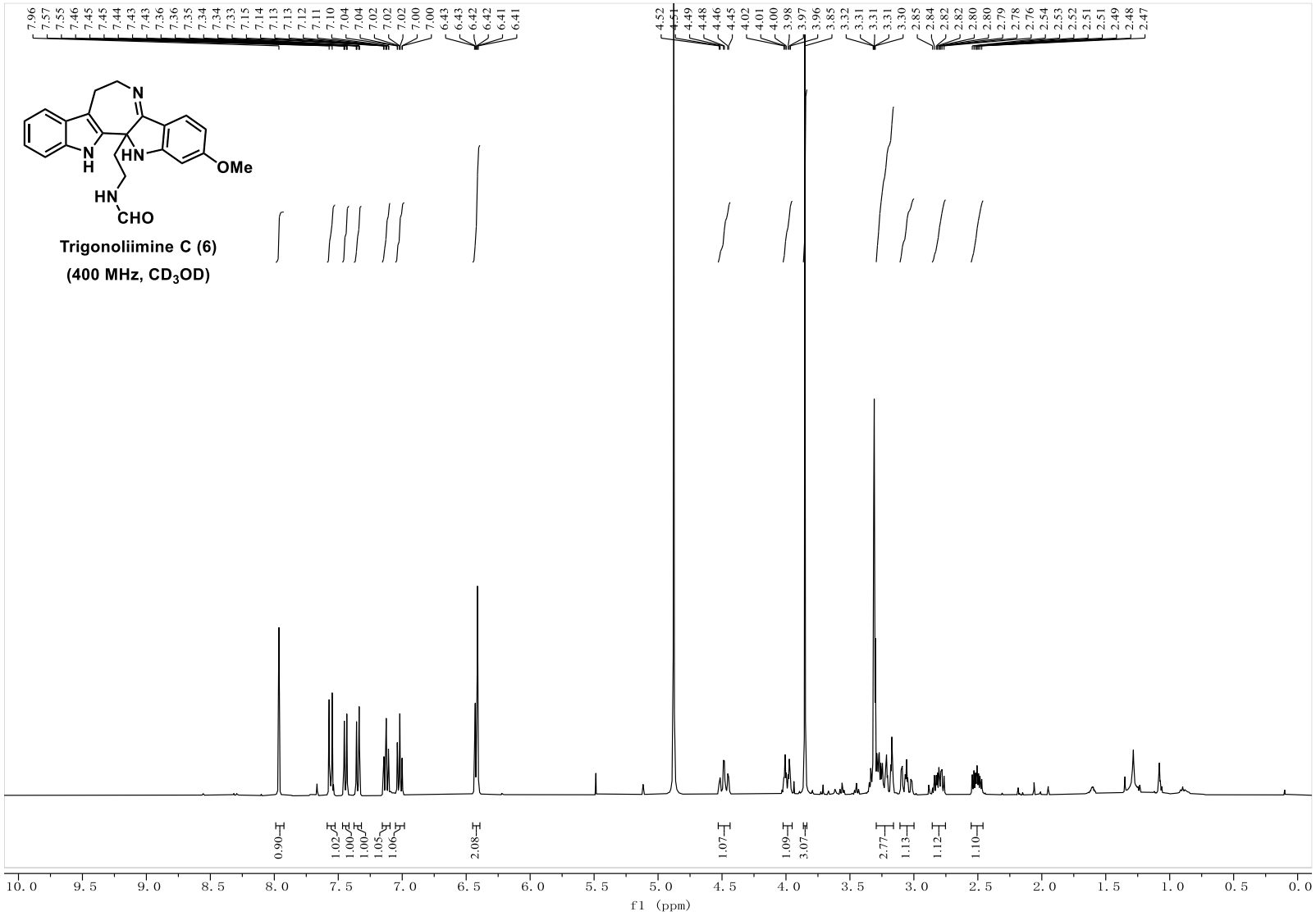

NPhth
MeO
NH2
S24
(101 MHz, CDCl3)
168.4
160.7
149.6
134.2
133.4
132.1
123.5
104.2
101.0
99.5
89.7
79.0
77.5
77.2
76.8
55.2
37.2
19.9
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

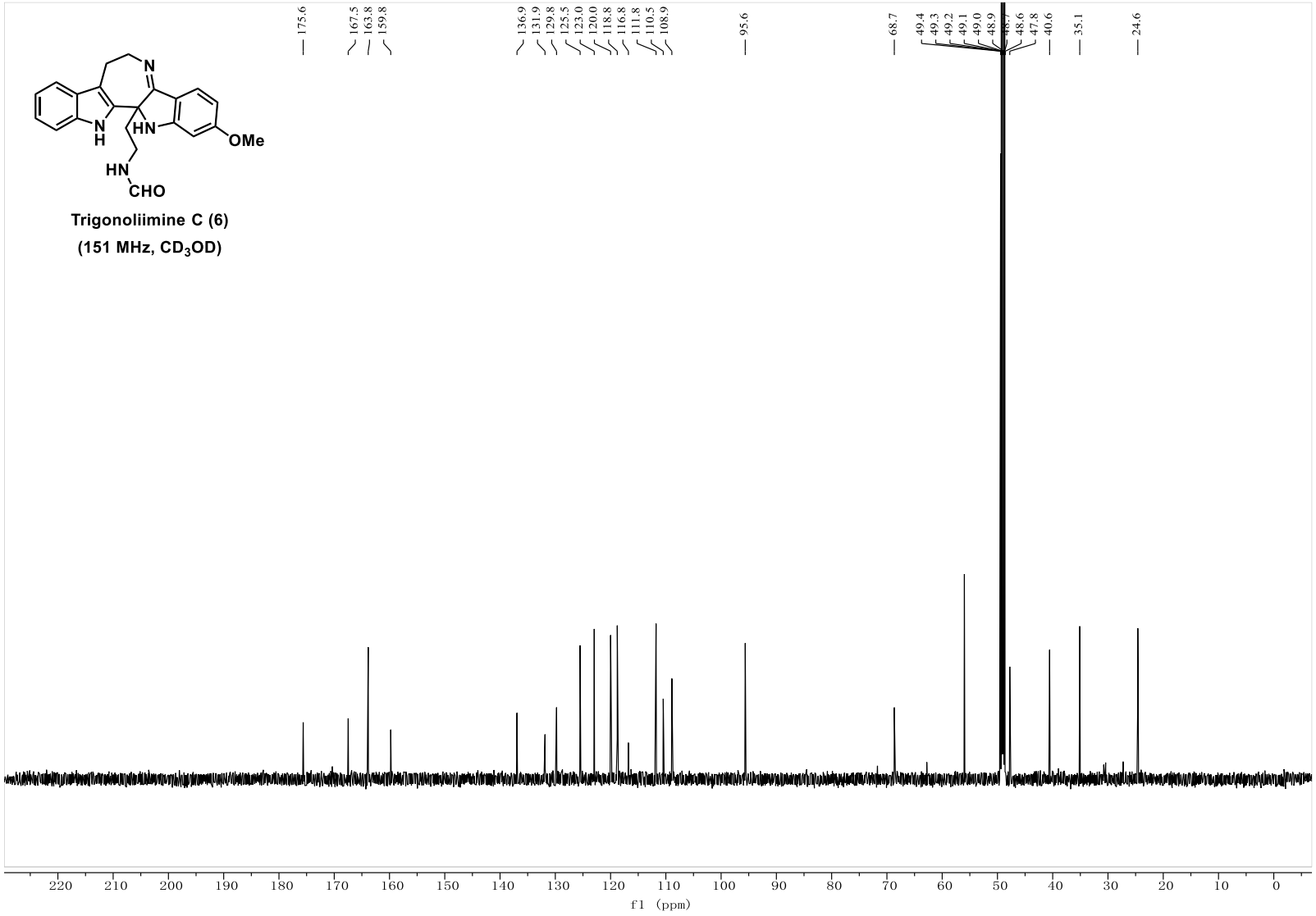

8.13
7.83
7.83
7.82
7.82
7.81
7.71
7.71
7.70
7.70
7.69
7.37
7.35
6.83
6.83
6.74
6.74
6.72
6.71
6.24
6.24
4.05
4.03
4.02
3.82
3.18
3.16
3.14
NPhth
MeO
N
H
77
(400 MHz, CDCl3)
0.94
2.15
2.20
1.01
1.00
1.00
0.98
2.12
3.24
2.11
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

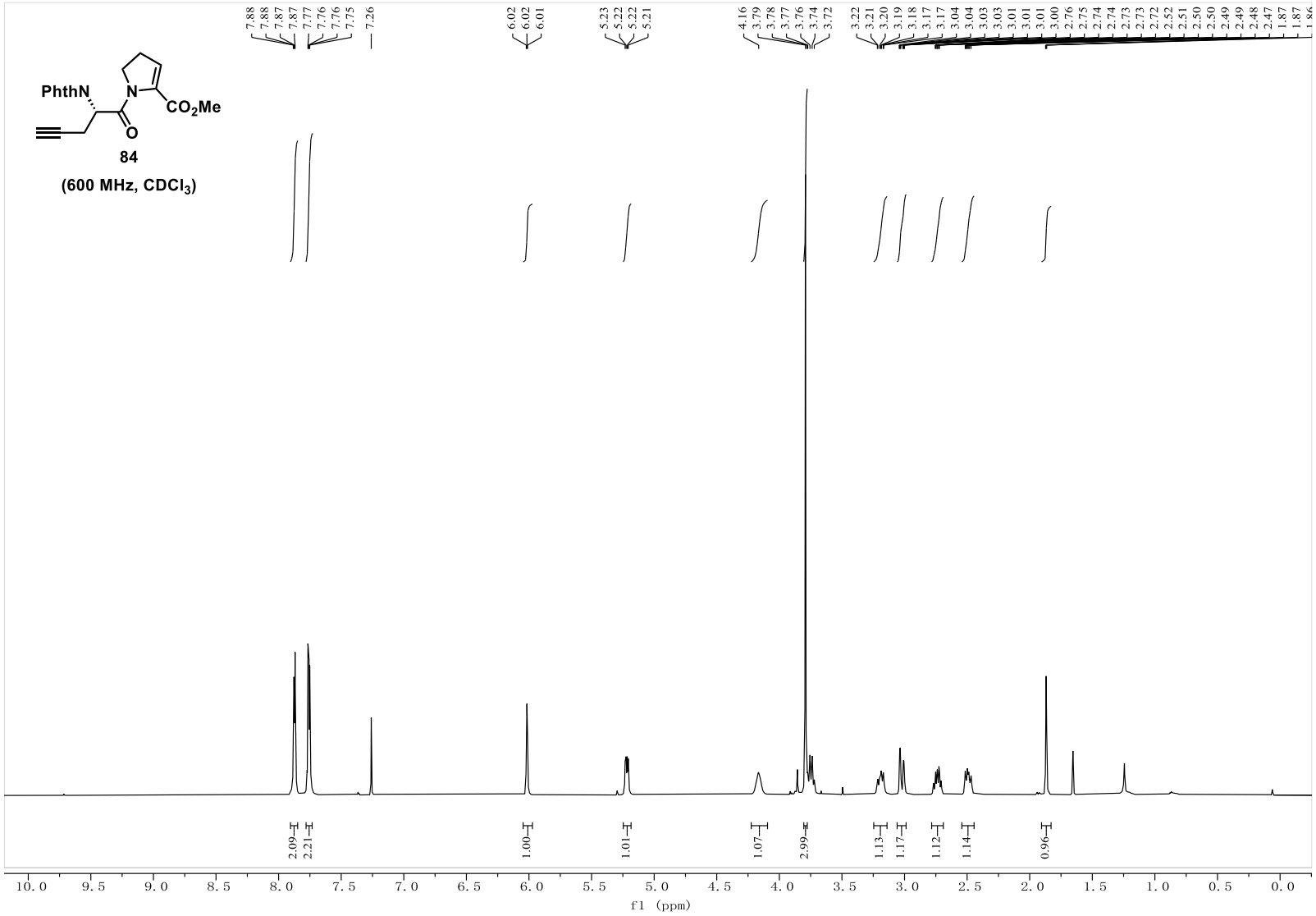

168.4
156.2
137.0
134.2
133.8
132.1
123.5
123.0
120.6
109.6
101.0
94.6
77.5
77.2
76.8
55.8
37.3
27.6
NPhth
MeO
N
H
77
(101 MHz, CDCl3)
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

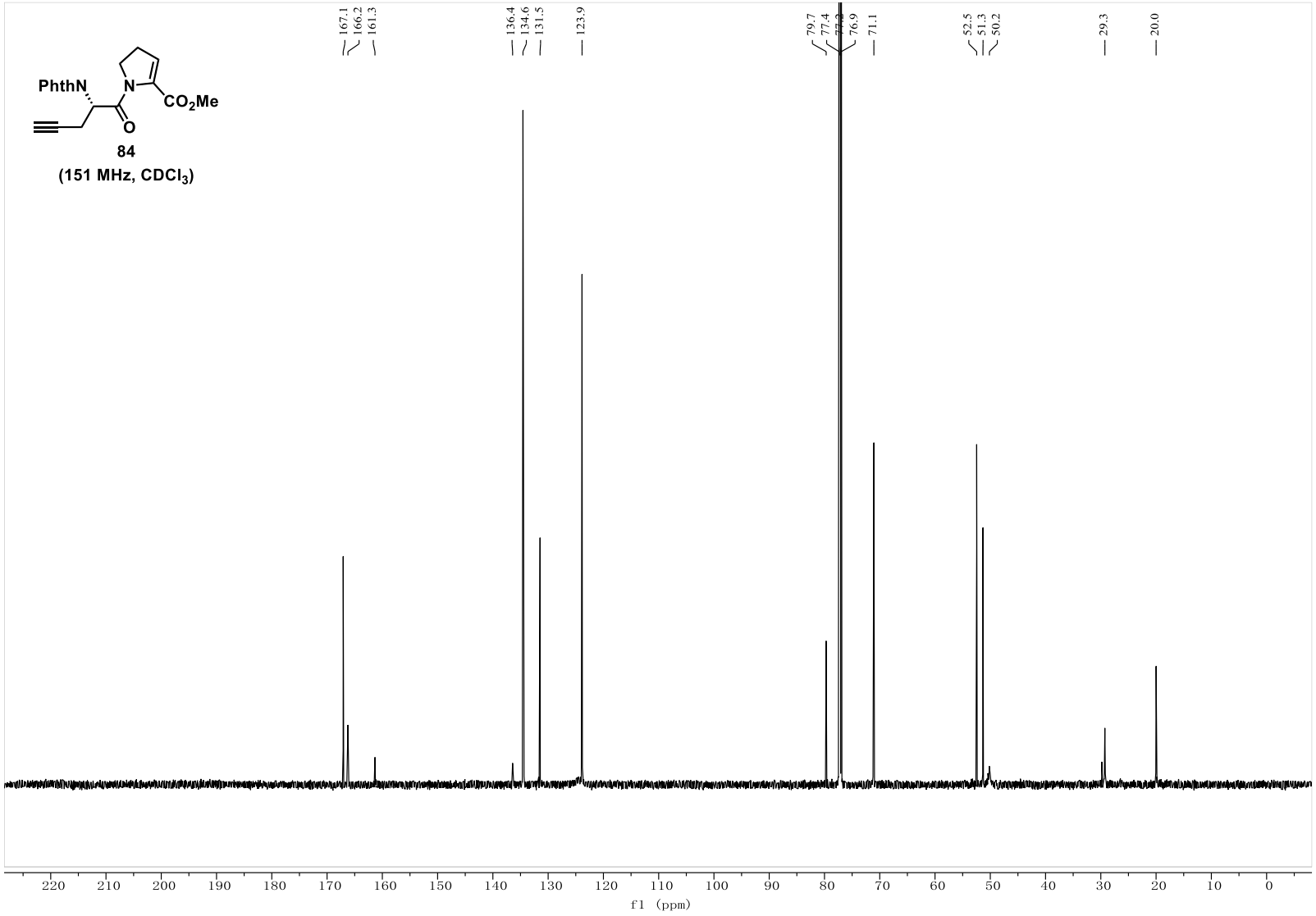

9.13
7.90
7.89
7.89
7.88
7.76
7.75
7.75
7.74
7.63
7.63
7.62
7.61
7.54
7.54
7.53
7.52
7.51
7.49
7.44
7.42
7.26
7.25
7.23
7.08
7.06
7.05
7.00
6.98
6.96
6.81
6.66
6.66
6.37
6.37
6.35
6.35
3.15
3.12
3.10
2.73
2.71
2.70
2.68
2.66
2.43
2.42
2.42
2.40
2.38
2.38
2.37
O
NPhth
H
N
MeO
N
H
PhthN
80
(400 MHz, CDCl3)
1.02
1.92
2.06
1.96
1.99
1.02
0.98
1.00
1.04
1.04
0.98
1.00
1.01
3.51
3.73
2.04
1.03
1.06
11.0
10.5
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
f1 (ppm)

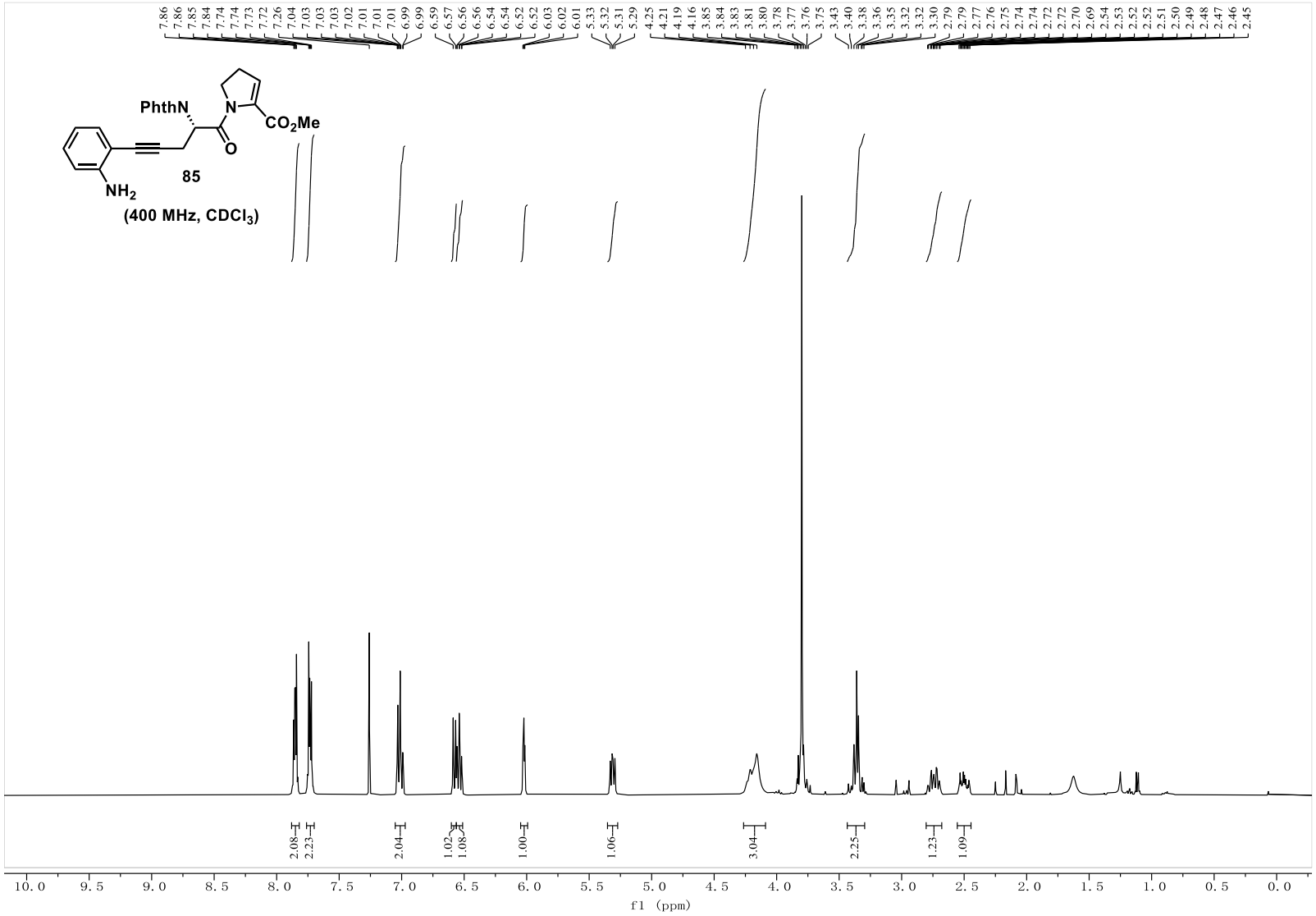

198.1
168.7
168.7
168.2
163.4
135.4
134.2
133.9
132.4
131.7
131.0
128.5
126.7
123.4
123.1
122.4
119.7
118.1
111.8
111.2
109.8
108.7
94.7
77.5
77.2
76.8
68.2
55.8
38.9
36.9
33.6
24.3
O
NPhth
H
N
MeO
N
H
PhthN
80
(101 MHz, CDCl3)
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

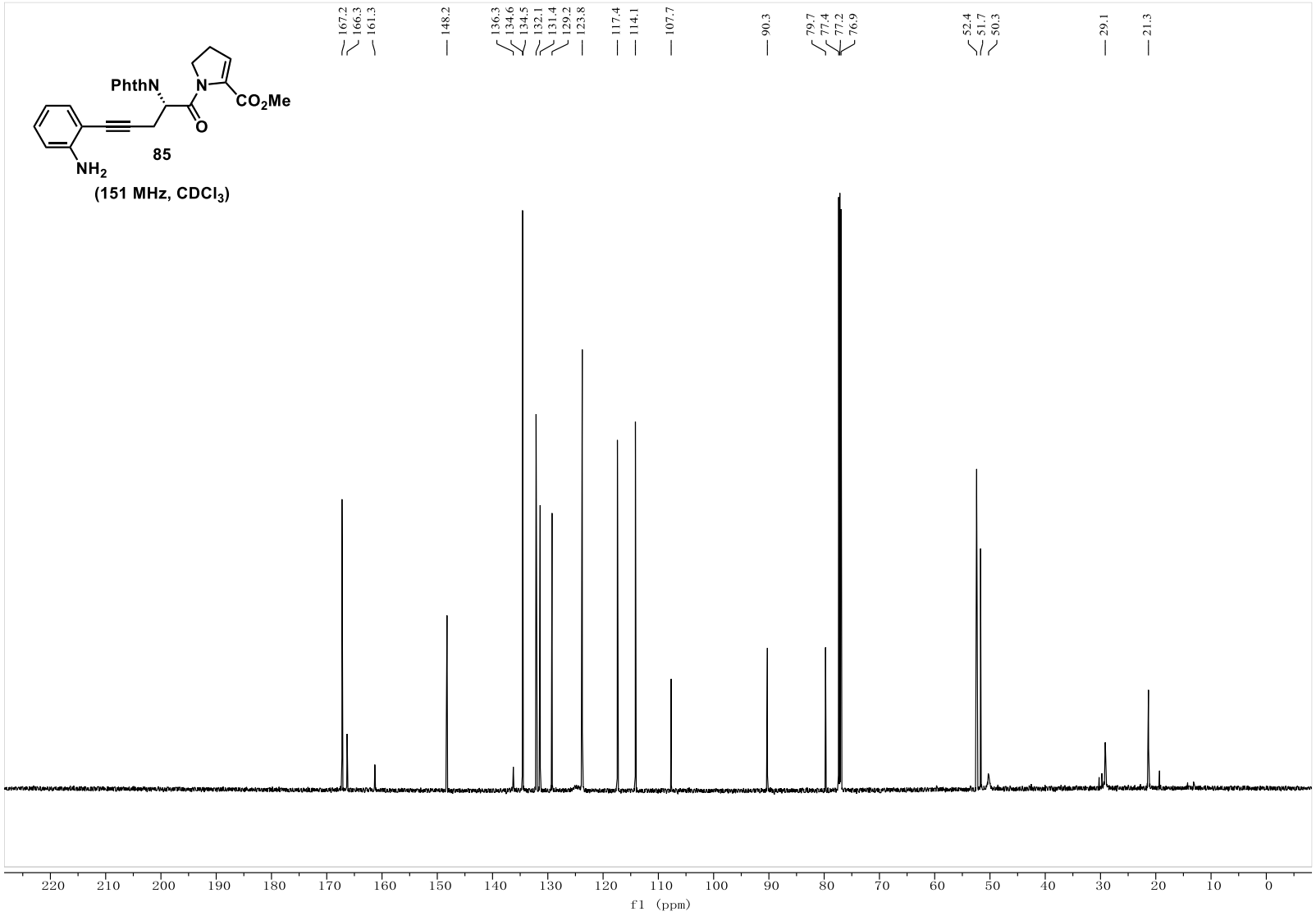

Trigonoliimine C (6)
(400 MHz, CD3OD)
f1 (ppm)

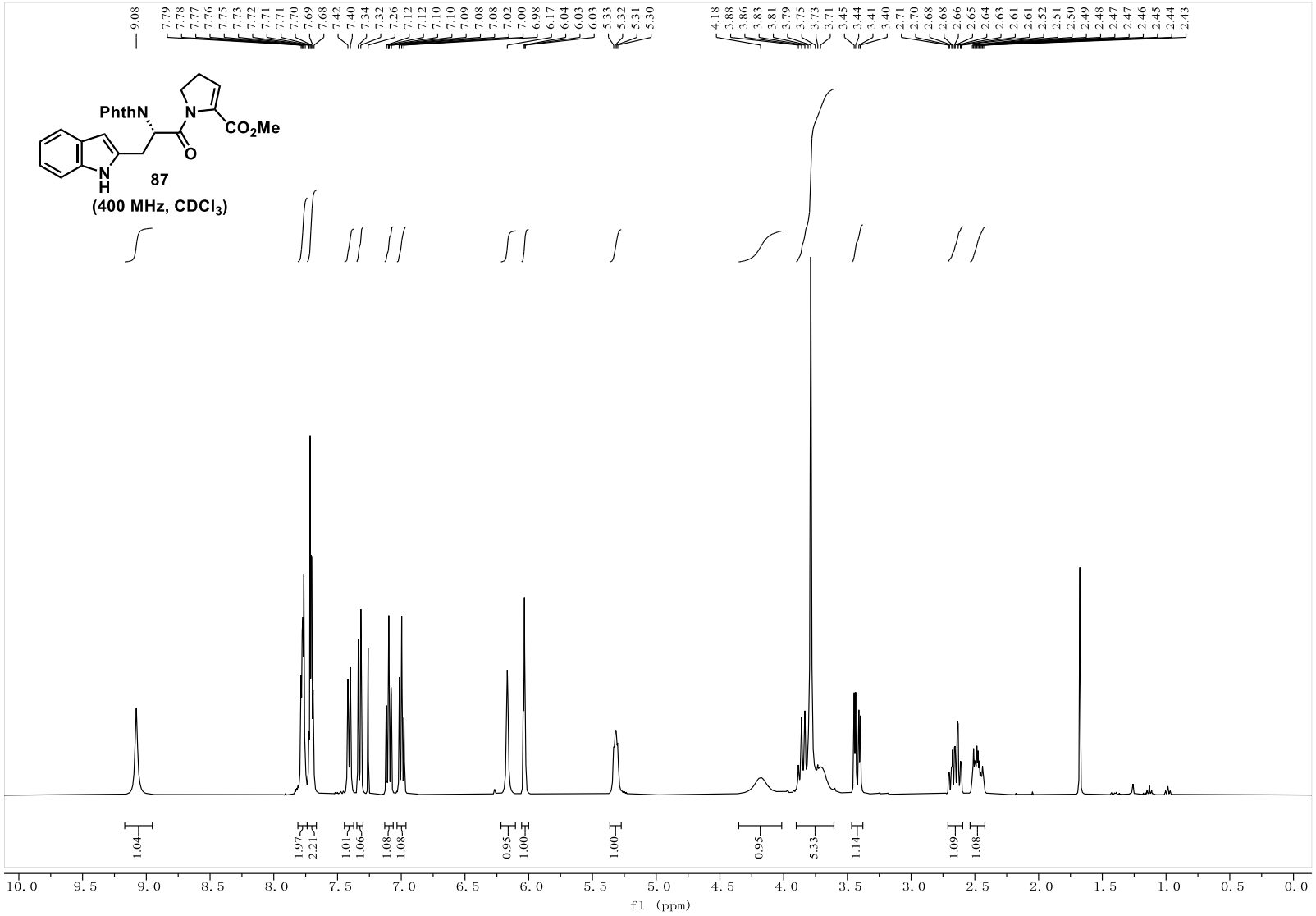

175.6
167.5
163.8
159.8
136.9
131.9
129.8
125.5
123.0
120.0
118.8
116.8
111.8
110.5
108.9
95.6
68.7
49.4
49.3
49.2
49.1
49.0
48.9
48.6
47.8
40.6
35.1
24.6
N
N
H
HN
OMe
HN
CHO
Trigonoliimine C (6)
(151 MHz, CD3OD)
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

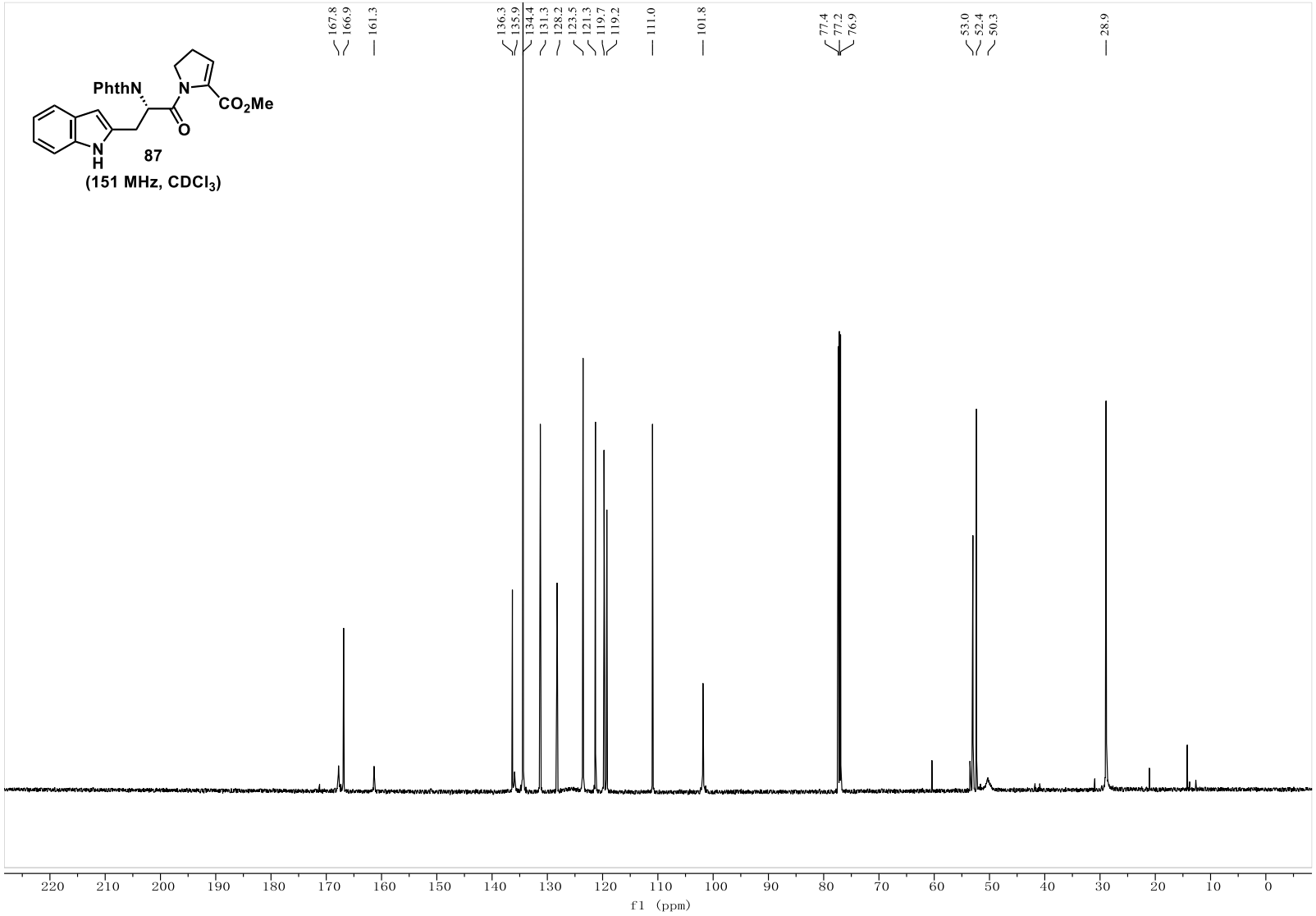

PhthN
N
CO2Me
O
84
(600 MHz, CDCl3)
f1 (ppm)

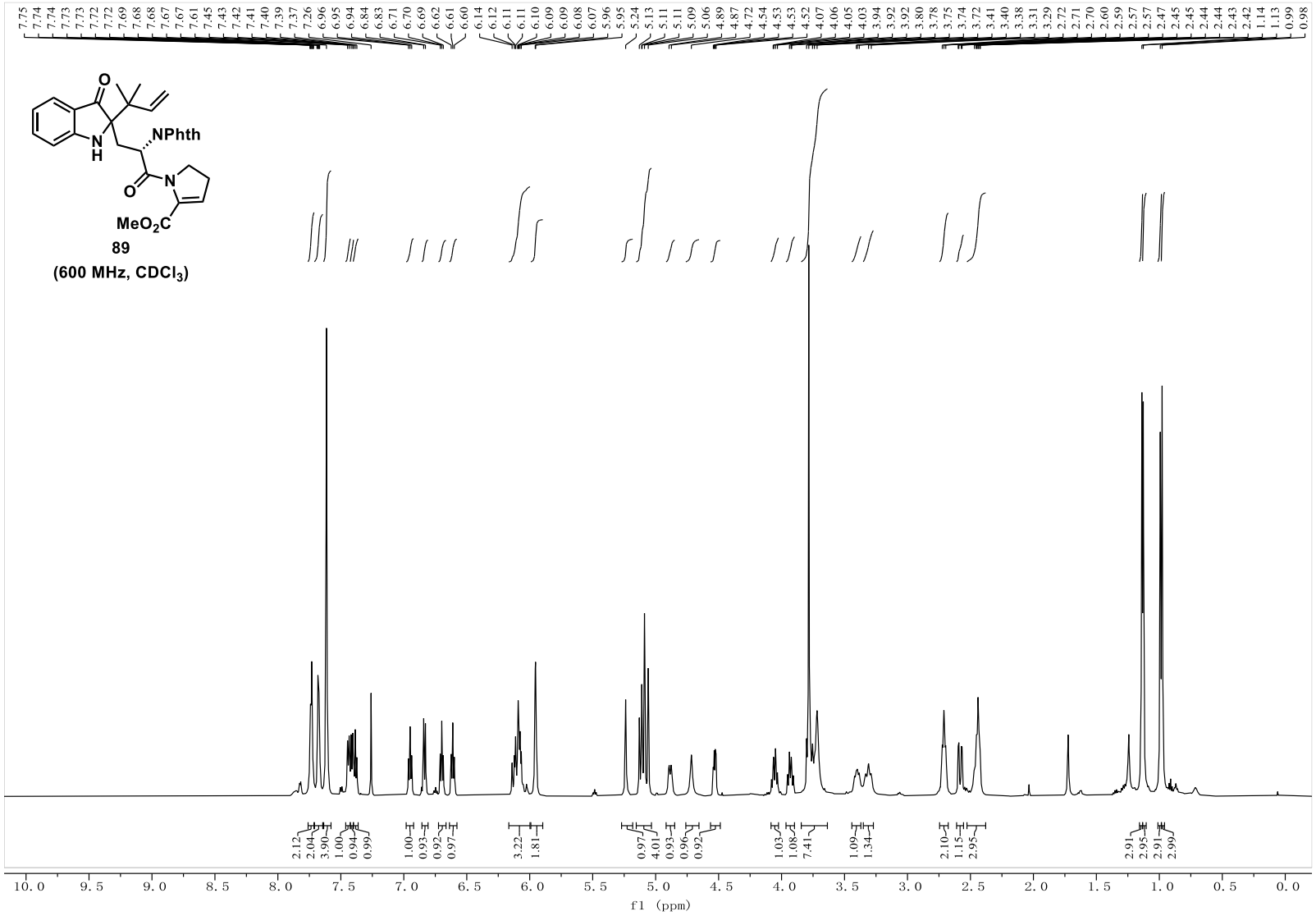

PhthN
N
CO2Me
O
84
(151 MHz, CDCl3)
167.1
166.2
161.3
136.4
134.6
131.5
123.9
79.7
77.4
77.2
76.9
71.1
52.5
51.3
50.2
29.3
20.0
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

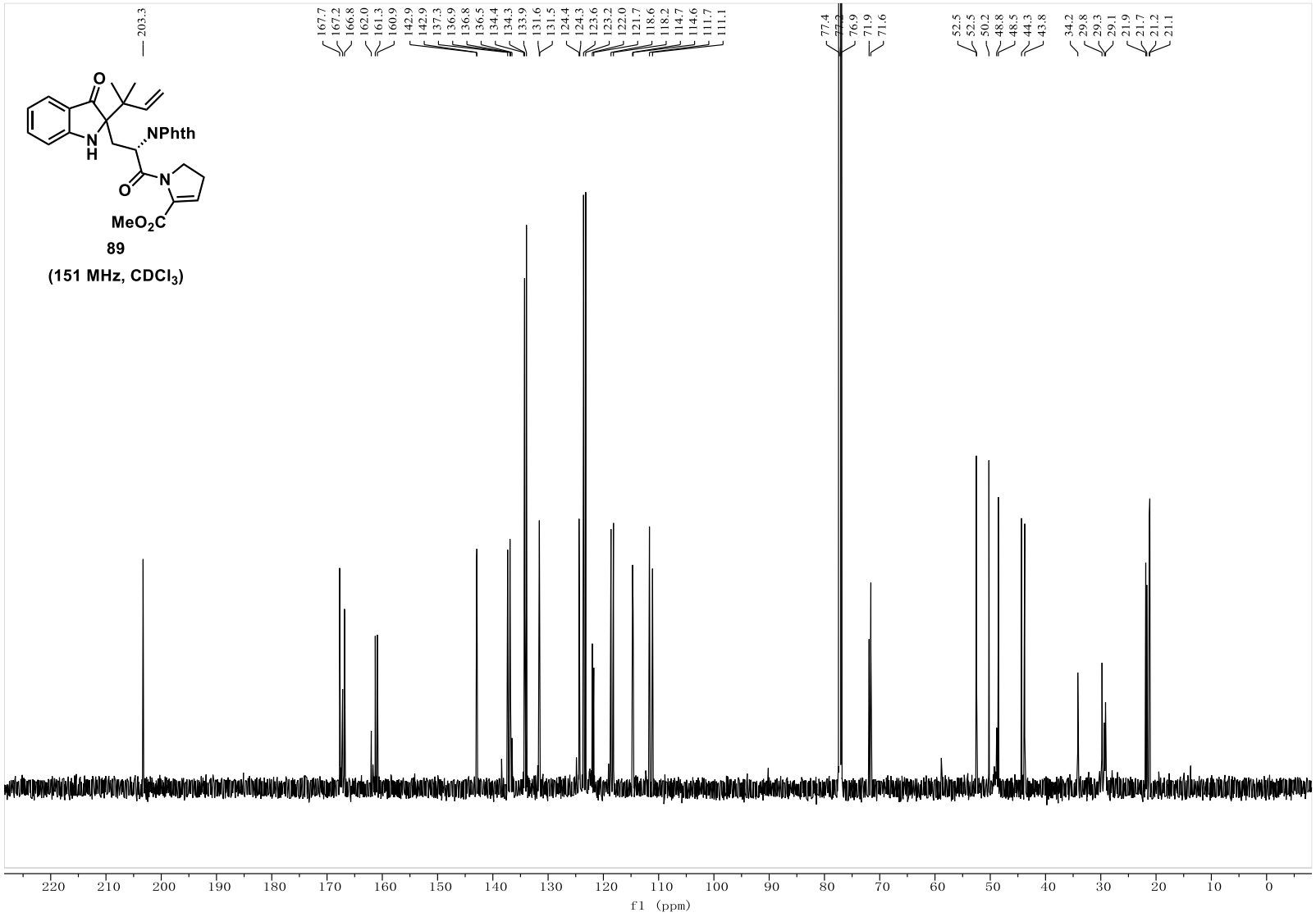

PhthN
N
CO2Me
O
NH2
85
(400 MHz, CDCl3)
f1 (ppm)

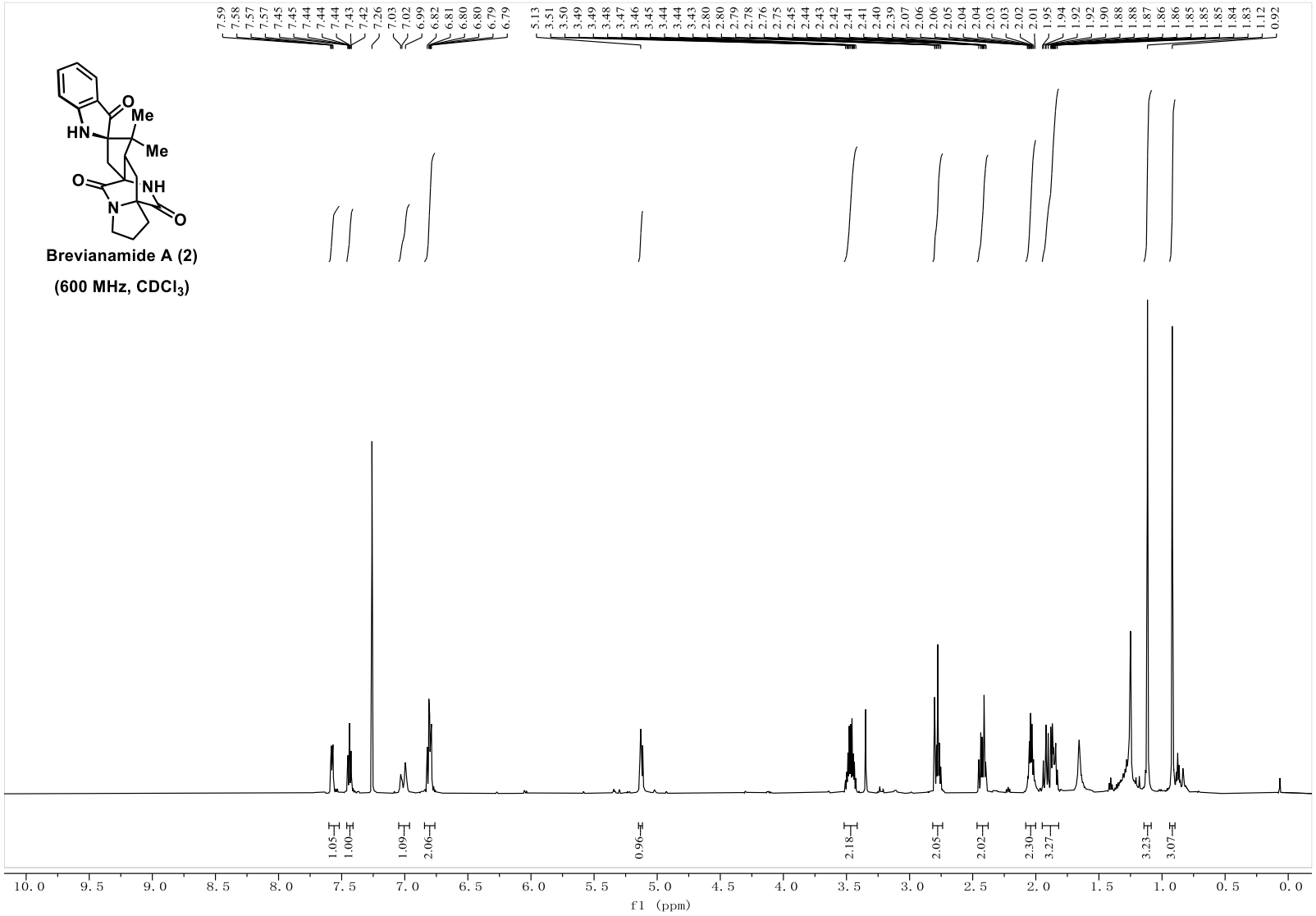

167.2
166.3
161.3
148.2
136.3
134.6
134.5
132.1
131.4
129.2
123.8
117.4
114.1
107.7
90.3
79.7
77.4
77.2
76.9
52.4
51.7
50.3
29.1
21.3
PhthN
N
CO2Me
O
NH2
85
(151 MHz, CDCl3)
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

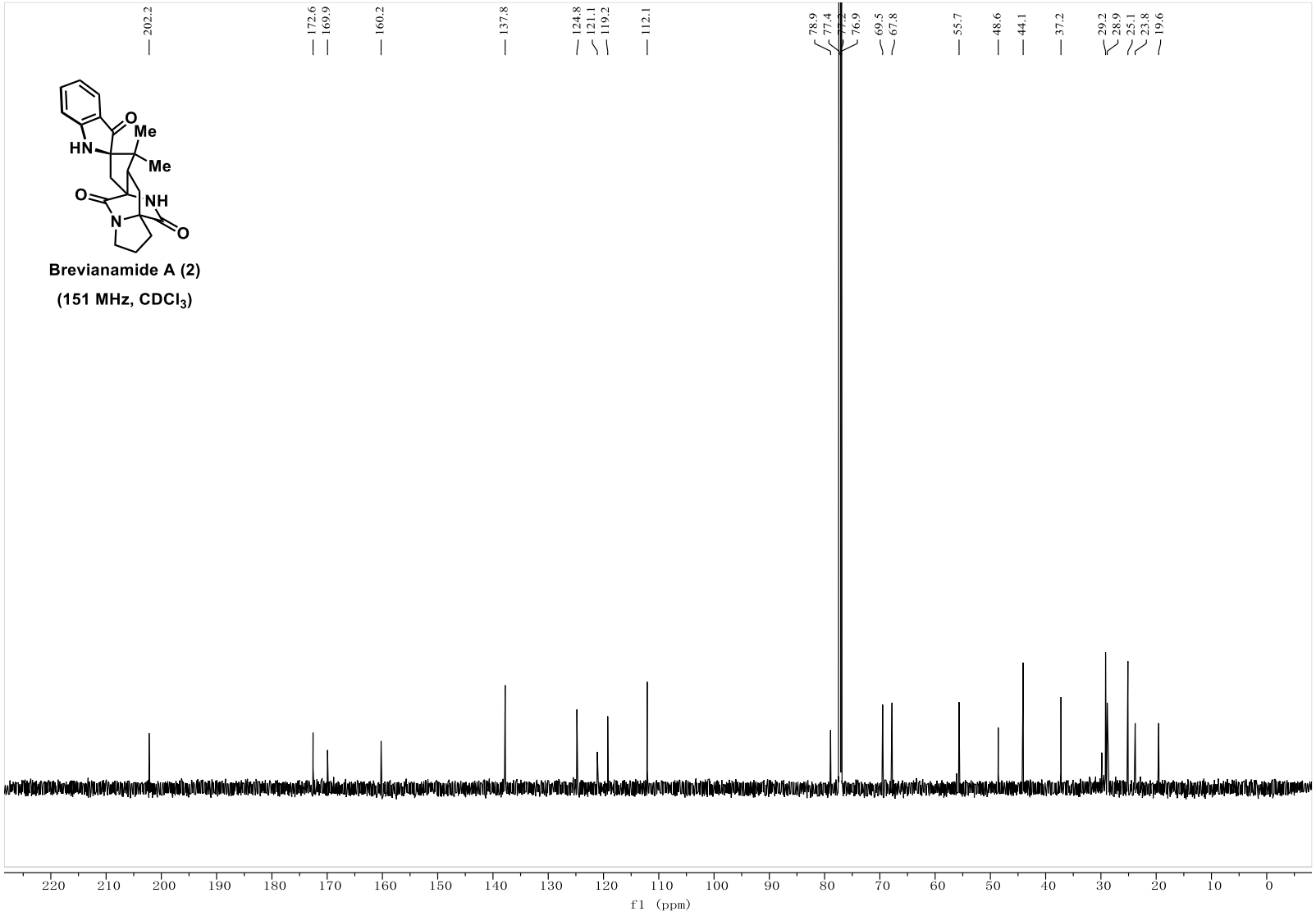

PhthN
N
CO2Me
O
N
H
87
(400 MHz, CDCl3)
f1 (ppm)


167.8
166.9
161.3
136.3
135.9
134.4
131.3
128.2
123.5
121.3
119.7
119.2
111.0
101.8
77.4
77.2
76.9
53.0
52.4
50.3
28.9
PhthN
N
CO2Me
O
N
H
87
(151 MHz, CDCl3)
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


NPhth
MeO2C
89
(600 MHz, CDCl3)
f1 (ppm)


203.3
167.7
167.2
166.8
162.0
161.3
160.9
142.9
142.9
137.3
136.9
136.8
136.5
134.4
134.3
133.9
131.6
131.5
124.4
124.3
123.6
123.2
122.0
121.7
118.6
118.2
114.7
114.6
111.7
111.1
77.4
76.9
71.9
71.6
52.5
52.5
50.2
48.8
48.5
44.3
43.8
34.2
29.8
29.3
29.1
21.9
21.7
21.2
21.1
NPhth
MeO2C
89
(151 MHz, CDCl3)
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


Brevianamide A (2)
(600 MHz, CDCl3)
f1 (ppm)


202.2
172.6
169.9
160.2
137.8
124.8
121.1
119.2
112.1
78.9
77.4
76.9
69.5
67.8
55.7
48.6
44.1
37.2
29.2
28.9
25.1
23.8
19.6
O
Me
HN
Me
O
NH
N
O
Brevianamide A (2)
(151 MHz, CDCl3)
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)