Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

for the manuscript entitled

Exhaustive Suzuki-Miyaura Reactions of Polyhalogenated Heteroarenes with Alkyl Boronic Pinacol Esters

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Table of Contents:

General considerations.

Reagents.
All reagents and chemicals were obtained commercially and used without further purification unless otherwise noted.

Acros	palladium(II) acetate, (dibenzylideneacetone)dipalladium(0), tricyclohexylphosphine, trimethylborate, pinacol, *N,N*-dimethylformamide (anhydrous), diethyl carbonate, allyl bromide, lithium *tert*-butoxide, potassim phosphate tribasic, *p*-toluenesulfonyl chloride, tricyclohexylphosphine
Alfa Aesar	magnesium turnings, 1-bromo-3-phenylpropane, 2-(2-bromoethyl)-1,3-dioxolane, copper iodide, 1,4-dichlorobenzene, lithium methoxide, triphenylphospine, pyridine, di(1-adamantyl)-*n*-butylphopshine
Ark Pharm Inc.	5-chloro-2-methoxypyridine, 1,3-dichloroisoquinoline, 2,6-dichloro-4-methylpyridine
Boehringer Mannheim	phenol
Chem Impex	2,6-dichloropyridine, 2,6-dibromopyridine, sodium *tert*-butoxide, potassium *tert*-butoxide, 4-chloroacetophenone, 1-bromo-3-hydroxypropane, cesium carbonate, Wilkinson's catalyst
Fisher Scientific	acetone, pentane, heptane, toluene, sodium iodide, iodine, diethyl ether, magnesium sulfate, chloroform
Gelest	*tert*-butyldimethylsilyl chloride
Matrix Scientific	magnesium turnings, phenylboronic acid, 1-bromo-5-chloropentane
Oakwook Chemical	1-bromo-4-(*tert*-butyl)benzene, 1-chloro-5-bromopentane, cesium fluoride, XPhos
Oxchem	bis(pinacolato)diboron, 2,6-dichloro-4-(trifluoromethyl)pyridine, 2,4,6-trichloropyridine, SPhos
Sigma-Aldrich	borane dimethylsulfide complex (2.0M in THF), sodium hydride (60% dispersion in mineral oil), hydrochloric acid (concentrated), 6-bromo-1-hexene, 1-chloro-4-nitrobenzene, dibromomethane, 1-iodoheptane, allyl alcohol, 7-bromo-1-heptene, RuPhos, BrettPhos
Strem Chemicals	di(1-adamantyl)-*n*-butylphosphine,
TCI	2-chloropyridine, 4-chloroanisole

Anhydrous 1,4-dioxane, tetrahydrofuran (THF), methylene chloride, and diethyl ether were obtained from Sigma Aldrich and were purified, dried, and degassed by passage through two columns of neutral, activated alumina under N_2 using an Innovative Technologies solvent purification system. Toluene was purified, dried, and degassed by passage through a column containing copper followed by a column of neutral, activated alumina under N_2 using an Innovative Technologies solvent purification system. Deionized (DI) water was degassed by sparging with argon for 20 minutes.

Preparation of Known Reagents.

4,4,5,5-tetramethyl-2-(3-phenylpropyl)-1,3,2-dioxaborolane (**6b**),[1] 2-(2-(1,3-dioxolan-2-yl)ethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**6s**),[1] 2-chloro-6-*tert*-butoxypyridine **(3q)** ,[2] 2-heptyl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**6a**),[3] 2-(hex-5-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**6m**),[3] 2-allyl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**6w**),[4] 4-(tris(4-(tert-butyl)phenyl)methyl)phenol (**9**),[5] *tert*-butyldimethyl(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propoxy)silane (**6u**)[6] were prepared according to the literature and stored at 2–8 °C. Ferrocenyl(diphenyl)phosphine was prepared according to the literature and store at –35 °C in and N_2-filled glovebox.[7]

Procedures.

Moisture-sensitive reactions were performed using flame-dried glassware under an atmosphere of dry nitrogen (N_2). Air- and water-sensitive reactions, where noted, were performed in an MBraun MB200 glove box held under an atmosphere of nitrogen gas (working pressure 2–6 mbar). Flame-dried equipment was stored in a 130 °C oven before use and either allowed to cool in a cabinet dessicator or assembled hot and allowed to cool under an inert atmosphere. Air- and moisture-sensitive liquids and solutions were transferred *via* plastic or glass syringe.

Chromatographic purification of products was accomplished using flash column chromatography Silicycle Silica flash F60 (particle size 40–63 μm, 230–400 mesh). Thin layer chromatography was performed on EMD Millipore silica gel 60 F254 glass-backed plates (layer thickness 250 μm, particle size 10–12 μm, impregnated with a fluorescent indicator). Visualization of the developed chromatogram was accomplished by fluorescence quenching under shortwave UV light and/or by staining with phosphomolybdic acid, *p*-anisaldehyde, or $KMnO_4$ stains. Room temperature is 23 °C.

Instrumentation.

NMR Spectrometry

NMR spectra were obtained on Varian iNOVA spectrometers operating at 400 or 500 MHz for ^{1}H NMR, 101 or 126 MHz for ^{13}C NMR, and 376 MHz for ^{19}F NMR at 23–25 °C, and are reported as chemical shifts (δ) in parts per million (ppm). Spectra were referenced internally according to residual solvent signals (^{1}H: $CDCl_3$, 7.26 ppm; ^{13}C: $CDCl_3$, 77.0 ppm; acetone-d_6,

[1] C.-T. Yang, Z.-Q. Zhang, H. Tajuddin, C.-C. Wu, J. Liang, J.-H. Liu, Y. Fu, M. Czyzewska, P. G. Steel, T. B. Marder, L Liu, *Angew. Chem. Int. Ed.* **2012**, *51*, 528–532.

[2] U. Gellrich, J. Huang, W. Seiche, M. Keller, M. Meuwly, B. Breit, *J. Am. Chem. Soc.* **2011**, *133*, 964.

[3] Laulhé, S.; Blackburn, J. M.; Roizen, J. L. *Org. Lett.* **2016**, *18*, 4440.

[4] Roush, W. R.; Adam, M. A.; Walts, A. E.; Harris, D. J. *J. Am. Chem. Soc.* **1986**, *108*, 3422.

[5] Hoekman, S.; Kitching, M. O.; Leigh, D. A.; Papmeyer, M; Roke, D. *J. Am. Chem. Soc.* **2015**, *137*, 7656.

[6] Bull, J. A., Charrette, A. B. *J. Am. Chem. Soc.* **2010**, *132*, 1895.

[7] D. A. Khobragade, S. G. Mahamulkar, L. Pospísil, I. Císarová, L. Rulísek, U. Jahn, *Chem. Eur. J.* **2012**, *18*, 12267.

29.2). Data for NMR spectra use the following abbreviations to describe multiplicity: s, singlet; br s, broad singlet; d, doublet; t, triplet; dd, doublet of doublet; td, triple of doublet; ddd, doublet of doublet of doublets; ddt, doublet of doublet of triplets; app dd, apparent doublet of doublets; m, multiplet. Coupling constant (*J*) are reported in units of Hertz (Hz).

IR Spectroscopy

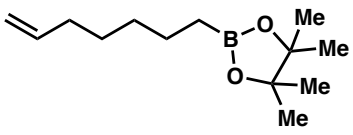
IR spectra were obtained on a Nicolet 6700 FT-IR system. Peaks are reported in cm^{-1} with indicated relative intensities: s (strong, 0–33% T); m (medium, 34-66% T); w (weak, 67-100% T); and br (broad).

Mass Spectrometry

High resolution mass spectra (HRMS, m/z) were recorded on a Agilent LCMS-TOF-DART spectrometer using electrospray ionization (ESI, Duke University Department of Chemistry Instrumentation Center).

Preparation of Reagents.

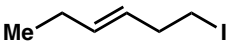
2-(hept-6-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (6n)



A flame-dried 50 mL round bottom flask was charged with a stir bar, Mg tunings (3312 mg, 12.9 mmol, 1.1 equiv), a small crystal of I_2, and anhydrous diethyl ether (30 mL) under nitrogen atmosphere. Then 7-bromohex-1-ene (2.07 g, 11.7 mmol, 1.0 equiv) was added dropwise to maintain a gentle reflux. Once the addition was over, the solution was reflux for 1 h at 40 °C. Then the solution was cooled at –78 °C and trimethylborate (2.43 g, 23.4 mmol, 2 equiv) was added drop-wise, which formed a white precipitate. The solution was stirred for 15 minutes and then warmed to 0 °C, and the solution was stirred for 30 min. Then the reaction was neutralized using 3N HCl (10 mL) at 0 °C and then allowed to warm at room temperature. The mixture was transferred to a separatory funnel with diethyl ether. The layers were separated and the aqueous layer was extracted with diethyl ether (4 x 20 mL). The organic layers were combined, dried over Na_2SO_4 and concentrated under reduced pressure until the crude contained 3–8 mL of solvent left. The resulting mixture was diluted in pentane and diethyl ether (4:1, 20 mL total), and pinacol (2.00 g, 17.6 mmol, 1.5 equiv) was added and stirred at room temperature for 48 h. The reaction crude was filtered through filter paper and then concentrated under reduced pressure. The resulting crude was then purified by silica gel column chromatography using hexanes:EtOAc (18:1, R_f = 0.4) to obtain the desired product as a colorless oil (1.27 g, 48% yield). The compound was stored at 2–8 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.81 (ddt, J = 17.0, 10.3, 6.9 Hz, 1H), 4.98 (dd, J = 17.0, 1.8 Hz, 1H); 4.91 (dd, J = 10.3, 1.8 Hz, 1H), 2.08– 2.00 (m, 2H), 1.46–1.34 (m, 4H), 1.24 (s, 12H), 0.78 (t, J = 7.2 Hz, 2H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 139.2, 114.0, 82.8, 33.7, 31.9, 28.7, 24.8, 23.8.
IR (neat) ν 2978 (m), 2926 (w), 2857 (w), 1408 (w), 1378 (m), 1317 (m), 1216 (w), 1146 (m), 1112 (w), 993 (m), 968 (w), 910 (w), 883 (w), 885 (w), 847 (w) cm^{-1}.
HRMS (EI) calcd for [M + H]= 225.2020, found = 225.2023.
TLC R_f = 0.56 (hexanes:EtOAc, 9:1).

(*E*)-1-Iodohex-3-ene (S1a)



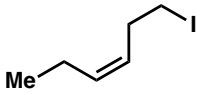
The compound was prepared according to a modified literature procedure.[8]
A flame-dried 250 mL round bottom flask equipped with a stir bar was charged with *p*-toluenesulfonyl chloride (22.88 g, 120 mmol, 1.2 equiv) and fitted with a rubber septum. Chloroform (60 mL) and pyridine (15 mL) were added sequentially by syringe and the mixture was stirred for five minutes, during which time the *p*-toluenesulfonyl chloride fully dissolved and the solution turned yellow. (*E*)-3-Hexen-1-ol (10.00 g, 100 mmol, 1.0 equiv) was then added dropwise by syringe and the reaction was allowed to stir at room temperature for 12 h. Diethyl ether (200 mL) was added and the mixture was transferred to a separatory funnel. The mixture was washed sequentially with 1N HCl (200 mL), saturated aqueous sodium bicarbonate solution (200 mL), and brine (200 mL). The organic layer was then dried over $MgSO_4$ and

[8] Fisher, M. J.; Overman, L. E. *J. Org. Chem.* **1990**, *55*, 1447.

concentrated under reduced pressure. The resulting crude product was passed over a silica plug (eluting with hexanes:EtOAc (9:1) until UV active spots with $R_f > 0.3$ ceased eluting) and again concentrated under reduced pressure to provide the crude tosylate as a pale yellow oil.
A flame-dried 250 mL round bottom flask equipped with a stir bar was charged with the crude tosylate and then capped with a rubber septum. The crude tosylate was dissolved in anhydrous acetone (125 mL, added by syringe). The septum was removed and the solution was treated with solid sodium iodide (30.00 g, 200 mmol, 2.0 equiv) before the reaction was resealed. The mixture was then heated in an oil bath at 55 °C with stirring for 2 h, during which a time a white precipitate formed. The mixture was allowed to cool to room temperature, filtered through a silica plug eluting with diethyl ether (2 x 250 mL). The resulting organic layer was concentrated under reduced pressure (not below 50 Torr) and purified by silica gel column chromatography using 100% pentane to give the desired product as a colorless to pale yellow oil (9.13 g, 43% yield; E:$Z \geq 19$:1). The compound was stored at 2–8 °C under an inert atmosphere.

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.61–5.53 (m, 1H), 5.39–5.31 (m, 1H), 3.14 (t, J = 6.9 Hz, 2H), 2.58–2.51 (m, 2H), 2.06–1.97 (m, 2H), 0.98 (t, J = 7.0 Hz, 3H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 135.0, 127.3, 36.7, 25.5, 13.6, 6.1.
IR (neat) ν 2960 (m), 2931 (w), 2871 (w), 1459 (w), 1422 (w), 1375 (w), 1309 (w), 1228 (w), 1168 (m), 1050 (w), 964 (m), 931 (w), 883 (w), 819 (w), 731 (w), 596 (m), 557 (w) cm^{-1}.
TLC R_f = 0.73 (hexanes).
HRMS (EI) calcd for [M + H]= 209.9906, found = 209.9902.

(*Z*)-1-Iodohex-3-ene (S1b)

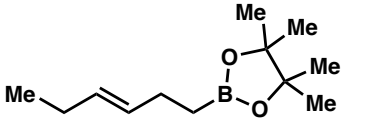


The compound was prepared according to a modified literature procedure.[8]
A flame-dried 250 mL round bottom flask equipped with a stir bar was charged with *p*-toluenesulfonyl chloride (22.88 g, 120 mmol, 1.2 equiv) and fitted with a rubber septum. Chloroform (60 mL) and pyridine (15 mL) were added sequentially by syringe and the mixture was stirred for five minutes, during which time the *p*-toluenesulfonyl chloride fully dissolved and the solution turned yellow. Then, (*Z*)-3-Hexen-1-ol (10.00 g, 100 mmol, 1.0 equiv) was added dropwise by syringe and the reaction was allowed to stir at room temperature for 12 h. Diethyl ether (200 mL) was added and the mixture was transferred to a separatory funnel. The mixture was washed sequentially with 1N HCl (200 mL), saturated aqueous sodium bicarbonate solution (200 mL), and brine (200 mL). The organic layer was then dried over $MgSO_4$ and concentrated under reduced pressure. The resulting crude product was passed over a silica plug (eluting with hexanes:EtOAc (9:1) until UV active spots with $R_f > 0.3$ ceased eluting) and concentrated under reduced pressure to provide the crude tosylate as a pale yellow oil.
A flame-dried 250 mL round bottom flask equipped with a stir bar was charged with the crude tosylate and then capped with a rubber septum. Anhydrous acetone (125 mL) was added by syringe, followed by sodium iodide (30.00 g, 200 mmol, 2.0 equiv) as a solid. The mixture was then heated in an oil bath at 55 °C with stirring for 2 h, during which a time a white precipitate formed. The mixture was then allowed to cool to room temperature, filtered through a silica plug eluting with ether (2 x 250 mL). The resulting organic layer was concentrated under reduced pressure (not below 50 Torr) and purified by silica gel column chromatography using pentane

(100%) to yield the desired product as a colorless to pale yellow oil (12.23 g, 58% yield; *Z*:*E* ≥ 19:1). The compound was stored at 2–8 °C under an inert atmosphere.

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.57–5.50 (m, 1H), 5.34–5.25 (m, 1H), 3.13 (t, J = 6.8 Hz, 2H), 2.67–2.59 (m, 2H), 2.06–1.98 (m, 2H), 0.98 (t, J = 7.1 Hz, 3H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 134.3, 127.1, 31.4, 20.7, 14.1, 5.6
IR (neat) ν 3008 (w), 2961 (m), 2931 (w), 2872 (w), 1454 (w), 1423 (w), 1300 (w), 1238 (m), 1168 (m), 1088 (w), 1069 (w), 968 (w), 924 (w), 866 (w), 794 (w), 707 (m), 596 (w) cm^{-1}.
TLC R_f = 0.70 (hexanes).
HRMS (EI) calcd for [M + H]= 209.9906, found = 209.9913.

(*E*)-2-(hex-3-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (6o)



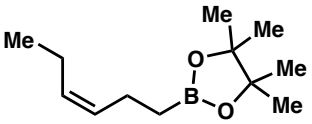
The compound was prepared according to modified literature procedures.[9]
A flame-dried 100 mL round bottom flask was charged with a stir bar, Mg tunings (576 mg, 24.0 mmol, 1.2 equiv), a small crystal of I_2, and anhydrous diethyl ether (30 mL) under nitrogen atmosphere. Then, (*E*)-1-iodohex-3-ene (4.20 g, 20.0 mmol, 1.0 equiv) was added dropwise to maintain a gentle reflux. Once the addition was over, the solution was reflux for 1 h at 40 °C. The solution was cooled at 0 °C and trimethylborate (2.68 mL, 24.0 mmol, 1.2 equiv) was added dropwise, which formed a white precipitate. The solution was stirred for 15 minutes and then warmed to room temperature. The reaction was neutralized using 1N HCl (10 mL). The mixture was transferred to a separatory funnel with diethyl ether. The layers were separated and the aqueous layer was extracted with diethyl ether (2 x 20 mL). The organic layers were combined, washed with brine, dried over $MgSO_4$ and concentrated under reduced pressure.
The resulting crude product was dissolved in diethyl ether (25 mL) in a flame-dried 100 mL round bottom flask containing a stir bar. Pinacol (2.36 g, 20 mmol, 1.0 equiv) and $MgSO_4$ (2.41 g, 20 mmol, 1.0 equiv) were added and the flask was capped with a rubber septum and the mixture stirred at room temperature for 16 h. The reaction crude was filtered through a plug of silica, eluting with additional diethyl ether (2 x 15 mL) and then concentrated under reduced pressure. The resulting crude was then purified by silica gel column chromatography using hexanes (100%) to hexanes:EtOAc (19:1) to obtain the desired product as a colorless oil (736 mg, 18% yield; *E*:*Z* ≥ 19:1). The compound was stored at 2–8 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.45–5.41 (m, 2H), 2.17–2.13 (m, 2H), 2.01–1.93 (m, 2H), 1.23 (s, 12H), 0.94 (t, J = 7.4 Hz, 3H), 0.85 (t, J = 7.7 Hz, 2H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 130.9, 82.9, 26.8, 25.5, 24.8, 13.9.
^{13}C NMR (126 MHz, acetone-d_6) δ 131.3, 130.8, 82.9, 26.9, 25.5, 24.5, 13.7.
IR (neat) ν 2977(w), 2931 (w), 1462 (w), 1406 (w), 1370 (m), 1313 (m), 1272 (w), 1238 (w), 1214 (w), 1144 (s), 1111 (w), 966 (m), 867 (w), 847 (w), 738 (w), 672 (w), 578 (w), 543 (w) cm^{-1}.
TLC R_f = 0.59 (hexanes:EtOAc, 9:1).

[9] Borylation: Susnik, P.; Hilt, G. *Organometallics,* **2014**, *33*, 5907. Esterification: Stymiest, J. L.; Dutheuil, G.; Mahmood, A.; Aggarwal, V. K. *Angew. Chem. Int. Ed.* **2007**, *46*, 7491.

HRMS (ESI) calcd for [M + H]= 211.1864, found = 211.1858.

(*Z*)-2-(hex-3-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (6p)



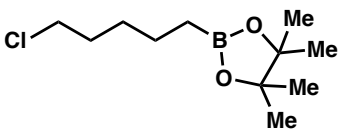
The compound was prepared according to modified literature procedures.[9]

A flame-dried 100 mL round bottom flask was charged with a stir bar, Mg tunings (576 mg, 24.0 mmol, 1.2 equiv), a small crystal of I_2, and anhydrous diethyl ether (30 mL) under nitrogen atmosphere. Then (*Z*)-1-iodohex-3-ene (4.20 g, 20.0 mmol, 1.0 equiv) was added dropwise to maintain a gentle reflux. Once the addition was over, the solution was reflux for 1 h at 40 °C. Then the solution was cooled at 0 °C and trimethylborate (2.68 mL, 24.0 mmol, 1.2 equiv) was added dropwise, which formed a white precipitate. The solution was stirred for 15 minutes and then warmed to room temperature. The reaction was neutralized using 1N HCl (10 mL). The mixture was transferred to a separatory funnel with diethyl ether. The layers were separated and the aqueous layer was extracted with diethyl ether (2 x 20 mL). The organic layers were combined, washed with brine, dried over $MgSO_4$ and concentrated under reduced pressure to yield the crude organoboron compound.

A flame-dried 100 mL round bottom flask equipped with a stir bar was charged with the resulting crude organoboron compound dissolved in diethyl ether (25 mL). Pinacol (2.36 g, 20 mmol, 1.0 equiv) and $MgSO_4$ (2.41 g, 20 mmol, 1.0 equiv) were added and the flask was capped with a rubber septum. The mixture stirred at room temperature for 16 h. The reaction crude was filtered through a plug of silica, eluted with additional diethyl ether (2 x 15 mL) and then concentrated under reduced pressure. The resulting crude borolane was then purified by silica gel column chromatography using hexanes (100%) to hexanes:EtOAc (19:1) to obtain the desired product as a colorless oil (527 mg, 13% yield; *Z*:*E* ≥ 19:1). The compound was stored at 2–8 °C.

^{1}H NMR (500 MHz, $CDCl_3$) δ 5.37–5.26 (m, 2H), 2.17–2.10 (m, 2H), 2.08–2.00 (m, 2H), 1.24 (s, 12H), 0.94 (t, J = 7.5 Hz, 3H), 0.83 (t, J = 7.0 Hz, 2H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 131.1, 130.8, 83.0, 24.8, 21.6, 20.4, 14.4.
IR (neat) ν 2976 (w), 2933 (w), 1463 (w), 1408 (w), 1370 (m), 1313 (m), 1271 (w), 1240 (m), 1214 (w), 1144 (s), 1111 (w), 967 (m), 869 (w), 846 (w), 801 (w), 673 (w), 578 (w), 542 (w) cm^{-1}.
TLC R_f = 0.62 (hexanes:EtOAc, 9:1).
HRMS (ESI) calcd for [M + H]= 211.1864, found = 211.1870.

2-(5-chloropentyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (6x)



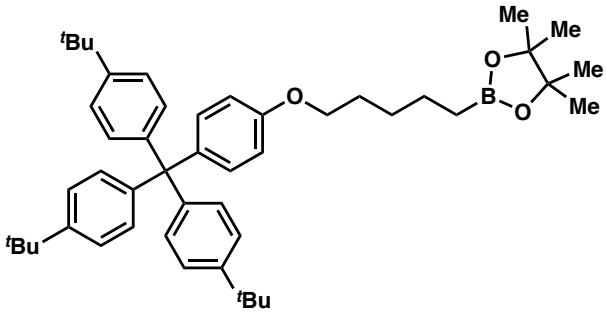
The compound was prepared according to a modified literature procedure.[1]

In a N_2-filled glove box, a flame dried 250 mL round bottom flask equipped with a stir bar was charged with CuI (514 mg, 2.7 mmol, 0.1 equiv), PPh_3 (921 mg, 3.5 mmol, 0.13 equiv), B_2pin_2 (10.30 g, 40.7 mmol, 1.5 equiv), and LiOMe (2.07 g, 54 mmol, 2 equiv), and anhydrous DMF (54 mL) and fitted with a rubber septum. The flask was removed from the glove box and fitted with nitrogen inlet line before 1-bromo-5-chloropentane (2.15 g, 11.7 mmol, 1 equiv) was added by syringe. The resulting

reaction mixture was stirred vigorously at room temperature for 12 h. The reaction mixture was then filtered through a pad of silica (ca. 50 g) eluting with hexanes:EtOAc (1:1, ca. 250 mL) and concentrated under reduced pressure. The mixture was then taken up in EtOAc (ca. 200 mL) and washed with water (3 x 200 mL) and brine (200 mL). The organic layer was then dried over $MgSO_4$ and concentrated under reduced pressure. The resulting crude was then purified by silica gel column chromatography using hexanes:PhMe (gradient elution, 4:1 to 1:1), to obtain the desired product as a colorless oil (5.52 g, 88% yield; contained trace 2-(5-bromopentyl)-4,4,5,5,-tetramethyl-1,3,2-dioxaborolane as an impurity (< 5%) but could be used without further purification). The compound was stored at 2–8 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 3.52 (t, J = 6.8 Hz, 2H), 1.80–1.73 (m, 2H), 1.47–1.40 (m 4H), 1.24 (s, 12H), 0.79 (t, J = 6.9 Hz, 2H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 82.9, 45.1, 32.4, 29.5, 24.8, 23.3.
IR (neat) ν 2978 (w), 2931 (w), 2862 (w), 1462 (w), 1407 (w), 1371 (m), 1315 (m), 1270 (w), 1214 (w), 1165 (w), 1143 (s), 1109 (w), 1005 (w), 968 (m), 870 (w), 847 (m), 722 (w), 697 (w), 673 (w), 651 (w), 578 (w), 542 (w) cm^{-1}.
TLC R_f = 0.47 (hexanes:EtOAc, 9:1).
HRMS (ESI) calcd for [M + H]= 233.1474, found =233.1479.

4,4,5,5-tetramethyl-2-(5-(4-(tris(4-(*tert*-butyl)phenyl)methyl)phenoxy)pentyl)-1,3,2-dioxaborolane (6y)



A flame-dried 100 mL round bottom flask equipped with a stir bar was charged with 4-(tris(4-(tert-butyl)phenyl)methyl)phenol (10.0 g, 19.8 mmol, 1.0 equiv) and fitted with a rubber septum. Anhydrous DMF (20 mL) was added by syringe and the mixture was allowed to stir for 5 minutes at room temperature. The mixture was cooled to 0 °C in an ice bath before sodium hydride (60% dispersion in mineral oil; 872 mg, 21.8 mmol, 1.1 equiv) was added quickly as a solid. The ice bath was then removed and the reaction mixture was stirred for 30 minutes at room temperature during which time evolution of hydrogen was observed. 2-(5-chloropentyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (5.58g, 24.0 mmol, 1.1 equiv) was next added by syringe followed by sodium iodide (327 mg, 2.18 mmol, 0.1 equiv) as a solid. The reaction mixture was then heated with stirring in an oil bath at 80 °C for 18 h. The mixture was then allowed to cool to room temperature before 1N HCl (20 mL) was added. The mixture was transferred to a separatory funnel and EtOAc (ca. 100 mL) and water (ca. 100 mL) was added. The organic layer was separated and the aqueous layer was extracted with additional EtOAc (ca. 100 mL). The combined organic layers were then washed with water (3 x 150 mL) and brine (150 mL), dried over $MgSO_4$ and concentrated. The resulting white solid was purified by silica gel column chromatography using hexanes (100%) to hexanes:EtOAc (19:1) to give the desired product as a white solid (11.77 g, 85% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 (d, J = 8.6 Hz, 6H), 7.10–7.04 (m, 8H), 6.74 (d, J = 8.9 Hz, 2H), 3.91 (t, J = 6.6 Hz, 2H), 1.80–1.72 (m, 2H), 1.48–1.42 (m, 4H), 1.29 (s, 27H), 1.24 (s, 12H), 0.80 (t, J = 6.9 Hz, 2H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 156.9, 148.2, 144.2, 139.3, 132.2, 130.7, 124.0, 112.9, 82.9, 67.7, 63.0, 34.3, 31.4, 29.1, 28.8, 24.8, 23.8.
IR (neat) ν 2953 (w), 1605 (w), 1504 (w), 1370 (m), 1313 (w), 1244 (w), 1183 (w), 1145 (w), 1017 (w), 967 (m), 823 (w), 625 (w), 579 (w) cm^{-1}.
TLC R_f = 0.47 (hexanes:EtOAc, 9:1).
HRMS (ESI) calcd for [M + H]= 700.5099, found = 700.5101.

General Procedure A.

Reactions were performed on 0.42 mmol scale, unless otherwise specified.
Inside a nitrogen-filled glove box, a flame-dried 10 mL Chem-Glass microwave vial equipped with a stir bar was charged with $Pd(OAc)_2$ (0.9 mg, 0.0042 mmol, 0.01 equiv), Ad_2P^nBu (4.5 mg, 0.0126 mmol, 0.03 equiv), aryl halide (0.42 mmol, 1 equiv), and LiO^tBu (203 mg, 2.53 mmol, 6 equiv). The vial was sealed with a crimp cap lined with a disposable Teflon septum and then removed from the glove box and placed in a pie-block. 1,4-Dioxane (3.2 mL) was added to the vial *via* syringe and the resulting mixture was stirred at room temperature for 5 minutes. Then alkyl boronic ester (1.06 mmol, 2.5 equiv) and degassed DI water (0.8 mL) were added sequentially to the reaction *via* syringe. The pie-block was heated to 100 °C and held at that temperature for 24 h. The reaction mixture was allowed to cool at room temperature, and the resulting crude was filtered through a plug of silica gel eluting with CH_2Cl_2:EtOAc (1:1, ca. 15 mL). The filtrate was concentrated under reduced pressure. Isolation of the desired product was achieved by silica gel column chromatography (conditions given below).
Deviations from this procedure are specified below.

General Procedure B.

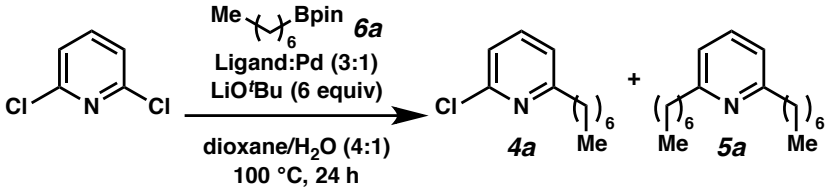
Reactions were performed on 0.42 mmol scale, unless otherwise specified.
Inside a nitrogen-filled glove box, a flame-dried 10 mL Chem-Glass microwave vial equipped with a stir bar was charged with $Pd(OAc)_2$ (0.9 mg, 0.0042 mmol, 0.01 equiv), Ad_2P^nBu (4.5 mg, 0.0126 mmol, 0.03 equiv), aryl halide (0.42 mmol, 1 equiv), and LiO^tBu (101 mg, 1.26 mmol, 3 equiv). The vial was sealed with a crimp cap lined with a disposable Teflon septum and then removed from the glove box and placed in a pie-block. 1,4-Dioxane (3.2 mL) was added to the vial *via* syringe and the resulting mixture was stirred at room temperature for 5 minutes. Then alkyl boronic ester (0.63 mmol, 1.5 equiv) and degassed DI water (0.8 mL) were added sequentially to the reaction *via* syringe. The pie-block was heated to 100 °C and held at that temperature for 24 h. The reaction mixture was allowed to cool at room temperature, and the resulting crude was filtered through a plug of silica gel eluting with CH_2Cl_2:EtOAc (1:1, ca. 15 mL). The filtrate was concentrated under reduced pressure. Isolation of the desired product was achieved by silica gel column chromatography (conditions given below).
Deviations from this procedure are specified below.

General Procedure C.

Reactions were performed on 0.42 mmol scale, unless otherwise specified.
Inside a nitrogen-filled glove box, a flame-dried 10 mL Chem-Glass microwave vial equipped with a stir bar was charged with $Pd(OAc)_2$ (0.9 mg, 0.0042 mmol, 0.01 equiv), Ad_2P^nBu (4.5 mg, 0.0126 mmol, 0.03 equiv), aryl halide (0.42 mmol, 1 equiv), and LiO^tBu (101 mg, 1.26 mmol, 3 equiv). The vial was sealed with a crimp cap lined with a disposable Teflon septum and then removed from the glove box and placed in a pie-block. 1,4-Dioxane (3.2 mL) was added to the vial *via* syringe and the resulting mixture was stirred at room temperature for 5 minutes. Then alkyl boronic ester (0.63 mmol, 1.5 equiv) and degassed DI water (0.8 mL) were added sequentially to the reaction *via* syringe. The pie-block was heated to 100 °C and held at that temperature for 24 h. The reaction mixture was allowed to cool at room temperature, and the

resulting crude was filtered through a plug of silica gel eluting with CH_2Cl_2:EtOAc (1:1, ca. 15 mL). The filtrate was concentrated under reduced pressure. The resulting crude was dissolved in CH_2Cl_2:trifluoroacetic acid (1:1, total 2 mL) and stirred for 30 min at room temperature. Then, the yellow mixture was quenched by slow addition of saturated aqueous sodium bicarbonate solution (ca. 2 mL) until the mixture attained a pH of 9–11. The resulting mixture was transferred to a separatory funnel with CH_2Cl_2 and was extracted with additional CH_2Cl_2 (4 x 15 mL). The combined organic layers were dried with Na_2SO_4 and concentrated under reduced pressure. Isolation of the desired product was achieved by silica gel column chromatography (conditions given below).

Additional Ligands Screened Under Otherwise Optimized Reaction Conditions:

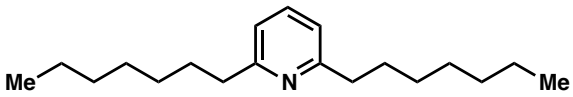


Ligand	**4a** (%)[a]	**5a** (%)[a]
PPh_3	27	10
SPhos	nd[b]	nd[b]
XPhos	nd[b]	nd[b]
RuPhos	nd[b]	nd[b]
BrettPhos	nd[b]	nd[b]

[a]Determined by ^{1}H NMR. [b]nd = not detected.

Preparation and characterization of substituted pyridines and benzenes.

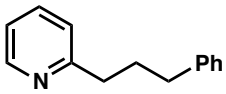
2,6-diheptylpyridine (5a)



Prepared from 2,6-dichloropyridine and 2-heptyl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane following general procedure A. The product was obtained as a colorless oil (98 mg, 84% yield) after silica gel column chromatography using CH_2Cl_2 (100%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.48 (t, J = 7.6 Hz, 1H), 6.93 (d, J = 7.6 Hz, 2H), 2.74 (app dd, J = 7.8, 7.8 Hz, 4H), 1.74–1.64 (m, 4H), 1.37–1.21 (m, 16H), 0.87 (t, J = 6.8 Hz, 6H).
^{13}C NMR (126 MHz, $CDCl_3$): δ 161.8, 136.2, 119.5, 38.6, 31.8, 30.2, 29.4, 29.2, 22.6, 14.0.
IR (neat) ν 2954 (w), 2921 (m), 2852 (m), 1589 (w), 1576 (w), 1454 (m), 1377 (w), 1217 (w), 1153 (w), 1080 (w), 991 (w), 750 (w), 723 (w), cm^{-1}.
TLC R_f = 0.45 (hexanes:CH_2Cl_2, 1:1).
HRMS (ESI): calcd for $C_{19}H_{34}N$ [M + H]= 276.2691, found 276.2687.

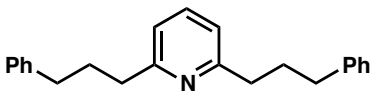
2-(3-phenylpropyl)pyridine (5b)



Prepared from 2-chloropyridine and following general procedure B using $Pd(OAc)_2$ (1.9 mg, 0.0084 mmol, 0.02 equiv), Ad_2P^nBu (9.0 mg, 0.0252 mmol, 0.06 equiv), 2-(3-phenylpropyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (0.260 mg, 1.055 mmol, 2.5 equiv), and LiO^tBu (203 mg, 2.53 mmol, 6 equiv). The product was obtained as a pale yellow oil (68 mg, 81% yield) after silica gel column chromatography using CH_2Cl_2:EtOAc (9:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.54 (dd, J = 5.0, 1.9 Hz, 1H), 7.58 (ddd, J = 7.7, 7.7, 1.9 Hz, 1H), 7.32–7.26 (m, 2H), 7.22–7.08 (m, 5H), 2.83 (app dd, J = 7.8, 7.8 Hz, 2H), 2.69 (app dd, J = 7.7, 7.7 Hz, 2H), 2.08 (m, 2H).
TLC R_f = 0.81 (hexanes:EtOAc, 4:1).
The characterization data for the compound were in agreement with previously published information.[3]

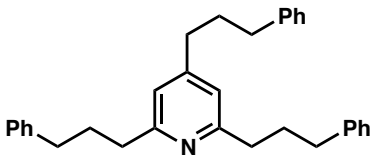
2,6-bis(3-phenylpropyl)pyridine (5c)



Prepared from 2,6-dichloropyridine following general procedure A using 2-(3-phenylpropyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (0.260 mg, 1.055 mmol, 2.5 equiv). The product was obtained as a pale yellow oil after silica gel column chromatography using CH_2Cl_2 (100%).
From 2,6-dichloropyridine: 95 mg, 95% yield.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (t, J = 7.7 Hz, 1H), 7.29–7.25 (m, 4H), 7.21–7.15 (m, 6H), 6.95 (d, J = 7.7 Hz, 2H), 2.82 (app dd, J = 7.8, 7.8 Hz, 4H), 2.69 (app dd, J = 7.8, 7.8 Hz, 4H), 2.05 (m, 4H).
TLC R_f = 0.31 (CH_2Cl_2).

The characterization data for the compound were in agreement with previously published information.[3]

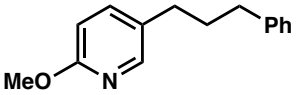
2,4,6-tris(3-phenylpropyl)pyridine (5d)



Prepared from 2,4,6-trichloropyridine and 2-(3-phenylpropyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (363 mg, 1.39 mmol, 3.5 equiv) and LiO^tBu (304 mg, 3.78 mmol, 9 equiv) following general procedure A. The product was obtained as a pale yellow oil (150 mg, 82% yield) after silica gel column chromatography using a solvent gradient CH_2Cl_2 (100%) to CH_2Cl_2/EtOAc (18:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.31–7.25 (m, 6H), 7.23–7.14 (m, 8H), 6.77 (s, 2H), 2.78 (app dd, J = 7.8, 7.8 Hz, 4H), 2.68 (app dd, J = 7.7, 7.7 Hz, 4H), 2.64 (app dd, J = 7.6, 7.6 Hz, 2H), 2.56 (app dd, J = 7.8, 7.8 Hz, 2H), 2.09–1.99 (m, 4H), 1.98–1.89 (m, 2H).
^{13}C NMR (126 MHz, $CDCl_3$): δ 161.1, 151.5, 142.3, 141.7, 128.4, 128.3, 128.3, 128.2, 125.9, 125.6, 120.1, 37.9, 35.6, 35.4, 34.6, 31.9, 31.8.
IR (neat) ν 3083 (w), 3060 (w), 2927 (w), 2856 (w), 1603 (w), 1562 (w), 1495 (w), 1453 (w), 1349 (w), 1178 (w), 1079 (w), 1030 (w), 878 (w), 745 (w), 698 (w), cm^{-1}.
TLC R_f = 0.34 (CH_2Cl_2).
HRMS (ESI): calcd for $C_{32}H_{36}N$ [M + H]= 434.2848, found 434.2845.

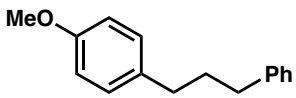
2-methoxy-5-(3-phenylpropyl)pyridine (5e)



Prepared from 2-methoxy-5-chloropyridine and 2-(3-phenylpropyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane following general procedure B with $Pd(OAc)_2$ (1.9 mg, 0.0084 mmol, 0.02 equiv) and Ad_2P^nBu (9.0 mg, 0.252 mmol, 0.06 equiv). The product was obtained as a pale yellow oil (94 mg, 98% yield) after silica gel column chromatography using a solvent gradient CH_2Cl_2 (100%) to CH_2Cl_2:EtOAc (9:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, J = 2.4 Hz, 1H), 7.40 (dd, J = 8.3, 2.4 Hz, 1H), 7.31–7.26 (m, 2H), 7.22–7.16 (m, 3H), 6.68 (d, J = 8.6 Hz, 1H), 3.92 (s, 3H), 2.64 (app dd, J = 7.6, 7.6 Hz, 2H), 2.57 (app dd, J = 7.6, 7.6 Hz, 2H), 1.96–1.87 (m, 2H).
TLC R_f = 0.35 (hexanes:CH_2Cl_2, 1:1).
The characterization data for the compound were in agreement with previously published information.[3]

1-methoxy-4-(3-phenylpropyl)benzene (5f)

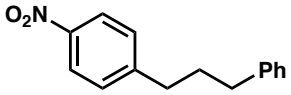


Prepared from 1-chloro-4-methoxybenzene and 2-(3-phenylpropyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane following general procedure B for 20 h using dioxane (2.1 mL). The product was obtained as a pale yellow oil (90 mg, 94% yield) after silica gel column chromatography using CH_2Cl_2:hexanes (1:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31–7.27 (m, 2H), 7.23–7.15 (m, 3H), 7.11 (d, J = 8.0 Hz, 2H), 6.84 (d, J = 8.0 Hz, 2H), 3.80 (s, 3H), 2.66–2.58 (m, 4H), 1.98–1.89 (m, 2H).
TLC R_f = 0.67 (hexanes:CH_2Cl_2, 1:1).

The characterization data for the compound was in agreement with previously published information.[10]

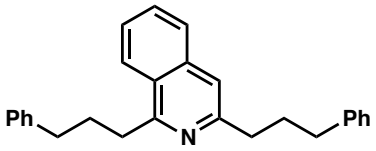
1-nitro-4-(3-phenylpropyl)benzene (5g)



Prepared from 4-nitrochlorobenzene and 2-(3-phenylpropyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane following general procedure B for 20 h using dioxane (2.1 mL) and water (0.5 mL). The product was obtained as a pale yellow oil (91 mg, 90% yield) after silica gel column chromatography using CH_2Cl_2:hexanes (1:2).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (d, J = 8.8 Hz, 2H), 7.37–7.27 (m, 4H), 7.24–7.14 (m, 3H), 2.75 (app dd, J = 7.8, 7.8 Hz, 1H), 2.66 (app dd, J = 7.6, 7.6 Hz, 1H), 2.04–1.95 (m, 1H).
TLC R_f = 0.17 (hexanes:CH_2Cl_2, 3:1).
The characterization data for the compound were in agreement with previously published information.[11]

1,3-bis(3-phenylpropyl)isoquinoline (5h)

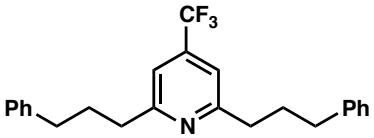


Prepared from 1,3-dichloroisoquinoline and 2-(3-phenylpropyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane following general procedure A for 16 h. The product was obtained as a colorless oil (124 mg, 80% yield) after silica gel column chromatography using CH_2Cl_2/hexanes (1:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.99 (d, J = 8.3 Hz, 1H), 7.72 (d, J = 8.1 Hz, 1H), 7.60 (dd, J = 8.1, 6.8 Hz, 1H), 7.47 (dd, J = 8.3, 6.8 Hz, 1H), 7.33–7.26 (m, 5H), 7.25–7.15 (m, 6H), 3.32 (app dd, J = 7.7, 7.7 Hz, 2H), 2.96 (app dd, J = 7.6, 7.6 Hz, 2H), 2.80 (app dd, J = 7.8, 7.8 Hz, 2H), 2.73 (app dd, J = 7.7, 7.7 Hz, 2H), 2.24–2.11 (m, 4H).
^{13}C NMR (126 MHz, $CDCl_3$): δ 161.3, 154.0, 142.4, 142.2, 136.9, 129.5, 128.5, 128.2, 128.2, 126.9, 126.0, 125.7, 125.6, 125.2, 125.1, 116.6, 37.6, 35.9, 35.6, 34.9, 31.5, 31.4.
^{13}C NMR (126 MHz, acetone-d_6): δ 161.0, 154.2, 142.7, 142.7, 137.2, 129.8, 128.7, 128.6, 128.5, 128.4, 127.2, 126.3, 125.9, 125.8, 125.5, 125.2, 116.7, 37.5, 35.7, 35.5, 34.2, 31.7, 31.0.
IR (neat) ν 3025 (w), 2926 (w), 2857 (w), 1702 (w), 1624 (w), 1592 (w), 1567 (w), 1496 (w), 1453 (w), 1345 (w), 1271 (w), 1179 (w), 1067 (w), 1030 (w), 747 (w), 699 (w), cm^{-1}.
TLC R_f = 0.47 (CH_2Cl_2).
HRMS (ESI): calcd for $C_{27}H_{28}N$ [M + H]= 366.2222, found 366.2216.

[10] R. Soler-Yanes, M. Guisán-Ceinos, E. Buñuel, D. J. Cárdenas, *Eur. J. Org. Chem.* **2014**, *3*, 6625–6629.
[11] Molander, G. A., Yun, C.-S. *Tetrahedron* **2002**, *58*, 1465–1470.

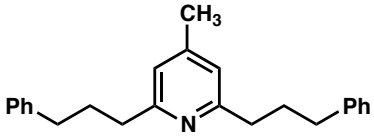
2,6-bis(3-phenylpropyl)-4-(trifluoromethyl)pyridine (5i)



Prepared from 2,6-dichloro-4-(trifluoromethyl)pyridine and 2-(3-phenylpropyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (260 mg, 1.055 mmol, 2.5 equiv) following general procedure A. Following concentration, the crude product was heated to 90 °C in concentrated HCl:EtOH (1:1, total 2 mL) for 8 h. Saturated aqueous sodium bicarbonate solution (ca. 10 mL) was then added dropwise and the resulting mixture was extracted with dichloromethane (5 x 10 mL). The combined organic layers were dried over Na_2SO_4 and concentrated under reduced pressure. The product was obtained as a colorless oil (84 mg, 52% yield) after silica gel column chromatography using CH_2Cl_2/hexanes (1:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.33–7.25 (m, 4H), 7.23–7.16 (m, 6H), 7.15 (s, 2H), 2.88 (app dd, J = 7.8, 7.8 Hz, 4H), 2.70 (dd, J = 7.7, 7.7 Hz, 4H), 2.14–2.04 (m, 4H).
^{13}C NMR (126 MHz, $CDCl_3$): δ 162.9, 141.8, 138.7 (q, J = 32.4 Hz), 128.4, 128.3, 125.9, 123.1 (q, J = 273.4 Hz), 115.5, 37.9, 35.5, 31.3.
^{19}F NMR (376 MHz, $CDCl_3$): δ –64.68.
IR (neat) ν 3062 (w), 3026 (w), 2927 (w), 2859 (w), 1603 (w), 1578 (w), 1496 (w), 1453 (w), 1420 (w), 1375 (m), 1321 (w), 1227 (w), 1166 (m), 1132 (m), 1106 (w), 1078 (w), 1030 (w), 883 (w), 743 (w), 698 (m), 674 (w), 560 (w) cm^{-1}.
TLC R_f = 0.42 (hexanes:CH_2Cl_2, 1:1).
HRMS (ESI): calcd for $C_{24}H_{25}F_3N$ [M + H]= 384.1939, found 384.1936.

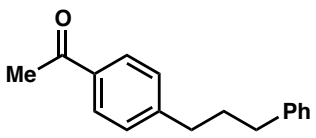
4-methyl-2,6-bis(3-phenylpropyl)pyridine (5j)



Prepared from 2,6-dichloro-4-methylpyridine and 2-(3-phenylpropyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane following general procedure A. The product was obtained as a colorless oil (146 mg, 96% yield) after silica gel column chromatography using CH_2Cl_2/hexanes (1:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.30–7.25 (m, 4H), 7.21–7.15 (m, 6H), 6.78 (s, 2H), 2.77 (app dd, J = 7.8, 7.8 Hz, 4H), 2.68 (app dd, J = 7.8, 7.8 Hz, 4H), 2.27 (s, 3H), 2.08–1.99 (m, 4H).
^{13}C NMR (126 MHz, $CDCl_3$): δ 161.1, 147.3, 142.3, 128.4, 128.2, 125.6, 120.8, 37.9, 35.6, 31.8, 20.8.
IR (neat) ν 3060 (w), 3025 (w), 2922 (w), 2856 (w), 1605 (m), 1566 (w), 1496 (w), 1452 (w), 1355 (w), 1179 (w), 1155 (w), 1079 (w), 1030 (w), 846 (w), 745 (w), 698 (m), 563 (w), cm^{-1}.
TLC R_f = 0.33 (CH_2Cl_2).
HRMS (ESI): calcd for $C_{24}H_{28}N$ [M + H]= 330.2222, found 330.2219.

1-(4-(3-phenylpropyl)phenyl)ethanone (5k)

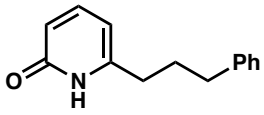


Prepared from 4-chloroacetophenone and 2-(3-phenylpropyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane following general procedure B. Following concentration, the crude product was heated to 80 °C in

concentrated HCl:EtOH (1:1, total 2 mL) for 12 h. Saturated aqueous sodium bicarbonate solution (ca. 10 mL) was then added dropwise and the resulting mixture was extracted with dichloromethane (5 x 10 mL). The combined organic layers were dried over Na_2SO_4 and concentrated under reduced pressure. The product was obtained as a pale yellow oil (18 mg, 18% yield) after silica gel column chromatography using CH_2Cl_2:hexanes (1:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, J = 8.1 Hz, 2H), 7.32–7.24 (m, 4H), 7.23–7.14 (m, 3H), 2.71 (app dd, J = 7.7, 7.7 Hz, 2H), 2.65 (app dd, 7.7, 7.7 Hz, 2H) 2.59 (s, 3H), 2.02–1.94 (m, 2H).
TLC R_f = 0.15 (hexanes:CH_2Cl_2, 1:1).
The characterization data for the compound were in agreement with previously published information.[12]

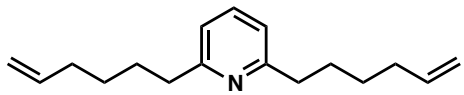
6-(3-phenylpropyl)pyridin-2(1*H*)-one (5l)



Prepared from 2-chloro-6-(*tert*-butoxy)-pyridine and 2-(3-phenylpropyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane following general procedure C. The product was obtained as pale yellow oil (89 mg, 98% yield) after silica gel column chromatography using EtOAc.

^{1}H NMR (400 MHz, $CDCl_3$) δ 12.39 (br s, 1H), 7.37 (dd, J = 8.9, 6.8 Hz, 1H), 7.31–7.25 (m, 2H), 7.22–7.16 (m, 3H), 6.41 (d, J = 8.9 Hz, 1H), 6.04 (d, J = 6.8 Hz, 1H), 2.69 (app dd, J = 7.6, 7.6 Hz, 2H), 2.63 (app dd, J = 7.6, 7.6 Hz, 2H), 2.08–1.99 (m, 2H).
TLC R_f = 0.25 (EtOAc).
The characterization data for the compound were in agreement with previously published information.[3]

2,6-di(hex-5-en-1-yl)pyridine (5m)



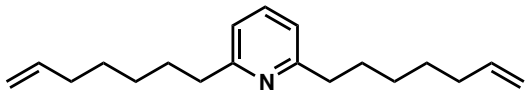
Prepared from 2,6-dichloropyridine and 2-(hex-5-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (221 mg, 1.055 mmol, 2.5 equiv) following general procedure A. The product was obtained as a pale yellow oil (92 mg, 90% yield) after silica gel column chromatography using a solvent gradient from CH_2Cl_2 (100%) to CH_2Cl_2:EtOAc (20:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.48 (t, J = 7.7 Hz, 1H), 6.93 (d, J = 7.7 Hz, 2H), 5.80 (ddt, J = 16.9, 10.1, 6.7 Hz, 2H), 5.02–4.90 (m, 4H), 2.75 (app dd, J = 7.8, 7.8 Hz, 4H), 2.08–2.01 (m, 4H), 1.76–1.67 (m, 4H), 1.46–1.35 (m, 4H).
^{13}C NMR (126 MHz, $CDCl_3$): δ 161.6, 138.9, 136.4, 119.6, 114.3, 38.4, 33.6, 29.6, 28.6.
IR (neat) ν 3074 (w), 2975 (w), 2925 (w), 2856 (w), 1640 (w), 1589 (w), 1576 (w), 1455 (w), 1155 (w), 1088 (w), 991 (w), 792 (w), 752 (w), 632 (w), cm^{-1}.
TLC R_f = 0.24 (CH_2Cl_2:hexanes, 1:1).

[12] Molander, G. A.; Ito, T. *Org. Lett.* **2001**, *3*, 393–396.

HRMS (ESI): calcd for $C_{17}H_{26}N$ [M + H]= 244.2065, found 244.2063.

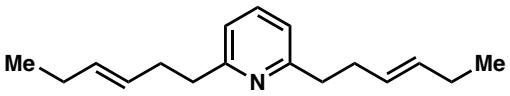
2,6-di(hept-6-en-1-yl)pyridine (5n)



Prepared from 2,6-dichloropyridine and 2-(hept-6-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (236 mg, 1.055 mmol, 2.5 equiv) following general procedure A. The product was obtained as a pale yellow oil (97 mg, 85% yield) after silica gel column chromatography using a solvent gradient CH_2Cl_2 (100%) to CH_2Cl_2:EtOAc (20:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.47 (t, J = 7.7 Hz, 1H), 6.93 (d, J = 7.7 Hz, 2H), 5.80 (ddt, J = 17.0, 10.3, 6.7 Hz, 2H), 5.02–4.88 (m, 4H), 2.75 (app dd, J = 7.8, 7.8 Hz, 4H), 2.07–2.00 (m, 4H), 1.77–1.65 (m, 4H), 1.47–1.33 (m, 8H).
^{13}C NMR (126 MHz, $CDCl_3$): δ 161.8, 139.0, 136.3, 119.6, 114.2, 38.5, 33.7, 30.0, 28.9, 28.8.
IR (neat) ν 3075 (w), 2976 (w), 2925 (w), 2854 (w), 1640 (w), 1589 (w), 1576 (w), 1455 (w), 1154 (w), 1088 (w), 992 (w), 908 (w), 798 (w), 751 (w), 637 (w), cm^{-1}.
TLC R_f = 0.27 (CH_2Cl_2:hexanes, 1:1).
HRMS (ESI): calcd for $C_{19}H_{30}N$ [M + H]= 272.2378, found 272.2373.

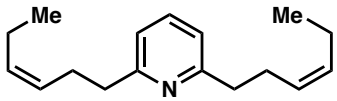
2,6-di((*E*)-hex-3-en-1-yl)pyridine (5o)



Prepared from 2-2,6-dichloropyridine and (*E*)-2-(hex-3-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane following general procedure A. The product was obtained as a pale yellow oil (47.6 mg, 47% yield; *E*:*Z* ≥ 19:1) after silica gel column chromatography using hexanes:CH_2Cl_2 (9:1 to 4:1) .

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (t, J = 7.6 Hz, 1H), 6.93 (d, J = 7.6 Hz, 2H), 5.51–5.40 (m, 4H), 2.81 (t, J = 7.8 Hz, 4H), 2.43–2.36 (m, 4H), 2.01–1.94 (m, 4H), 0.93 (t, J = 7.5 Hz, 6H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 161.1, 136.2, 132.7, 128.1, 119.9, 38.5, 33.0, 25.6, 13.9.
IR (neat) ν 2960 (w), 2923 (w), 2872 (w), 2849 (w), 1589 (w), 1576 (m), 1455 (m), 1373 (w), 1260 (w), 1216 (w), 1146 (w), 1091 (w), 964 (m), 895 (w), 798 (w), 749 (w), 542 (w) cm^{-1}.
TLC R_f = 0.77 (CH_2Cl_2).
HRMS (ESI) calcd for [M + H]= 244.2060, found = 244.2063.

2,6-di((*Z*)-hex-3-en-1-yl)pyridine (5p)

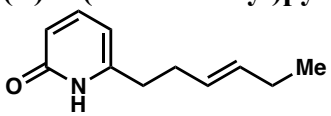


Prepared from 2-2,6-dichloropyridine and (*Z*)-2-(hex-3-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane following general procedure A. The product was obtained as a pale yellow oil (48.4 mg, 47% yield; *Z*:*E* ≥ 19:1) after silica gel column chromatography using hexanes:CH_2Cl_2 (9:1 to 4:1) .

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (t, J = Hz, 1H), 6.95 (d, J = Hz, 2H), 5.36 (m, 4H), 2.80 (app dd, J = 7.7, 7.7 Hz, 4H), 2.46 (m, 4H), 1.98 (m, 4H), 0.88 (t, J = 7.6 Hz, 6H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 161.1, 136.2, 132.3, 128.0, 120.0, 38.4, 27.6, 20.5, 14.2.
IR (neat) ν 3060 (w), 3004 (w), 2961 (w), 2931 (w), 2872 (w), 1653 (m), 1589 (w), 1576 (m), 1455 (m), 1404 (w), 1371 (w), 1326 (w), 1270 (w), 1240 (w), 1215 (w), 1145 (w), 1088 (w), 1069 (w), 991 (w), 967 (w), 868 (w), 830 (w), 795 (w), 703 (m), 578 (w) cm^{-1}.
TLC R_f = 0.80 (CH_2Cl_2).
HRMS (ESI) calcd for [M + H]= 244.2060, found = 244.2064.

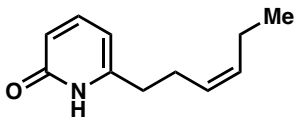
(*E*)-6-(hex-3-en-1-yl)pyridin-2-(1*H*)-one (5q)



Prepared from 2-chloro-6-(*tert*-butoxy)-pyridine and (*E*)-2-(hex-3-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane following general procedure C. The product was obtained as a pale yellow solid (63.5 mg, 85% yield; *E*:*Z* ≥ 19:1) after silica gel column chromatography using EtOAc.

^{1}H NMR (400 MHz, $CDCl_3$) δ 12.12 (bs, 1H), 7.34 (dd, *J* = 9.1, 6.9 Hz, 1H), 6.39 (d, *J* = 9.1 Hz, 1H), 6.02 (d, *J* = 6.9 Hz, 1H), 5.55–5.46 (m, 1H), 5.44–5.35 (m, 1H), 2.62 (t, *J* = 7.5 Hz, 2H), 2.42–2.33 (m, 2H), 2.02–1.93 (m, 2H), 0.91 (t, *J* = 7.5 Hz, 3H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 165.9, 149.5, 141.6, 133.9,126.7, 116.7, 105.2, 33.1, 31.3, 15.5, 13.7.
IR (neat) ν 3028 (w), 2960 (m), 2931 (m), 2872 (w), 2845 (w), 2779 (w), 1638 (s), 1624 (s), 1548 (m), 1465 (m), 1416 (w), 1379 (w), 1240 (w), 1207 (w), 1162 (m), 1079 (w), 1002 (m), 965 (m), 870 (w), 795 (w), 736 (w), 561 (m), 527 (m) cm^{-1}.
TLC R_f = 0.21 (CH_2Cl_2:EtOAc, 1:1).
HRMS (ESI) calcd for [M + H]= 178.1226, found = 178.1230.

(*Z*)-6-(hex-3-en-1-yl)pyridin-2-(1*H*)-one (5r)

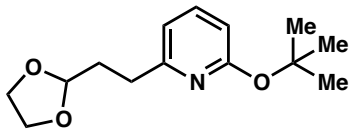


Prepared from 2-chloro-6-(*tert*-butoxy)-pyridine and (*Z*)-2-(hex-3-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane following general procedure C. The product was obtained as a pale yellow solid (62.5 mg, 84% yield; E:Z ≥ 19:1) after silica gel column chromatography using EtOAc.

^{1}H NMR (400 MHz, $CDCl_3$) δ 12.36 (bs, 1H), 7.34 (dd, *J* = 9.1, 6.9 Hz, 1H), 6.38 (d, *J* = 9.1 Hz, 1H), 6.03 (d, *J* = 6.9 Hz, 1H), 5.47–5.38 (m, 1H), 5.36–5.28 (m, 1H), 2.62 (t, *J* = 7.4 Hz, 2H), 2.48–2.40 (m, 2H), 2.05–1.95 (m, 2H), 0.89 (t, *J* = 7.6 Hz, 3H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 165.9, 149.5, 141.6, 133.4, 126.5, 116.8, 105.3, 33.0, 26.1, 20.5, 14.2.
IR (neat) ν 3001 (w), 2964 (m), 2932 (m), 2779 (m), 1642 (w), 1621 (w), 1547 (m), 1466 (m), 1414 (m), 1381 (m), 1335 (w), 1306 (w), 1269 (w), 1243 (w), 1209 (m), 1162 (m), 1072 (w), 1024 (w), 999 (m), 945 (m), 860 (m), 800 (m), 775 (m), 755 (w), 732 (m), 700 (m), 593 (w), 559 (s) cm^{-1}.

TLC R_f = 0.24 (CH_2Cl_2:EtOAc, 1:1).
HRMS (ESI) calcd for [M + H]= 178.1226, found = 178.1229.

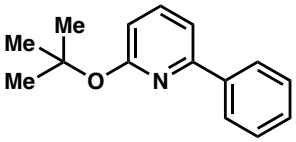
2-(2-(1,3-dioxolan-2-yl)ethyl)-6-(*tert*-butoxy)pyridine (5s)



Prepared from 2-chloro-6-(*tert*-butoxy)-pyridine and 2-(2-(1,3-dioxolan-2-yl)ethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane following general procedure B. The product was obtained as a pale yellow oil (96 mg, 90% yield) after silica gel column chromatography using hexanes:EtOAc (9:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.39 (dd, J = 8.3, 7.2 Hz, 1H), 6.66 (d, J = 7.2 Hz, 1H), 6.44 (d, J = 8.3 Hz, 1H), 4.92 (t, J = 4.8 Hz, 1H), 4.04–3.95 (m, 2H), 3.91–3.83 (m, 2H), 2.82–2.76 (m, 2H), 2.17–2.06 (m, 2H), 1.57 (s, 9H).
^{13}C NMR (126 MHz, $CDCl_3$): δ 163.4, 158.2, 138.3, 114.6, 110.2, 104.1, 79.2, 64.9, 33.1, 32.1, 28.8.
IR (neat) ν 2973 (w), 2929 (w), 2882 (w), 1592 (m), 1574 (m), 1477 (w), 1443 (m), 1388 (w), 1362 (m), 1302 (w), 1286 (w), 1247 (w), 1172 (m), 1135 (m), 1086 (w), 1065 (w), 1034 (m), 991 (m), 944 (m), 868 (w), 803 (w), 787 (w), 739 (w) cm^{-1}.
TLC R_f = 0.25 (CH_2Cl_2).
HRMS (ESI): calcd for $C_{14}H_{22}NO_3$ [M + H]= 252.1600, found 252.1595.

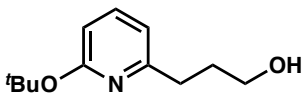
2-(*tert*-butoxy)-6-phenylpyridine (5t)



Prepared from 2-chloro-6-(*tert*-butoxy)-pyridine and phenylboronic acid following general procedure B with for 18 h. The product was obtained as a pale yellow oil (102 mg, 99% yield) after silica gel column chromatography using hexanes:CH_2Cl_2 (3:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (m, 2H), 7.58 (t, J = 8.2, 7.6 Hz, 1H), 7.51–7.43 (m, 2H), 7.41–7.36 (m, 1H), 7.31 (d, J, = 7.6 Hz, 1H), 6.60 (d, J = 8.2 Hz, 1H), 1.68 (s, 9H).
TLC R_f = 0.63 (hexanes:EtOAc, 9:1).
The characterization data for the compound were in agreement with previously published information.[13]

3-(6-(*tert*-butoxy)pyridin-2-yl)propan-1-ol (5u)

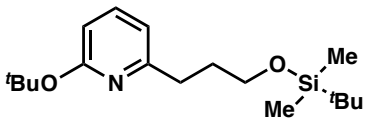


Prepared from 2-chloro-6-(*tert*-butoxy)-pyridine and *tert*-butyldimethyl(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propoxy)silane following general procedure B. The product was obtained as a pale yellow oil (74 mg, 84% yield) after silica gel column chromatography using CH_2Cl_2 (100%) to CH_2Cl_2:EtOAc (3:1).

[13] Fier, P. S.; Hartwig, J. F. *J. Am. Chem. Soc.* **2014***, 136*, 10139.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (dd, J = 8.2, 7.2 Hz, 1H), 6.68 (t, J = 7.2 Hz, 1H), 6.48 (d, J = 8.2 Hz, 1H), 3.56 (t, J = 7.7 Hz, 2H), 2.78 (t, J = 7.3 Hz, 2H), 2.03–1.96 (m, 2H), 1.57 (s, 9H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 163.3, 158.8, 138.6, 115.1, 110.7, 79.3, 62.3, 34.2, 31.9, 28.8.
IR (neat) ν 3349 (br, w), 2976 (w), 1592 (m), 1574 (m), 1443 (m), 1362 (m), 1292 (m), 1245 (m), 1173 (m), 1144 (m), 1058 (m), 1035 (m), 991 (m), 878 (m), 846 (w), 800 (m), 782 (m), 737 (w), 673 (w), 580 (w) cm^{-1}.
TLC R_f = 0.71 (CH_2Cl_2:EtOAc, 1:1).
HRMS (ESI) calcd for [M + H]= 210.1489, found =210.1491.

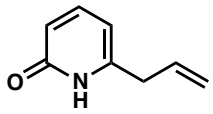
2-(*tert*-butoxy)-6-(3-((*tert*-butyldimethylsilyl)oxy)propyl)pyridine (5v)



Prepared from 2-chloro-6-(*tert*-butoxy)-pyridine and *tert*-butyldimethyl(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propoxy)silane following general procedure B, substituting K_3PO_4 for LiO^tBu. The product was obtained as a pale yellow oil (120 mg, 88% yield) after silica gel column chromatography using hexanes (100%) to hexanes:EtOAc (19:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (dd, J = 8.2, 7.2 Hz, 1H), 6.64 (d, J = 7.2 Hz, 1H), 6.44 (d, J = 8.2 Hz, 1H), 3.66 (t, J = 6.4 Hz, 2H), 2.73–2.68 (m, 2H), 1.98–1.91 (m, 2H), 1.58 (s, 9H), 0.90 (s, 9H), 0.04 (s, 6H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 138.3, 114.8, 110.0, 79.1, 62.7, 34.2, 32.33, 28.8, 26.0, 18.3, -5.3.
IR (neat) ν 2955 (w), 2928 (w), 2856 (w), 1593 (w), 1576 (w), 1472 (w), 1444 (m), 1388 (w), 1361 (m), 1318 (w), 1293 (w) 1249 (m), 1174 (m), 1146 (m), 1099 (m), 1036 (w), 1004 (m), 966 (w), 938 (w), 833 (s), 808 (m), 773 (s), 736 (w), 662 (m), 578 (w) cm^{-1}.
TLC R_f = 0.63 (hexanes:EtOAc, 9:1).
HRMS (ESI) calcd for [M + H]= 324.2353, found =324.2353.

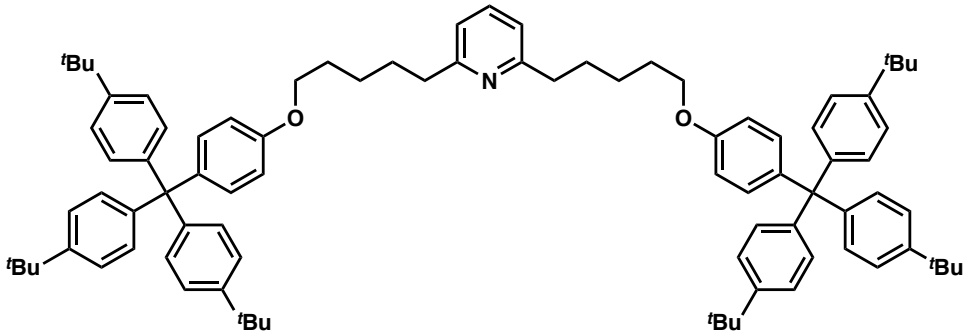
6-allylpyridin-2(1*H*)-one (5w)



Prepared from 2-chloro-6-(*tert*-butoxy)-pyridine and 2-allyl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane following general procedure, using CsF (4.76 mmol, 4 equiv) in place of LiO^tBu and 100% dioxane as the solvent (no water). The product was obtained as a white solid (26.6 mg, 47% yield) after silica gel column chromatography using EtOAc (100%) to EtOAc:MeOH (19:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ 12.55 (bs, 1H), 7.38 (dd, J = 9.1, 6.9 Hz, 1H), 6.43 (d, J = 9.1 Hz, 1H), 6.07 (d, J = 6.9 Hz, 1H), 5.92 (ddt, J = 17.0, 10.2, 6.8 Hz, 1H), 5.28–5.19 (m, 2H), 3.37 (d, J = 6.8 Hz, 2H).
^{13}C NMR (126 MHz, $CDCl_3$): δ 165.7, 147.6, 141.8, 132.5, 119.0, 117.3, 105.2, 37.2.
IR (neat) ν 2922 (w), 2779 (w), 1650 (m), 1622 (w), 1545 (w), 1464 (w), 1167 (w), 1007 (w), 962 (w), 922 (w), 814 (w), 561 (w), 528 (w) cm^{-1}.
TLC R_f = 0.18 (EtOAc).
HRMS (ESI): calcd for $C_8H_{10}NO$ [M + H]= 136.0762, found 136.0757.

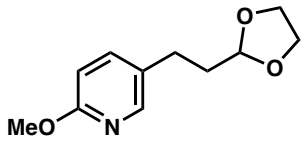
2,6-bis(5-(4-(tris(4-(*tert*-butyl)phenyl)methyl)phenoxy)pentyl)pyridine (1)



Prepared from 2-2,6-dichloropyridine and 4,4,5,5-tetramethyl-2-(5-(4-(tris(4-(*tert*-butyl)phenyl)methyl)phenoxy)pentyl)-1,3,2-dioxaborolane following general procedure A with varying $Pd(OAc)_2$ and Ad_2P^nBu loadings on a 0.21 mmol scale. The product was obtained as a white solid after silica gel column chromatography using hexanes:EtOAc (49:1 to 9:1).
Yield using 1 mol% $Pd(OAc)_2$ and 3 mol% Ad_2P^nBu: 109 mg, 42%.
Yield using 2 mol% $Pd(OAc)_2$ and 6 mol% Ad_2P^nBu: 169 mg, 66%.
Yield using 3 mol% $Pd(OAc)_2$ and 9 mol% Ad_2P^nBu: 192 mg, 75%.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.47 (t, J = 7.4 Hz, 1H), 7.22 (d, J = 8.4 Hz, 12H), 7.11–7.03 (m, 16H), 6.94 (d, J = 7.4 Hz, 2H), 6.73 (d, J = 8.8 Hz, 4H), 3.91 (t, J = 6.3 Hz, 4H), 2.77 (app dd, J = 7.5, 7.5 Hz, 4H), 1.83–21.72 (m, 8H), 1.56–1.48 (m, 4H), 1.29 (s, 54H).
TLC R_f = 0.24 (hexanes:EtOAc, 9:1).
The characterization data for the compound were in agreement with previously published information.[14]

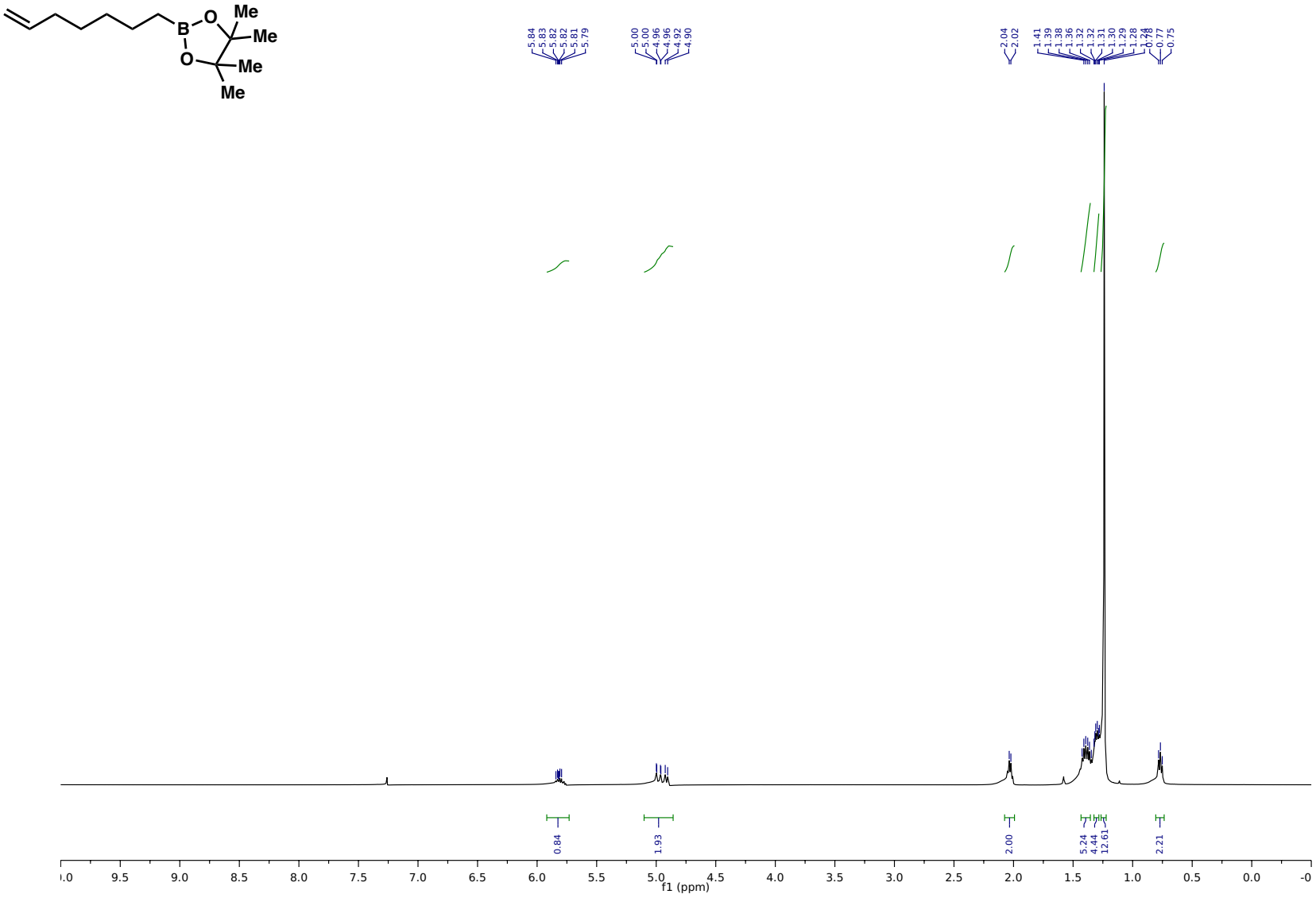
5-(2-(1,3-dioxolan-2-yl)ethyl)-2-methoxypyridine (S5a)



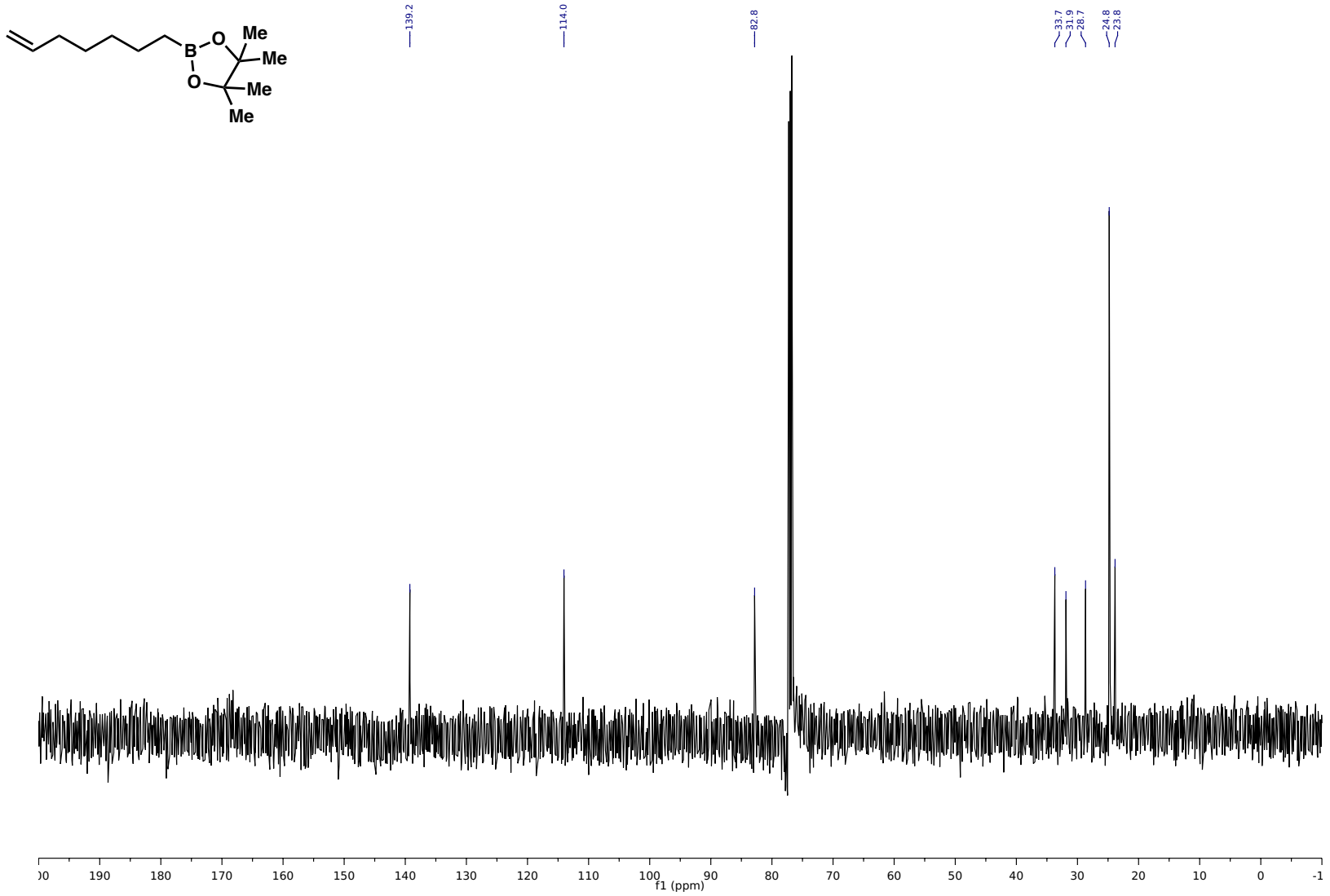
Prepared from 2-chloro-6-(*tert*-butoxy)-pyridine and 2-(2-(1,3-dioxolan-2-yl)ethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane following the general procedure C. The product was obtained as a pale yellow oil (41 mg, 46% yield) after silica gel column chromatography using hexanes:EtOAc (3:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.00 (d, J = 2.5 Hz, 1H), 7.42 (dd, J = 8.5, 2.5 Hz, 1H), 6.68 (d, J = 8.5 Hz, 1H), 4.88 (t, J = 4.6 Hz, 1H), 4.04–3.94 (m, 2H), 3.91 (s, 3H), 3.89–3.84 (m, 2H), 2.70–2.64 (m, 2H), 1.98–1.90 (m, 2H).
^{13}C NMR (126 MHz, $CDCl_3$): δ 162.7, 146.0, 138.9, 129.4, 110.5, 103.5, 65.0, 53.3, 35.3, 26.3.
IR (neat) ν 2948 (w), 2883 (w), 1609 (m), 1572 (w), 1493 (m), 1462 (w), 1391 (m), 1362 (w), 1307 (w), 1290 (w), 1255 (w), 1137 (w), 1056 (w), 1028 (m), 969 (w), 944 (w), 925 (w), 896 (w), 829 (w), 640 (w), 548 (w) cm^{-1}.
TLC R_f = 0.74 (CH_2Cl_2:EtOAc, 4:1).
HRMS (ESI): calcd for $C_{11}H_{16}NO_3$ [M + H]= 210.1130, found 210.1124.

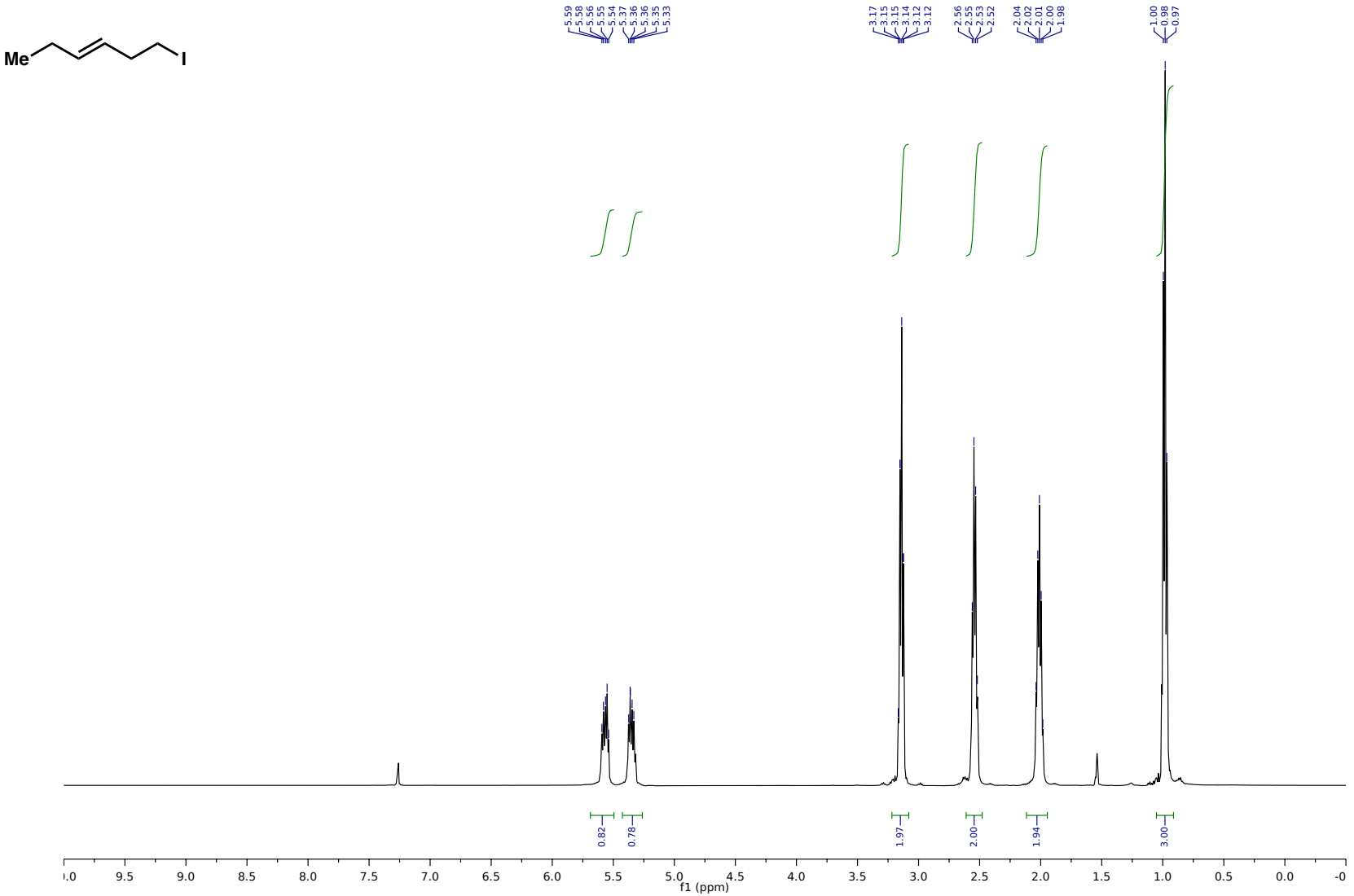
[14] Goldup, S. M; Leigh, D. A.; Lusby, P. J.; McBurney, R. T.; Slawin, A. M. Z. *Angew. Chem. Int. Ed.* **2008**, *47*, 6999.



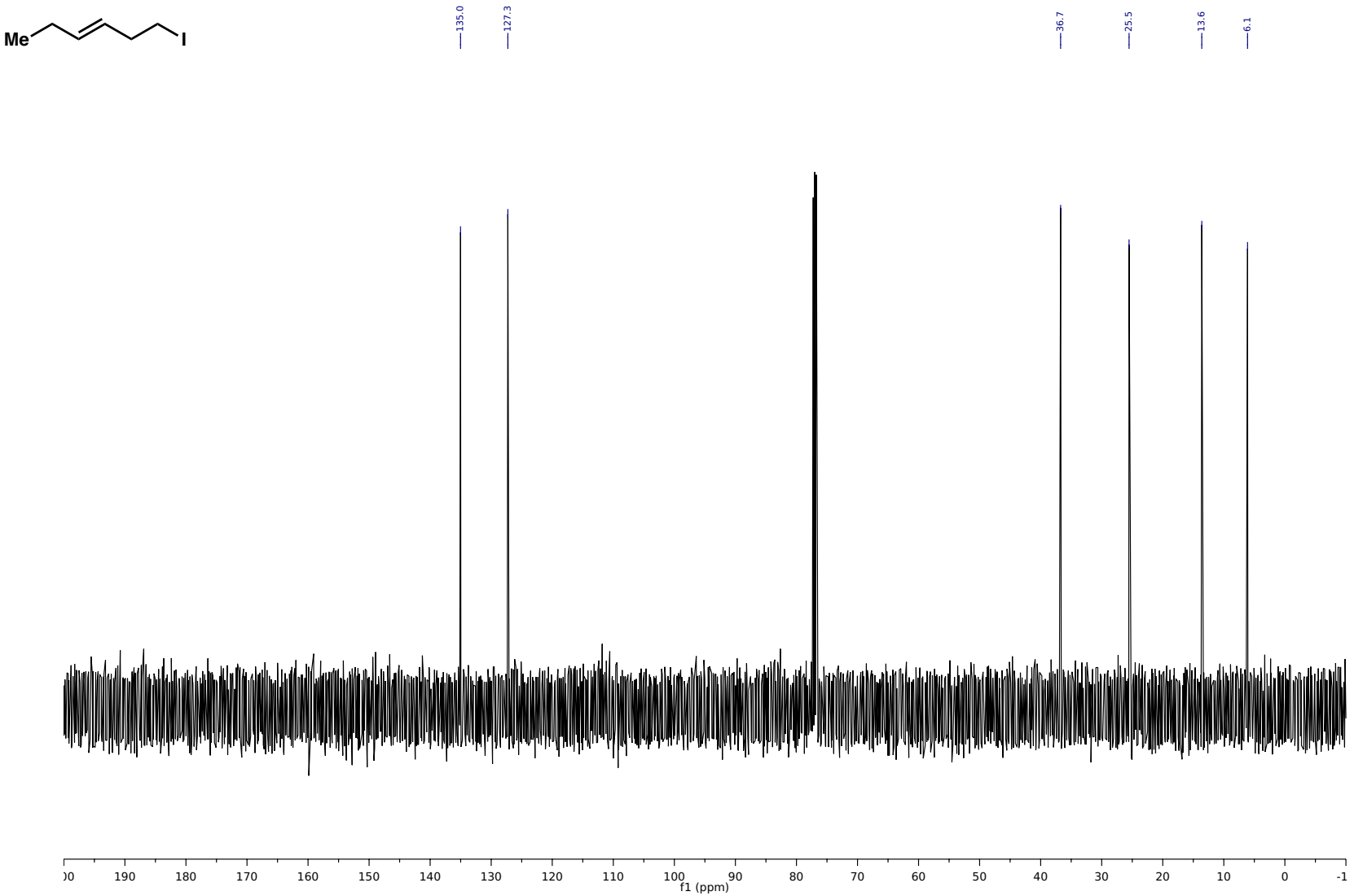
^{1}H NMR (126 MHz, $CDCl_3$) of 2-(hept-6-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**6n**)



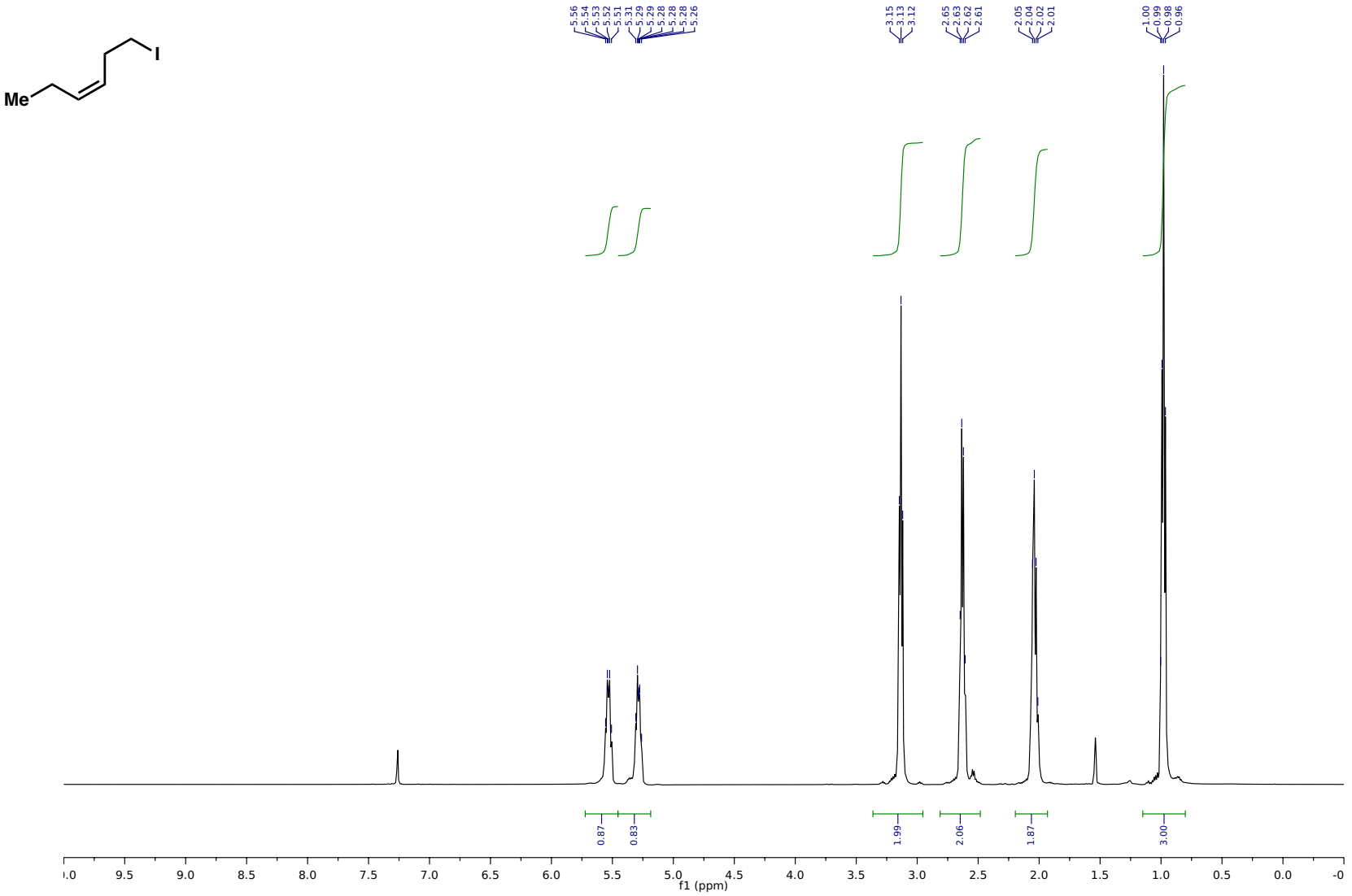
^{13}C NMR (126 MHz, $CDCl_3$) of 2-(hept-6-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**6n**)



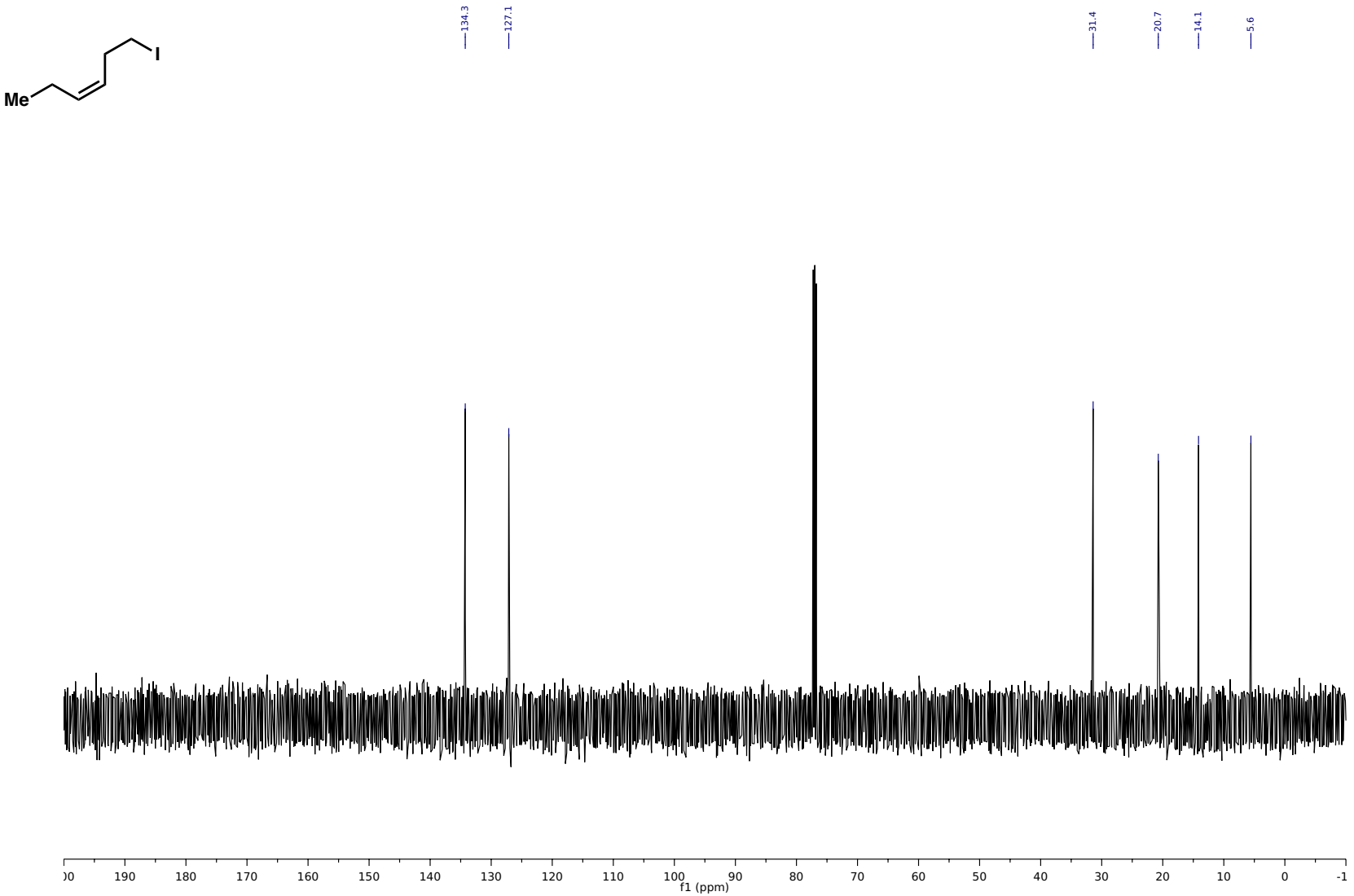
^{1}H NMR (400 MHz, $CDCl_3$) of (*E*)-1-iodohex-3-ene (**S1a**)



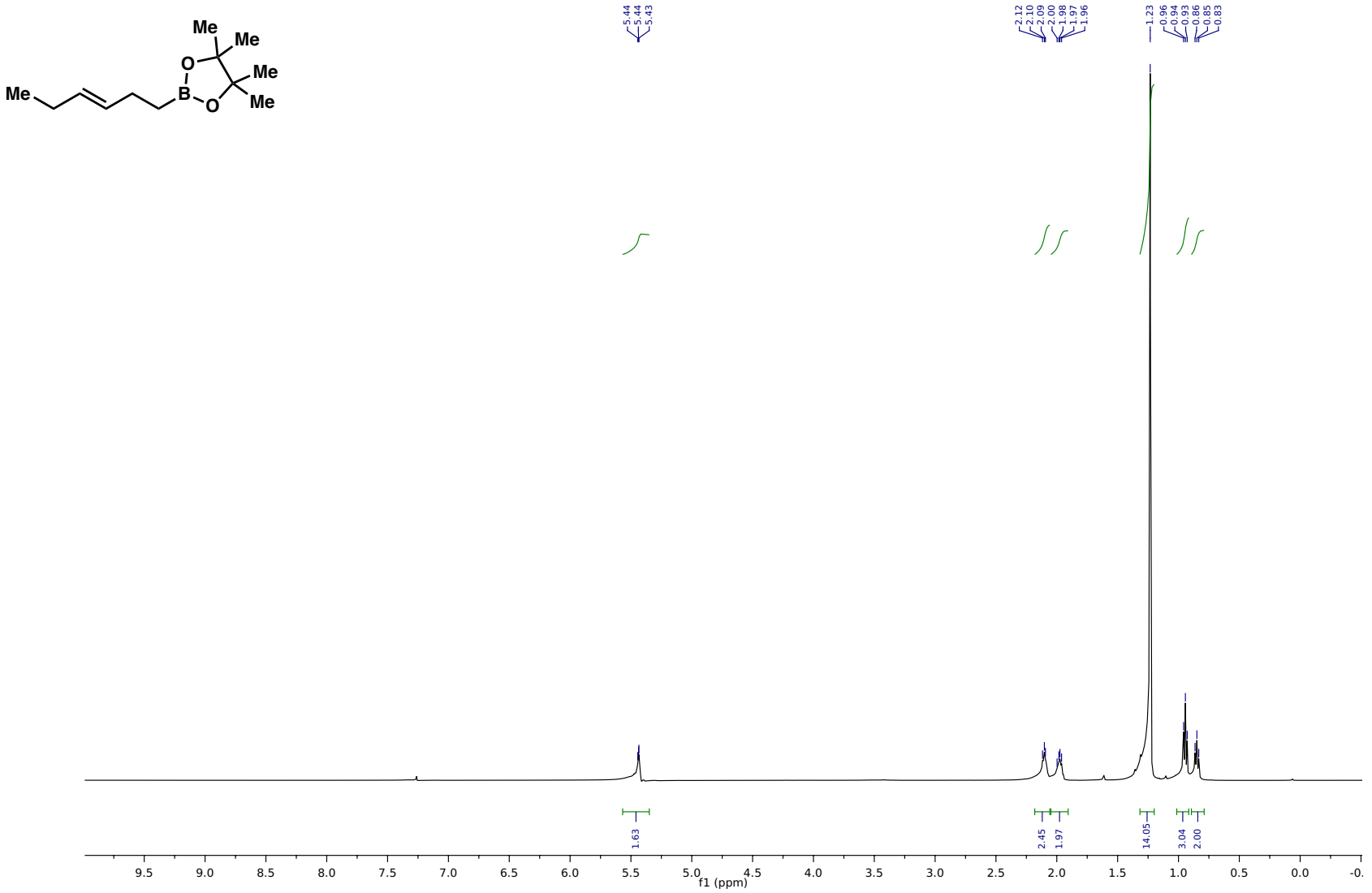
^{13}C NMR (126 MHz, $CDCl_3$) of (*E*)-1-iodohex-3-ene (**S1a**)



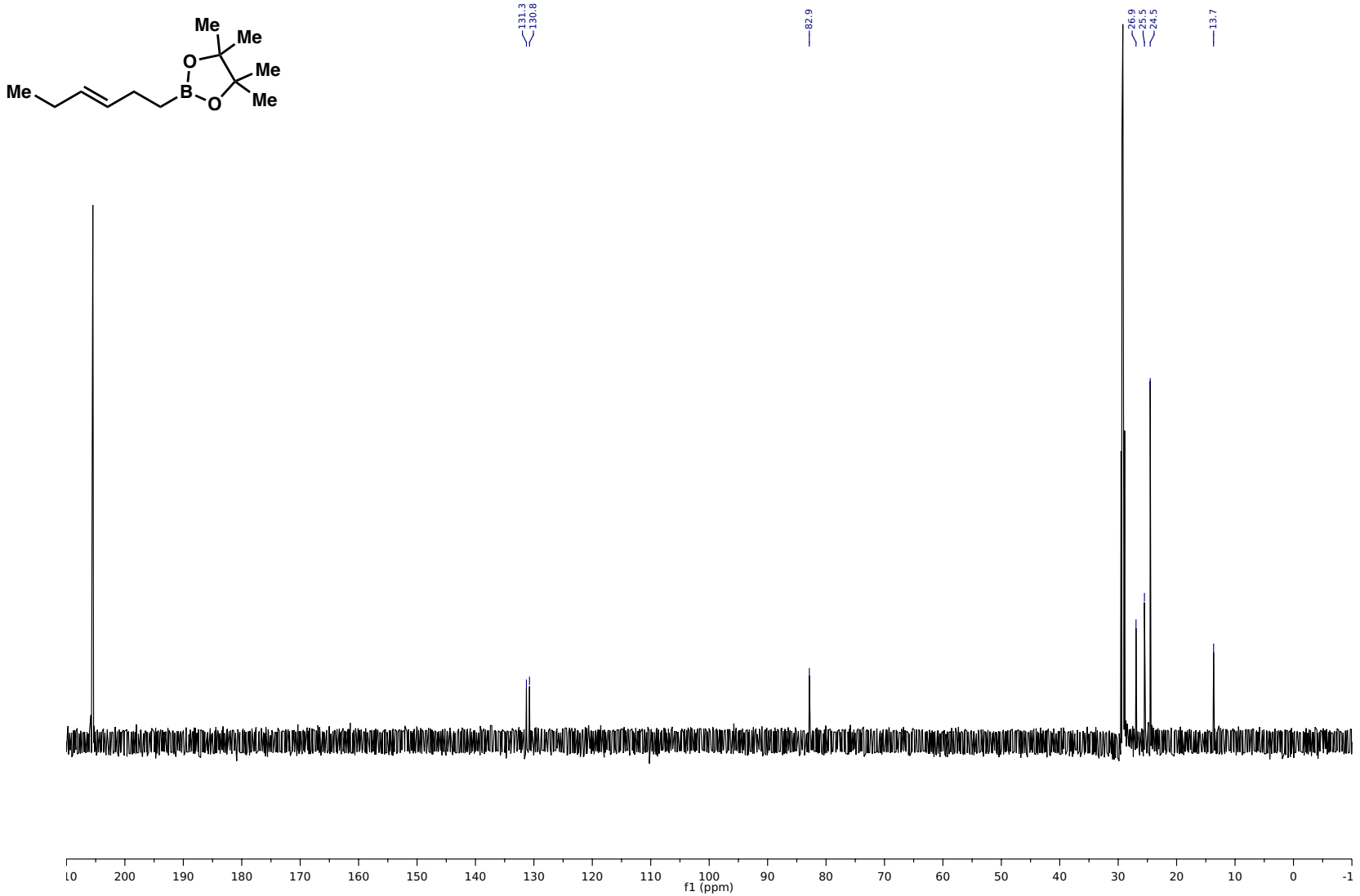
^{1}H NMR (400 MHz, $CDCl_3$) of (*Z*)-1-iodohex-3-ene (**S1b**)



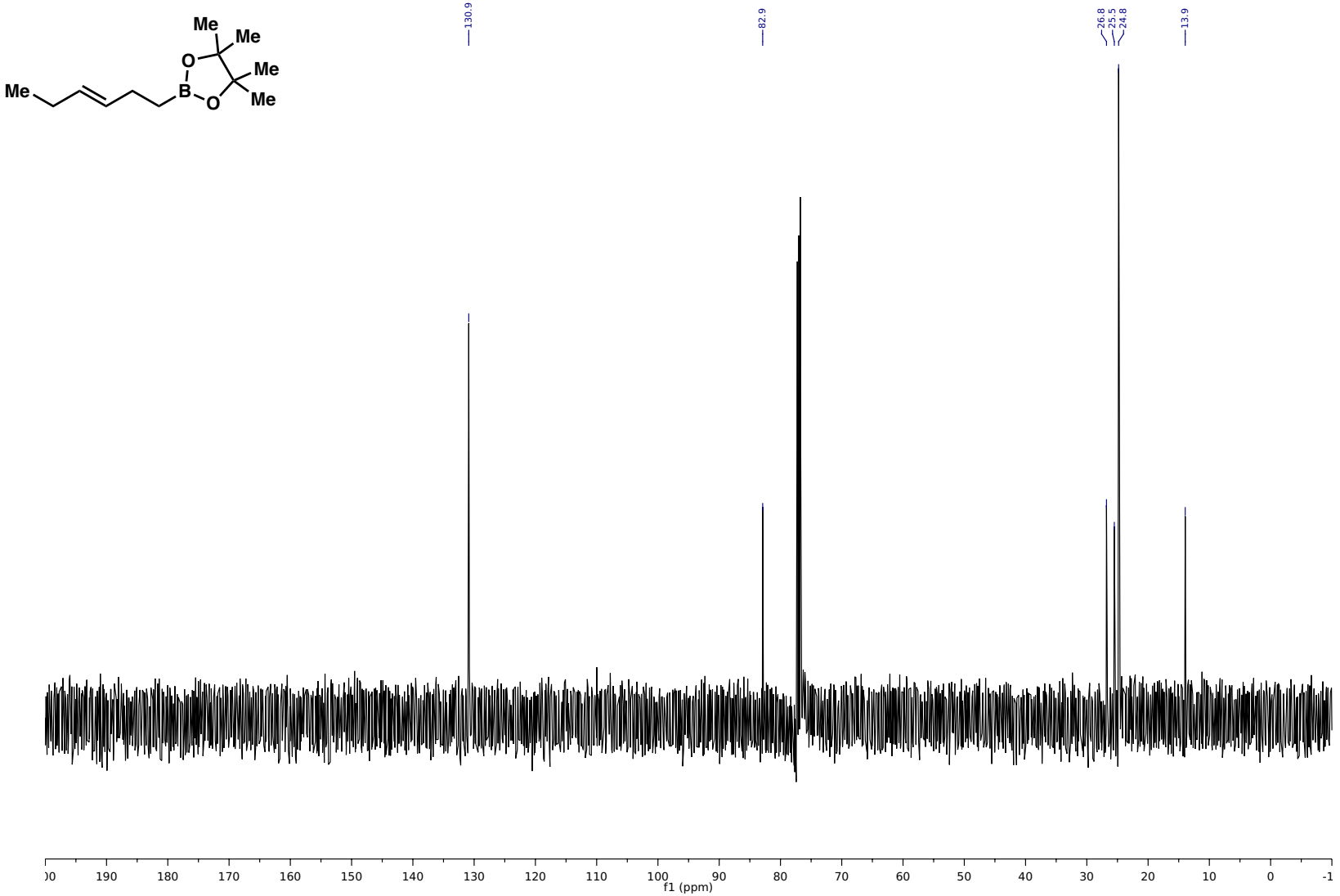
^{13}C NMR (126 MHz, $CDCl_3$) of (*Z*)-1-iodohex-3-ene (**S1b**)



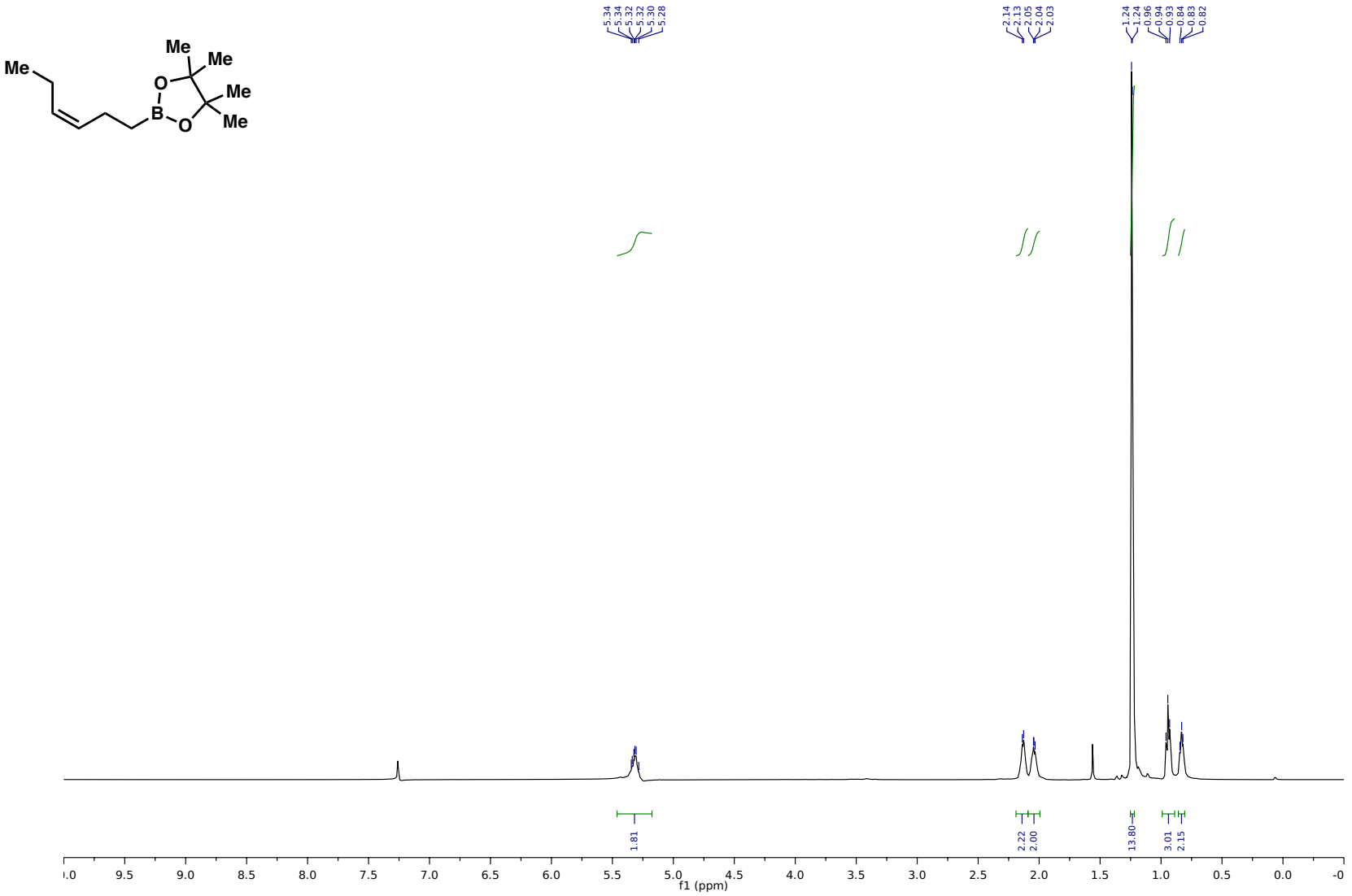
^{1}H NMR (400 MHz, $CDCl_3$) of (*E*)-2-(hex-3-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**6o**)



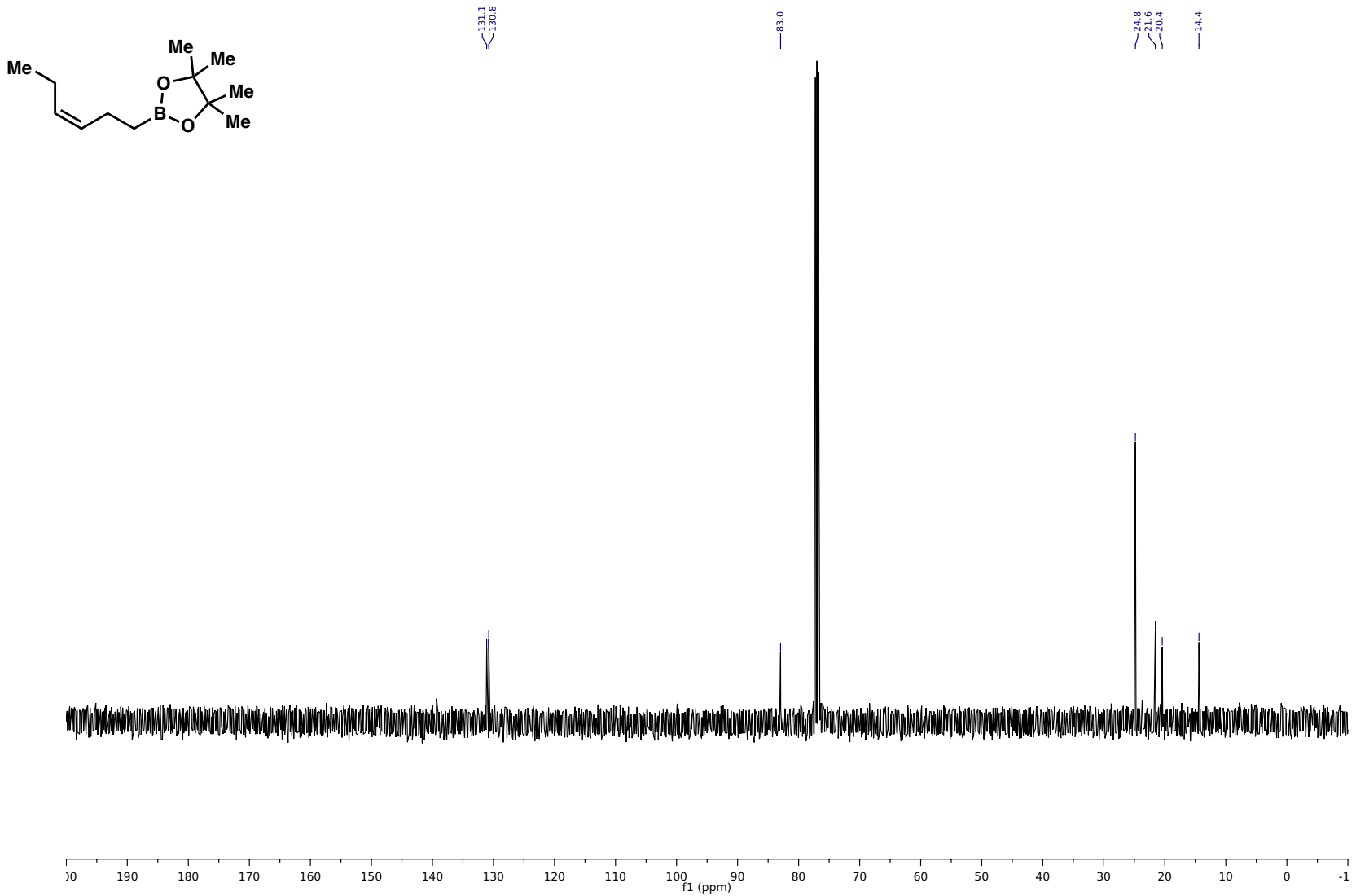
^{13}C NMR (126 MHz, acetone-d_6) of (*E*)-2-(hex-3-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**6o**)



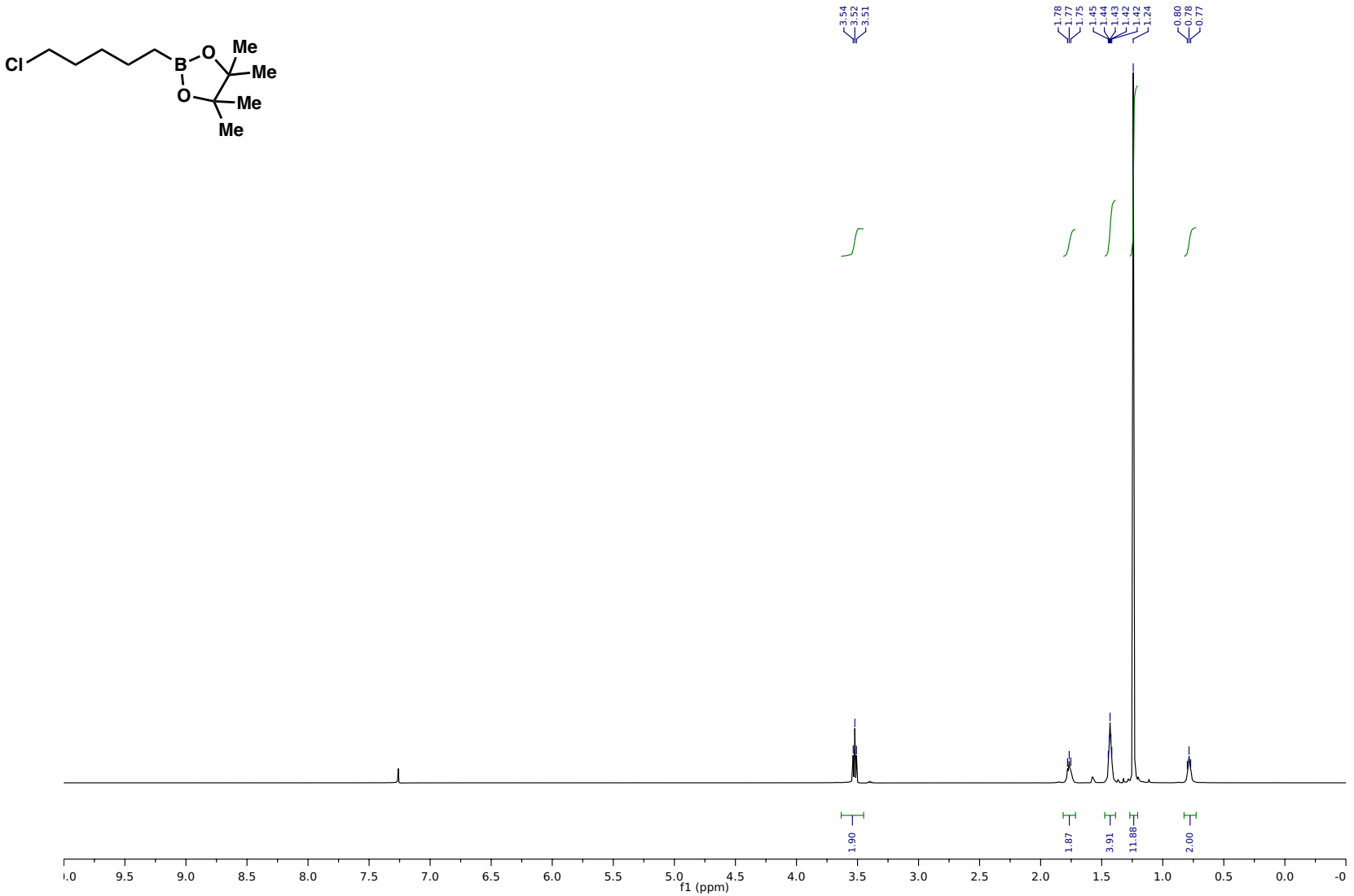
^{13}C NMR (126 MHz, $CDCl_3$) of (*E*)-2-(hex-3-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**6p**)



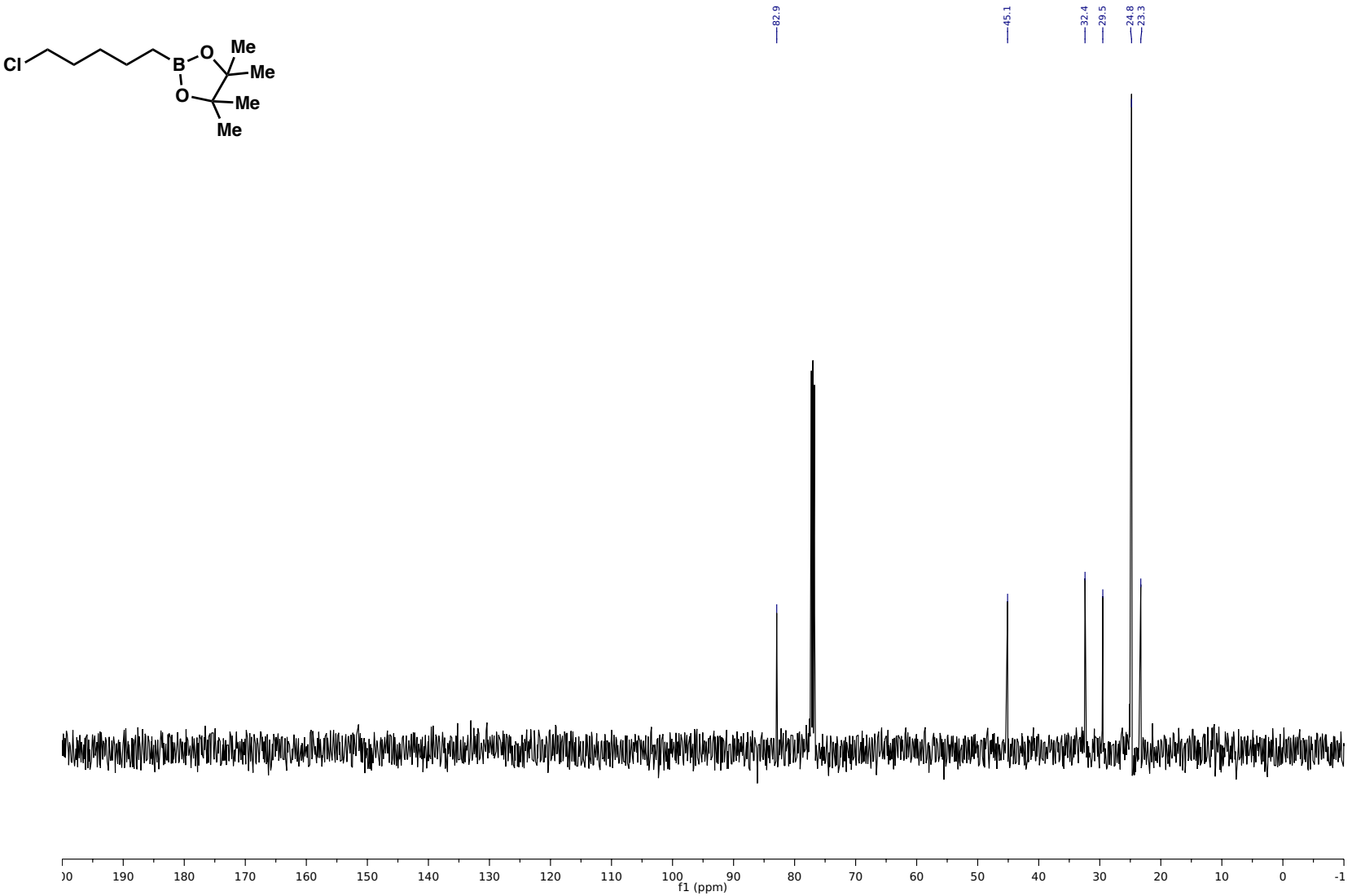
^{1}H NMR (400 MHz, $CDCl_3$) of (*Z*)-2-(hex-3-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**6p**)



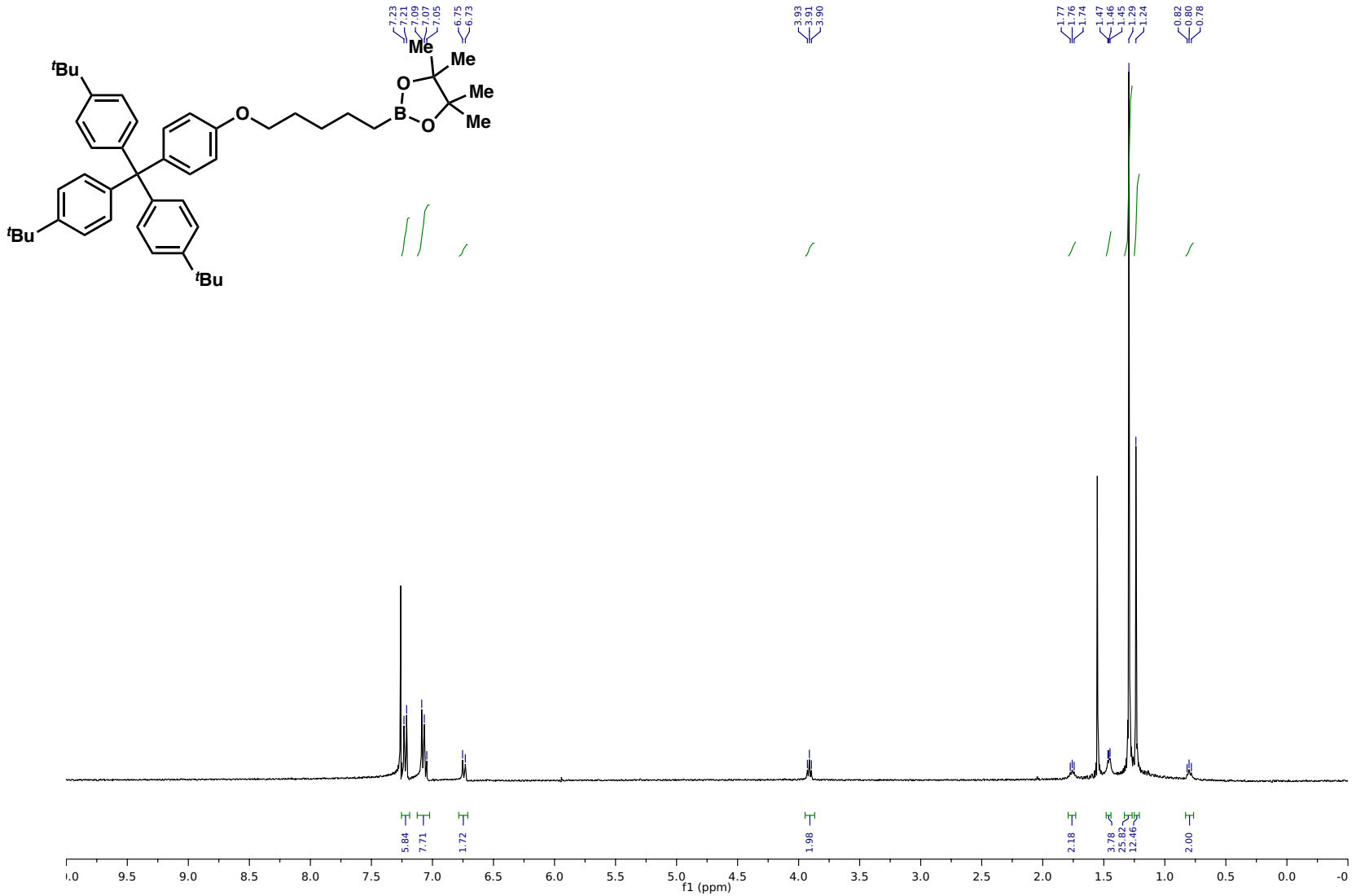
^{13}C NMR (126 MHz, $CDCl_3$) of (*Z*)-2-(hex-3-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**6p**)



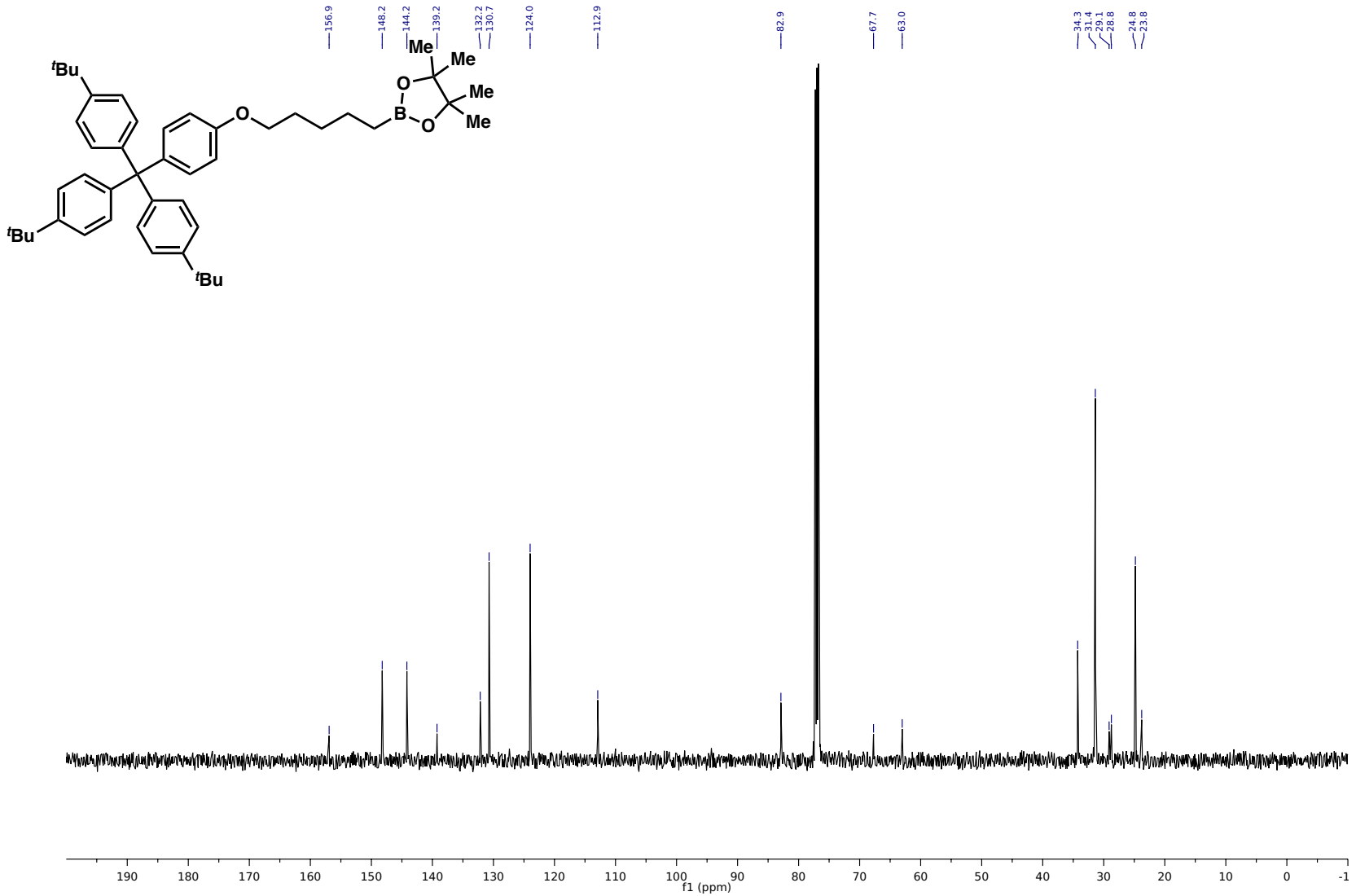
^{1}H NMR (400 MHz, $CDCl_3$) of 2-(5-chloropentyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**6x**)



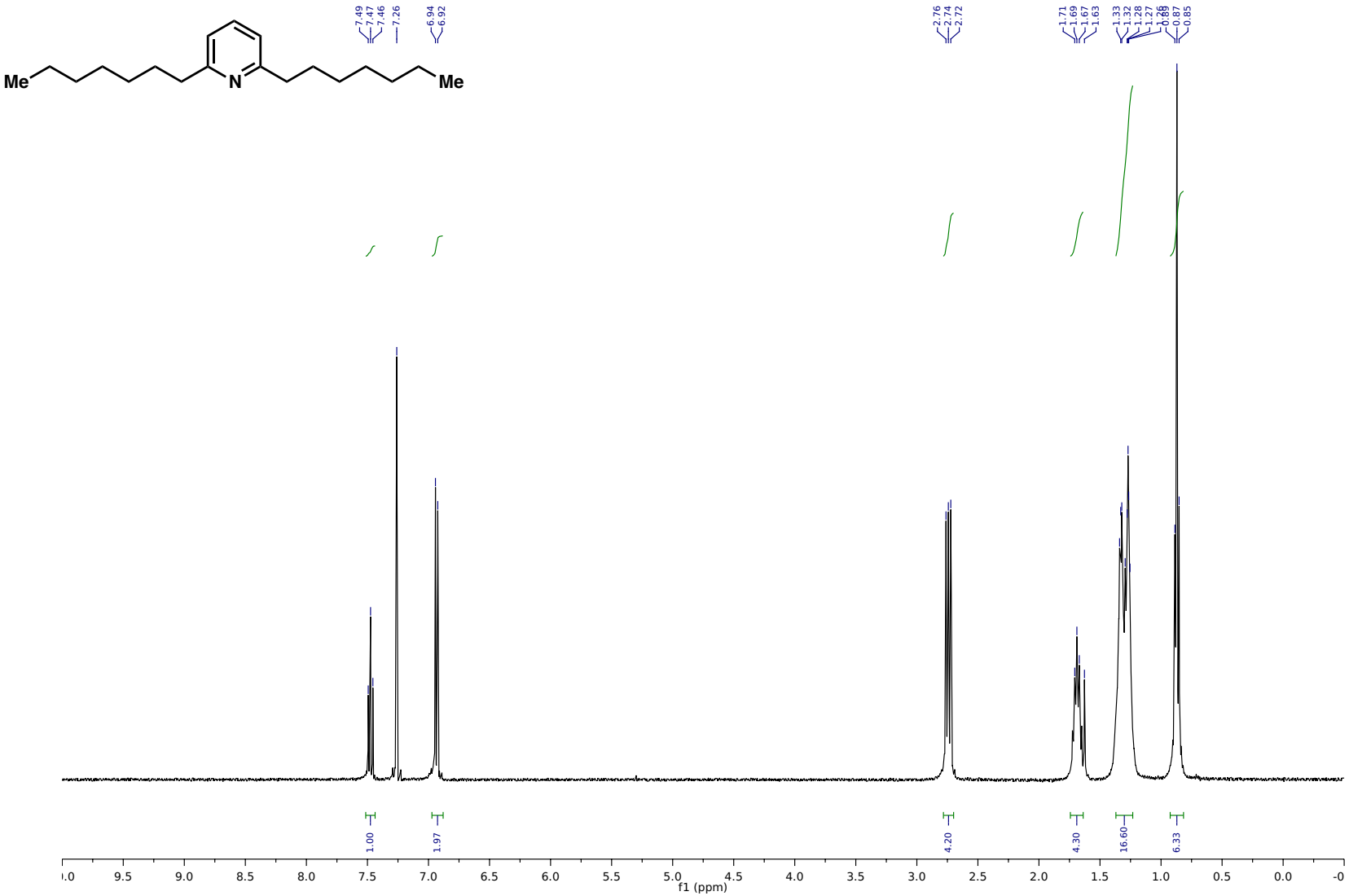
^{13}C NMR (126 MHz, $CDCl_3$) of 2-(5-chloropentyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**6x**)



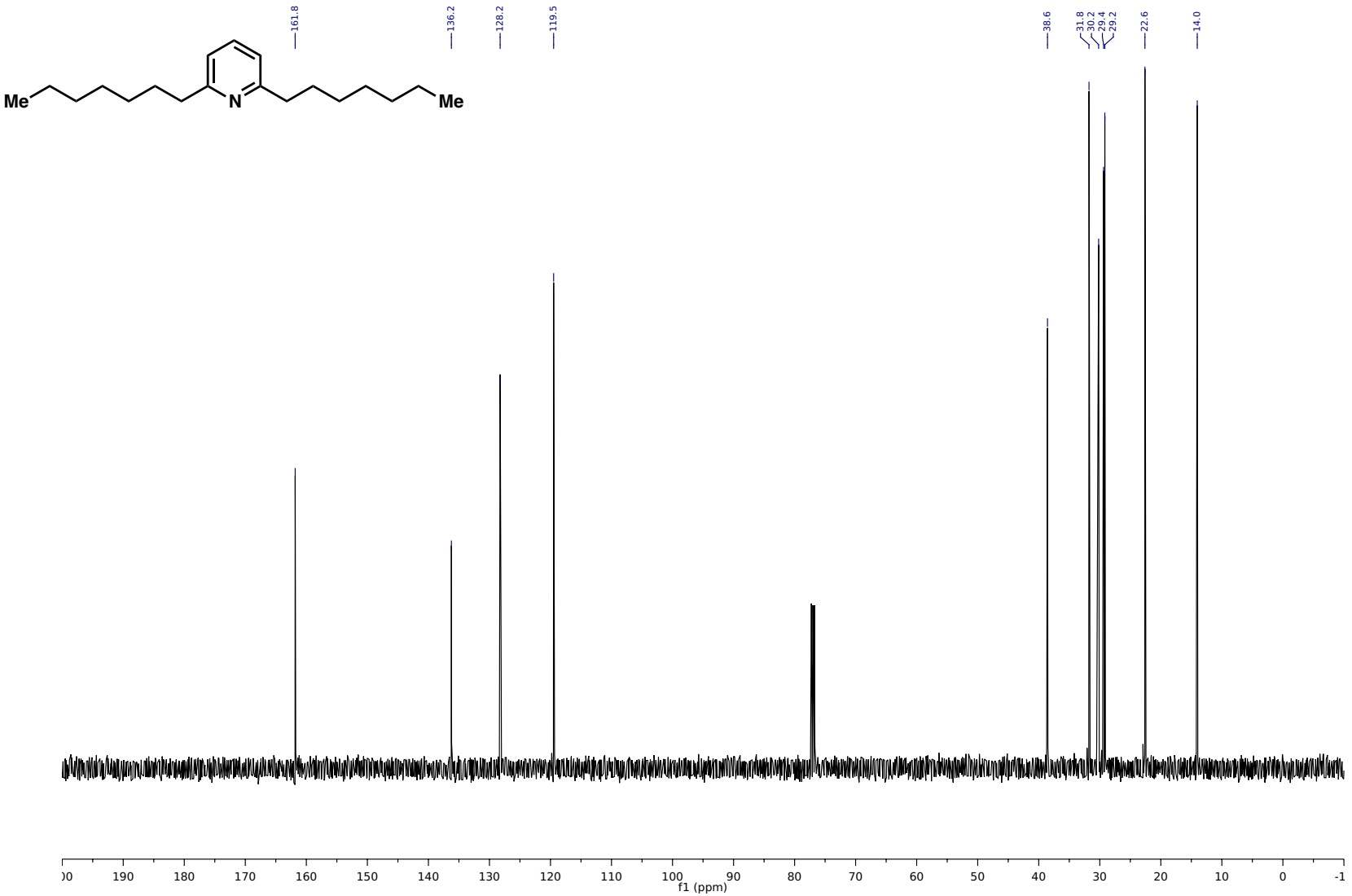
^{1}H NMR (400 MHz, $CDCl_3$) of 4,4,5,5-tetramethyl-2-(5-(4-(tris(4-(*tert*-butyl)phenyl)methyl)phenoxy)pentyl)-1,3,2-dioxaborolane (**6y**)



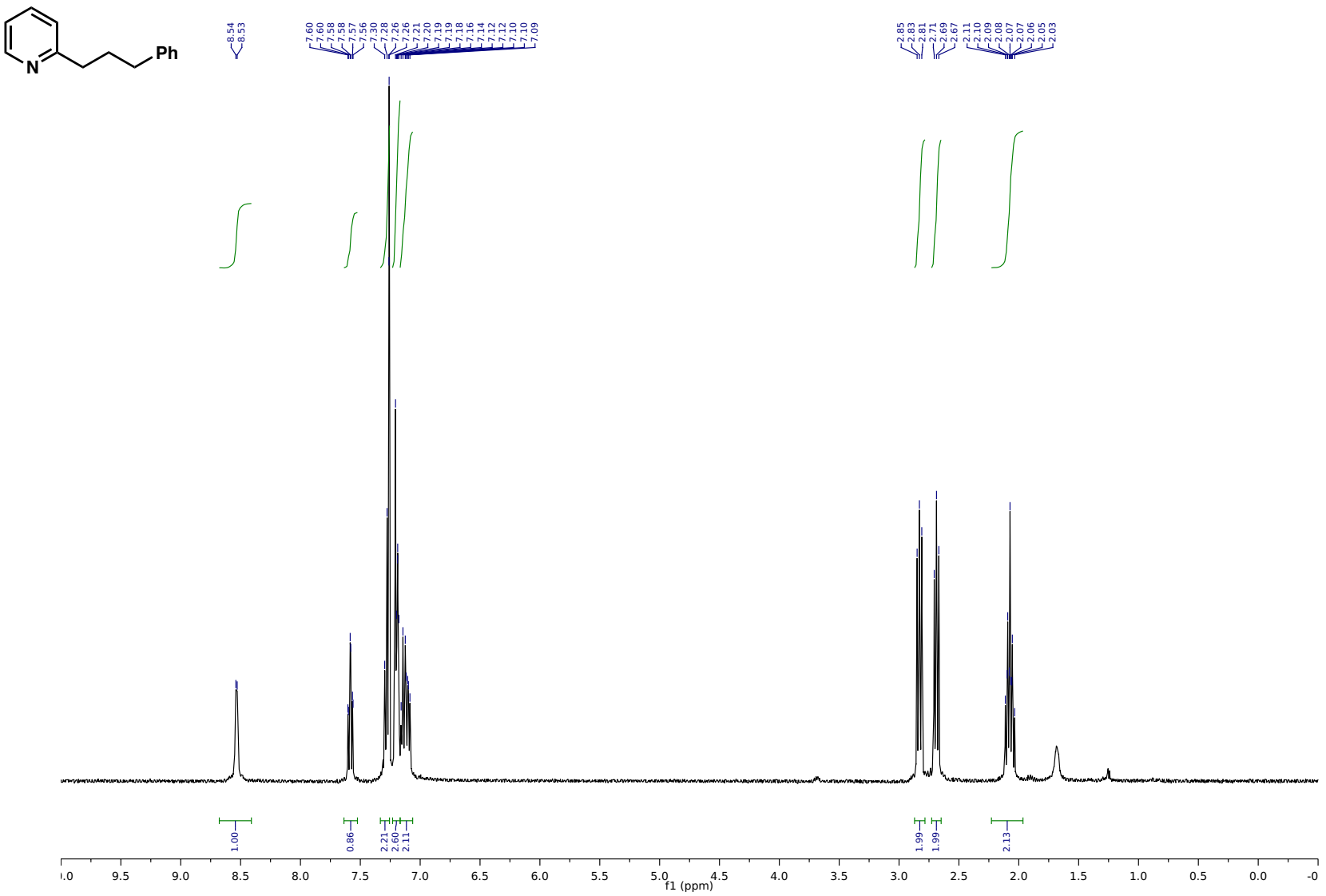
^{13}C NMR (126 MHz, $CDCl_3$) of 4,4,5,5-tetramethyl-2-(5-(4-(tris(4-(*tert*-butyl)phenyl)methyl)phenoxy)pentyl)-1,3,2-dioxaborolane (**6y**)



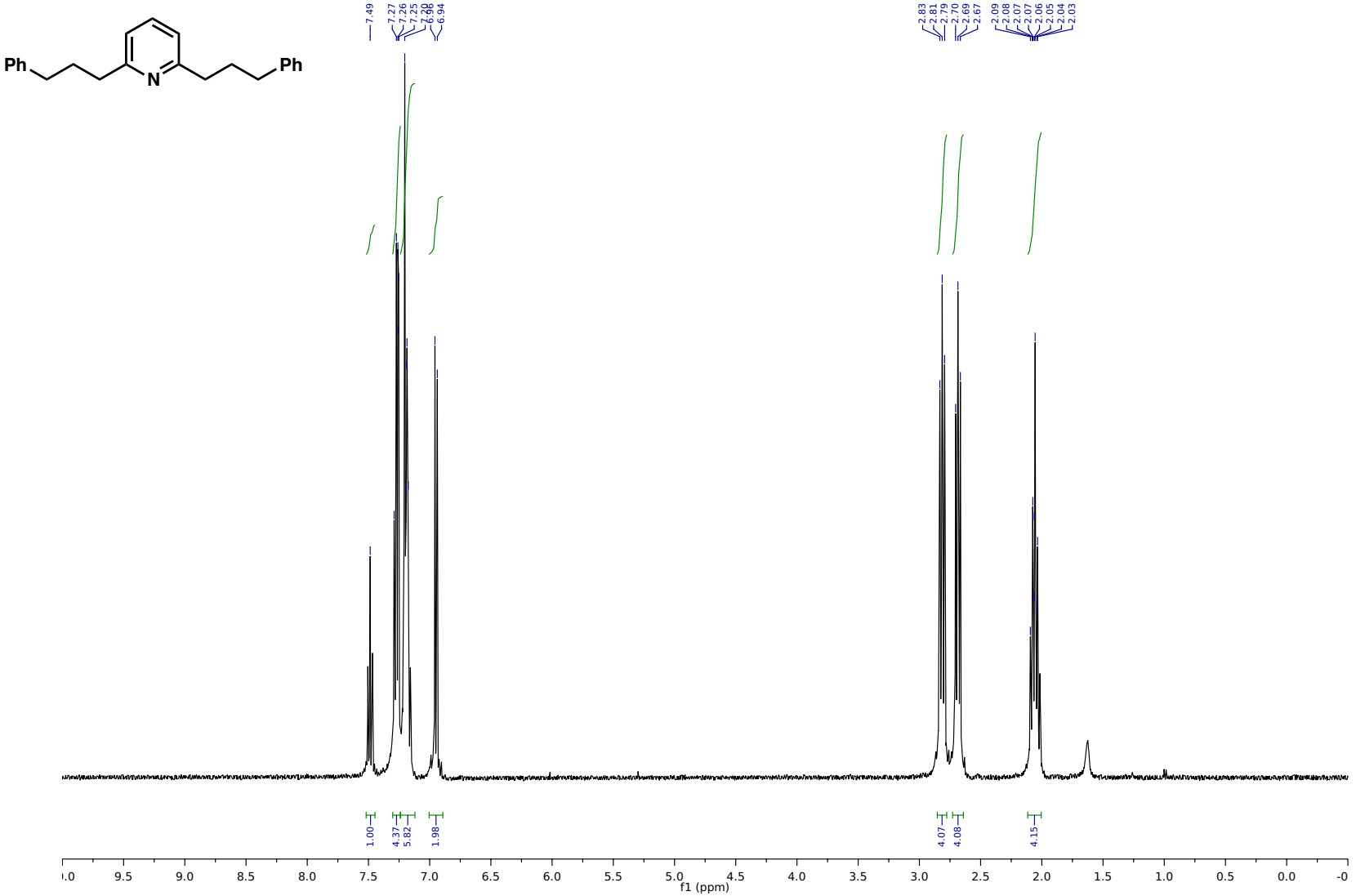
^{1}H NMR (400 MHz, $CDCl_3$) of 2,6-diheptylpyridine (**5a**)



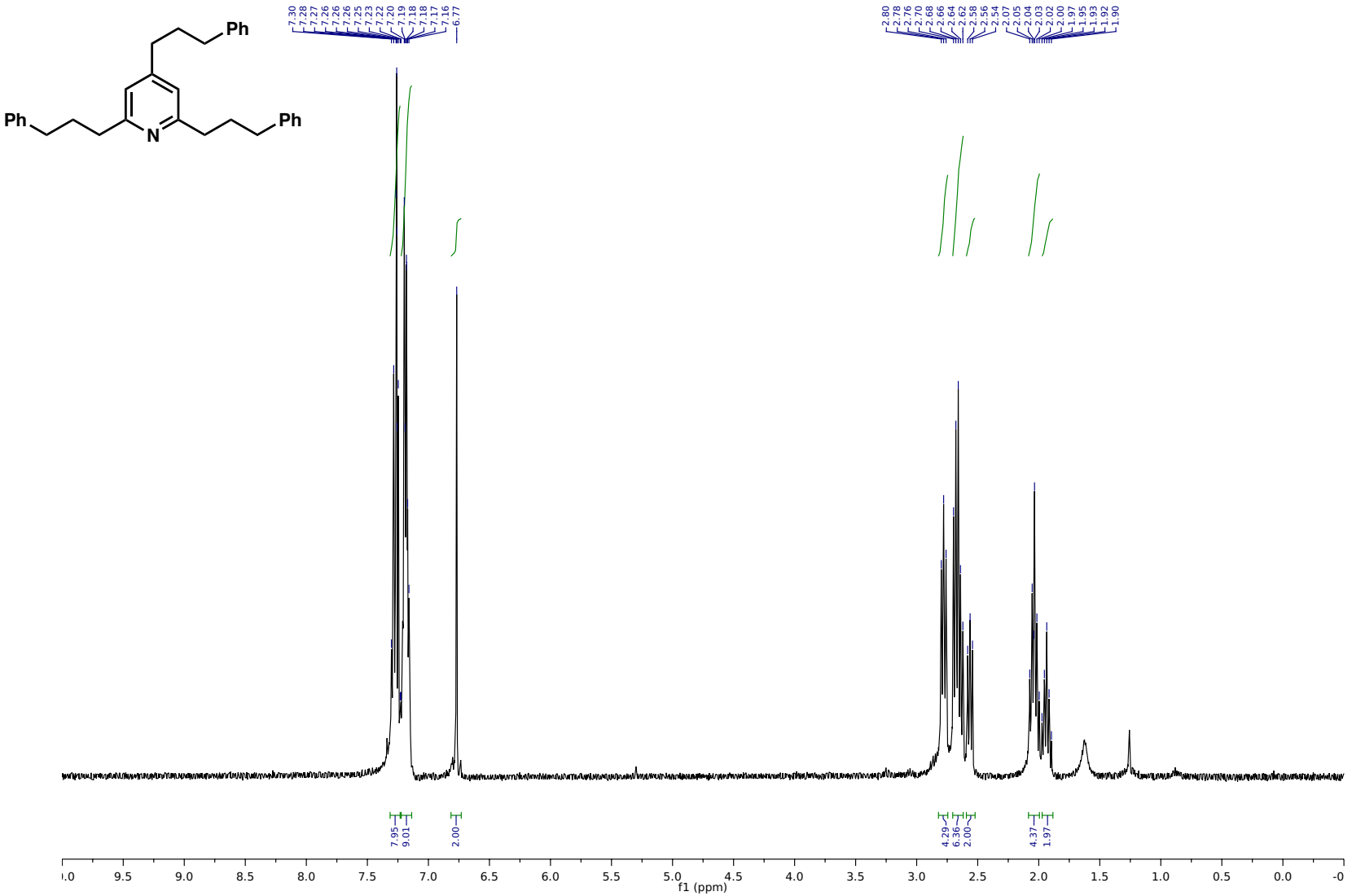
^{13}C NMR (126 MHz, $CDCl_3$) of 2,6-diheptylpyridine (**5a**)



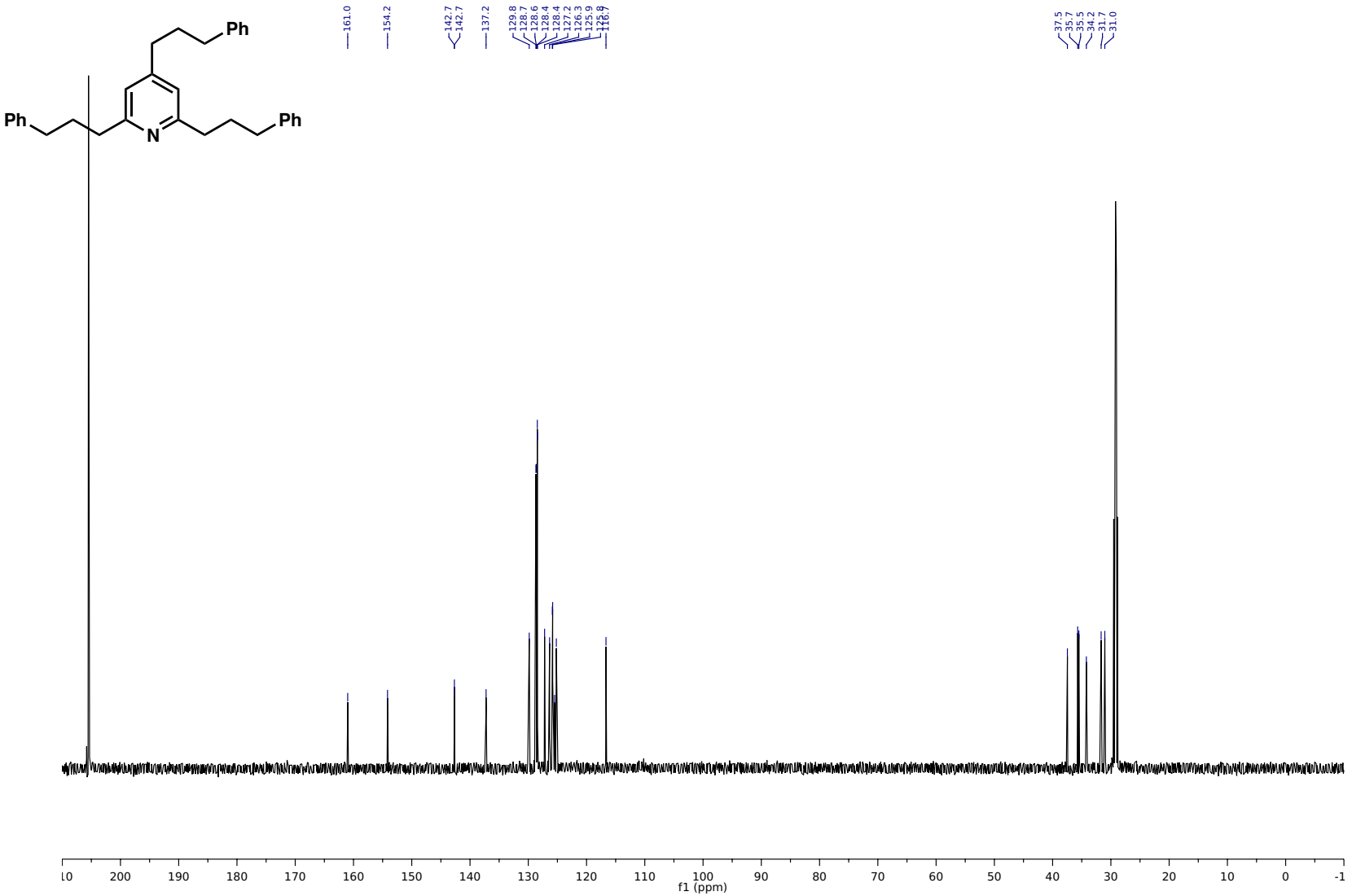
^{1}H NMR (400 MHz, $CDCl_3$) of 2-(3-phenylpropyl)pyridine (**5b**)



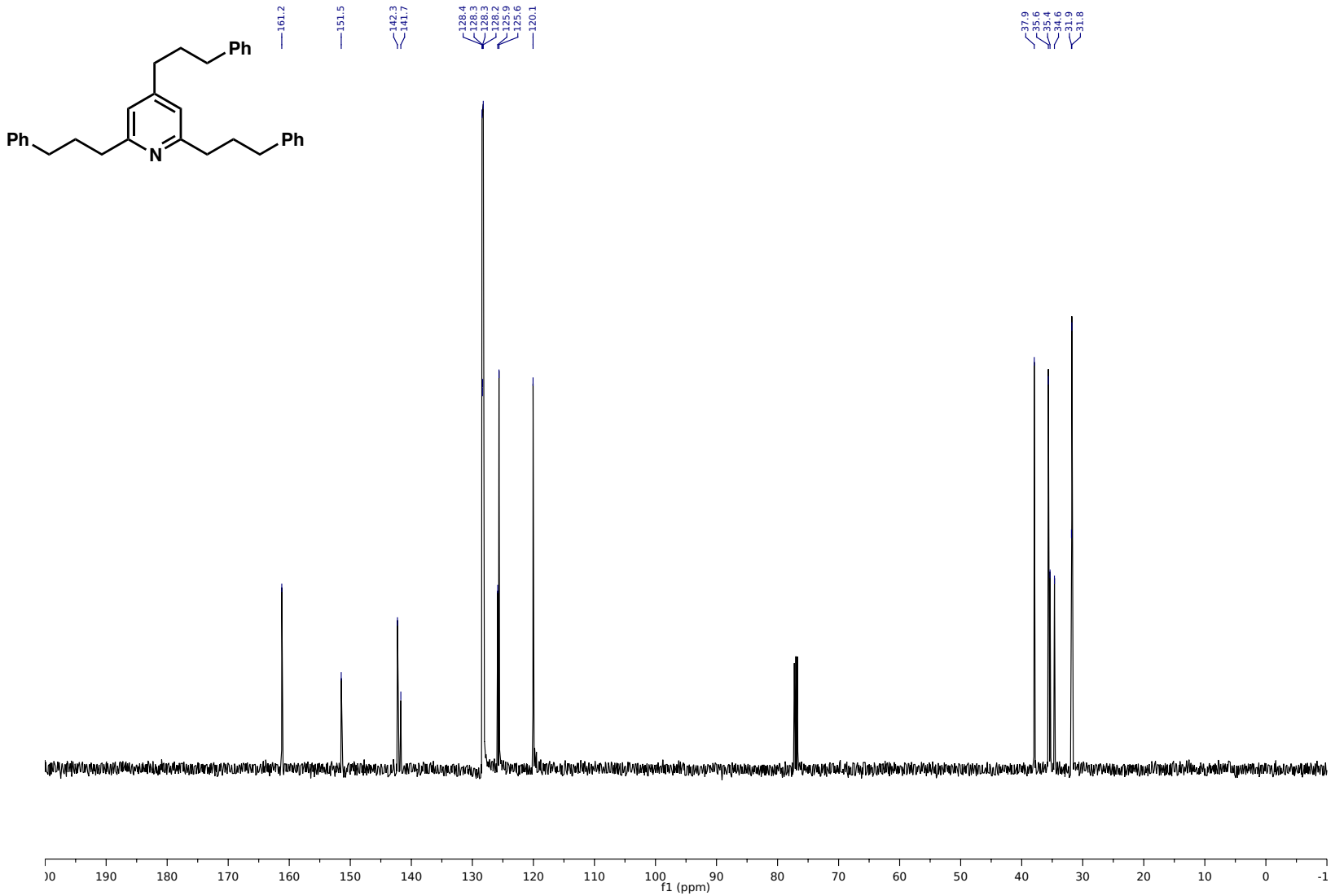
^{1}H NMR (400 MHz, $CDCl_3$) of 2,6-bis(3-phenylpropyl)pyridine (**5c**)



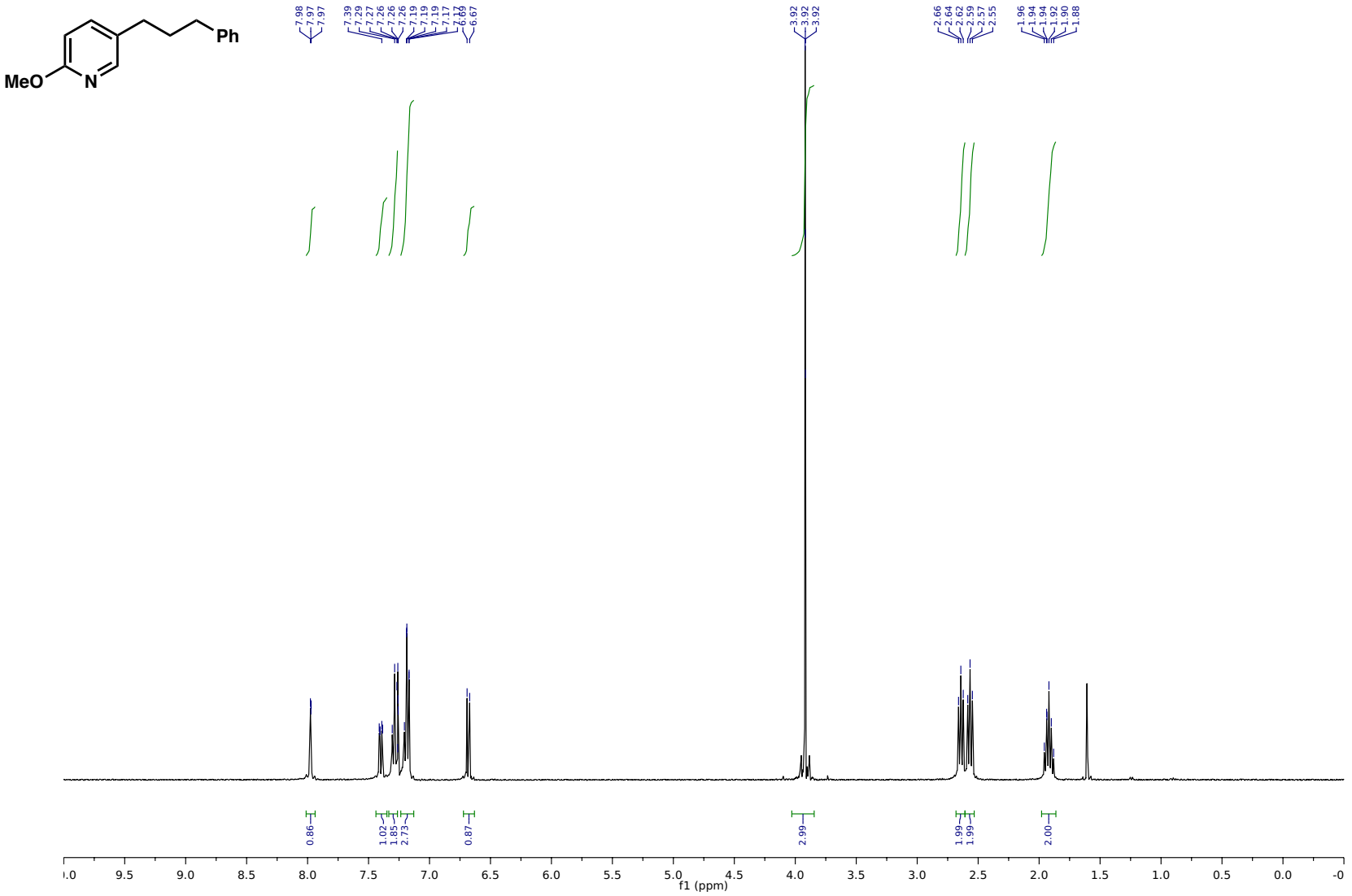
^{1}H NMR (400 MHz, $CDCl_3$) of 2,4,6-tris(3-phenylpropyl)pyridine (**5d**)



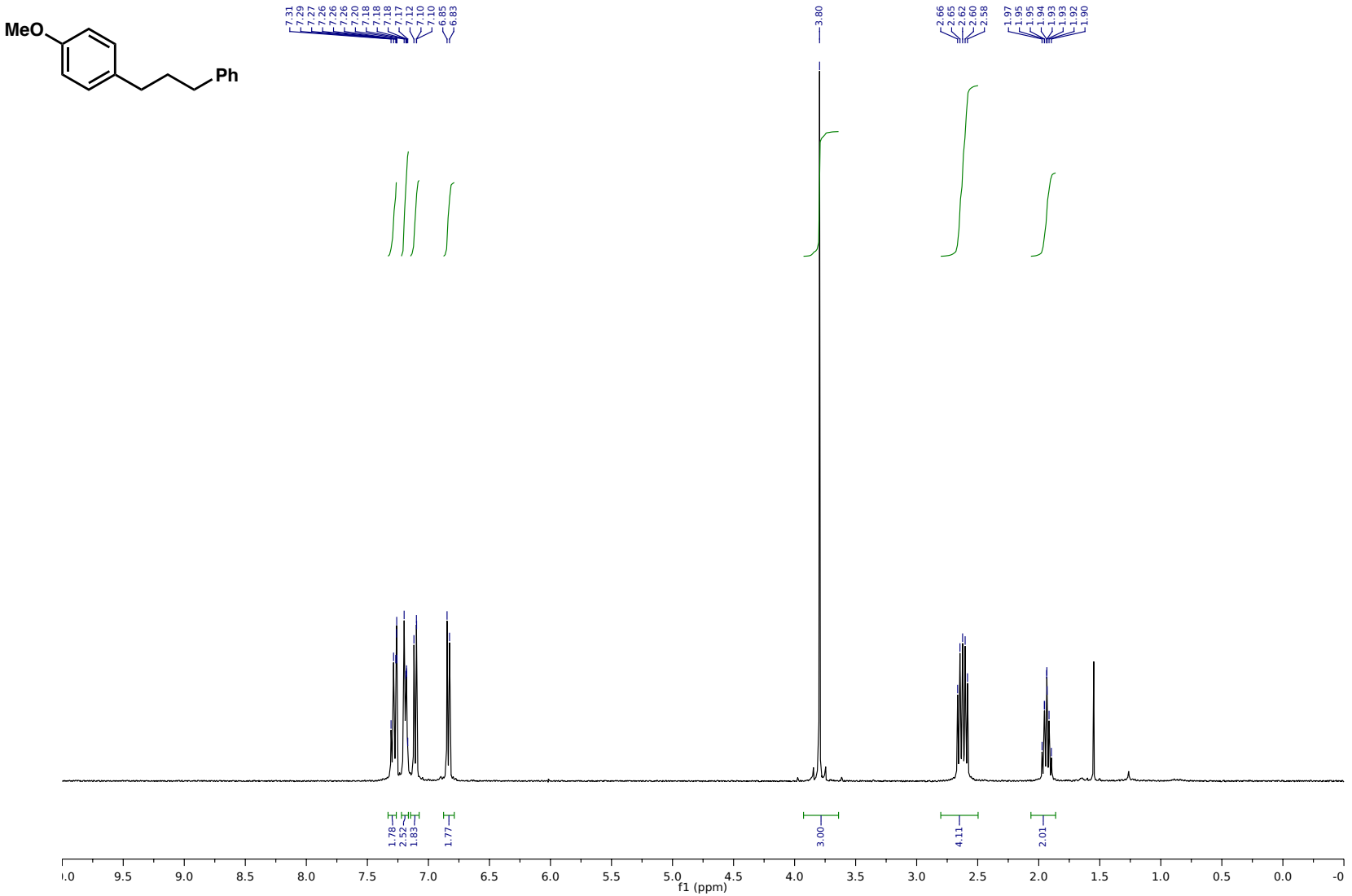
^{13}C NMR (125 MHz, acetone-d_6) of 2,4,6-tris(3-phenylpropyl)pyridine (**5d**)



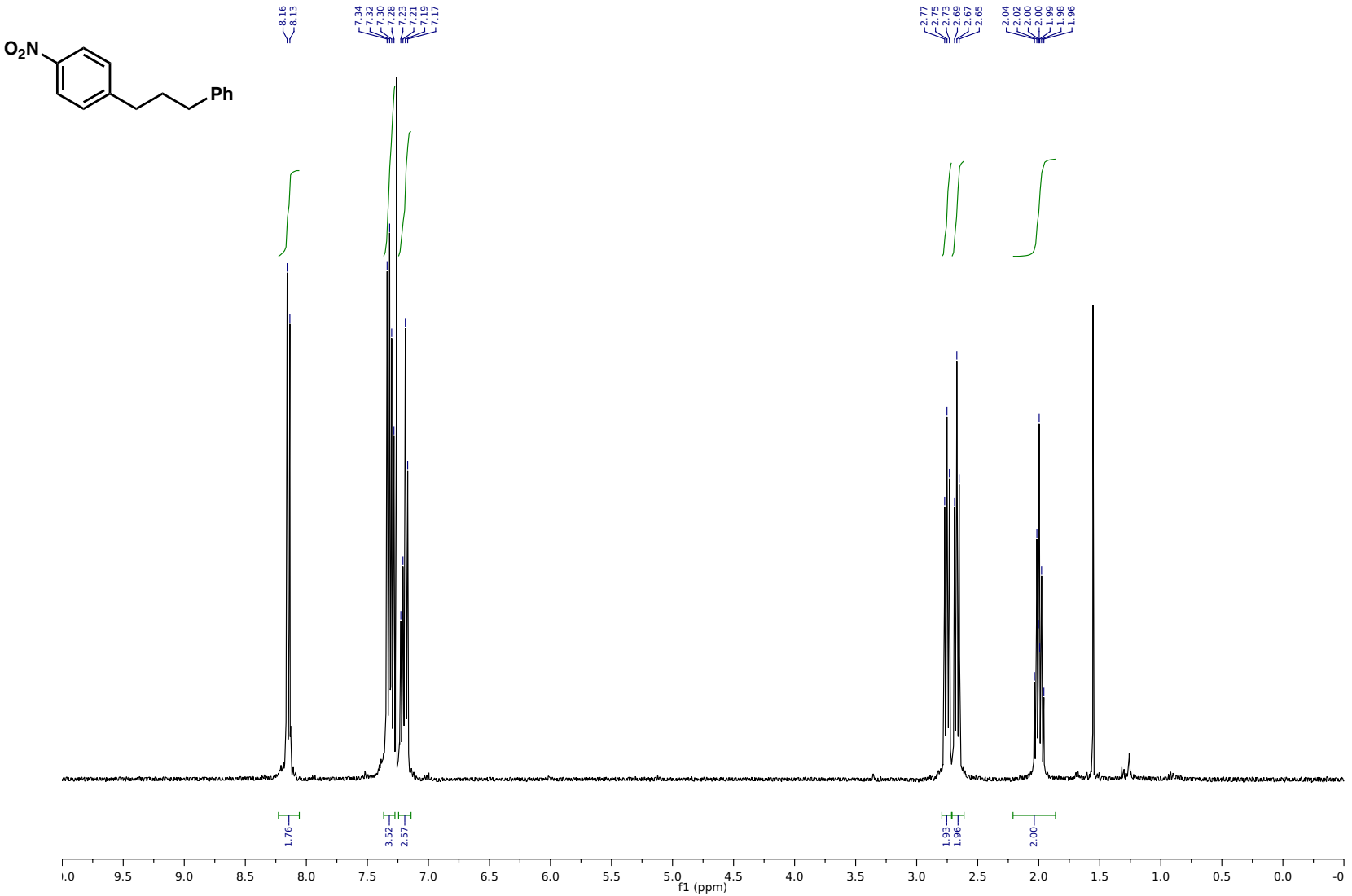
^{13}C NMR (125 MHz, $CDCl_3$) of 2,4,6-tris(3-phenylpropyl)pyridine (**5d**)



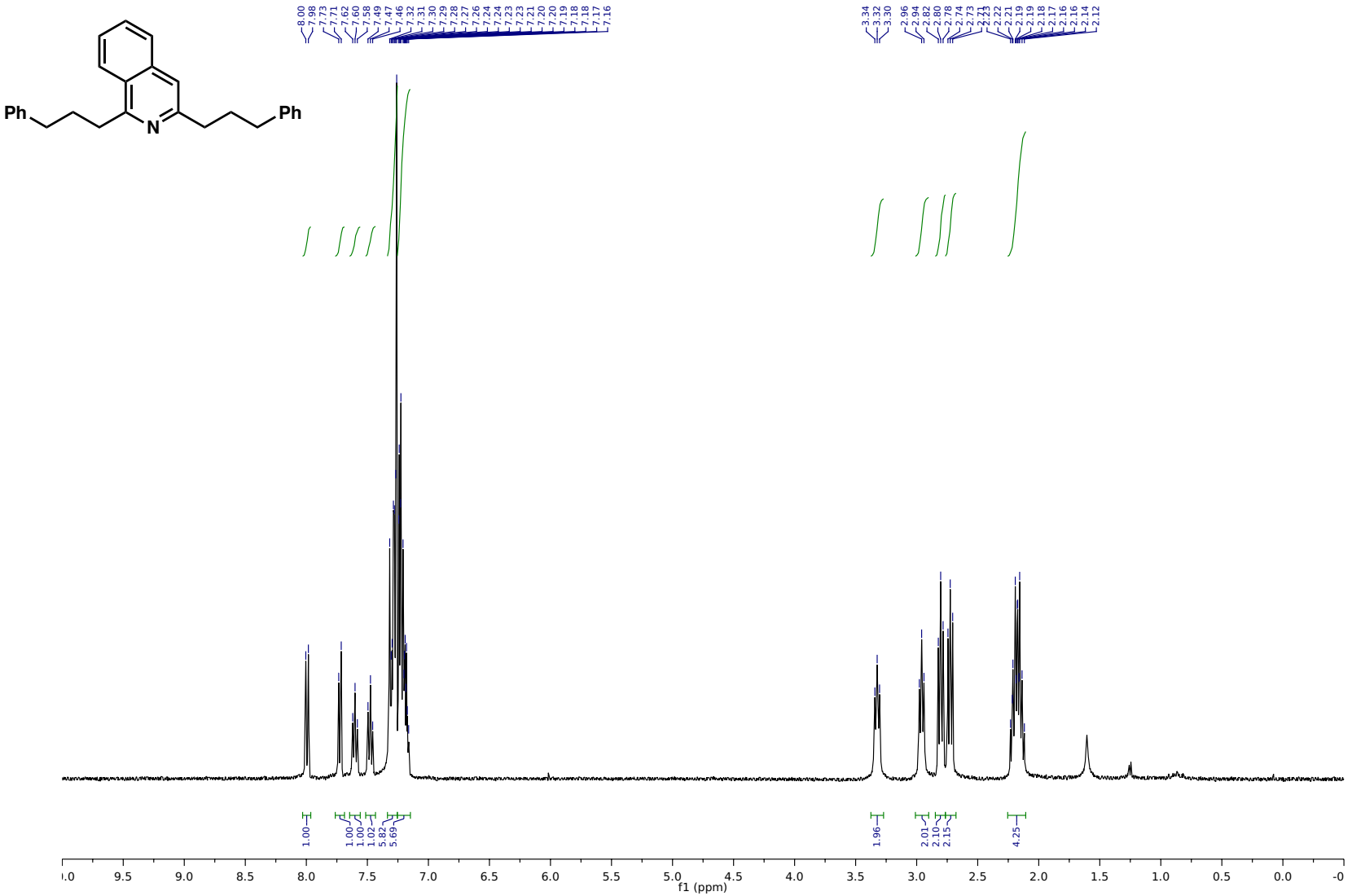
^{1}H NMR (400 MHz, $CDCl_3$) of 2-methoxy-5-(3-phenylpropyl)pyridine (**5e**)



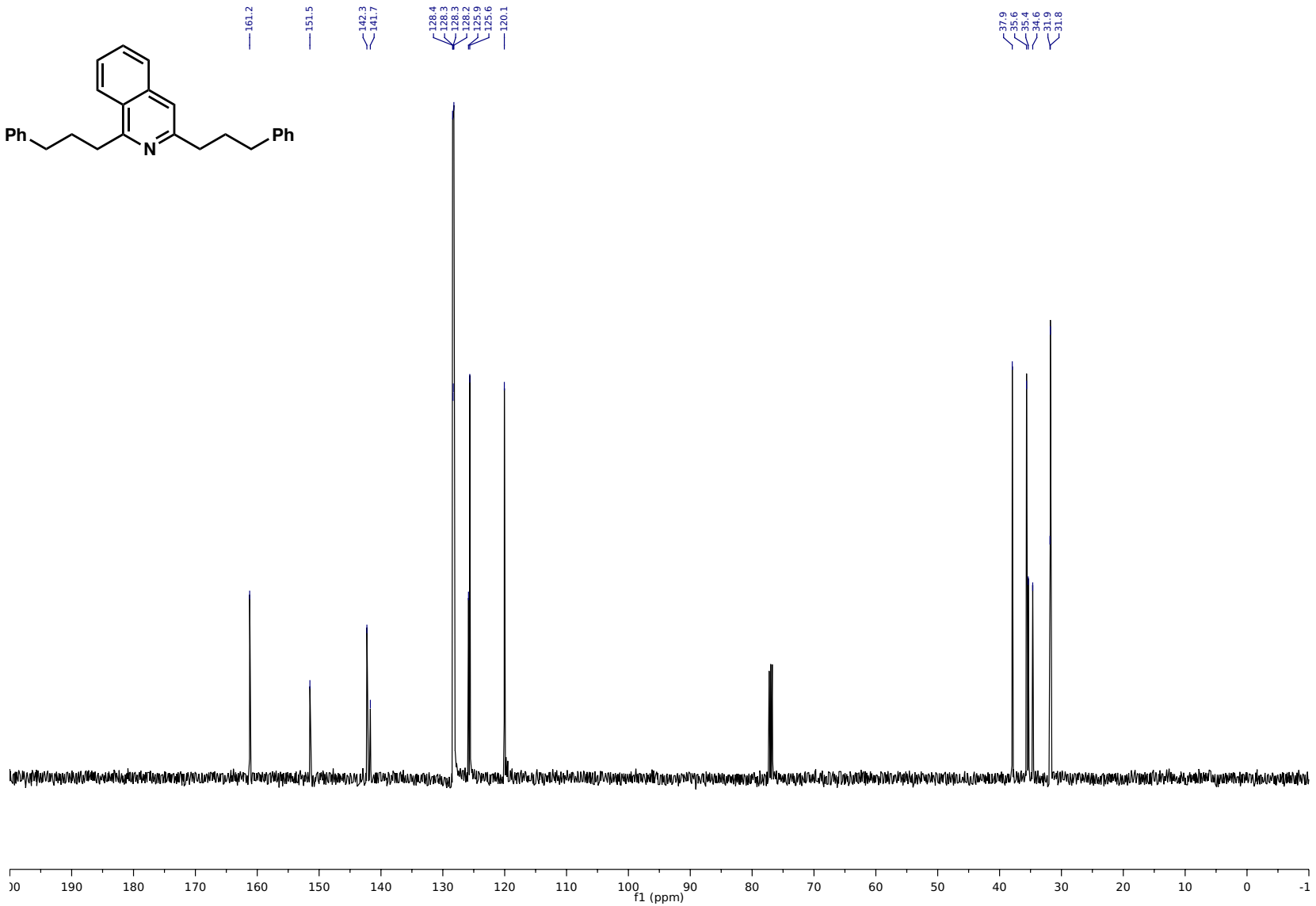
^{1}H NMR (400 MHz, $CDCl_3$) of 1-methoxy-4-(3-phenylpropyl)benzene (**5f**)



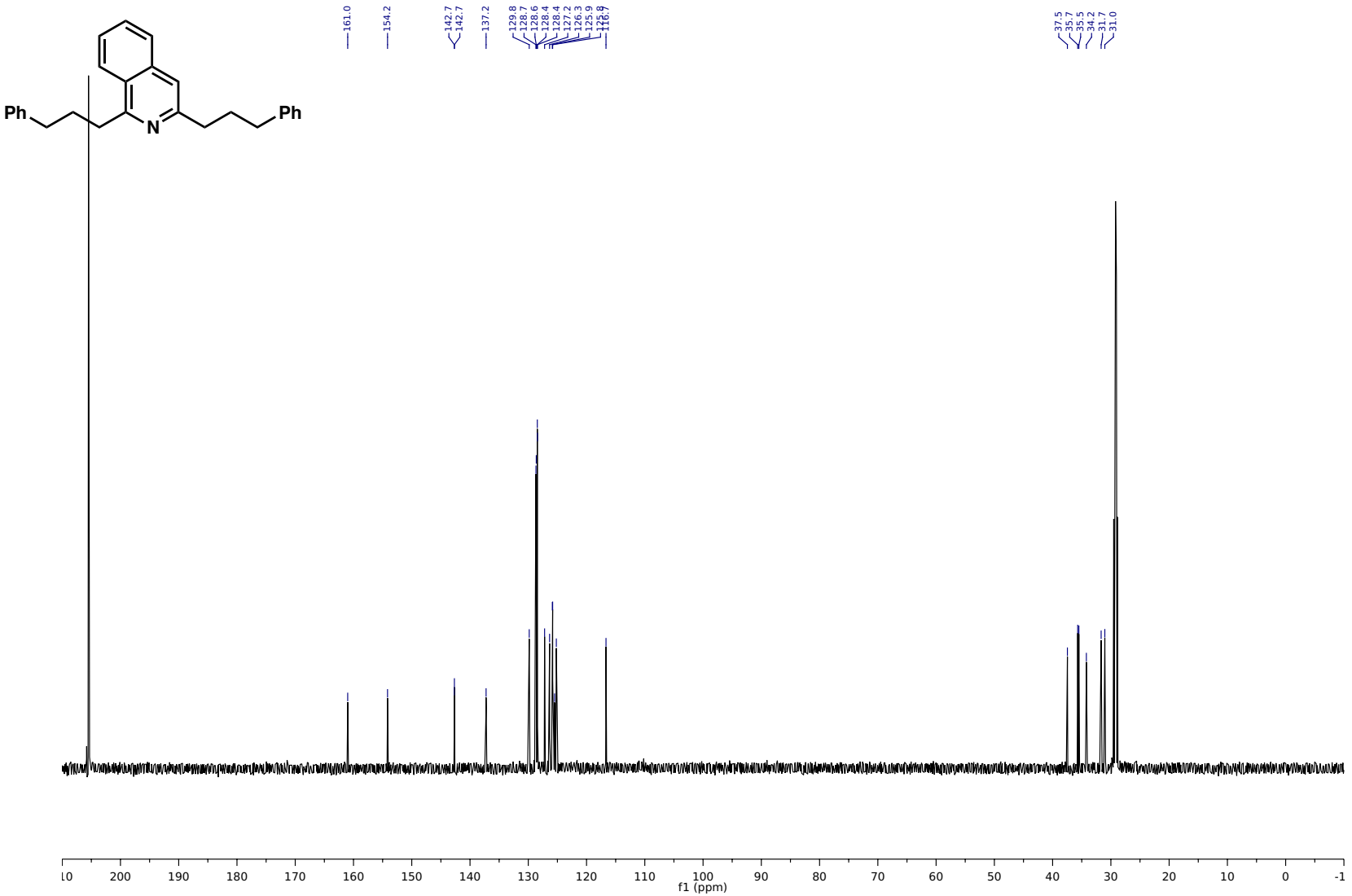
^{1}H NMR (400 MHz, $CDCl_3$) of 1-nitro-4-(3-phenylpropyl)benzene (**5g**)



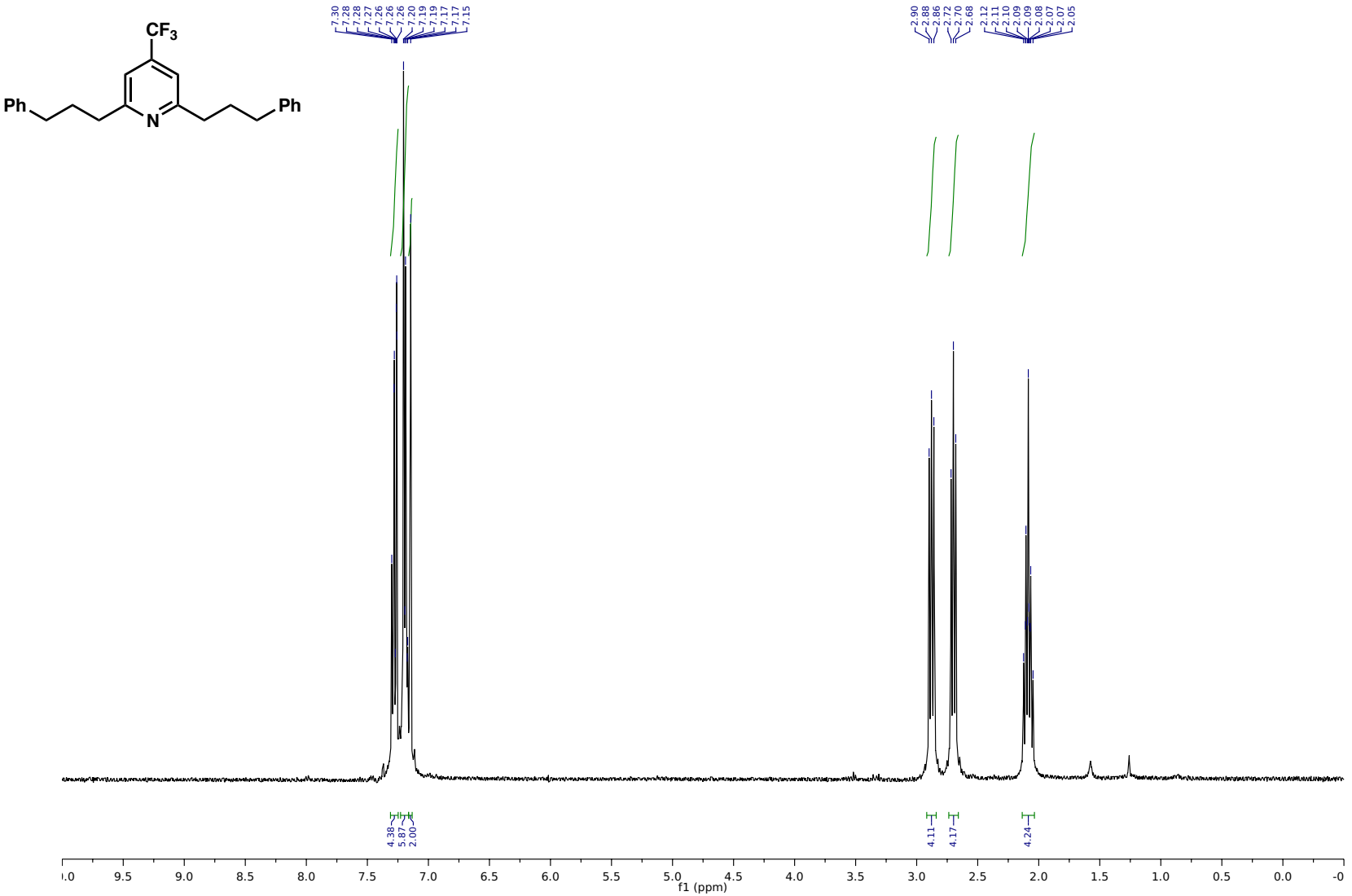
^{1}H NMR (400 MHz, $CDCl_3$) of 1,3-bis(3-phenylpropyl)isoquinoline (**5h**)



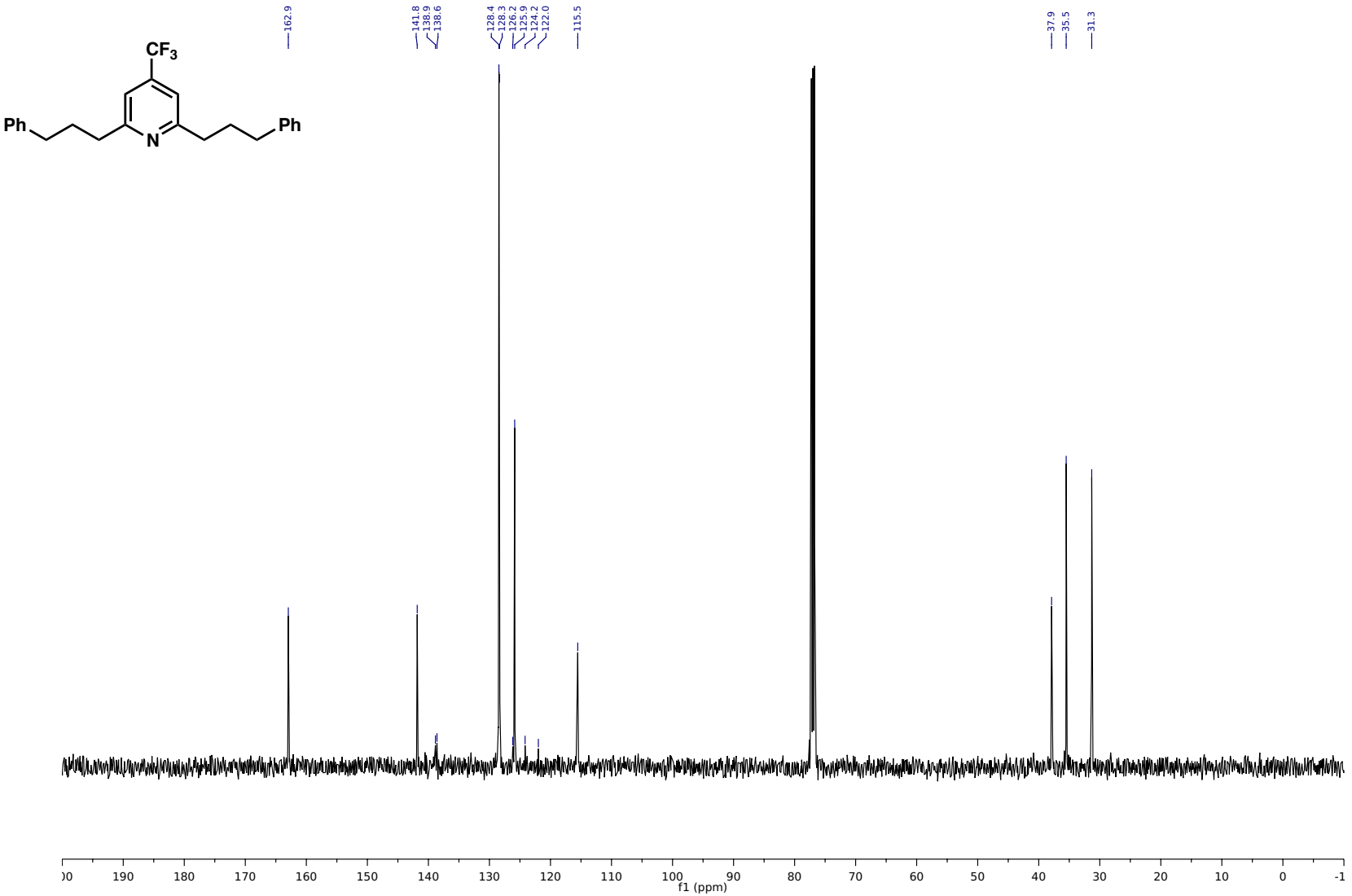
^{13}C NMR (125 MHz, $CDCl_3$) of 1,3-bis(3-phenylpropyl)isoquinoline (**5h**)



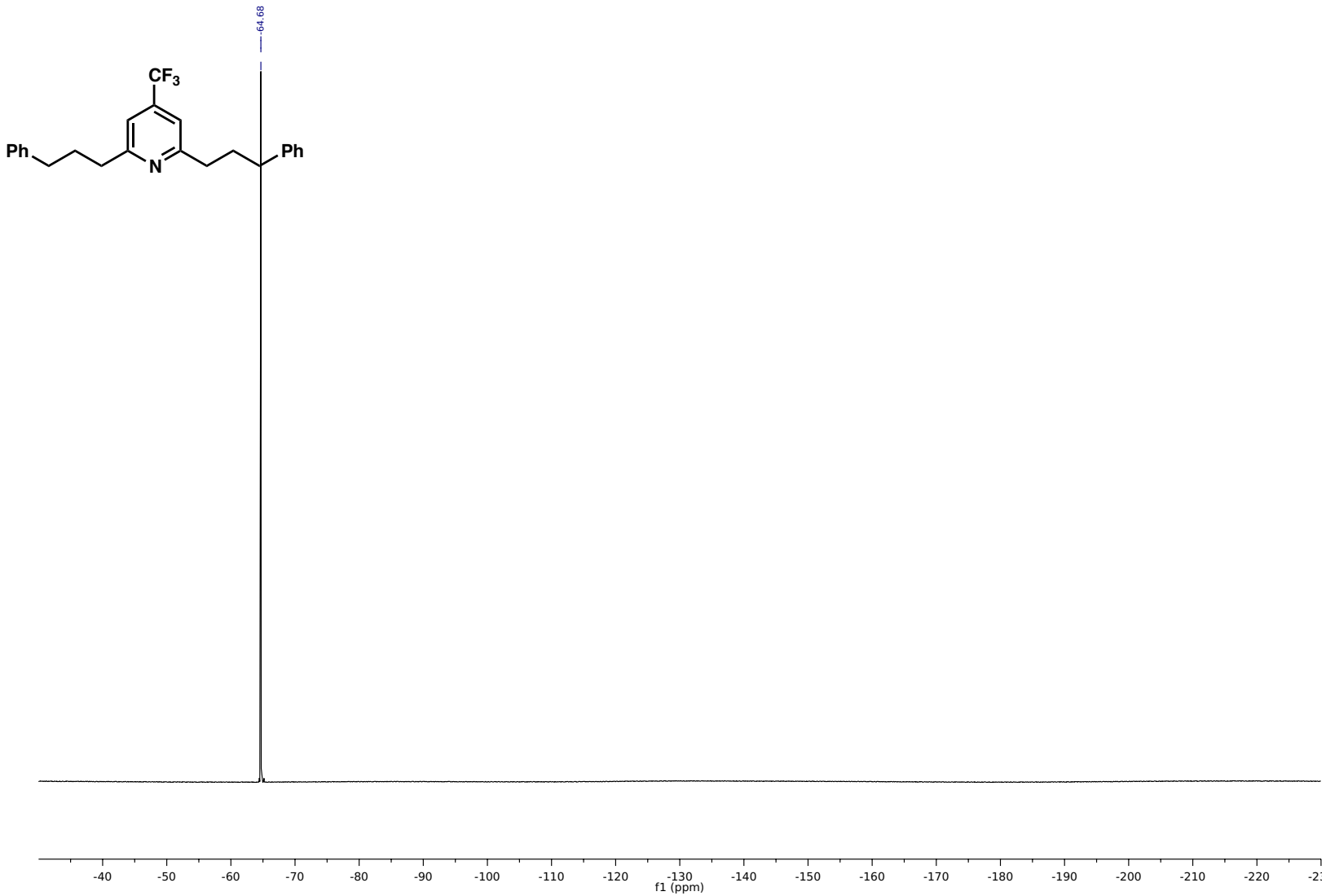
^{13}C NMR (125 MHz, acetone-d_6) of 1,3-bis(3-phenylpropyl)isoquinoline (**5h**)



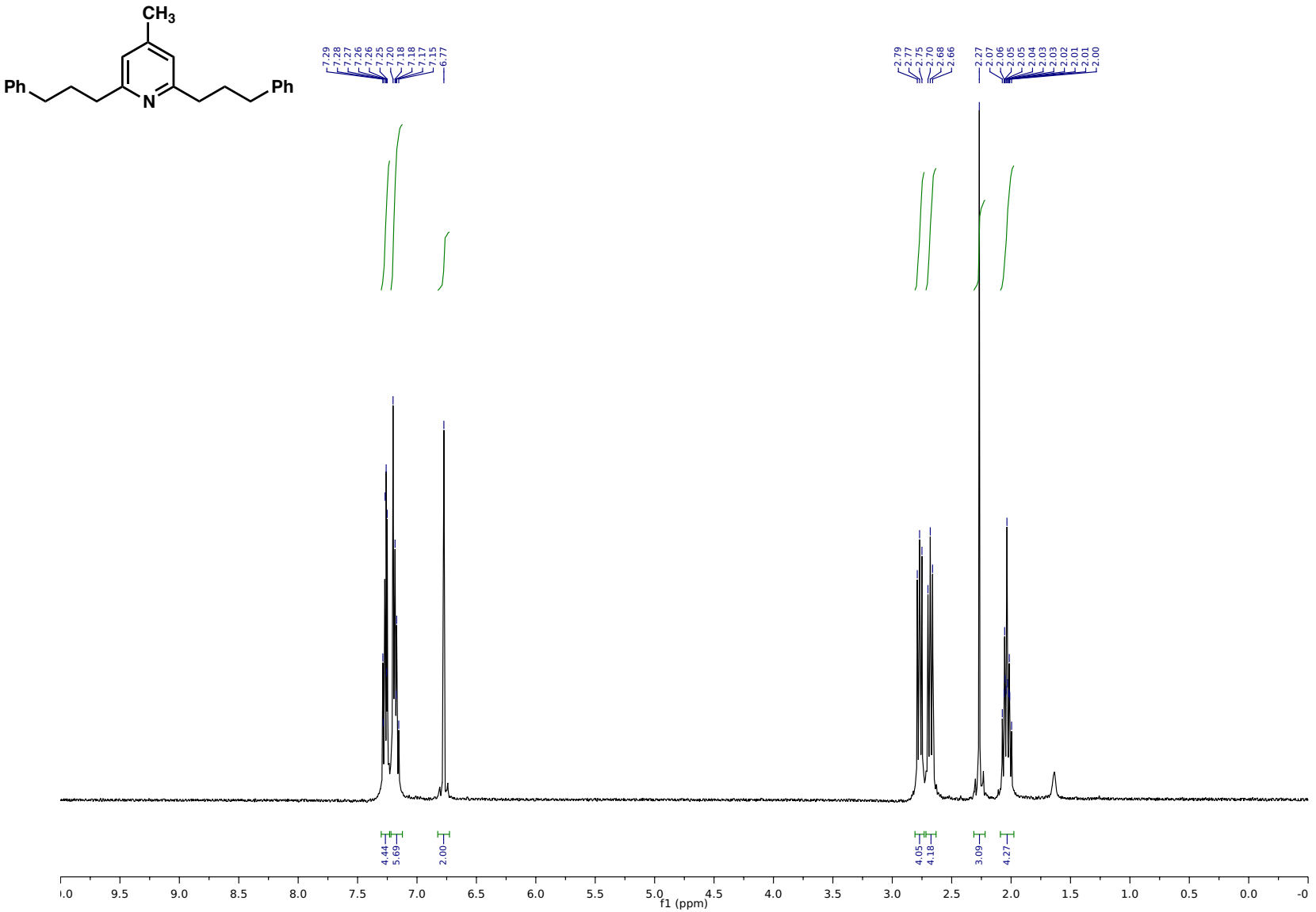
^{1}H NMR (400 MHz, $CDCl_3$) of 2,6-bis(3-phenylpropyl)-4-(trifluoromethyl)pyridine (**5i**)



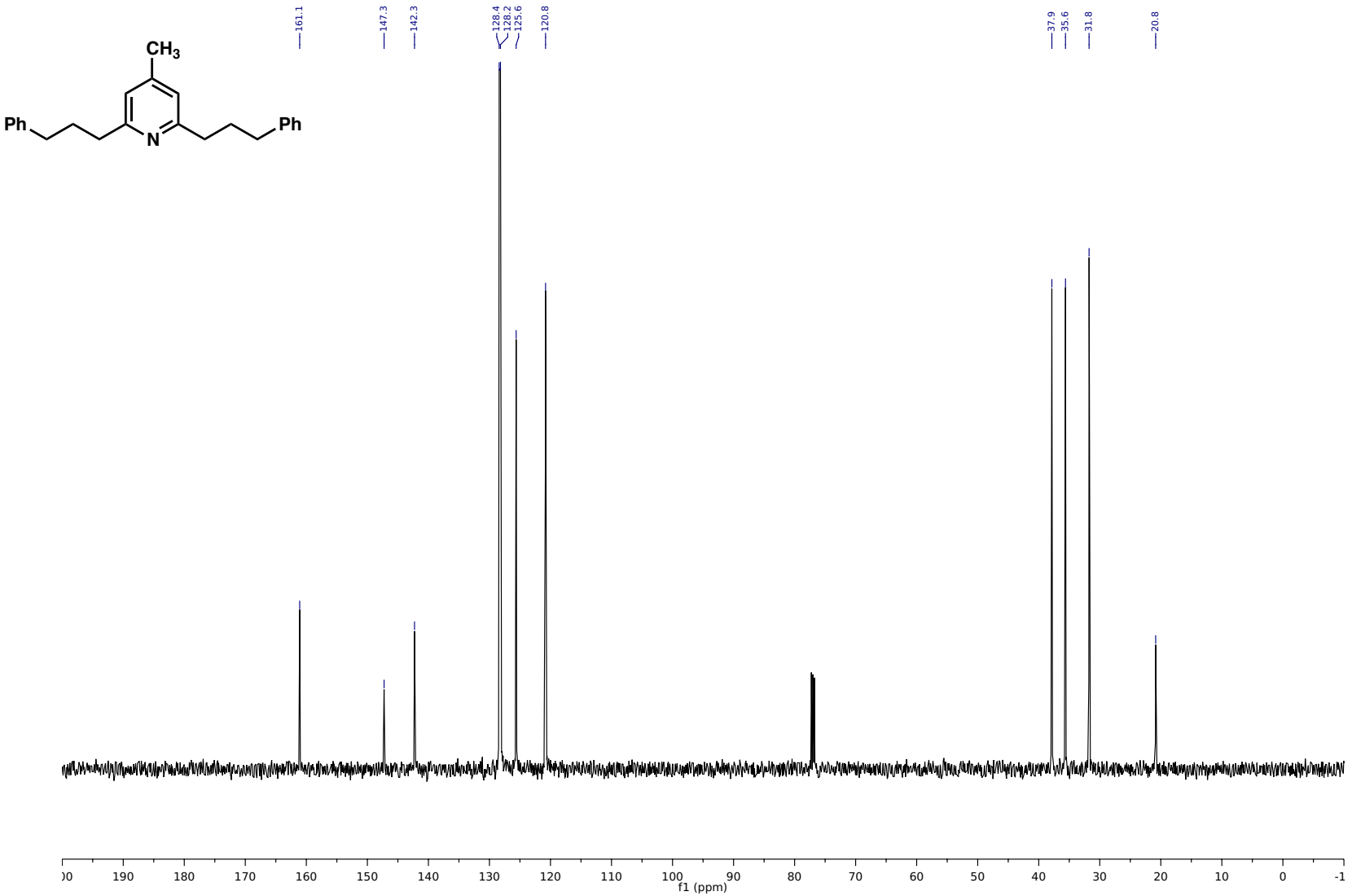
^{13}C NMR (125 MHz, $CDCl_3$) of 2,6-bis(3-phenylpropyl)-4-(trifluoromethyl)pyridine (**5i**)



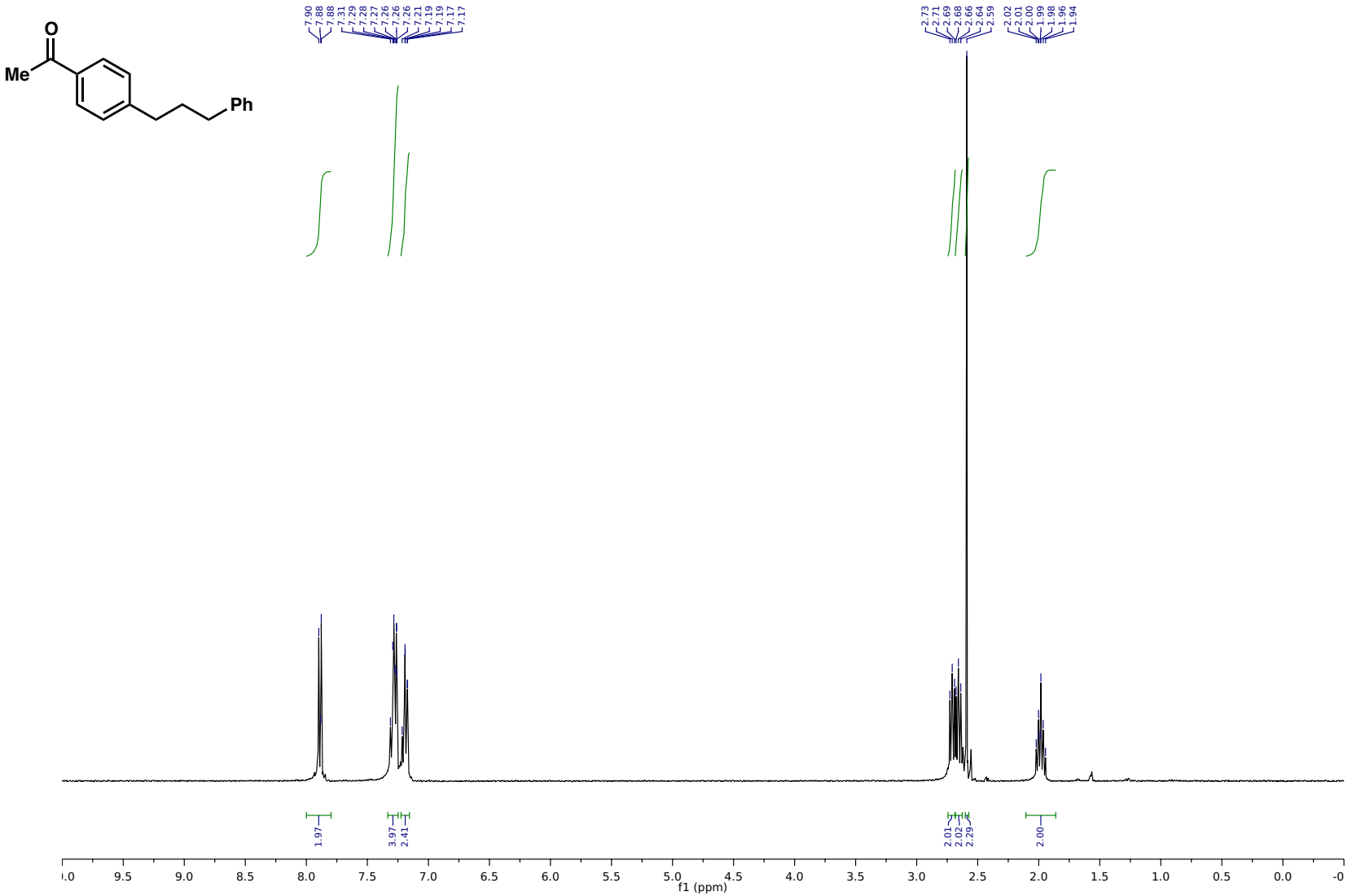
^{19}F NMR (376 MHz, $CDCl_3$) of 2,6-bis(3-phenylpropyl)-4-(trifluoromethyl)pyridine (**5i**)



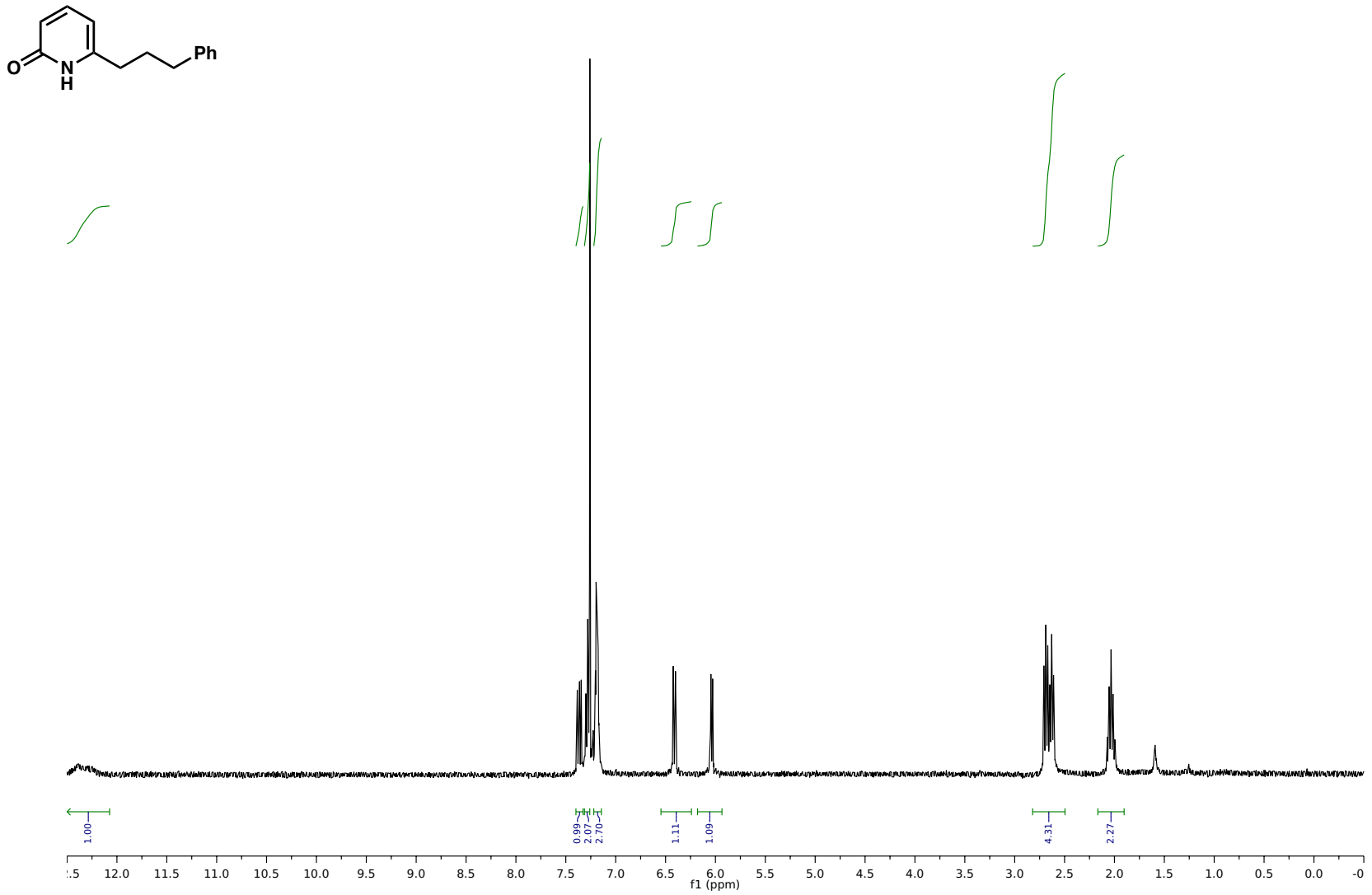
^{1}H NMR (400 MHz, $CDCl_3$) of 4-methyl-2,6-bis(3-phenylpropyl)pyridine (**5j**)



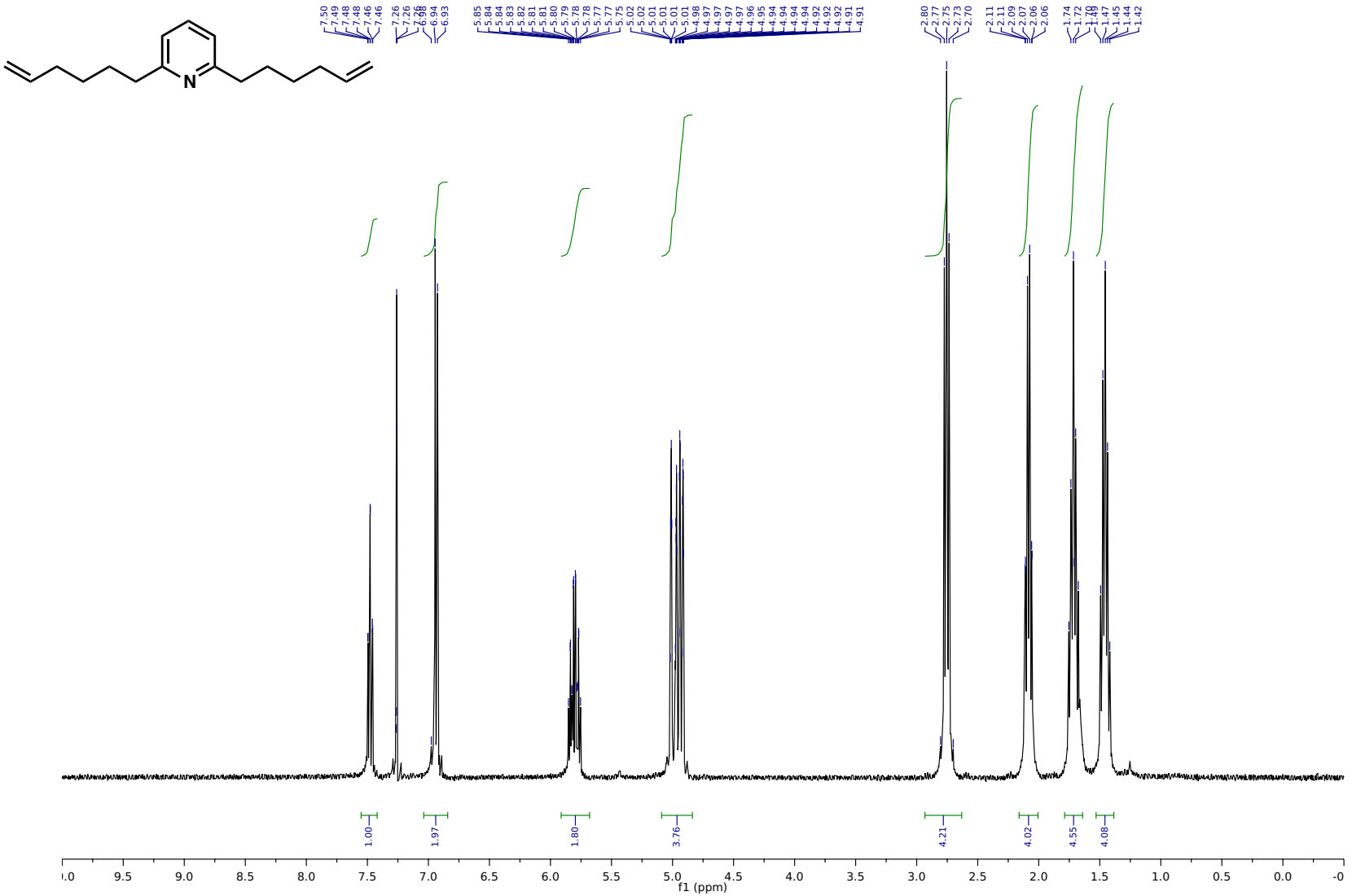
^{13}C NMR (125 MHz, $CDCl_3$) of 4-methyl-2,6-bis(3-phenylpropyl)pyridine (**5j**)



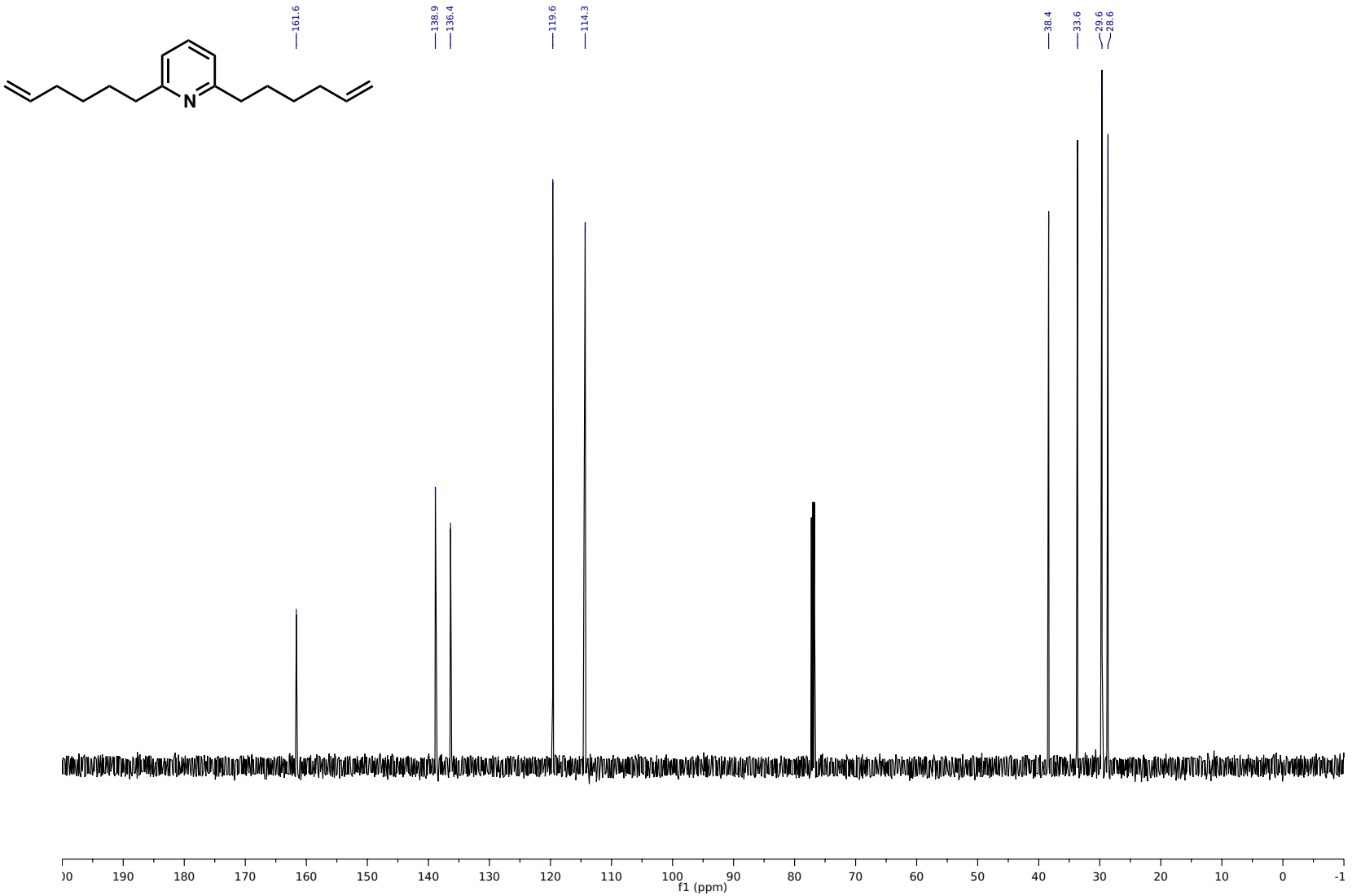
^{1}H NMR (400 MHz, $CDCl_3$) of 1-(4-(3-phenylpropyl)phenyl)ethanone (**5k**)



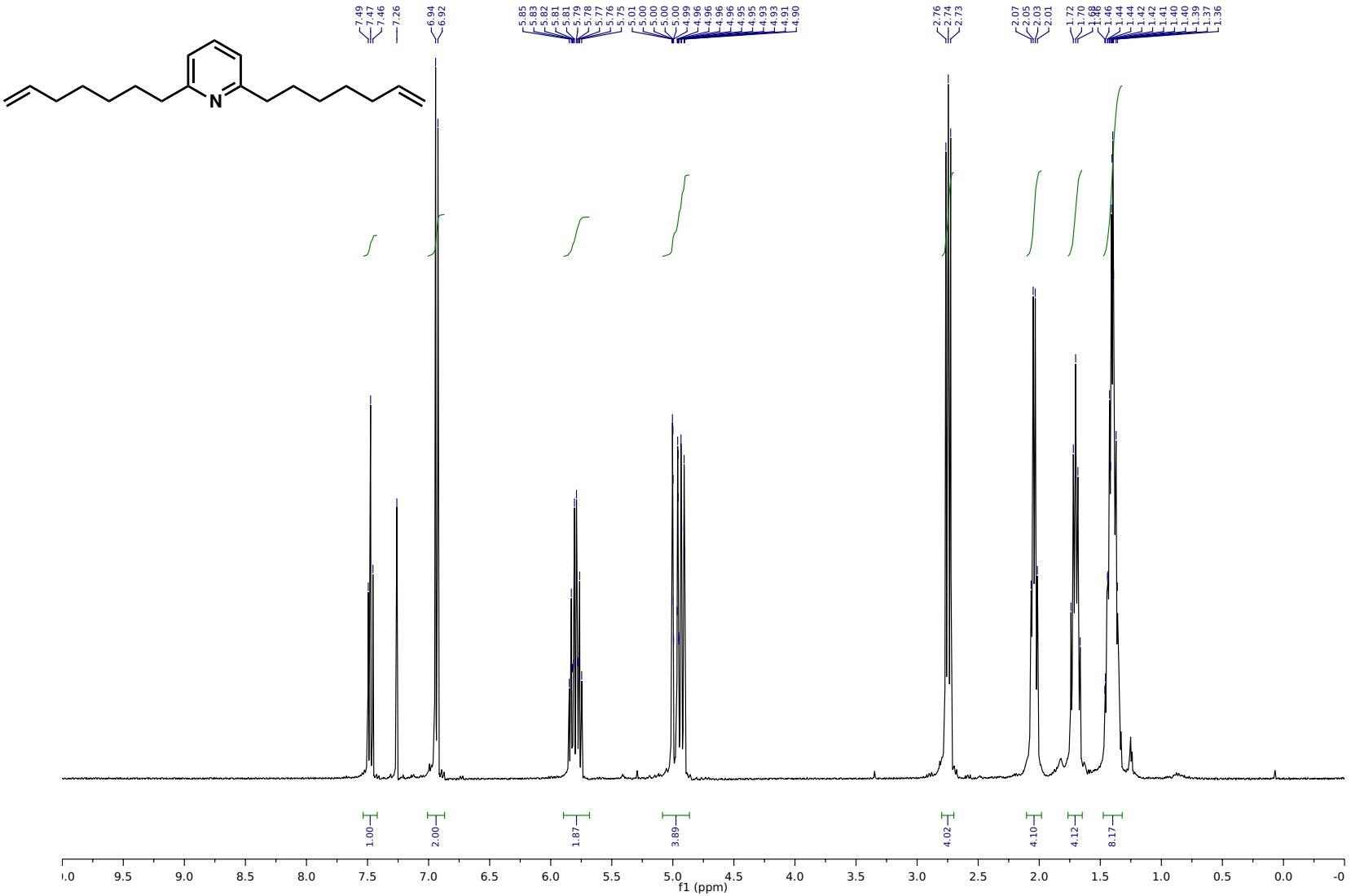
^{1}H NMR (400 MHz, $CDCl_3$) of 6-(3-phenylpropyl)pyridin-2(1*H*)-one (**5l**)



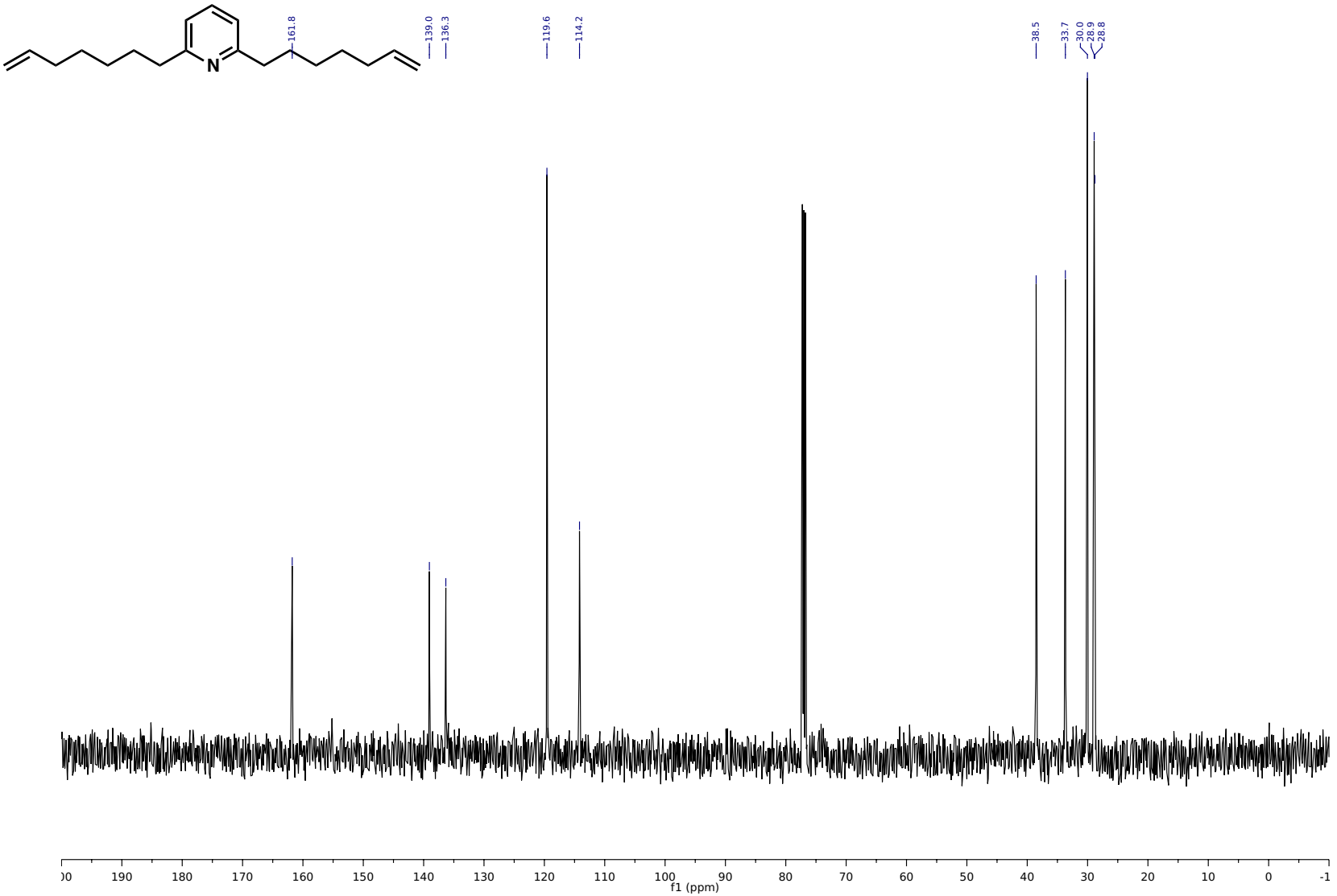
^{1}H NMR (400 MHz, $CDCl_3$) of 2,6-di(hex-5-en-1-yl)pyridine (**5m**)



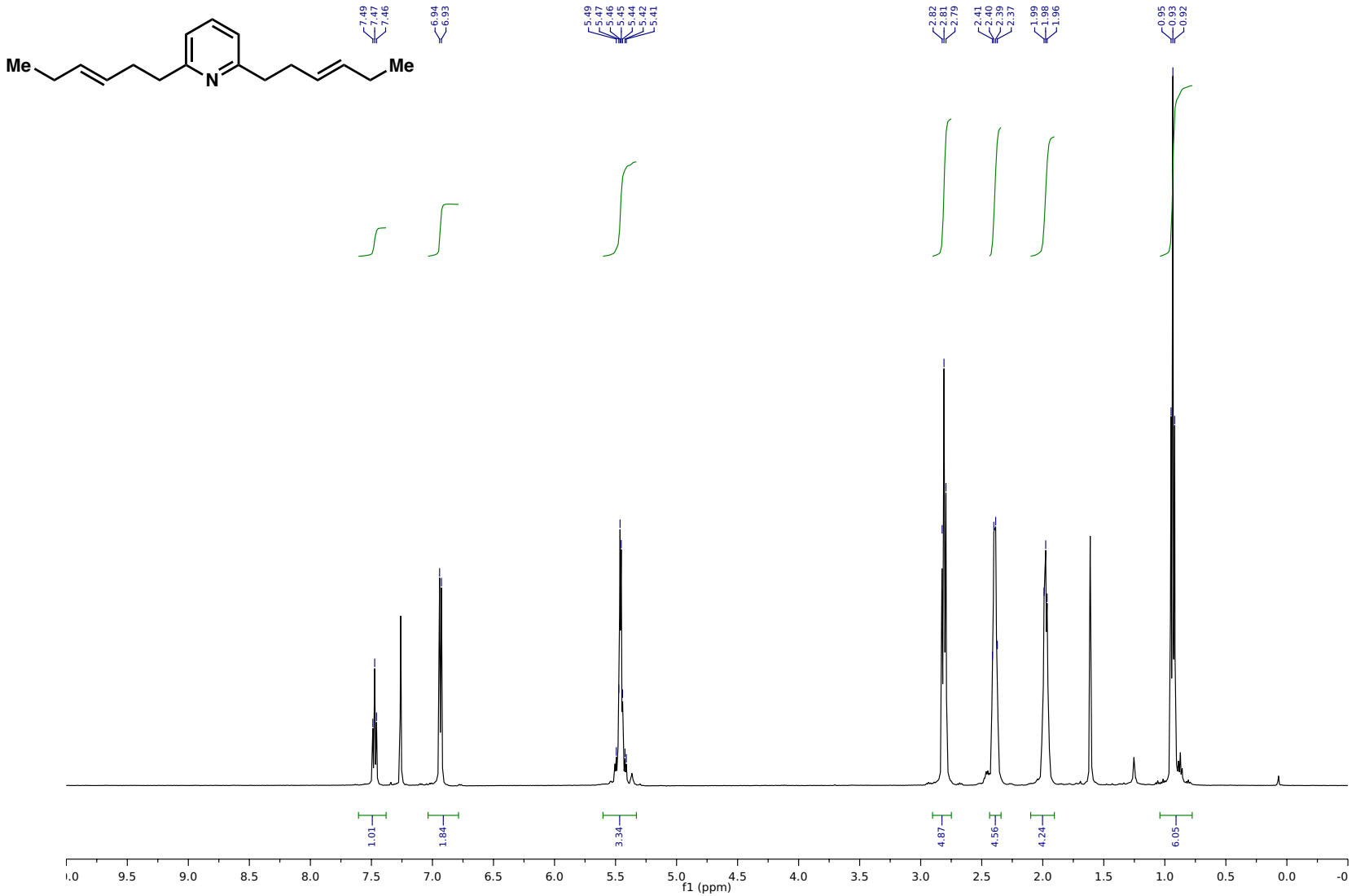
^{13}C NMR (125 MHz, $CDCl_3$) of 2,6-di(hex-5-en-1-yl)pyridine (**5m**)



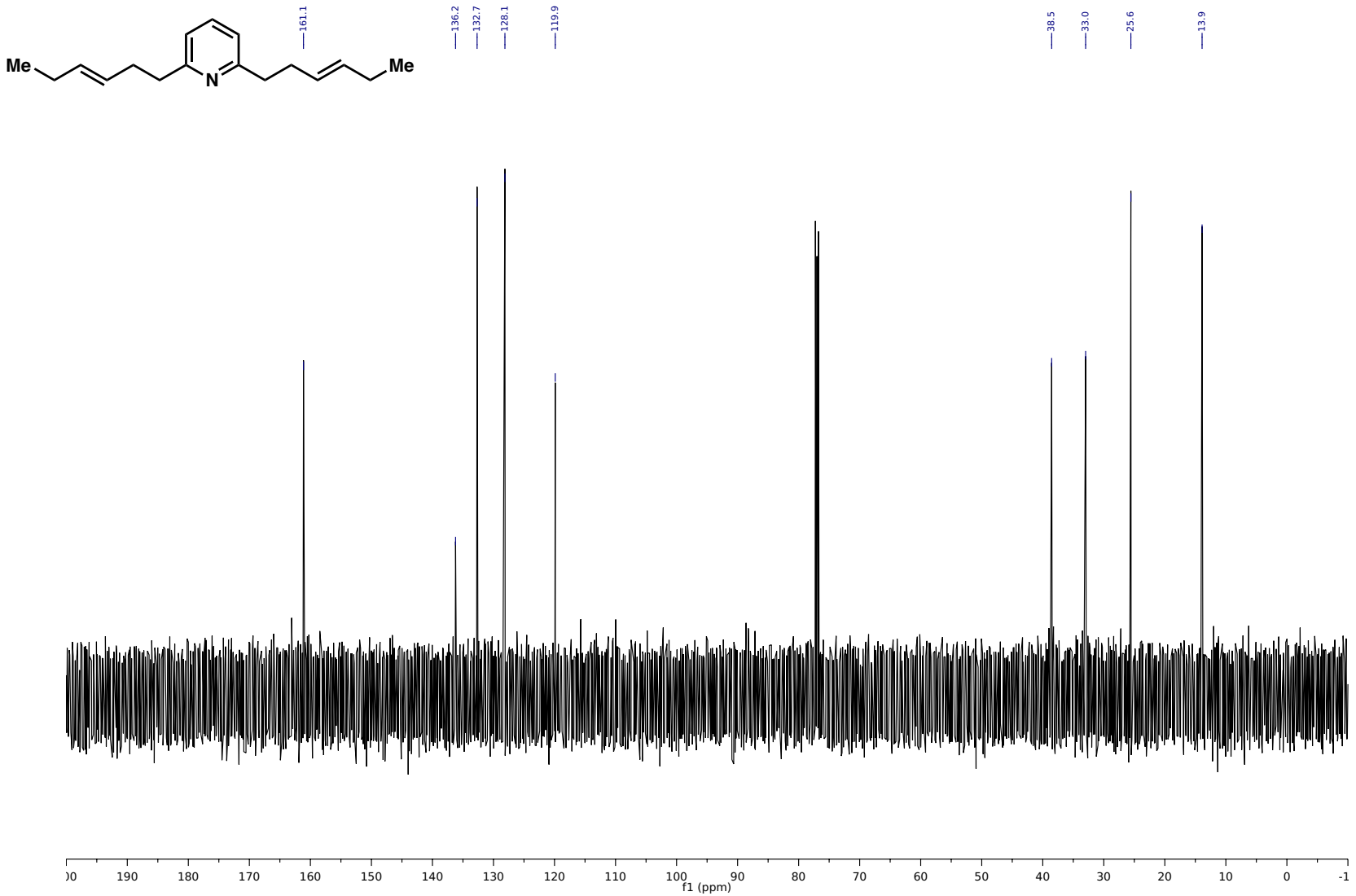
^{1}H NMR (400 MHz, $CDCl_3$) of 2,6-di(hept-6-en-1-yl)pyridine (**5n**)



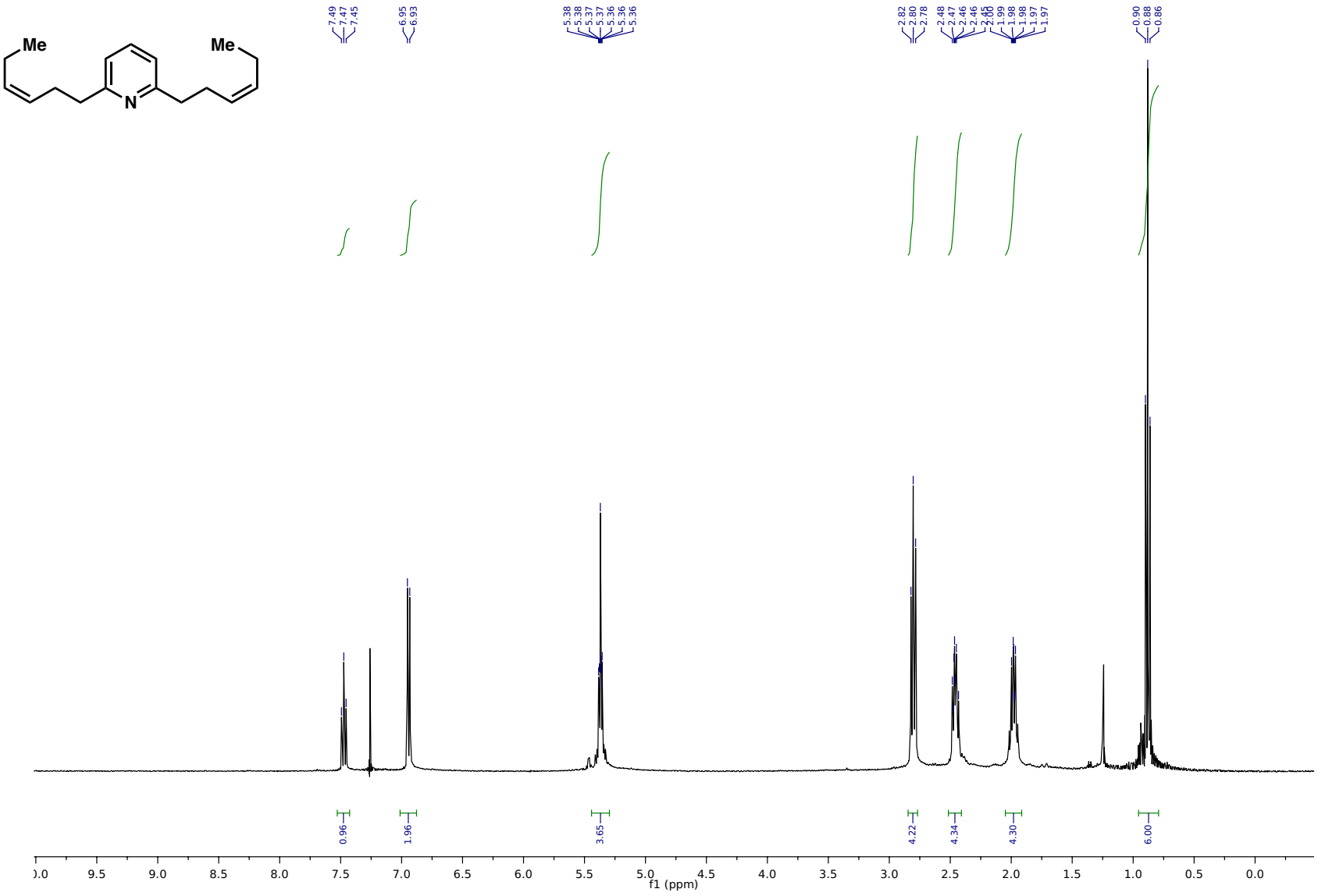
^{13}C NMR (125 MHz, $CDCl_3$) of 2,6-di(hept-6-en-1-yl)pyridine (**5n**)

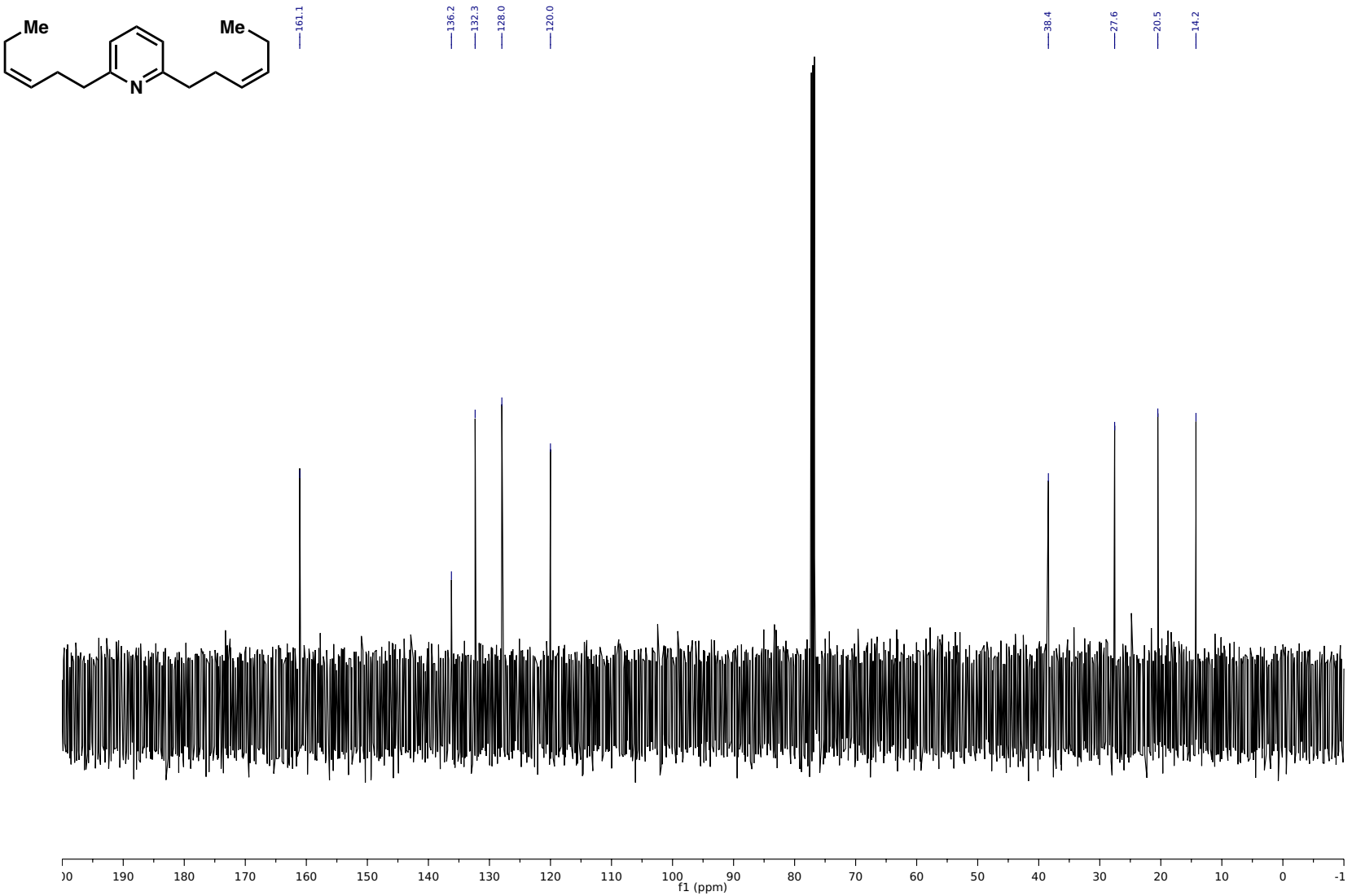


^{1}H NMR (500 MHz, $CDCl_3$) of 2,6-di((*E*)-hex-3-en-1-yl)pyridine (**5o**)

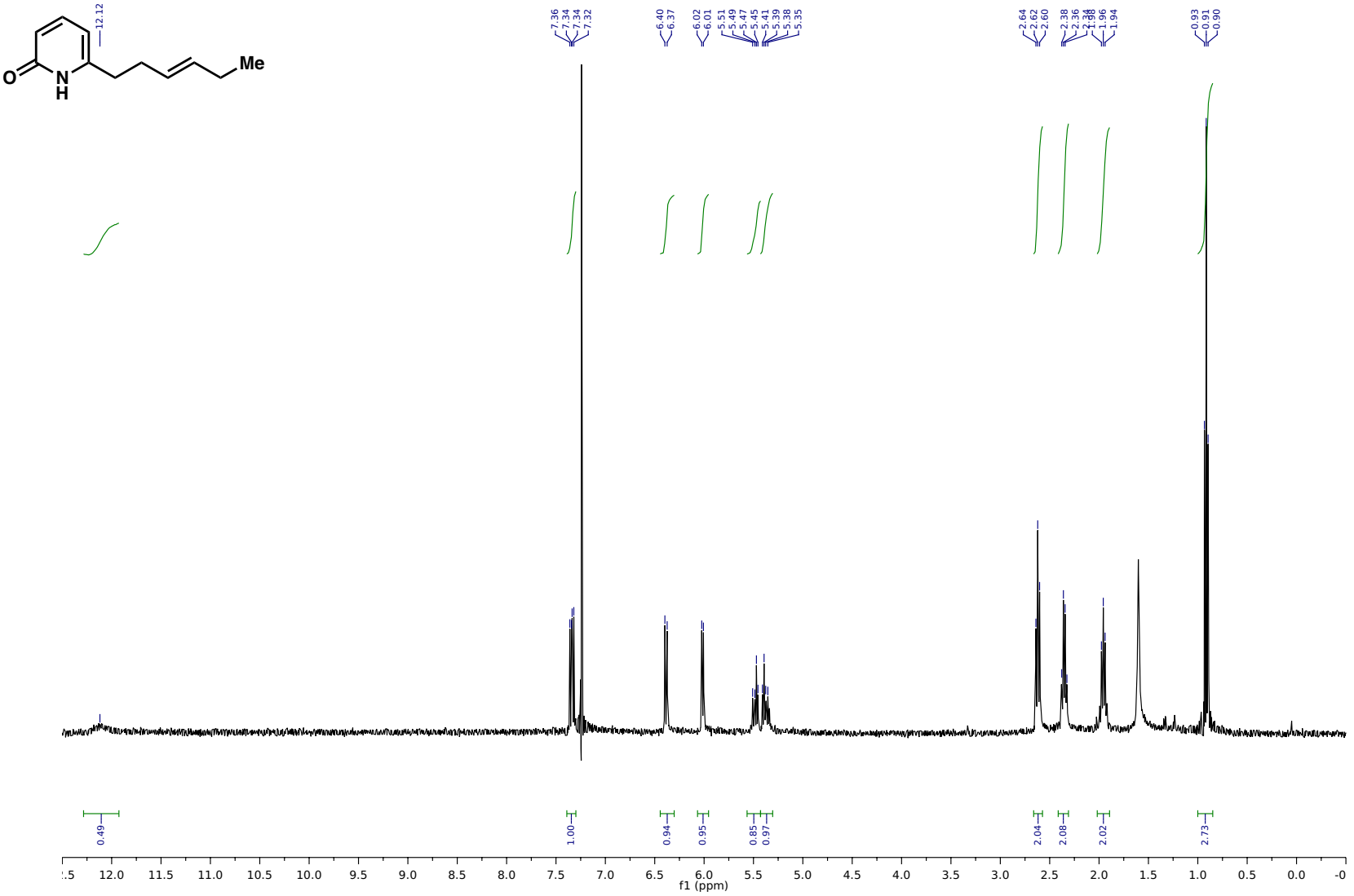


^{13}C NMR (125 MHz, $CDCl_3$) of 2,6-di((*E*)-hex-3-en-1-yl)pyridine (**5o**)

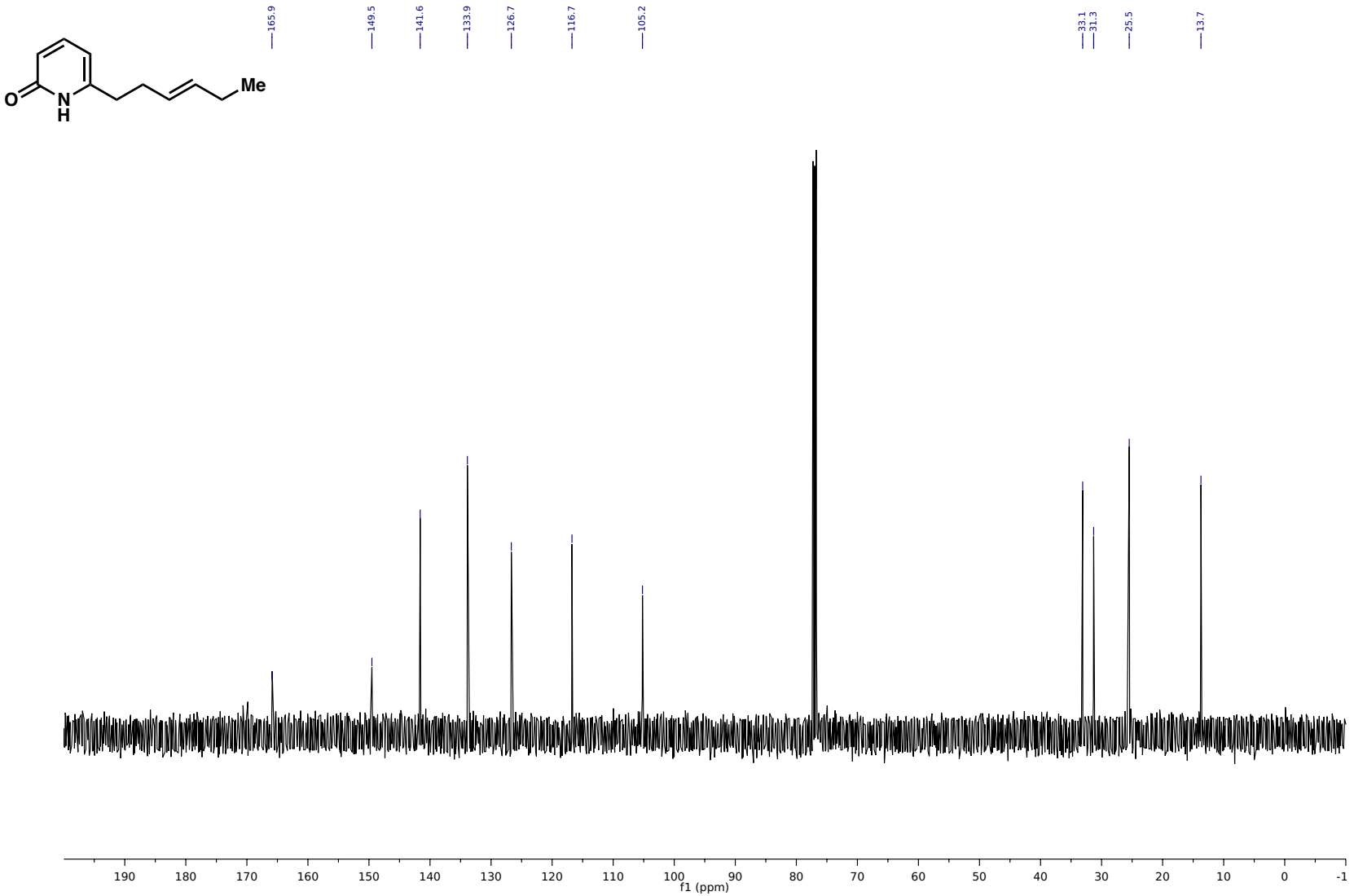

Me
Me
N
7.49
7.47
7.45
6.95
6.93
5.38
5.38
5.37
5.37
5.36
5.36
5.36
2.82
2.80
2.78
2.48
2.47
2.46
2.46
2.45
2.00
1.99
1.98
1.98
1.97
1.97
0.90
0.88
0.86
0.96
1.96
3.65
4.22
4.34
4.30
6.00
f1 (ppm)



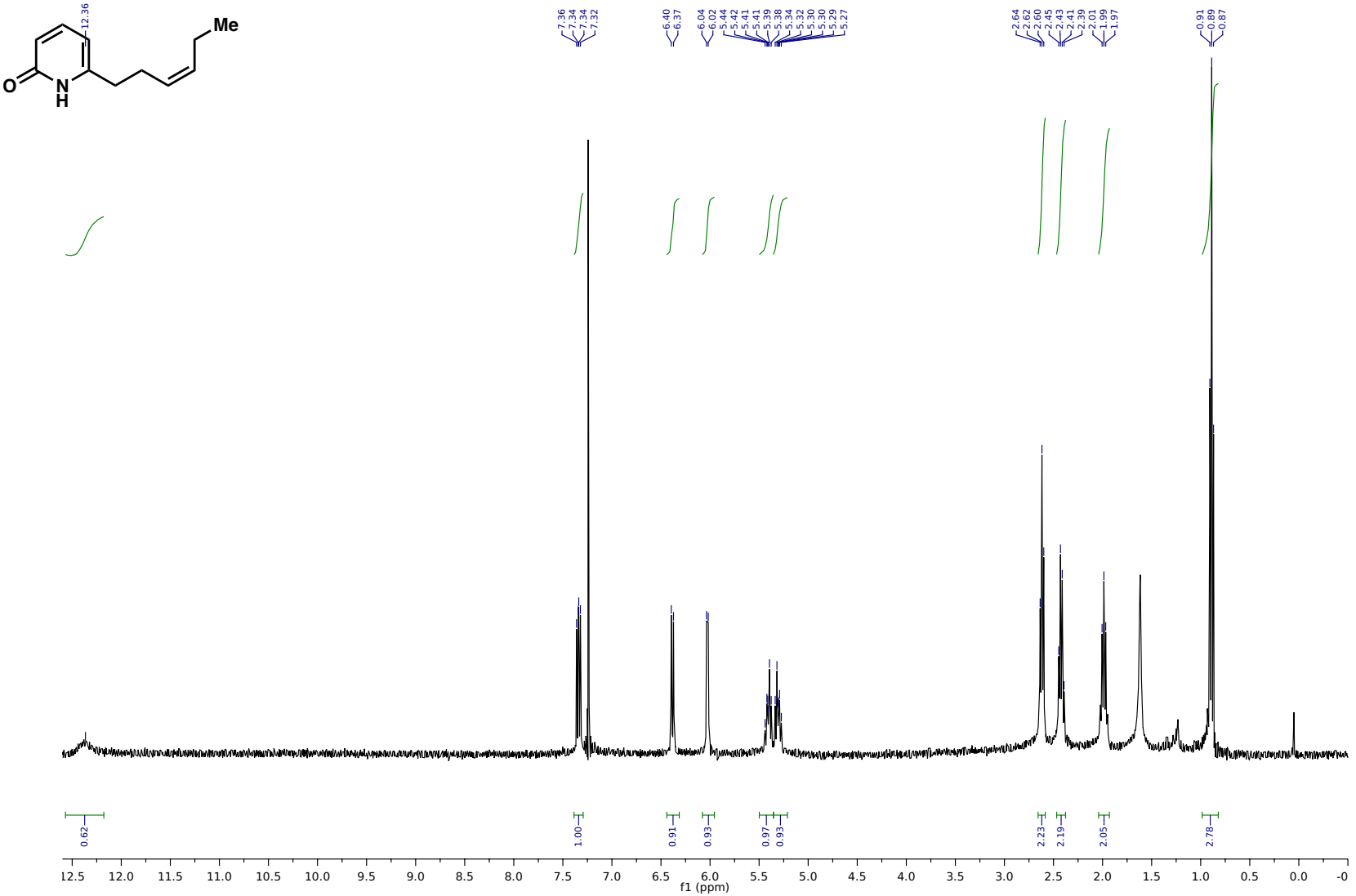
^{13}C NMR (125 MHz, $CDCl_3$) of 2,6-di((*Z*)-hex-3-en-1-yl)pyridine (**5q**)



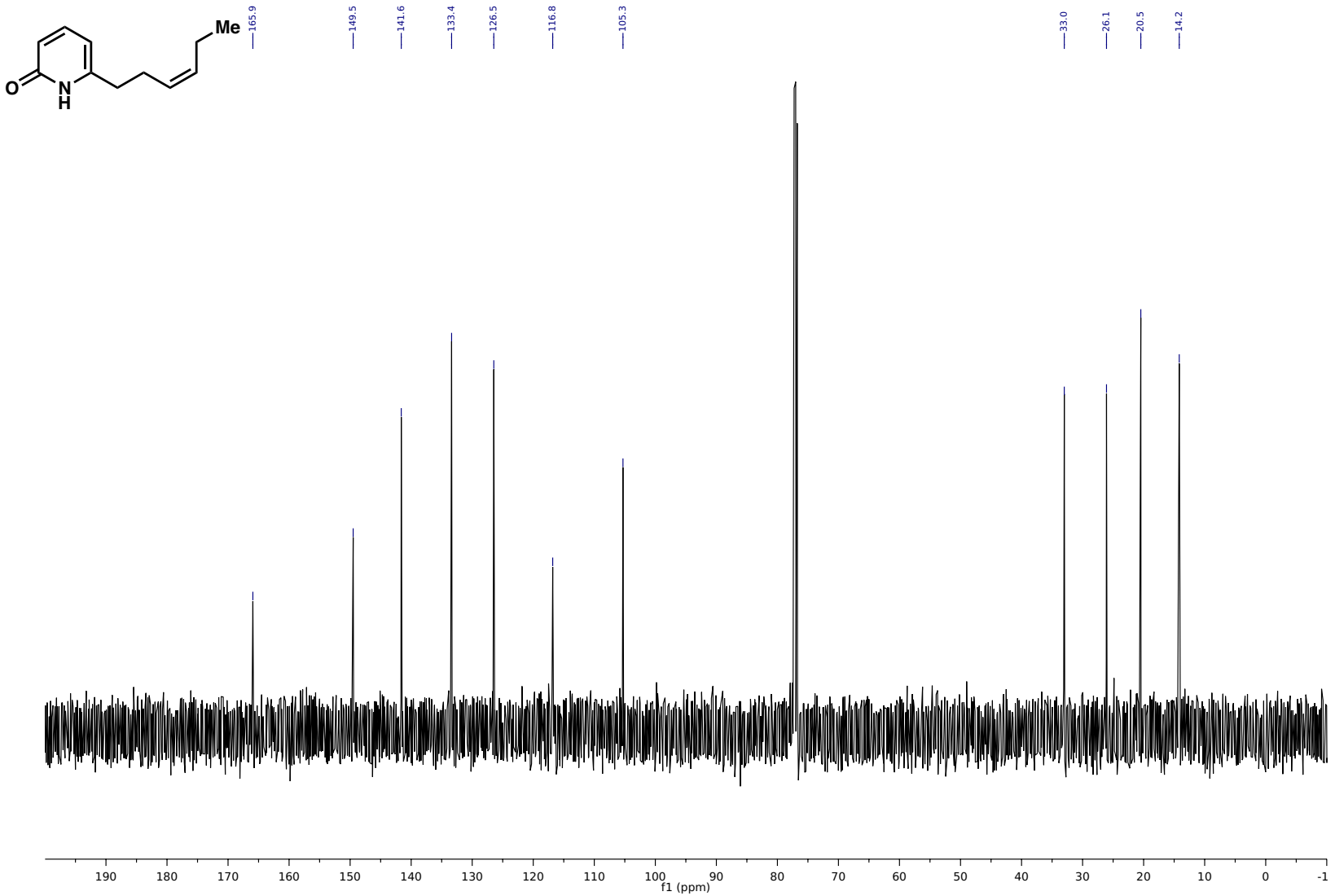
^{1}H NMR (400 MHz, $CDCl_3$) of (*E*)-6-(hex-3-en-1-yl)pyridin-2(1*H*)-one (**5q**)



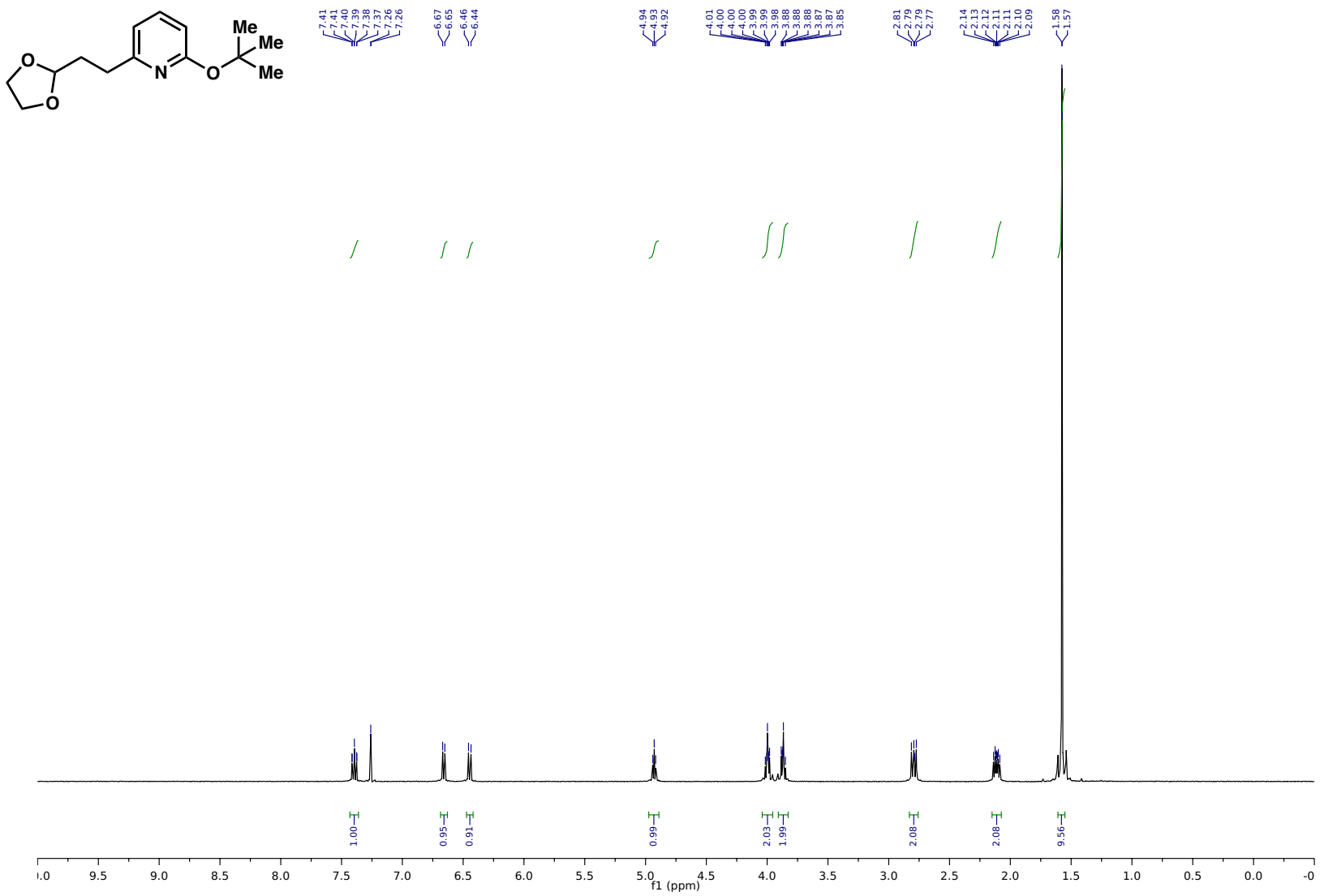
^{13}C NMR (125 MHz, $CDCl_3$) of (*E*)-6-(hex-3-en-1-yl)pyridin-2(1*H*)-one (**5q**)



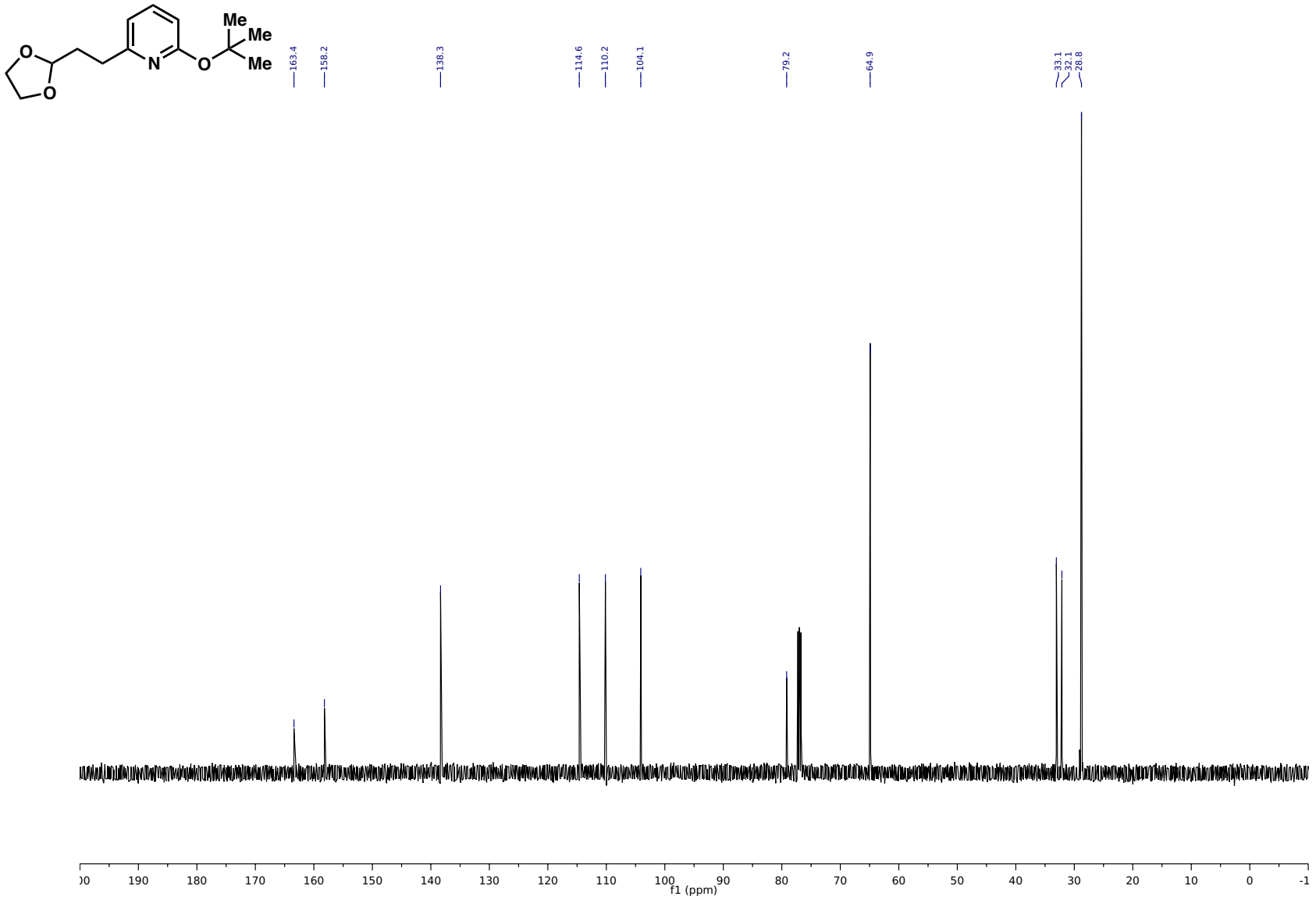
^{1}H NMR (400 MHz, $CDCl_3$) of (*Z*)-6-(hex-3-en-1-yl)pyridin-2(1*H*)-one (**5r**)



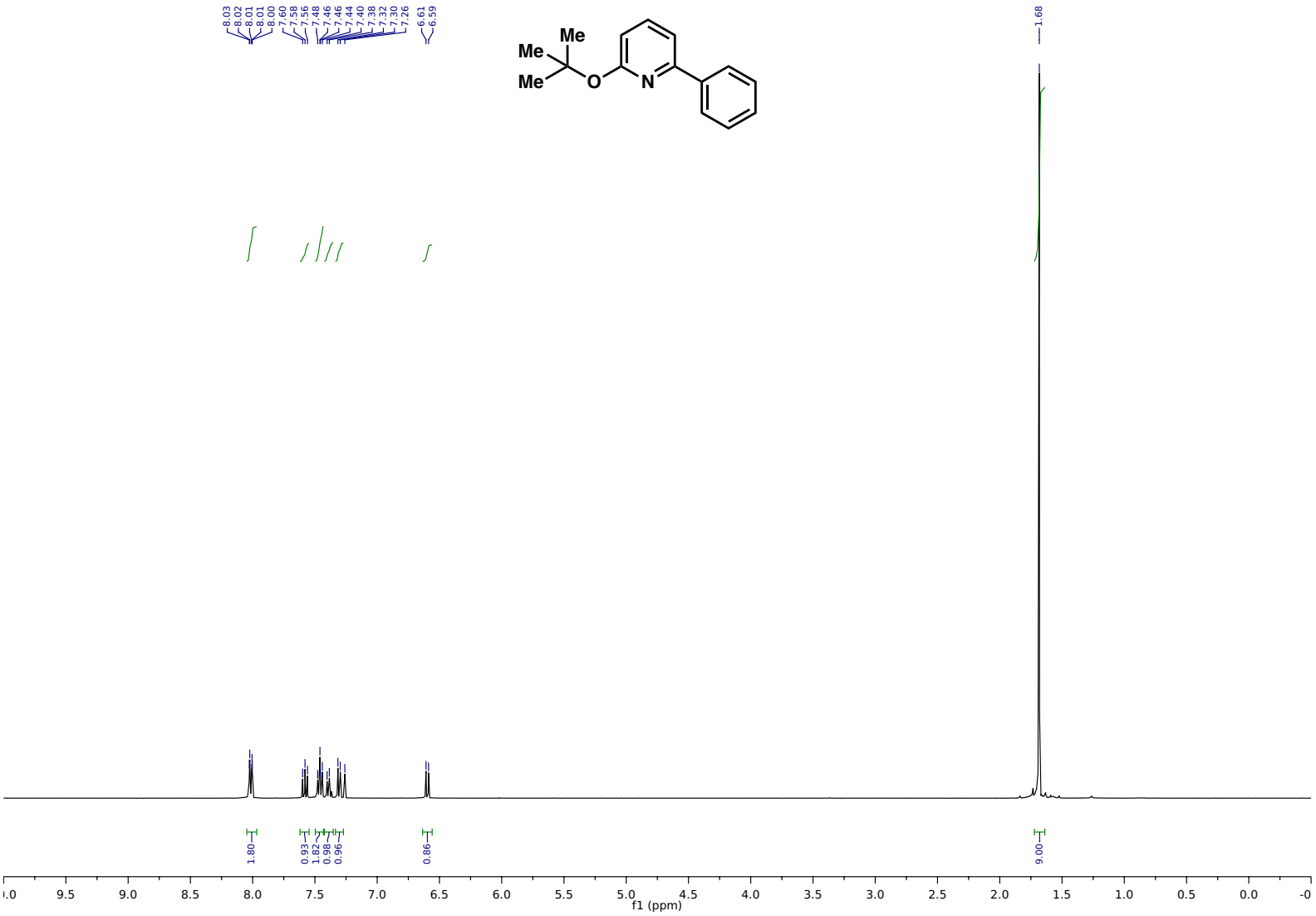
^{13}C NMR (125 MHz, $CDCl_3$) of (*Z*)-6-(hex-3-en-1-yl)pyridin-2(1*H*)-one (**5r**)



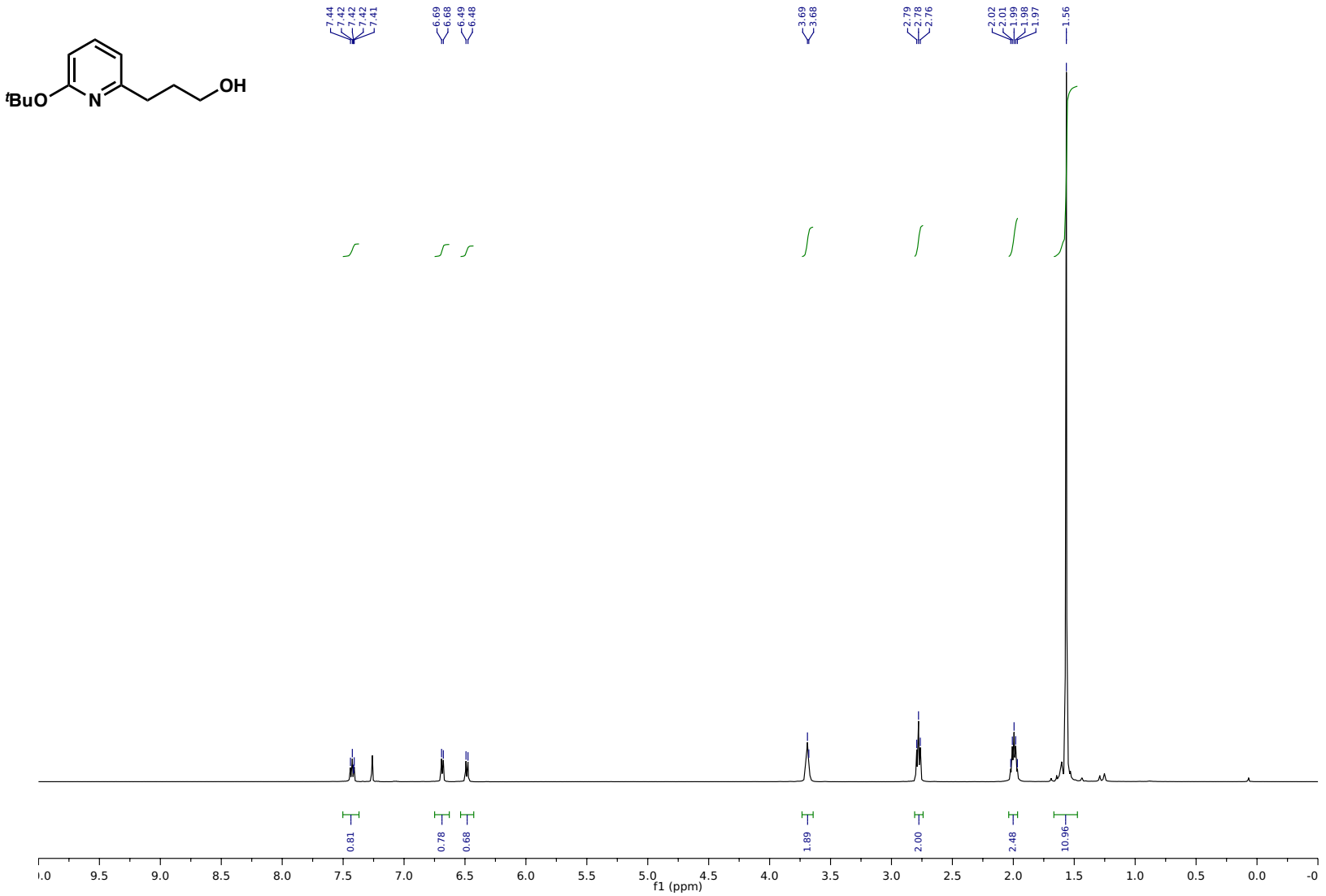
^{1}H NMR (400 MHz, $CDCl_3$) of 2-(2-(1,3-dioxolan-2-yl)ethyl)-6-(*tert*-butoxy)pyridine (**5t**)



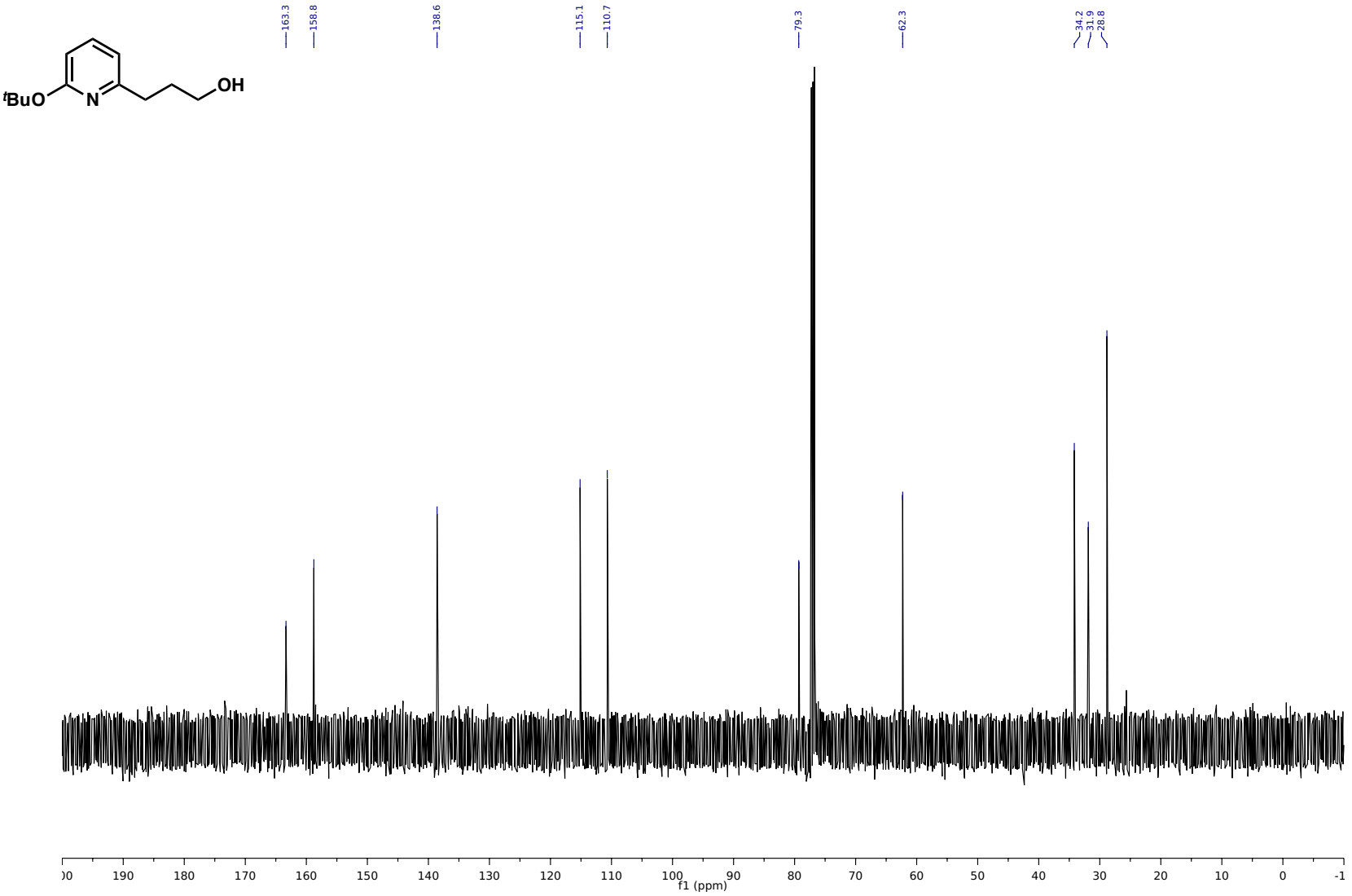
^{13}C NMR (125 MHz, $CDCl_3$) of 2-(2-(1,3-dioxolan-2-yl)ethyl)-6-(*tert*-butoxy)pyridine (**5t**)



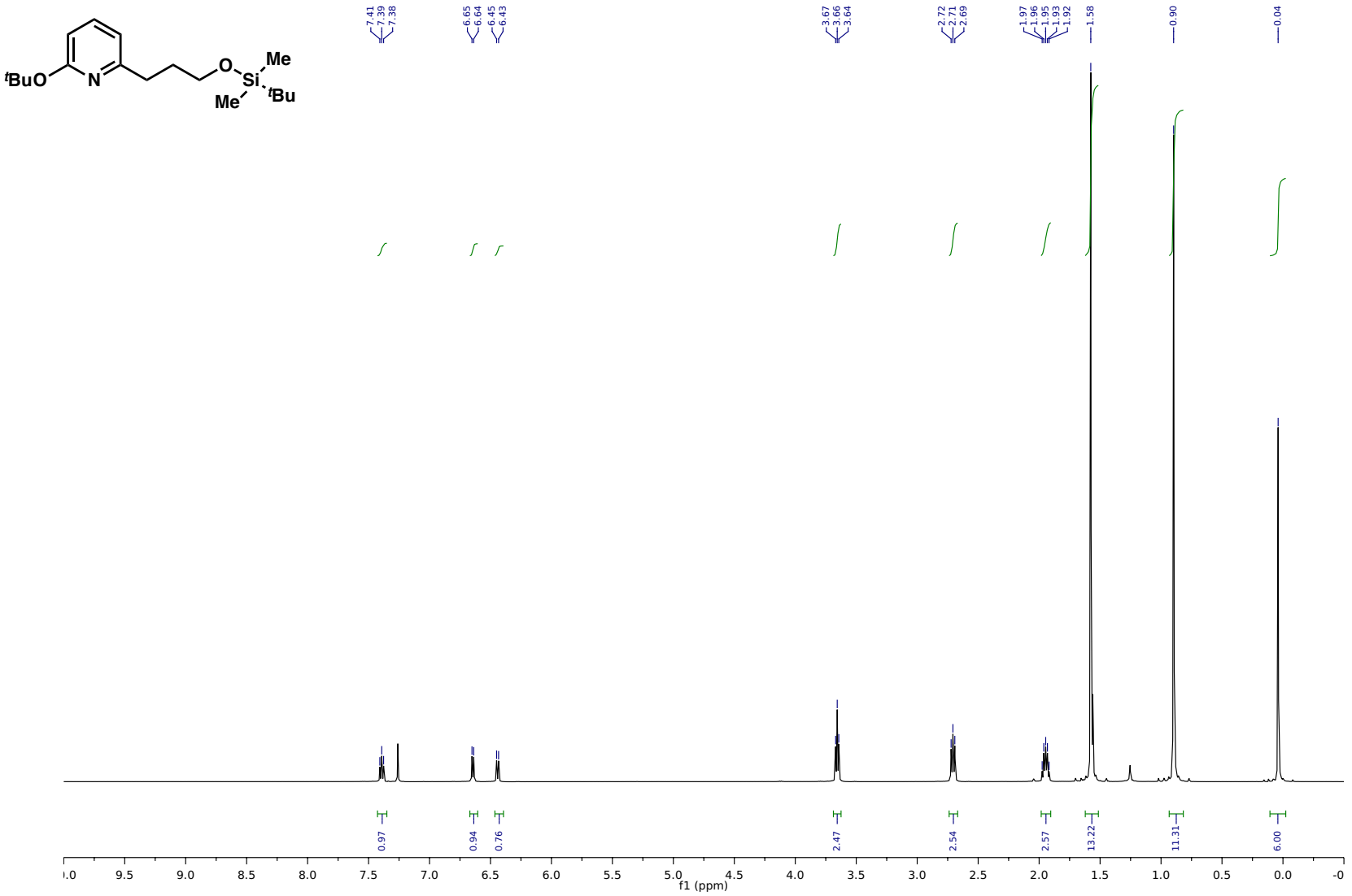
^{1}H NMR (125 MHz, $CDCl_3$) of 2-(*tert*-butoxy)-6-phenylpyridine (**5t**)



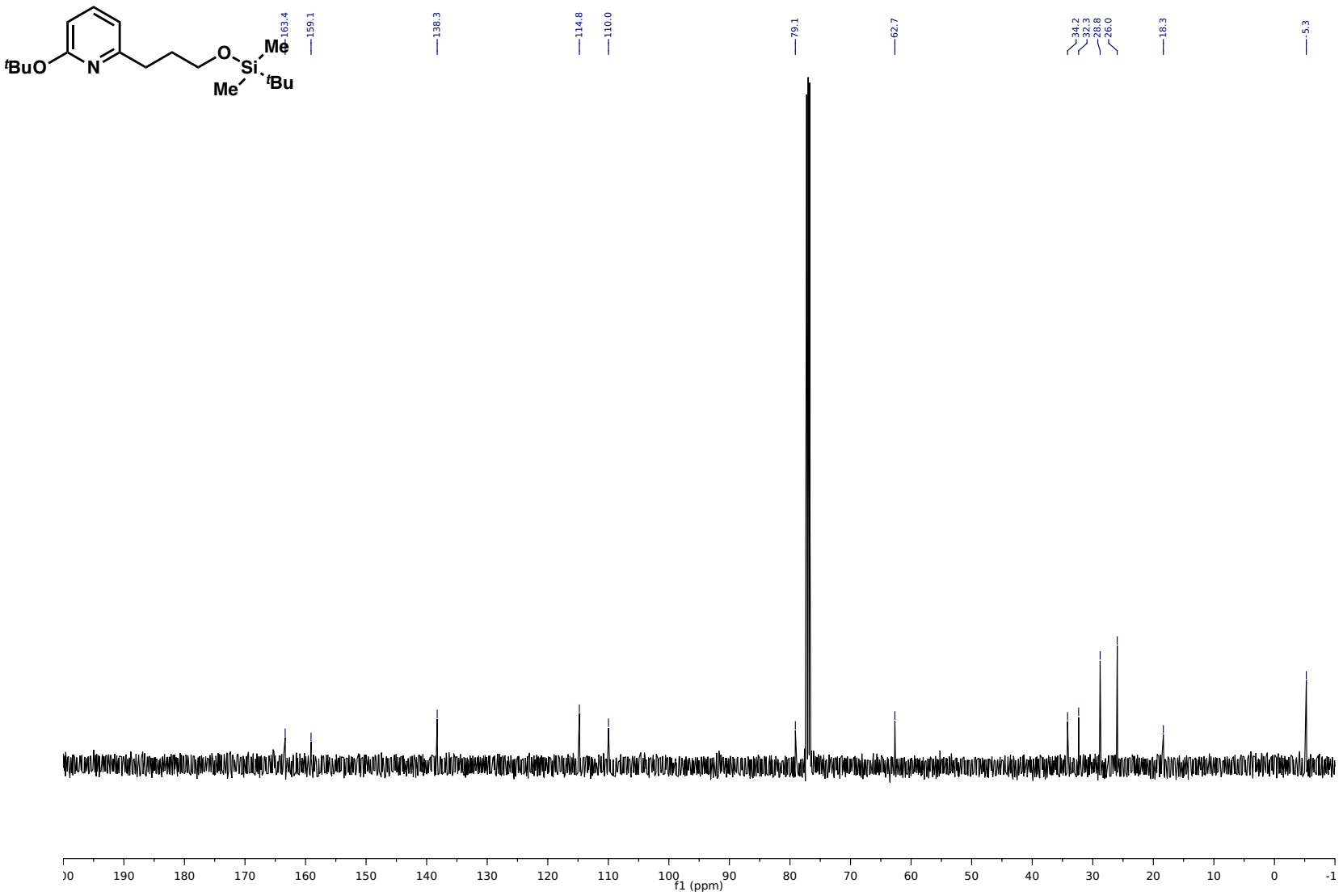
^{1}H NMR (500 MHz, $CDCl_3$) of 3-(6-(*tert*-butoxy)pyridine-2-yl)propan-1-ol (**5u**)



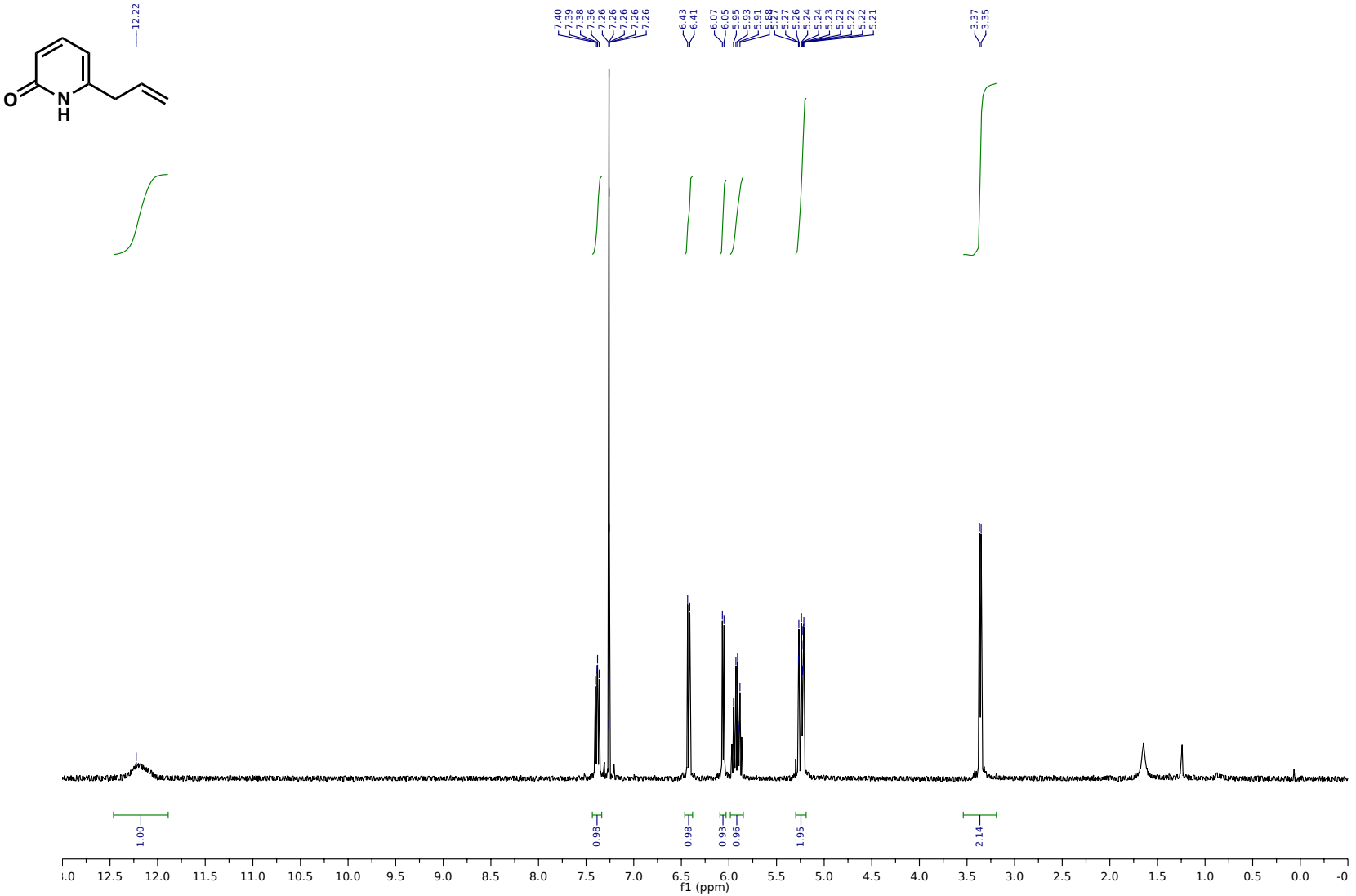
^{13}C NMR (125 MHz, $CDCl_3$) of 3-(6-(*tert*-butoxy)pyridine-2-yl)propan-1-ol (**5u**)



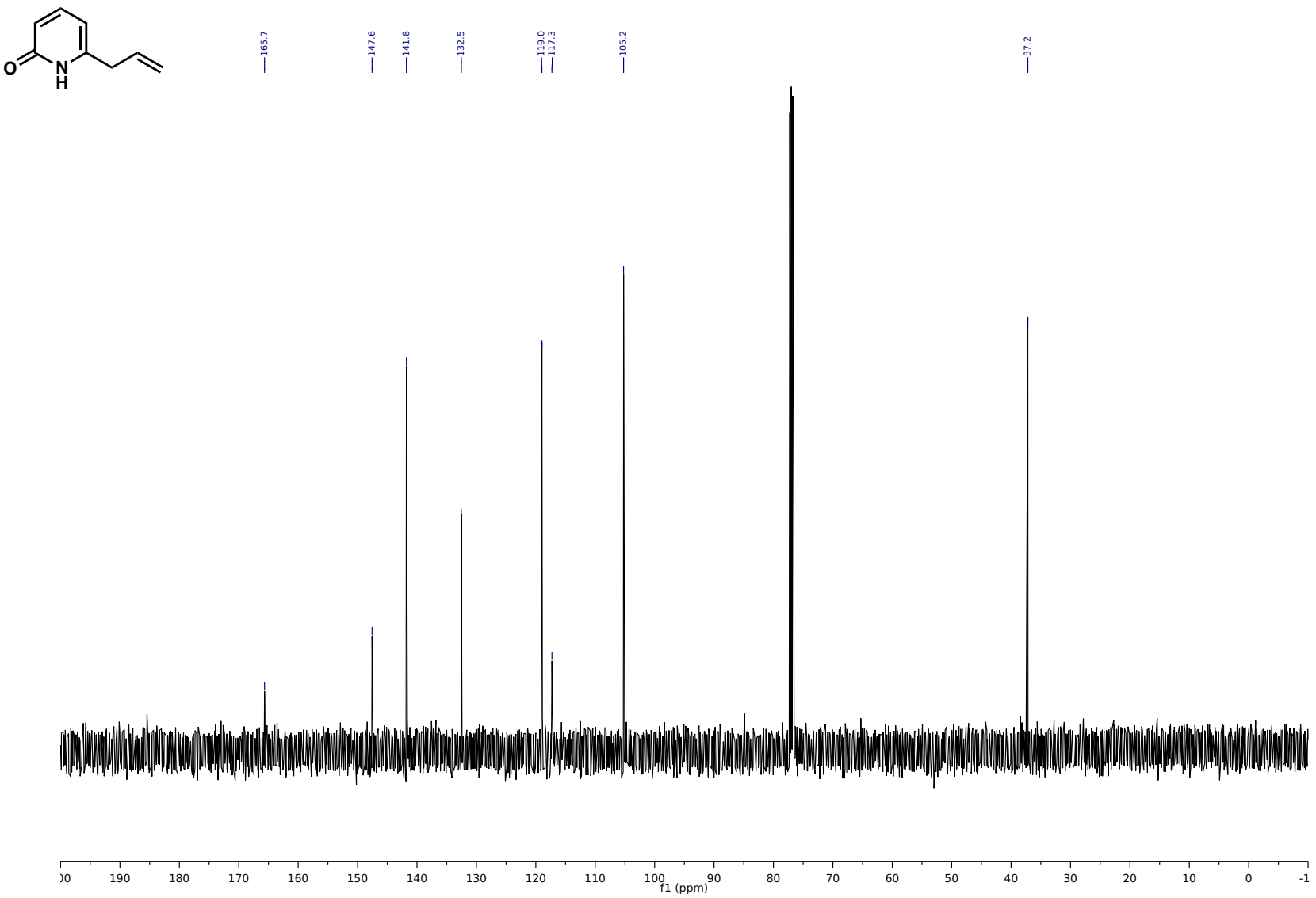
^{1}H NMR (500 MHz, $CDCl_3$) of 2-(*tert*-butoxy)-6-(3-((*tert*-butyldimethylsilyl)oxy)propyl)pyridine (**5v**)



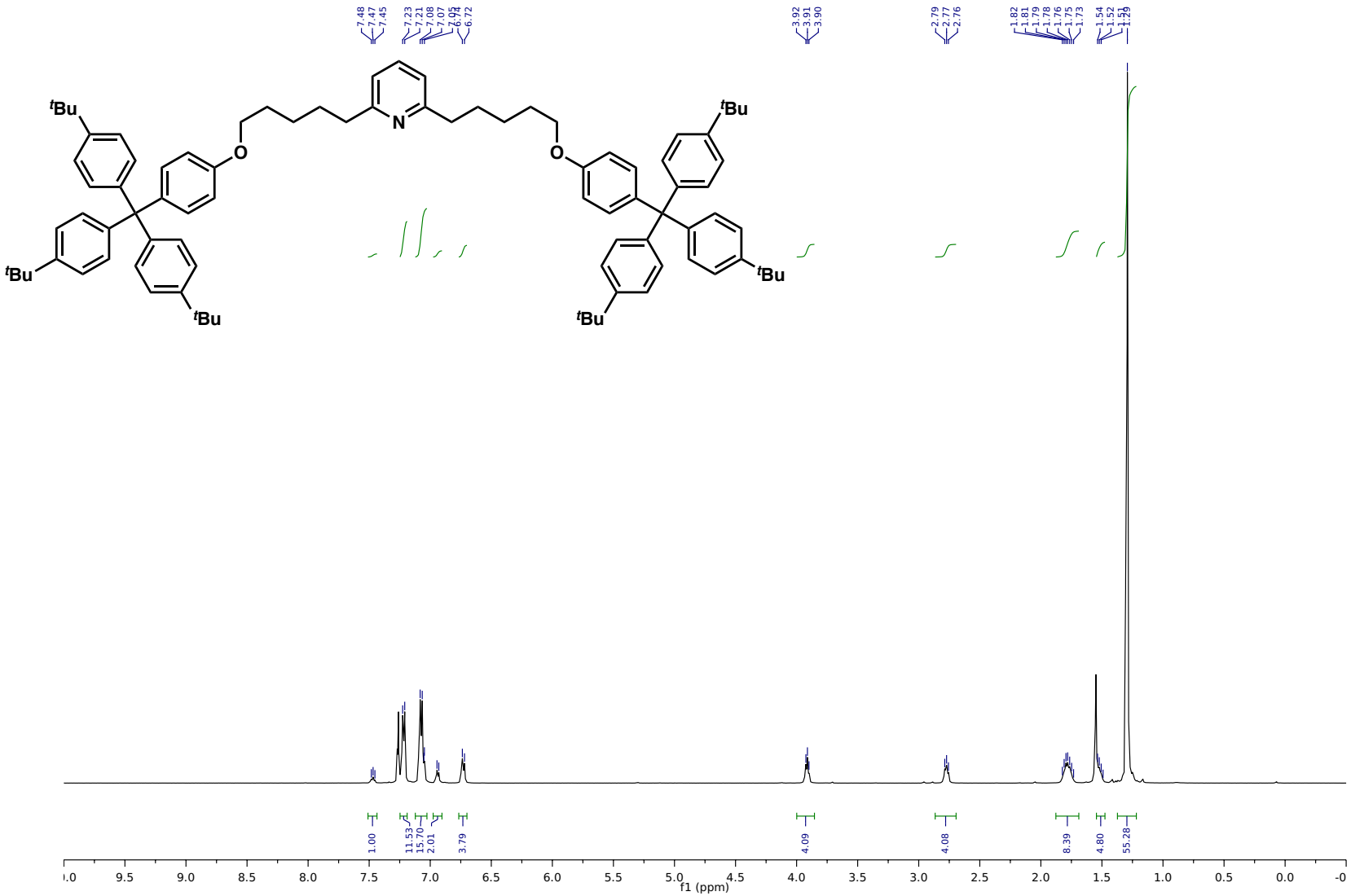
^{13}C NMR (125 MHz, $CDCl_3$) of 2-(*tert*-butoxy)-6-(3-((*tert*-butyldimethylsilyl)oxy)propyl)pyridine (**5v**)



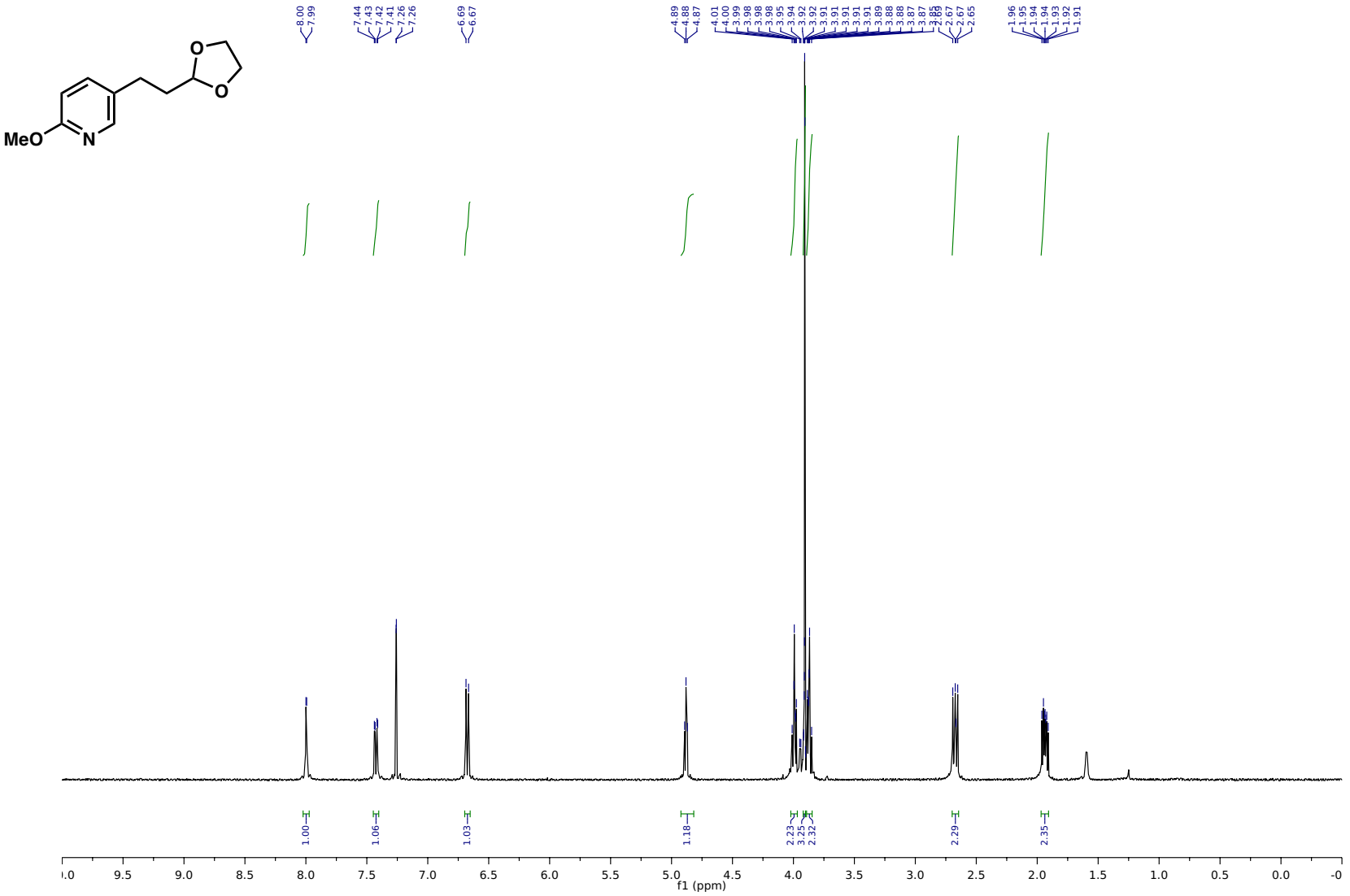
^{1}H NMR (400 MHz, $CDCl_3$) of 6-allylpyridin-2(1*H*)-one (**5w**)



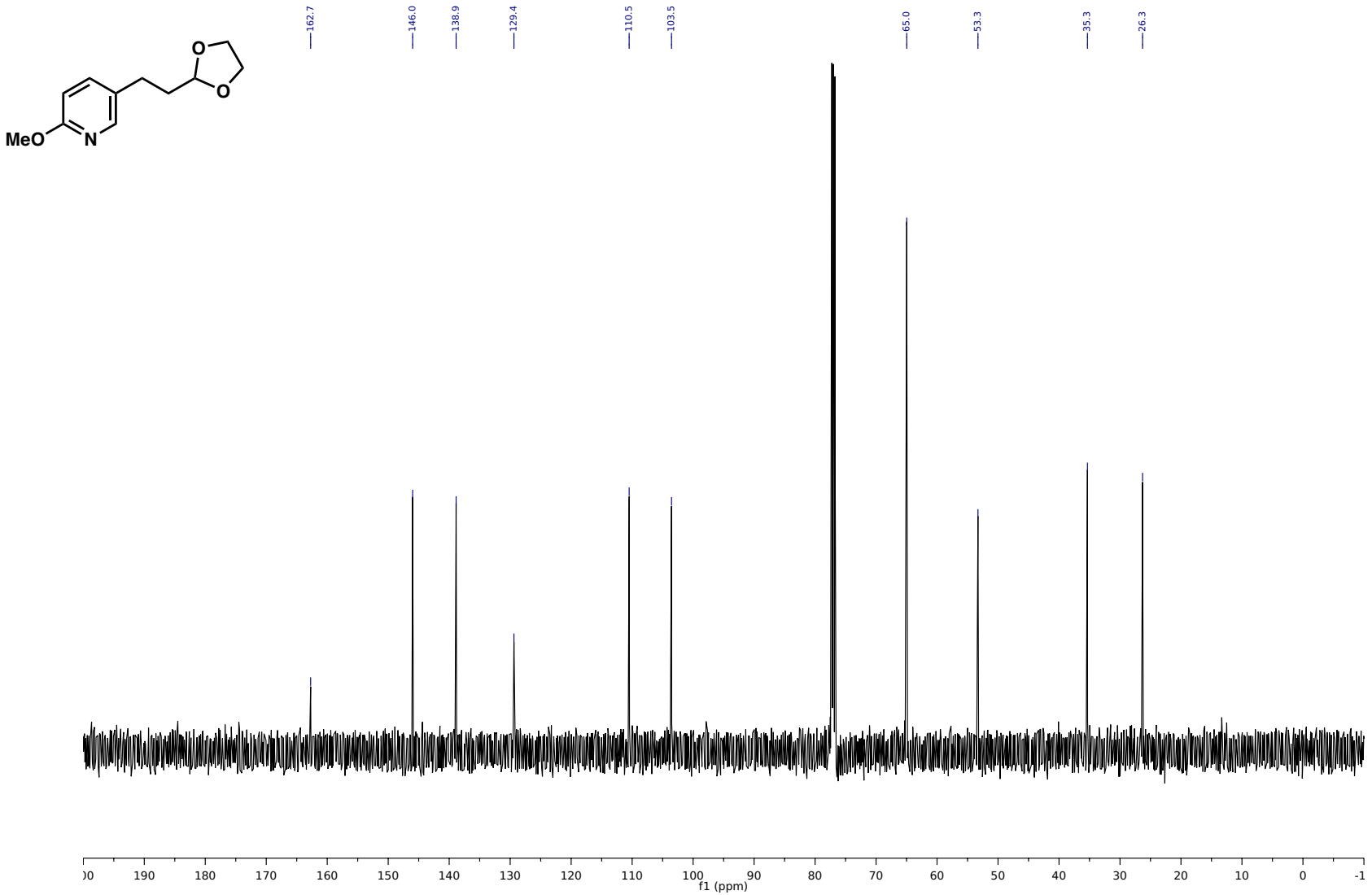
^{13}C NMR (125 MHz, $CDCl_3$) of 6-allylpyridin-2(1*H*)-one (**5w**)



^{1}H NMR (500 MHz, $CDCl_3$) of 2,6-bis(5-(4-(tris(4-(*tert*-butyl)phenyl)methyl)phenoxy)pentyl)pyridine (**5x**)



^{1}H NMR (400 MHz, $CDCl_3$) of 5-(2-(1,3-dioxolan-2-yl)ethyl)-2-methoxypyridine (**S5a**)



^{13}C NMR (125 MHz, $CDCl_3$) of 5-(2-(1,3-dioxolan-2-yl)ethyl)-2-methoxypyridine (**S5a**)