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Supplementary Materials for

Controlling Ni redox states by dynamic ligand exchange for electroreductive Csp3–Csp2 coupling

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General Remarks

Unless otherwise noted, all experiments were conducted under a dry atmosphere of nitrogen, and reaction cells were assembled in a nitrogen-filled glove box. Anhydrous, degassed DMF was obtained by sparging with nitrogen and storing over 3 Å molecular sieves for at least 24 hours prior to use. All alkyl and aryl bromides were purchased from chemical suppliers and used as received unless otherwise noted. Quinazolinap derivatives and bpp were synthesized according to modified literature procedure as detailed below.(*51*)

^{1}H NMR spectra were obtained at 400 or 600 MHz and chemical shifts were recorded relative to $CHCl_3$ in $CDCl_3$ (δ7.26 ppm), H_2O in D_2O (δ4.79 ppm), and $(CH_3)_2CO$ in $(CD_3)_2CO$ (δ2.05 ppm). ^{13}C NMR were obtained at 101 MHz. Proof of purity is demonstrated by copies of NMR spectra. NMR multiplicities are reported as follows: singlet (s), doublet (d), triplet (t), quartet (q), multiplet (m), broad signal (br). GC analysis was performed on an Agilent 7890B GC equipped with an HP-5 column (30 m x 0.32 mm x 0.25 μm film) and an FID detector. Quantitative GC analysis was performed by adding dodecane as an internal standard to the reaction mixture upon completion of the reaction. Response factors for the products relative to the internal standard were measured for reaction development.

All electrochemical analyses were carried out in a nitrogen-filled glovebox. The supporting electrolyte was potassium hexafluorophosphate which was dried under vacuum at 120 °C for 24 hours prior to use. Cyclic voltammetry was performed with a Biologic VSP multichannel potentiostat/galvanostat. Cyclic voltammetry was carried out in a three-electrode electrochemical cell, consisting of a glassy carbon disk working electrode (0.07 cm^2, BASi), a Ag/Ag^+ quasi-reference electrode (BASi) with 0.01 M $AgBF_4$ (Sigma) in DMF, and a platinum wire counter electrode (23 cm, ALS). The glassy carbon disk electrode was polished in a nitrogen filled glovebox using diamond polish (15 μm micron, BASi) and anhydrous DMF. All experiments were performed at a scan rate of 100 mV/s in a DMF electrolyte containing 0.5 M KPF_6. Reference electrodes were calibrated against an internal voltage reference of ferrocene (1-10 mM). Reactions were conducted as two-electrode cells with a LANHE LAND battery testing system using Ni foam (1.5 x 300 x 10,000 mm, 110 ppi, 99.8% purity, purchased from alibaba.com) and zinc (0.0234 x 3 x 600 in, purchased from Amazon.com) electrodes. Reactions were conducted in Fisherbrand disposable borosilicate glass tubes with a threaded end (16 x 100 mm).

UV-vis spectroscopy was performed on with an AvaLight-DHc compact deuterium-halogen lamp equipped with an Avantes Avaspec-ULS2048-USB2 equipped with a 2048 pixel CCD detector. Samples for UV-vis spectroscopy were prepared using 0.1 M KPF_6 in DMF as the electrolyte solution in quartz cuvette with a 0.17 mm path length. Spectroelectrochemistry was performed with a Pine Research Honeycomb Spectroelectrochemistry Cell with a gold honeycomb spectroelectrochemical electrode card (AB01STC1AU). Potentials were recorded against a nonaqueous electrode that was separately calibrated against Fc/Fc^+. Spectra were recorded using AvaSoft-Basic, exported to Microsoft Excel, and analyzed.

General Procedures

General Procedure A: Cross Coupling of Aryl Bromides with Tertiary Alkyl Bromides
In a nitrogen-filled glove-box, a 4 mL screw-cap vial was charged with (dme)$NiCl_2$ (11 mg, 0.050 mmol, 0.10 equiv), (bpp)$MnCl_2$ (17 mg, 0.050 mmol, 0.10 equiv), dimethylformamide (0.5 mL), and a stir bar. To a separate 4 mL screw-cap vial was charged **iPrQ** (24 mg, 0.05 mmol, 0.1 equiv), dimethylformamide (0.5 mL), and a stir bar. To a 4 mL screw-cap vial was charged KPF_6 (46 mg, 0.25 mmol, 100 mM), aryl bromide (1.00 mmol, 2.00 equiv), alkyl bromide (0.500 mmol, 1.00 equiv), dimethylformamide (1.5 mL), and a magnetic stir bar. These solutions were allowed to stir at room temperature for 10 minutes before transferring to a 12 mL screw-cap vial equipped with a septum. A Ni foam cathode and a Zn anode were inserted into the test tube and the leads were pierced through a septum cap. The sealed test tube was removed from the glovebox. The reaction mixture was stirred on a magnetic stir plate at room temperature for 5 minutes prior to electrolysis. A reductive, constant current was applied at the Ni cathode (3 mA, 53.6 mAh, 4.0 equiv e^-). After electrolysis, the product was extracted from the crude reaction mixture with ethyl acetate (3 x 50 mL) and water (50 mL). The organic layers were combined and washed with brine (50 mL). The organic layer was dried over Na_2SO_4, filtered, and concentrated by rotary evaporation. The product was purified by flash chromatography on silica gel. Variations to this general procedure and specific conditions for isolation are detailed for each substrate below.

General Procedure for the Cross Coupling of Aryl Chlorides with Secondary Alkyl Bromides
In a nitrogen-filled glove-box, a 4 mL screw-cap vial was charged with (dme)$NiCl_2$ (11 mg, 0.050 mmol, 0.10 equiv), (bpp)$NiCl_2$ (18 mg, 0.050 mmol, 0.10 equiv), dimethylformamide (0.5 mL), and a stir bar. To a separate 4 mL screw-cap vial was charged **iPrQ** (24 mg, 0.05 mmol, 0.1 equiv), dimethylformamide (0.5 mL), and a stir bar. To a 4 mL screw-cap vial was charged KPF_6 (46 mg, 0.25 mmol, 100 mM), aryl chloride (1.00 mmol, 2.00 equiv), alkyl bromide (0.500 mmol, 1.00 equiv), dimethylformamide (1.5 mL), and a magnetic stir bar. These solutions were allowed to stir at room temperature for 10 minutes before transferring to a 12 mL screw-cap vial equipped with a septum. A Ni foam cathode and a Zn anode were inserted into the test tube and the leads were pierced through a septum cap. The sealed test tube was removed from the glovebox. The reaction mixture was stirred on a magnetic stir plate at 40 °C for 5 minutes prior to electrolysis. A reductive, constant current was applied at the Ni cathode (3 mA, 53.6 mAh, 4.0 equiv e^-). After electrolysis, the product was extracted from the crude reaction mixture with ethyl acetate (3 x 50 mL) and water (50 mL). The organic layers were combined and washed with brine (50 mL). The organic layer was dried over Na_2SO_4, filtered, and concentrated by rotary evaporation. The product was purified by flash chromatography on silica gel. Variations to this general procedure and specific conditions for isolation are detailed for each substrate below.

General Procedure for the Cross Coupling of Aryl and Vinyl Triflates with Alkyl Bromides
In a nitrogen-filled glove-box, a 4 mL screw-cap vial was charged with (dme)$NiCl_2$ (11 mg, 0.050 mmol, 0.10 equiv), (bpp)$NiCl_2$ (18 mg, 0.050 mmol, 0.10 equiv), dimethylformamide (0.5 mL), and a stir bar. To a separate 4 mL screw-cap vial was charged **iPrQ** (24 mg, 0.05 mmol, 0.1 equiv), dimethylformamide (0.5 mL), and a stir bar. To a 4 mL screw-cap vial was charged KPF_6 (46 mg, 0.25 mmol, 100 mM), aryl/vinyl triflate (1.00 mmol, 2.00 equiv), alkyl bromide (0.500 mmol, 1.00 equiv), dimethylformamide (1.5 mL), and a magnetic stir bar. These solutions were allowed to stir at room temperature for 10 minutes before transferring to a 12 mL screw-cap vial equipped with a septum. A Ni foam cathode and a Zn anode were inserted into the test tube and the leads were pierced through a septum cap. The sealed test tube was removed from the glovebox. The reaction mixture was stirred on a magnetic stir plate at 40 °C for 5 minutes prior to electrolysis. A reductive, constant current was applied at the Ni cathode (3 mA, 53.6 mAh, 4.0 equiv e^-). After electrolysis, the product was extracted from the crude reaction mixture with ethyl acetate (3 x 50 mL) and water (50 mL). The organic layers were combined and washed with brine (50 mL). The organic layer was dried over Na_2SO_4, filtered, and concentrated by rotary evaporation. The product was purified by flash chromatography on silica gel. Variations to this general procedure and specific conditions for isolation are detailed for each substrate below.

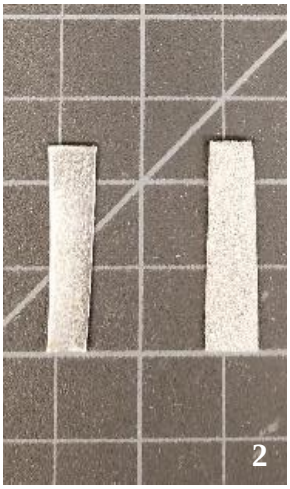
General Procedure for Pseudo-Stoichiometric Reactions in Figure 2A: Reactions of Preformed (phosphine)Ni-Ar Complexes
A 12 mL screw-cap vial was charged with $Ni(COD)_2$ (21 mg, 0.075 mmol,), ligand (0.083 mmol), dimethylformamide (0.5 mL), and a stir bar. To a 4 mL screw-cap vial was charged KPF_6 (46 mg, 0.25 mmol, 100 mM), ^{t}BuBr (34 mg, 0.25 mmol), 1-bromo-4-butylbenzene (53 mg, 0.25 mmol), dimethylformamide (2.0 mL), and a magnetic stir bar. These solutions were allowed to stir at room temperature for 10 minutes before transferring to a 12 mL screw-cap vial

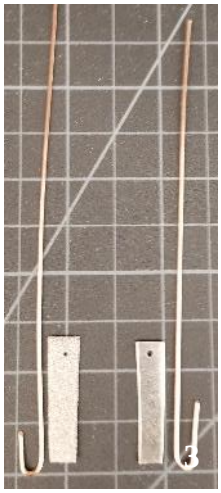
equipped with a septum. A Ni foam cathode and a Zn anode were inserted into the test tube and the leads were pierced through a septum cap. The sealed test tube was removed from the glovebox. The reaction mixture was stirred on a magnetic stir plate at room temperature for 5 minutes prior to electrolysis. A reductive, constant current was applied at the Ni cathode (3 mA, 13.4 mAh, 2.00 equiv e^-). After electrolysis, the product was extracted from the crude reaction mixture with ethyl acetate (2 mL) and brine (5 mL). The reaction mixture was analyzed by gas chromatography against a calibrated internal standard of dodecane.

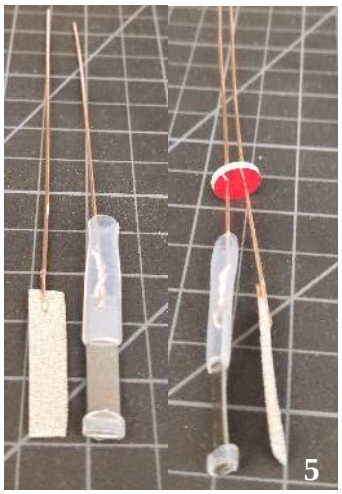
General Procedure for the Synthesis of Vinyl Triflates

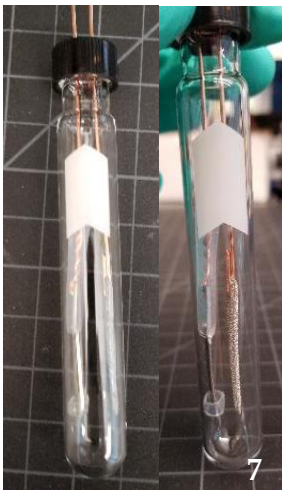
In a nitrogen-filled glove-box, an oven-dried 50 mL round-bottom flask was charged with ketone (5.00 mmol, 1 eq.), N-phenylbistriflamide (1.96 g, 5.50 mmol, 1.1 eq.), tetrahydrofuran (20 mL), and a magnetic stir bar. The mixture was cooled to -78 °C, and a solution of sodium hexamethyldisilazane (1.01 g, 5.50 mmol, 1.1 eq.) in tetrahydrofuran (5.5 mL) was added dropwise. The reaction was warmed to room temperature and allowed to stir for 12 hours. The product was extracted from the crude reaction mixture with ethyl acetate (3 x 50 mL) and water (50 mL). The organic layers were combined and washed with brine (50 mL), dried over anhydrous Na_2SO_4, filtered, and concentrated by rotary evaporation. The product was purified by flash column chromatography on silica gel. Variations to this general procedure and specific conditions for isolation are detailed for each substrate below.

Standard Electrochemical Cell Preparation







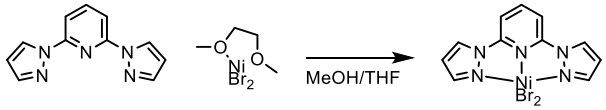


<u>Electrode Preparation Procedure</u>:

1. Materials required: 12 mL threaded reaction test tube, PTFE septa, threaded test tube cap, copper wire (18 ga), nickel foam, zinc sheet, PTFE tubing (3/16” ID, 1/4” OD, 1/32” WT), pliers, hole punch, and aviation snips.
2. Use aviation snips to cut nickel foam and zinc plate into 6 mm x 32 mm strips.
3. Use hole punch to make 1.2 mm hole in nickel foam and zinc strips.
4. Secure nickel foam and zinc strip to copper wire. For the nickel foam cathode, copper wire was threaded through hole and the copper was folded back on itself to clamp the nickel foam in place. For the zinc anode, the copper wire was threaded through hole and then twisted over itself to ensure secure connection.
5. On the zinc anode, 2 segments of PTFE tubing were cut one being 3 cm and the other being 3 mm. The larger segment was placed over the zinc-copper connection and the smaller segment was placed over the end of the zinc electrode; this was done to prevent electrodes from touching causing the cell to short circuit.
6. Copper wire from nickel foam and zinc electrodes was pushed through PTFE septa and electrodes were positioned parallel to each other to prevent them from touching.
7. The pair of electrodes were located into threaded reaction test tube with a 1 cm gap from the bottom of the test tube, the septa was then secured with the threaded cap.

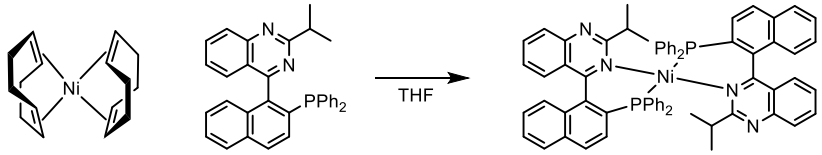
Synthesis and Characterization of Metal Complexes

(bpp)NiBr$_2$ (1)



A 100 mL round-bottom flask was charged with bpp (2.121 g, 10.00 mmol, 1 equiv), THF (35 mL), and a stir bar. This solution was allowed to stir for 5 minutes. To the reaction mixture was added a solution of (dme)NiBr$_2$ (3.090 g, 15.00 mmol, 1 equiv) in MeOH (15 mL). The resulting mixture was allowed to stir at 60 °C for one hour. The reaction was allowed to cool to room temperature. To the cooled mixture was slowly added Et$_2$O until a green powder precipitated. This powder was filtered, washed with Et$_2$O, and collected to afford **1** as a bright green powder (2.944 g, 6.75 mmol, 67%). Note: addition of superstoichiometric amounts of bpp lead to bis-ligated complex; recrystallization affords bis ligated complex. The title compound is paramagnetic.

(iPrQ)$_2$Ni^0 (2)

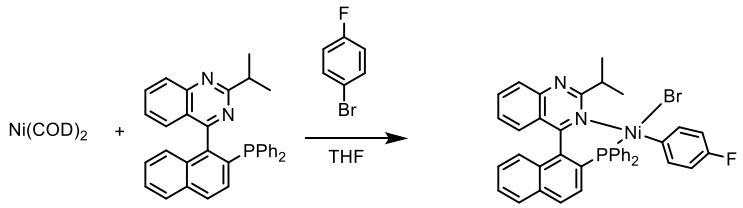


Inside a nitrogen-filled glovebox, to a 20 mL screw-cap vial was charged Ni(COD)$_2$ (200. mg, 0.727 mmol, 1 equiv) a stir bar, and 2 mL of THF. This mixture was allowed to stir at room temperature for 5 minutes. To this yellow solution was added **iPrQ** (877 mg, 1.82 mmol, 2.5 equiv) in 2 mL of THF. Upon addition, the yellow solution immediately changed color to reddish-orange. The resulting mixture was allowed to stir for 1 hour at room temperature. The orange solution was concentrated in vacuo to afford a sticky orange powder. The powder was washed with pentane (3x15 mL) and cold Et$_2$O (2x5 mL) and filtered. The resulting orange powder was dried in vacuo to afford the product as a light orange powder (531 mg, 0.519 mmol, 71%).

^{31}P NMR (243 MHz, C6D6) δ 38.8 (br)

Elemental Analysis Calculated for $C_{66}H_{54}N_4P_2$7·2(H_2O): C, 74.80; H, 5.14; N, 5.29. Found: C, 74.97; H, 5.48; N, 5.15

(iPrQ)NiBr(4-F-Ph) (**3**)

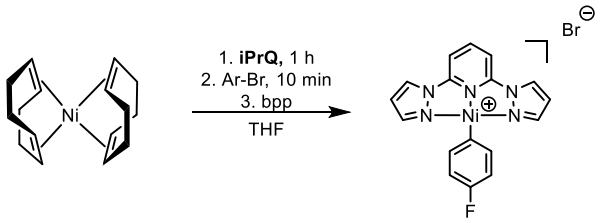


Inside a nitrogen-filled glovebox, to a 20 mL screw-cap vial was charged Ni(COD)$_2$ (55 mg, 0.20 mmol, 1 equiv) a stir bar, and 2 mL of THF. This mixture was allowed to stir at room temperature for 5 minutes. To this yellow solution was added **iPrQ** (241 mg, 0.499 mmol, 2.5 equiv) in 2 mL of THF. Upon addition, the yellow solution immediately changed color to reddish-orange. The resulting mixture was allowed to stir for 1 hour at room temperature. To this orange solution was added 4-fluorobromobenzene (349 mg, 2.00 mmol, 10 equiv). The reaction mixture was allowed to stir for 10 minutes at room temperature. The reaction mixture was then concentrated under vacuum. The resulting brown solid was suspended in pentane and filtered, washing with cold pentane (10x5 mL) and cold ether (2x5 mL). The solid was collected by filtration to afford **3** as a dark brown solid (95 mg, 0.13 mmol, 66%). Note: **3** is unstable in solution without added ArBr, likely because oxidative addition-reductive elimination are reversible processes. Due to the need for an equimolar (or greater) quantity of added ArBr, we were unable to characterize the complex 1H and 13C NMR spectroscopy.

^{31}P NMR (243 MHz, C6D6) δ 26.3

^{19}F NMR (565 MHz, CD$_3$CN) δ -124

(bpp)Ni^{II}-(Aryl) (4)

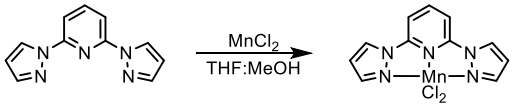


Inside a nitrogen-filled glovebox, a 20 mL screw-cap vial was charged with $Ni(COD)_2$ (55 mg, 0.20 mmol, 1 equiv) a stir bar, and 2 mL of THF. This mixture was allowed to stir at room temperature for 5 minutes. To this yellow solution was added **iPrQ** (241 mg, 0.499 mmol, 2.5 equiv) in 2 mL of THF. Upon addition, the yellow solution immediately changed color to reddish-orange. The resulting mixture was allowed to stir for 1 hour at room temperature. To this orange solution was added 4-fluorobromobenzene (175 mg, 1.00 mmol, 5.0 equiv). The reaction mixture was allowed to stir for 10 minutes at room temperature. Then, bpp (46 mg, 0.22 mmol, 1.1 equiv) in THF (1 mL) was added in one portion at which point the reaction immediately precipitated a yellow-orange solid. The solid was filtered and washed with pentane (3x15 mL) and cold ether (3x 10 mL). The resulting powder was dried in vacuo to afford the product as a bright yellow powder (60 mg, 0.135 mmol, 68%). Note: the title compound is unstable in solution for extended periods of time (>5 h).

^{1}H NMR (600 MHz, CD_3CN) δ 8.73 (s, 2H), 8.42 (dd, J = 7.3 Hz, 1H), 7.87 (d, J = 8.2 Hz, 2H), 7.56 (d, J = 6.0 Hz, 2H), 7.27 (s, 2H), 7.00 (dd, J = 8.8 Hz, 2H), 6.70 (s, 2H).

^{19}F NMR (565 MHz, CD_3CN) δ -123

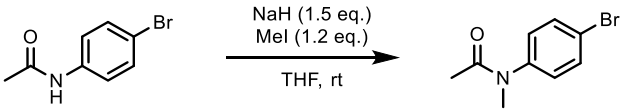
(bpp)$MnCl_2$



To a 100 mL round-bottom flask was charged bpp (3.492 g, 16.53 mmol, 1.1 equiv), THF (35 mL), and a stir bar. This solution was allowed to stir for 5 minutes. To the reaction mixture was added a solution of $MnCl_2$ (1.890 g, 15.00 mmol, 1 equiv) in MeOH (10 mL). The resulting mixture was allowed to stir at 60 °C for one hour. The reaction was allowed to cool to room temperature. To the cooled mixture was slowly added Et_2O until a white powder precipitated. This powder was filtered, washed with Et_2O, and collected (4.884 g, 14.49 mmol, 96%). Suitable crystals can be grown by dissolving the title compound in DMF and layering with a mixture of 2:1 Toluene:Et_2O to afford the product as small rectangular prisms. The title compound is paramagnetic.

Synthesis of Starting Materials

N-(4-bromophenyl)-N-methylacetamide

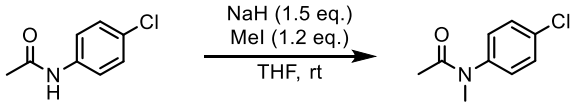


N-(4-bromophenyl)acetamide (3.00 g, 14.1 mmol, 1.00 equiv) was dissolved in THF (15 mL) and the resulting solution was slowly added to a suspension of NaH (60% dispersion in mineral oil, 841 mg, 21.0 mmol, 1.50 equiv) in THF (30 mL). After stirring for 5 minutes, MeI (2.39 g, 16.8 mmol, 1.20 equiv) was added dropwise and the reaction was stirred at room temperature overnight. The reaction mixture was diluted with water (50 mL) and DCM (50 mL). The aqueous layer was then extracted with DCM (3 × 30 mL). The combined organic phase was dried over anhydrous Na2SO4, and then concentrated *in vacuo*. The crude product was purified by flash column chromatography (25:75 EtOAc:Hexanes) to yield the title compound (2.54 g, 11.1 mmol 79%) as a white solid. Analysis by ^{1}H NMR spectroscopy and ^{13}C NMR spectroscopy matches characterization of previously reported literature for the title compound.(*52*)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (d, *J* = 8.6 Hz, 1H), 7.07 (d, *J* = 8.6 Hz, 1H), 3.24 (s, 2H), 1.87 (s, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.4, 143.8, 133.1, 129.0, 121.6, 37.2, 22.6.

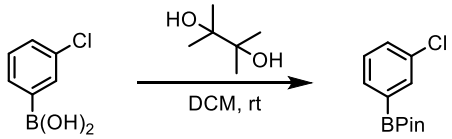
N-(4-chlorophenyl)-N-methylacetamide



N-(4-chlorophenyl)acetamide (2.00 g, 11.8 mmol, 1.00 equiv) was dissolved in THF (15 mL) and the resulting solution was slowly added to a suspension of NaH (60% dispersion in mineral oil, 707 mg, 17.7 mmol, 1.50 equiv) in THF (30 mL). After stirring for 5 minutes, MeI (2.01 g, 14.2 mmol, 1.20 equiv) was added dropwise and the reaction was stirred at room temperature overnight. The reaction mixture was diluted with water (50 mL) and DCM (50 mL). The aqueous layer was then extracted with DCM (3 × 30 mL). The combined organic phase was dried over anhydrous Na2SO4, and then concentrated *in vacuo*. The crude product was purified by flash column chromatography (25:75 EtOAc:Hexanes) to yield the title compound (2.54 g, 11.1 mmol 79%) as a white solid. Analysis by ^{1}H NMR spectroscopy matches characterization of previously reported literature for the title compound. (*53*)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (d, *J* = 8.8 Hz, 1H), 7.28 (d, *J* = 8.9 Hz, 1H), 3.42 (s, 3H), 2.17 (s, 3H).

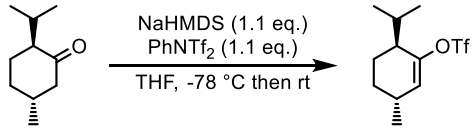
2-(3-chlorophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane



(3-chlorophenyl)boronic acid (3.91 g, 25 mmol, 1.00 equiv) and 2,3-dimethylbutane-2,3-diol (3.55 g, 30 mmol, 1.2 equiv) were dissolved in dichloromethane (50 mL) and allowed to stir at room temperature for 6 h. Upon completion, to the reaction mixture was added DI water (50 mL) and the aqueous layer was then extracted with DCM (3 x 50 mL). The combined organic phases were dried over anhydrous sodium sulfate and concentrated *in vacuo*. The crude product was purified by flash column chromatography (100% Hexanes) to yield the title compound (5.34 g, 22.4 mmol, 90%). Analysis by ^{1}H NMR spectroscopy matches characterization of previously reported literature for the title compound.(*54*)

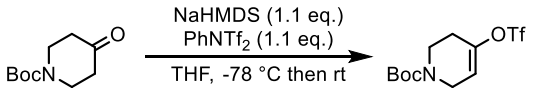
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (dd, *J* = 2.4, 1.2 Hz, 1H), 7.69 (dd, *J* = 7.3, 1.1 Hz, 1H), 7.41 (dd, *J* = 2.3, 1.2 Hz, 1H), 7.30 (t, *J* = 7.7 Hz, 1H), 1.35 (s, 12H).

(3R,6S)-6-isopropyl-3-methylcyclohex-1-en-1-yl trifluoromethanesulfonate



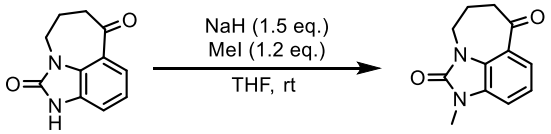
Following the general procedure for the synthesis of vinyl triflates, to the reaction was added (2S,5R)-2-isopropyl-5-methylcyclohexan-1-one (771 mg, 5.00 mmol, 1.00 equiv). The resulting product was purified via flash column chromatography (10:90 EtOAc:Hexanes) as a colorless oil (996 mg, 3.48 mmol, 70%). Analysis by ^{1}H NMR spectroscopy matches characterization of previously reported literature for the title compound.(*55*)
^{1}H NMR (400 MHz, $CDCl_3$) δ 5.64 (s, 1H), 2.48 (ddtd, J = 9.9, 5.9, 3.9, 1.9 Hz, 1H), 2.38 – 2.28 (m, 1H), 2.16 (pd, J = 7.0, 4.0 Hz, 1H), 1.81 (dddd, J = 11.2, 7.3, 5.6, 4.1 Hz, 2H), 1.47 – 1.36 (m, 1H), 1.15 (ddd, J = 12.7, 10.3, 2.7 Hz, 1H), 1.04 (d, J = 7.1 Hz, 3H), 1.02 – 0.97 (m, 1H), 0.95 (d, J = 7.0 Hz, 3H), 0.82 (d, J = 6.9 Hz, 3H).

tert-butyl 4-(((trifluoromethyl)sulfonyl)oxy)-3,6-dihydropyridine-1(2H)-carboxylate



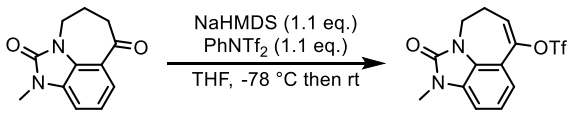
Following the general procedure for the synthesis of vinyl triflates, to the reaction was added tert-butyl 4-oxopiperidine-1-carboxylate (996 mg, 5.00 mmol, 1.00 equiv). The resulting product was purified via flash column chromatography (10:90 EtOAc:Hexanes) as a colorless oil (1.05 g, 3.17 mmol, 63%). Analysis by ^{1}H NMR spectroscopy matches characterization of previously reported literature for the title compound.(*56*)
1H NMR (400 MHz, $CDCl_3$) δ 5.76 (s, 1H), 4.04 (q, J = 3.0 Hz, 2H), 3.62 (t, J = 5.7 Hz, 2H), 2.43 (td, J = 2.9, 1.4 Hz, 2H), 1.47 (s, 9H).

2-methyl-8,9-dihydro-2,9a-diazabenzo[cd]azulene-1,6(2H,7H)-dione



8,9-dihydro-2,9a-diazabenzo[cd]azulene-1,6(2H,7H)-dione (1.00 g, 5.00 mmol, 1.00 equiv) was dissolved in THF (10 mL) and the resulting solution was slowly added to a suspension of NaH (60% dispersion in mineral oil, 299 mg, 7.50 mmol, 1.50 equiv) in THF (20 mL). After stirring for 5 minutes, MeI (851 mg, 6.00 mmol, 1.20 equiv) was added dropwise and the reaction was stirred at room temperature overnight. The reaction mixture was diluted with water (50 mL) and DCM (50 mL). The aqueous layer was then extracted with DCM (3 × 30 mL). The combined organic phase was dried over anhydrous Na2SO4, and then concentrated in vacuo. The crude product was purified by flash column chromatography (35:65 EtOAc:Hexanes) to yield the title compound (852 mg, 3.94 mmol 79%) as a white solid.
^{1}H NMR (400 MHz, $CDCl_3$)δ 7.79 (dd, J = 5.5, 3.9 Hz, 1H), 7.18 – 7.07 (m, 2H), 4.25 – 3.99 (m, 2H), 3.46 (s, 3H), 3.25 – 3.01 (m, 2H), 2.33 – 2.10 (m, 2H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 197.1, 153.8, 131.1, 128.9, 122.6, 120.6, 118.6, 111.7, 45.4, 44.5, 27.3, 20.3.

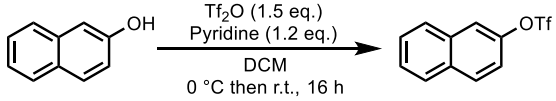
2-methyl-1-oxo-1,2,8,9-tetrahydro-2,9a-diazabenzo[cd]azulen-6-yl trifluoromethanesulfonate



Following the general procedure for the synthesis of vinyl triflates, to the reaction was added 2-methyl-8,9-dihydro-2,9a-diazabenzo[cd]azulene-1,6(2H,7H)-dione (1.08 g, 5.00 mmol, 1.00 equiv). The resulting product was purified via flash column chromatography (30:70 EtOAc:Hexanes) as a white solid (943 mg, 2.71 mmol, 54%).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 (dd, *J* = 8.1, 1.0 Hz, 1H), 7.15 (t, *J* = 8.0 Hz, 1H), 7.00 (dd, *J* = 7.7, 1.0 Hz, 1H), 6.26 (t, *J* = 7.2 Hz, 1H), 4.13 – 4.07 (m, 2H), 3.43 (s, 3H), 2.67 (td, *J* = 7.1, 4.7 Hz, 2H).

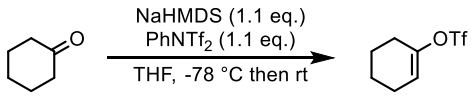
^{13}C NMR (101 MHz, $CDCl_3$) δ 153.3, 145.8, 130.4, 125.9, 122.2, 121.2, 118.45 (q, J = 320.2 Hz), 118.2, 114.2, 108.5, 42.5, 27.3, 25.6.

naphthalen-2-yl trifluoromethanesulfonate



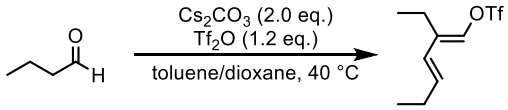
Following a published procedure,(*57*) to a scintered glass 20 mL vial was added naphthalen-2-ol (721 mg, 5.00 mmol, 1.00 equiv.) and pyridine (475 mg, 6.00 mmol, 1.20 equiv.). The two compounds were dissolved in DCM (10 mL) and the solution cooled to 0 °C. Triflic anhydride (2.12 g, 7.50 mmol, 1.50 equiv. was added dropwise and the solution allowed to warm to room temperature. Afterwards, saturated NaHCO3-solution (30 mL) was added, and the aqueous phase was extracted with DCM (3 × 25 mL). The combined organic phases were dried over sodium sulfate, and the mixture concentrated *in vacuo*. The crude product was purified by column chromatography (100 % Hexanes) to afford the title compound as an off white solid (836 mg, 3.03 mmol, 61%).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 – 7.85 (m, 3H), 7.77 (d, J = 2.5 Hz, 1H), 7.62 – 7.53 (m, 2H), 7.39 (dd, J = 9.0, 2.5 Hz, 1H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 147.1, 133.3z, 132.3, 130.6, 128.0, 127.9, 127.8, 127.7, 127.5, 127.2, 119.5, 119.2, 118.8 (q, *J* = 320.8 Hz).

cyclohex-1-en-1-yl trifluoromethanesulfonate



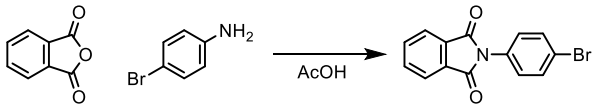
Following the general procedure for the synthesis of vinyl triflates, to the reaction was added cyclohexanone (4.00 g, 40.8 mmol, 1.00 equiv). The resulting product was purified via flash column chromatography (100% Hexanes) as a colorless oil (6.14 g, 26.7 mmol, 65%). Analysis by 1H NMR spectroscopy matches characterization of previously reported literature for the title compound.
^{1}H NMR (400 MHz, $CDCl_3$) δ 5.78 – 5.71 (m, 1H), 2.35 – 2.24 (m, 2H), 2.22 – 2.13 (m, 3H), 1.84 – 1.71 (m, 3H), 1.65 – 1.54 (m, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 149.4, 118.7- (q, J = 319.6 Hz), 118.3, 27.4, 23.7, 22.5, 20.9.

(1E,3E)-2-ethylhexa-1,3-dien-1-yl trifluoromethanesulfonate



Following a published procedure,(*58*) in a nitrogen-filled glove-box, to an oven-dried 50 mL round-bottom flask equipped with a magnetic stir bar was charged with butyraldehyde (361 mg, 5.00 mmol, 1 equiv), cesium carbonate (3.26 g, 10.0 mmol, 2.00 equiv) and toluene/dioxane (20 mL/20 mL). The mixture was removed from the glove-box after which a portion of triflic anhydride (1.69 g, 6.00 mmol, 1.2 equiv) was added dropwise. The reaction was heated to 40 °C and allowed to stir for 5 hours. The product was extracted from the crude reaction mixture with ethyl acetate (3 x 50 mL) and water (50 mL). The organic layers were combined and washed with brine (50 mL), dried over anhydrous Na_2SO_4, filtered, and concentrated by rotary evaporation. The product was purified by flash column chromatography (100% Hexanes) providing the title compound (556 mg, 2.15 mmol, 86%).
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.60 (s, 1H), 6.00 – 5.87 (m, 1H), 5.81 (dq, *J* = 15.6, 1.2 Hz, 1H), 2.34 (q, *J* = 7.6 Hz, 2H), 2.23 – 2.06 (m, 2H), 1.09 – 1.05 (m, 3H), 1.05 – 1.01 (m, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 135.5, 133.2, 133.2, 122.9, 118.60 (q, J = 321.0 Hz), 26.0, 18.2, 13.3, 12.9.

(2-(4-bromophenyl)isoindoline-1,3-dione

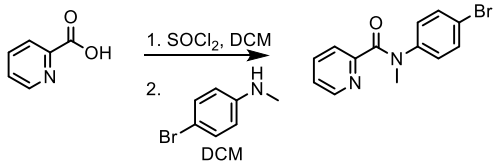


Following a published procedure,(*59*) to a 250 mL round-bottom flask was added isobenzofuran-1,3-dione (2.964 g, 19.81 mmol, 0.2 M, 1.00 equiv), AcOH (100 mL), and a large stir bar. While stirring, 4-bromoaniline was added in one portion. The resulting reaction mixture was allowed to reflux at 120 °C for 3 hours. Upon cooling to room temperature, a white solid precipitated and was collected by filtration, washing with water. The resulting mixture was dissolved in CH_2Cl_2 and the organic layer was extracted with brine, dried over Na_2SO_4, and concentrated by rotary evaporation to afford a white solid (5.322 g, 17.62 mmol, 88%). Analysis by ^{1}H NMR spectroscopy and ^{13}C NMR spectroscopy matches characterization of previously reported literature for the title compound.(*17~~60~~*)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (d, *J* = 8.6 Hz, 1H), 7.07 (d, *J* = 8.6 Hz, 1H), 3.24 (s, 2H), 1.87 (s, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.4, 143.8, 133.1, 129.0, 121.6, 37.2, 22.6.

N-(4-bromophenyl)picolinamide

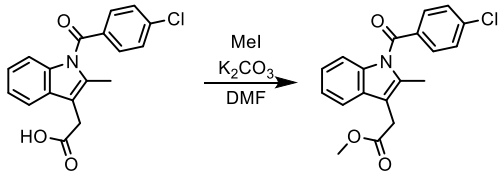


To a 40 mL screw-cap scintillation vial was added picolinic acid (1.231 g, 10.00 mmol), CH_2Cl_2 (15 mL), and a stir bar. The reaction mixture was to 0 °C in an ice bath. To this cooled solution was slowly added $SOCl_2$ (2.9 mL, 4 equiv) and then sealed with a Teflon-coated scintillation cap. The reaction mixture was allowed to stir at 0 °C for 5 minutes and then at 50 °C for 3 hours. The solvent was removed by stirring under high vacuum. The resulting solid was dissolved in CH_2Cl_2 (10 mL) and cooled to 0 °C in an ice bath. To this cooled solution as added triethylamine (3 mL) and then 4-bromo-N-methylaniline (2.887 g, 15.52 mmol, 1.5 equiv). The resulting reaction mixture was allowed to stir for 12 hours at room temperature. After this time, the reaction was poured into CH_2Cl_2 and extracted with water (3x15 mL), brine (2x10 mL), dried over sodium sulfate, and concentrated by rotary evaporation. The crude mixture was purified by column chromatography (40:60 EtOAc:Hexanes) to afford the title compound as a brown solid (2.182 g, 7.870 mmol, 79%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.34 (s, 1H), 7.65 (t, J = 7.8 Hz, 1H), 7.53 (d, J = 7.6 Hz, 1H), 7.33 (d, J = 8.1 Hz, 2H), 7.19 (d, J = 6.2 Hz, 1H), 6.95 (s, 2H), 3.49 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$ δ 168.6, 153.8, 148.4, 143.5, 136.5, 132.1, 128.2, 124.2, 123.8, 120.0, 38.1 (br).

methyl 2-(1-(4-chlorobenzoyl)-2-methyl-1H-indol-3-yl)acetate

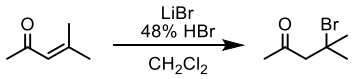


Following a published procedure,(*60~~1~~*) to a 20 mL screw-neck vial was added indomethacin (1.00 g, 2.79 mmol, 0.4 M, 1.00 equiv), Na_2CO_3 (592 mg, 5.60 mmol, 2.0 equiv), DMF (7 mL), and a stir bar. While stirring, methyl iodide (0.35 mL, 5.8 mmol, 2 equiv) was added dropwise over the course of 5 minutes. The reaction mixture was allowed to stir overnight at room temperature. The yellow solution was poured into ethyl acetate (25 mL) and extracted with water (50 mL), saturated $NaHCO_3$ (50 mL), water (50 mL), brine (50 mL), dried over Na_2SO_4, and concentrated by rotary evaporation. The product was isolated following column chromatography in 10:90 EtOAc: Hex to afford the title compound as a yellow solid (884 mg, 2.38 mmol, 85%). Analysis by ^{1}H NMR spectroscopy and ^{13}C NMR spectroscopy matches characterization of previously reported literature for the title compound.(*60~~1~~*)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 – 7.56 (m, 2H), 7.42 – 7.37 (m, 2H), 6.90 – 6.87 (m, 1H), 6.79 (dd, J = 9.0, 0.5 Hz, 1H), 6.60 (dd, J = 9.0, 2.6 Hz, 1H), 3.77 (s, 3H), 3.63 (s, 3H), 3.60 (s, 2H), 2.31 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 171.3, 168.3, 156.1, 139.3, 136.0, 133.9, 131.2, 130.8, 130.7, 129.1, 115.0, 112.5, 111.6, 101.3, 55.7, 52.2, 30.2, 13.4.

4-bromo-4-methylpentan-2-one

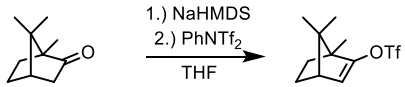


To a 40 mL screw-cap scintillation vial was added 4-methylpent-3-en-2-one (1.534 g, 15.63 mmol), LiBr (4.011 g, 46.19 mmol, 3 equiv), CH_2Cl_2 (2 mL) and a stir bar. While stirring, HBr (48%, 10 mL) was added in one portion. The resulting reaction mixture was allowed to stir at room temperature for 12 hours. The resulting mixture was dissolved in CH_2Cl_2 and the organic layer was extracted with water (3x20 mL), brine (2x10 mL), dried over Na_2SO_4, and concentrated by rotary evaporation. Elution of the crude material by flash column chromatography (0.1:5:94.9 NEt_3:EtOAc:Hexanes) afforded the product as a red oil (1.578 g, 8.81 mmol, 56%). Analysis by ^{1}H NMR spectroscopy and ^{13}C NMR spectroscopy matches characterization of previously reported literature for the title compound.(*16*~~62~~)

^{1}H NMR (400 MHz, $CDCl_3$) δ 3.07 (s, 2H), 2.19 (s, 3H), 1.88 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 205.1, 61.4, 58.3, 34.1, 31.8.

(1S,4S)-1,7,7-trimethylbicyclo[2.2.1]hept-2-en-2-yl trifluoromethanesulfonate



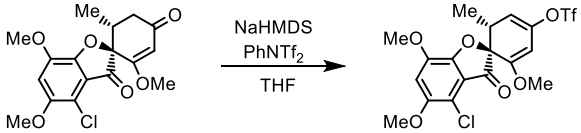
To a 40 mL screw-cap scintillation vial was added (1S,4S)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-one (5.420 g, 35.60 mmol), THF (70 mL), and a stir bar. The reaction mixture was cooled to –78 °C and allowed to stir for 5 minutes. While stirring, a solution of NaHMDS (7.155 g, 39.02 mmol, 1.1 equiv) in THF (30 mL) was slowly added over 10 minutes. The resulting reaction mixture was allowed to warm to room temperature and stir for 20 minutes. The reaction mixture was then cooled to -78 °C and to this cooled solution was slowly added $PhNTf_2$ (15.129 g, 43.32 mmol, 1.2 equiv) as a solution in THF (15 mL). The resulting mixture was allowed to warm to room temperature and to stir for 12 hours. The crude mixture was dissolved in CH_2Cl_2 and the organic layer was extracted with water (3x20 mL), brine (2x10 mL), dried over Na_2SO_4, and concentrated by rotary evaporation. Elution of the crude material by flash column chromatography (Hexanes) afforded the product as a colorless oil (7.819 g, 27.48 mmol, 77%). Analysis by ^{1}H NMR spectroscopy and ^{13}C NMR spectroscopy matches characterization of previously reported literature for the title compound.(*6*~~13~~)

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.67 (d, J = 3.8 Hz, 1H), 2.45 (t, J = 3.7 Hz, 1H), 1.93 (ddt, J = 12.2, 8.6, 3.7 Hz, 1H), 1.65 (dddd, J = 12.2, 8.5, 3.6, 0.7 Hz, 1H), 1.33 (ddd, J = 12.4, 9.1, 3.6 Hz, 1H), 1.15 (ddd, J = 12.5, 9.1, 3.6 Hz, 1H), 1.03 (s, 3H), 0.92 (s, 3H), 0.79 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 155.2, 120.1 (q, J = 321.3 Hz), 117.7, 57.0, 53.8, 50.1, 30.8, 25.3, 19.7, 19.0, 9.4.

^{19}F NMR (376 MHz, $CDCl_3$) δ -74.2.

(2S,6'R)-4-chloro-2',5,7-trimethoxy-6'-methyl-3-oxo-3H-spiro[benzofuran-2,1'-cyclohexane]-2',4'-dien-4'-yl trifluoromethanesulfonate



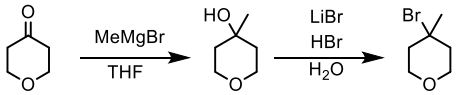
To a 40 mL screw-cap scintillation vial was added (2S,6'R)-4-chloro-2',5,7-trimethoxy-6'-methyl-3H-spiro[benzofuran-2,1'-cyclohexan]-2'-ene-3,4'-dione (1.00 g, 2.83 mmol), $PhNTf_2$ (1.244 g, 3.480 mmol, 1.2 equiv) THF (7 mL), and a stir bar. The reaction mixture was cooled to –78 °C and allowed to stir for 5 minutes. While stirring, a solution of NaHMDS (581 mg, 3.17 mmol, 1.1 equiv) in THF (5 mL) was slowly added over 10 minutes. The resulting mixture was allowed to warm to room temperature and to stir for 12 hours. The crude mixture was dissolved in CH_2Cl_2 and the organic layer was extracted with water (3x20 mL), brine (2x10 mL), dried over Na_2SO_4, and concentrated by rotary evaporation. Elution of the crude material by flash column chromatography (45:55 EtOAc:Hexanes) afforded the product as a yellow-brown solid (679 mg, 1.40 mmol, 49%). Analysis by ^{1}H NMR spectroscopy and ^{13}C NMR spectroscopy matches characterization of previously reported literature for the title compound.(*6*~~24~~)

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.10 (s, 1H), 5.40 (dd, J = 4.1, 1.9 Hz, 1H), 5.19 (d, J = 1.9 Hz, 1H), 4.00 (s, 3H), 3.95 (s, 3H), 3.58 (s, 3H), 3.23 (qd, J = 7.3, 4.0 Hz, 1H), 1.13 (d, J = 7.3 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 191.8, 168.6, 164.4, 157.8, 156.7, 143.8, 118.6 (q, J = 321 Hz), 111.7, 104.9, 97.3, 94.8, 91.2, 89.5, 56.9, 56.3, 56.3, 37.6, 13.4.

^{19}F NMR (376 MHz, $CDCl_3$) δ -73.0.

4-bromo-4-methyltetrahydro-2H-pyran



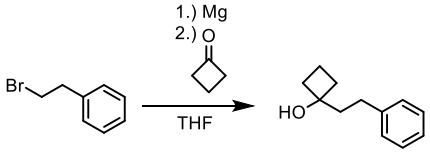
To a 100 mL round-bottom flask was added tetrahydro-4H-pyran-4-one (1.509 g, 15.00 mmol), THF (30 mL) and a stir bar. The resulting mixture was cooled to 0 °C in an ice bath. While stirring, a MeMgBr (1 M in Et_2O, 18 mL, 18 mmol, 1.2 equiv) was slowly added. The resulting mixture was allowed to stir at room temperature for 5 hours, then quenched with 10 mL of H_2O. EtOAc (30 mL) was added and the organic layer was extracted with water (3x20 mL), brine (2x10 mL), dried over Na_2SO_4, and concentrated by rotary evaporation to afford the crude product as a colorless oil (1.540 g, 13.26 mmol, 88%). The resulting crude mixture was used without further purification.

To a 40 mL screw-cap scintillation vial was added 4-methyltetrahydro-2H-pyran-4-ol (1.540 g, 13.26 mmol), LiBr (3.450 g, 39.77 mmol, 3 equiv), CH_2Cl_2 (2 mL) and a stir bar. While stirring, HBr (48%, 10 mL) was added in one portion. The resulting reaction mixture was allowed to stir at room temperature for 12 hours. The resulting mixture was dissolved in hexanes and the organic layer was extracted with water (3x20 mL), brine (2x10 mL), dried over Na_2SO_4, and concentrated by rotary evaporation. Elution of the crude material by flash column chromatography (0.1:5:94.9 NEt_3:EtOAc:Hexanes) afforded the product as a colorless oil (1.644 g, 9.18 mmol, 69%). Analysis by ^{1}H NMR spectroscopy and ^{13}C NMR spectroscopy matches characterization of previously reported literature for the title compound.(*6~~3~~5*)

^{1}H NMR (400 MHz, $CDCl_3$) δ 3.89 – 3.76 (m, 4H), 1.97 (dd, J = 14.6, 2.4 Hz, 2H), 1.87 (s, 3H), 1.81 – 1.68 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 68.3, 63.7, 43.3, 37.4.

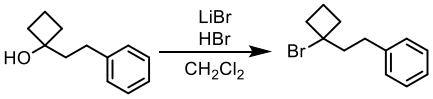
(2-(1-bromocyclobutyl)ethyl)benzene



To a 500 mL round-bottom flask was added magnesium turnings (2.633 g, 108.1 mmol), THF (250 mL), a crystal of I_2, and a stir bar. The resulting mixture was cooled to 0 °C in an ice bath and allowed to stir in an ice bath until the solution changed colors from yellow to clear. While stirring, a (2-bromoethyl)benzene (10.00 g, 54.04 mmol,) was slowly added. The resulting mixture was allowed to stir at room temperature for 5 hours. After this time, the reaction was cooled to 0 °C. To this solution was slowly added cyclobutanone (6.0 mL, 81 mmol, 1.5 equiv). This reaction was allowed to stir at room temperature for 12 hours after which it was quenched with 10 mL of H_2O. EtOAc (30 mL) was added, and the organic layer was extracted with water (3x20 mL), brine (2x10 mL), dried over Na_2SO_4, and concentrated by rotary evaporation. Purification by flash column chromatography (10:90 EtOAc:Hexanes) afforded 1-phenethylcyclobutan-1-ol as a colorless oil (8.411 g, 47.71 mmol, 88%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.30 (m, 2H), 7.28 – 7.25 (m, 2H), 7.24 – 7.19 (m, 1H), 2.81 – 2.68 (m, 2H), 2.15 (dddd, J = 12.6, 8.7, 3.8, 2.5 Hz, 2H), 2.07 (q, J = 9.6 Hz, 2H), 2.02 – 1.92 (m, 2H), 1.87 – 1.76 (m, 1H), 1.59 (dp, J = 11.3, 8.8 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 142.5, 128.4, 128.3, 125.7, 75.2, 41.3, 36.0, 29.9, 12.1.

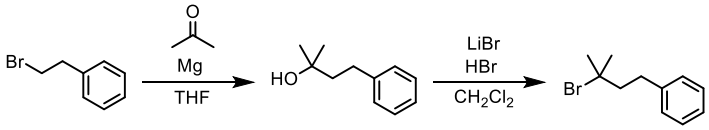


To a 40 mL screw-cap scintillation vial was added 1-phenethylcyclobutan-1-ol (8.411 g, 47.71 mmol), LiBr (12.428 g, 143.21 mmol, 3 equiv), CH_2Cl_2 (10 mL) and a stir bar. While stirring, HBr (48%, 25 mL) was added in one portion. The resulting reaction mixture was allowed to stir at room temperature for 12 hours. The resulting mixture was dissolved in hexanes and the organic layer was extracted with water (3x20 mL), brine (2x10 mL), dried over Na_2SO_4, and concentrated by rotary evaporation. Elution of the crude material by flash column chromatography (Hexanes) afforded the product as a colorless oil (7.291 g, 30.50 mmol, 63%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 – 7.28 (m, 2H), 7.24 (s, 2H), 7.23 – 7.18 (m, 1H), 2.86 – 2.82 (m, 2H), 2.78 – 2.65 (m, 2H), 2.48 – 2.37 (m, 2H), 2.31 – 2.16 (m, 1H), 2.28 – 2.19 (m, 2H), 1.89 (dtt, J = 11.2, 8.6, 6.9 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 141.5, 128.5, 128.4, 125.9, 68.0, 46.0, 40.0, 32.6, 17.1.

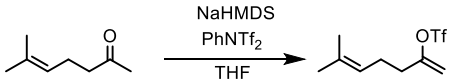
(3-bromo-3-methylbutyl)benzene



To a 250 mL round-bottom flask was added magnesium turnings (1.311 g, 54.04 mmol), THF (70 mL), a crystal of I_2, and a stir bar. The resulting mixture was cooled to 0 °C in an ice bath and allowed to stir in an ice bath until the solution changed colors from yellow to clear. While stirring, a (2-bromoethyl)benzene (5.004 g, 27.02 mmol) was slowly added. The resulting mixture was allowed to stir at room temperature for 5 hours. After this time, the reaction was cooled to 0 °C. To this solution was slowly added acetone (4.0 mL, 54 mmol, 2.0 equiv). This reaction was allowed to stir at room temperature for 12 hours after which it was quenched with 10 mL of H_2O. EtOAc (30 mL) was added, and the organic layer was extracted with water (3x20 mL), brine (2x10 mL), dried over Na_2SO_4, and concentrated by rotary evaporation. Purification by flash column chromatography (10:90 EtOAc:Hexanes) afforded 2-methyl-4-phenylbutan-2-ol as a colorless oil (3.682 g, 22.42 mmol, 83%).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 – 7.29 (m, 2H), 7.23 (d, J = 7.0 Hz, 2H), 7.21 – 7.18 (m, 1H), 2.77 – 2.70 (m, 2H), 2.19 (s, 1H), 1.90 – 1.77 (m, 3H), 1.32 (s, 6H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 142.5, 128.3, 128.3, 125.7, 70.8, 45.7, 30.7, 29.3.

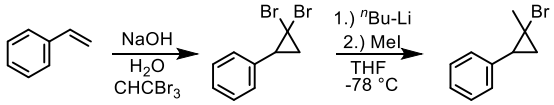
To a 40 mL screw-cap scintillation vial was added 2-methyl-4-phenylbutan-2-ol (3.682 g, 22.42 mmol), LiBr (5.384 g, 67.22 mmol, 3 equiv), CH_2Cl_2 (2 mL) and a stir bar. While stirring, HBr (48%, 15 mL) was added in one portion. The resulting reaction mixture was allowed to stir at room temperature for 12 hours. The resulting mixture was dissolved in hexanes and the organic layer was extracted with water (3x20 mL), brine (2x10 mL), dried over Na_2SO_4, and concentrated by rotary evaporation. Elution of the crude material by flash column chromatography (Hexanes) afforded the product as a colorless oil (3.284 g, 14.46 mmol, 64%). Analysis by ^{1}H NMR spectroscopy and ^{13}C NMR spectroscopy matches characterization of previously reported literature for the title compound.(*16*~~62~~)
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 – 7.28 (m, 2H), 7.25 – 7.19 (m, 2H), 2.94 – 2.83 (m, 2H), 2.16 – 2.04 (m, 2H), 1.85 (d, J = 1.7 Hz, 6H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 141.6, 128.4, 128.4, 125.9, 67.4, 49.4, 34.3, 32.9.

6-methylhepta-1,5-dien-2-yl trifluoromethanesulfonate



To a 40 mL screw-cap scintillation vial was added 6-methylhept-5-en-2-one (1.042 g, 7.920 mmol), THF (20 mL), and a stir bar. The reaction mixture was cooled to –78 °C and allowed to stir for 5 minutes. While stirring, a solution of NaHMDS (1.822 g, 9.946 mmol, 1.1 equiv) in THF (30 mL) was slowly added over 10 minutes. The resulting reaction mixture was allowed to warm to room temperature and stir for 20 minutes. The reaction mixture was then cooled to -78 °C and to this cooled solution was slowly added $PhNTf_2$ (3.386 g, 9.941 mmol, 1.2 equiv) as a solution in THF (15 mL). The resulting mixture was allowed to warm to room temperature and to stir for 12 hours. The crude mixture was dissolved in CH_2Cl_2 and the organic layer was extracted with water (3x20 mL), brine (2x10 mL), dried over Na_2SO_4, and concentrated by rotary evaporation. Elution of the crude material by flash column chromatography (Hexanes) afforded the product as a colorless oil (847 mg, 3.28 mmol, 41%). Analysis by ^{1}H NMR spectroscopy and ^{13}C NMR spectroscopy matches characterization of previously reported literature for the title compound.(*6*~~46~~)
^{1}H NMR (400 MHz, $CDCl_3$) δ 5.10 (d, J = 3.5 Hz, 1H), 5.07 (ddq, J = 7.0, 2.9, 1.4 Hz, 1H), 4.93 (dt, J = 3.6, 1.1 Hz, 1H), 2.36 (ddt, J = 7.7, 6.6, 1.1 Hz, 2H), 2.24 (dtdd, J = 8.0, 7.0, 2.0, 1.0 Hz, 2H), 1.70 (d, J = 1.4 Hz, 3H), 1.62 (d, J = 1.2 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$ δ 156.6, 133.7, 121.5, 119.1 (q, J = 320.0 Hz), 104.3, 34.0, 25.6, 24.6, 17.7.

(2-bromo-2-methylcyclopropyl)benzene



Following a modification of a published procedure,(6~~5~~7) to a 40 mL screw-cap scintillation vial was added styrene (3.0 mL, 26 mmol), bromoform (10.0 mL, 90.6 mmol), and a stir bar. The reaction mixture was cooled to 0 °C, and to this cooled solution was slowly added aqueous NaOH (20 M, 10 mL). The resulting mixture was allowed to stir at 60 °C for 2 hours. After this time, the reaction was allowed to cool to room temperature, poured into EtOAc (50 mL), and extracted with water (50 mL), brine (20 mL), dried over sodium sulfate, and concentrated by rotary evaporation. Distillation of the crude product under vacuum (150°C) afforded (2,2-dibromocyclopropyl)benzene as a colorless liquid (3.3 g, 12 mmol, 46%). Analysis by ^{1}H NMR spectroscopy and ^{13}C NMR spectroscopy matches characterization of previously reported literature for the title compound.(6~~6~~8)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (dtd, J = 11.2, 6.3, 2.1 Hz, 3H), 7.31 (d, J = 6.7 Hz, 2H), 3.01 (t, J = 9.4 Hz, 1H), 2.18 (dd, J = 30.1, 9.0 Hz, 1H), 2.06 (t, J = 8.0 Hz, 1H).

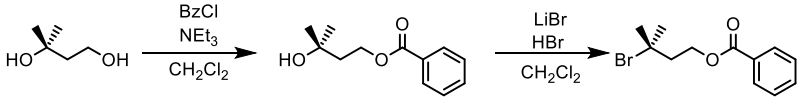
^{13}C NMR (101 MHz, $CDCl_3$ δ 132.9, 130.6, 127.9, 1275, 40.8, 35.0, 26.4.

To a 40 mL screw-cap scintillation vial was added (2,2-dibromocyclopropyl)benzene (1.122 g, 4.070 mmol), THF (20 mL), and a stir bar. This reaction was placed under N_2 and cooled to -78 °C while stirring. To this mixture was slowly added ^{n}BuLi (2.5 M in hexanes, 1.6 mL, 4.0 mmol, 1 equiv). The reaction mixture was allowed to stir for 10 minutes at -78 °C and promptly quenched with MeI (0.25 mL, 4.1 mmol, 1 equiv). The reaction was allowed to stir at -78 °C for 1 hour and then at room temperature for 30 minutes. The resulting reddish orange liquid was diluted in EtOAc (10 mL) and extracted with water (2x10 mL), brine (2x10 mL), dried over sodium sulfate, and concentrated by rotary evaporation. The red-orange oil was purified by distillation to afford the product as an orange oil (654 mg, 3.10 mmol, 76%) Analysis by ^{1}H NMR spectroscopy and ^{13}C NMR spectroscopy matches characterization of previously reported literature for the title compound.(6~~6~~8)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 – 7.30 (m, 2H), 7.29 – 7.25 (m, 1H), 7.26 – 7.20 (m, 2H), 1.94 – 1.82 (m, 1H), 1.62 (dd, J = 9.9, 6.7 Hz, 1H), 1.49 (s, 3H), 1.28 (t, J = 6.9 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 136.7, 128.7, 128.3, 126.7, 33.9, 32.5, 25.0, 21.3.

3-bromo-3-methylbutyl benzoate



Following a modification of a published procedure, to a 250 mL round-bottom flask was added 3-methylbutane-1,3-diol (5.204 g, 49.97 mmol), NEt3 (20.3 mL, 0.149 mmol, 3 equiv), and a stir bar. The reaction mixture was cooled to 0 °C, and to this cooled solution was slowly added benzoyl chloride (8.7 mL, 75 mmol, 1.5 equiv). The resulting mixture was allowed to stir at 60 °C for 2 hours. After this time, the reaction was allowed to cool to room temperature, filtered to remove any solid and washed with CH_2Cl_2. The filtrate was poured into EtOAc (50 mL), and extracted with water (50 mL), brine (20 mL), dried over sodium sulfate, and concentrated by rotary evaporation. Elution of the crude mixture by flash column chromatography (25:75 EtOAc:Hexanes) afforded 3-hydroxy-3-methylbutyl benzoate as a colorless liquid (7.573 g, 36.33 mmol, 73%).

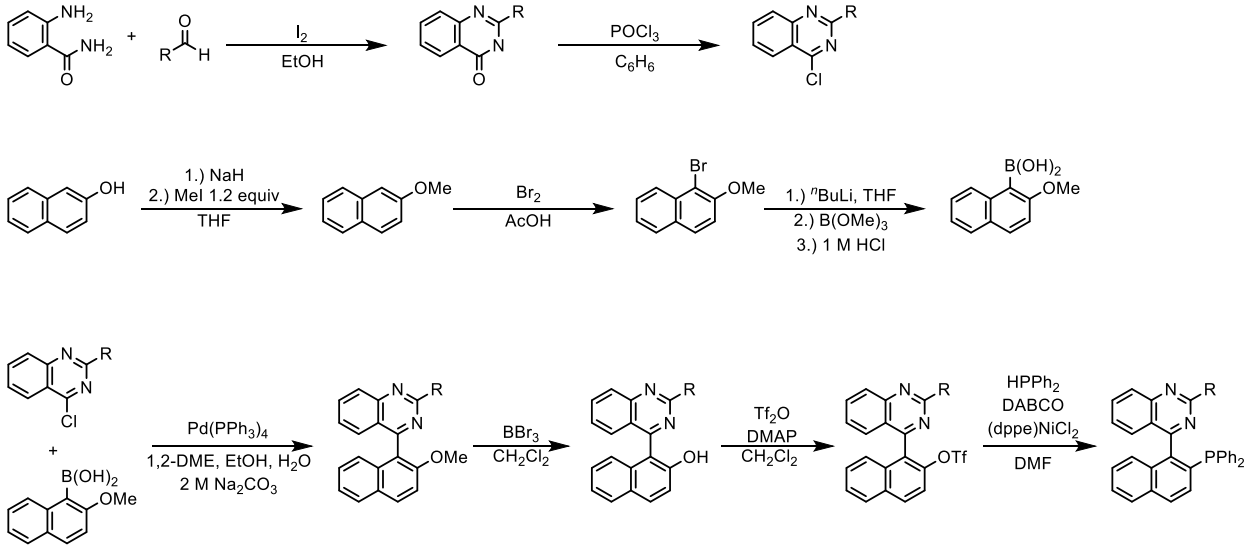
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 – 7.95 (m, 2H), 7.52 (ddt, J = 8.4, 6.6, 1.5 Hz, 1H), 7.46 – 7.35 (m, 2H), 4.48 (t, J = 6.9 Hz, 2H), 2.77 (s, 1H), 1.96 (t, J = 6.9 Hz, 2H), 1.36 – 1.26 (m, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 141.56, 128.45, 128.39, 125.95, 67.44, 49.42, 34.26, 32.88.

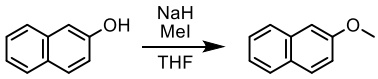
To a 40 mL screw-cap scintillation vial was added 3-hydroxy-3-methylbutyl benzoate (4.198 g, 20.16 mmol), LiBr (5.251 g, 60.47 mmol, 3 equiv), CH_2Cl_2 (2 mL) and a stir bar. While stirring, HBr (48%, 20 mL) was added in one portion. The resulting reaction mixture was allowed to stir at room temperature for 12 hours. The resulting mixture was dissolved in hexanes and the organic layer was extracted with water (3x20 mL), brine (2x10 mL), dried over Na_2SO_4, and concentrated by rotary evaporation. Elution of the crude material by flash column chromatography (5:95 EtOAc:Hexanes) afforded 3-bromo-3-methylbutyl benzoate as a yellow oil (3.559 g, 13.13 mmol, 65%). Analysis by ^{1}H NMR spectroscopy and ^{13}C NMR spectroscopy matches characterization of previously reported literature for the title compound(6~~6~~8)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 – 7.99 (m, 2H), 7.55 (ddt, J = 8.4, 6.6, 1.4 Hz, 1H), 7.43 (t, J = 7.4 Hz, 2H), 4.57 (t, J = 6.7 Hz, 2H), 2.30 (t, J = 6.8 Hz, 2H), 1.85 (s, 6H).
^{13}C NMR (101 MHz, $CDCl_3$ δ 167.1, 133.8, 130.4, 128.9, 128.1, 67.2, 61.6, 44.6, 35.7.

Overall synthetic route to Quinazolinap ligands

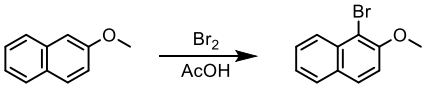


2-methoxynaphpthalene



Following a published procedure,(*5169*) a 2 L round-bottom flask was charged with 2-naphthol (100 g, 0.693 mol, 1 equiv), a stir bar, and 1.40 L of THF. This mixture was allowed to stir in an ice bath for 20 minutes before slowly adding NaH (60% dispersion in mineral oil, 18.31 g, 0.763 mol, 1.2 equiv) over the course of 30 minutes. To the resulting dark blue mixture was added MeI (52.8 mL, 0.83 mmol, 1.2 equiv). The reaction mixture was allowed to stir at room temperature for 12 hours. The reaction was quenched with 20 mL of H_2O and concentrated by rotary evaporation. The resulting slurry was redissolved in hexanes (1 L) and extracted with H_2O (3x100 mL), brine (2x 100 mL), and dried over Na_2SO_4 and filtered over a 3 in. pad of silica gel. The resulting clear solution was concentrated by rotary evaporation to afford a white powder (102.33 g, 0.646 mol, 93%. Analysis by ^{1}H NMR spectroscopy and ^{13}C NMR spectroscopy matches characterization of previously reported literature for the title compound.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (dd, J = 12.0, 8.2 Hz, 3H), 7.48 (ddd, J = 8.3, 6.9, 1.4 Hz, 1H), 7.37 (ddd, J = 8.1, 6.8, 1.3 Hz, 1H), 7.22 – 7.15 (m, 2H), 3.95 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 157.7, 134.6, 129.4, 129.10, 127.7, 126.8, 126.4, 123.6, 118.8, 105.8, 55.3.

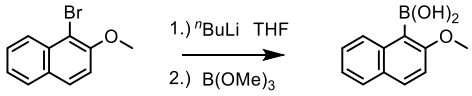
1-bromo-2-methoxynaphpthalene



Following a published procedure,(*5169*) 2-methoxynaphpthalene (50 g, 0.316 mol, 400 mM) was dissolved in AcOH (800 mL). A stir bar was added and the reaction mixture was allowed to stir while adding a solution Br_2 (16.2 mL, 0.316 mol, 1 equiv, 1 M) in AcOH (300 mL) over the course of an hour. The reaction mixture was allowed to stir for 12 hours at which point a white solid had precipitated. This solid was collected by vacuum filtration and washed with water. To the filtrate was added water until a white solid precipitated and was collected by filtration. Together these solids were combined and dissolved in DCM (300 mL) and dried over sodium sulfate. Concentration by rotary evaporation afforded the title compound as a colorless crystalline solid (57.87 g, 0.244 mol, 77%) Analysis by ^{1}H NMR spectroscopy and ^{13}C NMR spectroscopy matches characterization of previously reported literature for the title compound.

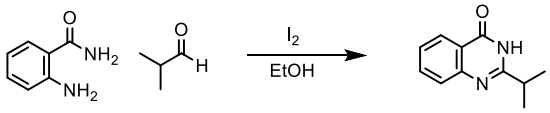
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.33 – 8.22 (m, 1H), 7.83 – 7.75 (m, 2H), 7.59 (ddd, J = 8.4, 6.7, 1.2 Hz, 1H), 7.41 (ddd, J = 8.1, 6.8, 1.2 Hz, 1H), 7.23 (d, J = 9.0 Hz, 1H), 4.01 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 133.2,129.9, 129.0, 129.0, 127.8, 126.2, 124.4, 113.6, 57.1

(2-methoxynaphthalen-1-yl)boronic acid



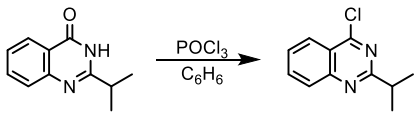
Following a modified version of a published procedure,(*5169*) 1-bromo-2-methoxynapthalene (10.00 g, 42.18 mmol, 1 equiv) was dissolved in anhydrous THF (200 mL) and allowed to stir under an inert atmosphere at -78 °C for 15 minutes. To this mixture was slowly added ^{n}BuLi (2.5 M in hexanes, 18.6 mL, 46.4 mmol, 1.1 equiv). Upon complete addition, the mixture was removed from the cold well and allowed to stir for 1 hours at room temperature. The solution was cooled down to -78 °C and trimethyl borate (7.0 mL, 63.3 mmol, 1.5 equiv) was slowly added over 15 minutes. The resulting solution was allowed to warm to room temperature and stir for 12 hours. The reaction mixture was quenched with 1 M HCl in water (50 mL) and allowed to stir for 1 hour. The resulting slurry was concentrated by rotary evaporation, dissolved in DCM, and extracted with brine(2x50 mL). The organic layer was separated and dried over Na_2SO_4 and concentrated by rotary evaporation. The resulting solid was allowed to stir in hexanes for 30 minutes and filtered and collected, washing with hexanes, to afford the title compound as a white solid (Analysis by ^{1}H NMR spectroscopy and ^{13}C NMR spectroscopy matches characterization of previously reported literature for the title compound.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.87 (dq, J = 8.7, 0.9 Hz, 1H), 7.97 (dt, J = 9.0, 0.6 Hz, 1H), 7.81 (ddd, J = 8.1, 1.4, 0.7 Hz, 1H), 7.54 (ddd, J = 8.6, 6.8, 1.5 Hz, 1H), 7.40 (ddd, J = 8.0, 6.8, 1.2 Hz, 1H), 7.31 (d, J = 9.1 Hz, 1H), 6.23 (s, 2H), 4.06 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 163.4, 137.9, 133.4, 129.5, 128.2, 128.1, 127.2, 123.9, 112.4, 56.7.

2-isopropylquinazolin-4(3H)-one



Following a modified version of a published procedure,(*6770*) a 1 L round-bottom flask was charged with 2-aminobenzamide (20.00 g, 146.9 mmol, 1 equiv), EtOH (~700 mL, 200 mM), and a stir bar. The reaction mixture was allowed to stir at room temperature for five minutes to ensure homogeneity upon which isobutyraldehyde (20.1 mL, 220 mmol, 1.5 equiv) was added. The resulting solution was allowed to stir for 15 minutes followed by addition of I_2 (44.74 g, 176.2 mmol, 1.2 equiv). This dark purple reaction mixture was allowed to stir for 12 hours at 90 °C. Upon completion, the mixture was allowed to cool to room temperature and the excess I_2 was quenched with sodium thiosulfate. After concentrating by rotary evaporation, the resulting mixture was dissolved in DCM and extracted with water (3x100 mL), brine (2x50 mL), and dried over sodium sulfate. The organic layer was concentrated by rotary evaporation to afford an off white solid. Recrystallization in DCM afforded the product as a white powder (22.77 g, 121.6 mmol, 83%). Analysis by ^{1}H NMR spectroscopy and ^{13}C NMR spectroscopy matches characterization of previously reported literature for the title compound.
^{1}H NMR (400 MHz, $CDCl_3$) δ 11.65 (s, 1H), 8.29 (dt, J = 8.0, 1.0 Hz, 1H), 7.79 – 7.69 (m, 2H), 7.46 (ddd, J = 8.1, 6.8, 1.5 Hz, 1H), 3.06 (hept, J = 7.0 Hz, 1H), 1.45 (d, J = 6.9 Hz, 6H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 164.2, 160.9, 149.5, 134.7, 127.4, 126.3, 126.2, 120.7, 34.9, 20.4.

4-chloro-2-isopropylquinazoline



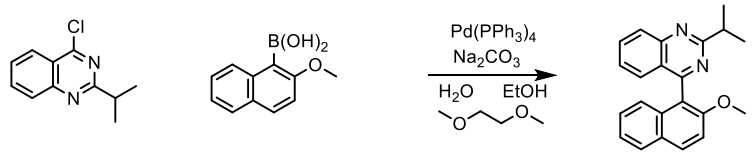
Following a published procedure,(*5169*) 2-isopropylquinazolin-4(3H)-one(5.014, 26.64 mmol), dry benzene (150 mL), N,N-diethylaniline (6.3 mL, 40 mmol, 1.5 equiv), and a stir bar were added to a 250 mL round-bottom flask. This solution was allowed to stir at 100 °C for 15 minutes after which time phosphorus oxychloride (2.2 mL, 24 mmol, 0.9 equiv) was added in one portion and allowed to stir for 4 hours at 100 °C. After this time, the mixture was cooled

to room temperature and filtered, washing with dry benzene. The organic layer was washed with cold water (1x100 mL), cold 2 M NaOH (2x100 mL), 2 M HCl (2x100 mL), water (1x100 mL), brine (1x100 mL), and dried over sodium sulfate. Concentration by rotary evaporation afforded 4-chloro-2-isopropylquinazoline as a yellow solid (3.86 g, 19 mmol, 70%). Analysis by ^{1}H NMR spectroscopy and ^{13}C NMR spectroscopy matches characterization of previously reported literature for the title compound.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (ddd, J = 8.3, 1.4, 0.7 Hz, 1H), 7.88 (ddd, J = 8.5, 1.2, 0.7 Hz, 1H), 7.78 (ddd, J = 8.4, 6.9, 1.4 Hz, 1H), 7.52 (ddd, J = 8.3, 6.9, 1.2 Hz, 1H), 3.24 (hept, J = 6.9 Hz, 1H), 1.34 (d, J = 6.9 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 153.8, 133.2, 129.9, 129.0, 128.1, 127.8, 126.1, 124.4, 113.6, 108.7, 57.0.

2-isopropyl-4-(2-methoxynaphthalen-1-yl)quinazoline

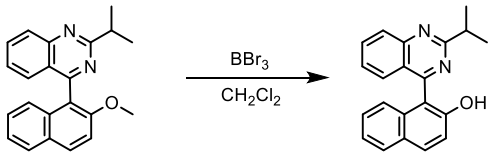


Following a published procedure,(*5169*) $Pd(PPh_3)_4$ (1.164 g, 1.000 mmol, 2.5 mol%) was dissolved in 1,2,-dimethoxyethane (40 mL, ~25 mM). To this yellow solution was added 2-isopropyl-4-chloroquinazoline (8.122 g, 40.19 mmol, 1 equiv) as a solid and stirred for 10 min under a nitrogen atmosphere. 2-Methyloxy-1-naphthylboronic acid (31.40 mmol), dissolved in the minimum amount of degassed ethanol (~30 mL), was then added to the 2-isopropyl-chloroquinazoline solution. Then, sodium carbonate solution (35 mL, 2M) was added, and the solution was allowed to stir at reflux under nitrogen for 36 hours. The solution was then cooled to room temperature and filtered to remove any solid, washing with CH_2Cl_2. The solvent was removed in vacuo to afford a brown oil, which was redissolved in dichloromethane (50 mL), washed with brine (2x30 mL), dried over sodium sulfate, and concentrated in vacuo. The resulting brown solid was allowed to stir in ether for 30 minutes and then filtered and washed with cold ether to afford pure 2-isopropyl-4-(2-methoxynaphthalen-1-yl)quinazoline (10.281 g, 31.30 mmol, 78%). Analysis by ^{1}H NMR spectroscopy and ^{13}C NMR spectroscopy matches characterization of previously reported literature for the title compound.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (dt, J = 8.5, 0.9 Hz, 1H), 8.03 (dd, J = 9.1, 0.8 Hz, 1H), 7.91 – 7.86 (m, 1H), 7.82 (ddd, J = 8.4, 6.8, 1.5 Hz, 1H), 7.47 – 7.41 (m, 2H), 7.40 – 7.31 (m, 2H), 7.32 – 7.27 (m, 1H), 7.11 (dt, J = 8.4, 1.0 Hz, 1H), 3.78 (s, 3H), 1.51 (dd, J = 6.9, 2.5 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 171.5, 167.2, 154.7, 150.8, 133.4, 133.1, 131.1, 129.2, 128.4, 128.1, 127.1, 126.9, 126.5, 124.4, 123.9, 123.6, 120.2, 113.6.

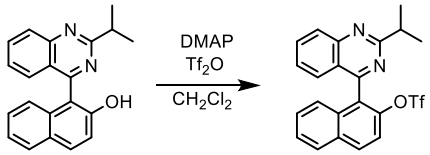
1-(2-isopropylquinazolin-4-yl)naphthalen-2-ol



Following a published procedure,(*5169*) 2-isopropyl-4-(2-methoxy-naphthalen-1-yl)-quinazoline (5.768 g, 17.54 mmol) was dissolved in CH_2Cl_2 (100 mL). BBr_3 (1.7 mL, 18 mmol, 2 equiv) dissolved in CH_2Cl_2 (~1 M) was added slowly via syringe. Upon complete addition, the reaction was covered in aluminum foil and allowed to stir for 12 hours at room temperature. The reaction was slowly quenched with water (100 mL) forming an orange precipitate. This precipitate was isolated by filtration giving pure 1-(2-substituted-quinazolin4-yl)-naphthalen-2-ol. The filtrate was neutralized with 1 M NaOH (2x50 mL) and extracted with dichloromethane, and the organic layer was then stirred with 2 M HCl (150 mL) for 10 min. Dichloromethane was added to dissolve any additional solid that precipitated from solution. To this solution was added the collected solid and 2 M Na_2CO_3 (100 mL) solution was added and allowed stir for 30 min. The organic layer was isolated from the black solution, the aqueous layer was extracted twice with dichloromethane, and the combined solutions were dried over sodium sulfate and concentrated by rotary evaporation to afford 1-(2-isopropyl-quinazolin-4-yl)-naphthalen-2-ol was as a light orange powder (4.414 g, 14.04 mmol, 80%). Analysis by ^{1}H NMR spectroscopy and ^{13}C NMR spectroscopy matches characterization of previously reported literature for the title compound.

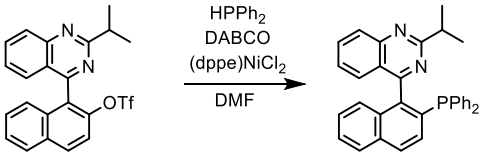
^{1}H NMR (400 MHz, $CDCl_3$) δ 10.11 (s, 1H), 8.07 (dt, J = 8.2, 0.8 Hz, 1H), 7.91 (d, J = 8.9 Hz, 1H), 7.89 – 7.81 (m, 2H), 7.60 – 7.56 (m, 1H), 7.39 – 7.33 (m, 3H), 7.34 – 7.30 (m, 1H), 7.30 – 7.27 (m, 1H), 3.47 (hept, J = 6.9 Hz, 1H), 1.52 (d, J = 6.9 Hz, 6H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 170.2, 166.1, 155.1, 151.9, 134.1, 132.6, 132.5, 128.7, 128.7, 128.4, 128.0, 126.6, 126.4, 125.1, 123.6, 122.2, 119.1, 114.5, 37.8, 22.1, 21.5.

1-(2-isopropylquinazolin-4-yl)naphthalen-2-yl trifluoromethanesulfonate



Following a published procedure,(*5169*) to a solution of 1-(2-isopropyl-quinazolin4-yl)-naphthalen-2-ol (4.414 g, 14.03 mmol), and 4-(dimethylamino)pyridine, (5.147 g, 42.10 mmol, 3 equiv), and CH_2Cl_2 (70 mL) was slowly added trifluoromethanesulfonic anhydride (2.8 mL, 17 mmol, 1.2 equiv). The reaction was allowed to stir for 12 hours. The dark orange solution was then washed with 1 M HCl (3x25 mL), water (2x25 mL), and brine (2x20 mL), dried over sodium sulfate, and concentrated by rotary evaporation to afford an orange solid. Purification by flash column chromatography (5:95 EtOAc:Hexanes) afforded 1-(2-isopropyl-quinazolin4-yl)-2-naphthyl(trifluoromethyl) sulfonate as a slightly yellow solid (5.424 g, 12.15 mmol, 86%). Analysis by ^{1}H NMR spectroscopy and ^{13}C NMR spectroscopy matches characterization of previously reported literature for the title compound.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 – 8.10 (m, 2H), 8.03 – 7.98 (m, 1H), 7.88 (ddd, J = 8.5, 6.7, 1.6 Hz, 1H), 7.64 – 7.57 (m, 2H), 7.48 – 7.39 (m, 2H), 7.36 (ddd, J = 8.3, 1.6, 0.7 Hz, 1H), 7.31 – 7.27 (m, 1H), 3.49 (p, J = 6.9 Hz, 1H), 1.50 (dd, J = 6.9, 6.0 Hz, 6H).
^{13}C NMR (101 MHz, $CDCl_3$) 171.5, 163.3, 150.7, 144.5, 134.2, 132.4, 132.4, 131.9, 128.5, 128.4, 128.2, 127.4 127.3 127.2, 126.2, 126.1, 123.0, 119.5, 118.1 (q, J = 320.3 Hz), 38.0, 21.8, 21.6.

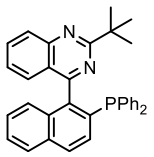
4-(2-(diphenylphosphaneyl)naphthalen-1-yl)-2-isopropylquinazoline (iPrQ)



Following a published procedure,(*5169*) ~~T~~to a solution of (dppe)$NiCl_2$ (467 mg, 0.884 mmol, 10 mol%) in anhydrous DMF (25 mL, ~35 mM) was added diphenyl phosphine (0.9 mL, 10 mmol, 0.6 equiv) at room temperature. The resulting solution was allowed to stir at 100 °C for 30 min under nitrogen. After this time, 1-(2-isopropyl-quinazolin-4-yl)2-naphthyl(trifluoromethyl) sulfonate (3.951 g, 8.853 mmol) and DABCO (3.970 g, 35.39 mmol) in DMF (35 mL) were subsequently added. The dark green solution was allowed to stir at 100 °C for 1 h after which another portion of diphenyl phosphine (0.9 mL, 10 mmol, 0.6 equiv) was added. The reaction was allowed to stir at 100 °C, under a nitrogen atmosphere 3 days. The reaction was allowed to cool, and the solvent was removed by rotary evaporation. The black residue was purified by chromatography (silica gel, 3:97 EtOAc:Hexanes) to afford (R,S)-diphenyl(1-(2-isopropyl-quinazolin-4-yl)(2-naphthyl)phosphine (3.460 g, 6.931 mmol, 78%). Analysis by ^{1}H NMR spectroscopy and ^{13}C NMR spectroscopy matches characterization of previously reported literature for the title compound.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (dt, J = 8.5, 0.9 Hz, 1H), 7.94 – 7.88 (m, 2H), 7.81 (ddd, J = 8.4, 6.6, 1.7 Hz, 1H), 7.51 (ddd, J = 8.2, 6.8, 1.2 Hz, 1H), 7.38 (dd, J = 8.5, 3.2 Hz, 1H), 7.35 – 7.21 (m, 11H), 7.20 – 7.14 (m, 2H), 7.12 (dd, J = 8.5, 1.0 Hz, 1H), 3.29 (hept, J = 6.9 Hz, 1H), 1.27 (dd, J = 8.3, 6.9 Hz, 6H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 171.1, 169.1 (d, J = 6.5 Hz), 150.5, 142.2 (d, J = 33.0 Hz), 137.3 (d, J = 12.0 Hz), 136.5 (d, J = 11.0 Hz), 134.3 (d, J = 14.8 Hz), 133.5 (d, J = 18.0 Hz), 133.34 (d, J = 19.2 Hz), 133.2, 131.8 (d, J = 7.9 Hz), 130.0 (d, J = 1.4 Hz), 129.0, 128.5, 128.4, 128.3, 128.3, 128.3, 128.2, 128.2, 128.0, 127.0, 126.9, 126.7, 126.6, 126.2 (d, J = 2.3 Hz), 123.6 (d, J = 2.6 Hz). 37.9, 21.8, 21.1.
^{31}P NMR (162 MHz, CDCl3) δ -14.1

Quinazolinap derivatives were prepared following the general route detailed above and previous reports.(*5169*)

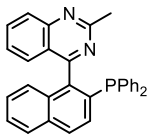
tBu-Quinazolinap



Synthesized according the procedure given above. 987 mg, 2.05 mmol, 76%. Analysis by ^{1}H NMR spectroscopy and ^{13}C NMR spectroscopy matches characterization of previously reported literature for the title compound.(*5169*)

^{1}H NMR (400 MHz, CDCl$_3$) δ 8.14 (s, 1H), 7.91 (dd, J = 8.6, 0.9 Hz, 2H), 7.81 (dddd, J = 8.5, 6.1, 2.5, 0.9 Hz, 1H), 7.51 (ddd, J = 8.2, 6.9, 1.2 Hz, 1H), 7.38 – 7.34 (m, 1H), 7.34 – 7.30 (m, 4H), 7.28 (dd, J = 5.9, 1.4 Hz, 3H), 7.25 – 7.18 (m, 3H), 7.16 (ddt, J = 7.7, 7.0, 1.1 Hz, 2H), 7.08 (dt, J = 8.5, 1.0 Hz, 1H), 1.32 (s, 9H).
^{13}C NMR (101 MHz, CDCl$_3$) δ 172.96, 168.44 (d, J = 6.6 Hz), 150.34, 142.75 (d, J = 33.4 Hz), 137.62 (d, J = 12.3 Hz), 136.63 (d, J = 11.2 Hz), 134.13 (d, J = 14.4 Hz), 133.84, 133.63, 133.56 (d, J = 17.6 Hz), 133.31 (d, J = 18.8 Hz), 133.30 (d, J = 27.4 Hz), 131.94 (d, J = 8.0 Hz), 130.16 (d, J = 1.7 Hz), 129.01, 128.78, 128.62 (d, J = 18.3 Hz), 128.39 (d, J = 15.4 Hz), 128.31 (d, J = 14.8 Hz), 128.17, 128.08, 126.99, 126.81, 126.55 (d, J = 2.3 Hz), 126.36 (d, J = 2.2 Hz), 123.29 (d, J = 2.5 Hz), 39.55, 29.35.
^{31}P NMR (162 MHz, CDCl3) δ -13.8

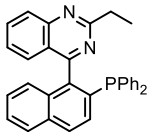
Me-Quinazolinap



Synthesized according a literature procedure.(*5169*) 138 mg, 0.303 mmol, 48%. Analysis by ^{1}H NMR spectroscopy and ^{13}C NMR spectroscopy matches characterization of previously reported literature for the title compound.(*5169*)

^{1}H NMR (400 MHz, CDCl$_3$) 8.09 (d, J = 8.5 Hz, 1H), 7.96 (d, J = 8.5 Hz, 1H), 7.93 (d, J = 8.5 Hz, 1H), 7.81 (t, J = 7.5 Hz, 1H), 7.51 (t, J = 7.6 Hz, 1H,), 7.43 (dd, J = 8.6 Hz, 3.2 Hz, 1H,), 7.34-7.17 (m, 13H), 7.13 (d, J=8.5 Hz, 1H) and 2.82 (s, 3H)
^{13}C NMR (101 MHz, CDCl$_3$) 169.5, 164.1 (d, J = 6.3 Hz), 150.8, 141.8 (d, J = 36.2 Hz), 137.1 (d, J = 14.3 Hz), 137.0 (d, J = 11.8 Hz), 135.0 (d, J = 18.8 Hz), 134.4 (d, J = 3.4 Hz), 133.7 (d, J = 16.8 Hz), 132.1, 130.1, 129.4, 128.7 (d, J = 2.3 Hz), 128.3, 128.3, 127.3, 127.2, 127.2, 126.9, 126.3, 123.6, 26.6
^{31}P NMR (162 MHz, CDCl$_3$) -13.4

Et-Quinazolinap

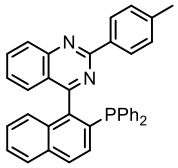


Synthesized according the procedure given above. 184 mg, 0.393 mmol, 74%.

^{1}H NMR (400 MHz, CDCl$_3$) δ 8.05 (s, 1H), 7.92 (d, J = 6.1 Hz, 2H), 7.90 (d, J = 5.6 Hz, 2H), 7.81 (ddd, J = 8.4, 6.6, 1.7 Hz, 3H), 7.50 (ddd, J = 8.2, 6.8, 1.2 Hz, 3H), 7.39 (dd, J = 8.5, 3.2 Hz, 3H), 7.34 – 7.32 (m, 2H), 7.31 – 7.27 (m, 11H), 7.25 – 7.19 (m, 20H), 7.15 (td, J = 7.8, 1.6 Hz, 5H), 7.11 (dd, J = 8.5, 1.0 Hz, 3H), 3.04 (q, J = 7.6 Hz, 4H), 1.26 (t, J = 7.6 Hz, 8H).
^{13}C NMR (101 MHz, CDCl$_3$) 13C NMR (101 MHz, Chloroform-d) δ 169.3 (d, J = 6.5 Hz), 168.1, 150.6, 141.9 (d,

J = 32.8 Hz), 137.1 (d, J = 11.6 Hz), 136.6 (d, J = 10.9 Hz), 134.5 (d, J = 15.1 Hz), 133.7, 133.5, 133.3, 131.8 (d, J = 7.7 Hz), 123.0, 129.2, 128.5, 128.4, 128.4, 128.3, 128.3, 128.2, 128.1, 127.1, 127.0, 126.9 126.7, 126.2 (d, J = 2.3 Hz), 123.5 (d, J = 2.6 Hz), 33.2, 12.9.
^{31}P NMR (162 MHz, CDCl3) δ -13.7

pTol-Quinazolinap



Synthesized according the procedure given above. 267 mg, 0.503 mmol, 50%.

^{1}H NMR (400 MHz, CDCl$_3$) δ 8.17 (dd, J = 8.6, 1.0 Hz, 1H), 8.09 (d, J = 8.1 Hz, 2H), 7.97 – 7.90 (m, 2H), 7.84 (ddd, J = 8.5, 6.7, 1.6 Hz, 1H), 7.50 (ddd, J = 8.1, 6.8, 1.2 Hz, 1H), 7.42 (dd, J = 8.5, 3.2 Hz, 1H), 7.37 (dd, J = 8.4, 1.6 Hz, 1H), 7.35 – 7.26 (m, 9H), 7.25 – 7.23 (m, 1H), 7.21 – 7.12 (m, 5H), 2.39 (s, 3H).
^{13}C NMR (101 MHz, CDCl$_3$) δ 169.04 (d, J = 6.2 Hz), 160.47, 151.06, 142.05 (d, J = 32.4 Hz), 140.34, 137.51 (d, J = 11.9 Hz), 136.69 (d, J = 10.8 Hz), 135.44, 134.63 (d, J = 15.0 Hz), 133.76, 133.66, 133.62, 133.56, 133.42, 131.90 (d, J = 7.5 Hz), 130.06, 129.11, 129.02, 128.95, 128.72, 128.41, 128.37, 128.34, 128.30, 128.07, 126.96, 126.88, 126.86, 126.80, 126.43 (d, J = 2.3 Hz), 123.84 (d, J = 2.1 Hz), 53.42, 21.48.
^{31}P NMR (162 MHz, CDCl3) δ -13.3

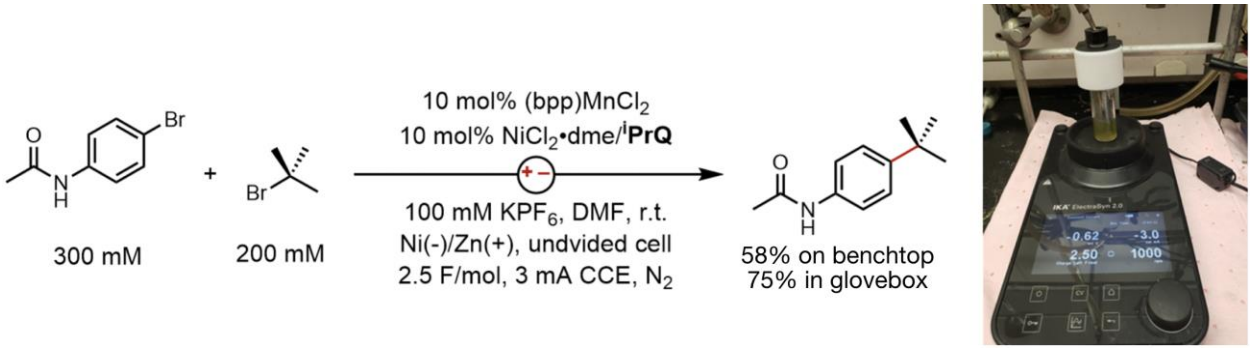


Figure S1. Results from reactions performed with an IKA ElectraSyn. **Reaction Procedure:** Inside an N_2-filled glovebox, an IKA ElectraSyn electrochemical cell equipped with a magnetic stir bar was charged with N-(4-bromophenyl)acetamide (308 mg, 1.61 mmol, 2.0 equiv), ^{t}BuBr (109 mg, 0.796 mmol, 1 equiv), KPF_6 (74 mg, 0.40 mmol), (bpp)$MnCl_2$ (27 mg, 0.15 mmol, 0.080 equiv), **^{i}PrQ** (39 mg, 0.081 mmol), (dme)$NiCl_2$ (18 mg, 0.082 mmol, 0.1 equiv), DMF (4.0 mL), and dodecane (27 mg, 0.16 mmol) as an internal standard. The electrochemical cell was sealed with a Teflon cap equipped with a Ni-foam cathode and a Zn anode. This mixture was allowed to stir for 5 minutes at room temperature before removing from the glovebox. The reaction was placed under active N_2 and a negative current was applied to the Ni-foam cathode (-3.0 mA). The reaction was allowed to run for 2.5 F/mol of electrons. Upon completion, the dark red mixture was diluted with ethyl acetate (20 mL) and extracted with brine (10 mL). The resulting mixture was analyzed by calibrated gas chromatography against the internal standard of dodecane.

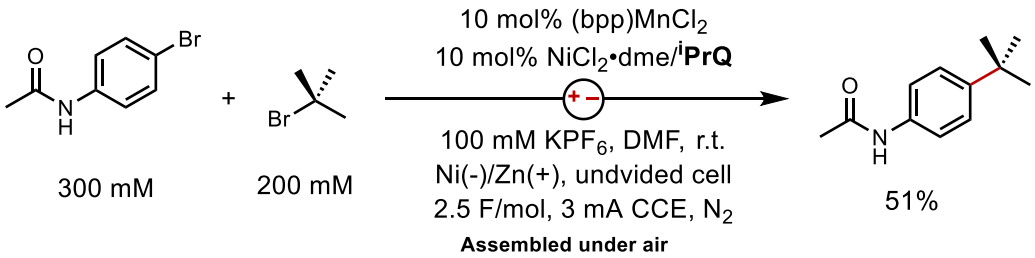


Figure S2: Evaluation of eXEC reaction that was assembled under atmospheric conditions. The vial headspace was exchanged with N_2 following vacuum/refill cycling. Lower yields compared to the standard reaction are attributed to the presence of oxygen, which unproductively consumes some of the 2.5e- equivalents that were passed. This is also consistent with a prolonged initial period of electrolysis before we observed the formation of a dark red solution that is consistent with the standard reactions.

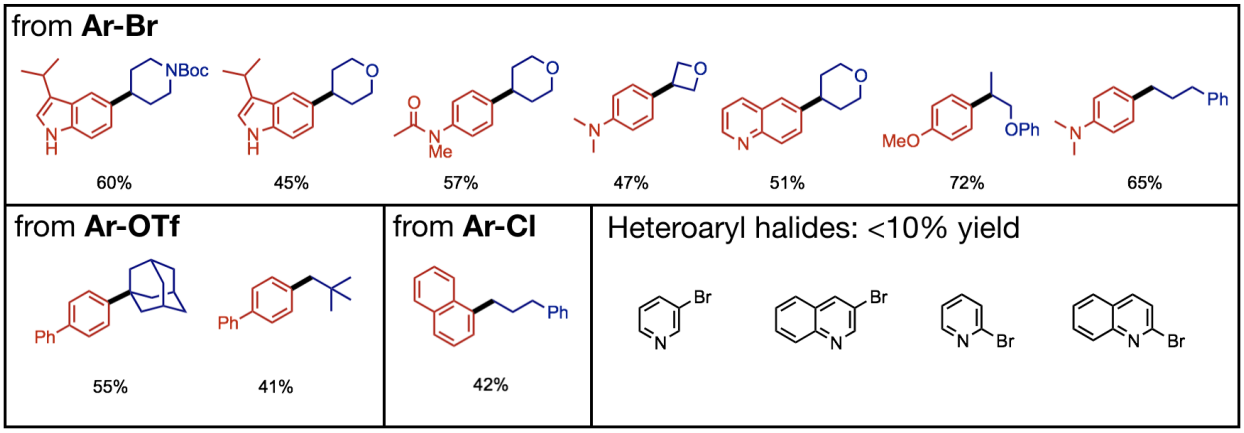


Figure S3. Additional examples of electrophilic couplings under the standard conditions.

Mechanistic Studies

Cyclic Voltammetry

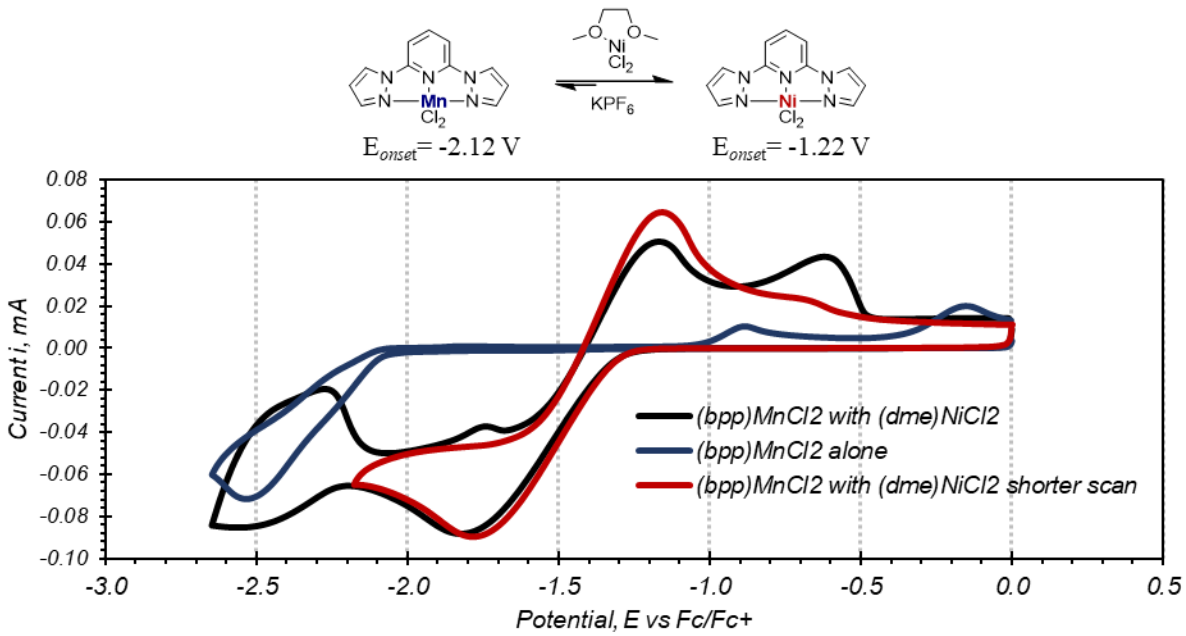


Figure S4. CV's of 10 mM (bpp)$MnCl_2$ (blue trace) with 10 mM (dme)$NiCl_2$ revealing the disappearance of (bpp)$MnCl_2$ and the growth of (bpp)$NiCl_2$. Glassy carbon WE, Pt CE, 0.1 M, DMF, KPF_6, 100 mV/s scan rate.

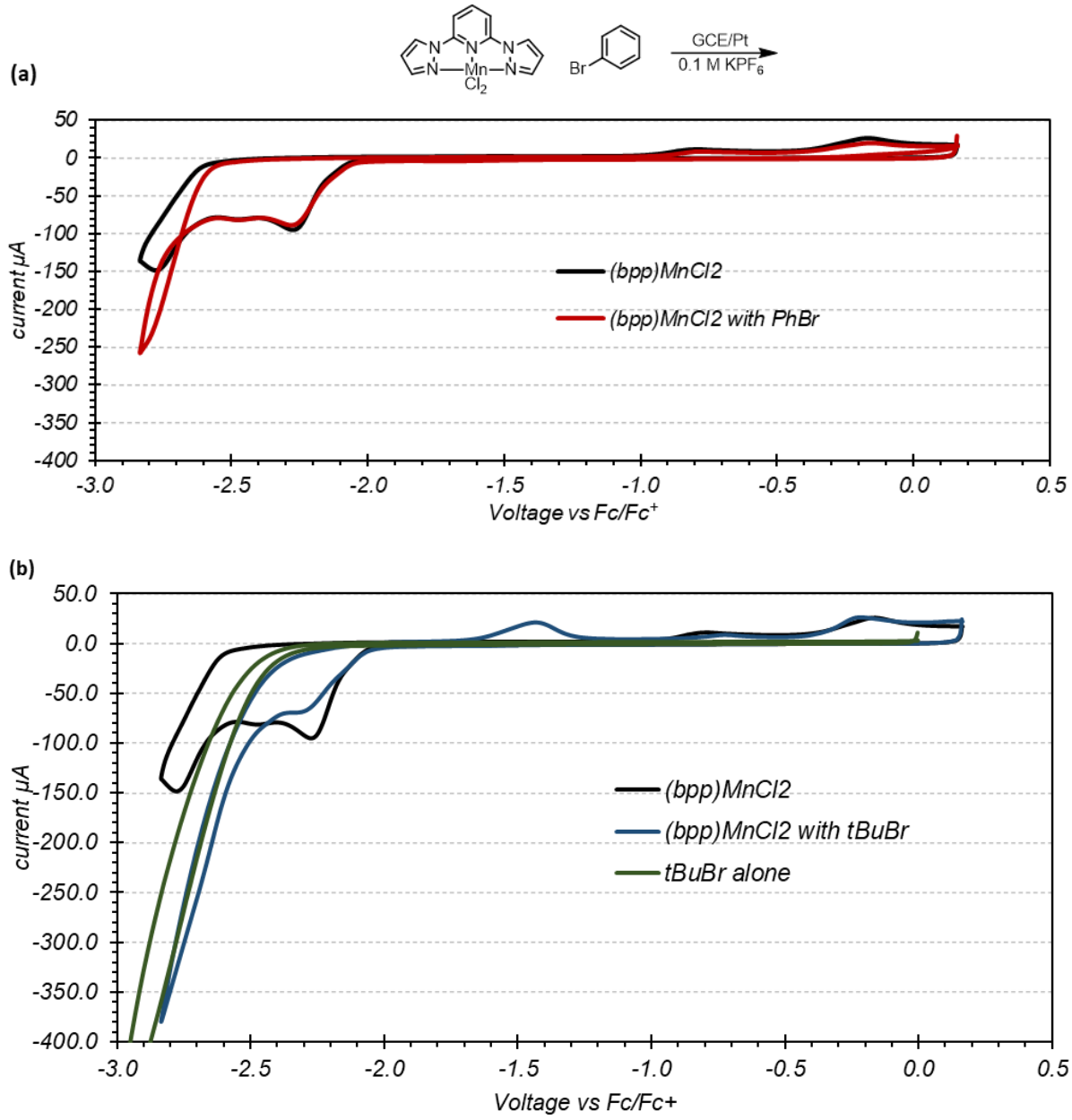


Figure S5. CV's of 10 mM (bpp)$MnCl_2$ (black trace) with electrophiles. (a) CV of of 10 mM (bpp)$MnCl_2$ in the presence of 50 mM PhBr (red trace). (b) CV of 10 mM (bpp)$MnCl_2$ in the presence of 50 mM ^{t}BuBr (blue trace) compared to ^{t}BuBr alone (green) Glassy carbon WE, Pt CE, 0.1 M, DMF, KPF_6, 100 mV/s scan rate.

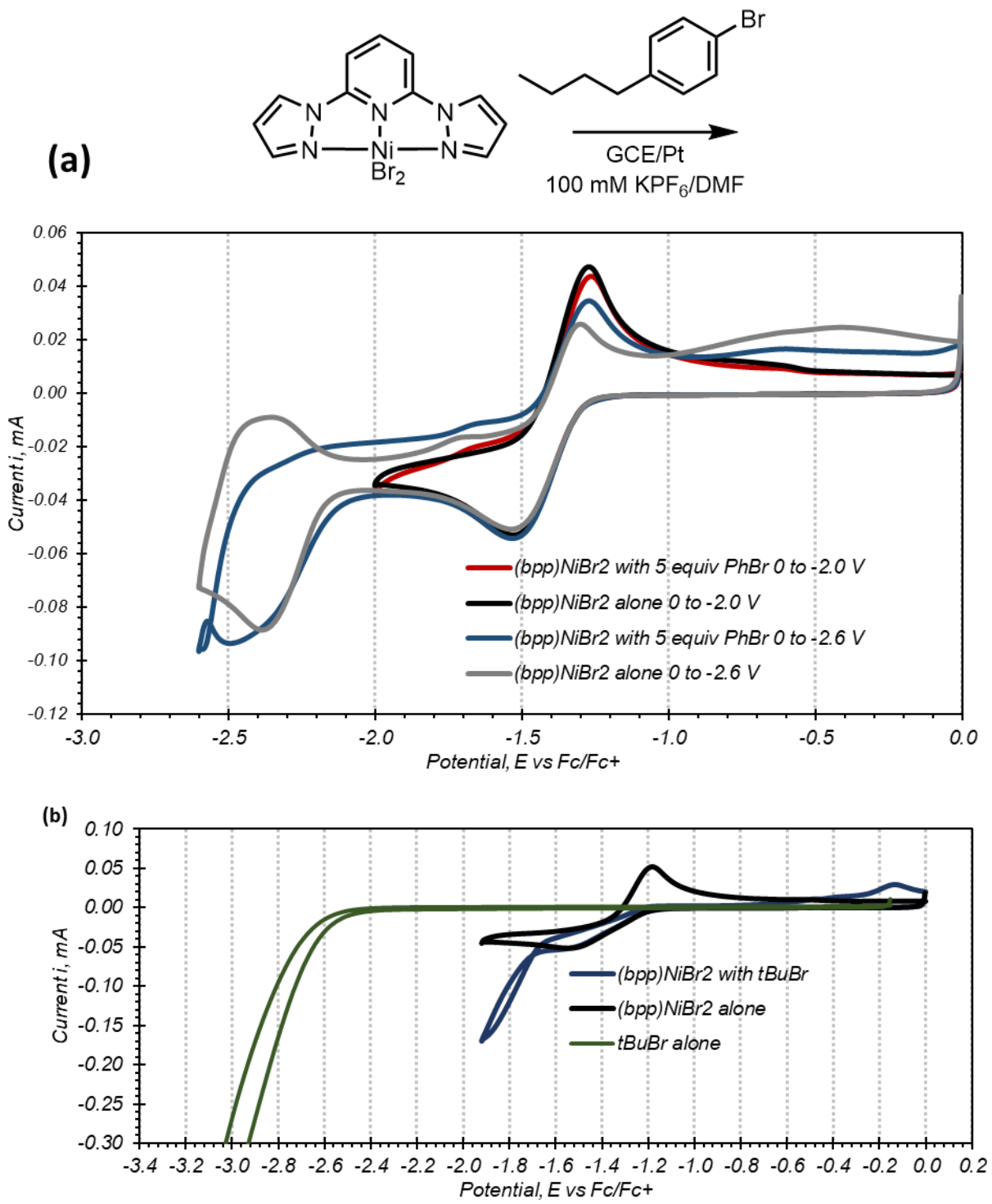


Figure S6. CV's of 10 mM (bpp)$NiBr_2$ (black trace) with electrophiles. (a) CV of of 10 mM (bpp)$NiBr_2$ in the presence of 50 mM PhBr (red trace). (b) CV of 10 mM (bpp)$NiBr_2$ in the presence of 50 mM ^{t}BuBr (blue trace) Glassy carbon WE, Pt CE, 0.1 M, DMF, KPF_6, 100 mV/s scan rate.

Additional Spectroelectrochemical Studies

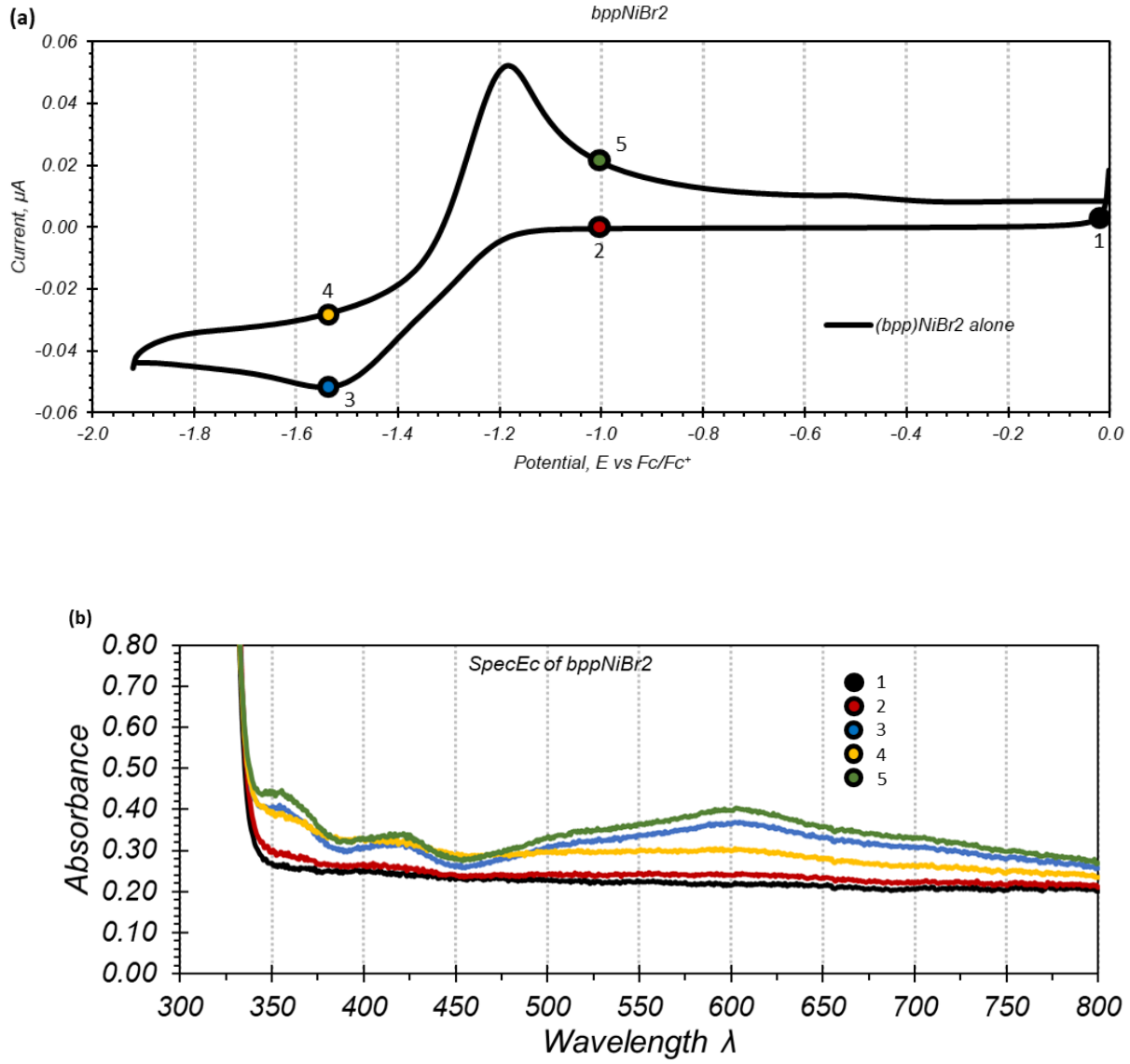


Figure S7. CV and spectroelectrochemical analysis of 10 mM (bpp)$NiBr_2$. (a) CV of of 10 mM (bpp)$NiBr_2$. (b) UV-vis taken at various potentials (see labelled dots). Gold WE, Gold CE, 0.1 M, DMF, KPF_6, 100 mV/s scan rate.

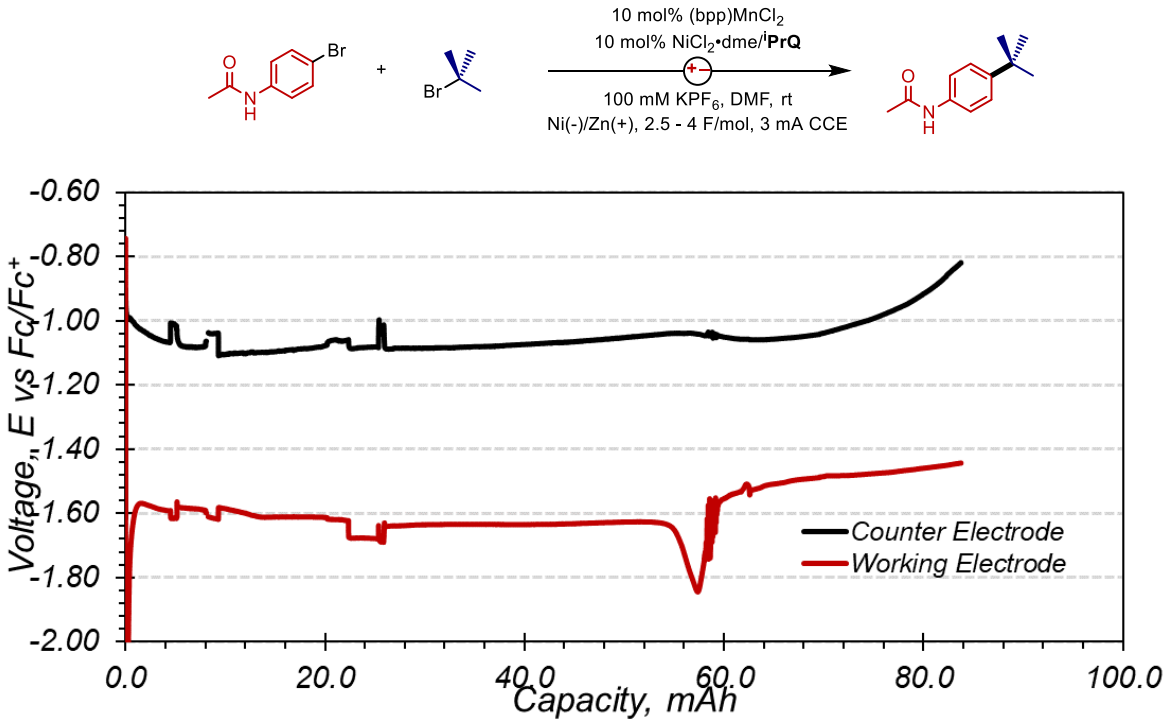


Figure S8. Voltage profile of a generic reaction. 300 mM ArBr, 200 mM ^{t}BuBr, Zn anode (counter electrode), Ni foam cathode (working electrode).

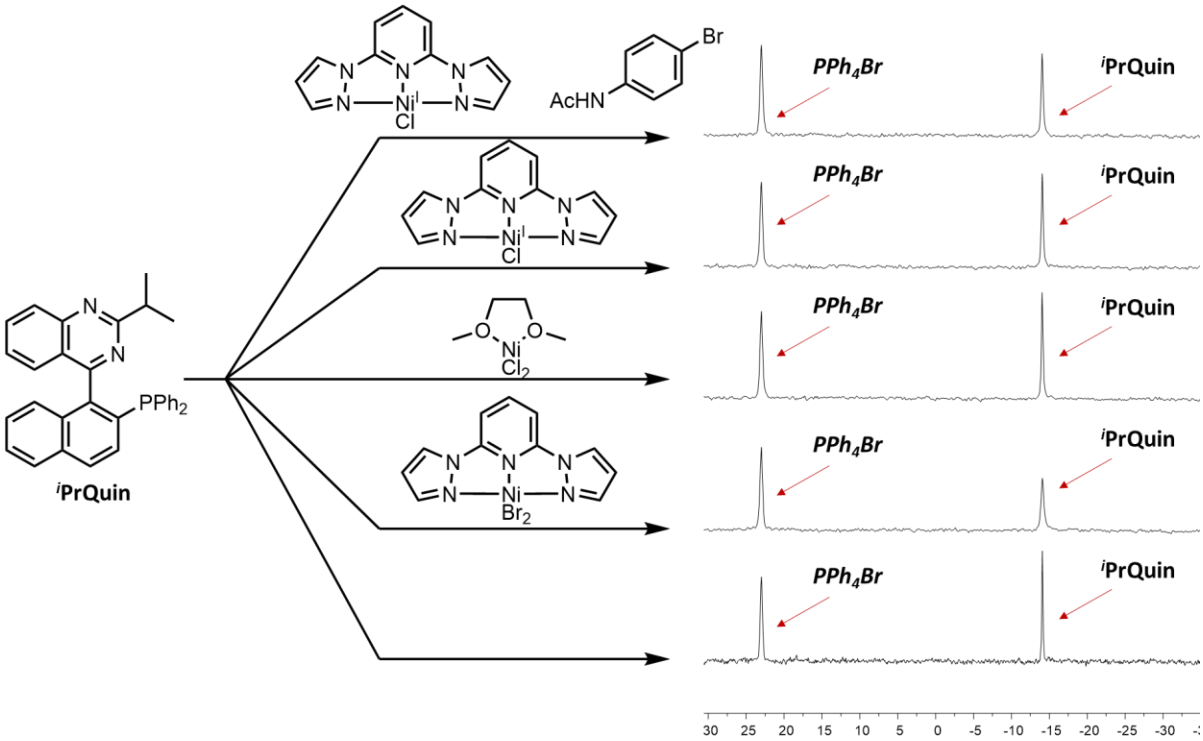


Figure S9. Analysis of interactions between phosphine and bpp complexes of Ni by ^{31}P NMR spectroscopy. **^{i}PrQ** does not appear to form a complex to (bpp)Ni complexes as only free ligand is observed in all instances.

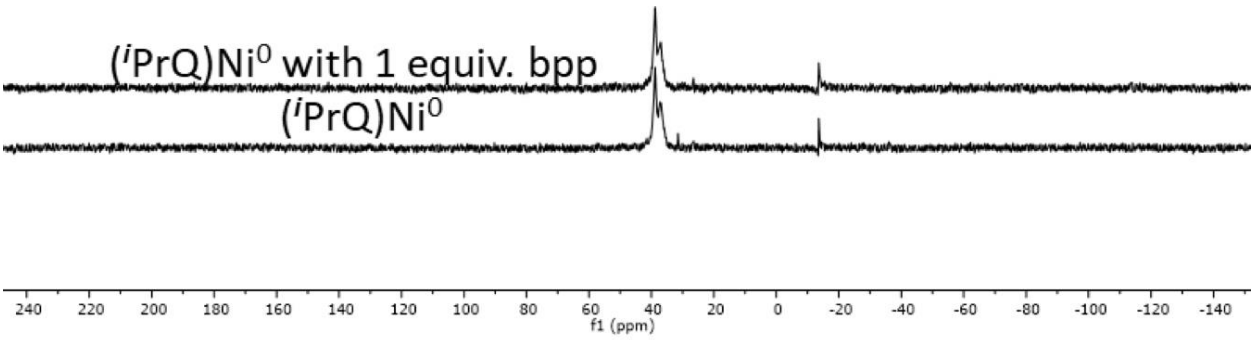


Figure S10. Analysis of a 50 mM solution of Ni^{0}(**^{i}PrQ**)$_2$ with (top) and without 1 equiv bpp (bottom) in a 1:1 DMF/benzene mixture by ^{31}P NMR spectroscopy. The bpp ligand does not displace phosphine from the Ni(0) complex as evidenced by a lack of free phosphine.

Stoichiometric Reactions

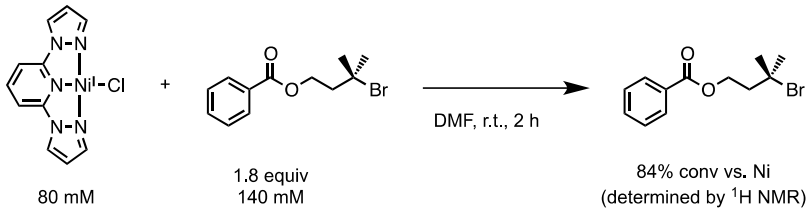


Figure S11. Stoichiometric reaction of isolated (bpp)Ni(I)Cl with a tertiary alkyl bromide.

Procedure: In a nitrogen-filled glove-box, a 4 mL screw-cap vial was charged with (bpp)Ni(I)Cl (36 mg, 0.12 mmol) and DMF(1.0 mL) to afford a deep forest green solution. In a separate 4 mL screw-cap vial was charged 1,3,5-trimethoxybenzene (11 mg, 0.065 mmol, internal standard), 3-bromo-3-methylbutyl benzoate (56 mg, 0.21 mmol, 1.8 equiv), and 0.5 mL of DMF. Both solutions were stirred vigorously for 1 minute at which point, the alkyl bromide solution was added in one portion to the Ni-containing solution. A color change from dark green to light green was observed immediately. This mixture was allowed to stir for 2 hours at room temperature. After this time, the reaction mixture was removed from the glovebox, dissolved in EtOAc (10 mL), washed with water (3x15 mL), brine (1x10 mL) and concentrated by rotary evaporation. The resulting mixture was dissolved in $CDCl_3$ and analyzed by ^{1}H NMR spectroscopy (400 MHz). Analysis reveals only 0.11 mmol of alkyl bromide remain corresponding to 84% activation relative to the added bppNi(I)Cl.

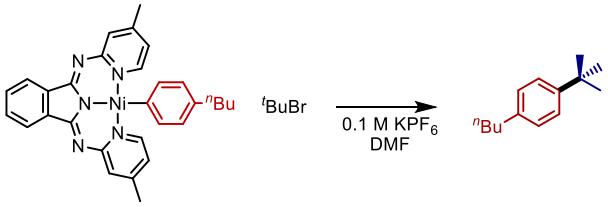


Figure S12. Preliminary Studies: Stoichiometric Reaction of (BPI)Ni-Ar and tBuBr without a cocatalyst.

Procedure: In a nitrogen-filled glove-box, a three-neck electrochemical cell was charged with (30. mg, 0.069 mmol, 28 mM, 1.0 equiv), ^{t}BuBr (40 mg mmol, 0.29 mmol, 5.0 equiv), dodecane as an internal standard (12 mg, 0.070 mM), KPF_6 (46 mg, 0.25 mmol, 100 mM), DMF (2.5 mL), a magnetic stirbar. This solution was allowed to stir at room temperature for 5 minutes before adding a nickel foam cathode, and a zinc anode. The electrodes were threaded through a septum and the reaction was sealed with a screw-cap. The vial was removed from the glove-box and was allowed to stir on a magnetic stir plate at room temperature. A reductive current of 3 mA was applied to the Ni foam electrode (2.04 mAh, 1.1 equiv e- vs (BPI)Ni-Ar). Upon completion, the product was dissolved in ethyl acetate, extracted with brine (1x5 mL), and quantified by calibrated gas chromatography. No product was detected.

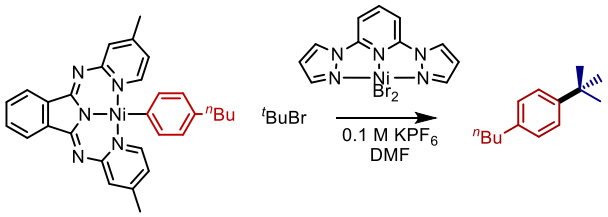
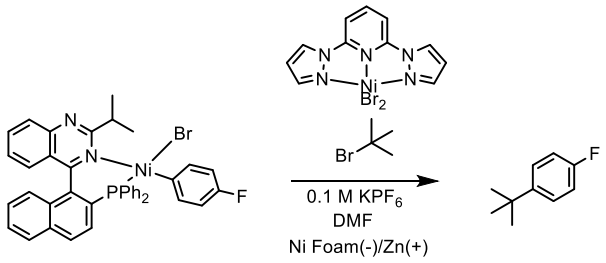


Figure S13. Preliminary Studies: Stoichiometric Coupling with tBuBr with **1** as a cocatalyst.

In a nitrogen-filled glove-box, a three-neck electrochemical cell was charged with (BPI)Ni(aryl) (30. mg, 0.058 mmol, 28 mM, 1.0 equiv) as prepared from a previous procedure,(*11*) ^{t}BuBr (40 mg mmol, 0.29 mmol, 5.0 equiv), dodecane as an internal standard (12 mg, 0.070 mM), KPF_6 (46 mg, 0.25 mmol, 100 mM), DMF (2.5 mL), a magnetic stirbar.

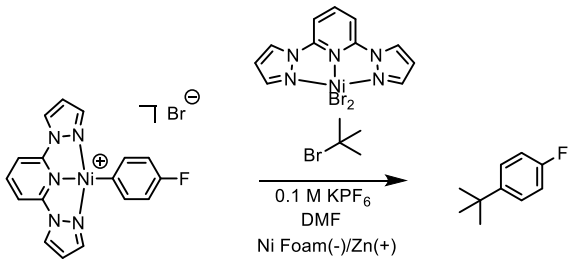
This solution was allowed to stir at room temperature for 5 minutes before adding **1** (5 mg, 0.01 mmol, 0.2 equiv), a nickel foam cathode, and a zinc anode. The electrodes were threaded through a septum and the reaction was sealed with a screw-cap. The vial was removed from the glove-box and was allowed to stir on a magnetic stir plate at room temperature. A reductive current of 3 mA was applied to the Ni electrode (2.04 mAh, 1.1 equiv e- vs complex 2). Upon completion, the product was dissolved in ethyl acetate, extracted with brine (1x5 mL), and quantified by calibrated gas chromatography (calc'd mmol: 0.045 mmol, 77% yield).



Aryl Homocoupling	Protodemetallated Aryl	Cross Product
68	27	0

Figure S14. Stoichiometric reactions of **3**

To a 12 mL screw-cap vial was charged with **3** (89 mg, 0.13 mmol, 1.0 equiv). In a separate vial, ^{t}BuBr (40 mg, 0.29 mmol, 5.0 equiv), KPF_6 (46 mg, 0.25 mmol), **1** (11 mg, 0.026 mmol, 0.2 equiv) and DMF (2.5 mL) equipped with a stir bar were allowed to stir for 5 minutes at room temperature. This solution was then added to **3** and the mixture was allowed to stir for 5 minutes before equipping the vial with a Ni foam cathode and a Zn anode. A reductive, constant current was applied at the Ni cathode (3 mA, 3.35 mAh, 1.00 equiv e^-). After electrolysis, the product was extracted from the crude reaction mixture with ethyl acetate (2 mL) and brine (5 mL). The reaction mixture was analyzed by ^{19}F NMR spectroscopy against an internal standard of KPF_6. No product was detected.



Aryl Homocoupling	Protodemetallated Aryl	Cross Product
17	3	85

Figure S15: Stoichiometric reactions of **4**

To a 12 mL screw-cap vial was charged with **4** (55 mg, 0.13 mmol, 1.0 equiv). In a separate vial, ^{t}BuBr (40 mg, 0.29 mmol, 5.0 equiv), KPF_6 (46 mg, 0.25 mmol), **1** (11 mg, 0.026 mmol, 0.2 equiv), and DMF (2.5 mL) equipped with a stir bar were allowed to stir for 5 minutes at room temperature. This solution was then added to **4** and the mixture was allowed to stir for 5 minutes before equipping the vial with a Ni foam cathode and a Zn anode. A reductive, constant current was applied at the Ni cathode (3 mA, 3.35 mAh, 1.00 equiv e^-). After electrolysis, the product was extracted from the crude reaction mixture with ethyl acetate (2 mL) and brine (5 mL). The reaction mixture was analyzed by ^{19}F NMR against an internal standard of KPF_6. Analysis by ^{19}F NMR reveals 0.11 mmol (85%) of the product.

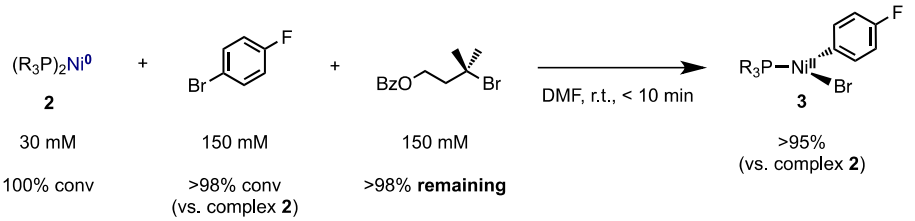
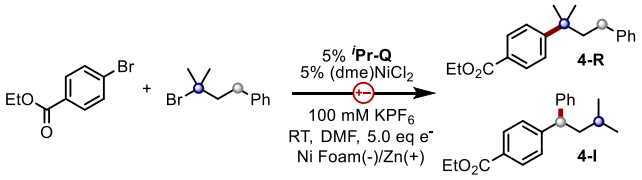
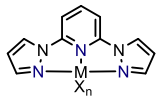


Figure S16. Stoichiometric reaction of $Ni^0(^i\mathbf{PrQ})_2$ with aryl bromide and alkyl bromide

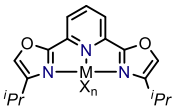
Inside a nitrogen-filled glovebox, a 4 mL screw-cap vial was charged with $Ni^0(^i\mathbf{PrQ})_2$ (31 mg, 0.031 mmol, complex **2**), benzene (0.3 mL), and a stir bar. This mixture was allowed to stir for 15 minutes at room temperature to ensure homogeneity. A separate 4 mL screw-cap vial was charged with 1-bromo-4-fluorobenzene (26 mg, 0.15 mmol, 5 equiv), 3-bromo-3-methylbutyl benzoate (41 mg, 0.15 mmol, 5 equiv), KPF_6 (5 mg, 0.03 mmol, 1 equiv), DMF (0.7 mL) and a stir bar. This mixture was allowed to stir for 15 minutes at room temperature to ensure homogeneity. To the dark red solution of $Ni^0(^i\mathbf{PrQ})_2$ was added the electrophile mixture in one portion. The resulting mixture was allowed to stir at room temperature for 30 minutes, noting a rapid color change from dark red to a yellow solution. Upon completion, 0.3 mL of the solution was diluted with 0.3 mL of DMF and was analyzed by ^{31}P and ^{19}F to quantify the generation of **3**. Analysis of the organic substrates was performed by ^1H NMR spectroscopy on the remaining sample following workup. Specifically, the remaining 0.6 mL of solution was transferred outside of the glovebox, quenched with water, and extracted with ethyl acetate. The organic layer was washed with water (3x10 mL), brine (1x10 mL), and concentrated by rotary evaporation. To the residue was added an internal standard (1,3,5-trimethoxybenzene, 5 mg, 0.03 mmol) and 0.6 mL of $CDCl_3$ prior to analysis by ^1H NMR spectroscopy.

Evaluation of Alternative Electrocatalysts for Activation of Alkyl Halides

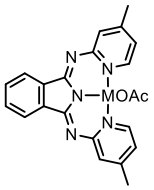




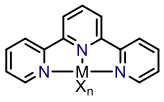
MX$_n$=
Cu(OTf)$_2$ 49% **R:l** =21:1
Co(OAc)$_2$ 22% **R:l** = 22:1
FeBr$_2$ 51% **R:l** = 5:1
MnCl$_2$ 71%**R:l** = >50:1
NiCl$_2$ 84%**R:l** = 29:1



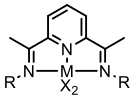
MX$_n$=
Cu(OTf)$_2$ 0% **R:l** = ND
Co(OAc)$_2$ 0% **R:l** = ND
FeBr$_2$ 0% **R:l** = ND
MnCl$_2$ 0% **R:l** = ND
NiCl$_2$ 0% **R:l** = ND



M=
Cu 0% **R:l** = ND
Co 0% **R:l** = ND
Fe 0% **R:l** = ND
Mn 6% **R:l** = ND
Ni 2% **R:l** = ND



MX$_n$=
Cu(OTf)$_2$ 17% **R:l** = 1:20
Co(OAc)$_2$ 0% **R:l** = ND
FeBr$_2$ 22% **R:l** =5:1
MnCl$_2$ 0% **R:l** = ND
NiCl$_2$ 2% **R:l** = ND



R=Cy
MX= NiCl$_2$, 14% **R:l** = 9:1

R=Me
MX= NiCl$_2$, 6% **R:l** = 6:1

Following a modified general procedure A, a 4 mL screw-cap vial was charged with metal salt (0.050 mmol, 0.10 equiv), ligand (0.050 mmol, 0.10 equiv), dimethylformamide (0.5 mL), and a stir bar. To a separate 4 mL screw-cap vial was charged **iPrQ** (24 mg, 0.050 mmol, 0.10 equiv), dimethylformamide (0.5 mL), and a stir bar. To a 4 mL screw-cap vial was charged KPF_6 (46 mg, 0.25 mmol, 100 mM), aryl bromide (1.00 mmol, 2.00 equiv), alkyl bromide (0.500 mmol, 1.00 equiv), dimethylformamide (1.5 mL), and a magnetic stir bar. These solutions were allowed to stir at room temperature for 10 minutes before transferring to a 12 mL screw-cap vial equipped with a septum. A Ni foam cathode and a Zn anode were inserted into the test tube and the leads were pierced through a septum cap. The sealed test tube was removed from the glovebox. The reaction mixture was stirred on a magnetic stir plate at room temperature for 5 minutes prior to electrolysis. A reductive, constant current was applied at the Ni cathode (3 mA, 53.6 mAh, 4.00 equiv e^-). After electrolysis, an aliquot (0.1 mL) was removed and the product was extracted from the crude reaction mixture with ethyl acetate (2 mL) and brine (5 mL). The reaction mixture was analyzed by gas chromatography against a calibrated internal standard of dodecane.

These results are consistent with the dual role that is require of the radical-generator. Not only is the cocatalyst responsible for activation of the alkyl halide, but it must undergo multiple ligand exchanges with the phosphine to form a reactive Ni(0) intermediate.

Proposed Role of (bpp)$MnCl_2$

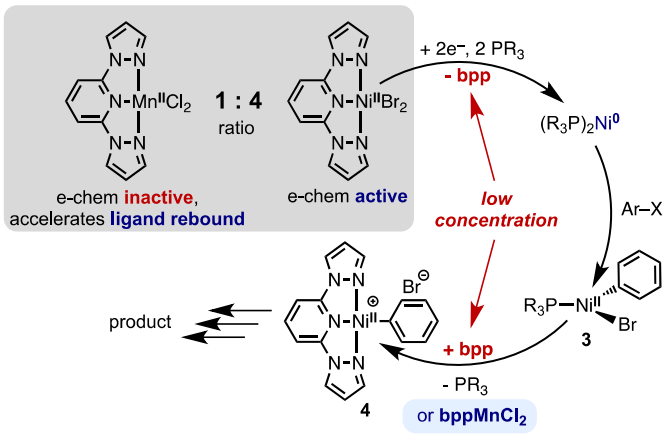


Figure S17. Proposed role of (bpp)$MnCl_2$ as a source of bpp for ligand rebound to form complex **4**.

Studies suggest that (bpp)$MnCl_2$ facilitates the ligand rebound step to form the (bpp)Ni-Ar complex (**4**) that is critical for radical capture and C–C coupling. The proposed role of Mn is summarized in **Figure S17** below and is based on CV and $^{31}P/^{19}F$ NMR spectroscopic studies detailed in **Figure S18** and **Figure S19** below. To summarize **Figure S17**, we discovered that NiX_2 does not fully displace Mn^{II} from (bpp)$MnCl_2$. Rather, a low but significant concentration of (bpp)$MnCl_2$ is present in solution (roughly 1:4 ratio vs complex **4**). NMR spectroscopic studies demonstrate that Mn from this complex is easily exchanged by the Ni-aryl of the phosphine complex **3** to form complex (bpp)Ni-aryl **4**. As noted above, this is a critical step prior to radical capture and C–C coupling. In contrast to combinations of (bpp)$MnCl_2$ and phosphine complex **3**, the (bpp)$NiBr_2$ analog binds tightly to bpp and does not undergo ligand exchange with the phosphine complex **3** to form complex **4**. Without the (bpp)$MnCl_2$ present in solution, the ligand rebound event to form **4** relies entirely on the concentration of free bpp in solution. This concentration is presumably low because free bpp is only transiently formed after the first ligand exchange event. We believe that slow formation of **4** or low concentrations of **4** allow competing capture/isomerization events to occur that degrade the reaction selectivity.

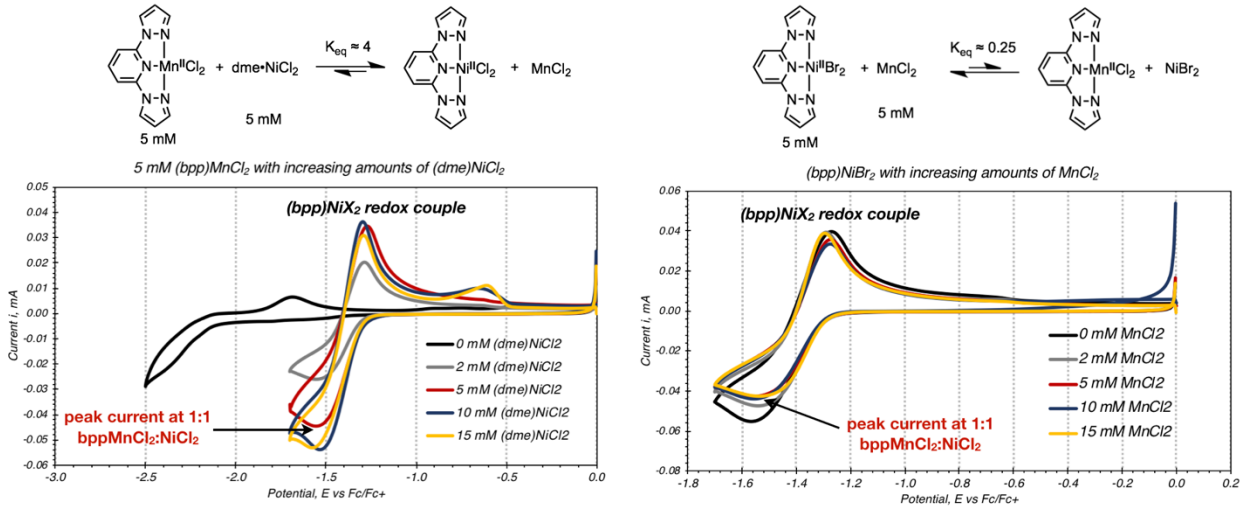


Figure S18. Equilibrium studies by CV under the standard conditions (DMF, 0.1 M KPF_6).

One component of the additional data to support the mechanistic proposal is detailed in **Figure S18**. These studies reveal that a 1:1 ratio of (bpp)$MnCl_2$ and dme•$NiCl_2$ does not completely form (bpp)$NiCl_2$ (**1**). CVs reveal that adding additional dme•$NiCl_2$ beyond 1 equivalent (vs. Mn) continues forms additional **1**, as evidenced by the further increase in peak reductive current. At a 1:1 ratio, the peak current corresponding to only 83% of the peak current with excess Ni added. It is assumed that **1** is completely formed in the presence of excess Ni. Conversely, $MnCl_2$ can be added to (bpp)$NiBr_2$ and a decrease in the reductive peak current for is observed (right CV plots). With 1 equivalent $MnCl_2$ added to (bpp)$NiBr_2$, the decrease in current – and thus loss of (bpp)$NiBr_2$ – corresponds to 20%. From these data, we

conclude that when equimolar amounts of dme•$NiCl_2$ and (bpp)$MnCl_2$ are mixed, the ratio of (bpp)$MnCl_2$ to (bpp)$NiBr_2$ at equilibrium under the reaction conditions is 1:4.

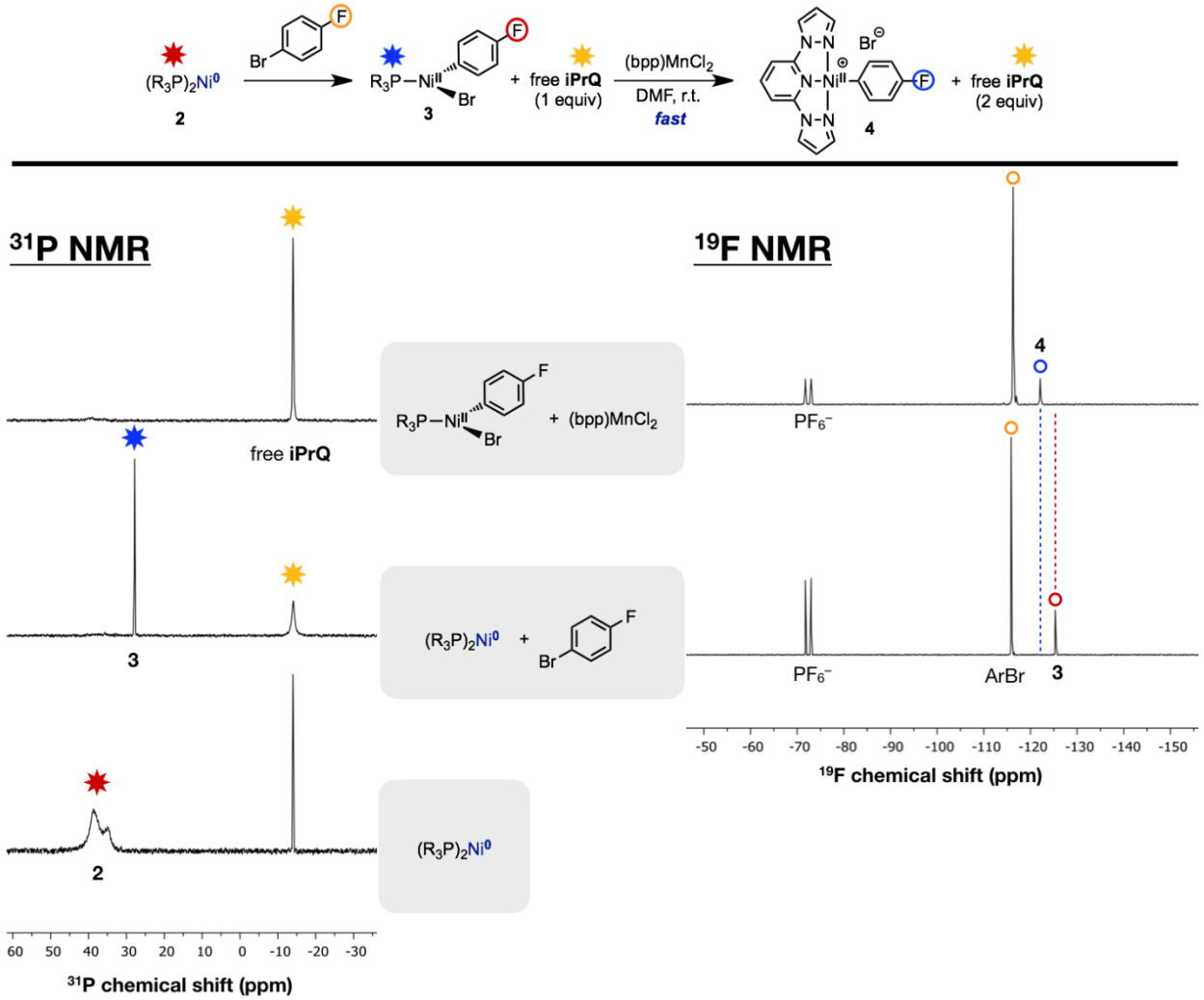


Figure S19. Stoichiometric ligand exchange reactions monitored by ^{31}P (left) and ^{19}F (right) NMR spectroscopy.

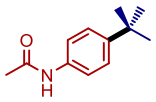
NMR spectroscopic studies revealed that the (bpp)$MnCl_2$ present in solution during catalytic reactions undergoes rapid ligand exchange with the (phosphino)Ni-aryl complex **3** to form complex **4**. This conclusion is supported by the disappearance of the ^{31}P resonance of **3** and the appearance of additional free ligand (**Figure S19**, left). Reactions of a para-fluoro substituted aryl analog allowed us to monitor the reaction by ^{19}F NMR spectroscopy. The ^{19}F resonance of the phosphine complex **3** immediately disappears upon addition of (bpp)$MnCl_2$ and a new ^{19}F resonance that is consistent with the (bpp)Ni-aryl complex (**Figure S19**, right).

Collectively, these data suggest that (bpp)$MnCl_2$ exists in significant concentrations during catalytic reactions and that the Mn complex can participate in the critical ligand-rebound step to form complex **4**. We attribute the efficient formation of **4** to the mitigation of isomerized byproducts that result from radical capture at competing complexes.

Note: Adding higher loadings of free bpp to catalytic reactions in an effort to promote ligand rebound inhibits the reaction because the bis homoleptic complex $[(bpp)_2Ni]^{2+}$is formed. Consequently, the role of (bpp)$MnCl_2$ as a masked source of free bpp is a serendipitous discovery.

Characterization of Products from eXEC

N-(4-(tert-butyl)phenyl)acetamide (5)



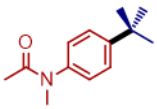
Following general procedure A, N-(4-bromophenyl)acetamide (214 mg, 1.00 mmol) was allowed to react with ^{t}BuBr (68 mg, 0.50 mmol) under reductive electrolysis (3 mA, 4 equiv e^-). The title compound was isolated following purification by flash column chromatography (26:74 EtOAc:Hexanes) as a white solid (76 mg, 0.40 mmol, 80%). Analysis by ^{1}H NMR spectroscopy and ^{13}C NMR spectroscopy matches characterization of previously reported literature for the title compound.(*68~~71~~*)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (d, J = 8.8 Hz, 2H), 7.33 (d, J = 8.7 Hz, 2H), 2.16 (s, 3H), 1.30 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 168.2, 147.3, 135.2, 125.8, 119.7, 34.3, 31.3, 24.5.

HRMS-ESI (m/z): for $C_{12}H_{17}NO$ [M + Na^+]: calcd 214.1203, found 214.1203

N-(4-tert-butylphenyl)-N-methylacetamide (6)



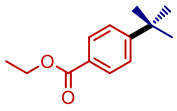
Following general procedure A, N-(4-bromophenyl)-N-methylacetamide (231 mg, 1.01 mmol) was allowed to react with ^{t}BuBr (68 mg, 0.20 mmol) under reductive electrolysis (3 mA, 4 equiv e^-). The title compound was isolated following purification by flash column chromatography (22:78 EtOAc:Hexanes) as an off-white solid (69 mg, 0.34 mmol, 67%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (d, *J* = 8.5 Hz, 2H), 1.86 (s, 3H), 7.08 (d, *J* = 8.5 Hz, 2H), 3.23 (s, 3H), 1.32 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.7, 150.7, 141.9, 126.5, 126.5, 77.4, 77.1, 76.7, 37.1, 34.6, 31.3, 22.4, 22.3.

HRMS-ESI (m/z): for $C_{13}H_{19}NO$ [M + Na^+]: calcd 228.1359, found 228.1349

ethyl 4-(tert-butyl)benzoate (7)



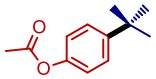
Following general procedure A, ethyl 4-bromobenzoate (227 mg, 0.990 mmol) was allowed to react with ^{t}BuBr (68 mg, 0.50 mmol) under reductive electrolysis (3 mA, 4 equiv e^-). The title compound was isolated following purification by flash column chromatography (0.5:99.5 EtOAc:Hexanes) as colorless oil (50 mg, 0.24 mmol, 48%). Analysis by ^{1}H NMR spectroscopy and ^{13}C NMR spectroscopy matches characterization of previously reported literature for the title compound.(*17~~60~~*)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (dt, J = 8.8, 1.9 Hz, 2H), 7.45 (dd, J = 8.7, 2.0 Hz, 2H), 4.37 (q, J = 7.1 Hz, 2H), 1.39 (t, J = 7.1 Hz, 3H), 1.34 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.6, 156.4, 129.4, 127.7, 125.2, 60.7, 35.0, 31.1, 14.3.

HRMS-ESI (m/z): for $C_{13}H_{18}O_2$ [M + Na^+]: calcd 229.1199, found 229.1204

4-(tert-butyl)phenyl acetate (8)



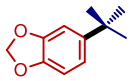
Following general procedure A, 4-bromophenyl acetate (220 mg, 1.02 mmol) was allowed to react with with ^{t}BuBr (70 mg, 0.51 mmol) under reductive electrolysis (3 mA, 4 equiv e^-). The title compound was isolated following purification by flash column chromatography (2:98 EtOAc:Hexanes) as colorless oil (56 mg, 0.291 mmol, 57%). Analysis by ^{1}H NMR spectroscopy and ^{13}C NMR spectroscopy matches characterization of previously reported literature for the title compound.(*69~~72~~*)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (d, J = 9.0 Hz, 2H), 7.01 (d, J = 9.0 Hz, 2H), 2.29 (s, 3H), 1.32 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 169.7, 148.6, 148.3, 126.3, 120.8, 34.4, 31.4, 21.1.

HRMS-ESI (m/z): for $C_{12}H_{16}O_2$ [M + Na^+]: calcd 215.1043, found 215.1037

5-(tert-butyl)benzo[*d*][1,3]dioxole (9)



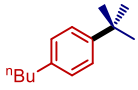
Following general procedure A, 5-bromobenzo[d][1,3]dioxole (199 mg, 0.999 mmol) was allowed to react with ^{t}BuBr (68 mg, 0.496 mmol) under reductive electrolysis (3 mA, 4 equiv e^-). The title compound was isolated following purification by flash column chromatography (2:98 EtOAc:Hexanes) as colorless oil (58 mg, 0.33 mmol, 66%). Analysis by ^{1}H NMR spectroscopy and ^{13}C NMR spectroscopy matches characterization of previously reported literature for the title compound.(*70~~3~~*)

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.91 (d, J = 1.9 Hz, 1H), 6.84 (dd, J = 8.1, 1.9 Hz, 1H), 6.75 (d, J = 8.2 Hz, 1H), 5.92 (s, 2H), 1.29 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 147.4, 145.4, 145.1, 117.8, 107.6, 106.4, 100.7, 34.6, 31.6.

HRMS-ESI (m/z): for $C_{11}H_{14}O_2$ [M + Na^+]: calcd 201.0886, found 201.0898

1-(tert-butyl)-4-butylbenzene (10)



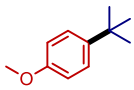
Following general procedure A, 1-bromo-4-butylbenzene (211 mg, 0.990 mmol) was allowed to react with ^{t}BuBr (68 mg, 0.50 mmol) under reductive electrolysis (3 mA, 4 equiv e^-) The title compound was isolated along with a small aryl dehalogenation byproduct following purification by flash column chromatography (0:100 EtOAc:Hexanes) as a colorless oil (79 mg, 0.42 mmol, 84%). Analysis by ^{1}H NMR spectroscopy and ^{13}C NMR spectroscopy matches characterization of previously reported literature for the title compound.(*7*[14])

^{1}H NMR (400 MHz, CDCl$_3$) (d, J = 8.3 Hz, 2H), 7.14 (d, J = 8.6 Hz, 2H), 2.63 – 2.56 (m, 2H), 1.69 – 1.56 (m, 2H), 1.38 (dd, J = 14.9, 7.5 Hz, 2H), 1.33 (s, 9H), 0.95 (t, J = 7.3 Hz, 3H).

^{13}C NMR (101 MHz, CDCl$_3$) δ 148.3, 139.8, 128.0, 125.1, 35.1, 34.3, 33.7, 31.4, 22.5, 14.0.

HRMS-ESI (m/z): for $C_{14}H_{22}$ [M + H^+] calcd 191.1795, found 191.1794

1-(tert-butyl)-4-methoxybenzene (11)



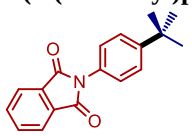
Following general procedure A, 1-bromo-4-methoxybenzene (112 mg, 0.995 mmol) was allowed to react with ^{t}BuBr (68 mg, 0.50 mmol) under reductive electrolysis (2 mA, 4 equiv e^-). The title compound was isolated following purification by flash column chromatography (0:100 EtOAc:Hexanes) as a colorless oil (58 mg, 0.35 mmol, 71%). Analysis by ^{1}H NMR spectroscopy and ^{13}C NMR spectroscopy matches characterization of previously reported literature for the title compound.(*7*[25])

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.31 (d, J = 8.9 Hz, 2H), 6.85 (d, J = 8.9 Hz, 2H), 3.80 (s, 3H), 1.30 (s, 9H).

^{13}C NMR (101 MHz, CDCl$_3$) δ 157.3, 143.3, 126.2, 113.3, 55.2, 34.1, 31.5.

HRMS-ESI (m/z): for $C_{11}H_{16}O$ [M + Na^+]: calcd 187.1094, found 187.1093

2-(4-(tert-butyl)phenyl)isoindoline-1,3-dione (12)



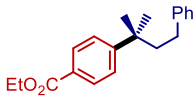
Following general procedure A, 2-(4-bromophenyl)isoindoline-1,3-dione (302 mg, 1.00 mmol) was allowed to react with ^{t}BuBr (67 mg, 0.49 mmol) under reductive electrolysis (3 mA, 4.0 equiv e^-). The title compound was isolated following purification by flash column chromatography (10:90) EtOAc:Hexanes) as light pink solid(86 mg, 0.31 mmol, 62%) with trace amounts of bpp ligand. Analysis by ^{1}H NMR spectroscopy and ^{13}C NMR spectroscopy matches characterization of previously reported literature for the title compound.(*7*[36])

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.95 (dd, J = 5.5, 3.0 Hz, 2H), 7.78 (dd, J = 5.5, 3.1 Hz, 2H), 7.55 – 7.50 (m, 2H), 7.40 – 7.34 (m, 2H), 1.36 (s, 9H).

^{13}C NMR (101 MHz, CDCl$_3$) δ 167.4, 151.1, 134.3, 131.8, 126.1, 126.0, 123.7, 31.3.

HRMS-ESI (m/z): for $C_{18}H_{17}NO_2$ [M + H^+] calcd 280.1333, found 280.1332

ethyl 4-(2-methyl-4-phenylbutan-2-yl)benzoate (13)



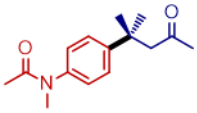
Following general procedure A, ethyl 4-bromobenzoate (241 mg, 1.05 mmol) was allowed to react with (3-bromo-3-methylbutyl)benzene (112 mg, 0.493 mmol) under reductive electrolysis (3 mA, 4 equiv e^-). The title compound along with its isomers was isolated following purification by flash column chromatography (1:99 EtOAc:Hexanes) as a white solid (9:1 selectivity) (89 mg, 0.30 mmol, 61%). Analysis by ^{1}H NMR spectroscopy and ^{13}C NMR spectroscopy matches characterization of previously reported literature for the title compound.(*16*[62])

^{1}H NMR (400 MHz, CDCl$_3$) δ 8.01 (d, J = 8.7 Hz, 2H), 7.46 (d, J = 8.8 Hz, 2H), 7.24 (t, J = 7.4 Hz, 2H), 7.15 (t, J = 7.3 Hz, 1H), 7.07 (d, J = 6.8 Hz, 2H), 4.38 (q, J = 7.1 Hz, 2H), 2.37 – 2.28 (m, 2H), 2.00 – 1.91 (m, 2H), 1.40 (s, 6H).

^{13}C NMR (101 MHz, CDCl$_3$) δ 166.7, 154.5, 142.7, 129.5, 128.3, 128.2, 127.9, 125.9, 125.7, 60.8, 46.6, 38.4, 31.3, 28.8, 14.4.

HRMS-ESI (m/z): for $C_{20}H_{24}O_2$ [M + H^+] calcd 297.1850, found 297.1848

N-methyl-N-(4-(2-methyl-4-oxopentan-2-yl)phenyl)acetamide (14)



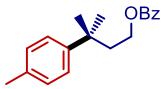
Following general procedure A, N-(4-bromophenyl)-N-methylacetamide (229 mg, 1.00 mmol) was allowed to react with 4-bromo-4-methylpentan-2-one (89 mg, 0.50 mmol) under reductive electrolysis (3 mA, 4 equiv e^-). The title compound was isolated following purification by flash column chromatography (28:72 EtOAc:Hexanes) as a white solid (76 mg, 0.31 mmol, 62%).

^{1}H NMR (400 MHz, $CDCl_3$) 7.38 (d, J = 8.1 Hz, 2H), 7.11 (d, J = 8.3 Hz, 2H), 3.24 (s, 3H), 2.77 (s, 2H), 1.88 (s, 3H), 1.85 (s, 3H), 1.43 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 207.3, 170.7, 148.0, 142.3, 126.8, 126.7, 56.5, 37.1, 31.8, 29.0, 22.4.

HRMS-ESI (m/z): for $C_{15}H_{21}NO_2$ found [M + Na^+]: calcd 270.1465, found 270. 1445

4-methyl-1-phenyl-4-(p-tolyl)pentan-1-one (15)



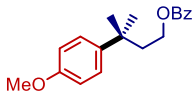
Following general procedure A, 1-bromo-4-methylbenzene (170 mg, 0.994 mmol) was allowed to react with 4-bromo-4-methyl-1-phenylpentan-1-one (127 mg, 0.498 mmol) under reductive electrolysis (3 mA, 4 equiv e^-). The title compound was isolated following purification by flash column chromatography (0.5:99.5 EtOAc:Hexanes) as a colorless oil (84 mg, 0.32 mmol, 63%). Analysis by ^{1}H NMR spectroscopy and ^{13}C NMR spectroscopy matches characterization of previously reported literature for the title compound.(*17*~~*60*~~)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (dd, J = 8.4, 1.4 Hz, 2H), 7.56 – 7.49 (m, 1H), 7.40 (ddt, J = 7.9, 6.7, 1.2 Hz, 2H), 7.32 – 7.26 (m, 2H), 7.17 – 7.10 (m, 2H), 4.22 – 4.14 (m, 2H), 2.31 (s, 3H), 2.13 (t, J = 7.2 Hz, 2H), 1.40 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$ δ 166.6, 145.3, 135.2, 132.7, 130.4, 129.5, 129.0, 128.2, 125.6, 62.6, 42.5, 36.4, 29.3, 20.9.

HRMS-ESI (m/z): for $C_{19}H_{22}O_2$ [M + H^+] calcd 283.1693, found 283.1693

3-(4-methoxyphenyl)-3-methylbutyl benzoate (16)



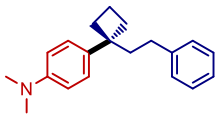
Following general procedure B, 1-bromo-4-methoxybenzene (140 mg, 0.752 mmol) was allowed to react with 3-bromo-3-methylbutyl benzoate (136 mg, 0.501 mmol) under reductive electrolysis (2 mA, 4 equiv e^-). The title compound was isolated following purification by flash column chromatography (1:99 EtOAc:Hexanes) as a colorless oil (81 mg, 0.27 mmol, 54%). Analysis by ^{1}H NMR spectroscopy and ^{13}C NMR spectroscopy matches characterization of previously reported literature for the title compound.(*17*~~*60*~~)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (dd, J = 8.4, 1.3 Hz, 2H), 7.53 (t, J = 7.4 Hz, 1H), 7.40 (dd, J = 8.2, 7.1 Hz, 2H), 6.85 (d, J = 8.9 Hz, 2H), 4.18 (t, J = 7.3 Hz, 2H), 3.78 (s, 3H), 2.12 (t, J = 7.3 Hz, 2H), 1.40 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.5, 157.5, 140.4, 132.7, 129.5, 128.2, 126.6, 113.6, 62.6, 55.2, 42.5, 36.1, 29.4.

HRMS-ESI (m/z): for $C_{19}H_{22}O_3$ [M + H^+] calcd 299.1642, found 299.1642

N,N-dimethyl-4-(1-phenethylcyclobutyl)aniline (17)



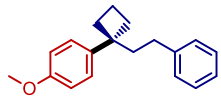
Following general procedure A, 4-bromo-N,N-dimethylaniline (152 mg, 0.760 mmol) was allowed to react with (2-(1-bromocyclobutyl)ethyl)benzene (121 mg, 0.506 mmol) under reductive electrolysis (3 mA, 4 equiv e^-). The title compound was isolated following purification by flash column chromatography (2:98 EtOAc:Hexanes) as a colorless oil (109 mg, 0.390 mmol, 77%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 (t, J = 7.3 Hz, 2H), 7.16 (d, J = 7.3 Hz, 1H), 7.11 (d, J = 17.6 Hz, 4H), 6.77 (d, J = 8.8 Hz, 2H), 2.96 (s, 6H), 2.40 (ddd, J = 9.6, 7.8, 2.2 Hz, 2H), 2.36 – 2.30 (m, 2H), 2.21 – 2.11 (m, 2H), 2.12 – 2.01 (m, 3H), 1.92 – 1.83 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 148.5, 143.2, 138.0, 128.3, 128.2, 126.4, 125.4, 112.6, 45.9, 45.1, 40.9, 32.9, 31.2, 16.0.

HRMS-ESI (m/z): for $C_{20}H_{25}N$ [M + H^+]: calcd 280.2021, found 280.2031

1-methoxy-4-(1-phenethylcyclobutyl)benzene (18)



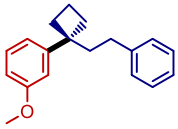
Following general procedure A, 1-bromo-4-methoxybenzene (185 mg,0.989 mmol) was allowed to react with (2-(1-bromocyclobutyl)ethyl)benzene (118 mg, 0.493 mmol) under reductive electrolysis (3 mA, 4 equiv e^-). The title compound was isolated following purification by flash column chromatography (1:99 EtOAc:Hexanes) as a colorless oil (102 mg, 0.383 mmol, 76%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 (t, J = 7.3 Hz, 2H), 7.20 – 7.11 (m, 4H), 7.11 – 7.09 (m, 1H), 6.90 (d, J = 8.8 Hz, 2H), 2.39 (ddd, J = 10.7, 9.2, 7.5 Hz, 2H), 2.35 – 2.28 (m, 2H), 2.17 (dddd, J = 13.6, 7.9, 3.6, 1.9 Hz, 2H), 2.13 – 2.04 (m, 3H), 1.95 – 1.80 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 157.2, 142.9, 142.0, 128.3, 128.2, 126.7, 125.5, 113.3, 55.2, 46.0, 44.9, 32.9, 31.2, 16.0.

HRMS-ESI (m/z): for $C_{19}H_{22}O$ [M + H^+]: calcd 267.1744, found 267.1716

1-methoxy-3-(1-phenethylcyclobutyl)benzene (19)



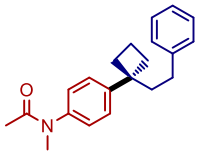
Following general procedure A, 1-bromo-3-methoxybenzene (189 mg, 1.01 mmol) was allowed to react with (2-(1-bromocyclobutyl)ethyl)benzene (118 mg, 0.493 mmol) under reductive electrolysis (3 mA, 4 equiv e^-). The title compound was isolated following purification by flash column chromatography (1:99 EtOAc:Hexanes) as a colorless oil (76 mg, 0.285 mmol, 56%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 – 7.19 (m, 3H), 7.14 (dd, J = 7.3, 2.0 Hz, 1H), 7.10 (dd, J = 7.9, 1.1 Hz, 2H), 3.83 (s, 3H), 2.40 (ddd, J = 11.0, 9.3, 7.9 Hz, 2H), 2.36 – 2.28 (m, 2H), 2.24 – 2.13 (m, 2H), 2.13 – 2.06 (m, 3H), 1.94 – 1.80 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 159.4, 151.8, 142.8, 128.9, 128.3, 128.2, 125.5, 118.3, 112.0, 110.1, 55.2, 46.7, 44.6, 32.8, 31.2, 16.0.

HRMS-ESI (m/z): for $C_{19}H_{22}O$ [M + Na^+]: calcd 289.1563, found 289.1566

N-methyl-N-(4-(1-phenethylcyclobutyl)phenyl)acetamide (20)



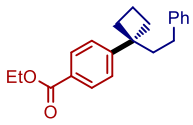
Following general procedure A, N-(4-bromophenyl)-N-methylacetamide (227 mg, 0.995 mmol) was allowed to react with (2-(1-bromocyclobutyl)ethyl)benzene (120 mg, 0.502 mmol) under reductive electrolysis (3 mA, 4 equiv e^-). The title compound was isolated following purification by flash column chromatography (24:76 EtOAc:Hexanes) as a colorless oil (128 mg, 0.412 mmol, 83%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 – 7.19 (m, 2H), 7.21 – 7.17 (m, 2H), 7.17 – 7.11 (m, 3H), 7.08 (d, J = 6.8 Hz, 2H), 3.27 (s, 3H), 2.46 – 2.35 (m, 2H), 2.35 – 2.28 (m, 2H), 2.20 (dddd, J = 14.0, 8.1, 5.7, 4.0 Hz, 2H), 2.16 – 2.07 (m, 3H), 1.89 (s, 3H), 1.95 – 1.82 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.7, 149.7, 142.4, 141.8, 128.3, 128.2, 127.0, 126.5, 125.7, 46.4, 44.4, 37.2, 32.8, 31.1, 22.4, 16.0.

HRMS-ESI (m/z): for $C_{21}H_{25}NO$ [M + Na^+]: calcd 330.1829, found 330.1829

Ethyl 4-(1-phenethylcyclobutyl)benzoate (21)



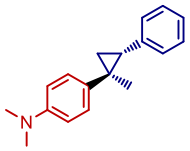
Following general procedure A, Ethyl-4-bromobenzoate (214 mg, 1.00 mmol) was allowed to react with (2-(1-bromocyclobutyl)ethyl)benzene (120 mg, 0.502 mmol) under reductive electrolysis (3 mA, 4.0 equiv e^-). The title compound was isolated following purification by flash column chromatography (1:99) EtOAc:Hexanes) as colorless oil (110 mg, 0.357 mmol, 71%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, J = 8.4 Hz, 2H), 7.14 (dd, J = 8.5, 7.0 Hz, 3H), 7.08 – 7.02 (m, 2H), 7.01 – 6.95 (m, 2H), 4.30 (q, J = 7.1 Hz, 2H), 2.33 (ddd, J = 11.3, 9.4, 8.1 Hz, 2H), 2.24 – 2.17 (m, 2H), 2.12 (dddd, J = 9.6, 5.8, 3.6, 1.8 Hz, 2H), 2.06 – 1.96 (m, 3H), 1.87 – 1.72 (m, 1H), 1.32 (t, J = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.7, 155.3, 142.4, 129.4, 128.3, 128.2, 127.7, 125.7, 125.6, 60.7, 46.9, 44.5, 32.7, 31.1, 16.0, 14.4.

HRMS-ESI (m/z): for $C_{21}H_{24}O_2$ [M + Na^+]: calcd 331.1669, found 331.1666

N,N-dimethyl-4-(1-methyl-2-phenylcyclopropyl)aniline (22)



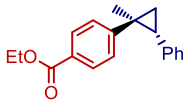
Following general procedure A, 4-bromo-N,N-dimethylaniline (202 mg, 1.01 mmol) was allowed to react with (2-bromo-2-methylcyclopropyl)benzene (107 mg, 0.507 mmol) under reductive electrolysis (3 mA, 4 equiv e^-). The title compound was isolated following purification by flash column chromatography (2:98 EtOAc:Hexanes) as a yellow solid as a mixture of diastereomers 7:1 trans to cis. (97 mg, 0.386 mmol, 76%). Relative stereochemistry is confirmed by NOESY analysis.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.34 (m, 4H), 7.30 (d, J = 8.8 Hz, 2H), 7.27 – 7.21 (m, 1H), 6.77 (d, J = 8.8 Hz, 2H), 2.97 (s, 6H), 2.39 (ddd, J = 8.8, 6.3, 0.7 Hz, 1H), 1.44 – 1.37 (m, 1H), 1.20 (dd, J = 6.3, 5.0 Hz, 1H), 1.12 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 148.9, 139.5, 136.0, 129.1, 128.0, 127.7, 125.7, 112.8, 40.9, 31.0, 26.3, 21.3, 18.3.

HRMS-ESI (m/z): for $C_{18}H_{21}N$ [M + Na^+]: calcd 274.1567, found 274.1564

ethyl 4-(1-methyl-2-phenylcyclopropyl)benzoate (23)



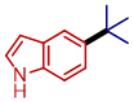
Following a modified general procedure A, ethyl 4-bromobenzoate (115 mg, 0.502 mmol) was allowed to react with (2-bromo-2-methylcyclopropyl)benzene (106 mg, 0.502 mmol) under reductive electrolysis (2 mA, 2.5 equiv e^-). The title compound was isolated following purification by flash column chromatography (1:99 EtOAc:Hexanes) as a colorless oil (71 mg, 0.25 mmol, 50%). Relative stereochemistry is confirmed by NOESY analysis.

^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.99 (d, J = 8.7 Hz, 2H), 7.44 – 7.40 (m, 2H), 7.32 (d, J = 7.1 Hz, 2H), 7.30 – 7.27 (m, 2H), 7.26 – 7.21 (m, 1H), 4.35 (q, J = 7.1 Hz, 2H), 2.44 (dd, J = 8.8, 6.7 Hz, 2H), 1.60 – 1.48 (m, 2H), 1.39 (t, J = 7.1 Hz, 2H), 1.40 – 1.30 (m, 3H).

^{13}C NMR (101 MHz, CD_2Cl_2) δ 166.7, 153.4, 139.0, 129.9, 129.5, 128.5, 128.4, 126.8, 126.6, 61.2, 32.7, 27.0, 20.4, 19.6, 14.5.

HRMS-ESI (m/z): for $C_{19}H_{20}O_2$ [M + Na^+]: calcd 303.1356, found 303.1345

5-(tert-butyl)-1H-indole (24)



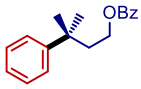
Following general procedure A, 5-bromo-1H-indole (194 mg, 0.989 mmol) was allowed to react with ^{t}BuBr (68 mg, 0.496 mmol) under reductive electrolysis (3 mA, 4 equiv e^-). The title compound was isolated following purification by flash column chromatography (3:97 EtOAc:Hexanes) as a yellow oil (52 mg, 0.30 mmol, 60%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (s, 1H), 7.67 – 7.66 (m, 1H), 7.39 – 7.28 (m, 2H), 7.18 (dd, *J* = 3.2, 2.4 Hz, 1H), 6.54 (ddd, *J* = 3.0, 2.0, 0.9 Hz, 1H), 1.41 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 142.6, 133.9, 127.6, 124.2, 120.3, 116.5, 110.5, 102.6, 34.5, 31.9.

HRMS-ESI (m/z): for $C_{12}H_{15}N$ [M + H^+] calcd 174.1278, found 174.1277

4-methyl-1,4-diphenylpentan-1-one (25)



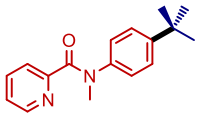
Following general procedure A, bromobenzene (156 mg, 0.994 mmol) was allowed to react with 4-bromo-4-methyl-1-phenylpentan-1-one (127 mg, 0.498 mmol) under reductive electrolysis (3 mA, 4 equiv e^-). The title compound was isolated following purification by flash column chromatography 0.5:99.5 EtOAc:Hexanes) as a colorless oil (79 mg, 0.31 mmol, 61%). Analysis by ^{1}H NMR spectroscopy and ^{13}C NMR spectroscopy matches characterization of previously reported literature for the title compound.(*16~~62~~*)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (dd, J = 8.3, 1.4 Hz, 2H), 7.53 (t, J = 7.4 Hz, 1H), 7.43 – 7.37 (m, 4H), 7.32 (dd, J = 8.2, 7.4 Hz, 2H), 7.28 – 7.14 (m, 1H), 4.36 – 3.63 (m, 2H), 2.16 (t, J = 7.3 Hz, 2H), 1.42 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.6, 148.3, 132.8, 130.4, 129.5, 128.3, 128.2, 125.8, 125.7, 62.6, 42.5, 36.7, 29.3.

HRMS-ESI (m/z): for $C_{18}H_{20}O_2$ [M + H^+] calcd 269.1537, found 269.1536

N-(4-(tert-butyl)phenyl)-N-methylpicolinamide (26)



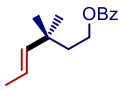
Following general procedure A, N-(4-bromophenyl)-N-methylpicolinamide (217 mg, 0.745 mmol) was allowed to react with with ^{t}BuBr (68 mg, 0.50 mmol) under reductive electrolysis (3 mA, 4 equiv e^-). The title compound was isolated following purification by flash column chromatography (20:80 EtOAc:Hexanes) as an orange oil (81 mg, 0.30 mmol, 61%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.34 (s, 1H), 7.56 (s, 1H), 7.38 (s, 1H), 7.21 – 7.16 (m, 2H), 7.13 – 7.06 (m, 1H), 6.95 (s, 2H), 3.49 (s, 3H), 1.23 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 168.8, 154.4, 149.4, 148.4, 141.5, 136.0, 126.0, 125.8, 123.7, 123.5, 37.9, 34.39, 31.2.

HRMS-ESI (m/z): for $C_{17}H_{20}N_2O$ [M + Na^+]: calcd 291.1468, found 291.1468

(E)-3,3-dimethylhex-4-en-1-yl benzoate (27)



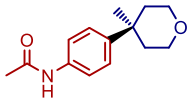
Following general procedure A, (E)-1-bromoprop-1-ene (125 mg, 1.03 mmol) was allowed to react with 3-bromo-3-methylbutyl benzoate (142 mg, 0.524 mmol) under reductive electrolysis (3 mA, 4 equiv e^-). The title compound was isolated as a 2:1 mixture of the title compound and isopentyl benzoate (116 mg total) following purification by flash column chromatography (0.5:99.5 EtOAc:Hexanes) a colorless oil (90 mg, 0.39 mmol, 75%). Analysis by ^{1}H NMR spectroscopy and ^{13}C NMR spectroscopy matches characterization of previously reported literature for the title compound.(16) ~~(62)~~

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 – 8.00 (m, 2H), 7.59 – 7.51 (m, 1H), 7.47 – 7.39 (m, 2H), 5.49 – 5.41 (m, 1H), 5.42 – 5.33 (m, 1H), 4.31 (dd, J = 7.5, 7.0 Hz, 2H), 1.80 – 1.72 (m, 2H), 1.65 (d, J = 4.8 Hz, 3H), 1.07 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.7, 140.1, 132.8, 130.5, 129.5, 128.3, 128.3, 121.4, 62.7, 41.1, 37.4, 27.7, 18.1.

HRMS-ESI (m/z): for $C_{15}H_{20}O_2$ [M + Na^+]: calcd 255.1356 found 255.1356

N-methyl-N-(4-(4-methyltetrahydro-2H-pyran-4-yl)phenyl)acetamide (28)



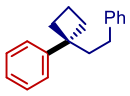
Following general procedure A, N-(4-bromophenyl)-N-methylacetamide (225 mg, 0.990 mmol) was allowed to react with 4-bromo-4-methyltetrahydro-2H-pyran (90 mg, 0.50 mmol) under reductive electrolysis (3 mA, 4 equiv e^-). The title compound was isolated following purification by flash column chromatography (0.5:29.5:71 TEA:EtOAc:Hexanes) as an off-white solid (51 mg, 0.22 mmol, 43%).

^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.45 (d, J = 8.7 Hz, 2H), 7.30 (s, 1H), 7.27 (d, J = 8.7 Hz, 2H), 3.72 (ddd, J = 11.2, 7.7, 3.2 Hz, 2H), 3.61 (ddd, J = 11.5, 6.7, 3.6 Hz, 2H), 2.12 (s, 3H), 2.05 (dddd, J = 12.2, 7.5, 3.6, 0.9 Hz, 2H), 1.72 (ddd, J = 12.7, 6.7, 3.4 Hz, 2H), 1.26 (s, 3H).

^{13}C NMR (101 MHz, CD_2Cl_2) δ 168.5, 145.4, 136.3, 126.5, 120.2, 64.6, 38.0, 35.7, 29.4, 24.7.

HRMS-ESI (m/z): for $C_{14}H_{19}NO_2$ [M + Na^+]: calcd 256.1308, found 256.1308

(1-phenethylcyclobutyl)benzene (29)



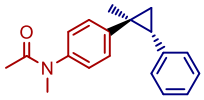
Following a modified general procedure B, chlorobenzene (111 mg, 0.986 mmol) was allowed to react with (2-(1-bromocyclobutyl)ethyl)benzene (119 mg, 0.497 mmol) under reductive electrolysis (3 mA, 4.0 equiv e^-) at 63 °C. The title compound was isolated as a mixture of products following purification by flash column chromatography (0:100) EtOAc:Hexanes) as yellow oil (0.27 mmol, 59% by gas chromatography).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 – 7.38 (m, 2H), 7.35 – 7.27 (m, 5H), 7.25 – 7.20 (m, 1H), 7.19 (s, 2H), 2.59 – 2.45 (m, 2H), 2.44 – 2.36 (m, 2H), 2.33 – 2.23 (m, 2H), 2.23 – 2.15 (m, 3H), 2.01 – 1.89 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 149.9, 142.8, 128.2, 128.2, 127.9, 125.7, 125.5, 125.3, 46.6, 44.7, 32.8, 31.2, 16.0.

HRMS-ESI (m/z): for $C_{18}H_{20}$ [M + Na^+]: calcd 259.1458, found 259.1452

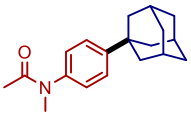
N-methyl-N-(4-((1S)-1-methyl-2-phenylcyclopropyl)phenyl)acetamide (30)



Following a modified general procedure A, -(4-chlorophenyl)-N-methylacetamide (181 mg, 0.986 mmol) was allowed to react with (2-bromo-2-methylcyclopropyl)benzene (105 mg, 0.497 mmol) under reductive electrolysis (2 mA, 2.5 equiv e^-). The title compound was isolated following purification by flash column chromatography (22:78 EtOAc:Hexanes) as a yellow mixture of products (0.20 mmol, 41% by gas chromatography). Relative stereochemistry is confirmed by NOESY analysis.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (d, J = 8.5 Hz, 2H), 7.32 (d, J = 7.0 Hz, 1H), 7.31 – 7.27 (m, 2H), 7.24 (t, J = 7.2 Hz, 1H), 7.13 (d, J = 8.4 Hz, 2H), 3.26 (s, 3H), 2.41 (dd, J = 8.9, 6.4 Hz, 1H), 1.90 (s, 3H), 1.45 (dd, J = 8.9, 5.2 Hz, 1H), 1.29 (dd, J = 6.5, 5.2 Hz, 1H), 1.12 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 170.7, 147.4, 142.2, 138.6, 129.1, 128.2, 128.0, 126.9, 126.2, 37.2, 31.8, 26.4, 22.5, 20.8, 19.0.
HRMS-ESI (m/z): for $C_{19}H_{21}NO$ [M + Na^+]: calcd 302.1516, found 302.1517

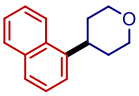
N-(4-((3r,5r,7r)-adamantan-1-yl)phenyl)-N-methylacetamide (31)



Following a modified general procedure B, N-(4-chlorophenyl)-N-methylacetamide (184 mg, 1.00 mmol) was allowed to react with 1-bromoadamantane (108 mg, 0.500 mmol) under reductive electrolysis (2 mA, 2.5 equiv e^-) at 60 °C. The title compound was isolated following purification by flash column chromatography (20:80 EtOAc:Hexanes) as a faint yellow powder (75 mg, 0.26 mmol, 52%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 (d, J = 8.6 Hz, 2H), 7.04 (d, J = 8.5 Hz, 2H), 3.18 (s, 3H), 2.05 (s, 3H), 1.85 (d, J = 2.9 Hz, 6H), 1.80 (s, 3H), 1.78 – 1.62 (m, 6H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 170.8, 151.0, 141.9, 126.5, 126.1, 43.2, 37.2, 36.7, 36.2, 28.9, 22.5.
HRMS-ESI (m/z): for $C_{19}H_{25}NO$ [M + Na^+]: calcd 306.1829, found 306.1828

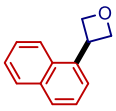
4-(naphthalen-1-yl)tetrahydro-2H-pyran (32)



Following general procedure B, 1-chloronaphthalene (203 mg, 0.980 mmol) was allowed to react with 4-bromotetrahydro-2H-pyran (81 mg, 0.49 mmol) under reductive electrolysis (2 mA, 2.5 equiv e^-). The title compound was isolated following purification by flash column chromatography (2% EtOAc:Hexanes) as a white solid (74 mg, 0.35 mmol, 71%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 – 8.10 (m, 1H), 7.89 (dd, J = 8.0, 1.7 Hz, 1H), 7.75 (dt, J = 8.2, 1.1 Hz, 1H), 7.59 – 7.47 (m, 2H), 7.47 (d, J = 7.8 Hz, 1H), 7.41 (d, J = 7.3 Hz, 1H), 4.17 (ddd, J = 11.8, 3.9, 1.9 Hz, 2H), 3.72 (td, J = 11.5, 2.6 Hz, 2H), 3.60 (dtd, J = 14.3, 7.8, 7.4, 3.6 Hz, 1H), 2.08 – 1.88 (m, 4H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 141.5, 134.0, 131.1, 129.1, 126.8, 125.9, 125.7, 125.4, 122.8, 122.6, 68.7, 36.7, 33.8.
HRMS-ESI (m/z): for $C_{15}H_{16}O$ [M + Na^+]: calcd 235.1094, found 235.1085

3-(naphthalen-1-yl)oxetane (33)

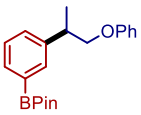


Following a modified general procedure B, 1-chloronaphthalene (121 mg, 0.744 mmol) was allowed to react with 3-bromooxetane (68 mg, 0.50 mmol) under reductive electrolysis (2 mA, 2.5 equiv e^-). The title compound was isolated following purification by flash column chromatography (2:98 EtOAc:Hexanes) as a white solid (62 mg, 0.34 mmol, 68%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (dd, J = 6.2, 3.4 Hz, 1H), 7.79 (d, J = 7.8 Hz, 1H), 7.66 – 7.59 (m, 1H), 7.51 (dd, J = 6.4, 3.4 Hz, 2H), 7.47 (dd, J = 8.1, 6.8 Hz, 2H), 5.28 – 5.20 (m, 2H), 5.05 (dd, J = 7.2, 5.4 Hz, 2H), 4.99 (t, J = 7.3 Hz, 1H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 136.8, 133.8, 131.2, 129.0, 127.4, 126.3, 125.8, 125.5, 123.1, 123.0, 77.1, 37.3.
HRMS-ESI (m/z): for $C_{13}H_{12}O$ [M + Na^+]: calcd 207.0781, found 207.0782

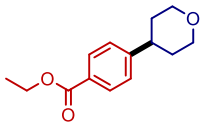
4,4,5,5-tetramethyl-2-(3-(1-phenoxypropan-2-yl)phenyl)-1,3,2-dioxaborolane (34)

Following general procedure B, 2-(3-chlorophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (239 mg, 1.00 mmol)



was allowed to react with (2-bromopropoxy)benzene (132 mg, 0.500 mmol) under reductive electrolysis (2 mA, 2.5 equiv e^-). The title compound was isolated following purification by flash column chromatography (2:98 EtOAc:Hexanes) as a yellow oil (118 mg, 0.348 mmol, 70%).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 – 7.65 (m, 2H), 7.40 (dddd, *J* = 7.7, 1.9, 1.5, 1H), 7.37 – 7.31 (m, 1H), 7.29 – 7.23 (m, 3H), 6.97 – 6.85 (m, 3H), 4.10 (dd, *J* = 9.1, 5.7 Hz, 1H), 3.96 (dd, *J* = 9.1, 8.1 Hz, 1H), 3.32 – 3.21 (m, 1H), 1.42 (d, *J* = 7.0 Hz, 3H), 1.35 (s, 12H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 159.0, 142.9, 133.7, 133.2, 130.4, 129.4, 127.9, 120.6, 114.7, 83.8, 73.4, 39.6, 29.7, 24.9, 24.9, 18.2.
HRMS-ESI (m/z): for $C_{21}H_{27}BO_3$ [M + Na^+]: calcd 361.1946, found 361.1960

ethyl 4-(tetrahydro-2H-pyran-4-yl)benzoate (35)



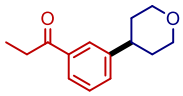
Following a modified general procedure B, ethyl 4-chlorobenzoate (139 mg mg, 0.752 mmol) was allowed to react with 4-bromotetrahydro-2H-pyran (83 mg, 0.50 mmol) under reductive electrolysis (3 mA, 4 equiv e^-) at 60 °C. The title compound was isolated following purification by flash column chromatography (5:95 EtOAc:Hexanes) as white solid (101 mg, 0.43 mmol, 86%). Analysis by ^{1}H NMR spectroscopy and ^{13}C NMR spectroscopy matches characterization of previously reported literature for the title compound.(*14~~77~~*)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, J = 8.4 Hz, 2H), 7.29 (d, J = 8.1 Hz, 2H), 4.37 (t, J = 7.1 Hz, 2H), 4.09 (dd, J = 9.8, 3.8 Hz, 2H), 3.53 (td, J = 11.5, 2.6 Hz, 2H), 2.82 (tt, J = 11.5, 4.3 Hz, 1H), 1.93 – 1.70 (m, 4H), 1.38 (t, J = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.5, 150.9, 129.8, 128.6, 126.7, 68.2, 60.8, 41.6, 33.6, 14.3.

HRMS-ESI (m/z): for $C_{14}H_{18}O_3$ [M + Na^+]: calcd 257.1149, found 257.1148

1-(3-(tetrahydro-2H-pyran-4-yl)phenyl)propan-1-one (36)



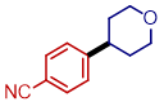
Following general procedure B, 1-(3-chlorophenyl)propan-1-one (175 mg, 1.04 mmol) was allowed to react with (24-bromotetrahydro-2H-pyran (86 mg, 0.52 mmol) under reductive electrolysis (3 mA, 4 equiv e^-). The title compound was isolated following purification by flash column chromatography (10:90 EtOAc:Hexanes) as a white solid (79 mg, 0.36 mmol, 69%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (dd, J = 1.6, 0.9 Hz, 1H), 7.80 (ddd, J = 6.3, 2.6, 1.8 Hz, 1H), 7.46 – 7.36 (m, 2H), 4.09 (ddt, J = 11.6, 4.4, 1.4 Hz, 2H), 3.54 (td, J = 11.5, 2.5 Hz, 2H), 3.00 (q, J = 7.3 Hz, 2H), 2.83 (tt, J = 11.6, 4.4 Hz, 1H), 1.95 – 1.71 (m, 5H), 1.23 (t, J = 7.2 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 200.9, 146.3, 137.2, 131.3, 128.8, 126.3, 126.2, 68.3, 41.5, 33.8, 31.9, 8.3.

HRMS-ESI (m/z): for $C_{14}H_{18}O_2$ [M + Na^+]: calcd 241.1199, found 241.1198

4-(tetrahydro-2H-pyran-4-yl)benzonitrile (37)



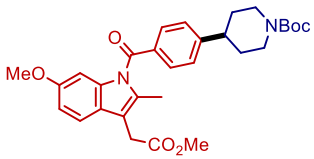
Following general procedure B, 4-chlorobenzonitrile (135 mg, 0.981 mmol) was allowed to react with 4-bromotetrahydro-2H-pyran (84 mg, 0.51 mmol) under reductive electrolysis (2 mA, 2.85 equiv e^-). The title compound was isolated following purification by flash column chromatography (3:97 EtOAc:Hexanes) as an off-white solid (71 mg, 0.38 mmol, 74%). Analysis by ^{1}H NMR spectroscopy and ^{13}C NMR spectroscopy matches characterization of previously reported literature for the title compound.(*14~~77~~*)

^{1}H NMR (400 MHz, $CDCl_3$) 1H NMR δ 7.58 (d, J = 8.0 Hz, 1H), 7.31 (d, J = 7.9 Hz, 1H), 4.07 (dd, J = 10.2, 3.7 Hz, 1H), 3.51 (td, J = 11.2, 3.6 Hz, 1H), 2.81 (tt, J = 10.9, 5.1 Hz, 0H), 1.89 – 1.65 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 151.0, 132.3, 127.5, 118.8, 110.1, 67.9, 41.6, 33.3.

HRMS-ESI (m/z): for $C_{12}H_{13}NO$ [M + H^+] calcd 188.1070, found 188.1070

tert-butyl 4-(4-(6-methoxy-3-(2-methoxy-2-oxoethyl)-2-methyl-1H-indole-1-carbonyl)phenyl)piperidine-1-carboxylate (38)



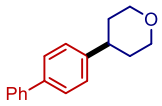
Following a modification of general procedure A, ethyl 2-(1-(4-chlorobenzoyl)-6-methoxy-2-methyl-1H-indol-3-yl)acetate (193 mg, 0.500 mmol) was allowed to react with tert-butyl 4-chloropiperidine-1-carboxylate (165 mg, 0.751 mmol) under reductive electrolysis (3 mA, 4 equiv e^-). The title compound was isolated following purification by flash column chromatography (15:85 EtOAc:Hexanes) as an off-white solid (146 mg, 0.280 mmol, 56%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (d, J = 8.1 Hz, 2H), 7.31 (d, J = 7.9 Hz, 2H), 6.95 (d, J = 2.6 Hz, 1H), 6.88 (d, J = 9.0 Hz, 1H), 6.65 (dd, J = 9.0, 2.5 Hz, 1H), 4.28 (d, J = 13.2 Hz, 2H), 3.83 (s, 3H), 3.70 (s, 3H), 3.67 (s, 2H), 2.80 (s, 2H), 2.80 – 2.69 (m, 1H), 2.37 (s, 3H), 1.94 – 1.83 (m, 2H), 1.65 (qd, J = 12.6, 4.2 Hz, 2H), 1.48 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 171.4, 169.2, 155.8, 154.7, 151.2, 136.0, 133.5, 130.9, 130.4, 130.2, 127.1, 114.9, 111.9, 111.4, 101.1, 55.7, 52.1, 44.2, 42.8, 32.9, 30.1, 28.4, 13.2.

HRMS-ESI (m/z): for $C_{30}H_{36}N_2O_6$ found [M + Na^+]: calcd 543.2466, found 543.2470

4-([1,1'-biphenyl]-4-yl)tetrahydro-2H-pyran (39)



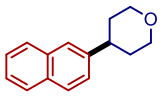
Following general procedure C, [1,1'-biphenyl]-4-yl trifluoromethanesulfonate (304 mg, 1.01 mmol) was allowed to react with 4-bromotetrahydro-2H-pyran (83 mg, 0.502 mmol) under reductive electrolysis (2 mA, 4 equiv e^-). The title compound was isolated following purification by flash column chromatography (0.5:99.5 EtOAc:Hexanes) as a white solid. (76 mg, 0.319 mmol, 63%). Analysis by ^{1}H NMR spectroscopy and ^{13}C NMR spectroscopy matches characterization of previously reported literature for the title compound.(*14~~77~~*)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (dd, J = 8.4, 1.3 Hz, 2H), 7.56 (d, J = 8.4 Hz, 2H), 7.43 (t, J = 7.5 Hz, 2H), 7.34 (d, J = 7.3 Hz, 1H), 7.33 – 7.29 (m, 2H), 4.11 (ddd, J = 10.7, 4.0, 1.3 Hz, 2H), 3.56 (td, J = 11.4, 2.7 Hz, 2H), 2.81 (tt, J = 11.3, 4.5 Hz, 1H), 2.00 – 1.74 (m, 4H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 145.0, 140.9, 139.3, 128.7, 127.3, 127.2, 127.1, 127.0, 68.4, 41.2, 33.9.

HRMS-ESI (m/z): for $C_{17}H_{18}O$ [M + H^+] calcd 239.1431 found 239.1430

4-(naphthalen-2-yl)tetrahydro-2H-pyran (40)



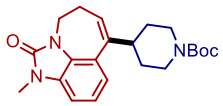
Following general procedure C, naphthalen-2-yl trifluoromethanesulfonate (276 mg, 1.00 mmol) was allowed to react with 4-bromotetrahydro-2H-pyran (83 mg, 0.5 mmol) under reductive electrolysis (2 mA, 2.5 equiv e^-). The title compound was isolated following purification by flash column chromatography (2.5:97.5 EtOAc:Hexanes) as a colorless oil (87 mg, 0.41 mmol, 82%). Analysis by ^{1}H NMR spectroscopy and ^{13}C NMR spectroscopy matches characterization of previously reported literature for the title compound.(*7~~48~~*)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 – 7.75 (m, 3H), 7.70 – 7.63 (m, 1H), 7.50 – 7.41 (m, 2H), 7.39 (dd, *J* = 8.5, 1.8 Hz, 1H), 4.13 (ddt, *J* = 11.7, 4.5, 0.9 Hz, 2H), 3.59 (td, *J* = 11.6, 2.5 Hz, 2H), 3.00 – 2.82 (m, 1H), 2.06 – 1.77 (m, 4H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 143.4, 133.8, 132.4, 128.2, 127.8, 127.7, 126.1, 125.8, 125.5, 124.9, 68.6, 41.8, 34.0.

HRMS-ESI (m/z): for $C_{15}H_{16}O$ [M + H^+] calcd 213.1274, found 213.1274

tert-butyl 4-(2-methyl-1-oxo-1,2,8,9-tetrahydro-2,9a-diazabenzo[cd]azulen-6-yl)piperidine-1-carboxylate (41)



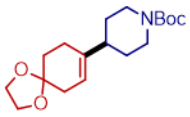
Following a modified general procedure C, 2-methyl-1-oxo-1,2,8,9-tetrahydro-2,9a-diazabenzo[cd]azulen-6-yl trifluoromethanesulfonate (348 mg, 1.00 mmol) was allowed to react with tert-butyl 4-bromopiperidine-1-carboxylate (132 mg, 0.500 mmol) under reductive electrolysis (1 mA, 2.5 equiv e^-). The title compound was isolated following purification by flash column chromatography (100% Hexanes) as a yellow resin (64 mg, 0.17 mmol, 34%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.19 – 7.14 (m, 1H), 7.10 (dd, *J* = 8.2, 7.6 Hz, 1H), 6.90 (dd, *J* = 7.6, 1.1 Hz, 1H), 5.99 (td, *J* = 7.3, 1.1 Hz, 1H), 4.21 (bs, 2H), 4.04 – 3.97 (m, 2H), 3.43 (s, 3H), 2.84 – 2.72 (m, 3H), 2.52 (td, *J* = 7.0, 3.5 Hz, 2H), 1.82 (d, *J* = 13.1 Hz, 2H), 1.46 (s, 9H), 1.47 – 1.36 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 154.8, 153.8, 142.0, 130.8, 127.3, 126.7, 121.3, 120.6, 119.0, 106.2, 79.4, 45.9, 40.1, 32.6, 28.5, 28.4, 27.7, 27.2.

HRMS-ESI (m/z): for $C_{22}H_{29}N_3O_3$ [M + Na^+]: calcd 406.2102, found 406.2099

tert-butyl 4-(1,4-dioxaspiro[4.5]dec-7-en-8-yl)piperidine-1-carboxylate (42)



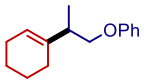
Following general procedure C, 1,4-dioxaspiro[4.5]dec-7-en-8-yl trifluoromethanesulfonate (290 mg, 1.01 mmol) was allowed to react with tert-butyl 4-bromopiperidine-1-carboxylate (133 mg, 0.503 mmol) under reductive electrolysis (2 mA, 2.5 equiv e^-). The title compound was isolated following purification by flash column chromatography (4:96 EtOAc:Hexanes) as a white solid (64 mg, 0.20 mmol, 39%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.31 (ddt, J = 3.8, 2.3, 1.3 Hz, 1H), 4.13 (s, 2H), 3.97 (d, J = 1.0 Hz, 4H), 2.66 (t, J = 13.7 Hz, 2H), 2.30 – 2.22 (m, 2H), 2.17 (tt, J = 6.6, 2.0 Hz, 2H), 1.95 (t, J = 12.0 Hz, 1H), 1.80 – 1.72 (m, 2H), 1.71 – 1.60 (m, 2H), 1.45 (s, 9H), 1.34 (tdd, J = 12.3, 4.1 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 154.8, 140.5, 117.1, 108.0, 79.3, 64.4, 43.0, 41.0, 35.7, 31.3, 30.7, 28.5, 25.8.

HRMS-ESI (m/z): for $C_{18}H_{29}NO_4$ [M + Na^+]: calcd 346.1989, found 346.1987

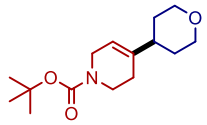
(2-(cyclohex-1-en-1-yl)propoxy)benzene (43)



Following general procedure C, cyclohex-1-en-1-yl trifluoromethanesulfonate (239 mg, 1.04 mmol) was allowed to react with (2-bromopropoxy)benzene (109 mg, 0.507 mmol) under reductive

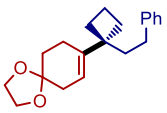
electrolysis (2 mA, 2.5 equiv e^-). The title compound was isolated following purification by flash column chromatography (0:100 EtOAc:Hexanes) as a colorless oil (90 mg, 0.42 mmol, 82%).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 – 7.19 (m, 2H), 6.94 – 6.84 (m, 3H), 5.50 (dddd, J = 3.7, 3.0, 2.2, 1.2 Hz, 1H), 3.93 (dd, J = 9.1, 5.8 Hz, 1H), 3.72 (dd, J = 9.1, 7.8 Hz, 1H), 2.49 (h, J = 6.5 Hz, 1H), 2.09 – 1.84 (m, 4H), 1.68 – 1.46 (m, 4H), 1.11 (d, J = 6.9 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 159.2, 139.0, 129.4, 121.8, 120.5, 114.7, 72.0, 40.7, 26.5, 25.3, 23.1, 22.6, 16.4.
HRMS-ESI (m/z): for $C_{15}H_{20}O$ [M + Na^+]: calcd 239.1407, found 239.1410

tert-butyl 4-(tetrahydro-2H-pyran-4-yl)-3,6-dihydropyridine-1(2H)-carboxylate (44)



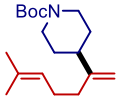
Following general procedure C, tert-butyl 4-(((trifluoromethyl)sulfonyl)oxy)-3,6-dihydropyridine-1(2H)-carboxylate (330 mg, 0.99 mmol) was allowed to react with 4-bromotetrahydro-2H-pyran (83 mg, 0.500 mmol) under reductive electrolysis (2 mA, 2.5 equiv e^-). The title compound was isolated following purification by flash column chromatography (10:90 EtOAc:Hexanes) as a colorless oil (84 mg, 0.322 mmol, 64%).
^{1}H NMR (400 MHz, $CDCl_3$) δ 5.36 (s, 1H), 4.08 – 3.96 (m, 2H), 3.86 (d, *J* = 3.1 Hz, 2H), 3.47 (t, *J* = 5.7 Hz, 2H), 3.40 (td, *J* = 11.5, 2.5 Hz, 2H), 2.06 (s, 3H), 1.64 – 1.55 (m, 2H), 1.55 – 1.49 (m, 2H), 1.46 (s, 9H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 154.9, 139.8, 116.9, 79.4, 68.1, 43.5, 41.9, 40.2, 31.1, 28.4, 26.6.
HRMS-ESI (m/z): for $C_{15}H_{25}NO_3$ [M + Na^+]: calcd 290.1727, found 290.1722

8-(1-phenethylcyclobutyl)-1,4-dioxaspiro[4.5]dec-7-ene (45)



Following general procedure C, 1,4-dioxaspiro[4.5]dec-7-en-8-yl trifluoromethanesulfonate (288 mg, 1.00 mmol) was allowed to react with ((1-bromocyclobutyl)methyl)benzene (112 mg, 0.500 mmol) under reductive electrolysis (2 mA, 2.5 equiv e-). The title compound was isolated as an inseparable mixture following purification by flash column chromatography (2:98 EtOAc:Hexanes) as a yellow oil (63 mg, 0.22 mmol, 44% based on NMR yield).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 – 7.23 (m, 2H), 7.20 – 7.13 (m, 3H), 5.33 – 5.26 (m, 1H), 3.99 (s, 4H), 2.40 – 2.34 (m, 2H), 2.35 – 2.32 (m, 2H), 2.28 (dd, J = 2.3, 1.3 Hz, 2H), 2.11 (d, J = 1.7 Hz, 2H), 2.08 (dq, J = 4.4, 1.9 Hz, 2H), 1.92 – 1.87 (m, 2H), 1.79 – 1.74 (m, 4H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 143.2, 142.1, 128.3, 128.2, 126.5, 125.4, 124.2, 39.9, 35.7, 35.7, 31.2, 31.2, 30.9, 30.9, 22.6, 15.2.
HRMS-ESI (m/z): for $C_{20}H_{26}O_2$ [M + Na^+]: calcd 321.1825, found 321.1823

tert-butyl 4-(6-methylhepta-1,5-dien-2-yl)piperidine-1-carboxylate (46)



Following general procedure C, 6-methylhepta-1,5-dien-2-yl trifluoromethanesulfonate (258 mg, 0.999 mmol) was allowed to react with tert-butyl 4-bromopiperidine-1-carboxylate (132 mg, 0.499 mmol) under reductive electrolysis (2 mA, 2.5 equiv e^-). The title compound was isolated following purification by flash column chromatography (4:96 EtOAc:Hexanes) as a colorless oil (92 mg, 0.31 mmol, 62%).
^{1}H NMR (400 MHz, $CDCl_3$) δ 5.11 (dddd, J = 6.9, 5.4, 2.8, 1.4 Hz, 1H), 4.76 (d, J = 1.4 Hz, 1H), 4.75 (s, 1H), 4.16 (s, 2H), 2.68 (t, J = 11.8 Hz, 2H), 2.15 – 2.08 (m, 2H), 2.07 – 2.01 (m, 2H), 1.98 (ddd, J = 15.3, 12.0, 2.9 Hz, 1H), 1.70 (d, J = 8.8 Hz, 2H), 1.69 (d, J = 1.3 Hz, 3H), 1.62 – 1.61 (m, 3H), 1.46 (s, 9H), 1.34 (qd, J = 12.6, 4.4 Hz, 2H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 154.8, 153.0, 131.7, 124.0, 107.9, 79.3, 77.2, 42.4, 34.7, 31.3, 28.5, 26.7, 25.7, 17.7.

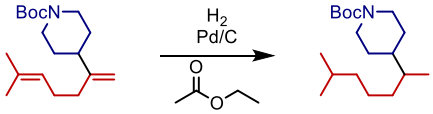
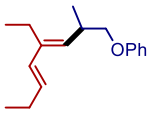


Figure S20: Product hydrogenation to form products of formal alkyl-alkyl coupling **.**

To a 20 mL round-bottom flask was added tert-butyl 4-(6-methylhepta-1,5-dien-2-yl)piperidine-1-carboxylate (92 mg, 0.31 mmol) a stir bar, 10% Pd/C (40 mg, 1 equiv) and 10 mL of EtOAc. The reaction mixture was allowed to stir at room temperature under 1 atm of H_2 for one hour. The resulting slurry was filtered over Celite and concentrated by rotary evaporation to afford the title compound as a colorless oil. (78 mg, 0.26 mmol, 84%)
^{1}H NMR (400 MHz, $CDCl_3$) δ 4.12 (q, J = 7.2 Hz, 2H), 2.61 (s, 2H), 1.54 (dt, J = 13.0, 4.4 Hz, 4H), 1.45 (s, 9H), 1.38 (s, 1H), 1.34 – 1.29 (m, 4H), 1.26 (d, J = 1.7 Hz, 4H), 0.87 (dd, J = 6.6, 1.1 Hz, 6H), 0.82 (d, J = 6.4 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 192.2, 79.1, 41.2, 39.3, 37.4, 34.1, 29.7, 28.5, 28.0, 25.1, 22.7, 22.6, 16.1.
HRMS-ESI (m/z): for $C_{18}H_{35}NO_2$ [M + Na^+]: calcd 320.2560, found 320.2560

((3E,5E)-4-ethyl-2-methylocta-3,5-dien-1-yl)oxy)benzene (47)



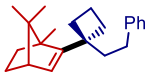
Following general procedure C, (1E,3E)-2-ethylhexa-1,3-dien-1-yl trifluoromethanesulfonate (250 mg, 1.00 mmol) was allowed to react with (2-bromopropoxy)benzene (108 mg, 0.500 mmol) under reductive electrolysis (2 mA, 2.5 equiv e^-). The title compound was isolated following purification by flash column chromatography (100% Hexanes) as a colorless oil (64 mg, 0.26 mmol, 4:1 d.r., 52%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 – 7.24 (m, 2H), 6.99 – 6.81 (m, 3H), 5.96 (dd, *J* = 15.8, 0.9 Hz, 1H), 5.72 (dt, *J* = 15.8, 6.5 Hz, 1H), 5.21 (d, *J* = 9.7 Hz, 1H), 3.87 (ddd, *J* = 9.0, 7.0, 5.7 Hz, 1H), 3.75 (dd, *J* = 8.9, 7.4 Hz, 1H), 3.07 – 2.81 (m, 1H), 2.31 (q, *J* = 7.5 Hz, 2H), 2.20 – 2.05 (m, 2H), 1.14 (d, *J* = 6.7 Hz, 3H), 1.10 – 1.07 (m, 3H), 1.06 – 0.98 (m, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 159.1, 140.7, 131.8, 131.1, 130.0, 129.4, 120.5, 114.5, 72.5, 32.7, 25.9, 20.4, 18.0, 14.3, 13.8.

HRMS-ESI (m/z): for $C_{17}H_{24}O$ [M + Na^+]: calcd 267.1720, found 267.1719

(1S,4S)-1,7,7-trimethyl-2-(1-phenethylcyclobutyl)bicyclo[2.2.1]hept-2-ene (48)



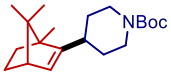
Following a modified general procedure C, (1S,4S)-1,7,7-trimethylbicyclo[2.2.1]hept-2-en-2-yl trifluoromethanesulfonate (170 mg, 0.598 mmol) was allowed to react with (2-(1-bromocyclobutyl)ethyl)benzene (119 mg, 0.498 mmol) under reductive electrolysis (2 mA, 4 equiv e^-) at 33 °C. The title compound was isolated following purification by flash column chromatography (0:100 EtOAc:Hexanes) as a colorless oil (105 mg, 0.357 mmol, 72%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 – 7.23 (m, 2H), 7.21 – 7.13 (m, 3H), 5.61 (d, J = 3.3 Hz, 1H), 2.56 – 2.46 (m, 1H), 2.36 – 2.25 (m, 2H), 2.24 – 2.17 (m, 2H), 1.97 – 1.81 (m, 6H), 1.81 – 1.75 (m, 1H), 1.51 (ddd, J = 12.2, 8.5, 3.6 Hz, 1H), 1.21 (ddd, J = 12.2, 9.2, 3.5 Hz, 1H), 1.07 – 1.02 (m, 1H), 1.02 (s, 3H), 0.90 (s, 3H), 0.75 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 152.4, 143.3, 128.3, 128.3, 128.1, 125.5, 57.3, 55.2, 51.2, 45.3, 39.7, 32.8, 32.3, 30.9, 30.8, 26.0, 19.9, 19.6, 16.4, 12.9.

HRMS-ESI (m/z): for $C_{22}H_{30}$ [M + Na^+]: calcd 317.2240, found 317.2244

tert-butyl 4-((1S,4S)-1,7,7-trimethylbicyclo[2.2.1]hept-2-en-2-yl)piperidine-1-carboxylate (49)



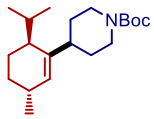
Following general procedure C, (1S,4S)-1,7,7-trimethylbicyclo[2.2.1]hept-2-en-2-yl trifluoromethanesulfonate (282 mg, 0.991 mmol) was allowed to react with tert-butyl 4-bromopiperidine-1-carboxylate (131 mg, 0.496 mmol) under reductive electrolysis (2 mA, 4 equiv e^-). The title compound was isolated following purification by flash column chromatography (2:98 EtOAc:Hexanes) as a white solid (87 mg, 0.27 mmol, 57%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.54 (dd, J = 3.4, 1.3 Hz, 1H), 4.11 (s, 2H), 2.70 (s, 2H), 2.21 (t, J = 3.5 Hz, 1H), 2.05 (ttd, J = 11.6, 3.5, 1.3 Hz, 1H), 1.79 (ddt, J = 11.1, 6.8, 3.6 Hz, 1H), 1.68 (t, J = 13.7 Hz, 2H), 1.52 – 1.47 (m, 1H), 1.45 (s, 9H), 1.41 – 1.15 (m, 2H), 1.01 (s, 3H), 0.99 – 0.86 (m, 2H), 0.75 (s, 3H), 0.74 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 154.8, 152.5, 126.0, 79.2, 56.6, 54.3, 51.1, 35.4, 32.2, 32.0, 30.8, 28.5, 25.6, 19.7, 19.7, 11.7.

HRMS-ESI (m/z): for $C_{20}H_{33}NO_2$ [M + Na^+]: calcd 342.2404, found 342.2403

tert-butyl 4-((3R,6S)-6-isopropyl-3-methylcyclohex-1-en-1-yl)piperidine-1-carboxylate (50)



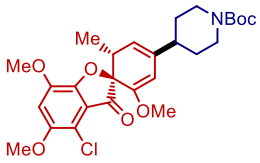
Following general procedure C, (3R,6S)-6-isopropyl-3-methylcyclohex-1-en-1-yl trifluoromethanesulfonate (286 mg, 1.00 mmol) was allowed to react with tert-butyl 4-bromopiperidine-1-carboxylate (132 mg, 0.500 mmol) under reductive electrolysis (2 mA, 2.5 equiv e^-). The title compound was isolated following purification by flash column chromatography (10:90 EtOAc:Hexanes) as a colorless oil (114 mg, 0.355 mmol, 71%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.28 (dt, *J* = 1.9, 0.9 Hz, 1H), 4.14 (dd, *J* = 31.0, 12.6 Hz, 2H), 2.68 (q, *J* = 11.4 Hz, 2H), 2.25 – 1.88 (m, 2H), 1.74 (ddt, *J* = 12.7, 8.9, 2.9 Hz, 2H), 1.66 (dddd, *J* = 13.1, 6.2, 5.0, 2.9 Hz, 1H), 1.62 – 1.54 (m, 1H), 1.53 – 1.48 (m, 1H), 1.46 (s, 11H), 1.35 – 1.23 (m, 1H), 1.04 (tdd, *J* = 12.9, 11.8, 4.3 Hz, 1H), 0.93 (d, *J* = 6.8 Hz, 3H), 0.91 (d, *J* = 7.0 Hz, 3H), 0.69 (d, *J* = 6.8 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 154.8, 142.6, 128.6, 79.2, 41.2, 38.2, 33.1, 31.0, 30.6, 30.2, 28.5, 27.8, 22.4, 21.8, 20.9, 16.1.

HRMS-ESI (m/z): for $C_{20}H_{35}NO_2$ [M + Na^+]: calcd 344.2560, found 344.2560

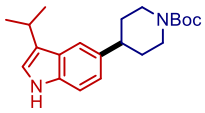
tert-butyl 4-((2S,6'R)-4-chloro-2',5,7-trimethoxy-6'-methyl-3-oxo-3H-spiro[benzofuran-2,1'-cyclohexane]-2',4'-dien-4'-yl)piperidine-1-carboxylate (51)



Following a modified version of general procedure B, (2S,6'R)-4-chloro-2',5,7-trimethoxy-6'-methyl-3-oxo-3H-spiro[benzofuran-2,1'-cyclohexane]-2',4'-dien-4'-yl trifluoromethanesulfonate (194 mg, 0.400 mmol) was allowed to react with tert-butyl 4-bromopiperidine-1-carboxylate (158 mg, 0.598 mmol) under reductive electrolysis (2 mA, 4 equiv e^-). The title compound was isolated following purification by flash column chromatography (15:85 EtOAc:Hexanes) as a yellow solid (71 mg, 0.14 mmol, 34%).

^{1}H NMR (400 MHz, CDCl$_3$ δ 6.06 (s, 1H), 5.14 (d, J = 1.1 Hz, 1H), 5.07 (dt, J = 3.7, 1.2 Hz, 1H), 4.16 (s, 2H), 3.98 (s, 3H), 3.93 (s, 3H), 3.52 (s, 3H), 3.11 (ddd, J = 7.3, 3.4, 1.3 Hz, 1H), 2.72 (t, J = 12.3 Hz, 2H), 2.09 (dd, J = 14.0, 10.3 Hz, 1H), 1.81 – 1.69 (m, 2H), 1.46 (s, 9H), 1.38 (dt, J = 12.6, 3.9 Hz, 2H), 1.02 (d, J = 7.4 Hz, 3H).
^{13}C NMR (101 MHz, CDCl$_3$) δ 193.6, 168.9, 163.8, 157.5, 154.8, 153.8, 136.5, 116.6, 105.5, 98.8, 97.1, 93.6, 89.0, 79.3, 65.8, 56.8, 56.2, 55.4, 41.8, 38.8, 28.5, 15.3, 14.1.
HRMS-ESI (m/z): for $C_{27}H_{34}ClNO_7$ [M + Na^+]: calcd 542.1916, found 542.1890

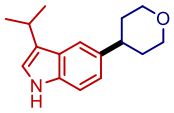
tert-butyl 4-(3-isopropyl-1H-indol-5-yl)piperidine-1-carboxylate



Following a modified general procedure B, 5-bromo-3-isopropyl-1H-indole (238 mg, 1.00 mmol) was allowed to react with tert-butyl 4-bromopiperidine-1-carboxylate (132 mg, 328 mmol) under reductive electrolysis (3 mA, 2.5 equiv e^-) at 40 °C. The title compound was isolated following purification by flash column chromatography (25:75) EtOAc:Hexanes) as a colorless solid (102 mg, 0.298 mmol, 60%).

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.91 (s, 1H), 7.47 (d, *J* = 0.9 Hz, 1H), 7.32 – 7.27 (m, 1H), 7.05 (dd, *J* = 8.4, 1.7 Hz, 1H), 6.94 (dd, *J* = 2.4, 0.9 Hz, 1H), 4.28 (s, 2H), 3.27 – 3.13 (m, 1H), 2.96 – 2.79 (m, 2H), 2.81 – 2.69 (m, 1H), 1.96 – 1.84 (m, 2H), 1.78 – 1.66 (m, 2H), 1.51 (s, 9H), 1.37 (d, *J* = 6.9 Hz, 6H).
^{13}C NMR (101 MHz, CDCl$_3$) δ 154.9, 136.6, 135.3, 126.9, 123.8, 121.1, 119.6, 116.7, 111.0, 79.3, 44.6, 43.0, 34.0, 28.5, 25.4, 23.3.
HRMS-ESI (m/z): for $C_{21}H_{30}N_2O_2$ [M + H^+]: calcd 343.2381, found 343.2380

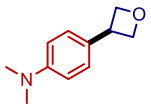
3-isopropyl-5-(tetrahydro-2H-pyran-4-yl)-1H-indole



Following a modified general procedure B, 5-bromo-3-isopropyl-1H-indole (238 mg, 1.00 mmol) was allowed to react with 4-bromotetrahydro-2H-pyran (82 mg, 0.50 mmol) under reductive electrolysis (3 mA, 2.5 equiv e^-) at 40 °C. The title compound was isolated following purification by flash column chromatography (15:85) EtOAc:Hexanes) as a colorless solid (55 mg, 0.23 mmol, 45%).

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.83 (s, 1H), 7.49 (dd, *J* = 1.7, 0.8 Hz, 1H), 7.30 (dd, *J* = 8.4, 0.7 Hz, 1H), 7.07 (dd, *J* = 8.4, 1.7 Hz, 1H), 6.95 (dd, *J* = 2.4, 0.9 Hz, 1H), 4.16 – 4.07 (m, 2H), 3.57 (td, *J* = 11.7, 2.4 Hz, 2H), 3.20 (qd, *J* = 6.8, 0.9 Hz, 1H), 2.93 – 2.81 (m, 1H), 1.97 – 1.87 (m, 2H), 1.86 – 1.79 (m, 2H), 1.37 (d, *J* = 6.9 Hz, 6H).
^{13}C NMR (101 MHz, CDCl$_3$) δ 136.8, 135.3, 126.9, 123.8, 121.1, 119.6, 116.8, 111.0, 68.7, 41.8, 34.8, 25.4, 23.3.
HRMS-ESI (m/z): for $C_{16}H_{21}NO$ [M + Na^+]: calcd 266.1516, found 266.1515

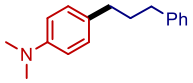
N,N-dimethyl-4-(oxetan-3-yl)aniline



Following a modified general procedure B, 4-bromo-N,N-dimethylaniline (199 mg, 0.99 mmol) was allowed to react with 3-bromooxetane (68 mg, 0.50 mmol) under reductive electrolysis (3 mA, 2.5 equiv e^-) at 40 °C. The title compound was isolated following purification by flash column chromatography (5:95) EtOAc:Hexanes) as a colorless solid (42 mg, 0.24 mmol, 47%).

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.30 – 7.26 (m, 2H), 6.75 (d, *J* = 8.9 Hz, 2H), 5.03 (dd, *J* = 8.4, 6.0 Hz, 2H), 4.76 (dd, *J* = 7.0, 5.9 Hz, 2H), 4.16 (tt, *J* = 8.5, 7.0 Hz, 1H), 2.95 (s, 6H).
^{13}C NMR (101 MHz, CDCl$_3$) δ 149.8, 129.3, 127.6, 112.9, 79.5, 40.7, 39.7.

N,N-dimethyl-4-(3-phenylpropyl)aniline

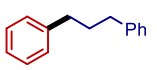


Following a modified general procedure B, 4-bromo-N,N-dimethylaniline (201 mg, 1.01 mmol) was allowed to react with (3-bromopropyl)benzene (99 mg, 0.50 mmol) under reductive electrolysis (3 mA, 2.5 equiv e^-) at 60 °C. The title compound was isolated following purification by flash column chromatography (3:97) EtOAc:Hexanes) as a colorless oil (78 mg, 0.33 mmol, 65%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.27 (m, 2H), 7.26 – 7.16 (m, 2H), 7.14 – 7.05 (m, 2H), 6.77 – 6.68 (m, 2H), 2.94 (s, 6H), 2.67 (td, *J* = 8.1, 5.1 Hz, 2H), 2.59 (dd, *J* = 9.9, 5.3 Hz, 2H), 2.01 – 1.88 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 149.0, 142.5, 130.5, 129.0, 128.4, 128.2, 125.6, 113.0, 77.3, 77.0, 76.7, 40.9, 35.4, 34.4, 33.2.

1,3-diphenylpropane

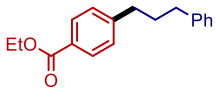


Following a modified general procedure B, bromobenzene (157 mg, 1.00 mmol) was allowed to react with (3-bromopropyl)benzene (mg, mmol) under reductive electrolysis (3 mA, 2.5 equiv e^-) at 60 °C. The title compound was confirmed by GCMS and quantified by gas chromatography, 47%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (dddd, *J* = 8.2, 5.6, 2.3, 1.2 Hz, 5H), 7.35 (ddd, *J* = 6.0, 2.2, 1.2 Hz, 7H), 2.85 – 2.78 (m, 4H), 2.17 – 2.07 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 142.2, 128.4, 128.2, 125.7, 35.4, 31.6.

ethyl 4-(3-phenylpropyl)benzoate

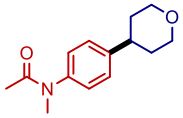


Following a modified general procedure B, ethyl 4-bromobenzoate (229 mg, 1.00 mmol) was allowed to react with (3-bromopropyl)benzene (99 mg, 0.50 mmol) under reductive electrolysis (3 mA, 2.5 equiv e^-) at 60 °C. The title compound was confirmed by GCMS and quantified by gas chromatography, 36%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 – 8.00 (m, 2H), 7.37 – 7.27 (m, 4H), 7.24 – 7.18 (m, 3H), 4.42 (qd, *J* = 7.1, 5.9 Hz, 2H), 2.77 – 2.58 (m, 4H), 2.07 – 1.95 (m, 2H), 1.46 – 1.41 (m, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.5, 147.6, 141.8, 132.7, 129.6, 129.4, 128.3, 128.3, 125.8, 125.5, 60.8, 60.7, 35.9, 35.3, 35.2, 32.5, 31.3, 29.1.

N-methyl-N-(4-(tetrahydro-2H-pyran-4-yl)phenyl)acetamide

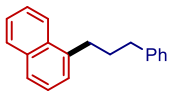


Following a modified general procedure B, N-(4-bromophenyl)-N-methylacetamide (230 mg, 1.00 mmol) was allowed to react with 4-bromotetrahydro-2H-pyran (mg, mmol) under reductive electrolysis (3 mA, 2.5 equiv e^-) at 40 °C. The title compound was isolated following purification by flash column chromatography (5:95) EtOAc:Hexanes) as a faint yellow solid (57% by gas chromatography).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (d, *J* = 8.5 Hz, 2H), 7.15 (d, *J* = 8.6 Hz, 2H), 4.12 – 4.00 (m, 2H), 3.52 (td, *J* = 11.3, 3.2 Hz, 2H), 2.71 (td, *J* = 10.8, 5.0 Hz, 1H), 2.17 (s, 3H), 2.15 (d, *J* = 3.9 Hz, 3H), 1.84 – 1.68 (m, 4H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 168.6, 168.5, 141.9, 138.0, 136.1, 129.0, 127.2, 124.3, 120.3, 119.9, 68.4, 41.0, 34.0, 24.5.

1-(3-phenylpropyl)naphthalene

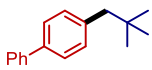


Following a modified general procedure B, 1-chloronaphthalene (mg, mmol) was allowed to react with (3-bromopropyl)benzene (mg, mmol) under reductive electrolysis (3 mA, 2.5 equiv e^-) at 60 °C. The title compound was isolated as a mixture of products following purification by flash column chromatography (0:100) EtOAc:Hexanes) as a colorless oil (42% yield by gas chromoatography).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (dt, *J* = 7.2, 3.2 Hz, 1H), 7.91 – 7.85 (m, 1H), 7.74 (d, *J* = 7.6 Hz, 1H), 7.54 – 7.48 (m, 2H), 7.48 – 7.40 (m, 1H), 7.40 – 7.29 (m, 4H), 7.25 (q, *J* = 7.5, 5.2 Hz, 2H), 3.14 (t, *J* = 7.7 Hz, 2H), 2.79 (t, *J* = 7.6 Hz, 2H), 2.25 – 2.01 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 142.2, 138.4, 133.9, 131.9, 128.5, 128.4, 126.6, 126.0, 125.7, 125.5, 125.4, 123.8, 35.9, 32.6, 32.3.

4-neopentyl-1,1'-biphenyl

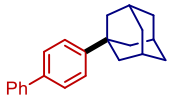


Following a modified general procedure C, [1,1'-biphenyl]-4-yl trifluoromethanesulfonate (302 mg, 1.00 mmol) was allowed to react with 1-bromo-2,2-dime thylpropane (76 mg, 0.51 mmol) under reductive electrolysis (3 mA, 2.5 equiv e^-) at 60 °C. The title compound was isolated as a mixture of products following purification by flash column chromatography (0:100) EtOAc:Hexanes) as a colorless oil (41% yield by gas chromatography).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 – 7.49 (m, 2H), 7.23 – 7.17 (m, 2H), 2.55 (s, 2H), 0.95 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 141.2, 138.9, 138.6, 130.9, 128.7, 127.2, 127.2, 127.0, 126.9, 49.9, 31.8, 29.4.

(3r,5r,7r)-1-([1,1'-biphenyl]-4-yl)adamantane

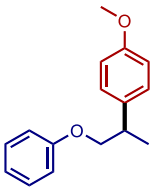


Following a modified general procedure C, [1,1'-biphenyl]-4-yl trifluoromethanesulfonate (302 mg, 1.00 mmol) was allowed to react with (3s,5s,7s)-1-bromoadamantane (108 mg, 0.500 mmol) under reductive electrolysis (3 mA, 2.5 equiv e^-) at 60 °C. The title compound was isolated as a mixture of products following purification by flash column chromatography (0:100) EtOAc:Hexanes) as a colorless oil (55% yield by gas chromatography).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 – 7.59 (m, 5H), 7.48 – 7.43 (m, 6H), 2.38 (d, *J* = 2.9 Hz, 6H), 2.13 – 2.08 (m, 3H), 1.74 (t, *J* = 3.2 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 141.2, 128.7, 128.6, 127.2, 127.1, 127.0, 126.8, 125.3, 49.3, 43.2, 36.8, 35.5, 32.6, 28.9.

1-methoxy-4-(1-phenoxypropan-2-yl)benzene



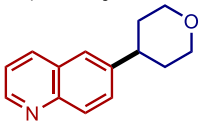
Following a modified general procedure B, 1-bromo-4-methoxybenzene (107 mg, 0.497 mmol) was allowed to react with (2-bromopropoxy)benzene (116 mg, 0.620 mmol) under reductive electrolysis (3 mA, 2.5 equiv e^-) at 25 °C. The title compound was isolated following purification by flash column chromatography (2:98) EtOAc:Hexanes) as a colorless oil (87 mg, 0.36 mmol, 72%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 – 7.26 (m, 2H), 7.27 – 7.18 (m, 2H), 6.93 (t, *J* = 7.4 Hz, 1H), 6.91 – 6.86 (m, 4H), 4.05 (dd, *J* = 9.1, 5.8 Hz, 1H), 3.92 (dd, *J* = 9.1, 7.9 Hz, 1H), 3.80 (s, 3H), 3.20 (dq, *J* = 13.9, 7.0 Hz, 1H), 1.39 (d, *J* = 6.9 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 158.98, 158.27, 135.75, 129.40, 128.32, 120.62, 114.62, 113.87, 73.55, 55.28, 38.72, 18.31.

HRMS-ESI (m/z): for $C_{16}H_{18}O_2$ [M + H^+]: calcd 243.1380, found 243.1380

6-(tetrahydro-2*H*-pyran-4-yl)quinoline



Following a modified general procedure B, 6-bromoquinoline (104 mg, 0.500 mmol) was allowed to react with 4-bromotetrahydro-2H-pyran (83 mg, 0.50 mmol) under reductive electrolysis (3 mA, 2.5 equiv e^-) at 25 °C. The title compound was isolated as a mixture of products following purification by flash column chromatography (5:95) EtOAc:Hexanes) as a yellow oil (54 mg, 0.25 mmol, 51%).

^{1}H NMR (400 MHz, $CDCl_3$) 8.87 (dd, *J* = 4.2, 1.8 Hz, 1H), 8.12 (d, *J* = 8.3 Hz, 1H), 8.06 (d, *J* = 9.3 Hz, 1H), 7.65 – 7.57 (m, 2H), 7.38 (dd, *J* = 8.3, 4.2 Hz, 1H), 4.24 – 4.05 (m, 2H), 3.58 (td, *J* = 11.4, 2.9 Hz, 2H), 2.95 (dq, *J* = 11.4, 6.8, 5.6 Hz, 1H), 1.89 (qd, *J* = 12.0, 3.9 Hz, 4H).

^{13}C NMR (101 MHz, $CDCl_3$) 149.90, 147.33, 144.07, 135.75, 129.55, 129.33, 128.32, 124.41, 121.15, 68.29, 41.45, 33.78.

HRMS-ESI (m/z): for $C_{14}H_{15}NO$ [M + H^+]: calcd 214.1227 found 214.1226

Single Crystal Analysis of (bpp)$MnCl_2$

The single crystal X-ray diffraction studies were carried out on a Bruker Kappa Photon II CPAD diffractometer equipped with Cu K_α radiation (λ = 1.54178). A 0.183 x 0.074 x 0.067 mm piece of a colorless plank was mounted on a Cryoloop with Paratone 24EX oil. Data were collected in a nitrogen gas stream at 100(2) K using ϕ and ϖ scans. Crystal-to-detector distance was 40 mm using variable exposure time (10s-60s) depending on θ with a scan width of 2.0°. Data collection was 100% complete to 68.00° in θ (0.83Å). A total of 29729 reflections were collected covering the indices, -13<=h<=13, -9<=k<=9, -19<=l<=18. 2669 reflections were found to be symmetry independent, with a R_{int} of 0.0357. Indexing and unit cell refinement indicated a primitive, monoclinic lattice. The space group was found to be $P2_1/c$. The data were integrated using the Bruker SAINT software program and scaled using the SADABS software program. Solution by direct methods (SHELXT) produced a complete phasing model for refinement.

All nonhydrogen atoms were refined anisotropically by full-matrix least-squares (SHELXL-2014). All hydrogen atoms were placed using a riding model. Their positions were constrained relative to their parent atom using the appropriate HFIX command in SHELXL-2014. Crystallographic data are summarized below.

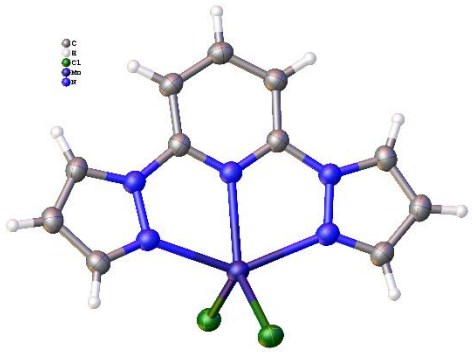


Figure S21. ORTEP illustration of (bpp)$MnCl_2$

Crystal data and structure refinement for (bpp)$MnCl_2$

Report date	2022-01-05	
Identification code	TBH-1255	
Empirical formula	C11 H9 Cl2 Mn N5	
Molecular formula	C11 H9 Cl2 Mn N5	
Formula weight	337.07	
Temperature	100.0 K	
Wavelength	1.54178 Å	
Crystal system	Monoclinic	
Space group	P 1 21/c 1	
Unit cell dimensions	a = 10.8214(3) Å	α= 90°.
	b = 7.9452(2) Å	β= 93.2600(10)°.
	c = 15.2117(4) Å	γ = 90°.
Volume	1305.76(6) $Å^3$	
Z	4	
Density (calculated)	1.715 Mg/m^3	
Absorption coefficient	11.929 mm^{-1}	
F(000)	676	
Crystal size	0.183 x 0.074 x 0.067 mm^3	
Crystal color, habit	Colorless Plank	
Theta range for data collection	4.092 to 74.646°.	
Index ranges	-13<=h<=13, -9<=k<=9, -19<=l<=18	
Reflections collected	29279	
Independent reflections	2669 [R(int) = 0.0357, R(sigma) = 0.0185]	
Completeness to theta = 68.000°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.1738 and 0.0514	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2669 / 0 / 172	
Goodness-of-fit on F^2	1.053	
Final R indices [I>2sigma(I)]	R1 = 0.0226, wR2 = 0.0619	
R indices (all data)	R1 = 0.0236, wR2 = 0.0627	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.219 and -0.242 $e.Å^{-3}$	

Single Crystal Analysis of 4

The single crystal X-ray diffraction studies were carried out on a Bruker Kappa Photon II CPAD diffractometer equipped with Cu K_α radiation (λ = 1.54178 Å). A 0.253 x 0.145 x 0.068 mm piece of a yellow block was mounted on a Cryoloop with Paratone 24EX oil. Data were collected in a nitrogen gas stream at 100(2) K using ϕ and ϖ scans. Crystal-to-detector distance was 50 mm using variable exposure time (5s-10s) depending on θ with a scan width of 1.0°. Data collection was 99.9% complete to 25.00° in θ (0.83Å). A total of 145700 reflections were collected covering the indices, -13<=h<=13, -19<=k<=19, -27<=l<=27. 14244 reflections were found to be symmetry independent, with a R_{int} of 0.0512. Indexing and unit cell refinement indicated a primitive, triclinic lattice. The space group was found to be *P*-1. The data were integrated using the Bruker SAINT software program and scaled using the SADABS software program. Solution by direct methods (SHELXT) produced a complete phasing model for refinement.

All nonhydrogen atoms were refined anisotropically by full-matrix least-squares (SHELXL-2014). All hydrogen atoms were placed using a riding model. Their positions were constrained relative to their parent atom using the appropriate HFIX command in SHELXL-2014. Crystallographic data are summarized below.

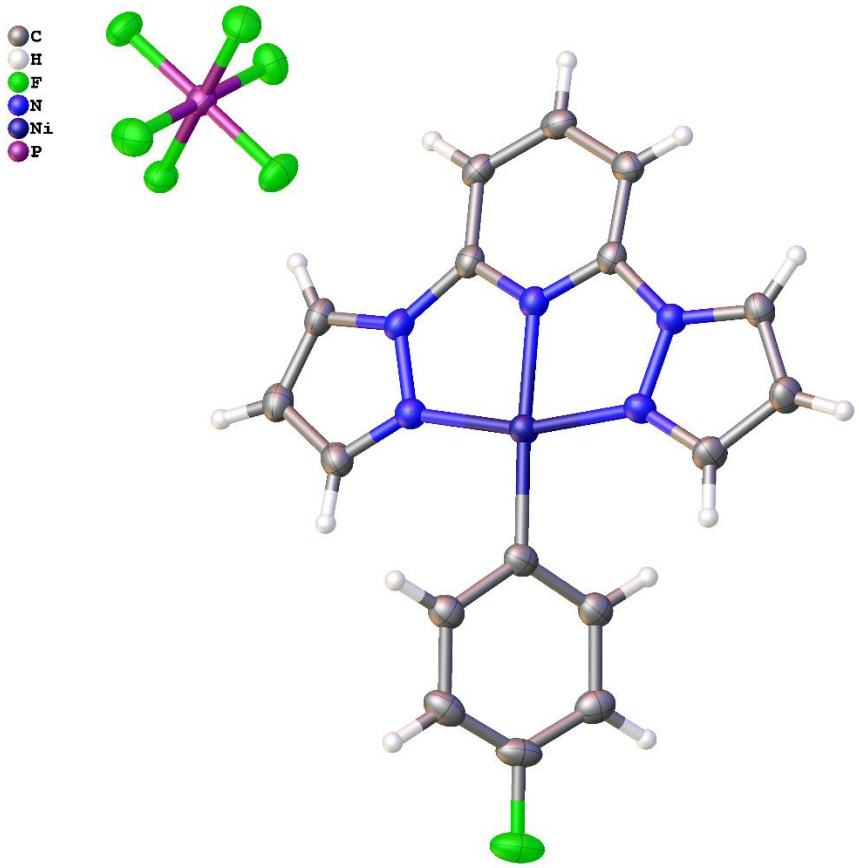
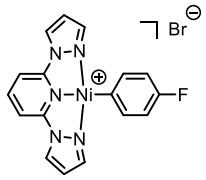


Figure S22. ORTEP illustration of **4** as the PF_6^- salt.

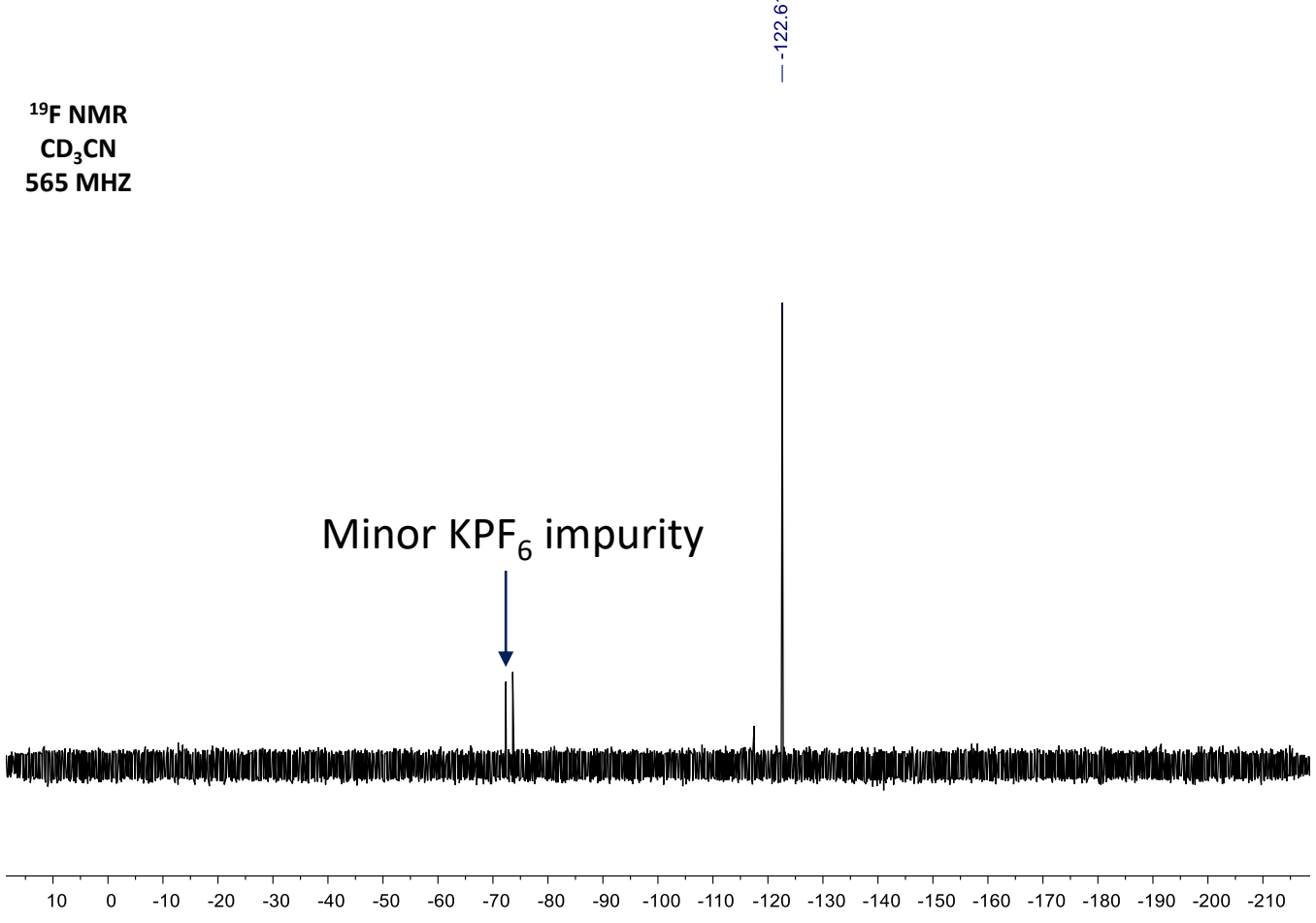
Crystal data and structure refinement for 4

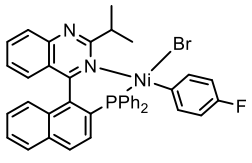
Report date	2022-01-06	
Identification code	TBH-1542	
Empirical formula	C19.67 H18.33 F7 N5 Ni O0.67 P	
Molecular formula	C17 H13 F N5 Ni. F6 P, 0.667(C4 H8 O)	
Formula weight	558.07	
Temperature	100.0 K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 10.2019(4) Å	α= 105.6390(10)°.
	b = 15.4564(6) Å	β= 98.1360(10)°.
	c = 21.6200(8) Å	γ = 93.7850(10)°
Volume	3230.4(2) $Å^3$	
Z	6	
Density (calculated)	1.721 Mg/m^3	
Absorption coefficient	1.058 mm^{-1}	
F(000)	1696	
Crystal size	0.253 x 0.145 x 0.068 mm^3	
Crystal color, habit	yellow block	
Theta range for data collection	4.092 to 74.646°.	
Index ranges	-13<=h<=13, -19<=k<=19, -27<=l<=27	
Reflections collected	145700	
Independent reflections	14244 [R(int) = 0.0512, R(sigma) = 0.0251]	
Completeness to theta = 68.000°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.0943 and 0.0678	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	14244 / 19 / 953	
Goodness-of-fit on F^2	1.016	
Final R indices [I>2sigma(I)]	R1 = 0.0283, wR2 = 0.0645	
R indices (all data)	R1 = 0.0379, wR2 = 0.0694	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.413 and -0.298 e.$Å^{-3}$	

^{1}H NMR
CD_3CN
600 MHZ



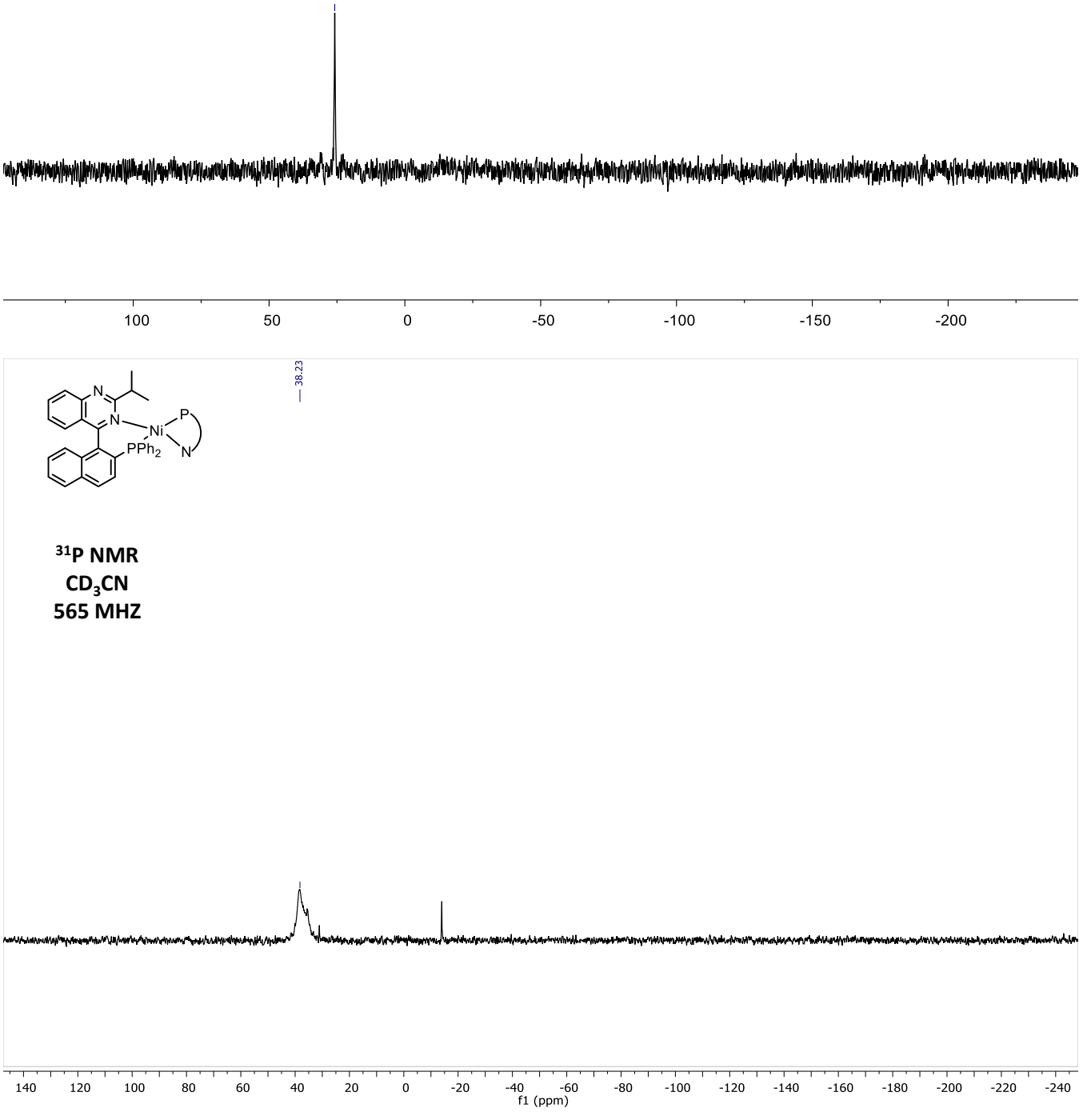
^{19}F NMR
CD_3CN
565 MHZ





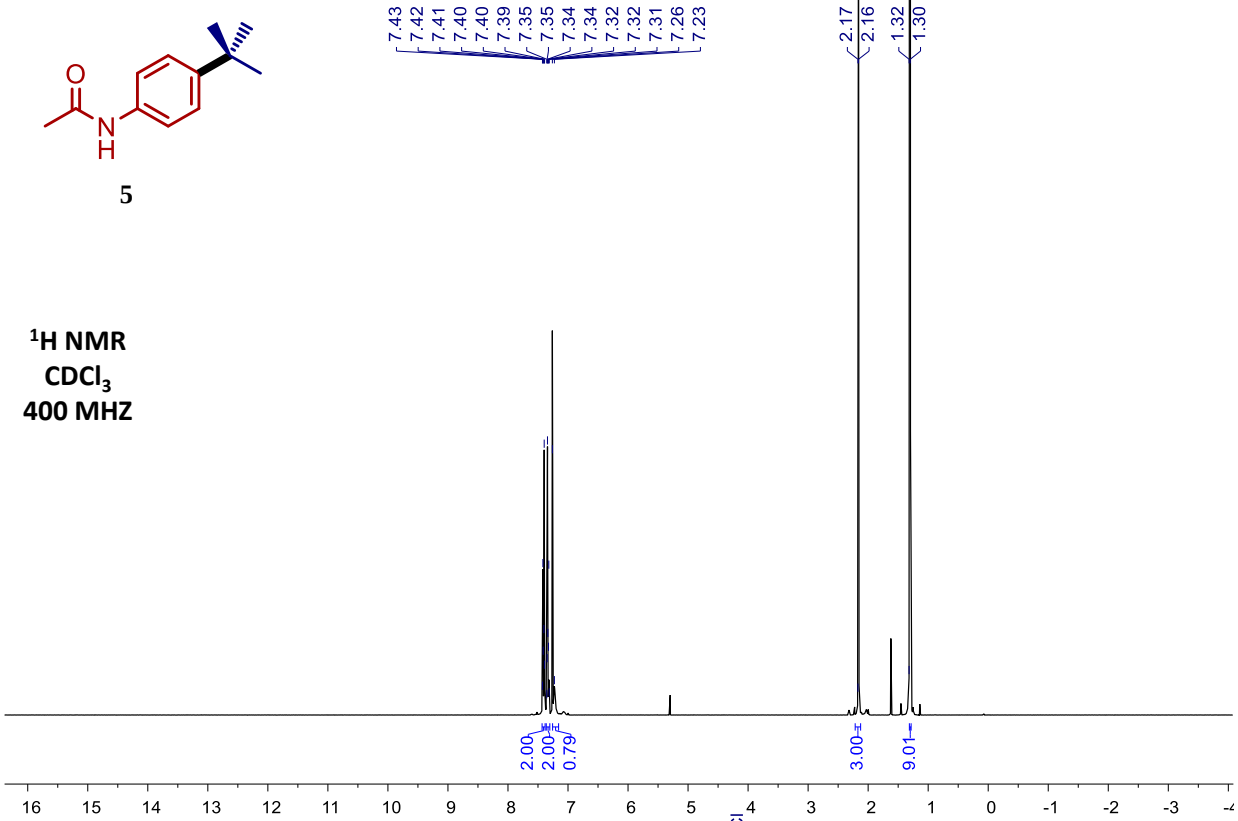
25.82

^{31}P NMR
CD_3CN
565 MHZ



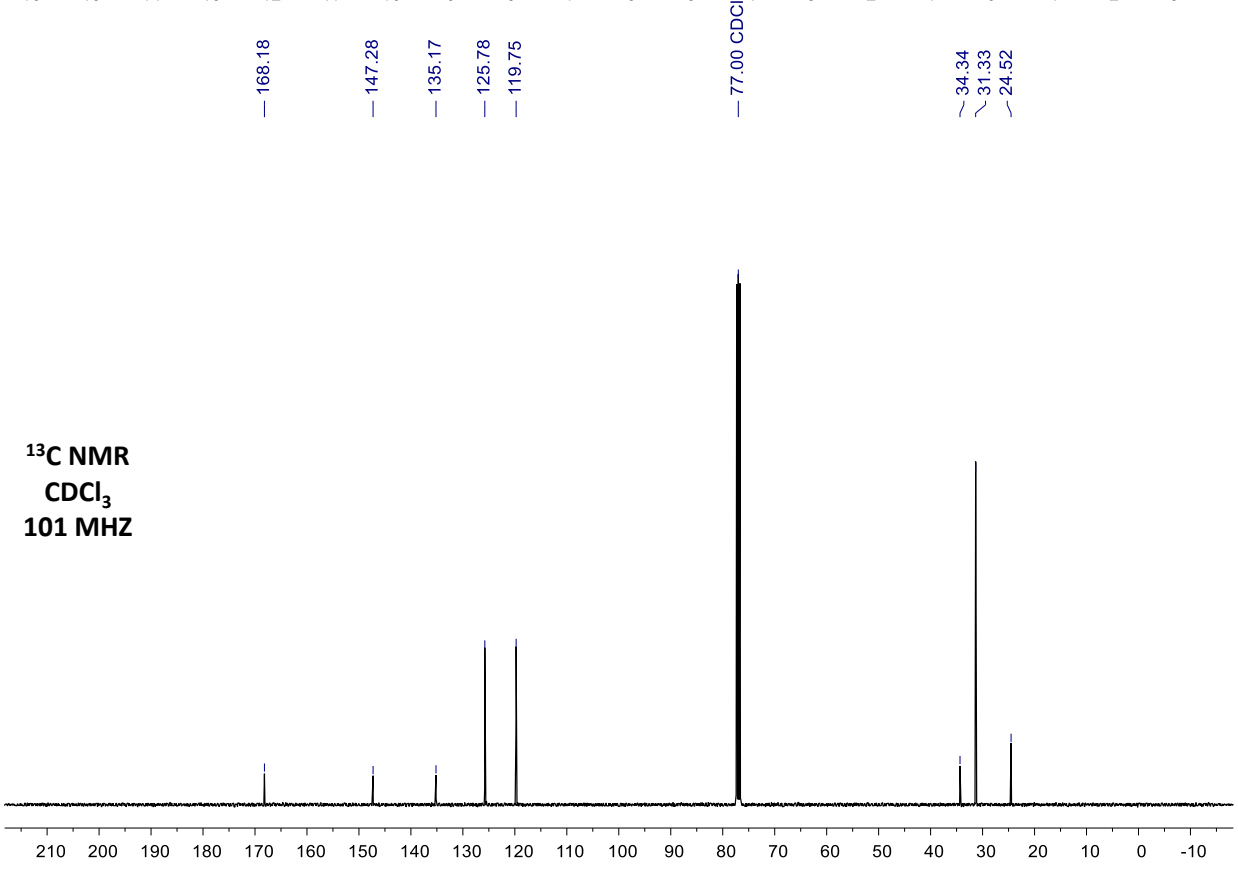
38.23

^{31}P NMR
CD_3CN
565 MHZ

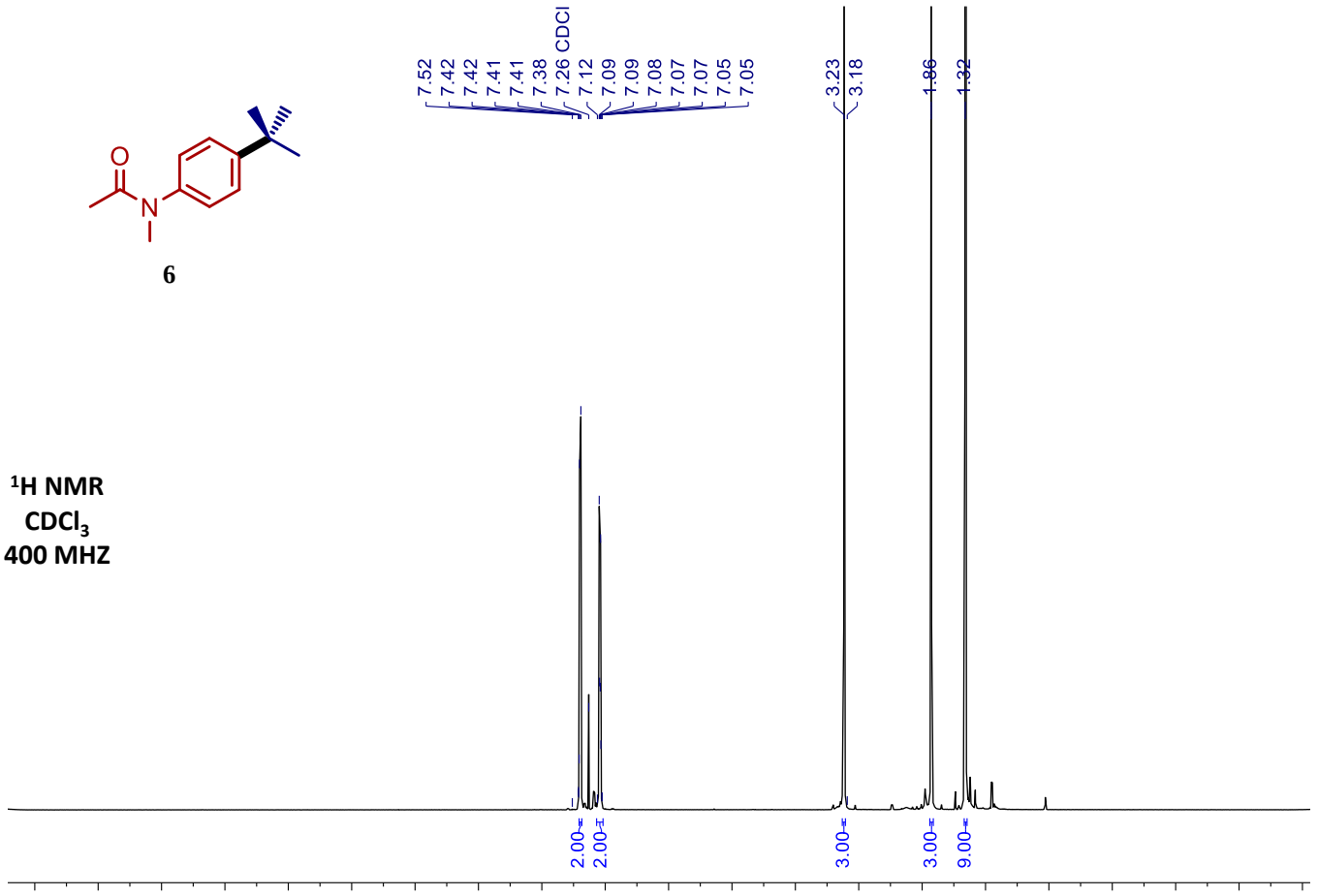


5

^{1}H NMR
$CDCl_3$
400 MHZ

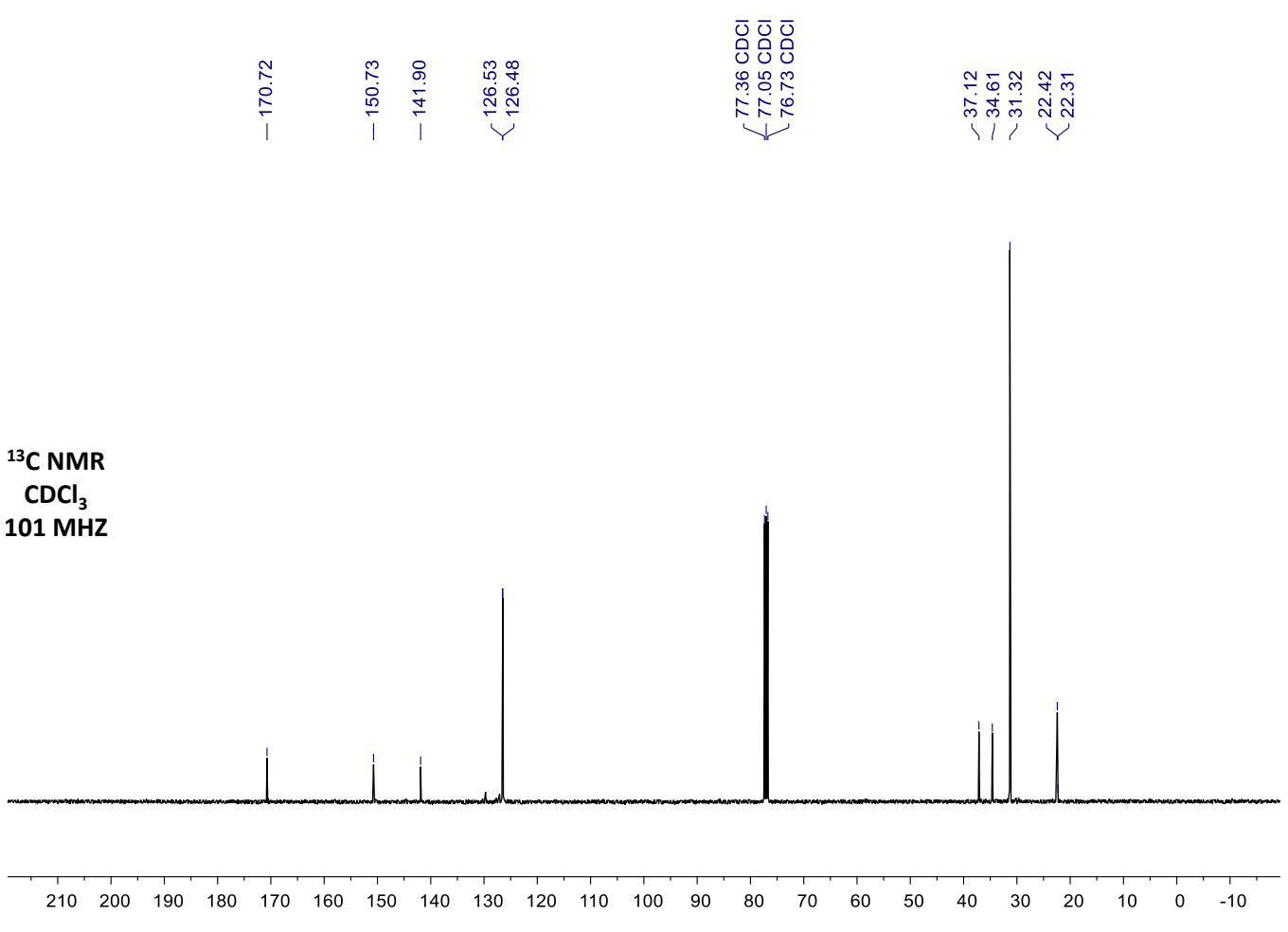


^{13}C NMR
$CDCl_3$
101 MHZ

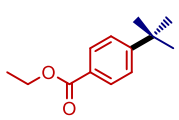


6

^{1}H NMR
$CDCl_3$
400 MHZ



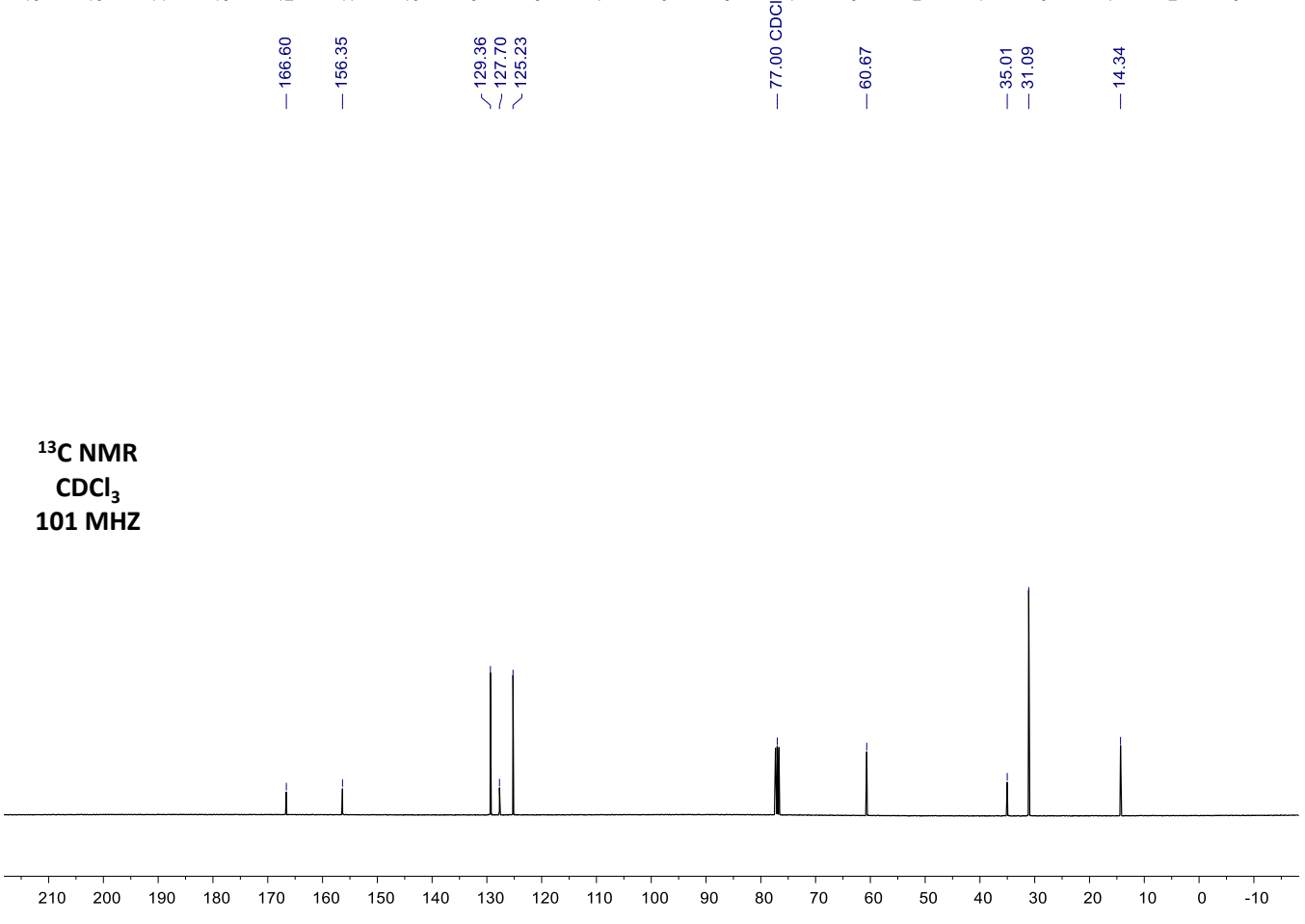
^{13}C NMR
$CDCl_3$
101 MHZ

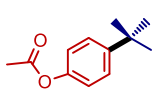


7

^{1}H NMR
$CDCl_3$
400 MHZ

^{13}C NMR
$CDCl_3$
101 MHZ

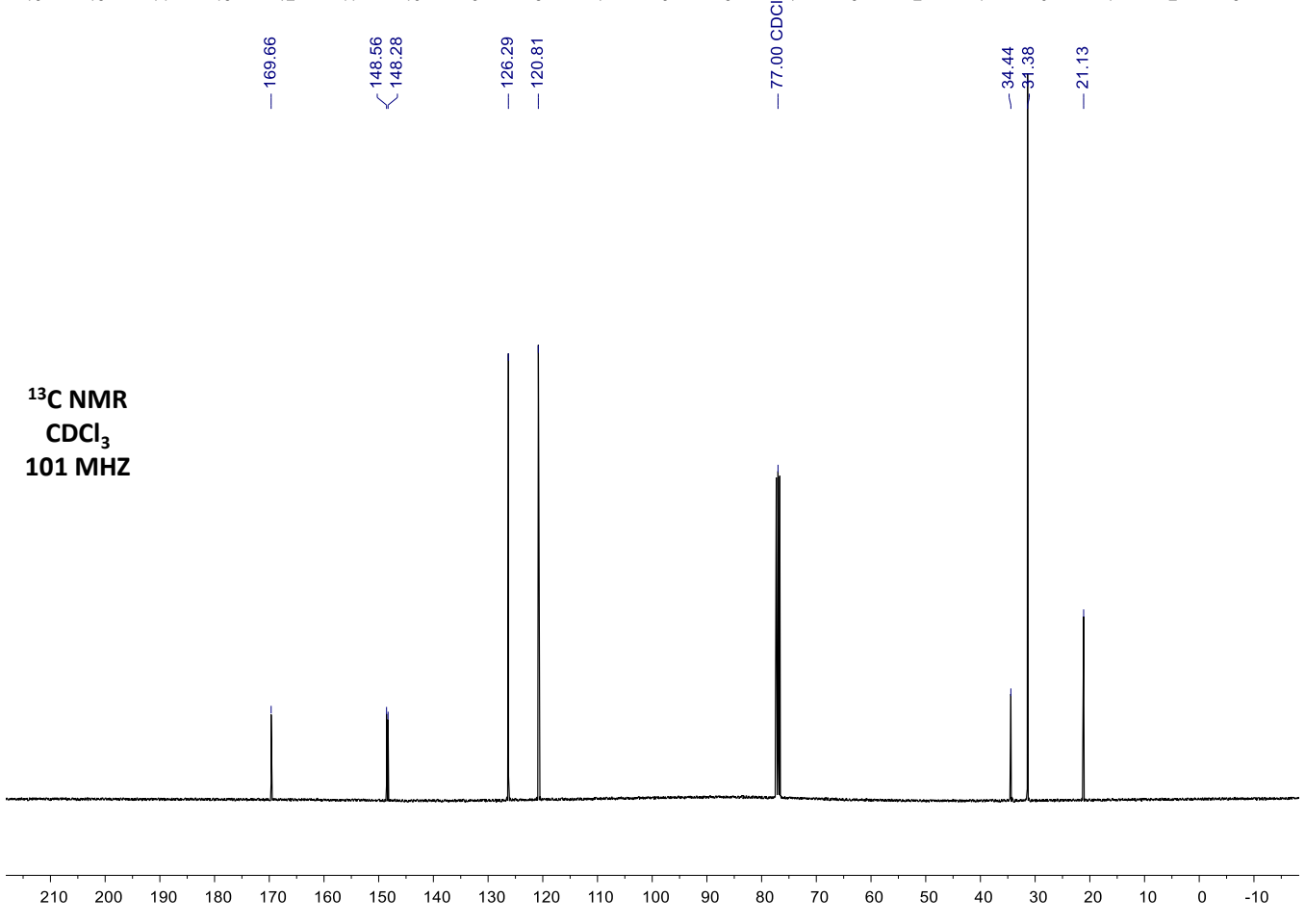


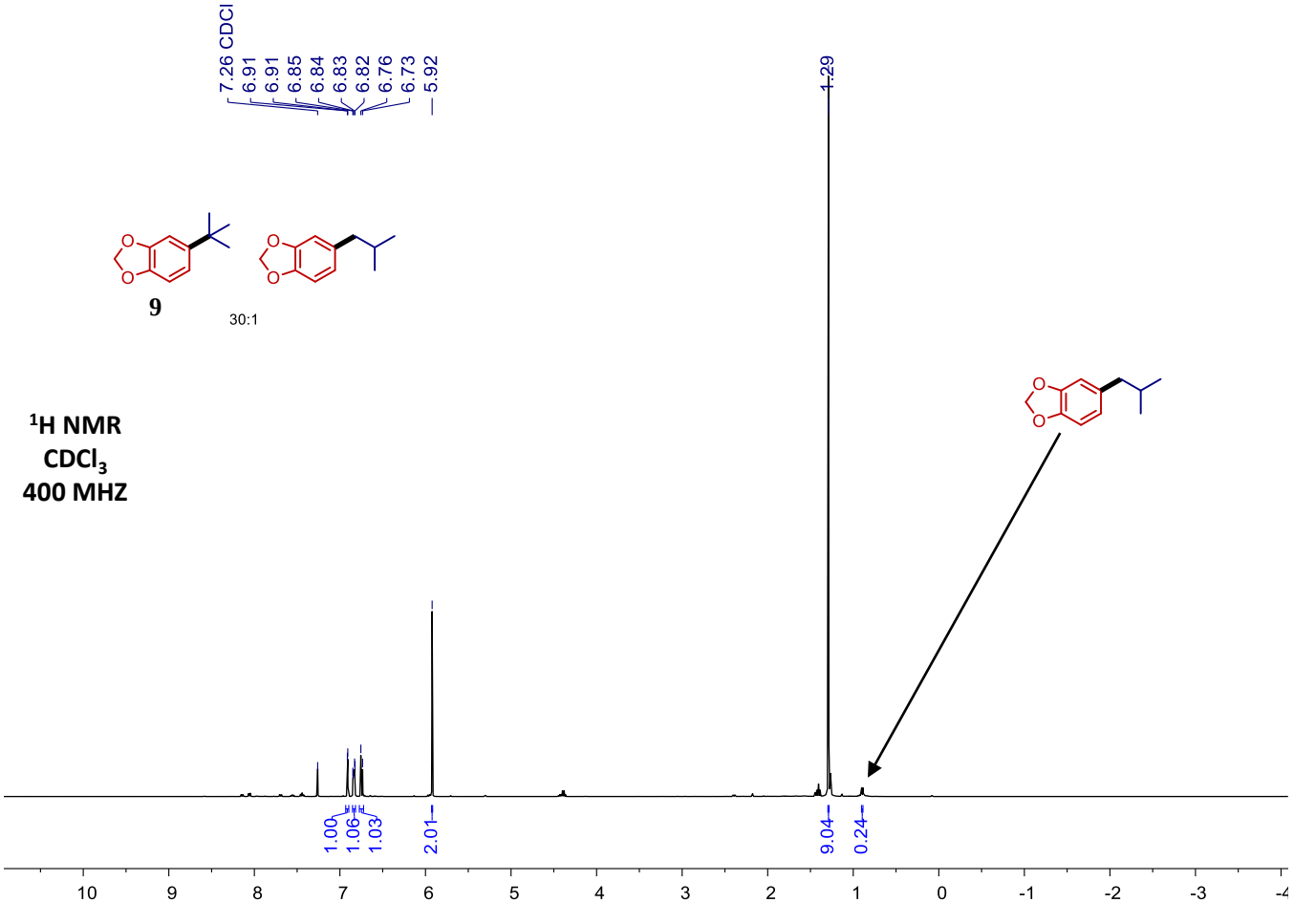


8

^{1}H NMR
$CDCl_3$
400 MHZ

^{13}C NMR
$CDCl_3$
101 MHZ

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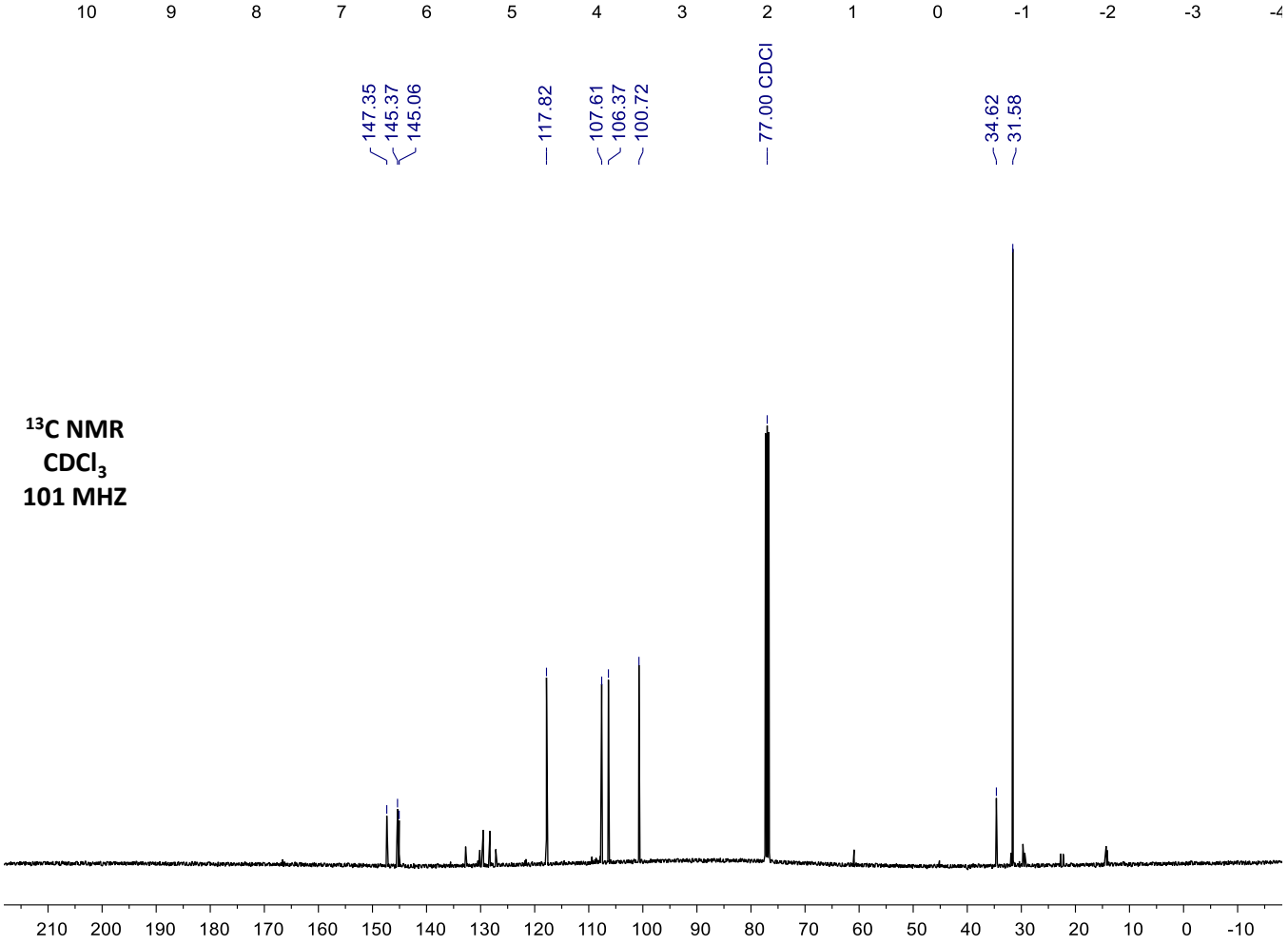
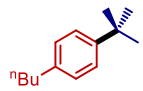
6.91
6.85
6.84
6.83
6.82
6.76
6.73
5.92
1.29
9
30:1
¹H NMR
CDCl₃
400 MHZ
1.00
1.06
1.03
2.01
9.04
0.24
10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3

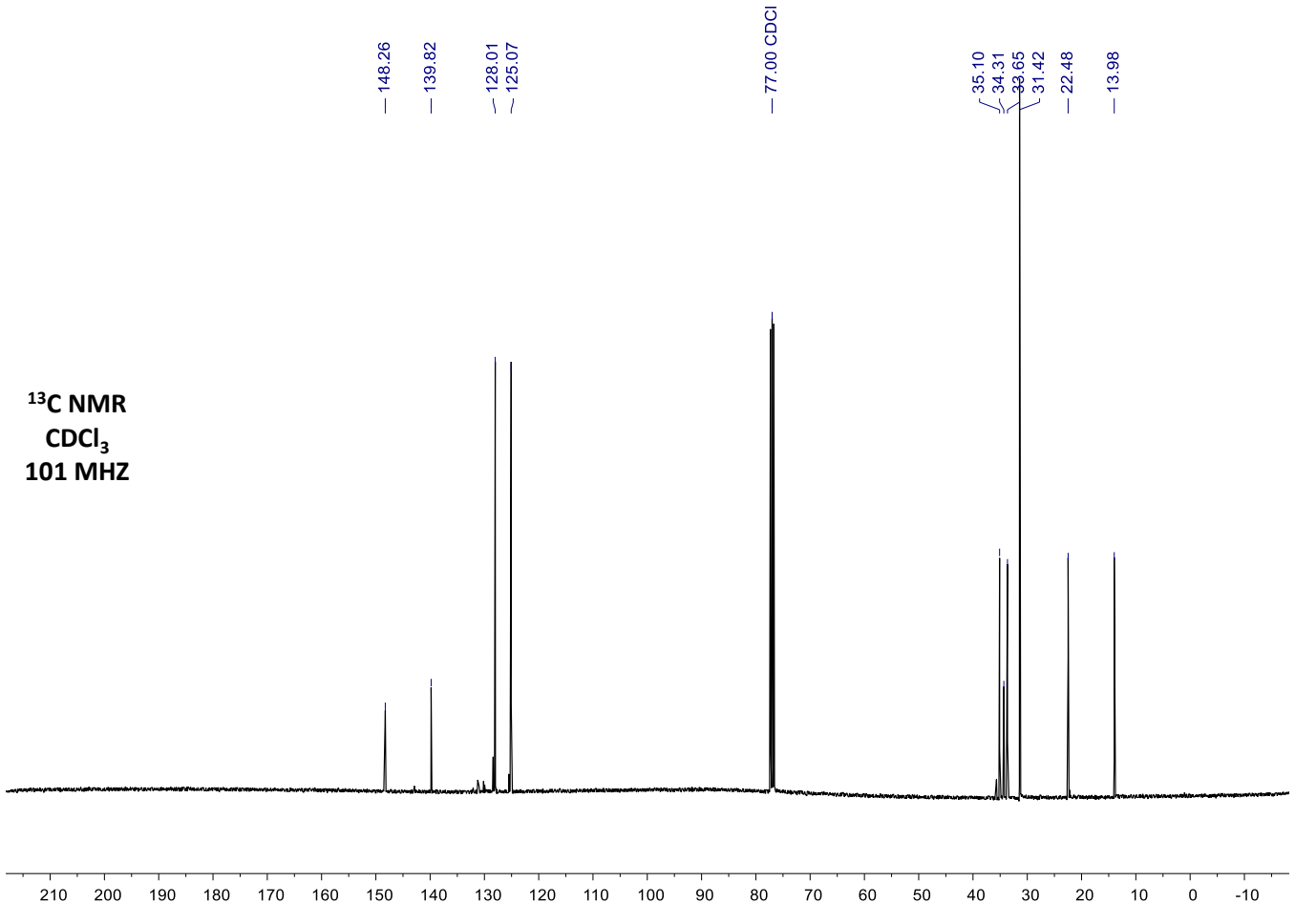

147.35
145.37
145.06
117.82
107.61
106.37
100.72
77.00 CDCl
34.62
31.58
¹³C NMR
CDCl₃
101 MHZ
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

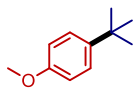


10

^{1}H NMR
$CDCl_3$
400 MHZ

^{13}C NMR
$CDCl_3$
101 MHZ

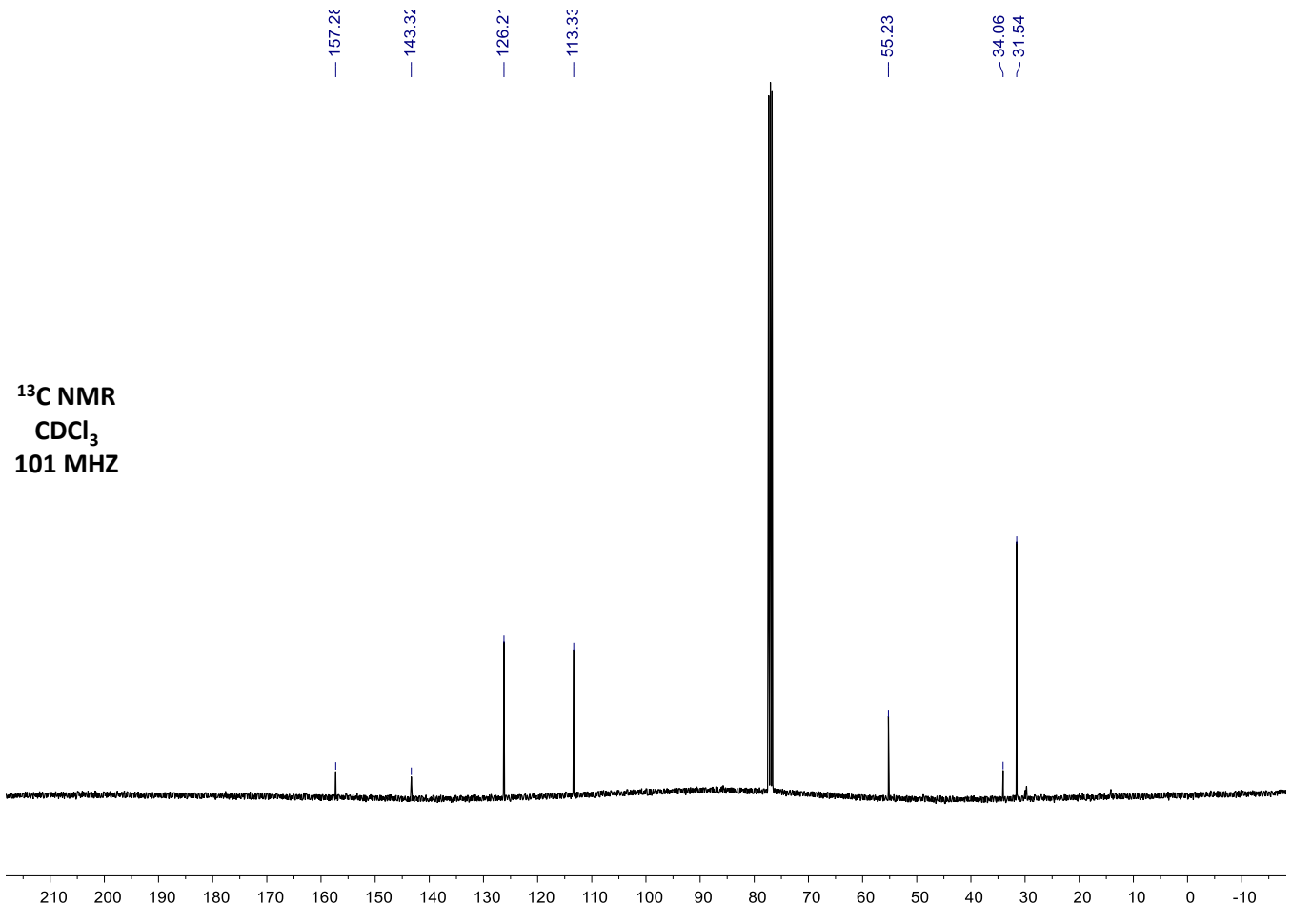


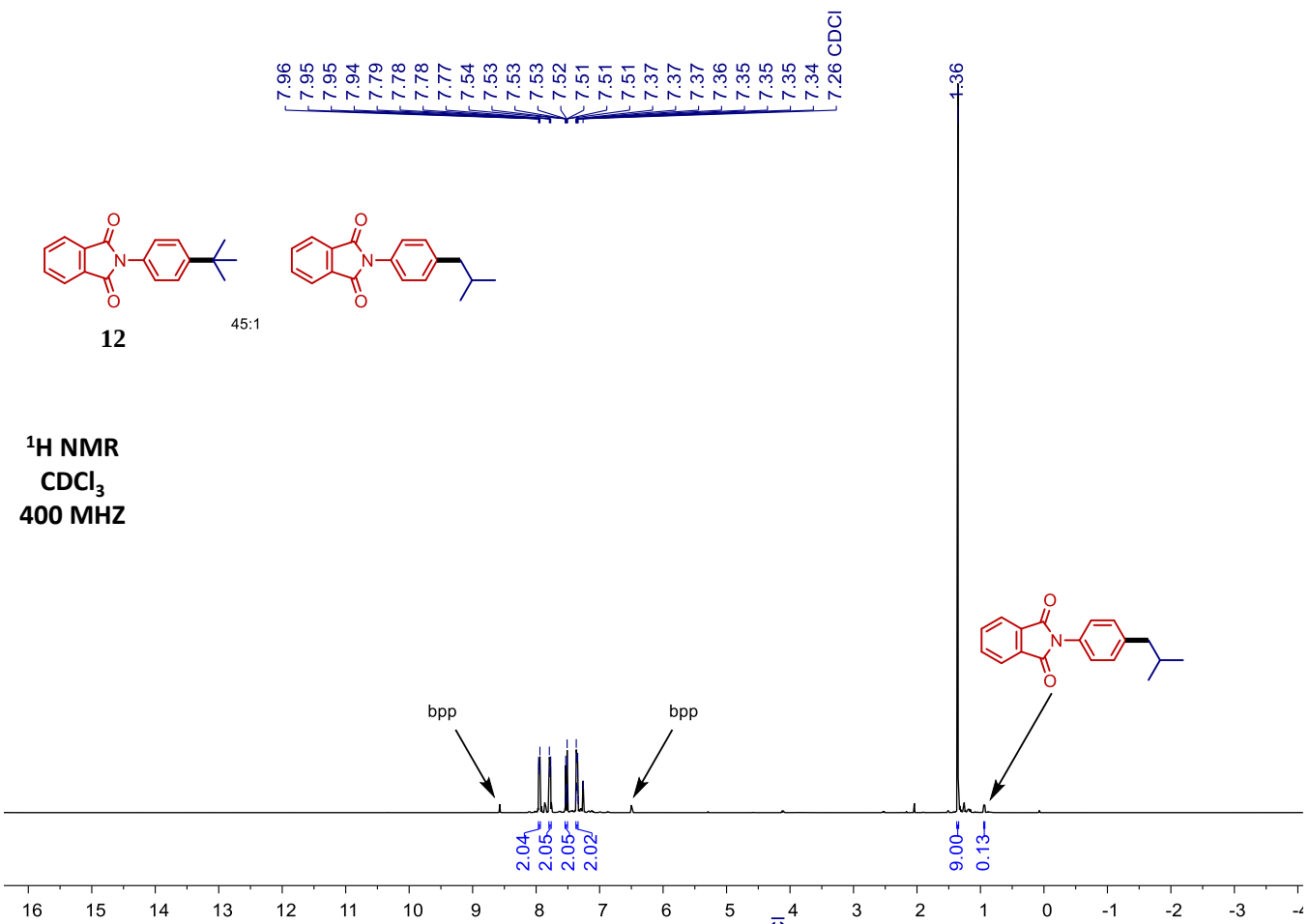


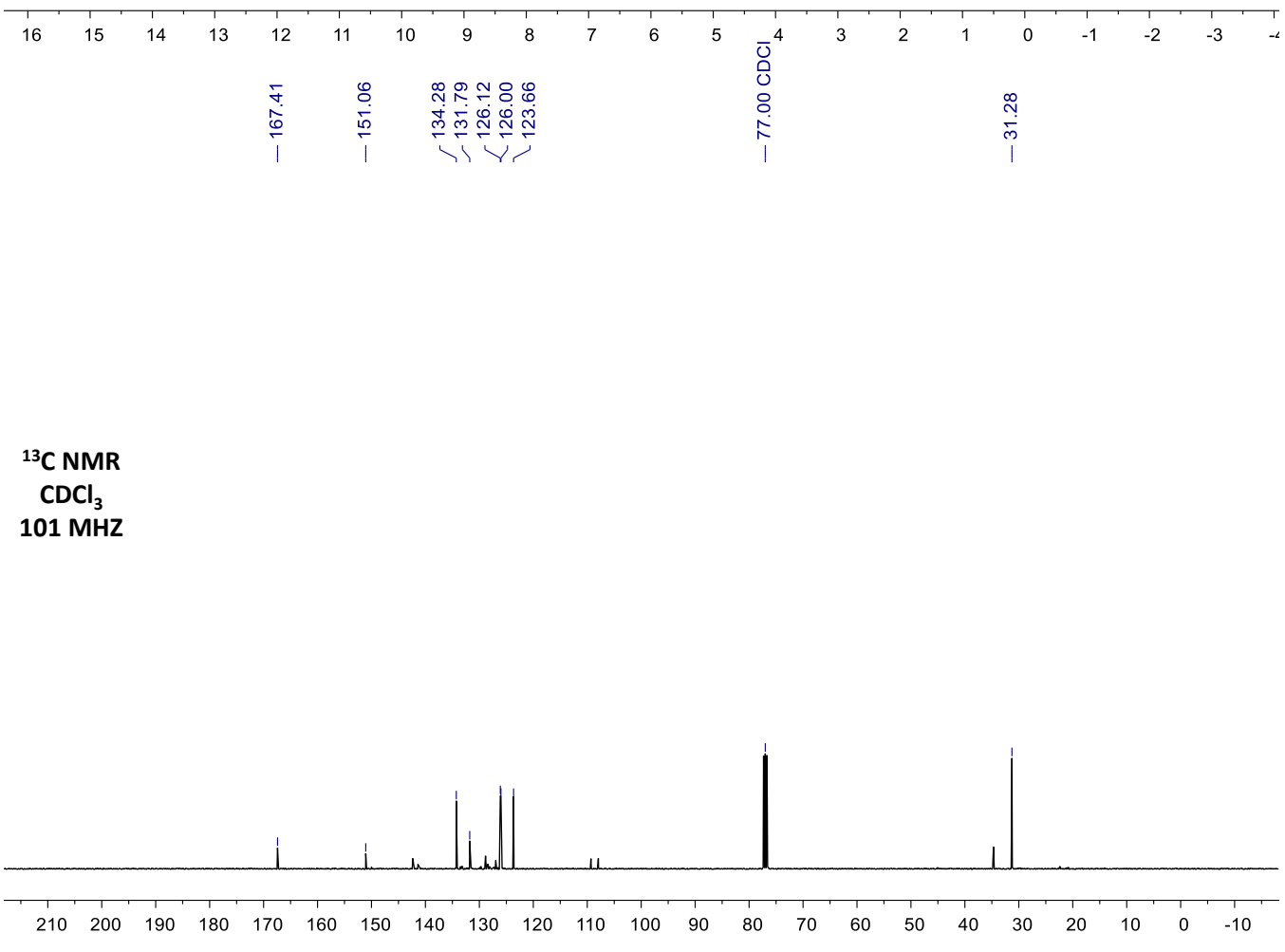
11

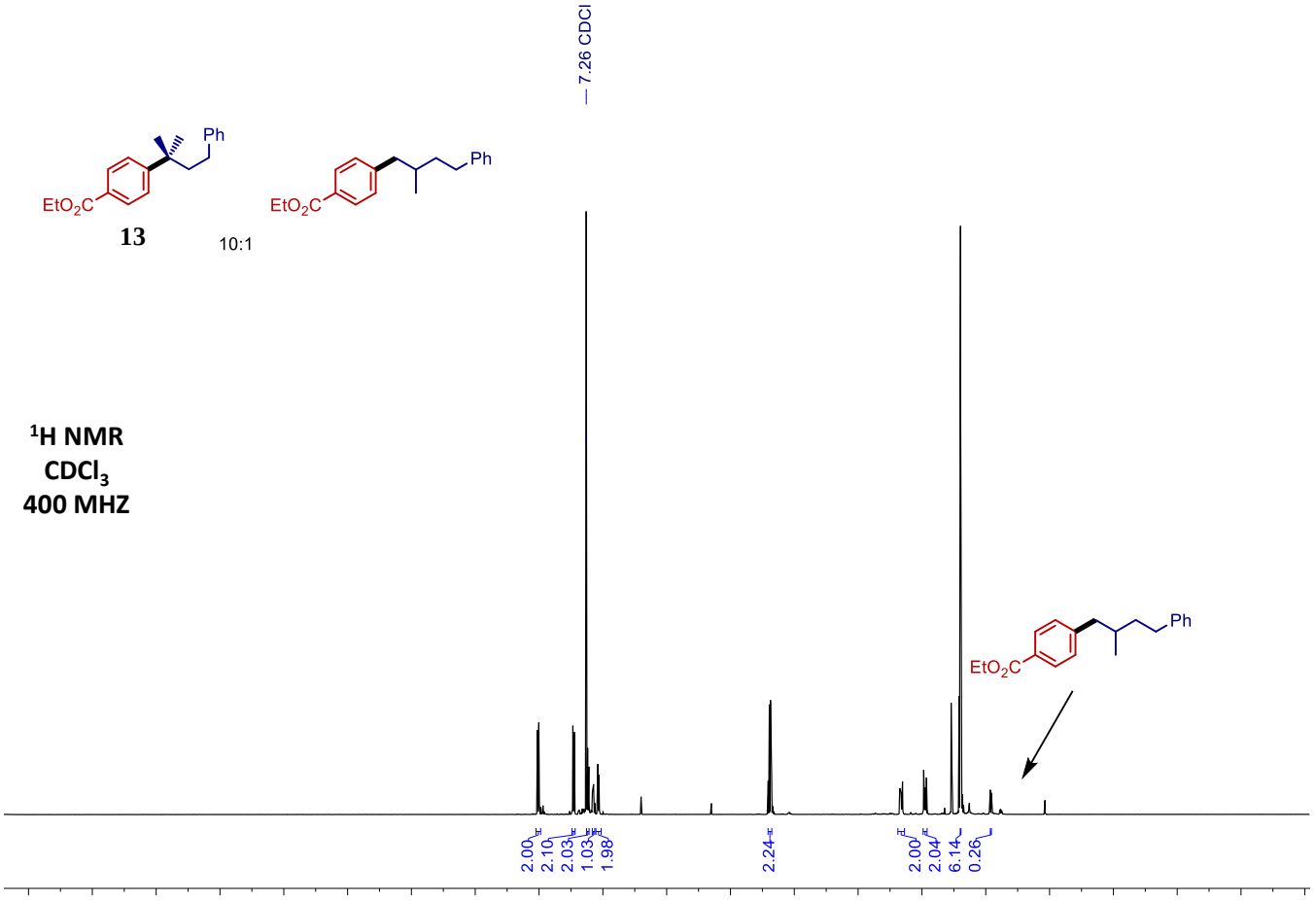
^{1}H NMR
$CDCl_3$
400 MHZ

^{13}C NMR
$CDCl_3$
101 MHZ

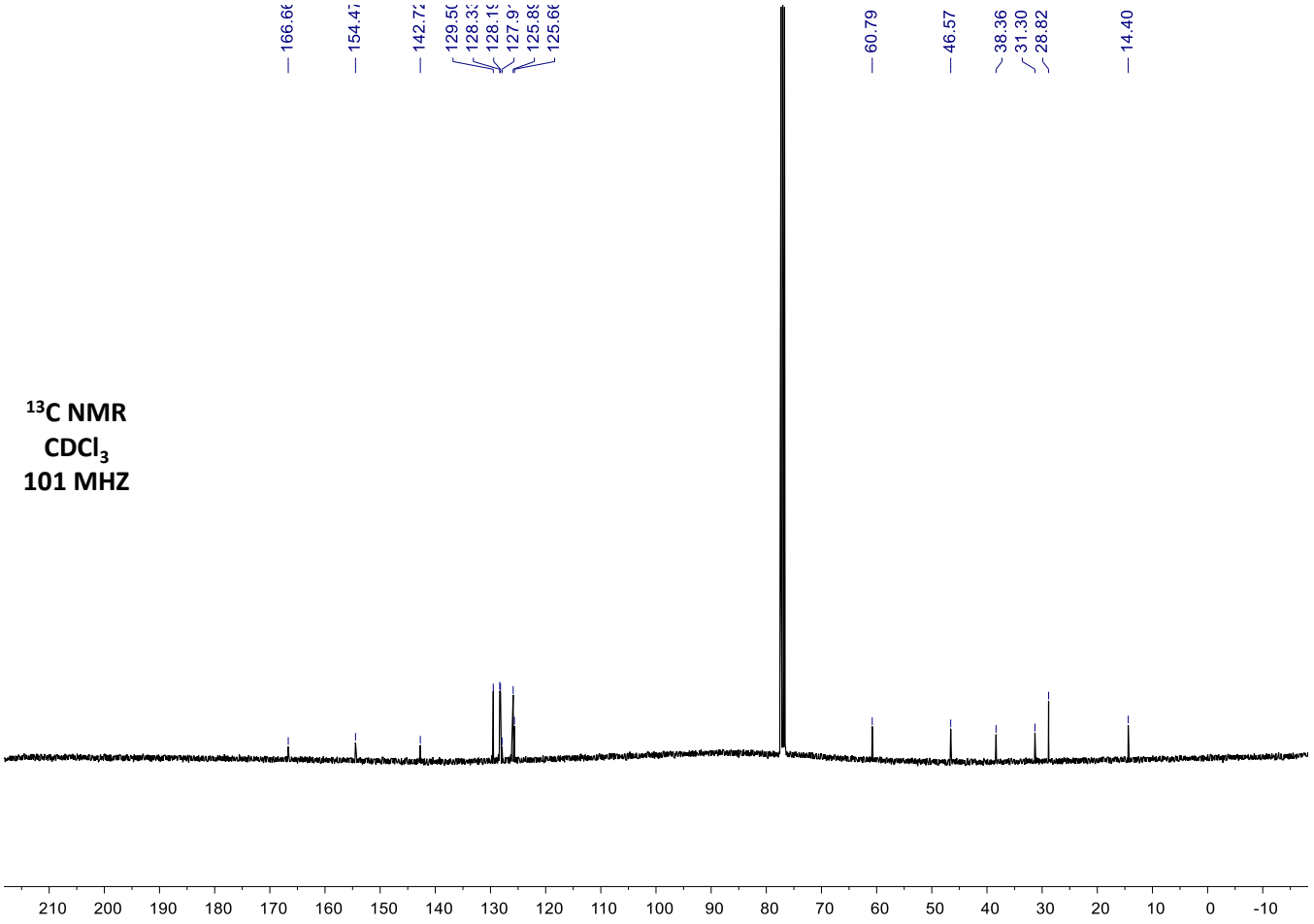



7.96
7.95
7.95
7.94
7.79
7.78
7.78
7.77
7.54
7.53
7.53
7.53
7.52
7.51
7.51
7.51
7.37
7.37
7.36
7.35
7.35
7.35
7.34
7.26 CDCl
1.36
45:1
12
1H NMR
CDCl3
400 MHZ
bpp
bpp
2.04
2.05
2.05
2.02
9.00
0.13
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3

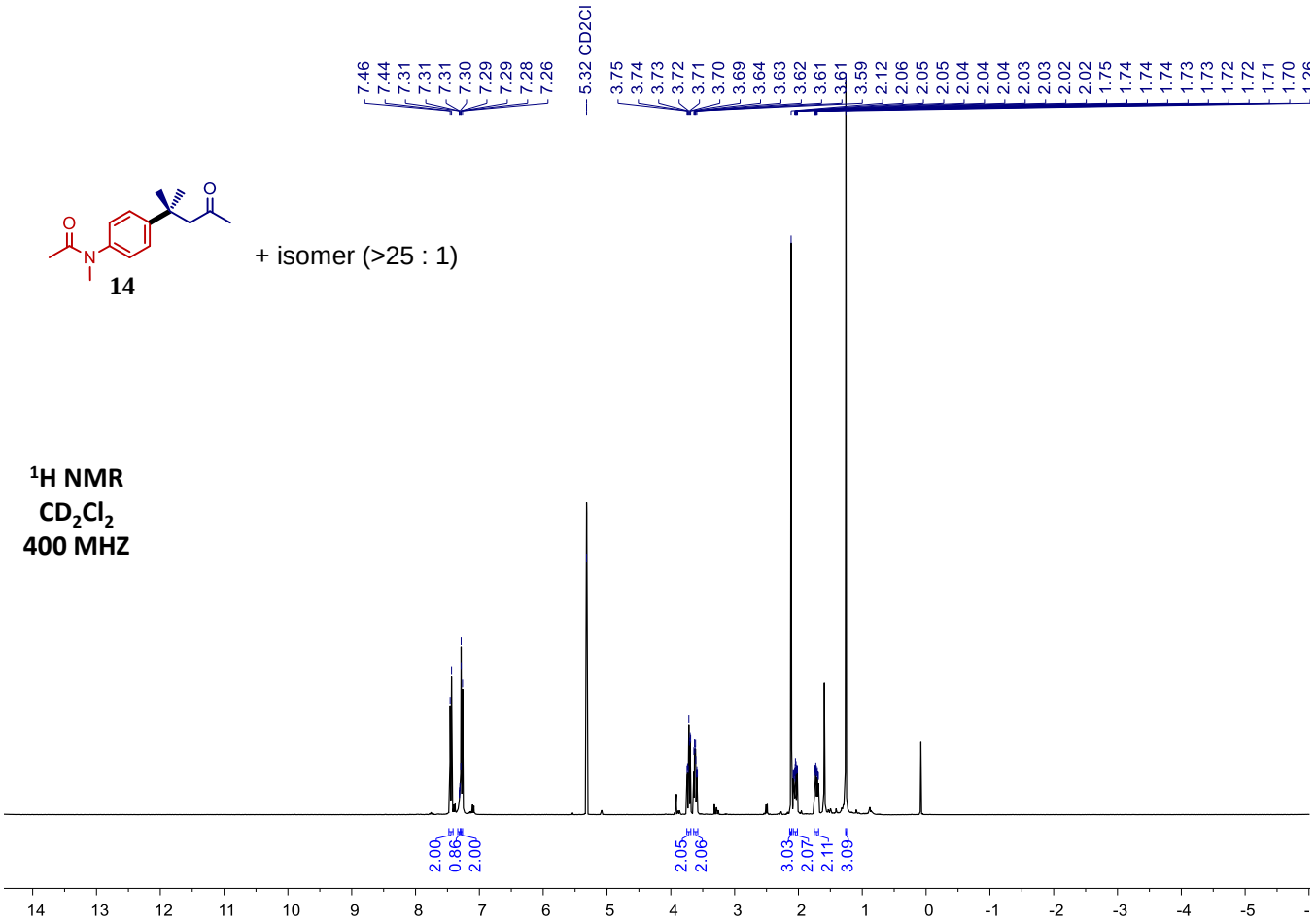

167.41
151.06
134.28
131.79
126.12
126.00
123.66
77.00 CDCl
31.28
13C NMR
CDCl3
101 MHZ
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

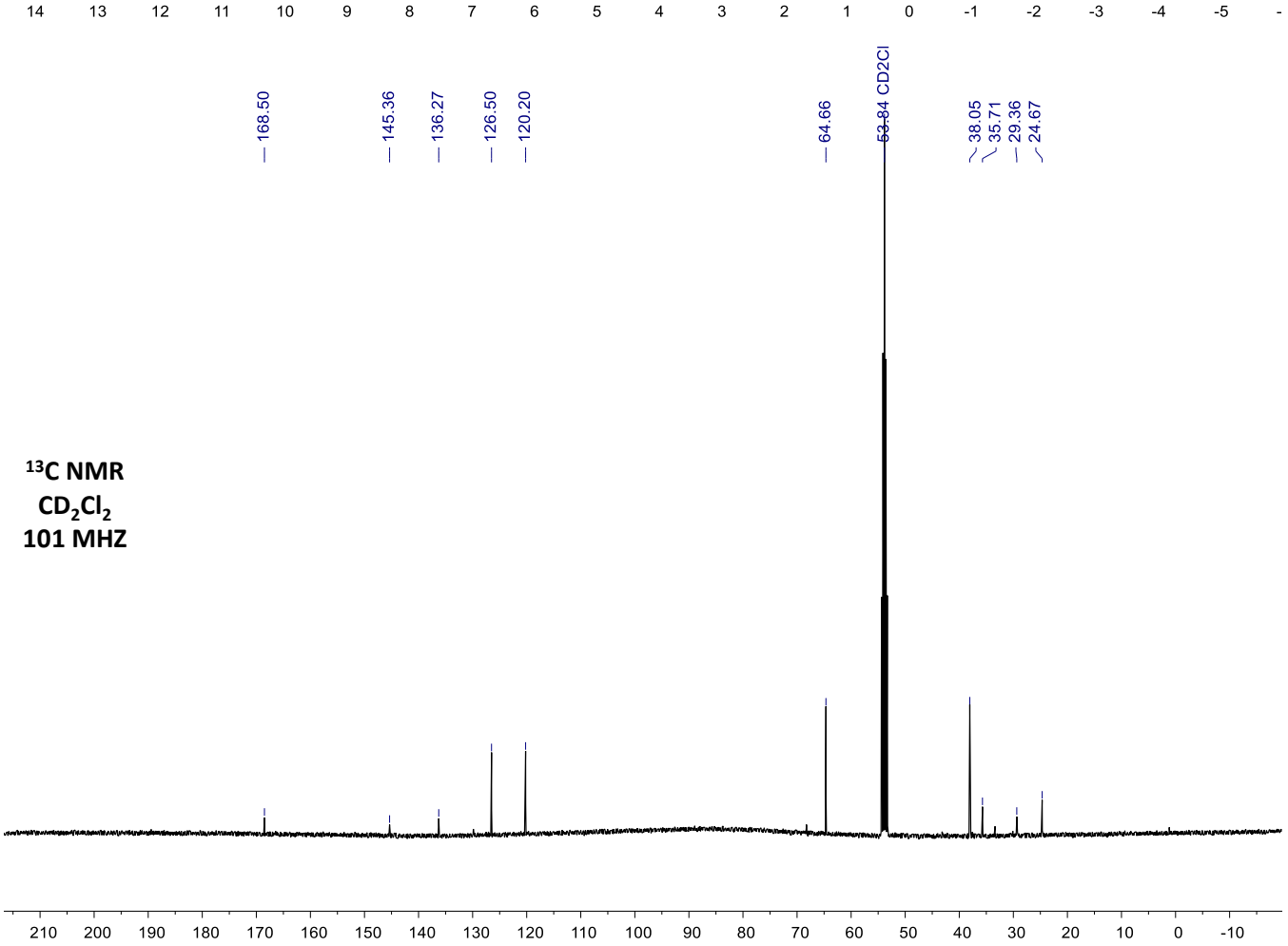


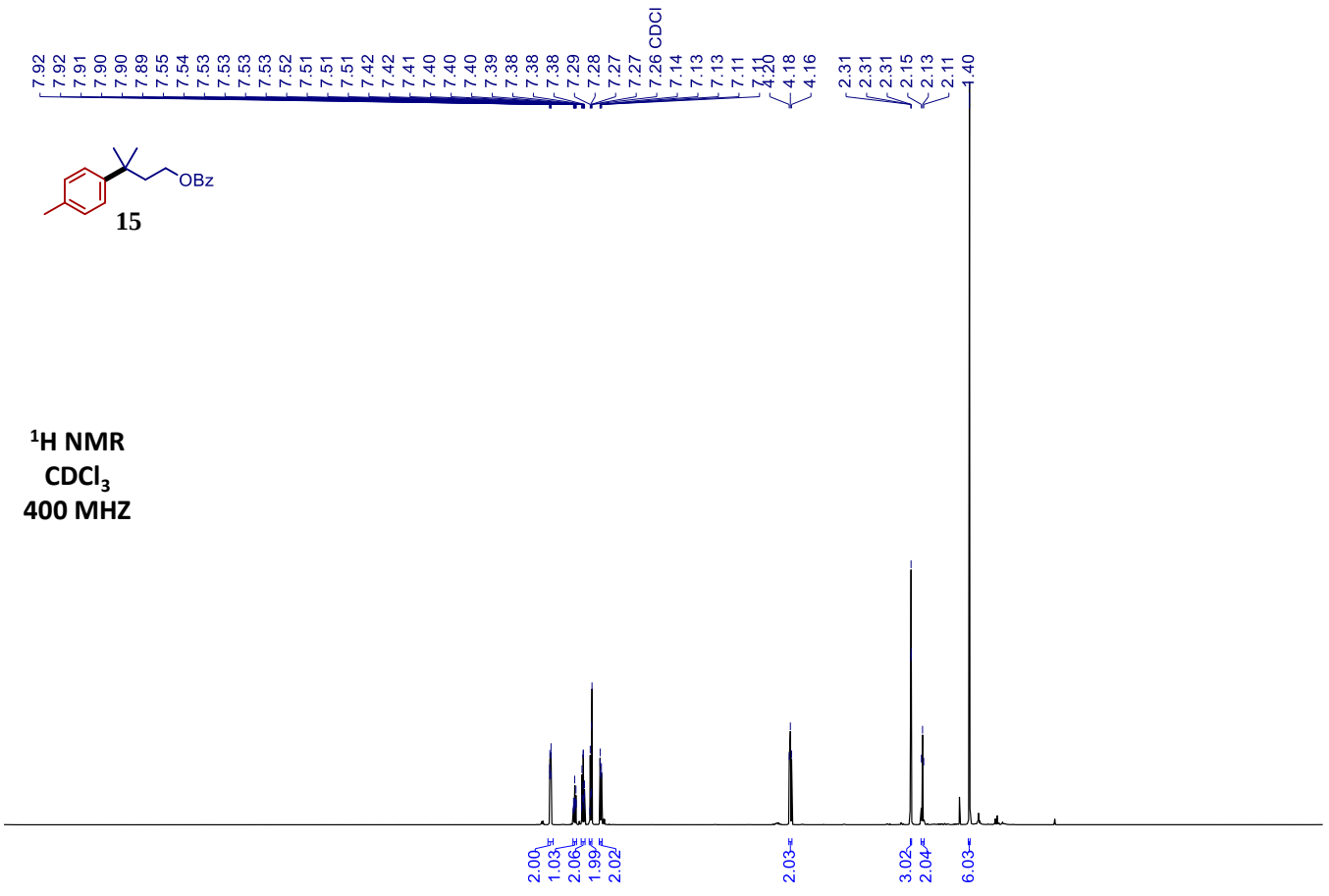
^{1}H NMR
$CDCl_3$
400 MHZ

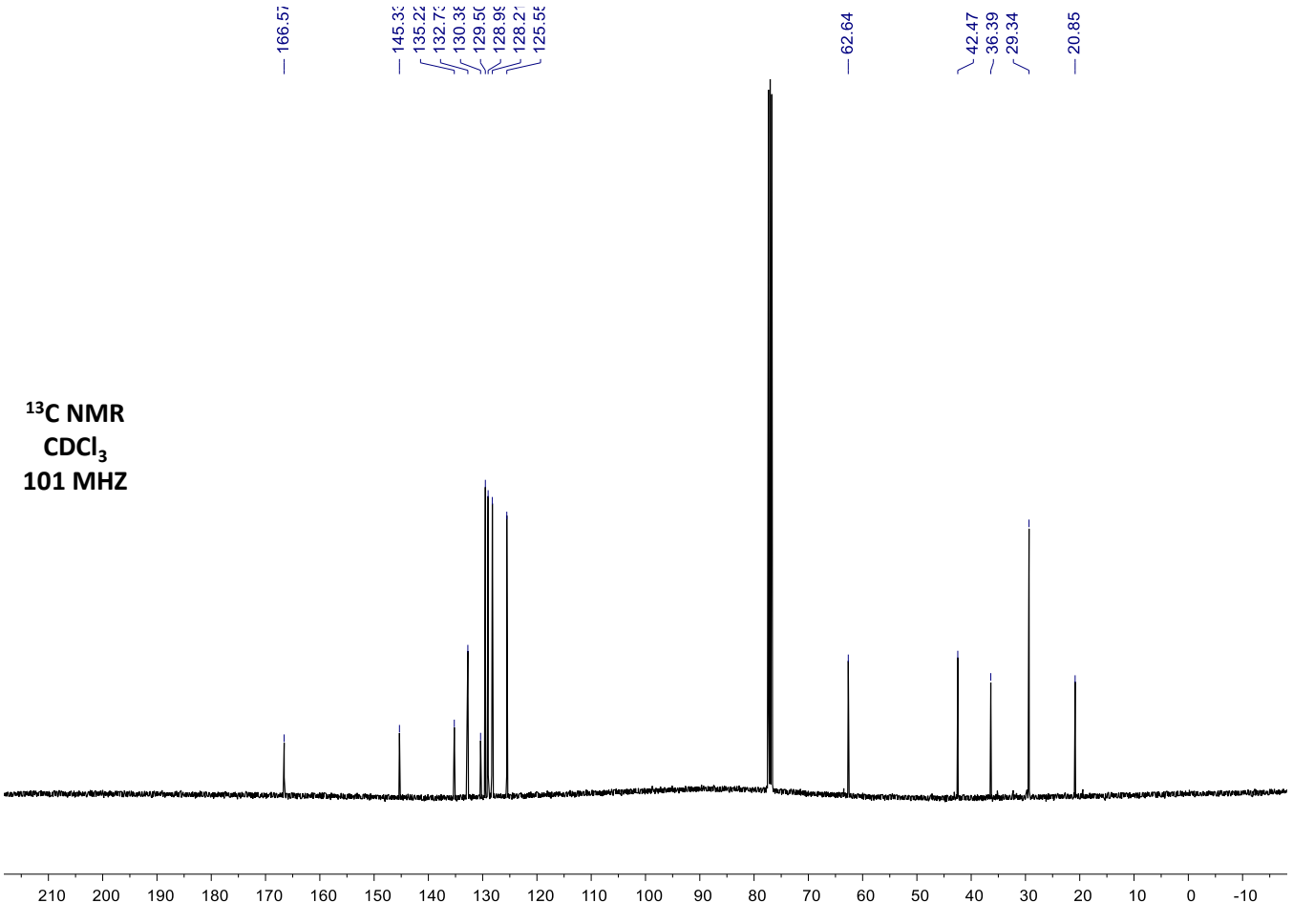


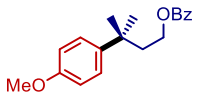
^{13}C NMR
$CDCl_3$
101 MHZ


7.46
7.44
7.31
7.31
7.31
7.30
7.29
7.29
7.28
7.26
5.32 CD2Cl
3.75
3.74
3.73
3.72
3.71
3.70
3.69
3.64
3.63
3.62
3.61
3.61
3.59
2.12
2.06
2.05
2.05
2.04
2.04
2.04
2.03
2.03
2.02
2.02
1.75
1.74
1.74
1.74
1.73
1.73
1.72
1.72
1.71
1.70
O
O
N
14
+ isomer (>25 : 1)
1H NMR
CD2Cl2
400 MHZ
2.00
0.86
2.00
2.05
2.06
3.03
2.07
2.11
3.09
14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3 -4 -5


168.50
145.36
136.27
126.50
120.20
64.66
53.84 CD2Cl2
38.05
35.71
29.36
24.67
13C NMR
CD2Cl2
101 MHZ
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10


7.92 7.92 7.91 7.90 7.90 7.89 7.55 7.54 7.53 7.53 7.53 7.53 7.52 7.51 7.51 7.51 7.42 7.42 7.41 7.40 7.40 7.40 7.39 7.38 7.38 7.29 7.28 7.27 7.26 CDCl 7.14 7.13 7.13 7.11 7.11 4.20 4.18 4.16 2.31 2.31 2.31 2.15 2.13 2.11 1.40
OBz
15
1H NMR
CDCl3
400 MHZ
2.00 1.03 2.06 1.99 2.02 2.03 3.02 2.04 6.03
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3

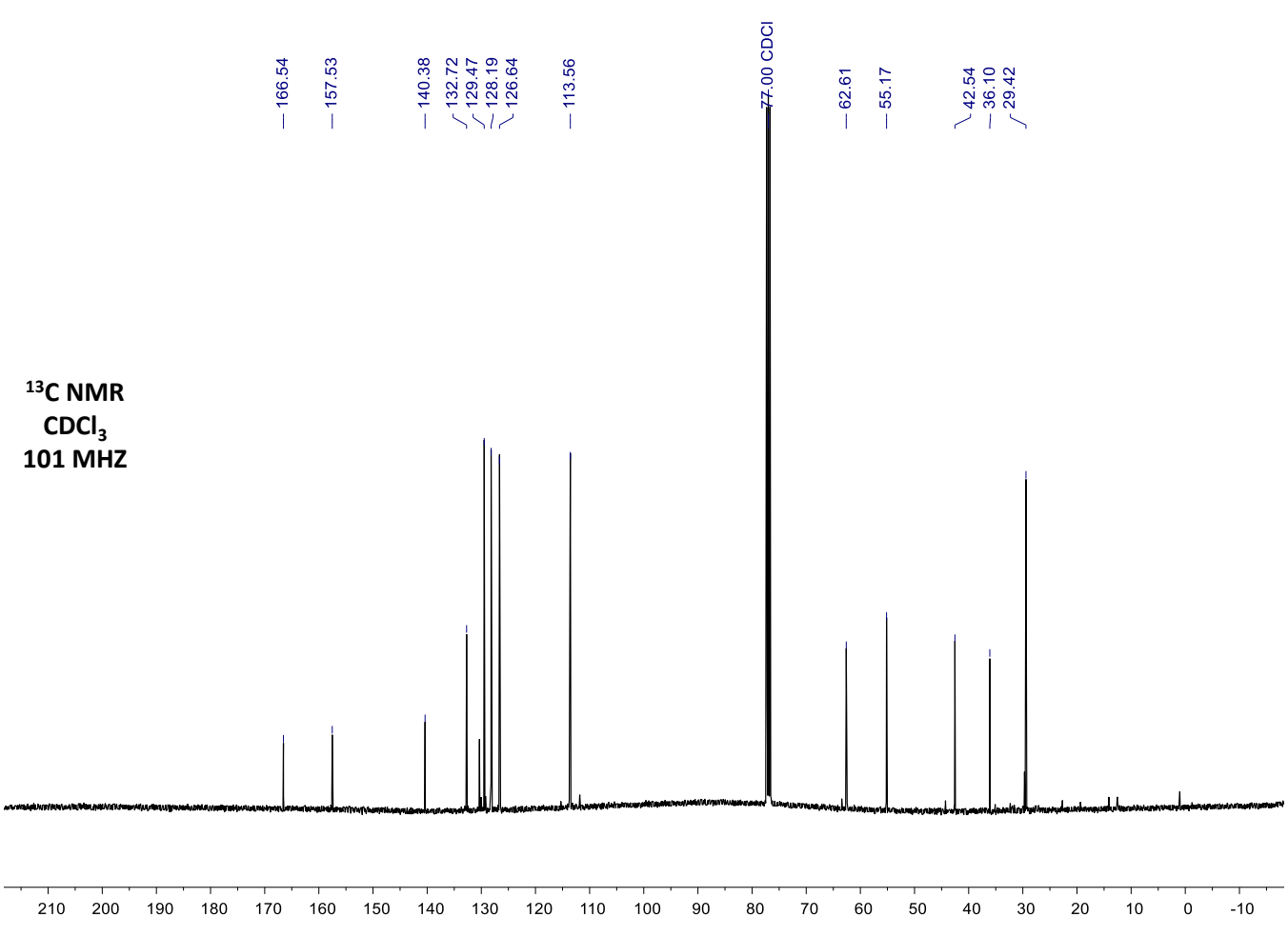

166.57 145.33 135.22 132.73 130.38 129.50 128.99 128.21 125.58 62.64 42.47 36.39 29.34 20.85
13C NMR
CDCl3
101 MHZ
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

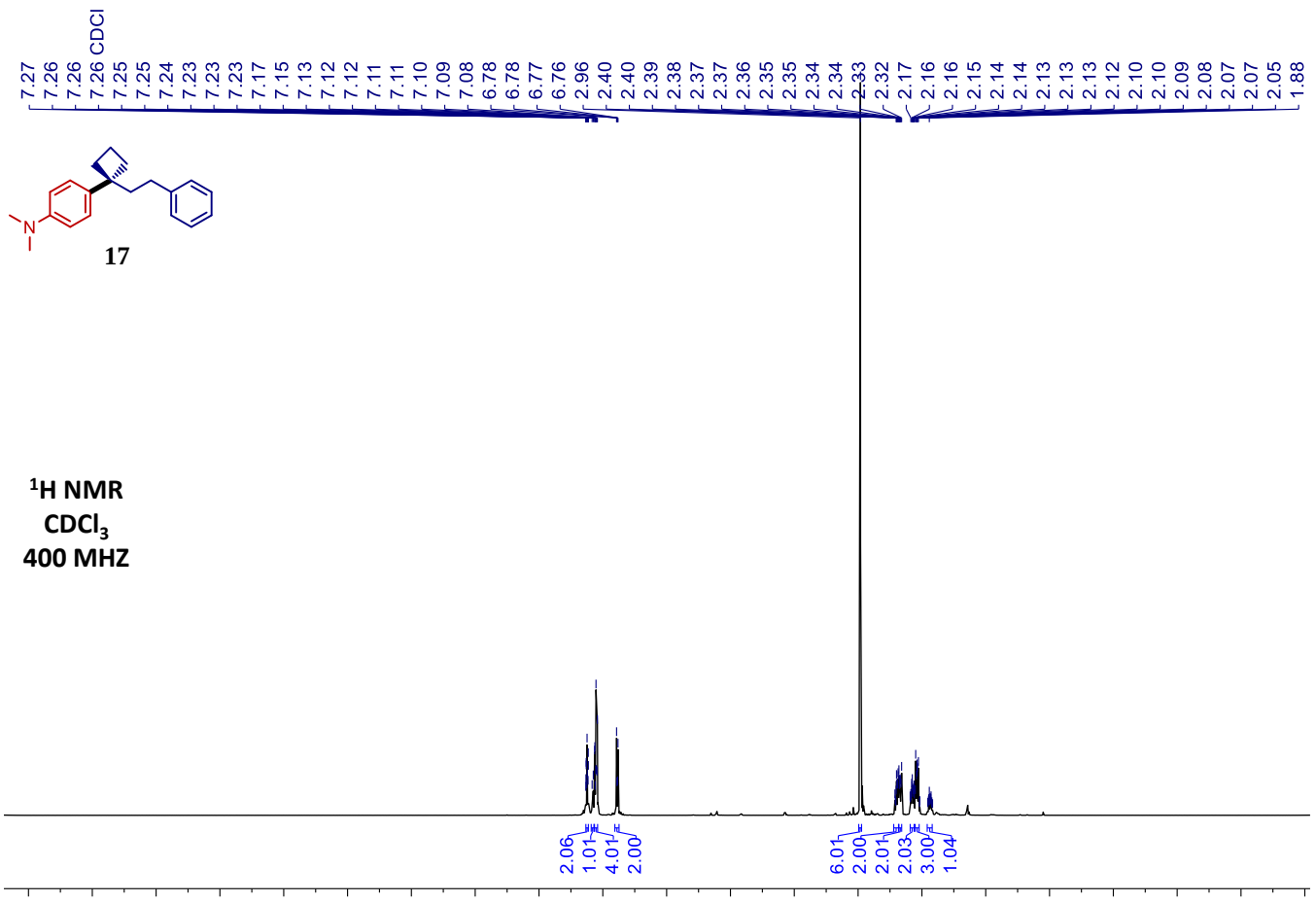


16

^{1}H NMR
$CDCl_3$
400 MHZ

^{13}C NMR
$CDCl_3$
101 MHZ




7.27
7.26
7.26
7.26 CDCl
7.25
7.25
7.24
7.23
7.23
7.23
7.17
7.15
7.13
7.12
7.12
7.11
7.11
7.10
7.09
7.08
6.78
6.78
6.77
6.76
2.96
2.40
2.40
2.39
2.38
2.37
2.37
2.36
2.35
2.35
2.34
2.34
2.33
2.32
2.17
2.16
2.16
2.15
2.14
2.14
2.13
2.13
2.12
2.10
2.10
2.09
2.08
2.07
2.07
2.05
1.88
17
1H NMR
CDCl3
400 MHZ
2.06
1.01
4.01
2.00
6.01
2.00
2.01
2.03
3.00
1.04
16
15
14
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11
10
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7
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5
4
3
2
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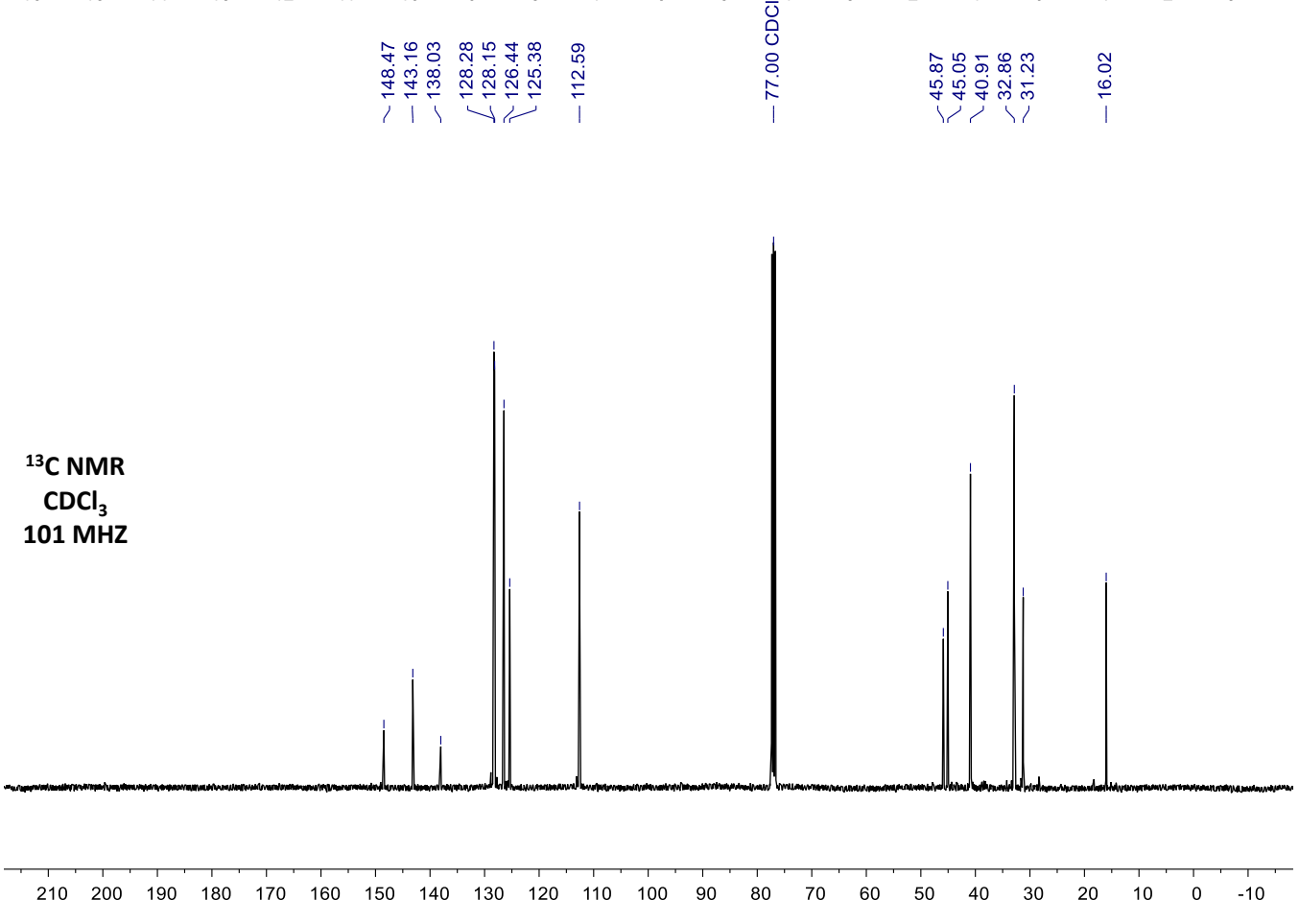
-1
-2
-3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143.16
138.03
128.28
128.15
126.44
125.38
112.59
77.00 CDCl3
45.87
45.05
40.91
32.86
31.23
16.02
13C NMR
CDCl3
101 MHZ
210
200
190
180
170
160
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140
130
120
110
100
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60
50
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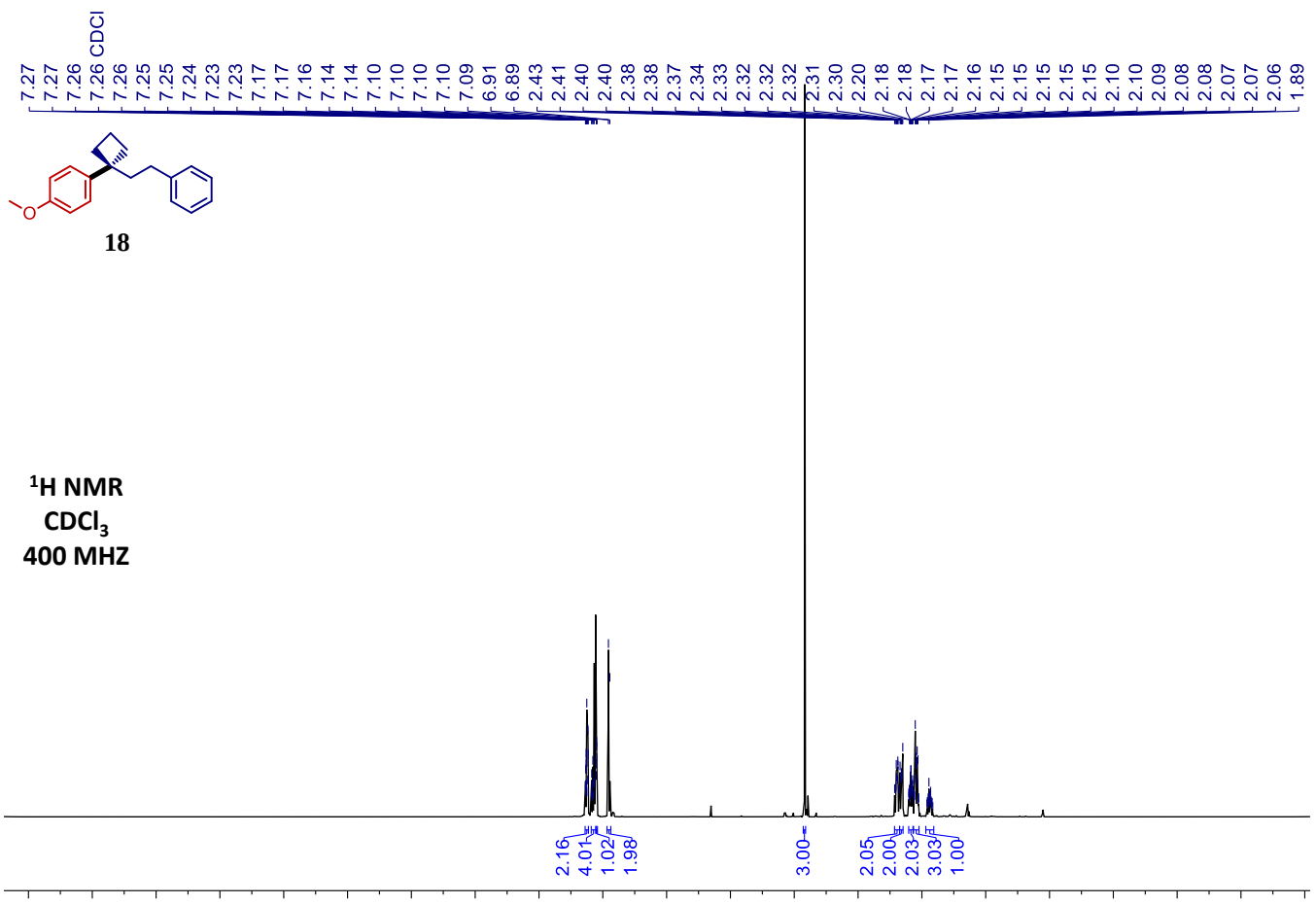
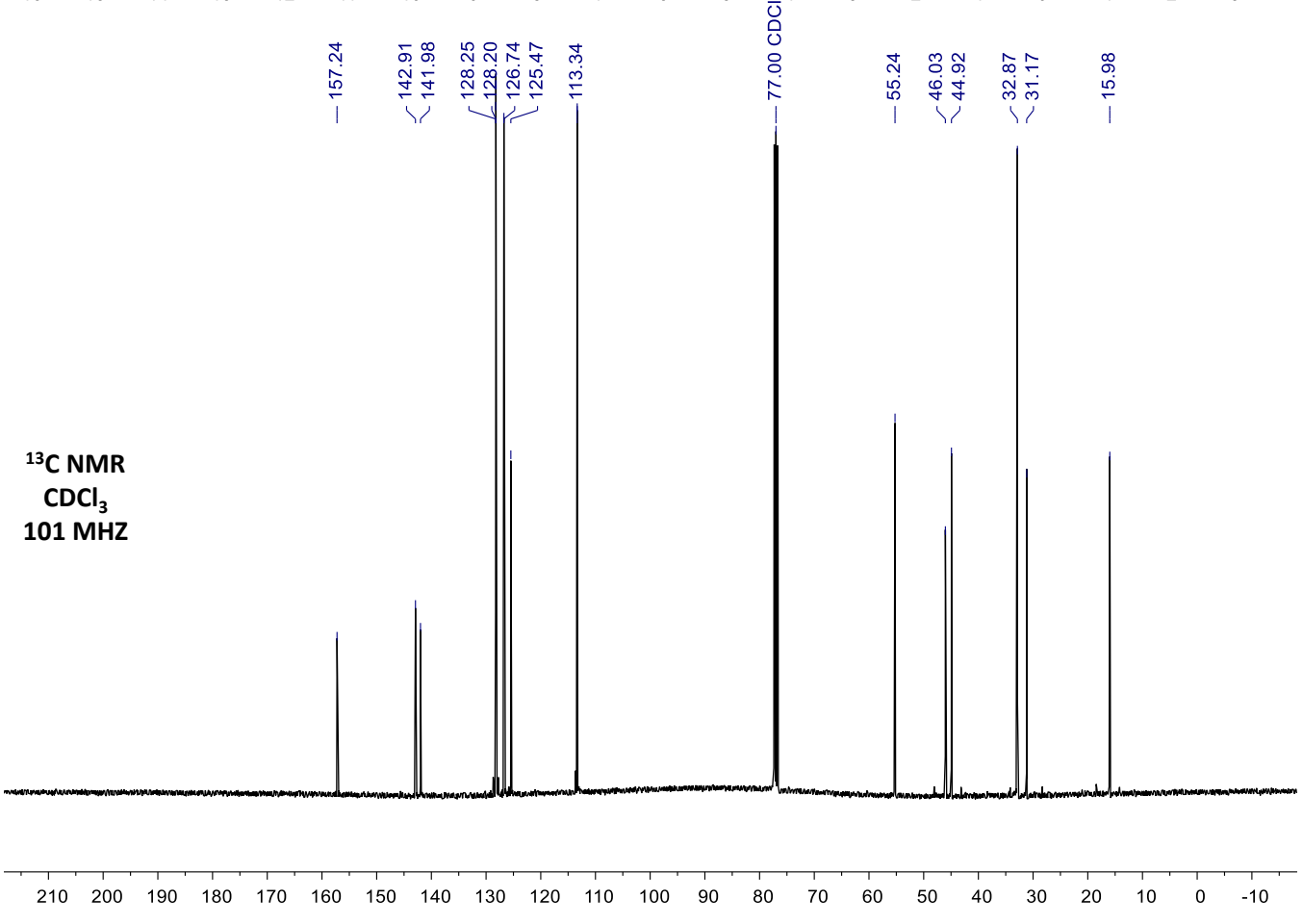
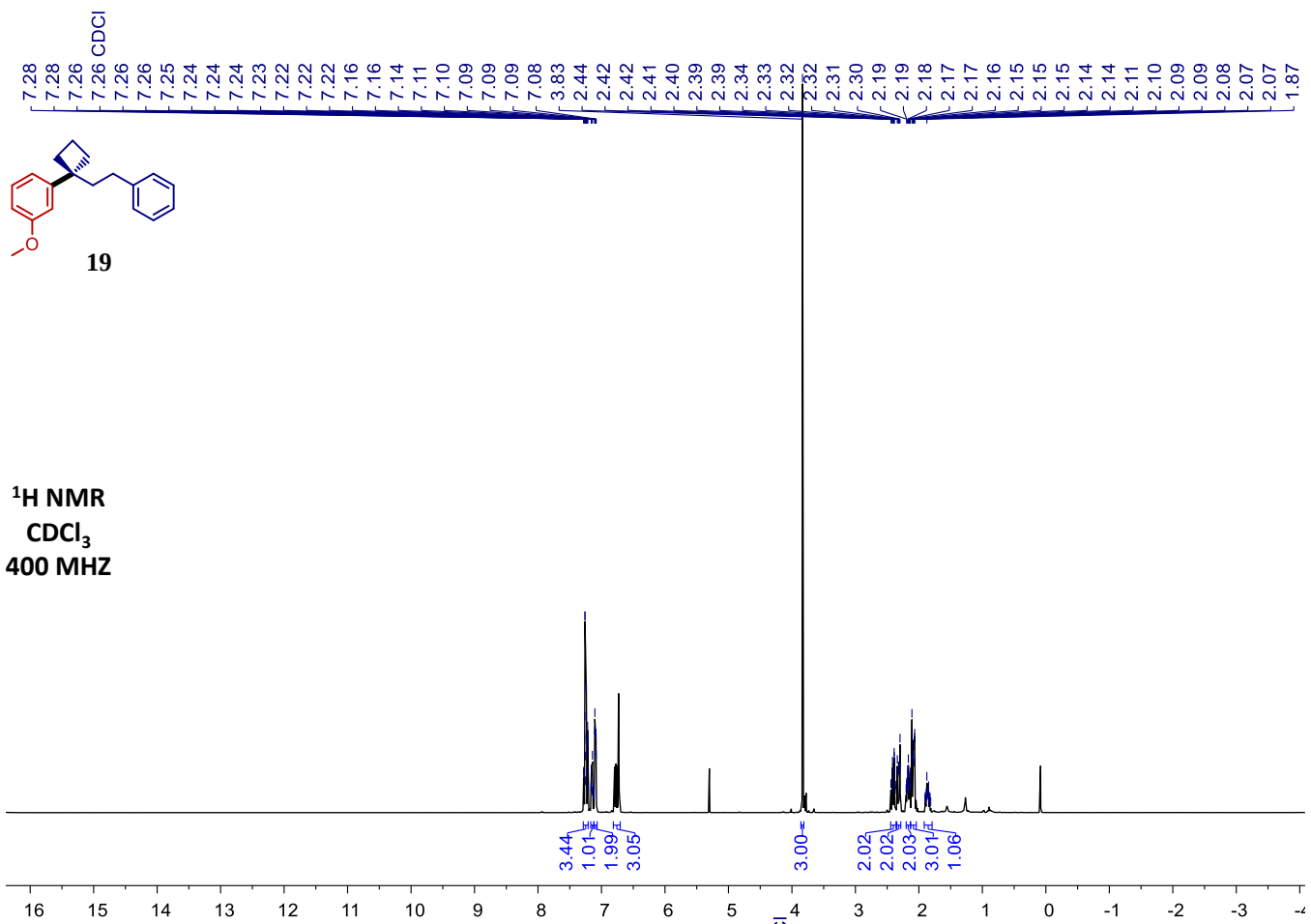
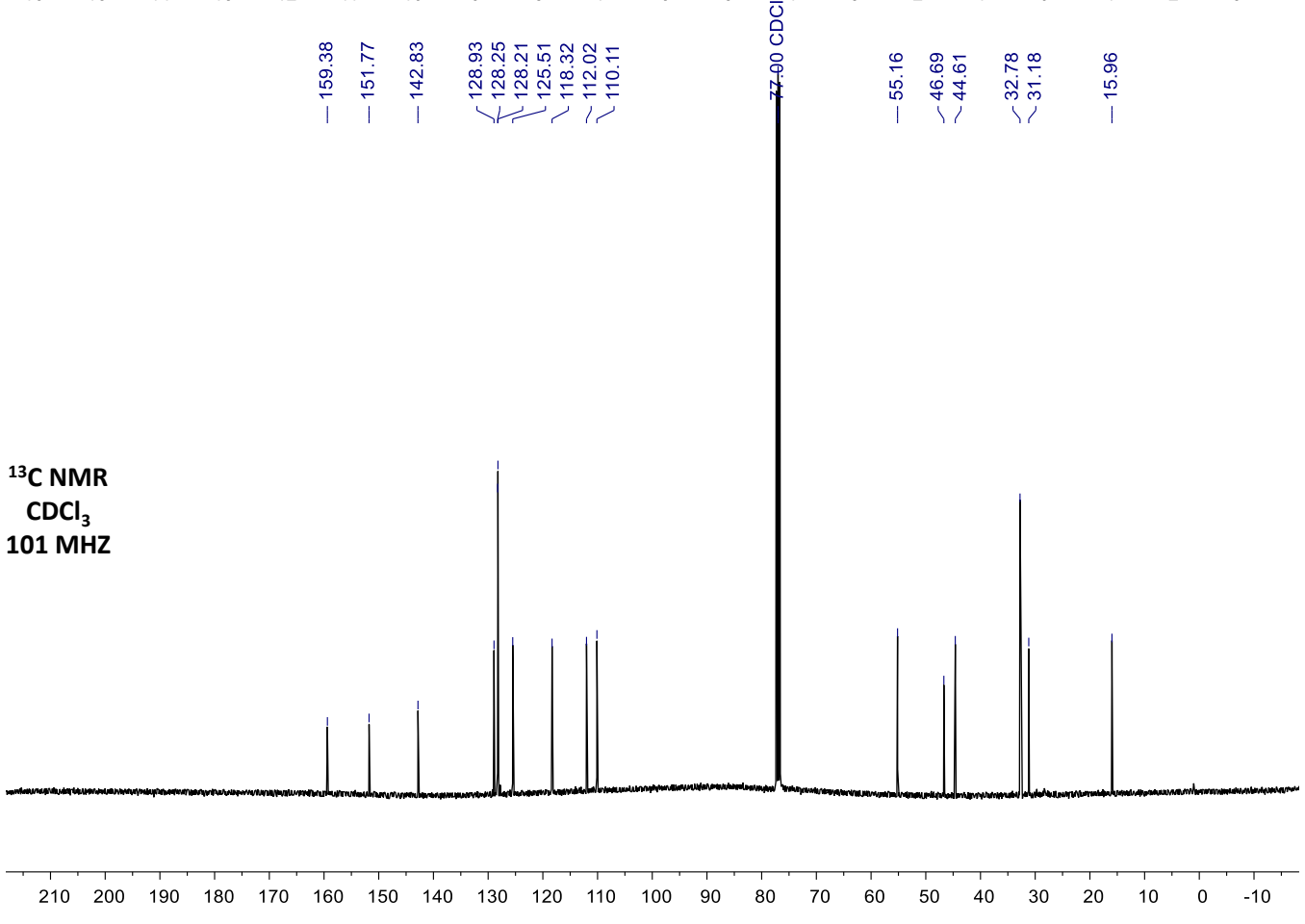
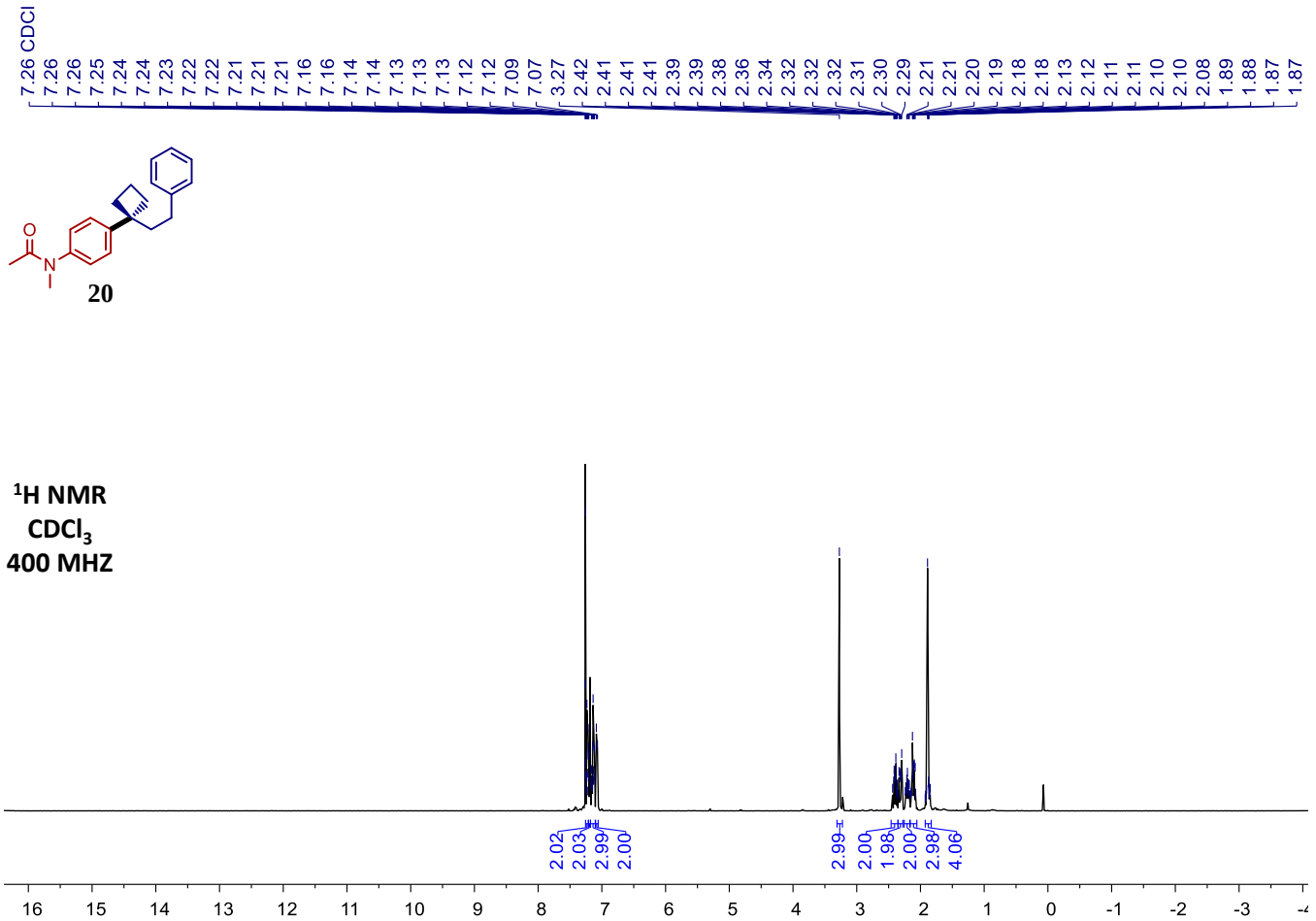
20
10
0
-10


7.27 7.27 7.26 7.26 CDCl 7.26 7.25 7.25 7.24 7.23 7.23 7.17 7.17 7.16 7.14 7.14 7.10 7.10 7.10 7.10 7.09 6.91 6.89 2.43 2.41 2.40 2.40 2.38 2.37 2.34 2.33 2.32 2.32 2.32 2.31 2.30 2.20 2.18 2.18 2.17 2.17 2.16 2.15 2.15 2.15 2.15 2.15 2.10 2.10 2.09 2.08 2.08 2.07 2.07 2.06 1.89
18
1H NMR
CDCl3
400 MHZ
2.16 4.01 1.02 1.98 3.00 2.05 2.00 2.03 3.03 1.00
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3


157.24 142.91 141.98 128.25 128.20 126.74 125.47 113.34 77.00 CDCl3 55.24 46.03 44.92 32.87 31.17 15.98
13C NMR
CDCl3
101 MHZ
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10


7.28 7.28 7.26 7.26 CDCl 7.26 7.26 7.25 7.24 7.24 7.24 7.23 7.22 7.22 7.22 7.16 7.16 7.14 7.11 7.10 7.09 7.09 7.09 7.08 3.83 2.44 2.42 2.41 2.40 2.39 2.39 2.34 2.33 2.32 2.32 2.31 2.30 2.19 2.19 2.18 2.17 2.17 2.16 2.15 2.15 2.15 2.14 2.14 2.11 2.10 2.09 2.09 2.08 2.07 2.07 1.87
19
1H NMR
CDCl3
400 MHZ
3.44 1.01 1.99 3.05 3.00 2.02 2.02 2.03 3.01 1.06
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3


159.38 151.77 142.83 128.93 128.25 128.21 125.51 118.32 112.02 110.11 77.00 CDCl3 55.16 46.69 44.61 32.78 31.18 15.96
13C NMR
CDCl3
101 MHZ
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10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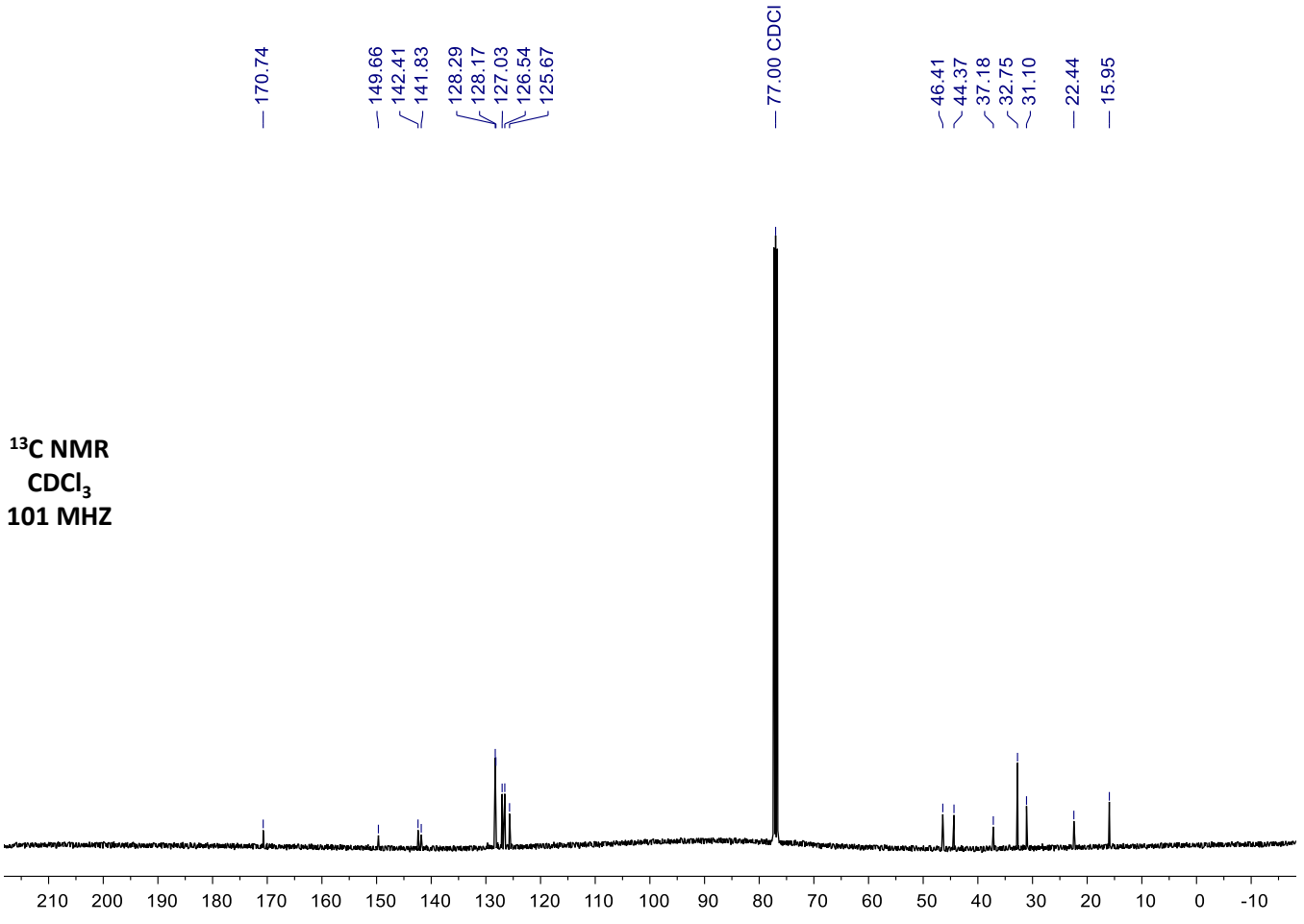
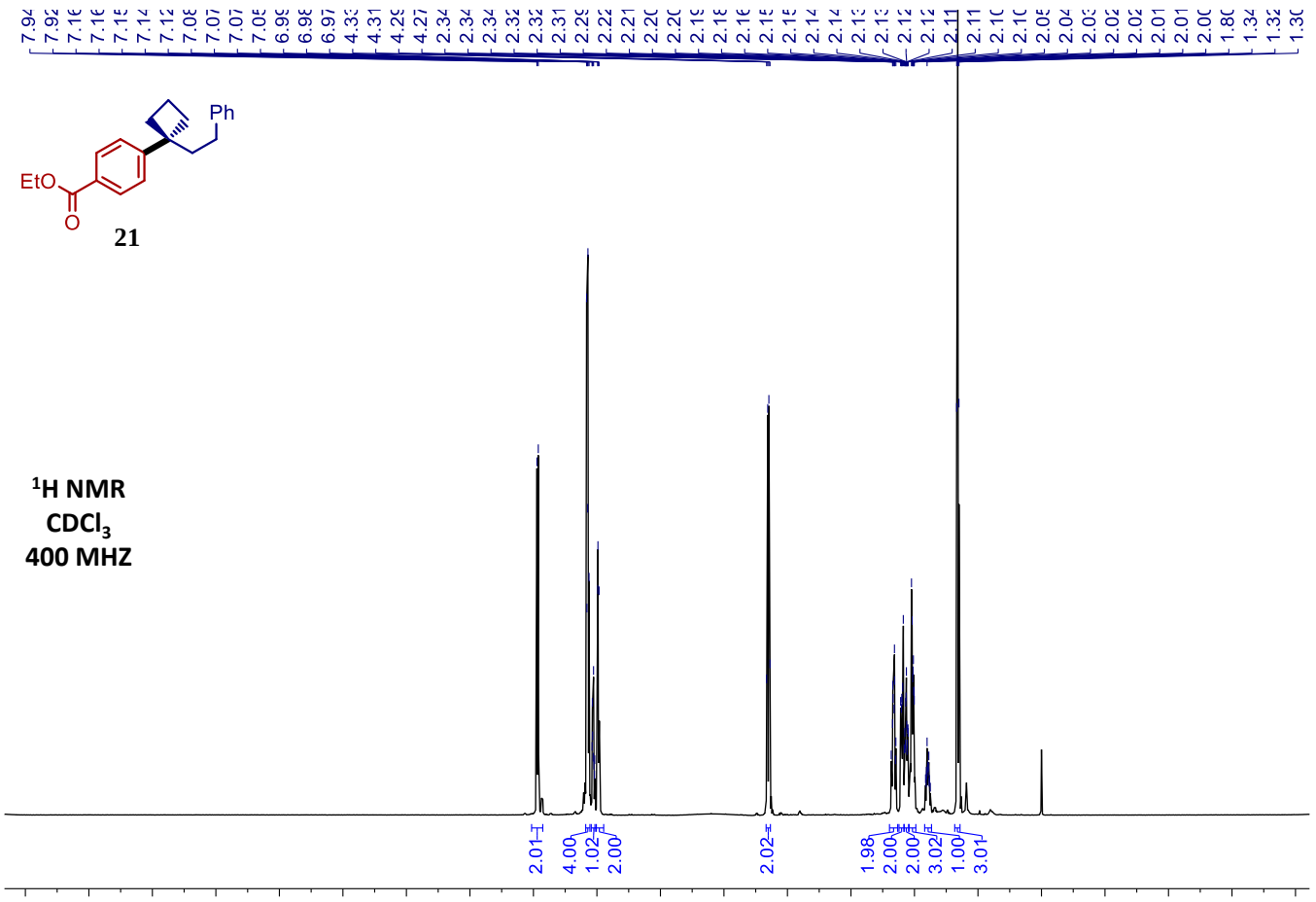
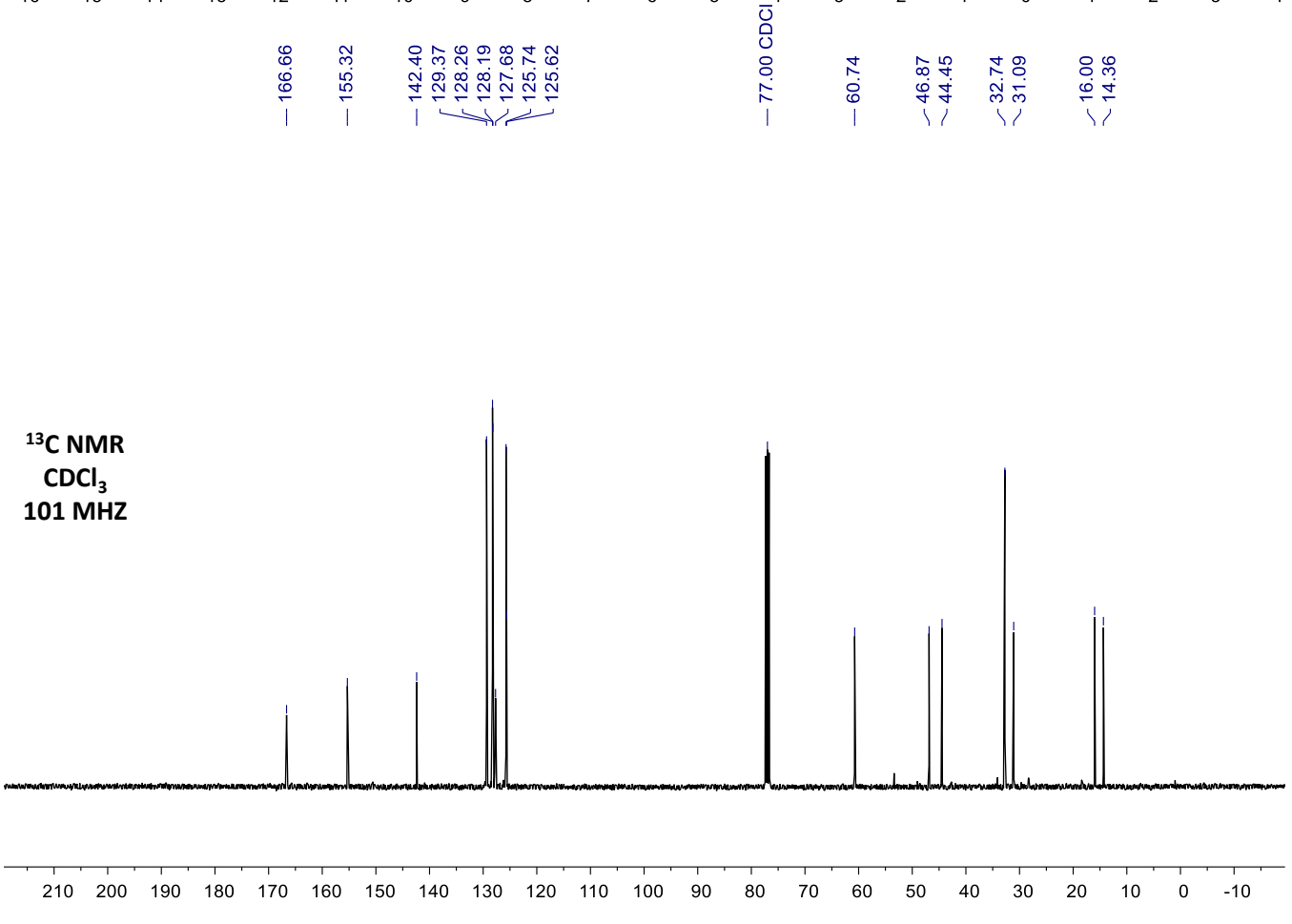
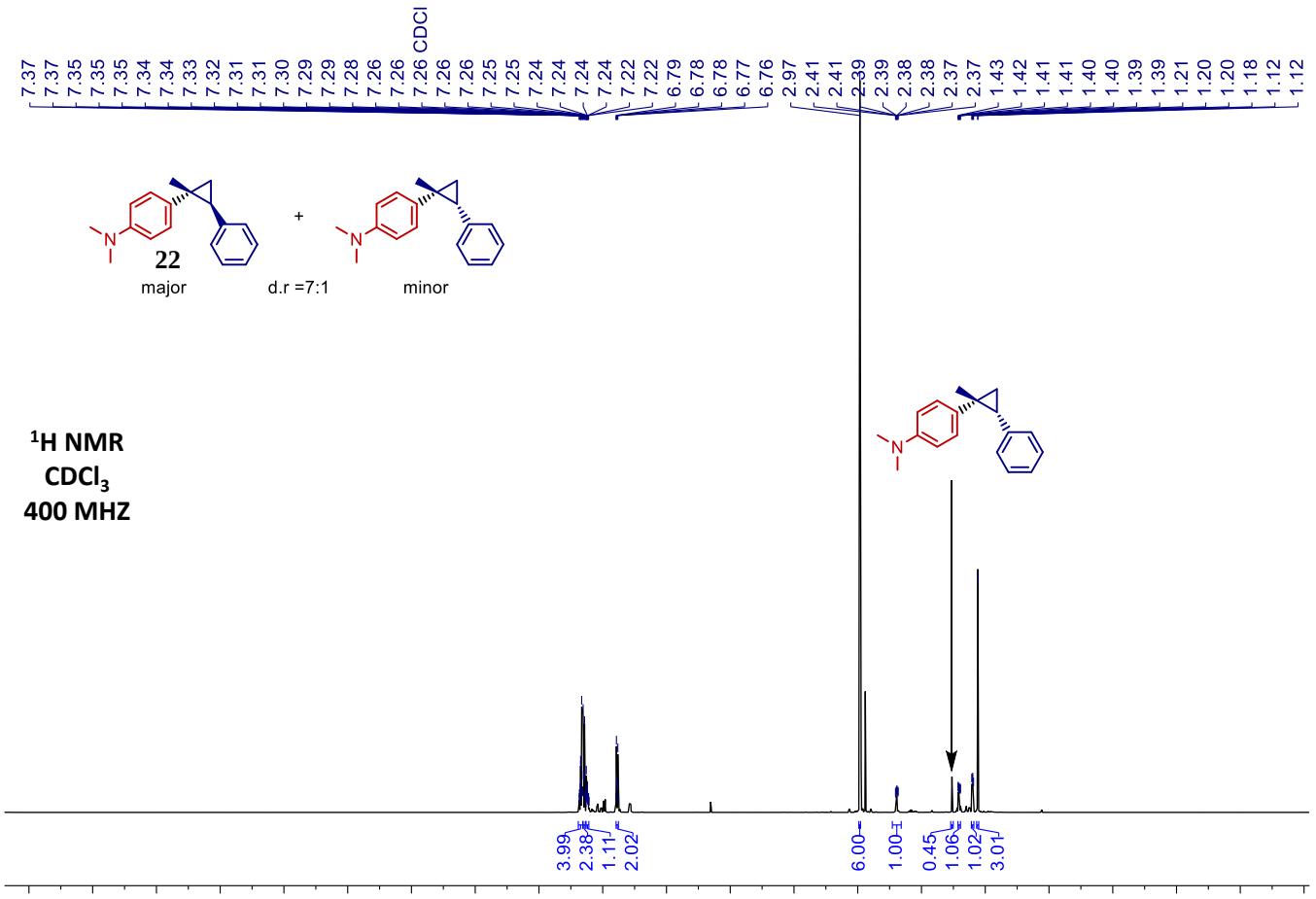
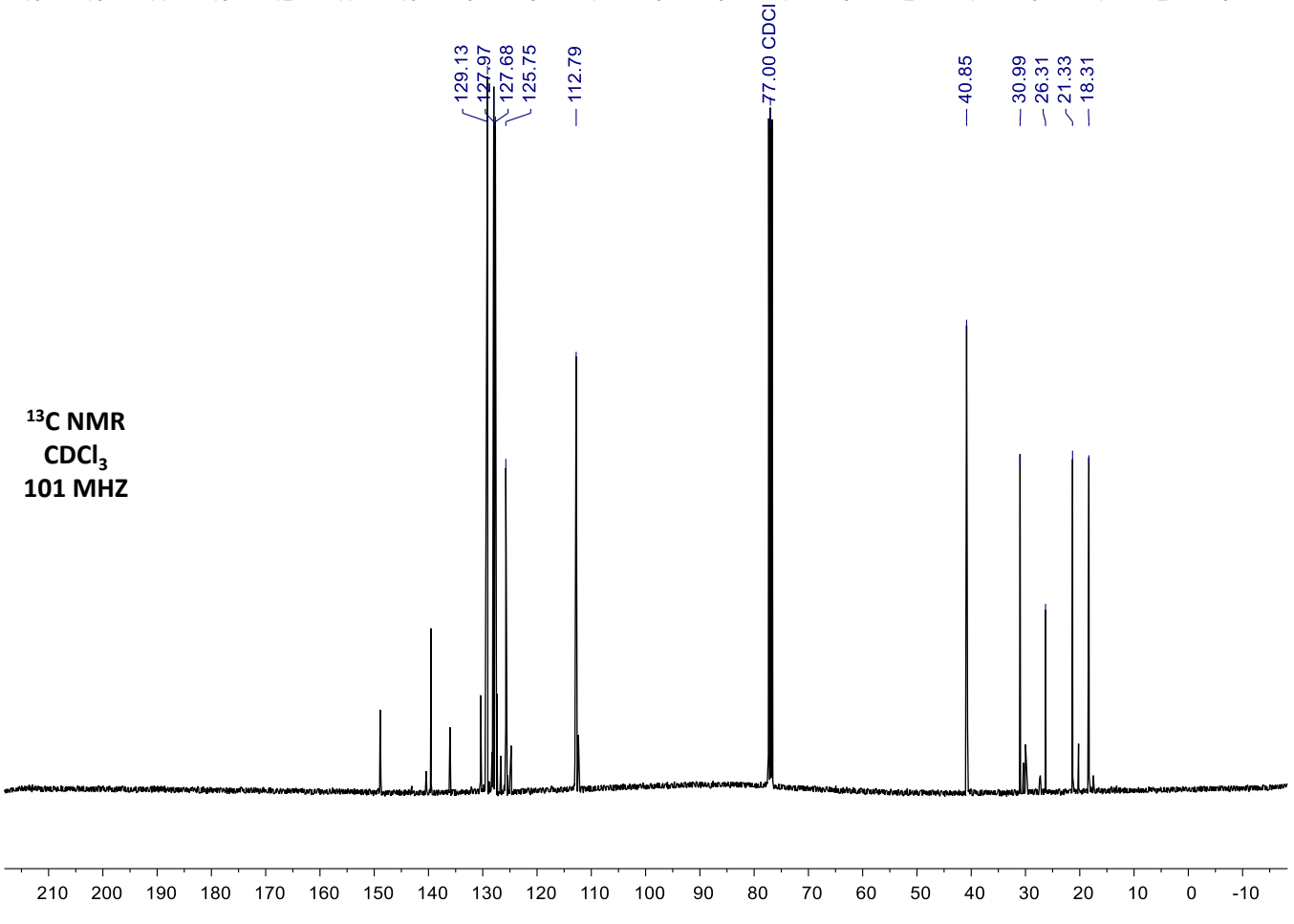
7.26 7.26 7.25 7.24 7.24 7.23 7.22 7.22 7.21 7.21 7.21 7.16 7.16 7.14 7.14 7.13 7.13 7.13 7.12 7.12 7.09 7.07 3.27 2.42 2.41 2.41 2.39 2.39 2.38 2.36 2.34 2.32 2.32 2.32 2.31 2.30 2.29 2.21 2.21 2.20 2.19 2.18 2.18 2.13 2.12 2.11 2.11 2.10 2.10 2.08 1.89 1.88 1.87 1.87
O
N
20
1H NMR
CDCl3
400 MHZ
2.02 2.03 2.99 2.00 2.99 2.00 1.98 2.00 2.98 4.06
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3


170.74
149.66
142.41
141.83
128.29
128.17
127.03
126.54
125.67
77.00 CDCl
46.41
44.37
37.18
32.75
31.10
22.44
15.95
13C NMR
CDCl3
101 MHZ
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

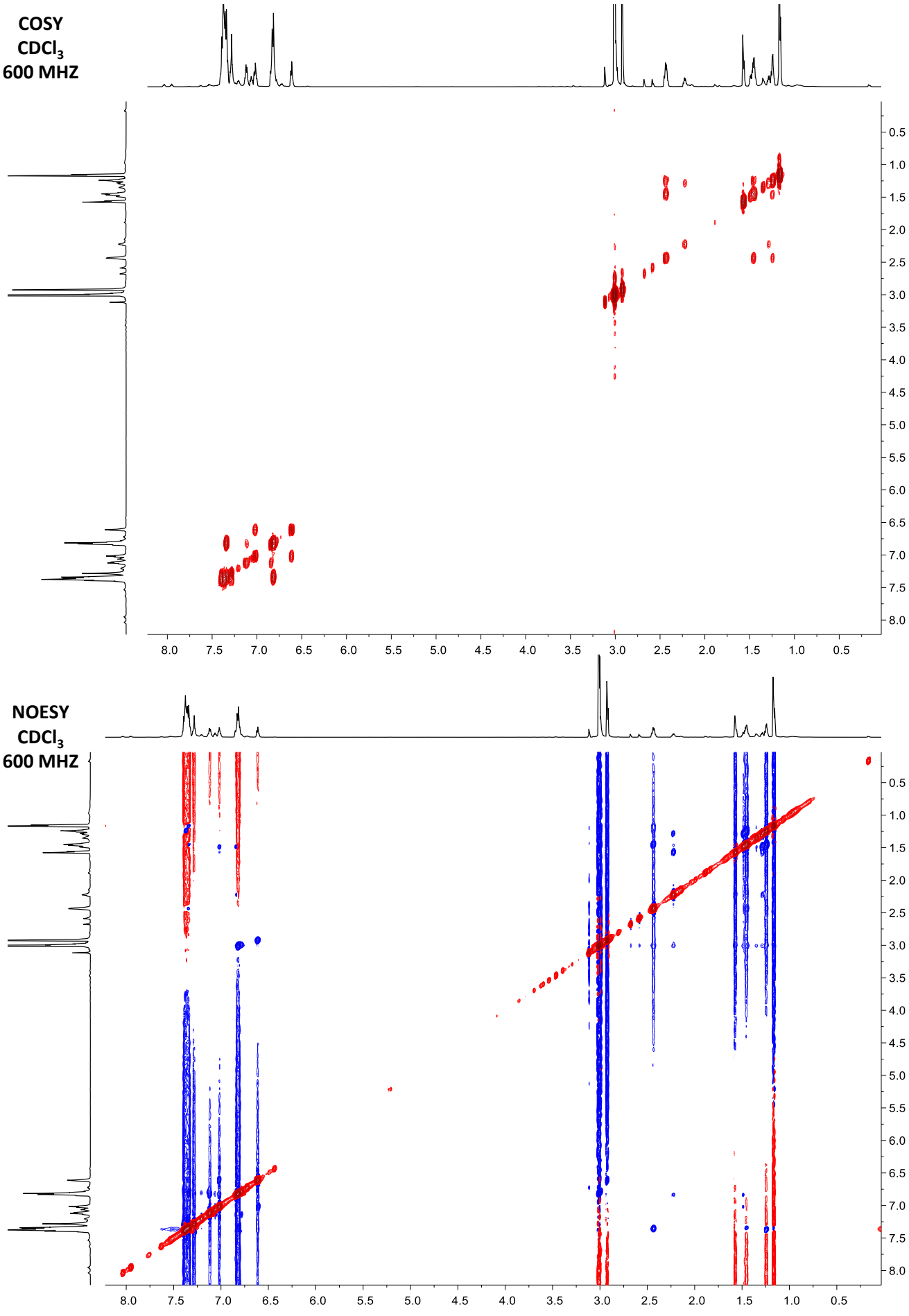

Ph
EtO
O
21
^{1}H NMR
$CDCl_3$
400 MHZ


166.66
155.32
142.40
129.37
128.26
128.19
127.68
125.74
125.62
77.00 CDCl
60.74
46.87
44.45
32.74
31.09
16.00
14.36
^{13}C NMR
$CDCl_3$
101 MHZ

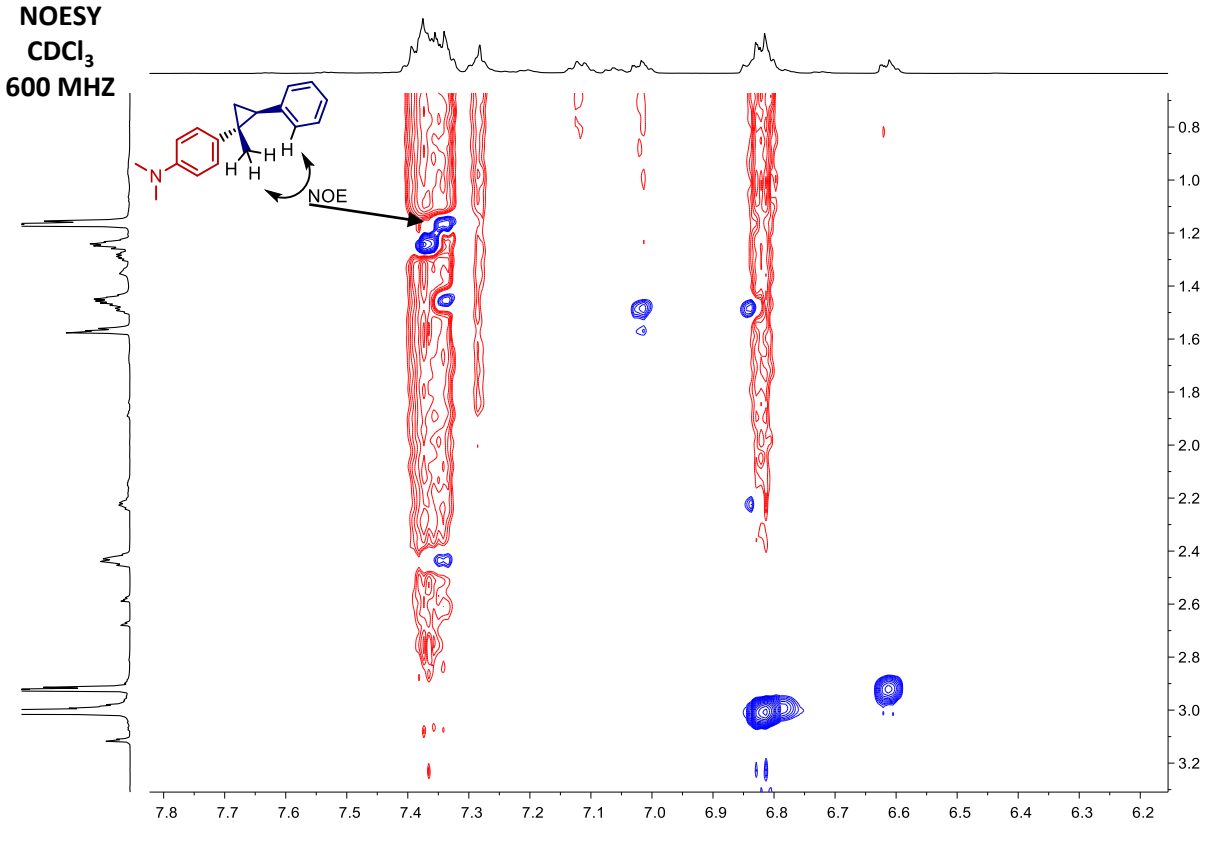

7.37 7.37 7.35 7.35 7.35 7.34 7.34 7.33 7.32 7.31 7.31 7.30 7.29 7.29 7.28 7.26 7.26 7.26 CDCl 7.26 7.26 7.25 7.25 7.24 7.24 7.24 7.24 7.22 7.22 6.79 6.78 6.78 6.77 6.76 2.97 2.41 2.41 2.39 2.39 2.38 2.38 2.37 2.37 1.43 1.42 1.41 1.41 1.40 1.40 1.39 1.39 1.21 1.20 1.20 1.18 1.12 1.12
22
major
d.r =7:1
minor
1H NMR
CDCl3
400 MHZ
3.99 2.38 1.11 2.02 6.00 1.00 0.45 1.06 1.02 3.01
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3


129.13 127.97 127.68 125.75 112.79 77.00 CDCl3 40.85 30.99 26.31 21.33 18.31
13C NMR
CDCl3
101 MHZ
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

COSY
$CDCl_3$
600 MHZ



NOESY
$CDCl_3$
600 MHZ


NOESY
CDCl3
600 MHZ
N
H
H
H
H
NOE
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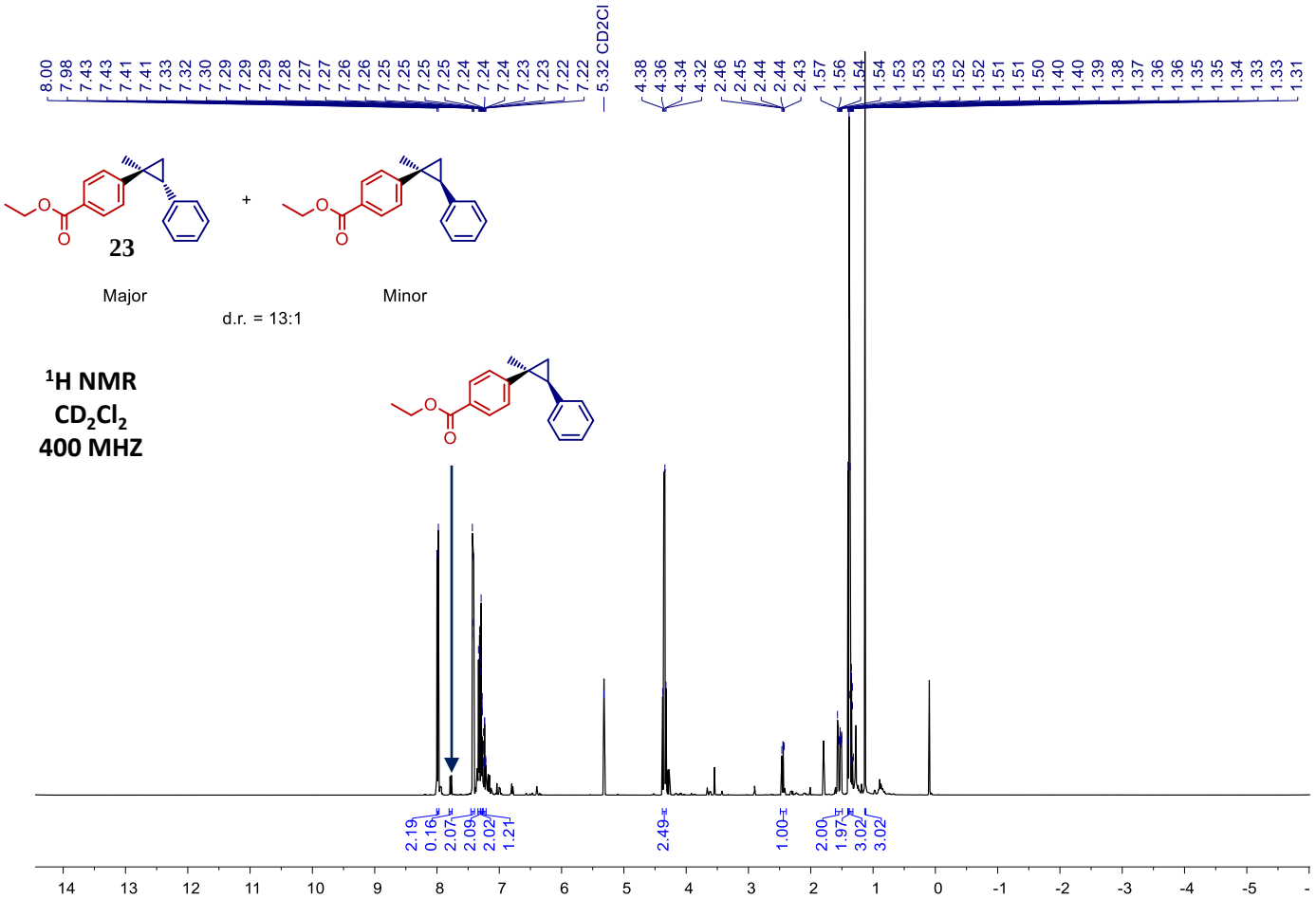
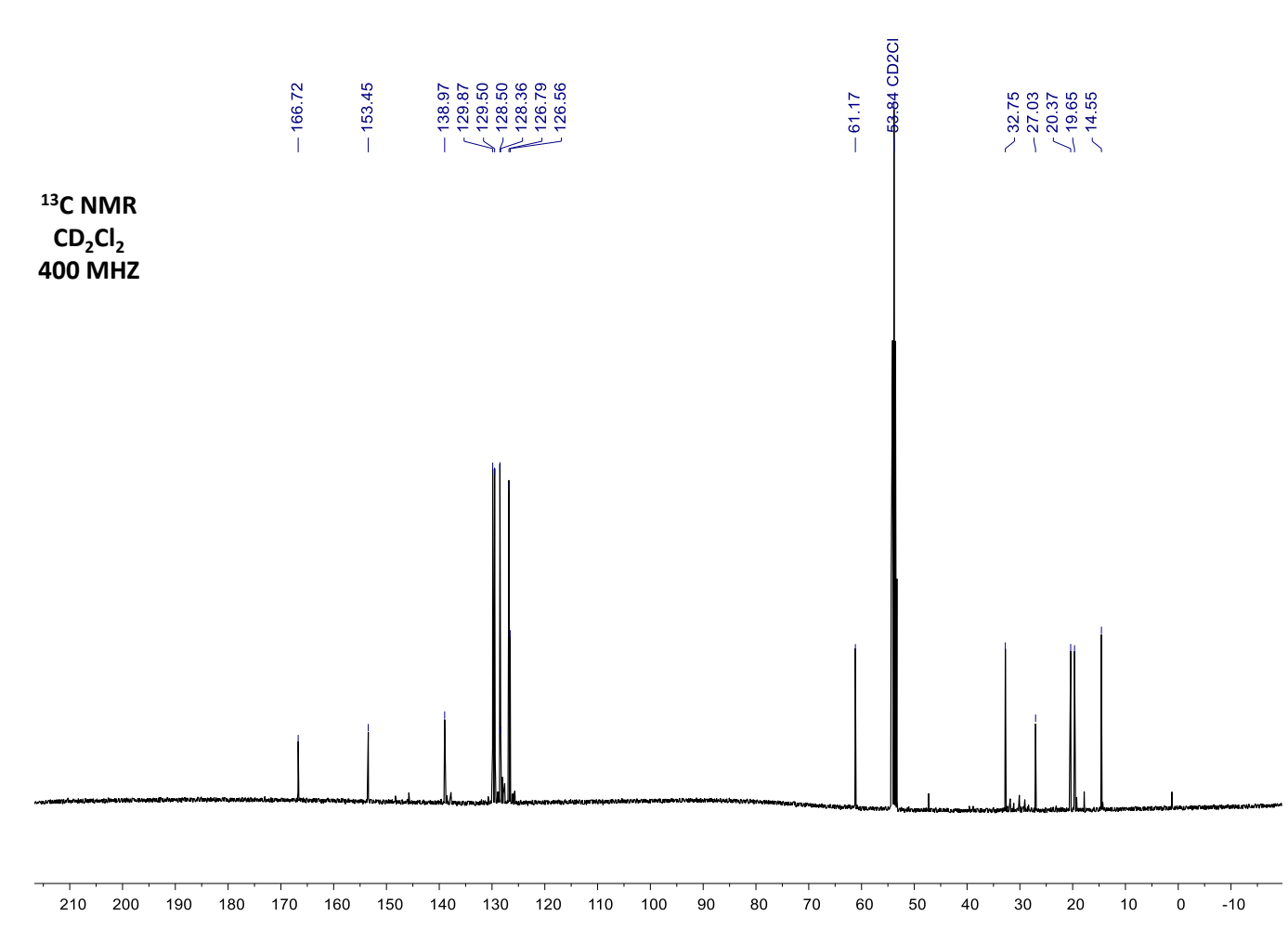
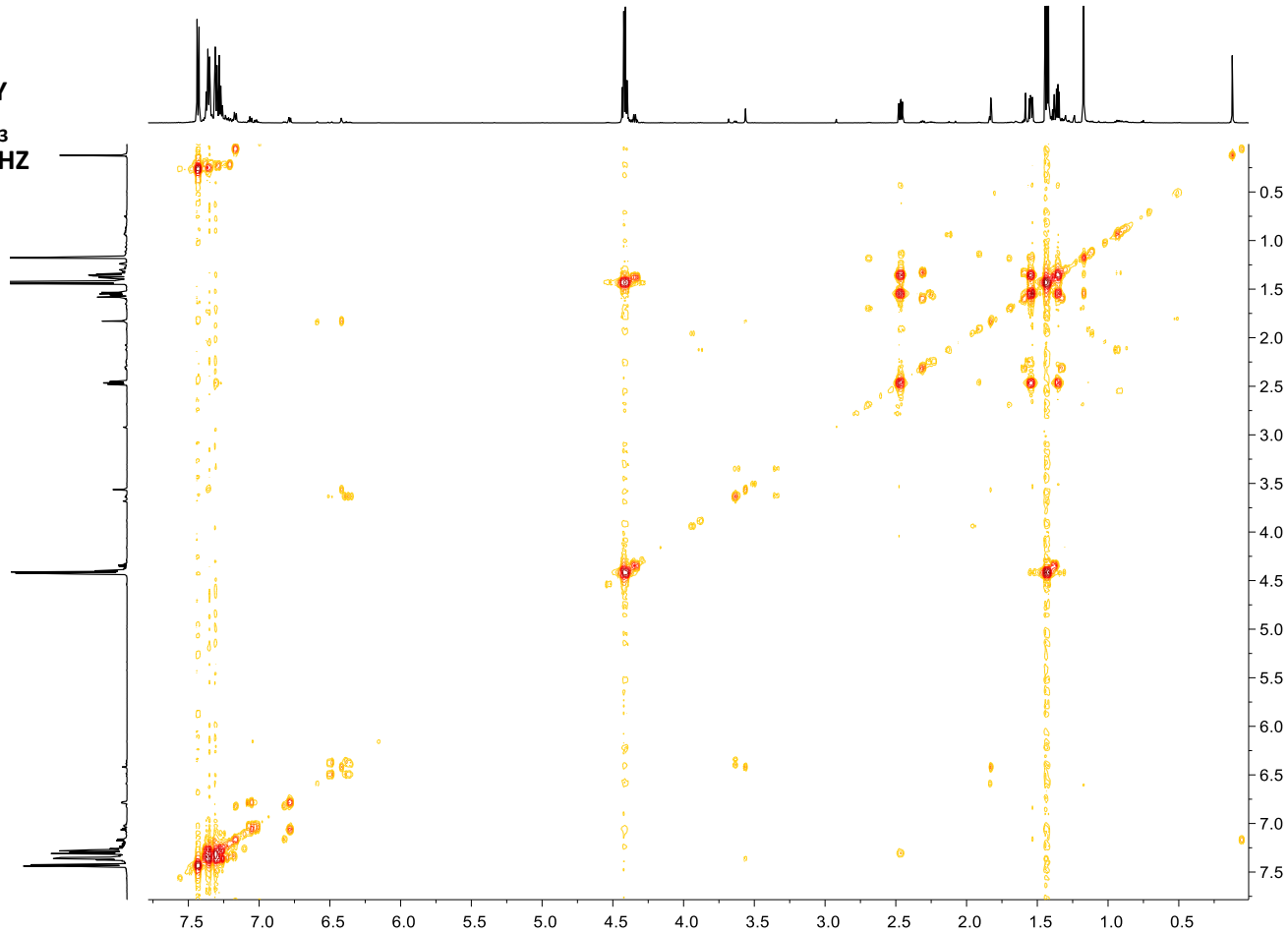
1.0
1.2
1.4
1.6
1.8
2.0
2.2
2.4
2.6
2.8
3.0
3.2
7.8
7.7
7.6
7.5
7.4
7.3
7.2
7.1
7.0
6.9
6.8
6.7
6.6
6.5
6.4
6.3
6.2

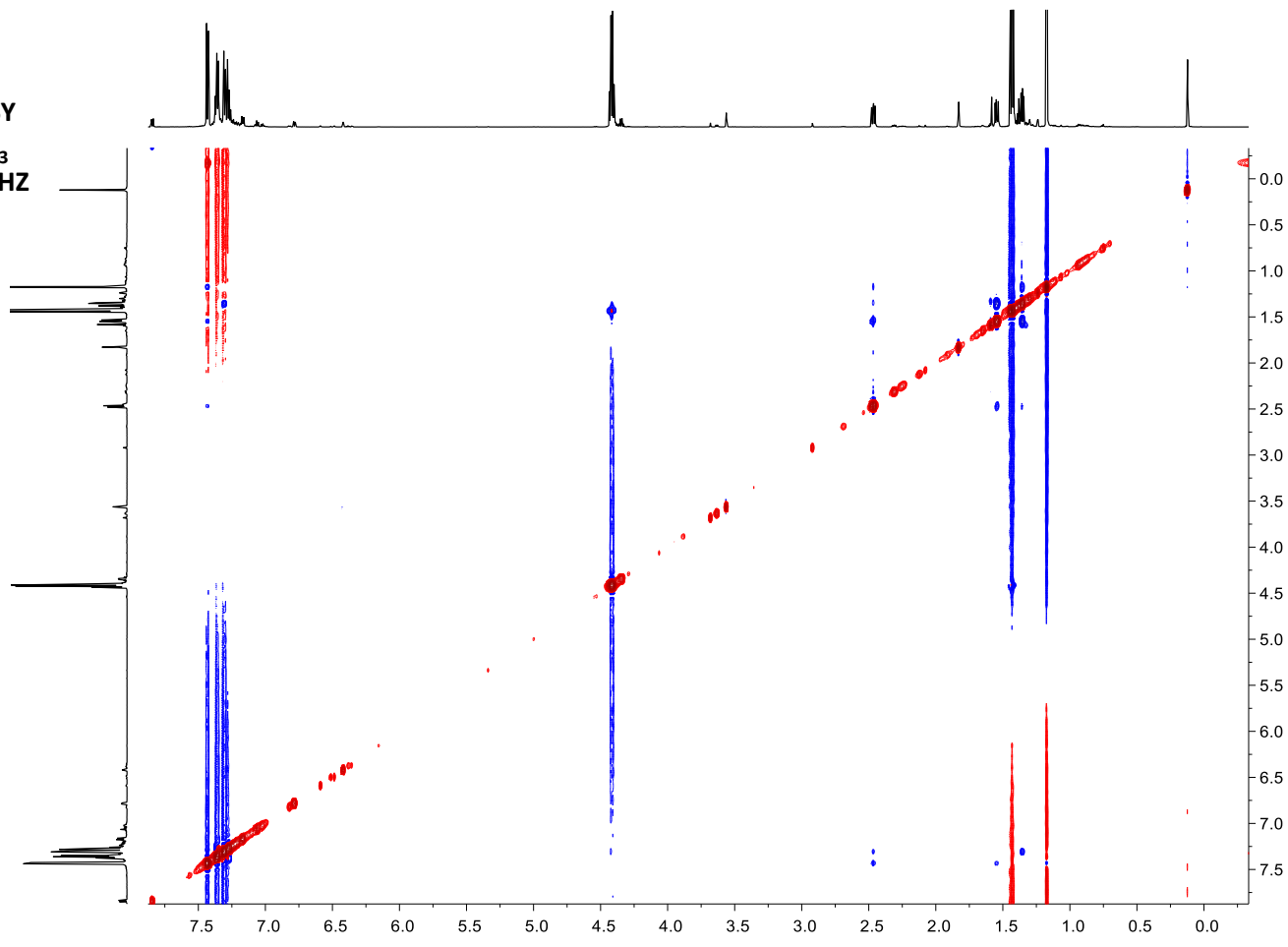

8.00 7.98 7.43 7.43 7.41 7.41 7.33 7.32 7.30 7.29 7.29 7.29 7.28 7.27 7.27 7.26 7.26 7.25 7.25 7.25 7.25 7.24 7.24 7.24 7.23 7.23 7.22 7.22 5.32 CD2Cl
4.38 4.36 4.34 4.32 2.46 2.45 2.44 2.44 2.43 1.57 1.56 1.54 1.54 1.53 1.53 1.53 1.52 1.52 1.51 1.51 1.50 1.40 1.40 1.39 1.38 1.37 1.36 1.36 1.35 1.35 1.34 1.33 1.33 1.31
23
Major
Minor
d.r. = 13:1
1H NMR
CD2Cl2
400 MHZ
2.19 0.16 2.07 2.09 2.02 1.21 2.49 1.00 2.00 1.97 3.02 3.02
14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3 -4 -5

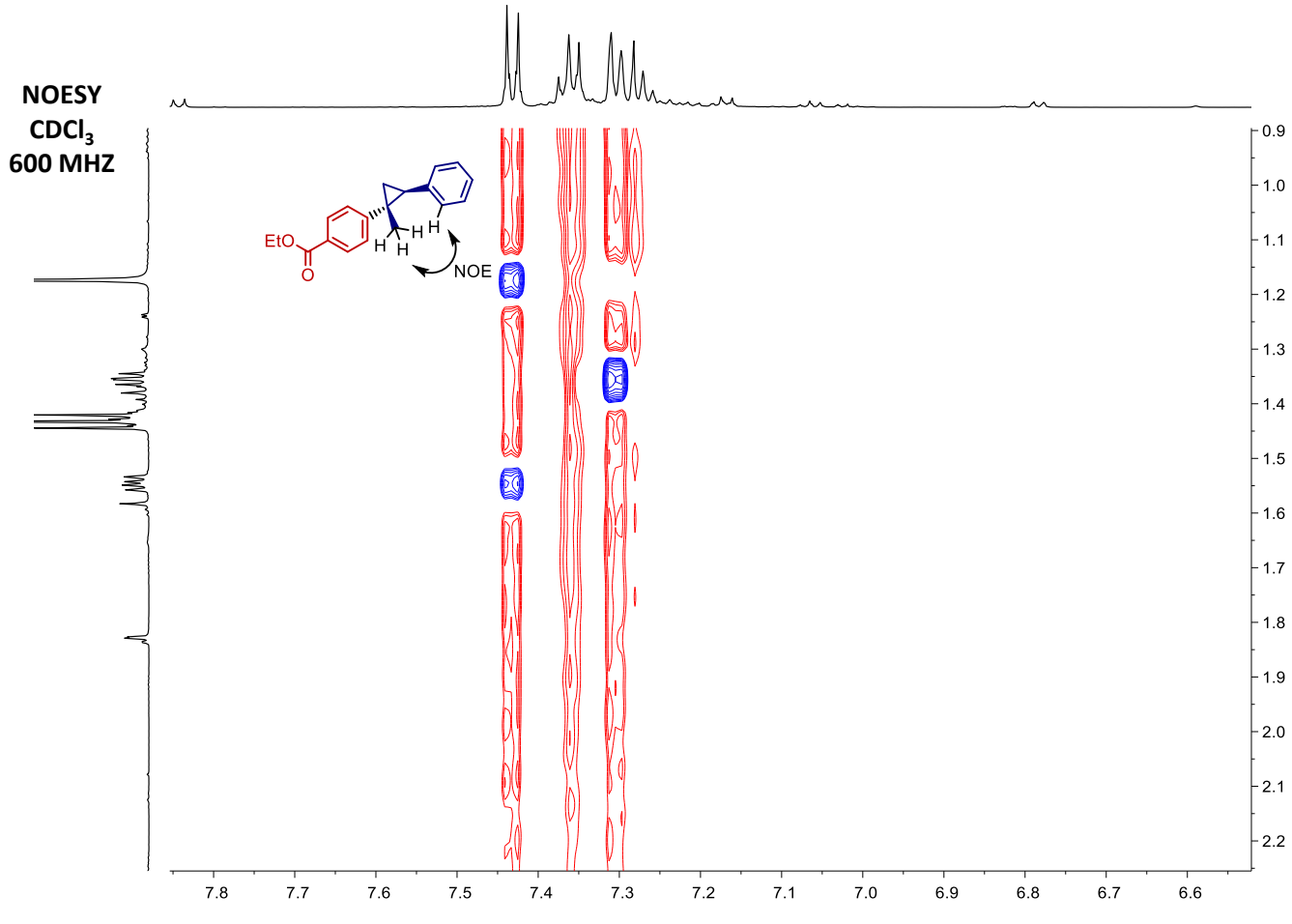

166.72 153.45 138.97 129.87 129.50 128.50 128.36 126.79 126.56 61.17 53.84 CD2Cl 32.75 27.03 20.37 19.65 14.55
13C NMR
CD2Cl2
400 MHZ
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

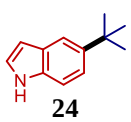
COSY
$CDCl_3$
600 MHZ



NOESY
$CDCl_3$
600 MHZ



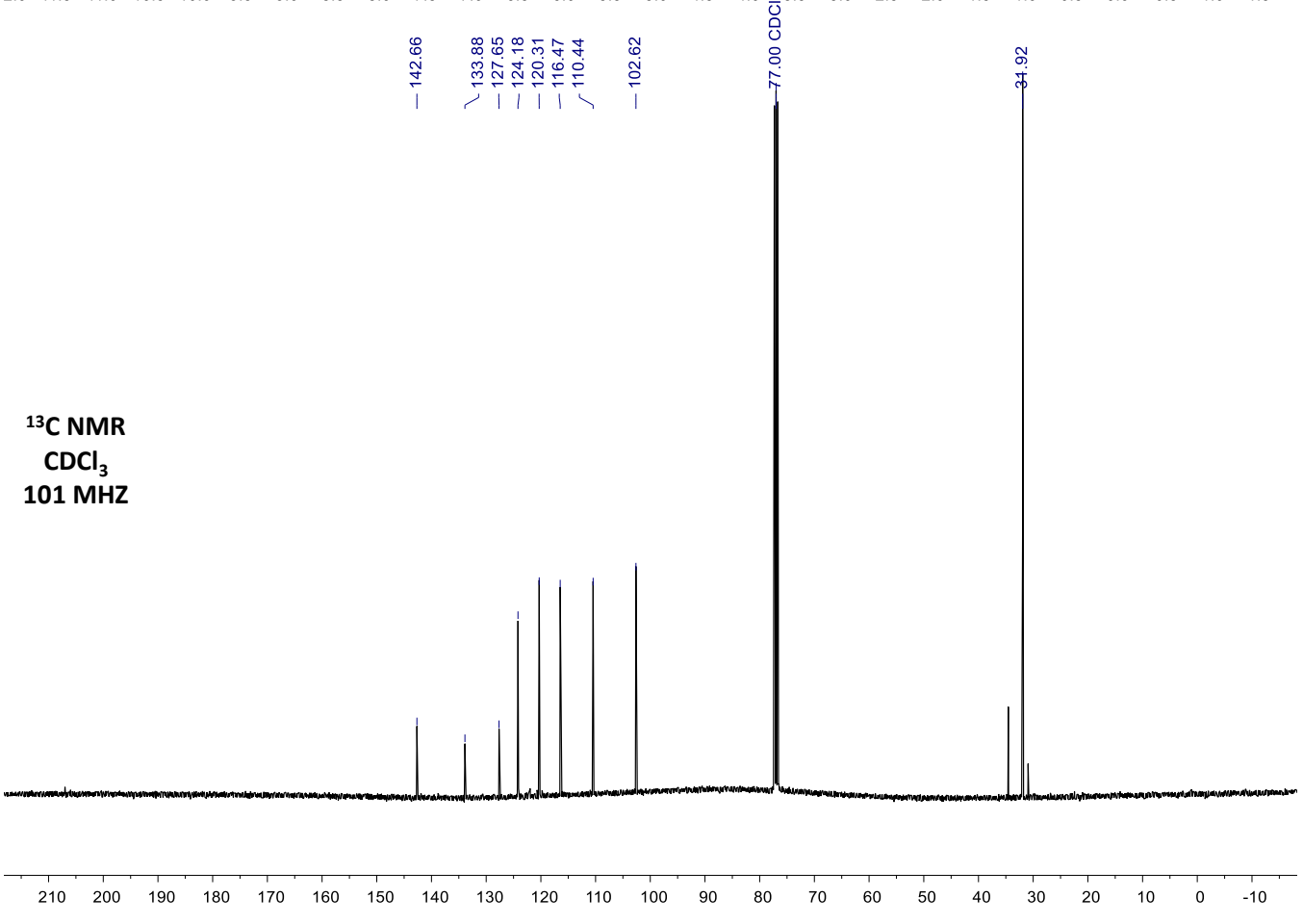

NOESY
CDCl3
600 MHZ
EtO
O
H
H
H
H
NOE
0.9
1.0
1.1
1.2
1.3
1.4
1.5
1.6
1.7
1.8
1.9
2.0
2.1
2.2
7.8
7.7
7.6
7.5
7.4
7.3
7.2
7.1
7.0
6.9
6.8
6.7
6.6

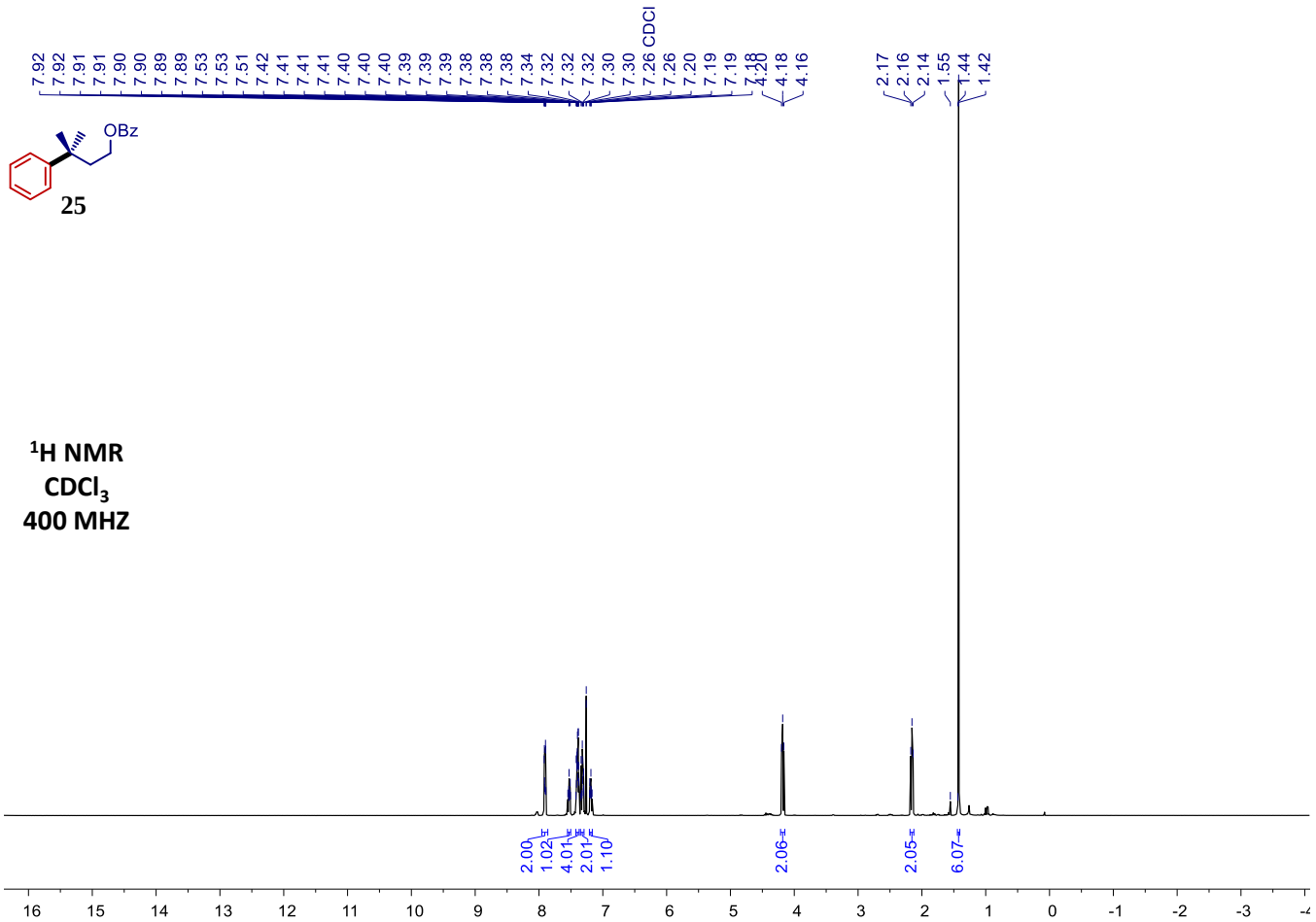


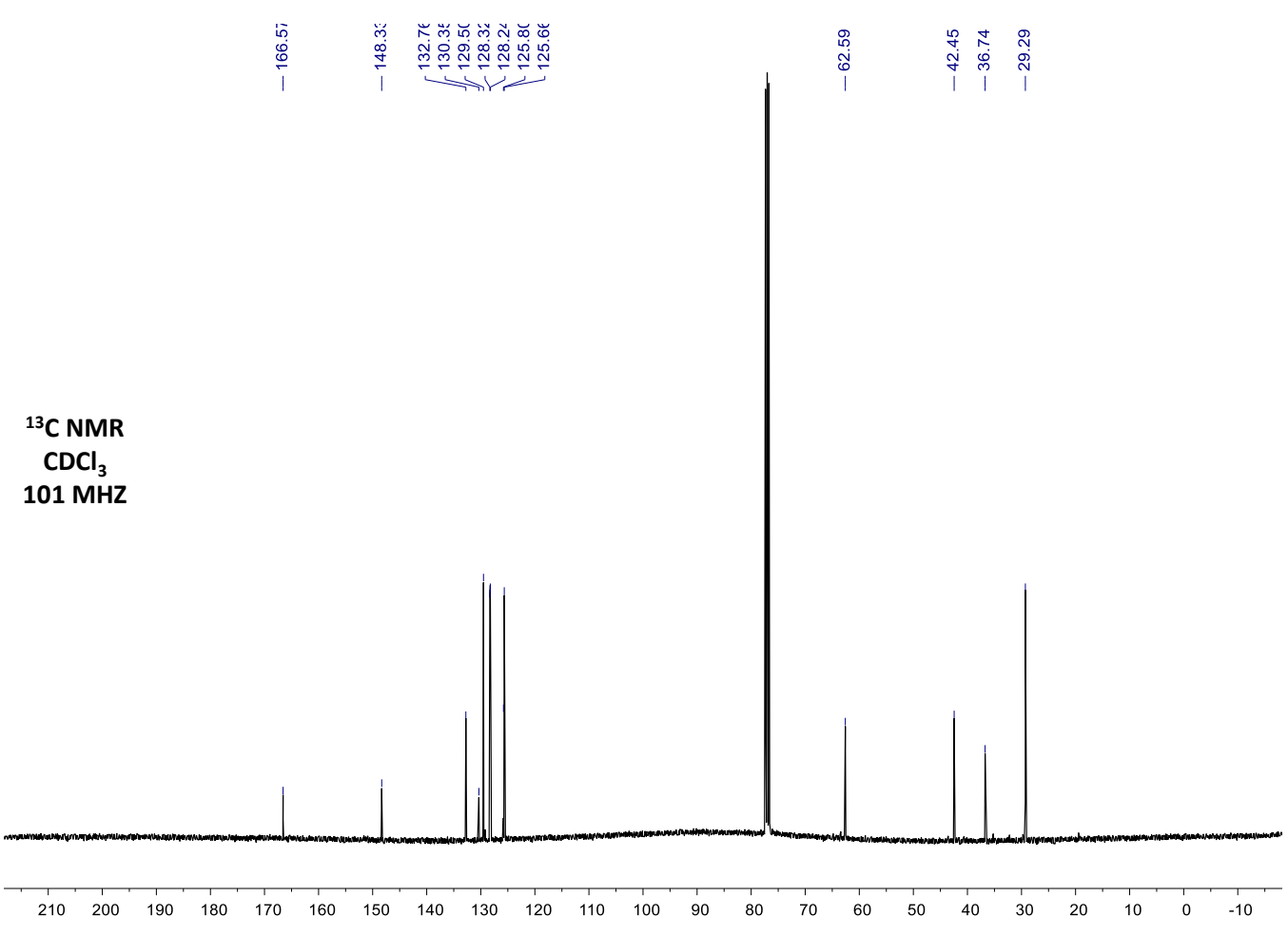
24

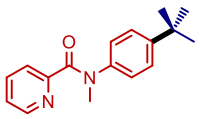
^{1}H NMR
$CDCl_3$
400 MHZ

^{13}C NMR
$CDCl_3$
101 MHZ




7.92 7.92 7.91 7.91 7.90 7.90 7.89 7.89 7.53 7.53 7.51 7.42 7.41 7.41 7.41 7.40 7.40 7.40 7.39 7.39 7.39 7.38 7.38 7.38 7.34 7.32 7.32 7.32 7.30 7.30 7.26 CDCl 7.26 7.20 7.19 7.19 7.18 4.20 4.18 4.16 2.17 2.16 2.14 1.55 1.44 1.42
OBz
25
^{1}H NMR
$CDCl_3$
400 MHZ
2.00 1.02 4.01 2.01 1.10 2.06 2.05 6.07
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3

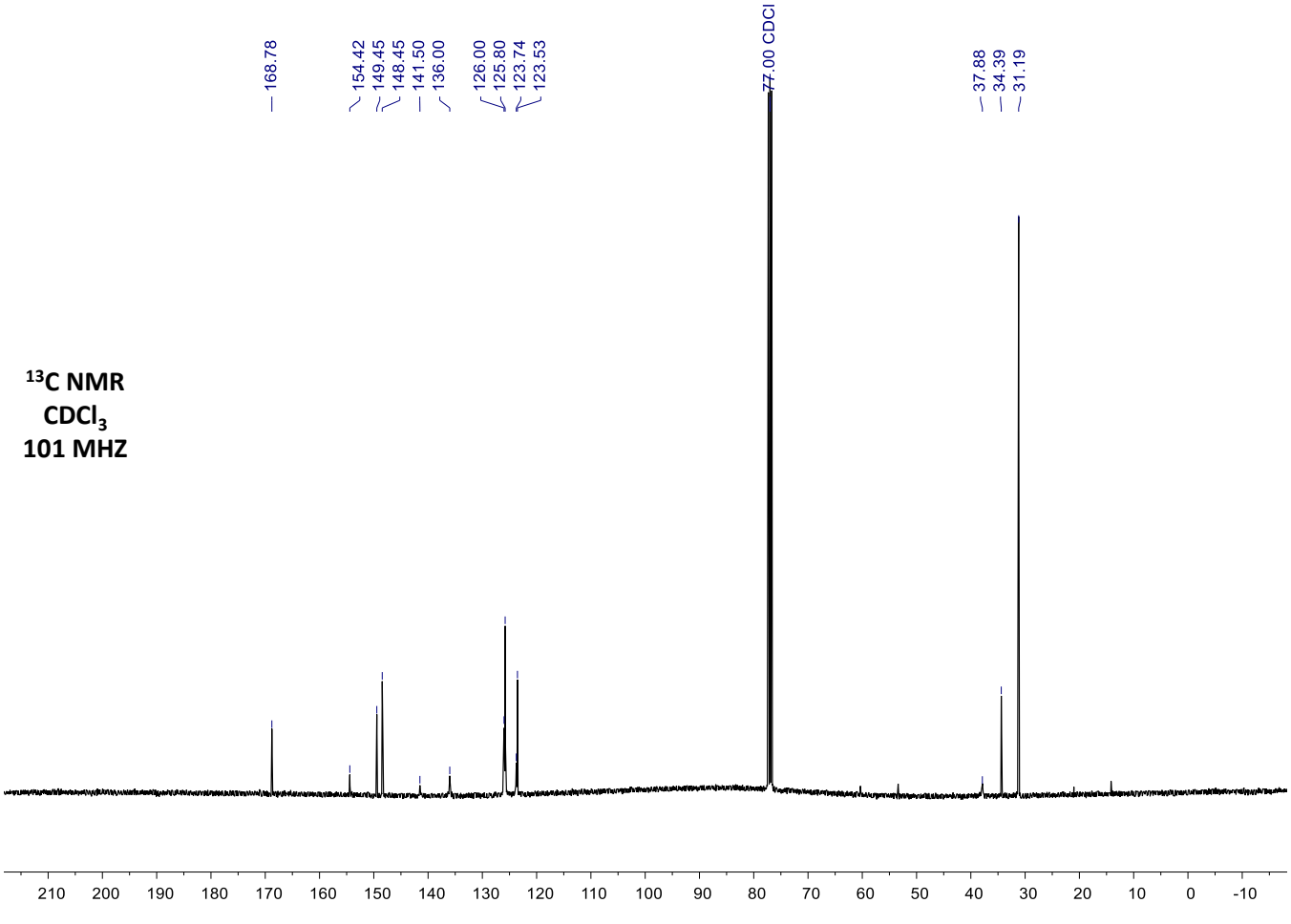

166.57 148.33 132.76 130.38 129.50 128.33 128.24 125.80 125.66 62.59 42.45 36.74 29.29
^{13}C NMR
$CDCl_3$
101 MHZ
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

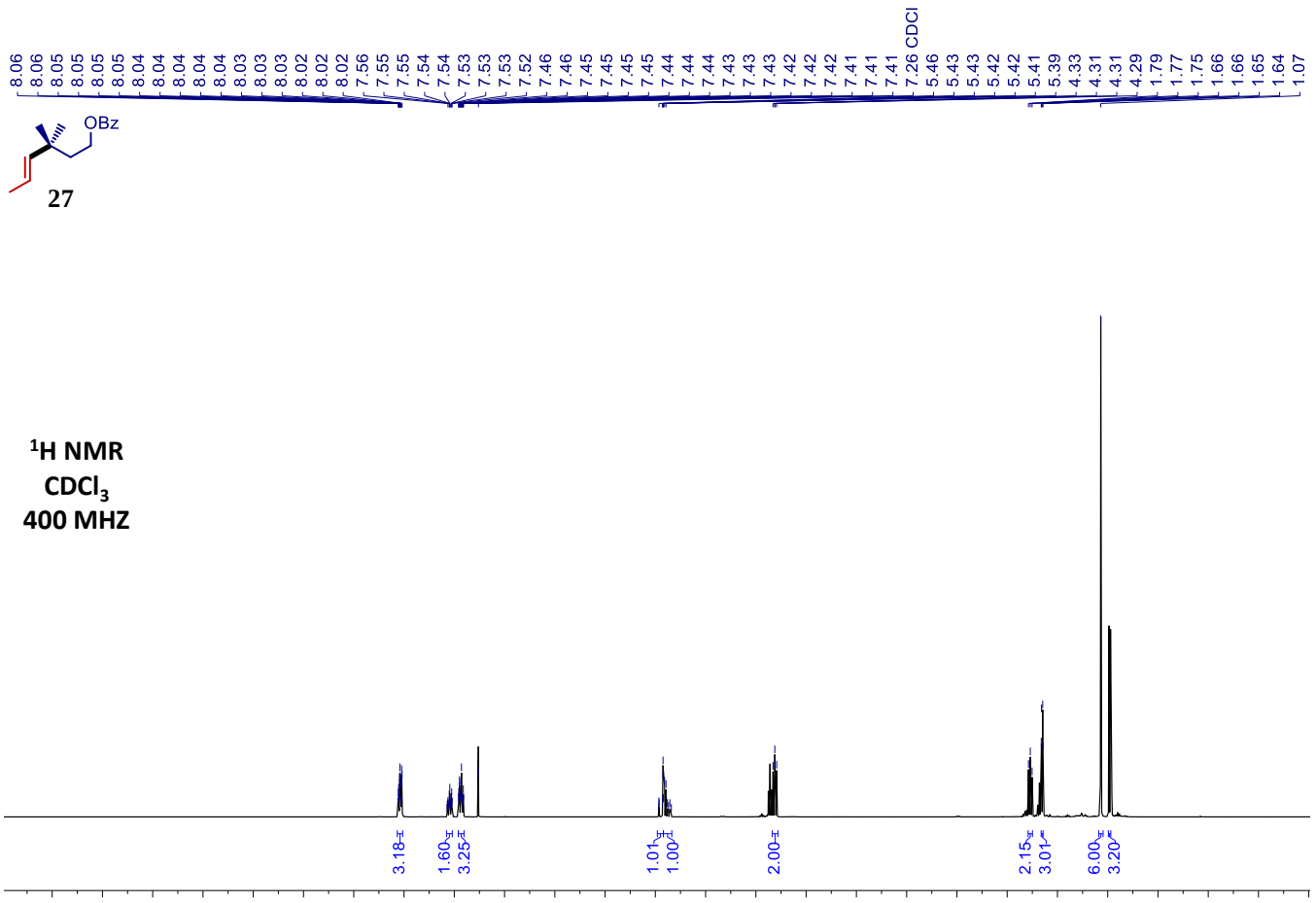


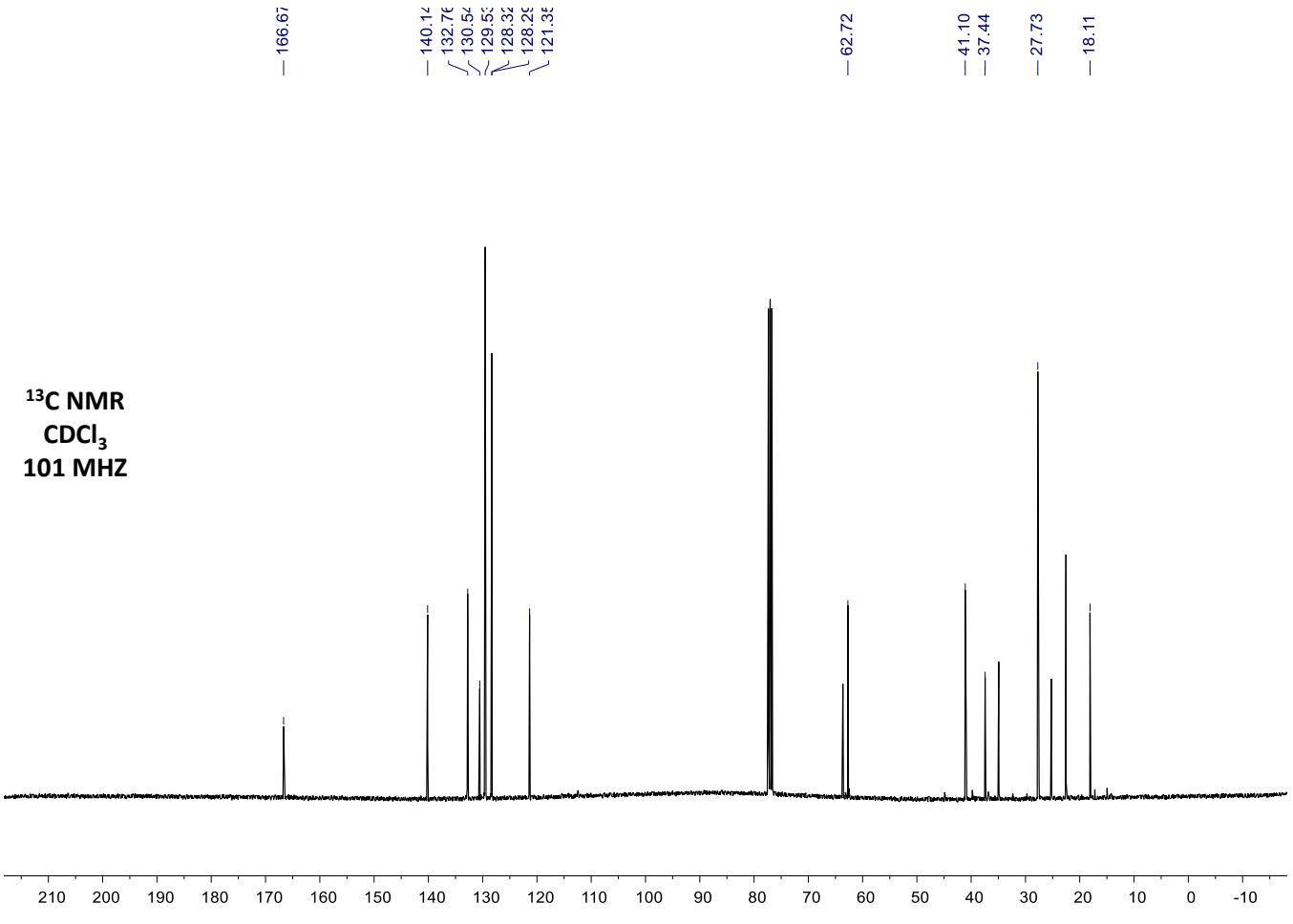
26

^{1}H NMR
$CDCl_3$
400 MHZ

^{13}C NMR
$CDCl_3$
101 MHZ




8.06 8.06 8.05 8.05 8.05 8.05 8.04 8.04 8.04 8.04 8.04 8.03 8.03 8.03 8.02 8.02 8.02 7.56 7.55 7.55 7.54 7.54 7.53 7.53 7.53 7.52 7.46 7.46 7.45 7.45 7.45 7.45 7.44 7.44 7.44 7.43 7.43 7.43 7.42 7.42 7.42 7.41 7.41 7.41 7.26 CDCl 5.46 5.43 5.43 5.42 5.42 5.41 5.39 4.33 4.31 4.31 4.29 1.79 1.77 1.75 1.66 1.66 1.65 1.64 1.07
OBz
27
1H NMR
CDCl3
400 MHZ
3.18 1.60 3.25 1.01 1.00 2.00 2.15 3.01 6.00 3.20
11.5 11.0 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 -1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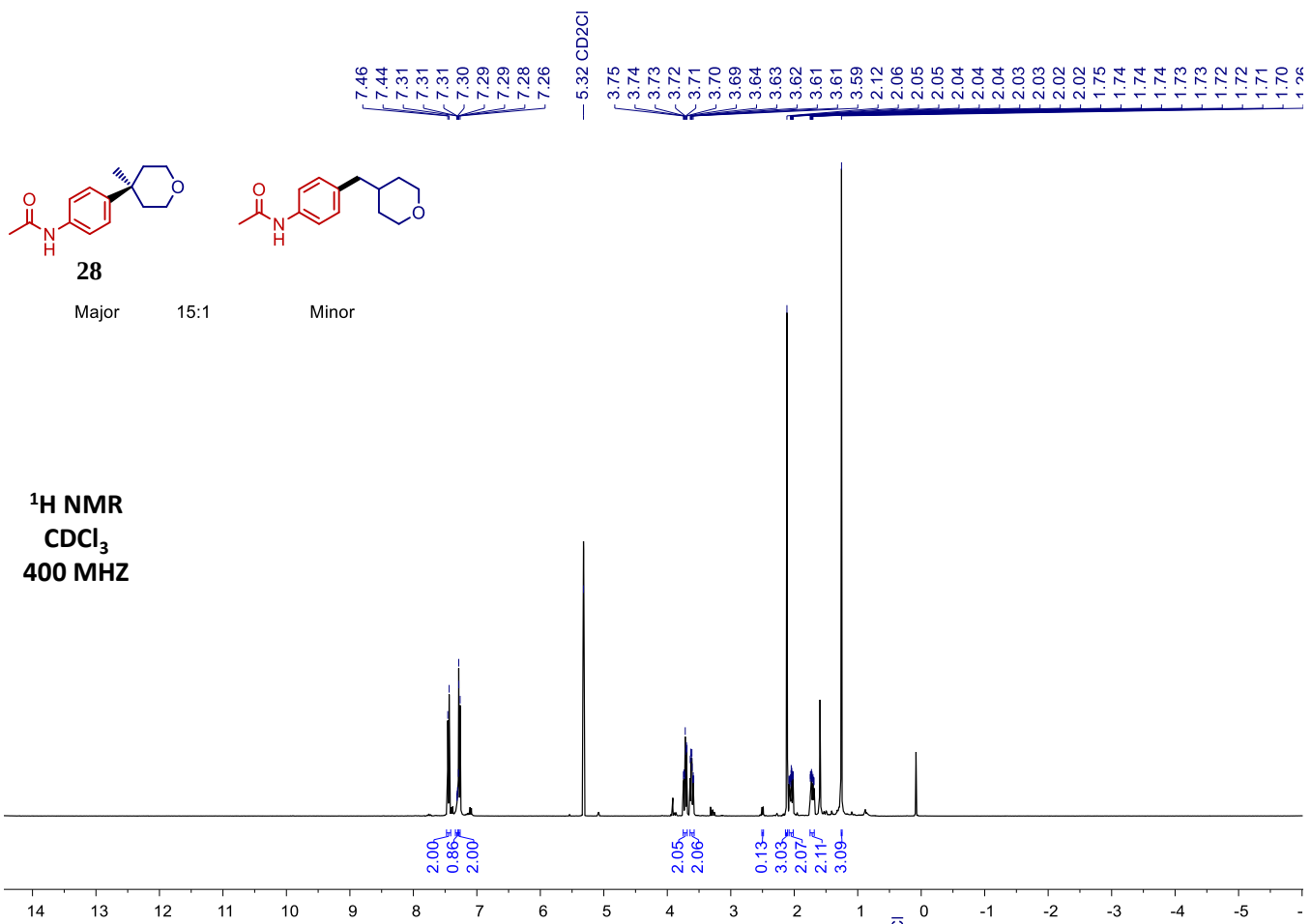
132.76
130.54
129.55
128.32
128.29
121.35
62.72
41.10
37.44
27.73
18.11
13C NMR
CDCl3
101 MHZ
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10


7.46
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7.30
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7.29
7.28
7.26
5.32 CD2Cl
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3.74
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3.71
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3.64
3.63
3.62
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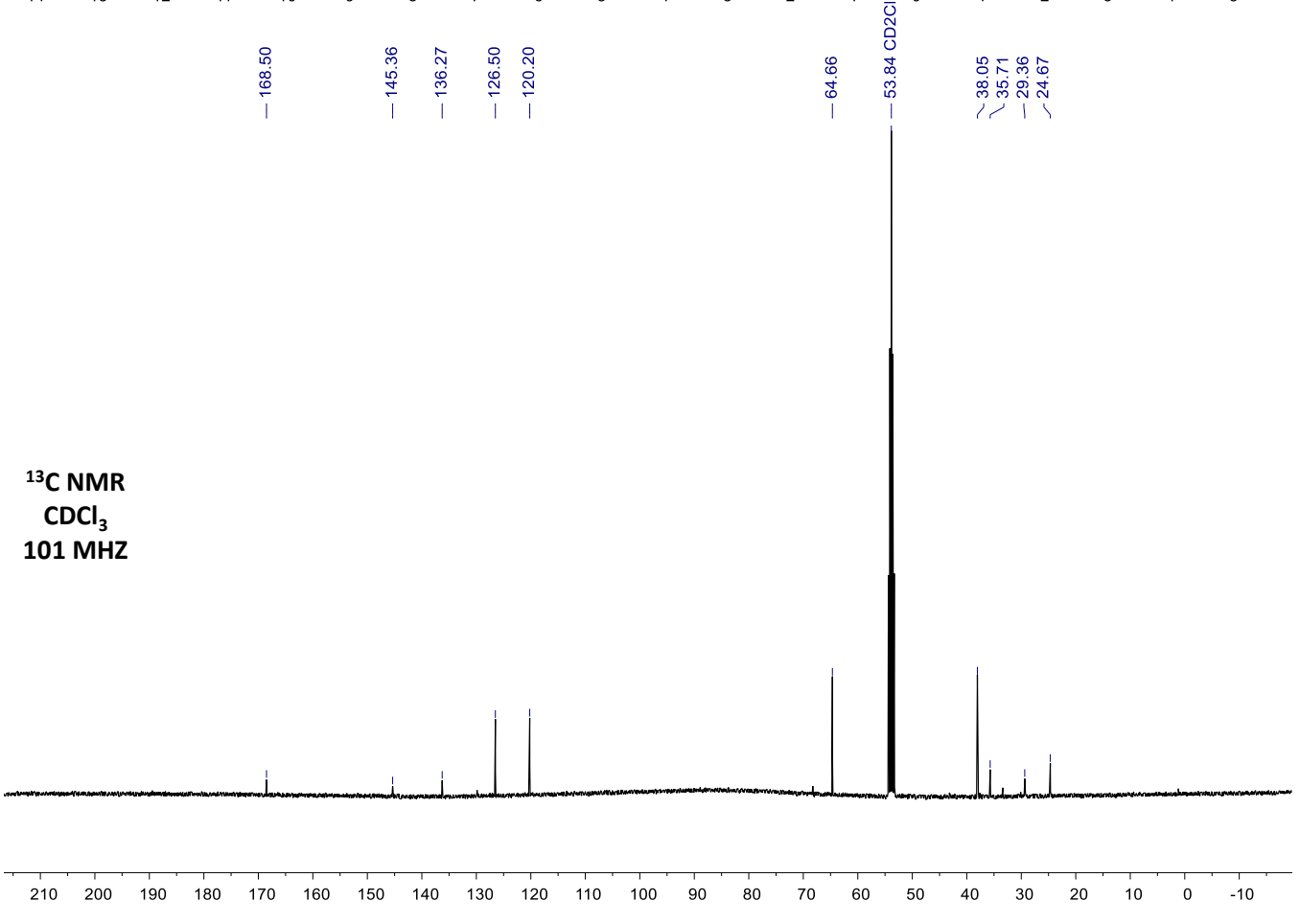
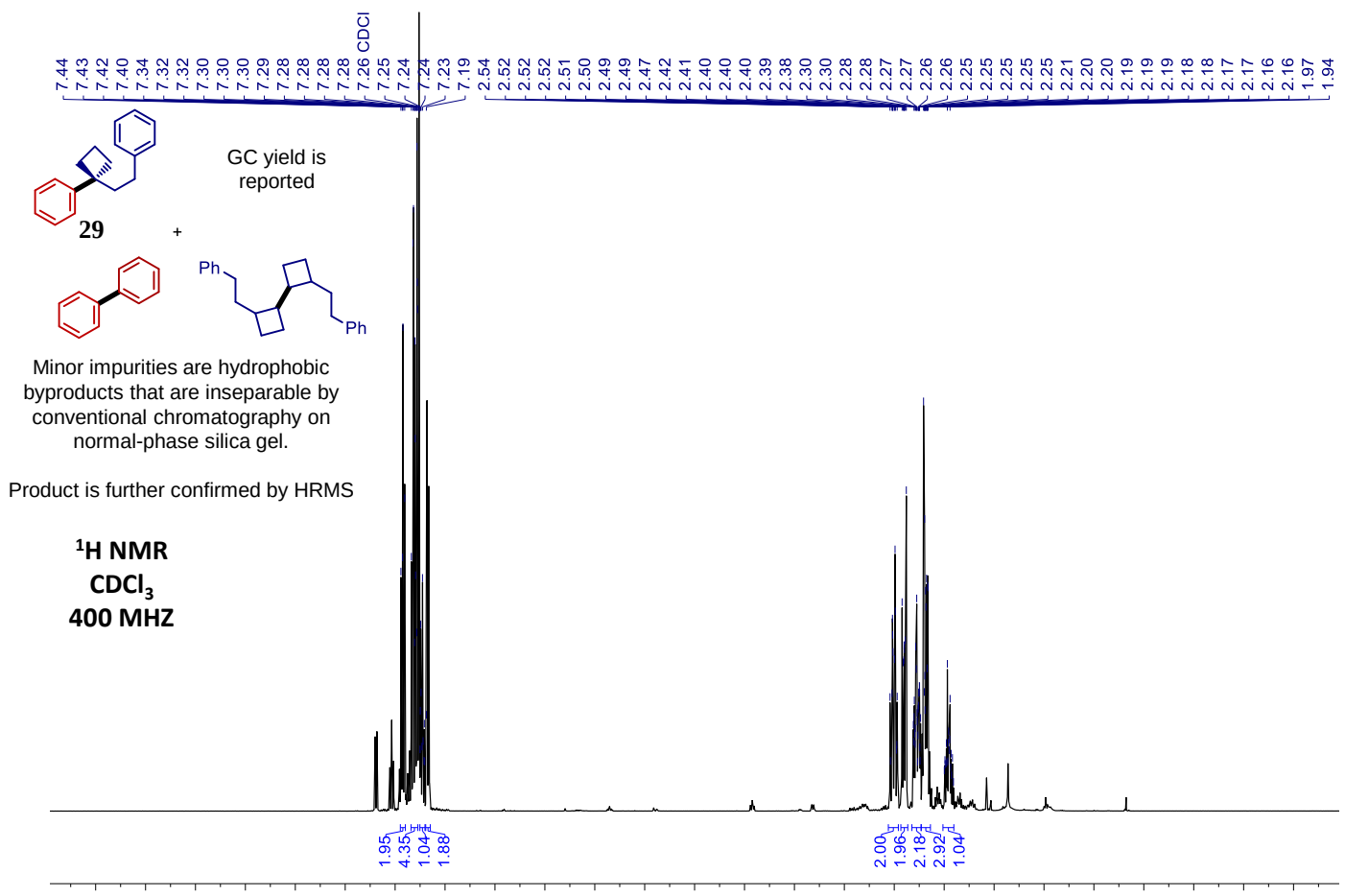
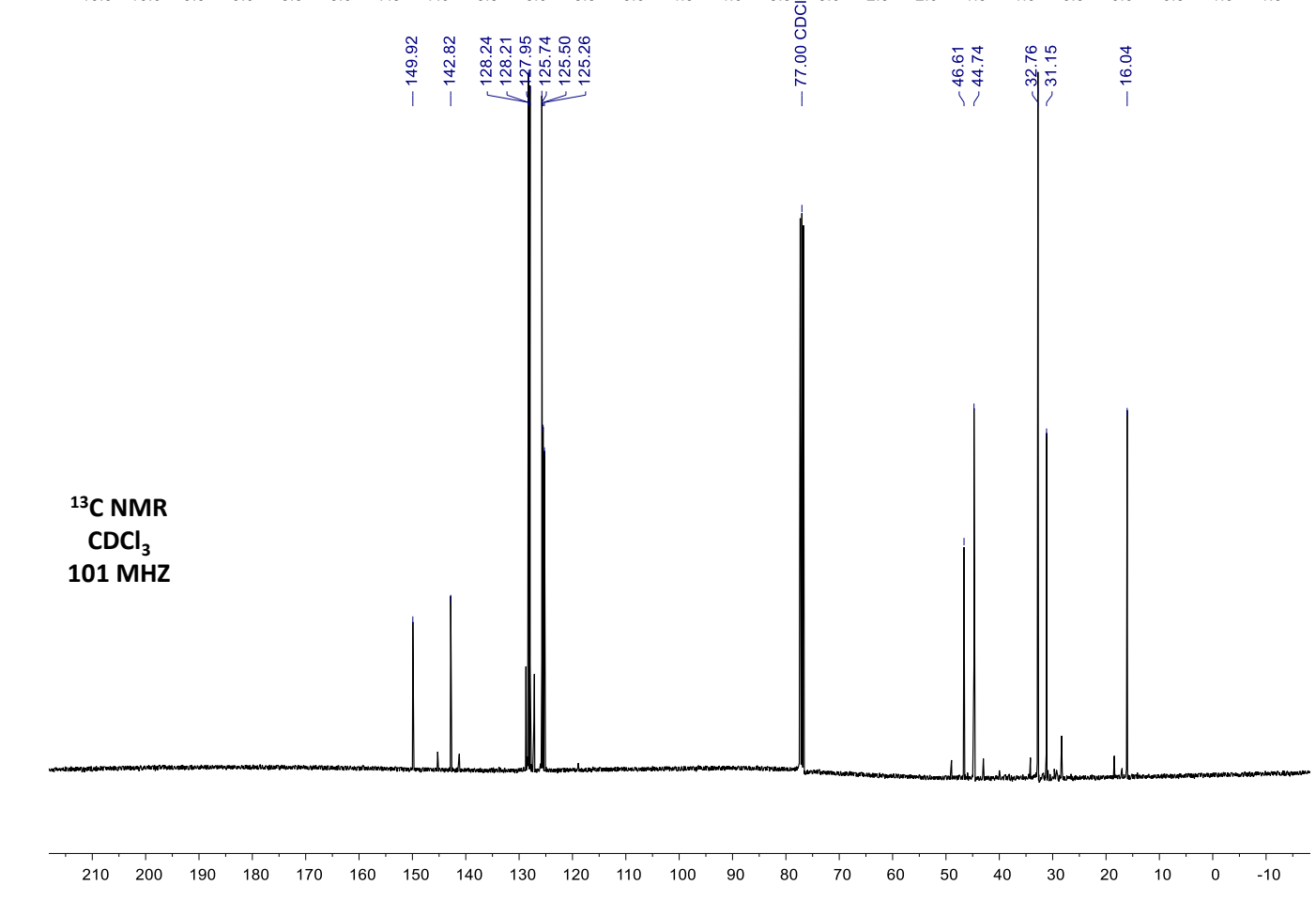
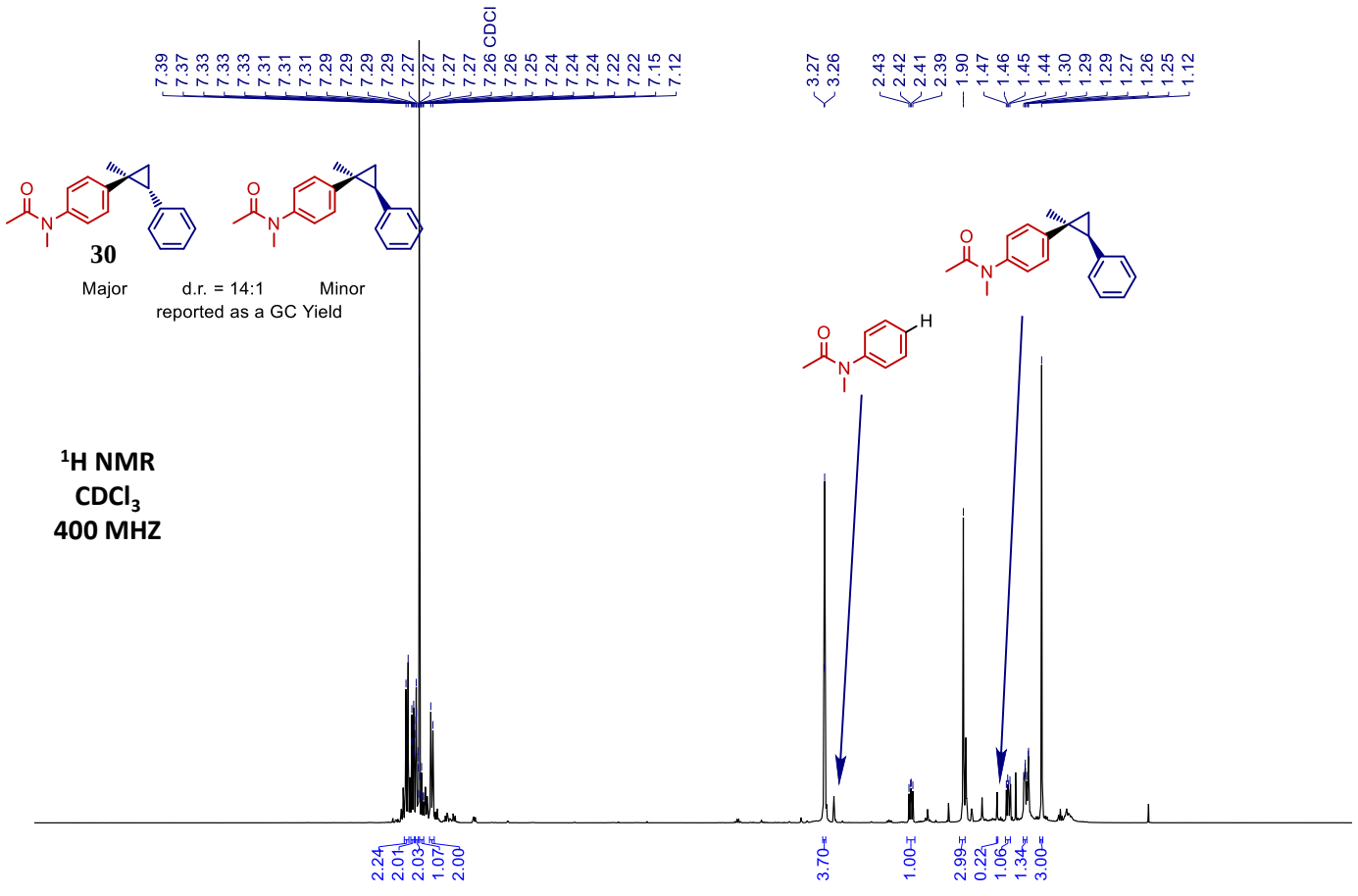
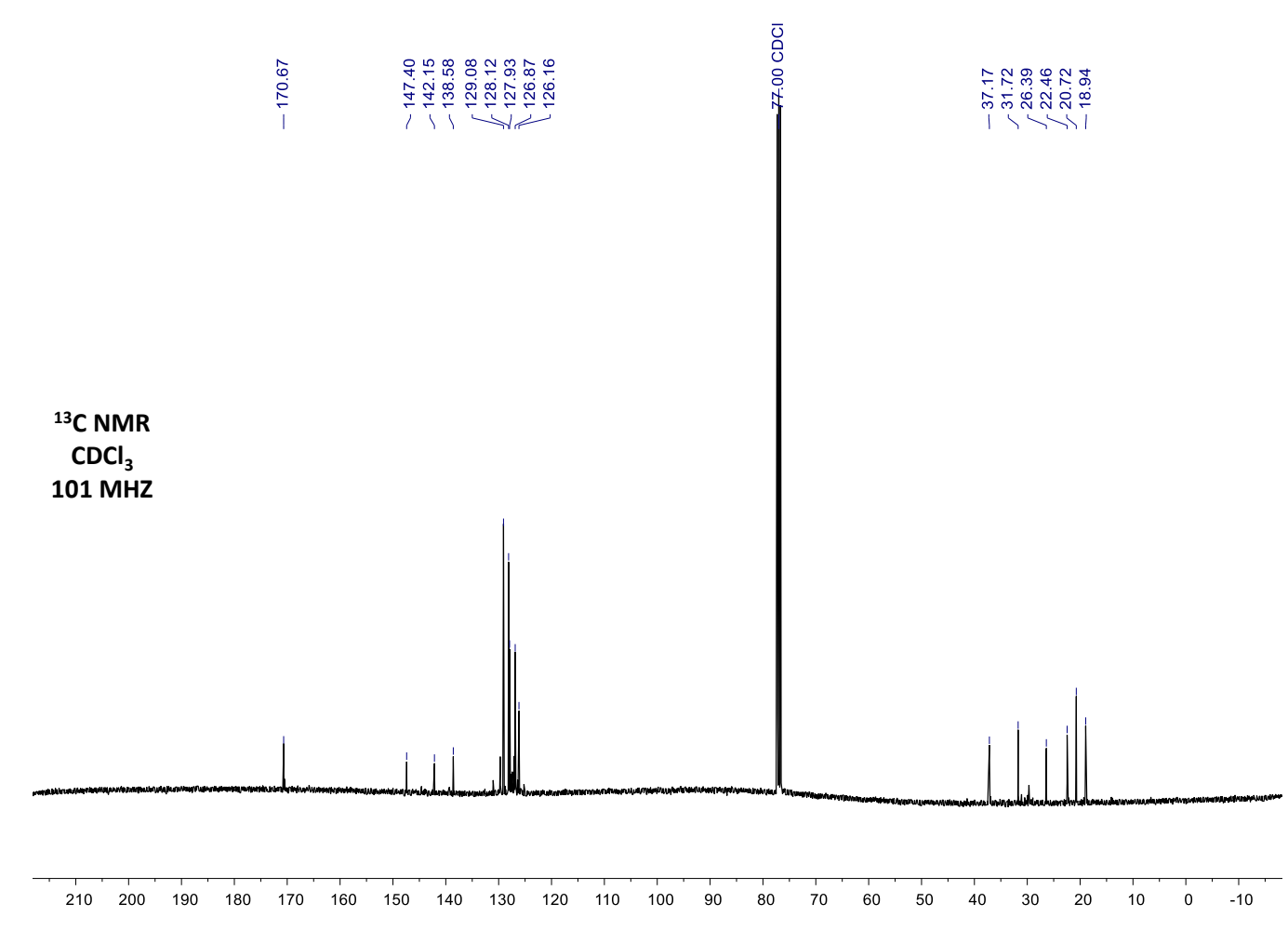
1.75
1.74
1.74
1.74
1.73
1.73
1.72
1.72
1.71
1.70
28
Major
15:1
Minor
1H NMR
CDCl3
400 MHZ
2.00
0.86
2.00
2.05
2.06
0.13
3.03
2.07
2.11
3.09
14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3 -4 -5


168.50
145.36
136.27
126.50
120.20
64.66
53.84 CD2Cl2
38.05
35.71
29.36
24.67
13C NMR
CDCl3
101 MHZ
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

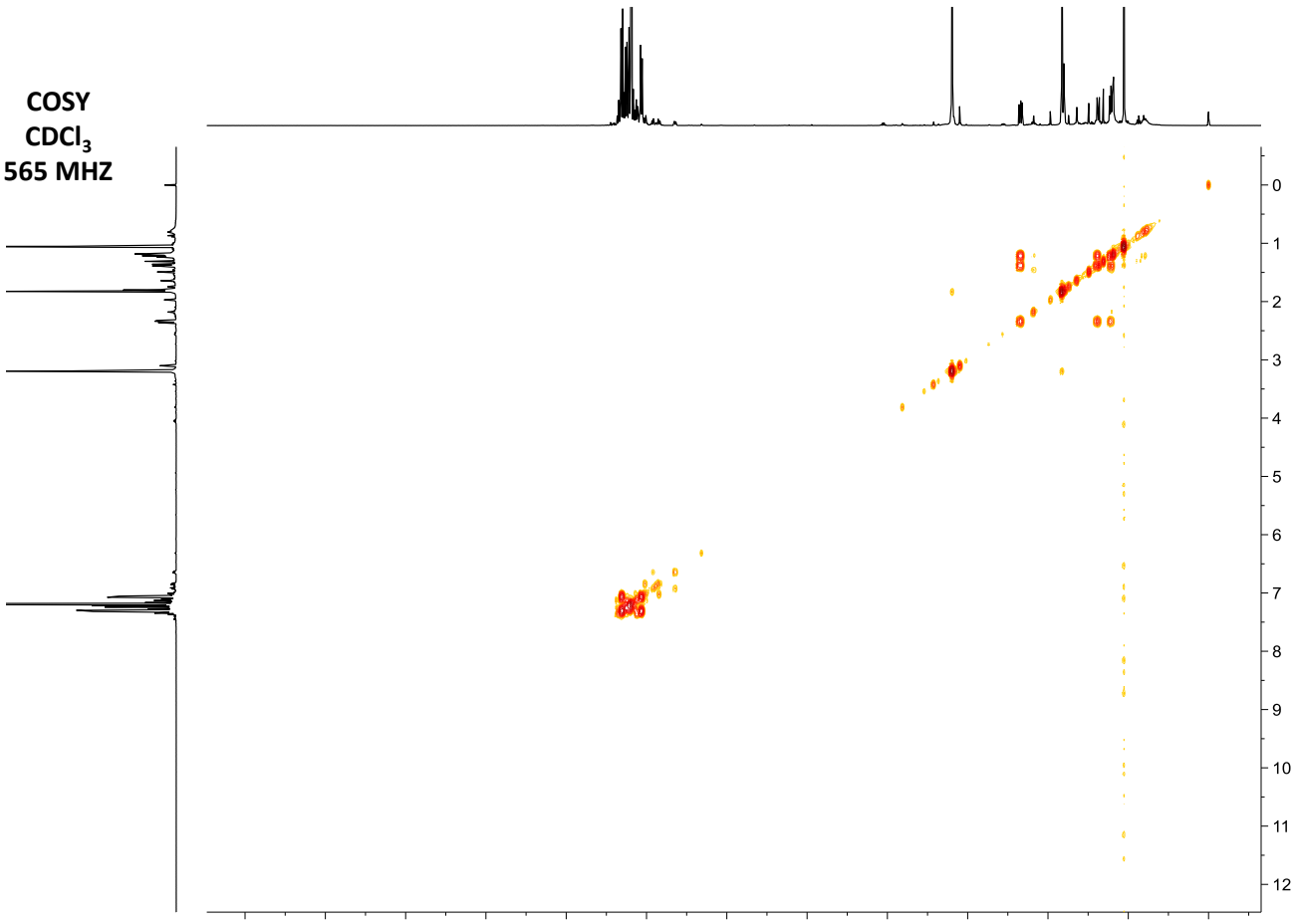

7.44 7.43 7.42 7.40 7.34 7.32 7.32 7.30 7.30 7.30 7.29 7.28 7.28 7.28 7.28 7.26 CDCl 7.25 7.24 7.24 7.23 7.19 2.54 2.52 2.52 2.52 2.51 2.50 2.49 2.49 2.47 2.42 2.41 2.40 2.40 2.40 2.39 2.38 2.30 2.30 2.28 2.28 2.27 2.27 2.26 2.26 2.25 2.25 2.25 2.25 2.25 2.21 2.20 2.20 2.19 2.19 2.19 2.18 2.18 2.17 2.17 2.16 2.16 1.97 1.94
GC yield is reported
29
+
Ph
Ph
Minor impurities are hydrophobic byproducts that are inseparable by conventional chromatography on normal-phase silica gel.
Product is further confirmed by HRMS
1H NMR
CDCl3
400 MHZ
1.95
4.35
1.04
1.88
2.00
1.96
2.18
2.92
1.04
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 -1.0 -1.5


149.92
142.82
128.24
128.21
127.95
125.74
125.50
125.26
77.00 CDCl3
46.61
44.74
32.76
31.15
16.04
13C NMR
CDCl3
101 MHZ
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

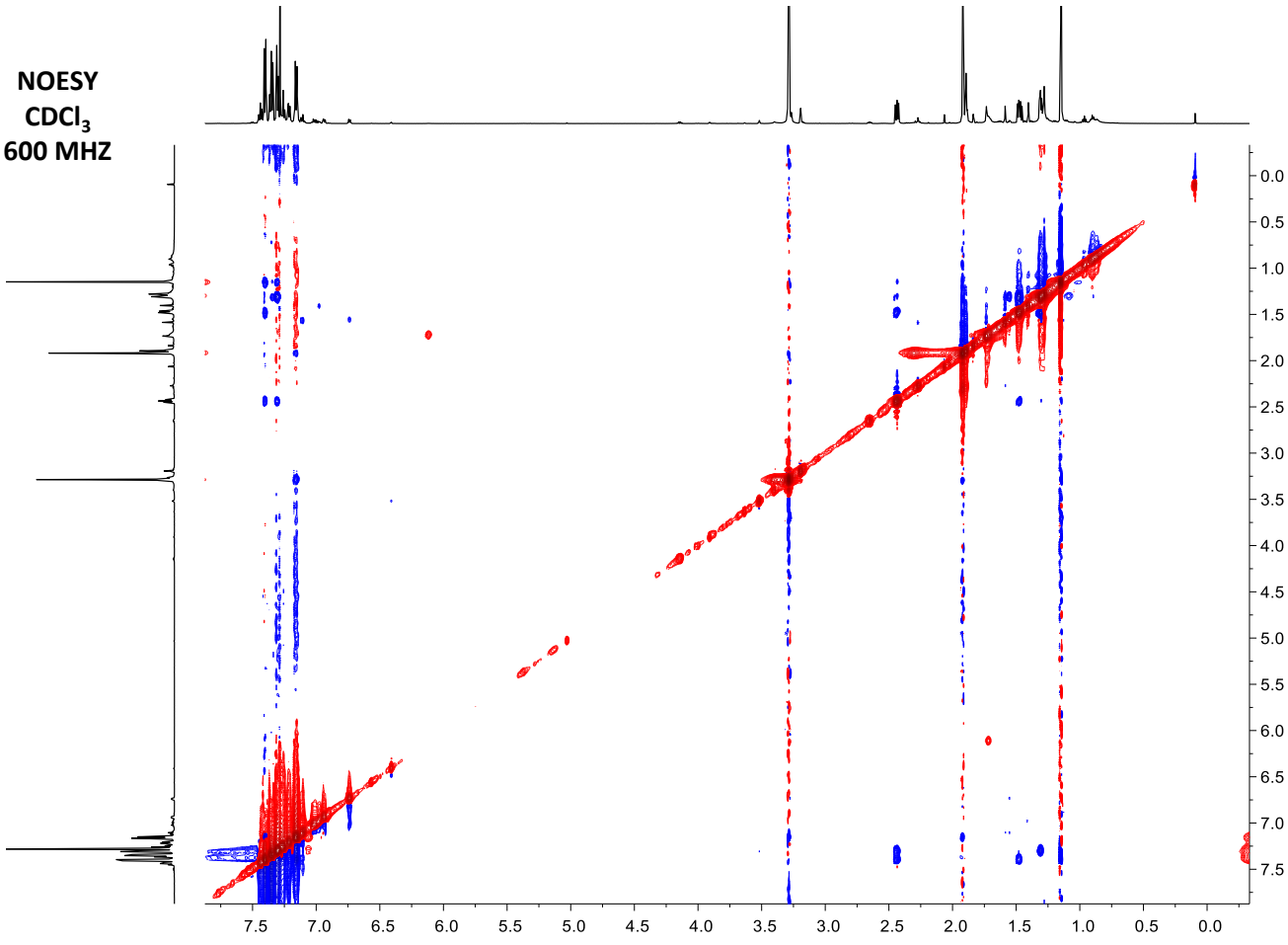

7.39 7.37 7.33 7.33 7.33 7.31 7.31 7.31 7.29 7.29 7.29 7.29 7.27 7.27 7.27 7.27 7.26 CDCl 7.26 7.25 7.24 7.24 7.24 7.22 7.22 7.15 7.12
3.27 3.26
2.43 2.42 2.41 2.39
1.90
1.47 1.46 1.45 1.44 1.30 1.29 1.29 1.27 1.26 1.25 1.12
30
Major
d.r. = 14:1
Minor
reported as a GC Yield
1H NMR
CDCl3
400 MHZ
2.24 2.01 2.03 1.07 2.00
3.70
1.00
2.99 0.22 1.06 1.34 3.00
1.0 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 -1.0 -1.5


170.67
147.40 142.15 138.58 129.08 128.12 127.93 126.87 126.16
77.00 CDCl
37.17 31.72 26.39 22.46 20.72 18.94
13C NMR
CDCl3
101 MHZ
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

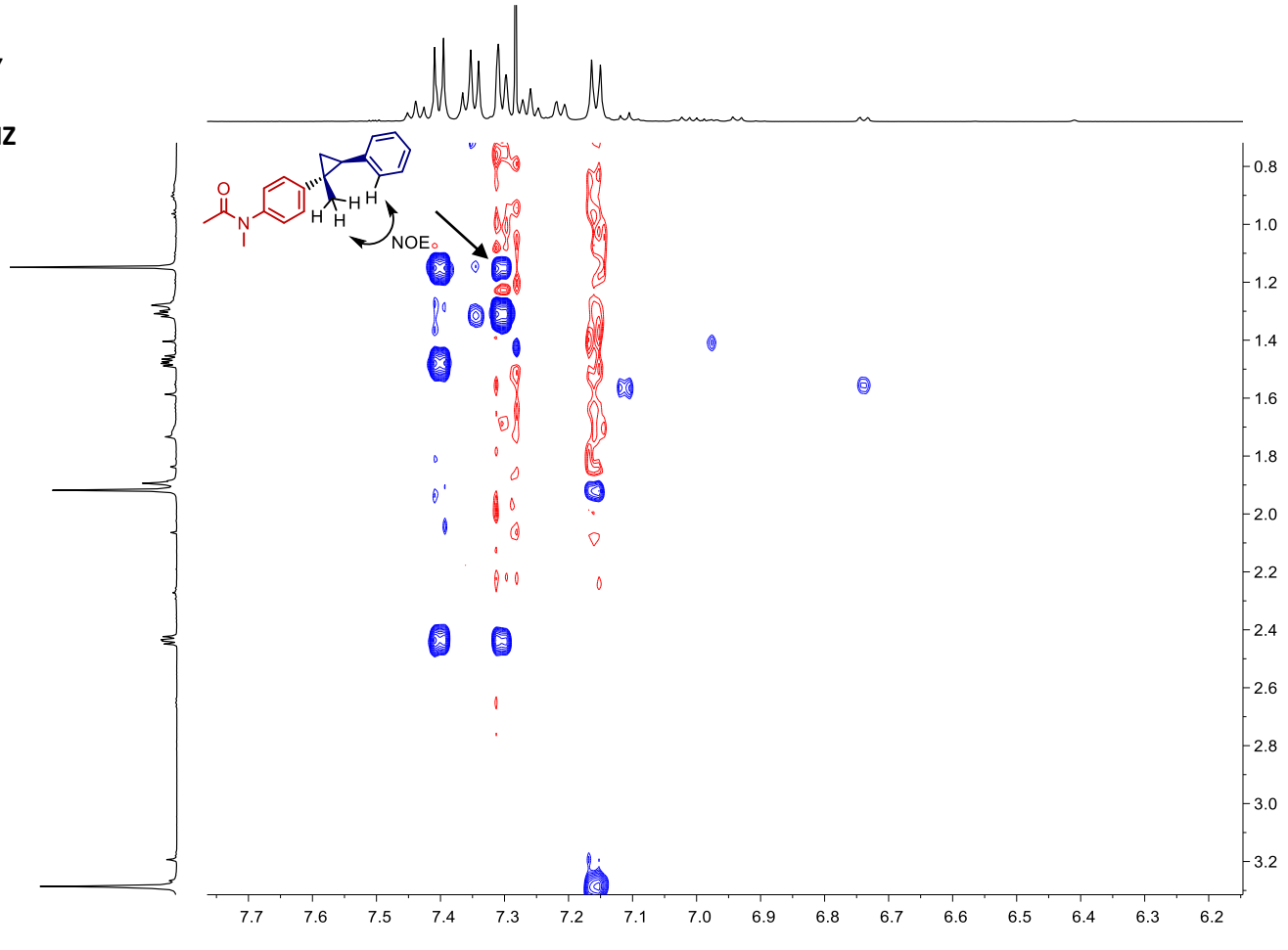
COSY
$CDCl_3$
565 MHZ

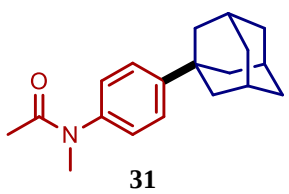


NOESY
$CDCl_3$
600 MHZ



NOESY
$CDCl_3$
600 MHZ

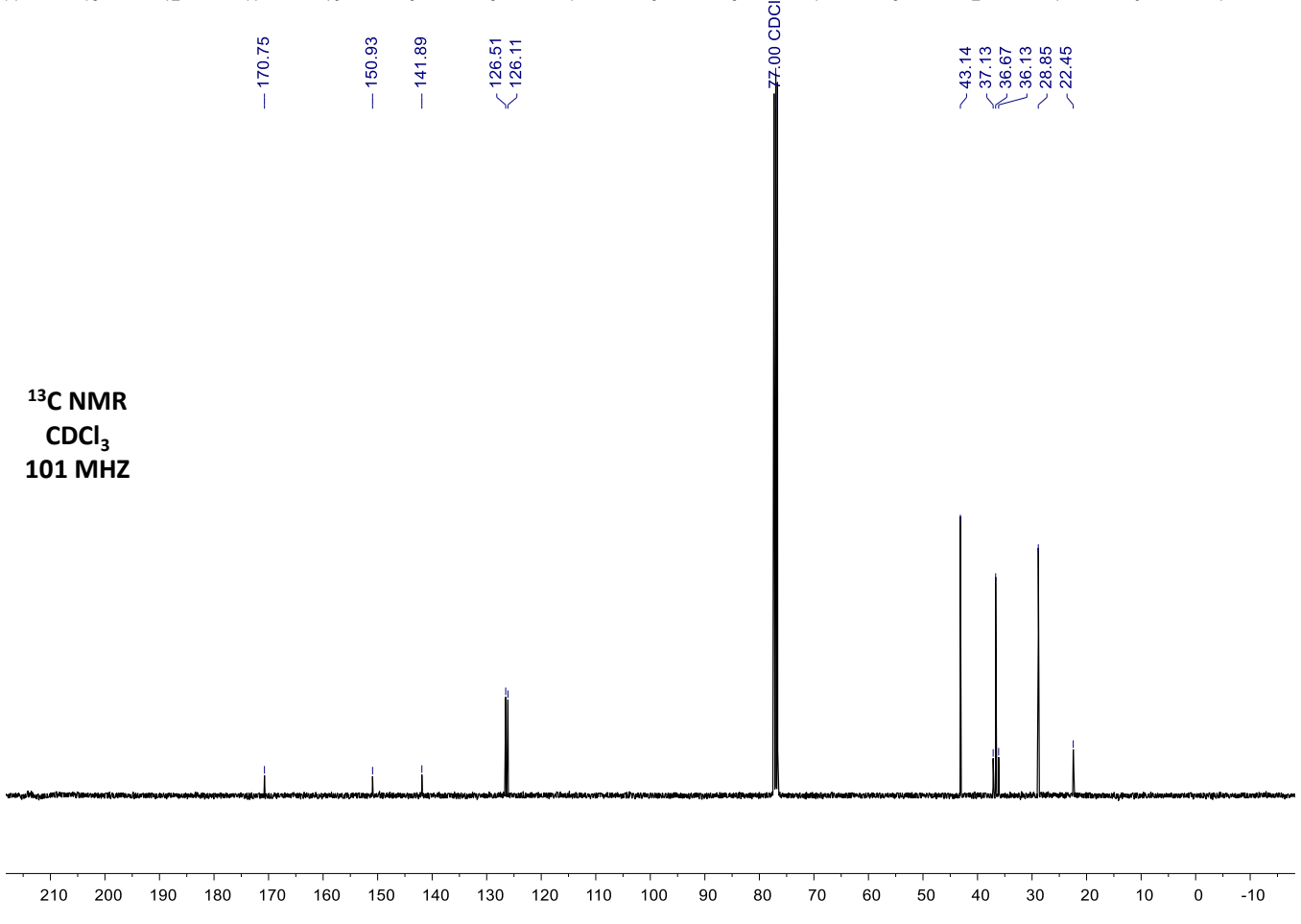


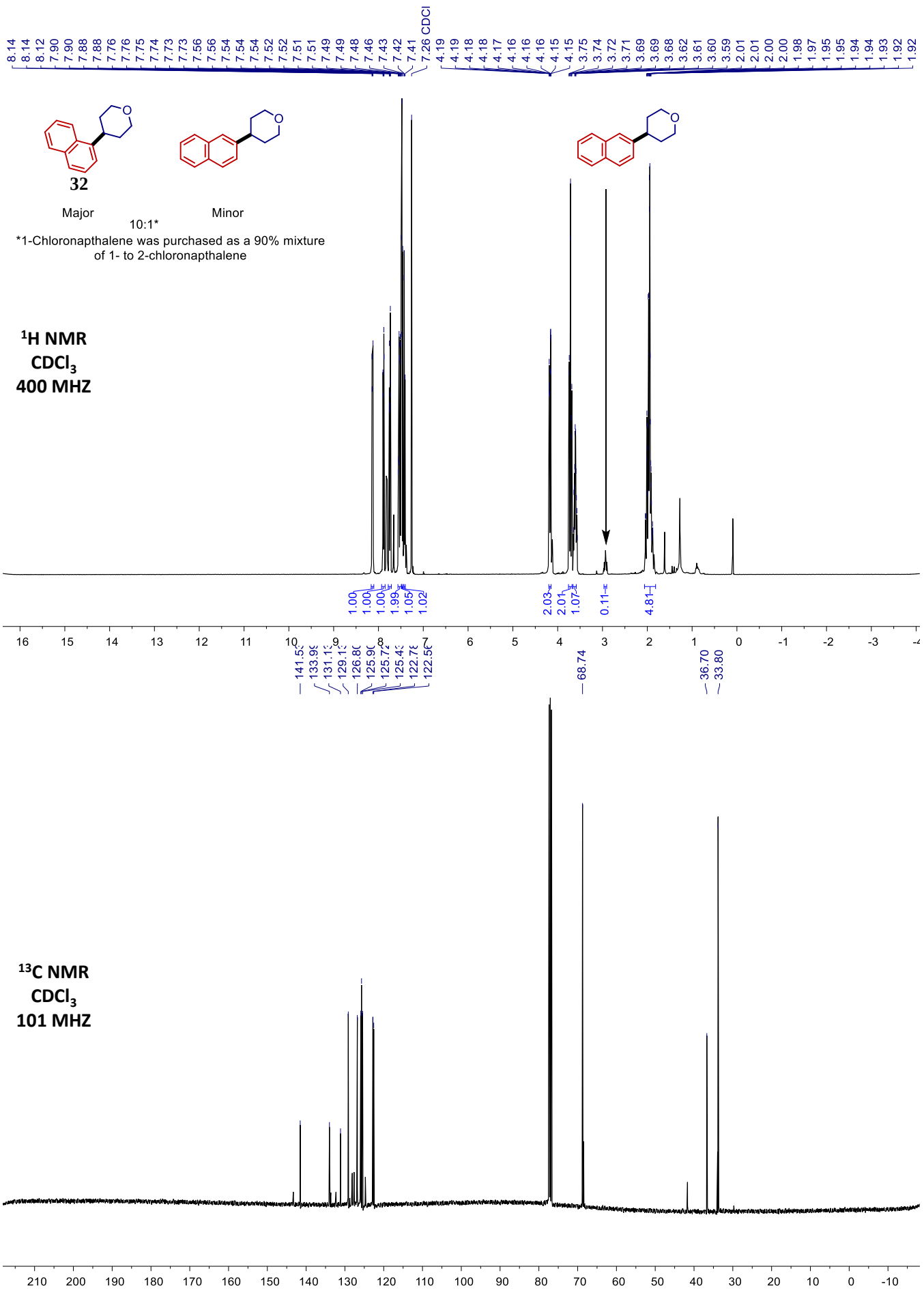


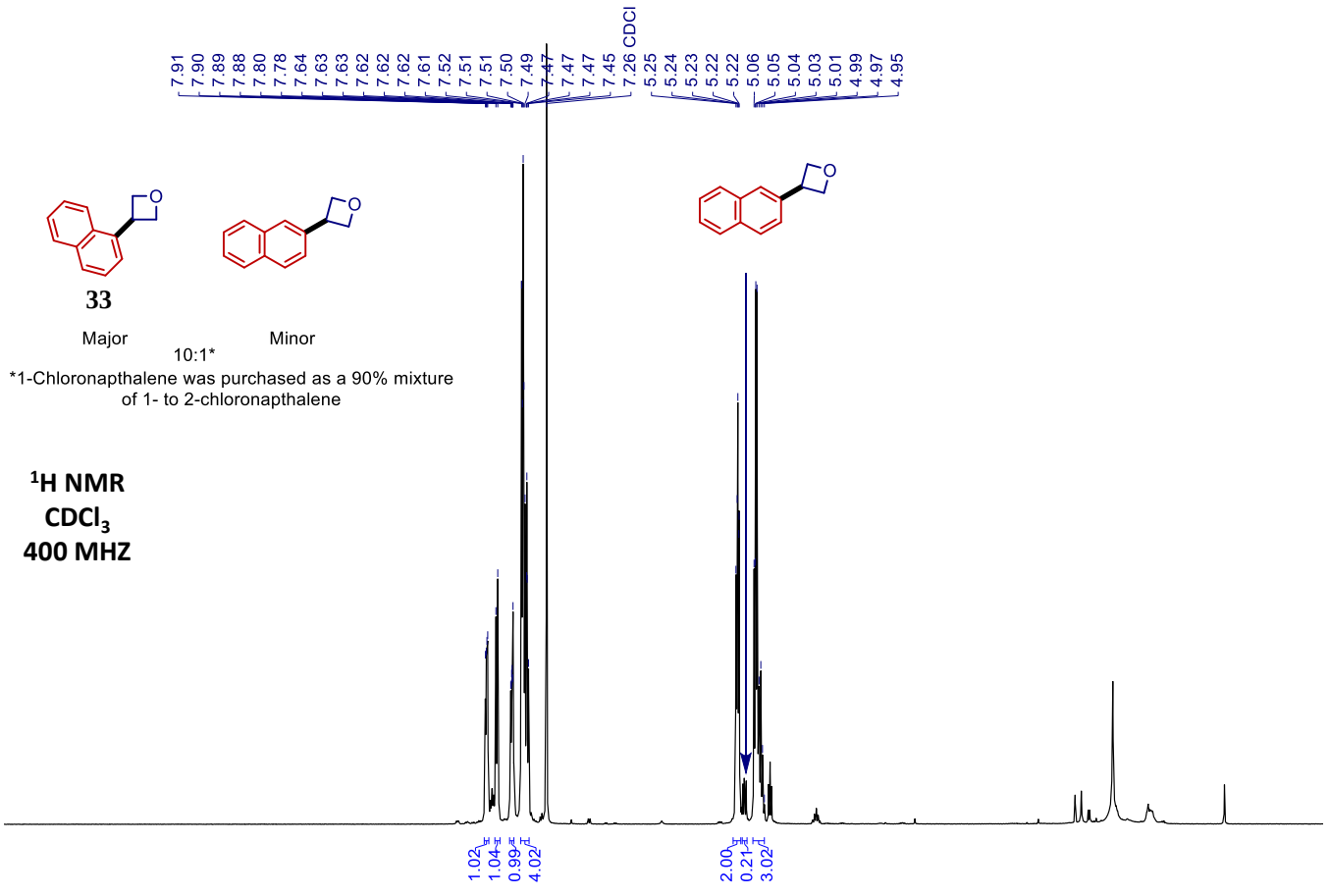
31

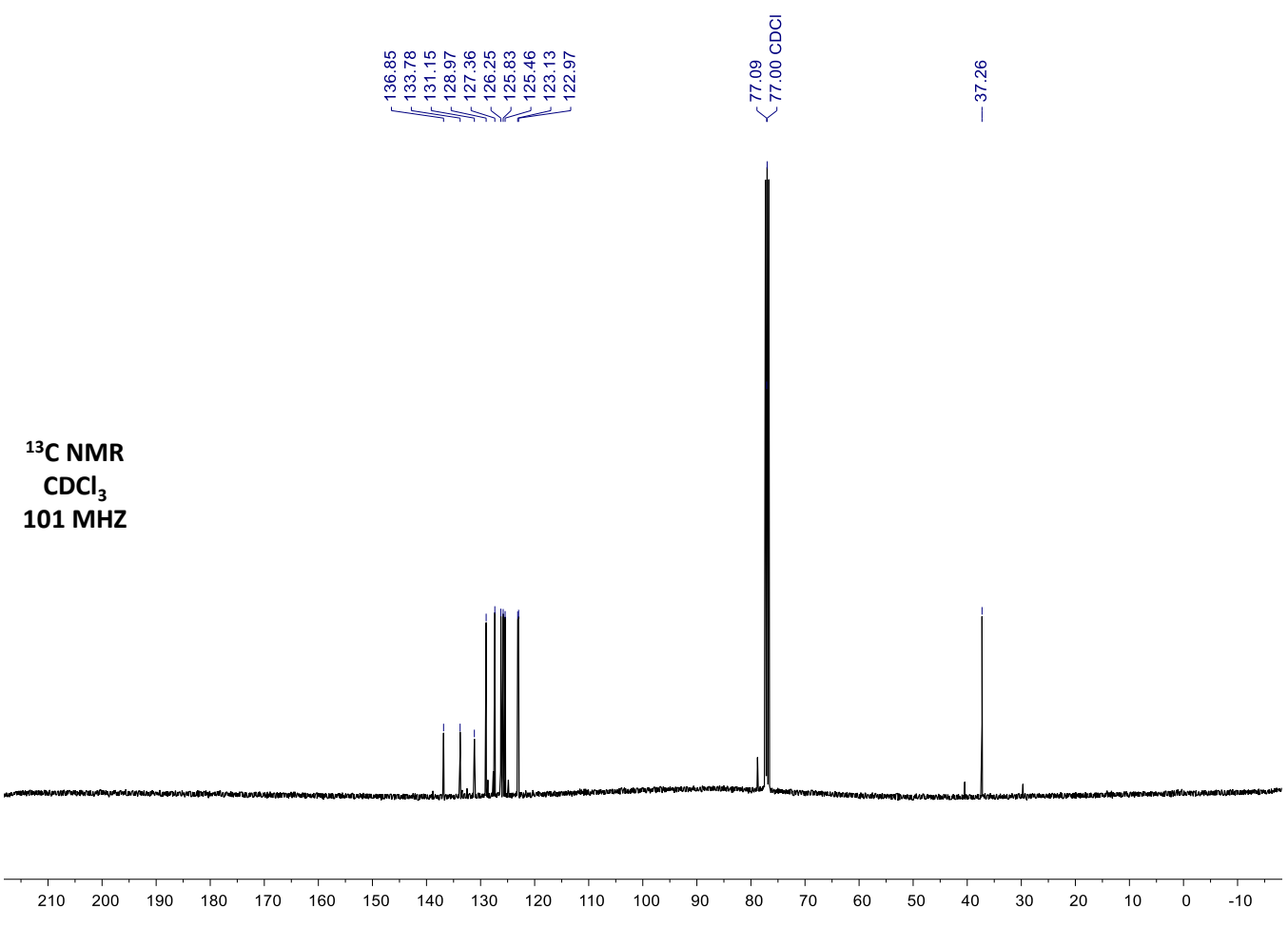
^{1}H NMR
$CDCl_3$
400 MHZ

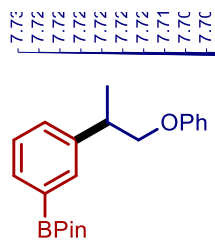
^{13}C NMR
$CDCl_3$
101 MHZ




32
Major
10:1*
Minor
*1-Chloronapthalene was purchased as a 90% mixture of 1- to 2-chloronapthalene
1H NMR
CDCl3
400 MHZ
13C NMR
CDCl3
101 MHZ


7.91
7.90
7.89
7.88
7.80
7.78
7.64
7.63
7.63
7.62
7.62
7.62
7.61
7.52
7.51
7.51
7.50
7.49
7.47
7.47
7.47
7.45
7.26 CDCl
5.25
5.24
5.23
5.22
5.22
5.06
5.05
5.04
5.03
5.01
4.99
4.97
4.95
33
Major
10:1*
Minor
*1-Chloronapthalene was purchased as a 90% mixture
of 1- to 2-chloronapthalene
1H NMR
CDCl3
400 MHZ
1.02
1.04
0.99
4.02
2.00
0.21
3.02
3.0 12.5 12.0 11.5 11.0 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

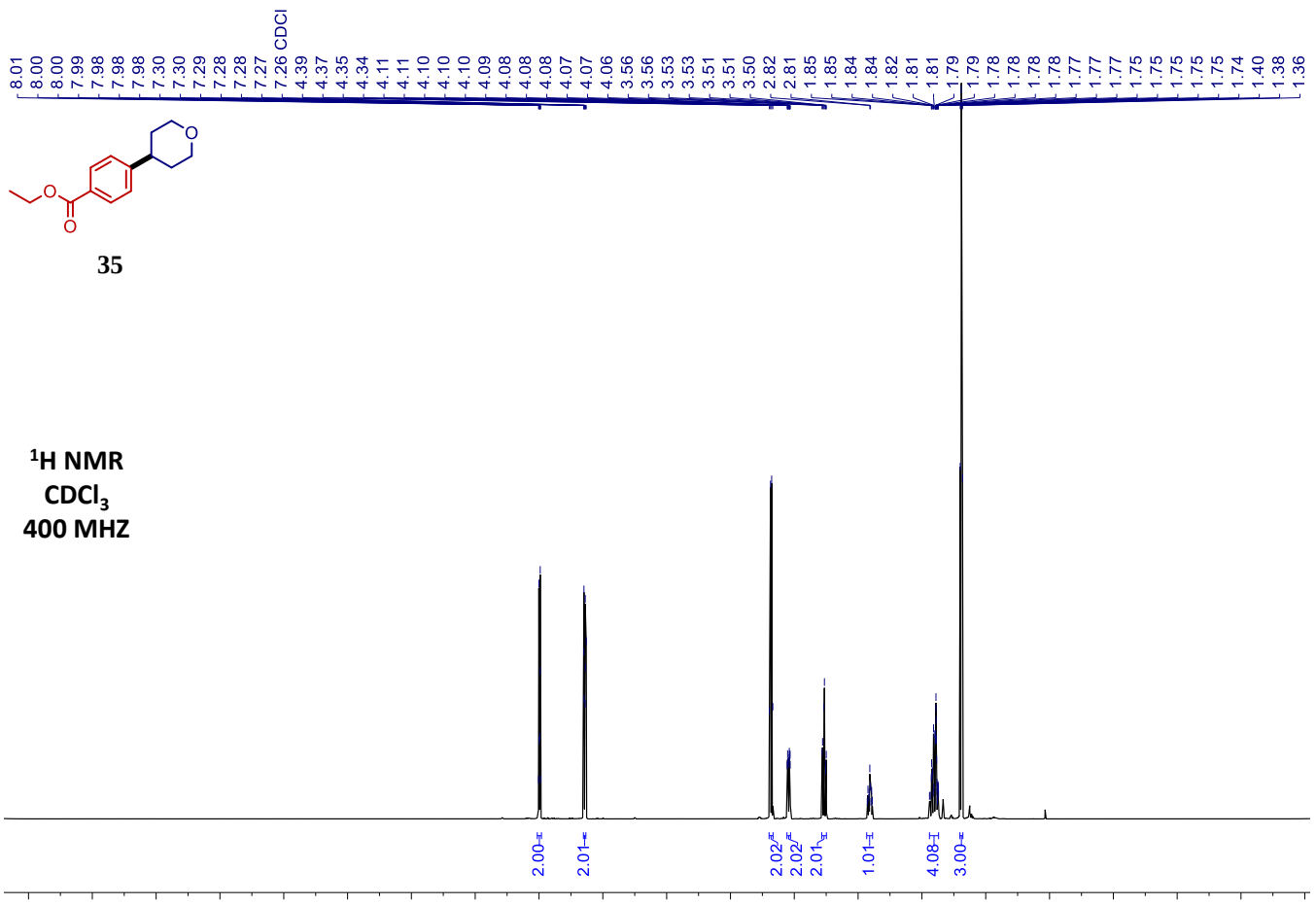

136.85
133.78
131.15
128.97
127.36
126.25
125.83
125.46
123.13
122.97
77.09
77.00 CDCl
37.26
13C NMR
CDCl3
101 MHZ
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

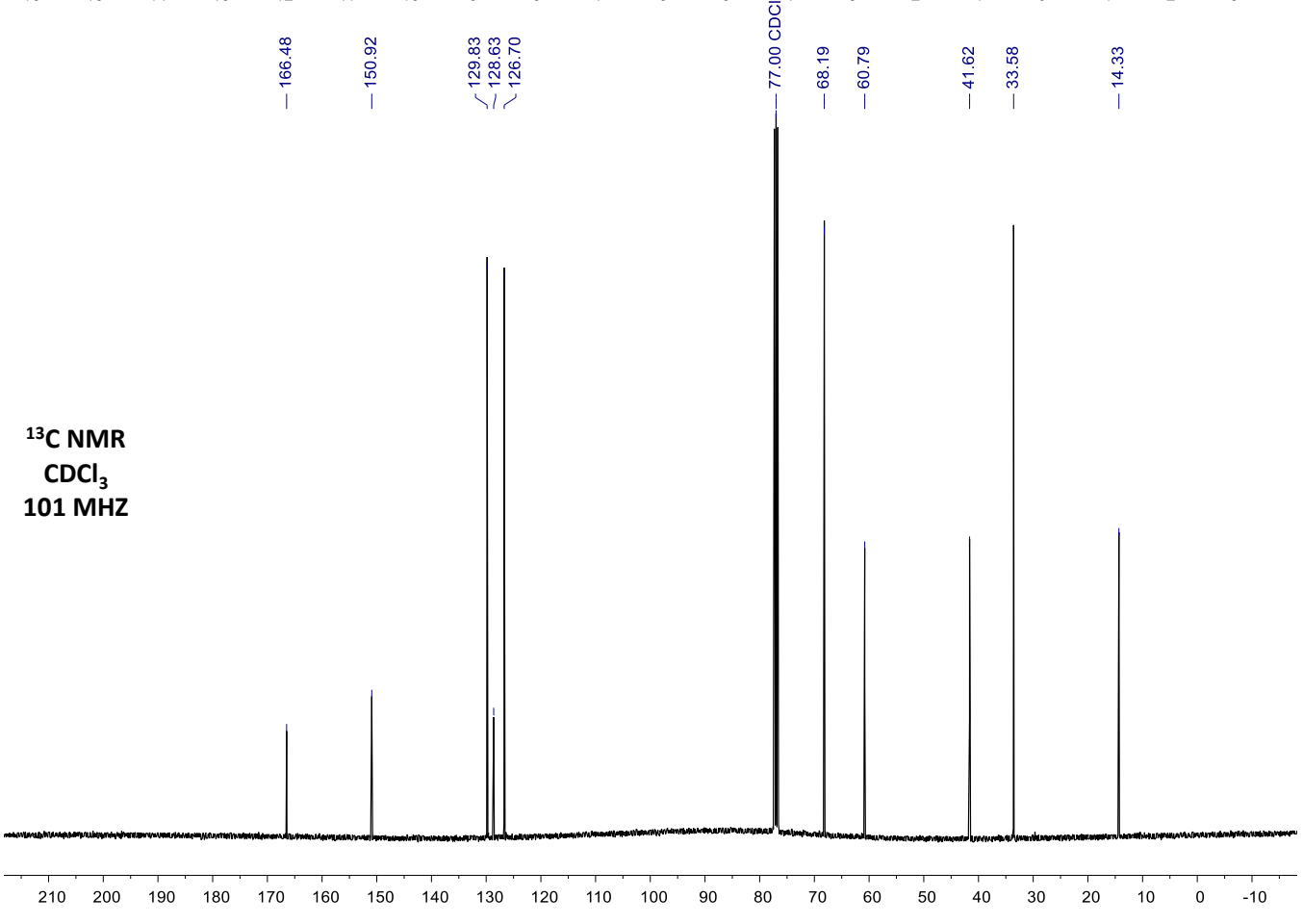


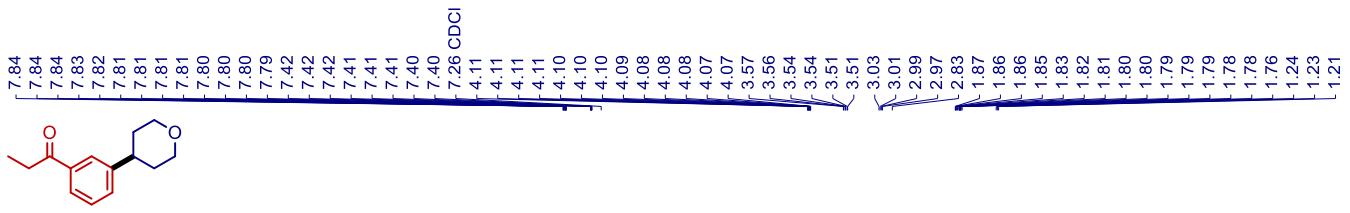
34

^{1}H NMR
$CDCl_3$
400 MHZ

^{13}C NMR
$CDCl_3$
101 MHZ

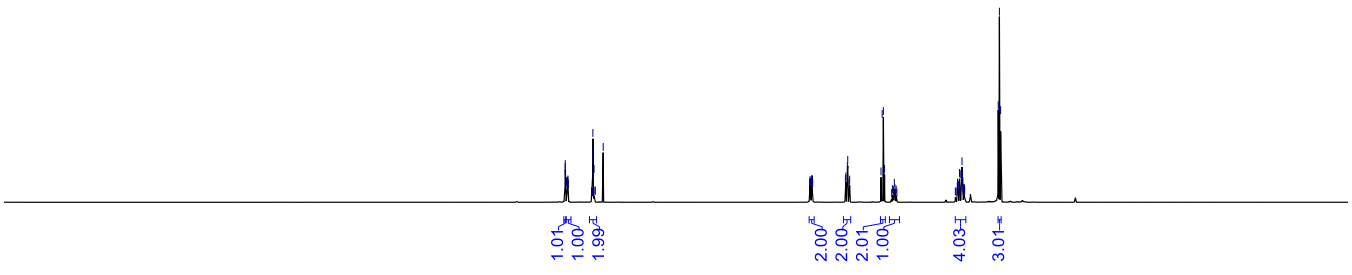

8.01 8.00 8.00 7.99 7.98 7.98 7.98 7.30 7.30 7.29 7.28 7.28 7.27 7.26 CDCl 4.39 4.37 4.35 4.34 4.11 4.11 4.10 4.10 4.10 4.09 4.08 4.08 4.08 4.07 4.07 4.06 3.56 3.56 3.53 3.53 3.51 3.51 3.50 2.82 2.81 1.85 1.85 1.84 1.84 1.82 1.81 1.81 1.79 1.79 1.78 1.78 1.78 1.78 1.77 1.77 1.77 1.75 1.75 1.75 1.75 1.74 1.40 1.38 1.36
35
1H NMR
CDCl3
400 MHZ
2.00 2.01 2.02 2.02 2.01 1.01 4.08 3.00
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3


166.48 150.92 129.83 128.63 126.70 77.00 CDCl3 68.19 60.79 41.62 33.58 14.33
13C NMR
CDCl3
101 MHZ
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

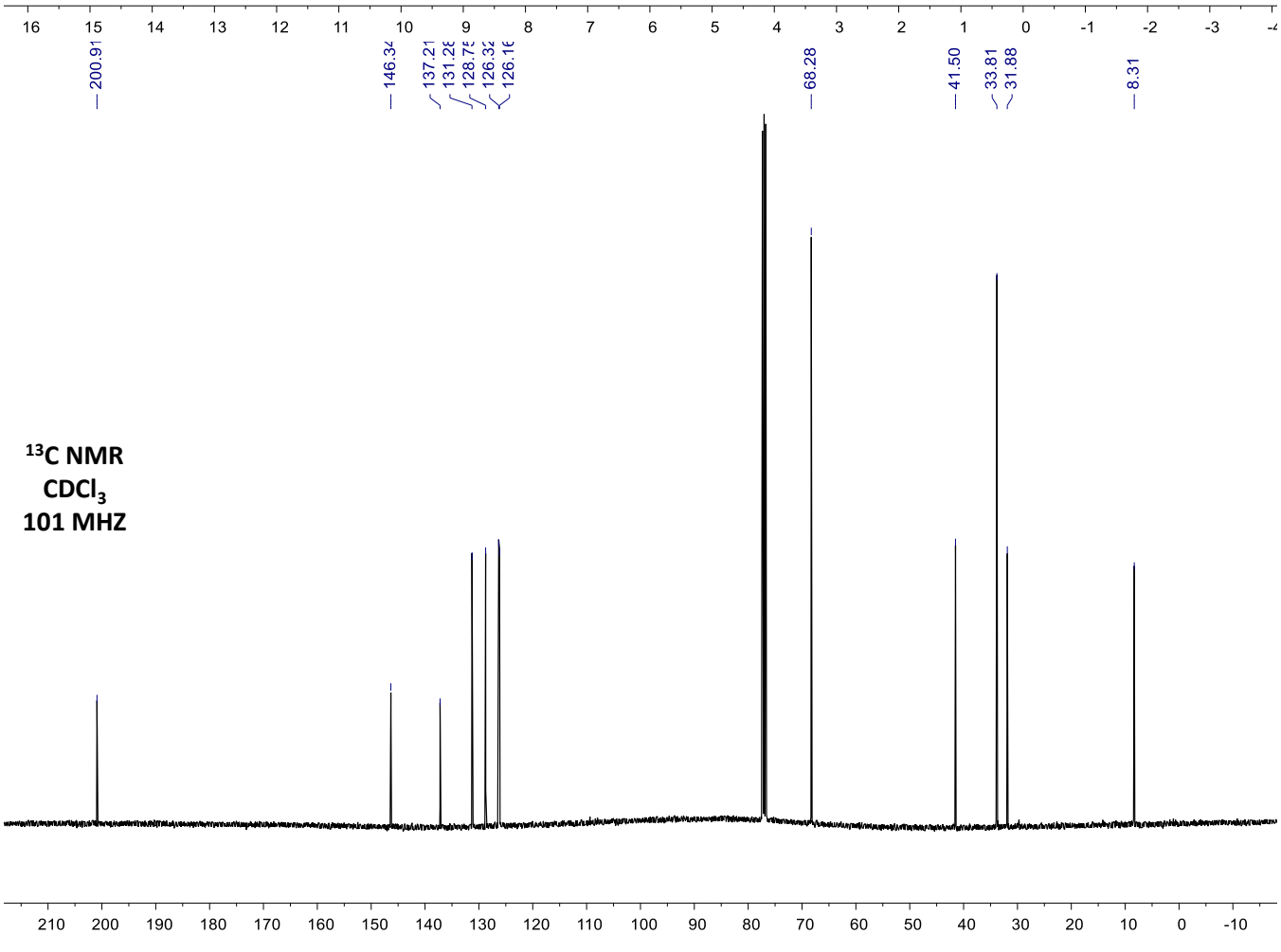


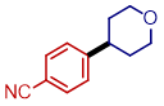
36

^{1}H NMR
$CDCl_3$
400 MHZ



^{13}C NMR
$CDCl_3$
101 MHZ

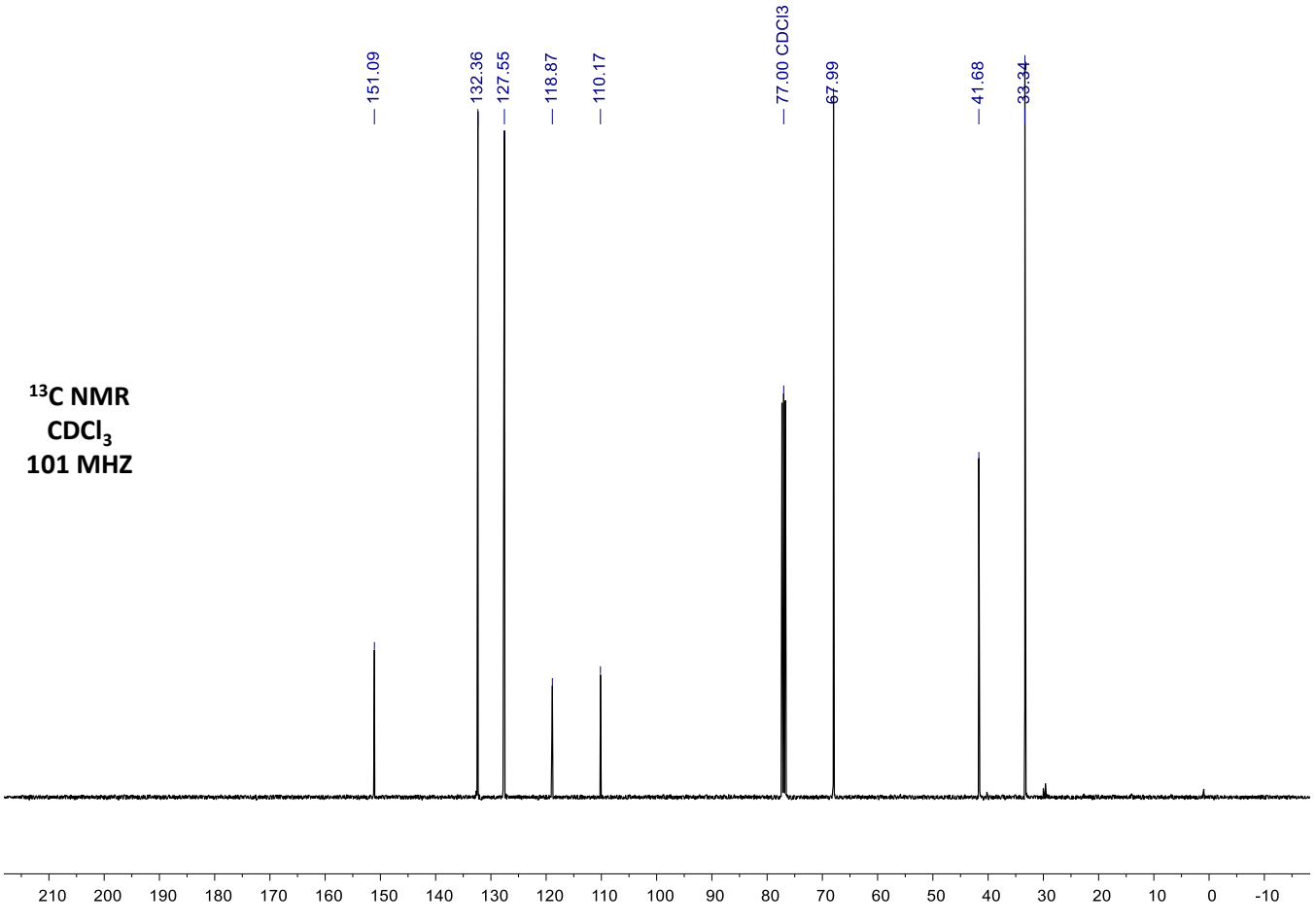


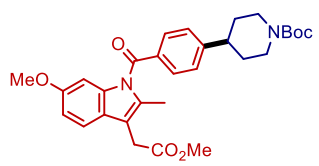


37

^{1}H NMR
$CDCl_3$
400 MHZ

^{13}C NMR
$CDCl_3$
101 MHZ

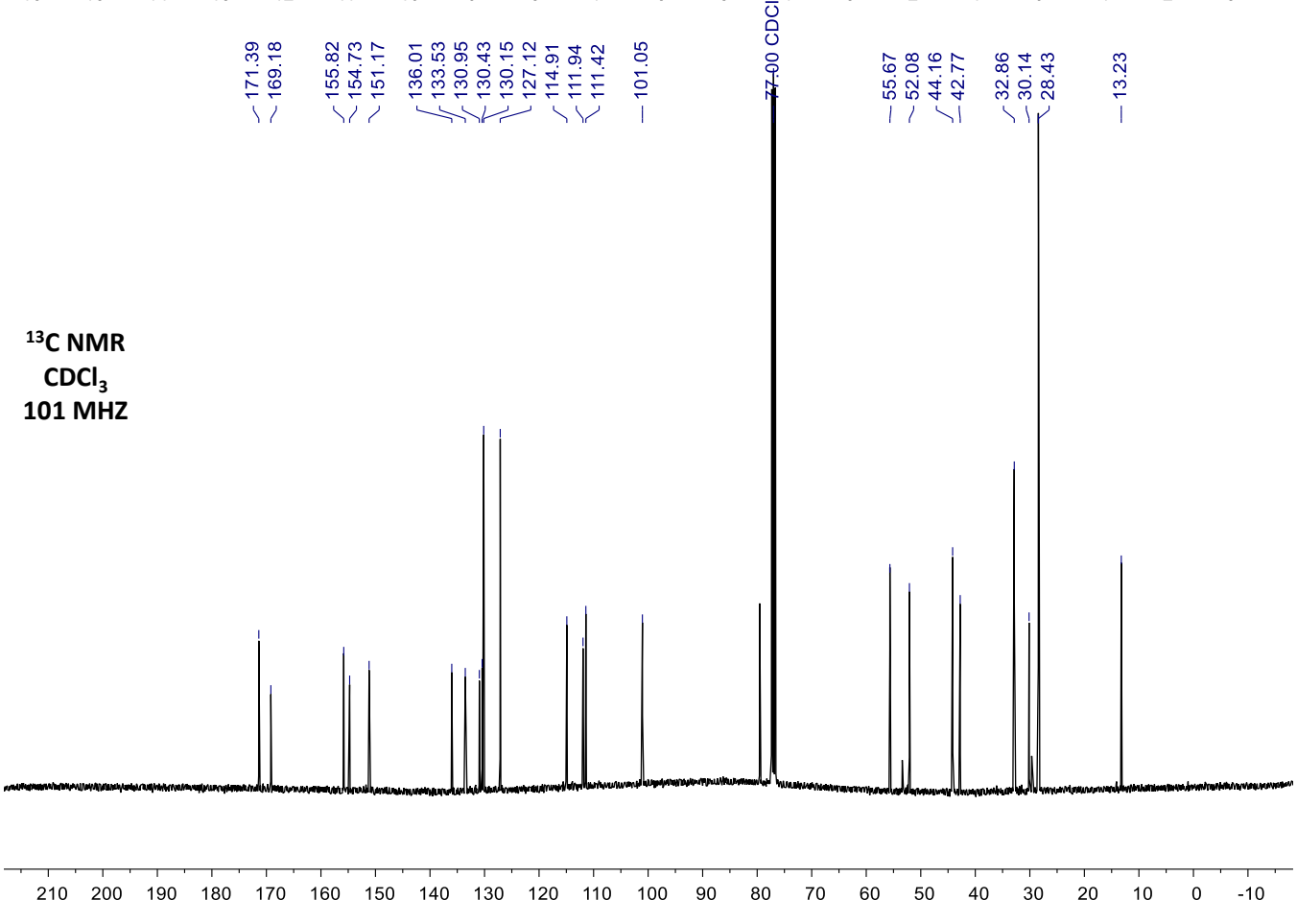


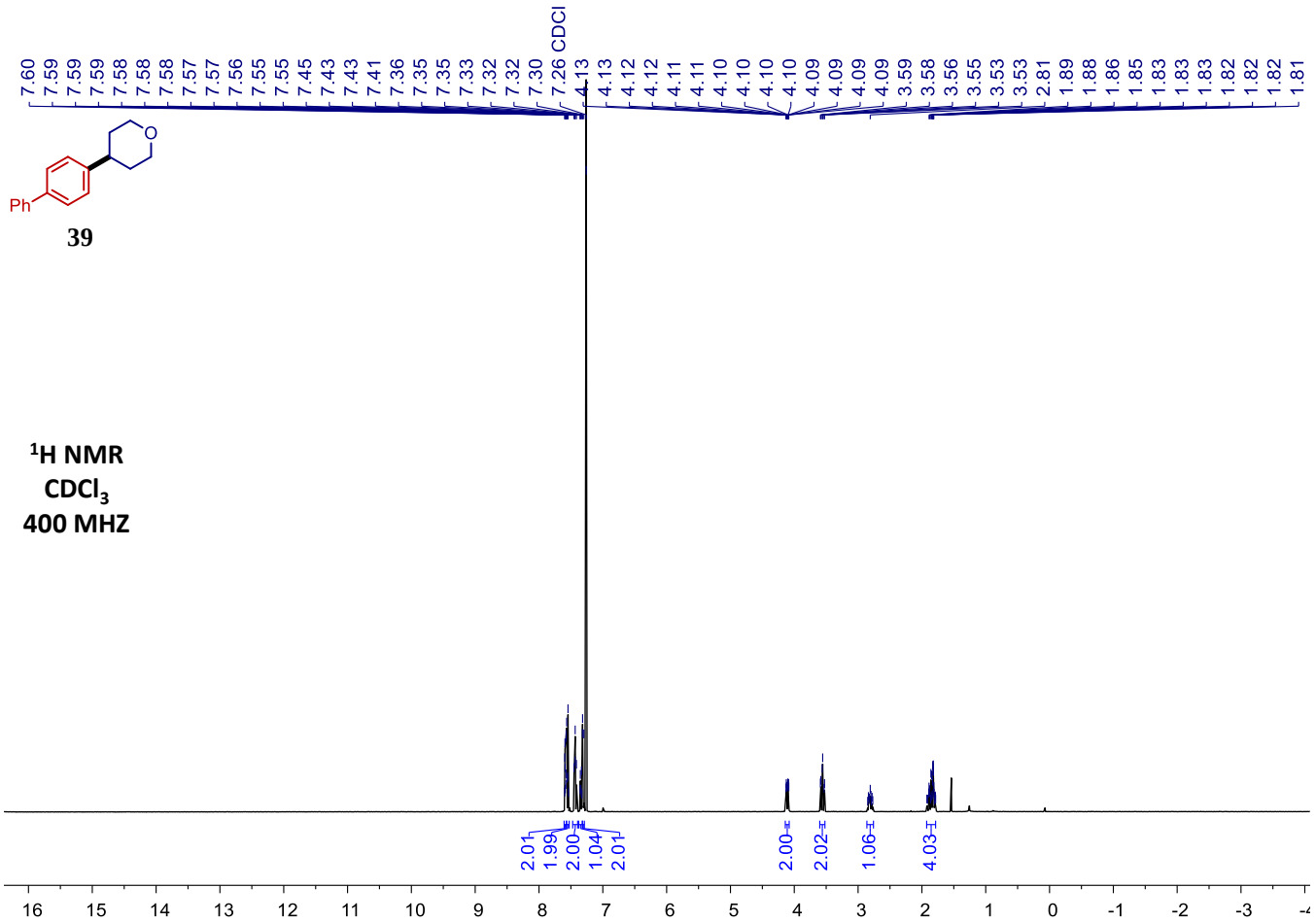


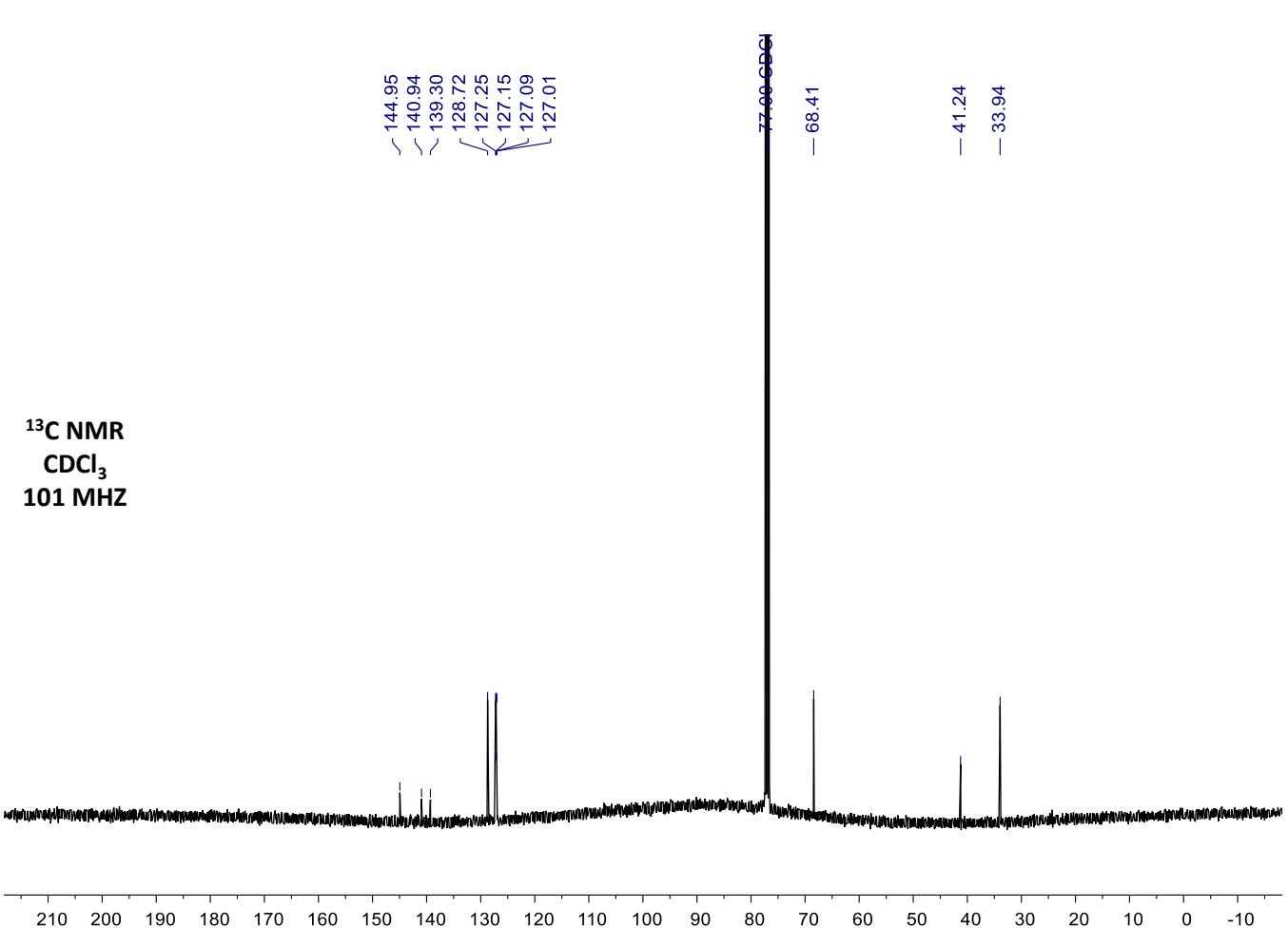
38

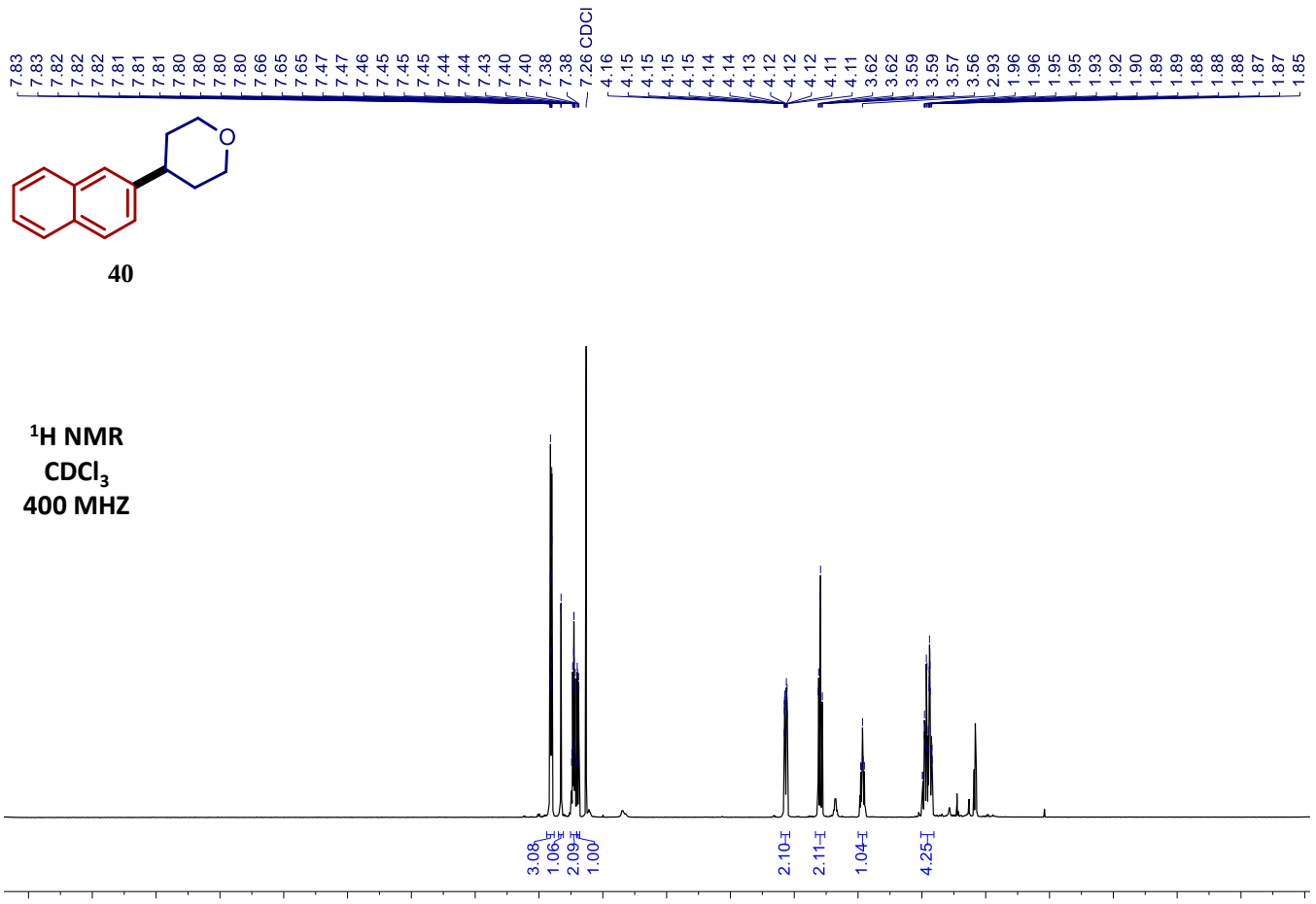
^{1}H NMR
$CDCl_3$
400 MHZ

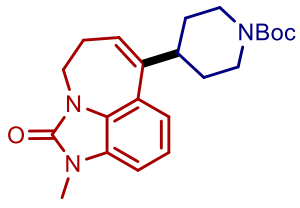
^{13}C NMR
$CDCl_3$
101 MHZ




7.60 7.59 7.59 7.59 7.58 7.58 7.58 7.57 7.57 7.56 7.55 7.55 7.45 7.43 7.43 7.41 7.36 7.35 7.35 7.33 7.32 7.32 7.30 7.26 CDCl 4.13 4.13 4.12 4.12 4.11 4.11 4.10 4.10 4.10 4.10 4.09 4.09 4.09 4.09 3.59 3.58 3.56 3.55 3.53 3.53 2.81 1.89 1.88 1.86 1.85 1.83 1.83 1.83 1.82 1.82 1.82 1.81
Ph
O
39
1H NMR
CDCl3
400 MHZ
2.01 1.99 2.00 1.04 2.01 2.00 2.02 1.06 4.03
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3


144.95 140.94 139.30 128.72 127.25 127.15 127.09 127.01 77.00 CDCl 68.41 41.24 33.94
13C NMR
CDCl3
101 MHZ
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

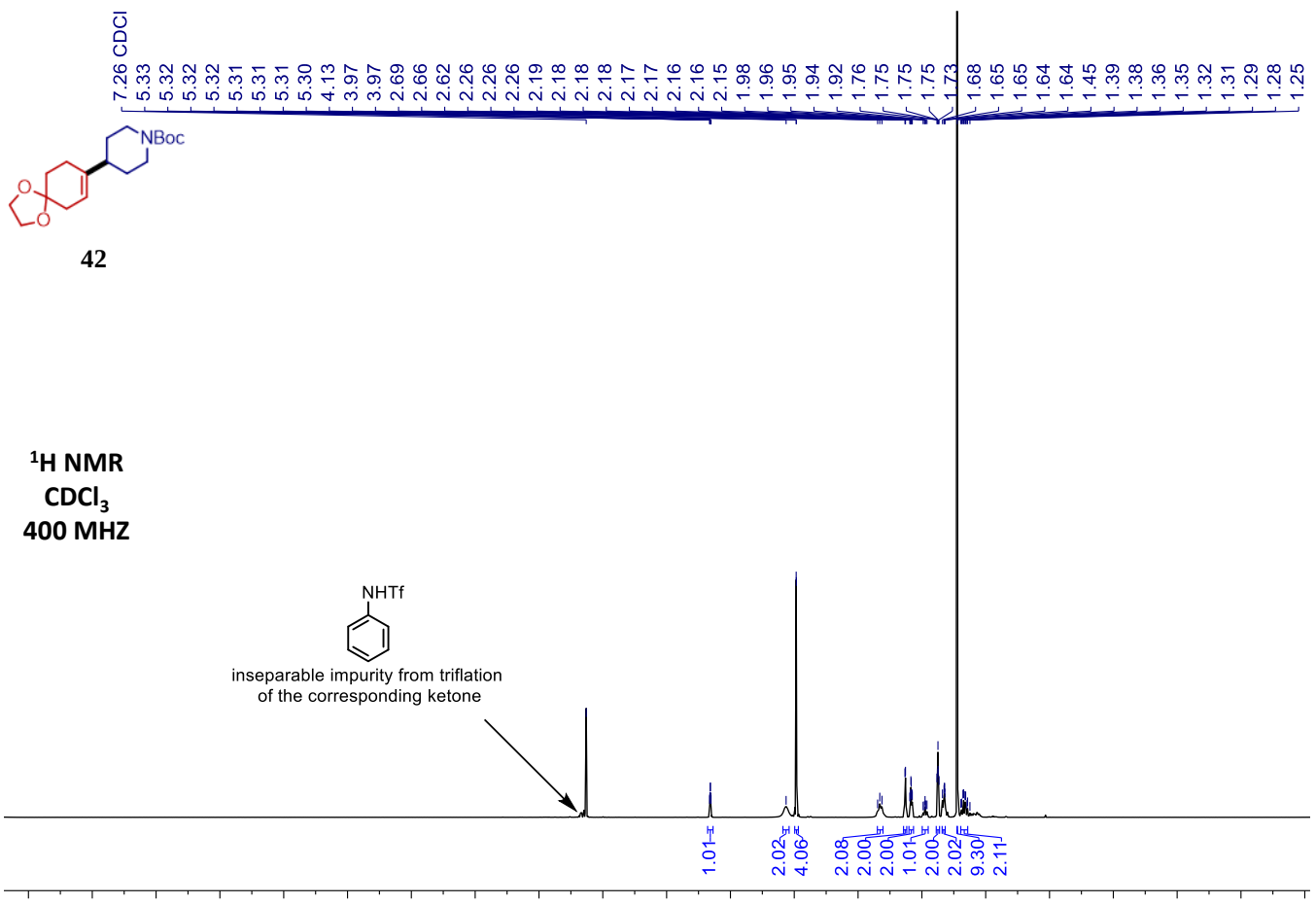

7.83 7.83 7.82 7.82 7.82 7.81 7.81 7.81 7.80 7.80 7.80 7.80 7.66 7.65 7.65 7.47 7.47 7.46 7.45 7.45 7.45 7.44 7.44 7.43 7.40 7.40 7.38 7.38 7.26 CDCl
4.16 4.15 4.15 4.15 4.15 4.14 4.14 4.13 4.12 4.12 4.12 4.11 4.11 3.62 3.62 3.59 3.59 3.57 3.56 2.93 1.96 1.96 1.95 1.95 1.93 1.92 1.90 1.89 1.89 1.88 1.88 1.88 1.87 1.87 1.85
O
40
1H NMR
CDCl3
400 MHZ
3.08
1.06
2.09
1.00
2.10
2.11
1.04
4.25
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3
143.27
133.59
132.25
128.06
127.61
127.57
125.98
125.68
125.35
124.69
77.00 CDCl3
68.42
41.65
33.88
13C NMR
CDCl3
101 MHZ
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10

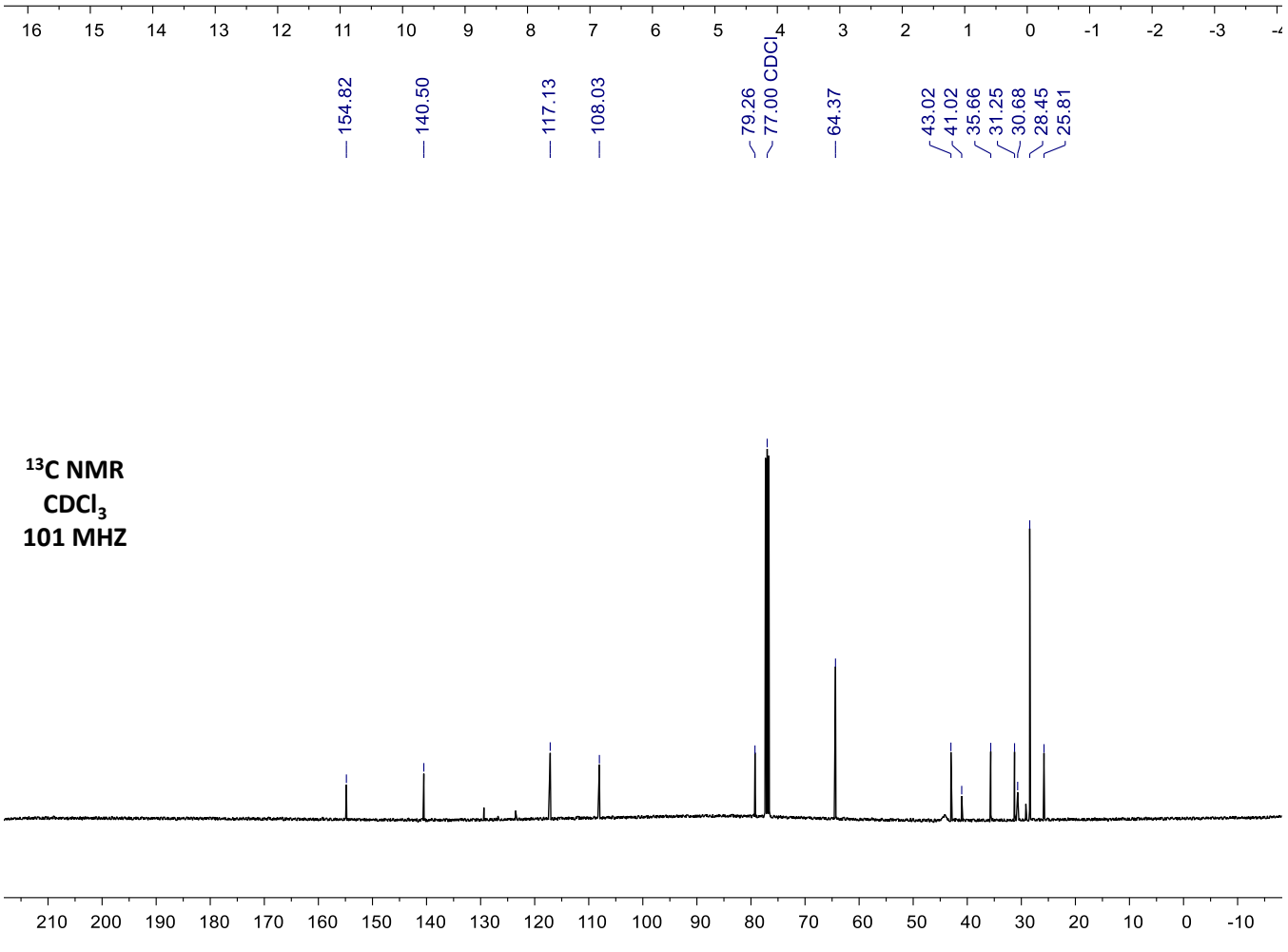


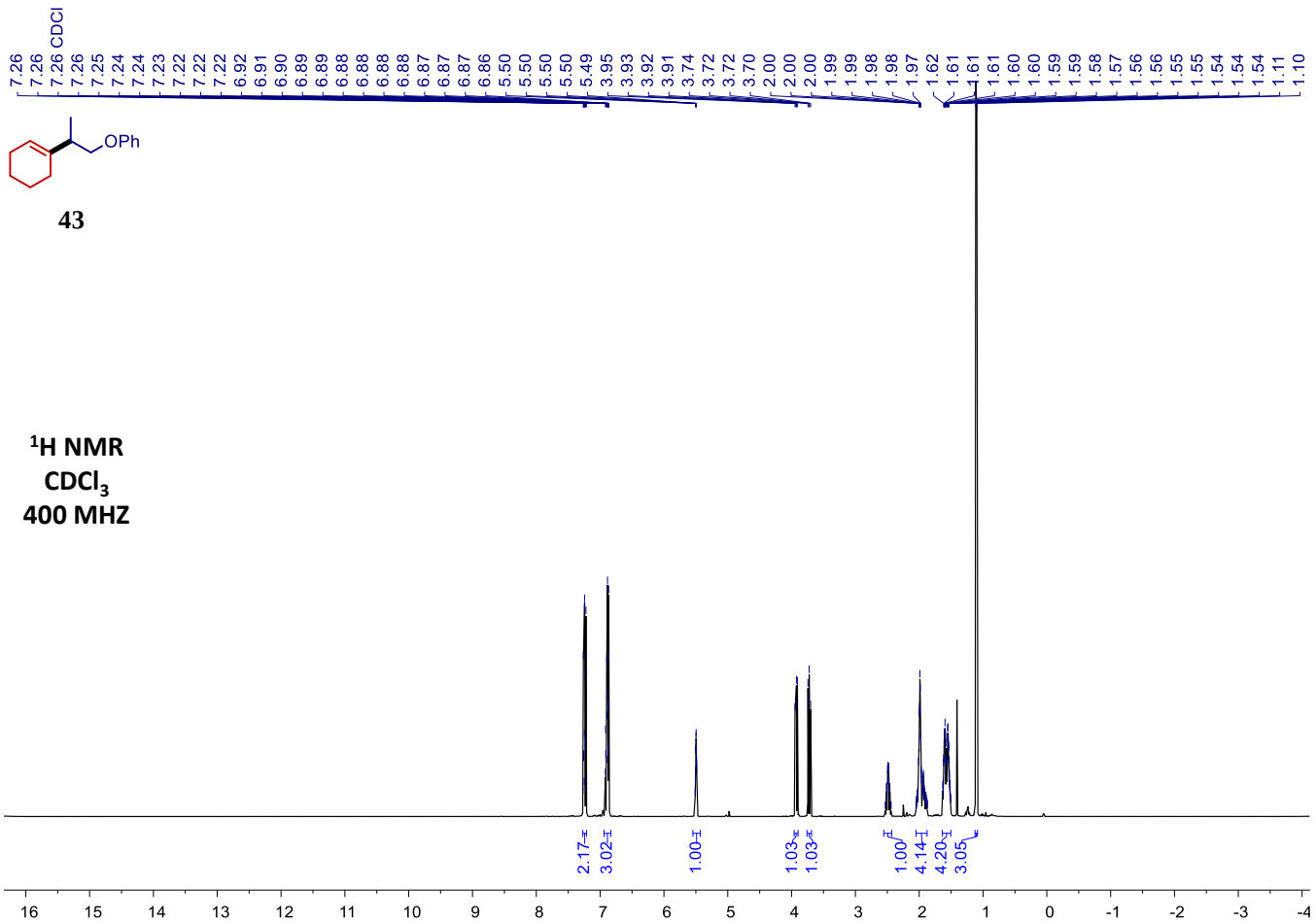
41

^{1}H NMR
$CDCl_3$
400 MHZ

^{13}C NMR
$CDCl_3$
101 MHZ


7.26 CDCl
5.33
5.32
5.32
5.32
5.31
5.31
5.31
5.30
4.13
3.97
3.97
2.69
2.66
2.62
2.26
2.26
2.26
2.19
2.18
2.18
2.18
2.17
2.17
2.16
2.16
2.15
1.98
1.96
1.95
1.94
1.92
1.76
1.75
1.75
1.75
1.73
1.68
1.65
1.65
1.64
1.64
1.45
1.39
1.38
1.36
1.35
1.32
1.31
1.29
1.28
1.25
NBoc
O
O
42
1H NMR
CDCl3
400 MHZ
NHTf
inseparable impurity from triflation
of the corresponding ketone
1.01
2.02
4.06
2.08
2.00
2.00
1.01
2.00
2.02
9.30
2.11
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
-3


154.82
140.50
117.13
108.03
79.26
77.00 CDCl
64.37
43.02
41.02
35.66
31.25
30.68
28.45
25.81
13C NMR
CDCl3
101 MHZ
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10


7.26
7.26
7.26 CDCl
7.26
7.25
7.24
7.24
7.23
7.22
7.22
6.92
6.91
6.90
6.89
6.89
6.88
6.88
6.88
6.88
6.87
6.87
6.87
6.86
5.50
5.50
5.50
5.49
3.95
3.93
3.92
3.91
3.74
3.72
3.72
3.70
2.00
2.00
1.99
1.99
1.98
1.98
1.97
1.62
1.61
1.61
1.61
1.60
1.60
1.59
1.59
1.58
1.57
1.56
1.56
1.55
1.55
1.54
1.54
1.54
1.11
1.10
OPh
43
1H NMR
CDCl3
400 MHZ
2.17
3.02
1.00
1.03
1.03
1.00
4.14
4.20
3.05
16
15
14
13
12
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10
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8
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6
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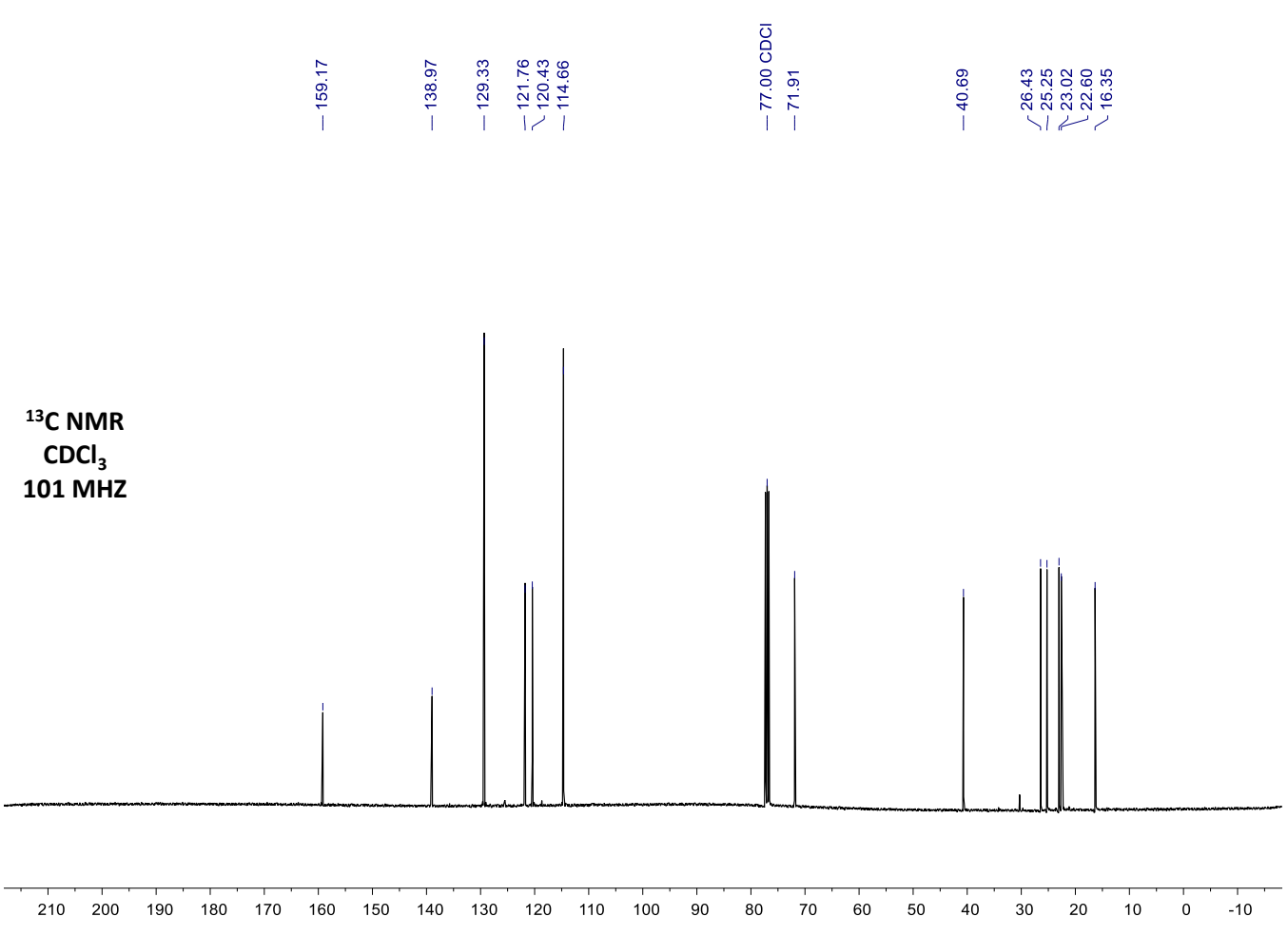
4
3
2
1
0
-1
-2
-3
-4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138.97
129.33
121.76
120.43
114.66
77.00 CDCl
71.91
40.69
26.43
25.25
23.02
22.60
16.35
13C NMR
CDCl3
101 MHZ
210
200
190
180
170
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100
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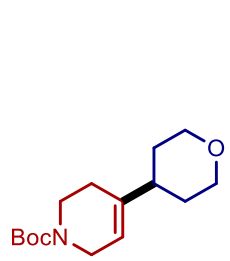

44

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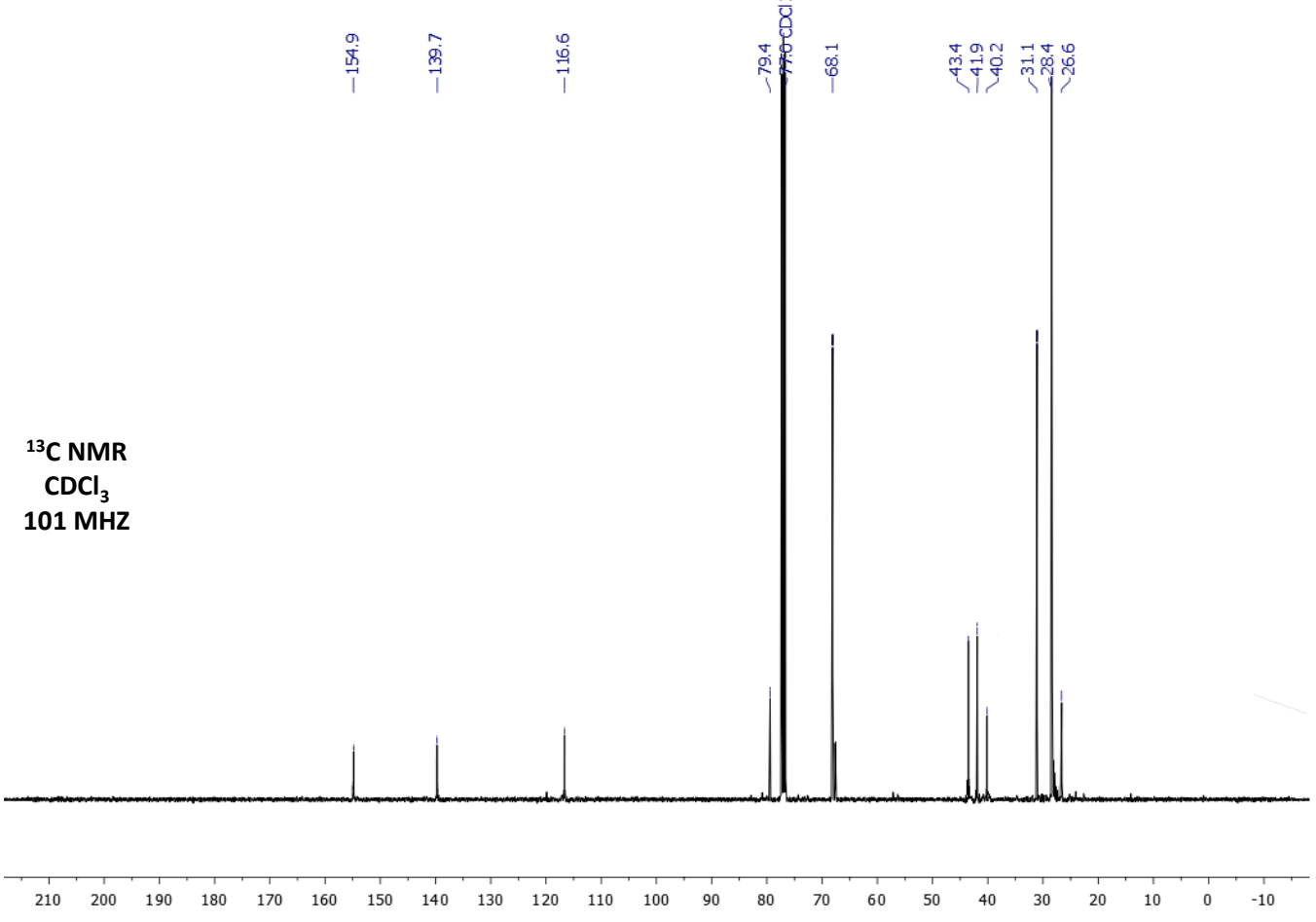
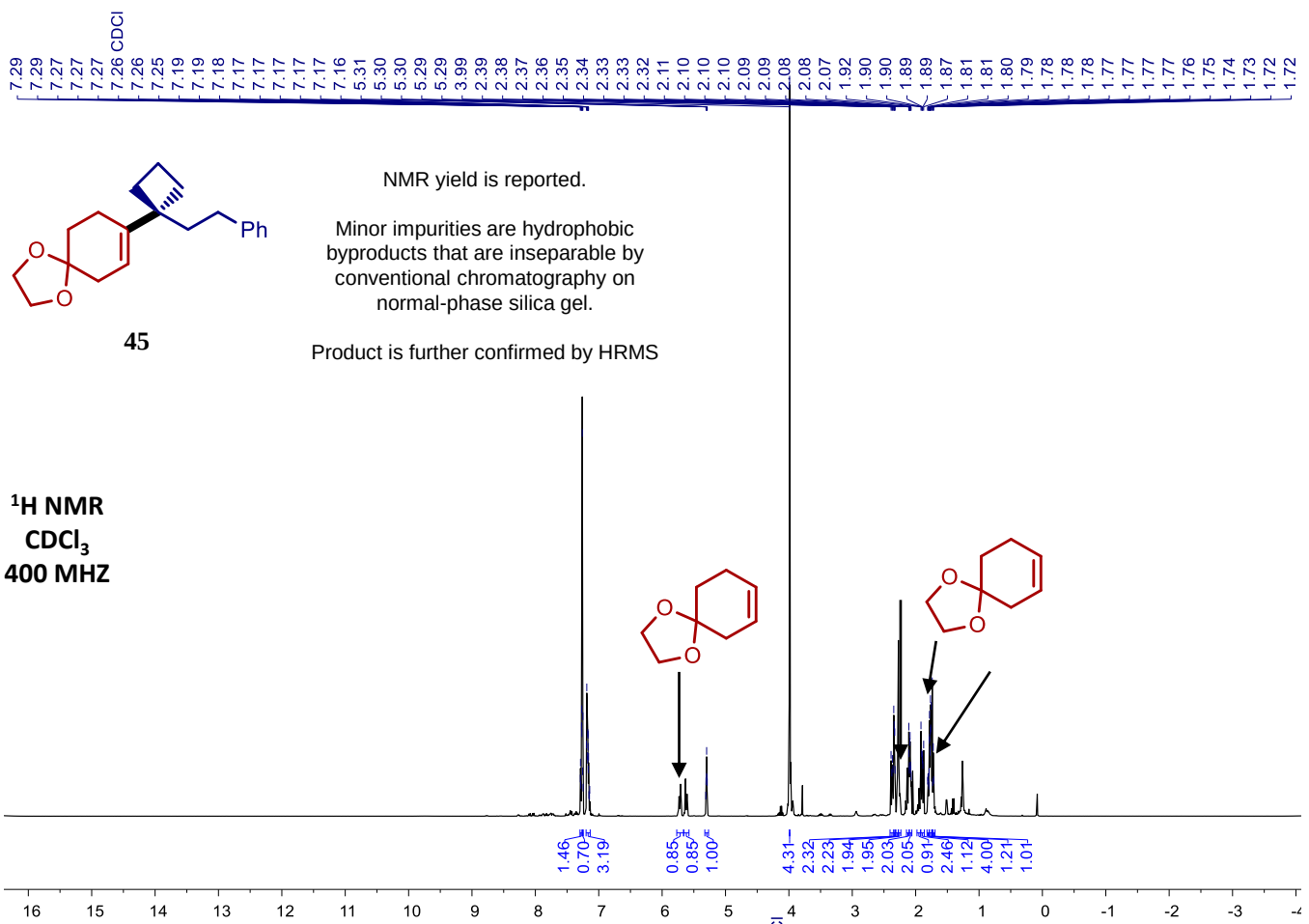
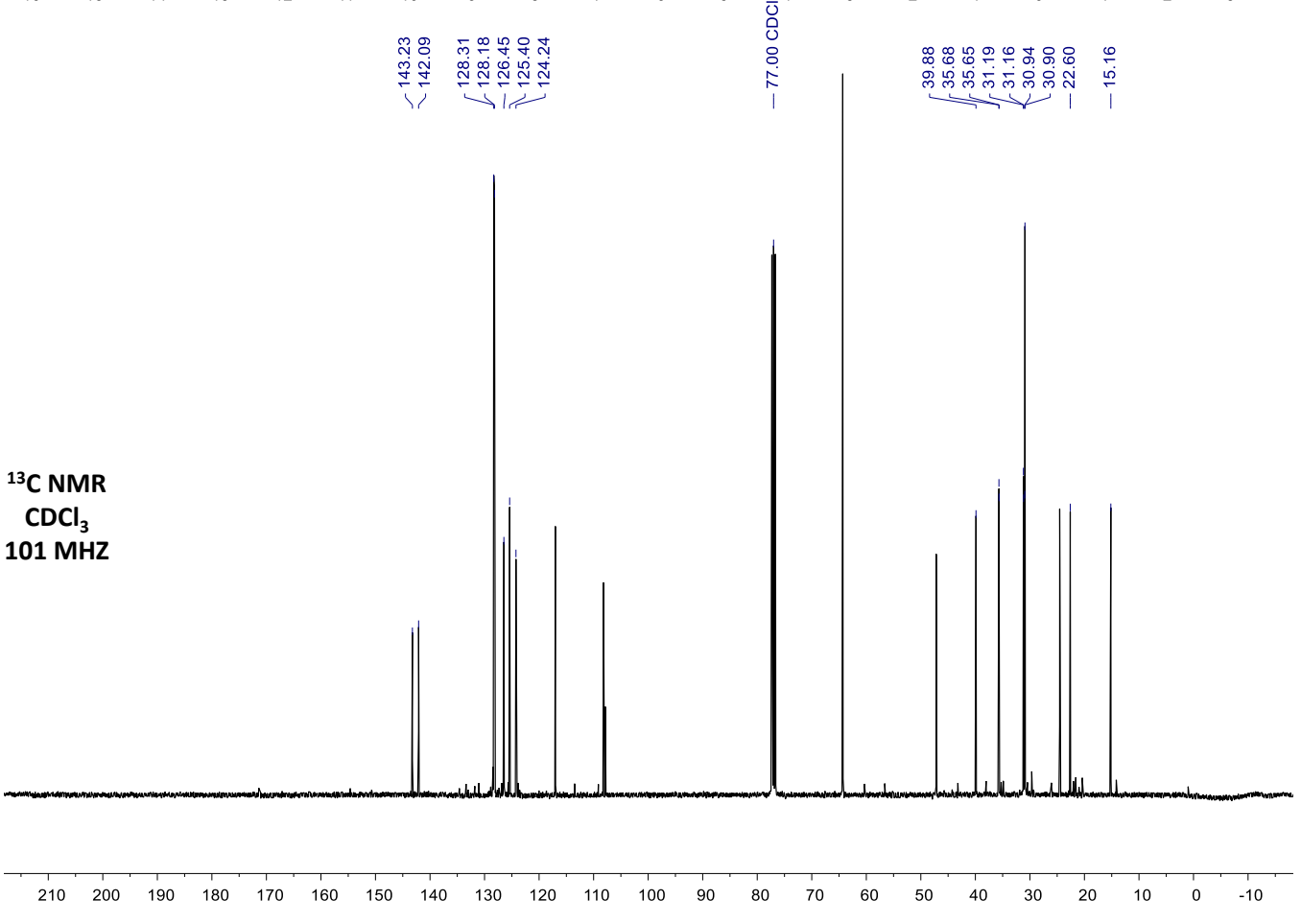
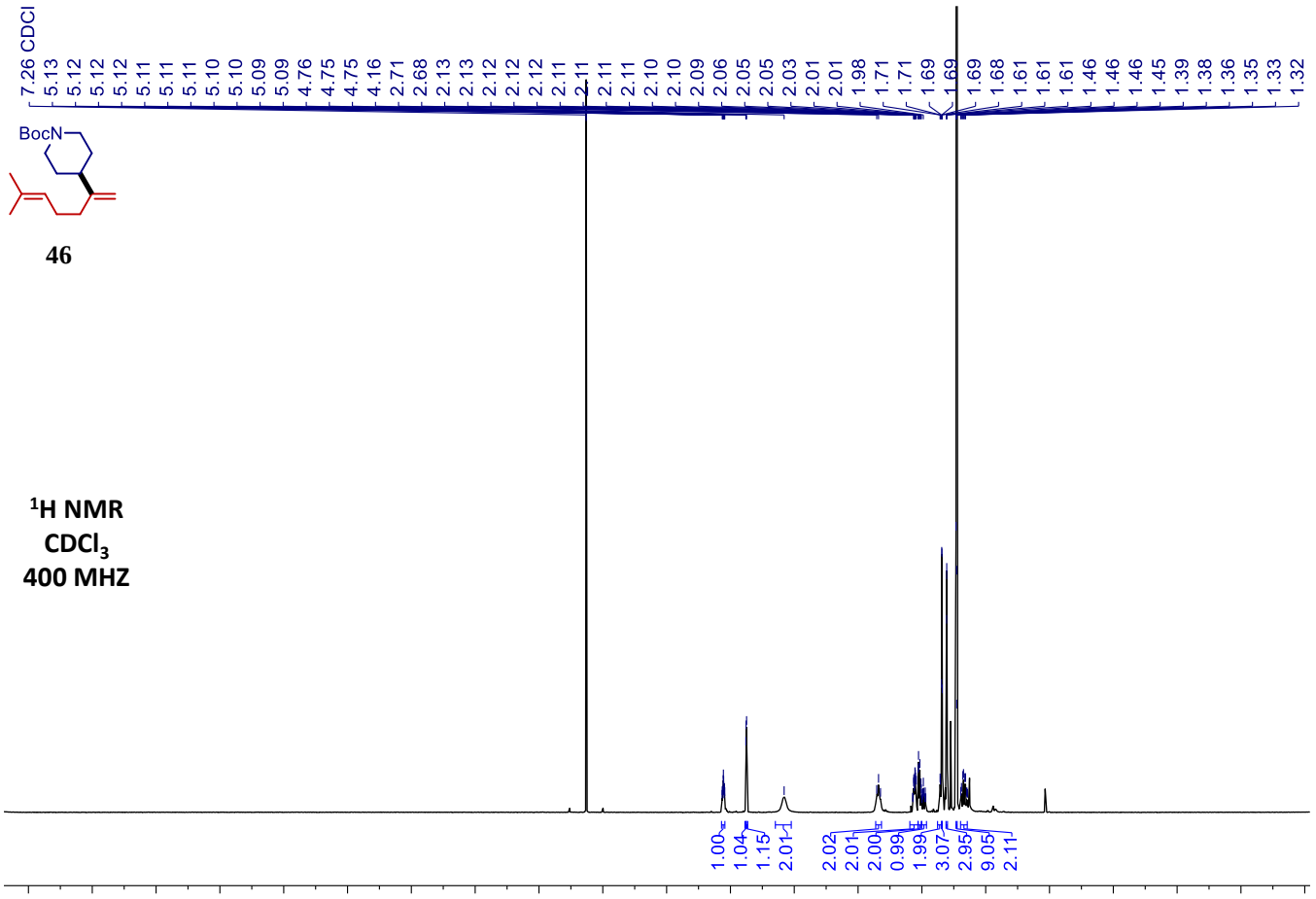
$CDCl_3$
400 MHZ

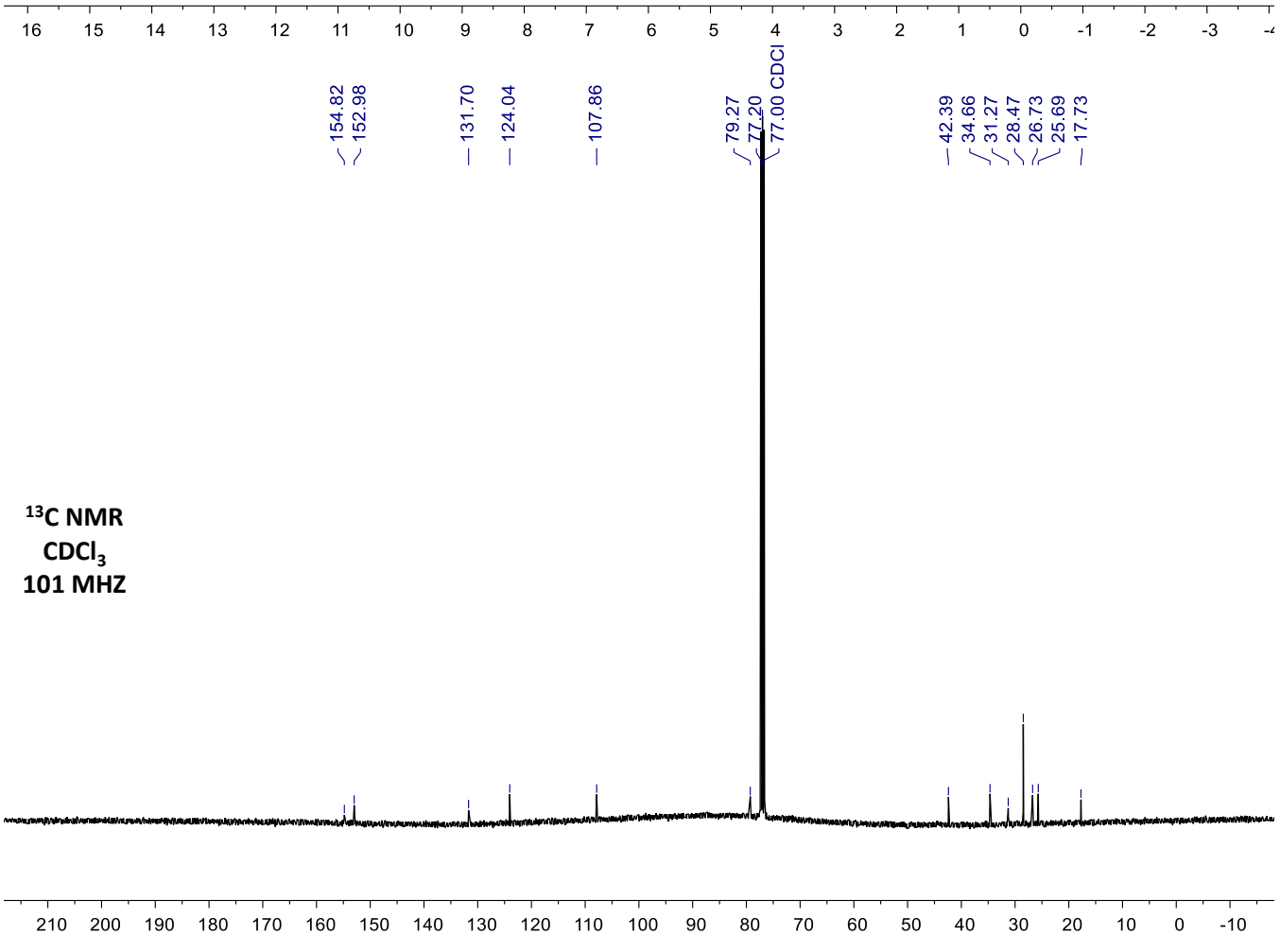
^{13}C NMR
$CDCl_3$
101 MHZ

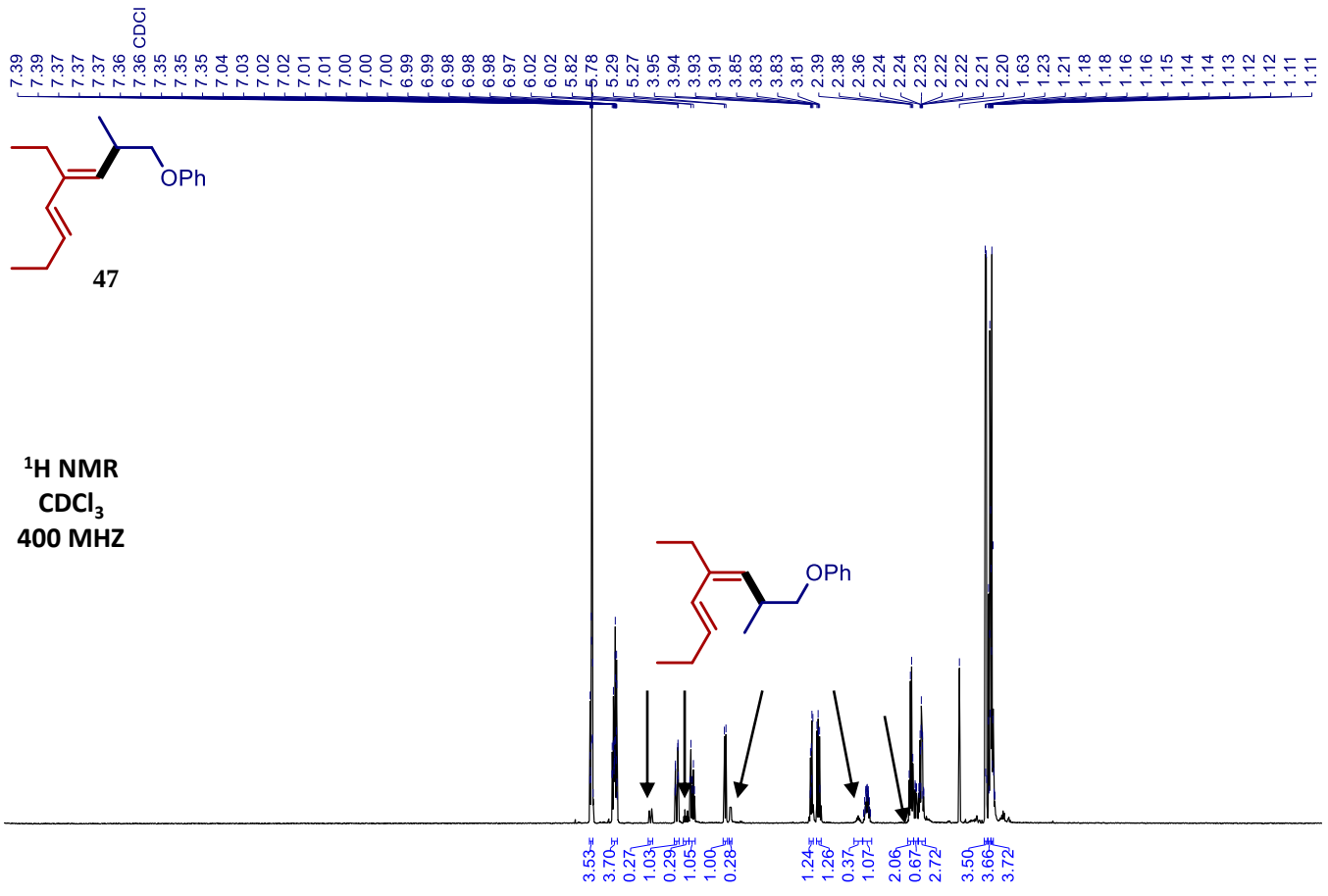


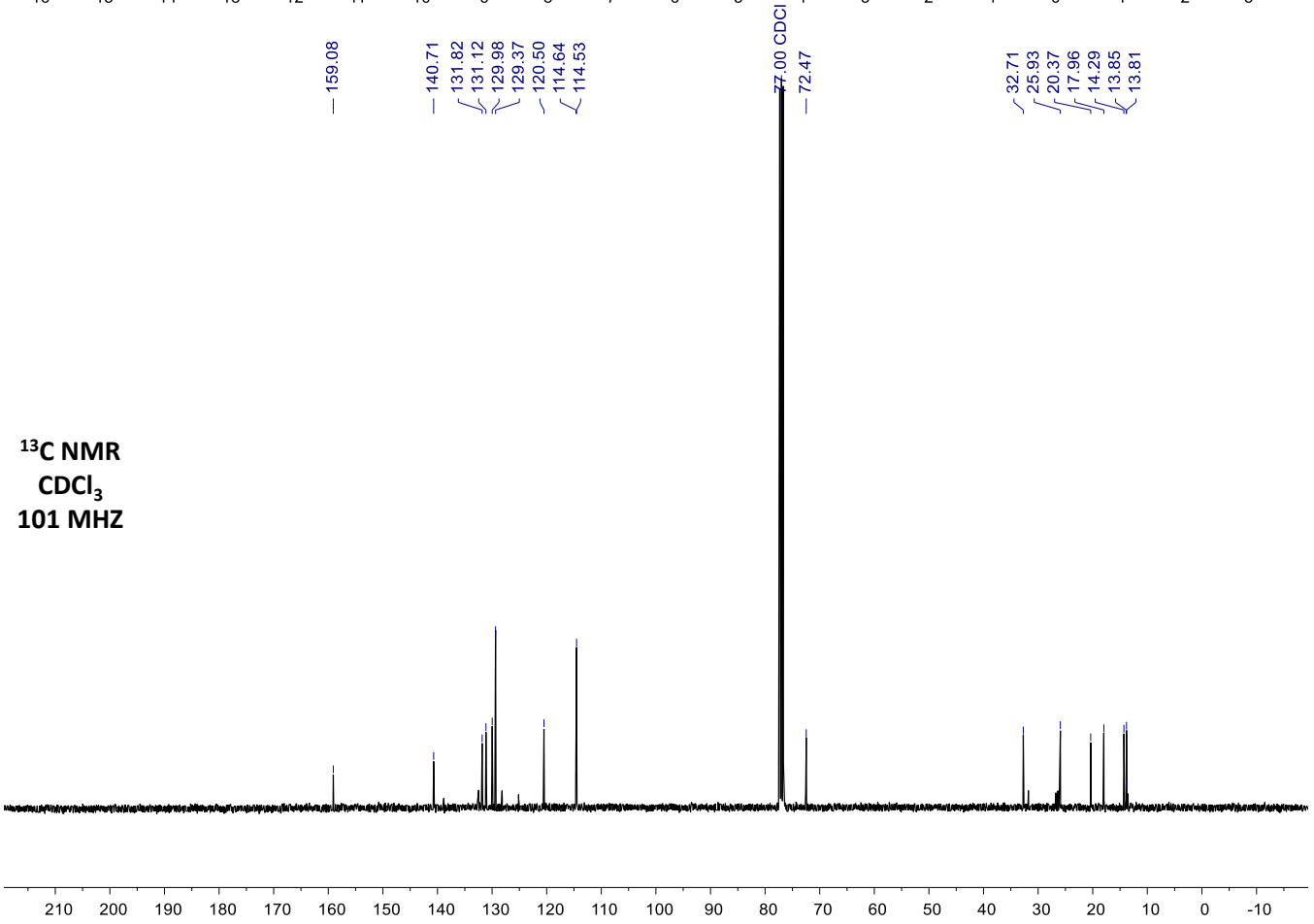

7.29 7.29 7.27 7.27 7.27 7.26 CDCl 7.26 7.25 7.19 7.19 7.18 7.17 7.17 7.17 7.17 7.17 7.16 5.31 5.30 5.30 5.29 5.29 3.99 2.39 2.38 2.37 2.36 2.35 2.34 2.33 2.33 2.32 2.11 2.10 2.10 2.09 2.09 2.08 2.08 2.07 1.92 1.90 1.90 1.89 1.89 1.87 1.81 1.81 1.80 1.79 1.78 1.78 1.77 1.77 1.77 1.77 1.76 1.75 1.74 1.73 1.72 1.72
Ph
O
O
45
NMR yield is reported.
Minor impurities are hydrophobic byproducts that are inseparable by conventional chromatography on normal-phase silica gel.
Product is further confirmed by HRMS
1H NMR
CDCl3
400 MHZ
1.46 0.70 3.19 0.85 0.85 1.00 4.31 2.32 2.23 1.94 1.95 2.03 2.05 0.91 2.46 1.12 4.00 1.21 1.01
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3

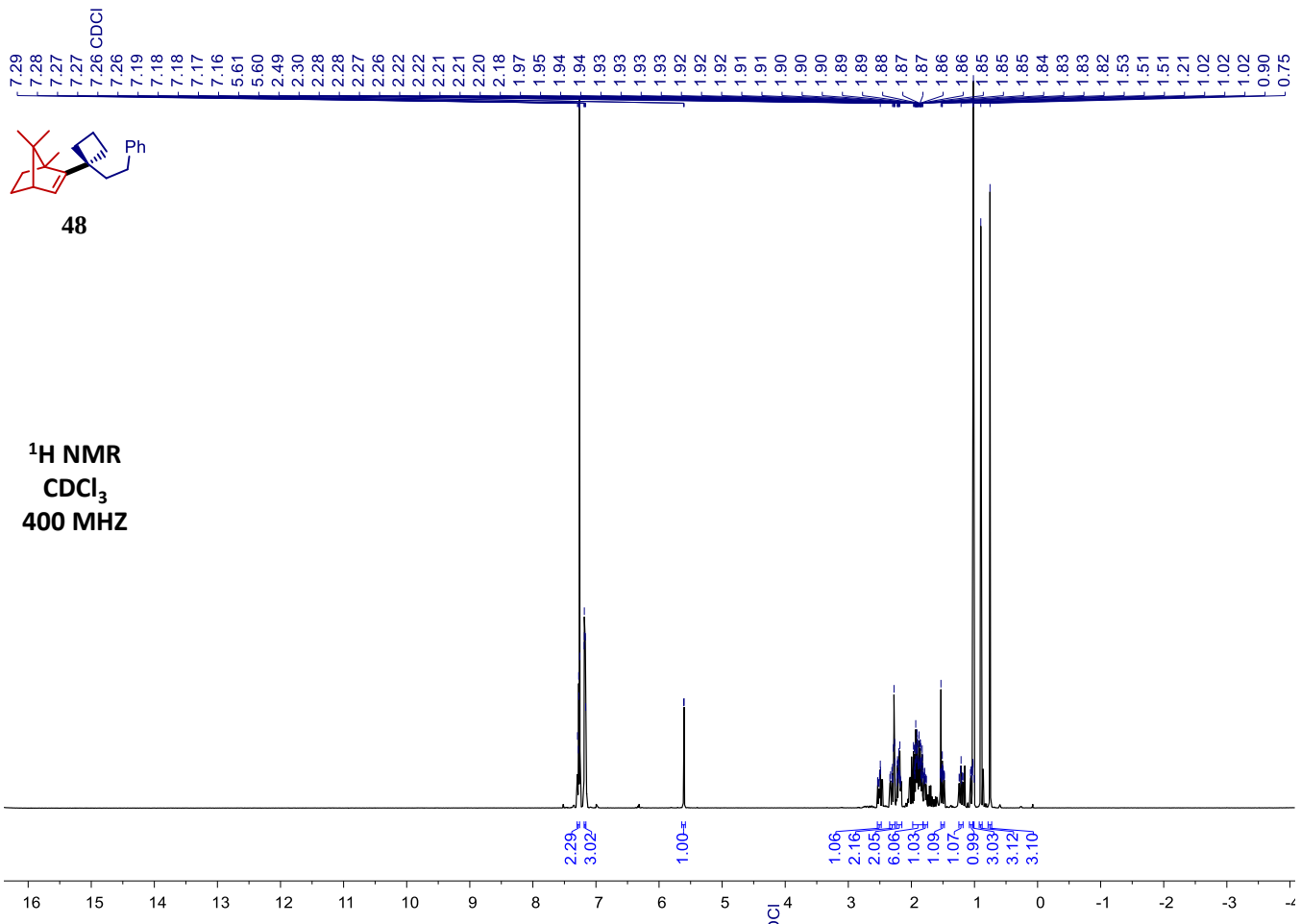

143.23 142.09 128.31 128.18 126.45 125.40 124.24 77.00 CDCl3 39.88 35.68 35.65 31.19 31.16 30.94 30.90 22.60 15.16
13C NMR
CDCl3
101 MHZ
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

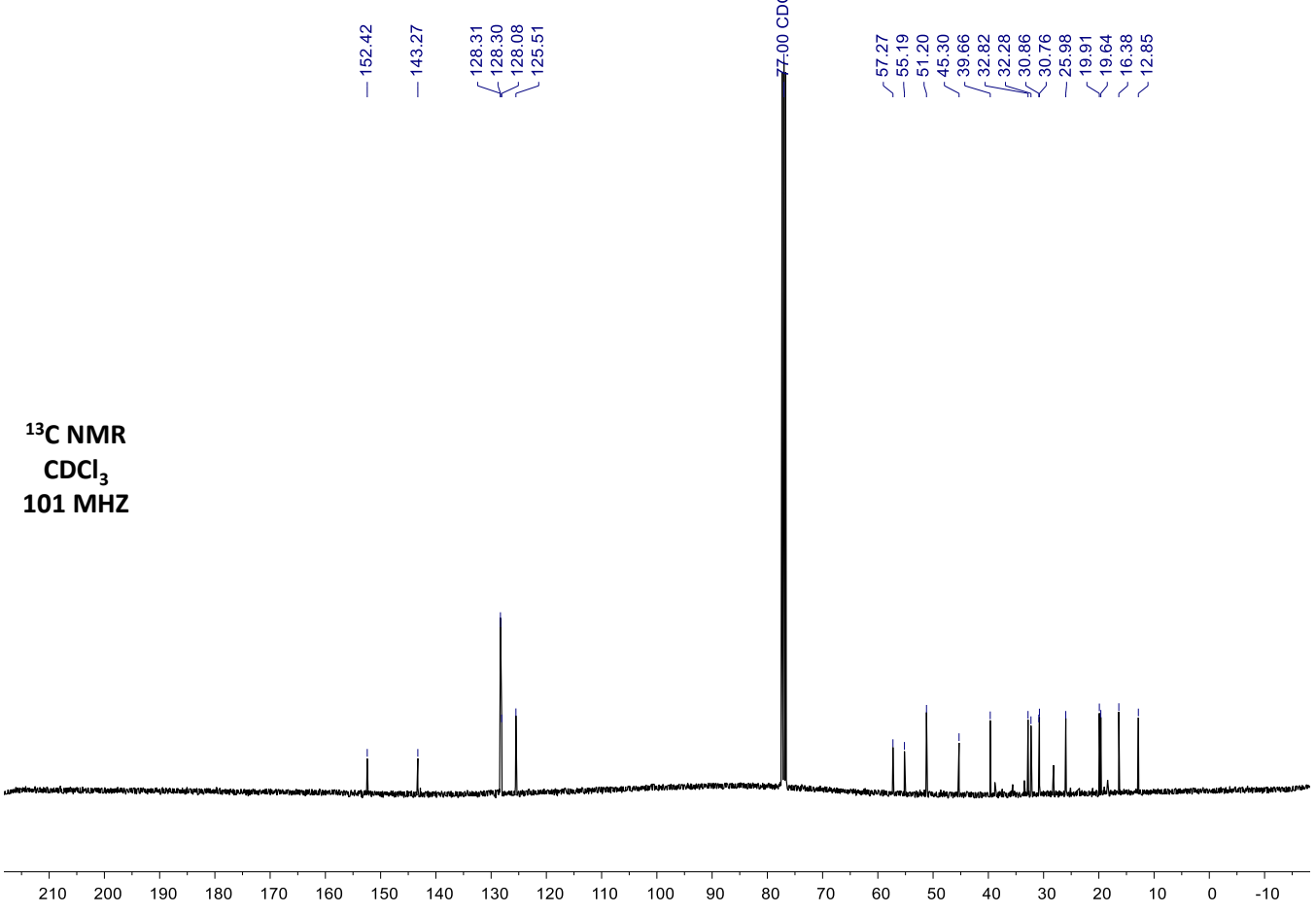

7.26 CDCl
5.13 5.12 5.12 5.12 5.11 5.11 5.11 5.10 5.10 5.09 5.09 4.76 4.75 4.75 4.16 2.71 2.68 2.13 2.13 2.12 2.12 2.12 2.11 2.11 2.11 2.11 2.10 2.10 2.09 2.06 2.05 2.05 2.03 2.01 2.01 1.98 1.71 1.71 1.69 1.69 1.69 1.68 1.61 1.61 1.61 1.46 1.46 1.46 1.45 1.39 1.38 1.36 1.35 1.33 1.32
BocN
46
1H NMR
CDCl3
400 MHZ
1.00 1.04 1.15 2.01 2.02 2.01 2.00 0.99 1.99 3.07 2.95 9.05 2.11
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3

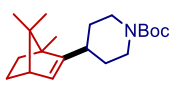

154.82 152.98 131.70 124.04 107.86 79.27 77.20 77.00 CDCl 42.39 34.66 31.27 28.47 26.73 25.69 17.73
13C NMR
CDCl3
101 MHZ
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10


7.39 7.39 7.37 7.37 7.37 7.36 7.36 CDCl 7.35 7.35 7.35 7.04 7.03 7.02 7.02 7.01 7.01 7.00 7.00 7.00 6.99 6.99 6.98 6.98 6.98 6.97 6.02 6.02 5.82 5.78 5.29 5.27 3.95 3.94 3.93 3.91 3.85 3.83 3.83 3.81 2.39 2.38 2.36 2.24 2.24 2.23 2.22 2.22 2.21 2.20 1.63 1.23 1.21 1.18 1.18 1.16 1.16 1.15 1.14 1.14 1.13 1.12 1.12 1.11 1.11
OPh
47
1H NMR
CDCl3
400 MHZ
OPh
3.53 3.70 0.27 1.03 0.29 1.05 1.00 0.28 1.24 1.26 0.37 1.07 2.06 0.67 2.72 3.50 3.66 3.72
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3


159.08 140.71 131.82 131.12 129.98 129.37 120.50 114.64 114.53 77.00 CDCl 72.47 32.71 25.93 20.37 17.96 14.29 13.85 13.81
13C NMR
CDCl3
101 MHZ
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10


7.29 7.28 7.27 7.27 7.26 CDCl 7.26 7.19 7.18 7.18 7.17 7.16 5.61 5.60 2.49 2.30 2.28 2.28 2.27 2.26 2.22 2.22 2.21 2.21 2.20 2.18 1.97 1.95 1.94 1.94 1.93 1.93 1.93 1.92 1.92 1.92 1.91 1.91 1.90 1.90 1.90 1.89 1.89 1.88 1.87 1.87 1.86 1.86 1.85 1.85 1.85 1.84 1.83 1.83 1.82 1.53 1.51 1.51 1.21 1.02 1.02 1.02 0.90 0.75
Ph
48
1H NMR
CDCl3
400 MHZ
2.29 3.02 1.00 1.06 2.16 2.05 6.06 1.03 1.09 1.07 0.99 3.03 3.12 3.10
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3
CDCl3

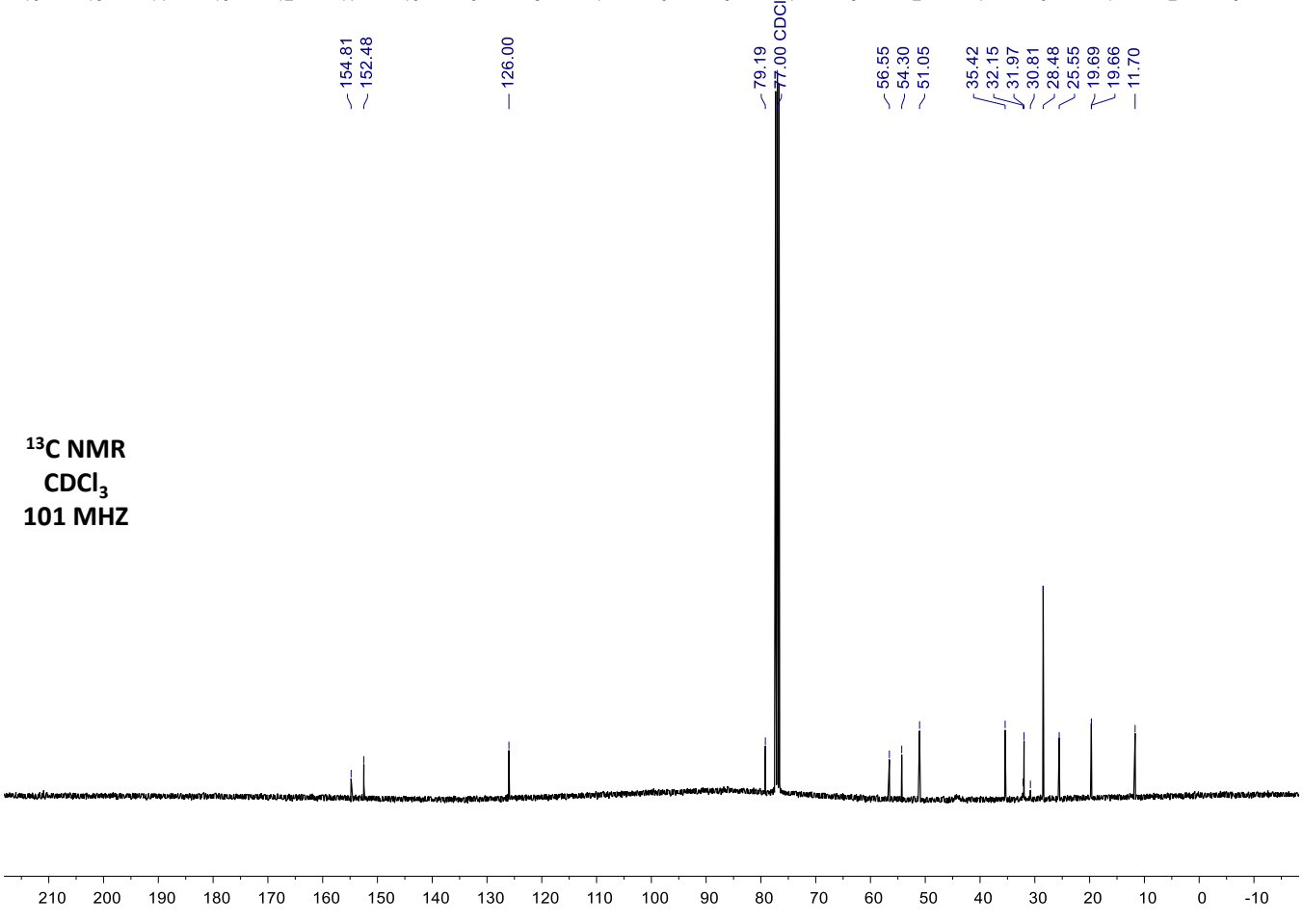

152.42 143.27 128.31 128.30 128.08 125.51 77.00 CDCl3 57.27 55.19 51.20 45.30 39.66 32.82 32.28 30.86 30.76 25.98 19.91 19.64 16.38 12.85
13C NMR
CDCl3
101 MHZ
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

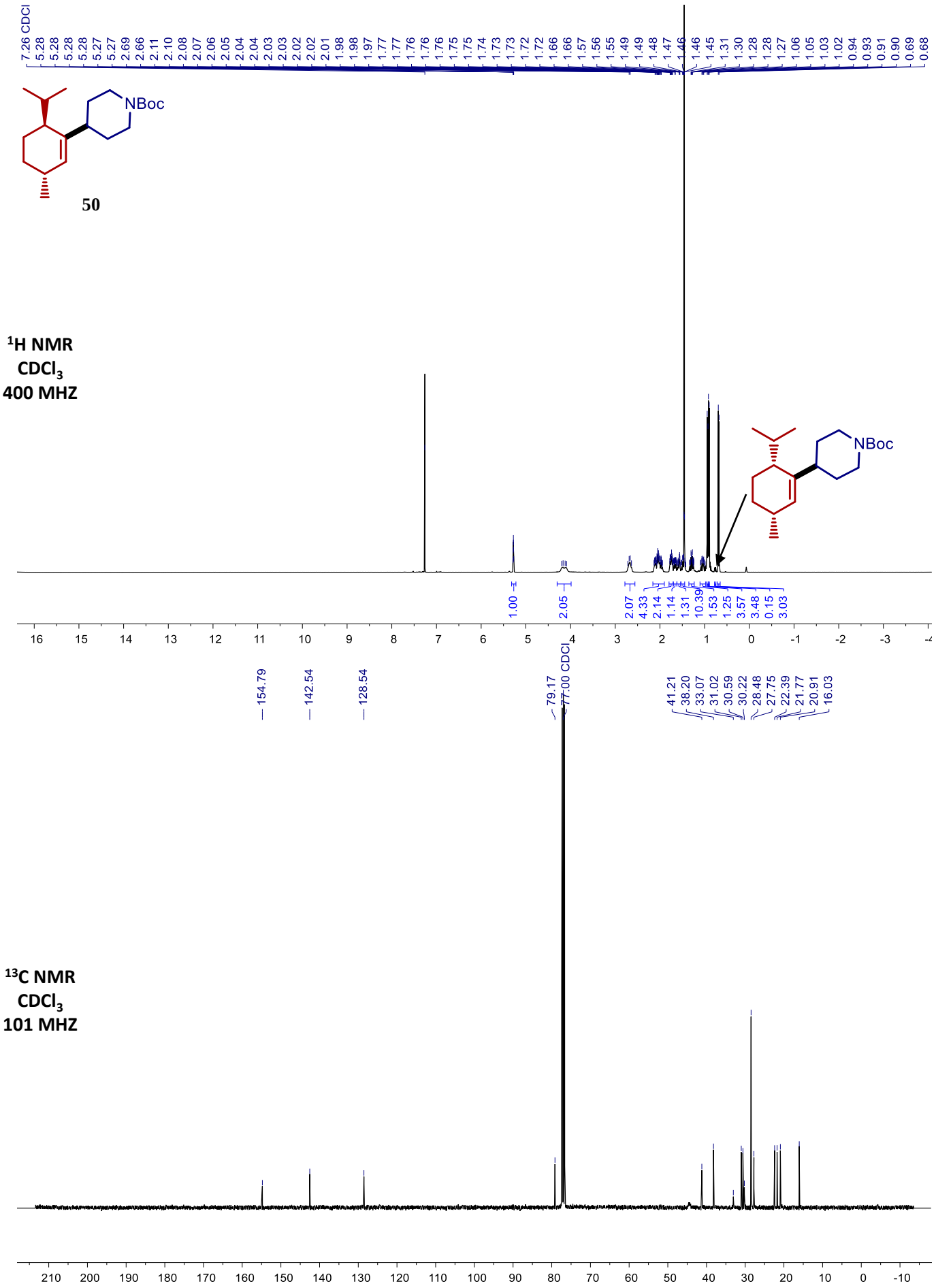


49

^{1}H NMR
$CDCl_3$
400 MHZ

^{13}C NMR
$CDCl_3$
101 MHZ

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5.28
5.28
5.28
5.27
5.27
2.69
2.66
2.11
2.10
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2.07
2.06
2.05
2.04
2.04
2.03
2.03
2.02
2.02
2.01
1.98
1.98
1.97
1.77
1.77
1.76
1.76
1.76
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1.74
1.73
1.73
1.72
1.72
1.66
1.66
1.57
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1.49
1.48
1.47
1.46
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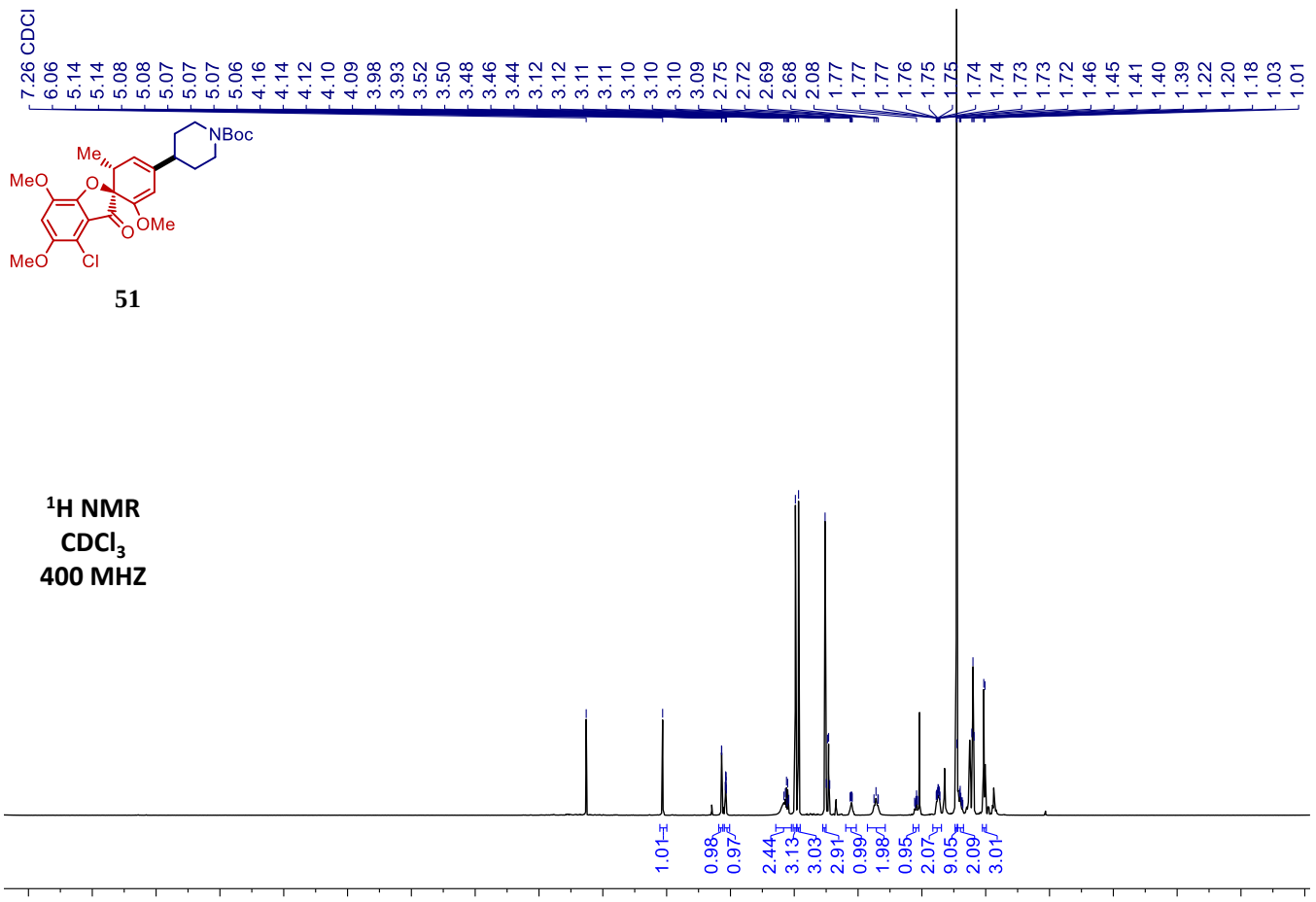
1.45
1.31
1.30
1.28
1.28
1.27
1.06
1.05
1.03
1.02
0.94
0.93
0.91
0.90
0.69
0.68
NBoc
50
1H NMR
CDCl3
400 MHZ
NBoc
1.00
2.05
2.07
4.33
2.14
1.14
1.31
10.39
1.53
1.25
3.57
3.48
0.15
3.03
DCl
154.79
142.54
128.54
79.17
77.00 CDCl3
41.21
38.20
33.07
31.02
30.59
30.22
28.48
27.75
22.39
21.77
20.91
16.03
13C NMR
CDCl3
101 MHZ


7.26 CDCl
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5.14
5.14
5.08
5.08
5.07
5.07
5.07
5.06
4.16
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4.12
4.10
4.09
3.98
3.93
3.52
3.50
3.48
3.46
3.44
3.12
3.12
3.11
3.11
3.10
3.10
3.10
3.09
2.75
2.72
2.69
2.68
2.08
1.77
1.77
1.77
1.76
1.75
1.75
1.74
1.74
1.73
1.73
1.72
1.46
1.45
1.41
1.40
1.39
1.22
1.20
1.18
1.03
1.01
NBoc
Me
MeO
O
OMe
O
MeO
Cl
51
1H NMR
CDCl3
400 MHZ
1.01
0.98
0.97
2.44
3.13
3.03
2.91
0.99
1.98
0.95
2.07
9.05
2.09
3.01
16
15
14
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11
10
9
8
7
6
5
4
3
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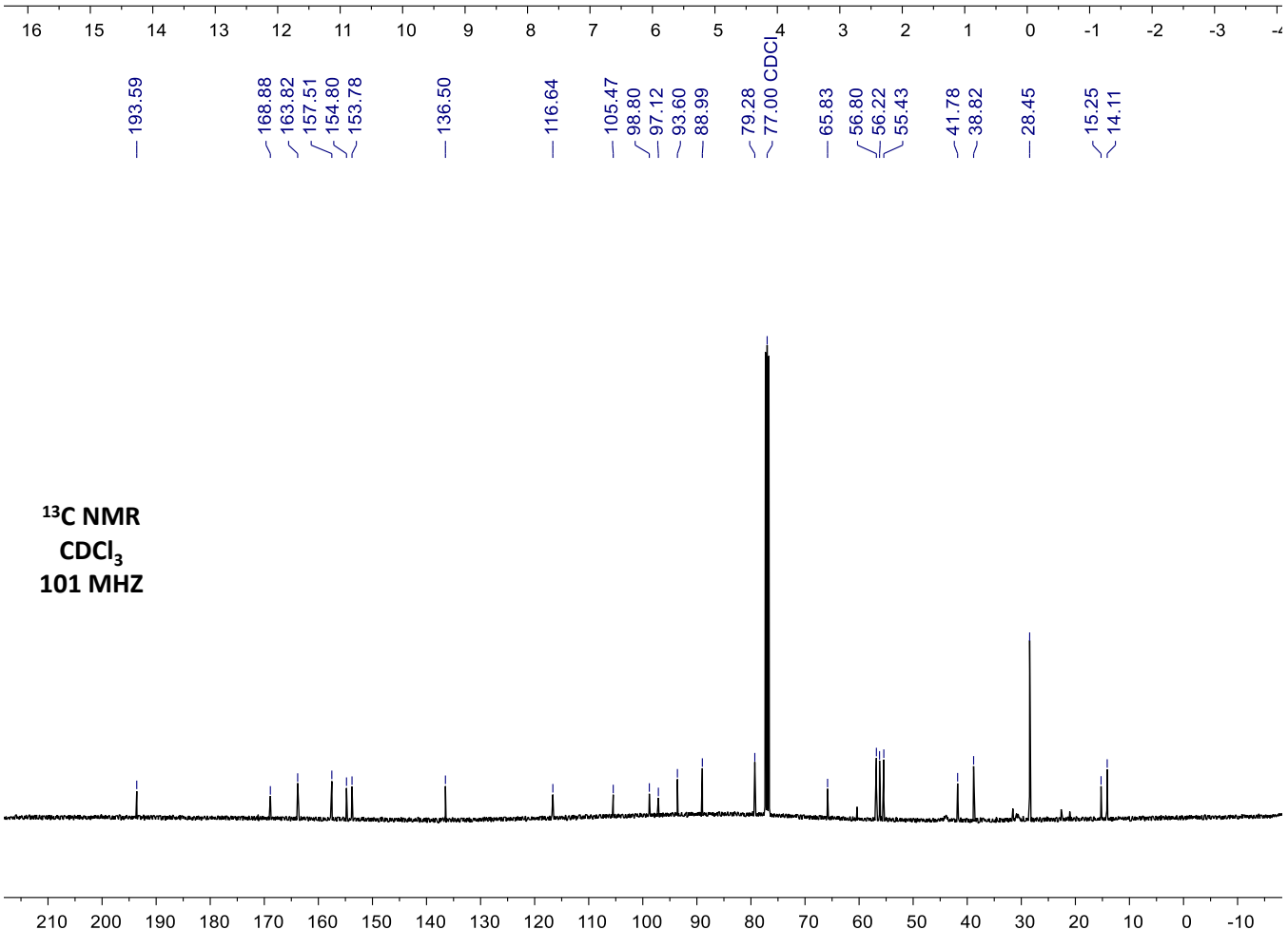
-1
-2
-3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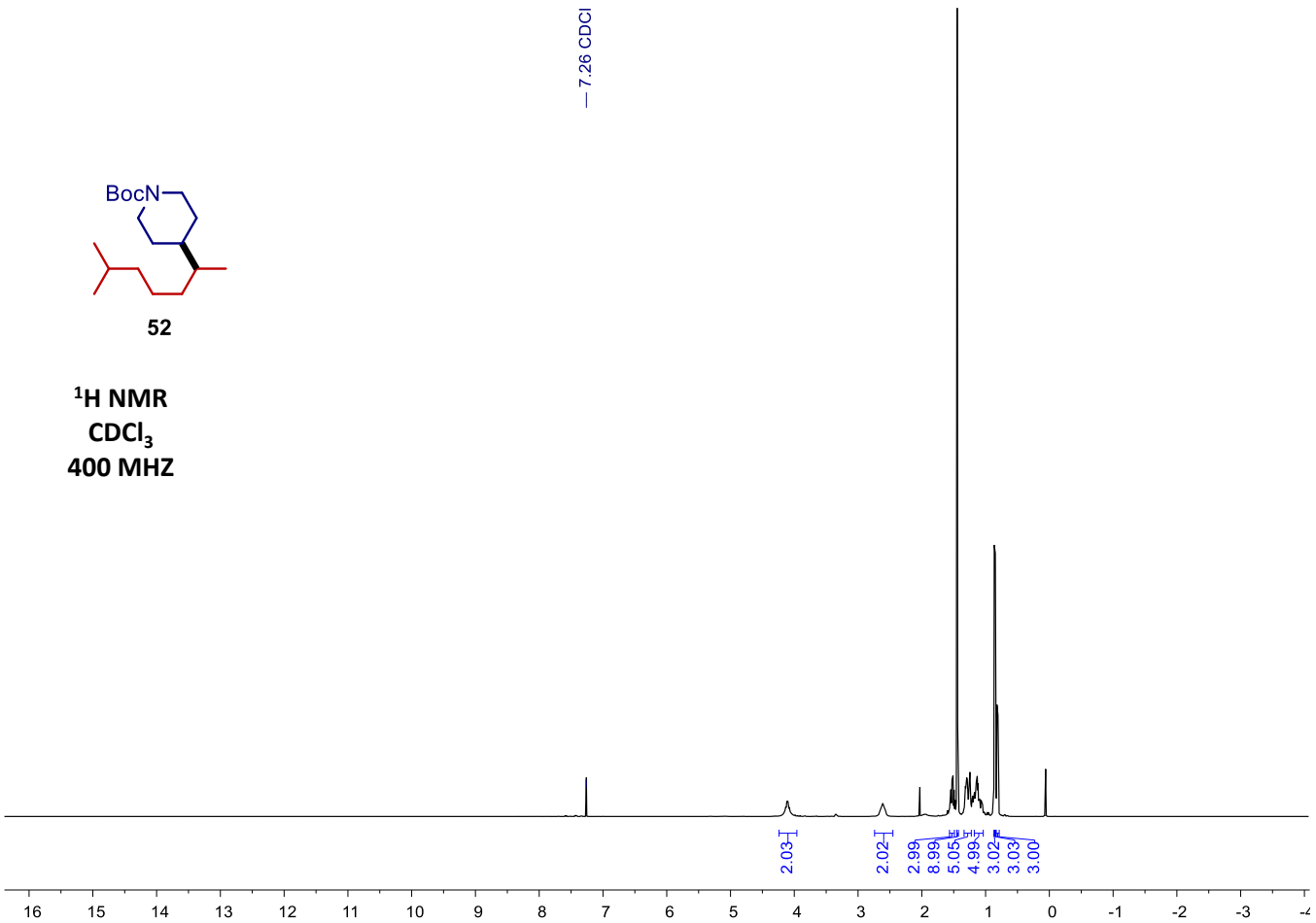
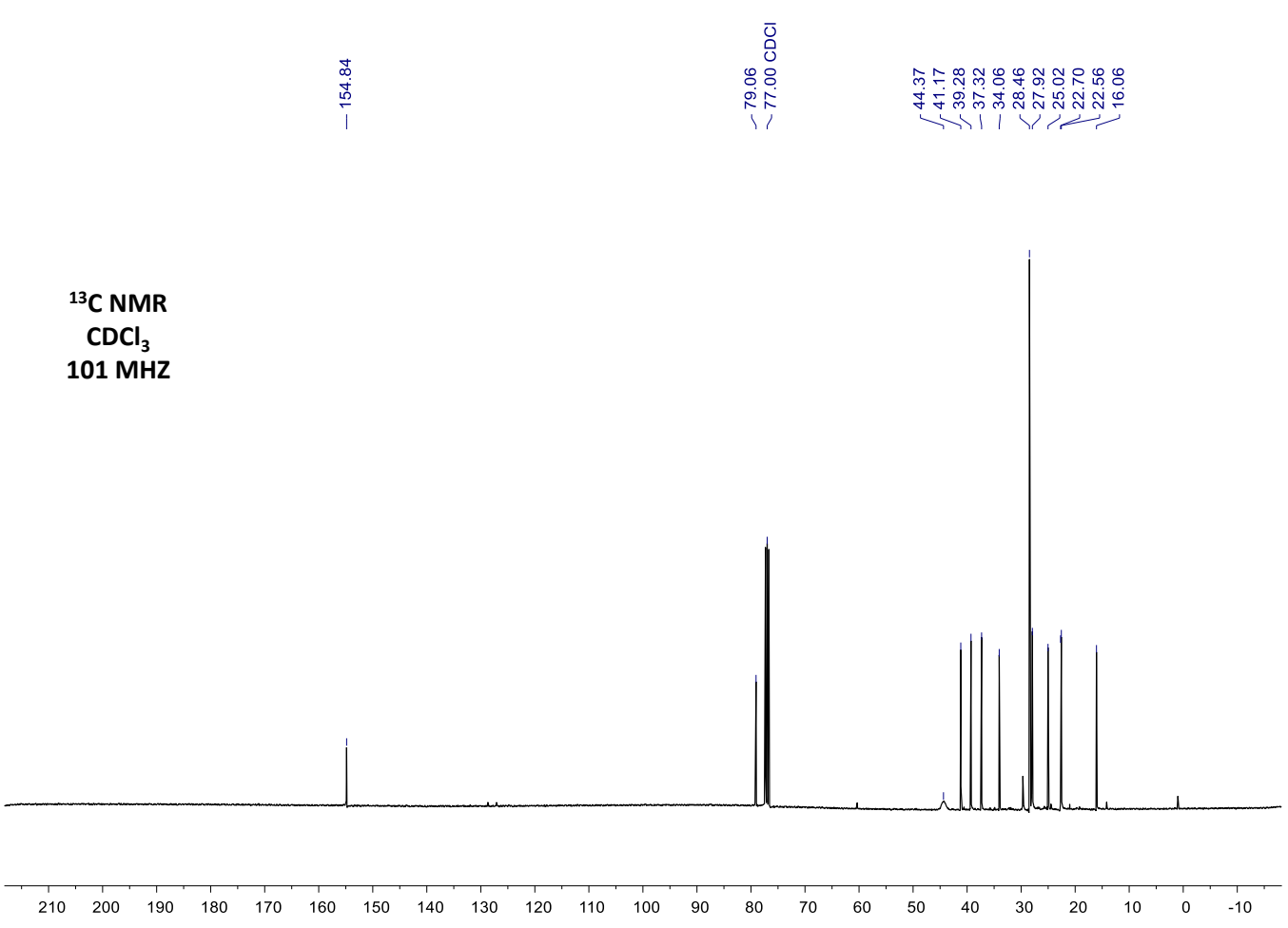
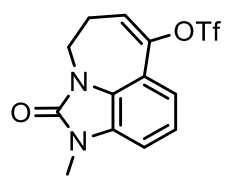
163.82
157.51
154.80
153.78
136.50
116.64
105.47
98.80
97.12
93.60
88.99
79.28
77.00 CDCl
65.83
56.80
56.22
55.43
41.78
38.82
28.45
15.25
14.11
13C NMR
CDCl3
101 MHZ
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10

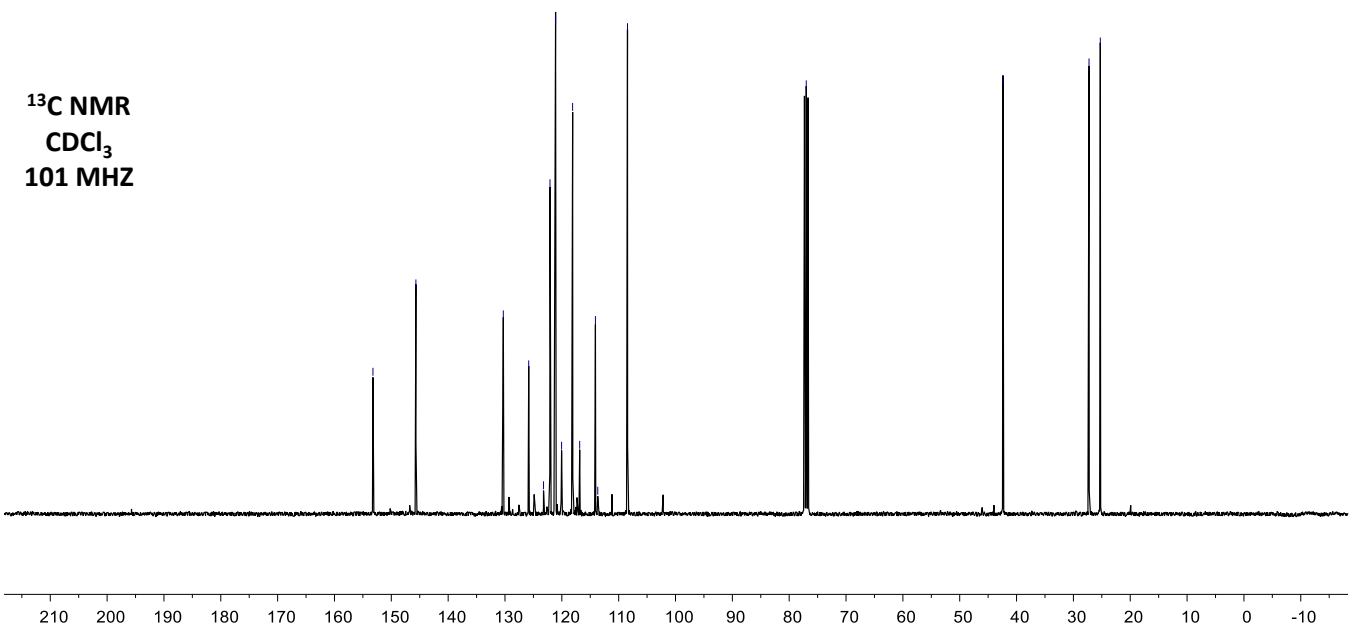

BocN
52
^{1}H NMR
$CDCl_3$
400 MHZ
7.26 CDCl
2.03
2.02
2.99
8.99
5.05
4.99
3.02
3.03
3.00
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3

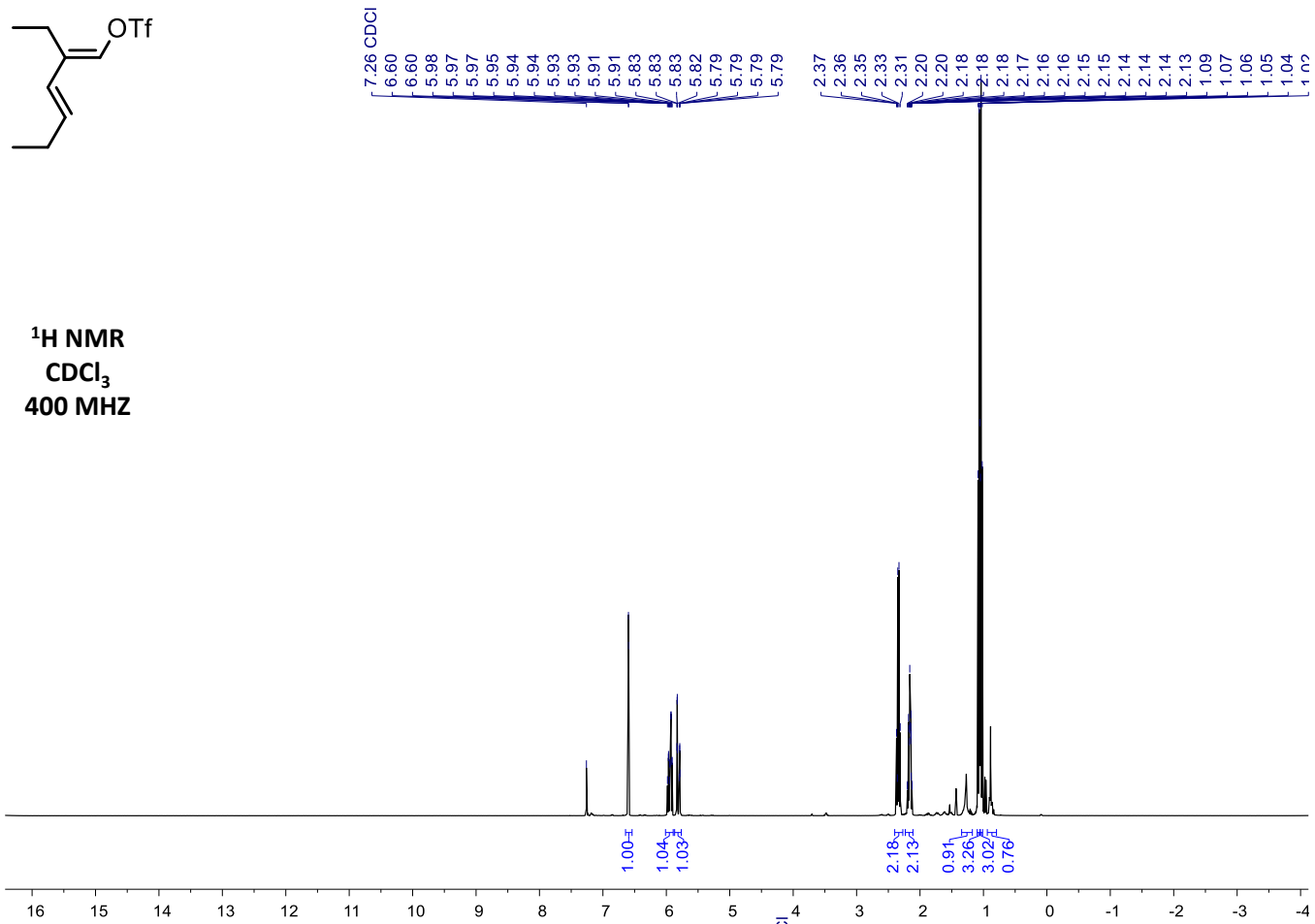

154.84
79.06
77.00 CDCl
44.37
41.17
39.28
37.32
34.06
28.46
27.92
25.02
22.70
22.56
16.06
^{13}C NMR
$CDCl_3$
101 MHZ
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10



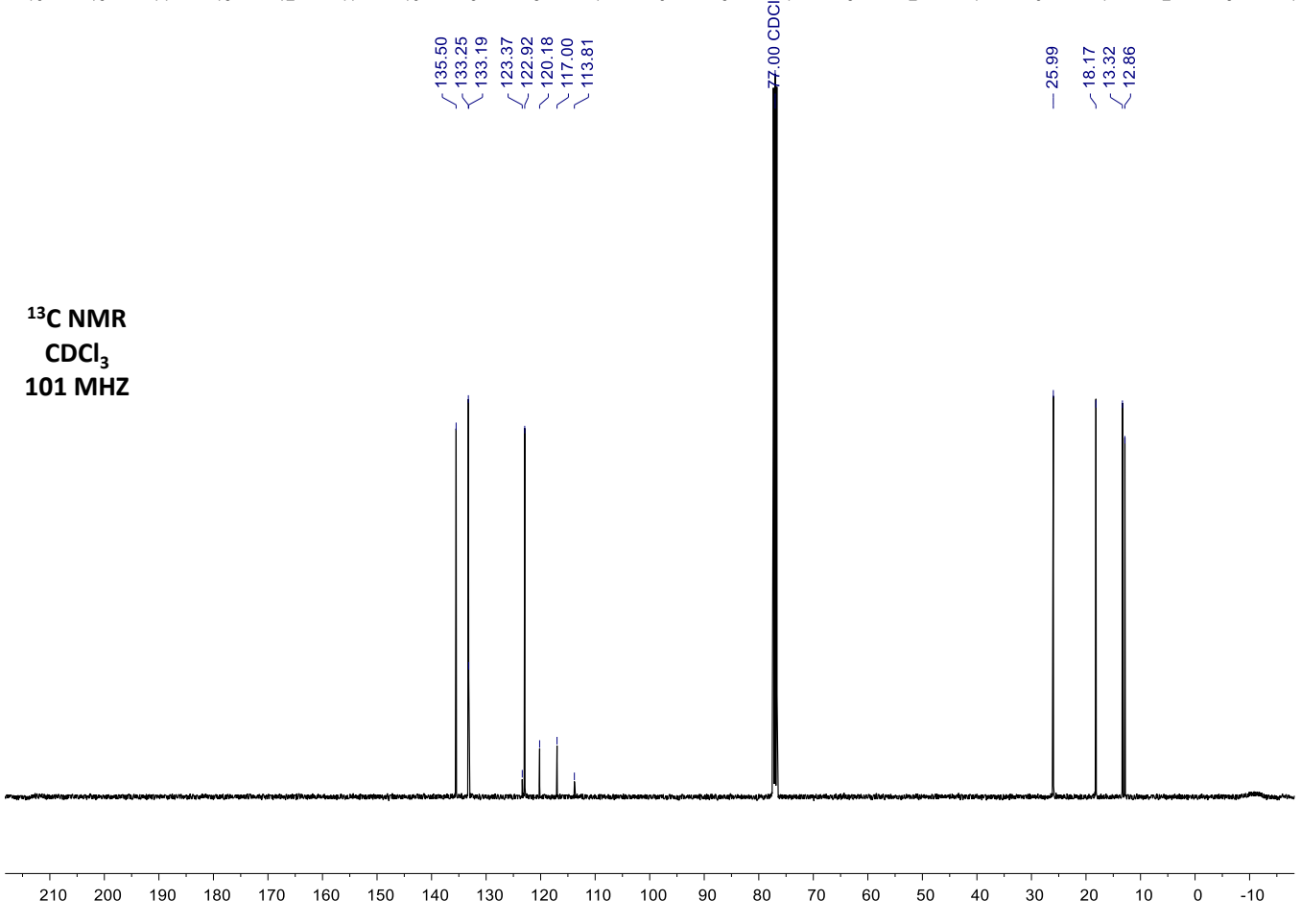
^{1}H NMR
$CDCl_3$
400 MHZ

^{13}C NMR
$CDCl_3$
101 MHZ

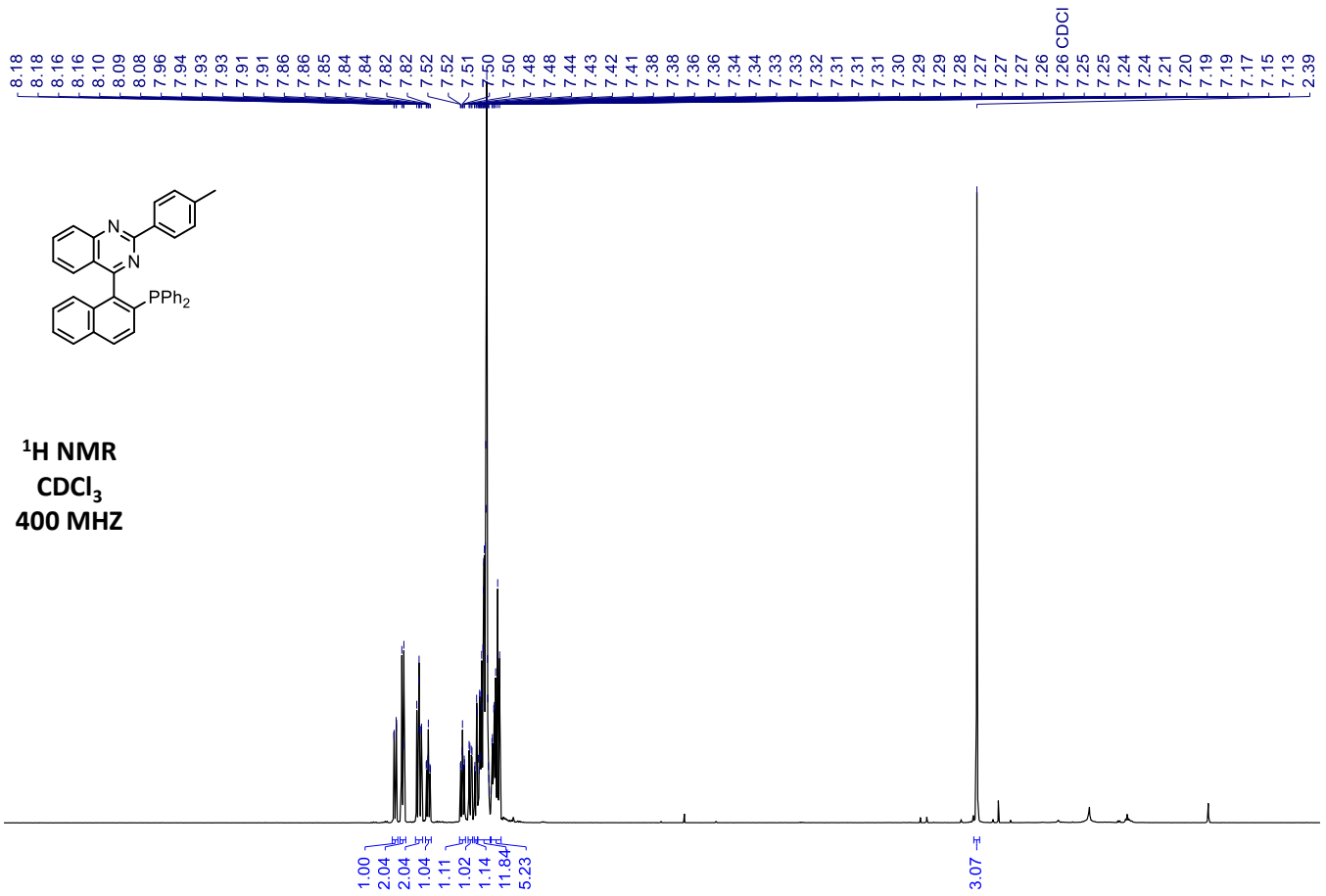


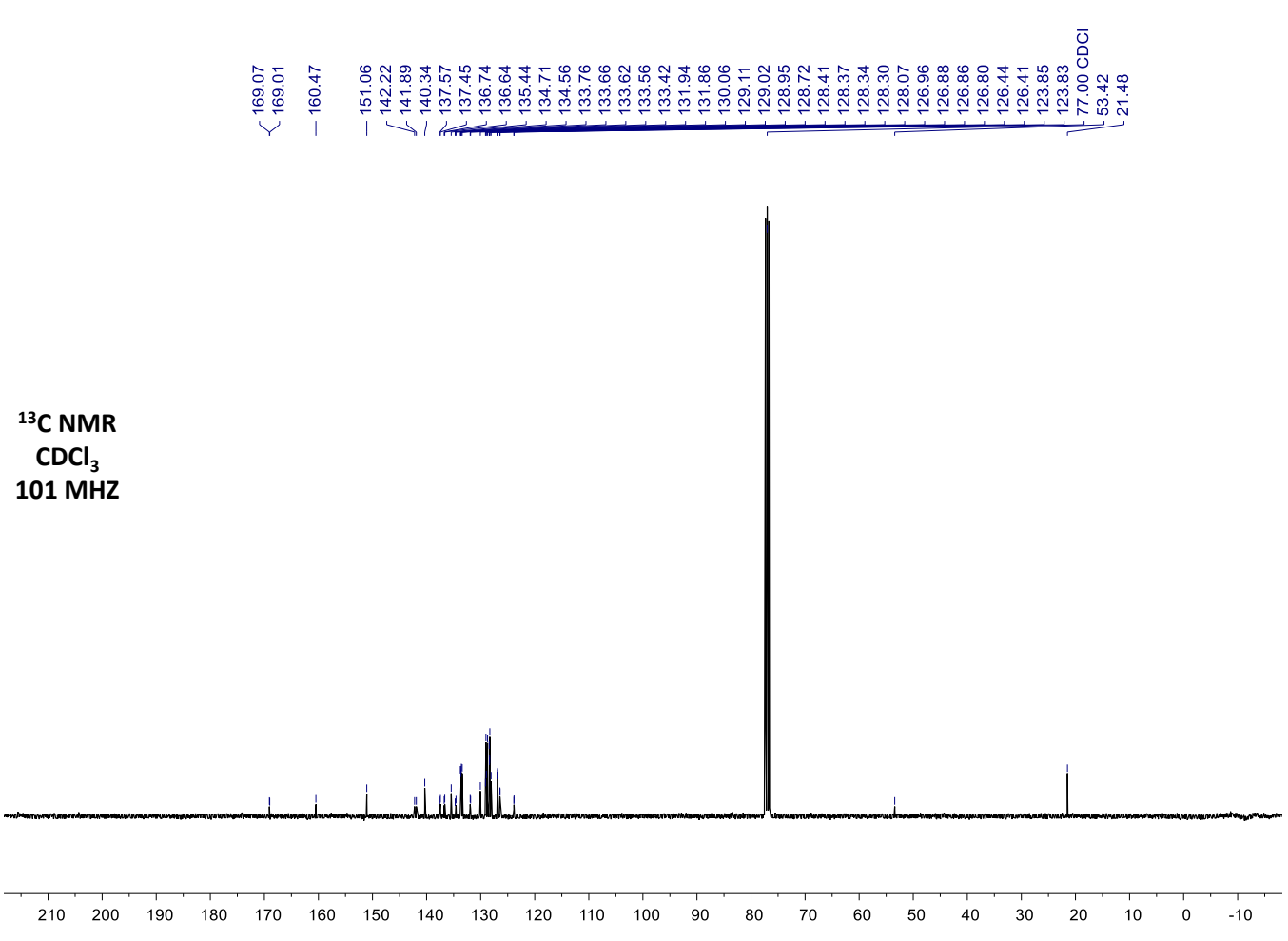


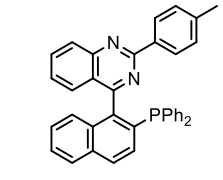
^{1}H NMR
$CDCl_3$
400 MHZ



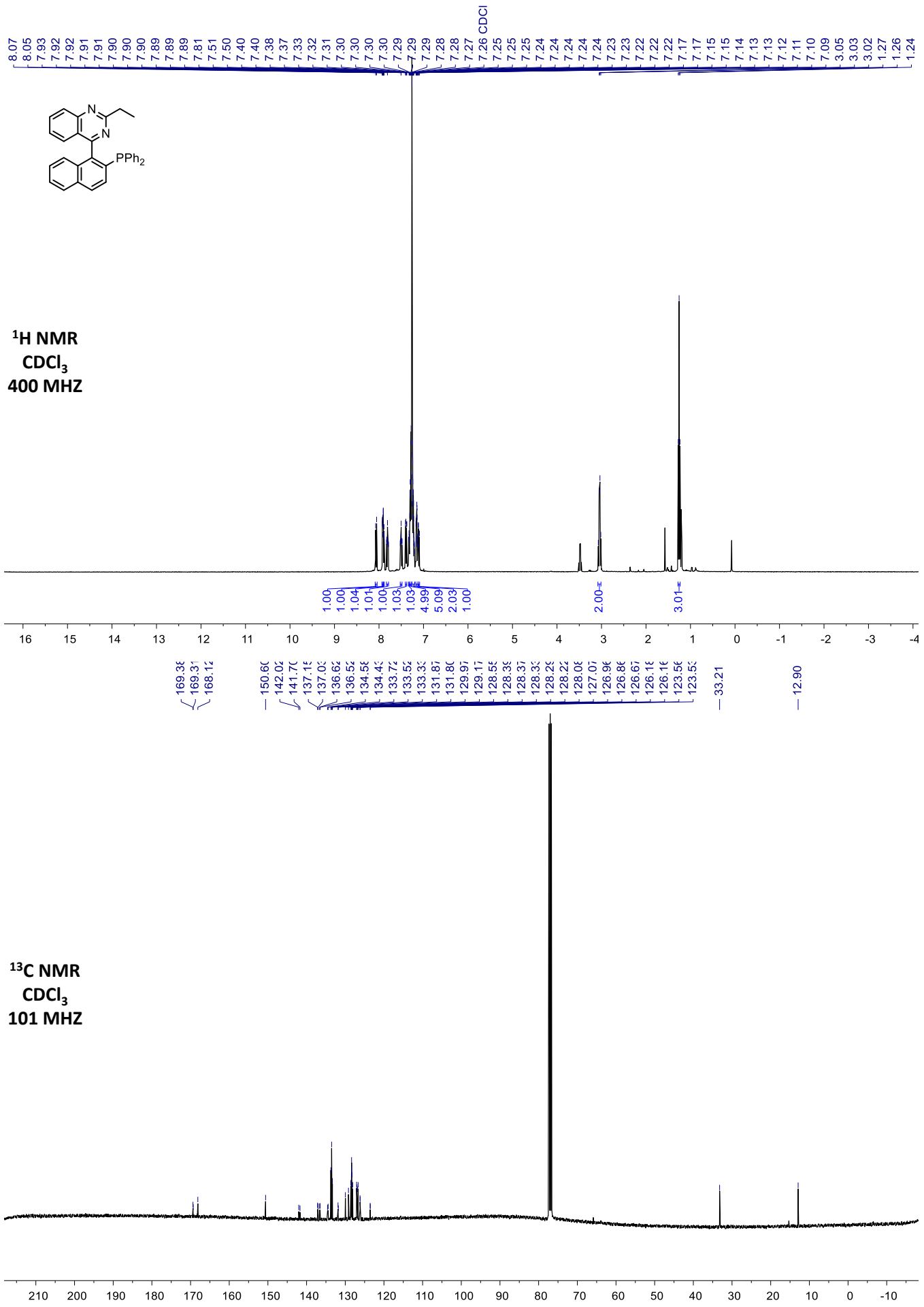
^{13}C NMR
$CDCl_3$
101 MHZ


8.18 8.18 8.16 8.16 8.10 8.09 8.08 7.96 7.94 7.93 7.93 7.91 7.91 7.86 7.86 7.85 7.84 7.84 7.82 7.82 7.52 7.52 7.51 7.50 7.50 7.48 7.48 7.44 7.43 7.42 7.41 7.38 7.38 7.36 7.36 7.34 7.34 7.33 7.33 7.32 7.31 7.31 7.31 7.30 7.29 7.29 7.28 7.27 7.27 7.27 7.26 7.26 CDCl 7.25 7.25 7.24 7.24 7.21 7.20 7.19 7.19 7.17 7.15 7.13 2.39
PPh2
1H NMR
CDCl3
400 MHZ
1.00 2.04 2.04 1.04 1.11 1.02 1.14 11.84 5.23
3.07
2.0 11.5 11.0 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 -1


169.07 169.01 160.47 151.06 142.22 141.89 140.34 137.57 137.45 136.74 136.64 135.44 134.71 134.56 133.76 133.66 133.62 133.56 133.42 131.94 131.86 130.06 129.11 129.02 128.95 128.72 128.41 128.37 128.34 128.30 128.07 126.96 126.88 126.86 126.80 126.44 126.41 123.85 123.83 77.00 CDCl 53.42 21.48
13C NMR
CDCl3
101 MHZ
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10



^{31}P NMR
$CDCl_3$
162 MHZ


8.07 8.05 7.93 7.92 7.92 7.91 7.91 7.90 7.90 7.90 7.89 7.89 7.89 7.81 7.51 7.50 7.40 7.40 7.38 7.37 7.33 7.32 7.31 7.30 7.30 7.30 7.29 7.29 7.29 7.28 7.28 7.27 7.26 CDCl 7.25 7.25 7.25 7.24 7.24 7.24 7.24 7.24 7.23 7.23 7.22 7.22 7.22 7.17 7.17 7.15 7.15 7.14 7.13 7.13 7.12 7.11 7.10 7.09 3.05 3.03 3.02 1.27 1.26 1.24
N
N
PPh2
1H NMR
CDCl3
400 MHZ
1.00 1.00 1.04 1.01 1.00 1.03 1.03 4.99 5.09 2.03 1.00 2.00 3.01
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3 -4
169.38 169.31 168.12 150.60 142.02 141.70 137.15 137.03 136.62 136.52 134.58 134.43 133.72 133.52 133.33 131.87 131.80 129.97 129.17 128.55 128.38 128.37 128.33 128.25 128.22 128.08 127.07 126.98 126.88 126.67 126.18 126.16 123.58 123.53 33.21 12.90
13C NMR
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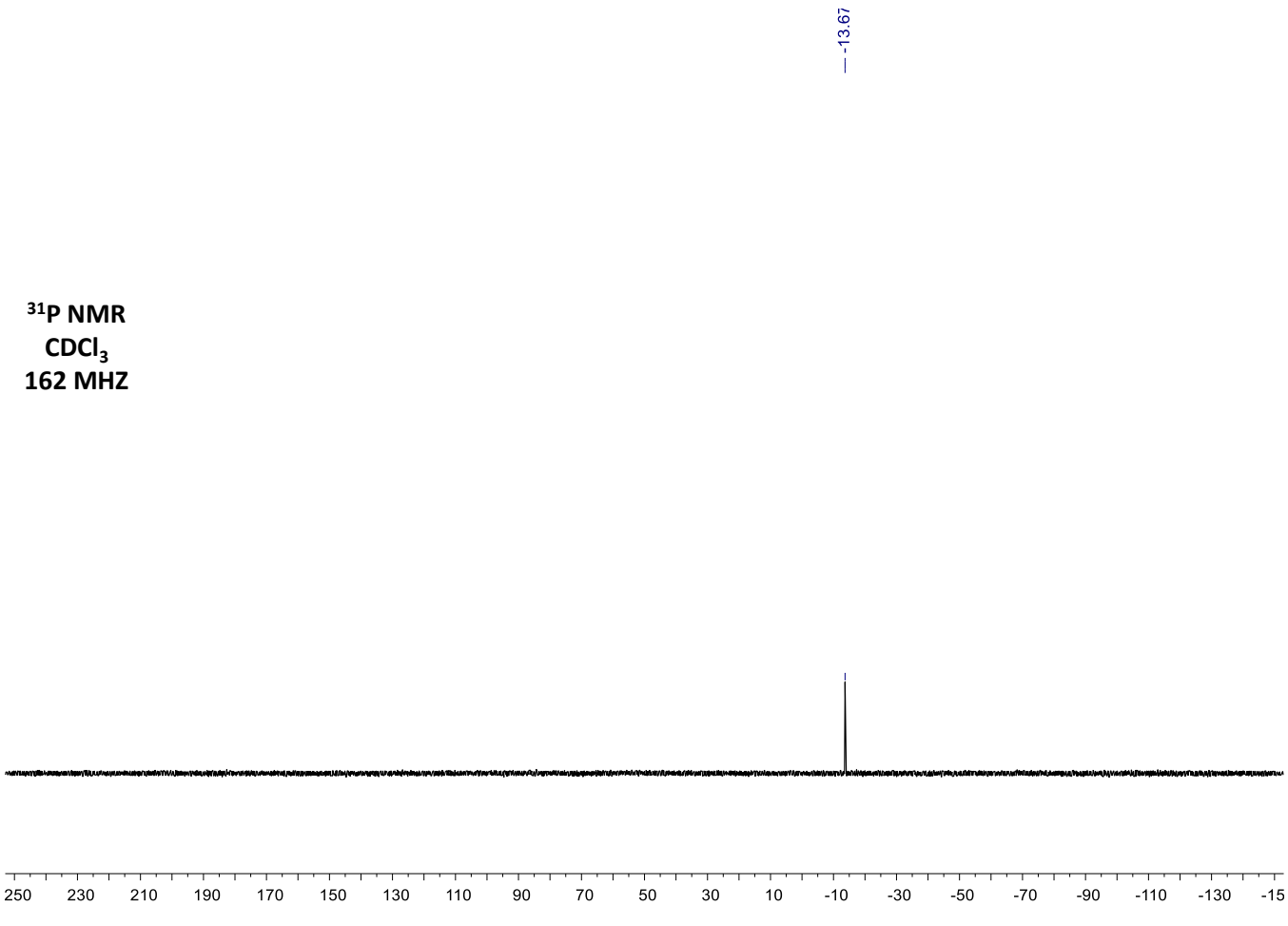

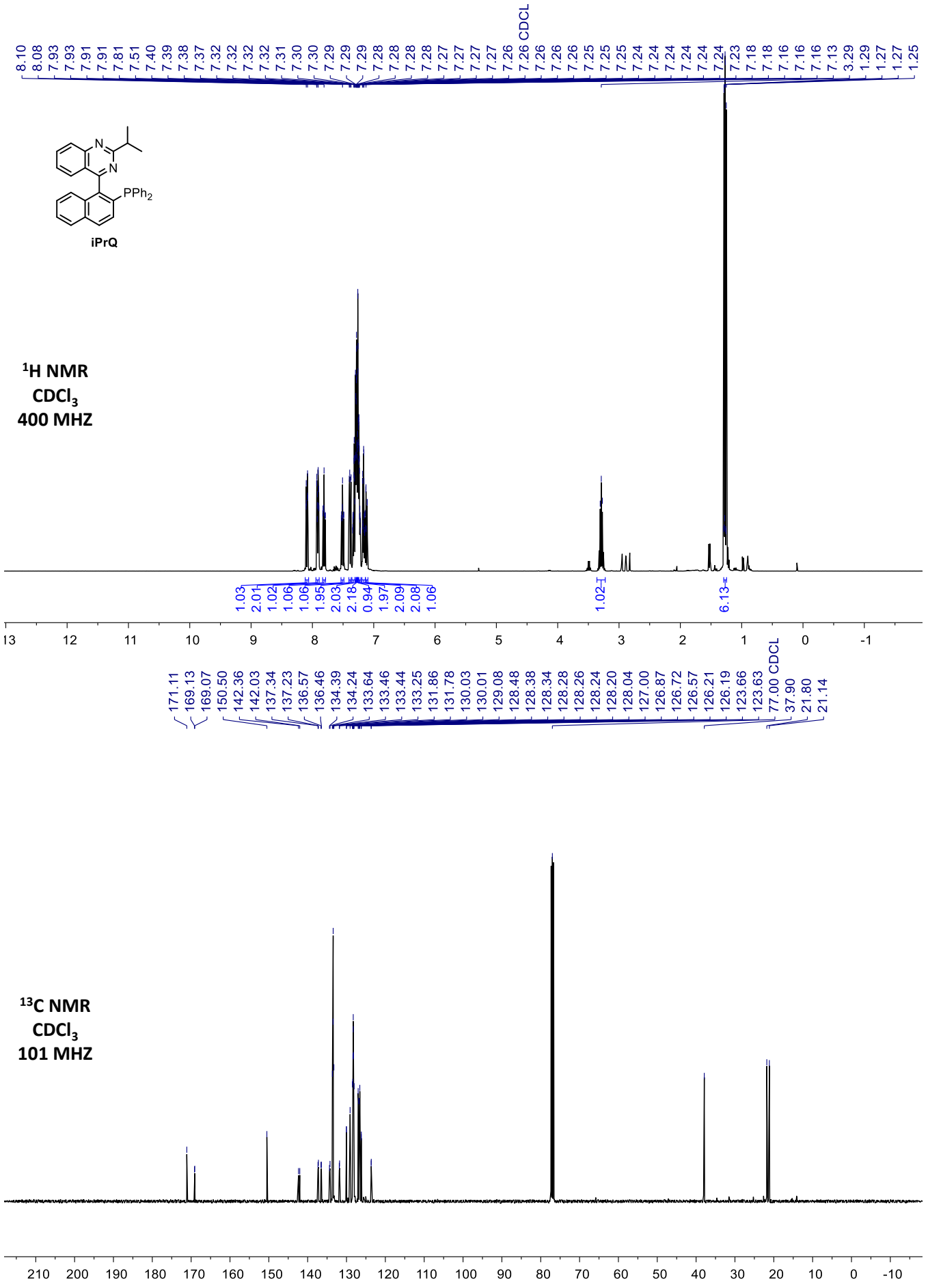
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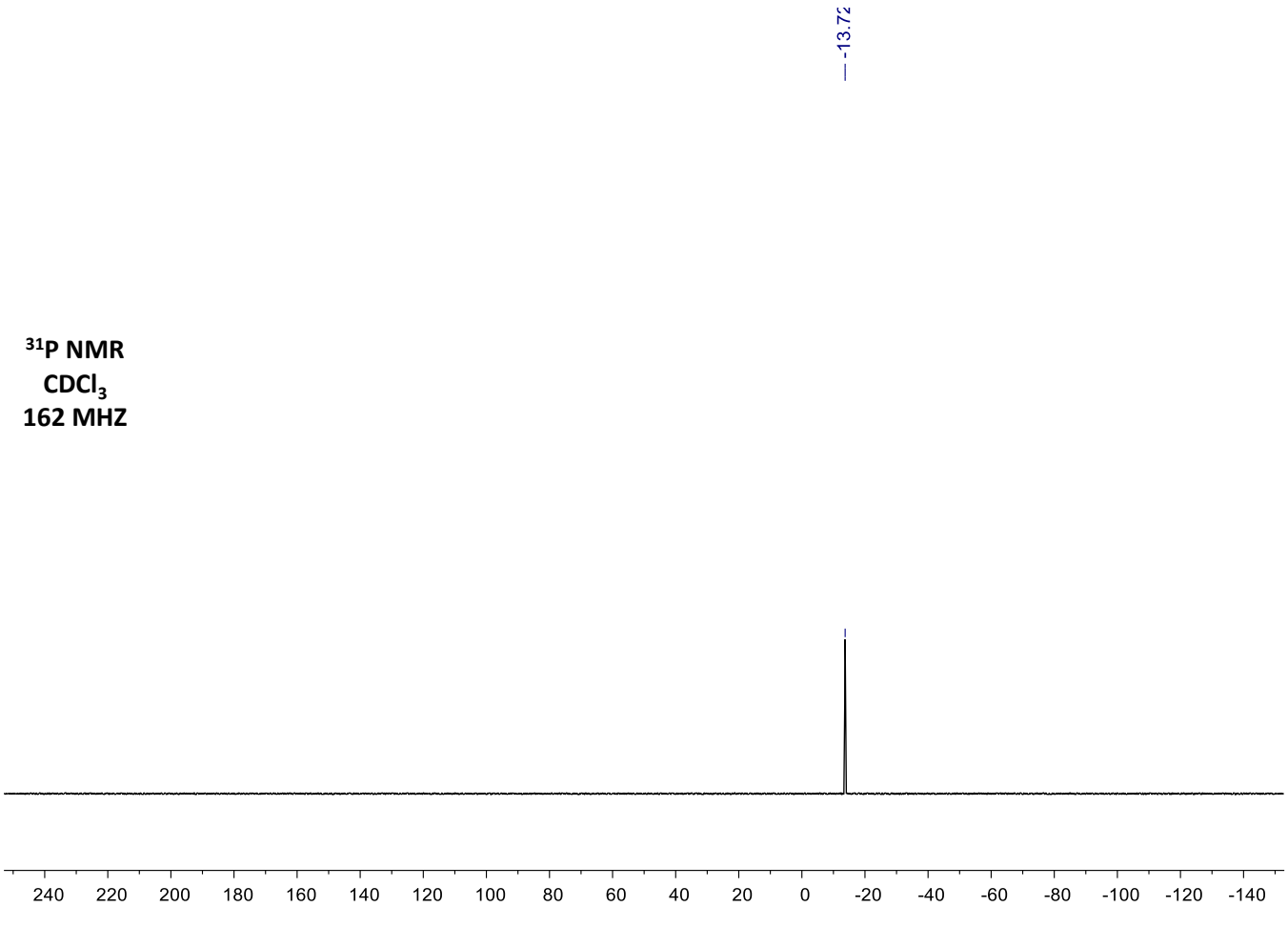

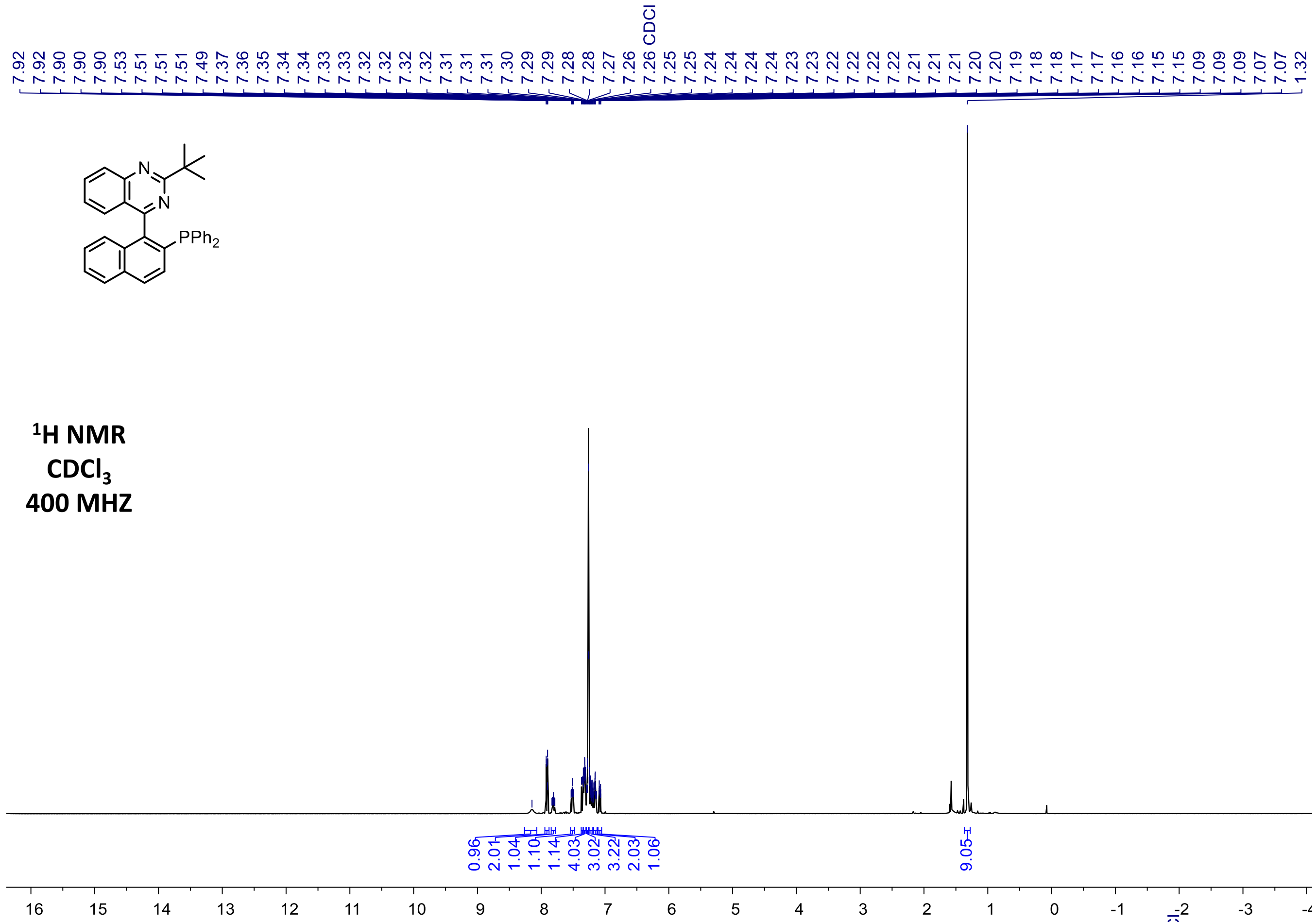
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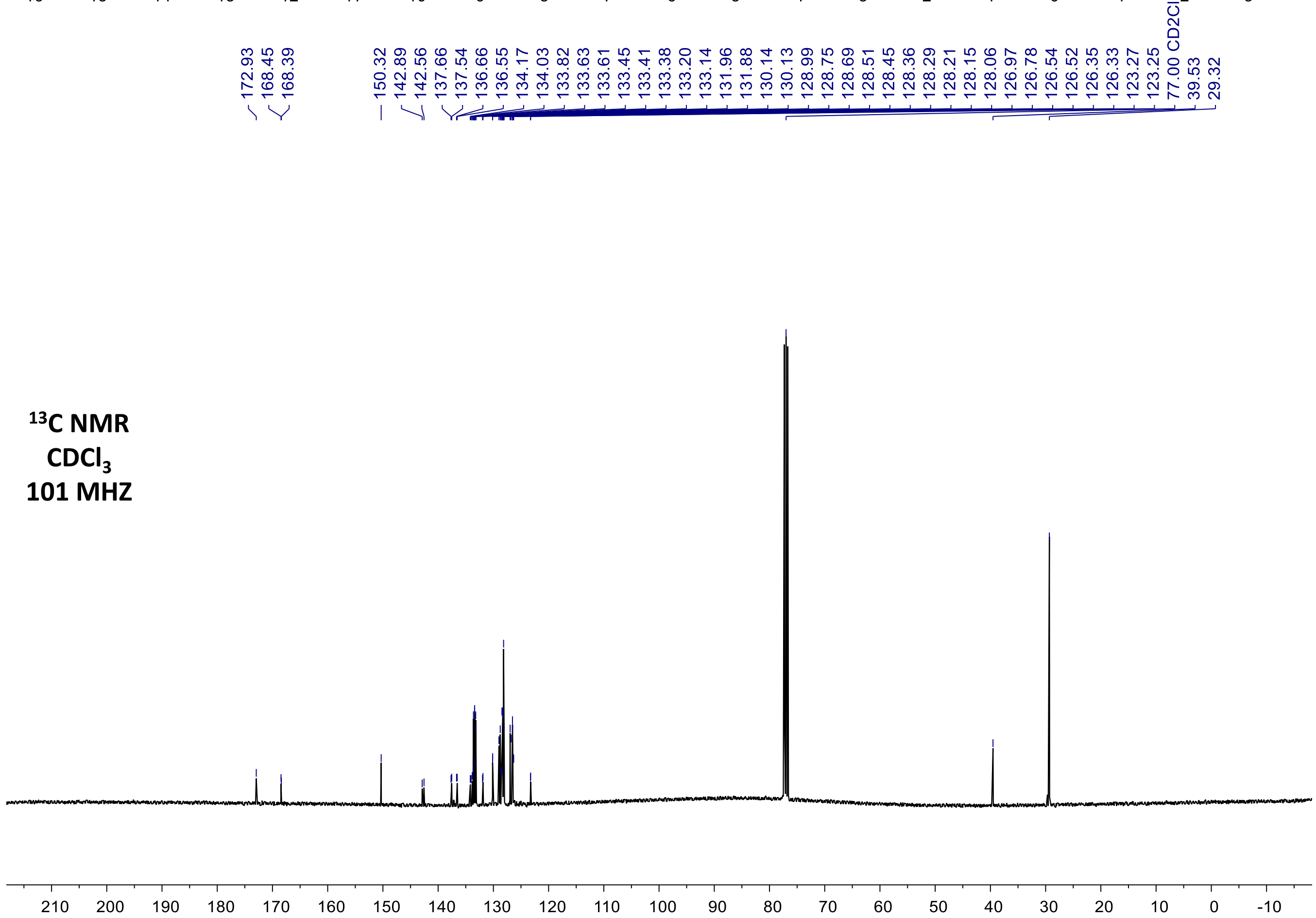
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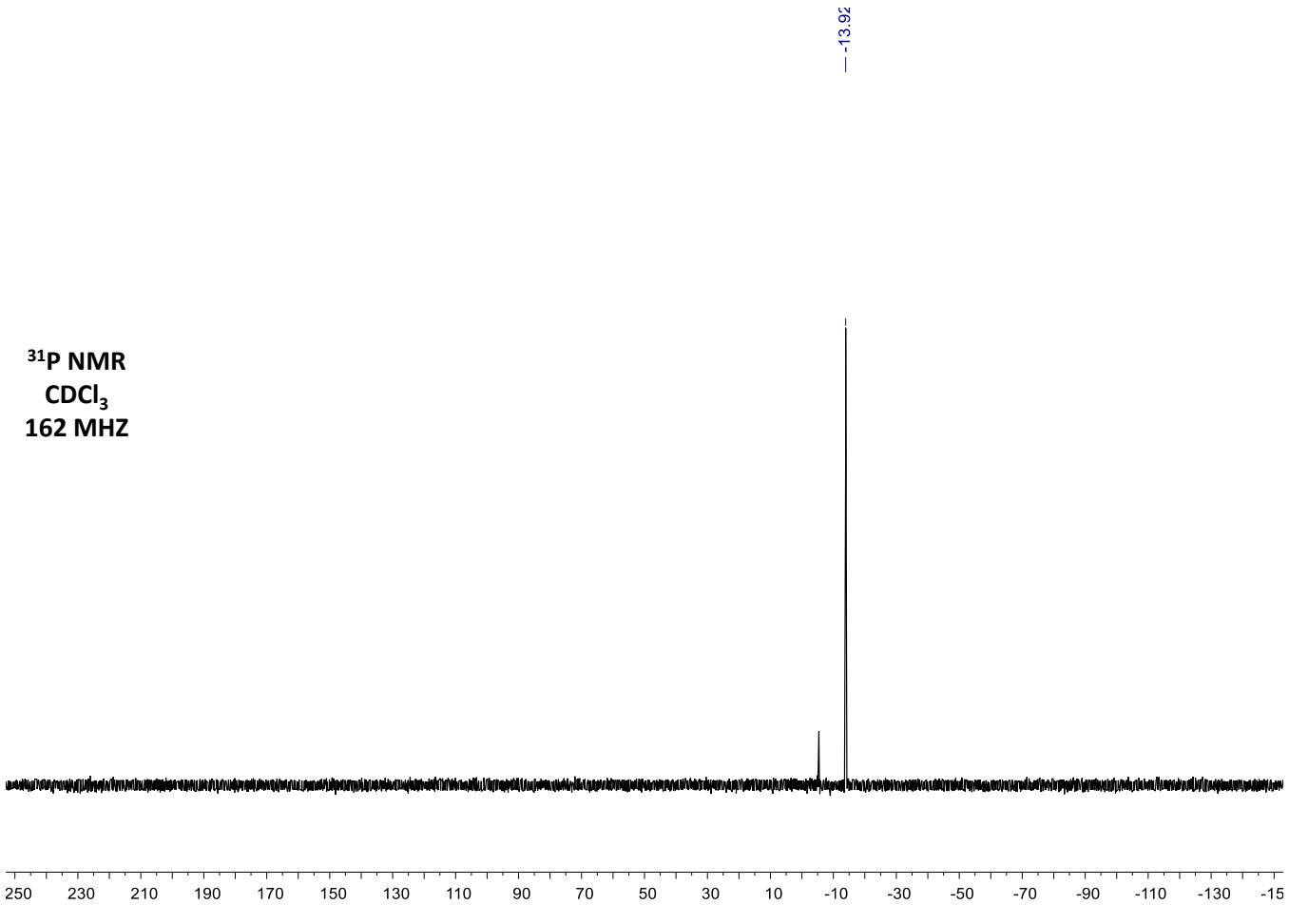
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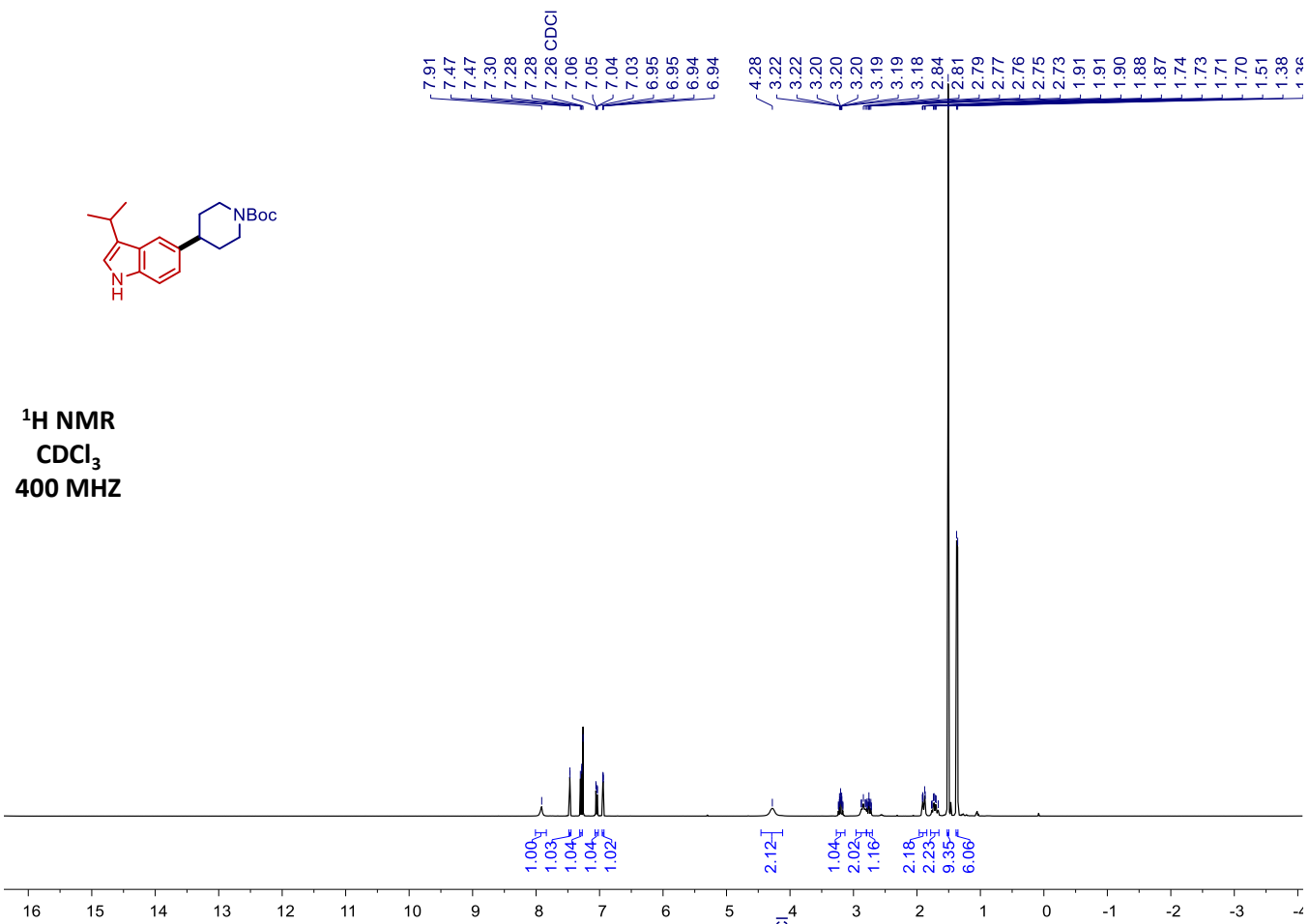

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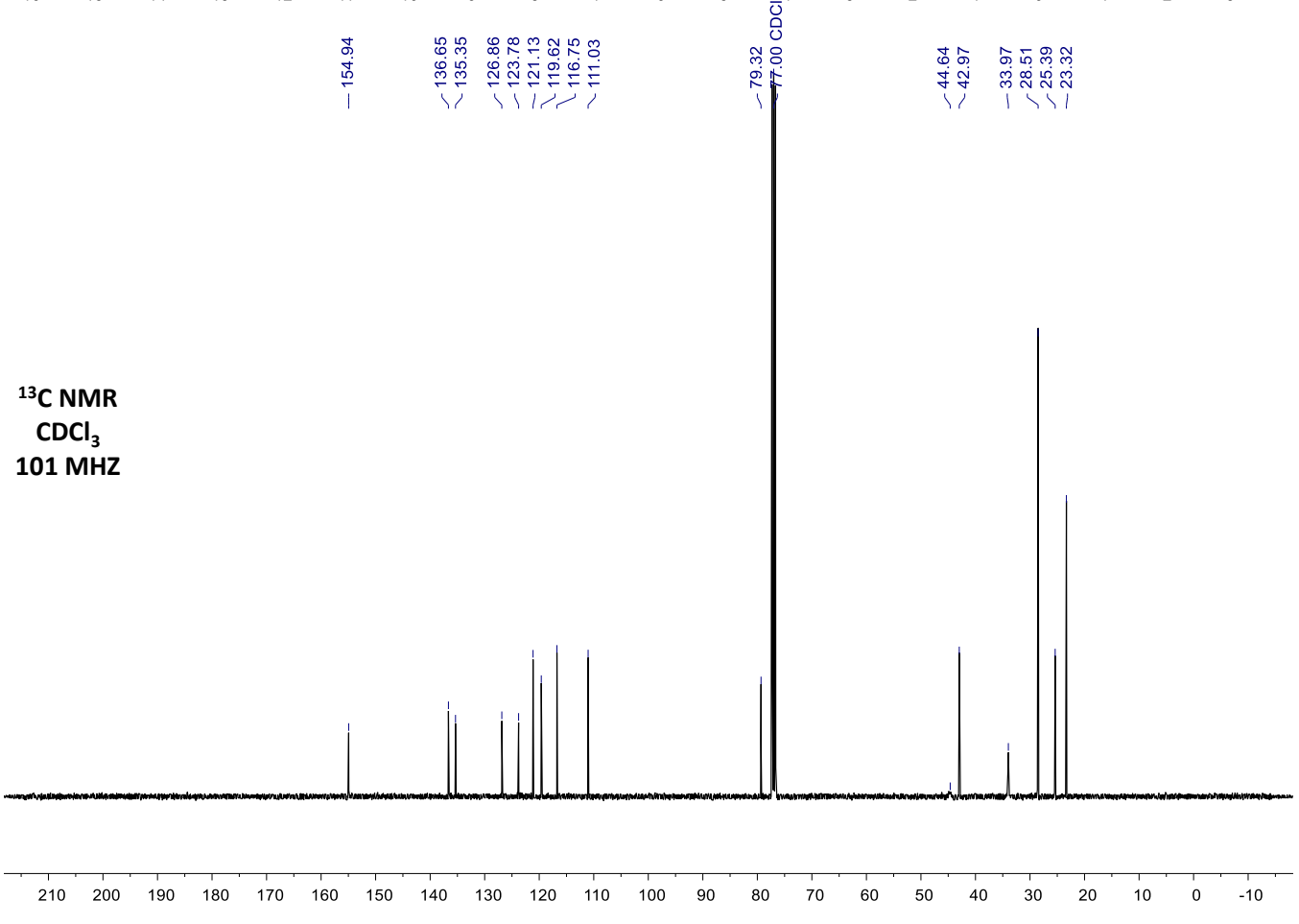

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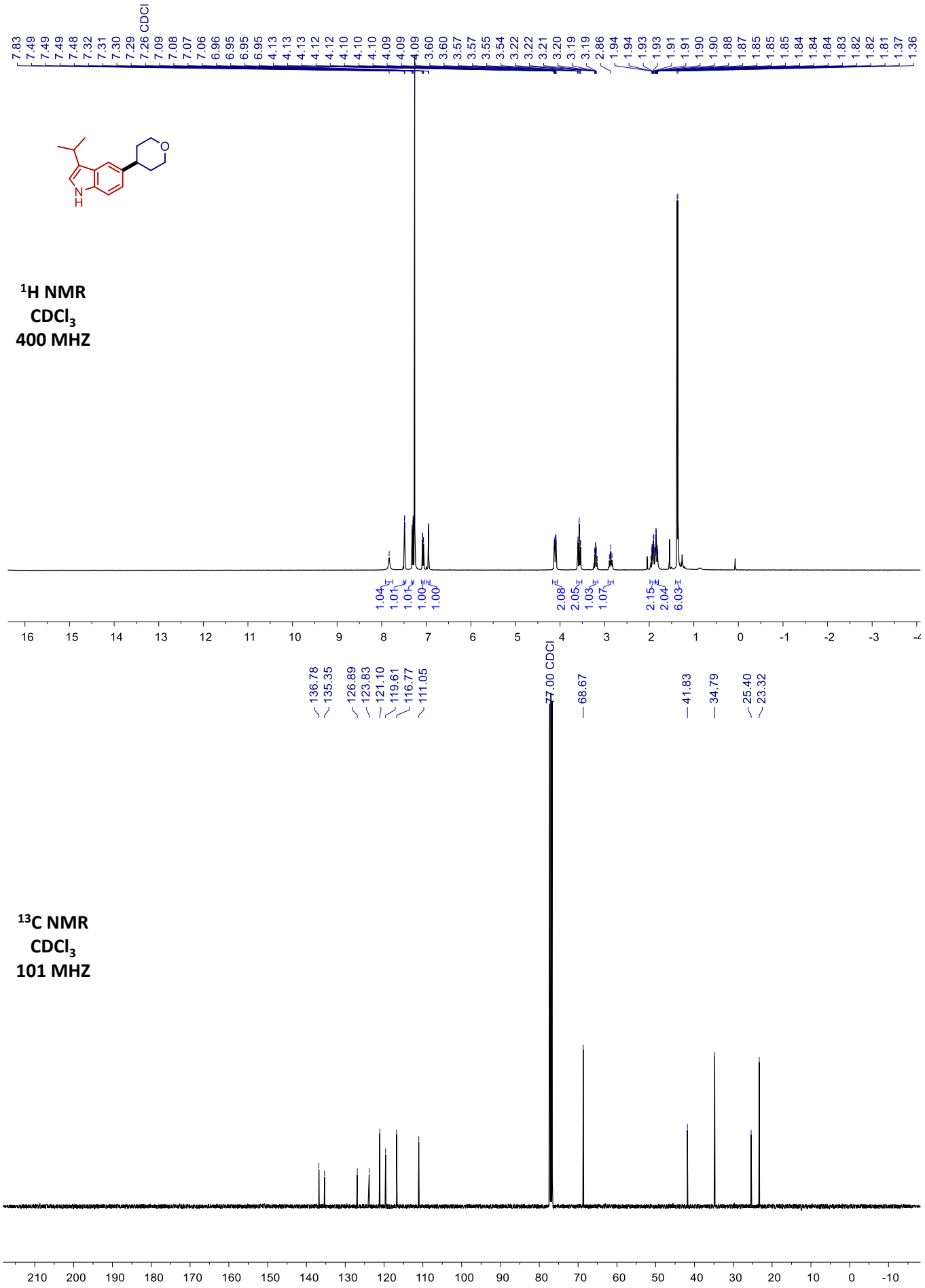
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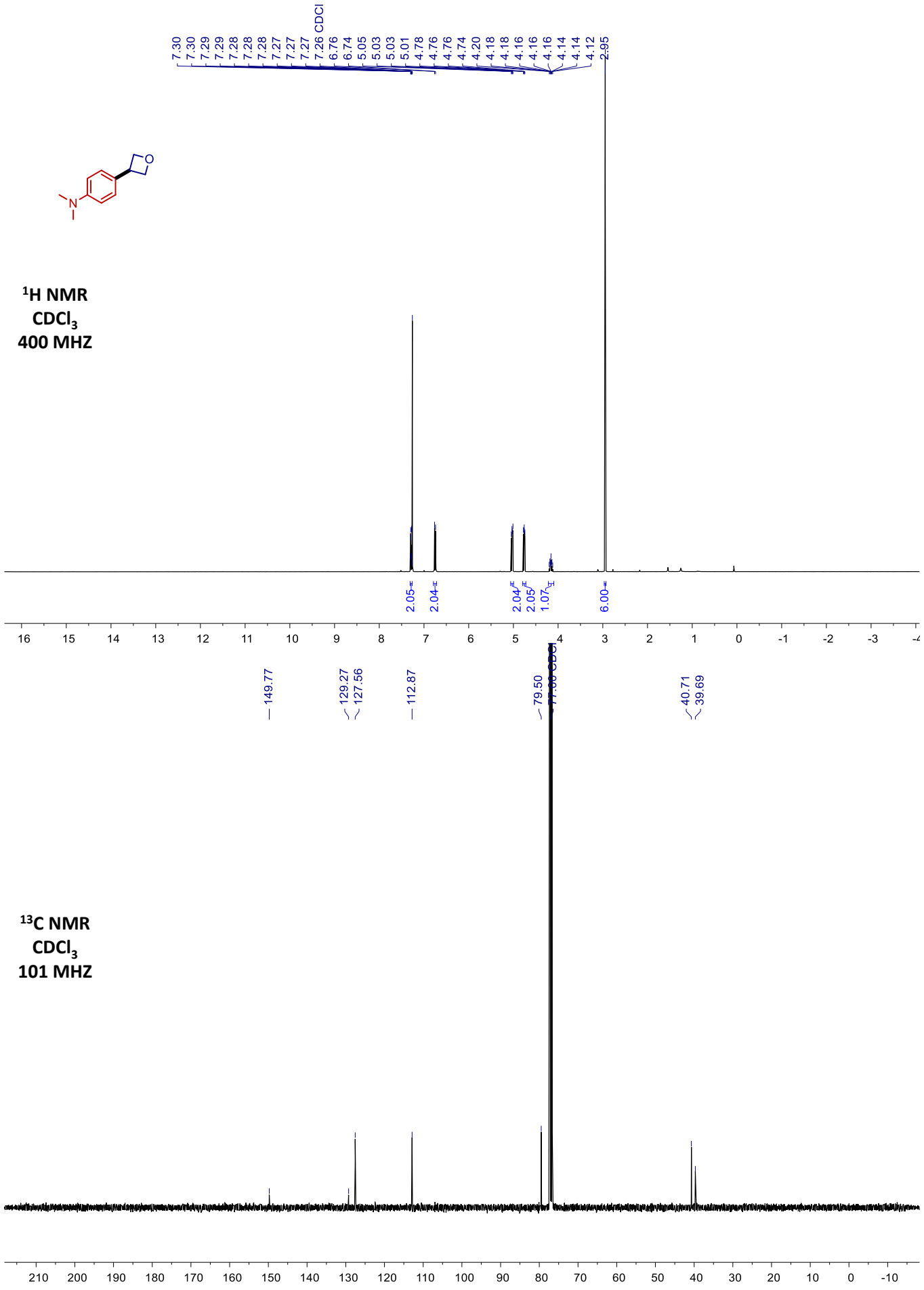
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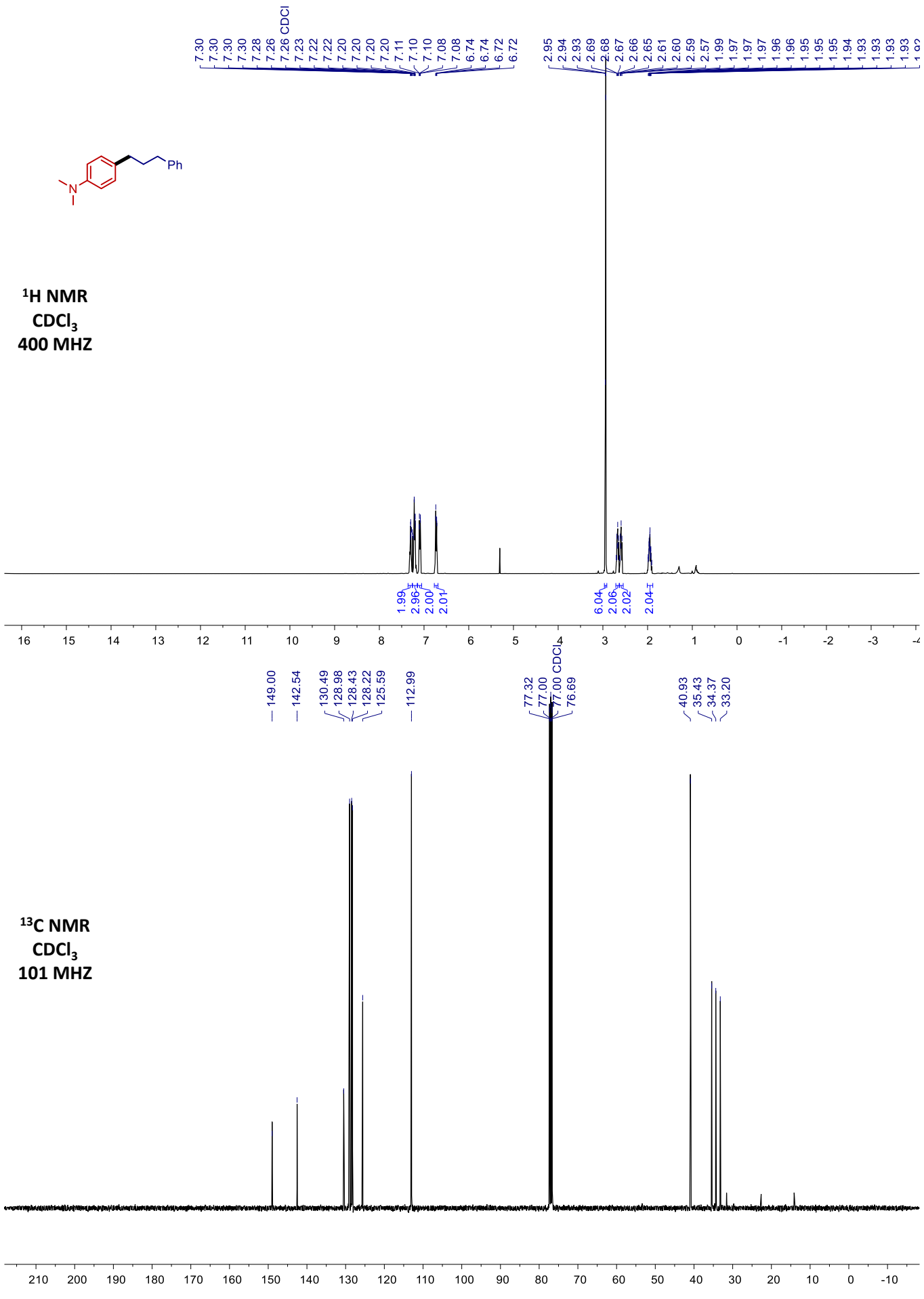
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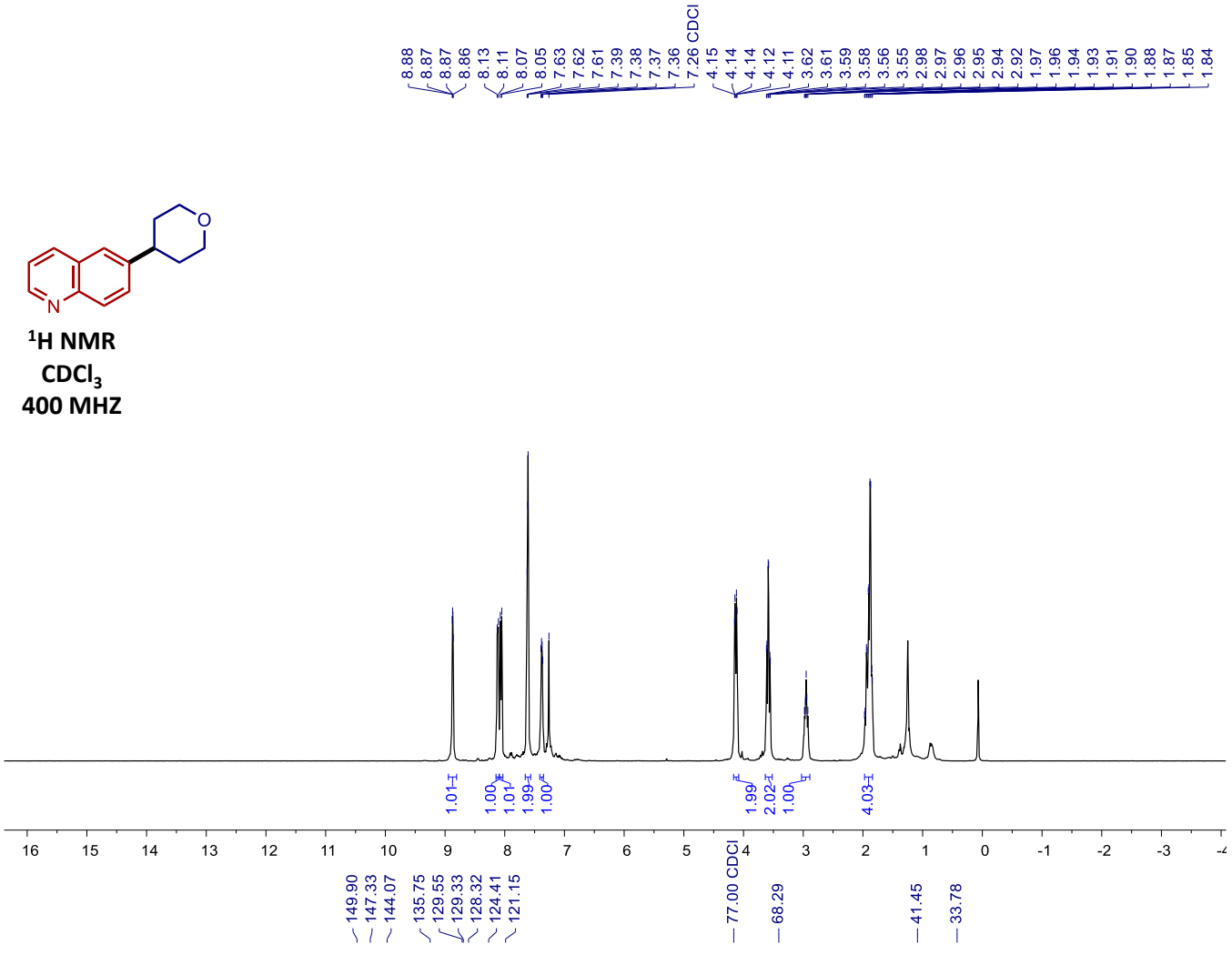
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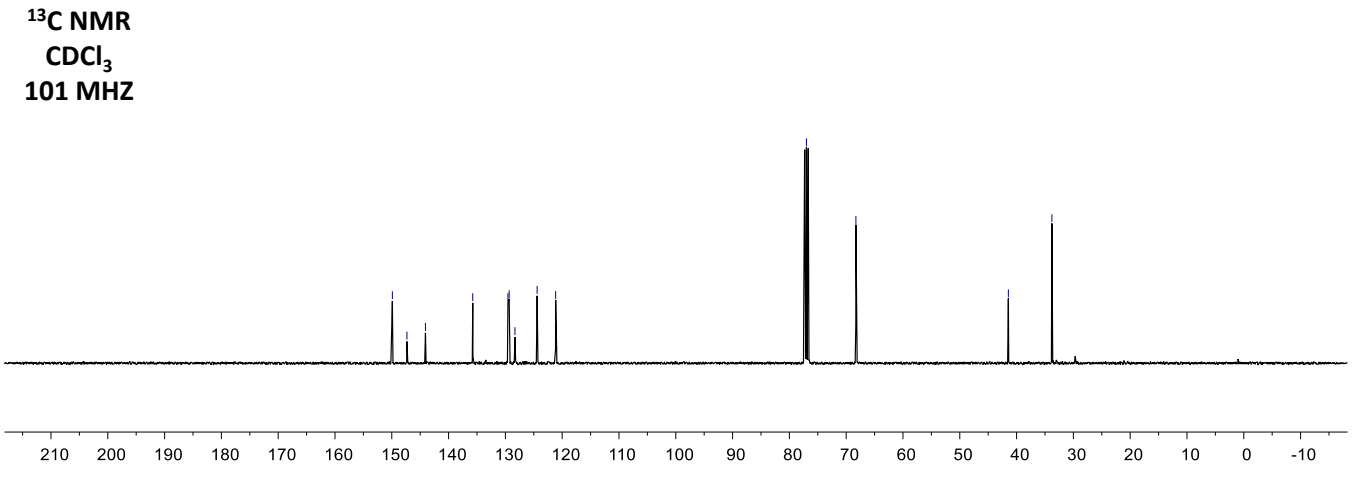
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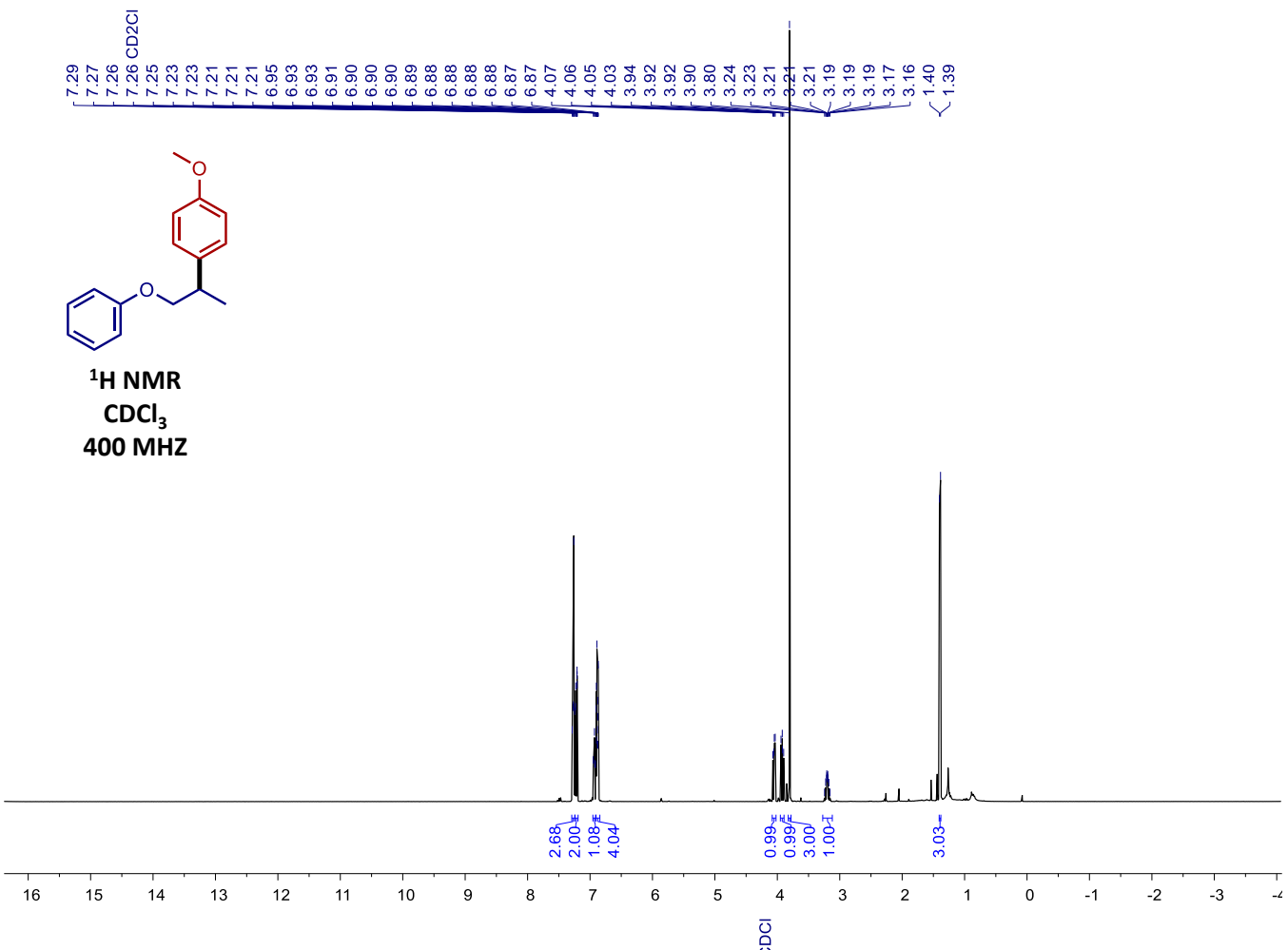
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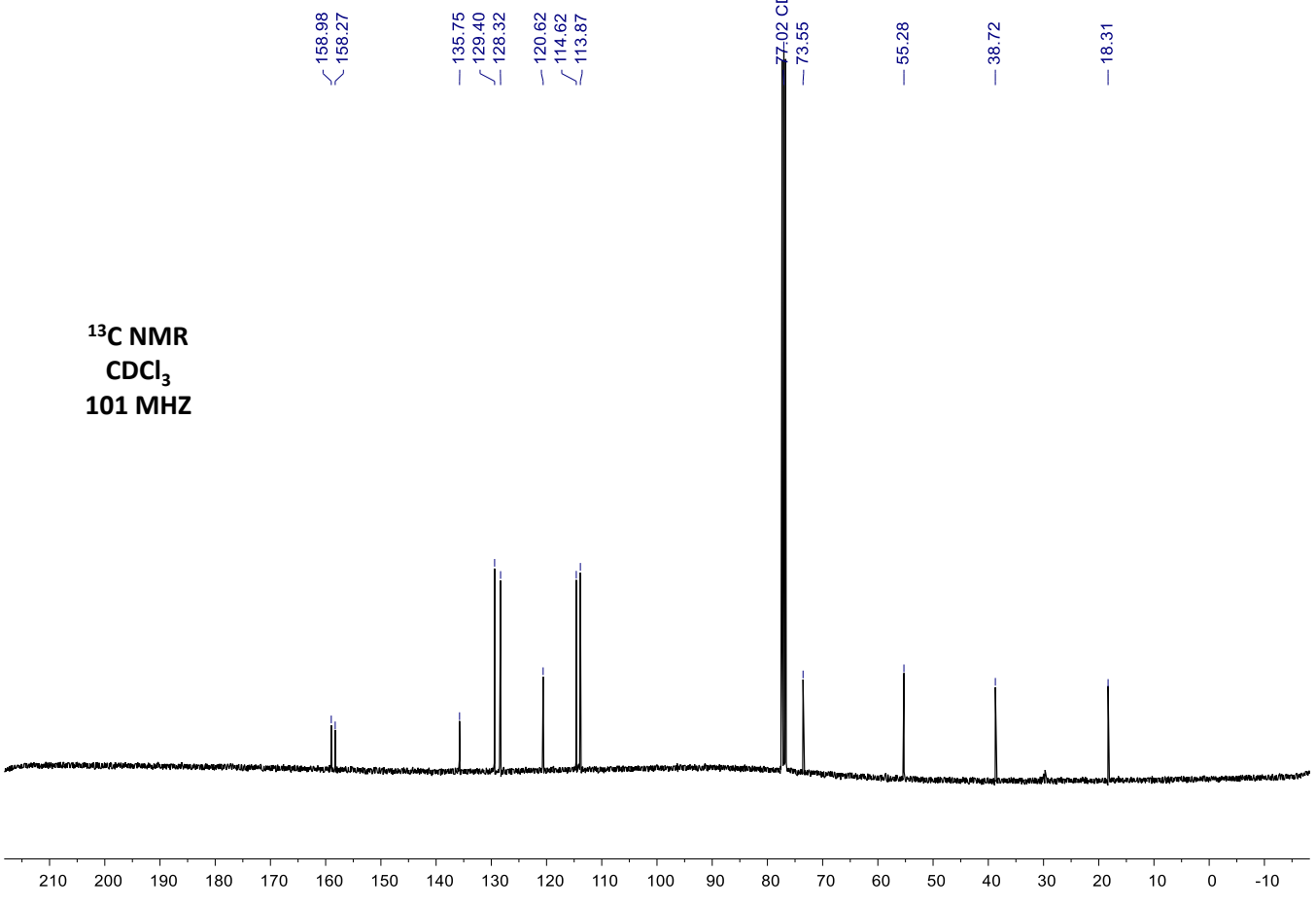
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