Supporting Information

Transition Metal-Catalyzed Cross Coupling with *N*-Acyliminium Ions Derived from Quinolines and Isoquinolines

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I. General Information

General Procedures. Unless otherwise noted, reactions were performed with rigorous exclusion of air or moisture. Ar-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 thin-layer chromatography (TLC) on EMD Silica Gel 60 F_{254} plates, visualizing with UV-light (254 nm). 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 purchased from Sigma Aldrich, Acros, Alfa Aesar, or TCI, and used as received with the following exceptions. *N*-Ethoxycarbonyl-2-ethoxy-1,2-dihydroquinoline (EEDQ), was purchased from Aldrich and stored at 0 °C. Quinoline, 6-methyl-quinoline, isoquinoline and 3-methyl-quinoline were freshly distilled from CaH_2 (Heat gun, <0.1 torr) and stored under Ar with exclusion of light. The use of aged samples (1-2 days) provided inferior results. 6-*N*-acetyl-quinoline,[1] and 6-benzoloxyquinoline[2] were prepared according to literature procedures. 1,4-dioxane (inhibitor free, ACS reagent grade >99%), and toluene (ACS reagent grade, >99%) were freshly distilled from Na under an atmosphere of dry N_2 prior to use. Methylene chloride (CH_2Cl_2), pyridine, and methanol (MeOH) were bubble degassed and dried by passage through two columns of activated alumina.[3] Anhydrous 2-methyl-2-butanol (*t*-AmOH, 1 L Sure/Seal™ bottle) was purchased from Aldrich and dispensed via cannula to a Schlenk flask containing activated 4Å molecular sieves (beads, activated by heating under reduced pressure at 300 °C for 12 h, <0.1 torr); it was then subject to 3 successive freeze-pump-thaw cycles and used for no longer than 4 days before degassing again.

$Ni(cod)_2$ was purchased from Strem and stored at −20 °C in a N_2 filled glovebox. Triphenylphosphine was purchased from Aldrich and stored in a N_2 filled glovebox. Sodium carbonate (99%, Fisher) was finely powdered and dried at 300 °C under reduced pressure (<0.1 torr) for 6 h. It was subsequently stored in a desiccator over anhydrous $CaSO_4$.

Instrumentation. Proton nuclear magnetic resonance (^{1}H NMR) spectra and carbon nuclear magnetic resonance (^{13}C NMR) spectra were recorded on a Bruker 500 AVANCE spectrometer (500 and 125 MHz, respectively). Chemical shifts for protons are reported in parts per million downfield from tetramethylsilane and are referenced to residual protium in the NMR solvent ($CHCl_3$ = δ 7.26). Chemical shifts for carbon are reported in parts per million downfield from tetramethylsilane and are referenced to the carbon resonances of the solvent residual peak ($CDCl_3$ = δ 77.16 ppm). ^{19}F spectra were recorded on a Varian Inova 300 (282 MHz) spectrometer; chemical shifts are reported in parts per millions and are referenced to $CFCl_3$ (δ 0 ppm). NMR data are represented as follows: chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, t =

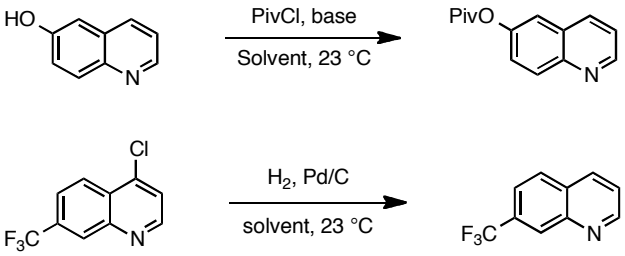
[1] Pitts, M. R.; Harrison, J. R.; Moody, C. J. *J. Chem. Soc., Perkin Trans. 1* **2001,** 955–977.
[2] Valeur, E.; Bradley, M. *Tetrahedron* **2007,** *63,* 8855–8871.
[3] Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J. *Organometallics* **1996,** *15,* 1518.

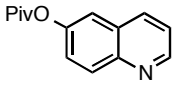
triplet, q = quartet, m = multiplet), coupling constant in Hertz (Hz), integration. High-resolution mass spectra were obtained on an Agilent 6220 Accurate-Mass Time-of-Flight LC/MS. FT-IR spectra were recorded on a Perkin-Elmer Paragon 500 and are reported in terms of frequency of absorption (cm^{-1}). X-ray diffraction data were collected on a Bruker Kappa APEX II Duo CCD diffractometer at the University of Pennsylvania. Data processing was performed using the APEX2 software package (Bruker), and structure solution and refinement were performed using the SHELXTL package (Bruker). Gas chromatography (GC) was performed on an Agilent 7890A series instrument equipped with a split-mode capillary injection system and flame ionization detectors. Optical rotations were recorded on a Perkin Elmer Model 341 polarimeter (1-mL cell, 1 dm path length); concentration (c) is in g/mL and $[a]_D$ values are in degrees. High-performance liquid chromatography (HPLC) was performed on an Agilent 1200 series instrument with a binary pump and a diode array detector

II. General Procedure for Reaction Optimization and Evaluation

An oven-dried 16 mL screw-cap test tube equipped with PTFE-coated stir-bar and PTFE-tape lined screw-thread was brought into a N_2-filled glovebox and charged with the prescribed amount of transition metal (7.5 mol%), *p*-F-phenylboronic acid (1.5 eq or 0.5 eq of the anhydride), and ligand(7.5 mol%, if required). The tube was sealed with a PTFE-lined screw-cap and the cap lined with electrical tape. The tube was removed from the glovebox and connected to an inert gas line. A positive pressure of Ar was maintained for the duration of the reaction. 1,4-dioxane (0.50 mL) was added via Ar-flushed gas-tight syringe and the catalyst mixture allowed to stir for 15-30 min at 23 °C. The mixture was then charged with a solution of EEDQ in 1,4-dioxane/*t*-AmOH (10:1, 0.02 M) and stirred vigorously for 10-15 min at 23 °C. It was then placed into a preheated (40 °C) oil bath and allowed to stir for the allotted time. The reaction mixture was filtered through a small plug of Celite, and the pad rinsed with 1 mL of CH_2Cl_2. Trifluorotoluene (1.0 eq) was added as an internal standard, and the resulting solutions subject to ^{19}F-NMR analysis.

III. Preparation of Quinolines





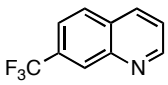
A 100 mL RBF was purged with Ar and then charged with 6-hydroxy-quinoline (1.45 g, 10.0 mmol), pyridine (1.63 mL, 20.0 mmol) and CH_2Cl_2 (50 mL). The flask was cooled to 0 °C (ice water) and the brown suspension stirred vigorously while pivaloyl chloride (1.35 mL, 11.0 mmol) was introduced dropwise. The ice bath was allowed to expire and the reaction stirred overnight. The reaction was then diluted with sat. $NaHCO_3$, transferred to a separatory funnel and extracted (2 x 50 mL DCM, 2 x 50 mL EtOAc). The combined extracts were dried over anhydrous Na_2SO_4 and concentrated to give thick dark oil. Chromatography on silica gel (3% MeOH/CH_2Cl_2) gave the desired product as a colorless oil (1.99 g, 87%).

IR (neat, cm^{-1}): 3047, 2873, 1740, 1120, 1102, 902, 808.

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.91 (dd, J = 4.1, 1.4 Hz, 1H), 8.12 (dd, J = 9.1, 2.5 Hz, 2H), 7.54 (d, J = 2.2 Hz, 1H), 7.46 – 7.39 (m, 2H), 1.41 (s, 9H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 177.28, 150.31, 149.04, 146.37, 135.88, 131.10, 128.68, 124.93, 121.70, 118.44, 39.34, 27.29.

HRMS: (ESI-TOF) calculated for $C_{14}H_{16}NO_2$ ($[M+H]^+$): 230.1176, found: 230.1177.



A 200 mL Schlenk flask equipped with a magnetic stir-bar was charged with anhydrous MeOH (50 mL), 4-chloro-7-trifluoro-methyl-quinoline (1.15 g, 5.00 mmol), triethylamine (1.04 mL, 7.50 mmol) and flushed with Ar. Pd/C (5 wt. %, dry basis) was introduced and the flask purged with, and stirred under H_2 (ambient pressure). The reaction was aged for 1 h, at which point direct inject MS (MeOH, 0.1% formic acid (v/v), APCI+) indicated complete consumption of 4-Chloro-7-trifluoro-methyl-quinoline (232 $[M+1]^+$) to the desired product (198 $[M+1]^+$) without the presence of over hydrogenated material (202 $[M+1]^+$) (Allowing the reaction to continue leads to complete conversion to the undesired 1,2,3,4-tetrahydro-7-trifluoro-methyl-quinoline). The reaction was

filtered, concentrated, and the residue purified on silica gel (60:40 hexanes:EtOAc) to give the desired product as a pale yellow solid (720 mg, 73%).

IR (neat, cm^{-1}): 3057, 1310, 1106, 931, 839, 683.

^{1}H NMR (500 MHz, $CDCl_3$): δ 9.03 (dd, J = 4.1, 1.4 Hz, 1H), 8.43 (s, 1H), 8.24 (d, J = 8.3 Hz, 1H), 7.96 (d, J = 8.5 Hz, 1H), 7.74 (d, J = 8.5 Hz, 1H), 7.54 (dd, J = 8.3, 4.2 Hz, 1H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 151.95, 147.38, 136.08, 131.37 (q, J = 32.3 Hz, 1C), 129.83, 129.20, 127.53 (q, J = 4.5 Hz, 1C), 124.04 (q, J = 272.7 Hz, 1C), 123.07, 122.41 (q, J = 3.1 Hz, 1C).

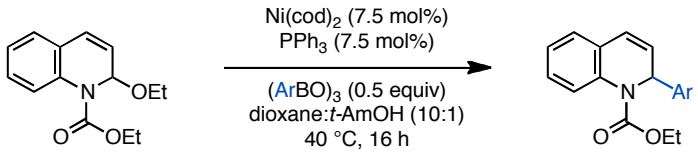
^{19}F NMR (282 MHz, $CDCl_3$): δ −63.08.

HRMS: (ESI-TOF) calculated for $C_{10}H_7F_3N$ ($[M+H]^+$): 198.0525, found: 198.0526.

IV. Procedure for Preparation of Boroxines

General Procedure for Preparation of Boroxines. A 25 mL conical flask was charged with Boronic acid (1-2 g) and connected in line with a P_2O_5-filled collection flask; the set-up was then placed into a Kugelrohr distillation apparatus. The flask was set to rotate (25 rpm), placed under high-vac (0.1 torr), and then heated to 150 °C for 4-6 h. The set up was then evacuated/back-filled with Ar 3-4 times and the flask containing the boroxine was transferred into a N_2 filled glovebox.

VI. Procedure for Preparation of *N*-ethoxycarbamate-2-aryl-1,2-dihydroquinolines

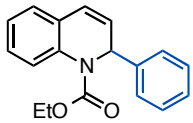


General Procedure for Preparation of *N*-ethoxycarbamate-2-aryl-1,2-dihydroquinolines. An oven-dried 50 mL pear-shaped Schlenk flask equipped with a PTFE-coated stir-bar was brought into a N_2 filled glovebox and charged with the prescribed amount of boroxine (0.25 mmol), sealed with a rubber septum and removed from the glovebox. The flask was connected to an Ar line and a under positive pressure of Ar was charged with EEDQ (0.50 mmol). The septum was replaced, and the flask was subjected to 3-4 evacuation/purge cycles with Ar.

A separate oven dried 2-dram vial equipped with a PTFE-coated stir-bar and PTFE-tape-lined screw-thread was brought into a N_2 filled glovebox, charged with $Ni(cod)_2$ (0.0375 mmol) and PPh_3 (0.0375 mmol). The vial was tightly sealed with a PTFE-lined screw-cap and the vial further sealed with electrical tape. It was removed from the glovebox and placed on an Ar line, charged with freshly distilled 1,4-dioxane (1 mL) and allowed to stir for 15-20 mins.

The Schlenk flask containing EEDQ/boroxine was charged with 1,4-dioxane:*t*-AmOH (25.0 mL, 10:1) immediately before addition of the catalyst mixture. The blood-red, homogenous catalyst mixture was rapidly added via Ar-flushed gas-tight syringe, and the reaction mixture stirred vigorously for 15 min at 23 °C. Under positive pressure of Ar, the septum was replaced with a greased glass-stopper and the flask sealed. The reaction was then aged for 16 h in a pre-heated oil bath (40 °C).

After this time, the reaction mixture is filtered through a short plug of silica gel, with the flask and plug being rinsed several times with EtOAc. Combined filtrate was then concentrated under reduced pressure, and the residue purified on silica gel (10 g pre-packed silica gel cartridge, linear gradient 100:0 to 80:20 Hexanes:EtOAc). The 1,4-adduct co-elutes and the regioisomeric ratio (rr) is determined by ^{1}H-NMR analysis.



Prepared according to the general procedure, the title compound[4] was isolated as a thick colorless oil (138 mg, 99%, >20:1 rr).

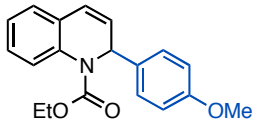
IR (neat, cm^{-1}): 3029, 1693, 1488, 1395, 1262, 1124, 1029, 760, 677.

[4] This compound has previously been reported, but did not possess full characterization data. Scopes, D. I. C.; Joule, J. A. *J. Chem. Soc., Perk. Trans. 1* **1972,** 2810-2811.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.53 (br s, 1H), 7.31 – 7.20 (m, 5H), 7.20 – 7.15 (m, 1H), 7.12 (dd, *J* = 7.5, 1.6 Hz, 1H), 7.05 (td, *J* = 7.4, 1.0 Hz, 1H), 6.65 (dt, *J* = 9.1, 4.2 Hz, 1H), 6.25 – 6.14 (m, 2H), 4.41 – 4.20 (m, 2H), 1.34 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 154.71, 139.70, 134.74, 128.54, 128.25, 127.81, 127.74, 127.10, 126.33, 125.36, 124.59, 124.18, 62.37, 55.53, 14.55; One peak is obscured due to overlap.

HRMS: (ESI-TOF) calculated for $C_{18}H_{18}NO_2$ ([M+H]$^+$): 280.1332, found: 280.1337.



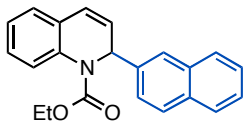
Prepared according to the general procedure, the title compound was isolated as a thick colorless oil (148 mg, 96%, >20:1 rr).

IR (neat, cm^{-1}): 3035, 1693, 1608, 1509, 1377, 1238, 1174, 1030, 756, 678.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.48 (br s, 1H), 7.21 – 7.14 (m, 3H), 7.12 (d, *J* = 7.5 Hz, 1H), 7.05 (t, *J* = 7.4 Hz, 1H), 6.78 – 6.72 (m, 2H), 6.64 (d, J = 8.7 Hz, 1H), 6.18 – 6.09 (br m, 2H), 4.37 – 4.21 (m, 2H), 3.73 (s, 3H), 1.34 (t, J = 7.1 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 159.27, 154.75, 134.68, 131.74, 128.64, 128.58, 127.76, 127.21, 126.34, 125.24, 124.70, 124.20, 113.90, 62.38, 55.30, 55.11,14.64.

HRMS: (ESI-TOF) calculated for $C_{19}H_{20}NO_3$ ([M+H]$^+$): 310.1438, found: 310.1435.



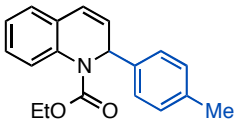
Prepared according to the general procedure, the title compound was isolated as a thick colorless oil (128 mg, 78%, >20:1 rr).

IR (neat, cm^{-1}): 3055, 2980, 1692, 1488, 1371, 1262, 1122, 1031, 733.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.78 – 7.67 (m, 4H), 7.51 (br s, 1H), 7.44 – 7.39 (m, 3H), 7.19 – 7.12 (m, 2H), 7.05 (td, J = 7.5, 1.1 Hz, 1H), 6.72 (d, J = 9.5 Hz, 1H), 6.35 (br d, J = 5.7 Hz, 1H), 6.28 (dd, J = 9.5, 6.1 Hz, 1H), 4.40 – 4.24 (m, 2H), 1.35 (t, J = 7.1 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 154.86, 137.05, 134.79, 133.19, 132.98, 128.49, 128.18, 128.11, 127.85, 127.63, 127.19, 126.45, 126.13, 126.07, 125.83, 125.36, 124.71, 124.32, 62.49, 55.58, 14.63; One peak is obscured due to overlap.

HRMS: (ESI-TOF) calculated for $C_{22}H_{20}NO_2$ ([M+H]$^+$): 330.1489, found: 330.1491.



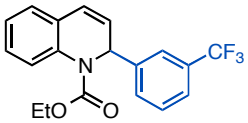
Prepared according to the general procedure, the title compound was isolated as a thick colorless oil (128 mg, 98%, >20:1 rr).

IR (neat, cm^{-1}): 3033, 1695, 1265, 1032, 756, 675, 507.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.51 (br s, 1H), 7.18 – 7.09 (m, 4H), 7.06 – 7.01 (m, 3H), 6.63 (d, J = 9.1 Hz, 1H), 6.19 – 6.11 (m, 2H), 4.36 – 4.20 (m, 2H), 2.26 (s, 3H), 1.33 (t, J = 7.1 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 154.73, 137.62, 136.74, 134.79, 129.27, 128.50, 127.74, 127.19, 127.15, 126.35, 125.25, 124.64, 124.18, 62.36, 55.38, 21.20,14.61.

HRMS: (ESI-TOF) calculated for $C_{19}H_{20}NO_2$ ($[M+H]^+$): 294.1489, found: 294.1492.



Prepared according to the general procedure, the title compound was isolated as a thick colorless oil (125 mg, 72%, >20:1 rr).

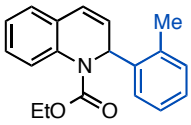
IR (neat, cm^{-1}): 3042, 1696, 1324, 1119, 785.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.57 – 7.41 (m, 4H), 7.38 – 7.31 (m, 1H), 7.19 (t, J = 7.7 Hz, 1H), 7.13 (d, J = 7.4 Hz, 1H), 7.06 (t, J = 7.4 Hz, 1H), 6.70 (d, J = 8.8 Hz, 1H), 6.28 – 6.15 (m, 2H), 4.42 – 4.20 (m, 2H), 1.35 (t, J = 7.1 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 154.70, 140.76, 134.44, 130.79 (q, J = 32.2 Hz, 1C), 130.53, 129.13, 128.11, 127.21, 126.85, 126.59, 126.30, 124.72 (q, J = 3.7 Hz, 1C), 124.64, 124.53, 124.10 (q, J = 272.4 Hz, 1C), 124.05 (q, J = 3.8 Hz, 1C), 62.68, 54.90, 14.56.

^{19}F NMR (282 MHz, $CDCl_3$): δ −63.03.

HRMS: (ESI-TOF) calculated for $C_{19}H_{17}F_3NO_2$ ($[M+H]^+$): 348.1206, found: 348.1207.



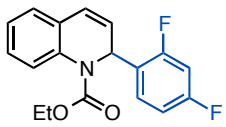
Prepared according to the general procedure, the title compound was isolated as a thick colorless oil (92 mg, 63%, >20:1 rr).

IR (neat, cm^{-1}): 3023, 1703, 1489, 1282, 1125.

^1H NMR (500 MHz, $CDCl_3$): δ 7.62 (br s, 1H), 7.25 – 7.19 (m, 1H), 7.16 – 7.03 (m, 5H), 6.97 (t, *J* = 7.4 Hz, 1H), 6.52 (d, J = 9.4 Hz, 1H), 6.33 (br d, J = 4.6 Hz, 1H), 6.10 (dd, *J* = 9.5, 6.0 Hz, 1H), 4.35 – 4.11 (m, 2H), 2.54 (s, 3H), 1.29 (t, J = 7.1 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 154.87, 139.25, 135.72, 134.25, 130.67, 128.48, 127.97, 127.82, 127.02, 126.64, 126.54, 126.49, 124.57, 124.33, 124.22, 62.45, 53.74, 19.67, 14.57.

HRMS: (ESI-TOF) calculated for $C_{19}H_{20}NO_2$ ($[M+H]^+$): 294.1489, found: 294.1488.



Prepared according to the general procedure, the title compound was isolated as a thick colorless oil (101 mg, 64%, >20:1 rr).

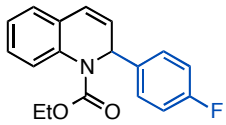
IR (neat, cm^{-1}): 3074, 1702, 1489, 1262, 964, 761.

^1H NMR (500 MHz, $CDCl_3$): δ 7.65 (br s, 1H), 7.25 – 7.21 (m, 1H), 7.12 – 7.00 (m, 3H), 6.81 – 6.74 (m, 1H), 6.68 – 6.61 (m, 1H), 6.58 (d, J = 9.6 Hz, 1H), 6.42 (d, J = 6.0 Hz, 1H), 6.18 – 6.11 (m, 1H), 4.35 – 4.20 (m, 2H), 1.31 (t, J = 7.1 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 162.42 (dd, *J* = 248.6, 11.9 Hz, 1C), 159.13 (dd, *J* = 250.0, 11.9 Hz, 1C), 154.38, 135.02, 128.83 (dd, *J* = 9.6, 5.7 Hz, 1C), 128.11, 127.04, 126.64, 126.56, 125.28, 124.41, 124.31, 123.52 (d, *J* = 12.6 Hz, 1C), 111.28 (dd, *J* = 21.0, 3.5 Hz, 1C), 104.01 (t, *J* = 25.6 Hz, 1C), 62.55, 49.95, 14.42.

^{19}F NMR (282 MHz, $CDCl_3$): δ −111.46 (m, 1F), −113.22 (br s, 1F).

HRMS: (ESI-TOF) calculated for $C_{18}H_{16}F_2NO_2$ ($[M+H]^+$): 316.1144, found: 316.1145.



Prepared according to the general procedure, the title compound was isolated as a thick colorless oil (139 mg, 94%, >20:1 rr).

IR (neat, cm^{-1}): 3037, 1693, 1488, 1221, 1030, 756.

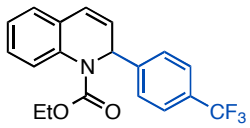
^1H NMR (500 MHz, $CDCl_3$): δ 7.46 (s, 1H), 7.23 – 7.19 (m, 2H), 7.18 – 7.12 (m, 1H), 7.10 (dd, J = 7.5, 1.6 Hz, 1H), 7.06 – 7.01 (m, 1H), 6.95 – 6.84 (m, 2H), 6.69 – 6.59 (m, 1H), 6.19 –

6.09 (m, 2H), 4.38 – 4.19 (m, 2H), 1.32 (t, J = 7.1 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 163.39, 161.44, 154.69, 134.94 (d, J = 112.5 Hz, 1C), 129.06 (d, J = 8.3 Hz, 1C), 128.07, 127.91, 127.03, 126.43, 125.68, 124.68, 124.36, 115.42 (d, J = 21.4 Hz, 1C), 62.51, 54.80, 14.61.

^{19}F NMR (282 MHz, $CDCl_3$): δ −114.69.

HRMS: (ESI-TOF) calculated for $C_{18}H_{17}FNO_2$ ($[M+H]^+$): 298.1238, found: 298.1243.



Prepared according to the general procedure, the title compound was isolated as a thick colorless oil (95 mg, 55%, >20:1 rr). A sample of the 1,4-adduct was obtained by repeated chromatography. ^{1}H-NMR spectra and key NOE's are presented below.

IR (neat, cm^{-1}): 2983, 1697, 1319, 1118, 757.

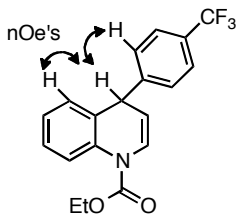
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.52 (br s, 1H), 7.49 (d, *J* = 7.9 Hz, 2H), 7.39 (d, *J* = 7.9 Hz, 2H), 7.20 (t, *J* = 7.6 Hz, 1H), 7.13 (d, *J* = 7.4 Hz, 1H), 7.07 (t, *J* = 7.3 Hz, 1H), 6.69 (d, *J* = 9.1 Hz, 1H), 6.29 – 6.15 (m, *J* = 15.2, 6.6 Hz, 2H), 4.41 – 4.23 (m, *J* = 31.4, 8.1 Hz, 2H), 1.34 (t, *J* = 7.0 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 154.73, 143.72, 134.54, 129.96 (q, J = 32.4 Hz, 1C), 128.12, 127.44, 127.33, 126.88, 126.61, 126.19, 125.61 (q, J = 3.7 Hz, 1C), 124.62, 124.54, 124.01 (q, J = 239.4 Hz, 1C), 62.70, 54.99, 14.60.

^{19}F NMR (282 MHz, $CDCl_3$): δ −62.99.

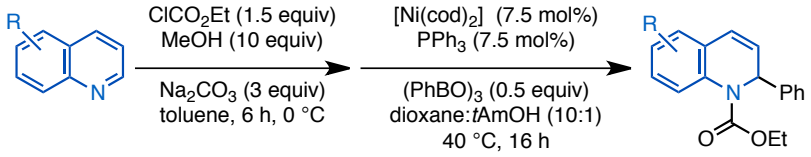
HRMS: (ESI-TOF) calculated for $C_{19}H_{17}F_3NO_2$ ($[M+H]^+$): 348.1206, found: 348.1210.

1,4-adduct:



^{1}H NMR (500 MHz, $CDCl_3$): δ 8.12 (d, J = 8.4 Hz, 1H), 7.54 (d, J = 7.6 Hz, 2H), 7.30 (d, J = 7.7 Hz, 2H), 7.28 – 7.21 (m, 1H), 7.17 (d, J = 7.7 Hz, 1H), 7.08 (t, J = 7.5 Hz, 1H), 6.96 (d, J = 7.6 Hz, 1H), 5.37 (t, J = 5.4 Hz, 1H), 4.70 (s, 1H), 4.36 (q, J = 6.7 Hz, 2H), 1.39 (t, J = 6.8 Hz, 3H).

VI. Procedure for Preparation of *N*-ethoxycarbamate-2-aryl-1,2-dihydroquinolines from Substituted Quinolines

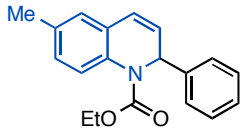


General Procedure for Preparation of *N*-ethoxycarbamate-2-aryl-1,2-dihydroquinolines. An oven-dried 50 mL pear-shaped Schlenk flask equipped with PTFE-coated stir-bar was cooled under vacuum, and backfilled with Ar. The reaction vessel was sequentially charged with Na_2CO_3 (1.50 mmol), quinoline derivative (0.50 mmol), MeOH (5.00 mmol) and toluene (1.5 mL). The reaction mixture was allowed to stir in an ice-bath for 15 min, and then ethyl chloroformate (1.5 mmol) was added dropwise. The reaction mixture was allowed to stir for 6 h between 0−10 °C. The rubber septum was then replaced with a greased glass stopper, and the volatiles removed under vacuum (0.1 torr, 23 °C, 15-20 mins). Residual water/MeOH was removed via azeotropic distillation (3 x 1 mL, freshly distilled toluene, 23 °C, 0.1 torr, 10-15 mins each cycle).

A 2-dram screw cap vial with PTFE-coated stir-bar was brought into the glove box and charged with $Ni(cod)_2$ (0.0375 mmol), and PPh_3 (0.0375 mmol mmol). An additional 2-dram screw-cap vial equipped with PTFE-coated stir-bar was brought into the glovebox and charged with phenylboroxine (0.25 mmol). Both vials were sealed with a PTFE-lined screw-cap, lined with electrical tape, removed from the glove box and placed onto an Ar line. The vial containing the nickel catalyst was charged with 1 mL of freshly distilled 1,4-dioxane and allowed to stir for 15 min (the solution takes on a deep red color during this time). The vial containing the boroxine was charged with 1-2 mL of freshly distilled 1,4-dioxane (enough to dissolve the boroxine) and stirred for ~2-3 mins.

For the pear-shaped Schlenk flask containing the *N,O*-acetal, the stopper was replaced with a rubber septum and the flask subjected to 3 brief evacuation/purge cycles with Ar; it was then charged with 1,4-dioxane:*t*-AmOH (25.0 mL, 10:1). The pre-stirred homogenous solution of boroxine was added rapidly followed by the nickel catalyst solution (via gas-tight, Ar-flushed syringes). The resulting orange reaction mixture was allowed to stir at 23 °C for 15 mins, then placed into a pre-heated oil bath (40 °C) and aged for 16 h.

After this time, the reaction mixture was filtered through a short plug of silica gel, with the flask and plug being rinsed several times with EtOAc. Combined filtrate was then concentrated under reduced pressure, and the residue purified on silica gel (10 g pre-packed silica gel cartridge, linear gradient 100:0 to 70:30 Hexanes:EtOAc). The 1,4-adduct co-elutes and the regioisomeric ratio (r.r.) is determined by ^{1}H-NMR analysis.



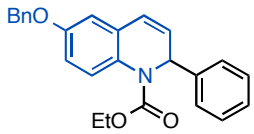
Prepared according to the general procedure, the title compound was isolated as a thick colorless oil (139 mg, 55%, >20:1 rr).

IR (neat, cm^{-1}): 3029, 2865, 1690, 1493, 1267, 1031, 696.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.46 (br s, 1H), 7.34 (d, J = 7.6 Hz, 2H), 7.29 (t, J = 7.4 Hz, 2H), 7.27 – 7.23 (m, 1H), 7.04 (d, J = 8.2 Hz, 1H), 6.98 (s, 1H), 6.67 (dd, J = 7.7, 4.5 Hz, 1H), 6.29 – 6.18 (br m, 2H), 4.43 – 4.26 (m, 2H), 2.35 (s, 3H), 1.39 (t, J = 7.1 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 154.82, 139.81, 133.71, 132.24, 128.54, 128.45, 128.27, 127.78, 127.15, 126.96, 126.87, 125.47, 124.46, 62.31, 55.55, 20.88,14.60.

HRMS: (ESI-TOF) calculated for $C_{19}H_{20}NO_2$ ($[M+H]^+$): 294.1489, found: 294.1488.



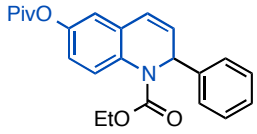
Prepared according to the general pr ocedure, the title compound was isolated as a thick colorless oil (152 mg, 79%, >20:1 rr).

IR (neat, cm^{-1}): 3032, 1623, 1500, 1225, 833, 730.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.47 (d, J = 7.0 Hz, 2H), 7.43 (t, J = 7.4 Hz, 2H), 7.40 – 7.35 (m, 1H), 7.33 – 7.23 (m, 6H), 6.85 (dd, J = 8.8, 2.1 Hz, 1H), 6.78 (d, J = 2.8 Hz, 1H), 6.64 (d, J = 9.2 Hz, 1H), 6.32 – 6.14 (m, 2H), 5.07 (d, J = 1.4 Hz, 2H), 4.41 – 4.24 (m, 2H), 1.37 (t, J = 6.9 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 155.36, 154.82, 139.51, 136.97, 128.96, 128.65, 128.53, 128.19, 128.06, 127.81, 127.59, 127.15, 125.82, 125.44, 114.01, 112.05, 70.25, 62.28, 55.43, 14.60; One peak was missing due to overlap.

HRMS: (ESI-TOF) calculated for $C_{25}H_{24}NO_3$ ($[M+H]^+$): 386.1751, found: 386.1747.



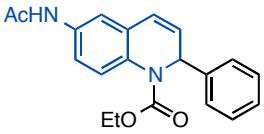
Prepared according to the general procedure, the title compound was isolated as a white foam (172 mg, 91%, >20:1 rr).

IR (neat, cm^{-1}): 3032, 2873, 1749, 1697, 1247, 1109, 902, 728.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.55 (br s, 1H), 7.35 – 7.19 (m, 5H), 6.89 (d, J = 8.5 Hz, 1H), 6.88 (s, 1H), 6.63 (d, J = 9.2 Hz, 1H), 6.32 – 6.15 (m, 2H), 4.45 – 4.19 (m, 2H), 1.37 (s, 9H), 1.35 (t, J = 7.1 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 177.18, 154.67, 147.19, 139.37, 132.09, 129.24, 128.63, 128.05, 127.97, 127.19, 125.54, 124.92, 120.45, 118.92, 62.48, 55.62, 39.15, 27.21, 14.57.

HRMS: (ESI-TOF) calculated for $C_{23}H_{26}NO_4$ ($[M+H]^+$): 380.1883, found: 380.1886.



Prepared according to the general procedure with the following exception: the residue was purified on a 10 g prepacked silica cartridge (100:0 CH_2Cl_2:MeOH to 94:6 CH_2Cl_2:MeOH, linear gradient), and the title compound was isolated as a pale yellow foam (161 mg, 92%, >20:1 rr). On the second run, the product was contaminated with ca. 5 mol. % $O=PPh_3$. A crystal suitable for X-Ray analysis was obtained from benzene.

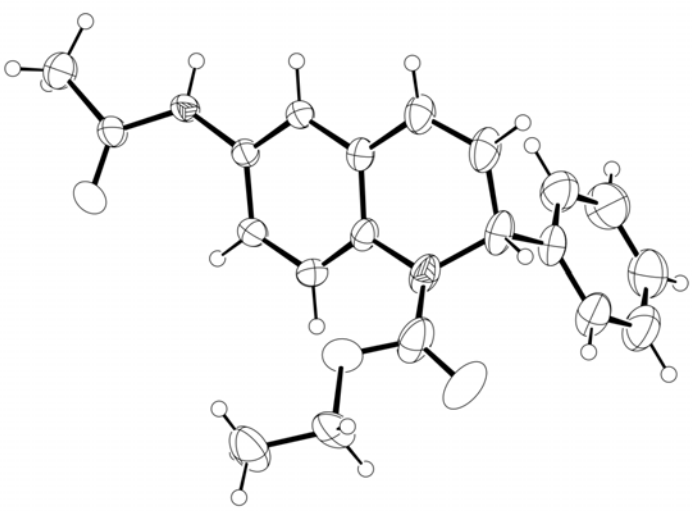
IR (neat, cm^{-1}): 3055, 1703, 1664, 1493, 1261, 1031, 733.

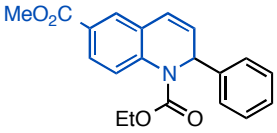
^{1}H NMR (500 MHz, MeOD): δ 7.45 (d, J = 1.9 Hz, 1H), 7.27 (dd, J = 8.8, 2.4 Hz, 2H), 7.25 – 7.15 (m, 5H), 6.65 (d, J = 9.6 Hz, 1H), 6.29 (dd, J = 9.4, 6.2 Hz, 1H), 6.13 (d, J = 5.9 Hz, 1H), 4.32 – 4.22 (m, 2H), 2.10 (s, J = 8.4 Hz, 3H), 1.32 (t, J = 7.1 Hz, 3H).

^{13}C NMR (125 MHz, MeOD): δ 170.18, 154.83, 139.38, 134.90, 130.53, 128.80, 128.06, 127.61, 127.42, 126.60, 124.88, 124.61, 118.92, 117.41, 62.17, 55.34, 22.36,13.4.

HRMS: (ESI-TOF) calculated for $C_{20}H_{21}N_2O_3$ ($[M+H]^+$): 337.1547, found: 337.1554.

X-Ray:





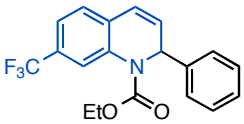
Prepared according to the general procedure, the title compound was isolated as a white foam (135 mg, 80%, >20:1 rr).

IR (neat, cm^{-1}): 3089, 2984, 1760, 1701, 1274, 1199, 1030, 759.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.88 – 7.78 (m, 2H), 7.63 (br d, J = 7.9 Hz, 1H), 7.25 – 7.21 (m, 5H), 6.69 (d, J = 9.4 Hz, 1H), 6.27 – 6.12 (m, 2H), 4.38 – 4.24 (m, 2H), 3.90 (s, 3H), 1.35 (t, J = 7.1 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 166.67, 154.34, 139.34, 139.09, 129.15, 128.90, 128.65, 128.10, 127.84, 127.06, 126.75, 125.54, 124.78, 124.07, 62.75, 56.04, 52.13,14.47.

HRMS: (ESI-TOF) calculated for $C_{20}H_{20}NO_4$ ($[M+H]^+$): 338.1387, found: 338.1387.



Prepared according to the general procedure, the title compound was isolated as thick colorless oil (99 mg, 57%, >20:1 rr).

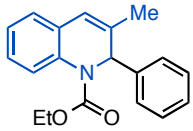
IR (neat, cm^{-1}): 3089, 2984, 1703, 1325, 1117, 676.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.86 (br s, 1H), 7.34 – 7.18 (m, 7H), 6.70 (d, J = 9.5 Hz, 1H), 6.31 (dd, J = 9.5, 6.1 Hz, 1H), 6.24 (br d, J = 5.4 Hz, 1H), 4.43 – 4.21 (m, 2H), 1.36 (t, J = 7.1 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 154.45, 139.09, 135.09, 130.70, 129.92, 129.61 (q, J = 32.3 Hz, 1C), 128.79, 128.25, 127.19, 126.66, 124.49, 124.06 (q, J = 272.2 Hz, 1C), 121.68, 120.88 (q, J = 3.7 Hz, 1C), 62.86, 55.77, 14.41.

^{19}F NMR (282 MHz, $CDCl_3$): δ −63.04.

HRMS: (ESI-TOF) calculated for $C_{19}H_{17}F_3NO_2$ ($[M+H]^+$): 348.1206, found: 348.1211.



Prepared according to the general procedure, the title compound was isolated as a thick colorless oil, which slowly crystallizes over the course of days (76 mg, 57%, >20:1 rr).

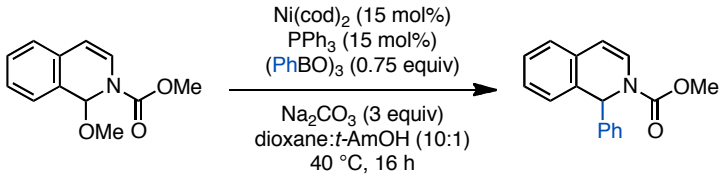
IR (neat, cm^{-1}): 3062, 1692, 1488, 1241, 1027, 696.

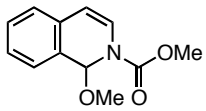
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.35 (br s, 1H), 7.20 – 7.08 (m, 5H), 7.07 – 6.91 (m, 3H), 6.35 (br s, 1H), 5.83 (br s, 1H), 4.31 – 4.09 (m, 2H), 1.79 (s, 3H), 1.25 (t, J = 7.1 Hz, 3H).

^{13}C NMR (125 MHz, MeOD): δ 156.05, 139.62, 138.83, 134.42, 129.59, 129.55, 129.19, 128.61, 127.74, 126.63, 125.49, 125.35, 122.76, 63.50, 61.35, 21.06,14.80.

HRMS: (ESI-TOF) calculated for $C_{19}H_{20}NO_2$ ($[M+H]^+$): 294.1488, found: 294.1492.

VII. Procedure for Preparation of N-methoxycarbamate-1-phenyl-1,2-dihydroisoquinoline





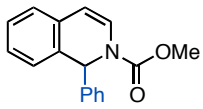
Neat isoquinoline (5.0 g, 38.0 mmol) (freshly distilled from CaH_2), was added to a 20 mL scintillation vial equipped with a magnetic stir bar. Dimethylpyrocarbonate was then added in 500 μL portions via plastic micropipette until the evolution of gas ceased (~10 portions) (the use of glass pipettes leads to decomposition of the pyrocarbonate). The resulting thick oil was stirred for 2 hours at r.t., then placed under reduced pressure (0.1 torr) and heated to 40 °C for 1 h to remove dimethylcarbonate. The resulting mixture was then fractionally distilled under reduced pressure, collecting three 1 g portions (126-130 °C, 0.1 torr) of the desired product as a thick colorless oil (3.0 g, 36%).

IR (neat, cm^{-1}): 2992, 1718, 1315, 1237, 1059, 767.

^{1}H NMR (500 MHz, MeOD): δ 7.39 – 7.32 (m, 2H), 7.28 (t, J = 7.4 Hz, 1H), 7.22 (d, J = 7.7 Hz, 1H), 7.03 (br s, 1H; minor rotamer 7.12, br s), 6.42 (br s, 1H), 6.07 (br s, 1H), 3.88 (s, 3H), 3.24 (s, 3H; minor rotamer 3.16, br s).

^{13}C NMR (125 MHz, MeOD): δ 155.94, 131.82, 130.31, 129.42, 128.88, 127.92, 126.03, 125.22, 124.55, 109.06, 83.40, 54.3.

LRMS: (APCI+) calculated for $C_{11}H_{10}NO_2$ ($[M\text{-}OCH_3]^+$): 188, found: 188.



An oven-dried Ar-flushed 50 mL pear-shaped Schlenk flask equipped with a PTFE-coated stir-bar and rubber septum was charged with Na_2CO_3 (158 mg, 1.50 mmol), *N*-methoxycarbamate-1-methoxy-1,2-dihydroisoquinoline (109 mg, 5.00 mmol) and evacuated/purged with Ar over 3 cycles.

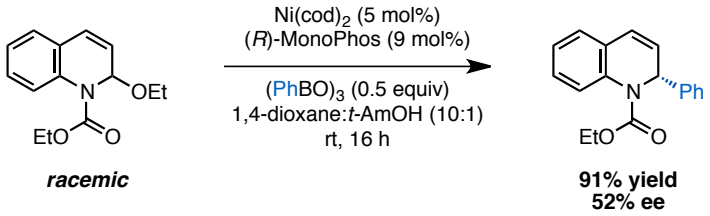
A 2-dram screw cap vial with PTFE-coated stir-bar was brought into the glove box and charged with $Ni(cod)_2$ (20.6 mg, 0.0750 mmol), and PPh_3 (19.7 mg, 0.0750 mmol). An additional 2-dram screw-cap vial equipped with PTFE-coated stir-bar was brought into the glovebox and charged with phenylboroxine (117 mg, 0.375 mmol). Both vials were sealed with a PTFE-lined screw-cap, lined with electrical tape, removed from the glove box and placed onto an Ar line. The vial

containing the nickel catalyst was charged with 1 mL of freshly distilled 1,4-dioxane and allowed to stir for 15 min (the reaction takes on a deep red color during this time). The vial containing the boroxine was charged with 1-2 mL of freshly distilled 1,4-dioxane (enough to dissolve the boroxine) and stirred for ~2-3 mins.

The Schlenk flask was charged with 1,4-dioxane:*t*-AmOH (25.0 mL, 10:1), followed by rapid addition of the phenylboroxine solution, followed by the blood red nickel catalyst solution (via gas-tight, Ar-flushed syringes). The vigorously stirred flask was aged for 12 h, and then filtered through a short pad of silica gel with the flask and pad being washed with EtOAc several times. Combined filtrate is then concentrated under reduced pressure, and the residue purified on silica gel (10 g pre-packed silica gel cartridge, linear gradient 100:0 to 80:20 Hexanes:EtOAc)affording the desired product as a colorless oil (94 mg, 71%). Spectral data were in accordance with previously reported values.[5]

[5] Lu, S.; Wang, Y.; Han, X.; Zhou, Y. *Angew. Chem., Int. Ed.* **2006,** *45,* 2260 –2263.

VIII. Procedure for the Asymmetric Preparation of *N*-ethoxycarbamate-2-phenyl-1,2-dihydroquinoline.



An oven-dried 50 mL pear-shaped Schlenk flask equipped with a PTFE-coated stir-bar was brought into a N2 filled glovebox and charged with the prescribed amount of phenylboroxine (0.25 mmol), sealed with a rubber septum and removed from the glovebox. The flask was connected to an N_2 line and a under positive pressure of N_2 was charged with EEDQ (0.50 mmol). The septum was replaced, and the flask was subjected to 3 evacuation/purge cycles with N_2.

A separate oven dried 2-dram vial equipped with a PTFE-coated stir-bar and PTFE-tape-lined screw-thread was brought into a N_2 filled glovebox, charged with Ni(cod)2 (0.025 mmol) and (*R*)-Monophos (0.045 mmol). The vial was tightly sealed with a PTFE-lined screw-cap and the vial further sealed with electrical tape. It was removed from the glovebox and placed on an N_2 line, charged with freshly distilled 1,4-dioxane (1 mL) and allowed to stir for 1 h.

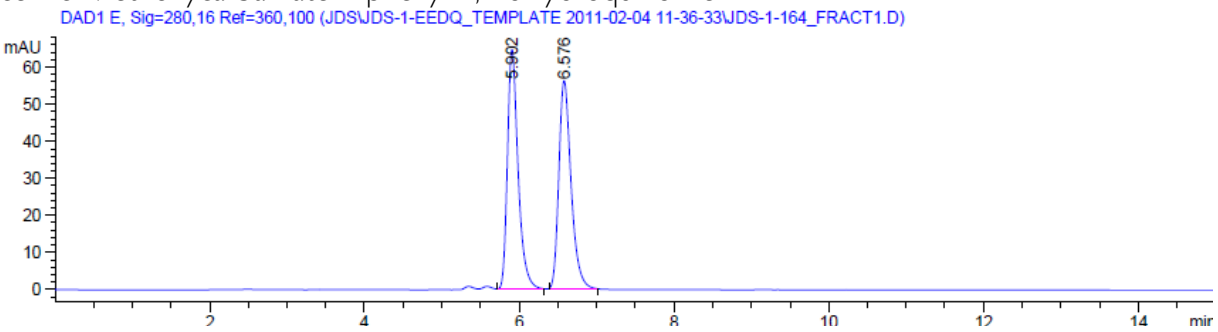
The Schlenk flask containing EEDQ/boroxine was charged with 1,4-dioxane:*t*-AmOH (25.0 mL, 10:1) immediately before addition of the catalyst mixture. The bright yellow, homogenous catalyst mixture was rapidly added via N_2-flushed gas-tight syringe, and the reaction mixture stirred vigorously at room temperature for 16 h.

After this time, the reaction mixture was filtered through a short plug of silica gel, with the flask and plug being rinsed several times with EtOAc. Combined filtrate was then concentrated under reduced pressure, and the residue purified on silica gel (25 g pre-packed silica gel cartridge, linear gradient 100:0 to 90:10 Hexanes:EtOAc) to afford the product (127 mg, 91%, >20:1 rr, 52% ee).

Enantiomeric excess of the product was determined by chiral HPLC (Chiralpak AS-H, 0.46 cm x 25 cm, 97:3 hexanes:*i*-PrOH, 1 mL/min, t_R(minor) = 5.9 min, t_R(major)= 6.6 min, 280 nm). $[\alpha]^{20}_D$ = –350.9 ($CHCl_3$, c = 1.00, path length = 1 dm). The absolute stereochemistry was tentatively assigned as the *R*-isomer by analogy.[6]

[6] Amiot, F.; Cointeaux, L.; Silve, E. J.; Alexakis, A. *Tetrahedron* **2004,** *60,* 8221-8231.

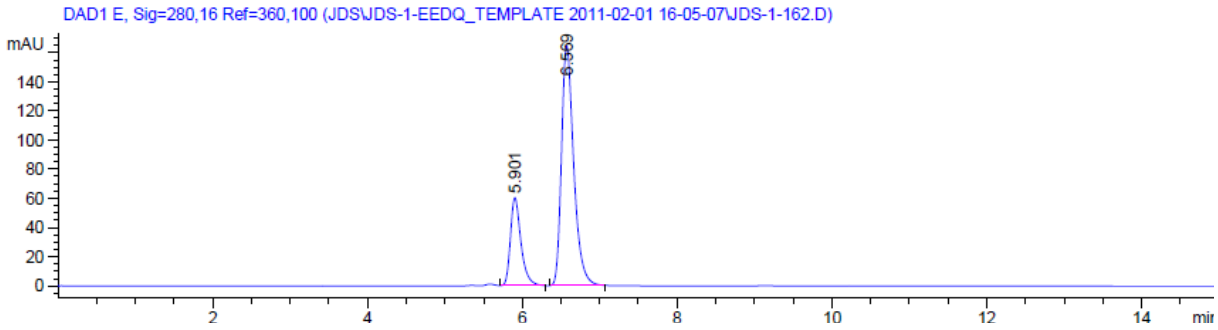
Racemic *N*-ethoxycarbamate-2-phenyl-1,2-dihydroquinoline:



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

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.902	VB	0.1442	623.95923	64.88611	50.0165
2	6.576	BB	0.1670	623.54687	56.41059	49.9835
Totals :				1247.50610	121.29670	

Enantioenriched *N*-ethoxycarbamate-2-phenyl-1,2-dihydroquinoline:



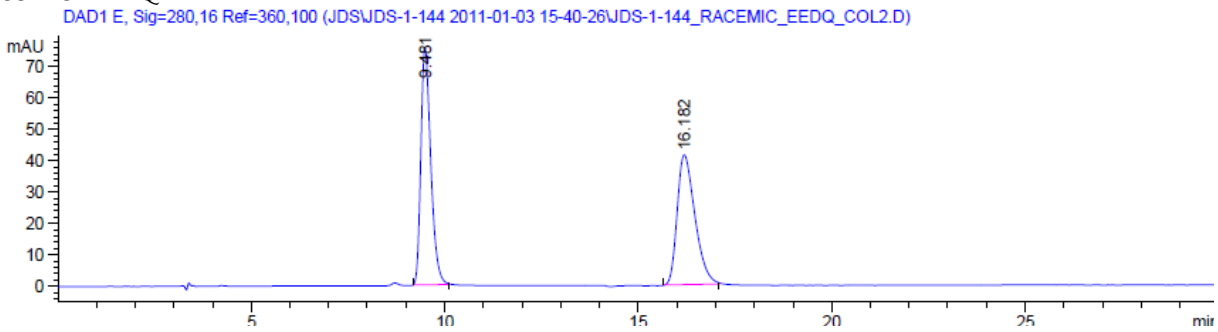
Signal 3: DAD1 E, Sig=280,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.901	VB	0.1428	574.51550	60.49106	24.0937
2	6.569	BB	0.1660	1809.98914	164.92657	75.9063
Totals :				2384.50464	225.41763	

IX. Racemization Studies

Racemic EEDQ was separated into both enantiomers using preparative chiral SFC (Chiralcel OJ-H column, 2 cm x 25 cm, 65 mL/min, 85:15:0.1 sCO_2:EtOH:DEA). The enantiomeric excess of the obtained material was determined to be 84% by chiral HPLC (Chiralcel OJ-H column, 0.46 cm x 25 cm, 95:5 hexanes:*i*-PrOH, 1 mL/min, $t_R(-)$ = 9.5 min, $t_R(+)$= 16.2 min, 280 nm). The optical rotation of the enantioenriched EEDQ was measured in chloroform $[\alpha]^{20}_D$ = +229.7 ($CHCl_3$, c = 1.00, path length = 1 dm). The absolute stereochemistry was not determined.

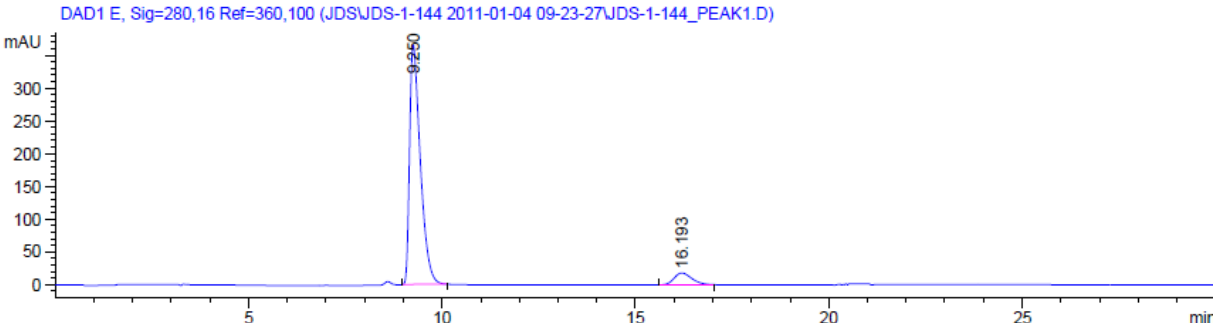
Racemic EEDQ:



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

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.481	BB	0.2747	1349.60120	75.42911	50.5496
2	16.182	BB	0.4902	1320.25281	41.38726	49.4504
Totals :				2669.85400	116.81636	

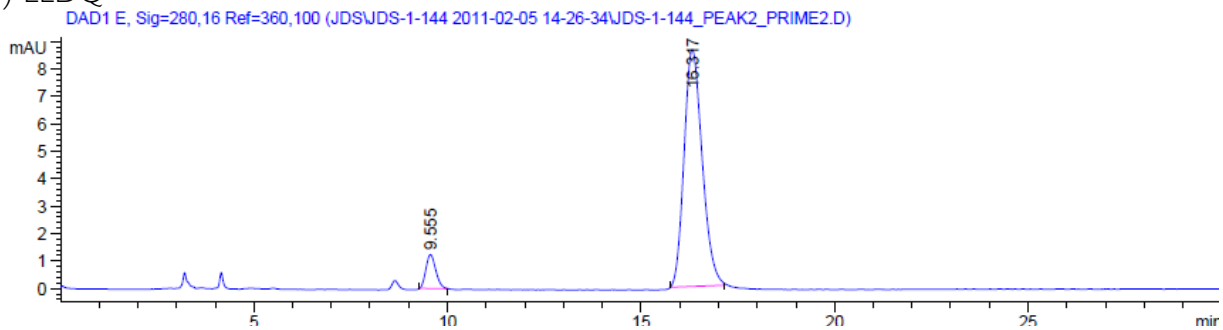
(–)-EEDQ



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

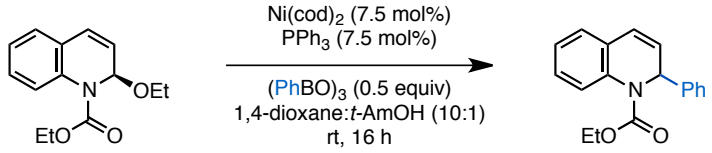
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.250	BB	0.2911	7068.48828	366.37482	92.4372
2	16.193	BB	0.4882	578.31372	18.12515	7.5628
Totals :				7646.80200	384.49996	

(+)-EEDQ



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

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.555	BB	0.2733	22.26668	1.24132	7.3241
2	16.317	BB	0.4964	281.75375	8.64236	92.6759
Totals :				304.02044	9.88368	

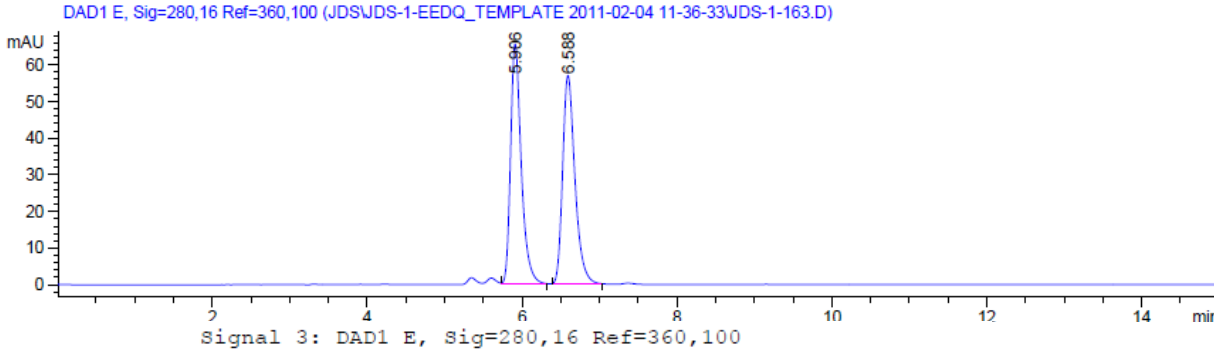


An oven-dried scintillation vial equipped with a PTFE-coated stir-bar was charged with enantioenriched (+)-EEDQ (0.1 mmol) and brought into a N2 filled glovebox. A 0.011M stock solution was then prepared by the addition of 1,4-dioxane/*t*-AmOH (9 mL, 8:1).

A separate oven dried 2-dram vial equipped with a PTFE-coated stir-bar was brought into a N_2 filled glovebox, charged with Ni(cod)2 (0.0075 mmol) and PPh_3 (0.0075 mmol). The vial was charged with 1,4-dioxane (0.5 mL) and the solution was stirred for 20 min.

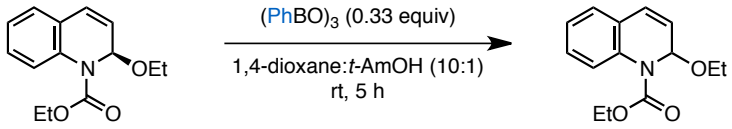
A separate oven dried 2-dram vial equipped with a PTFE-coated stir-bar and PTFE-tape-lined screw-thread was brought into a N_2 filled glovebox and charged with triphenylboroxine (0.05 mmol). Immediately before addition of the catalyst mixture, this vial was charged with 4.5 mL of the (+)-EEDQ stock solution. The dark red, homogeneous catalyst mixture was rapidly added by micropipette. The reaction was sealed with a PTFE-lined screw-cap and the vial further sealed with electrical tape. It was removed from the glovebox and stirred for 16 h at room temperature. The reaction mixture was then concentrated under reduced pressure to give the crude product. Conversion was determined to be >95% by GC analysis (HP-1, 80 °C to 300 °C, 20 °C/min, 5mL/min, t_R(starting material)= 3.84 min, t_R(product)= 8.99 min). Enantiomeric excess was determined to be 0% by chiral HPLC.

Racemic *N*-ethoxycarbamate-2-phenyl-1,2-dihydroquinoline:



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

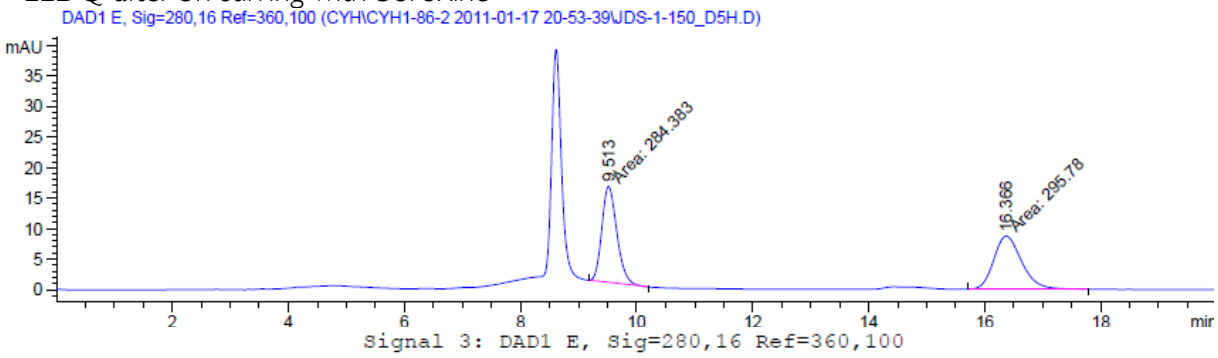
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.906	VB	0.1444	633.95911	65.80261	50.0767
2	6.588	BB	0.1671	632.01630	57.12250	49.9233
Totals :				1265.97540	122.92511	



84% ee ***racemic***

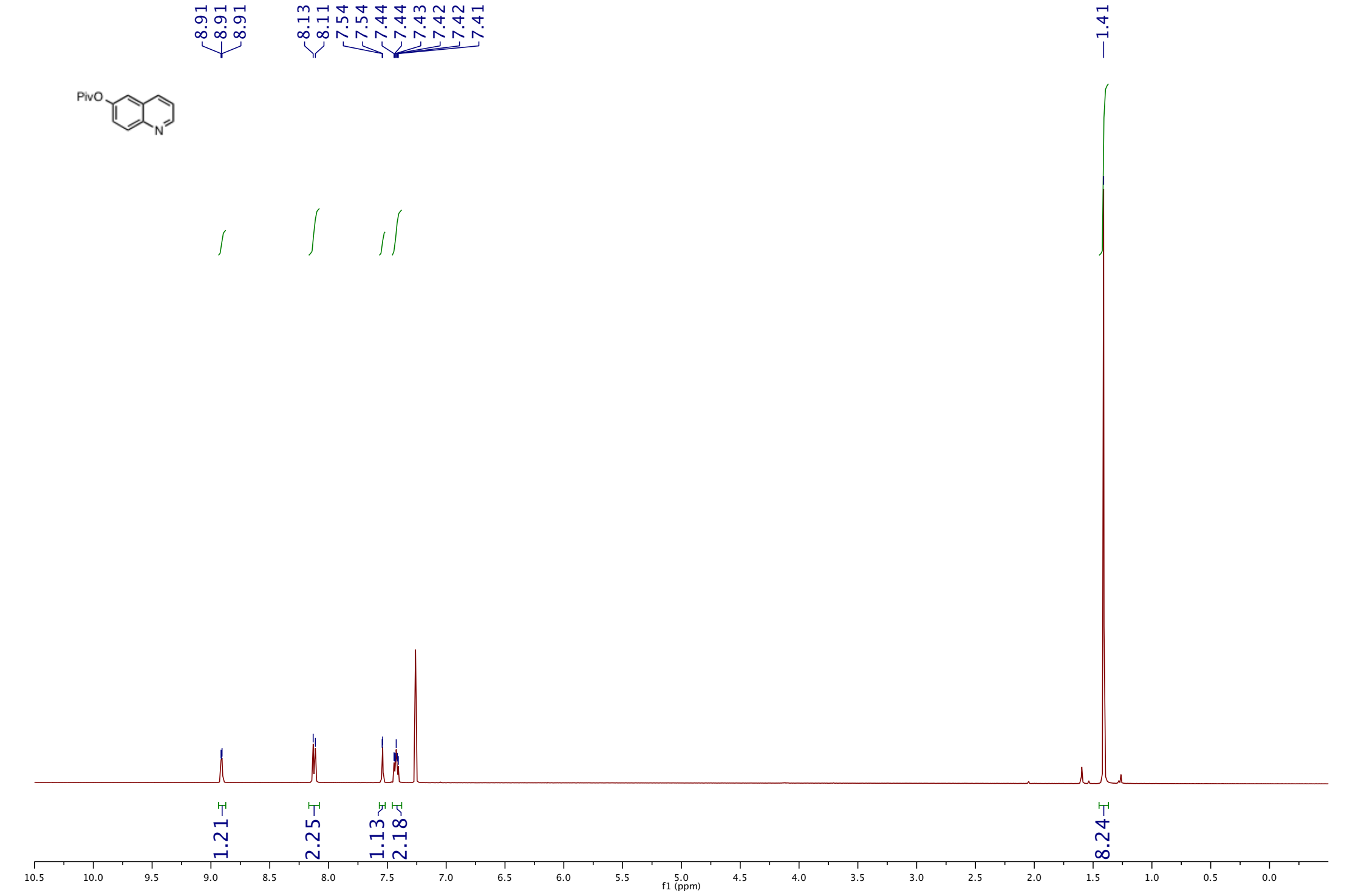
An oven-dried scintillation vial equipped with a PTFE-coated stir-bar was charged with enantioenriched (–)-EEDQ (0.05 mmol) and brought into a N2 filled glovebox. It was then charged with phenylboroxine (0.025 mmol), sealed and removed from the glovebox. The vial was charged with 1,4-dioxane/*t*-AmOH (5 mL, 9:1) and stirred. After 5 h, the reaction mixture was concentrated under reduced pressure. The EEDQ was found to be racemic by chiral HPLC, while no racemization was observed under identical conditions without phenylboroxine.

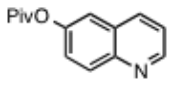
EEDQ after 5h stirring with boroxine



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

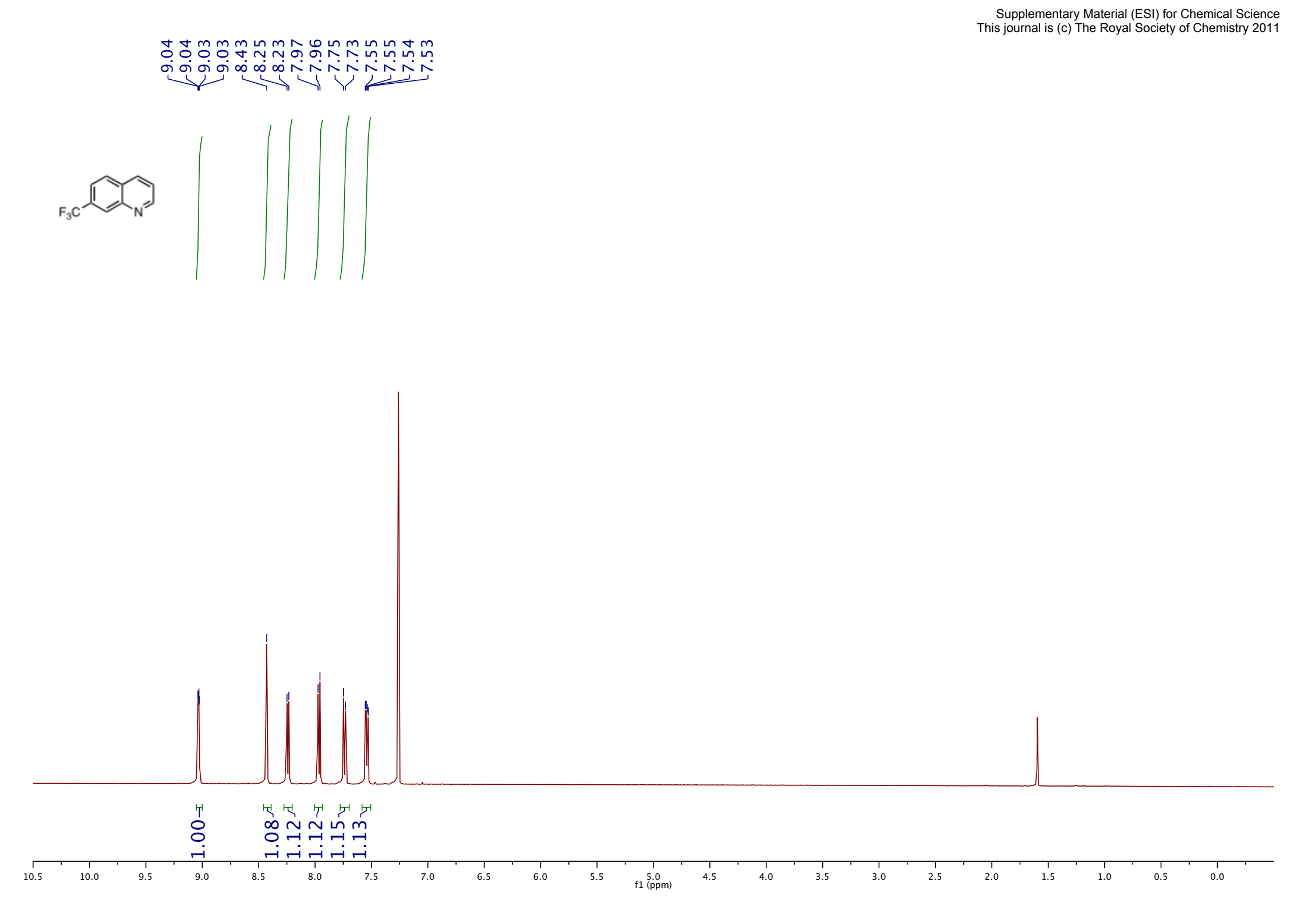
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.513	MM	0.3008	284.38266	15.75574	49.0177
2	16.366	MM	0.5640	295.78018	8.74043	50.9823
Totals :				580.16284	24.49617	

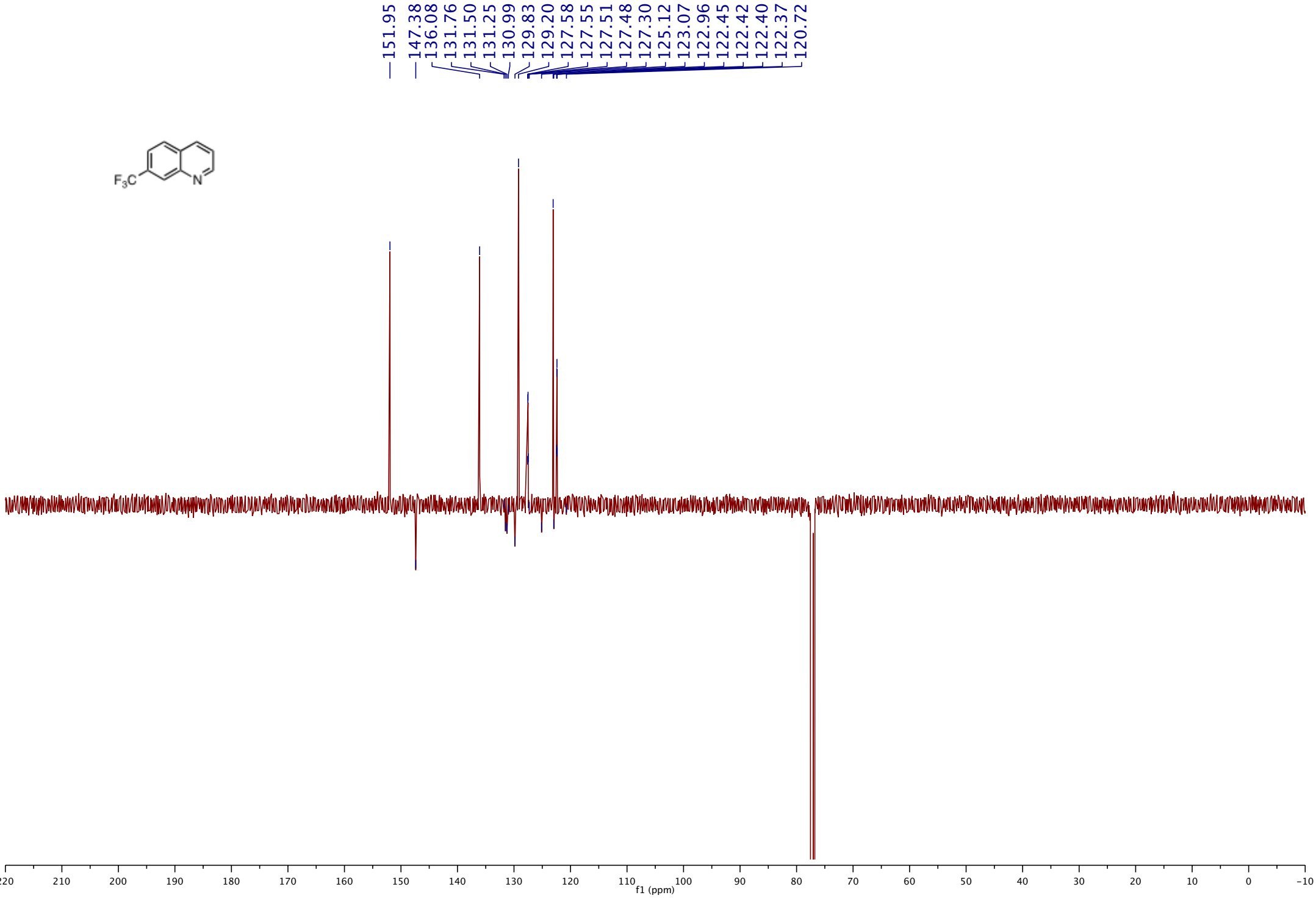


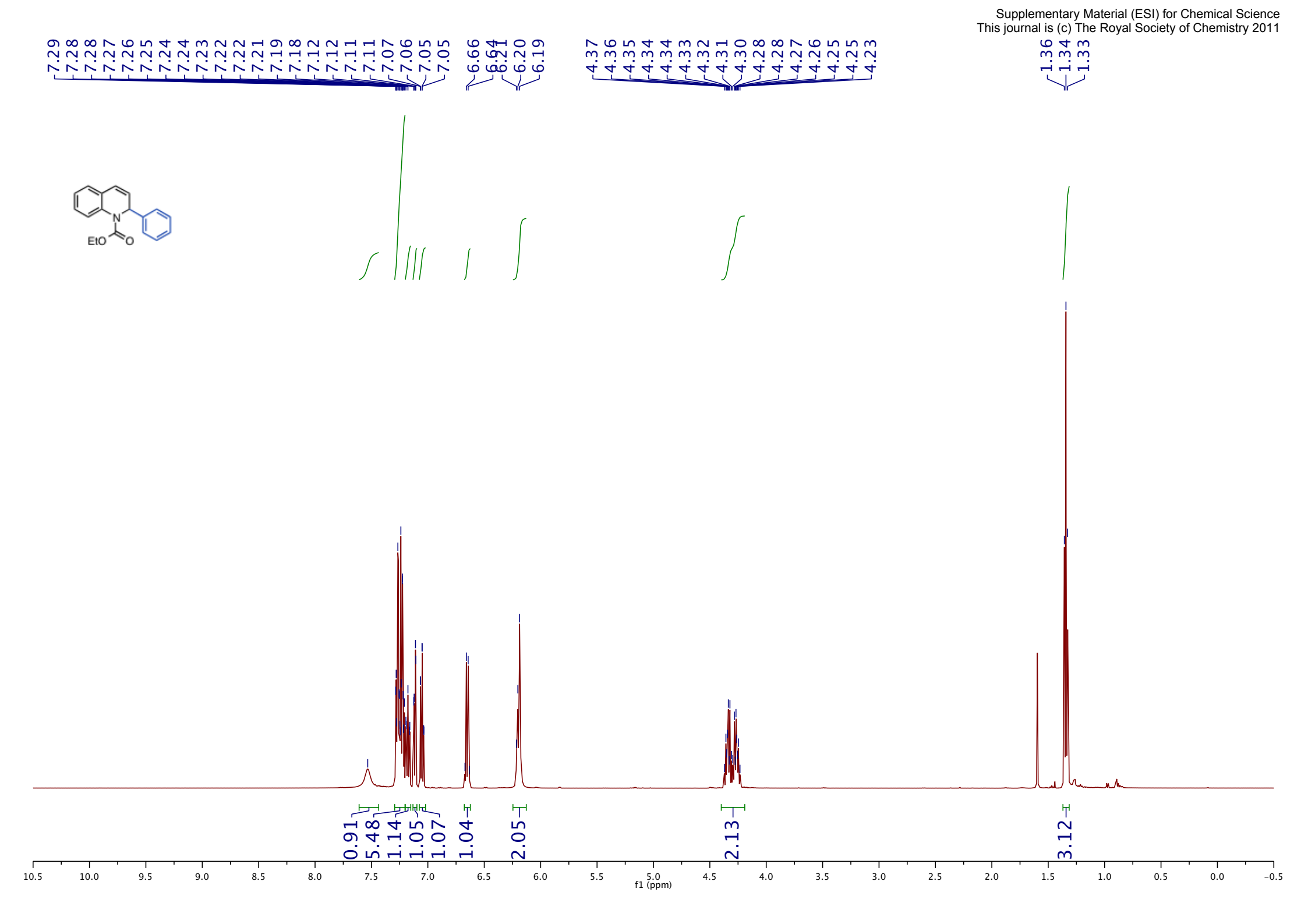


177.28
150.31
149.04
146.37
135.88
131.10
128.68
124.93
121.70
118.44
39.34
27.29

220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)


9.04
9.04
9.03
9.03
8.43
8.25
8.23
7.97
7.96
7.75
7.73
7.55
7.55
7.54
7.53
F3C
N
1.00
1.08
1.12
1.12
1.15
1.13
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


151.95
147.38
136.08
131.76
131.50
131.25
130.99
129.83
129.20
127.58
127.55
127.51
127.48
127.30
125.12
123.07
122.96
122.45
122.42
122.40
122.37
120.72
F3C
N
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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7.25
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7.22
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7.19
7.18
7.12
7.12
7.11
7.11
7.07
7.06
7.05
7.05
6.66
6.64
6.21
6.20
6.19
4.37
4.36
4.35
4.34
4.34
4.33
4.32
4.31
4.30
4.28
4.28
4.27
4.26
4.25
4.25
4.23
1.36
1.34
1.33
N
EtO
O
0.91
5.48
1.14
1.05
1.07
1.04
2.05
2.13
3.12
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
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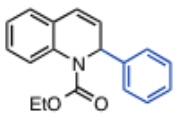
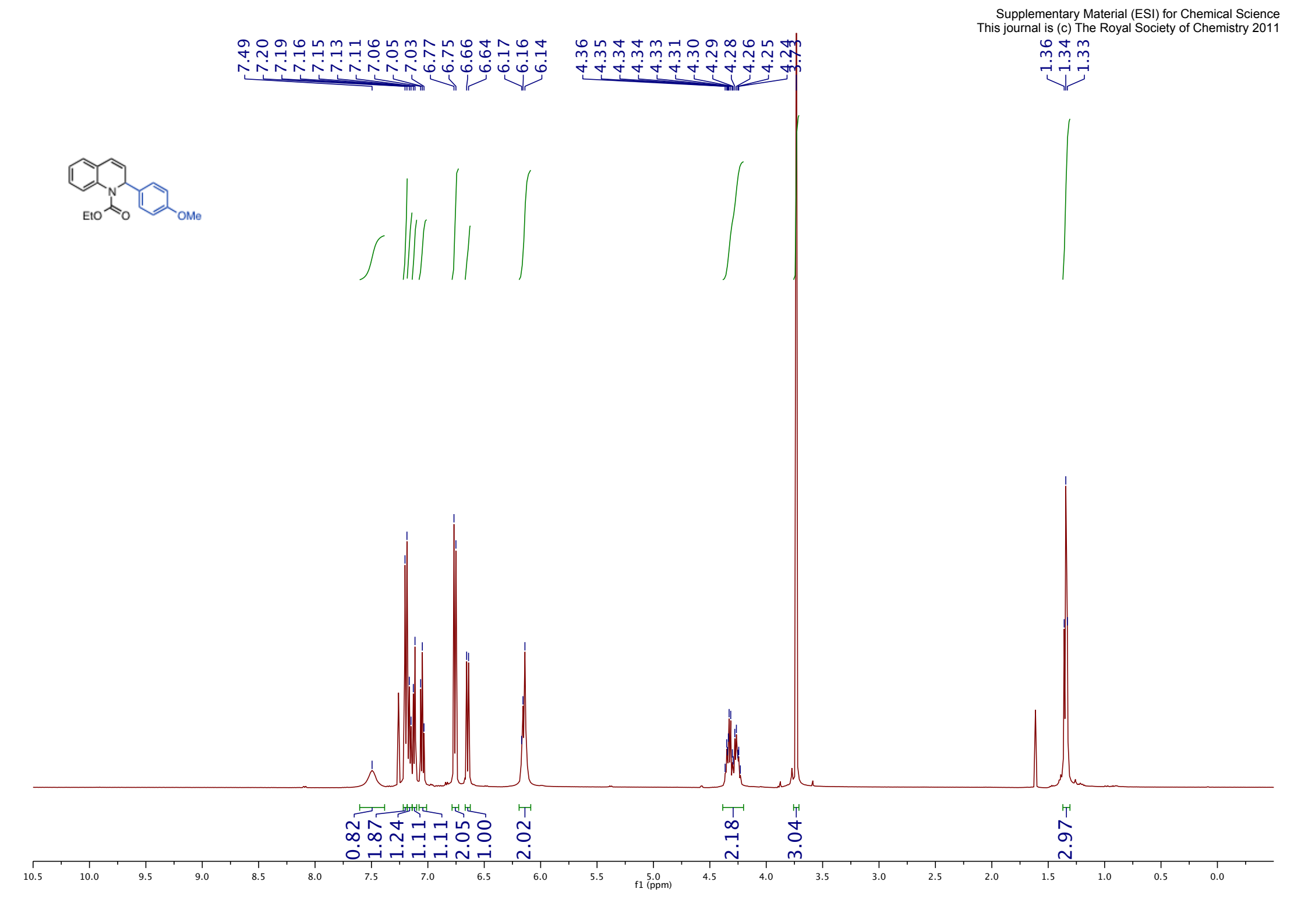
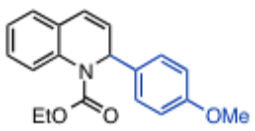
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

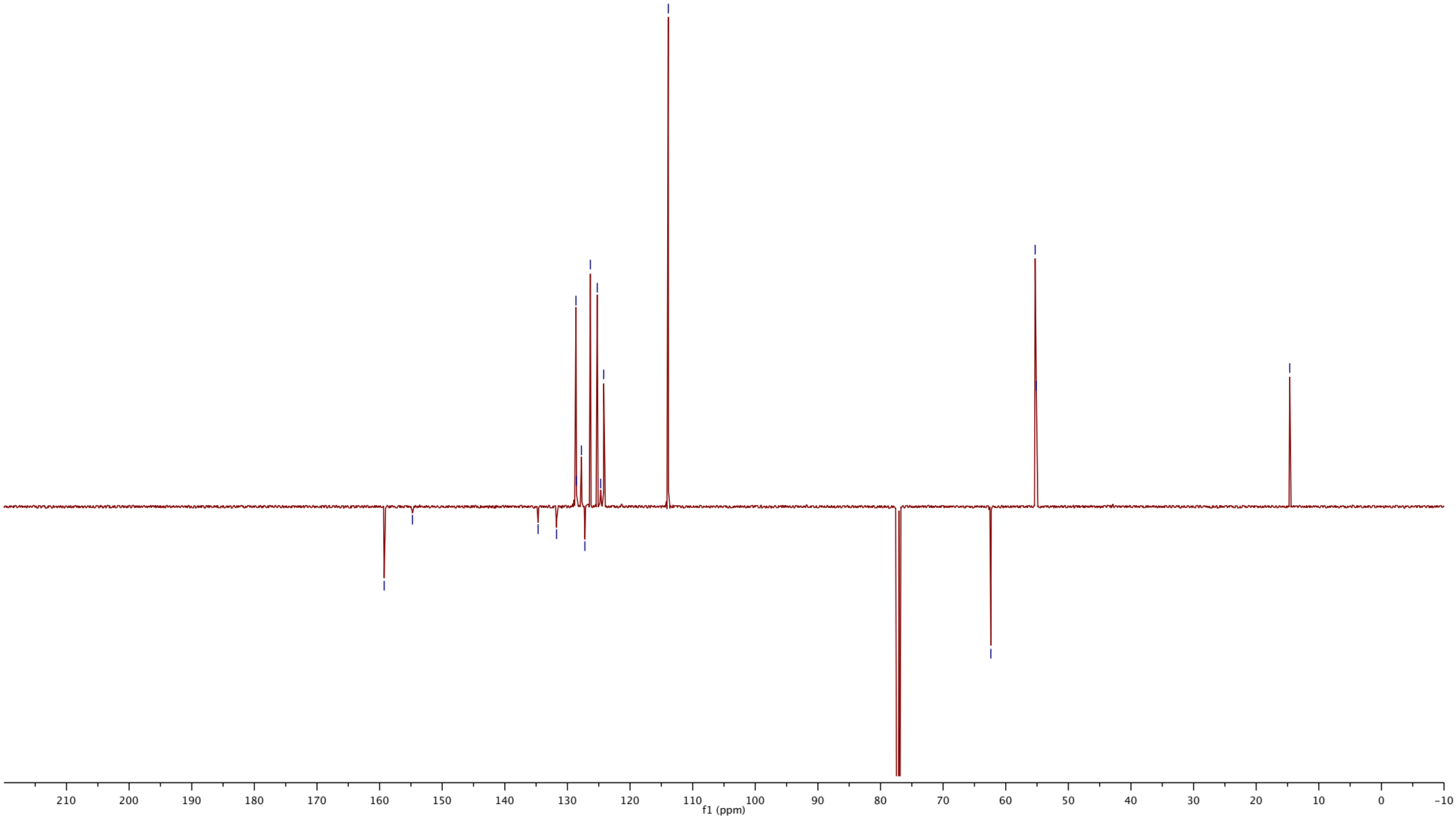

N
EtO
O

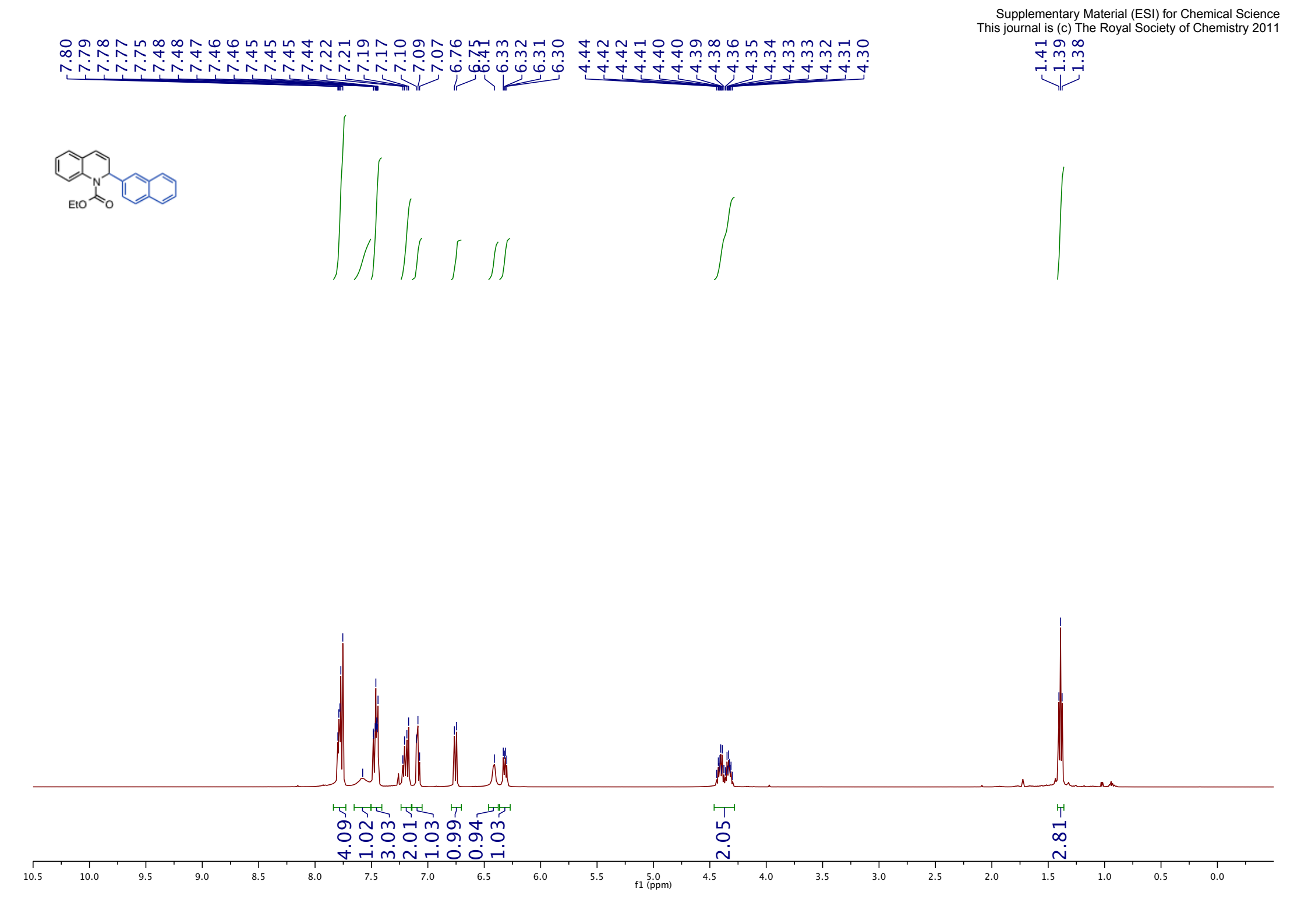
154.71
139.70
134.74
128.54
128.26
127.81
127.74
127.10
126.33
125.36
124.61
124.18
62.38
55.53
14.55
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)





159.27
154.75
134.68
131.74
128.64
128.58
127.76
127.21
126.34
125.24
124.70
124.20
113.90
62.38
55.30
55.11
14.64

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7.45
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7.45
7.44
7.22
7.21
7.19
7.17
7.10
7.09
7.07
6.76
6.75
6.41
6.33
6.32
6.31
6.30
4.44
4.42
4.42
4.41
4.40
4.40
4.39
4.38
4.36
4.35
4.34
4.33
4.33
4.32
4.31
4.30
1.41
1.39
1.38
EtO
O
N
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1.02
3.03
2.01
1.03
0.99
0.94
1.03
2.05
2.81
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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2.5
2.0
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1.0
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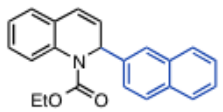
0.0
f1 (ppm)



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128.18
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127.85
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126.13
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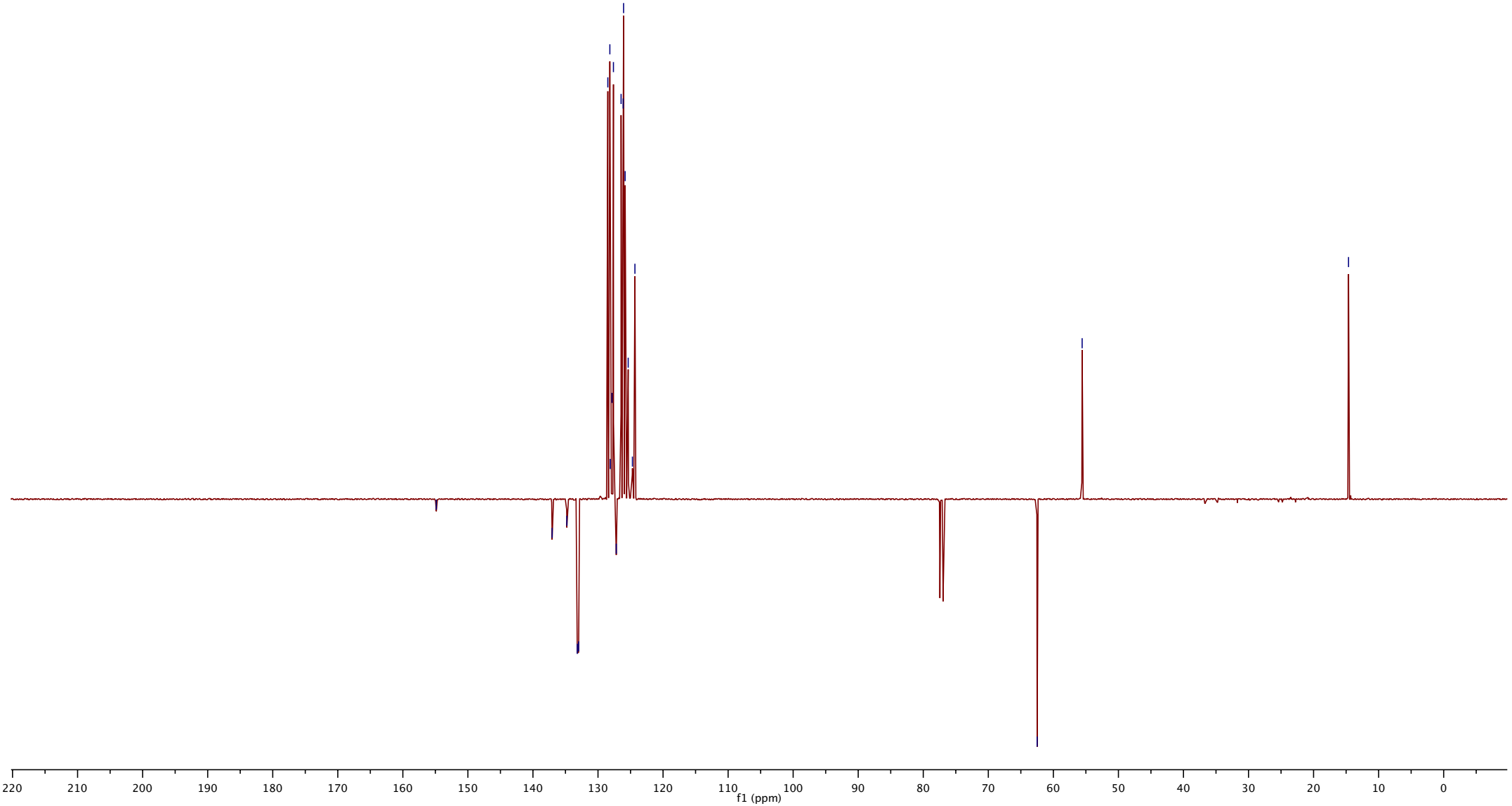
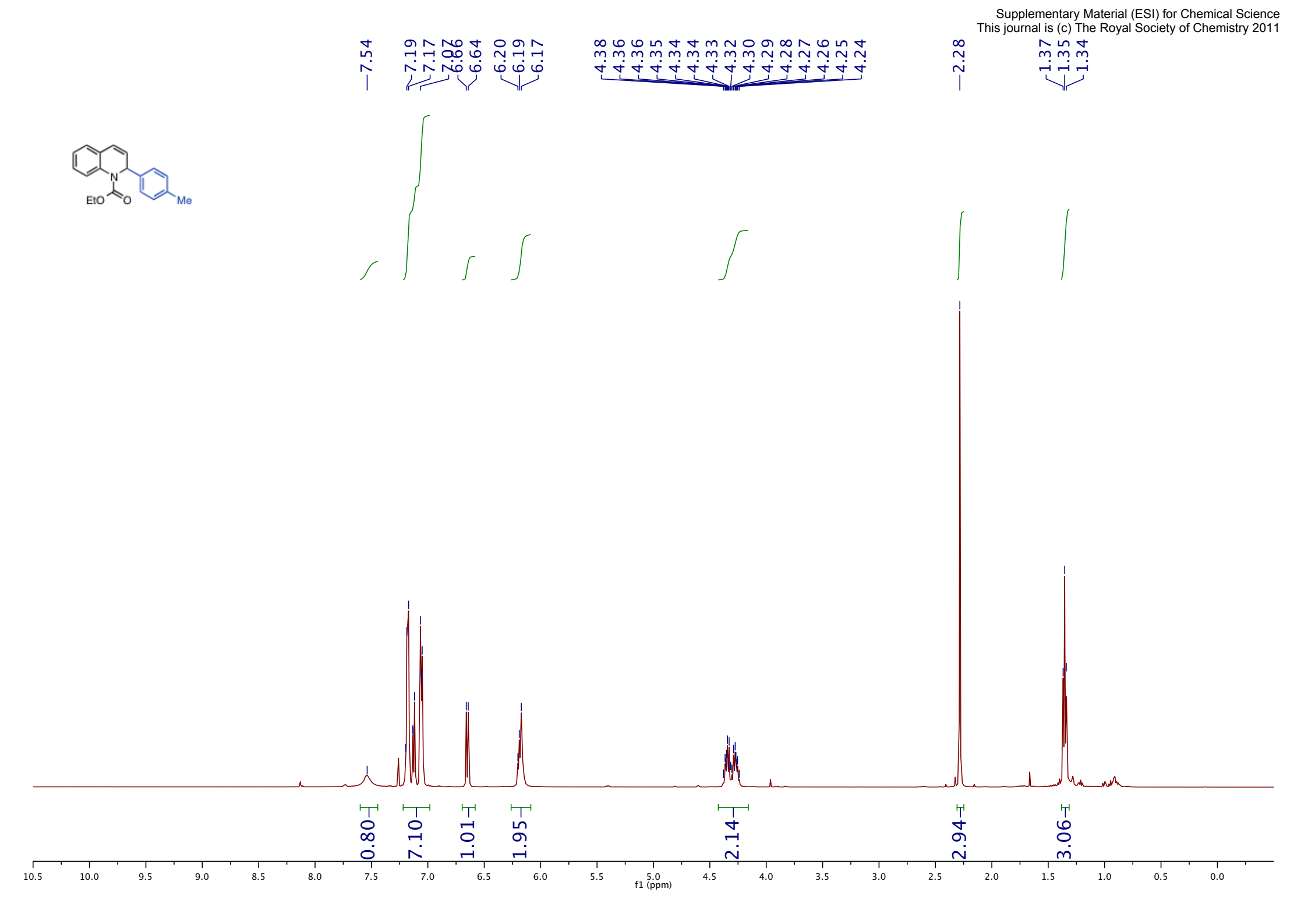
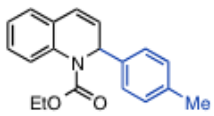
124.71
124.32
62.49
55.58
14.63






N
EtO
O
Me

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128.50
127.74
127.19
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126.35
125.25
124.64
124.18
62.36
55.38
21.20
14.61
220
210
200
190
180
170
160
150
140
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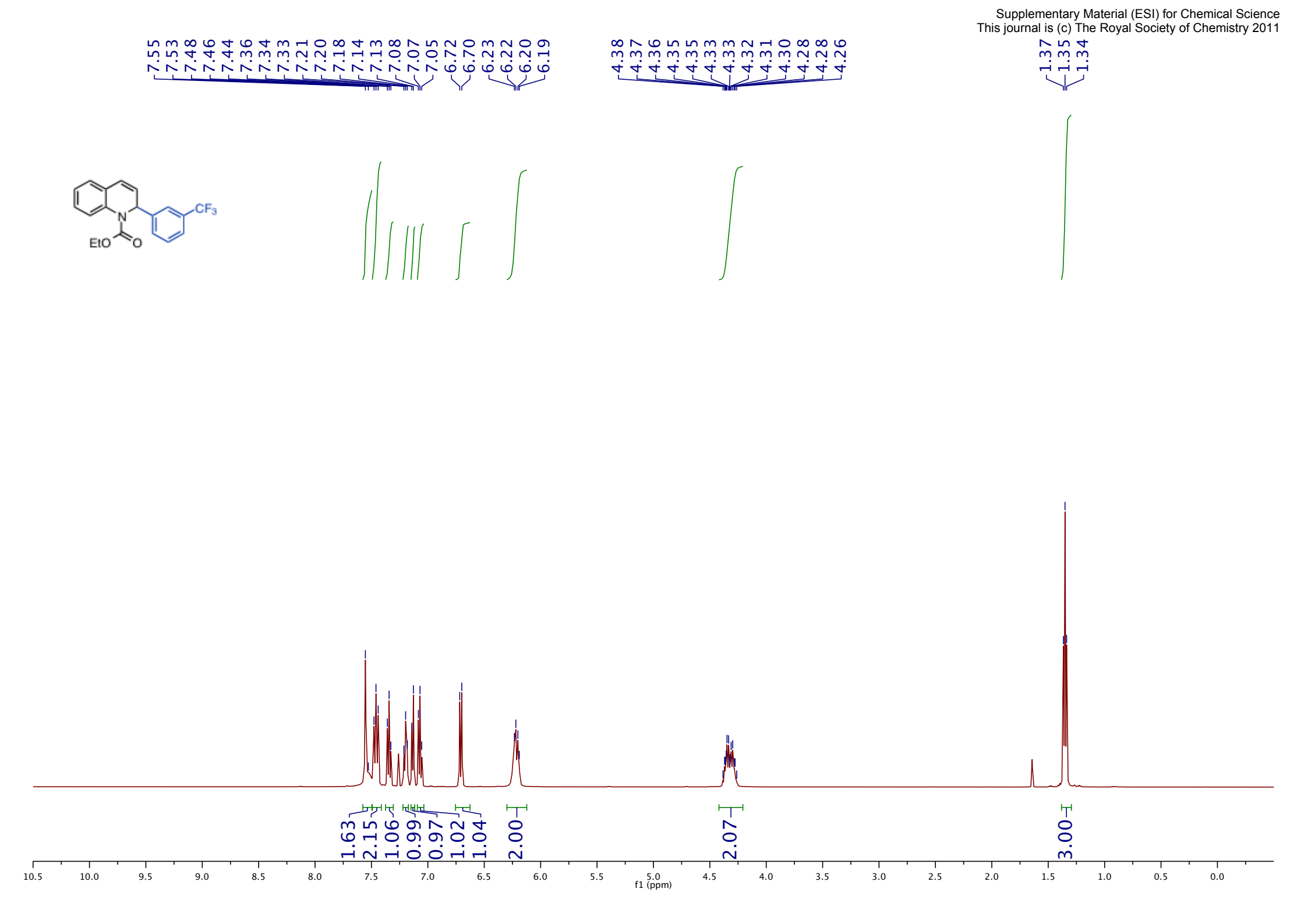
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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7.18
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7.13
7.08
7.07
7.05
6.72
6.70
6.23
6.22
6.20
6.19
4.38
4.37
4.36
4.35
4.35
4.33
4.33
4.32
4.31
4.30
4.28
4.28
4.26
1.37
1.35
1.34
CF3
N
EtO
O
1.63
2.15
1.06
0.99
0.97
1.02
1.04
2.00
2.07
3.00
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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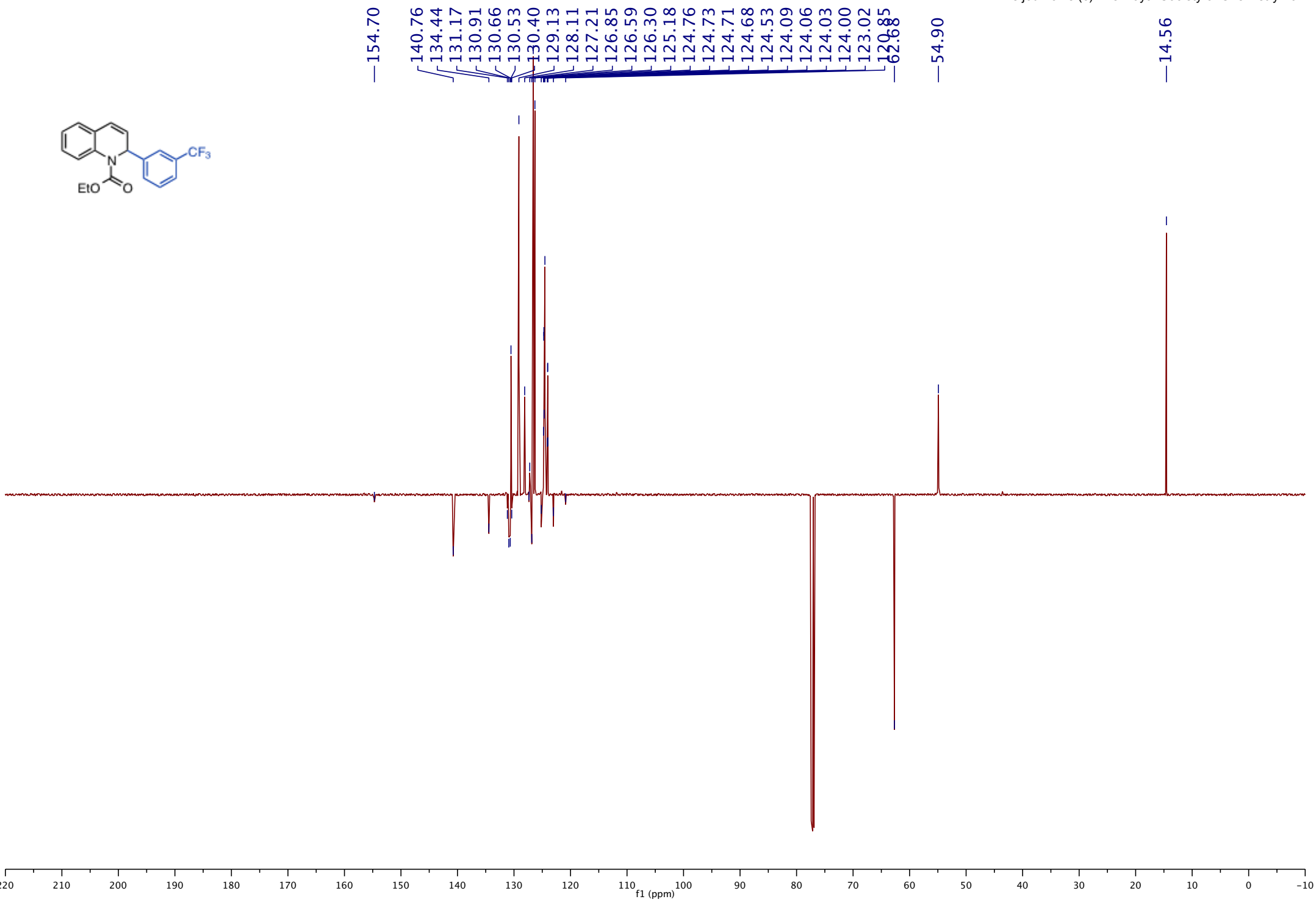
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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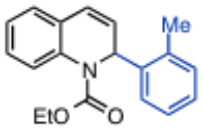
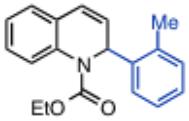
130.53
130.40
129.13
128.11
127.21
126.85
126.59
126.30
125.18
124.76
124.73
124.71
124.68
124.53
124.09
124.06
124.03
124.00
123.02
120.85
62.68
54.90
14.56
CF3
N
EtO
O
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)


Me
N
EtO
O

7.63
7.14
7.11
7.10
7.10
6.54
6.52
6.35
6.34
6.11
6.10
6.10
6.08
4.34
4.32
4.31
4.31
4.30
4.29
4.29
4.27
4.22
4.21
4.20
4.19
4.19
4.18
4.17
4.16
2.55
1.31
1.30
1.28
0.34
0.35
1.80
0.38
0.36
0.36
0.36
0.75
1.00
1.12
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)



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127.02
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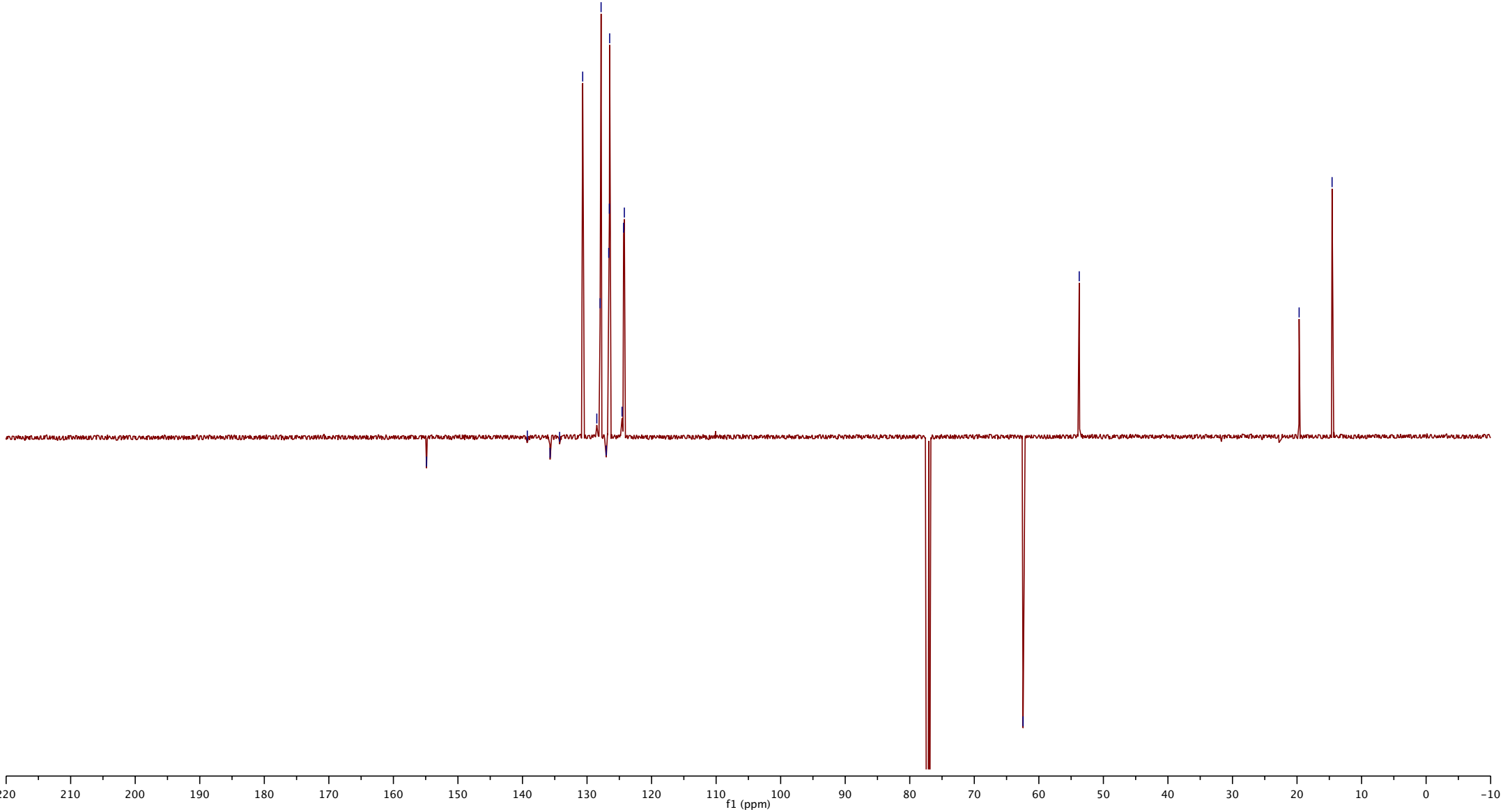
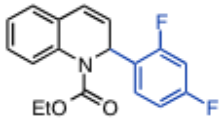
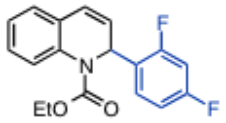
126.54
126.49
124.57
124.33
124.22

62.45
53.74

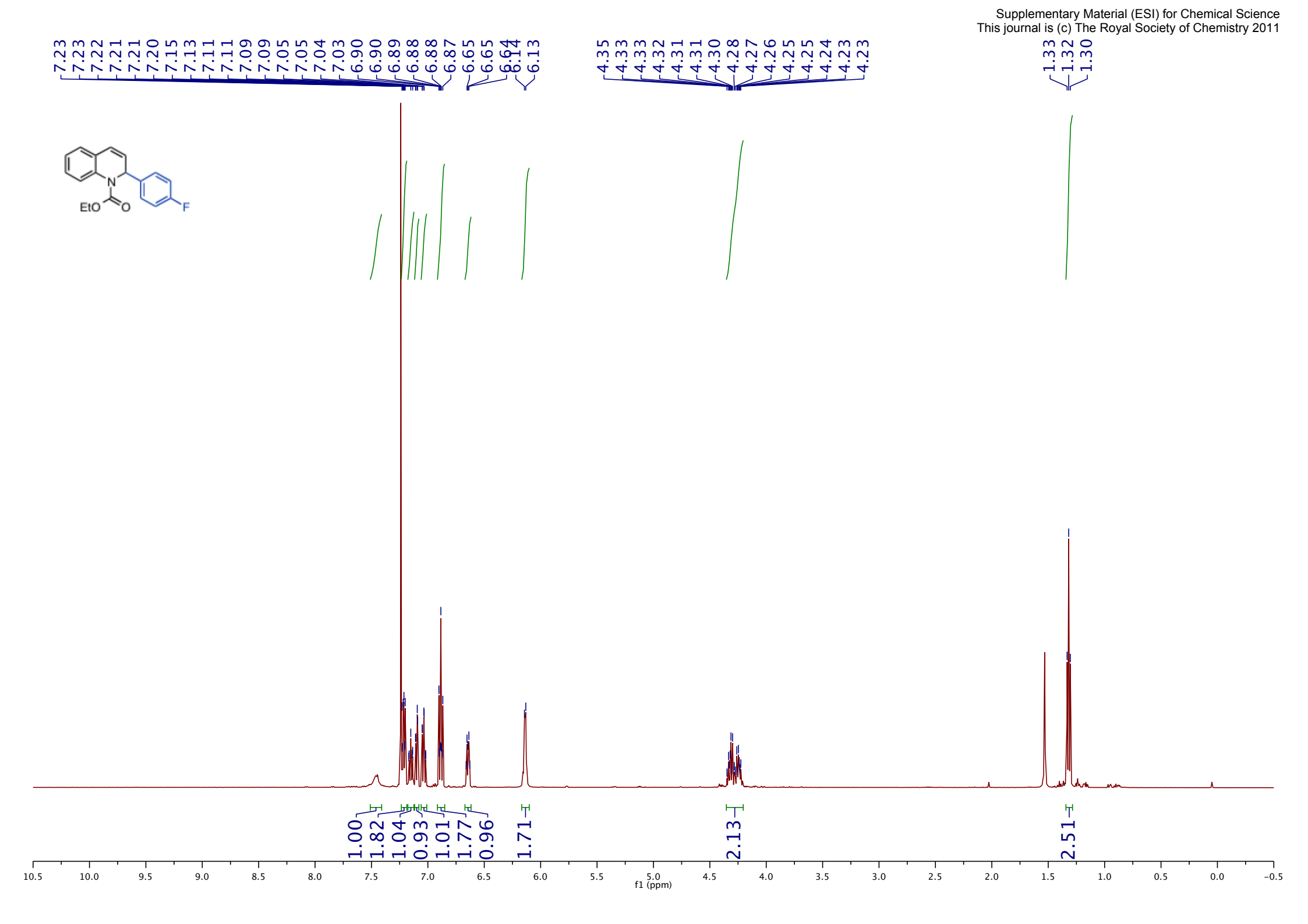
19.67
14.57

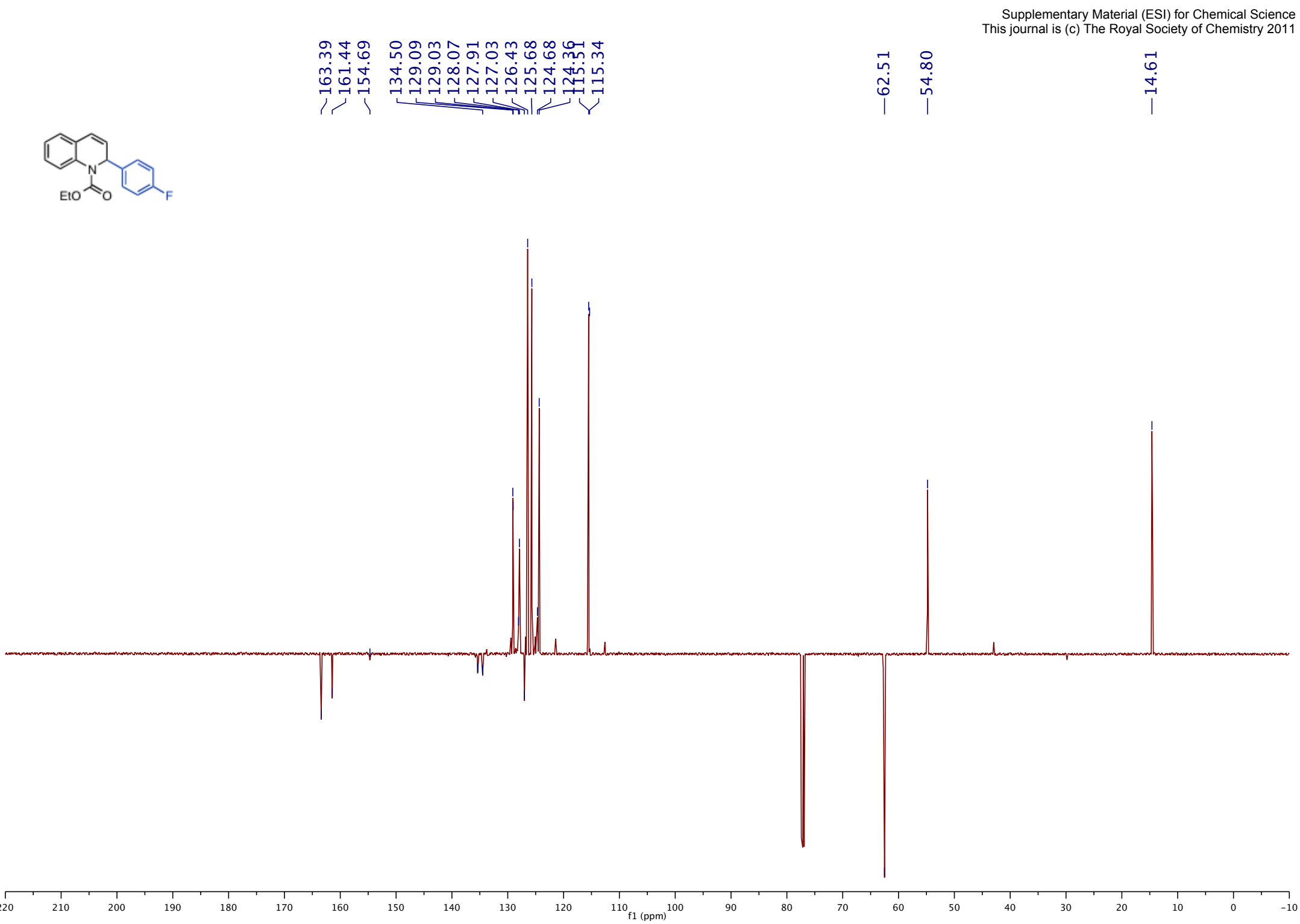


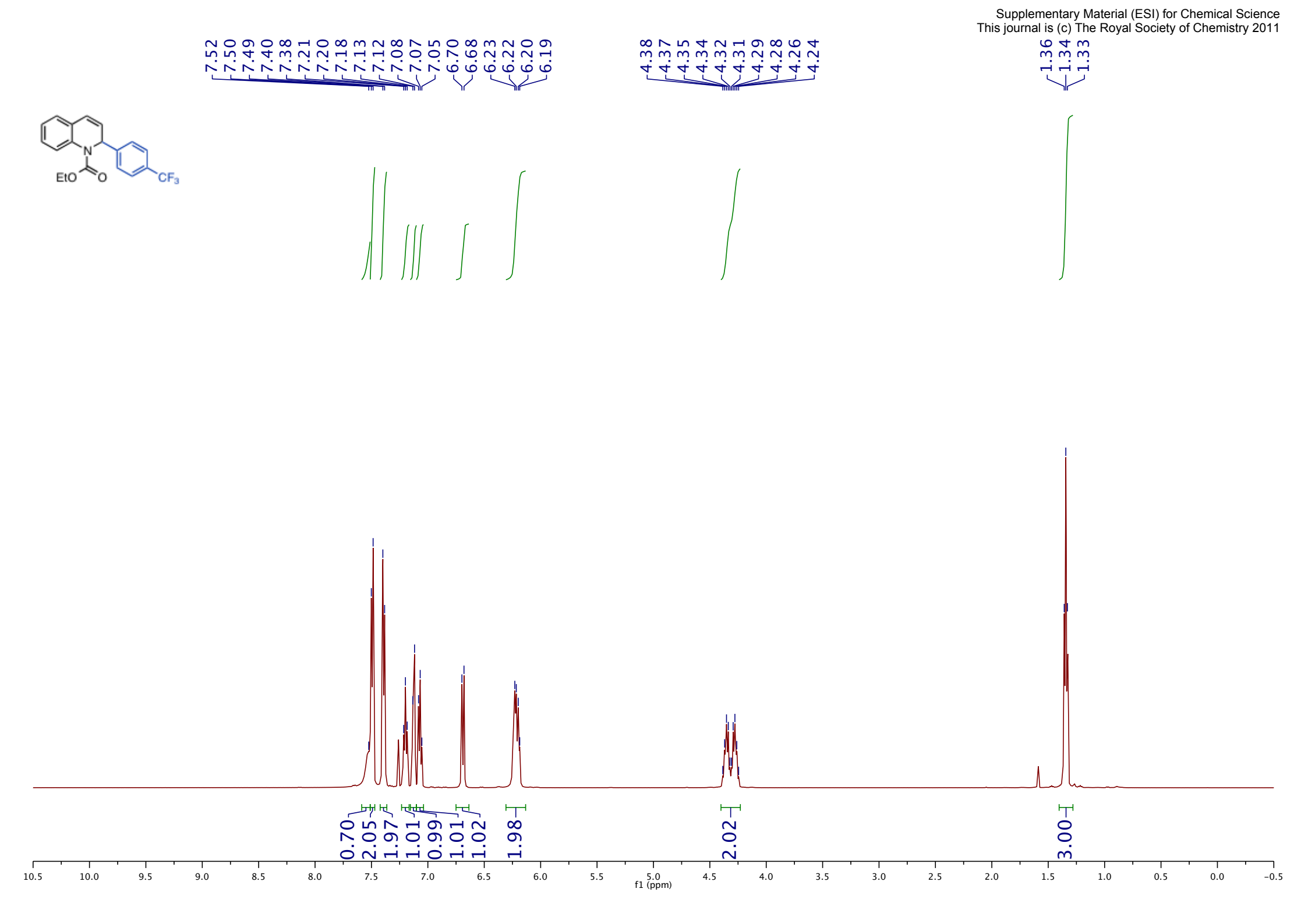


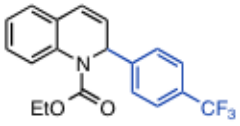


163.46
163.36
161.48
161.39
160.17
160.08
158.19
158.09
154.38
128.89
128.85
128.82
128.11
126.56
125.28
124.41
111.38
111.21
104.21
104.01
103.81
62.55
49.95
14.42



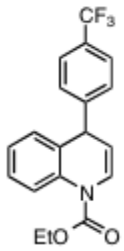

163.39
161.44
154.69
134.50
129.09
129.03
128.07
127.91
127.03
126.43
125.68
124.68
124.36
115.51
115.34
62.51
54.80
14.61
EtO
O
N
F
f1 (ppm)

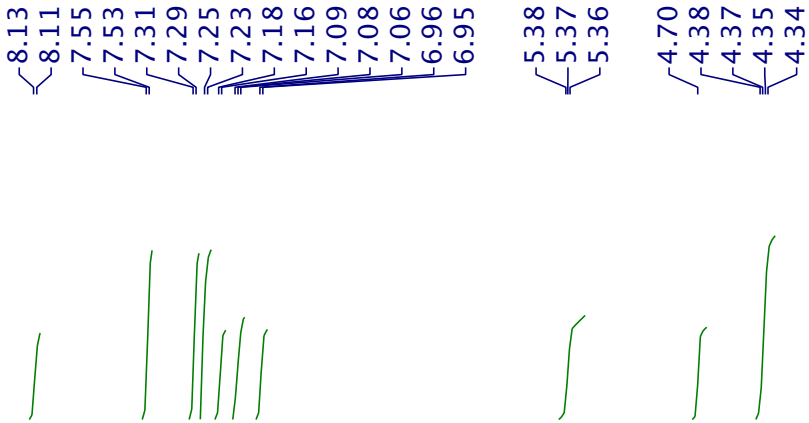


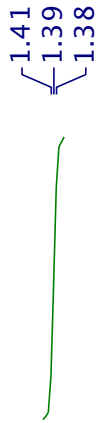


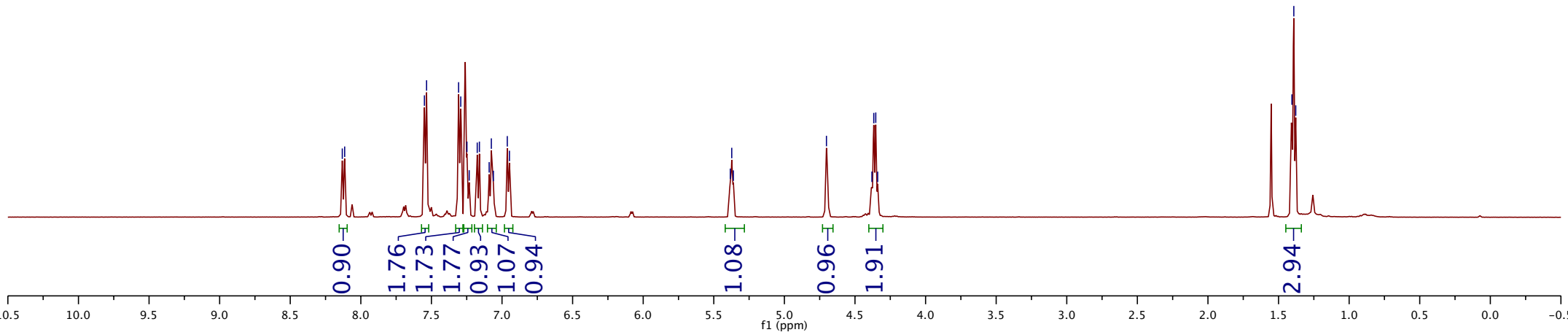
154.73
143.72
134.54
130.35
130.09
129.83
129.58
128.12
127.44
127.33
126.88
126.85
126.61
126.19
125.65
125.62
125.59
125.56
125.22
124.62
124.54
123.06
120.90
62.70
54.99
14.60

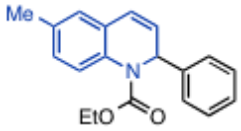
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)


CF3
N
EtO
O

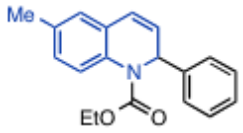

8.13
8.11
7.55
7.53
7.31
7.29
7.25
7.23
7.18
7.16
7.09
7.08
7.06
6.96
6.95
5.38
5.37
5.36
4.70
4.38
4.37
4.35
4.34


1.41
1.39
1.38


0.90
1.76
1.73
1.77
0.93
1.07
0.94
1.08
0.96
1.91
2.94
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

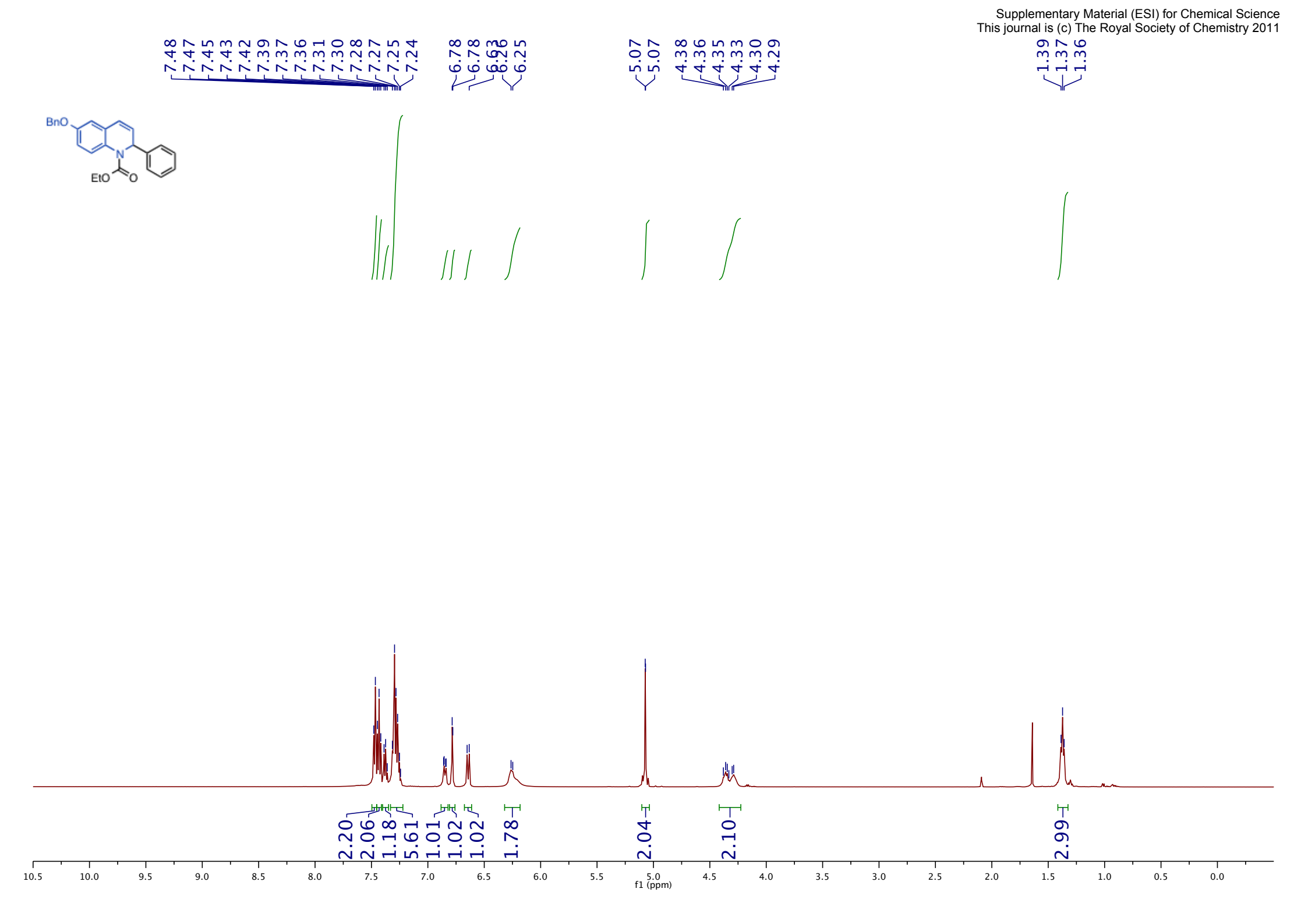

Me
N
EtO
O

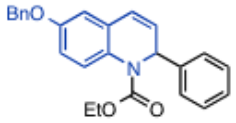
7.46
7.34
7.33
7.31
7.29
7.28
7.27
7.26
7.24
7.05
7.04
6.98
6.67
6.65
6.24
6.23
4.42
4.40
4.39
4.38
4.37
4.35
4.34
4.32
4.31
4.29
4.28
2.35
1.40
1.39
1.37
0.99
1.91
2.07
0.98
0.99
0.96
1.03
2.02
2.11
3.12
3.03
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)



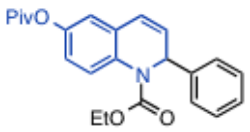
154.82
139.81
133.71
132.24
128.54
128.45
128.27
127.78
127.15
126.96
126.87
125.47
124.46
62.31
55.55
20.88
14.60

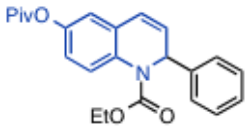
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)


7.48
7.47
7.45
7.43
7.42
7.39
7.37
7.36
7.31
7.30
7.28
7.27
7.25
7.24
6.78
6.78
6.63
6.26
6.25
5.07
5.07
4.38
4.36
4.35
4.33
4.30
4.29
1.39
1.37
1.36
BnO
N
EtO
O
2.20
2.06
1.18
5.61
1.01
1.02
1.02
1.78
2.04
2.10
2.99
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


BnO
N
EtO
O

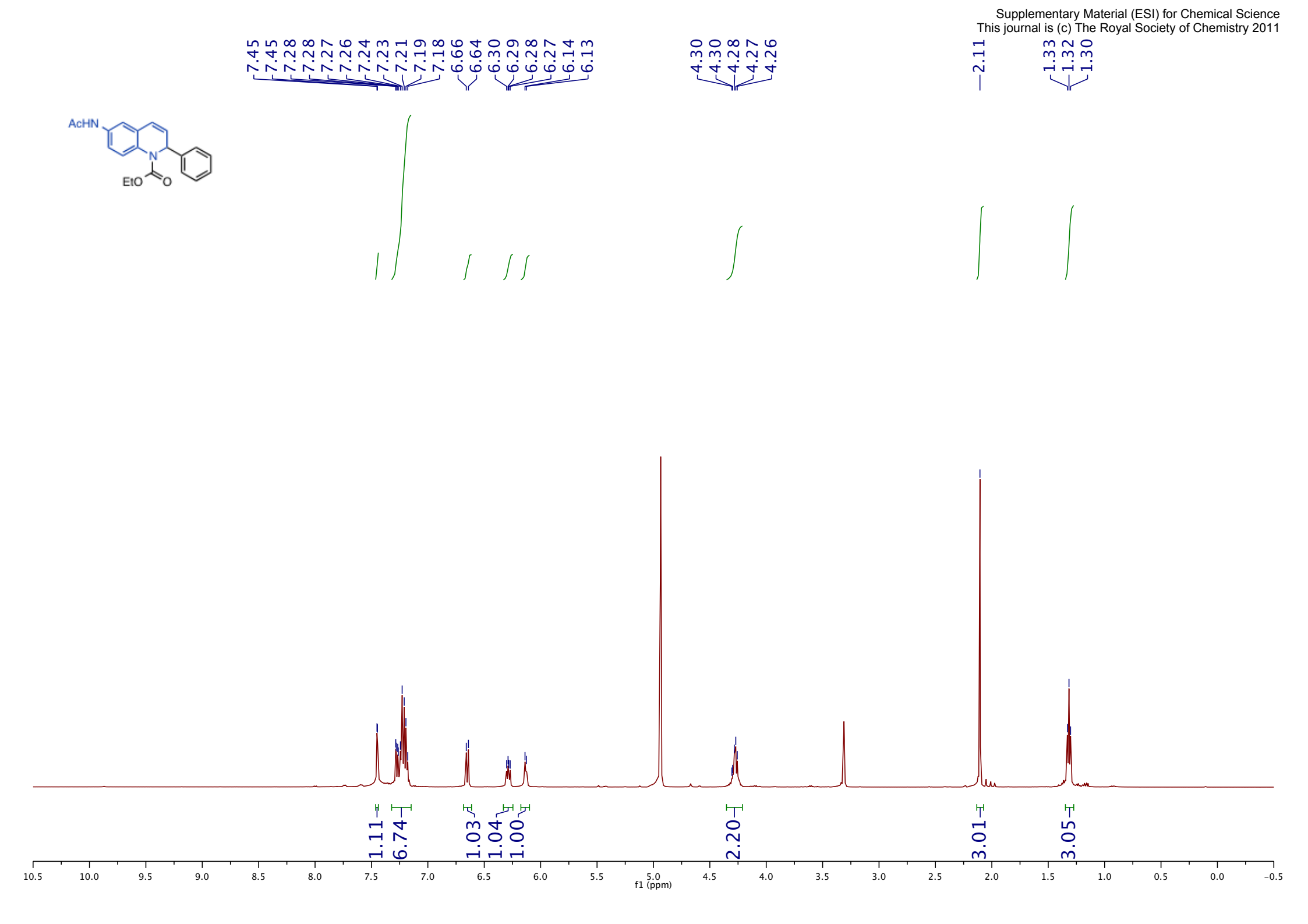
155.44
154.89
139.58
137.04
128.72
128.60
128.14
127.88
127.67
114.08
112.13
70.33
62.35
55.50
14.67
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

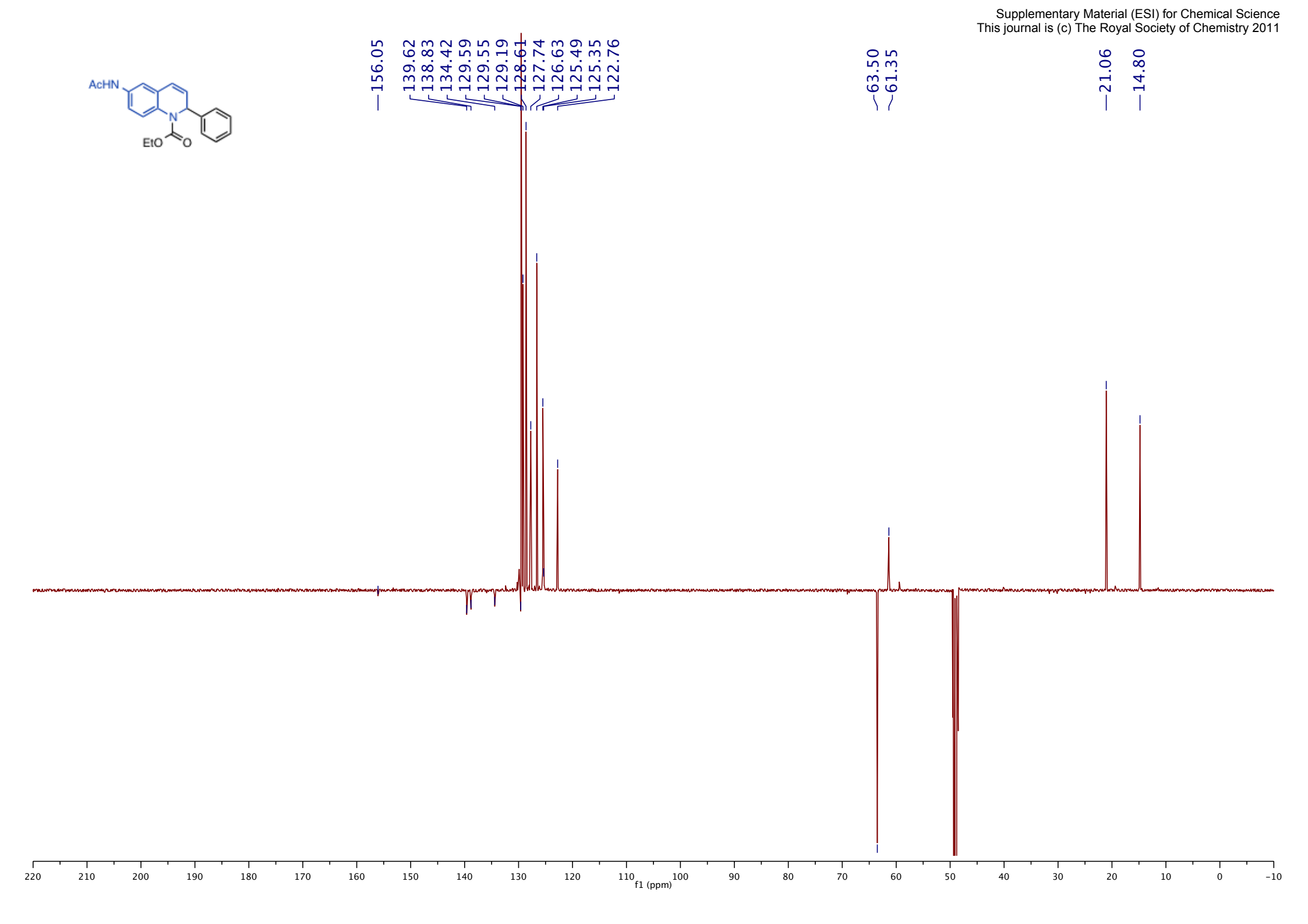


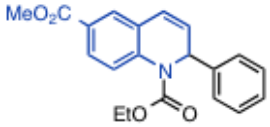


177.18
154.67
147.19
139.37
132.09
129.24
128.63
128.05
127.97
127.19
125.54
124.92
120.45
118.92
62.48
55.62
39.15
27.21
14.57

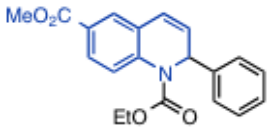
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)


7.45
7.45
7.28
7.28
7.27
7.26
7.24
7.23
7.21
7.19
7.18
6.66
6.64
6.30
6.29
6.28
6.27
6.14
6.13
4.30
4.30
4.28
4.27
4.26
2.11
1.33
1.32
1.30
AcHN
N
EtO
O
1.11
6.74
1.03
1.04
1.00
2.20
3.01
3.05
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

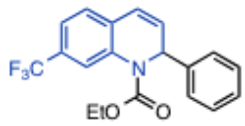



MeO2C
N
EtO
O

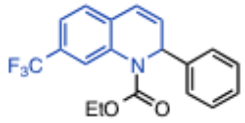
7.86
7.85
7.84
7.83
7.81
7.81
7.64
7.62
7.25
7.23
7.23
6.70
6.68
6.23
6.22
6.21
6.20
6.18
6.17
4.36
4.34
4.33
4.32
4.30
4.29
4.28
4.27
3.90
1.36
1.35
1.33
2.00
0.88
5.00
0.99
1.97
2.07
2.94
3.00
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)



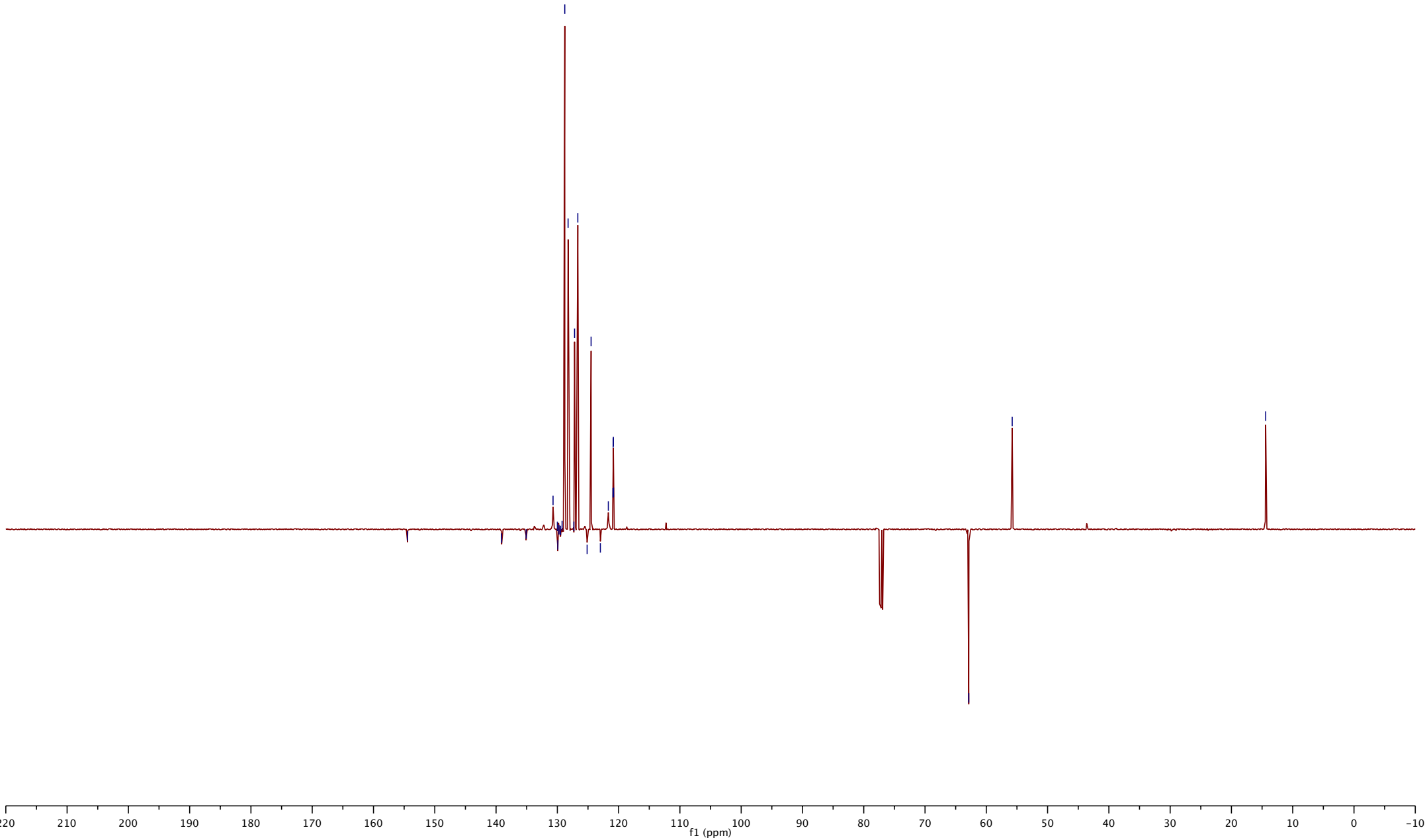
166.67
154.34
139.34
139.09
129.15
128.90
128.65
128.10
127.84
127.06
126.75
125.54
124.78
124.07
62.75
56.04
52.13
14.47

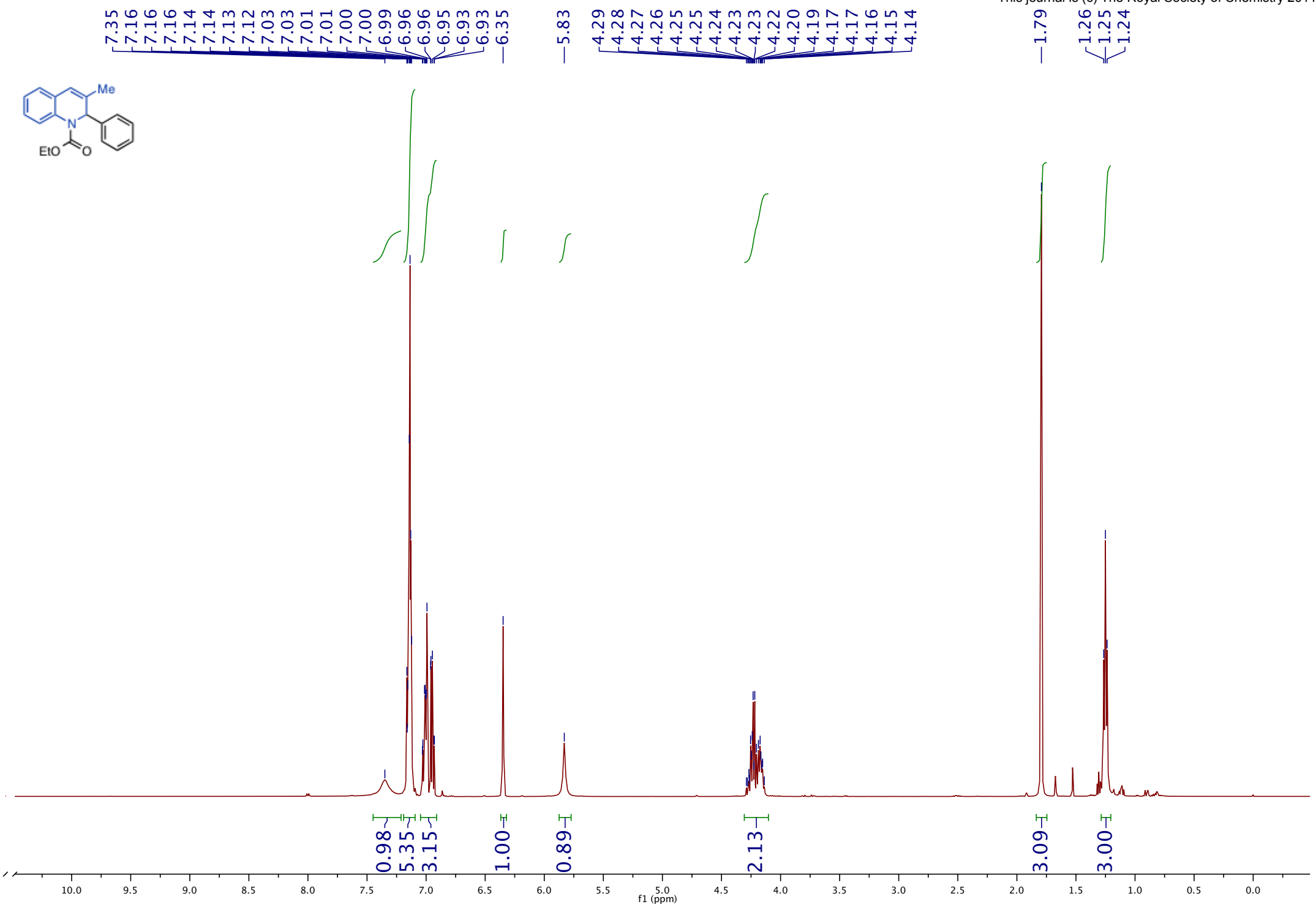

F3C
N
EtO
O

7.86
7.29
7.27
7.27
7.26
7.23
6.71
6.69
6.32
6.31
6.30
6.29
6.24
6.23
4.40
4.39
4.38
4.38
4.37
4.36
4.35
4.34
4.31
4.30
4.29
4.29
4.28
4.27
4.26
4.25
1.37
1.36
1.34
0.88
2.34
2.35
1.09
1.11
1.01
2.29
3.30
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)



154.45
139.09
135.09
130.70
130.00
129.92
129.74
129.48
129.23
128.79
128.25
127.30
127.19
126.66
125.14
124.49
122.98
121.68
120.92
120.89
120.86
120.83
62.86
55.77
14.41




7.35
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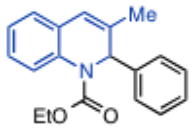
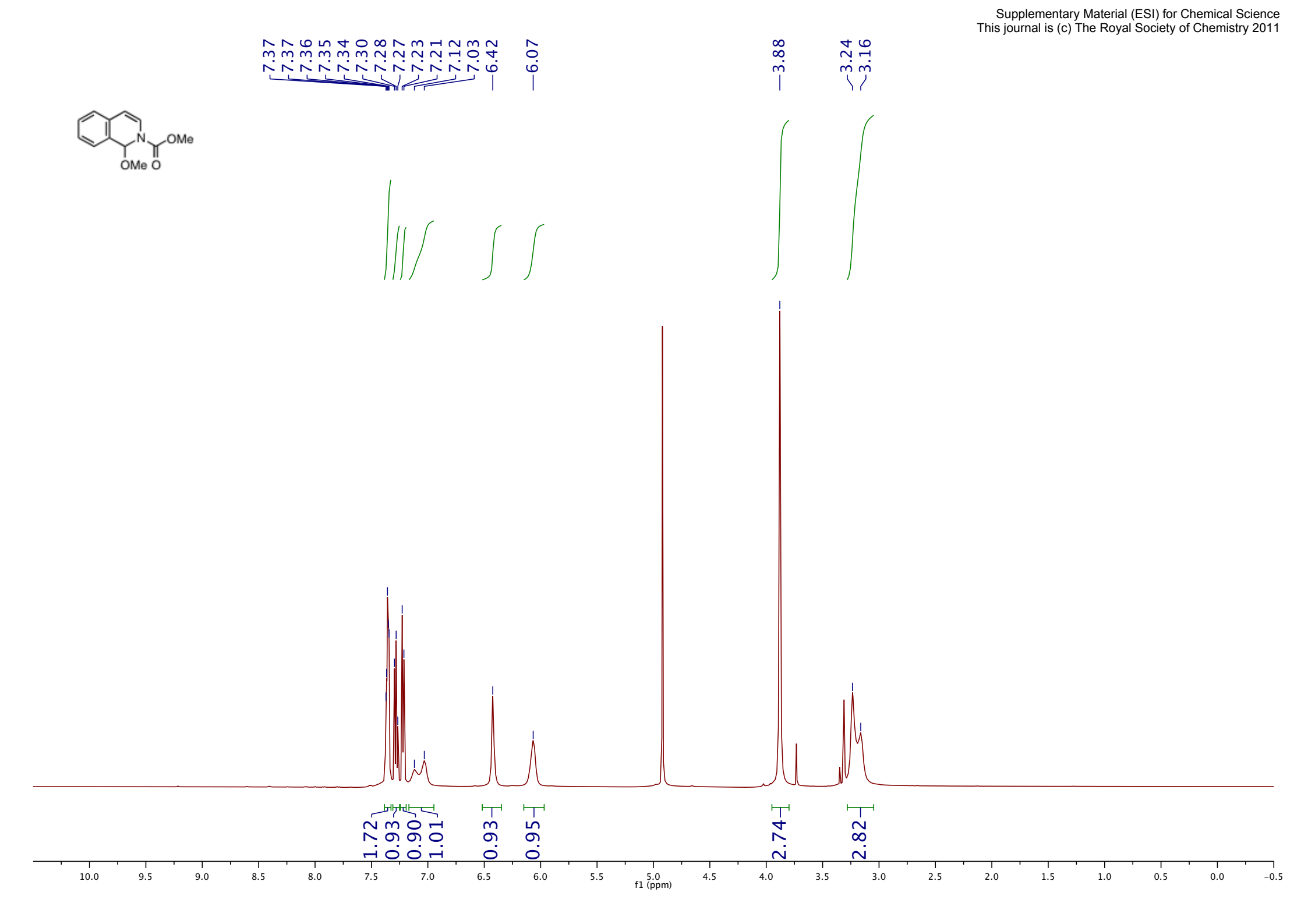
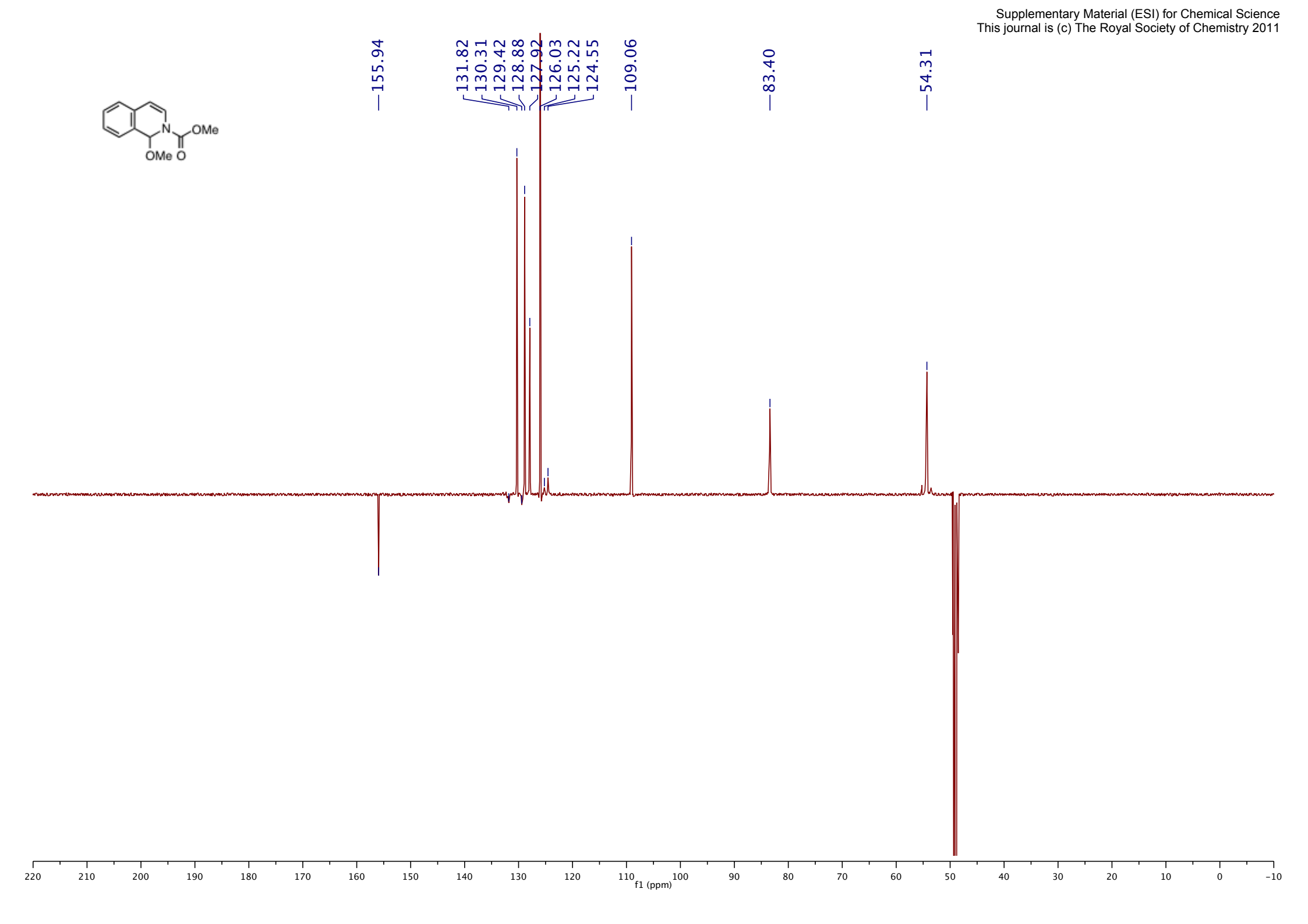
7.16
7.16
7.14
7.14
7.13
7.12
7.03
7.03
7.01
7.01
7.00
7.00
6.99
6.96
6.96
6.95
6.93
6.93
6.35
5.83
4.29
4.28
4.27
4.26
4.25
4.25
4.24
4.23
4.23
4.22
4.20
4.19
4.17
4.17
4.16
4.15
4.14
1.79
1.26
1.25
1.24
Me
N
EtO
O
0.98
5.35
3.15
1.00
0.89
2.13
3.09
3.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)



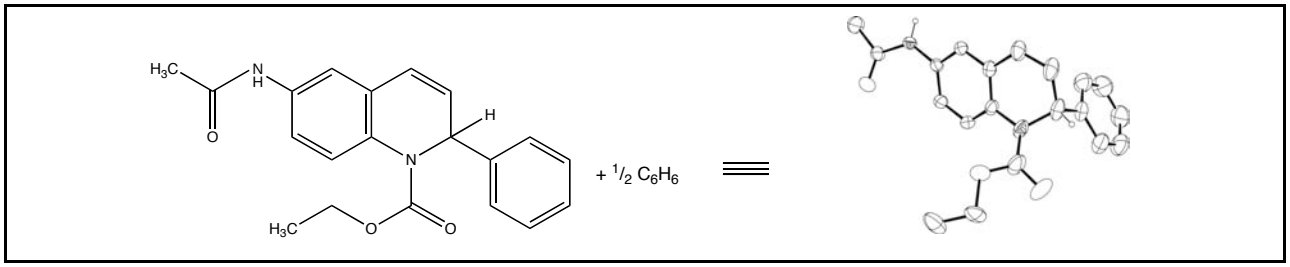
156.05
139.62
138.83
134.42
129.59
129.55
129.19
128.61
127.74
126.63
125.49
125.35
122.76
63.50
61.35
21.06
14.80

220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)





X-ray Structure Determination of Compound 99167



Compound 99167, $C_{23}H_{23}N_2O_3$, crystallizes in the monoclinic space group $P2_1/c$ (systematic absences 0k0: k=odd and h0l: l=odd) with a=12.0405(3)Å, b=17.1549(4)Å, c=10.0631(3)Å, β=90.4060(10)°, V=2078.52(9)Å^3, Z=4, and d_{calc}=1.200 g/cm^3 . X-ray intensity data were collected on a Bruker APEXII CCD area detector employing graphite-monochromated Mo-Kα radiation (λ=0.71073 Å) at a temperature of 296(1)K. Preliminary indexing was performed from a series of thirty-six 0.5° rotation frames with exposures of 20 seconds. A total of 2461 frames were collected with a crystal to detector distance of 37.628 mm, rotation widths of 0.5° and exposures of 20 seconds:

scan type	2θ	ω	ϕ	χ	frames
ϕ	24.50	78.84	-15.62	-35.57	739
ϕ	12.00	90.98	73.22	-20.60	118
ω	22.00	-31.37	-182.23	39.97	126
ϕ	-20.50	295.58	78.84	30.75	404
ϕ	24.50	12.92	-351.92	19.46	739
ϕ	-25.50	262.32	-333.54	55.93	335

Rotation frames were integrated using SAINT[1], producing a listing of unaveraged F^2 and $\sigma(F^2)$ values which were then passed to the SHELXTL[2] program package for further processing and structure solution on a Dell Pentium 4 computer. A total of 36138 reflections were measured over the ranges $1.69 \leq \theta \leq 25.08°$, $-14 \leq h \leq 14$, $-20 \leq k \leq 20$, $-11 \leq l \leq 12$ yielding 3689 unique reflections (Rint = 0.0222). The intensity data were corrected for Lorentz and polarization effects and for absorption using SADABS[3] (minimum and maximum transmission 0.6850, 0.7452).

The structure was solved by direct methods (SHELXS-97[4]). The structure includes a molecule of benzene that lies on a crystallographic center of symmetry (at ½, ½, ½); thus, the asymmetric unit consists of one molecule of the title compound plus ½ of a molecule of benzene. The C20-C19-O3-C18-O2 moiety is

disordered by a slight rotation about the N1-C18 bond. The two disorder contributions are present in a relative ratio of 0.55/0.45. Refinement was by full-matrix least squares based on F^2 using SHELXL-97.[5] All reflections were used during refinement. The weighting scheme used was $w=1/[\sigma^2(F_o^2)+ (0.0675P)^2 + 0.5956P]$ where $P = (F_o^2 + 2F_c^2)/3$. Non-hydrogen atoms were refined anisotropically and hydrogen atoms were refined using a riding model. Refinement converged to R1=0.0479 and wR2=0.1272 for 3058 observed reflections for which $F > 4\sigma(F)$ and R1=0.0580 and wR2=0.1376 and GOF =1.018 for all 3689 unique, non-zero reflections and 291 variables.[6] The maximum Δ/σ in the final cycle of least squares was 0.000 and the two most prominent peaks in the final difference Fourier were +0.208 and -0.274 e/Å^3.

Table 1. lists cell information, data collection parameters, and refinement data. Final positional and equivalent isotropic thermal parameters are given in Tables 2. and 3. Anisotropic thermal parameters are in Table 4. Tables 5. and 6. list bond distances and bond angles. Figure 1. is an ORTEP[7] representation of the molecule with 30% probability thermal ellipsoids displayed.

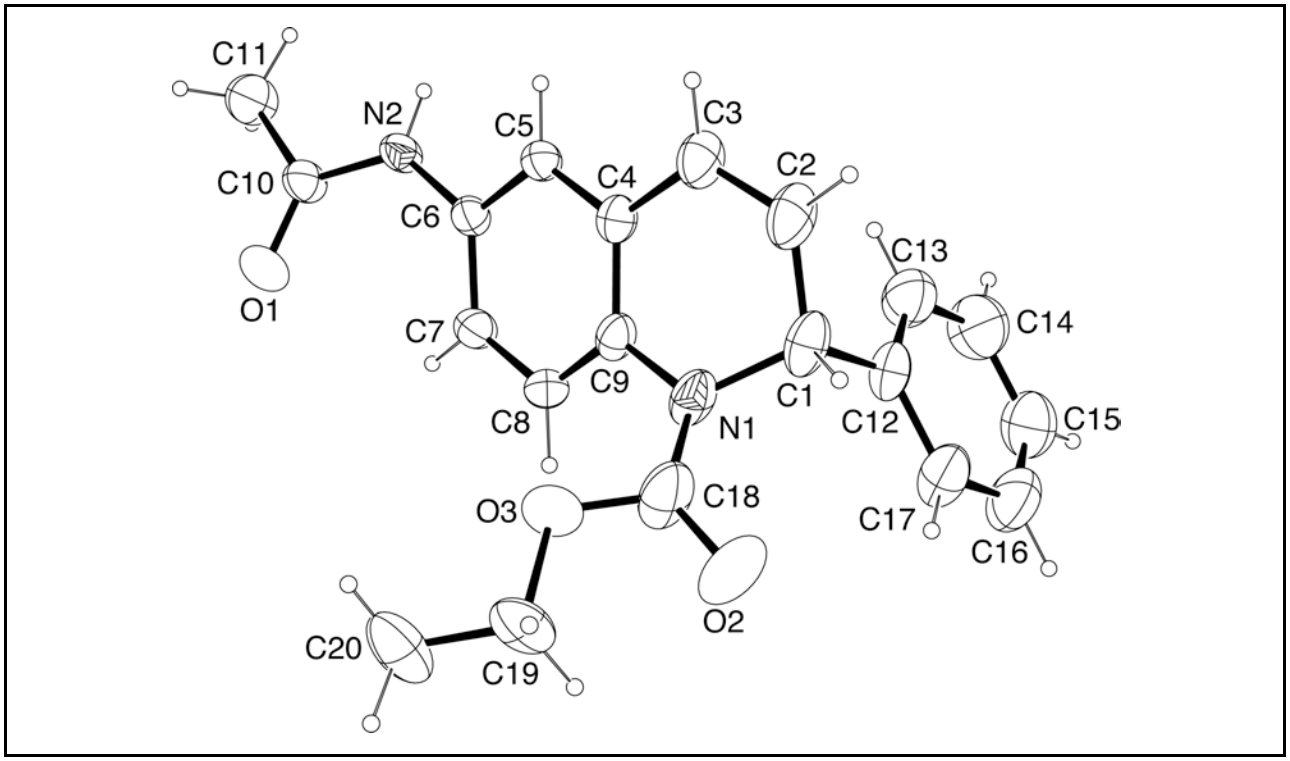


Figure 1. ORTEP drawing of the title compound with 30% probability thermal ellipsoids.

Table 1. Summary of Structure Determination of Compound 99167

Empirical formula	$C_{23}H_{23}N_2O_33$
Formula weight	375.43
Temperature	296(1) K
Wavelength	0.71073 Å
Crystal system	monoclinic
Space group	$P2_1/c$
Cell constants:	
a	12.0405(3) Å
b	17.1549(4) Å
c	10.0631(3) Å
β	90.4060(10)°
Volume	2078.52(9) $Å^3$
Z	4
Density (calculated)	1.200 Mg/m^3
Absorption coefficient	0.080 mm^{-1}
F(000)	796
Crystal size	0.38 x 0.15 x 0.10 mm^3
Theta range for data collection	1.69 to 25.08°
Index ranges	$-14 \le h \le 14, -20 \le k \le 20, -11 \le l \le 12$
Reflections collected	36138
Independent reflections	3689 [R(int) = 0.0222]
Completeness to theta = 25.08°	99.8 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7452 and 0.6850
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3689 / 36 / 291
Goodness-of-fit on F^2	1.018
Final R indices [I>2sigma(I)]	R1 = 0.0479, wR2 = 0.1272
R indices (all data)	R1 = 0.0580, wR2 = 0.1376
Largest diff. peak and hole	0.208 and -0.274 $e.Å^{-3}$

Table 2. Refined Positional Parameters for Compound 99167

Atom	x	y	z	U_{eq}, Å^2
C1	0.23839(17)	0.34926(10)	0.8690(2)	0.0697(6)
C2	0.17078(18)	0.37839(12)	0.9822(3)	0.0768(6)
C3	0.13632(16)	0.45152(11)	0.9881(2)	0.0649(5)
C4	0.16594(13)	0.50733(9)	0.88544(17)	0.0474(4)
C5	0.15184(13)	0.58696(9)	0.90305(15)	0.0442(4)
C6	0.18362(13)	0.63943(9)	0.80644(14)	0.0429(4)
C7	0.23379(15)	0.61195(10)	0.69219(16)	0.0510(4)
C8	0.24717(15)	0.53269(10)	0.67332(16)	0.0536(4)
C9	0.21033(13)	0.48007(9)	0.76697(17)	0.0487(4)
C10	0.14439(16)	0.77552(10)	0.74079(17)	0.0545(4)
C11	0.1253(2)	0.85571(12)	0.7967(2)	0.0854(7)
C12	0.36205(17)	0.34253(11)	0.8980(2)	0.0655(5)
C13	0.4148(2)	0.38785(15)	0.9911(3)	0.0866(7)
C14	0.5283(2)	0.3808(2)	1.0128(3)	0.1065(9)
C15	0.5887(2)	0.3287(2)	0.9420(3)	0.1037(9)
C16	0.5381(2)	0.28362(17)	0.8485(3)	0.0998(8)
C17	0.4249(2)	0.29035(13)	0.8257(3)	0.0846(7)
C21	0.5302(3)	0.4710(3)	0.6199(4)	0.1347(14)
C22	0.5395(3)	0.5493(3)	0.5950(4)	0.1312(12)
C23	0.5087(4)	0.5775(2)	0.4749(5)	0.1315(13)
O1	0.14244(14)	0.76328(8)	0.62170(12)	0.0723(4)
C18	0.1885(2)	0.35882(13)	0.6384(3)	0.0972(9)
O2	0.2115(7)	0.2922(4)	0.6052(8)	0.113(3)
O3	0.1343(4)	0.4040(3)	0.5574(4)	0.0707(12)
C19	0.1138(6)	0.3638(2)	0.4328(4)	0.0760(12)
C20	0.0805(7)	0.4246(3)	0.3394(6)	0.1024(19)
O2'	0.1723(9)	0.2873(4)	0.6447(10)	0.096(3)
O3'	0.1806(5)	0.4133(4)	0.5225(5)	0.094(2)
C19'	0.1762(6)	0.3907(5)	0.3743(7)	0.108(2)
C20'	0.0597(8)	0.3740(8)	0.3627(14)	0.174(5)
N1	0.21686(13)	0.39754(8)	0.75018(17)	0.0634(4)
N2	0.16507(13)	0.71963(7)	0.83155(13)	0.0502(4)

$U_{eq}={}^1/_3[U_{11}(aa^*)^2+U_{22}(bb^*)^2+U_{33}(cc^*)^2+2U_{12}aa^*bb^*\cos\gamma+2U_{13}aa^*cc^*\cos\beta+2U_{23}bb^*cc^*\cos\alpha]$

Table 3. Positional Parameters for Hydrogens in Compound 99167

Atom	x	y	z	U_{iso}, Å^2
H1	0.2117	0.2966	0.8484	0.093
H2	0.1524	0.3443	1.0504	0.102
H3	0.0926	0.4675	1.0589	0.086
H5	0.1205	0.6053	0.9812	0.059
H7	0.2585	0.6468	0.6281	0.068
H8	0.2814	0.5146	0.5967	0.071
H11a	0.1861	0.8890	0.7732	0.128
H11b	0.1201	0.8526	0.8917	0.128
H11c	0.0575	0.8766	0.7608	0.128
H13	0.3742	0.4237	1.0402	0.115
H14	0.5632	0.4120	1.0762	0.142
H15	0.6647	0.3239	0.9574	0.138
H16	0.5796	0.2481	0.7997	0.133
H17	0.3909	0.2595	0.7612	0.112
H21	0.5508	0.4512	0.7025	0.179
H22	0.5668	0.5827	0.6603	0.174
H23	0.5144	0.6306	0.4576	0.175
H19a	0.0552	0.3255	0.4425	0.101
H19b	0.1805	0.3376	0.4026	0.101
H20a	0.0633	0.4016	0.2547	0.154
H20b	0.1402	0.4612	0.3294	0.154
H20c	0.0162	0.4511	0.3725	0.154
H19a'	0.1982	0.4335	0.3173	0.144
H19b'	0.2216	0.3453	0.3556	0.144
H20a'	0.0438	0.3541	0.2754	0.261
H20b'	0.0179	0.4208	0.3771	0.261
H20c'	0.0395	0.3357	0.4279	0.261
H2a	0.1672	0.7341	0.9133	0.067

Table 4. Refined Thermal Parameters (U's) for Compound 99167

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C1	0.0709(12)	0.0337(9)	0.1045(16)	0.0067(9)	-0.0102(11)	0.0022(8)
C2	0.0743(13)	0.0478(11)	0.1085(17)	0.0243(11)	0.0140(12)	0.0041(9)
C3	0.0640(11)	0.0494(10)	0.0814(13)	0.0180(9)	0.0107(10)	0.0019(8)
C4	0.0469(8)	0.0398(8)	0.0554(9)	0.0035(7)	-0.0035(7)	0.0003(7)
C5	0.0526(9)	0.0401(8)	0.0399(8)	0.0004(6)	0.0011(6)	0.0019(7)
C6	0.0543(9)	0.0362(8)	0.0382(8)	-0.0013(6)	-0.0048(6)	-0.0003(6)
C7	0.0660(11)	0.0469(9)	0.0403(8)	0.0017(7)	0.0033(7)	0.0026(8)
C8	0.0654(11)	0.0527(10)	0.0427(9)	-0.0099(7)	-0.0020(7)	0.0107(8)
C9	0.0515(9)	0.0375(8)	0.0570(10)	-0.0068(7)	-0.0130(7)	0.0052(7)
C10	0.0779(12)	0.0400(9)	0.0455(10)	0.0062(7)	0.0039(8)	-0.0002(8)
C11	0.140(2)	0.0444(11)	0.0717(14)	0.0039(9)	0.0072(13)	0.0156(12)
C12	0.0683(12)	0.0445(10)	0.0837(14)	0.0117(9)	-0.0064(10)	0.0090(9)
C13	0.0832(16)	0.0867(16)	0.0897(16)	-0.0094(13)	-0.0143(13)	0.0141(13)
C14	0.0858(18)	0.130(3)	0.103(2)	-0.0115(18)	-0.0294(15)	0.0099(17)
C15	0.0743(16)	0.126(2)	0.111(2)	0.0066(19)	-0.0205(15)	0.0216(16)
C16	0.0824(17)	0.0971(19)	0.120(2)	-0.0020(17)	-0.0044(15)	0.0329(14)
C17	0.0818(15)	0.0648(13)	0.1069(18)	-0.0045(13)	-0.0105(13)	0.0155(11)
C21	0.137(3)	0.163(4)	0.105(3)	0.029(3)	0.036(2)	0.047(3)
C22	0.130(3)	0.144(4)	0.120(3)	-0.014(3)	0.036(2)	0.013(2)
C23	0.147(3)	0.108(3)	0.140(3)	0.014(3)	0.056(3)	0.028(2)
O1	0.1190(12)	0.0556(8)	0.0424(7)	0.0106(6)	0.0029(7)	0.0071(7)
C18	0.117(2)	0.0581(13)	0.116(2)	-0.0373(13)	-0.0518(17)	0.0227(13)
O2	0.121(5)	0.069(3)	0.149(7)	-0.063(4)	-0.046(4)	0.030(3)
O3	0.087(3)	0.0653(18)	0.0599(19)	-0.0196(15)	-0.0105(17)	-0.012(2)
C19	0.099(3)	0.072(3)	0.056(2)	-0.0171(19)	-0.022(2)	-0.027(2)
C20	0.131(5)	0.109(4)	0.067(3)	0.007(3)	-0.039(3)	-0.028(4)
O2'	0.148(8)	0.040(2)	0.102(4)	-0.028(2)	0.011(4)	-0.003(3)
O3'	0.110(5)	0.084(4)	0.088(4)	-0.047(3)	-0.047(3)	0.046(3)
C19'	0.113(5)	0.098(5)	0.113(5)	-0.024(4)	-0.020(5)	0.005(4)
C20'	0.102(6)	0.239(16)	0.182(11)	-0.003(11)	-0.037(7)	-0.036(8)
N1	0.0686(10)	0.0378(8)	0.0834(11)	-0.0138(7)	-0.0186(8)	0.0065(7)
N2	0.0784(10)	0.0364(7)	0.0357(7)	-0.0005(5)	0.0003(6)	0.0020(6)

The form of the anisotropic displacement parameter is:

$\exp[-2\pi^2(a^{*2}U_{11}h^2+b^{*2}U_{22}k^2+c^{*2}U_{33}l^2+2b^*c^*U_{23}kl+2a^*c^*U_{13}hl+2a^*b^*U_{12}hk)]$

Table 5. Bond Distances in Compound 99167, Å

C1-N1	1.476(3)	C1-C2	1.491(3)	C1-C12	1.520(3)
C2-C3	1.323(3)	C3-C4	1.455(2)	C4-C5	1.388(2)
C4-C9	1.391(2)	C5-C6	1.381(2)	C6-C7	1.385(2)
C6-N2	1.417(2)	C7-C8	1.382(2)	C8-C9	1.380(2)
C9-N1	1.428(2)	C10-O1	1.217(2)	C10-N2	1.346(2)
C10-C11	1.504(3)	C12-C13	1.371(3)	C12-C17	1.382(3)
C13-C14	1.388(4)	C14-C15	1.357(4)	C15-C16	1.359(4)
C16-C17	1.385(4)	C21-C23#1	1.347(6)	C21-C22	1.372(5)
C22-C23	1.351(5)	C23-C21#1	1.347(6)	C18-O2	1.223(6)
C18-O2'	1.245(7)	C18-O3	1.297(5)	C18-N1	1.349(3)
C18-O3'	1.497(6)	O3-C19	1.451(5)	C19-C20	1.459(6)
O3'-C19'	1.541(7)	C19'-C20'	1.436(8)		

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,-y+1,-z+1

Table 6. Bond Angles in Compound 99167, °

N1-C1-C2	109.71(15)	N1-C1-C12	111.36(17)	C2-C1-C12	114.72(19)
C3-C2-C1	121.68(19)	C2-C3-C4	120.90(19)	C5-C4-C9	119.23(15)
C5-C4-C3	121.74(16)	C9-C4-C3	119.02(16)	C6-C5-C4	121.12(15)
C5-C6-C7	119.15(14)	C5-C6-N2	117.55(14)	C7-C6-N2	123.28(14)
C8-C7-C6	120.04(15)	C9-C8-C7	120.73(15)	C8-C9-C4	119.51(15)
C8-C9-N1	123.32(16)	C4-C9-N1	117.16(16)	O1-C10-N2	123.20(16)
O1-C10-C11	121.60(16)	N2-C10-C11	115.20(15)	C13-C12-C17	118.3(2)
C13-C12-C1	122.5(2)	C17-C12-C1	119.2(2)	C12-C13-C14	120.6(2)
C15-C14-C13	120.4(3)	C14-C15-C16	119.9(3)	C15-C16-C17	120.2(3)
C12-C17-C16	120.6(2)	C23#1-C21-C22	120.3(4)	C23-C22-C21	119.5(4)
C21#1-C23-C22	120.2(4)	O2-C18-O3	120.0(5)	O2-C18-N1	129.2(5)
O2'-C18-N1	118.8(6)	O3-C18-N1	110.7(3)	O2'-C18-O3'	130.3(6)
N1-C18-O3'	110.9(3)	C18-O3-C19	109.9(4)	O3-C19-C20	105.1(4)
C18-O3'-C19'	126.8(5)	C20'-C19'-O3'	98.9(8)	C18-N1-C9	124.97(17)
C18-N1-C1	116.21(17)	C9-N1-C1	118.04(15)	C10-N2-C6	126.82(13)

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,-y+1,-z+1

[1]Bruker (2009) SAINT. Bruker AXS Inc., Madison, Wisconsin, USA.

[2]Bruker (2009) SHELXTL. Bruker AXS Inc., Madison, Wisconsin, USA.

[3]Sheldrick, G.M. (2007) SADABS. University of Gottingen, Germany.

[4]Sheldrick, G.M. (2008) Acta Cryst. A64,112-122.

[5]Sheldrick, G.M. (2008) Acta Cryst. A64,112-122.

[6]$R1 = \Sigma||F_o| - |F_c|| / \Sigma |F_o|$
$wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{½}$
$GOF = [\Sigma w(F_o^2 - F_c^2)^2/(n - p)]^{½}$
where n = the number of reflections and p = the number of parameters refined.

[7]"ORTEP-II: A Fortran Thermal Ellipsoid Plot Program for Crystal Structure Illustrations". C.K. Johnson (1976) ORNL-5138.