CdS Quantum Dots as Potent Photoreductants for Organic Chemistry Enabled by Auger Processes

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Supporting Information

1. General Information

Caution: Cadmium chalcogenide nanomaterials are known to be highly toxic and require special handling procedures.[1,2] For safety reasons, CdS QDs should not be stored in powdered form. In many cases the described reaction conditions led to pressure buildup within the reaction vessels throughout the course of the reaction. While the authors never experienced reaction vessel failure at the operative scales, caution should be exercised to prevent excessive pressure buildup by employing a pressure outlet, especially at larger reaction scales (>0.5 mmol). While small-scale (≤0.5 mmol) reactions were typically not vented to a nitrogen bubbler during irradiation, pressure was carefully relieved before workup with the insertion of a needle into the reaction headspace or cautious opening of the cap inside a fume hood, with extreme care taken to avoid hazardous expulsion or atomization of the reaction mixture containing CdS QDs. Cd-contaminated aqueous and organic waste is considered hazardous, and must be disposed of according to local guidelines.

1.1 Reagents

All solvents, substrates, reagents, starting materials, and metals were purchased from Sigma Aldrich, Acros Organics, TCI America, VWR International, or Chem-Impex International and used as received unless otherwise specified.

Substrates
Sulfonamides and non-commercially available aryl chlorides were prepared according to literature procedures (*vide infra*) and purified via flash chromatography on silica prior to use. Diethyl (7'-methoxy-3',4'-dihydro-2'H-spiro[cyclohexane-1,1'-isoquinolin]-6'-yl) phosphate and 4-(tert-butyl)-2,6-dimethoxyphenyl diethyl phosphate were graciously provided by members of the Wickens group at UW-Madison and used without further purification.[3]

Solvents
Anhydrous acetonitrile (MeCN) was purchased from Acros Organics, stored in a glovebox, and used as received. Anhydrous 1,3-dimethyltetrahydropyrimidin-2(1H)-one (DMPU), dimethyl sulfoxide (DMSO), *N,N*-dimethylformamide (DMF), and *N,N*-dimethylacetamide (DMA) were purchased from Sigma Aldrich, stored in a glovebox, and used as received. Anhydrous toluene, benzene, tetrahydrofuran (THF) and hexanes were obtained by passage of pure, degassed commercial solvent through activated alumina and molecular sieves in a solvent purification system.

Synthesis of 5.8-6.0 nm CdS Quantum Dots
CdS QDs were synthesized via hot-injection methods as adapted from Yu and Peng.[4] In an example synthesis, precipitated sulfur (80 mg, 2.49 mmol, 1 equiv) was combined with octadecene (ODE, 38 mL) and sonicated for 2 hours in a 100 mL round-bottom flask under air, affording a clear, colorless solution. To a 250 mL oven dried three-necked flask was added CdO (640 mg, 4.98 mmol, 2 equiv), ODE (89 mL), and oleic acid (OA) (33 mL). The flask was fitted with a reflux condenser and digital temperature control thermometer(J-Kem), and heated under vacuum to 120 °C in a heating mantle controlled by a digital temperature regulator (J-Kem). The mixture was degassed under vacuum for 2 h, before being heated to 280 °C under nitrogen at a rate of 10 °C per minute.

At 280 °C, half of the sulfur solution was rapidly injected, and the temperature dropped quickly to 250 °C, assisted by air blowing. Once the temperature had dropped to 250 °C, the remainder of the sulfur solution was added over a period of 120 s while the temperature was held at 250 °C with heating. After the addition was complete, the temperature was held at 250 °C for a further two minutes before cooling to room temperature with acetone spraying and air blowing. QDs were then purified from remaining precursors and ODE: The crude mixture was shaken in a 1 L separatory funnel with 50 mL hexanes and 200 mL MeOH. The hexanes/ODE layer containing the QDs was concentrated under reduced pressure on a rotary evaporator to remove excess hexanes, and the remaining ODE/QD mixture was washed in a 1 L separatory funnel with 1:1 iPrOH/MeOH (200 mL). The ODE/QD phase was divided into 4 mL aliquots in 15 mL HDPE centrifuge tubes, and 8 mL acetone was added to each tube to precipitate QDs, followed by centrifugation at 3300 rpm for 10 min. The supernatant was decanted, and the QD pellets re-suspended in 2 mL toluene. A second precipitation and centrifugation was performed using 5 mL EtOH as antisolvent. The resulting pellets were dried under vacuum briefly (**Caution:** Cd nanomaterials are highly hazardous when powdered; ensure that QD pellets are not dried to the point of powder formation), brought into a nitrogen-filled glovebox, and redispersed in 12 mL dry toluene or benzene. QDs were stored in the glovebox with ambient light excluded prior to use and dispensed as a solution. QD size and solution concentration were determined using published calibration curves and methods by Yu et al.[5] Average QD size obtained by this method was 5.9 nm.

Solvent Exchange of CdS QDs into alternative solvents

In a nitrogen filled glovebox, 2mL of CdS QD solution (~1.0×10^{-4} mmol) was added to a 15 mL centrifuge tube, and dry acetone was added to precipitate QDs. The centrifuge tube was sealed with electrical tape, removed from the glovebox, and centrifuged at 3300 rpm for 10 minutes. The centrifuge tube was brought back into the glovebox, the supernatant decanted, and the pelleted QDs were dried briefly under vacuum before resuspension in dry benzene or hexanes (2 mL). The QDs were re-characterized using published calibration curves and methods by Yu et al.[5]

1.2 Methods

NMR Spectroscopy

^{1}H and ^{13}C spectra were acquired on a 500 MHz Bruker Avance spectrometer equipped with a DCH cryoprobe. Heteronuclear spectra were acquired on a 400 MHz Bruker Avance spectrometer equipped with a BBFO probe. NMR chemical shifts are reported in ppm and are referenced to $CDCl_3$ at 7.26 ppm (^{1}H NMR) and 77.16 ppm (^{13}C NMR). Coupling constants (*J*) are reported in Hertz. Quantitative ^{1}H NMR experiments were performed using a d1 time of 15 s with 32 scans on a 500 MHz Bruker Avance spectrometer equipped with a DCH cryoprobe.

Gas Chromatography

GC analyses were performed on an Agilent 7890A GC equipped with dual DB-5 columns (20 m × 180 μm × 0.18 μm), dual FID detectors, and hydrogen as the carrier gas. A sample volume of 1 μL was injected at a temperature of 300 °C and a 100:1 split ratio. The initial inlet pressure was 20.3 psi but varied as the column flow was held constant at 1.8 mL/min for the duration of the run. The initial oven temperature of 50 °C was held for 0.46 min followed by a temperature ramp of 65 °C/min up to 300 °C. The total run time was 5.0 min and the FID temperature was 325 °C.

GC/MS Analysis

GC/MS analyses were performed on a Shimadzu GCMS-QP2010 equipped with an RTX-5MS column (30 m × 0.25 mm × 0.25 μm) with a quadrupole mass analyzer using helium as the carrier gas. The analysis method used in all cases was 1 μL injection of sample, an injection temp of 250 °C, and a 20:1 split ratio. The initial inlet pressure was 8.1 psi, but varied as the column flow was held constant at 1.0 mL/min for the duration of the run. The interface temperature was held at 275 °C, and the ion source (EI^+, 30 eV) was held at 200 °C. The initial oven temperature was held at 60 °C for 1 min with the detector off, followed by a temperature ramp, with the detector on, to 300 °C at 20 °C/min. Total run time was 13.00 min.

Supercritical Fluid Chromatography Mass Spectrometry

SFC/MS analyses were performed on a Waters ACQUITY UPC^2 equipped with ACQUITY UPC^2 PDA and ACQUITY QDa Detector. A Daicel Dcpack SFC-A column (3 mm ID × 150 mm L, 3 μm PS) was used for separations. The eluent was a mixture (97:3 CO_2/MeOH) with a flow rate of 2 mL/min at 40 °C with a ABPR at 1500 psi. We are grateful to Joe Barendt and Chiral Technologies for the donation of the SFC-A column used in this work.

UV-Vis Spectroscopy

Samples for UV-Vis analysis were prepared in a schlenk-type glass or quartz cuvette (10 mm path length) with PTFE stopcock in a nitrogen filled glovebox unless otherwise specified. Samples were analysed on an Agilent Cary 60 UV-Vis spectrophotometer and baseline correction was performed using blank cuvettes of the appropriate solvents. Data analysis and plotting was performed in Microsoft Excel.

Fluorescence Measurements

Fluorescence measurements were performed using a Hitachi F-4500 FL Fluorescence spectrophotometer using an excitation wavelength of 400 nm unless otherwise specified.

Chromatography

Chromatography was performed on silica gel (EMD, silica gel 60, particle size 0.040-0.063 mm) using standard flash techniques, on a Teledyne Isco Rf-200 (detection at 210 nm and 280 nm) or on a Biotage Isolera One (detection at 210 nm and 400 nm, on KPsil columns). Products were visualized by UV, PMA stain, or fractions were analyzed by GC or SFC-MS.

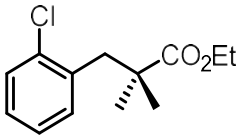
High Resolution Mass Spectrometry

Mass spectrometry data was collected on a Thermo Q Exactive Plus (thermofisher.com) via flow injection with electrospray ionization or via ASAP-MS (asap-ms.com) by the chemistry mass spectrometry facility at the University of Wisconsin – Madison. The purchase of the Thermo Q Exactive Plus in 2015 was funded by NIH Award 1S10 OD020022 to the Department of Chemistry.

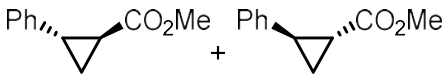
1.3 Compounds prepared according to literature procedures

1-(but-3-en-1-yl)-2-chlorobenzene (1b)[6]
2-chloro-1,3,5-trimethoxybenzene (1e)[7]
2-chloro-1,1'-biphenyl (1f)[8]
cyclopropyl(morpholino)methanone (3a)[9]
1-morpholinobutan-1-one (4a)[10]
1-(2-(benzyloxy)ethyl)-4-methoxybenzene (11)[11]

1.4 Preparation and characterization of substrates:

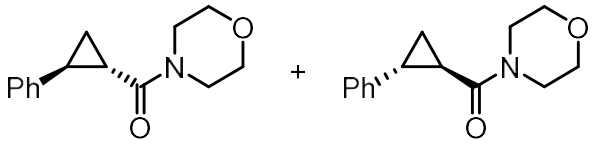


ethyl 3-(2-chlorophenyl)-2,2-dimethylpropanoate (1c) was synthesized according to modified literature methods.[12] To a flame dried 50 mL round bottom flask equipped with a stir bar under nitrogen atmosphere was added ethyl isobutyate (1.34 mL, 10.0 mmol, 1 equiv), and dry THF (10 mL) via syringe. The reaction vessel was lowed into a dry ice/acetone bath and the solution stirred for 30 min followed by the dropwise addition of potassium bis(trimethylsilyl)amide solution (1.0 M in THF) via syringe (12 mL, 12 mmol, 1.2 equiv). The mixture was stirred for 45 minutes, then 1-chloro-2-(chloromethyl)benzene (1.26 mL, 10.0 mmol, 1 equiv) was added dropwise via syringe. The cooling bath was removed and the reaction was allowed to warm to rt with stirring overnight. The reaction was quenched with the dropwise addition of saturated aqueous NH_4Cl (10 mL). The reaction mixture was was poured into a separatory funnel containing water (50 mL) and extracted with dichloromethane (3 × 25 mL). The combined organics were dried over Na_2SO_4, filtered and concentrated under reduced pressure on a rotary evaporator. The residue was purified by flash chromatography on silica (hexanes to 5% EtOAc in hexanes) to afford the product as a clear oil (1.28 g, 53% yield).
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37 – 7.32 (m, 1H), 7.19 – 7.11 (m, 3H), 4.14 (q, J = 7.1 Hz, 2H), 3.09 (s, 2H), 1.24 (t, J = 7.1 Hz, 3H), 1.22 (s, 6H).
^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 177.6, 136.3, 135.3, 131.9, 129.8, 127.9, 126.5, 60.7, 44.2, 42.0, 25.0, 14.3.
HRMS (ESI-MS) $[M+H]^+$ m/z calculated for $C_{13}H_{18}ClO_2$ 241.0990, found 241.0986.

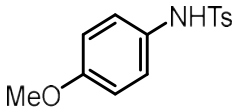


trans-(+/-)-methyl-2-phenyl-1-cyclopropanecarboxylate (3b) To a 20 mL scinitilation vial equipped with a stir bar was added trans-(+/-)-2-phenyl-1-cyclopropanecarboxylic acid (324 mg, 2.00 mmol, 1 equiv). MeOH (6 mL) was added, followed by H_2SO_4 (1 drop). The mixture was sealed with a PTFE-faced septum cap under air atmosphere and stirred at 60 °C for 24 h, followed by passage of the reaction mixture through a 1 cm silica pad into a round bottom flask. The silica pad was rinsed with DCM (10 mL) and the rinse collected in the round bottom flask. The residue was concentrated under reduced pressure on a rotary evaporator and purified via flash chromatography on silica (5% EtOAc/hexanes) to afford the product as a clear oil (258 mg, 75% yield) contaminated with trans-(+/-)-ethyl-2-phenyl-1-cyclopropanecarboxylate (approximately 7%). Spectroscopic data were consistent with literature reports.[13]

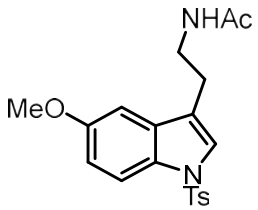
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.28 (dd, *J* = 8.3, 6.8 Hz, 2H), 7.23 – 7.18 (m, 1H), 7.14 – 7.06 (m, 2H), 3.72 (s, 3H), 2.53 (ddd, *J* = 9.4, 6.6, 4.2 Hz, 1H), 1.91 (ddd, *J* = 8.3, 5.4, 4.2 Hz, 1H), 1.61 (dt, *J* = 9.6, 4.9 Hz, 1H), 1.33 (ddd, *J* = 8.4, 6.6, 4.6 Hz, 1H).
^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 174.0, 140.1, 128.7, 128.6, 126.7, 126.4, 52.0, 26.4, 24.1, 17.2.



trans-(+/-)-4-[(2-phenylcyclopropyl)carbonyl]morpholine (3c) was synthesized according to literature methods from trans-(+/-)-2-phenyl-1-cyclopropanecarboxylic acid and morpholine,[9] and purified by flash chromatography on silica (20% EtOAc/hexanes), affording the product as a yellow oil. Spectroscopic data were consistent with literature reports.[14]
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.31 – 7.26 (m, 2H), 7.23 – 7.18 (m, 1H), 7.14 – 7.09 (m, 2H), 3.74 – 3.58 (m, 8H), 2.50 (ddd, *J* = 9.0, 6.3, 4.2 Hz, 1H), 1.93 (ddd, *J* = 8.3, 5.3, 4.2 Hz, 1H), 1.68 (ddd, *J* = 8.9, 5.4, 4.4 Hz, 1H), 1.30 (ddd, *J* = 8.3, 6.3, 4.3 Hz, 1H).
^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 170.8, 140.9, 128.7, 126.5, 126.2, 67.0, 66.9, 46.2, 42.7, 25.7, 23.1, 16.3.



N-(4-methoxyphenyl)-*p*-toluenesulfonamide (9a) was synthesized according to modified literature methods.[15] A scintillation vial equipped with a stir bar was charged with *p*-anisidine (616 mg, 5.00 mmol, 1 equiv) and pyridine (10 mL). The reaction vessel was then placed in an ice/water bath. *p*-Toluenesulfonyl chloride (1240 mg, 6.50 mmol, 1.3 equiv) was added, and the mixture was stirred overnight or until the reaction was complete via TLC analysis. Pyridine was removed by rotary evaporation under reduced pressure on a rotary evaporator, and the residue was purified by flash chromatography on silica gel (50% EtOAc/hexanes) to afford the product as a white solid. Spectroscopic data were consistent with literature reports.[16]
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.57 (d, *J* = 8.4 Hz, 2H), 7.21 (d, *J* = 7.9 Hz, 2H), 6.98 – 6.92 (m, 2H), 6.79 – 6.74 (m, 2H), 6.18 (br s, 1H), 3.76 (s, 3H), 2.39 (s, 3H).
^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 158.2, 143.8, 136.2, 129.7, 128.9, 127.5, 125.8, 114.6, 55.6, 21.7.

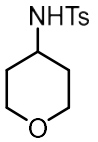


1-*p*-toluenesulfonyl-melatonin (9b) To an oven-dried 100 mL Schlenk flask equipped with a stir bar under nitrogen atmosphere was added melatonin (929 mg, 4.00 mmol, 1 equiv) and a stir bar. Dry THF (15 mL) was added via syringe, and the flask was placed in an ice/water bath. NaH (60 wt% in mineral oil, 176 mg, 4.40 mmol, 1.1 equiv) was added under stream of nitrogen, and the mixture was stirred for 15 minutes before *p*-toluenesulfonyl chloride (992 mg, 5.20 mmol, 1.3

equiv) was added. The cooling bath was then removed and the reaction mixture was allowed to return to rt with stirring overnight. The reaction was quenched with the dropwise addition of saturated aqueous NH_4Cl (10 mL). The crude mixture was poured into water (50 mL) and extracted with EtOAc (3 × 25 mL). The combined organics were washed with water (25 mL) and dried over Na_2SO_4,. The solids were filtered out, and the filtrate concentrated by rotary evaporation under reduced pressure. The residue was purified by flash chromatography on silica gel (1% MeOH/dichloromethane) to afford the product as a white solid. Spectroscopic data were consistent with literature reports (823 mg, 53% yield).[17]

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.94 – 7.85 (m, 1H), 7.75 – 7.68 (m, 2H), 7.32 (s, 1H), 7.23 – 7.18 (m, 2H), 6.96 – 6.90 (m, 2H), 3.82 (s, 3H), 3.53 (q, *J* = 6.7 Hz, 2H), 2.84 (td, *J* = 6.9, 1.0 Hz, 2H), 2.34 (s, 3H), 1.94 (s, 3H).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 170.2, 156.6, 145.0, 135.4, 131.8, 130.2, 130.0, 126.9, 124.2, 120.0, 114.9, 114.1, 102.0, 55.9, 39.0, 25.4, 23.5, 21.7.



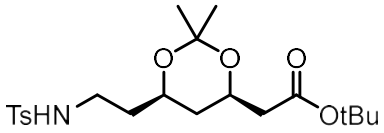
N-(tetrahydro-2H-pyran-4-yl)-*p*-toluensulfonamide (9c) A flame-dried 3-neck 100 mL round-bottom flask equipped with a stir bar under nitrogen atmosphere was charged sequentially with tetrahydro-2H-pyran-4-amine (414 µL, 4.00 mmol, 1 equiv), anhydrous dichloromethane (20 mL), and anhydrous triethylamine (1.7 mL, 12 mmol, 3 equiv). The mixture was cooled to 0 °C and *p*-toluenesulfonyl chloride (915 mg, 4.80 mmol, 1.2 equiv) was added. The reaction mixture was allowed to return to rt with stirring overnight, and then diluted with 30 mL dichloromethane. The mixture was washed with saturated $NaHCO_3$ and then brine. The organic phase was dried over Na_2SO_4, filtered to remove solids, and concentrated by rotary evaporation under reduced pressure. The residue was purified by flash chromatography on silica gel (hexanes to 50% EtOAc/hexanes) to afford the product as a white solid (958 mg, 94% yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.80 – 7.74 (m, 2H), 7.34 – 7.28 (m, 2H), 4.48 (d, *J* = 7.6 Hz, 1H), 3.86 (dt, *J* = 12.0, 3.8 Hz, 2H), 3.40 – 3.29 (m, 3H), 2.43 (s, 3H), 1.73 (ddt, *J* = 12.7, 4.6, 2.3 Hz, 2H), 1.45 (dtd, *J* = 13.1, 10.8, 4.3 Hz, 2H).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 143.6, 138.4, 129.9, 127.1, 66.6, 50.0, 34.1, 21.7.

HRMS (ESI-MS) $[M+H]^+$ m/z calculated for $C_{12}H_{18}NO_3S^+$ 256.1002, found 256.0998.

Melting point: 133.0-134.0 °C



***tert*-butyl 2-((4R,6R)-2,2-dimethyl-6-(2-((4-methylphenyl)sulfonamido)ethyl)-1,3-dioxan-4-yl)acetate (9d)** A flame-dried 3-neck 100 mL round-bottom flask with a stir bar under nitrogen atmosphere was charged sequentially with tert-butyl 2-((4R,6R)-6-(2-aminoethyl)-2,2-dimethyl-1,3-dioxan-4-yl)acetate (1.1 mL, 4.0 mmol, 1 equiv), dry dichloromethane (20 mL), and dry triethylamine (1.7 mL, 12 mmol, 3 equiv). The mixture was placed in an ice/water bath and *p*-toluenesulfonyl chloride (915 mg, 4.80 mmol, 1.2 equiv) was added. The reaction mixture was allowed to return to room temperature with stirring overnight, and then diluted with 30 mL dichloromethane. The mixture was washed with saturated $NaHCO_3$ and then brine. The organic

phase was dried over Na_2SO_4, filtered, and the filtrate was concentrated by rotary evaporation under reduced pressure. The residue was purified by flash chromatography on silica gel (hexanes to 50% EtOAc/hexanes) to afford the product as a white solid (1210 mg, 70% yield)

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.76 – 7.70 (m, 2H), 7.34 – 7.26 (m, 2H), 5.10 (dd, *J* = 6.8, 4.5 Hz, 1H), 4.24 – 4.15 (m, 1H), 3.92 (ddt, *J* = 11.3, 8.2, 3.0 Hz, 1H), 3.12 (dtd, *J* = 12.0, 7.2, 4.7 Hz, 1H), 2.99 (ddt, *J* = 12.4, 7.6, 4.6 Hz, 1H), 2.43 (s, 3H), 2.37 (dd, *J* = 15.2, 7.0 Hz, 1H), 2.24 (dd, *J* = 15.2, 6.1 Hz, 1H), 1.64 (dddd, *J* = 14.4, 7.8, 4.7, 3.4 Hz, 1H), 1.55 (dtd, *J* = 14.5, 7.9, 4.7 Hz, 1H), 1.43 (s, 9H), 1.37 (s, 3H), 1.35 (s, 3H), 1.12 (dt, *J* = 12.8, 11.6 Hz, 1H).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 170.2, 143.4, 137.1, 129.8, 127.3, 99.0, 80.9, 68.7, 66.2, 42.6, 40.9, 36.0, 34.7, 30.2, 28.2, 21.6, 19.8.

HRMS (ESI-MS) $[M+NH_4]^+$ m/z calculated for $C_{21}H_{37}N_2O_6S^+$ 445.2367, found 445.2364.

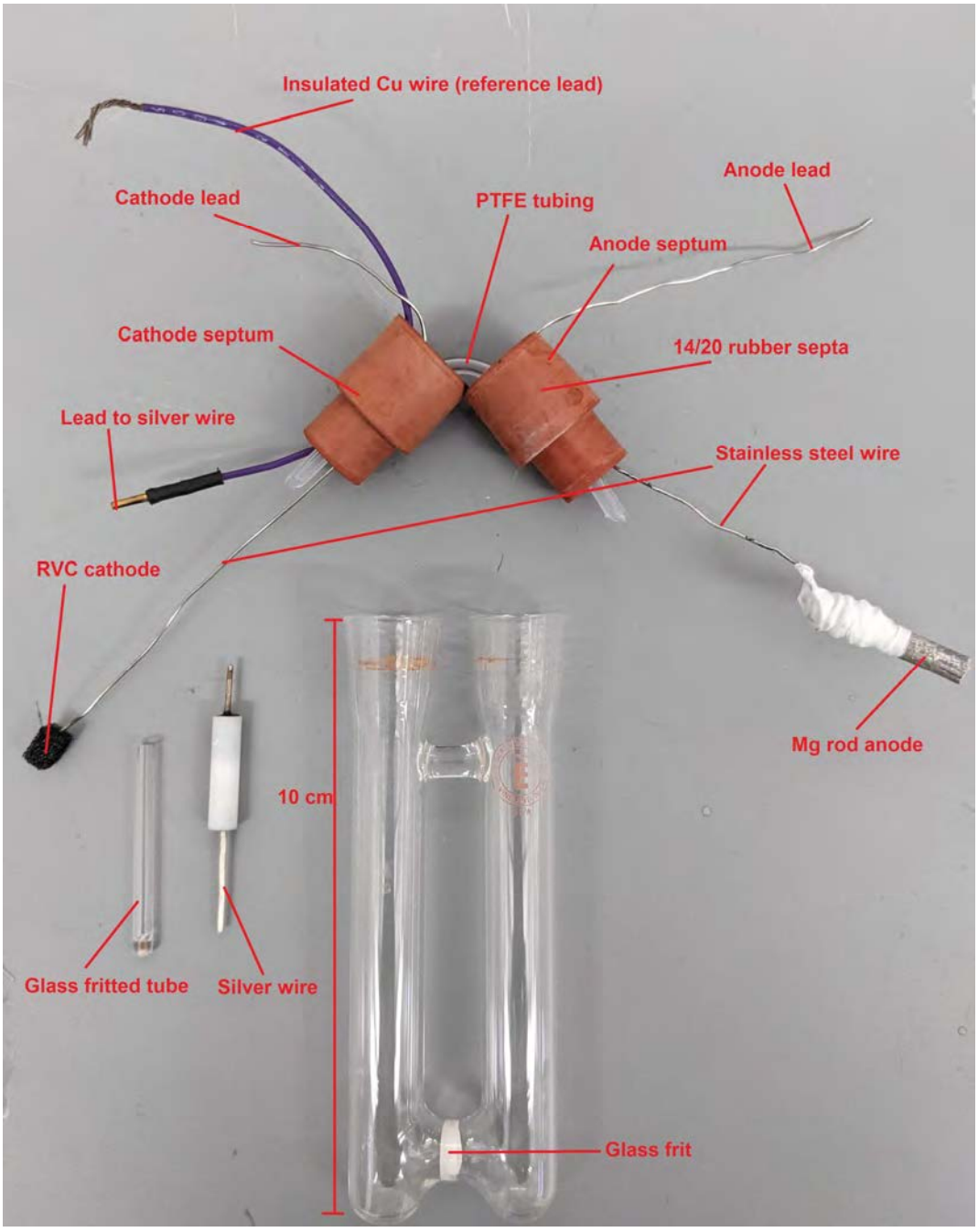
Melting point: 85.5-87.5 °C

1.5 Photochemical and Electrochemical Setups

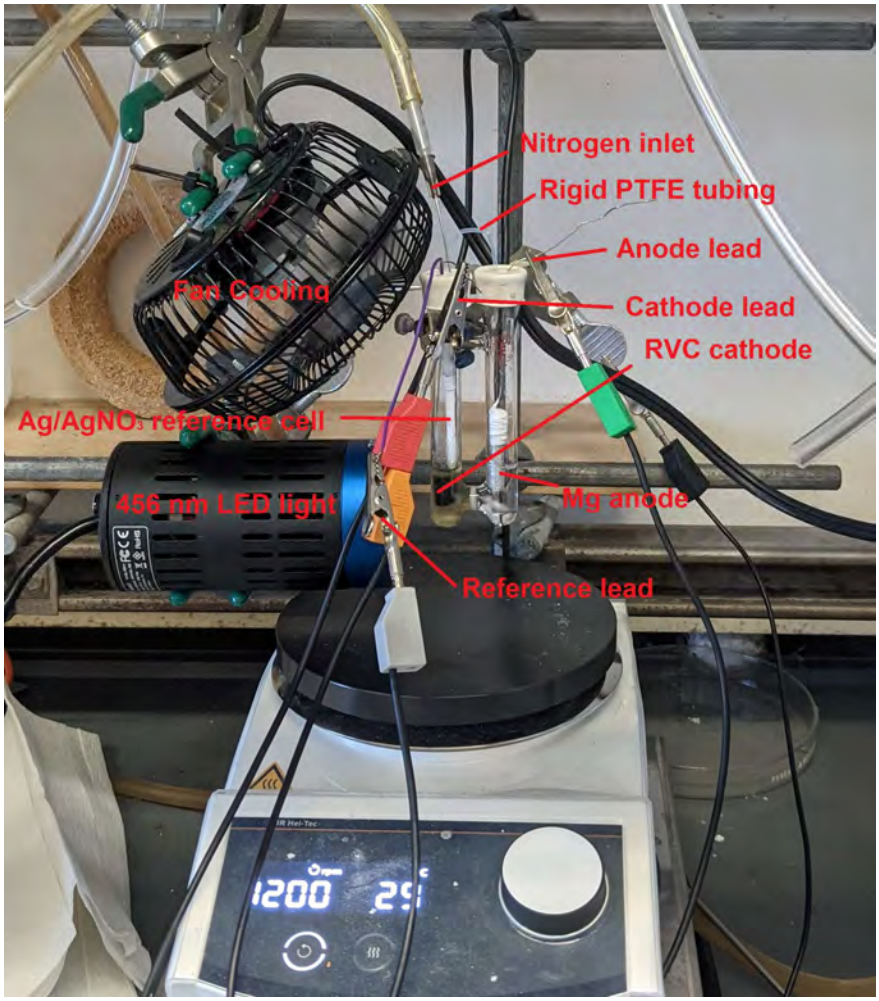
Photoreactor Setup

Royal-Blue LEDs (typical wavelength of 447.5 nm, range from 440 to 460 nm, catalog # SR-01-R0500), dimmable LED drivers (700 mA, 5-32 VDC, catalog # 3023-D-E-700), and collimators (Dialight 7° 11 mm Circular Beam Optic, catalog # OPC1-1-COL) were purchased from Luxeon Star LEDs. Two LEDs with collimators were attached to opposite sides of a small aluminum cylinder containing appropriately sized holes. The cylinder was bored to fit a 1-dram vial and the two LEDs were affixed to small heat sinks. These pieces were attached to an aluminum plate. This plate could be placed onto a standard magnetic stirrer. Shims were added to the cylinders, ensuring that the vials were elevated so that the LEDs were entirely covered by the reaction mixture. A fan was employed to maintain cooling, however, reaction temperatures were approximately 30°C. This arrangement provided 520 mW of 450 nm light as measured at the vial for the Royal-Blue LEDs.

Photoelectrochemistry



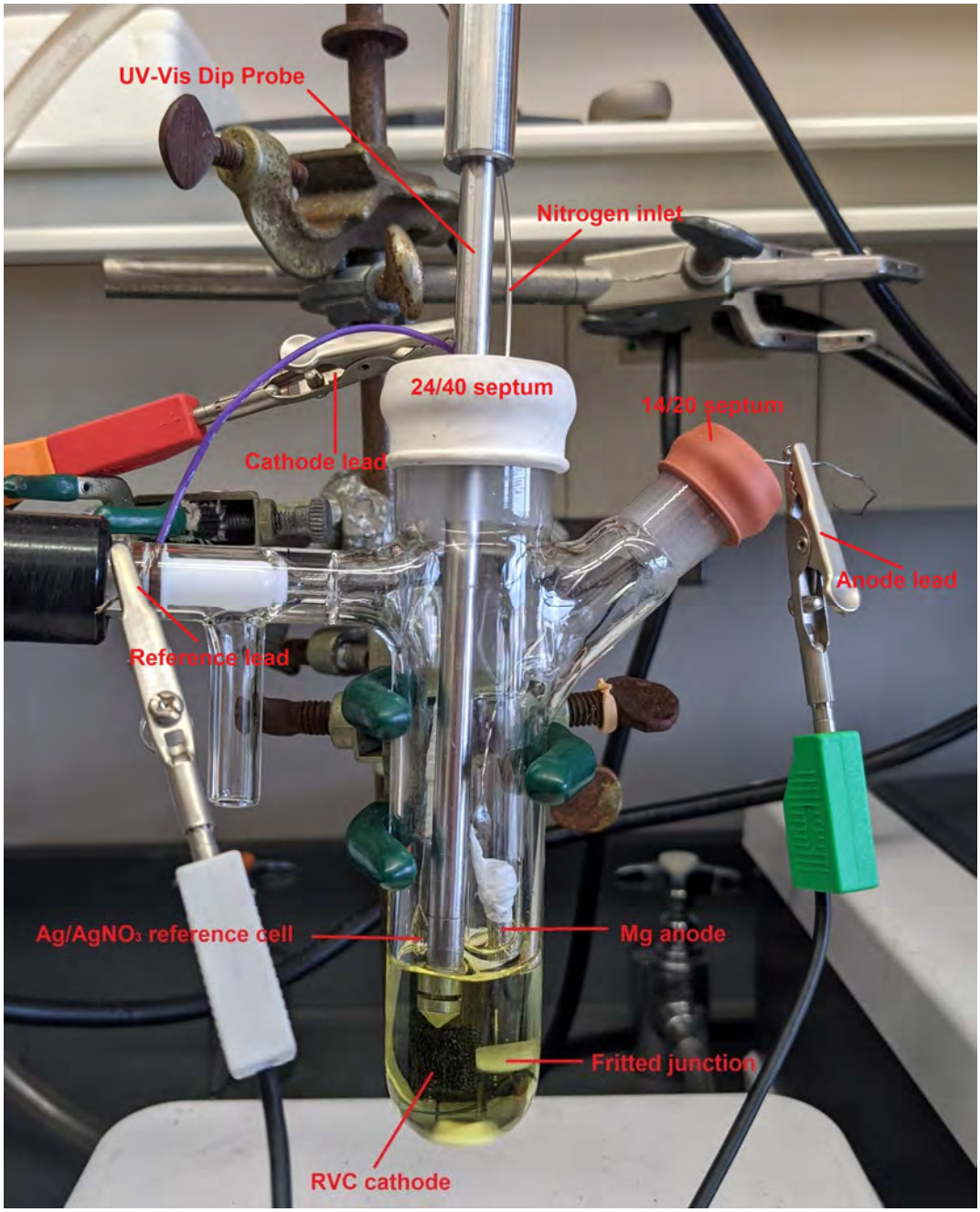
Divided cell electrochemical tube was made in-house using a porosity E glass frit from Ace Glass (8 mm diameter, part number 7176-21). Glass fritted tube and silver wire assembly purchased from Pine research (part number RREF0153L2). RVC purchased from Goodfellow Cambridge Ltd. (part number VC003830).



Fully assembled experimental setup for photoelectrochemistry experiments.

Spectroelectrochemistry

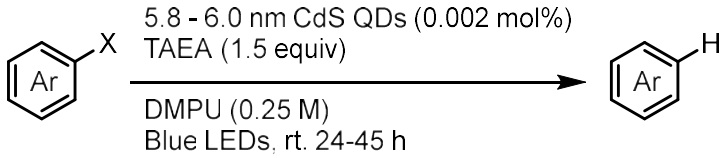
Schlenk-type divided cell apparatus used for spectroelectrochemical experiments.



Fully assembled experimental setup for spectroelectrochemical experiments.

2. General Reaction Procedures

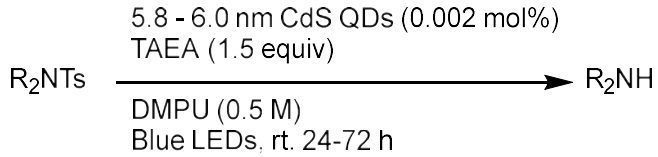
2.1 General Procedure A – Hydrodefunctionalization of Aryl Electrophiles



Reactions were set up in a N_2 filled glove box. An oven dried dram vial was charged with aryl chloride or aryl phosphate ester (0.25 mmol, 1 equiv), and a PTFE-coated stir bar. DMPU was added (1 mL) followed by TAEA (56 µL, 0.375 mmol, 1.5 equiv) and the mixture was shaken or stirred for 30 s, forming a homogeneous clear solution. CdS QDs were added in toluene solution (approximately 50 µL depending on QD solution concentration, 5.0 nmol, 2.0×10^{-3} mol%). For optimization and mechanistic studies, n-dodecane (10 µL, 7.5 mg) was added as an internal standard; this was omitted for reactions where the product was to be isolated. The reactions were sealed with a screw cap fitted with a PTFE-faced silicone septum before being removed from the glovebox. Reactions were placed into photoreactor plates equipped with two LEDs per reaction and irradiated with stirring (1250 RPM) and fan cooling for 24 h or until the reaction was complete. For images of the photoreactor plates, see section 1.5.

If desired, the QDs can be precipitated from the crude reaction mixture and reused in other reactions: After the reaction was judged complete, the reaction was quenched via exposure to atmosphere, and MeOH (1 mL) was added. The opaque yellow reaction mixture was transferred to a 15 mL screw cap centrifuge tube and centrifuged at 3300 RPM for 15 minutes. The supernatant containing the organic products was decanted and analyzed via GC-FID. The pelleted QDs were washed to remove remaining organic products by the addition of acetone (1 mL) and sonication for 1 minute. The yellow cloudy suspension was centrifuged at 3300 RPM for 15 minutes, and the supernatant was discarded. The QD pellet was then transferred to a N_2 filled glove box, and used in another reaction.

2.2 General Procedure B – Detosylation of *p*-toluenesulfonamides



Reactions were set up in a N_2 filled glove box. An oven dried dram vial was charged with tosylated substrate (0.25 mmol, 1 equiv), and a PTFE-coated stir bar. DMPU was added (0.5 mL) followed by TAEA (56 µL, 0.375 mmol, 1.5 equiv) and the mixture was stirred for 5 min, resulting in a homogeneous, clear solution. CdS QDs were added in toluene solution (~50 µL depending on QD concentration, 5.0 nmol, 2.0×10^{-3} mol%). For optimization and mechanistic studies, n-dodecane (10uL, 7.5mg) was added, however this was omitted for reactions to be isolated. The reactions were sealed with a screw cap fitted with a PTFE-faced silicone septum before being removed from the glovebox. Reactions were placed into photoreactor plates equipped with two LEDs per reaction and irradiated with stirring (1250 RPM) and fan cooling for 24 h or until the reaction was complete. For images of the photoreactor plates, see section 1.5.

For substrates **10c** and **10d**, Boc-protection of the amine product was performed in-situ prior to isolation: After the photochemical detosylation reaction was judged complete by SFC/MS,

the reaction was quenched via exposure to air, and charged with triethylamine (174 µL, 1.25 mmol, 5 equiv), di-*tert*-butyl dicarbonate (287 µL, 1.25 mmol, 5 equiv), and MeOH (1 mL). The vial was re-sealed and stirred at room temperature for 3 h.

2.3 Electron-Primed Photoredox Studies: Reduction of 1a

Reactions were set up in a N_2 filled glove box. An electrolyte solution containing 0.1 M tetrabutylammonium hexafluorophosphate in 1:1 toluene/DMPU was prepared by charging an oven-dried scintillation vial with tetrabutylammonium hexafluorophosphate (774.9 mg, 2 mmol), followed by DMPU (10 mL) and toluene (10 mL), then mixing until dissolved. A 1 cm Mg rod (Sigma Aldrich) was attached to a steel wire (8 in, 22 AWG) via graphite glue and PTFE tape to create a sacrificial anode, and the steel wire was inserted through an (anode) 14/20 rubber septum. A second (cathode) 14/20 rubber septum was pierced with stainless steel wire (8 in, 22 AWG) and an insulated Cu wire attached to the reference cell lead. An ~8 mm × ~8 mm × ~12 mm piece of RVC (Goodfellow Cambridge Ltd. part number VC003830) was pierced with the cathodic steel wire. The two rubber septa were connected by insertion of a 5 cm rigid PTFE tube to permit gas exchange between the anode and cathode after cell assembly (see section 1.5 for images of setup). An oven-dried dram vial was charged sequentially with 1,3-di-tert-butyl-5-chloro-2-methoxybenzene (127.4 mg, 0.5 mmol, 1 equiv), *n*-dodecane (20 µL, 15.0 mg) as internal standard, and 2 mL of elelctrolyte solution. The contents were shaken until fully homogeneous before 5.9 nm CdS QDs were added (10.0 nmol, 125 µL of 7.97×10^{-5} M solution in toluene), completing the reaction mixture. A non-aqueous Ag / $AgNO_3$ reference cell was assembled by filling a 3.5 mm OD ceramic-fritted glass tube (Pine research part number RREF0153L2) with 0.01M $AgNO_3$ / 0.1M $TBAPF_6$ solution in MeCN and capping with a PTFE-sleeved cap containing Ag wire as the reference electrode. The assembled reference cell was then wrapped with PTFE tape to exclude light, and connected to the lead inserted through the cathode 14/20 rubber septum. The oven-dried divided electrochemical cell was charged with PTFE-coated stir bars, and the anodic chamber was filled with 2.5 mL of electrolyte solution via pipette. The cathodic chamber was charged with the entire reaction mixture via pipette. The electrode/septa assembly was then lowered into and sealed with the electrochemical cell, ensuring contact between the all electrodes and appropriate solutions (RVC cathode and reference cell contacting reaction mixtute in cathodic chamber; Mg anode contacting electrolyte solution in anodic chamber). The assembled cell was removed from the glovebox, clamped above a stir plate 1 cm from the employed light source with stirring at 1250 RPM, and connected to the potentiostat (Pine research, WaveNow[XV]). Electrolysis was conducted for 24 h with irradiation, and yields were determined via GC-FID.

2.4 Analysis and Purification of Reaction Products

GC Analysis

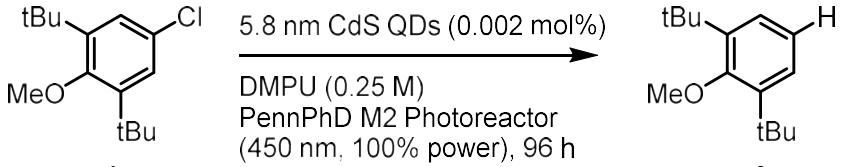
The reactions were monitored by GC analysis, by taking a 20 μL aliquot of the crude reaction mixture with a gas-tight syringe. The aliquot was filtered through a 1-cm silica or celite plug in a Pasteur pipette using 1.5 mL EtOAc, and collected in a GC vial. The resulting solution was analyzed by GC and yields were determined based on the peak area of the analyte compared to n-dodecane as an internal standard.

Isolation and Purification

Purification A. The crude reaction mixture was filtered through a 1 cm celite pad, diluted with dichloromethane (20 mL) and slurried with silica gel (5 g). Volatile solvents were removed under reduced pressure on a rotary evaporator and the resulting dry loaded product was purified by automated column chromatography on silica to provide the desired products.

Purification B. The crude reaction mixture was poured into water (50 mL) and extracted with DCM (3 × 20 mL), the organic layers were combined, washed with water (1 × 20 mL), and dried over Na_2SO_4. Solids were removed by filtration, silica gel (5 g) was added, and solvent was removed under reduced pressure on a rotary evaporator. The resulting dry-loaded product was purified by automated column chromatography on silica to provide the desired products.

2.5 Large-Scale Dehalogenation Procedure



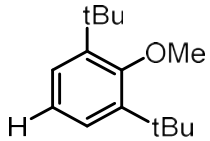
1a
4 mmol

2a
87% yield

An oven-dried 20 mL scintillation vial was charged with 1,3-di-*tert*-butyl-5-chloro-2-methoxybenzene (1.019 g, 4.000 mmol, 1 equiv) under air. The vial was brought into a nitrogen-filled glovebox and DMPU was added (16 mL) followed by TAEA (1.2 mL, 8.0 mmol, 2 equiv), 5.8 nm CdS QDs (80 nmol, 2.0×10^{-3} mol%) and a magnetic PTFE-coated stir bar. The vial was sealed with a PTFE-faced septum cap, and removed from the glovebox. The vial was placed in a photoreactor (Penn PhD Photoreactor M2, 450 nm) and vented to a nitrogen bubbler to preclude pressure buildup. The reaction mixture was irradiated for 96 h with 450 nm light at the maximum power setting, with stirring at 1200 RPM and fan cooling.

After completion, the reaction mixture was poured into water (200 mL) and extracted with Et_2O (3 × 50 mL). The combined organic layers were washed with water (2 × 50 mL) and brine (50 mL), then dried over Na_2SO_4 and concentrated under reduced pressure on a rotary evaporator. The residue was passed through a 1 inch silica plug using EtOAc to remove QDs and ionic impurities, and solvent was removed under reduced pressure on a rotary evaporator, affording an inseparable mixture of the product (767 mg, 87%) and starting material (51 mg, 5% RSM) by ^1H NMR analysis.

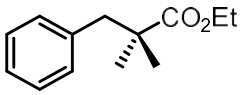
3. Specific Procedures and Product Characterization



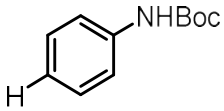
1,3-di-*tert*-butyl-5-chloro-2-methoxybenzene (2a) [CAS: 1516-95-6]

General procedure A was followed using 1,3-di-*tert*-butyl-5-chloro-2-methoxybenzene (63.7 mg, 0.25 mmol, 1 equiv). After 45 h, the reaction was poured into water (50 mL) and extracted with Et_2O (3 × 25 mL). The combined organic layers were washed with water (2 × 25 mL) and saturated brine (25 mL), dried over Na_2SO_4, and concentrated under reduced pressure on a rotary evaporator

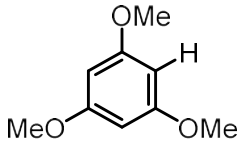
affording an inseparable mixture of the product (42.4 mg, 77% yield) and starting material (3.2 mg, 5% RSM) as a clear oil. Characterization data matched an authentic sample of product.
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.32 (d, *J* = 7.8 Hz, 2H), 7.04 (t, *J* = 7.8 Hz, 1H), 3.76 (s, 3H), 1.50 (s, 18H).
^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 159.6, 143.8, 126.7, 123.0, 64.4, 35.9, 32.3.



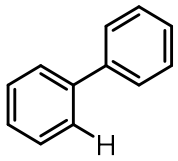
ethyl 2,2-dimethyl-3-phenylpropanoate (2c) [CAS: 94800-92-7]
General procedure A was followed using ethyl 3-(2-chlorophenyl)-2,2-dimethylpropanoate (60.2 mg, 0.25 mmol, 1 equiv). After 48 h, an aliquot of the crude reaction mixture was analyzed by SFC-MS, and the indanone product was not observed. The reaction was purified according to **Purification A** (10% EtOAc/Hexanes), affording an inseparable mixture of product (75% yield) and starting aryl chloride (4% yield) as a clear oil via ^{1}H NMR analysis. Characterization data were consistent with literature reports.[18] No indanone products were detected via SFC-MS, indicating that no anionic cyclization occurs.
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.29 – 7.17 (m, 3H), 7.14 – 7.09 (m, 2H), 4.11 (q, *J* = 7.1 Hz, 2H), 2.86 (s, 2H), 1.23 (t, *J* = 7.2 Hz, 3H), 1.18 (s, 6H).
^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 177.6, 138.1, 130.3, 128.1, 126.5, 60.5, 46.4, 43.6, 25.1, 14.3.



tert-butyl phenylcarbamate (2d) [CAS: 3422-01-3]
General procedure A was followed using tert-butyl (4-chlorophenyl)carbamate (56.9 mg, 0.25 mmol, 1 equiv). After 48 h, the reaction was quenched and purified according to **Purification A** (5% EtOAc/Hexanes) affording the product as a white solid (38.8 mg, 80% yield). Characterization data matched an authentic sample of product.
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36 (d, *J* = 8.7 Hz, 2H), 7.32 – 7.23 (m, 2H), 7.03 (tt, *J* = 7.3, 1.2 Hz, 1H), 6.49 (s, 1H), 1.52 (s, 9H).
^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 152.9, 138.5, 129.1, 129.1, 123.2, 118.7, 80.6, 28.5.



1,3,5-trimethoxybenzene (2e) [CAS: 621-23-8]
General procedure A was followed using 2-chloro-1,3,5-trimethoxybenzene (50.7mg, 0.26 mmol, 1 equiv). After 45 h, the reaction was quenched and purified according to **Purification A** (5-20% EtOAc/hexanes) affording the product as a white solid (31.8mg, 76%). Characterization data matched an authentic sample of product.
^{1}H NMR (500 MHz, $CDCl_3$) δ 6.09 (s, 3H), 3.77 (s, 9H).
^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 161.7, 93.1, 55.5.

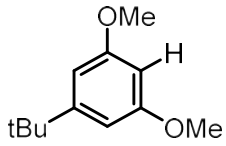


1,1'-biphenyl (2f) [CAS: 92-52-4]

General procedure A was followed using 2-chloro-1,1'-biphenyl (47.2 mg, 0.25 mmol, 1 equiv). After 24 h, the reaction was quenched and purified according to **Purification A** (5% EtOAc/Hexanes) affording the product as a white solid (32.4 mg, 84% yield). Characterization data matched an authentic sample of product.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.64 – 7.58 (m, 4H), 7.49 – 7.42 (m, 4H), 7.40 – 7.33 (m, 2H).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 141.4, 128.9, 127.4, 127.3.

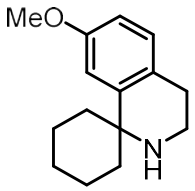


1-(tert-butyl)-3,5-dimethoxybenzene (2g) [CAS: 143029-45-2]

General procedure A was followed using 4-(tert-butyl)-2,6-dimethoxyphenyl diethyl phosphate (86.6 mg, 0.25 mmol, 1 equiv) and employing DIPEA (174 µL, 1 mmol, 4 equiv) instead of TAEA as the terminal reductant. After 48 h, the reaction was quenched and purified according to **Purification A** (hexanes) affording the product as a white solid (35.0 mg, 72 % yield). Characterization data were consistent with literature reports.[3]

^{1}H NMR (500 MHz, $CDCl_3$) δ 6.55 (d, J = 2.2 Hz, 2H), 6.31 (t, J = 2.3 Hz, 1H), 3.80 (s, 6H), 1.30 (s, 9H).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 160.7, 154.0, 104.2, 96.9, 55.4, 35.1, 31.4.

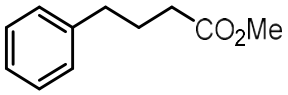


7'-methoxy-3',4'-dihydro-2'H-spiro[cyclohexane-1,1'-isoquinoline] (2h)

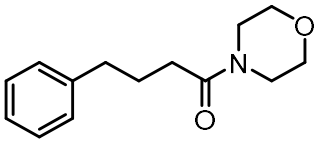
General procedure A was followed using diethyl (7'-methoxy-3',4'-dihydro-2'H-spiro[cyclohexane-1,1'-isoquinolin]-6'-yl) phosphate (95.9 mg, 0.25 mmol, 1 equiv) and employing $NaCHO_2$ (51.0 mg, 0.75 mmol, 3 equiv) instead of TAEA as the terminal reductant. After 48 h, the reaction was quenched by exposure to air and CH_2Br_2 (10 µL) was added via glass syringe. A 100 µL aliquot of the crude mixture was poured into 1M NaOH (1 mL), and extracted with $CDCl_3$ for ^{1}H NMR analysis. Resolved ^{1}H and all ^{13}C NMR signals were consistent with literature reports.[3] The yield was determined to be 47% via integration of the methoxy resonance at 3.79 ppm vs. CH_2Br_2.

^{1}H NMR (500 MHz, $CDCl_3$) Visible signals: δ 6.98 (dd, J = 8.4, 1.0 Hz, 1H), 6.80 (d, J = 2.7 Hz, 1H), 6.69 (dd, J = 8.3, 2.7 Hz, 1H), 3.79 (s, 3H), 2.70 (t, J = 6.0 Hz, 2H). Reported ^{1}H multiplets at 1.83-1.64 ppm, and 1.38-1.28 ppm were obscured by impurities.

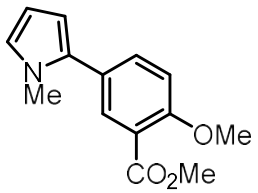
^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 157.6, 145.9, 129.8, 127.1, 111.4, 111.2, 55.2, 54.6, 38.3, 37.7, 29.9, 25.6, 21.6.



methyl 4-phenylbutanoate (4b) [CAS: 2046-17-5]
In a nitrogen-filled glovebox, an oven dried dram vial was charged with methyl 2-phenylcyclopropane-1-carboxylate (44.1 mg, 0.25 mmol, 1 equiv), TAEA (56 µL, 0.375 mmol, 1.5 equiv), and a PTFE-coated stir bar. DMPU (1 mL) was added, followed by CdS QDs in hexane solution (~50 µL depending on QD concentration, 5.0 nmol, 2.0×10^{-3} mol %). The vial was sealed with a screw cap fitted with a PTFE-faced silicone septum before being removed from the glovebox. The vial was placed into a photoreactor equipped with two LEDs and irradiated with stirring (1250 RPM) and fan cooling for 45 h. After the reaction was complete, the reaction mixture was purified according to **Purification B** (5% EtOAc / hexanes), affording the product as a clear oil (31.5 mg, 71% yield) contaminated with ethyl 4-phenylbutanoate (2.3 mg, 0.012 mmol) as a byproduct due to an impurity of ethyl 2-phenylcyclopropane-1-carboxylate in the starting material.
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.32 – 7.26 (m, 1H), 7.23 – 7.15 (m, 1H), 3.67 (s, 1H), 2.68 – 2.63 (m, 1H), 2.34 (t, *J* = 7.5 Hz, 1H), 1.97 (p, *J* = 7.6 Hz, 1H).
^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 174.1, 141.5, 128.6, 128.5, 126.1, 51.6, 35.3, 33.5, 26.6.



1-morpholino-4-phenylbutan-1-one (4c)
In a nitrogen-filled glovebox, an oven dried dram vial was charged with morpholino(2-phenylcyclopropyl)methanone (57.8 mg, 0.25 mmol, 1 equiv), TAEA (56 µL, 0.375 mmol, 1.5 equiv), and a PTFE-coated stirbar. DMPU (1 mL) was added, followed by CdS QDs in hexane solution (~50 µL depending on QD concentration, 5.0 nmol, 2.0×10^{-3} mol %). The vial was sealed with a screw cap fitted with a PTFE-faced silicone septum before being removed from the glovebox. The vial was placed into a photoreactor equipped with two LEDs and irradiated with stirring (1250 RPM) and fan cooling for 45 h. The reaction mixture was partially purified according to **Purification B** (1% MeOH in DCM), affording the product contaminated with DMPU. The yield was determined to be 75% via integration of the methylene resonance at 2.67 ppm vs. CH_2Br_2. Visible signals matched those reported in the literature.[19]
^{1}H NMR (500 MHz, $CDCl_3$) Visible signals: δ 7.30 – 7.23 (m, 2H), 7.20 – 7.15 (m, 3H), 3.68 – 3.55 (m, 6H), 3.36 (t, *J* = 5.0 Hz, 2H), 2.67 (t, *J* = 7.5 Hz, 2H), 2.29 (dd, *J* = 8.1, 7.0 Hz, 2H).
^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 171.4, 141.6, 128.5, 128.4, 126.0, 67.0, 66.6, 45.9, 41.9, 35.3, 32.1, 26.6.



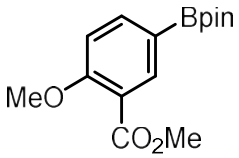
Methyl 2-methoxy-5-(1-methyl-1*H*-pyrrol-2-yl)benzoate (6)
In a nitrogen-filled glovebox, an oven dried dram vial was charged with methyl 5-chloro-2-methoxybenzoate (50.2 mg, 0.25 mmol, 1 equiv), and a PTFE-coated stirbar. DMSO was added (1.67 mL) followed by TAEA (56 µL, 0.375 mmol, 1.5 equiv) and heteroarene trapping agent

(12.5 mmol, 50 equiv) before the mixture was stirred for 5 minutes forming a homogeneous clear solution. CdS QDs were added in hexane solution (~50 µL depending on QD concentration, 5.0 nmol, 2.0×10^{-3} mol %). The vial was sealed with a screw cap fitted with a PTFE-faced silicone septum before being removed from the glovebox. The vial was placed into a photoreactor equipped with two LEDs per reaction and irradiated with stirring (1250 RPM) and fan cooling for 24 h. The crude reaction mixture was subjected to Purification B and the resulting dry-loaded product was purified by column chromatography on silica (15% EtOAc/Hexanes) affording the product as a colorless oil (25.7 mg, 42% yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.84 (d, *J* = 2.4 Hz, 1H), 7.50 (dd, *J* = 8.6, 2.4 Hz, 1H), 7.02 (d, *J* = 8.6 Hz, 1H), 6.70 (t, *J* = 2.3 Hz, 1H), 6.22 – 6.16 (m, 2H), 3.94 (s, 3H), 3.90 (s, 3H), 3.63 (s, 3H).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 166.7, 158.2, 133.8, 133.3, 132.1, 125.8, 123.5, 120.1, 112.3, 108.6, 107.9, 56.3, 52.2, 35.0.

HRMS (ESI) $[M+H]^+$ m/z calc'd for $C_{14}H_{16}NO_3^+$ 246.1125, found 246.1122.



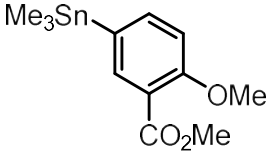
methyl 2-methoxy-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzoate (7) [CAS: 478375-37-0]

In a nitrogen-filled glovebox, an oven dried dram vial was charged with methyl 5-chloro-2-methoxybenzoate (50.2 mg, 0.25 mmol, 1 equiv), $NaCHO_2$ (51.0 mg, 0.75 mmol, 3 equiv), bis(pinacolato)diboron (190.5 mg, 0.75 mmol, 3 equiv), Cs_2CO_3 (244.4 mg, 0.75 mmol, 3 equiv), and a PTFE-coated stirbar. DMSO (1.25 mL) was added, followed by CdS QDs in hexane solution (~50 µL depending on QD concentration, 5.0 nmol, 2.0×10^{-3} mol %). The vial was sealed with a screw cap fitted with a PTFE-faced silicone septum before being removed from the glovebox. The vial was placed into a photoreactor equipped with two LEDs and irradiated with stirring (1250 RPM) and fan cooling for 24 h. The crude reaction mixture was subjected to Purification B and the resulting dry-loaded product was partially purified by column chromatography on silica (10% EtOAc/Hexanes). The product was obtained as white solid (40.2 mg, 55%) contaminated with bis(pinacolato)diboron (9.8 mg, 0.039 mmol), as determined via ^{1}H NMR spectroscopy using CH_2Br_2 as internal standard. Spectroscopic data was consistent with literature reports.[20]

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.21 (d, *J* = 1.7 Hz, 1H), 7.89 (dd, *J* = 8.3, 1.7 Hz, 1H), 6.95 (d, *J* = 8.4 Hz, 1H), 3.91 (s, 3H), 3.87 (s, 3H), 1.32 (s, 12H).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 166.7, 161.5, 140.3, 138.5, 119.8, 111.3, 84.0, 56.0, 52.0, 25.0. (C_{ipso} to boron does not appear due to quadrupolar broadening)

HRMS (ESI) $[M+H]^+$ m/z calc'd for $C_{15}H_{22}BO_5^+$ 293.1555, found 293.1551.



methyl 2-methoxy-5-(trimethylstannyl)benzoate (8)

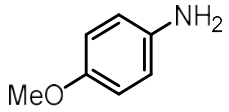
In a nitrogen-filled glovebox, an oven dried dram vial was charged with methyl 5-chloro-2-methoxybenzoate (50.2 mg, 0.25 mmol, 1 equiv), $NaCHO_2$ (102.0 mg, 1.5 mmol, 6 equiv),

hexamethylditin (245.7 mg, 0.75 mmol, 3 equiv), and a PTFE-coated stirbar. DMSO (1.00 mL) was added, followed by CdS QDs in hexane solution (~50 µL depending on QD concentration, 5.0 nmol, 2.0×10^{-3} mol %). The vial was sealed with a screw cap fitted with a PTFE-faced silicone septum before being removed from the glovebox. The vial was placed into a photoreactor equipped with two LEDs and irradiated with stirring (1250 RPM) and fan cooling for 48 h. After the reaction was complete, CH_2Br_2 (10 µL) was added via glass syringe. A 100 µL aliquot of the crude mixture was poured into water (1 mL), and extracted with $CDCl_3$ for ^{1}H NMR anlysis. The yield was determined to be 43% via integration of the aromatic resonance at 7.83 ppm vs. CH_2Br_2. Thereaction mixture was then purified according to **Purification A** (hexanes to 5% EtOAc in hexanes), affording the product as a clear oil (28.2 mg, 34% yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.91 – 7.80 (m, 1H), 7.62 – 7.50 (m, 1H), 7.00 – 6.94 (m, 1H), 3.90 (s, 3H), 3.89 (s, 3H), 0.29 (s, 9H).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 167.4, 159.4, 141.0, 138.7, 132.4, 120.2, 112.0, 56.0, 52.2, -9.3.

HRMS (ESI) $[M+H]^+$ m/z calc'd for $C_{12}H_{19}O_3Sn^+$ 331.0351, found 331.0340.

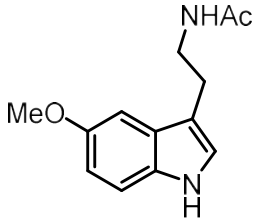


4-methoxyaniline (10a) [CAS: 104-94-9]

General procedure B was followed using N-(4-methoxyphenyl)-4-methylbenzenesulfonamide (138.7 mg, 0.5 mmol, 1 equiv). After 24 h, the reaction was quenched by exposure to air and purified according to **Purification A** (50% EtOAc/Hexanes) affording the product as a white solid (42.0 mg, 68% yield). Characterization data matched an authentic sample of product.

^{1}H NMR (500 MHz, $CDCl_3$) δ 6.77 – 6.72 (m, 2H), 6.69 – 6.62 (m, 2H), 3.75 (s, 3H), 3.41 (br, 2H).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 153.0, 140.1, 116.6, 115.0, 55.9.

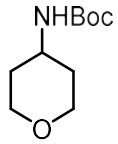


Melatonin (10b) [CAS: 77-31-4]

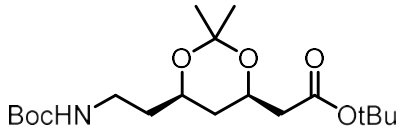
General procedure B was followed using N-(2-(5-methoxy-1-tosyl-1H-indol-3-yl)ethyl)acetamide (193.2 mg, 0.5 mmol, 1 equiv). After 24 h, the reaction was quenched and purified according to **Purification A** (1% MeOH/DCM), affording the product contaminated with DMPU. The yield was determined to be 89% via ^{1}H NMR spectroscopy using CH_2Br_2 as internal standard. DCM (100 uL) and hexanes (2 mL) were sequentially added to the impure product, and a white precipitate formed overnight at -40 °C. The mother liquor was decanted, and the process was repeated on the precipitate, yielding the pure product as a white powder (78.7 mg, 68% yield). Characterization data matched an authentic sample of product.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.95 (br, 1H), 7.27 (d, J = 8.5 Hz, 1H), 7.07 – 7.00 (m, 2H), 6.88 (dd, J = 8.8, 2.4 Hz, 1H), 5.51 (br, 1H), 3.87 (s, 3H), 3.60 (q, J = 6.6 Hz, 2H), 2.95 (td, J = 6.7, 0.9 Hz, 2H), 1.93 (s, 3H).

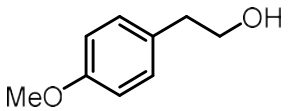
$^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 170.1, 154.3, 131.7, 127.9, 122.9, 113.0, 112.7, 112.1, 100.6, 56.1, 39.9, 25.5, 23.6.



tert-butyl (tetrahydro-2H-pyran-4-yl)carbamate (10c) [CAS: 1324000-32-9]
General procedure B was followed using 4-methyl-N-(tetrahydro-2H-pyran-4-yl)benzenesulfonamide (63.8 mg, 0.25 mmol, 1 equiv). After 72 h of irradiation and subsequent Boc protection, the reaction was quenched and purified according to **Purification A** (hexanes to 50% EtOAc/hexanes), affording the product as a white solid (44.3 mg, 88% yield). Characterization data were consistent with literature reports.[21]
^1H NMR (500 MHz, $CDCl_3$) δ 4.44 (br, 1H), 3.94 (ddd, *J* = 11.6, 4.1, 2.3 Hz, 2H), 3.66 (br, 1H), 3.44 (td, *J* = 11.7, 2.2 Hz, 2H), 1.90 (ddt, *J* = 12.6, 4.5, 2.3 Hz, 2H), 1.50 – 1.40 (m, 11H).
$^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 155.2, 79.6, 67.0, 47.0, 33.7, 28.6.ff
HRMS (ESI) $[M+H]^+$ m/z calc'd for $C_{10}H_{20}NO_3^+$ 202.1438, found 202.1436.



tert-butyl 2-((4R,6R)-6-(2-((tert-butoxycarbonyl)amino)ethyl)-2,2-dimethyl-1,3-dioxan-4-yl)acetate (10d)
General procedure B was followed using tert-butyl 2-((4R,6R)-2,2-dimethyl-6-(2-((4-methylphenyl)sulfonamido)ethyl)-1,3-dioxan-4-yl)acetate (106.9 mg, 0.25 mmol, 1 equiv). After 72 h of irradiation and subsequent Boc protection, the reaction was quenched and purified according to **Purification A** (hexanes to 50% EtOAc/hexanes), affording the product as a white solid (74.7 mg, 80% yield).
^1H NMR (500 MHz, $CDCl_3$) δ 4.83 (br, 1H), 4.29 – 4.21 (m, 1H), 4.01 – 3.87 (m, 1H), 3.34 – 3.12 (m, 2H), 2.42 (dd, *J* = 15.1, 7.0 Hz, 1H), 2.29 (dd, *J* = 15.1, 6.1 Hz, 1H), 1.70 – 1.57 (m, 2H), 1.54 (dt, *J* = 12.8, 2.4 Hz, 1H), 1.49 – 1.42 (m, 21H), 1.37 (s, 3H), 1.23 (dt, *J* = 12.8, 11.5 Hz, 1H).
$^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 170.4, 156.1, 98.9, 80.8, 79.8, 79.1, 67.9, 66.3, 42.8, 37.6, 36.4, 36.1, 30.2, 28.6, 28.4, 28.3, 19.8.
Melting point: 71.5-73.5 °C
HRMS (ESI) $[M+H]^+$ m/z calc'd for $C_{19}H_{36}NO_6^+$ 374.2537, found 374.2531.



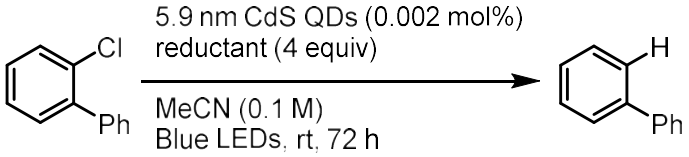
2-(4-methoxyphenyl)ethan-1-ol (12) [CAS: 702-23-8]
In a nitrogen-filled glovebox, an oven dried dram vial was charged with 1-(2-(benzyloxy)ethyl)-4-methoxybenzene (60.6 mg, 0.25 mmol, 1 equiv), TAEA (56 µL, 0.375 mmol, 1.5 equiv), and a PTFE-coated stirbar. DMPU (1 mL) was added, followed by CdS QDs in hexane solution (~50 µL depending on QD concentration, 5.0 nmol, 2.0×10^{-3} mol %). The vial was sealed with a screw cap fitted with a PTFE-faced silicone septum before being removed from the glovebox. The vial was placed into a photoreactor equipped with two LEDs and irradiated with stirring (1250 RPM)

and fan cooling for 72 h. The reaction mixture was quenched and purified according to **Purification A** (5% EtOAc/hexanes to 20% EtOAc/hexanes), affording the product as a clear oil (30.1 mg, 79%). Characterization data matched an authentic sample of product.
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.18 – 7.12 (m, 2H), 6.90 – 6.83 (m, 2H), 3.83 (t, J = 6.6 Hz, 2H), 3.80 (s, 3H), 2.82 (t, J = 6.5 Hz, 2H), 1.36 (br, 1H).
^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 158.5, 130.5, 130.1, 114.2, 64.0, 55.4, 38.4.

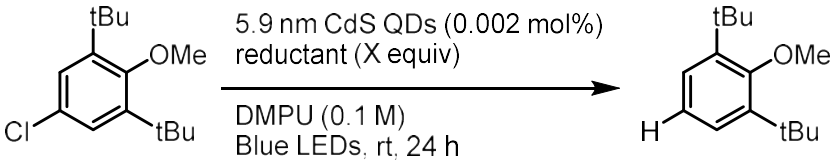
4. Supplemental Data

4.1 Figure S1. Additional Optimization Studies

Reductant Optimization

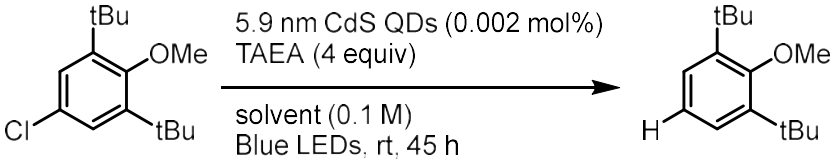


Reductant	% Yield
DIPEA	27
Triethanolamine	5
Tris(2-aminoethyl)amine (TAEA)	78
NaSPh	17
N,N-diisopropylethylenediamine	53
Hexamethylenediamine	50
tetrasodium EDTA	0
Mn	0



Reductant	% Yield
TAEA (4 equiv)	65
TAEA (1.5 equiv)	95
DIPEA (4 equiv)	91
DIPEA (1.5 equiv)	68
No reductant	0
TAEA (1.5 equiv), 0.25 M	86

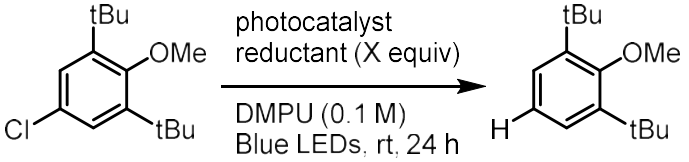
Solvent Optimization



Solvent	% Yield
DMA	65
DMF	51
DMPU	91
NMP	58
Cyrene	0

Reactions were assembled according to **General procedure A** and yields were determined via corrected GC-FID *vs*. *n*-dodecane as internal standard.

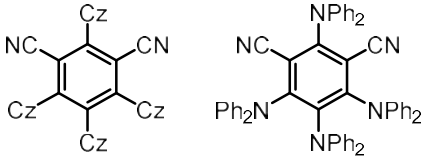
4.2 Figure S2. Alternative Two-Photon Photocatalyst Comparisons



Photocatalyst (1.5 equiv TAEA)	% Yield at 24 h	TON (per cat.)	mg pdt per mg cat.
5.9 nm CdS QDs (0.002 mol%)	95	47500	33
4-CzIPN (10 mol%)	24	2.4	0.66
4-DPAIPN (10 mol%)	96	9.6	2.7
$[Ir(dFCF_3ppy)_2(dtbbpy)]PF_6$ (2 mol%)	54	27	5.3
PDI (10 mol%)	16	1.6	0.59

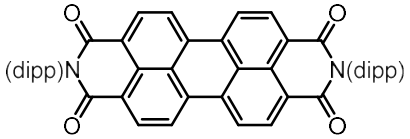
Photocatalyst (3 equiv $NaCHO_2$)	% Yield at 24 h (48 h)	TON (per cat.)	mg pdt per mg cat.
5.9 nm CdS QDs (0.002 mol%)	83 (95)	47500	33
4-CzIPN (10 mol%)	21 (23)	2.3	0.64
4-DPAIPN (10 mol%)	25 (38)	3.8	1.1
$[Ir(dFCF_3ppy)_2(dtbbpy)]PF_6$ (2 mol%)	16 (23)	13.5	2.2
PDI (10 mol%)	10 (12)	1.2	0.44

Photocatalyst (3 equiv DIPEA)	% Yield at 24 h (48 h)	TON (per cat.)	mg pdt per mg cat.
5.9 nm CdS QDs (0.002 mol%)	86 (95)	47500	33
4-CzIPN (10 mol%)	28 (29)	2.9	0.81
4-DPAIPN (10 mol%)	49 (74)	7.4	2.0
$[Ir(dFCF_3ppy)_2(dtbbpy)]PF_6$ (2 mol%)	76 (90)	45	9.0
PDI (10 mol%)	3 (3)	0.3	0.11



4-CzIPN

4-DPAIPN

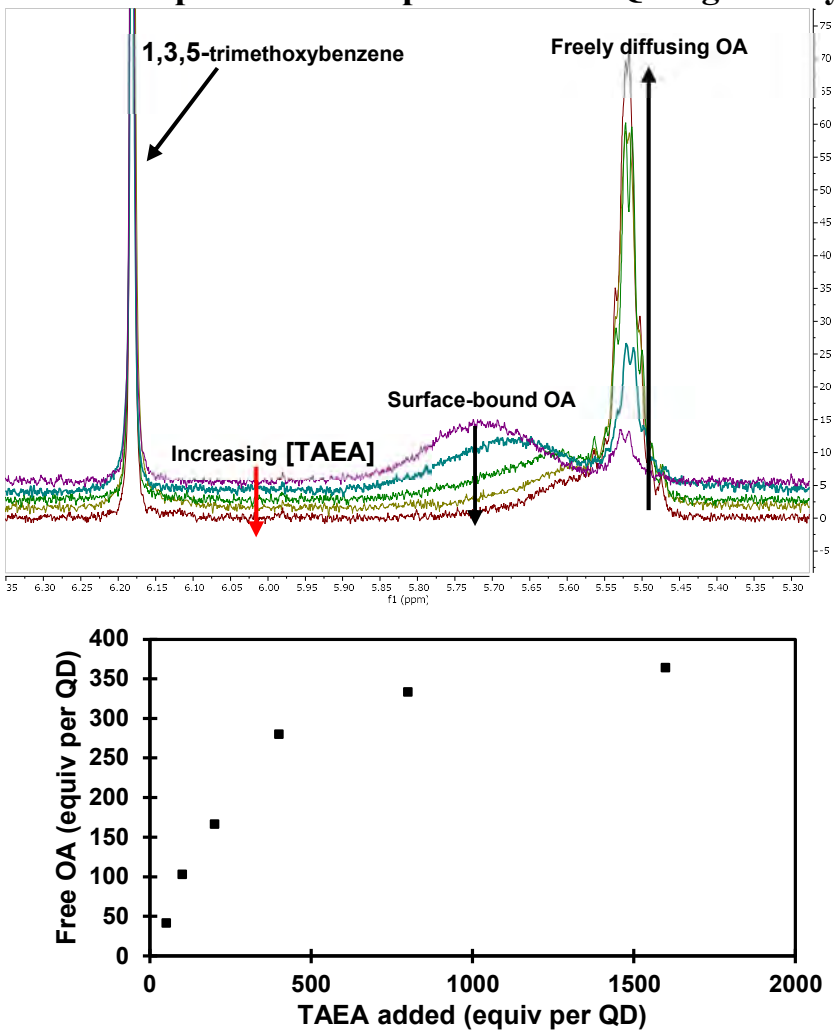


PDI

Experimental procedure: Reactions were set up in a N_2 filled glove box. An oven dried dram vial was charged with photocatalyst if solid, aryl chloride (0.1 mmol), reductant if solid, and a PTFE-coated stirbar. Solvent was added (1 mL) followed by reductant if liquid, and the mixture was stirred for 5 minutes forming a homogeneous clear solution. Unless a different photocatalyst was used, CdS QDs were added in toluene solution (approximately 50 µL depending on QD solution concentration, 5.0 nmol, 2×10^{-3} mol%). *n*-Dodecane (10 µL, 7.5mg) was added as internal standard, and the reactions were sealed with a screw cap fitted with a PTFE-faced silicone septum before being removed from the glovebox. Reactions were placed into photoreactor plates equipped with two LEDs per reaction and irradiated with stirring (1250 RPM) and fan cooling for 24 – 48

h. Yields were determined via corrected GC-FID. For images of the photoreactor plates, see section 1.5.

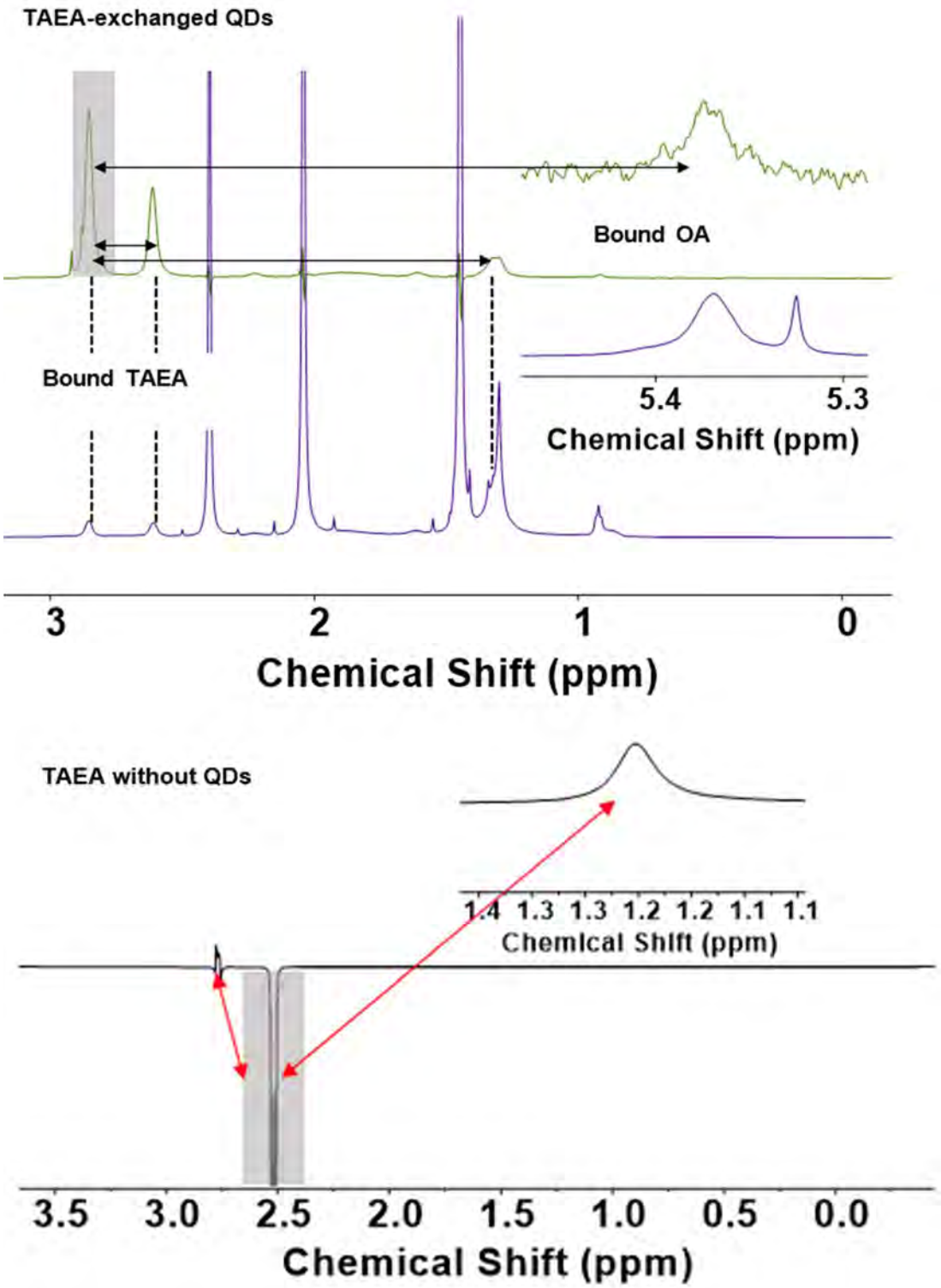
4.3 Figure S3. NMR experiments: displacement of QD ligands by TAEA



Experimental procedure: In a nitrogen-fileld glovebox, 1 mL of CdS QD solution (5.8 nm, ~5 × 10^{-5} M in toluene) was added to a centrifuge tube and 2 mL dry acetone was added to precipitate QDs. The QDs were centrifuged outside of the glovebox (3300 rpm, 10 min), and the supernatant was decanted. The QDs were brought into the glovebox and re-suspended in 1 mL toluene-d_8. The concentration was determined to be 4.52 × 10^{-5} M via UV-Vis spectroscopy.[5] In the glovebox, stock solutions of TAEA (5.25 mg/mL) and 1,3,5-trimethoxybenzene as an internal standard (1 mg/mL) were prepared in toluene-d_8. Samples for analysis were prepared by combining toluene-d_8 solutions of 1,3,5-trimethoxybenzene (200 µL, 0.2 mg, 1.19 × 10^{-3} mmol), CdS QDs (133 µL, 6 × 10^{-6} mmol), and TAEA (8.3 – 267 µL, 3 × 10^{-4} mmol – 9.6 × 10^{-3} mmol) in oven-dried dram vials equipped with PTFE-coated stir bars. Excess toluene-d_8 was added to maintain a constant volume of 600 µL. The solutions were stirred for 1 h at rt in the glovebox, then transferred to oven-dried NMR tubes for ^{1}H NMR analysis. Samples were analyzed for the presence of free OA signal via ^{1}H NMR using 32 scans and a d1 delay time of 30 s. Amounts of free OA were determined as described in the literature[22] by integration of the vinylic ^{1}H resonances of freely diffusing OA compared to 1,3,5-trimethoxybenzene, using MestReNova peak fitting to account for broad overlapping resonances of QD-bound OA. Integration of the total amount of OA in each sample (bound and unbound) yielded an average of 502 OA per QD. Plotting free OA *vs*. added TAEA

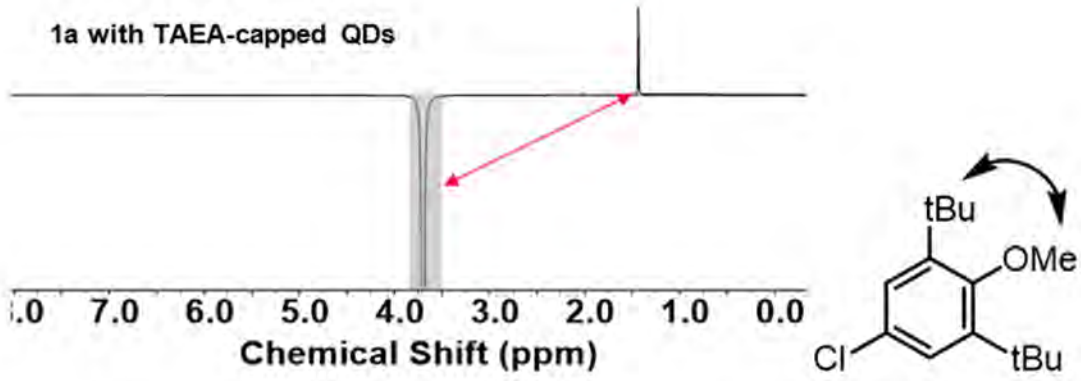
shows that increasing amounts of TAEA displace the bound OA, however a fraction of the OA remains bound even at the highest employed concentration of TAEA.

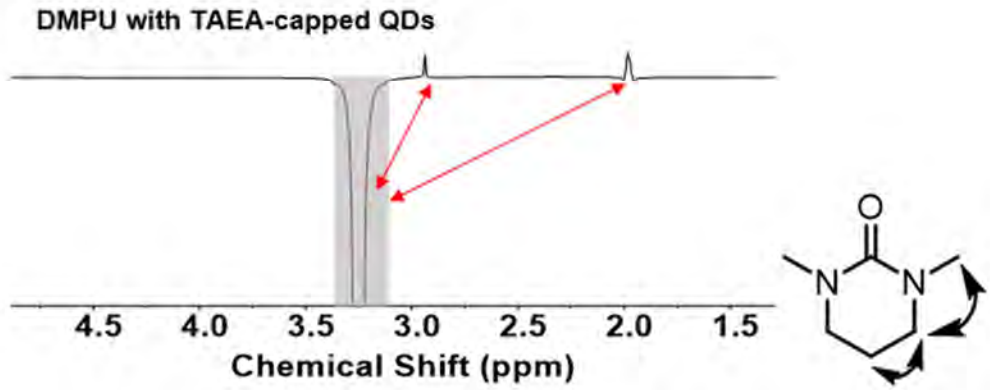
4.4 Figure S4. Study of QD ligand shell via NOE spectroscopy



Experimental procedure: Soluble TAEA-capped 6.0 nm CdS QDs were prepared: In the glovebox, an oven-dried dram vial was charged with 6.0 nm CdS QDs (6×10^{-6} mmol, 83 µL in toluene solution) and toluene (1 mL). TAEA was added (8.6 mg, 6×10^{-2} mmol, 600 µL in toluene solution),

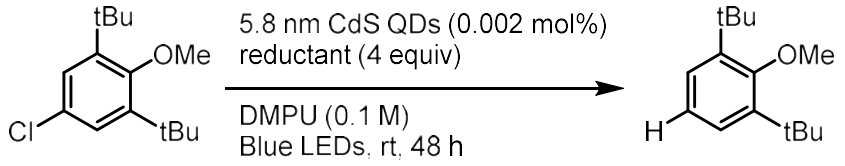
and a stir bar was added. The mixture was stirred protected from light for 3 h, remaining completely homogeneous throughout. The mixture was removed from the glovebox and transferred to a 15 mL centrifuge tube, and MeCN was added (5 mL). The mixture was centrifuged for 15 minutes at 3300 rpm to pellet the QDs. The clear colorless supernatant was discarded, and the yellow QD pellet dried briefly under vacuum before resuspension in $CDCl_3$ (650 μL) under air. The middle spectrum (purple) shows the standard ^1H spectrum of the sample; broadedned TAEA resonances are visible at 2.86 and 2.60 ppm, while residual oleate resonances are visible from incomplete exchange of the oleate ligands by TAEA. Additional peaks are visible from residual solvent signals of MeCN and toluene. Selective 1D NOESY spectra were obtained (top spectrum, green) on a Bruker Avance 600 MHz spectrometer with a TCI-F cryoprobe. The 180° pulse was applied to the TAEA methylene resonance at 2.86 ppm. 400 scans were obtained with a d1 delay of 10 s to allow complete relaxation, with a mixing time of 420 ms. The NOESY spectrum is phased positive to allow easier comparison with the ^1H spectrum. Negative NOE (same phase as pulsed resonance) is observed between the pulsed TAEA signal and other TAEA resonances, and also with residual surface-bound OA resonances (black arrows) which remain after treatment with TAEA, confirming the presence of TAEA on the QD surface. As a control experiment, selective 1D NOESY was performed on TAEA without QDs (bottom spectrum, black), and only weak positive NOE (anti-phase to the pulsed resonance) was observed between the resonance at 2.60 ppm and other resonances on the TAEA molecule (red arrows), as expected for a small molecule.

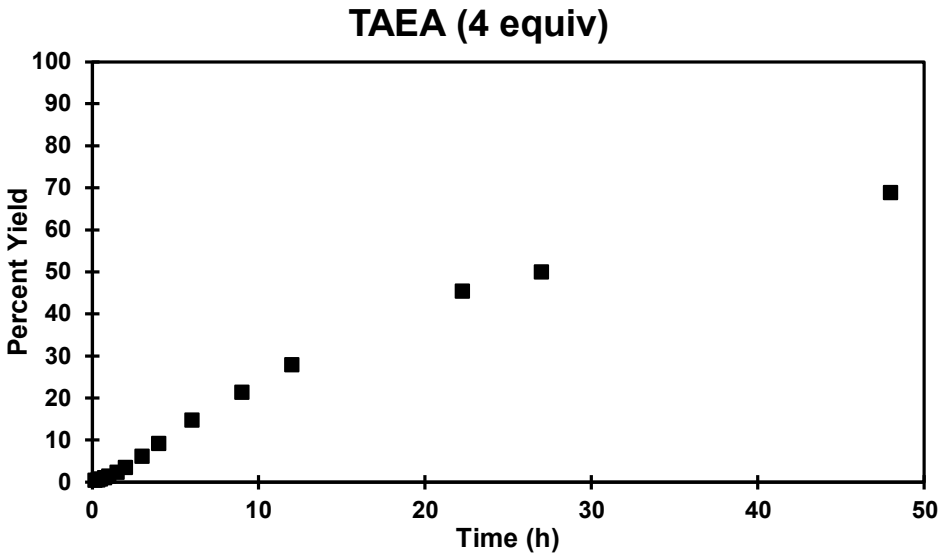


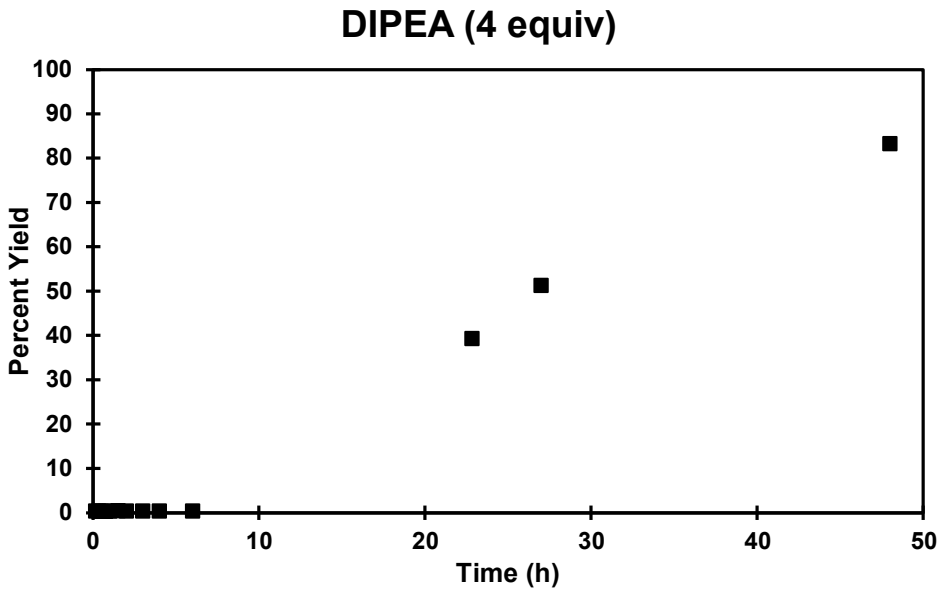


The NOE experiments were repeated, with **1a** (7.6 mg, 3×10^{-2} mmol) or DMPU (7.7 mg, 6×10^{-2} mmol) added to the sample after resuspension in $CDCl_3$. In the case of **1a**, the 180° pulse was applied to the methoxyl resonance of **1a** at 3.70 ppm. Weak positive NOE is observed between the pulsed methoxyl resonance and the *t*Bu signal at 1.4 ppm. In the case of DMPU, the 180° pulse was applied to the α-nitrogen methylene resonance at 3.25 ppm. Weak positive NOE is observed between the pulsed methylene resonance and both other ^{1}H resonances, In contrast to TAEA, only positive NOE (anti-phase to the pulsed peak, shown with red arrows) was observed, for **1a** and DMPU, with no negative NOE observed between the pulsed resonances and other resonances on the same molecule, or surface-bound TAEA or OA resonances. These results show that DMPU and **1a** do not associate with the QD surface under these conditions, however they cannot rule out that such interactions occur under the catalytic reaction conditions employing solvent quantities of DMPU and higher concentrations of substrate.

4.5 Figure S5. Reaction Kinetics – comparison of TAEA and DIPEA



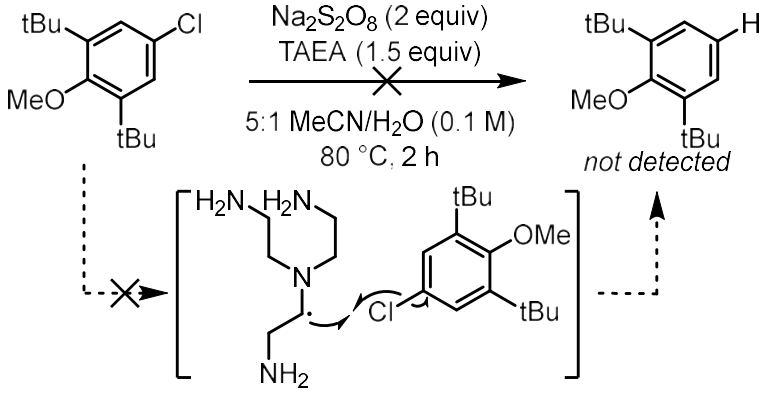




Experimental procedure: In the glovebox, to an oven-dried 5 mL Schlenk flask was added 1,3-di-*tert*-butyl-5-chloro-2-methoxybenzene (63.7 mg, 0.250 mmol, 1 equiv), followed by *n*-dodecane (20.0 µL, 15.0 mg) as internal standard and a PTFE-coated stir bar. DMPU (2.5 mL) was added via pipette followed by tris-(2-aminoethyl)amine (150 µL, 1.00 mmol, 4 equiv) or DIPEA (174 µL, 1.00 mmol, 4 equiv), and the mixture was stirred until solids had dissolved. 5.8 nm CdS QDs (5.0 nmol, 88.2 µL of 5.67×10^{-5} M solution in toluene) were added via pipette and the vessel sealed with a 14/20 rubber septum. The vessel was removed from the glovebox, placed 1 cm from a 456 nm Kessil lamp, and vented to a nitrogen bubbler via the side arm. The headspace was purged

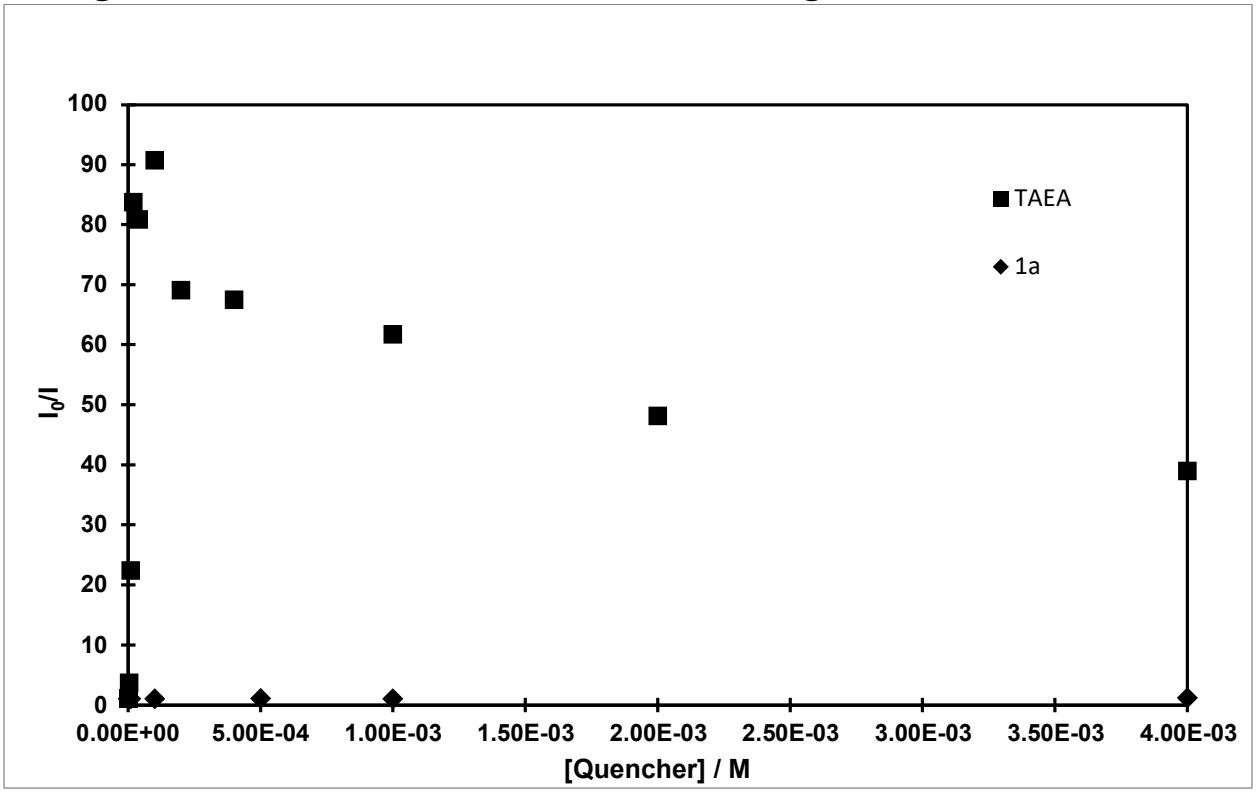
with nitrogen for 5 minutes, and then the vessel was irradiated at maximum lamp intensity for 48 h with stirring at 1250 RPM. Over the course of the reaction, 20 μL aliquots were removed from the reaction mixture using a syringe and analyzed via GC-FID.

4.6 Figure S6. Persulfate Oxidation Controls



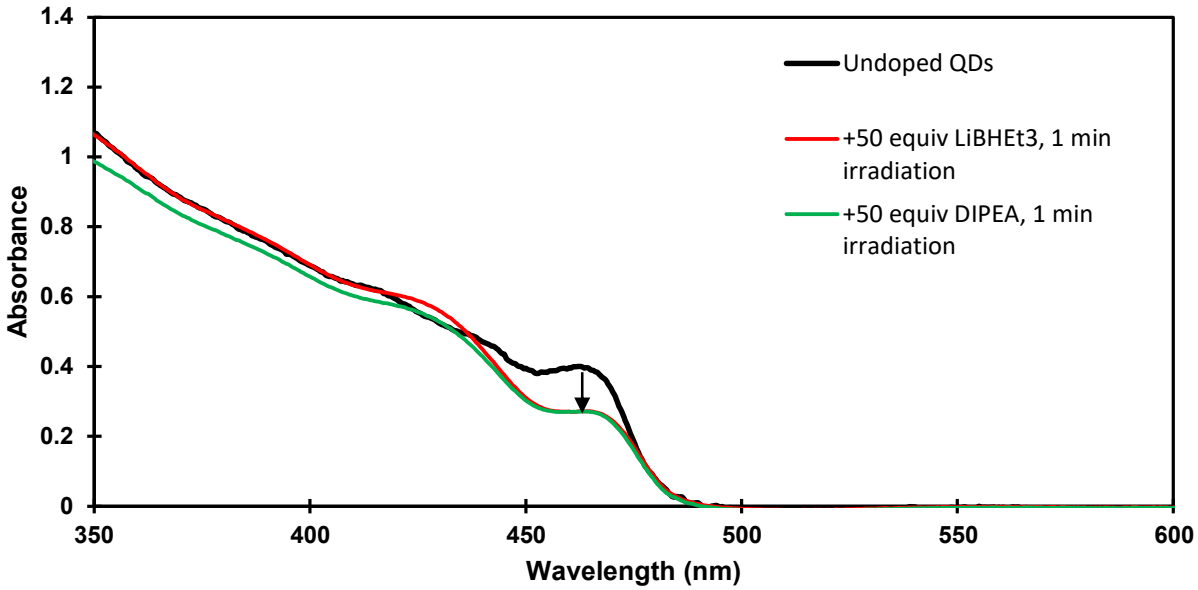
Experimental procedure was adapted from literature methods to generate alpha-amino radicals from tertiary amines and persulfate salts for organohalide activation.[23] In the glovebox, an oven dried dram vial was charged with 1,3-di-*tert*-butyl-5-chloro-2-methoxybenzene (63.7 mg, 0.25 mmol, 1 equiv), Sodium persulfate (119.1 mg, 0.500 mmol, 2 equiv), and a PTFE-coated stirbar. MeCN was added (0.867 mL) followed by TAEA (56 µL, 0.375 mmol, 1.5 equiv). CdS QDs were added in toluene solution (approximately 50 µL depending on QD concentration, 5.0 nmol, 2.0×10^{-3} mol%). The vial was removed from the glovebox and degassed water was added (166 µL), and the mixture was stirred for 2 h at 80 °C. After completion, the reaction mixture was analyzed via GC-FID *vs*. *n*-dodecane and product formation was not detected. The experiment was repeated employing 2-chlorobiphenyl as aryl chloride, and no dehalogenated product was observed.

4.7 Figure S7. Static Photoluminescence Quenching Plots



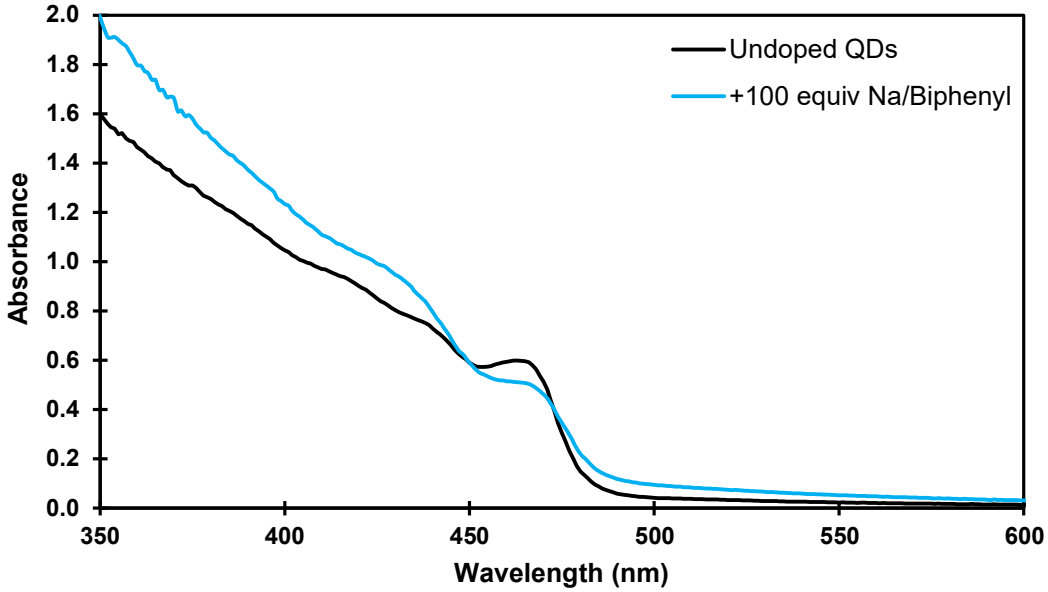
Experimental procedure: In the glovebox, a Schlenk type cuvette with PTFE stopcock was charged with 2 mL of toluene, 6.0 nm CdS QDs (8×10^{-8} mmol in toluene solution), and quencher ($0 – 8 \times 10^{-3}$ mmol dispensed in toluene solution). The cuvette was sealed, kept in the dark, and measured on a Lambda 950 UV-Vis blanked with toluene and a home-built fluorimeter system with a 450 W xenon arc lamp source coupled to an excitation SpectraPro 150 monochromator. A photomultiplier tube (PMT) was used for emission detection with an emission SpectraPro 300 monochromator every 1 nm with an integration time of 250 ms. The excitation wavelength was 450 nm for all of the PL spectra obtained. PL intensity at 474 nm were used to construct quenching plots. No significant quenching of QD PL by 1a was observed, however TAEA significantly quenched PL at all concentrations, with higher equivalents causing slight recovery of PL, possibly due to enhanced passivation of QD surface sites at high concentrations of TAEA. Due to nonlinearity of PL quenching effects by TAEA owing to surface modification of QDs combined with reductive quenching, no quantitative relationship can be extracted.

4.8 Figure S8. Photochemical preparation of n-doped QDs



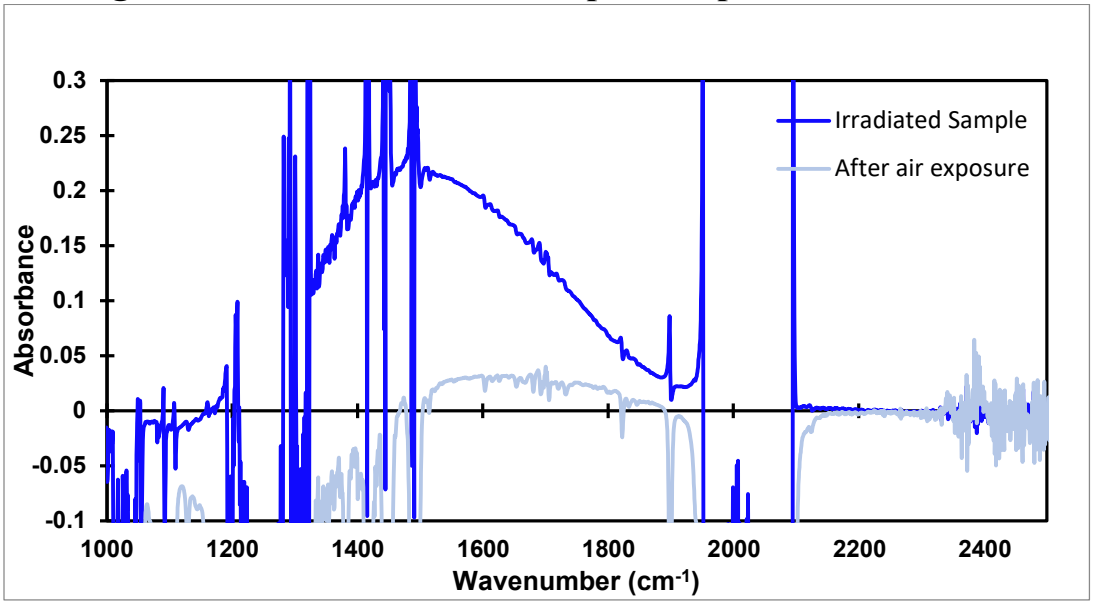
Experimental procedure: Photodoped CdS QDs were prepared using methods adapted from Cohn et al.[24] In the glovebox, 10 µL of 1 M $LiBHEt_3$ solution in THF was brought to a final volume of 2.7 mL with dry THF, for a final concentration of 3.7 mM. An oven-dried Schlenk-type quartz cuvette (path length 1 cm) was charged with 5.9 nm CdS QDs (7.4×10^{-7} mmol, 2 mL of 3.7×10^{-7} M solution in toluene) and $LiBHEt_3$ (3.7×10^{-5} mmol, 10 µL of 3.7 mM solution in THF, 50 equiv per QD). The cuvette was removed from the glovebox and irradiated with a 456 nm Kessil lamp for 1 minute (approx. 2 cm from bulb) with gentle shaking of the cuvette, before UV-Vis spectra were obtained. A control sample of QDs was additionally prepared with no $LiBHEt_3$. As observed in literature reports, partial bleaching of the excitonic peak of the QDs was observed, which was fully reversible upon exposure to air, consistent with photo-induced electron injection into the CB of the QDs. The above procedure was repeated, substituting $LiBHEt_3$ for N-ethyl-N-isopropylpropan-2-amine (DIPEA) (3.7×10^{-5} mmol, 10 uL of 3.7 mM solution in THF).

4.9 Figure S9. Chemical preparation of n-doped QDs



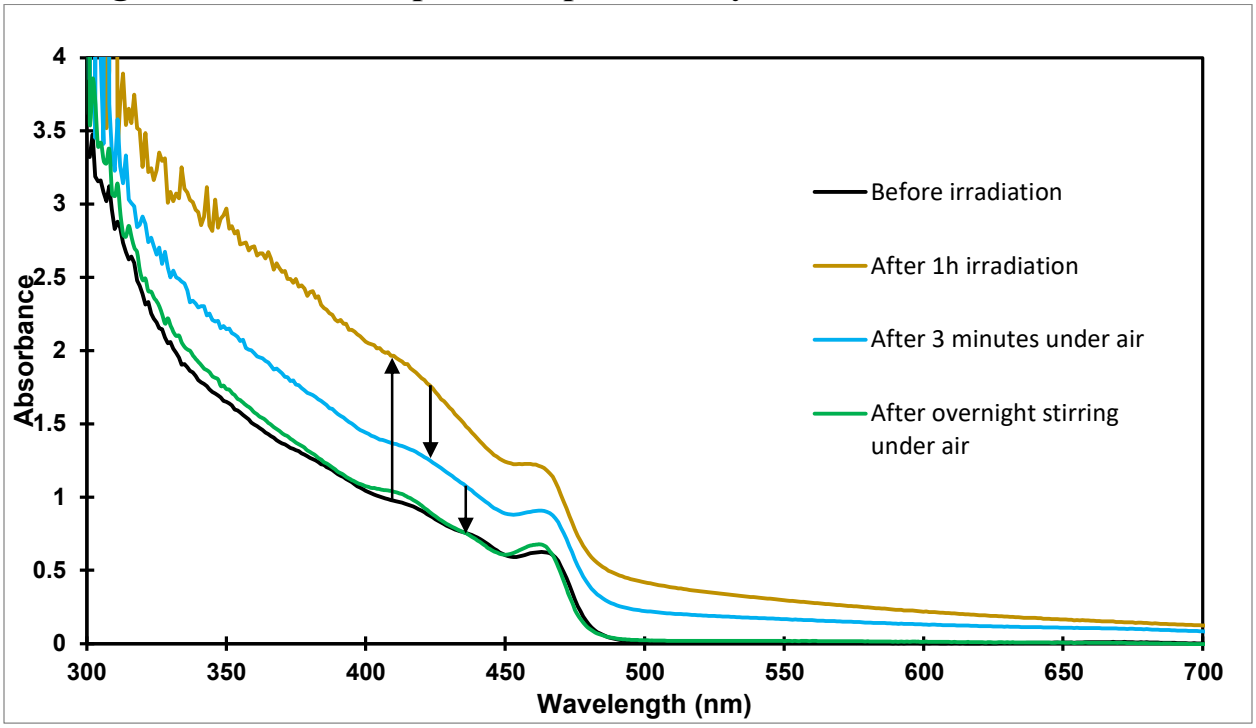
Experimental procedure: In the glovebox, biphenyl (42.4 mg, 0.280 mmol) and Na metal (5.8 mg, 0.25 mmol) were sequentially added to an oven-dried 1 dram vial with a PTFE-coated stir bar, followed by DMPU (2.5 mL). The solution was stirred until homogenous, turning deep blue as the Na dissolved. An oven-dried scintillation vial was charged with 5.9 nm CdS QDs (1.4×10^{-6} mmol, 3.5 mL of 4×10^{-7} M solution in toluene) followed by Na/biphenyl solution (7.4×10^{-4} mmol, 7 µL of 0.1 M solution in DMPU, 500 equiv per QD). The solution was shaken for 30 s, and 2 mL was transferred to an oven-dried Schlenk-type quartz cuvette (path length 1 cm). The cuvette was sealed, removed from the glovebox, and UV-vis spectra were obtained before and after exposure to air. A control sample of QDs was additionally prepared with no Na/biphenyl solution. As observed in literature reports, bleaching of the excitonic peak at 463 nm indicates electron occupation of the $1S_e$ state in the conduction band.[25]

4.10 Figure S10. IR measurement of photodoped QDs



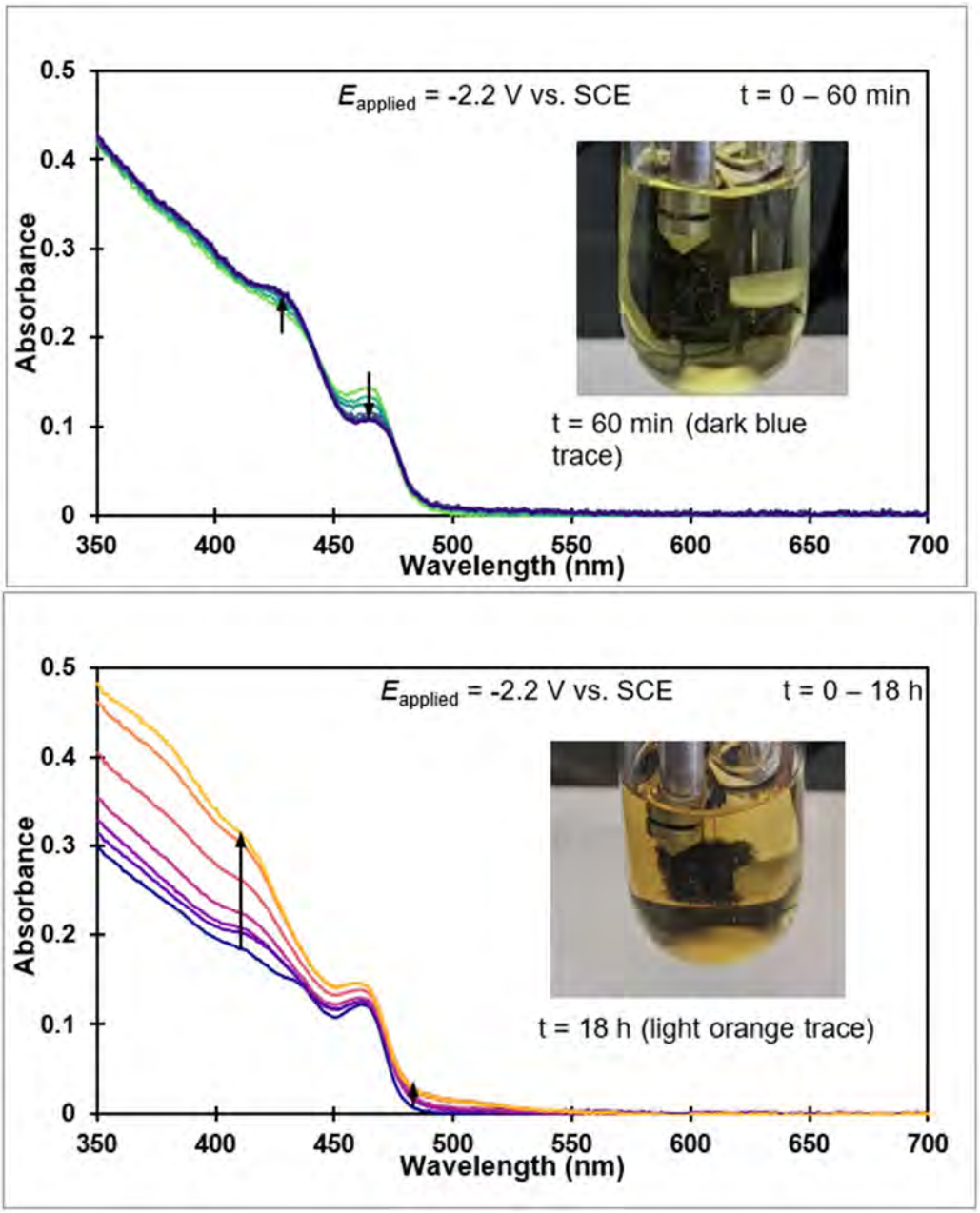
Experimental procedure: In the glovebox, a FTIR sandwich cell (International Crystal part number 0004D-1190W) equipped with CaF_2 windows and a 0.1 mm lead spacer was charged with 6.0 nm CdS QDs (6×10^{-6} M in hexanes). FTIR spectra were collected on the sample after irradiation with two 250 mW blue LEDs with stirring for 20 min. The sample was then exposed to air for 3 min and remeasured.

4.11 Figure S11. UV-Vis spectra of photocatalytic reaction mixture



Experimental procedure: To a dram vial in the glovebox was added 1,3-di-*tert*-butyl-5-chloro-2-methoxybenzene (51 mg, 0.2 mmol), 1 mL toluene, 1 mL DMPU, and DIPEA (140 µL, 0.8 mmol, 4 equiv). 5.85 nm CdS QDs were added in toluene solution (10 µL QD solution, 9.87×10^{-5} M, 1×10^{-6} mmol QDs, 5×10^{-6} equiv), and the mixture was stirred briefly then transferred to a schlenk cuvette sealed with a teflon stopcock along with a teflon-coated stir bar. UV-vis spectra were obtained before irradiation, and were completely homogeneous, and showed no appreciable light scattering due to QD precipitation. The cuvette was placed 1 cm in front of a Kessil lamp with emission centered at 456 nm, with an approximate power entering the cuvette of 1W. The cuvette was irradiated with stirring at 800 RPM for 1 h, and the solution turned from a light yellow to a dark golden color while remaining visibly homogeneous. UV-vis spectra were obtained again, and broad absorbance enhancement was observed across the entire visible and UV region with simultaneous flattening of the QD excitonic peak (yellow trace), ascribed to photodoping of the QD conduction band states. The cuvette was then opened to atmosphere and air was blown into the cuvette headspace for 3 min using a compressed air line, with vigorous stirring to facilitate gas equilibration. The cuvette was re-sealed to prevent significant solvent evaporation, and the solution was stirred overnight while the color gradually returned to light yellow. UV-vis spectra were obtained immediately after exposure to air (blue trace), and after stirring overnight (green trace). The blue trace after air exposure showed significant decreases in the broad absorbance that first appeared during irradiation, and the QD excitonic peak had returned to the original shape (black trace). After overnight stirring under air atmosphere, the spectrum (green trace) strongly resembled the QDs before irradiation (black trace), but had been blueshifted by ca. 3 nm.

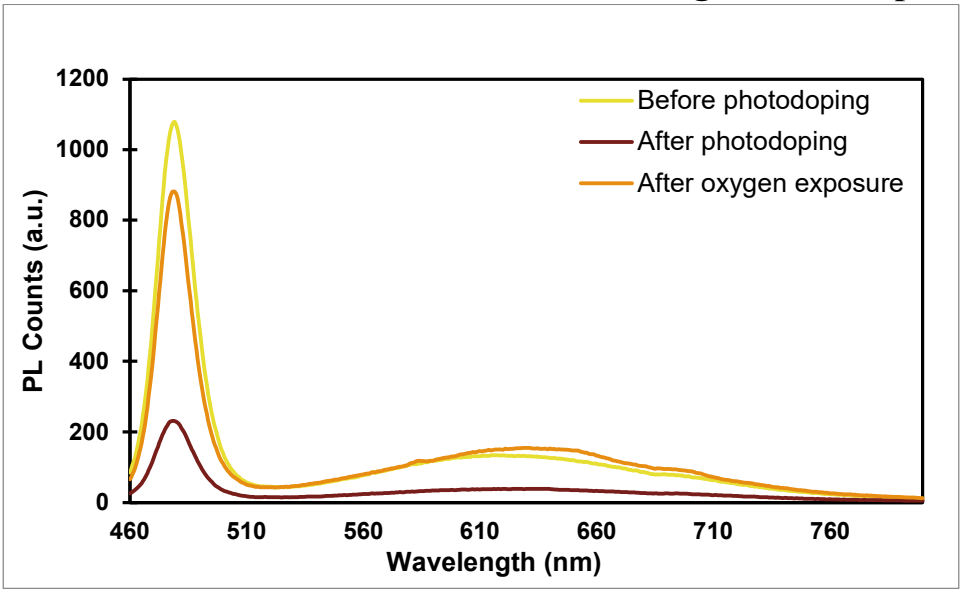
4.12 Figure S12. Spectroelectrochemistry of 5.9 nm CdS QDs



Experimental procedure: In the glovebox, to prepare the cathode QD solution, tetrabutylammonium hexafluorophosphate ($TBAPF_6$, 387.4 mg, 1 mmol) was dissolved in 2.5 mL DMPU in an oven-dried dram vial. 5.9 nm CdS QDs (5.0 nmol, 60.3 µL of 8.29×10^{-5} M solution in toluene) were added to 7.5 mL toluene in an oven-dried scintillation vial to create a clear yellow solution. The entire $TBAPF_6$ solution in DMPU was added dropwise to the QD solution with stirring over 1 min to prevent QD precipitation. To prepare the anode solution, $TBAPF_6$ (193.7 mg, 0.5 mmol) was dissolved in a mixture of toluene (3.75 mL) and DMPU (1.25 mL). The QD solution was added via pipette to the main chamber of an oven-dried two-necked Schlenk-type divided cell electrolysis tube equipped with an inner fritted tube and charged with a PTFE-coated stir bar (see image, section S1.5). Anode solution was then added to the interior fritted tube to equal the level

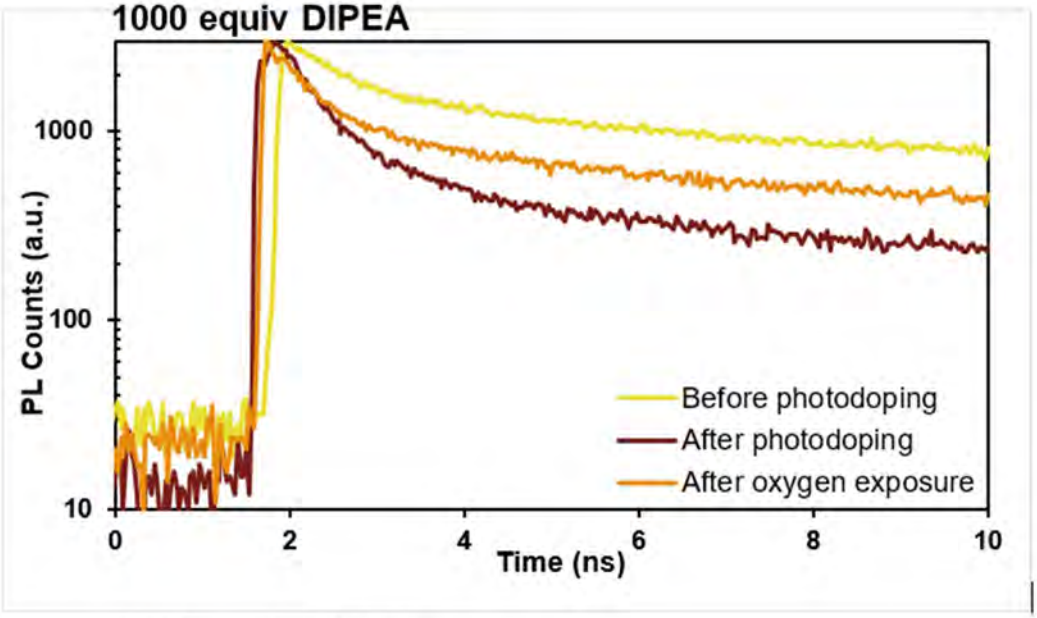
of the QD solution. A non-aqueous Ag / $AgNO_3$ reference cell was assembled by filling a 2 mm ID fritted glass tube (Pine research) with 0.01 M $AgNO_3$ / 0.1 M $TBAPF_6$ solution in MeCN and capping with a PTFE-sleeved cap containing Ag wire as the reference electrode. The assembled reference cell was then wrapped with PTFE tape to exclude light, and connected to a lead inserted through a 24/40 rubber septum. An RVC cathode was pierced with a steel wire which was then inserted through the 24/40 rubber septum, and the septum/electrode assembly was inserted into the top of the Schlenk tube, allowing both electrodes to contact the QD solution. A 1 cm Mg rod (Sigma Aldrich) was attached to a steel wire via graphite glue and PTFE tape to create a sacrificial anode, and the steel wire was inserted through a 14/20 rubber septum, which was then inserted into the side-arm of the Schlenk tube, allowing the Mg anode to contact the anode solution in the inner fritted tube. The assembly was removed from the glovebox, and a UV-vis dip probe (Agilent, 2 mm path length) was inserted into a pre-drilled hole in the 24/40 septum until the detector was immersed in the QD solution. A needle was inserted through the 24/40 septum, and the headspace was placed under a slow stream of nitrogen. Cathodic reduction of the QD solution was then conducted for 120 min at a potential of -2.5 V vs. Ag/$AgNO_3$ (-2.2 V vs. SCE) using a Pine WaveNowXV potentiostat, with absorbance scans taken every minute for the first hour and every 5 minutes thereafter. Over this period, the solution remained completely homogeneous, and slow bleaching of the excitonic peak of the QDs was observed (top spectra). The average number of electrons per QD was estimated to be 0.5, based on the magnitude of bleaching. The experiment was repeated over 18 h with scans taken every 30 min, and the excitonic bleaching was accompanied by other absorbance changes (bottom spectra). Throughout this period, the QD sample remained completely homogeneous with no QD flocculation visible to the naked eye.

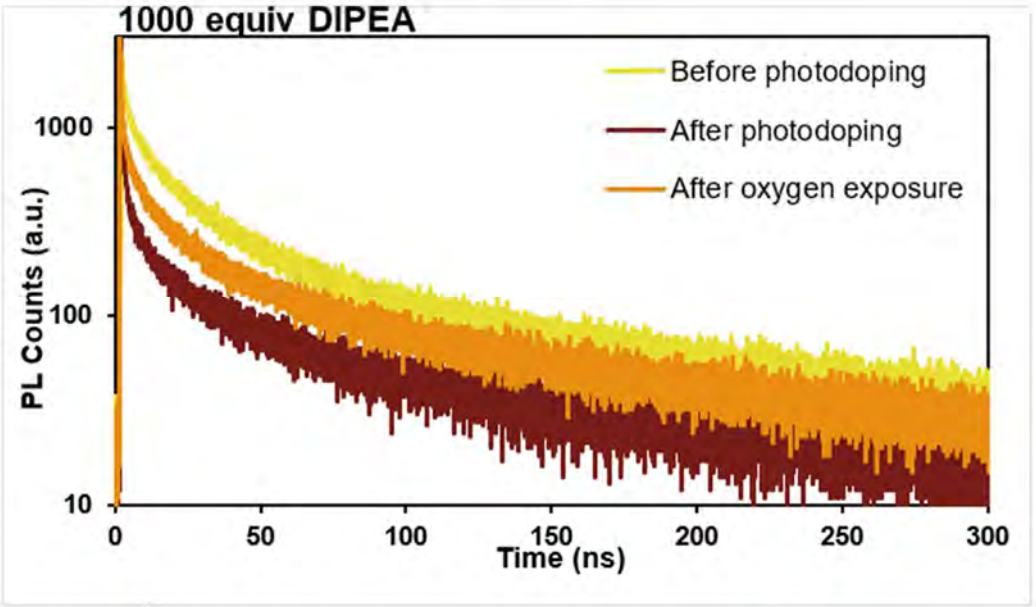
4.13 Figure S13. Static Photoluminescence Quenching of Photodoped QDs



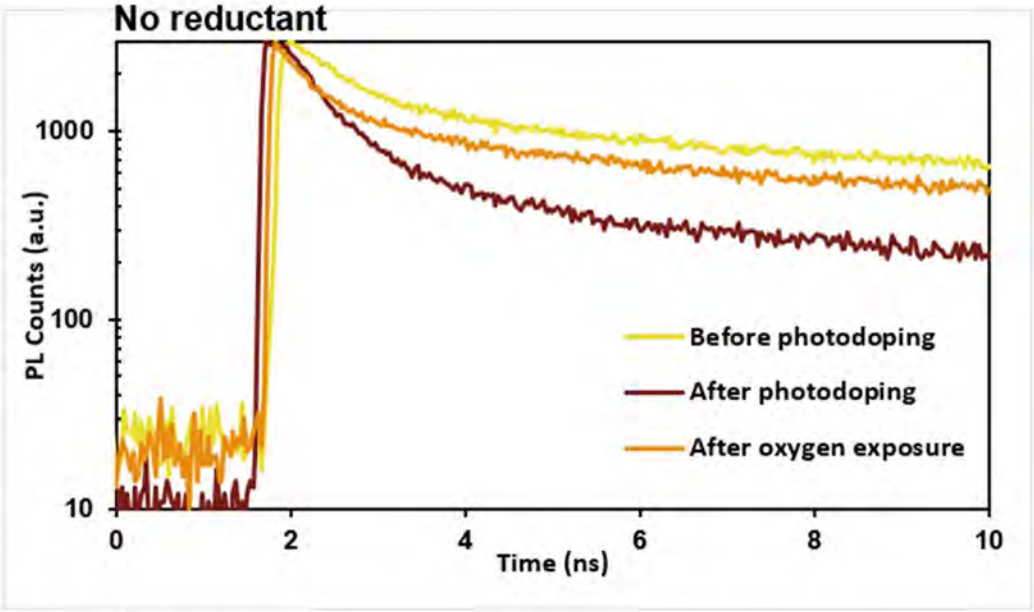
A Schlenk type cuvette with PTFE stopcock was charged with 2 mL toluene, 6.0 nm CdS QDs (0.3 nmol in toluene solution), and DIPEA (0.3 μmol, 1000 equiv). The cuvette was sealed, kept in the dark, and measured on a Lambda 950 UV-Vis blanked with toluene and a home-built fluorimeter system with a 450 W xenon arc lamp source coupled to an excitation SpectraPro 150 monochromator. A photomultiplier tube (PMT) was used for emission detection with an emission SpectraPro 300 monochromator every 1 nm with an integration time of 250 ms. The excitation wavelength was 450 nm for all of the PL spectra obtained. The sample was then irradiated with four 250 mW blue LED lights for 20 minutes with stirring, and then measured again on both instruments. Finally, the solution was exposed to air for 3 min and a final set of scans were performed.

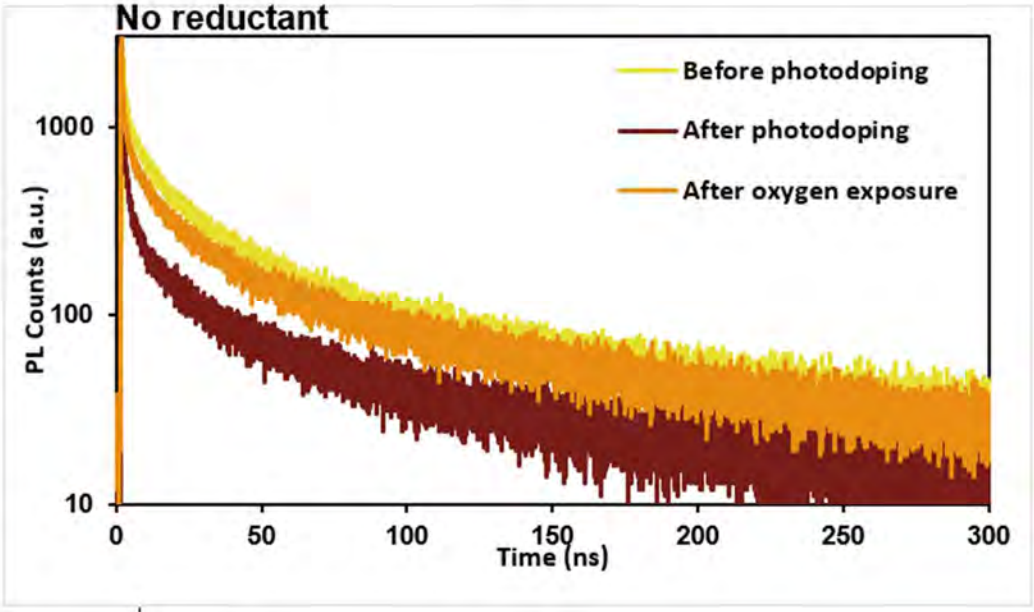
4.14 Figure S14. Time-Resolved Photoluminescence Decay of Photodoped QDs





Sample	A1 (%)	t1 (ns)	A2 (%)	t2 (ns)	A3 (%)	t3 (ns)	Average Lifetime (ns)
Initial	59.5	1.04	32.2	16.0	8.38	140	**17.5**
Doped	85.6	0.577	11.1	10.9	3.27	143	**6.4**
Oxygen	73.8	0.660	20.2	12.3	6.00	140	**11.4**



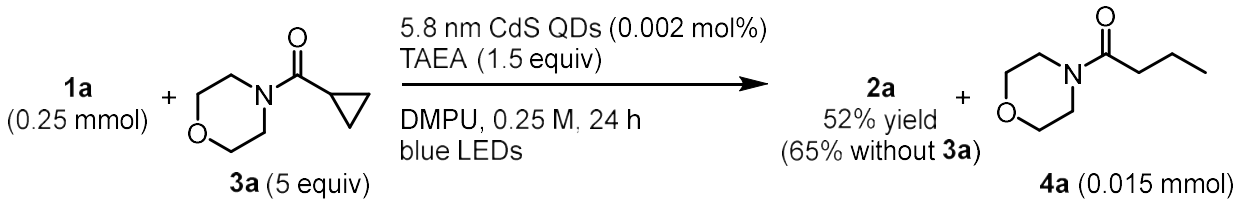


Sample	A1 (%)	t1 (ns)	A2 (%)	t2 (ns)	A3 (%)	t3 (ns)	Average Lifetime (ns)
Initial	64.7	0.924	28.0	15.3	7.24	137	**14.8**
Doped	88.2	0.730	9.2	12.6	2.59	143	**5.5**
Oxygen	69.8	0.650	23.6	12.2	6.66	131	**12.1**

Experimental procedure: In an air-free Schlenk-type 1 cm quartz cuvette, 2 mL of toluene, 0.3 nmol of 6.0 nm CdS QDs, and 0.3 μmol of DIPEA were combined. The cuvette was sealed, kept in the dark, and measured on a Lambda 950 UV-Vis blanked with Toluene. The sample was then irradiated with four 250 mW blue LED lights for 20 min with stirring, and then measured again. Finally, the solution was exposed to air for 3 min and a final scan was observed. The PL decay

curves were measured on a home-built apparatus. A neutral density filter (Thorlabs, Inc.) was placed in the excitation pathway to ensure the photon flux was no higher than 10^{12} photons per cm^2 per pulse. Single photon PL emission was collected by a gated InGaAs/InP avalanche photodiode (APD) (Micro Photon Devices, 25 μm active sensing area diameter) with a fast-timing resolution of less than 100 ps. All components of the TCSPC setup were incorporated in the PicoHarp 300 module (PicoQuant). The instrument response function (IRF) was measured from residual scattering of the IR laser beam from the optical parametric oscillator. The PL decay curves were analyzed and fit by FluoFit software (PicoQuant) using an iterative reconvolution method (first set of plots and data table). The experiment was repeated without DIPEA as a reductant (second set of plots and data table), and reductant-free photodoping was observed, as previously documented in CdS QDs through auto-oxidation of the QD ligands[26] or trapped water at the QD-ligand interface.[27] These oxidizable species enable the formation of anionic QDs for PL study without reductant, but are not present in large enough quantities to sustain the supply of electrons required by the catalytic reaction beyond unmeasurably low conversion, necessitating the presence of stoichiometric reductants for the catalytic reaction. The samples prepared with and without reductant displayed similar lifetime reduction after photodoping, resulting from the production of anionic QDs.

4.15 Figure S15. Inhibitory effect of trialkyl amides

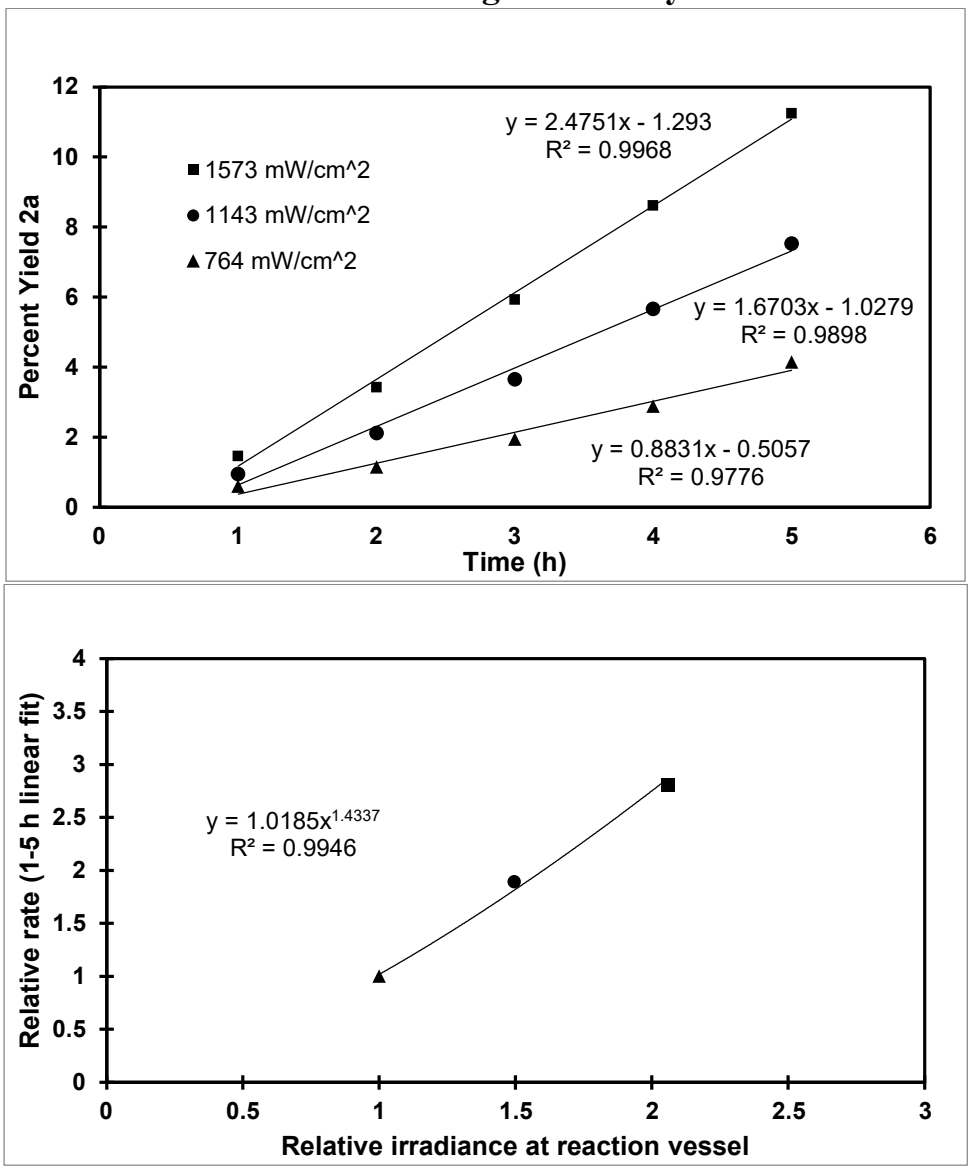


Experimental procedure: General procedure A was followed using 1,3-di-*tert*-butyl-5-chloro-2-methoxybenzene (63.7 mg, 0.25 mmol, 1 equiv), with and without cyclopropyl(morpholino)methanone (194.0 mg, 1.25 mmol, 5 equiv) as an additive. After 24 h, the reactions were quenched with addition of EtOAc (1 mL) and yields of **2a** and 1-morpholinobutan-1-one were determined via GC-FID *vs. n*-dodecane as internal standard.

4.16 Figure S16. Aryl radical cyclization probe

Experimental procedure: General procedure A was followed using 1-(but-3-en-1-yl)-2-chlorobenzene (41.7 mg, 0.25 mmol, 1 equiv). After 48 h, the reaction was quenched by exposure to air, and trimethoxybenzene was added as internal standard. A 100 µL aliquot of the crude reaction mixture was diluted in $CDCl_3$ for yield determination via ^1H NMR analysis, and resolved signals of each product were in agreement with literature reports.[28]

4.17 Figure S17. Reaction Kinetics – Light Intensity



Experimental procedure: In the glovebox, to an oven-dried 5 mL Schlenk flask was added 1,3-di-*tert*-butyl-5-chloro-2-methoxybenzene (63.7 mg, 0.25 mmol, 1 equiv), followed by *n*-dodecane (20 µL, 15.0 mg) as internal standard and a PTFE-coated stir bar. DMPU (2.5 mL) was added via pipette followed by tris-(2-aminoethyl)amine (150 µL, 1 mmol, 4 equiv), and the mixture was stirred until solids had dissolved. 5.8 nm CdS QDs (5.0 nmol, 88.2 µL of 5.67×10^{-5} M solution in toluene) were added via pipette and the vessel sealed with a 14/20 rubber septum. The vessel was removed from the glovebox, placed 1 cm from a 456 nm Kessil lamp, and vented to a nitrogen bubbler via the side arm. The headspace was purged with nitrogen for 5 min, and then the vessel was irradiated at 100%, 75%, or 50% power for 5 h with stirring at 1250 RPM. The irradiance of the lamp was measured at a distance of 1 cm with a power meter (Thorlabs) to quantify power delivered to the reaction vessel. Over the course of the reaction, 20 µL aliquots were removed from the reaction mixture using a syringe and analyzed via GC-FID. Rate order of photons was estimated using a power fitting function in Excel.

5. References

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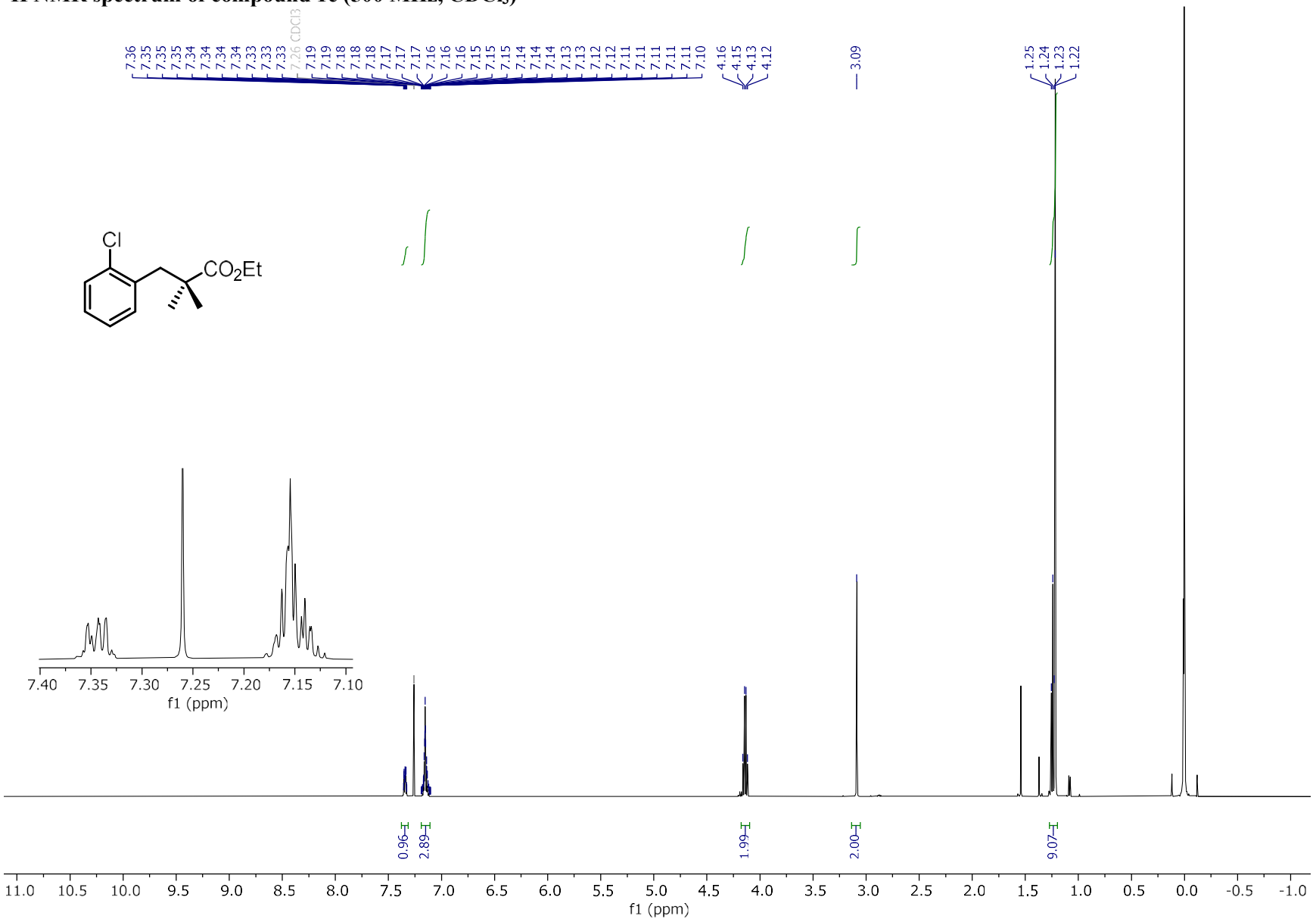
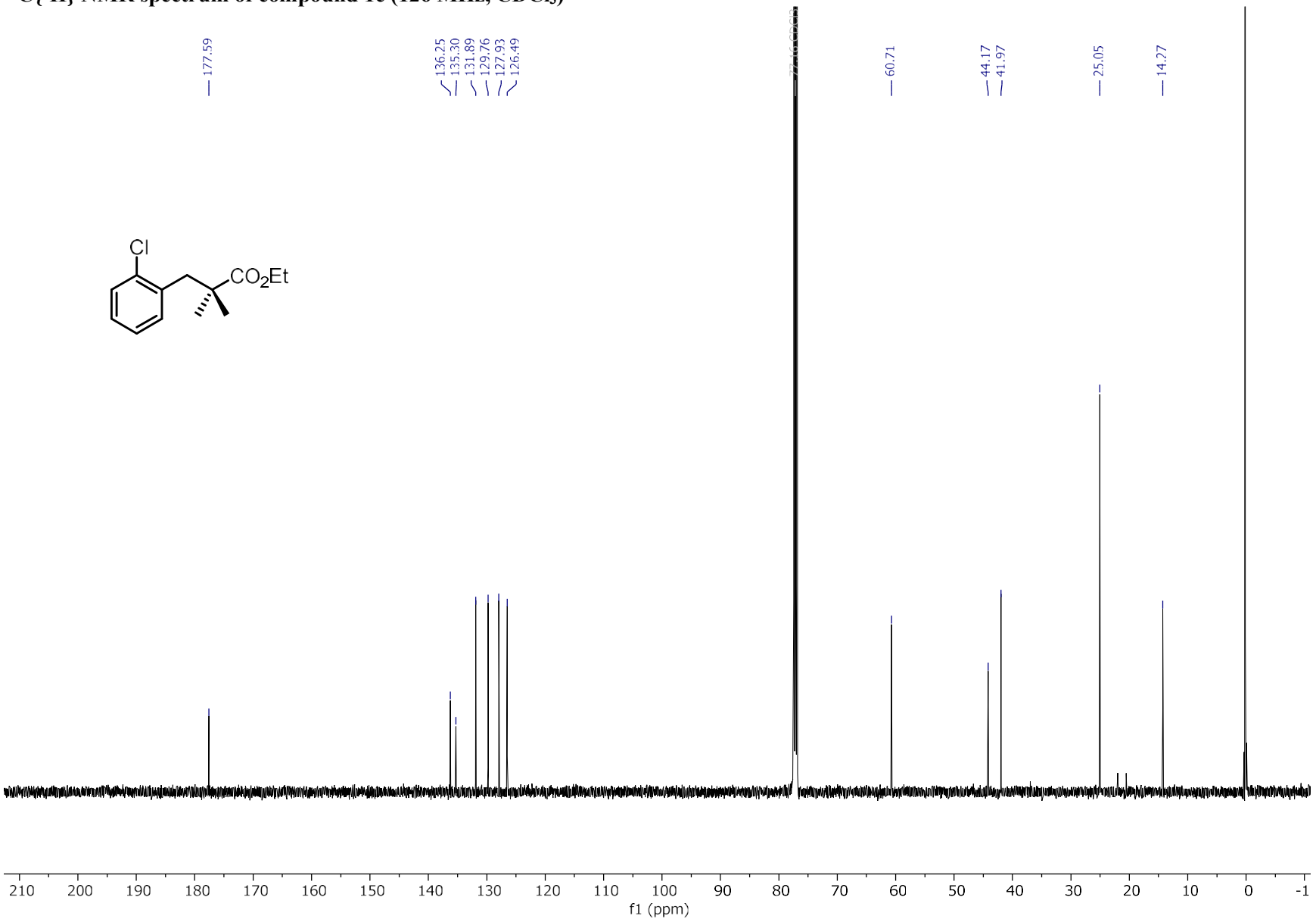
6. NMR Spectra

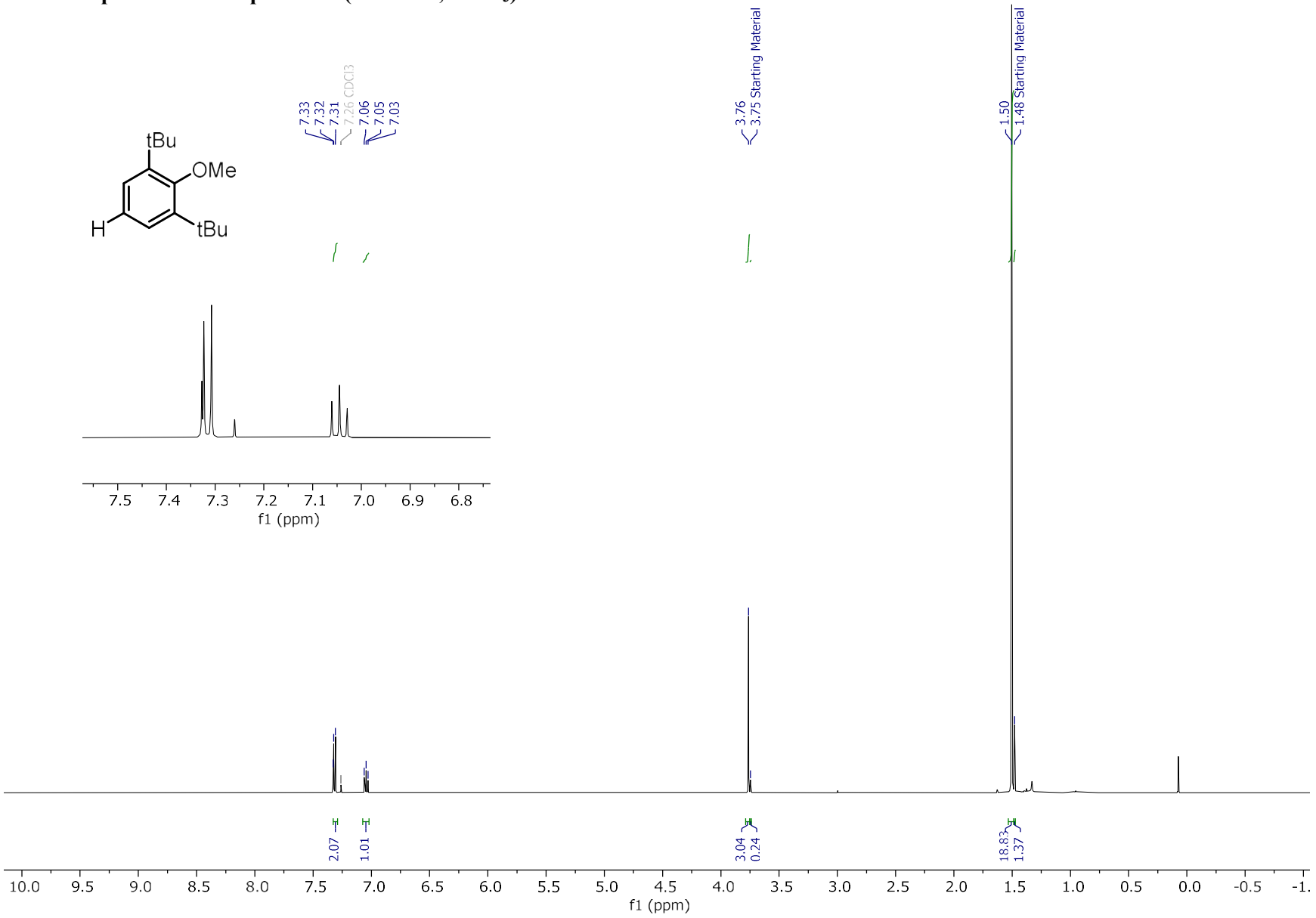
^{1}H NMR spectrum of compound 1c (500 MHz, $CDCl_3$)



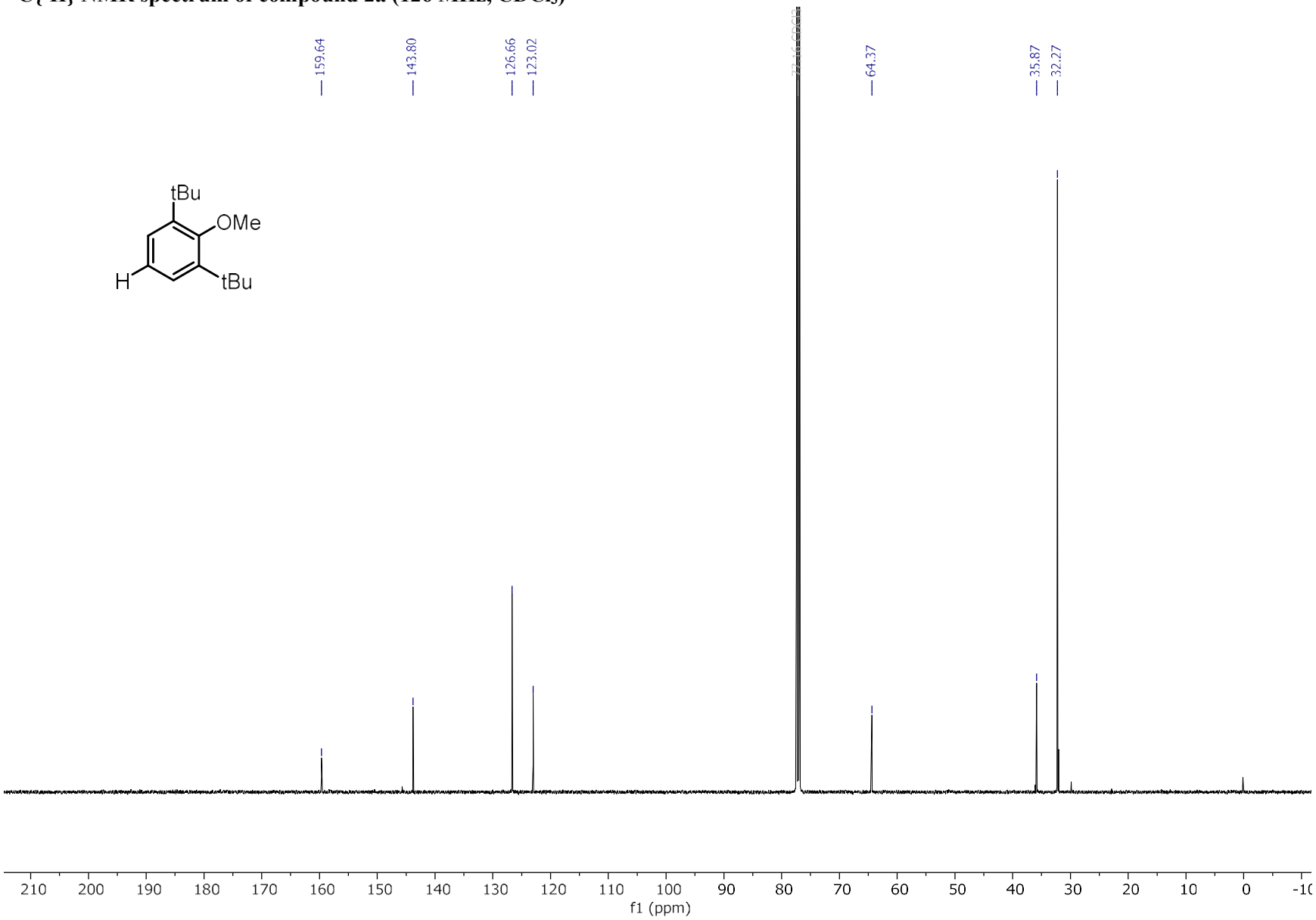
$^{13}C\{^{1}H\}$ NMR spectrum of compound 1c (126 MHz, $CDCl_3$)



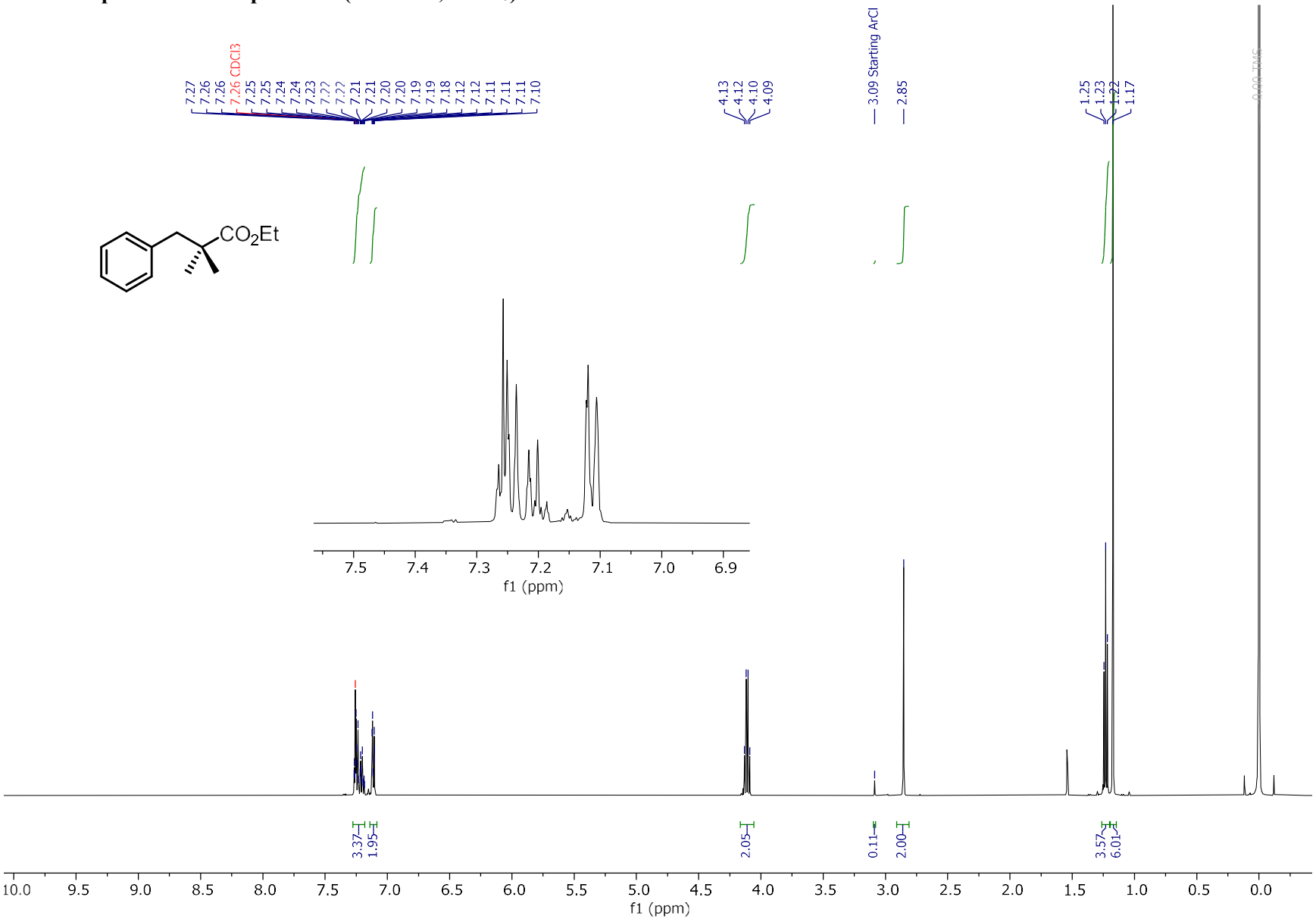
^{1}H NMR spectrum of compound 2a (500 MHz, $CDCl_3$)



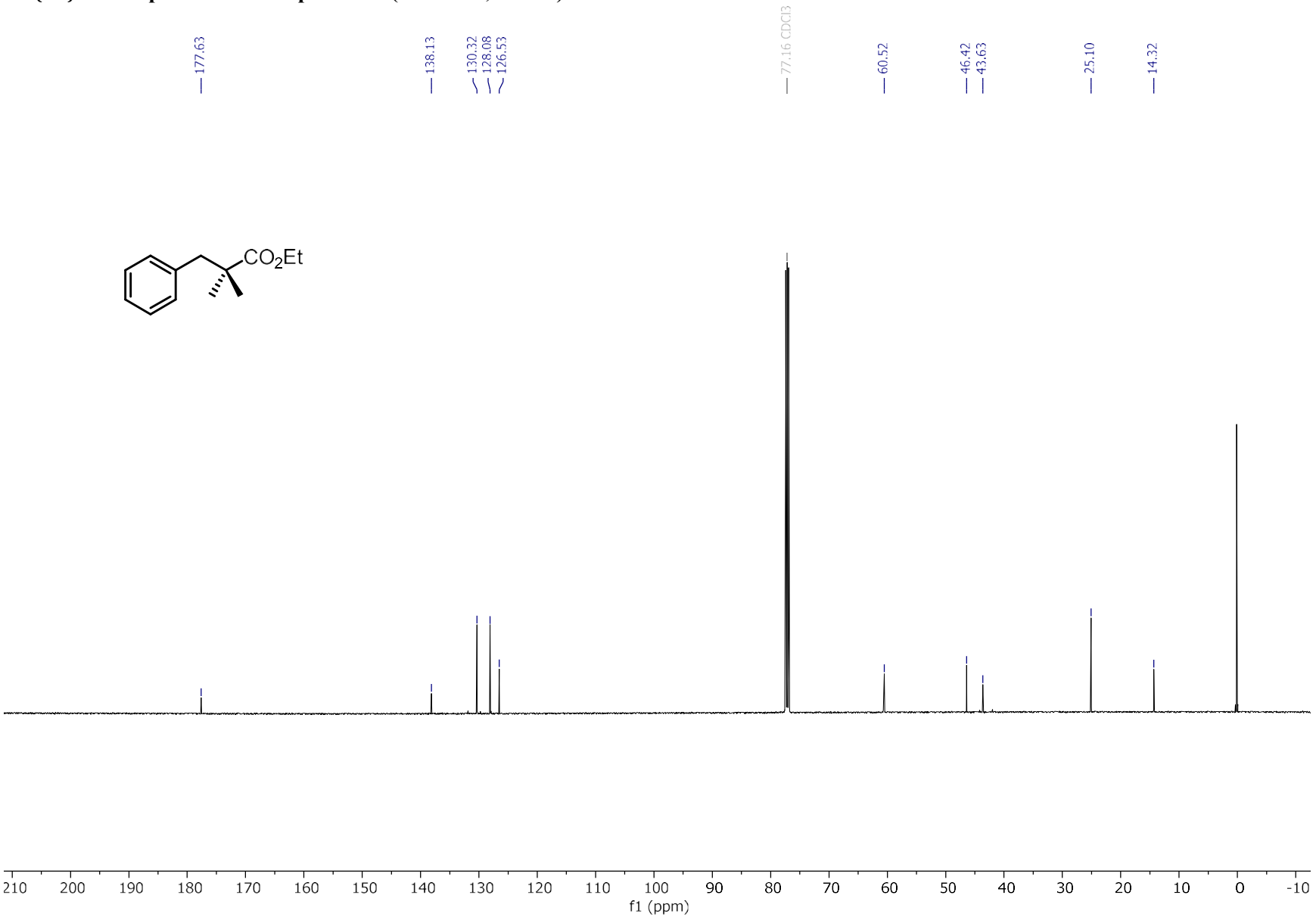
$^{13}C\{^{1}H\}$ NMR spectrum of compound 2a (126 MHz, $CDCl_3$)



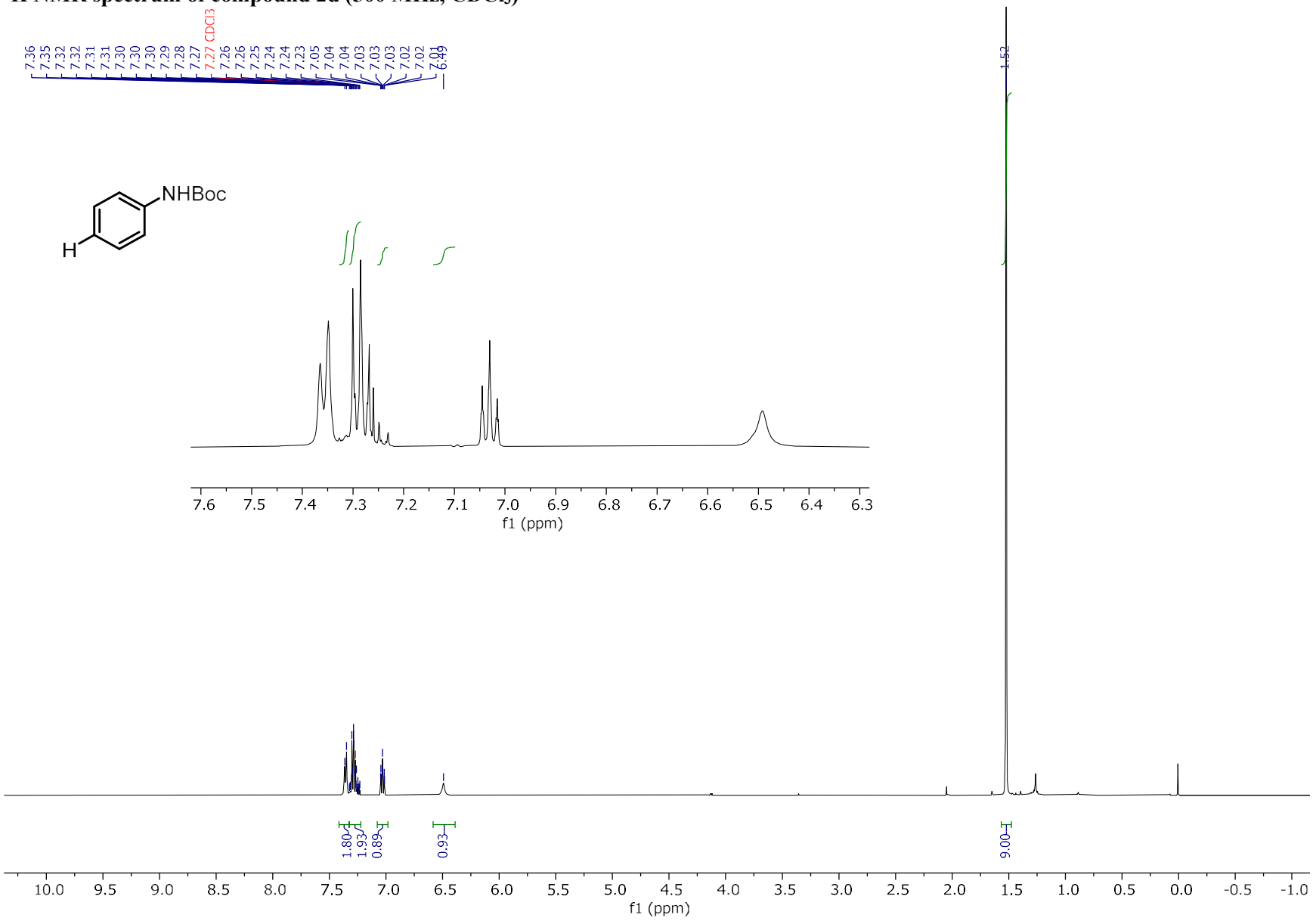
^{1}H NMR spectrum of compound 2c (500 MHz, $CDCl_3$)



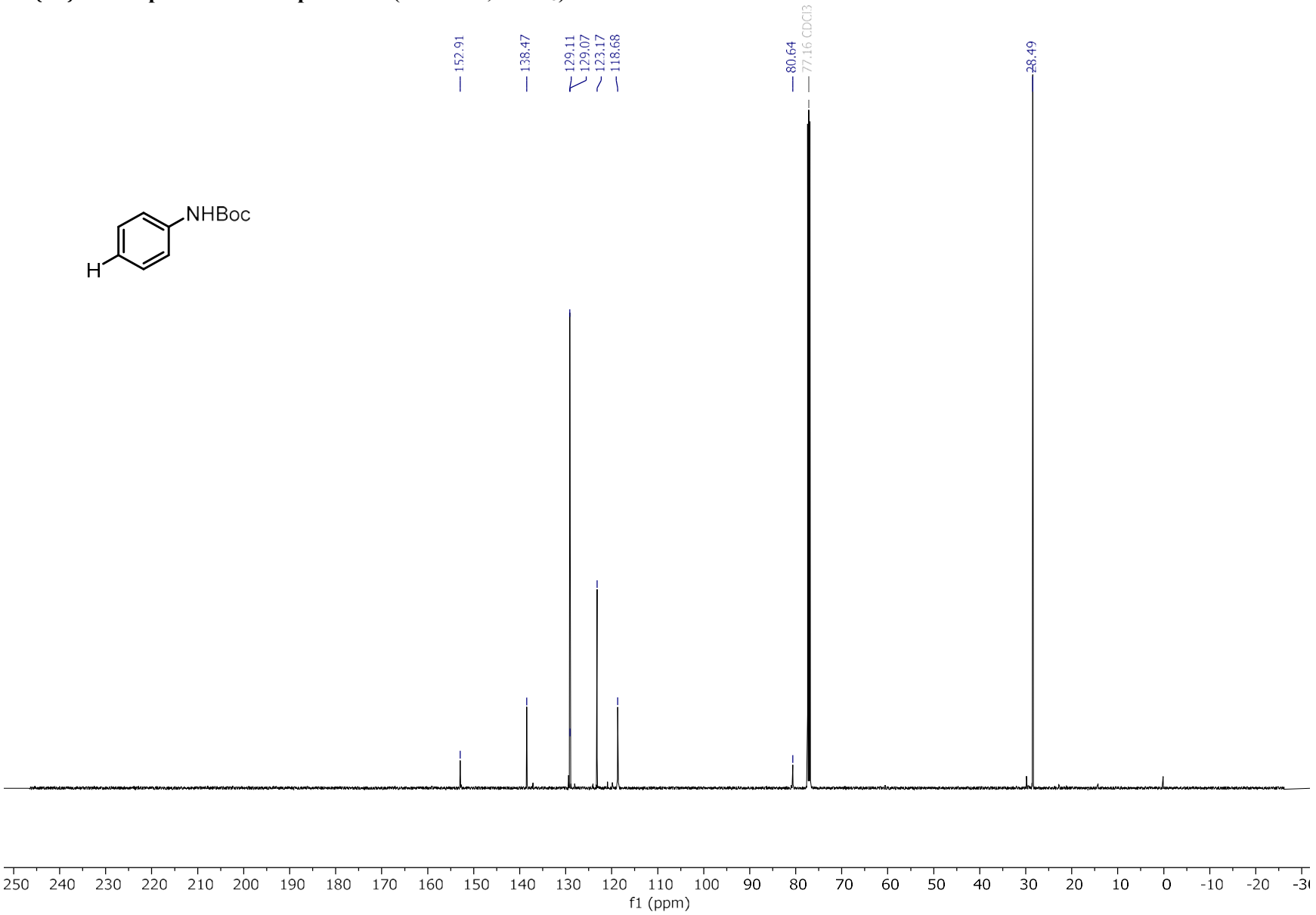
$^{13}C\{^{1}H\}$ NMR spectrum of compound 2c (126 MHz, $CDCl_3$)



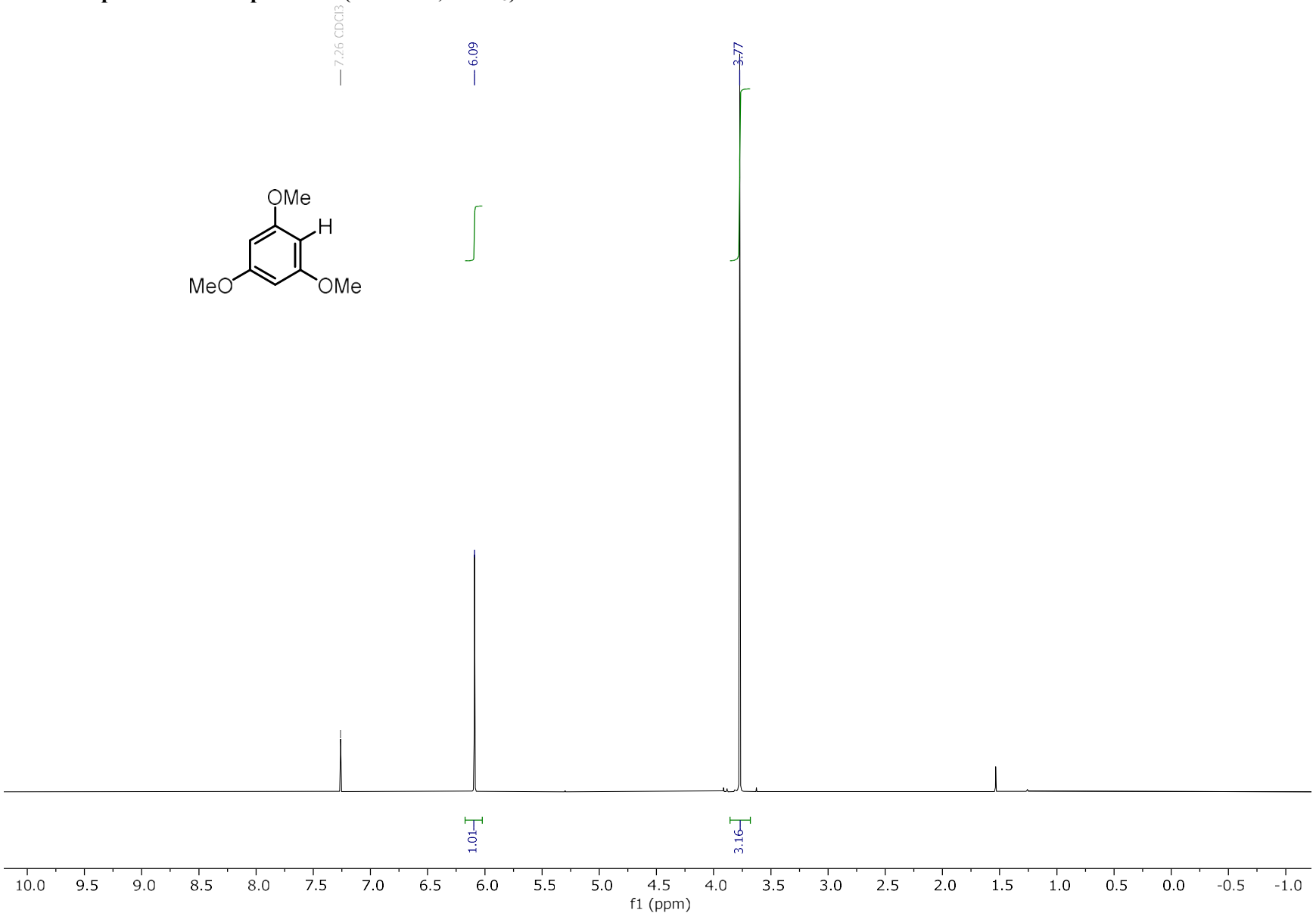
^{1}H NMR spectrum of compound 2d (500 MHz, $CDCl_3$)



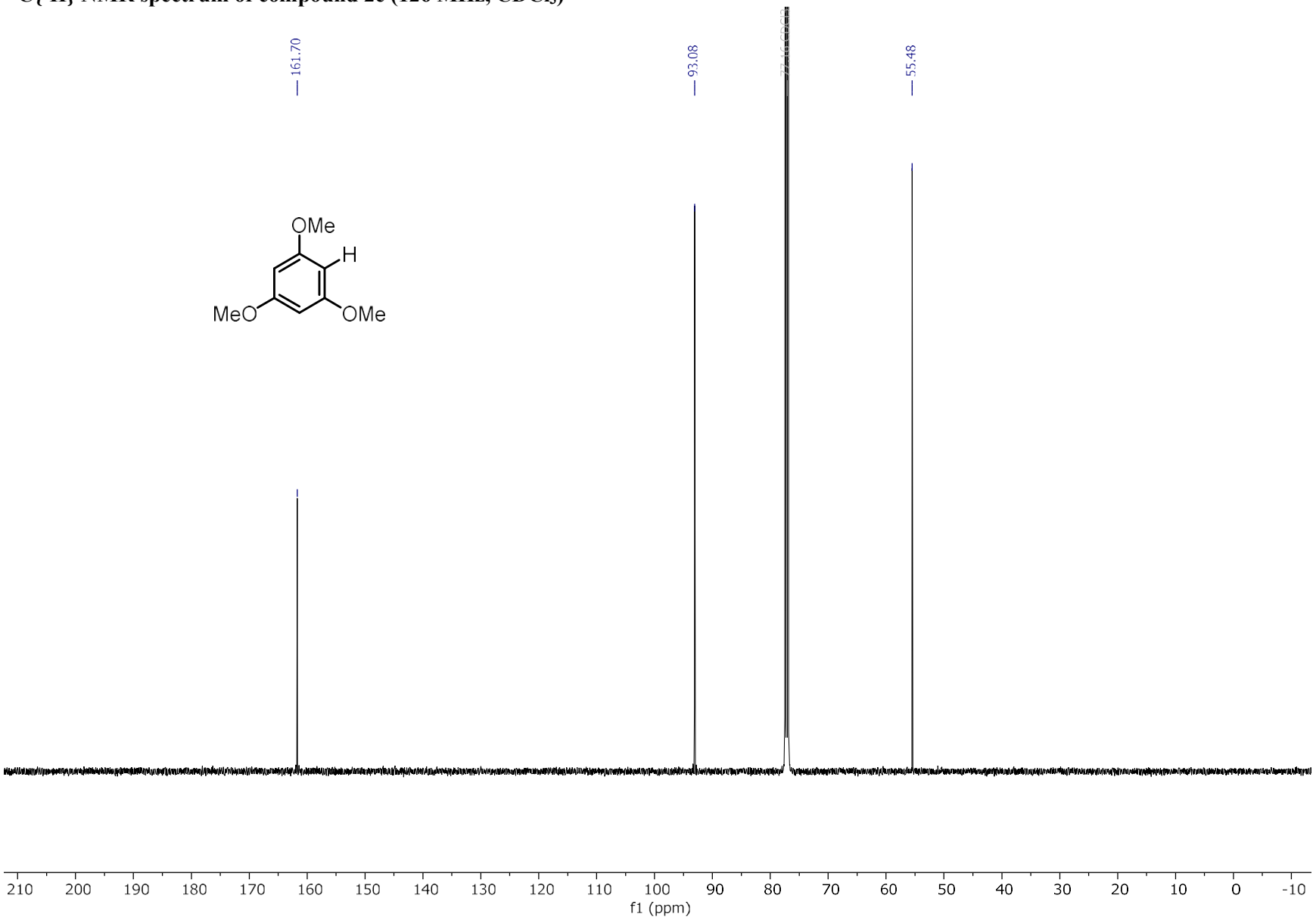
$^{13}C\{^{1}H\}$ NMR spectrum of compound 2d (126 MHz, $CDCl_3$)



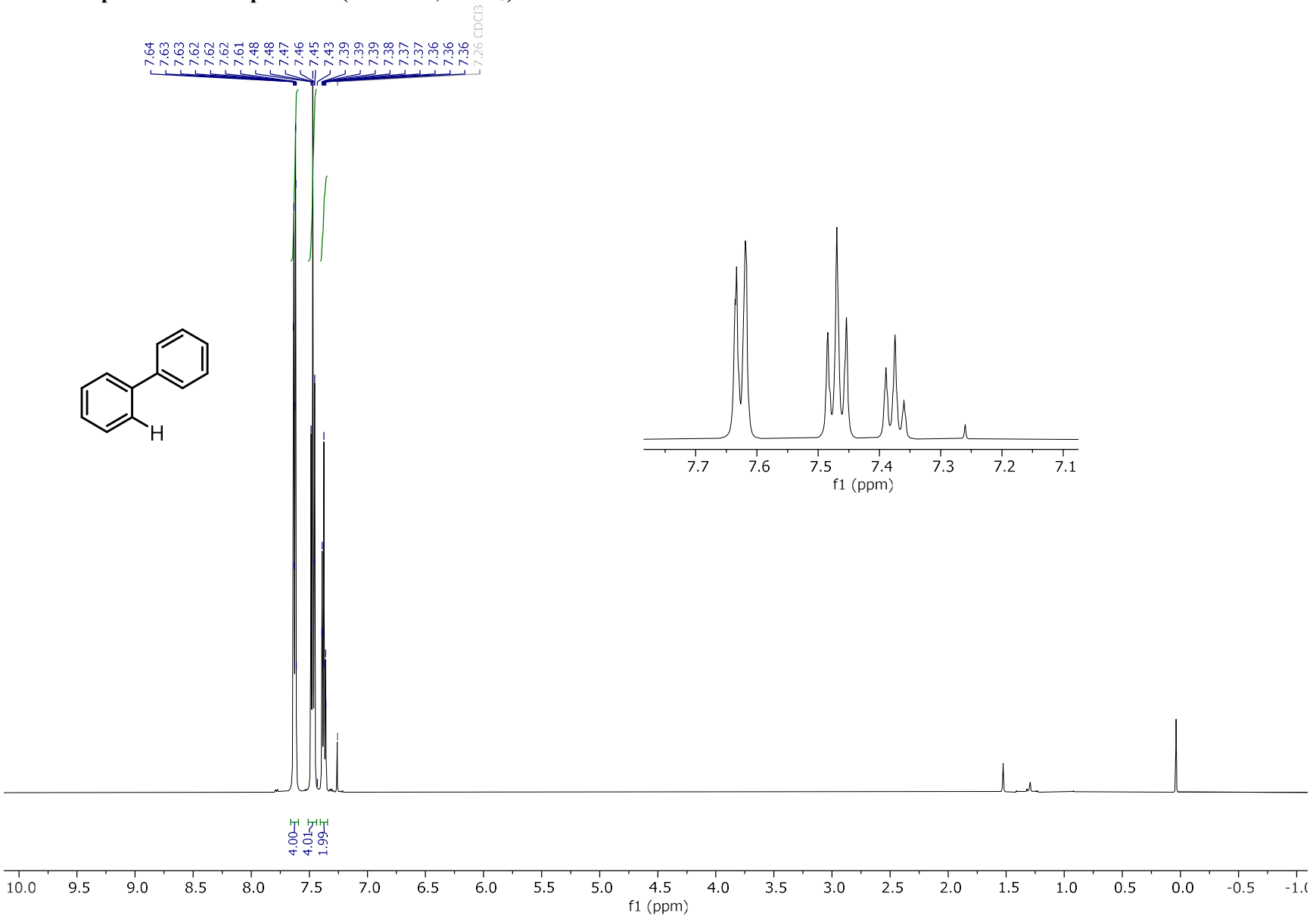
^{1}H NMR spectrum of compound 2e (500 MHz, $CDCl_3$)



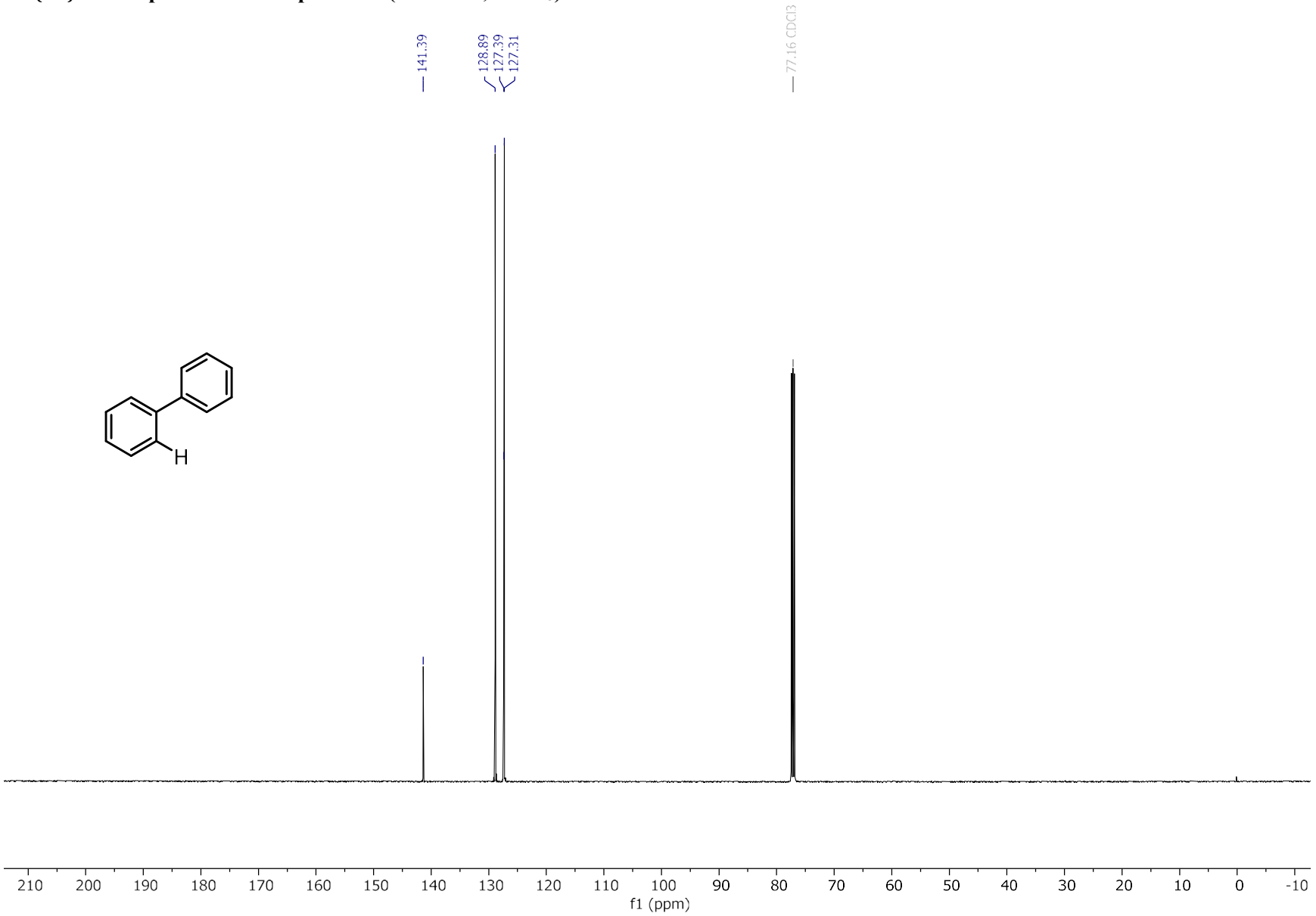
$^{13}C\{^{1}H\}$ NMR spectrum of compound 2e (126 MHz, $CDCl_3$)



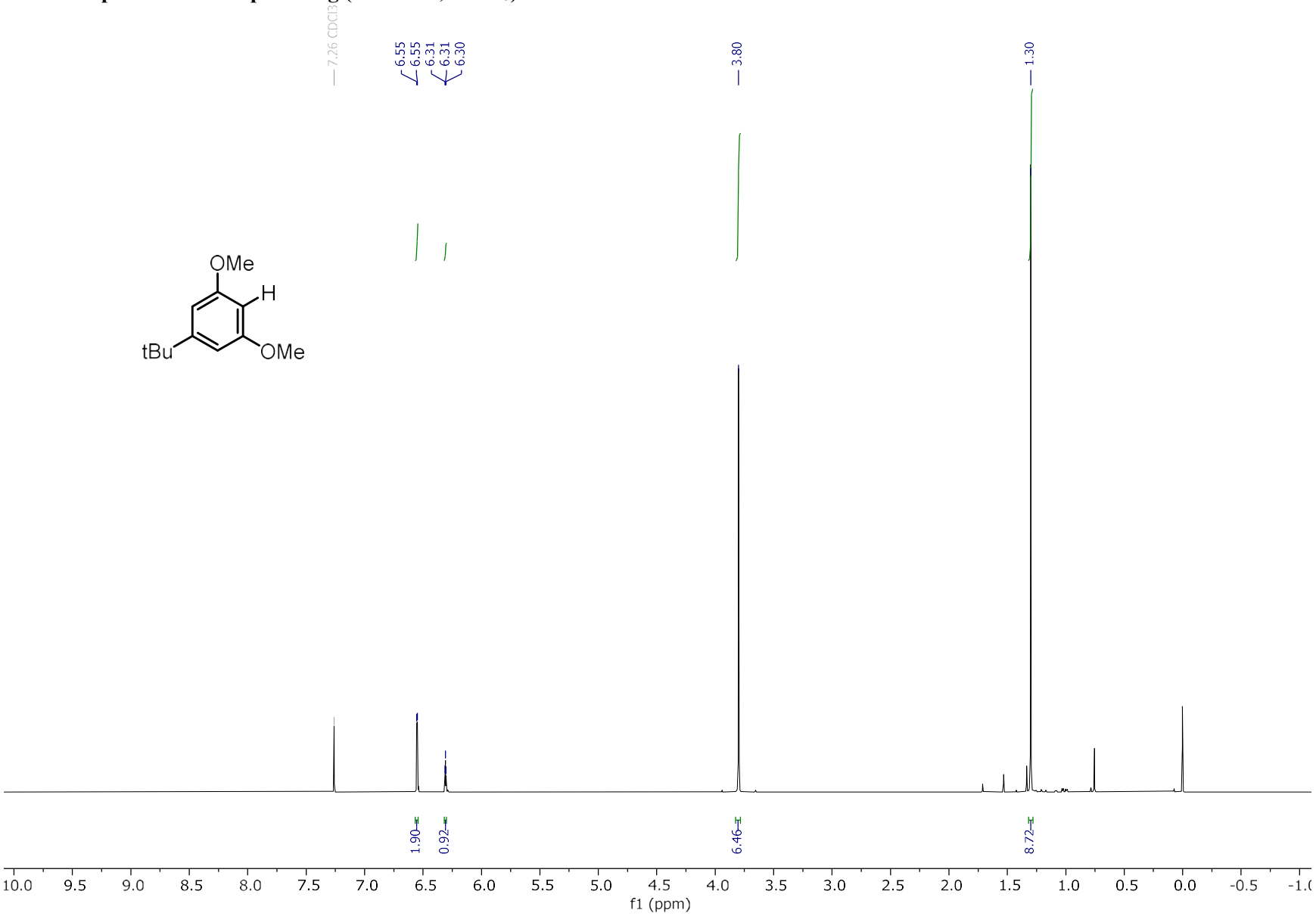
^{1}H NMR spectrum of compound 2f (500 MHz, $CDCl_3$)



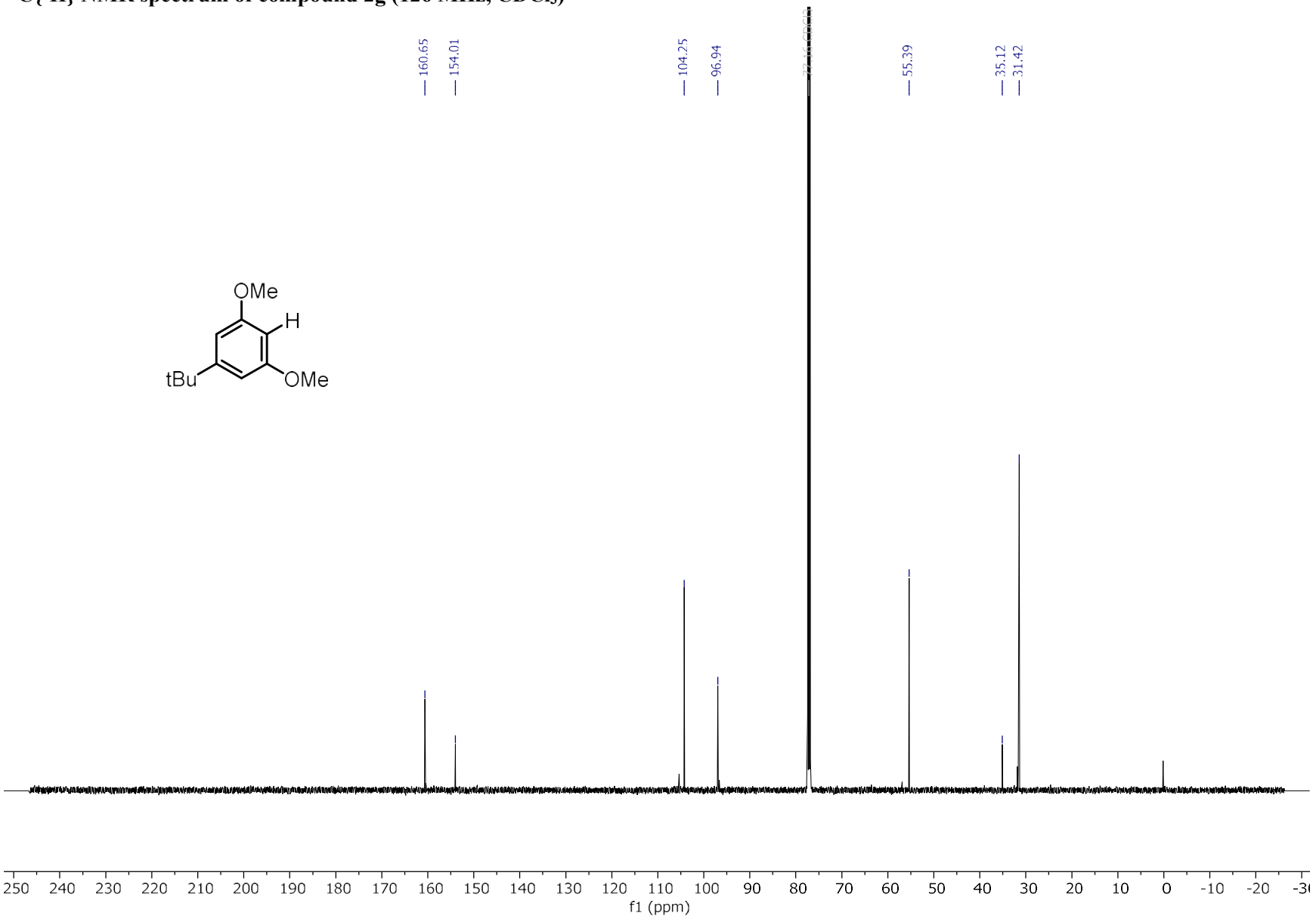
$^{13}C\{^{1}H\}$ NMR spectrum of compound 2f (126 MHz, $CDCl_3$)



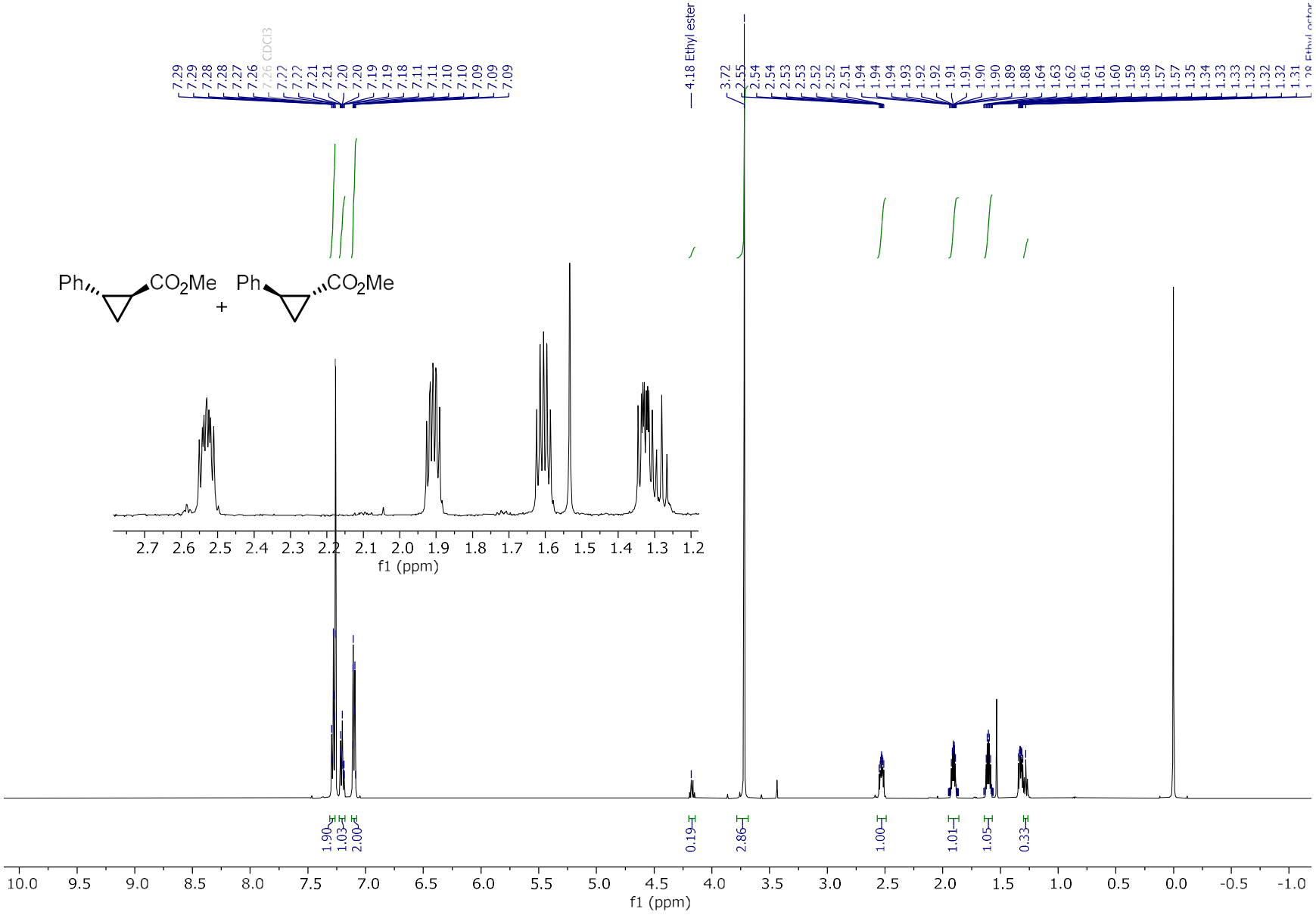
^{1}H NMR spectrum of compound 2g (500 MHz, $CDCl_3$)



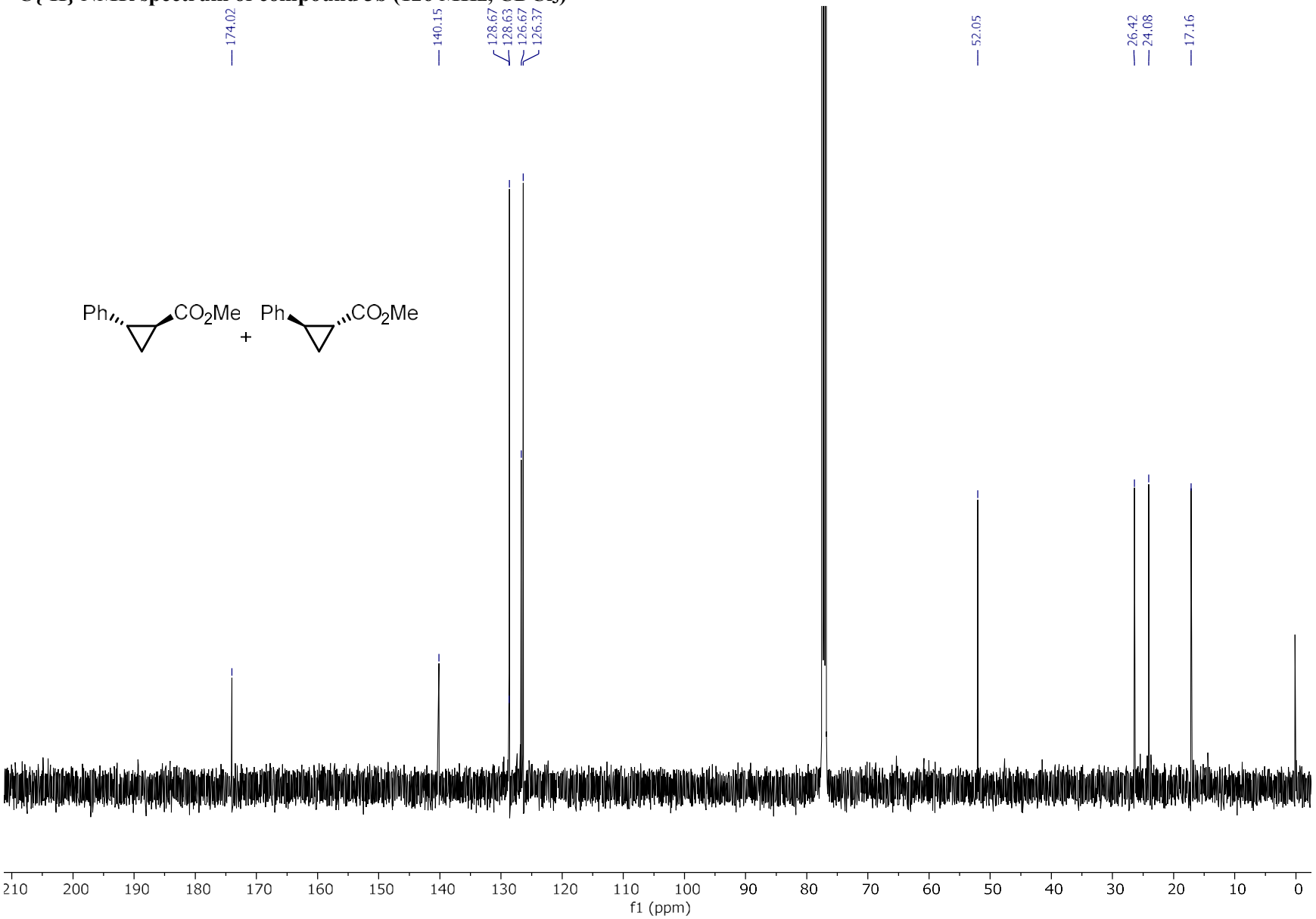
$^{13}C\{^{1}H\}$ NMR spectrum of compound 2g (126 MHz, $CDCl_3$)



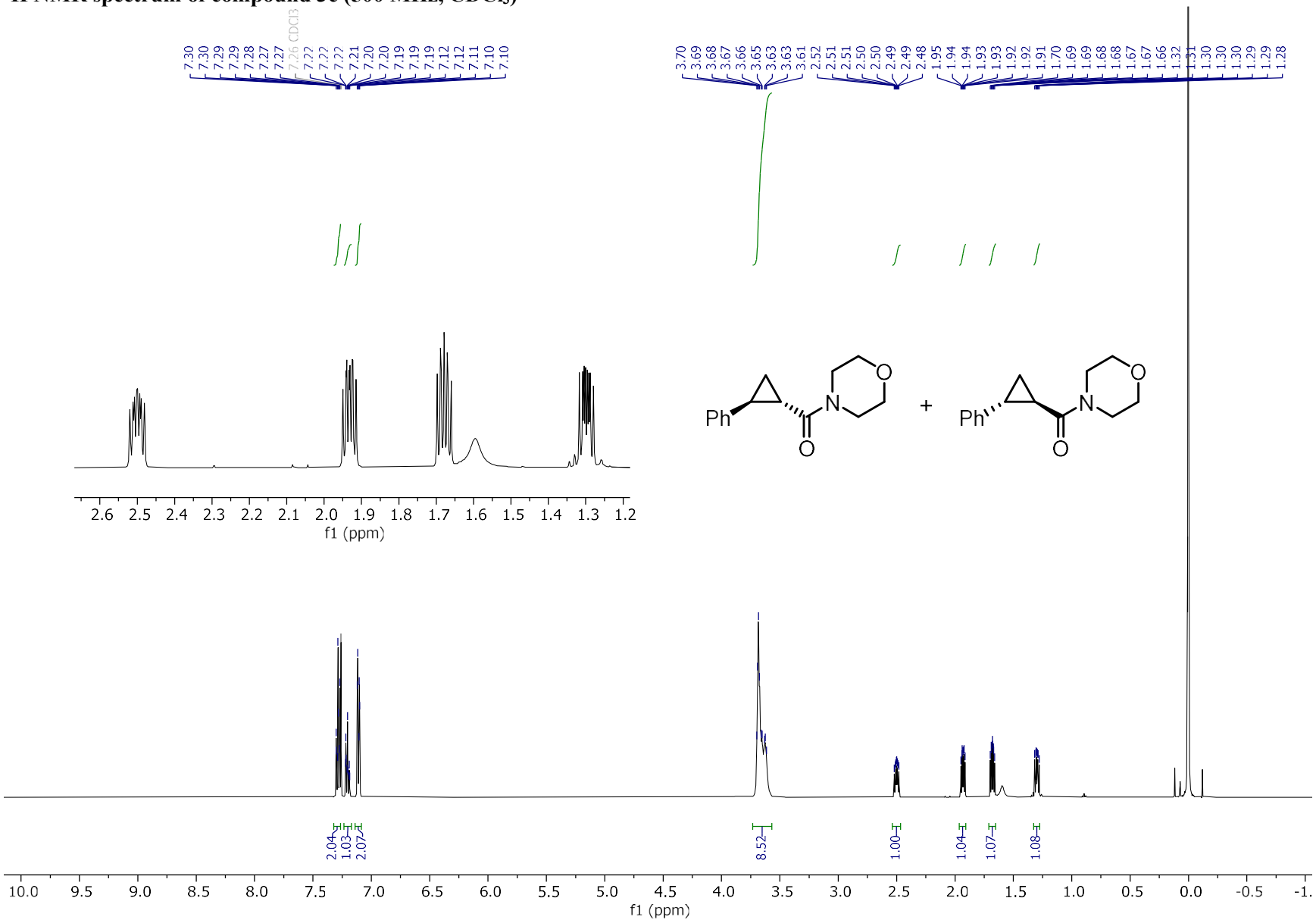
^{1}H NMR spectrum of compound 3b (500 MHz, $CDCl_3$)



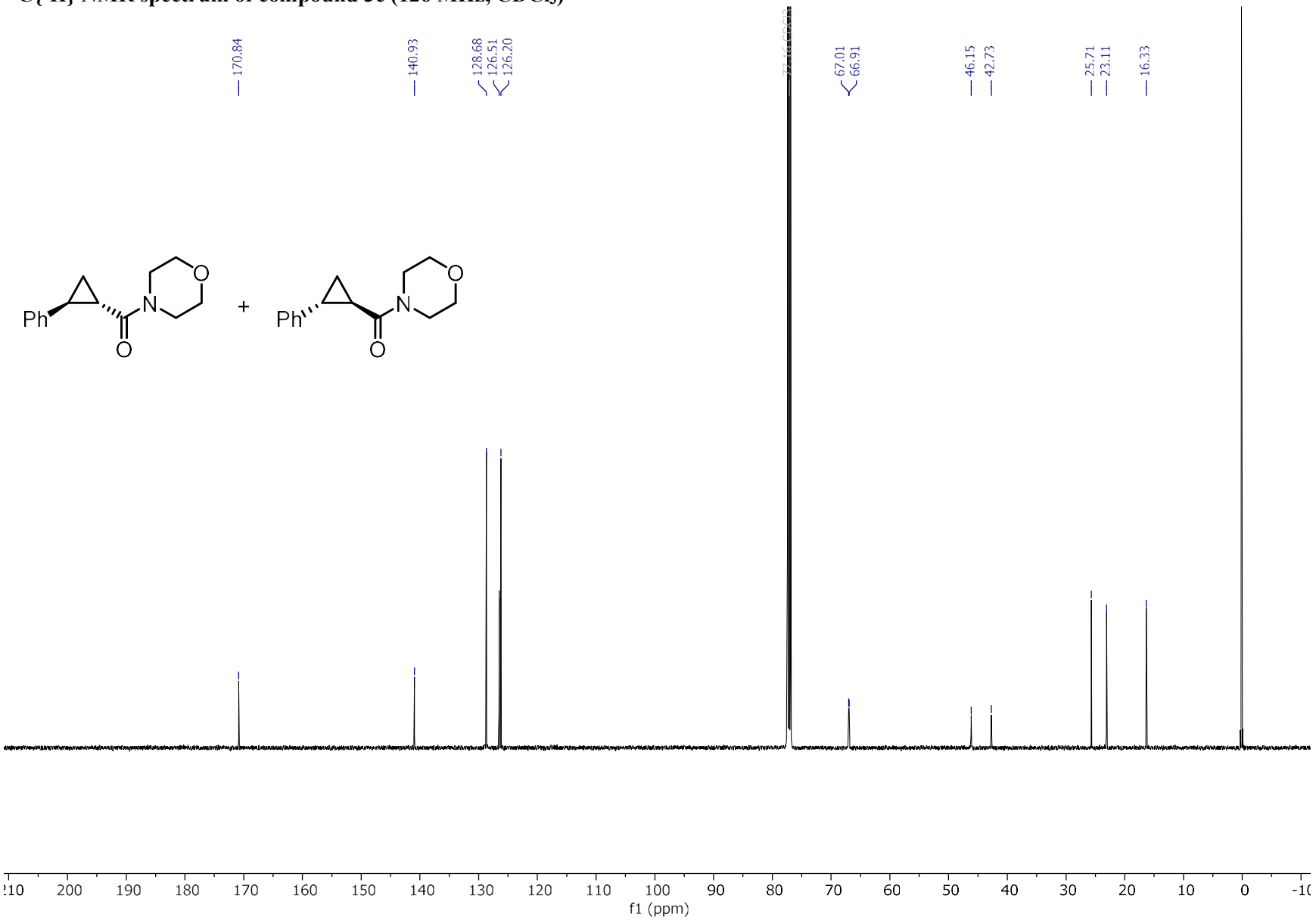
$^{13}C\{^{1}H\}$ NMR spectrum of compound 3b (126 MHz, $CDCl_3$)



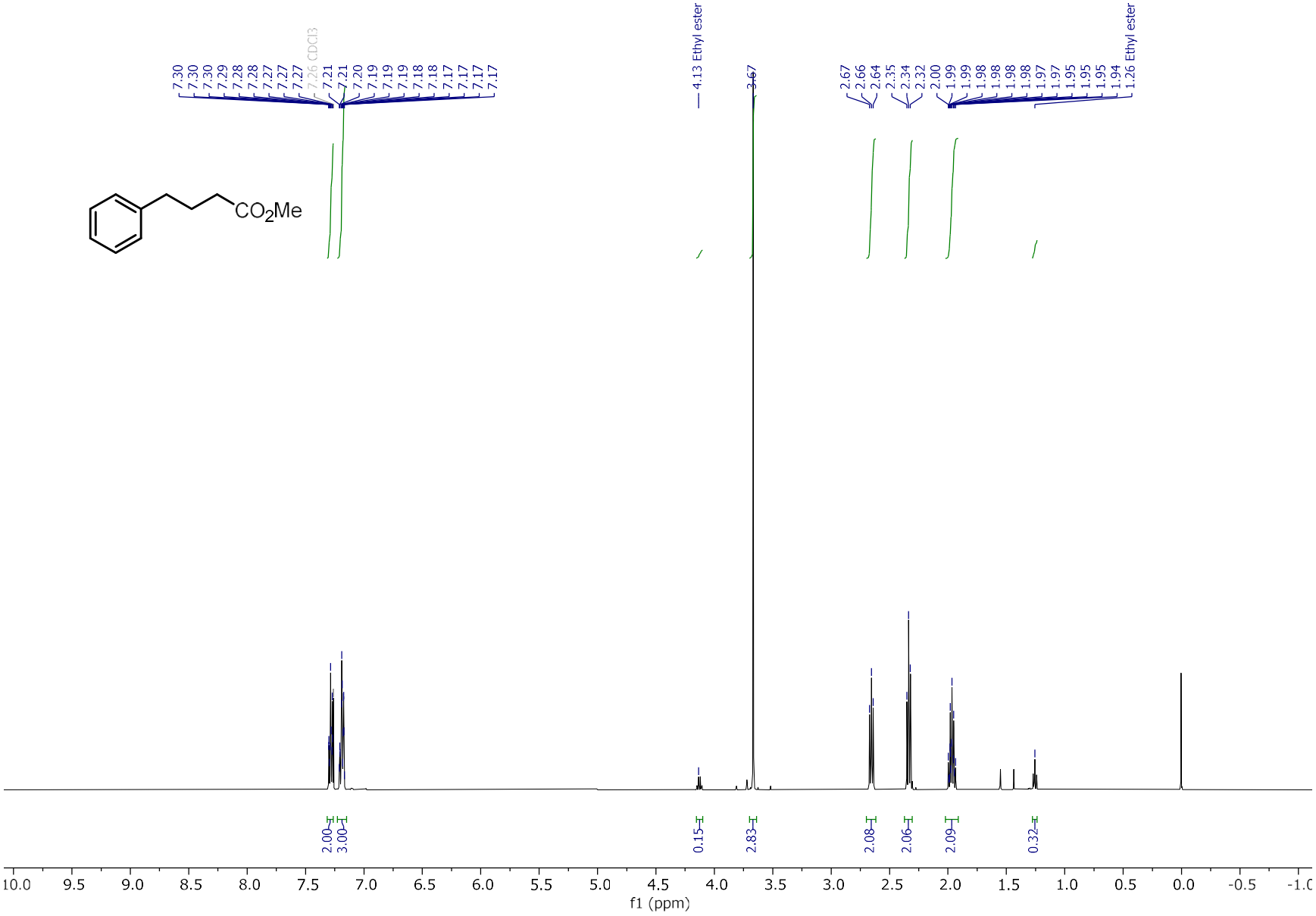
^{1}H NMR spectrum of compound 3c (500 MHz, $CDCl_3$)



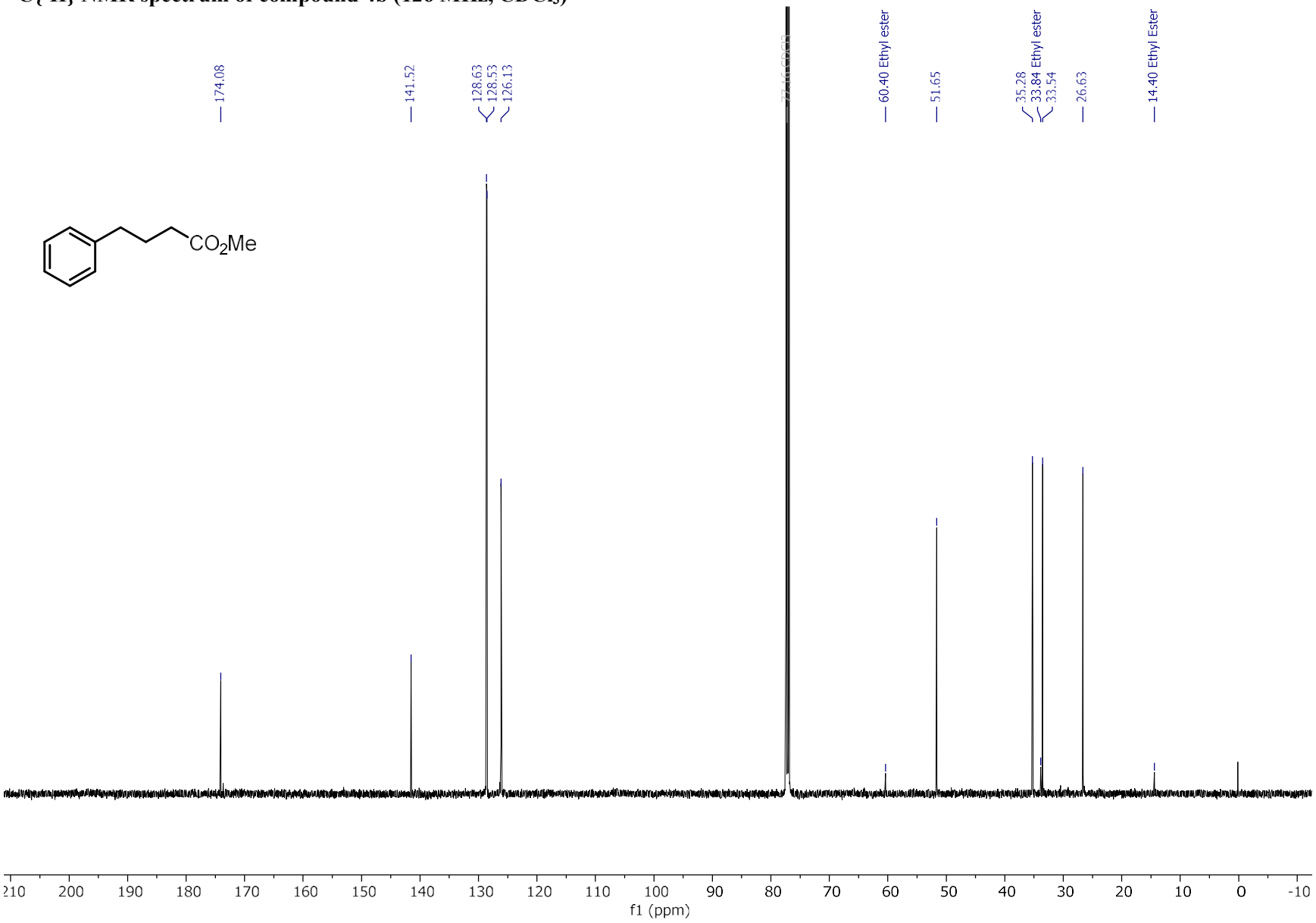
$^{13}C\{^{1}H\}$ NMR spectrum of compound 3c (126 MHz, $CDCl_3$)



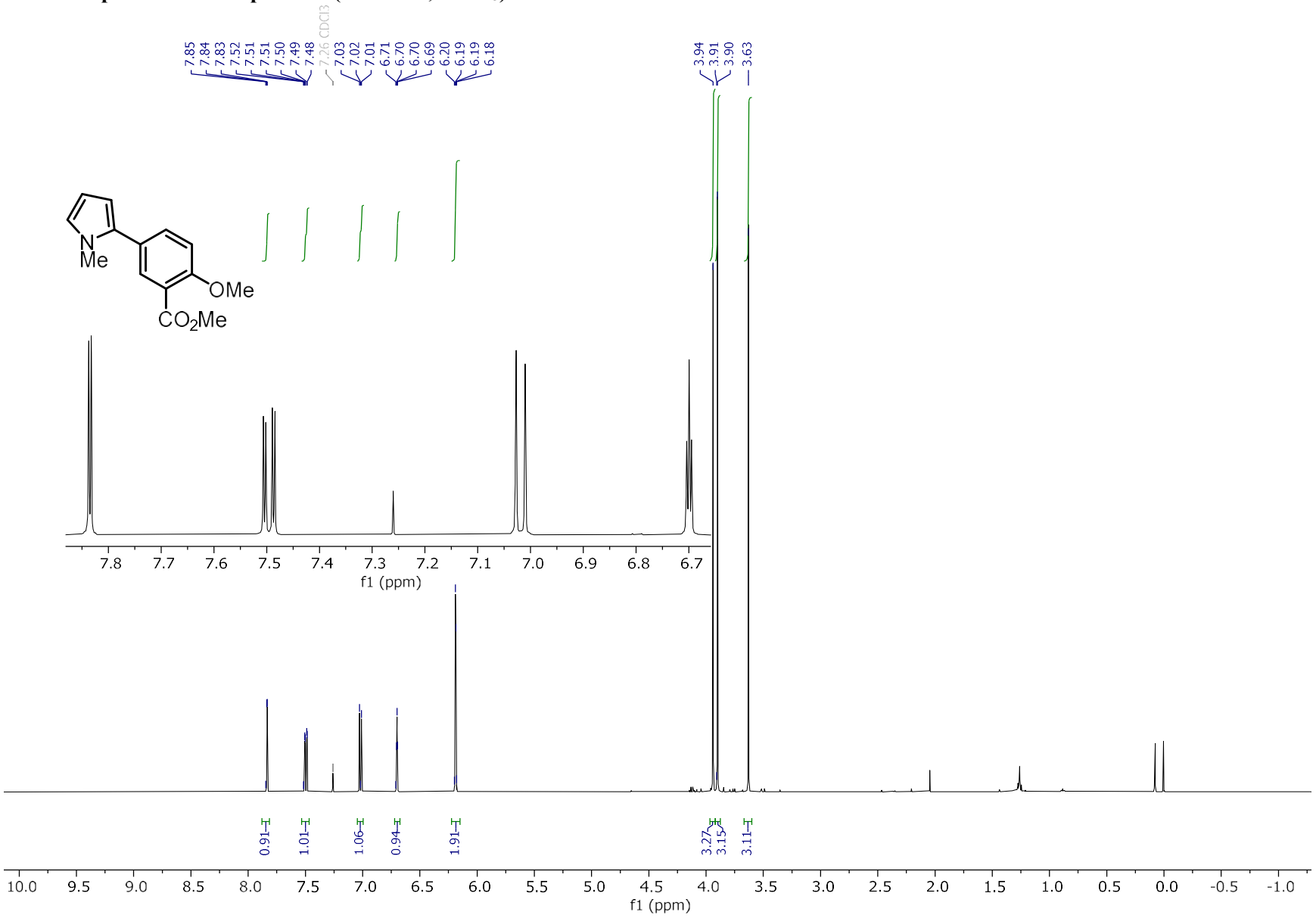
^{1}H NMR spectrum of compound 4b (500 MHz, $CDCl_3$)



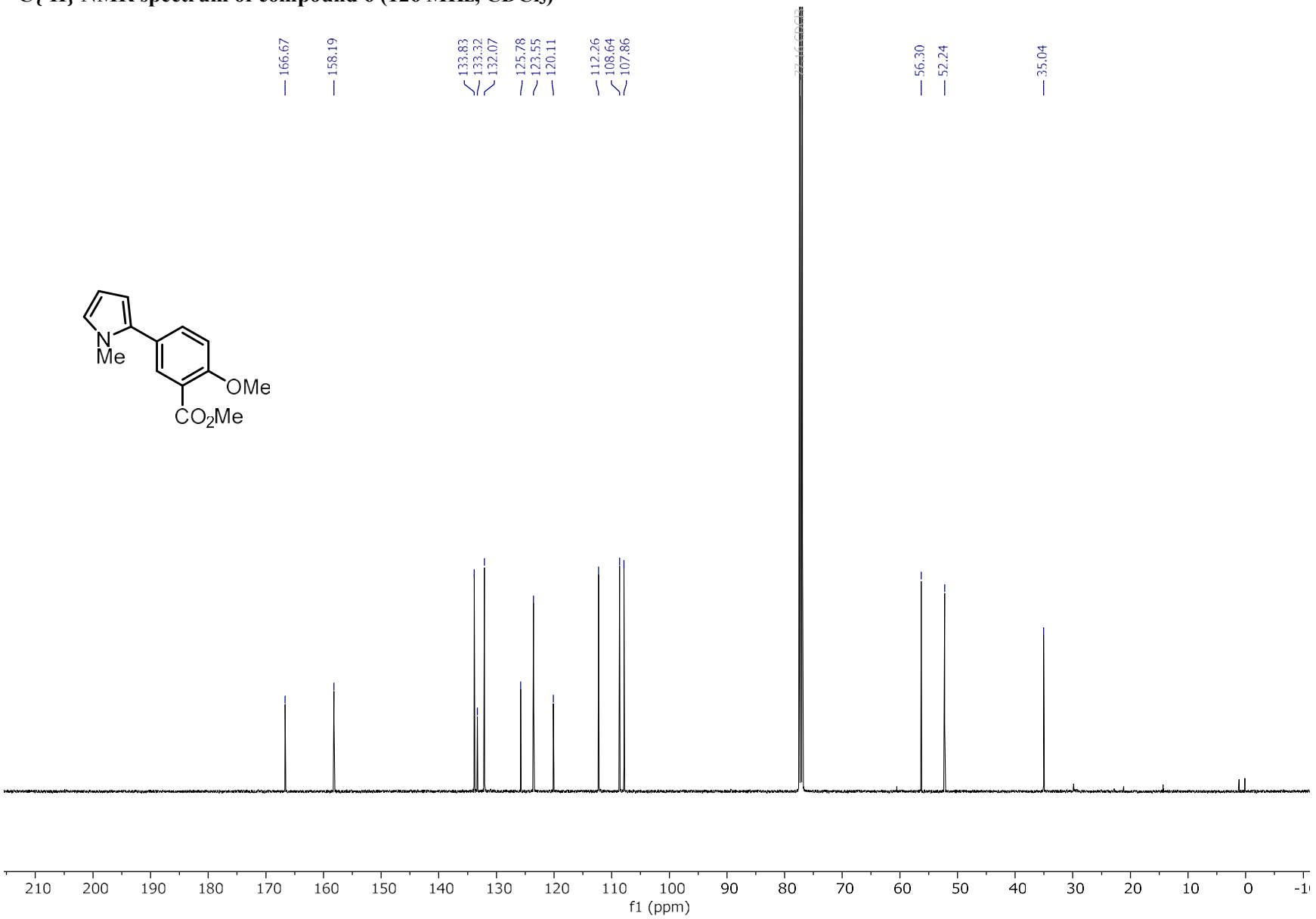
$^{13}C\{^{1}H\}$ NMR spectrum of compound 4b (126 MHz, $CDCl_3$)



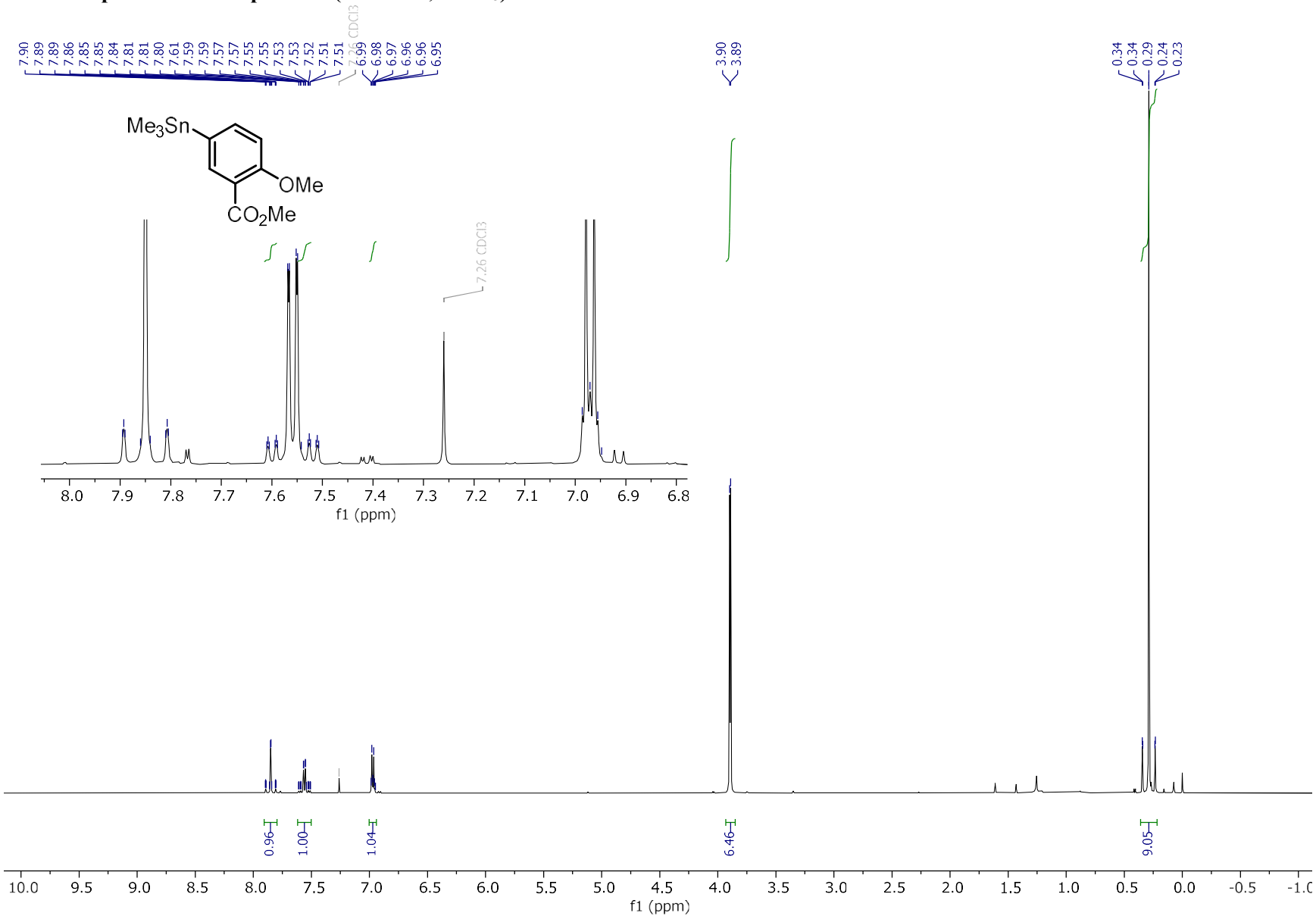
^{1}H NMR spectrum of compound 6 (500 MHz, $CDCl_3$)



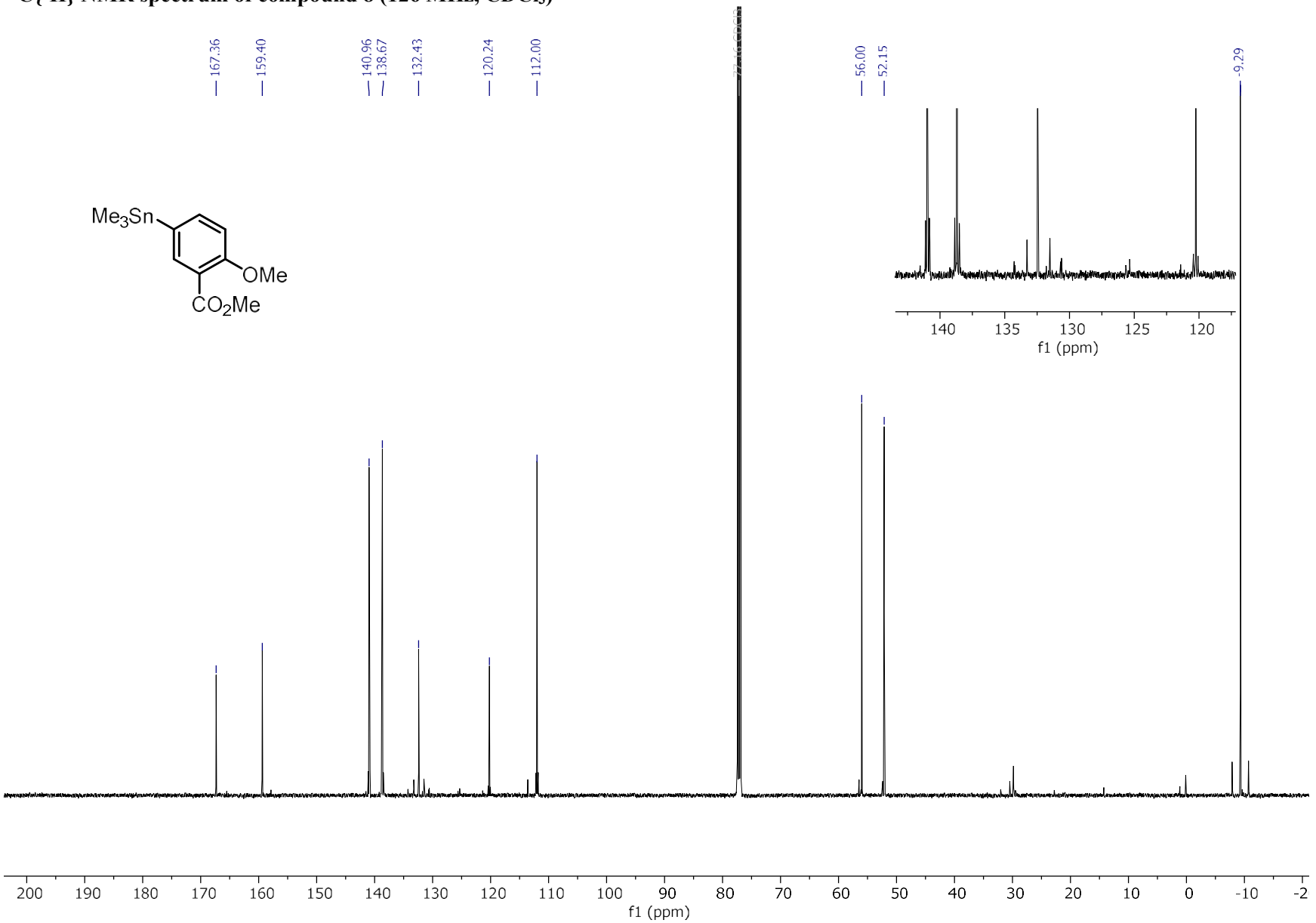
$^{13}C\{^{1}H\}$ NMR spectrum of compound 6 (126 MHz, $CDCl_3$)



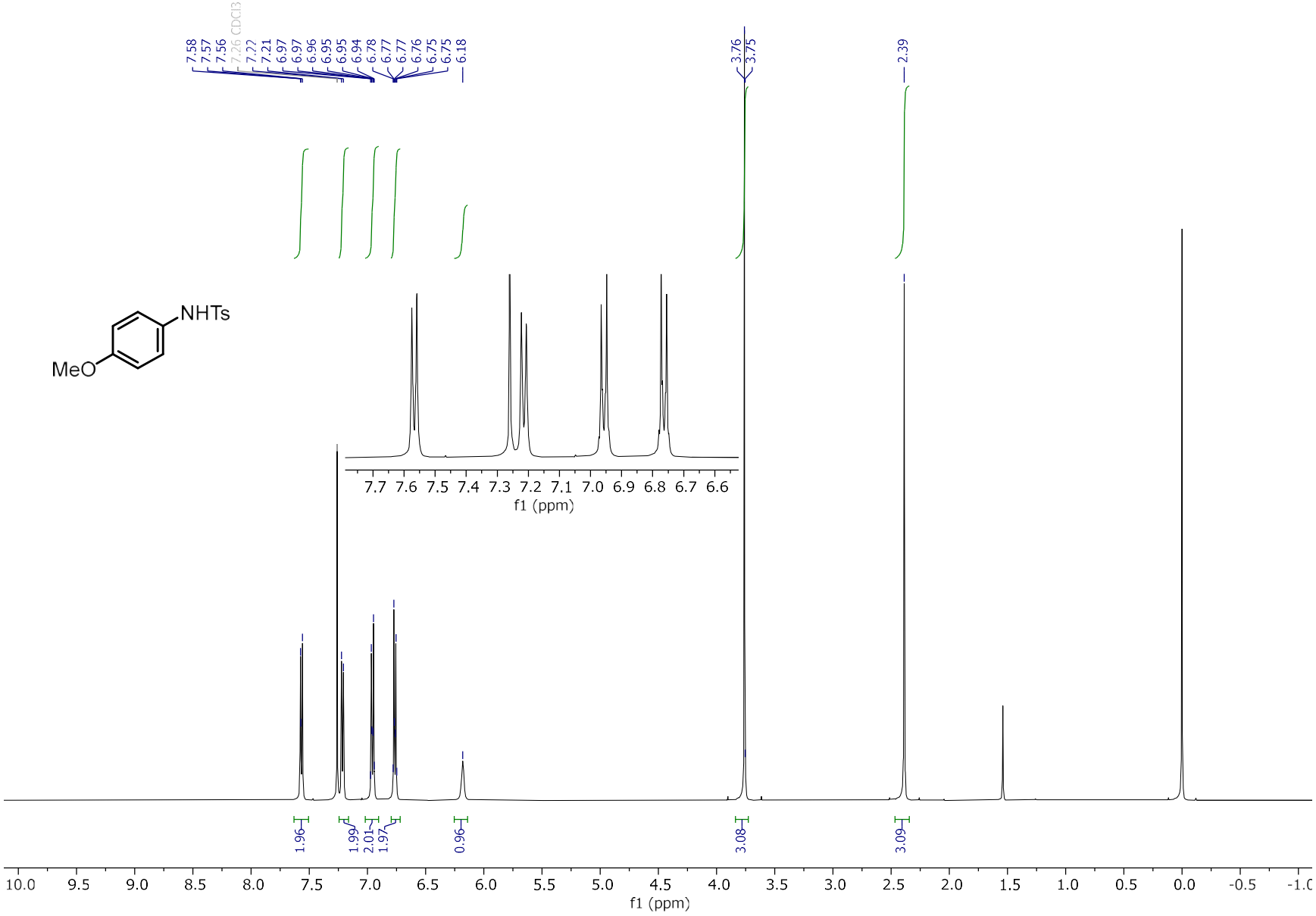
^{1}H NMR spectrum of compound 8 (500 MHz, $CDCl_3$)



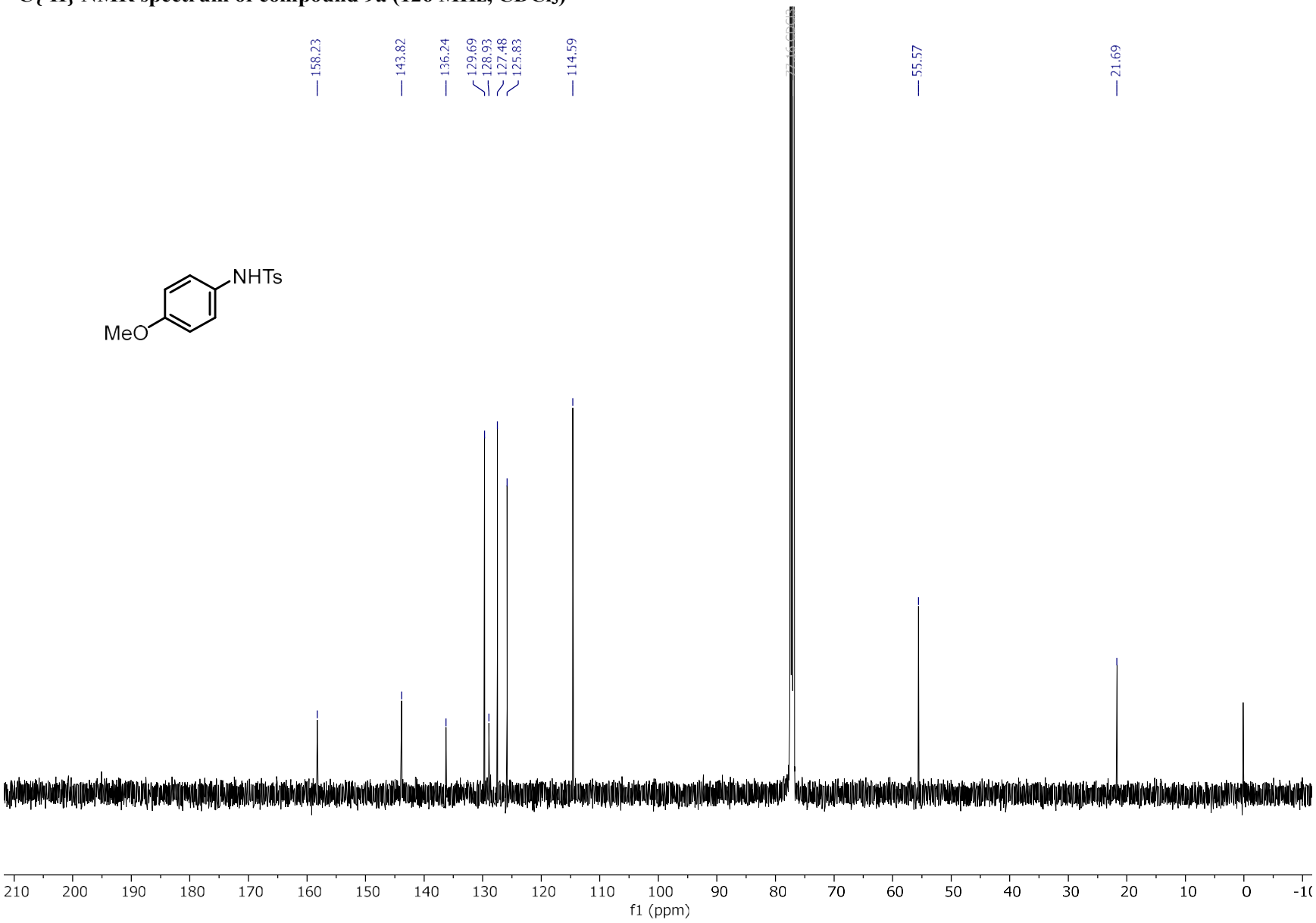
$^{13}C\{^{1}H\}$ NMR spectrum of compound 8 (126 MHz, $CDCl_3$)



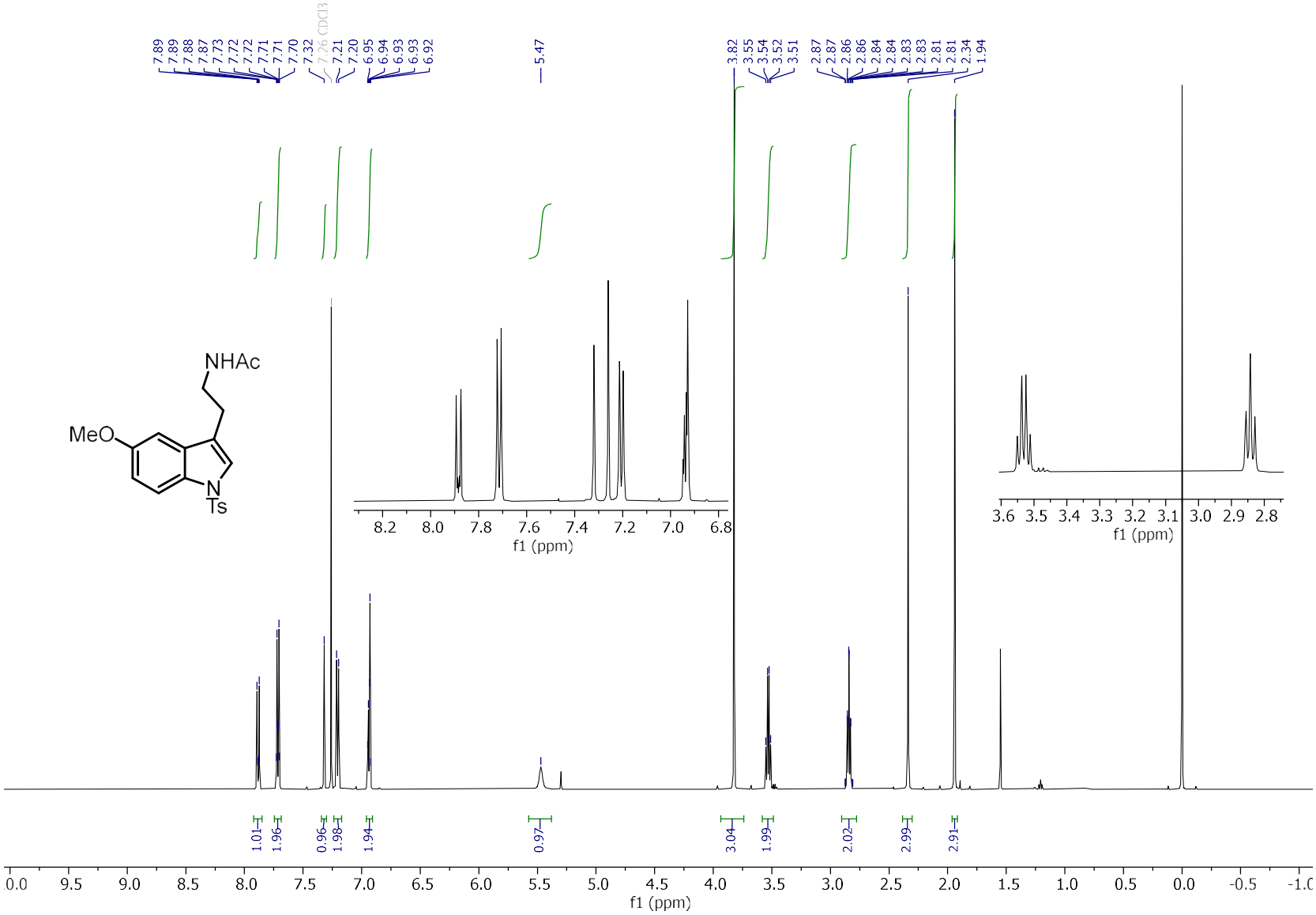
^{1}H NMR spectrum of compound 9a (500 MHz, $CDCl_3$)



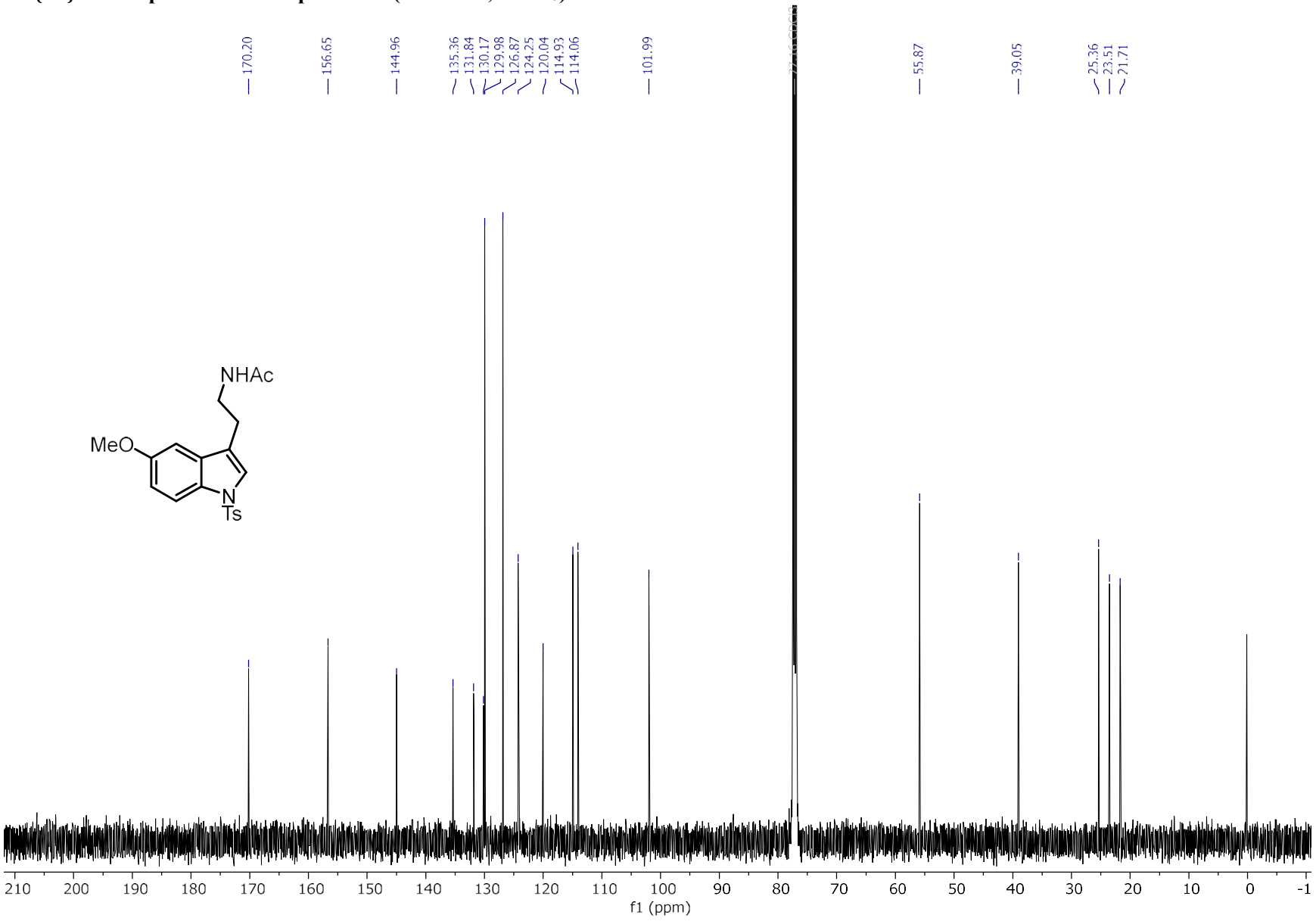
$^{13}C\{^{1}H\}$ NMR spectrum of compound 9a (126 MHz, $CDCl_3$)



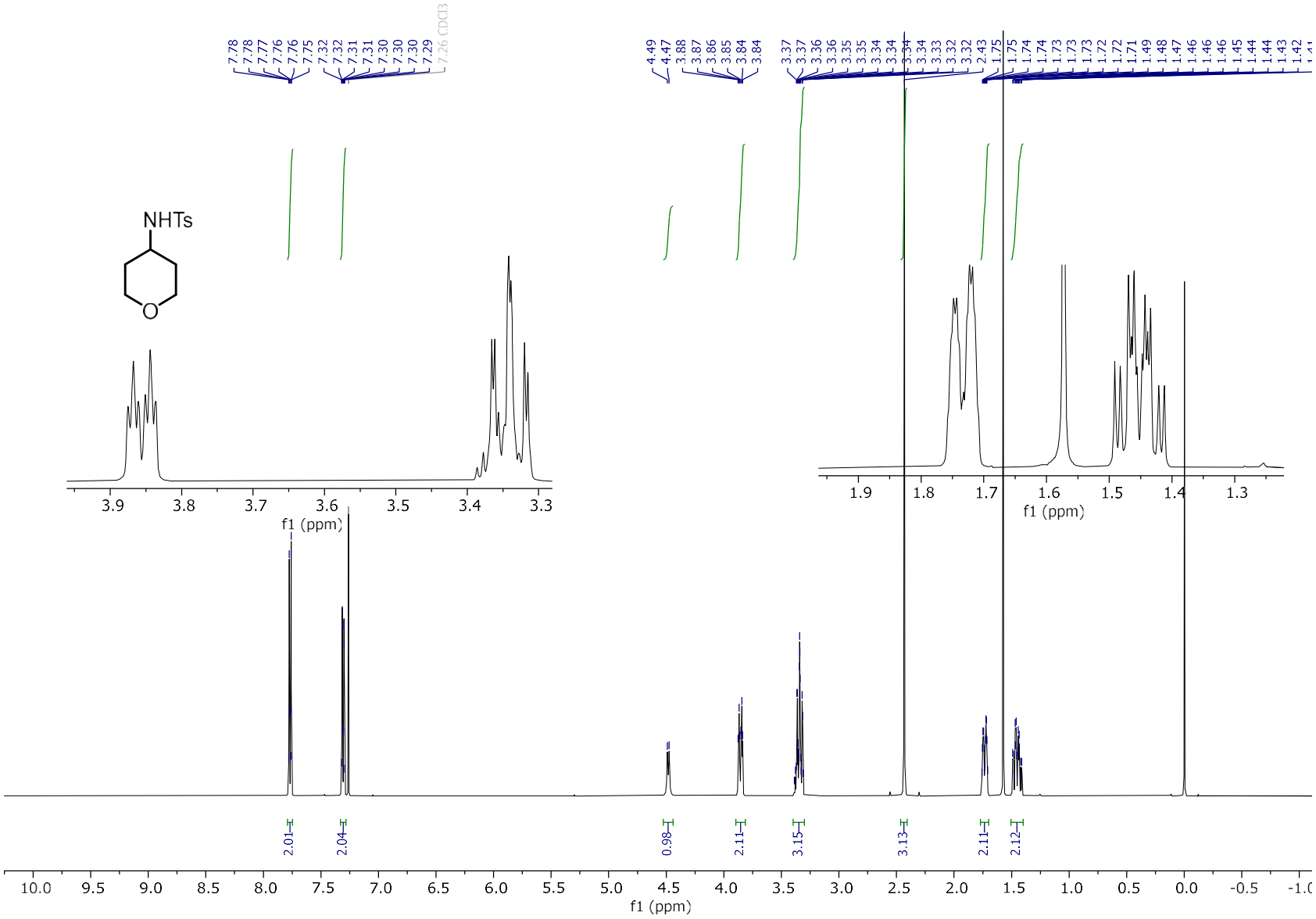
^{1}H NMR spectrum of compound 9b (500 MHz, $CDCl_3$)



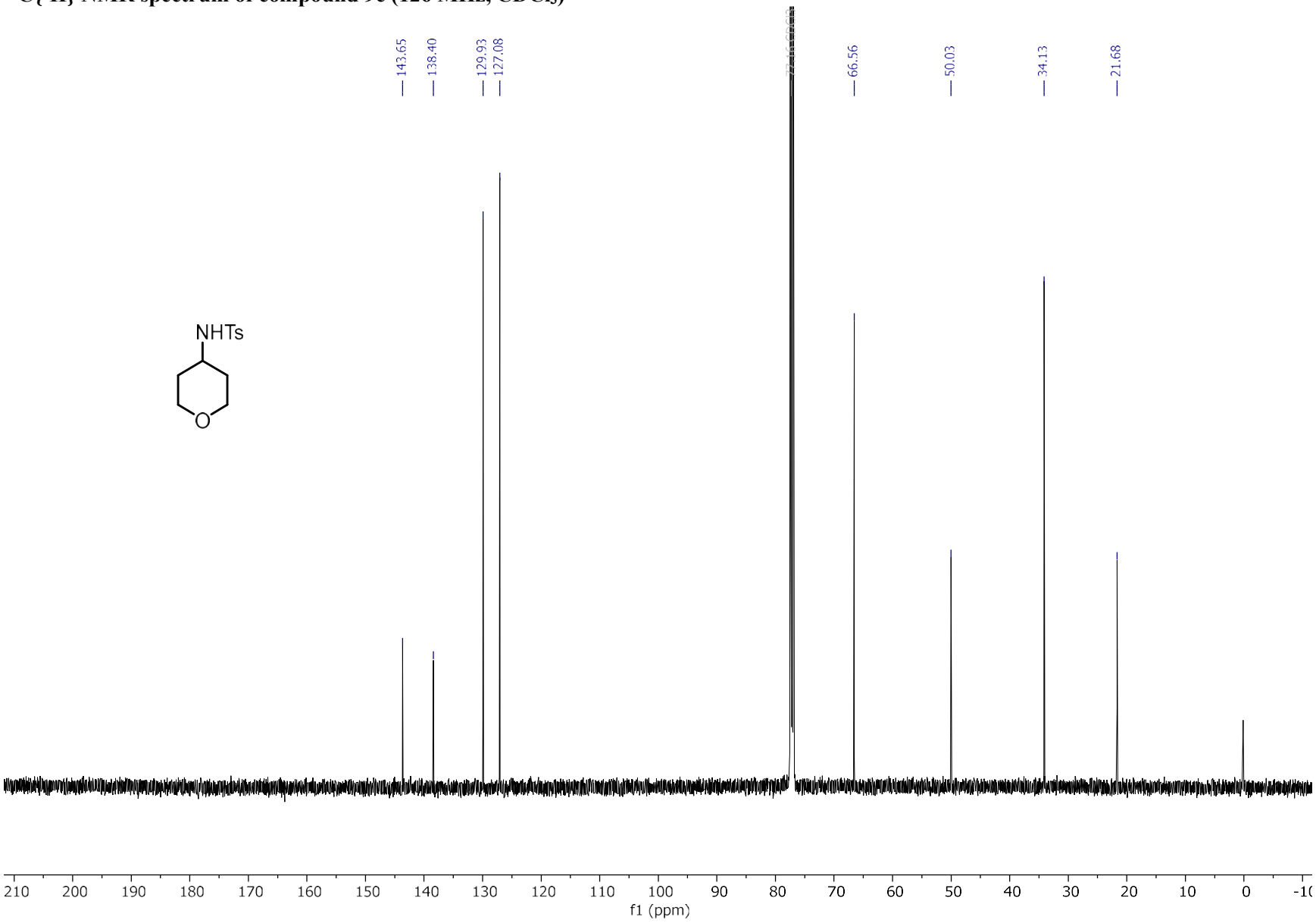
$^{13}C\{^{1}H\}$ NMR spectrum of compound 9b (126 MHz, $CDCl_3$)



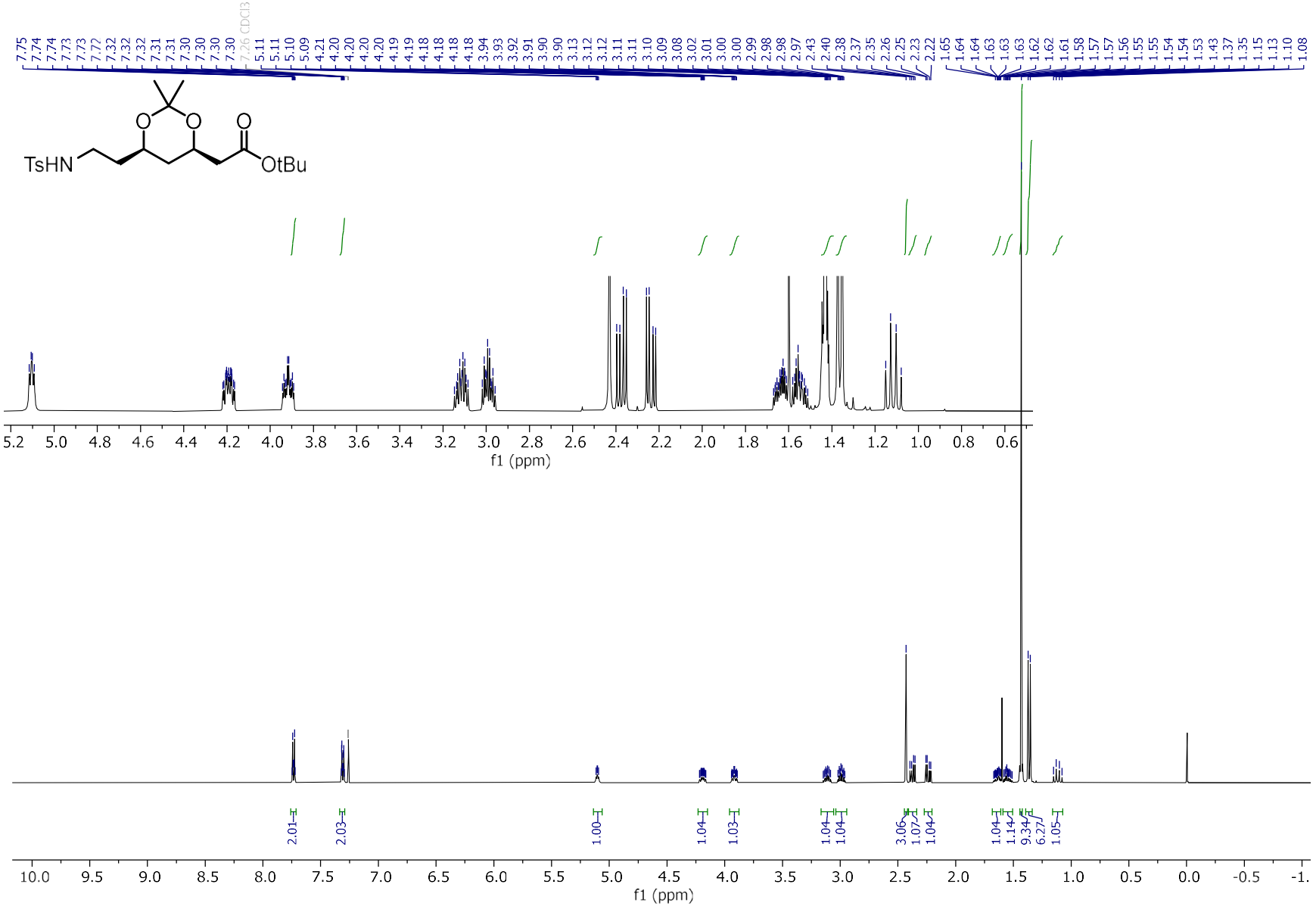
^{1}H NMR spectrum of compound 9c (500 MHz, $CDCl_3$)



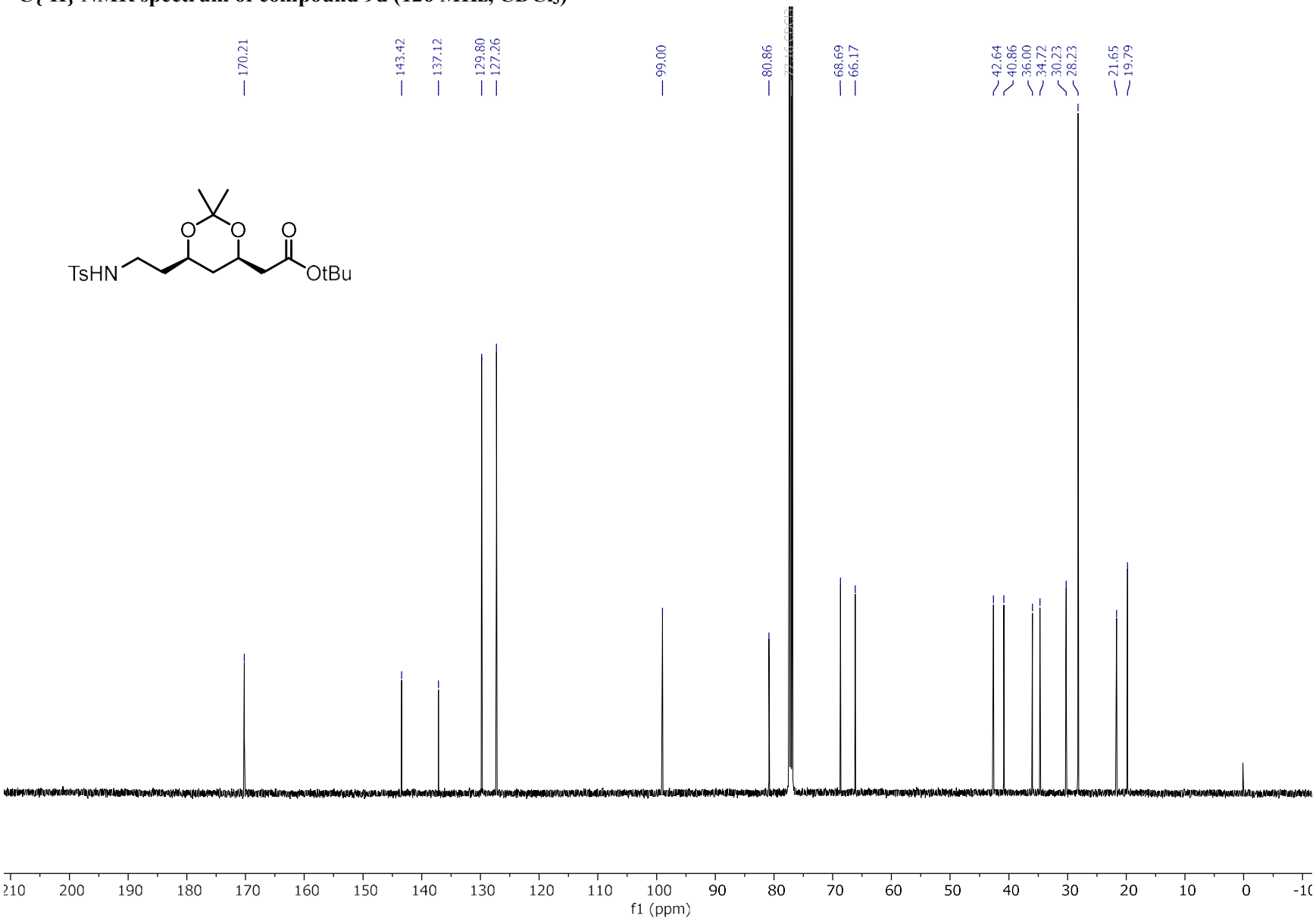
$^{13}C\{^{1}H\}$ NMR spectrum of compound 9c (126 MHz, $CDCl_3$)



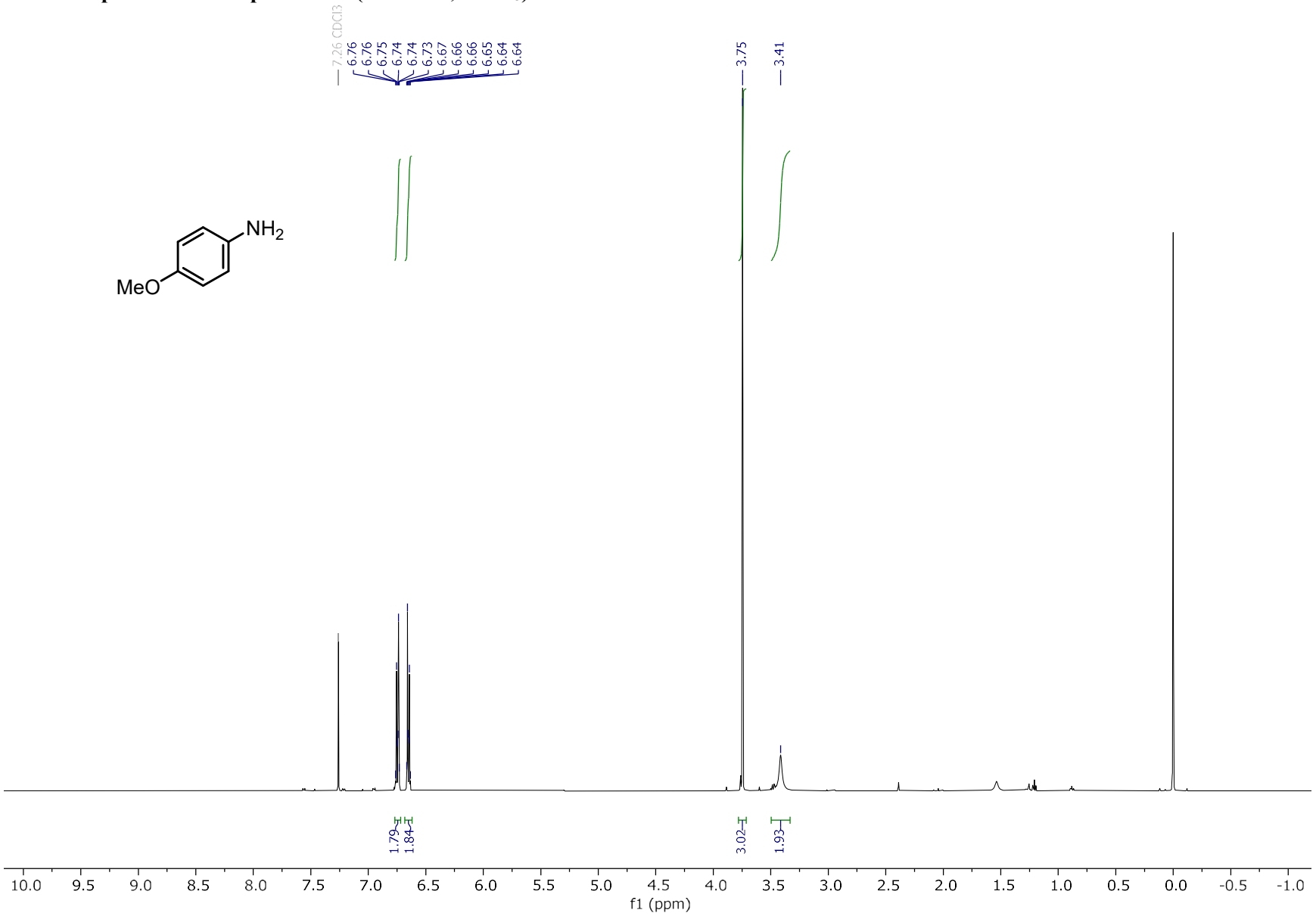
^{1}H NMR spectrum of compound 9d (500 MHz, $CDCl_3$)



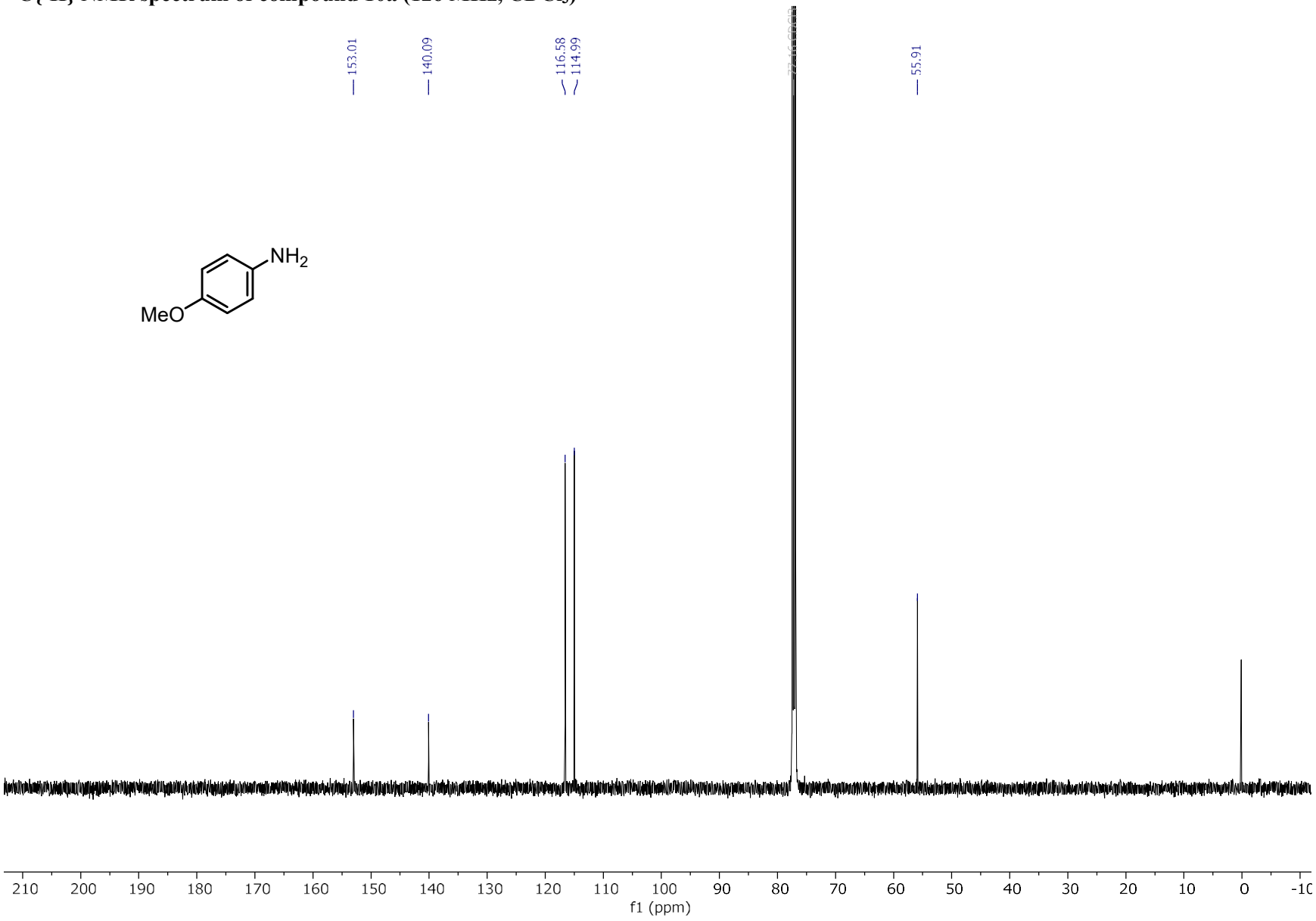
$^{13}C\{^{1}H\}$ NMR spectrum of compound 9d (126 MHz, $CDCl_3$)



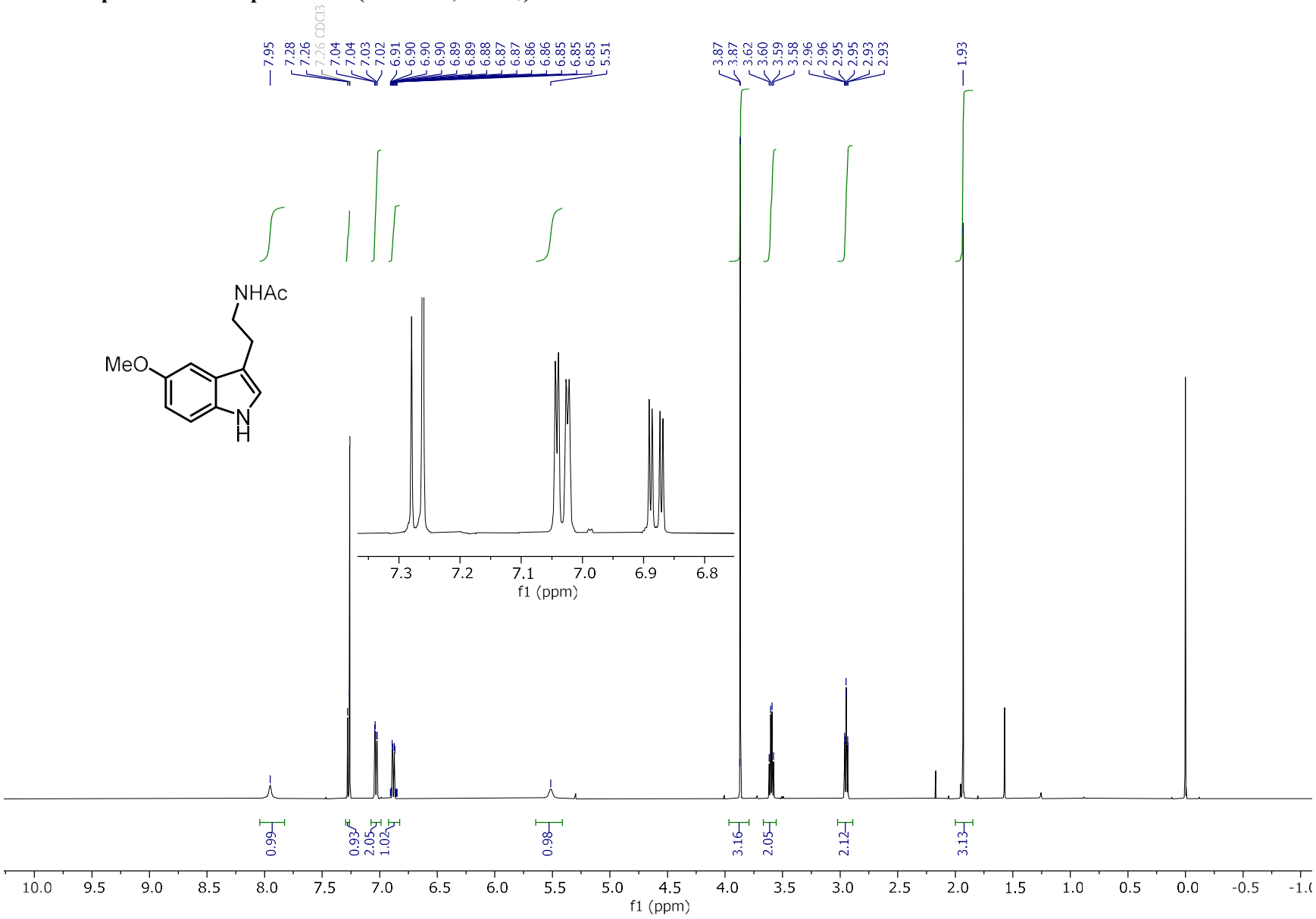
^{1}H NMR spectrum of compound 10a (500 MHz, $CDCl_3$)



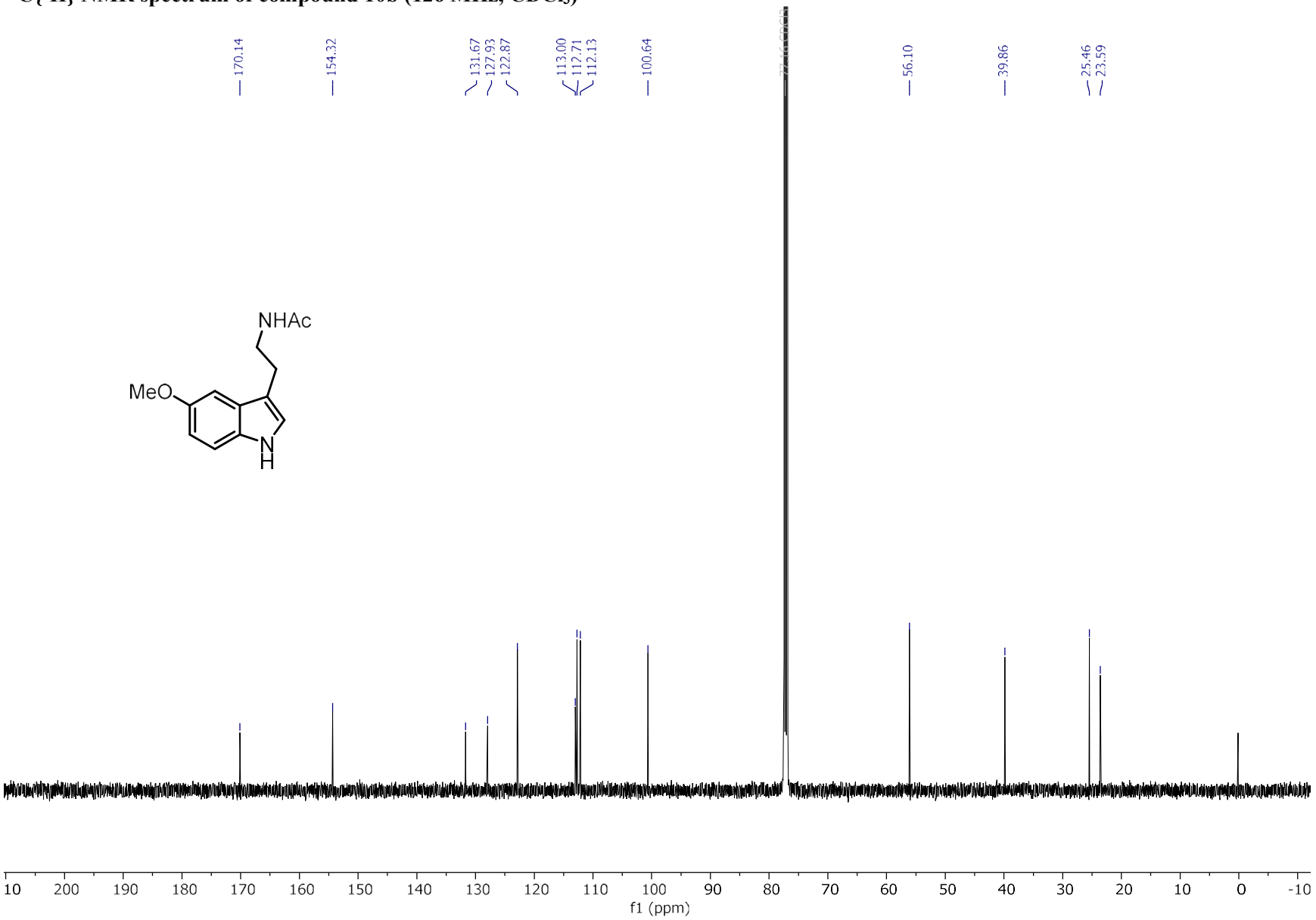
$^{13}C\{^{1}H\}$ NMR spectrum of compound 10a (126 MHz, $CDCl_3$)



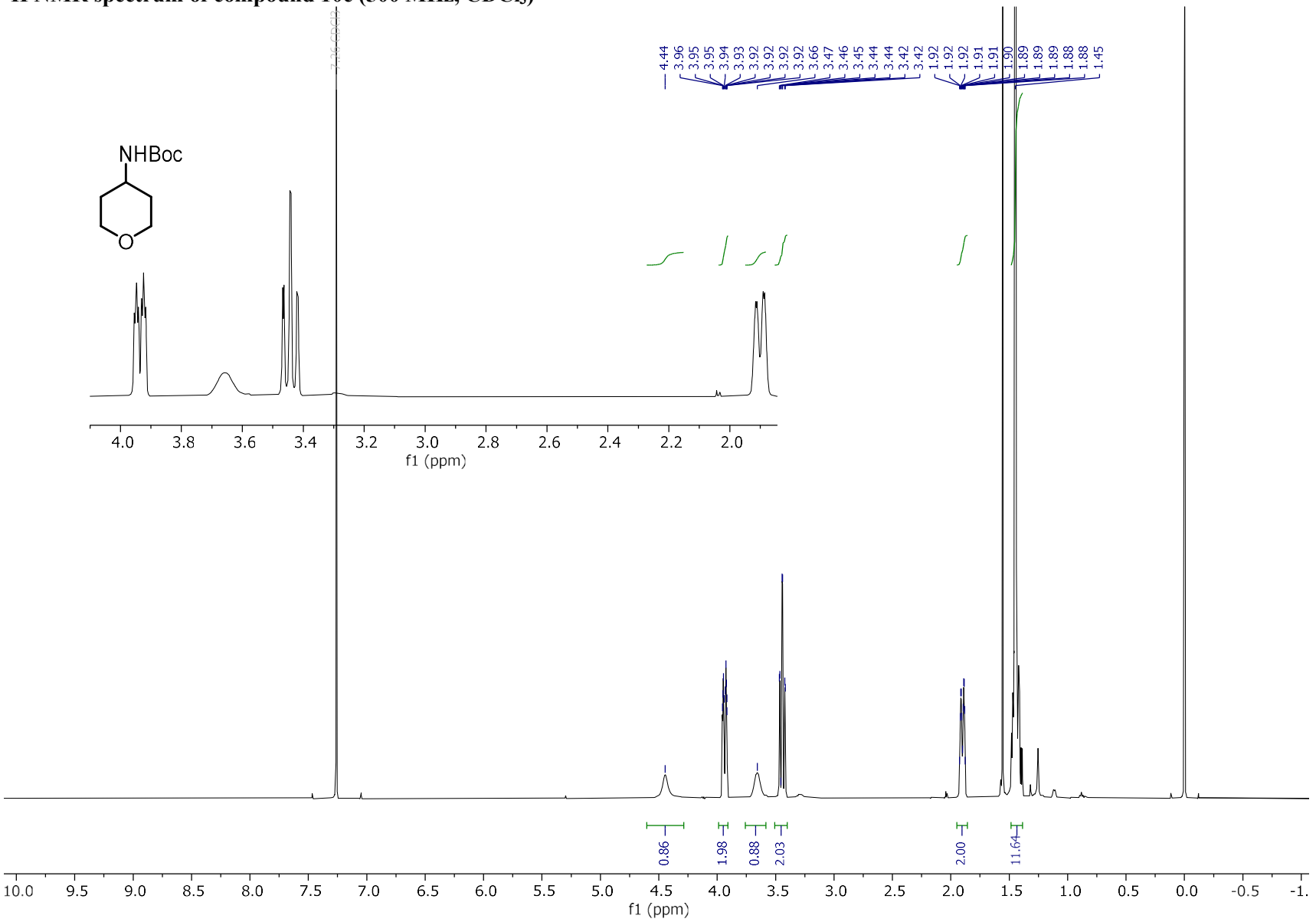
^{1}H NMR spectrum of compound 10b (500 MHz, $CDCl_3$)



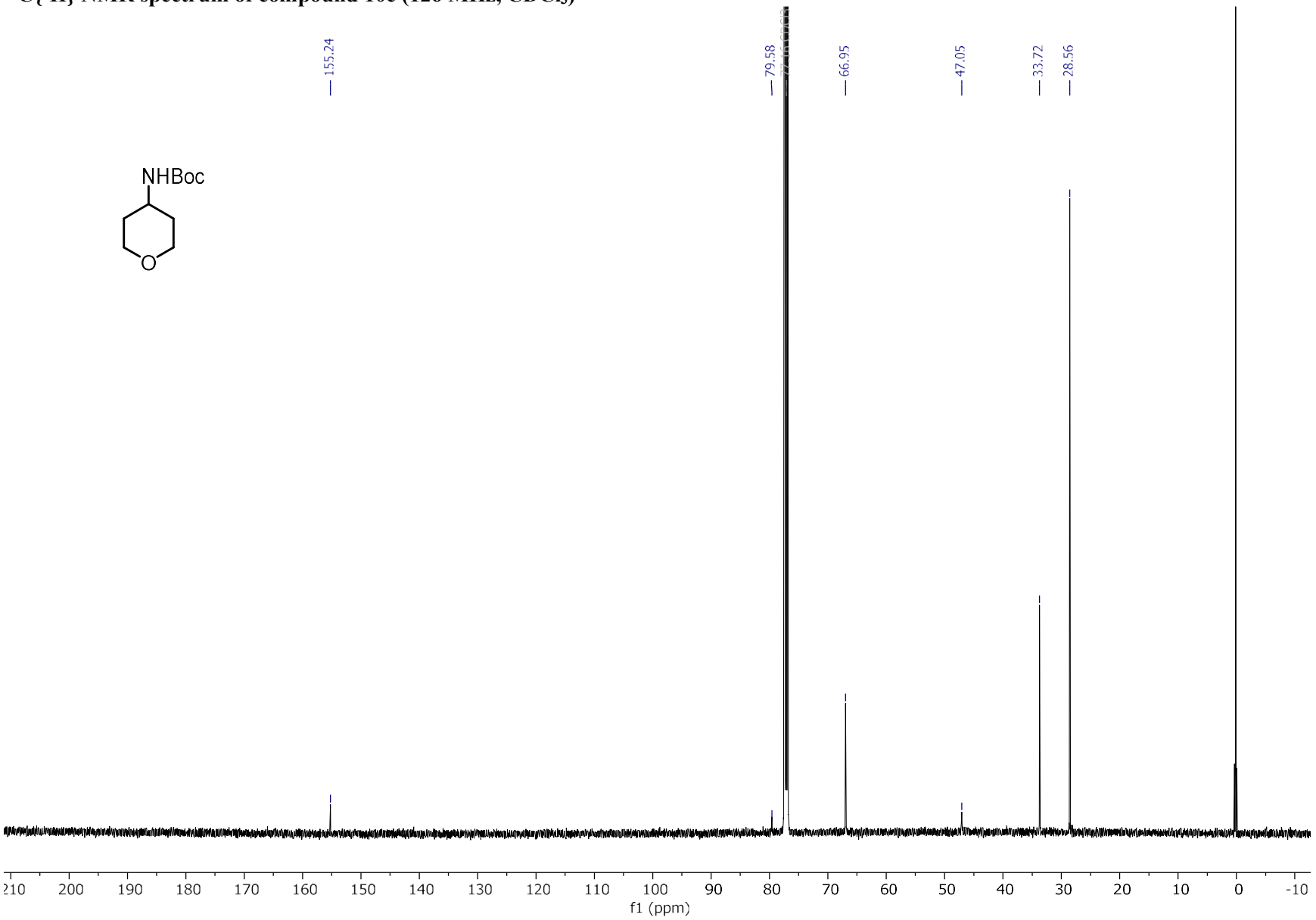
$^{13}C\{^{1}H\}$ NMR spectrum of compound 10b (126 MHz, $CDCl_3$)



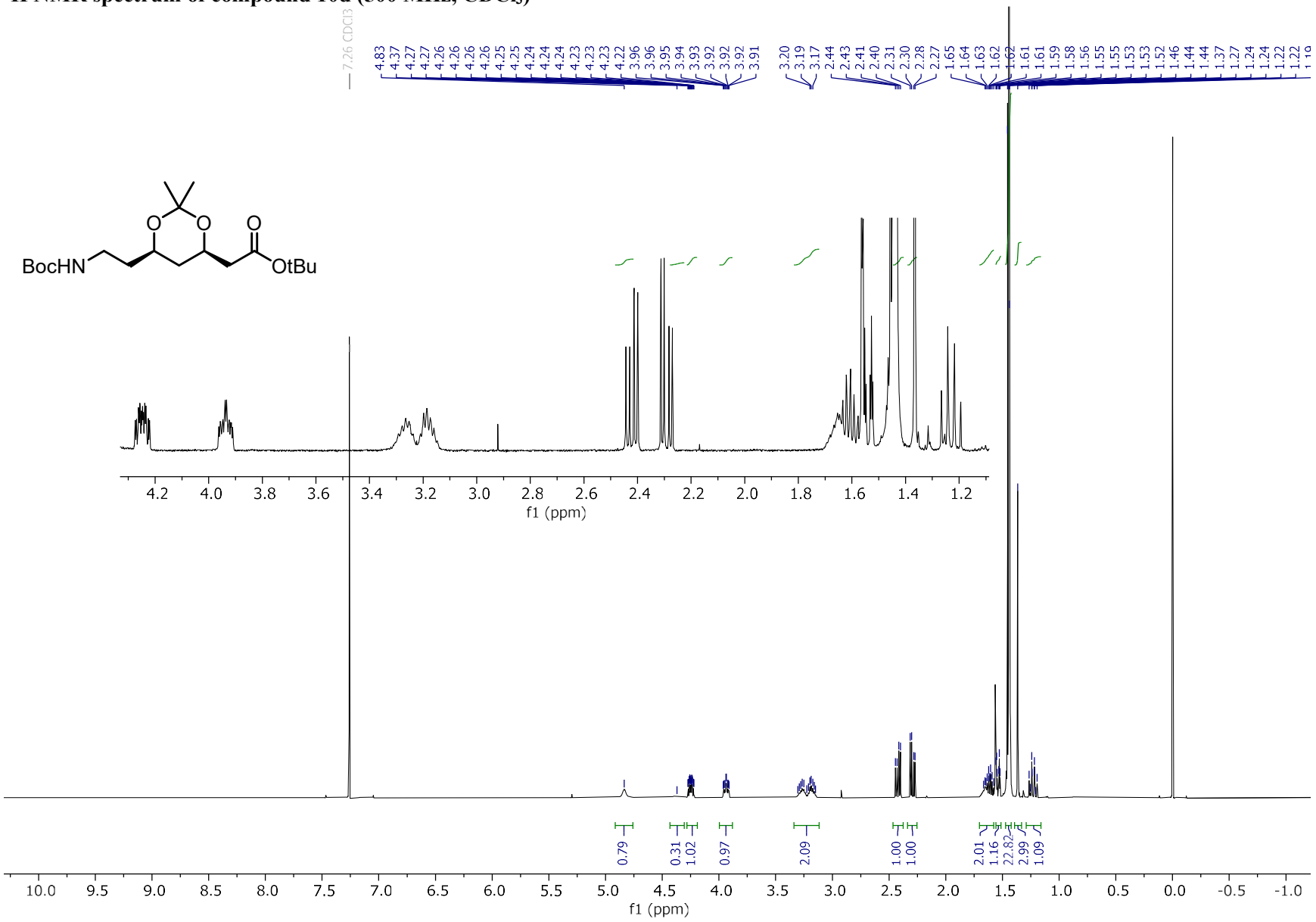
^{1}H NMR spectrum of compound 10c (500 MHz, $CDCl_3$)



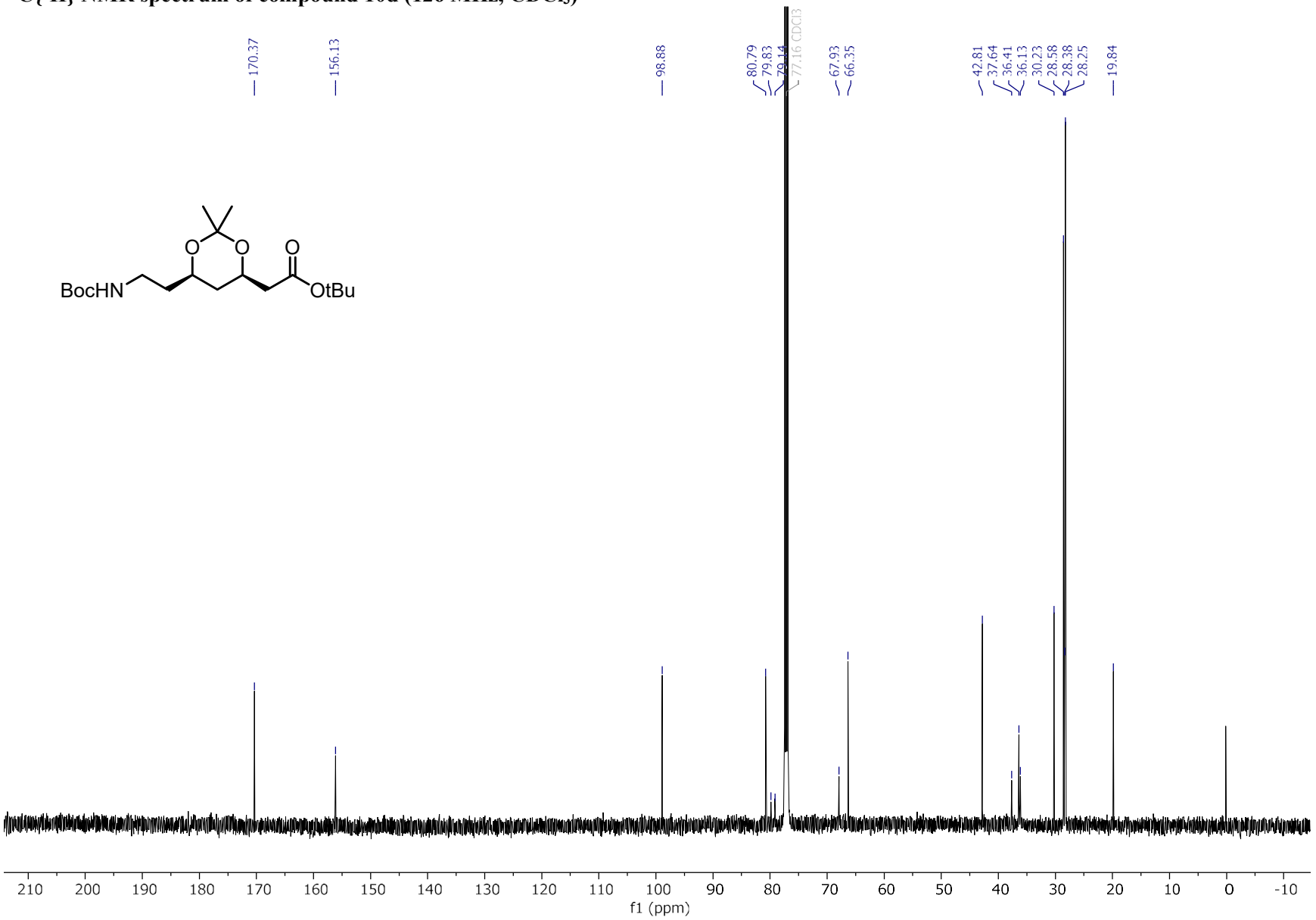
$^{13}C\{^{1}H\}$ NMR spectrum of compound 10c (126 MHz, $CDCl_3$)



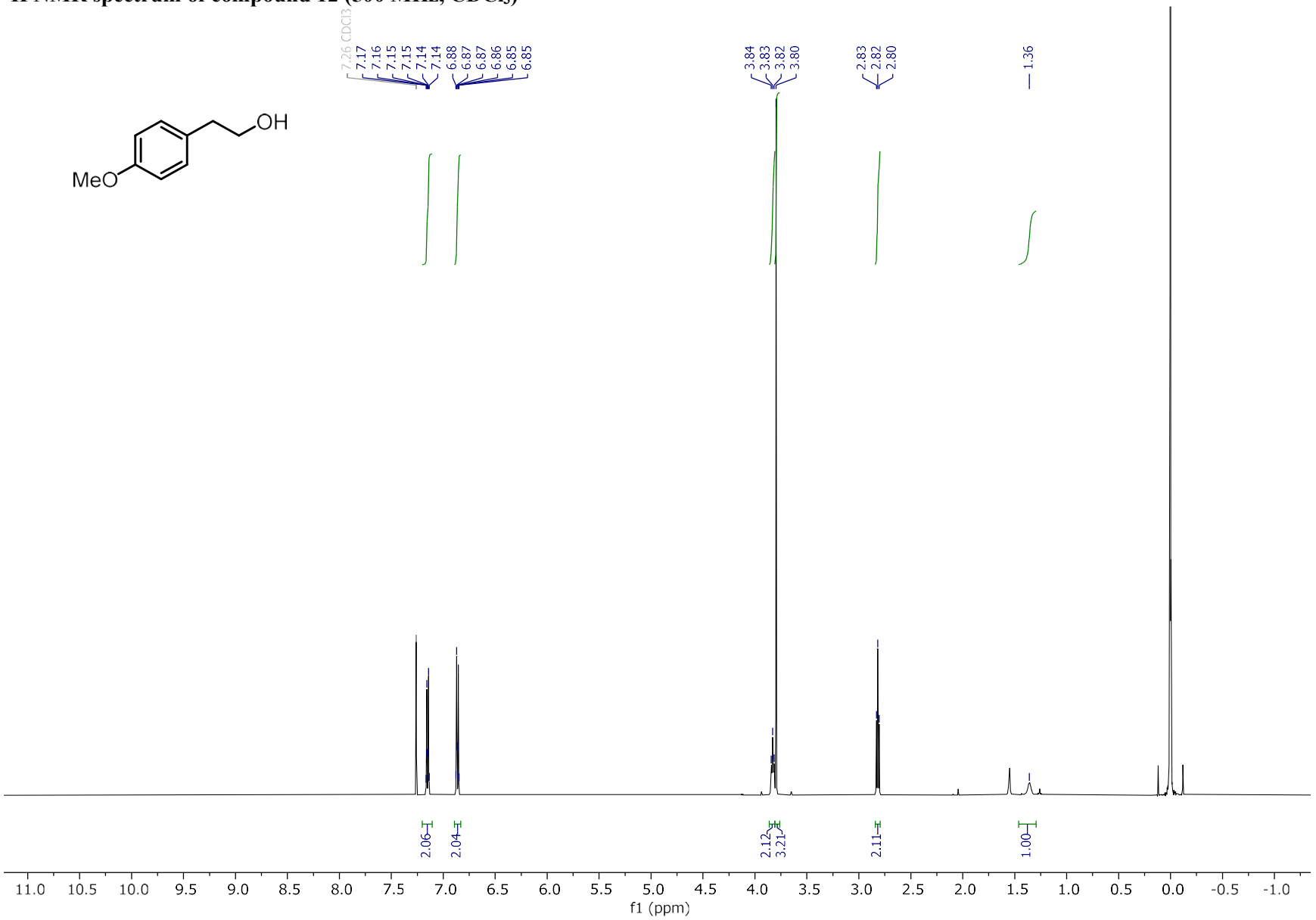
^{1}H NMR spectrum of compound 10d (500 MHz, $CDCl_3$)



$^{13}C\{^{1}H\}$ NMR spectrum of compound 10d (126 MHz, $CDCl_3$)



^{1}H NMR spectrum of compound 12 (500 MHz, $CDCl_3$)



$^{13}C\{^{1}H\}$ NMR spectrum of compound 12 (126 MHz, $CDCl_3$)