
Supplementary information

Reductive alkyl–alkyl coupling from isolable nickel–alkyl complexes

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Reductive Alkyl-Alkyl Coupling from Isolable Nickel-Alkyl Complexes

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General Information

Reagents

Unless otherwise noted, commercial reagents were purchased from either Sigma, TCI, Ambeed, or Oakwood Chemical and used as received.

Solvents

Anhydrous, degassed N,N-dimethylformamide (DMF), HPLC-grade tetrahydrofuran (THF) were purchased from Fischer, sparged with nitrogen (20 min), passed through activated alumina (PureSolv solvent system) and stored over 3 Å molecular sieves for at least 24 hours prior to use.

Coupling Partners and Organometallic Complexes

Non-commercial substrates were synthesized via modified literature procedures (*vide infra*).

Safety note: the toxicology of the organonickel complexes has not been studied. Handling of organonickel complexes should be done with care.^{1,2}

Instrumentation

Unless otherwise noted, all experiments were conducted under a dry atmosphere of nitrogen, and reaction cells were assembled in a nitrogen-filled glovebox.

NMR Spectroscopy

¹H NMR spectra were obtained at 400 or 600 MHz and chemical shifts were recorded relative to CHCl₃ in Chloroform-d (δ7.26 ppm), DMSO in DMSO-d₆ (δ2.50 ppm), C₆D₆ (δ7.16 ppm) ¹³C NMR spectra were obtained at 101 or 150 MHz. NMR multiplicities are reported as follows: singlet (s), doublet (d), triplet (t), quartet (q), multiplet (m), broad signal (br).

Gas Chromatography (GC)

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 decane as an internal standard to the reaction mixture upon completion of the reaction. Response factors for the products relative to the decane internal standard were measured.

GC-MS Instrumentation

Analysis and characterization of compounds via a GC-MS was performed using the Agilent 6850 GC equipped with the 5975 Series mass spectrometer (MS). Samples were analyzed via a positive electron-impact (EI) ionization method.

Chromatography

Chromatography was performed on silica gel (SiliCycle, silica gel 60) using standard flash techniques or using a Biotage Isolera One (detection at 253 nm and 400 nm). Products were visualized by UV light or stained using iodine or phosphomolybdic acid (PMA).

High Resolution Mass Spectrometry (HRMS)

High resolution mass spectra were collected using a ThermoFisher Exploris MX (Orbitrap) with Vanquish HPLC with ESI source. Samples were analyzed using a positive-ion ionization method.

Electrochemical Methods and Instrumentation

Electrochemical reactions were carried out in a nitrogen-filled glovebox. Supporting electrolytes and salts were used as received (TBAPF₆, TBABF₄) or were dried at 120 °C under vacuum for 24 hours (LiBr, LiCl). 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 10 mM AgBF₄ (Sigma) with 100 mM TBAPF₆ supporting electrolyte 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. Reference electrodes were calibrated against an internal voltage reference of ferrocene (1-10 mM). Electrolytic 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 plate (0.0234 x 3 x 600 in, purchased from Amazon.com) electrodes. Alternative electrode materials that were used included Cobalt wire (0.5 mm diameter, 2m, 99.995% purity, purchased from Puratonic) and stainless steel plate (10" x 10", 0.024" thickness, 304 grade, purchased from Grainger, item number 787Z88). Reactions were conducted in Fisherbrand disposable borosilicate glass tubes with a threaded end (16 x 100 mm). IKA Electrosyn 2.0 reactions were performed using a standard Zn-plate anode (Ident. No.: 0040002850) and a standard Ni-plate cathode (Ident. No.: 0040002859) (electrode dimensions: 8 x 52.5 x 2 mm).

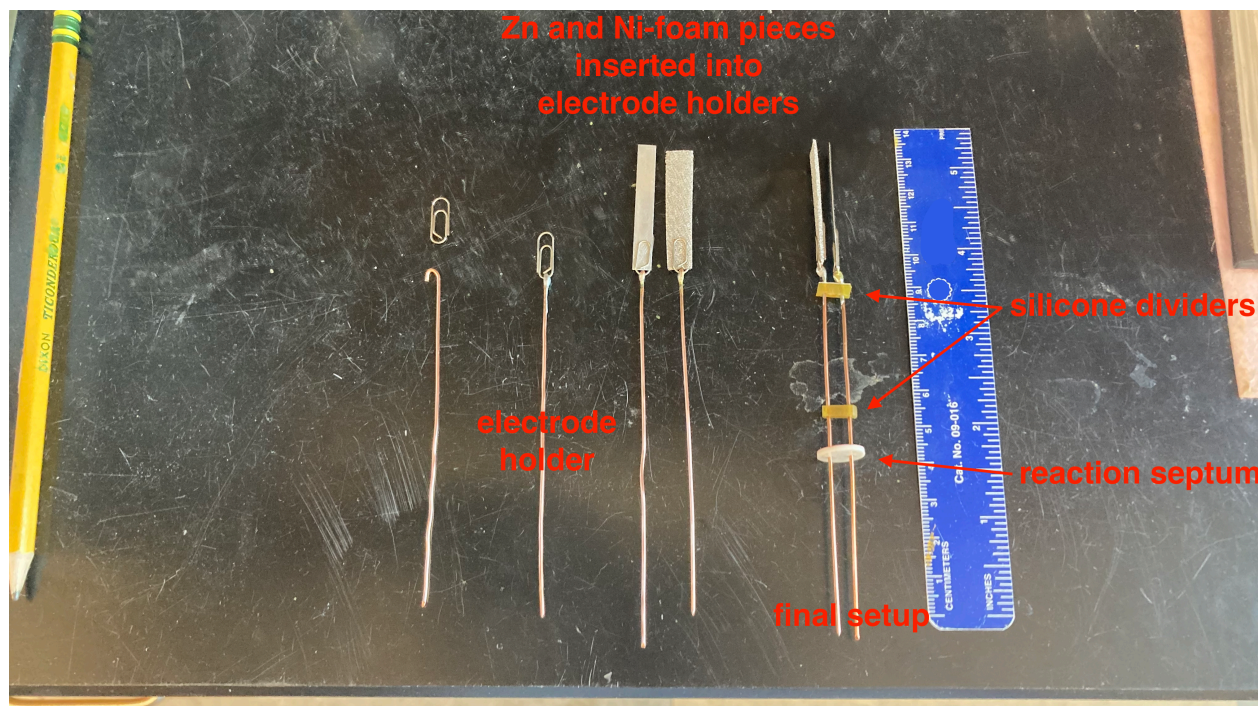
Electrochemical cell preparation procedures

Materials required:

12 mL threaded reaction test tube (12 mL threaded culture tube),
threaded test tube cap,
copper wire (18 ga),
cobalt wire (0.5 mm diameter),
nichrome wire (0.8 mm diameter, from Fischer, catalog #155402B),
nickel foam, zinc sheet,
PTFE septa (13 mm diameter, from Fischer, item #0334010G),
PTFE/Silicone septa (22 mm diameter, from Fischer, catalog #111016140),
stainless-steel paper clips (15 mm x 5.6 mm, purchased from Outus via Amazon.com)
coarse sandpaper,
pliers, hole punch, and aviation snips.

Ni(-)Zn(+) electrochemical cell setup

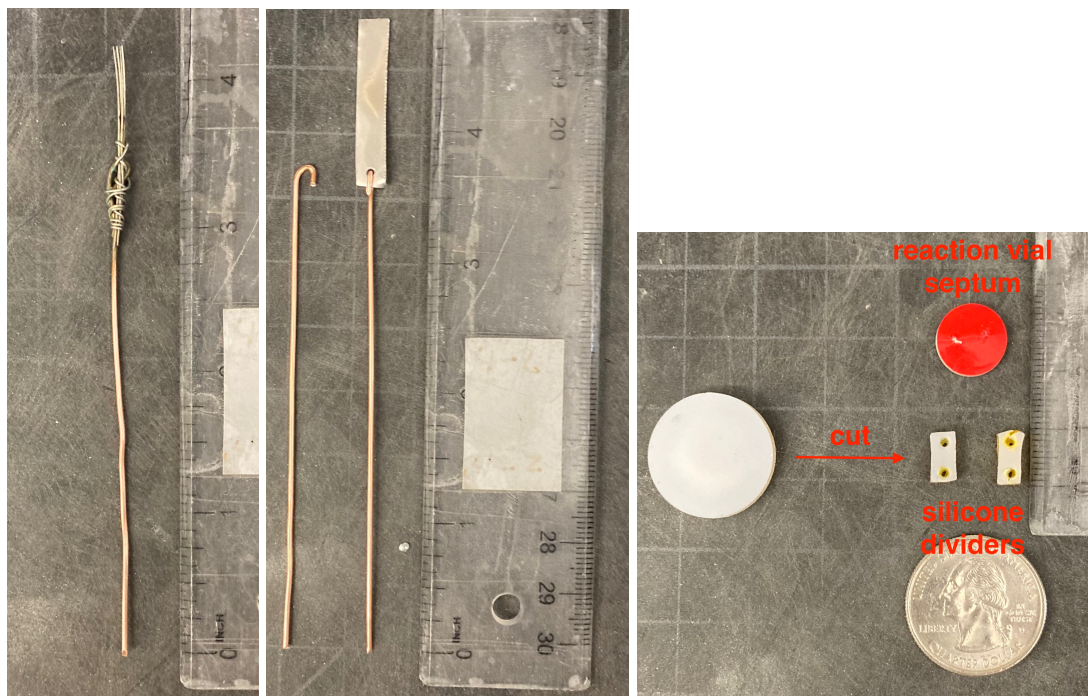
Electrode holders were prepared by soldering a piece of copper wire (3" length) to a small stainless steel paper clip. Aviation snips were used to cut a 0.25" x 1.5" piece of Zn plate and 0.25" x 1.5" piece of Ni-foam. Both electrodes were pierced through two 0.0625" x 0.25" pieces of silicone dividers (cut from silicone septum) and were subsequently pierced through a reaction vial septum. Both sides of the Zn electrode were sanded with a coarse sandpaper before use.



Electrodes were inserted into a threaded reaction vial with a 0.39" gap from the bottom of the vial, with reaction vial septum secured with the threaded cap.

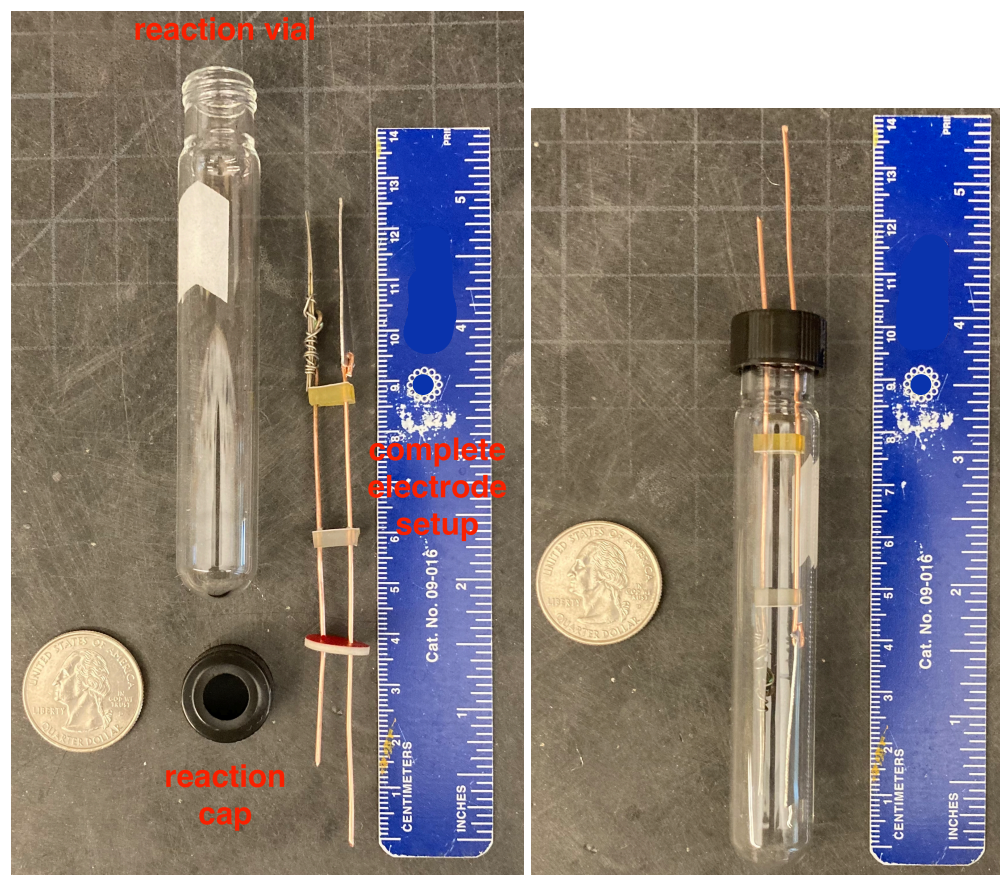
Co(+)SS(+) electrochemical cell setup

Cobalt wire electrode was prepared by bundling 4 pieces of cobalt wire (1.25" length) around a copper wire (3" length) and fixing them in place with nichrome wire as shown below. Co wires were sanded with a coarse sandpaper before use.



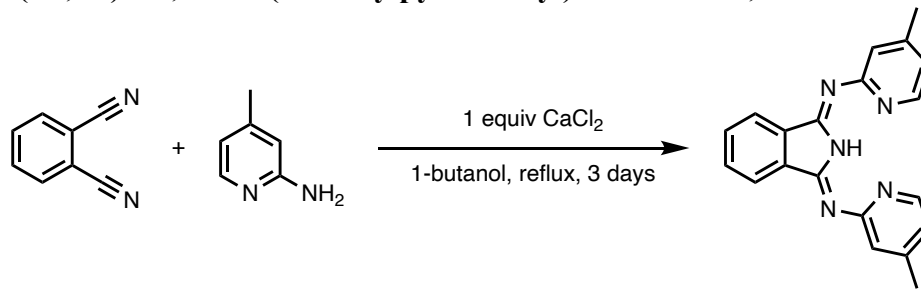
Stainless-steel (SS) electrode was prepared as follows. Aviation snips were used to cut a 1.25" L 0.2" W piece of stainless steel. A 1.2 mm hole was punched and the resulting SS electrode was secured to copper wire via pliers. Both sides of the SS electrode were sanded with a coarse sandpaper before use.

Both electrodes were pierced through two 0.0625" x 0.25" pieces of silicone dividers (cut from silicone septum) and were subsequently pierced through a reaction vial septum. The silicone separators prevent accidental contact between wires. Electrodes were inserted into a threaded reaction vial with a 0.39" gap from the bottom of the vial, with reaction vial septum secured with the threaded cap.



Synthesis of starting materials

Synthesis of (1Z,3Z)-N1,N3-bis(4-methylpyridin-2-yl)isoindoline-1,3-diimine BPI Ligand



The title product was prepared following a published procedure with modifications.³

Calcium chloride was dried in a vacuum oven at 120 °C for 16 hours before use. A 1 L round-bottom flask equipped with a stir bar was charged with phthalonitrile (50.0 g, 390.2 mmol, 1.00 equiv), 4-methylpyridin-2-amine (105.5 g, 975.5 mmol, 2.500 equiv), calcium chloride (43.3 g, 390 mmol, 1.00 equiv), and 1-butanol (500 mL, 780 mM). The reaction was allowed to reflux for at least 3 days, with longer reaction times improving the yield. During reflux, the reaction slowly evolves ammonia gas and gradually turns yellow-orange. After cooling to room temperature, large solid clumps were broken down with a spatula. The reaction was diluted with hexanes (1 L), causing further precipitation. The resulting suspension was vigorously stirred for 30 minutes, filtered, and washed with hexanes (2 x 150 mL). Solids were dissolved in DCM (600-900 mL), and the resulting solution was filtered through a Celite bed to remove insoluble calcium salts. If the DCM filtrate appears green, the solution needs to be stirred with activated charcoal (2-5 g) for 1 hour and filtered through Celite.

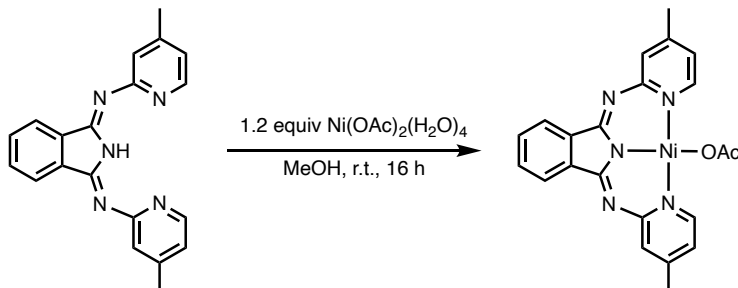
The DCM filtrate was washed with water (3 x 150 mL), followed by brine (100 mL). The solvent was removed via rotary evaporation to afford crude BPI ligand.

The crude product was recrystallized in boiling ethanol (0.7-1 L) to afford pure BPI ligand as a flaky yellow solid (50.1 g, 153 mmol, 39%).

¹H NMR (400 MHz, Chloroform-d) δ 13.96 (s, 1H), 8.44 (dd, J = 5.0, 0.7 Hz, 2H), 8.12 – 7.98 (m, 2H), 7.69 – 7.55 (m, 2H), 7.36 – 7.19 (m, 2H), 6.92 (ddd, J = 5.1, 1.6, 0.8 Hz, 2H), 2.37 (s, 6H).

¹³C NMR (101 MHz, Chloroform-d) δ 160.2, 157.1, 153.1, 138.5, 135.7, 131.8, 122.7, 119.7, 118.6, 24.8.

Synthesis of (1Z,3Z)-N1,N3-bis(4-methylpyridin-2-yl)isoindoline-1,3-diimineNickelAcetate, BPI-Ni-OAc (1)

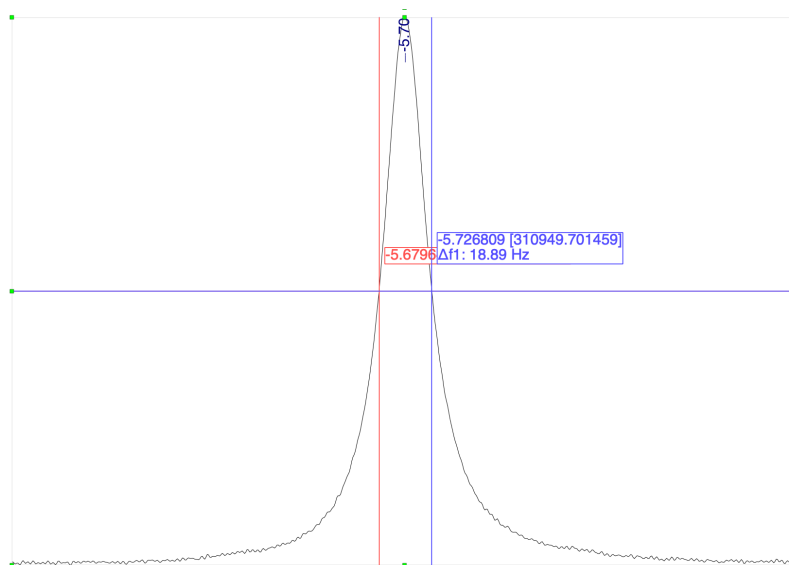


The title product was prepared following a previously reported procedure.⁴

This reaction was performed under an ambient atmosphere. A 1 L round-bottom flask equipped with a stir bar was charged with (1Z,3Z)-N1,N3-bis(4-methylpyridin-2-yl)isoindoline-1,3-diimine (BPI) (25.0 g, 76.4 mmol, 1.00 equiv), nickel(II) acetate tetrahydrate (22.8 g, 91.6 mmol, 1.20 equiv), and methanol (610 mL, 125 mM). The resulting suspension was stirred at room temperature for 16 hours, gradually turning golden-yellow. The resulting suspension was filtered, washing with methanol (3 x 100 mL) to afford product as a golden-yellow clumpy solid (10.0 g, 22.5 mmol, 74%).

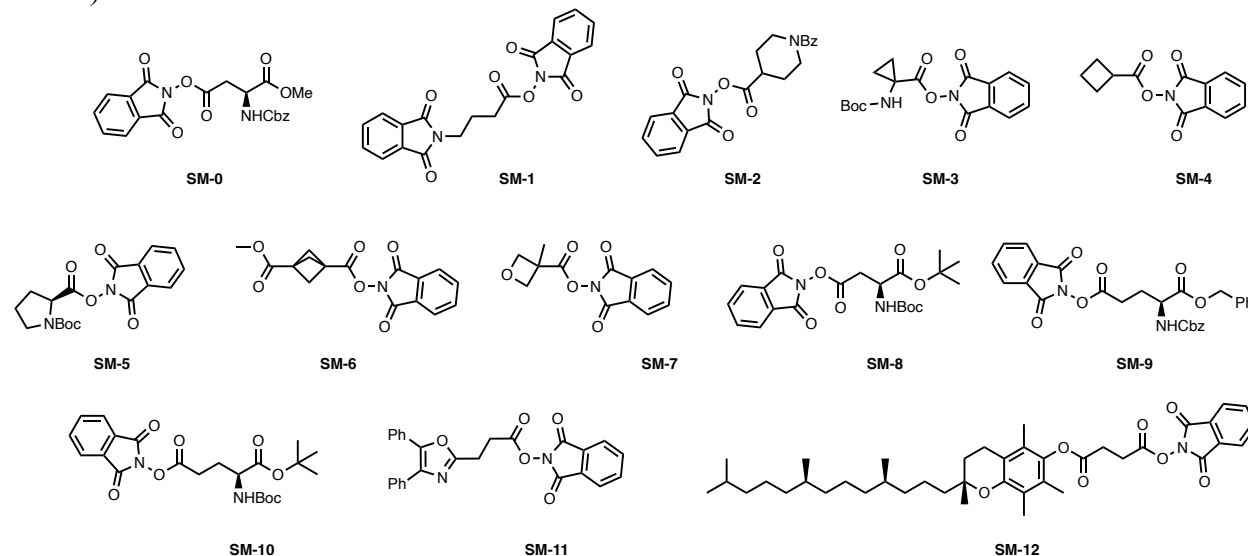
The presence of residual nickel salts in the final product was assessed by measuring the half-width frequency of a singlet at -5.71 ppm (¹H NMR, 400 MHz, DMSO-*d*6). The product is pure if the half-width frequency is less than 23 Hz (see details below).

¹H NMR (400 MHz, DMSO-*d*6) δ 52.72 (s, 2H), 42.95 (s, 3H), 36.60 (s, 2H), 13.79 (s, 2H), 12.53 (s, 2H), -5.71 (s, 6H).



Synthesis of redox-active esters

The following redox-active esters were prepared following published procedures (referenced below).



SM-1,⁵ [SM-2, SM-4, SM-5],⁶ SM-3,⁷ SM-6,⁸ SM-7,⁹ SM-8,¹⁰ SM-9,¹¹ SM-10,¹⁰ SM-11.¹²

4-(1,3-dioxoisindolin-2-yl) 1-methyl ((benzyloxy)carbonyl)-L-aspartate (SM-0)

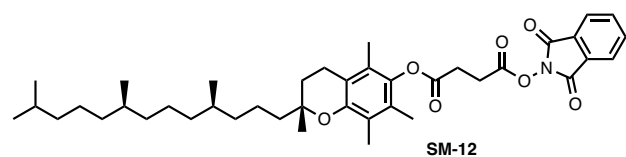
This reaction was carried out under an atmosphere of nitrogen. An oven-dried 100 mL round bottom flask equipped with a PTFE-coated stir bar was charged with (S)-3-(((benzyloxy)carbonyl)amino)-4-methoxy-4-oxobutanoic acid (1.97 g, 7.00 mmol, 1.00 equiv), 2-hydroxyisindoline-1,3-dione (1.14 g, 7.00 mmol, 1.00 equiv), dicyclohexylmethanediimine (2.17 g, 10.5 mmol, 1.50 equiv), and DCM (23 mL, 0.30 M). The reaction was allowed to stir for 16 hours at room temperature. The reaction was diluted with DCM (50 mL) and was washed with aqueous NaHCO₃ (3 x 30 mL) followed by brine (30 mL). The organic layer was dried over an anhydrous sodium sulfate, solvent was removed via a rotary evaporation. The resulting product-containing residue was recrystallized in ethanol to afford the title compound as a white powder (2.02 g, .4.74 mmol, 68%).

¹H NMR (400 MHz, Chloroform-*d*) δ 7.94 – 7.85 (m, 2H), 7.82 – 7.75 (m, 2H), 7.40 – 7.29 (m, 5H), 5.83 (d, J = 8.0 Hz, 1H), 5.21 – 5.11 (m, 2H), 4.80 (dt, J = 8.5, 4.8 Hz, 1H), 3.81 (s, 3H), 3.43 – 3.22 (m, 2H).

¹³C NMR (101 MHz, Chloroform-*d*) δ 170.1, 167.3, 161.7, 155.9, 136.2, 135.0, 128.9, 128.7, 128.3, 128.2, 124.2, 67.5, 53.3, 50.4, 34.3.

1,3-dioxoisindolin-2-yl ((R)-2,5,7,8-tetramethyl-2-((4R,8R)-4,8,12-trimethyltridecyl)chroman-6-yl) succinate (SM-12)

This reaction was carried out under an atmosphere of nitrogen. An oven-dried 100 mL round bottom flask equipped with a PTFE stir bar was charged with a 4-oxo-4-(((R)-2,5,7,8-tetramethyl-2-((4R,8R)-4,8,12-



trimethyltridecyl)chroman-6-yl)oxy)butanoic acid (4.01 g, 7.55 mmol, 1.00 equiv), 2-hydroxyisindoline-1,3-dione (1.48 g, 9.06 mmol, 1.20 equiv), N,N-dimethylpyridin-4-amine (92 mg, 0.76 mmol, 0.10 equiv) and anhydrous DCM (38 mL, 0.20 M). The resulting suspension was stirred on ice for 5 minutes. 3-(((ethylimino)methylene)amino)-N,N-dimethylpropan-1-amine hydrochloride (EDC) (1.73 g, 9.06 mmol, 1.20 equiv) was suspended in DCM (10 mL) and syringed into the first suspension over the course of 30 seconds at 0 °C. The reaction was allowed to gradually warm up to room temperature and was stirred for an additional 16 hour period.

The reaction was diluted with DCM (150 mL) and was washed with 2M HCl (2 x 50 mL), followed by a saturated aqueous sodium bicarbonate (2 x 50 mL) and brine (30 mL). The organic layer was dried over an anhydrous sodium sulfate, solvent was removed via a rotary evaporation. Purification via a flash column chromatography (0-5% EtOAc in hexanes) afforded the title compound as a waxy pale-yellow solid (4.80 g, 7.10 mmol, 94%).

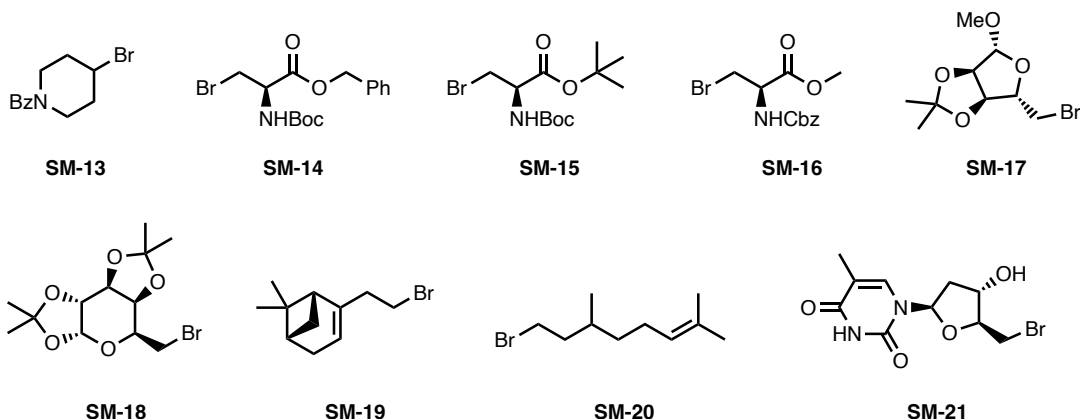
¹H NMR (400 MHz, Chloroform-*d*) δ 7.94 – 7.85 (m, 2H), 7.84 – 7.75 (m, 2H), 3.18 (td, *J* = 6.9, 1.2 Hz, 2H), 3.08 (td, *J* = 6.9, 1.2 Hz, 2H), 2.58 (t, *J* = 6.8 Hz, 2H), 2.08 (s, 3H), 2.01 (s, 3H), 1.97 (s, 3H), 1.89 – 1.65 (m, 3H), 1.58 – 1.01 (m, 23H), 0.88 – 0.82 (m, 12H).

¹³C NMR (101 MHz, Chloroform-*d*) δ 169.9, 168.7, 161.8, 149.7, 140.5, 134.9, 129.0, 126.8, 125.0, 124.2, 123.2, 117.6, 75.2, 39.5, 37.6, 37.6, 37.6, 37.4, 33.0, 32.9, 31.2 (broad, 2C), 28.6, 28.1, 26.5, 25.0, 24.6, 22.9, 22.8, 21.2, 20.7, 19.9, 19.8, 13.1, 12.3, 12.0 (some of the alkyl resonances overlap).

HRMS-ESI (m/z): for C₄₁H₅₇NO₇ [M + Na]⁺: calcd 698.4027, found 698.4026

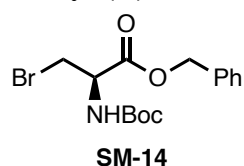
Synthesis of alkyl bromides

Synthesis of reported alkyl bromides was carried out following literature procedures.



SM-13,¹³ SM-15,¹⁴ SM-16,¹⁵ SM-17,¹⁶ SM-18,¹⁶ SM-19,¹⁷ SM-20,¹⁸ SM-21.¹⁹

benzyl (R)-3-bromo-2-((tert-butoxycarbonyl)amino)propanoate (SM-14)



Following a published literature procedure with modifications,¹³ this reaction was carried out under an atmosphere of nitrogen. An oven-dried 100 mL round-bottom flask equipped with a PTFE-coated stir bar was charged with triphenylphosphine (4.49 g, 17.1 mmol, 1.50 equiv), imidazole (1.16 g, 17.1 mmol, 1.50 equiv), and anhydrous DCM (23 mL, 0.50 M). The

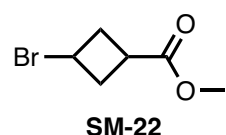
resulting mixture was cooled to 0 °C when bromine (0.88 mL, 17 mmol, 1.5 equiv) was added dropwise (~1 drop per second). The resulting clear yellow solution was allowed to stir for 10 min at 0 °C. A solution of benzyl (tert-butoxycarbonyl)-L-serinate (3.37 g, 11.4 mmol, 1.00 equiv) in anhydrous DCM (11 mL, 1.0 M) was added portion-wise into the previous solution over the course of 10 minutes. The reaction mixture was allowed to gradually warm up to room temperature and was stirred for 16 hours. DCM was removed via a rotary evaporation, the product-containing residue was re-dissolved in ethyl acetate (300 mL) and successively washed with a 10% aqueous sodium thiosulfate (50 mL) and brine (50 mL). The organic fraction was dried over an anhydrous sodium sulfate, the solvent was removed via a rotary evaporation. The title compound was isolated following a purification via a flash column chromatography (5-30% EtOAc in hexanes) as a white solid (2.94 g, 8.21 mmol, 72%).

¹H NMR (400 MHz, Chloroform-*d*) δ 7.43 – 7.30 (m, 5H), 5.42 (d, *J* = 7.9 Hz, 1H), 5.28 – 5.16 (m, 2H), 4.79 (dt, *J* = 7.6, 3.4 Hz, 1H), 3.90 – 3.64 (m, 2H), 1.45 (s, 9H).

¹³C NMR (101 MHz, Chloroform-*d*) δ 169.2, 155.0, 134.9, 128.7, 128.6, 128.5, 80.5, 67.9, 54.0, 34.1, 28.3.

HRMS-ESI (*m/z*): for C₁₅H₂₀BrNO₄ [*M* + Na]⁺: calcd 380.0468, found 380.0468

methyl 3-bromocyclobutane-1-carboxylate (SM-22)



Methyl 3-bromocyclobutane-1-carboxylate was prepared following a published procedure with modifications.²⁰

This reaction was carried out under an atmosphere of nitrogen. An oven-dried 100 mL round-bottom flask equipped with a PTFE stir bar was charged with methyl 3-hydroxycyclobutane-1-carboxylate (2.00 g, 15.37 mmol, 1.00 equiv), triphenylphosphine (16.1 g, 61.5 mmol, 4.00 equiv), anhydrous lithium bromide (5.34 g, 61.5 mmol, 4.00 equiv), and anhydrous THF (71 mL, 216 mM). Mixture was stirred at 0 °C until homogeneous and was then purged with nitrogen for 5 minutes. Carbon tetrabromide (20.4 g, 61.5 mmol, 4.00 equiv) was added portion-wise into the reaction mixture over a period of 10 minutes. Following a complete addition of CBr₄, the reaction vessel was purged with nitrogen for 5 minutes. After 10 minutes of stirring, a copious amount of white precipitate has formed. The resulting suspension was allowed to stir for 16 hours at room temperature. The reaction was slowly poured into diethyl ether (200 mL), the resulting suspension was filtered over Celite, washing with diethyl ether (2x50 mL). The filtrate was evaporated via a rotary evaporation, affording a crude product as a thick oil. Pure product was afforded following a purification via a flash column chromatography (0—5% EtOAc in hexanes) as a pale yellow oil (2.19 g, 11.3 mmol, 74%).

Caution: carbon tetrabromide is a suspected carcinogen.

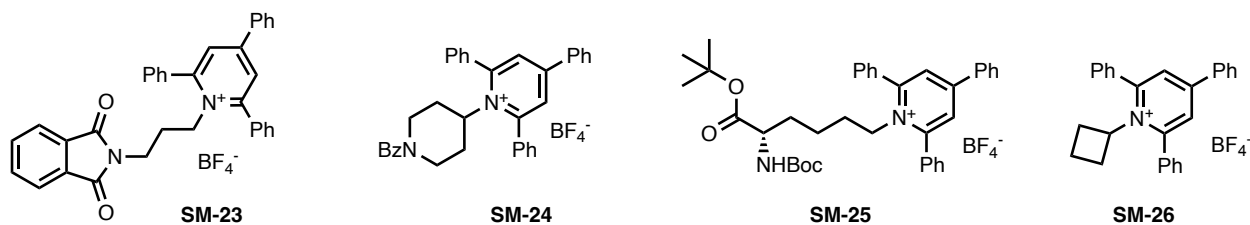
¹H NMR (400 MHz, Chloroform-*d*) δ 4.66 (ttd, *J* = 7.4, 6.3, 0.9 Hz, 1H), 3.70 (s, 3H), 3.39 (ttd, *J* = 9.6, 5.1, 1.0 Hz, 1H), 2.97 – 2.87 (m, 2H), 2.75 – 2.64 (m, 2H).

¹³C NMR (101 MHz, Chloroform-*d*) δ 175.2, 52.2, 41.0, 37.7, 36.0.

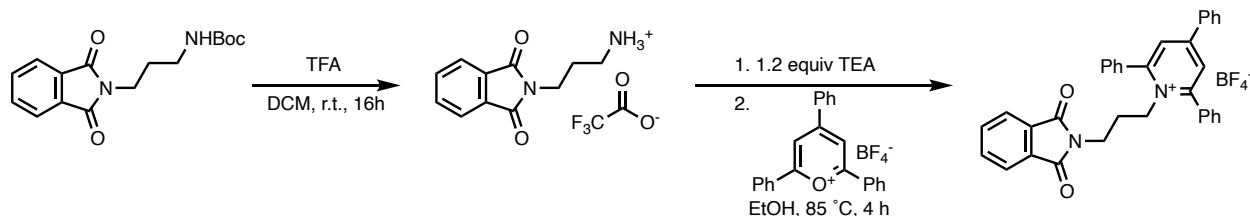
HRMS-ESI (*m/z*): for C₆H₉BrO₂ [*M* + H]⁺: calcd 192.9859, found 192.9859

Synthesis of N-alkyl pyridinium (Katritzky) salts

Syntheses of reported N-Alkyl pyridinium salts were carried out following literature procedures: **SM-25**,²¹ **SM-26**.²²



1-(3-(1,3-dioxoisindolin-2-yl)propyl)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate (SM-23)



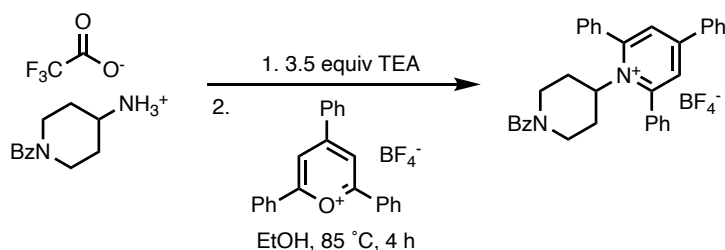
3-(1,3-dioxoisindolin-2-yl)propan-1-aminium 2,2,2-trifluoroacetate was prepared following a literature procedure with modifications.²³ This reaction was carried out under air.

An oven-dried 250 mL round bottom flask equipped with a PTFE-coated stir bar was charged with tert-butyl (3-(1,3-dioxoisindolin-2-yl)propyl)carbamate (3.04 g, 10.0 mmol, 1.00 equiv), DCM (133 mL, 75 mM), and trifluoroacetic acid (TFA) (50 mL, 0.20 M). The resulting homogenous solution was loosely capped and allowed to stir at room temperature for 16 hours. The solvent was evaporated in vacuo. To induce crystallization of salt, oily residue was co-evaporated with diethyl ether to remove residual TFA. Pure 3-(1,3-dioxoisindolin-2-yl)propan-1-aminium 2,2,2-trifluoroacetate salt was afforded following sonication with n-heptane and subsequent filtration, as a white powder (3.02 g, 9.49 mmol, 95%). This salt was used in the next step without further purification.

1-(3-(1,3-dioxoisindolin-2-yl)propyl)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate was prepared via a modified literature procedure.²⁴

This reaction was setup under air. A oven-dried 20 mL scintillation vial equipped with a PTFE-coated stir bar was charged with 3-(1,3-dioxoisindolin-2-yl)propan-1-aminium 2,2,2-trifluoroacetate (309 mg, 0.971 mmol, 1.10 equiv) and ethanol (1.8 mL, 0.50 M). The resulting suspension was stirred for 3 minutes when triethylamine (0.14 mL, 1.0 mmol, 1.2 equiv) was added dropwise, resulting in a clear homogeneous solution which was stirred for additional 10 minutes at room temperature. Into the resulting solution was added 2,4,6-triphenylpyridinium tetrafluoroborate (350 mg, 0.880 mmol, 1.00 equiv). The vial was capped with a PTFE-lined cap, contents were heated to 85 °C for 4 hours. The resulting clear red solution was gradually cooled to room temperature and dropwise added into vigorously stirred diethyl ether (250 mL), causing precipitation of the pyridinium salt. 1-(3-(1,3-dioxoisindolin-2-yl)propyl)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate product was afforded following filtration, washing with diethyl ether (3 x 20 mL) as an off-white powder (325 mg, 0.558 mmol, 63%) which was directly used in cross-coupling reactions without further purification.

1-(1-benzoylpiperidin-4-yl)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate (SM-24)



The title compound was prepared via a modified literature procedure.²⁴ This reaction was setup under air.

An oven-dried 20 mL scintillation vial equipped with a PTFE-coated stir bar was charged with 1-benzoylpiperidin-4-aminium trifluoroacetate (2.60 g, 8.18 mmol, 1.20 equiv) and ethanol (6.81 mL, 1.00 M). The resulting suspension was stirred for 3 minutes when triethylamine (3.32 mL, 23.8 mmol, 3.50 equiv) was added, resulting in a clear homogeneous solution which was stirred for additional 10 minutes at room temperature. Into the resulting solution was added 2,4,6-triphenylpyrylium tetrafluoroborate (2.70 g, 6.81 mmol, 1.00 equiv). The vial was capped with a PTFE-lined cap, contents were heated to 85 °C for 4 hours. The resulting clear red solution was gradually cooled to room temperature causing precipitation of the pyridinium salt. 1-(1-benzoylpiperidin-4-yl)-2,4,6-triphenylpyridinium tetrafluoroborate product was afforded following filtration, washing with ethanol (3 x 5 mL) and diethyl ether (3 x 5 mL) as an off-white powder (2.62 g, 4.50 mmol, 66%) which was directly used in cross-coupling reactions without further purification.

Preparation of Grignard reagents

All operations were performed inside of a nitrogen-filled glovebox. An oven-dried 125 mL 3-neck flask equipped with a PTFE-coated magnetic stir bar was charged with magnesium turnings (3.00 equiv), and diethyl ether (0.75 M). The flask was stoppered with a rubber septa and was equipped with a Vigreux condenser column. Next, a primary or a secondary alkyl bromide (1.0 equiv) was slowly syringed into a stirred mixture of Mg turnings in ether at a rate that maintains a steady reflux of ether, over the course of 15 minutes. Following a complete addition of an alkyl bromide, the reaction was allowed to stir for additional 10 minutes. After stirring was stopped, solids were allowed to settle for 5 minutes. The resulting clear brown Grignard solution was filtered through a short plug of Celite to remove micro-dispersed Mg solids.

Titration of Grignard reagents

An oven-dried 4 mL scintillation vial equipped with a PTFE-coated stir bar was charged with 25 mg of iodine followed by a 1 mL of saturated LiCl solution in THF. The Grignard solution was then added dropwise (~2 drops per second) into a stirred solution of iodine until a complete discoloration of the iodine solution (endpoint). The concentration of an organomagnesium reagent was calculated based on the volume of added Grignard used to achieve the endpoint via the following titration equation: $[Y = 0.0985 / X]$ where Y is the concentration of Grignard (M) and X is the volume of added Grignard (mL).

General procedures

General Procedure A: synthesis of Ni(alkyl) complexes by transmetalation

All operations were conducted inside of a nitrogen-filled glovebox. Basic alumina was dried at 120 °C in a vacuum oven for 24 hours before use.

A 250 mL round-bottom flask, equipped with a PTFE stir bar, was charged with BPI-Ni-OAc (**1**) (1.00 equiv) and THF (25 mM). The resulting suspension underwent vigorous stirring for 5 minutes to disperse any large BPI-Ni-OAc clumps. The reaction was then cooled to -10 °C using a cold well (iPrOH/dry ice). At lower temperatures, the BPI-Ni-OAc suspension thickens.

A Grignard solution or an organozinc solution (1.00 equiv, 0.5-1 M in ether or THF) was added dropwise to the cooled suspension of BPI-Ni-OAc, with active swirling. Upon complete addition of the organometallic reagent, the reaction darkened to a purple hue and transformed into a solution.

While the reaction mixture was still cold, it was promptly filtered through a short plug of basic alumina, and THF was removed under vacuum. Depending on the compound, the product-containing residue was either triturated twice with pentanes, a THF-pentane mixture, or recrystallized from a THF-pentane mixture before being dried under high vacuum for 30 minutes. Conditions specific to each complex are described below.

The purity of the Ni(alkyl) complex was assessed via a quantitative ¹H NMR spectroscopy with 1,3,5-trimethoxybenzene internal standard.

General Procedure B: synthesis of Ni(alkyl) complexes by chemical reduction with Zn

All operations were carried out in a nitrogen-filled glovebox. Zn powder was purchased from Oakwood Chemical (325 mesh, item # 044742-1Kg).

Activation of Zn powder

A 40 mL scintillation vial equipped with a stir bar was charged with Zn powder (20.0 g, 306 mmol, 1.00 equiv), lithium chloride (324 mg, 7.65 mmol, 0.0250 equiv), and THF (30 mL). The resulting suspension was vigorously stirred for 15 minutes at room temperature. Next, 1,2-dibromoethane (0.26 mL, 3.1 mmol, 0.010 equiv) was injected, the mixture was allowed to stir for an additional hour at room temperature. *Caution: ethylene gas is produced during activation – the reaction vial should not be tightly capped.* Zn suspension was filtered through a glass fritted funnel, thoroughly washed with THF (3 x 25 mL) and dried under high vacuum for 1 hour.

Unactivated Zn powder (used directly from the commercial bottle) was successfully employed without any noticeable effect on yield. However, the use of activated Zn powder resulted in a faster formation of organonickel complexes.

Formation of Ni(alkyl) via Zn

A 20 mL scintillation vial equipped with a PTFE stir bar was charged with BPI-Ni-OAc (**1**) (1.00 equiv), lithium chloride (2.00 equiv), activated Zn powder (5.00 equiv) and either a primary alkyl bromide (1.5 equiv), or a secondary alkyl bromide (1.5 equiv), followed by a 9:1 mixture of THF:DMF (50 mM).

The resulting suspension was allowed to vigorously stir at 0 °C for 2-4 hours. When necessary, Ni alkyl solutions were filtered through a short plug of Celite to remove remaining Zn powder.

Solutions of organonickel complexes could be used as-is for subsequent cross-coupling reactions or could be used for isolation of pure complexes via recrystallization with THF-pentanes.

General Procedure C: coupling of isolated Ni(Alkyl) complexes via Zn

All operations were carried out in a nitrogen-filled glovebox. An oven-dried, threaded 4 mL vial equipped with a PTFE-coated stir bar was charged with a given nickel complex (0.050 mmol, 1.0 equiv), lithium chloride (4 mg, 0.1 mmol, 2 equiv), Zn powder (16 mg, 0.25 mmol, 5.0 equiv), electrophile-2 (0.75 mmol, 1.5 equiv), decane internal standard (10 mg), and THF (1.0 mL, 50 mM). The vial was capped with a PTFE-lined cap. The reaction was allowed to stir for 16 hours at room temperature. A 0.5 mL reaction aliquot was collected, shaken with ethyl acetate (3 mL) and brine (3 mL), and analyzed via a gas chromatography (GC).

Couplings with tertiary redox-active esters were carried out with a higher loading of the ester coupling partner (35 mg, 0.10 mmol, 2.0 equiv) and with ZnBr₂ additive (23 mg, 0.10 mmol, 2.0 equiv) in addition to the conditions described above.

General Procedure D: coupling of secondary alkyl bromides with secondary Ni(Alkyl) complexes via e-chem

Reactions were performed in a nitrogen-filled glovebox. An oven-dried, threaded 12 mL culture tube equipped with a PTFE-coated stir bar was charged with a secondary Ni(Alkyl) (0.090 mmol, 1.0 equiv), a secondary alkyl bromide (0.135 mmol, 1.50 equiv), tetrabutylammonium tetrafluoroborate (247 mg, 0.750 mmol, 8.33 equiv) electrolyte, decane internal standard (20 mg), and DMF (1.5 mL). The culture tube was equipped with a Ni-foam cathode and Zn-plate anode. The reaction was taken out of the glovebox. Freshly-degassed methanol (1.5 mL, 30 mM final concentration) was syringed into the vial. The contents were pre-stirred for 1 minute before a reductive, constant current was applied at the Ni cathode (10 mA, 9.65 mAh, 4 equiv e-) at room temperature. Following the electrolysis, a 0.5 mL reaction aliquot was collected, shaken with ethyl acetate (3 mL) and brine (3 mL), and analyzed via a gas chromatography (GC).

General Procedure E: coupling of secondary redox-active esters with secondary Ni(Alkyl) complexes via e-chem

Reactions were performed in a nitrogen-filled glovebox. An oven-dried threaded 12 mL culture tube equipped with a PTFE-coated stir bar was charged with a secondary Ni(Alkyl) (0.090 mmol, 1.0 equiv), a secondary redox-active ester (0.135 mmol, 1.50 equiv), lithium bromide (65 mg, 0.750 mmol, 8.33 equiv) electrolyte, decane internal standard (20 mg), and 1:1 DMF:THF solvent mixture (3.0 mL, 30 mM final concentration). The culture tube was equipped with a Ni-foam cathode and Zn-plate anode. The reaction was taken out of the glovebox. The contents were pre-stirred for 1 minute when a reductive, constant current was applied at the Ni cathode (5 mA, 9.65 mAh, 4 equiv e-) at room temperature. Following the electrolysis, a 0.5 mL reaction aliquot was collected, shaken with ethyl acetate (3 mL) and brine (3 mL), and analyzed via a gas chromatography (GC).

General Procedure F: coupling of primary N-alkyl pyridinium (Katritzky) salts via e-chem

Reactions were setup in a nitrogen-filled glovebox. An oven-dried threaded 12 mL culture tube equipped with a PTFE-coated stir bar was charged with Ni(Alkyl) (0.090 mmol, 1.0 equiv), a primary N-alkyl pyridinium salt (0.135 mmol, 1.50 equiv), sodium iodide (113 mg, 0.75 mmol, 8.3 equiv) electrolyte, decane internal standard (20 mg), and a 2:1 DMA:THF solvent mixture (3.0 mL, 30 mM final concentration). The culture tube was equipped with a stainless steel (SS)

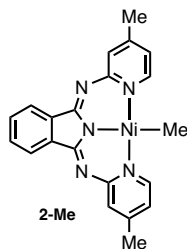
plate cathode and a cobalt-wire anode. The reaction was taken out of the glovebox. Contents were pre-stirred for 1 minute when a reductive, constant current was applied at the Ni cathode (5 mA, 4.82 mAh, 2.00 equiv e-) at 60 °C. Following the electrolysis, a 0.5 mL reaction aliquot was shaken with ethyl acetate (3 mL) and brine (3 mL) and analyzed via a gas chromatography (GC).

General Procedure G: coupling of secondary N-alkyl pyridinium (Katritzky) salts with Ni(Alkyl) complexes via Zn

Reactions were setup in a nitrogen-filled glovebox. An oven-dried, threaded 4 mL vial equipped with a PTFE-coated stir bar was charged with a given nickel complex (0.050 mmol, 1.0 equiv), Zn powder (6 mg, 0.1 mmol, 2 equiv), secondary Ni-alkyl pyridinium salt (0.75 mmol, 1.5 equiv), decane internal standard (10 mg), and THF (0.5 mL). The vial was covered with a PTFE-lined septum and capped with an open-top screw cap. The cap was taped with an electrical tape and taken out of the glovebox. Degassed methanol (0.5 mL, 50 mM final concentration) was syringed and the reaction was allowed to stir for 16 hours at room temperature. A 0.5 mL reaction aliquot was collected, shaken with ethyl acetate (3 mL) and brine (3 mL), and analyzed via a gas chromatography (GC).

Preparation of Ni(Alkyl) complexes

2-Me



This complex was prepared and isolated following a **General Procedure A** for the synthesis 1° or 2° nickel alkyls via a transmetalation.

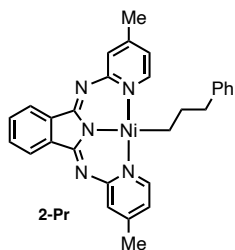
BPI-Ni-OAc (**1**) (3.00 g, 6.75 mmol, 1.00 equiv) and ethereal methylmagnesium bromide (7.00 mL, 985 mM, 6.89 mmol, 1.02 equiv) were reacted to afford BPI-Ni-Me as a fluffy grape-colored solid (2.41 g, 6.02 mmol, 89%).

¹H NMR (600 MHz, C₆D₆) δ 8.54 (d, J = 6.3 Hz, 2H), 8.25 (dd, J = 5.5, 3.1 Hz, 2H), 7.24 (s, 2H), 7.21 (dd, J = 5.7, 2.9 Hz, 2H), 6.13 (d, J = 5.2 Hz, 2H), 1.70

(s, 6H), 0.13 (s, 3H).

¹³C NMR (151 MHz, C₆D₆) δ 160.2, 157.3, 151.4, 148.3, 140.7, 130.6, 126.0, 122.1, 120.0, 20.2, -1.8.

2-Pr



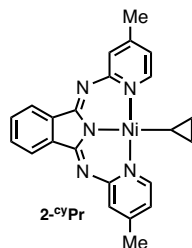
This complex was prepared and isolated following a **General Procedure A** for the synthesis 1° or 2° nickel alkyls via a transmetalation.

BPI-Ni-OAc (**1**) (2.00 g, 4.50 mmol, 1.00 equiv) and ethereal (3-phenylpropyl)magnesium bromide (4.60 mL, 985 mM, 4.50 mmol, 1.00 equiv) were reacted to afford product which was triturated with pentanes (2 x 50 mL) and dried to afford the title complex as a dark purple powder (2.16 g, 4.28 mmol, 95%).

¹H NMR (600 MHz, C₆D₆) δ 8.57 (d, J = 6.2 Hz, 2H), 8.28 (dd, J = 5.4, 3.0 Hz, 2H), 7.25 – 7.22 (m, 2H), 7.21 (dd, J = 5.5, 3.0 Hz, 2H), 7.10 – 7.04 (m, 4H), 6.94 (tt, J = 6.5, 2.1 Hz, 1H), 6.16 (dd, J = 6.3, 2.1 Hz, 2H), 2.96 (t, J = 7.5 Hz, 2H), 1.69 (s, 6H), 1.39 (p, 2H), 0.69 (t, J = 7.4 Hz, 2H).

¹³C NMR (151 MHz, C₆D₆) δ 160.1, 157.0, 150.7, 147.8, 143.2, 140.5, 130.3, 128.6, 125.2, 125.2, 121.8, 119.7, 38.5, 34.3, 19.9, 19.0 (one Ph signal overlapped with C₆D₆ signals).

2-cyPr



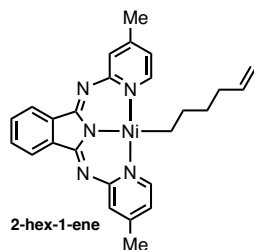
This complex was prepared and isolated following a **General Procedure A** for the synthesis 1° or 2° nickel alkyls via a transmetalation.

BPI-Ni-OAc (**1**) (700 mg, 1.58 mmol, 1.00 equiv) and a THF solution of cyclopropylmagnesium bromide (11.2 mL, 141 mM, 1.58 mmol, 1.00 equiv) were reacted to afford product as a cocoa-colored fluffy solid (646 mg, 1.52 mmol, 96%).

¹H NMR (600 MHz, C₆D₆) δ 9.05 (d, J = 6.3 Hz, 2H), 8.22 (dd, J = 5.4, 3.1 Hz, 2H), 7.30 (s, 2H), 6.28 (d, J = 5.3 Hz, 2H), 1.76 (s, 6H), 0.45 – 0.39 (m, 2H), 0.10 (d, J = 5.4 Hz, 2H), -0.66 (q, J = 6.9 Hz, 1H).

¹³C NMR (151 MHz, C₆D₆) δ 159.8, 157.2, 152.2, 148.4, 140.6, 130.6, 126.1, 122.1, 119.7, 20.2, 10.5, 3.2.

2-hex-1-ene



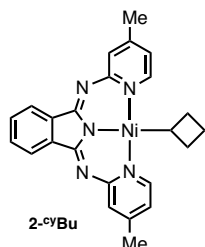
This complex was prepared and isolated following a **General Procedure A** for the synthesis 1° or 2° nickel alkyls via a transmetalation with modifications.

BPI-Ni-OAc (**1**) (1.00 g, 2.25 mmol, 1.00 equiv) was reacted with hex-5-en-1-ylmagnesium bromide (6.00 mL, 4.55 mmol, 2.02 equiv) at -10 °C. Reaction was promptly filtered through basic alumina, THF was evaporated *in vacuo*. Residue was triturated with minimal pentanes (2 x 15 mL) and dried affording a title complex as a purple-brown flaky solid (456 mg, 43%). Product is soluble in pentanes.

¹H NMR (600 MHz, C₆D₆) δ 8.65 (d, J = 6.2 Hz, 2H), 8.27 (dd, J = 5.5, 2.9 Hz, 2H), 7.24 (s, 2H), 7.21 (dd, J = 5.5, 2.9 Hz, 2H), 6.21 (d, J = 6.5 Hz, 2H), 5.71 (ddt, J = 17.3, 10.8, 6.9 Hz, 1H), 4.92 (d, J = 16.8 Hz, 1H), 4.83 (d, J = 10.0 Hz, 1H), 2.06 (q, J = 6.6 Hz, 2H), 1.78 (p, J = 7.3 Hz, 2H), 1.71 (s, 6H), 1.13 (p, J = 7.5 Hz, 2H), 0.71 (t, J = 7.7 Hz, 2H).

¹³C NMR (151 MHz, C₆D₆) δ 160.6, 157.4, 151.2, 148.1, 140.8, 139.7, 130.6, 125.6, 122.2, 120.1, 114.0, 34.2, 32.0, 31.9, 20.2, 20.0.

2-cyBu



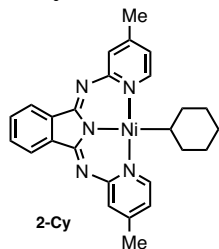
This complex was prepared and isolated following a **General Procedure A** for the synthesis 1° or 2° nickel alkyls via a transmetalation with modifications.

BPI-Ni-OAc (**1**) (1.00 g, 2.25 mmol, 1.00 equiv) was reacted with cyclobutylmagnesium bromide (3.20 mL, 2.25 mmol, 1.00 equiv) to afford product as a fluffy dark solid (950 mg, 2.16 mmol, 96%).

¹H NMR (600 MHz, C₆D₆) δ 8.57 (d, J = 6.2 Hz, 2H), 8.29 (dd, J = 5.4, 3.0 Hz, 2H), 7.28 (s, 2H), 7.23 (dd, J = 5.5, 3.0 Hz, 2H), 6.23 – 6.17 (m, 2H), 2.13 (h, J = 8.9 Hz, 1H), 1.89 (p, J = 8.4 Hz, 1H), 1.71 (s, 6H), 1.70 – 1.64 (m, 2H), 1.62 (t, J = 9.3 Hz, 1H), 1.52 (pd, J = 9.2, 3.1 Hz, 2H).

¹³C NMR (151 MHz, C₆D₆) δ 160.1, 156.9, 151.0, 147.6, 140.6, 130.2, 125.6, 121.8, 119.3, 35.0, 33.1, 19.9.

2-Cy



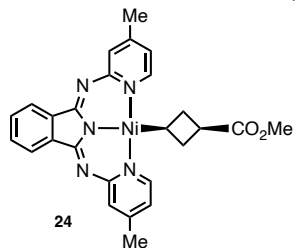
This complex was prepared and isolated following a **General Procedure A** for the synthesis 1° or 2° nickel alkyls via a transmetalation.

BPI-Ni-OAc (**1**) (300 mg, 0.675 mmol, 1.00 equiv) was reacted with cyclohexylmagnesium bromide (1.03 mL, 657 mM, 0.675 mmol, 1.00 equiv) to afford product as a fluffy purple-brown solid (262 mg, 0.560 mmol, 83%).

¹H NMR (600 MHz, C₆D₆) δ 8.87 (d, J = 6.1 Hz, 2H), 8.38 – 8.23 (m, 2H), 7.21 (t, J = 4.5 Hz, 2H), 7.19 (s, 2H), 6.20 (d, J = 6.0 Hz, 2H), 1.92 – 1.82 (m, 2H), 1.70 (s, 6H), 1.50 – 1.40 (m, 5H), 1.30 (p, J = 13.5 Hz, 3H), 0.95 (d, J = 10.1 Hz, 1H).

¹³C NMR (151 MHz, C₆D₆) δ 160.9, 157.1, 151.3, 147.5, 140.7, 130.2, 124.5, 121.8, 119.4, 36.7, 28.2, 28.0, 25.4, 20.0.

BPI-Ni-cBu-CO₂Me (24)



This complex was prepared and isolated following a **General Procedure B**.

BPI-Ni-OAc (**1**) (333 mg, 0.750 mmol, 1.00 equiv), lithium chloride (63 mg, 1.5 mmol, 2.0 equiv), Zn powder (294 mg, 4.50 mmol, 6.00 equiv), and methyl 3-bromocyclobutane-1-carboxylate (304 mg, 1.57 mmol, 2.10 equiv) were stirred in THF (15 mL, 50 mM) for 16 hours at 0 °C. The resulting dark purple solution was filtered through a short plug of basic alumina and diluted with pentanes (30 mL) causing product to precipitate. Product was collected via filtration, washing with pentanes (10 mL), and dried. Title complex was isolated as a 2 : 1 mixture of diastereomers (determined by ¹H NMR spectroscopy) as a plum-colored solid (307 mg, 82%).

¹H NMR (600 MHz, C₆D₆) (major syn diastereomer) δ 8.42 (d, J = 6.2 Hz, 2H), 8.21 (dd, J = 5.4, 3.0 Hz, 2H), 7.26 – 7.24 (m, 2H), 7.18 (dd, J = 5.5, 3.0 Hz, 2H), 6.18 (dd, J = 6.2, 2.2 Hz, 2H), 3.21 (s, 3H), 3.17 (q, J = 8.7 Hz, 1H), 1.88 (t, J = 8.7 Hz, 4H), 1.73 (s, 6H), 1.39 (p, J = 8.6 Hz, 1H).

¹³C NMR (151 MHz, C₆D₆) (major syn diastereomer) δ 172.9, 160.4, 157.3, 151.1, 148.2, 140.7, 130.5, 126.1, 122.2, 119.7, 50.8, 36.6, 35.6, 27.7, 20.3.

Comparison of synthetic routes for 2-^{cy}Bu (Figure 1 in the manuscript)

Synthesis of 2-^{cy}Bu via electrochemistry (Figure 1 in the manuscript)

All operations were carried out in a nitrogen-filled glovebox. An oven-dried 12 mL vial equipped with a PTFE stir bar was charged with BPI-Ni-OAc (**1**) (67 mg, 0.15 mmol, 1.0 equiv), lithium bromide (65 mg, 0.75 mmol, 5.0 equiv), bromocyclobutane (30 mg, 0.23 mmol, 1.5 equiv), 1,3,5-trimethoxybenzene (25 mg) internal standard, and 1:1 DMF:THF solvent (3.0 mL, 50 mM). Mixture was stirred for 2 minutes, the vial was equipped with a Ni-foam cathode and Zn-plate anode. A reductive, constant current was applied at the Ni cathode (1 mA, 8.04 mAh, 2 equiv e⁻) at room temperature. Following the electrolysis, the reaction vial was brought back into the glovebox. A 0.4 mL reaction aliquot was diluted with 0.2 mL of benzene-d₆ and promptly analyzed via ¹H NMR spectroscopy.

Synthesis of 2-^{cy}Bu via a chemical reduction (Figure 1 in the manuscript)

Formation of 2-^{cy}Bu from ^{cy}Bu-Br or ^{cy}Bu-RAE

All operations were carried out in a nitrogen-filled glovebox. An oven-dried 4 mL threaded vial equipped with a PTFE-coated stir bar was charged with BPI-Ni-OAc (**1**) (22 mg, 0.050 mmol, 1.0 equiv), lithium chloride (4 mg, 0.1 mmol, 2 equiv), Zn powder (16 mg, 0.25 mmol, 5.0 equiv), and either bromocyclobutane (7.1 μ L, 10 mg, 0.075 mmol, 1.5 equiv) or 1,3-dioxoisindolin-2-yl cyclobutanecarboxylate (18 mg, 0.075 mmol, 1.5 equiv), 1,3,5-trimethoxybenzene internal standard (8 mg), and a 9:1 THF:DMF (1.0 mL, 50 mM). Reaction vial was capped with a PTFE-lined cap and sealed with an electrical tape to delay exposure to air. The reaction vial was taken out of the glovebox and stirred at 0 °C (ice bath) for 4 hours. The reaction vial was brought back into the glovebox. A 0.4 mL reaction aliquot was diluted with 0.2 mL of benzene-d₆ and promptly analyzed via ¹H NMR spectroscopy.

Formation of 2-^{cy}Bu from ^{cy}Bu-[Py⁺] (SM-26)

Formation of 2-^{cy}Bu from the ^{cy}Bu-[Py⁺]-N-alkyl pyridinium was carried out as follows.

An oven-dried 4 mL scintillation vial equipped with a PTFE-coated stir bar was charged with BPI-Ni-OAc (**1**) (11 mg, 0.025 mmol, 1.0 equiv), 1-cyclobutyl-2,4,6-triphenylpyridinium tetrafluoroborate N-alkyl pyridinium salt (17 mg, 0.037 mmol, 1.5 equiv), lithium chloride (2 mg, 0.05 mmol, 2 equiv), zinc powder (16 mg, 0.25 mmol, 10 equiv), a decane internal standard (10 mg), and a 1:1 DMA:THF solvent mixture (0.50 mL, 50 mM). The reaction vial was removed from the glovebox and stirred at 40 °C for 30 minutes, during which it darkened over time. The resulting Ni(Alkyl) complex was found to be relatively short-lived under these reaction conditions. Hence, the yield of the 2-^{cy}Bu was inferred from the yield of the resulting C-C cross-coupled product.

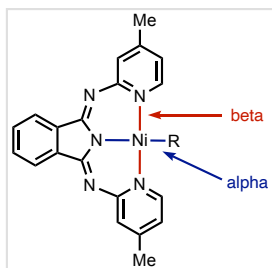
After stirring for 30 minutes at 40 °C, the reaction vial was returned to the glovebox and charged with 1,3-dioxoisindolin-2-yl 5-phenylpentanoate 1° redox-active ester (12 mg, 0.037 mmol, 1.5 equiv). The mixture was then stirred for 1 hour at room temperature. Afterward, the reaction mixture was shaken with ethyl acetate (1 mL) and brine (1 mL). The organic layer was analyzed via GC. The yield of Ni(Alkyl) was inferred from the yield of the resulting C-C cross-coupled product.

Formation of 2-^{cy}Bu via transmetalation (Figure 1 in the manuscript)

All operations were carried out in a nitrogen-filled glovebox. An oven-dried 4 mL threaded vial equipped with a PTFE-coated stir bar was charged with BPI-Ni-OAc (**1**) (22 mg, 0.050 mmol, 1.0 equiv) and 1,3,5-trimethoxybenzene (8 mg) internal standard. A pre-chilled (0 °C) THF solution of a given cyclobutyl organozinc (1.0 mL, 50 mM, 0.050 mmol, 1.0 equiv) was promptly syringed with stirring. After 5 minutes of stirring a 0.4 mL reaction aliquot was diluted with 0.2 mL of benzene-d₆ and promptly analyzed via ¹H NMR spectroscopy.

Characterization of Ni(Alkyl) complexes (Figure 1 in the manuscript)

Tau-4 calculations



τ_4 geometry index was calculated using the following formula derived from a previous report:²⁵

$\tau_4 = [360^\circ - (\alpha - \beta)] / (360^\circ - 2 \times 109.5^\circ)$ where α is the phthN-Ni-N angle and β is the Py-Ni-Py angle. Bond angles were analyzed and determined from X-ray crystallographic data.

τ_4 parameter varies from 0 for square planar to 1 for tetrahedral geometries.

Figure S1. β : Py-Ni-Py bond angle (RED), α : phthN-Ni-R bond angle (BLUE).

Percent buried volume calculations

Buried volume was calculated via SambVca 2.1 web application software.²⁶ While calculating the buried volume:

1. The Ni atom was assumed to be the center of the complex.
2. Hydrogen atoms were included in the calculation.
3. Bondi radii were scaled to default 1.17 Å, sphere radius was assumed to be 3.5 Å and mesh spacing was set to be 0.10 Å.

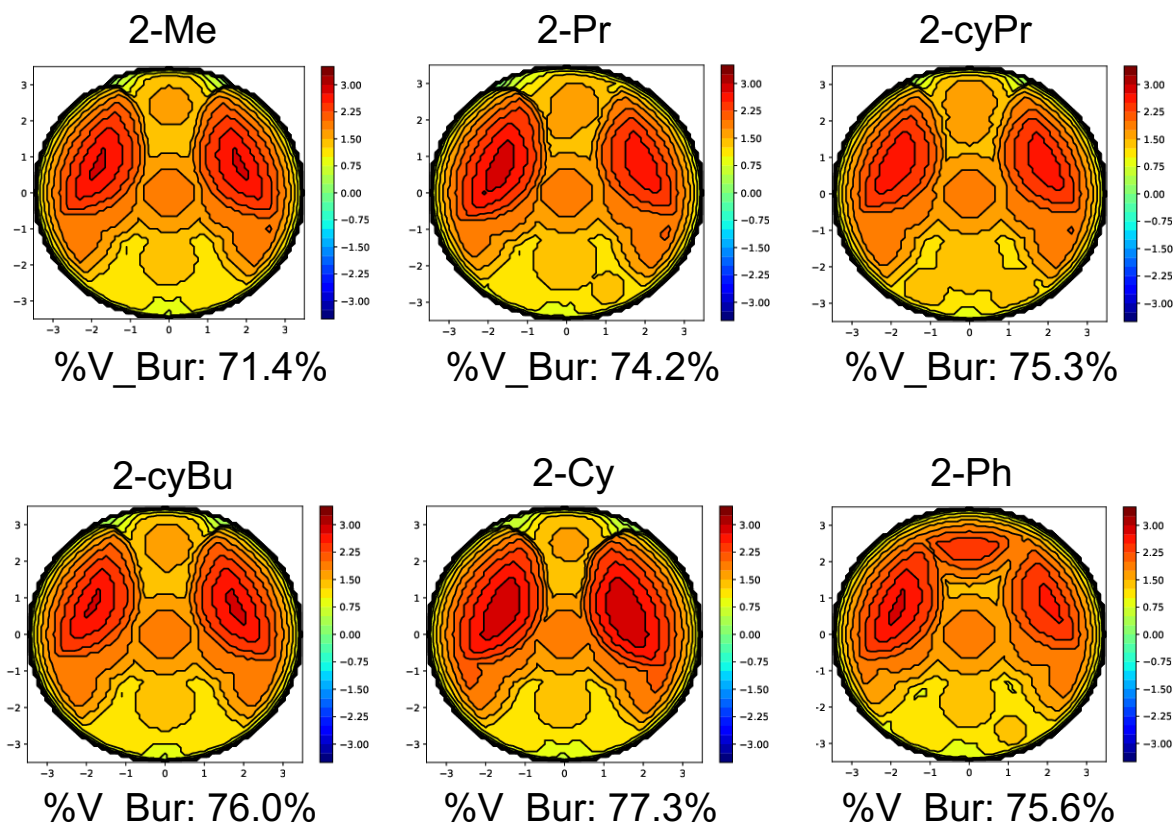


Figure S2. Buried volume heat maps.

Preliminary reactions of isolated Ni(Alkyl) complexes with an alkyl redox-active ester (Figure 1D in the manuscript)

All operations were carried out in the nitrogen-filled glovebox. Complexes **2-Me**, **2-Pr**, **2-cyPr**, **2-cyBu**, **2-Cy** were prepared via transmetalation following a **General Procedure A**. Complex **2-Ph** was prepared following a published procedure.⁽⁴⁾

A oven-dried threaded 4 mL vial equipped with a stir bar was charged with a given nickel complex (0.050 mmol, 1.0 equiv), lithium chloride (4 mg, 0.1 mmol, 2 equiv), Zn powder (16 mg, 0.25 mmol, 5.0 equiv), primary redox-active ester 1,3-dioxoisindolin-2-yl 4-(1,3-dioxoisindolin-2-yl)butanoate (28 mg, 0.75 mmol, 1.5 equiv), decane internal standard (10 mg), and THF (1.0 mL, 50 mM). Vial was capped with a PTFE-lined cap. The reaction was allowed to stir for 16 hours at room temperature. A 0.5 mL reaction aliquot was collected, shaken with ethyl acetate (3 mL) and brine (3 mL), and analyzed via a gas chromatography (GC).

Reactions of organonickel complexes (Figure 2A in the manuscript)

Stoichiometric coupling reactions with Ni(Alkyl) complexes

Unless noted otherwise, stoichiometric coupling reactions were performed following a **General Procedure C**.

Coupling reaction between a secondary alkyl bromide and **2-cyPr** was performed following a **General Procedure D**.

Coupling reaction between a secondary redox-active ester and **2-cyPr** was performed following a **General Procedure E**.

Coupling reactions of primary N-alkyl pyridinium salts were performed following a **General Procedure F**.

Coupling reactions of secondary N-alkyl pyridinium salts were performed following a **General Procedure G**.

Catalytic coupling reactions with 10 mol% of BPI-Ni-OAc (**1**)

Unless noted otherwise, catalytic coupling reactions were performed following the **General Procedure C** with modifications (see below).

An oven-dried threaded 4 mL vial equipped with a PTFE-coated stir bar was charged with a given electrophile-1 (either methyl iodide, (3-bromopropyl)benzene, or bromocyclopropane) (0.050 mmol, 1.0 equiv) instead of a respective Ni(Alkyl) complex along with the BPI-Ni-OAc (**1**) (2 mg, 0.005 mmol, 0.1 equiv) as catalyst.

Catalytic coupling reactions with 10 mol% (**1**) between the bromocyclopropane and a secondary alkyl bromide were performed following the **General Procedure D** with modifications.

Bromocyclopropane (11 mg, 0.090 mmol, 1.0 equiv) was used instead of the **2-cyPr** along with the BPI-Ni-OAc (**1**) (4 mg, 0.009 mmol, 0.1 equiv) as catalyst.

Catalytic coupling reactions with 10 mol% (**1**) between the bromocyclopropane and a secondary redox-active ester were performed following the **General Procedure E** with modifications.

Bromocyclopropane (11 mg, 0.090 mmol, 1.0 equiv) was used instead of the **2-cyPr** along with the BPI-Ni-OAc (**1**) (4 mg, 0.009 mmol, 0.1 equiv) as catalyst.

Catalytic coupling reactions with 10 mol% (**1**) employing primary N-alkyl pyridinium salts were performed following the **General Procedure F** with modifications.

An oven-dried threaded 4 mL vial equipped with a PTFE-coated stir bar was charged with a given electrophile-1 (either methyl iodide, (3-bromopropyl)benzene, or bromocyclopropane) (0.090 mmol, 1.0 equiv) instead of a respective Ni(Alkyl) complex along with the BPI-Ni-OAc (**1**) (4 mg, 0.009 mmol, 0.1 equiv) as catalyst.

Catalytic coupling reactions with 10 mol% (**1**) employing secondary N-alkyl pyridinium salts were performed following the **General Procedure G** with modifications.

An oven-dried threaded 4 mL vial equipped with a PTFE-coated stir bar was charged with a given electrophile-1 (either methyl iodide, (3-bromopropyl)benzene, or bromocyclopropane) (0.050 mmol, 1.0 equiv) instead of a respective Ni(Alkyl) complex along with the BPI-Ni-OAc (**1**) (2 mg, 0.005 mmol, 0.1 equiv) as catalyst.

Comparison of cross-coupling reactions employing either e-chem or Zn as a reductant (discussed in Fig. 2A of the manuscript).

(echem)
or
Zn powder

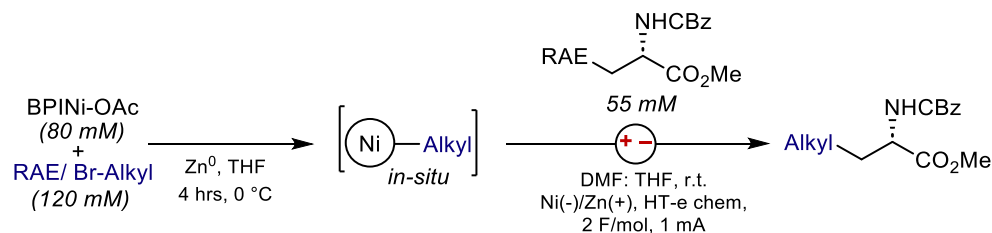
isolated Ni-R + X-CH₂-CH₂-R' (1.5 equiv) → R-CH₂-CH₂-R' (X = Br, RAE, or Py⁺)

	 1° RBr	 2° RBr	 1° RAE	 2° RAE	 3° RAE	 1° [Py⁺]
Ni-Me, 2-Me	79% (82%)	98% (95%)	91% (96%)	98% (95%)	88% (95%)	1% (58%)
Ni-Pr(Ph), 2-Pr	72% (95%)	84% (95%)	79% (95%)	81% (95%)	85% (95%)	8% (48%)
Ni-cyPr, 2-cyPr	98% (95%)	25% (98%)	98% (95%)	4% (52%)	70% (22%)	51% (73%)

Figure S3. Comparison of cross-coupling reactions employing either e-chem or Zn as a reductant. Yields in parentheses correspond to e-chem yields.

Reactions with stoichiometric Ni(Alkyl) complexes were performed following **General Procedures A-G**. Catalytic coupling reactions with 10 mol% (**1**) were performed following modified **General Procedures A-G** (see the “Reactions of organonickel complexes” section above).

Procedures for high-throughput experiments (HTE) (Figure 2B in the manuscript)



HTE-Chem cross-coupling reactions.

In a nitrogen-filled glovebox, 1-mL vials (secured in a 24-well aluminum block) equipped with tumble stir bars were charged with the Ni(Alkyl) solution (see below for preparation, 195 μL , 80.0 mM in THF, 15.6 μmol , 1.50 equiv) and ASP RAE (**SM-0**) solution (see below for preparations, 195 μL , 54 mM in DMF, 10.4 μmol , 1.0 equiv). The electrodes were inserted, and the HTE-Chem reaction block was assembled inside the glovebox. The reactor was then taken outside of the glovebox and stirred briefly on an IKA stir plate. The reactions were electrolyzed at constant current (1 mA, 2.0 F/mol). After electrolysis, reactions were worked up with 2 mL of EtOAc and 2 mL of water. The organic layer was then analyzed by GC and products were determined by GC-MS.

Stock Solution for HTE-Chem reactions.

Ni(Alkyl) stock solution preparation: In a nitrogen-filled glovebox, a 4 mL screw-cap vial was charged with BPI-Ni-OAc (**1**) (71.1 mg, 0.160 mmol, 80.0 mM, 1.00 equiv), C(sp³) electrophile (0.240 mmol, 120 mM, 1.50 equiv), LiCl (13.6 mg, 0.320 mmol, 160 mM, 2.00 equiv), THF (2 mL), dodecane internal standard (27.5 mg, 0.0160 mmol, 80.0 mM, 1.00 equiv), and a magnetic stir bar. The reactions were then sealed and removed from the glovebox. The reactions were then stirred at 0 °C for 4 hours.

ASP RAE (**SM-0**) stock solution: In a nitrogen filled glove box, a 4 mL screw cap vial was charged with 4-(1,3-dioxoisindolin-2-yl) 1-methyl ((benzyloxy)carbonyl)-L-aspartate (ASP RAE, **SM-0**) (23 mg, 0.054 mmol, 54 mM), lithium bromide (44 mg, 0.500 mmol, 500 mM), DMF (1 mL), and a magnetic stir bar. The solution was then stirred for 5 minutes.

Mechanistic investigation

Radical clock experiment with 2-hex-1-ene

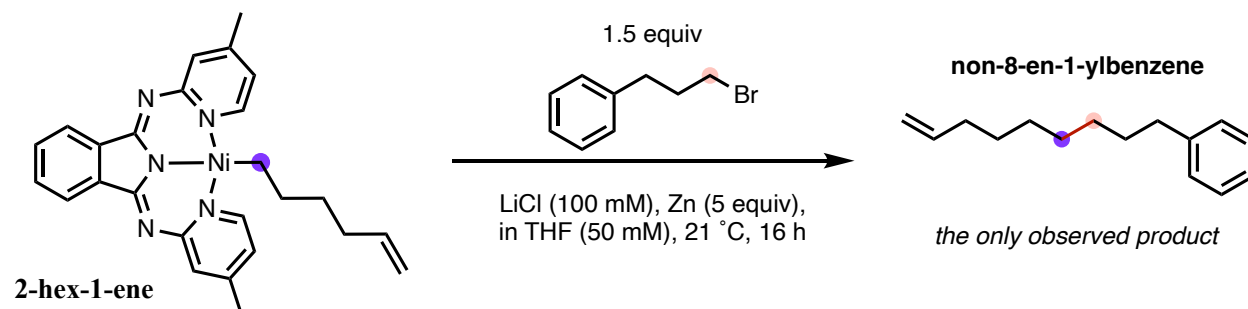


Figure S4. Radical clock experiment with **2-hex-1-ene**.

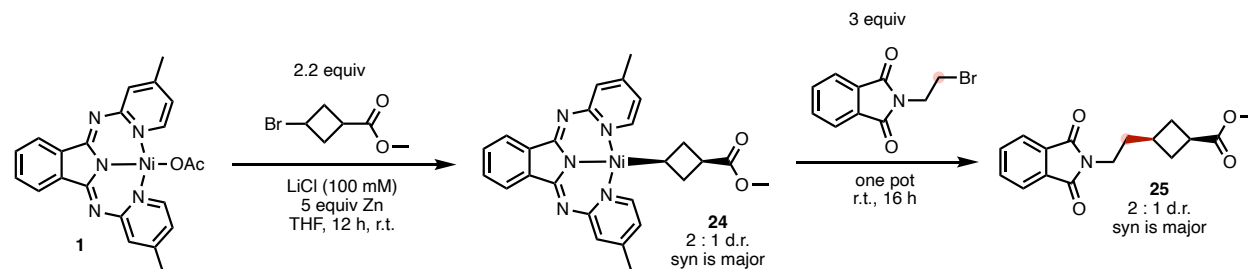
Following a **General Procedure C**, an oven-dried 4 mL scintillation vial equipped with a PTFE-coated stir bar was charged with **2-hex-1-ene** (47 mg, 0.10 mmol, 1.0 equiv), lithium chloride (8 mg, 0.2 mmol, 2 equiv), (3-bromopropyl)benzene (30 mg, 0.15 mmol, 1.5 equiv), zinc powder (33 mg, 0.50 mmol, 5.0 equiv), and THF (2.0 mL, 50 mM). Contents were allowed to stir for 16 hours at room temperature. The reaction was diluted with hexanes (10 mL), the resulting suspension was filtered through a short plug of silica. Filtrate was evaporated *in vacuo*. A single uncyclized non-8-en-1-ylbenzene product was isolated following a purification via a preparatory thin layer chromatography (hexanes) as a colorless oil (10 mg, 0.049 mmol, 49%).

¹H NMR (400 MHz, Chloroform-*d*) δ 7.30 – 7.24 (m, 2H), 7.20 – 7.13 (m, 3H), 5.80 (ddt, *J* = 16.9, 10.1, 6.7 Hz, 1H), 5.03 – 4.85 (m, 2H), 2.65 – 2.55 (m, 2H), 2.09 – 1.98 (m, 2H), 1.63 – 1.57 (m, 2H), 1.43 – 1.25 (m, 8H).

¹³C NMR (101 MHz, Chloroform-*d*) δ 142.9, 139.2, 128.4, 128.2, 125.6, 114.1, 36.0, 33.8, 31.5, 29.3, 29.3, 29.1, 28.9.

GC-MS-EI (m/z): for C₁₅H₂₂ [M]⁺: calcd 202.2, found 202.2

Stereochemical probe (Figure 4B in the manuscript)



Reactions were carried out in a nitrogen-filled glovebox. An oven-dried 20 mL scintillation vial equipped with a PTFE-coated stir bar was charged with BPI-Ni-OAc (**1**) (133 mg 0.300 mmol, 1.00 equiv), lithium chloride (25 mg, 0.60 mmol, 2.0 equiv), zinc powder (98 mg, 1.5 mmol, 5.0 equiv), methyl 3-bromocyclobutane-1-carboxylate (127 mg, 0.660 mmol, 2.20 equiv) and THF (6.0 mL, 50 mM). Contents were allowed to stir for 12 hours at room temperature. A 0.4 mL reaction aliquot was analyzed via a crude ¹H NMR spectroscopy. Complex **24** was formed as a 2:1 mixture of syn:anti diastereomers.

The remaining 5.6 mL of the reaction mixture, 2-(2-bromoethyl)isoindoline-1,3-dione (213 mg, 0.840 mmol, 3.00 equiv) was added, and the mixture was allowed to stir for additional 16 hours at room temperature. The reaction mixture was diluted with ethyl acetate (20 mL), and the resulting precipitates were removed following a filtration through a pad of Celite.

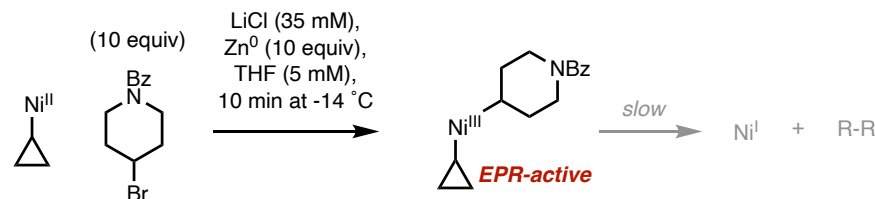
The filtrate was evaporated via a rotary evaporation and purified by column chromatography (silica, 0-10% EtOAc in hexanes) to afford methyl 3-(2-(1,3-dioxoisindolin-2-yl)ethyl)cyclobutane-1-carboxylate as a 2:1 mixture of syn:anti diastereomers (54 mg, 0.19 mmol, 67%) as determined via ^1H NMR NOESY spectroscopy.

^1H NMR (600 MHz, Chloroform- d) (major syn diastereomer) δ 7.81 (dd, J = 5.4, 3.0 Hz, 2H), 7.69 (dd, J = 5.4, 3.0 Hz, 2H), 3.63 (s, 3H), 3.61 – 3.58 (m, 2H), 2.95 (tt, J = 9.6, 8.3 Hz, 1H), 2.34 – 2.27 (m, 2H), 2.27 – 2.15 (m, 1H), 1.98 – 1.88 (m, 2H), 1.77 (q, J = 7.1 Hz, 2H).

^{13}C NMR (101 MHz, Chloroform- d) (major syn diastereomer) δ 175.5, 168.4, 134.0, 132.2, 123.3, 51.7, 36.0, 35.3, 34.5, 31.4, 29.4.

HRMS-ESI (m/z): for $\text{C}_{16}\text{H}_{17}\text{NO}_4$ $[\text{M}+\text{H}]^+$: calcd 288.1231, found 288.1230

EPR study of Ni(III)(dialkyl) complex (26) (Figure 4C in the manuscript)



All operations were carried out in a nitrogen-filled glovebox prior to the analysis. An oven-dried 4 mL vial equipped with a PTFE-stir bar was charged with **2-cyPr** (6 mg, 0.01 mmol, 1 equiv), lithium chloride (4 mg, 0.1 mmol, 7 equiv), (4-bromopiperidin-1-yl)(phenyl)methanone (40 mg, 0.15 mmol, 10 equiv), and THF (3 mL, 5 mM). The resulting stock solution was allowed to stir for 5 minutes.

A separate 4 mL vial equipped with PTFE-coated stir bar was charged with zinc powder (10 mg, 0.15 mmol, 10 equiv). Next, 1 mL of the above stock solution was dispensed into the second vial. The vial was covered with a PTFE-lined septum and capped with an open-top screw cap. The vial cap was wrapped with electrical tape to delay exposure to air. Empty 1 mL syringe was inserted into the vial through the PTFE septum. The vial was taken out of the glovebox. Contents were allowed to stir at -14 °C (slurry of ice and CaCl_2) for 10 minutes.

In the glovebox, an oven-dried quartz EPR tube (4 mm diameter, 250 mm long) was capped with a rubber septum. The septum was covered in multiple layers of parafilm to delay exposure to air. The EPR tube was taken out of the glovebox 1 minute before being injected with the reaction mixture.

After a 10 minute period, the reaction was allowed to stand for 30 seconds at -14 °C. A 0.3 mL aliquot was syringed from the reaction vial directly into a pre-chilled (ca. -20 °C) EPR tube. Following transfer, the EPR sample was promptly frozen in liquid nitrogen. EPR analysis was carried out at -196 °C

EPR analyses were carried out using a Bruker Magnetech ESR5000 instrument at X-band frequency with a 103s sweep time, 1.0 modulation, 100 kHz modulation frequency, 1 μ W microwave power, at -196 °C, at 9.45 GHz, -1 QFactor, at 5 mM sample concentration in THF.

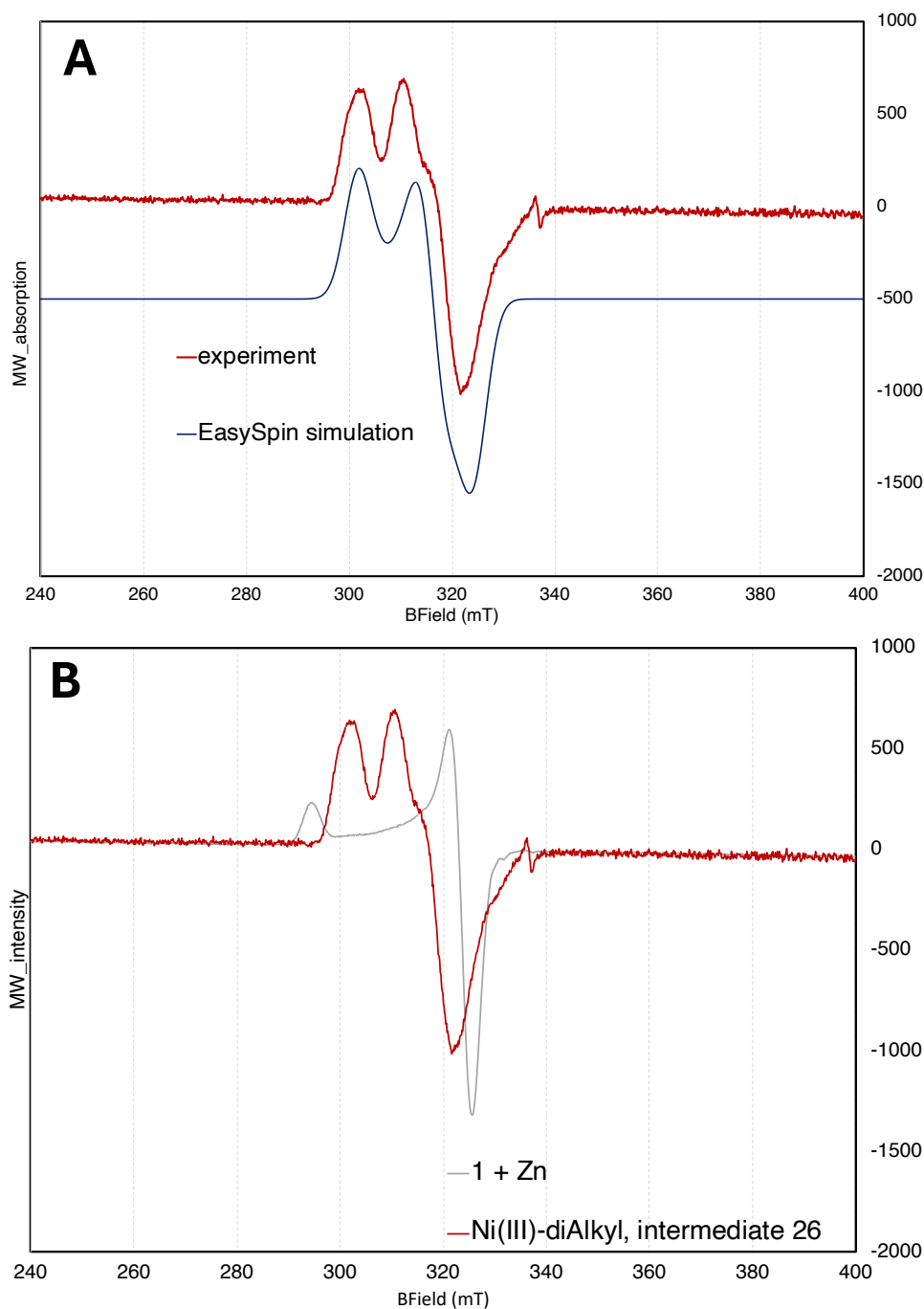


Figure S5. (A) EPR spectrum of the Ni(III)(dialkyl) intermediate **26** with the overlaid EasySpin simulation. (B) EPR spectrum of a mixture of **1** and Zn overlaid with the spectrum of intermediate **26**.

To distinguish Ni(III) intermediate **26** from a potential EPR-active Ni(I) intermediate, a control experiment was performed to generate Ni(I) by mixing **1** with an excess of Zn powder under similar reaction conditions as described below.

An oven-dried 4 mL vial equipped with a PTFE stir bar was charged with **1** (4 mg, 0.01 mmol, 1 equiv), lithium chloride (8 mg, 0.02 mmol, 20 equiv), zinc powder (13 mg, 0.020 mmol, 20 equiv), and THF (2 mL, 5 mM). The vial was covered with a PTFE-lined septum and capped with an open-top screw cap. The vial cap was wrapped with electrical tape to delay exposure to air. An empty 1 mL syringe was inserted into the vial through the PTFE septum. The vial was taken out of the glovebox, and the contents were allowed to stir at 0 °C (ice) for 30 minutes.

In the glovebox, an oven-dried quartz EPR tube (4 mm diameter, 250 mm long) was capped with a rubber septum. The septum was covered in multiple layers of parafilm to delay exposure to air. The EPR tube was taken out of the glovebox 1 minute before being injected with the reaction mixture.

After a 30-minute period, the reaction was allowed to stand for 30 seconds at 0 °C. A 0.3 mL aliquot was syringed from the reaction vial directly into a pre-chilled (ca. -20 °C) EPR tube. Following transfer, the EPR sample was promptly frozen in liquid nitrogen. EPR analysis was carried out at -196 °C using the same instrument and acquisition conditions as previously described. The acquired EPR spectrum of a putative Ni(I) intermediate is overlaid with the EPR spectrum of intermediate **26** in Figure S5(B). We found the EPR spectrum of the supposed Ni(I) intermediate to be distinct compared to the EPR spectrum of the Ni(III)-diAlkyl intermediate **26**.

Simulation of the EPR spectrum of intermediate **26**

Simulation of the EPR spectrum was performed using the EasySpin (5.2.36) plugin for MATLAB (version 2023b) using the following parameters:

```
Sys0.g = [2.2372, 2.1343, 2.0816];  
Sys0.lw = 6.01; % mT  
Sys0.gStrain = [0.01, 0.01, 0.01]  
Vary.lw = 0.1; % mT  
Vary.g = [0.01, 0.01, 0.01];  
Exp.mwFreq = 9.446271; % GHz  
Exp.Range = [240 400]; % mT  
esfit('pepper', spc, Sys0, Vary, Exp);
```

Best-fit simulated values of g-factor: $g_1=2.2372$, $g_2=2.1343$, $g_3=2.0816$

Probing oxidative addition via cyclic voltammetry

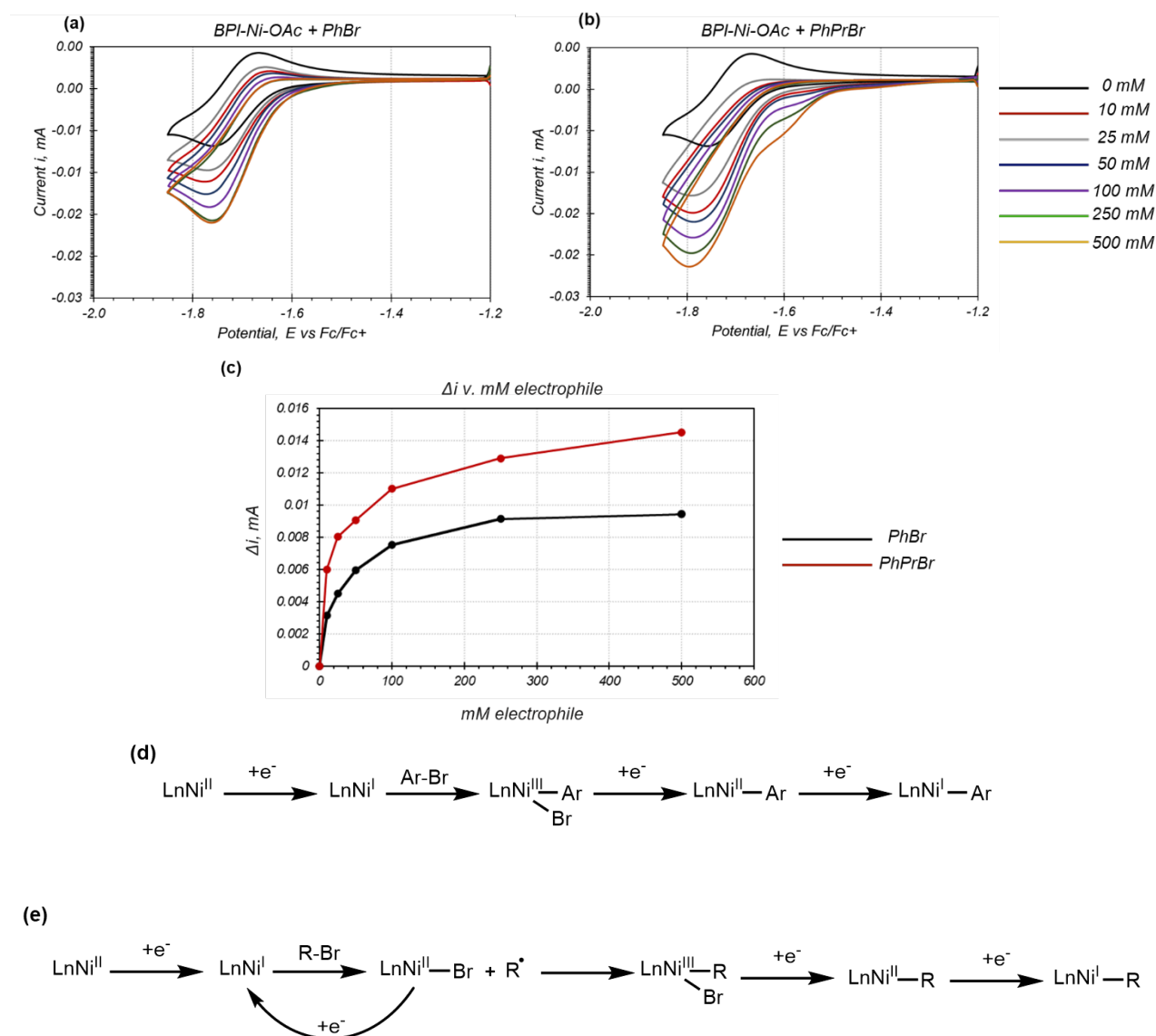
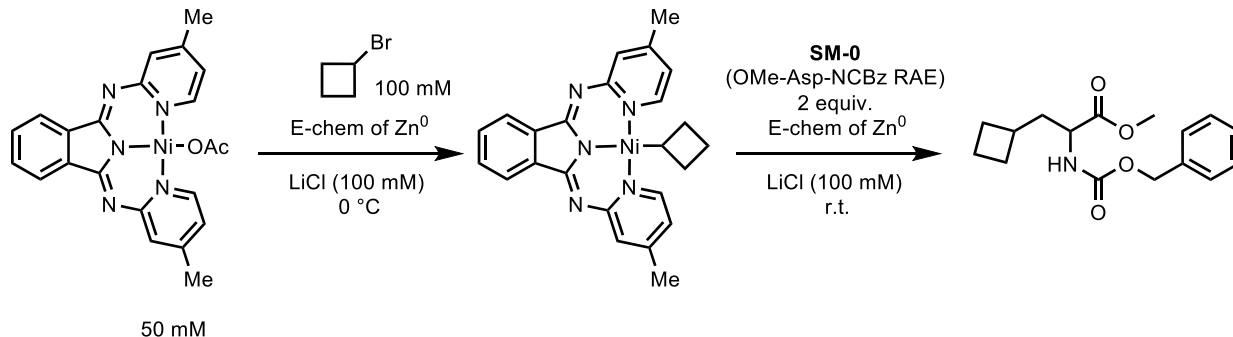


Figure S6. CVs of 1 mM BPI-Ni-OAc with varying concentrations of electrophile, and the change in i_c/i_0 with respect to the concentration of electrophile. (a) 1 mM BPI-Ni-OAc (black trace) in the presence of 10 mM PhBr (red trace), 25 mM PhBr (grey trace), 50 mM PhBr (navy trace), 100 mM PhBr (violet trace), 250 mM PhBr (green trace), and 500 mM PhBr (orange trace). (b) 1 mM BPI-Ni-OAc (black trace) in the presence of 10 mM PhPrBr (red trace), 25 mM PhPrBr (grey trace), 50 mM PhPrBr (navy trace), 100 mM PhPrBr (violet trace), 250 mM PhPrBr (green trace), and 500 mM PhPrBr (orange trace). (c) plot of Δi vs mM of PhBr (black trace) and PhPrBr (red trace) (d) Mechanistic hypothesis for PhBr oxidative addition. (e) Mechanistic hypothesis for PhPrBr oxidative addition. Glassy carbon working electrode, Pt counter electrode, 2 mL DMF, 250 mM TBAPF₆ supporting electrolyte, 10 mV/s scan rate.

Testing Robustness of the Method: The Use of IKA Electrosyn, Wet Solvents, Performing Reactions Outside of the Glovebox or Under Air



Atmosphere Preparation Cond.	Solvent	Reductant for the entire reaction	Yield (GC)
Glovebox	Dry (1:1) THF:DMF	E-chem	71%
Glovebox	Dry (1:1) THF:DMF	E-chem (IKA)	62%
atmosphere, N ₂ pump cycle	Wet (1:1) THF:DMF	E-chem	42%
atmosphere, N ₂ pump cycle	Wet (1:1) THF:DMF	E-chem (IKA)	41%
Open to air	Wet (1:1) THF:DMF	E-chem	0%
Glovebox	Dry (9:1) THF: DMF	Zn	83%
atmosphere, N ₂ pump cycle	Wet (9:1) THF: DMF	Zn	66%
Open to air	Wet (9:1) THF: DMF	Zn	0%

Figure S7. Evaluating robustness of the method. Glovebox: reactions were setup inside of a nitrogen-filled glovebox and **SM-0** was added to the reaction inside of a nitrogen-filled glovebox. Pump cycle: reactions were setup on a benchtop and were evacuated then backfilled with nitrogen via a Schlenk line three times. Air: reactions were set up on a benchtop then sealed with no further modifications to the atmosphere. Dry solvents: solvents were degassed via sparging with nitrogen and stored in a glovebox over 3 Å mol-sieves before use. Wet solvents: unstabilized THF and DMF were taken from the PureSolv solvent system and were stored in an open container under ambient air for 1 hour to saturate solvents with moisture. Both solvents were used “as-is” for subsequent reactions. E-chem: the reaction was preformed using our standard E-chem setup (see section “Electrochemical cell preparation procedures” for details). E-chem (IKA): the reactions were preformed using an IKA ElectraSyn 2.0. instrument outside of the glovebox. Zn: reactions were performed using a Zn powder as a reductant.

Glovebox reactions with Zn

In a nitrogen-filled glovebox, a 12 mL screw-cap vial was charged with BPI-Ni-OAc (**1**) (44 mg, 0.10 mmol, 50 mM, 1.0 equiv), bromocyclobutane (27 mg, 0.20 mmol, 100 mM, 2.0 equiv), LiCl (8 mg, 0.2 mmol, 100 mM, 2 equiv), THF (1.9 mL), DMF (0.1 mL), Zn powder (33 mg, 0.50

mmol, 5.0 equiv), dodecane as internal standard (27 mg), and a magnetic stir bar. The reactions were then sealed and removed from the glovebox. The reactions were stirred at 0 °C for 4 hours. The reactions were then brought back inside the glovebox, and 4-(1,3-dioxoisindolin-2-yl) 1-methyl ((benzyloxy)carbonyl)aspartate (**SM-0**) (85 mg, 0.20 mmol, 2.0 equiv) was added to the reaction. The reactions were then re-sealed and removed from the glovebox. The reactions were stirred at room temperature for 4 hours. A 0.5 mL aliquot of the reaction mixture was shaken with 2 mL of EtOAc and 2 mL of water. The organic layer was then analyzed by GC to determine yield.

Pump cycle reactions with Zn

On a benchtop, a 12 mL screw-cap vial was charged with BPI-Ni-OAc (**1**) (44 mg, 0.10 mmol, 50 mM, 1.0 equiv), bromocyclobutane (27 mg, 0.20 mmol, 100 mM, 2.0 equiv), LiCl (8 mg, 0.2 mmol, 100 mM, 2 equiv), THF (1.9 mL), DMF (0.1 mL), Zn powder (33 mg, 0.50 mmol, 5.0 equiv), dodecane as internal standard (27 mg), and a magnetic stir bar. The vial was sealed, evacuated, and backfilled with nitrogen three times before stirring at 0 °C for 4 hours. **SM-0** (85 mg, 0.20 mmol, 2.0 equiv) was dissolved in 0.5 mL of DMF and added to the reaction mixture via syringe. The reaction continued at room temperature for 4 hours. After completion, a 0.5 mL aliquot of the reaction mixture was shaken with 2 mL of EtOAc and 2 mL of water. The organic layer was then analyzed by GC to determine the yield.

Air reactions with Zn

On a benchtop, a 12 mL screw-cap vial was charged with BPI-Ni-OAc (**1**) (44 mg, 0.10 mmol, 50 mM, 1.0 equiv), bromocyclobutane (27 mg, 0.20 mmol, 100 mM, 2.0 equiv), LiCl (8 mg, 0.2 mmol, 100 mM, 2 equiv), THF (1.9 mL), DMF (0.1 mL), Zn powder (33 mg, 0.50 mmol, 5.0 equiv), dodecane as an internal standard (27 mg), and a magnetic stir bar. The vial was sealed and stirred at 0 °C for 4 hours. **SM-0** (85 mg, 0.20 mmol, 2.0 equiv) was dissolved in 0.5 mL of DMF and added to the reaction vial via syringe. The reaction was then stirred at room temperature for 4 hours. Following completion, a 0.5 mL aliquot of the reaction mixture was shaken with 2 mL of EtOAc and 2 mL of water. The organic layer was then analyzed by GC to determine the yield.

Glovebox E-chem reactions

Inside a nitrogen-filled glovebox, a 12 mL screw-cap vial was charged with BPI-Ni-OAc (**1**) (44 mg, 0.10 mmol, 50 mM, 1.0 equiv), bromocyclobutane (27 mg, 0.20 mmol, 100 mM, 2.0 equiv), LiCl (8 mg, 0.2 mmol, 100 mM, 2 equiv), THF (1.0 mL), DMF (1.0 mL), dodecane as an internal standard (27 mg), and a magnetic stir bar. A Ni-foam cathode and a Zn-plate anode were inserted into the vial, with the leads pierced through a septum cap, and the vial was sealed with a screw-cap. The sealed vial was removed from the glovebox, and the reaction mixture was stirred while a reductive, constant current was applied at the Ni cathode (3 mA, 5.36 mAh, 2.00 equiv e-) at 0 °C. The vial was then brought back inside the glovebox, and **SM-0** (85 mg, 0.20 mmol, 2.0 equiv) was dissolved in 0.5 mL of DMF and added to the reaction vial via syringe. The sealed vial was removed from the glovebox again, and the reaction mixture was stirred while a reductive, constant current was applied at the Ni cathode (3 mA, 5.36 mAh, 2.00 equiv e-) at room temperature. Following completion, a 0.5 mL aliquot of the reaction mixture was shaken with 2 mL of EtOAc and 2 mL of water. The organic layer was then analyzed by GC to determine the yield.

Pump cycle E-chem reaction

On a benchtop, a 12 mL screw-cap vial was charged with BPI-Ni-OAc (**1**) (44 mg, 0.10 mmol, 50 mM, 1.0 equiv), bromocyclobutane (27 mg, 0.20 mmol, 100 mM, 2.0 equiv), LiCl (8 mg, 0.2 mmol, 100 mM, 2 equiv), THF (1.0 mL), DMF (1.0 mL), dodecane as an internal standard (27 mg), and a magnetic stir bar. A Ni-foam cathode and Zn-plate anode were inserted into the vial, with the leads pierced through a septum cap, and the vial was sealed with a screw-cap. The sealed vial was then evacuated and backfilled with nitrogen three times via a Schlenk line. The reaction mixture was stirred while a reductive, constant current was applied at the Ni cathode (3 mA, 5.36 mAh, 2.00 equiv e-) at 0 °C. **SM-0** (85 mg, 0.20 mmol, 2.0 equiv) was dissolved in 0.5 mL of DMF and added to the reaction vial via syringe. The mixture was stirred at room temperature while the same reductive, constant current was applied at the Ni cathode. Following completion, a 0.5 mL aliquot of the reaction mixture was shaken with 2 mL of EtOAc and 2 mL of water. The organic layer was then analyzed by GC to determine the yield.

Air E-chem reaction

On a benchtop, a 12 mL screw-cap vial was charged with BPI-Ni-OAc (**1**) (44 mg, 0.10 mmol, 50 mM, 1.0 equiv), bromocyclobutane (27 mg, 0.20 mmol, 100 mM, 2.0 equiv), LiCl (8 mg, 0.2 mmol, 100 mM, 2 equiv), THF (1.0 mL), DMF (1.0 mL), dodecane as an internal standard (27 mg), and a magnetic stir bar. A Ni-foam cathode and Zn-plate anode were inserted into the vial, with the leads pierced through a septum cap, and the vial was sealed with a screw-cap. The reaction mixture was stirred while a reductive, constant current was applied at the Ni cathode (3 mA, 5.36 mAh, 2.00 equiv e-) at 0 °C. **SM-0** (85 mg, 0.20 mmol, 2.0 equiv) was dissolved in 0.5 mL of DMF and added to the reaction vial via syringe. The mixture was then stirred at room temperature while the same reductive, constant current was applied at the Ni cathode. Following completion, a 0.5 mL aliquot of the reaction mixture was shaken with 2 mL of EtOAc and 2 mL of water. The organic layer was then analyzed by GC to determine the yield.

Glovebox IKA ElectroSyn reaction

Inside a nitrogen-filled glovebox, a 4 mL screw-cap IKA vial was charged with BPI-Ni-OAc (**1**) (44 mg, 0.10 mmol, 50 mM, 1.0 equiv), bromocyclobutane (27 mg, 0.20 mmol, 100 mM, 2.0 equiv), LiCl (8 mg, 0.2 mmol, 100 mM, 2 equiv), THF (1.0 mL), DMF (1.0 mL), dodecane as an internal standard (27 mg), and a magnetic stir bar. A Ni-plate IKA electrode and Zn-plate IKA electrode were attached to the top of the IKA reactor cap. The IKA 4 mL reaction vial was then capped and sealed with the IKA reactor cap. The sealed vial was removed from the glovebox, and the reaction mixture was stirred (700 rpm) while a reductive, constant current was applied at the Ni cathode (3 mA, 5.36 mAh, 2.00 equiv e-) at room temperature. **SM-0** (85 mg, 0.20 mmol, 2.0 equiv) was dissolved in 0.5 mL of DMF and injected into the reaction vial via syringe. The mixture was then stirred again (700 rpm) with the same reductive, constant current applied at the Ni cathode. Following completion, a 0.5 mL aliquot of the reaction mixture was shaken with 2 mL of EtOAc and 2 mL of water. The organic layer was then analyzed by GC to determine the yield.

Pump cycle IKA ElectroSyn reaction

On a benchtop, a 4 mL screw-cap IKA vial was charged with BPI-Ni-OAc (**1**) (44 mg, 0.10 mmol, 50 mM, 1.0 equiv), bromocyclobutane (27 mg, 0.20 mmol, 100 mM, 2.0 equiv), LiCl (8 mg, 0.2 mmol, 100 mM, 2 equiv), THF (1.0 mL), DMF (1.0 mL), dodecane as an internal standard (27 mg), and a magnetic stir bar. A Ni-plate IKA electrode and Zn-plate IKA electrode were attached

to the top of the IKA reactor cap. The IKA 4 mL reaction vial was then capped and sealed with the IKA reactor cap. The sealed vial was evacuated and backfilled with nitrogen three times, and the reaction mixture was stirred (700 rpm) while a reductive, constant current was applied at the Ni cathode (3 mA, 5.36 mAh, 2.00 equiv e-) at room temperature. **SM-0** (85 mg, 0.20 mmol, 2.0 equiv) was dissolved in 0.5 mL of DMF and injected to the reaction vial via syringe. The mixture was stirred again (700 rpm) with the same reductive, constant current applied at the Ni cathode. Following completion, a 0.5 mL aliquot of the reaction mixture was shaken with 2 mL of EtOAc and 2 mL of water. The organic layer was then analyzed by GC to determine the yield.

Evaluating Functional Group Tolerance Through an Additive-Based Screening

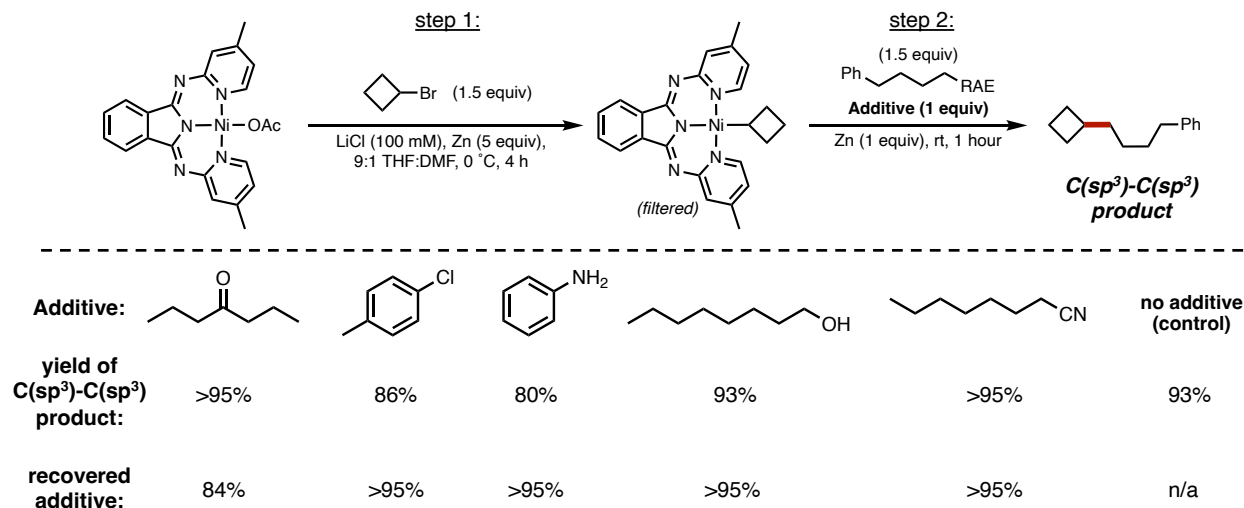


Figure S8. Yield of the C(sp³)-C(sp³) cross-coupled product with functional group additives added in step 2 of the reaction scheme.

Reactions with additive added during step 2

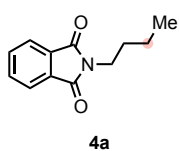
1,3-dioxoisindolin-2-yl 5-phenylpentanoate redox-active ester was prepared following a published procedure.²⁷

In a nitrogen-filled glovebox, a 40 mL oven-dried screw-cap vial was charged with BPI-Ni-OAc (**1**) (533 mg, 1.20 mmol, 1.00 equiv, 60.0 mM), bromocyclobutane (243 mg, 1.80 mmol, 1.50 equiv), lithium chloride (102 mg, 2.40 mmol, 2.00 equiv), zinc powder (392 mg, 6.00 mmol, 5.00 equiv), THF (18 mL), DMF (2 mL), decane as an internal standard, and a PTFE-coated magnetic stir bar. The vial was capped with a PTFE-lined cap, wrapped with electrical tape, and stirred for 4 hours at 0 °C. The resulting dark purple stock solution of **2-cyBu** was filtered through a plug of Celite to remove Zn powder.

Separately, stock solutions of each additive (1.0 mL, 294 mM) were prepared in THF. Cross-coupling reactions were performed in 4 mL oven-dried screw-cap vials with each vial charged with a magnetic stir bar, 1,3-dioxoisindolin-2-yl 5-phenylpentanoate redox-active ester (24 mg, 0.075 mmol, 1.5 equiv), zinc powder (3 mg, 0.05 mmol, 1 equiv), a solution of the **2-cyBu** prepared in the previous step (0.83 mL, 60 mM, 0.050 mmol, 1.0 equiv) and a solution of a respective additive (0.17 mL, 294 mM, 0.050 mmol, 1.0 equiv). The reactions were stirred at room temperature for 1 hour. Following completion, a 0.5 mL aliquot of each reaction mixture was shaken with 2 mL of EtOAc and 2 mL of brine. The organic layer was then analyzed by GC to determine the yield.

Characterization Data for Isolated Compounds (Figures 2-4 in the manuscript)

2-butylisoindoline-1,3-dione (4a)



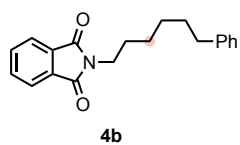
The title compound was isolated from the combination of reactions performed in Figure 2A and purified by flash chromatography with 0-10% EtOAc in hexanes as eluent.

¹H NMR (400 MHz, Chloroform-*d*) δ 7.89 – 7.76 (m, 2H), 7.75 – 7.64 (m, 2H), 3.67 (t, *J* = 7.2 Hz, 2H), 1.74 – 1.59 (m, 2H), 1.42 – 1.26 (m, 2H), 0.93 (t, *J* = 7.3 Hz, 3H).

¹³C NMR (101 MHz, Chloroform-*d*) δ 168.6, 133.9, 132.3, 123.2, 37.9, 30.8, 20.2, 13.7.

HRMS-ESI (m/z): for C₁₂H₁₃NO₂ [*M* + *H*]⁺: calcd 204.1019, found 204.1017

2-(6-phenylhexyl)isoindoline-1,3-dione (4b)



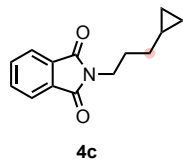
The title compound was isolated from the combination of reactions performed in Figure 2A and purified by flash chromatography with 0-5% EtOAc in hexanes as eluent.

¹H NMR (400 MHz, Chloroform-*d*) δ 7.88 – 7.81 (m, 2H), 7.73 – 7.68 (m, 2H), 7.29 – 7.23 (m, 2H), 7.19 – 7.11 (m, 3H), 3.70 – 3.65 (m, 2H), 2.63 – 2.55 (m, 2H), 1.76 – 1.56 (m, 4H), 1.38 (p, *J* = 3.6 Hz, 4H).

¹³C NMR (101 MHz, Chloroform-*d*) δ 168.6, 142.8, 134.0, 132.3, 128.5, 128.4, 125.7, 123.3, 38.2, 36.0, 31.4, 29.0, 28.7, 26.9.

HRMS-ESI (m/z): for C₂₀H₂₁NO₂ [*M* + *H*]⁺: calcd 308.1645, found 308.1645

2-(3-cyclopropylpropyl)isoindoline-1,3-dione (4c)



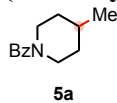
The title compound was isolated from the combination of reactions performed in Figure 2A and purified by flash chromatography with 0-5% EtOAc in hexanes as eluent.

¹H NMR (400 MHz, Chloroform-*d*) δ 7.87 – 7.78 (m, 2H), 7.72 – 7.67 (m, 2H), 3.73 – 3.67 (m, 2H), 1.82 – 1.73 (m, 2H), 1.29 – 1.19 (m, 2H), 0.76 – 0.64 (m, 1H), 0.44 – 0.37 (m, 2H), 0.04 – -0.02 (m, 2H).

¹³C NMR (101 MHz, Chloroform-*d*) δ 168.6, 134.0, 132.3, 123.3, 38.0, 32.0, 28.7, 10.5, 4.6.

HRMS-ESI (m/z): for C₁₄H₁₅NO₂ [*M* + *H*]⁺: calcd 230.1176, found 230.1174

(4-methylpiperidin-1-yl)(phenyl)methanone (5a)

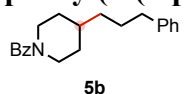


The title compound was isolated from the combination of reactions performed in Figure 2A and purified by flash chromatography with 10-20% EtOAc in hexanes as eluent.

¹H NMR (400 MHz, Chloroform-*d*) δ 7.39 – 7.35 (m, 5H), 4.66 (bs, 1H), 3.69 (bs, 1H), 3.02 – 2.65 (m, 2H), 1.79 – 1.53 (m, 3H), 1.24 – 1.04 (m, 2H), 0.96 (d, *J* = 6.4 Hz, 3H).

¹³C NMR (101 MHz, Chloroform-*d*) δ 170.3, 136.6, 129.4, 128.5, 126.9, 48.2, 42.6, 34.8, 34.0, 31.3, 21.8.

HRMS-ESI (m/z): for C₁₃H₁₇NO [*M* + *H*]⁺: calcd 204.1383, found 204.1380

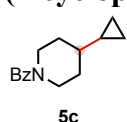
phenyl(4-(3-phenylpropyl)piperidin-1-yl)methanone (5b)

The title compound was isolated from the combination of reactions performed in Figure 2A and purified by flash chromatography with 5-20% EtOAc in hexanes as eluent.

¹H NMR (400 MHz, Chloroform-*d*) δ 7.42 – 7.35 (m, 5H), 7.30 – 7.24 (m, 2H), 7.22 – 7.15 (m, 3H), 4.69 (bs, 1H), 3.72 (bs, 1H), 3.09 – 2.67 (m, 2H), 2.61 (t, *J* = 7.7 Hz, 2H), 1.86 – 1.49 (m, 5H), 1.35 – 1.06 (m, 4H).

¹³C NMR (101 MHz, Chloroform-*d*) δ 170.4, 142.5, 136.6, 129.5, 128.5, 128.5, 128.4, 126.9, 125.9, 48.2, 42.6, 36.2, 36.2, 36.1, 33.0, 32.1, 28.6.

HRMS-ESI (m/z): for C₂₁H₂₅NO [M + H]⁺: calcd 308.2009, found 308.2005

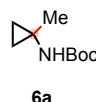
(4-cyclopropylpiperidin-1-yl)(phenyl)methanone (5c)

The title compound was isolated from the combination of reactions performed in Figure 2A and purified by flash chromatography with 5-20% EtOAc in hexanes as eluent.

¹H NMR (400 MHz, Chloroform-*d*) δ 7.41 – 7.36 (m, 5H), 4.67 (s, 1H), 3.72 (s, 1H), 3.03 – 2.64 (m, 2H), 1.94 – 1.60 (m, 2H), 1.52 – 1.20 (m, 2H), 0.82 – 0.70 (m, 1H), 0.63 – 0.51 (m, 1H), 0.48 – 0.37 (m, 2H), 0.18 – 0.03 (m, 2H).

¹³C NMR (101 MHz, Chloroform-*d*) δ 170.4, 136.7, 129.5, 128.5, 127.0, 48.1, 42.6, 41.7, 32.8, 31.9, 16.7, 3.3.

HRMS-ESI (m/z): for C₁₅H₁₉NO [M + H]⁺: calcd 230.1540, found 230.1538

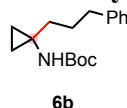
tert-butyl (1-methylcyclopropyl)carbamate (6a)

The title compound was isolated from the combination of reactions performed in Figure 2A and purified by flash chromatography with 0-10% EtOAc in hexanes as eluent.

¹H NMR (400 MHz, Chloroform-*d*) δ 4.84 (bs, 1H), 1.43 (s, 9H), 1.33 (s, 3H), 0.75 – 0.66 (m, 2H), 0.62 – 0.52 (m, 2H).

¹³C NMR (101 MHz, Chloroform-*d*) δ 155.6, 79.1, 29.7, 29.2, 28.4, 23.2, 14.6.

HRMS-ESI (m/z): for C₉H₁₇NO₂ [M + H]⁺: calcd 172.1332, found 172.1332

tert-butyl (1-(3-phenylpropyl)cyclopropyl)carbamate (6b)

The title compound was isolated from the combination of reactions performed in Figure 2A and purified by flash chromatography with 0-5% EtOAc in hexanes as eluent.

¹H NMR (400 MHz, Chloroform-*d*) δ 7.31 – 7.24 (m, 2H), 7.23 – 7.11 (m, 3H), 4.85 (bs, 1H), 2.63 (t, *J* = 7.7 Hz, 2H), 1.80 – 1.68 (m, 2H), 1.66 – 1.50 (m, 2H), 1.43 (s, 9H), 0.75 – 0.66 (m, 2H), 0.62 – 0.51 (m, 2H).

¹³C NMR (101 MHz, Chloroform-*d*) δ 155.6, 142.6, 128.5, 128.4, 125.8, 79.2, 36.2, 35.9, 33.1, 29.8, 28.5, 28.3, 13.9.

HRMS-ESI (m/z): for C₁₇H₂₅NO₂ [M + H]⁺: calcd 276.1958, found 276.1957

tert-butyl [1,1'-bi(cyclopropan)]-1-ylcarbamate (6c)



The title compound was isolated from the combination of reactions performed in Figure 2A and purified by flash chromatography with 0-5% EtOAc in hexanes as eluent.

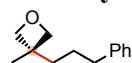
6c

¹H NMR (400 MHz, Chloroform-*d*) δ 4.88 (bs, 1H), 1.44 (s, 9H), 1.36 – 1.28 (m, 1H), 0.71 – 0.62 (m, 2H), 0.58 – 0.49 (m, 2H), 0.43 – 0.36 (m, 2H), 0.16 – 0.07 (m, 2H).

¹³C NMR (101 MHz, Chloroform-*d*) δ 155.8, 79.2, 34.3, 29.8, 28.5, 15.7, 12.0, 2.9.

HRMS-ESI (m/z): for C₁₁H₁₉NO₂ [M + H]⁺: calcd 198.1489, found 198.1488

3-methyl-3-(3-phenylpropyl)oxetane (8)



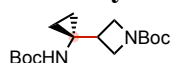
Following a **General Procedure B**, an oven-dried 4 mL scintillation vial equipped with a PTFE-coated stir bar was charged with BPI-Ni-OAc (**1**) (88 mg, 0.20 mmol, 1.0 equiv), (3-bromopropyl)benzene (60 mg, 0.30 mmol, 1.5 equiv), zinc powder (65 mg, 1.0 mmol, 5.0 equiv), lithium chloride (17 mg, 0.40 mmol, 2.0 equiv), and THF (4.0 mL, 50 mM). The resulting suspension was stirred for 1 hour at room temperature, darkening over time. Cross-coupling reaction was performed following a **General Procedure C**. 1,3-dioxoisindolin-2-yl 3-methyloxetane-3-carboxylate (78 mg, 0.3 mmol, 1.5 equiv) and zinc bromide (90 mg, 0.40 mmol, 2.0 equiv) were introduced into the solution of Ni(Alkyl) from the previous step (one pot). Contents were allowed to react for 16 hours while stirring at room temperature. The title compound was isolated following a purification by flash column chromatography (1% EtOAc in hexanes) as a colorless oil (22 mg, 0.12 mmol, 58%).

¹H NMR (400 MHz, Chloroform-*d*) 7.32 – 7.26 (m, 2H), 7.23 – 7.15 (m, 3H), 4.41 (d, J = 5.5 Hz, 2H), 4.33 (d, J = 5.5 Hz, 2H), 2.63 (t, J = 7.5 Hz, 2H), 1.71 – 1.65 (m, 2H), 1.62 – 1.54 (m, 2H), 1.28 (s, 3H).

¹³C NMR (101 MHz, Chloroform-*d*) δ 142.3, 128.5, 128.5, 126.0, 83.1, 39.3, 38.8, 36.4, 26.6, 23.4.

HRMS-ESI (m/z): for C₁₃H₁₈O [M + H]⁺: calcd 191.1431, found 191.1431

tert-butyl 3-(1-((tert-butoxycarbonyl)amino)cyclopropyl)azetidine-1-carboxylate (9)



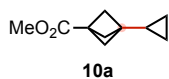
Following a **General Procedure B**, an oven-dried 20 mL scintillation vial equipped with a PTFE-coated stir bar was charged with BPI-Ni-OAc (**1**) (178 mg, 0.400 mmol, 1.00 equiv), *tert*-butyl 3-iodoazetidine-1-carboxylate (125 mg, 0.440 mmol, 1.10 equiv), zinc powder (130 mg, 2.00 mmol, 5.00 equiv), lithium chloride (34 mg, 0.80 mmol, 2.0 equiv), and THF (8.0 mL, 50 mM). The resulting suspension was stirred for 1 hour at room temperature, darkening over time. Cross-coupling reaction was performed following a **General Procedure C**. 1,3-dioxoisindolin-2-yl 1-((tert-butoxycarbonyl)amino)cyclopropane-1-carboxylate (277 mg, 0.800 mmol, 2.00 equiv) and zinc bromide (180 mg, 0.800 mmol, 2.00 equiv) were introduced into the Ni-alkyl solution from the previous step (one pot). Contents were allowed to react for 16 hours while stirring at room temperature. The title compound was isolated following a purification by flash column chromatography (20% EtOAc in hexanes) as yellow oil (82 mg, 0.26 mmol, 66%).

¹H NMR (400 MHz, Chloroform-*d*) δ 5.04 (s, 1H), 3.88 (t, J = 8.7 Hz, 2H), 3.58 (s, 2H), 2.78 (tt, J = 8.4, 5.9 Hz, 1H), 1.39 (s, 18H), 0.87 – 0.76 (m, 2H), 0.73 – 0.67 (m, 2H).

¹³C NMR (101 MHz, Chloroform-*d*) δ 156.5, 155.7, 79.6, 79.4, 52.3, 51.0, 33.9, 33.4, 28.5, 28.4, 11.7.

HRMS-ESI (m/z): for C₁₆H₂₈N₂O₄ [M + Na]⁺: calcd 335.1941, found 335.1939

methyl 3-cyclopropylbicyclo[1.1.1]pentane-1-carboxylate (10a)



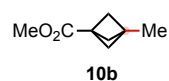
Following a **General Procedure C**, an oven-dried 20 mL scintillation vial equipped with a PTFE-coated stir bar was charged with **2-cyPr** (107 mg, 0.250 mmol, 1.00 equiv), lithium chloride (21 mg, 0.50 mmol, 2.0 equiv), zinc powder (33 mg, 0.50 mmol, 2.0 equiv), 1-(1,3-dioxoisindolin-2-yl) 3-methyl bicyclo[1.1.1]pentane-1,3-dicarboxylate (158 mg, 0.500 mmol, 2.00 equiv), zinc bromide (113 mg, 0.500 mmol, 2.00 equiv) and THF (5.0 mL, 50 mM). Contents were allowed to react for 16 hours while stirring at room temperature. Pure product was afforded following a purification via a flash column chromatography (0-5% EtOAc in hexanes) (22 mg, 0.13 mmol, 52%) as a clear oil.

¹H NMR (400 MHz, Chloroform-*d*) δ 3.65 (s, 3H), 1.81 (s, 5H), 0.86 (tt, *J* = 8.3, 5.0 Hz, 1H), 0.46 – 0.28 (m, 2H), 0.18 – 0.07 (m, 2H).

¹³C NMR (101 MHz, Chloroform-*d*) δ 168.1, 48.7, 47.9, 38.5, 34.0, 8.1, -0.6.

HRMS-ESI (m/z): for C₁₀H₁₄O₂ [M + H]⁺: calcd 167.1067, found 167.1065

methyl 3-methylbicyclo[1.1.1]pentane-1-carboxylate (10b)



Following a **General Procedure B**, an oven-dried 20 mL scintillation vial equipped with a PTFE-coated stir bar was charged with a BPI-Ni-OAc (**1**) (167 mg, 0.375 mmol, 1.00 equiv), methyl iodide (80 mg, 0.56 mmol, 1.5 equiv), zinc powder (123 mg, 1.89 mmol, 5.00 equiv), lithium chloride (32 mg, 0.75 mmol, 2.0 equiv), and THF (7.5 mL, 50 mM). The resulting suspension was stirred for 2 hours at room temperature, darkening over time. The resulting Ni(Alkyl) solution was filtered through a short plug of basic alumina before use.

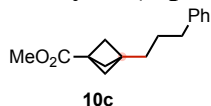
Cross-coupling reaction was carried out following a **General Procedure C**. An oven-dried 20 mL scintillation vial equipped with a PTFE-coated stir bar was charged with the previous Ni(Alkyl) solution, 1-(1,3-dioxoisindolin-2-yl) 3-methyl bicyclo[1.1.1]pentane-1,3-dicarboxylate (221 mg, 0.700 mmol, 2.00 equiv), and zinc bromide (158 mg, 0.700 mmol, 2.00 equiv). Contents were allowed to react for 4 hours while stirring at room temperature. Pure product was afforded following a purification via a flash column chromatography (0-5% EtOAc in hexanes) (21 mg, 0.15 mmol, 42%) as a volatile clear oil with a potent aroma.

¹H NMR (400 MHz, Chloroform-*d*) δ 3.66 (s, 3H), 1.90 (s, 6H), 1.26 (s, 3H).

¹³C NMR (101 MHz, Chloroform-*d*) δ 170.7, 51.6, 50.6, 38.9, 36.8, 14.1.

HRMS-ESI (m/z): for C₈H₁₂O₂ [M + H]⁺: calcd 141.0910, found 141.0910

methyl 3-(3-phenylpropyl)bicyclo[1.1.1]pentane-1-carboxylate (10c)



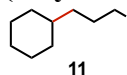
Following a **General Procedure C**, an oven-dried 20 mL scintillation vial equipped with a PTFE-coated stir bar was charged with **2-Pr** (101 mg, 0.200 mmol, 1.00 equiv), lithium chloride (17 mg, 0.40 mmol, 2.0 equiv), zinc powder (26 mg, 0.40 mmol, 2.0 equiv), 1-(1,3-dioxoisindolin-2-yl) 3-methyl bicyclo[1.1.1]pentane-1,3-dicarboxylate (126 mg, 0.400 mmol, 2.00 equiv), zinc bromide (90 mg, 0.40 mmol, 2.0 equiv) and THF (4.0 mL, 50 mM). Contents were allowed to react for 24 hours while stirring at room temperature. Pure product was afforded following a purification via a flash column chromatography (25 mg, 0.10 mmol, 52%) as a clear oil.

¹H NMR (600 MHz, Chloroform-*d*) δ 7.31 – 7.25 (m, 2H), 7.21 – 7.15 (m, 3H), 3.66 (s, 3H), 2.60 (t, *J* = 7.6 Hz, 2H), 1.90 (s, 6H), 1.61 – 1.56 (m, 2H), 1.52 – 1.47 (m, 2H).

¹³C NMR (101 MHz, Chloroform-*d*) δ 170.8, 142.4, 128.4, 128.3, 125.8, 51.6, 51.5, 40.1, 37.7, 36.0, 30.9, 28.3.

HRMS-ESI (m/z): for $C_{16}H_{20}O_2$ $[M + H]^+$: calcd 245.1536, found 245.1534

(3-cyclohexylpropyl)benzene (11)



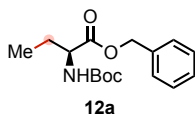
Complexes **2-Pr** and **2-Cy** were prepared following a **General Procedure A**. Cross-coupling between **2-Pr** and bromocyclohexane was carried out following a **General Procedure C**. Electrochemical cross-coupling between **2-Cy** and (3-bromopropyl)benzene was carried out following a **General Procedure D**, while an analogous cross-coupling reaction with Zn powder was carried out following a **General Procedure C**. The title compound was isolated from the combination of reactions performed in Figure 3 and was isolated following a purification via a preparatory thin layer chromatography with hexanes as eluent.

1H NMR (400 MHz, Chloroform-*d*) δ 7.31 – 7.25 (m, 2H), 7.24 – 7.13 (m, 3H), 2.61 – 2.55 (m, 2H), 1.74 – 1.59 (m, 7H), 1.27 – 1.10 (m, 6H), 0.92 – 0.83 (m, 2H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 143.1, 128.5, 128.3, 125.7, 37.7, 37.3, 36.4, 33.5, 29.0, 26.9, 26.6.

GC-MS-EI (m/z): for $C_{15}H_{22}$ $[M]^+$: calcd 202.2, found 202.1

benzyl (S)-2-((tert-butoxycarbonyl)amino)butanoate (12a)



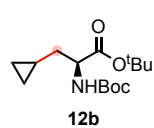
Following a **General Procedure C**, an oven-dried 4 mL scintillation vial containing PTFE-coated stir bar was charged with **2-Me** (60 mg, 0.15 mmol, 1.0 equiv), benzyl (R)-3-bromo-2-((tert-butoxycarbonyl)amino)propanoate (73 mg, 0.23 mmol, 1.5 equiv), zinc powder (10 mg, 0.15 mmol, 1.0 equiv), lithium chloride (13 mg, 0.30 mmol, 2.0 equiv) and THF (3.0 mL, 50 mM). Contents were allowed to react for 16 hours while stirring at room temperature. The title compound isolated following a purification by flash column chromatography (15% EtOAc in hexanes) as a colorless oil (33 mg, 0.12 mmol, 78%).

1H NMR (400 MHz, Chloroform-*d*) δ 7.38 – 7.30 (m, 5H), 5.22 – 5.11 (m, 2H), 5.06 (d, J = 8.5 Hz, 1H), 4.31 (q, J = 7.7 Hz, 1H), 1.84 (m, 1H), 1.68 (m, 1H), 1.44 (s, 9H), 0.90 (t, J = 7.5 Hz, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 172.7, 155.4, 135.5, 128.6, 128.4, 128.2, 79.8, 66.9, 54.6, 28.3, 25.9, 9.6.

HRMS-ESI (m/z): for $C_{16}H_{23}NO_4$ $[M + Na]^+$: calcd 316.1519, found 316.1519

tert-butyl (S)-2-((tert-butoxycarbonyl)amino)-3-cyclopropylpropanoate (12b)



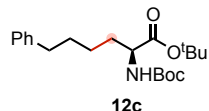
Following a **General Procedure C**, an oven-dried 4 mL scintillation vial equipped with a PTFE-coated stir bar was charged with **2-cyPr** (64 mg, 0.15 mmol, 1.0 equiv), 1-(tert-butyl) 4-(1,3-dioxoisindolin-2-yl) (tert-butoxycarbonyl)-L-aspartate (98 mg, 0.23 mmol, 1.5 equiv), zinc powder (10 mg, 0.15 mmol, 1.0 equiv), lithium chloride (13 mg, 0.30 mmol, 2.0 equiv), and THF (3.0 mL, 50 mM). Contents were allowed to react for 24 hours while stirring at room temperature. The title compound was isolated following a purification by flash column chromatography (15% EtOAc in hexanes) as a colorless oil (26 mg, 0.092 mmol, 61%).

1H NMR (400 MHz, Chloroform-*d*) δ 5.13 (d, J = 8.3 Hz, 1H), 4.23 (dt, J = 8.3, 5.9 Hz, 1H), 1.69 – 1.54 (m, 2H), 1.46 (s, 9H), 1.43 (s, 9H), 0.76 – 0.62 (m, 1H), 0.52 – 0.39 (m, 2H), 0.14 – 0.03 (m, 2H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 171.9, 155.2, 81.6, 79.5, 54.5, 37.6, 28.4, 28.0, 6.9, 4.4, 4.2.

HRMS-ESI (*m/z*): for $\text{C}_{15}\text{H}_{27}\text{NO}_4$ [$\text{M} + \text{Na}$] $^{+}$: calcd 308.1832, found 308.1832

tert-butyl (S)-2-((tert-butoxycarbonyl)amino)-6-phenylhexanoate (12c)



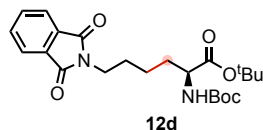
Following a **General Procedure C**, an oven-dried 4 mL scintillation vial equipped with a PTFE-coated stir bar was charged with **2-Pr** (76 mg, 0.15 mmol, 1.0 equiv), 1-(tert-butyl) 4-(1,3-dioxoisindolin-2-yl) (tert-butoxycarbonyl)-L-aspartate (98 mg, 0.23 mmol, 1.5 equiv), zinc powder (10 mg, 0.15 mmol, 1.0 equiv), lithium chloride (13 mg, 0.30 mmol, 2.0 equiv), and THF (3.0 mL, 50 mM). Contents were allowed to react for 24 hours while stirring at room temperature. The title compound was isolated following a purification by flash column chromatography (15% EtOAc in hexanes) as a colorless oil (20 mg, 0.056 mmol, 37%).

^1H NMR (400 MHz, Chloroform-*d*) δ 7.31 – 7.22 (m, 2H), 7.21 – 7.13 (m, 2H), 5.00 (d, J = 8.4 Hz, 1H), 4.17 (q, J = 7.1 Hz, 1H), 2.61 (t, J = 7.6 Hz, 2H), 1.77 (m, 1H), 1.71 – 1.55 (m, 3H), 1.44 (s, 9H), 1.43 (s, 9H), 1.41 – 1.29 (m, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 172.05, 155.35, 142.30, 128.40, 128.30, 125.72, 81.69, 79.55, 53.89, 35.68, 32.88, 31.04, 28.35, 27.99, 24.71.

HRMS-ESI (*m/z*): for $\text{C}_{21}\text{H}_{33}\text{NO}_4$ [$\text{M} + \text{Na}$] $^{+}$: calcd 386.2302, found 386.2301

tert-butyl (S)-2-((tert-butoxycarbonyl)amino)-6-(1,3-dioxoisindolin-2-yl)hexanoate (12d)



Following a **General Procedure B**, an oven-dried 4 mL scintillation vial equipped with a PTFE-coated stir bar was charged with BPI-Ni-OAc (**1**) (40 mg, 0.090 mmol, 1.0 equiv), 2-(3-bromopropyl)isindoline-1,3-dione (48 mg, 0.18 mmol, 2.0 equiv), zinc powder (30 mg, 0.45 mmol, 5.0 equiv), lithium chloride (8 mg, 0.2 mmol, 2.0 equiv), and THF (3.0 mL, 30 mM). The resulting suspension was stirred for 4 hours at room temperature, darkening over time. The resulting Ni(Alkyl) solution was filtered through a short plug of basic alumina before being evaporated to dryness *in vacuo*.

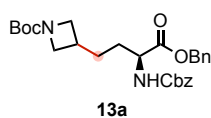
Cross-coupling reaction was performed following a **General Procedure D**. A 12 mL threaded reaction vial equipped with a PTFE-coated stir bar was charged with the Ni(Alkyl) complex from the previous step, tetrabutylammonium tetrafluoroborate (247 mg, 0.750 mmol, 8.33 equiv, 250 mM), tert-butyl (R)-3-bromo-2-((tert-butoxycarbonyl)amino)propanoate (44 mg, 0.14 mmol, 1.5 equiv), and DMF (1.5 mL). The reaction was equipped with a Ni-foam cathode and Zn-plate anode and was taken out of the glovebox before being injected with degassed methanol (1.5 mL, net 30 mM). A reductive constant current was passed through the Ni-foam cathode (5 mA, 4 equiv e $^{-}$) at room temperature. The title compound was isolated following a purification by flash column chromatography (20% EtOAc in hexanes) as a colorless oil (20 mg, 0.047 mmol, 52%).

^1H NMR (400 MHz, Chloroform-*d*) δ 7.83 (dd, J = 5.5, 3.0 Hz, 2H), 7.70 (dd, J = 5.5, 3.0 Hz, 2H), 5.01 (d, J = 8.4 Hz, 1H), 4.17 – 4.11 (m, 1H), 3.68 (t, J = 7.2 Hz, 2H), 1.87 – 1.64 (m, 5H), 1.43 (s, 9H), 1.42 (s, 9H), 1.27 – 1.23 (m, 1H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 171.86, 168.36, 155.35, 133.89, 132.14, 123.19, 81.79, 79.57, 53.77, 37.63, 32.54, 28.32, 28.23, 27.98, 22.53, 14.11.

HRMS-ESI (*m/z*): for $\text{C}_{23}\text{H}_{32}\text{N}_2\text{O}_6$ [$\text{M} + \text{Na}$] $^{+}$: calcd 455.2152, found 455.2152

tert-butyl (S)-3-(4-(benzyloxy)-3-(((benzyloxy)carbonyl)amino)-4-oxobutyl)azetidine-1-carboxylate (13a)



Following a **General Procedure B**, an oven-dried 4 mL scintillation vial equipped with a PTFE-coated stir bar was charged with BPI-Ni-Oac (**1**) (88 mg, 0.20 mmol, 1.0 equiv), *tert*-butyl 3-iodoazetidine-1-carboxylate (62 mg, 0.22 mmol, 1.1 equiv), zinc powder (65 mg, 1.0 mmol, 5.0 equiv), lithium chloride (17 mg, 0.40 mmol, 2.0 equiv), and THF (4.0 mL, 50 mM). The resulting suspension was stirred for 1 hour at room temperature, darkening over time.

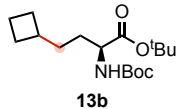
Cross-coupling reaction was performed following a **General Procedure C**. 1-benzyl 5-(1,3-dioxoisindolin-2-yl) ((benzyloxy)carbonyl)-L-glutamate (155 mg, 0.300 mmol, 1.50 equiv) was added to the Ni(Alkyl) solution from the previous step (one pot). Contents were allowed to react for 16 hours while stirring at room temperature. The title compound was isolated following a purification by flash column chromatography (15% EtOAc in hexanes) as a colorless oil (65 mg, 0.13 mmol, 67%).

¹H NMR (400 MHz, Chloroform-*d*) δ 7.42 – 7.27 (m, 10H), 5.38 (d, *J* = 8.2 Hz, 1H), 5.24 – 5.12 (m, 2H), 5.10 (s, 2H), 4.45 – 4.24 (m, 1H), 4.09 – 3.76 (m, 2H), 3.60 – 3.28 (m, 2H), 2.55 – 2.25 (m, 1H), 1.83 – 1.52 (m, 4H), 1.43 (s, 9H).

¹³C NMR (101 MHz, Chloroform-*d*) δ 172.1, 156.6, 155.5, 81.9, 79.7, 79.3, 53.9, 34.4, 33.1, 28.9, 28.6, 28.5, 28.2, 26.8, 25.1.

HRMS-ESI (m/z): for C₂₇H₃₄N₂O₆ [M + Na]⁺: calcd 505.2309, found 505.2308

tert-butyl (S)-2-((tert-butoxycarbonyl)amino)-4-cyclobutylbutanoate (13b)



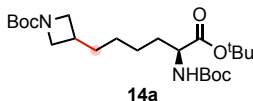
Following a **General Procedure C**, a 4 mL scintillation vial equipped with a PTFE-coated stir bar was charged with 2-^cBu (66 mg, 0.15 mmol, 1.0 equiv), 1-(tert-butyl) 5-(1,3-dioxoisindolin-2-yl) (tert-butoxycarbonyl)-L-glutamate (121 mg, 0.270 mmol, 1.80 equiv), zinc powder (49 mg, 0.75 mmol, 5.0 equiv), lithium chloride (13 mg, 0.30 mmol, 2.0 equiv), and THF (3.0 mL, 50 mM). Contents were allowed to react for 24 hours while stirring at room temperature. The title compound was isolated following a purification by flash column chromatography (10% EtOAc in hexanes) as a colorless oil (24 mg, 0.078 mmol, 52%).

¹H NMR (400 MHz, Chloroform-*d*) δ 4.99 (d, *J* = 8.3 Hz, 1H), 4.18 – 4.06 (m, 1H), 2.30 – 2.14 (m, 1H), 2.08 – 1.96 (m, 2H), 1.89 – 1.71 (m, 2H), 1.68 – 1.47 (m, 4H), 1.46 (s, 9H), 1.43 (s, 9H), 1.44 – 1.21 (m, 2H).

¹³C NMR (101 MHz, Chloroform-*d*) δ 172.1, 155.3, 81.6, 79.5, 53.9, 35.6, 32.1, 30.4, 28.3, 28.1, 28.1, 28.0, 18.4.

HRMS-ESI (m/z): for C₁₇H₃₁NO₄ [M + Na]⁺: calcd 336.2145, found 336.2146

tert-butyl (S)-3-(6-(tert-butoxy)-5-((tert-butoxycarbonyl)amino)-6-oxohexyl)azetidine-1-carboxylate (14a)



Following a **General Procedure B**, an oven-dried 4 mL scintillation vial containing a PTFE-coated stir bar was charged with BPI-Ni-Oac (**1**) (44 mg, 0.10 mmol, 1.0 equiv), lithium chloride (8 mg, 0.2 mmol, 2 equiv), zinc powder (33 mg, 0.50 mmol, 5.0 equiv), *tert*-butyl 3-iodoazetidine-1-carboxylate (34 mg, 0.12 mmol, 1.2 equiv), and THF (1.0 mL, 100 mM). Contents were stirred for 1.5 hours at room temperature, darkening over time. The resulting purple solution of Ni(Alkyl) was filtered through a short plug of Celite.

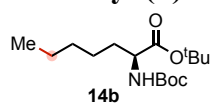
Cross-coupling reaction was performed following a **General Procedure F**. An oven-dried 12 mL culture tube equipped with a PTFE-coated stir bar was charged with sodium iodide (112 mg, 0.750 mmol, 7.50 equiv, 250 mM) electrolyte, (S)-1-(6-(tert-butoxy)-5-((tert-butoxycarbonyl)amino)-6-oxohexyl)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate N-alkyl pyridinium salt (102 mg, 0.150 mmol, 1.50 equiv), DMA (2 mL), and the Ni(Alkyl) solution from the previous step (1 mL, 33 mM final concentration). Tube was equipped with a Co-wire anode and a stainless steel cathode and was taken out of the glovebox. A reductive constant current was passed through the cathode (5 mA, 5.36 mAh, 2.00 equiv e-) at 60 °C. The title compound was isolated following a purification by flash column chromatography (10-30% EtOAc in hexanes) as a waxy solid (25 mg, 0.056 mmol, 56%).

¹H NMR (400 MHz, Chloroform-*d*) δ 5.00 (d, *J* = 8.5 Hz, 1H), 4.15 (q, *J* = 7.3, 6.7 Hz, 1H), 3.97 (t, *J* = 8.3 Hz, 2H), 3.50 (dd, *J* = 8.5, 5.5 Hz, 2H), 2.50 – 2.39 (m, 1H), 1.78 – 1.71 (m, 1H), 1.62 – 1.52 (m, 4H), 1.45 (s, 9H), 1.44 (s, 9H), 1.42 (s, 9H), 1.28 – 1.21 (m, 3H).

¹³C NMR (101 MHz, Chloroform-*d*) δ 172.1, 156.6, 155.5, 81.9, 79.7, 79.3, 53.9, 34.4, 33.1, 28.9, 28.6, 28.5, 28.2, 26.8, 25.1.

HRMS-ESI (m/z): for C₂₃H₄₂N₂O₆ [M]⁺: calcd 442.3043, found 442.3008

tert-butyl (S)-2-((tert-butoxycarbonyl)amino)heptanoate (14b)



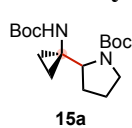
Following a **General Procedure F**, an oven-dried 12 mL culture tube equipped with a PTFE-coated stir bar was charged with sodium iodide (112 mg, 0.750 mmol, 8.33 equiv, 250 mM) electrolyte, (S)-1-(6-(tert-butoxy)-5-((tert-butoxycarbonyl)amino)-6-oxohexyl)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate N-alkyl pyridinium salt (92 mg, 0.13 mmol, 1.5 equiv), **2-Me** (36 mg, 0.090 mmol, 1.0 equiv), and a 2:1 mixture of DMA:THF (3.0 mL, 30 mM). Reaction tube was equipped with a Co-wire anode and a stainless steel cathode and was taken out of the glovebox. A reductive constant current was passed through the cathode (5 mA, 4.82 mAh, 2.00 equiv e-) at 60 °C. The title compound was isolated following a purification by flash column chromatography (5-10% EtOAc in hexanes) as a clear oil (22 mg, 0.073 mmol, 81%).

¹H NMR (400 MHz, Chloroform-*d*) δ 5.14 – 4.58 (m, 1H), 4.27 – 3.90 (m, 1H), 1.79 – 1.69 (m, 1H), 1.62 – 1.55 (m, 1H), 1.45 (s, 9H), 1.43 (s, 9H), 1.35 – 1.23 (m, 6H), 0.91 – 0.84 (m, 3H).

¹³C NMR (101 MHz, Chloroform-*d*) δ 172.3, 155.5, 81.7, 79.6, 54.1, 33.0, 31.6, 28.5, 28.1, 24.9, 22.6, 14.1.

HRMS-ESI (m/z): for C₁₆H₃₁NO₄ [M + Na]⁺: calcd 324.2145, found 324.2145

tert-butyl 2-(1-((tert-butoxycarbonyl)amino)cyclopropyl)pyrrolidine-1-carboxylate (15a)



Following a **General Procedure B**, an oven-dried 20 mL scintillation vial containing a PTFE-coated stir bar was charged with BPI-Ni-Oac (**1**) (133 mg, 0.300 mmol, 1.00 equiv), lithium chloride (25 mg, 0.60 mmol, 2.0 equiv), zinc powder (392 mg, 6.00 mmol, 20.0 equiv), 1-(tert-butyl) 2-(1,3-dioxoisindolin-2-yl) pyrrolidine-1,2-dicarboxylate (162 mg, 0.450 mmol, 1.50 equiv), and THF (6.0 mL, 50 mM). Contents were stirred for 2 hours at 0 °C, darkening over time. The resulting solution of Ni(Alkyl) was filtered through a short plug of Celite.

Cross-coupling reaction was performed following a **General Procedure C**. An oven-dried 20 mL scintillation vial equipped with a PTFE-coated stir bar was charged with zinc powder (196 mg, 1.5 mmol, 10.0 equiv), zinc bromide (135 mg, 0.600 mmol, 2.00 equiv), 1,3-dioxoisindolin-2-yl 1-((tert-butoxycarbonyl)amino)cyclopropane-1-carboxylate (208 mg, 0.600

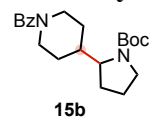
mmol, 2.00 equiv), and the Ni(Alkyl) solution from the previous step. Contents were reacted for 16 hours at room temperature. The title compound was isolated following a purification by flash column chromatography (15% EtOAc in hexanes) as a colorless oil (39, 0.12 mmol, 40%).

¹H NMR (400 MHz, Chloroform-*d*) δ 4.89 (bs, 1H), 3.59 – 3.29 (m, 3H), 2.30 – 2.10 (m, 1H), 1.96 – 1.85 (m, 2H), 1.79 – 1.71 (m, 1H), 1.46 (s, 9H), 1.40 (s, 9H), 1.11 – 0.87 (m, 2H), 0.80 – 0.66 (m, 2H).

¹³C NMR (101 MHz, Chloroform-*d*) δ 155.6, 155.4, 79.4, 79.2, 63.3, 47.9, 35.8, 28.7, 28.5, 23.9, 15.7, 11.5.

HRMS-ESI (*m/z*): for C₁₇H₃₀N₂O₄ [M + Na]⁺: calcd 349.2098, found 349.2097

tert-butyl 2-(1-benzoylpiperidin-4-yl)pyrrolidine-1-carboxylate (**15b**)



Following a **General Procedure B**, an oven-dried 4 mL scintillation vial containing a PTFE-coated stir bar was charged with BPI-Ni-Oac (**1**) (89 mg, 0.20 mmol, 1.0 equiv), lithium chloride (8 mg, 0.2 mmol, 1 equiv), zinc powder (65 mg, 1.0 mmol, 5.0 equiv), 1-(tert-butyl) 2-(1,3-dioxoisindolin-2-yl) pyrrolidine-1,2-dicarboxylate (108 mg, 0.300 mmol, 1.50 equiv), and THF (2.0 mL, 100 mM). Contents were stirred for 2 hours at room temperature, darkening over time. The resulting solution of Ni(Alkyl) was filtered through a short plug of Celite.

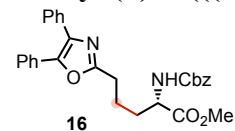
Cross-coupling reaction was performed following a **General Procedure D**. A 12 mL threaded reaction vial equipped with a PTFE-coated stir bar was charged with the Ni(Alkyl) solution from the previous step, tetrabutylammonium tetrafluoroborate (494 mg, 1.50 mmol, 7.50 equiv, 250 mM) electrolyte, (4-bromopiperidin-1-yl)(phenyl)methanone (80 mg, 0.30 mmol, 1.5 equiv), and DMF (2 mL). The reaction was equipped with a Ni-foam cathode and a Zn-plate anode and was taken out of the glovebox. A degassed methanol (2 mL, net 33 mM) was syringed and a reductive constant current was passed through the Ni-foam cathode (10 mA, 21.4 mAh, 4 equiv e⁻) at room temperature. The reaction mixture was diluted with ethyl acetate (200 mL) and successively washed with an aqueous solution of citric acid (2M, 2 x 25 mL) and brine (25 mL). Organic fraction was dried over an anhydrous sodium sulfate, solvent was removed via a rotary evaporation. The title compound was isolated following a purification by flash column chromatography (10-30% EtOAc in hexanes) as a colorless oil (29 mg, 0.081 mmol, 40%).

¹H NMR (400 MHz, Chloroform-*d*) δ 7.44 – 7.33 (m, 5H), 4.77 (s, 1H), 3.93 – 3.63 (m, 2H), 3.57 – 3.37 (m, 1H), 3.27 – 3.13 (m, 1H), 3.02 – 2.57 (m, 3H), 2.18 – 1.56 (m, 7H), 1.44 (s, 9H), 1.33 – 1.18 (m, 2H).

¹³C NMR (101 MHz, Chloroform-*d*) δ 170.4, 155.2, 136.4, 129.5, 128.5, 126.9, 79.5, 79.3, 61.0, 48.3, 47.2, 46.5, 42.7, 42.4, 40.5, 39.5, 30.2, 29.8, 27.7, 27.0, 26.7, 24.4, 23.6.

HRMS-ESI (*m/z*): for C₂₁H₃₀N₂O₃ [M + Na]⁺: calcd 381.2148, found 381.2148

methyl (S)-2-(((benzyloxy)carbonyl)amino)-5-(4,5-diphenyloxazol-2-yl)pentanoate (**16**)



Following a **General Procedure B**, an oven-dried 4 mL scintillation vial equipped with a PTFE-coated stir bar was charged with BPI-Ni-Oac (**1**) (67 mg, 0.15 mmol, 1.0 equiv), methyl 2-(((benzyloxy)carbonyl)amino)-3-bromopropanoate (71 mg, 0.22 mmol, 1.5 equiv), zinc powder (49 mg, 0.75 mmol, 5.0 equiv), lithium chloride (13 mg, 0.30 mmol, 2.0 equiv), and THF (3.0 mL, 50 mM). The resulting suspension was stirred for 2 hours at 0 °C, darkening over time.

Cross-coupling reaction was performed following a **General Procedure C**. 1,3-dioxoisindolin-2-yl 3-(4,5-diphenyloxazol-2-yl)propanoate (99 mg, 0.22 mmol, 1.5 equiv) was introduced into

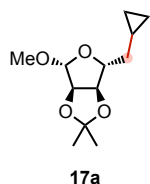
the solution of Ni(Alkyl) from the previous step (one pot). Contents were reacted for 16 hours at 0 °C. The title compound was isolated following a purification by flash column chromatography (20% EtOAc in hexanes) as an amorphous white solid (26 mg, 0.054 mmol, 36%).

¹H NMR (400 MHz, Chloroform-*d*) δ 7.67 – 7.61 (m, 2H), 7.60 – 7.54 (m, 2H), 7.40 – 7.29 (m, 11H), 5.53 (d, *J* = 8.1 Hz, 1H), 5.11 (s, 2H), 4.45 (td, *J* = 7.7, 4.7 Hz, 1H), 3.74 (s, 3H), 3.05 – 2.79 (m, 2H), 2.09 – 1.79 (m, 4H).

¹³C NMR (101 MHz, Chloroform-*d*) δ 172.8, 162.8, 156.1, 145.4, 136.4, 135.2, 132.6, 129.1, 128.8, 128.7, 128.7, 128.6, 128.3, 128.2, 128.2, 128.0, 126.6, 67.2, 53.8, 52.6, 32.0, 27.7, 22.9.

HRMS-ESI (*m/z*): for C₂₉H₂₈N₂O₅ [*M* + Na]⁺: calcd 507.1890, found 507.1888

(3*a*R,4*R*,6*R*,6*a*R)-4-(cyclopropylmethyl)-6-methoxy-2,2-dimethyltetrahydrofuro[3,4-*d*][1,3]dioxole (17a)



Following a **General Procedure C**, an oven-dried 4 mL scintillation vial equipped with a PTFE-coated stir bar was charged with **2-cyPr** (64 mg, 0.15 mmol, 1.0 equiv), (3*a*R,4*R*,6*S*,6*a*S)-4-(bromomethyl)-6-methoxy-2,2-dimethyltetrahydrofuro[3,4-*d*][1,3]dioxole (60 mg, 0.22 mmol, 1.5 equiv), lithium chloride (13 mg, 0.30 mmol, 2.0 equiv), zinc powder (49 mg, 0.75 mmol, 5.0 equiv), and THF (3.0 mL, 50 mM). Contents were allowed to react for 16 hours

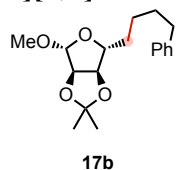
while stirring at room temperature. The title compound was isolated following a purification by flash column chromatography (1% EtOAc in hexanes) as a colorless oil (25 mg, 0.11 mmol, 74%).

¹H NMR (400 MHz, Chloroform-*d*) δ 4.94 (s, 1H), 4.60 (s, 2H), 4.26 (t, *J* = 7.7 Hz, 1H), 3.33 (s, 3H), 1.65 (ddd, *J* = 13.8, 7.5, 6.2 Hz, 1H), 1.49 (s, 3H), 1.32 (s, 3H), 1.28 – 1.24 (m, 1H), 0.80 – 0.72 (m, 1H), 0.53 – 0.46 (m, 2H), 0.12 – 0.05 (m, 2H).

¹³C NMR (101 MHz, Chloroform-*d*) δ 112.3, 109.5, 87.8, 85.8, 83.9, 54.9, 40.0, 26.7, 25.2, 8.0, 4.7, 4.4.

HRMS-ESI (*m/z*): for C₁₂H₂₀O₄ [*M*]⁺: calcd 228.1362, found 228.1383

(3*a*R,4*R*,6*R*,6*a*R)-4-methoxy-2,2-dimethyl-6-(4-phenylbutyl)tetrahydrofuro[3,4-*d*][1,3]dioxole (17b)



Following a **General Procedure C**, an oven-dried 4 mL scintillation vial equipped with a PTFE-coated stir bar was charged with **2-Pr** (76 mg, 0.15 mmol, 1.0 equiv), (3*a*R,4*R*,6*S*,6*a*S)-4-(bromomethyl)-6-methoxy-2,2-dimethyltetrahydrofuro[3,4-*d*][1,3]dioxole (60 mg, 0.22 mmol, 1.5 equiv),

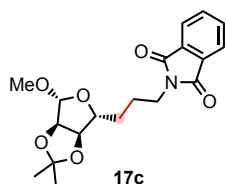
lithium chloride (13 mg, 0.30 mmol, 2.0 equiv), zinc powder (49 mg, 0.75 mmol, 5.0 equiv), and THF (3.0 mL, 50 mM). Contents were allowed to react for 16 hours while stirring at room temperature. The title compound was isolated following a purification by flash column chromatography (1% EtOAc in hexanes) as a colorless oil (30 mg, 0.10 mmol, 67%).

¹H NMR (400 MHz, Chloroform-*d*) δ 7.31 – 7.24 (m, 2H), 7.22 – 7.14 (m, 3H), 4.94 (s, 1H), 4.60 (d, *J* = 6.0 Hz, 1H), 4.52 (dd, *J* = 6.0, 1.1 Hz, 1H), 4.18 – 4.10 (m, 1H), 3.31 (s, 3H), 2.63 (t, *J* = 7.7 Hz, 2H), 1.74 – 1.49 (m, 6H), 1.48 (s, 3H), 1.32 (s, 3H).

¹³C NMR (101 MHz, Chloroform-*d*) δ 142.6, 128.5, 128.4, 125.8, 112.3, 109.6, 87.3, 85.7, 84.3, 55.0, 35.9, 35.1, 31.3, 26.7, 26.0, 25.2.

HRMS-ESI (*m/z*): for C₁₈H₂₆O₄ [*M* + H]⁺: calcd 307.1904, found 307.1805

2-(3-((3aR,4R,6R,6aR)-6-methoxy-2,2-dimethyltetrahydrofuro[3,4-d][1,3]dioxol-4-yl)propyl)isoindoline-1,3-dione (17c)



Following a **General Procedure B**, an oven-dried 4 mL scintillation vial equipped with a PTFE-coated stir bar was charged with BPI-Ni-Oac (**1**) (67 mg, 0.15 mmol, 1.5 equiv), 2-(2-bromoethyl)isoindoline-1,3-dione (76 mg, 0.20 mmol, 2.0 equiv), zinc powder (49 mg, 0.75 mmol, 5.0 equiv), lithium chloride (13 mg, 0.30 mmol, 2.0 equiv), and THF (3.0 mL, 50 mM). The resulting suspension was stirred for 2 hours at room temperature, darkening over time.

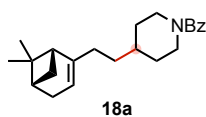
Cross-coupling reaction was performed following a **General Procedure C**. (3aR,4R,6S,6aS)-4-(bromomethyl)-6-methoxy-2,2-dimethyltetrahydrofuro[3,4-d][1,3]dioxole (60 mg, 0.22 mmol, 1.5 equiv) was introduced into the Ni(Alkyl) solution from the previous step (one pot). Contents were allowed to react for 16 hours while stirring at room temperature. The title compound was isolated following a purification by flash column chromatography (3% EtOAc in hexanes) as a colorless oil (35 mg, 0.096 mmol, 64%).

¹H NMR (400 MHz, Chloroform-*d*) δ 7.86 – 7.80 (m, 2H), 7.73 – 7.68 (m, 2H), 4.91 (s, 1H), 4.56 (d, *J* = 5.9 Hz, 1H), 4.54 – 4.47 (m, 1H), 4.15 (dd, *J* = 9.2, 6.1 Hz, 1H), 3.71 (t, *J* = 7.1 Hz, 2H), 3.30 (s, 3H), 1.95 – 1.82 (m, 1H), 1.81 – 1.70 (m, 1H), 1.67 – 1.51 (m, 2H), 1.45 (s, 3H), 1.29 (s, 3H).

¹³C NMR (101 MHz, Chloroform-*d*) δ 168.5, 134.1, 132.2, 123.3, 112.4, 109.7, 86.7, 85.6, 84.2, 6.1, 37.8, 32.5, 26.6, 25.7, 25.1.

HRMS-ESI (m/z): for C₁₉H₂₃NO₆ [M+Na]⁺: calcd 384.1417, found 384.1416

(4-(2-((1R,5S)-6,6-dimethylbicyclo[3.1.1]hept-2-en-2-yl)ethyl)piperidin-1-yl)(phenyl)methanone (18a)



Following a **General Procedure B**, an oven-dried 4 mL scintillation vial equipped with a PTFE-coated stir bar was charged with BPI-Ni-Oac (**1**) (67 mg, 0.15 mmol, 1.0 equiv), lithium chloride (13 mg, 0.30 mmol, 2.0 equiv), zinc powder (49 mg, 0.75 mmol, 5.0 equiv), (1R,5S)-2-(2-bromoethyl)-6,6-dimethylbicyclo[3.1.1]hept-2-ene (52 mg, 0.22 mmol, 1.5 equiv), and THF (1.5 mL, 100 mM).

Contents were reacted for 2 hours at room temperature. The resulting Ni(Alkyl) solution was filtered through a short plug of Celite.

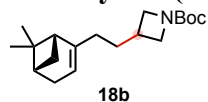
Cross-coupling reaction was performed following a **General Procedure G**. An oven-dried 4 mL scintillation vial equipped with a PTFE-coated stir bar was charged with the 1-(1-benzoylpiperidin-4-yl)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate N-alkyl pyridinium salt (131 mg, 0.225 mmol, 1.50 equiv), zinc powder (49 mg, 0.75 mmol, 5.0 equiv), and the Ni(Alkyl) solution from the previous step. The reaction vial was covered with a PTFE septum and capped with an open-top screw cap and taped with an electrical tape. The reaction vial was taken out of the glovebox and injected with degassed methanol (1.5 mL, net 50 mM). Contents were allowed to react for 16 hours while stirring at room temperature. The title compound was isolated following a purification by flash column chromatography (5-20% EtOAc in hexanes) as a colorless oil (26 mg, 0.077 mmol, 51%).

¹H NMR (400 MHz, Chloroform-*d*) δ 7.41 – 7.35 (m, 5H), 5.22 – 5.13 (m, 1H), 4.69 (s, 1H), 3.72 (s, 1H), 3.01 – 2.67 (m, 2H), 2.35 (dt, *J* = 8.6, 5.6 Hz, 1H), 2.27 – 2.13 (m, 2H), 2.10 – 2.05 (m, 1H), 2.00 – 1.92 (m, 3H), 1.86 – 1.75 (m, 1H), 1.68 – 1.62 (m, 1H), 1.54 – 1.45 (m, 1H), 1.34 – 1.22 (m, 7H), 1.13 (d, *J* = 8.4 Hz, 1H), 0.82 (s, 3H).

¹³C NMR (101 MHz, Chloroform-*d*) δ 170.4, 148.3, 136.6, 129.5, 128.5, 126.9, 116.0, 48.3, 45.9, 42.7, 40.9, 38.1, 36.0, 34.0, 33.9, 33.0, 32.1, 31.8, 31.4, 26.5, 21.3.

HRMS-ESI (m/z): for C₂₃H₃₁NO [M + Na]⁺: calcd 360.2298, found 360.2297.

tert-butyl 3-(2-((1*R*,5*S*)-6,6-dimethylbicyclo[3.1.1]hept-2-en-2-yl)ethyl)azetidine-1-carboxylate (18b)



Following a **General Procedure B**, an oven-dried 4 mL scintillation vial equipped with a PTFE-coated stir bar was charged with BPI-Ni-Oac (**1**) (67 mg, 0.15 mmol, 1.0 equiv), lithium chloride (13 mg, 0.30 mmol, 2.0 equiv), zinc powder (49 mg, 0.75 mmol, 5.0 equiv), (1*R*,5*S*)-2-(2-bromoethyl)-6,6-dimethylbicyclo[3.1.1]hept-2-ene (52 mg, 0.22 mmol, 1.5 equiv), and THF (3.0 mL, 50 mM). Contents were reacted for 2 hours at room temperature.

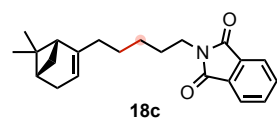
Cross-coupling reaction was performed following a **General Procedure C**. tert-butyl 3-iodoazetidine-1-carboxylate (64 mg, 0.22 mmol, 1.5 equiv) was introduced into the solution of Ni(Alkyl) from the previous step (one pot). Contents were allowed to react for 16 hours while stirring at room temperature. The title compound was isolated following a purification by flash column chromatography (0-10% EtOAc in hexanes) as a colorless oil (42 mg, 0.14 mmol, 92%).

¹H NMR (400 MHz, Chloroform-*d*) δ 5.22 – 5.12 (m, 1H), 3.97 (t, *J* = 8.3 Hz, 2H), 3.54 – 3.49 (m, 2H), 2.50 – 2.41 (m, 1H), 2.34 (dt, *J* = 8.4, 5.6 Hz, 1H), 2.26 – 2.13 (m, 2H), 2.07 (s, 1H), 1.97 (td, *J* = 5.6, 1.5 Hz, 1H), 1.90 – 1.80 (m, 2H), 1.66 – 1.56 (m, 2H), 1.43 (s, 9H), 1.26 (s, 3H), 1.12 (d, *J* = 8.5 Hz, 1H), 0.81 (s, 3H).

¹³C NMR (101 MHz, Chloroform-*d*) δ 156.6, 147.6, 116.5, 79.2, 45.9, 40.9, 38.1, 34.3, 32.3, 31.8, 31.4, 28.7, 28.6, 26.4, 21.3.

HRMS-ESI (m/z): for C₁₉H₃₁NO₂ [M + H]⁺: calcd 306.2428, found 306.2427.

2-(5-((1*R*,5*S*)-6,6-dimethylbicyclo[3.1.1]hept-2-en-2-yl)pentyl)isoindoline-1,3-dione (18c)



Following a **General Procedure B**, an oven-dried 4 mL scintillation vial equipped with a PTFE-coated stir bar was charged with BPI-Ni-Oac (**1**) (44 mg, 0.10 mmol, 1.0 equiv), lithium chloride (8 mg, 0.2 mmol, 2 equiv), zinc powder (33 mg, 0.50 mmol, 5.0 equiv), (1*R*,5*S*)-2-(2-bromoethyl)-6,6-dimethylbicyclo[3.1.1]hept-2-ene (34 mg, 0.15 mmol, 1.5 equiv), and THF (1.0 mL, 100 mM). Contents were reacted for 2 hours at room temperature. The resulting solution of Ni(Alkyl) was filtered through a short plug of Celite.

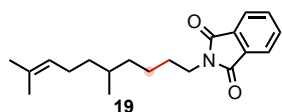
Cross-coupling reaction was performed following a **General Procedure F**. An oven-dried 12 mL culture tube equipped with a PTFE-coated stir bar was charged with sodium iodide (112 mg, 0.750 mmol, 7.50 equiv, 250 mM) electrolyte, 1-(3-(1,3-dioxoisoindolin-2-yl)propyl)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate N-alkyl pyridinium salt (88 mg, 0.15 mmol, 1.5 equiv), DMA (2 mL, net 33 mM), and the Ni(Alkyl) solution from the previous step. The reaction tube was equipped with a Co-wire anode and a stainless steel cathode and was taken out of the glovebox. A reductive constant current was passed through the cathode (5 mA, 5.36 mAh, 2.00 equiv e⁻) at 60 °C. The title compound was isolated following a purification by flash column chromatography (0-5% EtOAc in hexanes) as a colorless oil (29 mg, 0.086 mmol, 86%).

¹H NMR (400 MHz, Chloroform-*d*) δ 7.87 – 7.80 (m, 2H), 7.73 – 7.67 (m, 2H), 5.17 – 5.09 (m, 1H), 3.67 (t, *J* = 7.3, 2H), 2.31 (dt, *J* = 8.5, 5.6 Hz, 1H), 2.24 – 2.09 (m, 2H), 2.08 – 2.00 (m, 1H), 1.96 (td, *J* = 5.6, 1.5 Hz, 1H), 1.96 – 1.86 (m, 2H), 1.72 – 1.63 (m, 2H), 1.40 – 1.28 (m, 4H), 1.24 (s, 3H), 1.09 (d, *J* = 8.4 Hz, 1H), 0.78 (s, 3H).

¹³C NMR (101 MHz, Chloroform-*d*) δ 168.6, 148.4, 134.0, 132.3, 123.3, 116.0, 45.9, 41.0, 38.2, 38.0, 36.8, 31.8, 31.4, 28.6, 26.9, 26.8, 26.5, 21.3.

HRMS-ESI (m/z): for C₂₂H₂₇NO₂ [M + H]⁺: calcd 338.2115, found 338.2115.

2-(6,10-dimethylundec-9-en-1-yl)isoindoline-1,3-dione (19)



Following a **General Procedure B**, an oven-dried 4 mL scintillation vial equipped with a PTFE-coated stir bar was charged with BPI-Ni-Oac (**1**) (67 mg, 0.15 mmol, 1.0 equiv), lithium chloride (13 mg, 0.30 mmol, 2.0 equiv), zinc powder (49 mg, 0.75 mmol, 5.0 equiv), 8-bromo-2,6-dimethyloct-2-ene (49 mg, 0.22 mmol, 1.5 equiv), and THF (3.0 mL, 50 mM). Contents were stirred for 2 hours at room temperature.

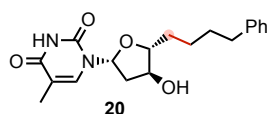
Cross-coupling reaction was performed following a **General Procedure C**. 2-(2-bromoethyl)isoindoline-1,3-dione (57 mg, 0.22 mmol, 1.5 equiv) was introduced into the solution of Ni(Alkyl) from the previous step (one pot). Contents were allowed to react for 16 hours while stirring at room temperature. The title compound was isolated following a purification by flash column chromatography (0-5% EtOAc in hexanes) as a colorless oil (36 mg, 0.12 mmol, 77%).

¹H NMR (600 MHz, Chloroform-*d*) δ 7.86 (dd, *J* = 5.4, 3.0 Hz, 2H), 7.73 (dd, *J* = 5.5, 3.0 Hz, 2H), 5.10 (td, *J* = 7.0, 3.8 Hz, 1H), 3.70 (t, *J* = 7.4 Hz, 2H), 1.97 (dhept, *J* = 30.2, 6.9 Hz, 2H), 1.73 – 1.64 (m, 5H), 1.61 (s, 3H), 1.47 – 1.24 (m, 4H), 1.15 (dddd, *J* = 22.8, 13.6, 7.8, 4.1 Hz, 2H), 1.03 – 0.92 (m, 1H), 0.87 (d, *J* = 6.5 Hz, 3H).

¹³C NMR (101 MHz, Chloroform-*d*) δ 168.4, 133.8, 132.2, 131.0, 124.9, 123.1, 38.1, 37.1, 36.5, 32.3, 28.9, 25.7, 25.5, 24.3, 19.5, 17.6.

HRMS-ESI (m/z): for C₂₀H₂₇NO₂ [M + H]⁺: calcd 314.2115, found 314.2115.

1-((2R,4S,5R)-4-hydroxy-5-(4-phenylbutyl)tetrahydrofuran-2-yl)-5-methylpyrimidine-2,4(1H,3H)-dione (20)



Following a **General Procedure B**, an oven-dried 4 mL scintillation vial equipped with a PTFE-coated stir bar was charged with BPI-Ni-Oac (**1**) (44 mg, 0.10 mmol, 1.0 equiv), lithium chloride (8 mg, 0.2 mmol, 2 equiv), zinc powder (65 mg, 1.0 mmol, 10 equiv), (3-bromopropyl)benzene (30 mg, 0.15 mmol, 1.5 equiv), and THF (2.0 mL, 50 mM). Contents were stirred for 2 hours at room temperature.

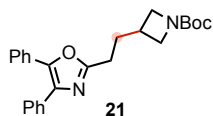
Cross-coupling reaction was performed following a **General Procedure C**. 1-((2R,4S,5S)-5-(bromomethyl)-4-hydroxytetrahydrofuran-2-yl)-5-methylpyrimidine-2,4(1H,3H)-dione (46 mg, 0.15 mmol, 1.5 equiv) and anhydrous DMSO co-solvent (0.2 mL) were introduced into the solution of Ni(Alkyl) from the previous step (one pot). Contents were allowed to react for 16 hours while stirring at room temperature. The title compound was isolated following a purification by flash column chromatography (0-7.5% MeOH in DCM) as a white solid (21 mg, 0.061 mmol, 61%).

¹H NMR (400 MHz, Chloroform-*d*) δ 11.28 (s, 1H), 7.36 (q, *J* = 1.1 Hz, 1H), 7.32 – 7.23 (m, 2H), 7.23 – 7.10 (m, 3H), 6.11 (t, *J* = 6.9 Hz, 1H), 5.21 (d, *J* = 4.4 Hz, 1H), 4.08 – 3.95 (m, 1H), 3.67 – 3.55 (m, 1H), 2.58 (t, *J* = 7.6 Hz, 2H), 2.16 (dt, *J* = 13.8, 6.9 Hz, 1H), 2.02 (ddd, *J* = 13.5, 6.6, 4.0 Hz, 1H), 1.78 (d, *J* = 1.2 Hz, 3H), 1.71 – 1.49 (m, 4H), 1.48 – 1.28 (m, 2H).

¹³C NMR (101 MHz, Chloroform-*d*) δ 163.7, 150.5, 142.2, 136.0, 128.2, 128.2, 125.6, 109.7, 85.7, 83.2, 73.1, 38.4, 35.0, 32.8, 30.9, 3.19, 12.2.

HRMS-ESI (m/z): for C₁₉H₂₄N₂O₄ [M + H]⁺: calcd 345.1809, found 345.1807.

tert-butyl 3-(2-(4,5-diphenyloxazol-2-yl)ethyl)azetidine-1-carboxylate (21)



Following a **General Procedure B**, an oven-dried 4 mL scintillation vial equipped with a PTFE-coated stir bar was charged with BPI-Ni-Oac (**1**) (88 mg, 0.20 mmol, 1.0 equiv), *tert*-butyl 3-iodoazetidine-1-carboxylate (62 mg, 0.22 mmol, 1.1 equiv), zinc powder (65 mg, 1.0 mmol, 5.0 equiv), lithium chloride (17 mg, 0.40 mmol, 2.0 equiv), and THF (4.0 mL, 50 mM). The resulting suspension was stirred for 1 hour at room temperature, darkening over time.

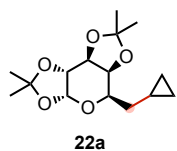
Cross-coupling reaction was performed following a **General Procedure C**. 1,3-dioxoisindolin-2-yl 3-(4,5-diphenyloxazol-2-yl)propanoate (132 mg, 0.300 mmol, 1.50 equiv) was added to the Ni(Alkyl) solution from the previous step. Contents were allowed to react for 16 hours while stirring at room temperature. The title compound was isolated following purification by flash column chromatography (3% EtOAc in hexanes) as a colorless oil (57 mg, 0.14 mmol, 71%).

¹H NMR (400 MHz, Chloroform-*d*) δ 7.64 – 7.60 (m, 2H), 7.59 – 7.55 (m, 2H), 7.39 – 7.29 (m, 6H), 4.05 (t, *J* = 8.4 Hz, 2H), 3.60 (dd, *J* = 8.6, 5.5 Hz, 2H), 2.82 (t, *J* = 7.5 Hz, 2H), 2.72 – 2.55 (m, 1H), 2.15 (q, *J* = 7.6 Hz, 2H), 1.43 (s, 9H).

¹³C NMR (101 MHz, Chloroform-*d*) 162.6, 156.5, 145.4, 135.2, 132.5, 129.1, 128.8, 128.7, 128.6, 128.2, 128.0, 126.5, 79.4, 31.8, 28.5, 28.5, 25.9.

HRMS-ESI (m/z): for C₂₅H₂₈N₂O₃ [M + Na]⁺: calcd 427.1992, found 427.1992.

(3aR,5R,5aS,8aS,8bR)-5-(cyclopropylmethyl)-2,2,7,7-tetramethyltetrahydro-5H-bis([1,3]dioxolo)[4,5-b:4',5'-d]pyran (22a)



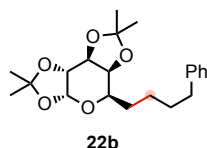
Following a **General Procedure C**, an oven-dried 4 mL scintillation vial equipped with PTFE-coated stir bar was charged with 2-^cPr (43 mg, 0.10 mmol, 1.0 equiv), (3aR,5S,5aR,8aS,8bR)-5-(bromomethyl)-2,2,7,7-tetramethyltetrahydro-5H-bis([1,3]dioxolo)[4,5-b:4',5'-d]pyran (49 mg, 0.15 mmol, 1.5 equiv), zinc powder (33 mg, 0.51 mmol, 5.1 equiv), lithium chloride (8 mg, 0.2 mmol, 2 equiv), and THF (2.0 mL, 50 mM). Contents were allowed to react for 16 hours while stirring at room temperature. The title compound was isolated following a purification by flash column chromatography (20% EtOAc in hexanes) as a colorless oil (23 mg, 0.081 mmol, 81%).

¹H NMR (400 MHz, Chloroform-*d*) δ 5.52 (d, *J* = 5.0 Hz, 1H), 4.59 (dd, *J* = 8.0, 2.3 Hz, 1H), 4.29 (dd, *J* = 5.1, 2.3 Hz, 1H), 4.22 (dd, *J* = 8.0, 1.8 Hz, 1H), 3.83 (td, *J* = 6.9, 1.8 Hz, 1H), 1.72 – 1.63 (m, 1H), 1.54 (s, 3H), 1.45 (s, 3H), 1.41 – 1.34 (m, 1H), 1.34 (s, 3H), 1.33 (s, 3H), 0.86 – 0.76 (m, 1H), 0.50 – 0.40 (m, 2H), 0.13 – 0.06 (m, 2H).

¹³C NMR (101 MHz, Chloroform-*d*) δ 108.9, 108.3, 96.6, 72.5, 70.8, 70.7, 67.9, 35.1, 26.1, 26.0, 25.0, 24.4, 7.4, 4.3, 4.3.

HRMS-ESI (m/z): for C₁₅H₂₄O₅ [M + H]⁺: calcd 285.1697, found 285.1697.

(3aR,5R,5aS,8aS,8bR)-2,2,7,7-tetramethyl-5-(4-phenylbutyl)tetrahydro-5H-bis([1,3]dioxolo)[4,5-b:4',5'-d]pyran (22b)



Following a **General Procedure B**, an oven-dried 4 mL scintillation vial equipped with a PTFE-coated stir bar was charged with BPI-Ni-OAc (**1**) (67 mg, 0.15 mmol, 1.0 equiv), (3aR,5S,5aR,8aS,8bR)-5-(bromomethyl)-2,2,7,7-tetramethyltetrahydro-5H-bis([1,3]dioxolo)[4,5-b:4',5'-d] (73 mg, 0.23 mmol, 1.5 equiv), zinc powder (49 mg, 0.75 mmol, 5.0 equiv), lithium chloride (13 mg, 0.30 mmol, 2.0 equiv), and THF (3.0 mL, 50 mM). The resulting suspension was stirred for 5 hours at 0 °C, darkening over time.

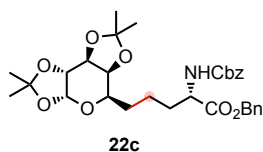
Cross-coupling reaction was performed following a **General Procedure C**. (3-bromopropyl)benzene (45 mg, 0.23 mmol, 1.5 equiv) was introduced into the Ni(Alkyl) solution from the previous step (one pot). Contents were allowed to react for 16 hours while stirring at 0 °C. The title compound was isolated following a purification by flash column chromatography (20% EtOAc in hexanes) as a colorless oil (25 mg, 0.069 mmol, 46%).

¹H NMR (400 MHz, Chloroform-*d*) δ 7.31 – 7.10 (m, 5H), 5.54 (d, *J* = 5.1 Hz, 1H), 4.58 (dd, *J* = 8.0, 2.3 Hz, 1H), 4.29 (dd, *J* = 5.1, 2.3 Hz, 1H), 4.12 (dd, *J* = 8.0, 1.8 Hz, 1H), 3.71 (ddd, *J* = 8.7, 4.6, 1.8 Hz, 1H), 2.62 (t, *J* = 7.8 Hz, 2H), 1.77 – 1.53 (m, 5H), 1.51 (s, 3H), 1.47 (s, 3H), 1.45 – 1.39 (m, 1H), 1.35 (s, 3H), 1.33 (s, 3H).

¹³C NMR (101 MHz, Chloroform-*d*) δ 142.7, 128.4, 128.2, 125.6, 109.0, 108.3, 96.6, 72.8, 70.9, 70.6, 67.4, 35.9, 31.4, 29.9, 26.1, 26.0, 25.5, 24.9, 24.4.

HRMS-ESI (m/z): for C₂₁H₃₀O₅ [M + H]⁺: calcd 363.2166, found 363.2143.

benzyl (S)-2-(((benzyloxy)carbonyl)amino)-5-((3aR,5R,5aS,8aS,8bR)-2,2,7,7-tetramethyltetrahydro-5H-bis([1,3]dioxolo)[4,5-b:4',5'-d]pyran-5-yl)pentanoate (22c**)**



Following a **General Procedure B**, an oven-dried 4 mL scintillation vial equipped with a PTFE-coated stir bar was charged with BPI-Ni-OAc (**1**) (89 mg, 0.20 mmol, 1.0 equiv), (3aR,5S,5aR,8aS,8bR)-5-(bromomethyl)-2,2,7,7-tetramethyltetrahydro-5H-bis([1,3]dioxolo)[4,5-b:4',5'-d]pyran (97 mg, 0.30 mmol, 1.5 equiv), zinc powder (65 mg, 1.0 mmol, 5.0 equiv), lithium chloride (17 mg, 0.40 mmol, 2.0 equiv), and THF (4.0 mL, 50 mM). The resulting suspension was stirred for 4 hours at 0 °C, darkening over time.

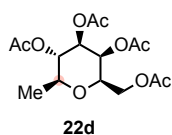
Cross-coupling reaction was performed following a **General Procedure C**. 1-benzyl 5-(1,3-dioxoisindolin-2-yl) ((benzyloxy)carbonyl)-L-glutamate (156 mg, 0.300 mmol, 1.50 equiv) was introduced into the solution of Ni(Alkyl) from the previous step (one pot). Contents were allowed to react for 16 hours while stirring at 0 °C. The title compound was isolated following purification by flash column chromatography (20% EtOAc in hexanes) as a colorless oil (77 mg, 0.14 mmol, 68 %).

¹H NMR (400 MHz, Chloroform-*d*) δ 7.34 (dt, *J* = 7.1, 4.1 Hz, 10H), 5.50 (d, *J* = 5.1 Hz, 1H), 5.28 (d, *J* = 8.6 Hz, 1H), 5.16 (d, *J* = 2.8 Hz, 2H), 5.10 (s, 2H), 4.56 (dd, *J* = 7.9, 2.3 Hz, 1H), 4.42 (td, *J* = 8.1, 4.7 Hz, 1H), 4.27 (dd, *J* = 5.1, 2.3 Hz, 1H), 4.06 (dd, *J* = 8.1, 1.8 Hz, 1H), 3.65 (d, *J* = 6.0 Hz, 1H), 1.90 (td, *J* = 9.6, 5.0 Hz, 1H), 1.77 – 1.48 (m, 5H), 1.47 (s, 3H), 1.44 (s, 3H), 1.33 (s, 3H), 1.31 (s, 3H).

¹³C NMR (101 MHz, Chloroform-*d*) δ 172.4, 155.9, 136.3, 135.3, 128.6, 128.5, 128.4, 128.3, 128.2, 128.1, 109.0, 108.3, 96.5, 72.7, 70.9, 70.5, 67.1, 67.0, 53.9, 32.4, 29.6, 26.1, 26.0, 24.9, 24.4, 21.5.

HRMS-ESI (m/z): for C₃₁H₃₉NO₉ [M + H]⁺: calcd 570.2698, found 570.2696.

(2R,3S,4R,5S,6S)-2-(acetoxymethyl)-6-methyltetrahydro-2H-pyran-3,4,5-triyl triacetate (22d)



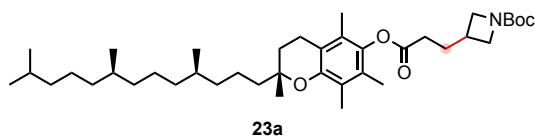
Following a **General Procedure B** with modifications, an oven-dried 4 mL scintillation vial equipped with a PTFE-coated stir bar was charged with BPI-Ni-OAc (**1**) (44 mg, 0.10 mmol, 1.0 equiv), zinc powder (33 mg, 0.50 mmol, 5.0 equiv), lithium chloride (8 mg, 0.2 mmol, 2 equiv), iodomethane (21 mg, 0.15 mmol, 1.5 equiv), and THF (2.0 mL, 50 mM). The resulting suspension was stirred for 1 hour at 21 °C, turning purple over time.

Cross-coupling reaction was performed following a **General Procedure C** with modifications. (2R,3S,4S,5R,6R)-2-(acetoxymethyl)-6-bromotetrahydro-2H-pyran-3,4,5-triyl triacetate (CAS: 3068-32-4) (82 mg, 0.20 mmol, 2.00 equiv) was introduced into the solution of Ni(Alkyl) from the previous step (one pot). Contents were allowed to react for 16 hours while stirring at 21 °C. The title compound was isolated following purification by flash column chromatography (20% EtOAc in hexanes) as a colorless oil (36 mg, 0.10 mmol, >95%).

¹H NMR (400 MHz, CDCl₃) δ 5.37 (dd, J = 3.1, 1.2 Hz, 1H), 5.01 (dd, J = 10.2, 8.8 Hz, 1H), 4.96 (dd, J = 9.8, 3.1 Hz, 1H), 4.05 (d, J = 6.6 Hz, 2H), 3.83 (td, J = 6.6, 1.3 Hz, 1H), 3.50 (dq, J = 8.9, 6.2 Hz, 1H), 2.11 (s, 3H), 2.01 (s, 3H), 2.00 (s, 3H), 1.93 (s, 3H), 1.20 (d, J = 6.2 Hz, 3H). **¹³C NMR (151 MHz, CDCl₃)** δ 170.5, 170.3, 170.2, 169.9, 74.7, 74.1, 72.0, 70.7, 67.9, 61.9, 20.8, 20.7, 20.7, 20.6, 17.7.

HRMS-ESI (m/z): for C₁₅H₂₂O₉ [M + Na]⁺: calcd 369.1156, found 369.1155.

tert-butyl 3-(3-oxo-3-(((R)-2,5,7,8-tetramethyl-2-((4R,8R)-4,8,12-trimethyltridecyl)chroman-6-yl)oxy)propyl)azetidine-1-carboxylate (23a)



The **Ni-azetidine** complex was isolated and purified via trituration with a 2:1 solution of pentanes and diethyl ether following a **General Procedure B** from the tert-butyl 3-iodoazetidine-1-carboxylate.

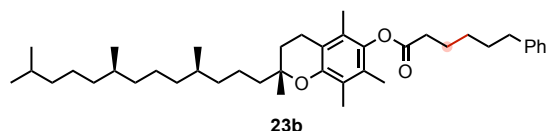
Cross-coupling reaction was performed following a **General Procedure C**. An oven-dried 4 mL scintillation vial equipped with a PTFE-coated stir bar was charged with **Ni-azetidine** (54 mg, 0.10 mmol, 1.0 equiv), 1,3-dioxoisindolin-2-yl ((R)-2,5,7,8-tetramethyl-2-((4R,8R)-4,8,12-trimethyltridecyl)chroman-6-yl) succinate (101 mg, 0.150 mmol, 1.50 equiv), lithium chloride (8 mg, 0.2 mmol, 2 equiv), zinc powder (33 mg, 0.50 mmol, 5.0 equiv), and THF (2.0 mL, 50 mM). Contents were allowed to react for 16 hours while stirring at room temperature. The title compound was isolated following a purification by flash column chromatography (2% EtOAc in hexanes) as a colorless oil (46 mg, 0.072 mmol, 72%).

¹H NMR (400 MHz, Chloroform-*d*) δ 4.05 (t, J = 8.4 Hz, 2H), 3.63 (dd, J = 8.6, 5.4 Hz, 2H), 2.63 – 2.52 (m, 4H), 2.09 (s, 3H), 2.00 (s, 3H), 1.95 (s, 3H), 1.85 – 1.00 (m, 38H), 0.90 – 0.82 (m, 12H).

¹³C NMR (101 MHz, Chloroform-*d*) δ 171.6, 156.5, 149.6, 140.5, 126.7, 124.9, 123.2, 117.6, 79.5, 75.2, 39.5, 37.6, 37.6, 37.4, 32.9, 32.8, 31.6, 31.2, 29.8, 29.7, 28.6, 28.5, 28.1, 24.9, 24.6, 22.9, 22.8, 21.2, 20.7, 19.9, 19.8, 13.1, 12.3, 12.0.

HRMS-ESI (m/z): for C₄₀H₆₇NO₅ [M + Na]⁺: calcd 664.4911, found 664.4907.

(R)-2,5,7,8-tetramethyl-2-((4R,8R)-4,8,12-trimethyltridecyl)chroman-6-yl 6-phenylhexanoate (23b)



Following a **General Procedure C**, an oven-dried 4 mL scintillation vial equipped with a PTFE-coated stir bar was charged with **2-Pr** (50 mg, 0.10 mmol, 1.0 equiv), 1,3-dioxoisindolin-2-yl ((R)-2,5,7,8-

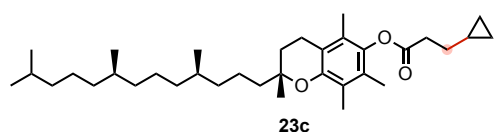
tetramethyl-2-((4R,8R)-4,8,12-trimethyltridecyl)chroman-6-yl) succinate (101 mg, 0.150 mmol, 1.50 equiv), lithium chloride (8 mg, 0.2 mmol, 2 equiv), zinc powder (33 mg, 0.50 mmol, 5.0 equiv), and THF (2.0 mL, 50 mM). Contents were allowed to react for 16 hours while stirring at room temperature. The title compound was isolated following a purification by flash column chromatography (1% EtOAc in hexanes) as a colorless oil (38 mg, 0.063 mmol, 63%).

¹H NMR (400 MHz, Chloroform-*d*) δ 7.32 – 7.26 (m, 2H), 7.22 – 7.16 (m, 3H), 2.70 – 2.55 (m, 6H), 2.10 (s, 3H), 2.00 (s, 3H), 1.96 (s, 3H), 1.89 – 1.03 (m, 32H), 0.90 – 0.84 (m, 12H).

¹³C NMR (101 MHz, Chloroform-*d*) δ 172.4, 149.5, 142.6, 140.6, 128.5, 128.4, 126.8, 125.8, 125.0, 123.1, 117.5, 75.2, 39.5, 37.6, 37.6, 37.4, 35.9, 34.2, 33.0, 32.9, 31.2, 29.1, 28.1, 25.2, 25.0, 24.6, 22.9, 22.8, 21.2, 20.8, 19.9, 19.8, 13.1, 12.3, 12.0.

HRMS-ESI (m/z): for C₄₁H₆₄O₃ [M + Na]⁺: calcd 627.4747, found 627.4742.

(R)-2,5,7,8-tetramethyl-2-((4R,8R)-4,8,12-trimethyltridecyl)chroman-6-yl 3-cyclopropylpropanoate (23c)



Following a **General Procedure C**, an oven-dried 4 mL scintillation vial equipped with a PTFE-coated stir bar was charged with **2-cyPr** (43 mg, 0.10 mmol, 1.0 equiv), 1,3-dioxoisindolin-2-yl ((R)-2,5,7,8-tetramethyl-2-

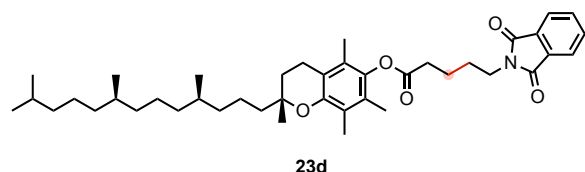
((4R,8R)-4,8,12-trimethyltridecyl)chroman-6-yl) succinate (101 mg, 0.150 mmol, 1.50 equiv), lithium chloride (8 mg, 0.2 mmol, 2 equiv), zinc powder (33 mg, 0.50 mmol, 5.0 equiv), and THF (2.0 mL, 50 mM). Contents were allowed to react for 16 hours while stirring at room temperature. The title compound was isolated following a purification by flash column chromatography (1% EtOAc in hexanes) as a colorless oil (30 mg, 0.057 mmol, 57%).

¹H NMR (400 MHz, Chloroform-*d*) δ 2.74 – 2.66 (m, 2H), 2.59 (t, *J* = 6.8 Hz, 2H), 2.09 (s, 3H), 2.01 (s, 3H), 1.97 (s, 3H), 1.87 – 0.99 (m, 29H), 0.90 – 0.82 (m, 12H), 0.54 – 0.45 (m, 2H), 0.18 – 0.10 (m, 2H).

¹³C NMR (101 MHz, Chloroform-*d*) δ 172.4, 149.5, 140.7, 126.8, 125.1, 123.1, 117.5, 75.2, 39.5, 37.6, 37.6, 37.4, 34.3, 33.0, 32.9, 31.3, 30.4, 28.1, 25.0, 24.6, 22.9, 22.8, 21.2, 20.8, 19.9, 19.8, 13.1, 12.3, 12.0, 10.8, 4.7.

HRMS-ESI (m/z): for C₃₅H₅₈O₃ [M + Na]⁺: calcd 549.4278, found 549.4274.

(R)-2,5,7,8-tetramethyl-2-((4R,8R)-4,8,12-trimethyltridecyl)chroman-6-yl 5-(1,3-dioxoisindolin-2-yl)pentanoate (23d)



Following a **General Procedure B**, an oven-dried 4 mL scintillation vial equipped with a PTFE-coated stir bar was charged with BPI-Ni-Oac (**1**) (44 mg, 0.10 mmol, 1.0 equiv), 2-(2-bromoethyl)isindoline-1,3-dione (38 mg, 0.15

mmol, 1.5 equiv), zinc powder (33 mg, 0.50 mmol, 5.0 equiv), lithium chloride (8 mg, 0.2 mmol, 2 equiv), and THF (2 mL, 50 mM). The resulting suspension was stirred for 2 hours at room temperature, darkening over time.

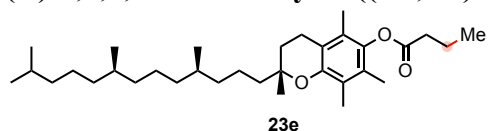
Cross-coupling reaction was performed following a **General Procedure C**. 1,3-dioxoisindolin-2-yl ((R)-2,5,7,8-tetramethyl-2-((4R,8R)-4,8,12-trimethyltridecyl)chroman-6-yl) succinate (101 mg, 0.15 mmol, 1.5 equiv) was added to the Ni(Alkyl) solution from the previous step. Contents were allowed to react for 16 hours while stirring at room temperature. The title compound was isolated following a purification by flash column chromatography (3% EtOAc in hexanes) as a colorless oil (38 mg, 0.057 mmol, 57%).

¹H NMR (400 MHz, Chloroform-*d*) δ 7.89 – 7.80 (m, 2H), 7.73 – 7.68 (m, 2H), 3.80 – 3.67 (m, 2H), 2.69 – 2.54 (m, 4H), 2.08 (s, 3H), 1.99 (s, 3H), 1.95 (s, 3H), 1.87 – 1.01 (m, 30H), 0.88 – 0.81 (m, 12H).

¹³C NMR (101 MHz, Chloroform-*d*) δ 171.9, 168.5, 149.5, 140.6, 134.1, 132.3, 126.8, 125.0, 123.4, 123.1, 117.5, 75.2, 39.5, 37.6, 37.6, 37.6, 37.4, 33.6, 32.9, 32.8, 31.2, 28.4, 28.1, 24.9, 24.6, 22.9, 22.8, 22.5, 21.2, 20.7, 19.9, 19.8, 13.1, 12.3, 11.9.

HRMS-ESI (m/z): for C₄₂H₆₁NO₅ [M + Na]⁺: calcd 682.4442, found 682.4435.

(R)-2,5,7,8-tetramethyl-2-((4R,8R)-4,8,12-trimethyltridecyl)chroman-6-yl butyrate (23e)



Following a **General Procedure C**, an oven-dried 4 mL scintillation vial equipped with a PTFE-coated stir bar was charged with **2-Me** (40 mg, 0.10 mmol, 1.0 equiv), 1,3-dioxoisindolin-2-yl ((R)-2,5,7,8-tetramethyl-2-

((4R,8R)-4,8,12-trimethyltridecyl)chroman-6-yl) succinate (101 mg, 0.150 mmol, 1.50 equiv), lithium chloride (8 mg, 0.2 mmol, 2 equiv), zinc powder (33 mg, 0.50 mmol, 5.0 equiv), and THF (2.0 mL, 50 mM). Contents were allowed to react for 16 hours while stirring at room temperature. The title compound was isolated following a purification by flash column chromatography (1% EtOAc in hexanes) as a colorless oil (40 mg, 0.080 mmol, 80%).

¹H NMR (400 MHz, Chloroform-*d*) δ 2.62 – 2.55 (m, 4H), 2.10 (s, 3H), 2.02 (s, 3H), 1.98 (s, 3H), 1.89 – 1.71 (m, 4H), 1.60 – 1.48 (m, 4H), 1.44 – 1.22 (m, 15H), 1.19 – 1.03 (m, 9H), 0.89 – 0.84 (m, 12H).

¹³C NMR (101 MHz, Chloroform-*d*) δ 172.3, 149.5, 140.7, 126.8, 125.0, 123.1, 117.5, 75.2, 39.5, 37.6, 37.6, 37.6, 37.4, 36.2, 33.0, 32.9, 31.3, 31.2, 28.1, 25.0, 24.6, 22.9, 22.8, 21.2, 20.8, 19.9, 19.8, 18.8, 14.0, 13.1, 12.3, 12.0.

HRMS-ESI (m/z): for C₃₃H₅₆O₃ [M + Na]⁺: calcd 523.4121, found 523.4119.

References

1. Egorova, K. S. & Ananikov, V. P. Toxicity of Metal Compounds: Knowledge and Myths. *Organometallics* **36**, 4071–4090 (2017).
2. Egorova, K. S. & Ananikov, V. P. Welche Katalysatormetalle sind harmlos, welche giftig? Vergleich der Toxizitäten von Ni-, Cu-, Fe-, Pd-, Pt-, Rh- und Au-Salzen. *Angewandte Chemie* **128**, 12334–12347 (2016).
3. Siegl, W. O. A template type synthesis using phthalonitrile. Metal complexes of 1,3-bis(2-pyridylimnio)isoindolines. *Inorganic and Nuclear Chemistry Letters* **10**, 825–829 (1974).
4. Dinh, L. P. *et al.* Persistent organonickel complexes as general platforms for Csp²–Csp³ coupling reactions. *Nat. Chem.* (2024) doi:10.1038/s41557-024-01528-7.
5. Chen, F. *et al.* Decarboxylative Selective Phosphorylation of Aliphatic Acids: A Transition-Metal- and Photocatalyst-Free Avenue to Dialkyl and Trialkyl Phosphine Oxides from White Phosphorus. *Angewandte Chemie International Edition* **61**, e202210334 (2022).
6. Mills, L. R., Zhou, C., Fung, E. & Rousseaux, S. A. L. Ni-Catalyzed β -Alkylation of Cyclopropanol-Derived Homoenoates. *Org. Lett.* **21**, 8805–8809 (2019).
7. West, M. S., Gabbey, A. L., Huestis, M. P. & Rousseaux, S. A. L. Ni-Catalyzed Reductive Cross-Coupling of Cyclopropylamines and Other Strained Ring NHP Esters with (Hetero)Aryl Halides. *Org. Lett.* **24**, 8441–8446 (2022).
8. Toriyama, F. *et al.* Redox-Active Esters in Fe-Catalyzed C–C Coupling. *J. Am. Chem. Soc.* **138**, 11132–11135 (2016).
9. Maharaj, V., Chandrachud, P. P., Che, W., Wojtas, L. & Lopchuk, J. M. Photodecarboxylative Amination of Redox-Active Esters with Diazirines. *Org. Lett.* **23**, 8838–8842 (2021).
10. Palkowitz, M. D. *et al.* Overcoming Limitations in Decarboxylative Arylation via Ag–Ni Electrocatalysis. *J. Am. Chem. Soc.* **144**, 17709–17720 (2022).
11. Kingston, C. *et al.* Direct Carbon Isotope Exchange through Decarboxylative Carboxylation. *J. Am. Chem. Soc.* **141**, 774–779 (2019).
12. Donald, J. R. & Berrell, S. L. Radical cyanomethylation via vinyl azide cascade-fragmentation. *Chem. Sci.* **10**, 5832–5836 (2019).
13. Yu, X., Yang, T., Wang, S., Xu, H. & Gong, H. Nickel-Catalyzed Reductive Cross-Coupling of Unactivated Alkyl Halides. *Org. Lett.* **13**, 2138–2141 (2011).
14. Carson II, W. P., Sarver, P. J., Goudy, N. S. & MacMillan, D. W. C. Photoredox Catalysis-Enabled Sulfination of Alcohols and Bromides. *J. Am. Chem. Soc.* **145**, 20767–20774 (2023).
15. Siebum, A. H. G., Woo, W. S., Raap, J. & Lugtenburg, J. Access to Any Site-Directed Isotopomer of Methionine, Selenomethionine, Cysteine, and Selenocysteine – Use of Simple, Efficient Modular Synthetic Reaction Schemes for Isotope Incorporation. *European J. Org. Chem.* **2004**, 2905–2913 (2004).
16. Classon, B., Liu, Z. & Samuelsson, B. New halogenation reagent systems useful for the mild one-step conversion of alcohols into iodides or bromides. *J. Org. Chem.* **53**, 6126–6130 (1988).

17. Adamson, C., Kajino, H., Kawashima, S. A., Yamatsugu, K. & Kanai, M. Live-Cell Protein Modification by Boronate-Assisted Hydroxamic Acid Catalysis. *J. Am. Chem. Soc.* **143**, 14976–14980 (2021).
18. Watanabe Kazuki; Ekuni Kento; Edagawa Ryota; Akagi Yuta; Okuda Yasuhiro; Wakamatsu Kan; Orita Akihiro, H. N. Custom-Made Pyrene Photocatalyst-Promoted Desulfonylation of Arylethenyl Sulfones Using Green-Light-Emitting Diodes. *Synthesis (Stuttg)* **53**, 2984–2994 (2021).
19. Hunger, M. *et al.* Organometallic B12–DNA Conjugate: Synthesis, Structure Analysis, and Studies of Binding to Human B12-Transporter Proteins. *Chemistry – A European Journal* **20**, 13103–13107 (2014).
20. Tokunaga, K. *et al.* Bicyclobutane Carboxylic Amide as a Cysteine-Directed Strained Electrophile for Selective Targeting of Proteins. *J. Am. Chem. Soc.* **142**, 18522–18531 (2020).
21. Basch, C. H., Liao, J., Xu, J., Piane, J. J. & Watson, M. P. Harnessing Alkyl Amines as Electrophiles for Nickel-Catalyzed Cross Couplings via C–N Bond Activation. *J. Am. Chem. Soc.* **139**, 5313–5316 (2017).
22. Martin-Montero, R., Yatham, V. R., Yin, H., Davies, J. & Martin, R. Ni-catalyzed Reductive Deaminative Arylation at sp³ Carbon Centers. *Org. Lett.* **21**, 2947–2951 (2019).
23. Hutton, C. A. & Bartlett, P. A. Preparation of Diazabicyclo[4.3.0]nonene-Based Peptidomimetics. *J. Org. Chem.* **72**, 6865–6872 (2007).
24. Liao, J. *et al.* Deaminative Reductive Cross-Electrophile Couplings of Alkylpyridinium Salts and Aryl Bromides. *Org. Lett.* **21**, 2941–2946 (2019).
25. Yang, L., Powell, D. R. & Houser, R. P. Structural variation in copper(i) complexes with pyridylmethanamide ligands: structural analysis with a new four-coordinate geometry index, τ_4 . *Dalton Transactions* 955–964 (2007) doi:10.1039/B617136B.
26. Falivene, L. *et al.* Towards the online computer-aided design of catalytic pockets. *Nat Chem* **11**, 872–879 (2019).
27. Sherwood, T. C. *et al.* Decarboxylative Intramolecular Arene Alkylation Using N-(Acyloxy)phthalimides, an Organic Photocatalyst, and Visible Light. *Journal of Organic Chemistry* **84**, 8360–8379 (2019).
28. M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. *et al.* Gaussian 16 B.01. Gaussian 16, Revision C.01, Gaussian, Inc., Wallin Preprint at (2016).
29. Grimme, S., Antony, J., Ehrlich, S. & Krieg, H. A consistent and accurate ab initio parametrization of density functional dispersion correction (DFT-D) for the 94 elements H–Pu. *J. Chem. Phys.* **132**, 154104 (2010).
30. P Fuentealba, H Stoll, L von Szentpaly, P Schwerdtfeger & H Preuss. On the reliability of semi-empirical pseudopotentials: simulation of Hartree-Fock and Dirac-Fock results. *Journal of Physics B: Atomic and Molecular Physics* **16**, L323 (1983).
31. Hay, P. J. & Wadt, W. R. Ab initio effective core potentials for molecular calculations. Potentials for the transition metal atoms Sc to Hg. *J. Chem. Phys.* **82**, 270–283 (1985).
32. Marenich, A. V, Cramer, C. J. & Truhlar, D. G. Universal Solvation Model Based on Solute Electron Density and on a Continuum Model of the Solvent Defined by the Bulk Dielectric Constant and Atomic Surface Tensions. *J. Phys. Chem. B* **113**, 6378–6396 (2009).

33. Hehre, W. J., Ditchfield, R. & Pople, J. A. Self—Consistent Molecular Orbital Methods. XII. Further Extensions of Gaussian—Type Basis Sets for Use in Molecular Orbital Studies of Organic Molecules. *J. Chem. Phys.* **56**, 2257–2261 (1972).
34. Hariharan, P. C. & Pople, J. A. The influence of polarization functions on molecular orbital hydrogenation energies. *Theor. Chim. Acta* **28**, 213–222 (1973).
35. Becke, A. D. Density-functional thermochemistry. III. The role of exact exchange. *J. Chem. Phys.* **98**, 5648–5652 (1993).

X-ray characterization Data

X-ray characterization of complex 2-Me

Experimental Summary

The single crystal X-ray diffraction studies were carried out on a Bruker Kappa Photon III CPAD diffractometer equipped with Mo K_{α} radiation ($\lambda = 0.71073 \text{ \AA}$). A 0.218 x 0.035 x 0.018 mm piece of an orangell needle was mounted on a MiTeGen MicroMount with Paratone 24EX oil. Data were collected in a nitrogen gas stream at 100(2) K using ϕ and ω scans. Crystal-to-detector distance was 60 mm using variable exposure time (1s-20s) depending on θ with a scan width of 0.75° . Data collection was 99.8% complete to 25.00° in θ ($0.83 \text{ \AA}$). A total of 82435 reflections were collected covering the indices, $-18 \leq h \leq 18$, $-5 \leq k \leq 5$, $-42 \leq l \leq 42$. 4604 reflections were found to be symmetry independent, with a R_{int} of 0.0401. 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 dual-space method (SHELXT) produced a complete phasing model for refinement.

All nonhydrogen atoms were refined anisotropically by full-matrix least-squares (SHELXL-2014). All carbon bonded 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. All other hydrogen atoms (water molecule) were located in the difference map. Their relative positions were restrained using DFIX commands and their thermals freely refined. Crystallographic data are summarized below.

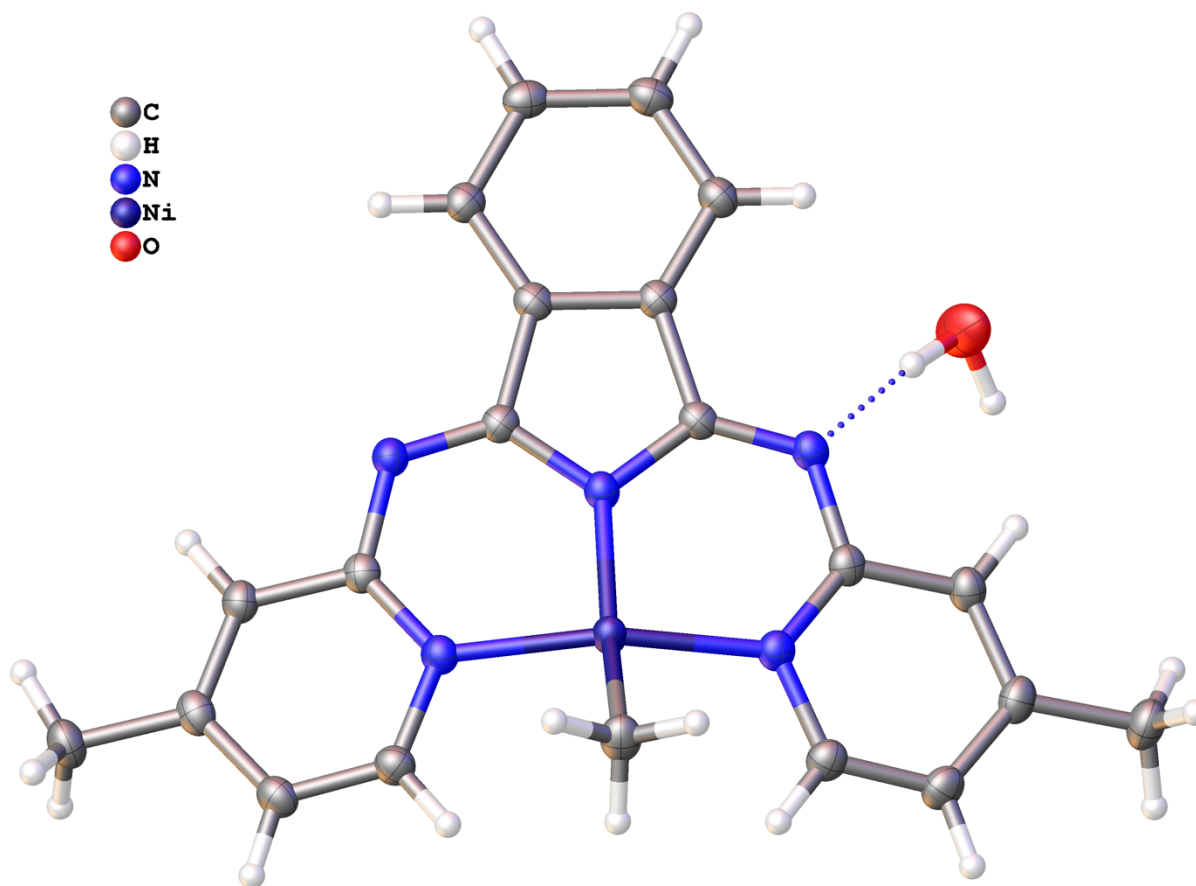


Table S1. Crystal data and structure refinement for Sevov_SA1-1005.

Report date	2024-04-30	
Identification code	SA1-1005	
Empirical formula	C ₂₁ H ₂₁ N ₅ Ni O	
Molecular formula	C ₂₁ H ₁₉ N ₅ Ni, H ₂ O	
Formula weight	418.14	
Temperature	100.0 K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 1 21/c 1	
Unit cell dimensions	a = 13.6374(8) Å	α = 90°.
	B = 4.3625(2) Å	β = 101.594(2)°.
	C = 31.807(2) Å	γ = 90°.
Volume	1853.68(18) Å ³	
Z	4	
Density (calculated)	1.498 Mg/m ³	
Absorption coefficient	1.069 mm ⁻¹	
F(000)	872	
Crystal size	0.218 x 0.035 x 0.018 mm ³	
Crystal color, habit	orange needle	
Theta range for data collection	2.199 to 28.343°.	
Index ranges	-18 ≤ h ≤ 18, -5 ≤ k ≤ 5, -42 ≤ l ≤ 42	
Reflections collected	82435	
Independent reflections	4604 [R(int) = 0.0401, R(sigma) = 0.0143]	
Completeness to theta = 25.000°	99.8 %	
Absorption correction	None	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	4604 / 5 / 268	
Goodness-of-fit on F ²	1.045	
Final R indices [I > 2σ(I)]	R1 = 0.0273, wR2 = 0.0715	
R indices (all data)	R1 = 0.0319, wR2 = 0.0744	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.392 and -0.232 e.Å ⁻³	

Table S2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for Sevov_SA1-1005. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Ni(1)	1718(1)	5284(1)	6201(1)	18(1)
N(1)	1908(1)	6102(3)	5629(1)	20(1)
N(2)	3357(1)	2837(3)	5643(1)	20(1)
N(3)	2978(1)	3347(3)	6344(1)	19(1)
N(4)	3101(1)	2604(3)	7101(1)	19(1)
N(5)	1687(1)	5856(3)	6797(1)	20(1)
C(1)	265(1)	5571(4)	6026(1)	26(1)
C(2)	1308(1)	8264(4)	5396(1)	23(1)
C(3)	1393(1)	9256(4)	4995(1)	24(1)
C(4)	2137(1)	8015(4)	4801(1)	24(1)
C(5)	2759(1)	5872(4)	5034(1)	23(1)
C(6)	2659(1)	4955(3)	5448(1)	20(1)
C(7)	2258(1)	8980(4)	4358(1)	30(1)
C(8)	3485(1)	2171(3)	6050(1)	19(1)
C(9)	4251(1)	-17(3)	6264(1)	19(1)
C(10)	4175(1)	-80(3)	6695(1)	19(1)
C(11)	3359(1)	2061(3)	6737(1)	18(1)
C(12)	4962(1)	-1754(3)	6114(1)	22(1)
C(13)	5597(1)	-3561(4)	6414(1)	24(1)
C(14)	5529(1)	-3600(3)	6845(1)	23(1)
C(15)	4811(1)	-1843(3)	6993(1)	21(1)
C(16)	2362(1)	4697(3)	7135(1)	19(1)
C(17)	2335(1)	5547(3)	7561(1)	21(1)
C(18)	1644(1)	7597(4)	7654(1)	23(1)
C(19)	969(1)	8821(4)	7305(1)	23(1)
C(20)	1014(1)	7927(4)	6895(1)	23(1)
C(21)	1617(1)	8508(4)	8109(1)	29(1)
O(1S)	5077(1)	2510(4)	5262(1)	45(1)

Table S3. Bond lengths [Å] and angles [°] for Sevov_SA1-1005.

Ni(1)-N(1)	1.9199(12)	C(12)-C(13)	1.395(2)
Ni(1)-N(3)	1.8857(12)	C(13)-H(13)	0.9500
Ni(1)-N(5)	1.9226(12)	C(13)-C(14)	1.395(2)
Ni(1)-C(1)	1.9517(15)	C(14)-H(14)	0.9500
N(1)-C(2)	1.3661(19)	C(14)-C(15)	1.398(2)
N(1)-C(6)	1.3662(18)	C(15)-H(15)	0.9500
N(2)-C(6)	1.3802(19)	C(16)-C(17)	1.412(2)
N(2)-C(8)	1.3034(18)	C(17)-H(17)	0.9500
N(3)-C(8)	1.3708(17)	C(17)-C(18)	1.375(2)
N(3)-C(11)	1.3731(18)	C(18)-C(19)	1.400(2)
N(4)-C(11)	1.2983(18)	C(18)-C(21)	1.506(2)
N(4)-C(16)	1.3803(18)	C(19)-H(19)	0.9500
N(5)-C(16)	1.3648(19)	C(19)-C(20)	1.375(2)
N(5)-C(20)	1.3667(19)	C(20)-H(20)	0.9500
C(1)-H(1A)	0.9800	C(21)-H(21A)	0.9800
C(1)-H(1B)	0.9800	C(21)-H(21B)	0.9800
C(1)-H(1C)	0.9800	C(21)-H(21C)	0.9800
C(2)-H(2)	0.9500	O(1S)-H(1S)	0.917(15)
C(2)-C(3)	1.373(2)	O(1S)-H(1SA)	0.930(19)
C(3)-H(3)	0.9500	O(1S)-H(1SB)	0.942(19)
C(3)-C(4)	1.400(2)		
C(4)-C(5)	1.375(2)	N(1)-Ni(1)-N(5)	160.71(6)
C(4)-C(7)	1.510(2)	N(1)-Ni(1)-C(1)	92.33(6)
C(5)-H(5)	0.9500	N(3)-Ni(1)-N(1)	91.29(5)
C(5)-C(6)	1.409(2)	N(3)-Ni(1)-N(5)	91.13(5)
C(7)-H(7A)	0.9800	N(3)-Ni(1)-C(1)	157.03(7)
C(7)-H(7B)	0.9800	N(5)-Ni(1)-C(1)	92.88(6)
C(7)-H(7C)	0.9800	C(2)-N(1)-Ni(1)	117.51(10)
C(8)-C(9)	1.477(2)	C(2)-N(1)-C(6)	116.28(12)
C(9)-C(10)	1.396(2)	C(6)-N(1)-Ni(1)	125.85(10)
C(9)-C(12)	1.388(2)	C(8)-N(2)-C(6)	122.47(12)
C(10)-C(11)	1.4793(19)	C(8)-N(3)-Ni(1)	124.27(10)
C(10)-C(15)	1.383(2)	C(8)-N(3)-C(11)	108.50(12)
C(12)-H(12)	0.9500	C(11)-N(3)-Ni(1)	124.28(9)

C(11)-N(4)-C(16)	121.60(13)	C(12)-C(9)-C(10)	121.36(14)
C(16)-N(5)-Ni(1)	125.72(10)	C(9)-C(10)-C(11)	106.32(12)
C(16)-N(5)-C(20)	116.34(12)	C(15)-C(10)-C(9)	121.67(13)
C(20)-N(5)-Ni(1)	117.32(10)	C(15)-C(10)-C(11)	131.98(13)
Ni(1)-C(1)-H(1A)	109.5	N(3)-C(11)-C(10)	109.32(12)
Ni(1)-C(1)-H(1B)	109.5	N(4)-C(11)-N(3)	128.05(13)
Ni(1)-C(1)-H(1C)	109.5	N(4)-C(11)-C(10)	122.60(13)
H(1A)-C(1)-H(1B)	109.5	C(9)-C(12)-H(12)	121.4
H(1A)-C(1)-H(1C)	109.5	C(9)-C(12)-C(13)	117.14(14)
H(1B)-C(1)-H(1C)	109.5	C(13)-C(12)-H(12)	121.4
N(1)-C(2)-H(2)	117.7	C(12)-C(13)-H(13)	119.2
N(1)-C(2)-C(3)	124.62(14)	C(12)-C(13)-C(14)	121.53(14)
C(3)-C(2)-H(2)	117.7	C(14)-C(13)-H(13)	119.2
C(2)-C(3)-H(3)	120.2	C(13)-C(14)-H(14)	119.5
C(2)-C(3)-C(4)	119.54(14)	C(13)-C(14)-C(15)	120.96(14)
C(4)-C(3)-H(3)	120.2	C(15)-C(14)-H(14)	119.5
C(3)-C(4)-C(7)	121.95(14)	C(10)-C(15)-C(14)	117.33(14)
C(5)-C(4)-C(3)	116.55(14)	C(10)-C(15)-H(15)	121.3
C(5)-C(4)-C(7)	121.49(14)	C(14)-C(15)-H(15)	121.3
C(4)-C(5)-H(5)	118.9	N(4)-C(16)-C(17)	114.19(13)
C(4)-C(5)-C(6)	122.20(14)	N(5)-C(16)-N(4)	124.82(13)
C(6)-C(5)-H(5)	118.9	N(5)-C(16)-C(17)	120.98(13)
N(1)-C(6)-N(2)	124.35(13)	C(16)-C(17)-H(17)	119.0
N(1)-C(6)-C(5)	120.74(13)	C(18)-C(17)-C(16)	122.01(14)
N(2)-C(6)-C(5)	114.91(13)	C(18)-C(17)-H(17)	119.0
C(4)-C(7)-H(7A)	109.5	C(17)-C(18)-C(19)	116.48(14)
C(4)-C(7)-H(7B)	109.5	C(17)-C(18)-C(21)	121.99(14)
C(4)-C(7)-H(7C)	109.5	C(19)-C(18)-C(21)	121.53(14)
H(7A)-C(7)-H(7B)	109.5	C(18)-C(19)-H(19)	120.0
H(7A)-C(7)-H(7C)	109.5	C(20)-C(19)-C(18)	119.91(14)
H(7B)-C(7)-H(7C)	109.5	C(20)-C(19)-H(19)	120.0
N(2)-C(8)-N(3)	127.52(13)	N(5)-C(20)-C(19)	124.25(14)
N(2)-C(8)-C(9)	122.96(13)	N(5)-C(20)-H(20)	117.9
N(3)-C(8)-C(9)	109.50(12)	C(19)-C(20)-H(20)	117.9
C(10)-C(9)-C(8)	106.35(12)	C(18)-C(21)-H(21A)	109.5
C(12)-C(9)-C(8)	132.28(13)	C(18)-C(21)-H(21B)	109.5

C(18)-C(21)-H(21C)	109.5
H(21A)-C(21)-H(21B)	109.5
H(21A)-C(21)-H(21C)	109.5
H(21B)-C(21)-H(21C)	109.5
H(1S)-O(1S)-H(1SA)	96(2)
H(1S)-O(1S)-H(1SB)	94(2)

Table S4. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for Sevov_SA1-1005. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U^{11} + \dots + 2 h k a^* b^* U^{12}]$

	U ¹¹	U ²²	U ³³	U ²³	U ¹³	U ¹²
Ni(1)	15(1)	22(1)	17(1)	0(1)	4(1)	0(1)
N(1)	18(1)	23(1)	19(1)	0(1)	2(1)	-1(1)
N(2)	18(1)	23(1)	19(1)	-1(1)	4(1)	-1(1)
N(3)	17(1)	21(1)	18(1)	-1(1)	4(1)	-1(1)
N(4)	20(1)	20(1)	18(1)	0(1)	4(1)	-1(1)
N(5)	18(1)	22(1)	20(1)	0(1)	6(1)	-1(1)
C(1)	19(1)	35(1)	23(1)	0(1)	4(1)	0(1)
C(2)	19(1)	26(1)	23(1)	1(1)	3(1)	0(1)
C(3)	20(1)	28(1)	23(1)	3(1)	0(1)	0(1)
C(4)	23(1)	29(1)	19(1)	1(1)	2(1)	-5(1)
C(5)	20(1)	29(1)	20(1)	-1(1)	5(1)	-2(1)
C(6)	18(1)	23(1)	18(1)	-2(1)	3(1)	-3(1)
C(7)	30(1)	40(1)	21(1)	6(1)	5(1)	1(1)
C(8)	17(1)	19(1)	21(1)	-2(1)	4(1)	-2(1)
C(9)	18(1)	19(1)	21(1)	-1(1)	4(1)	-2(1)
C(10)	18(1)	18(1)	22(1)	-2(1)	4(1)	-3(1)
C(11)	17(1)	19(1)	20(1)	0(1)	3(1)	-3(1)
C(12)	21(1)	23(1)	23(1)	-2(1)	6(1)	-1(1)
C(13)	21(1)	23(1)	30(1)	-3(1)	6(1)	1(1)
C(14)	20(1)	20(1)	28(1)	0(1)	1(1)	0(1)
C(15)	22(1)	20(1)	21(1)	-1(1)	2(1)	-2(1)
C(16)	18(1)	20(1)	20(1)	1(1)	6(1)	-3(1)
C(17)	22(1)	24(1)	19(1)	0(1)	5(1)	-2(1)
C(18)	23(1)	24(1)	23(1)	-2(1)	9(1)	-5(1)
C(19)	22(1)	24(1)	26(1)	-2(1)	9(1)	0(1)
C(20)	20(1)	24(1)	24(1)	1(1)	6(1)	1(1)
C(21)	30(1)	35(1)	23(1)	-5(1)	10(1)	1(1)
O(1S)	37(1)	57(1)	49(1)	16(1)	26(1)	13(1)

Table S5. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^{-3}$) for Sevov_SA1-1005.

	x	y	z	U(eq)
H(1A)	-49	4452	6231	39
H(1B)	53	4677	5739	39
H(1C)	63	7729	6019	39
H(2)	795	9143	5520	27
H(3)	950	10774	4851	29
H(5)	3273	4981	4912	27
H(7A)	2955	8681	4331	45
H(7B)	2079	11149	4314	45
H(7C)	1818	7738	4142	45
H(12)	5013	-1715	5821	27
H(13)	6088	-4793	6321	29
H(14)	5978	-4838	7042	28
H(15)	4761	-1861	7287	26
H(17)	2809	4676	7790	26
H(19)	481	10268	7351	28
H(20)	547	8805	6664	27
H(21A)	2121	7335	8308	43
H(21B)	952	8078	8167	43
H(21C)	1761	10703	8147	43
H(1S)	4535(14)	2500(60)	5392(7)	55(7)
H(1SA)	4970(40)	4470(70)	5149(17)	69(18)
H(1SB)	4820(30)	970(100)	5064(13)	57(16)

Table S6. Hydrogen bonds for Sevov_SA1-1005 [$\text{\AA}$ and $^\circ$].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O(1S)-H(1S)...N(2)	0.917(15)	1.937(15)	2.8516(17)	175(2)
O(1S)-H(1SA)...O(1S)#1	0.930(19)	1.85(2)	2.722(3)	156(4)
O(1S)-H(1SB)...O(1S)#2	0.942(19)	1.86(2)	2.735(4)	154(4)

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,-y+1,-z+1 #2 -x+1,-y,-z+1

X-ray characterization of complex 2-Pr

Experimental Summary

The single crystal X-ray diffraction studies were carried out on a Bruker Kappa Photon III CPAD diffractometer equipped with Mo K α radiation ($\lambda = 0.71073 \text{ \AA}$). A 0.212 x 0.207 x 0.164 mm piece of a red block was mounted on a MiTeGen MicroMount with Paratone 24EX oil. Data were collected in a nitrogen gas stream at 100(2) K using ϕ and ω scans. Crystal-to-detector distance was 70 mm using variable exposure time (1s-3s) depending on θ with a scan width of 0.75° . Data collection was 99.8% complete to 25.00° in θ ($0.83 \text{ \AA}$). A total of 63801 reflections were collected covering the indices, $-9 \leq h \leq 9$, $-20 \leq k \leq 20$, $-25 \leq l \leq 25$. 10232 reflections were found to be symmetry independent, with a R_{int} of 0.0488. Indexing and unit cell refinement indicated a primitive, monoclinic lattice. The space group was found to be $P2_1/n$. The data were integrated using the Bruker SAINT software program and scaled using the SADABS software program. Solution by dual-space method (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.

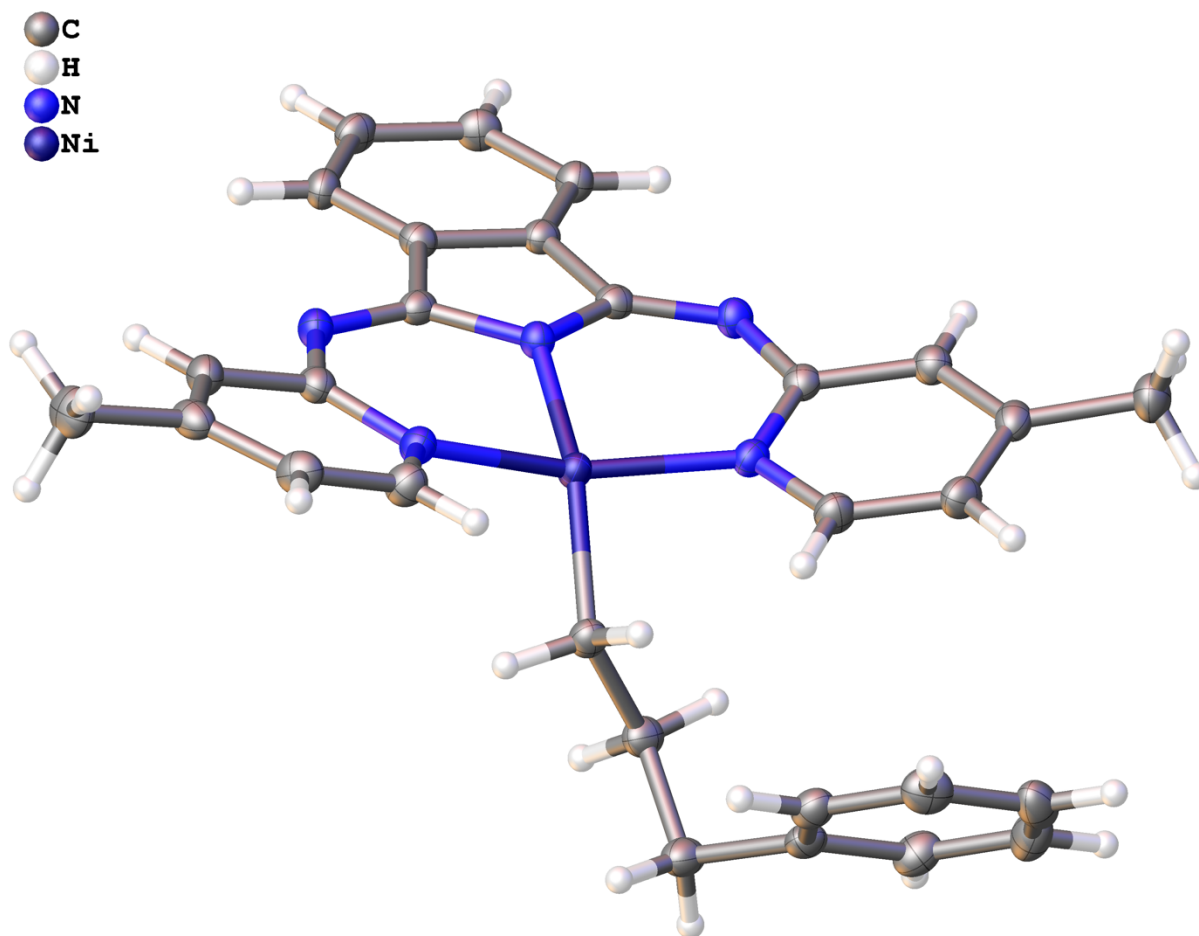


Table S7. Crystal data and structure refinement for Sevov_SA1-1028.

Report date	2024-04-30	
Identification code	SA1-1028	
Empirical formula	C ₂₉ H ₂₇ N ₅ Ni	
Molecular formula	C ₂₉ H ₂₇ N ₅ Ni	
Formula weight	504.26	
Temperature	100.0 K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 1 2 ₁ /n 1	
Unit cell dimensions	a = 7.3490(4) Å	α = 90°.
	b = 16.3706(7) Å	β = 95.092(2)°.
	c = 19.6942(9) Å	γ = 90°.
Volume	2360.0(2) Å ³	
Z	4	
Density (calculated)	1.419 Mg/m ³	
Absorption coefficient	0.851 mm ⁻¹	
F(000)	1056	
Crystal size	0.212 x 0.207 x 0.164 mm ³	
Crystal color, habit	red block	
Theta range for data collection	2.883 to 27.100°.	
Index ranges	-9 ≤ h ≤ 9, -20 ≤ k ≤ 20, -25 ≤ l ≤ 25	
Reflections collected	63801	
Independent reflections	10232 [R(int) = 0.0488, R(sigma) = 0.0364]	
Completeness to theta = 25.000°	99.8 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.094308 and 0.064126	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	10232 / 0 / 319	
Goodness-of-fit on F ²	1.065	
Final R indices [I > 2σ(I)]	R1 = 0.0347, wR2 = 0.0812	
R indices (all data)	R1 = 0.0398, wR2 = 0.0839	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.289 and -0.501 e.Å ⁻³	

Table S8. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for Sevov_SA1-1028. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	$U(\text{eq})$
Ni(1)	4150(1)	7767(1)	5171(1)	17(1)
N(1)	4591(3)	8108(1)	4268(1)	19(1)
N(2)	5909(3)	6838(1)	3898(1)	20(1)
N(3)	5802(3)	6883(1)	5114(1)	17(1)
N(4)	6027(3)	6408(1)	6270(1)	19(1)
N(5)	4352(3)	7691(1)	6157(1)	18(1)
C(1)	1860(3)	8382(1)	5117(1)	20(1)
C(2)	291(4)	7966(1)	5444(1)	22(1)
C(3)	-1300(4)	8556(2)	5555(1)	25(1)
C(4)	-868(3)	9098(1)	6170(1)	21(1)
C(5)	-1126(4)	8804(2)	6819(1)	27(1)
C(6)	-692(4)	9273(2)	7395(1)	31(1)
C(7)	5(4)	10051(2)	7337(1)	30(1)
C(8)	279(4)	10352(2)	6694(1)	28(1)
C(9)	-155(3)	9879(1)	6118(1)	23(1)
C(10)	4249(3)	8902(1)	4091(1)	24(1)
C(11)	4501(4)	9230(2)	3466(1)	25(1)
C(12)	5119(3)	8734(2)	2956(1)	24(1)
C(13)	5534(3)	7938(1)	3134(1)	22(1)
C(14)	5324(3)	7632(1)	3787(1)	20(1)
C(15)	5299(4)	9050(2)	2247(1)	30(1)
C(16)	6152(3)	6532(1)	4507(1)	18(1)
C(17)	6897(3)	5704(1)	4636(1)	18(1)
C(18)	6934(3)	5575(1)	5332(1)	18(1)
C(19)	6219(3)	6328(1)	5625(1)	18(1)
C(20)	7455(3)	5112(1)	4199(1)	21(1)
C(21)	8059(3)	4373(1)	4489(1)	22(1)
C(22)	8093(3)	4240(1)	5188(1)	22(1)
C(23)	7530(3)	4841(1)	5626(1)	21(1)
C(24)	5301(3)	7106(1)	6535(1)	18(1)
C(25)	5606(3)	7169(1)	7250(1)	20(1)

C(26)	4998(3)	7827(1)	7601(1)	21(1)
C(27)	4032(4)	8421(1)	7213(1)	23(1)
C(28)	3748(3)	8335(1)	6521(1)	22(1)
C(29)	5390(4)	7911(2)	8361(1)	28(1)

Table S9. Bond lengths [Å] and angles [°] for Sevov_SA1-1028.

Ni(1)-N(1)	1.9186(19)	C(10)-H(10)	0.9500
Ni(1)-N(3)	1.8987(18)	C(10)-C(11)	1.371(3)
Ni(1)-N(5)	1.9385(18)	C(11)-H(11)	0.9500
Ni(1)-C(1)	1.956(2)	C(11)-C(12)	1.399(3)
N(1)-C(10)	1.364(3)	C(12)-C(13)	1.377(3)
N(1)-C(14)	1.373(3)	C(12)-C(15)	1.505(3)
N(2)-C(14)	1.381(3)	C(13)-H(13)	0.9500
N(2)-C(16)	1.298(3)	C(13)-C(14)	1.401(3)
N(3)-C(16)	1.370(3)	C(15)-H(15A)	0.9800
N(3)-C(19)	1.370(3)	C(15)-H(15B)	0.9800
N(4)-C(19)	1.297(3)	C(15)-H(15C)	0.9800
N(4)-C(24)	1.383(3)	C(16)-C(17)	1.475(3)
N(5)-C(24)	1.366(3)	C(17)-C(18)	1.386(3)
N(5)-C(28)	1.371(3)	C(17)-C(20)	1.382(3)
C(1)-H(1A)	0.9900	C(18)-C(19)	1.478(3)
C(1)-H(1B)	0.9900	C(18)-C(23)	1.387(3)
C(1)-C(2)	1.531(3)	C(20)-H(20)	0.9500
C(2)-H(2A)	0.9900	C(20)-C(21)	1.393(3)
C(2)-H(2B)	0.9900	C(21)-H(21)	0.9500
C(2)-C(3)	1.547(3)	C(21)-C(22)	1.391(3)
C(3)-H(3A)	0.9900	C(22)-H(22)	0.9500
C(3)-H(3B)	0.9900	C(22)-C(23)	1.395(3)
C(3)-C(4)	1.512(3)	C(23)-H(23)	0.9500
C(4)-C(5)	1.395(3)	C(24)-C(25)	1.411(3)
C(4)-C(9)	1.388(3)	C(25)-H(25)	0.9500
C(5)-H(5)	0.9500	C(25)-C(26)	1.375(3)
C(5)-C(6)	1.384(4)	C(26)-C(27)	1.393(3)
C(6)-H(6)	0.9500	C(26)-C(29)	1.505(3)
C(6)-C(7)	1.381(4)	C(27)-H(27)	0.9500
C(7)-H(7)	0.9500	C(27)-C(28)	1.367(3)
C(7)-C(8)	1.390(4)	C(28)-H(28)	0.9500
C(8)-H(8)	0.9500	C(29)-H(29A)	0.9800
C(8)-C(9)	1.388(3)	C(29)-H(29B)	0.9800
C(9)-H(9)	0.9500	C(29)-H(29C)	0.9800

		C(5)-C(4)-C(3)	119.6(2)
N(1)-Ni(1)-N(5)	160.55(8)	C(9)-C(4)-C(3)	122.4(2)
N(1)-Ni(1)-C(1)	90.84(9)	C(9)-C(4)-C(5)	117.9(2)
N(3)-Ni(1)-N(1)	90.31(8)	C(4)-C(5)-H(5)	119.4
N(3)-Ni(1)-N(5)	91.05(8)	C(6)-C(5)-C(4)	121.3(2)
N(3)-Ni(1)-C(1)	160.17(9)	C(6)-C(5)-H(5)	119.4
N(5)-Ni(1)-C(1)	94.39(9)	C(5)-C(6)-H(6)	119.9
C(10)-N(1)-Ni(1)	118.20(15)	C(7)-C(6)-C(5)	120.3(2)
C(10)-N(1)-C(14)	115.99(19)	C(7)-C(6)-H(6)	119.9
C(14)-N(1)-Ni(1)	125.71(15)	C(6)-C(7)-H(7)	120.4
C(16)-N(2)-C(14)	121.77(19)	C(6)-C(7)-C(8)	119.2(2)
C(16)-N(3)-Ni(1)	122.82(15)	C(8)-C(7)-H(7)	120.4
C(19)-N(3)-Ni(1)	124.33(15)	C(7)-C(8)-H(8)	119.8
C(19)-N(3)-C(16)	108.38(18)	C(9)-C(8)-C(7)	120.3(2)
C(19)-N(4)-C(24)	122.10(19)	C(9)-C(8)-H(8)	119.8
C(24)-N(5)-Ni(1)	125.48(15)	C(4)-C(9)-H(9)	119.5
C(24)-N(5)-C(28)	115.33(19)	C(8)-C(9)-C(4)	121.0(2)
C(28)-N(5)-Ni(1)	118.39(15)	C(8)-C(9)-H(9)	119.5
Ni(1)-C(1)-H(1A)	108.5	N(1)-C(10)-H(10)	117.7
Ni(1)-C(1)-H(1B)	108.5	N(1)-C(10)-C(11)	124.6(2)
H(1A)-C(1)-H(1B)	107.5	C(11)-C(10)-H(10)	117.7
C(2)-C(1)-Ni(1)	115.13(15)	C(10)-C(11)-H(11)	120.2
C(2)-C(1)-H(1A)	108.5	C(10)-C(11)-C(12)	119.7(2)
C(2)-C(1)-H(1B)	108.5	C(12)-C(11)-H(11)	120.2
C(1)-C(2)-H(2A)	109.0	C(11)-C(12)-C(15)	121.8(2)
C(1)-C(2)-H(2B)	109.0	C(13)-C(12)-C(11)	116.5(2)
C(1)-C(2)-C(3)	112.85(19)	C(13)-C(12)-C(15)	121.7(2)
H(2A)-C(2)-H(2B)	107.8	C(12)-C(13)-H(13)	119.0
C(3)-C(2)-H(2A)	109.0	C(12)-C(13)-C(14)	122.1(2)
C(3)-C(2)-H(2B)	109.0	C(14)-C(13)-H(13)	119.0
C(2)-C(3)-H(3A)	109.2	N(1)-C(14)-N(2)	124.0(2)
C(2)-C(3)-H(3B)	109.2	N(1)-C(14)-C(13)	120.9(2)
H(3A)-C(3)-H(3B)	107.9	N(2)-C(14)-C(13)	115.1(2)
C(4)-C(3)-C(2)	111.9(2)	C(12)-C(15)-H(15A)	109.5
C(4)-C(3)-H(3A)	109.2	C(12)-C(15)-H(15B)	109.5
C(4)-C(3)-H(3B)	109.2	C(12)-C(15)-H(15C)	109.5

H(15A)-C(15)-H(15B)	109.5	C(26)-C(27)-H(27)	120.0
H(15A)-C(15)-H(15C)	109.5	C(28)-C(27)-C(26)	120.0(2)
H(15B)-C(15)-H(15C)	109.5	C(28)-C(27)-H(27)	120.0
N(2)-C(16)-N(3)	128.5(2)	N(5)-C(28)-H(28)	117.5
N(2)-C(16)-C(17)	122.1(2)	C(27)-C(28)-N(5)	125.0(2)
N(3)-C(16)-C(17)	109.37(18)	C(27)-C(28)-H(28)	117.5
C(18)-C(17)-C(16)	106.52(19)	C(26)-C(29)-H(29A)	109.5
C(20)-C(17)-C(16)	131.6(2)	C(26)-C(29)-H(29B)	109.5
C(20)-C(17)-C(18)	121.8(2)	C(26)-C(29)-H(29C)	109.5
C(17)-C(18)-C(19)	106.38(19)	H(29A)-C(29)-H(29B)	109.5
C(17)-C(18)-C(23)	121.5(2)	H(29A)-C(29)-H(29C)	109.5
C(23)-C(18)-C(19)	132.1(2)	H(29B)-C(29)-H(29C)	109.5
N(3)-C(19)-C(18)	109.31(19)		
N(4)-C(19)-N(3)	128.0(2)		
N(4)-C(19)-C(18)	122.6(2)		
C(17)-C(20)-H(20)	121.4		
C(17)-C(20)-C(21)	117.1(2)		
C(21)-C(20)-H(20)	121.4		
C(20)-C(21)-H(21)	119.4		
C(22)-C(21)-C(20)	121.2(2)		
C(22)-C(21)-H(21)	119.4		
C(21)-C(22)-H(22)	119.3		
C(21)-C(22)-C(23)	121.3(2)		
C(23)-C(22)-H(22)	119.3		
C(18)-C(23)-C(22)	117.0(2)		
C(18)-C(23)-H(23)	121.5		
C(22)-C(23)-H(23)	121.5		
N(4)-C(24)-C(25)	113.9(2)		
N(5)-C(24)-N(4)	124.7(2)		
N(5)-C(24)-C(25)	121.4(2)		
C(24)-C(25)-H(25)	119.0		
C(26)-C(25)-C(24)	122.0(2)		
C(26)-C(25)-H(25)	119.0		
C(25)-C(26)-C(27)	116.3(2)		
C(25)-C(26)-C(29)	122.0(2)		
C(27)-C(26)-C(29)	121.7(2)		

Table S10. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for Sevov_SA1-1028. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U^{11} + \dots + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Ni(1)	17(1)	18(1)	15(1)	0(1)	3(1)	2(1)
N(1)	19(1)	21(1)	17(1)	1(1)	3(1)	1(1)
N(2)	22(1)	22(1)	16(1)	0(1)	2(1)	1(1)
N(3)	18(1)	17(1)	15(1)	1(1)	2(1)	0(1)
N(4)	21(1)	18(1)	18(1)	-1(1)	1(1)	0(1)
N(5)	18(1)	19(1)	18(1)	-2(1)	3(1)	1(1)
C(1)	20(1)	21(1)	19(1)	0(1)	2(1)	4(1)
C(2)	21(1)	23(1)	24(1)	-5(1)	2(1)	-1(1)
C(3)	19(1)	28(1)	27(1)	-5(1)	3(1)	-1(1)
C(4)	17(1)	24(1)	24(1)	-3(1)	3(1)	4(1)
C(5)	26(1)	25(1)	30(1)	2(1)	9(1)	-1(1)
C(6)	36(2)	35(1)	23(1)	3(1)	7(1)	10(1)
C(7)	32(2)	33(1)	25(1)	-7(1)	-3(1)	10(1)
C(8)	28(1)	21(1)	36(1)	-2(1)	2(1)	2(1)
C(9)	22(1)	24(1)	24(1)	2(1)	5(1)	4(1)
C(10)	25(1)	23(1)	23(1)	2(1)	4(1)	2(1)
C(11)	25(1)	24(1)	26(1)	6(1)	3(1)	1(1)
C(12)	20(1)	30(1)	22(1)	6(1)	0(1)	-3(1)
C(13)	21(1)	28(1)	18(1)	0(1)	2(1)	-1(1)
C(14)	17(1)	23(1)	18(1)	1(1)	1(1)	-1(1)
C(15)	34(2)	34(1)	23(1)	9(1)	4(1)	-2(1)
C(16)	15(1)	19(1)	20(1)	-3(1)	2(1)	-1(1)
C(17)	16(1)	19(1)	19(1)	0(1)	1(1)	-1(1)
C(18)	15(1)	19(1)	19(1)	-2(1)	2(1)	0(1)
C(19)	15(1)	19(1)	20(1)	-1(1)	0(1)	-1(1)
C(20)	21(1)	24(1)	17(1)	-3(1)	3(1)	0(1)
C(21)	22(1)	21(1)	24(1)	-6(1)	4(1)	1(1)
C(22)	23(1)	17(1)	26(1)	1(1)	2(1)	2(1)
C(23)	22(1)	21(1)	19(1)	0(1)	3(1)	0(1)
C(24)	17(1)	19(1)	18(1)	0(1)	3(1)	-2(1)
C(25)	20(1)	22(1)	19(1)	2(1)	3(1)	0(1)

C(26)	20(1)	25(1)	18(1)	-2(1)	3(1)	-5(1)
C(27)	23(1)	23(1)	24(1)	-5(1)	3(1)	2(1)
C(28)	23(1)	21(1)	22(1)	-1(1)	3(1)	4(1)
C(29)	32(1)	32(1)	19(1)	-4(1)	2(1)	1(1)

Table S11. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^{-3}$) for Sevov_SA1-1028.

	x	y	z	U(eq)
H(1A)	2096	8919	5339	24
H(1B)	1466	8485	4631	24
H(2A)	764	7733	5890	27
H(2B)	-179	7509	5150	27
H(3A)	-1551	8901	5145	30
H(3B)	-2414	8235	5618	30
H(5)	-1608	8270	6866	32
H(6)	-873	9059	7833	37
H(7)	293	10376	7732	36
H(8)	766	10885	6649	34
H(9)	41	10092	5682	28
H(10)	3806	9252	4424	28
H(11)	4256	9793	3379	30
H(13)	5978	7584	2803	27
H(15A)	6216	8727	2033	45
H(15B)	5679	9624	2271	45
H(15C)	4120	9004	1975	45
H(20)	7429	5204	3722	25
H(21)	8454	3952	4204	27
H(22)	8509	3729	5371	27
H(23)	7554	4752	6103	25
H(25)	6251	6745	7497	24
H(27)	3571	8887	7429	28
H(28)	3081	8753	6274	26
H(29A)	5796	7384	8556	41
H(29B)	4279	8085	8561	41
H(29C)	6352	8320	8461	41

Table S12. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for Sevov_SA1-1005. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U^{11} + \dots + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Ni(1)	15(1)	22(1)	17(1)	0(1)	4(1)	0(1)
N(1)	18(1)	23(1)	19(1)	0(1)	2(1)	-1(1)
N(2)	18(1)	23(1)	19(1)	-1(1)	4(1)	-1(1)
N(3)	17(1)	21(1)	18(1)	-1(1)	4(1)	-1(1)
N(4)	20(1)	20(1)	18(1)	0(1)	4(1)	-1(1)
N(5)	18(1)	22(1)	20(1)	0(1)	6(1)	-1(1)
C(1)	19(1)	35(1)	23(1)	0(1)	4(1)	0(1)
C(2)	19(1)	26(1)	23(1)	1(1)	3(1)	0(1)
C(3)	20(1)	28(1)	23(1)	3(1)	0(1)	0(1)
C(4)	23(1)	29(1)	19(1)	1(1)	2(1)	-5(1)
C(5)	20(1)	29(1)	20(1)	-1(1)	5(1)	-2(1)
C(6)	18(1)	23(1)	18(1)	-2(1)	3(1)	-3(1)
C(7)	30(1)	40(1)	21(1)	6(1)	5(1)	1(1)
C(8)	17(1)	19(1)	21(1)	-2(1)	4(1)	-2(1)
C(9)	18(1)	19(1)	21(1)	-1(1)	4(1)	-2(1)
C(10)	18(1)	18(1)	22(1)	-2(1)	4(1)	-3(1)
C(11)	17(1)	19(1)	20(1)	0(1)	3(1)	-3(1)
C(12)	21(1)	23(1)	23(1)	-2(1)	6(1)	-1(1)
C(13)	21(1)	23(1)	30(1)	-3(1)	6(1)	1(1)
C(14)	20(1)	20(1)	28(1)	0(1)	1(1)	0(1)
C(15)	22(1)	20(1)	21(1)	-1(1)	2(1)	-2(1)
C(16)	18(1)	20(1)	20(1)	1(1)	6(1)	-3(1)
C(17)	22(1)	24(1)	19(1)	0(1)	5(1)	-2(1)
C(18)	23(1)	24(1)	23(1)	-2(1)	9(1)	-5(1)
C(19)	22(1)	24(1)	26(1)	-2(1)	9(1)	0(1)
C(20)	20(1)	24(1)	24(1)	1(1)	6(1)	1(1)
C(21)	30(1)	35(1)	23(1)	-5(1)	10(1)	1(1)
O(1S)	37(1)	57(1)	49(1)	16(1)	26(1)	13(1)

Table S13. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^{-3}$) for Sevov_SA1-1005.

	x	y	z	U(eq)
H(1A)	-49	4452	6231	39
H(1B)	53	4677	5739	39
H(1C)	63	7729	6019	39
H(2)	795	9143	5520	27
H(3)	950	10774	4851	29
H(5)	3273	4981	4912	27
H(7A)	2955	8681	4331	45
H(7B)	2079	11149	4314	45
H(7C)	1818	7738	4142	45
H(12)	5013	-1715	5821	27
H(13)	6088	-4793	6321	29
H(14)	5978	-4838	7042	28
H(15)	4761	-1861	7287	26
H(17)	2809	4676	7790	26
H(19)	481	10268	7351	28
H(20)	547	8805	6664	27
H(21A)	2121	7335	8308	43
H(21B)	952	8078	8167	43
H(21C)	1761	10703	8147	43
H(1S)	4535(14)	2500(60)	5392(7)	55(7)
H(1SA)	4970(40)	4470(70)	5149(17)	69(18)
H(1SB)	4820(30)	970(100)	5064(13)	57(16)

Table S14. Hydrogen bonds for Sevov_SA1-1005 [$\text{\AA}$ and $^\circ$].

D-H...A	d(D-H)	d(H...A)	d(D...A)	$\angle$ (DHA)
O(1S)-H(1S)...N(2)	0.917(15)	1.937(15)	2.8516(17)	175(2)
O(1S)-H(1SA)...O(1S)#1	0.930(19)	1.85(2)	2.722(3)	156(4)
O(1S)-H(1SB)...O(1S)#2	0.942(19)	1.86(2)	2.735(4)	154(4)

Symmetry transformations used to generate equivalent atoms:

#1 $-x+1, -y+1, -z+1$ #2 $-x+1, -y, -z+1$

X-ray characterization of complex 2-^{cy}Pr

Experimental Summary

The single crystal X-ray diffraction studies were carried out on a Bruker Kappa Photon III CPAD diffractometer equipped with Mo K_α radiation ($\lambda = 0.71073 \text{ \AA}$). A 0.383 x 0.111 x 0.035 mm piece of a red needle was mounted on a MiTeGen MicroMount with Paratone 24EX oil. Data were collected in a nitrogen gas stream at 100(2) K using ϕ and ω scans. Crystal-to-detector distance was 60 mm using variable exposure time (5s-10s) depending on θ with a scan width of 1.0° . Data collection was 99.8% complete to 25.00° in θ ($0.83 \text{ \AA}$). A total of 31049 reflections were collected covering the indices, $-23 \leq h \leq 23$, $-6 \leq k \leq 6$, $-26 \leq l \leq 28$. 4183 reflections were found to be symmetry independent, with a R_{int} of 0.0593. 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 dual-space method (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.

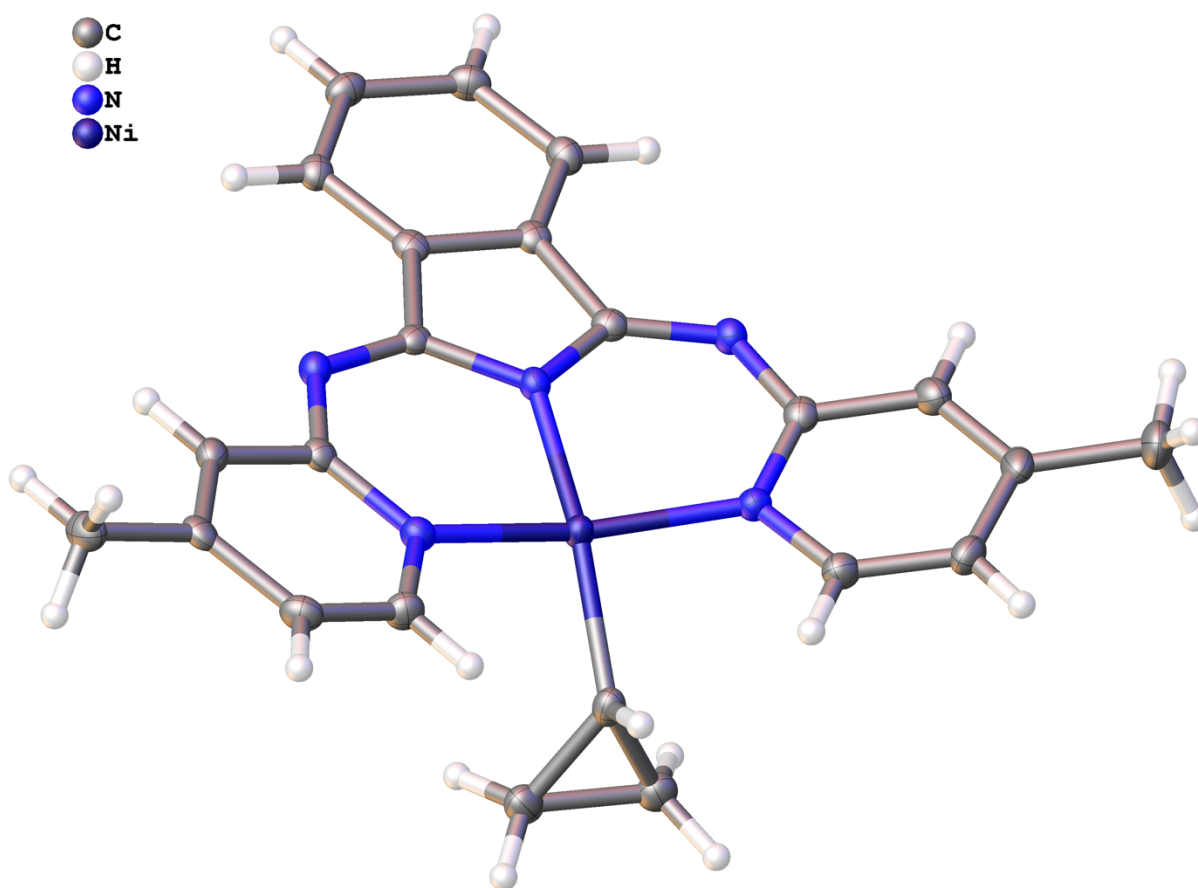


Table S15. Crystal data and structure refinement for Sevov_SA1-1004.

Report date	2024-04-30	
Identification code	SA1-1004	
Empirical formula	C23 H21 N5 Ni	
Molecular formula	C23 H21 N5 Ni	
Formula weight	426.16	
Temperature	100.0 K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 1 21/c 1	
Unit cell dimensions	a = 18.1443(10) Å	$\alpha = 90^\circ$.
	b = 4.7089(2) Å	$\beta = 95.595(2)^\circ$.
	c = 22.4414(12) Å	$\gamma = 90^\circ$.
Volume	1908.25(17) Å ³	
Z	4	
Density (calculated)	1.483 Mg/m ³	
Absorption coefficient	1.037 mm ⁻¹	
F(000)	888	
Crystal size	0.383 x 0.111 x 0.035 mm ³	
Crystal color, habit	red needle	
Theta range for data collection	3.036 to 27.118°.	
Index ranges	-23 ≤ h ≤ 23, -6 ≤ k ≤ 6, -26 ≤ l ≤ 28	
Reflections collected	31049	
Independent reflections	4183 [R(int) = 0.0593, R(sigma) = 0.0406]	
Completeness to theta = 25.000°	99.8 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.2612 and 0.2309	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	4183 / 0 / 264	
Goodness-of-fit on F ²	1.039	
Final R indices [I > 2sigma(I)]	R1 = 0.0337, wR2 = 0.0684	
R indices (all data)	R1 = 0.0533, wR2 = 0.0743	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.444 and -0.327 e.Å ⁻³	

Table S16. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for Sevov_SA1-1004. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	$U(\text{eq})$
Ni(1)	7887(1)	2869(1)	3178(1)	14(1)
N(1)	7400(1)	2278(4)	2383(1)	16(1)
N(2)	6380(1)	5595(4)	2435(1)	15(1)
N(3)	7080(1)	5035(4)	3393(1)	14(1)
N(4)	7439(1)	5748(4)	4440(1)	16(1)
N(5)	8242(1)	2347(4)	4010(1)	16(1)
C(1)	8844(1)	1877(5)	2927(1)	18(1)
C(2)	9500(1)	3700(5)	3119(1)	22(1)
C(3)	9173(1)	3708(5)	2476(1)	22(1)
C(4)	7674(1)	224(4)	2036(1)	19(1)
C(5)	7346(1)	-654(5)	1493(1)	19(1)
C(6)	6683(1)	588(4)	1254(1)	17(1)
C(7)	6401(1)	2668(4)	1595(1)	16(1)
C(8)	6750(1)	3489(4)	2156(1)	15(1)
C(9)	6299(1)	-336(5)	663(1)	22(1)
C(10)	6544(1)	6218(4)	2995(1)	14(1)
C(11)	6139(1)	8408(4)	3303(1)	15(1)
C(12)	6457(1)	8468(4)	3894(1)	15(1)
C(13)	7048(1)	6299(4)	3939(1)	15(1)
C(14)	5548(1)	10134(4)	3114(1)	16(1)
C(15)	5286(1)	11975(4)	3532(1)	18(1)
C(16)	5613(1)	12036(4)	4122(1)	19(1)
C(17)	6202(1)	10266(4)	4313(1)	17(1)
C(18)	7968(1)	3642(4)	4483(1)	17(1)
C(19)	8230(1)	2923(5)	5078(1)	21(1)
C(20)	8754(1)	853(5)	5206(1)	21(1)
C(21)	9019(1)	-495(5)	4716(1)	21(1)
C(22)	8757(1)	275(5)	4148(1)	20(1)
C(23)	9027(1)	78(6)	5839(1)	31(1)

Table S17. Bond lengths [Å] and angles [°] for Sevov_SA1-1004.

Ni(1)-N(1)	1.9328(17)	C(11)-C(12)	1.393(3)
Ni(1)-N(3)	1.8853(17)	C(11)-C(14)	1.378(3)
Ni(1)-N(5)	1.9301(17)	C(12)-C(13)	1.477(3)
Ni(1)-C(1)	1.934(2)	C(12)-C(17)	1.378(3)
N(1)-C(4)	1.364(3)	C(14)-H(14)	0.9500
N(1)-C(8)	1.363(3)	C(14)-C(15)	1.394(3)
N(2)-C(8)	1.382(3)	C(15)-H(15)	0.9500
N(2)-C(10)	1.296(3)	C(15)-C(16)	1.397(3)
N(3)-C(10)	1.374(3)	C(16)-H(16)	0.9500
N(3)-C(13)	1.369(3)	C(16)-C(17)	1.390(3)
N(4)-C(13)	1.296(3)	C(17)-H(17)	0.9500
N(4)-C(18)	1.377(3)	C(18)-C(19)	1.414(3)
N(5)-C(18)	1.360(3)	C(19)-H(19)	0.9500
N(5)-C(22)	1.365(3)	C(19)-C(20)	1.372(3)
C(1)-H(1)	1.0000	C(20)-C(21)	1.394(3)
C(1)-C(2)	1.497(3)	C(20)-C(23)	1.503(3)
C(1)-C(3)	1.496(3)	C(21)-H(21)	0.9500
C(2)-H(2A)	0.9900	C(21)-C(22)	1.366(3)
C(2)-H(2B)	0.9900	C(22)-H(22)	0.9500
C(2)-C(3)	1.505(3)	C(23)-H(23A)	0.9800
C(3)-H(3A)	0.9900	C(23)-H(23B)	0.9800
C(3)-H(3B)	0.9900	C(23)-H(23C)	0.9800
C(4)-H(4)	0.9500		
C(4)-C(5)	1.368(3)	N(1)-Ni(1)-C(1)	92.19(8)
C(5)-H(5)	0.9500	N(3)-Ni(1)-N(1)	91.00(7)
C(5)-C(6)	1.397(3)	N(3)-Ni(1)-N(5)	90.92(7)
C(6)-C(7)	1.372(3)	N(3)-Ni(1)-C(1)	161.21(8)
C(6)-C(9)	1.502(3)	N(5)-Ni(1)-N(1)	162.57(7)
C(7)-H(7)	0.9500	N(5)-Ni(1)-C(1)	91.55(8)
C(7)-C(8)	1.407(3)	C(4)-N(1)-Ni(1)	117.98(14)
C(9)-H(9A)	0.9800	C(8)-N(1)-Ni(1)	125.85(13)
C(9)-H(9B)	0.9800	C(8)-N(1)-C(4)	115.67(17)
C(9)-H(9C)	0.9800	C(10)-N(2)-C(8)	121.75(18)
C(10)-C(11)	1.476(3)	C(10)-N(3)-Ni(1)	124.90(13)

C(13)-N(3)-Ni(1)	124.53(14)	N(1)-C(8)-N(2)	124.90(18)
C(13)-N(3)-C(10)	108.42(17)	N(1)-C(8)-C(7)	121.15(18)
C(13)-N(4)-C(18)	121.63(18)	N(2)-C(8)-C(7)	113.95(18)
C(18)-N(5)-Ni(1)	125.78(14)	C(6)-C(9)-H(9A)	109.5
C(18)-N(5)-C(22)	115.92(18)	C(6)-C(9)-H(9B)	109.5
C(22)-N(5)-Ni(1)	117.87(14)	C(6)-C(9)-H(9C)	109.5
Ni(1)-C(1)-H(1)	115.6	H(9A)-C(9)-H(9B)	109.5
C(2)-C(1)-Ni(1)	119.27(15)	H(9A)-C(9)-H(9C)	109.5
C(2)-C(1)-H(1)	115.6	H(9B)-C(9)-H(9C)	109.5
C(3)-C(1)-Ni(1)	119.12(15)	N(2)-C(10)-N(3)	128.27(19)
C(3)-C(1)-H(1)	115.6	N(2)-C(10)-C(11)	122.31(19)
C(3)-C(1)-C(2)	60.36(14)	N(3)-C(10)-C(11)	109.41(17)
C(1)-C(2)-H(2A)	117.8	C(12)-C(11)-C(10)	106.33(18)
C(1)-C(2)-H(2B)	117.8	C(14)-C(11)-C(10)	132.49(19)
C(1)-C(2)-C(3)	59.77(14)	C(14)-C(11)-C(12)	121.16(19)
H(2A)-C(2)-H(2B)	114.9	C(11)-C(12)-C(13)	106.36(17)
C(3)-C(2)-H(2A)	117.8	C(17)-C(12)-C(11)	121.79(19)
C(3)-C(2)-H(2B)	117.8	C(17)-C(12)-C(13)	131.83(19)
C(1)-C(3)-C(2)	59.87(14)	N(3)-C(13)-C(12)	109.48(17)
C(1)-C(3)-H(3A)	117.8	N(4)-C(13)-N(3)	128.43(19)
C(1)-C(3)-H(3B)	117.8	N(4)-C(13)-C(12)	122.07(18)
C(2)-C(3)-H(3A)	117.8	C(11)-C(14)-H(14)	121.1
C(2)-C(3)-H(3B)	117.8	C(11)-C(14)-C(15)	117.75(19)
H(3A)-C(3)-H(3B)	114.9	C(15)-C(14)-H(14)	121.1
N(1)-C(4)-H(4)	117.6	C(14)-C(15)-H(15)	119.7
N(1)-C(4)-C(5)	124.9(2)	C(14)-C(15)-C(16)	120.64(19)
C(5)-C(4)-H(4)	117.6	C(16)-C(15)-H(15)	119.7
C(4)-C(5)-H(5)	120.0	C(15)-C(16)-H(16)	119.3
C(4)-C(5)-C(6)	119.9(2)	C(17)-C(16)-C(15)	121.46(19)
C(6)-C(5)-H(5)	120.0	C(17)-C(16)-H(16)	119.3
C(5)-C(6)-C(9)	121.68(19)	C(12)-C(17)-C(16)	117.19(19)
C(7)-C(6)-C(5)	116.07(19)	C(12)-C(17)-H(17)	121.4
C(7)-C(6)-C(9)	122.2(2)	C(16)-C(17)-H(17)	121.4
C(6)-C(7)-H(7)	118.8	N(4)-C(18)-C(19)	114.01(18)
C(6)-C(7)-C(8)	122.32(19)	N(5)-C(18)-N(4)	125.00(19)
C(8)-C(7)-H(7)	118.8	N(5)-C(18)-C(19)	120.97(19)

C(18)-C(19)-H(19)	119.0
C(20)-C(19)-C(18)	122.0(2)
C(20)-C(19)-H(19)	119.0
C(19)-C(20)-C(21)	116.33(19)
C(19)-C(20)-C(23)	121.9(2)
C(21)-C(20)-C(23)	121.8(2)
C(20)-C(21)-H(21)	120.0
C(22)-C(21)-C(20)	120.0(2)
C(22)-C(21)-H(21)	120.0
N(5)-C(22)-C(21)	124.7(2)
N(5)-C(22)-H(22)	117.6
C(21)-C(22)-H(22)	117.6
C(20)-C(23)-H(23A)	109.5
C(20)-C(23)-H(23B)	109.5
C(20)-C(23)-H(23C)	109.5
H(23A)-C(23)-H(23B)	109.5
H(23A)-C(23)-H(23C)	109.5
H(23B)-C(23)-H(23C)	109.5

Table S18. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for Sevov_SA1-1004. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U^{11} + \dots + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Ni(1)	14(1)	16(1)	12(1)	0(1)	1(1)	2(1)
N(1)	17(1)	16(1)	15(1)	0(1)	3(1)	0(1)
N(2)	16(1)	16(1)	13(1)	1(1)	1(1)	0(1)
N(3)	15(1)	15(1)	12(1)	1(1)	1(1)	-1(1)
N(4)	16(1)	19(1)	14(1)	-1(1)	1(1)	0(1)
N(5)	14(1)	18(1)	15(1)	1(1)	2(1)	1(1)
C(1)	18(1)	20(1)	15(1)	0(1)	0(1)	5(1)
C(2)	20(1)	23(1)	22(1)	1(1)	3(1)	4(1)
C(3)	21(1)	24(1)	22(1)	4(1)	4(1)	6(1)
C(4)	19(1)	19(1)	20(1)	-1(1)	3(1)	3(1)
C(5)	20(1)	19(1)	19(1)	-3(1)	6(1)	0(1)
C(6)	19(1)	18(1)	13(1)	2(1)	4(1)	-4(1)
C(7)	16(1)	19(1)	15(1)	3(1)	1(1)	-1(1)
C(8)	16(1)	14(1)	14(1)	2(1)	3(1)	-2(1)
C(9)	21(1)	28(1)	17(1)	-3(1)	2(1)	-3(1)
C(10)	12(1)	13(1)	16(1)	2(1)	3(1)	-2(1)
C(11)	16(1)	13(1)	16(1)	0(1)	4(1)	-4(1)
C(12)	15(1)	13(1)	16(1)	1(1)	2(1)	-4(1)
C(13)	15(1)	15(1)	16(1)	0(1)	3(1)	-2(1)
C(14)	16(1)	16(1)	16(1)	2(1)	1(1)	-2(1)
C(15)	15(1)	14(1)	25(1)	2(1)	2(1)	2(1)
C(16)	20(1)	17(1)	21(1)	-4(1)	6(1)	0(1)
C(17)	20(1)	18(1)	15(1)	-1(1)	2(1)	-2(1)
C(18)	15(1)	17(1)	17(1)	2(1)	0(1)	-3(1)
C(19)	18(1)	29(1)	16(1)	-1(1)	1(1)	-1(1)
C(20)	15(1)	31(1)	17(1)	6(1)	-1(1)	-3(1)
C(21)	16(1)	23(1)	22(1)	5(1)	0(1)	3(1)
C(22)	18(1)	23(1)	20(1)	3(1)	3(1)	3(1)
C(23)	26(1)	47(2)	19(1)	9(1)	-4(1)	6(1)

Table S19. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^{-3}$) for Sevov_SA1-1004.

	x	y	z	U(eq)
H(1)	8946	-202	2898	21
H(2A)	9984	2748	3214	26
H(2B)	9420	5396	3365	26
H(3A)	8891	5410	2328	27
H(3B)	9456	2762	2177	27
H(4)	8126	-661	2184	23
H(5)	7569	-2107	1278	23
H(7)	5953	3585	1447	20
H(9A)	6114	-2278	697	33
H(9B)	6650	-277	357	33
H(9C)	5883	944	548	33
H(14)	5327	10072	2713	19
H(15)	4882	13199	3415	22
H(16)	5428	13316	4399	23
H(17)	6420	10295	4715	21
H(19)	8038	3902	5399	25
H(21)	9381	-1948	4778	25
H(22)	8947	-702	3826	24
H(23A)	9548	629	5919	46
H(23B)	8980	-1977	5894	46
H(23C)	8732	1075	6116	46

X-ray characterization of complex 2-^{cy}Bu

Experimental Summary

The single crystal X-ray diffraction studies were carried out on a Bruker Kappa Photon III CPAD diffractometer equipped with Mo K $_{\alpha}$ radiation ($\lambda = 0.71073 \text{ \AA}$). A 0.128 x 0.035 x 0.020 mm piece of a purple needle was mounted on a MiTeGen MicroMount 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 (10s-120s) 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 34124 reflections were collected covering the indices, $-19 \leq h \leq 19$, $-5 \leq k \leq 5$, $-31 \leq l \leq 31$. 3682 reflections were found to be symmetry independent, with a R_{int} of 0.0960. 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 dual-space method (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.

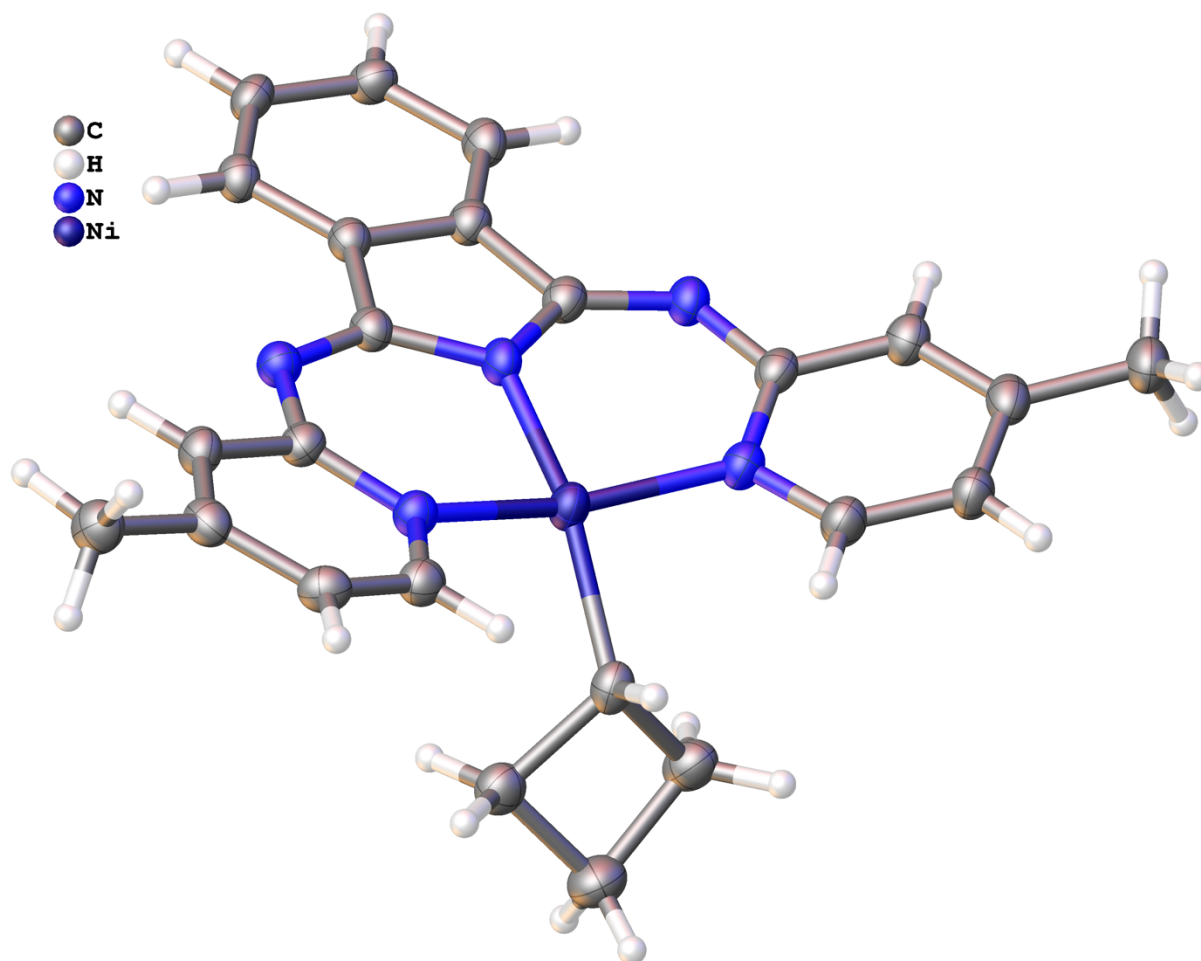


Table S20. Crystal data and structure refinement for Sevov_SA1-1591.

Report date	2024-05-01	
Identification code	SA1-1591	
Empirical formula	C ₂₄ H ₂₃ N ₅ Ni	
Molecular formula	C ₂₄ H ₂₃ N ₅ Ni	
Formula weight	440.18	
Temperature	100.0 K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 1 21/c 1	
Unit cell dimensions	a = 16.0232(15) Å	α = 90°.
	b = 4.8395(4) Å	β = 97.521(3)°.
	c = 26.219(2) Å	γ = 90°.
Volume	2015.6(3) Å ³	
Z	4	
Density (calculated)	1.451 Mg/m ³	
Absorption coefficient	0.984 mm ⁻¹	
F(000)	920	
Crystal size	0.128 x 0.035 x 0.020 mm ³	
Crystal color, habit	purple needle	
Theta range for data collection	2.564 to 25.359°.	
Index ranges	-19 ≤ h ≤ 19, -5 ≤ k ≤ 5, -31 ≤ l ≤ 31	
Reflections collected	34124	
Independent reflections	3682 [R(int) = 0.0960, R(sigma) = 0.0533]	
Completeness to theta = 25.000°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.0916 and 0.0598	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	3682 / 0 / 273	
Goodness-of-fit on F ²	1.030	
Final R indices [I > 2sigma(I)]	R1 = 0.0383, wR2 = 0.0767	
R indices (all data)	R1 = 0.0672, wR2 = 0.0860	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.270 and -0.321 e.Å ⁻³	

Table S21. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for Sevov_SA1-1591. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	$U(\text{eq})$
Ni(1)	2428(1)	6166(1)	6062(1)	25(1)
N(1)	3594(1)	6781(5)	5994(1)	24(1)
N(2)	4209(1)	3410(5)	6627(1)	24(1)
N(3)	2733(1)	4061(5)	6665(1)	24(1)
N(4)	1376(1)	3444(5)	6950(1)	26(1)
N(5)	1317(1)	6760(5)	6244(1)	26(1)
C(1)	2073(2)	6917(6)	5336(1)	27(1)
C(2)	1255(2)	5481(7)	5070(1)	35(1)
C(3)	1718(2)	4790(7)	4607(1)	40(1)
C(4)	2559(2)	5342(6)	4946(1)	31(1)
C(5)	3788(2)	8884(6)	5684(1)	27(1)
C(6)	4585(2)	9712(6)	5623(1)	28(1)
C(7)	5279(2)	8353(6)	5894(1)	28(1)
C(8)	5097(2)	6271(6)	6214(1)	27(1)
C(9)	4269(2)	5499(6)	6275(1)	25(1)
C(10)	6168(2)	9195(7)	5840(1)	33(1)
C(11)	3507(2)	2833(6)	6794(1)	23(1)
C(12)	3432(2)	662(6)	7186(1)	23(1)
C(13)	2596(2)	662(6)	7277(1)	24(1)
C(14)	2167(2)	2840(6)	6945(1)	25(1)
C(15)	4020(2)	-1106(6)	7445(1)	25(1)
C(16)	3737(2)	-2904(6)	7801(1)	26(1)
C(17)	2899(2)	-2918(6)	7887(1)	26(1)
C(18)	2312(2)	-1111(6)	7629(1)	27(1)
C(19)	988(2)	5545(6)	6648(1)	25(1)
C(20)	206(2)	6360(6)	6779(1)	28(1)
C(21)	-265(2)	8446(6)	6520(1)	30(1)
C(22)	82(2)	9692(6)	6118(1)	29(1)
C(23)	849(2)	8839(6)	5999(1)	29(1)
C(24)	-1096(2)	9328(7)	6665(1)	35(1)

Table S22. Bond lengths [Å] and angles [°] for Sevov_SA1-1591.

Ni(1)-N(1)	1.924(2)	C(10)-H(10B)	0.9800
Ni(1)-N(3)	1.890(2)	C(10)-H(10C)	0.9800
Ni(1)-N(5)	1.923(2)	C(11)-C(12)	1.486(4)
Ni(1)-C(1)	1.948(3)	C(12)-C(13)	1.391(4)
N(1)-C(5)	1.364(4)	C(12)-C(15)	1.383(4)
N(1)-C(9)	1.375(3)	C(13)-C(14)	1.478(4)
N(2)-C(9)	1.380(4)	C(13)-C(18)	1.379(4)
N(2)-C(11)	1.290(3)	C(15)-H(15)	0.9500
N(3)-C(11)	1.377(3)	C(15)-C(16)	1.394(4)
N(3)-C(14)	1.374(4)	C(16)-H(16)	0.9500
N(4)-C(14)	1.303(3)	C(16)-C(17)	1.391(4)
N(4)-C(19)	1.385(4)	C(17)-H(17)	0.9500
N(5)-C(19)	1.375(4)	C(17)-C(18)	1.392(4)
N(5)-C(23)	1.365(4)	C(18)-H(18)	0.9500
C(1)-H(1)	1.0000	C(19)-C(20)	1.400(4)
C(1)-C(2)	1.564(4)	C(20)-H(20)	0.9500
C(1)-C(4)	1.563(4)	C(20)-C(21)	1.384(4)
C(2)-H(2A)	0.9900	C(21)-C(22)	1.392(4)
C(2)-H(2B)	0.9900	C(21)-C(24)	1.495(4)
C(2)-C(3)	1.542(4)	C(22)-H(22)	0.9500
C(3)-H(3A)	0.9900	C(22)-C(23)	1.371(4)
C(3)-H(3B)	0.9900	C(23)-H(23)	0.9500
C(3)-C(4)	1.538(4)	C(24)-H(24A)	0.9800
C(4)-H(4A)	0.9900	C(24)-H(24B)	0.9800
C(4)-H(4B)	0.9900	C(24)-H(24C)	0.9800
C(5)-H(5)	0.9500		
C(5)-C(6)	1.367(4)	N(1)-Ni(1)-C(1)	92.46(11)
C(6)-H(6)	0.9500	N(3)-Ni(1)-N(1)	90.77(9)
C(6)-C(7)	1.402(4)	N(3)-Ni(1)-N(5)	91.13(10)
C(7)-C(8)	1.368(4)	N(3)-Ni(1)-C(1)	158.12(11)
C(7)-C(10)	1.506(4)	N(5)-Ni(1)-N(1)	160.36(10)
C(8)-H(8)	0.9500	N(5)-Ni(1)-C(1)	93.02(11)
C(8)-C(9)	1.407(4)	C(5)-N(1)-Ni(1)	118.12(18)
C(10)-H(10A)	0.9800	C(5)-N(1)-C(9)	115.6(2)

C(9)-N(1)-Ni(1)	125.82(19)	C(5)-C(6)-H(6)	120.2
C(11)-N(2)-C(9)	121.8(2)	C(5)-C(6)-C(7)	119.6(3)
C(11)-N(3)-Ni(1)	124.33(19)	C(7)-C(6)-H(6)	120.2
C(14)-N(3)-Ni(1)	124.26(18)	C(6)-C(7)-C(10)	121.5(3)
C(14)-N(3)-C(11)	108.6(2)	C(8)-C(7)-C(6)	116.0(3)
C(14)-N(4)-C(19)	121.6(2)	C(8)-C(7)-C(10)	122.5(3)
C(19)-N(5)-Ni(1)	125.98(18)	C(7)-C(8)-H(8)	118.5
C(23)-N(5)-Ni(1)	117.59(19)	C(7)-C(8)-C(9)	123.0(3)
C(23)-N(5)-C(19)	115.8(2)	C(9)-C(8)-H(8)	118.5
Ni(1)-C(1)-H(1)	111.0	N(1)-C(9)-N(2)	124.8(2)
C(2)-C(1)-Ni(1)	118.3(2)	N(1)-C(9)-C(8)	120.4(3)
C(2)-C(1)-H(1)	111.0	N(2)-C(9)-C(8)	114.8(2)
C(4)-C(1)-Ni(1)	116.21(19)	C(7)-C(10)-H(10A)	109.5
C(4)-C(1)-H(1)	111.0	C(7)-C(10)-H(10B)	109.5
C(4)-C(1)-C(2)	87.2(2)	C(7)-C(10)-H(10C)	109.5
C(1)-C(2)-H(2A)	113.8	H(10A)-C(10)-H(10B)	109.5
C(1)-C(2)-H(2B)	113.8	H(10A)-C(10)-H(10C)	109.5
H(2A)-C(2)-H(2B)	111.0	H(10B)-C(10)-H(10C)	109.5
C(3)-C(2)-C(1)	89.2(2)	N(2)-C(11)-N(3)	128.3(3)
C(3)-C(2)-H(2A)	113.8	N(2)-C(11)-C(12)	122.8(2)
C(3)-C(2)-H(2B)	113.8	N(3)-C(11)-C(12)	108.9(2)
C(2)-C(3)-H(3A)	113.8	C(13)-C(12)-C(11)	106.6(2)
C(2)-C(3)-H(3B)	113.8	C(15)-C(12)-C(11)	131.7(3)
H(3A)-C(3)-H(3B)	111.0	C(15)-C(12)-C(13)	121.7(3)
C(4)-C(3)-C(2)	89.0(2)	C(12)-C(13)-C(14)	106.5(2)
C(4)-C(3)-H(3A)	113.8	C(18)-C(13)-C(12)	121.6(3)
C(4)-C(3)-H(3B)	113.8	C(18)-C(13)-C(14)	131.9(3)
C(1)-C(4)-H(4A)	113.7	N(3)-C(14)-C(13)	109.5(2)
C(1)-C(4)-H(4B)	113.7	N(4)-C(14)-N(3)	128.3(3)
C(3)-C(4)-C(1)	89.4(2)	N(4)-C(14)-C(13)	122.2(3)
C(3)-C(4)-H(4A)	113.7	C(12)-C(15)-H(15)	121.5
C(3)-C(4)-H(4B)	113.7	C(12)-C(15)-C(16)	117.0(3)
H(4A)-C(4)-H(4B)	111.0	C(16)-C(15)-H(15)	121.5
N(1)-C(5)-H(5)	117.4	C(15)-C(16)-H(16)	119.4
N(1)-C(5)-C(6)	125.3(3)	C(17)-C(16)-C(15)	121.1(3)
C(6)-C(5)-H(5)	117.4	C(17)-C(16)-H(16)	119.4

C(16)-C(17)-H(17)	119.2
C(16)-C(17)-C(18)	121.5(3)
C(18)-C(17)-H(17)	119.2
C(13)-C(18)-C(17)	117.1(3)
C(13)-C(18)-H(18)	121.5
C(17)-C(18)-H(18)	121.5
N(4)-C(19)-C(20)	114.5(3)
N(5)-C(19)-N(4)	124.5(2)
N(5)-C(19)-C(20)	121.0(3)
C(19)-C(20)-H(20)	118.9
C(21)-C(20)-C(19)	122.2(3)
C(21)-C(20)-H(20)	118.9
C(20)-C(21)-C(22)	116.2(3)
C(20)-C(21)-C(24)	122.0(3)
C(22)-C(21)-C(24)	121.7(3)
C(21)-C(22)-H(22)	120.0
C(23)-C(22)-C(21)	120.1(3)
C(23)-C(22)-H(22)	120.0
N(5)-C(23)-C(22)	124.7(3)
N(5)-C(23)-H(23)	117.7
C(22)-C(23)-H(23)	117.7
C(21)-C(24)-H(24A)	109.5
C(21)-C(24)-H(24B)	109.5
C(21)-C(24)-H(24C)	109.5
H(24A)-C(24)-H(24B)	109.5
H(24A)-C(24)-H(24C)	109.5
H(24B)-C(24)-H(24C)	109.5

Table S23. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for Sevov_SA1-1591. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U^{11} + \dots + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Ni(1)	19(1)	28(1)	27(1)	2(1)	2(1)	1(1)
N(1)	23(1)	25(1)	25(1)	2(1)	3(1)	0(1)
N(2)	22(1)	26(1)	25(1)	1(1)	4(1)	0(1)
N(3)	16(1)	28(1)	26(1)	-2(1)	2(1)	-1(1)
N(4)	19(1)	29(1)	29(1)	0(1)	2(1)	1(1)
N(5)	22(1)	28(1)	28(1)	1(1)	0(1)	2(1)
C(1)	22(2)	26(2)	32(2)	4(1)	2(1)	2(1)
C(2)	30(2)	44(2)	30(2)	4(2)	1(1)	-2(1)
C(3)	38(2)	48(2)	33(2)	-3(2)	-3(2)	0(2)
C(4)	30(2)	32(2)	31(2)	3(1)	3(1)	1(1)
C(5)	27(2)	27(2)	27(2)	0(1)	2(1)	1(1)
C(6)	30(2)	28(2)	25(2)	2(1)	4(1)	-6(1)
C(7)	25(2)	32(2)	28(2)	-6(1)	5(1)	-4(1)
C(8)	21(1)	31(2)	29(2)	-2(2)	2(1)	0(1)
C(9)	22(2)	27(2)	24(2)	-2(1)	1(1)	-1(1)
C(10)	27(2)	39(2)	34(2)	3(2)	5(1)	-4(1)
C(11)	20(2)	26(2)	24(2)	-3(1)	3(1)	-2(1)
C(12)	20(1)	24(2)	24(2)	-2(1)	3(1)	-1(1)
C(13)	21(1)	25(2)	25(2)	-1(1)	1(1)	0(1)
C(14)	21(2)	26(2)	26(2)	-2(1)	0(1)	-1(1)
C(15)	20(1)	26(2)	28(2)	-2(1)	3(1)	-1(1)
C(16)	22(2)	26(2)	27(2)	0(1)	-3(1)	3(1)
C(17)	25(2)	30(2)	24(2)	3(1)	2(1)	-2(1)
C(18)	20(1)	31(2)	30(2)	-3(1)	3(1)	-2(1)
C(19)	21(2)	26(2)	26(2)	-1(1)	-2(1)	1(1)
C(20)	22(2)	30(2)	31(2)	1(1)	1(1)	0(1)
C(21)	23(2)	33(2)	32(2)	-8(1)	0(1)	3(1)
C(22)	24(2)	32(2)	31(2)	3(1)	2(1)	6(1)
C(23)	26(2)	32(2)	30(2)	3(2)	2(1)	3(1)
C(24)	24(2)	43(2)	38(2)	-3(2)	3(1)	7(1)

Table S24. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^{-3}$) for Sevov_SA1-1591.

	x	y	z	U(eq)
H(1)	2060	8949	5266	32
H(2A)	1088	3833	5256	42
H(2B)	774	6759	4987	42
H(3A)	1646	2852	4488	48
H(3B)	1597	6094	4316	48
H(4A)	2949	6527	4780	38
H(4B)	2845	3645	5089	38
H(5)	3333	9851	5495	33
H(6)	4668	11199	5398	33
H(8)	5551	5302	6405	32
H(10A)	6251	11138	5939	50
H(10B)	6268	8956	5482	50
H(10C)	6562	8039	6064	50
H(15)	4591	-1095	7384	30
H(16)	4124	-4141	7988	31
H(17)	2722	-4189	8127	32
H(18)	1742	-1101	7692	32
H(20)	-9	5451	7055	33
H(22)	-213	11135	5926	35
H(23)	1070	9762	5726	35
H(24A)	-1547	8260	6466	53
H(24B)	-1182	11300	6590	53
H(24C)	-1106	9004	7033	53

X-ray characterization of Complex 2-Cy

Experimental Summary

The single crystal X-ray diffraction studies were carried out on a Bruker Kappa Photon III CPAD diffractometer equipped with Mo K_{α} radiation ($\lambda = 0.71073 \text{ \AA}$). A 0.200 x 0.021 x 0.011 mm piece of a yellow needle was mounted on a MiTeGen MicroMount with Paratone 24EX oil. Data were collected in a nitrogen gas stream at 100(2) K using ϕ and ω scans. Crystal-to-detector distance was 50 mm using variable exposure time (10s-60s) depending on θ with a scan width of 1.0° . Data collection was 99.9% complete to 25.00° in θ ($0.83 \text{ \AA}$). A total of 41925 reflections were collected covering the indices, $-30 \leq h \leq 30$, $-6 \leq k \leq 6$, $-20 \leq l \leq 20$. 3957 reflections were found to be symmetry independent, with a R_{int} of 0.0826. Indexing and unit cell refinement indicated a *C*-centered, monoclinic lattice. The space group was found to be *C*2. The data were integrated using the Bruker SAINT software program and scaled using the SADABS software program. Solution by dual-space method (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. The crystal collected was refined as a racemic twin with a Flack parameter of 0.27(3). Crystallographic data are summarized below.



Table S25. Crystal data and structure refinement for Sevov_SA1-1634.

Report date	2024-05-01	
Identification code	SA1-1634	
Empirical formula	C ₂₆ H ₂₇ N ₅ Ni	
Molecular formula	C ₂₆ H ₂₇ N ₅ Ni	
Formula weight	468.23	
Temperature	100.0 K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	C 1 2 1	
Unit cell dimensions	a = 26.020(3) Å	α = 90°.
	b = 4.9969(5) Å	β = 94.189(3)°.
	c = 16.7347(18) Å	γ = 90°.
Volume	2170.1(4) Å ³	
Z	4	
Density (calculated)	1.433 Mg/m ³	
Absorption coefficient	0.919 mm ⁻¹	
F(000)	984	
Crystal size	0.200 x 0.021 x 0.011 mm ³	
Crystal color, habit	yellow needle	
Theta range for data collection	1.916 to 25.393°.	
Index ranges	-30 ≤ h ≤ 30, -6 ≤ k ≤ 6, -20 ≤ l ≤ 20	
Reflections collected	41925	
Independent reflections	3957 [R(int) = 0.0826, R(sigma) = 0.0412]	
Completeness to theta = 25.000°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.0916 and 0.0632	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	3957 / 98 / 391	
Goodness-of-fit on F ²	1.102	
Final R indices [I > 2sigma(I)]	R1 = 0.0445, wR2 = 0.1010	
R indices (all data)	R1 = 0.0518, wR2 = 0.1044	
Absolute structure parameter	0.27(3)	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.692 and -0.418 e.Å ⁻³	

Table S26. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for Sevov_SA1-1634. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	$U(\text{eq})$
Ni(1)	6071(1)	6430(2)	2481(1)	22(1)
N(1)	6302(2)	7090(9)	1438(3)	23(1)
N(2)	6990(2)	3845(9)	1464(3)	22(1)
N(3)	6693(2)	4627(10)	2770(3)	21(1)
N(4)	6640(2)	4258(10)	4195(3)	24(1)
N(5)	6002(2)	7306(9)	3574(3)	22(1)
C(1)	5318(2)	6756(14)	2130(3)	25(1)
C(2)	4954(3)	5600(20)	2728(5)	31(2)
C(3)	4386(2)	5926(15)	2441(4)	29(2)
C(4)	4263(2)	4614(15)	1634(4)	31(2)
C(5)	4624(3)	5654(13)	1030(4)	32(2)
C(6)	5187(3)	5340(30)	1331(5)	30(2)
C(7)	6076(2)	9226(12)	1033(3)	26(1)
C(8)	6228(4)	10100(30)	316(6)	25(2)
C(9)	6618(2)	8830(12)	-64(3)	25(1)
C(10)	6853(2)	6673(16)	345(3)	27(1)
C(11)	6704(2)	5898(11)	1105(3)	21(1)
C(12)	6772(5)	9760(40)	-869(6)	34(2)
C(13)	6982(2)	3362(11)	2223(3)	22(1)
C(14)	7307(2)	1285(16)	2644(3)	23(1)
C(15)	7209(2)	1455(16)	3453(3)	22(1)
C(16)	6819(2)	3560(11)	3516(3)	22(1)
C(17)	7656(2)	-527(12)	2369(3)	24(1)
C(18)	7906(2)	-2210(12)	2931(3)	27(1)
C(19)	7816(2)	-2057(11)	3746(4)	26(1)
C(20)	7462(2)	-240(13)	4017(3)	24(1)
C(21)	6286(2)	6318(16)	4233(3)	22(1)
C(22)	6229(2)	7345(12)	5001(3)	26(1)
C(23)	5908(2)	9467(12)	5128(3)	26(1)
C(24)	5640(7)	10580(30)	4449(4)	26(2)
C(25)	5693(2)	9468(13)	3715(3)	27(1)

C(26)	5849(9)	10590(50)	5945(4)	32(2)
Ni(1B)	6069(3)	4074(14)	2524(4)	22(1)
N(1B)	6298(12)	3290(70)	1482(15)	23(1)
N(2B)	7030(12)	6320(80)	1479(15)	22(1)
N(3B)	6676(11)	5980(80)	2763(14)	21(1)
N(4B)	6651(14)	6400(90)	4197(15)	24(1)
N(5B)	5993(13)	3420(70)	3631(12)	22(1)
C(1B)	5313(9)	3650(90)	2180(20)	25(1)
C(2B)	4960(16)	5100(200)	2750(30)	31(2)
C(3B)	4391(16)	4640(140)	2460(30)	29(2)
C(4B)	4267(17)	5790(120)	1650(30)	31(2)
C(5B)	4628(19)	4670(170)	1060(30)	32(2)
C(6B)	5191(17)	5000(300)	1360(30)	30(2)
C(7B)	6072(15)	1090(80)	1110(20)	26(1)
C(8B)	6150(40)	300(300)	350(40)	25(2)
C(9B)	6587(15)	1270(100)	0(20)	25(1)
C(10B)	6869(16)	3280(90)	430(20)	27(1)
C(11B)	6701(17)	4400(100)	1140(20)	21(1)
C(12B)	6770(50)	-100(400)	-730(70)	34(2)
C(13B)	6997(14)	6980(70)	2223(15)	22(1)
C(14B)	7320(16)	9120(80)	2628(17)	23(1)
C(15B)	7225(16)	9030(80)	3442(17)	22(1)
C(16B)	6826(14)	6990(80)	3512(14)	22(1)
C(17B)	7683(18)	10840(90)	2360(20)	24(1)
C(18B)	7938(18)	12600(90)	2880(20)	27(1)
C(19B)	7830(17)	12560(90)	3690(20)	26(1)
C(20B)	7470(20)	10840(100)	3970(20)	24(1)
C(21B)	6281(18)	4480(100)	4273(16)	22(1)
C(22B)	6222(19)	3480(90)	5044(18)	26(1)
C(23B)	5919(16)	1300(100)	5199(19)	26(1)
C(24B)	5640(60)	200(300)	4530(20)	26(2)
C(25B)	5707(16)	1160(90)	3780(20)	27(1)
C(26B)	5830(80)	400(400)	6020(30)	32(2)

Table S27. Bond lengths [Å] and angles [°] for Sevov_SA1-1634.

Ni(1)-N(1)	1.917(5)	C(8)-C(9)	1.391(11)
Ni(1)-N(3)	1.884(5)	C(9)-C(10)	1.394(9)
Ni(1)-N(5)	1.901(5)	C(9)-C(12)	1.506(13)
Ni(1)-C(1)	2.012(5)	C(10)-H(10)	0.9500
N(1)-C(7)	1.373(7)	C(10)-C(11)	1.410(7)
N(1)-C(11)	1.359(7)	C(12)-H(12A)	0.9800
N(2)-C(11)	1.379(7)	C(12)-H(12B)	0.9800
N(2)-C(13)	1.296(7)	C(12)-H(12C)	0.9800
N(3)-C(13)	1.380(7)	C(13)-C(14)	1.485(9)
N(3)-C(16)	1.375(7)	C(14)-C(15)	1.398(6)
N(4)-C(16)	1.306(7)	C(14)-C(17)	1.383(8)
N(4)-C(21)	1.385(8)	C(15)-C(16)	1.470(9)
N(5)-C(21)	1.375(7)	C(15)-C(20)	1.397(8)
N(5)-C(25)	1.378(7)	C(17)-H(17)	0.9500
C(1)-H(1)	1.0000	C(17)-C(18)	1.388(8)
C(1)-C(2)	1.539(10)	C(18)-H(18)	0.9500
C(1)-C(6)	1.529(13)	C(18)-C(19)	1.403(8)
C(2)-H(2A)	0.9900	C(19)-H(19)	0.9500
C(2)-H(2B)	0.9900	C(19)-C(20)	1.393(8)
C(2)-C(3)	1.528(8)	C(20)-H(20)	0.9500
C(3)-H(3A)	0.9900	C(21)-C(22)	1.402(7)
C(3)-H(3B)	0.9900	C(22)-H(22)	0.9500
C(3)-C(4)	1.514(8)	C(22)-C(23)	1.376(9)
C(4)-H(4A)	0.9900	C(23)-C(24)	1.404(13)
C(4)-H(4B)	0.9900	C(23)-C(26)	1.495(16)
C(4)-C(5)	1.521(8)	C(24)-H(24)	0.9500
C(5)-H(5A)	0.9900	C(24)-C(25)	1.365(14)
C(5)-H(5B)	0.9900	C(25)-H(25)	0.9500
C(5)-C(6)	1.521(8)	C(26)-H(26A)	0.9800
C(6)-H(6A)	0.9900	C(26)-H(26B)	0.9800
C(6)-H(6B)	0.9900	C(26)-H(26C)	0.9800
C(7)-H(7)	0.9500	Ni(1B)-N(1B)	1.92(2)
C(7)-C(8)	1.362(11)	Ni(1B)-N(3B)	1.863(19)
C(8)-H(8)	0.9500	Ni(1B)-N(5B)	1.907(19)

Ni(1B)-C(1B)	2.02(2)	C(12B)-H(12D)	0.9800
N(1B)-C(7B)	1.37(3)	C(12B)-H(12E)	0.9800
N(1B)-C(11B)	1.35(2)	C(12B)-H(12F)	0.9800
N(2B)-C(11B)	1.38(2)	C(13B)-C(14B)	1.49(2)
N(2B)-C(13B)	1.30(2)	C(14B)-C(15B)	1.40(2)
N(3B)-C(13B)	1.37(2)	C(14B)-C(17B)	1.38(2)
N(3B)-C(16B)	1.38(2)	C(15B)-C(16B)	1.46(2)
N(4B)-C(16B)	1.30(2)	C(15B)-C(20B)	1.38(2)
N(4B)-C(21B)	1.37(2)	C(17B)-H(17B)	0.9500
N(5B)-C(21B)	1.37(2)	C(17B)-C(18B)	1.38(3)
N(5B)-C(25B)	1.38(3)	C(18B)-H(18B)	0.9500
C(1B)-H(1B)	1.0000	C(18B)-C(19B)	1.40(3)
C(1B)-C(2B)	1.54(3)	C(19B)-H(19B)	0.9500
C(1B)-C(6B)	1.54(3)	C(19B)-C(20B)	1.39(3)
C(2B)-H(2BA)	0.9900	C(20B)-H(20B)	0.9500
C(2B)-H(2BB)	0.9900	C(21B)-C(22B)	1.40(2)
C(2B)-C(3B)	1.53(3)	C(22B)-H(22B)	0.9500
C(3B)-H(3BA)	0.9900	C(22B)-C(23B)	1.38(3)
C(3B)-H(3BB)	0.9900	C(23B)-C(24B)	1.41(3)
C(3B)-C(4B)	1.50(3)	C(23B)-C(26B)	1.49(3)
C(4B)-H(4BA)	0.9900	C(24B)-H(24B)	0.9500
C(4B)-H(4BB)	0.9900	C(24B)-C(25B)	1.37(3)
C(4B)-C(5B)	1.52(3)	C(25B)-H(25B)	0.9500
C(5B)-H(5BA)	0.9900	C(26B)-H(26D)	0.9800
C(5B)-H(5BB)	0.9900	C(26B)-H(26E)	0.9800
C(5B)-C(6B)	1.52(3)	C(26B)-H(26F)	0.9800
C(6B)-H(6BA)	0.9900		
C(6B)-H(6BB)	0.9900	N(1)-Ni(1)-C(1)	94.8(2)
C(7B)-H(7B)	0.9500	N(3)-Ni(1)-N(1)	89.76(19)
C(7B)-C(8B)	1.36(3)	N(3)-Ni(1)-N(5)	90.14(19)
C(8B)-H(8B)	0.9500	N(3)-Ni(1)-C(1)	156.1(3)
C(8B)-C(9B)	1.39(3)	N(5)-Ni(1)-N(1)	153.4(2)
C(9B)-C(10B)	1.40(3)	N(5)-Ni(1)-C(1)	96.0(2)
C(9B)-C(12B)	1.51(3)	C(7)-N(1)-Ni(1)	115.6(4)
C(10B)-H(10B)	0.9500	C(11)-N(1)-Ni(1)	126.9(4)
C(10B)-C(11B)	1.41(2)	C(11)-N(1)-C(7)	116.9(5)

C(13)-N(2)-C(11)	121.2(5)	C(6)-C(5)-H(5A)	109.3
C(13)-N(3)-Ni(1)	123.3(4)	C(6)-C(5)-H(5B)	109.3
C(16)-N(3)-Ni(1)	124.3(4)	C(1)-C(6)-H(6A)	109.0
C(16)-N(3)-C(13)	108.6(5)	C(1)-C(6)-H(6B)	109.0
C(16)-N(4)-C(21)	121.3(5)	C(5)-C(6)-C(1)	112.9(7)
C(21)-N(5)-Ni(1)	127.4(4)	C(5)-C(6)-H(6A)	109.0
C(21)-N(5)-C(25)	115.4(5)	C(5)-C(6)-H(6B)	109.0
C(25)-N(5)-Ni(1)	116.3(4)	H(6A)-C(6)-H(6B)	107.8
Ni(1)-C(1)-H(1)	108.0	N(1)-C(7)-H(7)	118.5
C(2)-C(1)-Ni(1)	114.3(4)	C(8)-C(7)-N(1)	122.9(8)
C(2)-C(1)-H(1)	108.0	C(8)-C(7)-H(7)	118.5
C(6)-C(1)-Ni(1)	111.6(4)	C(7)-C(8)-H(8)	119.2
C(6)-C(1)-H(1)	108.0	C(7)-C(8)-C(9)	121.6(13)
C(6)-C(1)-C(2)	106.7(6)	C(9)-C(8)-H(8)	119.2
C(1)-C(2)-H(2A)	109.1	C(8)-C(9)-C(10)	115.9(8)
C(1)-C(2)-H(2B)	109.1	C(8)-C(9)-C(12)	121.3(11)
H(2A)-C(2)-H(2B)	107.8	C(10)-C(9)-C(12)	122.8(9)
C(3)-C(2)-C(1)	112.4(6)	C(9)-C(10)-H(10)	119.4
C(3)-C(2)-H(2A)	109.1	C(9)-C(10)-C(11)	121.1(5)
C(3)-C(2)-H(2B)	109.1	C(11)-C(10)-H(10)	119.4
C(2)-C(3)-H(3A)	109.2	N(1)-C(11)-N(2)	123.8(5)
C(2)-C(3)-H(3B)	109.2	N(1)-C(11)-C(10)	121.3(5)
H(3A)-C(3)-H(3B)	107.9	N(2)-C(11)-C(10)	114.9(5)
C(4)-C(3)-C(2)	111.8(5)	C(9)-C(12)-H(12A)	109.5
C(4)-C(3)-H(3A)	109.2	C(9)-C(12)-H(12B)	109.5
C(4)-C(3)-H(3B)	109.2	C(9)-C(12)-H(12C)	109.5
C(3)-C(4)-H(4A)	109.6	H(12A)-C(12)-H(12B)	109.5
C(3)-C(4)-H(4B)	109.6	H(12A)-C(12)-H(12C)	109.5
C(3)-C(4)-C(5)	110.1(5)	H(12B)-C(12)-H(12C)	109.5
H(4A)-C(4)-H(4B)	108.1	N(2)-C(13)-N(3)	127.9(5)
C(5)-C(4)-H(4A)	109.6	N(2)-C(13)-C(14)	123.1(5)
C(5)-C(4)-H(4B)	109.6	N(3)-C(13)-C(14)	108.9(4)
C(4)-C(5)-H(5A)	109.3	C(15)-C(14)-C(13)	106.2(5)
C(4)-C(5)-H(5B)	109.3	C(17)-C(14)-C(13)	131.6(5)
C(4)-C(5)-C(6)	111.8(5)	C(17)-C(14)-C(15)	122.2(6)
H(5A)-C(5)-H(5B)	107.9	C(14)-C(15)-C(16)	106.8(5)

C(20)-C(15)-C(14)	120.4(6)	H(26A)-C(26)-H(26C)	109.5
C(20)-C(15)-C(16)	132.8(5)	H(26B)-C(26)-H(26C)	109.5
N(3)-C(16)-C(15)	109.5(4)	N(1B)-Ni(1B)-C(1B)	94.4(13)
N(4)-C(16)-N(3)	127.5(5)	N(3B)-Ni(1B)-N(1B)	89.1(11)
N(4)-C(16)-C(15)	123.1(5)	N(3B)-Ni(1B)-N(5B)	91.5(11)
C(14)-C(17)-H(17)	121.4	N(3B)-Ni(1B)-C(1B)	155(2)
C(14)-C(17)-C(18)	117.3(5)	N(5B)-Ni(1B)-N(1B)	155.2(18)
C(18)-C(17)-H(17)	121.4	N(5B)-Ni(1B)-C(1B)	95.3(13)
C(17)-C(18)-H(18)	119.3	C(7B)-N(1B)-Ni(1B)	114.8(19)
C(17)-C(18)-C(19)	121.4(5)	C(11B)-N(1B)-Ni(1B)	127.1(19)
C(19)-C(18)-H(18)	119.3	C(11B)-N(1B)-C(7B)	117(2)
C(18)-C(19)-H(19)	119.5	C(13B)-N(2B)-C(11B)	119(2)
C(20)-C(19)-C(18)	121.0(5)	C(13B)-N(3B)-Ni(1B)	126.4(17)
C(20)-C(19)-H(19)	119.5	C(13B)-N(3B)-C(16B)	108.7(18)
C(15)-C(20)-H(20)	121.1	C(16B)-N(3B)-Ni(1B)	124.1(17)
C(19)-C(20)-C(15)	117.7(5)	C(16B)-N(4B)-C(21B)	122(3)
C(19)-C(20)-H(20)	121.1	C(21B)-N(5B)-Ni(1B)	127.2(19)
N(4)-C(21)-C(22)	115.5(5)	C(21B)-N(5B)-C(25B)	117(2)
N(5)-C(21)-N(4)	123.3(5)	C(25B)-N(5B)-Ni(1B)	114(2)
N(5)-C(21)-C(22)	121.1(6)	Ni(1B)-C(1B)-H(1B)	109.8
C(21)-C(22)-H(22)	119.0	C(2B)-C(1B)-Ni(1B)	113(2)
C(23)-C(22)-C(21)	122.1(6)	C(2B)-C(1B)-H(1B)	109.8
C(23)-C(22)-H(22)	119.0	C(6B)-C(1B)-Ni(1B)	110(2)
C(22)-C(23)-C(24)	116.8(9)	C(6B)-C(1B)-H(1B)	109.8
C(22)-C(23)-C(26)	122.3(12)	C(6B)-C(1B)-C(2B)	105(4)
C(24)-C(23)-C(26)	120.9(14)	C(1B)-C(2B)-H(2BA)	109.5
C(23)-C(24)-H(24)	120.3	C(1B)-C(2B)-H(2BB)	109.5
C(25)-C(24)-C(23)	119.3(16)	H(2BA)-C(2B)-H(2BB)	108.1
C(25)-C(24)-H(24)	120.3	C(3B)-C(2B)-C(1B)	111(4)
N(5)-C(25)-H(25)	117.5	C(3B)-C(2B)-H(2BA)	109.5
C(24)-C(25)-N(5)	125.0(10)	C(3B)-C(2B)-H(2BB)	109.5
C(24)-C(25)-H(25)	117.5	C(2B)-C(3B)-H(3BA)	109.3
C(23)-C(26)-H(26A)	109.5	C(2B)-C(3B)-H(3BB)	109.3
C(23)-C(26)-H(26B)	109.5	H(3BA)-C(3B)-H(3BB)	108.0
C(23)-C(26)-H(26C)	109.5	C(4B)-C(3B)-C(2B)	111(4)
H(26A)-C(26)-H(26B)	109.5	C(4B)-C(3B)-H(3BA)	109.3

C(4B)-C(3B)-H(3BB)	109.3	C(9B)-C(12B)-H(12F)	109.5
C(3B)-C(4B)-H(4BA)	109.5	H(12D)-C(12B)-H(12E)	109.5
C(3B)-C(4B)-H(4BB)	109.5	H(12D)-C(12B)-H(12F)	109.5
C(3B)-C(4B)-C(5B)	111(3)	H(12E)-C(12B)-H(12F)	109.5
H(4BA)-C(4B)-H(4BB)	108.1	N(2B)-C(13B)-N(3B)	129(2)
C(5B)-C(4B)-H(4BA)	109.5	N(2B)-C(13B)-C(14B)	123(2)
C(5B)-C(4B)-H(4BB)	109.5	N(3B)-C(13B)-C(14B)	108.2(19)
C(4B)-C(5B)-H(5BA)	109.3	C(15B)-C(14B)-C(13B)	107(2)
C(4B)-C(5B)-H(5BB)	109.3	C(17B)-C(14B)-C(13B)	133(2)
C(4B)-C(5B)-C(6B)	112(4)	C(17B)-C(14B)-C(15B)	121(2)
H(5BA)-C(5B)-H(5BB)	107.9	C(14B)-C(15B)-C(16B)	106.1(19)
C(6B)-C(5B)-H(5BA)	109.3	C(20B)-C(15B)-C(14B)	120(2)
C(6B)-C(5B)-H(5BB)	109.3	C(20B)-C(15B)-C(16B)	134(2)
C(1B)-C(6B)-H(6BA)	109.2	N(3B)-C(16B)-C(15B)	109.6(19)
C(1B)-C(6B)-H(6BB)	109.2	N(4B)-C(16B)-N(3B)	129(2)
C(5B)-C(6B)-C(1B)	112(4)	N(4B)-C(16B)-C(15B)	122(2)
C(5B)-C(6B)-H(6BA)	109.2	C(14B)-C(17B)-H(17B)	120.0
C(5B)-C(6B)-H(6BB)	109.2	C(18B)-C(17B)-C(14B)	120(3)
H(6BA)-C(6B)-H(6BB)	107.9	C(18B)-C(17B)-H(17B)	120.0
N(1B)-C(7B)-H(7B)	118.2	C(17B)-C(18B)-H(18B)	120.5
C(8B)-C(7B)-N(1B)	124(4)	C(17B)-C(18B)-C(19B)	119(3)
C(8B)-C(7B)-H(7B)	118.2	C(19B)-C(18B)-H(18B)	120.5
C(7B)-C(8B)-H(8B)	120.5	C(18B)-C(19B)-H(19B)	119.2
C(7B)-C(8B)-C(9B)	119(3)	C(20B)-C(19B)-C(18B)	122(3)
C(9B)-C(8B)-H(8B)	120.5	C(20B)-C(19B)-H(19B)	119.2
C(8B)-C(9B)-C(10B)	116(3)	C(15B)-C(20B)-C(19B)	119(3)
C(8B)-C(9B)-C(12B)	120(4)	C(15B)-C(20B)-H(20B)	120.7
C(10B)-C(9B)-C(12B)	124(4)	C(19B)-C(20B)-H(20B)	120.7
C(9B)-C(10B)-H(10B)	119.0	N(4B)-C(21B)-N(5B)	123(2)
C(9B)-C(10B)-C(11B)	122(3)	N(4B)-C(21B)-C(22B)	117(2)
C(11B)-C(10B)-H(10B)	119.0	N(5B)-C(21B)-C(22B)	119(2)
N(1B)-C(11B)-N(2B)	126(2)	C(21B)-C(22B)-H(22B)	118.1
N(1B)-C(11B)-C(10B)	119(2)	C(23B)-C(22B)-C(21B)	124(3)
N(2B)-C(11B)-C(10B)	114(2)	C(23B)-C(22B)-H(22B)	118.1
C(9B)-C(12B)-H(12D)	109.5	C(22B)-C(23B)-C(24B)	116(3)
C(9B)-C(12B)-H(12E)	109.5	C(22B)-C(23B)-C(26B)	123(4)

C(24B)-C(23B)-C(26B)	121(4)
C(23B)-C(24B)-H(24B)	120.1
C(25B)-C(24B)-C(23B)	120(3)
C(25B)-C(24B)-H(24B)	120.1
N(5B)-C(25B)-H(25B)	117.9
C(24B)-C(25B)-N(5B)	124(3)
C(24B)-C(25B)-H(25B)	117.9
C(23B)-C(26B)-H(26D)	109.5
C(23B)-C(26B)-H(26E)	109.5
C(23B)-C(26B)-H(26F)	109.5
H(26D)-C(26B)-H(26E)	109.5
H(26D)-C(26B)-H(26F)	109.5
H(26E)-C(26B)-H(26F)	109.5

Table S28. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for Sevov_SA1-1634. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U^{11} + \dots + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Ni(1)	24(1)	22(1)	22(1)	0(1)	2(1)	2(1)
N(1)	26(2)	20(3)	24(2)	2(2)	-1(2)	1(2)
N(2)	21(3)	21(3)	24(2)	1(2)	2(2)	3(2)
N(3)	24(2)	19(3)	20(2)	0(2)	4(2)	2(2)
N(4)	28(3)	20(2)	24(2)	1(2)	2(2)	3(2)
N(5)	23(2)	19(3)	26(2)	0(2)	2(2)	-1(2)
C(1)	29(3)	20(3)	26(2)	1(3)	4(2)	2(3)
C(2)	27(3)	31(7)	35(3)	6(3)	1(2)	1(2)
C(3)	25(3)	24(5)	37(3)	5(3)	5(2)	0(3)
C(4)	20(3)	27(4)	45(3)	2(3)	-1(3)	-2(3)
C(5)	36(3)	33(6)	27(3)	-5(3)	1(2)	-5(3)
C(6)	29(3)	26(5)	35(3)	-3(2)	3(2)	-1(3)
C(7)	27(3)	22(3)	27(3)	-1(3)	1(2)	7(3)
C(8)	26(4)	22(4)	26(3)	2(2)	-2(2)	4(4)
C(9)	24(3)	27(3)	24(3)	4(2)	3(2)	-1(3)
C(10)	25(3)	29(3)	26(2)	1(3)	1(2)	4(3)
C(11)	22(3)	15(4)	26(2)	-2(2)	-2(2)	0(2)
C(12)	34(3)	40(5)	28(6)	11(4)	5(4)	3(3)
C(13)	19(3)	16(3)	29(3)	-3(2)	2(2)	-1(2)
C(14)	24(3)	18(3)	25(2)	-1(3)	-1(2)	1(3)
C(15)	26(3)	18(2)	24(2)	2(3)	0(2)	1(4)
C(16)	25(3)	18(3)	23(3)	-4(2)	2(2)	-2(2)
C(17)	23(3)	23(3)	25(3)	-3(3)	1(2)	1(3)
C(18)	30(3)	20(3)	30(3)	-1(2)	2(3)	3(3)
C(19)	25(3)	21(3)	32(3)	3(2)	2(3)	1(2)
C(20)	23(3)	25(4)	24(3)	4(3)	3(2)	-3(3)
C(21)	23(3)	21(3)	24(2)	-1(3)	4(2)	-2(4)
C(22)	22(3)	29(3)	26(3)	2(2)	-1(2)	-3(2)
C(23)	23(3)	28(3)	27(3)	-3(3)	5(2)	-6(3)
C(24)	25(3)	22(7)	32(3)	-4(2)	4(3)	0(3)
C(25)	22(3)	30(3)	29(3)	-1(3)	3(2)	3(3)

C(26)	33(4)	39(6)	25(3)	-6(3)	8(3)	-2(3)
Ni(1B)	24(1)	22(1)	22(1)	0(1)	2(1)	2(1)
N(1B)	26(2)	20(3)	24(2)	2(2)	-1(2)	1(2)
N(2B)	21(3)	21(3)	24(2)	1(2)	2(2)	3(2)
N(3B)	24(2)	19(3)	20(2)	0(2)	4(2)	2(2)
N(4B)	28(3)	20(2)	24(2)	1(2)	2(2)	3(2)
N(5B)	23(2)	19(3)	26(2)	0(2)	2(2)	-1(2)
C(1B)	29(3)	20(3)	26(2)	1(3)	4(2)	2(3)
C(2B)	27(3)	31(7)	35(3)	6(3)	1(2)	1(2)
C(3B)	25(3)	24(5)	37(3)	5(3)	5(2)	0(3)
C(4B)	20(3)	27(4)	45(3)	2(3)	-1(3)	-2(3)
C(5B)	36(3)	33(6)	27(3)	-5(3)	1(2)	-5(3)
C(6B)	29(3)	26(5)	35(3)	-3(2)	3(2)	-1(3)
C(7B)	27(3)	22(3)	27(3)	-1(3)	1(2)	7(3)
C(8B)	26(4)	22(4)	26(3)	2(2)	-2(2)	4(4)
C(9B)	24(3)	27(3)	24(3)	4(2)	3(2)	-1(3)
C(10B)	25(3)	29(3)	26(2)	1(3)	1(2)	4(3)
C(11B)	22(3)	15(4)	26(2)	-2(2)	-2(2)	0(2)
C(12B)	34(3)	40(5)	28(6)	11(4)	5(4)	3(3)
C(13B)	19(3)	16(3)	29(3)	-3(2)	2(2)	-1(2)
C(14B)	24(3)	18(3)	25(2)	-1(3)	-1(2)	1(3)
C(15B)	26(3)	18(2)	24(2)	2(3)	0(2)	1(4)
C(16B)	25(3)	18(3)	23(3)	-4(2)	2(2)	-2(2)
C(17B)	23(3)	23(3)	25(3)	-3(3)	1(2)	1(3)
C(18B)	30(3)	20(3)	30(3)	-1(2)	2(3)	3(3)
C(19B)	25(3)	21(3)	32(3)	3(2)	2(3)	1(2)
C(20B)	23(3)	25(4)	24(3)	4(3)	3(2)	-3(3)
C(21B)	23(3)	21(3)	24(2)	-1(3)	4(2)	-2(4)
C(22B)	22(3)	29(3)	26(3)	2(2)	-1(2)	-3(2)
C(23B)	23(3)	28(3)	27(3)	-3(3)	5(2)	-6(3)
C(24B)	25(3)	22(7)	32(3)	-4(2)	4(3)	0(3)
C(25B)	22(3)	30(3)	29(3)	-1(3)	3(2)	3(3)
C(26B)	33(4)	39(6)	25(3)	-6(3)	8(3)	-2(3)

Table S29. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^{-3}$) for Sevov_SA1-1634.

	x	y	z	U(eq)
H(1)	5236	8700	2056	30
H(2A)	5031	3678	2811	37
H(2B)	5019	6521	3250	37
H(3A)	4170	5116	2839	34
H(3B)	4301	7855	2401	34
H(4A)	3902	5007	1443	37
H(4B)	4301	2650	1687	37
H(5A)	4550	7569	922	39
H(5B)	4561	4663	520	39
H(6A)	5407	6072	925	36
H(6B)	5267	3411	1394	36
H(7)	5802	10133	1263	31
H(8)	6063	11618	69	30
H(10)	7117	5710	109	32
H(12A)	6496	9335	-1281	51
H(12B)	7089	8845	-996	51
H(12C)	6830	11695	-855	51
H(17)	7720	-615	1818	28
H(18)	8144	-3494	2759	32
H(19)	7999	-3209	4118	31
H(20)	7395	-157	4567	29
H(22)	6417	6551	5448	31
H(24)	5424	12093	4500	32
H(25)	5503	10244	3268	32
H(26A)	5934	12495	5950	48
H(26B)	6081	9642	6337	48
H(26C)	5492	10351	6083	48
H(1B)	5223	1705	2138	30
H(2BA)	5026	4343	3296	37
H(2BB)	5038	7005	2762	37

H(3BA)	4314	2702	2456	34
H(3BB)	4171	5503	2849	34
H(4BA)	4302	7764	1668	37
H(4BB)	3907	5358	1463	37
H(5BA)	4566	5595	536	39
H(5BB)	4552	2742	970	39
H(6BA)	5272	6934	1405	36
H(6BB)	5413	4219	962	36
H(7B)	5846	40	1404	31
H(8B)	5920	-841	64	30
H(10B)	7182	3891	236	32
H(12D)	6757	-2033	-658	51
H(12E)	7120	471	-811	51
H(12F)	6540	413	-1200	51
H(17B)	7757	10821	1811	28
H(18B)	8183	13818	2700	32
H(19B)	8011	13742	4057	31
H(20B)	7381	10914	4514	29
H(22B)	6401	4357	5485	31
H(24B)	5408	-1251	4595	32
H(25B)	5545	239	3333	32
H(26D)	5552	1388	6236	48
H(26E)	6149	605	6373	48
H(26F)	5740	-1545	6008	48

X-ray characterization of complex 24

Experimental Summary

The single crystal X-ray diffraction studies were carried out on a Bruker Kappa Photon III CPAD diffractometer equipped with Mo K $_{\alpha}$ radiation ($\lambda = 0.71073 \text{ \AA}$). A 0.416 x 0.311 x 0.178 mm piece of a purple block was mounted on a MiTeGen MicroMount with Paratone 24EX oil. Data were collected in a nitrogen gas stream at 100(2) K using ϕ and ω scans. Crystal-to-detector distance was 50 mm using variable exposure time (1s-3s) depending on θ with a scan width of 1.0°. Data collection was 99.5% complete to 25.00° in θ (0.83Å). A total of 57946 reflections were collected covering the indices, $-10 \leq h \leq 10$, $-14 \leq k \leq 14$, $-16 \leq l \leq 15$. 4637 reflections were found to be symmetry independent, with a R_{int} of 0.0263. Indexing and unit cell refinement indicated a primitive, triclinic lattice. The space group was found to be $P\bar{1}$. The data were integrated using the Bruker SAINT software program and scaled using the SADABS software program. Solution by dual-space method (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.

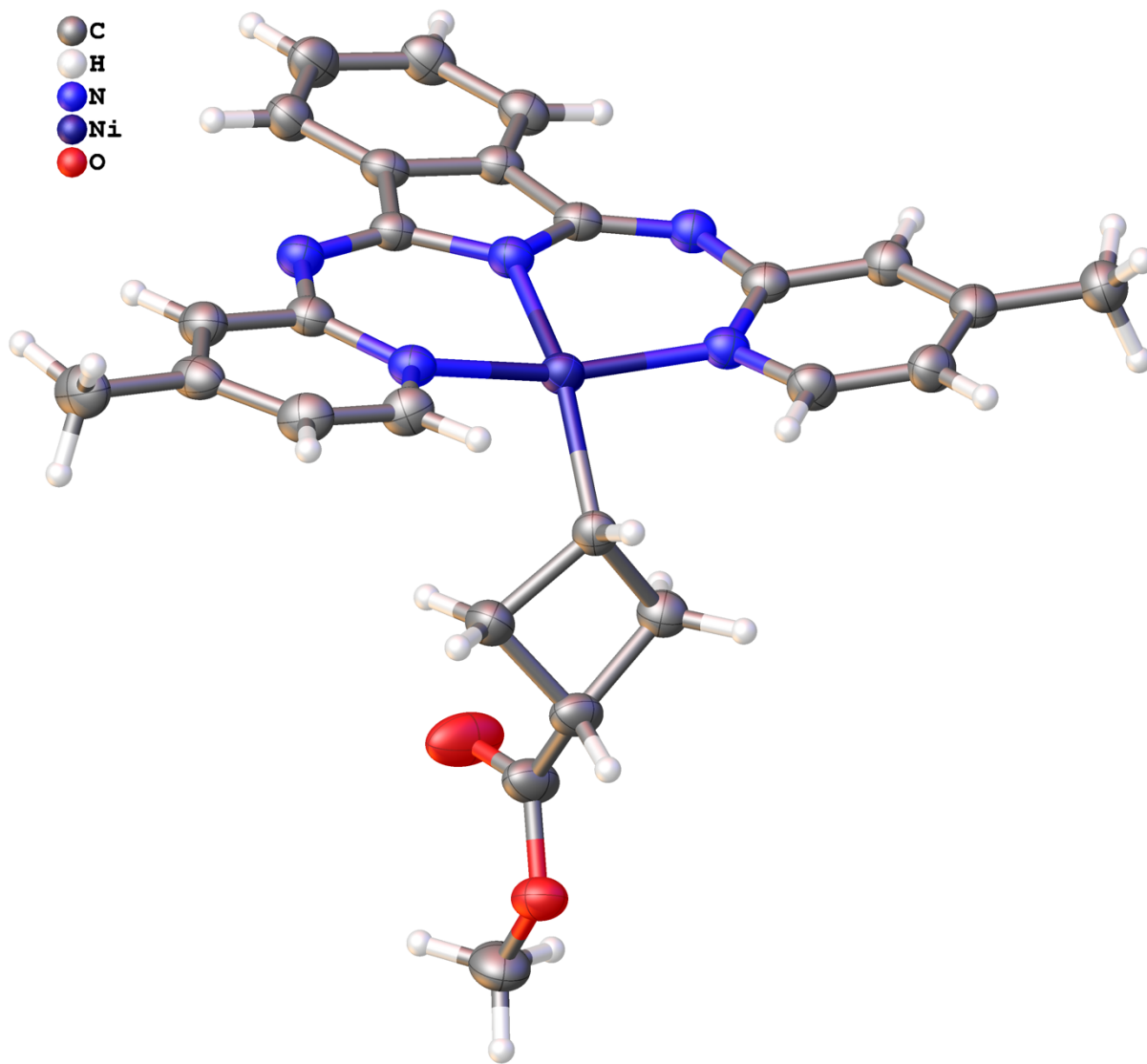


Table S30. Crystal data and structure refinement for Sevov_SA1-1382.

Report date	2024-05-01	
Identification code	SA1-1382	
Empirical formula	C ₂₆ H ₂₅ N ₅ Ni O ₂	
Molecular formula	C ₂₆ H ₂₅ N ₅ Ni O ₂	
Formula weight	498.22	
Temperature	100.00 K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 8.1484(4) Å	α = 96.308(2)°.
	b = 11.4532(7) Å	β = 92.804(2)°.
	c = 12.7770(8) Å	γ = 106.925(2)°.
Volume	1129.75(11) Å ³	
Z	2	
Density (calculated)	1.465 Mg/m ³	
Absorption coefficient	0.894 mm ⁻¹	
F(000)	520	
Crystal size	0.416 x 0.311 x 0.178 mm ³	
Crystal color, habit	purple block	
Theta range for data collection	3.180 to 26.479°.	
Index ranges	-10 ≤ h ≤ 10, -14 ≤ k ≤ 14, -16 ≤ l ≤ 15	
Reflections collected	57946	
Independent reflections	4637 [R(int) = 0.0263, R(sigma) = 0.0140]	
Completeness to theta = 25.000°	99.5 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.0932 and 0.0661	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	4637 / 45 / 356	
Goodness-of-fit on F ²	1.083	
Final R indices [I > 2σ(I)]	R1 = 0.0261, wR2 = 0.0666	
R indices (all data)	R1 = 0.0294, wR2 = 0.0694	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.277 and -0.202 e.Å ⁻³	

Table S31. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for Sevov_SA1-1382. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	$U(\text{eq})$
Ni(1)	7333(1)	3564(1)	7085(1)	25(1)
O(1)	1408(11)	1301(6)	6670(6)	57(2)
O(1B)	2058(8)	-951(5)	6096(6)	60(2)
O(1C)	1579(11)	1075(7)	7087(5)	62(2)
O(2)	903(2)	-701(2)	6075(1)	38(1)
O(2B)	551(6)	346(5)	6493(4)	40(2)
N(1)	8011(2)	3074(1)	8383(1)	27(1)
N(2)	7466(2)	4680(1)	9600(1)	29(1)
N(3)	7341(2)	5104(1)	7798(1)	26(1)
N(4)	6752(2)	6078(1)	6309(1)	27(1)
N(5)	7411(2)	4176(1)	5741(1)	27(1)
C(1)	6348(2)	1863(1)	6434(1)	27(1)
C(2)	4711(2)	1655(2)	5675(1)	33(1)
C(3)	3789(3)	533(2)	6180(2)	35(1)
C(3B)	3583(8)	1191(6)	6621(5)	30(2)
C(4)	5176(2)	991(2)	7128(1)	38(1)
C(5)	1971(6)	411(3)	6422(4)	41(1)
C(5B)	2010(18)	66(10)	6371(11)	33(2)
C(6)	-909(2)	-832(2)	6267(2)	49(1)
C(7)	8675(2)	2103(2)	8313(1)	32(1)
C(8)	9129(2)	1606(2)	9168(1)	35(1)
C(9)	8920(2)	2088(2)	10186(1)	33(1)
C(10)	8363(2)	3118(2)	10269(1)	32(1)
C(11)	7949(2)	3625(1)	9376(1)	28(1)
C(12)	9278(3)	1511(2)	11138(2)	41(1)
C(13)	7214(2)	5323(1)	8864(1)	27(1)
C(14)	6681(2)	6450(1)	9088(1)	28(1)
C(15)	6416(2)	6835(1)	8118(1)	27(1)
C(16)	6842(2)	5969(1)	7308(1)	26(1)
C(17)	6472(2)	7103(2)	10027(1)	32(1)
C(18)	5986(2)	8164(2)	9951(1)	36(1)

C(19)	5691(2)	8538(2)	8977(1)	35(1)
C(20)	5888(2)	7875(1)	8036(1)	30(1)
C(21)	7186(2)	5274(1)	5559(1)	27(1)
C(22)	7373(2)	5669(2)	4560(1)	30(1)
C(23)	7824(2)	5001(2)	3723(1)	30(1)
C(24)	8122(2)	3902(2)	3932(1)	33(1)
C(25)	7905(2)	3537(2)	4912(1)	32(1)
C(26)	7975(2)	5429(2)	2654(1)	37(1)

Table S32. Bond lengths [Å] and angles [°] for Sevov_SA1-1382.

Ni(1)-N(1)	1.9151(13)	C(3B)-C(4)	1.510(7)
Ni(1)-N(3)	1.8928(13)	C(3B)-C(5B)	1.521(15)
Ni(1)-N(5)	1.9208(13)	C(4)-H(4AA)	0.9900
Ni(1)-C(1)	1.9493(15)	C(4)-H(4AB)	0.9900
O(1)-C(5)	1.251(7)	C(4)-H(4BC)	0.9900
O(1B)-C(5B)	1.191(12)	C(4)-H(4BD)	0.9900
O(1C)-C(5)	1.194(7)	C(6)-H(6AA)	0.9800
O(2)-C(5)	1.330(4)	C(6)-H(6AB)	0.9800
O(2)-C(6)	1.476(3)	C(6)-H(6AC)	0.9800
O(2B)-C(5B)	1.331(13)	C(6)-H(6BD)	0.9800
O(2B)-C(6)	1.506(5)	C(6)-H(6BE)	0.9800
N(1)-C(7)	1.367(2)	C(6)-H(6BF)	0.9800
N(1)-C(11)	1.364(2)	C(7)-H(7)	0.9500
N(2)-C(11)	1.381(2)	C(7)-C(8)	1.369(2)
N(2)-C(13)	1.299(2)	C(8)-H(8)	0.9500
N(3)-C(13)	1.371(2)	C(8)-C(9)	1.394(3)
N(3)-C(16)	1.372(2)	C(9)-C(10)	1.377(2)
N(4)-C(16)	1.297(2)	C(9)-C(12)	1.503(2)
N(4)-C(21)	1.386(2)	C(10)-H(10)	0.9500
N(5)-C(21)	1.365(2)	C(10)-C(11)	1.406(2)
N(5)-C(25)	1.364(2)	C(12)-H(12A)	0.9800
C(1)-H(1)	1.0000	C(12)-H(12B)	0.9800
C(1)-C(2)	1.554(2)	C(12)-H(12C)	0.9800
C(1)-C(4)	1.554(2)	C(13)-C(14)	1.481(2)
C(2)-H(2AA)	0.9900	C(14)-C(15)	1.389(2)
C(2)-H(2AB)	0.9900	C(14)-C(17)	1.387(2)
C(2)-H(2BC)	0.9900	C(15)-C(16)	1.478(2)
C(2)-H(2BD)	0.9900	C(15)-C(20)	1.392(2)
C(2)-C(3)	1.516(3)	C(17)-H(17)	0.9500
C(2)-C(3B)	1.598(6)	C(17)-C(18)	1.394(2)
C(3)-H(3)	1.0000	C(18)-H(18)	0.9500
C(3)-C(4)	1.550(3)	C(18)-C(19)	1.392(3)
C(3)-C(5)	1.498(5)	C(19)-H(19)	0.9500
C(3B)-H(3B)	1.0000	C(19)-C(20)	1.392(2)

C(20)-H(20)	0.9500	C(4)-C(1)-Ni(1)	115.31(11)
C(21)-C(22)	1.401(2)	C(4)-C(1)-H(1)	112.9
C(22)-H(22)	0.9500	C(1)-C(2)-H(2AA)	113.6
C(22)-C(23)	1.373(2)	C(1)-C(2)-H(2AB)	113.6
C(23)-C(24)	1.401(2)	C(1)-C(2)-H(2BC)	114.0
C(23)-C(26)	1.499(2)	C(1)-C(2)-H(2BD)	114.0
C(24)-H(24)	0.9500	C(1)-C(2)-C(3B)	88.1(3)
C(24)-C(25)	1.367(2)	H(2AA)-C(2)-H(2AB)	110.8
C(25)-H(25)	0.9500	H(2BC)-C(2)-H(2BD)	111.2
C(26)-H(26A)	0.9800	C(3)-C(2)-C(1)	90.42(14)
C(26)-H(26B)	0.9800	C(3)-C(2)-H(2AA)	113.6
C(26)-H(26C)	0.9800	C(3)-C(2)-H(2AB)	113.6
		C(3B)-C(2)-H(2BC)	114.0
N(1)-Ni(1)-N(5)	162.05(6)	C(3B)-C(2)-H(2BD)	114.0
N(1)-Ni(1)-C(1)	92.36(6)	C(2)-C(3)-H(3)	111.2
N(3)-Ni(1)-N(1)	90.75(6)	C(2)-C(3)-C(4)	88.49(15)
N(3)-Ni(1)-N(5)	91.62(6)	C(4)-C(3)-H(3)	111.2
N(3)-Ni(1)-C(1)	156.80(6)	C(5)-C(3)-C(2)	116.6(2)
N(5)-Ni(1)-C(1)	92.43(6)	C(5)-C(3)-H(3)	111.2
C(5)-O(2)-C(6)	113.7(2)	C(5)-C(3)-C(4)	116.3(3)
C(5B)-O(2B)-C(6)	107.6(6)	C(2)-C(3B)-H(3B)	111.0
C(7)-N(1)-Ni(1)	117.22(11)	C(4)-C(3B)-C(2)	87.0(3)
C(11)-N(1)-Ni(1)	126.25(11)	C(4)-C(3B)-H(3B)	111.0
C(11)-N(1)-C(7)	116.50(14)	C(4)-C(3B)-C(5B)	116.6(7)
C(13)-N(2)-C(11)	121.73(14)	C(5B)-C(3B)-C(2)	118.2(7)
C(13)-N(3)-Ni(1)	123.96(10)	C(5B)-C(3B)-H(3B)	111.0
C(13)-N(3)-C(16)	108.94(13)	C(1)-C(4)-H(4AA)	113.8
C(16)-N(3)-Ni(1)	123.14(11)	C(1)-C(4)-H(4AB)	113.8
C(16)-N(4)-C(21)	122.00(13)	C(1)-C(4)-H(4BC)	113.4
C(21)-N(5)-Ni(1)	125.55(11)	C(1)-C(4)-H(4BD)	113.4
C(25)-N(5)-Ni(1)	118.32(11)	C(3)-C(4)-C(1)	89.16(14)
C(25)-N(5)-C(21)	115.77(14)	C(3)-C(4)-H(4AA)	113.8
Ni(1)-C(1)-H(1)	112.9	C(3)-C(4)-H(4AB)	113.8
C(2)-C(1)-Ni(1)	113.48(11)	C(3B)-C(4)-C(1)	91.3(3)
C(2)-C(1)-H(1)	112.9	C(3B)-C(4)-H(4BC)	113.4
C(2)-C(1)-C(4)	87.01(12)	C(3B)-C(4)-H(4BD)	113.4

H(4AA)-C(4)-H(4AB)	111.0	N(2)-C(11)-C(10)	114.64(15)
H(4BC)-C(4)-H(4BD)	110.7	C(9)-C(12)-H(12A)	109.5
O(1)-C(5)-O(2)	120.9(6)	C(9)-C(12)-H(12B)	109.5
O(1)-C(5)-C(3)	124.3(5)	C(9)-C(12)-H(12C)	109.5
O(1C)-C(5)-O(2)	120.5(6)	H(12A)-C(12)-H(12B)	109.5
O(1C)-C(5)-C(3)	123.9(6)	H(12A)-C(12)-H(12C)	109.5
O(2)-C(5)-C(3)	112.5(3)	H(12B)-C(12)-H(12C)	109.5
O(1B)-C(5B)-O(2B)	123.3(12)	N(2)-C(13)-N(3)	128.64(14)
O(1B)-C(5B)-C(3B)	124.6(11)	N(2)-C(13)-C(14)	122.44(14)
O(2B)-C(5B)-C(3B)	112.0(8)	N(3)-C(13)-C(14)	108.90(13)
O(2)-C(6)-H(6AA)	109.5	C(15)-C(14)-C(13)	106.45(14)
O(2)-C(6)-H(6AB)	109.5	C(17)-C(14)-C(13)	132.09(15)
O(2)-C(6)-H(6AC)	109.5	C(17)-C(14)-C(15)	121.45(15)
O(2B)-C(6)-H(6BD)	109.5	C(14)-C(15)-C(16)	106.68(13)
O(2B)-C(6)-H(6BE)	109.5	C(14)-C(15)-C(20)	121.77(15)
O(2B)-C(6)-H(6BF)	109.5	C(20)-C(15)-C(16)	131.53(15)
H(6AA)-C(6)-H(6AB)	109.5	N(3)-C(16)-C(15)	108.93(13)
H(6AA)-C(6)-H(6AC)	109.5	N(4)-C(16)-N(3)	128.54(14)
H(6AB)-C(6)-H(6AC)	109.5	N(4)-C(16)-C(15)	122.52(14)
H(6BD)-C(6)-H(6BE)	109.5	C(14)-C(17)-H(17)	121.5
H(6BD)-C(6)-H(6BF)	109.5	C(14)-C(17)-C(18)	117.00(16)
H(6BE)-C(6)-H(6BF)	109.5	C(18)-C(17)-H(17)	121.5
N(1)-C(7)-H(7)	118.0	C(17)-C(18)-H(18)	119.2
N(1)-C(7)-C(8)	123.91(16)	C(19)-C(18)-C(17)	121.57(16)
C(8)-C(7)-H(7)	118.0	C(19)-C(18)-H(18)	119.2
C(7)-C(8)-H(8)	120.0	C(18)-C(19)-H(19)	119.3
C(7)-C(8)-C(9)	120.09(16)	C(20)-C(19)-C(18)	121.34(15)
C(9)-C(8)-H(8)	120.0	C(20)-C(19)-H(19)	119.3
C(8)-C(9)-C(12)	121.70(16)	C(15)-C(20)-H(20)	121.6
C(10)-C(9)-C(8)	116.42(15)	C(19)-C(20)-C(15)	116.84(16)
C(10)-C(9)-C(12)	121.88(17)	C(19)-C(20)-H(20)	121.6
C(9)-C(10)-H(10)	119.0	N(4)-C(21)-C(22)	114.39(14)
C(9)-C(10)-C(11)	122.00(16)	N(5)-C(21)-N(4)	124.57(14)
C(11)-C(10)-H(10)	119.0	N(5)-C(21)-C(22)	121.04(14)
N(1)-C(11)-N(2)	124.72(14)	C(21)-C(22)-H(22)	118.7
N(1)-C(11)-C(10)	120.63(15)	C(23)-C(22)-C(21)	122.61(15)

C(23)-C(22)-H(22)	118.7
C(22)-C(23)-C(24)	115.80(15)
C(22)-C(23)-C(26)	121.62(15)
C(24)-C(23)-C(26)	122.58(15)
C(23)-C(24)-H(24)	120.0
C(25)-C(24)-C(23)	119.96(15)
C(25)-C(24)-H(24)	120.0
N(5)-C(25)-C(24)	124.74(15)
N(5)-C(25)-H(25)	117.6
C(24)-C(25)-H(25)	117.6
C(23)-C(26)-H(26A)	109.5
C(23)-C(26)-H(26B)	109.5
C(23)-C(26)-H(26C)	109.5
H(26A)-C(26)-H(26B)	109.5
H(26A)-C(26)-H(26C)	109.5
H(26B)-C(26)-H(26C)	109.5

Table S33. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for Sevov_SA1-1382. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U^{11} + \dots + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Ni(1)	28(1)	21(1)	28(1)	3(1)	3(1)	8(1)
O(1)	48(3)	33(2)	85(5)	-6(3)	29(4)	8(2)
O(1B)	43(3)	28(2)	105(5)	-12(2)	17(3)	7(2)
O(1C)	46(3)	53(4)	75(4)	-26(3)	20(3)	5(3)
O(2)	37(1)	28(1)	43(1)	2(1)	1(1)	4(1)
O(2B)	30(3)	33(3)	56(3)	6(2)	7(2)	9(2)
N(1)	26(1)	23(1)	32(1)	4(1)	1(1)	7(1)
N(2)	32(1)	24(1)	31(1)	4(1)	2(1)	7(1)
N(3)	27(1)	22(1)	30(1)	4(1)	2(1)	7(1)
N(4)	27(1)	24(1)	31(1)	3(1)	2(1)	9(1)
N(5)	26(1)	23(1)	30(1)	3(1)	3(1)	7(1)
C(1)	32(1)	23(1)	28(1)	3(1)	3(1)	10(1)
C(2)	31(1)	32(1)	36(1)	4(1)	3(1)	8(1)
C(3)	36(1)	26(1)	38(1)	-4(1)	7(1)	5(1)
C(3B)	31(3)	24(3)	33(3)	-5(2)	10(2)	7(2)
C(4)	43(1)	30(1)	34(1)	6(1)	3(1)	2(1)
C(5)	41(2)	31(2)	44(2)	-5(2)	14(1)	2(1)
C(5B)	35(3)	26(3)	35(5)	-1(3)	5(2)	8(3)
C(6)	34(1)	52(1)	53(1)	8(1)	2(1)	-3(1)
C(7)	32(1)	30(1)	37(1)	2(1)	0(1)	14(1)
C(8)	33(1)	31(1)	43(1)	5(1)	-2(1)	14(1)
C(9)	28(1)	29(1)	40(1)	9(1)	-4(1)	5(1)
C(10)	33(1)	29(1)	32(1)	5(1)	0(1)	7(1)
C(11)	24(1)	24(1)	33(1)	4(1)	2(1)	4(1)
C(12)	45(1)	36(1)	43(1)	12(1)	-6(1)	13(1)
C(13)	24(1)	22(1)	32(1)	2(1)	3(1)	4(1)
C(14)	26(1)	22(1)	34(1)	3(1)	5(1)	4(1)
C(15)	23(1)	22(1)	33(1)	2(1)	4(1)	5(1)
C(16)	23(1)	21(1)	33(1)	3(1)	2(1)	5(1)
C(17)	35(1)	28(1)	33(1)	4(1)	8(1)	8(1)
C(18)	42(1)	30(1)	38(1)	0(1)	13(1)	12(1)

C(19)	36(1)	27(1)	44(1)	5(1)	11(1)	13(1)
C(20)	29(1)	26(1)	38(1)	6(1)	7(1)	10(1)
C(21)	22(1)	25(1)	32(1)	2(1)	0(1)	6(1)
C(22)	29(1)	28(1)	34(1)	5(1)	1(1)	9(1)
C(23)	25(1)	32(1)	32(1)	4(1)	1(1)	4(1)
C(24)	34(1)	31(1)	32(1)	1(1)	7(1)	9(1)
C(25)	35(1)	26(1)	35(1)	3(1)	6(1)	10(1)
C(26)	39(1)	38(1)	33(1)	7(1)	5(1)	9(1)

Table S34. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^{-3}$) for Sevov_SA1-1382.

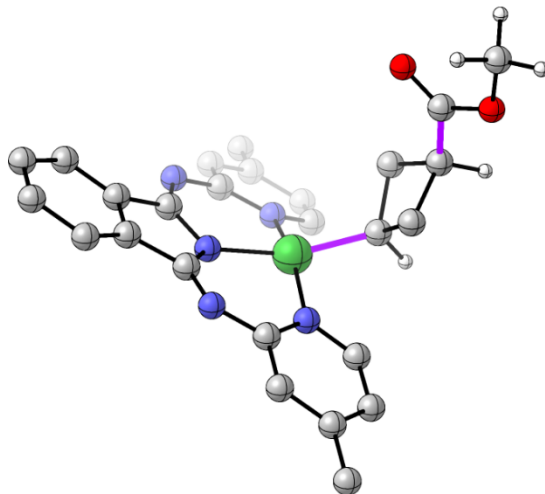
	x	y	z	U(eq)
H(1)	7220	1509	6110	33
H(2AA)	4180	2331	5773	40
H(2AB)	4887	1463	4922	40
H(2BC)	4581	1013	5065	40
H(2BD)	4571	2420	5443	40
H(3)	3879	-240	5772	42
H(3B)	3287	1885	7032	36
H(4AA)	5654	345	7347	45
H(4AB)	4808	1428	7742	45
H(4BC)	5204	129	6993	45
H(4BD)	5390	1295	7893	45
H(6AA)	-1335	-291	5855	74
H(6AB)	-990	-604	7021	74
H(6AC)	-1607	-1688	6053	74
H(6BD)	-883	-1221	5548	74
H(6BE)	-2007	-651	6332	74
H(6BF)	-789	-1391	6774	74
H(7)	8830	1752	7630	39
H(8)	9586	932	9068	42
H(10)	8255	3497	10952	39
H(12A)	9309	2073	11781	62
H(12B)	10391	1348	11103	62
H(12C)	8368	736	11154	62
H(17)	6653	6840	10691	39
H(18)	5852	8642	10579	44
H(19)	5348	9260	8954	42
H(20)	5671	8121	7369	36
H(22)	7179	6429	4457	36
H(24)	8475	3410	3393	39
H(25)	8112	2784	5024	38
H(26A)	6986	4927	2173	56

H(26B)	9040	5346	2376	56
H(26C)	7995	6294	2714	56

Transition state calculations (Figure 4B in the manuscript)

All calculations were performed using the Gaussian 16 suite of programs.²⁸ The geometries were optimized using the B3LYP-D3 hybrid density functional along with Pople's 6-311+G** triple- ζ basis set for all atoms except for the Ni atom.²⁹ The Stuttgart–Dresden double- ζ basis set (SDD) with an effective core potential was used for the nickel atom.^{30,31} Solvation effects were included via SMD, Cramer-Truhlar's continuum solvation model for the solvent tetrahydrofuran (THF).³² All the stationary points were characterized as minima or a first-order saddle point (transition state). The transition states (TSs) were verified by examining whether the stationary point has a unique imaginary frequency representing the desired reaction coordinate. The zero-point vibrational energy (ZPVE), thermal, and entropic corrections obtained at 298.15 K with SMD_(THF)/B3LYP-D3/6-311+G**, SDD(Ni) level of theory are included in the Gibbs free energies.^{33–35}

Complex 24 (syn diastereomer)



E(RB3LYP) = -1601.530857

H - Sum of electronic and thermal Enthalpies = -1601.034086

G - Sum of electronic and thermal Free Energies = -1601.129680

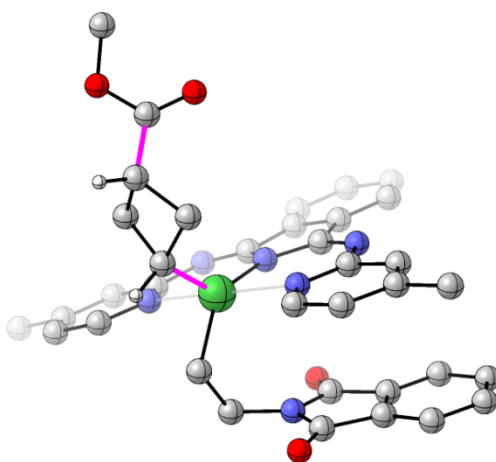
Number of imaginary frequencies: 0

Cartesian Coordinates

C	-4.04984500	0.60013700	-2.01159300
C	-4.05366900	-0.79804100	-1.93112800
C	-2.92830300	-1.49786900	-1.48270100
C	-1.81229900	-0.75637300	-1.12169200
C	-1.80860900	0.63925900	-1.20191900
C	-2.92057600	1.34057400	-1.64583700
C	-0.47881700	-1.15019300	-0.61340100
N	0.27737700	-0.02219800	-0.43144100
C	-0.47314500	1.08194600	-0.74143100
N	2.02202300	1.97754400	0.39496000
C	1.10692900	2.76165100	-0.24461000
N	-0.13330300	2.33260500	-0.66230400
N	-0.14489700	-2.38565600	-0.39223300
C	1.09368200	-2.77027400	0.07054500
N	2.01209300	-1.92336100	0.61915500
C	1.37547000	-4.14885000	-0.05197000
C	2.59551900	-4.67923800	0.32500800
C	3.54207600	-3.77960800	0.84400200
C	3.21112500	-2.44913200	0.97388900
C	3.22349200	2.53417000	0.68821900
C	3.56037600	3.84020600	0.40997200
C	2.61705600	4.68047000	-0.20525900
C	1.39426500	4.11675900	-0.51990200
C	2.93723600	6.11726800	-0.50403600
C	2.90842100	-6.14231500	0.19209200
Ni	1.80059000	0.04267100	0.76900300
H	-4.93733600	1.11519300	-2.36212500
H	-4.94409400	-1.34503300	-2.22054500
H	-2.92621100	-2.57954900	-1.41746700
H	-2.91242400	2.42257000	-1.70487100
H	0.59866100	-4.77612500	-0.47110800
H	4.52619400	-4.11482000	1.14953200
H	3.92481700	-1.74859700	1.37945300
H	3.93377300	1.88009700	1.17016700
H	4.54599300	4.20334800	0.67614800
H	0.61963500	4.69724700	-1.00519700
H	3.16862100	6.65745600	0.41951800
H	3.81942000	6.18779900	-1.14807400
H	2.10554300	6.62090000	-0.99954500
H	3.09344900	-6.58349100	1.17688300
H	2.09068700	-6.68825100	-0.28131400
H	3.81545800	-6.28961500	-0.40217200
C	2.75002200	0.13960600	2.47358200
C	2.27317200	1.28100400	3.42879300
C	2.27858700	-0.88948000	3.54892000

H	3.84674400	0.13415100	2.40045000
C	2.25543900	0.27147700	4.59451300
H	1.26094300	1.61720500	3.19099600
H	2.91342400	2.15785300	3.54567100
H	1.26919300	-1.25924700	3.34444000
H	2.92203700	-1.74060600	3.77835000
H	3.18314300	0.27992100	5.16988500
C	1.08419300	0.27501800	5.53465300
O	0.05762800	0.90435500	5.39173900
O	1.28814800	-0.56941600	6.56847900
C	0.19712000	-0.71844200	7.50268800
H	0.54376700	-1.43462900	8.24569000
H	-0.03500500	0.23641500	7.97822100
H	-0.69232500	-1.09920100	6.99697800

Ni^{III}(dialkyl) Complex



E(UB3LYP) = -2192.819539

H - Sum of electronic and thermal Enthalpies= -2192.149309

G - Sum of electronic and thermal Free Energies= -2192.272239

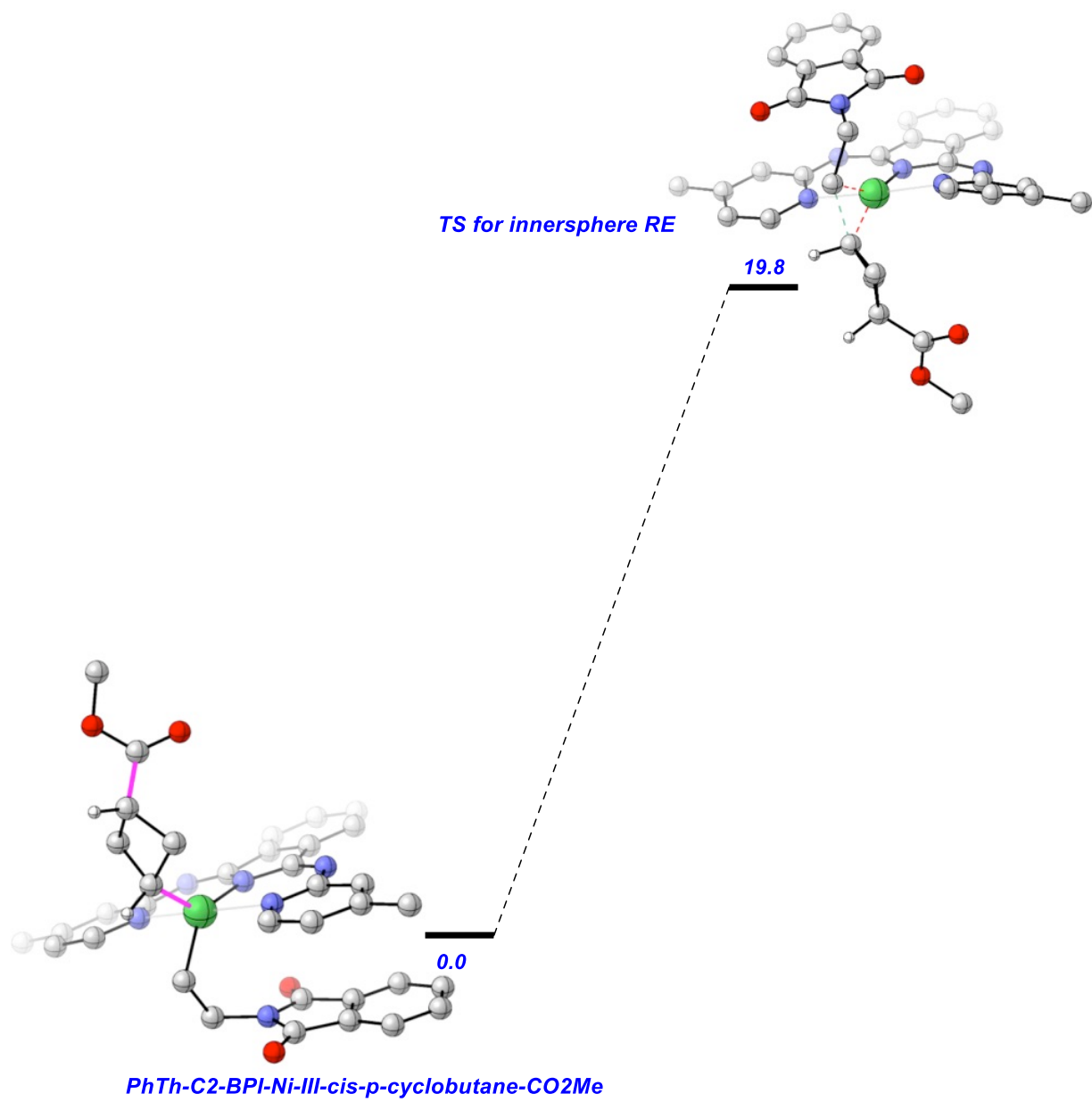
Number of imaginary frequencies: 0

Cartesian Coordinates

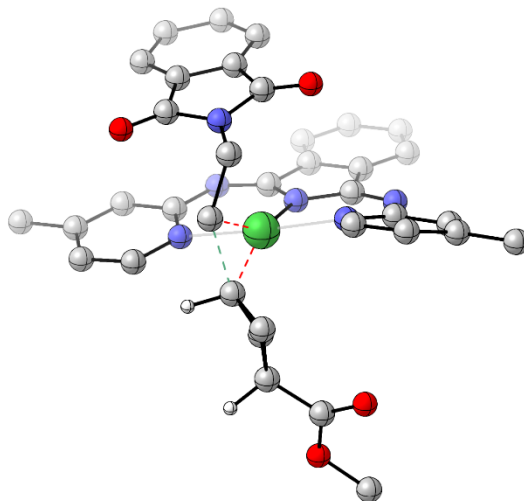
C	-0.61405800	1.19316100	-0.47908300
C	-0.88335600	-0.17782500	-0.35664600
C	0.02850100	-1.03759400	0.26108400
C	1.20433200	-0.48261600	0.75098200

C	1.47056400	0.87543300	0.63024900
C	0.57414600	1.73912200	0.01304600
C	2.37160100	-1.08642600	1.43411500
N	3.29502000	-0.09537900	1.72892600
C	2.80121600	1.10355100	1.23738100
N	5.39323600	1.87327800	2.32168600
C	4.53707900	2.69493500	1.67622200
N	3.31066600	2.29497500	1.19824200
N	2.38722200	-2.36890700	1.62870400
C	3.37718200	-3.11207200	2.22849600
N	4.49291200	-2.57612500	2.76755600
C	3.14466300	-4.50638000	2.26693700
C	4.04557400	-5.36581700	2.87261200
C	5.18616000	-4.78406100	3.45156500
C	5.35446300	-3.41525800	3.37260200
C	6.55229400	2.40283500	2.75484900
C	6.93318900	3.71486500	2.55262800
C	6.07188800	4.57600700	1.85397300
C	4.86605000	4.04577200	1.42950100
C	6.45998100	5.99996900	1.57209700
C	3.82323900	-6.85145100	2.92479300
Ni	5.06830200	-0.35786100	2.68573400
H	-1.33984900	1.83616700	-0.96486100
H	-1.81299000	-0.57417700	-0.75011500
H	-0.16896600	-2.09890900	0.35473900
H	0.79289200	2.79623200	-0.08078000
H	2.23538000	-4.87916900	1.81142700
H	5.92872500	-5.39033600	3.95756000
H	6.22056000	-2.95125400	3.82418100
H	7.20430200	1.72555300	3.28825900
H	7.89306100	4.05901600	2.91989600
H	4.14944300	4.64829800	0.88564700
H	6.60258800	6.55326600	2.50589200
H	7.40839100	6.03755100	1.02736200
H	5.70097100	6.51357000	0.97943000
H	3.79883100	-7.20058600	3.96186500
H	2.88637000	-7.13588200	2.44241900
H	4.64236400	-7.37950800	2.42639100
C	5.67988000	-0.34277200	4.56043900
C	5.38995500	0.97806100	5.31775700
C	4.61631900	-1.05375800	5.43596500
H	6.68669300	-0.71703800	4.74589500
C	4.75327200	0.13489400	6.44309300
H	4.62705100	1.58334700	4.82696000
H	6.23806200	1.61162300	5.57848800
H	3.62600400	-1.05522800	4.97209900

H	4.83688200	-2.05493700	5.80415000
H	5.46230800	-0.11827900	7.23234500
C	3.46397200	0.61854100	7.04814700
O	2.79304300	1.54159900	6.64060800
O	3.10689300	-0.14650800	8.09863800
C	1.84085700	0.16615700	8.72180300
H	1.72826400	-0.55323700	9.53086400
H	1.84959800	1.18309300	9.11814400
H	1.02489800	0.06025400	8.00447000
C	6.49712000	4.37468300	-1.98705000
C	5.26012000	3.89084300	-2.42478400
C	4.85192900	2.58284800	-2.13648800
C	5.71856200	1.79561800	-1.39842800
C	6.94810900	2.28002600	-0.95545200
C	7.36520400	3.56836200	-1.24145900
C	5.56468600	0.39842400	-0.90070300
N	6.69568300	0.14753200	-0.11044800
C	7.60009500	1.21218000	-0.14579400
O	8.69186900	1.21954200	0.38547800
O	4.67507500	-0.39279300	-1.12407200
H	6.78241800	5.39396900	-2.22107200
H	4.60464800	4.54225900	-2.99148900
H	3.88983500	2.20642900	-2.46218200
H	8.31842300	3.94202700	-0.88775100
C	6.90281300	-1.06541100	0.67934700
H	7.85520600	-1.51127100	0.36676000
H	6.10871700	-1.75864800	0.39768800
C	6.92863900	-0.81893600	2.18919800
H	7.25695400	-1.73435300	2.67939100
H	7.63753000	-0.03346600	2.44200100



Transition state for reductive elimination C(sp³)-C(sp³).



E(UB3LYP) = -2192.790688

H - Sum of electronic and thermal Enthalpies= -2192.119843

G - Sum of electronic and thermal Free Energies= -2192.240647

Number of imaginary frequencies: 1

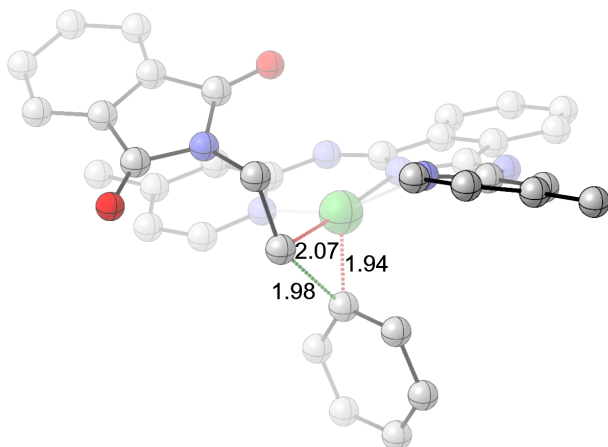
Cartesian Coordinates

C	-3.18048300	-3.38854000	3.54237600
C	-2.10960200	-4.28338100	3.40937200
C	-0.96770400	-3.93615800	2.68067500
C	-0.93477800	-2.67510600	2.09968700
C	-1.99671900	-1.78656500	2.23400100
C	-3.13599800	-2.12101800	2.95370800
C	0.06743100	-2.00357000	1.23812900
N	-0.39199800	-0.75117000	0.88931500
C	-1.61481600	-0.56007800	1.49554300
N	-1.00332800	2.07854300	0.39390600
C	-2.16740600	1.71068600	0.98641100
N	-2.41364100	0.46260300	1.50493700
N	1.16385600	-2.62448300	0.92657000
C	2.09199700	-2.23911600	-0.01106500
N	1.95004000	-1.15728100	-0.81681000
C	3.19625800	-3.11293500	-0.14419400
C	4.13421000	-2.94221600	-1.14674400
C	3.91559800	-1.87711500	-2.03482200
C	2.83830000	-1.03949900	-1.82326400

C	-0.89616700	3.37800000	0.04822800
C	-1.88681400	4.32784200	0.19908400
C	-3.12201100	3.94456700	0.74539900
C	-3.23665600	2.62508500	1.14109900
C	-4.25049700	4.92677400	0.88725700
C	5.32025600	-3.85229800	-1.29970200
Ni	0.57373200	0.52462400	-0.29587700
H	-4.05560800	-3.68686400	4.10941900
H	-2.17141400	-5.26007200	3.87682300
H	-0.13837300	-4.62454300	2.56787400
H	-3.96098900	-1.42468600	3.04645400
H	3.26496600	-3.94192200	0.54980300
H	4.58147600	-1.69570300	-2.87055600
H	2.67909600	-0.21270000	-2.49902000
H	0.04602700	3.68045100	-0.38240300
H	-1.70399300	5.34879100	-0.11596300
H	-4.14784200	2.25386600	1.59366400
H	-3.93127400	5.80589600	1.45548100
H	-4.57455900	5.27981400	-0.09732600
H	-5.11008200	4.48174500	1.39200500
H	6.24840800	-3.29986800	-1.11919400
H	5.27883600	-4.68880600	-0.59949300
H	5.37503100	-4.25190900	-2.31685800
C	1.95291200	2.04509600	-0.81713600
C	2.36032600	1.90326300	0.71800500
C	3.45499900	2.03547000	-1.17135600
H	1.63362100	3.07779200	-0.90898600
C	3.75253100	2.46330700	0.27960300
H	2.46730200	0.88079500	1.08654500
H	1.78247100	2.48988900	1.42870500
H	3.86676000	1.04524300	-1.34072600
H	3.76865800	2.70476400	-1.97460600
H	3.78374000	3.54608100	0.40941800
C	4.93665400	1.83542500	0.96302000
O	5.63879700	0.96244300	0.50144100
O	5.10291500	2.34466300	2.19781200
C	6.16616200	1.77309100	2.99315100
H	6.13442700	2.30105900	3.94437600
H	5.99675300	0.70577800	3.14625300
H	7.13160400	1.92508000	2.50716500
C	-5.48435900	-0.49847900	-0.74818000
C	-5.01829400	-1.80459200	-0.56871300
C	-3.73736300	-2.17898400	-0.99090700
C	-2.95384200	-1.20351200	-1.58285900
C	-3.41602300	0.10005800	-1.75760100
C	-4.68356000	0.47866000	-1.35114700

C	-1.55954100	-1.27452800	-2.09880400
N	-1.22168600	0.04211400	-2.46534000
C	-2.32100100	0.90172300	-2.37343900
O	-2.33822100	2.05677300	-2.74689000
O	-0.84334300	-2.24146400	-2.22722400
H	-6.47907800	-0.23719500	-0.40536700
H	-5.65670100	-2.53622800	-0.08695000
H	-3.36639000	-3.18605600	-0.84397600
H	-5.03410700	1.49556900	-1.47838800
C	0.08623400	0.42887800	-2.98162000
H	-0.05185900	0.78934100	-4.00853000
H	0.67069600	-0.48414100	-3.02923600
C	0.79838500	1.58800500	-2.22751000
H	1.59592900	1.87982700	-2.91168600
H	0.09643800	2.41461400	-2.18672700

Transition state for reductive elimination C(sp²)-C(sp³).



E(UB3LYP) = -2038.489774

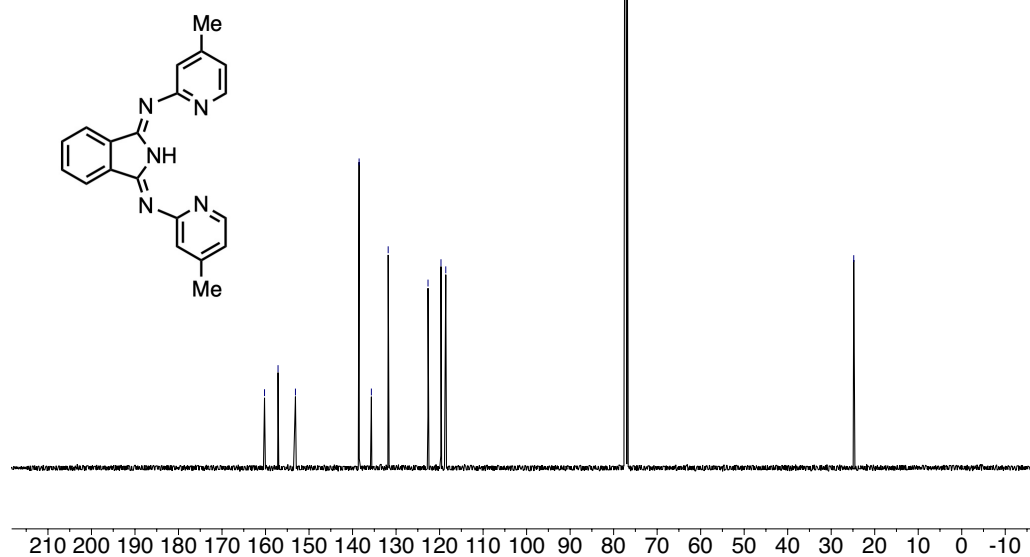
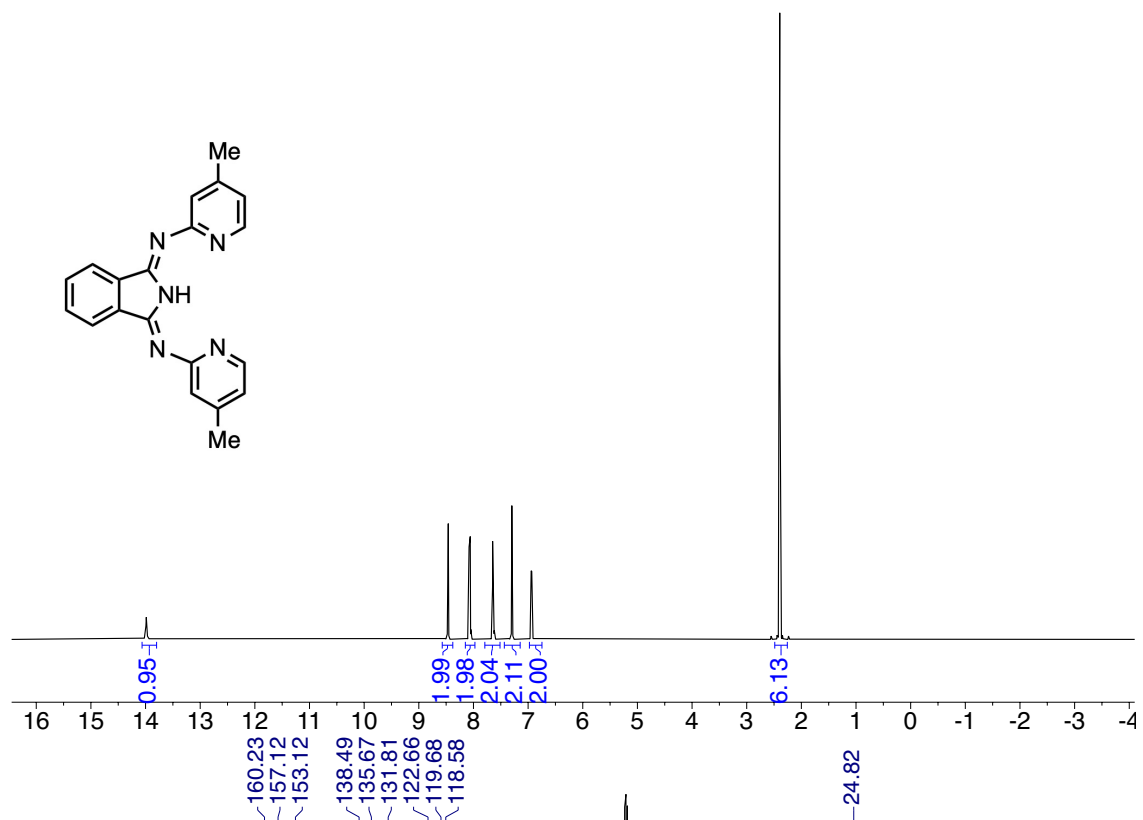
Number of imaginary frequencies: 1

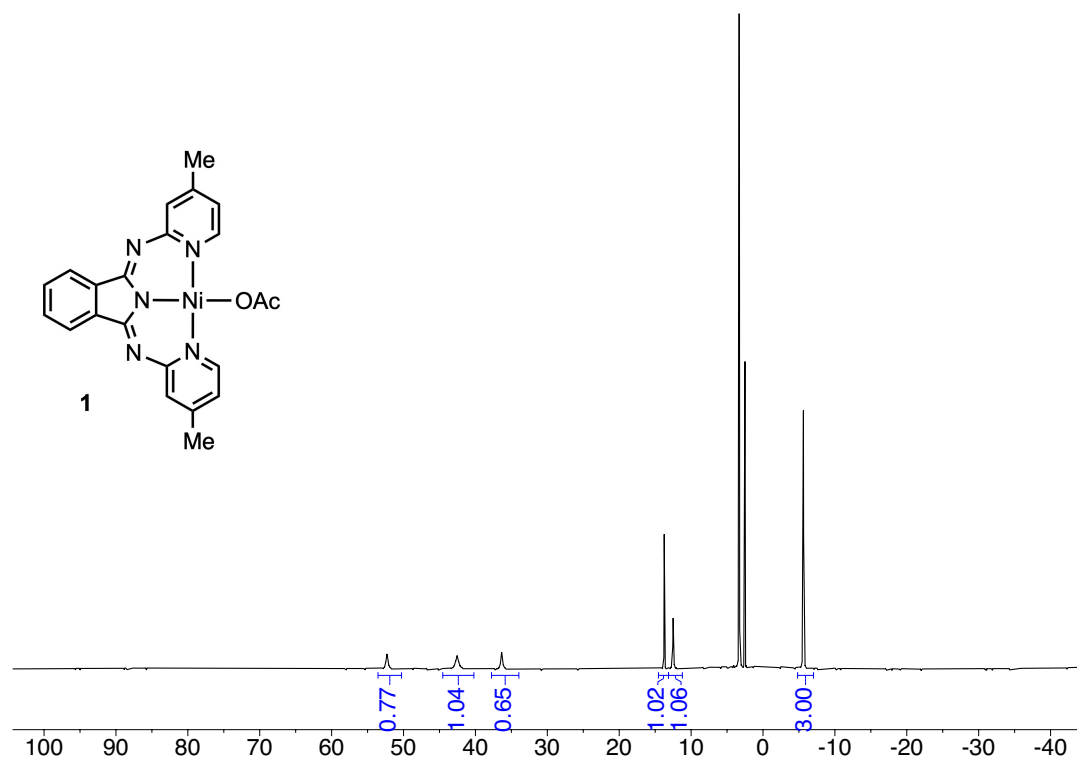
C	0.68725300	4.70453800	-4.30673200
C	-0.69870900	4.54526500	-4.27366200
C	-1.29109800	3.57596100	-3.46905400
C	-0.45279200	2.78050100	-2.70953900
C	0.92216900	2.93761300	-2.74318200
C	1.52112100	3.90073600	-3.53441400
C	-0.72449900	1.66893700	-1.77728500
N	0.45775200	1.20425700	-1.26453700
C	1.47966700	1.95255400	-1.79550900
N	2.75391700	1.92259100	-1.58657000
N	-1.94594000	1.30369500	-1.56267900
C	3.40980800	1.22262600	-0.60518100
C	-2.35747300	0.22196600	-0.83062900
N	2.78723000	0.53803200	0.37418400

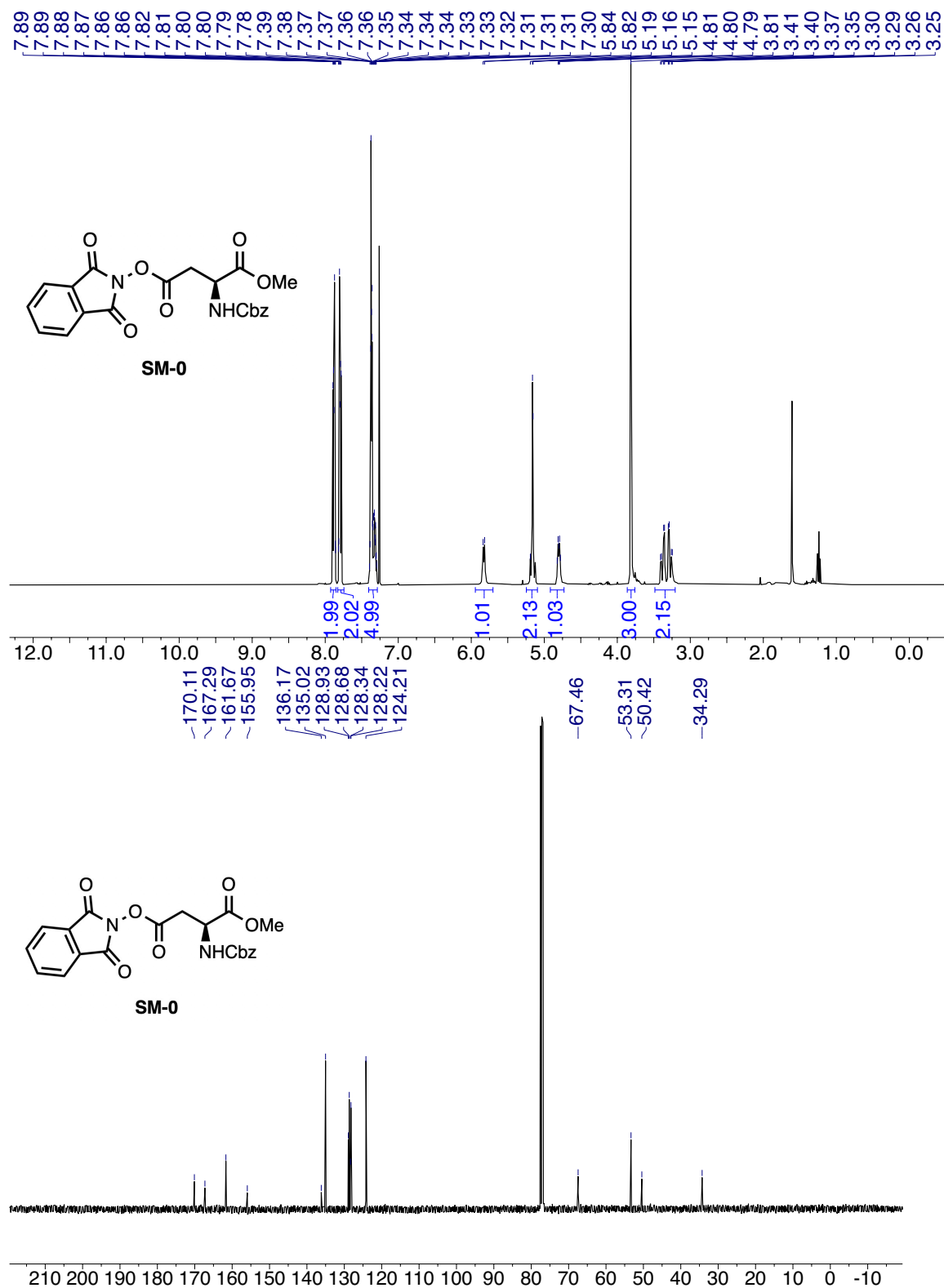
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C	5.60314600	0.75743900	0.32655100
C	4.81339500	1.31635600	-0.65527000
C	-3.75065900	0.13236100	-0.64503100
C	-4.32641700	-0.96140000	-0.03614000
C	-3.45963500	-1.98131300	0.37122300
C	-2.10654100	-1.81098800	0.19805100
N	-1.52745100	-0.73041800	-0.35400300
C	-5.80097000	-1.07632200	0.15468300
C	7.09130600	0.84844200	0.30027500
H	1.11890100	5.46972000	-4.94538300
H	-1.32224900	5.18995200	-4.88628100
H	-2.36897300	3.44738500	-3.43553400
H	2.60023800	4.02124400	-3.55196600
H	3.06182000	-0.48184200	2.15751000
H	5.48992600	-0.32317500	2.20419000
H	5.25320700	1.86232700	-1.48480700
H	-4.35946300	0.95114300	-1.01764700
H	-3.83509300	-2.88805300	0.83758900
H	-1.43881100	-2.59774600	0.53369600
H	-6.03706300	-1.53744400	1.11913600
H	-6.28999600	-0.09990400	0.10167300
H	-6.23940600	-1.71386300	-0.62229700
H	7.45123400	1.33931700	-0.60716100
H	7.45697000	1.41340000	1.16525100
H	7.54204600	-0.14819100	0.35991300
Ni	0.69611800	-0.41255800	-0.17279500
C	1.40576100	-2.11385600	-0.77817600
C	0.51950300	-2.83972400	-1.58172100
C	2.77760500	-2.25071400	-1.02406800
C	0.98810400	-3.61755100	-2.63363900
H	-0.54921400	-2.78535000	-1.41685700
C	3.23899400	-3.02642500	-2.07774200
H	3.50217400	-1.75039600	-0.38984900
C	2.34783400	-3.71250700	-2.89312200
H	0.27405500	-4.15168500	-3.25486800
H	4.30886100	-3.09743400	-2.25464000
H	2.71067800	-4.32287500	-3.71468700
C	-5.11320200	-0.69131100	4.04277000
C	-4.99218000	0.61679200	3.57873100
C	-3.78256900	1.09422100	3.07662100
C	-2.71736300	0.21789400	3.05760400
C	-2.84029800	-1.08807400	3.51092400
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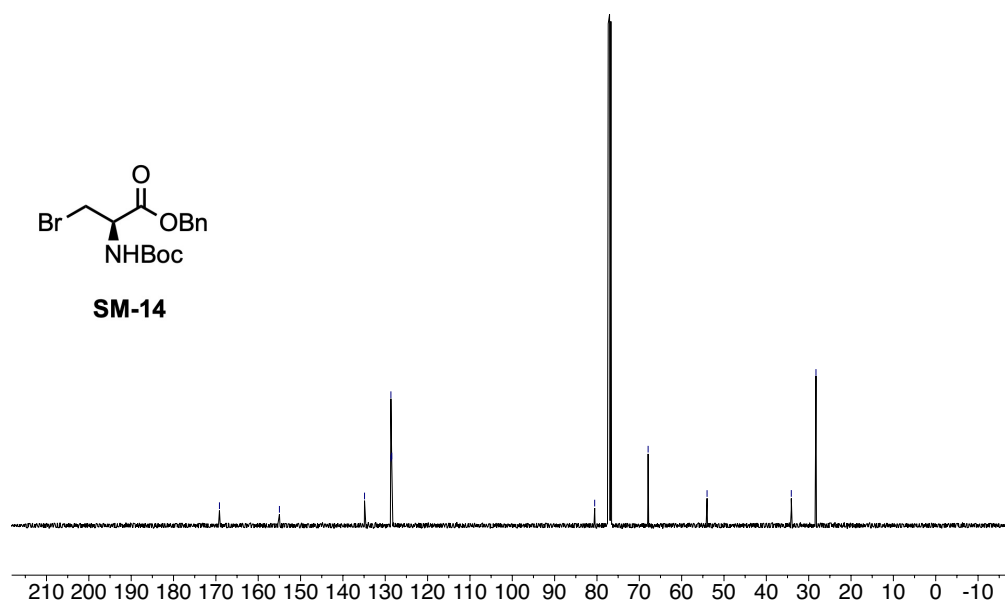
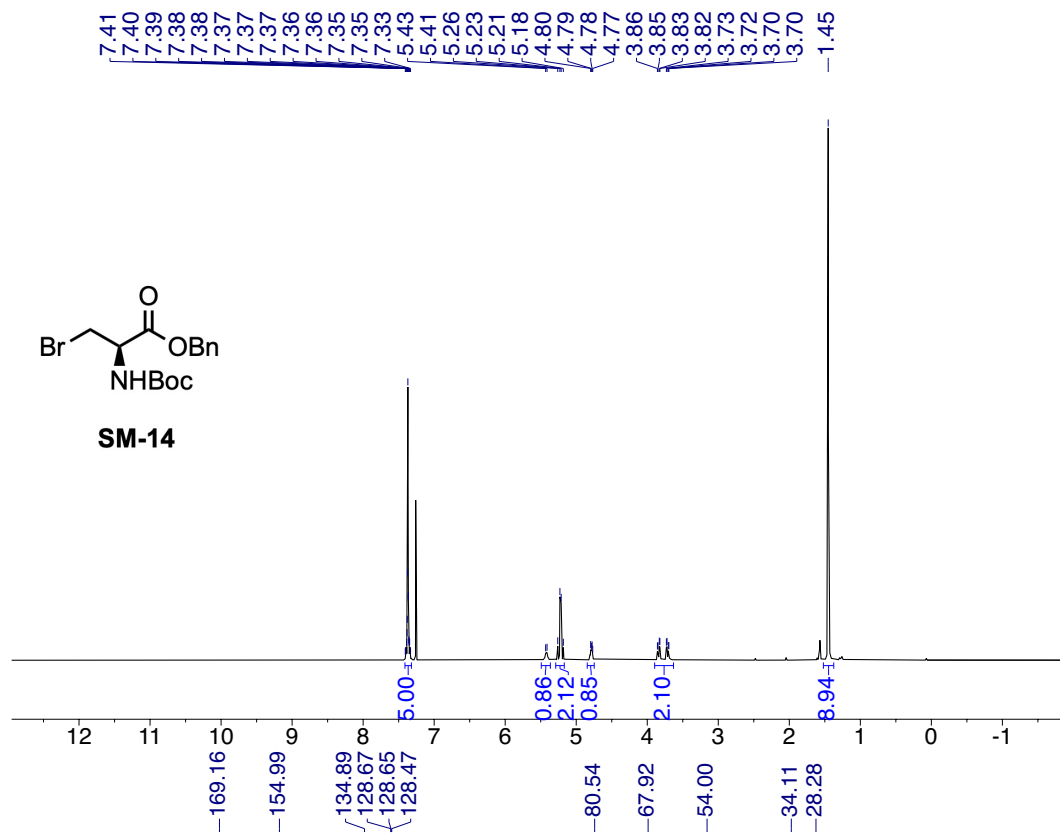
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O	-1.23391000	-2.91304000	3.56427100
O	-0.80376800	1.40600800	2.14368500
H	-6.06992400	-1.03180000	4.42688200
H	-5.85724100	1.27229000	3.60608700
H	-3.68267900	2.10926900	2.70385800
H	-4.12282700	-2.59403500	4.36302600
C	0.67608000	-1.07349500	2.36167900
H	1.12218700	-1.57858600	3.22980100
H	1.13096400	-0.08123000	2.29774000
C	1.02151200	-1.97960100	1.14291800
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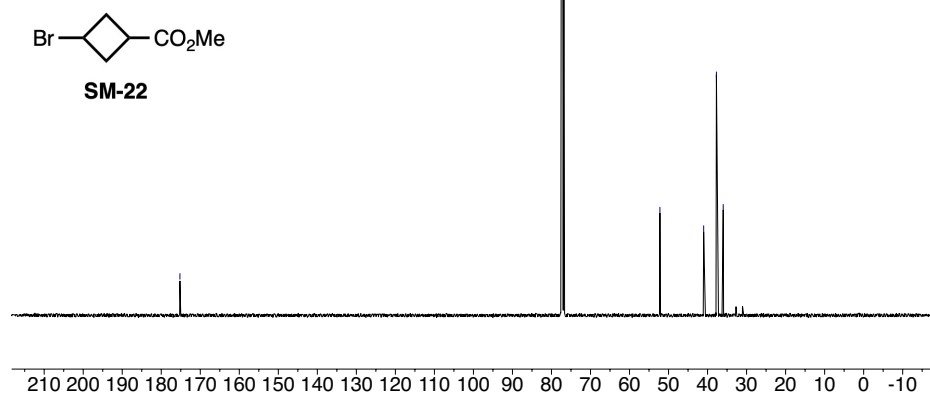
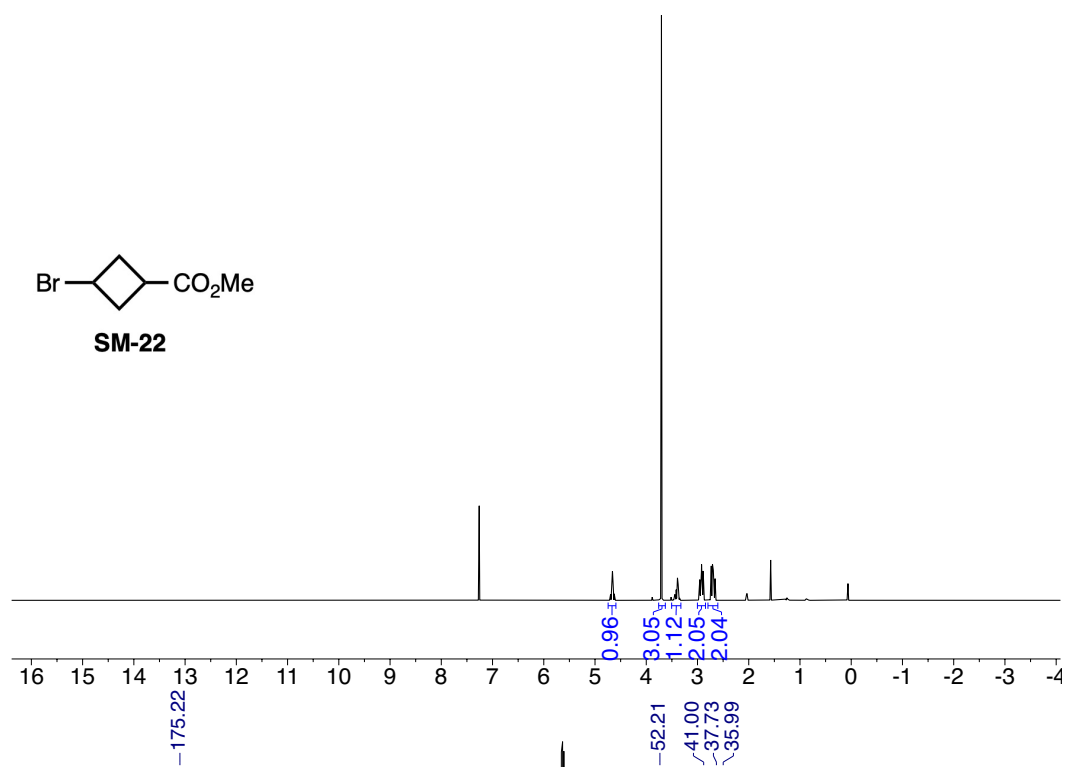
NMR spectra of characterized compounds

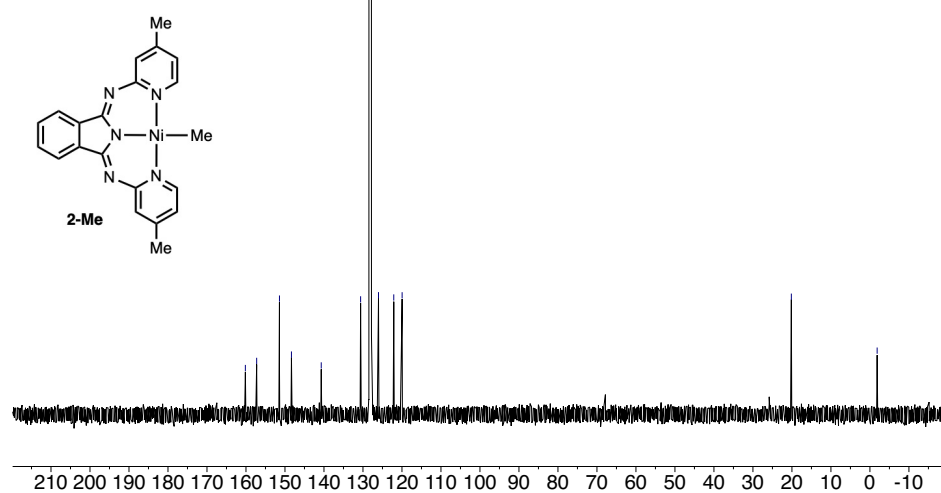
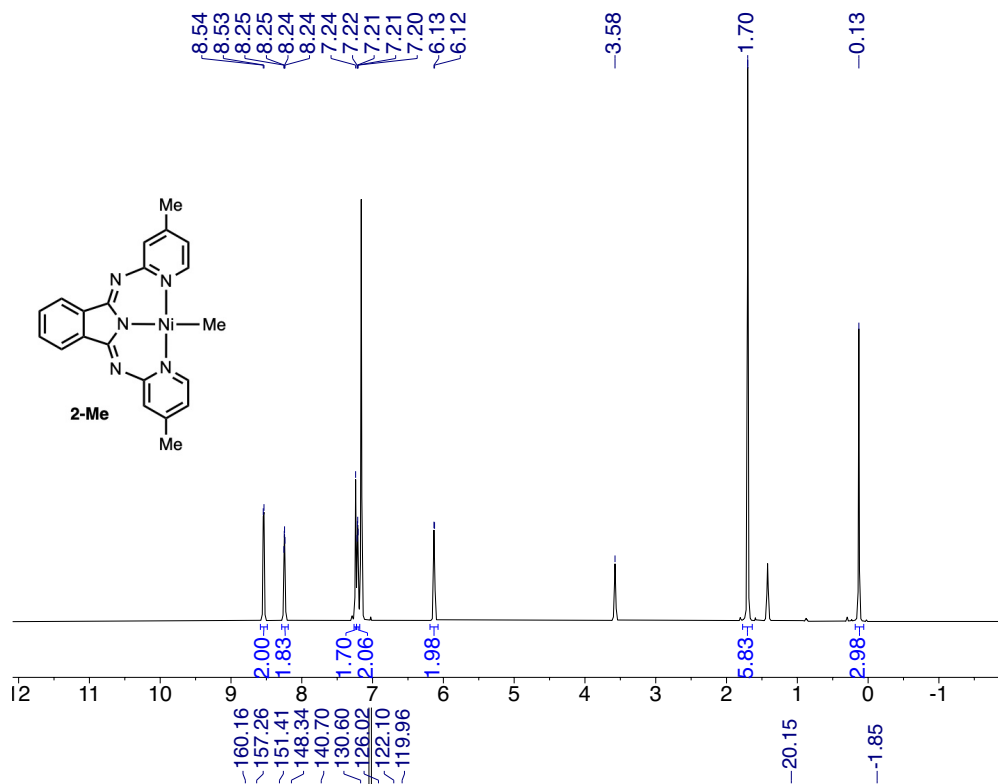


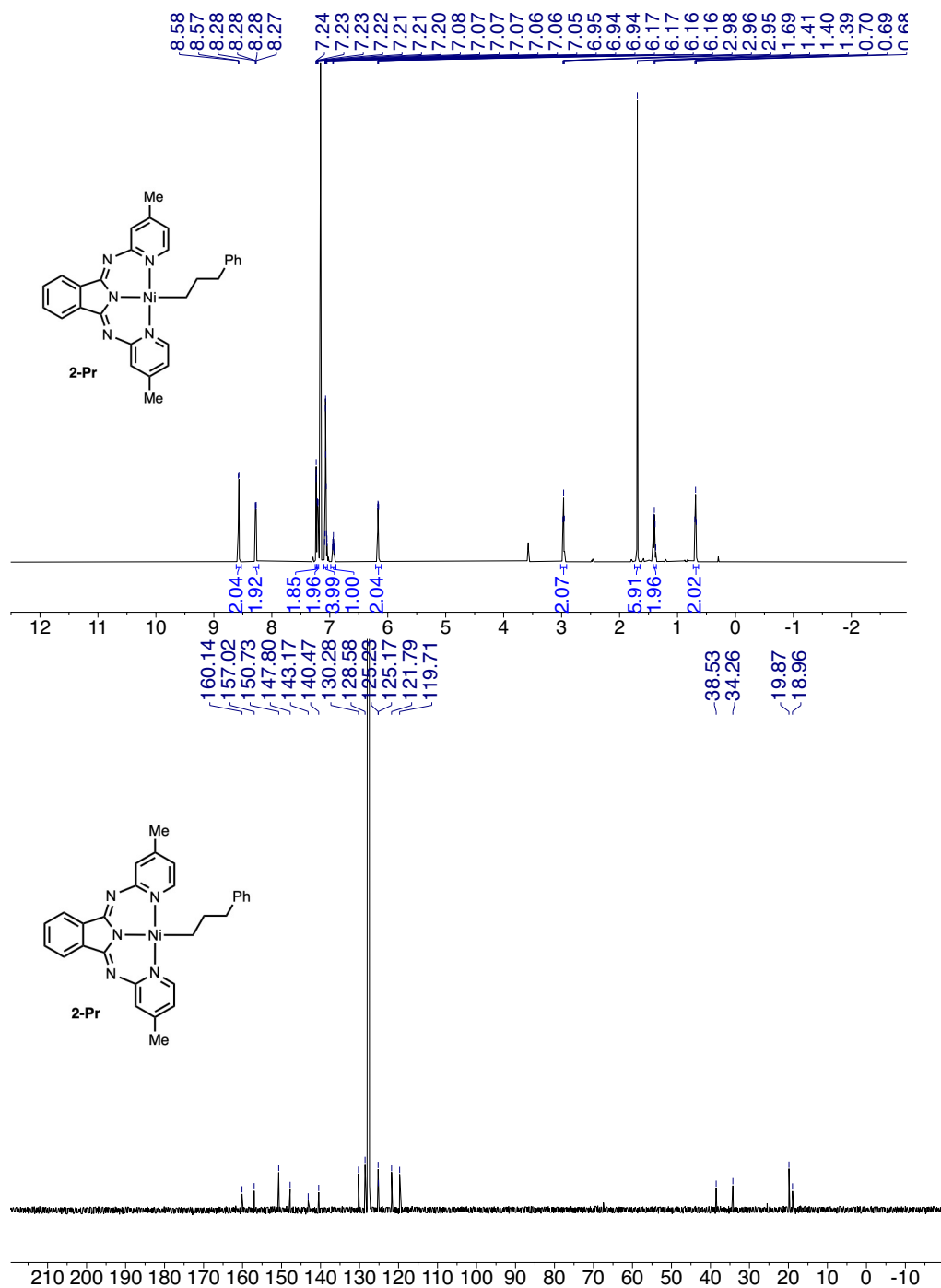


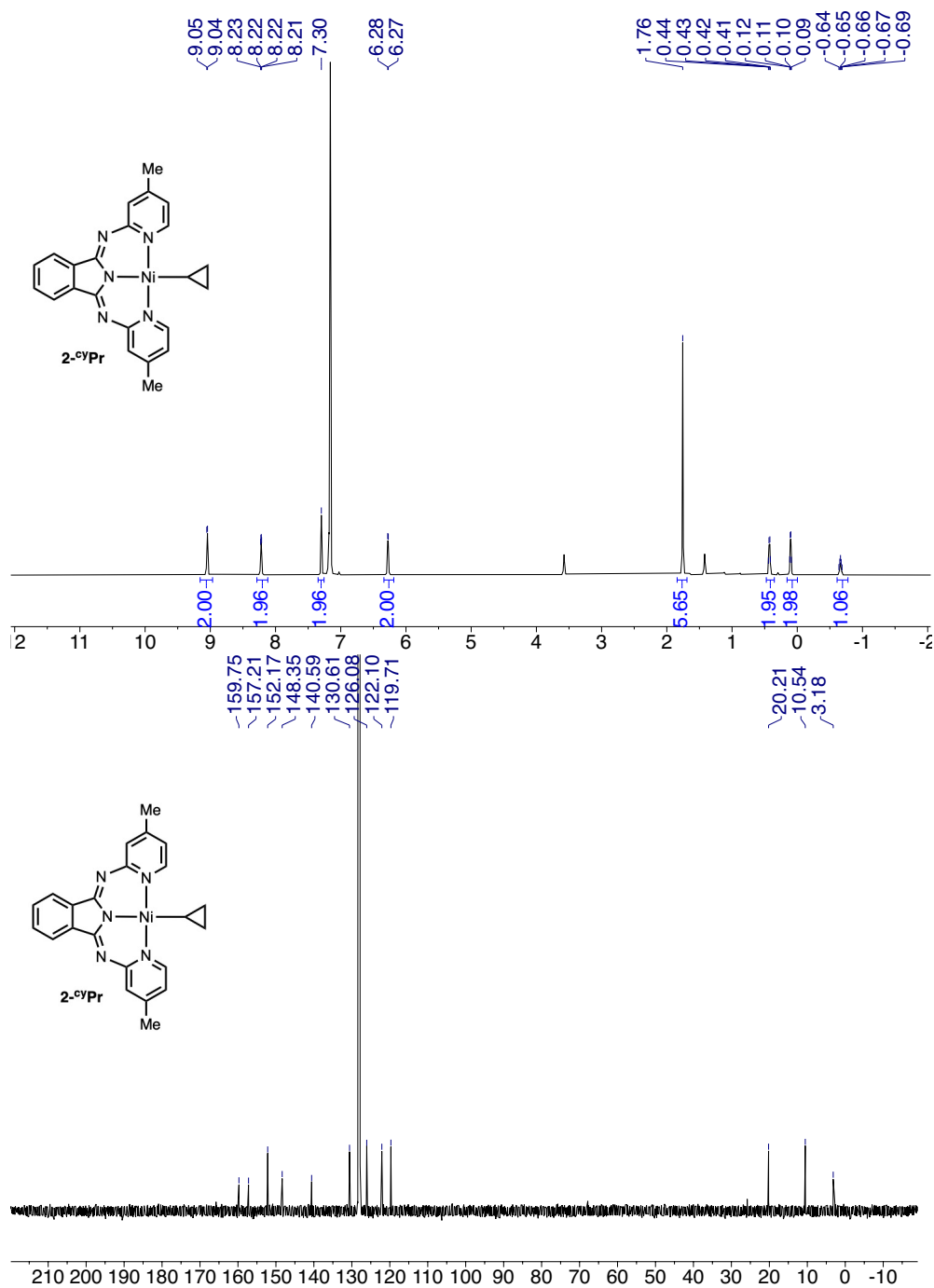


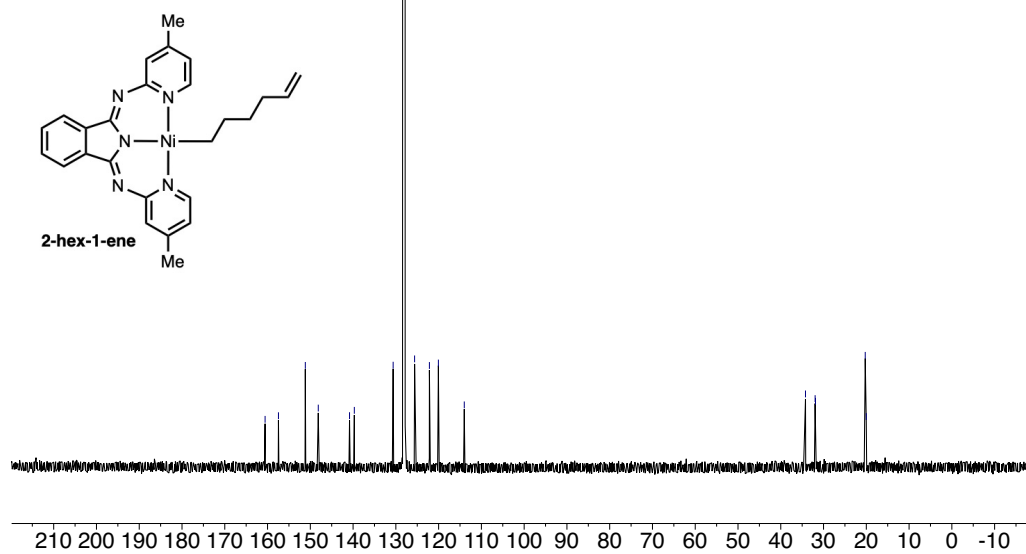
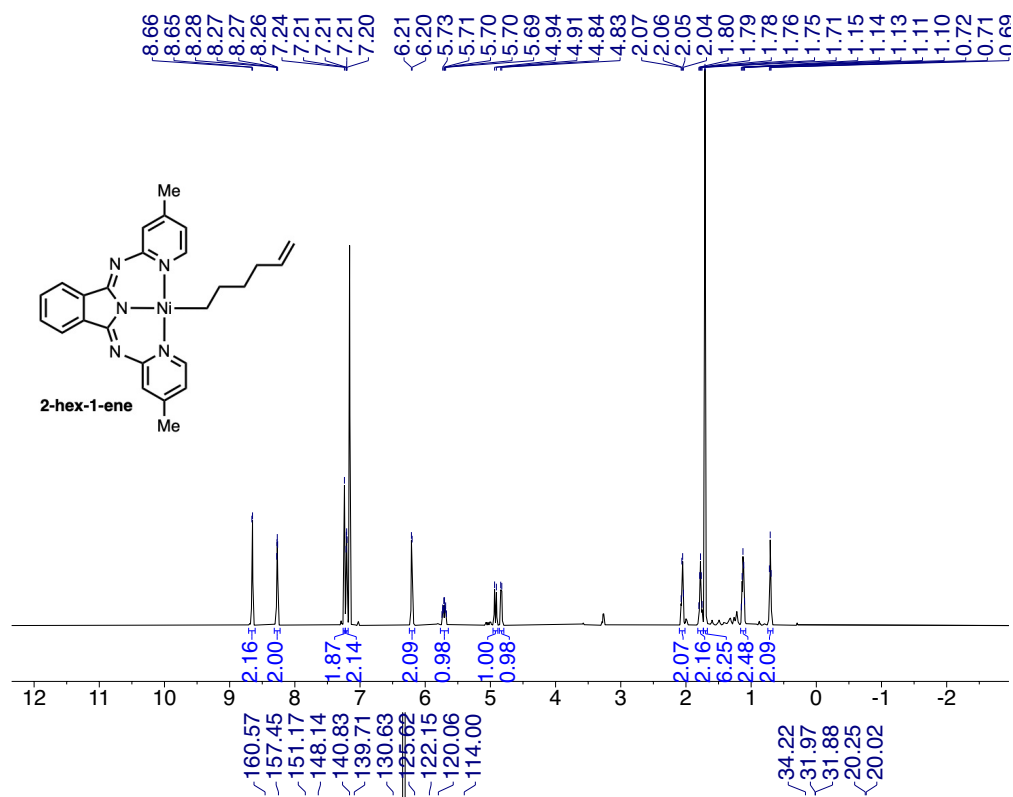


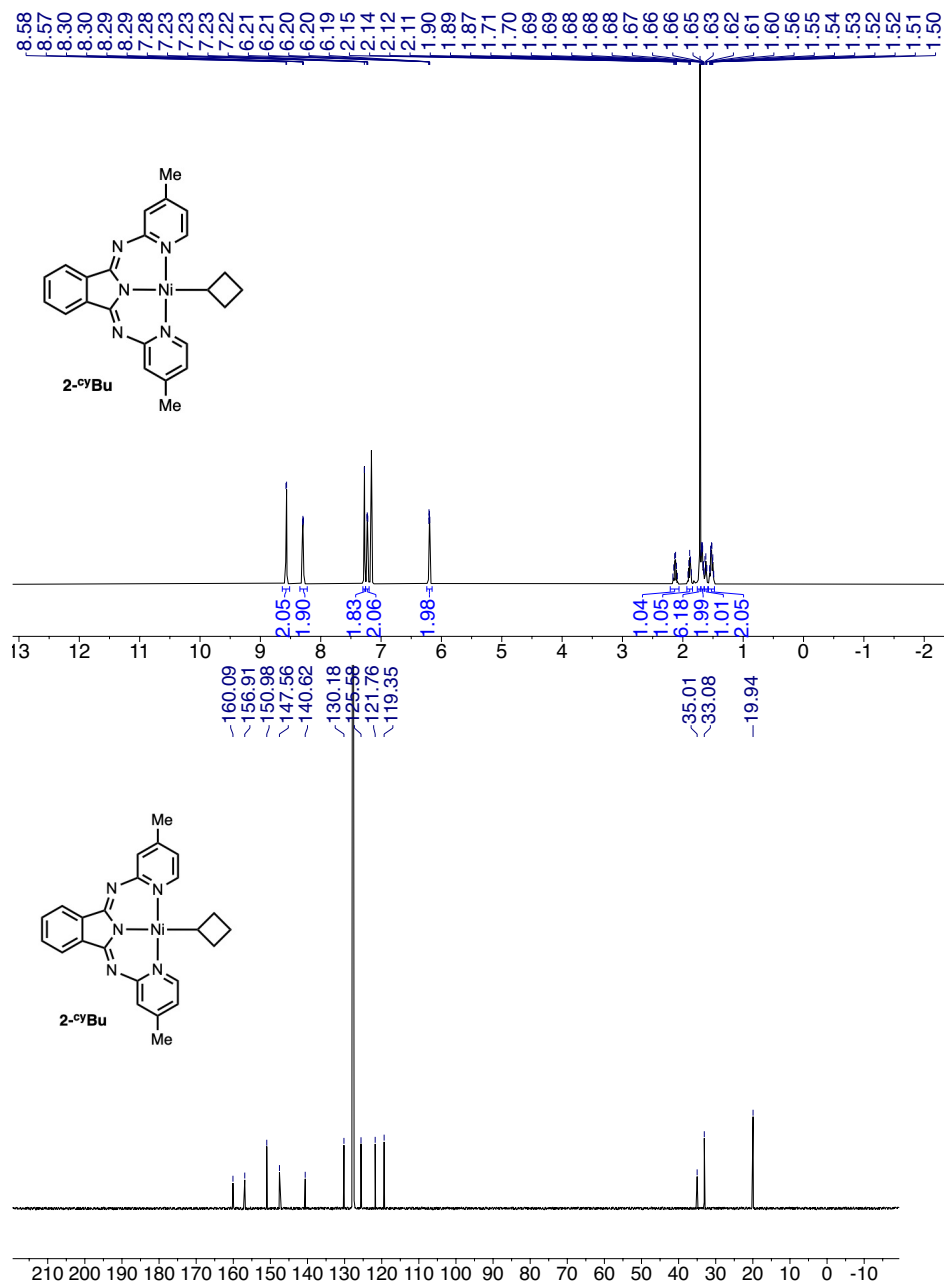


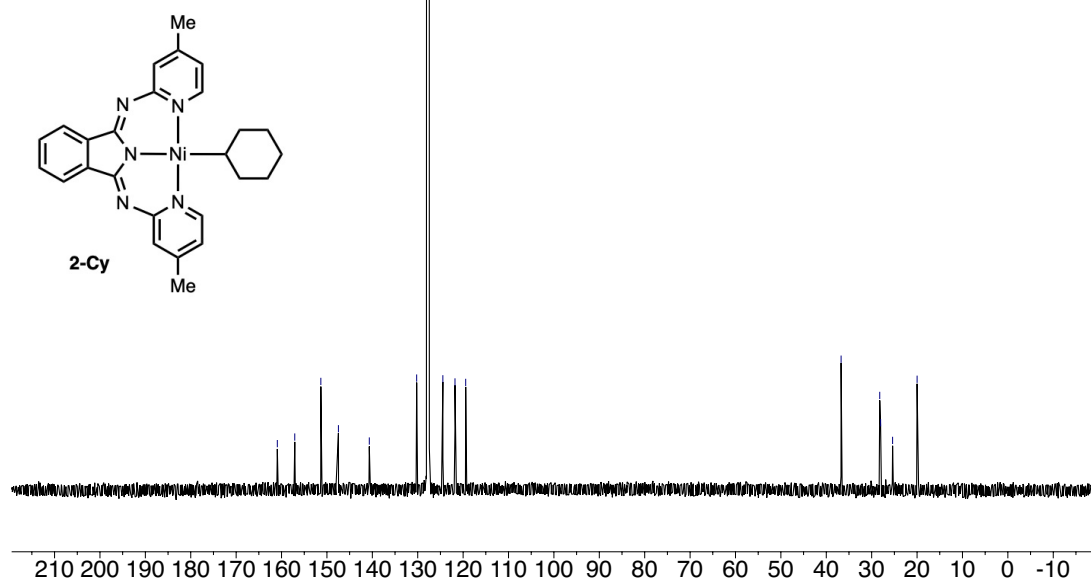
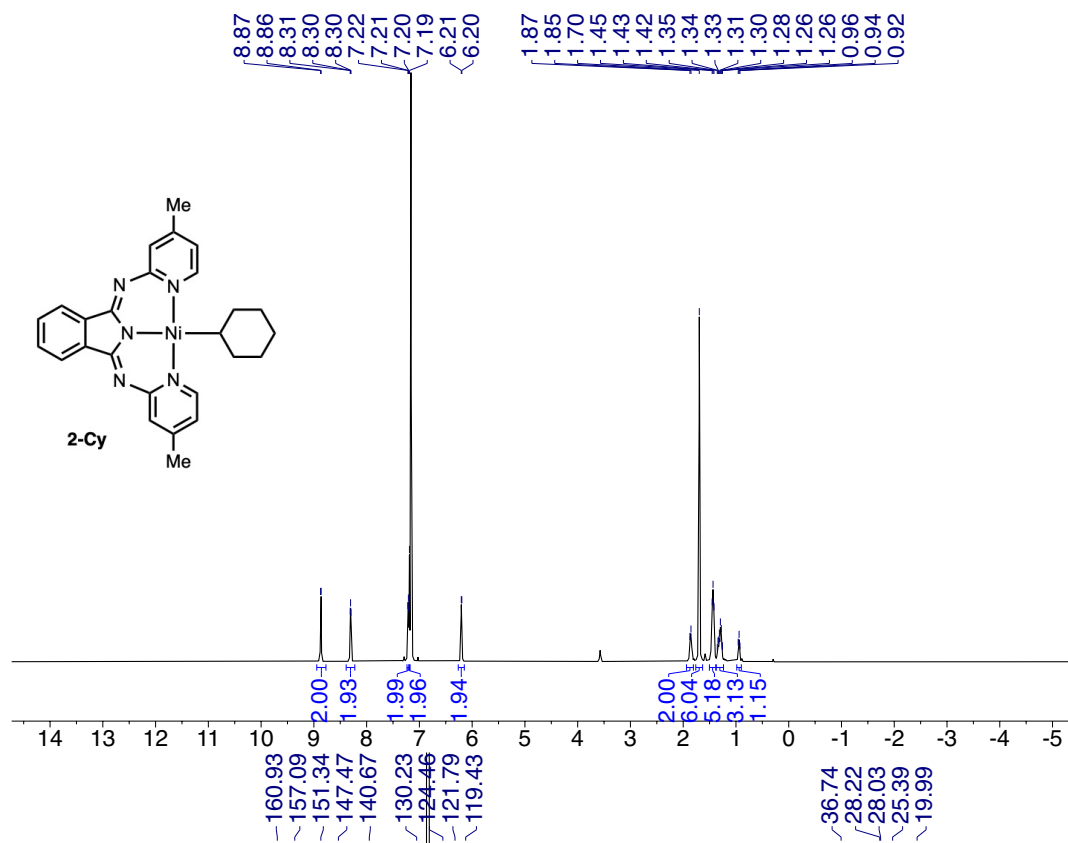


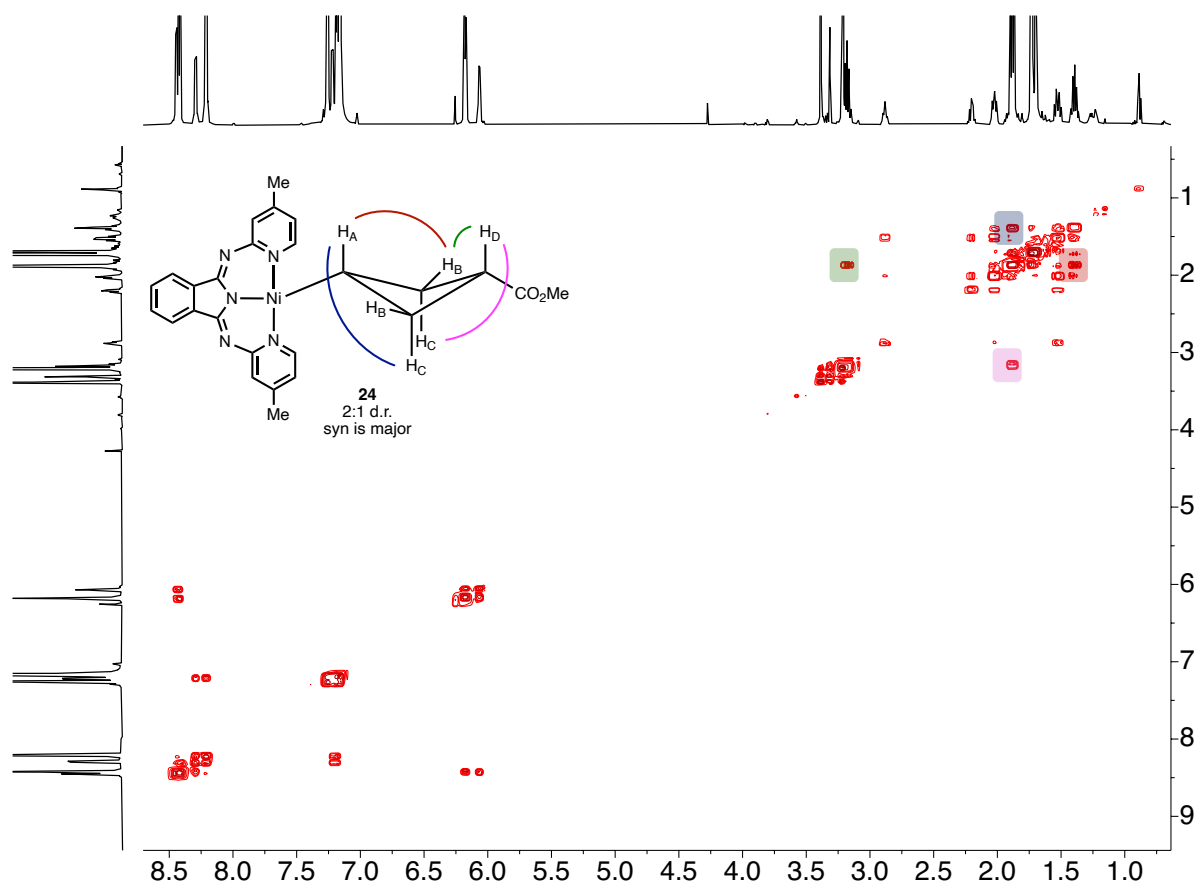


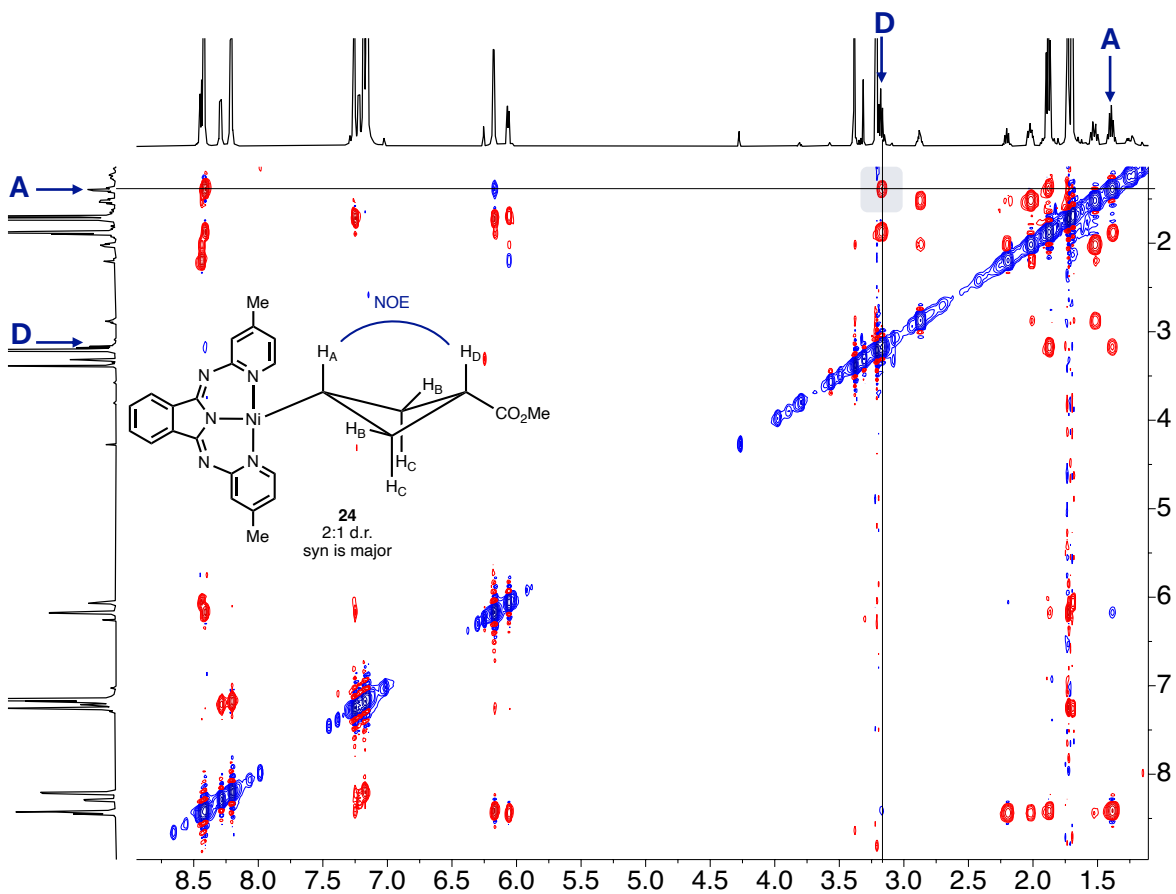


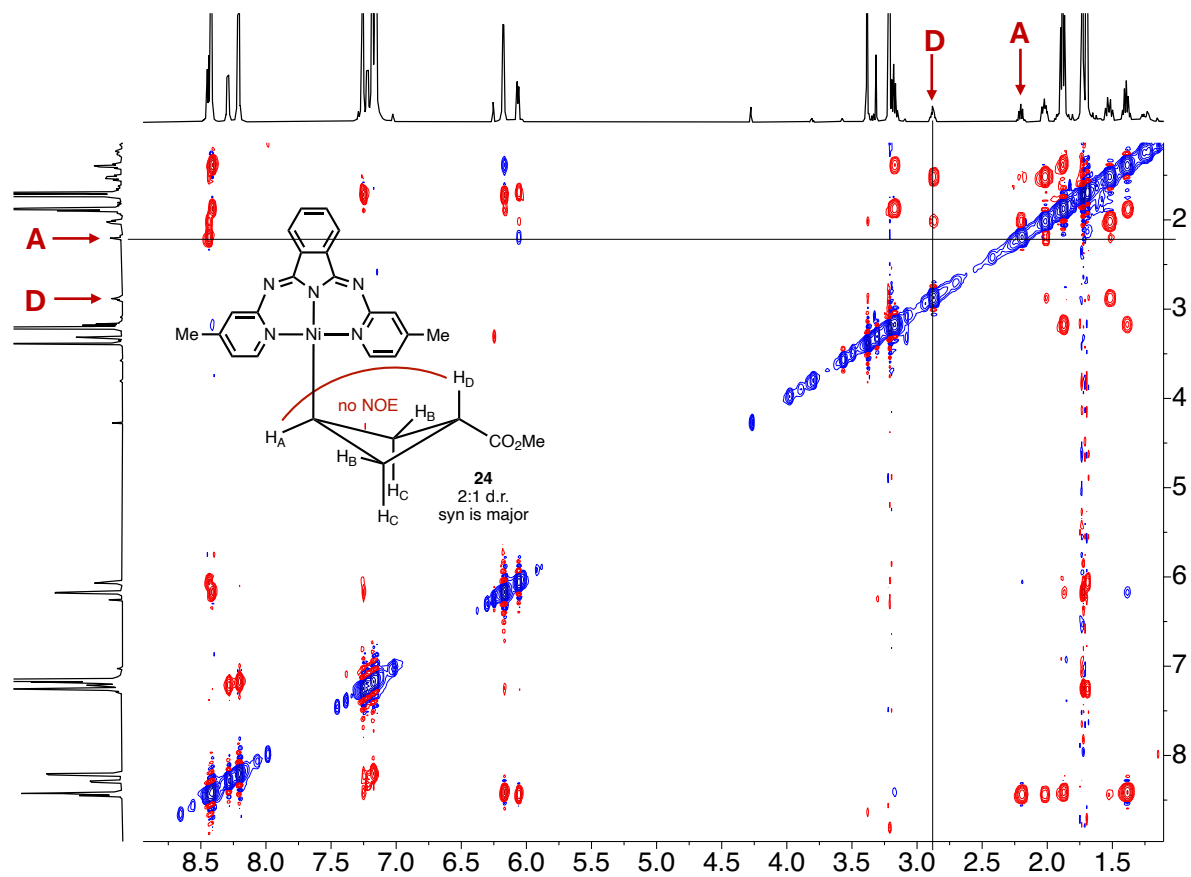


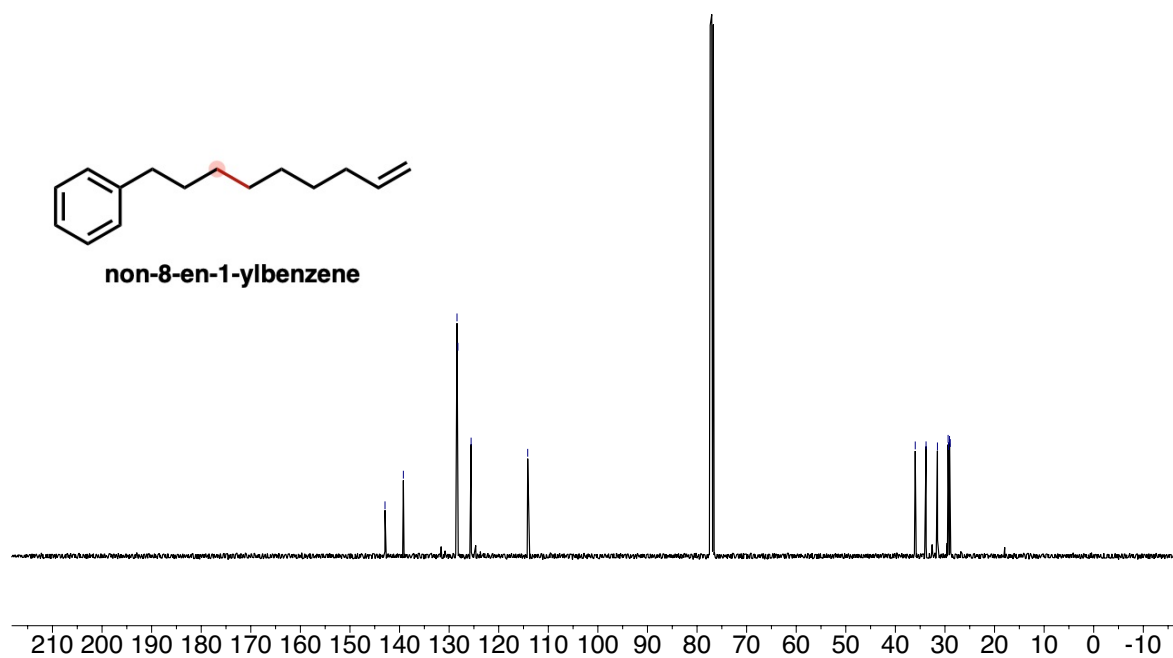
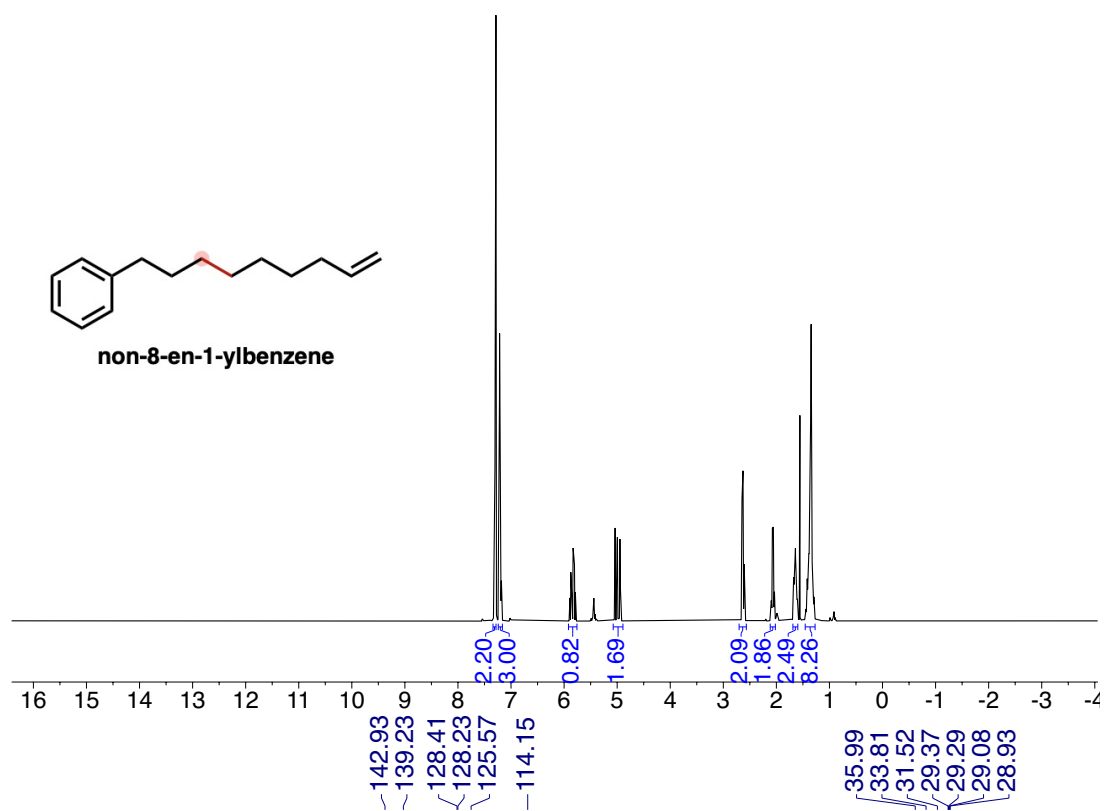


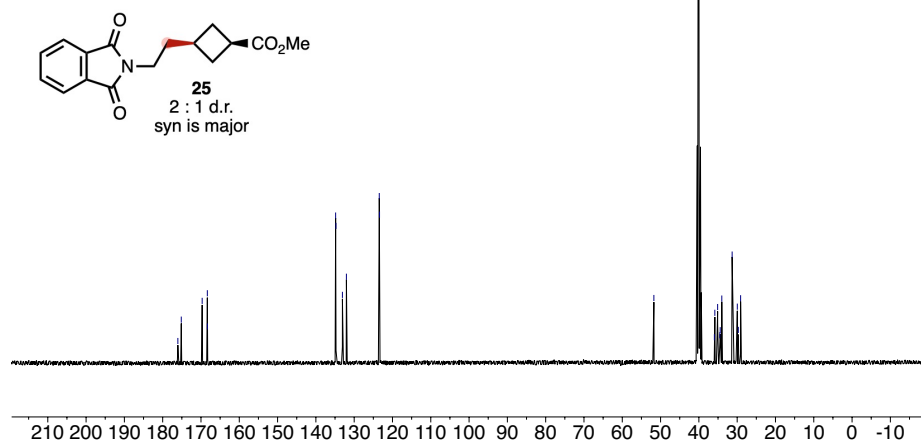
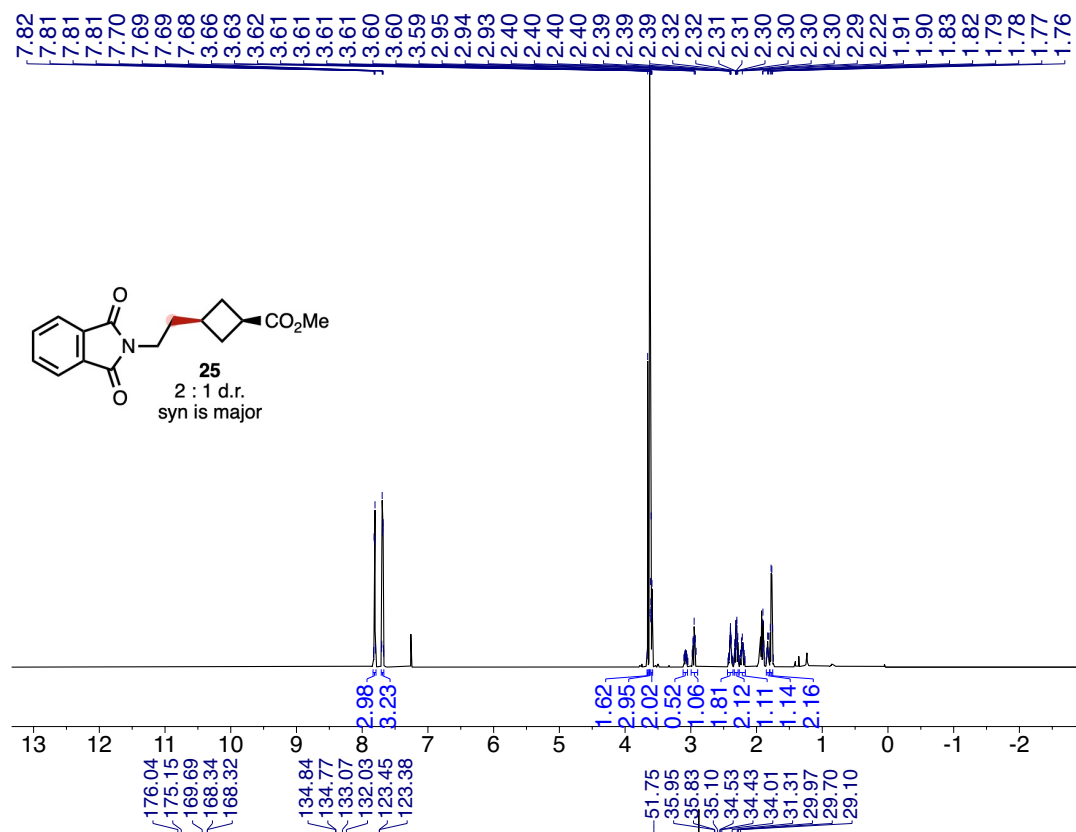


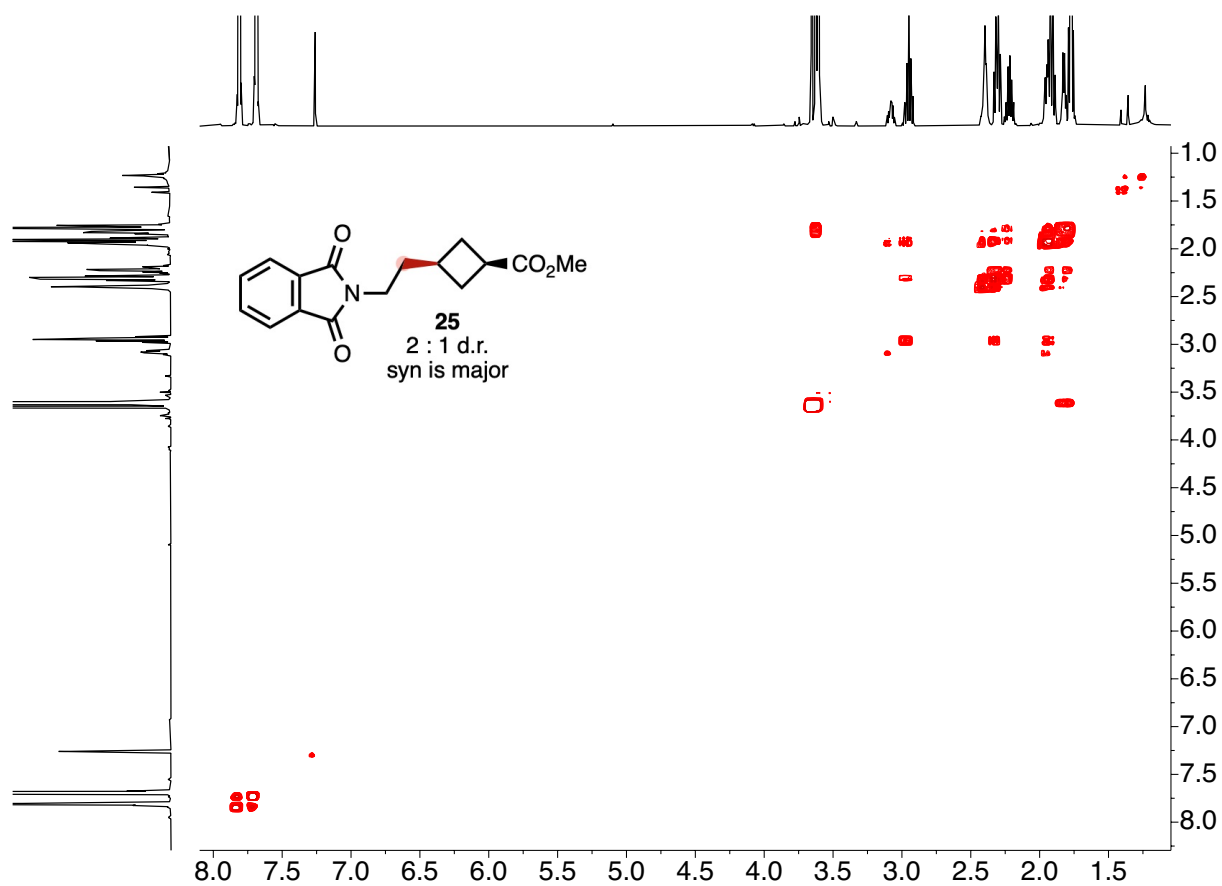


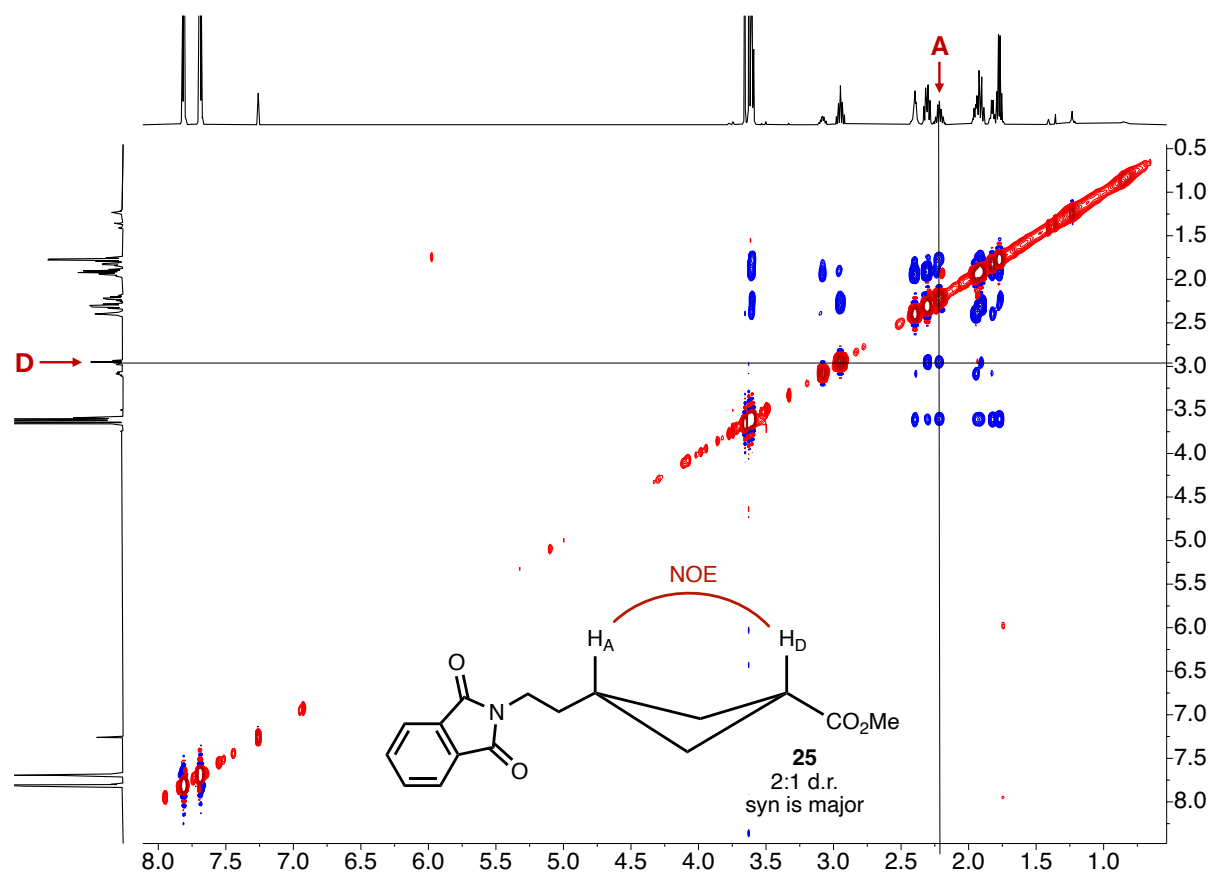


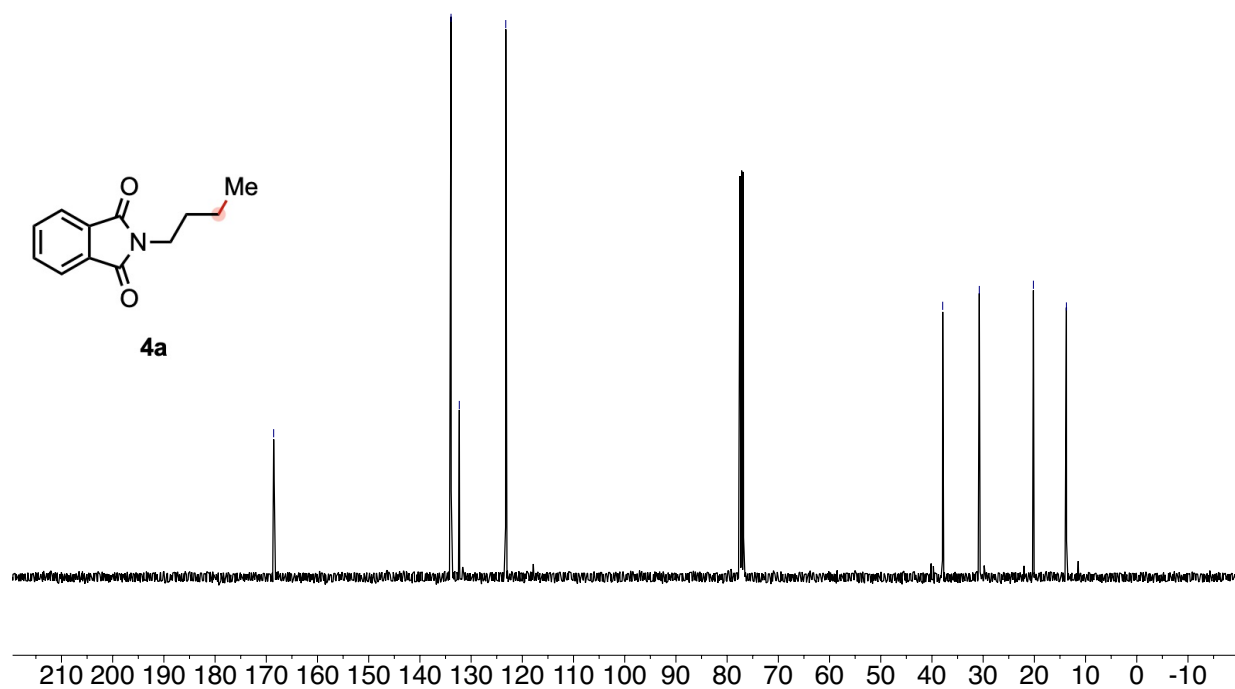
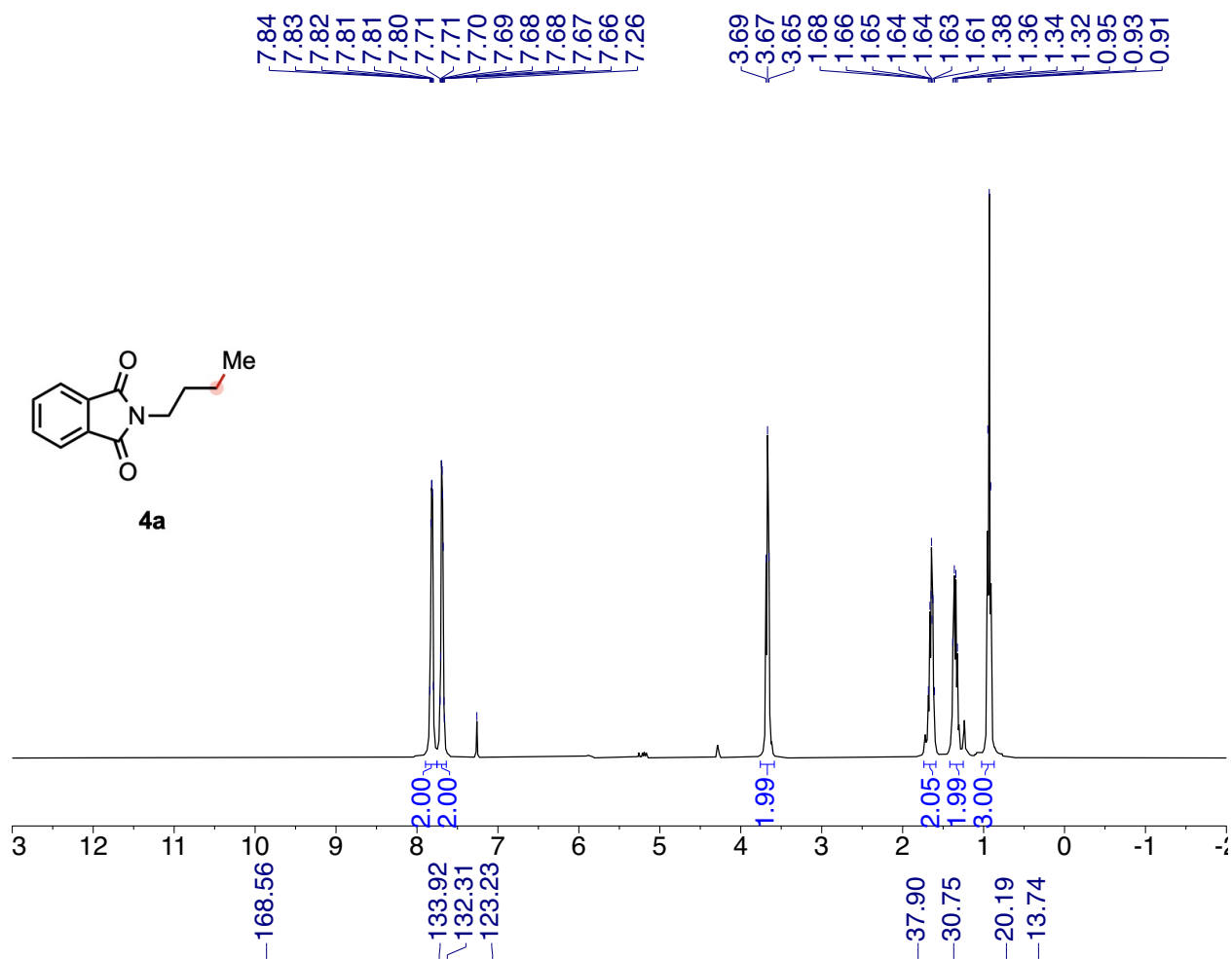




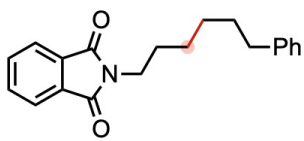




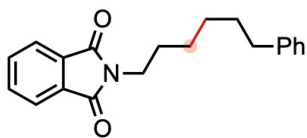
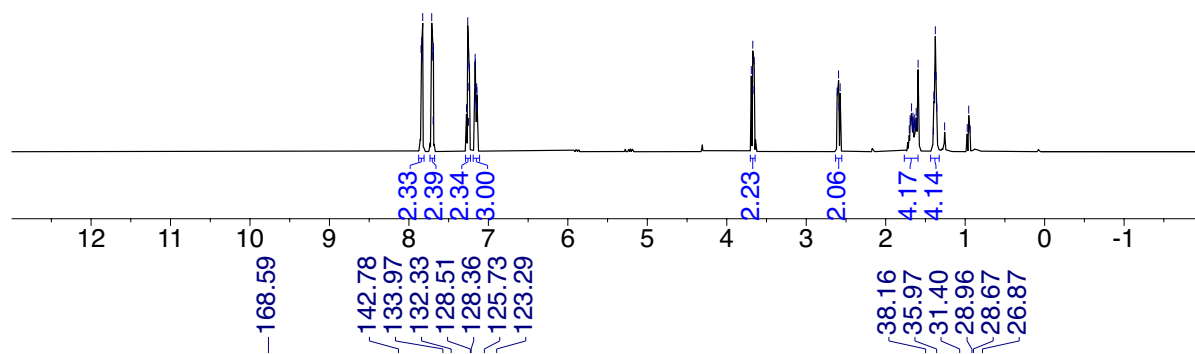




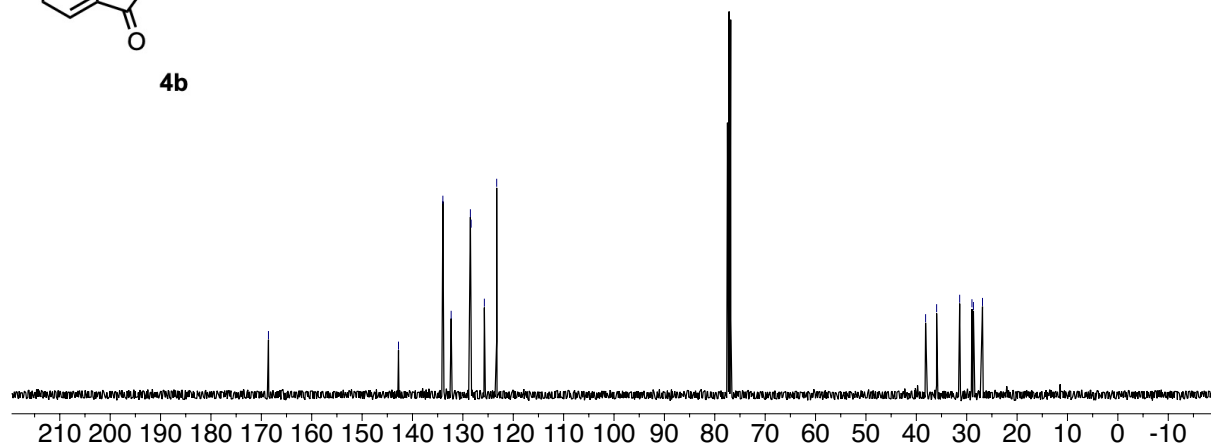
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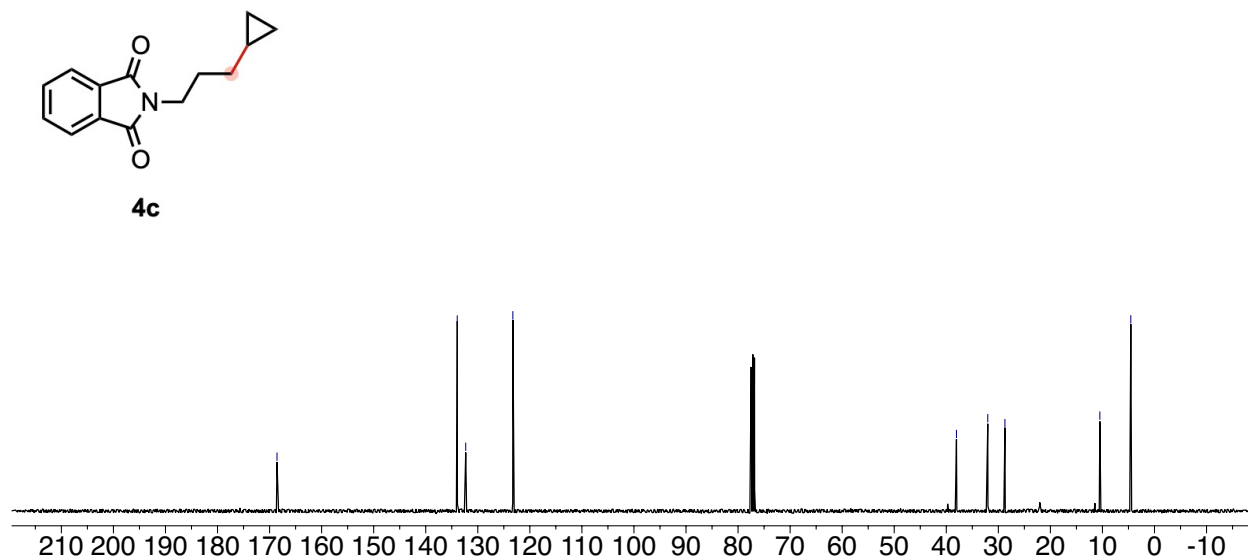
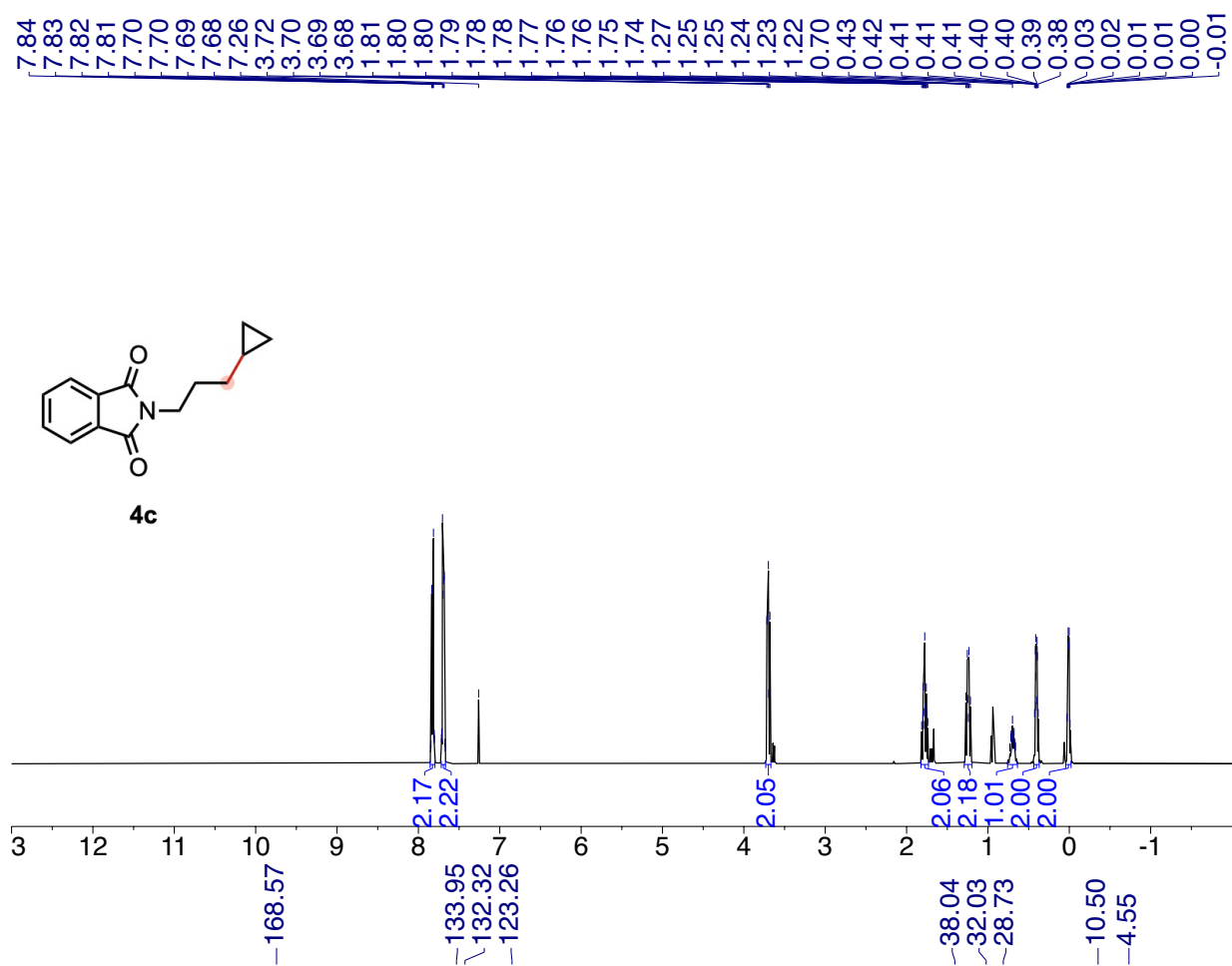


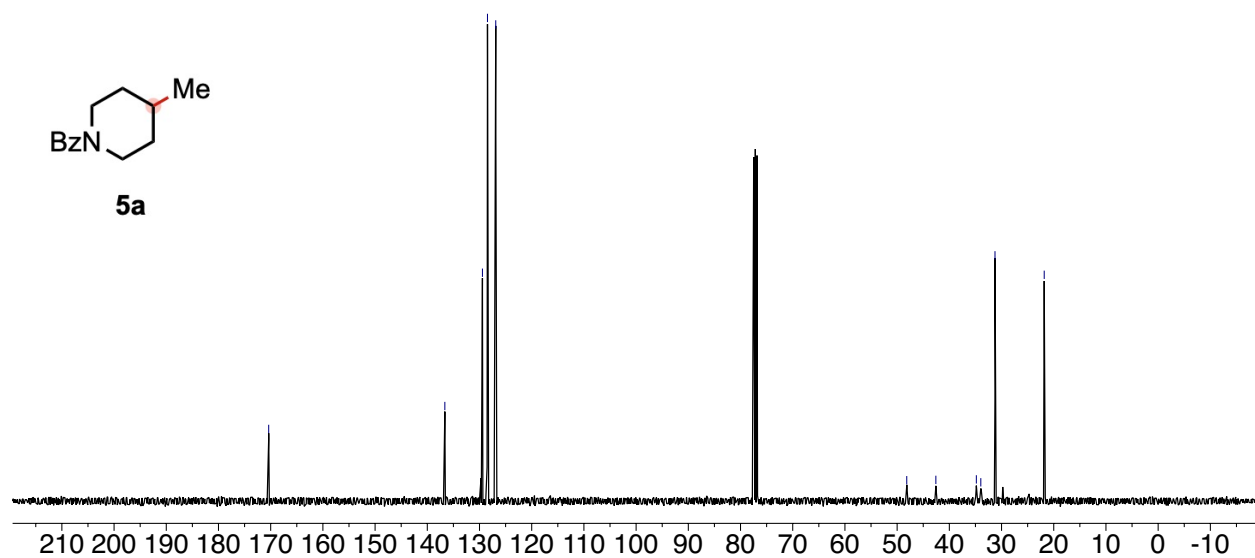
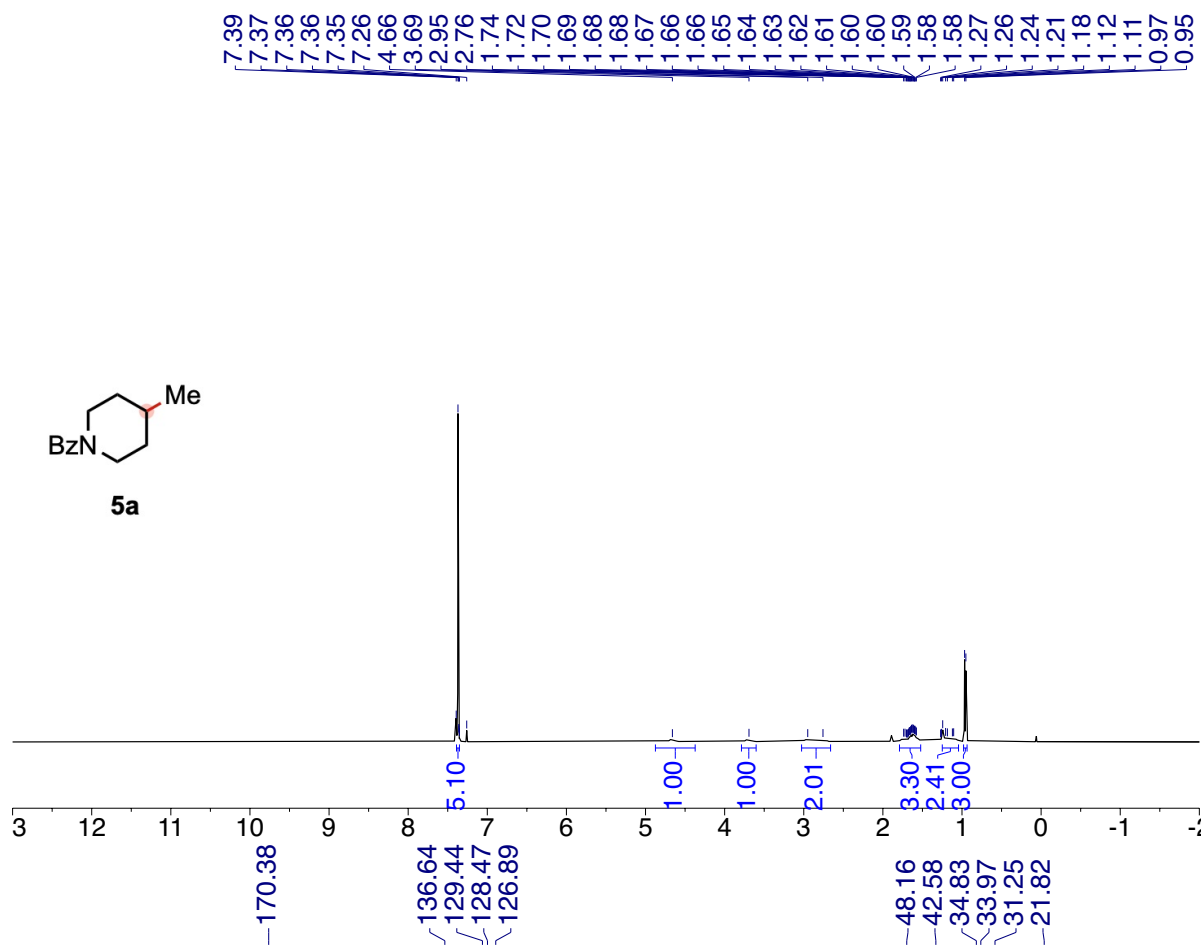
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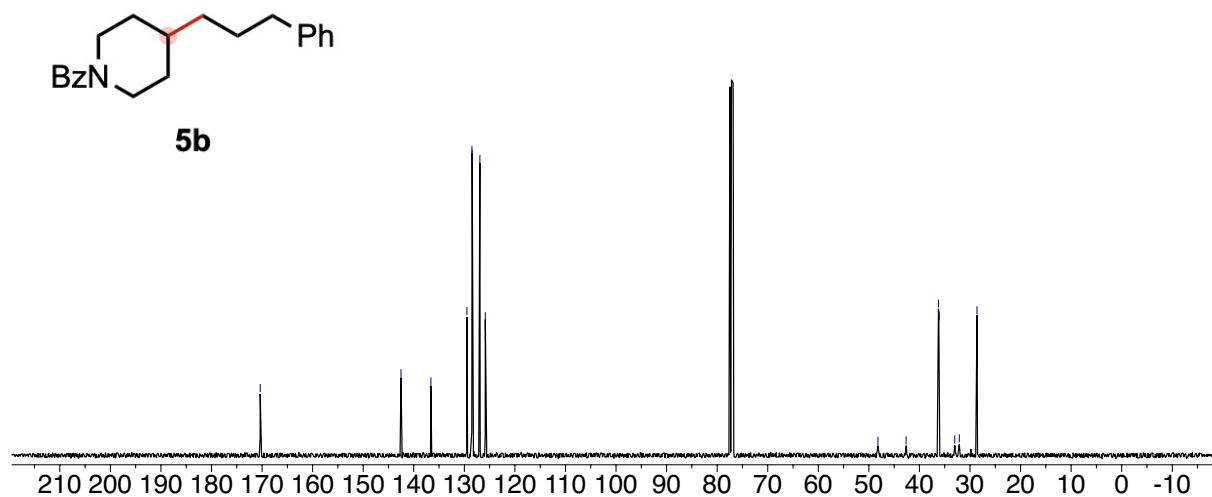
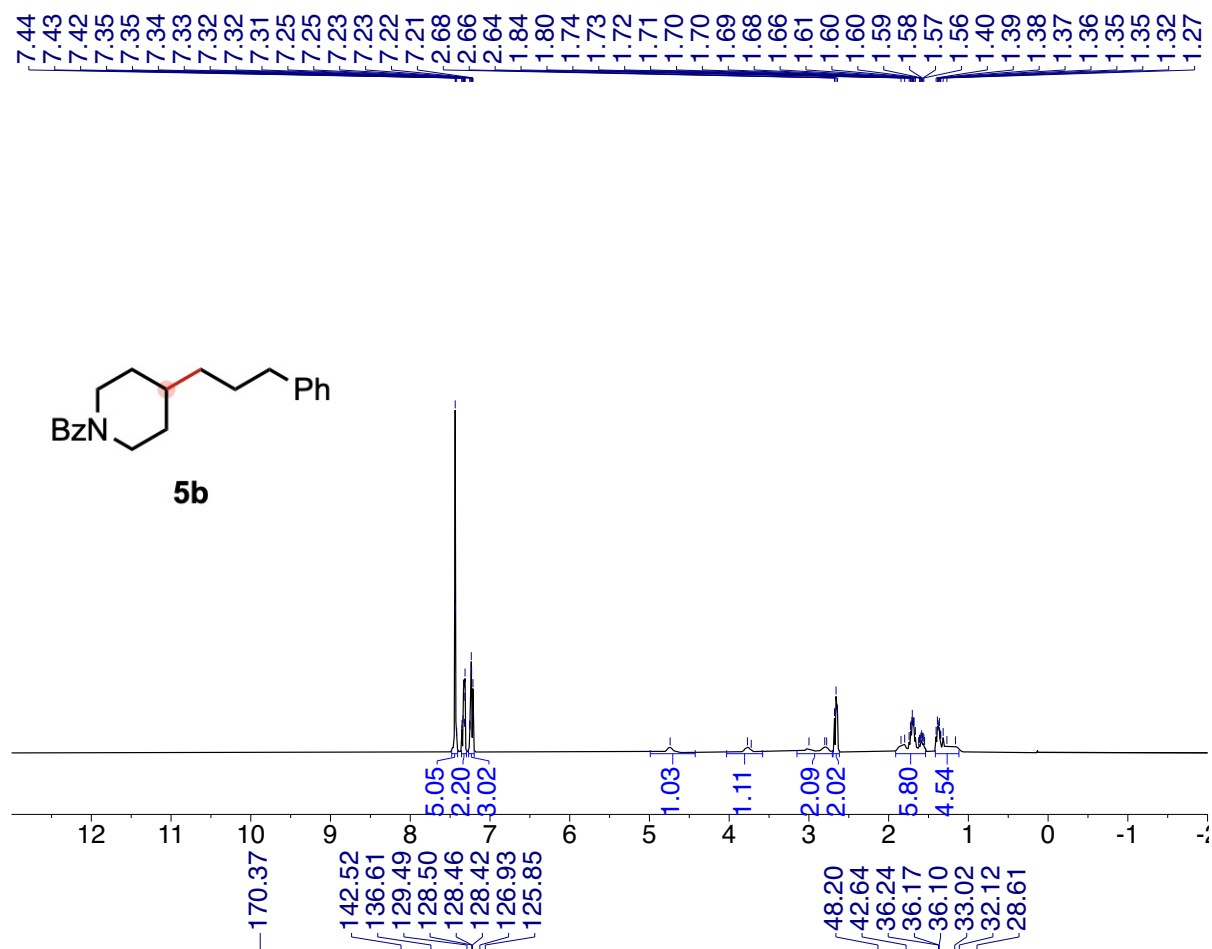


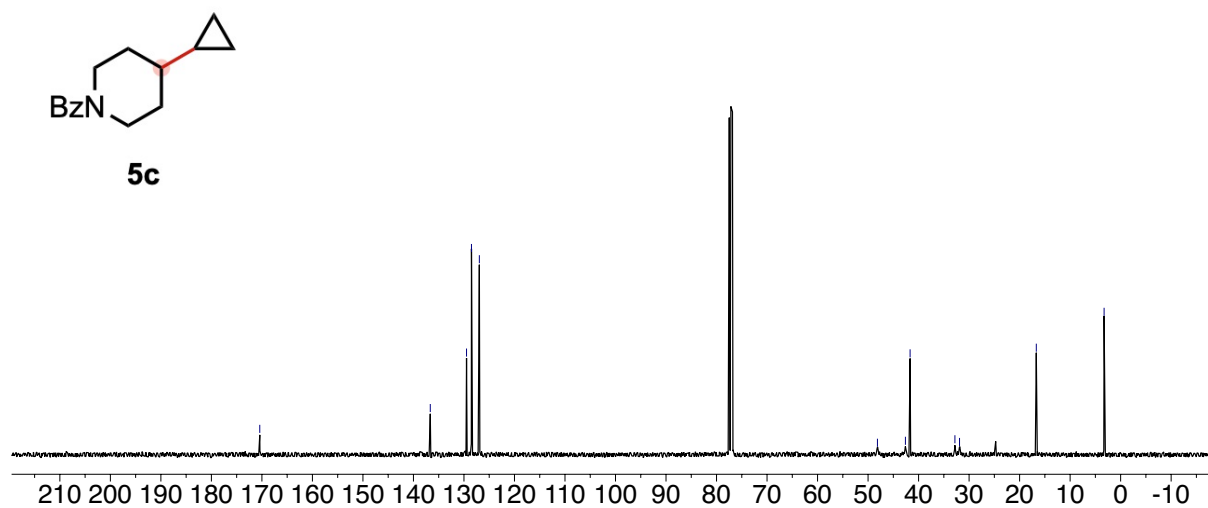
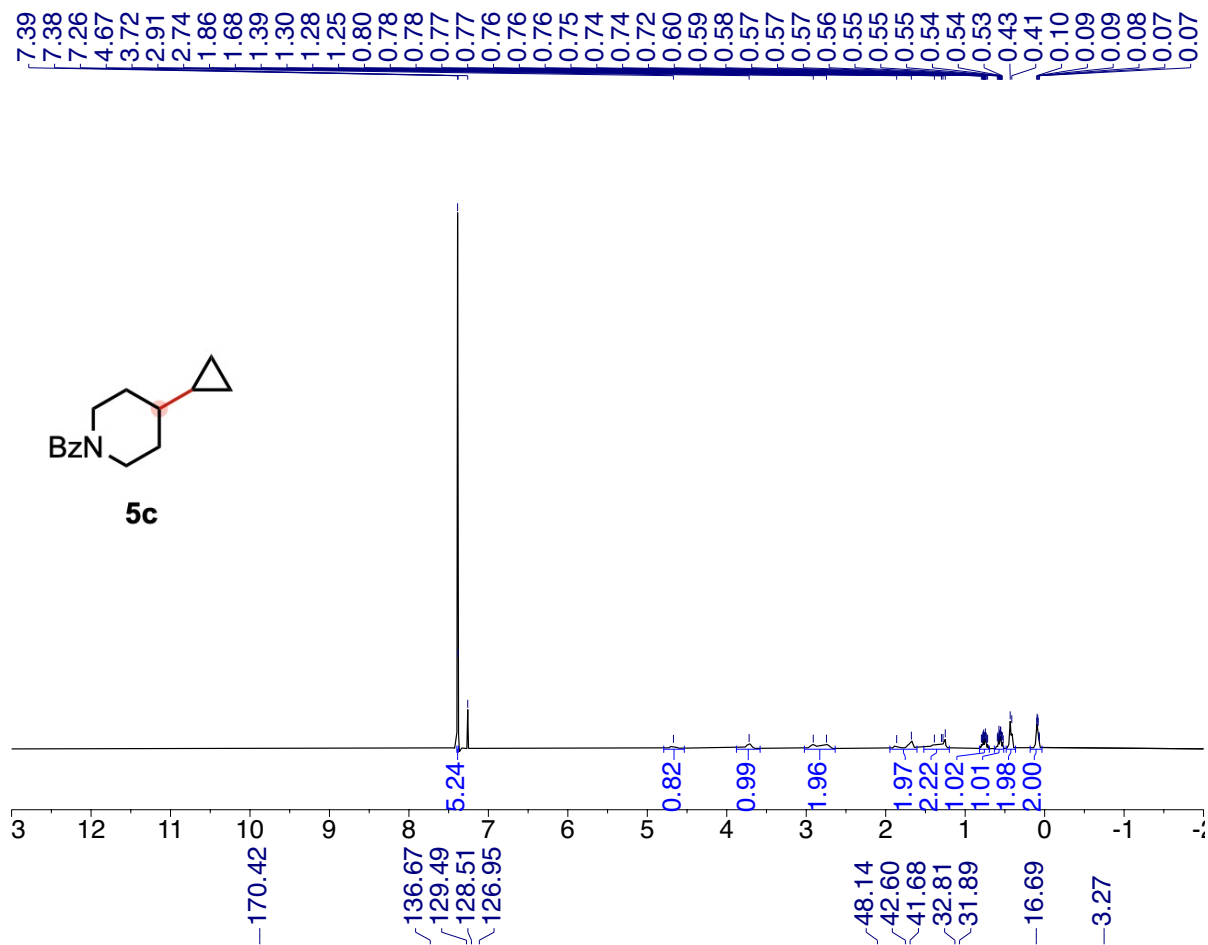
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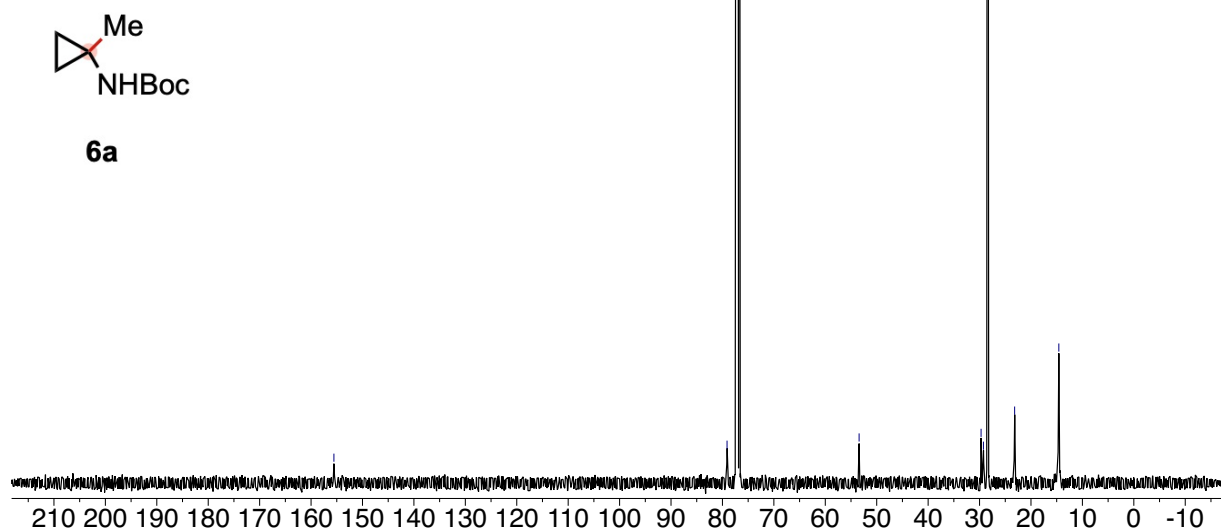
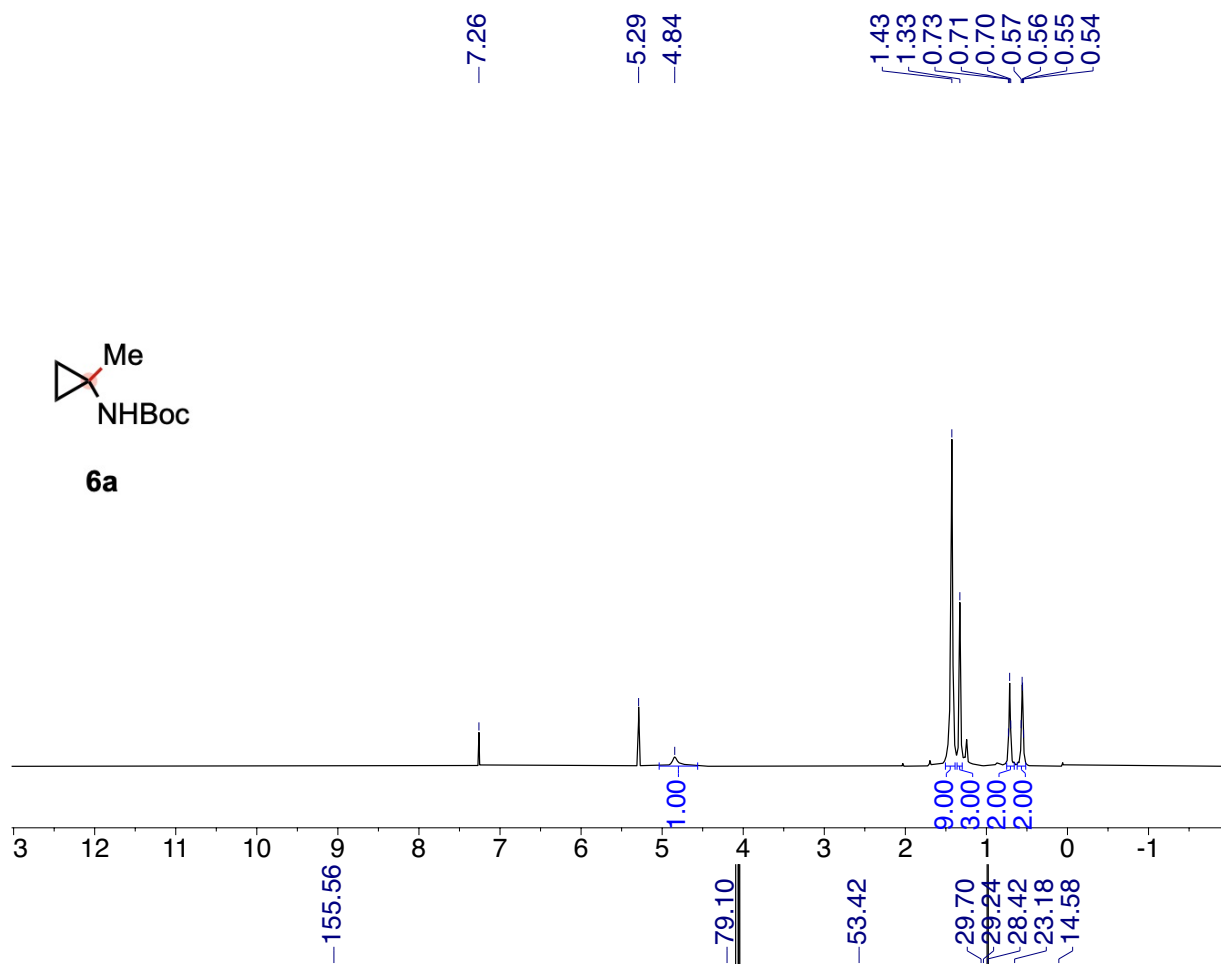


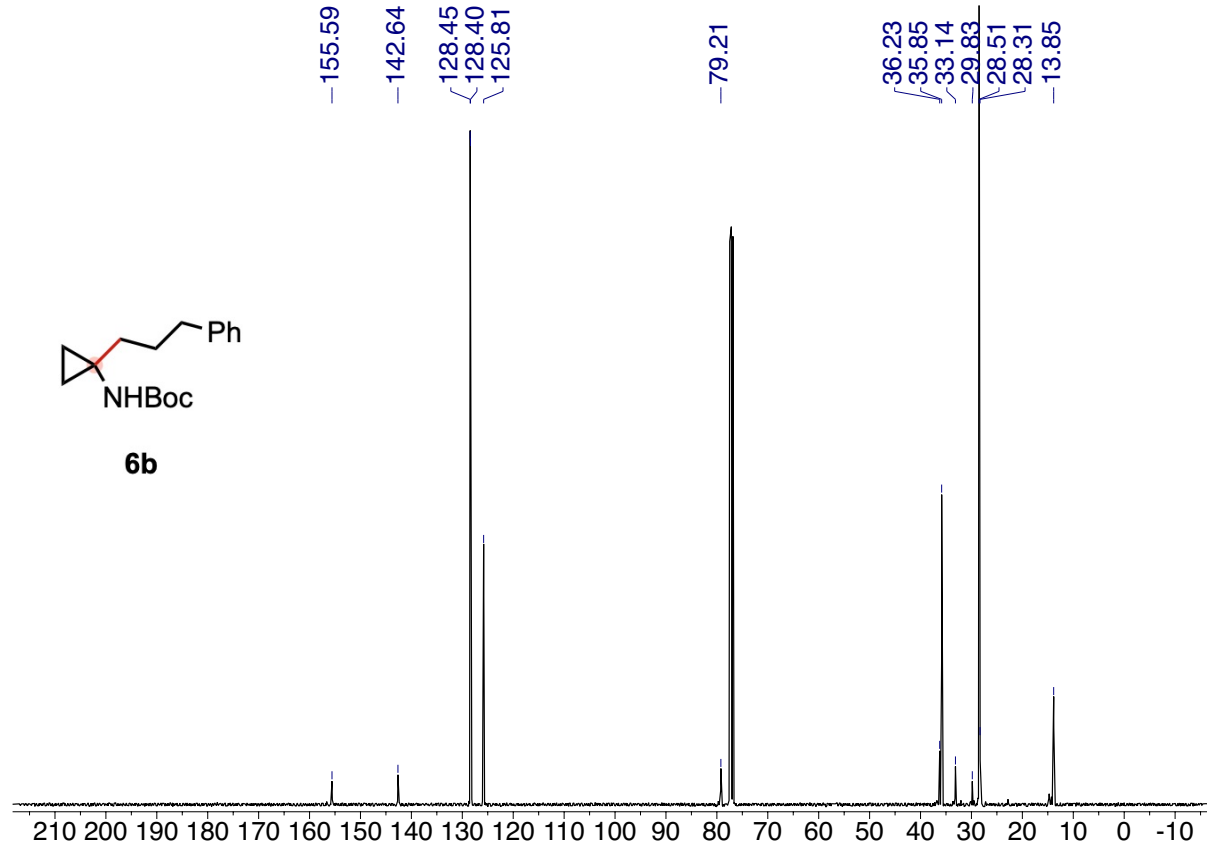
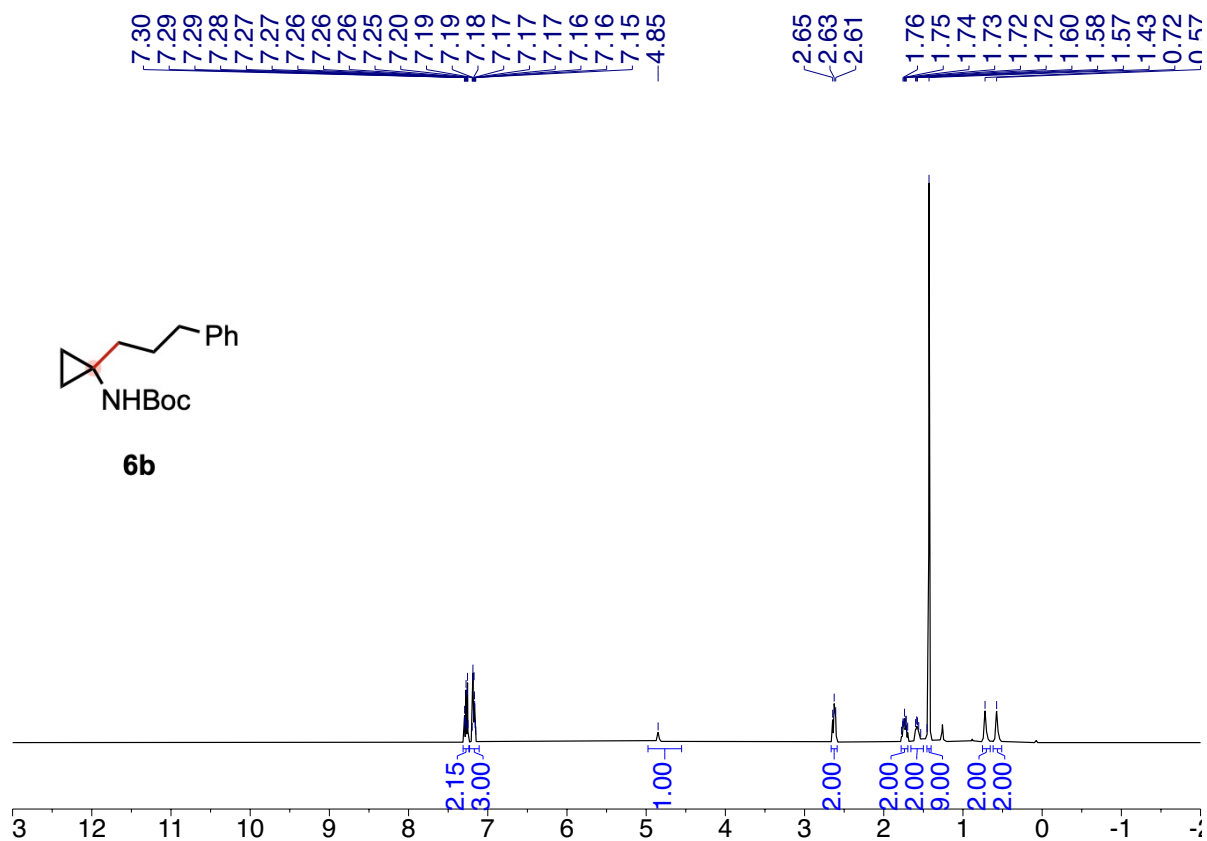


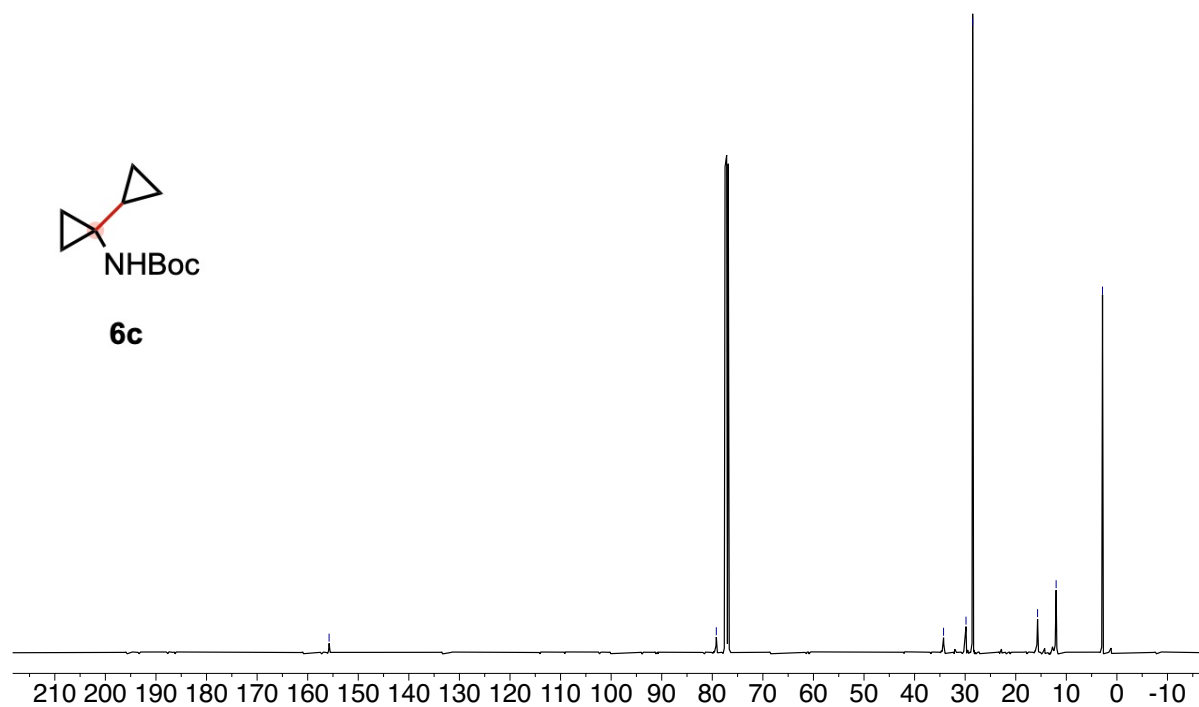
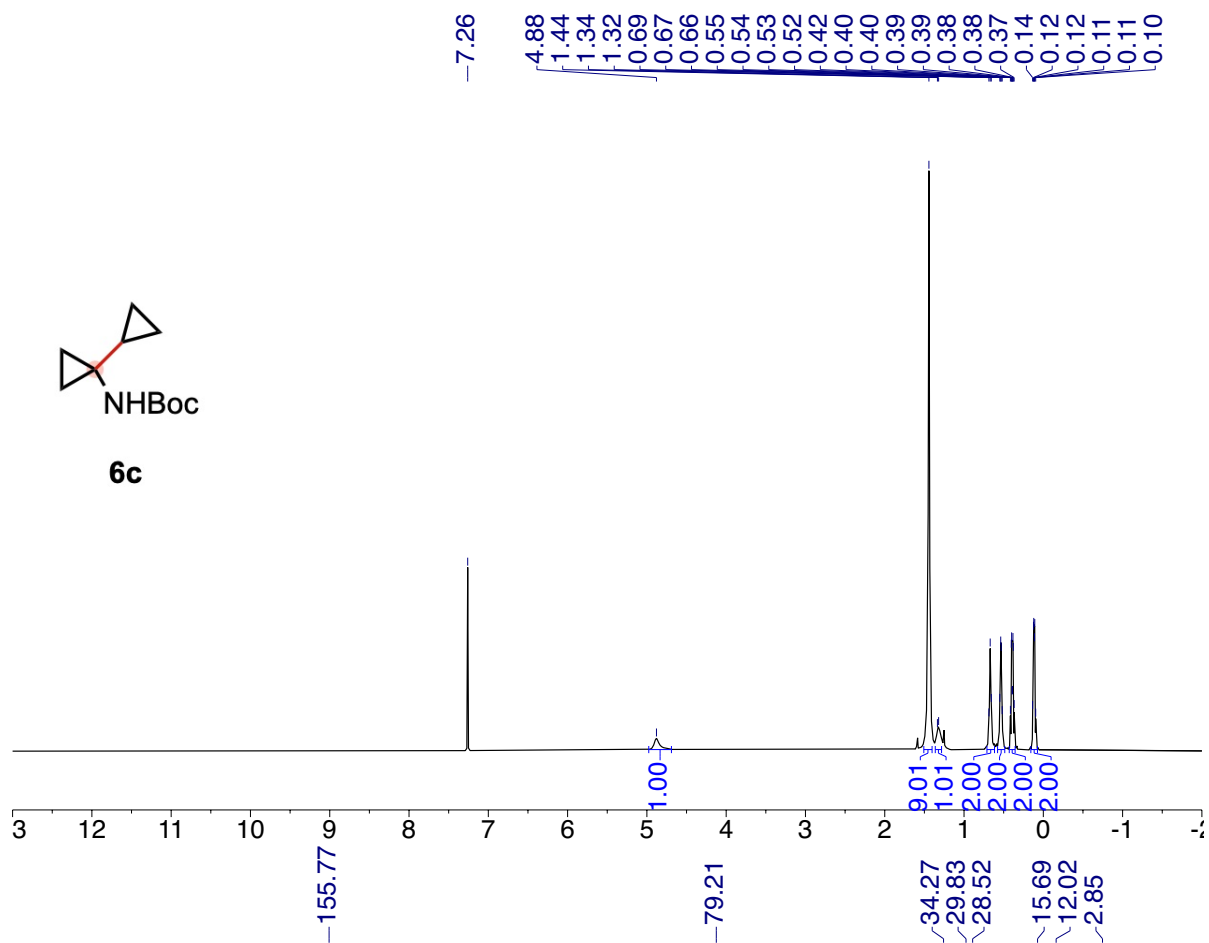


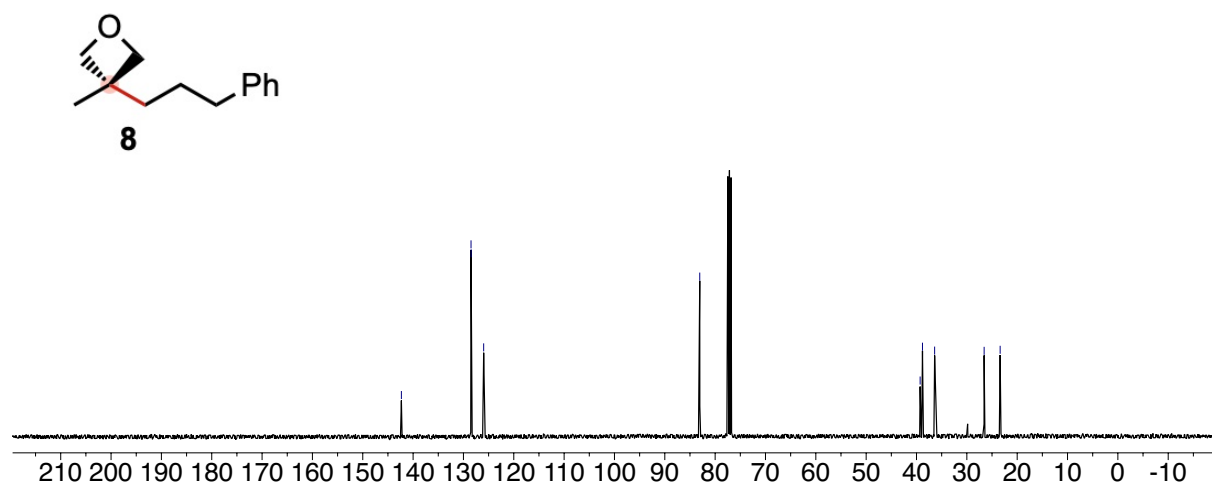
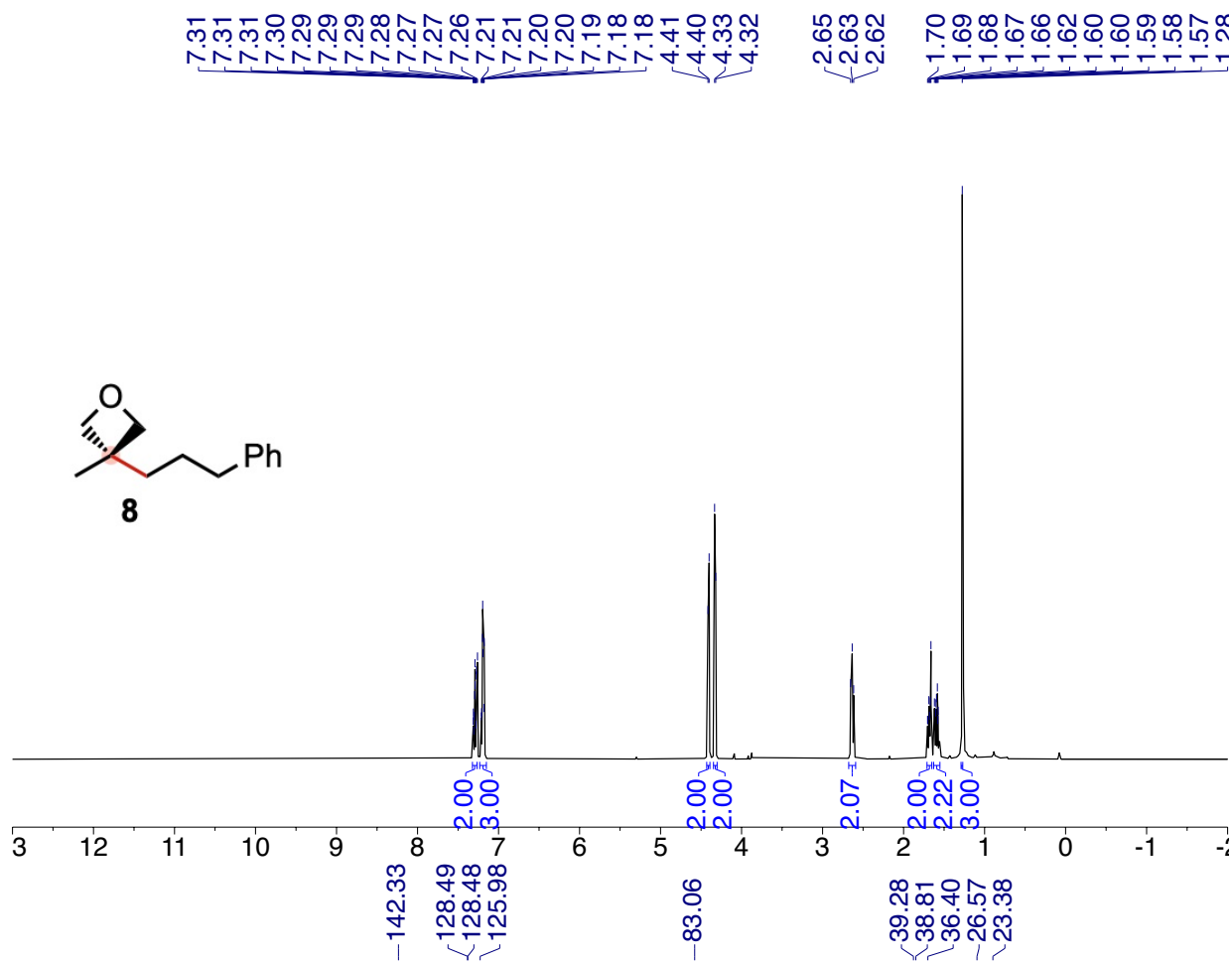


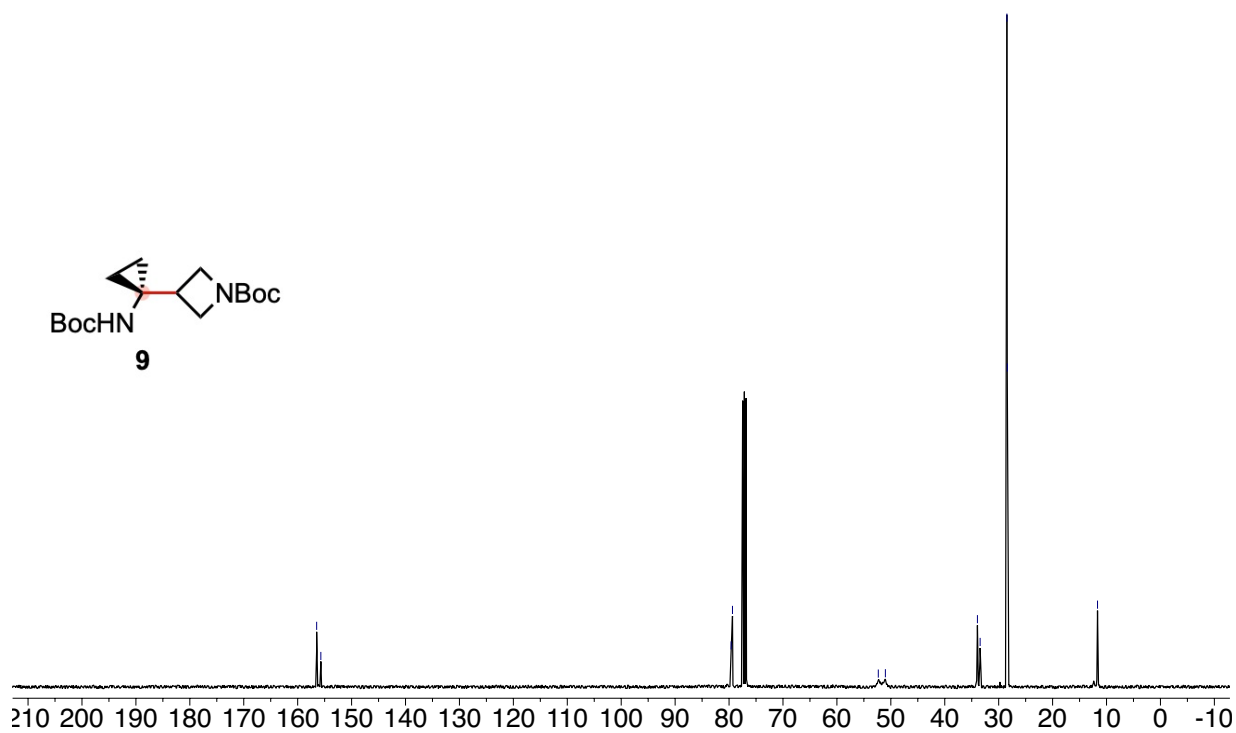
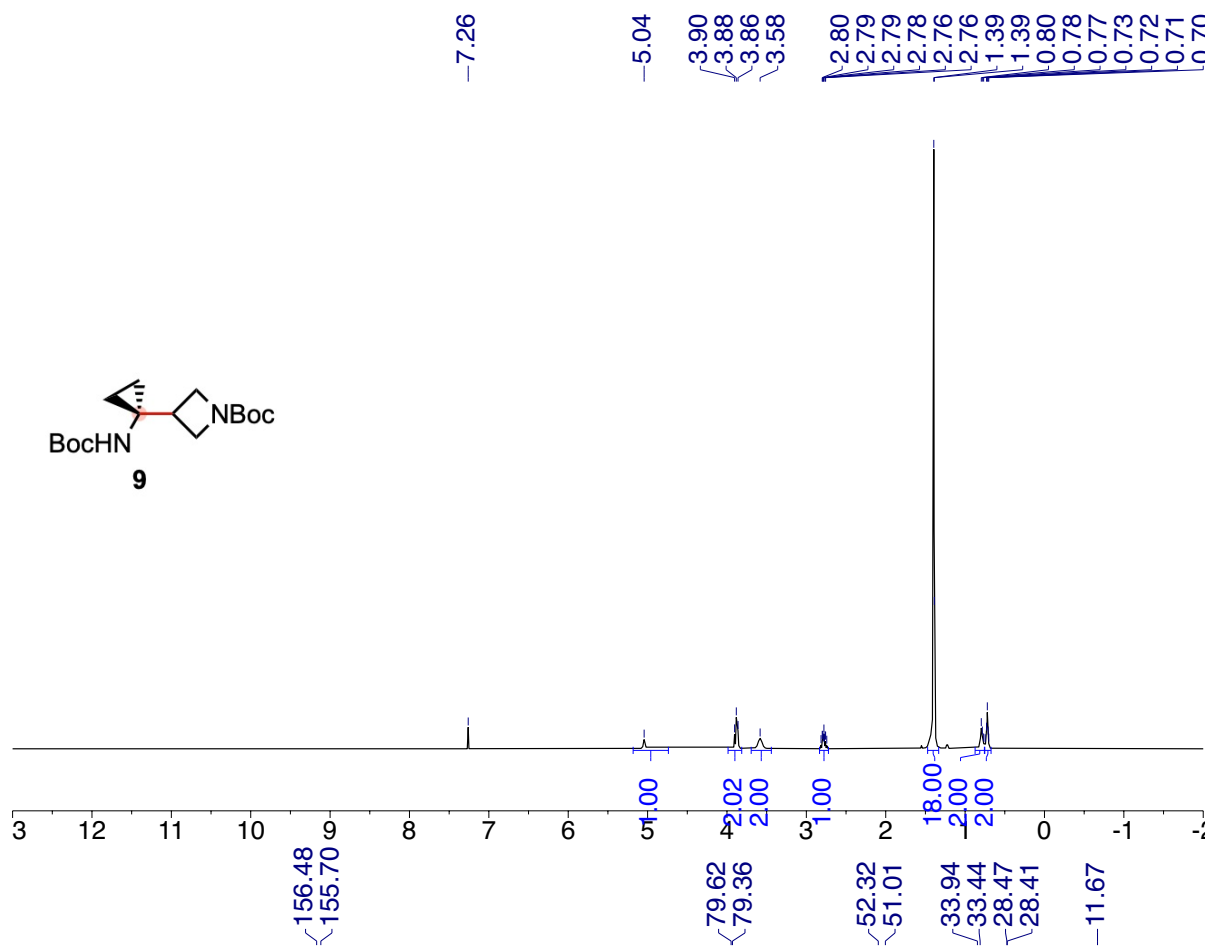


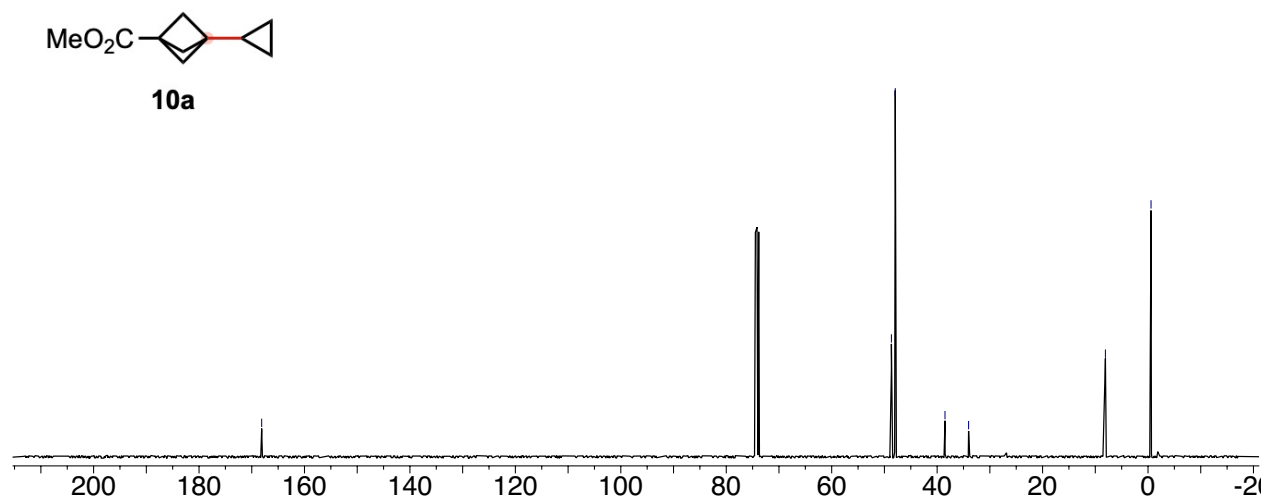
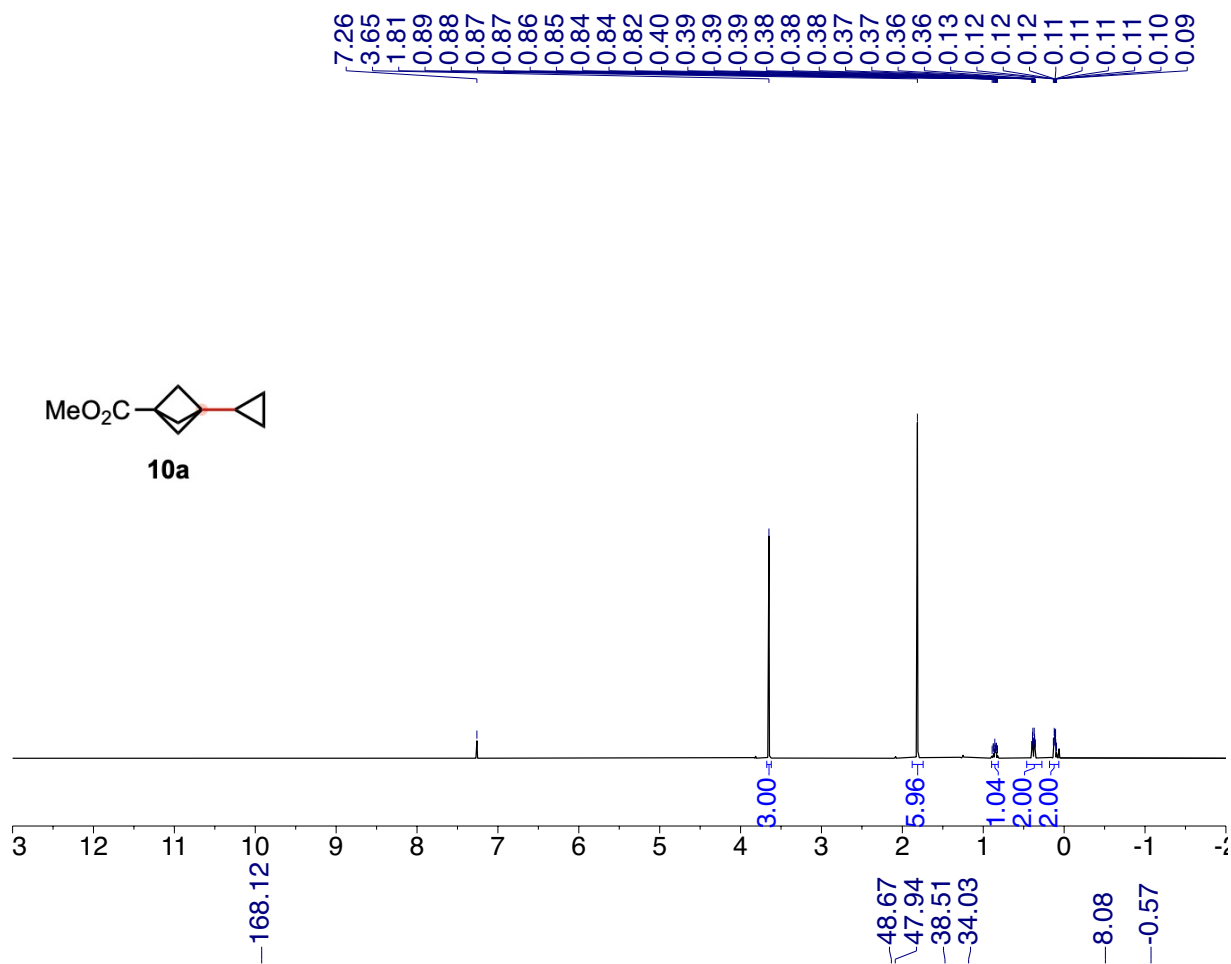


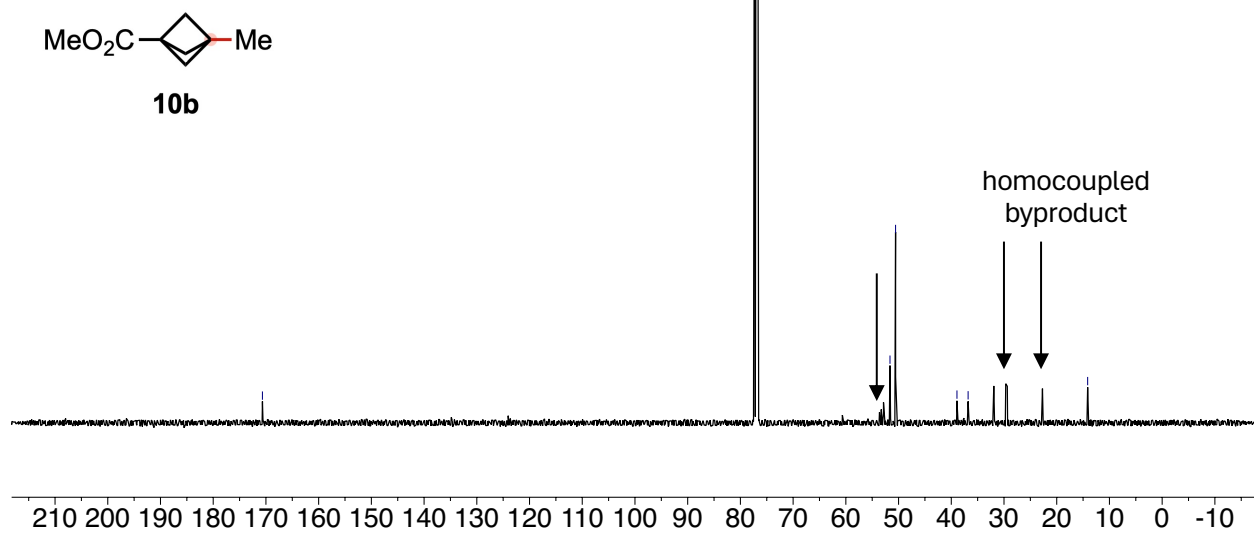
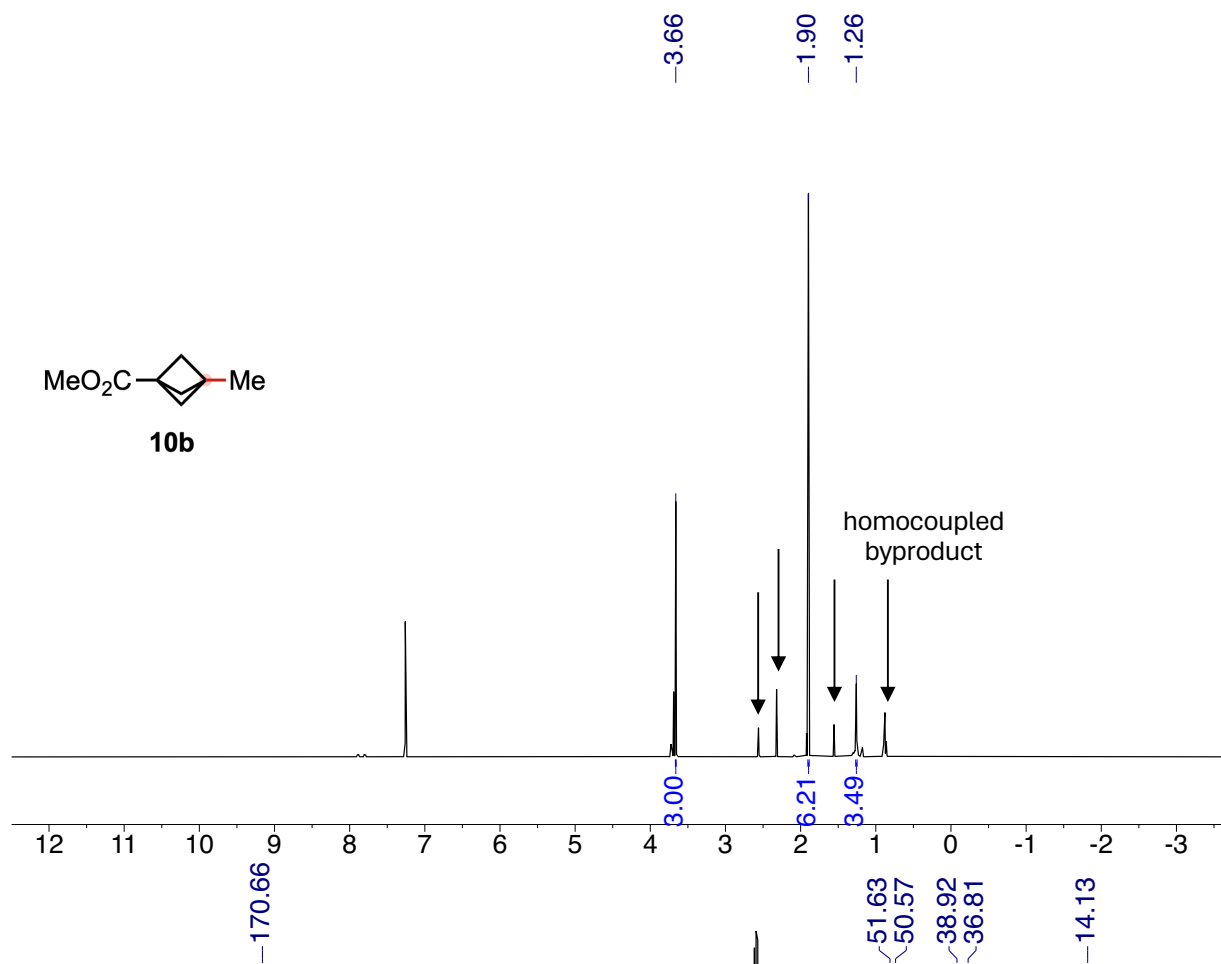


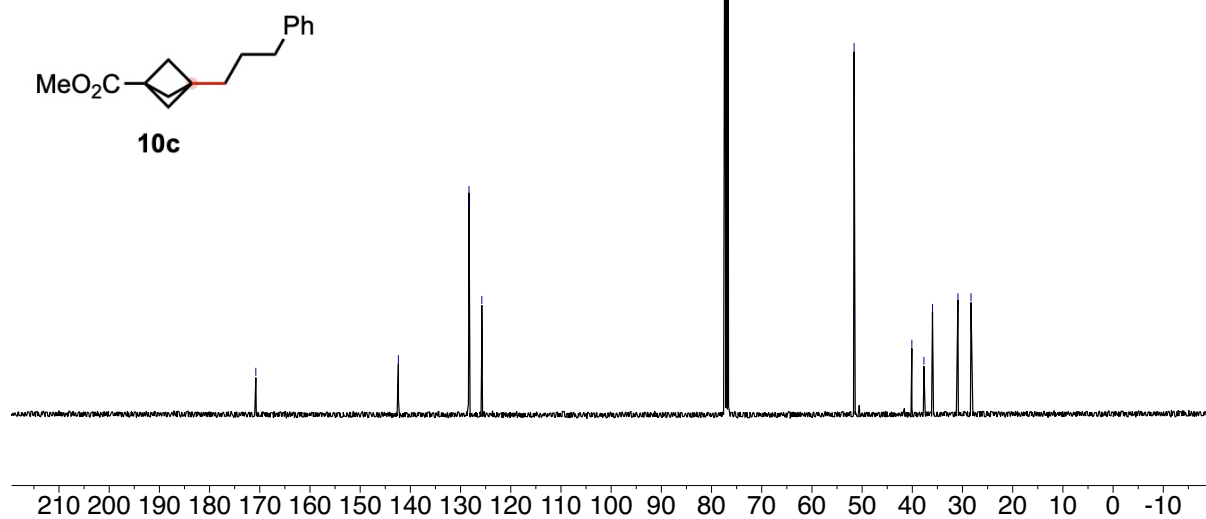
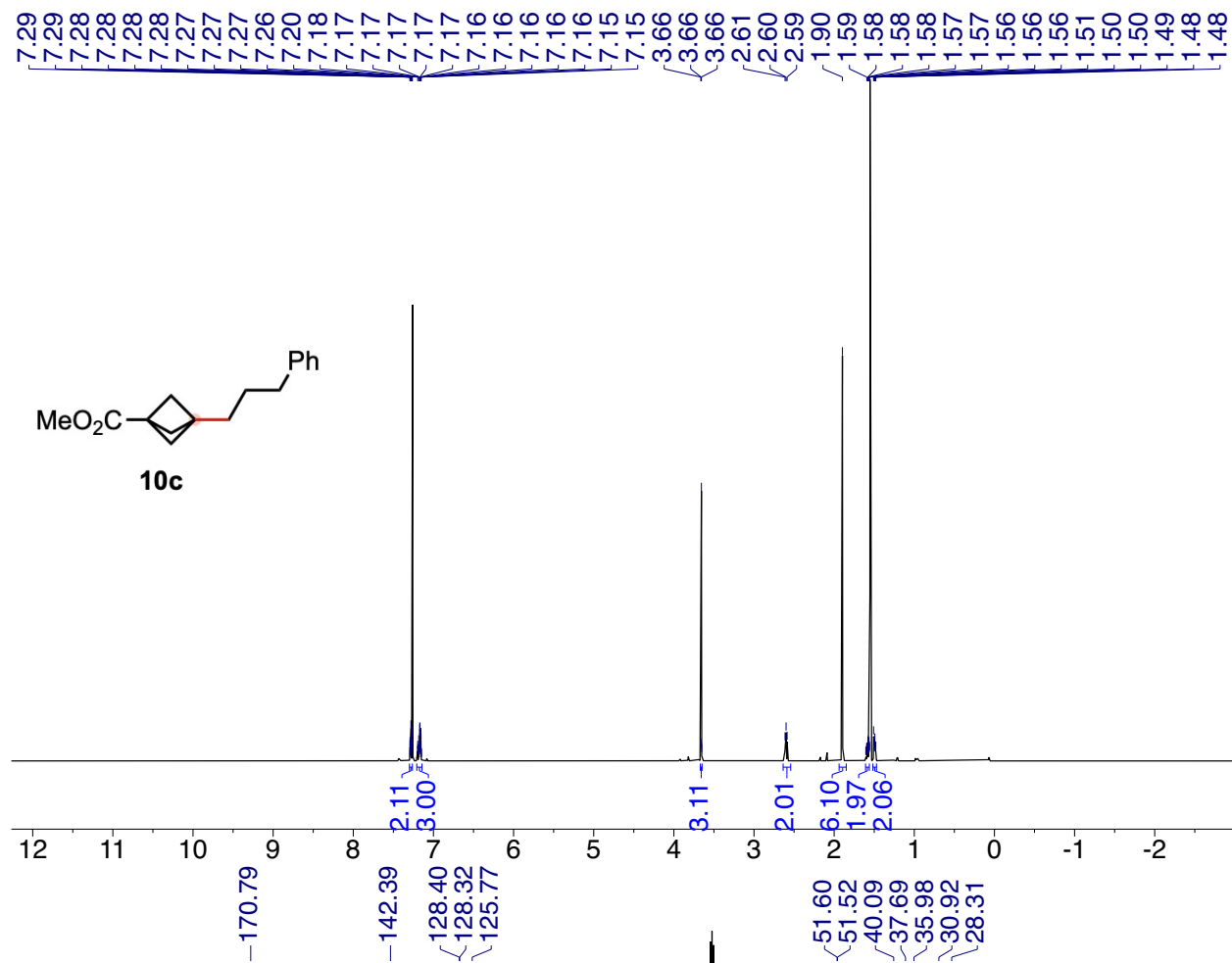


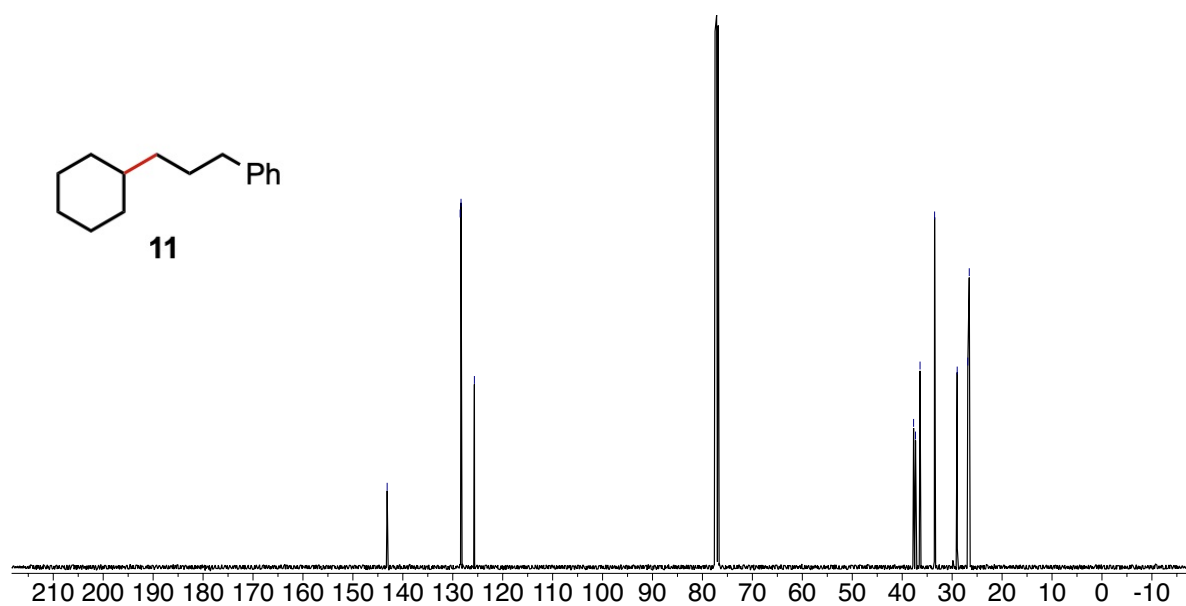
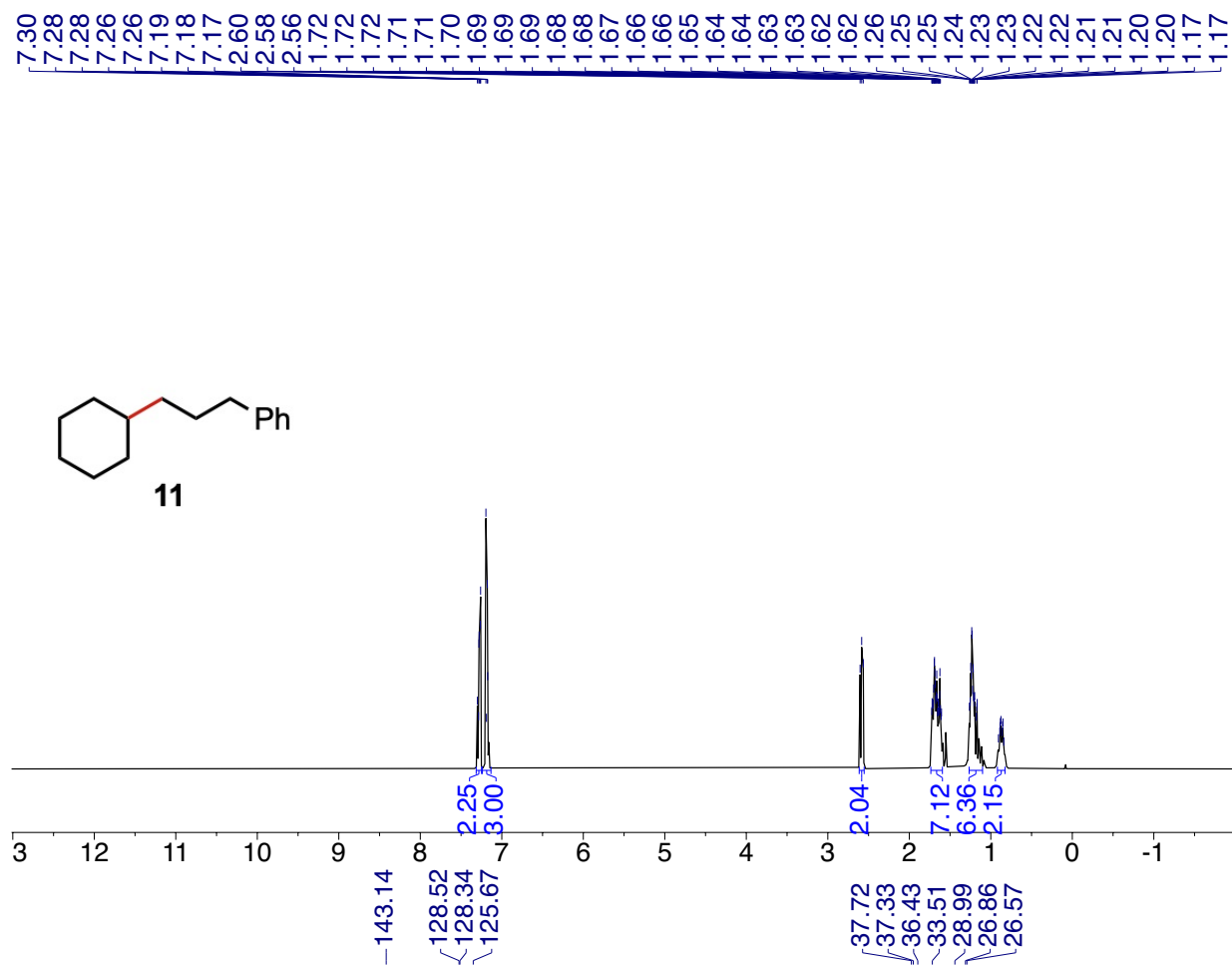


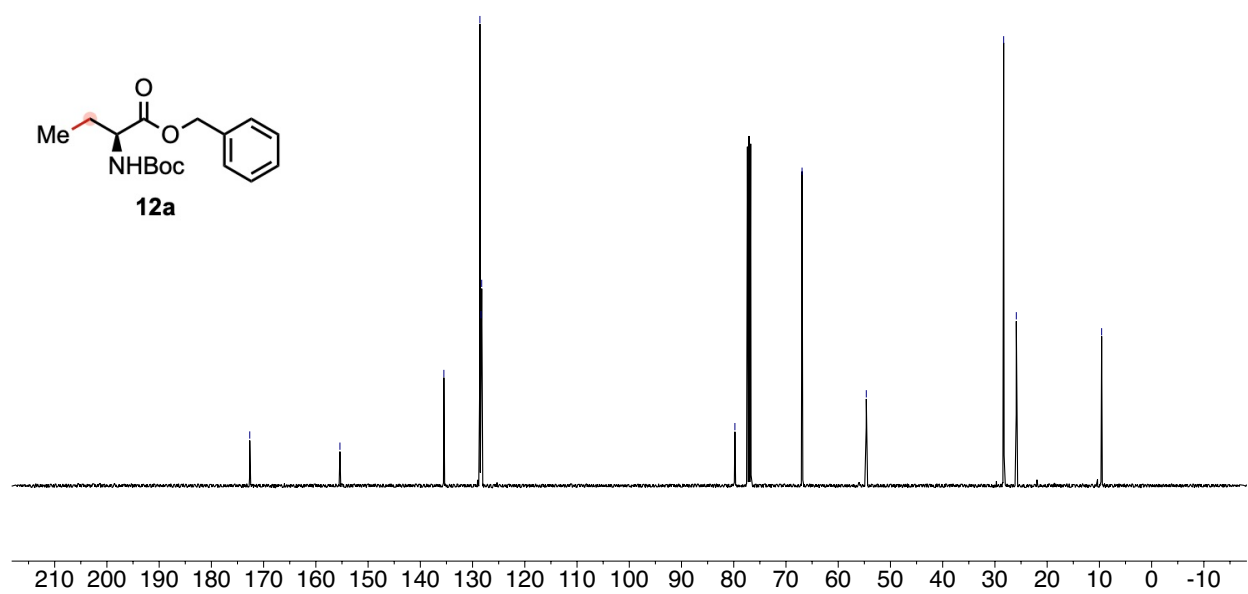
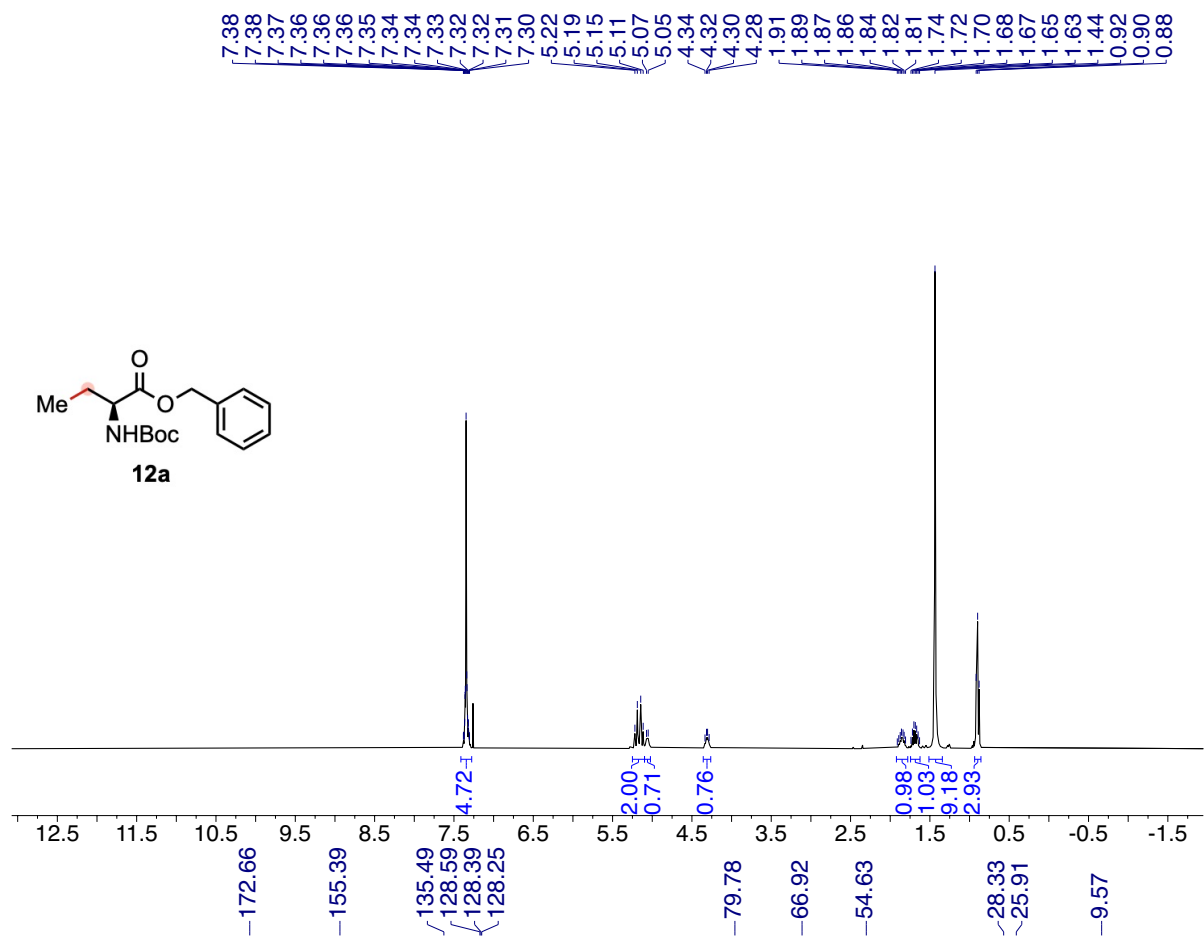


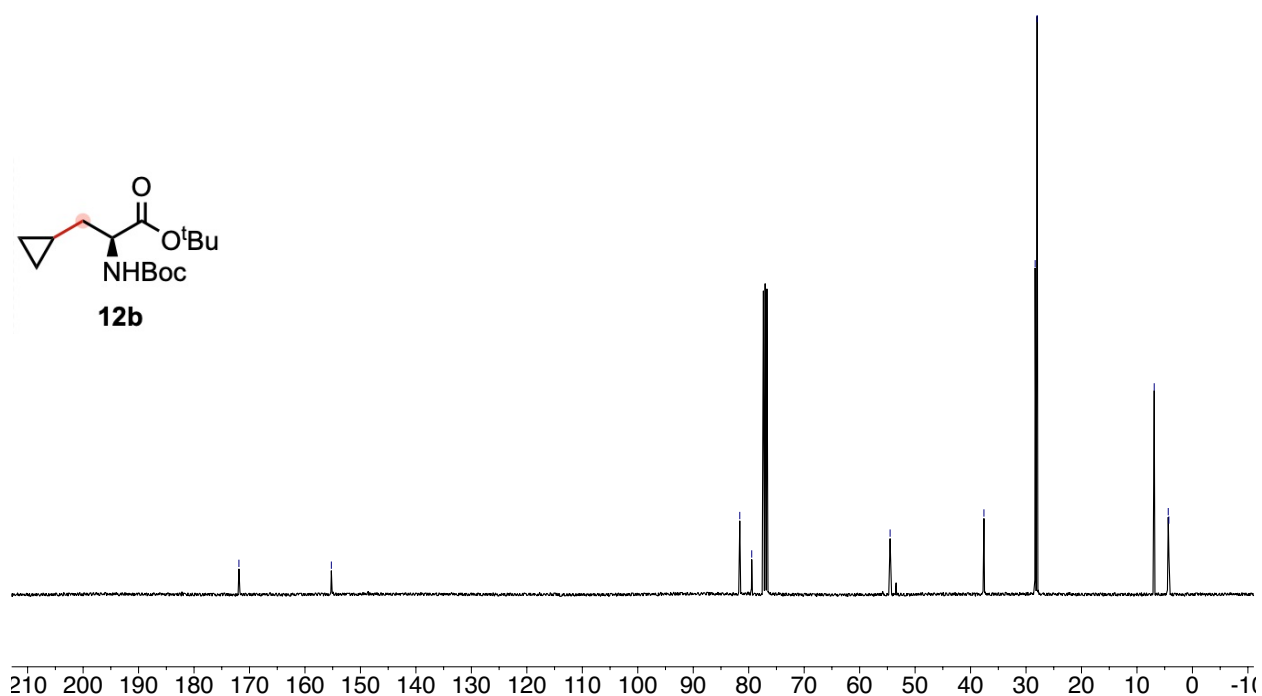
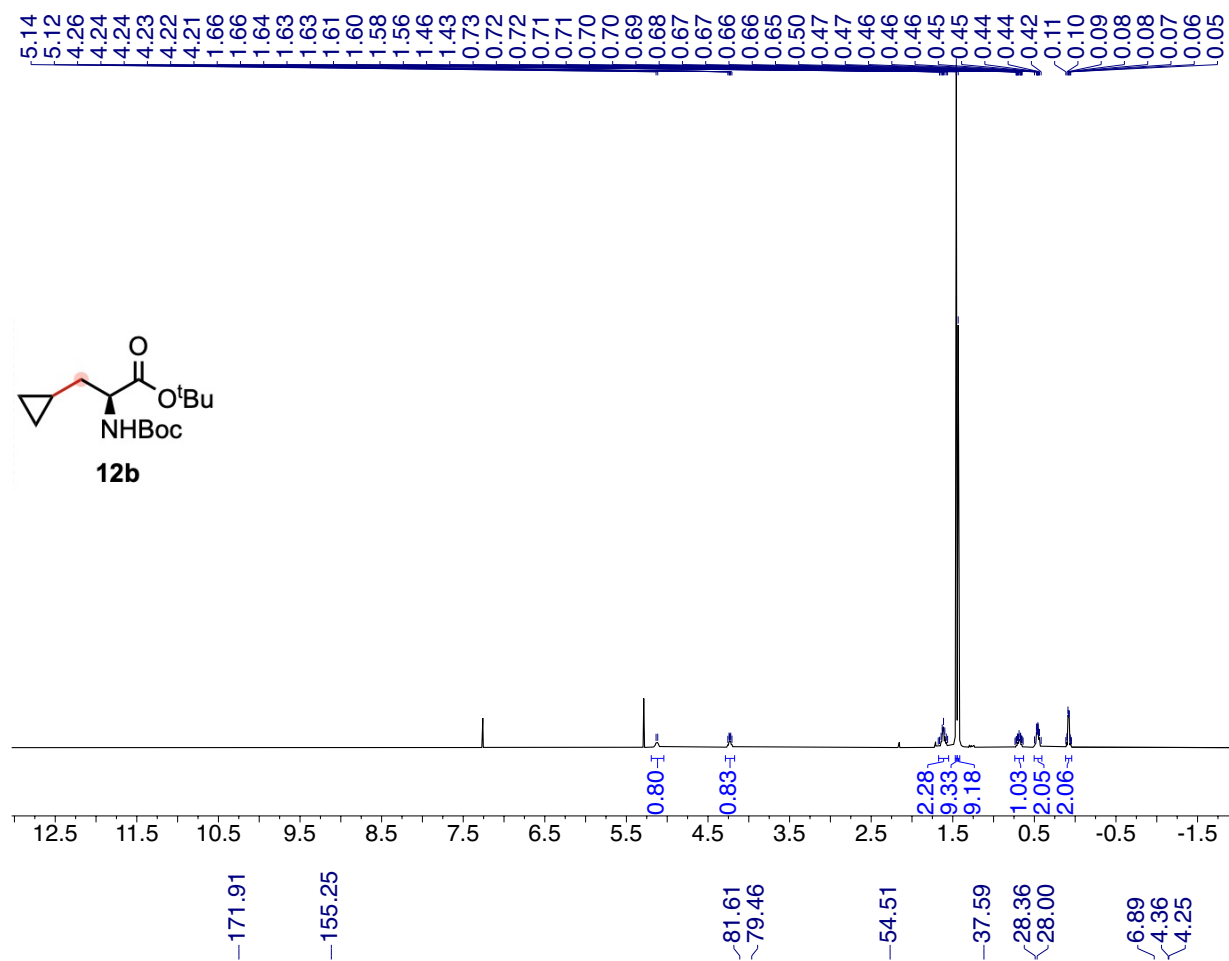


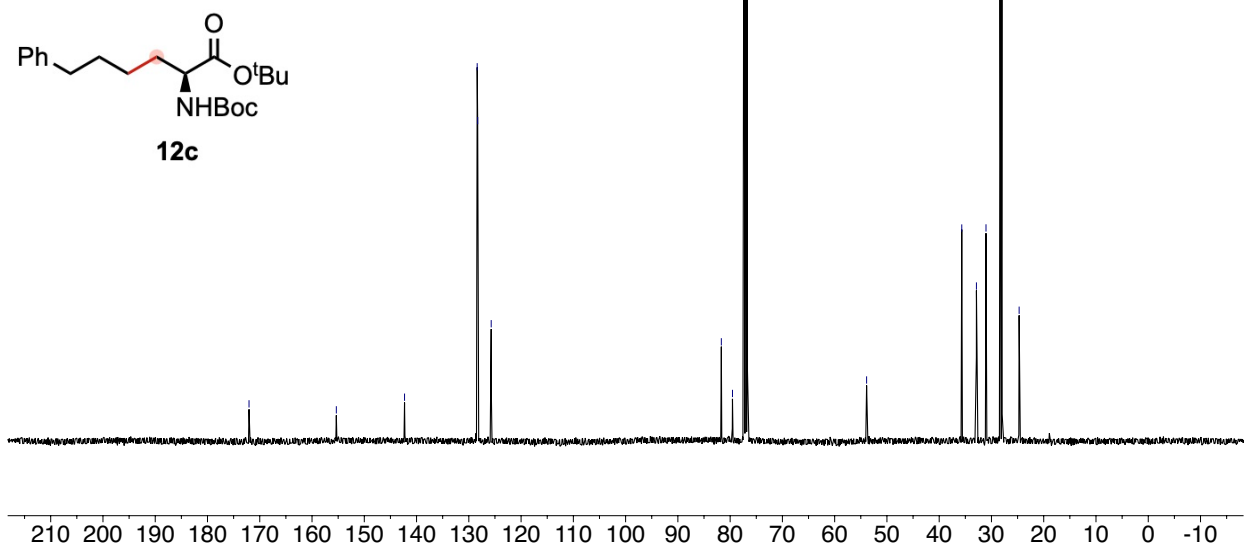
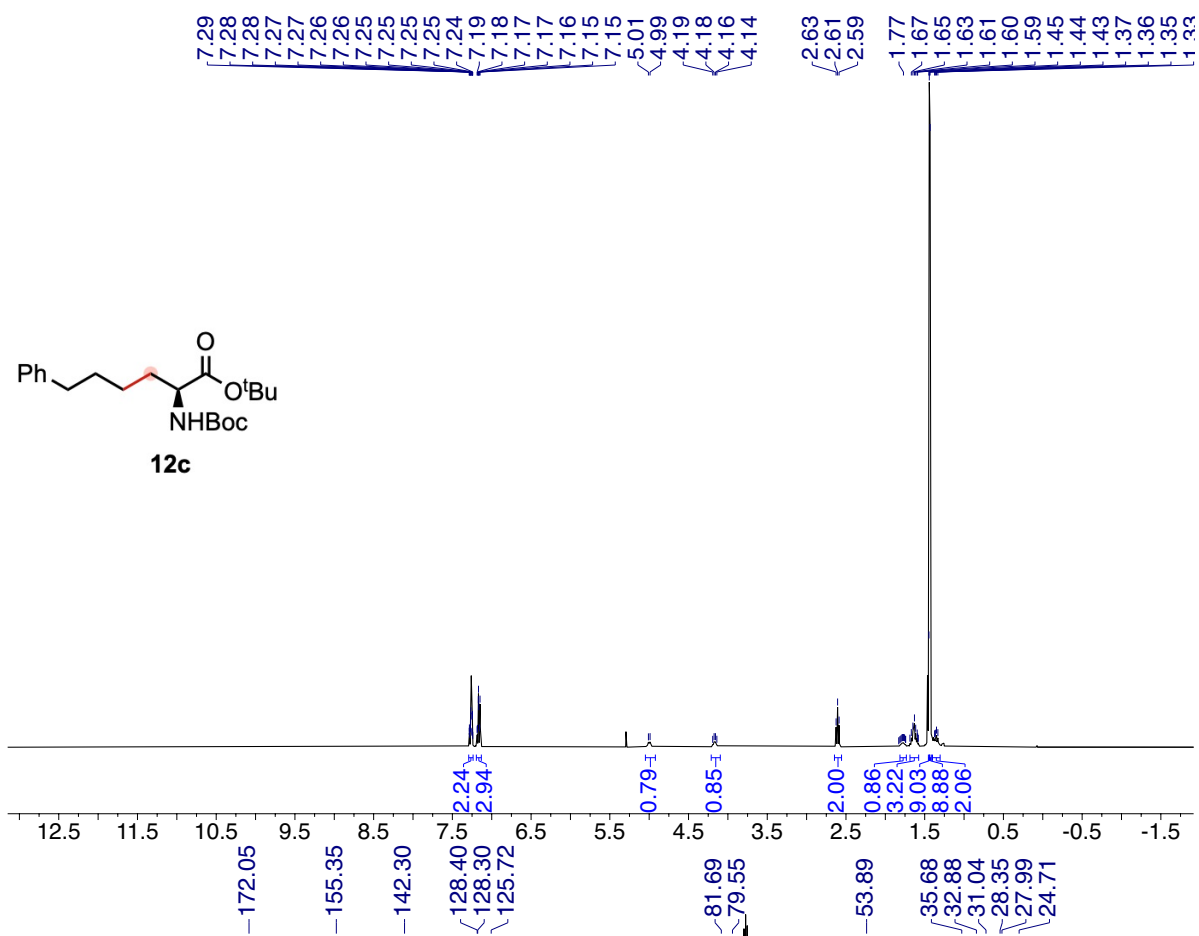


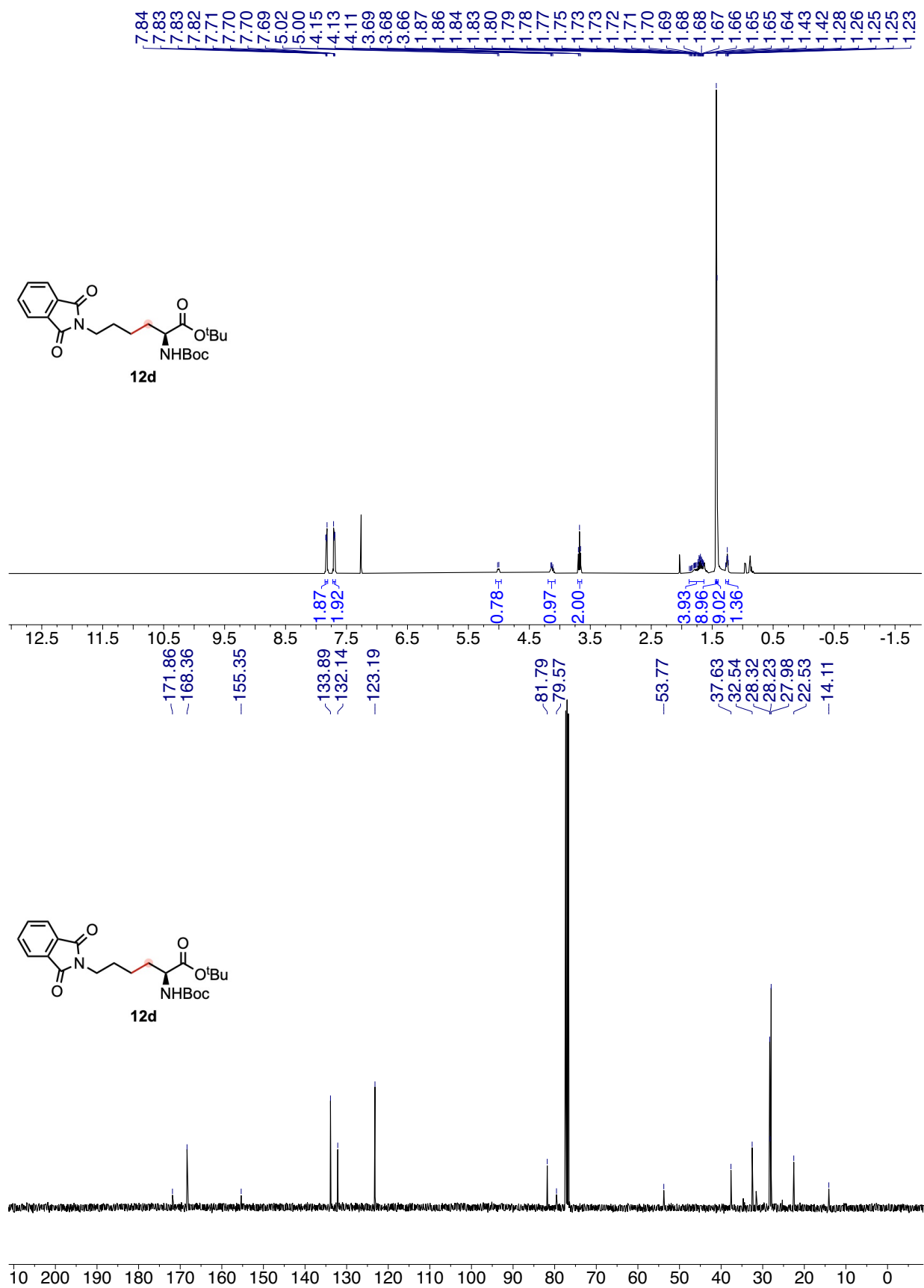


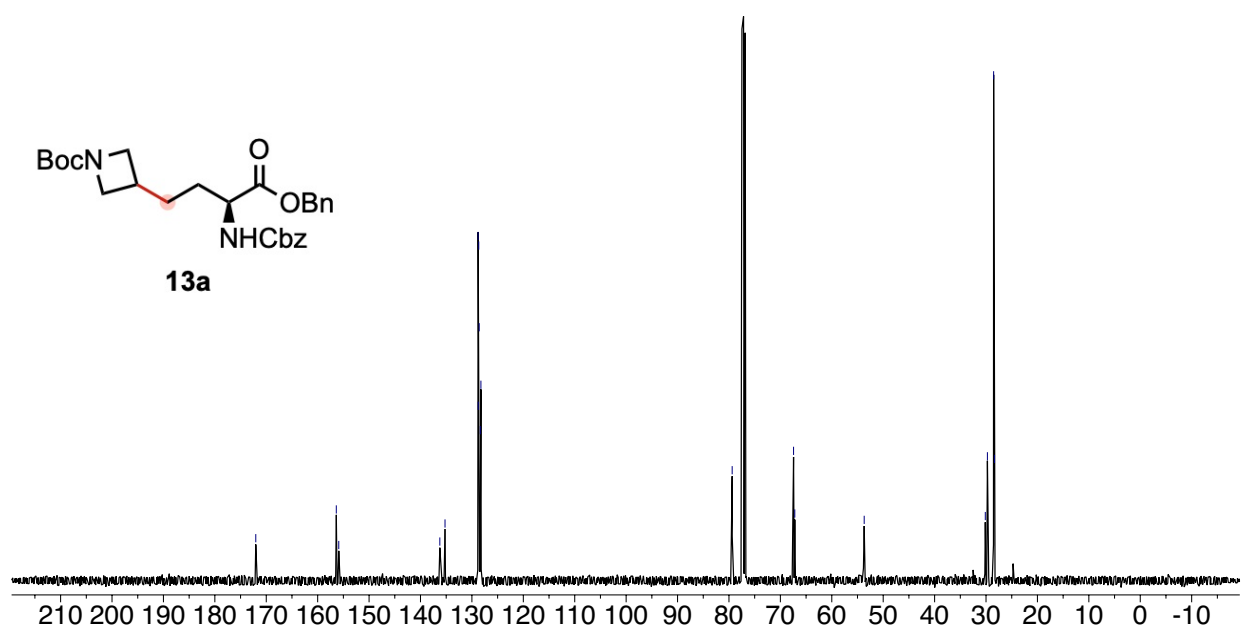
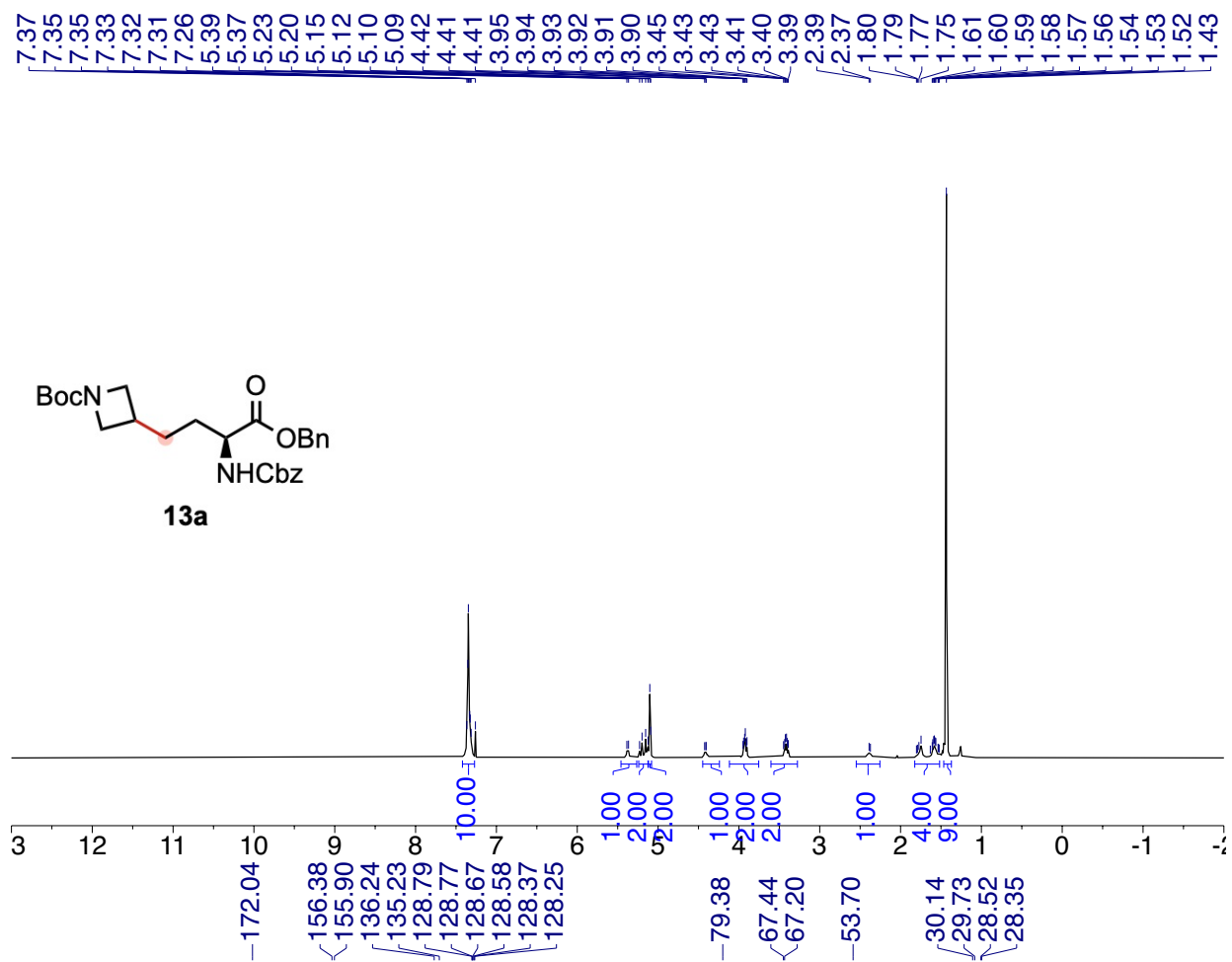


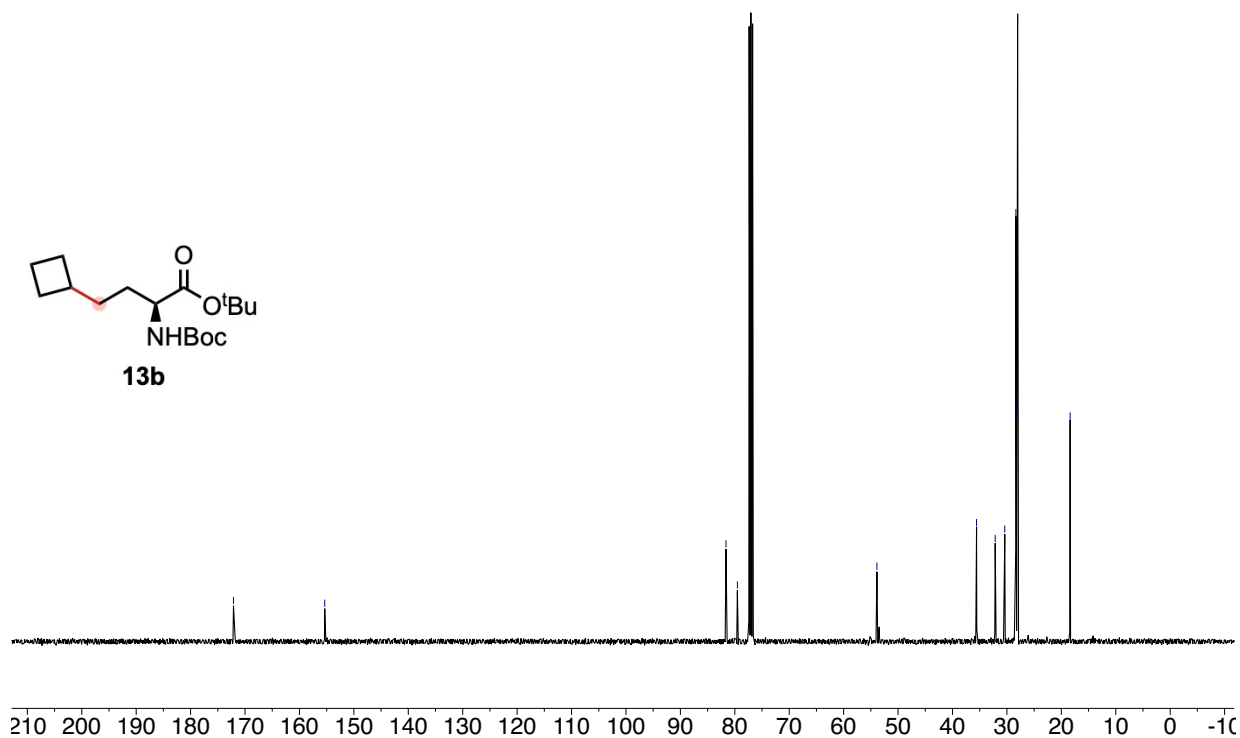
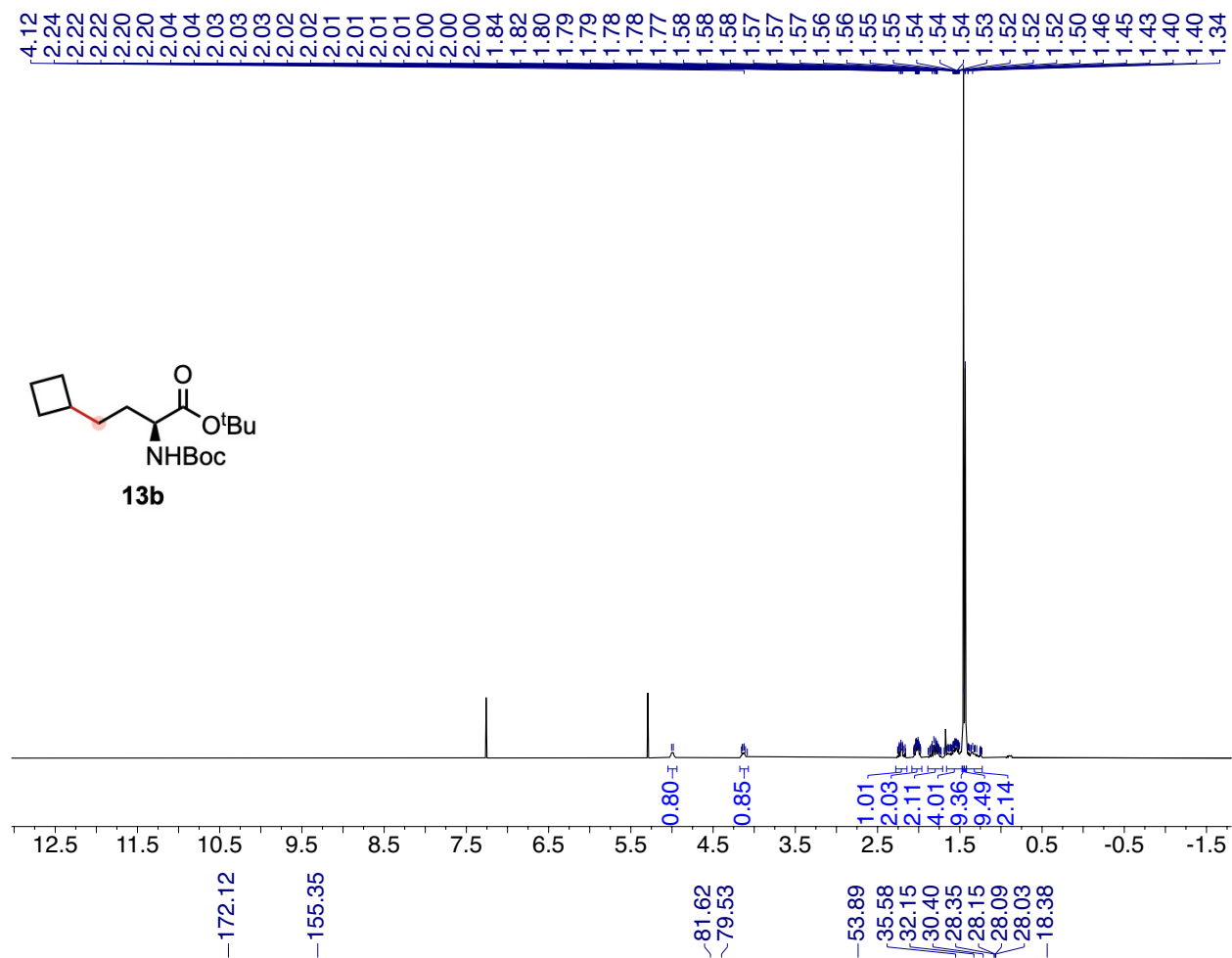


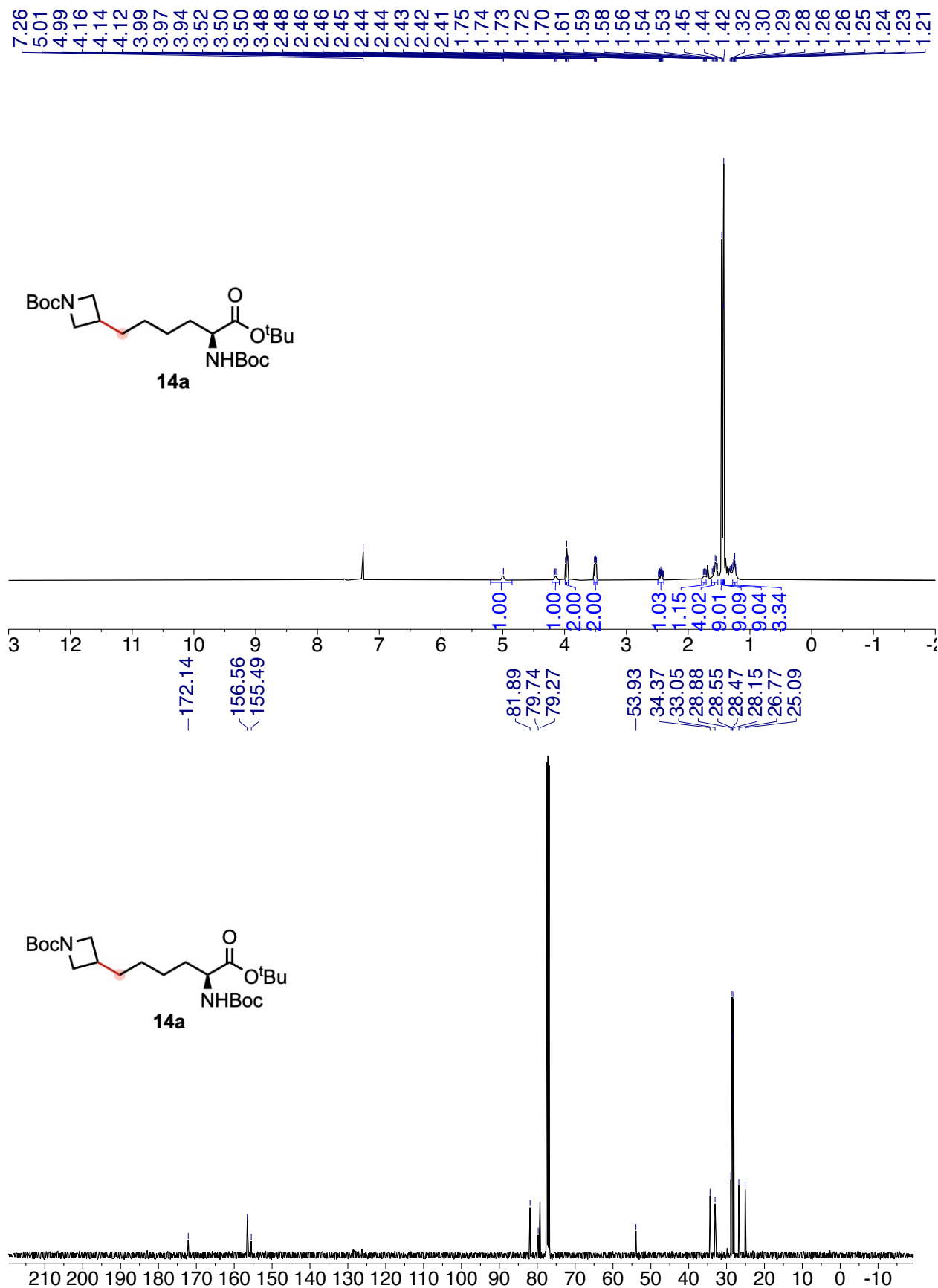


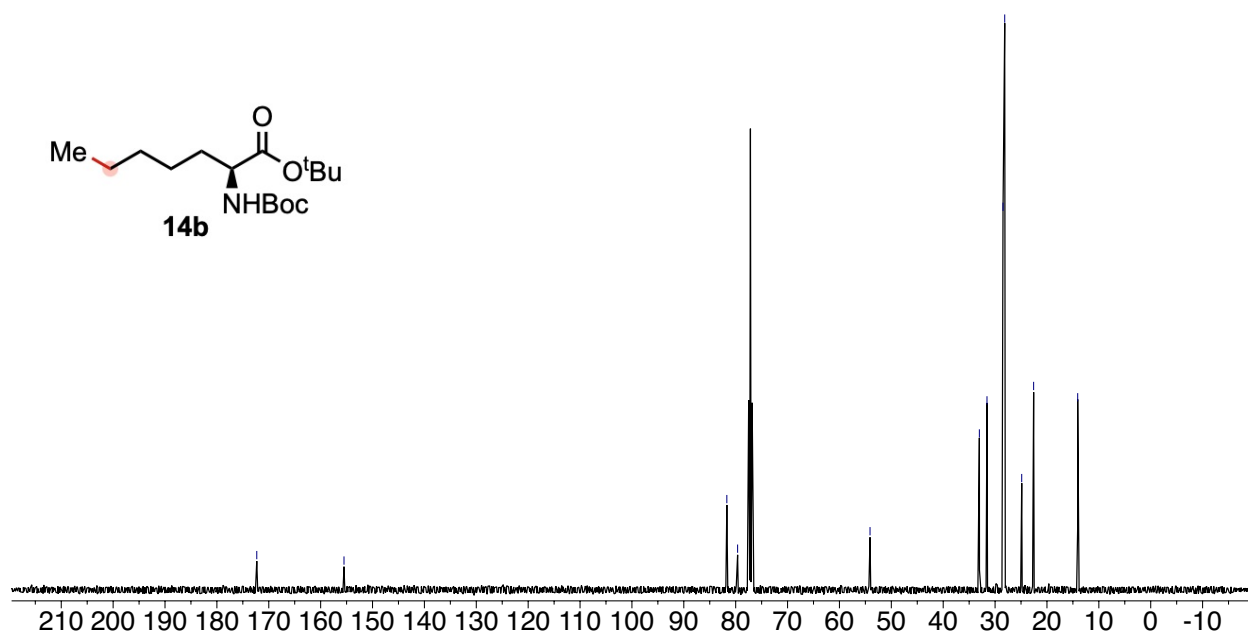
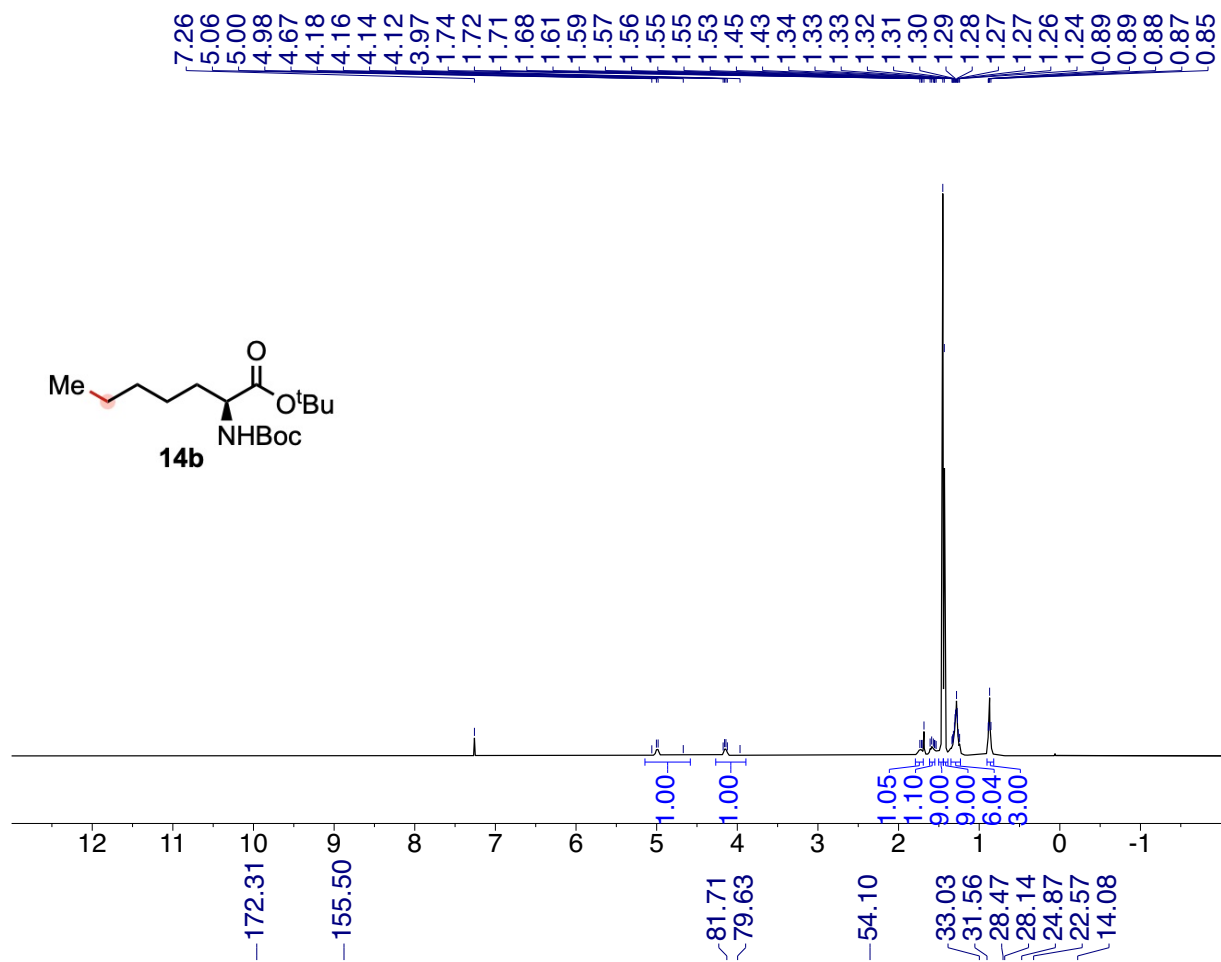


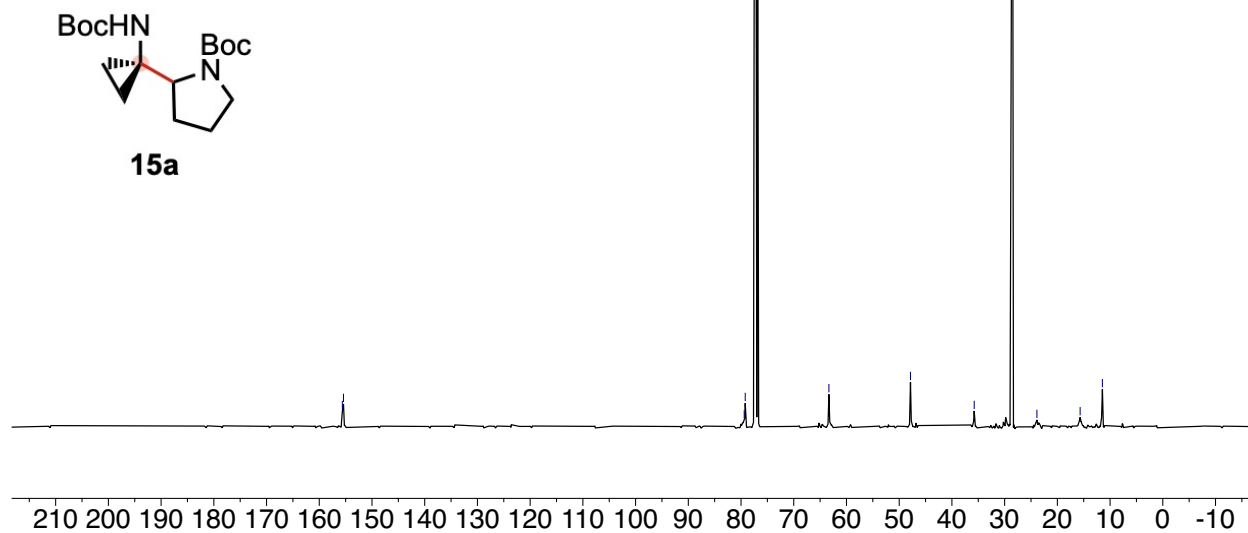
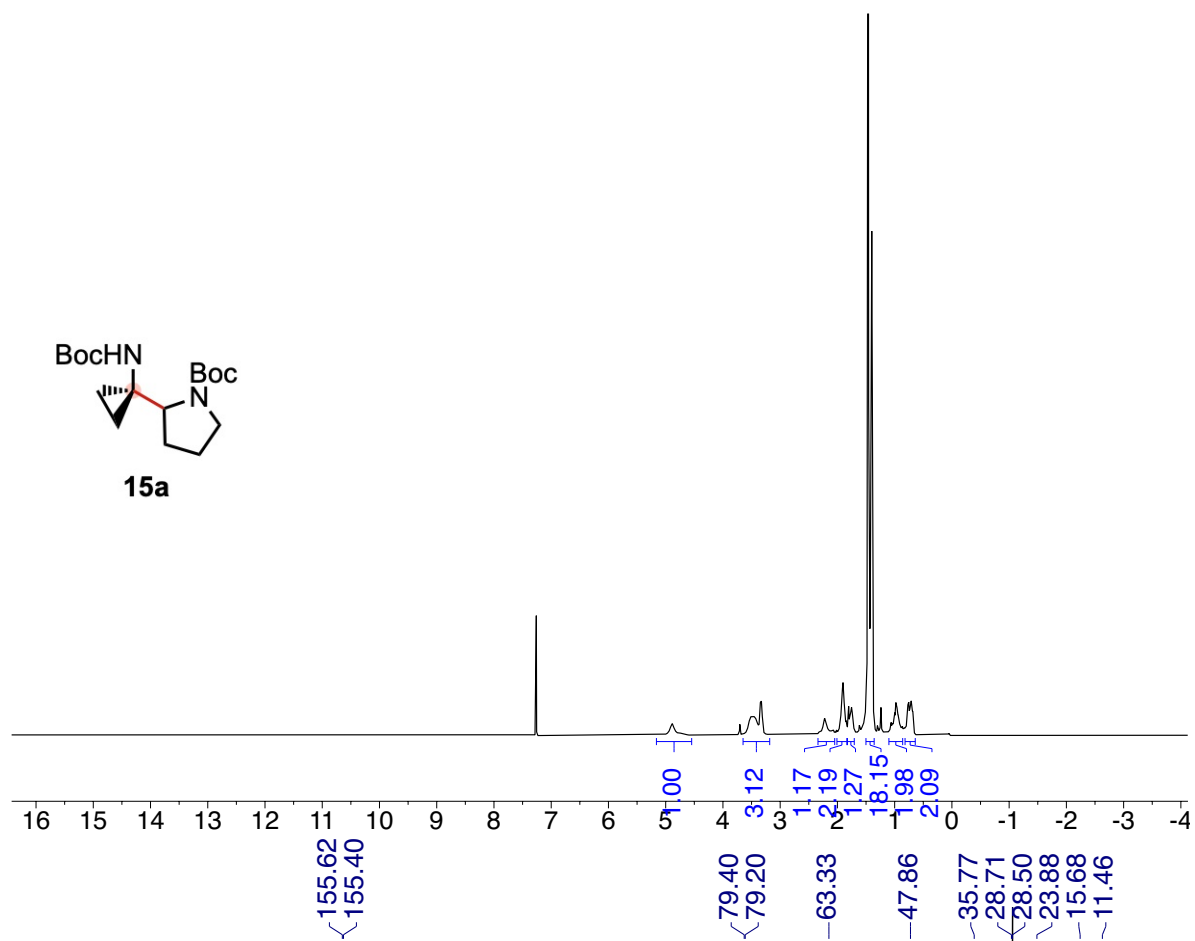


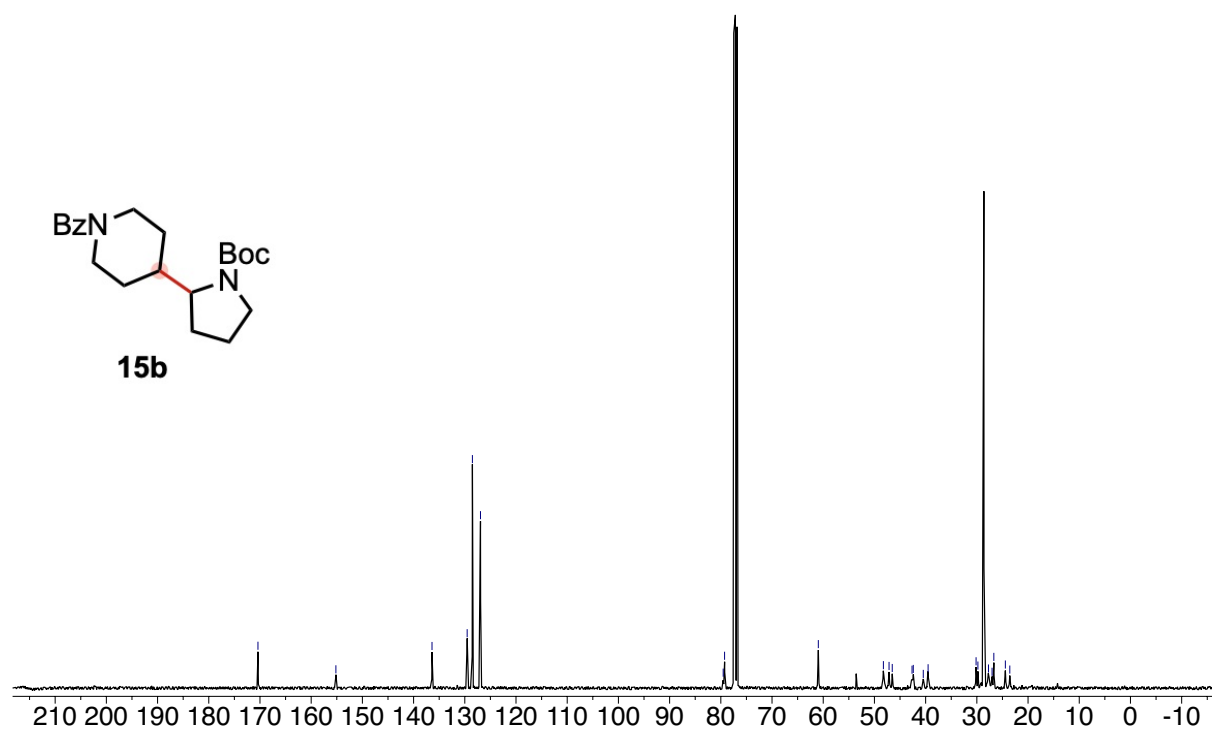
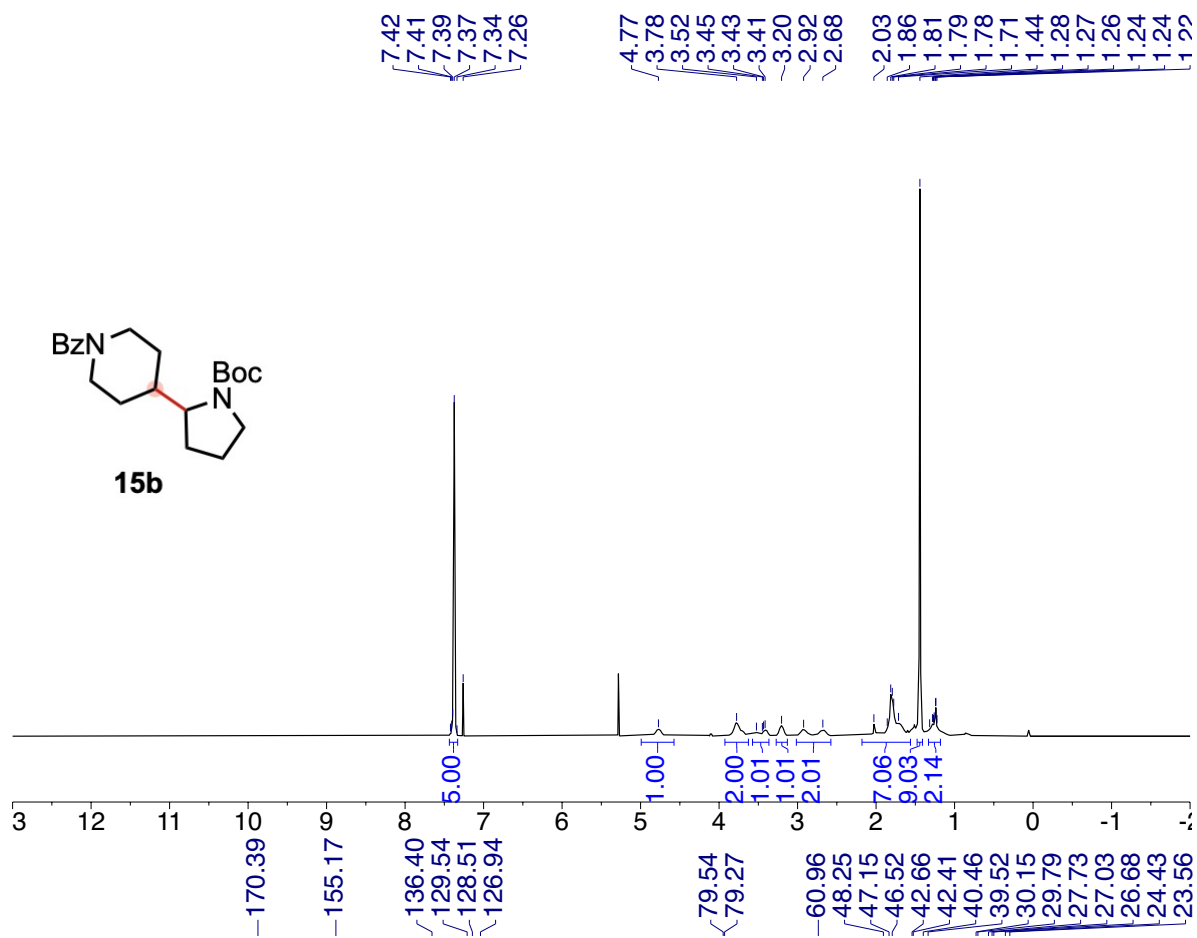


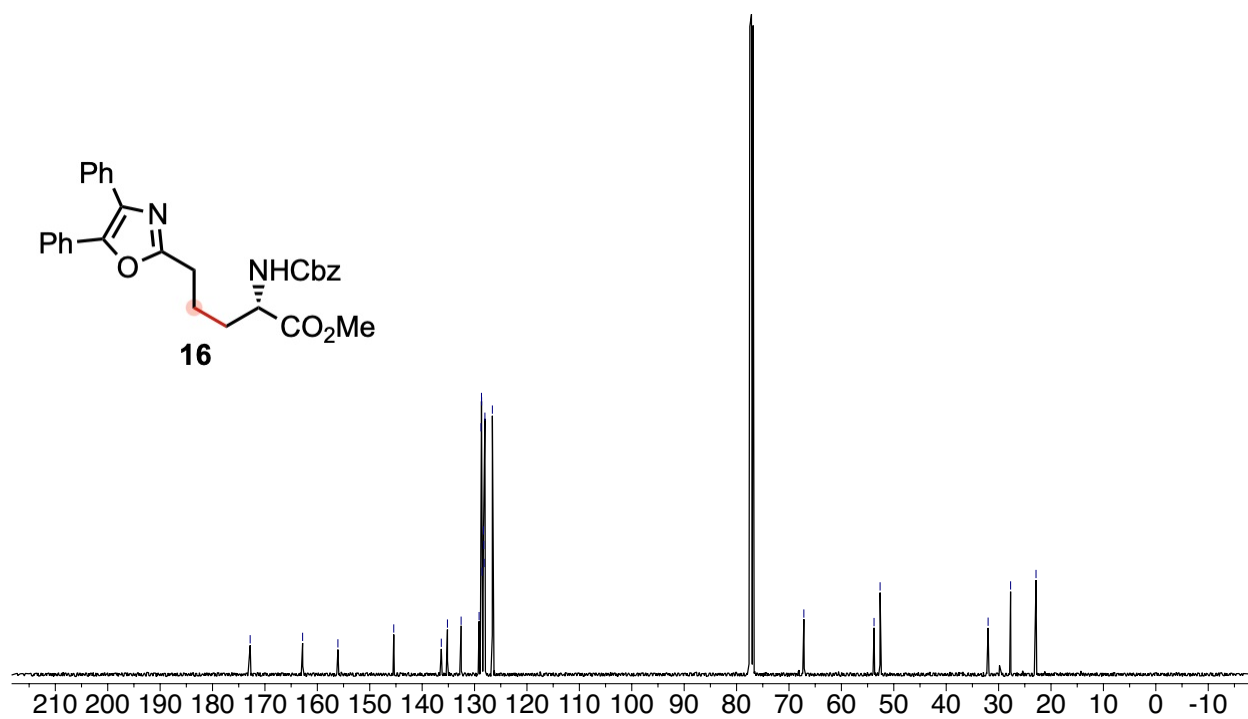
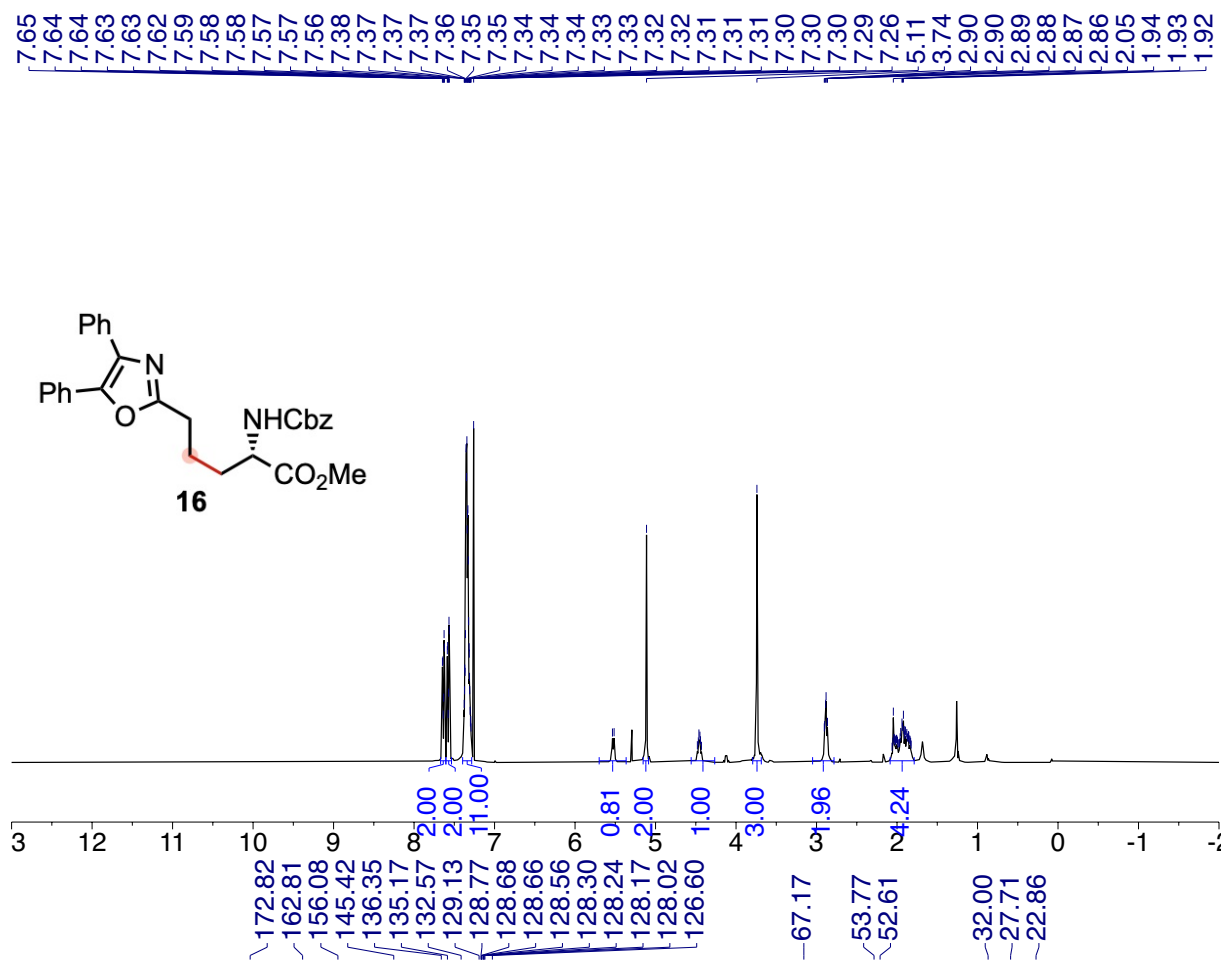


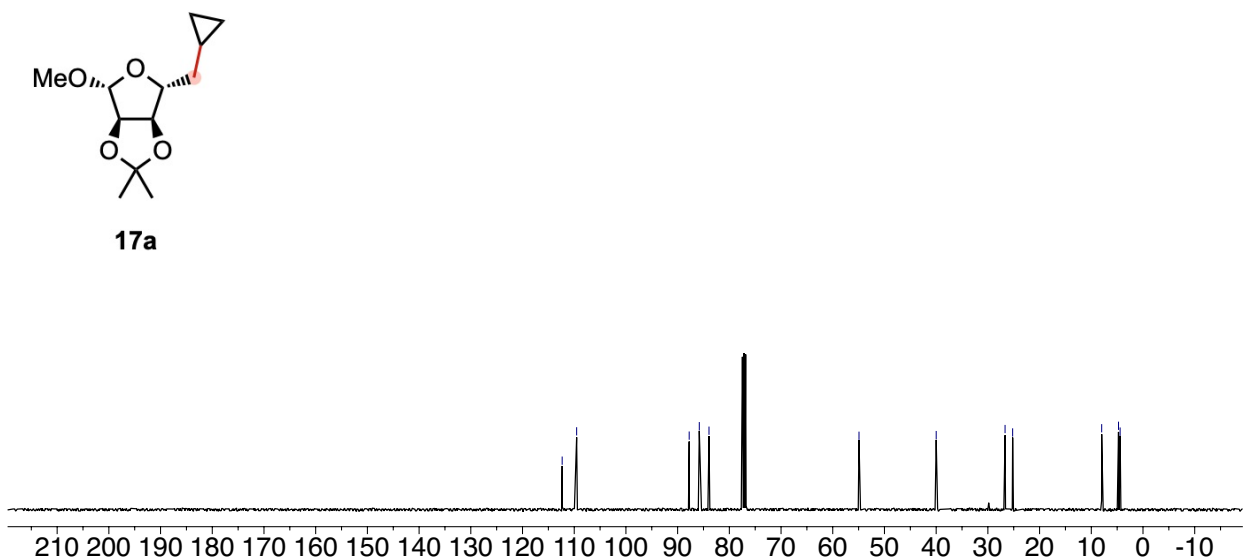
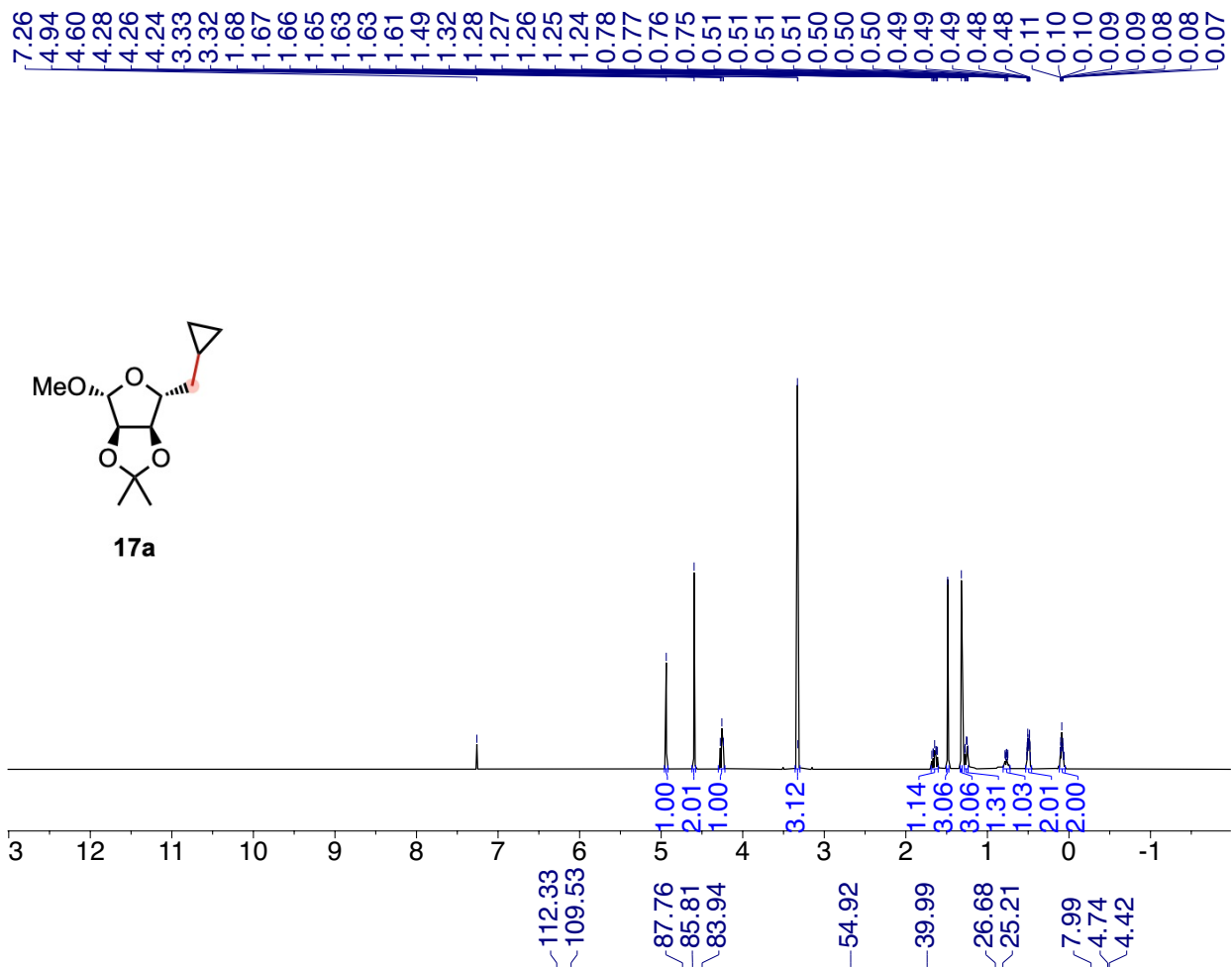


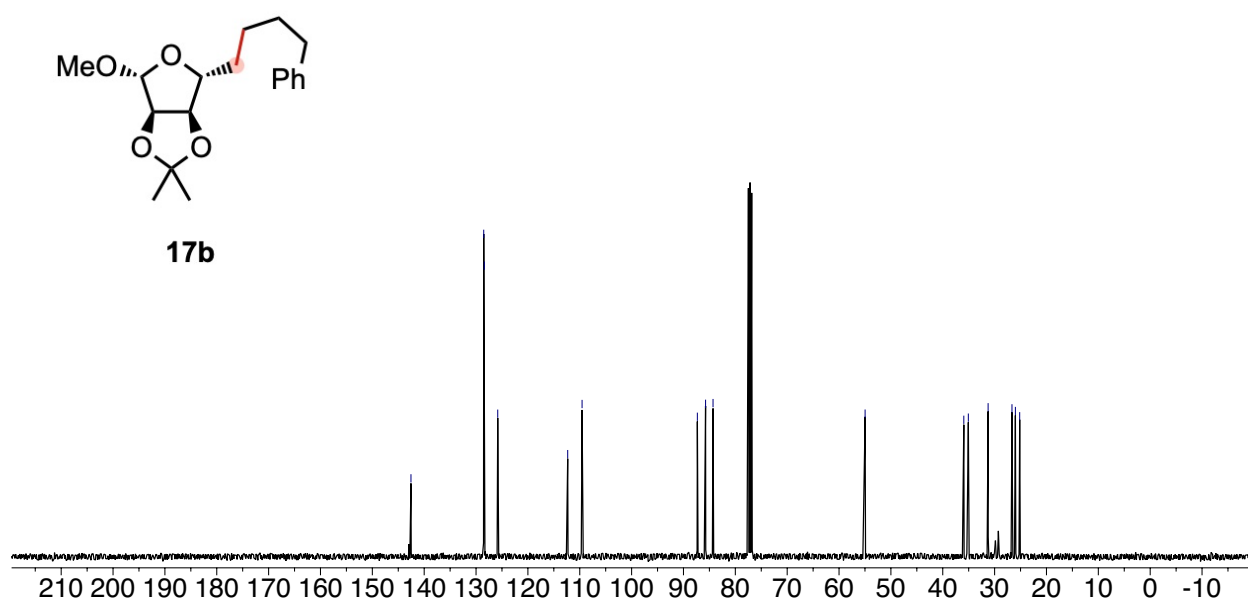
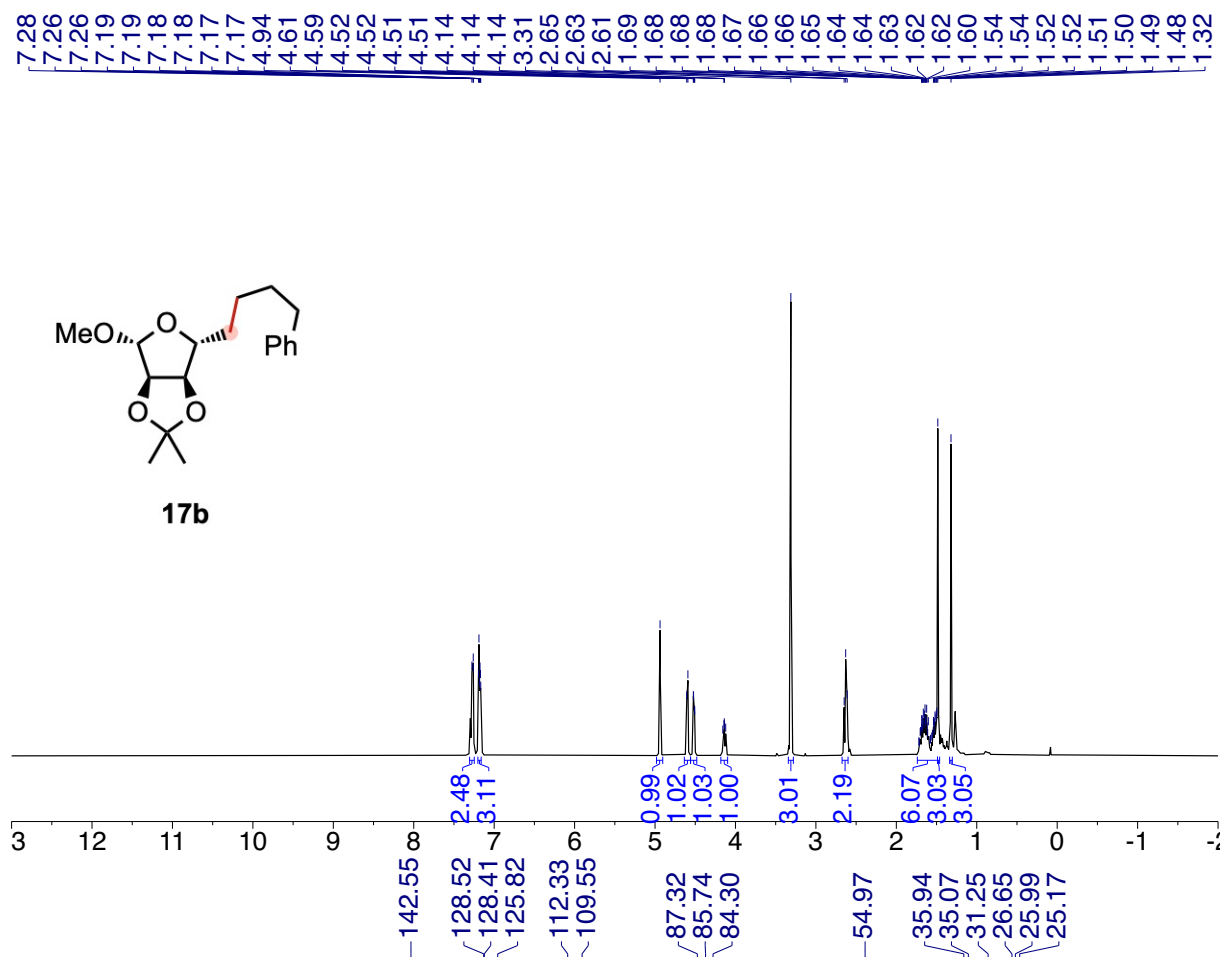


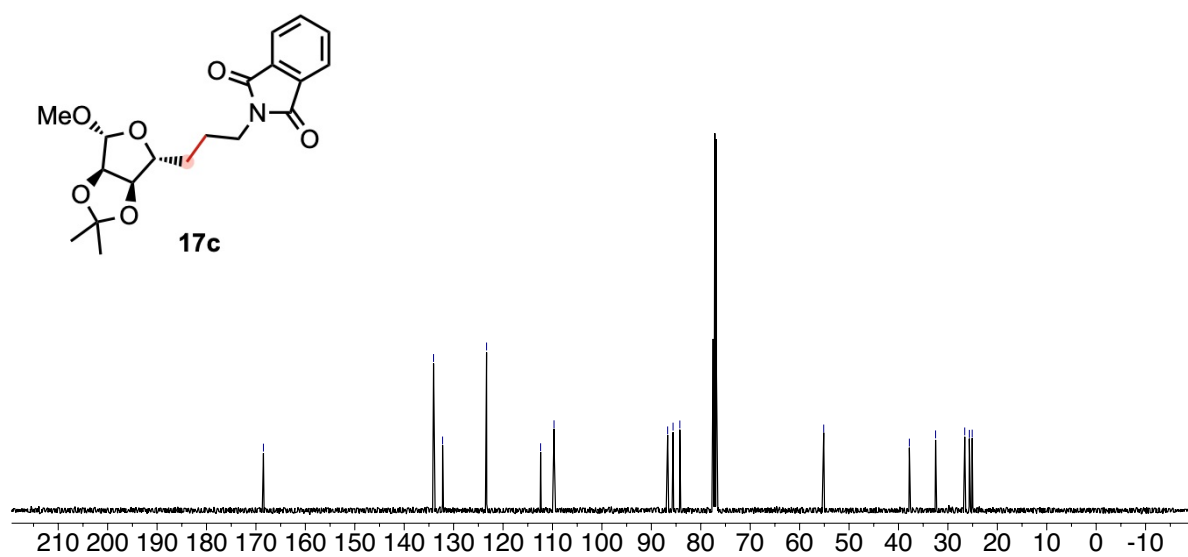
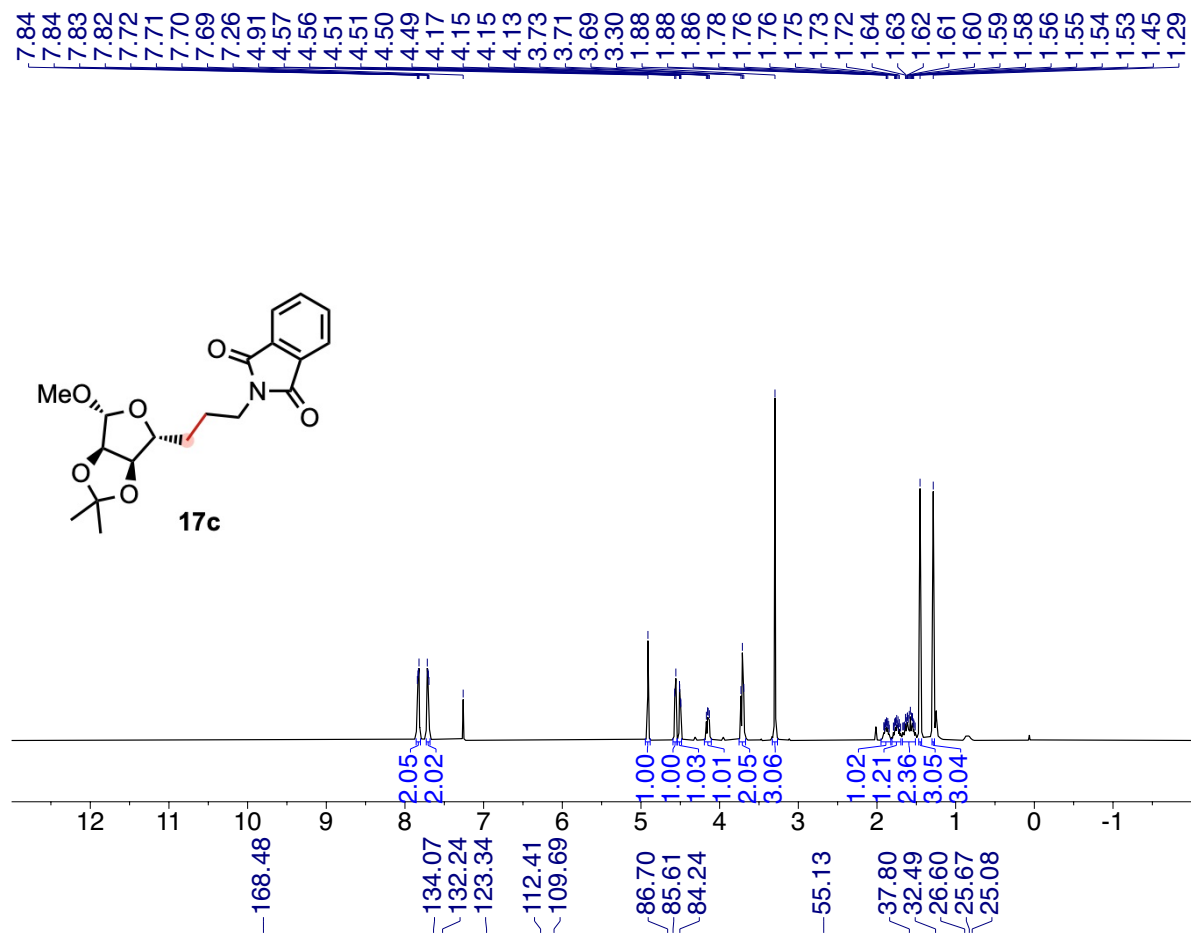


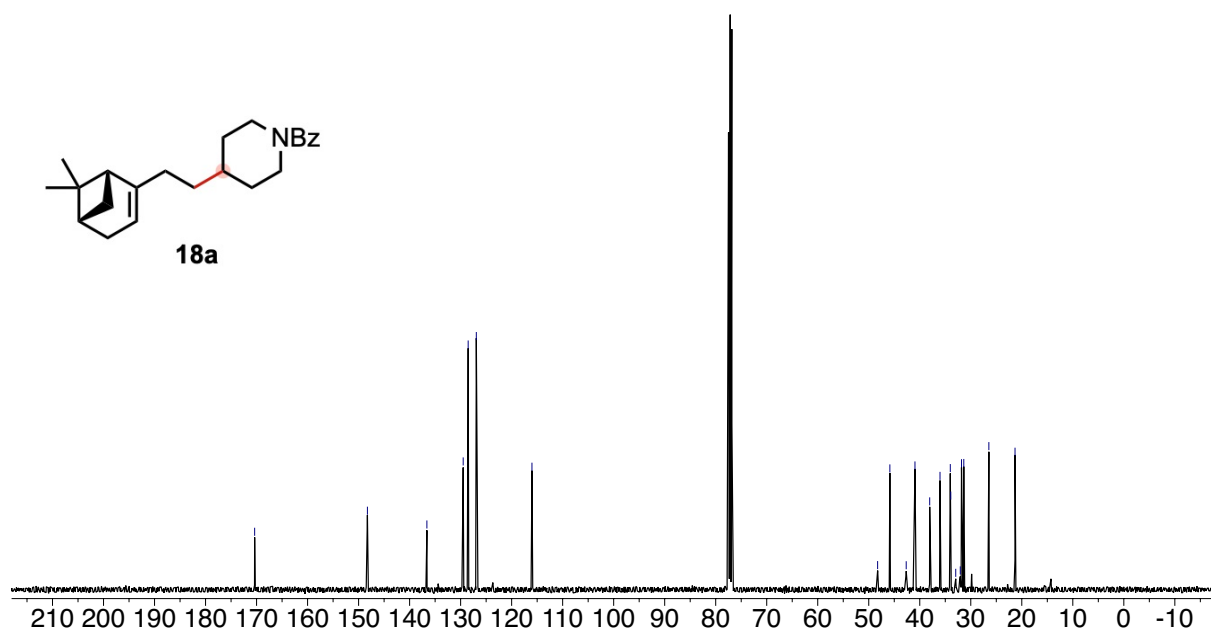
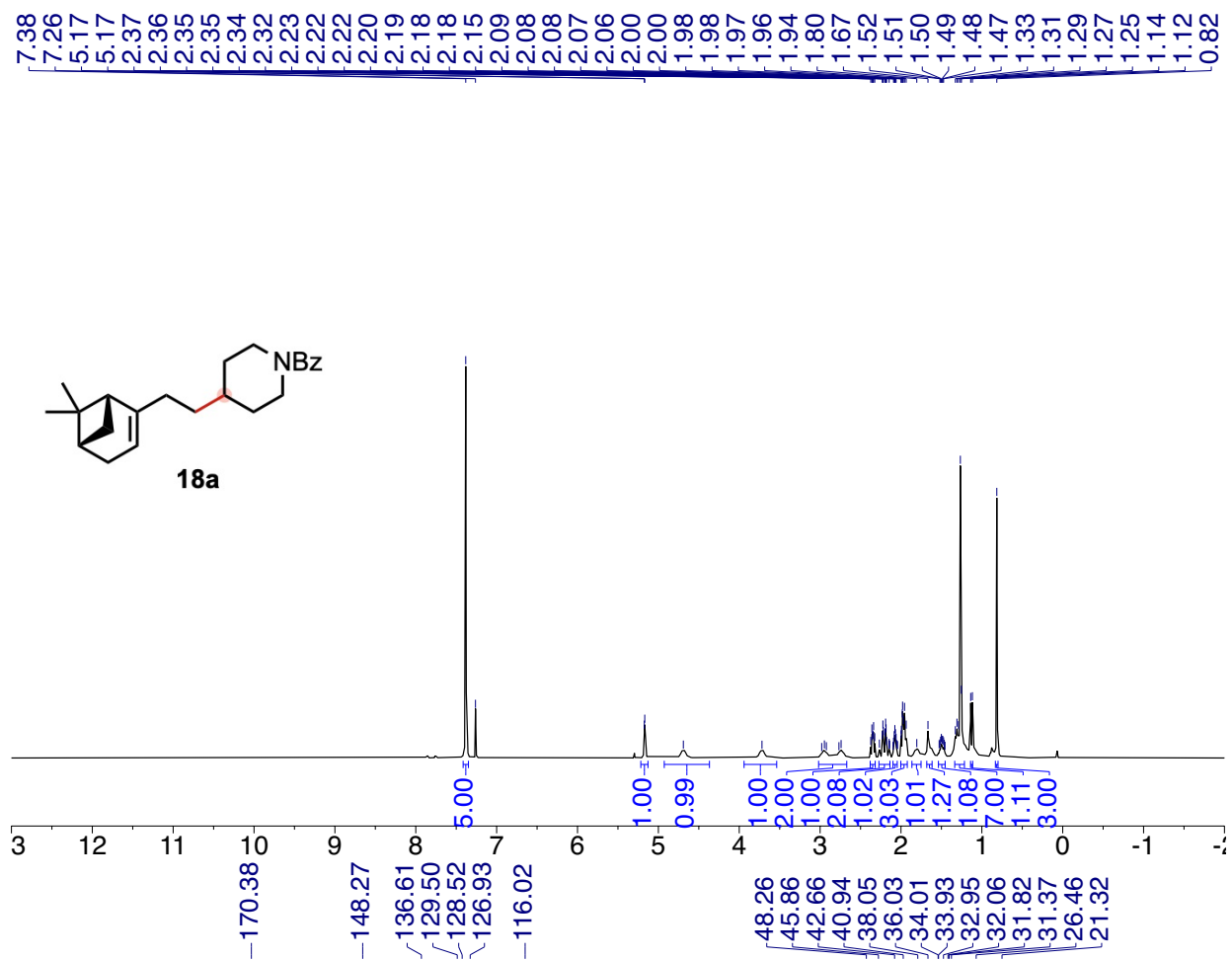


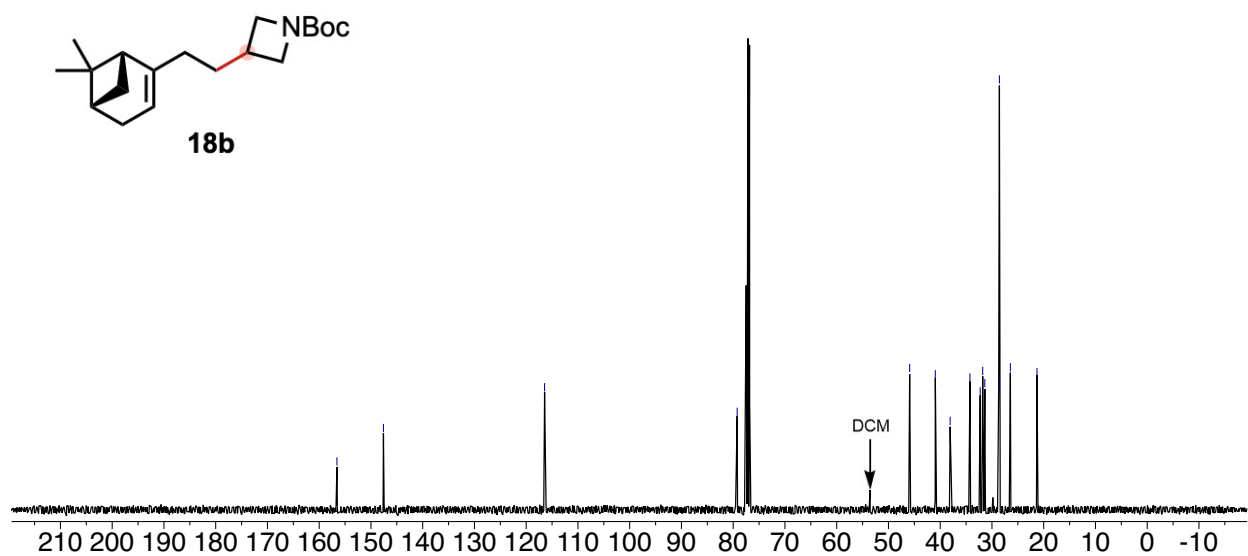
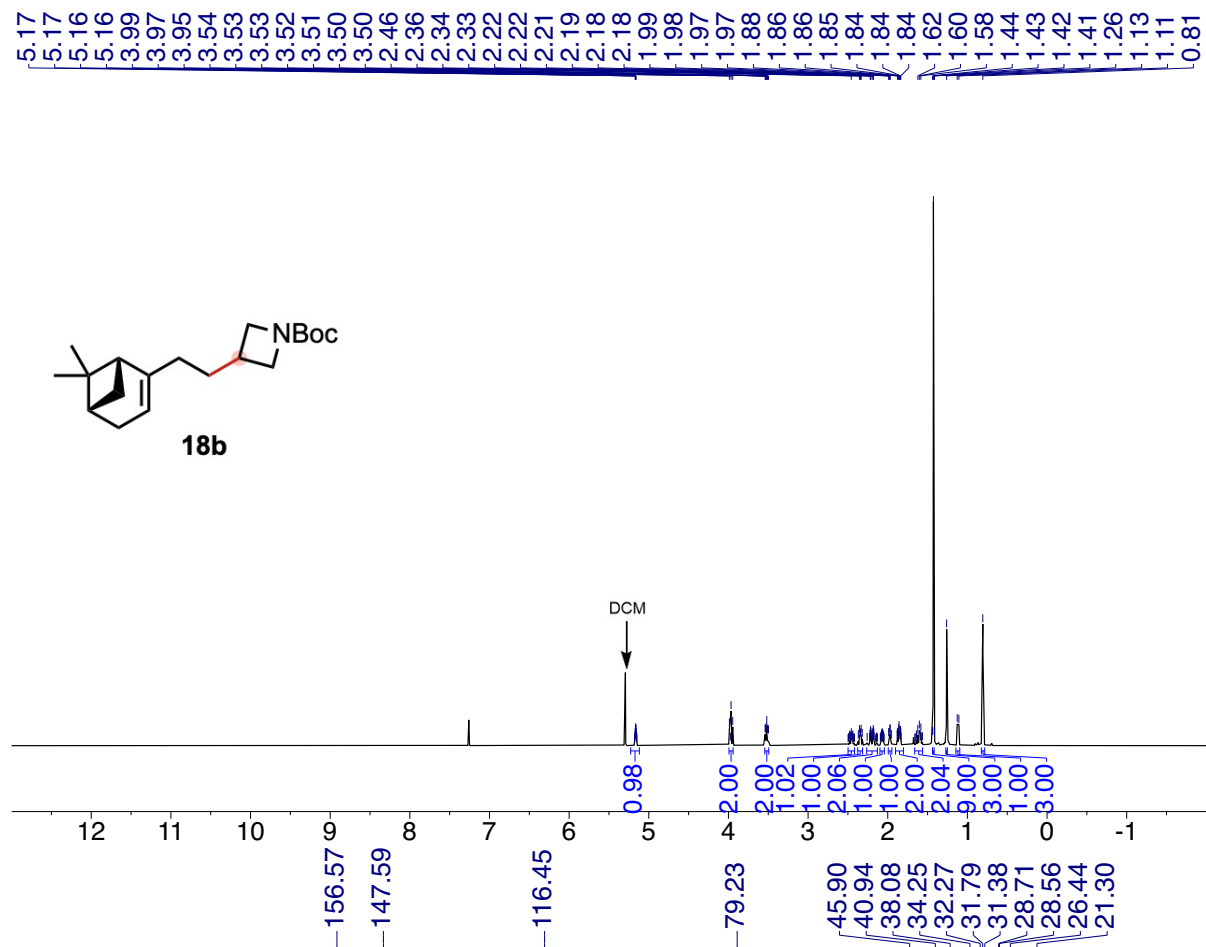


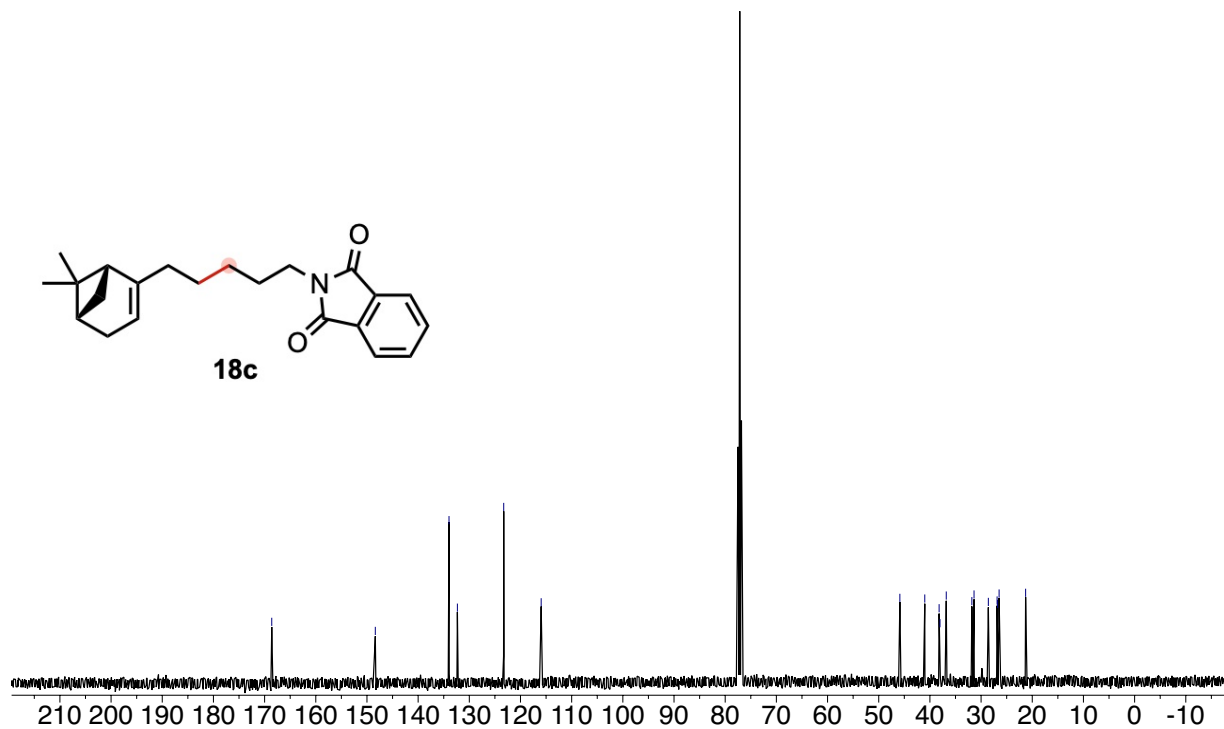
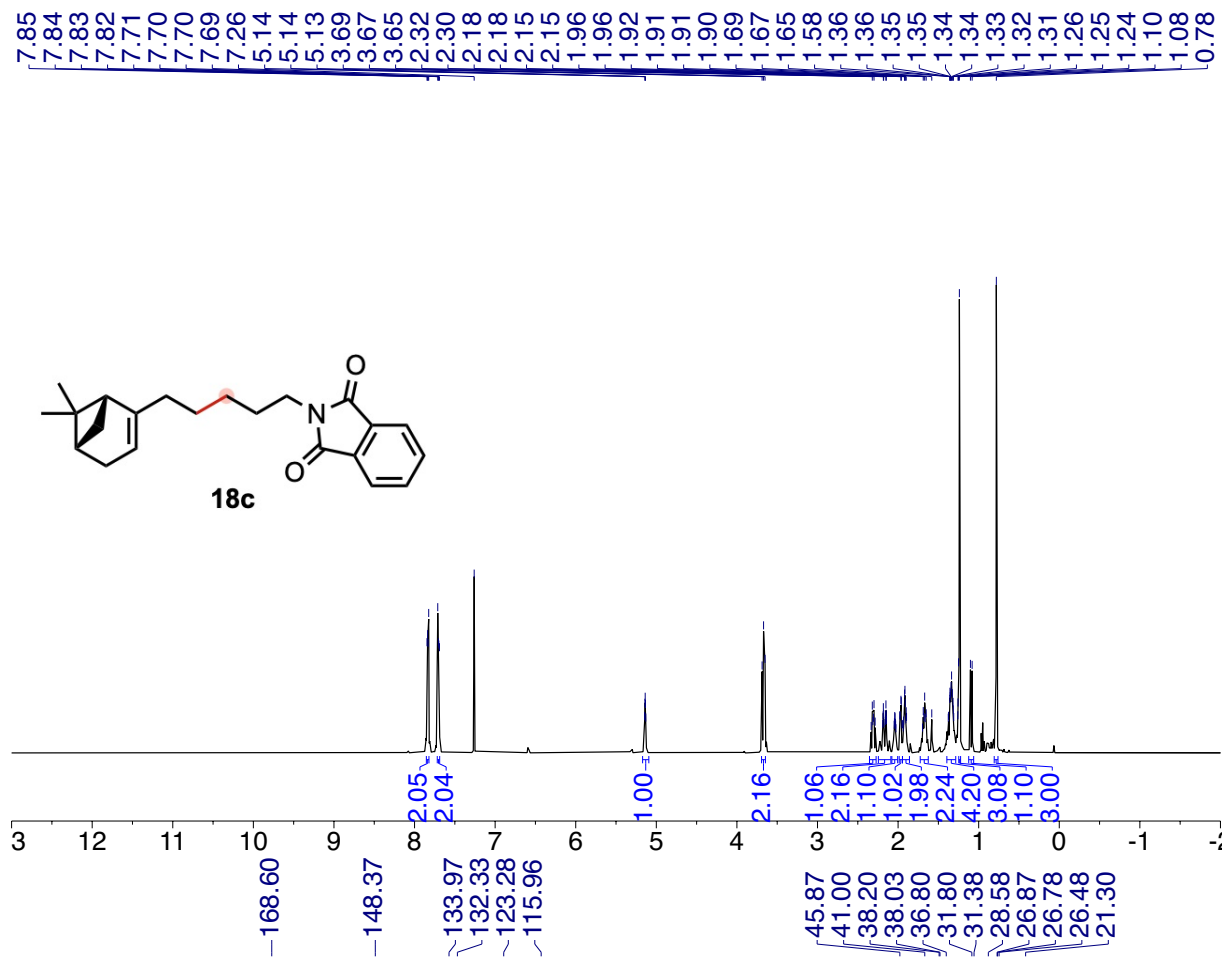


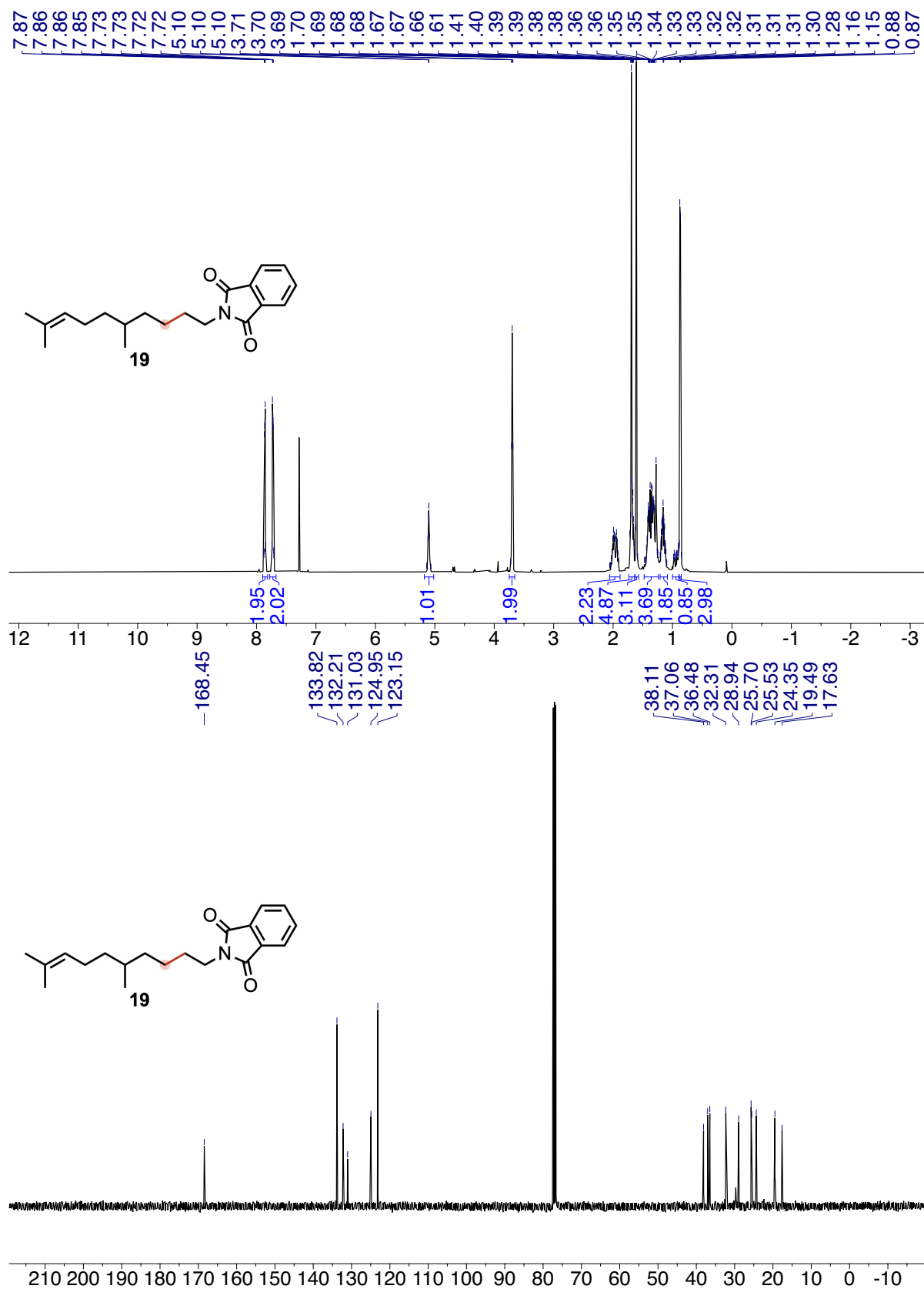


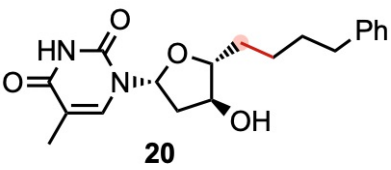


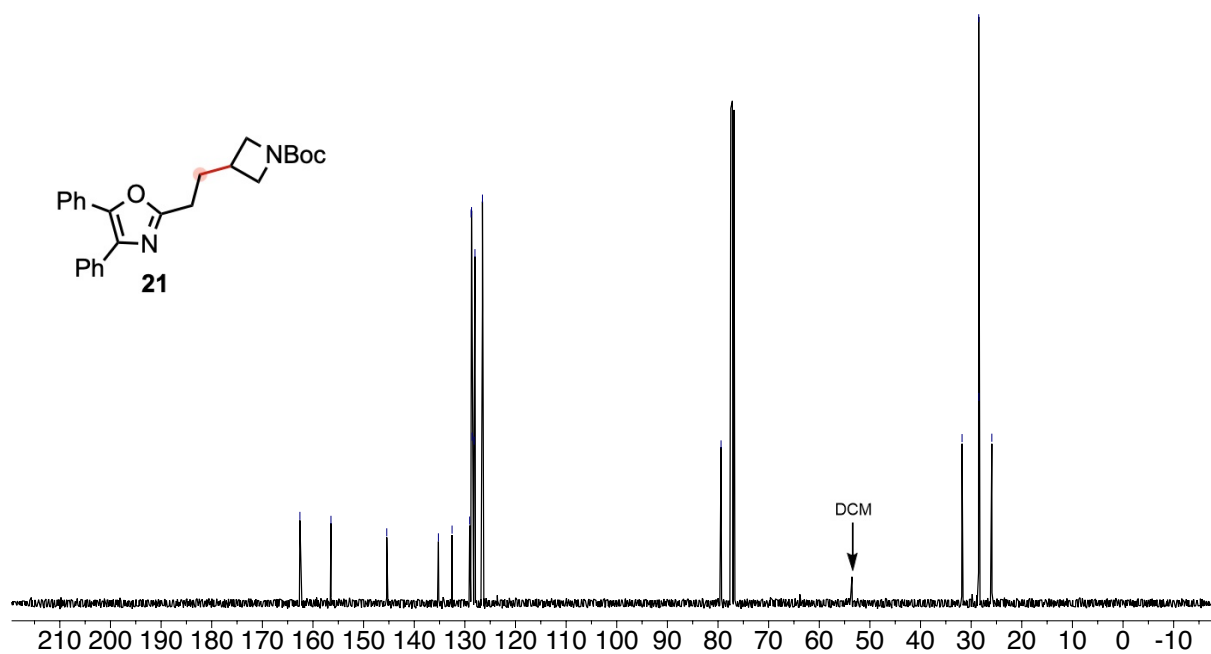
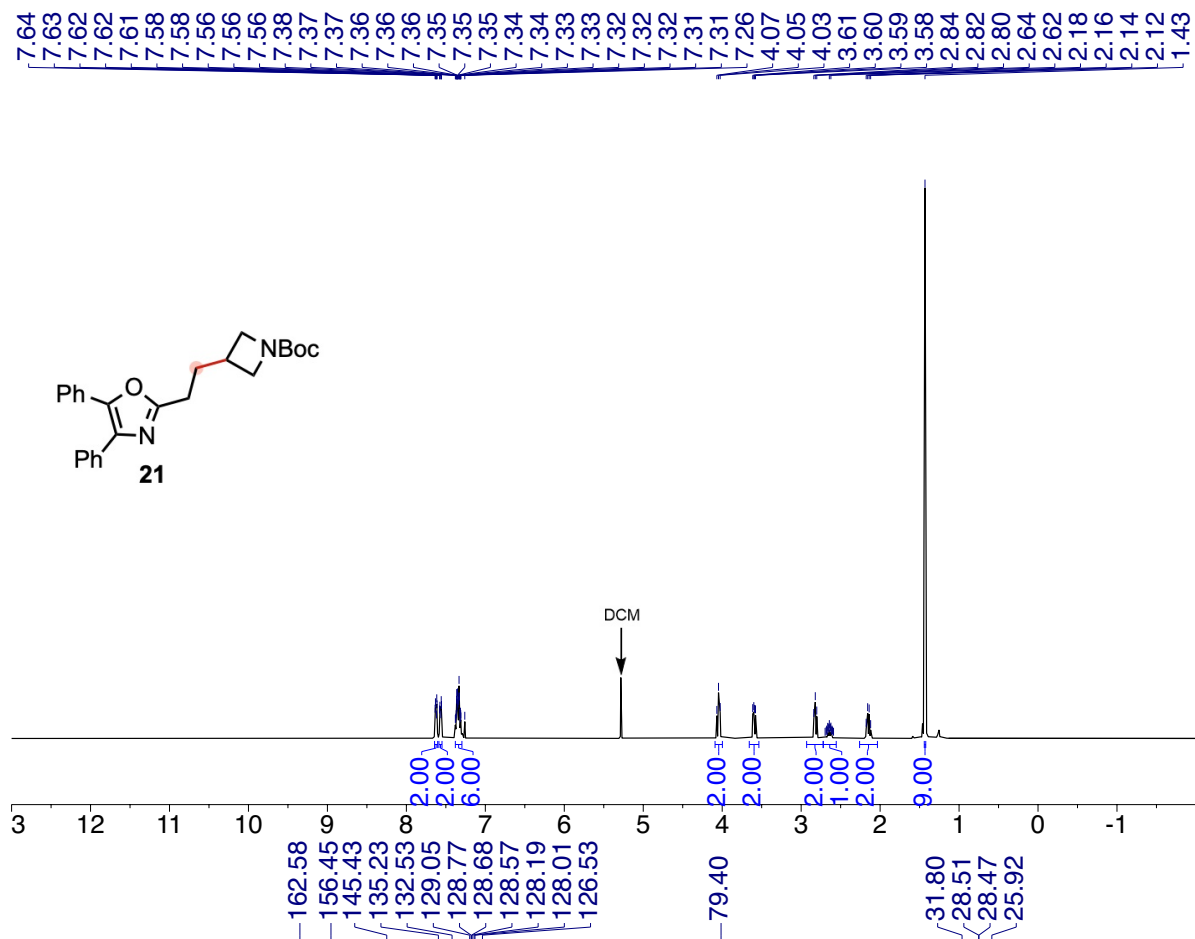


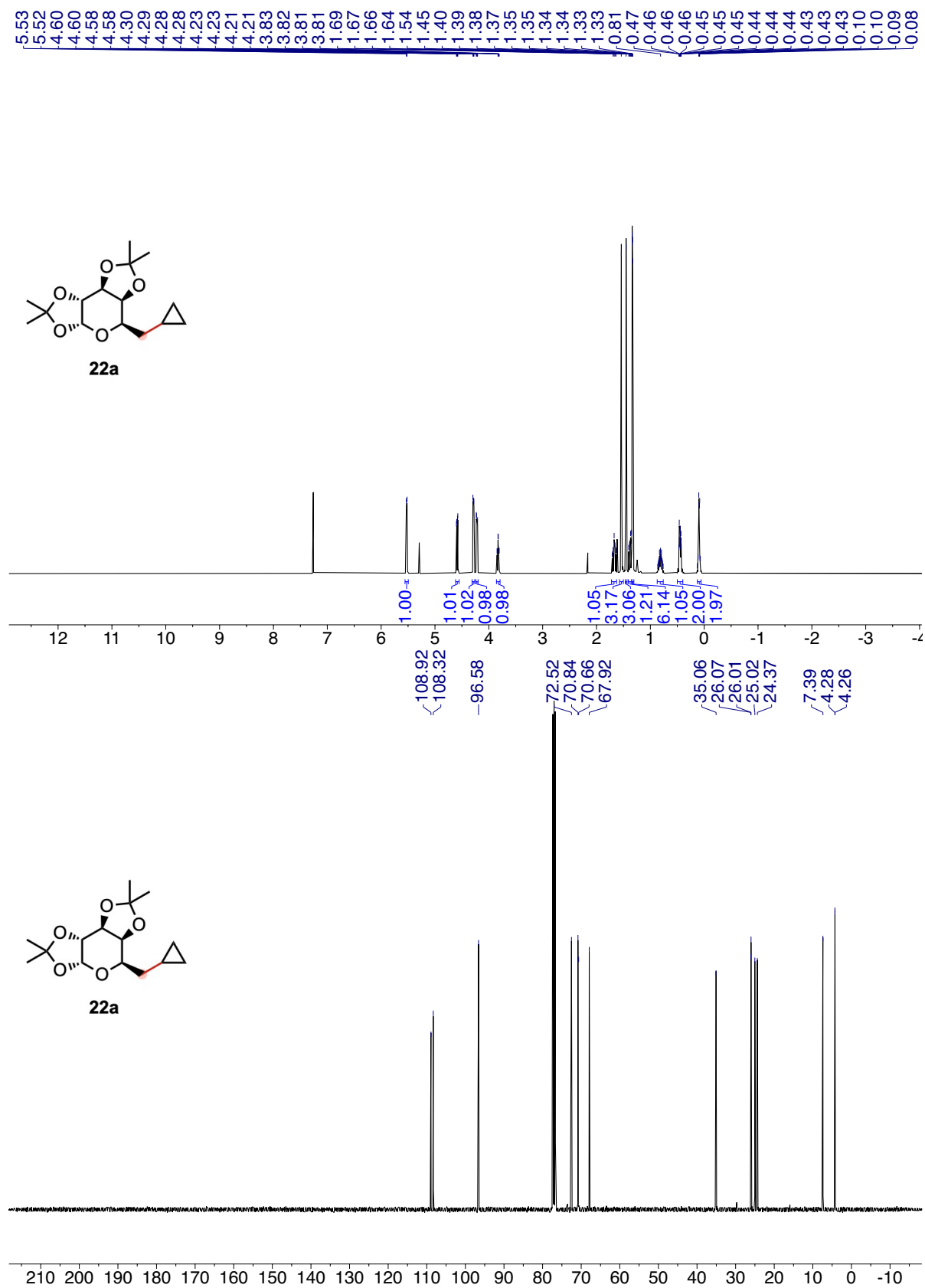


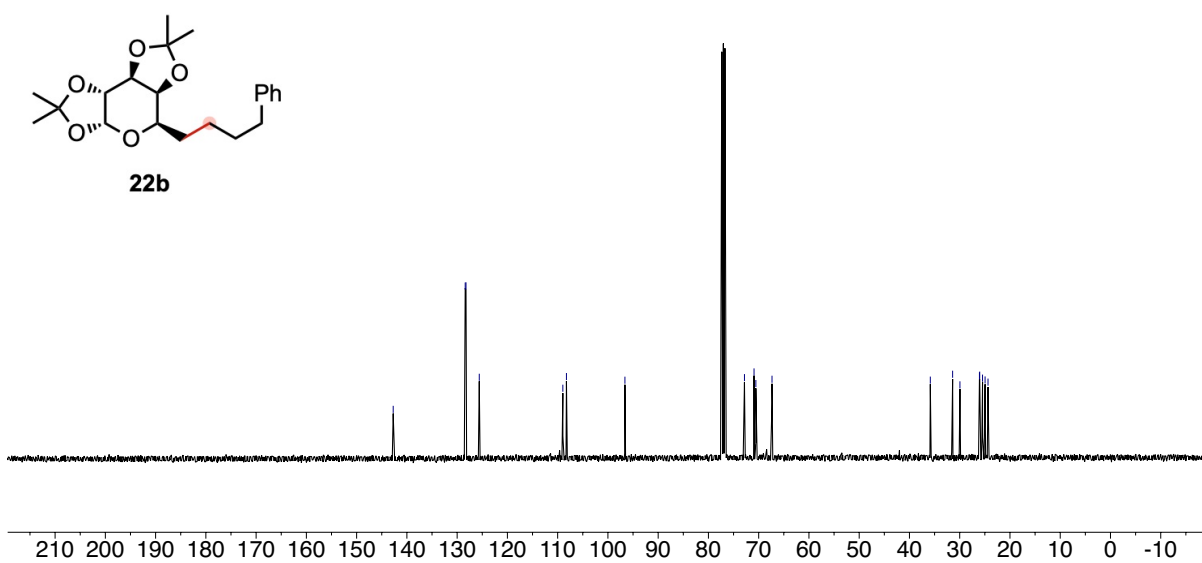
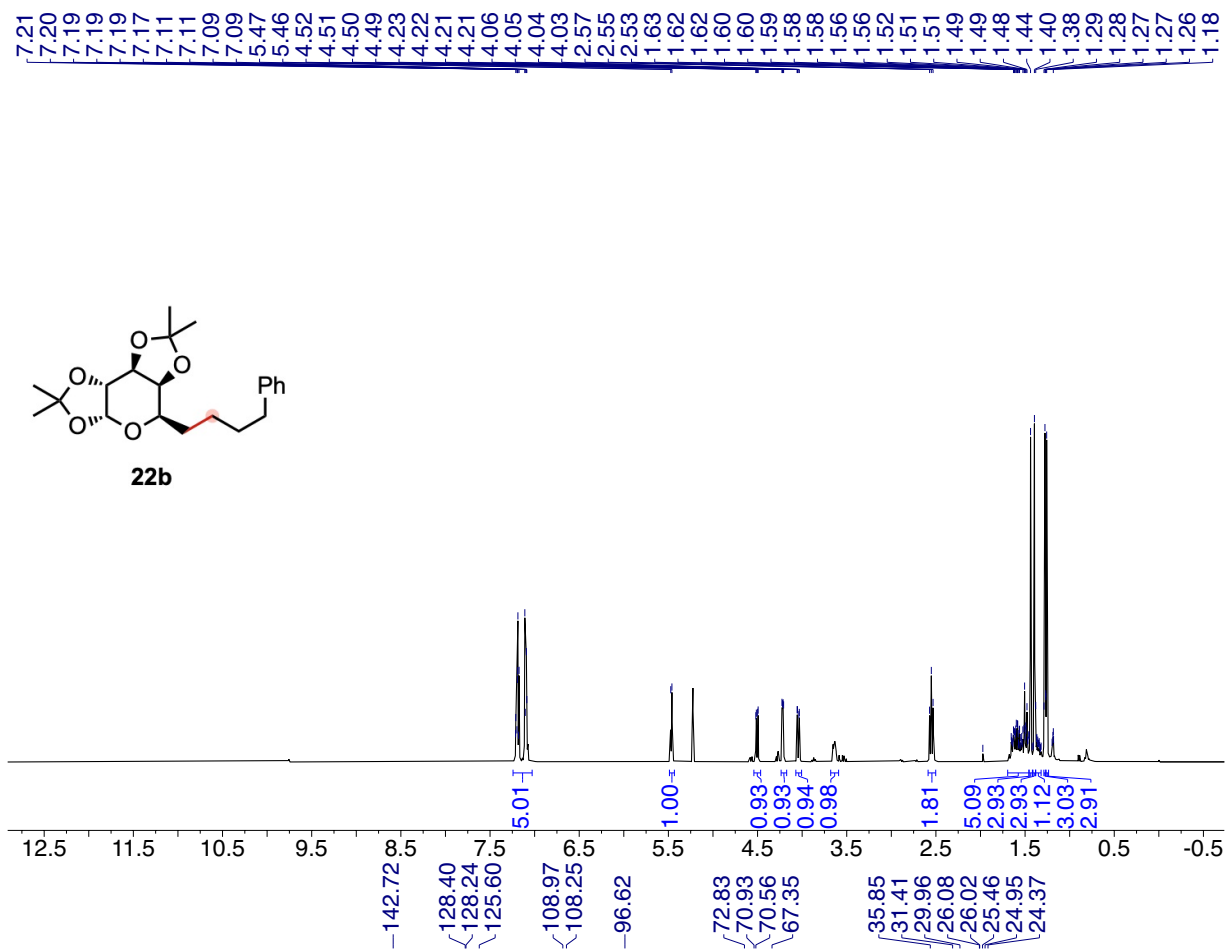


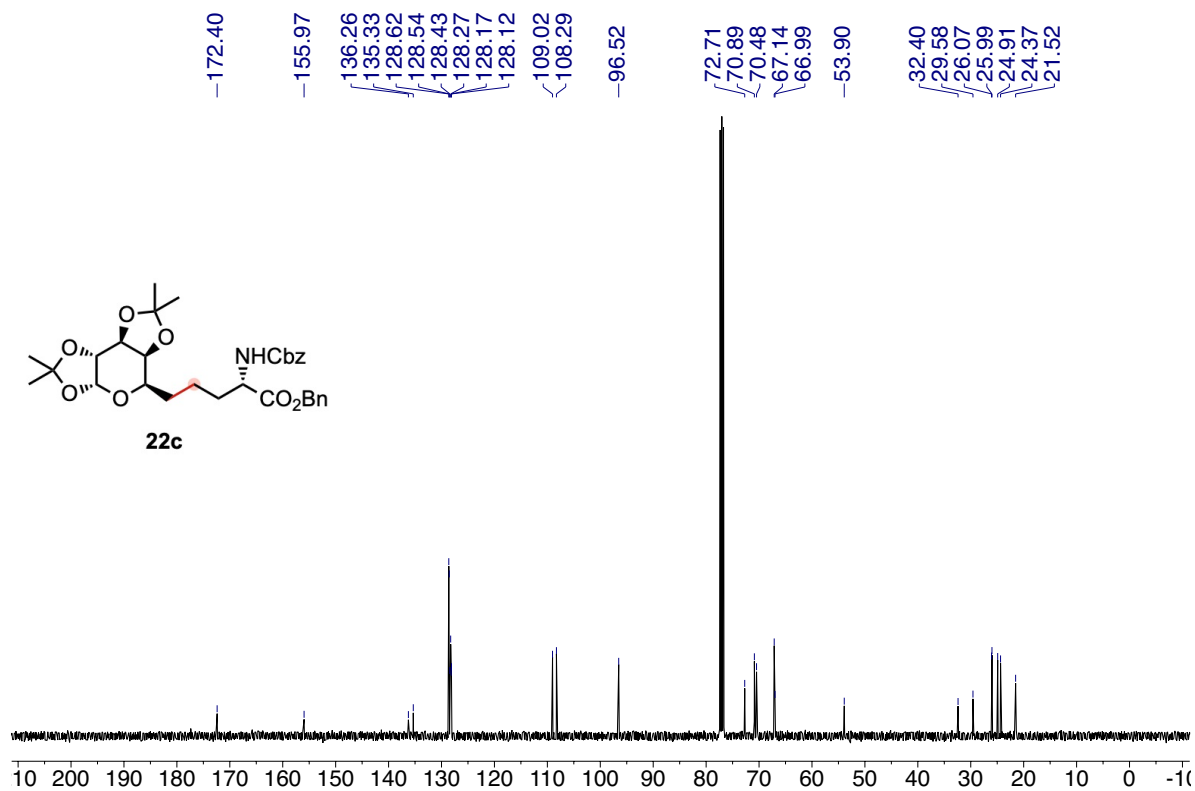
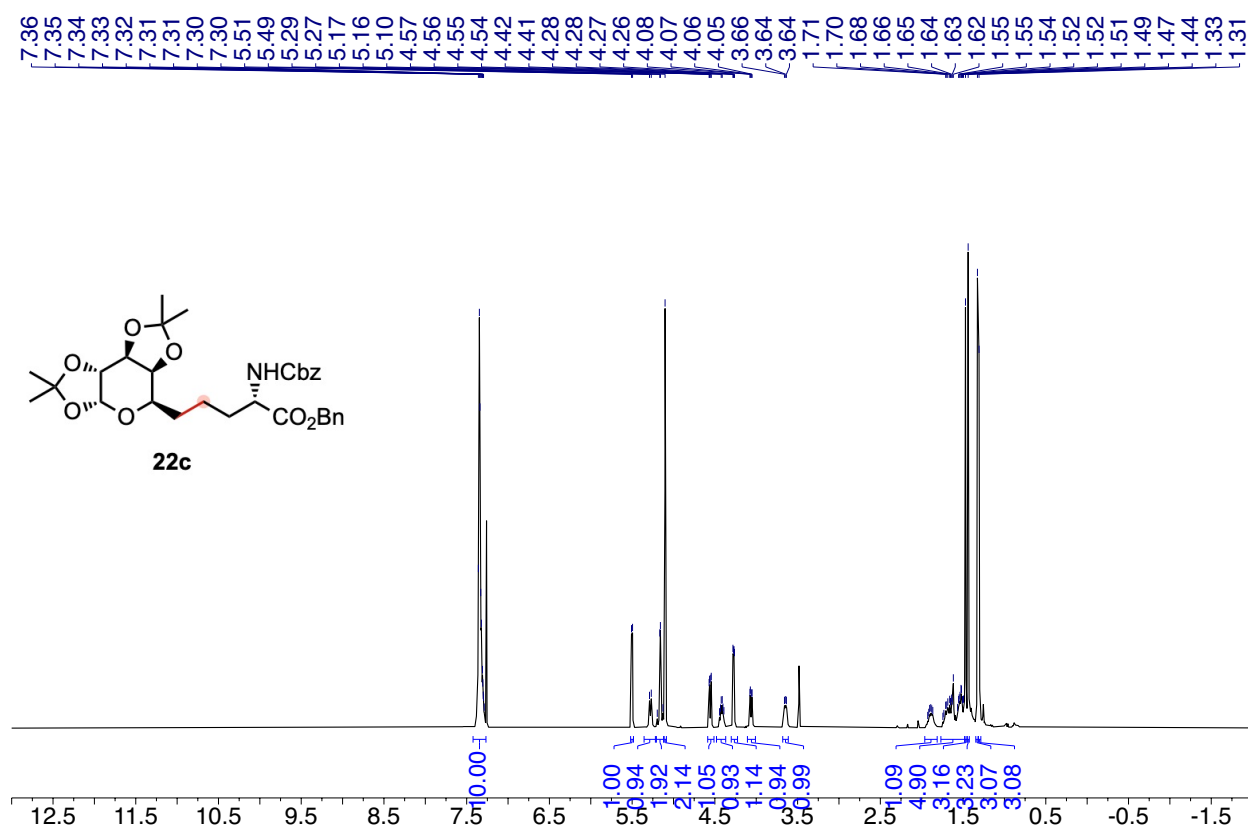


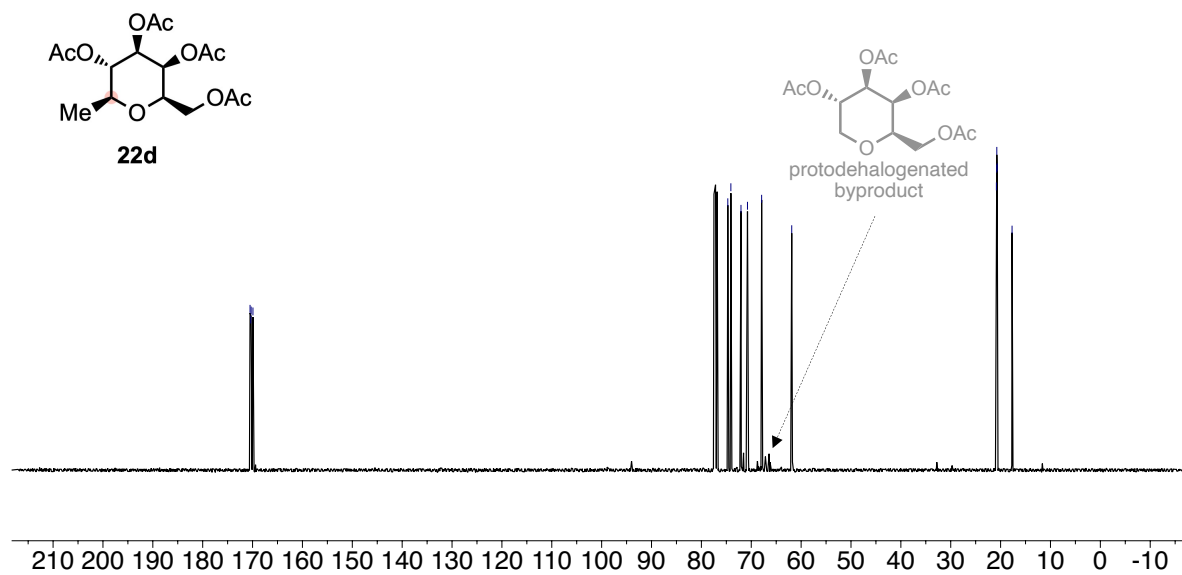
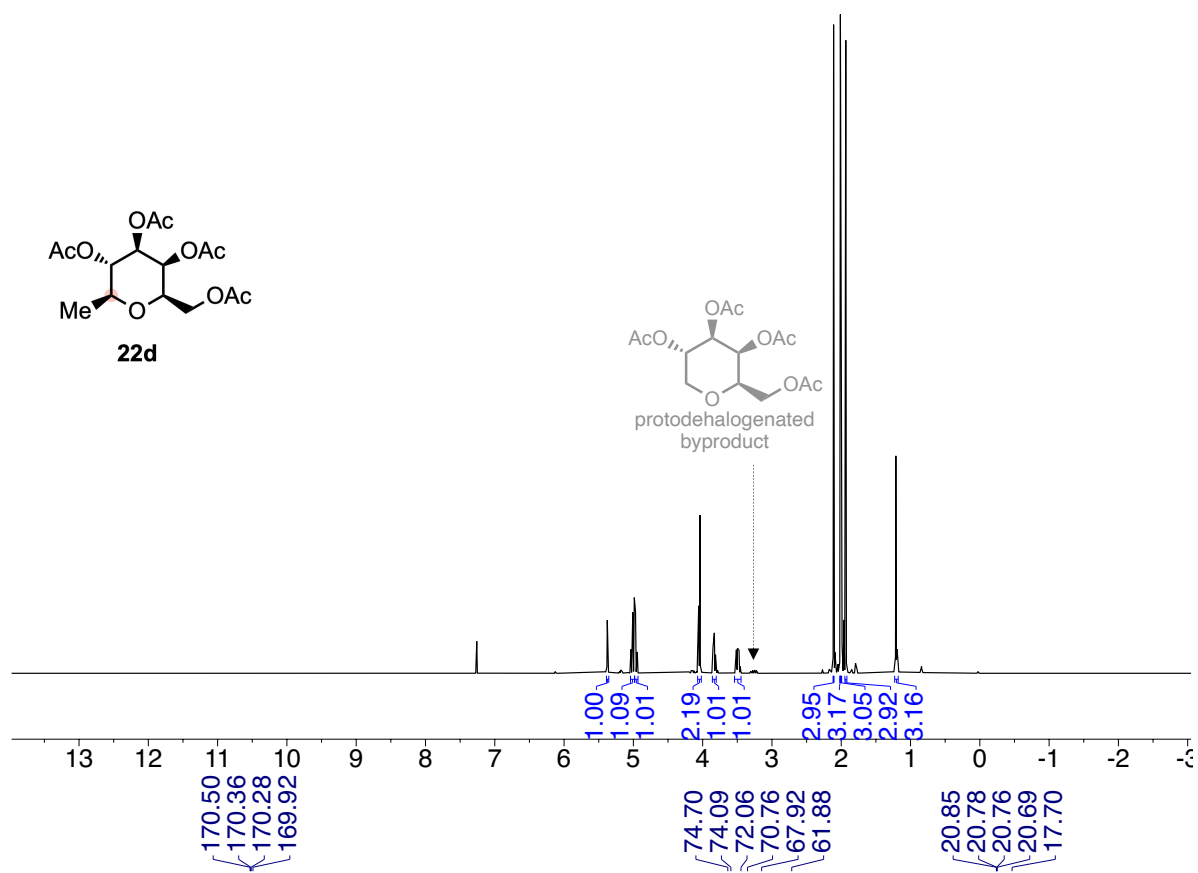


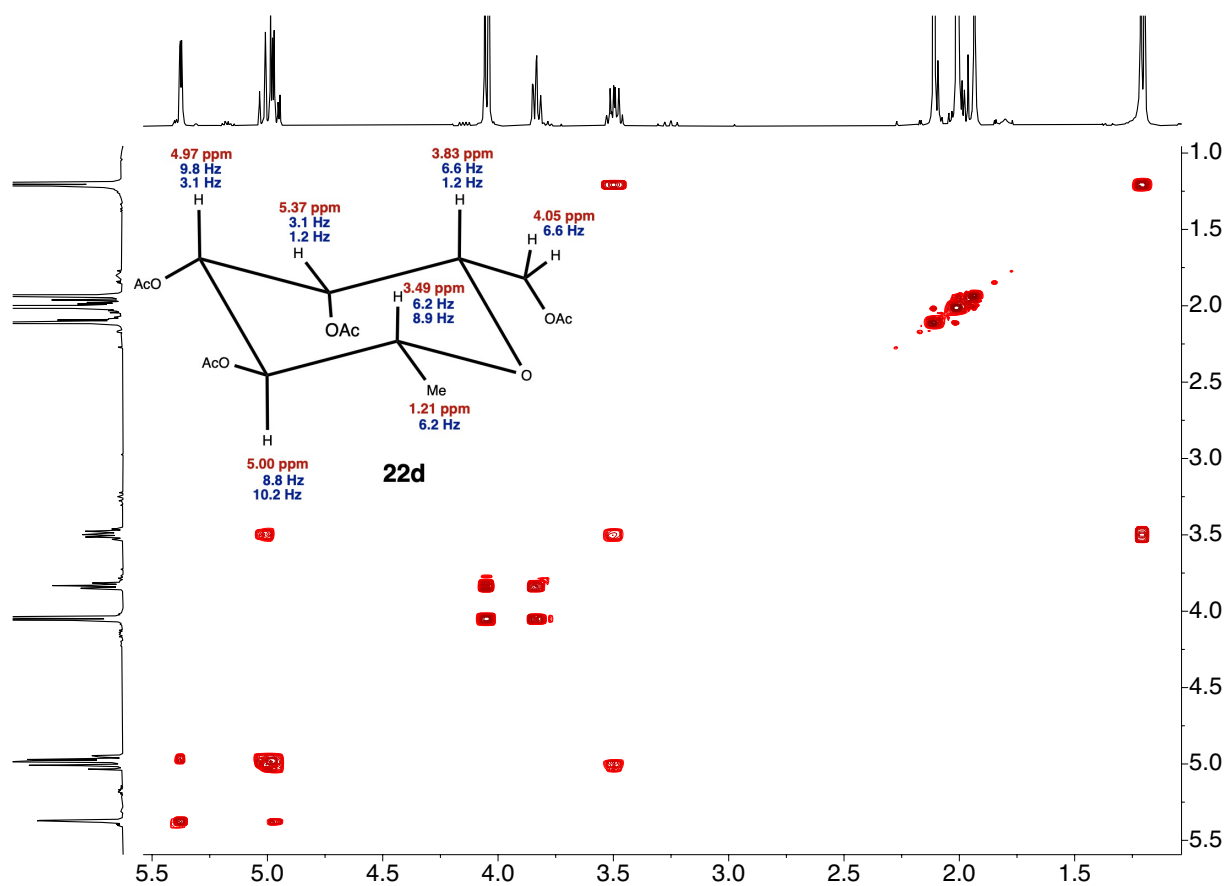


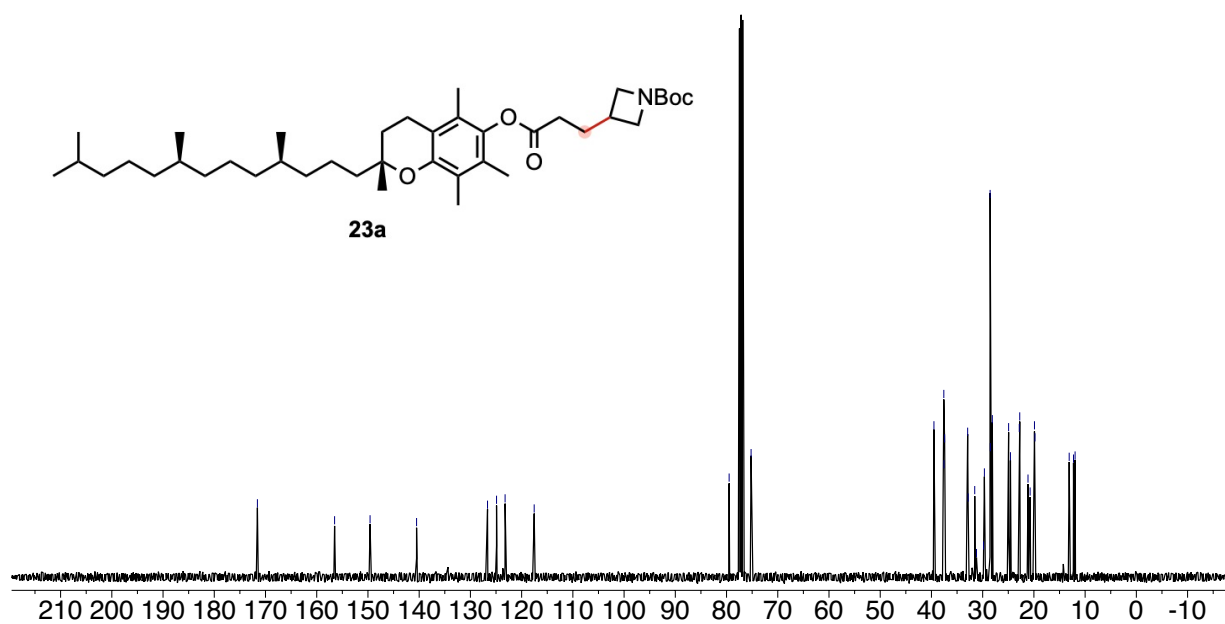
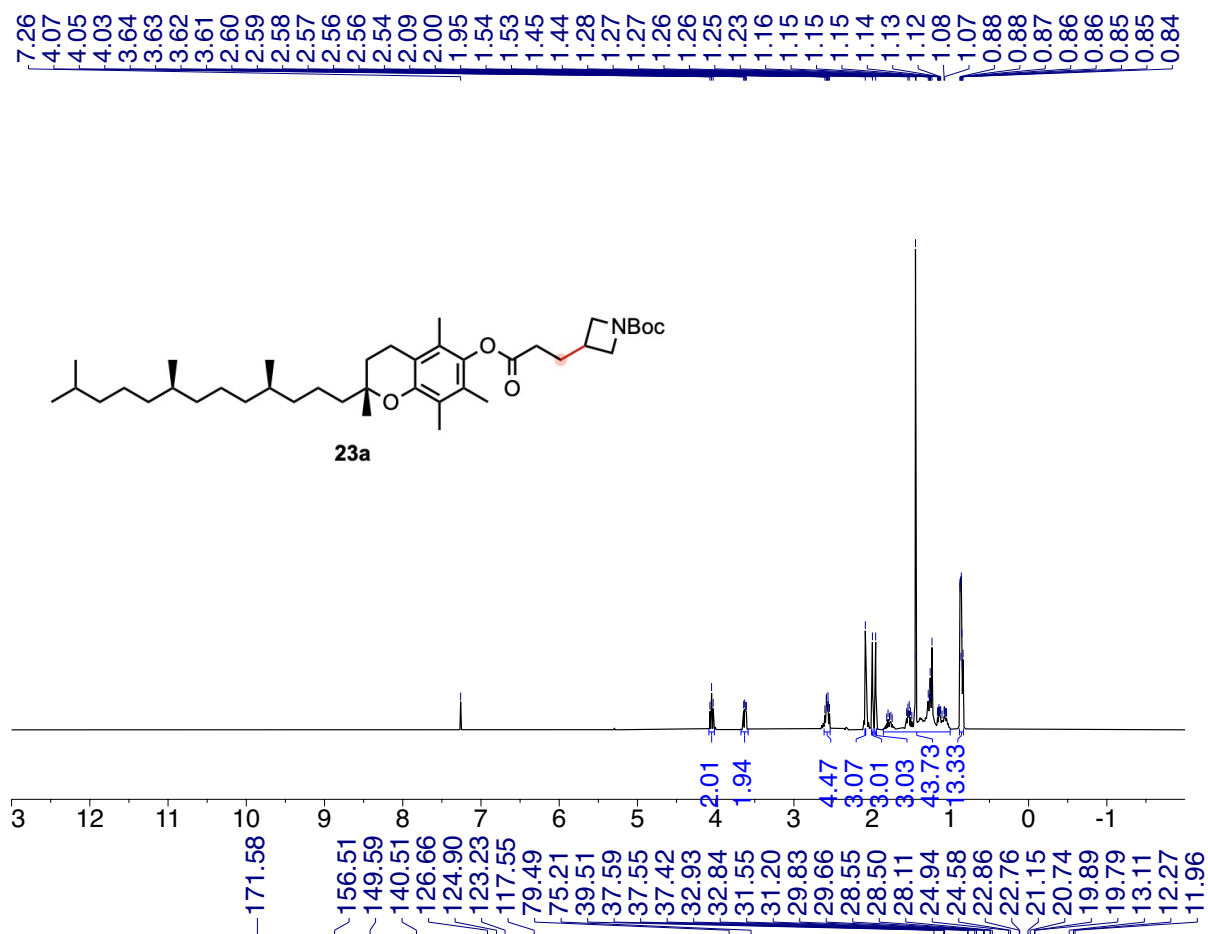


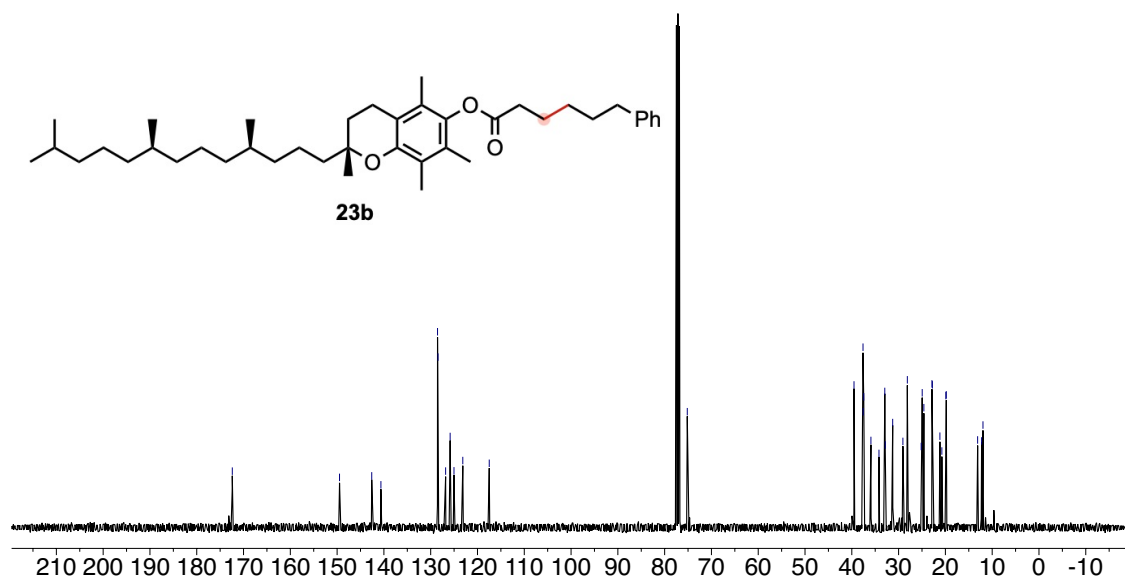
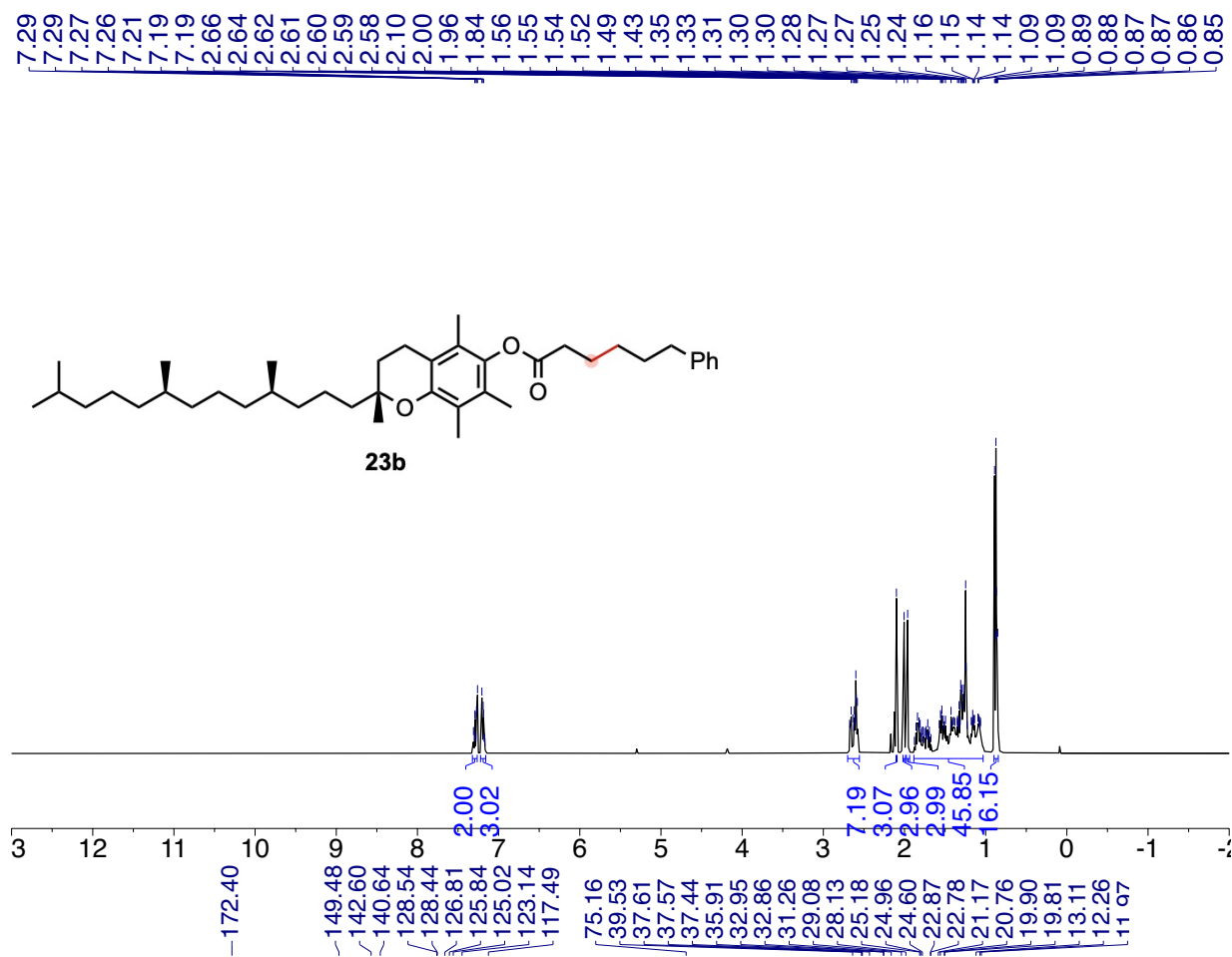


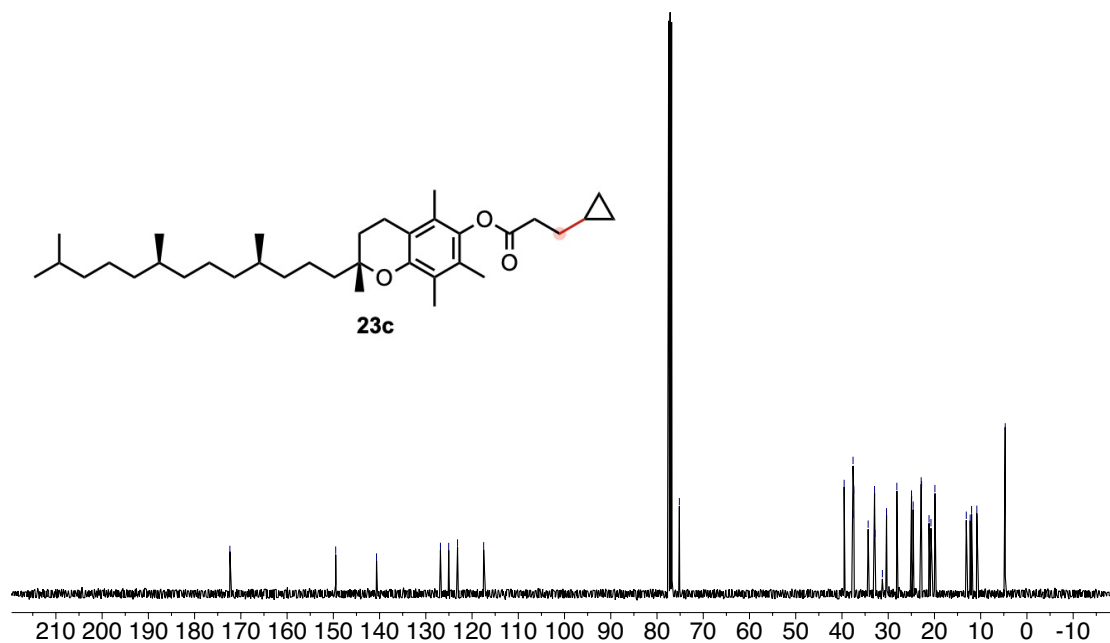
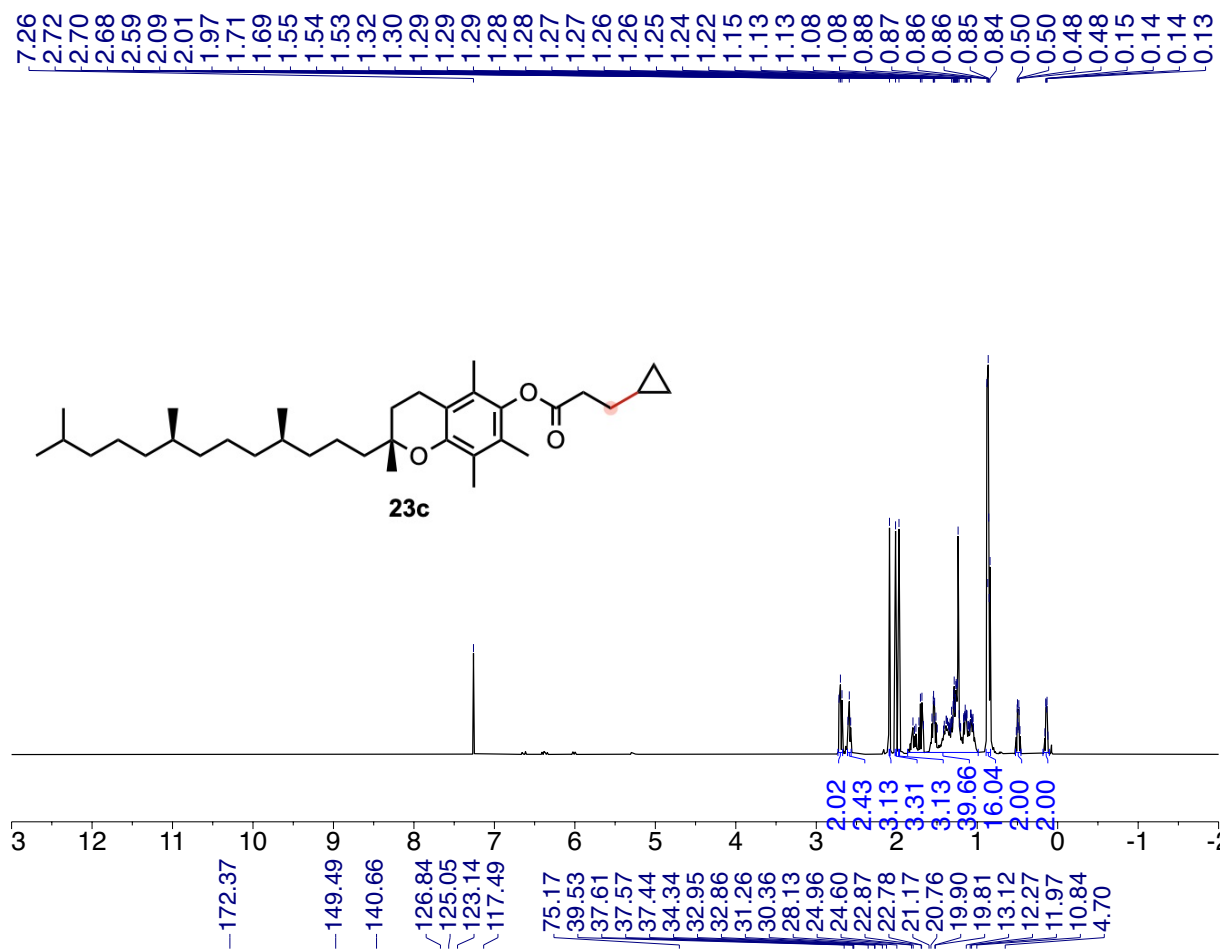


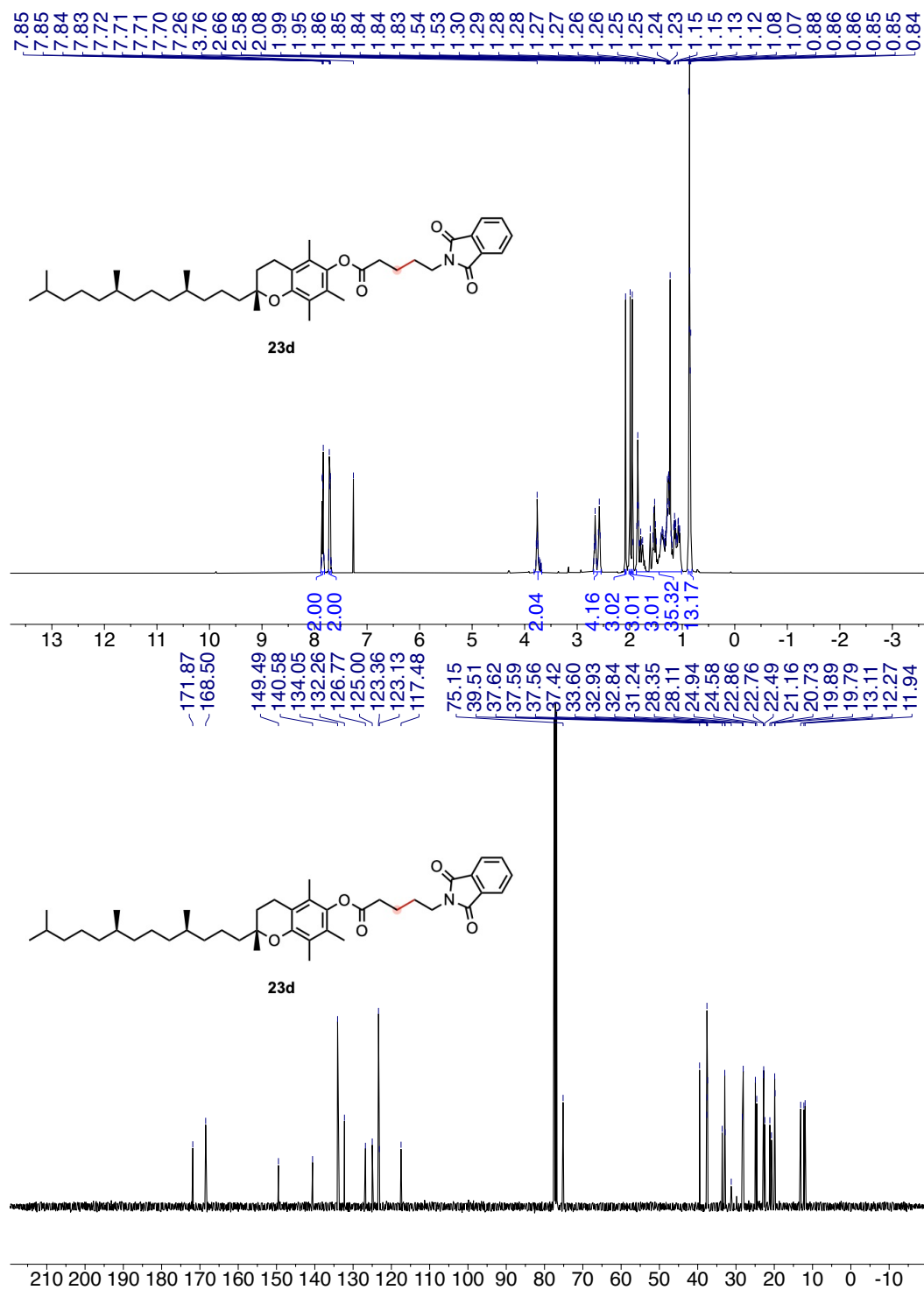












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