Supporting Information

Mechanistic Investigation of the Nickel-Catalyzed Suzuki Reaction of *N,O*-Acetals: Evidence for Boronic Acid-Assisted Oxidative Addition and an Iminium Activation Pathway

Kevin T. Sylvester, Kevin Wu, and Abigail G. Doyle

Department of Chemistry, Princeton University
Frick Chemical Laboratory, Princeton, NJ 08544 USA
E-mail: agdoyle@princeton.edu

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A) General considerations.

General information. Unless otherwise noted, reactions were performed with rigorous exclusion of air or moisture. Argon-flushed stainless steel cannulae or gas-tight syringes were used to transfer air- and moisture-sensitive reagents. Solvent was freshly distilled/degassed prior to use unless otherwise noted. Reactions were monitored by LCMS gas chromatography or NMR spectrometry. Organic solutions were concentrated under reduced pressure using a rotary evaporator (30 °C, <50 torr). Automated column chromatography was performed using pre-packed silica gel cartridges on a Biotage SP4 (40-53 µm, 60 Å).

Materials. Commercial reagents were used as received with the following exceptions. All boroxines[1] were prepared by heating the commercial boronic acid under vacuum using P_2O_5 as a desiccant and then were stored in a nitrogen-filled glovebox. 1,4-dioxane (inhibitor free, ACS reagent grade >99%) was refluxed over sodium, distilled, and degassed before being stored in a nitrogen-filled glove box over activated 4 Å sieves. Pentane (Fisher, HPLC grade) was stored over activated sieves and degassed before being stored in a nitrogen-filled glovebox over over activated 4 Å sieves. Anhydrous 2-methyl-2-butanol (t-AmOH, 1 L Sure/Seal^{TM} bottle) was purchased from Aldrich and sparged with N_2 for 30 minutes under sonication. The degassed *t*-AmOH was stored over activated 4 Å sieves in a nitrogen-filled glovebox. All other solvents (toluene, diethyl ether, hexanes, tetrahydrofuran) were HPLC grade, degassed for 30 minutes, and dried by passing through a neutral alumina column.[2] Deuterated solvents were purchased from Aldrich (dichloromethane-d_2 and toluene-d_8) and Cambridge Isotopes (C_6D_6 and chloroform-d_1) degassed and stored activated 4 Å sieves in a nitrogen-filled glovebox. All other solvents (toluene, diethyl ether, hexanes, tetrahydrofuran) were HPLC grade, degassed for 30 minutes, and dried by passing through a neutral alumina column. Ni(cod)$_2$ was purchased from Strem and stored at −40 °C in a nitrogen-filled glovebox. DPEPhos and tris(pentafluorophenyl)borane was purchased from Strem and stored in a nitrogen-filled glovebox.

Instrumentation. Proton nuclear magnetic resonance (^1H NMR) spectra, carbon nuclear magnetic resonance (^{13}C NMR) spectra, and phosphorus nuclear magnetic resonance (^{31}P NMR) spectra were recorded on a Bruker 500 AVANCE spectrometer (500, 125, and 203 MHz, respectively). Chemical shifts for proton are reported in parts per million (ppm) downfield from tetramethylsilane and are referenced to residual protium in the NMR solvent ($CHCl_3$ = δ 7.26, C_6D_6 = δ 7.16). Chemical shifts for carbon are reported in ppm downfield from tetramethylsilane and are referenced to the carbon resonances of the solvent residual peak ($CDCl_3$ = δ 77.16, C_6D_6 = δ 128.06). Chemical shifts for phosphorus are reported in ppm and are referenced to triphenylphosphine oxide shift. Fluorine nuclear magnetic resonance (^{19}F NMR) spectra were recorded on a Varian Inova 300 (282 MHz) or 400 (376 MHz) spectrometer; chemical shifts are reported in parts per millions and are referenced to $CFCl_3$ (δ 0 ppm). NMR data are presented as follows: chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad), coupling constant in Hertz (Hz), integration. FT-IR spectra were recorded on a Perkin-Elmer Paragon 500 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. Optical rotations were recorded using a 1-mL cell with a 1.0 dm path length; concentration (c) is in g/100 mL and $[\alpha]_D$ values are in degrees

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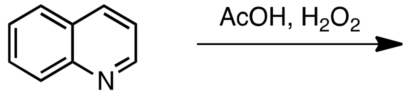
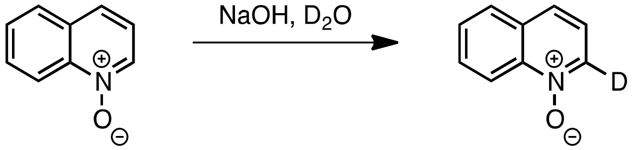
[1] Graham, T. J. A.; Shields, J. D.; Doyle, A. G. *Chem. Sci.* **2011**, *2*, 980–984.

[2] Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J. *Organometallics* **1996**, *15*, 1518–1520.

B) Preparation of organic substrates and fluorinated DPEPhos.

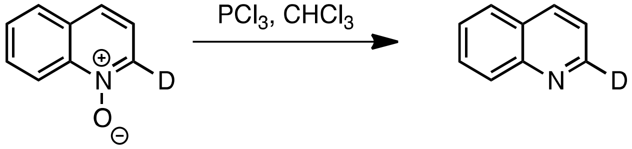


Synthesis of quinoline-N-oxide. Quinoline (12.5 g, 96.8 mmol) was dissolved in 40 mL of acetic acid in a 250-mL round bottom flask equipped with a Teflon®-coated stir bar. The reaction was placed behind a blast shield and cooled in a water bath. Aqueous hydrogen peroxide (20 mL, 25% w/w) was added dropwise resulting in a pale yellow solution. The reaction was heated at 70 °C for 30 hours (shorter reaction times resulted in lower isolated yields). The dark solution was cooled to room temperature and neutralized with 350 mL of 2M NaOH (pH~8). The aqueous mixture was extracted with methylene chloride (600 mL, 4 x 150 mL). The organic extracts were dried over sodium sulfate, filtered, and concentrated. The product was isolated as a yellow-orange solid (8.2 g, 57% yield). Spectral data were consistent with previous reports.[3]



Synthesis of 2-d_1-quinoline-N-oxide. D_2O (15 mL) was added to a 30-mL screw cap tube followed by NaOH (2.0 g, 50 mmol). To that solution, quinoline-*N*-oxide (3.0 g, 20.7 mmol) was added along with a stir bar. The tube was sealed with Teflon®-tape and a cap. The brown suspension was heated at 100 °C for five hours during which time two homogenous layers formed. The tube was cooled to room temperature. Chloroform (120 mL) was used to separate the organic product from the aqueous layer. The tan colored extract was dried over magnesium sulfate, and filtered. Chloroform was removed in vacuou to reveal a beige solid (2.4 g, 75% yield). Deuterium incorporation was measured to be 89% by ^{1}H NMR in d_1-chloroform. Peak areas at 8.76 ppm and 8.53 ppm were compared to measure the deuterium incorporation (see data below). Spectral data were consistent with previous reports.[4]

Quinoline-N-Oxide	*Peak 1 Area (8.76 ppm, d)*	*Peak 2 Area (8.53 ppm, d)*
no deuterium incorporation	*1.0*	*0.96*
mono-deuterium incorporation	*1.0*	*0.11*



Synthesis of 2-d_1-quinoline. . 2-d_1-Quinoline-*N*-oxide (3.4 g, 32.3 mmol) was dissolved in dry, degassed chloroform (125 mL). PCl_3 (4.1 mL, 6.5 g, 47.0 mmol) was added under nitrogen. The

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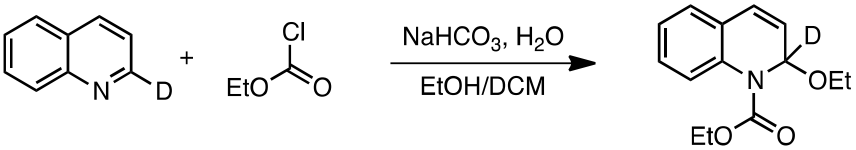
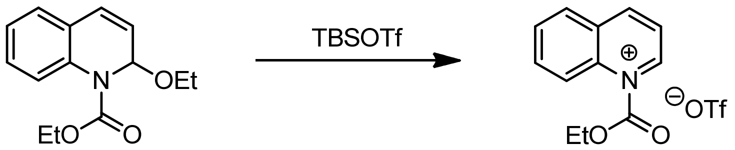
[3] Heitman, L. H.; Göblyös, A.; Zweemer, A. J. M.; Bakker, R.; Mulder-Krieger, T.; van Veldhoven, J. P. D.; de Vries, H.; Brussee, J.; Ijzerman, A. P. *J. Med. Chem.* **2009**, *52*, 926–931.

[4] Kametani, T.; Nemoto, H.; *Chem. Pharm. Bull.* **1968**, *16*, 1696–1699.

solution was heated at reflux overnight. The reaction was cooled and kept under nitrogen. The reflux condenser was removed and replaced with a short path distillation apparatus. The excess volatiles were removed by atmospheric distillation at ~100 °C. The remaining oil was diluted with 30 mL of ether and neutralized with 25 mL of saturated sodium bicarbonate. The layers were separated and the organic layer was removed. The remaining aqueous layer was extracted with 50 mL of ether. The combined organic layers were dried over K_2CO_3 overnight. The drying agent was removed via filtration and concentration of the organic layer under vacuum yield 1.95 g of a pale brown oil identified as of 2-d_1-quinoline (65% yield). (The procedure was repeated with 2.45 g of 2-d_1-quinoline-*N*-oxide and 1.35 g of product was isolated, 62% yield). Spectral data were consistent with previous reports.[4]



Synthesis of 2-d_1-N-ethoxycarbonyl-2-ethoxy-1,2-dihydroquinoline (**1-d_1**).[5] Immediately before reaction set up, pale, brown 2-d_1-quinoline (3.30 g) was freshly distilled from calcium hydride to yield 2.5 g (19.2 mmol) of colorless and clear quinoline. In a 200-mL three-neck round bottom flask, the distilled quinoline, water (2.0 mL), absolute ethanol (20 mL), and dichloromethane (20 mL) were combined and stirred under nitrogen. Solid sodium bicarbonate (2.37 g, 28.2 mmol) was added through one of the necks and the suspension was stirred for 10 minutes. The heterogeneous reaction was cooled to 0 °C in an ice/salt bath. Ethyl chloroformate (2.2 mL, 23.1 mmol) was added dropwise over ten minutes so that the temperature did not rise above 5 °C. The reaction was stirred for four hours while allowing the bath to expire. Analysis by ^{1}H NMR showed complete consumption of quinoline. Water (50 mL) was added to the suspension and stirred for five minutes. The organic layer was separated and the aqueous layer was extracted with 2 x 75 mL chloroform. The combined organic layers were washed with brine and dried over sodium sulfate. The drying agent was removed by filtration and the solvent removed by rotary evaporation. The remaining clear, colorless, viscous oil was diluted with 20 mL of ether and stored at 0 °C overnight. After 16 hours, a white precipitate was collected via vacuum filtration (3.2 g 67% yield) which was identified as 2-d_1-EEDQ (**1-d_1**). The spectral properties were consistent with commercial undeuterated sample.



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8

Synthesis of quinolinium triflate (**8**).[6] In an oven dried 250-mL round bottom flask with a Teflon®-coated stir bar, EEDQ (3.00 g, 12.1 mmol) was dissolved in 50 mL of dry toluene. The

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[5] Procedure was adapted from: Moquist, P. N. Asymmetric Catalytic Reactions of Boronate Nucleophiles. Ph.D. Dissertation, Boston University, Boston, MA, 2011. The only change was the use of deuterated quinoline.

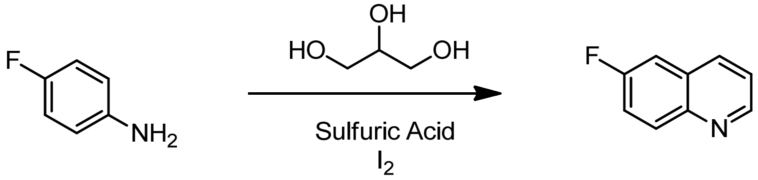
[6] See the following references for similar substrates and procedures: (a) Yamaguchi, R.; Hatano, B.; Nakayasu, T.; Kozima, S. *Tetrahedron Lett.* **1997**, *38*, 403–406. (b) Yamaguchi, R.; Nakayasu, T.; Hatano, B.; Nagura, T.; Kozima, S.; Fujita, K. *Tetrahedron* **2001**, *57*, 109–117.

flask was purged with argon and cooled in an ice bath. *t*-Butyldimethylsilyl triflate (3.21 g, 12.1 mmol) was dissolved in 5 mL of toluene and added dropwise to the solution of EEDQ. Immediately, a white precipitate began to form and the reaction was stirred for one hour during which time the reaction was allowed to warm to room temperature. The white solid was quickly filtered on a frit and washed with dry diethyl ether (100 mL). The collected white solid was dried under reduced pressure to yield 3.37 g (80 % yield) of the expected quinolinium triflate **6**.

^{1}H NMR (300 MHz, CD_2Cl_2): δ 9.85 (dd, J = 6.2, 1.5 Hz, 1H), 9.37 (dt, J = 8.3, 1.2 Hz, 1H), 8.68 (dd, J = 9.1, 0.8 Hz, 1H), 8.42 (dd, J = 8.3, 1.5 Hz, 1H), 8.34 – 8.18 (m, 2H), 8.10 – 7.98 (m, 1H), 4.90 (q, J = 7.2 Hz, 2H), 1.60 (t, J = 7.2 Hz, 3H).

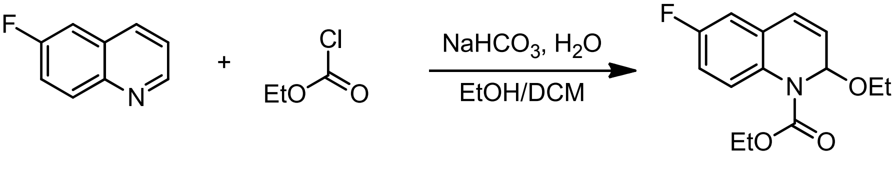
^{13}C NMR (125 MHz, CD_2Cl_2): δ 153.57, 148.81, 148.44, 138.24, 136.65, 131.53, 131.19, 130.39, 121.91, 121.12 (q, J = 321 Hz), 120.16, 71.02, 13.82.

^{19}F NMR (282 MHz, CD_2Cl_2): δ –78.92.



Synthesis of 6-fluoroquinoline. 4-fluoroaniline (12.79 ml, 135 mmol), glycerol (14.80 ml, 201 mmol), and Iodine (3.43 g, 13.50 mmol) were weighed out into a 250 ml round bottom flask equipped with a PTFE stirbar. The flask was placed in a water bath and sulfuric acid (39.7 ml, 730 mmol) was added dropwise to avoid exotherm. The reaction was then heated to 140 °C in an oil bath for 14 hours.

The crude reaction was poured into ice water and basified with ammonium hydroxide. The aqueous layer was extracted (3x400 ml DCM). The combined organic layers were first filtered through celite, dried over sodium sulfate, and then concentrated under reduced pressure. The crude product was then distilled under reduced pressure (bp = 65–70 °C, 0.1 torr) to give 6-fluoroquinoline (1.91 g, 12.98 mmol, 9.6% yield) as a clear liquid. The spectral properties were consistent with literature reports.[7]



(6-F)EEDQ

Synthesis of 6-fluoro-N-ethoxycarbonyl-2-ethoxy-1,2-dihydroquinoline (**[6-F]EEDQ)**. The EEDQ was prepared according to the procedure for **1-*d*$_1$**. 6-fluoroquinoline (0.900 g, 6.12 mmol) was dissolved in DCM, ethanol, and water (10:10:1) in a 100 ml rbf. The solution was then cooled to 0°C and sodium bicarbonate (0.771 g, 9.17 mmol) was added. Ethyl Chloroformate (0.700 ml, 7.31 mmol) was then added dropwise at 0 °C. The reaction was then allowed to warm to room

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[7] Furuya, T.; Strom, A. E.; Ritter, T. *J. Am. Chem. Soc.* **2009**, *131*, 1662–1663.

temperatue (23 °C) and allowed to stir for 36 h. The reaction was then quenched with water (50 ml). The aqueous layer was then extracted with chloroform (3 x 75 ml. The combined organic layers were then washed with brine (50 ml), dried with Na_2SO_4, filtered, and concentrated under reduced pressure.

The crude product was passed through a silica gel plug pretreated with 10% triethylamine in hexanes. After evaporation under reduced pressure, **(6-F)EEDQ** was obtained as a translucent oil (1.50 g, 5.65 mmol, 92% yield). The oil then spontaneously crystallized to give white crystals after 12 hours in a 0 °C freezer.

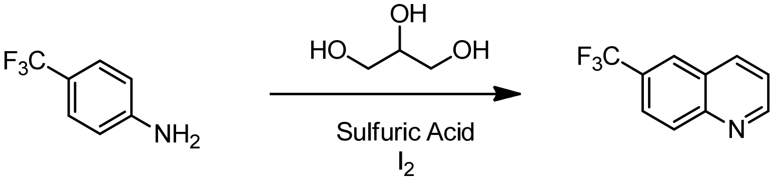
IR (neat, cm^{-1}): 2978, 1709, 1493, 1371, 1295, 1227, 1116, 1064, 1010, 873, 765.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.64 (s, 1H), 6.98 (td, J = 8.7, 2.9 Hz, 1H), 6.92 (dd, J = 8.6, 2.9 Hz, 1H), 6.68 (d, J = 9.4 Hz, 1H), 6.21 (dd, J = 9.4, 5.4 Hz, 1H), 6.13 (d, J = 5.5 Hz, 1H), 4.42 – 4.18 (m, 2H), 3.74 – 3.46 (m, 2H), 1.35 (t, J = 7.1 Hz, 3H), 1.13 (t, J = 7.1 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 159.20 (d, *J* = 243.0 Hz), 154.87, 129.82 (d, *J* = 2.7 Hz), 127.39 (d, *J* = 8.4 Hz), 127.10 (d, *J* = 2.2 Hz), 126.04 (d, *J* = 8.1 Hz), 125.34, 114.65 (d, *J* = 22.8 Hz), 112.95 (d, *J* = 22.9 Hz), 78.12, 62.84, 62.74, 15.28, 14.55.

^{19}F NMR (282 MHz, $CDCl_3$): δ –118.92 (td, J = 8.4, 4.9 Hz).

HRMS: (ESI-TOF) calculated for $C_{12}H_{11}FNO_2^+$ ($[M-OEt]^+$): 220.0774, found: 220.0772.



Synthesis of 6-trifluoromethylquinoline. The compound was prepared according to the procedure for 6-fluoroquinoline. 4-trifluoromethylaniline (7.79 ml, 62.1 mmol), glycerol (6.80 ml, 92 mmol), and Iodine (1.58 g, 6.21 mmol) were weighed out into a 100 ml round bottom flask equipped with a PTFE stirbar. The flask was placed in a water bath and sulfuric acid (9.92 ml, 186 mmol) was added dropwise to avoid exotherm. The reaction was then heated to 140 °C in an oil bath for 14 hours.

The crude reaction was poured into ice water and basified with ammonium hydroxide. The aqueous layer was extracted (3x400 ml DCM). The combined organic layers were first filtered through celite, dried over sodium sulfate, and then concentrated under reduced pressure. The crude product was then purified by flash chromatography (100 g pre-packed cartridge, hexanes:EtOAc gradient from 90:10 to 40:60) to give 6-trifluoromethylquinoline as a clear liquid (1.94 g, 9.89 mmol, 16% yield). The spectral properties were consistent with literature reports.[8]

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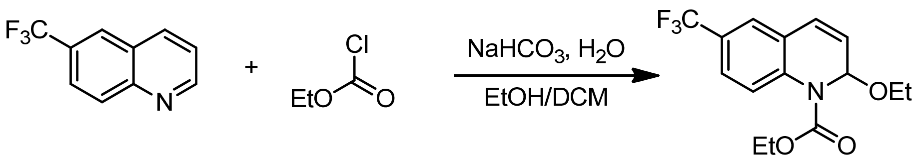
[8] Honel, M.; Vierhapper, F.W.; *J. Chem. Soc. Perkin Trans 1* **1980**, 1933–1939.



(6-CF_3)EEDQ

Synthesis of 6-trifluoromethyl-N-ethoxycarbonyl-2-ethoxy-1,2-dihydroquinoline **([6-CF_3]EEDQ)**. The EEDQ was prepared according to the procedure for **1-d_1**. 6-trifluoromethylquinoline (1.50 g, 7.61 mmol) was dissolved in DCM, ethanol, and water (10:10:1) in a 100 ml rbf. The solution was then cooled to 0°C and Sodium Bicarbonate (0.951 g, 11.41 mmol) was added. Ethyl Chloroformate (0.869 ml, 9.13 mmol) was then added dropwise at 0°C. The reaction was then allowed to warm to room temperatue (23°C) and allowed to stir for 36 h. The reaction was then quenched with water (50 ml). The aqueous layer was then extracted with chloroform (3 x 75 ml. The combined organic layers were then washed with brine (50 ml), dried with Na_2SO_4, filtered, and concentrated under reduced pressure.

The crude product was purified by flash chromatography (100 g pre-packed cartridge primed with 10% triethylamine in hexanes, hexanes:EtOAc gradient from 98:2 to 80:20) to give **(6-CF_3)EEDQ** as a colorless oil (1.01 g, 3.20 mmol, 42% yield). The oil then spontaneously crystallized to give white crystals after 12 hours in a 0 °C freezer.

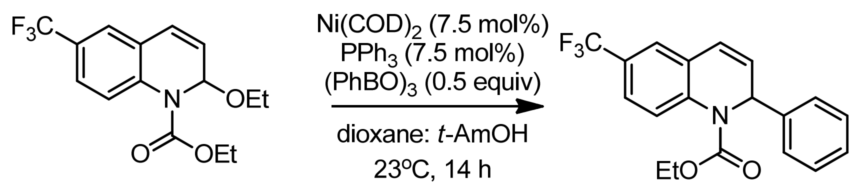
IR (neat, cm^{-1}): 2981, 1716, 1501, 1447, 1401, 1371, 1324, 1293, 1166, 1118, 1079, 1010, 830, 766.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.82 (d, J = 8.6 Hz, 1H), 7.52 (dd, J = 8.6, 2.1 Hz, 1H), 7.48 (d, J = 2.1 Hz, 1H), 6.77 (d, J = 9.4 Hz, 1H), 6.25 (dd, J = 9.4, 5.4 Hz, 1H), 6.16 (d, J = 5.5 Hz, 1H), 4.39 – 4.30 (m, 2H), 3.70 – 3.55 (m, 2H), 1.37 (t, J = 7.1 Hz, 3H), 1.13 (t, J = 7.1 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 154.64, 136.87 (d, *J* = 1.4 Hz), 126.97, 126.19 (q, *J* = 32.8 Hz), 126.02, 125.43, 124.61, 124.59, 124.20 (q, *J* = 271.7 Hz), 124.13 (q, *J* = 3.9 Hz), 78.24, 63.21, 62.92, 15.31, 14.54.

^{19}F NMR (282 MHz, $CDCl_3$): δ –62.27.

HRMS: (ESI-TOF) calculated for $C_{13}H_{11}F_3NO_2^+$ ([M-OEt]$^+$): 270.0742, found: 270.0734.



Synthesis of ethyl 2-phenyl-6-(trifluoromethyl)quinoline-1(2H)-carboxylate. Ni(COD)$_2$ (4.9 mg, 0.018 mmol) and triphenylphosphine (4.7 mg, 0.018 mmol) were weighed inside the glovebox into a 2-dram vial equipped with a PTFE stirbar and dissolved in 1 ml dioxane. The precatalyst solution was stirred for 15 minutes.

Ethyl 2-ethoxy-6-(trifluoromethyl)quinoline-1(2H)-carboxylate (75 mg, 0.238 mmol) and phenyl boroxine (37.1 mg, 0.119 mmol) were added to a threaded tube equipped with a PTFE stirbar in the glovebox. The reagents were then dissolved with dioxane (10 ml) and *t*-AmOH (1.00 ml). The precatalyst solution was then added and the reaction was sealed, brought out of the glovebox, and stirred at 23 °C for 18 hours.

The reaction mixture was passed through a celite plug and concentrated under reduced pressure. The crude product was purified by flash chromatography (25 g pre-packed silica gel cartridge, hexanes:EtOAc gradient from 98:2 to 80:20) to yield ethyl 2-phenyl-6-(trifluoromethyl)quinoline-1(2H)-carboxylate (74.9 mg, 0.216 mmol, 91 % yield) as a clear, colorless oil.

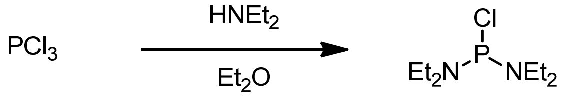
IR (neat, cm^{-1}): 2983, 1708, 1499, 1386, 1328, 1282, 1165, 1120, 1079, 897, 831, 762.

^{1}H NMR (500 MHz, CDCl$_3$): δ 7.67 (d, J = 8.7 Hz, 1H), 7.41 (dd, J = 8.7, 2.1 Hz, 1H), 7.37 (d, J = 2.1 Hz, 1H), 7.30 – 7.21 (m, 5H), 6.67 (d, J = 9.5 Hz, 1H), 6.26 (dd, J = 9.5, 6.1 Hz, 1H), 6.19 (d, J = 6.2 Hz, 1H), 4.41 – 4.22 (m, 2H), 1.35 (t, J = 7.1 Hz, 3H).

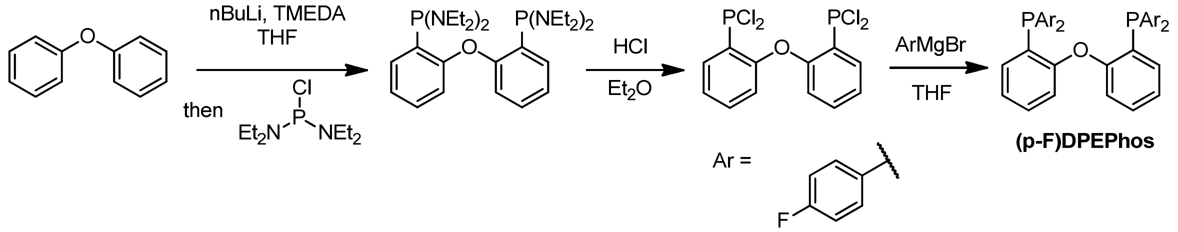
^{13}C NMR (125 MHz, CDCl$_3$): δ 154.51, 139.32, 137.96, 129.86, 128.86, 128.32, 127.27, 127.20, 126.12 (q, J = 32.8 Hz), 124.76 (q, J = 3.6 Hz), 124.67, 124.59, 124.22 (q, J = 271.7 Hz), 123.47 (q, J = 3.8 Hz), 62.96, 56.03, 14.66.

^{19}F NMR (282 MHz, CDCl$_3$): δ –62.30.

HRMS: (ESI-TOF) calculated for $C_{19}H_{17}F_3NO_2^+$ ($[M+H]^+$): 347.1133, found: 347.1138



Synthesis of bis(diethylamino)chlorophosphine. The compound was prepared according to the literature.[9] Diethylamine (50 ml, 481 mmol) in Et$_2$O (100 ml) was added dropwise to a solution of PCl$_3$ (8.35 ml, 96 mmol) in Et$_2$O (250 ml) at –78°C over 2 hours. The reaction was then allowed to warm to 23 °C. The product was then filtered in air and then concentrated under reduced pressure. The product was then distilled under reduced pressure (bp= ~75–80 °C, 0.1 torr). The product (14.67 g, 69.6 mmol, 73% yield) was obtained as a viscous clear liquid.



Synthesis of 2,2'-oxybis(2,1-phenylene)bis(bis(4-fluorophenyl)phosphine) **(*p*-F)DPEPhos**. The compound was prepared according to the literature.[10] Into a flask charged with *n*-BuLi (25.08 ml, 48.4 mmol, 1.93M) placed in a water bath at 23 °C, TMEDA (7.31 ml, 48.8 mmol) was added dropwise with rapid stirring. After addition is finished, the mixture was placed in an ice-water

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[9] Sakaki, J-i.; Schweizer, W. B.; Seebach, D. *Helv. Chim. Acta.* **1993**, *76*, 2654–2665.

[10] Zhu, Y.; Rawal, V. H. *J. Am. Chem. Soc.* **2012**, *134*, 111–114.

bath, and a THF (11.75 ml) solution of phenyl ether (3.73 ml, 23.50 mmol) was added dropwise with stirring. The mixture was warmed up and stirred at rt for 16 hours and then cooled to –78°C. A THF (23.50 ml) solution of bis(diethylamino)chlorophosphine (10.20 g, 48.4 mmol) was added to the above reaction mixture over 1 hour with stirring at –78 °C. After addition was complete, the resulitng mixture was warmed and allowed to stir at 23 °C for 16 hours. The mixture was filtered under N_2 in the glovebox, and then concentrated under vacuum to give the product (12.19 g, 23.50 mmol) as a viscous deep red liquid which was used in the next step without further purification.

Crude 1,1'-(oxybis(2,1-phenylene))bis(N,N,N',N'-tetraethylphosphinediamine) (12.19 g, 23.50 mmol) was dissolved in Et_2O and cooled to –78 °C. Hydrochloric acid (2M in Et_2O) (150 ml, 300 mmol) was added to the reaction mixture at –78 °C over 2 hours. The reaction mixture was then warmed up and stirred at 23 °C for 12 h. The mixture was filtered under N_2 with a Schlenk filter, and then concentrated under vacuum to give a yellow oil, which was then carried on to the next step without purification.

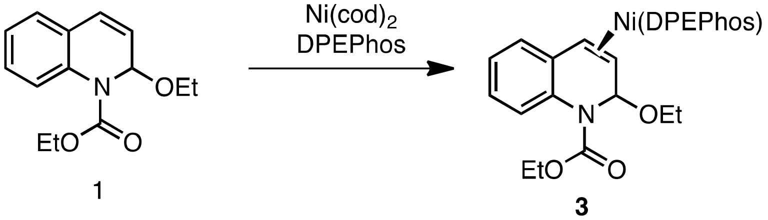
Part of the crude (oxybis(2,1-phenylene))bis(dichlorophosphine) (2.000 g, 5.38 mmol) was dissolved in THF (Volume: 90 ml) and the reaction cooled down to –78 °C. (4-fluorophenyl)magnesium bromide, 1M solution in THF (37.6 ml, 37.6 mmol) was then added batchwise over 1 hour and the reaction was allowed to stir at –78 °C for 1 hour. The temperature was then raised to 0°C and the reaction allowed to stir for 2 hours. The reaction was then allowed to warm to 23°C and allowed to stir for 16 hours.

The reaction was then cooled to 0°C and then quenched by the addition of saturated aqueous NH_4Cl (25 mL). The mixture was then warmed to room temperature and then extracted with Et_2O (2x60 mL) and CH_2Cl_2 (50 ml) sequentially. The combined organic layers were dried with Na_2SO_4 and then concentrated under reduced pressure. While the phosphine did not oxidize significantly over the course of workup, oxidation was observed over longer periods of time in solution (>5 hours). The crude product was then purified by recrystallization from hot i-PrOH (anhydrous, deegassed) under N_2. The solvent was removed via filtration in the glovebox. The solid was rinsed with ~5 ml pentanes and then dried under high vacuum to give (oxybis(2,1-phenylene))bis(bis(4-fluorophenyl)phosphine) **(*p*-F)DPEPhos** (1.881 g, 3.08 mmol, 57% yield) as a white solid. Spectral data matched the literature report.[9]

^{19}F NMR (282 MHz, $CDCl_3$): δ –112.68 (tq, J = 9.7, 5.3 Hz).

C) Preparation of organometallic complexes.

Syntheses of nickel olefin complexes



Synthesis of racemic **3**. DPEPhos (560 mg, 1.04 mmol, 1.1 equiv) and Ni(cod)$_2$ (265 mg, 0.96 mmol, 1.0 equiv) were combined in a 20-mL scintillation vial equipped with a Teflon®-coated stir bar. Toluene (3 mL) was added to the vial and the suspension quickly turned dark red and homogenous upon stirring. The reaction was stirred for 20 minutes at room temperature until a dark orange precipitate formed (indicating the presence of (DPEPhos)Ni(cod)). Subsequently, EEDQ (280 mg, 1.13 mmol, 1.2 equiv) was added and the reaction became bright orange and homogenous. Stirring was continued for another hour and a bright yellow precipitate formed. The yellow precipitate was collected by vacuum filtration and washed with ~20 mL of pentanes. After drying under vacuum, 789 mg of a bright yellow powder was isolated identified as **3** (97% isolated yield). A crystal suitable for single X-ray crystallographic analysis was grown from a mixture of toluene and hexanes (~1:2).

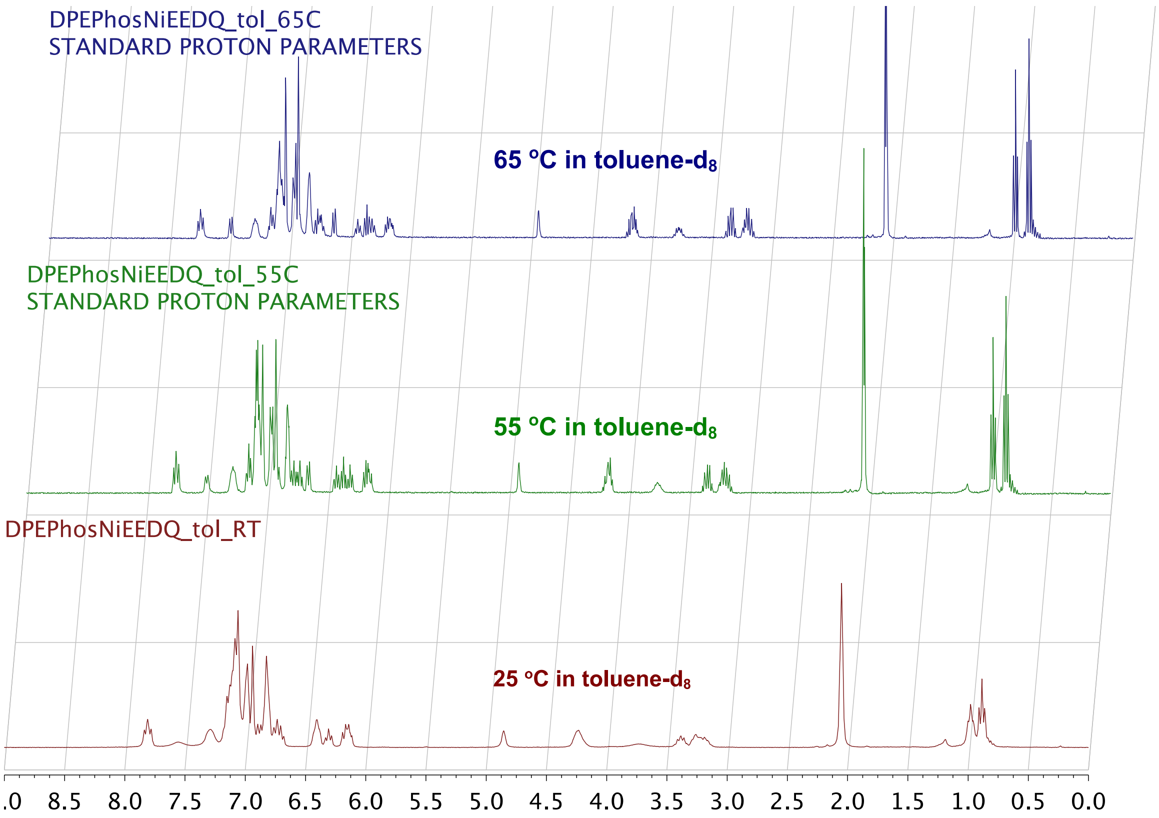
^{1}H NMR (500 MHz, toluene-d$_8$, 60 °C): δ 7.84 (t, *J* = 7.8 Hz, 2H), 7.62 (d, *J* = 8.1 Hz, 1H), 7.42 – 7.32 (m, 2H), 7.24 – 7.00 (m, 14H), 6.96 – 6.83 (m, 6H), 6.81 – 6.71 (m, 2H), 6.46 (t, *J* = 7.6 Hz, 2H), 6.40 (td, *J* = 7.7, 1.6 Hz, 1H), 6.25 – 6.17 (m, 2H), 5.06 – 4.99 (m, 1H), 4.34 – 4.19 (m, 2H), 3.90 – 3.76 (m, 1H), 3.45 (dq, *J* = 9.8, 7.1 Hz, 1H), 3.36 (tdd, *J* = 8.7, 4.0, 2.5 Hz, 1H), 3.27 (dq, *J* = 9.8, 7.1 Hz, 1H), 1.00 (t, *J* = 7.1 Hz, 3H), 0.92 (t, *J* = 7.0 Hz, 3H)

^{13}C NMR (125 MHz, C$_6$D$_6$): δ 159.76 (d, *J* = 9.0 Hz), 159.09 (d, *J* = 12.3 Hz), 154.65, 135.76, 135.48, 134.94 (d, *J* = 14.8 Hz), 133.48 (d, *J* = 13.0 Hz), 133.14 (d, *J* = 20.4 Hz), 132.04, 130.66, 129.70, 129.20, 129.00, 128.68, 128.45, 128.37, 125.57, 125.39, 125.25 (d, *J* = 6.2 Hz), 125.06 (d, *J* = 5.9 Hz), 124.73, 124.09, 122.57 (d, *J* = 7.4 Hz), 116.46, 82.50, 59.10 (d, *J* = 21.6 Hz), 55.55 (d, *J* = 18.6 Hz), 15.51, 14.58. Some peaks obscured by overlap.

^{31}P NMR (121 MHz, C$_6$D$_6$): δ 35.76 (1 P, d, *J* = 36.5 Hz), 32.25 (1 P, d, *J* = 36.6 Hz).

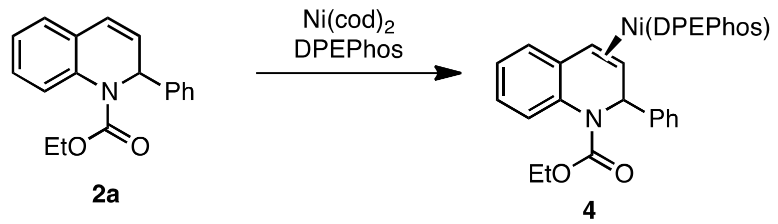
NMR analysis of complex **3** was complicated by rotomers specifically resulting from the carbamate group and the dynamic nature of the DPEPhos ligand. Consequently, variable temperature NMR was conducted with ~20 mg of racemic **3** dissolved in 0.80 mL toluene-d$_8$ and the rotomers were resolved as exhibited by the sharpening of peaks in the ethoxy region (1.0-2.0 ppm), the olefinic region (3.0 to 5.0 ppm), and the aromatic region (6.0 to 8.0 ppm). The spectra as a function of temperature are shown below.

Variable temperature ^1H NMR of racemic ***3*** *in toluene-d_8.*



Synthesis of partially deuterated **3**. In the drybox, a 20-mL scintillation vial was charged with an overn-dried Teflon®-coated stir bar, DPEPhos (558 mg, 1.04 mmol), $Ni(cod)_2$ (280 mg, 1.02 mmol) followed by 3.0 mL toluene. The suspension quickly turned dark red and was stirred until the mixture became homogenous (10 minutes). Subsequently, an approximately ~1:1 mixture of d_0 and d_1-EEDQ (280 mg, ~1.13 mmol) was added to the red suspension. The solution quickly lightened to dark orange and a yellow precipitate began to form. The suspension was stirred for 10 more minutes and diluted with 10 mL of pentanes. The solid was collected on a glass frit and dried in vacuo for an hour. A yellow powder (790 mg, 92% yield) was isolated and identified as the partially deuterated analog of olefin complex **3**. Spectral data were consistent with proteo-**3.**

Synthesis of enantioenriched **3**. (+)-EEDQ (99% ee) was prepared from commercially available racemic **1** by preparative SFC (Chiralcel OJ-H column, 2 cm x 25 cm, 65 mL/min 85:15:1 sCO_2:EtOH:DEA). DPEPhos (0.646 g, 1.200 mmol, 1.1 equiv) and $Ni(cod)_2$ (0.300 g, 1.091 mmol, 1.0 equiv) were combined in a 20-mL scintillation vial equipped with a Teflon® coated stir bar. Toluene (3 mL) was added to the vial and the suspension quickly turned dark red and homogenous upon stirring. The reaction was allowed to stir for 20 minutes at room temperature until a dark orange precipitate formed (indicating the presence of (DPEPhos)Ni(cod)). Subsequently, enantioenriched (+)-EEDQ (0.326 g, 1.309 mmol, 1.2 equiv, 99% ee) was added and the reaction became bright orange and homogenous. Stirring was continued for another hour and a bright yellow precipitate formed. The yellow precipitate was collected by vacuum filtration on a medium frit filter and washed with 20 mL of pentanes. After drying under vacuum, a bright yellow-orange powder (0.906 g, 98% yield) was isolated. $[\alpha]^{20}_D = -237.0$ (Toluene, c=1.00, path length = 1 dm). Spectral data were consistent with racemic complex **3**.

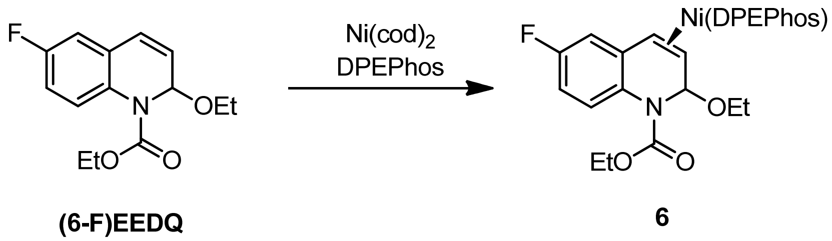


Synthesis of complex **4**. In the drybox, a 2-dram vial was charged with a Teflon®-coated stir bar, DPEPhos (118 mg, 0.22 mmol), Ni(cod)$_2$ (60 mg, 0.22 mmol) and finally 1 mL diethyl ether. The suspension quickly turned dark red and was stirred until the mixture became homogenous (10 minutes). Then, **2a** (63 mg, 0.23 mmol) dissolved in 3 mL hexanes was added and the dark red solution quickly turned pale orange. Stirring was continued for one hour and then the reaction was cooled in the glovebox freezer overnight. A yellow powder precipitated after one day, which was collected on a medium glass fit via filtration. The yellow powder was dried under vacuum to yield 112 mg bright yellow solid identified as **4 (**58 % isolated yield).

^{1}H NMR (500 MHz, toluene-d$_8$, 60 °C): δ 7.89 (d, *J* = 8.9 Hz, 2H), 7.52 – 7.33 (m, 3H), 7.33 – 7.10 (m, 11H), 7.10 – 7.02 (m, 6H), 6.99 (t, *J* = 7.6 Hz, 2H), 6.89 (ddt, *J* = 17.1, 7.6, 3.5 Hz, 5H), 6.80 – 6.69 (m, 3H), 6.49 (td, *J* = 7.8, 1.7 Hz, 1H), 6.42 (q, *J* = 7.3 Hz, 2H), 6.31 – 6.16 (m, 2H), 5.08 (d, *J* = 6.2 Hz, 1H), 4.40 – 4.28 (m, 1H), 4.20 (dq, *J* = 10.7, 7.1 Hz, 1H), 3.98 – 3.78 (m, 1H), 3.39 (tdd, *J* = 8.2, 4.0, 2.0 Hz, 1H), 0.98 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (125 MHz, C$_6$D$_6$): δ 159.77 (d, *J* = 9.3 Hz), 154.67 , 136.46 , 134.92 (d, *J* = 14.9 Hz), 133.60 (d, *J* = 12.9 Hz), 132.13 , 130.64 , 129.68 , 129.02 , 128.39 , 126.76 , 125.33 – 124.87 (m), 124.04 , 122.61 (d, *J* = 7.1 Hz), 116.50 , 14.60.

^{31}P NMR (121 MHz, C$_6$D$_6$): δ 34.51 (1 P, d, *J* = 39.1 Hz), 33.04 (1 P, d, *J* = 39.2 Hz).



Synthesis of complex **6**. The complex was prepared using the general procedure for the preparation of **3**. DPEPhos (0.668 g, 1.240 mmol) and Ni(cod)$_2$ (0.310 g, 1.127 mmol) were weighed out into a 20 ml scintillation vial equipped with a PTFE stirbar in the glovebox and toluene (2.00 ml) was added to dissolve the solids, forming a deep red solution. The solution was then stirred for 20 mininutes before the addition of ethyl 2-ethoxy-6-fluoroquinoline-1(2H)-carboxylate (0.359 g, 1.352 mmol) with 3 ml toluene. The orange solution was then stirred for an additional 10 minutes before the slow addition of 6.5 ml pentanes with rapid stirring. Pentane was added slowly until the precipitate that formed upon addition no longer dissipated with stirring and the solution turned cloudy. The solution was then allowed to stir rapidly until a yellow precipitate begans to form. The reaction was then placed in a –30 °C freezer overnight.

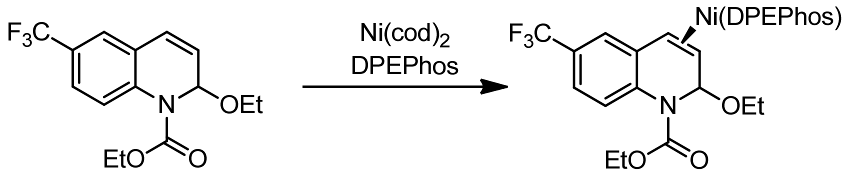
The yellow precipitate was collected by vacuum filtration in the glovebox and rinsed with 10 ml pentanes. The resulting yellow powder was dried under reduced pressure and identified as **6** (0.9227 g, 1.070 mmol, 95 % yield).

^{1}H NMR (400 MHz, C_6D_6, 60 °C): δ 7.86 – 7.72 (m, 2H), 7.52 – 7.43 (m, 1H), 7.37 (td, J = 8.3, 7.7, 3.8 Hz, 2H), 7.25 – 7.00 (m, 14H), 6.99 – 6.82 (m, 5H), 6.76 (t, J = 7.6 Hz, 1H), 6.55 (tdd, J = 8.7, 2.7, 1.2 Hz, 1H), 6.52 – 6.44 (m, 2H), 6.41 (dd, J = 9.6, 2.8 Hz, 1H), 6.26 (t, J = 7.5 Hz, 1H), 6.20 (dd, J = 8.3, 4.3 Hz, 1H), 5.00 (dd, J = 3.9, 2.1 Hz, 1H), 4.30 – 4.11 (m, 2H), 3.90 – 3.73 (m, 1H), 3.43 (dq, J = 9.9, 7.0 Hz, 1H), 3.34 – 3.20 (m, 2H), 1.00 (t, J = 7.1 Hz, 3H), 0.95 (t, J = 7.0 Hz, 3H).

^{13}C NMR (125 MHz, C_6D_6): δ 161.09, 159.74, 159.18, 159.09, 159.00, 140.38, 136.41, 135.17 (d, J = 3.1 Hz), 134.89 (d, J = 3.3 Hz), 134.54 (d, J = 14.0 Hz), 133.71 (d, J = 12.8 Hz), 132.12, 130.87, 129.89, 129.33, 129.23, 129.10, 128.98, 128.67 (d, J = 8.9 Hz), 128.57, 125.86 (d, J = 8.4 Hz), 125.41 (d, J = 3.9 Hz), 125.17 (d, J = 3.9 Hz), 122.69 (d, J = 5.1 Hz), 116.41 (d, J = 3.2 Hz), 111.53 (d, J = 2.7 Hz), 111.35 (d, J = 2.7 Hz), 82.46, 62.41, 58.23 (d, J = 3.0 Hz), 58.06 (d, J = 3.0 Hz), 54.52 (d, J = 18.4 Hz), 15.61, 14.66. Some peaks obscured by overlap.

^{31}P NMR (121 MHz, C_6D_6): δ 35.57 (1 P, d, J = 34.5 Hz), 32.66 (1 P, d, J = 35.1 Hz).

^{19}F NMR (282 MHz, $CDCl_3$): δ –120.79.



(6-CF$_3$)EEDQ

([6-CF$_3$]EEDQ)Ni(DPEPhos)

Synthesis of complex **([6-CF$_3$]EEDQ)Ni(DPEPhos)**. The complex was prepared using the general procedure for the preparation of **3**. DPEPhos (0.431 g, 0.800 mmol) and Ni(cod)2 (0.200 g, 0.727 mmol) were weighed out into a 20 ml scintillation vial equipped with a PTFE stirbar in the glovebox and toluene (3.00 ml) was added to dissolve the solids, forming a deep red solution. The solution was then stirred for 20 mininutes before the addition of ethyl 2-ethoxy-6-(trifluoromethyl)quinoline-1(2H)-carboxylate (0.275 g, 0.873 mmol). The orange solution was then stirred for an additional 10 minutes before the slow addition of 6.5 ml pentanes with rapid stirring. Pentane was added slowly until the precipitate that formed upon addition no longer dissipated with stirring and the solution turned cloudy. The solution was then allowed to stir rapidly until a yellow precipitate began to form. The reaction was then placed in a –30 °C freezer overnight.

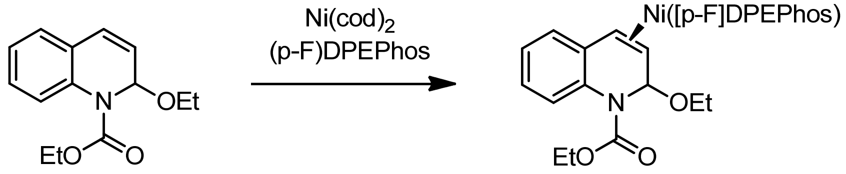
The yellow precipitate was collected by vacuum filtration in the glovebox and rinsed with 10 ml pentanes. The resulting yellow powder was dried under reduced pressure and identified as **([6-CF$_3$]EEDQ)Ni(DPEPhos)** (0.4692 g, 0.514 mmol, 71 % yield).

^{1}H NMR (400 MHz, C_6D_6, 60 °C): δ 7.78 (t, J = 8.7 Hz, 2H), 7.57 (d, J = 8.6 Hz, 1H), 7.40 – 7.29 (m, 3H), 7.24 – 6.97 (m, 14H), 6.95 (t, J = 7.7 Hz, 2H), 6.92 – 6.84 (m, 4H), 6.76 (t, J = 7.5 Hz, 1H), 6.48 (t, J = 7.8 Hz, 1H), 6.41 (t, J = 7.7 Hz, 1H), 6.24 (t, J = 7.4 Hz, 1H), 6.19 (dd, J = 8.4, 4.5 Hz, 1H), 5.00 (dt, J = 4.0, 1.9 Hz, 1H), 4.28 – 4.15 (m, 2H), 3.82 (q, J = 9.6, 8.5 Hz, 1H), 3.48 – 3.34 (m, 1H), 3.34 – 3.16 (m, 2H), 0.99 (td, *J* = 7.2, 1.7 Hz, 3H), 0.94 (td, *J* = 7.0, 1.5 Hz, 3H).

^{13}C NMR (125 MHz, C_6D_6): δ 159.68 (d, *J* = 8.8 Hz), 159.04 (d, *J* = 11.7 Hz), 138.84, 137.89, 136.40, 136.14, 134.91 (d, *J* = 3.2 Hz), 134.63 (d, *J* = 3.2 Hz), 134.46 (d, *J* = 14.0 Hz), 133.53 (d, *J* = 12.7 Hz), 133.17 (d, *J* = 11.3 Hz), 132.13, 130.95, 129.93, 129.33, 129.28 (t, *J* = 22.4 Hz), 128.65 (m), 125.70, 125.32 (dd, *J* = 29.0, 4.0 Hz), 124.81 (d, *J* = 1.8 Hz), 82.59, 62.62, 61.46, 58.06 (dd, *J* = 21.9, 3.0 Hz), 54.08 (dd, *J* = 18.4, 2.6 Hz), 15.58, 14.56. Some peaks obscured by overlap.

^{31}P NMR (121 MHz, C_6D_6): δ 35.44 (1 P, d, J = 34.0 Hz), 32.64 (1 P, d, J = 34.1 Hz).

^{19}F NMR (282 MHz, C_6D_6): δ –61.55.



1 **7**

Synthesis of complex **7**. The complex was prepared using the general procedure. ([p-F]DPEPhos) (0.488 g, 0.800 mmol) and $Ni(cod)_2$ (0.200 g, 0.727 mmol) were weighed out into a 20 ml scintillation vial equipped with a PTFE stirbar in the glovebox and toluene (1.50 ml) was added to dissolve the solids, forming a deep red solution. The solution was then stirred for 20 mininutes before the addition of ethyl 2-ethoxyquinoline-1(2H)-carboxylate (0.216 g, 0.873 mmol). The brown solution was then stirred for an additional 10 minutes before the slow addition of pentanes with rapid stirring. Pentane was added slowly until the precipitate that formed upon addition no longer dissipated with stirring and the solution turned cloudy. The solution was then allowed to stir rapidly until a yellow precipitate begins to form. The reaction was then placed in a –30 °C freezer overnight.

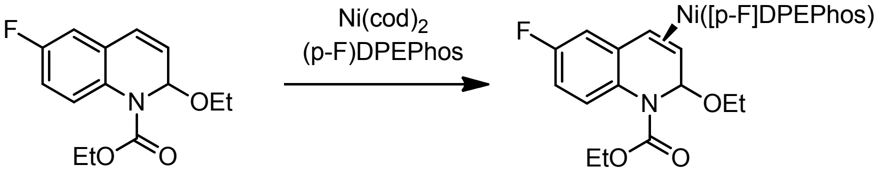
The yellow precipitate was collected by vacuum filtration in the glovebox and rinsed with 10 ml pentanes. The resulting yellow powder was dried under reduced pressure and identified as **7** (0.595 g, 0.649 mmol, 89 % yield).

^{1}H NMR (400 MHz, C_6D_6, 60 °C): δ 7.60 (td, *J* = 8.7, 5.8 Hz, 2H), 7.43 (d, *J* = 8.1 Hz, 1H), 7.19 – 7.04 (m, 2H), 7.02 – 6.89 (m, 7H), 6.87 – 6.74 (m, 7H), 6.71 (t, *J* = 8.5 Hz, 2H), 6.67 – 6.61 (m, 1H), 6.53 (t, *J* = 8.5 Hz, 1H), 6.43 (t, *J* = 7.5 Hz, 2H), 6.31 – 6.18 (m, 2H), 6.08 (dd, *J* = 8.2, 4.3 Hz, 1H), 4.89 (dd, *J* = 3.9, 2.1 Hz, 1H), 4.16 (dt, *J* = 10.4, 5.6 Hz, 1H), 4.06 (dq, *J* = 10.7, 7.0 Hz, 1H), 3.84 – 3.63 (m, 1H), 3.39 (dtd, *J* = 10.1, 8.0, 7.6, 6.6 Hz, 1H), 3.24 (dqd, *J* = 9.5, 7.1, 4.3 Hz, 2H). 1.01 – 0.85 (m, 6H).

^{13}C NMR (126 MHz, C_6D_6): δ 163.91 (d, *J* = 249.4 Hz), 163.82 (d, *J* = 249.3 Hz), 163.69 (d, *J* = 250.1 Hz), 163.33 (d, *J* = 248.9 Hz), 159.62 (d, *J* = 8.7 Hz), 158.84 (d, *J* = 11.9 Hz), 154.69, 137.90, 136.72 (dd, *J* = 16.1, 8.1 Hz), 135.95, 135.44 (dd, *J* = 14.5, 7.9 Hz), 135.02, 133.88, 133.09, 131.84, 131.21, 130.23, 129.33, 128.57, 127.56, 127.00, 125.72 (d, *J* = 4.5 Hz), 125.51, 125.24 (d, *J* = 4.1 Hz), 125.08, 124.44 (d, *J* = 13.5 Hz), 124.11, 122.82 (d, *J* = 5.0 Hz), 122.25, 116.57 (d, *J* = 3.2 Hz), 115.84 (dd, *J* = 20.9, 10.0 Hz), 115.37 (dd, *J* = 20.9, 9.4 Hz), 114.99 (dd, *J* = 20.8, 10.5 Hz), 82.25, 62.45, 61.33, 59.50 (dd, *J* = 21.4, 3.1 Hz), 55.91 (d, *J* = 18.7 Hz), 34.45, 15.41, 14.57, 14.32.

<u>^{31}P NMR (121 MHz, C_6D_6):</u> δ 33.67 (1 P, d, J = 38.4 Hz), 30.75 (1 P, d, J = 38.4 Hz).

<u>^{19}F NMR (282 MHz, $CDCl_3$):</u> δ –111.01, –111.46, –111.75, –112.48 .



(6-F)EEDQ

([6-F]EEDQ)Ni([p-F]DPEPhos)

Synthesis of complex **([6-F]EEDQ)Ni([p-F]DPEPhos)**. ([p-F]DPEPhos) (0.366 g, 0.600 mmol) and Ni(cod)$_2$ (0.150 g, 0.545 mmol) were weighed out into a 20 ml scintillation vial equipped with a PTFE stirbar in the glovebox and toluene (1.00 ml) was added to dissolve the solids, forming a deep red solution. The solution was then stirred for 20 mininutes before the addition of ethyl 2-ethoxy-6-fluoroquinoline-1(2H)-carboxylate (0.174 g, 0.654 mmol). The brown solution was then stirred for an additional 10 minutes before the slow addition of pentanes with rapid stirring. Pentane was added slowly until the precipitate that formed upon addition no longer dissipated with stirring and the solution turned cloudy. The solution was then allowed to stir rapidly until a brown-yellow precipitate begins to form. The reaction was then placed in a –30 °C freezer overnight.

The product was collected by vacuum filtration and rinsed with 10 ml of pentanes. The resulting brown-yellow solid was identified as **([6-F]EEDQ)Ni([*p*-F]DPEPhos)** (0.427 g, 0.457 mmol, 84 % yield).

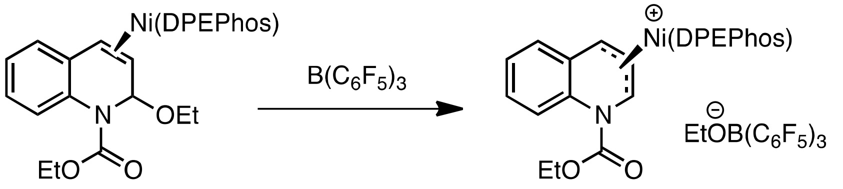
<u>^{1}H NMR (400 MHz, C_6D_6, 60°C):</u> δ 7.68 – 7.47 (m, 2H), 7.32 (d, *J* = 7.1 Hz, 1H), 7.24 – 7.07 (m, 1H), 7.04 – 6.93 (m, 7H), 6.92 – 6.73 (m, 8H), 6.64 – 6.52 (m, 3H), 6.48 (t, *J* = 8.6 Hz, 1H), 6.41 – 6.23 (m, 3H), 6.10 (dd, *J* = 8.2, 4.4 Hz, 1H), 4.88 (dd, *J* = 4.0, 2.1 Hz, 1H), 4.18 – 3.98 (m, 2H), 3.73 (s, 1H), 3.47 – 3.34 (m, 1H), 3.28 (tt, *J* = 10.0, 7.0 Hz, 1H), 3.19 (tdd, *J* = 8.3, 3.9, 1.9 Hz, 1H), 1.01 – 0.90 (m, 6H).

<u>^{13}C NMR (126 MHz, C_6D_6):</u> δ 163.99 (d, *J* = 250.0 Hz), 163.87 (d, *J* = 249.7 Hz), 163.73 (d, *J* = 250.2 Hz), 163.37 (d, *J* = 249.3 Hz), 161.14, 159.45 (d, *J* = 8.9 Hz), 159.22, 158.65, 154.55, 140.01, 137.90, 136.23 (dd, *J* = 15.6, 8.2 Hz), 135.56 (dd, *J* = 14.6, 8.0 Hz), 135.00, 131.77, 131.31, 130.28, 130.02, 129.33, 128.82, 128.57, 127.24, 126.21 (d, *J* = 8.7 Hz), 125.76 (d, *J* = 4.0 Hz), 125.70, 125.25 (d, *J* = 4.1 Hz), 122.82 (d, *J* = 5.1 Hz), 116.43, 116.00 (dd, *J* = 21.0, 10.0 Hz), 115.40 (dd, *J* = 21.1, 9.3 Hz), 115.04 (dd, *J* = 20.8, 10.1 Hz), 111.45 (d, *J* = 21.5 Hz), 108.71 (d, *J* = 22.3 Hz), 82.09, 62.46, 61.36, 58.45 (dd, *J* = 21.9, 2.9 Hz), 54.76 (d, *J* = 18.7 Hz), 34.45, 15.38, 14.54, 14.33.

<u>^{31}P NMR (121 MHz, C_6D_6):</u> δ 33.51 (1 P, d, J = 36.6 Hz), 31.26 (1 P, d, J = 37.2 Hz).

<u>^{19}F NMR (282 MHz, C_6D_6):</u> δ –110.78, –111.02, –111.51, –112.29, –120.42.

Synthesis of nickel allyl complexes.



3 **5-borate**

Synthesis of **5-borate.** (DPEPhos)Ni(EEDQ), **3**, (200 mg, 0.237 mmol, 1.05 equiv) and tris(pentafluorophenyl) borane (115 mg, 0.225 mmol, 1.0 equiv) were added to a 2-dram vial with an oven-dried stir bar in a nitrogen-filled glovebox. The solids were suspended in 5 mL of hexanes and capped with a Teflon®-lined screw-cap. The suspension was stirred vigorously overnight (~16 h) during which time the yellow suspension turned dark red-orange. The solid material was collected on a medium-glass frit and washed with 50 mL of hexanes. The red-orange solids (250 mg, 82% yield) was identified as **5-borate**. A crystal suitable for single X-ray crystallography analysis was grown from a solvent mixture of hexanes:toluene:THF (6:2:1).

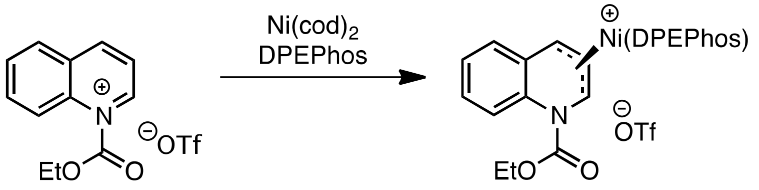
^{1}H NMR (300 MHz, C_6D_6): δ 7.83 (d, *J* = 8.6 Hz, 1H), 7.60-6.00 (br, m, 30H) 6.49 (t, *J* = 7.5 Hz, 1H), 5.63-5.56 (m, 2H), 5.51 (d, *J* = 6.5 Hz, 1H), 3.77 (q, *J* = 6.9 Hz, 2H), 3.48 (ddd, *J* = 97.5, 10.6, 7.1 Hz, 2H), 1.35 (t, *J* = 6.9 Hz, 3H), 0.76 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (125 MHz, C_6D_6): δ 158.32 (d, *J* = 8.4 Hz), 150.75, 149.95 (d, J = 12.1 Hz), 148.07 (d, J = 11.6 Hz), 139.70, 138.01, 136.08, 133.62, 132.73, 130.13, 129.07 (d, J = 9.6 Hz), 127.39, 126.46, 126.00, 125.57, 123.55, 121.53, 120.76, 117.96, 84.29, 81.10, 63.51, 60.26, 19.43, 13.32. Some peaks obscured by overlap.

^{11}B NMR (96 MHz, C_6D_6): δ –2.16.

^{19}F NMR (282 MHz, C_6D_6): δ –132.78 (m), –163.07 (t, J = 20.7 Hz), –166.54 (m).

^{31}P NMR (121 MHz, C_6D_6): δ (referenced to external $O{=}PPh_3$) 19.32 (d, *J* = 848.8 Hz).



6 **5-triflate**

Synthesis of **5-triflate***:* In the dry box, $Ni(cod)_2$ (276 mg, 1.0 mmol, 1.03 equiv) and DPEPhos (551 mg, 1.02 mmol, 1.05 equiv) were dissolved in 3 mL THF in a 20-mL scintillation vial equipped with an oven-dried Teflon®-coated stir bar. The quinolinium triflate (340 mg, 0.97 mmol, 1.0 equiv) was added to the dark red reaction, which was then diluted with 3 mL THF. The resulting suspension was stirred for 1 hour at room temperature. The reaction was diluted with 5 mL of pentanes and filtered. The red-orange solid was collected by vacuum filtration on a glass frit and dried in vacuo for one hour. The product was isolated as 857 mg of a bright red-orange solid (93% isolated yield). A crystal suitable for single X-ray crystallography analysis was grown from a solvent mixture of hexanes and dichloromethane (~1:1).

^{1}H NMR (300 MHz, CD_2Cl_2): δ 8.65 (s, 1H), 8.00-6.35 (br, 30 H), 6.82 (t, *J* = 7.5 Hz, 1H), 5.75 (dd, *J* = 14.5, 6.8 Hz, 2H), 5.54 (t, *J* = 6.3 Hz, 1H), 3.82 (ddq, *J* = 68.1, 10.6, 7.1 Hz, 2H), 1.07 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (125 MHz, CD_2Cl_2): δ 158.56, 151.37, 134.71, 133.84, 133.09, 131.60, 130.98, 130.84, 130.73, 129.52 (d, J = 9.7 Hz), 129.18, 126.84, 126.19, 124.34, 121.31, 121.27, 82.20, 80.86, 64.07, 14.00. Some peaks obscured by overlap.

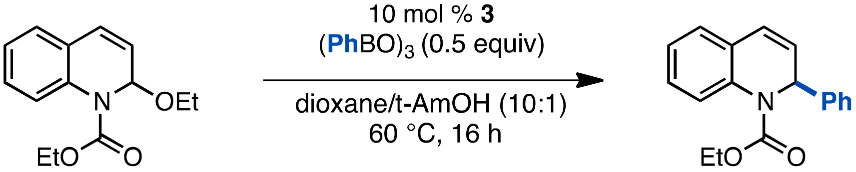
^{19}F NMR (282 MHz, CD_2Cl_2): δ –78.81.

^{31}P NMR (121 MHz, CD_2Cl_2): δ(referenced to external O=PPh_3) 19.07 (d, J = 906.3 Hz).

D) Comparison of activity between DPEPhos and PPh_3

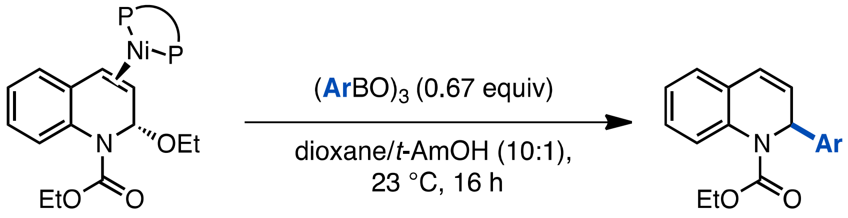
It was shown that a Ni(cod)$_2$/DPEPhos (10 mol%) catalyst system was effective at 60 °C, providing 60% yield of **2a** after 16 h compared with 66 % yield with 10 mol % Ni(cod)$_2$ and PPh_3 under the same conditions. Nevertheless, a significant rate difference was observed between PPh_3 and DPEPhos ligands. In order to compare the two ligands under equivalent ligand stoichiometry and to exclude the possibility of cyclooctadiene affecting the catalyst, we prepared the triphenylphosphine analog of **3** using the same procedure and compared its catalytic activity with that of **3**. While the reaction of **1** with *p*-fluorophenyl boronic acid using **3** as a catalyst (10 mol%) showed only trace product (<1%) after 3 hours at 23 °C (by ^{19}F NMR), the reaction using the triphenylphosphine analog provided the product in 14% yield after 3 hours.

E) Catalytic reactions with racemic 3.



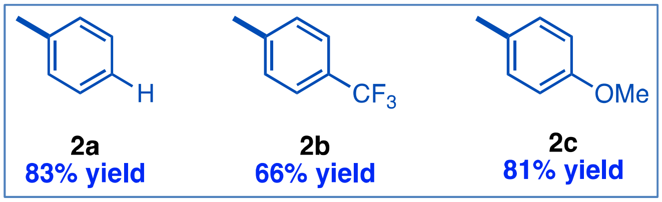
In a nitrogen-filled glovebox, EEDQ (120 mg, 0.49 mmol, 1.0 equiv), phenyl boroxine (75 mg, 0.24 mmol, 0.5 equiv), **3** (41 mg, 0.049 mmol, 0.1 equiv) were added to a 30-mL screw cap tube equipped with an oven-dried Teflon®-coated stir bar. Dioxane (15 mL) and *t-amyl* alcohol (1.5 mL) were added to the solids. The tube was sealed with a Teflon®-coated screw cap and electrical tape. The reaction was removed from the glovebox and heated at 60 °C in an oil bath until the orange color dissipated (turned greenish). The solvent was removed under reduced pressure. The crude green reaction mixture was taken up in 2 mL of toluene and purified using flash chromatography (ethyl acetate/hexane). Reaction was repeated twice. Isolated yields were 77.3 mg (52% yield) and 86.1 mg (57% yield). Average yield was calculated to be 54 %. Spectral data were consistent with the expected product **2a**.

F) Stoichiometric arylation of 3 with boroxines.



3 **2**

In the glovebox, aryl boroxine (0.198 mmol, 0.67 equiv) and **3** (250 mg, 0.296 mmol, 1.0 equiv) were added to a 30-mL screw cap tube charged with a Teflon®-coated stir bar. Solvent (13.3 mL dioxane and 1.33 mL *t-amyl* alcohol) was added and the tube was sealed with a Teflon®-lined cap and electrical tape. The reaction was removed from the glovebox and stirred overnight at room temperature. After 16 hours, dioxane and *t*-AmOH were removed under reduced pressure. The crude was purified on silica gel using 0% to 10% ethyl acetate/hexane as the eluent. The yields for phenyl boroxine, *para*-trifluoromethylphenyl boroxine, and *para*-methoxyphenyl boroxine were 68 mg, 67 mg, and 74 mg, respectively. The percent yields are reported in the box below. ***Note:*** The reactions turned dark red upon addition of solvent and eventually turn orange and finally dark green with precipitation of nickel black.

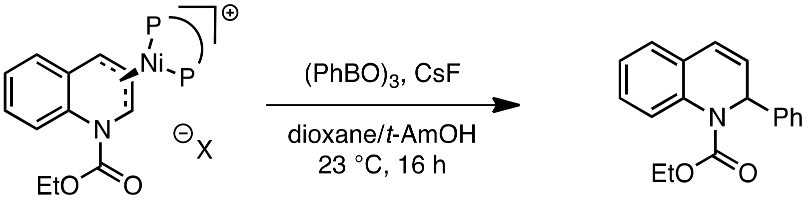


2a 83% yield

2b 66% yield

2c 81% yield

G) Stoichiometric arylation of nickel allyl complexes with phenyl boroxine.



5 **2a**

*Stoichiometric reaction between **5-borate** and phenyl boroxine.* In the dry box, phenyl boroxine (31 mg, 0.099 mmol, 0.67 equiv) and cesium fluoride[11] (45 mg, 0.296 mmol, 2.0 equiv) were added to a 10-mL threaded tube with a Teflon®-coated stir bar and Teflon®-lined cap. The solids were suspended in solvent (6.7 mL dioxane and 0.67 mL t-amyl alcohol) and stirred vigorously for 3 hours until dissolution occurred. **5-borate** (200 mg, 0.148 mmol, 1.0 equiv) was then added

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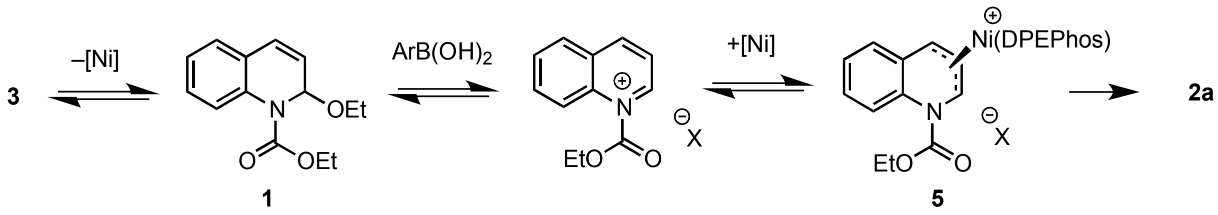
[11] A base is required in this case to activate the boroxine for transmetalation because abstraction/removal of the ethoxide from the Lewis acidic $B(C_6F_5)_3$ is highly unfavorable. As such a few different bases were screened for this reaction. They included CsF, KOH, Na_2CO_3, KOEt, KO^tBu, and NaO^tBu. The most effective/reactive base was determined to be CsF with KOEt and KOH also showing some product formation.

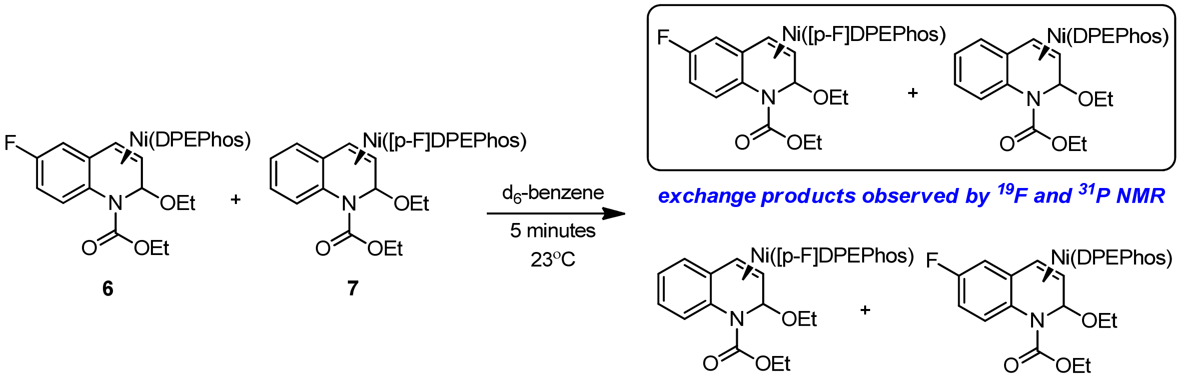
to the solution resulting in a dark red suspension. The reaction was sealed with electrical tape and removed from the glovebox. After stirring began, the dark red precipitate dissolved and stirring was continued at room temperature overnight. After 16 hours, dioxane and *t*-AmOH were removed under reduced pressure. The crude was suspended in toluene and filtered to remove solid salts. The toluene was then removed under reduced pressure. The crude material was purified on silica gel using ethyl acetate/hexane as the eluent. The isolated yield of **2a** for the reaction was 27 mg (65 % yield). Spectral data was consistent with the expected product.

*Stoichiometric reaction between **5-triflate** and phenyl boroxine.* In the dry box, phenyl boroxine (31 mg, 0.099 mmol, 0.67 equiv) and cesium fluoride (45 mg, 0.296 mmol, 2.0 equiv) were added to a 10-mL threaded tube with a Teflon®-coated stir bar and Teflon®-lined cap. The solids were suspended in solvent (6.7 mL dioxane and 0.67 mL t-amyl alcohol) and stirred vigorously for 2 hours until dissolution occurred. **5-triflate** (140 mg, 0.148 mmol, 1.0 equiv) was then added to the solution resulting in a dark red-orange suspension. The reaction was sealed with electrical tape and removed from the glovebox. After stirring began, the dark red-orange precipitate dissolved and stirring was continued at room temperature overnight. After 16 hours, dioxane and *t*-AmOH were removed under reduced pressure. The crude was suspended in toluene and filtered to remove solid salts. The toluene was then removed under reduced pressure. The crude material was purified on silica gel using ethyl acetate/hexane as the eluent. The isolated yield of **2a** for the reaction was 29 mg (70 % yield). Spectral data were consistent with the expected product.

H) Exchange experiments

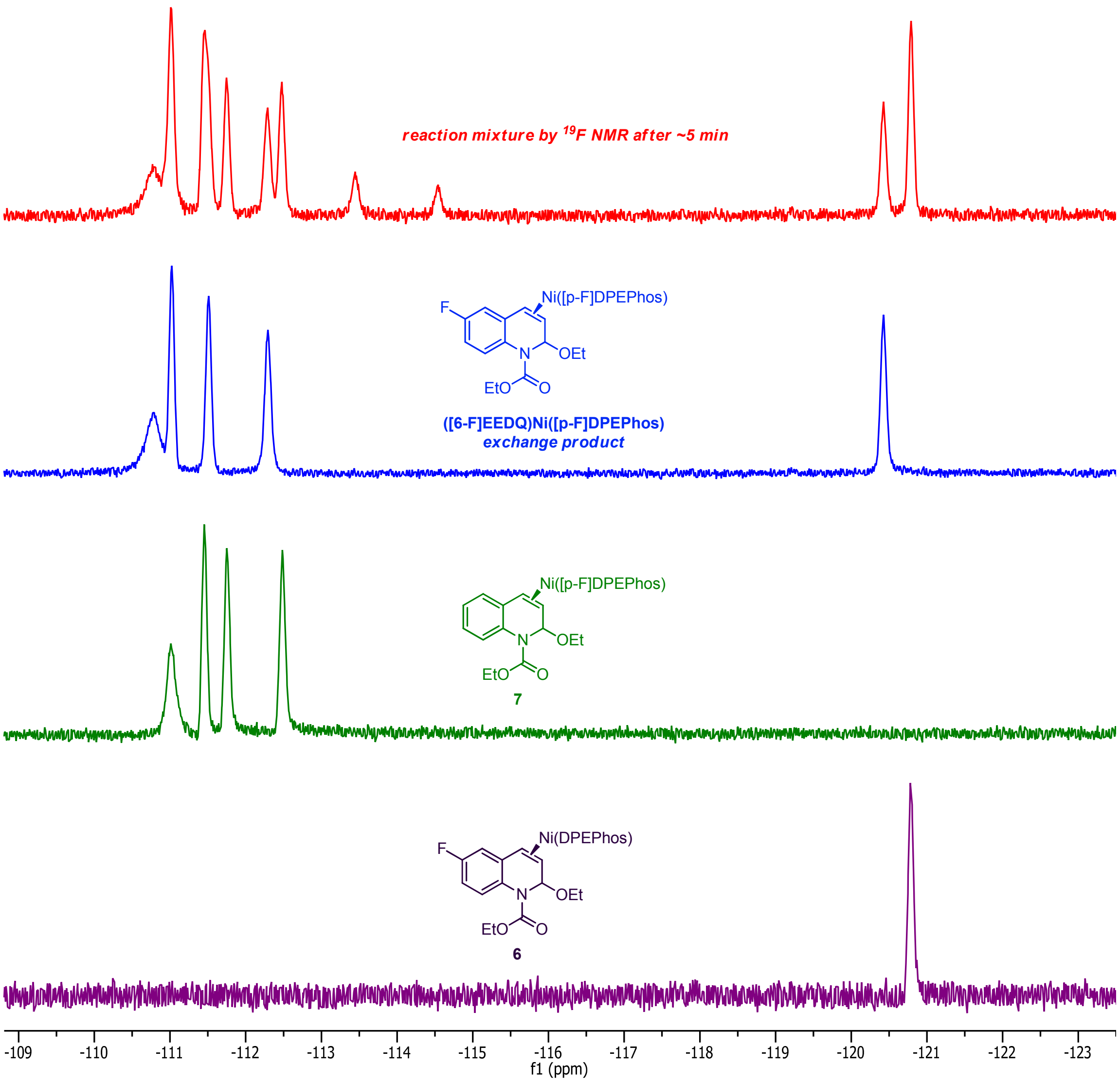


In order for an S_N1 mechanism such as that in Scheme 1 path (i) to be stereoconvergent from **3**, Ni must dissociate prior to ionization. An exchange experiment was conducted in order to determine whether Ni can dissociate from complex **3** as shown below:

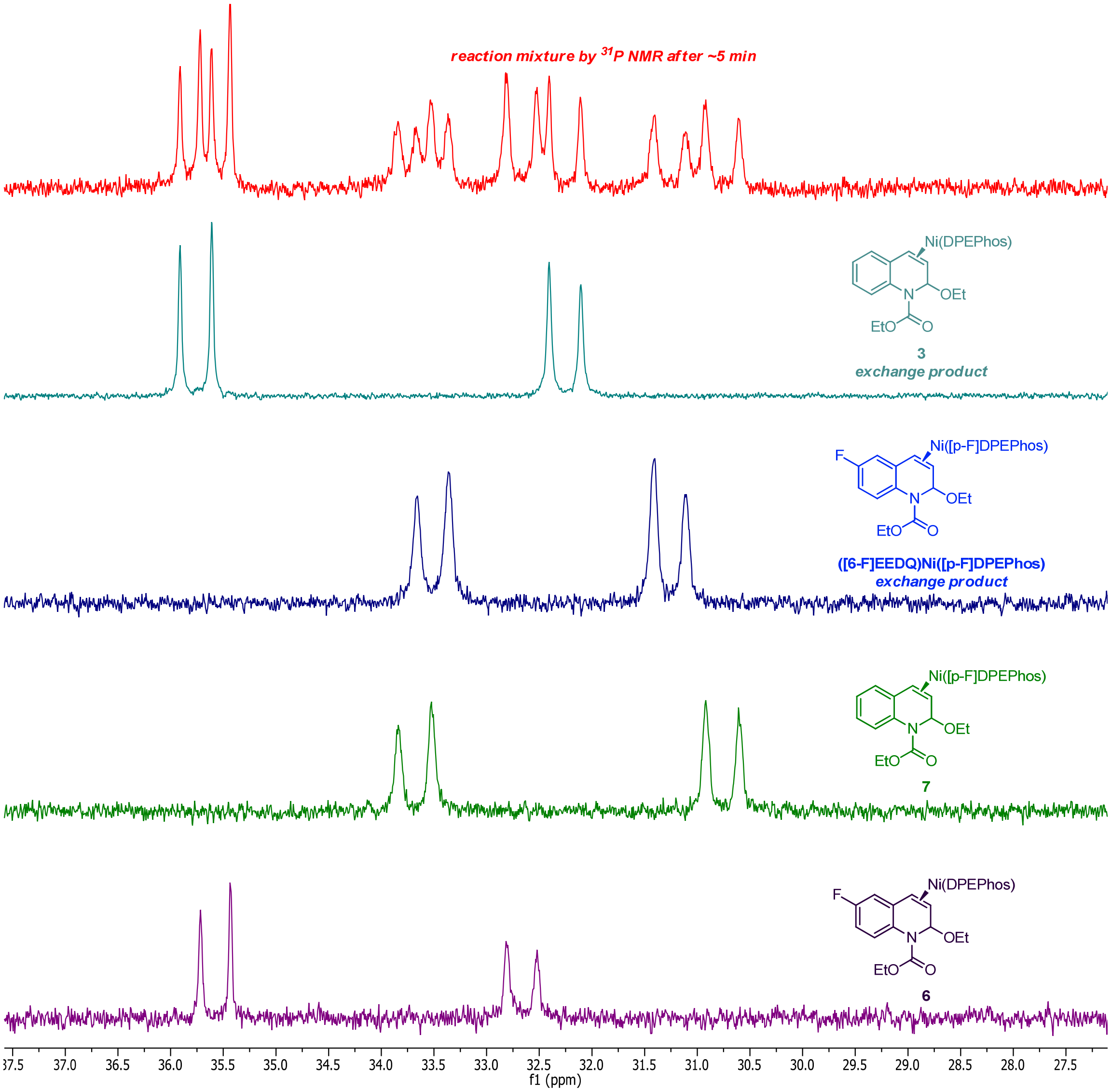


Exchange expermient. **6** (31.9 mg, 0.035 mmol) and **7** (30 mg, 0.035 mmol) were weighed out inside the glovebox into an oven-dried vial equipped with a PTFE stirbar. d_6-Benzene (Volume: 1.5 ml) was added and the reaction was stirred until all solids were dissolved. 0.7 ml of the reaction was then transferred to a J. Young tube and monitored by NMR after 5 minutes. Presence of exchange products indicates olefin dissociation.

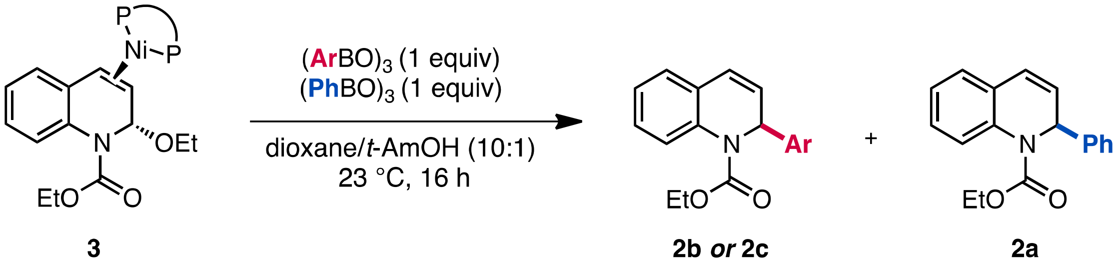
^{19}F NMR of reaction after 5 min and individual reaction components



^{31}P NMR of reaction after 5 min and individual reaction components

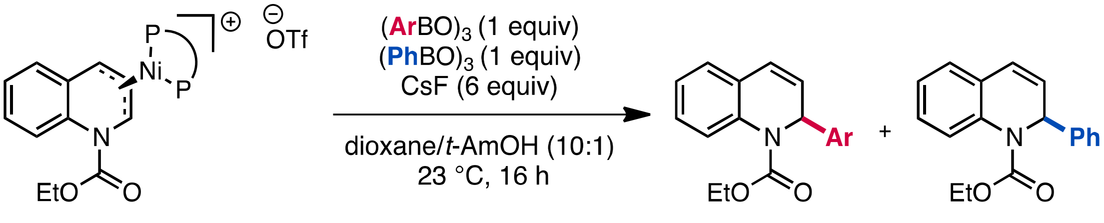


I) *Competition experiments.*



*Competition experiment with **3** and electronically different boroxines.* In the glovebox, complex **3** (40.0 mg, 0.047 mmol) was added to a 10-mL screw cap tube equipped with an oven-dried Teflon®-coated stir bar. Teflon® tape was also wrapped around the tube's threads. In a separate 2-dram vial, a boroxine mixture was prepared (6 equiv of aryl group) and dissolved in 2.2 mL dioxane/*t*-AmOH(10:1). The boroxine mixture consisted of phenyl boroxine (14.6 mg, 0.047 mmol, 1 equiv) and **either** *para*-trifluoromethylphenyl boroxine (24.2 mg, 0.047 mmol, 1 equiv) or *para*-methoxyphenyl boroxine (18.9 mg, 0.047 mmol, 1.0 equiv). The solution containing the boroxine mixture was added to the tube containing **3** and sealed with a cap and electrical tape. The tube was removed from the glovebox and stirred a room temperature for 16 hours. Analysis by GC and LCMS showed complete consumption of EEDQ and the product ratio was measured by GC. Each competition reaction (phenyl vs. *para*-CF_3 and phenyl vs. *para*-MeO) was done in duplicate. The results of the competition experiments are shown below. We found that CF_3 is favored over H which is favored over MeO by a ratio of 9.5:2.3:1.0.

Experiment	Relative Area *p*-CF_3	Relative Area *p*-H	Relative Area *p*-MeO
1A	4.5	1.0	N/A
1B	4.0	1.0	N/A
2A	N/A	2.4	1.0
2B	N/A	2.1	1.0

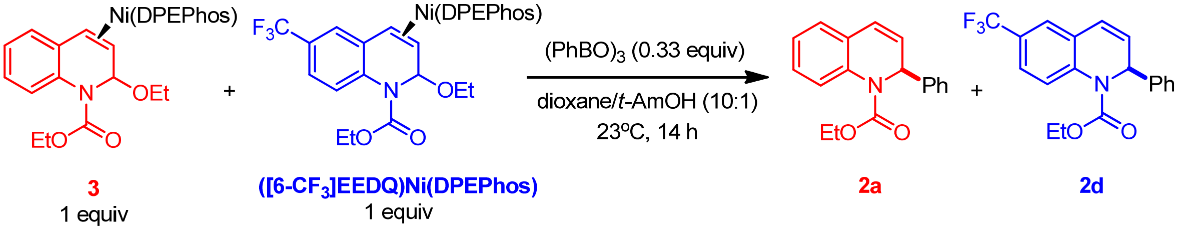


5-triflate **2b *or* 2c** **2a**

Competition experiment with 5-triflate and electronically different boroxines. In the glovebox, complex **5-triflate** (44.6 mg, 0.047 mmol) was added to a 10-mL screw cap tube equipped with an oven-dried Teflon®-coated stir bar. Teflon® tape was also wrapped around the tube's threads. In a separate 2-dram vial, a boroxine mixture (6 equiv of aryl group) and CsF (42.8 mg, 0.282 mmol, 6 equiv) was prepared and dissolved in 2.2 mL dioxane/*t*-AmOH(10:1). The boroxine mixture consisted of phenyl boroxine (14.6 mg, 0.047 mmol, 1 equiv) and **either** *para*-trifluoromethylphenyl boroxine (24.2 mg, 0.047 mmol, 1 equiv) or *para*-methoxyphenyl boroxine (18.9 mg, 0.047 mmol, 1.0 equiv). The suspension of boroxines and CsF was stirred for 2-3 hours at room temperature until dissolution occurred. The boroxine mixture/CsF solution was added to the tube containing **5-triflate** and sealed with a cap and electrical tape. The tube was removed from the glovebox and stirred a room temperature for 20 hours. Analysis by GC and LCMS showed complete consumption of EEDQ and the product ratio was measured by GC.

The results of the competition experiments are shown below. We found that CF_3 is favored over H which is favored over MeO by a ratio of 1.8:1.1:1.0.

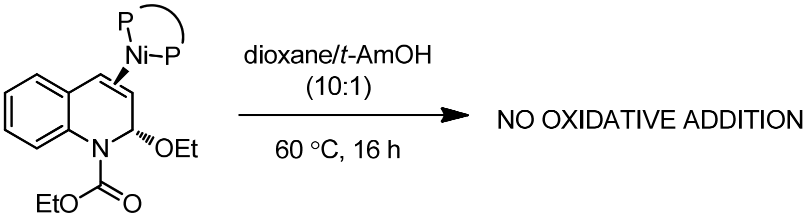
Experiment	Relative Area *p*-CF_3	Relative Area *p*-H	Relative Area *p*-MeO
1A	1.5	1.0	N/A
1B	1.8	1.0	N/A
2A	N/A	1.1	1.0
2B	N/A	1.1	1.0



Competition experiment of electronically different EEDQ olefin complexes with phenyl boroxine. **([6-CF3]EEDQ)Ni(DPEPhos)** (43.2 mg, 0.047 mmol, 1 equiv) and **3** (40.0 mg, 0.047 mmol, 1 equiv) weighed into an oven-dried threaded tube equipped with a PTFE stirbar in the glovebox. A mixture of dioxane (1.500 ml):tAmOH (0.200 ml) was added to dissolve the mixture and the solution was allowed to stir vigorously for 10 minutes. Phenyl boroxine (4.87 mg, 0.016 mmol, 0.33 equiv) in 0.5 ml dioxane was added and the vial was capped, sealed with electrical tape, and brought out of the glovebox. The reaction was allowed to stir for 16 hours at 23 °C before analysis by GC. We found that 6-H EEDQ is favored over 6-CF_3 EEDQ by a ratio of 3.1:1.0, consistent with the formation of a cationic intermediate.

Experiment	Relative Area 6-H	Relative Area 6-CF_3
1A	3.2	1.0
1B	3.0	1.0
Relative areas corrected using response factor.		

J) Oxidative addition studies with enantioenriched 3



3
99% ee

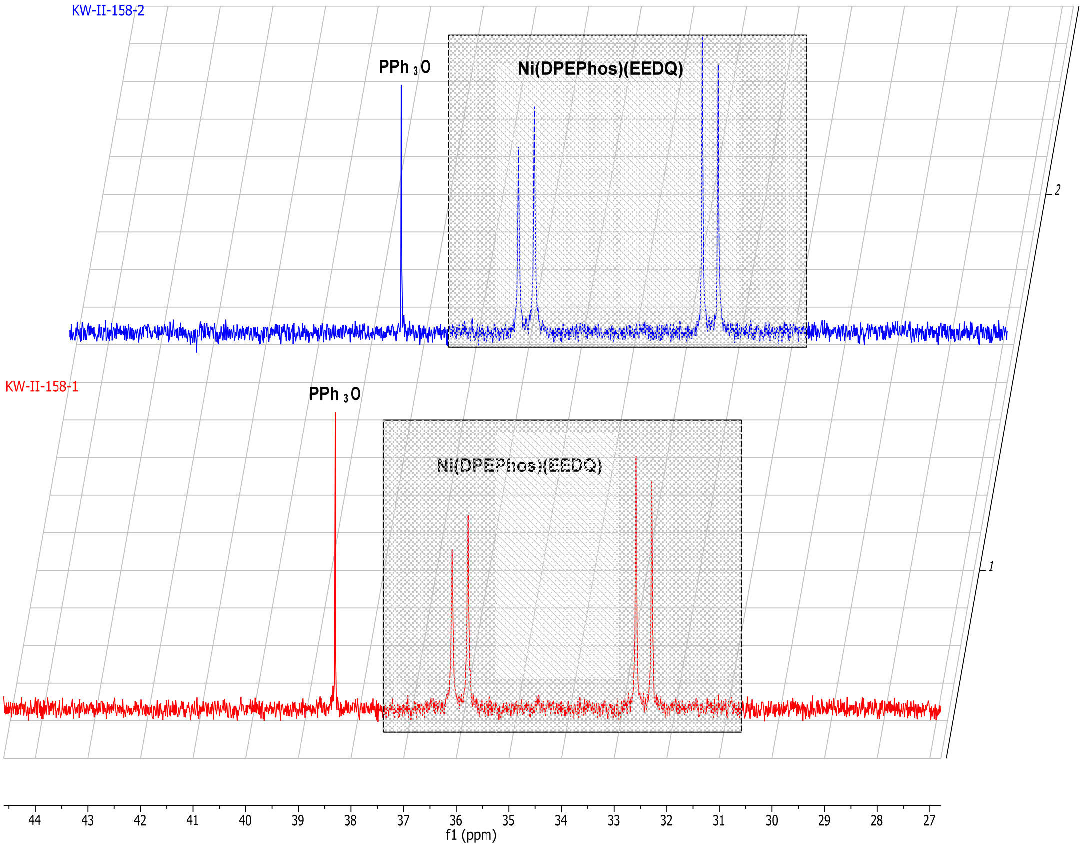
Oxidative addition studies in dioxane/t-AmOH. (DPEPhos)Ni((+)-EEDQ) (10 mg) was added to 1.1 ml dioxane/*t*-AmOH (10:1). The mixture was allowed to stir rapidly for 10 minutes resulting in a bright yellow suspension. The mixture was then transferred to a J. Young tube and a capillary containing triphenylphosphine oxide dissolved in d_8-toluene was added and the tube sealed. The initial ^{31}P and ^{1}H NMR spectra were measured. The olefin complex was subsequently heated at 60 °C for 16 hours. NMR analysis of the reactionwas conducted. Over the course of the reaction no reaction was observed by either ^{31}P or ^{1}H NMR. The data for the ^{31}P NMR analysis are shown below including the spectra taken at 0 hours and 16 hours.

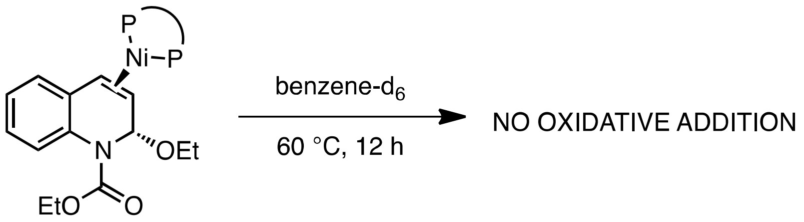
Time (h)	PPh_3O		DPEPhosNiEEDQ (**complex 3**)				Average Internal Ratio*	% Conv**
	δ (ppm)	Area	δ (ppm) Pk 1	Area Pk 1	δ (ppm) Pk 2	Area Pk 2		
0	38.3	1	35.9	4.4	32.4	4.4	4.4	N/A
16	38.3	1	35.9	5.0	32.4	5.4	5.2	-19.9

*Average Internal Ratio = (Pk 1 Area + Pk 2 Area/2)

Negative conversion results from increased solubility of **3 in dioxane/*t*-AmOH at 60 °C

Analysis of ^{31}*P NMR over time (initial = red; 16 hr = blue)*





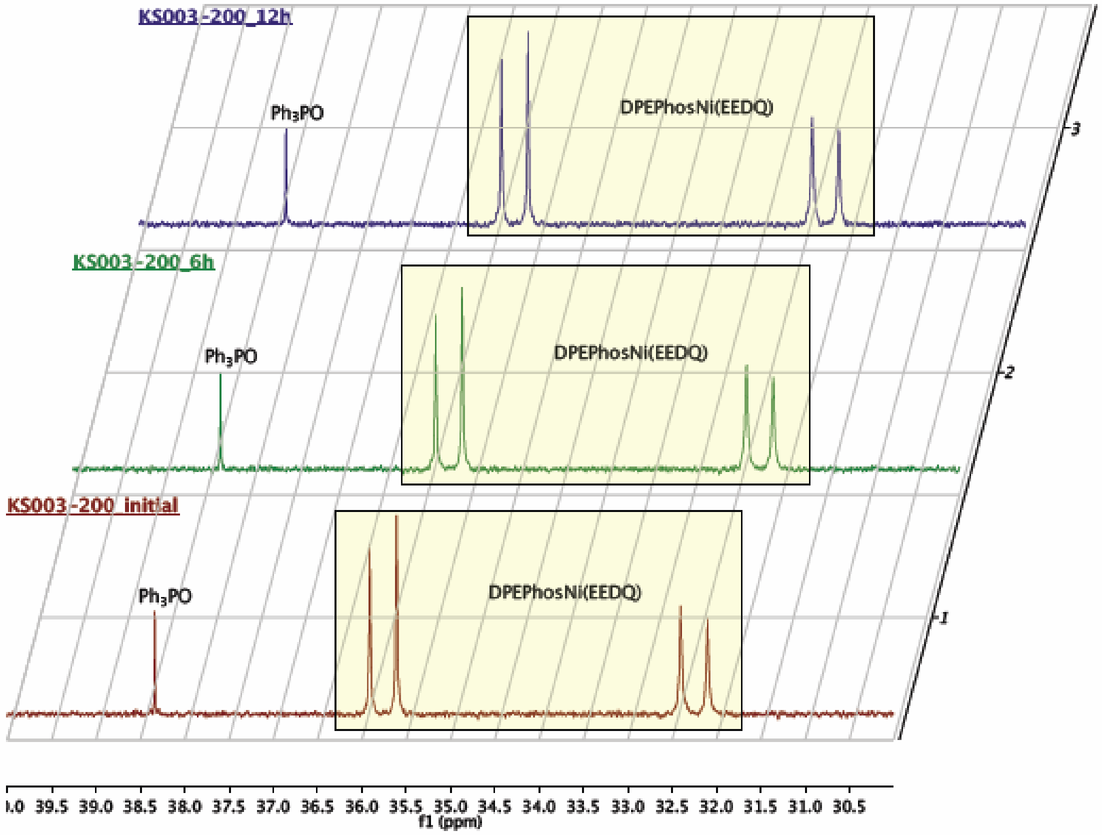
3
99% ee

Oxidative addition studies in C_6D_6. (DPEPhos)Ni((+)-EEDQ) (20 mg) was added to 1.0 mL of C_6D_6. The mixture was dissolved with rapid stirring resulting in a dark amber solution. The solution was transfered to a J. Young tube and monitored at 6 and 12 hours according to the procedure above. Over the course of the reaction no reaction was observed by ^{31}P or ^{1}H NMR.

Time (h)	PPh$_3$O		DPEPhosNiEEDQ **(complex 3)**				Average IR*	% Conv.
	δ (ppm)	Area	δ (ppm) Pk 1	Area Pk 1	δ (ppm) Pk 2	Area Pk 2		
0	38.3	1.0	35.8	11.8	32.3	11.3	11.6	N/A
6	38.3	1.0	35.8	11.1	32.3	10.6	10.9	6.0
12	38.3	1.0	35.8	11.8	32.3	10.9	11.4	1.7

*Average IR = average internal ratio = (Pk 1 Area + Pk 2 Area/2)

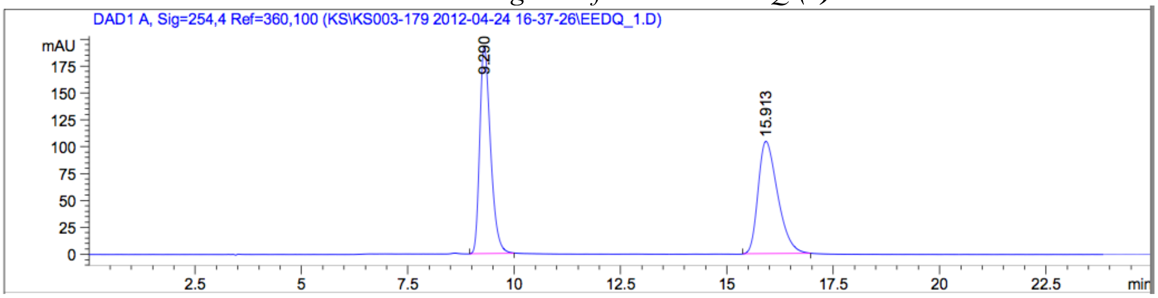
Analysis of ^{31}P NMR over time (initial = red; 6 hr = green; 12 hr = blue)



K) Stereochemical studies with enantioenriched 3.

EEDQ was analyzed by chiral HPLC. Separation of enantiomers was achieved using a Chiral OJ-H column; 0.46 cm x 25 cm; 95:5 hexanes:isopropanol, 1mL/min; $t_R(–)$ = 9.3 min, $t_R(+)$ = 15.9 min, 254 nm).

HPLC chromatogram of racemic EEDQ ***(1)***.

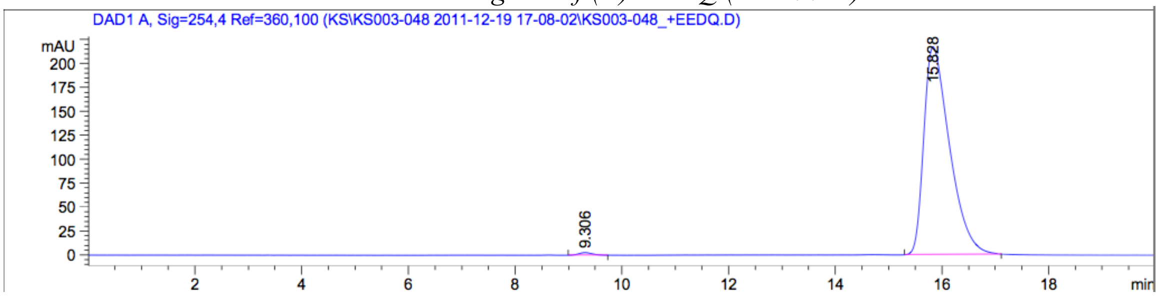


```
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]        %
----|-------|----|-------|----------|----------|--------|
   1   9.290 BB    0.2698 3400.00562  192.78893  50.2334
   2  15.913 BB    0.4912 3368.41040  104.72926  49.7666

Totals :                  6768.41602  297.51819
```

HPLC chromatogram of (+)-EEDQ (98.7 % ee)



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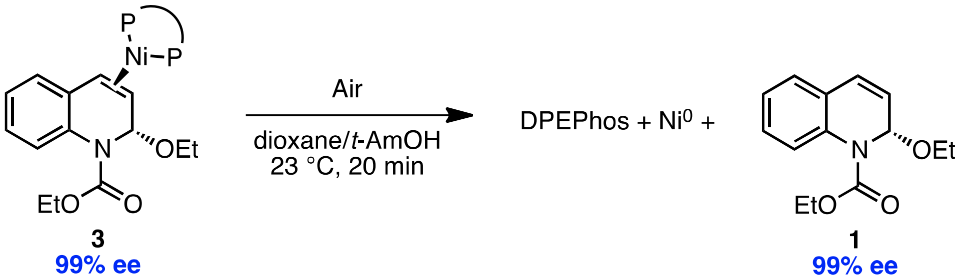
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

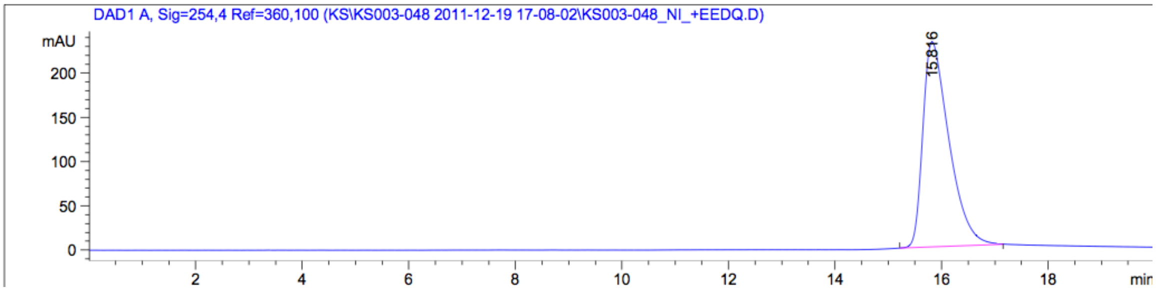
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]        %
----|-------|----|-------|----------|----------|--------|
   1   9.306 BB    0.2667   47.55773    2.71075   0.6478
   2  15.828 BB    0.5080 7293.57080  217.06354  99.3522

Totals :                  7341.12853  219.77429
```



*Effect of (DPEPhos)Ni binding on stereochemistry of enantiopure **1**.* About 30 mg enantioenriched **3**, (DPEPhos)Ni((+)-EEDQ), was added to 1.5 mL dioxane/*t*-amyl alcohol (10:1) and stirred in air for 20 minutes. The yellow suspension eventually turned dark greenish and nickel precipitated. The slurry was passed through a small celite plug and the solvent was removed. The residue was dissolved in 2 mL 5% isopropanol/hexanes and filtered through a celite pad. The resultant solution was analyzed by chiral HPLC to measure the enantiomeric excess of the recovered EEDQ. It was found that the secondary isomer was not present in the recovered EEDQ, so ee is greater than 99%. Thus, the binding of nickel does not effect the stereochemical integrity of EEDQ.

*HPLC chromatograph of recovered EEDQ from oxidizing enantiopure **3***



```
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]        %
----|-------|----|-------|----------|----------|--------|
   1  15.816 BB    0.5170 7928.61572  231.85246 100.0000

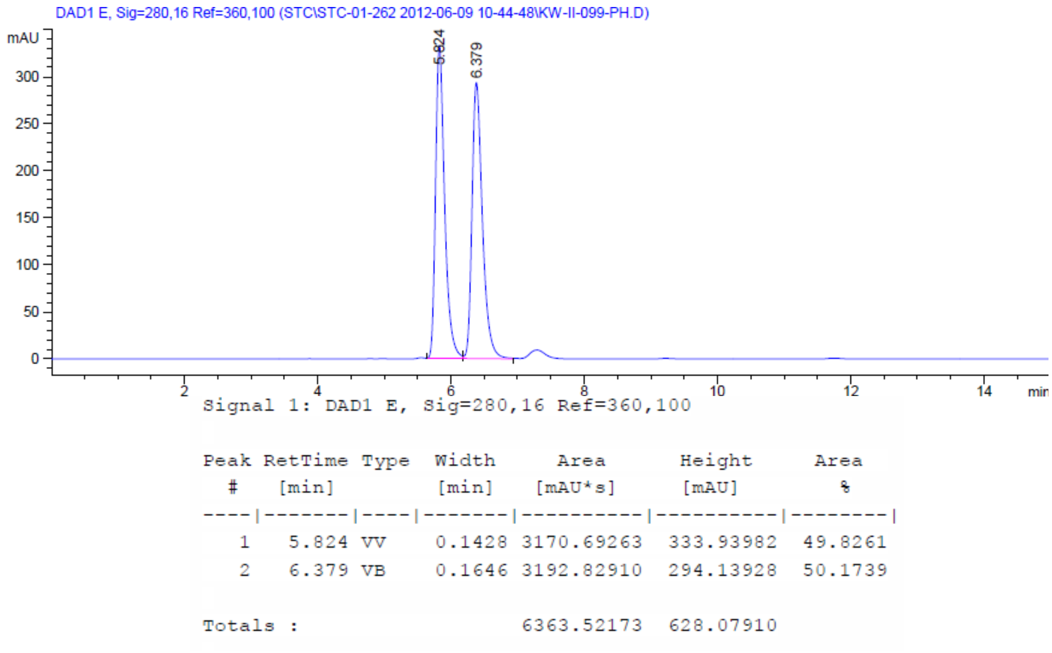
Totals :                  7928.61572  231.85246
```

*Effect of temperature on enantioenriched **3**.* When the oxidative addition study was conducted with enantioenriched **3**, the reaction was then exposed to air. Subsequently, the recovered EEDQ was analyzed by chiral HPLC. It was found that heating complex **3** at 60 °C for 12 hours did not induce racemization as the recovered EEDQ had an ee of 99.6%.

L) Stoichiometric reactions of enantioenriched 3 with various nucleophiles

Enantiomeric excess of **2a** was determined by chiral HPLC (Chiralpak AS-H, 0.46 cm x 25 cm, 97:3 hexanes:isopropanol, 1.0 mL/min, t_R(major) = 6.31 min, t_R(minor) = 5.82 min, 280 nm). A racemic trace is shown below.

HPLC chromatogram of racemic N-ethoxycarbamate-2-phenyl-1,2-dihydroquinoline ***(2a)***

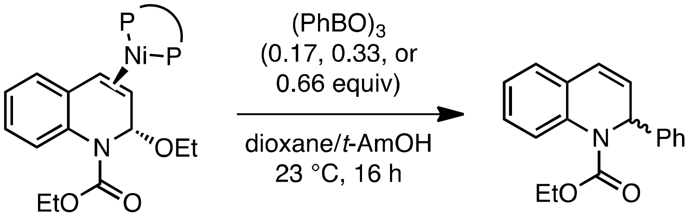


```
Signal 1: DAD1 E, Sig=280,16 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]        %
----|-------|----|-------|----------|----------|--------|
   1   5.824 VV    0.1428 3170.69263  333.93982  49.8261
   2   6.379 VB    0.1646 3192.82910  294.13928  50.1739

Totals :                  6363.52173  628.07910
```

Reactions with enantioenriched 3 and boroxines



3

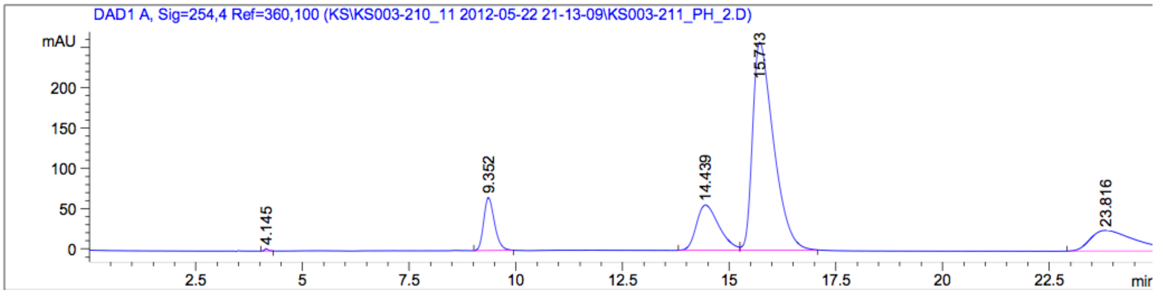
99% ee

2a

Reactions with phenyl boroxine. In the glovebox, 40 mg of enantioenriched **3** (0.047 mmol, 1.0 equiv) was added to a 7-mL screw cap tube charged with a Teflon®-coated stir bar. In a separate 2-dram vial, boroxine (0.17, 0.33, or 0.67 equiv) was dissolved in 2.2 mL solvent (10:1 dioxane:*t*-AmOH). The boroxine solution was added to the tube containing **3** and was sealed with a cap and electrical tape. The reaction was removed from the glovebox and stirred for a certain time depending on the equivalents of boroxine added.

0.17 equiv boroxine: The reaction was quenched after 2 hours with 3.0 mL saturated sodium bicarbonate and extracted with diethyl ether (6 mL). The organic layer was dried over sodium sulfate and passed through a small silica gel plug (that had been washed with 2 mL of triethylamine). The ether was removed and the crude was dissolved in 2 mL 5% isopropanol in hexanes. The crude contained recovered EEDQ and arylated product which was analyzed by chiral HPLC. It was found that the recovered EEDQ was 72% enriched and the product **2a** was essentially racemic with an enantiomeric excess of 6.7%.

HPLC chromatograph of crude reaction mixture from 0.17 equiv boroxine (EEDQ assay)

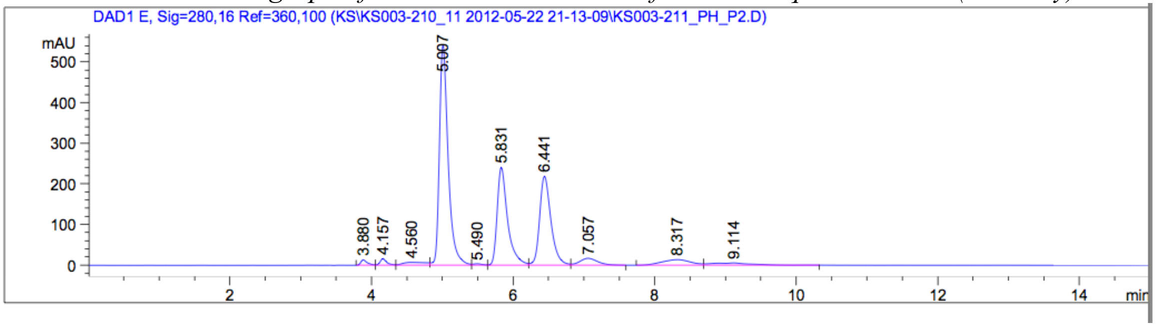


```
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   4.145 BB    0.0954   17.63058    2.80135   0.1271
   2   9.352 BB    0.2724 1158.74878   65.49090   8.3534
   3  14.439 BV    0.5606 2066.60986   56.24945  14.8982
   4  15.713 VB    0.5178 8837.78223  257.87625  63.7116
   5  23.816 BBA   1.0033 1790.77039   25.68716  12.9097

Totals :                  1.38715e4   408.10511
```

*HPLC chromatograph of crude reaction mixture from 0.17 equiv boroxine (**2a** assay)*

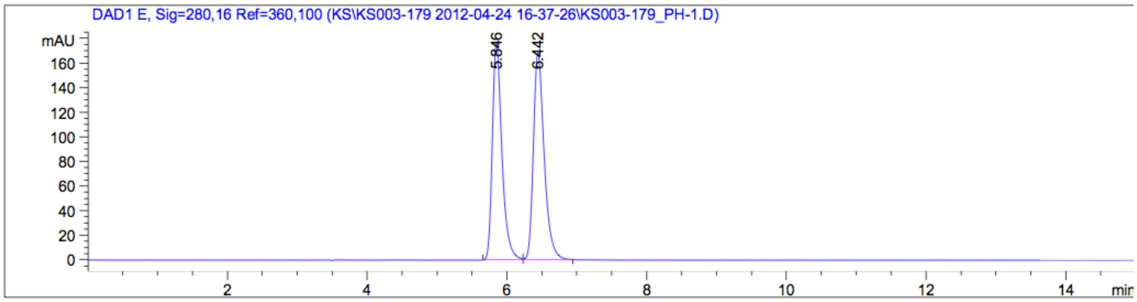


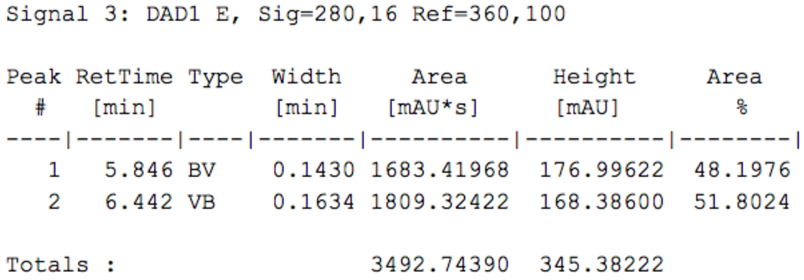
```
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak RetTime Type  Width      Area       Height      Area
  #    [min]        [min]    [mAU*s]     [mAU]        %
----|-------|----|-------|----------|----------|--------|
   1   3.879 BV    0.0938  775.95154  122.61273   3.6264
   2   4.130 VV    0.1275   75.24423    8.47816   0.3516
   3   4.568 VV    0.3257  451.09689   19.66245   2.1082
   4   5.007 VV    0.1300 1.21712e4  1419.58240  56.8813
   5   5.493 VV    0.1332  121.63680   13.49506   0.5685
   6   5.834 VV    0.1853 2894.90039  220.38387  13.5291
   7   6.438 VV    0.1769 2531.41919  212.56038  11.8304
   8   7.057 VB    0.2690  835.87030   47.57892   3.9064
   9   8.325 BV    0.4162  982.49792   36.25379   4.5916
  10   8.902 VB    0.4084  557.73193   19.11333   2.6065
```

0.33 or 0.67 equiv boroxine: These reactions were stirred overnight and were purified by preparative TLC (eluent 10 % EtOAc/hexanes). In both cases, the isolated product **2a** was determined to be racemic with the measured enantiomeric excesses being -3.6% for 0.33 equiv boroxine and -5.7% for 0.67 equiv boroxine.

*HPLC chromatograph of **2a** isolated from 0.33 equiv boroxine*



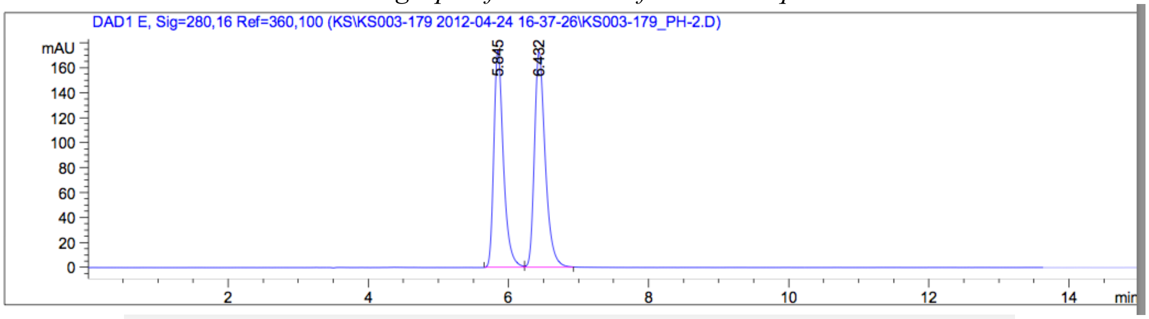


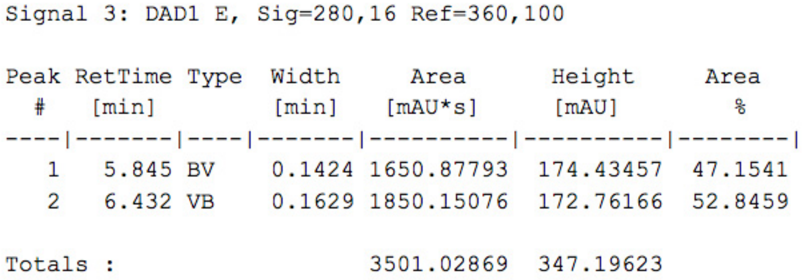
```
Signal 3: DAD1 E, Sig=280,16 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]        %
----|-------|----|-------|----------|----------|--------|
   1    5.846 BV    0.1430 1683.41968  176.99622  48.1976
   2    6.442 VB    0.1634 1809.32422  168.38600  51.8024

Totals :                   3492.74390  345.38222
```

*HPLC chromatograph of **2a** isolated from 0.67 equiv boroxine*



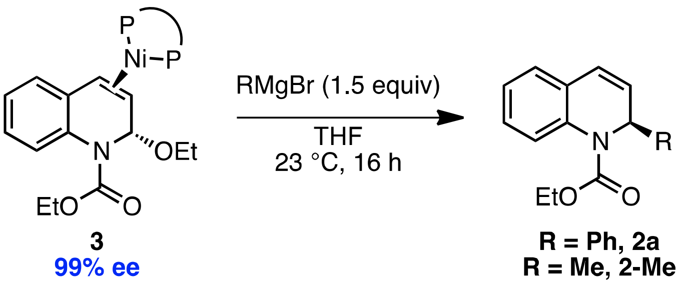


```
Signal 3: DAD1 E, Sig=280,16 Ref=360,100

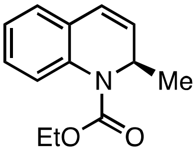
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]        %
----|-------|----|-------|----------|----------|--------|
   1    5.845 BV    0.1424 1650.87793  174.43457  47.1541
   2    6.432 VB    0.1629 1850.15076  172.76166  52.8459

Totals :                   3501.02869  347.19623
```

Reactions with enantioenriched 3 and Grignard reagents.



Reactions with Grignard reagents. An oven-dried threaded tube equipped with a PTFE-coated stirbar and PTFE-lined threading was brought into a nitrogen-filled glovebox and 100 mg (0.118 mmol) of the (DPEPhos)Ni(EEDQ) complex **3** (99% ee) was weighed into the tube. The solid was then dissolved in 2.00 mL THF and 0.178 mmol (1.5 equiv) of Grignard solution in THF was added dropwise to the reaction. The tube was then sealed with a PTFE-lined cap, wrapped in electrical tape, and removed from the glovebox. The reaction was then allowed to stir for 16 hours at 23°C. After this time, 1 mL of saturated aqueous NH_4Cl was added to the reaction and the biphasic mixture was stirred for 10 minutes. The mixture was then diluted with 3 mL of water and extracted with CH_2Cl_2. The combined organic layers were dried with Na_2SO_4, filtered, and concentrated under reduced pressure. The crude products were then purified using flash chromatography (silica gel packed in a pipette, hexanes:Et_2O 30:1 to 15:1). The products were then analyzed by ^1H and ^{13}C NMR.



2-Me

Prepared according to the general procedure for Grignard addition, the title compound **2-Me** was obtained as a thick, colorless oil. (21.7 mg, 84% yield)

IR (neat, cm^{-1}): 3042, 2975, 1695, 1490, 1397, 1298, 1128, 1049, 904, 762

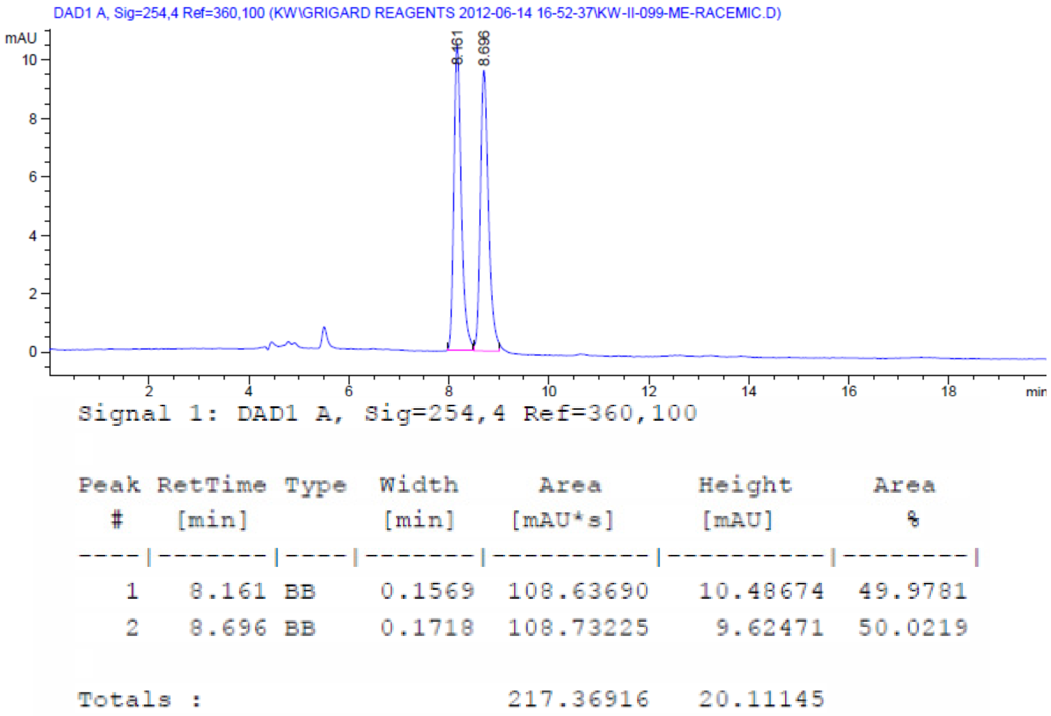
^1H NMR (300 MHz, $CDCl_3$): δ 7.60 (br s, J = 8.4 Hz, 1H), 7.20 (ddd, J = 8.2, 5.9, 3.1 Hz, 1H), 7.10 – 7.00 (m, 2H), 6.42 (dt, J = 9.6, 0.8 Hz, 1H), 6.00 (dd, J = 9.5, 5.9 Hz, 1H), 5.20 – 4.97 (m, 1H), 4.41 – 4.10 (m, 2H), 1.32 (t, J = 7.1 Hz, 3H), 1.11 (d, J = 6.7 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 154.39, 134.40, 130.87, 127.54, 127.08, 126.37, 124.63, 124.34, 124.15, 62.17, 49.03, 18.75, 14.73.

MS: (ES-APCI) Calculated for $C_{13}H_{15}NO_2$ (M+H): 218.1, found: 218.1.

The enantiomeric excess of the product was determined by chiral HPLC (Chiralpak AS-H, 0.46 cm x 25 cm, 99.5:0.5 hexanes:*i*-PrOH, 0.75 mL/min, 20 min, t_R(major) = 8.09 min, t_R(minor) = 8.60 min, 254 nm). The enantiomeric excess was determined to be 95%. The absolute stereochemistry was not determined. $[\alpha]^{20}_D = -212.0$ (CH_2Cl_2, c=0.567, path length = 1 dm)

*HPLC chromatogram of racemic N-ethoxycarbamate-2-methyl-1,2-dihydroquinoline (**2-Me**)*

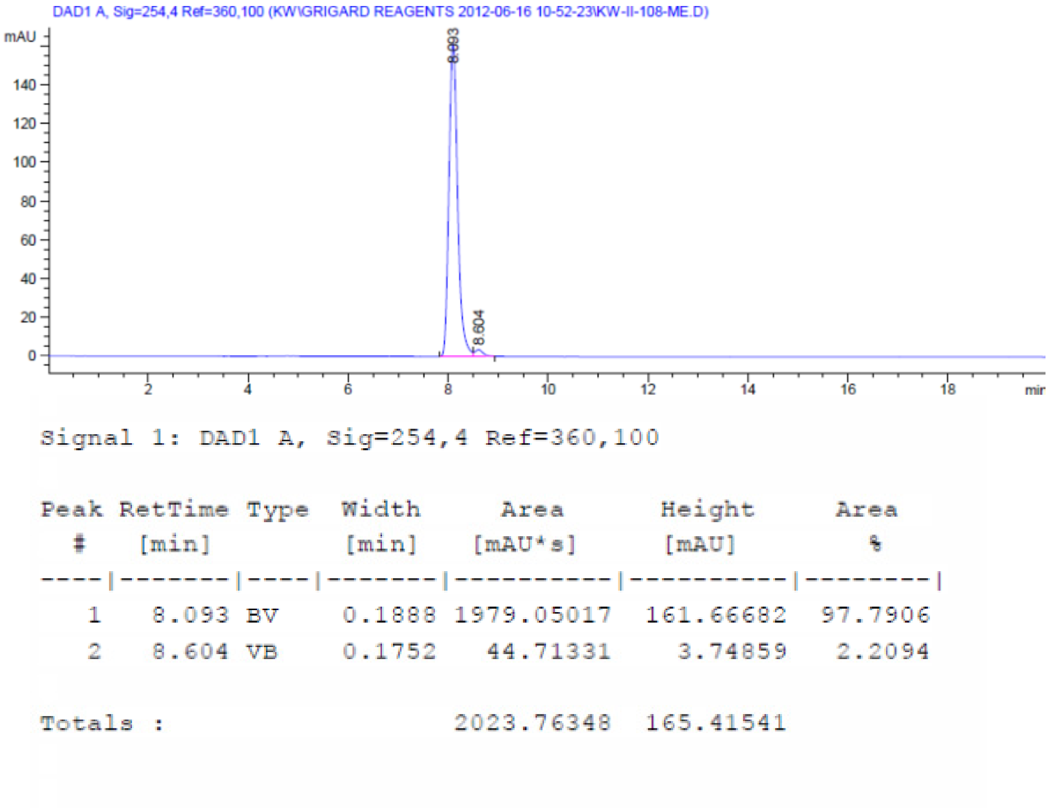


```
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak RetTime Type  Width     Area       Height      Area
  #   [min]        [min]   [mAU*s]      [mAU]        %
----|-------|----|-------|----------|----------|--------|
   1   8.161 BB    0.1569  108.63690   10.48674  49.9781
   2   8.696 BB    0.1718  108.73225    9.62471  50.0219

Totals :                   217.36916   20.11145
```

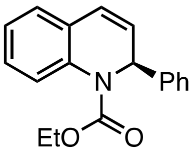
*HPLC chromatogram of product **2-Me** from addition of MeMgBr to enantiopure **3***



```
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak RetTime Type  Width     Area       Height      Area
  #   [min]        [min]   [mAU*s]      [mAU]        %
----|-------|----|-------|----------|----------|--------|
   1   8.093 BV    0.1888 1979.05017  161.66682  97.7906
   2   8.604 VB    0.1752   44.71331    3.74859   2.2094

Totals :                  2023.76348  165.41541
```



2a

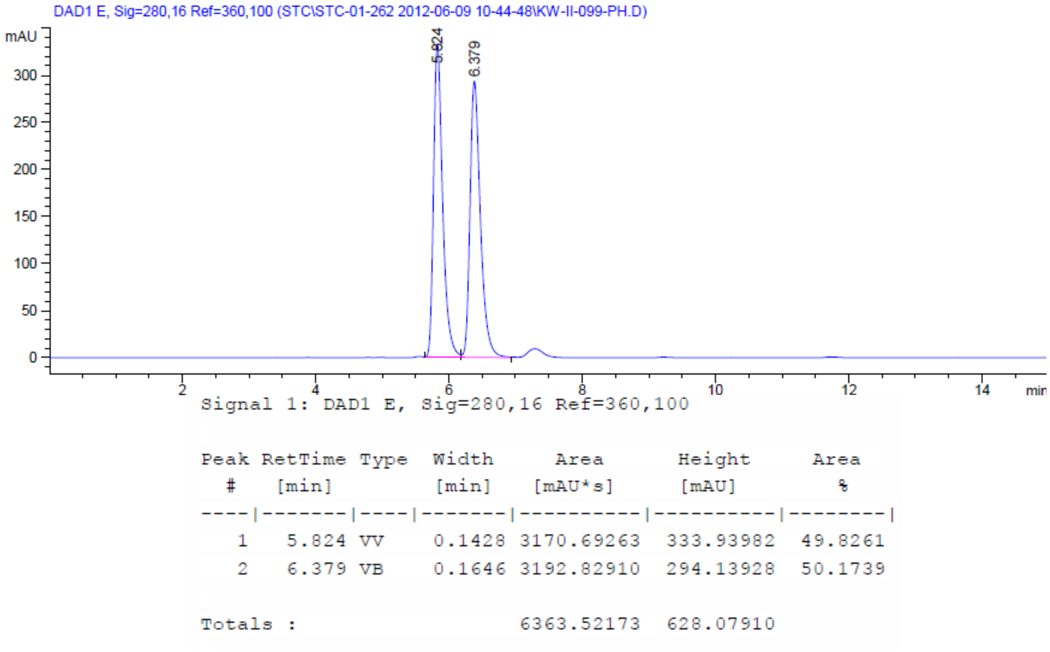
Prepared according to the general procedure for Grignard addition, the title compound **2a** was isolated as a thick, colorless oil. (29.8 mg, 90% yield). The spectra match the literature values.[12]

<u>^{1}H NMR (300 MHz, CDCl$_3$):</u> δ 7.54 (br s, 1H), 7.31 – 7.19 (m, 5H), 7.19 – 7.14 (m, 1H), 7.11 (dd, J = 7.5, 1.9 Hz, 1H), 7.05 (td, J = 7.3, 1.0 Hz, 1H) 6.71 – 6.58 (m, 1H), 6.26 – 6.12 (m, 2H), 4.43 – 4.17 (m, 2H), 1.34 (t, J = 7.1 Hz, 3H).

<u>^{13}C NMR (125 MHz, CDCl$_3$):</u> δ 154.86, 139.84, 134.88, 128.68, 128.41, 127.96, 127.89, 127.25, 126.48, 125.50, 124.75, 124.33, 62.53, 55.68, 14.71. One peak is obscured due to overlap.

Enantiomeric excess was determined by chiral HPLC (Chiralpak AS-H, 0.46 cm x 25 cm, 97:3 hexanes:*i*-PrOH, 1.0 mL/min, t_R(major) = 6.31 min, t_R(minor) = 5.82 min, 280 nm). The enantiomeric excess was determined to be 73% ee. The erosion in ee in this example could be a result of PhMgBr-induced racemization of EEDQ. Alternatively, racemization could proceed by a Ni(0)-mediated pathway. This pathway is also available to the boronic acids especially since these reactions should be characterized by a higher concentration of [Ni(0)] due to slower oxidative addition. Nevertheless, the KIE, quinolinium experiment, and stereochemical results taken together are most consistent with the proposed S_N1-type process.

HPLC chromatogram of racemic N-ethoxycarbamate-2-phenyl-1,2-dihydroquinoline ***(2a)***



```
Signal 1: DAD1 E, Sig=280,16 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]        %
----|-------|----|-------|----------|----------|--------|
   1   5.824 VV    0.1428 3170.69263  333.93982  49.8261
   2   6.379 VB    0.1646 3192.82910  294.13928  50.1739

Totals :                  6363.52173  628.07910
```

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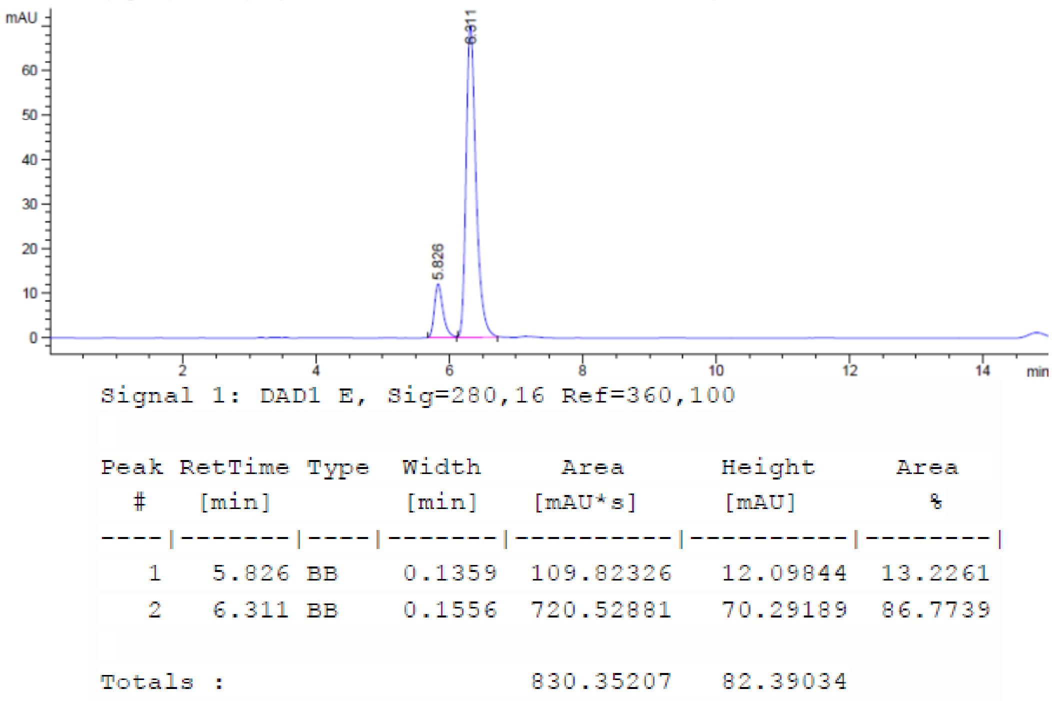
[12] Graham, T. J. A.; Shields, J. D.; Doyle, A. G. *Chem. Sci.* **2011**, *2*, 980–984.

*HPLC chromatogram of product **2a** from addition of PhMgBr to enantiopure **3***

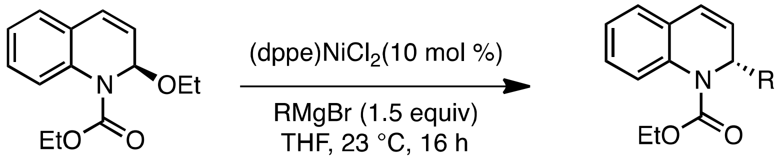


```
Signal 1: DAD1 E, Sig=280,16 Ref=360,100

Peak RetTime Type  Width     Area       Height     Area
  #   [min]        [min]   [mAU*s]      [mAU]        %
----|-------|----|-------|----------|----------|--------|
   1   5.826 BB    0.1359  109.82326   12.09844 13.2261
   2   6.311 BB    0.1556  720.52881   70.29189 86.7739

Totals :                   830.35207   82.39034
```

M) Catalytic Reaction of Enantioenriched 1 with Grignard Reagents.[13]



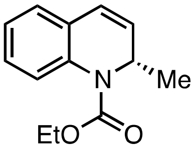
1
99% ee

R = Ph, 2a
R = Me, 2-Me

An oven-dried threaded tube equipped with a PTFE-coated stirbar and PTFE-lined threading was brought into a N_2 filled glovebox. The tube was then charged with 94 mg (0.379 mmol) of enantioenriched EEDQ **1** (99% ee) and 10 mg (0.019 mmol, 10 mol%) of Ni(dppe)Cl_2 (dppe = diphenylphosphinoethane). The solid was then dissolved in 2.00 mL THF and 0.178 mmol (1.5 equiv) of Grignard solution in THF or Et_2O was added dropwise to the reaction. The tube was then sealed with a PTFE-lined cap, wrapped in electrical tape, and removed from the glovebox. The reaction was then allowed to stir for 16 hours at 23°C. The reaction was then worked up using the same procedure as the stoichiometric reaction. The products were then analyzed by ^1H and ^{13}C NMR, and the enantiomeric excess of the product was determined by chiral HPLC (Chiralpak AS-H, 0.46 cm x 25 cm).

---

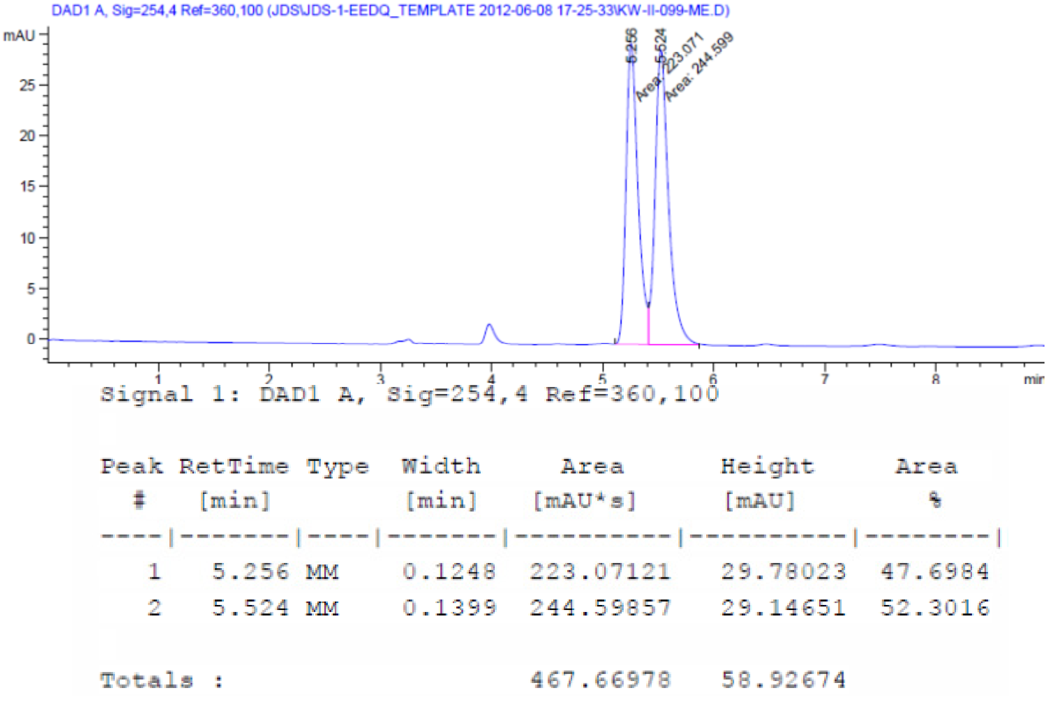
[13] The control reaction with PhMgBr and MeMgBr was run using the same procedure as the catalytic reaction of **1** while omitting the catalyst. No reaction was observed with MeMgBr and an unidentified side product was observed with PhMgBr



2-Me

Enantiomeric excess determined by chiral HPLC (Chiralpak AS-H, 0.46 cm x 25 cm, 99:1 hexanes:*i*-PrOH, 1.00 mL/min, t_R(major) = 5.25 min, t_R(minor) = 5.52 min, 254 nm) enantiomeric excess was determined to be 99%. The absolute configuration was not determined.

Racemic N-ethoxycarbamate-2-methyl-1,2-dihydroquinoline ***(2-Me)****:*

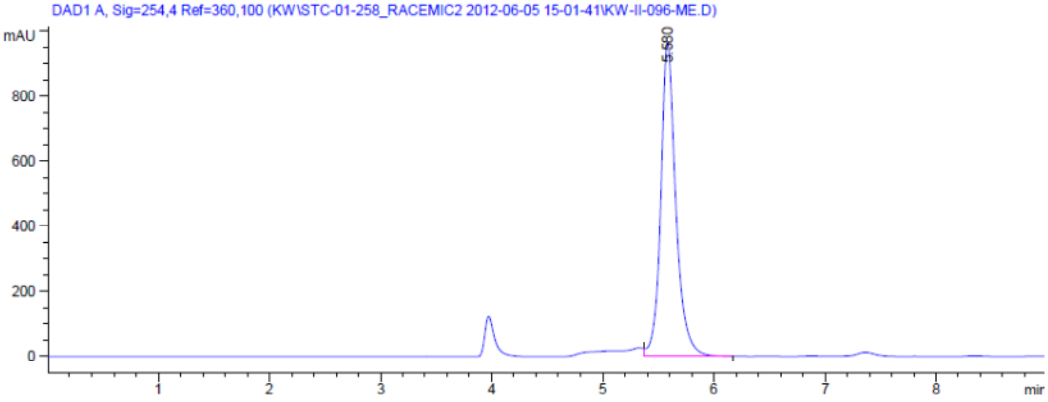


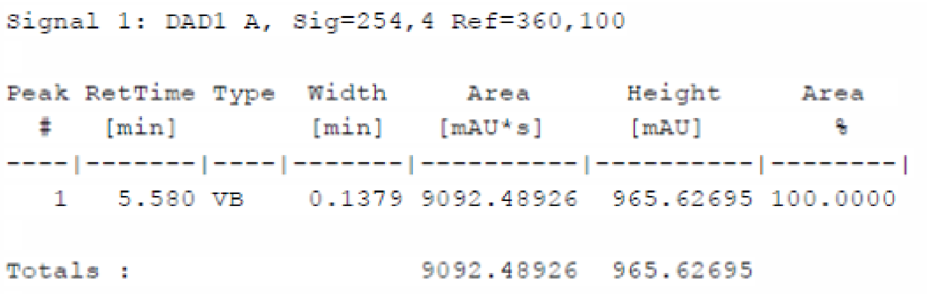
```
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]        %
----|-------|----|-------|----------|----------|--------|
   1   5.256 MM    0.1248  223.07121   29.78023  47.6984
   2   5.524 MM    0.1399  244.59857   29.14651  52.3016

Totals :                   467.66978   58.92674
```

HPLC chromatogram of product ***2-Me*** *from Ni-cat addition of MeMgBr to enantiopure* ***1***

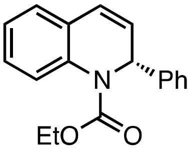




```
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak RetTime Type  Width     Area       Height     Area
  #   [min]        [min]   [mAU*s]      [mAU]        %
----|-------|----|-------|----------|----------|--------|
   1   5.580 VB     0.1379 9092.48926  965.62695 100.0000

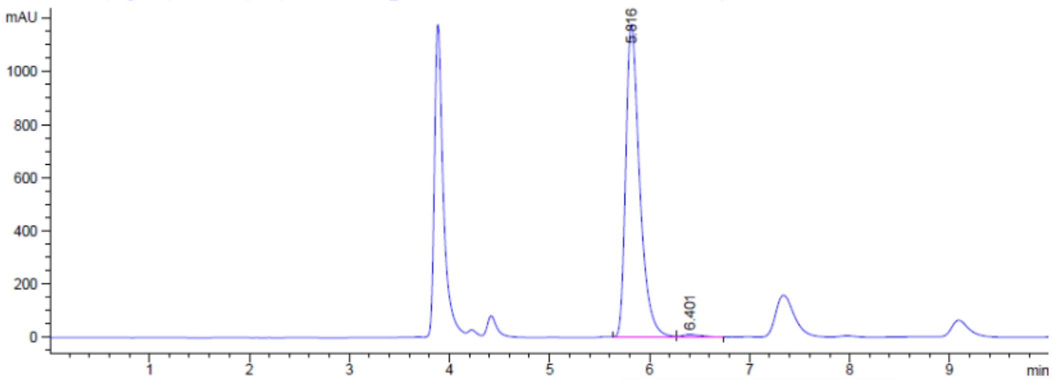
Totals :                   9092.48926  965.62695
```

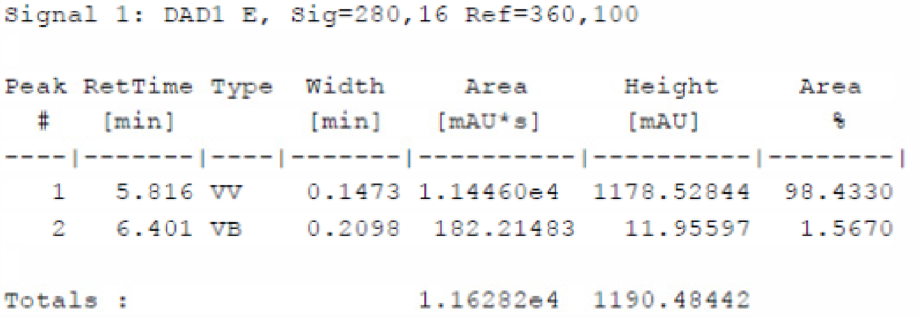


2a

Enantiomeric excess was determined by chiral HPLC (Chiralpak AS-H, 0.46 cm x 25 cm, 97:3 hexanes:*i*-PrOH, 1.0 mL/min, t_R(major) = 5.82 min, t_R(minor) = 6.40 min, 280 nm). The enantiomeric excess was determined to be 97%.

*HPLC chromatogram of product **2a** from Ni-cat. addition of PhMgBr to enantiopure **1***



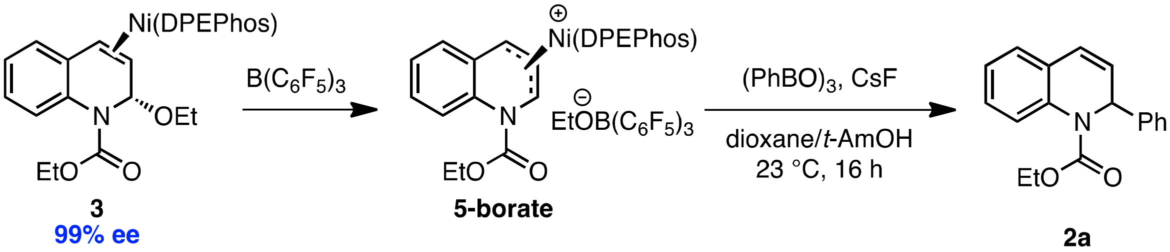


```
Signal 1: DAD1 E, Sig=280,16 Ref=360,100

Peak RetTime Type  Width     Area       Height     Area
  #   [min]        [min]   [mAU*s]      [mAU]        %
----|-------|----|-------|----------|----------|--------|
   1   5.816 VV     0.1473 1.14460e4 1178.52844  98.4330
   2   6.401 VB     0.2098  182.21483   11.95597   1.5670

Totals :                   1.16282e4 1190.48442
```

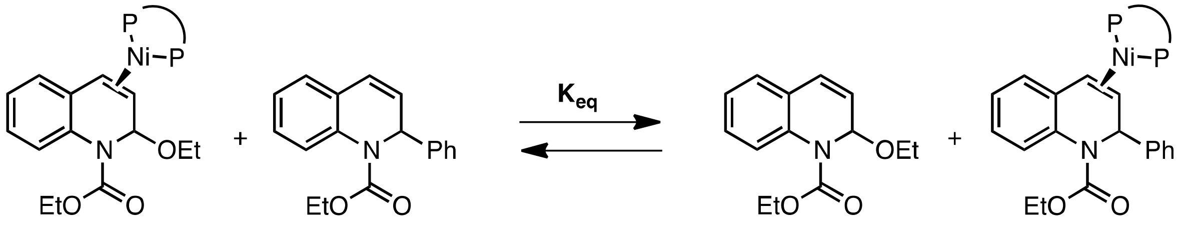
N) Preparation of the Allyl Complex from Enantioenriched 3 and Subsequent Reaction.



Enantioenriched (99% ee) (DPEPhos)Ni(EEDQ) **3** (0.200 g, 0.237 mmol, 1.05 equiv) and tris(pentafluorophenyl) borane (0.115 g, 0.225 mmol, 1.0 equiv) were added to an oven dried 2-dram vial with a PTFE-coated stirbar in a nitrogen-filled glovebox. The solids were dissolved in 2.0 mL of toluene and capped with a PTFE-lined screw-cap. The solution was allowed to stir vigorously overnight (16 h) during which time the yellow solution turned dark red-orange. Solids were precipitated using 10 mL of pentane and collected using a medium frit filter. The solids were then washed with 25 mL of pentanes and dried under high vacuum. The red-orange solids (0.246 g, 81% yield) were identified as **5-borate**. Optical rotation identifies the allyl complex as racemic. $[\alpha]^{20}_{D}$ = +2.6 (Dioxane, c=0.11, path length = 1 dm) (control with **5-borate** from racemic EEDQ $[\alpha]^{20}_{D}$ = +3.0 (Dioxane, c=0.10, path length = 1 dm))

Phenyl boroxine (7.3 mg, 0.023 mmol, 0.66 equiv) and cesium fluoride (10.8 mg, 0.071 mmol, 2.00 equiv) were added to an oven-dried threaded tube equipped with a PTFE-coated stirbar and PTFE lined threading. The solids were then dissolved in dioxane:*t*-AmOH (10:1 1.5 mL:0.15 mL, 0.02 M) and allowed to stir for 3 hours. **5-borate** derived from enantioenriched **3** (50 mg, 0.035 mmol, 1.00 equiv) was then added. The tube was then sealed with a PTFE-lined cap, wrapped in electrical tape, and removed from the glovebox. The reaction was then allowed to stir for 16 hours at 23°C. The reaction was then worked up using the same procedure as the reaction of racemic **3**. The identity of the product **2a** was confirmed by LCMS, ^{1}H, and ^{13}C NMR and the product was confirmed to be racemic by chiral HPLC (Chiralpak AS-H, 0.46 cm x 25 cm, 97:3 Hexanes:*i*-PrOH, 1.0 mL/min, 280 nm).

O) Measurement of equilibrium constant.



3 **2a** **1** **4**

Two experiments were conducted to measure the equilibrium constant, K_{eq}, for **1** and product **2a** binding to (DPEPhos)Ni. The equilibrium constant was calculated according to the following equation:

$$\mathbf{K_{eq}} = \frac{[\mathbf{1}][\mathbf{4}]}{[\mathbf{3}][\mathbf{2a}]}$$

In the glovebox, 40.0 mg (0.0474 mmol, 0.0237 M) **3** and 7.3 mg (0.0261 mmol, 0.0131 M) **2a** were added to a 2-mL volumetric flask. The two solids were dissolved in 2.00 mL deuterated benzene. An aliquot was transferred to a screw cap NMR tube. The ^{31}P NMR spectrum was collected after 1 hour and after 24 hours. The ratio of **3** and **4** were determined by relative areas as measured by ^{31}P NMR and used to determine the equilibrium concentration of both **1** and **2a**. The calculated equilibrium constants were 0.26 and 0.24 after one hour and 24 hours, respectively; showing the reaction quickly reaches equilibrium.

*Concentration data for substoichiometric addition of **2a** to **3**.*

Time (hr)	Initial [3], M	Initial [2a], M	Initial [1], M	Initial [4], M	Final [3], M	Final [2a], M	Final [1], M	Final [4], M
1	0.0237	0.0131	0.00	0.00	0.0179	0.0073	0.0058	0.0058
24	0.0237	0.0131	0.00	0.00	0.0181	0.0074	0.0057	0.0057

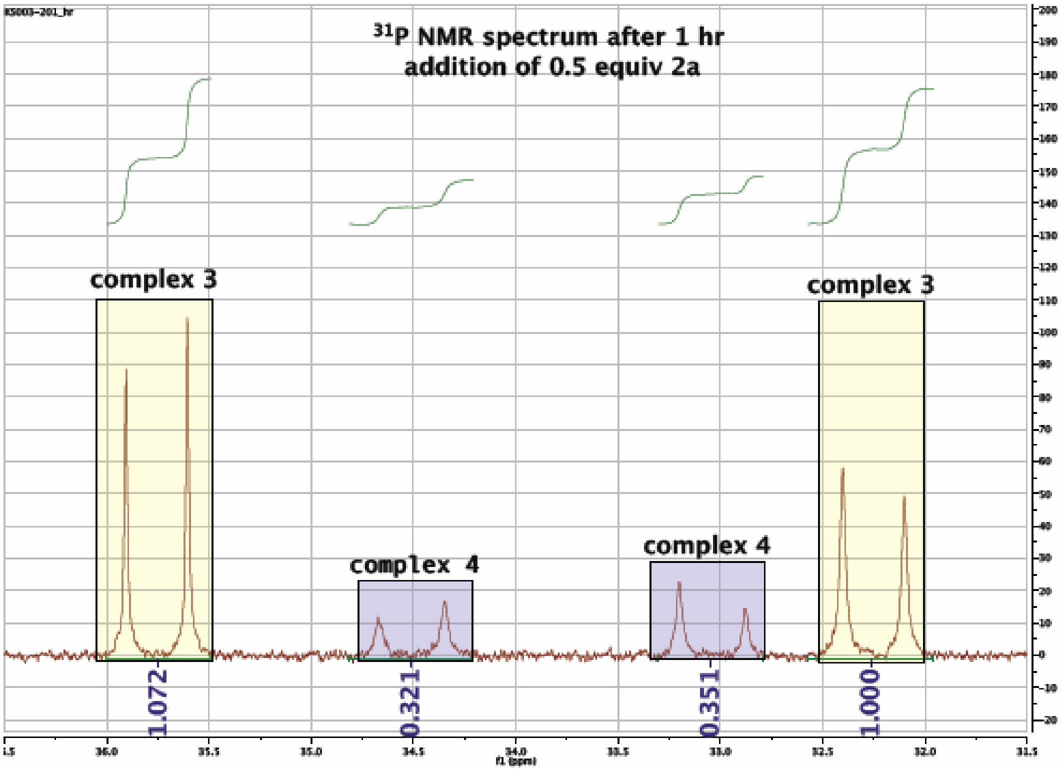
Additionally, the reaction was set up under conditions in which **2a** was in excess. In a 2-mL volumetric flask inside the glovebox, **3** (40.6 mg, 0.481 mmol, 0.0241 M) and **2a** (24.3 mg, 0.087 mmol, 0.0435 M) were dissolved in 2.00 mL of deuterated benzene. ^{31}P NMR spectra were collected after 1 hour and 24 hours. Analogous calculations to the previous conditions were performed. The equilibrium constants were measured to be 0.30 and 0.29 after 1 hour and 24 hour respectively.

*Concentration data for addition of excess **2a** to **3**.*

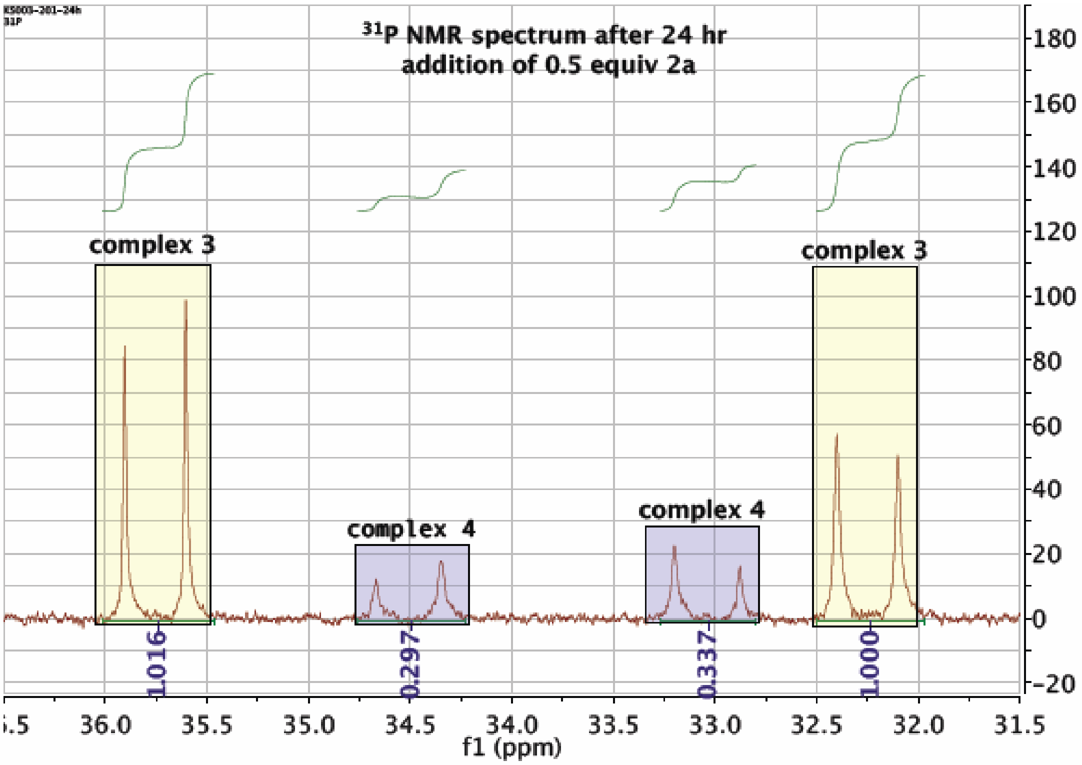
Time (hr)	Initial [3], M	Initial [2a], M	Initial [1], M	Initial [4], M	Final [3], M	Final [2a], M	Final [1], M	Final [4], M
1	0.0241	0.0435	0.00	0.00	0.0129	0.0323	0.0112	0.0112
24	0.0241	0.0435	0.00	0.00	0.0129	0.0324	0.0111	0.0111

Taking the two final measurements (after 24 hours) into account, the average equilibrium constant is 0.27±0.04, highlighting the higher binding affinity of (DPEPhos)Ni for **1** most likely on the basis of sterics. This result is consistent with the ability of **3** to function as a catalyst for the arylation reaction.

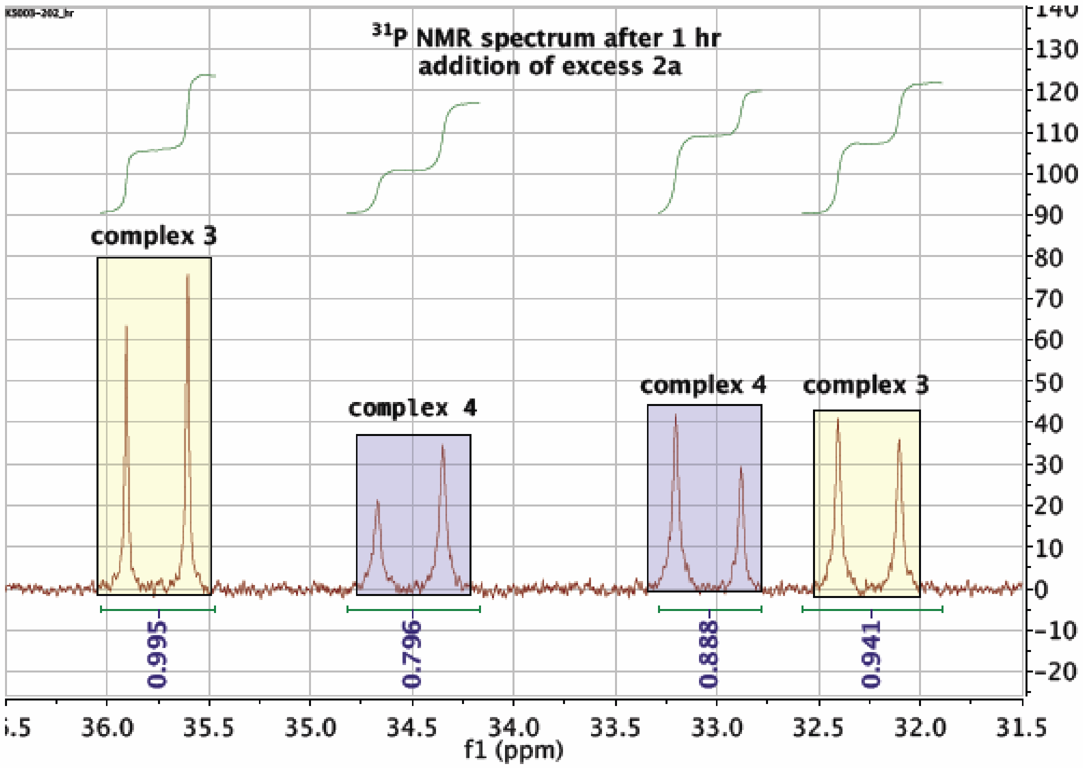
*^{31}P NMR spectrum of addition of **3** and substoichiometric **2a** after 1 hour*



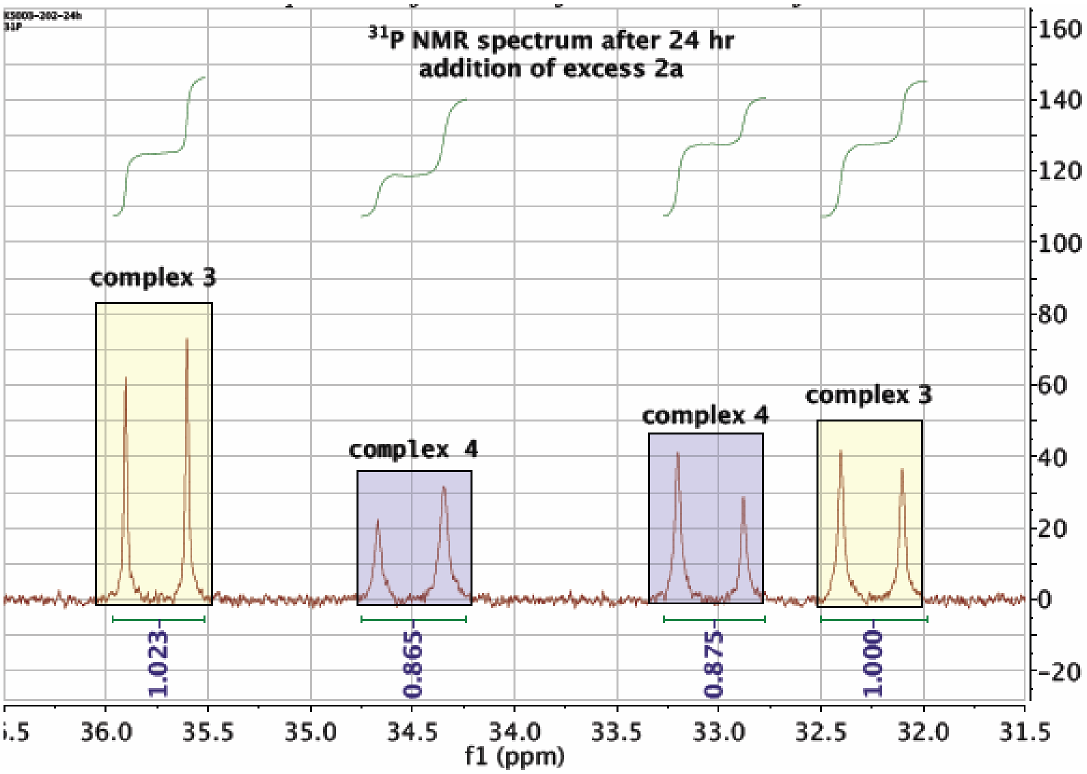
*^{31}P NMR spectrum of addition of **3** and substoichiometric **2a** after 24 hour*



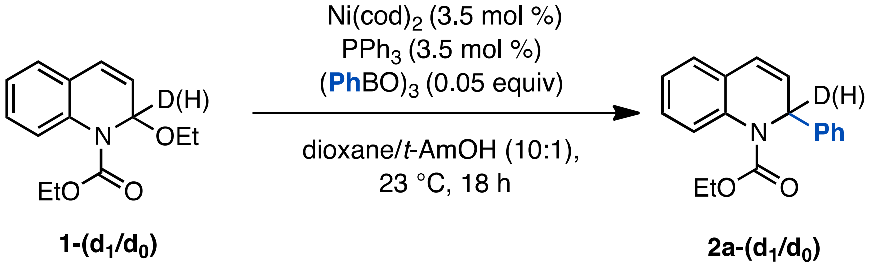
*^{31}P NMR spectrum of addition of **3** and excess **2a** after 1 hour*



*^{31}P NMR spectrum of addition of **3** and excess **2a** after 24 hour*



P) Kinetic isotope effect experiments for catalytic system.



Catalytic system. The secondary kinetic isotope effect was measured for the catalytic reaction using a competition experiment between EEDQ and d_1-EEDQ and Ni(cod)$_2$/PPh$_3$ as the catalyst system. Below is the experimental procedures.

Preparation of catalyst stock solution. Ni(cod)$_2$ (14.6 mg) and PPh$_3$ (13.9 mg) were weighed into an oven-dried vial equipped with a stirbar in a glovebox under nitrogen atmosphere. 1.5 ml of dioxane was added and the resulting blood red solution was stirred for 10 min under nitrogen in the glovebox.

Preparation of boroxine stock solution. Phenyl boroxine (23.6 mg) was weighed into an oven-dried vial equipped with a stirbar in a glovebox under nitrogen atmosphere. 1.5 ml of dioxane was added and the resulting solution was stirred for 10 min under nitrogen in the glovebox.

Preparation of reaction solution and addition of stock solutions. EEDQ (111 mg, 0.447 mmol), d_1-EEDQ (150 mg, 0.603 mmol) and 1,3,5-trimethoxybenzene (internal standard, 71 mg, 0.420 mmol, 0.4 equiv) were weighed out into a 100 ml air-dried round-bottomed flask equipped with a stirbar in a glovebox under nitrogen atmosphere. 23.4 ml of dioxane and 2.6 ml of *t*-AmOH (10:1) was added and the solution was stirred for 5 min. An aliquot (1 mL) of the solution was then withdrawn and analyzed ^{1}H NMR spectroscopy, leaving a 25 ml solution (1.01 mmol of EEDQ, 0.404 mmol of standard). Integration of the C-2 proton provided the initial isotopic ratio. The catalyst stock solution (1 ml, 0.035 mmol of Ni, 3.5 mol% 0.035 mmol of PPh$_3$, 3.5 mol%) was added and the resulting orange solution was stirred for 1 min. The boroxine stock solution (1 ml, 0.051 mmol, 0.050 eq) was then added. The flask was then sealed with a rubber septum, wrapped with electrical tape, and brought out of the glovebox. The reaction was then allowed to stir at room temperature (23 °C) for 18 h.

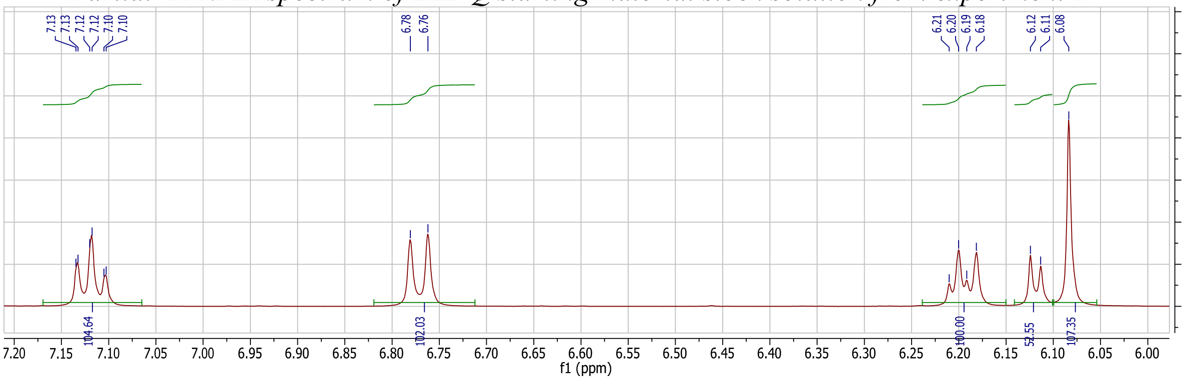
Reaction work up. The reaction vessel was exposed to air to quench the reaction and filtered through Celite. The flask and celite was then rinsed several times with ethyl acetate. The filtrate was then concentrated under reduced pressure and the crude reaction mixture was analyzed by ^{1}H NMR to determine conversion. The crude mixture was then purified by flash chromatography (hexanes:EtOAc 30:1), TLC plate visualized in CAM stain (hexanes:EtOAc 5:1, Rf ~ 0.5), to obtain the purified product and to determine the final isotopic ratio.

Data Analysis of catalytic reaction. KIE = $k_H/k_D = \ln(1-F)/\ln(1-F(R_p/R_o))$ where F = conversion of deuterated starting material, $R_o = [D]_o/[H]_o$ = initial isotopic ratio, $R_p = [D]/[H]$ = final isotopic ratio. At low conversion (where F approaches zero), the expression reduces to KIE = $k_H/k_D = R_o/R_p$. The simplification is valid because a large excess of deuterated starting material is used.

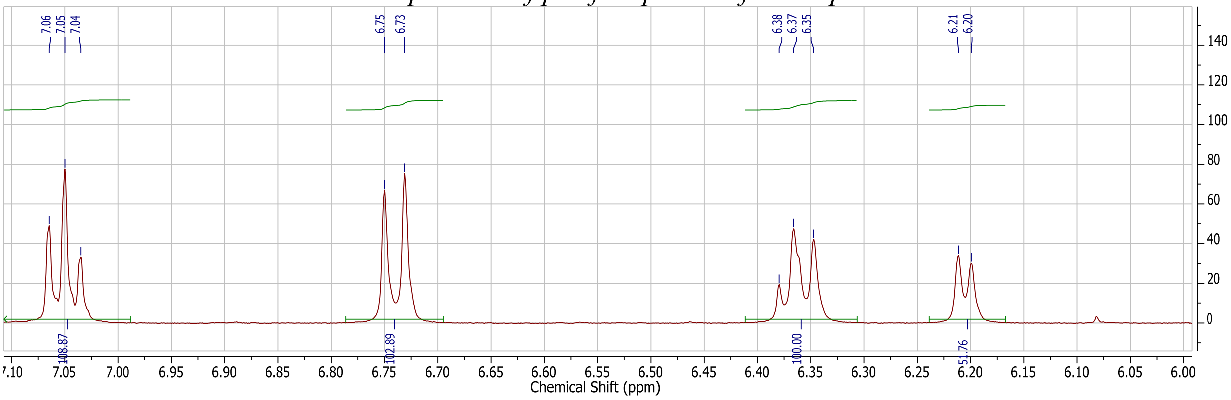
KIE data for catalytic reaction

Expt.	***Ro***	***Rp***	***KIE***
1	0.902	0.931	0.968
2	0.887	0.893	0.993
3	0.902	0.860	1.04
4	0.895	0.899	0.996
5	0.899	0.895	1.00
		Ave. KIE	***1.00 ± 0.02***

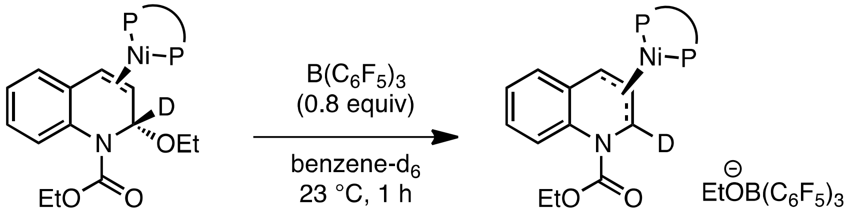
Partial ^1H NMR spectrum of EEDQ starting material stock solution from experiment 1



Partial ^1H NMR spectrum of purified product from experiment 1



Q) Secondary KIE for stoichiometric abstraction of ethoxide from 3 by B(C_6F_5)$_3$.



3-(d_1/d_0) ~50 % d_1 **5-borate-(d_1/d_0)**

Measurement of secondary KIE for ethoxide abstraction by tris(pentafluorophenyl)borane. In a nitrogen-filled glovedox, a 2-dram vial was charged with 80 mg of **3-(*d_1/d_0*)** (0.947 mmol) followed by 4.75 g deuterated benzene (5.0 mL). An aliquot (750 mg) was removed and analyzed by ^{1}H NMR spectroscopy at 40 °C to measure the ratio of starting material to internal standard (durene, 3mg). Also, the initial H/D ratio was measured using the first aliquot but the sample was oxidized in air before analysis by ^{1}H NMR spectroscopy (in which the integrated areas of the allylic CH/CD was compared to the olefinic CH peak). To the remaining reaction mixture was added 27 mg of B(C_6F_5)$_3$ (0.8 equiv). The reaction immediately turned dark red and was stirred for five minutes. An aliquot was removed (750 mg) and analyzed at 40 °C to measure the conversion. The remaining reaction mixture was exposed to air. The EEDQ was recovered by passing through a buffered silica gel plug (rinsed with 3 mL triethylamine) and analyzed by ^{1}H NMR in order to determine the final isotopic ratio (by analyzing the allylic CH/CD and olefinic CH peaks by ^{1}H NMR spectroscopy).

As calculated[14]:

$$\boldsymbol{KIE = \frac{k_H}{k_D} = \frac{\log(1-F_H)}{\log[(1-F_H)\left(\frac{R}{R0}\right)]}}$$

KIE = kinetic isotope effect
F_H = fractional conversion of protiated starting material (EEDQ)
R^0 = initial isotopic ratio (determined from EEDQ recovered from oxidized starting olefin complex)
R = final isotopic ratio (determined from EEDQ recovered from oxidized reaction mixture after borane addition)
% Conv = percent conversion

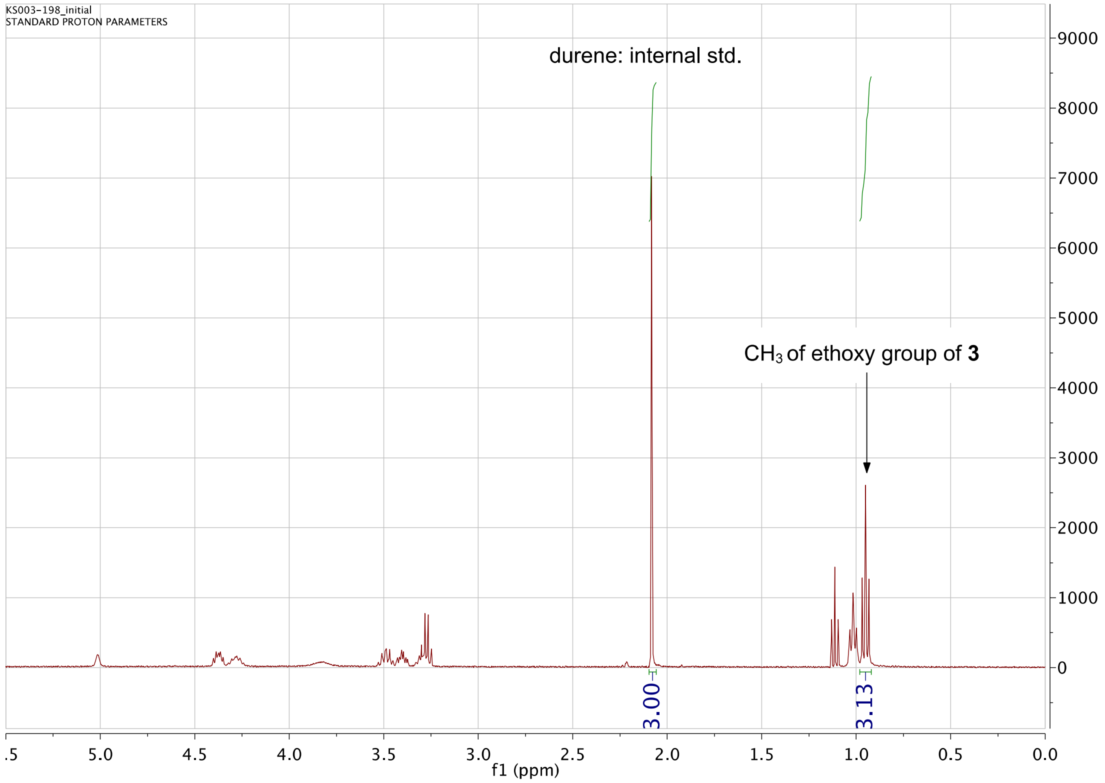
KIE data for stoichiometric reaction

Experiment	***% Conv.***	***1-F_H***	***R^0***	***R***	***R/R_0***	***KIE***
1	0.722	0.263	0.792	0.898	1.133	1.10
2	0.849	0.131	0.890	1.179	1.320	1.16
3	0.765	0.215	0.835	1.004	1.203	1.14
					Ave. KIE	***1.13 ± 0.02***

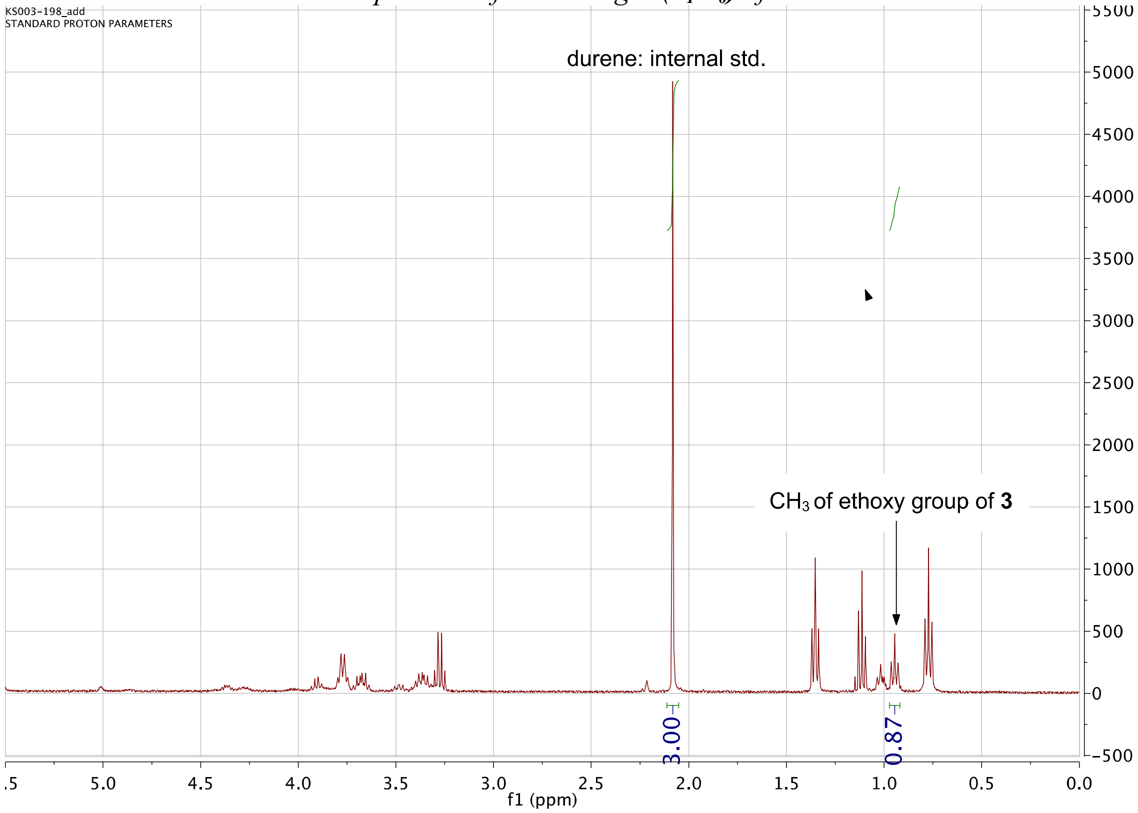
---

[14] KIE equation derived from: Klausen, R.S. Benzoic Acid and Thiourea Cocatalysis. Ph.D. Dissertation, Harvard University, Cambridge, MA, 2010.

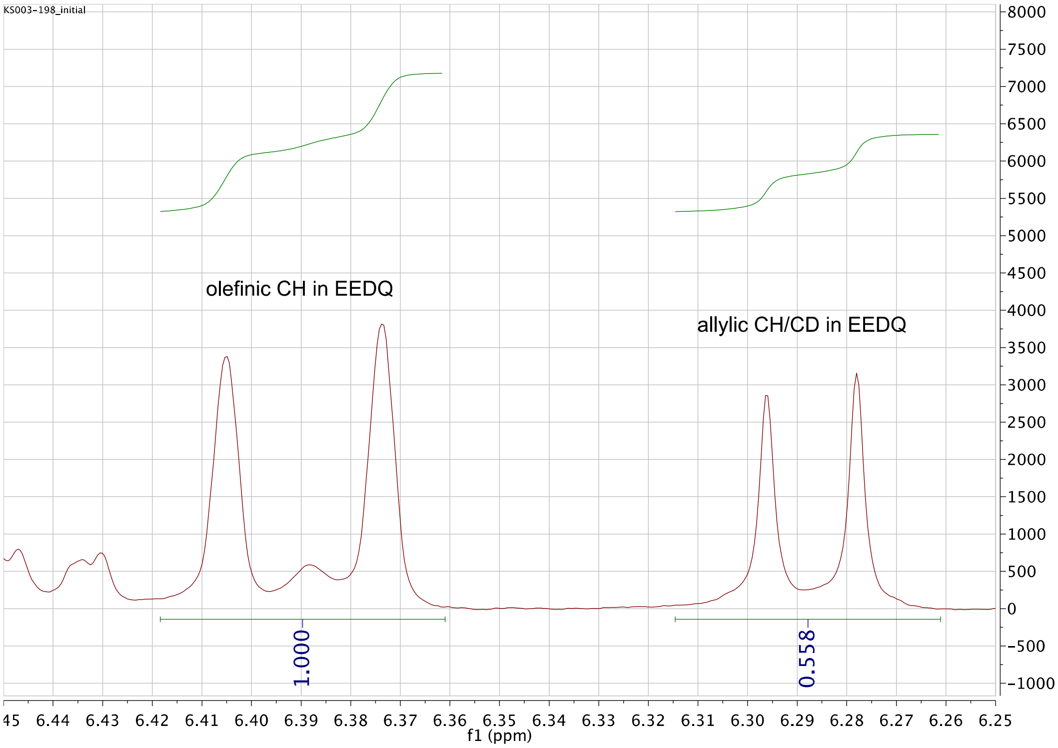
*Partial initial ^{1}H NMR spectrum of **3-(d_1/d_0)** used to determine conversion for experiment 1.*



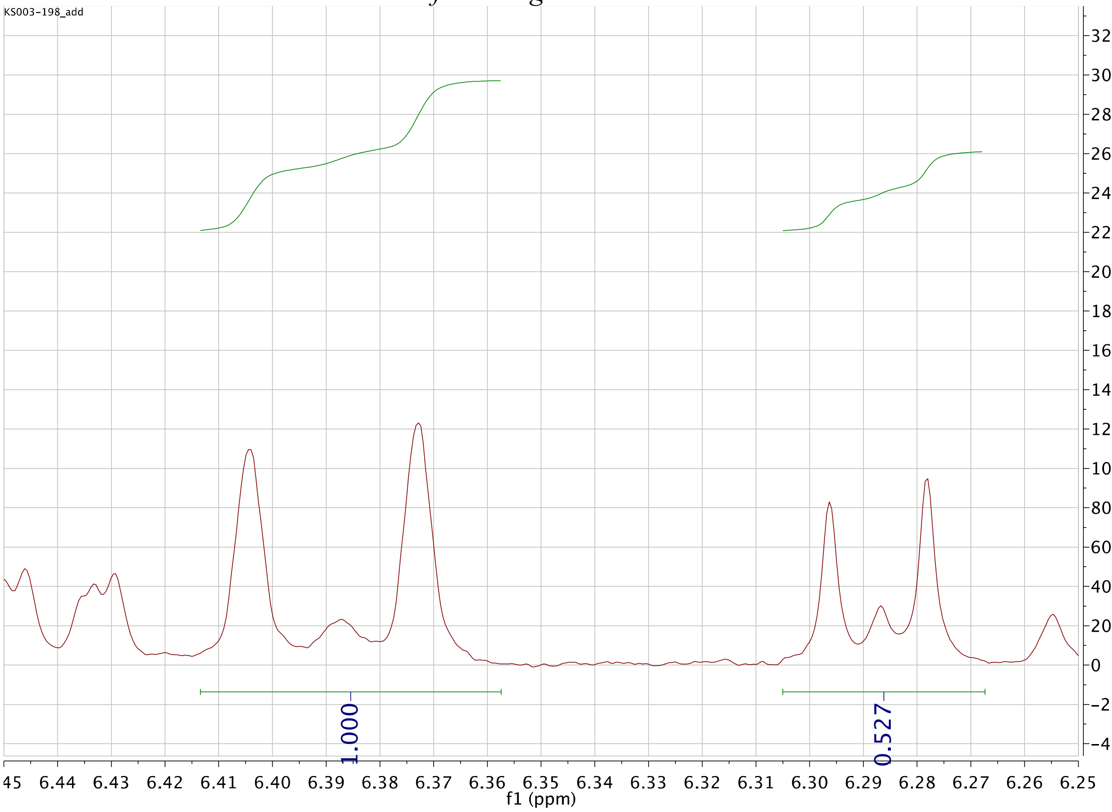
*Partial ^{1}H NMR spectrum of remaining **3-(d_1/d_0)** after borane addition*



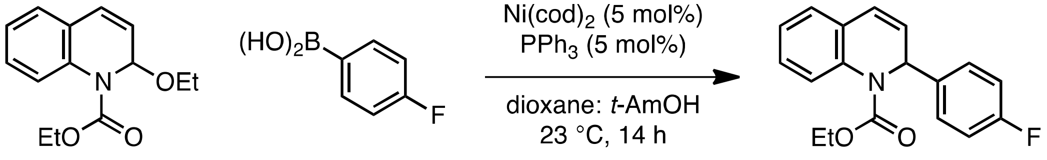
Partial ^{1}H NMR spectrum of ***1-(d_1/d_0)*** *used to determine initial H/D ratio in experiment 1.*



Partial ^{1}H NMR spectrum of ***1-(d_1/d_0)*** *used to determine final H/D ratio for experiment 1 after air oxidation following borane addition.*

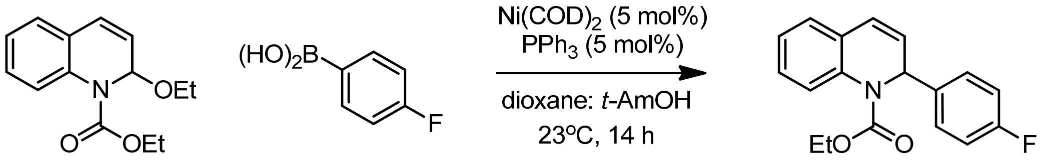


R) Reactions with radical inhibitors.



no additive: **41% yield** by ^{19}F NMR
20 mol% TEMPO: **37% yield**
20 mol% 9,10-dihydroanthracene: **47% yield**

A stock solution of Ni(COD)$_2$ (4.5 mg, 0.016 mmol) and triphenylphosphine (4.3 mg, 0.016 mmol) in 2.0 mL dioxane was prepared in a N$_2$ filled glovebox and allowed to stir for 15 minutes, forming a blood red solution. A second stock solution of (4-fluorophenyl)boronic acid (45.25 mg, 0.324 mmol) in 4.0 mL dioxane and a third stock solution of EEDQ (80 mg, 0.324 mmol) and trifluorotoluene (internal standard, 18.9 mg, 0.128 mmol) in dioxane:*t*-amyl alcohol (2 mL dioxane, 0.8 mL *t*-AmOH, 5:2) were also prepared. Then, 0.7 mL of the stock solution of EEDQ (0.081 mmol) and trifluorotoluene (0.032 mmol, 40 mol%) was added to three threaded tubes, one containing 9,10-dihydroanthracene (2.9 mg, 0.016 mmol, 20 mol%), one containing TEMPO (2.5 mg, 0.016 mmol, 20 mol%), and one with no radical inhibitor as a control. 0.5 mL of the Ni(COD)$_2$ stock solution was added, followed by 1.0 mL of the boronic acid (0.081 mmol, 1.0 equiv) stock solution. The reactions were then capped, wrapped with electrical tape, and brought out of the glovebox. The reactions were allowed to stir at room temperature (23 °C) for 14 h. An aliquot (0.3 mL) of each reaction was removed and added to an NMR tube containing 0.5 mL of d$_6$-benzene. The yields of the reactions were determined by ^{19}F NMR. The yield of the control was 41%, the yield of the 9,10-dihydroanthracene reaction was 47%, and the yield of the TEMPO reaction was 37%.



No additive: **46% Yield** by ^{19}F NMR
20 mol% nitrobenzene: **no product**
20 mol% phenanthroquinone: **no product**

A radical inhibitor experiment with phenanthroquinone and nitrobenzene was conducted with the same procedure.[15] No product was observed with phenanthroquinone or nitrobenzene, but the addition of either of these inhibitors to the catalyst in the absence of any substrate results in the binding of the inhibitor to the catalyst. We suspect that this binding accounts for the observed inhibition rather than inhibition by radical quenching.

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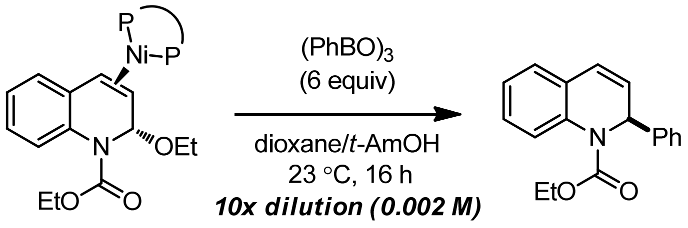
[15] Kochi, J. K. *Pure & Appl. Chem.* **1980**, *52*, 571–605.

S) Dilution Experiment.



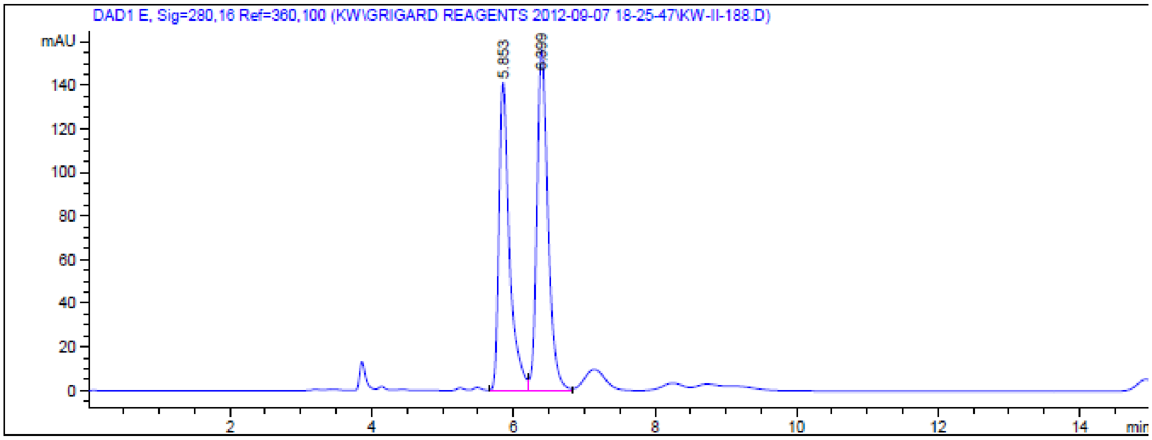
3

To examine the possibility of Ni-mediated racemization post oxidative addition, we performed the stoichiometric exeriment at low [**3**] while holding [Boroxine] constant.

Enantioenriched **3** (50 mg, 0.059 mmol) and phenyl boroxine (111 mg, 0.355 mmol) were weighed out into an oven-dried 100 ml rbf equipped with a PTFE coated stirbar inside an N_2 filled glovebox. Dioxane (25.8 ml) and t-AmOH (2.58 ml) were then added and the flask was sealed with a septum, wrapped in electrical tape, and removed from the glovebox. The reaction was then allowed to stir at 23 °C for 14 hours.

The reaction was then exposed to air and filtered over celite. The reaction concentrated under reduced pressure and the crude product was purified via flash chromatography (hexanes:Et_2O 30:1 to 15:1). The enantiomeric ratio of the product was then analyzed by chiral HPLC (Chiralpak AS-H, 0.46 cm x 25 cm, 99:1 hexanes:*i*-PrOH, 1.00 mL/min, t_R= 5.25 min, t_R= 5.52 min, 254 nm). The product was found to be racemic (~6% ee), indicating Ni-mediated racemization is minimal.

HPLC chromatogram of product from dilution experiment.

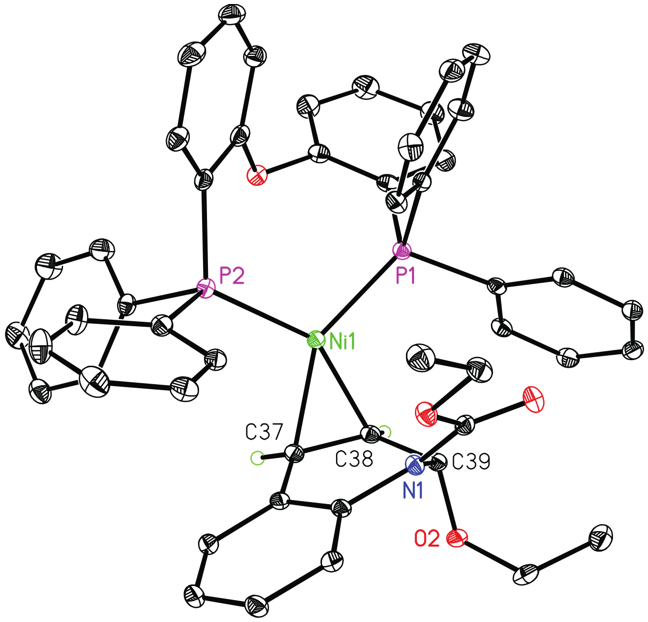


```
Signal 1: DAD1 E, Sig=280,16 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]        %
----|-------|----|-------|----------|----------|--------|
   1   5.853 VV    0.1554 1470.81238  141.40091  46.2351
   2   6.399 VV    0.1654 1710.34875  156.66176  53.7649

Totals :                  3181.16113  298.06267
```

T) X-ray Crystal Structural Information for 1



Computing details

Data collection: Bruker *APEX2*; cell refinement: Bruker *SAINT*; data reduction: Bruker *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3* (Farraguia, 1997).

Crystal data

$C_{57}H_{53}NNiO_4P_2$	$F(000) = 1968$
$M_r = 936.65$	$D_x = 1.320$ Mg m^{-3}
Monoclinic, $P2_1/c$	Cu K□ radiation, □ = 1.54178 Å
$a = 10.765$ (4) Å	Cell parameters from 9898 reflections
$b = 42.779$ (12) Å	□ = 4.5–64.8°
$c = 11.074$ (3) Å	□ = 1.62 mm^{-1}
□ = 112.420 (9)°	$T = 100$ K
$V = 4714$ (3) Å^3	Shard, yellow
$Z = 4$	0.07 × 0.06 × 0.03 mm

Data collection

Bruker APEX II CCD diffractometer	7855 independent reflections
Radiation source: fine-focus sealed tube	6893 reflections with $I > 2$□(I)
graphite	$R_{int} = 0.032$
phi and □ scans	□$_{max}$ = 66.2°, □$_{min}$ = 4.1°
Absorption correction: multi-scan *SADABS* V2008/1 (Bruker AXS)	$h = -12$□12
$T_{min} = 0.694$, $T_{max} = 0.753$	$k = -50$□48
29266 measured reflections	$l = -12$□12

Refinement

Refinement on F^2	Primary atom site location: structure-invariant direct methods
Least-squares matrix: full	Secondary atom site location: difference Fourier map
$R[F^2 > 2\sigma(F^2)] = 0.047$	Hydrogen site location: inferred from neighbouring sites
$wR(F^2) = 0.121$	H atoms treated by a mixture of independent and constrained refinement
$S = 1.12$	$w = 1/[\sigma^2(F_o^2) + (0.0415P)^2 + 8.2586P]$ where $P = (F_o^2 + 2F_c^2)/3$
7855 reflections	$(\Delta/\sigma)_{max} = 0.001$
591 parameters	$\Delta\rho_{max} = 1.47$ e Å^{-3}
0 restraints	$\Delta\rho_{min} = -1.17$ e Å^{-3}

Special details

Experimental. Collected, solved and refined by Scott P. Semproni

Geometry. All s.u.'s (except the s.u. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell s.u.'s are taken into account individually in the estimation of s.u.'s in distances, angles and torsion angles; correlations between s.u.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell s.u.'s is used for estimating s.u.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2, conventional R-factors R are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > 2\sigma(F^2)$ is used only for calculating R-factors(gt) etc. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R- factors based on ALL data will be even larger.

*Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters for X-ray structure **1** (Å^2)*

	x	*y*	*z*	U_{iso}*/U_{eq}
C1	0.4617 (3)	0.09015 (7)	0.4794 (3)	0.0193 (6)
C1S	0.6376 (5)	0.26393 (10)	0.5710 (5)	0.0573 (8)
H1S1	0.5859	0.2482	0.5074	0.086*
H1S2	0.7124	0.2538	0.6408	0.086*
H1S3	0.6729	0.2795	0.5273	0.086*
C2S	0.5462 (5)	0.28010 (10)	0.6293 (5)	0.0573 (8)
C3S	0.4109 (4)	0.28511 (9)	0.5517 (5)	0.0540 (11)
H3S	0.3761	0.2787	0.4629	0.065*
C4S	0.3274 (4)	0.29941 (9)	0.6038 (5)	0.0565 (12)
H4S	0.2351	0.3024	0.5507	0.068*
C5	0.6598 (3)	0.07880 (7)	0.4320 (3)	0.0255 (7)
H5	0.7236	0.0850	0.3964	0.031*
C5S	0.3763 (5)	0.30947 (10)	0.7325 (5)	0.0612 (13)
H5S	0.3183	0.3196	0.7667	0.073*

C6S	0.5085 (5)	0.30474 (9)	0.8100 (5)	0.0530 (11)
H6S	0.5427	0.3115	0.8984	0.064*
C7	0.2427 (3)	0.09959 (6)	0.5650 (3)	0.0184 (6)
C7S	0.5928 (4)	0.28995 (9)	0.7586 (5)	0.0499 (10)
H7S	0.6842	0.2865	0.8132	0.060*
C8	0.3037 (3)	0.10003 (7)	0.7010 (3)	0.0260 (7)
H8	0.3895	0.1094	0.7422	0.031*
C9	0.2401 (3)	0.08686 (7)	0.7765 (3)	0.0288 (7)
H9	0.2826	0.0873	0.8691	0.035*
C10	0.1151 (3)	0.07300 (7)	0.7181 (3)	0.0262 (7)
H10	0.0719	0.0640	0.7702	0.031*
C11	0.0536 (3)	0.07239 (7)	0.5834 (3)	0.0258 (7)
H11	-0.0322	0.0629	0.5427	0.031*
C12	0.1171 (3)	0.08563 (7)	0.5072 (3)	0.0222 (6)
H12	0.0741	0.0851	0.4147	0.027*
C13	0.4128 (3)	0.14997 (7)	0.5613 (3)	0.0213 (6)
C14	0.5457 (3)	0.14740 (7)	0.6506 (3)	0.0259 (7)
H14	0.5923	0.1282	0.6579	0.031*
C15	0.6105 (3)	0.17251 (8)	0.7285 (3)	0.0313 (7)
H15	0.7004	0.1703	0.7892	0.038*
C16	0.5450 (4)	0.20066 (8)	0.7183 (3)	0.0357 (8)
H16	0.5904	0.2179	0.7709	0.043*
C18	0.3491 (3)	0.17852 (7)	0.5556 (3)	0.0221 (6)
C26	-0.1603 (3)	0.10026 (7)	0.1578 (3)	0.0208 (6)
H26	-0.0797	0.0884	0.1916	0.025*
C28	-0.4010 (3)	0.10206 (8)	0.0530 (3)	0.0322 (7)
H28	-0.4849	0.0916	0.0160	0.039*
C29	-0.3970 (3)	0.13449 (8)	0.0588 (4)	0.0346 (8)
H29	-0.4779	0.1462	0.0249	0.042*
C30	-0.2742 (3)	0.14965 (8)	0.1143 (3)	0.0296 (7)
H30	-0.2716	0.1718	0.1174	0.036*
C31	-0.0115 (3)	0.18903 (7)	0.1644 (3)	0.0205 (6)
C32	-0.0536 (3)	0.18882 (7)	0.0286 (3)	0.0254 (7)
H32	-0.0718	0.1695	-0.0169	0.030*
C33	-0.0694 (3)	0.21673 (8)	-0.0409 (3)	0.0305 (7)
H33	-0.1001	0.2163	-0.1335	0.037*
C34	-0.0408 (4)	0.24480 (8)	0.0242 (3)	0.0346 (8)
H34	-0.0527	0.2638	-0.0231	0.042*
C35	0.0057 (4)	0.24515 (8)	0.1594 (3)	0.0382 (8)
H35	0.0284	0.2645	0.2048	0.046*
C36	0.0192 (4)	0.21761 (7)	0.2288 (3)	0.0319 (7)
H36	0.0499	0.2182	0.3214	0.038*
C46	0.3501 (3)	0.02386 (7)	0.0659 (3)	0.0277 (7)
H46A	0.3561	0.0180	-0.0182	0.033*
H46B	0.2718	0.0128	0.0718	0.033*
C47	0.4749 (3)	0.01298 (8)	0.1752 (3)	0.0344 (8)
H47A	0.5517	0.0254	0.1763	0.052*
H47B	0.4906	-0.0091	0.1624	0.052*

H47C	0.4638	0.0155	0.2586	0.052*
C48	0.1430 (3)	0.03444 (6)	0.2412 (3)	0.0183 (6)
C49	-0.0032 (3)	0.00860 (7)	0.3230 (3)	0.0246 (6)
H49A	0.0496	0.0156	0.4134	0.030*
H49B	0.0274	-0.0126	0.3112	0.030*
C50	-0.1505 (3)	0.00830 (8)	0.2979 (3)	0.0277 (7)
H50A	-0.1786	0.0293	0.3127	0.042*
H50B	-0.1673	-0.0066	0.3573	0.042*
H50C	-0.2017	0.0020	0.2073	0.042*
O1	0.2165 (2)	0.18213 (4)	0.46711 (19)	0.0220 (4)
O2	0.32699 (19)	0.05683 (5)	0.06542 (19)	0.0218 (4)
O3	0.2385 (2)	0.02245 (5)	0.3260 (2)	0.0248 (5)
O4	0.01421 (19)	0.03011 (5)	0.22972 (19)	0.0214 (4)
H38A	0.362 (3)	0.1126 (7)	0.166 (3)	0.014 (7)*
H37A	0.159 (3)	0.1368 (8)	0.029 (3)	0.022 (8)*
C2	0.4731 (3)	0.06082 (7)	0.5376 (3)	0.0206 (6)
H2	0.4100	0.0546	0.5739	0.025*
C3	0.5764 (3)	0.04068 (7)	0.5426 (3)	0.0237 (6)
H3	0.5832	0.0207	0.5819	0.028*
C4	0.6699 (3)	0.04963 (7)	0.4906 (3)	0.0262 (7)
H4	0.7407	0.0358	0.4952	0.031*
C6	0.5558 (3)	0.09882 (7)	0.4257 (3)	0.0221 (6)
H6	0.5482	0.1186	0.3846	0.026*
C17	0.4129 (3)	0.20394 (7)	0.6313 (3)	0.0308 (7)
H17	0.3670	0.2233	0.6239	0.037*
C19	0.1134 (3)	0.17297 (6)	0.5065 (3)	0.0223 (6)
C20	0.1229 (3)	0.17562 (7)	0.6346 (3)	0.0263 (7)
H20	0.2034	0.1830	0.7007	0.032*
C21	0.0135 (3)	0.16740 (7)	0.6654 (3)	0.0302 (7)
H21	0.0194	0.1690	0.7530	0.036*
C22	-0.1039 (3)	0.15685 (7)	0.5689 (3)	0.0309 (7)
H22	-0.1792	0.1517	0.5898	0.037*
C23	-0.1113 (3)	0.15384 (7)	0.4417 (3)	0.0250 (7)
H23	-0.1922	0.1465	0.3761	0.030*
C24	-0.0023 (3)	0.16140 (6)	0.4078 (3)	0.0205 (6)
C25	-0.1546 (3)	0.13280 (7)	0.1658 (3)	0.0211 (6)
C37	0.1522 (3)	0.11632 (7)	0.0683 (3)	0.0192 (6)
C38	0.2752 (3)	0.10286 (7)	0.1546 (3)	0.0187 (6)
C39	0.2836 (3)	0.06776 (7)	0.1654 (3)	0.0183 (6)
H39	0.3510	0.0617	0.2531	0.022*
C40	0.0402 (3)	0.06445 (7)	0.0344 (3)	0.0183 (6)
C41	-0.0612 (3)	0.04366 (7)	-0.0378 (3)	0.0209 (6)
H41	-0.0583	0.0225	-0.0106	0.025*
C42	-0.1656 (3)	0.05385 (7)	-0.1486 (3)	0.0235 (6)
H42	-0.2354	0.0399	-0.1967	0.028*
C43	-0.1682 (3)	0.08477 (7)	-0.1896 (3)	0.0243 (6)
H43	-0.2395	0.0918	-0.2660	0.029*
C44	-0.0668 (3)	0.10512 (7)	-0.1188 (3)	0.0216 (6)

H44	-0.0695	0.1261	-0.1476	0.026*
C45	0.0397 (3)	0.09551 (7)	-0.0056 (3)	0.0184 (6)
N1	0.1513 (2)	0.05461 (5)	0.1478 (2)	0.0179 (5)
P1	0.32069 (7)	0.116727 (16)	0.45850 (7)	0.01702 (16)
P2	0.00961 (7)	0.151253 (16)	0.25030 (7)	0.01798 (16)
Ni1	0.18480 (5)	0.124302 (11)	0.25670 (4)	0.01707 (13)
C27	-0.2830 (3)	0.08500 (7)	0.1011 (3)	0.0265 (7)
H27	-0.2858	0.0628	0.0953	0.032*

Atomic displacement parameters for X-ray structure ***1*** *(Å^2)*

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0160 (14)	0.0245 (15)	0.0134 (13)	0.0002 (11)	0.0010 (11)	-0.0033 (11)
C1S	0.060 (2)	0.0444 (17)	0.077 (2)	-0.0068 (15)	0.0375 (18)	-0.0010 (15)
C2S	0.060 (2)	0.0444 (17)	0.077 (2)	-0.0068 (15)	0.0375 (18)	-0.0010 (15)
C3S	0.052 (3)	0.039 (2)	0.070 (3)	-0.0075 (19)	0.022 (2)	0.000 (2)
C4S	0.044 (2)	0.038 (2)	0.091 (4)	0.0055 (18)	0.029 (2)	0.002 (2)
C5	0.0190 (15)	0.0365 (17)	0.0212 (15)	0.0001 (13)	0.0078 (13)	-0.0020 (13)
C5S	0.065 (3)	0.041 (2)	0.096 (4)	0.006 (2)	0.052 (3)	0.000 (2)
C6S	0.070 (3)	0.036 (2)	0.066 (3)	0.006 (2)	0.041 (2)	0.0033 (19)
C7	0.0191 (15)	0.0179 (14)	0.0191 (14)	0.0024 (11)	0.0081 (12)	0.0010 (11)
C7S	0.052 (2)	0.036 (2)	0.071 (3)	0.0005 (18)	0.033 (2)	0.0057 (19)
C8	0.0228 (16)	0.0329 (17)	0.0212 (15)	-0.0062 (13)	0.0072 (13)	-0.0013 (13)
C9	0.0340 (18)	0.0340 (17)	0.0190 (15)	-0.0023 (14)	0.0107 (14)	0.0004 (13)
C10	0.0324 (18)	0.0246 (15)	0.0282 (16)	0.0014 (13)	0.0191 (14)	0.0029 (13)
C11	0.0196 (15)	0.0272 (16)	0.0309 (17)	-0.0028 (12)	0.0097 (13)	0.0019 (13)
C12	0.0220 (16)	0.0240 (15)	0.0182 (14)	0.0009 (12)	0.0049 (12)	0.0019 (12)
C13	0.0228 (15)	0.0244 (15)	0.0180 (14)	-0.0052 (12)	0.0093 (12)	-0.0016 (12)
C14	0.0217 (16)	0.0288 (16)	0.0249 (16)	0.0001 (13)	0.0062 (13)	-0.0015 (13)
C15	0.0235 (17)	0.0353 (18)	0.0280 (17)	-0.0057 (14)	0.0019 (14)	-0.0056 (14)
C16	0.038 (2)	0.0307 (18)	0.0336 (18)	-0.0124 (15)	0.0084 (16)	-0.0091 (14)
C18	0.0224 (16)	0.0242 (15)	0.0199 (15)	-0.0035 (12)	0.0085 (13)	-0.0012 (12)
C26	0.0222 (15)	0.0228 (15)	0.0192 (14)	0.0015 (12)	0.0098 (12)	0.0022 (11)
C28	0.0219 (17)	0.0405 (19)	0.0319 (18)	-0.0086 (14)	0.0075 (14)	0.0016 (15)
C29	0.0193 (16)	0.0365 (19)	0.045 (2)	0.0036 (14)	0.0085 (15)	0.0064 (15)

C30	0.0220 (16)	0.0268 (16)	0.0403 (19)	0.0027 (13)	0.0122 (15)	0.0031 (14)
C31	0.0182 (15)	0.0197 (14)	0.0248 (15)	0.0012 (11)	0.0093 (12)	0.0025 (12)
C32	0.0261 (16)	0.0245 (15)	0.0246 (16)	-0.0015 (13)	0.0086 (13)	0.0007 (12)
C33	0.0305 (18)	0.0337 (18)	0.0264 (16)	0.0023 (14)	0.0096 (14)	0.0081 (14)
C34	0.044 (2)	0.0257 (17)	0.0362 (19)	0.0014 (15)	0.0177 (16)	0.0130 (14)
C35	0.055 (2)	0.0199 (16)	0.040 (2)	-0.0030 (15)	0.0189 (18)	0.0012 (14)
C36	0.045 (2)	0.0244 (16)	0.0276 (17)	0.0001 (15)	0.0152 (15)	0.0003 (13)
C46	0.0290 (17)	0.0264 (16)	0.0305 (17)	-0.0003 (13)	0.0147 (14)	-0.0098 (13)
C47	0.0326 (19)	0.0326 (18)	0.0380 (19)	0.0065 (15)	0.0133 (16)	-0.0008 (15)
C48	0.0189 (15)	0.0161 (13)	0.0190 (14)	0.0007 (11)	0.0064 (12)	-0.0019 (11)
C49	0.0285 (17)	0.0245 (15)	0.0217 (15)	-0.0025 (13)	0.0106 (13)	0.0039 (12)
C50	0.0277 (17)	0.0320 (17)	0.0264 (16)	-0.0009 (13)	0.0135 (14)	0.0035 (13)
O1	0.0223 (11)	0.0216 (10)	0.0228 (10)	0.0000 (8)	0.0092 (9)	-0.0004 (8)
O2	0.0221 (11)	0.0262 (11)	0.0186 (10)	0.0036 (8)	0.0093 (9)	-0.0025 (8)
O3	0.0212 (11)	0.0259 (11)	0.0234 (11)	0.0021 (9)	0.0042 (9)	0.0059 (9)
O4	0.0190 (10)	0.0245 (10)	0.0207 (10)	0.0005 (8)	0.0075 (8)	0.0045 (8)
C2	0.0181 (15)	0.0251 (15)	0.0167 (14)	-0.0026 (12)	0.0043 (12)	-0.0018 (12)
C3	0.0245 (16)	0.0218 (15)	0.0194 (15)	0.0005 (12)	0.0023 (13)	-0.0032 (12)
C4	0.0215 (16)	0.0317 (17)	0.0223 (15)	0.0057 (13)	0.0047 (13)	-0.0068 (13)
C6	0.0199 (15)	0.0272 (15)	0.0167 (14)	-0.0020 (12)	0.0041 (12)	-0.0003 (12)
C17	0.0336 (19)	0.0237 (16)	0.0325 (18)	-0.0032 (14)	0.0097 (15)	-0.0029 (13)
C19	0.0272 (16)	0.0149 (14)	0.0281 (16)	0.0037 (12)	0.0142 (14)	0.0012 (12)
C20	0.0348 (18)	0.0205 (15)	0.0252 (16)	0.0019 (13)	0.0133 (14)	-0.0002 (12)
C21	0.045 (2)	0.0260 (16)	0.0274 (17)	0.0022 (14)	0.0220 (16)	0.0007 (13)
C22	0.0361 (19)	0.0288 (17)	0.0378 (19)	0.0009 (14)	0.0254 (16)	0.0009 (14)
C23	0.0250 (16)	0.0228 (15)	0.0311 (17)	0.0013 (12)	0.0149 (14)	0.0012 (13)
C24	0.0231 (15)	0.0164 (13)	0.0242 (15)	0.0044 (12)	0.0114 (13)	0.0029 (11)
C25	0.0200 (15)	0.0234 (15)	0.0214 (15)	-0.0002 (12)	0.0097 (12)	0.0004 (12)
C37	0.0232 (15)	0.0199 (14)	0.0167 (14)	0.0013 (12)	0.0101 (12)	0.0026 (11)
C38	0.0177 (15)	0.0236 (15)	0.0164 (14)	-0.0013 (12)	0.0084 (12)	-0.0001 (11)
C39	0.0152 (14)	0.0243 (15)	0.0158 (14)	0.0013 (11)	0.0063 (11)	-0.0012 (11)
C40	0.0154 (14)	0.0251 (15)	0.0147 (14)	0.0020 (11)	0.0059 (11)	-0.0013 (11)

C41	0.0223 (15)	0.0217 (14)	0.0199 (15)	0.0018 (12)	0.0093 (12)	-0.0009 (11)
C42	0.0193 (15)	0.0286 (16)	0.0191 (15)	-0.0007 (12)	0.0034 (12)	-0.0030 (12)
C43	0.0203 (15)	0.0295 (16)	0.0196 (15)	0.0047 (13)	0.0036 (12)	0.0010 (12)
C44	0.0230 (16)	0.0230 (15)	0.0190 (14)	0.0041 (12)	0.0082 (13)	0.0015 (12)
C45	0.0193 (15)	0.0223 (14)	0.0152 (13)	0.0023 (12)	0.0084 (12)	-0.0003 (11)
N1	0.0161 (12)	0.0200 (12)	0.0164 (12)	0.0005 (10)	0.0047 (10)	0.0010 (9)
P1	0.0159 (4)	0.0190 (3)	0.0159 (3)	-0.0004 (3)	0.0058 (3)	0.0001 (3)
P2	0.0175 (4)	0.0172 (3)	0.0200 (4)	0.0008 (3)	0.0079 (3)	0.0007 (3)
Ni1	0.0165 (3)	0.0183 (2)	0.0163 (2)	0.00065 (19)	0.0062 (2)	0.00053 (18)
C27	0.0288 (17)	0.0265 (16)	0.0241 (16)	-0.0058 (13)	0.0099 (14)	-0.0018 (13)

*Bond distances (Å) for X-ray structure of **1***

C1—C2	1.394 (4)	C33—C34	1.374 (5)
C1—C6	1.406 (4)	C34—C35	1.386 (5)
C1—P1	1.839 (3)	C35—C36	1.384 (5)
C1S—C2S	1.532 (6)	C46—O2	1.432 (4)
C2S—C7S	1.390 (6)	C46—C47	1.499 (5)
C2S—C3S	1.398 (6)	C48—O3	1.210 (3)
C3S—C4S	1.382 (6)	C48—O4	1.356 (3)
C4S—C5S	1.386 (7)	C48—N1	1.376 (4)
C5—C6	1.391 (4)	C49—O4	1.448 (3)
C5—C4	1.392 (5)	C49—C50	1.502 (4)
C5S—C6S	1.368 (7)	O1—C19	1.395 (4)
C6S—C7S	1.393 (6)	O2—C39	1.434 (3)
C7—C12	1.391 (4)	C2—C3	1.392 (4)
C7—C8	1.395 (4)	C3—C4	1.390 (4)
C7—P1	1.841 (3)	C19—C20	1.387 (4)
C8—C9	1.387 (4)	C19—C24	1.397 (4)
C9—C10	1.385 (5)	C20—C21	1.390 (5)
C10—C11	1.383 (4)	C21—C22	1.383 (5)
C11—C12	1.393 (4)	C22—C23	1.386 (4)
C13—C18	1.391 (4)	C23—C24	1.400 (4)
C13—C14	1.399 (4)	C24—P2	1.848 (3)
C13—P1	1.855 (3)	C25—P2	1.834 (3)
C14—C15	1.388 (4)	C37—C38	1.426 (4)
C15—C16	1.378 (5)	C37—C45	1.474 (4)
C16—C17	1.387 (5)	C37—Ni1	2.009 (3)
C18—C17	1.385 (4)	C38—C39	1.506 (4)
C18—O1	1.398 (4)	C38—Ni1	1.976 (3)
C26—C27	1.390 (4)	C39—N1	1.473 (4)
C26—C25	1.394 (4)	C40—C41	1.399 (4)
C28—C27	1.383 (5)	C40—C45	1.400 (4)

C28—C29	1.389 (5)	C40—N1	1.428 (4)
C29—C30	1.388 (5)	C41—C42	1.380 (4)
C30—C25	1.394 (4)	C42—C43	1.395 (4)
C31—C36	1.391 (4)	C43—C44	1.382 (4)
C31—C32	1.394 (4)	C44—C45	1.399 (4)
C31—P2	1.845 (3)	P1—Ni1	2.1783 (10)
C32—C33	1.396 (4)	P2—Ni1	2.1885 (10)

*Bond angles for X-ray structure **1** (°)*

C2—C1—C6	118.9 (3)	C20—C19—O1	122.7 (3)
C2—C1—P1	122.5 (2)	C20—C19—C24	121.7 (3)
C6—C1—P1	118.5 (2)	O1—C19—C24	115.6 (3)
C7S—C2S—C3S	118.0 (4)	C19—C20—C21	119.4 (3)
C7S—C2S—C1S	122.3 (4)	C22—C21—C20	120.2 (3)
C3S—C2S—C1S	119.8 (4)	C21—C22—C23	119.8 (3)
C4S—C3S—C2S	120.2 (5)	C22—C23—C24	121.4 (3)
C3S—C4S—C5S	120.9 (4)	C19—C24—C23	117.4 (3)
C6—C5—C4	119.6 (3)	C19—C24—P2	117.4 (2)
C6S—C5S—C4S	119.7 (4)	C23—C24—P2	124.5 (2)
C5S—C6S—C7S	119.7 (4)	C30—C25—C26	118.6 (3)
C12—C7—C8	118.5 (3)	C30—C25—P2	123.1 (2)
C12—C7—P1	118.5 (2)	C26—C25—P2	118.2 (2)
C8—C7—P1	123.0 (2)	C38—C37—C45	119.0 (3)
C2S—C7S—C6S	121.6 (4)	C38—C37—Ni1	67.79 (16)
C9—C8—C7	120.6 (3)	C45—C37—Ni1	117.40 (19)
C10—C9—C8	120.5 (3)	C37—C38—C39	117.9 (3)
C11—C10—C9	119.5 (3)	C37—C38—Ni1	70.28 (16)
C10—C11—C12	120.2 (3)	C39—C38—Ni1	116.47 (19)
C7—C12—C11	120.8 (3)	O2—C39—N1	110.9 (2)
C18—C13—C14	117.0 (3)	O2—C39—C38	107.0 (2)
C18—C13—P1	120.4 (2)	N1—C39—C38	110.1 (2)
C14—C13—P1	122.5 (2)	C41—C40—C45	121.0 (3)
C15—C14—C13	121.0 (3)	C41—C40—N1	121.7 (3)
C16—C15—C14	120.4 (3)	C45—C40—N1	117.3 (2)
C15—C16—C17	120.1 (3)	C42—C41—C40	120.0 (3)
C17—C18—C13	122.7 (3)	C41—C42—C43	119.8 (3)
C17—C18—O1	118.4 (3)	C44—C43—C42	119.9 (3)
C13—C18—O1	118.9 (3)	C43—C44—C45	121.5 (3)
C27—C26—C25	120.6 (3)	C44—C45—C40	117.7 (3)
C27—C28—C29	120.1 (3)	C44—C45—C37	122.6 (3)
C30—C29—C28	119.7 (3)	C40—C45—C37	119.6 (2)
C29—C30—C25	121.0 (3)	C48—N1—C40	125.0 (2)
C36—C31—C32	118.3 (3)	C48—N1—C39	118.5 (2)
C36—C31—P2	123.2 (2)	C40—N1—C39	116.5 (2)
C32—C31—P2	118.4 (2)	C1—P1—C7	103.25 (13)
C31—C32—C33	120.7 (3)	C1—P1—C13	100.03 (13)
C34—C33—C32	120.1 (3)	C7—P1—C13	100.36 (13)

C33—C34—C35	119.5 (3)	C1—P1—Ni1	114.86 (9)
C36—C35—C34	120.6 (3)	C7—P1—Ni1	115.13 (10)
C35—C36—C31	120.6 (3)	C13—P1—Ni1	120.54 (10)
O2—C46—C47	114.2 (3)	C25—P2—C31	102.06 (13)
O3—C48—O4	123.4 (3)	C25—P2—C24	100.51 (13)
O3—C48—N1	124.7 (3)	C31—P2—C24	104.00 (13)
O4—C48—N1	111.9 (2)	C25—P2—Ni1	116.15 (10)
O4—C49—C50	106.7 (2)	C31—P2—Ni1	114.40 (9)
C19—O1—C18	118.1 (2)	C24—P2—Ni1	117.52 (10)
C46—O2—C39	115.2 (2)	C38—Ni1—C37	41.92 (12)
C48—O4—C49	115.2 (2)	C38—Ni1—P1	103.49 (9)
C3—C2—C1	120.2 (3)	C37—Ni1—P1	145.41 (9)
C4—C3—C2	120.5 (3)	C38—Ni1—P2	146.33 (9)
C3—C4—C5	120.0 (3)	C37—Ni1—P2	104.41 (9)
C5—C6—C1	120.9 (3)	P1—Ni1—P2	110.17 (4)
C18—C17—C16	118.8 (3)	C28—C27—C26	120.0 (3)

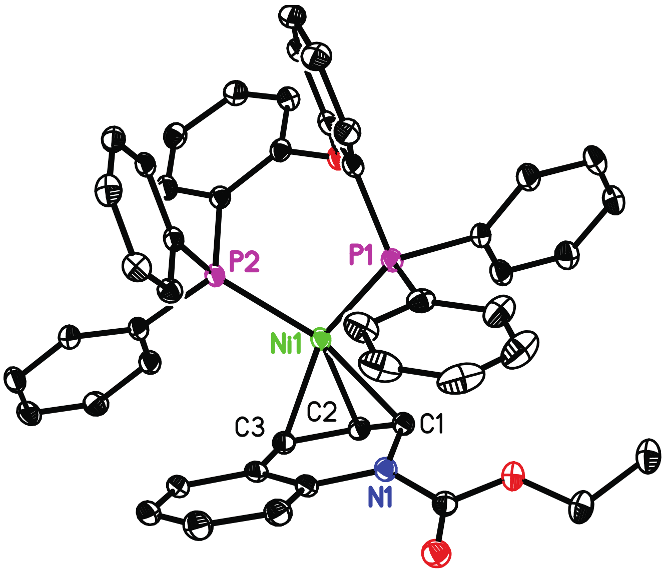
Dihedral angles for X-ray structure ***1*** *(°)*

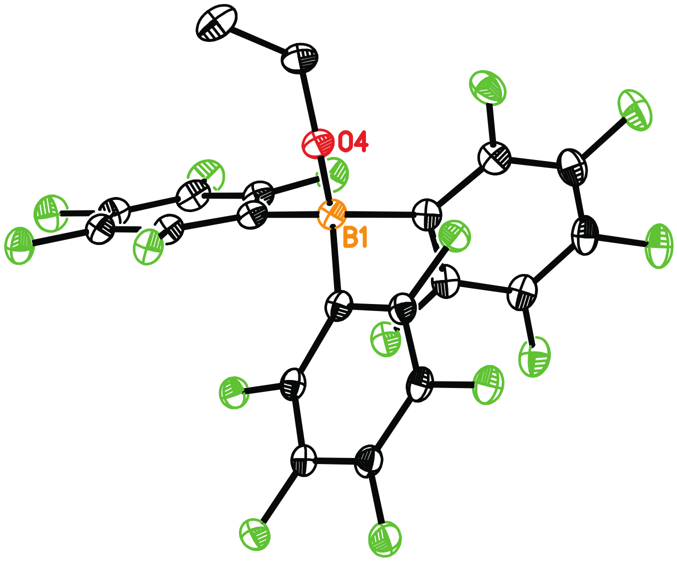
C7S—C2S—C3S—C4S	-0.1 (6)	N1—C40—C45—C44	178.2 (2)
C1S—C2S—C3S—C4S	179.4 (4)	C41—C40—C45—C37	-176.4 (3)
C2S—C3S—C4S—C5S	1.1 (6)	N1—C40—C45—C37	0.7 (4)
C3S—C4S—C5S—C6S	-1.2 (7)	C38—C37—C45—C44	-160.0 (3)
C4S—C5S—C6S—C7S	0.2 (6)	Ni1—C37—C45—C44	121.5 (3)
C3S—C2S—C7S—C6S	-0.8 (6)	C38—C37—C45—C40	17.4 (4)
C1S—C2S—C7S—C6S	179.7 (4)	Ni1—C37—C45—C40	-61.1 (3)
C5S—C6S—C7S—C2S	0.7 (6)	O3—C48—N1—C40	168.2 (3)
C12—C7—C8—C9	0.0 (5)	O4—C48—N1—C40	-13.5 (4)
P1—C7—C8—C9	179.8 (2)	O3—C48—N1—C39	-12.9 (4)
C7—C8—C9—C10	0.1 (5)	O4—C48—N1—C39	165.4 (2)
C8—C9—C10—C11	-0.1 (5)	C41—C40—N1—C48	-40.6 (4)
C9—C10—C11—C12	0.0 (5)	C45—C40—N1—C48	142.4 (3)
C8—C7—C12—C11	0.0 (4)	C41—C40—N1—C39	140.5 (3)
P1—C7—C12—C11	-179.8 (2)	C45—C40—N1—C39	-36.5 (3)
C10—C11—C12—C7	0.0 (5)	O2—C39—N1—C48	114.4 (3)
C18—C13—C14—C15	-0.7 (4)	C38—C39—N1—C48	-127.4 (3)
P1—C13—C14—C15	-178.2 (2)	O2—C39—N1—C40	-66.6 (3)
C13—C14—C15—C16	-0.6 (5)	C38—C39—N1—C40	51.6 (3)

C14—C15—C16—C17	1.0 (5)	C2—C1—P1—C7	14.0 (3)
C14—C13—C18—C17	1.7 (4)	C6—C1—P1—C7	-171.0 (2)
P1—C13—C18—C17	179.3 (2)	C2—C1—P1—C13	117.3 (2)
C14—C13—C18—O1	179.6 (2)	C6—C1—P1—C13	-67.7 (2)
P1—C13—C18—O1	-2.8 (4)	C2—C1—P1—Ni1	-112.1 (2)
C27—C28—C29—C30	-0.7 (5)	C6—C1—P1—Ni1	62.9 (2)
C28—C29—C30—C25	-0.7 (5)	C12—C7—P1—C1	-110.1 (2)
C36—C31—C32—C33	-2.4 (5)	C8—C7—P1—C1	70.1 (3)
P2—C31—C32—C33	-179.1 (2)	C12—C7—P1—C13	146.9 (2)
C31—C32—C33—C34	1.4 (5)	C8—C7—P1—C13	-32.9 (3)
C32—C33—C34—C35	0.9 (5)	C12—C7—P1—Ni1	15.8 (3)
C33—C34—C35—C36	-2.1 (6)	C8—C7—P1—Ni1	-164.0 (2)
C34—C35—C36—C31	1.0 (6)	C18—C13—P1—C1	167.8 (2)
C32—C31—C36—C35	1.3 (5)	C14—C13—P1—C1	-14.7 (3)
P2—C31—C36—C35	177.8 (3)	C18—C13—P1—C7	-86.6 (2)
C17—C18—O1—C19	-95.7 (3)	C14—C13—P1—C7	90.9 (3)
C13—C18—O1—C19	86.3 (3)	C18—C13—P1—Ni1	40.9 (3)
C47—C46—O2—C39	-73.0 (3)	C14—C13—P1—Ni1	-141.6 (2)
O3—C48—O4—C49	-3.0 (4)	C30—C25—P2—C31	-32.5 (3)
N1—C48—O4—C49	178.7 (2)	C26—C25—P2—C31	150.4 (2)
C50—C49—O4—C48	177.4 (2)	C30—C25—P2—C24	74.4 (3)
C6—C1—C2—C3	0.3 (4)	C26—C25—P2—C24	-102.7 (2)
P1—C1—C2—C3	175.3 (2)	C30—C25—P2—Ni1	-157.6 (2)
C1—C2—C3—C4	0.4 (4)	C26—C25—P2—Ni1	25.3 (3)
C2—C3—C4—C5	-0.6 (4)	C36—C31—P2—C25	129.5 (3)
C6—C5—C4—C3	-0.1 (4)	C32—C31—P2—C25	-53.9 (3)
C4—C5—C6—C1	0.9 (4)	C36—C31—P2—C24	25.3 (3)
C2—C1—C6—C5	-1.0 (4)	C32—C31—P2—C24	-158.2 (2)
P1—C1—C6—C5	-176.2 (2)	C36—C31—P2—Ni1	-104.2 (3)
C13—C18—C17—C16	-1.3 (5)	C32—C31—P2—Ni1	72.3 (2)
O1—C18—C17—C16	-179.2 (3)	C19—C24—P2—C25	172.6 (2)
C15—C16—C17—C18	-0.1 (5)	C23—C24—P2—C25	3.0 (3)
C18—O1—C19—C20	33.4 (4)	C19—C24—P2—C31	-82.0 (2)
C18—O1—C19—C24	-147.7 (2)	C23—C24—P2—C31	108.4 (3)
O1—C19—C20—C21	176.9 (3)	C19—C24—P2—Ni1	45.6 (2)
C24—C19—C20—C21	-1.8 (4)	C23—C24—P2—Ni1	-124.0 (2)

C19—C20—C21—C22	-0.3 (5)	C39—C38—Ni1—C37	-112.2 (3)
C20—C21—C22—C23	1.4 (5)	C37—C38—Ni1—P1	179.88 (15)
C21—C22—C23—C24	-0.3 (5)	C39—C38—Ni1—P1	67.7 (2)
C20—C19—C24—C23	2.9 (4)	C37—C38—Ni1—P2	0.6 (3)
O1—C19—C24—C23	-176.0 (2)	C39—C38—Ni1—P2	-111.5 (2)
C20—C19—C24—P2	-167.5 (2)	C45—C37—Ni1—C38	112.2 (3)
O1—C19—C24—P2	13.7 (3)	C38—C37—Ni1—P1	-0.2 (2)
C22—C23—C24—C19	-1.8 (4)	C45—C37—Ni1—P1	112.0 (2)
C22—C23—C24—P2	167.8 (2)	C38—C37—Ni1—P2	-179.64 (15)
C29—C30—C25—C26	1.4 (5)	C45—C37—Ni1—P2	-67.5 (2)
C29—C30—C25—P2	-175.7 (3)	C1—P1—Ni1—C38	-6.99 (14)
C27—C26—C25—C30	-0.7 (4)	C7—P1—Ni1—C38	-126.75 (13)
C27—C26—C25—P2	176.5 (2)	C13—P1—Ni1—C38	112.75 (14)
C45—C37—C38—C39	0.2 (4)	C1—P1—Ni1—C37	-6.85 (19)
Ni1—C37—C38—C39	110.2 (2)	C7—P1—Ni1—C37	-126.61 (18)
C45—C37—C38—Ni1	-110.0 (2)	C13—P1—Ni1—C37	112.89 (18)
C46—O2—C39—N1	-64.1 (3)	C1—P1—Ni1—P2	172.57 (10)
C46—O2—C39—C38	175.8 (2)	C7—P1—Ni1—P2	52.81 (11)
C37—C38—C39—O2	87.9 (3)	C13—P1—Ni1—P2	-67.69 (11)
Ni1—C38—C39—O2	168.58 (17)	C25—P2—Ni1—C38	57.18 (19)
C37—C38—C39—N1	-32.7 (3)	C31—P2—Ni1—C38	-61.39 (19)
Ni1—C38—C39—N1	48.0 (3)	C24—P2—Ni1—C38	176.20 (18)
C45—C40—C41—C42	-1.6 (4)	C25—P2—Ni1—C37	57.62 (14)
N1—C40—C41—C42	-178.5 (3)	C31—P2—Ni1—C37	-60.96 (14)
C40—C41—C42—C43	1.2 (4)	C24—P2—Ni1—C37	176.63 (13)
C41—C42—C43—C44	-0.4 (4)	C25—P2—Ni1—P1	-122.04 (11)
C42—C43—C44—C45	-0.1 (4)	C31—P2—Ni1—P1	119.38 (11)
C43—C44—C45—C40	-0.3 (4)	C24—P2—Ni1—P1	-3.03 (11)
C43—C44—C45—C37	177.2 (3)	C29—C28—C27—C26	1.4 (5)
C41—C40—C45—C44	1.2 (4)	C25—C26—C27—C28	-0.7 (4)

U) X-ray Crystal Structural Information for 5-borate





Computing details

Data collection: Bruker *APEX2*; cell refinement: Bruker *SAINT*; data reduction: Bruker *SAINT*; program(s) used to solve structure: *SIR92* (Giacavazzo, 1993); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3* (Farraguia, 1997).

Crystal data

$C_{79}H_{61}BF_{15}NNiO_5P_2$	$Z = 2$
$M_r = 1520.75$	$F(000) = 1560$
Triclinic, $P\bar{1}$	$D_x = 1.466$ Mg m^{-3}
$a = 14.2780$ (5) Å	Cu *K*□ radiation, □ = 1.54178 Å
$b = 16.2816$ (6) Å	Cell parameters from 9975 reflections

c = 17.9728 (10) Å	θ = 3.2–66.0°
α = 103.497 (3)°	μ = 1.68 mm^{-1}
β = 100.949 (3)°	T = 100 K
γ = 115.919 (2)°	Parallelipid, orange
V = 3444.4 (3) Å^3	0.10 × 0.07 × 0.04 mm

Data collection

Bruker APEX II CCD diffractometer	11205 independent reflections
Radiation source: fine-focus sealed tube	9538 reflections with $I > 2\sigma(I)$
graphite	R_{int} = 0.028
phi and ω scans	$\theta_{\max}$ = 66.2°, $\theta_{\min}$ = 2.7°
Absorption correction: multi-scan *SADABS* V2008/1 (Bruker AXS)	$h = -16 \rightarrow 16$
$T_{\min}$ = 0.673, $T_{\max}$ = 0.753	$k = -18 \rightarrow 19$
29624 measured reflections	$l = -20 \rightarrow 21$

Refinement

Refinement on F^2	Primary atom site location: structure-invariant direct methods
Least-squares matrix: full	Secondary atom site location: difference Fourier map
$R[F^2 > 2\sigma(F^2)]$ = 0.056	Hydrogen site location: inferred from neighbouring sites
$wR(F^2)$ = 0.168	H-atom parameters constrained
S = 1.05	$w = 1/[\sigma^2(F_o^2) + (0.0941P)^2 + 5.2115P]$ where $P = (F_o^2 + 2F_c^2)/3$
11205 reflections	$(\Delta/\sigma)_{\max}$ = 0.001
892 parameters	$\Delta\rho_{\max}$ = 1.13 e Å^{-3}
66 restraints	$\Delta\rho_{\min}$ = -0.89 e Å^{-3}

Special details

Experimental. Collected, solved and refined by Scott P. Semproni. The unit cell contained a molecule of disordered toluene and of tetra-hydrofuran, which were modeled using SIMU, DELU, DFIX and EADP least squares restraints.

Geometry. All s.u.'s (except the s.u. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell s.u.'s are taken into account individually in the estimation of s.u.'s in distances, angles and torsion angles; correlations between s.u.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell s.u.'s is used for estimating s.u.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2, conventional R-factors R are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > 2\sigma(F^2)$ is used only for calculating R-factors(gt) etc. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters for ***5-borate*** *($\AA^2$)*

	x	*y*	*z*	U_{iso}*/U_{eq}
C1	0.6585 (2)	0.0477 (2)	0.76789 (19)	0.0262 (7)
H1	0.6961	0.0549	0.8207	0.031*
C1S	-0.0616 (7)	0.6436 (7)	0.7856 (6)	0.1394 (14)
H1S	-0.1023	0.6521	0.8198	0.167*
C2	0.6179 (2)	-0.0391 (2)	0.70224 (19)	0.0267 (7)
H2	0.5913	-0.1009	0.7083	0.032*
C2S	0.0536 (7)	0.6958 (8)	0.8148 (6)	0.1394 (14)
H2S	0.0923	0.7465	0.8667	0.167*
C3	0.6190 (2)	-0.0288 (2)	0.62753 (19)	0.0284 (7)
H3	0.6114	-0.0801	0.5842	0.034*
C3S	0.1108 (8)	0.6731 (8)	0.7677 (6)	0.1394 (14)
H3S	0.1885	0.7008	0.7894	0.167*
C4	0.6317 (2)	0.0608 (3)	0.6158 (2)	0.0299 (7)
C4S	0.0504 (7)	0.6065 (7)	0.6850 (6)	0.1394 (14)
H4S	0.0917	0.5974	0.6515	0.167*
C5	0.6325 (3)	0.0708 (3)	0.5401 (2)	0.0351 (8)
H5	0.6226	0.0185	0.4964	0.042*
C5S	-0.0654 (7)	0.5540 (8)	0.6503 (6)	0.1394 (14)
C6	0.6476 (3)	0.1560 (3)	0.5290 (2)	0.0441 (10)
H6	0.6478	0.1624	0.4778	0.053*
C6S	-0.1168 (8)	0.5779 (8)	0.7041 (6)	0.1394 (14)
H6S	-0.1950	0.5474	0.6843	0.167*
C7	0.6625 (3)	0.2326 (3)	0.5928 (3)	0.0459 (10)
H7	0.6746	0.2918	0.5851	0.055*
C7S	-0.1152 (10)	0.4988 (9)	0.5579 (7)	0.260 (9)
H7S1	-0.1176	0.5436	0.5305	0.390*
H7S2	-0.1902	0.4446	0.5443	0.390*
H7S3	-0.0694	0.4731	0.5402	0.390*
C8	0.6599 (3)	0.2245 (3)	0.6678 (2)	0.0389 (8)
H8	0.6691	0.2772	0.7107	0.047*
C9	0.6438 (3)	0.1381 (3)	0.6794 (2)	0.0298 (7)
C9S	0.3772 (11)	0.5396 (10)	0.2337 (8)	0.175 (3)
H9S1	0.4058	0.5199	0.2768	0.210*
H9S2	0.3688	0.5949	0.2612	0.210*
C10	0.6172 (3)	0.1779 (2)	0.8122 (2)	0.0297 (7)
C11	0.6045 (3)	0.2088 (3)	0.9439 (2)	0.0388 (8)
H11A	0.5241	0.1840	0.9295	0.047*
H11B	0.6428	0.2795	0.9530	0.047*
C11S	0.2910 (11)	0.4345 (9)	0.1068 (7)	0.175 (3)
H11C	0.2458	0.4437	0.0641	0.210*
H11D	0.2727	0.3655	0.0872	0.210*
C12	0.6457 (3)	0.1919 (3)	1.0191 (2)	0.0432 (9)
H12A	0.6109	0.1215	1.0082	0.065*
H12B	0.6271	0.2225	1.0632	0.065*

H12C	0.7261	0.2207	1.0349	0.065*
C12S	0.4129 (11)	0.5008 (8)	0.1207 (6)	0.175 (3)
H12D	0.4493	0.4611	0.1181	0.210*
H12E	0.4190	0.5266	0.0761	0.210*
C13	1.0526 (3)	0.1836 (2)	0.83971 (18)	0.0274 (7)
C13S	0.4710 (10)	0.5818 (8)	0.1968 (6)	0.175 (3)
H13A	0.4845	0.6446	0.1909	0.210*
H13B	0.5409	0.5883	0.2272	0.210*
C14	1.1359 (3)	0.2810 (3)	0.8687 (2)	0.0327 (7)
H14	1.1200	0.3315	0.8874	0.039*
C15	1.2421 (3)	0.3044 (3)	0.8704 (2)	0.0378 (8)
H15	1.2987	0.3711	0.8899	0.045*
C16	1.2666 (3)	0.2317 (3)	0.8441 (2)	0.0358 (8)
H16	1.3399	0.2488	0.8458	0.043*
C17	1.1850 (3)	0.1342 (3)	0.81515 (19)	0.0299 (7)
H17	1.2014	0.0840	0.7971	0.036*
C18	1.0793 (3)	0.1116 (2)	0.81315 (18)	0.0265 (7)
C19	0.9855 (3)	-0.0510 (2)	0.71855 (18)	0.0256 (6)
C20	1.0251 (3)	-0.1128 (3)	0.7287 (2)	0.0311 (7)
H20	1.0598	-0.1073	0.7817	0.037*
C21	1.0140 (3)	-0.1828 (3)	0.6610 (2)	0.0326 (7)
H21	1.0390	-0.2268	0.6674	0.039*
C22	0.9665 (3)	-0.1880 (3)	0.5844 (2)	0.0333 (7)
H22	0.9614	-0.2342	0.5379	0.040*
C23	0.9262 (3)	-0.1261 (2)	0.5749 (2)	0.0300 (7)
H23	0.8932	-0.1308	0.5218	0.036*
C24	0.9331 (2)	-0.0570 (2)	0.64205 (19)	0.0250 (6)
C25	0.9053 (3)	0.2519 (2)	0.8743 (2)	0.0325 (7)
C26	0.8922 (3)	0.2811 (3)	0.9487 (2)	0.0436 (9)
H26	0.8907	0.2448	0.9833	0.052*
C27	0.8814 (4)	0.3629 (3)	0.9731 (3)	0.0567 (12)
H27	0.8728	0.3824	1.0242	0.068*
C28	0.8830 (3)	0.4158 (3)	0.9236 (3)	0.0595 (13)
H28	0.8736	0.4708	0.9400	0.071*
C29	0.8984 (4)	0.3892 (3)	0.8499 (3)	0.0569 (12)
H29	0.9019	0.4272	0.8165	0.068*
C30	0.9089 (3)	0.3070 (3)	0.8247 (2)	0.0454 (9)
H30	0.9184	0.2883	0.7737	0.054*
C31	0.8999 (3)	0.0868 (3)	0.91372 (19)	0.0294 (7)
C32	0.9861 (3)	0.1360 (3)	0.9887 (2)	0.0407 (9)
H32	1.0499	0.1959	0.9974	0.049*
C33	0.9785 (3)	0.0978 (3)	1.0496 (2)	0.0484 (10)
H33	1.0365	0.1316	1.1003	0.058*
C34	0.8855 (3)	0.0094 (3)	1.0365 (2)	0.0438 (9)
H34	0.8801	-0.0167	1.0786	0.053*
C35	0.8012 (3)	-0.0403 (3)	0.9625 (2)	0.0371 (8)
H35	0.7382	-0.1008	0.9535	0.045*
C36	0.8089 (3)	-0.0015 (3)	0.9012 (2)	0.0318 (7)

H36	0.7511	-0.0361	0.8502	0.038*
C37	0.7842 (3)	-0.0454 (2)	0.52152 (18)	0.0258 (7)
C38	0.6945 (3)	-0.1402 (2)	0.49368 (19)	0.0292 (7)
H38	0.6783	-0.1735	0.5305	0.035*
C39	0.6285 (3)	-0.1865 (3)	0.4123 (2)	0.0345 (8)
H39	0.5675	-0.2512	0.3938	0.041*
C40	0.6517 (3)	-0.1382 (3)	0.3581 (2)	0.0364 (8)
H40	0.6060	-0.1692	0.3027	0.044*
C41	0.7417 (3)	-0.0447 (3)	0.3852 (2)	0.0340 (8)
H41	0.7584	-0.0121	0.3479	0.041*
C42	0.8078 (3)	0.0018 (3)	0.46623 (19)	0.0288 (7)
H42	0.8694	0.0661	0.4842	0.035*
C43	0.9715 (3)	0.1337 (2)	0.63559 (18)	0.0254 (6)
C44	1.0793 (3)	0.1574 (2)	0.64019 (18)	0.0269 (7)
H44	1.1012	0.1101	0.6402	0.032*
C45	1.1544 (3)	0.2496 (3)	0.64473 (19)	0.0320 (7)
H45	1.2282	0.2658	0.6487	0.038*
C46	1.1225 (3)	0.3187 (3)	0.6435 (2)	0.0364 (8)
H46	1.1743	0.3818	0.6464	0.044*
C47	1.0154 (3)	0.2957 (3)	0.6382 (2)	0.0352 (8)
H47	0.9936	0.3428	0.6368	0.042*
C48	0.9400 (3)	0.2039 (2)	0.6348 (2)	0.0303 (7)
H48	0.8668	0.1886	0.6320	0.036*
C49	0.6638 (3)	0.7334 (3)	0.7639 (2)	0.0397 (8)
H49A	0.6213	0.6614	0.7366	0.048*
H49B	0.7075	0.7490	0.8202	0.048*
C50	0.7405 (3)	0.7782 (3)	0.7195 (3)	0.0476 (10)
H50A	0.6976	0.7587	0.6627	0.071*
H50B	0.7938	0.7554	0.7219	0.071*
H50C	0.7801	0.8496	0.7451	0.071*
C51	0.4226 (3)	0.6486 (2)	0.8000 (2)	0.0326 (7)
C52	0.4825 (3)	0.6630 (3)	0.8770 (2)	0.0394 (8)
C53	0.4349 (3)	0.6220 (3)	0.9289 (2)	0.0430 (9)
C54	0.3224 (3)	0.5653 (3)	0.9057 (2)	0.0406 (9)
C55	0.2581 (3)	0.5480 (3)	0.8306 (2)	0.0378 (8)
C56	0.3093 (3)	0.5893 (2)	0.7800 (2)	0.0343 (8)
C57	0.4159 (3)	0.7744 (2)	0.7370 (2)	0.0282 (7)
C58	0.4508 (3)	0.8509 (2)	0.8091 (2)	0.0299 (7)
C59	0.4095 (3)	0.9135 (2)	0.8197 (2)	0.0311 (7)
C60	0.3311 (3)	0.9033 (3)	0.7552 (2)	0.0345 (8)
C61	0.2931 (3)	0.8295 (3)	0.6818 (2)	0.0346 (8)
C62	0.3345 (3)	0.7667 (2)	0.6751 (2)	0.0305 (7)
C63	0.4342 (3)	0.6203 (2)	0.6457 (2)	0.0306 (7)
C64	0.3948 (3)	0.5208 (3)	0.6266 (2)	0.0348 (8)
C65	0.3670 (3)	0.4557 (2)	0.5503 (2)	0.0376 (8)
C66	0.3812 (3)	0.4898 (3)	0.4877 (2)	0.0370 (8)
C67	0.4242 (3)	0.5883 (3)	0.5035 (2)	0.0342 (8)
C68	0.4495 (3)	0.6498 (2)	0.5805 (2)	0.0316 (7)

N1	0.6434 (2)	0.1252 (2)	0.75528 (16)	0.0274 (6)
O1	0.99298 (17)	0.01557 (16)	0.78753 (12)	0.0269 (5)
O1S	0.2612 (12)	0.4548 (10)	0.1828 (8)	0.306 (7)
O2	0.5875 (2)	0.23470 (19)	0.80200 (15)	0.0390 (6)
O3	0.6276 (2)	0.15606 (17)	0.87925 (14)	0.0331 (5)
O4	0.58993 (18)	0.77001 (17)	0.76500 (14)	0.0324 (5)
F1	0.59366 (18)	0.71968 (17)	0.90628 (14)	0.0492 (6)
F2	0.4983 (2)	0.63931 (19)	1.00303 (14)	0.0581 (6)
F3	0.2740 (2)	0.52698 (16)	0.95662 (14)	0.0508 (6)
F4	0.14773 (18)	0.49236 (16)	0.80722 (14)	0.0488 (6)
F5	0.24210 (16)	0.56930 (15)	0.70634 (12)	0.0397 (5)
F6	0.52862 (16)	0.86652 (14)	0.87545 (11)	0.0352 (4)
F7	0.44395 (17)	0.98352 (14)	0.89201 (12)	0.0385 (5)
F8	0.2903 (2)	0.96450 (17)	0.76494 (13)	0.0469 (5)
F9	0.21546 (19)	0.81804 (18)	0.61815 (12)	0.0458 (5)
F10	0.28756 (16)	0.69322 (15)	0.60168 (11)	0.0367 (5)
F11	0.49195 (16)	0.74592 (13)	0.59003 (12)	0.0349 (4)
F12	0.43949 (19)	0.62245 (15)	0.44262 (12)	0.0428 (5)
F13	0.35443 (19)	0.42836 (16)	0.41261 (13)	0.0486 (6)
F14	0.32784 (19)	0.35993 (15)	0.53684 (15)	0.0492 (6)
F15	0.38173 (18)	0.48039 (14)	0.68449 (13)	0.0407 (5)
P1	0.90874 (6)	0.13969 (6)	0.83422 (5)	0.02576 (19)
P2	0.86590 (6)	0.01525 (6)	0.62998 (4)	0.02350 (18)
Ni1	0.77707 (4)	0.03994 (4)	0.71594 (3)	0.02387 (15)
B1	0.4717 (3)	0.7032 (3)	0.7368 (2)	0.0305 (8)

Atomic displacement parameters for ***5-borate*** *(Å^2)*

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0236 (15)	0.0273 (17)	0.0266 (16)	0.0101 (14)	0.0090 (12)	0.0130 (13)
C1S	0.116 (3)	0.174 (4)	0.156 (4)	0.086 (3)	0.050 (2)	0.075 (3)
C2	0.0208 (15)	0.0258 (17)	0.0276 (16)	0.0062 (13)	0.0088 (12)	0.0106 (13)
C2S	0.116 (3)	0.174 (4)	0.156 (4)	0.086 (3)	0.050 (2)	0.075 (3)
C3	0.0214 (15)	0.0307 (18)	0.0257 (16)	0.0086 (14)	0.0061 (12)	0.0086 (13)
C3S	0.116 (3)	0.174 (4)	0.156 (4)	0.086 (3)	0.050 (2)	0.075 (3)
C4	0.0193 (15)	0.039 (2)	0.0278 (17)	0.0115 (14)	0.0056 (13)	0.0138 (14)
C4S	0.116 (3)	0.174 (4)	0.156 (4)	0.086 (3)	0.050 (2)	0.075 (3)
C5	0.0266 (17)	0.054 (2)	0.0278 (18)	0.0202 (17)	0.0089 (14)	0.0195 (16)
C5S	0.116 (3)	0.174 (4)	0.156 (4)	0.086 (3)	0.050 (2)	0.075 (3)
C6	0.0366 (19)	0.073 (3)	0.042 (2)	0.032 (2)	0.0193 (17)	0.039 (2)
C6S	0.116 (3)	0.174 (4)	0.156 (4)	0.086 (3)	0.050 (2)	0.075 (3)
C7	0.046 (2)	0.055 (3)	0.056 (3)	0.030 (2)	0.0235 (19)	0.039 (2)
C7S	0.157 (10)	0.209 (12)	0.221 (10)	0.110 (9)	-0.108 (9)	-0.139 (10)
C8	0.040 (2)	0.045 (2)	0.045 (2)	0.0255 (18)	0.0180 (16)	0.0266 (17)
C9	0.0234 (15)	0.039 (2)	0.0280 (17)	0.0141 (15)	0.0078 (13)	0.0168 (14)
C9S	0.256 (8)	0.172 (7)	0.130 (5)	0.120 (6)	0.076 (6)	0.077 (4)
C10	0.0246 (15)	0.0278 (18)	0.0282 (17)	0.0085 (14)	0.0065 (13)	0.0074 (13)
C11	0.046 (2)	0.034 (2)	0.0335 (19)	0.0174 (17)	0.0198 (16)	0.0081 (15)

C11S	0.256 (8)	0.172 (7)	0.130 (5)	0.120 (6)	0.076 (6)	0.077 (4)
C12	0.048 (2)	0.039 (2)	0.0306 (19)	0.0136 (18)	0.0167 (16)	0.0080 (15)
C12S	0.256 (8)	0.172 (7)	0.130 (5)	0.120 (6)	0.076 (6)	0.077 (4)
C13	0.0272 (16)	0.0307 (18)	0.0183 (15)	0.0123 (14)	0.0044 (12)	0.0061 (12)
C13S	0.256 (8)	0.172 (7)	0.130 (5)	0.120 (6)	0.076 (6)	0.077 (4)
C14	0.0311 (17)	0.0278 (18)	0.0296 (18)	0.0109 (15)	0.0074 (14)	0.0047 (13)
C15	0.0288 (17)	0.0301 (19)	0.039 (2)	0.0066 (15)	0.0073 (15)	0.0064 (15)
C16	0.0251 (16)	0.040 (2)	0.0308 (18)	0.0119 (16)	0.0053 (14)	0.0071 (15)
C17	0.0287 (16)	0.0350 (19)	0.0223 (16)	0.0151 (15)	0.0053 (13)	0.0085 (13)
C18	0.0290 (16)	0.0270 (17)	0.0174 (15)	0.0104 (14)	0.0048 (12)	0.0078 (12)
C19	0.0243 (15)	0.0240 (17)	0.0239 (16)	0.0087 (13)	0.0092 (12)	0.0071 (12)
C20	0.0322 (17)	0.0356 (19)	0.0285 (17)	0.0177 (16)	0.0107 (14)	0.0144 (14)
C21	0.0370 (18)	0.0311 (19)	0.0344 (19)	0.0196 (16)	0.0132 (15)	0.0134 (14)
C22	0.0379 (18)	0.0316 (19)	0.0279 (18)	0.0176 (16)	0.0126 (14)	0.0053 (14)
C23	0.0313 (17)	0.0315 (18)	0.0232 (16)	0.0129 (15)	0.0085 (13)	0.0096 (13)
C24	0.0238 (15)	0.0237 (16)	0.0250 (16)	0.0088 (13)	0.0090 (12)	0.0102 (12)
C25	0.0229 (15)	0.0276 (18)	0.0335 (18)	0.0090 (14)	0.0036 (13)	0.0010 (14)
C26	0.0350 (19)	0.030 (2)	0.049 (2)	0.0073 (16)	0.0168 (17)	0.0011 (16)
C27	0.047 (2)	0.032 (2)	0.069 (3)	0.0099 (19)	0.028 (2)	-0.005 (2)
C28	0.035 (2)	0.029 (2)	0.090 (4)	0.0128 (18)	0.011 (2)	-0.006 (2)
C29	0.052 (2)	0.037 (2)	0.067 (3)	0.024 (2)	-0.001 (2)	0.008 (2)
C30	0.049 (2)	0.036 (2)	0.042 (2)	0.0241 (19)	0.0023 (17)	0.0051 (16)
C31	0.0306 (17)	0.0371 (19)	0.0207 (16)	0.0173 (15)	0.0097 (13)	0.0092 (13)
C32	0.0322 (18)	0.052 (2)	0.0266 (18)	0.0133 (17)	0.0085 (15)	0.0114 (16)
C33	0.044 (2)	0.070 (3)	0.0228 (19)	0.025 (2)	0.0063 (16)	0.0148 (18)
C34	0.050 (2)	0.062 (3)	0.0281 (19)	0.032 (2)	0.0158 (17)	0.0228 (18)
C35	0.045 (2)	0.037 (2)	0.0335 (19)	0.0224 (18)	0.0156 (16)	0.0154 (15)
C36	0.0393 (19)	0.0344 (19)	0.0226 (16)	0.0212 (16)	0.0083 (14)	0.0079 (13)
C37	0.0272 (16)	0.0280 (17)	0.0194 (15)	0.0130 (14)	0.0067 (12)	0.0065 (12)
C38	0.0285 (16)	0.0303 (18)	0.0249 (17)	0.0126 (15)	0.0078 (13)	0.0089 (13)
C39	0.0289 (17)	0.0332 (19)	0.0294 (18)	0.0118 (15)	0.0045 (14)	0.0037 (14)
C40	0.0366 (19)	0.045 (2)	0.0218 (17)	0.0223 (17)	0.0030 (14)	0.0043 (14)
C41	0.0428 (19)	0.043 (2)	0.0241 (17)	0.0261 (18)	0.0120 (15)	0.0148 (14)
C42	0.0302 (16)	0.0318 (18)	0.0250 (17)	0.0157 (15)	0.0103 (13)	0.0101 (13)
C43	0.0264 (15)	0.0258 (17)	0.0190 (15)	0.0097 (14)	0.0067 (12)	0.0077 (12)
C44	0.0289 (16)	0.0302 (18)	0.0181 (15)	0.0132 (14)	0.0067 (12)	0.0074 (12)
C45	0.0254 (16)	0.0329 (19)	0.0253 (17)	0.0065 (15)	0.0074 (13)	0.0075 (13)
C46	0.0373 (19)	0.0240 (18)	0.0332 (19)	0.0045 (15)	0.0113 (15)	0.0087 (14)
C47	0.0369 (19)	0.0265 (19)	0.0368 (19)	0.0135 (16)	0.0088 (15)	0.0101 (14)
C48	0.0281 (16)	0.0289 (18)	0.0300 (17)	0.0125 (15)	0.0075 (13)	0.0099 (13)
C49	0.0323 (18)	0.033 (2)	0.049 (2)	0.0149 (16)	0.0115 (16)	0.0120 (16)
C50	0.038 (2)	0.029 (2)	0.068 (3)	0.0119 (17)	0.0254 (19)	0.0089 (18)
C51	0.0345 (18)	0.0236 (17)	0.0346 (19)	0.0109 (15)	0.0116 (15)	0.0098 (14)
C52	0.0374 (19)	0.032 (2)	0.042 (2)	0.0126 (17)	0.0114 (16)	0.0146 (16)
C53	0.052 (2)	0.036 (2)	0.035 (2)	0.0169 (19)	0.0126 (17)	0.0156 (16)
C54	0.058 (2)	0.028 (2)	0.036 (2)	0.0167 (18)	0.0234 (18)	0.0155 (15)
C55	0.040 (2)	0.0226 (18)	0.041 (2)	0.0071 (16)	0.0180 (16)	0.0094 (14)
C56	0.0392 (19)	0.0254 (18)	0.0313 (18)	0.0113 (16)	0.0115 (15)	0.0088 (14)

C57	0.0255 (16)	0.0220 (17)	0.0330 (18)	0.0062 (14)	0.0135 (13)	0.0116 (13)
C58	0.0282 (16)	0.0275 (18)	0.0313 (18)	0.0091 (14)	0.0128 (14)	0.0136 (14)
C59	0.0361 (18)	0.0250 (18)	0.0306 (18)	0.0116 (15)	0.0174 (14)	0.0099 (13)
C60	0.046 (2)	0.036 (2)	0.0364 (19)	0.0263 (17)	0.0232 (16)	0.0195 (15)
C61	0.0387 (19)	0.044 (2)	0.0293 (18)	0.0229 (17)	0.0167 (15)	0.0176 (15)
C62	0.0318 (17)	0.0289 (18)	0.0281 (17)	0.0111 (15)	0.0141 (14)	0.0108 (13)
C63	0.0265 (16)	0.0232 (17)	0.0381 (19)	0.0096 (14)	0.0115 (14)	0.0097 (14)
C64	0.0296 (17)	0.0273 (19)	0.046 (2)	0.0110 (15)	0.0150 (15)	0.0146 (15)
C65	0.0348 (18)	0.0193 (18)	0.051 (2)	0.0100 (15)	0.0154 (16)	0.0065 (15)
C66	0.0349 (18)	0.0280 (19)	0.038 (2)	0.0140 (16)	0.0091 (15)	0.0015 (15)
C67	0.0347 (18)	0.0310 (19)	0.0362 (19)	0.0154 (16)	0.0139 (15)	0.0116 (15)
C68	0.0313 (17)	0.0209 (17)	0.0395 (19)	0.0108 (14)	0.0134 (14)	0.0095 (14)
N1	0.0268 (13)	0.0281 (15)	0.0268 (14)	0.0120 (12)	0.0097 (11)	0.0122 (11)
O1	0.0279 (11)	0.0268 (12)	0.0209 (11)	0.0112 (10)	0.0070 (9)	0.0061 (9)
O1S	0.42 (2)	0.267 (14)	0.286 (16)	0.222 (15)	0.082 (15)	0.130 (13)
O2	0.0440 (14)	0.0398 (15)	0.0384 (14)	0.0260 (13)	0.0127 (11)	0.0134 (11)
O3	0.0392 (13)	0.0332 (13)	0.0269 (12)	0.0170 (11)	0.0146 (10)	0.0104 (10)
O4	0.0271 (11)	0.0267 (12)	0.0393 (13)	0.0106 (10)	0.0116 (10)	0.0107 (10)
F1	0.0363 (11)	0.0513 (14)	0.0464 (13)	0.0121 (11)	0.0046 (10)	0.0227 (11)
F2	0.0650 (16)	0.0618 (16)	0.0410 (13)	0.0255 (13)	0.0108 (11)	0.0268 (11)
F3	0.0705 (15)	0.0379 (13)	0.0420 (13)	0.0184 (12)	0.0301 (11)	0.0198 (10)
F4	0.0406 (12)	0.0387 (13)	0.0467 (13)	0.0026 (10)	0.0199 (10)	0.0130 (10)
F5	0.0319 (10)	0.0360 (12)	0.0351 (11)	0.0054 (9)	0.0088 (9)	0.0118 (9)
F6	0.0319 (10)	0.0339 (11)	0.0308 (10)	0.0134 (9)	0.0059 (8)	0.0068 (8)
F7	0.0457 (12)	0.0302 (11)	0.0348 (11)	0.0160 (9)	0.0172 (9)	0.0071 (8)
F8	0.0696 (15)	0.0559 (14)	0.0409 (12)	0.0473 (13)	0.0263 (11)	0.0217 (10)
F9	0.0555 (13)	0.0664 (15)	0.0317 (11)	0.0426 (12)	0.0158 (10)	0.0192 (10)
F10	0.0370 (10)	0.0379 (11)	0.0278 (10)	0.0179 (9)	0.0077 (8)	0.0044 (8)
F11	0.0432 (11)	0.0226 (10)	0.0377 (11)	0.0137 (9)	0.0189 (9)	0.0107 (8)
F12	0.0559 (13)	0.0387 (12)	0.0369 (12)	0.0246 (11)	0.0206 (10)	0.0131 (9)
F13	0.0570 (14)	0.0360 (12)	0.0401 (12)	0.0220 (11)	0.0122 (10)	-0.0012 (9)
F14	0.0537 (13)	0.0211 (11)	0.0635 (15)	0.0139 (10)	0.0210 (11)	0.0087 (10)
F15	0.0460 (12)	0.0257 (11)	0.0512 (13)	0.0144 (9)	0.0217 (10)	0.0181 (9)
P1	0.0243 (4)	0.0264 (4)	0.0200 (4)	0.0102 (3)	0.0051 (3)	0.0047 (3)
P2	0.0235 (4)	0.0238 (4)	0.0191 (4)	0.0090 (3)	0.0063 (3)	0.0075 (3)
Ni1	0.0226 (3)	0.0243 (3)	0.0190 (3)	0.0082 (2)	0.0058 (2)	0.0067 (2)
B1	0.0304 (19)	0.024 (2)	0.034 (2)	0.0107 (16)	0.0118 (16)	0.0097 (15)

*Bond distances for **5-borate*** (Å)

C1—C2	1.403 (5)	C33—C34	1.393 (6)
C1—N1	1.430 (4)	C34—C35	1.383 (6)
C1—Ni1	2.118 (3)	C35—C36	1.391 (5)
C1S—C2S	1.395 (8)	C37—C38	1.394 (5)
C1S—C6S	1.415 (8)	C37—C42	1.396 (4)
C2—C3	1.394 (4)	C37—P2	1.835 (3)
C2—Ni1	1.991 (3)	C38—C39	1.392 (5)
C2S—C3S	1.378 (8)	C39—C40	1.389 (5)

C3—C4	1.458 (5)	C40—C41	1.383 (5)
C3—Ni1	2.115 (3)	C41—C42	1.387 (5)
C3S—C4S	1.440 (8)	C43—C44	1.393 (4)
C4—C9	1.409 (5)	C43—C48	1.403 (5)
C4—C5	1.411 (5)	C43—P2	1.820 (3)
C4S—C5S	1.407 (8)	C44—C45	1.384 (5)
C5—C6	1.377 (6)	C45—C46	1.389 (5)
C5S—C6S	1.403 (12)	C46—C47	1.383 (5)
C5S—C7S	1.538 (8)	C47—C48	1.386 (5)
C6—C7	1.386 (6)	C49—O4	1.422 (4)
C7—C8	1.391 (5)	C49—C50	1.507 (5)
C8—C9	1.396 (5)	C51—C52	1.387 (5)
C9—N1	1.428 (4)	C51—C56	1.390 (5)
C9S—O1S	1.525 (9)	C51—B1	1.674 (5)
C9S—C13S	1.565 (9)	C52—F1	1.350 (4)
C10—O2	1.209 (4)	C52—C53	1.384 (5)
C10—O3	1.334 (4)	C53—F2	1.348 (5)
C10—N1	1.392 (4)	C53—C54	1.369 (6)
C11—O3	1.458 (4)	C54—F3	1.354 (4)
C11—C12	1.503 (5)	C54—C55	1.369 (6)
C11S—O1S	1.513 (9)	C55—F4	1.343 (4)
C11S—C12S	1.524 (9)	C55—C56	1.385 (5)
C12S—C13S	1.439 (9)	C56—F5	1.350 (4)
C13—C14	1.390 (5)	C57—C62	1.385 (5)
C13—C18	1.394 (5)	C57—C58	1.393 (5)
C13—P1	1.829 (3)	C57—B1	1.669 (5)
C14—C15	1.384 (5)	C58—F6	1.352 (4)
C15—C16	1.383 (5)	C58—C59	1.379 (5)
C16—C17	1.385 (5)	C59—F7	1.344 (4)
C17—C18	1.379 (5)	C59—C60	1.371 (5)
C18—O1	1.393 (4)	C60—F8	1.351 (4)
C19—C20	1.382 (5)	C60—C61	1.378 (5)
C19—C24	1.393 (4)	C61—F9	1.345 (4)
C19—O1	1.394 (4)	C61—C62	1.381 (5)
C20—C21	1.388 (5)	C62—F10	1.359 (4)
C21—C22	1.380 (5)	C63—C68	1.387 (5)
C22—C23	1.389 (5)	C63—C64	1.389 (5)
C23—C24	1.399 (5)	C63—B1	1.670 (5)
C24—P2	1.838 (3)	C64—F15	1.356 (4)
C25—C26	1.389 (5)	C64—C65	1.380 (5)
C25—C30	1.398 (6)	C65—F14	1.346 (4)
C25—P1	1.826 (3)	C65—C66	1.378 (5)
C26—C27	1.386 (6)	C66—F13	1.344 (4)
C27—C28	1.371 (7)	C66—C67	1.373 (5)
C28—C29	1.385 (7)	C67—F12	1.351 (4)
C29—C30	1.392 (6)	C67—C68	1.376 (5)
C31—C36	1.383 (5)	C68—F11	1.360 (4)
C31—C32	1.406 (5)	O4—B1	1.450 (4)

C31—P1	1.829 (3)	P1—Ni1	2.2118 (9)
C32—C33	1.379 (6)	P2—Ni1	2.2488 (9)

Bond angles for ***5-borate*** *(º)*

C2—C1—N1	120.0 (3)	C52—C51—B1	126.9 (3)
C2—C1—Ni1	65.25 (17)	C56—C51—B1	119.4 (3)
N1—C1—Ni1	108.4 (2)	F1—C52—C53	115.3 (3)
C2S—C1S—C6S	118.9 (10)	F1—C52—C51	121.0 (3)
C3—C2—C1	115.7 (3)	C53—C52—C51	123.7 (4)
C3—C2—Ni1	75.01 (18)	F2—C53—C54	119.7 (3)
C1—C2—Ni1	74.97 (18)	F2—C53—C52	120.4 (4)
C3S—C2S—C1S	119.4 (10)	C54—C53—C52	119.8 (4)
C2—C3—C4	120.1 (3)	F3—C54—C53	120.7 (4)
C2—C3—Ni1	65.45 (17)	F3—C54—C55	119.6 (4)
C4—C3—Ni1	95.0 (2)	C53—C54—C55	119.7 (3)
C2S—C3S—C4S	118.6 (9)	F4—C55—C54	120.1 (3)
C9—C4—C5	119.1 (3)	F4—C55—C56	121.3 (3)
C9—C4—C3	121.0 (3)	C54—C55—C56	118.6 (3)
C5—C4—C3	119.9 (3)	F5—C56—C55	116.2 (3)
C5S—C4S—C3S	124.7 (9)	F5—C56—C51	119.0 (3)
C6—C5—C4	120.4 (4)	C55—C56—C51	124.8 (3)
C6S—C5S—C4S	112.3 (9)	C62—C57—C58	113.4 (3)
C6S—C5S—C7S	128.7 (9)	C62—C57—B1	129.0 (3)
C4S—C5S—C7S	117.4 (9)	C58—C57—B1	117.6 (3)
C5—C6—C7	119.8 (3)	F6—C58—C59	115.5 (3)
C5S—C6S—C1S	125.4 (9)	F6—C58—C57	120.2 (3)
C6—C7—C8	121.3 (4)	C59—C58—C57	124.3 (3)
C7—C8—C9	119.3 (4)	F7—C59—C60	119.6 (3)
C8—C9—C4	120.0 (3)	F7—C59—C58	121.2 (3)
C8—C9—N1	122.6 (3)	C60—C59—C58	119.2 (3)
C4—C9—N1	117.3 (3)	F8—C60—C59	119.5 (3)
O1S—C9S—C13S	123.0 (11)	F8—C60—C61	120.9 (3)
O2—C10—O3	124.4 (3)	C59—C60—C61	119.5 (3)
O2—C10—N1	124.8 (3)	F9—C61—C60	120.2 (3)
O3—C10—N1	110.8 (3)	F9—C61—C62	120.8 (3)
O3—C11—C12	106.9 (3)	C60—C61—C62	119.0 (3)
O1S—C11S—C12S	112.7 (11)	F10—C62—C61	114.5 (3)
C13S—C12S—C11S	114.3 (11)	F10—C62—C57	121.0 (3)
C14—C13—C18	118.3 (3)	C61—C62—C57	124.4 (3)
C14—C13—P1	125.7 (3)	C68—C63—C64	112.6 (3)
C18—C13—P1	116.0 (2)	C68—C63—B1	120.0 (3)
C12S—C13S—C9S	94.3 (10)	C64—C63—B1	127.2 (3)
C15—C14—C13	119.9 (3)	F15—C64—C65	114.6 (3)
C16—C15—C14	120.7 (3)	F15—C64—C63	120.6 (3)
C15—C16—C17	120.4 (3)	C65—C64—C63	124.9 (3)
C18—C17—C16	118.5 (3)	F14—C65—C66	119.8 (3)

C17—C18—O1	122.4 (3)	F14—C65—C64	120.9 (3)
C17—C18—C13	122.2 (3)	C66—C65—C64	119.3 (3)
O1—C18—C13	115.4 (3)	F13—C66—C67	120.5 (3)
C20—C19—C24	122.2 (3)	F13—C66—C65	120.8 (3)
C20—C19—O1	118.4 (3)	C67—C66—C65	118.7 (3)
C24—C19—O1	119.3 (3)	F12—C67—C66	119.0 (3)
C19—C20—C21	119.5 (3)	F12—C67—C68	121.3 (3)
C22—C21—C20	119.7 (3)	C66—C67—C68	119.7 (3)
C21—C22—C23	120.2 (3)	F11—C68—C67	115.2 (3)
C22—C23—C24	121.3 (3)	F11—C68—C63	120.0 (3)
C19—C24—C23	117.0 (3)	C67—C68—C63	124.8 (3)
C19—C24—P2	121.4 (2)	C10—N1—C9	122.2 (3)
C23—C24—P2	121.4 (2)	C10—N1—C1	119.8 (3)
C26—C25—C30	118.9 (3)	C9—N1—C1	117.6 (3)
C26—C25—P1	123.2 (3)	C18—O1—C19	116.7 (2)
C30—C25—P1	117.7 (3)	C11S—O1S—C9S	93.8 (11)
C27—C26—C25	120.6 (4)	C10—O3—C11	115.5 (3)
C28—C27—C26	120.3 (4)	C49—O4—B1	120.3 (3)
C27—C28—C29	120.0 (4)	C25—P1—C31	105.46 (16)
C28—C29—C30	120.1 (5)	C25—P1—C13	103.69 (15)
C29—C30—C25	120.0 (4)	C31—P1—C13	101.98 (15)
C36—C31—C32	119.1 (3)	C25—P1—Ni1	112.13 (11)
C36—C31—P1	120.8 (2)	C31—P1—Ni1	113.69 (11)
C32—C31—P1	120.1 (3)	C13—P1—Ni1	118.48 (10)
C33—C32—C31	120.3 (4)	C43—P2—C37	102.87 (14)
C32—C33—C34	119.9 (3)	C43—P2—C24	107.06 (14)
C35—C34—C33	120.1 (3)	C37—P2—C24	101.12 (14)
C34—C35—C36	119.9 (4)	C43—P2—Ni1	108.54 (10)
C31—C36—C35	120.6 (3)	C37—P2—Ni1	116.77 (10)
C38—C37—C42	119.0 (3)	C24—P2—Ni1	118.97 (10)
C38—C37—P2	119.3 (2)	C2—Ni1—C3	39.54 (13)
C42—C37—P2	121.8 (2)	C2—Ni1—C1	39.79 (13)
C39—C38—C37	120.5 (3)	C3—Ni1—C1	68.06 (12)
C40—C39—C38	120.0 (3)	C2—Ni1—P1	124.23 (9)
C41—C40—C39	119.7 (3)	C3—Ni1—P1	156.22 (10)
C40—C41—C42	120.5 (3)	C1—Ni1—P1	89.52 (9)
C41—C42—C37	120.3 (3)	C2—Ni1—P2	128.15 (10)
C44—C43—C48	119.2 (3)	C3—Ni1—P2	96.85 (9)
C44—C43—P2	124.1 (3)	C1—Ni1—P2	164.80 (9)
C48—C43—P2	116.6 (2)	P1—Ni1—P2	105.13 (3)
C45—C44—C43	120.2 (3)	O4—B1—C57	104.9 (3)
C44—C45—C46	120.2 (3)	O4—B1—C63	109.3 (3)
C47—C46—C45	120.1 (3)	C57—B1—C63	114.3 (3)
C46—C47—C48	120.0 (3)	O4—B1—C51	116.0 (3)
C47—C48—C43	120.1 (3)	C57—B1—C51	101.5 (3)
O4—C49—C50	110.2 (3)	C63—B1—C51	110.7 (3)
C52—C51—C56	113.4 (3)		

*Dihedral angles for **5-borate** (º)*

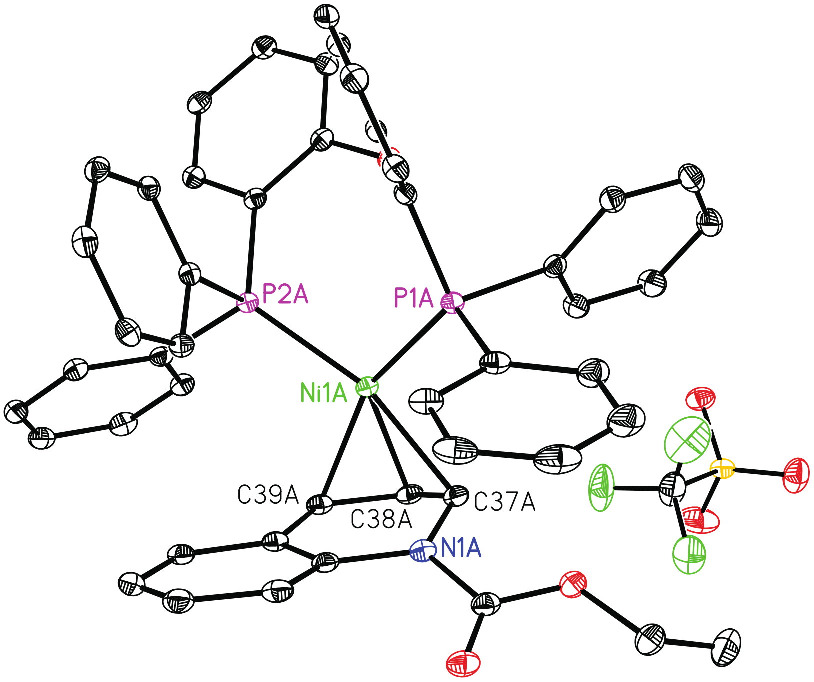
N1—C1—C2—C3	33.0 (4)	C63—C64—C65—C66	1.9 (6)
Ni1—C1—C2—C3	-64.7 (2)	F14—C65—C66—F13	1.2 (5)
N1—C1—C2—Ni1	97.8 (3)	C64—C65—C66—F13	-179.7 (3)
C6S—C1S—C2S—C3S	-8.4 (16)	F14—C65—C66—C67	-178.2 (3)
C1—C2—C3—C4	-16.5 (4)	C64—C65—C66—C67	0.9 (5)
Ni1—C2—C3—C4	-81.2 (3)	F13—C66—C67—F12	-0.2 (5)
C1—C2—C3—Ni1	64.7 (2)	C65—C66—C67—F12	179.2 (3)
C1S—C2S—C3S—C4S	9.3 (16)	F13—C66—C67—C68	179.1 (3)
C2—C3—C4—C9	0.4 (4)	C65—C66—C67—C68	-1.5 (5)
Ni1—C3—C4—C9	-64.1 (3)	F12—C67—C68—F11	-0.9 (5)
C2—C3—C4—C5	-179.9 (3)	C66—C67—C68—F11	179.8 (3)
Ni1—C3—C4—C5	115.7 (3)	F12—C67—C68—C63	178.6 (3)
C2S—C3S—C4S—C5S	-7.1 (17)	C66—C67—C68—C63	-0.6 (6)
C9—C4—C5—C6	1.6 (5)	C64—C63—C68—F11	-177.4 (3)
C3—C4—C5—C6	-178.2 (3)	B1—C63—C68—F11	-2.0 (5)
C3S—C4S—C5S—C6S	3.5 (16)	C64—C63—C68—C67	3.1 (5)
C3S—C4S—C5S—C7S	170.6 (11)	B1—C63—C68—C67	178.4 (3)
C4—C5—C6—C7	0.2 (5)	O2—C10—N1—C9	3.8 (5)
C4S—C5S—C6S—C1S	-2.6 (16)	O3—C10—N1—C9	-177.1 (3)
C7S—C5S—C6S—C1S	-167.9 (12)	O2—C10—N1—C1	-169.0 (3)
C2S—C1S—C6S—C5S	5.2 (17)	O3—C10—N1—C1	10.1 (4)
C5—C6—C7—C8	-1.5 (6)	C8—C9—N1—C10	25.0 (5)
C6—C7—C8—C9	1.0 (6)	C4—C9—N1—C10	-157.7 (3)
C7—C8—C9—C4	0.9 (5)	C8—C9—N1—C1	-162.1 (3)
C7—C8—C9—N1	178.1 (3)	C4—C9—N1—C1	15.2 (4)
C5—C4—C9—C8	-2.1 (5)	C2—C1—N1—C10	140.1 (3)
C3—C4—C9—C8	177.6 (3)	Ni1—C1—N1—C10	-148.4 (2)
C5—C4—C9—N1	-179.5 (3)	C2—C1—N1—C9	-33.0 (4)
C3—C4—C9—N1	0.3 (4)	Ni1—C1—N1—C9	38.5 (3)
O1S—C11S—C12S—C13S	-12.1 (16)	C17—C18—O1—C19	-43.0 (4)
C11S—C12S—C13S—C9S	13.5 (13)	C13—C18—O1—C19	139.4 (3)
O1S—C9S—C13S—C12S	-13.4 (15)	C20—C19—O1—C18	100.5 (3)
C18—C13—C14—C15	0.2 (5)	C24—C19—O1—C18	-83.0 (3)
P1—C13—C14—C15	179.3 (3)	C12S—C11S—O1S—C9S	2.6 (13)
C13—C14—C15—C16	-0.5 (5)	C13S—C9S—O1S—C11S	7.1 (15)
C14—C15—C16—C17	0.3 (6)	O2—C10—O3—C11	-2.2 (5)
C15—C16—C17—C18	0.2 (5)	N1—C10—O3—C11	178.7 (3)
C16—C17—C18—O1	-177.8 (3)	C12—C11—O3—C10	-167.2 (3)
C16—C17—C18—C13	-0.4 (5)	C50—C49—O4—B1	126.9 (3)
C14—C13—C18—C17	0.2 (5)	C26—C25—P1—C31	-3.1 (3)
P1—C13—C18—C17	-178.9 (2)	C30—C25—P1—C31	-178.9 (3)
C14—C13—C18—O1	177.8 (3)	C26—C25—P1—C13	-109.9 (3)

P1—C13—C18—O1	-1.3 (4)	C30—C25—P1—C13	74.3 (3)
C24—C19—C20—C21	0.7 (5)	C26—C25—P1—Ni1	121.1 (3)
O1—C19—C20—C21	177.0 (3)	C30—C25—P1—Ni1	-54.6 (3)
C19—C20—C21—C22	1.9 (5)	C36—C31—P1—C25	114.3 (3)
C20—C21—C22—C23	-2.4 (5)	C32—C31—P1—C25	-65.6 (3)
C21—C22—C23—C24	0.5 (5)	C36—C31—P1—C13	-137.6 (3)
C20—C19—C24—C23	-2.6 (5)	C32—C31—P1—C13	42.5 (3)
O1—C19—C24—C23	-178.9 (3)	C36—C31—P1—Ni1	-8.9 (3)
C20—C19—C24—P2	172.3 (3)	C32—C31—P1—Ni1	171.2 (3)
O1—C19—C24—P2	-4.0 (4)	C14—C13—P1—C25	0.3 (3)
C22—C23—C24—C19	2.0 (5)	C18—C13—P1—C25	179.3 (2)
C22—C23—C24—P2	-172.9 (3)	C14—C13—P1—C31	-109.1 (3)
C30—C25—C26—C27	0.9 (5)	C18—C13—P1—C31	69.9 (3)
P1—C25—C26—C27	-174.8 (3)	C14—C13—P1—Ni1	125.3 (3)
C25—C26—C27—C28	0.3 (6)	C18—C13—P1—Ni1	-55.7 (3)
C26—C27—C28—C29	-1.7 (7)	C44—C43—P2—C37	-100.5 (3)
C27—C28—C29—C30	2.0 (7)	C48—C43—P2—C37	79.3 (3)
C28—C29—C30—C25	-0.9 (6)	C44—C43—P2—C24	5.6 (3)
C26—C25—C30—C29	-0.5 (6)	C48—C43—P2—C24	-174.6 (2)
P1—C25—C30—C29	175.4 (3)	C44—C43—P2—Ni1	135.2 (2)
C36—C31—C32—C33	-1.7 (5)	C48—C43—P2—Ni1	-45.1 (3)
P1—C31—C32—C33	178.2 (3)	C38—C37—P2—C43	179.3 (3)
C31—C32—C33—C34	0.7 (6)	C42—C37—P2—C43	-2.2 (3)
C32—C33—C34—C35	0.4 (6)	C38—C37—P2—C24	68.7 (3)
C33—C34—C35—C36	-0.5 (6)	C42—C37—P2—C24	-112.8 (3)
C32—C31—C36—C35	1.5 (5)	C38—C37—P2—Ni1	-61.9 (3)
P1—C31—C36—C35	-178.4 (3)	C42—C37—P2—Ni1	116.6 (2)
C34—C35—C36—C31	-0.5 (5)	C19—C24—P2—C43	86.7 (3)
C42—C37—C38—C39	-1.1 (5)	C23—C24—P2—C43	-98.6 (3)
P2—C37—C38—C39	177.5 (3)	C19—C24—P2—C37	-165.9 (3)
C37—C38—C39—C40	0.0 (5)	C23—C24—P2—C37	8.7 (3)
C38—C39—C40—C41	1.1 (5)	C19—C24—P2—Ni1	-36.6 (3)
C39—C40—C41—C42	-1.1 (5)	C23—C24—P2—Ni1	138.0 (2)
C40—C41—C42—C37	0.0 (5)	C1—C2—Ni1—C3	-122.5 (3)
C38—C37—C42—C41	1.1 (5)	C3—C2—Ni1—C1	122.5 (3)
P2—C37—C42—C41	-177.5 (2)	C3—C2—Ni1—P1	156.12 (16)
C48—C43—C44—C45	0.6 (4)	C1—C2—Ni1—P1	33.6 (2)
P2—C43—C44—C45	-179.6 (2)	C3—C2—Ni1—P2	-44.5 (2)
C43—C44—C45—C46	-1.0 (5)	C1—C2—Ni1—P2	-167.00 (15)
C44—C45—C46—C47	0.3 (5)	C4—C3—Ni1—C2	120.9 (3)
C45—C46—C47—C48	0.6 (5)	C2—C3—Ni1—C1	-35.6 (2)
C46—C47—C48—C43	-1.0 (5)	C4—C3—Ni1—C1	85.3 (2)
C44—C43—C48—C47	0.3 (5)	C2—C3—Ni1—P1	-56.1 (3)
P2—C43—C48—C47	-179.4 (3)	C4—C3—Ni1—P1	64.8 (3)
C56—C51—C52—F1	-179.3 (3)	C2—C3—Ni1—P2	146.28 (18)
B1—C51—C52—F1	-6.0 (6)	C4—C3—Ni1—P2	-92.86 (19)
C56—C51—C52—C53	0.5 (5)	N1—C1—Ni1—C2	-115.3 (3)
B1—C51—C52—C53	173.9 (3)	C2—C1—Ni1—C3	35.4 (2)

F1—C52—C53—F2	-0.1 (5)	N1—C1—Ni1—C3	-79.9 (2)
C51—C52—C53—F2	-179.9 (3)	C2—C1—Ni1—P1	-152.76 (18)
F1—C52—C53—C54	178.4 (3)	N1—C1—Ni1—P1	92.0 (2)
C51—C52—C53—C54	-1.4 (6)	C2—C1—Ni1—P2	42.4 (4)
F2—C53—C54—F3	0.6 (6)	N1—C1—Ni1—P2	-72.8 (4)
C52—C53—C54—F3	-177.9 (3)	C25—P1—Ni1—C2	-73.91 (18)
F2—C53—C54—C55	179.8 (3)	C31—P1—Ni1—C2	45.60 (17)
C52—C53—C54—C55	1.3 (6)	C13—P1—Ni1—C2	165.33 (17)
F3—C54—C55—F4	-0.8 (5)	C25—P1—Ni1—C3	-34.2 (3)
C53—C54—C55—F4	179.9 (3)	C31—P1—Ni1—C3	85.3 (3)
F3—C54—C55—C56	178.9 (3)	C13—P1—Ni1—C3	-155.0 (3)
C53—C54—C55—C56	-0.4 (5)	C25—P1—Ni1—C1	-53.16 (15)
F4—C55—C56—F5	-0.8 (5)	C31—P1—Ni1—C1	66.35 (14)
C54—C55—C56—F5	179.5 (3)	C13—P1—Ni1—C1	-173.92 (15)
F4—C55—C56—C51	179.1 (3)	C25—P1—Ni1—P2	122.76 (13)
C54—C55—C56—C51	-0.6 (6)	C31—P1—Ni1—P2	-117.73 (12)
C52—C51—C56—F5	-179.6 (3)	C13—P1—Ni1—P2	2.00 (13)
B1—C51—C56—F5	6.5 (5)	C43—P2—Ni1—C2	144.61 (16)
C52—C51—C56—C55	0.5 (5)	C37—P2—Ni1—C2	29.00 (18)
B1—C51—C56—C55	-173.4 (3)	C24—P2—Ni1—C2	-92.75 (17)
C62—C57—C58—F6	178.8 (3)	C43—P2—Ni1—C3	117.91 (14)
B1—C57—C58—F6	1.1 (4)	C37—P2—Ni1—C3	2.29 (15)
C62—C57—C58—C59	0.3 (5)	C24—P2—Ni1—C3	-119.45 (15)
B1—C57—C58—C59	-177.4 (3)	C43—P2—Ni1—C1	111.3 (4)
F6—C58—C59—F7	-1.2 (5)	C37—P2—Ni1—C1	-4.3 (4)
C57—C58—C59—F7	177.4 (3)	C24—P2—Ni1—C1	-126.0 (4)
F6—C58—C59—C60	179.3 (3)	C43—P2—Ni1—P1	-52.94 (11)
C57—C58—C59—C60	-2.1 (5)	C37—P2—Ni1—P1	-168.56 (12)
F7—C59—C60—F8	0.7 (5)	C24—P2—Ni1—P1	69.70 (12)
C58—C59—C60—F8	-179.8 (3)	C49—O4—B1—C57	-172.9 (3)
F7—C59—C60—C61	-177.8 (3)	C49—O4—B1—C63	-50.0 (4)
C58—C59—C60—C61	1.6 (5)	C49—O4—B1—C51	76.0 (4)
F8—C60—C61—F9	0.9 (5)	C62—C57—B1—O4	127.9 (3)
C59—C60—C61—F9	179.4 (3)	C58—C57—B1—O4	-54.8 (4)
F8—C60—C61—C62	-178.0 (3)	C62—C57—B1—C63	8.2 (5)
C59—C60—C61—C62	0.5 (5)	C58—C57—B1—C63	-174.4 (3)
F9—C61—C62—F10	-2.2 (5)	C62—C57—B1—C51	-110.9 (4)
C60—C61—C62—F10	176.6 (3)	C58—C57—B1—C51	66.4 (3)
F9—C61—C62—C57	178.7 (3)	C68—C63—B1—O4	-62.2 (4)
C60—C61—C62—C57	-2.5 (5)	C64—C63—B1—O4	112.4 (4)
C58—C57—C62—F10	-177.0 (3)	C68—C63—B1—C57	55.0 (4)
B1—C57—C62—F10	0.4 (5)	C64—C63—B1—C57	-130.4 (4)
C58—C57—C62—C61	2.0 (5)	C68—C63—B1—C51	168.8 (3)
B1—C57—C62—C61	179.4 (3)	C64—C63—B1—C51	-16.6 (5)
C68—C63—C64—F15	175.8 (3)	C52—C51—B1—O4	2.2 (5)
B1—C63—C64—F15	0.8 (5)	C56—C51—B1—O4	175.2 (3)
C68—C63—C64—C65	-3.7 (5)	C52—C51—B1—C57	-110.8 (4)
B1—C63—C64—C65	-178.6 (3)	C56—C51—B1—C57	62.2 (4)

F15—C64—C65—F14	1.5 (5)	C52—C51—B1—C63	127.5 (4)
C63—C64—C65—F14	-179.0 (3)	C56—C51—B1—C63	-59.5 (4)
F15—C64—C65—C66	-177.6 (3)		

V) X-ray Crystal Structural Information for 5-triflate



Computing details

Data collection: Bruker *APEX2*; cell refinement: Bruker *SAINT*; data reduction: Bruker *SAINT*; program(s) used to solve structure: *SIR92* (Giacavazzo, 1993); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3* (Farraguia, 1997).

Crystal data

$C_{51}H_{44}Cl_4F_3NNiO_6P_2S$	$Z = 2$
$M_r = 1118.38$	$F(000) = 1148$
Triclinic, $P\bar{1}$	$D_x = 1.499$ Mg m^{-3}
$a = 10.2820$ (1) Å	Cu *K*□ radiation, □ = 1.54178 Å
$b = 15.9061$ (2) Å	Cell parameters from 9860 reflections
$c = 16.4165$ (2) Å	□ = 3.3–66.4°
□ = 110.974 (1)°	□ = 4.08 mm^{-1}
□ = 94.270 (1)°	$T = 100$ K
□ = 95.688 (1)°	Square, red
$V = 2477.10$ (5) Å^3	0.10 × 0.09 × 0.06 mm

Data collection

BRUKER APEX II CCD diffractometer	8199 independent reflections
Radiation source: fine-focus sealed tube	7557 reflections with $I > 2$□(I)
graphite	$R_{int} = 0.024$
phi and □ scans	□$_{max}$ = 66.6°, □$_{min}$ = 2.9°
Absorption correction: multi-scan *SADABS* V2008/1 (Bruker AXS)	h = -12□12
$T_{min} = 0.687$, $T_{max} = 0.753$	k = -18□18
22680 measured reflections	l = -19□19

Refinement

Refinement on F^2	Primary atom site location: structure-invariant direct methods
Least-squares matrix: full	Secondary atom site location: difference Fourier map
$R[F^2 > 2\sigma(F^2)] = 0.044$	Hydrogen site location: inferred from neighbouring sites
$wR(F^2) = 0.125$	H-atom parameters constrained
$S = 1.03$	$w = 1/[\sigma^2(F_o^2) + (0.0704P)^2 + 3.445P]$ where $P = (F_o^2 + 2F_c^2)/3$
8199 reflections	$(\Delta/\sigma)_{max} = 0.001$
657 parameters	$\Delta\rho_{max} = 0.56$ e Å^{-3}
2 restraints	$\Delta\rho_{min} = -0.88$ e Å^{-3}

Special details

Experimental. Collected, solved and refined by Scott P. Semproni

Geometry. All s.u.'s (except the s.u. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell s.u.'s are taken into account individually in the estimation of s.u.'s in distances, angles and torsion angles; correlations between s.u.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell s.u.'s is used for estimating s.u.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2, conventional R-factors R are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > 2\sigma(F^2)$ is used only for calculating R-factors(gt) etc. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters for ***5-triflate*** *(Å^2)*

	x	*y*	*z*	U_{iso}*/U_{eq}	Occ. (<1)
C1	0.0811 (2)	0.27325 (18)	0.26525 (16)	0.0229 (5)	
C1S	0.4229 (4)	0.9692 (3)	0.5928 (2)	0.0543 (9)	
H1S1	0.3783	0.9587	0.5338	0.065*	
H1S2	0.5018	1.0148	0.6044	0.065*	
C2	0.0485 (3)	0.3614 (2)	0.29595 (17)	0.0277 (6)	
H2	0.0941	0.4069	0.2798	0.033*	
C3	-0.0511 (3)	0.3827 (2)	0.35037 (19)	0.0354 (7)	
H3	-0.0738	0.4426	0.3711	0.043*	
C4	-0.1163 (3)	0.3164 (3)	0.37394 (19)	0.0408 (8)	
H4	-0.1850	0.3307	0.4102	0.049*	
C5	-0.0828 (3)	0.2300 (2)	0.3456 (2)	0.0405 (8)	
H5	-0.1276	0.1852	0.3630	0.049*	
C6	0.0169 (3)	0.2077 (2)	0.29129 (18)	0.0314 (6)	
H6	0.0406	0.1481	0.2723	0.038*	

C7	0.2202 (3)	0.12909 (17)	0.16428 (16)	0.0210 (5)	
C8	0.1155 (3)	0.06334 (18)	0.11631 (17)	0.0257 (6)	
H8	0.0394	0.0807	0.0936	0.031*	
C9	0.1219 (3)	-0.02757 (19)	0.10158 (19)	0.0317 (6)	
H9	0.0500	-0.0723	0.0691	0.038*	
C10	0.2333 (3)	-0.05321 (19)	0.13437 (19)	0.0320 (6)	
H10	0.2367	-0.1153	0.1257	0.038*	
C11	0.3392 (3)	0.01137 (19)	0.17951 (19)	0.0308 (6)	
H11	0.4164	-0.0066	0.2002	0.037*	
C12	0.3332 (3)	0.10260 (18)	0.19482 (17)	0.0252 (6)	
H12	0.4062	0.1469	0.2261	0.030*	
C13	0.1218 (2)	0.25134 (16)	0.09043 (16)	0.0190 (5)	
C14	-0.0037 (3)	0.27588 (17)	0.08326 (18)	0.0236 (5)	
H14	-0.0511	0.2920	0.1329	0.028*	
C15	-0.0600 (3)	0.27701 (18)	0.00404 (18)	0.0260 (6)	
H15	-0.1449	0.2952	0.0003	0.031*	
C16	0.0068 (3)	0.25181 (17)	-0.06939 (17)	0.0255 (6)	
H16	-0.0328	0.2519	-0.1235	0.031*	
C17	0.1317 (3)	0.22647 (17)	-0.06404 (17)	0.0232 (5)	
H17	0.1780	0.2090	-0.1142	0.028*	
C18	0.1876 (2)	0.22712 (16)	0.01580 (16)	0.0191 (5)	
C19	0.4084 (2)	0.23285 (17)	-0.01432 (16)	0.0202 (5)	
C20	0.4296 (3)	0.17802 (17)	-0.09825 (17)	0.0231 (5)	
H20	0.3774	0.1206	-0.1274	0.028*	
C21	0.5278 (3)	0.20780 (18)	-0.13936 (17)	0.0238 (5)	
H21	0.5430	0.1707	-0.1967	0.029*	
C22	0.6027 (3)	0.29112 (18)	-0.09671 (16)	0.0226 (5)	
H22	0.6694	0.3117	-0.1249	0.027*	
C23	0.5810 (2)	0.34534 (17)	-0.01236 (16)	0.0210 (5)	
H23	0.6334	0.4027	0.0164	0.025*	
C24	0.4837 (2)	0.31705 (17)	0.03088 (16)	0.0183 (5)	
C25	0.3196 (2)	0.44998 (16)	0.12274 (16)	0.0174 (5)	
C26	0.2668 (2)	0.50386 (17)	0.19716 (16)	0.0204 (5)	
H26	0.2966	0.5039	0.2534	0.024*	
C27	0.1716 (2)	0.55681 (17)	0.18928 (17)	0.0222 (5)	
H27	0.1382	0.5947	0.2402	0.027*	
C28	0.1249 (2)	0.55455 (18)	0.10687 (18)	0.0241 (5)	
H28	0.0587	0.5904	0.1013	0.029*	
C29	0.1747 (2)	0.49996 (18)	0.03278 (17)	0.0227 (5)	
H29	0.1414	0.4978	-0.0236	0.027*	
C30	0.2732 (2)	0.44830 (17)	0.04046 (16)	0.0200 (5)	
H30	0.3085	0.4121	-0.0104	0.024*	
C31	0.5974 (2)	0.47775 (17)	0.17226 (15)	0.0191 (5)	
C32	0.5881 (3)	0.56591 (18)	0.17681 (16)	0.0220 (5)	
H32	0.5052	0.5818	0.1623	0.026*	
C33	0.6993 (3)	0.63103 (18)	0.20246 (17)	0.0252 (6)	
H33	0.6917	0.6912	0.2060	0.030*	
C34	0.8213 (3)	0.60845 (19)	0.22287 (17)	0.0271 (6)	

H34	0.8971	0.6529	0.2404	0.033*	
C35	0.8315 (3)	0.5204 (2)	0.21746 (17)	0.0270 (6)	
H35	0.9148	0.5044	0.2309	0.032*	
C36	0.7206 (3)	0.45543 (18)	0.19258 (16)	0.0228 (5)	
H36	0.7286	0.3953	0.1893	0.027*	
C37	0.3805 (3)	0.31834 (18)	0.36684 (16)	0.0215 (5)	
H37	0.3351	0.2582	0.3431	0.026*	
C38	0.5117 (3)	0.33553 (18)	0.35153 (15)	0.0215 (5)	
H38	0.5704	0.2916	0.3443	0.026*	
C39	0.5509 (2)	0.41977 (18)	0.34747 (16)	0.0219 (5)	
H39	0.6285	0.4294	0.3222	0.026*	
C40	0.4726 (3)	0.49366 (18)	0.38214 (16)	0.0219 (5)	
C41	0.5120 (3)	0.57994 (18)	0.38009 (16)	0.0256 (6)	
H41	0.5944	0.5916	0.3608	0.031*	
C42	0.4336 (3)	0.64787 (19)	0.40541 (17)	0.0304 (6)	
H42	0.4624	0.7062	0.4046	0.037*	
C43	0.3120 (3)	0.63071 (19)	0.43226 (17)	0.0302 (6)	
H43	0.2559	0.6766	0.4470	0.036*	
C44	0.2716 (3)	0.54714 (19)	0.43782 (16)	0.0267 (6)	
H44	0.1891	0.5366	0.4575	0.032*	
C45	0.3524 (3)	0.47866 (18)	0.41450 (16)	0.0224 (5)	
C46	0.2360 (3)	0.37935 (19)	0.47938 (17)	0.0251 (6)	
C47	0.1456 (3)	0.2717 (2)	0.5367 (2)	0.0404 (8)	
H47A	0.0521	0.2520	0.5116	0.048*	
H47B	0.1508	0.3255	0.5917	0.048*	
C48A	0.207 (2)	0.1930 (12)	0.5549 (12)	0.053 (3)	0.53 (6)
H48A	0.1597	0.1766	0.5980	0.080*	0.53 (6)
H48B	0.2999	0.2131	0.5781	0.080*	0.53 (6)
H48C	0.1992	0.1400	0.5001	0.080*	0.53 (6)
C48B	0.154 (5)	0.1791 (16)	0.522 (3)	0.083 (11)	0.47 (6)
H48D	0.1109	0.1410	0.4633	0.124*	0.47 (6)
H48E	0.1090	0.1624	0.5662	0.124*	0.47 (6)
H48F	0.2461	0.1698	0.5274	0.124*	0.47 (6)
C49	0.1147 (5)	0.9175 (3)	0.3540 (3)	0.0591 (11)	
N1	0.3162 (2)	0.39134 (15)	0.41805 (13)	0.0216 (4)	
O1	0.31157 (16)	0.20179 (11)	0.02673 (11)	0.0196 (4)	
O2	0.18791 (19)	0.43935 (13)	0.53105 (12)	0.0294 (4)	
O3	0.2237 (2)	0.29329 (13)	0.47366 (12)	0.0308 (4)	
O4	0.2114 (2)	0.78999 (16)	0.24185 (14)	0.0407 (5)	
O5	0.1159 (3)	0.75868 (17)	0.35878 (19)	0.0571 (7)	
O6	0.3229 (3)	0.8555 (3)	0.3879 (2)	0.0791 (10)	
F1	-0.0016 (3)	0.8954 (2)	0.3044 (2)	0.0921 (10)	
F2	0.1836 (4)	0.98310 (16)	0.3373 (2)	0.1013 (12)	
F3	0.0889 (4)	0.95189 (16)	0.43632 (19)	0.0942 (11)	
P1	0.20846 (6)	0.24926 (4)	0.19099 (4)	0.01745 (15)	
P2	0.45361 (6)	0.38973 (4)	0.14168 (4)	0.01681 (15)	
S1	0.20024 (7)	0.81935 (5)	0.33348 (4)	0.03287 (18)	
Ni1	0.40066 (4)	0.33562 (3)	0.24613 (3)	0.01769 (12)	

Cl1	0.47095 (19)	0.86795 (8)	0.59468 (9)	0.1053 (6)	
Cl2	0.31578 (14)	1.01164 (10)	0.67201 (8)	0.0947 (5)	
C2S	0.6204 (5)	0.1229 (3)	0.0693 (3)	0.0369 (10)	0.762 (4)
H2S1	0.6476	0.1412	0.0208	0.044*	0.762 (4)
H2S2	0.5230	0.1151	0.0643	0.044*	0.762 (4)
Cl3	0.68406 (15)	0.20819 (10)	0.16996 (9)	0.0411 (4)	0.762 (4)
Cl4	0.67671 (15)	0.01880 (7)	0.05972 (8)	0.0531 (5)	0.762 (4)
Cl5	0.7778 (6)	0.0335 (4)	0.1200 (5)	0.093 (3)	0.238 (4)
Cl6	0.6403 (9)	0.1873 (7)	0.1329 (9)	0.112 (3)	0.238 (4)
C3S	0.6349 (19)	0.0698 (10)	0.0873 (19)	0.111 (9)*	0.238 (4)
H3S1	0.6230	0.0499	0.0224	0.133*	0.238 (4)
H3S2	0.5581	0.0409	0.1051	0.133*	0.238 (4)

Atomic displacement parameters for ***5-triflate*** *(Å^2)*

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0176 (12)	0.0306 (14)	0.0172 (12)	0.0037 (11)	0.0014 (9)	0.0049 (10)
C1S	0.066 (2)	0.053 (2)	0.0382 (19)	0.0008 (19)	-0.0011 (17)	0.0125 (16)
C2	0.0246 (13)	0.0335 (15)	0.0216 (13)	0.0074 (12)	0.0013 (11)	0.0055 (11)
C3	0.0265 (14)	0.0455 (17)	0.0246 (14)	0.0146 (13)	0.0019 (11)	-0.0010 (13)
C4	0.0240 (14)	0.065 (2)	0.0244 (15)	0.0066 (15)	0.0076 (12)	0.0048 (14)
C5	0.0341 (16)	0.054 (2)	0.0308 (16)	-0.0018 (15)	0.0125 (13)	0.0129 (14)
C6	0.0288 (14)	0.0380 (16)	0.0265 (14)	0.0024 (12)	0.0065 (11)	0.0105 (12)
C7	0.0243 (13)	0.0219 (12)	0.0182 (12)	0.0041 (10)	0.0058 (10)	0.0084 (10)
C8	0.0253 (13)	0.0258 (13)	0.0270 (14)	0.0024 (11)	-0.0002 (11)	0.0116 (11)
C9	0.0339 (15)	0.0239 (14)	0.0341 (15)	-0.0033 (12)	-0.0047 (12)	0.0103 (12)
C10	0.0416 (16)	0.0207 (13)	0.0334 (15)	0.0056 (12)	-0.0003 (12)	0.0102 (11)
C11	0.0339 (15)	0.0261 (14)	0.0322 (15)	0.0098 (12)	-0.0019 (12)	0.0104 (12)
C12	0.0256 (13)	0.0234 (13)	0.0246 (13)	0.0035 (11)	0.0002 (10)	0.0068 (10)
C13	0.0194 (12)	0.0161 (11)	0.0194 (12)	0.0005 (10)	-0.0008 (9)	0.0053 (9)
C14	0.0213 (12)	0.0207 (12)	0.0270 (13)	0.0021 (10)	0.0015 (10)	0.0071 (10)
C15	0.0218 (13)	0.0230 (13)	0.0321 (14)	0.0042 (11)	-0.0034 (11)	0.0100 (11)
C16	0.0287 (14)	0.0215 (13)	0.0248 (13)	-0.0018 (11)	-0.0074 (11)	0.0100 (10)
C17	0.0264 (13)	0.0199 (12)	0.0211 (12)	-0.0018 (10)	0.0012 (10)	0.0066 (10)
C18	0.0186 (12)	0.0150 (11)	0.0221 (12)	-0.0003 (10)	-0.0004 (9)	0.0059 (9)
C19	0.0185 (12)	0.0237 (13)	0.0208 (12)	0.0055 (10)	0.0031 (10)	0.0102 (10)
C20	0.0272 (13)	0.0200 (12)	0.0207 (13)	0.0037 (11)	0.0034 (10)	0.0054 (10)
C21	0.0277 (13)	0.0246 (13)	0.0204 (12)	0.0093 (11)	0.0066 (10)	0.0075 (10)

C22	0.0214 (12)	0.0291 (13)	0.0207 (13)	0.0072 (11)	0.0059 (10)	0.0116 (11)
C23	0.0194 (12)	0.0216 (12)	0.0222 (13)	0.0044 (10)	0.0016 (10)	0.0083 (10)
C24	0.0181 (11)	0.0200 (12)	0.0184 (12)	0.0065 (10)	0.0020 (9)	0.0079 (10)
C25	0.0153 (11)	0.0170 (11)	0.0198 (12)	0.0021 (9)	0.0013 (9)	0.0068 (9)
C26	0.0195 (12)	0.0216 (12)	0.0195 (12)	0.0025 (10)	0.0005 (10)	0.0074 (10)
C27	0.0181 (12)	0.0194 (12)	0.0270 (13)	0.0014 (10)	0.0043 (10)	0.0062 (10)
C28	0.0169 (12)	0.0229 (13)	0.0343 (14)	0.0036 (10)	0.0008 (10)	0.0130 (11)
C29	0.0198 (12)	0.0257 (13)	0.0246 (13)	0.0009 (11)	-0.0023 (10)	0.0130 (11)
C30	0.0188 (12)	0.0196 (12)	0.0210 (12)	-0.0008 (10)	0.0025 (9)	0.0076 (10)
C31	0.0195 (12)	0.0227 (12)	0.0143 (11)	0.0019 (10)	0.0035 (9)	0.0058 (9)
C32	0.0220 (12)	0.0260 (13)	0.0188 (12)	0.0039 (11)	0.0035 (10)	0.0089 (10)
C33	0.0297 (14)	0.0241 (13)	0.0213 (13)	0.0003 (11)	0.0049 (10)	0.0082 (10)
C34	0.0248 (13)	0.0325 (14)	0.0204 (13)	-0.0059 (11)	0.0027 (10)	0.0078 (11)
C35	0.0196 (13)	0.0388 (15)	0.0236 (13)	0.0032 (11)	0.0030 (10)	0.0126 (11)
C36	0.0232 (13)	0.0262 (13)	0.0201 (12)	0.0048 (11)	0.0038 (10)	0.0092 (10)
C37	0.0243 (13)	0.0240 (13)	0.0160 (12)	0.0044 (10)	0.0013 (10)	0.0071 (10)
C38	0.0219 (12)	0.0278 (13)	0.0149 (11)	0.0080 (11)	-0.0013 (9)	0.0075 (10)
C39	0.0194 (12)	0.0281 (13)	0.0156 (12)	0.0014 (10)	-0.0005 (9)	0.0060 (10)
C40	0.0227 (12)	0.0255 (13)	0.0148 (11)	0.0016 (10)	-0.0029 (9)	0.0057 (10)
C41	0.0296 (14)	0.0273 (14)	0.0159 (12)	-0.0018 (11)	-0.0023 (10)	0.0057 (10)
C42	0.0462 (17)	0.0215 (13)	0.0201 (13)	0.0029 (12)	-0.0012 (12)	0.0049 (10)
C43	0.0419 (16)	0.0275 (14)	0.0196 (13)	0.0115 (13)	0.0031 (11)	0.0052 (11)
C44	0.0314 (14)	0.0303 (14)	0.0165 (12)	0.0091 (12)	0.0030 (10)	0.0049 (10)
C45	0.0262 (13)	0.0252 (13)	0.0140 (12)	0.0033 (11)	-0.0016 (10)	0.0058 (10)
C46	0.0237 (13)	0.0307 (14)	0.0182 (12)	0.0004 (11)	-0.0004 (10)	0.0072 (11)
C47	0.0467 (18)	0.0418 (17)	0.0312 (16)	-0.0053 (15)	0.0184 (14)	0.0120 (13)
C48A	0.074 (8)	0.047 (5)	0.047 (6)	0.002 (5)	0.020 (6)	0.027 (5)
C48B	0.11 (2)	0.056 (9)	0.110 (19)	0.019 (10)	0.082 (18)	0.051 (11)
C49	0.090 (3)	0.0386 (19)	0.059 (2)	0.023 (2)	0.046 (2)	0.0185 (17)
N1	0.0222 (10)	0.0247 (11)	0.0172 (10)	0.0044 (9)	0.0032 (8)	0.0064 (8)
O1	0.0188 (8)	0.0215 (8)	0.0197 (8)	0.0031 (7)	0.0037 (7)	0.0083 (7)
O2	0.0299 (10)	0.0343 (10)	0.0219 (9)	0.0072 (8)	0.0082 (8)	0.0063 (8)
O3	0.0381 (11)	0.0293 (10)	0.0234 (10)	-0.0016 (9)	0.0118 (8)	0.0078 (8)
O4	0.0469 (13)	0.0437 (12)	0.0310 (11)	0.0167 (11)	0.0094 (9)	0.0095 (9)
O5	0.0728 (18)	0.0450 (14)	0.0658 (17)	0.0196 (13)	0.0364 (14)	0.0264 (13)
O6	0.0658 (19)	0.095 (2)	0.0514 (17)	-0.0028 (17)	-0.0193 (14)	0.0057 (16)
F1	0.082 (2)	0.112 (2)	0.112 (2)	0.0684 (19)	0.0395 (18)	0.056 (2)
F2	0.172 (3)	0.0408 (13)	0.115 (2)	0.0340 (17)	0.099 (2)	0.0367 (14)
F3	0.161 (3)	0.0430 (12)	0.0780 (18)	0.0239 (16)	0.084 (2)	0.0056 (12)

P1	0.0168 (3)	0.0188 (3)	0.0166 (3)	0.0033 (2)	0.0025 (2)	0.0060 (2)
P2	0.0164 (3)	0.0185 (3)	0.0156 (3)	0.0033 (2)	0.0020 (2)	0.0061 (2)
S1	0.0375 (4)	0.0336 (4)	0.0239 (3)	0.0041 (3)	0.0030 (3)	0.0066 (3)
Ni1	0.0176 (2)	0.0199 (2)	0.0156 (2)	0.00259 (17)	0.00140 (16)	0.00665 (16)
Cl1	0.1701 (15)	0.0576 (7)	0.0698 (8)	0.0328 (8)	-0.0486 (9)	0.0090 (6)
Cl2	0.0836 (8)	0.1015 (10)	0.0613 (7)	-0.0070 (7)	0.0192 (6)	-0.0122 (6)
C2S	0.053 (3)	0.026 (2)	0.027 (2)	0.0065 (19)	0.0004 (18)	0.0057 (17)
Cl3	0.0451 (8)	0.0345 (6)	0.0368 (7)	-0.0007 (6)	0.0131 (5)	0.0048 (5)
Cl4	0.0820 (11)	0.0312 (6)	0.0553 (8)	0.0190 (6)	0.0277 (7)	0.0202 (5)
Cl5	0.069 (4)	0.059 (3)	0.144 (6)	0.001 (2)	0.045 (4)	0.024 (3)
Cl6	0.094 (6)	0.108 (8)	0.150 (10)	0.003 (5)	-0.006 (6)	0.076 (8)

*Bond distances for **5-triflate** (Å)*

C1—C6	1.389 (4)	C31—C36	1.398 (4)
C1—C2	1.394 (4)	C31—P2	1.837 (2)
C1—P1	1.831 (3)	C32—C33	1.392 (4)
C1S—Cl1	1.741 (4)	C33—C34	1.388 (4)
C1S—Cl2	1.758 (4)	C34—C35	1.387 (4)
C2—C3	1.396 (4)	C35—C36	1.388 (4)
C3—C4	1.379 (5)	C37—C38	1.408 (4)
C4—C5	1.373 (5)	C37—N1	1.424 (3)
C5—C6	1.398 (4)	C37—Ni1	2.118 (2)
C7—C8	1.391 (4)	C38—C39	1.387 (4)
C7—C12	1.392 (4)	C38—Ni1	2.001 (2)
C7—P1	1.820 (3)	C39—C40	1.459 (4)
C8—C9	1.387 (4)	C39—Ni1	2.135 (2)
C9—C10	1.388 (4)	C40—C41	1.405 (4)
C10—C11	1.379 (4)	C40—C45	1.413 (4)
C11—C12	1.390 (4)	C41—C42	1.375 (4)
C13—C14	1.394 (4)	C42—C43	1.390 (4)
C13—C18	1.394 (4)	C43—C44	1.390 (4)
C13—P1	1.829 (2)	C44—C45	1.397 (4)
C14—C15	1.391 (4)	C45—N1	1.425 (3)
C15—C16	1.385 (4)	C46—O2	1.205 (3)
C16—C17	1.389 (4)	C46—O3	1.330 (3)
C17—C18	1.388 (4)	C46—N1	1.400 (3)
C18—O1	1.392 (3)	C47—C48B	1.418 (18)
C19—C20	1.389 (4)	C47—O3	1.469 (3)
C19—O1	1.389 (3)	C47—C48A	1.565 (17)
C19—C24	1.393 (4)	C49—F3	1.322 (4)
C20—C21	1.391 (4)	C49—F2	1.325 (5)
C21—C22	1.376 (4)	C49—F1	1.336 (6)
C22—C23	1.393 (4)	C49—S1	1.806 (4)
C23—C24	1.398 (4)	O4—S1	1.424 (2)
C24—P2	1.841 (2)	O5—S1	1.425 (3)
C25—C30	1.389 (4)	O6—S1	1.428 (3)

C25—C26	1.401 (3)	P1—Ni1	2.2174 (7)
C25—P2	1.823 (2)	P2—Ni1	2.2539 (7)
C26—C27	1.380 (4)	C2S—Cl3	1.749 (4)
C27—C28	1.388 (4)	C2S—Cl4	1.766 (4)
C28—C29	1.386 (4)	Cl5—C3S	1.747 (10)
C29—C30	1.392 (4)	Cl6—C3S	1.740 (10)
C31—C32	1.390 (4)		

Bond angles for ***5-triflate*** *(º)*

C6—C1—C2	119.6 (2)	C38—C39—C40	119.8 (2)
C6—C1—P1	122.8 (2)	C38—C39—Ni1	65.28 (14)
C2—C1—P1	117.6 (2)	C40—C39—Ni1	94.88 (16)
Cl1—C1S—Cl2	111.1 (2)	C41—C40—C45	118.6 (2)
C1—C2—C3	120.0 (3)	C41—C40—C39	120.7 (2)
C4—C3—C2	119.7 (3)	C45—C40—C39	120.6 (2)
C5—C4—C3	120.7 (3)	C42—C41—C40	121.3 (3)
C4—C5—C6	120.3 (3)	C41—C42—C43	119.6 (3)
C1—C6—C5	119.7 (3)	C44—C43—C42	120.7 (3)
C8—C7—C12	119.4 (2)	C43—C44—C45	119.9 (3)
C8—C7—P1	120.7 (2)	C44—C45—C40	119.7 (2)
C12—C7—P1	119.85 (19)	C44—C45—N1	122.6 (2)
C9—C8—C7	120.2 (3)	C40—C45—N1	117.6 (2)
C8—C9—C10	120.0 (3)	O2—C46—O3	125.3 (2)
C11—C10—C9	120.0 (3)	O2—C46—N1	124.3 (3)
C10—C11—C12	120.2 (3)	O3—C46—N1	110.3 (2)
C11—C12—C7	120.0 (3)	C48B—C47—O3	106.1 (7)
C14—C13—C18	118.0 (2)	O3—C47—C48A	105.8 (6)
C14—C13—P1	125.0 (2)	F3—C49—F2	107.5 (3)
C18—C13—P1	117.05 (19)	F3—C49—F1	106.0 (4)
C15—C14—C13	120.6 (2)	F2—C49—F1	108.2 (4)
C16—C15—C14	120.3 (3)	F3—C49—S1	112.3 (3)
C15—C16—C17	120.2 (2)	F2—C49—S1	111.7 (3)
C18—C17—C16	118.9 (2)	F1—C49—S1	110.8 (3)
C17—C18—O1	122.6 (2)	C46—N1—C37	119.9 (2)
C17—C18—C13	122.1 (2)	C46—N1—C45	121.6 (2)
O1—C18—C13	115.3 (2)	C37—N1—C45	117.8 (2)
C20—C19—O1	119.0 (2)	C19—O1—C18	116.00 (18)
C20—C19—C24	122.0 (2)	C46—O3—C47	116.1 (2)
O1—C19—C24	119.0 (2)	C7—P1—C13	103.11 (11)
C19—C20—C21	119.5 (2)	C7—P1—C1	104.51 (12)
C22—C21—C20	119.8 (2)	C13—P1—C1	101.45 (12)
C21—C22—C23	120.2 (2)	C7—P1—Ni1	112.34 (9)
C22—C23—C24	121.4 (2)	C13—P1—Ni1	119.39 (8)
C19—C24—C23	117.2 (2)	C1—P1—Ni1	114.31 (8)
C19—C24—P2	121.61 (19)	C25—P2—C31	102.61 (11)
C23—C24—P2	121.18 (19)	C25—P2—C24	104.48 (11)
C30—C25—C26	119.5 (2)	C31—P2—C24	100.92 (11)

C30—C25—P2	123.68 (19)	C25—P2—Ni1	106.89 (8)
C26—C25—P2	116.69 (18)	C31—P2—Ni1	116.09 (8)
C27—C26—C25	120.4 (2)	C24—P2—Ni1	123.53 (8)
C26—C27—C28	119.9 (2)	O4—S1—O5	114.88 (16)
C29—C28—C27	120.0 (2)	O4—S1—O6	113.90 (18)
C28—C29—C30	120.4 (2)	O5—S1—O6	115.1 (2)
C25—C30—C29	119.7 (2)	O4—S1—C49	103.51 (16)
C32—C31—C36	118.8 (2)	O5—S1—C49	103.94 (17)
C32—C31—P2	122.54 (19)	O6—S1—C49	103.4 (2)
C36—C31—P2	118.68 (19)	C38—Ni1—C37	39.85 (10)
C31—C32—C33	120.5 (2)	C38—Ni1—C39	39.01 (10)
C34—C33—C32	120.4 (2)	C37—Ni1—C39	68.04 (10)
C35—C34—C33	119.4 (2)	C38—Ni1—P1	124.03 (8)
C34—C35—C36	120.4 (2)	C37—Ni1—P1	89.10 (7)
C35—C36—C31	120.5 (2)	C39—Ni1—P1	155.97 (7)
C38—C37—N1	119.8 (2)	C38—Ni1—P2	130.05 (8)
C38—C37—Ni1	65.62 (14)	C37—Ni1—P2	164.54 (8)
N1—C37—Ni1	106.55 (16)	C39—Ni1—P2	97.46 (7)
C39—C38—C37	116.7 (2)	P1—Ni1—P2	104.40 (3)
C39—C38—Ni1	75.71 (15)	Cl3—C2S—Cl4	111.0 (3)
C37—C38—Ni1	74.53 (15)	Cl6—C3S—Cl5	112.3 (9)

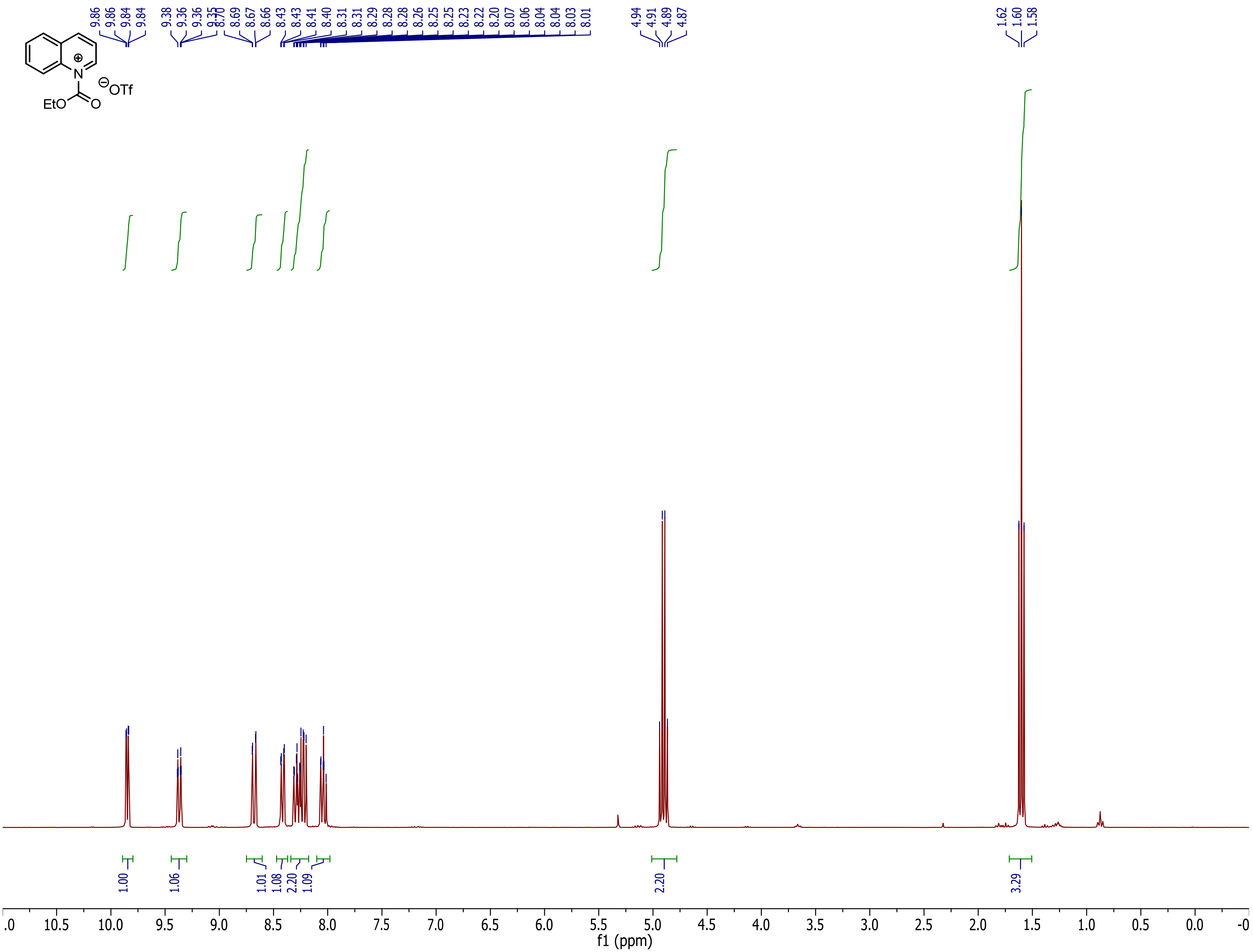
Dihedral angles for ***5-triflate*** *(º)*

C6—C1—C2—C3	-2.0 (4)	N1—C46—O3—C47	177.9 (2)
P1—C1—C2—C3	177.8 (2)	C48B—C47—O3—C46	-176 (3)
C1—C2—C3—C4	0.4 (4)	C48A—C47—O3—C46	-148.8 (9)
C2—C3—C4—C5	1.1 (5)	C8—C7—P1—C13	-39.8 (2)
C3—C4—C5—C6	-0.9 (5)	C12—C7—P1—C13	142.6 (2)
C2—C1—C6—C5	2.2 (4)	C8—C7—P1—C1	65.9 (2)
P1—C1—C6—C5	-177.7 (2)	C12—C7—P1—C1	-111.7 (2)
C4—C5—C6—C1	-0.7 (5)	C8—C7—P1—Ni1	-169.65 (18)
C12—C7—C8—C9	2.2 (4)	C12—C7—P1—Ni1	12.7 (2)
P1—C7—C8—C9	-175.5 (2)	C14—C13—P1—C7	114.2 (2)
C7—C8—C9—C10	-0.3 (4)	C18—C13—P1—C7	-66.3 (2)
C8—C9—C10—C11	-1.8 (5)	C14—C13—P1—C1	6.2 (2)
C9—C10—C11—C12	2.1 (5)	C18—C13—P1—C1	-174.36 (19)
C10—C11—C12—C7	-0.2 (4)	C14—C13—P1—Ni1	-120.4 (2)
C8—C7—C12—C11	-1.9 (4)	C18—C13—P1—Ni1	59.1 (2)
P1—C7—C12—C11	175.8 (2)	C6—C1—P1—C7	0.9 (3)
C18—C13—C14—C15	-0.8 (4)	C2—C1—P1—C7	-178.9 (2)
P1—C13—C14—C15	178.7 (2)	C6—C1—P1—C13	107.9 (2)
C13—C14—C15—C16	1.4 (4)	C2—C1—P1—C13	-71.9 (2)
C14—C15—C16—C17	-0.9 (4)	C6—C1—P1—Ni1	-122.3 (2)

C15—C16—C17—C18	-0.1 (4)	C2—C1—P1—Ni1	57.9 (2)
C16—C17—C18—O1	179.3 (2)	C30—C25—P2—C31	95.4 (2)
C16—C17—C18—C13	0.8 (4)	C26—C25—P2—C31	-81.5 (2)
C14—C13—C18—C17	-0.3 (4)	C30—C25—P2—C24	-9.6 (2)
P1—C13—C18—C17	-179.83 (19)	C26—C25—P2—C24	173.54 (18)
C14—C13—C18—O1	-178.9 (2)	C30—C25—P2—Ni1	-142.03 (19)
P1—C13—C18—O1	1.6 (3)	C26—C25—P2—Ni1	41.1 (2)
O1—C19—C20—C21	-178.9 (2)	C32—C31—P2—C25	0.2 (2)
C24—C19—C20—C21	-0.7 (4)	C36—C31—P2—C25	179.52 (19)
C19—C20—C21—C22	-0.1 (4)	C32—C31—P2—C24	107.9 (2)
C20—C21—C22—C23	0.4 (4)	C36—C31—P2—C24	-72.8 (2)
C21—C22—C23—C24	0.0 (4)	C32—C31—P2—Ni1	-116.02 (19)
C20—C19—C24—C23	1.0 (4)	C36—C31—P2—Ni1	63.3 (2)
O1—C19—C24—C23	179.3 (2)	C19—C24—P2—C25	-83.2 (2)
C20—C19—C24—P2	179.4 (2)	C23—C24—P2—C25	95.1 (2)
O1—C19—C24—P2	-2.4 (3)	C19—C24—P2—C31	170.6 (2)
C22—C23—C24—C19	-0.7 (4)	C23—C24—P2—C31	-11.1 (2)
C22—C23—C24—P2	-179.0 (2)	C19—C24—P2—Ni1	38.9 (2)
C30—C25—C26—C27	-1.7 (4)	C23—C24—P2—Ni1	-142.83 (17)
P2—C25—C26—C27	175.33 (19)	F3—C49—S1—O4	176.7 (3)
C25—C26—C27—C28	2.1 (4)	F2—C49—S1—O4	-62.4 (4)
C26—C27—C28—C29	-0.7 (4)	F1—C49—S1—O4	58.4 (3)
C27—C28—C29—C30	-1.1 (4)	F3—C49—S1—O5	56.3 (4)
C26—C25—C30—C29	-0.1 (3)	F2—C49—S1—O5	177.3 (3)
P2—C25—C30—C29	-176.87 (18)	F1—C49—S1—O5	-62.0 (3)
C28—C29—C30—C25	1.5 (4)	F3—C49—S1—O6	-64.3 (4)
C36—C31—C32—C33	-1.0 (4)	F2—C49—S1—O6	56.7 (4)
P2—C31—C32—C33	178.37 (19)	F1—C49—S1—O6	177.4 (3)
C31—C32—C33—C34	0.8 (4)	C39—C38—Ni1—C37	-123.5 (2)
C32—C33—C34—C35	0.0 (4)	C37—C38—Ni1—C39	123.5 (2)
C33—C34—C35—	-0.5 (4)	C39—C38—Ni1—P1	-156.53 (12)

C36			
C34—C35—C36—C31	0.3 (4)	C37—C38—Ni1—P1	-33.04 (18)
C32—C31—C36—C35	0.5 (4)	C39—C38—Ni1—P2	39.81 (18)
P2—C31—C36—C35	-178.90 (19)	C37—C38—Ni1—P2	163.30 (12)
N1—C37—C38—C39	-31.0 (3)	N1—C37—Ni1—C38	115.8 (2)
Ni1—C37—C38—C39	64.79 (19)	C38—C37—Ni1—C39	-34.47 (16)
N1—C37—C38—Ni1	-95.8 (2)	N1—C37—Ni1—C39	81.32 (17)
C37—C38—C39—C40	16.9 (3)	C38—C37—Ni1—P1	153.13 (15)
Ni1—C38—C39—C40	81.0 (2)	N1—C37—Ni1—P1	-91.07 (16)
C37—C38—C39—Ni1	-64.13 (19)	C38—C37—Ni1—P2	-55.6 (3)
C38—C39—C40—C41	178.8 (2)	N1—C37—Ni1—P2	60.2 (4)
Ni1—C39—C40—C41	-117.0 (2)	C40—C39—Ni1—C38	-120.7 (2)
C38—C39—C40—C45	-4.3 (4)	C38—C39—Ni1—C37	35.19 (15)
Ni1—C39—C40—C45	59.9 (2)	C40—C39—Ni1—C37	-85.48 (17)
C45—C40—C41—C42	-2.7 (4)	C38—C39—Ni1—P1	54.2 (3)
C39—C40—C41—C42	174.3 (2)	C40—C39—Ni1—P1	-66.5 (3)
C40—C41—C42—C43	-1.1 (4)	C38—C39—Ni1—P2	-150.38 (14)
C41—C42—C43—C44	3.1 (4)	C40—C39—Ni1—P2	88.95 (15)
C42—C43—C44—C45	-1.4 (4)	C7—P1—Ni1—C38	-55.58 (13)
C43—C44—C45—C40	-2.4 (4)	C13—P1—Ni1—C38	-176.43 (13)
C43—C44—C45—N1	-179.5 (2)	C1—P1—Ni1—C38	63.29 (14)
C41—C40—C45—C44	4.4 (4)	C7—P1—Ni1—C37	-76.03 (11)
C39—C40—C45—C44	-172.6 (2)	C13—P1—Ni1—C37	163.12 (12)
C41—C40—C45—N1	-178.4 (2)	C1—P1—Ni1—C37	42.84 (12)
C39—C40—C45—N1	4.6 (3)	C7—P1—Ni1—C39	-93.6 (2)
O2—C46—N1—C37	172.7 (2)	C13—P1—Ni1—C39	145.6 (2)
O3—C46—N1—C37	-5.7 (3)	C1—P1—Ni1—C39	25.3 (2)
O2—C46—N1—C45	2.7 (4)	C7—P1—Ni1—P2	111.58 (9)
O3—C46—N1—C45	-175.7 (2)	C13—P1—Ni1—P2	-9.27 (10)
C38—C37—N1—C46	-138.6 (2)	C1—P1—Ni1—P2	-129.56 (10)
Ni1—C37—N1—C46	150.39 (18)	C25—P2—Ni1—C38	-136.18 (13)

C38—C37—N1—C45	31.8 (3)	C31—P2—Ni1—C38	-22.43 (14)
Ni1—C37—N1—C45	-39.2 (2)	C24—P2—Ni1—C38	102.85 (14)
C44—C45—N1—C46	-30.5 (4)	C25—P2—Ni1—C37	-92.5 (3)
C40—C45—N1—C46	152.5 (2)	C31—P2—Ni1—C37	21.3 (3)
C44—C45—N1—C37	159.3 (2)	C24—P2—Ni1—C37	146.5 (3)
C40—C45—N1—C37	-17.8 (3)	C25—P2—Ni1—C39	-112.20 (11)
C20—C19—O1—C18	-92.8 (3)	C31—P2—Ni1—C39	1.55 (12)
C24—C19—O1—C18	88.9 (3)	C24—P2—Ni1—C39	126.83 (12)
C17—C18—O1—C19	41.8 (3)	C25—P2—Ni1—P1	57.75 (8)
C13—C18—O1—C19	-139.6 (2)	C31—P2—Ni1—P1	171.50 (9)
O2—C46—O3—C47	-0.5 (4)	C24—P2—Ni1—P1	-63.23 (10)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⊕
⊖OTf
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O
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9.86
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9.84
9.38
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8.69
8.67
8.66
8.43
8.43
8.41
8.40
8.31
8.31
8.29
8.28
8.28
8.26
8.25
8.25
8.23
8.22
8.20
8.07
8.06
8.04
8.04
8.03
8.01
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4.89
4.87
1.62
1.60
1.58
1.00
1.06
1.01
1.08
2.20
1.09
2.20
3.29
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10.0
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8.5
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7.5
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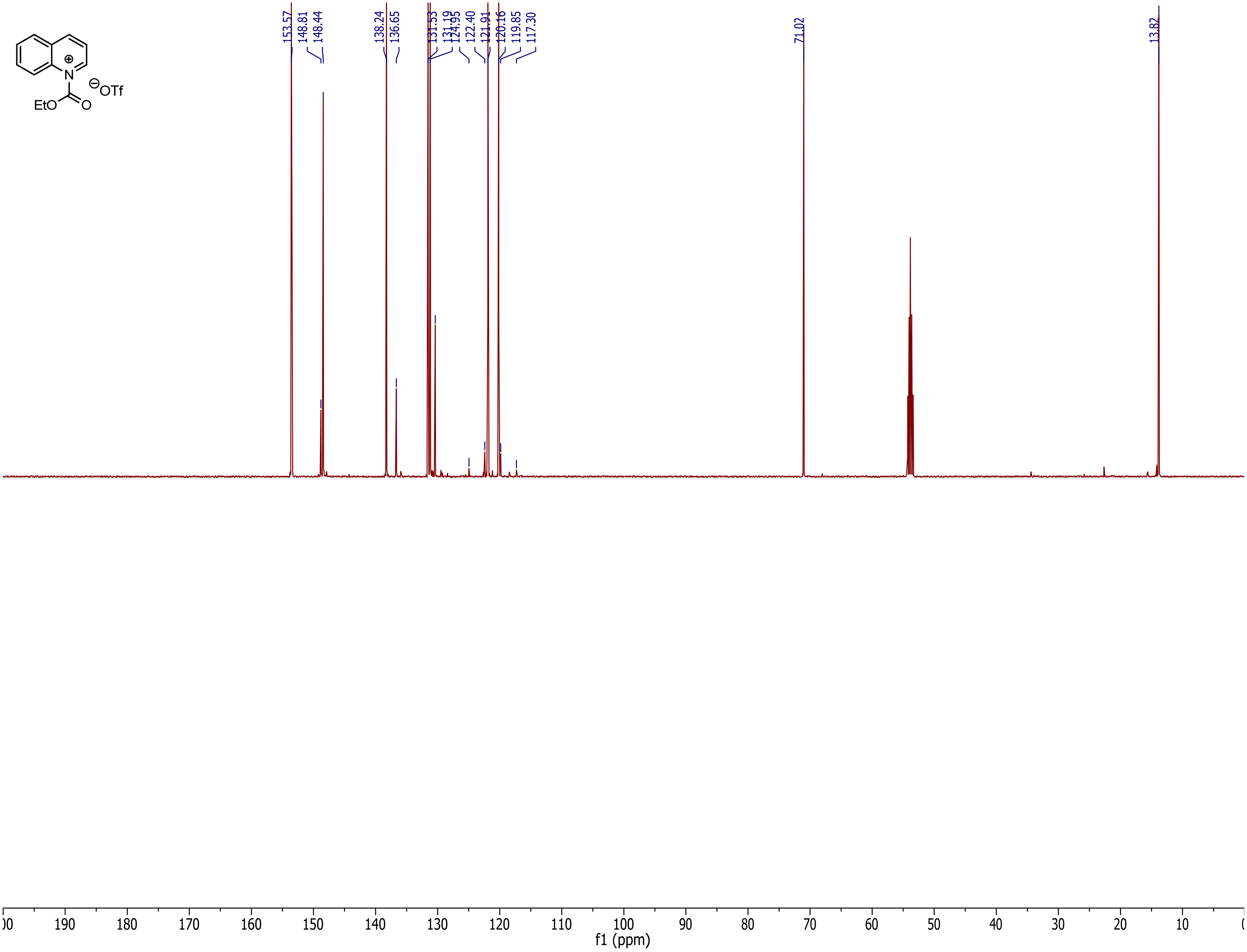
f1 (ppm)



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⊕
⊖OTf
EtO
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124.95
122.40
121.91
120.16
119.85
117.30
71.02
13.82
190
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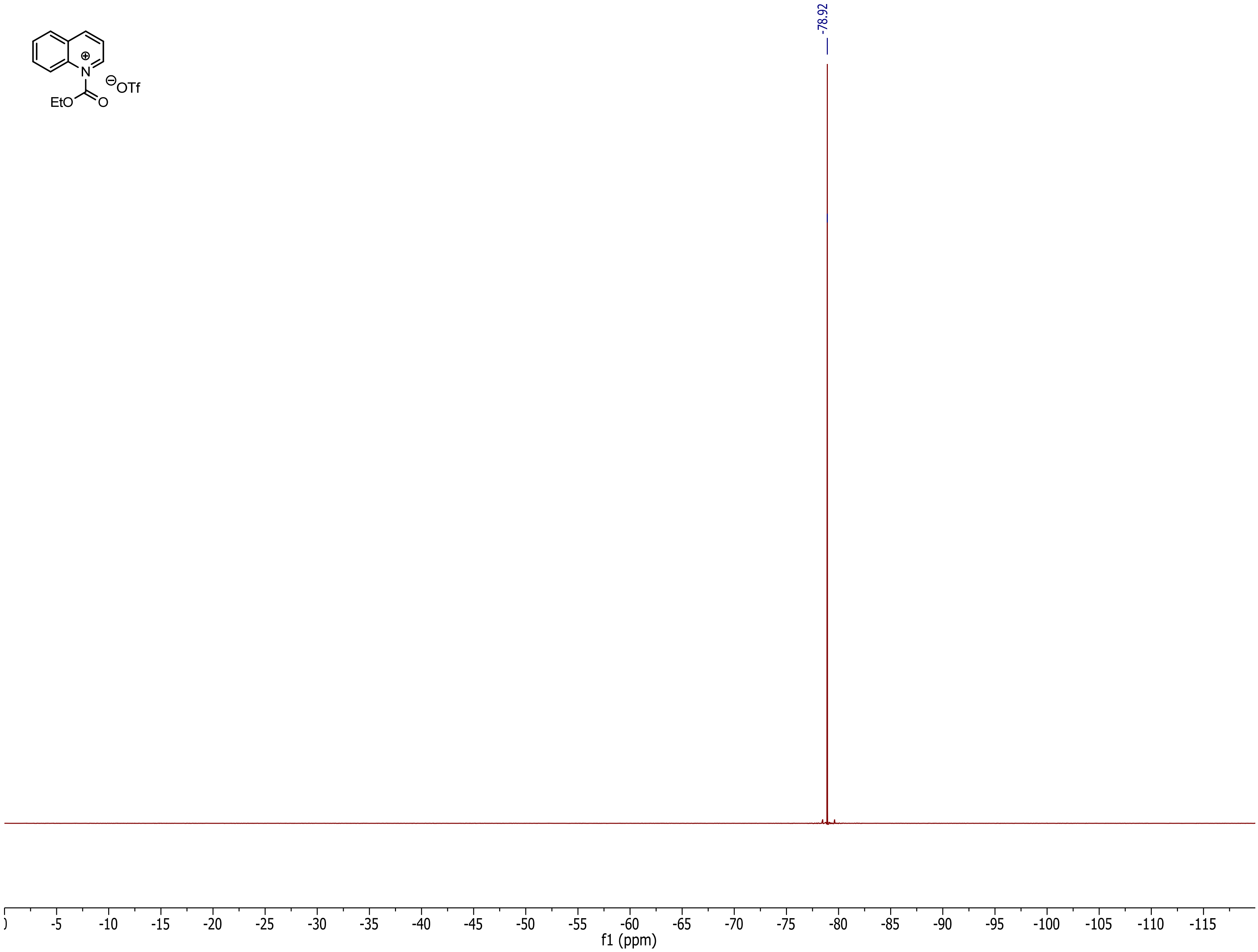
f1 (ppm)



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EtO
O
OTf
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-10
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-25
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-70
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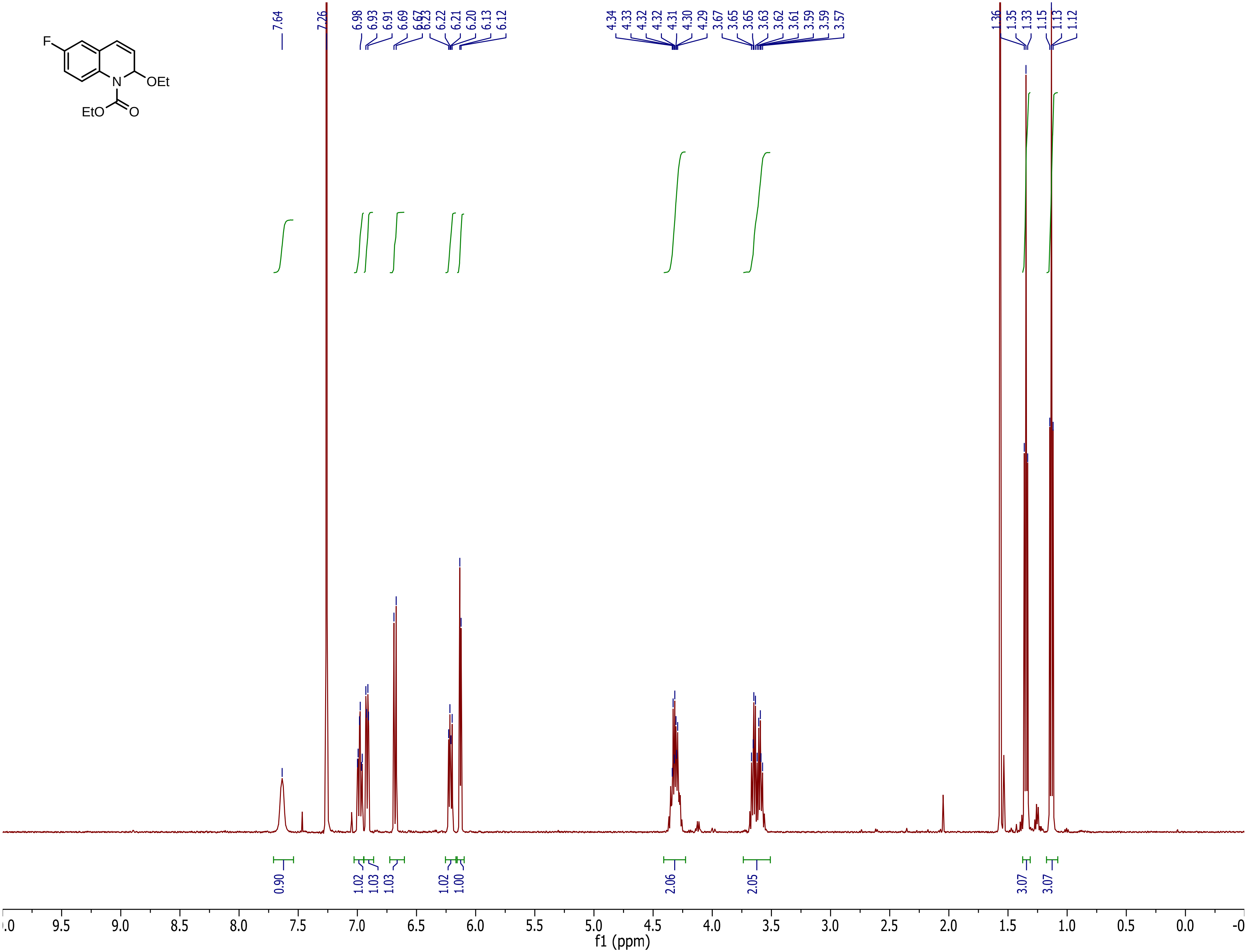
f1 (ppm)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OEt
EtO
O
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6.21
6.20
6.13
6.12
4.34
4.33
4.32
4.32
4.31
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4.29
3.67
3.65
3.65
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3.59
3.59
3.57
1.36
1.35
1.33
1.15
1.13
1.12
0.90
1.02
1.03
1.03
1.02
1.00
2.06
2.05
3.07
3.07
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8.0
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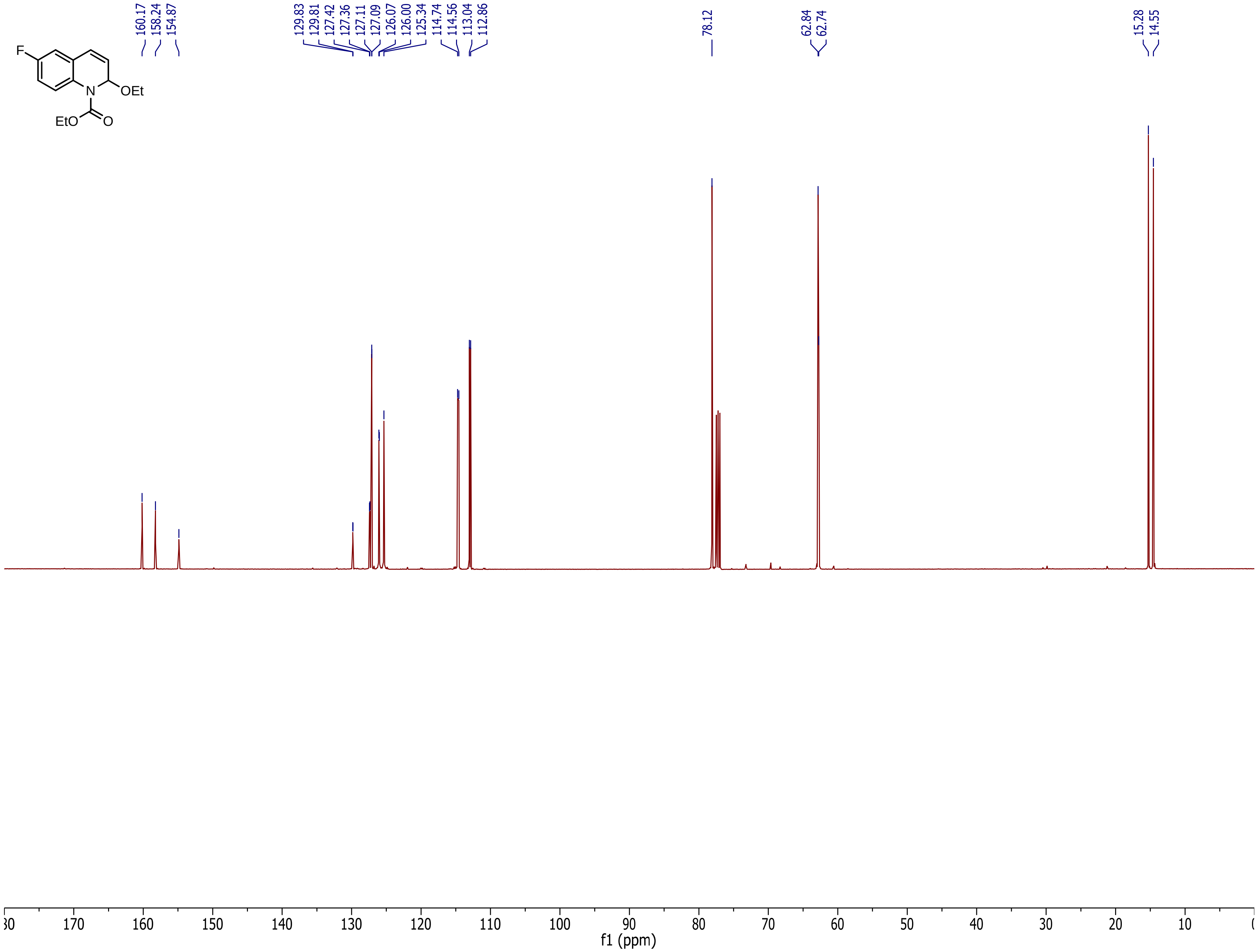
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114.56
113.04
112.86
78.12
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62.74
15.28
14.55
F
N
OEt
EtO
O
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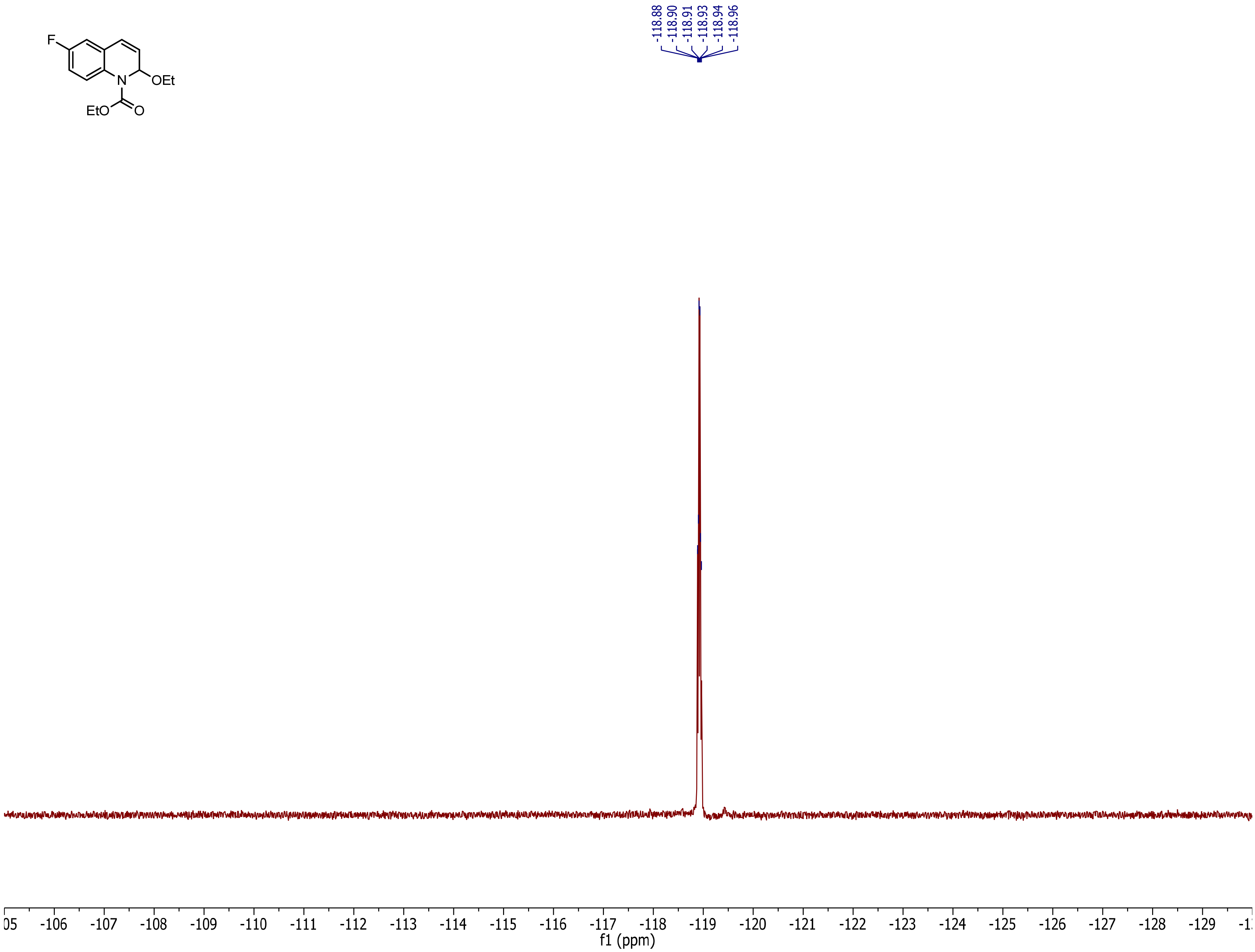
f1 (ppm)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-128
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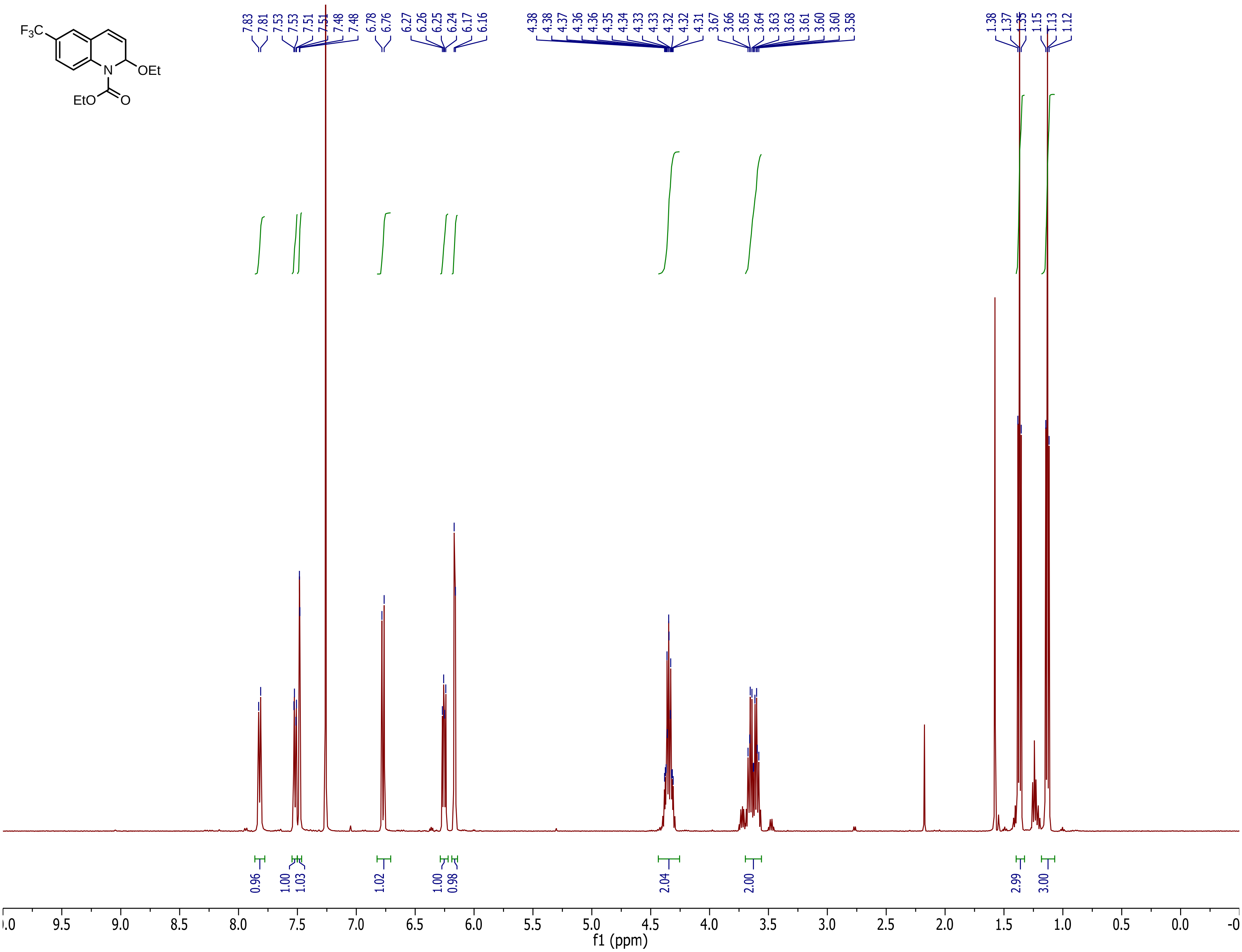
f1 (ppm)



F3C
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OEt
EtO
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7.81
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7.53
7.51
7.51
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6.76
6.27
6.26
6.25
6.24
6.17
6.16
4.38
4.38
4.37
4.36
4.36
4.35
4.34
4.33
4.33
4.32
4.32
4.31
3.67
3.66
3.65
3.64
3.63
3.63
3.61
3.60
3.60
3.58
1.38
1.37
1.35
1.15
1.13
1.12
0.96
1.00
1.03
1.02
1.00
0.98
2.04
2.00
2.99
3.00
.0
9.5
9.0
8.5
8.0
7.5
7.0
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6.0
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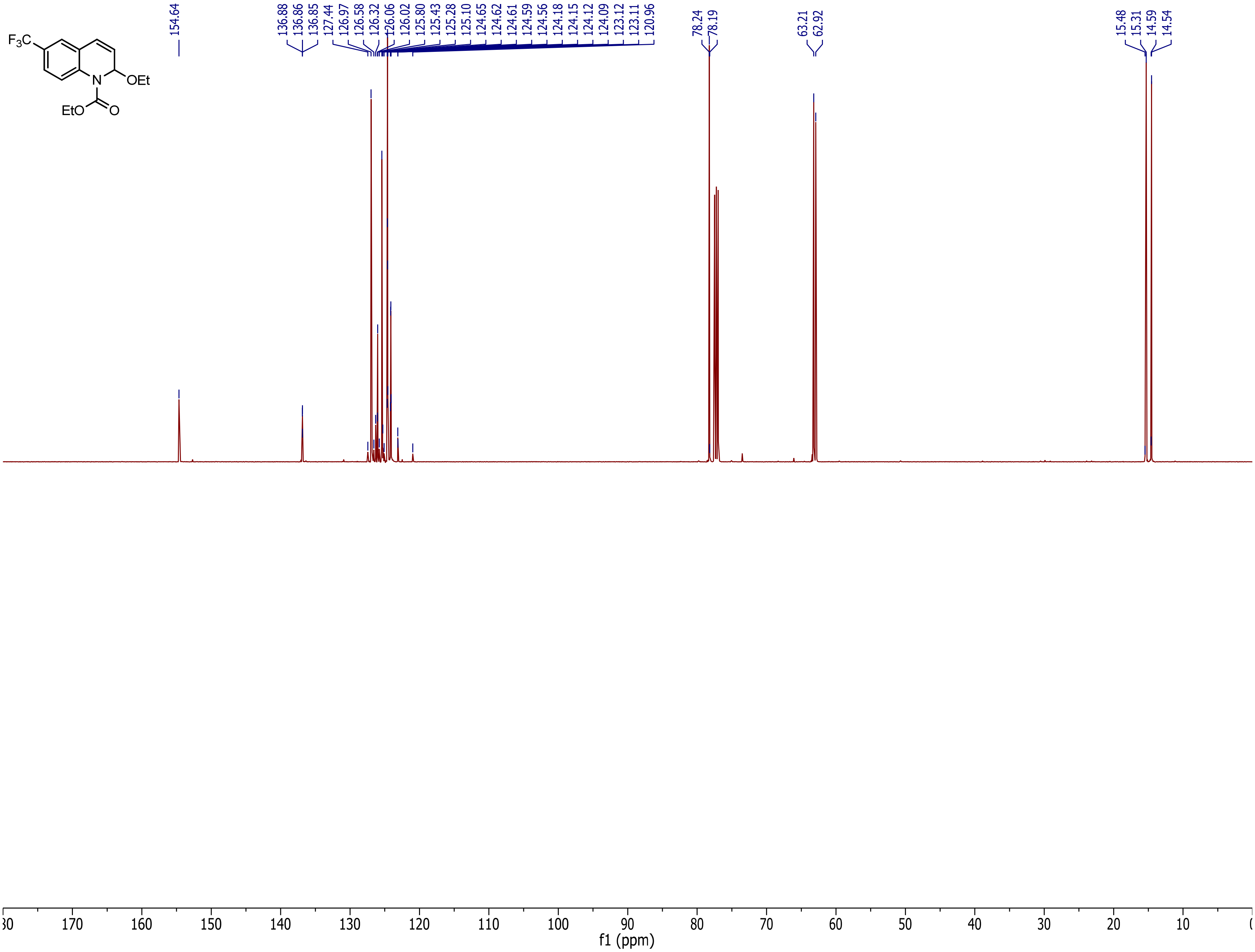
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OEt
EtO
O
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126.06
126.02
125.80
125.43
125.28
125.10
124.65
124.62
124.61
124.59
124.56
124.18
124.15
124.12
124.09
123.12
123.11
120.96
78.24
78.19
63.21
62.92
15.48
15.31
14.59
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120
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60
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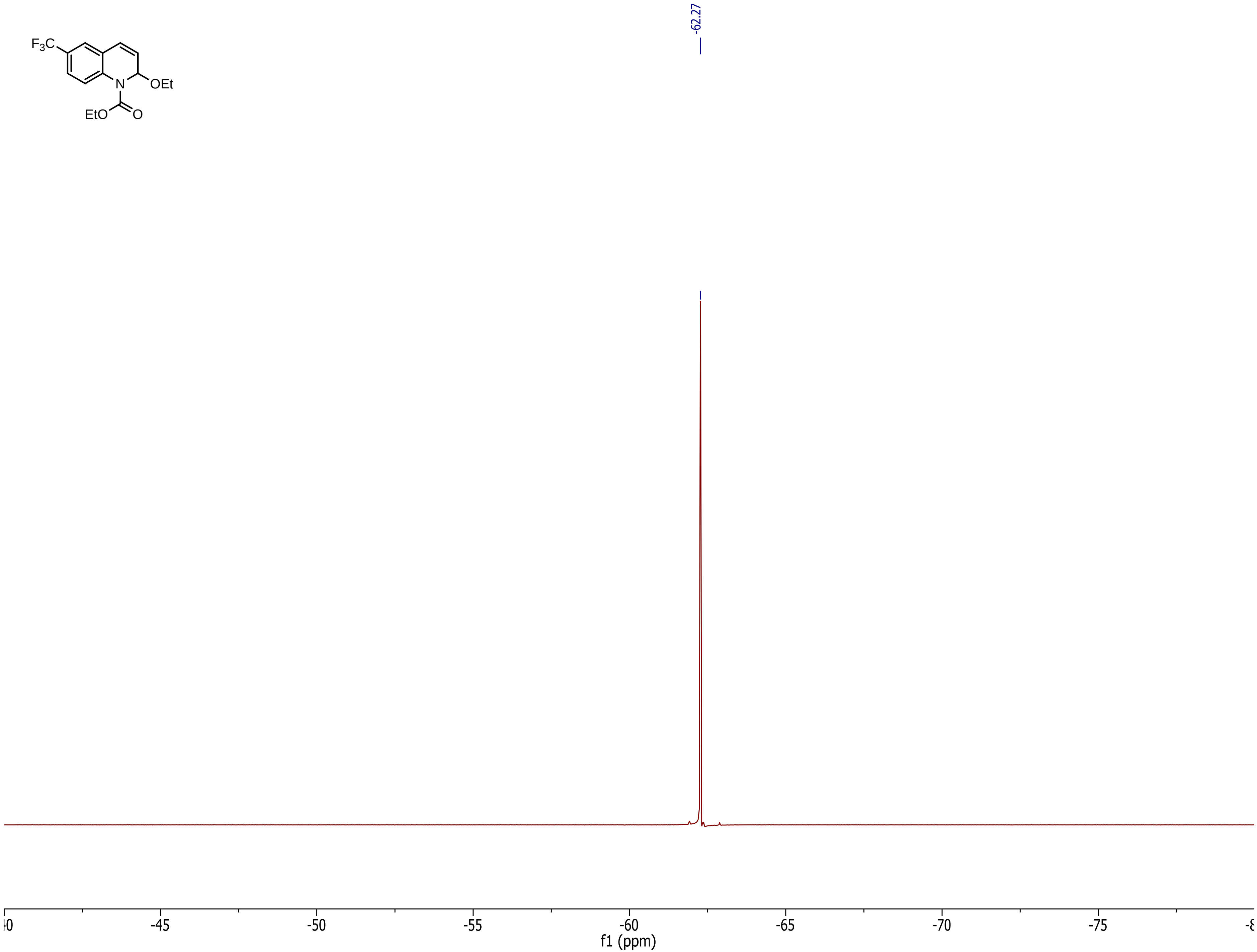
20
10
f1 (ppm)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OEt
EtO
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-55
-60
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-70
-75
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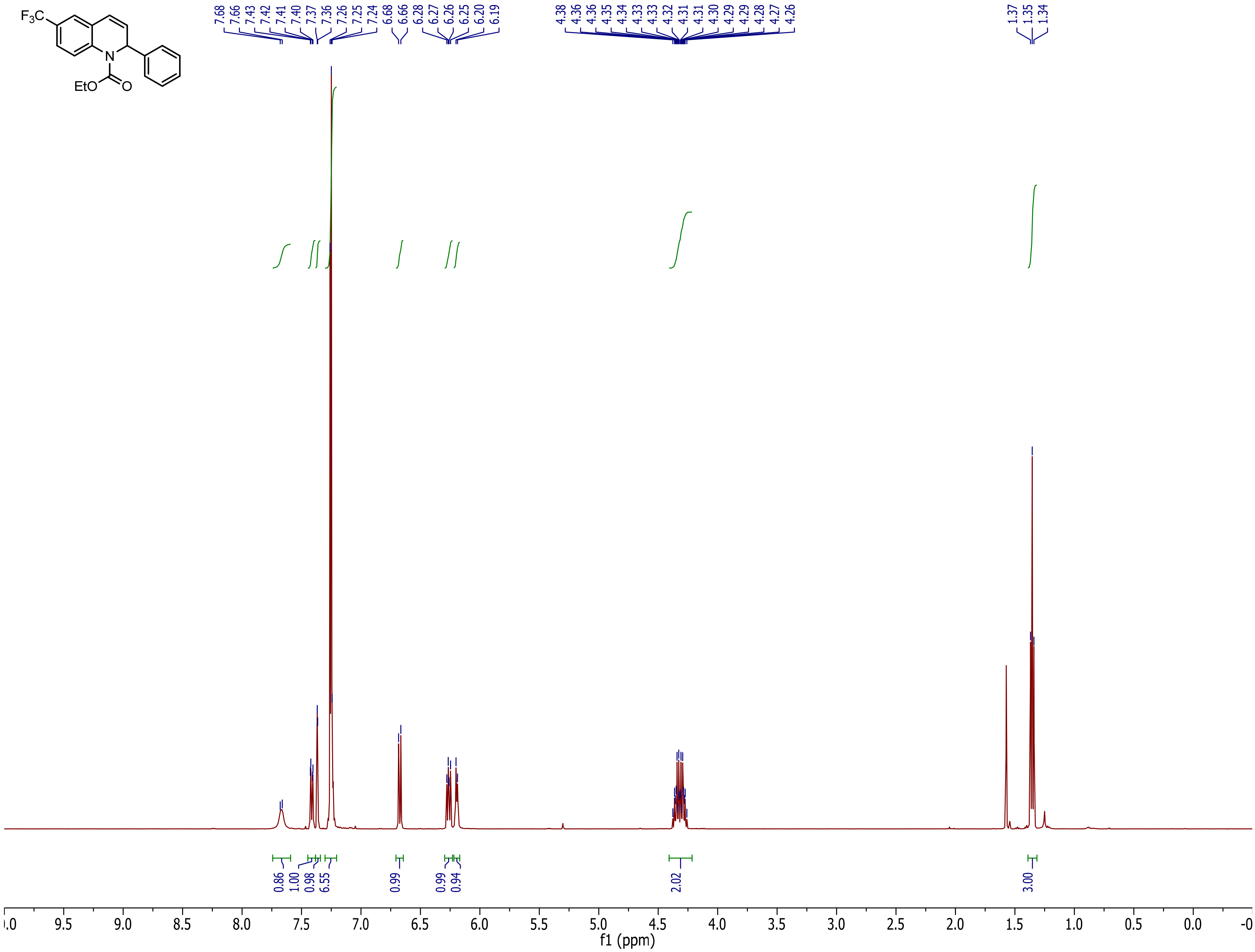

F3C
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EtO
O
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7.25
7.24
6.68
6.66
6.28
6.27
6.26
6.25
6.20
6.19
4.38
4.36
4.36
4.35
4.34
4.33
4.33
4.32
4.31
4.31
4.30
4.29
4.29
4.28
4.27
4.26
1.37
1.35
1.34
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1.00
0.98
6.55
0.99
0.99
0.94
2.02
3.00
.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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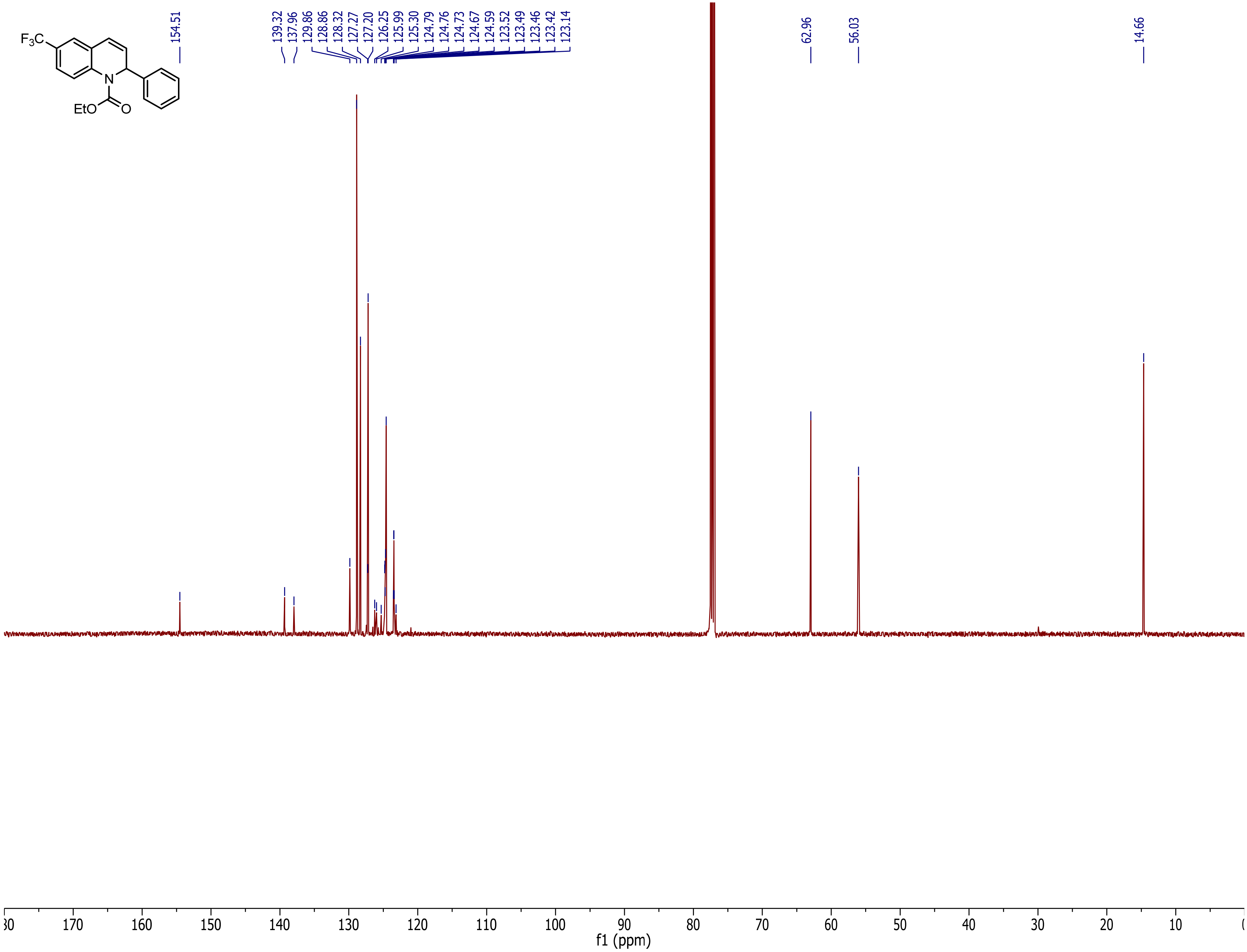
f1 (ppm)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O
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125.99
125.30
124.79
124.76
124.73
124.67
124.59
123.52
123.49
123.46
123.42
123.14
62.96
56.03
14.66
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140
130
120
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100
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50
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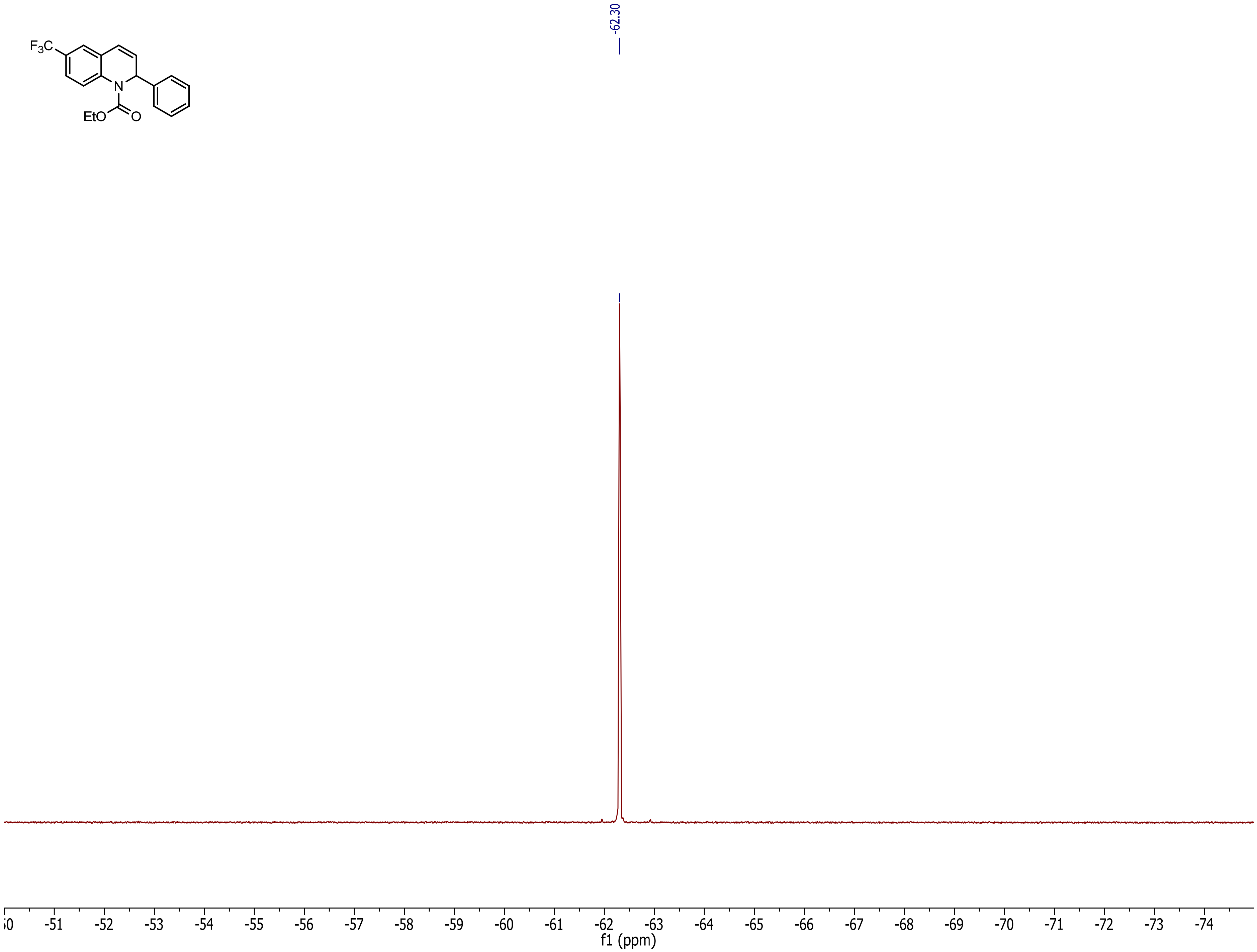
20
10
f1 (ppm)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-67
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-71
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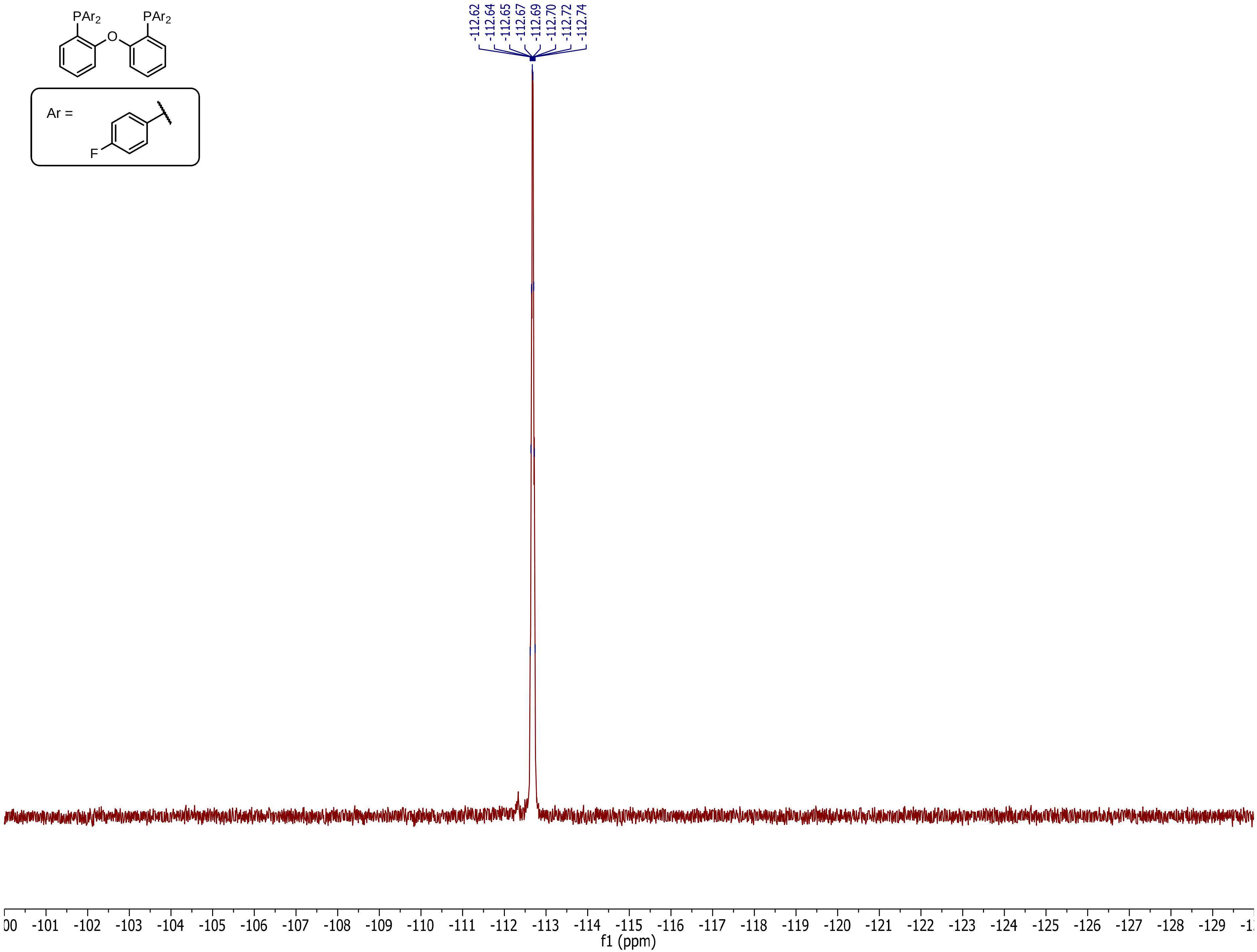
-73
-74
f1 (ppm)


PAr2
PAr2
O
Ar =
F
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-112.67
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-112.74
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-104
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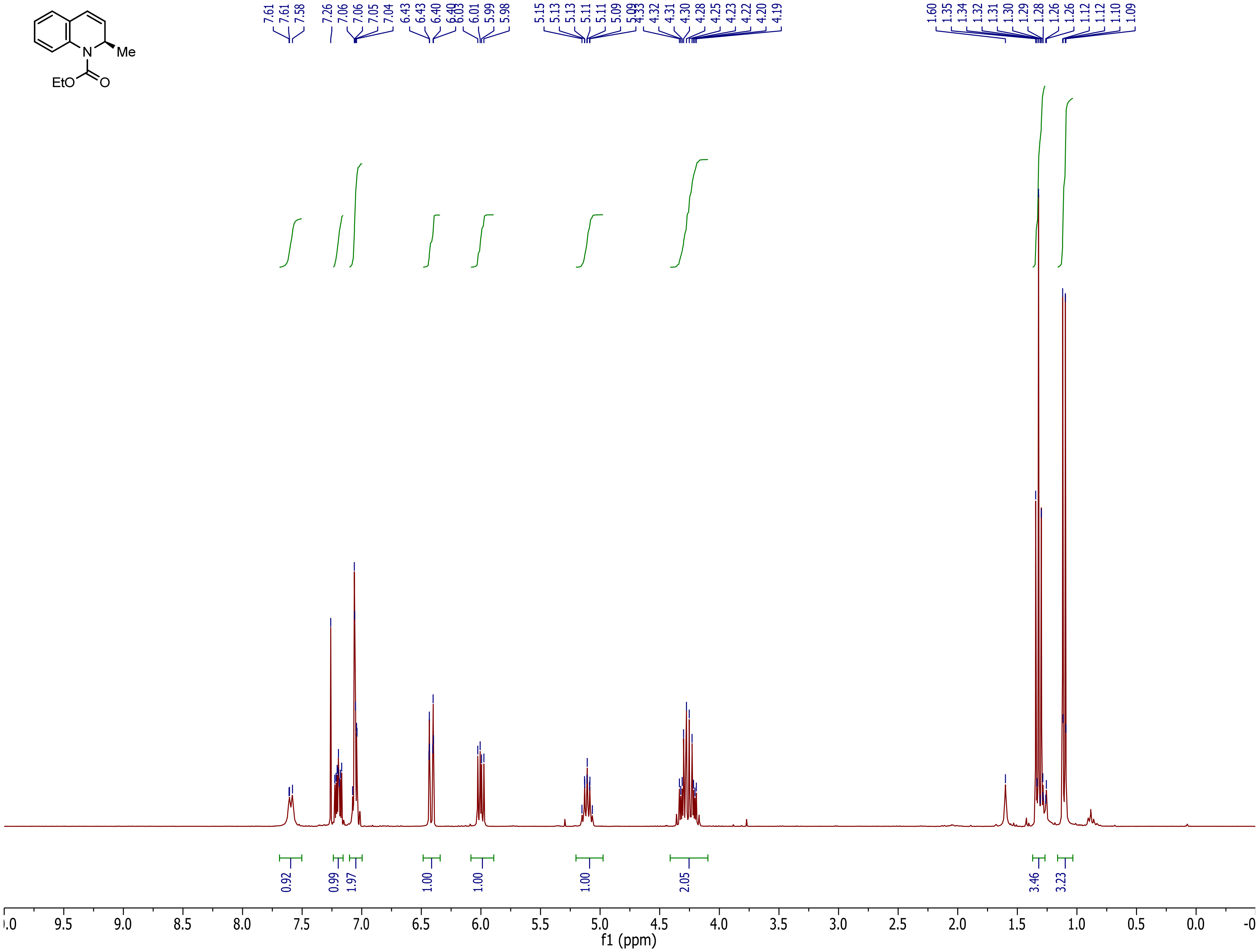
-129
f1 (ppm)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Me
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6.43
6.40
6.40
6.03
6.01
5.99
5.98
5.15
5.13
5.13
5.11
5.11
5.09
5.09
4.33
4.32
4.31
4.30
4.28
4.25
4.23
4.22
4.20
4.19
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1.35
1.34
1.32
1.31
1.30
1.29
1.28
1.26
1.26
1.12
1.12
1.10
1.09
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0.99
1.97
1.00
1.00
1.00
2.05
3.46
3.23
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9.0
8.5
8.0
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5.5
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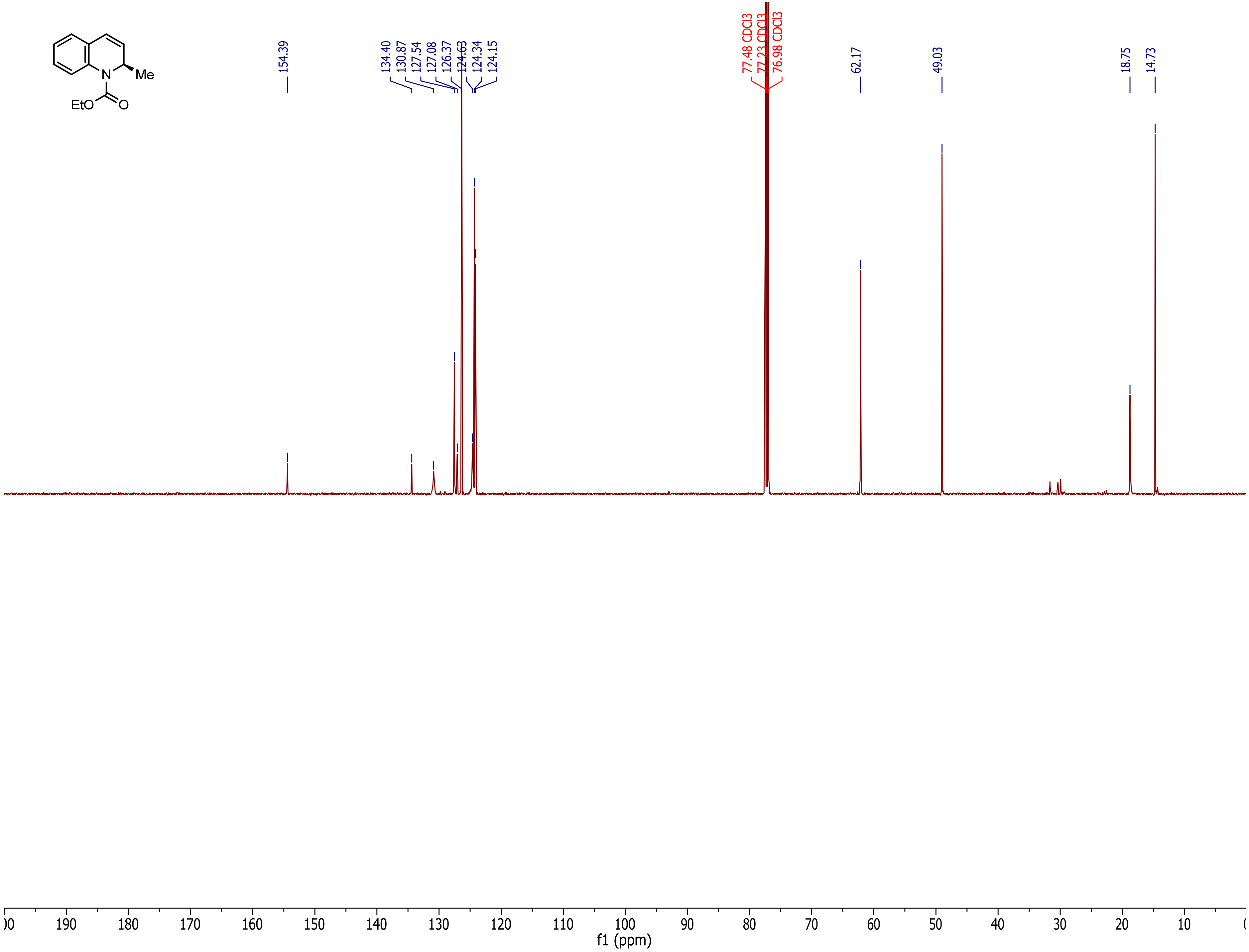
f1 (ppm)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O
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126.37
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124.34
124.15
77.48 CDCl3
77.23 CDCl3
76.98 CDCl3
62.17
49.03
18.75
14.73
190
180
170
160
150
140
130
120
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100
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80
70
60
50
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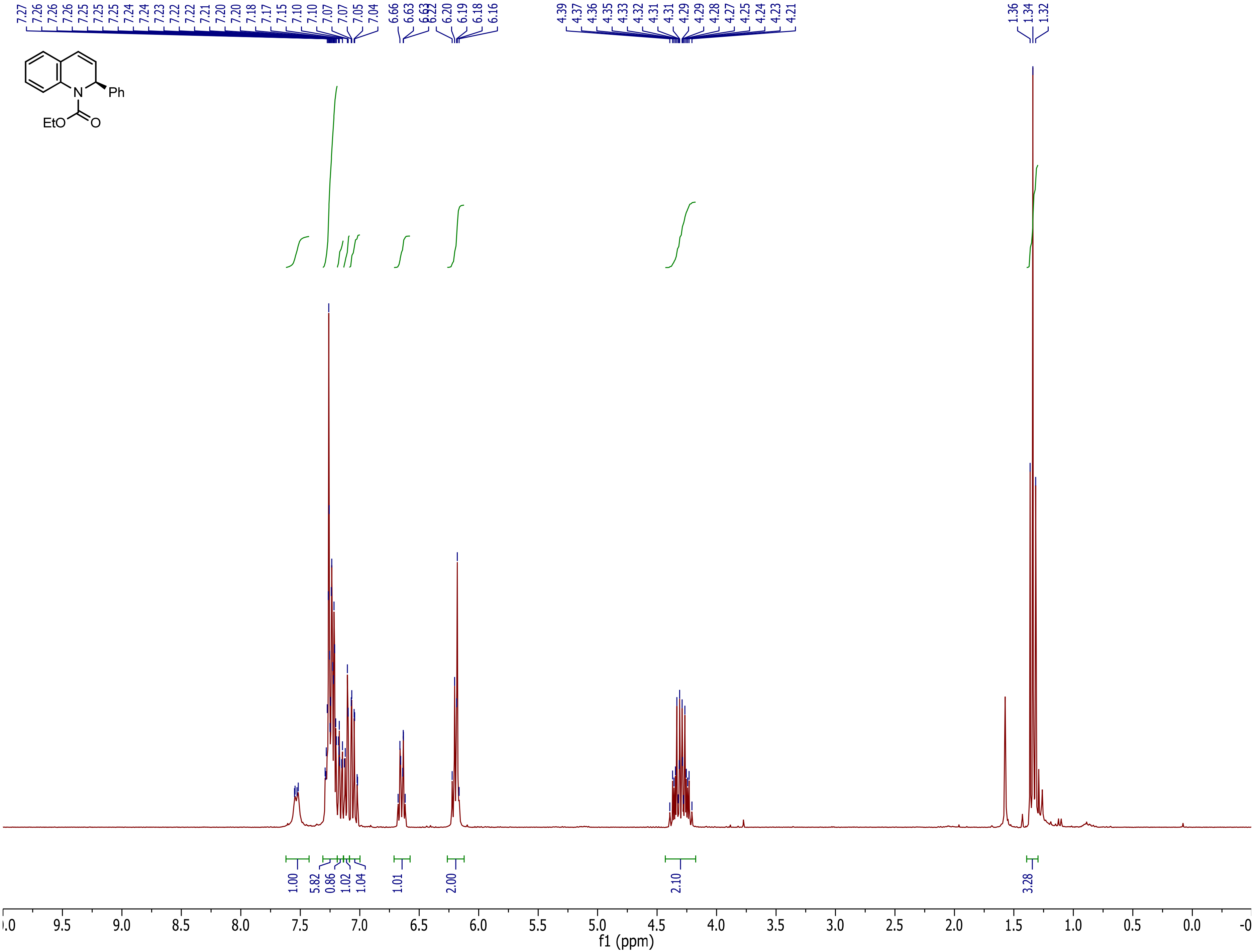
30
20
10
f1 (ppm)



EtO
O
N
Ph
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7.23
7.22
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7.21
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7.20
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7.07
7.05
7.04
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6.63
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6.19
6.18
6.16
4.39
4.37
4.36
4.35
4.33
4.32
4.31
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4.29
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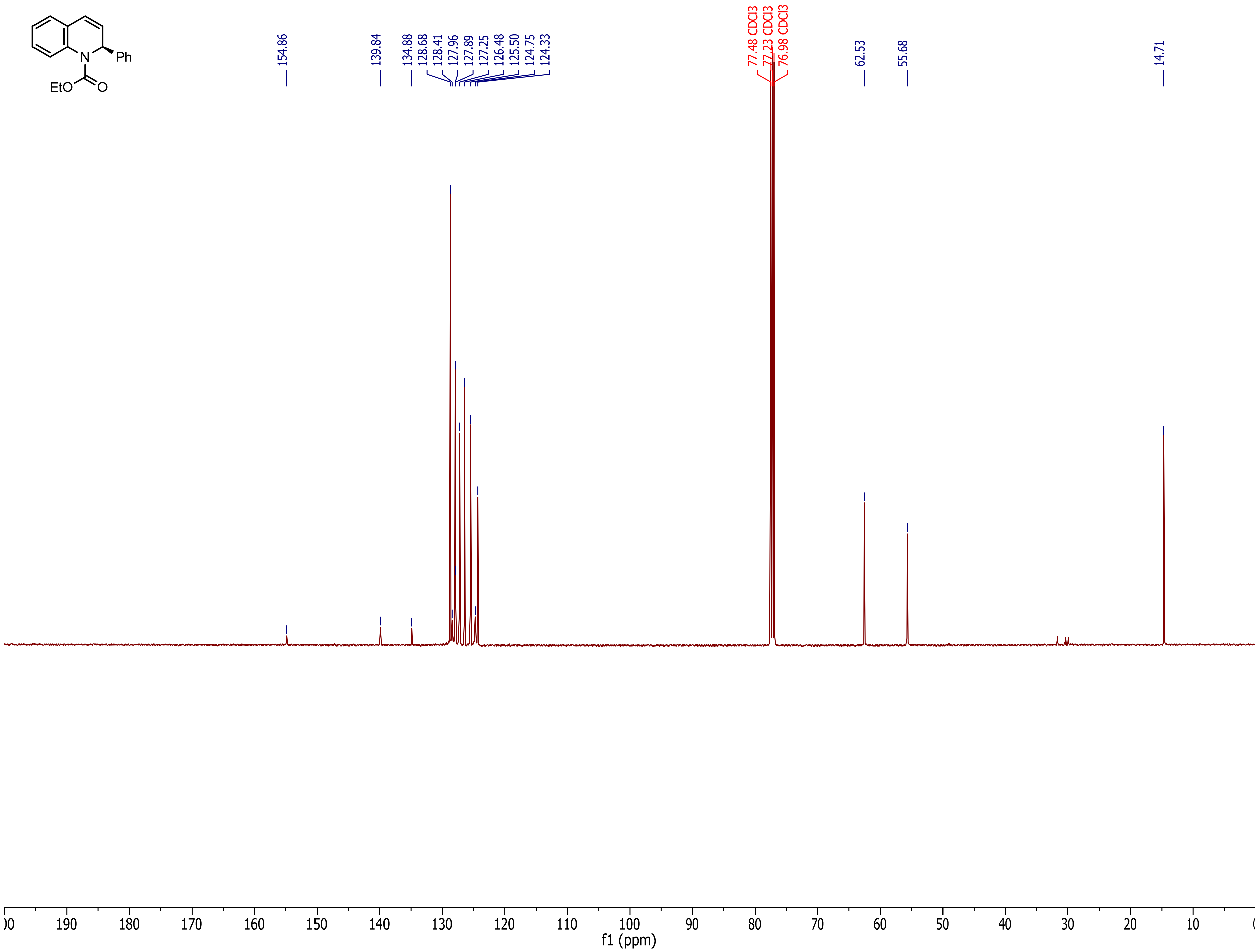
f1 (ppm)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124.33
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77.23 CDCl3
76.98 CDCl3
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55.68
14.71
190
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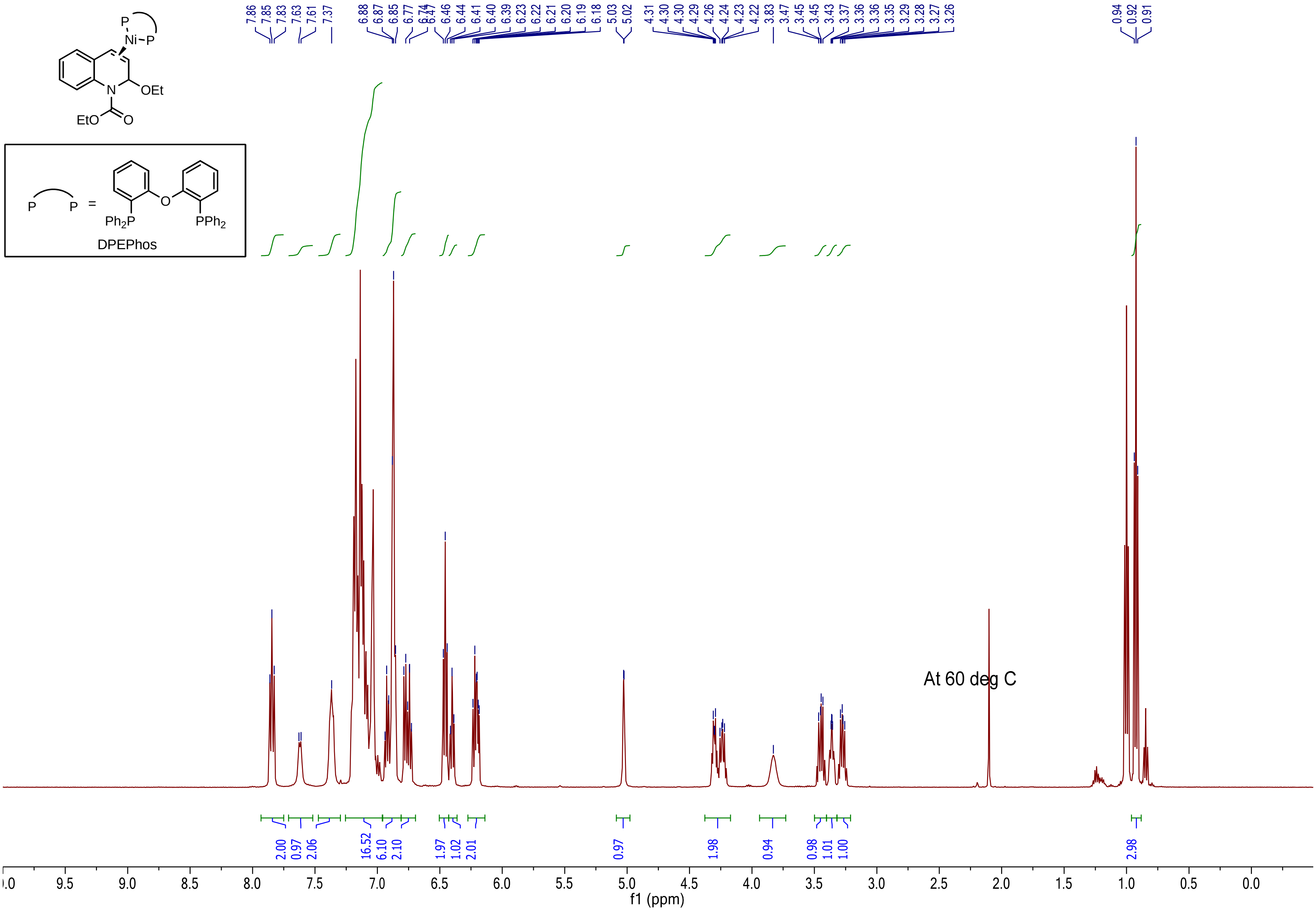
f1 (ppm)


P
Ni
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OEt
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EtO
O
P
P
=
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Ph$_2$P
PPh$_2$
DPEPhos
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7.85
7.83
7.63
7.61
7.37
6.88
6.87
6.85
6.77
6.74
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6.44
6.41
6.40
6.39
6.23
6.22
6.21
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6.19
6.18
5.03
5.02
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4.22
3.83
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3.45
3.43
3.37
3.36
3.36
3.35
3.29
3.28
3.27
3.26
0.94
0.92
0.91
At 60 deg C
2.00
0.97
2.06
16.52
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2.10
1.97
1.02
2.01
0.97
1.98
0.94
0.98
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1.00
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6.5
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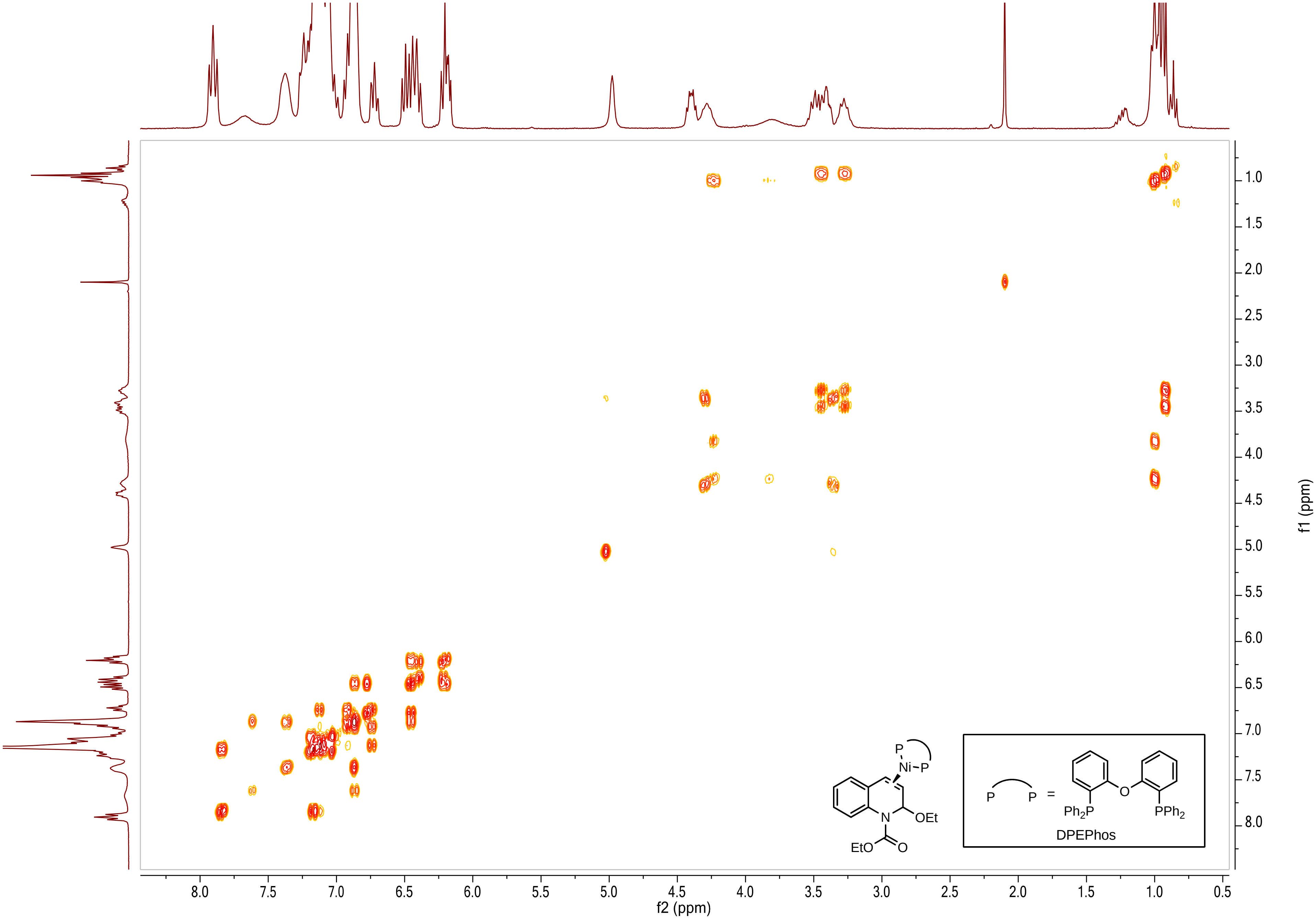
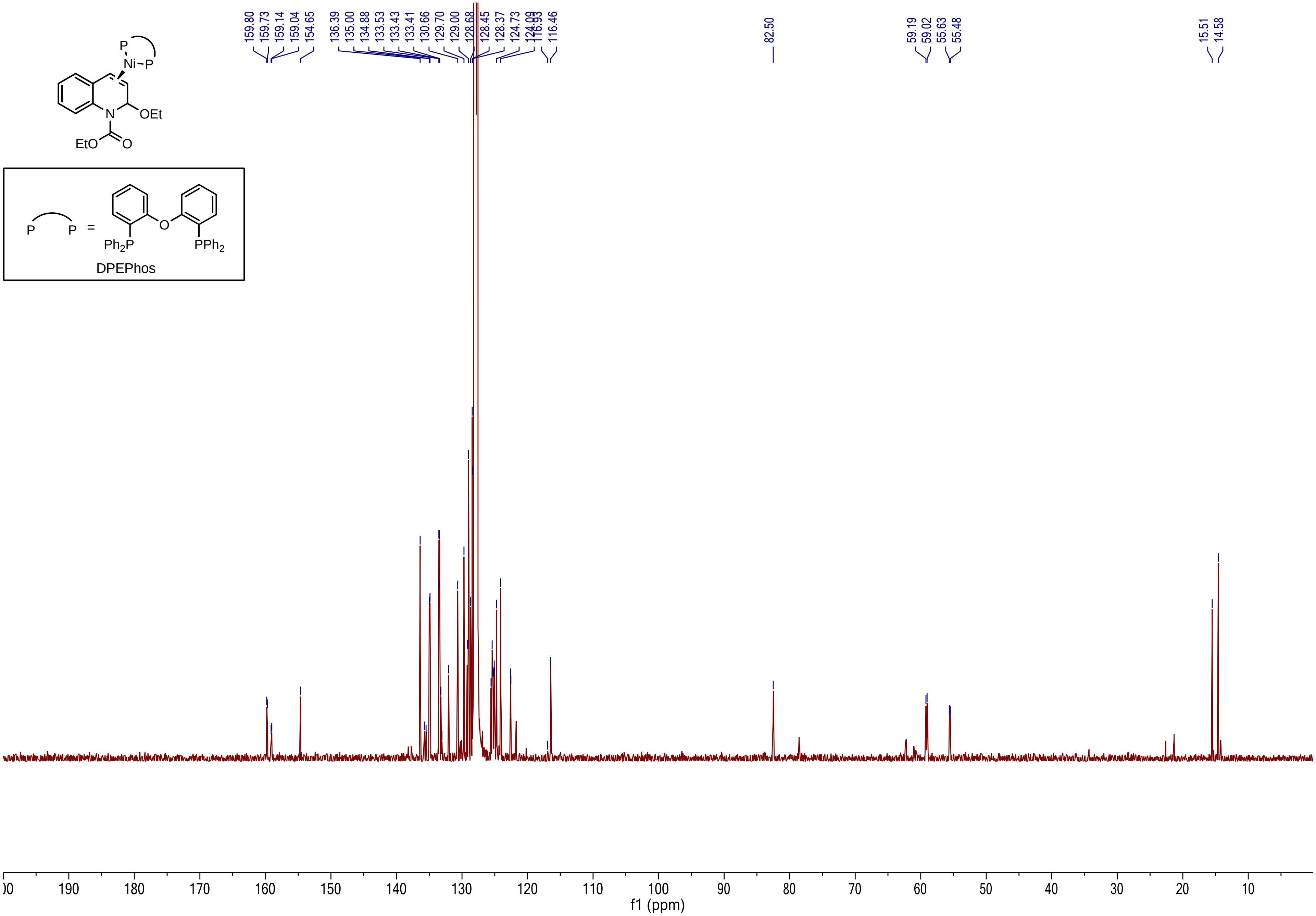
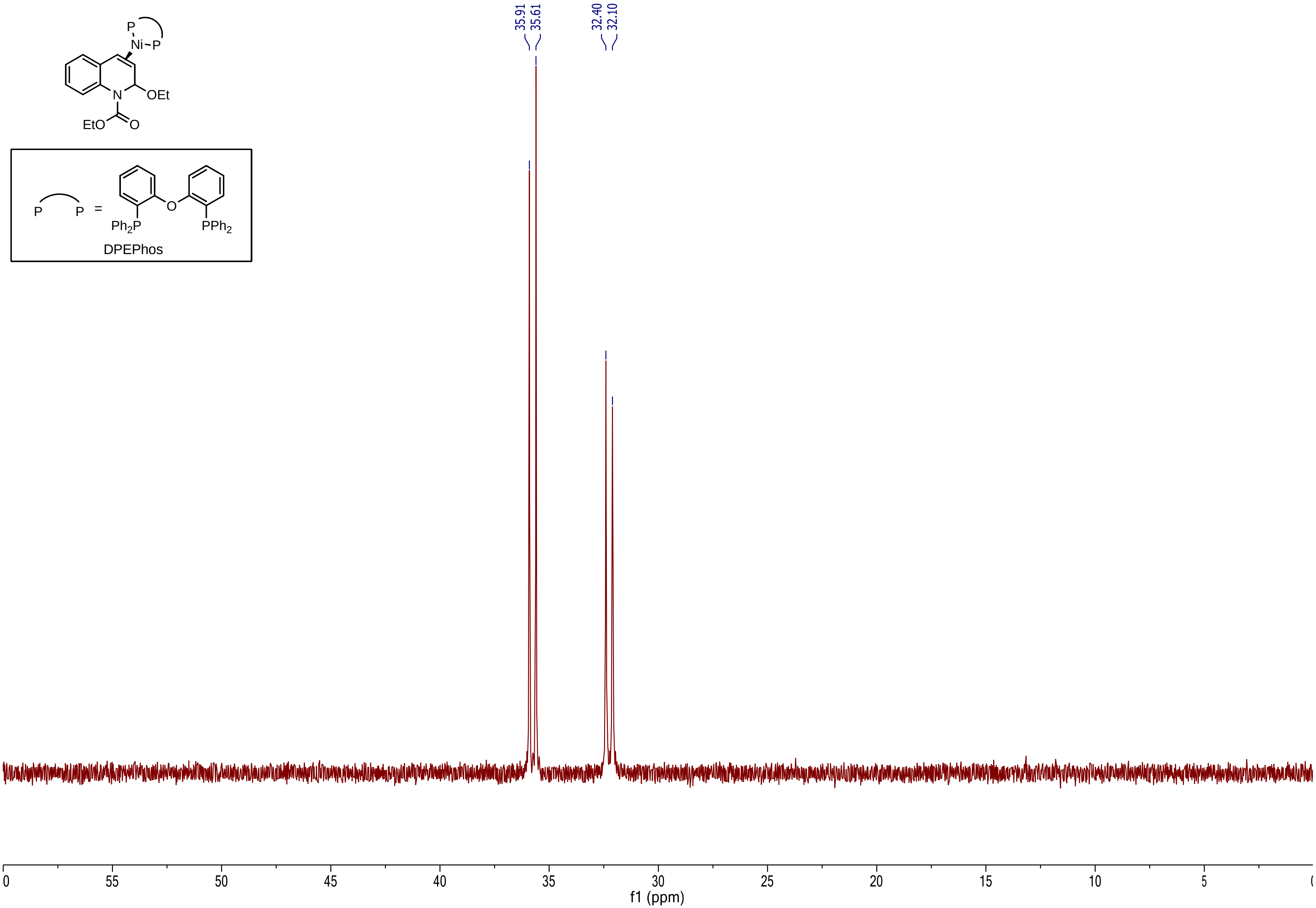
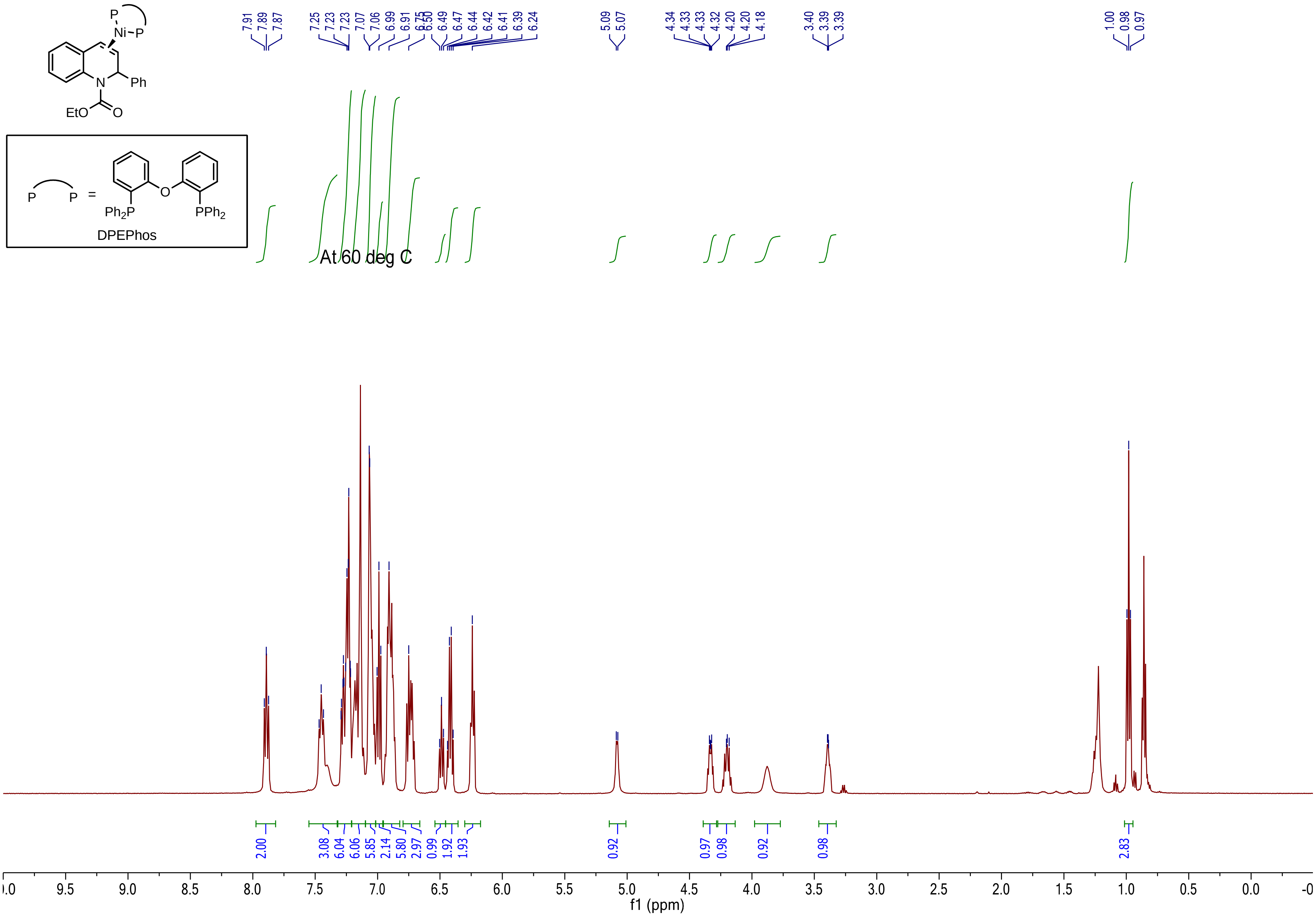
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

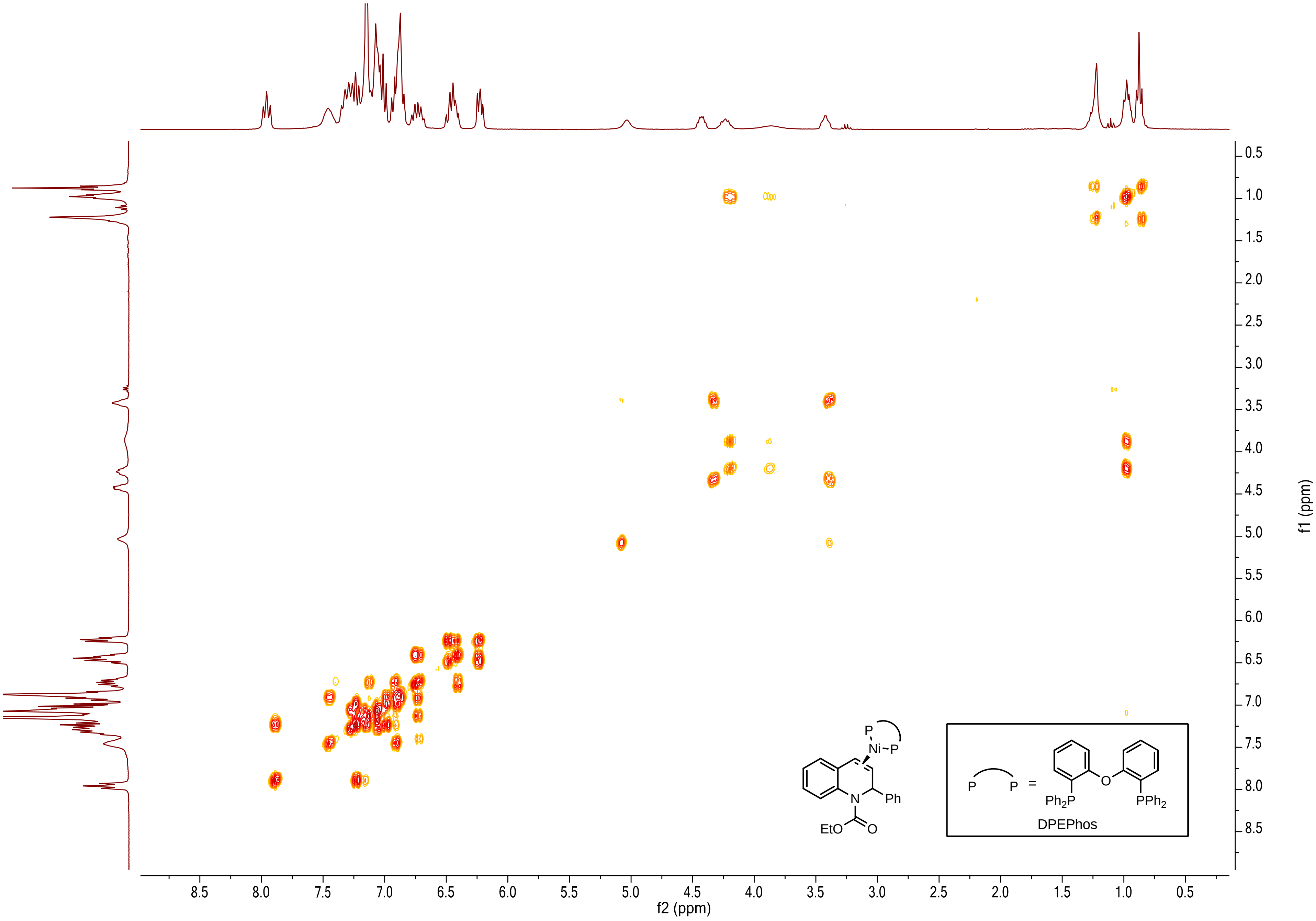


f2 (ppm)
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)
P
Ni
P
N
OEt
EtO
O
P
P
=
Ph2P
O
PPh2
DPEPhos

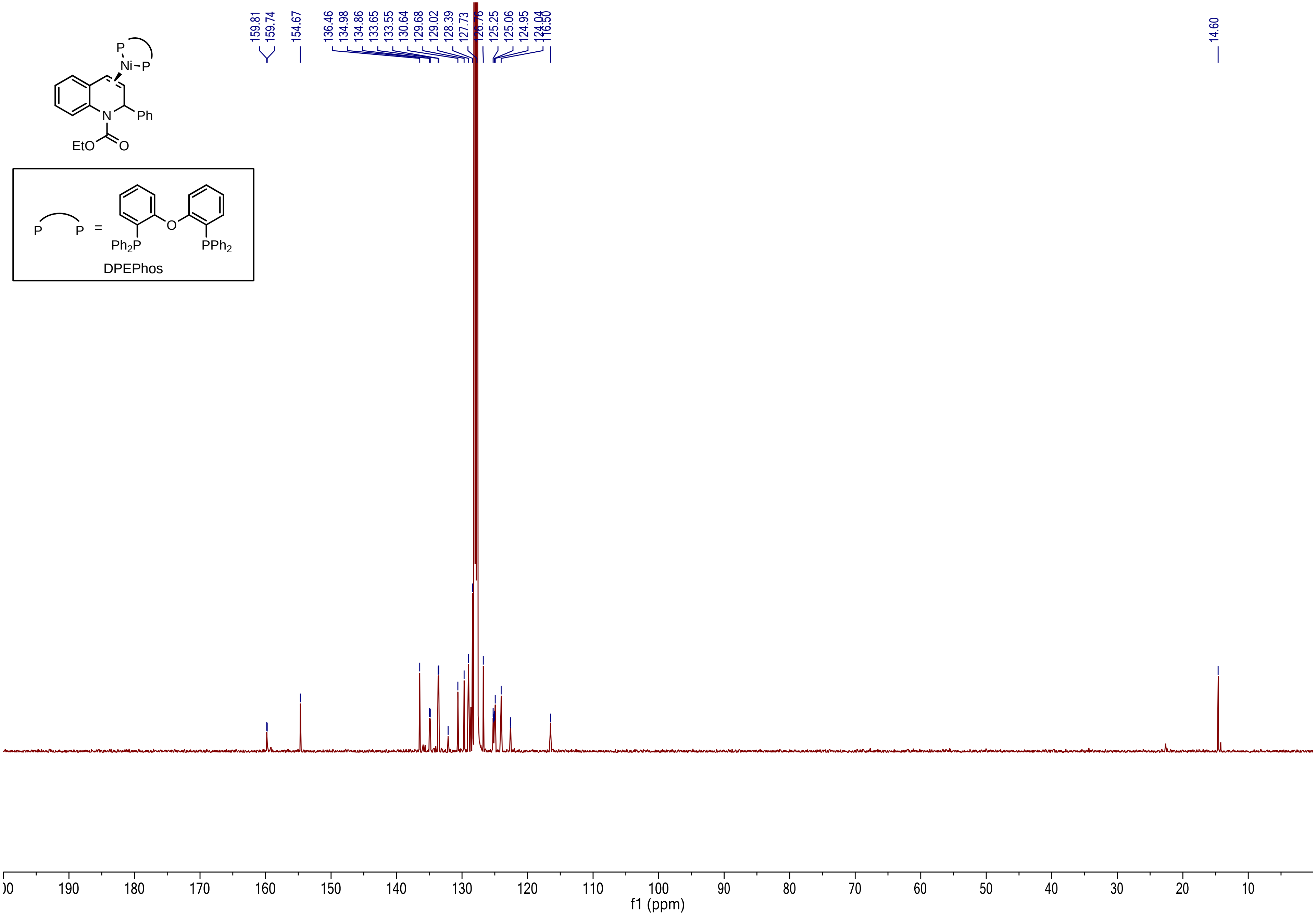

159.80
159.73
159.14
159.04
154.65
136.39
135.00
134.88
133.53
133.43
133.41
130.66
129.70
129.00
128.68
128.45
128.37
124.73
124.09
116.93
116.46
82.50
59.19
59.02
55.63
55.48
15.51
14.58
P
Ni
P
N
OEt
EtO
O
P
P
=
O
Ph2P
PPh2
DPEPhos
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

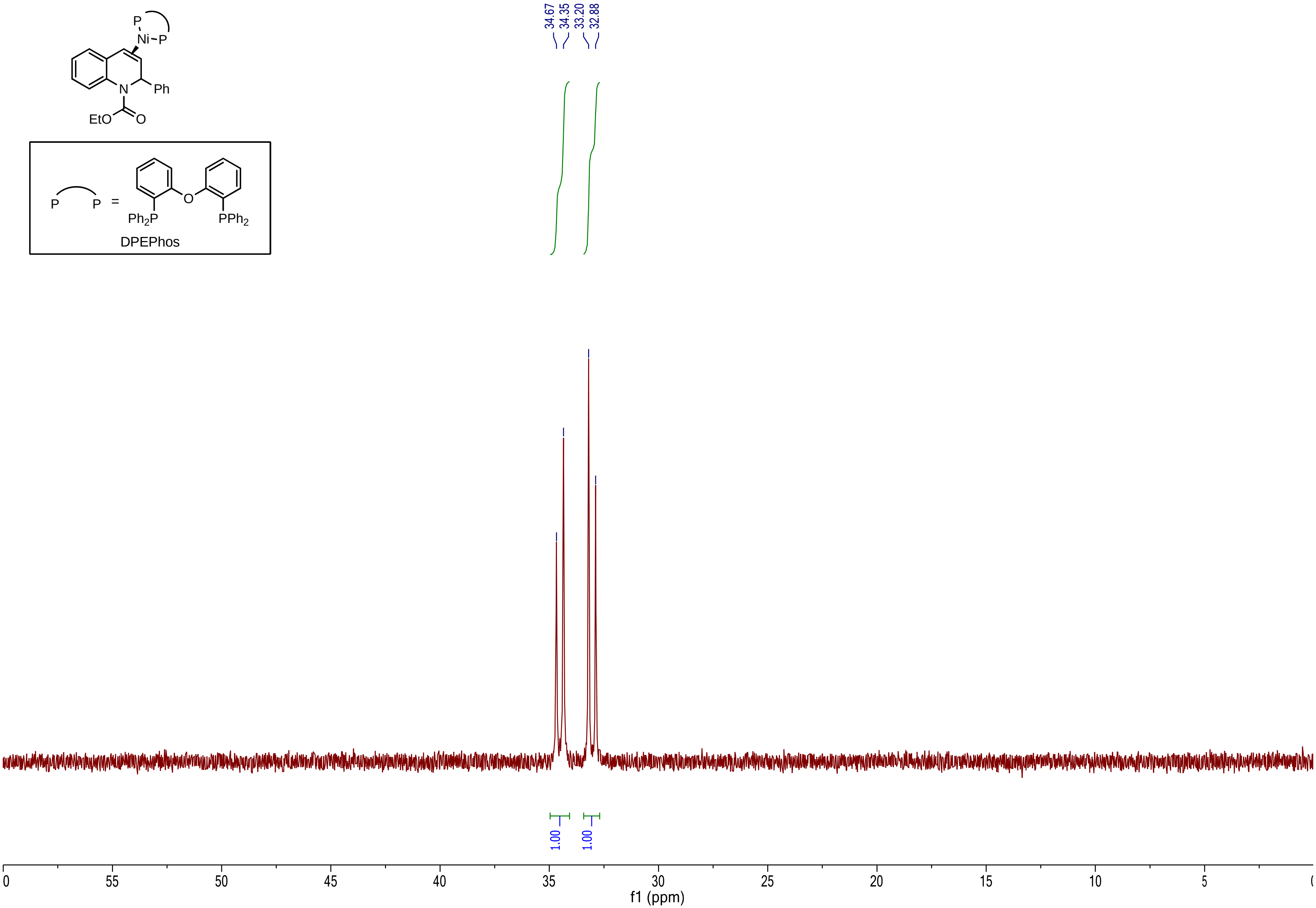

P
Ni
P
N
OEt
EtO
O
P
P
=
O
Ph2P
PPh2
DPEPhos
35.91
35.61
32.40
32.10
0
55
50
45
40
35
30
25
20
15
10
5
f1 (ppm)

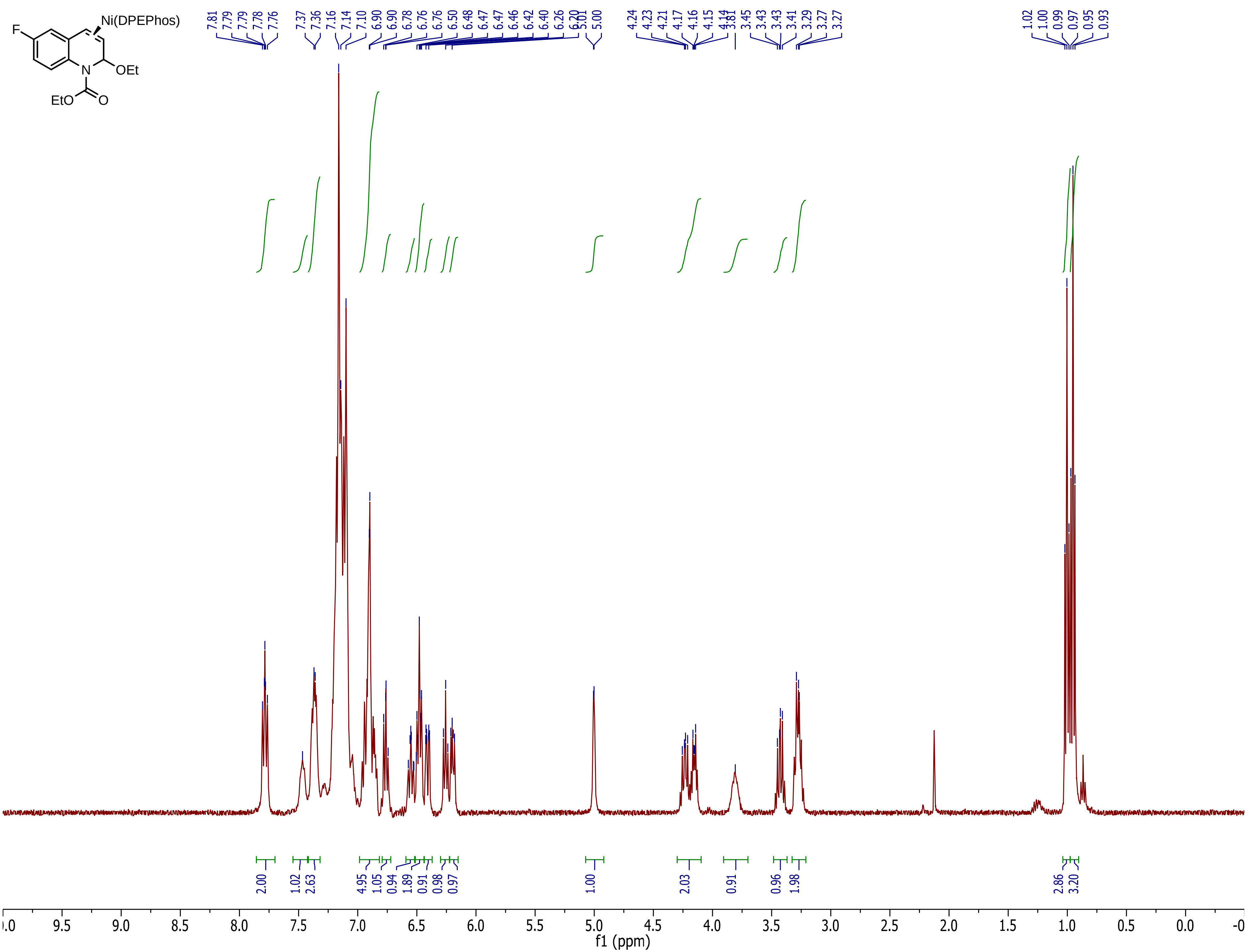

P
Ni
P
N
Ph
EtO
O
P
P
=
O
Ph2P
PPh2
DPEPhos
At 60 deg C
7.91
7.89
7.87
7.25
7.23
7.23
7.07
7.06
6.99
6.91
6.75
6.50
6.49
6.47
6.44
6.42
6.41
6.39
6.24
5.09
5.07
4.34
4.33
4.33
4.32
4.20
4.20
4.18
3.40
3.39
3.39
1.00
0.98
0.97
2.00
3.08
6.04
6.06
5.85
2.14
5.80
2.97
0.99
1.92
1.93
0.92
0.97
0.98
0.92
0.98
2.83
.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0
f1 (ppm)

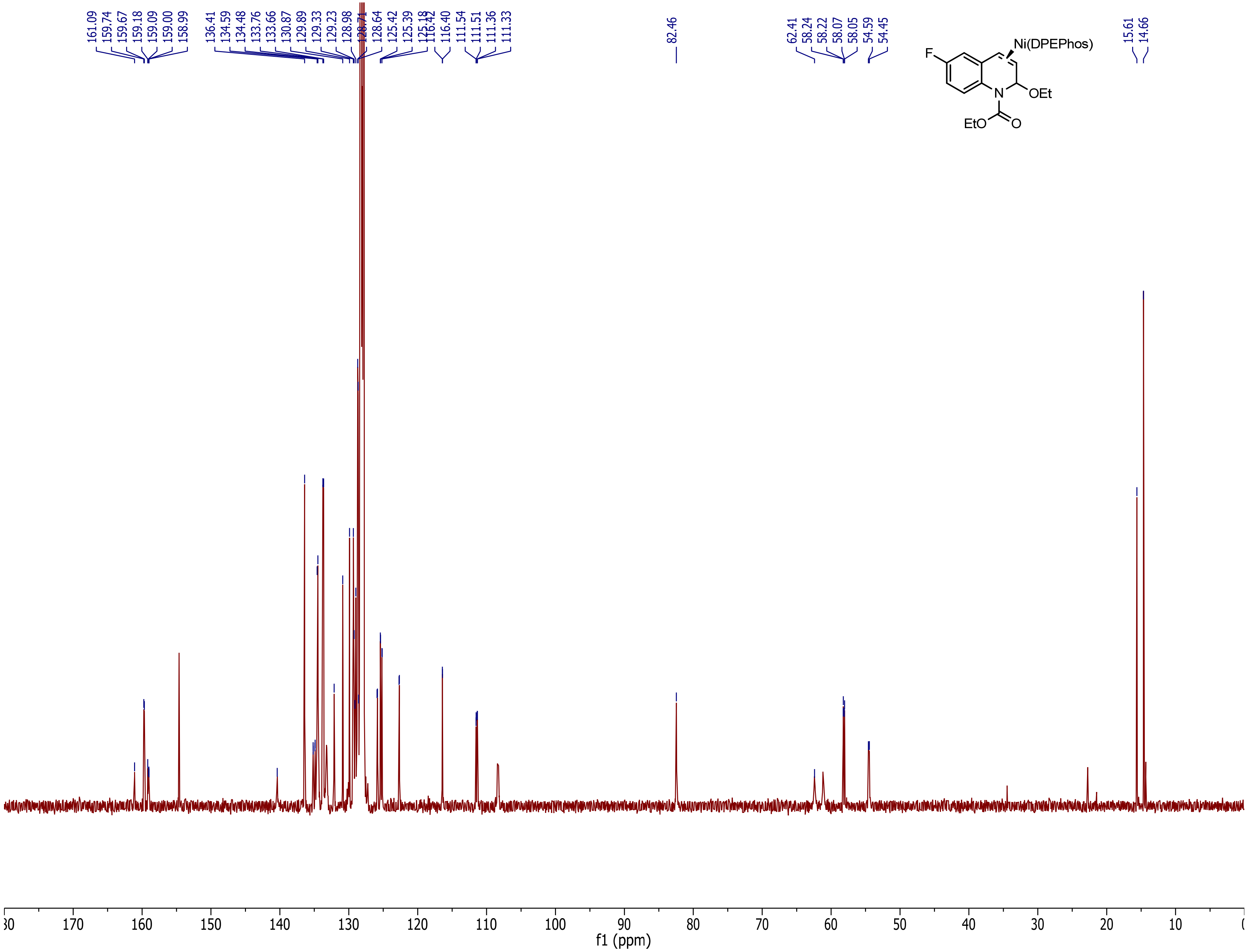


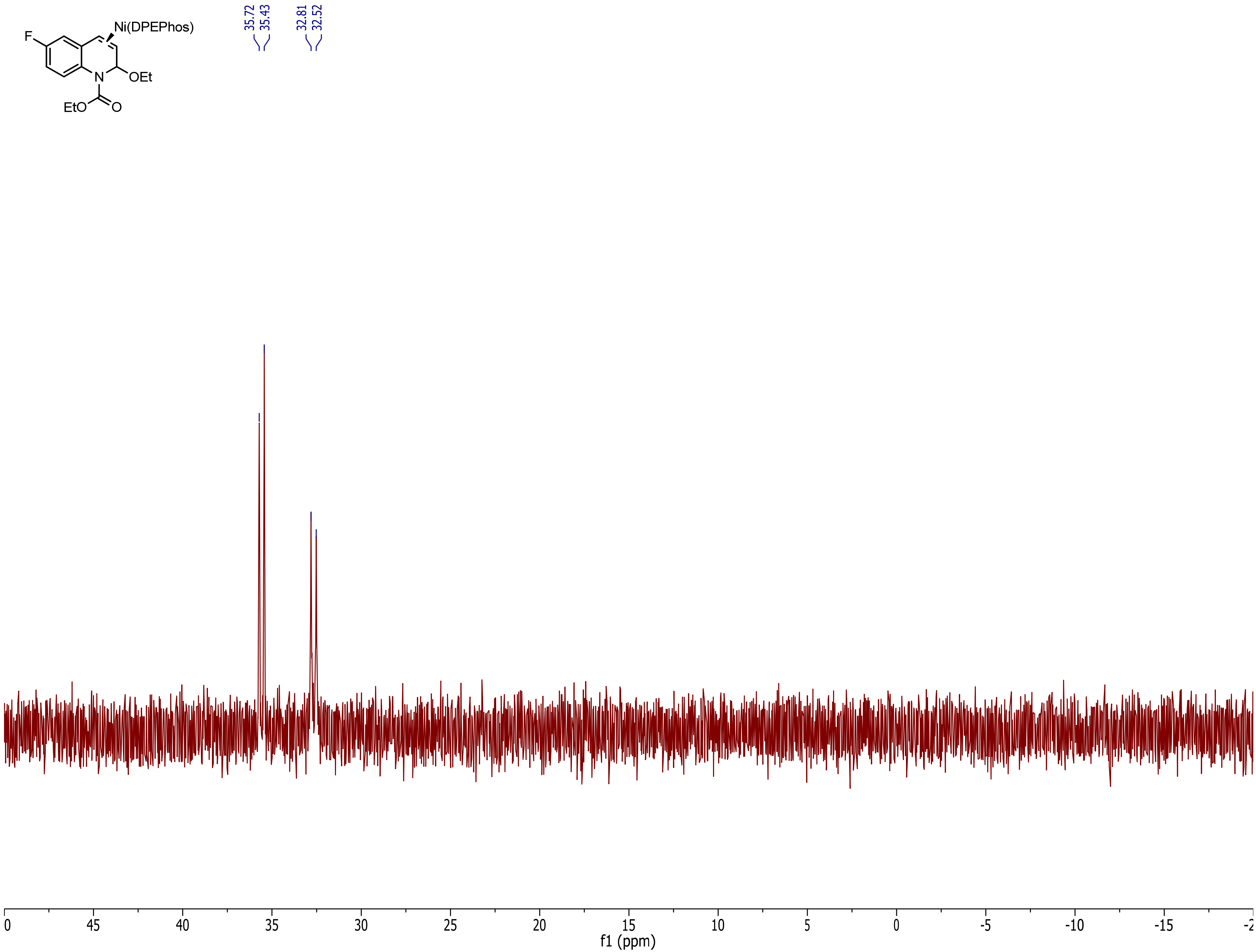
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f2 (ppm)
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
8.5
f1 (ppm)
P
Ni
P
N
Ph
EtO
O
P
P
=
O
Ph$_2$P
PPh$_2$
DPEPhos

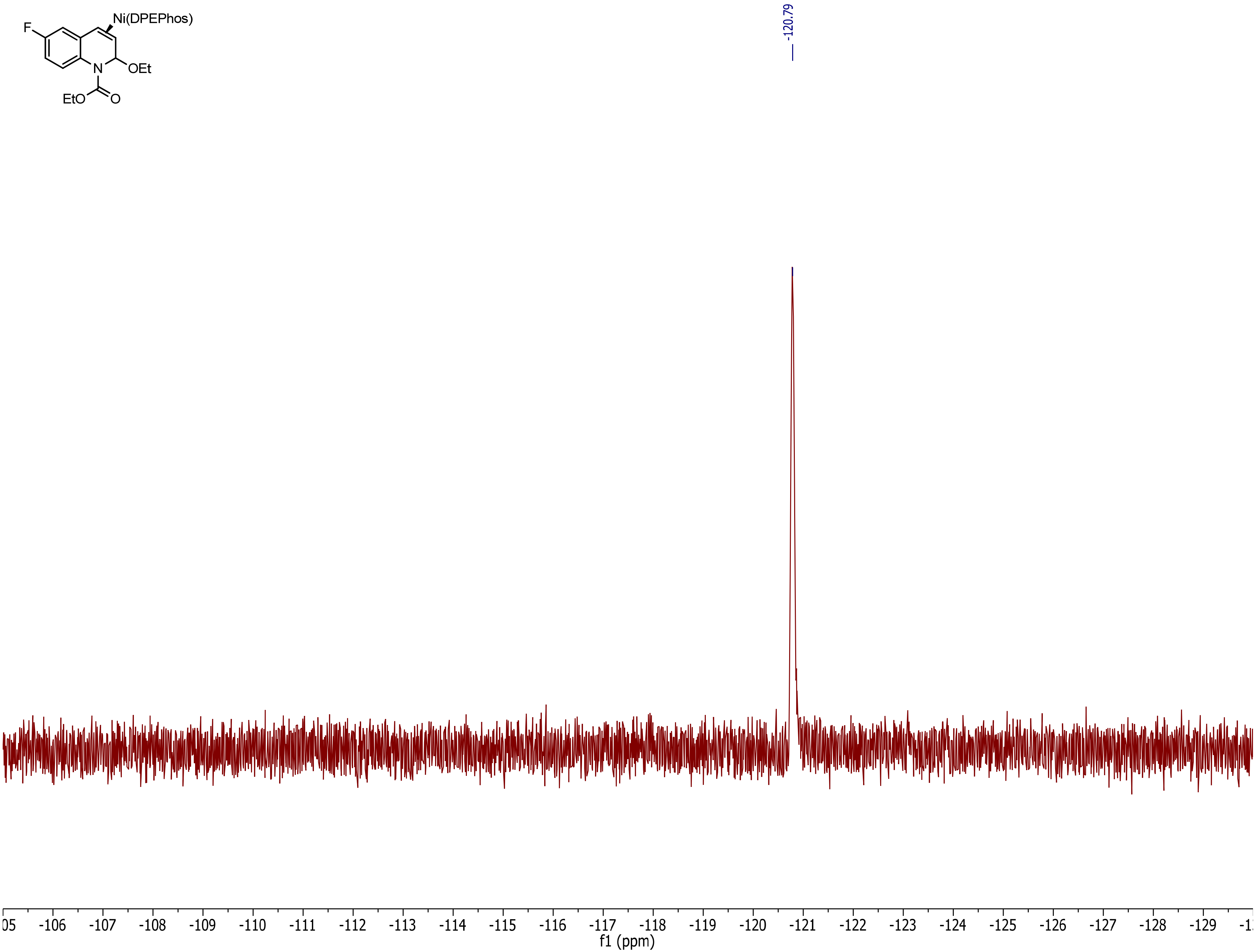

159.81
159.74
154.67
136.46
134.98
134.86
133.65
133.55
130.64
129.68
129.02
128.39
127.73
126.76
125.25
125.06
124.95
124.04
116.50
14.60
P
Ni
P
N
Ph
EtO
O
P
P
=
O
Ph2P
PPh2
DPEPhos
f1 (ppm)
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10

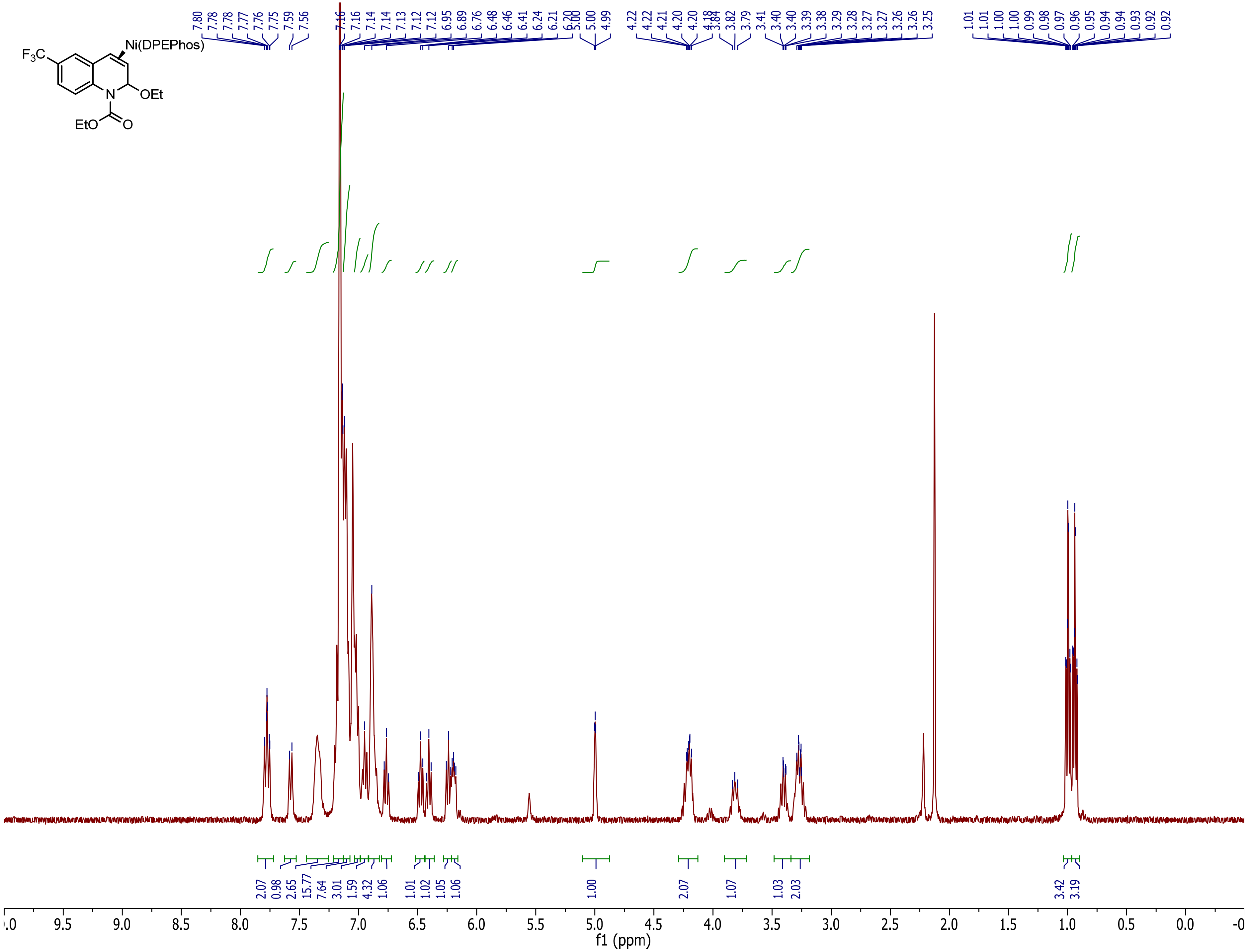

P
Ni
P
N
Ph
EtO
O
P
P
=
O
Ph2P
PPh2
DPEPhos
34.67
34.35
33.20
32.88
1.00
1.00
0
55
50
45
40
35
30
25
20
15
10
5
f1 (ppm)

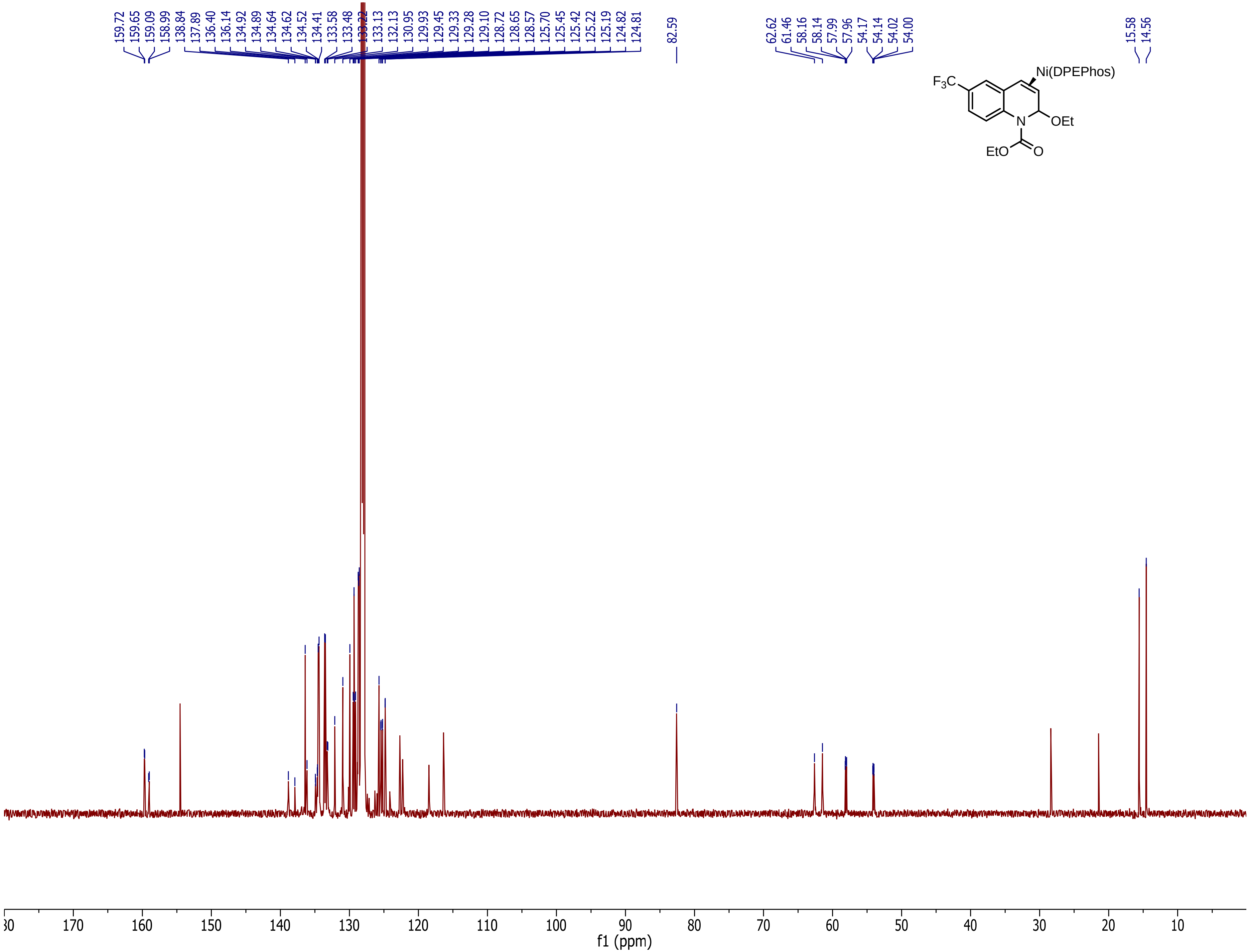

F
Ni(DPEPhos)
N
OEt
EtO
O
7.81
7.79
7.79
7.78
7.76
7.37
7.36
7.16
7.14
7.10
6.90
6.90
6.78
6.76
6.76
6.50
6.48
6.47
6.47
6.46
6.42
6.40
6.26
6.20
5.01
5.00
4.24
4.23
4.21
4.17
4.16
4.15
4.14
3.81
3.45
3.43
3.43
3.41
3.29
3.27
3.27
1.02
1.00
0.99
0.97
0.95
0.93
2.00
1.02
2.63
4.95
1.05
0.94
1.89
0.91
0.98
0.97
1.00
2.03
0.91
0.96
1.98
2.86
3.20
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0
f1 (ppm)

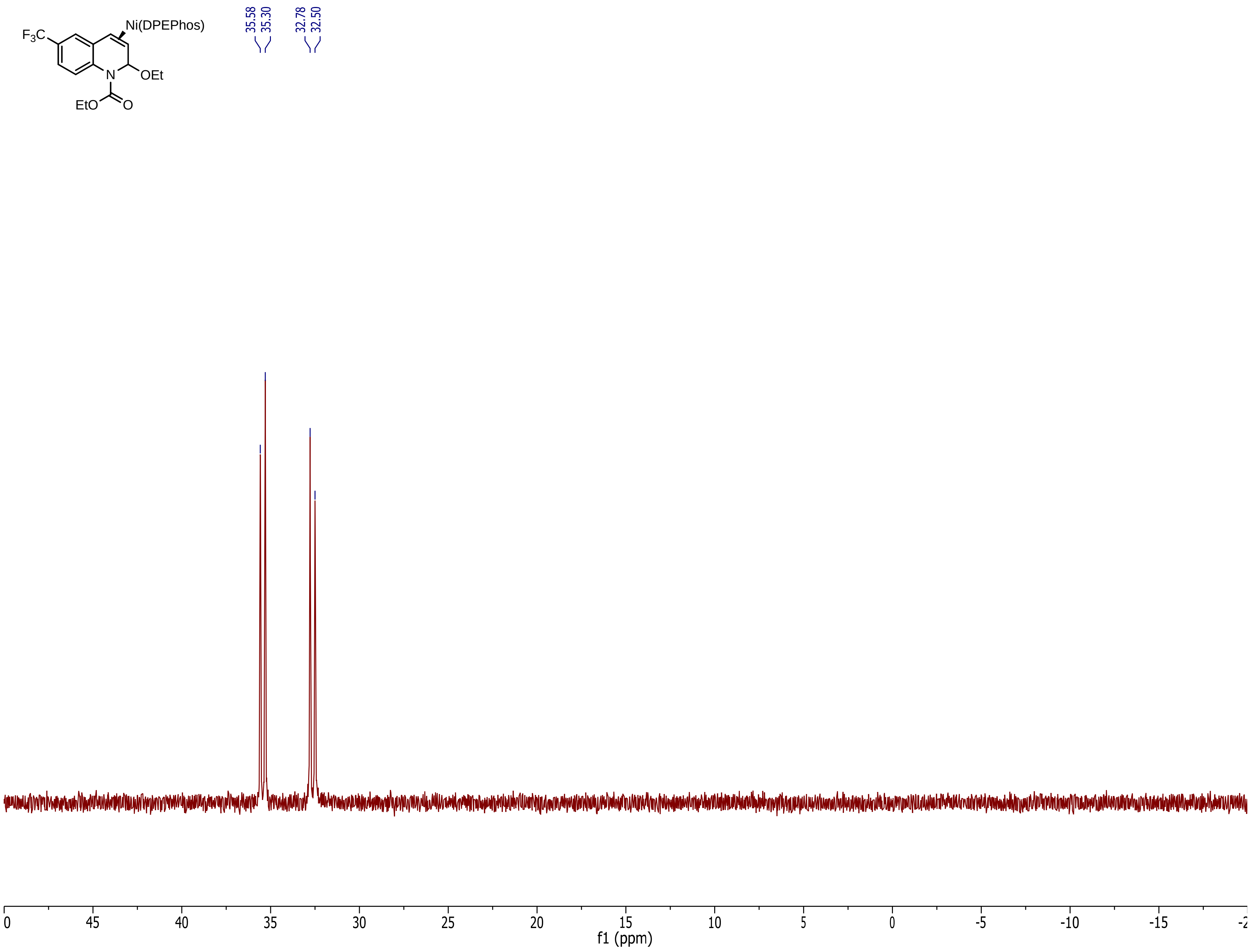

161.09
159.74
159.67
159.18
159.09
159.00
158.99
136.41
134.59
134.48
133.76
133.66
130.87
129.89
129.33
129.23
128.98
128.71
128.64
125.42
125.39
125.18
116.42
116.40
111.54
111.51
111.36
111.33
82.46
62.41
58.24
58.22
58.07
58.05
54.59
54.45
15.61
14.66
F
Ni(DPEPhos)
N
OEt
EtO
O
30
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

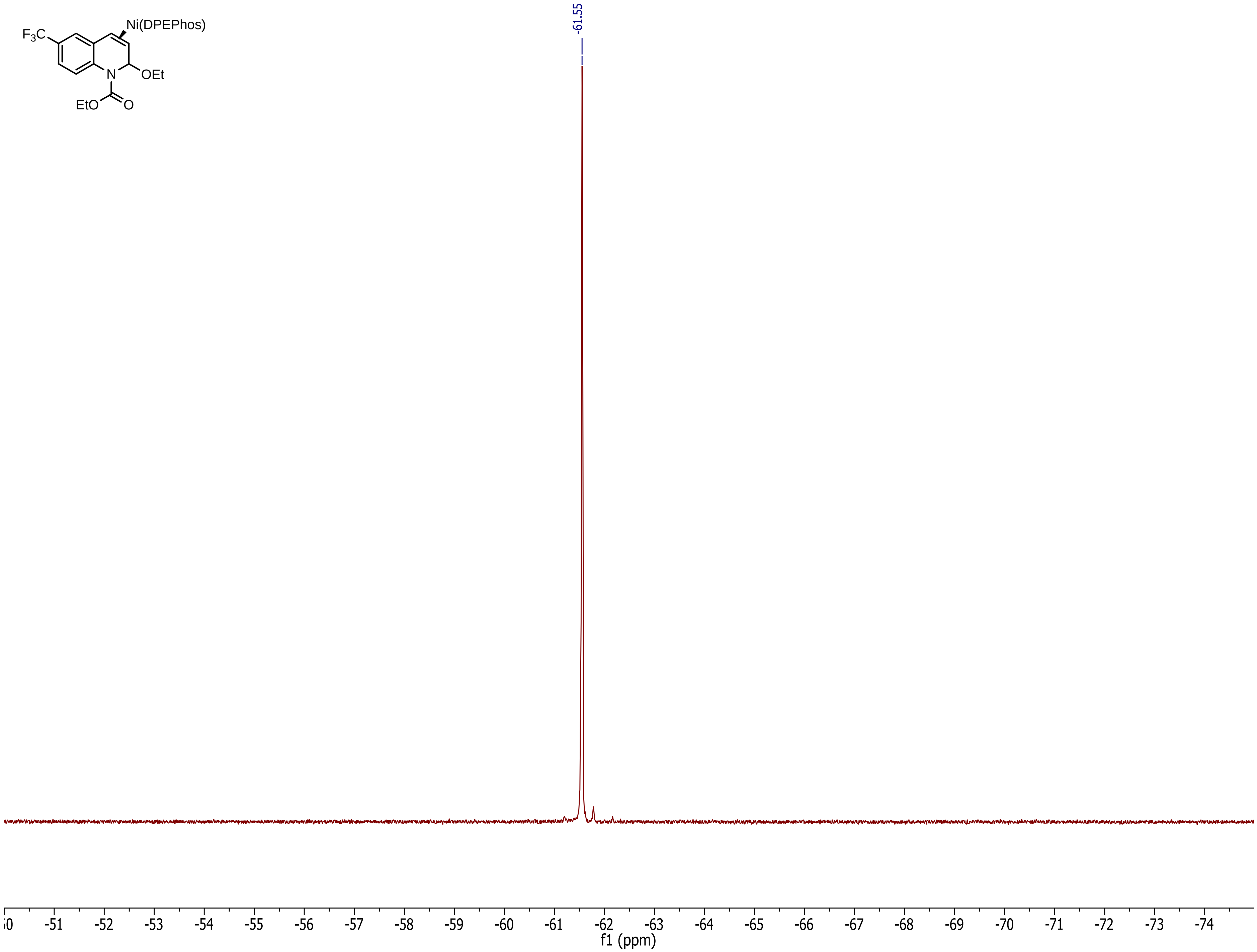

F
Ni(DPEPhos)
OEt
N
EtO
O
35.72
35.43
32.81
32.52
0
45
40
35
30
25
20
15
10
5
0
-5
-10
-15
-2
f1 (ppm)

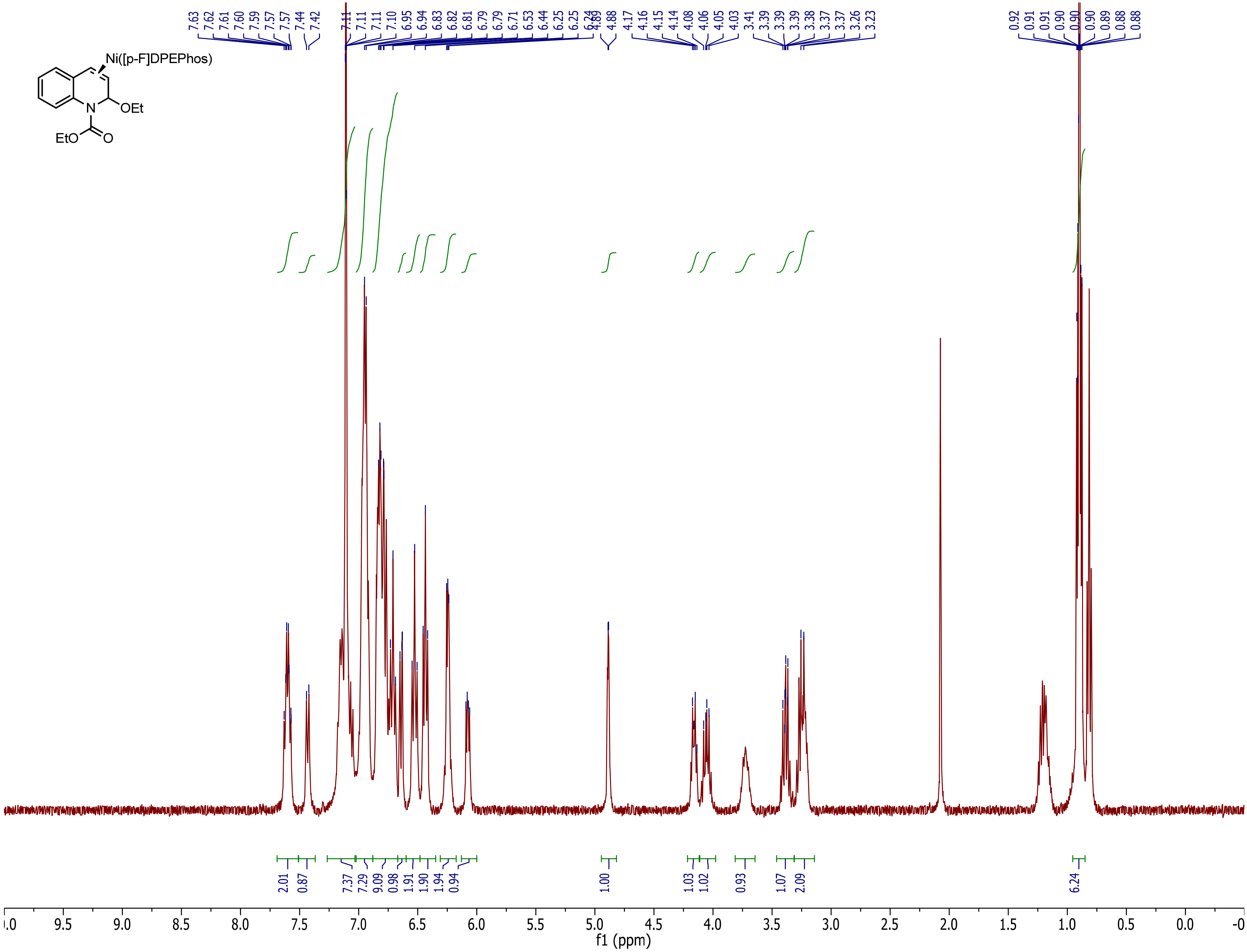

F
Ni(DPEPhos)
N
OEt
EtO
O
-120.79
05
-106
-107
-108
-109
-110
-111
-112
-113
-114
-115
-116
-117
-118
-119
-120
-121
-122
-123
-124
-125
-126
-127
-128
-129
f1 (ppm)

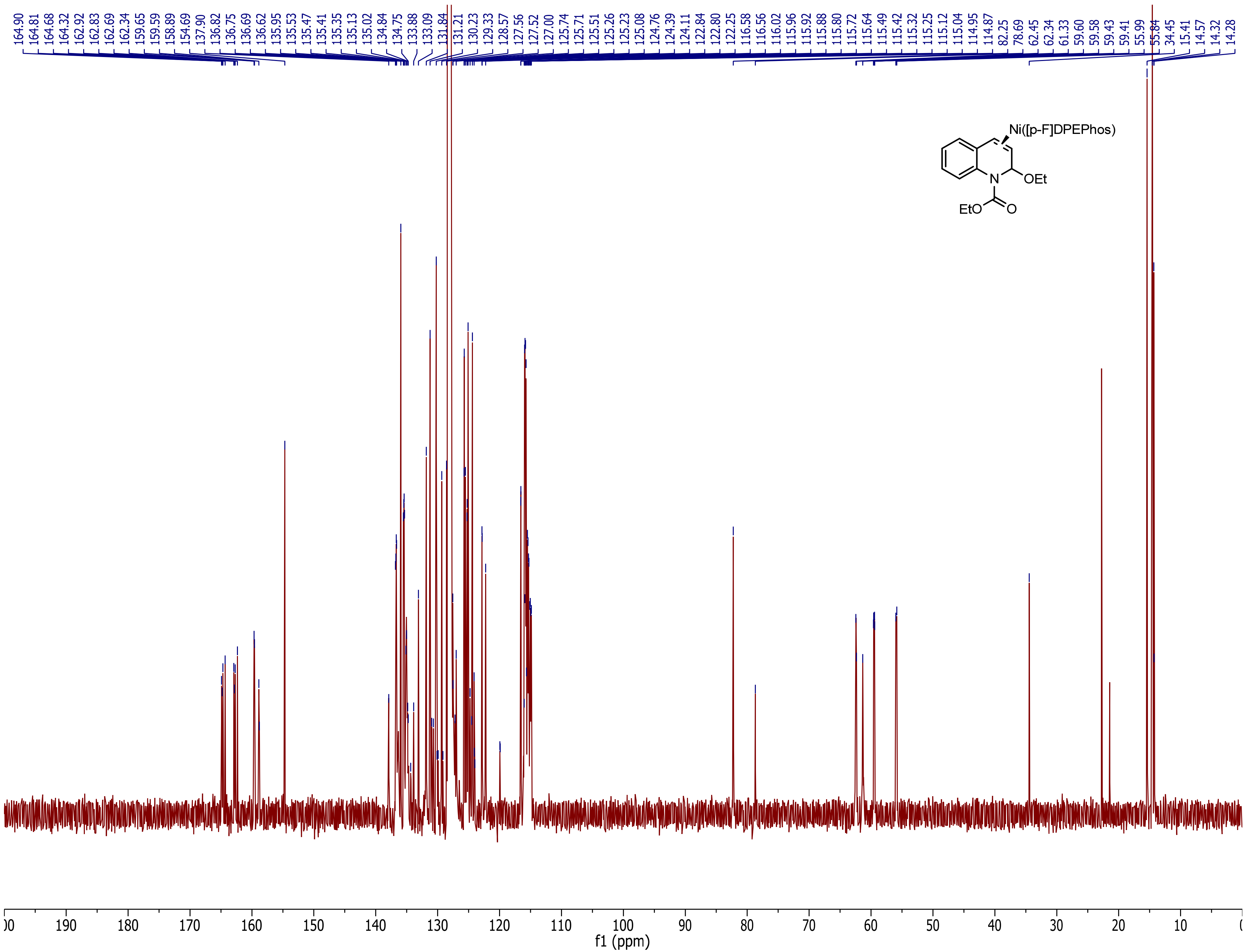

F$_3$C
Ni(DPEPhos)
N
OEt
EtO
O
7.80
7.78
7.78
7.77
7.76
7.75
7.59
7.56
7.16
7.16
7.14
7.14
7.13
7.12
7.12
6.95
6.89
6.76
6.48
6.46
6.41
6.24
6.21
6.20
5.00
5.00
4.99
4.22
4.22
4.21
4.20
4.20
4.18
3.84
3.82
3.79
3.41
3.40
3.40
3.39
3.38
3.29
3.28
3.27
3.27
3.26
3.26
3.25
1.01
1.01
1.00
1.00
0.99
0.98
0.97
0.96
0.95
0.94
0.94
0.93
0.92
0.92
2.07
0.98
2.65
15.77
7.64
3.01
1.59
4.32
1.06
1.01
1.02
1.05
1.06
1.00
2.07
1.07
1.03
2.03
3.42
3.19
.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0
f1 (ppm)

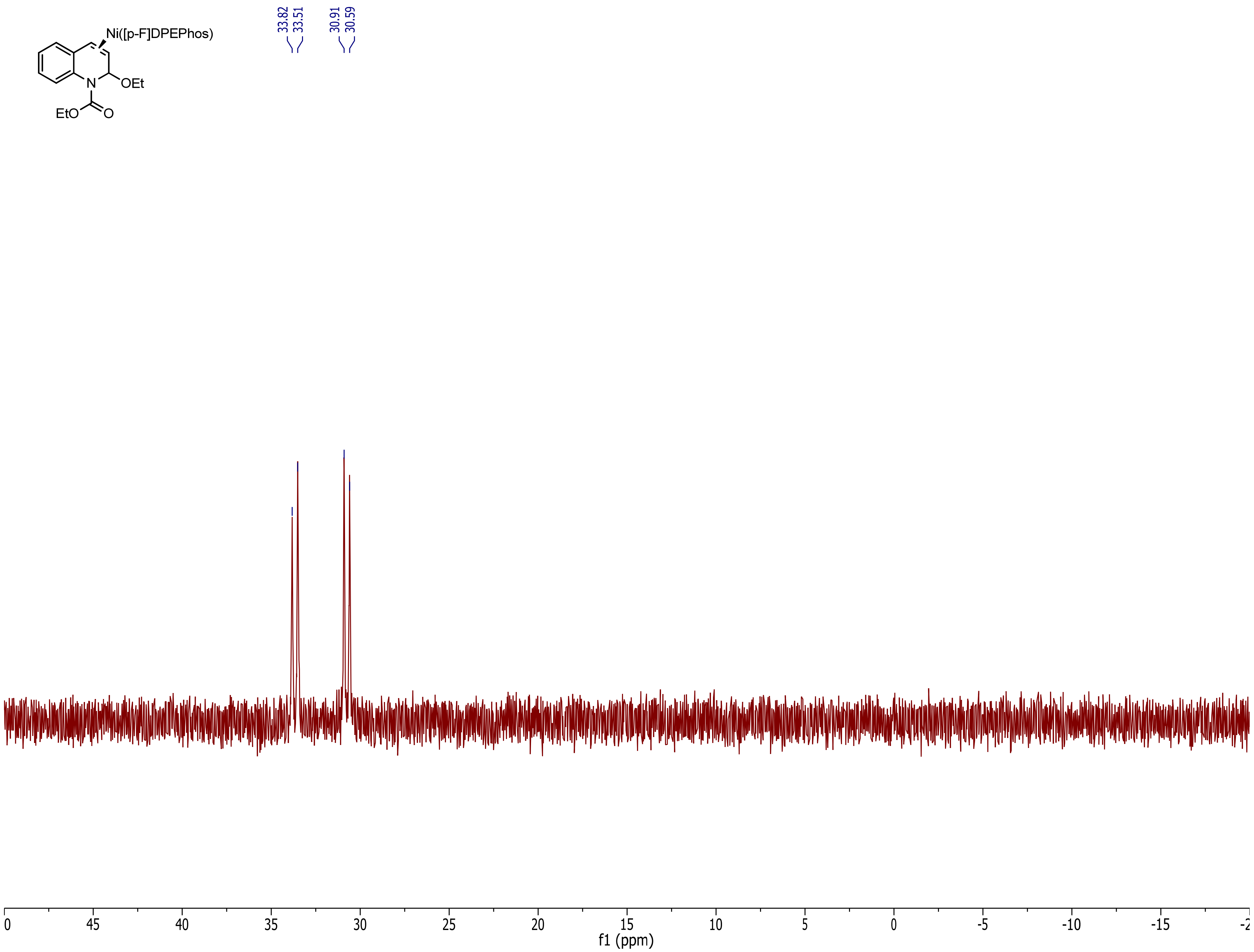

159.72
159.65
159.09
158.99
138.84
137.89
136.40
136.14
134.92
134.89
134.64
134.62
134.52
134.41
133.58
133.48
133.22
133.13
132.13
130.95
129.93
129.45
129.33
129.28
129.10
128.72
128.65
128.57
125.70
125.45
125.42
125.22
125.19
124.82
124.81
82.59
62.62
61.46
58.16
58.14
57.99
57.96
54.17
54.14
54.02
54.00
15.58
14.56
F_3C
Ni(DPEPhos)
N
OEt
EtO
O
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

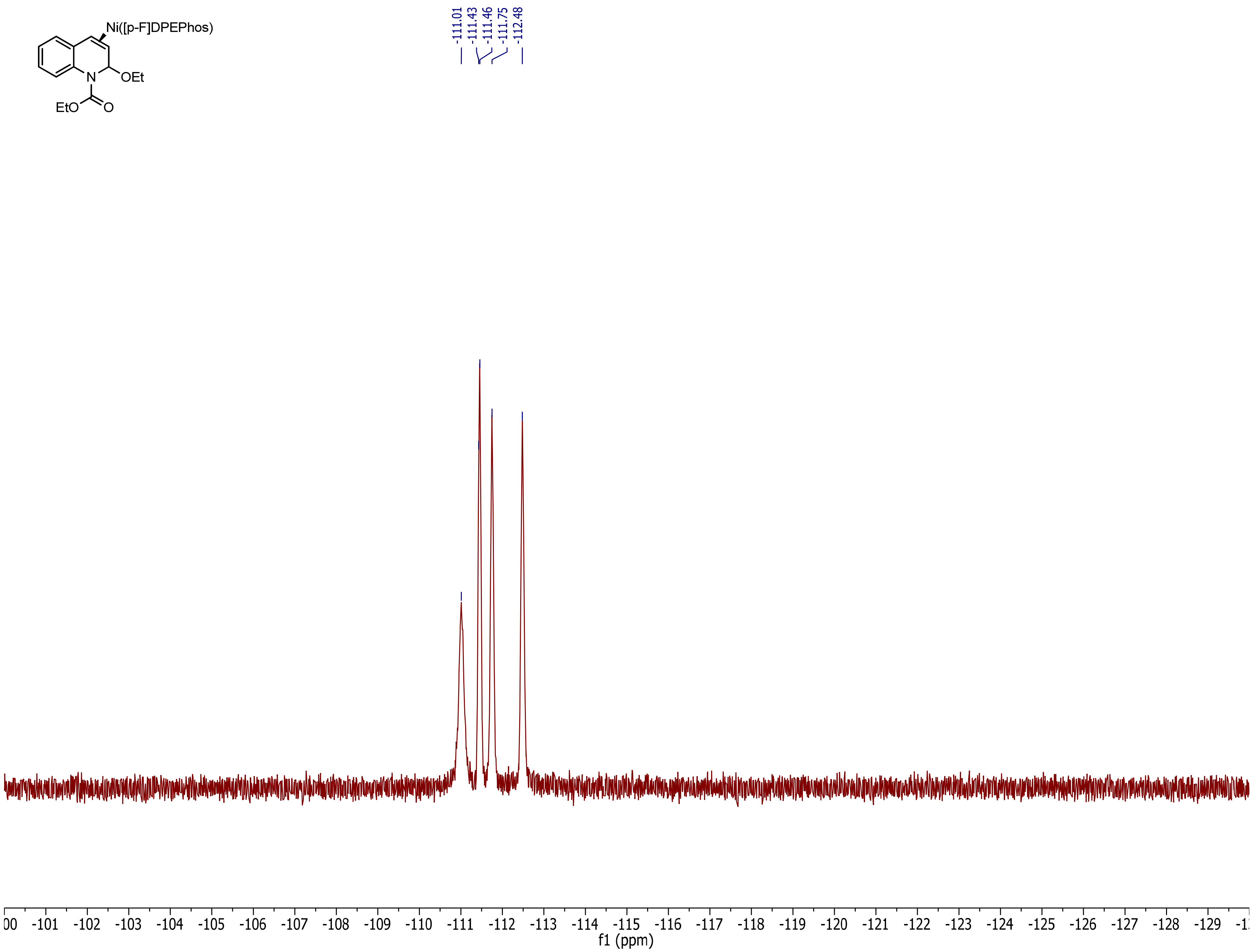

F3C
Ni(DPEPhos)
N
OEt
EtO
O
35.58
35.30
32.78
32.50
0
45
40
35
30
25
20
15
10
5
0
-5
-10
-15
-2
f1 (ppm)

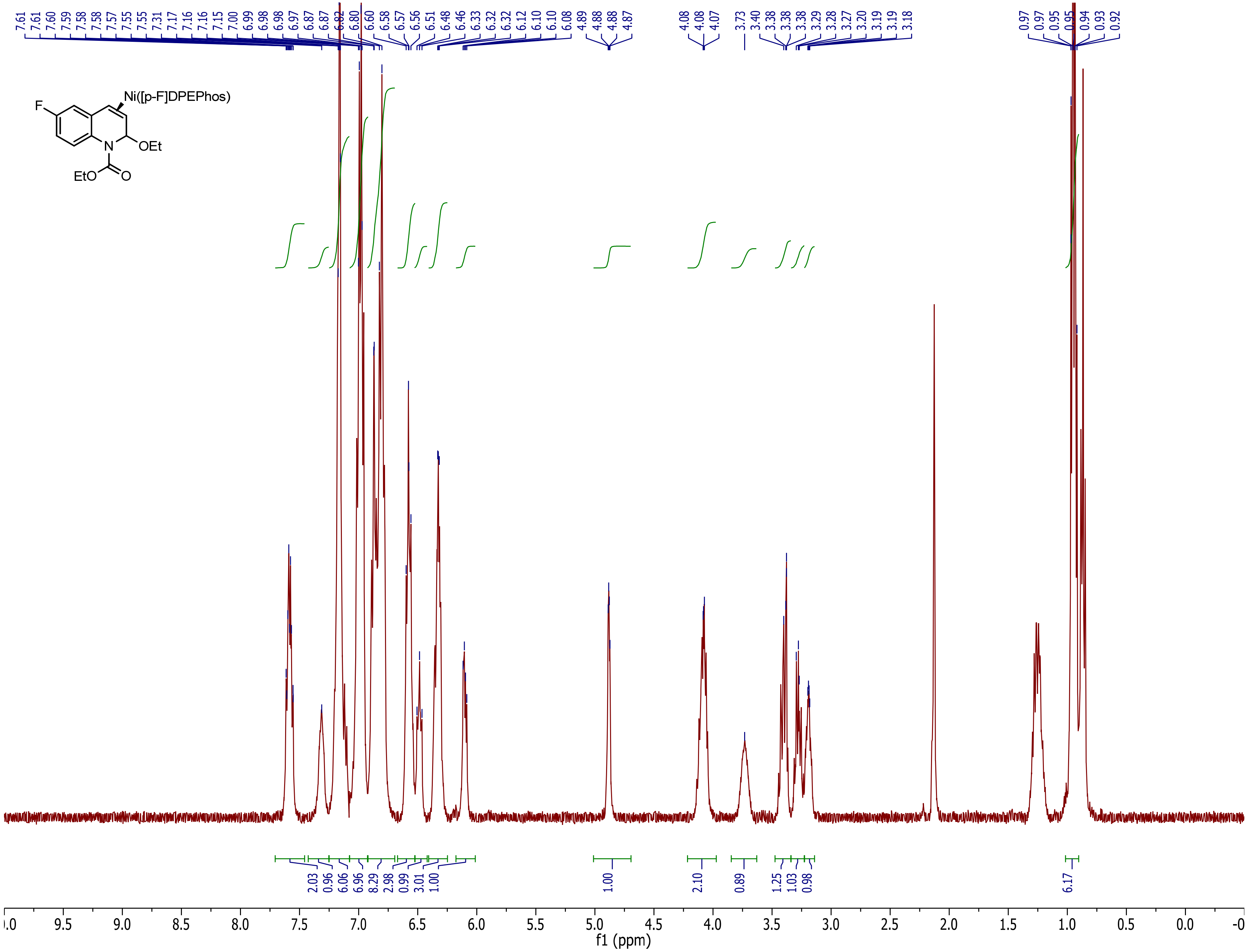

F3C
Ni(DPEPhos)
N
OEt
EtO
O
-61.55
-51
-52
-53
-54
-55
-56
-57
-58
-59
-60
-61
-62
-63
-64
-65
-66
-67
-68
-69
-70
-71
-72
-73
-74
f1 (ppm)


Ni([p-F]DPEPhos)
N
OEt
EtO
O
7.63
7.62
7.61
7.60
7.59
7.57
7.57
7.44
7.42
7.11
7.11
7.11
7.10
6.95
6.94
6.83
6.82
6.81
6.79
6.79
6.71
6.53
6.44
6.25
6.25
6.24
4.89
4.88
4.17
4.16
4.15
4.14
4.08
4.06
4.05
4.03
3.41
3.39
3.39
3.39
3.38
3.37
3.37
3.26
3.23
0.92
0.91
0.91
0.90
0.90
0.90
0.89
0.88
0.88
2.01
0.87
7.37
7.29
9.09
0.98
1.91
1.90
1.94
0.94
1.00
1.03
1.02
0.93
1.07
2.09
6.24
.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0
f1 (ppm)

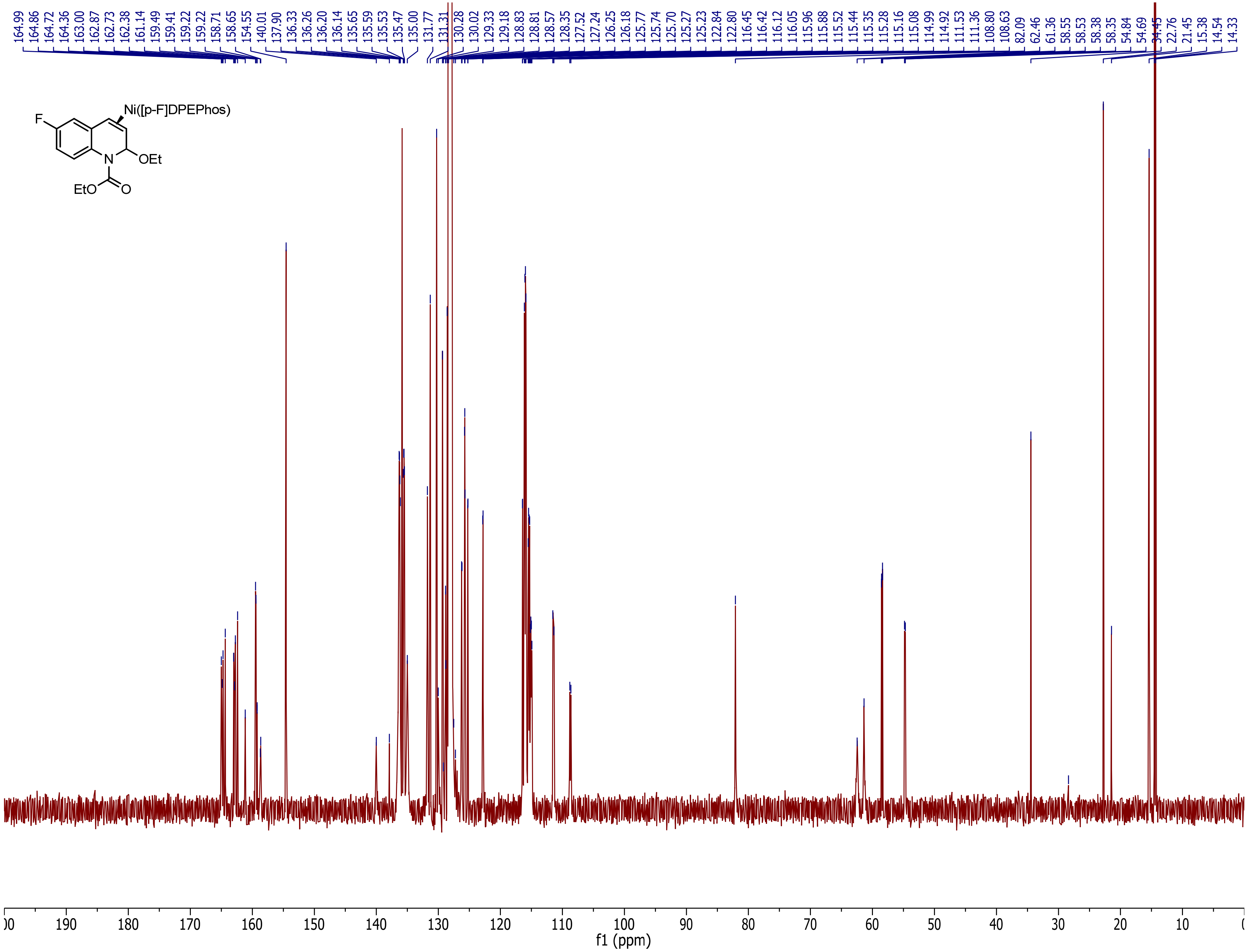

164.90
164.81
164.68
164.32
162.92
162.83
162.69
162.34
159.65
159.59
158.89
154.69
137.90
136.82
136.75
136.69
136.62
135.95
135.53
135.47
135.41
135.35
135.13
135.02
134.84
134.75
133.88
133.09
131.84
131.21
130.23
129.33
128.57
127.56
127.52
127.00
125.74
125.71
125.51
125.26
125.23
125.08
124.76
124.39
124.11
122.84
122.80
122.25
116.58
116.56
116.02
115.96
115.92
115.88
115.80
115.72
115.64
115.49
115.42
115.32
115.25
115.12
115.04
114.95
114.87
82.25
78.69
62.45
62.34
61.33
59.60
59.58
59.43
59.41
55.99
55.84
34.45
15.41
14.57
14.32
14.28
Ni([p-F]DPEPhos)
N
OEt
EtO
O
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

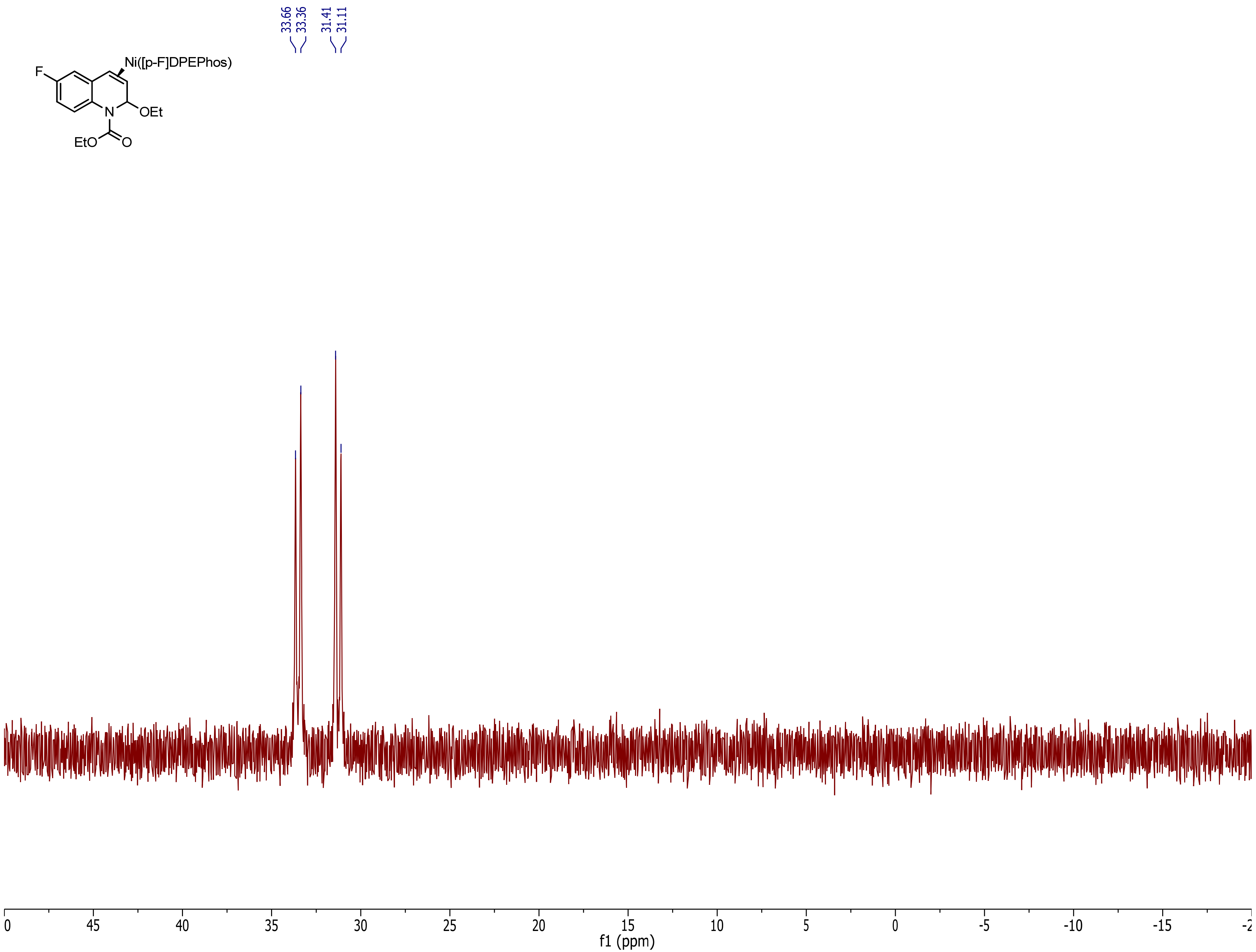

Ni([p-F]DPEPhos)
N
OEt
EtO
O
33.82
33.51
30.91
30.59
0
45
40
35
30
25
20
15
10
5
0
-5
-10
-15
-2
f1 (ppm)

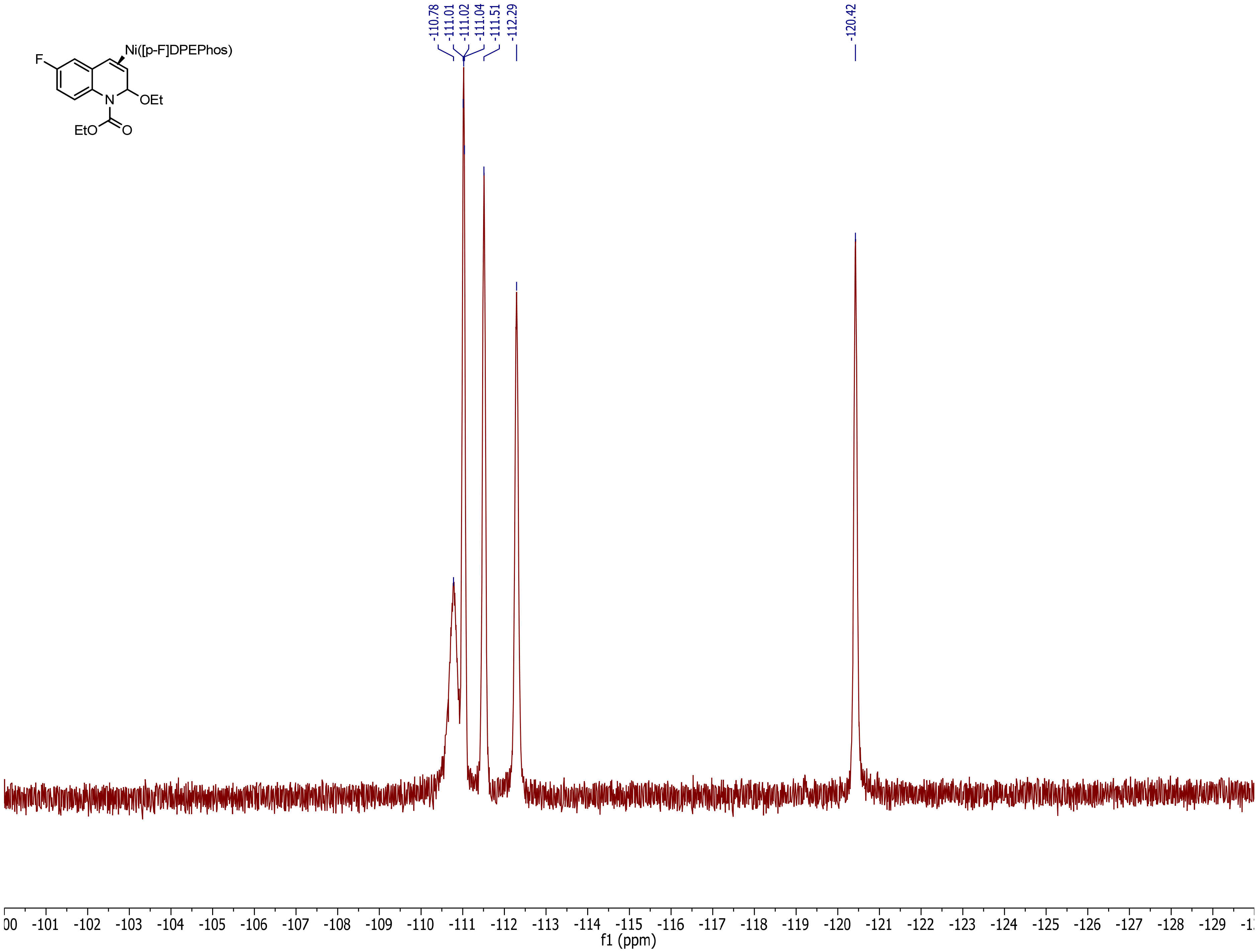

Ni([p-F]DPEPhos)
N
OEt
EtO
O
-111.01
-111.43
-111.46
-111.75
-112.48
00
-101
-102
-103
-104
-105
-106
-107
-108
-109
-110
-111
-112
-113
-114
-115
-116
-117
-118
-119
-120
-121
-122
-123
-124
-125
-126
-127
-128
-129
f1 (ppm)

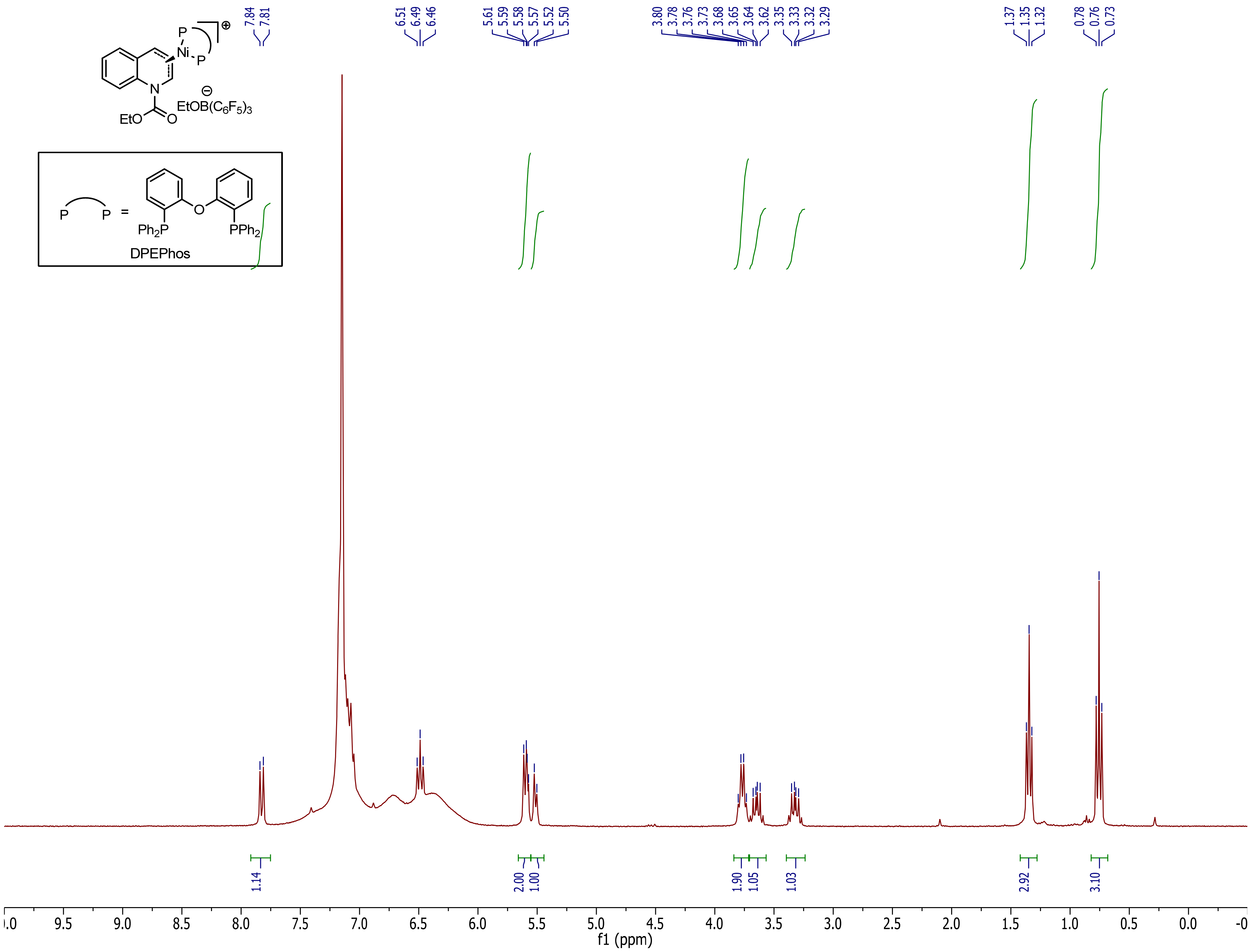


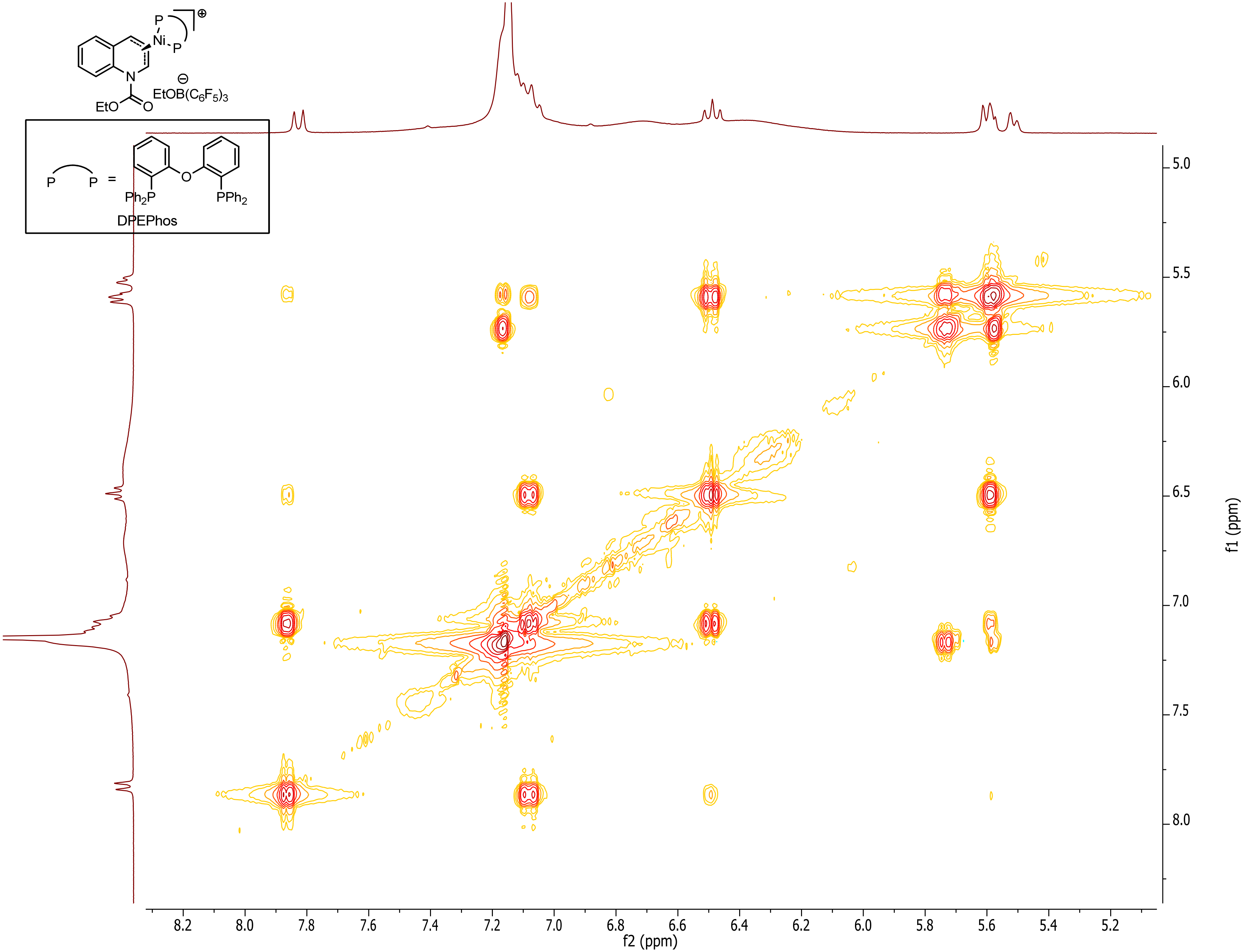
7.61
7.61
7.60
7.59
7.58
7.58
7.57
7.55
7.55
7.31
7.17
7.16
7.16
7.15
7.00
6.99
6.98
6.98
6.97
6.87
6.87
6.82
6.80
6.60
6.58
6.57
6.56
6.51
6.48
6.46
6.33
6.32
6.32
6.12
6.10
6.10
6.08
4.89
4.88
4.88
4.87
4.08
4.08
4.07
3.73
3.40
3.38
3.38
3.38
3.29
3.28
3.27
3.20
3.19
3.19
3.18
0.97
0.97
0.95
0.95
0.94
0.93
0.92
Ni([p-F]DPEPhos)
F
N
OEt
EtO
O
2.03
0.96
6.06
6.96
8.29
2.98
0.99
3.01
1.00
1.00
2.10
0.89
1.25
1.03
0.98
6.17
.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0
f1 (ppm)


164.99
164.86
164.72
164.36
163.00
162.87
162.73
162.38
161.14
159.49
159.41
159.22
159.22
158.71
158.65
154.55
140.01
137.90
136.33
136.26
136.20
136.14
135.65
135.59
135.53
135.47
135.00
131.77
131.31
130.28
130.02
129.33
129.18
128.83
128.81
128.57
128.35
127.52
127.24
126.25
126.18
125.77
125.74
125.70
125.27
125.23
122.84
122.80
116.45
116.42
116.12
116.05
115.96
115.88
115.52
115.44
115.35
115.28
115.16
115.08
114.99
114.92
111.53
111.36
108.80
108.63
82.09
62.46
61.36
58.55
58.53
58.38
58.35
54.84
54.69
34.45
22.76
21.45
15.38
14.54
14.33
F
Ni([p-F]DPEPhos)
N
OEt
EtO
O
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

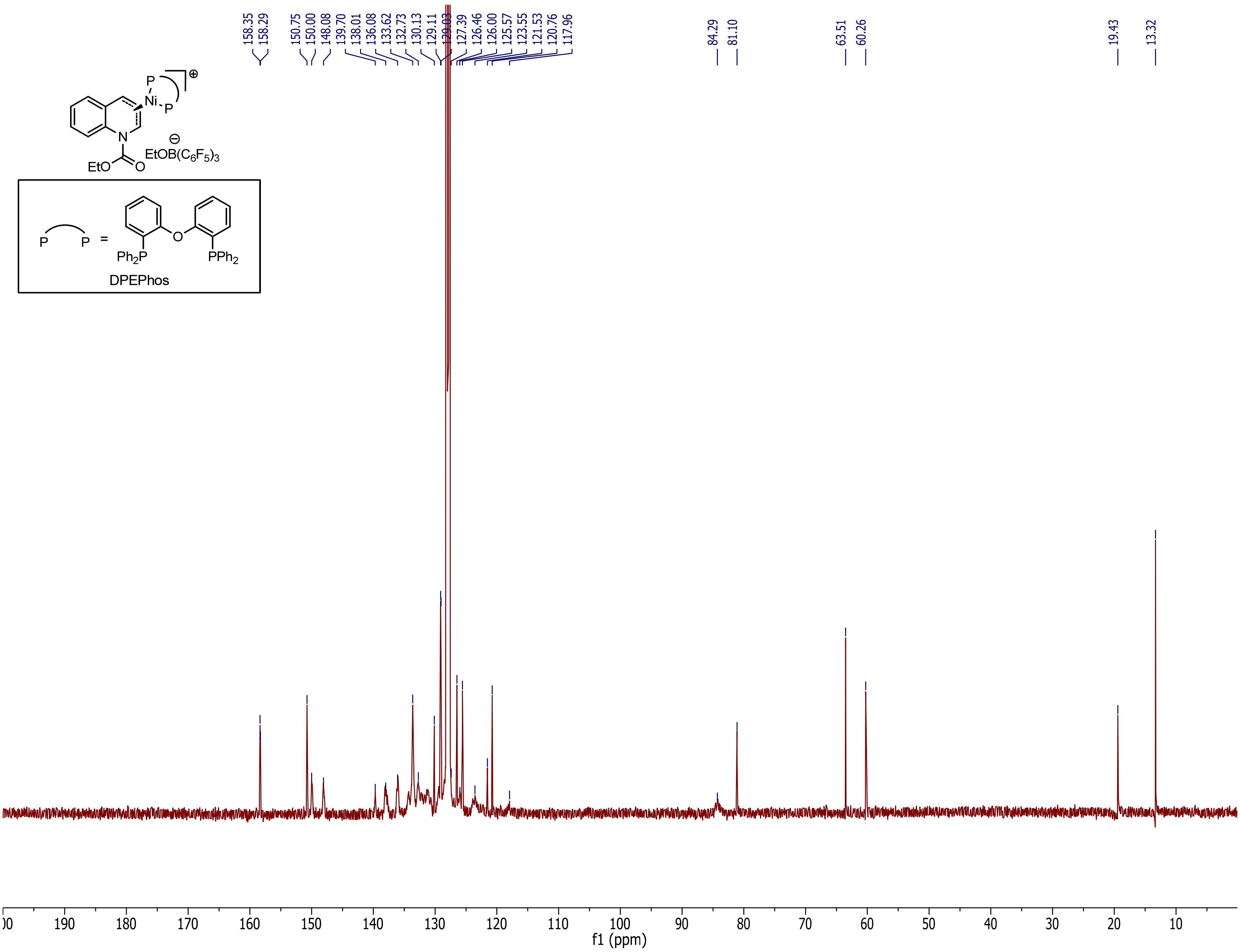

33.66
33.36
31.41
31.11
F
Ni([p-F]DPEPhos)
N
OEt
EtO
O
0
45
40
35
30
25
20
15
10
5
0
-5
-10
-15
-2
f1 (ppm)

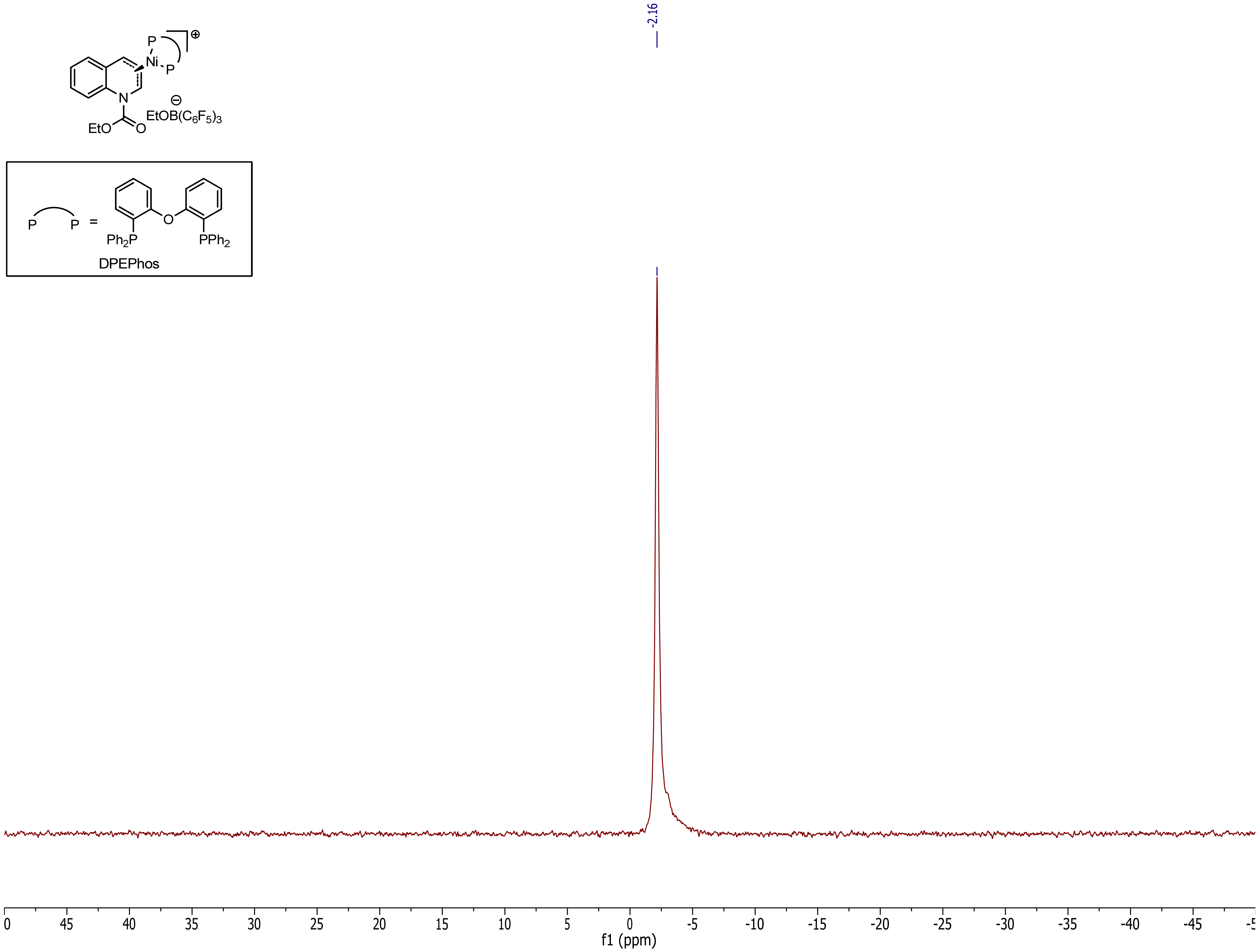

Ni([p-F]DPEPhos)
F
N
OEt
EtO
O
-110.78
-111.01
-111.02
-111.04
-111.51
-112.29
-120.42
00
-101
-102
-103
-104
-105
-106
-107
-108
-109
-110
-111
-112
-113
-114
-115
-116
-117
-118
-119
-120
-121
-122
-123
-124
-125
-126
-127
-128
-129
f1 (ppm)

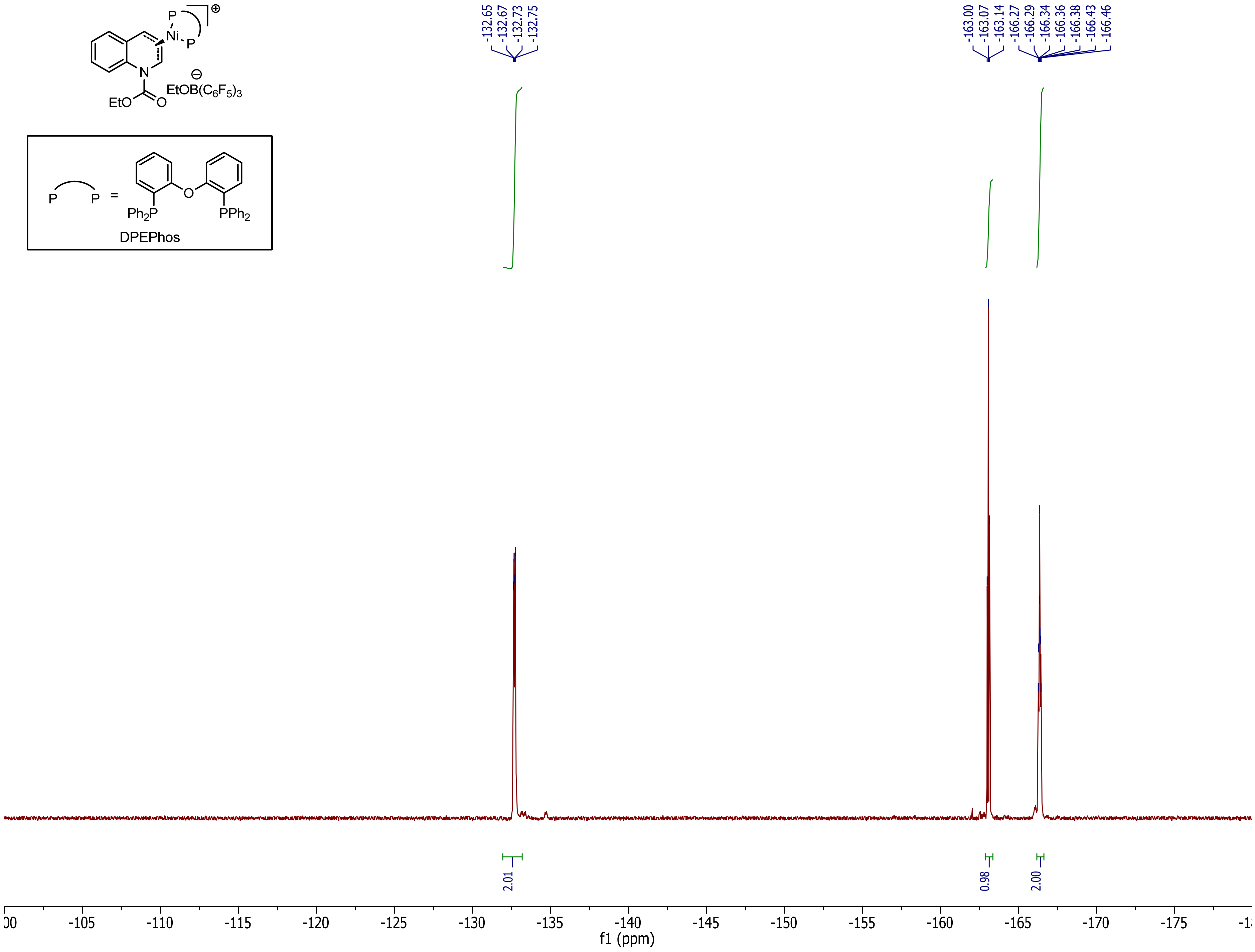

P
Ni
P
⊕
N
EtO
O
⊖
EtOB(C6F5)3
P
P
=
Ph2P
O
PPh2
DPEPhos
7.84
7.81
6.51
6.49
6.46
5.61
5.59
5.58
5.57
5.52
5.50
3.80
3.78
3.76
3.73
3.68
3.65
3.64
3.62
3.35
3.33
3.32
3.29
1.37
1.35
1.32
0.78
0.76
0.73
1.14
2.00
1.00
1.90
1.05
1.03
2.92
3.10
.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0
f1 (ppm)

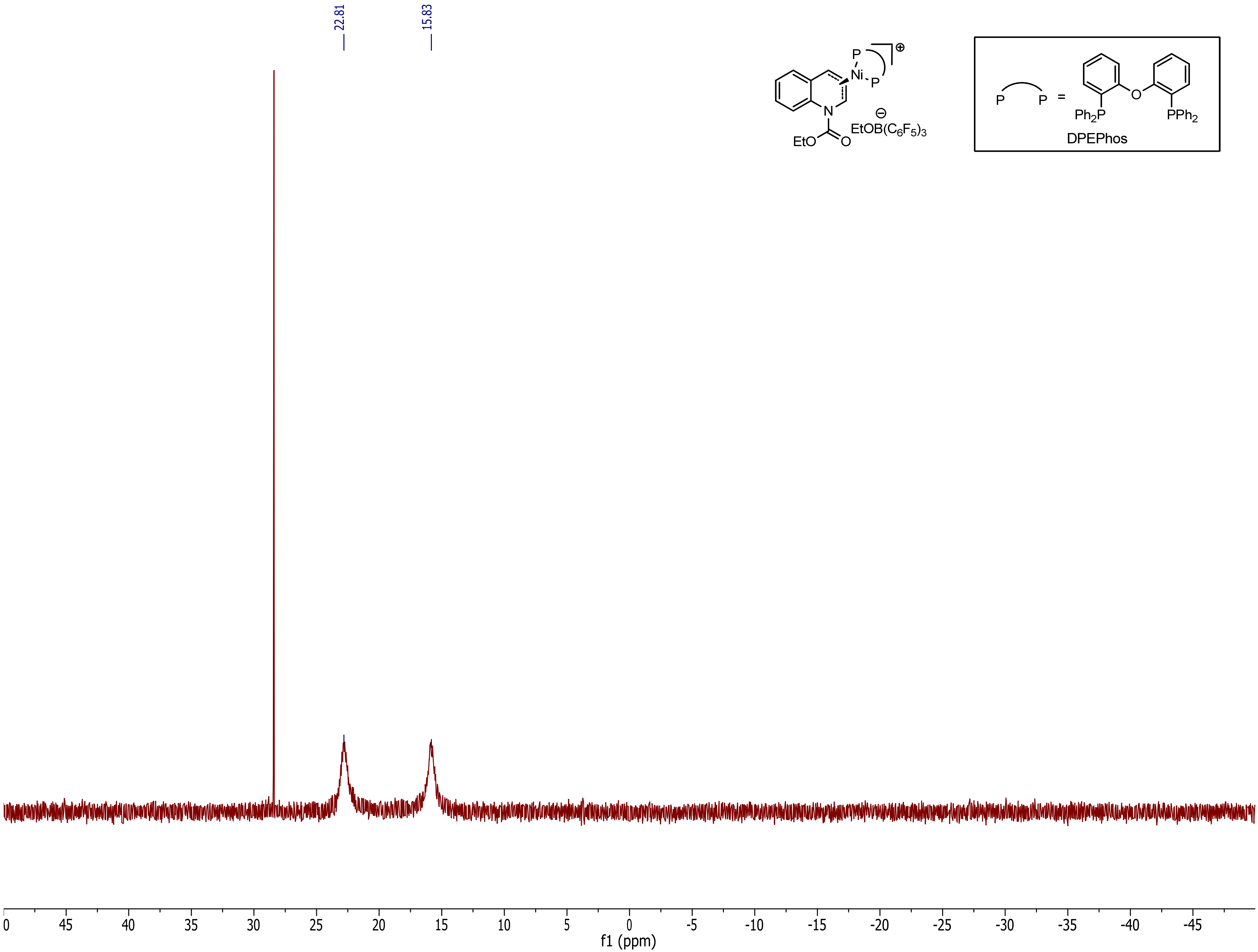


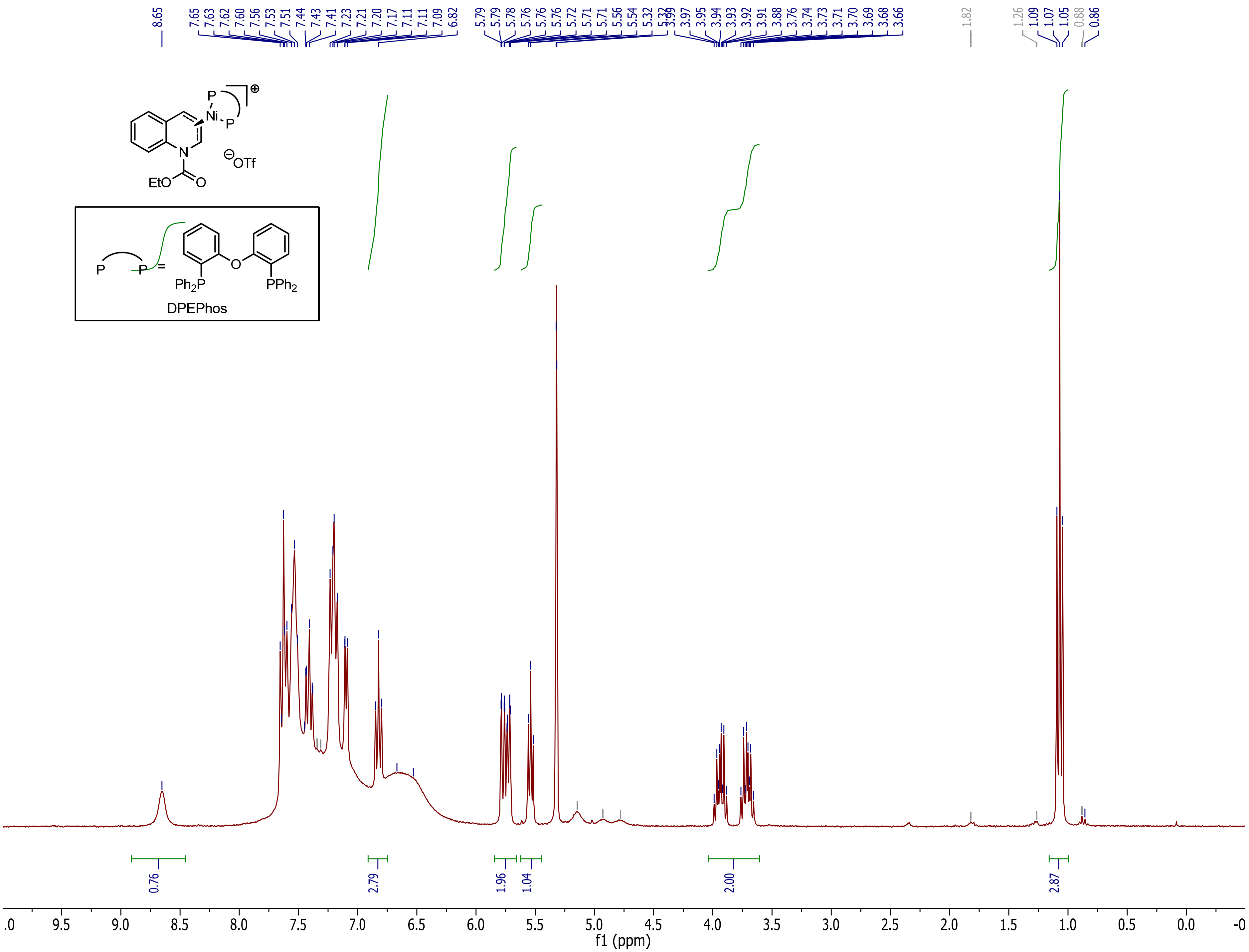
P
Ni
P
⊕
N
EtO
O
⊖
EtOB(C6F5)3
P
P
=
O
Ph2P
PPh2
DPEPhos
5.0
5.5
6.0
6.5
7.0
7.5
8.0
f1 (ppm)
8.2
8.0
7.8
7.6
7.4
7.2
7.0
6.8
6.6
6.4
6.2
6.0
5.8
5.6
5.4
5.2
f2 (ppm)

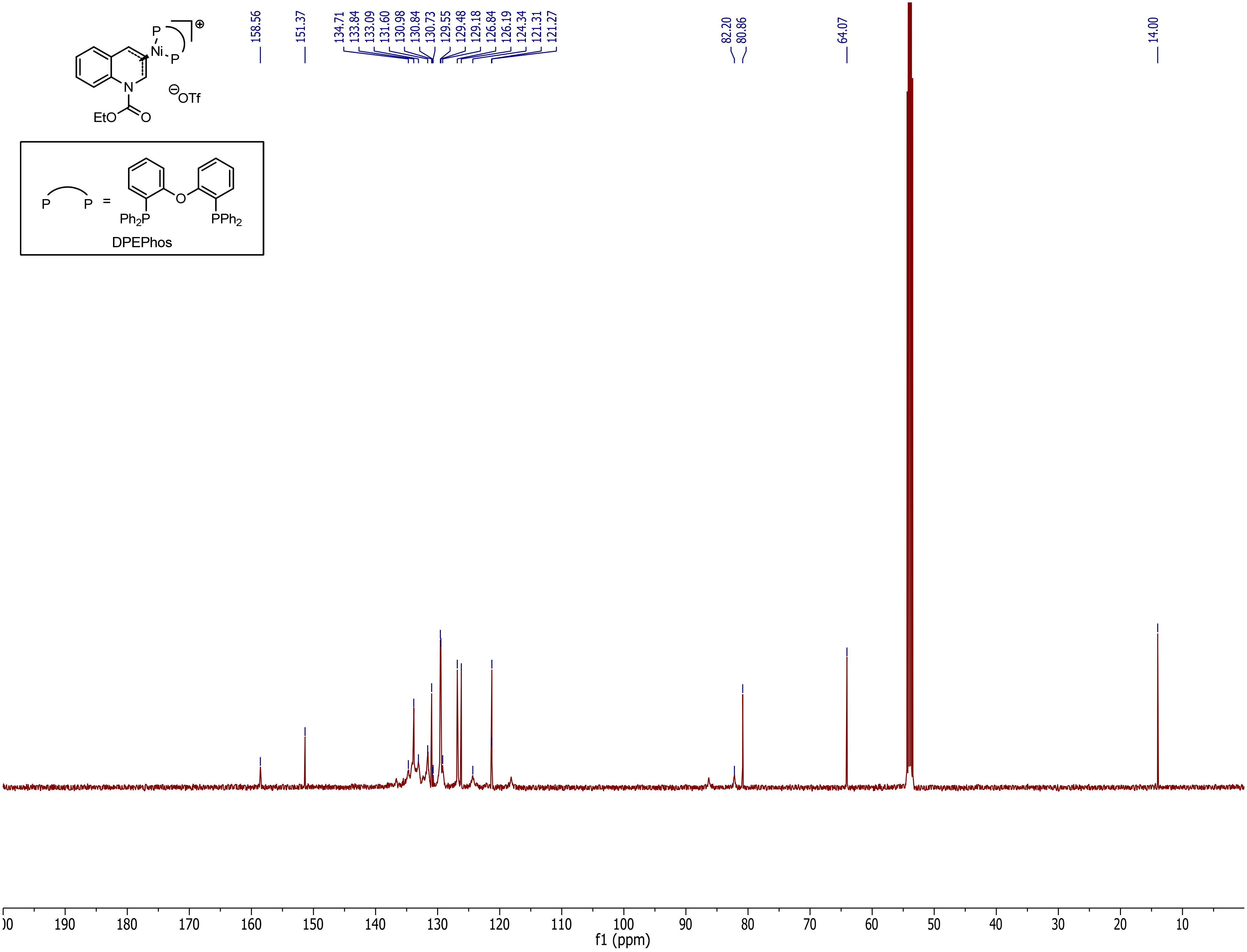

158.35
158.29
150.75
150.00
148.08
139.70
138.01
136.08
133.62
132.73
130.13
129.11
129.03
127.39
126.46
126.00
125.57
123.55
121.53
120.76
117.96
84.29
81.10
63.51
60.26
19.43
13.32
P
Ni
P
⊕
N
EtO
O
⊖
EtOB(C$_6$F$_5$)$_3$
P
P
=
Ph$_2$P
O
PPh$_2$
DPEPhos
)0
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

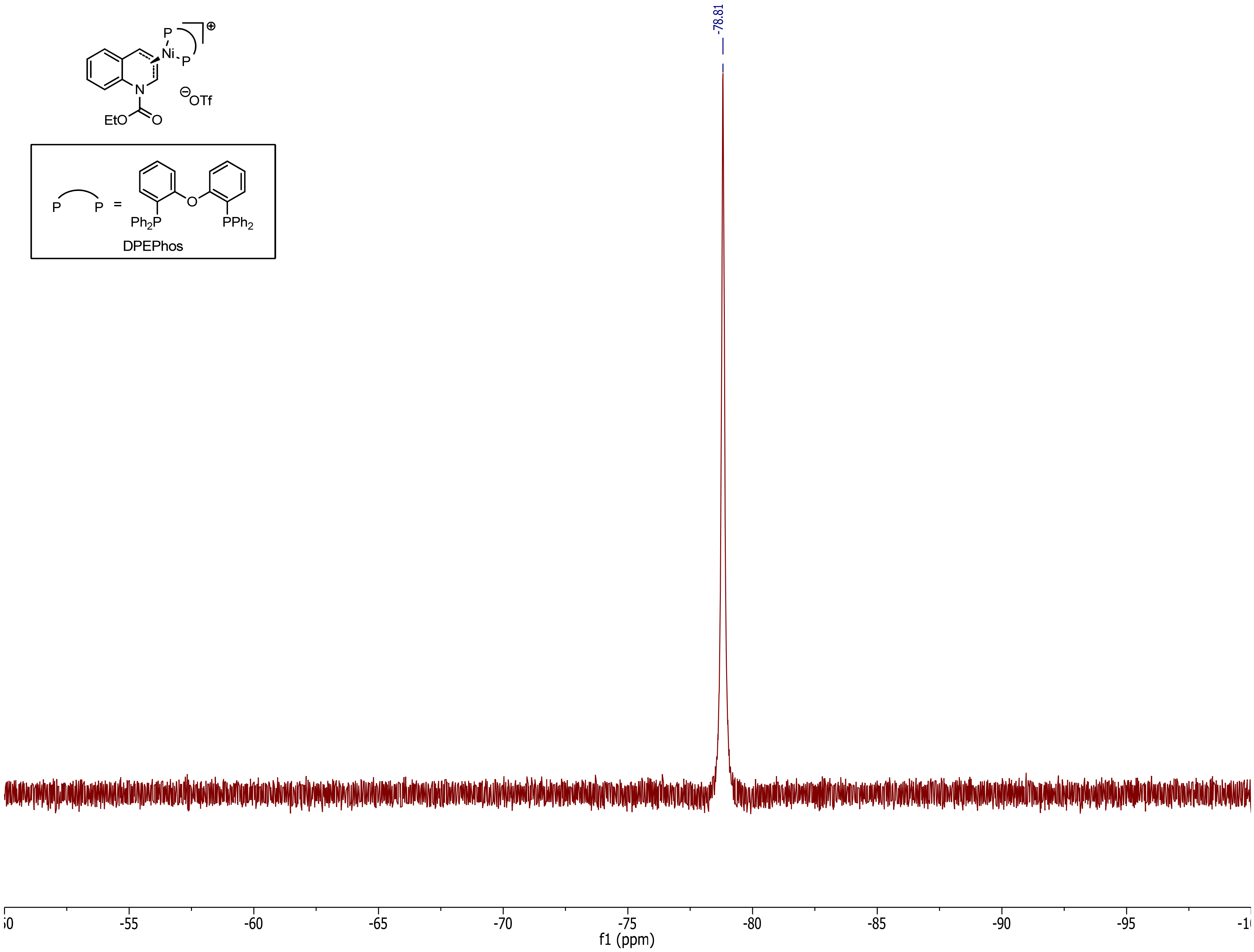

Ni
P
P
N
EtO
O
EtOB(C6F5)3
⊕
⊖
P
P
=
O
Ph2P
PPh2
DPEPhos
-2.16
0
45
40
35
30
25
20
15
10
5
0
-5
-10
-15
-20
-25
-30
-35
-40
-45
-5
f1 (ppm)

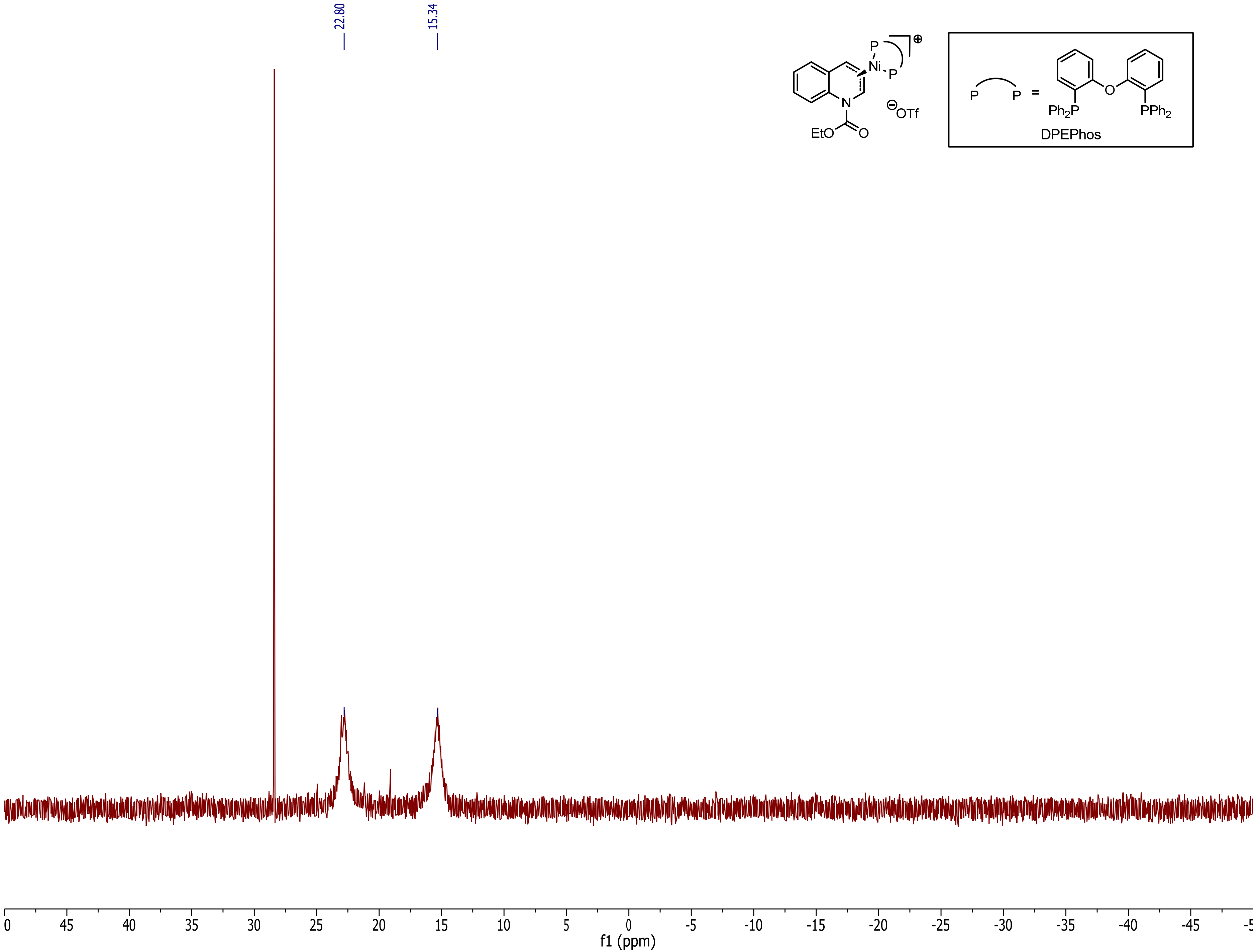

P
Ni
P
⊕
N
EtO
O
⊖
EtOB(C6F5)3
P
P
=
Ph2P
O
PPh2
DPEPhos
-132.65
-132.67
-132.73
-132.75
-163.00
-163.07
-163.14
-166.27
-166.29
-166.34
-166.36
-166.38
-166.43
-166.46
2.01
0.98
2.00
00
-105
-110
-115
-120
-125
-130
-135
-140
-145
-150
-155
-160
-165
-170
-175
-1
f1 (ppm)


22.81
15.83
P
Ni
P
N
EtO
O
⊕
⊖
EtOB(C6F5)3
P
P
=
Ph2P
O
PPh2
DPEPhos
0
45
40
35
30
25
20
15
10
5
0
-5
-10
-15
-20
-25
-30
-35
-40
-45
f1 (ppm)


8.65
7.65
7.63
7.62
7.60
7.56
7.53
7.51
7.44
7.43
7.41
7.23
7.21
7.20
7.17
7.11
7.11
7.09
6.82
5.79
5.79
5.78
5.76
5.76
5.76
5.72
5.71
5.71
5.56
5.54
5.32
3.99
3.97
3.95
3.94
3.93
3.92
3.91
3.88
3.76
3.74
3.73
3.71
3.70
3.69
3.68
3.66
1.82
1.26
1.09
1.07
1.05
0.88
0.86
P
Ni
P
N
EtO
O
⊕
⊖OTf
P
P =
O
Ph2P
PPh2
DPEPhos
0.76
2.79
1.96
1.04
2.00
2.87
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


P
Ni
P
N
EtO
O
⊕
⊖OTf
P
P
=
O
Ph2P
PPh2
DPEPhos
158.56
151.37
134.71
133.84
133.09
131.60
130.98
130.84
130.73
129.55
129.48
129.18
126.84
126.19
124.34
121.31
121.27
82.20
80.86
64.07
14.00
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


P
Ni
P
⊕
N
EtO
O
⊖OTf
P
P
=
O
Ph2P
PPh2
DPEPhos
-78.81
-55
-60
-65
-70
-75
-80
-85
-90
-95
f1 (ppm)


22.80
15.34
P
Ni
P
N
EtO
O
⊖OTf
⊕
P
P
=
O
Ph$_2$P
PPh$_2$
DPEPhos
0
45
40
35
30
25
20
15
10
5
0
-5
-10
-15
-20
-25
-30
-35
-40
-45
-5
f1 (ppm)