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Supporting Information

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Nickel-Catalyzed Enantioselective Arylation of Pyridinium Ions: Harnessing an Iminium Ion Activation Mode**

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I. General Information

General Procedures. Unless otherwise noted, reactions were performed with rigorous exclusion of air and moisture. Nitrogen-flushed stainless steel cannulae or plastic syringes were used to transfer air- and moisture-sensitive reagents. All reactions forming products **2a-2p** can be run without the use of a glovebox with vacuum evacuation and refilling of glassware with nitrogen. Solvent was freshly distilled/degassed prior to use unless otherwise noted. Reactions were monitored by thin-layer chromatography (TLC) on EMD Silica Gel 60 F_{254} plates, visualizing with UV-light (254 nm) fluorescence quenching, and $KMnO_4$ stain. Organic solutions were concentrated under reduced pressure using a rotary evaporator (25 °C, <50 torr). Automated column chromatography was performed using pre-packed silica gel cartridges on a Biotage SP4 (40-53 µm, 60 Å). Sigma Aldrich silica gel technical grade 60 Å, 230-400 mesh was buffered with 5% Et_3N. Iatrobeads 6RS-8060 was buffered with 5% Et_3N and used as indicated. SiliaFlash® Irregular silica gel P60 (40-63 µm, 230-400 mesh) was used as received.

Materials. Commercial reagents were purchased from Sigma Aldrich, Acros, Alfa Aesar, Strem, or TCI, and used as received with the following exceptions. Diethyl ether (Et_2O), dichloromethane (CH_2Cl_2), tetrahydrofuran (THF), and toluene were dried by passing through activated alumina columns; acetonitrile (CH_3CN) was dried by passing through a column of activated molecular sieves. Nickel(II) chloride glyme was purchased from Strem and stored at room temperature in a N_2-filled glovebox. Nickel(II) bromide diglyme was purchased from Sigma Aldrich and stored at room temperature in a N_2-filled glovebox. For storage purposes all zinc reagents, ligands, and nickel sources were kept in the glovebox protected from moisture and air.

Instrumentation. Proton nuclear magnetic resonance (^{1}H NMR) spectra and carbon nuclear magnetic resonance (^{13}C NMR) spectra were recorded on a Bruker 500 AVANCE spectrometer (500 and 125 MHz, respectively). Chemical shifts for protons are reported in parts per million downfield from tetramethylsilane and are referenced to residual protium in the NMR solvent ($CDCl_3$ = δ 7.26 ppm, MeOD = δ 3.35 ppm, C_6D_6 = δ 7.16 ppm). Chemical shifts for carbon are reported in parts per million downfield from tetramethylsilane and are referenced to the carbon resonances of the solvent residual peak ($CDCl_3$ = δ 77.00 ppm, MeOD = δ 49.30 ppm, C_6D_6 = δ 128.06 ppm). ^{19}F spectra (282 MHz) and ^{31}P spectra (121 MHz) were recorded on a Bruker NB 300 spectrometer; chemical shifts are reported in parts per million. NMR data are represented as follows: chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constant in Hertz (Hz), integration. High-resolution mass spectra were obtained on an Agilent 6220 using electrospray ionization time-of-flight (ESI-TOF). FT-IR spectra were recorded on a Perkin-Elmer Spectrum 100 and are reported in terms of frequency of absorption (cm^{-1}). Reversed-phase liquid chromatography/mass spectrometry (LC/MS) was performed on an Agilent 1260 Infinity analytical LC and Agilent 6120 Quadrupole LC/MS system, using electrospray ionization/atmospheric-pressure chemical ionization (ESI/APCI), and UV detection at 254 and 280 nm. High-performance liquid chromatography (HPLC) was performed on an Agilent 1200 series instrument with a binary pump and a diode array detector, using Chiralpak OD-H (25 cm x 0.46 cm) and Chiralpak AD-H (25 cm x 0.46 cm) columns. SFC separation performed on a Berger Analytical SFC System equipped with a dual pump (FCM1200), an auto sampler (ALS3100), a column oven (TCM200) and a diode array detector (DAD4100) using a Chiralpak IA (15 x 0.46cm) column. Single crystals suitable for X-ray diffraction were coated with polyisobutylene oil, transferred to a nylon loop and then quickly transferred to the goniometer head of a Bruker APEX2 Duo diffractometer equipped with molybdenum (λ = 0.71073 Å) and copper (λ = 1.54184 Å) X-ray tubes. Preliminary data revealed the crystal system. A hemisphere routine or optimization using COSMO was used for data collection and determination of lattice constants. The space group was identified, and the data were processed using the Bruker SAINT+ program and corrected for absorption using SADABS. The structures were solved using the SIR92 software suite, completed by subsequent Fourier synthesis and refined by full-matrix least-squares procedures. Optical rotations were taken with a Perkin Elmer 341 polarimeter Na/Hal lamp with a .998 dm/1mL cell in spectral grade $CHCl_3$.

II. General Procedure

0.05 mmol scale:

To a 10-mL glass vial charged with ligand **L7** (2.9 mg, 0.006 mmol, 0.12 equiv.) in THF (0.5 mL) at rt, was added nickel(II) bromide digylme (1.8 mg, 0.005 mmol, 0.1 equiv.) in THF (0.5 mL) and 4-F-PhZnBr solution (0.3 M in THF, 0.66 mL, 2 mmol, 4 equiv.) in a nitrogen filled glovebox. The vial was sealed with a plastic cap lined with a rubber septum, wrapped with electrical tape and removed from the glovebox.

To a separate 10-mL glass vial equipped with a stir bar were added 2 mL of THF, 4-methoxypyridine (5.45 mg, 0.05 mmol, 1 equiv.) and phenyl chloroformate (0.025 mL, 0.2 mmol, 4 equiv.) at 0 °C, and the solution was stirred for 15 min at this temperature. The resulting white slurry was then cooled to –78°C and the cocktail of ligand, nickel and aryl zinc bromide solution was added dropwise. Reaction was stirred overnight and allowed to warm to rt. The reaction was quenched with 2 mL of 1 M HCl and stirred for 20 min, extracted with diethyl ether (2 x 5 mL), filtered through a silica gel plug, dried over $MgSO_4$ and concentrated *in vacuo*. The crude material was evaluated via ^{19}F NMR versus an internal standard of *p*-difluorobenzene and chiral HPLC to determine yield and % ee respectively.

0.5 mmol scale:

To a 25-mL glass vial was added ligand **L7** (28.5 mg, 0.06 mmol, 0.12 equiv.) in 5 mL of THF. To this solution was added nickel(II) bromide diglyme (17.6 mg, 0.05 mmol, 0.1 equiv) in 5 mL of THF (allowed to stir 15 min in a separate glass vial with a stir bar until metal completely dissolves to give a solution that is purple in color) and arylzinc halide (0.3 M in THF, 6.66 mL, 2 mmol, 4 equiv.) in a nitrogen-filled glovebox. Upon addition of the arylzinc halide solution to the ligand and nickel source the solution immediately turned a dark brown color. The 25-mL glass vial was sealed with a plastic cap lined with a rubber septum, wrapped with electrical tape and removed from the glovebox.

Separately, a 50-mL Schlenk flask armed with a 1-inch bar-shaped stir bar was flame dried under vacuum and charged with nitrogen. To this flask were added 20 mL of THF, 4-methoxypyridine (54.5 mg, 0.5 mmol, 1 equiv.) and phenyl chloroformate (0.250 mL, 2 mmol, 4 equiv.) at 0 °C. Upon addition of phenyl chloroformate, a thick white slurry immediately formed and the solution was allowed to stir for an additional 15 min at 0 °C. The reaction was cooled to –78 °C and to the Schlenk flask was added the freshly prepared cocktail of ligand, nickel and arylzinc halide solution dropwise over 20 min. The reaction was allowed to warm to –40 °C and stirred overnight at this constant temperature unless otherwise noted. The reaction was quenched with 30 mL of 1 M HCl and stirred for 20 min at rt. The resulting mixture was diluted with diethyl ether, and the aqueous layer was extracted with diethyl ether (3 x 10 mL) and washed with sat. $NaHCO_3$ (2 x 10 mL) and brine (2 x 10 mL). The combined organic layers were dried over $MgSO_4$ and the filtrate was concentrated *in vacuo*. The crude mixture was purified with silica gel (SiO_2) column chromatography (buffered with 5% Et_3N as noted, 3:1, 2:1 hexanes: EtOAc unless otherwise stated) and the title compound was obtained as an oil unless otherwise stated.

Formation of Aryl Zinc Halide Solutions:

Method A[1]: To a 250-mL 3-neck round-bottomed flask equipped with a stir bar, nitrogen inlet and a thermocouple was added aryl bromide (35 mmol, 1 equiv.) in THF (70 mL) at rt. The solution was cooled to –100 °C and *n*-BuLi (2.0 M in hexanes, 17.5 mL, 35 mmol, 1 equiv.) was added dropwise, while maintaining the solution at –100 to –105 °C. After complete addition, the mixture was stirred for an additional 20 min at –100 °C and then warmed to –78 °C. At this temperature, a solution of $ZnBr_2$ (8.7 g, 38.5 mmol, 1.1 equiv.) in THF (12.5 mL) was added dropwise. After complete addition the flask was warmed to rt, cannulated into a vial and stored in a nitrogen glovebox.

Method B[2]: A 100-mL round-bottomed flask equipped with a stir bar was charged with LiCl (1.5 equiv.) and $ZnCl_2$ (1.2 equiv.) and heated with a heatgun under vacuum (0.1 torr) for 5 min. Mg dust (1.6 equiv.) and THF (12 mL at 8 mmol scale) was activated with DIBAL-H (1.0 M in hexanes, 0.01 equiv.) at 0 °C. Bubbling immediately occurred and after 5 min of stirring, aryl bromide (1 equiv.) was added. The resulting solution was warmed to rt and stirred for 3 h, diluted to 0.3 M with THF, cannulated into a vial, and stored in a nitrogen glovebox.

Preparation of Nickel Methallylchloride Dimer[3]:

A 200-mL Schlenk flask and Teflon stir bar were oven dried and brought into a nitrogen-filled glovebox. There, the flask was charged with anhydrous, degassed THF (70 mL), then $Ni(COD)_2$ (1.375 g, 5 mmol). The sides were rinsed with THF (10 mL). The flask was carefully sealed and then *quickly* removed from the glovebox and put into a –78 °C cooling bath. After cooling, methallyl chloride (0.54 mL, 5.5 mmol) was added via syringe. The bath was allowed to expire slowly. The mixture went from bright yellow to green-brown to dark red as it warmed. After warming to 0 °C, the THF was removed by vacuum via a Schlenk line, leaving a red-orange solid. The flask was brought to the glovebox, and the material was redissolved in anhydrous, degassed toluene and filtered through Celite (prepared according to the RajanBabu method). The resulting dark orange solution was concentrated to a flaky orange powder (0.55 g, 74% yield).

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[1] Jensen, A.E.; Kneisel, F.; Knochel, P. *Org. Synth*. **2004**, *Coll. Vol 10*, 391.

[2] (a) Schade, M.A.; Manolikakes, G.; Knochel, P. *Org. Lett*. **2010**, *12*, 3648-3650. (b) Piller, F. M.; Metzger, A.; Schade, M. A; Haag, B. A; Gavryushin, A.; Knochel, P. *Chem. Eur. J.* **2009**, *15*, 7192–202.

[3] (a) Shim, C. B.; Kim, Y. H.; Lee, B. Y.; Dong, Y.; Yun, H. *Organometallics* **2003**, *22*, 4272–4280. (b) Smith, C. R.; Zhang, A.; Mans, D. J.; RajanBabu, T. V. *Org. Synth*. **2008**, *85*, 248-266.

Preparation of gram-scale reaction under benchtop conditions:

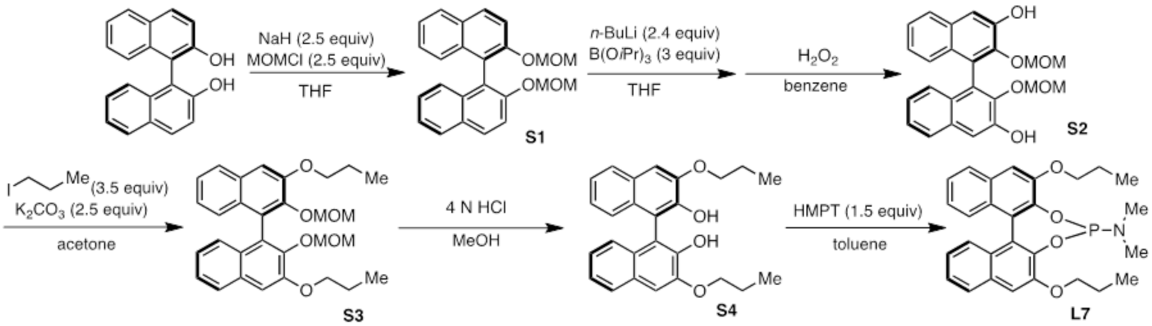
To a 250-mL round bottom flask was added ligand **L7** (143 mg, 0.30 mmol, 0.06 equiv.) evacuated and refilled with N_2 then added 50-mL of THF at rt. To the ligand solution was added nickel(II) bromide diglyme (88 mg, 0.250 mmol, 0.05 equiv) in 50 mL of THF (allowed to stir 15 min in a N_2 purged 50-mL pear shaped flask containing a septum armed with a stir bar, stirred until metal completely dissolves to give a solution that is purple in color) then arylzinc halide (0.3 M in THF, 66.7 mL, 20 mmol, 4 equiv.) was added via syringe. Upon addition of the arylzinc halide solution to the ligand and nickel source the solution immediately turned a dark brown color.

Separately, a 1 L round bottom flask armed with a 2-inch bar-shaped stir bar was flame dried under vacuum and charged with nitrogen. To this flask were added 100 mL of THF, 4-methoxypyridine (0.508 mL, 5 mmol, 1 equiv.) and phenyl chloroformate (2.509 mL, 20 mmol, 4 equiv.) at 0 °C. Upon addition of phenyl chloroformate, a thick white slurry immediately formed and the solution was allowed to stir for an additional 15 min at 0 °C. The reaction was cooled to –78 °C and to the round bottom flask was added the freshly prepared cocktail of ligand, nickel and arylzinc halide solution dropwise over 20 min and monitored with a thermocouple. The reaction was allowed to warm to –40 °C and stirred overnight at this constant temperature. The reaction was quenched with 30 mL of 1 M HCl and stirred for 20 min at rt. The resulting mixture was diluted with diethyl ether, and the aqueous layer was extracted with diethyl ether (3 x 30 mL) and washed with sat. $NaHCO_3$ (30 mL) and brine (2 x 10 mL). The combined organic layers were dried over $MgSO_4$ and the filtrate was concentrated *in vacuo*. The crude mixture was purified with silica gel (SiO_2) column chromatography (3:1, 2:1 hexanes: EtOAc unless otherwise stated) providing 2a (1.14 g, 73% yield) in 93% ee.

Preparation of racemates 2a-2p:

Racemic standards were developed using racemic (±)Monophos instead of L7 under otherwise identical reaction conditions for compounds 2a-2p under 0.05 mmol scale.

Ligand (**L7**) Synthesis:



(*R*)-2,2'-bis(methoxymethoxy)-1,1'-binaphthalene (S1)[4]: A flame-dried, 250-mL round-bottomed flask equipped with a stir bar was charged with (*R*)-BINOL (10 g, 35 mmol, 1.0 equiv.) in dry THF (30 mL). The reaction mixture was cooled to 0 °C and sodium hydride (3.5 g, 88 mmol, 2.5 equiv.) was added portionwise to give a yellow solution. The reaction mixture was warmed to rt and allowed to stir 1 h. The reaction mixture was cooled to 0 °C and MOMCl (6.6 mL, 88 mmol, 2.5 equiv.) was added via syringe. The reaction mixture was allowed to stir at 0 °C for 10 min, then warmed to rt and allowed to stir overnight. The reaction was quenched with sat. NH_4Cl (40 mL) and diluted with water (40 mL). The resulting mixture was extracted with Et_2O (3 x 30 mL) and the combined organic layers were dried with $MgSO_4$ and filtered. The filtrate was concentrated *in vacuo* and the crude product mixture was purified using flash chromatography with SiO_2 (rf=0.60 in 4:1 hex:EtOAc) to give the product as a beige solid (7.3 g, 20 mmol, 56%).

(*R*)-2,2'-bis(methoxymethoxy)-[1,1'-binaphthalene]-3,3'-diol (S2)[5]: A flame-dried, 100-mL recovery flask equipped with a stir bar was charged with **S1** (3.0 g, 8.0 mmol, 1.0 equiv.) in dry THF (30 mL). The reaction mixture was cooled to –78°C and fresh *n*-BuLi (2.0 M in hexanes, 9.6 mL, 19 mmol, 2.4 equiv.) was added to the stirring solution, and the solution was allowed to stir at 0 °C for 1 h. The solution was cooled to –78 °C and triisopropyl borate (5.6 mL, 24 mmol, 3.0 equiv.) was added dropwise. The reaction mixture was warmed to rt and stirred overnight, then concentrated *in vacuo* to give an orange solid. Benzene (40 mL) was added and the solution was cooled to 0 °C. Aqueous hydrogen peroxide (30 wt%, 6 mL) was added, and the solution was allowed to stir at 0 °C for 2 h. The reaction mixture was diluted with water (40 mL) and extracted with Et_2O (3 x 30 mL). The combined organic portions were dried with $MgSO_4$ and filtered, and the filtrate was concentrated *in vacuo* to give an orange oil. Hexanes were added to the oil and a solid precipitated from solution, and the hexanes were then removed *in vacuo*. The addition of hexanes to precipitate product followed by removing the hexanes *in vacuo* was carried out a total of three times to give an orange solid (2.9 g, 7.2 mmol, 90%) that was carried directly on to the next step of the synthesis without purification. Fresh *n*-BuLi was required for reproducible results.

(*R*)-2,2'-bis(methoxymethoxy)-[1,1'-binaphthalene]-3,3'-diol (S3)[5]: A 100-mL recovery flask equipped with a stir bar was charged with **S2** (2.9 g, 7.2 mmol, 1.0 equiv.) dissolved in acetone (10 mL). K_2CO_3 (2.5 g, 18 mmol, 2.5 equiv.) and 1-iodopropane (2.5 mL, 25 mmol, 3.5 equiv.) were added to the solution. The flask was capped with a reflux condenser and the solution was stirred at reflux overnight. The reaction was quenched with water (40 mL) and diluted with Et_2O (40 mL), then extracted with Et_2O

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[4] Wu, T. R; Shen, L.; Chong, J. M. *Org. Lett.* **2004**, *6*, 2701-2704.
[5] Ooi, T.; Kameda, M.; Maruoka, K.; *J. Am. Chem. Soc.* **2003**, *125*, 5139-5151.

(4x30 mL), dried with $MgSO_4$, and filtered. The filtrate was concentrated *in vacuo* to give an orange solid. The crude product was purified using flash chromatography with SiO_2 (rf=0.53 in 4:1 hex:EtOAc) to give the product as a yellow oil (1.3 g, 2.6 mmol, 36%).

(*R*)-3,3'-dipropoxy-[1,1'-binaphthalene]-2,2'-diol (S4): A 100-mL recovery flask was charged with **S3** (1.3 g, 2.6 mmol) dissolved in MeOH (30 mL). Aqueous HCl (4 M, 5 mL) was added, and the reaction mixture was allowed to stir at rt for 36 h. The reaction mixture was diluted with water (40 mL) and Et_2O (30 mL), then extracted with Et_2O (3 x 30 mL). The combined organic portions were dried with $MgSO_4$ and filtered, and the filtrate was concentrated *in vacuo* to give a yellow solid. The crude product mixture was purified using flash chromatography with SiO_2 (rf=0.36 in 4:1 hex:EtOAc) to give the product as a crystalline, beige solid (0.78 g, 1.9 mmol, 76%).

(*R*)-*N,N*-dimethyl-2,6-dipropoxydinaphtho[2,1-*d*:1',2'-*f*][1,3,2]dioxaphosphepin-4-amine (L7)[6]: A 50-mL round-bottomed flask equipped with a stir bar was charged with **S4** (0.78 g, 1.9 mmol, 1.0 equiv) in toluene (30 mL). HMPT (0.53 mL, 2.9 mmol, 1.5 equiv.) was added, and the reaction mixture was allowed to stir for 5 h at rt. The toluene was removed *in vacuo* to give a white solid that was purified using flash chromatography with SiO_2 (rf=0.63 in 4:1 hex:EtOAc) to give the product as a white, crystalline solid (0.77 g, 1.6 mmol, 83%).

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.77 (dd, *J* = 8.3, 5.0 Hz, 2H), 7.40 – 7.33 (m, 2H), 7.31 (d, *J* = 9.4 Hz, 2H), 7.24 (d, *J* = 12.2 Hz, 1H), 7.10 (dddd, *J* = 16.8, 8.3, 6.7, 1.3 Hz, 3H), 4.17 (dddt, *J* = 39.5, 29.8, 9.0, 6.5 Hz, 4H), 2.53 (d, *J* = 9.2 Hz, 6H), 1.98 (qd, *J* = 7.5, 3.9 Hz, 4H), 1.15 (t, *J* = 7.4 Hz, 3H), 1.11 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 150.59 (d, *J* = 14.6 Hz), 141.64 (d, *J* = 118.6 Hz), 131.37 (d, *J* = 72.8 Hz), 127.38 (d, *J* = 15.8 Hz), 126.91 (d, *J* = 4.8 Hz), 126.83 (d, *J* = 7.9 Hz), 125.61 (d, *J* = 5.2 Hz), 125.03 (d, *J* = 28.4 Hz), 123.49 (d, *J* = 7.6 Hz), 108.23 (d, *J* = 54.3 Hz), 70.19 (d, *J* = 15.3 Hz), 35.49 (d, *J* = 20.7 Hz), 22.52 (d, *J* = 44.8 Hz), 10.67 (d, *J* = 15.0 Hz).

^{31}P NMR (121 MHz, $CDCl_3$): 148.8 ppm.

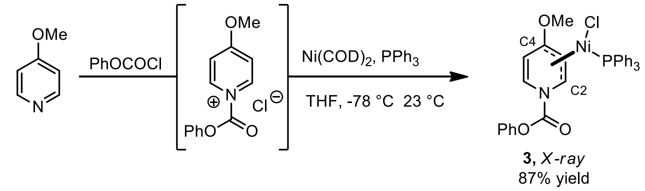
HRMS: (ESI-TOF) calculated for $C_{28}H_{30}NO_4P$ ($[M+H]^+$): 476.1985, found: 476.1988.

FTIR (thin film, cm^{-1}): 2963, 2924, 1619, 1595, 1504.

Optical rotation: $[\alpha]_D^{26}$ –666.1 (*c* 0.96, $CHCl_3$).

MP: 94-98 °C

Preparation of Oxidative Adduct **3**:



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[6] Kangying, L.; Zhenghong, Z.; Guofeng, Z.; Chuchi, T.; *Heteroatom Chem.* **2003**, *14*, 546-550.

A solution of the pyridinium salt was prepared by the dropwise addition of phenyl chloroformate (0.576 mL, 4.58 mmol) to a solution of 4-methoxypyridine (500 mg, 4.58 mmol) in THF (20 mL) at 0 °C. The solution was then allowed to stir at 0 °C for 30 min under N_2. $Ni(COD)_2$ (1.26 g, 4.58 mmol) and PPh_3 (1.31 g, 5.03 mmol) was weighed out into a flame-dried 50-mL Schlenk flask equipped with a PTFE stirbar in the glovebox under N_2 and dissolved in THF (10 mL), producing a dark orange solution. The flask was then removed from the glovebox and attached to a nitrogen line. The product was then cooled to –78 °C and the pyridinium salt solution was added dropwise. The pyridinium salt flask was then rinsed with THF (2 x 2 mL) and the rinses added dropwise to the Ni solution. The solution was then allowed to stir at –78 °C for 2 h and then allowed to warm to 23 °C. The flask was allowed to stir at 23 °C for 30 min. The reaction was brought into the glovebox and the solvent was removed under high vacuum. The residue was redissolved in THF/Toluene (2:1) and the product was precipitated by addition of pentane and storage overnight in a –30 °C freezer. The Ni-allyl complex **3** (2.355 g, 87 % yield) was collected by vacuum filtration as a light purple solid and dried *in vacuo* for 1 h. A crystal suitable for single crystal X-ray crystallography was grown from THF:Toluene:Pentane (5:1:5).

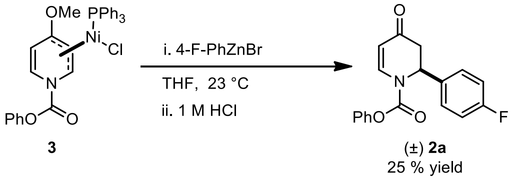
Crystallographic data: begins on page S-85.

^{1}H NMR (300 MHz, C_6D_6): δ 7.89 (t, *J* = 8.6 Hz, 6H), 7.21 – 6.69 (m, 14H), 5.96 (s, 1H), 5.70 (s, 1H), 5.00 (s, 1H), 4.40 (s, 1H), 3.70 (s, 3H).

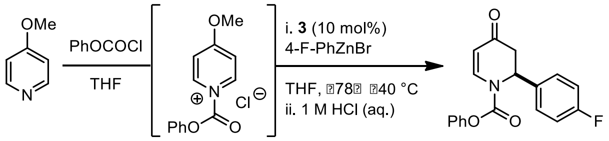
^{13}C NMR (125 MHz, C_6D_6): δ 150.83, 149.40, 148.03, 134.51, 134.42, 133.79, 133.48, 130.03, 129.25, 128.70, 125.86, 121.35, 88.35, 72.15, 56.51.

^{31}P NMR (121 MHz, C_6D_6): δ 33.66.

Stoichiometric/Catalytic Studies with **3**:



Stoichiometric study with 3: A 50-mL Schlenk flask armed with a stir bar was flame-dried under vacuum and charged with nitrogen. To this flask was added air-sensitive oxidative adduct **3** (120 mg, 0.205 mmol, 1 equiv.) and 1 mL of THF in the glovebox. The Schlenk flask was treated with 4-F-PhZnBr (0.8M in THF, 3.84 mL, 15 equiv.) was added dropwise via syringe pump addition at 1 mL/h. The reaction was allowed to stir over a period of 24 h at rt. The Schlenk flask was removed from the glovebox and was added 1 M HCl (20 mL) and the solution was stirred for 20 min. The resulting mixture was diluted with diethyl ether and the aqueous layer was extracted with diethyl ether (3 x 10 mL). The combined organic layers were dried over $MgSO_4$ and filtered, and the filtrate was concentrated *in vacuo*. The crude reaction mixture was purified with silica gel (SiO_2) column chromatography (3:1, 2:1 hexanes:EtOAc), providing (±) **2a** (15.8 mg, 25 % yield). Spectral data were determined to be identical to **2a**. The major byproduct is the unsubstituted pyridone adduct presumably formed from protodemetallation after addition of acid.



(±) **2a**
68% yield

Catalytic competency of 3: A solution of the pyridinium salt was prepared by the dropwise addition of phenyl chloroformate (0.256 mL, 2.04 mmol) to a solution of 4-methoxypyridine (0.056 g, 0.51 mmol) in THF (12.0 mL) at 0 °C. The solution was then allowed to stir at 0 °C for 30 min under N_2. Oxidative adduct **3** (0.029 g, 0.051 mmol) was weighed out into a 50-mL Schlenk flask equipped with a PTFE stirbar in the glovebox under N_2. THF (12.0 mL) was added to dissolve the complex and the flask was removed from the glovebox. The solution of the complex was then placed under N_2 and cooled to –78 °C. 4-F-PhZnBr 0.3 M in THF, (6.80 mL, 2.04 mmol) was then added dropwise, followed by the dropwise addition of the pyridinium solution. The flask containing the pyridinium solution was rinsed with THF (2 x 4 mL). The Schlenk flask was then transferred to a –40 °C bath and allowed to stir for 16 h. The reaction was quenched by the addition of aqueous HCl (1 M, 10 mL) at –40 °C. The solution was then allowed to warm to 23 °C and allowed to stir for 10 min. The reaction mixture was poured into a separatory funnel and extracted with Et_2O (3 x 20 mL). The combined organic extracts were rinsed sequentially with saturated aqueous $NaHCO_3$ (20 mL) and brine (20 mL), dried with $MgSO_4$, and filtered. The solution was concentrated under reduced pressure to yield a yellow oil. The crude product was purified by column chromatography (25 g pre-packed silica gel cartridge, hexanes:EtOAc gradient 96:4 to 50:50) to yield (±) **2a** (0.119 g, 0.383 mmol, 68 % yield) as a white foam. The identity of the product was confirmed by ^{1}H and ^{13}C NMR analysis to be identical to **2a**.

III. Additional Optimization Experiments

A. Additional ligand evaluation

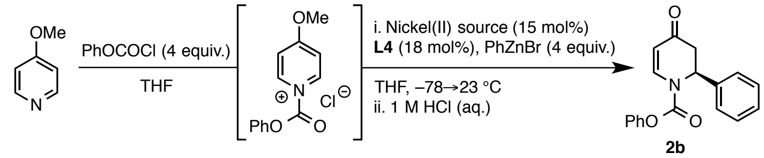
Further study of the (*S*,*S*,*S*) diastereomer of **L9** using otherwise identical procedures to those shown in Table 1 provided **2a** in 13% ^{19}F NMR yield (0.05 mmol) and –13% ee.

B. Confirmation of the role of the Ni catalyst

In conditions analogous to those depicted in Table 2 with the exception that no Ni source was added, **2a** was formed in 9.8% ^{19}F NMR yield and 0% ee.

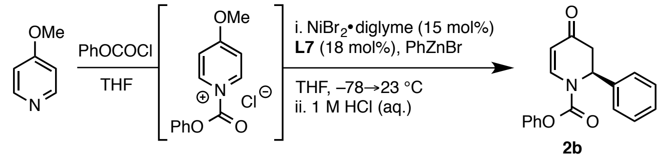
C. Miscellaneous optimization experiments

Table S1. Evaluation of Ni precatalysts.



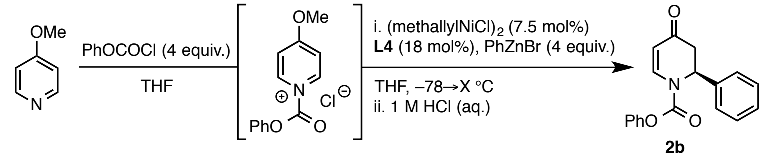
Entry	Ni source	Yield (%)	ee (%)
1	$NiBr_2$•diglyme	33	81
2	$NiCl_2$•diglyme	21	82
3	NiF_2	26	0
4	NiI_2	46	19
5	$Ni(OTf)_2$	37	0
6	$Ni(TMHD)_2$	13	37
7	$Ni(acac)_2$	17	70

Table S2. Evaluation of nucleophile and chloroformate equivalents.



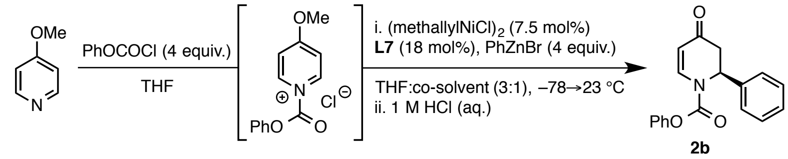
Entry	Equiv. PhCOCl	Equiv PhZnBr	Yield (%)	ee (%)
1	2	4	n.d.	26
2	4	4	54	85
3	2	6	n.d	11
4	4	6	52	85

Table S3. Evaluation of temperature.



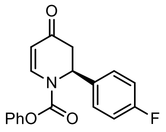
Entry	X (°C)	Yield (%)	ee (%)
1	–60	21	77
2	–40	32	76
3	–20	14	68
4	0	29	60

Table S4. Evaluation of co-solvent.



Entry	Co-solvent	Yield (%)	ee (%)
1	none	31	85
2	dioxane	40	67
3	toluene	10	67
4	DMA	10	27
5	*t*-AmOH	0	n.d
6	Et_2O	70	70
7	DCM	17	17

IV. Characterization



2a

(*S*)-phenyl 2-(4-fluorophenyl)-4-oxo-3,4-dihydropyridine-1(2H)-carboxylate (2a): The zincbromide solution was prepared via method A. General procedure was followed, providing **2a** in 88% yield, 93% ee as a clear oil (Run 1). Run 2 provided 80% yield and 93% ee.

^{1}H NMR (500 MHz, MeOD): δ 8.29 (d, *J* = 8.3 Hz, 1H), 7.44 (t, *J* = 7.9 Hz, 2H), 7.40 (dd, *J* = 8.6, 5.2 Hz, 2H), 7.31 (t, *J* = 7.4 Hz, 1H), 7.17 (s, 2H), 7.15 (t, *J* = 8.7 Hz, 2H), 5.96 (d, *J* = 6.9 Hz, 1H), 5.51 (d, *J* = 8.4 Hz, 1H), 3.40 (dd, *J* = 16.7, 7.5 Hz, 1H), 2.82 (d, *J* = 16.7 Hz, 1H).

^{13}C NMR (125 MHz, MeOD): δ 195.37, 164.45 (d, *J* = 245.2 Hz), 153.58, 152.72, 145.34, 136.63, 131.33, 129.64 (d, *J* = 8.3 Hz), 128.17, 123.17, 117.40 (d, *J* = 21.9 Hz), 109.76, 57.85, 43.70.

^{19}F NMR (282 MHz, $CDCl_3$): δ -113.45 – -113.59 (septet, *J* = 9.0, 5.0 Hz).

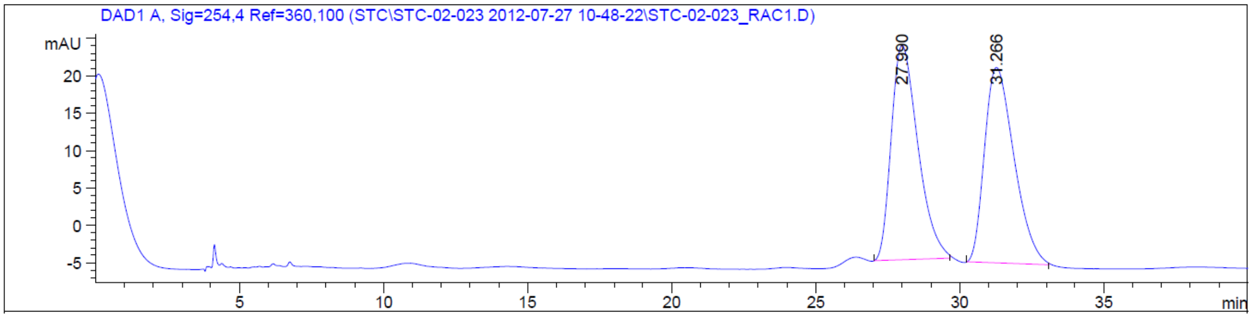
HRMS: (ESI-TOF) calculated for $C_{18}H_{14}FNO_3$ ($[M+H]^+$): 362.0925, found: 362.0988.

FTIR (thin film, cm^{-1}): 1738, 1671, 1607, 1510.

Optical rotation: $[\alpha]_D^{26}$ +45.9 (*c* 3.8, $CHCl_3$).

HPLC: Chiralpak OD-H, 1:4, IPA to Hexanes, 40 min run, 0.8 mL/min.

Racemic Standard:



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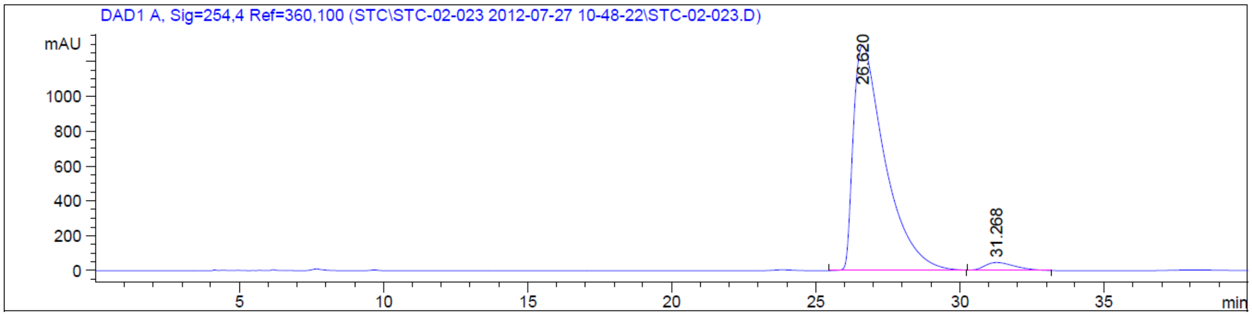
Peak RetTime Type  Width     Area       Height      Area
  #   [min]         [min]  [mAU*s]      [mAU]        %
----|-------|----|-------|----------|----------|--------|
   1  27.990 BB    0.9707 1851.09277   28.68992  49.7293
   2  31.266 BB    1.0462 1871.24280   26.17061  50.2707
```

Enantioenriched:



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Peak RetTime Type  Width     Area       Height      Area
  #   [min]         [min]  [mAU*s]      [mAU]        %
----|-------|----|-------|----------|----------|--------|
   1  26.620 BB    1.1300 9.91445e4  1293.81543  96.5802
   2  31.268 BB    1.1377 3510.57080   46.87749   3.4198
```
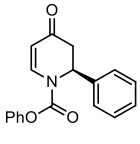



2b

(*S*)-phenyl 4-oxo-2-phenyl-3,4-dihydropyridine-1(2H)-carboxylate (2b): The zincbromide solution was prepared via method A. General procedure was followed and the crude material was purified with 5% Et$_3$N buffered Iatrobeads 6RS-8060 silica gel, providing **2b** in 81% yield, 93% ee as a white solid (Run 1). Run 2 provided 91% yield and 91% ee. Recystallized from hexane:ether (1:1) to provide 78% yield in >99% ee.

Crystallographic data: begins on page S-77.

^{1}H NMR (500 MHz, MeOD): δ 8.32 (d, *J* = 8.3 Hz, 1H), 7.50 – 7.25 (m, 8H), 7.15 (s, 2H), 5.97 (d, *J* = 7.0 Hz, 1H), 5.51 (d, *J* = 8.3 Hz, 1H), 3.41 (dd, *J* = 16.6, 7.5 Hz, 1H), 2.85 (d, *J* = 16.6 Hz, 1H).

^{13}C NMR (125 MHz, MeOD): δ 193.46, 151.61, 150.65, 143.41, 138.47, 129.23, 128.62, 127.67, 126.05, 125.38, 121.07, 107.70, 56.36, 41.66.

HRMS: (ESI-TOF) calculated for C$_{18}$H$_{15}$NO$_3$ ([M+H]$^+$): 294.1051, found: 294.1113.

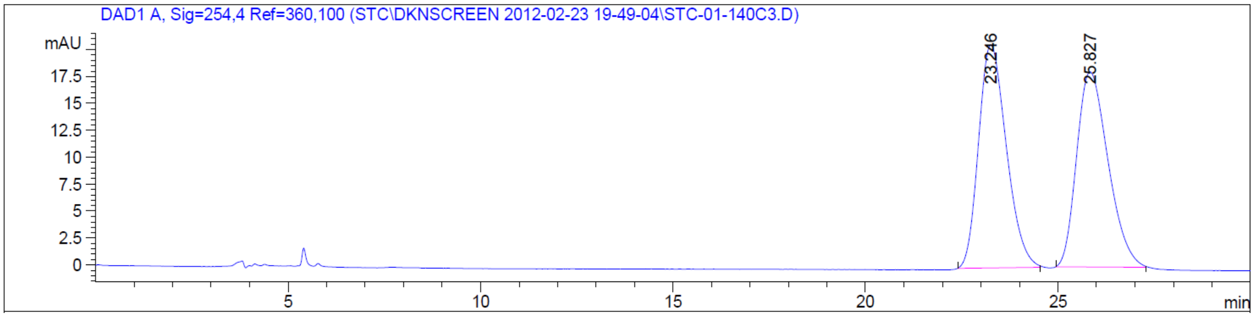
FTIR (thin film, cm^{-1}): 1733, 1666, 1605, 1494.

Optical rotation: $[\alpha]_D^{26}$ +25.4 (*c* 1.1, CHCl$_3$).

Melting point: 122-126°C.

HPLC: Chiralpak OD-H, 1:4, IPA to Hexanes, 30 min run, 0.8 mL/min.

Racemic standard:



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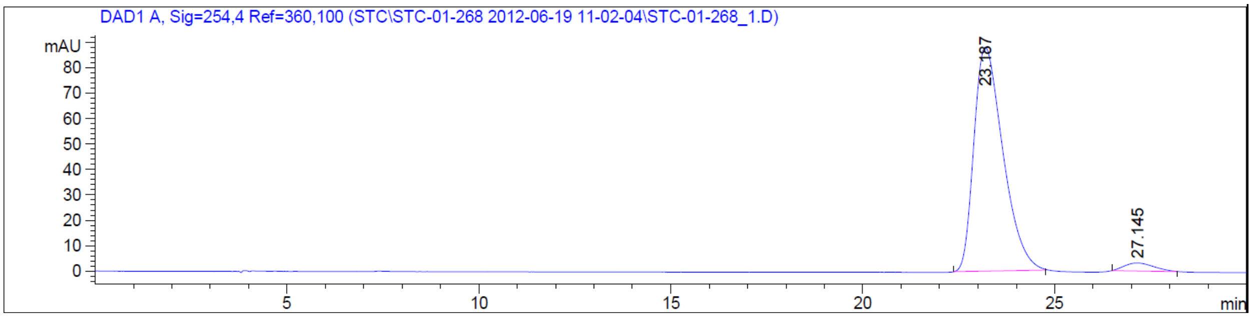
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]        %
----|-------|----|-------|----------|----------|--------|
   1  23.246 BB    0.7698 1040.75928   20.72812  50.2625
   2  25.827 BB    0.8504 1029.88733   18.13890  49.7375
```

Enantioenriched:



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Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]        %
----|-------|----|-------|----------|----------|--------|
   1  23.187 BB    0.8062 4659.59229   88.21658  96.3885
   2  27.145 BB    0.6374  174.58669    3.22595   3.6115
```
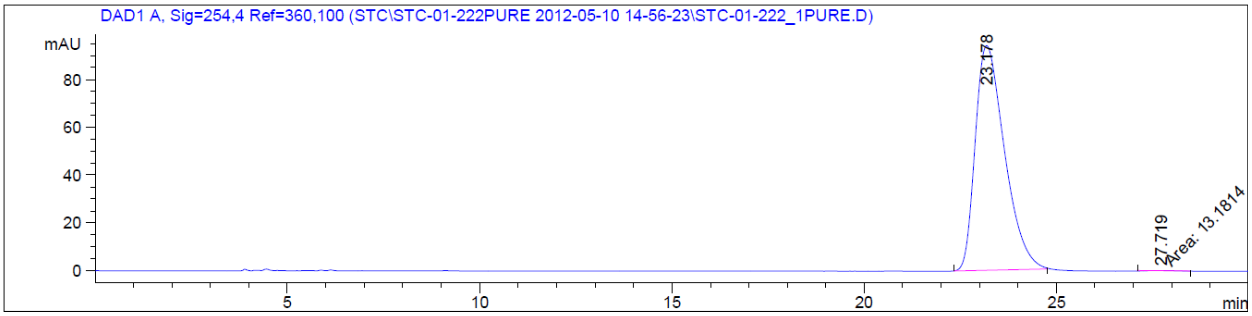

Recrystallized:



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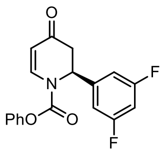
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]        %
----|-------|----|-------|----------|----------|--------|
   1  23.178 BB    0.8049 4995.19971   94.16082  99.7368
   2  27.719 MM    0.8260   13.18143 2.65954e-1   0.2632
```



2c

(*S*)-phenyl 2-(3,5-difluorophenyl)-4-oxo-3,4-dihydropyridine-1(2H)-carboxylate (2c): The zincbromide solution was prepared via method A. General procedure was followed, providing **2c** in 80% yield, >99% ee as a white foam (Run 1). Run 2 provided 79% yield and >99% ee.

^{1}H NMR (500 MHz, MeOD): δ 8.30 (d, *J* = 8.2 Hz, 1H), 7.44 (t, *J* = 7.9 Hz, 2H), 7.31 (t, *J* = 7.4 Hz, 1H), 7.19 (s, 2H), 7.00 (d, *J* = 6.5 Hz, 2H), 6.95 (t, *J* = 9.0 Hz, 1H), 5.96 (s, 1H), 5.51 (d, *J* = 8.3 Hz, 1H), 3.38 (dd, *J* = 17.2, 8.0 Hz, 1H), 2.82 (d, *J* = 16.7 Hz, 1H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 190.91, 164.28 (dd, *J* = 250.2, 12.7 Hz), 151.29, 150.19, 142.19, 141.77, 129.76, 126.69, 121.18, 110.16 (dd, *J* = 25.9, 5.9 Hz), 109.14, 103.96 (t, *J* = 25.2 Hz), 55.85, 41.51.

^{19}F NMR (282 MHz, $CDCl_3$): δ -107.71 (broad singlet).

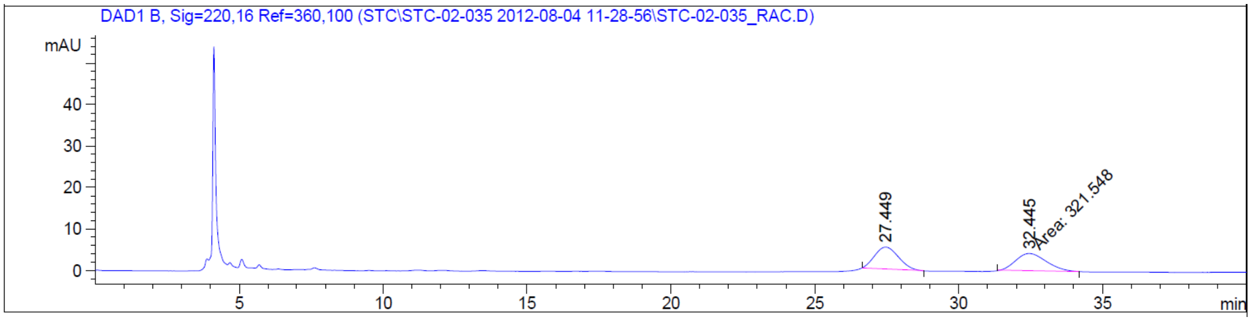
HRMS: (ESI-TOF) calculated for $C_{18}H_{13}F_2NO_3$ ($[M+H]^+$): 330.0863, found: 330.0960.

FTIR (thin film, cm^{-1}): 1739, 1672, 1607, 1419.

Optical rotation: $[\alpha]_D^{26}$ –17.5 (*c* 7.7, $CHCl_3$).

HPLC: Chiralpak OD-H, 1:4, IPA to Hexanes, 40 min run, 0.8 mL/min.

Racemic Standard:



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Peak RetTime Type  Width      Area       Height       Area
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----|-------|----|-------|----------|----------|--------|
   1  27.449 BB    0.7674  314.88690    5.37558  49.4767
   2  32.445 MM    1.2610  321.54761    4.24987  50.5233
```
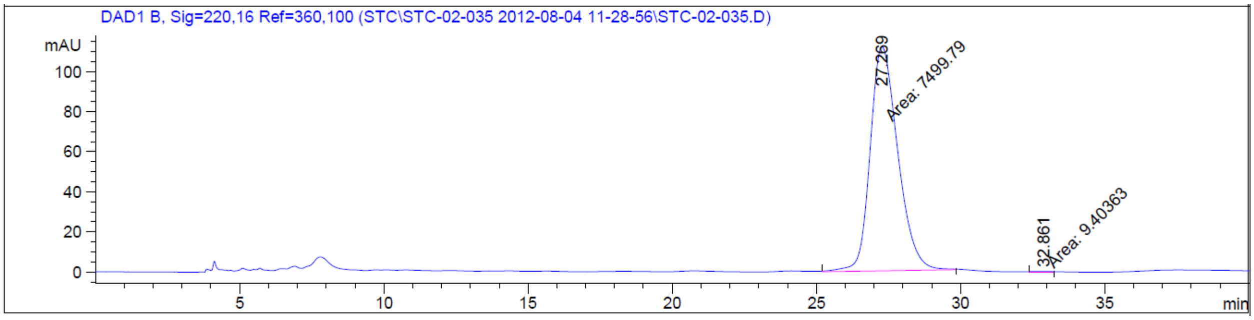

Enantioenriched:



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Peak RetTime Type  Width      Area       Height       Area
  #   [min]        [min]    [mAU*s]      [mAU]         %
----|-------|----|-------|----------|----------|--------|
   1  27.269 MM    1.1162 7499.79297  111.98203  99.8748
   2  32.861 MM    0.7863    9.40363 1.99332e-1   0.1252
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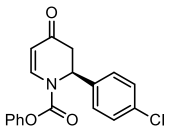


2d

(*S*)-phenyl 2-(4-chlorophenyl)-4-oxo-3,4-dihydropyridine-1(2H)-carboxylate (2d): The zincbromide solution was prepared via method A. General procedure was followed, providing **2d** in 85% yield, 95% ee as a clear oil (Run 1). Run 2 provided 83% yield and 96% ee.

^{1}H NMR (500 MHz, MeOD): δ 8.24 (d, *J* = 8.4 Hz, 1H), 7.43 – 7.25 (m, 7H), 7.15 (s, 2H), 5.91 (s, 1H), 5.47 (d, *J* = 8.4 Hz, 1H), 3.43 – 3.25 (dd, *J* = 16.7, 7,6 Hz, 1H), 2.78 (d, *J* = 16.7 Hz, 1H).

^{13}C NMR (125 MHz, MeOD): δ 194.67, 153.07, 152.23, 144.82, 138.88, 135.09, 130.92, 130.34, 128.84, 127.76, 122.74, 109.39, 57.41, 43.07.

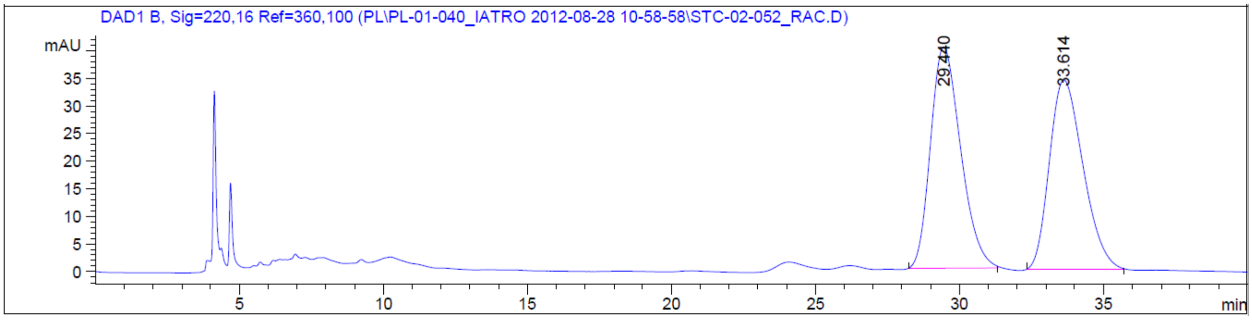
HRMS: (ESI-TOF) calculated for $C_{18}H_{14}ClNO_3$ ($[M+H]^+$): 328.0662, found: 328.0723.

FTIR (thin film, cm^{-1}): 1734, 1667, 1606, 1492.

Optical rotation: $[\alpha]_D^{26}$ +12.2 (*c* 1.0, $CHCl_3$).

HPLC: Chiralpak OD-H, 1:4, IPA to Hexanes, 40 min run, 0.8 mL/min.

Racemic Standard:



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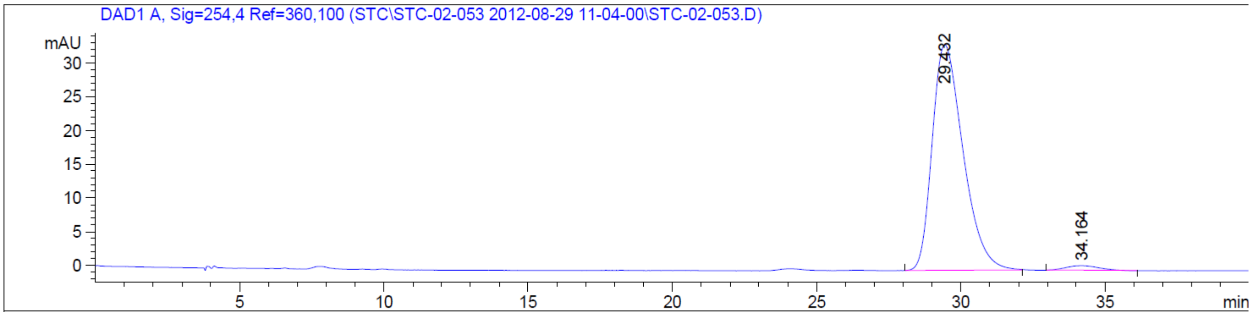
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  29.433 BB    0.9737  862.00659   12.12163  51.7299
   2  33.604 BB    1.0046  804.35516   10.14956  48.2701
```

Enantioenriched:



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Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  29.432 BB    1.1413 2493.43042   33.46296  97.7392
   2  34.164 BB    0.9624   57.67502 7.18551e-1   2.2608
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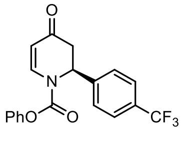


2e

(*S*)-phenyl 4-oxo-2-(4-(trifluoromethyl)phenyl)-3,4-dihydropyridine-1(2H)-carboxylate (2e): The zincbromide solution was prepared via method A. General procedure was followed, providing **2e** in 92% yield, 98% ee as a clear oil (Run 1). Run 2 provided 95% yield and 98% ee.

^{1}H NMR (500 MHz, MeOD): δ 8.31 (d, *J* = 8.3 Hz, 1H), 7.71 (d, *J* = 8.2 Hz, 2H), 7.56 (d, *J* = 8.2 Hz, 2H), 7.42 (t, *J* = 7.8 Hz, 2H), 7.30 (t, *J* = 7.4 Hz, 1H), 7.17 (s, 2H), 6.03 (s, 1H), 5.51 (d, *J* = 8.4 Hz, 1H), 3.41 (dd, *J* = 16.7, 7.6 Hz, 1H), 2.85 (d, *J* = 16.7 Hz, 1H).

^{13}C NMR (125 MHz, MeOD): δ 192.78 , 151.44 , 150.60 , 143.26 , 142.89 , 129.77 (q, *J* = 32.5 Hz), 129.29 , 126.25 , 126.14 , 125.57 (q, *J* = 3.3 Hz), 127.43 – 120.47 (q, *J* = 269.4 Hz.), 121.09 , 107.87 , 56.02 , 41.37 .

^{19}F NMR (282 MHz, CDCl$_3$): δ -62.64.

HRMS: (ESI-TOF) calculated for $C_{19}H_{14}F_3NO_3$ ($[M+H]^+$):362.0925, found: 362.0988.

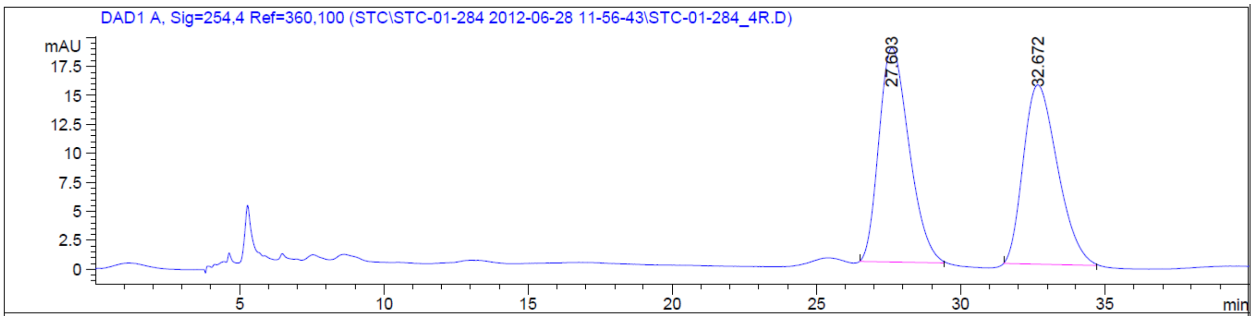
FTIR (thin film, cm^{-1}): 1736, 1670, 1606, 1493.

Optical rotation: $[\alpha]_D^{26}$ –4.2 (*c* 6.6, CHCl$_3$).

Melting point: 68-74°C.

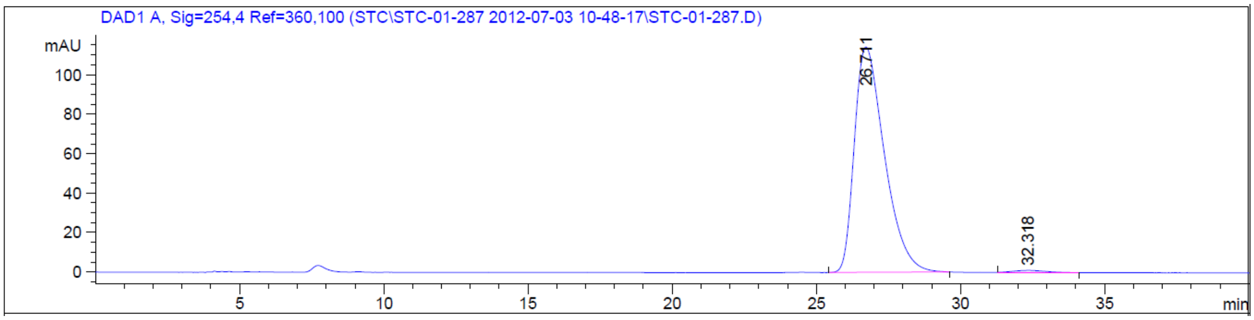
HPLC: Chiralpak OD-H, 1:4, IPA to Hexanes, 40 min run, 0.8 mL/min.

Racemic Standard:



```
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]        %
----|-------|----|-------|----------|----------|--------|
   1  27.603 BB    1.0021 1345.67505   18.51154  51.1702
   2  32.672 BB    0.9880 1284.12549   15.50898  48.8298
```

Enantioenriched:



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Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]        %
----|-------|----|-------|----------|----------|--------|
   1  26.711 BB    1.1112 8297.55176  114.26085  99.0091
   2  32.318 BB    0.9402   83.04057    1.05977   0.9909
```
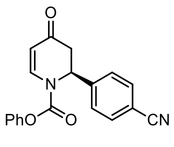



2f

(*S*)-phenyl 2-(4-cyanophenyl)-4-oxo-3,4-dihydropyridine-1(2H)-carboxylate (2f): The zincbromide solution was prepared via method A. General procedure was followed, providing **2f** in 90% yield, 97% ee as a white solid (Run 1). Run 2 provided 91% yield and 98% ee.

^{1}H NMR (500 MHz, MeOD): δ 8.34 (d, *J* = 7.5 Hz, 1H), 7.80 (d, *J* = 5.9 Hz, 2H), 7.58 (d, *J* = 8.0 Hz, 2H), 7.45 (t, *J* = 7.7 Hz, 2H), 7.32 (t, *J* = 7.4 Hz, 1H), 7.18 (s, 2H), 6.05 (s, 1H), 5.52 (d, *J* = 8.3 Hz, 1H), 3.46 (dd, *J* = 16.5, 7.2 Hz, 1H), 2.86 (d, *J* = 16.8 Hz, 1H).

^{13}C NMR (125 MHz, MeOD): δ 194.25, 153.08, 152.29, 145.73, 144.98, 134.25, 130.96, 128.28, 127.84, 122.75, 119.59, 113.30, 109.54, 57.81, 42.92.

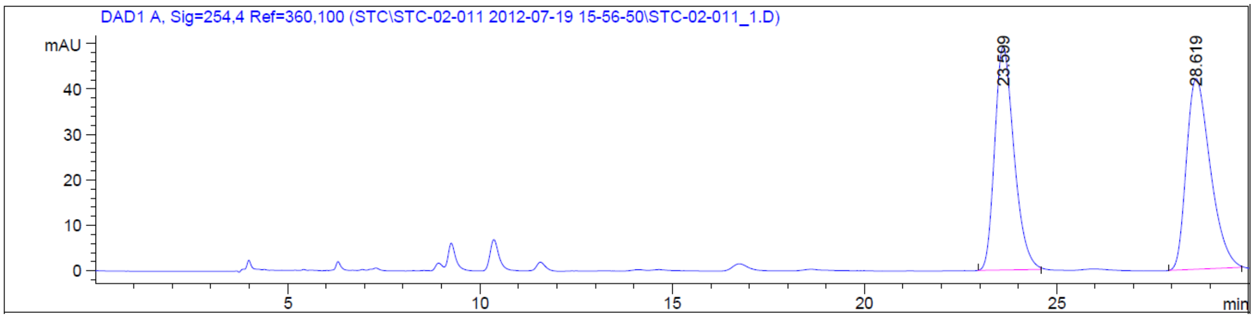
HRMS: (ESI-TOF) calculated for $C_{19}H_{14}N_2O_3$ ($[M+H]^+$): 308.1208, found: 308.1271.

FTIR (thin film, cm^{-1}): 2229, 1736, 1667, 1604, 1493.

Optical rotation: $[\alpha]_D^{26}$ –24.8 (*c* 1.7, $CHCl_3$).

HPLC: Chiralpak AD-H, 1:4, IPA to Hexanes, 30 min run, 0.8 mL/min.

Racemic standard:



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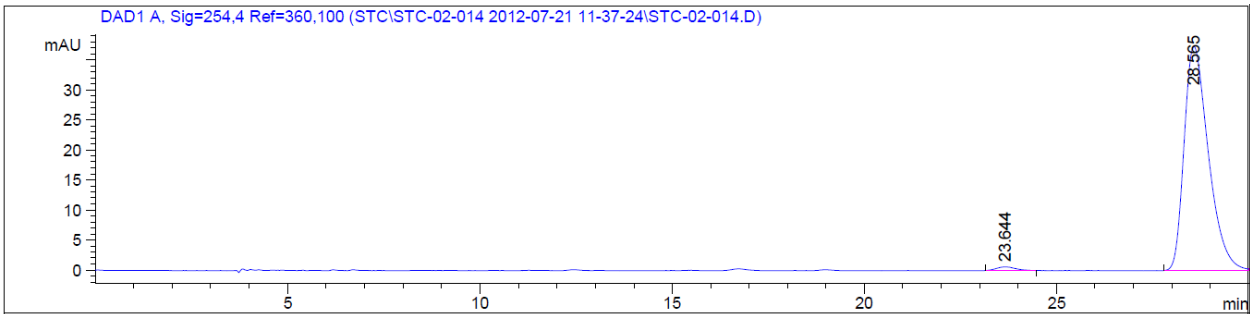
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]        %
----|-------|----|-------|----------|----------|--------|
   1  23.599 BB    0.5372 1725.95996   49.20678  48.6220
   2  28.619 BB    0.6640 1823.78784   42.05377  51.3780
```

Enantioenriched:



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Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]        %
----|-------|----|-------|----------|----------|--------|
   1  23.644 BB    0.4205   21.14775 6.12921e-1   1.2721
   2  28.565 BBA   0.6749 1641.29871   37.33656  98.7279
```
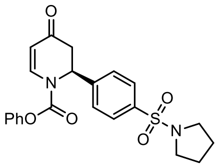



2g

(*S*)-phenyl 4-oxo-2-(4-(pyrrolidin-1-ylsulfonyl)phenyl)-3,4-dihydropyridine-1(2H)-carboxylate (2g): The zincbromide solution was prepared via method A. General procedure was followed with the exception of temperature (–78°C to rt) and the crude material was purified with flash chromatography (SiO_2) (1:1 hexanes: EtOAc), providing **2g** in 75% yield, 98% ee as a pale yellow foam (Run 1). Run 2 provided 66% yield and 97% ee.

^{1}H NMR (500 MHz, MeOD): δ 8.33 (d, *J* = 8.3 Hz, 1H), 7.88 (d, *J* = 8.0 Hz, 2H), 7.61 (d, *J* = 8.1 Hz, 2H), 7.42 (t, *J* = 7.8 Hz, 2H), 7.30 (t, *J* = 7.4 Hz, 1H), 7.17 (s, 2H), 6.05 (d, *J* = 7.8 Hz, 1H), 5.51 (d, *J* = 8.4 Hz, 1H), 3.45 (dd, *J* = 16.7, 7.6 Hz, 1H), 3.23 (q, *J* = 4.7, 3.3 Hz, 4H), 2.86 (d, *J* = 16.7 Hz, 1H), 1.84 – 1.63 (m, 4H).

^{13}C NMR (125 MHz, MeOD): δ 194.87, 153.58, 152.77, 145.89, 145.50, 138.53, 131.44, 130.13, 128.61, 128.31, 123.24, 110.04, 58.24, 49.91, 43.50, 26.99.

HRMS: (ESI-TOF) calculated for $C_{22}H_{22}N_2O_5S$ ($[M+H]^+$): 427.13222, found: 427.13105.

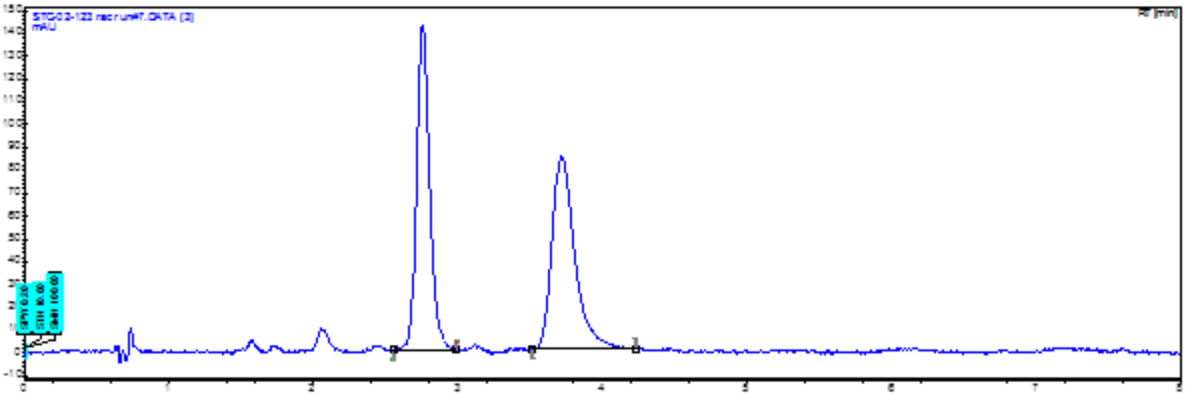
FTIR (thin film, cm^{-1}): 1739, 1671, 1607, 1333

Optical rotation: $[\alpha]_D^{26}$ +5.0 (*c* 1.0, $CHCl_3$).

SFC: Chiralpak IA, 40% MeOH (DEA)/CO_2 (100 bar) 40 °C, 3ml/min, 220 nm.

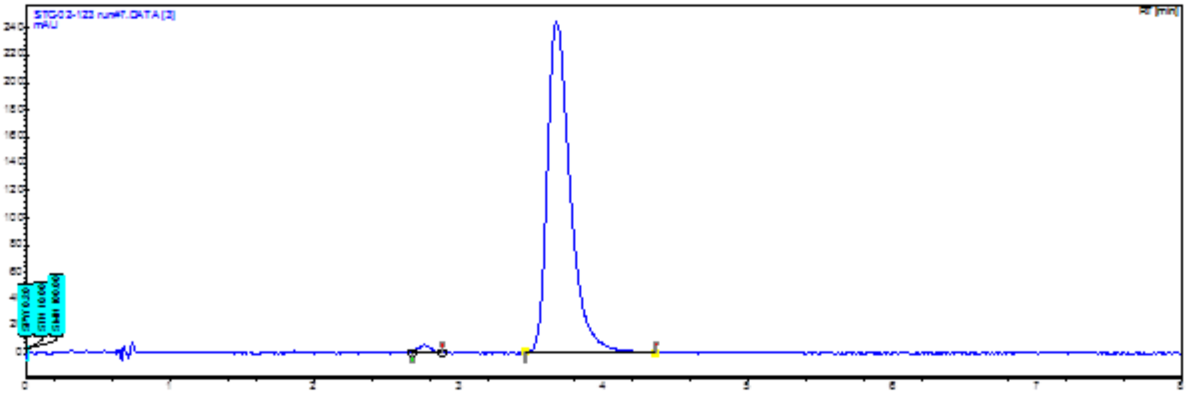
Melting Point: 118-120 °C.

Racemic Standard:

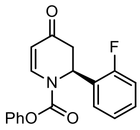


Index	Time	Width	Height	Res. HW	Selectivity	Area	Area
	[Min]	[Min]	[µV]			[µV.Min]	[%]
1	2.75	0.10	142.5	0.00	0.00	15.1	49.748
2	3.72	0.16	84.1	4.45	1.35	15.2	50.252
Total			226.6			30.3	100.000

Enantioenriched:



Index	Time	Width	Height	Res. HW	Selectivity	Area	Area
	[Min]	[Min]	[µV]			[µV.Min]	[%]
2	2.75	0.10	5.7	0.00	0.00	0.6	1.234
1	3.67	0.16	243.4	4.16	1.33	44.3	98.766
Total			249.2			44.8	100.000



2h

(*S*)-phenyl 2-(2-fluorophenyl)-4-oxo-3,4-dihydropyridine-1(2H)-carboxylate (2h): The zincbromide solution was prepared via method A. General procedure was followed with the following exceptions: the reaction was warmed to a constant –20°C and the crude material was purified with 5% Et_3N buffered Iatrobeads 6RS-8060 silica gel, providing **2h** in 62% yield, 92% ee as a white solid (Run 1). Run 2 provided 56% yield and 90% ee.

^{1}H NMR (500 MHz, MeOD): δ 8.39 (d, *J* = 8.4 Hz, 1H), 7.46 – 7.37 (m, 3H), 7.36 – 7.28 (m, 2H), 7.25 – 7.17 (m, 2H), 7.12 (s, 2H), 6.19 (d, *J* = 7.6 Hz, 1H), 5.75 – 5.38 (m, 1H), 3.44 (dd, *J* = 16.6, 7.9 Hz, 1H), 2.75 (dd, *J* = 16.8, 1.5 Hz, 1H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 191.45, 160.73 (d, *J* = 247.0 Hz), 151.25, 150.25, 142.52, 130.00 (d, *J* = 8.4 Hz), 129.63, 126.52, 126.14 (d, *J* = 3.2 Hz), 125.37 (d, *J* = 11.7 Hz), 124.52 (d, *J* = 3.1 Hz), 121.17, 116.41 (d, *J* = 21.7 Hz), 108.78, 51.50, 41.09.

^{19}F NMR (282 MHz, $CDCl_3$): δ –119.67 ppm.

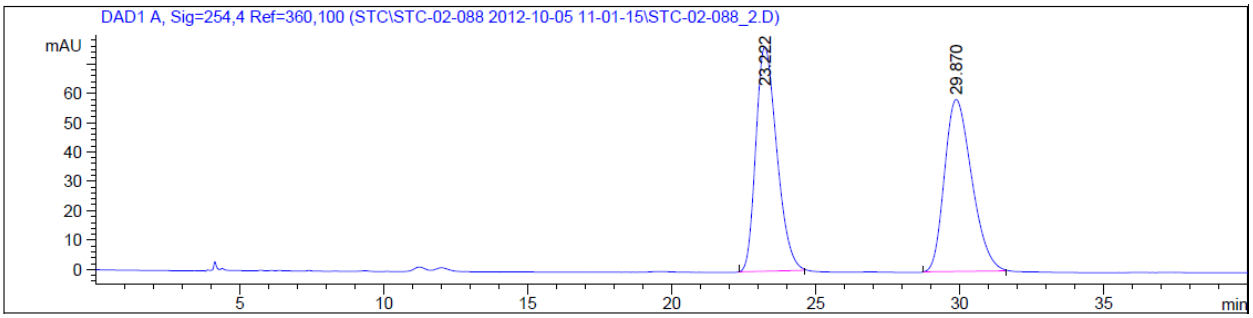
HRMS: (ESI-TOF) calculated for $C_{18}H_{14}FNO_3$ ($[M+H]^+$): 312.1030, found: 312.1025 .

FTIR (thin film, cm^{-1}): 1742, 1672, 1611, 1488.

Optical rotation: $[\alpha]_D^{26}$ +13.3 (*c* 1.0, $CHCl_3$).

HPLC: Chiralpak OD-H, 1:4, IPA to Hexanes, 40 min run, 0.8 mL/min.

Racemic Standard:



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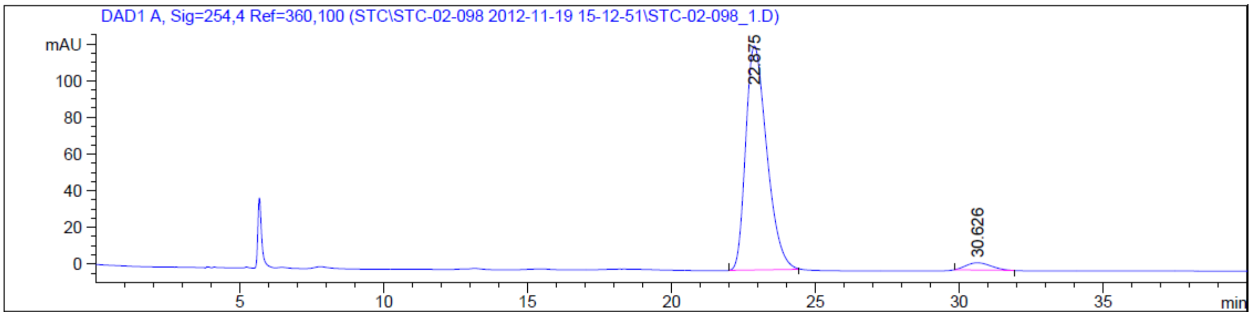
Peak RetTime Type  Width     Area      Height      Area
  #   [min]        [min]   [mAU*s]     [mAU]        %
----|-------|----|-------|----------|----------|--------|
   1  23.222 BB    0.7756 3874.73901   76.41698  50.0528
   2  29.870 BB    1.0178 3866.55884   58.60061  49.9472
```

Enantioenriched:



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Peak RetTime Type  Width     Area      Height      Area
  #   [min]        [min]   [mAU*s]     [mAU]        %
----|-------|----|-------|----------|----------|--------|
   1  22.875 BB    0.7890 6256.03564  122.25266  96.1654
   2  30.626 BB    0.7444  249.46289    4.05113   3.8346
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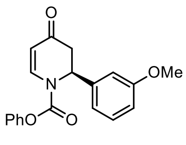


2i

(*S*)-phenyl 2-(3-methoxyphenyl)-4-oxo-3,4-dihydropyridine-1(2H)-carboxylate (2i): The zincbromide solution was prepared via method A. General procedure was followed, providing **2i** in 85% yield, 89% ee as a clear oil (Run 1). Run 2 provided 93% yield and 87% ee.

^{1}H NMR (500 MHz, MeOD): δ 8.28 (d, *J* = 8.4 Hz, 1H), 7.42 (t, *J* = 7.8 Hz, 2H), 7.30 (q, *J* = 7.3 Hz, 2H), 7.14 (s, 2H), 6.93 – 6.87 (m, 3H), 5.91 (d, *J* = 6.9 Hz, 1H), 5.48 (d, *J* = 8.4 Hz, 1H), 3.79 (s, 3H), 3.40 – 3.29 (dd, *J*= obscured 1H), 2.82 (d, *J* = 16.6 Hz, 1H).

^{13}C NMR (125 MHz, MeOD):δ 195.10, 161.84, 153.25, 152.29, 145.01, 141.72, 131.42, 130.92, 127.73, 122.75, 119.04, 114.33, 113.18, 109.32, 57.94, 55.98, 43.26.

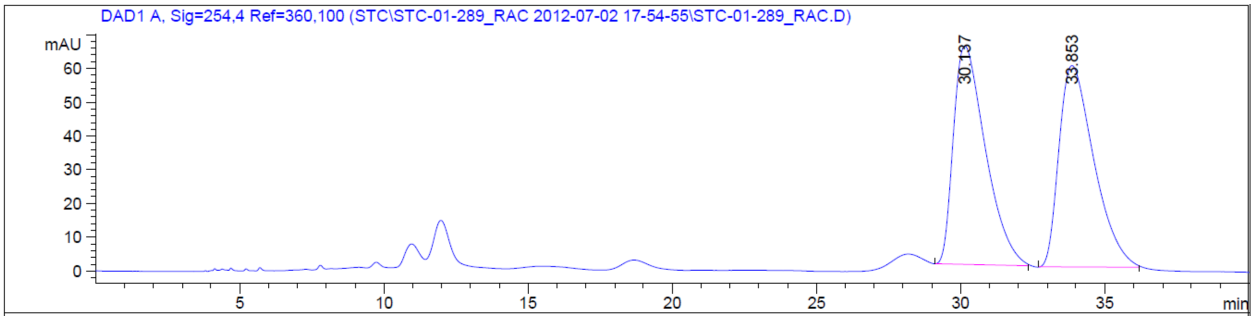
HRMS: (ESI-TOF) calculated for $C_{19}H_{17}NO_4$ ($[M+H]^+$): 324.1157, found: 324.1211.

FTIR (thin film, cm^{-1}): 1735, 1669, 1605, 1489.

Optical rotation: $[\alpha]_D^{26}$ +15.1 (*c* 3.2, $CHCl_3$).

HPLC: Chiralpak OD-H, 1:4, IPA to Hexanes, 40 min run, 0.8 mL/min.

Racemic standard:



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Peak RetTime Type  Width      Area        Height       Area
  #   [min]        [min]    [mAU*s]       [mAU]         %
----|-------|----|-------|----------|----------|--------|
  1   30.137 BB     1.1563 5017.29443   64.87373  49.9071
  2   33.853 BB     1.2686 5035.96533   59.79429  50.0929
```
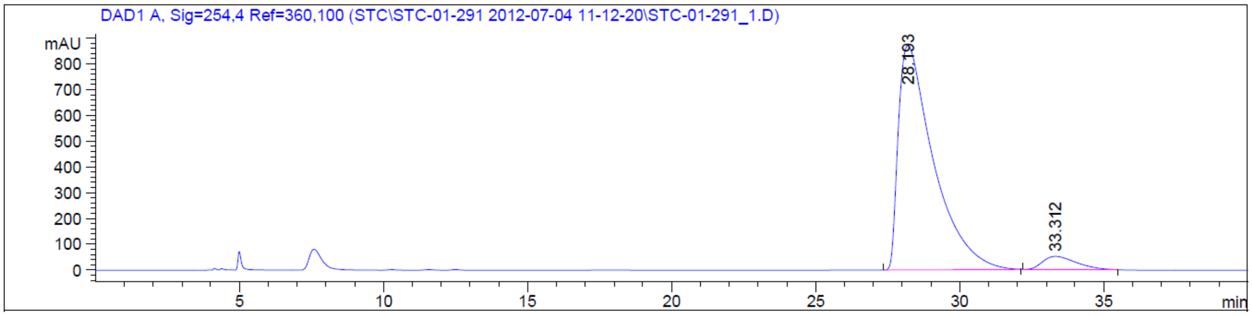

Enantioenriched:



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Peak RetTime Type  Width      Area       Height       Area
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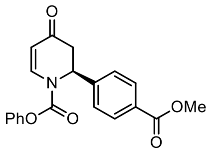
----|-------|----|-------|----------|----------|--------|
  1   28.193 BB     1.2459 7.40842e4   871.41205  94.3717
  2   33.312 BB     1.2280 4418.32227   52.81436   5.6283
```



2j

(*S*)-phenyl 2-(4-(methoxycarbonyl)phenyl)-4-oxo-3,4-dihydropyridine-1(2H)-carboxylate (2j): The zincchloride solution was prepared via method B. General procedure was followed, providing **2j** in 55% yield, 95% ee as a clear oil (Run 1). Run 2 provided 59% yield and 95% ee.

^{1}H NMR (500 MHz, MeOD): δ 8.27 (d, *J* = 8.3 Hz, 1H), 7.41 (t, *J* = 7.9 Hz, 2H), 7.30 (q, *J* = 7.4 Hz, 2H), 7.14 (s, 2H), 6.92 – 6.87 (m, 3H), 5.91 (d, *J* = 6.9 Hz, 1H), 5.48 (d, *J* = 8.4 Hz, 1H), 3.79 (s, 3H), 3.41 – 3.29 (dd, *J*= obscured, 1H), 2.81 (d, *J* = 17.9 Hz, 1H).

^{13}C NMR (125 MHz, MeOD): δ 193.46, 160.19, 150.64, 143.36, 140.06, 129.76, 129.26, 126.07, 121.09, 117.38, 112.68, 111.51, 107.66, 56.28, 54.32, 41.61.

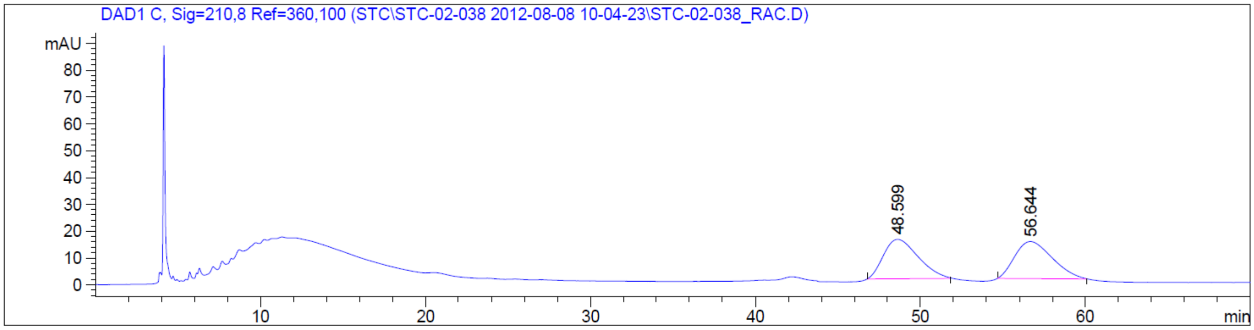
HRMS: (ESI-TOF) calculated for $C_{20}H_{17}NO_5$ ($[M+H]^+$): 352.1106, found: 352.1173.

FTIR (thin film, cm^{-1}): 1719, 1669, 1606, 1434.

Optical rotation: $[\alpha]_D^{26}$ +7.1 (*c* .81, $CHCl_3$).

HPLC: Chiralpak OD-H, 1:4, IPA to Hexanes, 70 min run, 0.8 mL/min.

Racemic Standard:



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Peak RetTime Type  Width     Area      Height     Area
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----|-------|----|-------|----------|----------|--------|
   1  48.599 BB    1.7515 2173.97656   14.78479  49.4881
   2  56.644 BB    1.8700 2218.95508   13.93283  50.5119
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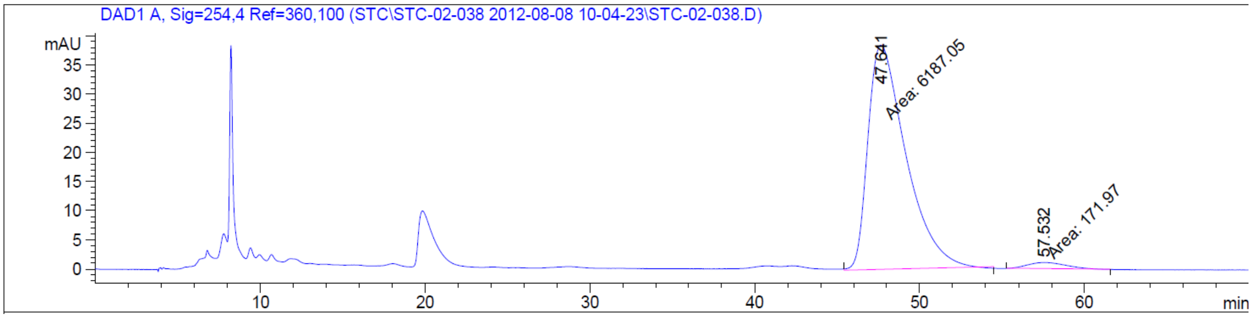
Enantioenriched:



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Peak RetTime Type  Width     Area      Height     Area
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----|-------|----|-------|----------|----------|--------|
   1  47.641 MM    2.6791 6187.04688   38.48969  97.2957
   2  57.532 MM    2.7038  171.96974    1.06005   2.7043
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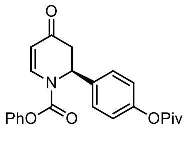


2k

(*S*)-phenyl 4-oxo-2-(4-(pivaloyloxy)phenyl)-3,4-dihydropyridine-1(2H)-carboxylate (2k): The zincchloride solution was prepared via method B. General procedure was followed, providing **2k** in 46% yield, 82% ee as a white foam. (Run 1). Run 2 provided 39% yield and 73% ee.

^{1}H NMR (500 MHz, MeOD): δ 8.29 (d, *J* = 8.4 Hz, 1H), 7.43 (dd, *J* = 12.3, 8.2 Hz, 3H), 7.30 (t, *J* = 7.4 Hz, 1H), 7.16 (d, *J* = 6.2 Hz, 3H), 7.11 (d, *J* = 8.5 Hz, 2H), 5.98 (d, *J* = 7.1 Hz, 1H), 5.51 (d, *J* = 8.4 Hz, 1H), 3.41 (dd, *J* = 16.7, 7.5 Hz, 1H), 2.85 (d, *J* = 16.7 Hz, 1H), 1.37 (s, 9H).

^{13}C NMR (125 MHz, MeOD): δ 193.32, 177.11, 151.54, 150.83, 150.64, 143.31, 136.09, 129.24, 126.73, 126.07, 121.79, 121.11, 107.70, 55.92, 41.54, 38.69, 26.04.

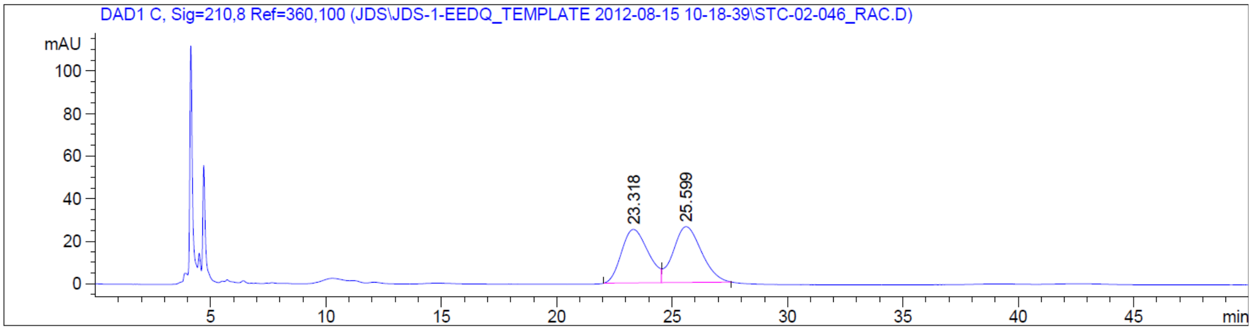
HRMS: (ESI-TOF) calculated for $C_{23}H_{23}NO_5$ ($[M+H]^+$): 394.1572, found: 394.1633.

FTIR (thin film, cm^{-1}): 1738, 1670,1606, 1507.

Optical rotation: $[\alpha]_D^{26}$ +15.1 (*c* 1.2, $CHCl_3$).

HPLC: Chiralpak OD-H, 1:4, IPA to Hexanes, 50 min run, 0.8 mL/min.

Racemic Standard:



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Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]        %
----|-------|----|-------|----------|----------|--------|
   1  23.318 BV    1.1427 2056.16797   25.33927  47.4051
   2  25.599 VB    1.1689 2281.27686   26.43262  52.5949
```
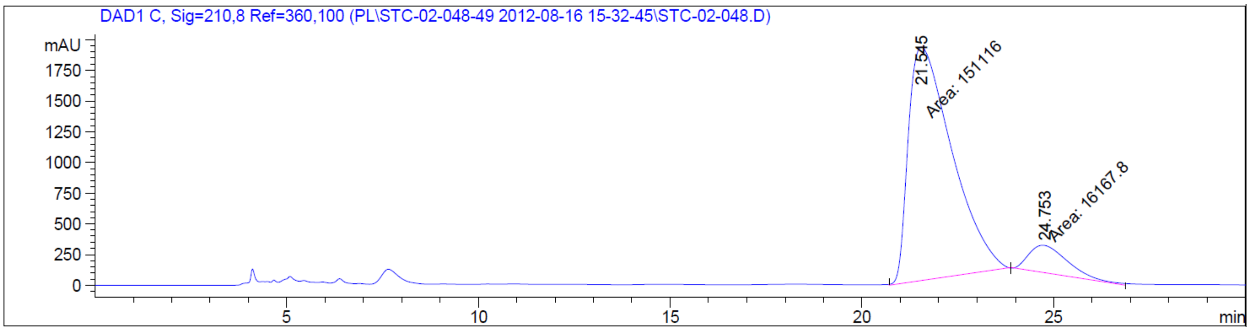

Enantioenriched:



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Peak RetTime Type  Width     Area      Height     Area
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----|-------|----|-------|----------|----------|--------|
   1  21.544 MM    1.2896 1.00250e5 1295.61719  90.9005
   2  24.746 MM    1.1576 1.00354e4  144.48186   9.0995
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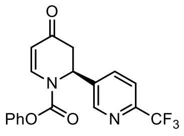


2l

(*S*)-phenyl 4-oxo-6'-(trifluoromethyl)-3,4-dihydro-[2,3'-bipyridine]-1(2H)-carboxylate (2l): The zincbromide solution was prepared via method A. General procedure was followed with the exception of temperature (–78°C to rt) and the crude material was purified with flash chromatography (SiO_2) (1:1 hexanes: EtOAc), providing **2l** in 70% yield, >99% ee as a yellow oil (Run 1). Run 2 provided 72% yield and >99% ee.

^{1}H NMR (500 MHz, MeOD): δ 8.77 (s, 1H), 8.29 (d, *J* = 8.2 Hz, 1H), 8.05 (d, *J* = 9.9 Hz, 1H), 7.83 (d, *J* = 8.2 Hz, 1H), 7.43 (t, *J* = 7.9 Hz, 2H), 7.30 (t, *J* = 7.4 Hz, 1H), 7.20 (s, 2H), 6.11 (s, 1H), 5.53 (d, *J* = 8.4 Hz, 1H), 3.45 (dd, *J* = 16.9, 7.6 Hz, 1H), 2.87 (d, *J* = 16.9 Hz, 1H).

^{13}C NMR (125 MHz, MeOD): δ 192.22 , 151.27 , 150.57 , 147.89 , 147.14 (q, *J* = 35.0 Hz), 143.10 , 138.11 , 135.72 , 129.32 , 126.22 , 124.87 – 117.88 (q, *J* = 268.2), 121.10 , 120.48 (d, *J* = 20.1 Hz), 107.93 , 54.17 , 40.85 .

^{19}F NMR (282 MHz, $CDCl_3$): δ -68.03.

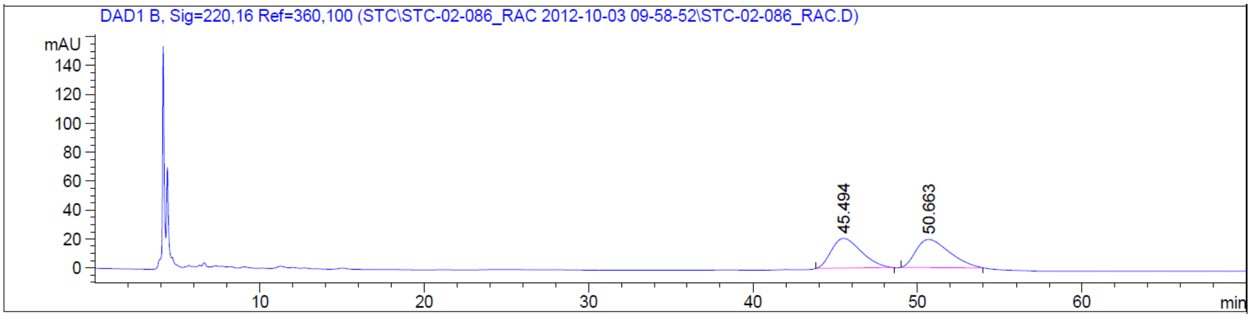
HRMS: (ESI-TOF) calculated for $C_{18}H_{13}F_3N_2O_3$ ($[M+H]^+$): 363.0878, found: 363.0943.

FTIR (thin film, cm^{-1}): 1735, 1669, 1605, 1493.

Optical rotation: $[\alpha]_D^{26}$ –4.5 (*c* 3.3, $CHCl_3$).

HPLC: Chiralpak OD-H, 1:4, IPA to Hexanes, 70 min run, 0.8 mL/min.

Racemic Standard:



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Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]        %
----|-------|----|-------|----------|----------|--------|
   1  45.494 BB    1.5463 2654.69141   20.75353  48.7617
   2  50.663 BB    1.6891 2789.51831   19.54519  51.2383
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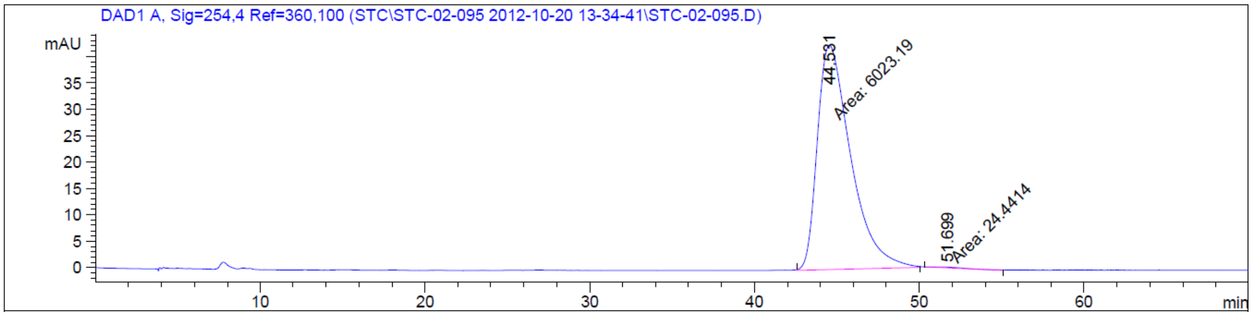
Enantioenriched:



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Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]        %
----|-------|----|-------|----------|----------|--------|
   1  44.531 MM    2.3561 6023.19141   42.60728  99.5959
   2  51.699 MM    2.3620   24.44138 1.72464e-1   0.4041
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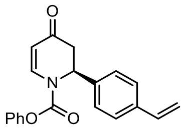


2m

(*S*)-phenyl 4-oxo-2-(4-vinylphenyl)-3,4-dihydropyridine-1(2H)-carboxylate (2m): The zincbromide solution was prepared via method A. General procedure was followed with the exception of temperature (–78°C to –50°C) and the crude material was purified with 5% Et_3N buffered Iatrobeads 6RS-8060 silica gel, providing **2m** in 90 % yield, 52% ee as a pale yellow oil (Run 1). Run 2 provided 87% yield and 50% ee.

^{1}H NMR (500 MHz, MeOD): δ 8.30 (d, *J* = 8.4 Hz, 1H), 7.48 (d, *J* = 8.0 Hz, 2H), 7.43 (t, *J* = 7.8 Hz, 2H), 7.31 (dd, *J* = 15.4, 7.7 Hz, 3H), 7.16 (s, 2H), 6.76 (dd, *J* = 17.6, 11.0 Hz, 1H), 5.96 (d, *J* = 7.2 Hz, 1H), 5.83 (d, *J* = 17.7 Hz, 1H), 5.50 (d, *J* = 8.5 Hz, 1H), 5.28 (d, *J* = 11.0 Hz, 1H), 3.41 (dd, *J* = 16.7, 7.5 Hz, 1H), 2.84 (d, *J* = 16.9 Hz, 1H).

^{13}C NMR (125 MHz, MeOD): δ 194.87, 153.02, 152.05, 144.76, 139.31, 138.85, 137.39, 130.63, 127.74, 127.45, 127.08, 122.48, 114.71, 109.09, 57.59, 42.92.

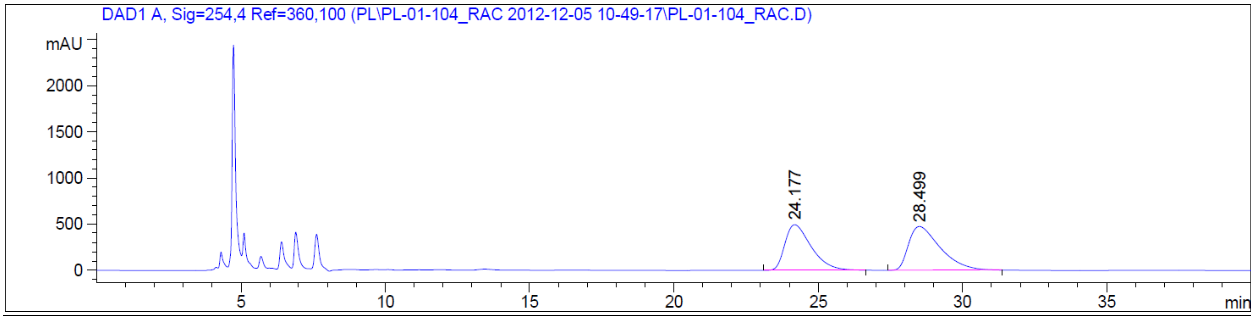
HRMS: (ESI-TOF) calculated for $C_{20}H_{17}NO_3$ ($[M+H]^+$): 320.1281, found: 320.1296.

FTIR (thin film, cm^{-1}): 1736, 1669, 1606, 1306.

Optical rotation: $[\alpha]_D^{26}$ –3.7 (*c* 11.6, $CHCl_3$).

HPLC: Chiralpak OD-H, 1:4, IPA to Hexanes, 40 min run, 0.8 mL/min.

Racemic Standard:



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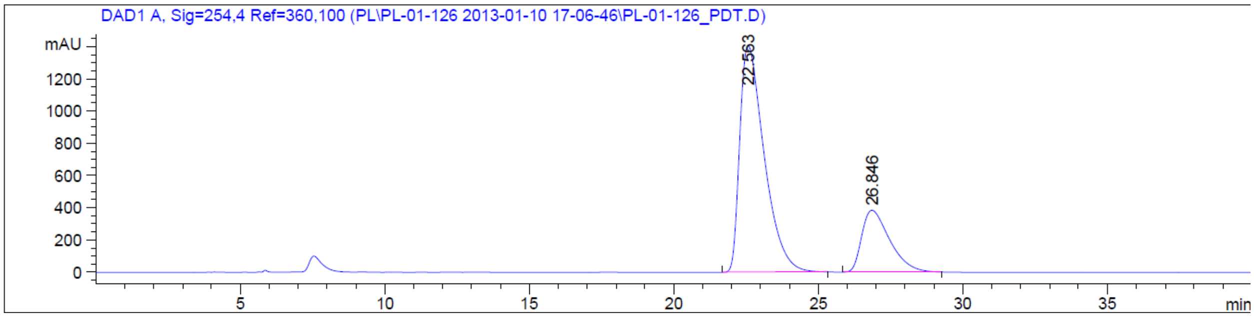
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]        %
----|-------|----|-------|----------|----------|--------|
   1  24.183 BB    1.0229 2.42971e4  362.07007  51.2368
   2  28.498 BB    1.1469 2.31240e4  302.82648  48.7632
```

Enantioenriched:



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Peak RetTime Type  Width     Area      Height     Area
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----|-------|----|-------|----------|----------|--------|
   1  22.563 BB    0.8975 8.29257e4 1407.22388  76.2129
   2  26.846 BB    1.0184 2.58822e4  383.96167  23.7871
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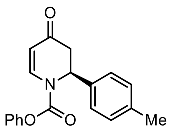


2n

(*S*)-phenyl 4-oxo-2-(p-tolyl)-3,4-dihydropyridine-1(2H)-carboxylate (2n): The zincbromide solution was prepared via method A. General procedure was followed with the exception of temperature (–78°C to –50°C), providing **2n** in 73% yield, 60% ee as a white foam (Run 1). Run 2 provided 69% yield and 53% ee.

^{1}H NMR (500 MHz, MeOD): δ 8.26 (d, *J* = 8.3 Hz, 1H), 7.41 (t, *J* = 7.8 Hz, 2H), 7.29 (t, *J* = 7.4 Hz, 1H), 7.24 – 7.18 (m, 4H), 7.14 (s, 2H), 5.90 (d, *J* = 6.5 Hz, 1H), 5.47 (d, *J* = 8.3 Hz, 1H), 3.37 – 3.27 (dd, *J* = obscured, 1H,), 2.80 (d, *J* = 16.6 Hz, 1H), 2.33 (s, 3H).

^{13}C NMR (125 MHz, MeOD): δ 195.29, 153.30, 152.32, 145.01, 139.28, 137.08, 130.91, 130.85, 127.72, 127.03, 122.77, 109.33, 57.83, 43.32, 21.35.

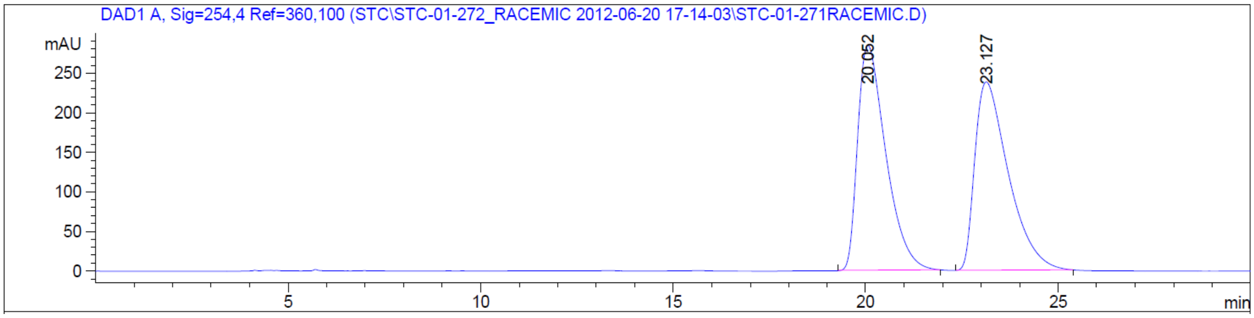
HRMS: (ESI-TOF) calculated for $C_{19}H_{17}NO_3$ ($[M+H]^+$): 308.1208, found: 308.1271.

FTIR (thin film, cm^{-1}): 1733, 1667, 1604, 1494.

Optical rotation: $[\alpha]_D^{26}$ –24.8 (*c* .77, $CHCl_3$).

HPLC: Chiralpak OD-H, 1:4, IPA to Hexanes, 30 min run, 0.8 mL/min.

Racemic Standard:



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Peak RetTime Type  Width     Area       Height     Area
  #   [min]        [min]   [mAU*s]      [mAU]       %
----|-------|----|-------|----------|----------|--------|
  1  20.052 BB    0.7784 1.45172e4  284.96182  50.0850
  2  23.127 BB    0.9090 1.44680e4  238.08754  49.9150
```
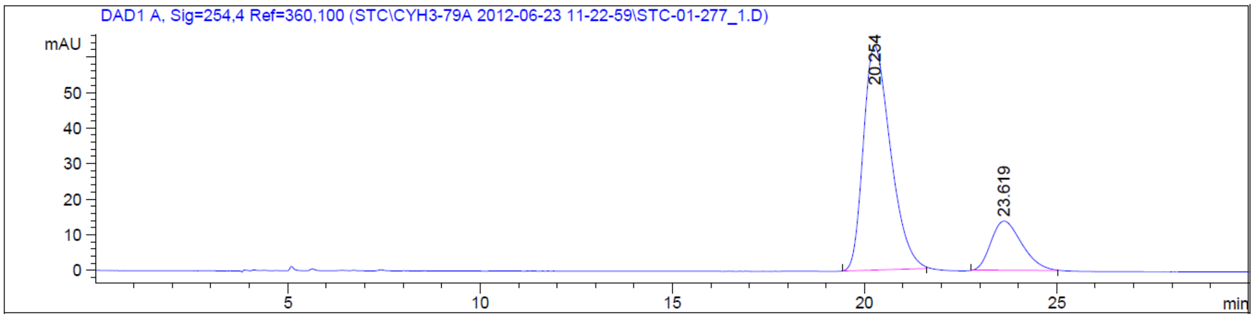

Enantioenriched:



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  1  20.254 BB    0.7535 3101.86646   63.09587  79.9411
  2  23.619 BB    0.8296  778.32428   13.89206  20.0589
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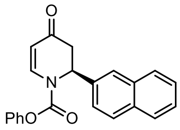


2o

(*S*)-phenyl 2-(naphthalen-2-yl)-4-oxo-3,4-dihydropyridine-1(2H)-carboxylate (2o): The zincbromide solution was prepared via method A. General procedure was followed, providing **2o** in 57% yield, 83% ee as a white solid (Run 1). Run 2 provided 51% yield and 79% ee.

^{1}H NMR (500 MHz, MeOD): δ 8.38 (d, *J* = 8.4 Hz, 1H), 7.93 (d, *J* = 8.6 Hz, 1H), 7.89 – 7.85 (m, 2H), 7.79 (s, 1H), 7.56 – 7.48 (m, 3H), 7.41 (t, *J* = 7.8 Hz, 2H), 7.29 (t, *J* = 7.4 Hz, 1H), 7.14 (s, 2H), 6.13 (d, *J* = 7.0 Hz, 1H), 5.54 (d, *J* = 8.4 Hz, 1H), 3.49 (dd, *J* = 16.7, 7.5 Hz, 1H), 2.97 (d, *J* = 16.7 Hz, 1H).

^{13}C NMR (125 MHz, MeOD): δ 195.20, 153.38, 152.36, 145.17, 137.40, 134.94, 134.65, 130.92, 130.37, 129.31, 128.96, 127.95, 127.74, 125.76, 125.13, 122.78, 109.47, 58.20, 43.22 (1 carbon overlap).

HRMS: (ESI-TOF) calculated for $C_{22}H_{17}NO_3$ ($[M+H]^+$): 344.1195, found: 344.1268.

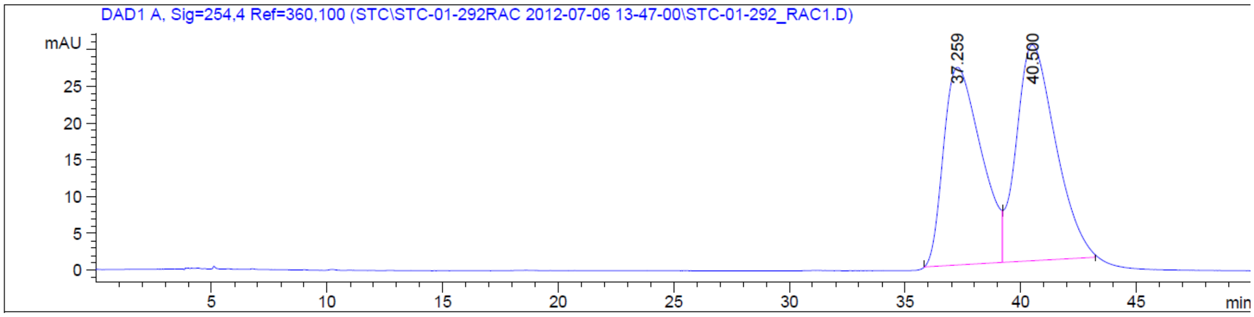
FTIR (thin film, cm^{-1}): 1736, 1669, 1606, 1494.

Optical rotation: $[\alpha]_D^{26}$ +6.4 (*c* .93, $CHCl_3$).

Melting point: 130-132°C.

HPLC: Chiralpak OD-H, 1:4, IPA to Hexanes, 50 min run, 0.8 mL/min.

Racemic standard:



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  1  37.259 BV    1.5268 3053.40234   26.89025  46.7997
  2  40.500 VB    1.5351 3470.99976   29.36287  53.2003
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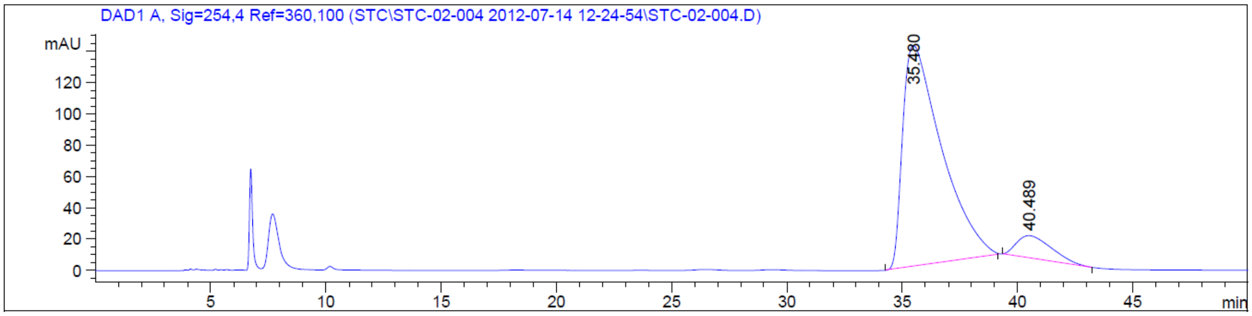
Enantioenriched:



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Peak RetTime Type  Width     Area       Height      Area
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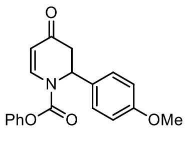
----|-------|----|-------|----------|----------|--------|
  1  35.480 BB    1.6748 1.65945e4  141.23099  91.5831
  2  40.489 BB    1.2849 1525.11084  14.24687   8.4169
```



2p

Phenyl 2-(4-methoxyphenyl)-4-oxo-3,4-dihydropyridine-1(2H)-carboxylate (2p): The zincbromide solution was prepared via method A. General procedure was followed, providing **2p** in 77% yield, 0% ee as a clear oil. Attempts to increase the selectivity included performing syringe pump addition of the nucleophile, the addition of additives including 1,4-dioxane, dimethoxyethane, and using different types of zinc based nucleophiles including $(4\text{-OMePh})_2Zn$, 4-OMePhZnEt, 4-OMePhZnCl·LiCl, and salt free $(4\text{-MeO})_2Zn$ provided only racemic **2p**.

^{1}H NMR (500 MHz, MeOD): δ 8.23 (d, *J* = 8.2 Hz, 1H), 7.42 (t, *J* = 7.8 Hz, 2H), 7.28 (dd, *J* = 16.2, 8.1 Hz, 3H), 7.15 (d, *J* = 7.9 Hz, 2H), 7.03 – 6.91 (m, 2H), 5.87 (d, *J* = 7.2 Hz, 1H), 5.47 (d, *J* = 8.3 Hz, 1H), 3.78 (s, 3H), 3.31 (dd, *J* = 16.6, 7.4 Hz, 1H), 2.79 (dt, *J* = 16.5, 1.6 Hz, 1H).

^{13}C NMR (125 MHz, MeOD): δ 193.73, 159.46, 151.60, 150.66, 143.24, 130.36, 129.27, 126.81, 126.06, 121.13, 113.89, 107.61, 55.87, 54.36, 41.65.

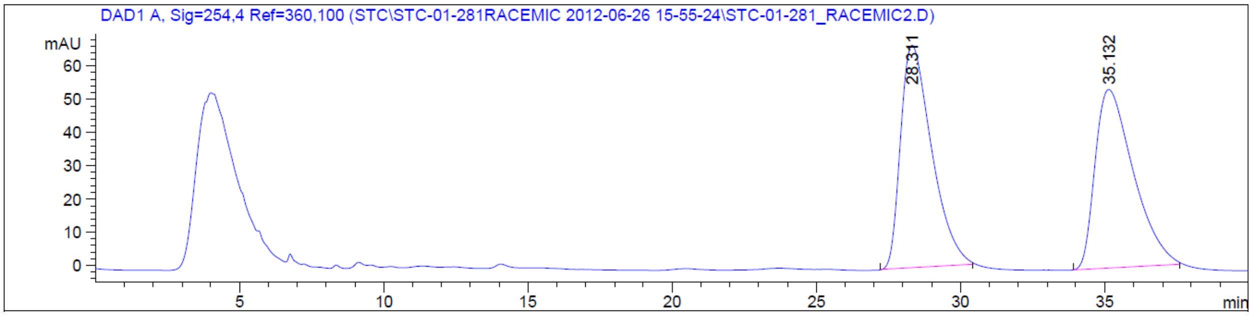
HRMS: (ESI-TOF) calculated for $C_{19}H_{17}NO_4$ ($[M+H]^+$): 324.1157, found: 324.1191.

FTIR (thin film, cm^{-1}): 1735, 1665, 1605, 1440.

Optical rotation: N/A.

HPLC: Chiralpak OD-H, 1:4, IPA to Hexanes, 40 min run, 0.8 mL/min.

Racemic Standard:



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   2  35.132 BB    1.3340 4956.03955   53.73827  49.5472
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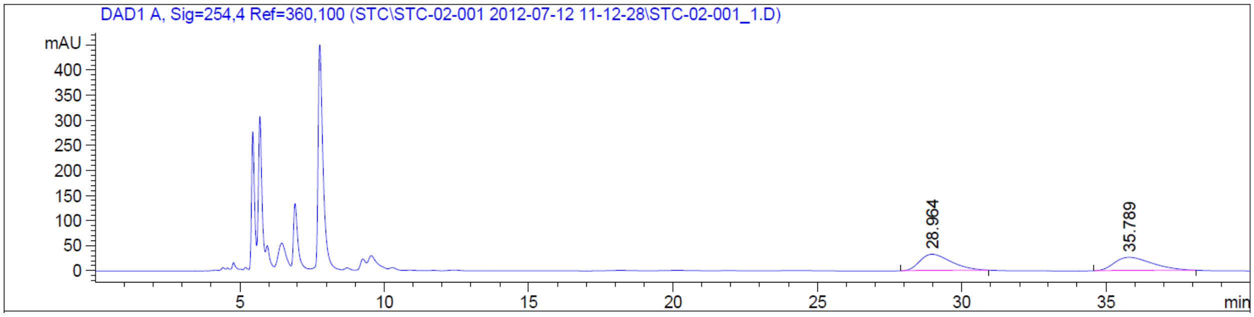
Enantioenriched:



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Peak RetTime Type  Width     Area      Height     Area
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   2  35.789 BB    1.2997 2493.02710   26.78967  49.7241
```
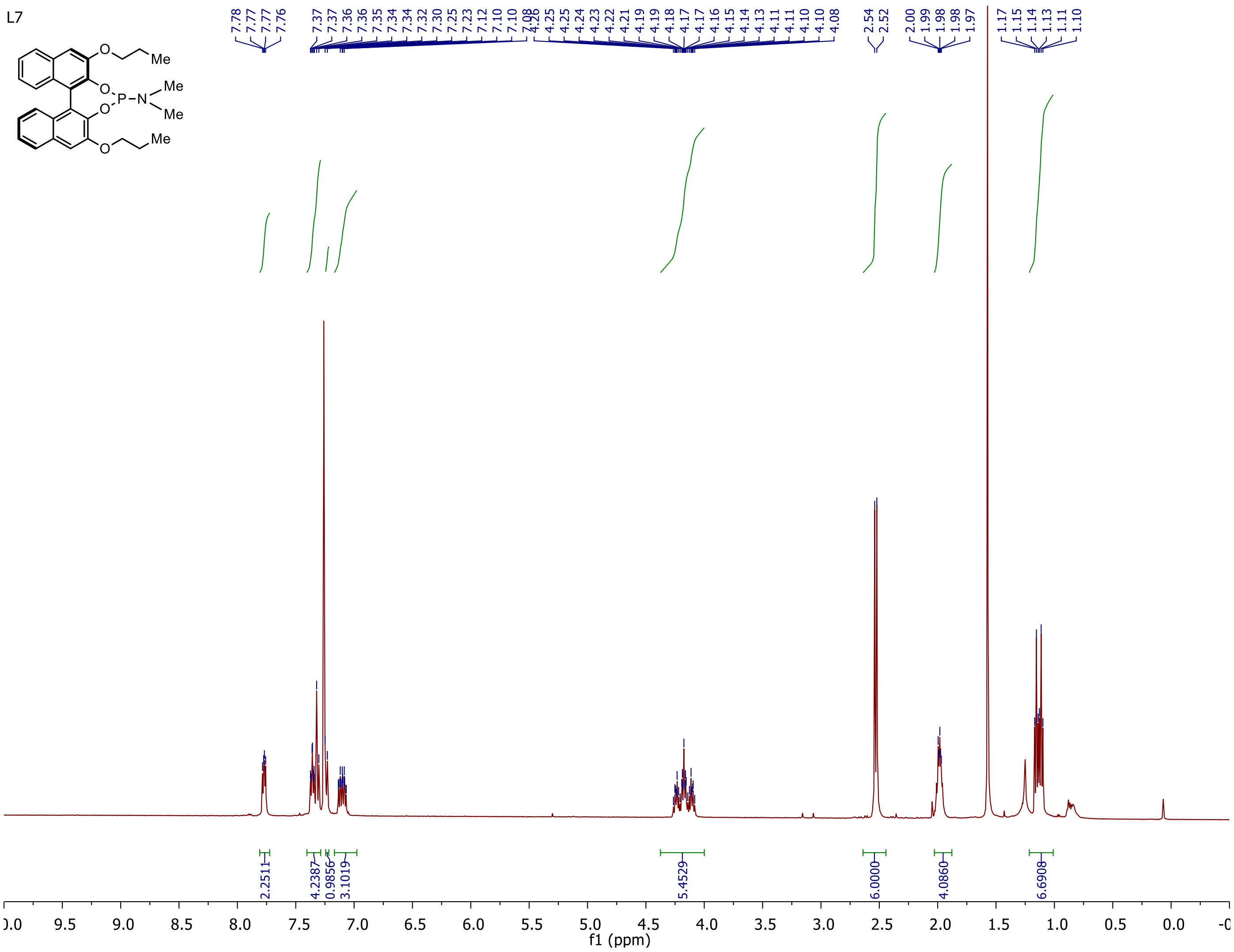
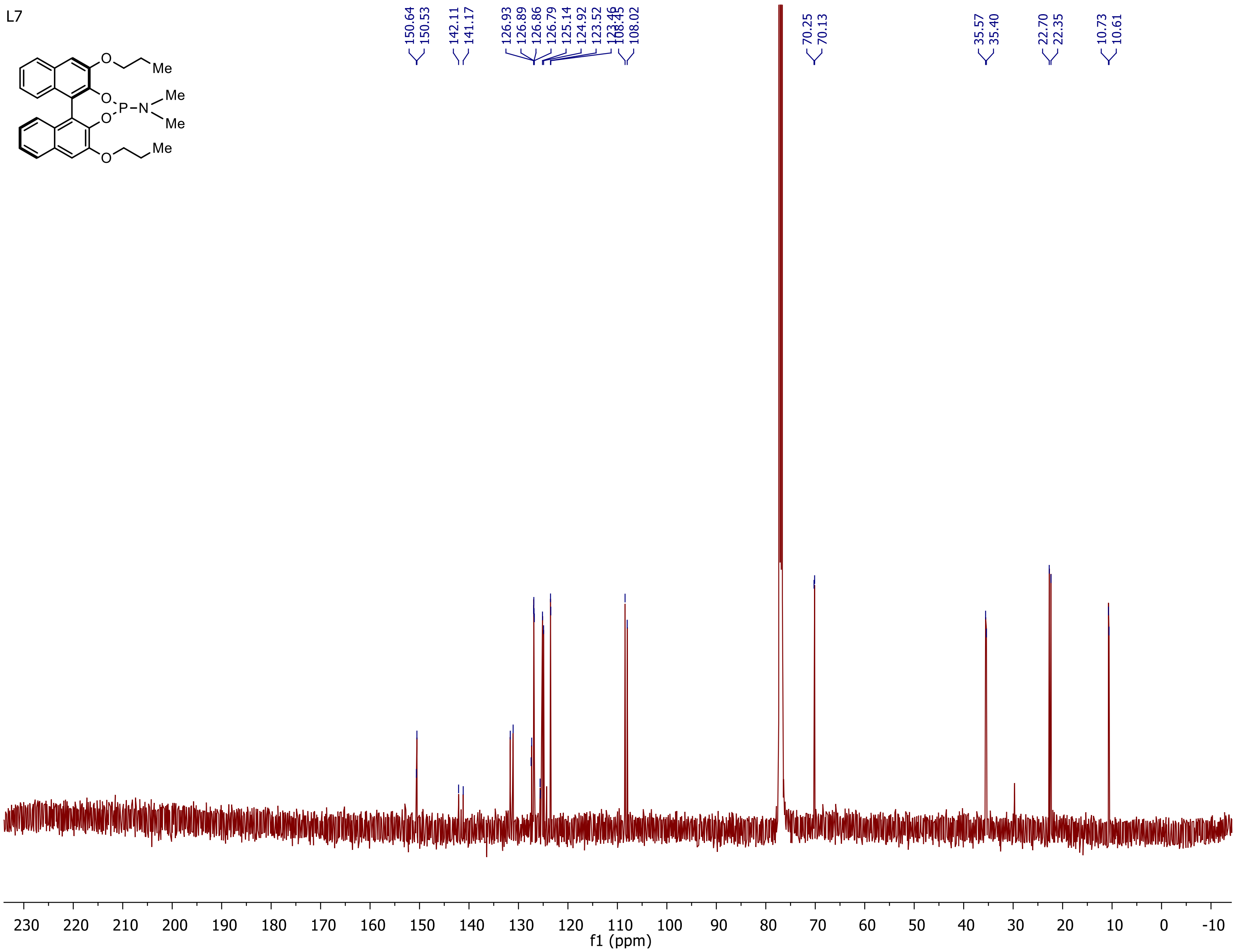
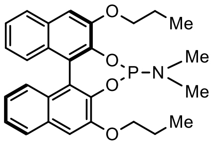

V. NMR Spectra



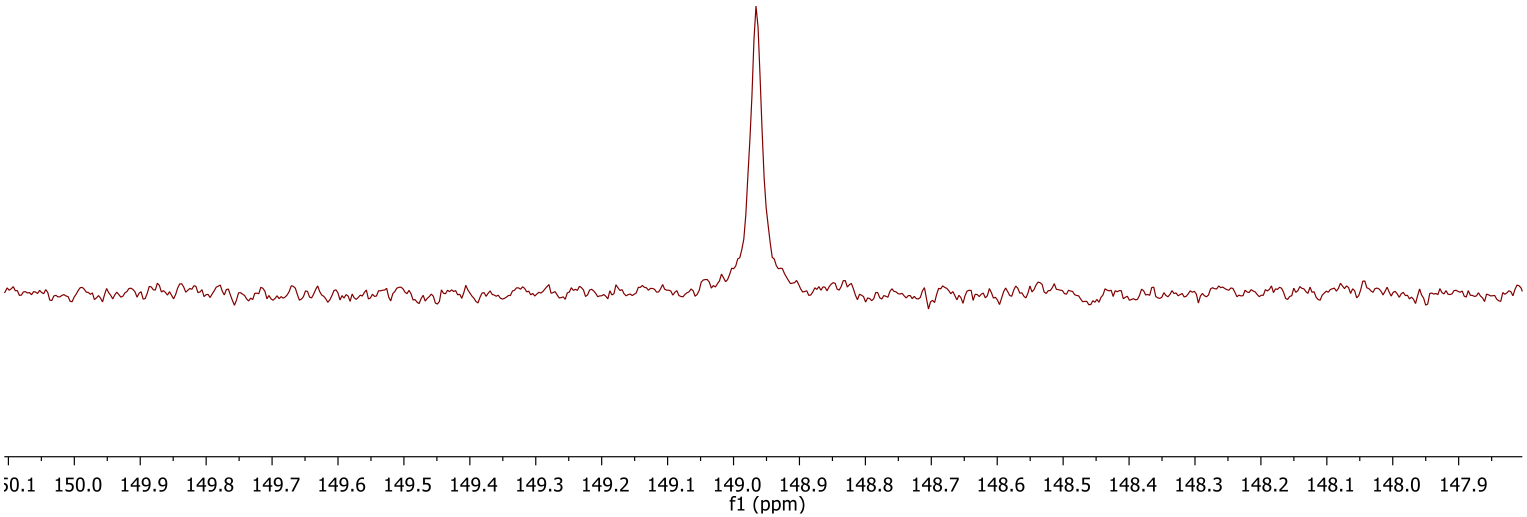
500 MHz ^{1}H-NMR spectrum of **L7** in $CDCl_3$



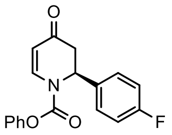
125 MHz ^{13}C-NMR spectrum of **L7** in $CDCl_3$



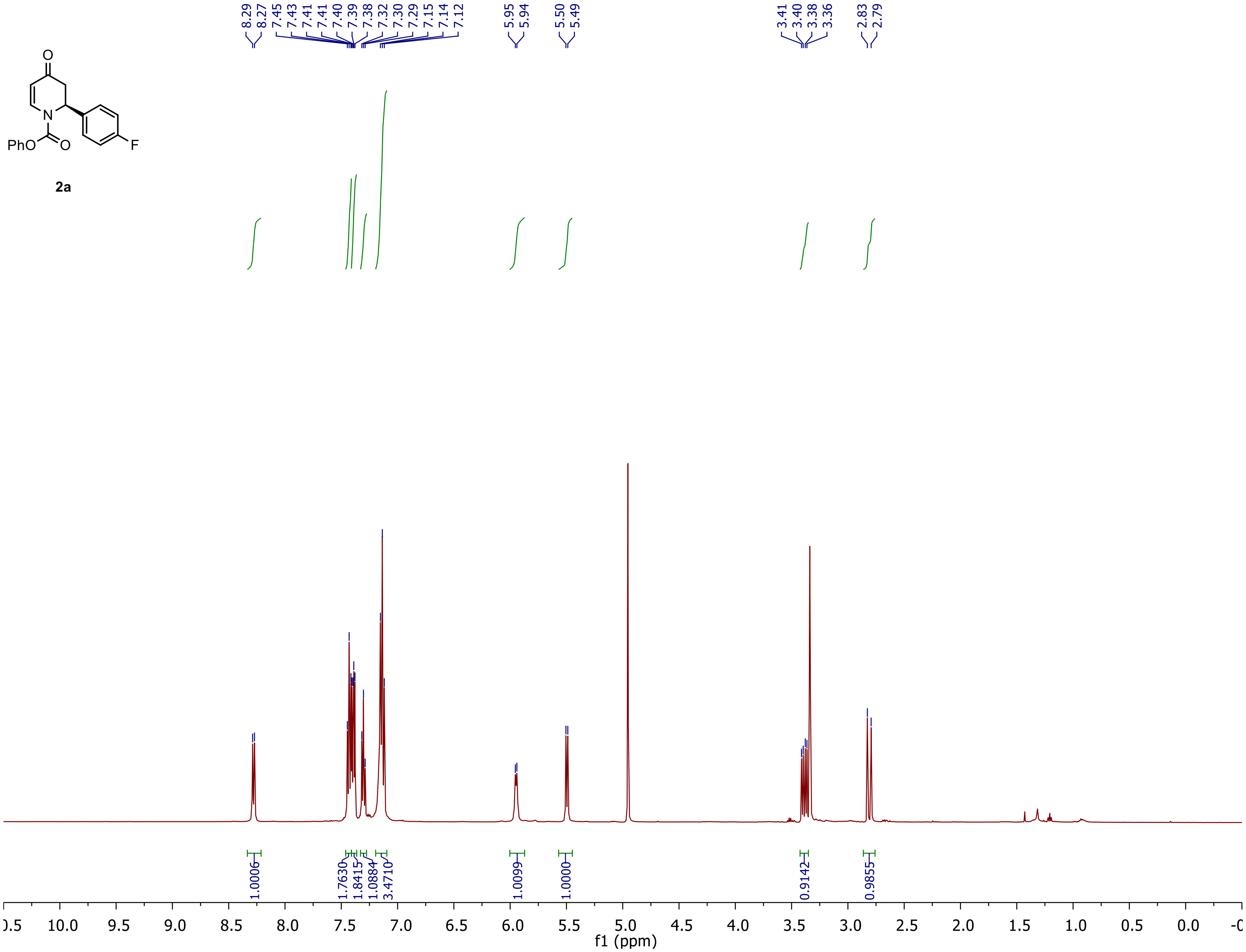
L7



121 MHz ^{31}P-NMR spectrum of **L7** in $CDCl_3$

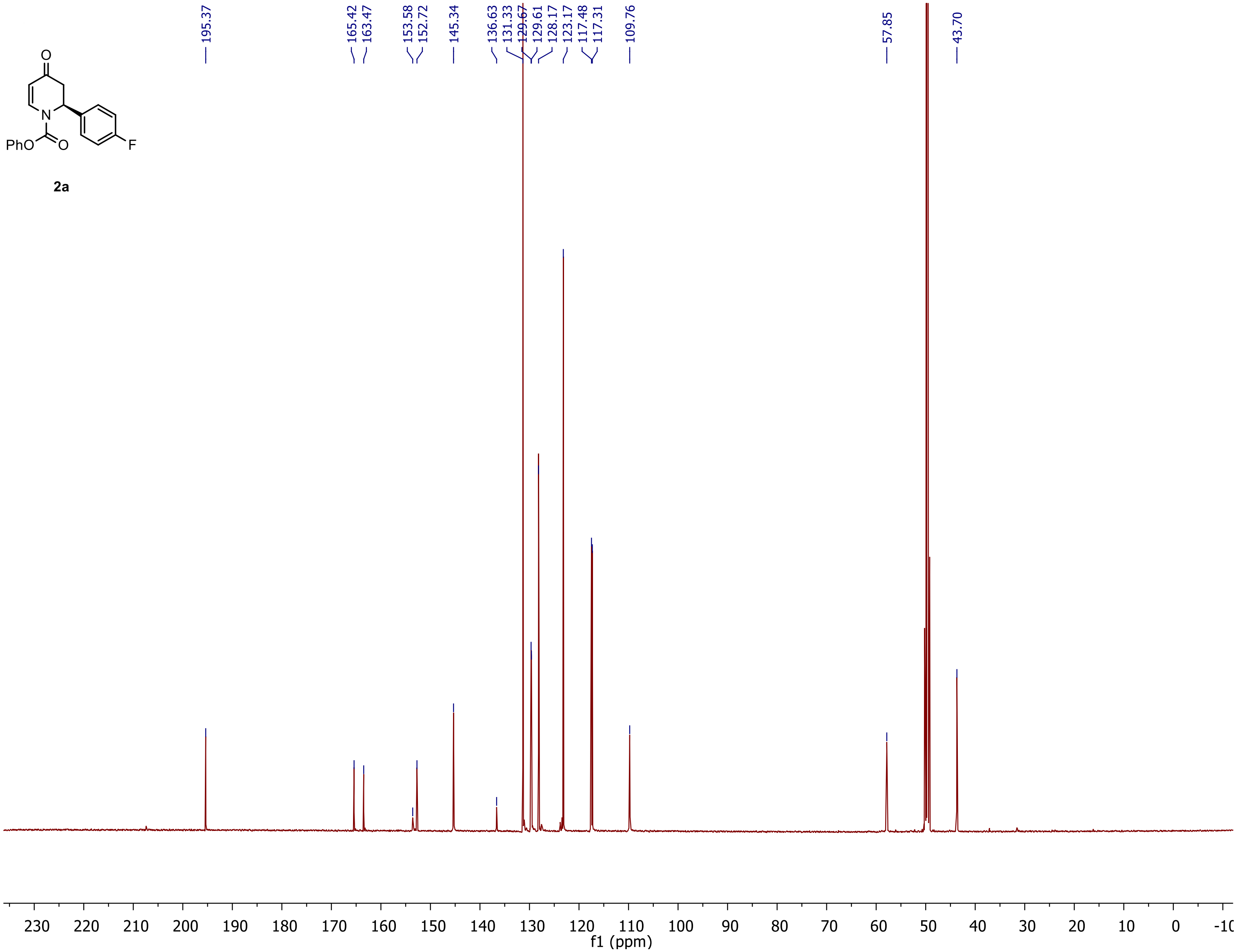


2a

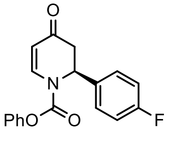


500 MHz ^{1}H-NMR spectrum of **2a** in MeOD

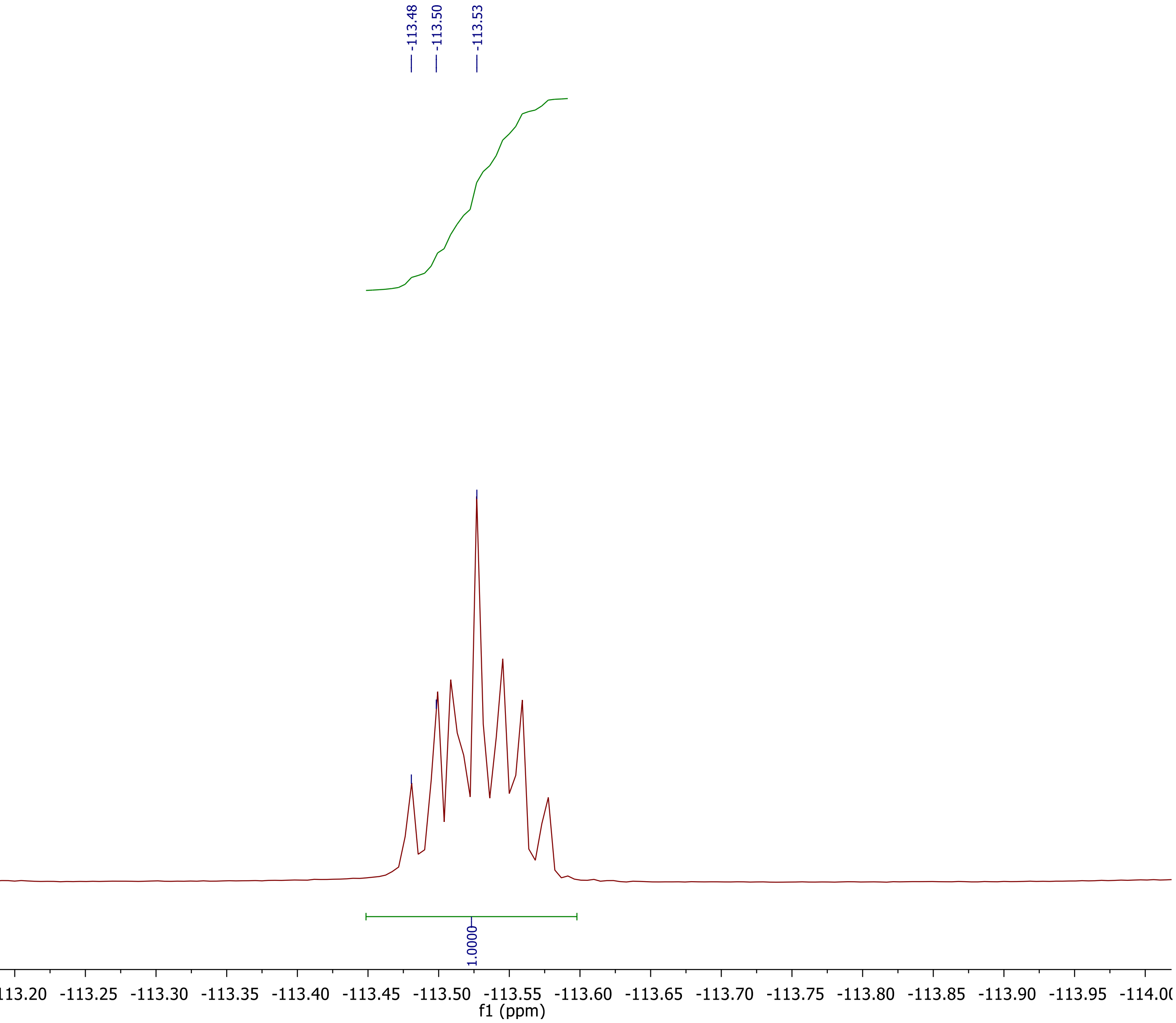
2a



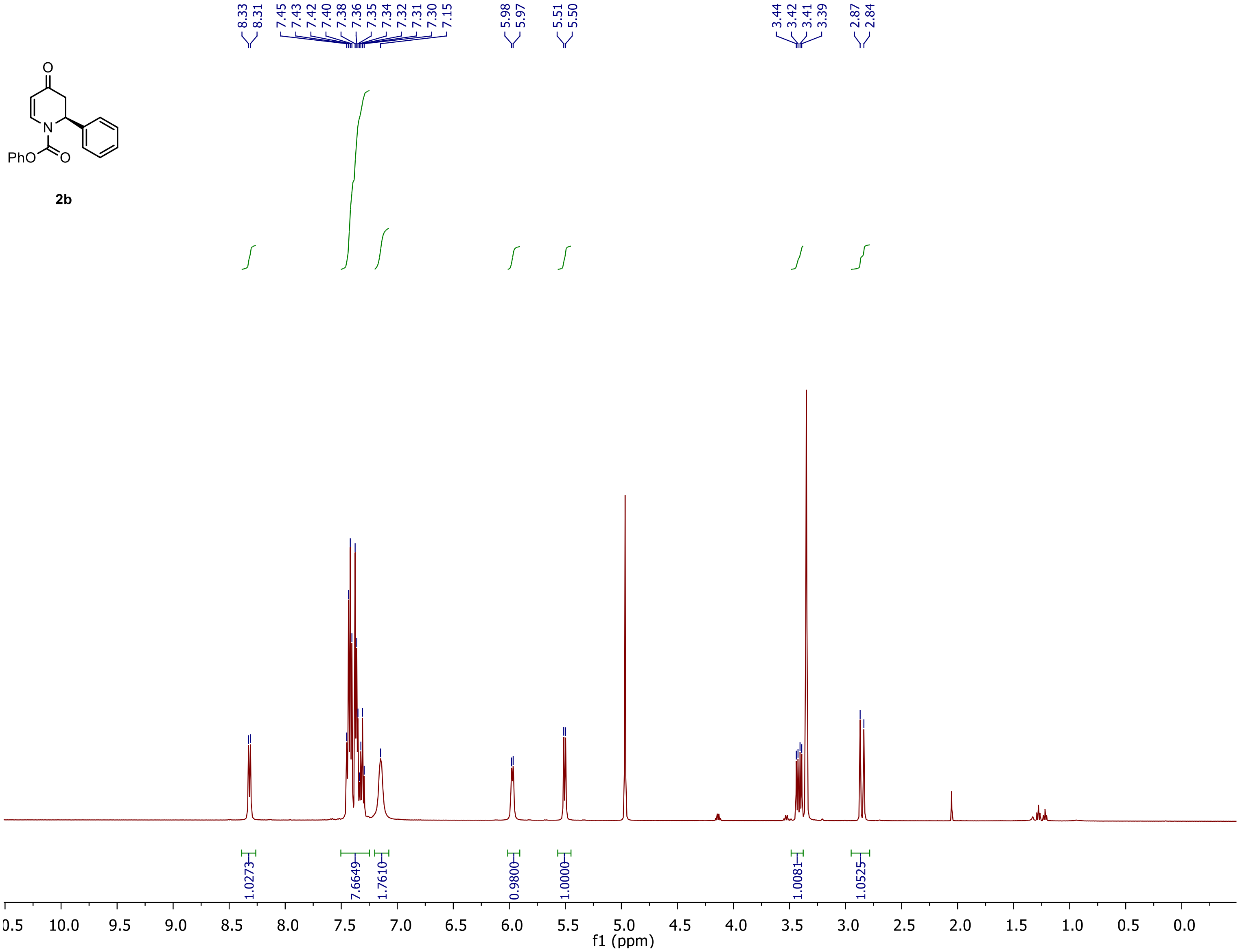
125 MHz ^{13}C-NMR spectrum of **2a** in MeOD



2a

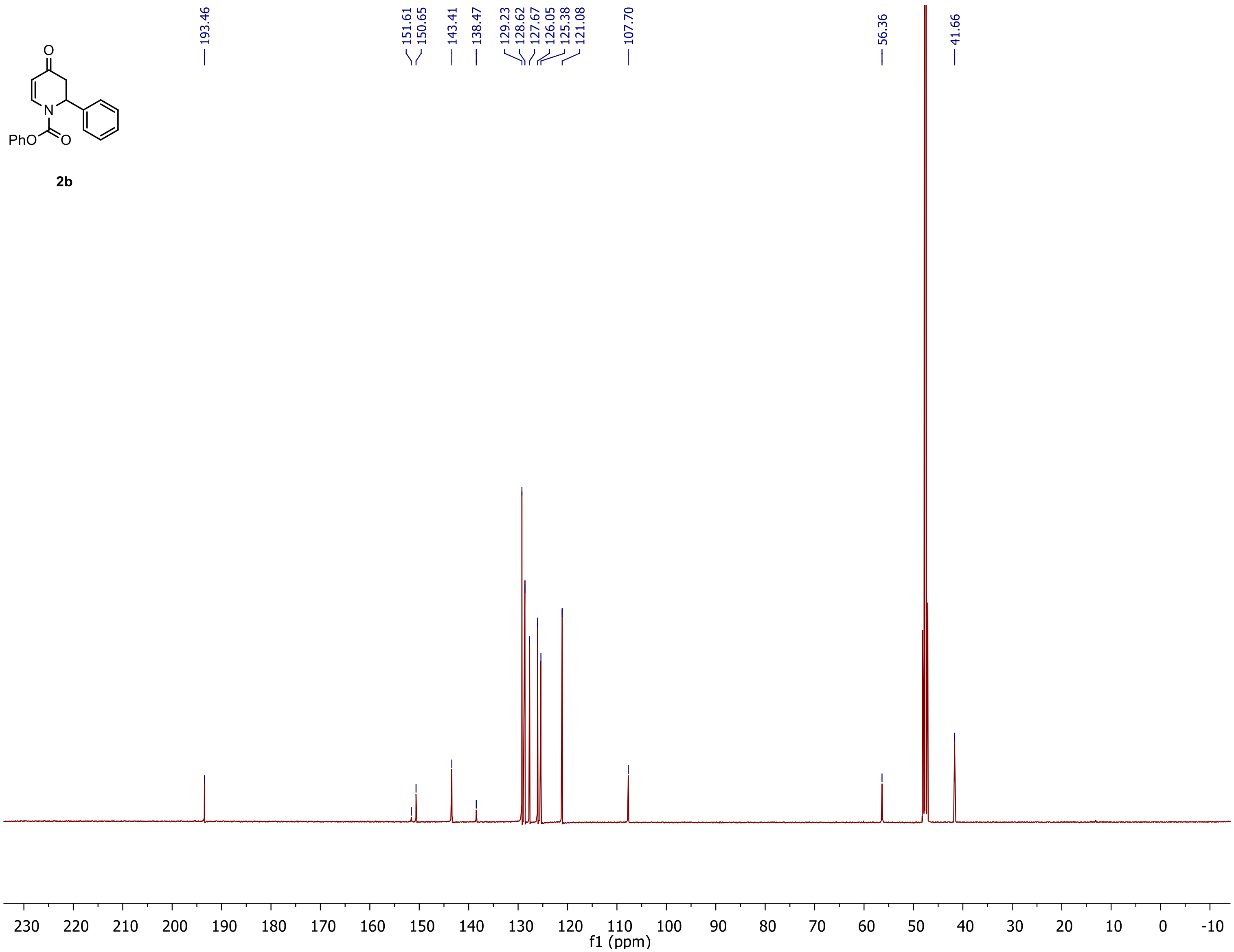


282 MHz ^{19}F NMR spectrum of **2a** in MeOD

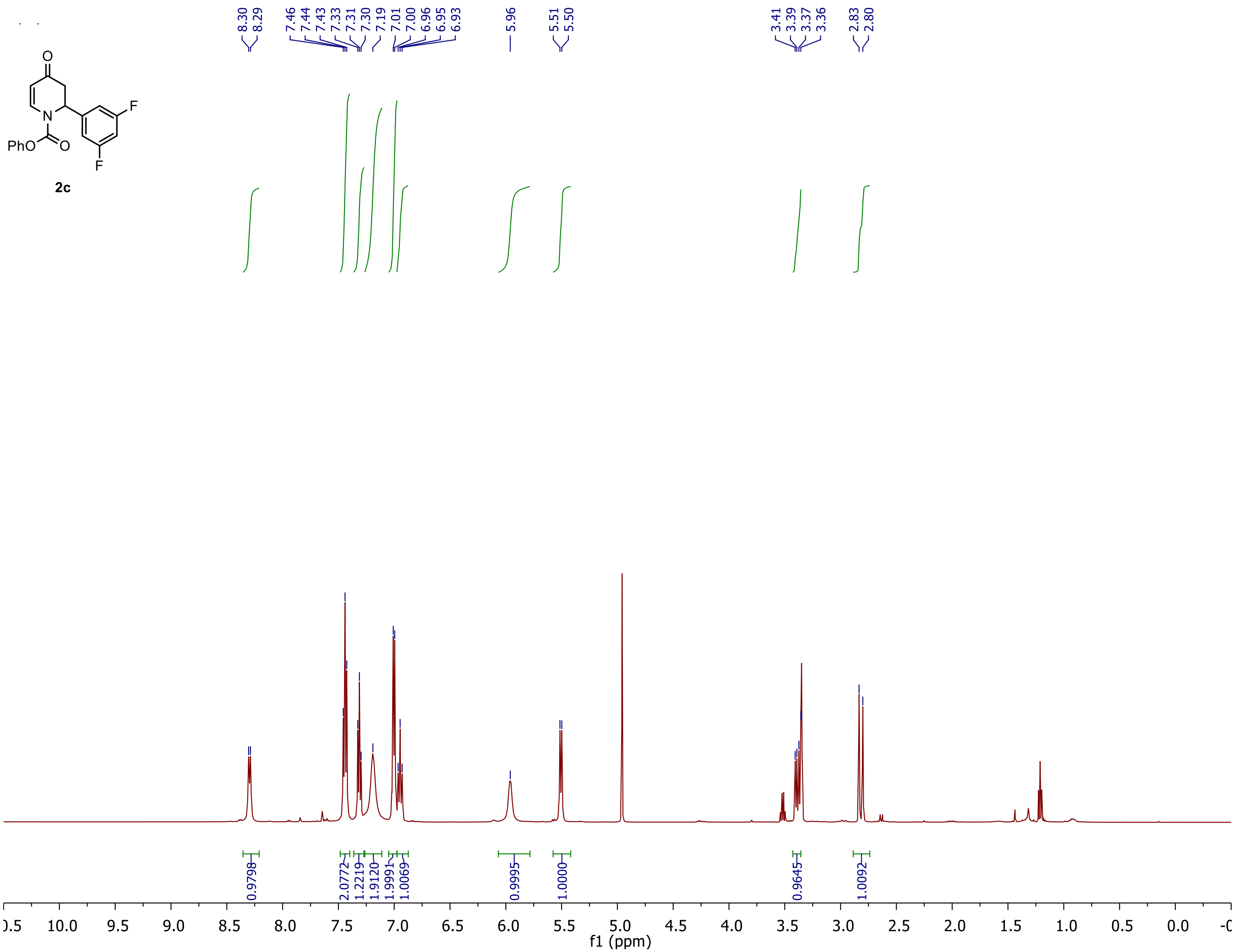


2b

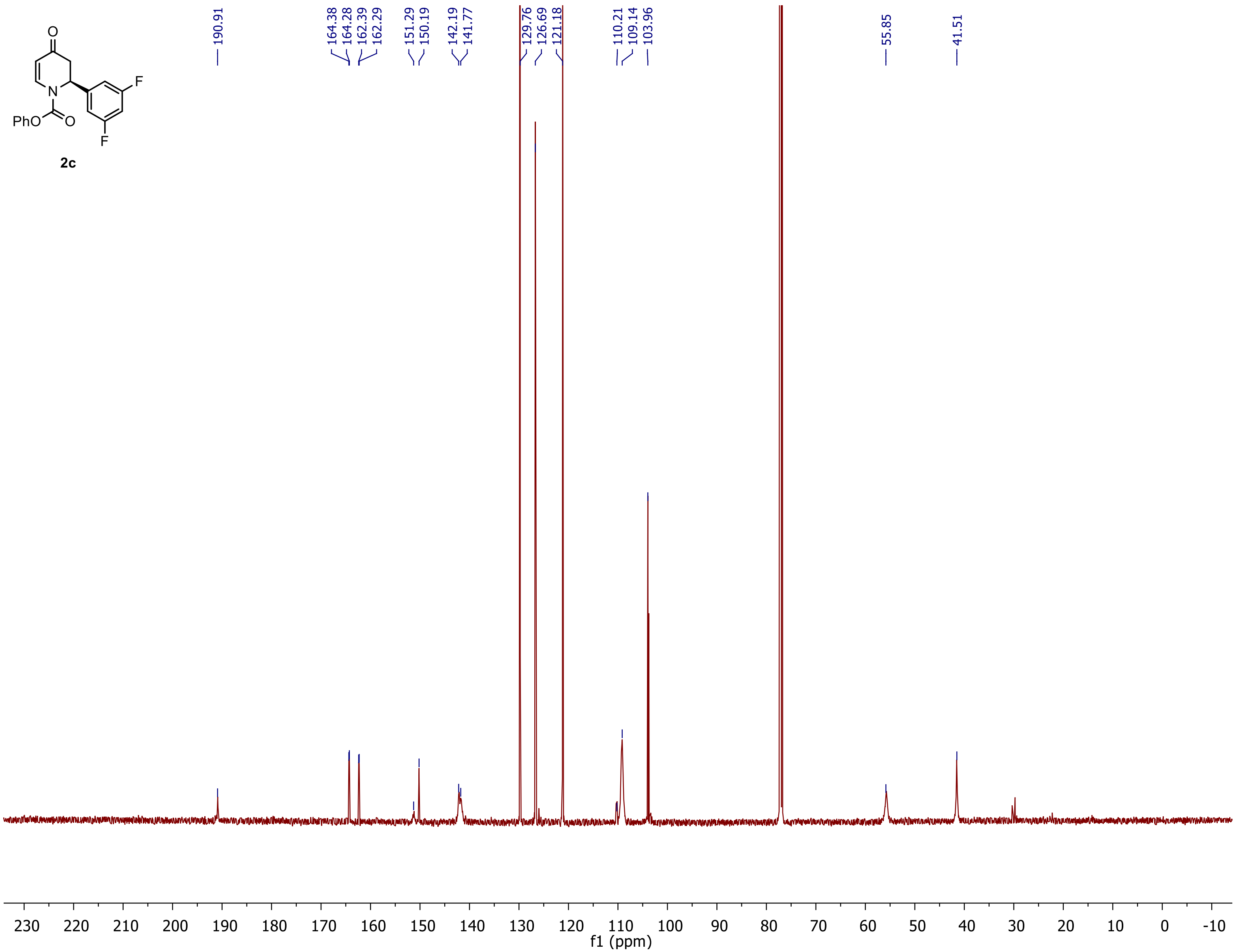
500 MHz ^{1}H-NMR spectrum of **2b** in MeOD



125 MHz ^{13}C-NMR spectrum of **2b** in MeOD

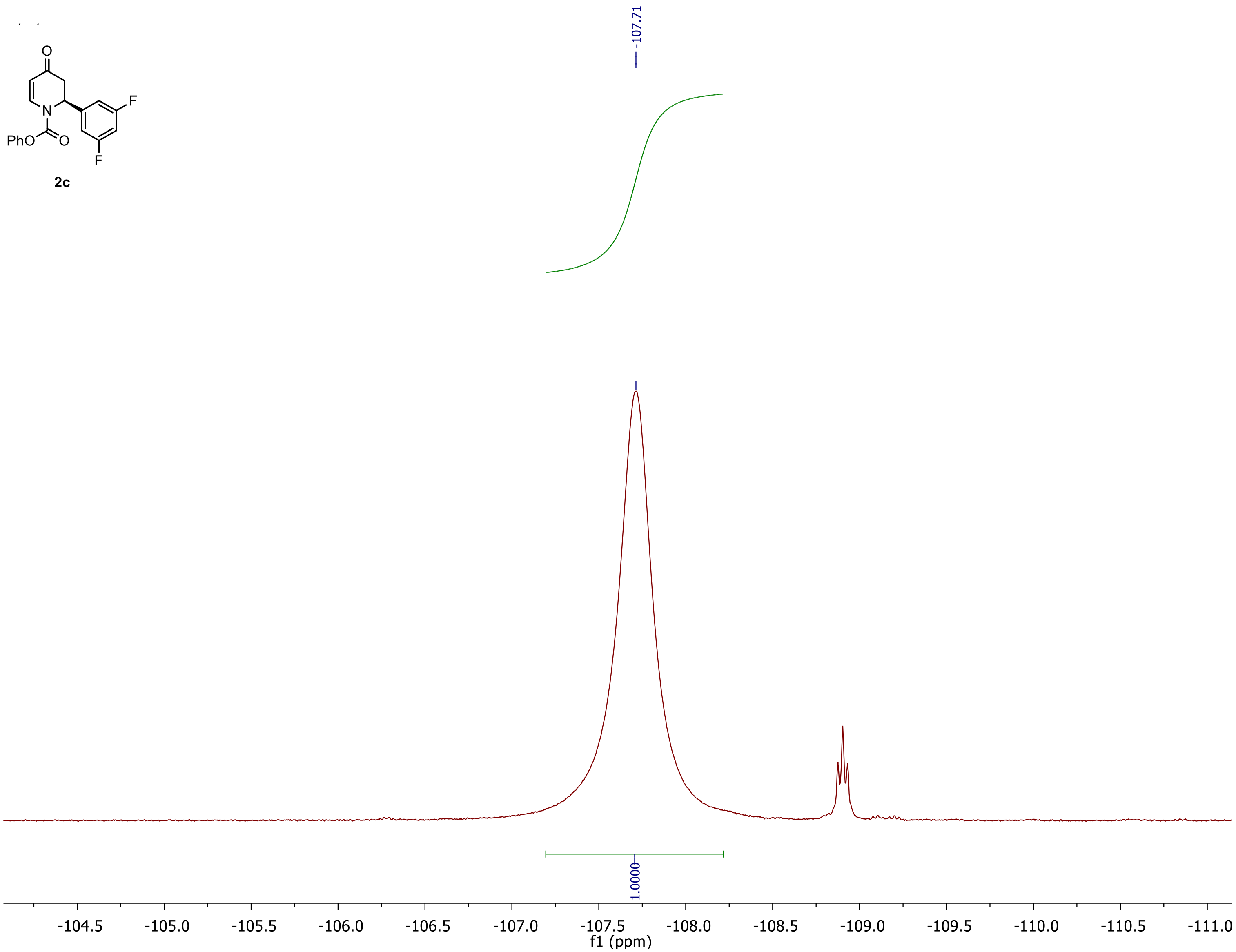


500 MHz ^{1}H-NMR spectrum of **2c** in MeOD

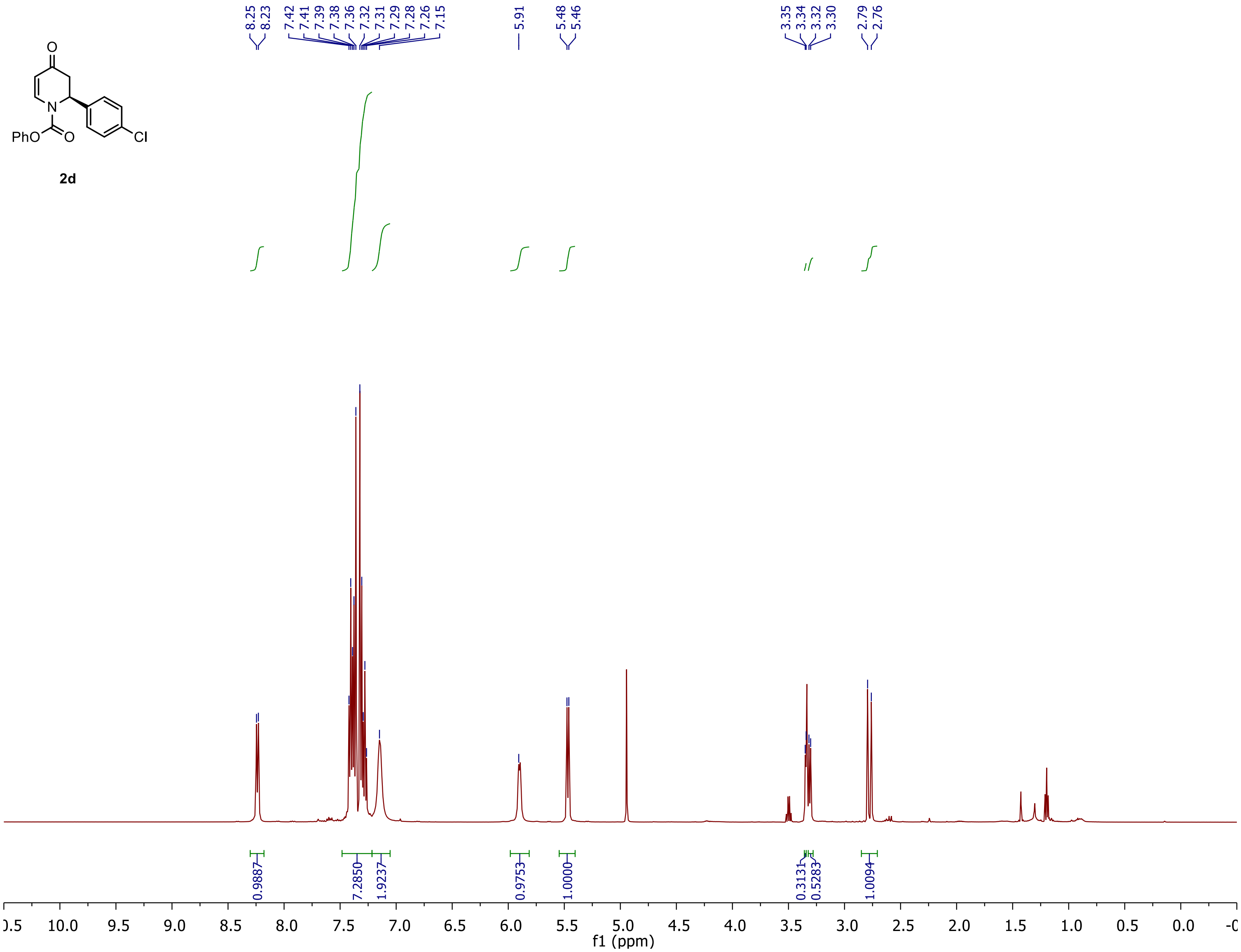


125 MHz ^{13}C-NMR spectrum of **2c** in $CDCl_3$

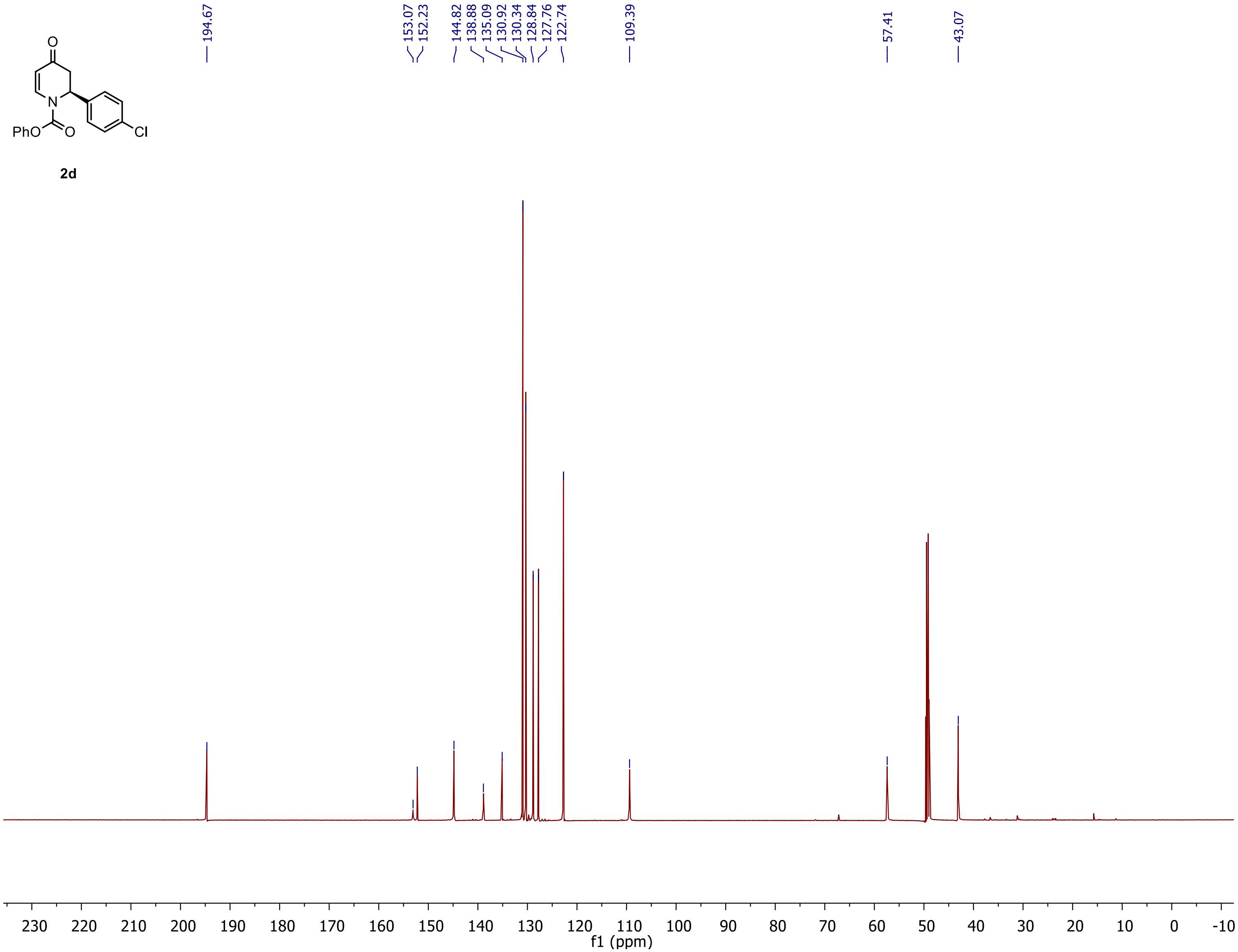
2c



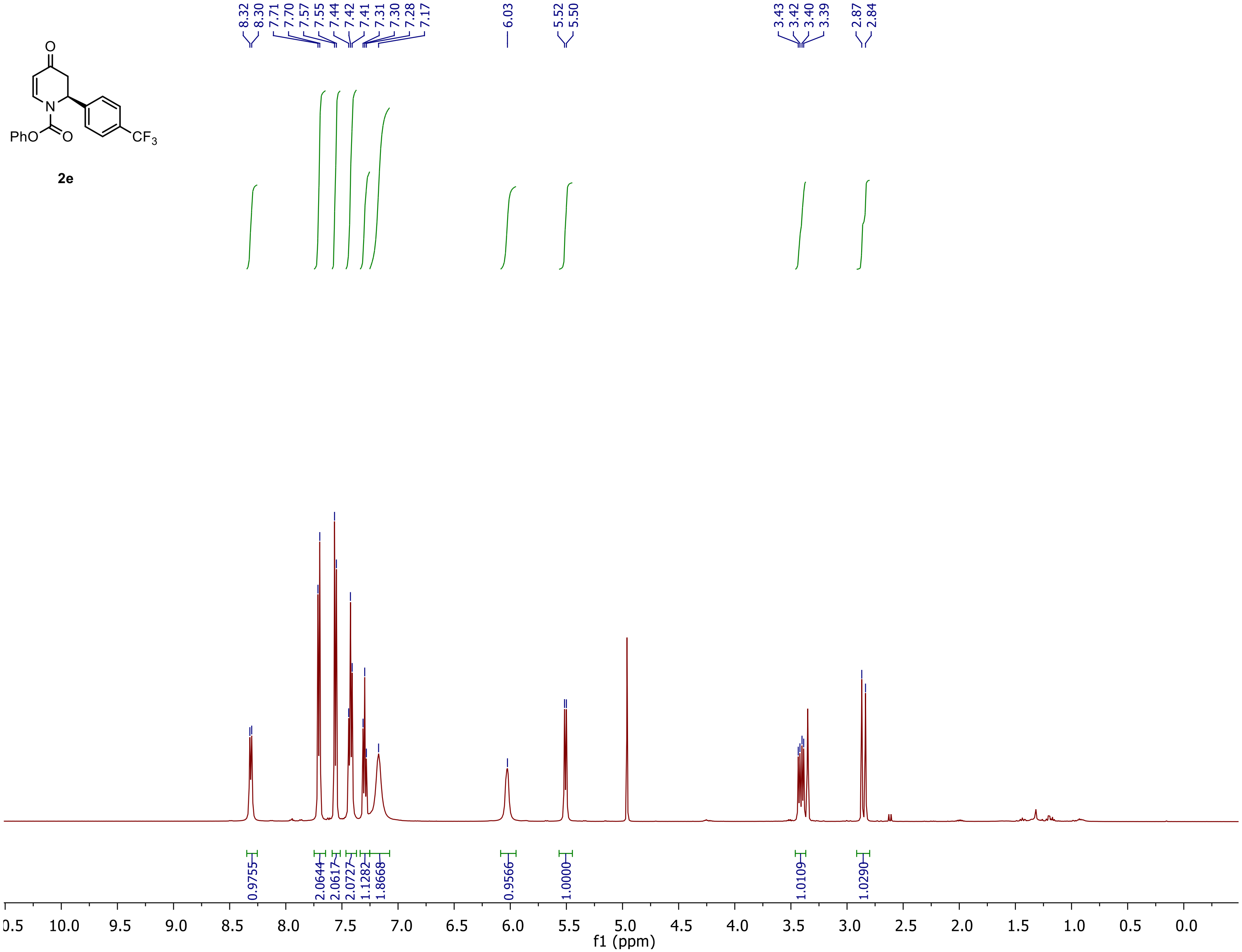
282 MHz ^{19}F NMR spectrum of **2c** in MeOD



500 MHz ^{1}H-NMR spectrum of **2d** in MeOD

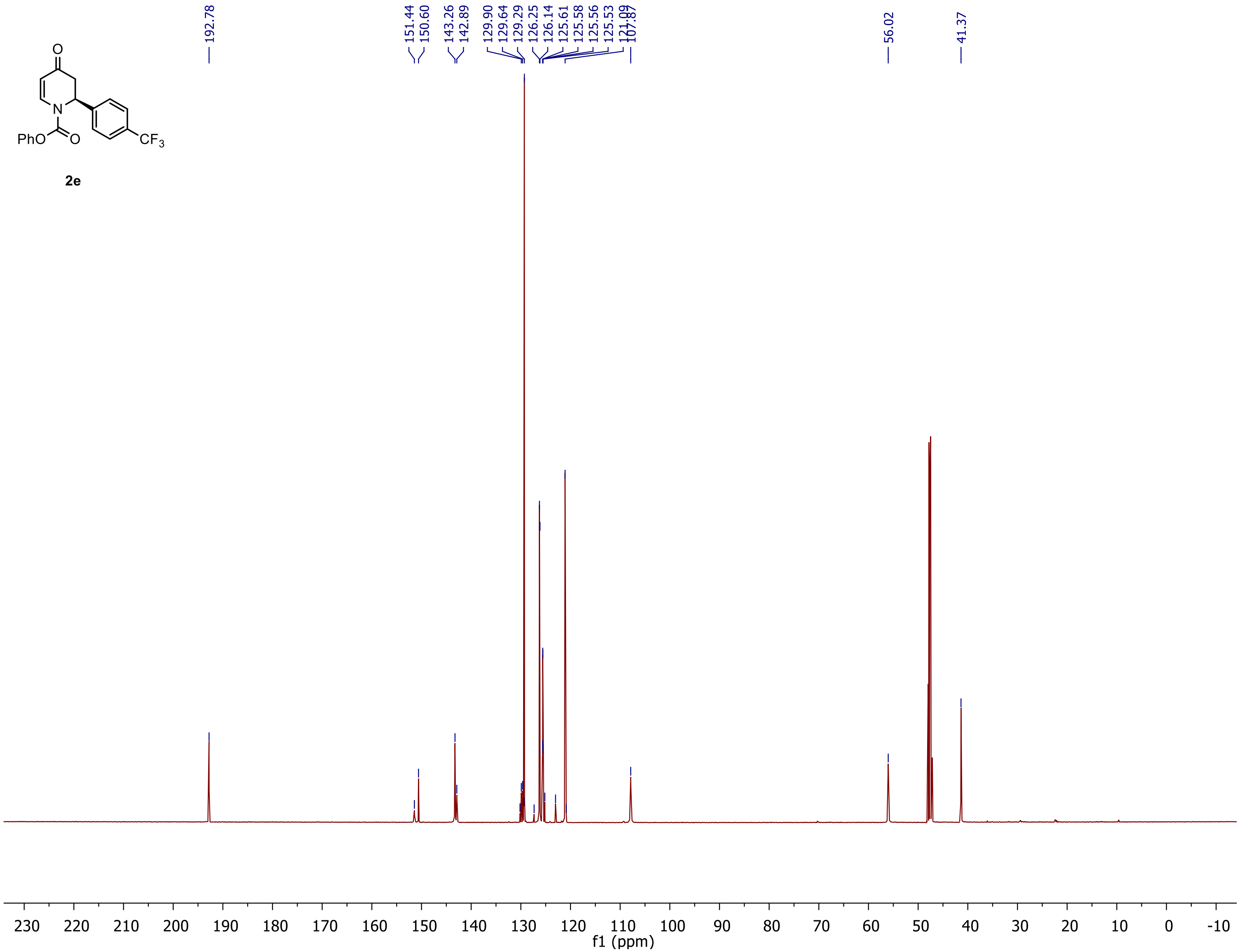


125 MHz ^{13}C-NMR spectrum of **2d** in MeOD



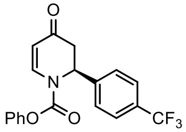
2e

500 MHz ^{1}H-NMR spectrum of **2e** in MeOD

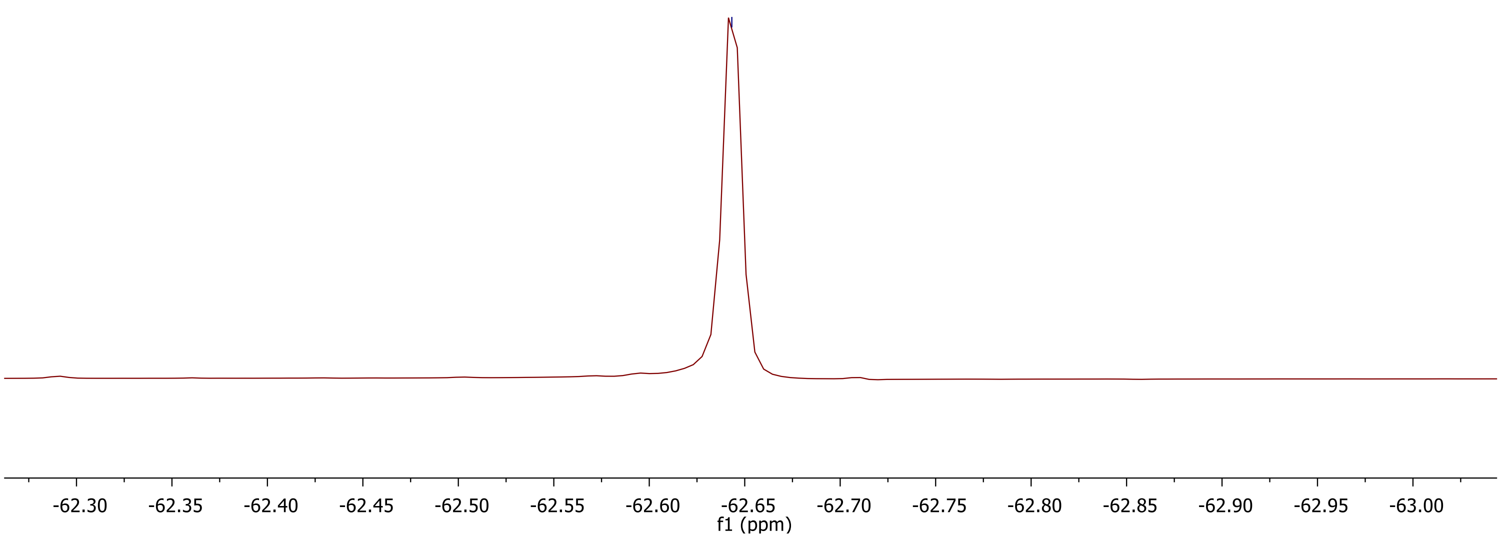


2e

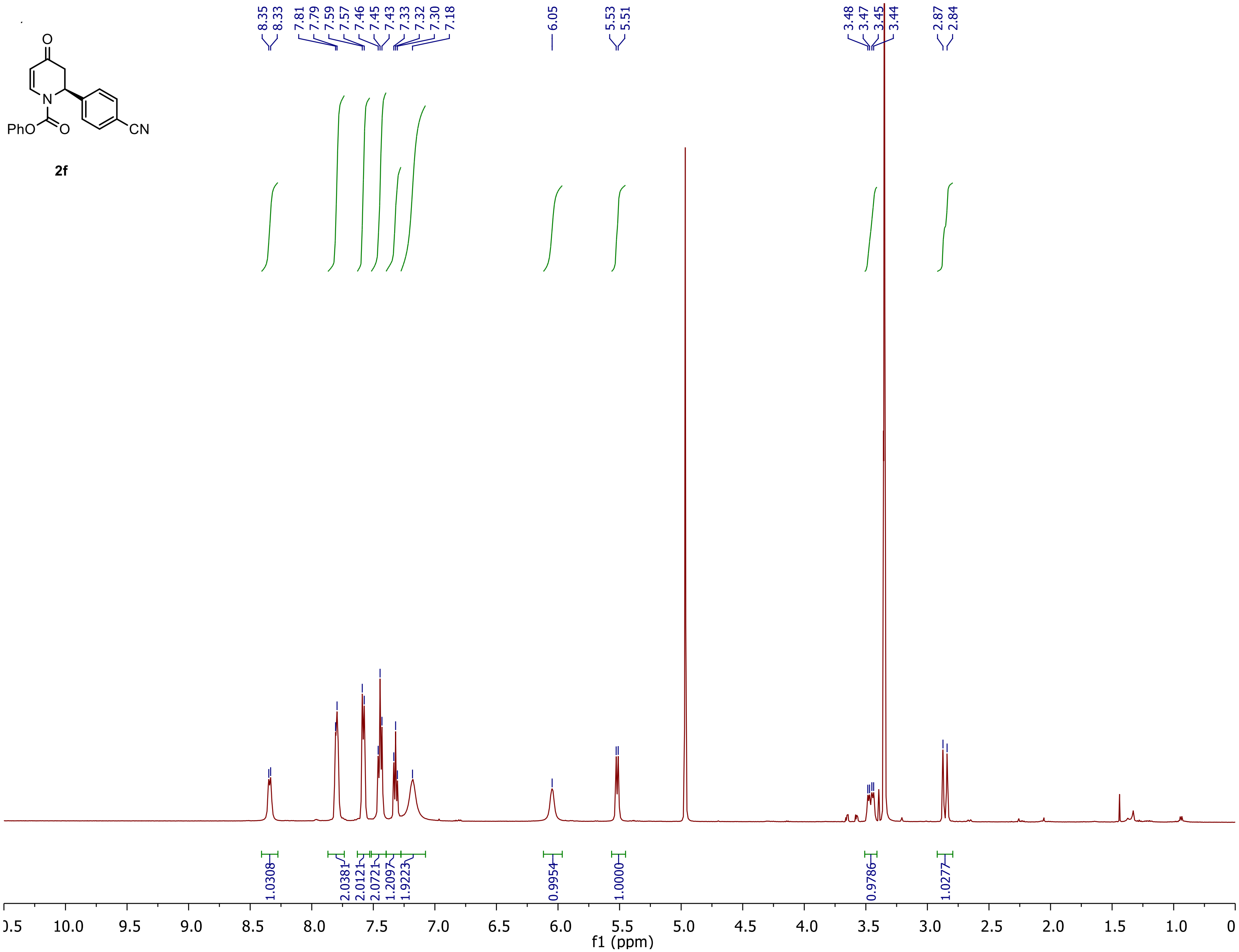
125 MHz ^{13}C-NMR spectrum of **2e** in MeOD



2e

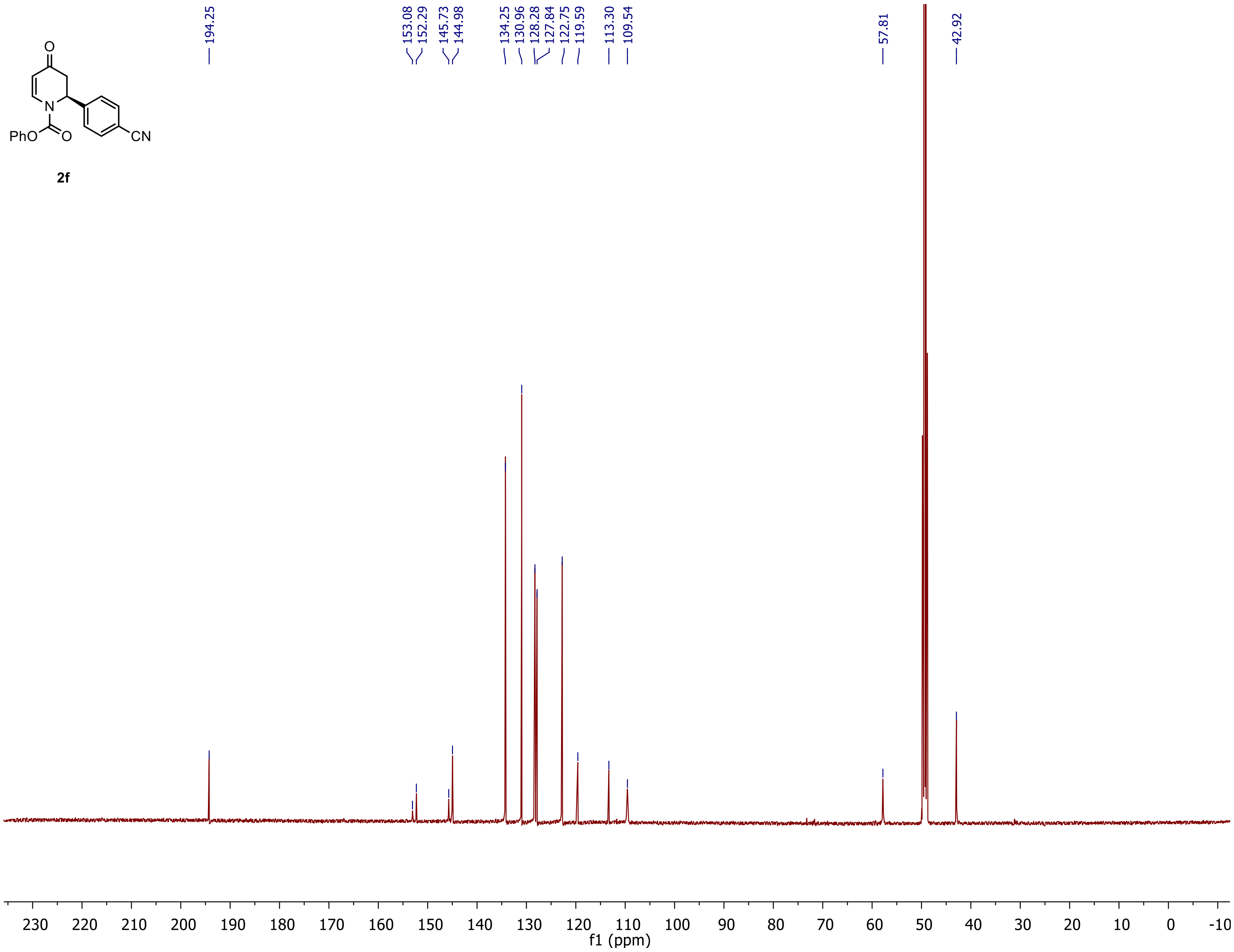


282 MHz ^{19}F NMR spectrum of **2e** in MeOD

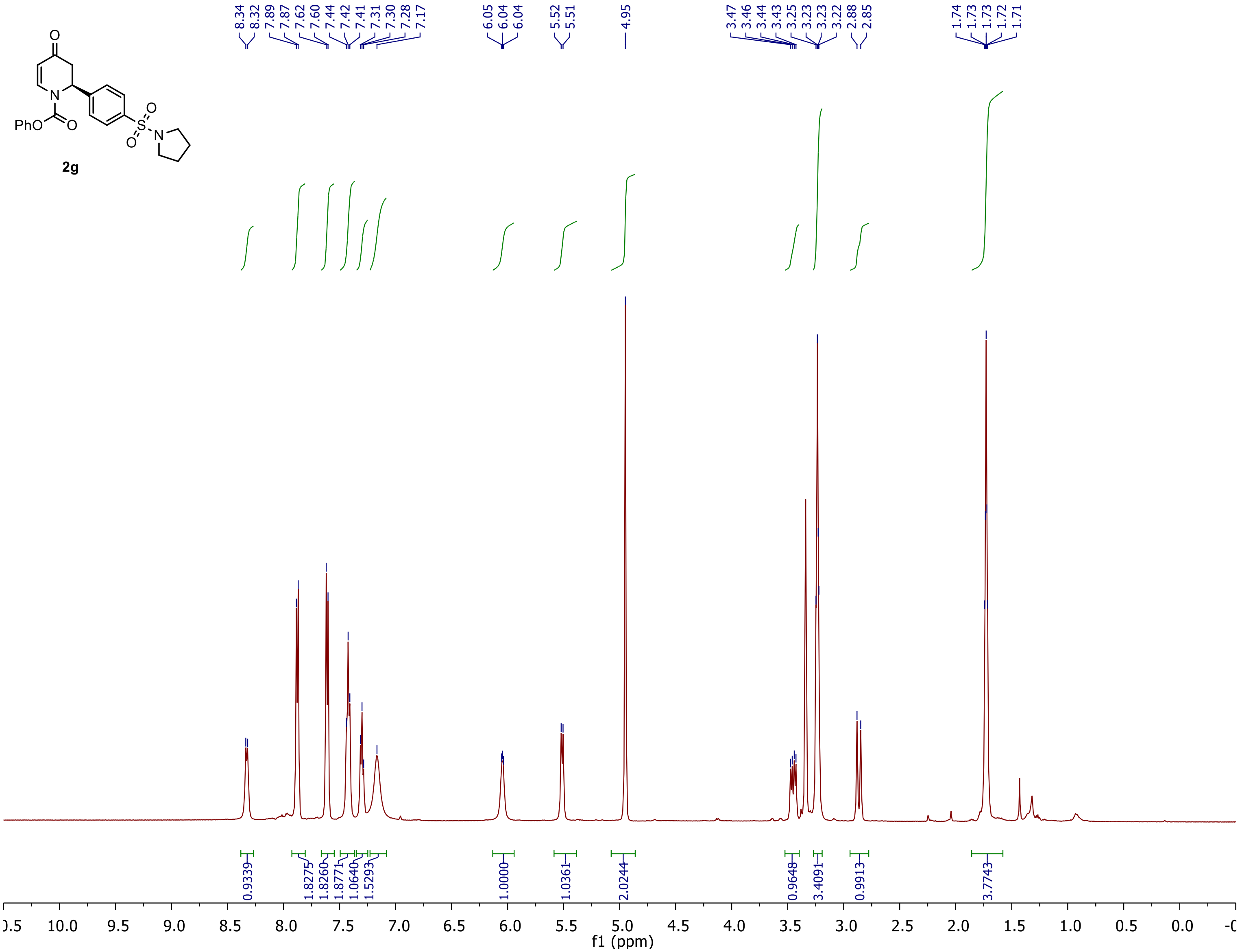


2f

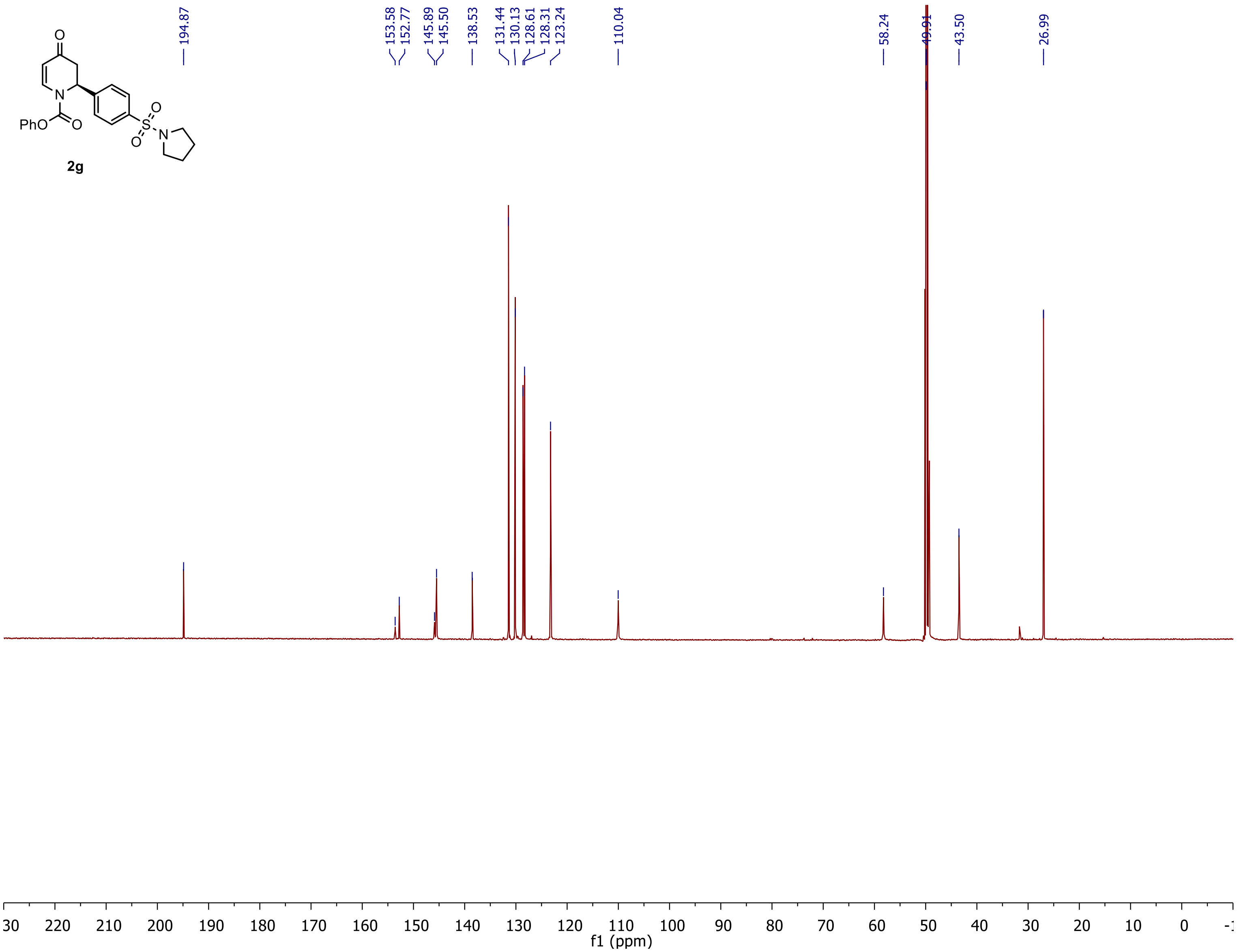
500 MHz ^{1}H-NMR spectrum of **2f** in MeOD



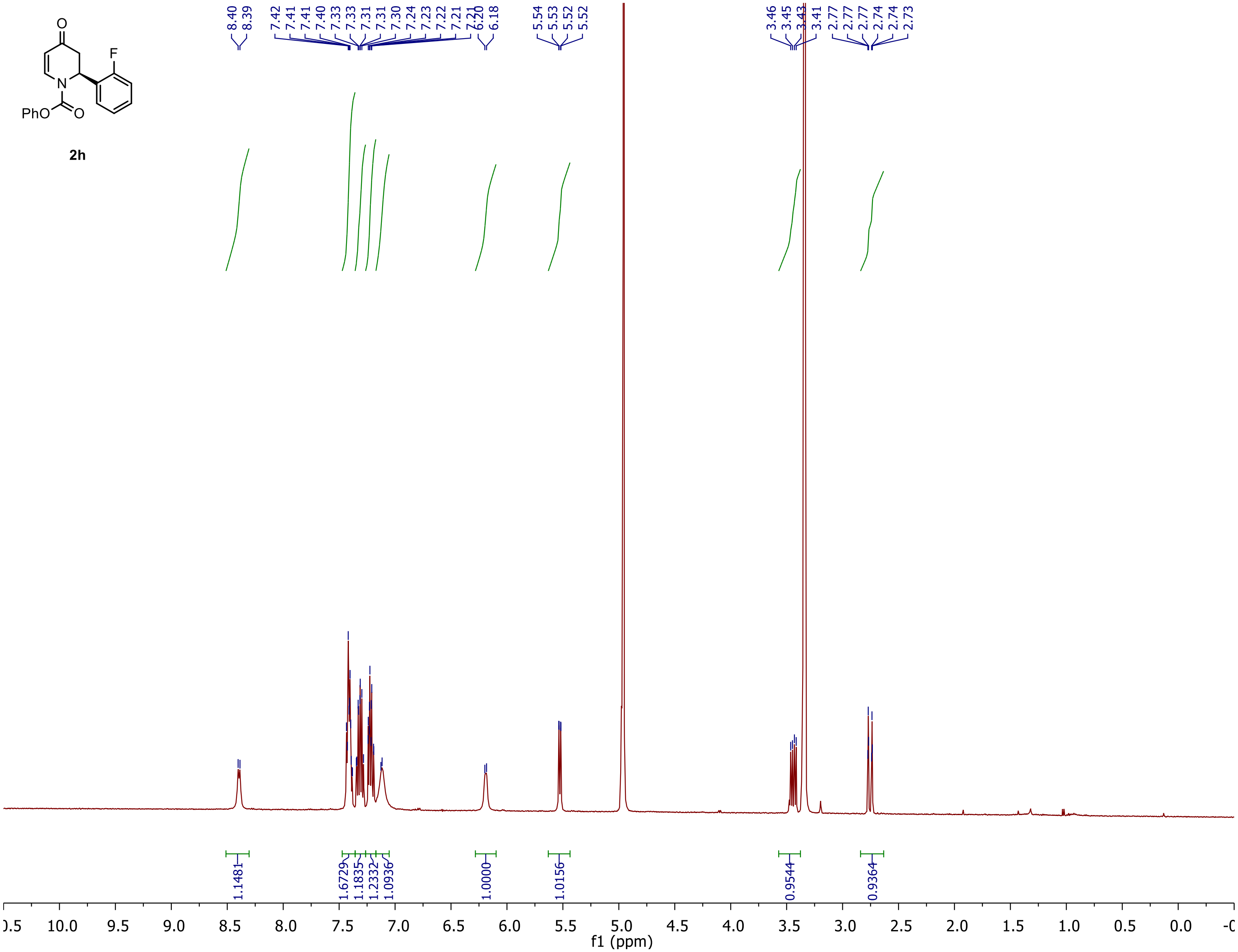
125 MHz ^{13}C-NMR spectrum of **2f** in MeOD



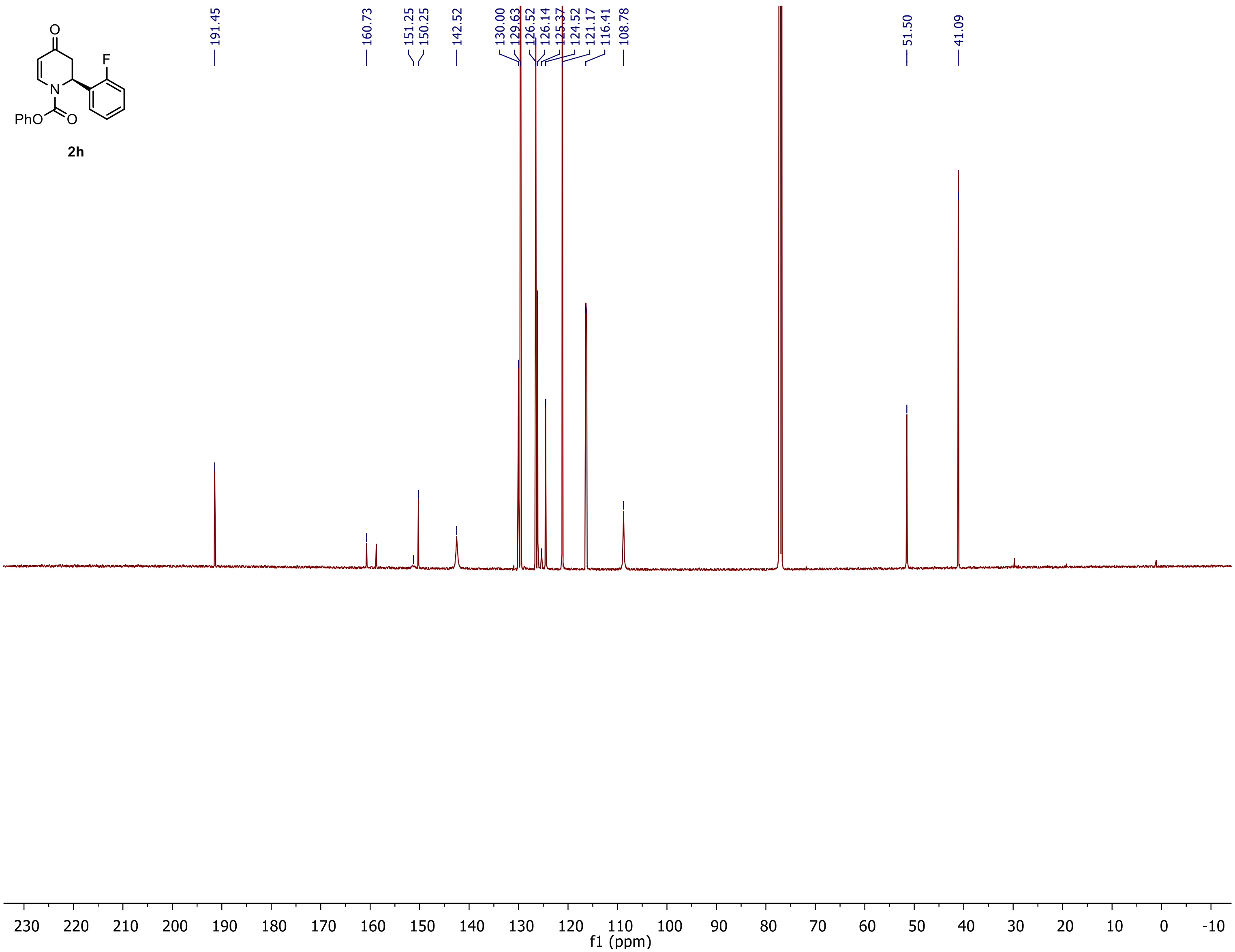
500 MHz ^{1}H-NMR spectrum of **2g** in MeOD



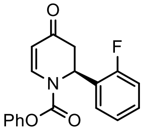
125 MHz ^{13}C-NMR spectrum of **2g** in MeOD



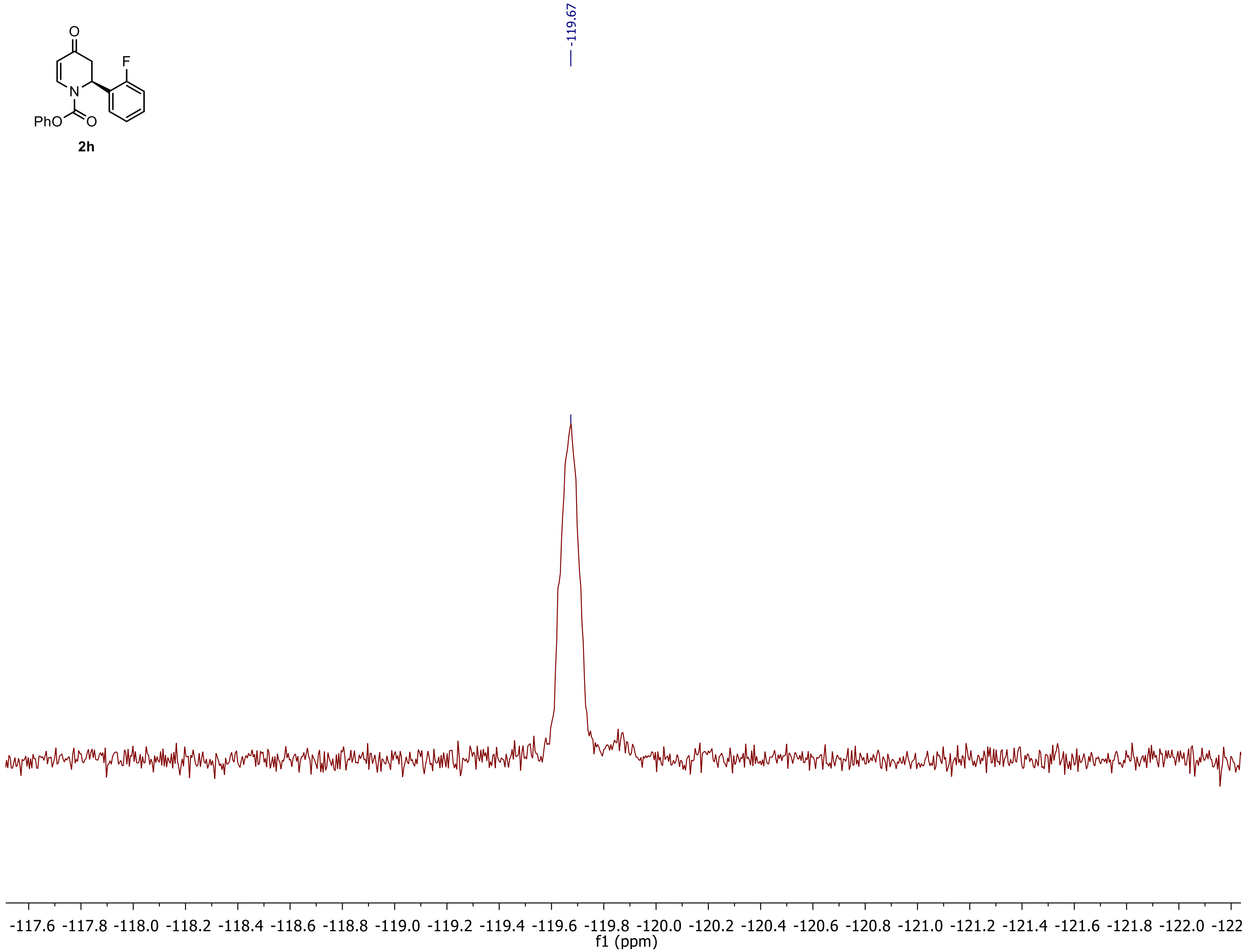
500 MHz ^{1}H-NMR spectrum of **2h** in MeOD



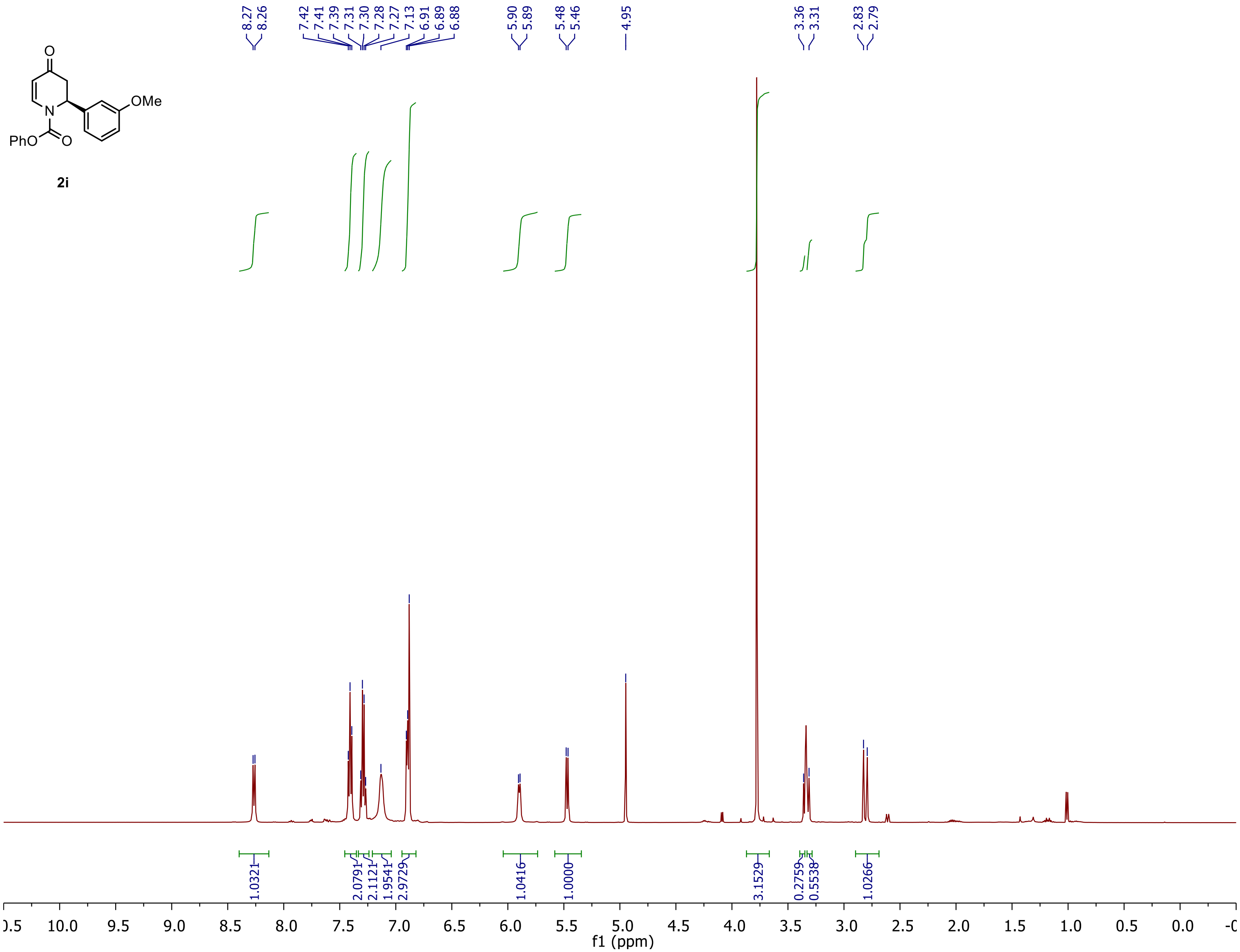
125 MHz ^{13}C-NMR spectrum of **2h** in $CDCl_3$



2h

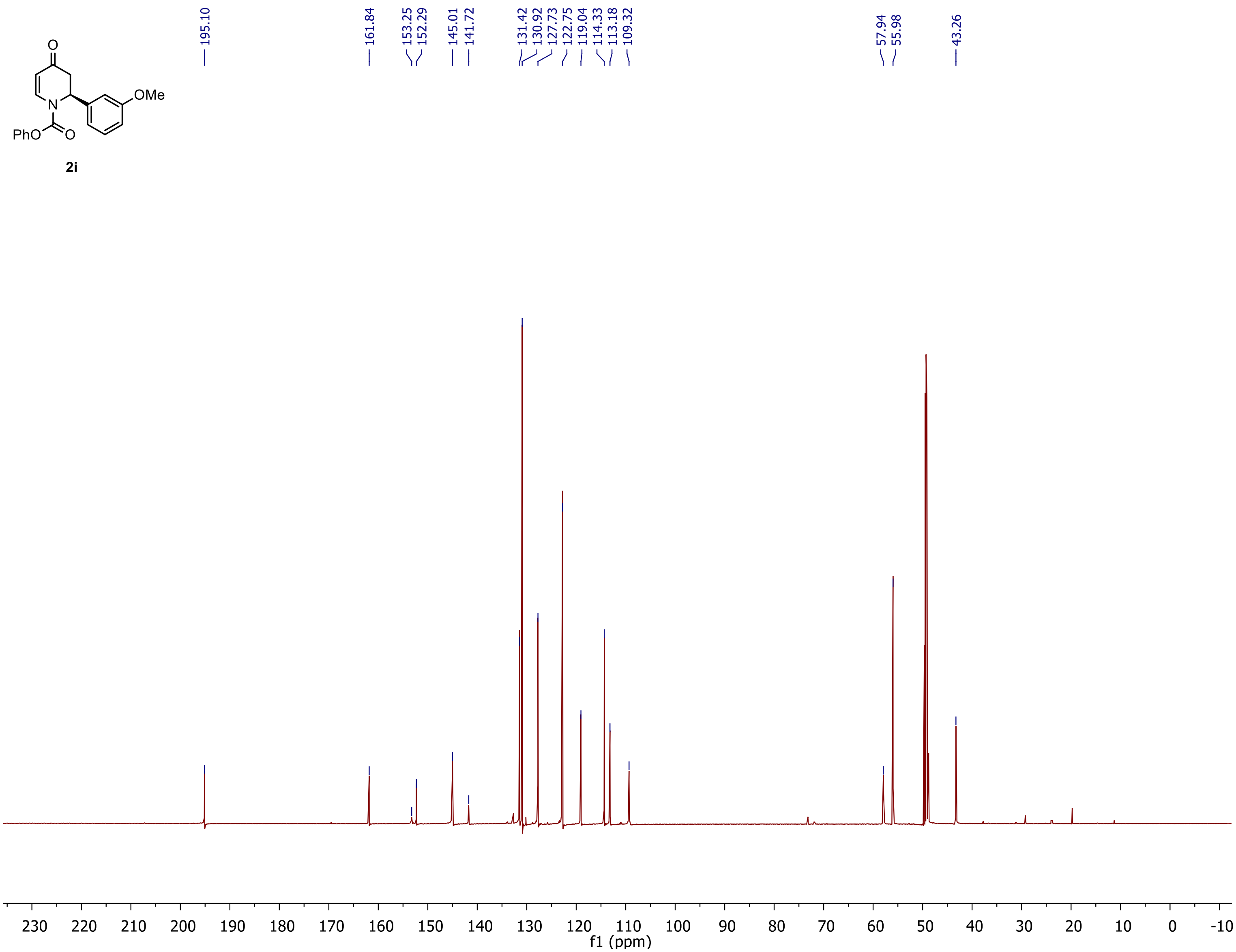


282 MHz ^{19}F NMR spectrum of **2h** in MeOD

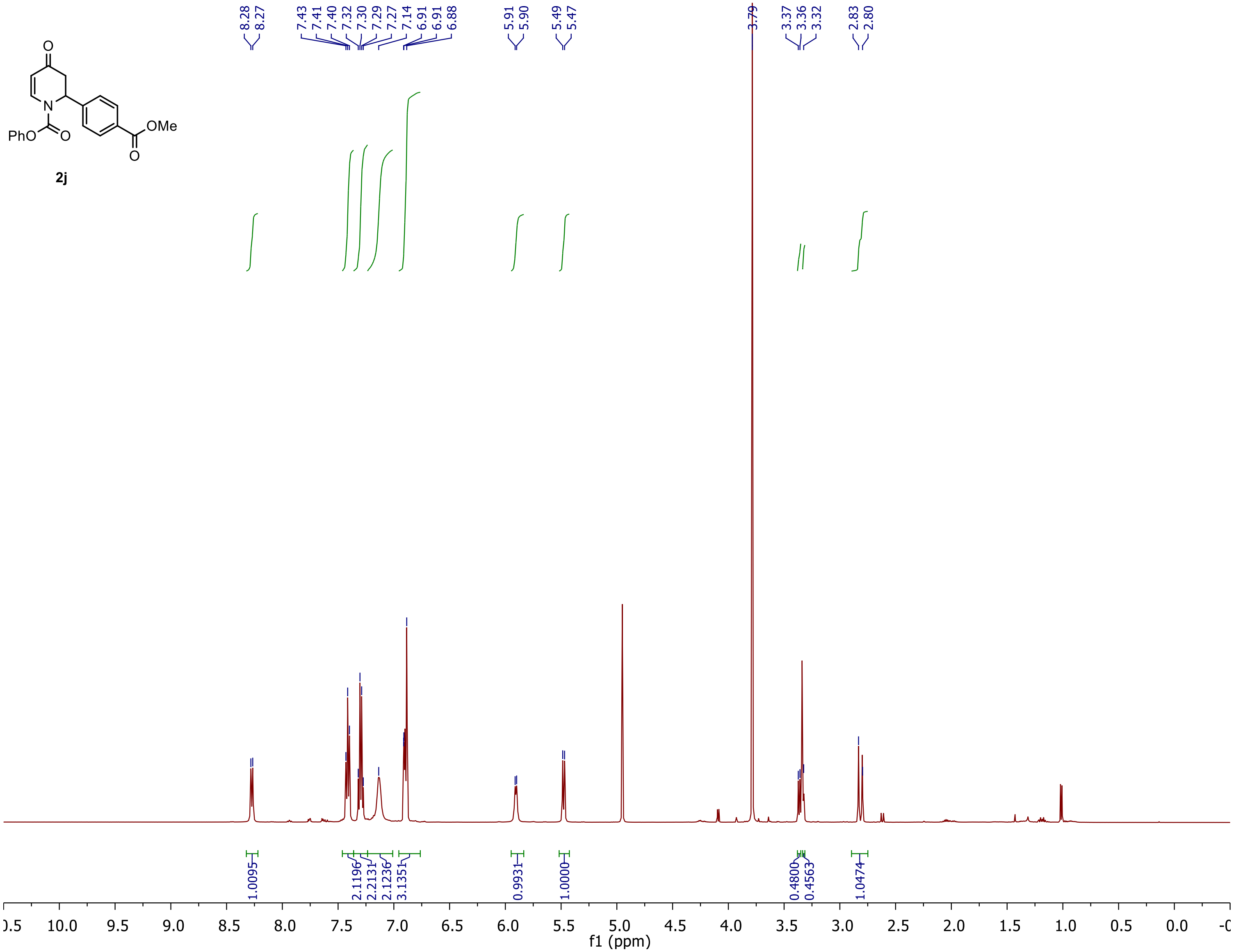


2i

500 MHz ^{1}H-NMR spectrum of **2i** in MeOD

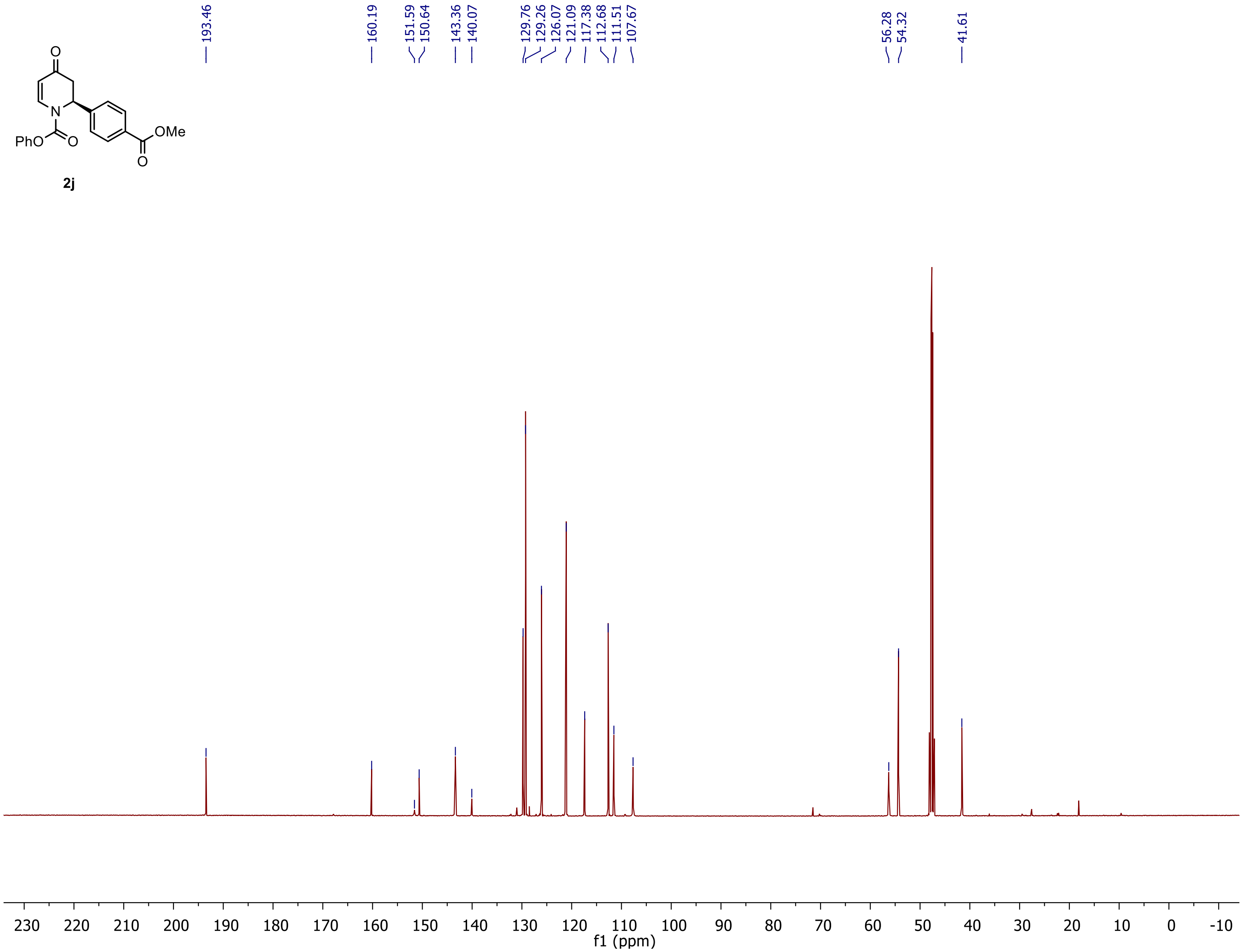


125 MHz ^{13}C-NMR spectrum of **2i** in MeOD



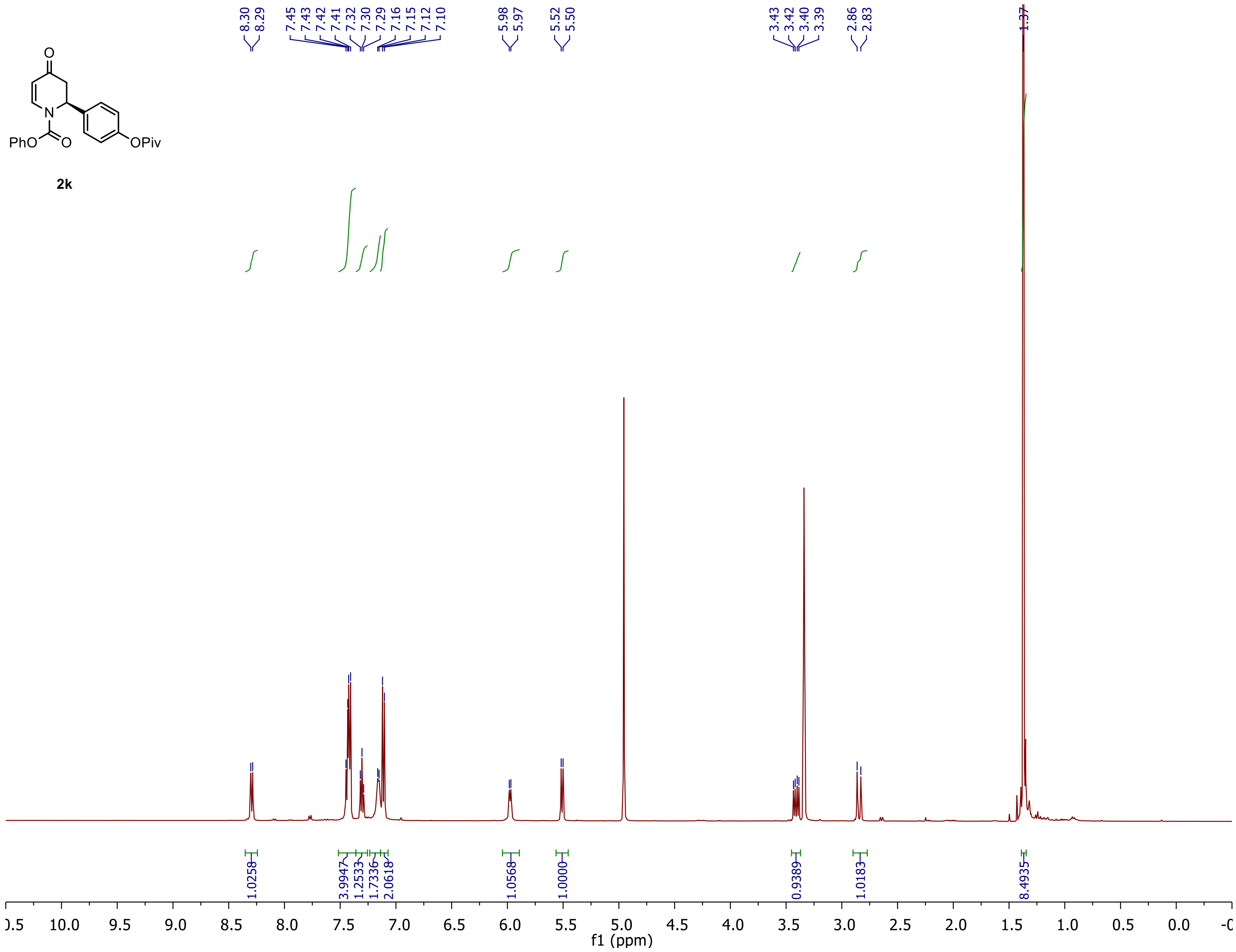
2j

500 MHz ^{1}H-NMR spectrum of **2j** in MeOD



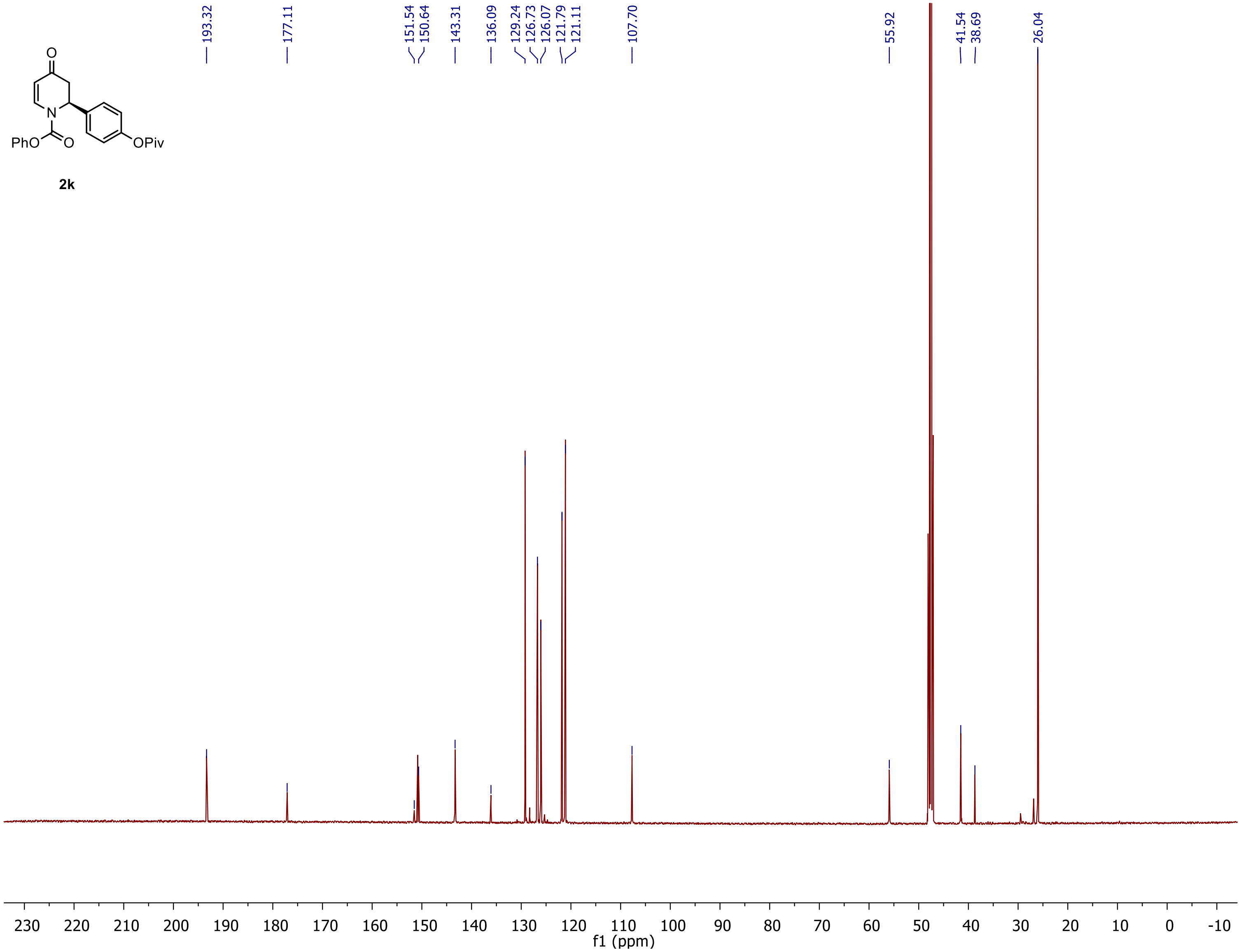
125 MHz ^{13}C-NMR spectrum of **2j** in MeOD

2k

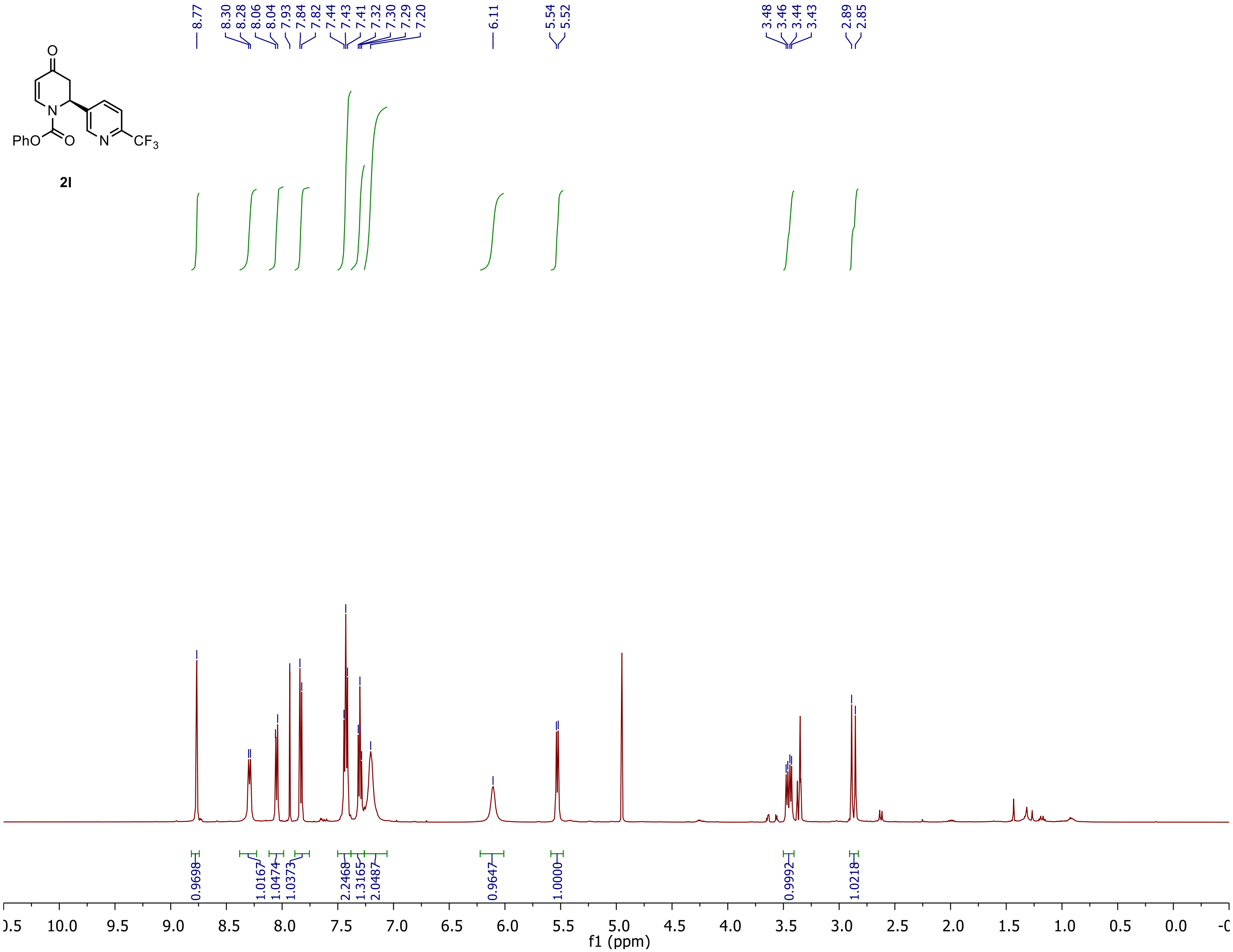


500 MHz ^{1}H-NMR spectrum of **2k** in MeOD

2k

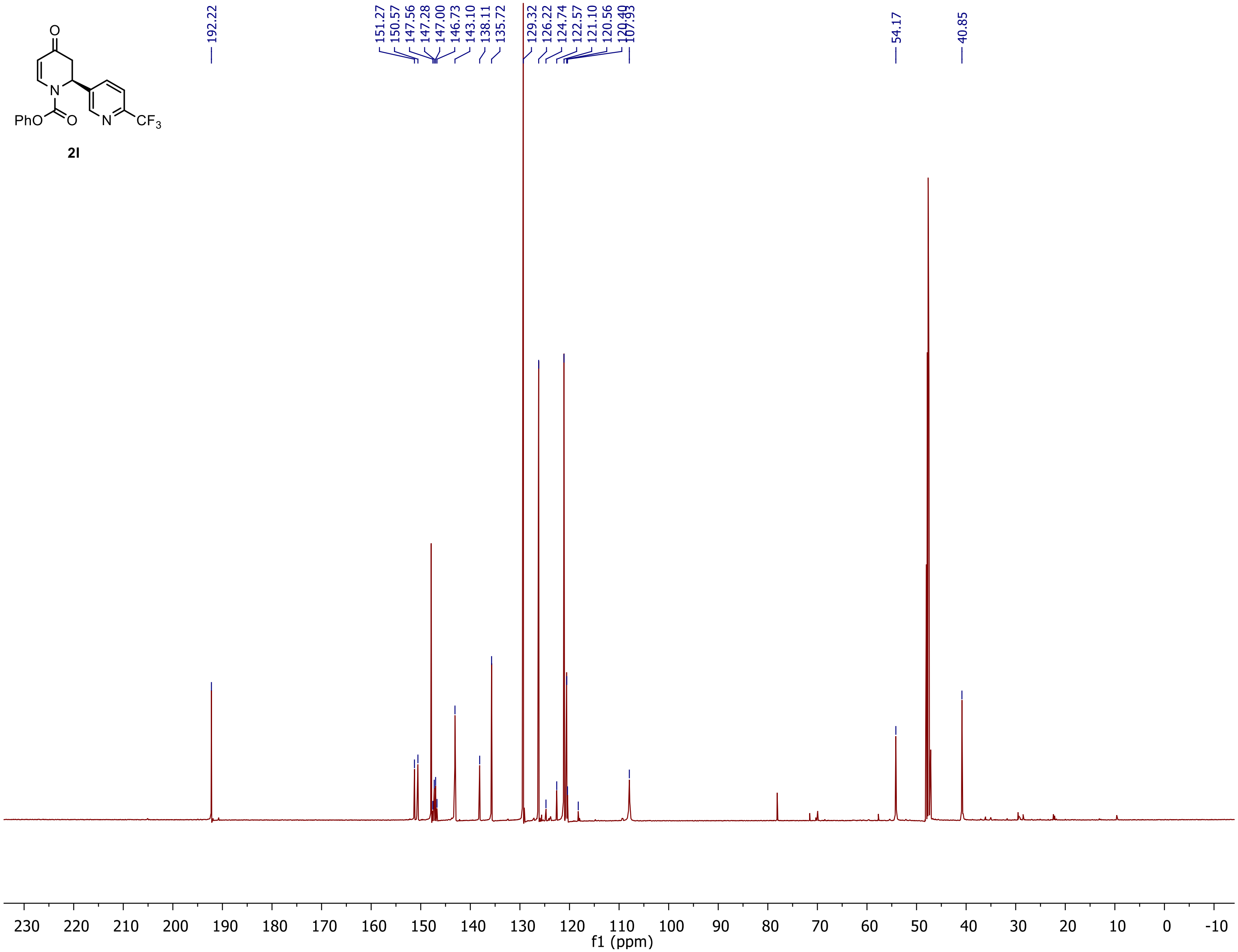


125 MHz ^{13}C-NMR spectrum of **2k** in MeOD

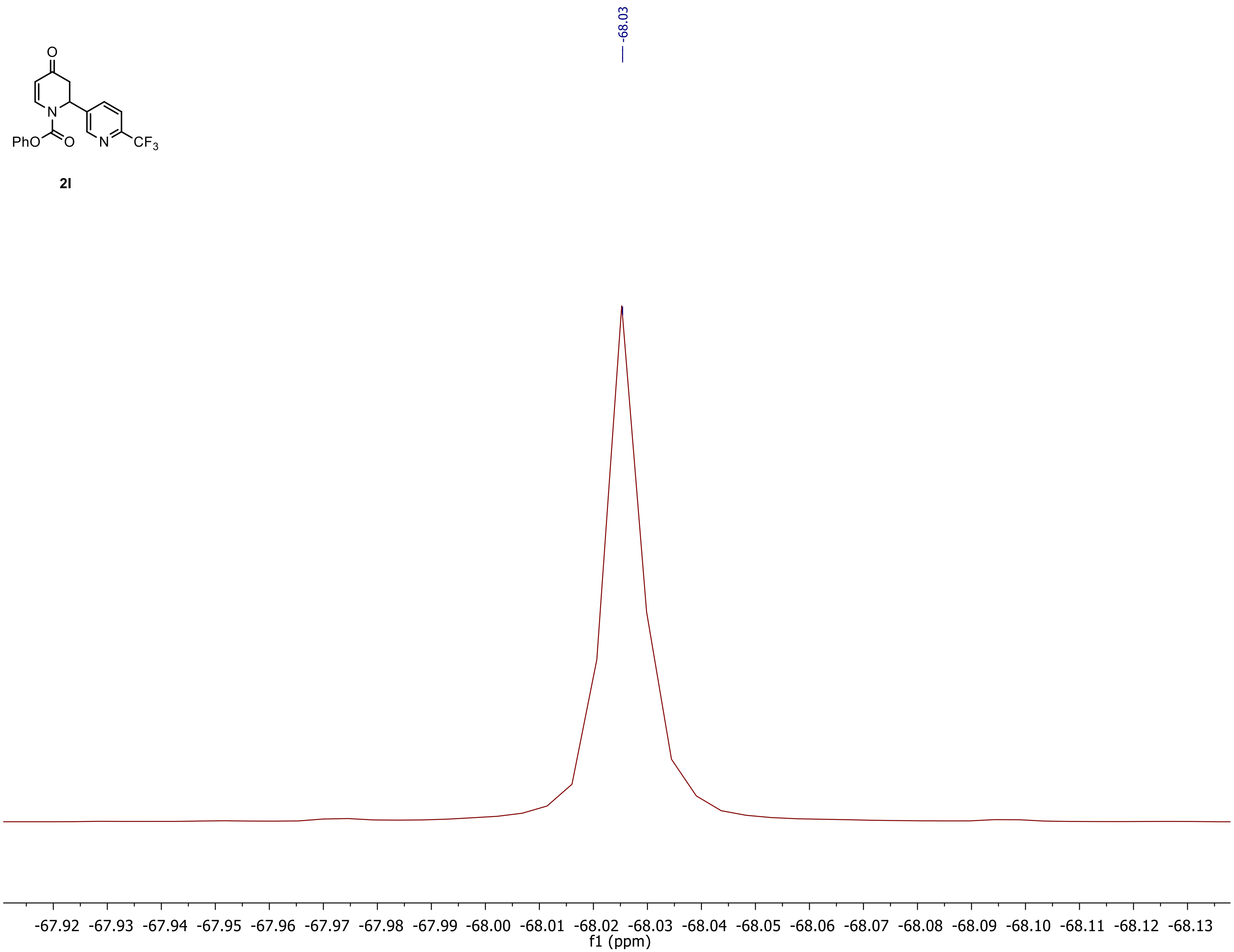


2l

500 MHz ^{1}H-NMR spectrum of **2l** in MeOD

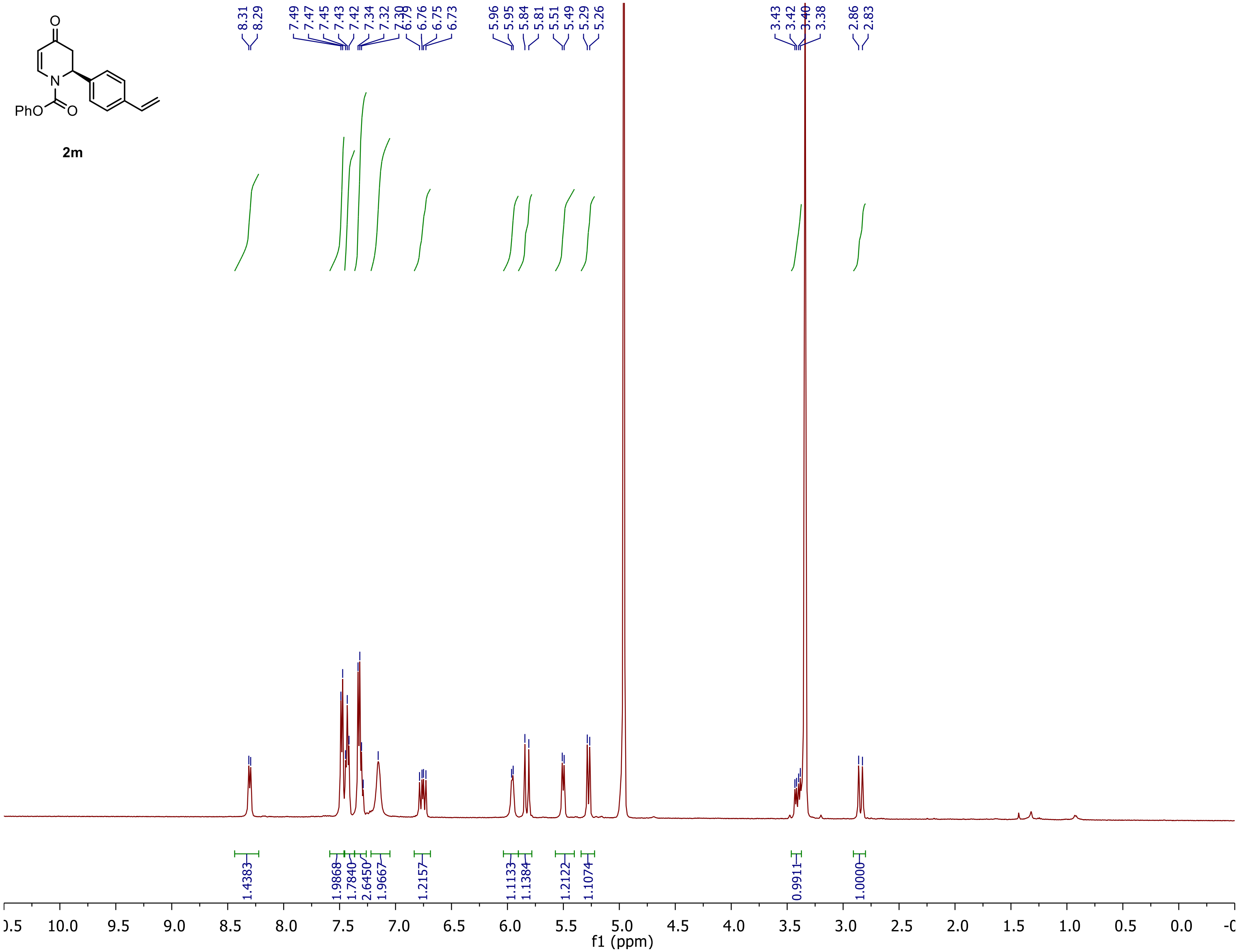


125 MHz ^{13}C-NMR spectrum of **2l** in MeOD

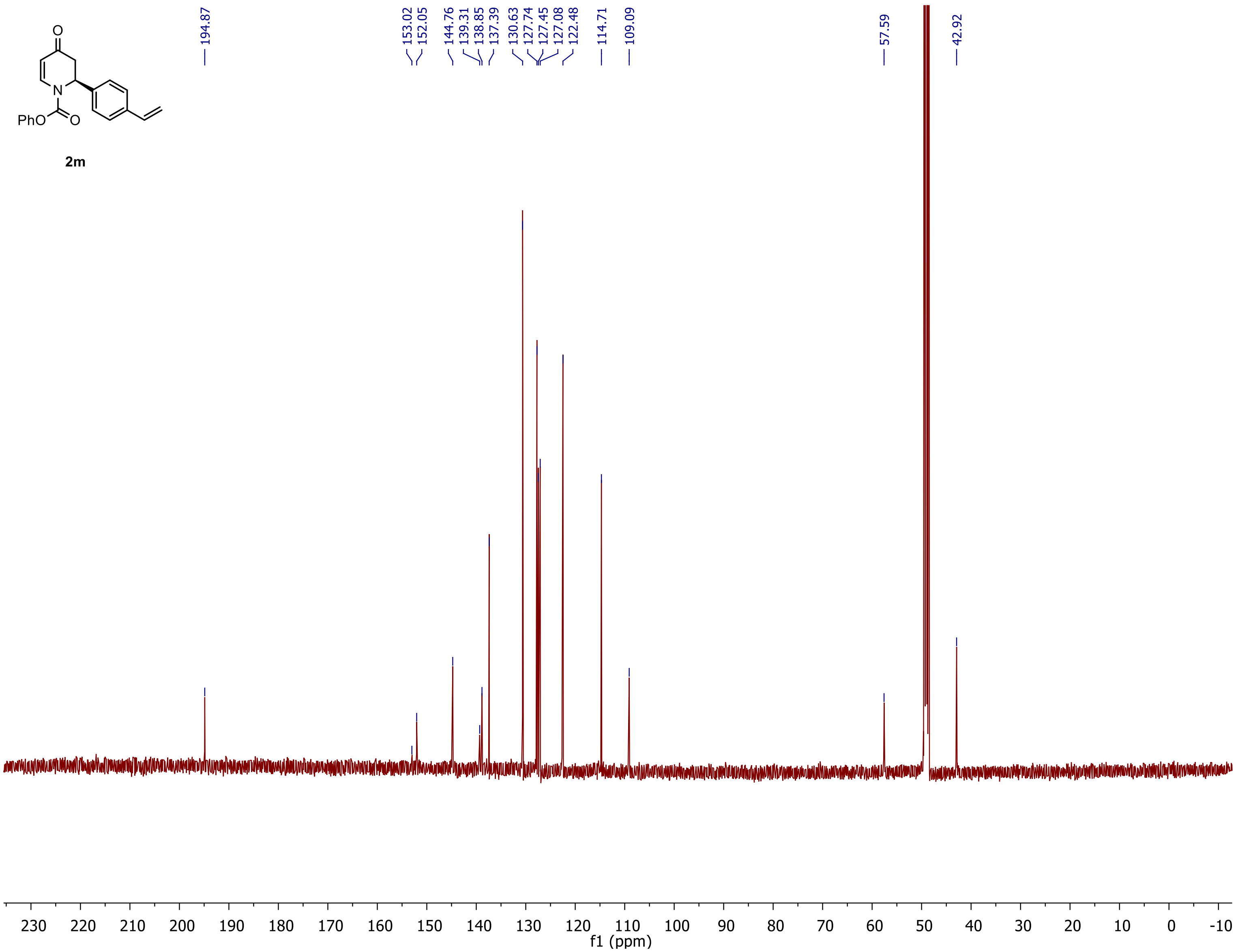


282 MHz ^{19}F NMR spectrum of **2l** in MeOD

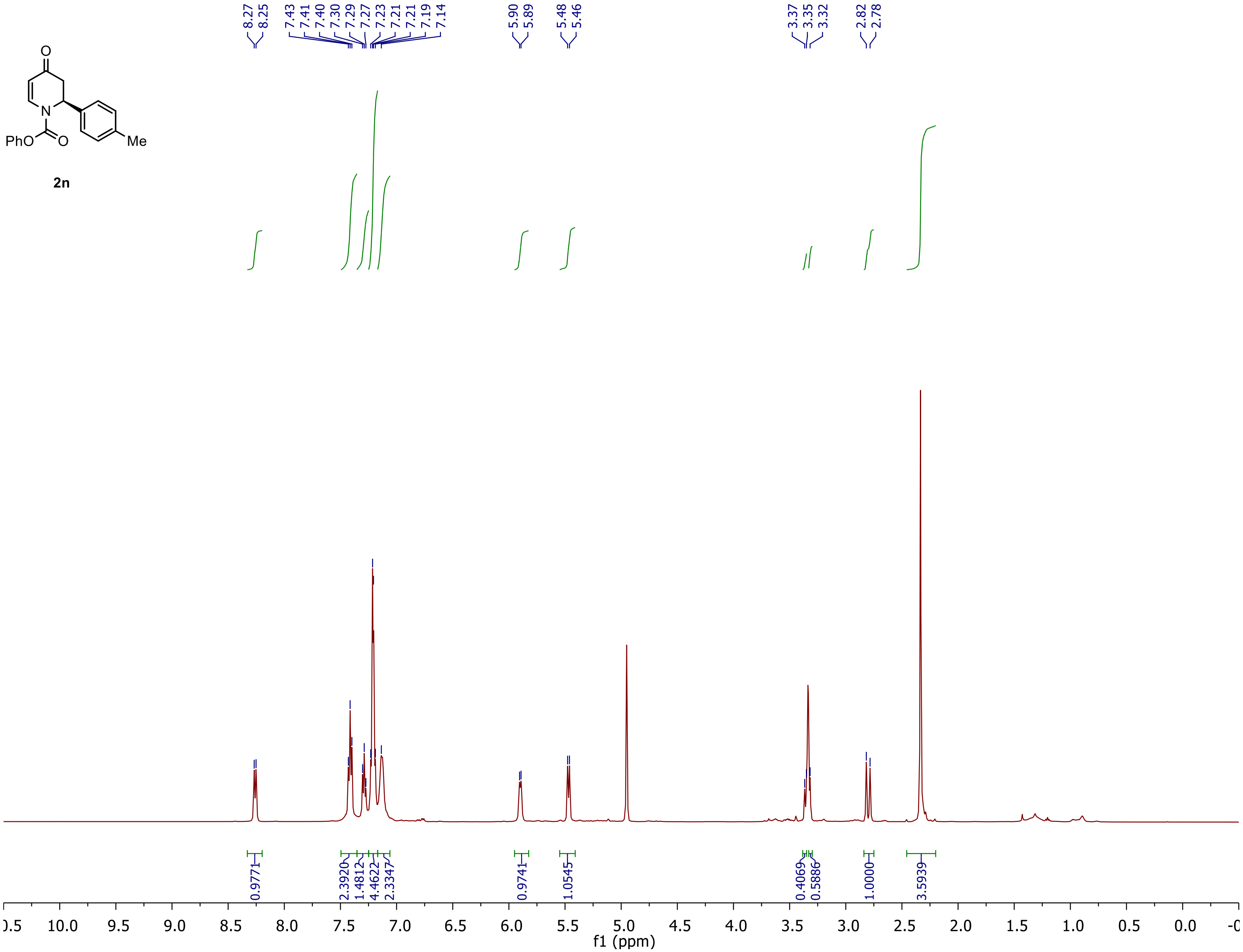
2m



500 MHz ^{1}H-NMR spectrum of **2m** in MeOD

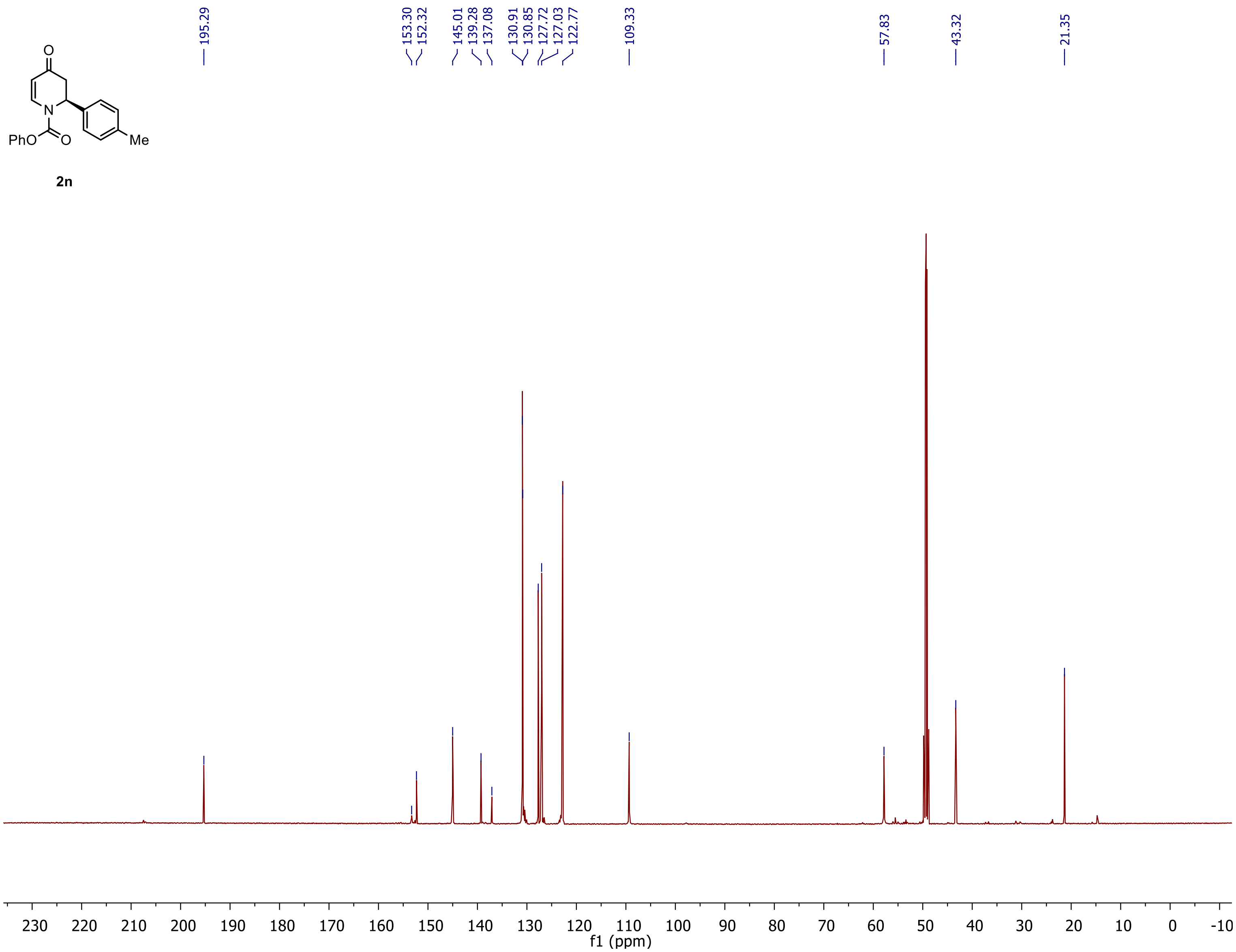


125 MHz ^{13}C-NMR spectrum of **2m** in MeOD



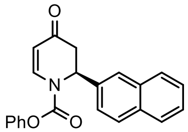
2n

500 MHz ^{1}H-NMR spectrum of **2n** in MeOD

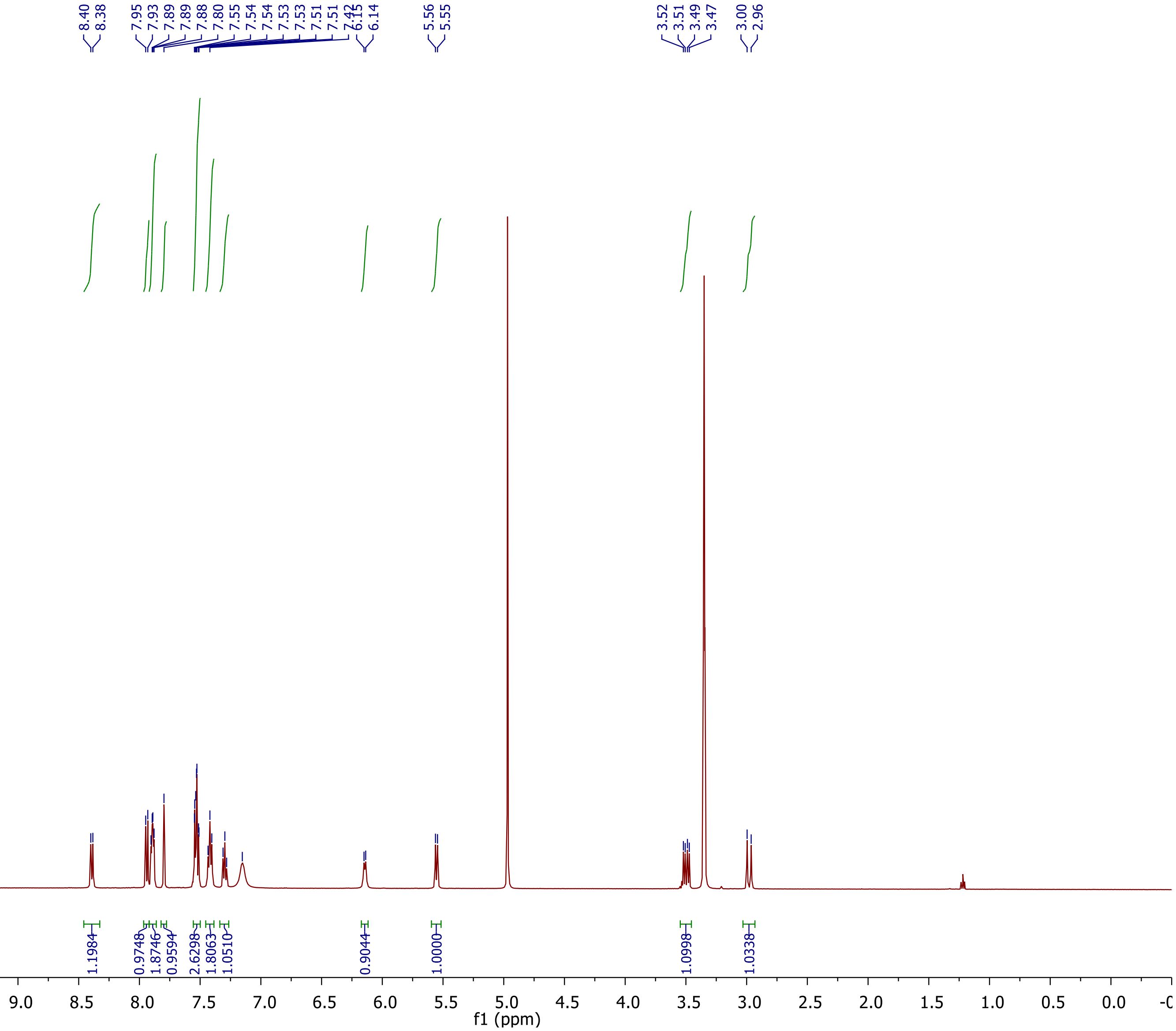


2n

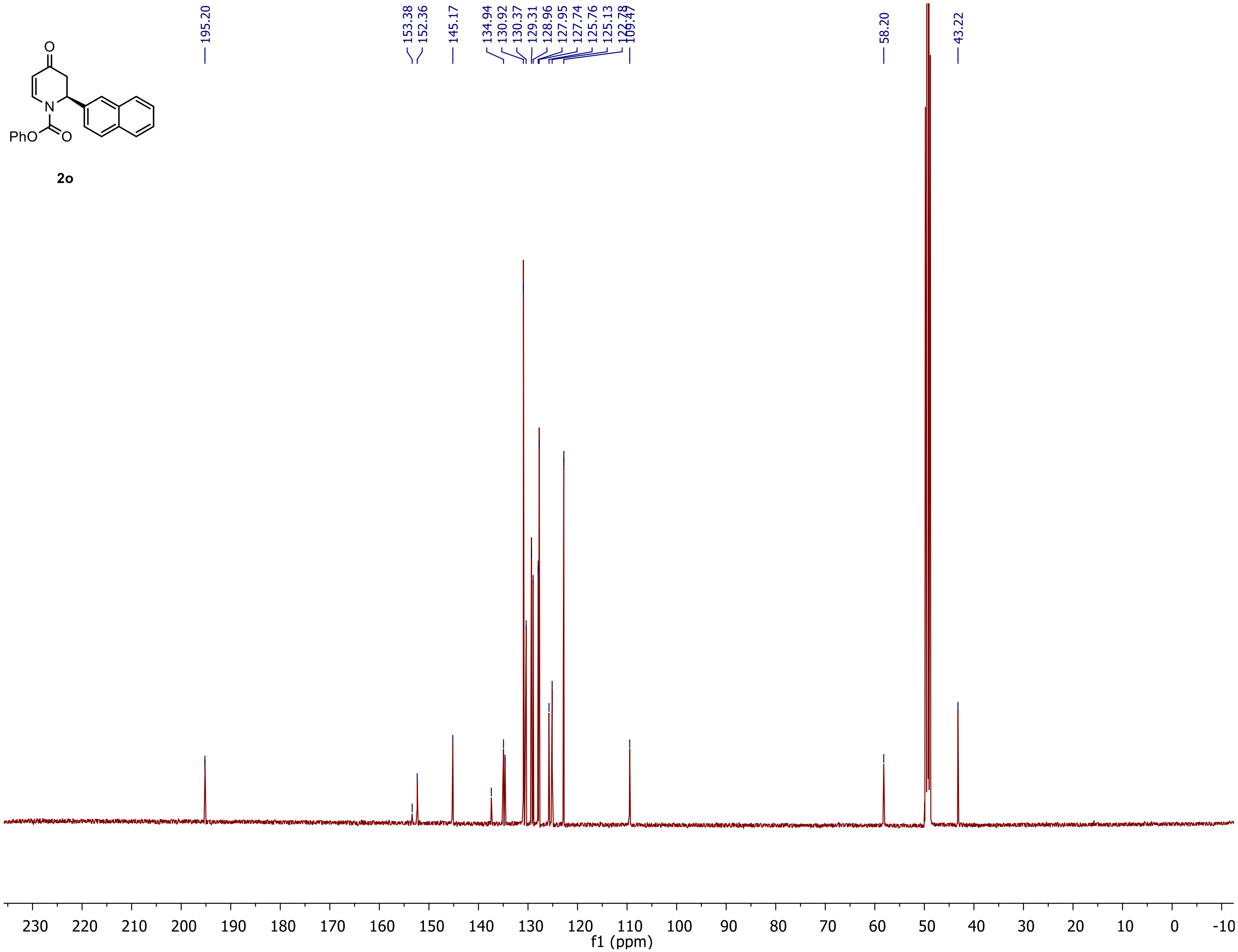
125 MHz ^{13}C-NMR spectrum of **2n** in MeOD



2o

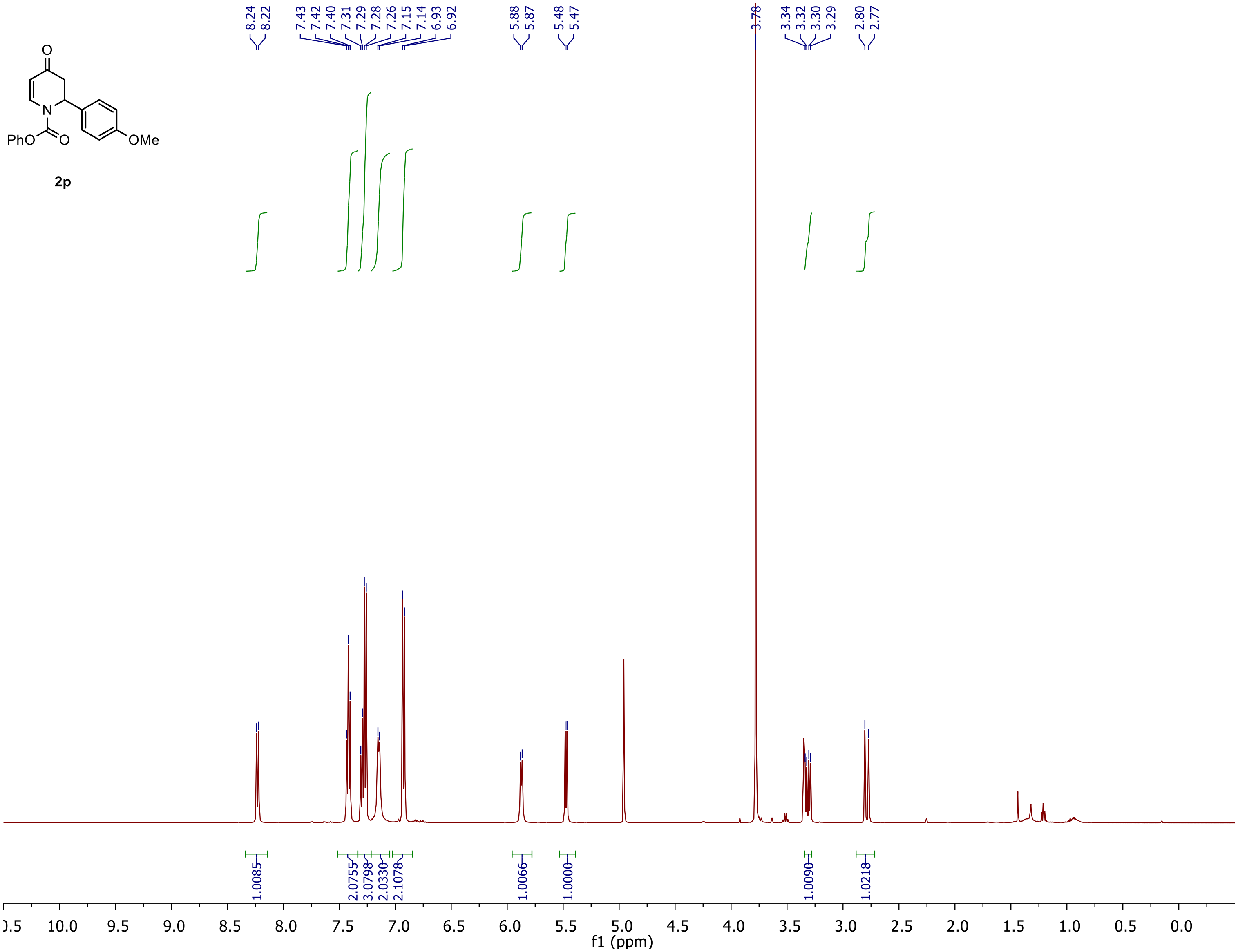


500 MHz ^{1}H-NMR spectrum of **2o** in MeOD

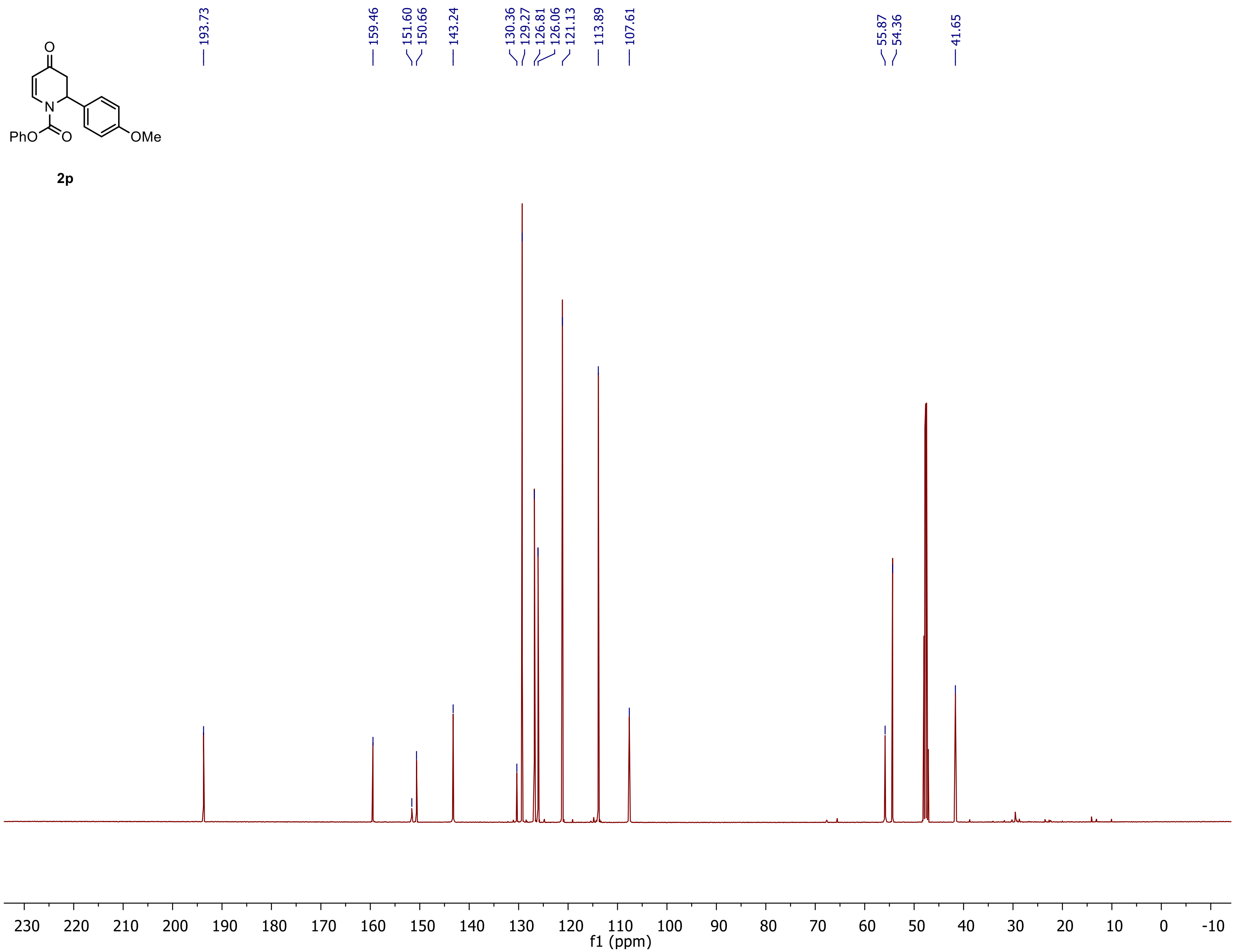


125 MHz ^{13}C-NMR spectrum of **2o** in MeOD

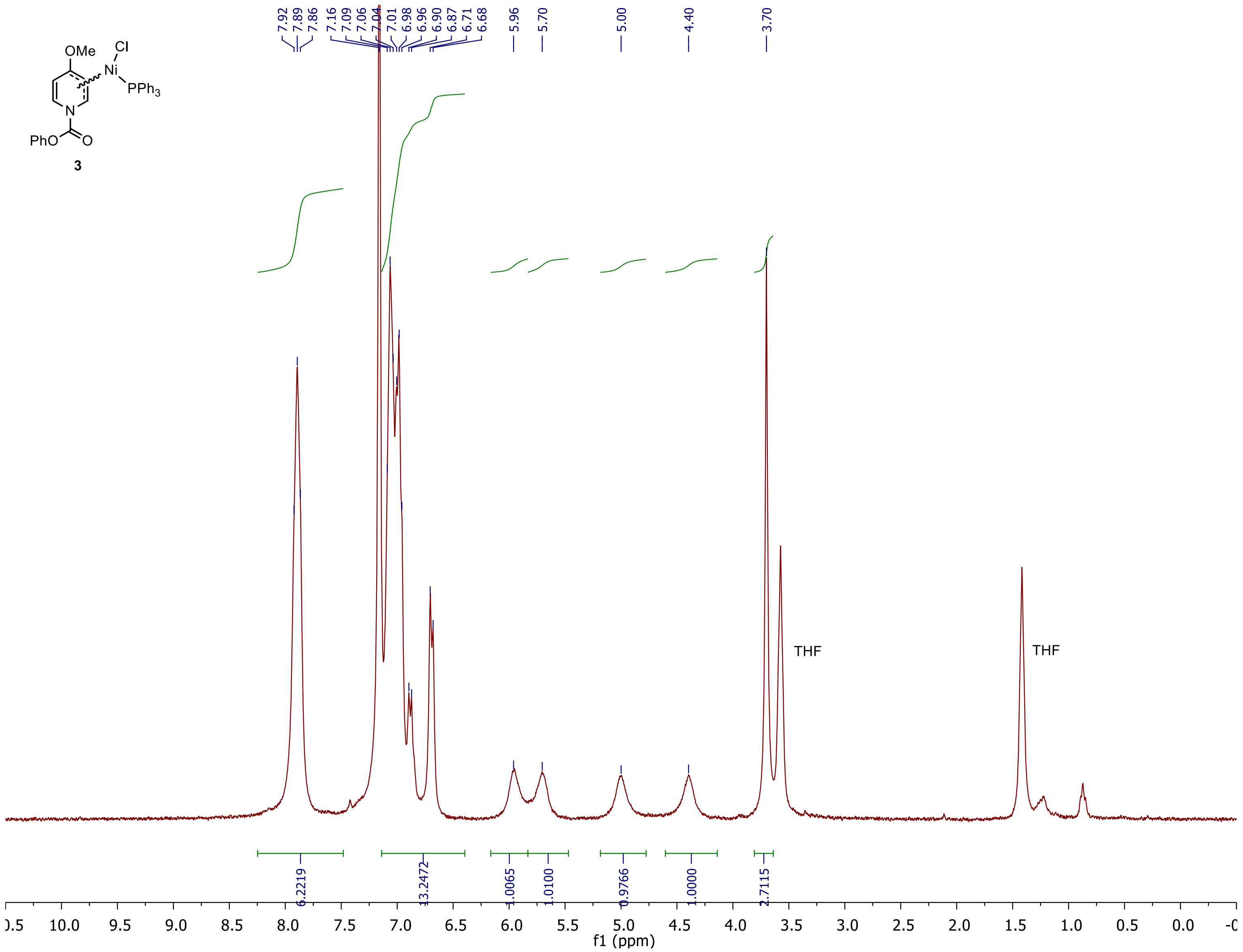
2p



500 MHz ^{1}H-NMR spectrum of **2p** in MeOD

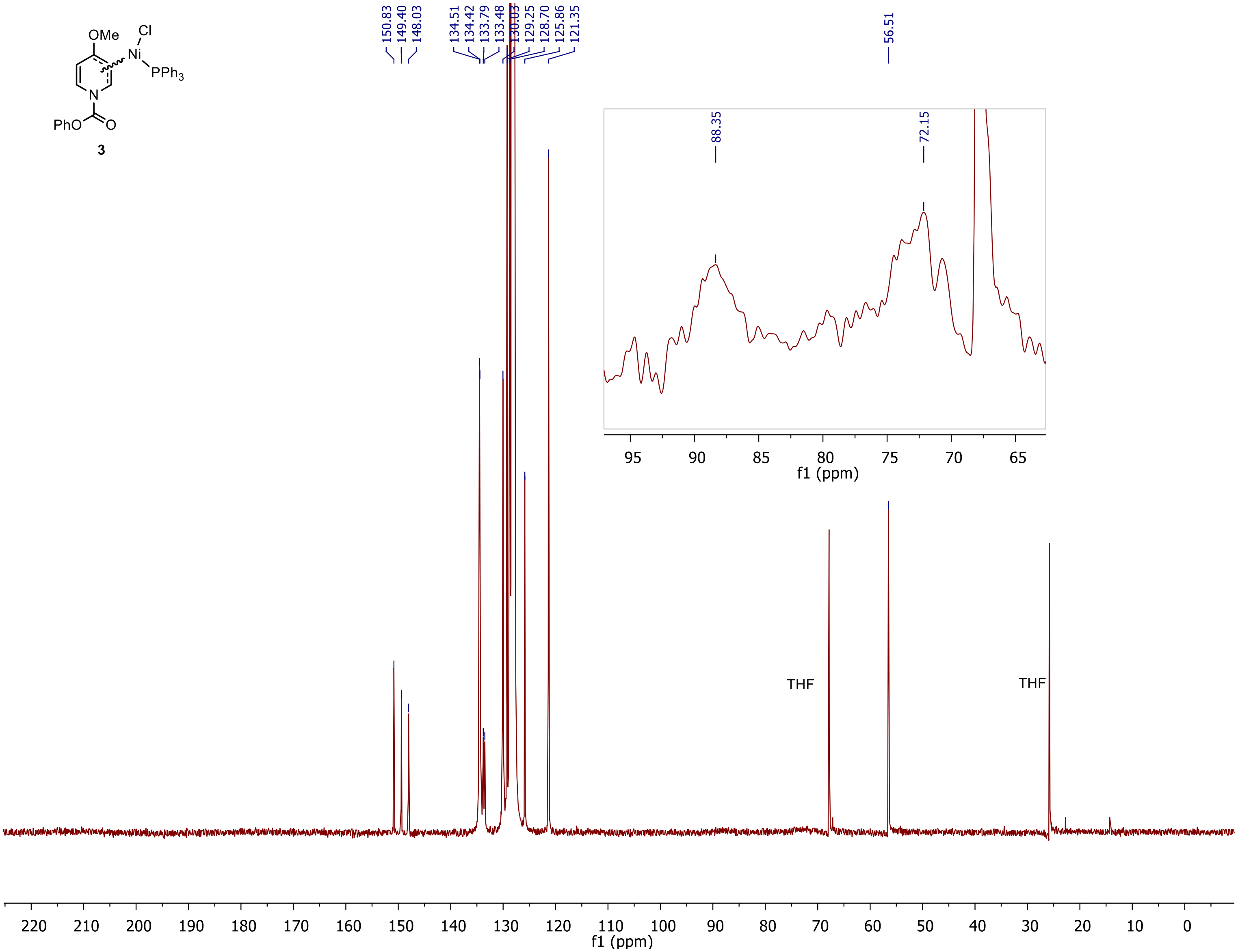


125 MHz ^{13}C-NMR spectrum of **2p** in MeOD

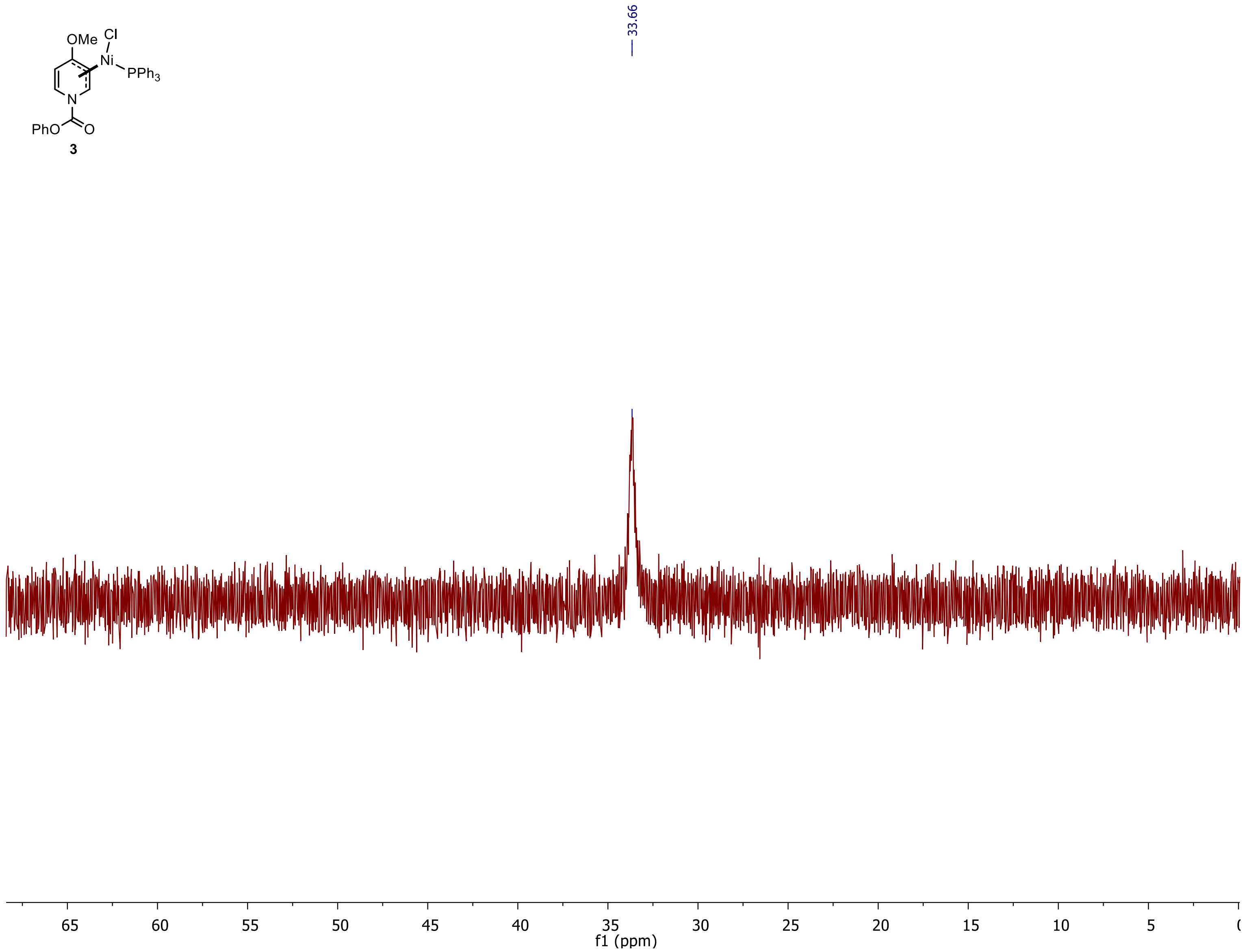


300 MHz ^{1}H-NMR spectrum of **3** in C_6D_6

3



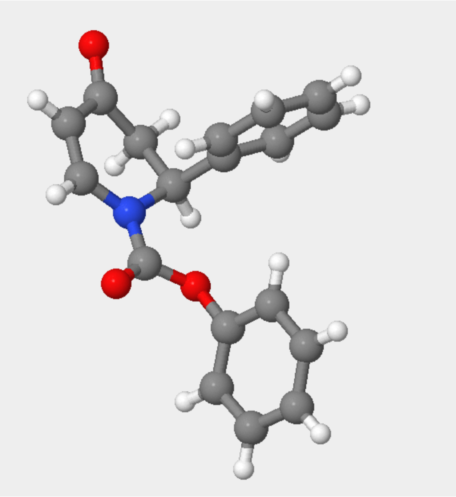
125 MHz ^{13}C-NMR spectrum of **3** in C_6D_6



121 MHz ^{31}P-NMR spectrum of **3** in C_6D_6

VI. Crystallographic Data

Crystal Structure Report for 2b[7]



A triangular plate-like specimen of $C_{18}H_{15}NO_3$, approximate dimensions 0.160 mm x 0.190 mm x 0.280 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured.

Table S5. Data collection details for 2b.

Axis	dx (mm)	2θ (°)	ω (°)	φ (°)	χ (°)	Width (°)	Frames	Time (s)	Wavelength (Å)	Voltage (kV)	Current (mA)	Temp. (K)
Omega	39.947	98.00	-86.00	-150.00	54.50	0.50	377	5.00	1.54184	45	0.7	100.01
Omega	39.947	100.00	-84.00	342.00	54.50	0.50	377	5.00	1.54184	45	0.7	100.01
Phi	39.947	-34.00	-214.00	-352.12	54.50	0.50	707	5.00	1.54184	45	0.7	100.01
Omega	39.947	94.00	-90.00	-220.00	54.50	0.50	272	5.00	1.54184	45	0.7	100.01
Omega	39.947	98.00	-86.00	32.00	54.50	0.50	377	5.00	1.54184	45	0.7	100.01
Omega	39.947	98.00	-86.00	-54.00	54.50	0.50	377	5.00	1.54184	45	0.7	100.01
Phi	39.947	62.00	-84.00	-45.20	54.50	0.50	101	5.00	1.54184	45	0.7	100.01
Phi	39.947	96.00	12.00	110.93	54.50	0.50	170	5.00	1.54184	45	0.7	100.01
Omega	39.947	98.00	-60.77	78.00	54.50	0.50	288	5.00	1.54184	45	0.7	100.01

A total of 3046 frames were collected. The total exposure time was 4.23 hours. The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. The integration of the data using an orthorhombic unit cell yielded a total of 9563 reflections to a maximum θ angle of 65.08° (0.85 Å resolution), of which 2408 were independent (average redundancy 3.971,

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[7] For further information on Flack parameters see Flack H.D. *Acta Cryst.* **1983**, A39, 876-881.

completeness = 99.7%, R_{int} = 1.96%, R_{sig} = 1.83%) and 2381 (98.88%) were greater than $2\sigma(F^2)$. The final cell constants of a = 8.309(10) Å, b = 8.760(11) Å, c = 19.63(2) Å, volume = 1429.(3) Å^3, are based upon the refinement of the XYZ-centroids of 221 reflections above 20 σ(I) with 5.324° < 2θ < 52.99°. Data were corrected for absorption effects using the multi-scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.917. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.8143 and 0.8881.

The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group P 21 21 21, with Z = 4 for the formula unit, $C_{18}H_{15}NO_3$. The final anisotropic full-matrix least-squares refinement on F^2 with 200 variables converged at R1 = 2.38%, for the observed data and wR2 = 6.88% for all data. The goodness-of-fit was 1.682. The largest peak in the final difference electron density synthesis was 0.145 e$^-$/Å^3 and the largest hole was -0.118 e$^-$/Å^3 with an RMS deviation of 0.028 e$^-$/Å^3. On the basis of the final model, the calculated density was 1.364 g/cm^3 and F(000), 616 e$^-$.

Table S6. Sample and crystal data for 2b.

Identification code	pdjstc	
Chemical formula	$C_{18}H_{15}NO_3$	
Formula weight	293.31	
Temperature	100(2) K	
Wavelength	1.54178 Å	
Crystal size	0.160 x 0.190 x 0.280 mm	
Crystal system	orthorhombic	
Space group	P 21 21 21	
Unit cell dimensions	a = 8.309(10) Å	α = 90°
	b = 8.760(11) Å	β = 90°
	c = 19.63(2) Å	γ = 90°
Volume	1429.(3) Å^3	
Z	4	
Density (calculated)	1.364 Mg/cm^3	
Absorption coefficient	0.760 mm^{-1}	
F(000)	616	

Table S7. Data collection and structure refinement for 2b.

Theta range for data collection	4.50 to 65.08°	
Index ranges	-9<=h<=9, -10<=k<=10, -23<=l<=22	
Reflections collected	9563	
Independent reflections	2408 [R(int) = 0.0196]	
Coverage of independent reflections	99.7%	
Absorption correction	multi-scan	
Max. and min. transmission	0.8881 and 0.8143	
Structure solution technique	direct methods	
Structure solution program	SHELXS-97 (Sheldrick, 2008)	
Refinement method	Full-matrix least-squares on F^2	
Refinement program	SHELXL-97 (Sheldrick, 2008)	
Function minimized	$\Sigma w(F_o^2 - F_c^2)^2$	
Data / restraints / parameters	2408 / 0 / 200	
Goodness-of-fit on F^2	1.682	
Δ/σ_{max}	0.012	
Final R indices	2381 data; $I>2\sigma(I)$	R1 = 0.0238, wR2 = 0.0686
	all data	R1 = 0.0242, wR2 = 0.0688
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.0338P)^2+0.0000P]$ where $P=(F_o^2+2F_c^2)/3$	
Absolute structure parameter	0.0(1)	
Extinction coefficient	0.0015(5)	
Largest diff. peak and hole	0.145 and -0.118 eÅ^{-3}	
R.M.S. deviation from mean	0.028 eÅ^{-3}	

Table S8. Atomic coordinates and equivalent isotropic atomic displacement parameters (Å^2) for 2b.

U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x/a	y/b	z/c	U(eq)
O1	0.82529(11)	0.92524(9)	0.75553(4)	0.0301(2)
O2	0.03192(11)	0.04206(9)	0.70171(4)	0.0311(2)
O3	0.30747(11)	0.89570(9)	0.98620(4)	0.0300(2)
N1	0.06373(11)	0.93344(10)	0.80717(5)	0.0238(2)
C1	0.46724(16)	0.10560(17)	0.63344(8)	0.0405(3)
C2	0.50248(17)	0.17225(15)	0.69511(8)	0.0416(3)
C3	0.62507(17)	0.11540(14)	0.73541(6)	0.0341(3)
C4	0.71032(13)	0.99119(12)	0.71203(5)	0.0247(2)
C5	0.97867(14)	0.97414(12)	0.74959(6)	0.0245(2)
C6	0.97771(14)	0.87675(12)	0.86781(5)	0.0223(2)
C7	0.88464(13)	0.00434(12)	0.90250(5)	0.0218(2)
C8	0.91417(14)	0.15840(13)	0.89128(6)	0.0260(3)
C9	0.82768(16)	0.26860(13)	0.92568(6)	0.0288(3)
C10	0.70997(16)	0.22698(13)	0.97169(6)	0.0302(3)
C11	0.55572(17)	0.98324(16)	0.61102(7)	0.0372(3)
C12	0.67824(16)	0.92445(13)	0.65050(6)	0.0301(3)
C13	0.21796(14)	0.98980(12)	0.81454(6)	0.0264(2)
C14	0.30218(14)	0.98082(12)	0.87234(6)	0.0273(2)
C15	0.24267(14)	0.89491(12)	0.93043(5)	0.0249(3)
C16	0.09762(14)	0.79833(12)	0.91524(6)	0.0241(2)
C17	0.67672(16)	0.07357(14)	0.98197(6)	0.0319(3)
C18	0.76431(15)	0.96391(13)	0.94804(6)	0.0277(3)

Table S9. Bond lengths (Å) for 2b.

O1-C5	1.349(2)	**O1-C4**	1.4055(17)
O2-C5	1.1973(17)	**O3-C15**	1.2200(19)
N1-C5	1.3800(19)	**N1-C13**	1.381(2)
N1-C6	1.4745(19)	**C1-C11**	1.372(2)
C1-C2	1.375(3)	**C1-H1**	0.95
C2-C3	1.383(2)	**C2-H2**	0.95
C3-C4	1.377(2)	**C3-H3**	0.95
C4-C12	1.368(2)	**C6-C7**	1.5202(19)
C6-C16	1.5269(19)	**C6-H6**	1.0
C7-C18	1.3872(19)	**C7-C8**	1.389(2)
C8-C9	1.380(2)	**C8-H8**	0.95
C9-C10	1.380(2)	**C9-H9**	0.95
C10-C17	1.387(2)	**C10-H10**	0.95
C11-C12	1.379(2)	**C11-H11**	0.95
C12-H12	0.95	**C13-C14**	1.335(2)
C13-H13	0.95	**C14-C15**	1.453(2)
C14-H14	0.95	**C15-C16**	1.502(2)
C16-H16A	0.99	**C16-H16B**	0.99
C17-C18	1.377(2)	**C17-H17**	0.95
C18-H18	0.95		

Table S10. Bond angles (°) for 2b.

C5-O1-C4	117.31(10)	**C5-N1-C13**	117.95(10)
C5-N1-C6	120.00(12)	**C13-N1-C6**	119.06(10)
C11-C1-C2	119.98(13)	**C11-C1-H1**	120.0
C2-C1-H1	120.0	**C1-C2-C3**	120.50(13)
C1-C2-H2	119.7	**C3-C2-H2**	119.7
C4-C3-C2	118.22(13)	**C4-C3-H3**	120.9
C2-C3-H3	120.9	**C12-C4-C3**	122.12(11)
C12-C4-O1	119.55(12)	**C3-C4-O1**	118.16(12)
O2-C5-O1	125.07(11)	**O2-C5-N1**	125.61(13)
O1-C5-N1	109.32(11)	**N1-C6-C7**	111.14(10)
N1-C6-C16	109.12(12)	**C7-C6-C16**	112.92(11)
N1-C6-H6	107.8	**C7-C6-H6**	107.8
C16-C6-H6	107.8	**C18-C7-C8**	118.52(10)
C18-C7-C6	117.88(11)	**C8-C7-C6**	123.59(12)
C9-C8-C7	120.66(13)	**C9-C8-H8**	119.7
C7-C8-H8	119.7	**C10-C9-C8**	120.29(12)
C10-C9-H9	119.9	**C8-C9-H9**	119.9
C9-C10-C17	119.50(11)	**C9-C10-H10**	120.3
C17-C10-H10	120.3	**C1-C11-C12**	120.45(14)
C1-C11-H11	119.8	**C12-C11-H11**	119.8
C4-C12-C11	118.71(13)	**C4-C12-H12**	120.6
C11-C12-H12	120.6	**C14-C13-N1**	123.66(11)
C14-C13-H13	118.2	**N1-C13-H13**	118.2
C13-C14-C15	121.27(12)	**C13-C14-H14**	119.4
C15-C14-H14	119.4	**O3-C15-C14**	123.45(13)
O3-C15-C16	122.37(11)	**C14-C15-C16**	114.13(11)
C15-C16-C6	113.03(11)	**C15-C16-H16A**	109.0
C6-C16-H16A	109.0	**C15-C16-H16B**	109.0
C6-C16-H16B	109.0	**H16A-C16-H16B**	107.8
C18-C17-C10	120.02(14)	**C18-C17-H17**	120.0
C10-C17-H17	120.0	**C17-C18-C7**	120.97(12)
C17-C18-H18	119.5	**C7-C18-H18**	119.5

Table S11. Anisotropic atomic displacement parameters (Å^2) for 2b.

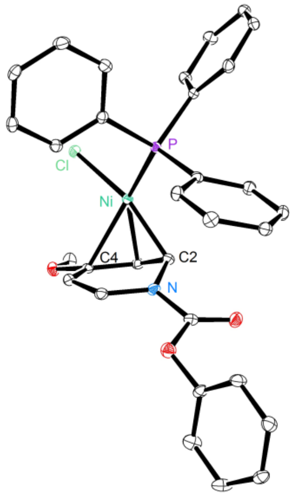
The anisotropic atomic displacement factor exponent takes the form: $-2\pi^2[\, h^2 a^{*2} U_{11} + ... + 2\, h\, k\, a^{*} b^{*} U_{12} \,]$

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
O1	0.0279(4)	0.0339(4)	0.0287(4)	0.0102(3)	-0.0064(3)	-0.0072(4)
O2	0.0318(4)	0.0344(4)	0.0271(4)	0.0101(4)	0.0030(3)	0.0008(4)
O3	0.0324(4)	0.0264(4)	0.0313(4)	0.0016(3)	-0.0072(4)	0.0004(3)
N1	0.0253(5)	0.0224(4)	0.0237(5)	0.0028(4)	0.0008(4)	-0.0002(4)
C1	0.0256(6)	0.0458(7)	0.0501(8)	0.0200(6)	-0.0014(6)	-0.0020(6)
C2	0.0362(7)	0.0298(6)	0.0587(9)	0.0090(6)	0.0177(6)	0.0072(6)
C3	0.0406(7)	0.0293(6)	0.0323(6)	-0.0022(5)	0.0079(5)	-0.0027(5)
C4	0.0252(5)	0.0241(5)	0.0248(5)	0.0062(4)	-0.0012(4)	-0.0042(4)
C5	0.0292(6)	0.0198(5)	0.0244(5)	0.0010(4)	-0.0001(4)	0.0006(5)
C6	0.0258(6)	0.0186(5)	0.0224(5)	0.0020(4)	0.0010(4)	-0.0022(4)
C7	0.0219(5)	0.0225(5)	0.0209(5)	0.0017(4)	-0.0047(4)	-0.0006(4)
C8	0.0242(6)	0.0232(5)	0.0307(6)	0.0011(4)	-0.0014(5)	-0.0025(5)
C9	0.0299(6)	0.0207(5)	0.0358(6)	-0.0006(4)	-0.0065(5)	-0.0002(5)
C10	0.0302(7)	0.0279(6)	0.0326(6)	-0.0035(5)	-0.0030(5)	0.0085(5)
C11	0.0350(6)	0.0433(7)	0.0335(6)	0.0044(5)	-0.0087(5)	-0.0092(6)
C12	0.0344(6)	0.0257(5)	0.0304(6)	-0.0003(5)	-0.0013(5)	-0.0020(5)
C13	0.0248(6)	0.0242(5)	0.0302(5)	0.0032(4)	0.0045(4)	0.0009(4)
C14	0.0221(5)	0.0246(5)	0.0352(6)	0.0018(5)	-0.0003(5)	-0.0007(5)
C15	0.0253(6)	0.0193(5)	0.0302(6)	-0.0007(4)	-0.0011(5)	0.0071(5)
C16	0.0273(6)	0.0189(5)	0.0259(5)	0.0020(4)	-0.0006(4)	0.0007(5)
C17	0.0311(6)	0.0338(6)	0.0309(6)	0.0022(5)	0.0058(5)	0.0007(6)
C18	0.0314(6)	0.0234(5)	0.0282(5)	0.0028(4)	0.0020(5)	-0.0012(5)

Table S12. Hydrogen atomic coordinates and isotropic atomic displacement parameters (Å^2) for 2b.

	x/a	**y/b**	**z/c**	**U(eq)**
H1	0.3817	0.1443	0.6064	0.049
H2	0.4421	0.2580	0.7101	0.05
H3	0.6498	0.1608	0.7781	0.041
H6	0.8983	-0.2017	0.8523	0.027
H8	0.9947	0.1882	0.8596	0.031
H9	0.8492	0.3736	0.9177	0.035
H10	0.6522	0.3029	0.9961	0.036
H11	0.5324	-0.0613	0.5680	0.045
H12	0.7392	-0.1607	0.6353	0.036
H13	1.2669	0.0376	0.7764	0.032
H14	1.4029	0.0316	0.8755	0.033
H16A	1.0428	-0.2271	0.9586	0.029
H16B	1.1333	-0.2985	0.8941	0.029
H17	0.5935	0.0441	1.0124	0.038
H18	0.7420	-0.1410	0.9559	0.033

Crystal Structure Report for 3



A translucent dark purple-brown irregular rod-like specimen of $C_{31}H_{27}ClNNiO_3P$, approximate dimensions 0.040 mm x 0.130 mm x 0.140 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured.

The structure of **3** is comparable to a quinolinium-derived π-allyl intermediate that we previously reported in the context of our mechanistic investigation of allylic *N*,*O*-acetal C–O oxidative addition of 1-ethoxycarbonyl-1,2-dihydroquinoline (EEDQ) (C2-C3,C3-C4 1.438, 1.394 Å [3] vs. C2-C3, C3-C4 1.404, 1.394 Å [1, Scheme 1]).

Table S13: Data collection details for 3.

Axis	Dx (mm)	2θ (°)	ω (°)	ϕ (°)	χ (°)	Width (°)	Frames	Time(s)	Wavelength (Å)	Voltage (kV)	Current (mA)	Temp. (K)
Omega	40.000	88.00	-95.62	-190.00	54.50	0.50	371	15.00	1.54184	45	0.7	99.99
Phi	40.000	94.00	-64.00	-360.00	54.50	0.50	739	15.00	1.54184	45	0.7	99.99
Phi	40.000	-52.00	-212.00	-358.32	54.50	0.50	720	15.00	1.54184	45	0.7	99.99
Phi	40.000	82.00	-38.00	-356.94	54.50	0.50	721	15.00	1.54184	45	0.7	99.99
Omega	40.000	100.00	-83.53	342.00	54.50	0.50	376	15.00	1.54184	45	0.7	99.99
Omega	40.000	92.00	-58.36	58.00	54.50	0.50	264	15.00	1.54184	45	0.7	99.99
Phi	40.000	-36.00	-70.00	-356.78	54.50	0.50	731	15.00	1.54184	45	0.7	99.99
Phi	40.000	96.00	58.00	-263.48	54.50	0.50	404	15.00	1.54184	45	0.7	99.99
Omega	40.000	-42.00	140.30	-112.00	54.50	0.50	134	15.00	1.54184	45	0.7	99.99
Omega	40.000	94.00	-51.91	-220.00	54.50	0.50	159	15.00	1.54184	45	0.7	99.99
Phi	40.000	-78.00	-200.00	17.40	54.50	0.50	184	15.00	1.54184	45	0.7	99.99

A total of 4803 frames were collected. The total exposure time was 20.01 hours. The integration of the data using a triclinic unit cell yielded a total of 10058 reflections to a maximum θ angle of 66.41° (0.84 Å resolution), of which 4173 were independent (average redundancy 2.410, completeness = 88.2%, R_{int} = 2.00%, R_{sig} = 2.59%) and 3877 (92.91%) were greater than 2σ(F^2). The final cell constants of a = 9.9071(12) Å, b = 11.3675(11) Å, c = 12.9176(19) Å, α = 84.179(11)°, β = 69.191(11)°, γ =80.417(8)°, volume = 1339.5(3) $Å^3$, are based upon the refinement of the XYZ-centroids of 238 reflections above 20 σ(I) with 51.12° < 2θ < 126.3°. Data were corrected for absorption effects using the multi-scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.814. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.6900 and 0.8938.

The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group P -1, with Z = 2 for the formula unit, $C_{31}H_{27}ClNNiO_3P$. The final anisotropic full-matrix least-squares refinement on F^2 with 344 variables converged at R1 = 2.68%, for the observed data and wR2 = 7.05% for all data. The goodness-of-fit was 0.894. The largest peak in the final difference electron density synthesis was 0.346 $e^-/Å^3$ and the largest hole was -0.314 $e^-/Å^3$ with an RMS deviation of 0.049 $e^-/Å^3$. On the basis of the final model, the calculated density was 1.455 g/cm^3 and F(000), 608 e^-.

Table S14. Sample and crystal data for 3.

Identification code	PDJKW2	
Chemical formula	$C_{31}H_{27}ClNNiO_3P$	
Formula weight	586.67	
Temperature	100(2) K	
Wavelength	1.54178 Å	
Crystal size	0.040 x 0.130 x 0.140 mm	
Crystal habit	translucent dark purple-brown irregular rod	
Crystal system	triclinic	
Space group	P -1	
Unit cell dimensions	a = 9.9071(12) Å	α = 84.179(11)°
	b = 11.3675(11) Å	β = 69.191(11)°
	c = 12.9176(19) Å	γ = 80.417(8)°
Volume	1339.5(3) $Å^3$	
Z	2	
Density (calculated)	1.455 Mg/cm^3	
Absorption coefficient	2.803 mm^{-1}	
F(000)	608	

Table S15. Data collection and structure refinement for 3.

Theta range for data collection	3.66 to 66.41°	
Index ranges	-11<=h<=11, -13<=k<=13, -15<=l<=15	
Reflections collected	10058	
Independent reflections	4173 [R(int) = 0.0200]	
Coverage of independent reflections	88.2%	
Absorption correction	multi-scan	
Max. and min. transmission	0.8938 and 0.6900	
Structure solution technique	direct methods	
Structure solution program	SHELXS-97 (Sheldrick, 2008)	
Refinement method	Full-matrix least-squares on F^2	
Refinement program	SHELXL-97 (Sheldrick, 2008)	
Function minimized	$\Sigma\ w(F_o^2 - F_c^2)^2$	
Data / restraints / parameters	4173 / 0 / 344	
Goodness-of-fit on F^2	0.894	
Δ/σ_{max}	0.003	
Final R indices	3877 data; $I>2\sigma(I)$	R1 = 0.0268, wR2 = 0.0686
	all data	R1 = 0.0293, wR2 = 0.0705
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.0401P)^2+1.2823P]$ where $P=(F_o^2+2F_c^2)/3$	
Largest diff. peak and hole	0.346 and -0.314 eÅ^{-3}	
R.M.S. deviation from mean	0.049 eÅ^{-3}	

Table S16. Atomic coordinates and equivalent isotropic atomic displacement parameters (Å^2) for 3.

U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x/a	**y/b**	**z/c**	**U(eq)**
Ni1	0.49238(3)	0.67105(2)	0.67650(2)	0.01497(10)
Cl1	0.59741(5)	0.48308(3)	0.68433(3)	0.01926(11)
P1	0.64215(5)	0.76979(4)	0.70903(3)	0.01418(11)
O1	0.22502(15)	0.04028(11)	0.65560(11)	0.0259(3)
O2	0.09459(15)	0.01141(12)	0.83872(11)	0.0268(3)
O3	0.24270(14)	0.50264(11)	0.72720(10)	0.0210(3)
N1	0.25139(16)	0.85883(13)	0.74717(12)	0.0186(3)
C1	0.35063(19)	0.80126(16)	0.64832(14)	0.0174(4)
C2	0.1936(2)	0.97786(16)	0.73870(15)	0.0205(4)

	x/a	y/b	z/c	U(eq)
C3	0.0086(2)	0.12383(17)	0.83994(15)	0.0217(4)
C4	0.0634(2)	0.22662(17)	0.84240(16)	0.0247(4)
C5	0.9737(2)	0.33518(17)	0.84862(16)	0.0249(4)
C6	0.8318(2)	0.33954(17)	0.85240(15)	0.0237(4)
C7	0.7786(2)	0.23481(19)	0.85044(18)	0.0309(5)
C8	0.8670(2)	0.12564(18)	0.84466(17)	0.0287(5)
C9	0.20128(19)	0.78507(16)	0.84099(15)	0.0198(4)
C10	0.21892(19)	0.66648(16)	0.83172(15)	0.0195(4)
C11	0.26823(19)	0.61570(16)	0.72368(15)	0.0179(4)
C12	0.2803(2)	0.44956(18)	0.62225(16)	0.0285(5)
C13	0.31977(19)	0.68791(16)	0.62812(15)	0.0179(4)
C14	0.82476(19)	0.76863(15)	0.60556(14)	0.0159(4)
C15	0.9125(2)	0.85593(16)	0.59718(15)	0.0199(4)
C16	0.0534(2)	0.84686(16)	0.52033(16)	0.0221(4)
C17	0.1065(2)	0.75214(17)	0.45045(15)	0.0230(4)
C18	0.0200(2)	0.66529(17)	0.45856(15)	0.0235(4)
C19	0.8794(2)	0.67309(16)	0.53650(15)	0.0192(4)
C20	0.67675(19)	0.71140(15)	0.83597(14)	0.0166(4)
C21	0.8089(2)	0.71355(17)	0.85029(16)	0.0237(4)
C22	0.8288(2)	0.66946(19)	0.94886(16)	0.0268(4)
C23	0.7178(2)	0.62258(16)	0.03341(15)	0.0219(4)
C24	0.5864(2)	0.61838(15)	0.01976(15)	0.0206(4)
C25	0.5661(2)	0.66214(15)	0.92111(14)	0.0184(4)
C26	0.57810(18)	0.92875(15)	0.73213(14)	0.0159(4)
C27	0.5110(2)	0.97165(16)	0.83874(15)	0.0202(4)
C28	0.4586(2)	0.09191(16)	0.85316(16)	0.0226(4)
C29	0.4727(2)	0.17104(16)	0.76216(15)	0.0204(4)
C30	0.5363(2)	0.12833(16)	0.65684(15)	0.0218(4)
C31	0.5878(2)	0.00820(16)	0.64108(15)	0.0206(4)

Table S17. Bond lengths (Å) for 3.

Ni1-C1	1.9640(17)	**Ni1-C13**	1.9943(18)
Ni1-P1	2.1752(6)	**Ni1-Cl1**	2.2247(5)
Ni1-C11	2.2638(18)	**P1-C14**	1.8267(18)
P1-C20	1.8302(18)	**P1-C26**	1.8303(17)
O1-C2	1.198(2)	**O2-C2**	1.361(2)
O2-C3	1.411(2)	**O3-C11**	1.344(2)
O3-C12	1.440(2)	**N1-C9**	1.387(2)
N1-C2	1.388(2)	**N1-C1**	1.445(2)
C1-C13	1.441(3)	**C1-H1**	1.0
C3-C4	1.375(3)	**C3-C8**	1.379(3)
C4-C5	1.387(3)	**C4-H4**	0.95
C5-C6	1.382(3)	**C5-H5**	0.95
C6-C7	1.385(3)	**C6-H6**	0.95
C7-C8	1.387(3)	**C7-H7**	0.95
C8-H8	0.95	**C9-C10**	1.342(3)
C9-H9	0.95	**C10-C11**	1.451(3)
C10-H10	0.95	**C11-C13**	1.394(3)
C12-H12A	0.98	**C12-H12B**	0.98
C12-H12C	0.98	**C13-H13**	0.95
C14-C19	1.388(3)	**C14-C15**	1.397(3)
C15-C16	1.390(3)	**C15-H15**	0.95
C16-C17	1.386(3)	**C16-H16**	0.95
C17-C18	1.385(3)	**C17-H17**	0.95
C18-C19	1.393(3)	**C18-H18**	0.95
C19-H19	0.95	**C20-C21**	1.390(3)
C20-C25	1.395(3)	**C21-C22**	1.389(3)
C21-H21	0.95	**C22-C23**	1.382(3)
C22-H22	0.95	**C23-C24**	1.383(3)
C23-H23	0.95	**C24-C25**	1.390(3)
C24-H24	0.95	**C25-H25**	0.95
C26-C31	1.393(3)	**C26-C27**	1.398(3)
C27-C28	1.385(3)	**C27-H27**	0.95
C28-C29	1.386(3)	**C28-H28**	0.95
C29-C30	1.381(3)	**C29-H29**	0.95
C30-C31	1.385(3)	**C30-H30**	0.95
C31-H31	0.95		

Table S18. Bond angles (°) for 3.

C1-Ni1-C13	42.70(7)	**C1-Ni1-P1**	101.51(6)
C13-Ni1-P1	143.90(5)	**C1-Ni1-Cl1**	156.14(6)
C13-Ni1-Cl1	113.45(5)	**P1-Ni1-Cl1**	102.12(2)
C1-Ni1-C11	68.03(7)	**C13-Ni1-C11**	37.56(7)
P1-Ni1-C11	150.44(5)	**Cl1-Ni1-C11**	92.47(5)
C14-P1-C20	103.57(8)	**C14-P1-C26**	103.44(8)
C20-P1-C26	103.94(8)	**C14-P1-Ni1**	117.84(6)
C20-P1-Ni1	111.00(6)	**C26-P1-Ni1**	115.49(6)
C2-O2-C3	116.34(14)	**C11-O3-C12**	116.62(14)
C9-N1-C2	123.63(15)	**C9-N1-C1**	116.47(14)
C2-N1-C1	118.96(14)	**C13-C1-N1**	116.52(15)
C13-C1-Ni1	69.77(10)	**N1-C1-Ni1**	113.83(12)
C13-C1-H1	116.2	**N1-C1-H1**	116.2
Ni1-C1-H1	116.2	**O1-C2-O2**	125.62(16)
O1-C2-N1	124.97(17)	**O2-C2-N1**	109.40(15)
C4-C3-C8	121.91(17)	**C4-C3-O2**	120.38(17)
C8-C3-O2	117.62(17)	**C3-C4-C5**	118.86(18)
C3-C4-H4	120.6	**C5-C4-H4**	120.6
C6-C5-C4	120.37(19)	**C6-C5-H5**	119.8
C4-C5-H5	119.8	**C5-C6-C7**	119.80(18)
C5-C6-H6	120.1	**C7-C6-H6**	120.1
C6-C7-C8	120.38(19)	**C6-C7-H7**	119.8
C8-C7-H7	119.8	**C3-C8-C7**	118.67(19)
C3-C8-H8	120.7	**C7-C8-H8**	120.7
C10-C9-N1	119.84(17)	**C10-C9-H9**	120.1
N1-C9-H9	120.1	**C9-C10-C11**	120.72(16)
C9-C10-H10	119.6	**C11-C10-H10**	119.6
O3-C11-C13	125.95(16)	**O3-C11-C10**	113.81(15)
C13-C11-C10	119.78(17)	**O3-C11-Ni1**	124.58(12)
C13-C11-Ni1	60.68(10)	**C10-C11-Ni1**	92.61(12)
O3-C12-H12A	109.5	**O3-C12-H12B**	109.5
H12A-C12-H12B	109.5	**O3-C12-H12C**	109.5
H12A-C12-H12C	109.5	**H12B-C12-H12C**	109.5
C11-C13-C1	113.97(16)	**C11-C13-Ni1**	81.76(11)
C1-C13-Ni1	67.53(10)	**C11-C13-H13**	123.0
C1-C13-H13	123.0	**Ni1-C13-H13**	118.8
C19-C14-C15	119.43(17)	**C19-C14-P1**	117.63(14)

C15-C14-P1	122.87(13)	**C16-C15-C14**	120.15(17)
C16-C15-H15	119.9	**C14-C15-H15**	119.9
C17-C16-C15	120.10(19)	**C17-C16-H16**	119.9
C15-C16-H16	119.9	**C18-C17-C16**	119.95(17)
C18-C17-H17	120.0	**C16-C17-H17**	120.0
C17-C18-C19	120.16(18)	**C17-C18-H18**	119.9
C19-C18-H18	119.9	**C14-C19-C18**	120.20(18)
C14-C19-H19	119.9	**C18-C19-H19**	119.9
C21-C20-C25	118.98(16)	**C21-C20-P1**	122.56(14)
C25-C20-P1	118.46(14)	**C22-C21-C20**	120.26(18)
C22-C21-H21	119.9	**C20-C21-H21**	119.9
C23-C22-C21	120.33(19)	**C23-C22-H22**	119.8
C21-C22-H22	119.8	**C22-C23-C24**	120.04(17)
C22-C23-H23	120.0	**C24-C23-H23**	120.0
C23-C24-C25	119.78(17)	**C23-C24-H24**	120.1
C25-C24-H24	120.1	**C24-C25-C20**	120.59(17)
C24-C25-H25	119.7	**C20-C25-H25**	119.7
C31-C26-C27	118.94(16)	**C31-C26-P1**	119.11(13)
C27-C26-P1	121.82(13)	**C28-C27-C26**	120.30(17)
C28-C27-H27	119.9	**C26-C27-H27**	119.9
C27-C28-C29	120.42(17)	**C27-C28-H28**	119.8
C29-C28-H28	119.8	**C30-C29-C28**	119.30(16)
C30-C29-H29	120.3	**C28-C29-H29**	120.3
C29-C30-C31	120.95(17)	**C29-C30-H30**	119.5
C31-C30-H30	119.5	**C30-C31-C26**	120.04(17)
C30-C31-H31	120.0	**C26-C31-H31**	120.0

Table S19. Anisotropic atomic displacement parameters (Å^2) for 3.

The anisotropic atomic displacement factor exponent takes the form:
$-2\pi^2[\ h^2\ a^{*2}\ U_{11} + \ldots + 2\ h\ k\ a^*\ b^*\ U_{12}\ ]$

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Ni1	0.01495(16)	0.01328(16)	0.01642(17)	-0.00066(11)	-0.00521(12)	-0.00171(12)
Cl1	0.0192(2)	0.0139(2)	0.0225(2)	0.00004(15)	-0.00563(17)	-0.00048(16)
P1	0.0146(2)	0.0129(2)	0.0141(2)	-0.00044(16)	-0.00390(18)	-0.00192(17)
O1	0.0277(7)	0.0196(7)	0.0252(7)	0.0014(6)	-0.0055(6)	0.0016(6)
O2	0.0282(7)	0.0211(7)	0.0229(7)	-0.0028(5)	-0.0028(6)	0.0071(6)
O3	0.0243(7)	0.0206(6)	0.0206(7)	0.0006(5)	-0.0087(5)	-0.0090(5)
N1	0.0172(8)	0.0184(8)	0.0185(8)	-0.0014(6)	-0.0054(6)	0.0009(6)
C1	0.0167(9)	0.0190(9)	0.0149(9)	-0.0002(7)	-0.0046(7)	0.0000(7)
C2	0.0176(9)	0.0196(9)	0.0235(10)	-0.0034(8)	-0.0070(8)	0.0007(8)
C3	0.0221(10)	0.0202(9)	0.0184(9)	-0.0039(7)	-0.0044(8)	0.0055(8)
C4	0.0164(9)	0.0264(10)	0.0307(11)	-0.0032(8)	-0.0076(8)	-0.0015(8)
C5	0.0247(10)	0.0203(9)	0.0284(10)	-0.0033(8)	-0.0065(8)	-0.0043(8)
C6	0.0232(10)	0.0235(10)	0.0221(10)	-0.0061(7)	-0.0076(8)	0.0057(8)
C7	0.0190(10)	0.0352(12)	0.0404(12)	-0.0140(9)	-0.0125(9)	0.0030(9)
C8	0.0252(11)	0.0254(10)	0.0354(12)	-0.0120(8)	-0.0071(9)	-0.0039(9)
C9	0.0168(9)	0.0234(10)	0.0167(9)	-0.0006(7)	-0.0044(7)	0.0006(8)
C10	0.0166(9)	0.0225(9)	0.0175(9)	0.0021(7)	-0.0047(7)	-0.0018(7)
C11	0.0140(8)	0.0190(9)	0.0220(9)	-0.0004(7)	-0.0080(7)	-0.0023(7)
C12	0.0435(12)	0.0244(10)	0.0229(10)	-0.0025(8)	-0.0149(9)	-0.0105(9)
C13	0.0156(9)	0.0218(9)	0.0166(9)	-0.0003(7)	-0.0069(7)	-0.0012(7)
C14	0.0155(9)	0.0165(8)	0.0152(9)	0.0020(7)	-0.0060(7)	-0.0012(7)
C15	0.0206(9)	0.0161(9)	0.0212(9)	0.0002(7)	-0.0052(8)	-0.0028(8)
C16	0.0189(9)	0.0179(9)	0.0282(10)	0.0048(7)	-0.0071(8)	-0.0050(8)
C17	0.0167(9)	0.0264(10)	0.0207(10)	0.0035(7)	-0.0022(8)	-0.0017(8)
C18	0.0220(10)	0.0255(10)	0.0200(10)	-0.0058(7)	-0.0038(8)	-0.0001(8)
C19	0.0198(9)	0.0192(9)	0.0193(9)	-0.0026(7)	-0.0065(8)	-0.0043(8)
C20	0.0194(9)	0.0132(8)	0.0158(9)	-0.0021(6)	-0.0052(7)	0.0004(7)
C21	0.0184(9)	0.0302(10)	0.0212(10)	0.0021(8)	-0.0052(8)	-0.0050(8)
C22	0.0207(10)	0.0361(11)	0.0249(10)	-0.0009(8)	-0.0112(8)	-0.0004(9)
C23	0.0285(10)	0.0179(9)	0.0181(9)	-0.0022(7)	-0.0093(8)	0.0040(8)
C24	0.0270(10)	0.0142(8)	0.0174(9)	-0.0005(7)	-0.0038(8)	-0.0030(7)
C25	0.0187(9)	0.0168(9)	0.0199(9)	-0.0012(7)	-0.0067(8)	-0.0028(7)
C26	0.0136(8)	0.0154(8)	0.0189(9)	-0.0020(7)	-0.0051(7)	-0.0033(7)
C27	0.0237(10)	0.0189(9)	0.0177(9)	0.0003(7)	-0.0072(8)	-0.0033(8)

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C28	0.0257(10)	0.0210(9)	0.0210(10)	-0.0071(7)	-0.0074(8)	-0.0008(8)
C29	0.0194(9)	0.0143(9)	0.0271(10)	-0.0028(7)	-0.0072(8)	-0.0020(7)
C30	0.0239(10)	0.0175(9)	0.0214(10)	0.0043(7)	-0.0055(8)	-0.0046(8)
C31	0.0221(10)	0.0191(9)	0.0172(9)	-0.0022(7)	-0.0033(8)	-0.0007(8)

Table S20. Hydrogen atomic coordinates and isotropic atomic displacement parameters (Å^2) for 3.

	x/a	y/b	z/c	U(eq)
H1	0.3889	0.8551	0.5815	0.021
H4	0.1609	1.2233	0.8399	0.03
H5	0.0100	1.4070	0.8503	0.03
H6	-0.2292	1.4141	0.8563	0.028
H7	-0.3189	1.2378	0.8531	0.037
H8	-0.1692	1.0535	0.8440	0.034
H9	0.1546	0.8184	0.9117	0.024
H10	0.1989	0.6152	0.8966	0.023
H12A	0.2243	0.4963	0.5792	0.043
H12B	0.2574	0.3675	0.6349	0.043
H12C	0.3848	0.4487	0.5812	0.043
H13	0.3333	0.6645	0.5562	0.021
H15	0.8759	0.9216	0.6441	0.024
H16	1.1134	0.9057	0.5157	0.027
H17	1.2021	0.7468	0.3971	0.028
H18	1.0565	0.6002	0.4109	0.028
H19	0.8208	0.6128	0.5424	0.023
H21	0.8858	0.7453	0.7924	0.028
H22	0.9192	0.6715	0.9582	0.032
H23	0.7317	0.5932	1.1009	0.026
H24	0.5102	0.5857	1.0776	0.025
H25	0.4762	0.6585	0.9115	0.022
H27	0.5012	0.9181	0.9016	0.024
H28	0.4128	1.1203	0.9259	0.027
H29	0.4389	1.2538	0.7721	0.024
H30	0.5448	1.1821	0.5943	0.026
H31	0.6298	0.9799	0.5681	0.025