Enantioselective Nickel-Catalyzed Mizoroki–Heck Cyclizations of Amide Electrophiles

Ana S. Bulger‡, Daniel J. Nasrallah‡, Arismel Tena Meza‡, and Neil K. Garg*

Department of Chemistry and Biochemistry,
University of California, Los Angeles, California 90095

Electronic Supplementary Information – Table of Contents

Materials and Methods. Unless stated otherwise, reactions were conducted in flame-dried glassware under an atmosphere of nitrogen, and commercially obtained reagents were used as received unless otherwise specified. Anhydrous solvents were either freshly distilled or passed through activated alumina columns, unless otherwise stated. Non-commercially available substrates were synthesized according to known preparations or following protocols specified in the Experimental Procedures. Prior to use in carbene generation or nickel-catalyzed reactions, toluene (PhMe) was distilled over CaH_2 and degassed by five freeze pump thaw cycles. Prior to use in carbene generation or nickel-catalyzed reactions, trifluorotoluene ($PhCF_3$), tetrahydrofuran (THF), 1,2-dimethoxyethane (DME), 1,4-dioxane (dioxane), and acetonitrile (MeCN) were passed through an activated alumina column and degassed by five freeze-pump-thaw cycles. Dichloromethane (CH_2Cl_2), diethyl ether (Et_2O), and triethylamine (NEt_3) were passed through an activated alumina column and ethanol (EtOH) was stored over activated 2Å molecular sieves prior to use. *t*-Amyl alcohol (**13**) was distilled over K_2CO_3 and stored over activated 2Å molecular sieves for 24 h prior to use. Additives were distilled and degassed prior to use in nickel-catalyzed reactions unless otherwise noted: 1-butanol (**14**), *n*-butylamine (**15**), *t*-butylamine (**16**), N,N′-dimethylethylenediamine (**19**), piperidine (**20**), morpholine (**21**), aniline (**37**), N,N-dimethylaniline (**38**), 4-methylmorpholine (**39**), pyrrolidine (**40**), 2-methoxyethan-1-amine (**41**), diisopropylamine (**42**), 1-methylpiperazine (**43**),2,6,6-tetramethyl piperidine (**44**), benzylamine (**45**), diethylamine (**17**), and triethylamine (**18**). Diphenylamine (**46**) and triphenylamine (**47**) were purified by flash chromatography on silica and then recrystallized prior to use. Piperazine (**48**) was recrystallized prior to use. Phenol (**49**) and potassium carbonate (K_2CO_3) were obtained from Acros Organics and used as received. Amine **(S)-50** was purchased from Enamine Building Blocks and used as received. Ammonium salt **(S)-51** was purchased from Ambeed and used as received. Amine **(+)-52**, amine **(+)-53**, **L20**, formaldehyde (37 wt% in H_2O, 1.0 equiv), glyoxal (40 wt% in H_2O, 1.0 equiv), (±)-BINAP, concentrated HCl, potassium *tert*-butoxide (KO*t*-Bu), lithium *tert*-butoxide (LiOt-Bu), sodium *tert*-pentoxide (NaO*t*-amyl), lithium bis(trimethylsilyl)amide (LiHMDS), potassium bis(trimethylsilyl)amide (KHMDS), sodium bis(trimethylsilyl)amide (NaHMDS), potassium phosphate tribasic (K_3PO_4), cesium carbonate (Cs_2CO_3), methyl chloroformate, pyridine, $MgCl_2$, tetrabutylammonium bromide (TBAB), dimethylacetamide (DMA), thiophenol (PhSH), phenylsilane ($PhSiH_3$), tetrabutylammonium fluoride (TBAF) (1.0 M in THF), urea hydrogen peroxide TFA, BF_3•OEt_2, *n*-butyllithium (*n*-BuLi, 2.4 M in hexanes),

allylMgCl (2.0 M in THF), *meta*-chloroperoxybenzoic acid (*m*-CPBA), $NaHCO_3$, and 4-bromobenzenesulfonohydrazide were all purchased from Sigma-Aldrich and used as received. amine **(–)-54**, amine **(–)-55**, amine **(–)-56**, acetic acid (AcOH), 1,2-dibromobenzene, $LiAlH_4$, triethyl orthoformate ($CH(OEt)_3$), triphenylphosphine (PPh_3), and acetyl chloride were obtained from Thermofisher Scientific. $Pd_2(dba)_3$, sodium *tert*-butoxide (NaOt-Bu), bis(1,5-cyclooctadiene)nickel(0) ($Ni(cod)_2$), NiI_2, Zn^0 dust**,** 1,3-dicyclohexylbenzimidazolium chloride (Benz-ICy•HCl), and iron(III) acetylacetonate ($Fe(acac)_3$) were obtained from Strem Chemicals. Di-*tert*-butyl azodicarboxylate (DBAD) and methyltriphenylphosphonium bromide (PPh_3MeBr) were obtained from CombiBlocks. Reaction temperatures at or above 23 °C were controlled using an IKAmag temperature modulator, and unless stated otherwise, performed at room temperature (approximately 23 °C). Thin-layer chromatography (TLC) was conducted with EMD gel 60 F_{254} pre-coated plates (0.25 mm for analytical chromatography and 0.50 mm for preparative chromatography) and visualized using a combination of UV, anisaldehyde, and potassium permanganate staining techniques. Silicycle Siliaflash P60 (particle size 40–63 μm) or Brockman Grade activated neutral alumina (58Å pore size) were used for flash column chromatography unless otherwise specified. ^{1}H-NMR and 2D-NOESY spectra were recorded on Bruker spectrometers (at 500 and 600 MHz) and are reported relative to the residual solvent signal. Data for ^{1}H-NMR spectra are reported as follows: chemical shift (δ ppm), multiplicity, coupling constant (Hz), and integration. ^{13}C-NMR spectra were recorded on Bruker spectrometers (at 125 and 150 MHz) and are reported relative to the residual solvent signal. Data for ^{13}C-NMR spectra are reported in terms of chemical shift (δ ppm) and, when necessary, multiplicity, and coupling constant (Hz). ^{19}F-NMR spectra were recorded on Bruker spectrometers (at 282 MHz) and are reported in terms of chemical shift (δ ppm), multiplicity, and integration. IR spectra were recorded on a Perkin-Elmer UATR Two FT-IR spectrometer and are reported in terms of frequency absorption (cm^{-1}). ESI-TOF measurements were carried out in positive ionization mode on a Waters LCT-Premier XE Time of Flight Instrument controlled by MassLynx 4.1 software (Waters Corporation, Milford MA). The instrument was equipped with the Multi Mode Ionization source operated in the electrospray mode. A solution of Leucine Enkephalin (Sigma Chemical, L9133) was used in the Lock-Spray to obtain accurate mass measurements. Samples were infused using direct loop injection on a Waters Acquity UPLC system. GC-MS measurements were carried out

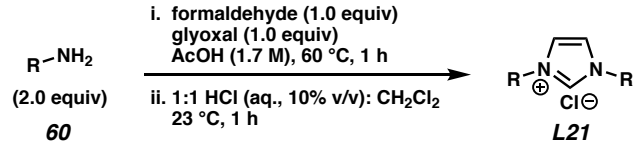
using an Agilent Model 7693 Autosampler, 7890B Gas Chromatograph, and 7250 Q-TOF Mass Selective Detector in the Electron Ionization mode. Sample injection was carried out in split mode with inlet temperature set to 280 °C. Separation was carried out on an Agilent HP5-MS column with dimensions 30m x 250 μm x 0.25 μm. Ultra High Purity Grade He (Airgas) was used as carrier gas with the flow set to 1.1 mL/min in constant flow mode. The initial oven temperature was set to 70 °C for 1 min followed by a 20 °C/min ramp to a final temperature of 300 °C which was maintained for 4 min. A 3.0 min solvent delay was used. EI energy was set to 70 eV. The MSD was set to scan the 50–500 m/z range. Data collection and analysis were performed using Mass Hunter Acquisition and Qualitative Analysis software (Agilent). Optical rotations were measured with a Rudolf Autopol III Automatic Polarimeter. Determination of enantiopurity was carried out on a JASCO SFC (supercritical fluid chromatography) and an Agilent 1260 SFC using Daicel ChiralPak IB N-3, IC, and ID columns. Data for SFC chromatograms are reported in enantiomeric excess (ee). Diastereomeric ratios (dr) and regioisomeric ratios (rr) were determined by ^{1}H analysis of crude reaction mixtures.

Ligand salts **L7**,[1] **L9**,[2] **L10**,[3] **L11**,[3] **L12**,[4] **L13**[3] and ligand **58**[5] were synthesized according to known literature procedures. Amides **6**, **11**, and **22** and indanones **9**, **12**, and **23** are known compounds.[6] Nitrile oxide precursor **59** was synthesized according to a known procedure.[7] Spectral data matched those reported in literature.

Experimental Procedures

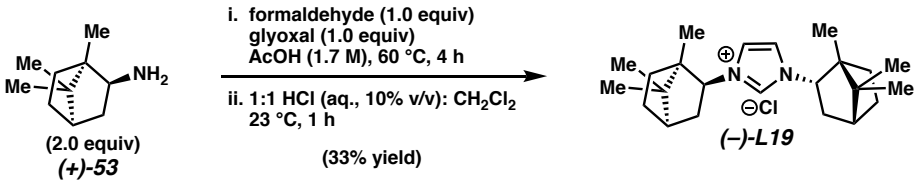
A. Ligand Syntheses

General procedure 1 for the syntheses of imidazolium salts:

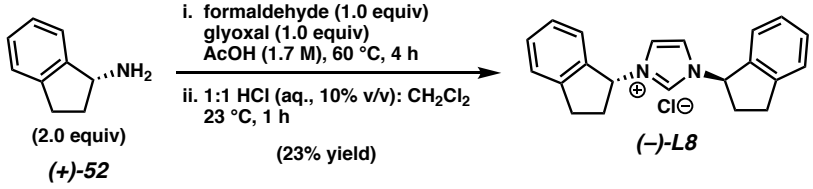


Imidazoliums L21. To a solution of amine **60** (2.0 equiv) in AcOH (1.7 M) was added formaldehyde (37 wt% in H_2O, 1.0 equiv) and glyoxal (40 wt% in H_2O, 1.0 equiv). The reaction was heated to 60 °C in a preheated aluminum block and stirred at this temperature for 1 h. The reaction was then cooled to 23 °C and transferred to a round bottom flask containing a stir bar. The mixture was diluted with CH_2Cl_2 (50 mL) and aqueous HCl (10% v/v, 50 mL) was added. The resulting biphasic mixture was stirred vigorously at 23 °C. After 1 h of stirring, the organic

and aqueous layers were separated, and the aqueous layer was extracted with CH_2Cl_2 (2 x 30 mL). The combined organic layers were dried with $MgSO_4$, filtered, and concentrated under reduced pressure. The crude material was purified by flash chromatography to provide imidazoliums **L21**. *Any modification of the reaction conditions shown in the general procedure above are specified in the following schemes.*

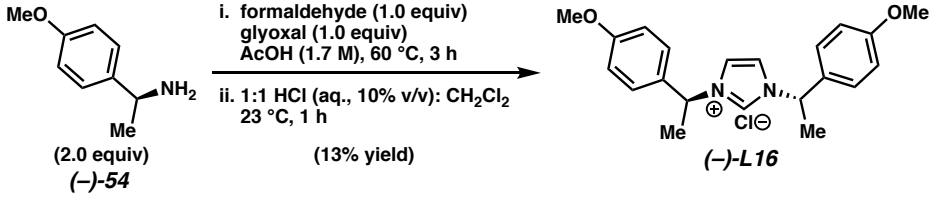


Imidazolium (–)-L19. Followed a modified version of General Procedure 1 using **(+)-53** (320 mg, 2.09 mmol, 2.0 equiv) by altering the reaction time in the first step to 4 h. Purification by flash chromatography on silica (14:1 CH_2Cl_2:MeOH) afforded imidazolium **(–)-L19** (110 mg, 0.34 mmol, 33% yield) as an off-white powder. **Imidazolium (–)-L19**: Mp: >250 °C; R_f 0.09 (9:1 CH_2Cl_2:MeOH); ^{1}H NMR (500 MHz, $CDCl_3$): δ 11.30 (s, 1H), 7.22 (s, 2H), 5.07 (dd, *J* = 12.0, 2.8, 2H), 2.54 (ddt, *J* = 15.0, 11.4, 3.8, 2H), 1.96–1.87 (m, 3H), 1.84 (dd, *J* = 14.4, 4.8, 2H), 1.81–1.74 (m, 1H), 1.68–1.59 (m, 2H), 1.49–1.38 (m, 2H), 1.14–1.03 (m, 8H), 0.97 (s, 6H), 0.96 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 139.9, 120.7, 66.8, 51.1, 49.8, 44.8, 34.3, 28.3, 27.7, 20.0, 18.7, 13.8; IR (film): 3051, 2951, 2888, 1544, 1392 cm^{-1}; HRMS-ESI (*m/z*) $[M - Cl]^+$ calcd for $C_{23}H_{37}N_2^+$, 341.2947; found 341.2957; $[\alpha]^{24.3}_D$–24.0° (c = 1.00, CH_2Cl_2).

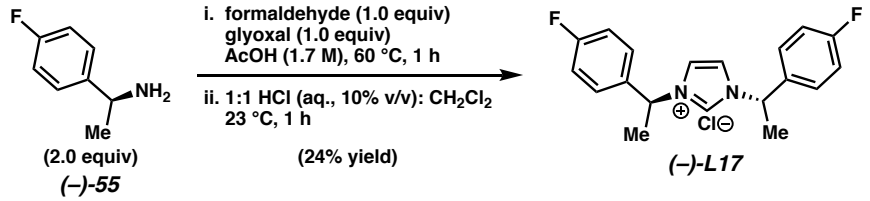


Imidazolium (–)-L8. Followed a modified version of General Procedure 1 using **(+)-52** (300 mg, 2.25 mmol, 2.0 equiv) by altering the reaction time in the first step to 4 h. Purification by flash chromatography on neutral alumina (50:3 EtOAc:*i*-PrOH → 1:1 EtOAc:*i*-PrOH) afforded imidazolium **(–)-L8** (89 mg, 0.26 mmol, 23% yield) as an off-white powder. **Imidazolium (–)-L8**: Mp: 58 °C; R_f 0.40 (9:1 CH_2Cl_2:MeOH); ^{1}H NMR (500 MHz, $CDCl_3$): δ 11.62–11.57 (m, 1H), 7.39–7.33 (m, 4H), 7.29–7.22 (m, 4H), 6.79 (d, *J* = 1.6, 2H), 6.53 (dd, *J* = 8.0, 5.4, 2H), 3.17 (ddd, *J* = 16.3, 8.7, 5.7, 2H), 3.07 (ddd, *J* = 16.3, 8.6, 5.8, 2H), 2.98 (dtd, *J* = 13.6, 8.7, 5.8, 2H), 2.28 (ddt, *J* = 13.6, 8.6, 5.7, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 144.3, 138.6, 138.2, 130.1, 127.9,

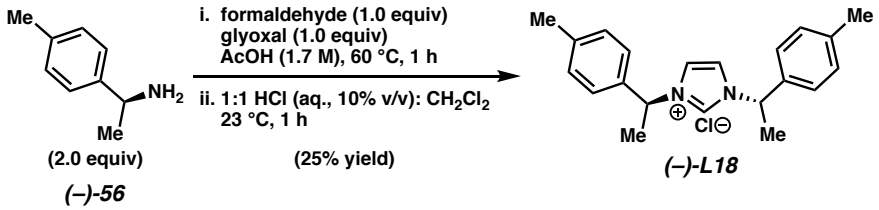
125.7, 125.2, 119.5, 65.2, 34.7, 30.5; IR (film): 3042, 2949, 1630, 1547, 1459 cm^{-1}; HRMS-ESI (*m/z*) $[M - Cl]^+$ calcd for $C_{21}H_{21}N_2^+$, 301.1705; found 301.1710; $[\alpha]^{24.5}_D$–14.0° (c = 1.00, CH_2Cl_2).



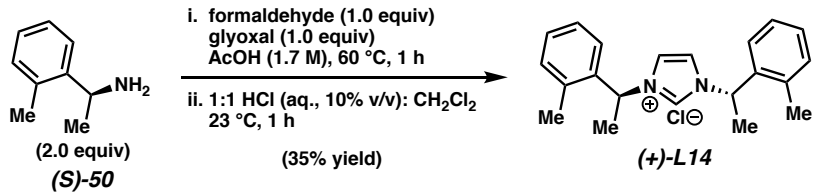
Imidazolium (–)-L16. Followed a modified version of General Procedure 1 using **(–)-54** (500 mg, 3.31 mmol, 2.0 equiv) by altering the reaction time in the first step to 3 h. Purification by flash chromatography on neutral alumina (20:1 EtOAc:*i*-PrOH → 1:1 EtOAc:*i*-PrOH) afforded imidazolium **(–)-L16** (80 mg, 0.22 mmol, 13% yield) as a light-yellow solid. **Imidazolium (–)-L16**: Mp: 79 °C; R_f 0.35 (9:1 CH_2Cl_2:MeOH); ^{1}H NMR (500 MHz, $CDCl_3$): δ 11.61–11.57 (m, 1H), 7.44–7.38 (m, 4H), 6.95–6.88 (m, 6H), 5.98 (q, *J* = 7.0, 2H), 3.80 (s, 6H), 2.01 (d, *J* = 7.0, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 160.3, 137.3, 129.7, 128.6, 119.4, 114.7, 59.5, 55.4, 21.3; IR (film): 3066, 2982, 1515, 1249, 1148 cm^{-1}; HRMS-ESI (*m/z*) $[M - Cl]^+$ calcd for $C_{21}H_{25}N_2O_2^+$, 337.1916; found 337.1923; $[\alpha]^{23.9}_D$–58.0° (c = 1.00, CH_2Cl_2).



Imidazolium (–)-L17. Followed General Procedure 1 using **(–)-55** (535 mg, 3.84 mmol, 2.0 equiv). Purification by flash chromatography on neutral alumina (15:1 EtOAc:*i*-PrOH → 1:2 EtOAc:*i*-PrOH) afforded imidazolium **(–)-L17** (160 mg, 0.46 mmol, 24% yield) as an off-white solid. **Imidazolium (–)-L17**: Mp: 177–178 °C; R_f 0.15 (9:1 CH_2Cl_2:MeOH); ^{1}H NMR (500 MHz, $CDCl_3$): δ 11.75 (s, 1H), 7.55–7.48 (m, 4H), 7.13–7.06 (m, 4H), 7.02–6.96 (m, 2H), 6.07 (q, *J* = 7.0, 2H), 2.03 (d, *J* = 7.1, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 163.3 (d, *J* = 249.1), 137.8, 133.7 (d, *J* = 3.3), 129.3 (d, *J* = 8.5), 119.7, 116.7 (d, *J* = 21.9), 59.4, 21.3; ^{19}F NMR (282 MHz, $CDCl_3$): δ –111.2 (m, 2F); IR (film): 3064, 2987, 1604, 1511, 1226 cm^{-1}; HRMS-ESI (*m/z*) $[M - Cl]^+$ calcd for $C_{19}H_{19}F_2N_2^+$, 313.1516; found 313.1527; $[\alpha]^{24.0}_D$–36.0° (c = 1.00, CH_2Cl_2).

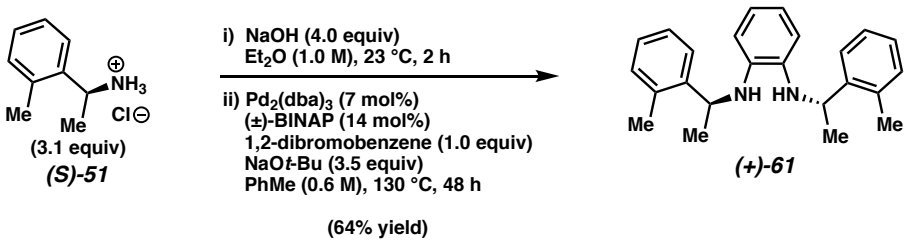


Imidazolium (–)-L18. Followed General Procedure 1 using **(–)-56** (500 mg, 3.70 mmol, 2.0 equiv). Purification by flash chromatography on neutral alumina (15:1 EtOAc:*i*-PrOH → 1:1 EtOAc:*i*-PrOH) afforded imidazolium **(–)-L18** (160 mg, 0.46 mmol, 25% yield) as a white solid. **Imidazolium (–)-L18**: Mp: 87–89 °C; R_f 0.45 (9:1 CH_2Cl_2:MeOH); ^{1}H NMR (500 MHz, $CDCl_3$): δ 11.61 (s, 1H), 7.33 (d, *J* = 8.0, 4H), 7.20 (d, *J* = 8.0, 4H), 6.96–6.92 (m, 2H), 6.00 (q, *J* = 6.9, 2H), 2.34 (s, 6H), 2.01 (d, J = 6.9, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 139.6, 137.6, 134.9, 130.2, 127.2, 119.7, 59.8, 21.4, 21.3; IR (film): 3060, 2982, 1614, 1546, 1150 cm^{-1}; HRMS-ESI (*m/z*) [M – Cl]$^+$ calcd for $C_{21}H_{25}N_2^+$, 305.2018; found 305.2033; $[\alpha]^{23.7}_D$–44.0° (c = 1.00, CH_2Cl_2).



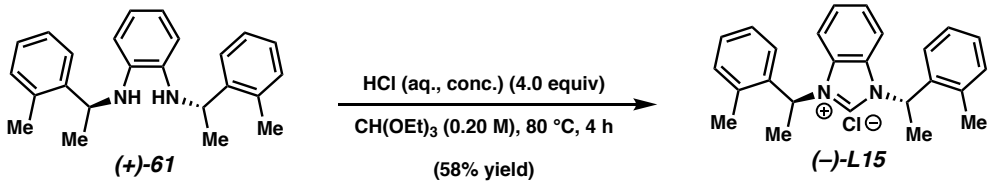
Imidazolium L14. Followed General Procedure 1 using **(S)-50** (590 mg, 4.36 mmol, 2.0 equiv). Purification by flash chromatography on neutral alumina (25:1 EtOAc:*i*-PrOH → 1:1 EtOAc:*i*-PrOH) afforded imidazolium **L14** (260 mg, 0.76 mmol, 35% yield) as a beige solid. **Imidazolium L14**: Mp: 146–147 °C; R_f 0.10 (9:1 CH_2Cl_2:MeOH); ^{1}H NMR (500 MHz, $CDCl_3$): δ 11.65 (s, 1H), 7.30–7.23 (m, 6H), 7.22–7.18 (m, 2H), 6.90–6.85 (m, 2H), 6.22 (q, *J* = 7.0, 2H), 2.36 (s, 6H), 2.04 (d, *J* = 7.0, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 138.2, 136.7, 135.8, 131.7, 129.5, 127.1, 125.8, 120.1, 56.9, 21.7, 19.5; IR (film): 3064, 2981, 1629, 1544, 1462 cm^{-1}; HRMS-ESI (*m/z*) [M – Cl]$^+$ calcd for $C_{21}H_{25}N_2^+$, 305.2018; found 305.2032; $[\alpha]^{23.3}_D$+8.0° (c = 1.00, CH_2Cl_2).

Synthesis of benzimidazolium salt L15:



Diamine (+)-61. To a flask containing a stir bar and **(S)-51** (4.73 g, 27.6 mmol, 3.1 equiv) in Et_2O (27.6 mL, 1.0 M) was added aqueous 1.0 M NaOH (55 mL, 2.0 equiv). The resulting mixture was stirred vigorously at 23 °C for 2 h. After this time, the organic and aqueous layers were separated and the aqueous layer was extracted with Et_2O (2 x 30 mL). The combined organic layers were dried with Na_2SO_4, filtered, and concentrated under reduced pressure. The resulting amine was immediately transferred to a flame-dried 8-dram vial, secured with a septum cap, and purged with an inlet needle using N_2 and an outlet needle open to air for 5 min. Subsequently, 1,2-dibromobenzene (1.96 g, 8.29 mmol, 1.0 equiv) was added to the vial. A separate 50 mL pressure tube containing a stir bar was fitted with a septum, flame-dried under reduced pressure, and backfilled with N_2. The 8-dram vial and pressure tube were then brought into a glovebox. In the glovebox, $Pd_2(dba)_3$ (529 mg, 0.578 mmol, 7 mol%), (±)-BINAP (720 mg, 1.16 mmol, 14 mol%), and toluene (7 mL) were added to the pressure tube. The tube was sealed and prestirred for 15 minutes at 130 °C in a preheated aluminum block in the glovebox. After this time, the reaction vessel was allowed to cool to 23 °C and the amine and 1,2-dibromobenzene mixture were transferred to the reaction tube using toluene (7 mL, 0.6 M). Then, NaO*t*-Bu (2.78 g, 28.9 mmol, 3.5 equiv) was added to the pressure tube, which was then sealed and brought out of the glovebox. The reaction was then heated to 130 °C in an oil bath and stirred at this temperature for 48 h. After this time, the reaction was allowed to cool to 23 °C and was filtered over a pad of Celite, eluting with EtOAc (250 mL). The eluate was concentrated under reduced pressure and the crude material was purified by flash chromatography on silica (4:1 hexanes:CH_2Cl_2 → 3:2 hexanes:CH_2Cl_2) to afford diamine **(+)-61** (1.83 g, 5.31 mmol, 64% yield) as a white solid. **Diamine (+)-61**: Mp: 94–95 °C; R_f 0.35 (4:1 CH_2Cl_2:MeOH); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.51–7.45 (m, 2H), 7.20–7.11 (m, 6H), 6.56 (dt, *J* = 9.5, 3.8, 2H), 6.30 (dt, *J* = 9.5, 3.8, 2H), 4.69 (q, *J* = 6.5, 2H), 3.72 (s, 2H), 2.46 (s, 6H), 1.54 (d, *J* = 6.5, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 143.0, 136.4, 134.6, 130.7, 126.7, 124.8, 119.2, 113.3, 50.1, 23.5, 19.2 (11 of 12 signals observed); IR (film): 3346, 3022,

2965, 1599, 1508 cm^{-1}; HRMS-ESI (*m/z*) $[M + H]^+$ calcd for $C_{24}H_{29}N_2^+$, 345.2331; found 345.2335; $[\alpha]^{25.9}_D$+308.0° (c = 1.00, CH_2Cl_2).

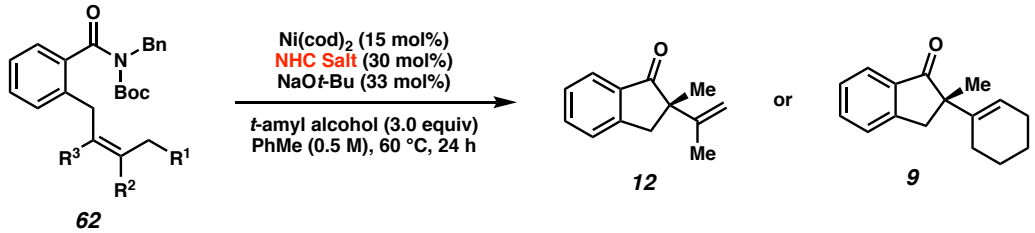


Benzimidazolium (–)-L15. To a round bottom flask containing a stir bar was added diamine **(+)-61** (1.83 g, 5.31 mmol, 1.0 equiv), followed by $CH(OEt)_3$ (26.6 mL, 0.20 M). Then, concentrated aqueous HCl (12 M, 1.8 mL, 21.2 mmol, 4.0 equiv) was added to the reaction vial. The reaction flask was fitted with an air condenser, which was capped with a septum that was pierced with a needle and left open to air. The resulting reaction was heated to 80 °C in an oil bath and stirred for 4 h. After this time, the reaction was allowed to cool to 23 °C and the reaction mixture was loaded directly onto a column and purification by flash chromatography on silica (EtOAc → 4:1 EtOAc:MeOH) affording an oily residue containing benzimidazolium (–)-**L15**. The resulting salt was crystallized by solvent diffusion after transferring the oily residue to a vial and dissolving it in MeOH (2 mL) followed by slow addition of Et_2O (10 mL) down the side of the vial. The resulting salt was allowed to crystallize over 14 h at –20 °C, after which, the mother liquor was decanted and the crystals were washed with cold Et_2O (10 mL), providing benzimidazolium (–)-**L15** (1.20 g, 3.08 mmol, 58% yield) as a white crystalline solid. **Benzimidazolium** (–)-**L15**: Mp: 234–235 °C; R_f 0.15 (9:1 CH_2Cl_2:MeOH); ^{1}H NMR (500 MHz, $CDCl_3$): δ 12.37 (s, 1H), 7.39–7.34 (m, 2H), 7.31–7.27 (m, 2H), 7.26–7.24 (m, 4H), 7.22–7.18 (m, 2H), 7.17–7.14 (m, 2H), 6.47 (q, *J* = 6.9, 2H), 2.43 (s, 6H), 2.31 (d, *J* = 6.9, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 143.4, 135.8, 135.6, 131.5, 131.2, 129.1, 127.2, 126.6, 125.8, 114.2, 56.6, 20.9, 19.6; IR (film): 3112, 2979, 1552, 1462, 1249 cm^{-1}; HRMS-ESI (*m/z*) $[M - Cl]^+$ calcd for $C_{25}H_{27}N_2^+$, 355.2174; found 355.2184; $[\alpha]^{22.3}_D$–14.0° (c = 1.00, CH_2Cl_2).

B. Reaction Discovery

B.1 Ligand Optimization

General procedure 2 for ligand optimization



62 **12** **9**

A flame-dried 1-dram vial containing a stir bar was charged with amide **62** (34.3 mg, 0.087 mmol, 1.0 equiv). The vial was brought into a glovebox and charged sequentially with $Ni(cod)_2$ (3.6 mg, 0.013 mmol, 15 mol%), NHC salt (0.026 mmol, 30 mol%), NaO*t*-Bu (2.8 mg, 0.029 mmol, 33 mol%), toluene (0.18 mL, 0.5 M), and *t*-amyl alcohol (29 μL, 0.26 mmol, 3.0 equiv). The vial was then sealed with a Teflon-lined screw cap, removed from the glovebox, the gap between the cap and the vial was sealed with electrical tape, and the vial was stirred at 60 °C for 24 h. After cooling to 23 °C, the mixture was filtered through a plug of silica, eluting with EtOAc (10 mL). The eluate was concentrated and then analyzed by ^1H NMR using hexamethylbenzene as an external standard. Purification by preparative thin layer silica chromatography (3:1 hexanes:EtOAc) afforded analytical samples of indanones **12** or **9**, which were then subjected to analysis by supercritical fluid chromatography to determine enantiomeric excess.

*The absolute stereochemistry shown for **12** and **9** is not necessarily representative of the major enantiomer observed for all ligands examined.*

A range of ligands (see Figure S1 below for structures) were examined using General Procedure 2, and results of these reactions appear below in Table S1. Apart from **L20**, which is commercially available, all chiral NHC salts in Table S1 were synthesized according to the procedures above or using known procedures referenced in the Materials and Methods section.

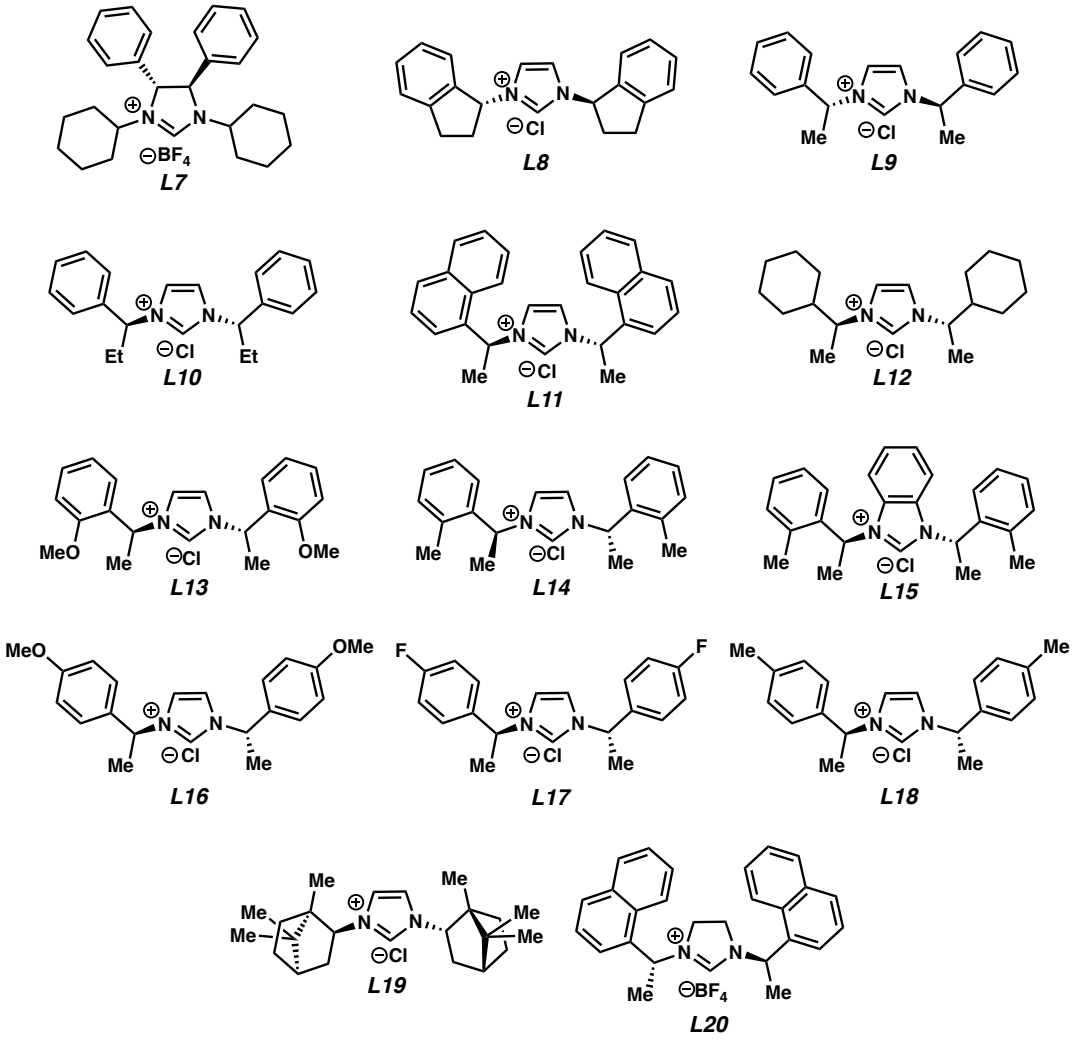
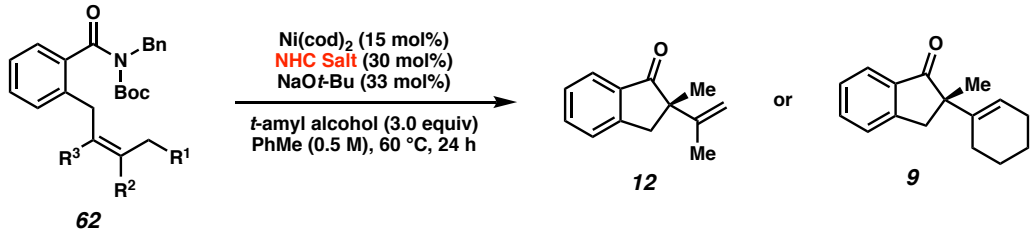


Figure S1. NHC salts evaluated during asymmetric reaction development.

Table S1. Ligand evaluation results. See Figure S1 above for NHC salts.



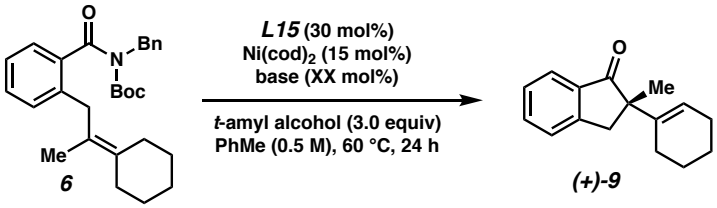
Entry	NHC Salt	Yield of 12[a]	% ee of 12	Yield of 9[a]	% ee of 9
1	**L7**	31%	11%	27%	26%
2	**L8**	16%	0%	N.D.	N.D.
3	**L9**	23%	39%	4%	58%
4	**L10**	17%	34%	2%	62%
5	**L11**	0%	N.D.	N.D.	N.D.
6	**L12**	18%	62%	20%	84%
7	**L13**	17%	70%	16%	76%
8	**L14**	14%	74%	17%	85%
9	**L15**	18%	75%	32%	88%
10	**L16**	10%	43%	N.D.	N.D.
11	**L17**	0%	N.D.	N.D.	N.D.
12	**L18**	2%	49%	7%	58%
13	**L19**	0%	N.D.	0%	N.D.
14	**L20**	0%	N.D.	2%	74%

[a]Yields determined via ^{1}H NMR analysis using hexamethylbenzene as an external standard

Ligand optimization revealed that **L15** gave the best combination of yield and enantioselectivity in the formation of products **12** and **9**.

B.2 Reaction optimization

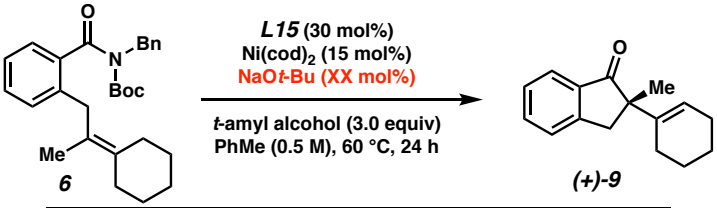
General procedure 3 for optimization of reaction conditions with L15



A flame-dried 1-dram vial containing a stir bar was brought into a glovebox and charged with **L15** (0.030 mmol, 30 mol%) followed by base (0.030–0.040 mmol, 30–65 mol%). Then, $Ni(cod)_2$ (0.015 mmol, 15 mol%) was added followed by **6** (0.060 mmol, 1.0 equiv). Subsequently, *t*-amyl alcohol (3 equiv) and toluene (0.5 M with respect to amide **6**) were added to the reaction vial. The vial was then sealed with a Teflon-lined screw cap, removed from the glovebox, the gap between the cap and the vial was sealed with electrical tape, and the vial was stirred at the indicated temperature for 24 h. After cooling to 23 °C, the mixture was filtered through a plug of silica, eluting with EtOAc (10 mL). The eluate was concentrated under reduced pressure and hexamethylbenzene was used as an external standard to determine ^{1}H NMR yields.

Any modification of the reaction conditions shown in the general procedure above are specified.

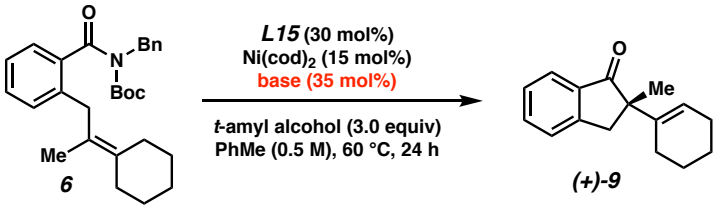
Table S2. Evaluation of stoichiometric loading of NaO*t*-Bu with **6** and **L15**.



Entry	mol%	Yield of (+)-9[a]	Recovered 6[a]
1	30	3%	88%
2	35	33%	46%
3	40	28%	36%

[a]Yields determined via ^{1}H NMR analysis using hexamethylbenzene as an external standard

Table S3. Variation of base employed with **6** and **L15**.

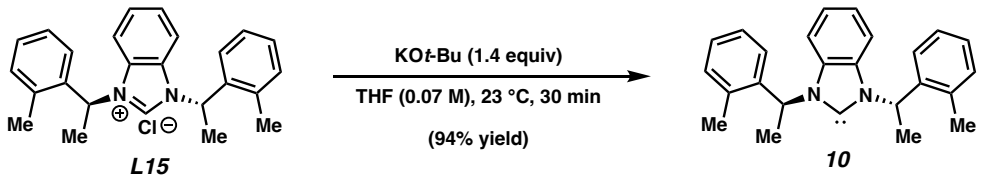


Entry	Base	Yield of (+)-9[a]	Recovered 6[a]
1	NaO*t*-Bu	33%	46%
2	LiO*t*-Bu	1%	75%
3	KO*t*-Bu	31%	50%
4	NaO*t*-amyl	30%	35%
5	LiHMDS	0%	84%
6	KHMDS	41%	37%
7	NaHMDS	23%	54%
8	K_2CO_3	0%	97%
9	K_3PO_4	0%	98%
10	Cs_2CO_3	0%	100%

[a]Yields determined via ^{1}H NMR analysis using hexamethylbenzene as an external standard

In-situ generation of the free carbene did not lead to significant increase in yield or catalyst turnover. Additionally, during our optimization efforts, we observed varying amounts of removal of the Boc group from the amide starting material which through control reactions we found could occur through the use of base, therefore, we sought to add the free carbene as a discrete reagent and omit the use of base overall.

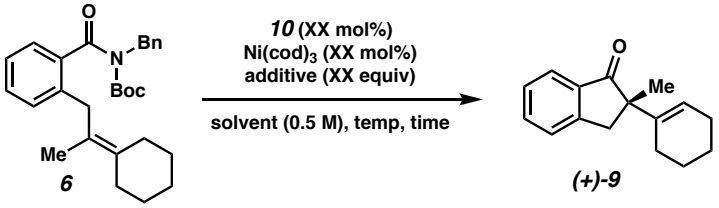
Generation of Free Carbene 10



Carbene 10. A flame-dried scintillation vial containing a stir bar was brought into a glovebox and charged with **L15** (145.6 mg, 0.37 mmol, 1 equiv) and KO*t*-Bu (58.5 mg, 0.52 mmol, 1.4 equiv). Next, THF (5.3 mL, 0.07 M) was added. The vial was capped with a Teflon-lined screw cap and stirred for 30 mins in the glovebox. The reaction was then eluted through a Celite plug with THF (2 x 0.5 mL) and collected in a flame-dried scintillation vial. The solvent was removed under

reduced pressure and a white residue was left on the sides of the vial. The material was then dissolved in toluene, and then eluted through another Celite plug with toluene (2 x 0.5 mL), and collected in a tared flame-dried scintillation vial in the glovebox. The solvent was removed under reduced pressure, providing free carbene **10** (123.9 mg, 0.35 mmol, 94% yield) as a white solid that was dissolved and stored in toluene (0.1 mg/μL) for ease of addition to reaction vials. **Carbene 10**: ^{1}H NMR (500 MHz, toluene-d_8): δ 7.40–7.34 (m, 2H), 6.96–6.89 (m, 6H), 6.84–6.79 (m, 2H), 6.73–6.68 (m, 2H), 5.66 (q, *J* = 6.9, 2H), 2.26 (s, 6H), 2.09 (d, *J* = 6.9, 6H); ^{13}C NMR (125 MHz, toluene-d_8): δ 225.0, 141.8, 135.9, 134.8, 130.8, 127.3, 126.8, 126.1, 121.4, 110.7, 54.7, 22.7, 19.2.

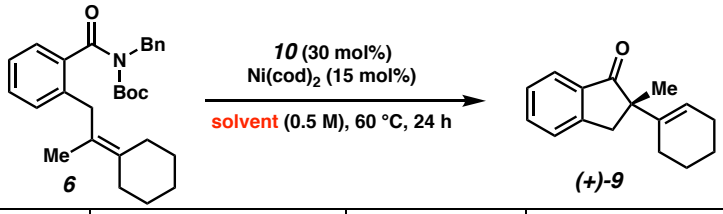
General procedure 4 for optimization of reaction conditions with free carbene 10



A flame-dried 1-dram vial containing a stir bar was brought into a glovebox and charged with a solution of **10** (0.015–0.080 mmol, 15–80 mol%) in solvent (0.5 M with respect to amide **6**). Then, the $Ni(cod)_2$ (0.015–0.040 mmol, 15–40 mol%) was added and the reaction was allowed to stir at 23 °C for 30 min. Subsequently, **6** (0.060 mmol, 1.0 equiv) and additive (0–3 equiv) were added to the reaction vial. The vial was then sealed with a Teflon-lined screw cap, removed from the glovebox, the gap between the cap and the vial was sealed with electrical tape, and the vial was stirred at the indicated temperature for a given time. After cooling to 23 °C, the mixture was filtered through a plug of silica, eluting with EtOAc (10 mL). The eluate was concentrated under reduced pressure, and hexamethylbenzene was used as an external standard to determine ^{1}H NMR yields. In cases where SFC data were obtained, purification by preparative thin-layer chromatography (benzene) afforded analytical samples of indanone **9**, which were then subjected to analysis by supercritical fluid chromatography to determine enantiomeric excess.

Any modification of the reaction conditions shown in the general procedure above are specified.

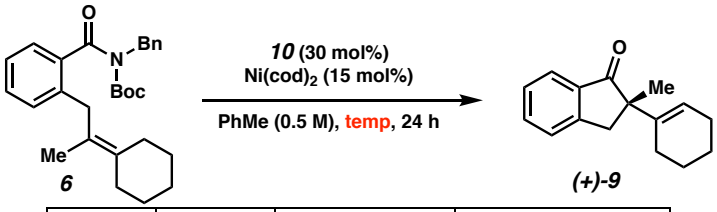
Table S4. Solvent variation with **6** and **10**.



Entry	Solvent	Yield of (+)-9[a]	Recovered 6[a]
1	PhMe	10%	70%
2	$PhCF_3$	7%	78%
3	THF	6%	83%
4	1,2-Dimethoxyethane	8%	70%
5	1,4-Dioxane	4%	81%
6	Acetonitrile	0%	82%

[a]Yields determined via ^{1}H NMR analysis using hexamethylbenzene as an external standard

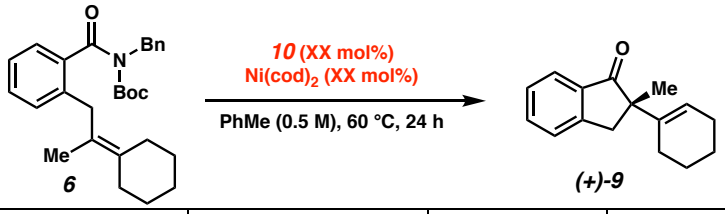
Table S5. Temperature variation with **6** and **10**.



Entry	Temp	Yield of (+)-9[a]	Recovered 6[a]
1	40 °C	3%	72%
2	60 °C	10%	70%
3	80 °C	0%	79%
4	100 °C	2%	71%
5	120 °C	2%	53%

[a]Yields determined via ^{1}H NMR analysis using hexamethylbenzene as an external standard

Table S6. Variation of catalyst stoichiometry with **6**.

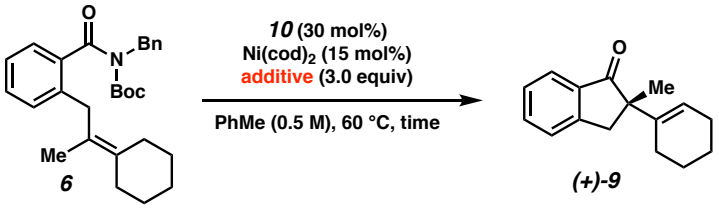


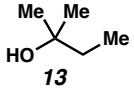
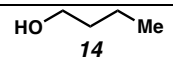
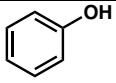
Entry	mol% of 10	$Ni(cod)_2$ mol%	Yield of (+)-9[a]	Recovered 6[a]
1	30	15	10%	70%
2	15	15	11%	62%
3	60	15	0%	80%
4	80	40	28%	40%

[a]Yields determined via ^{1}H NMR analysis using hexamethylbenzene as an external standard

Optimization attempts varying solvent, temperature, and catalyst loading did not improve the yield of the reaction using the free carbene without any additive. Optimization was investigated using alcohol and amine additives and select examples of these efforts are shown in tables S7–S9 below. Optimized conditions were found using 1.0 equivalent of morpholine as an additive (see Table S9, entry 3).

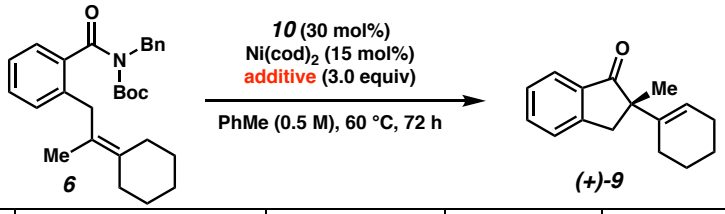
Table S7. Evaluation of alcohol additives with **6** and **10**.

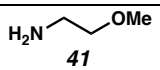
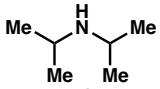
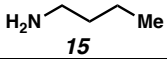
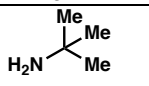
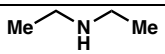
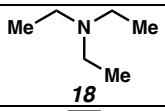
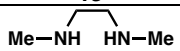
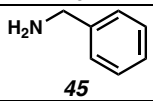
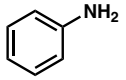
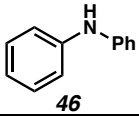
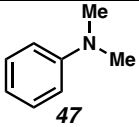


Entry	Additive	Time	Yield of (+)-9[a]	Recovered 6[a]
1	 13	72 h	24%	62%
2	 14	72 h	27%	34%
3	 49	24 h	0%	82%

[a]Yields determined via ^{1}H NMR analysis using hexamethylbenzene as an external standard

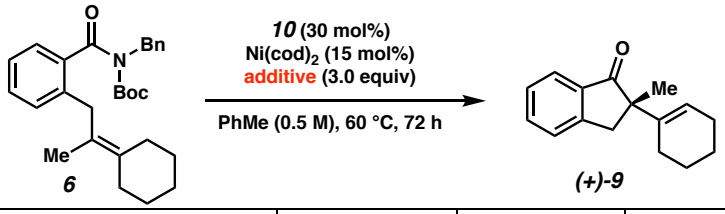
Table S8. Evaluation of acyclic amines additives with **6** and **10**.

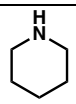
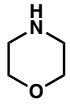
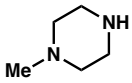
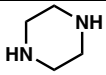
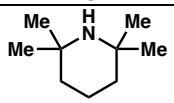
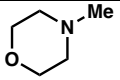


Entry	Additive	Yield of (+)-9[a]	% ee of (+)-9	Recovered 6[a]
1	 *41*	12%	N.D.	0%
2	 *42*	10%	N.D.	70%
3	 *15*	4%	N.D.	44%
4	 *16*	42%	N.D.	40%
5	 *17*	39%	N.D.	30%
6	 *18*	5%	N.D.	84%
7	 *19*	34%	N.D.	11%
8	 *45*	6%	N.D.	31%
9	 *37*	40%	89%	59%
10	 *46*	15%	N.D.	85%
11	 *47*	13%	N.D.	84%

[a]Yields determined via ^{1}H NMR analysis using hexamethylbenzene as an external standard

Table S9. Evaluation of cyclic amine additives with **6** and **10**.



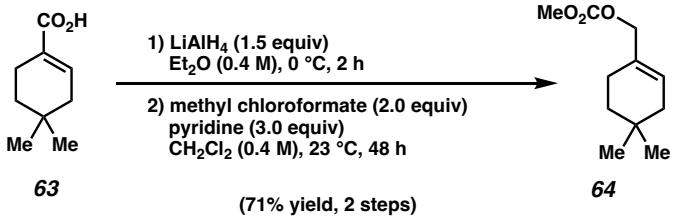
Entry	Additive	Yield of (+)-9[a]	% ee of (+)-9	Recovered 6[a]
1	 *20*	23%	N.D.	7%
2 3	 *21*	42% 55%[b]	89% 88%[b]	0% 0%[b]
4	 *40*	13%	N.D.	0%
5	 *43*	36%	N.D.	0%
6	 *48*	22%	N.D.	0%
7	 *44*	30%	87%	80%
8	 *39*	13%	N.D.	75%

[a]Yields determined via ^{1}H NMR analysis using hexamethylbenzene as an external standard

[b]Reaction run with 1 equiv of morpholine

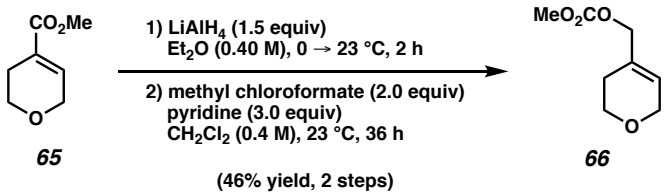
C. Syntheses of Heck Cyclization Substrates

C.1 Syntheses of Carbonate Reductive Coupling Partners



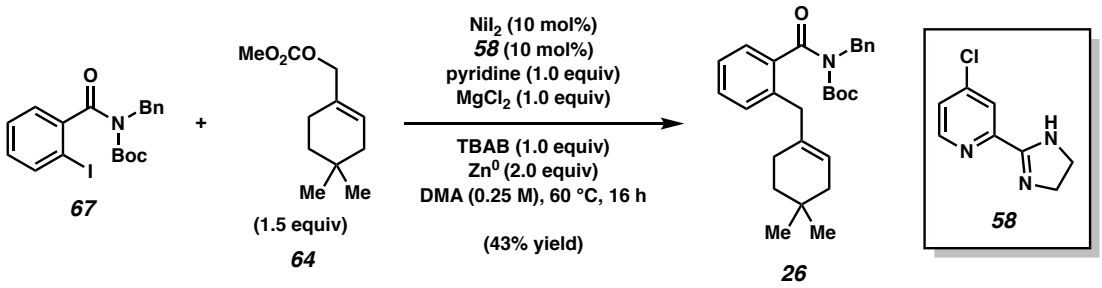
63 (71% yield, 2 steps) *64*

Carbonate 64. To a solution of carboxylic acid **63** (2.5 g, 16.0 mmol, 1.0 equiv) in Et_2O (41 mL, 0.4 M) at 0 °C was added $LiAlH_4$ (12 mL, 2 M in THF, 1.5 equiv) dropwise over 10 min via syringe. After stirring for 2 h, deionized water (20 mL) was added dropwise over 5 min at 0 °C. The resulting heterogeneous mixture was filtered through a plug of Celite, eluting with Et_2O (100 mL), and the filtrate was diluted with deionized water (50 mL). The layers were separated and the aqueous layer was extracted with $E_{t2}O$ (3 x 50 mL). The organic layers were combined, dried over $MgSO_4$, and concentrated under reduced pressure (100 mbar, at 23 °C) to afford the corresponding alcohol, which was used in the subsequent step without further purification. To a solution of the crude alcohol in CH_2Cl_2 (41 mL, 0.4 M) was added pyridine (4.0 mL, 49.0 mmol, 3.0 equiv from **63**). The reaction was cooled to 0 °C. After stirring for 5 min, methyl chloroformate (2.5 mL, 33.0 mmol, 2.0 equiv from **63**) was added dropwise over 1 min. The reaction was allowed to warm to 23 °C. After stirring for 48 h, the reaction mixture was poured into brine (150 mL) and diluted with CH_2Cl_2 (100 mL). The layers were separated and the aqueous layer was extracted with CH_2Cl_2 (3 x 100 mL). The organic layers were combined, washed with 1 N HCl (50 mL), dried over $MgSO_4$, and concentrated under reduced pressure (100 mbar, at 23 °C). The crude mixture was purified via flash chromatography on silica (95:5 hexanes:EtOAc) to afford carbonate **64** (2.3 g, 11.4 mmol, 71% yield, 2 steps) as a colorless oil. **Carbonate 64**: R_f 0.55 (9:1 hexanes:EtOAc); ^{1}H NMR (600 MHz, $CDCl_3$): δ 5.72–5.68 (m, 1H), 4.53–4.51 (m, 2H), 3.78 (s, 3H), 2.07–2.00 (m, 2H), 1.85–1.81 (m, 2H), 1.39 (t, J = 6.4, 2H), 0.90 (s, 6H) ^{13}C NMR (125 MHz, $CDCl_3$): δ 155.9, 131.0, 126.3, 72.2, 54.7, 38.9, 35.1, 28.5, 28.1, 23.6; IR (film): 3018, 2958, 2852, 1750, 1266 cm^{-1}; HRMS-ESI (*m/z*) $[M + H]^+$ calcd for $C_{11}H_{19}O_3^+$, 199.1334; found 199.1345.

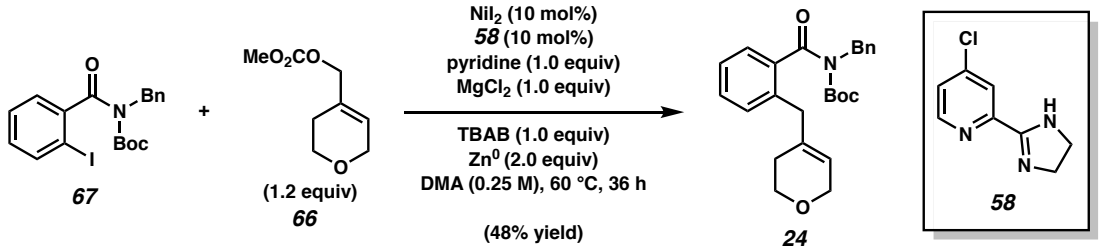


Carbonate 66. To a solution of methyl ester **65** (4.0 g, 28.0 mmol, 1.0 equiv) in Et_2O (70 mL, 0.4 M) at 0 °C was added $LiAlH_4$ (21.1 mL, 2 M in THF, 1.5 equiv) dropwise over 10 min via syringe. After stirring for 2 h, deionized water (40 mL) was added dropwise over 5 min at 0 °C. The resulting heterogeneous mixture was filtered through a plug of Celite eluting with Et_2O (150 mL) and the filtrate was diluted with deionized water (100 mL). The layers were separated and the aqueous layer was extracted with Et_2O (3 x 80 mL). The organic layers were combined, dried over $MgSO_4$, and concentrated under reduced pressure (100 mbar, at 23 °C) to afford the corresponding alcohol, which was used in the subsequent step without further purification. To a solution of the crude alcohol (1.0 equiv) in CH_2Cl_2 (55 mL) was added pyridine (5.3 mL, 65.7 mmol, 3.0 equiv from **65**). The reaction was cooled to 0 °C. After stirring for 5 min, methyl chloroformate (3.4 mL, 43.8 mmol, 2.0 equiv from **65**) was added dropwise over 1 min. The reaction was allowed to warm to 23 °C. After stirring for 36 h, the reaction mixture was poured into brine (150 mL) and diluted with CH_2Cl_2 (100 mL). The layers were separated and the aqueous layer was extracted with CH_2Cl_2 (3 x 100 mL). The organic layers were combined, washed with 1 N HCl (50 mL), dried over $MgSO_4$, and concentrated under reduced pressure (100 mbar, at 23 °C). The crude mixture was purified via flash chromatography on silica (95:5 hexanes:EtOAc) to afford carbonate **66** (1.8 g, 12.9 mmol, 46% yield, 2 steps) as a yellow oil. **Carbonate 66**: R_f 0.17 (9:1 hexanes:EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$): δ 5.83–5.77 (m, 1H), 4.55 (s, 2H), 4.17–4.13 (m, 2H), 3.83–3.80 (m, 2H), 3.79 (s, 3H), 2.17–2.10 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 155.8, 130.4, 125.2, 70.8, 65.1, 64.1, 55.0, 26.0 ; IR (film): 2962, 2826, 2849, 1749, 1268 cm^{-1}; HRMS-ESI (*m/z*) $[M + Na]^+$ calcd for $C_8H_{12}O_4Na^+$, 195.0633; found 195.0644.

C.2 Reductive Cross-Coupling of Imides and Carbonates

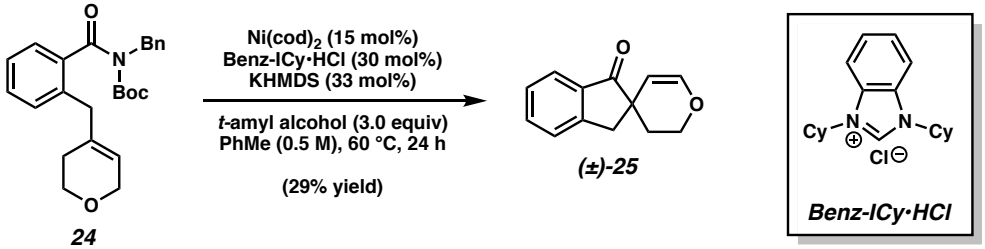


Amide 26. A flame-dried 250 mL round bottom flask equipped with a large 3 cm football-shaped stir bar was brought into a glovebox and charged with amide **67**[6] (3.5 g, 8.00 mmol, 1.0 equiv), ligand **58** (145 mg, 0.80 mmol, 10 mol%), NiI_2 (250 mg, 0.80 mmol, 10 mol%), $MgCl_2$ (726 mg, 8.00 mmol, 1.0 equiv), TBAB (2.58 g, 8.00 mmol, 1.0 equiv) and Zn^0 (1.1 g, 16.0 mmol, 2.0 equiv). The flask was removed from the glovebox, at which point DMA (32.0 mL, 0.25 M), pyridine (647 μL, 8.0 mmol, 1.0 equiv), and carbonate **64** (2.38 g, 12.0 mmol, 1.5 equiv) were added. The flask was quickly sealed with an air condenser and stirred at 60 °C for 16 h. After cooling to 23 °C, the mixture was passed through a plug of silica gel eluting with 5:2 hexanes:EtOAc (150 mL) until TLC indicated the desired product had eluted. The volatiles were removed under reduced pressure and the crude mixture was further purified by flash chromatography on silica (99:1 hexanes:EtOAc) to yield amide **26** (1.5 g, 3.50 mmol, 43% yield) as a colorless oil. **Amide 26**: R_f 0.55 (9:1 hexanes:EtOAc); ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.43 (d, J = 7.3, 2H), 7.35–7.26 (m, 4H), 7.22–7.13 (m, 3H), 5.38–5.34 (m, 1H), 5.01 (s, 2H), 3.31 (s, 2H), 1.85–1.80 (m, 2H), 1.79–1.76 (m, 2H), 1.30 (t, J = 6.4, 2H), 1.11 (s, 9H), 0.87 (s, 6H); ^{13}C NMR (150 MHz, $CDCl_3$, 23 of 24 signals observed): δ 172.4, 152.9, 138.4, 138.0, 137.5, 134.8, 129.7, 129.4, 128.5, 128.4, 127.5, 126.4, 125.7, 123.3, 83.3, 48.1, 40.9, 39.5, 35.8, 28.6, 28.4, 27.5, 26.1; IR (film): 2955, 2867, 1730, 1673, 1231 cm^{-1}; HRMS-ESI (*m/z*) $[M + Na]^+$ calcd for $C_{28}H_{35}NO_3Na^+$, 456.2515; found 456.2519.

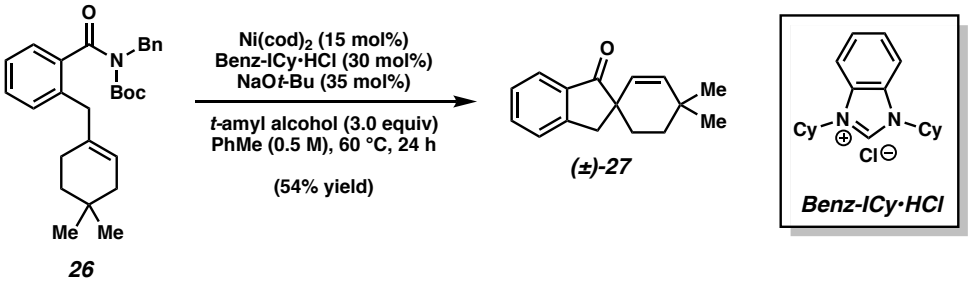


Amide 24. A flame-dried 250 mL round bottom flask equipped with a large 3 cm football-shaped stir bar was brought into a glovebox and charged with amide **67**[6] (3.8 g, 8.70 mmol, 1.0 equiv), ligand **58** (160 mg, 0.87 mmol, 10 mol%), NiI_2 (270 mg, 0.87 mmol, 10 mol%), $MgCl_2$ (83.0 mg, 8.70 mmol, 1.0 equiv), TBAB (2.80 g, 8.7 mmol, 1.0 equiv) and Zn^0 (1.1 g, 17.4 mmol, 2.0 equiv). The flask was removed from the glovebox, at which point DMA (35.0 mL), pyridine (700 μL, 8.7 mmol, 1.0 equiv), and carbonate **66** (1.80 g, 10.0 mmol, 1.2 equiv) were added. The flask was quickly sealed with an air condenser and stirred at 60 °C for 36 h. After cooling to 23 °C, the mixture was passed through a plug of silica gel and eluted with 5:2 hexanes:EtOAc (150 mL) until TLC indicated the desired product had eluted. The volatiles were removed under reduced pressure and the crude mixture was further purified by flash chromatography on silica (99:1 hexanes:EtOAc) to yield amide **24** (1.7 g, 4.2 mmol, 48% yield) as a colorless oil. **Amide 24**: R_f 0.34 (95:5 benzene: MeCN; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.43 (d, J = 7.3, 2H), 7.36–7.30 (m, 3H), 7.28 (overlapped with residual solvent peak, 1H), 7.24–7.13 (m, 3H), 5.39 (br s, 1H), 5.02 (s, 2H), 4.09–4.04 (m, 2H), 3.71 (t, J = 5.5, 2H), 3.37 (s, 2H), 2.00–1.91 (m, 2H), 1.12 (s, 9H), ^{13}C NMR (125 MHz, $CDCl_3$): δ 172.3, 152.9, 138.4, 137.9, 136.4, 134.2, 130.2, 129.5, 128.6, 128.4, 127.6, 126.4, 126.0, 122.6, 83.5, 65.6, 64.5, 48.1, 40.4, 28.4, 27.6; IR (film): 3037, 2983, 2849, 1725, 1140 cm^{-1}; HRMS-ESI (*m/z*) [M + Na]$^+$ calcd for $C_{25}H_{29}NO_4Na^+$, 430.1994; found 430.2018.

D. Syntheses of Racemic Indanones (±)-25 and (±)-27



Indanone (±)-25. A flame-dried 1-dram vial containing amide **24** (35.0 mg, 0.086 mmol, 1.0 equiv) and a magnetic stir bar was sequentially charged with Benz-ICy•HCl (8.2 mg, 0.026 mmol, 30 mol%), $Ni(cod)_2$ (3.5 mg, 0.013 mmol, 15 mol%), and KHMDS (6.0 mg, 0.030 mmol, 35 mol%) in a glovebox. Subsequently, toluene (172 μL, 0.5 M) and then *t*-amyl alcohol (28.2 μL, 0.26 mmol, 3.0 equiv) were added. The vial was sealed with a Teflon-lined screw cap, removed from the glovebox, the gap between the cap and the vial was sealed with electrical tape, and the vial was stirred at 60 °C for 24 h. After cooling to 23 °C, the mixture was diluted with hexanes (1.0 mL) and filtered through a plug of silica gel (10 mL of EtOAc eluent). Purification by preparative thin-layer chromatography (95:5 benzene: MeCN) afforded indanone **(±)-25** (5.0 mg, 0.025 mmol, 29% yield) as a colorless oil. **Indanone (±)-25**: R_f 0.53 (95:5 benzene: MeCN); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.77 (d, *J* = 7.6, 1H), 7.62 (t, *J* = 7.6, 1H), 7.44 (d, *J* = 7.6, 1H), 7.40 (t, *J* = 7.6, 1H), 6.64 (d, *J* = 6.1, 1H), 4.52 (d, *J* = 6.1, 1H), 4.44 (ddd, *J* = 10.9, 7.5, 3.0, 1H), 4.02 (ddd, *J* = 10.9, 7.5, 3.0, 1H), 3.23 (d, *J* = 17.1, 1H), 3.07 (d, *J* = 17.1, 1H), 2.13–2.04 (m, 1H), 1.77 (ddd, *J* = 13.9, 7.4, 3.0, 1H).^{13}C NMR (150 MHz, $CDCl_3$): δ 208.8, 151.8, 146.1, 135.5, 135.3, 127.9, 126.7, 124.8, 102.9, 63.1, 46.5, 43.2, 32.5; IR (film): 2916, 2849, 1712, 1641, 1250 cm^{-1}; HRMS-ESI (*m/z*) $[M + H]^+$ calcd for $C_{13}H_{13}O_2^+$, 201.0916; found 201.0920.

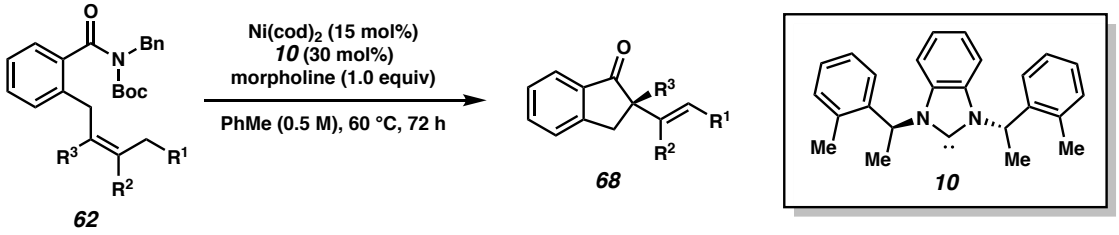


Indanone (±)-27. A flame-dried 1-dram vial containing amide **26** (40.2 mg, 0.093 mmol, 1.0 equiv) and a magnetic stir bar was sequentially charged with Benz-ICy•HCl (8.9 mg, 0.028 mmol,

30 mol%), $Ni(cod)_2$ (3.8 mg, 0.014 mmol, 15 mol%), and NaO*t*-Bu (3.1 mg, 0.033 mmol, 35 mol%) in a glovebox. Subsequently, toluene (185 μL, 0.5 M) and then *t*-amyl alcohol (31 μL, 0.28 mmol, 3.0 equiv) were added. The vial was sealed with a Teflon-lined screw cap, removed from the glovebox, the gap between the cap and the vial was sealed with electrical tape, and the vial was stirred at 60 °C for 24 h. After cooling to 23 °C, the mixture was diluted with hexanes (1.0 mL) and filtered through a plug of silica gel (10 mL of EtOAc eluent). The volatiles were removed under reduced pressure. Purification by preparative thin-layer chromatography (95:5 benzene:MeCN) afforded indanone **(±)-27** (11.3 mg, 0.050 mmol, 54% yield) as a colorless oil. **Indanone (±)-27**: R_f 0.76 (95:5 benzene:MeCN; ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.76 (d, *J* = 7.6, 1H), 7.59 (td, *J* = 7.4, 1.2, 1H), 7.43 (dt, *J* = 7.7, 0.9, 1H), 7.40–7.35 (m, 1H), 5.71 (dd, *J* = 9.9, 1.0, 1H), 5.30 (dd, *J* = 9.9, 1.0, 1H), 3.14–3.05 (m, 2H), 1.98 (ddd, *J* = 13.4, 10.8, 3.1, 1H), 1.81 (dddd, *J* = 13.3, 7.1, 3.2, 0.8, 1H), 1.60–1.53 (m, 1H), 1.52–1.47 (m, 1H), 1.11 (s, 3H), 1.05 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 209.7, 152.6, 140.4, 136.0, 134.9, 127.6, 126.7, 125.9, 124.7, 51.6, 42.2, 34.2, 31.5, 30.3, 30.2, 29.0; IR (film): 2991, 2962, 2852, 1710, 964 cm^{-1}; HRMS-ESI (*m/z*) $[M + H]^+$ calcd for $C_{16}H_{19}O^+$, 227.1436; found 227.1450.

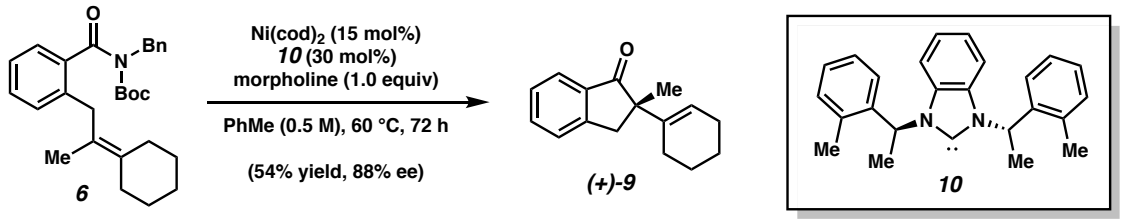
E. Scope of Methodology

General procedure 5 for the enantioselective nickel-catalyzed Mizoroki–Heck reaction

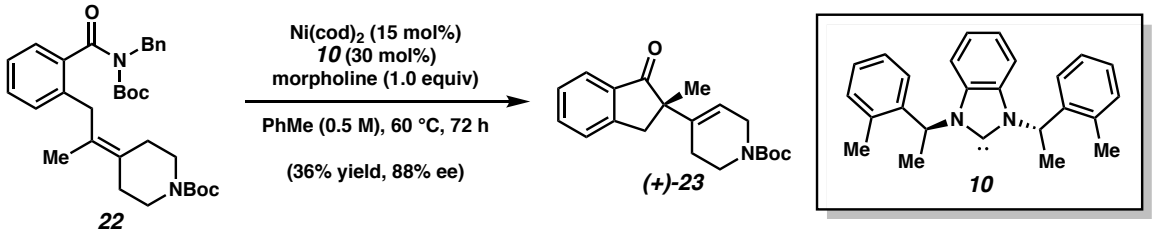


A flame-dried 1-dram vial containing a stir bar was brought into a glovebox and charged sequentially with amide **62** (0.1 mmol, 1.0 equiv), $Ni(cod)_2$ (4.1 mg, 0.015 mmol, 15 mol%), and a solution of **10** (0.1 mg/μL in PhMe, 106 μL, 10.6 mg, 0.030 mmol, 30 mol%) in toluene (95 μL, 0.5 M total accounting for the volume of the carbene solution). The mixture was then prestirred for 15 minutes in the glovebox at 23 °C. Then, morpholine (8.6 μL, 0.1 mmol, 1.0 equiv) was added to the vial using a micropipette. The vial was then sealed with a Teflon-lined screw cap, removed from the glovebox, the gap between the cap and the vial was sealed with electrical tape, and the vial was stirred at 60 °C for 72 h. After cooling to 23 °C, the mixture was filtered through

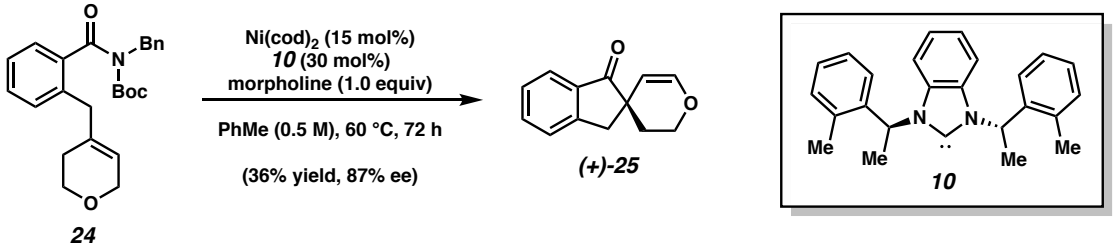
a plug of silica, eluting with EtOAc (10 mL). The eluate was concentrated under reduced pressure, then purified by flash chromatography on silica to provide products **68**.



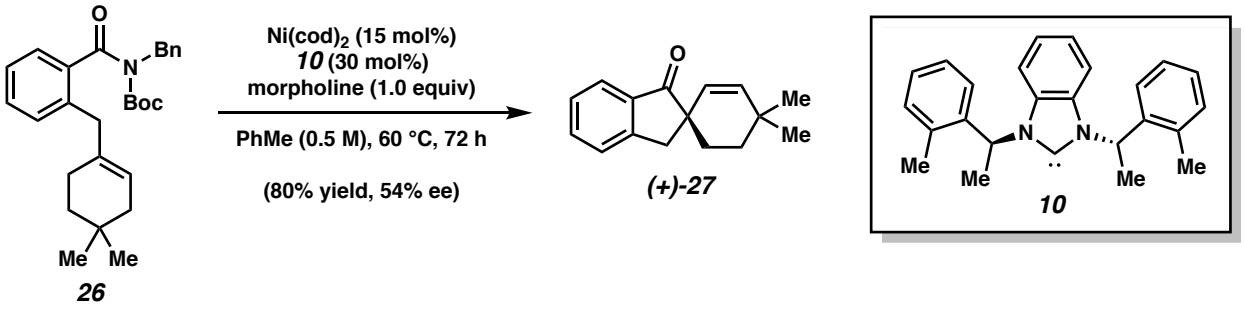
Indanone (+)-9. Followed General Procedure 5. Purification by preparative thin layer silica chromatography (95:5 benzene:MeCN) afforded indanone product **(+)-9** (54% yield, 88% ee, average of two experiments) as a colorless oil. Spectral data match those previously reported.[6] $[\alpha]^{27.9}_{D}$ +80° (*c* = 1.00, CH_2Cl_2).



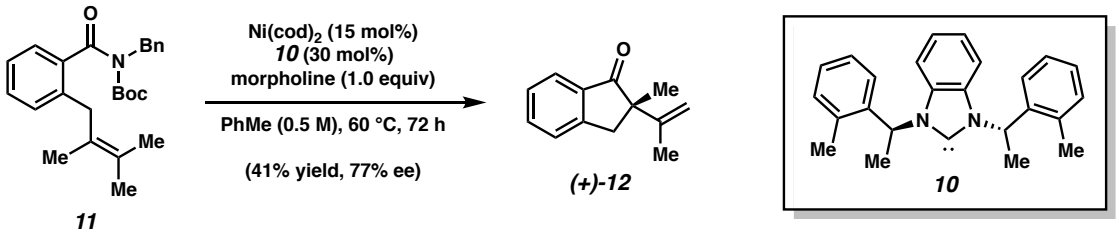
Indanone (+)-23. Followed General Procedure 5. Purification by preparative thin layer silica chromatography (2:1 hexanes:EtOAc) afforded indanone product **(+)-23** (36% yield, 88% ee, average of two experiments) as a colorless oil. Spectral data match those previously reported.[6] $[\alpha]^{24.0}_{D}$ +14° (*c* = 1.00, CH_2Cl_2).



Indanone (+)-25. Followed General Procedure 5. Purification by preparative thin layer silica chromatography (95:5 benzene:CH_3CN) afforded indanone product **(+)-25** (36% yield, 87% ee, average of two experiments) as a colorless oil. Spectral data match those previously reported in Section D. $[\alpha]^{26.4}_{D}$ +196° (*c* = 1.00, CH_2Cl_2).

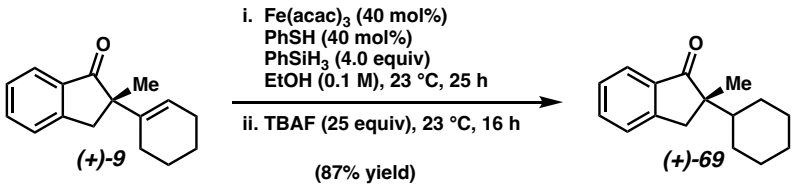


Indanone (+)-27. Followed General Procedure 5. Purification by preparative thin layer silica chromatography (95:5 benzene:MeCN) afforded indanone product **(+)-27** (80% yield, 54% ee, average of two experiments) as a colorless oil. Spectral data match those previously reported in Section D. $[\alpha]^{27.1}_{D}$ +82° (*c* = 1.00, CH_2Cl_2).



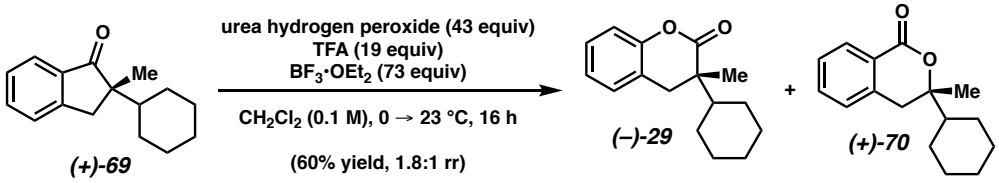
Indanone (+)-12. Followed General Procedure 5. Purification by preparative thin layer silica chromatography (3:1 hexanes:EtOAc) afforded indanone product **(+)-12** (41% yield, 77% ee, average of two experiments) as a colorless oil. Spectral data match those previously reported.[6] $[\alpha]^{23.6}_{D}$ +18° (*c* = 1.00, CH_2Cl_2).

F. Synthetic Elaboration of Mizoroki–Heck Cyclization Product (+)-9



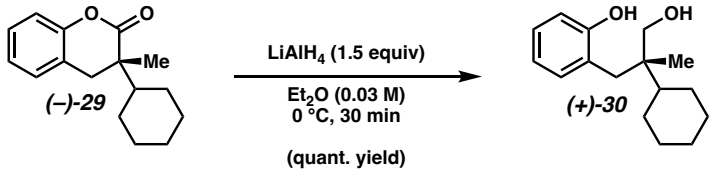
Indanone (+)-69. A flame-dried 1-dram vial containing a magnetic stir bar was charged with indanone **(+)-9** (30.0 mg, 0.12 mmol, 1.0 equiv) and $Fe(acac)_3$ (17.0 mg, 48 μmol, 40 mol%). The vial was then secured with a septum cap and purged with an inlet needle using N_2 and an outlet needle open to air for 5 min. Then, ethanol (1.2 mL, 0.1 M) was added to the vial and the mixture was stirred for 2 min until homogenous. Subsequently, phenylsilane (59 μL, 0.48 mmol, 4.00 equiv), and thiophenol (0.50 M in *n*-propanol, 95 μL, 48 μmol, 40 mol%) were added sequentially.

The reaction was allowed to stir at 23 °C under nitrogen for 25 h. After 25 h, TBAF (1.0 M in THF, 0.86 mL, 3.0 mmol, 25 equiv) was added to the reaction to eliminate excess phenylsilane and stirred at 23 °C under nitrogen for 16 h. After this time, the crude material was concentrated under reduced pressure. Purification by preparative thin layer silica chromatography (95:5 benzene:MeCN) afforded product **(+)-69** (22.9 mg, 0.10 mmol, 87% yield) as a colorless oil. **Indanone (+)-69**: R_f 0.33 (benzene); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.73 (d, J = 7.7, 1H), 7.57 (t, J = 7.4, 1H), 7.43 (d, J = 7.4, 1H), 7.35 (t, J = 7.4, 1H), 3.21 (d, J = 17.4, 1H), 2.69 (d, J = 17.4, 1H), 1.91–1.84 (m, 1H), 1.82–1.76 (m, 1H), 1.72 (tt, J = 12.1, 3.2, 1H), 1.67–1.55 (m, 2H), 1.39–1.33 (m, 1H), 1.31–1.17 (m, 5H), 1.09 (tt, J = 12.8, 3.1, 1H), 0.98 (qd, J = 12.6, 3.6, 1H), 0.86 (qd, J = 12.6, 3.6, 1H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 212.5, 153.5, 136.8, 134.8, 127.4, 126.5, 124.0, 52.6, 44.5, 37.6, 28.1, 27.6, 26.8, 26.6, 26.4, 23.0; IR (film): 2960, 2927, 2880, 2852, 1710 cm^{-1}; HRMS-ESI (*m/z*) $[M + H]^+$ calcd for $C_{16}H_{21}O^+$, 229.1587; found 229.1598. $[\alpha]^{26.6}_D$ –60° (*c* = 1.00, CH_2Cl_2).



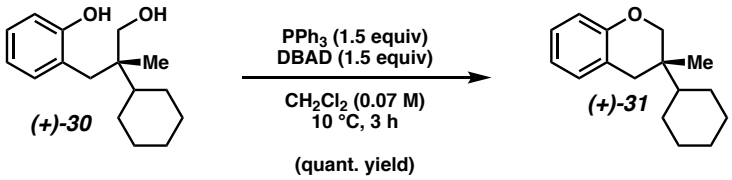
Lactones (–)-29 and **(+)-70.** To a solution of indanone **(+)-69** (17.0 mg, 75 μmol, 1 equiv) and urea hydrogen peroxide (298 mg, 3.16 mmol, 43 equiv) in CH_2Cl_2 (1.1 mL, 0.1 M) at –0 ºC was added TFA (109 μL, 1.41 mmol, 19 equiv). After stirring for 10 min, BF_3•OEt_2 (671 μL, 5.44 mmol, 73 equiv) was added dropwise via syringe. The reaction was allowed to warm to 23 °C over 16 h. After stirring for 16 h, the reaction mixture was poured into deionized water (50 mL) and diluted with CH_2Cl_2 (50 mL). The layers were separated and the aqueous layer was extracted with CH_2Cl_2 (3 x 10 mL). The organic layers were combined, washed with saturated aqueous $NaHCO_3$ (50 mL), dried over $MgSO_4$, and concentrated under reduced pressure (100 mbar, at 23 °C). Purification by preparative thin layer chromatography (95:5 benzene:MeCN) afforded lactone **(–)-29** and lactone **(+)-70**, each as a colorless oil (11.0 mg, 45 μmol, 60% combined yield, 1.8:1 rr determined by ^{1}H NMR analysis of the crude reaction mixture). **(–)-29**: R_f 0.66 (benzene); ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.26–7.22 (overlapped with residual solvent peak, 1H), 7.13 (d, J = 7.3, 1H), 7.07 (t, J = 7.3, 1H), 7.00 (d, J = 8.2, 1H), 2.99 (d, J = 16.1, 1H), 2.78 (d, J = 16.1, 1H),

1.80–1.70 (m, 2H), 1.69–1.64 (m, 1H), 1.63–1.59 (m, 2H), 1.57–1.50 (m, 1H), 1.22 (s, 3H), 1.17–0.96 (m, 5H); ^{13}C NMR (125 MHz, $CDCl_3$, 15 of 16 signals observed): δ 173.0, 151.8, 128.4, 128.2, 124.4, 122.0, 116.0, 44.1, 40.3, 33.9, 27.8, 26.7, 26.6, 26.4, 19.6; IR (film): 2929, 2880, 2853, 1762, 1458 cm^{-1}; HRMS-ESI (*m/z*) $[M + H]^+$ calcd for $C_{16}H_{21}O_2^+$, 245.1542; found 245.1553. $[\alpha]^{27.5}_D$ –10° (*c* = 1.00, CH_2Cl_2). **(+)-70**: R_f 0.38 (benzene); ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.10–8.07 (m, 1H), 7.52 (td, *J* = 7.6, 1.2, 1H), 7.37 (t, *J* = 7.6, 1H), 7.21 (d, *J* = 7.6 1H), 3.18 (d, *J* = 16.4, 1H), 2.83 (d, *J* = 16.4, 1H), 2.04–1.97 (m, 1H), 1.88–1.77 (m, 3H), 1.71–1.64 (m, 2H), 1.30 (s, 3H), 1.25–1.02 (m, 5H); ^{13}C NMR (125 MHz, $CDCl_3$): 165.3, 138.3, 133.9, 130.1, 128.3, 127.5, 125.3, 85.6, 53.6, 47.1, 35.8, 27.7, 27.0, 26.6, 26.5, 21.9 δ; IR (film): 2928, 2882, 2854, 1715, 1460 cm^{-1}; HRMS-ESI (*m/z*) $[M + H]^+$ calcd for $C_{16}H_{21}O_2^+$, 245.1542; found 245.1553. $[\alpha]^{25.5}_D$ +8° (*c* = 1.00, CH_2Cl_2).

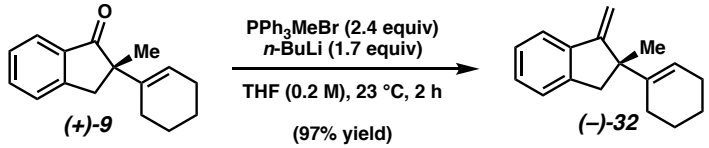


Diol (+)-30. To a solution of lactone **(–)-29** (2.6 mg, 11 μmol, 1.0 equiv) in Et_2O (0.5 mL, 0.03 M) at 0 °C was added $LiAlH_4$ (8 μL, 2 M in THF, 16 μmol, 1.5 equiv). After stirring for 30 min, deionized water (5 mL) was added dropwise over 5 min at 0 °C. The resulting heterogeneous mixture was filtered through a plug of Celite eluting with Et_2O (10 mL) and the filtrate was diluted with deionized water (10 mL). The layers were separated and the aqueous layer was extracted with Et_2O (3 x 10 mL). The organic layers were combined, dried over $MgSO_4$, and concentrated under reduced pressure (100 mbar, at 23 °C) to afford the corresponding diol **(+)-30**. Purification by preparative thin layer silica chromatography (95:5 benzene:MeCN) afforded diol **(+)-30** (2.6 mg, 11 μmol, quant. yield) as a colorless oil. **(+)-30**: R_f 0.32 (95:5 benzene:MeCN); ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.16–7.09 (m, 1H), 7.03–6.97 (m, 1H), 6.88 (d, *J* = 7.8, 1H), 6.85–6.79 (m, 1H), 3.45 (d, *J* = 10.9, 1H), 3.16 (d, *J* = 10.9, 1H), 2.77 (d, *J* = 14.2, 1H), 2.59 (d, *J* = 14.2, 1H), 1.99–1.92 (m, 1H), 1.89–1.82 (m, 1H), 1.81–1.75 (m, 1H), 1.74–1.62 (m, 3H), 1.51–1.43 (m, 2H), 1.23–1.02 (m, 5H), 0.75 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 156.1, 133.0, 127.9, 124.6, 120.0, 117.0, 66.3, 42.3, 41.2, 35.2, 29.9, 27.5, 27.23, 27.16, 26.8, 17.1; IR (film): 3208, 3000, 2925,

2882, 2853 cm^{-1}; HRMS-ESI (*m/z*) $[M + H]^+$ calcd for $C_{16}H_{25}O_2^+$, 249.1855; found 249.1869. $[\alpha]^{24.3}_D$ +50° (*c* = 1.00, CH_2Cl_2).

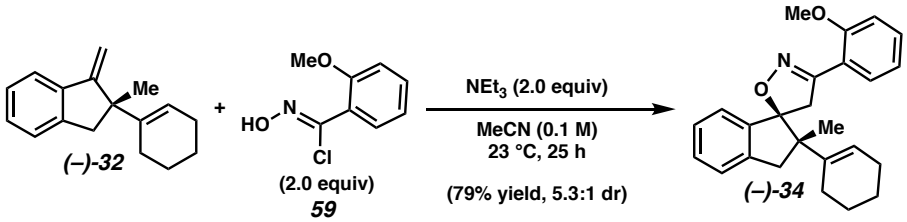


Chromane (+)-31. To a flame-dried 1-dram vial containing a stir bar was added diol **(+)-30** (2.0 mg, 8.1 μmol, 1 equiv), PPh_3 (3.2 mg, 12 μmol, 1.5 equiv), and DBAD (2.8 mg, 12 μmol, 1.5 equiv). The vial was then secured with a septum cap and purged with an inlet needle using N_2 and an outlet needle open to air for 5 min. Then, CH_2Cl_2 (120 μL, 0.07 M) was added and the vial was sealed with a Teflon-lined cap and cooled to 10 °C. The solution was allowed to stir at 10 °C for 3 h. After this time, the mixture was eluted through a pad of silica using CH_2Cl_2 (10 mL), and the eluate was concentrated under reduced pressure. Purification by flash chromatography on silica (benzene) afforded chromane **(+)-31** (1.9 mg, 8.2 μmol, quant. yield) as a volatile, colorless oil. **Chromane (+)-31**: R_f 0.61 (100% benzene); ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.08 (t, *J* = 7.0, 1H), 7.01 (d, *J* = 7.0, 1H), 6.84 (t, *J* = 7.0, 1H), 6.82–6.76 (m, 1H), 3.85 (s, 2H), 2.71 (d, *J* = 15.9, 1H), 2.45 (d, *J* = 15.9, 1H), 1.83–1.72 (m, 4H), 1.70–1.63 (m, 1H), 1.28–1.03 (m, 6H), 0.89 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 154.2, 130.4, 127.1, 121.9, 120.5, 116.3, 73.7, 43.3, 36.4, 33.7, 27.1, 27.03, 26.96, 26.8, 26.6, 18.0; IR (film): 2968, 2926, 2879, 2853, 1230 cm^{-1}; HRMS-ESI (*m/z*) $[M + Na]^+$ calcd for $C_{16}H_{22}ONa^+$, 253.1568; found 253.1664. $[\alpha]^{24.0}_D$ +200° (*c* = 1.00, CH_2Cl_2).



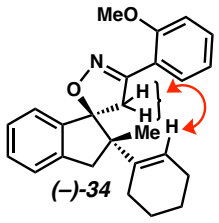
Olefin (–)-32. To a flame-dried 2-dram vial containing a stir bar was added PPh_3MeBr (200 mg, 0.56 mmol, 2.4 equiv). The vial was then secured with a septum cap and purged with an inlet needle using N_2 and an outlet needle open to air for 5 min. Then, THF (610 μL, 0.2 M) was added, followed by the dropwise addition of *n*-BuLi (2.4 M in hexanes, 152 μL, 1.7 equiv) over 1 min at 23 °C, resulting in an orange heterogeneous solution. The solution was allowed to stir at 23 °C for 1 h. Subsequently, indanone **(+)-9** (55.6 mg, 0.22 mmol, 1.0 equiv) was dissolved in THF (500 μL) in a separate flame-dried 1-dram vial and was transferred via syringe to the reaction vial and

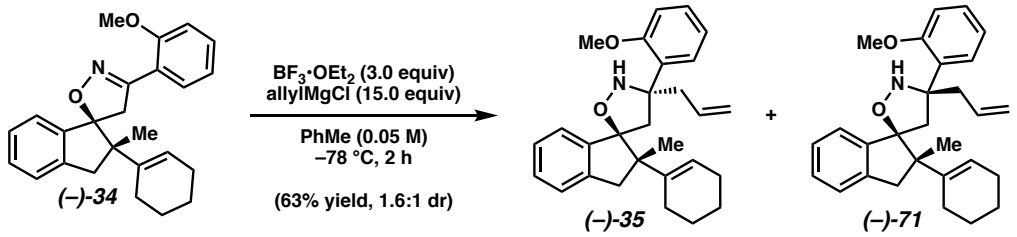
added dropwise over 1 minute. The reaction was allowed to stir at 23 °C for 1 h. After this time, the mixture was eluted through a pad of silica using CH_2Cl_2 (10 mL), and the eluate was concentrated under reduced pressure. Purification by flash chromatography on silica (pentanes) afforded olefin **(–)-32** (48.3 mg, 0.22 mmol, 97% yield) as a volatile, colorless oil. **Olefin (–)-32**: R_f 0.45 (9:1 hexanes:EtOAc); ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.49 (d, *J* = 7.0, 1H), 7.25–7.17 (m, 3H), 5.72–5.65 (m, 1H), 5.50 (s, 1H), 4.81 (s, 1H), 3.16 (d, *J* = 16.8, 1H), 2.69 (d, *J* = 16.8, 1H), 2.14–2.04 (m, 2H), 1.88–1.76 (m, 2H), 1.64–1.55 (m, 2H), 1.54–1.46 (m, 2H), 1.29 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 158.1, 144.3, 142.3, 140.7, 128.6, 126.6, 125.4, 121.1, 120.2, 102.9, 51.4, 44.6, 27.3, 25.70, 25.66, 23.4, 22.8; IR (film): 3075, 2959, 2925, 2854, 1636 cm^{-1}; GCMS-EI (*m/z*) $[M]^+$ calcd for $C_{17}H_{20}^+$, 224.1565; found 224.1559. $[\alpha]^{23.9}_D$ –36° (*c* = 1.00, CH_2Cl_2).



(–)-34. To a flame-dried 1-dram vial was added sequentially olefin **(–)-32** (21.8 mg, 0.092 mmol, 1.0 equiv), **59** (34.3 mg, 0.19 mmol, 2.0 equiv), MeCN (920 μL, 0.1 M), and NEt_3 (25.7 μL, 0.19 mmol, 2.0 equiv). The vial was sealed with a Teflon-lined cap and stirred at 23 °C for 25 h. After this time, the reaction was eluted through a pad of silica with EtOAc (10 mL), and the eluate was concentrated under reduced pressure. Purification by preparative thin layer silica chromatography (4:1 hexanes:EtOAc) afforded **(–)-34** (30.4 mg, 0.081 mmol, 79% yield, 5.3:1 dr determined by ^{1}H NMR analysis of the crude reaction mixture) as an off-white foam. **(–)-34**: R_f 0.65 (3:1 hexanes:EtOAc); ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.77–7.71 (m, 1H), 7.39–7.34 (m, 1H), 7.32–7.29 (m, 1H), 7.25–7.18 (m, 3H), 6.99 (td, *J* = 7.5, 0.9, 1H), 6.92 (d, *J* = 8.3, 1H), 5.75–5.66 (m, 1H), 3.81 (s, 3H), 3.75 (d, *J* = 18.2, 1H), 3.22–3.12 (m, 2H), 2.69 (d, *J* = 15.2, 1H), 2.16–2.01 (m, 3H), 1.99–1.90 (m, 1H), 1.68–1.42 (m, 4H), 1.27 (s, 3H); ^{13}C NMR (150 MHz, CDCl3, 24 of 25 signals observed): δ 157.7, 156.3, 146.9, 141.9, 139.7, 131.2, 129.6, 128.2, 127.1, 124.9, 122.9, 122.4, 120.9, 119.4, 111.5, 98.0, 56.7, 55.6, 46.1, 42.1, 25.9, 23.4, 22.6, 21.9; IR (film): 3042, 2922, 2854, 1600, 1253 cm^{-1}; HRMS-ESI (*m/z*) $[M + H]^+$ calcd for $C_{25}H_{28}NO_2^+$, 374.2120; found 374.2134. $[\alpha]^{22.2}_D$ –50° (*c* = 1.00, CH_2Cl_2).

The structure of **(–)-34** was verified by 2D-NOESY, as the following interactions were observed:

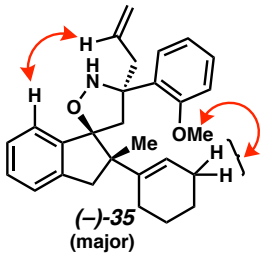


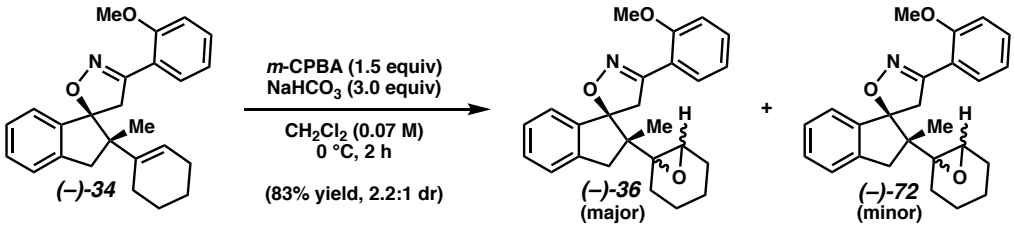


(–)-34 and **(–)-71.** A flame-dried 1-dram vial was charged with **(–)-34** (28.5 mg, 0.068 mmol, 1.0 equiv) and toluene (1.0 mL) and cooled to –78 °C. BF_3OEt_2 (26.0 µL, 0.21 mmol, 3.0 equiv) was then added and the reaction was allowed to stir at –78 °C for 1 h. Subsequently, a solution of allylMgCl (2.0 M in THF, 512 µL, 15.0 equiv) in toluene (0.95 mL) was prepared and added slowly dropwise over 15 min to the reaction vial. The resulting solution was allowed to stir for 1 h and after this time, the reaction was quenched at –78 °C with saturated aqueous $NaHCO_3$ (2 mL) and slowly allowed to warm to 23 °C. The mixture was then diluted with Et_2O (2 mL) and deionized water (2 mL). The organic and aqueous layers were separated, and the aqueous layer was extracted with Et_2O (2 x 2 mL). The combined organic layers were dried with Na_2SO_4, filtered, and concentrated under reduced pressure. Purification by preparative thin layer silica chromatography (4:1 hexanes:EtOAc) afforded major diastereomer **(–)-35** and minor diastereomer **(–)-71**, each as colorless oils (19.4 mg, 0.044 mmol, 63% combined yield, 1.6:1 dr determined by ^{1}H NMR analysis of the crude reaction mixture). **(–)-35** (major): R_f 0.55 (5:1 hexanes:EtOAc); ^{1}H NMR (600 MHz, $(CD_3)_2SO$): δ 7.65–7.54 (m, 2H), 7.29–7.20 (m, 3H), 7.20–7.15 (m, 1H), 7.04–6.99 (m, 1H), 6.90 (td, J = 7.5, 0.9, 1H), 6.18 (br s, 1H), 5.55 (ddt, J = 16.9, 10.1, 7.5, 1H), 5.24–5.14 (m, 1H), 4.95–4.83 (m, 2H), 3.79 (s, 3H), 3.00–2.90 (m, 2H), 2.84 (d, J = 15.5, 1H), 2.70 (dd, J = 14.2, 6.8, 1H), 2.63 (d, J = 15.5, 1H), 2.46 (d, J = 14.0, 1H), 1.85–1.69 (m, 2H), 1.47–1.37 (m, 1H), 1.34–1.13 (m, 4H), 1.07–0.95 (m, 1H), 0.72 (s, 3H); ^{13}C NMR (150 MHz, $(CD_3)_2SO$): δ 156.5, 147.7, 142.3, 142.0, 134.8, 132.2, 128.00, 127.95, 127.8, 126.6, 124.2, 122.3, 120.6, 119.8,

117.4, 111.7, 97.7, 69.0, 55.3, 53.8, 47.9, 43.5, 40.6, 26.0, 25.0, 22.5, 21.6, 20.0; IR (film): 3359, 3071, 2928, 1601, 1235 cm^{-1}; HRMS-ESI (*/z*) $[M + H]^+$ calcd for $C_{28}H_{34}NO_2^+$, 416.2589; found 416.2595. $[\alpha]^{21.9}_D$ –62° (*c* = 1.00, CH_2Cl_2). **(–)-71** (minor): R_f 0.65 (3:1 hexanes:EtOAc); ^1H NMR (500 MHz, $(CD_3)_2SO$): δ 7.65–7.48 (m, 1H), 7.34–7.25 (m, 1H), 7.13–6.99 (m, 3H), 6.96–6.85 (m, 1H), 6.84–6.64 (m, 1H), 6.16–5.71 (m, 2H), 5.71–5.60 (m, 1H), 5.59–5.46 (m, 1H), 4.98–4.83 (m, 2H), 3.86–3.79 (m, 3H), 2.97–2.86 (m, 1H), 2.85–2.68 (m, 3H), 2.61–2.57 (m, 1H), 2.56–2.52 (overlapped with residual solvent peak, 1H), 2.12–1.97 (m, 2H), 1.58–1.21 (m, 9H); ^{13}C NMR (125 MHz, $(CD_3)_2SO$, 27 of 28 peaks observed): δ 156.6, 146.0, 142.8, 141.4, 134.4, 131.0, 128.3, 128.2, 128.0, 126.1, 123.8, 122.6, 121.4, 120.1, 117.6, 111.8, 97.4, 69.0, 55.5, 54.9, 47.0, 43.5, 26.3, 25.2, 22.9, 21.7, 19.5; IR (film): 3075, 2928, 1600, 1436, 1236 cm^{-1}; HRMS-APCI (*m/z*) $[M + H]^+$ calcd for $C_{28}H_{34}NO_2^+$, 416.2589; found 416.2585. $[\alpha]^{25.2}_D$ –42° (*c* = 1.00, CH_2Cl_2).

The structure of **(–)-35** was verified by 2D-NOESY, as the following interactions were observed:

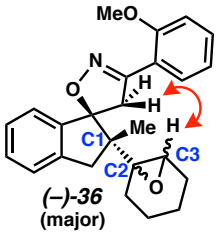




(–)-36 and **(–)-72.** A 1-dram vial containing a stir bar was charged with **(–)-34** (13.3 mg, 0.033 mmol, 1.0 equiv) and CH_2Cl_2 (490 µL, 0.07 M), and the solution was cooled to 0 °C. Then, $NaHCO_3$ (8.3 mg, 0.098 mmol, 3.0 equiv), and *m*-CPBA (77 wt% purity, 11.0 mg, 0.049 mmol, 1.5 equiv) were added sequentially as solids in singular portions and the reaction was stirred for 2 h at 0 °C. After this time, the reaction was quenched with EtOAc (2 mL) and diluted with saturated aqueous $NaHCO_3$ (2 mL). The organic and aqueous layers were separated, and the aqueous layer was extracted with EtOAc (2 x 2 mL). The combined organic layers were dried with Na_2SO_4, filtered, and concentrated under reduced pressure. Purification by preparative thin layer silica

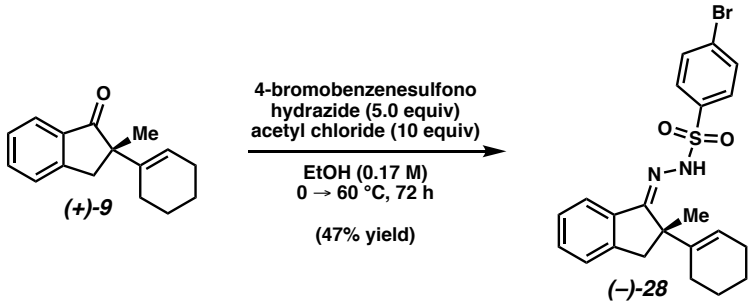
chromatography (4:1 hexanes: EtOAc) afforded unassigned diastereomers **(–)-36** and **(–)-72**, each as beige foams (11.3 mg, 0.027 mmol, 83% combined yield, 2.2:1 dr determined by ^{1}H NMR analysis of the crude reaction mixture). **(–)-36** (major): R_f 0.50 (3:1 hexanes: EtOAc); ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.82 (dd, *J* = 7.6, 1.7, 1H), 7.39 (ddd, *J* = 8.3, 7.6, 1.7, 1H), 7.32–7.28 (m, 1H), 7.25–7.19 (m, 2H), 7.18–7.14 (m, 1H), 7.01 (td, *J* = 7.6, 0.9, 1H), 6.94 (d, *J* = 8.3, 1H), 3.98 (d, *J* = 18.2, 1H), 3.83 (s, 3H), 3.51–3.46 (m, 1H), 3.28 (d, *J* = 18.2, 1H), 2.82 (d, *J* = 15.9, 1H), 2.55 (d, *J* = 15.9, 1H), 2.16–2.08 (m, 1H), 1.98 (dt, *J* = 15.6, 5.5, 1H), 1.85 (ddd, 15.6, 9.9, 5.4, 1H), 1.76 (dddd, *J* = 15.2, 8.7, 5.9, 3.0, 1H), 1.48–1.40 (m, 1H), 1.40–1.33 (m, 1H), 1.31 (s, 3H), 1.25–1.17 (m, 1H), 1.04 (dtdd, *J* = 13.7, 9.9, 5.4, 3.0, 1H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 157.6, 155.7, 146.2, 138.9, 131.5, 129.5, 128.6, 127.5, 125.1, 122.9, 121.1, 119.1, 111.6, 97.4, 62.8, 57.1, 55.6, 54.7, 46.0, 39.3, 26.2, 25.7, 21.0, 19.1, 18.9; IR (film): 2994, 2936, 2861, 1600, 1251 cm^{-1}; HRMS-ESI (*m/z*) $[M + H]^+$ calcd for $C_{25}H_{28}NO_3^+$, 390.2069; found 390.2071. $[\alpha]^{23.5}_D$ –72° (*c* = 1.00, CH_2Cl_2). **(–)-72** (minor): R_f 0.55 (3:1 hexanes: EtOAc); ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.81–7.75 (m, 1H), 7.40–7.33 (m, 1H), 7.31–7.26 (m, 1H), 7.24–7.18 (m, 2H), 7.18–7.12 (m, 1H), 6.99 (t, *J* = 7.4, 1H), 6.92 (d, *J* = 8.3, 1H), 4.29 (d, *J* = 18.8, 1H), 3.82 (s, 3H), 3.27 (d, *J* = 18.8, 1H), 3.09 (d, *J* = 15.1, 1H), 2.99–2.92 (m, 1H), 2.37–2.28 (m, 2H), 2.05 (dt, *J* = 15.5, 5.2, 1H), 1.86–1.76 (m, 1H), 1.65 (ddd, *J* = 15.5, 9.9, 5.2, 1H), 1.52–1.44 (m, 1H), 1.39–1.29 (m, 2H), 1.27 (s, 3H), 1.20–1.09 (m, 1H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 157.9, 156.2, 147.0. 138.1, 131.3, 129.6, 128.3, 127.4, 125.2, 122.7, 120.9, 119.2, 111.5, 97.1, 63.0, 55.6, 55.5, 54.2, 46.5, 38.0, 25.3, 25.1, 21.34, 21.26, 19.3; IR (film): 3029, 2934, 2854, 1600, 1253 cm^{-1}; HRMS-ESI (*m/z*) $[M + H]^+$ calcd for $C_{25}H_{28}NO_3^+$, 390.2069; found 390.2075. $[\alpha]^{22.4}_D$ –94° (*c* = 1.00, CH_2Cl_2).

The structure of **(–)-36** was analyzed by 2D-NOESY, and the following interaction was observed:



Attempts to assign the stereocenters at C2 and C3 were unsuccessful due to the free rotation about the C–C bond between C1 and C2, which resulted in observation of NOESY correlations with the H at C3 in both diastereomers. Efforts at obtaining an X-Ray crystal structure were unsuccessful, therefore, the stereocenters at C2 and C3 remain unassigned. Nonetheless, the ability to access isomers **(–)-36** and **(–)-72** in enantioenriched form demonstrates that complex structures bearing multiple stereocenters are readily accessible from Mizoroki–Heck cyclization products.

G. Assignment of Absolute Stereochemical Configuration of Indanone (+)-9



Brosyl hydrazone (–)-28. A flame-dried 1-dram vial containing a stir bar was charged with (+)-**9** (29.5 mg, 0.13 mmol, 1.0 equiv) followed by 4-bromobenzene-1-sulfonohydrazide (164 mg, 0.65 mmol, 5.0 equiv). Then, ethanol (1.86 mL, 0.07 M) was added and the vial was cooled to 0 °C. Lastly, acetyl chloride (91.1 µL, 1.30 mmol, 10.0 equiv) was added slowly over 1 minute. The vial was sealed with a Teflon-lined screw cap and then heated to 60 °C and allowed to stir for 72 h. The reaction was allowed to cool to 23 °C and then EtOAc (1.0 mL) was added. The solution was filtered through filter paper using a Buchner funnel and washed with EtOAc (1.0 mL). The solid was discarded and the filtrate was concentrated under reduced pressure. Purification by preparative thin layer silica chromatography (benzene) afforded product **(–)-28** (28.3 mg, 0.062 mmol, 47% yield) as a white solid.

Crystals suitable for X-ray diffraction studies were obtained by recrystallization from hot ethanol with the following procedure: **(–)-28** (28.3 mg) was added to a scintillation vial along with ethanol (1.2 mL, filtered through a 0.22 µm filter prior to use). The scintillation vial was heated to 75 °C for 5 min until the solid dissolved. The vial was allowed to cool slowly to 23 °C overnight with a septum cap pierced with a vent needle open to air. After 16 h, clear crystals were found on the bottom of the vial. The crystals of **(–)-28** that were evaluated by X-ray had the same sign by optical rotation ($[\alpha]^{26.1}_{D}$–294.0° (c = 1.00, CH_2Cl_2)) as the enantioenriched mixture observed after chromatography (i.e., $[\alpha]^{22.5}_{D}$–276.0°). **Brosyl hydrazone (–)-28**: Mp: 178–182 °C; R_f 0.65 (8:2 hexanes:EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.55 (s, 1H), 7.88–7.81 (m, 2H), 7.70–7.60 (m, 3H), 7.34 (td, *J* = 7.4, 1.3, 1H), 7.30–7.23 (overlapped with residual solvent peak, 1H), 7.22–7.16 (m, 1H), 5.91–5.82 (m, 1H), 3.09 (d, *J* = 17.3, 1H), 2.77 (d, *J* = 17.3, 1H), 2.22–1.95 (m, 2H), 1.83–1.68 (m, 1H), 1.66–1.15 (m, 8H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 163.0, 146.0, 139.2, 137.5, 137.0, 132.2, 131.2, 129.6, 128.3, 127.5, 125.5, 124.6, 122.5, 51.0, 45.8, 25.6, 25.0, 22.8, 22.2, 20.4; IR (film): 3206, 2928, 2858, 1574, 1355 cm^{-1}; HRMS-ESI (*m/z*) $[M + H]^+$ calcd for $C_{22}H_{24}BrN_2O_2S^+$, 459.0742; found 459.0759; $[\alpha]^{22.5}_{D}$–276.0° (c = 1.00, CH_2Cl_2).

Crystal Structure Analysis for (–)-28

Diffraction intensities were collected at 100 K on a Bruker Smart ApexII CCD diffractometer with CuKα radiation, 1.54178 Å. Absorption corrections were applied by SADABS.[8] All calculations were performed by the SHELXL-2014 packages.[9] Deposition Number 2271421 contains the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service www.ccdc.cam.ac.uk/structures.

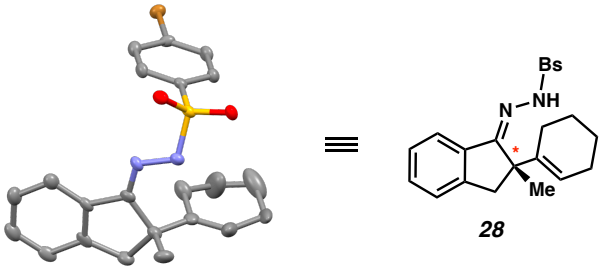


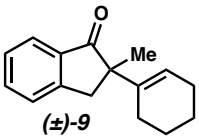
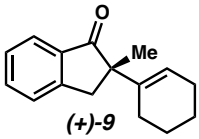
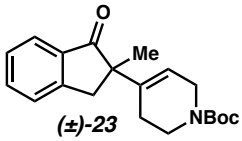
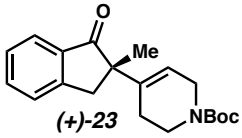
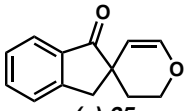
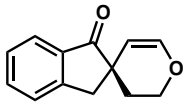
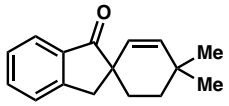
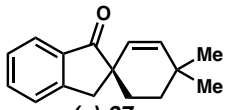
Figure S2: ORTEP representation of X-ray crystallographic structure of (–)-**28** (CCDC Registry #2271421).

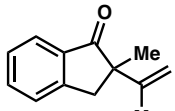
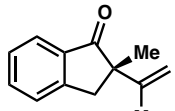
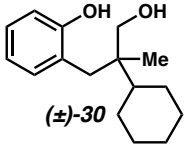
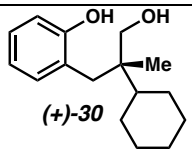
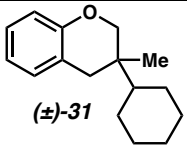
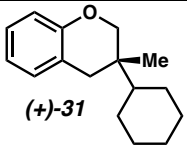
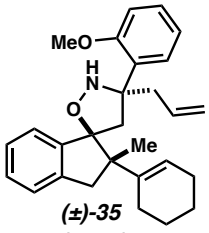
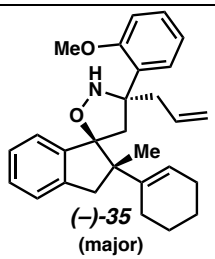
Table S10. Crystal data and structure refinement for compound (–)-**28**.

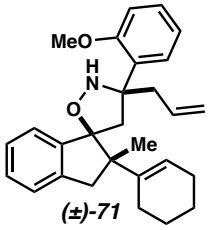
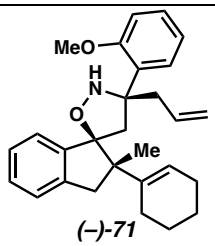
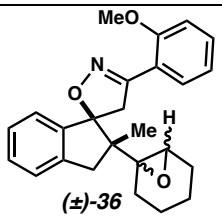
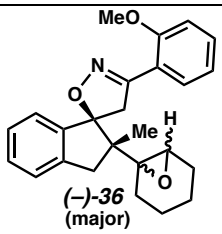
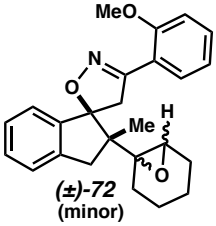
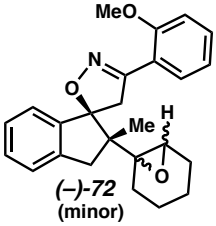
Identification code	cu_garg2304_a	
Empirical formula	C22 H23 Br N2 O2 S	
Formula weight	459.39	
Temperature	100(2) K	
Wavelength	1.54178 Å	
Crystal system	Monoclinic	
Space group	$P2_1$	
Unit cell dimensions	a = 9.5459(2) Å	α = 90°.
	b = 19.1854(5) Å	β = 93.0090(10)°.
	c = 11.5679(3) Å	γ = 90°.
Volume	2115.65(9) $Å^3$	
Z	4	
Density (calculated)	1.442 Mg/m^3	
Absorption coefficient	3.728 mm^{-1}	
F(000)	944	
Crystal size	0.18 x 0.04 x 0.04 mm^3	
Theta range for data collection	3.826 to 69.613°.	
Index ranges	-11<=h<=11, -22<=k<=23, -13<=l<=13	
Reflections collected	26366	
Independent reflections	7768 [R(int) = 0.0457]	
Completeness to theta = 67.679°	99.8	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.75 and 0.64	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	7768 / 1 / 513	
Goodness-of-fit on F^2	1.040	
Final R indices [I>2sigma(I)]	R1 = 0.0329, wR2 = 0.0700	
R indices (all data)	R1 = 0.0375, wR2 = 0.0712	
Absolute structure parameter	-0.009(8)	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.796 and -0.497 e.$Å^{-3}$	

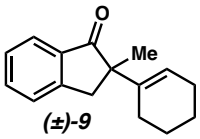
SFC Data

Table S4. SFC conditions and data.

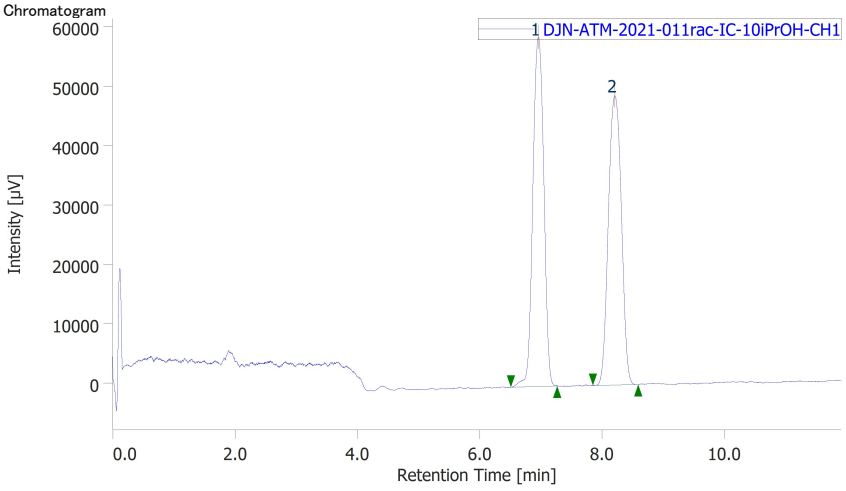
Compound	Column	Solvent	Flow Rate	Retention Times (min)	Enantiomeric Ratio (er)
 *(±)-9*	Daicel ChiralPak IC / 30 °C	10% isopropanol in CO_2	10.0 mL/min	6.96/8.21	50.5 : 49.5
 *(+)-9*	Daicel ChiralPak IC / 30 °C	10% isopropanol in CO_2	10.0 mL/min	6.83/7.98	6.2 : 93.8
 *(±)-23*	Daicel ChiralPak ID / 30 °C	15% isopropanol in CO_2	4.0 mL/min	4.93/5.66	49.9 : 50.1
 *(+)-23*	Daicel ChiralPak ID / 30 °C	15% isopropanol in CO_2	4.0 mL/min	4.67/5.29	6.1 : 93.9
 *(±)-25*	Daicel ChiralPak IC / 30 °C	10% isopropanol in CO_2	10.0 mL/min	9.32/11.13	50.0 : 50.0
 *(+)-25*	Daicel ChiralPak IC / 30 °C	10% isopropanol in CO_2	10.0 mL/min	9.34/11.18	93.6 : 6.4
 *(±)-27*	Daicel ChiralPak IC / 30 °C	10% isopropanol in CO_2	10.0 mL/min	6.05/6.53	50.3 : 49.7
 *(+)-27*	Daicel ChiralPak IC / 30 °C	10% isopropanol in CO_2	10.0 mL/min	5.98/6.42	22.9 : 77.1

 ***(±)-12***	Daicel ChiralPak IC / 30 °C	10% isopropanol in CO_2	10.0 mL/min	4.25/4.79	49.9 : 50.1
 ***(+)-12***	Daicel ChiralPak IC / 30 °C	10% isopropanol in CO_2	10.0 mL/min	4.25/4.78	11.5 : 88.5
 ***(±)-30***	Daicel ChiralPak IC / 30 °C	10% isopropanol in CO_2	1.5 mL/min	9.91/14.37	50.1 : 49.9
 ***(+)-30***	Daicel ChiralPak IC / 30 °C	10% isopropanol in CO_2	1.5 mL/min	9.89/14.34	5.8 : 94.2
 ***(±)-31***	Daicel ChiralPak IB N-3 / 30 °C	10% isopropanol in CO_2	1.5 mL/min	4.41/4.67	50.7 : 49.3
 ***(+)-31***	Daicel ChiralPak IB N-3 / 30 °C	10% isopropanol in CO_2	1.5 mL/min	4.51/4.79	94.1 : 5.9
 ***(±)-35*** **(major)**	Daicel ChiralPak IC / 30 °C	20% isopropanol in CO_2	1.5 mL/min	6.23/11.11	49.9 : 50.1
 ***(–)-35*** **(major)**	Daicel ChiralPak IC / 30 °C	20% isopropanol in CO_2	1.5 mL/min	6.30/11.23	93.9 : 6.1

 ***(±)-71*** **(minor)**	Daicel ChiralPak IB N-3 / 30 °C	10% isopropanol in CO_2	1.5 mL/min	9.87/18.36	50.2 : 49.8
 ***(–)-71*** **(minor)**	Daicel ChiralPak IB N-3 / 30 °C	10% isopropanol in CO_2	1.5 mL/min	9.88/18.52	93.9 : 6.1
 ***(±)-36*** **(major)**	Daicel ChiralPak IC / 30 °C	30% isopropanol in CO_2	1.5 mL/min	9.63/11.82	49.8 : 50.2
 ***(–)-36*** **(major)**	Daicel ChiralPak IC / 30 °C	30% isopropanol in CO_2	1.5 mL/min	9.61/11.82	93.8 : 6.2
 ***(±)-72*** **(minor)**	Daicel ChiralPak IC / 30 °C	20% isopropanol in CO_2	1.5 mL/min	12.82/17.89	50.0 : 50.0
 ***(–)-72*** **(minor)**	Daicel ChiralPak IC / 30 °C	20% isopropanol in CO_2	1.5 mL/min	12.77/17.76	93.8 : 6.2



(±)-9



Peak Information

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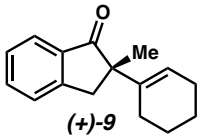
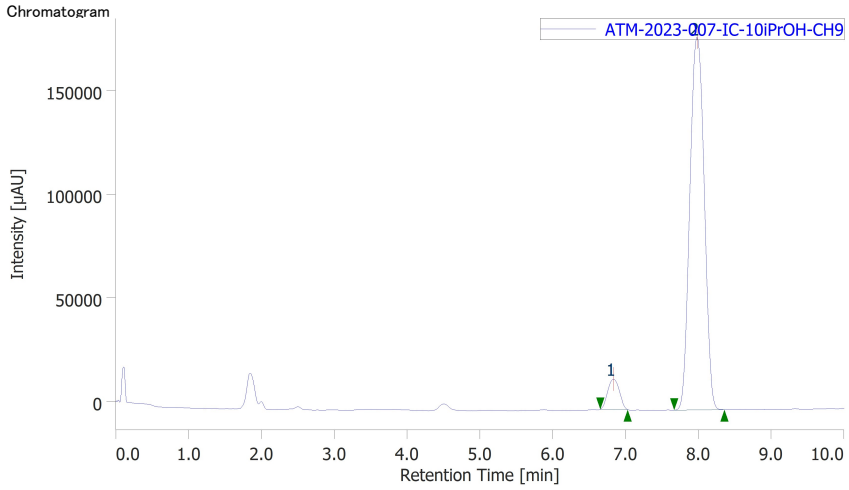


(+)-9



Peak Information

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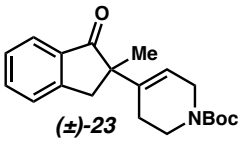
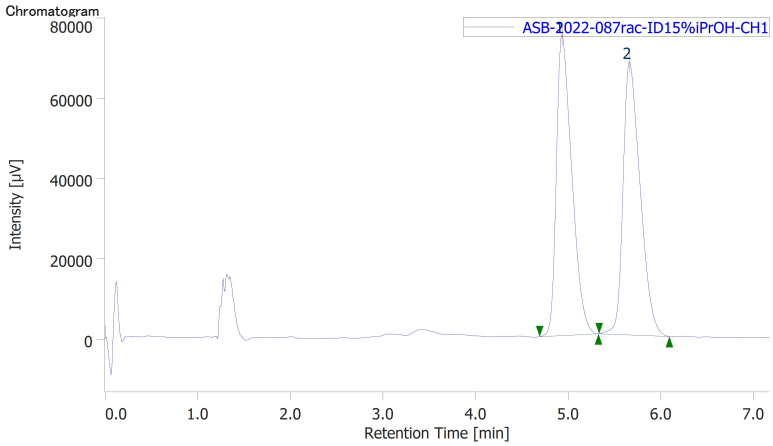


(±)-23



Peak Information

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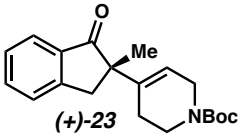
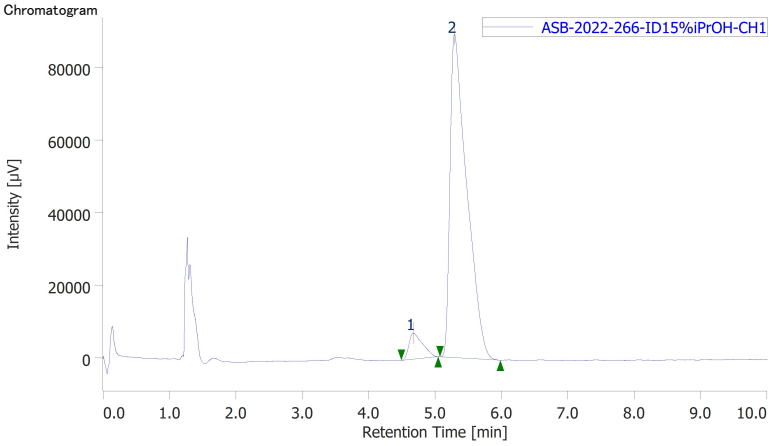


(+)-23



Peak Information

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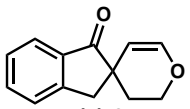
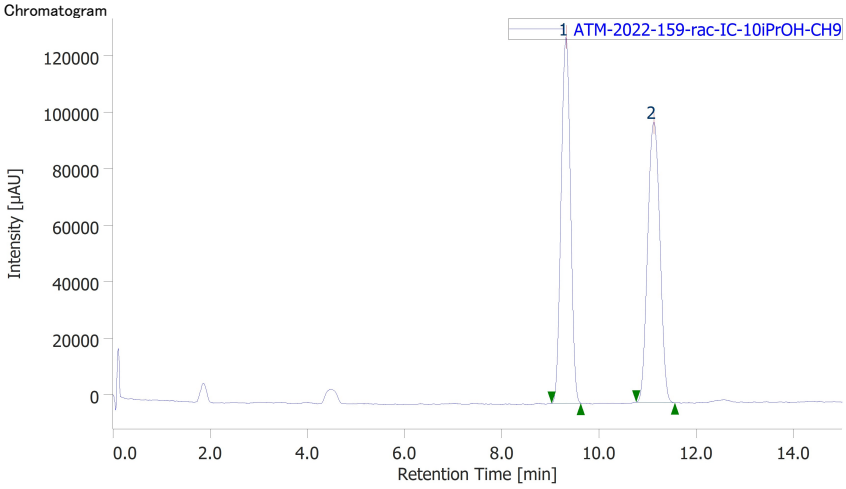
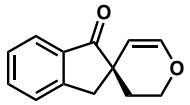


(±)-25



Peak Information

#	Peak Name	CH	tR [min]	Area [μV·sec]	Height [μV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	9	9.320	1735406	129569	50.000	56.651	N/A	10494	4.292	0.986	
2	Unknown	9	11.127	1735387	99147	50.000	43.349	N/A	8594	N/A	1.016	



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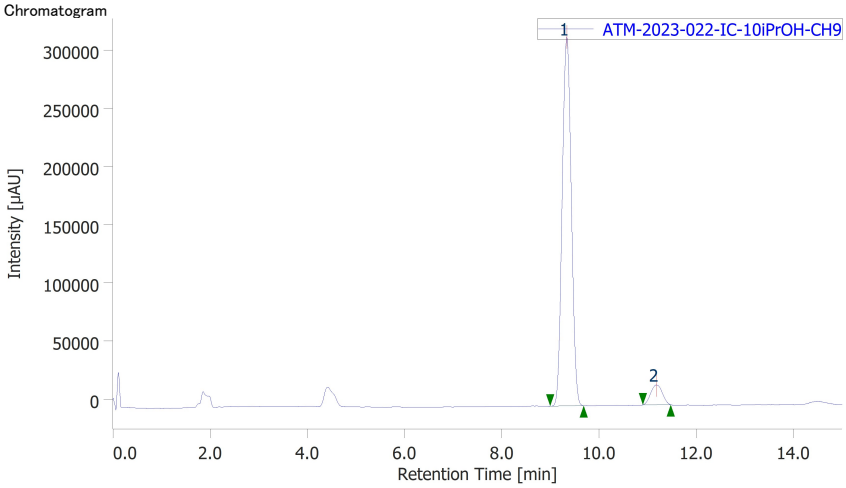
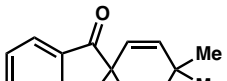
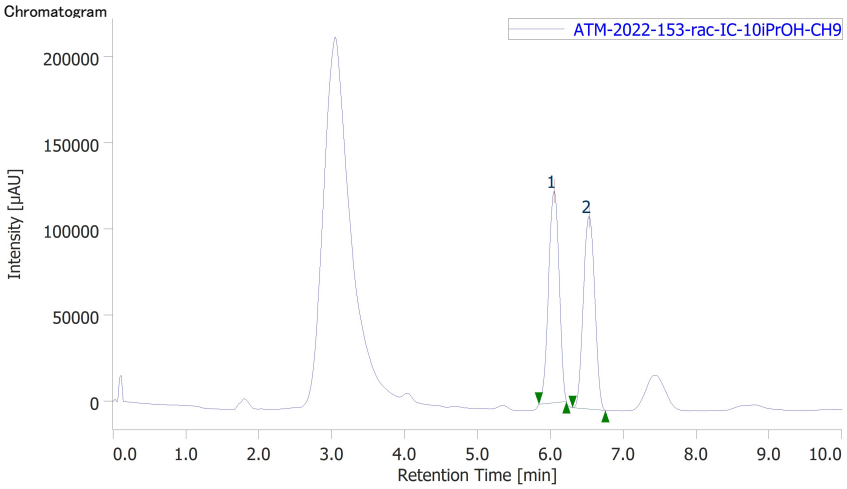


Peak Information

#	Peak Name	CH	tR [min]	Area [μV·sec]	Height [μV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	9	9.337	4124400	316946	93.554	94.903	N/A	11266	4.548	1.025	
2	Unknown	9	11.177	284158	17022	6.446	5.097	N/A	9466	N/A	1.033	

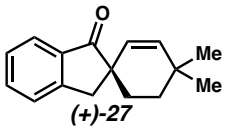


(±)-27



Peak Information

#	Peak Name	CH	tR [min]	Area [μV·sec]	Height [μV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	9	6.050	1235985	122833	50.324	52.344	N/A	7733	1.673	0.926	
2	Unknown	9	6.530	1220048	111832	49.676	47.656	N/A	7569	N/A	1.007	



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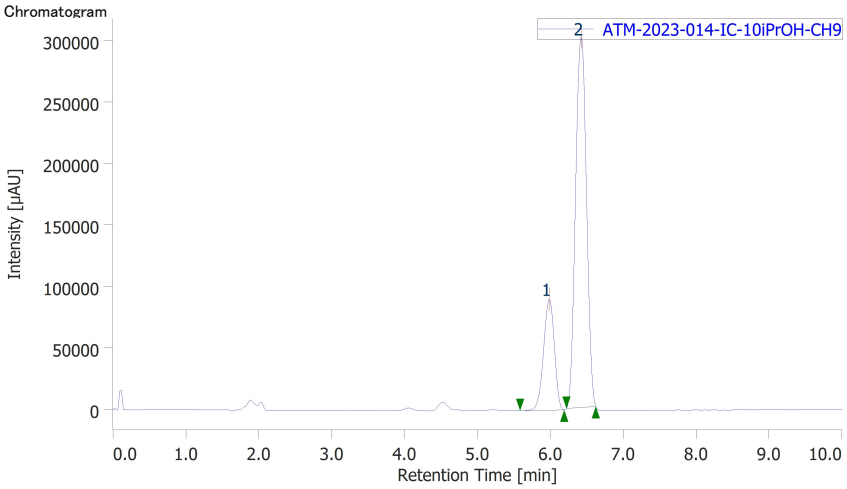
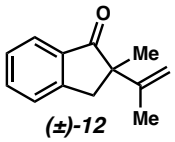


Peak Information

#	Peak Name	CH	tR [min]	Area [μV·sec]	Height [μV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	9	5.983	933483	90214	22.907	23.052	N/A	7469	1.553	0.918	
2	Unknown	9	6.420	3141658	301141	77.093	76.948	N/A	8021	N/A	1.017	



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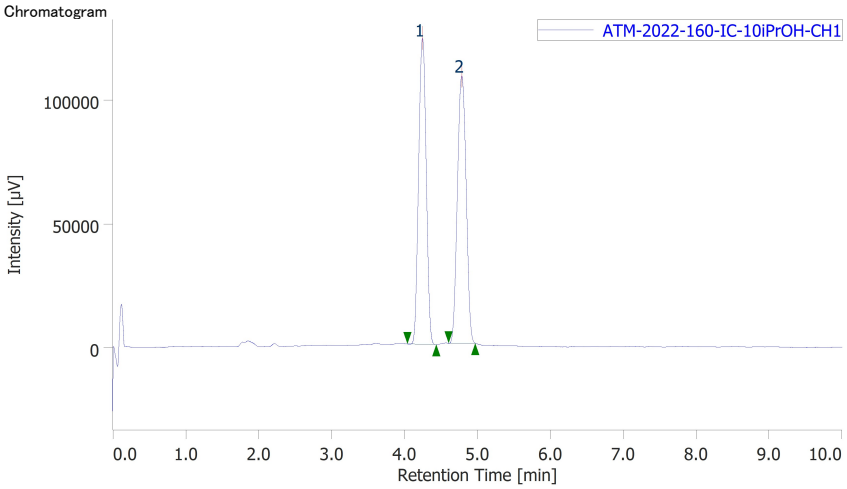
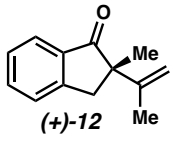


Peak Information

#	Peak Name	CH	tR [min]	Area [μV·sec]	Height [μV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	1	4.245	891091	123447	49.885	53.408	N/A	7385	2.531	1.008	
2	Unknown	1	4.785	895191	107693	50.115	46.592	N/A	6905	N/A	1.010	



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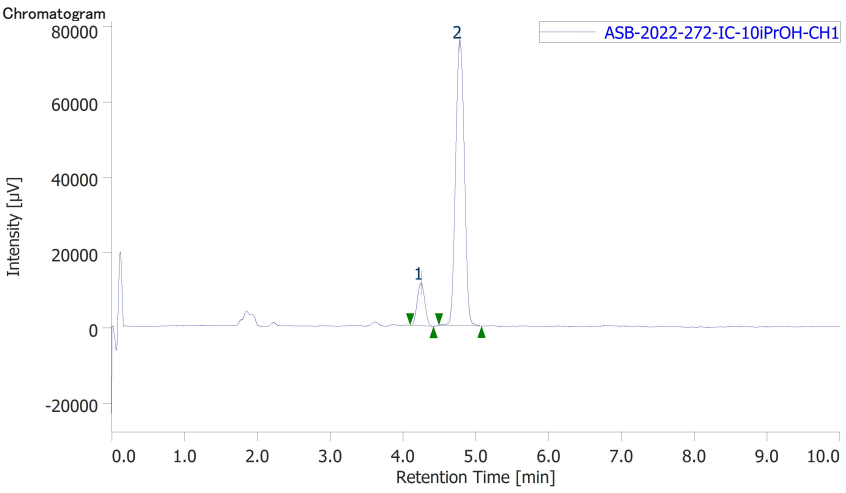
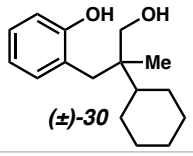


Peak Information

#	Peak Name	CH	tR [min]	Area [μV·sec]	Height [μV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	1	4.247	81956	11366	11.482	13.034	N/A	7371	2.519	1.009	
2	Unknown	1	4.780	631799	75841	88.518	86.966	N/A	7115	N/A	1.023	



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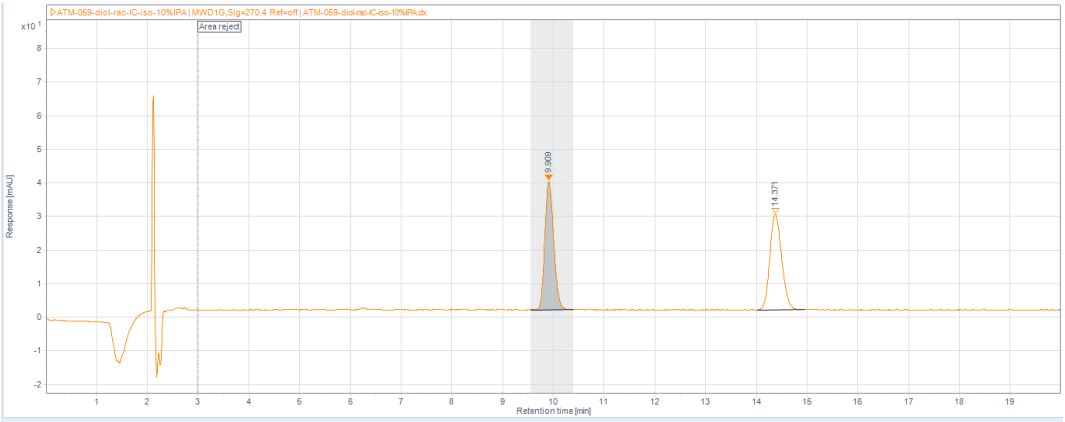
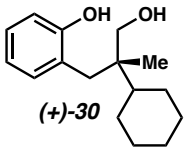


Injection Results

Peaks | Summary

#	Name	Signal description	RT (min)	Area (mAU·s)	Area%	Height (mAU)	Height%	Amount	Concentration	Start time (min)	End time (min)
1		MWD1G,Sig=270,4 Ref=off	9.909	463.312	50.136	38.194	57.34			9.552	10.389
2		MWD1G,Sig=270,4 Ref=off	14.371	460.791	49.864	28.411	42.66			14.002	14.948



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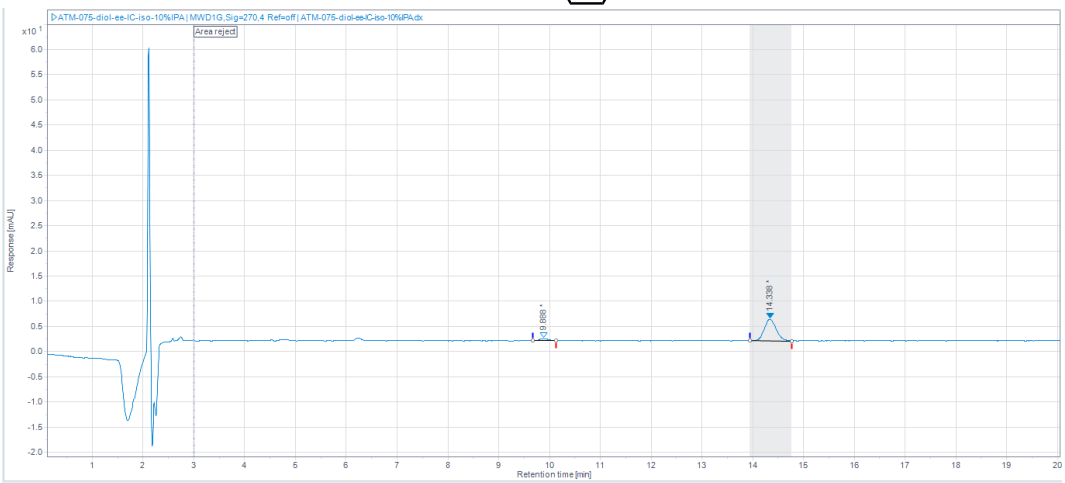
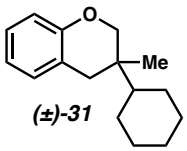


Injection Results

Peaks | Summary

#	Name	Signal description	RT (min)	Area (mAU·s)	Area%	Height (mAU)	Height%	Amount	Concentration	Start time (min)	End time (min)
1		MWD1G,Sig=270,4 Ref=off	9.888	4.292	5.850	0.387	8.35			9.668	10.128
2		MWD1G,Sig=270,4 Ref=off	14.338	69.080	94.150	4.248	91.65			13.940	14.768



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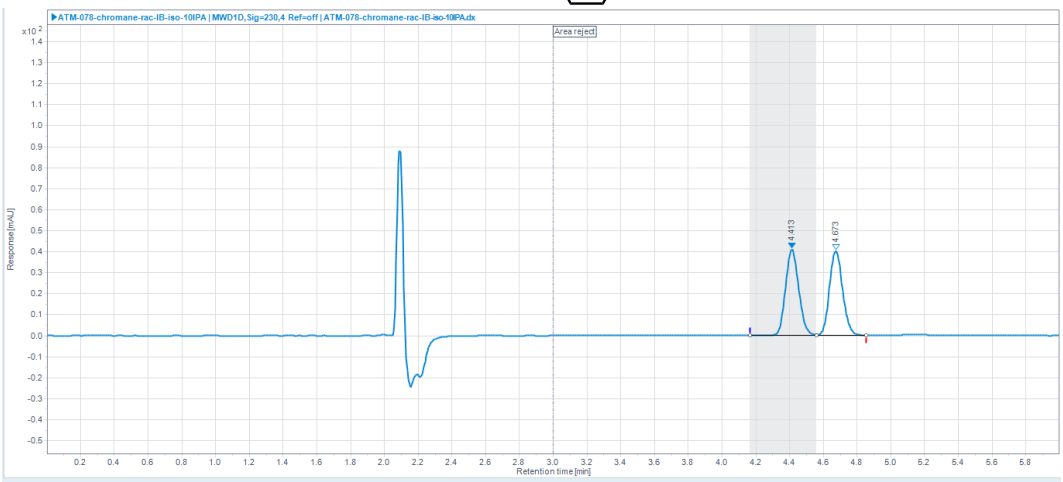
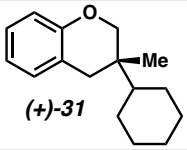


Injection Results

Peaks | Summary

#	Name	Signal description	RT (min)	Area (mAU·s)	Area%	Height (mAU)	Height%	Amount	Concentration	Start time (min)	End time (min)
1		MWD1D,Sig=230,4 Ref=off	4.413	223.789	50.666	40.954	50.46			4.166	4.561
2		MWD1D,Sig=230,4 Ref=off	4.673	217.909	49.334	40.212	49.54			4.561	4.854



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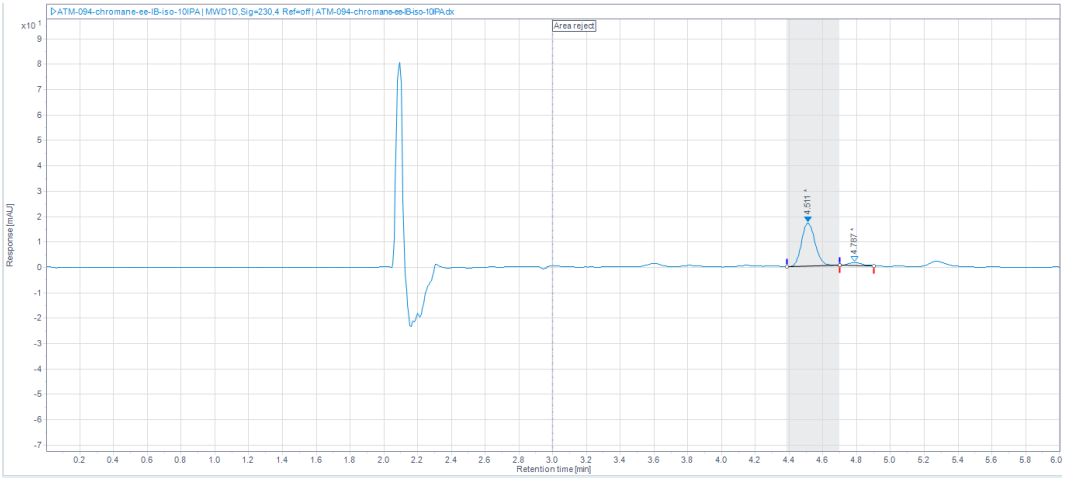
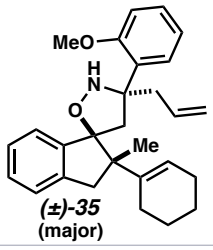


Injection Results

Peaks | Summary

#	Name	Signal description	RT (min)	Area (mAU·s)	Area%	Height (mAU)	Height%	Amount	Concentration	Start time (min)	End time (min)
1		MWD1D,Sig=230,4 Ref=off	4.511	94.408	94.145	16.972	93.97			4.388	4.701
2		MWD1D,Sig=230,4 Ref=off	4.787	5.871	5.855	1.090	6.03			4.701	4.901



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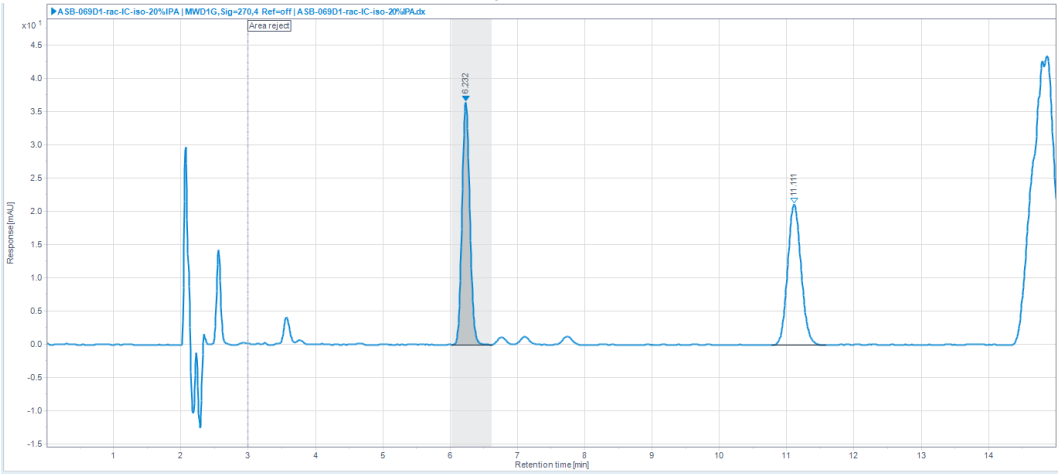
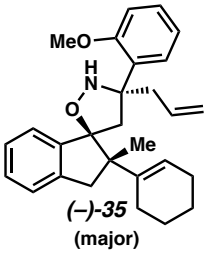


Injection Results

Peaks | Summary

#	Name	Signal description	RT (min)	Area (mAU·s)	Area%	Height (mAU)	Height%	Amount	Concentration	Start time (min)	End time (min)
1		MWD1G,Sig=270,4 Ref=off	6.232	293.453	49.873	36.520	63.31			6.028	6.624
2		MWD1G,Sig=270,4 Ref=off	11.111	294.943	50.127	21.166	36.69			10.777	11.576



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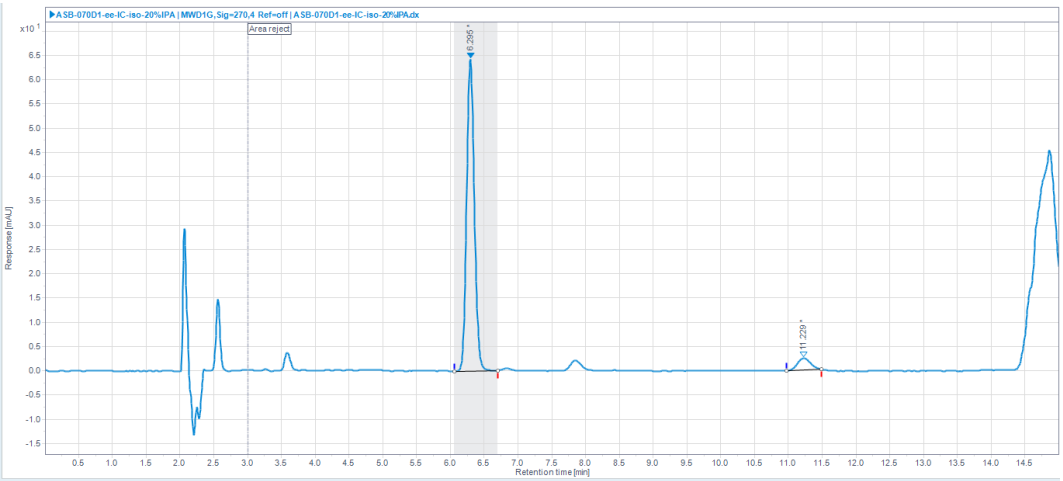
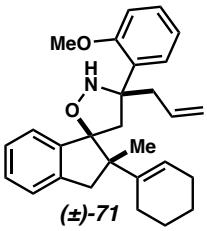


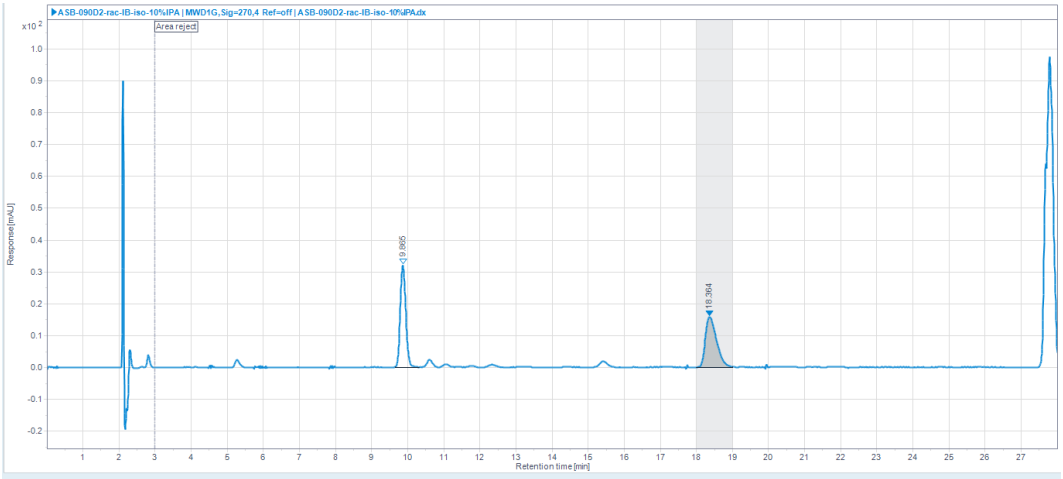
Injection Results

Peaks | Summary

#	Name	Signal description	RT (min)	Area (mAU·s)	Area%	Height (mAU)	Height%	Amount	Concentration	Start time (min)	End time (min)
1		MWD1G,Sig=270,4 Ref=off	6.295	510.868	93.865	64.237	96.28			6.058	6.697
2		MWD1G,Sig=270,4 Ref=off	11.229	33.389	6.135	2.480	3.72			10.976	11.484



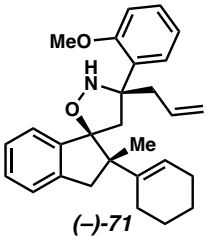
(±)-71
(minor)



Injection Results

Peaks | Summary

#	Name	Signal description	RT (min)	Area (mAU·s)	Area%	Height (mAU)	Height%	Amount	Concentration	Start time (min)	End time (min)
1		MWD1G,Sig=270,4 Ref=off	9.865	344.021	50.170	32.173	67.00			9.660	10.312
2		MWD1G,Sig=270,4 Ref=off	18.364	341.686	49.830	15.848	33.00			17.995	18.994



(–)-71
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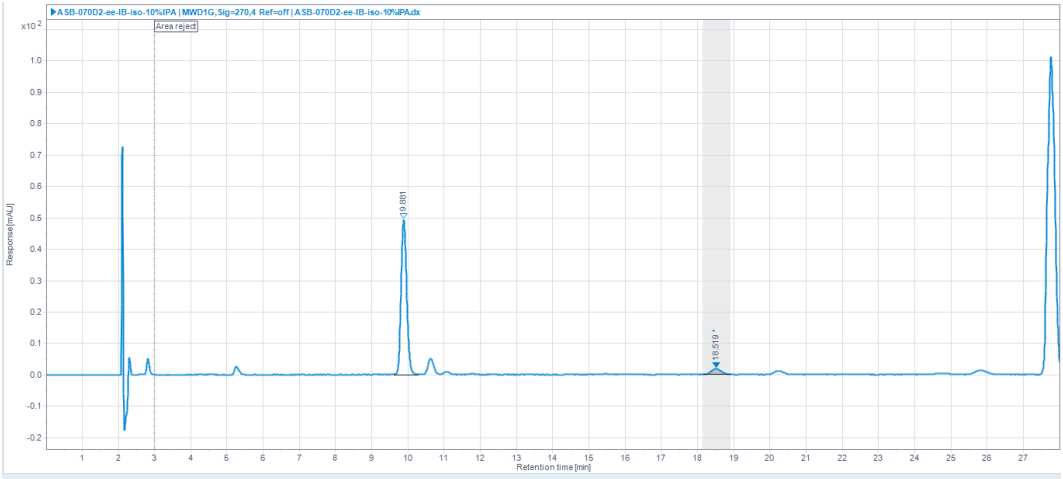
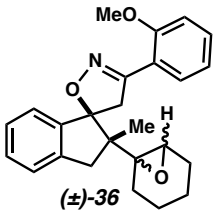


Injection Results

Peaks | Summary

#	Name	Signal description	RT (min)	Area (mAU·s)	Area%	Height (mAU)	Height%	Amount	Concentration	Start time (min)	End time (min)
1		MWD1G,Sig=270,4 Ref=off	9.881	533.540	93.944	49.424	96.44			9.622	10.294
2		MWD1G,Sig=270,4 Ref=off	18.519	34.393	6.056	1.827	3.56			18.148	18.920



(±)-36
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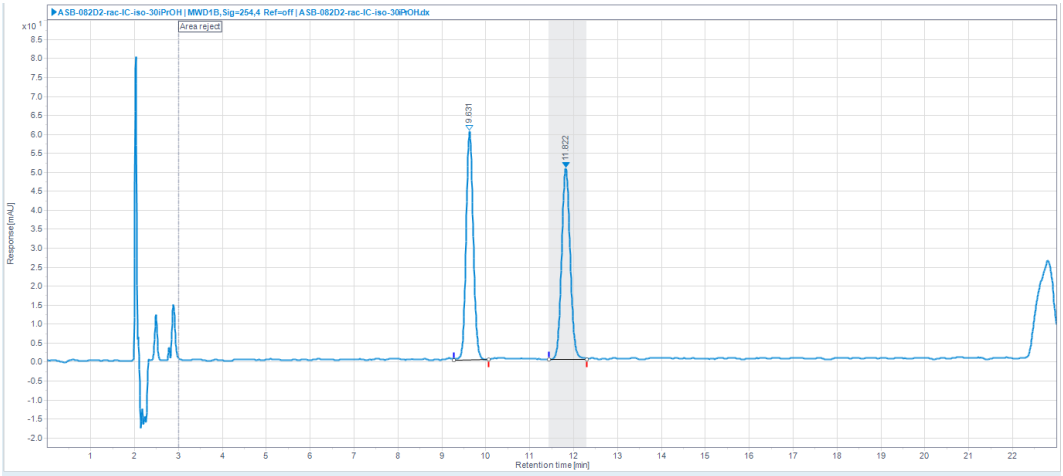
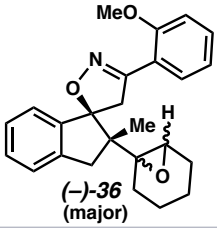


Injection Results

Peaks | Summary

#	Name	Signal description	RT (min)	Area (mAU·s)	Area%	Height (mAU)	Height%	Amount	Concentration	Start time (min)	End time (min)
1		MWD1B,Sig=254,4 Ref=off	9.631	680.050	49.840	60.217	54.43			9.267	10.060
2		MWD1B,Sig=254,4 Ref=off	11.822	684.413	50.160	50.423	45.57			11.436	12.297



(–)-36
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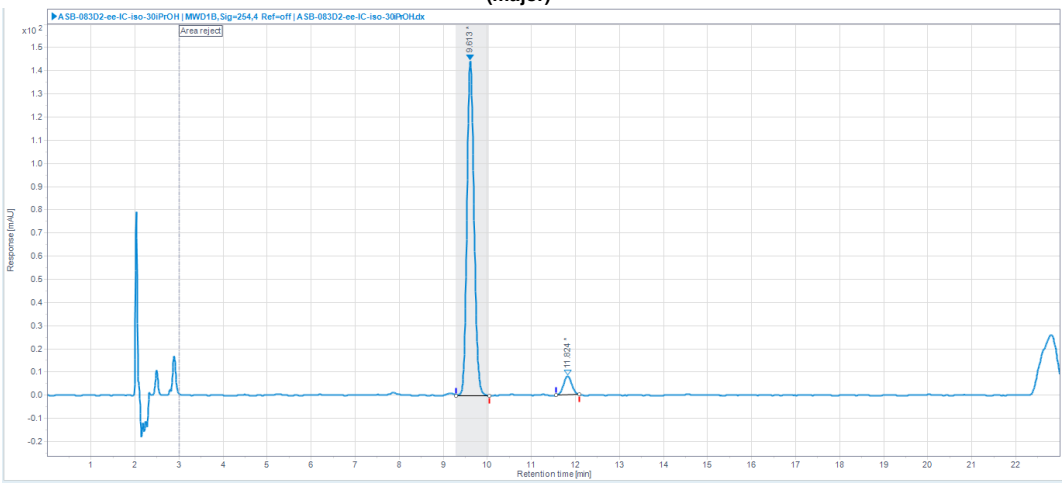
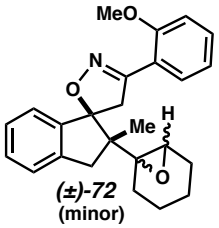


Injection Results

Peaks | Summary

#	Name	Signal description	RT (min)	Area (mAU·s)	Area%	Height (mAU)	Height%	Amount	Concentration	Start time (min)	End time (min)
1		MWD1B,Sig=254,4 Ref=off	9.613	1615.767	93.837	144.363	94.67			9.296	10.041
2		MWD1B,Sig=254,4 Ref=off	11.824	106.118	6.163	8.127	5.33			11.564	12.087



(±)-72
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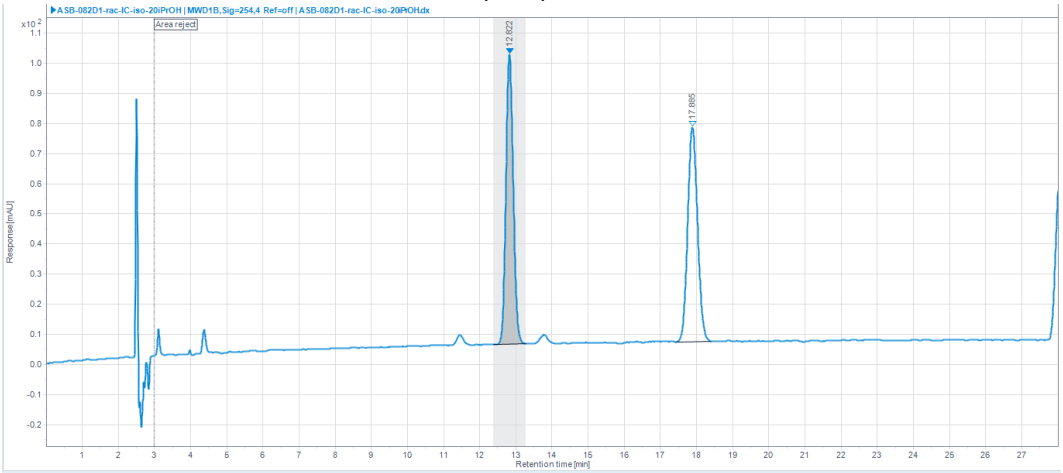
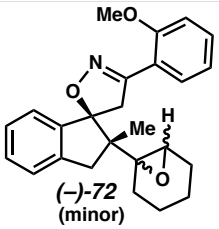


Injection Results

Peaks | Summary

#	Name	Signal description	RT (min)	Area (mAU·s)	Area%	Height (mAU)	Height%	Amount	Concentration	Start time (min)	End time (min)
1		MWD1B,Sig=254,4 Ref=off	12.822	1349.509	49.999	96.237	57.47			12.377	13.285
2		MWD1B,Sig=254,4 Ref=off	17.885	1349.575	50.001	71.226	42.53			17.411	18.415



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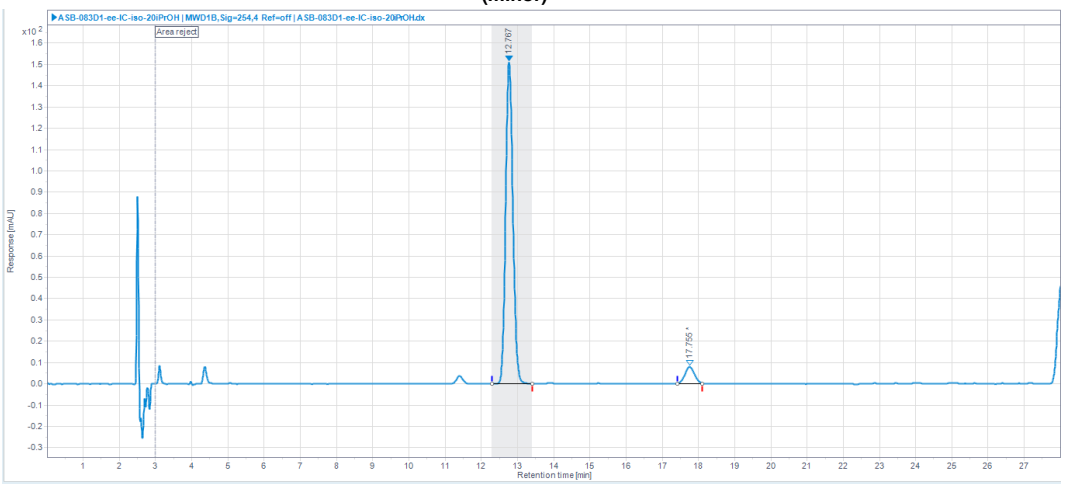


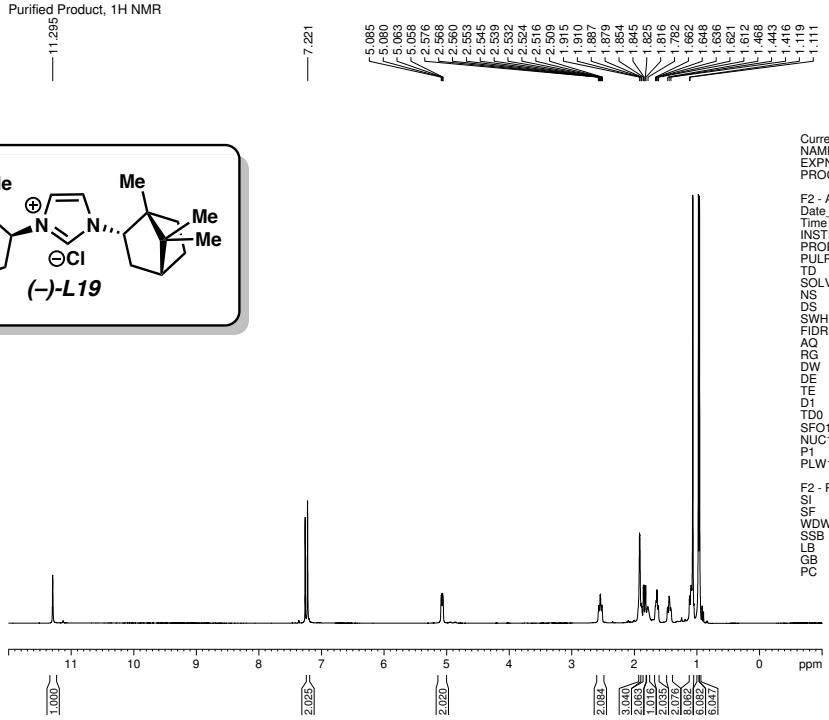
Injection Results

Peaks | Summary

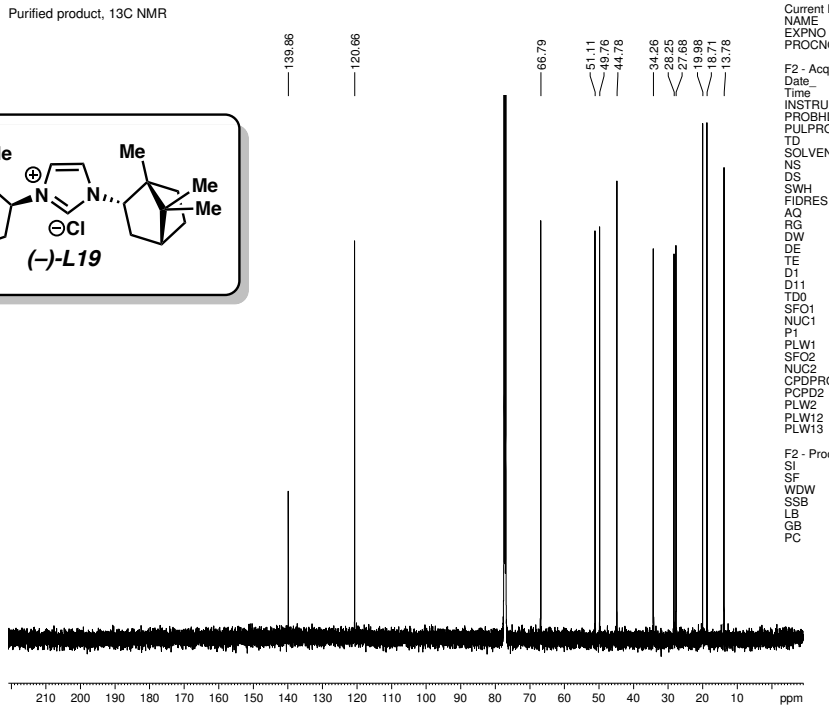
#	Name	Signal description	RT (min)	Area (mAU·s)	Area%	Height (mAU)	Height%	Amount	Concentration	Start time (min)	End time (min)
1		MWD1B,Sig=254,4 Ref=off	12.767	2107.617	93.769	151.118	95.11			12.288	13.407
2		MWD1B,Sig=254,4 Ref=off	17.755	140.042	6.231	7.770	4.89			17.420	18.111

NMR Spectra

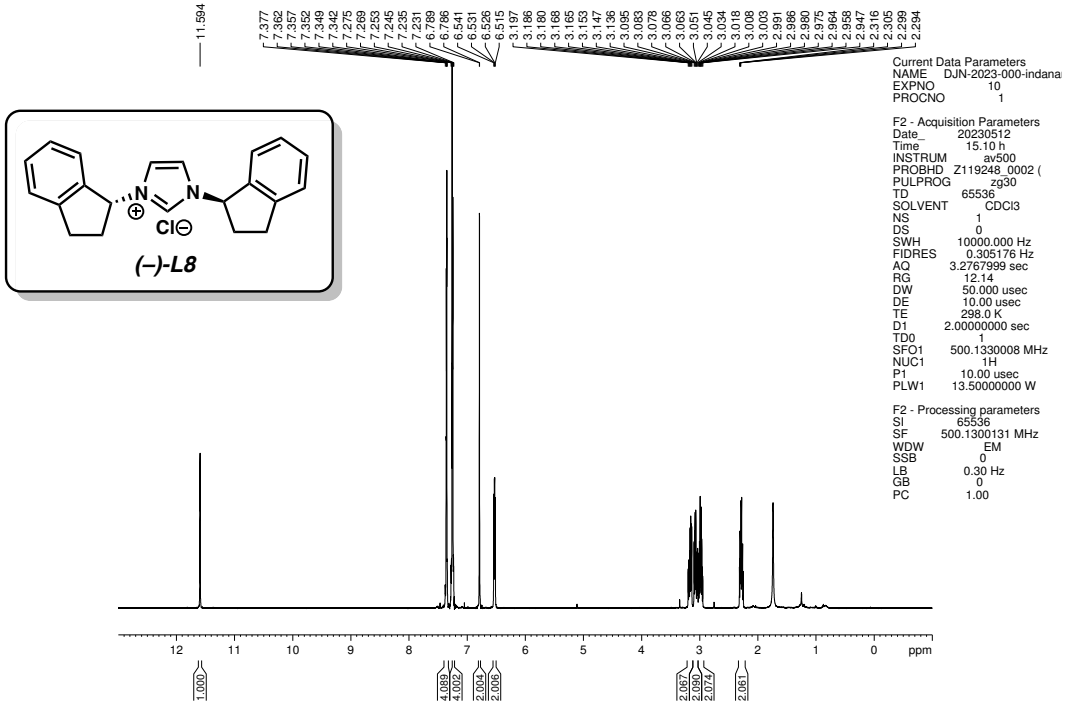
Purified Product, 1H NMR



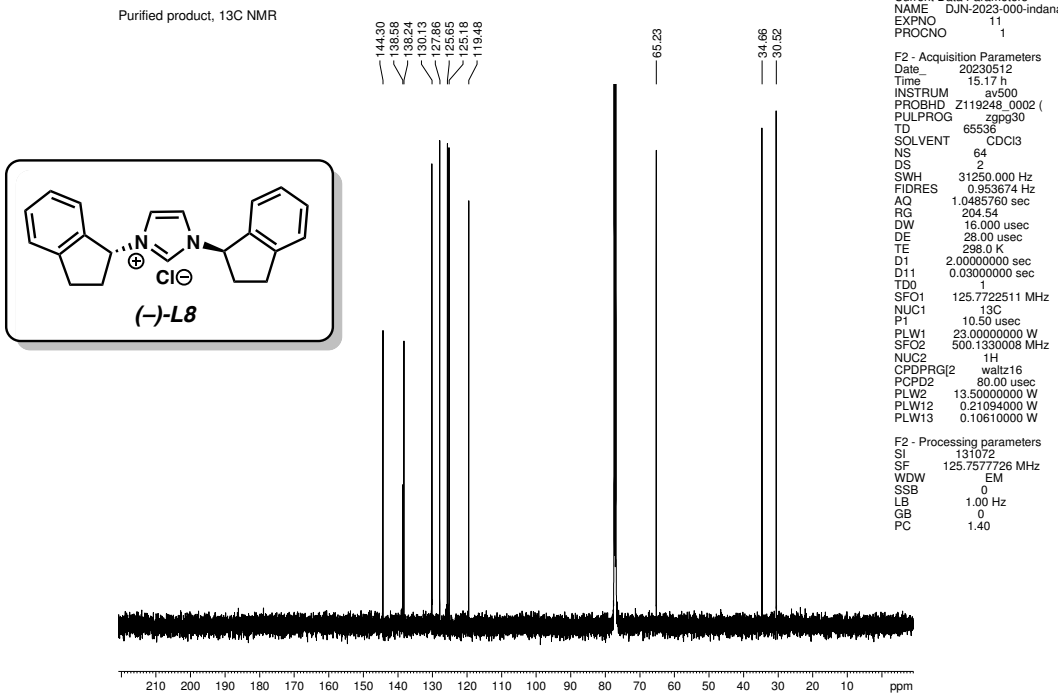
Purified product, 13C NMR



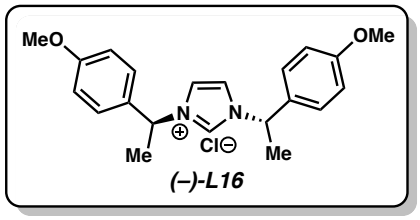
Purified product, 1H NMR



Purified product, 13C NMR



Purified product, 1H NMR



(–)-L16

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EXPNO 10
PROCNO 1

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SOLVENT CDCl3
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DS 0
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FIDRES 0.305176 Hz
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RG 12.14
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DE 10.00 usec
TE 298.0 K
D1 2.00000000 sec
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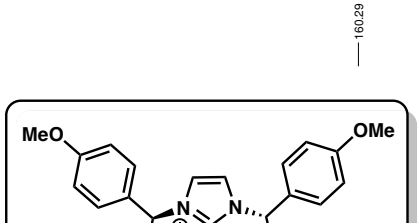
NUC1 1H
P1 10.00 usec
PLW1 13.50000000 W

F2 - Processing parameters
SI 65536
SF 500.1300127 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

Purified product, 13C NMR



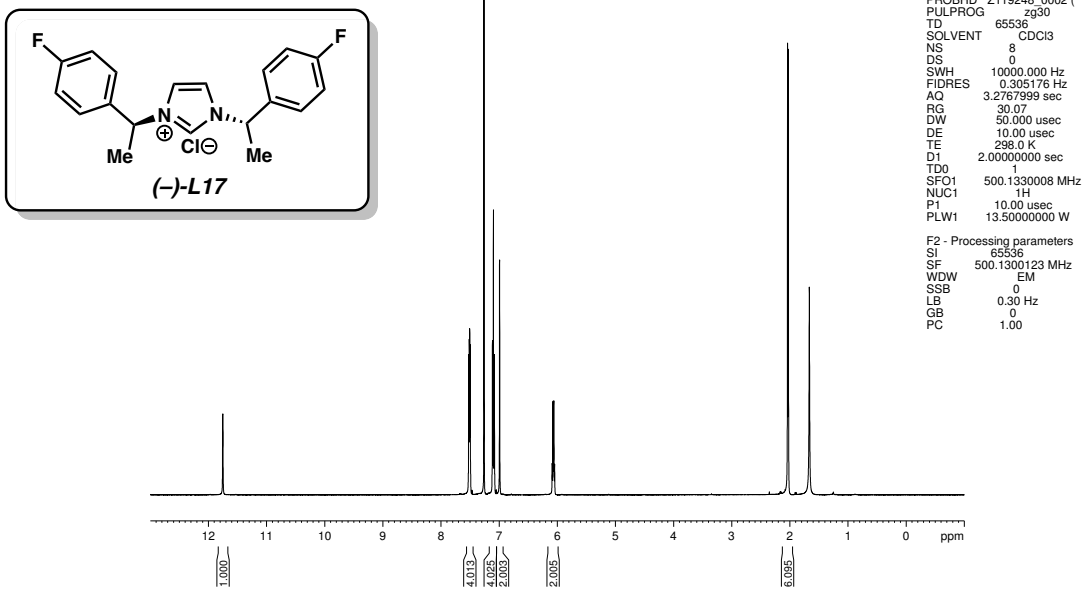
(–)-L16

Current Data Parameters
NAME ASB-2023-000
EXPNO 17
PROCNO 1

F2 - Acquisition Parameters
Date_ 20230412
Time 18.57 h
INSTRUM av500
PROBHD Z119248_0002 (
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 128
DS 2
SWH 31250.000 Hz
FIDRES 0.953674 Hz
AQ 1.0485760 sec
RG 204.54
DW 16.000 usec
DE 28.00 usec
TE 298.0 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
SFO1 125.7722511 MHz
NUC1 13C
P1 10.50 usec
PLW1 23.00000000 W
SFO2 500.1330008 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 80.00 usec
PLW2 13.50000000 W
PLW12 0.21094000 W
PLW13 0.10610000 W

F2 - Processing parameters
SI 131072
SF 125.7577892 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

Purified product, 1H NMR

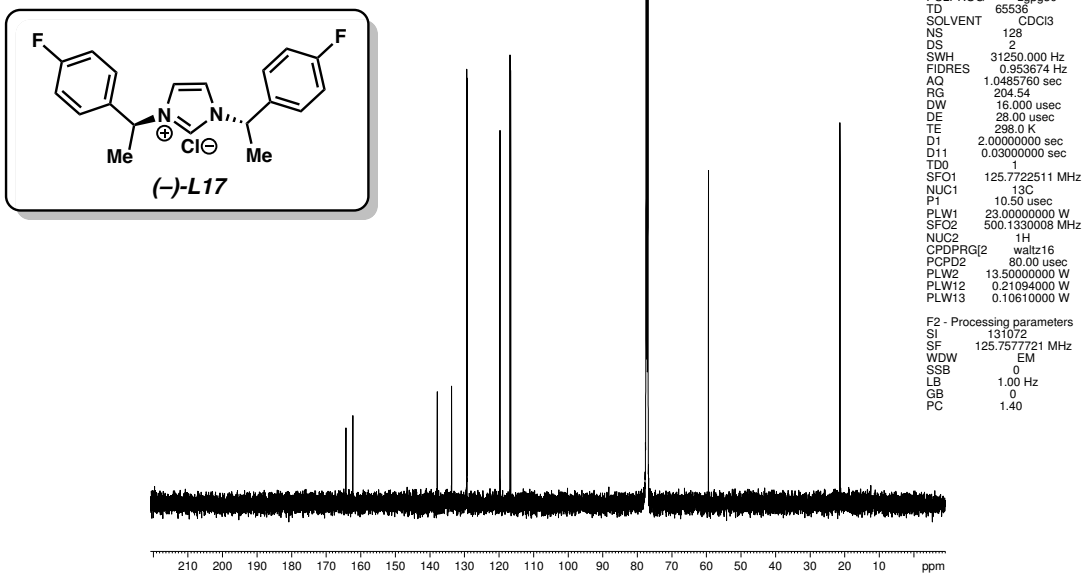


Current Data Parameters
NAME ASB-2023-000
EXPNO 18
PROCNO 1

F2 - Acquisition Parameters
Date_ 20230412
Time 19.01 h
INSTRUM av500
PROBHD Z119248_0002 (
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 8
DS 0
SWH 10000.000 Hz
FIDRES 0.305176 Hz
AQ 3.2767999 sec
RG 30.07
DW 50.000 usec
DE 10.00 usec
TE 298.0 K
D1 2.00000000 sec
TD0 1
SFO1 500.1330008 MHz
NUC1 1H
P1 10.00 usec
PLW1 13.50000000 W

F2 - Processing parameters
SI 65536
SF 500.1300123 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

Purified product, 13C NMR

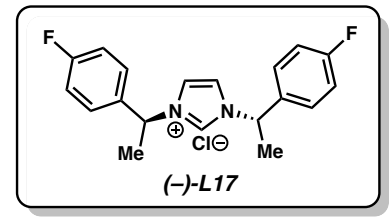


Current Data Parameters
NAME ASB-2023-000
EXPNO 19
PROCNO 1

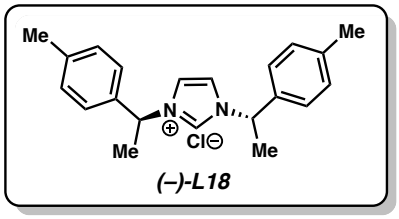
F2 - Acquisition Parameters
Date_ 20230412
Time 19.08 h
INSTRUM av500
PROBHD Z119248_0002 (
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 128
DS 2
SWH 31250.000 Hz
FIDRES 0.953674 Hz
AQ 1.0485760 sec
RG 204.54
DW 16.000 usec
DE 28.00 usec
TE 298.0 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
SFO1 125.7722511 MHz
NUC1 13C
P1 10.50 usec
PLW1 23.00000000 W
SFO2 500.1330008 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 80.00 usec
PLW2 13.50000000 W
PLW12 0.21094000 W
PLW13 0.10610000 W

F2 - Processing parameters
SI 131072
SF 125.7577721 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

Purified product, 19F NMR



Purified product, 1H NMR



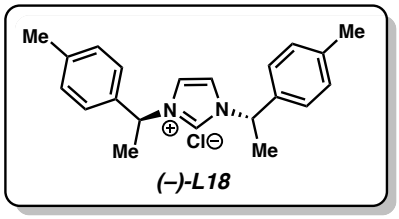
(–)-L18

Current Data Parameters
NAME ASB-2023-000
EXPNO 20
PROCNO 1

F2 - Acquisition Parameters
Date_ 20230412
Time 19.12 h
INSTRUM av500
PROBHD Z119248_0002 (
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 8
DS 0
SWH 10000.000 Hz
FIDRES 0.305176 Hz
AQ 3.2767999 sec
RG 26.59
DW 50.000 usec
DE 10.00 usec
TE 298.0 K
D1 2.00000000 sec
TD0 1
SFO1 500.1330008 MHz
NUC1 1H
P1 10.00 usec
PLW1 13.50000000 W

F2 - Processing parameters
SI 65536
SF 500.1300122 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

Purified product, 13C NMR



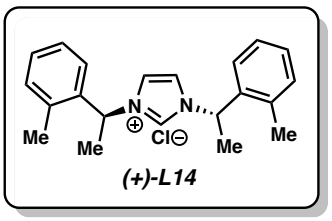
(–)-L18

Current Data Parameters
NAME ASB-2023-000
EXPNO 21
PROCNO 1

F2 - Acquisition Parameters
Date_ 20230412
Time 19.18 h
INSTRUM av500
PROBHD Z119248_0002 (
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 80
DS 2
SWH 31250.000 Hz
FIDRES 0.953674 Hz
AQ 1.0485760 sec
RG 204.54
DW 16.000 usec
DE 28.00 usec
TE 298.0 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
SFO1 125.7722511 MHz
NUC1 13C
P1 10.50 usec
PLW1 23.00000000 W
SFO2 500.1330008 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 80.00 usec
PLW2 13.50000000 W
PLW12 0.21094000 W
PLW13 0.10610000 W

F2 - Processing parameters
SI 131072
SF 125.7577725 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

Purified product, 1H NMR

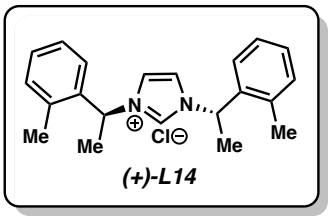


Current Data Parameters
NAME ASB-2023-000
EXPNO 14
PROCNO 1

F2 - Acquisition Parameters
Date_ 20230412
Time 18.43 h
INSTRUM av500
PROBHD Z119248_0002 (
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 8
DS 0
SWH 10000.000 Hz
FIDRES 0.305176 Hz
AQ 3.2767999 sec
RG 26.59
DW 50.000 usec
DE 10.00 usec
TE 298.0 K
D1 2.00000000 sec
TD0 1
SFO1 500.1330008 MHz
NUC1 1H
P1 10.00 usec
PLW1 13.50000000 W

F2 - Processing parameters
SI 65536
SF 500.1300128 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

Purified product, 13C NMR

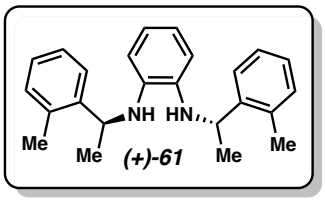


Current Data Parameters
NAME ASB-2023-000
EXPNO 15
PROCNO 1

F2 - Acquisition Parameters
Date_ 20230412
Time 18.45 h
INSTRUM av500
PROBHD Z119248_0002 (
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 33
DS 2
SWH 31250.000 Hz
FIDRES 0.953674 Hz
AQ 1.0485760 sec
RG 204.54
DW 16.000 usec
DE 28.00 usec
TE 298.0 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
SFO1 125.7722511 MHz
NUC1 13C
P1 10.50 usec
PLW1 23.00000000 W
SFO2 500.1330008 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 80.00 usec
PLW2 13.50000000 W
PLW12 0.21094000 W
PLW13 0.10610000 W

F2 - Processing parameters
SI 131072
SF 125.7577750 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

Purified product, 1H NMR

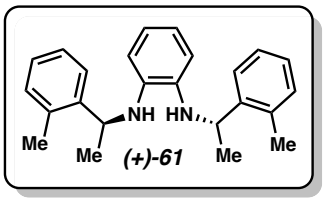


Current Data Parameters
NAME DJN-2021-172-Proton
EXPNO 10
PROCNO 1

F2 - Acquisition Parameters
Date_ 20210720
Time 17.58 h
INSTRUM av500
PROBHD Z119248_0002 (
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 8
DS 0
SWH 10000.000 Hz
FIDRES 0.305176 Hz
AQ 3.2767999 sec
RG 12.14
DW 50.000 usec
DE 10.00 usec
TE 298.0 K
D1 2.00000000 sec
TD0 1
SFO1 500.1330008 MHz
NUC1 1H
P1 10.00 usec
PLW1 13.50000000 W

F2 - Processing parameters
SI 65536
SF 500.1300122 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

Purified product, 13C NMR

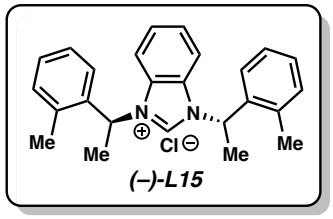


Current Data Parameters
NAME DJN-2021-172-Carbo
EXPNO 11
PROCNO 1

F2 - Acquisition Parameters
Date_ 20210720
Time 18.03 h
INSTRUM av500
PROBHD Z119248_0002 (
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 64
DS 2
SWH 31250.000 Hz
FIDRES 0.953674 Hz
AQ 1.0485760 sec
RG 204.54
DW 16.000 usec
DE 28.00 usec
TE 298.0 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
SFO1 125.7722511 MHz
NUC1 13C
P1 10.50 usec
PLW1 23.00000000 W
SFO2 500.1330008 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 80.00 usec
PLW2 13.50000000 W
PLW12 0.21094000 W
PLW13 0.10610000 W

F2 - Processing parameters
SI 131072
SF 125.7577740 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

Purified product, 1H NMR

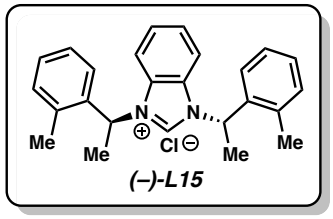


Current Data Parameters
NAME DJN-2023-000-o-tol-be
EXPNO 10
PROCNO 1

F2 - Acquisition Parameters
Date_ 20230512
Time 15.07 h
INSTRUM av500
PROBHD Z119248_0002 (
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 1
DS 0
SWH 10000.000 Hz
FIDRES 0.305176 Hz
AQ 3.2767999 sec
RG 12.14
DW 50.000 usec
DE 10.00 usec
TE 298.0 K
D1 2.00000000 sec
TD0 1
SFO1 500.1330008 MHz
NUC1 1H
P1 10.00 usec
PLW1 13.50000000 W

F2 - Processing parameters
SI 65536
SF 500.1300126 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

Purified product, 13C NMR

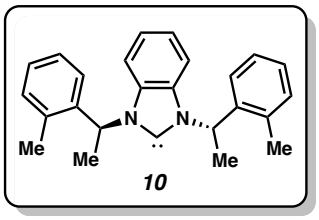


Current Data Parameters
NAME ASB-2023-000
EXPNO 11
PROCNO 1

F2 - Acquisition Parameters
Date_ 20230412
Time 18.30 h
INSTRUM av500
PROBHD Z119248_0002 (
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 88
DS 2
SWH 31250.000 Hz
FIDRES 0.953674 Hz
AQ 1.0485760 sec
RG 204.54
DW 16.000 usec
DE 28.00 usec
TE 298.0 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
SFO1 125.7722511 MHz
NUC1 13C
P1 10.50 usec
PLW1 23.00000000 W
SFO2 500.1330008 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 80.00 usec
PLW2 13.50000000 W
PLW12 0.21094000 W
PLW13 0.10610000 W

F2 - Processing parameters
SI 131072
SF 125.7577892 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

Purified product, 1H NMR

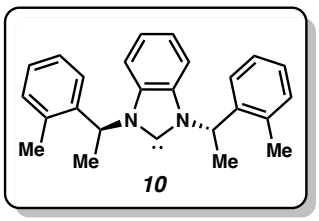


Current Data Parameters
NAME DJN-2023-064-carben
EXPNO 10
PROCNO 1

F2 - Acquisition Parameters
Date_ 20230504
Time 14.15 h
INSTRUM av500
PROBHD Z119248_0002 (
PULPROG zg30
TD 65536
SOLVENT Tol
NS 8
DS 0
SWH 10000.000 Hz
FIDRES 0.305176 Hz
AQ 3.2767999 sec
RG 12.14
DW 50.000 usec
DE 10.00 usec
TE 298.0 K
D1 2.00000000 sec
TD0 1
SFO1 500.1330008 MHz
NUC1 1H
P1 10.00 usec
PLW1 13.50000000 W

F2 - Processing parameters
SI 65536
SF 500.1300247 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

Purified product, 13C NMR

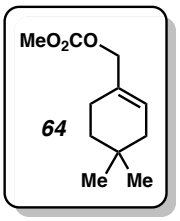


Current Data Parameters
NAME DJN-2023-064-carbe
EXPNO 10
PROCNO 1

F2 - Acquisition Parameters
Date_ 20230504
Time 14.20 h
INSTRUM av500
PROBHD Z119248_0002 (
PULPROG zgpg30
TD 65536
SOLVENT Tol
NS 72
DS 2
SWH 31250.000 Hz
FIDRES 0.953674 Hz
AQ 1.0485760 sec
RG 204.54
DW 16.000 usec
DE 28.00 usec
TE 298.0 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
SFO1 125.7722511 MHz
NUC1 13C
P1 10.50 usec
PLW1 23.00000000 W
SFO2 500.1330008 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 80.00 usec
PLW2 13.50000000 W
PLW12 0.21094000 W
PLW13 0.10610000 W

F2 - Processing parameters
SI 131072
SF 125.7577433 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

Purified product, 1H NMR

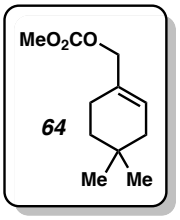


Current Data Parameters
NAME ATM-2022-142
EXPNO 2
PROCNO 1

F2 - Acquisition Parameters
Date_ 20221027
Time 14.45 h
INSTRUM Avance
PROBHD Z168773_0038 (
PULPROG zg30
TD 81920
SOLVENT CDCl3
NS 8
DS 0
SWH 11904.762 Hz
FIDRES 0.290644 Hz
AQ 3.4406400 sec
RG 90.5
DW 42.000 usec
DE 13.70 usec
TE 298.0 K
D1 1.00000000 sec
TD0 1
SFO1 600.1337058 MHz
NUC1 1H
P0 4.00 usec
P1 12.00 usec
PLW1 19.40099907 W

F2 - Processing parameters
SI 65536
SF 600.1300148 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

Purified product, 13C NMR

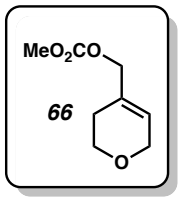


Current Data Parameters
NAME ATM-2022-142
EXPNO 16
PROCNO 1

F2 - Acquisition Parameters
Date_ 20230604
Time 17.42 h
INSTRUM av500
PROBHD Z119248_0002 (
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 8
DS 2
SWH 31250.000 Hz
FIDRES 0.953674 Hz
AQ 1.0485760 sec
RG 204.54
DW 16.000 usec
DE 28.00 usec
TE 298.0 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
SFO1 125.7722511 MHz
NUC1 13C
P1 10.50 usec
PLW1 23.00000000 W
SFO2 500.1330008 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 80.00 usec
PLW2 13.50000000 W
PLW12 0.21094000 W
PLW13 0.10610000 W

F2 - Processing parameters
SI 131072
SF 125.7577892 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

Purified product, 1H NMR

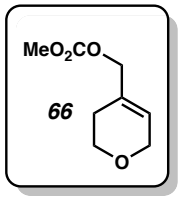


Current Data Parameters
NAME ATM-2022-117
EXPNO 23
PROCNO 1

F2 - Acquisition Parameters
Date_ 20230609
Time 10.13 h
INSTRUM av500
PROBHD Z119248_0002 (
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 8
DS 0
SWH 10000.000 Hz
FIDRES 0.305176 Hz
AQ 3.2767999 sec
RG 23.34
DW 50.000 usec
DE 10.00 usec
TE 298.0 K
D1 2.00000000 sec
TD0 1
SFO1 500.1330008 MHz
NUC1 1H
P1 10.00 usec
PLW1 13.50000000 W

F2 - Processing parameters
SI 65536
SF 500.1300121 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

Purified product, 13C NMR

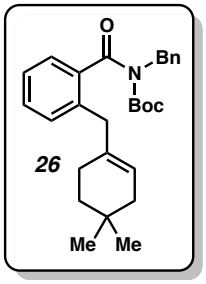


Current Data Parameters
NAME ATM-2022-117
EXPNO 27
PROCNO 1

F2 - Acquisition Parameters
Date_ 20230609
Time 10.41 h
INSTRUM av500
PROBHD Z119248_0002 (
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 100
DS 2
SWH 31250.000 Hz
FIDRES 0.953674 Hz
AQ 1.0485760 sec
RG 204.54
DW 16.000 usec
DE 28.00 usec
TE 298.0 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
SFO1 125.7722511 MHz
NUC1 13C
P1 10.50 usec
PLW1 23.00000000 W
SFO2 500.1330008 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 80.00 usec
PLW2 13.50000000 W
PLW12 0.21094000 W
PLW13 0.10610000 W

F2 - Processing parameters
SI 131072
SF 125.7577892 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

Purified product, 1H NMR

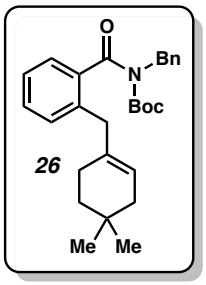


Current Data Parameters
NAME ATM-2022-145
EXPNO 81
PROCNO 1

F2 - Acquisition Parameters
Date_ 20230602
Time 13.21 h
INSTRUM Avance
PROBHD Z168773_0038 (
PULPROG zg30
TD 81920
SOLVENT CDCl3
NS 8
DS 0
SWH 11904.762 Hz
FIDRES 0.290644 Hz
AQ 3.4406400 sec
RG 101
DW 42.000 usec
DE 13.70 usec
TE 298.0 K
D1 1.00000000 sec
TD0 1
SFO1 600.1337058 MHz
NUC1 1H
P0 4.00 usec
P1 12.00 usec
PLW1 19.40099907 W

F2 - Processing parameters
SI 65536
SF 600.1300149 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

Purified product, 13C NMR

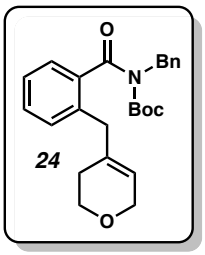


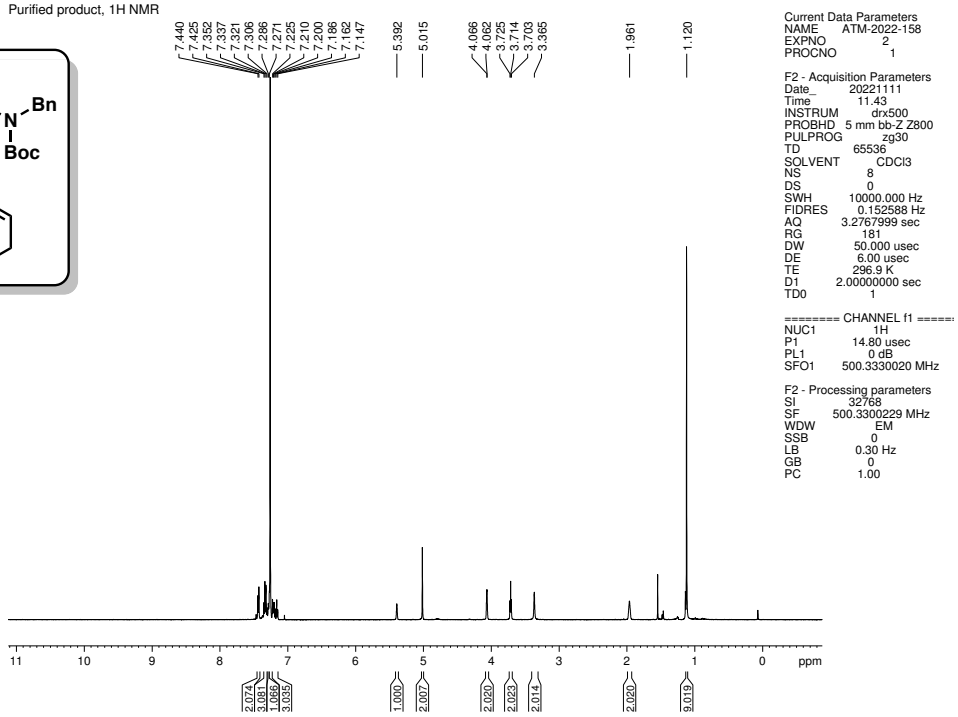
Current Data Parameters
NAME ATM-2022-145
EXPNO 21
PROCNO 1

F2 - Acquisition Parameters
Date_ 20230601
Time 17.53 h
INSTRUM Avance
PROBHD Z168773_0038 (
PULPROG zgpg30
TD 131072
SOLVENT CDCl3
NS 100
DS 0
SWH 35714.285 Hz
FIDRES 0.544957 Hz
AQ 1.8350080 sec
RG 101
DW 14.000 usec
DE 18.00 usec
TE 298.0 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
SFO1 150.9178988 MHz
NUC1 13C
P0 3.33 usec
P1 10.00 usec
PLW1 86.29599762 W
SFO2 600.1324005 MHz
NUC2 1H
CPDPRG[2 waltz65
PCPD2 80.00 usec
PLW2 19.40099907 W
PLW12 0.43652001 W
PLW13 0.21922000 W

F2 - Processing parameters
SI 65536
SF 150.9027910 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

Purified product, 1H NMR





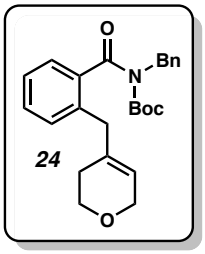
Current Data Parameters
NAME ATM-2022-158
EXPNO 2
PROCNO 1

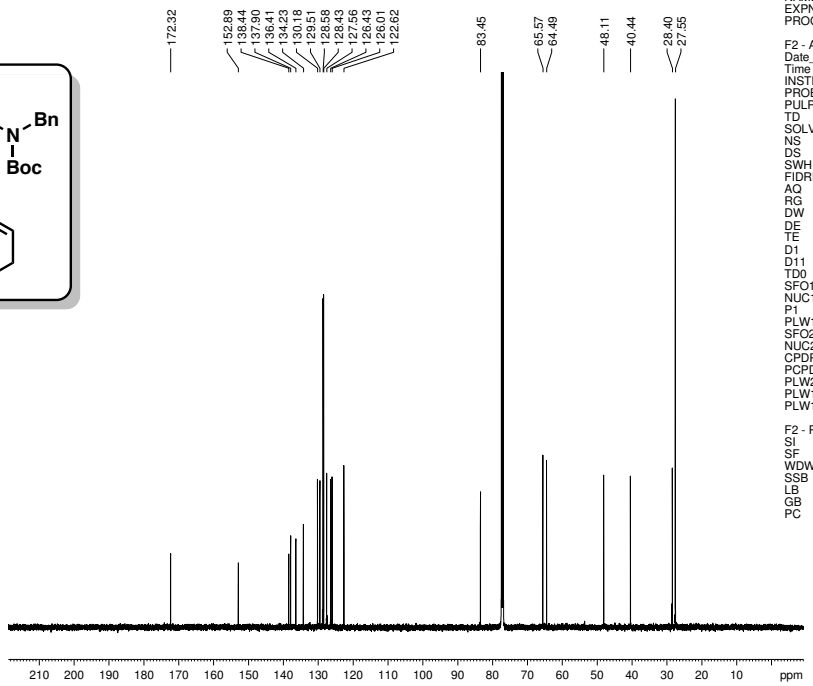
F2 - Acquisition Parameters
Date_ 20221111
Time 11.43
INSTRUM drx500
PROBHD 5 mm bb-Z Z800
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 8
DS 0
SWH 10000.000 Hz
FIDRES 0.152588 Hz
AQ 3.2767999 sec
RG 181
DW 50.000 usec
DE 6.00 usec
TE 296.9 K
D1 2.00000000 sec
TD0 1

======== CHANNEL f1 ======
NUC1 1H
P1 14.80 usec
PL1 0 dB
SFO1 500.3330020 MHz

F2 - Processing parameters
SI 32768
SF 500.3300229 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

Purified product, 13C NMR



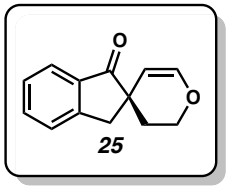


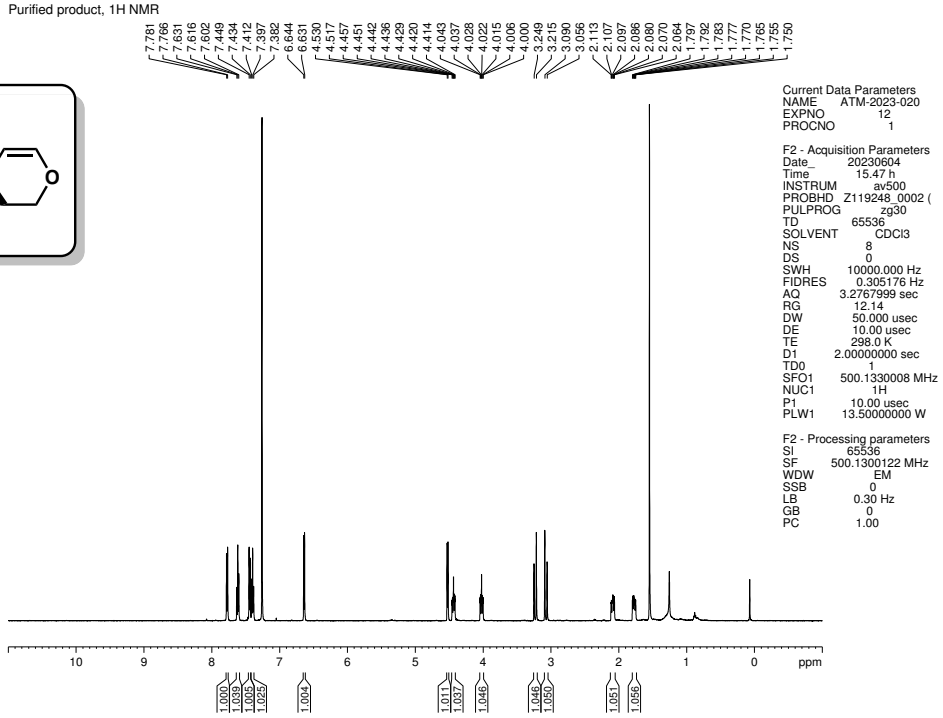
Current Data Parameters
NAME ATM-2022-158
EXPNO 18
PROCNO 1

F2 - Acquisition Parameters
Date_ 20230604
Time 18.04 h
INSTRUM av500
PROBHD Z119248_0002 (
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 64
DS 2
SWH 31250.000 Hz
FIDRES 0.953674 Hz
AQ 1.0485760 sec
RG 204.54
DW 16.000 usec
DE 28.00 usec
TE 298.0 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
SFO1 125.7722511 MHz
NUC1 13C
P1 10.50 usec
PLW1 23.00000000 W
SFO2 500.1330008 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 80.00 usec
PLW2 13.50000000 W
PLW12 0.21094000 W
PLW13 0.10610000 W

F2 - Processing parameters
SI 131072
SF 125.7577729 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

Purified product, 1H NMR



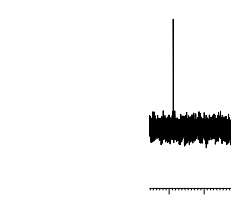


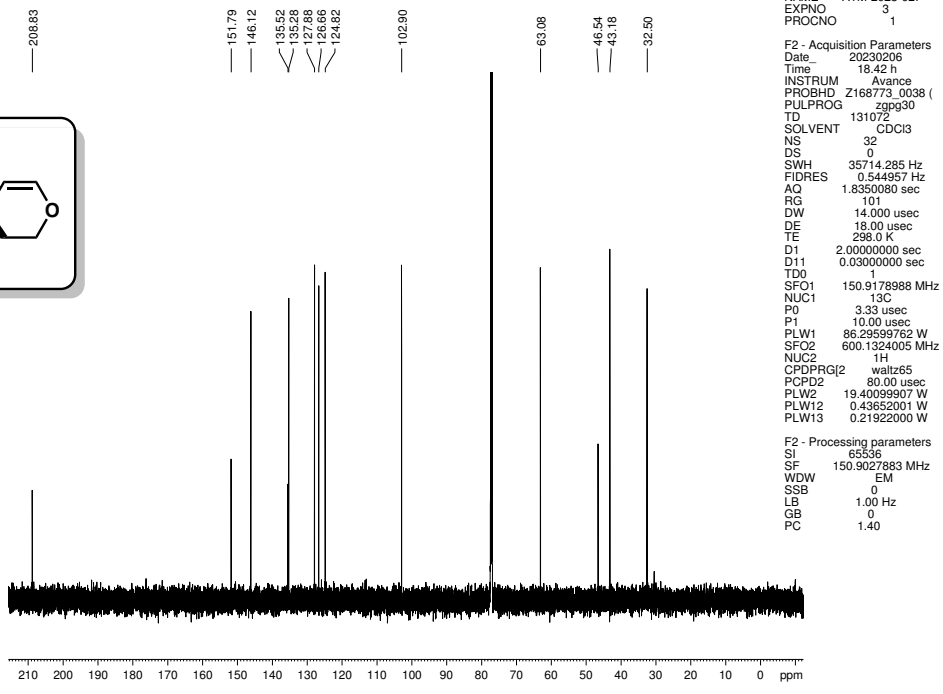
Current Data Parameters
NAME ATM-2023-020
EXPNO 12
PROCNO 1

F2 - Acquisition Parameters
Date_ 20230604
Time 15.47 h
INSTRUM av500
PROBHD Z119248_0002 (
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 8
DS 0
SWH 10000.000 Hz
FIDRES 0.305176 Hz
AQ 3.2767999 sec
RG 12.14
DW 50.000 usec
DE 10.00 usec
TE 298.0 K
D1 2.00000000 sec
TD0 1
SFO1 500.1330008 MHz
NUC1 1H
P1 10.00 usec
PLW1 13.50000000 W

F2 - Processing parameters
SI 65536
SF 500.1300122 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

Purified product, 13C NMR



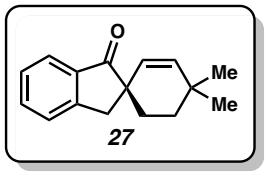


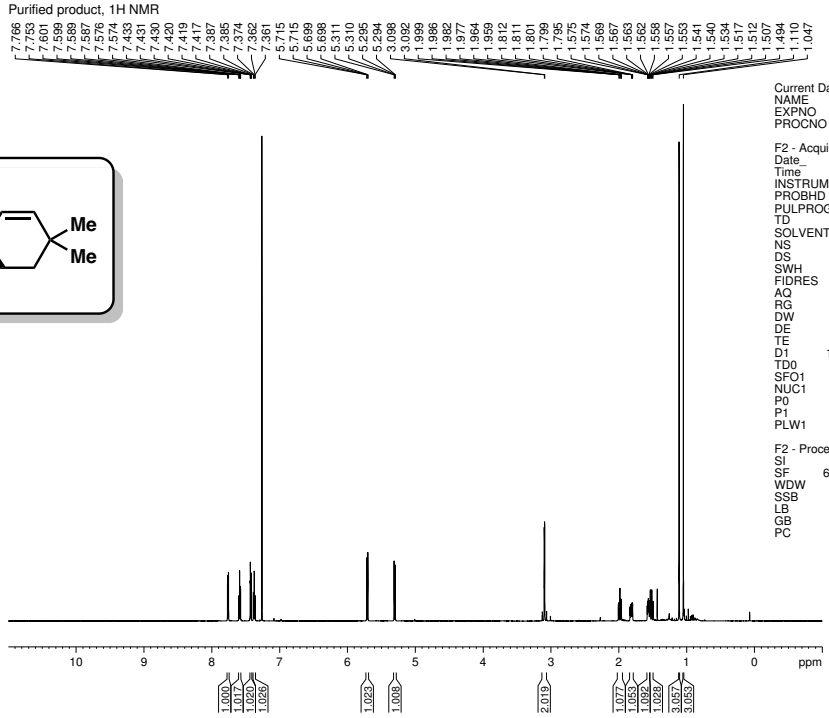
Current Data Parameters
NAME ATM-2023-027
EXPNO 3
PROCNO 1

F2 - Acquisition Parameters
Date_ 20230206
Time 18.42 h
INSTRUM Avance
PROBHD Z168773_0038 (
PULPROG zgpg30
TD 131072
SOLVENT CDCl3
NS 32
DS 0
SWH 35714.285 Hz
FIDRES 0.544957 Hz
AQ 1.8350080 sec
RG 101
DW 14.000 usec
DE 18.00 usec
TE 298.0 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
SFO1 150.9178988 MHz
NUC1 13C
P0 3.33 usec
P1 10.00 usec
PLW1 86.29599762 W
SFO2 600.1324005 MHz
NUC2 1H
CPDPRG[2 waltz65
PCPD2 80.00 usec
PLW2 19.40099907 W
PLW12 0.43652001 W
PLW13 0.21922000 W

F2 - Processing parameters
SI 65536
SF 150.9027883 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

Purified product, 1H NMR



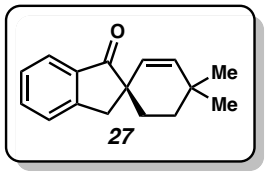


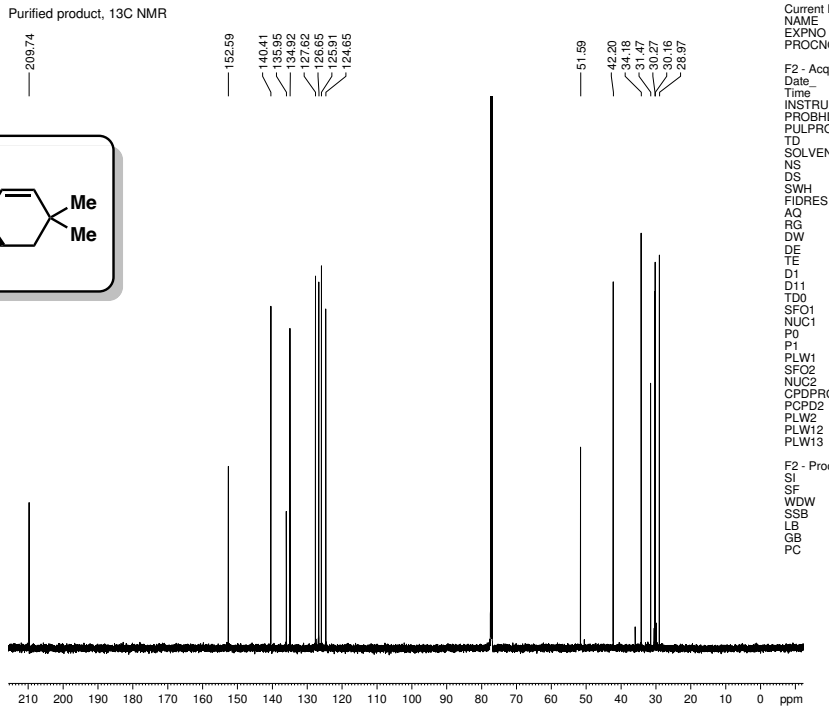
Current Data Parameters
NAME ATM-2023-017
EXPNO 2
PROCNO 1

F2 - Acquisition Parameters
Date_ 20230126
Time 17.58 h
INSTRUM Avance
PROBHD Z168773_0038 (
PULPROG zg30
TD 81920
SOLVENT CDCl3
NS 8
DS 0
SWH 11904.762 Hz
FIDRES 0.290644 Hz
AQ 3.4406400 sec
RG 101
DW 42.000 usec
DE 13.70 usec
TE 298.0 K
D1 1.00000000 sec
TD0 1
SFO1 600.1337058 MHz
NUC1 1H
P0 4.00 usec
P1 12.00 usec
PLW1 19.40099907 W

F2 - Processing parameters
SI 65536
SF 600.1300148 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

Purified product, 13C NMR

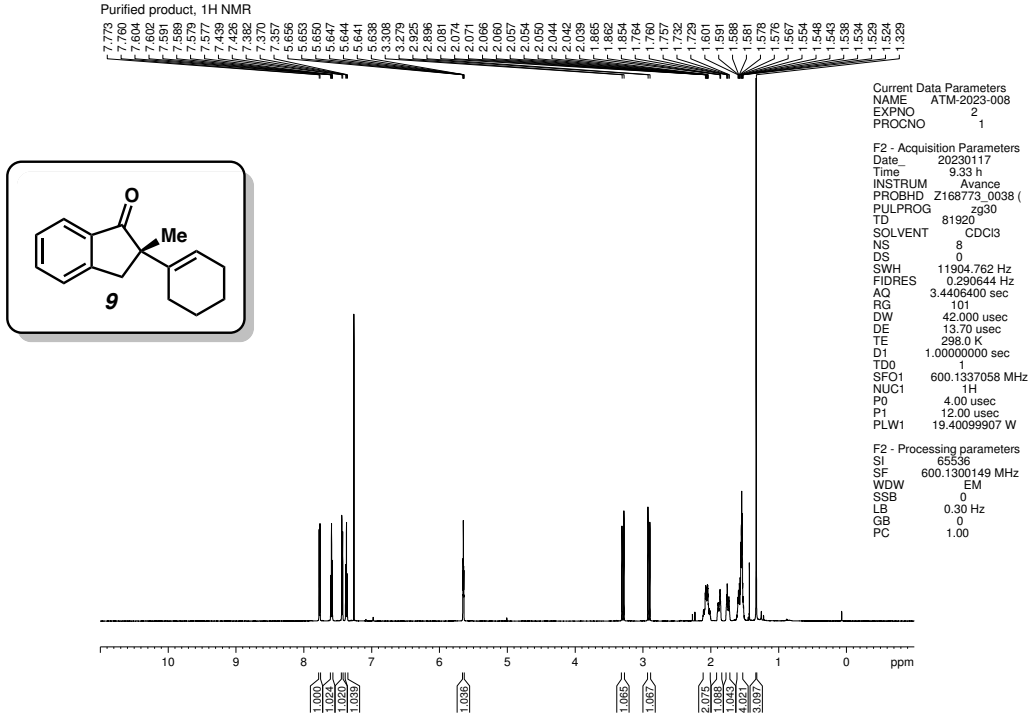


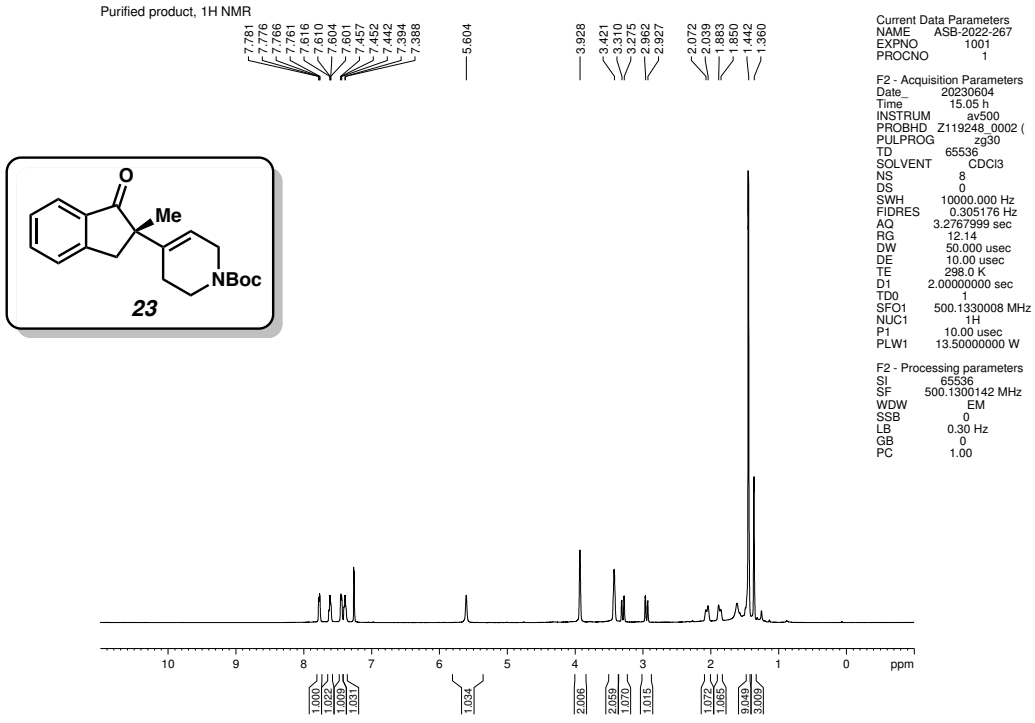


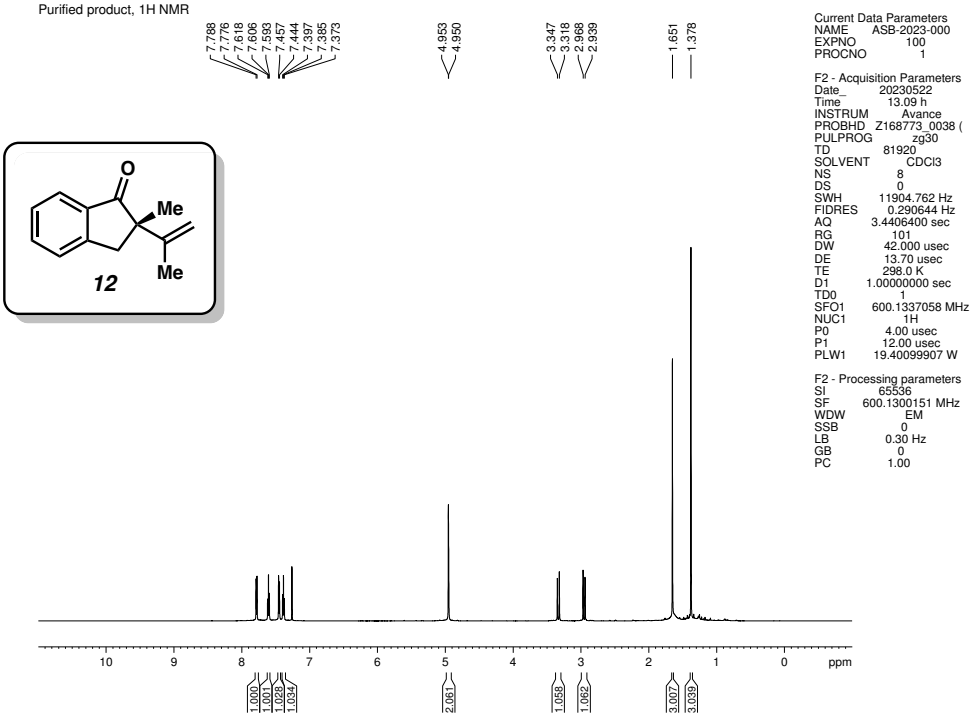
Current Data Parameters
NAME ATM-2023-014
EXPNO 3
PROCNO 1

F2 - Acquisition Parameters
Date_ 20230123
Time 17.07 h
INSTRUM Avance
PROBHD Z168773_0038 (
PULPROG zgpg30
TD 131072
SOLVENT CDCl3
NS 64
DS 0
SWH 35714.285 Hz
FIDRES 0.544957 Hz
AQ 1.8350080 sec
RG 101
DW 14.000 usec
DE 18.00 usec
TE 298.0 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
SFO1 150.9178988 MHz
NUC1 13C
P0 3.33 usec
P1 10.00 usec
PLW1 86.29599762 W
SFO2 600.1324005 MHz
NUC2 1H
CPDPRG[2 waltz65
PCPD2 80.00 usec
PLW2 19.40099907 W
PLW12 0.43652001 W
PLW13 0.21922000 W

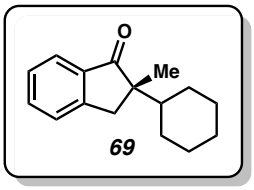
F2 - Processing parameters
SI 65536
SF 150.9027899 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

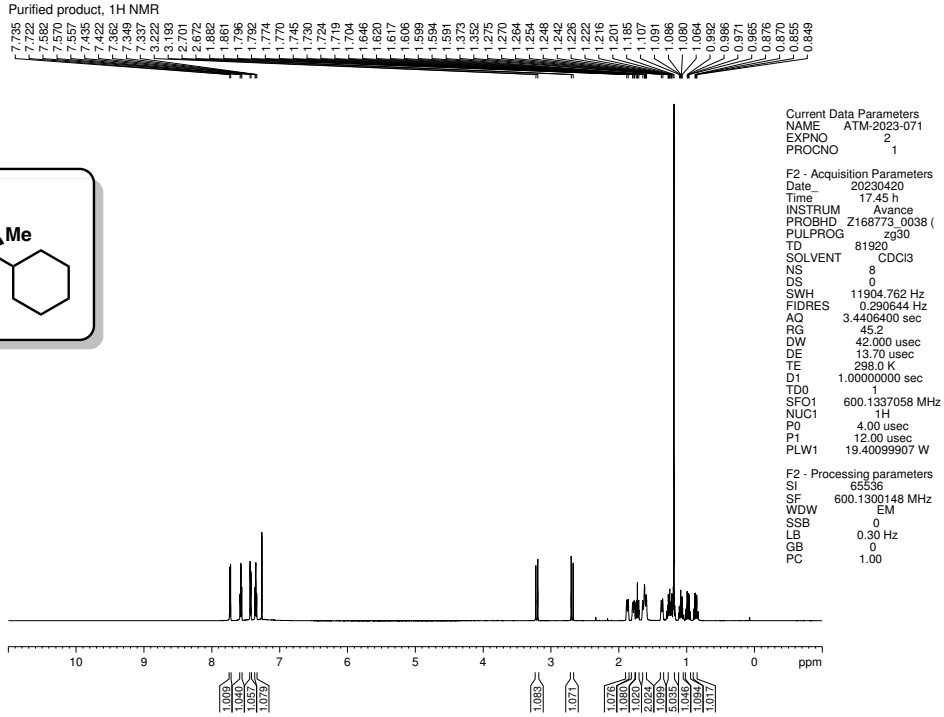

Purified product, 1H NMR
Me
9
Current Data Parameters
NAME ATM-2023-008
EXPNO 2
PROCNO 1
F2 - Acquisition Parameters
Date_ 20230117
Time 9.33 h
INSTRUM Avance
PULPROG zg30
TD 81920
SOLVENT CDCl3
NS 8
DS 0
SWH 11904.762 Hz
FIDRES 0.290644 Hz
AQ 3.4406400 sec
RG 101
DW 42.000 usec
DE 13.70 usec
TE 298.0 K
D1 1.00000000 sec
TD0 1
SFO1 600.1337058 MHz
NUC1 1H
P0 4.00 usec
P1 12.00 usec
PLW1 19.40099907 W
F2 - Processing parameters
SI 65536
SF 600.1300149 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
ppm


Purified product, 1H NMR
Me
NBoc
23
Current Data Parameters
NAME ASB-2022-267
EXPNO 1001
PROCNO 1
F2 - Acquisition Parameters
Date_ 20230604
Time 15.05 h
INSTRUM av500
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 8
DS 0
SWH 10000.000 Hz
FIDRES 0.305176 Hz
AQ 3.2767999 sec
RG 12.14
DW 50.000 usec
DE 10.00 usec
TE 298.0 K
D1 2.00000000 sec
TD0 1
SFO1 500.1330008 MHz
NUC1 1H
P1 10.00 usec
PLW1 13.50000000 W
F2 - Processing parameters
SI 65536
SF 500.1300142 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
ppm

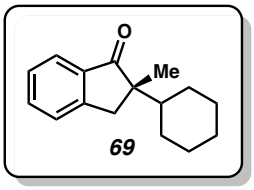

Purified product, 1H NMR
7.788
7.776
7.618
7.606
7.593
7.457
7.444
7.397
7.385
7.373
4.953
4.950
3.347
3.318
2.968
2.939
1.651
1.378
O
Me
Me
12
Current Data Parameters
NAME ASB-2023-000
EXPNO 100
PROCNO 1
F2 - Acquisition Parameters
Date_ 20230522
Time 13.09 h
INSTRUM Avance
PROBHD Z168773_0038 (
PULPROG zg30
TD 81920
SOLVENT CDCl3
NS 8
DS 0
SWH 11904.762 Hz
FIDRES 0.290644 Hz
AQ 3.4406400 sec
RG 101
DW 42.000 usec
DE 13.70 usec
TE 298.0 K
D1 1.00000000 sec
TD0 1
SFO1 600.1337058 MHz
NUC1 1H
P0 4.00 usec
P1 12.00 usec
PLW1 19.40099907 W
F2 - Processing parameters
SI 65536
SF 600.1300151 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
10
9
8
7
6
5
4
3
2
1
0
ppm
1.000
1.001
1.028
1.034
2.061
1.058
1.062
3.007
3.039

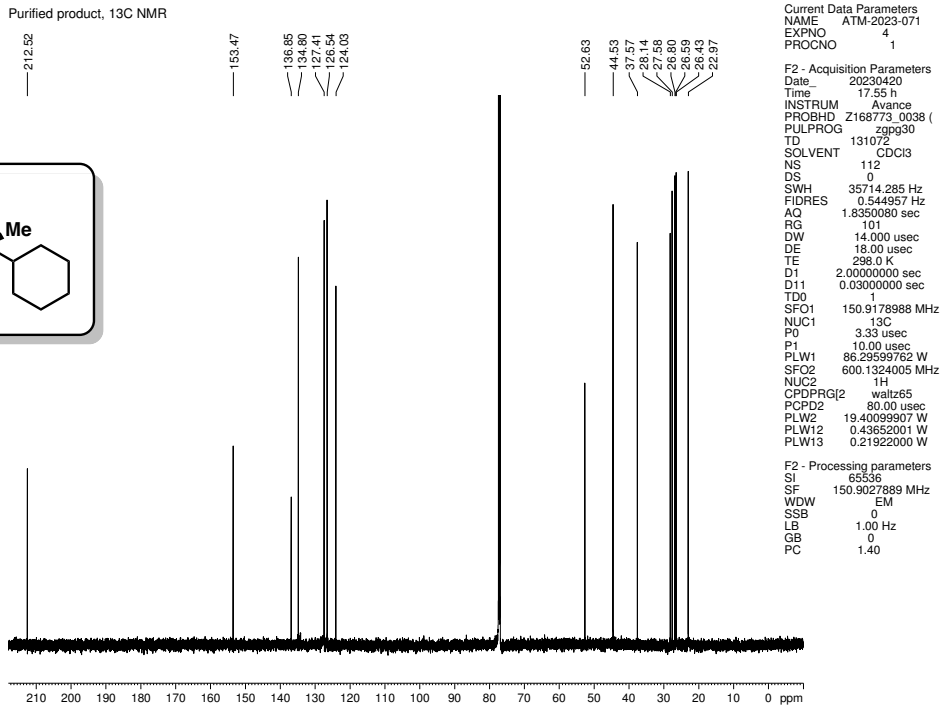
Purified product, 1H NMR



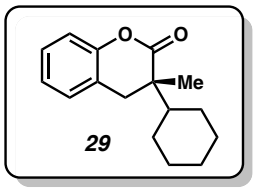


Purified product, 13C NMR





Purified product, 1H NMR

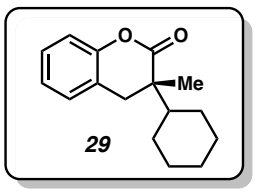


Current Data Parameters
NAME ATM-2023-051
EXPNO 8
PROCNO 1

F2 - Acquisition Parameters
Date_ 20230328
Time 18.49 h
INSTRUM Avance
PROBHD Z168773_0038 (
PULPROG zg30
TD 81920
SOLVENT CDCl3
NS 8
DS 0
SWH 11904.762 Hz
FIDRES 0.290644 Hz
AQ 3.4406400 sec
RG 57
DW 42.000 usec
DE 13.70 usec
TE 298.0 K
D1 1.00000000 sec
TD0 1
SFO1 600.1337058 MHz
NUC1 1H
P0 4.00 usec
P1 12.00 usec
PLW1 19.40099907 W

F2 - Processing parameters
SI 65536
SF 600.1300152 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

Purified product, 13C NMR

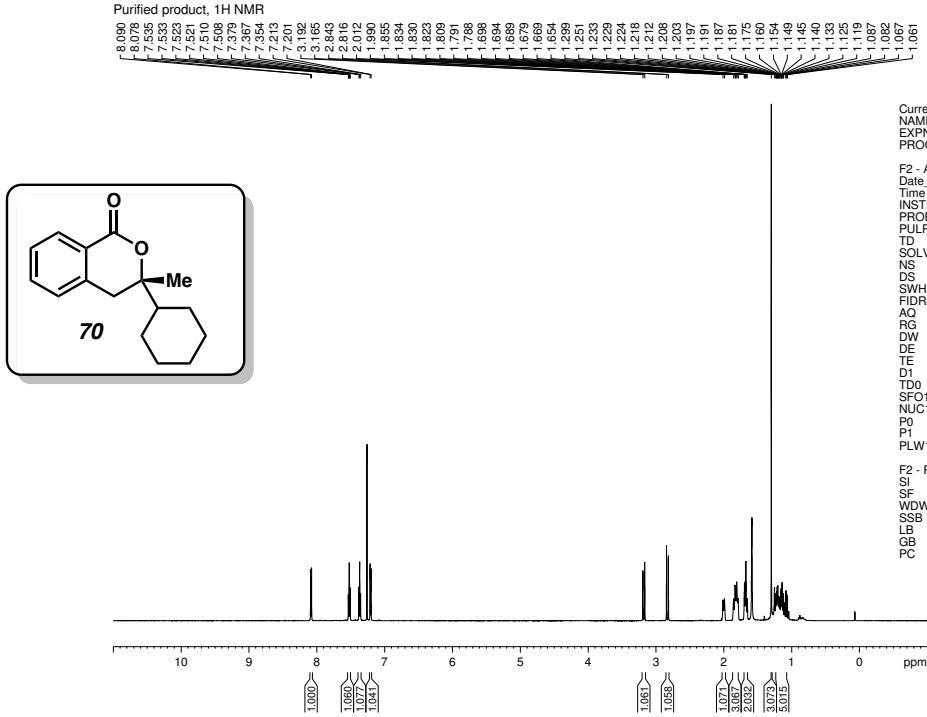


Current Data Parameters
NAME ATM-2023-051
EXPNO 3
PROCNO 1

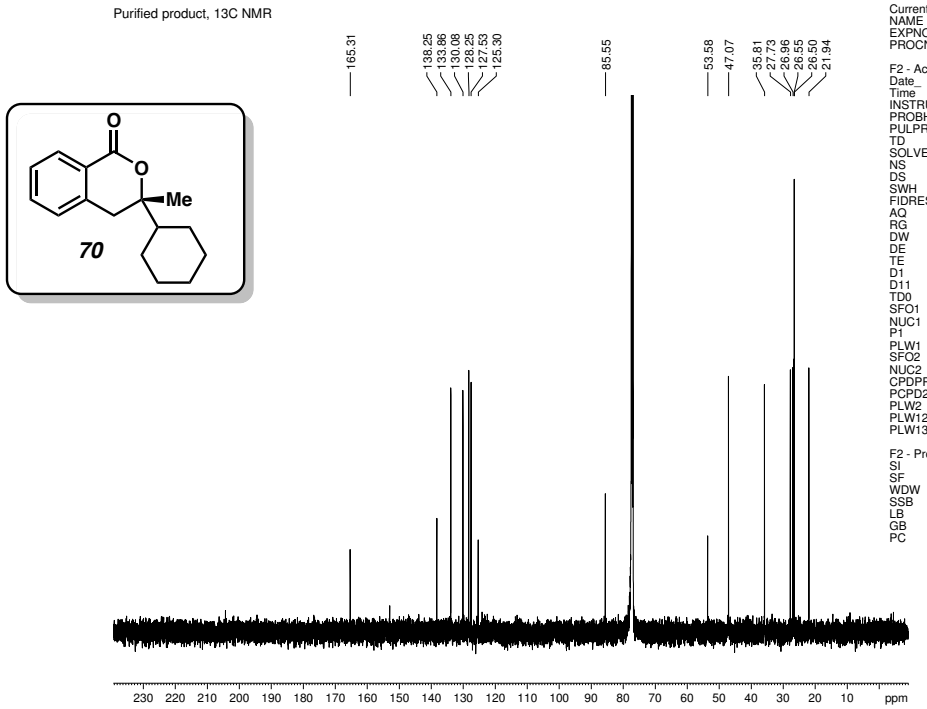
F2 - Acquisition Parameters
Date_ 20230328
Time 14.09 h
INSTRUM av500
PROBHD Z119248_0002 (
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 8
DS 2
SWH 31250.000 Hz
FIDRES 0.953674 Hz
AQ 1.0485760 sec
RG 204.54
DW 16.000 usec
DE 28.00 usec
TE 298.0 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
SFO1 125.7722511 MHz
NUC1 13C
P1 10.50 usec
PLW1 23.00000000 W
SFO2 500.1330008 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 80.00 usec
PLW2 13.50000000 W
PLW12 0.21094000 W
PLW13 0.10610000 W

F2 - Processing parameters
SI 131072
SF 125.7577892 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

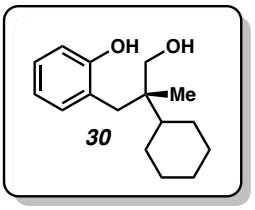
Purified product, 1H NMR



Purified product, 13C NMR



Purified product, 1H NMR

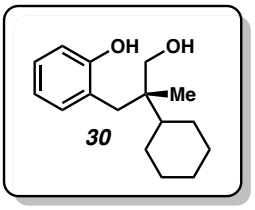


Current Data Parameters
NAME ATM-2023-075
EXPNO 2
PROCNO 1

F2 - Acquisition Parameters
Date_ 20230425
Time 16.50 h
INSTRUM Avance
PROBHD Z168773_0038 (
PULPROG zg30
TD 81920
SOLVENT CDCl3
NS 8
DS 0
SWH 11904.762 Hz
FIDRES 0.290644 Hz
AQ 3.4406400 sec
RG 101
DW 42.000 usec
DE 13.70 usec
TE 298.0 K
D1 1.00000000 sec
TD0 1
SFO1 600.1337058 MHz
NUC1 1H
P0 4.00 usec
P1 12.00 usec
PLW1 19.40099907 W

F2 - Processing parameters
SI 65536
SF 600.1300166 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

Purified product, 13C NMR

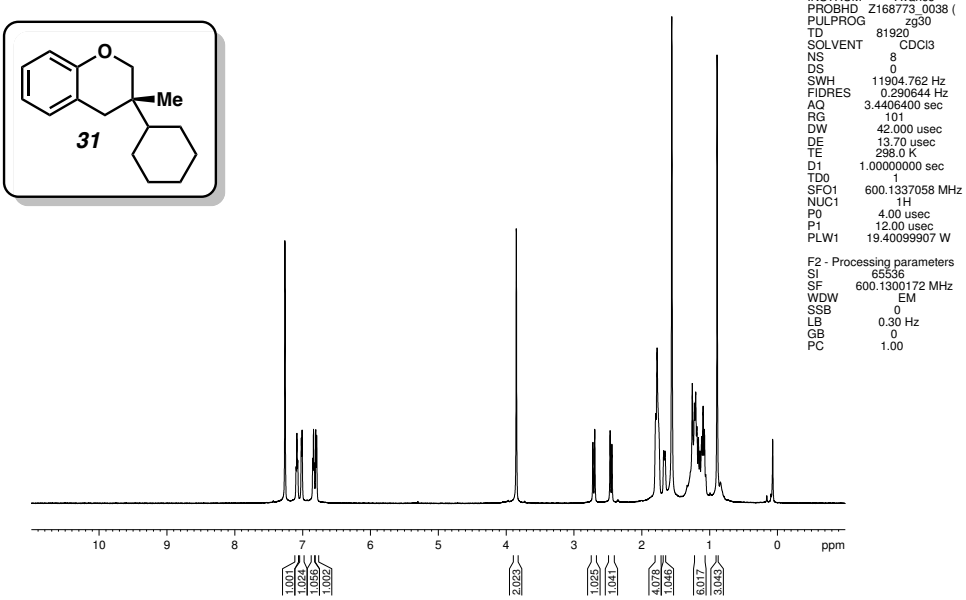


Current Data Parameters
NAME ATM-2023-075
EXPNO 15
PROCNO 1

F2 - Acquisition Parameters
Date_ 20230602
Time 11.43 h
INSTRUM Avance
PROBHD Z168773_0038 (
PULPROG zgpg30
TD 131072
SOLVENT CDCl3
NS 1700
DS 0
SWH 35714.285 Hz
FIDRES 0.544957 Hz
AQ 1.8350080 sec
RG 101
DW 14.000 usec
DE 18.00 usec
TE 298.0 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
SFO1 150.9178988 MHz
NUC1 13C
P0 3.33 usec
P1 10.00 usec
PLW1 86.29599762 W
SFO2 600.1324005 MHz
NUC2 1H
CPDPRG[2 waltz65
PCPD2 80.00 usec
PLW2 19.40099907 W
PLW12 0.43652001 W
PLW13 0.21922000 W

F2 - Processing parameters
SI 65536
SF 150.9027880 MHz
WDW no
SSB 0
LB 0 Hz
GB 0
PC 1.40

Purified product, 1H NMR

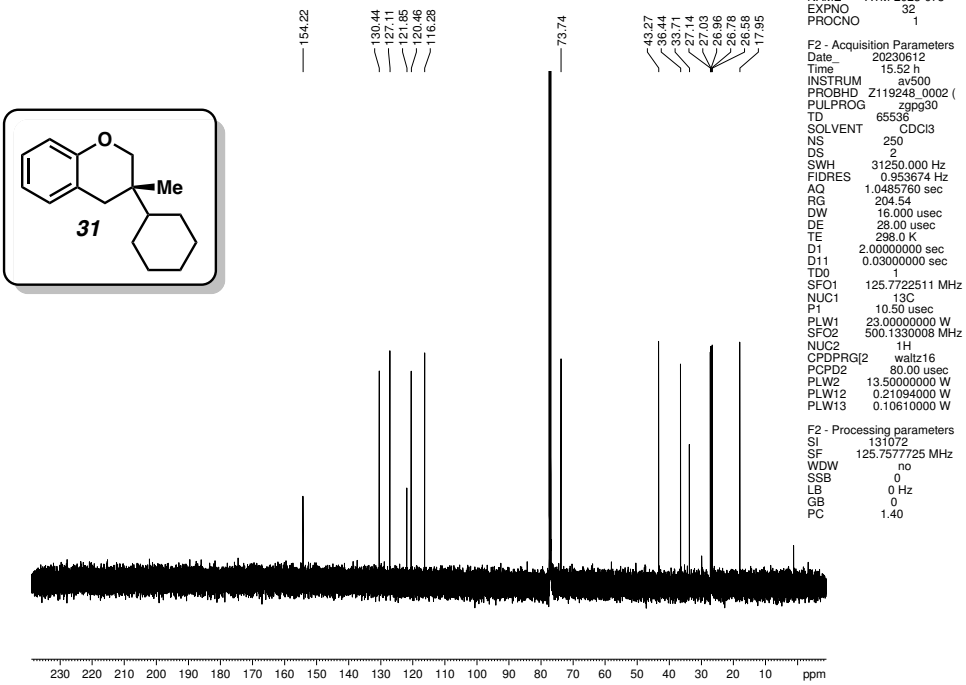


Current Data Parameters
NAME ATM-2023-078
EXPNO 2
PROCNO 1

F2 - Acquisition Parameters
Date_ 20230427
Time 16.27 h
INSTRUM Avance
PROBHD Z168773_0038 (
PULPROG zg30
TD 81920
SOLVENT CDCl3
NS 8
DS 0
SWH 11904.762 Hz
FIDRES 0.290644 Hz
AQ 3.4406400 sec
RG 101
DW 42.000 usec
DE 13.70 usec
TE 298.0 K
D1 1.00000000 sec
TD0 1
SFO1 600.1337058 MHz
NUC1 1H
P0 4.00 usec
P1 12.00 usec
PLW1 19.40099907 W

F2 - Processing parameters
SI 65536
SF 600.1300172 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

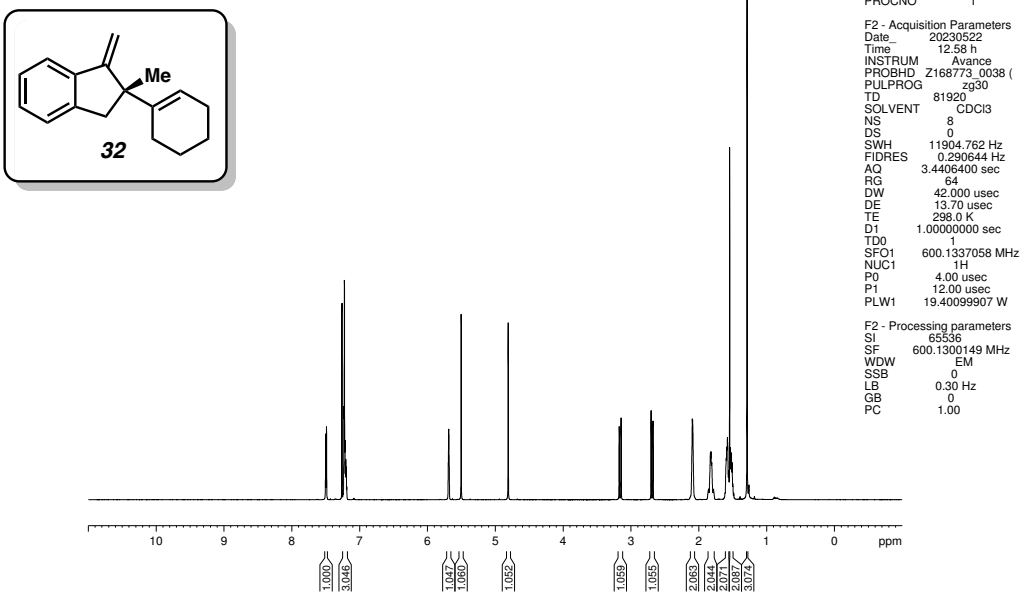
Purified product, 13C NMR

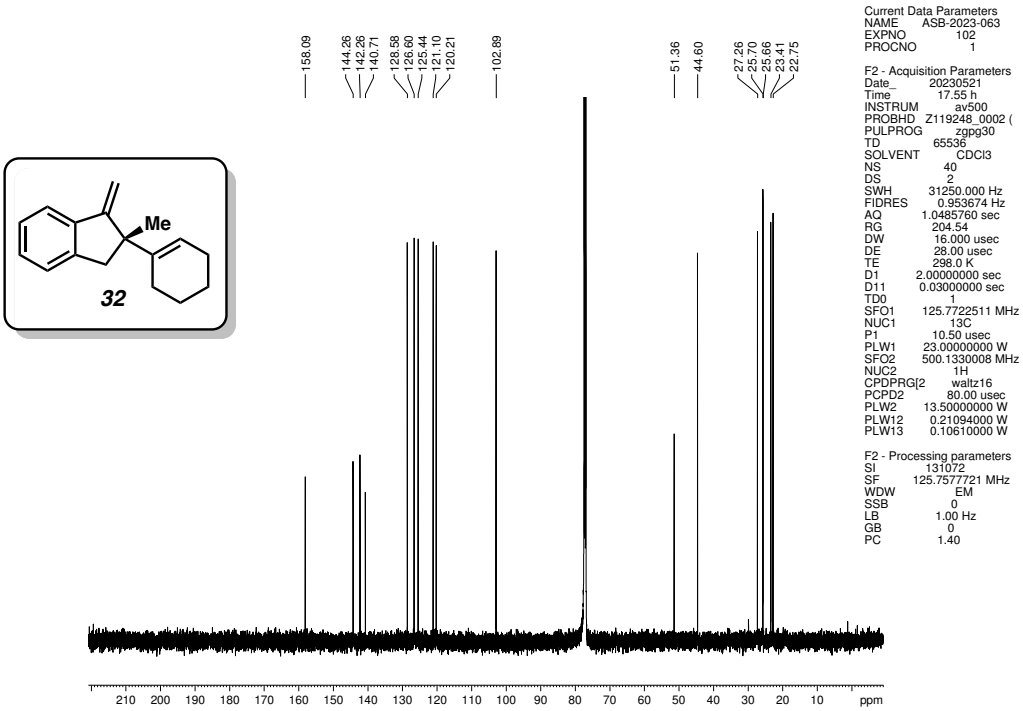


Current Data Parameters
NAME ATM-2023-078
EXPNO 32
PROCNO 1

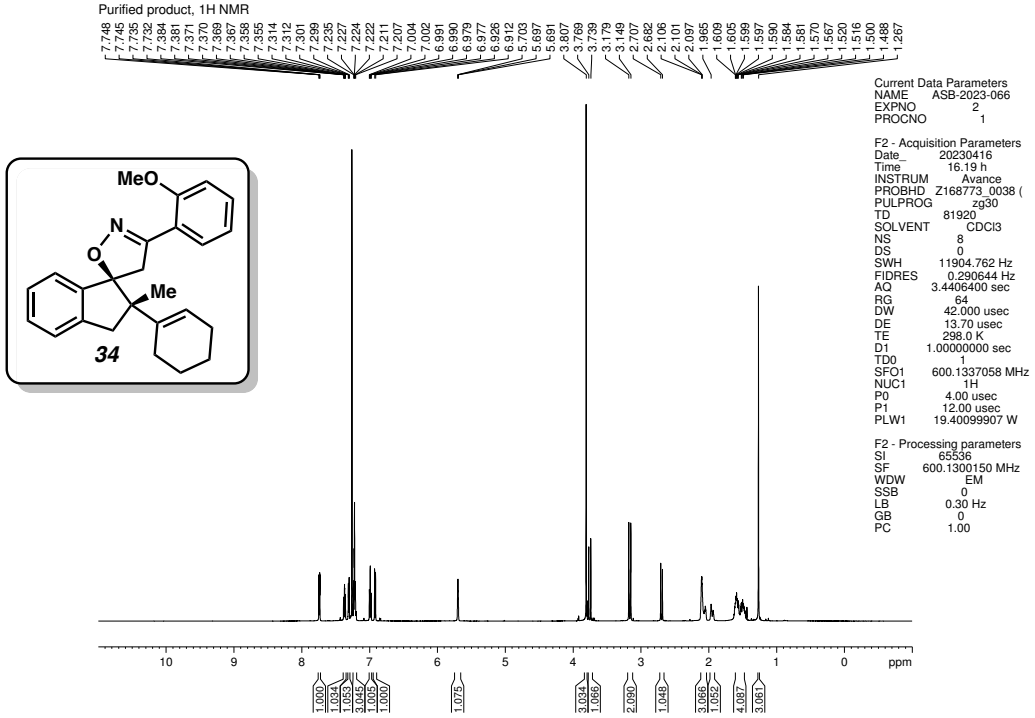
F2 - Acquisition Parameters
Date_ 20230612
Time 15.52 h
INSTRUM av500
PROBHD Z119248_0002 (
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 250
DS 2
SWH 31250.000 Hz
FIDRES 0.953674 Hz
AQ 1.0485760 sec
RG 204.54
DW 16.000 usec
DE 28.00 usec
TE 298.0 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
SFO1 125.7722511 MHz
NUC1 13C
P1 10.50 usec
PLW1 23.00000000 W
SFO2 500.1330008 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 80.00 usec
PLW2 13.50000000 W
PLW12 0.21094000 W
PLW13 0.10610000 W

F2 - Processing parameters
SI 131072
SF 125.7577725 MHz
WDW no
SSB 0
LB 0 Hz
GB 0
PC 1.40

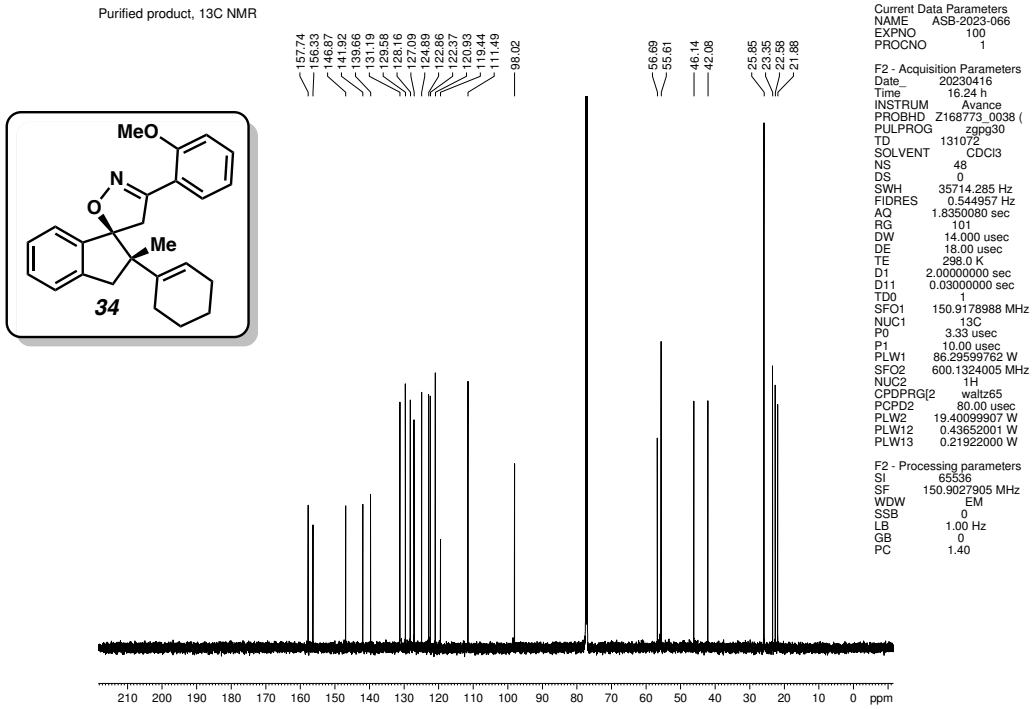

7.500
7.488
7.230
7.224
7.216
7.209
7.204
7.197
7.189
5.686
5.503
4.809
3.172
3.145
2.702
2.674
2.095
2.090
1.854
1.828
1.820
1.809
1.783
1.594
1.588
1.583
1.577
1.538
1.534
1.524
1.518
1.508
1.497
1.287
Me
32
Current Data Parameters
NAME ASB-2023-062
EXPNO 100
PROCNO 1
F2 - Acquisition Parameters
Date_ 20230522
Time 12.58 h
INSTRUM Avance
PROBHD Z168773_0038 (
PULPROG zg30
TD 81920
SOLVENT CDCl3
NS 8
DS 0
SWH 11904.762 Hz
FIDRES 0.290644 Hz
AQ 3.4406400 sec
RG 64
DW 42.000 usec
DE 13.70 usec
TE 298.0 K
D1 1.00000000 sec
TD0 1
SFO1 600.1337058 MHz
NUC1 1H
P0 4.00 usec
P1 12.00 usec
PLW1 19.40099907 W
F2 - Processing parameters
SI 65536
SF 600.1300149 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
10 9 8 7 6 5 4 3 2 1 0 ppm
1.000
3.046
1.047
1.060
1.052
1.059
1.055
2.063
2.044
2.077
2.087
3.074

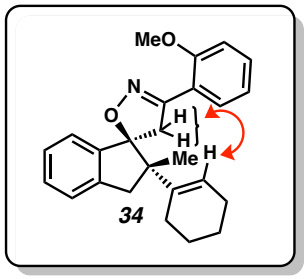

158.09
144.26
142.26
140.71
128.58
126.60
125.44
121.10
120.21
102.89
51.36
44.60
27.26
25.70
25.66
23.41
22.75
Me
32
Current Data Parameters
NAME ASB-2023-063
EXPNO 102
PROCNO 1
F2 - Acquisition Parameters
Date_ 20230521
Time 17.55 h
INSTRUM av500
PROBHD Z119248_0002 (
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 40
DS 2
SWH 31250.000 Hz
FIDRES 0.953674 Hz
AQ 1.0485760 sec
RG 204.54
DW 16.000 usec
DE 28.00 usec
TE 298.0 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
SFO1 125.7722511 MHz
NUC1 13C
P1 10.50 usec
PLW1 23.00000000 W
SFO2 500.1330008 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 80.00 usec
PLW2 13.50000000 W
PLW12 0.21094000 W
PLW13 0.10610000 W
F2 - Processing parameters
SI 131072
SF 125.7577721 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

Purified product, 1H NMR

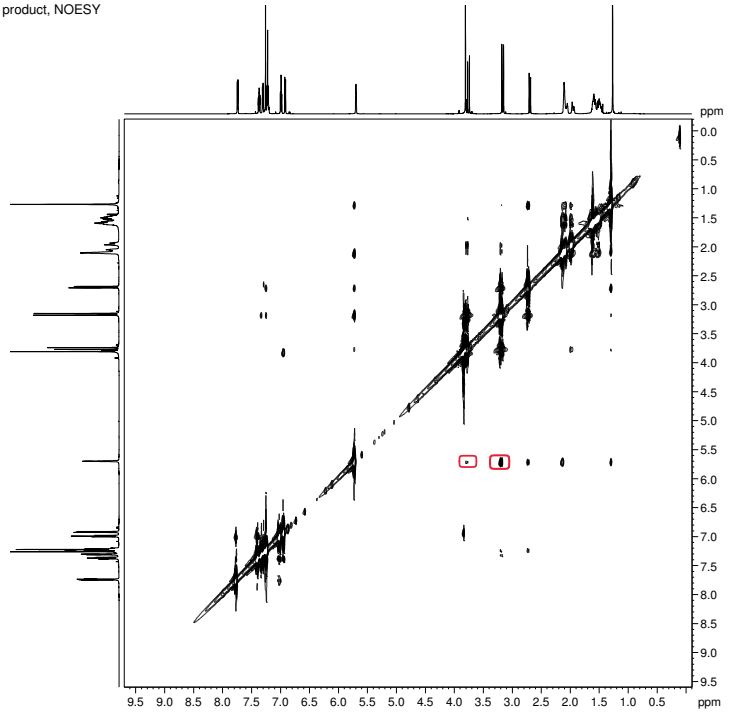


Purified product, 13C NMR





Purified product, NOESY

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Current Data Parameters
NAME        ASB-2023-074
EXPNO             1111
PROCNO               1

F2 - Acquisition Parameters
Date_         20230605
Time           7.48 h
INSTRUM         Avance
PROBHD  Z168773_0038 (
PULPROG      noesygpph
TD               2048
SOLVENT         CDCl3
NS                 72
DS                  4
SWH          5882.353 Hz
FIDRES       5.744485 Hz
AQ           0.1740800 sec
RG                101
DW             85.000 usec
DE             13.61 usec
TE             298.0 K
D0          0.00006972 sec
D1          2.00000000 sec
D8          0.30000001 sec
D16         0.00020000 sec
IN0         0.00017000 sec
TDav                1
SFO1        600.1328206 MHz
NUC1               1H
P1              12.00 usec
P2              24.00 usec
PLW1        19.40099907 W
GPNAM[1]    SMSQ10.100
GPZ1           40.00 %
P16          1000.00 usec

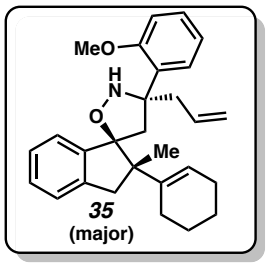
======== F1 INDIRECT DIMEN
td1      256
sw_F1    9.801752

F1 - Acquisition parameters
TD               256
SFO1        600.1328 MHz
FIDRES      45.955883 Hz
SW          9.802 ppm
FnMODE           TPPI

F2 - Processing parameters
SI              1024
SF        600.1300001 MHz
WDW             QSINE
SSB                2
LB              0 Hz
GB                 0
PC              1.00

F1 - Processing parameters
SI              1024
MC2             TPPI
SF        600.1300017 MHz
WDW             QSINE
SSB                2
LB              0 Hz
GB                 0
```

Purified product, 1H NMR

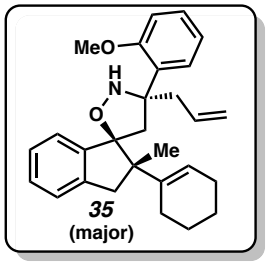


Current Data Parameters
NAME ASB-2023-070
EXPNO 3000
PROCNO 1

F2 - Acquisition Parameters
Date_ 20230522
Time 17.51 h
INSTRUM Avance
PROBHD Z168773_0038 (
PULPROG zg30
TD 81920
SOLVENT DMSO
NS 8
DS 0
SWH 11904.762 Hz
FIDRES 0.290644 Hz
AQ 3.4406400 sec
RG 101
DW 42.000 usec
DE 13.70 usec
TE 298.0 K
D1 1.00000000 sec
TD0 1
SFO1 600.1337058 MHz
NUC1 1H
P0 4.00 usec
P1 12.00 usec
PLW1 19.40099907 W

F2 - Processing parameters
SI 65536
SF 600.1300059 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

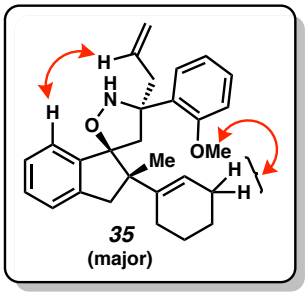
Purified product, 13C NMR



Current Data Parameters
NAME ASB-2023-070
EXPNO 3005
PROCNO 1

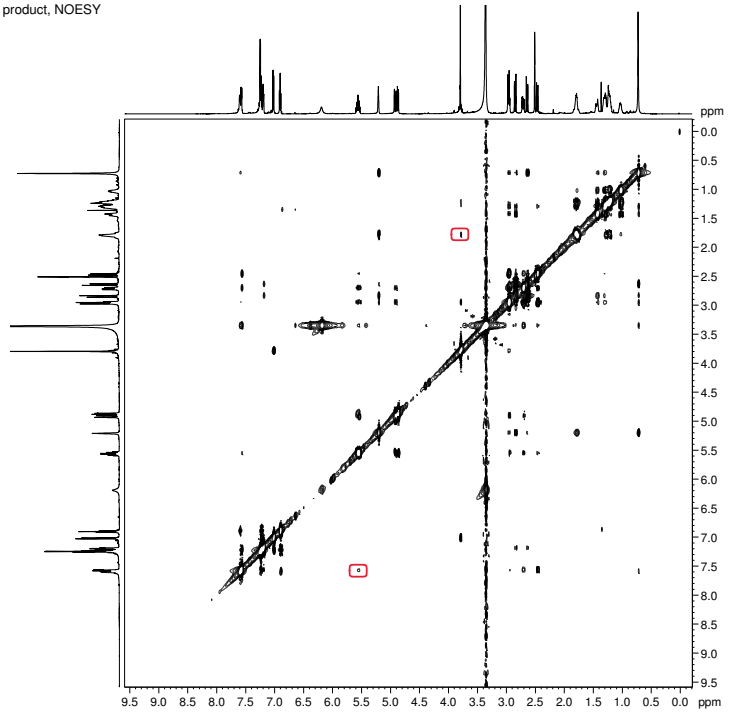
F2 - Acquisition Parameters
Date_ 20230522
Time 18.17 h
INSTRUM Avance
PROBHD Z168773_0038 (
PULPROG zgpg30
TD 131072
SOLVENT DMSO
NS 49
DS 0
SWH 35714.285 Hz
FIDRES 0.544957 Hz
AQ 1.8350080 sec
RG 101
DW 14.000 usec
DE 18.00 usec
TE 298.0 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
SFO1 150.9178988 MHz
NUC1 13C
P0 3.33 usec
P1 10.00 usec
PLW1 86.29599762 W
SFO2 600.1324005 MHz
NUC2 1H
CPDPRG[2 waltz65
PCPD2 80.00 usec
PLW2 19.40099907 W
PLW12 0.43652001 W
PLW13 0.21922000 W

F2 - Processing parameters
SI 65536
SF 150.9028776 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40



35
(major)

Purified product, NOESY



Current Data Parameters
NAME ASB-2023-070
EXPNO 5004
PROCNO 1

F2 - Acquisition Parameters
Date_ 20230527
Time 13.55 h
INSTRUM Avance
PROBHD Z168773_0038 (
PULPROG noesygpph
TD 2048
SOLVENT DMSO
NS 8
DS 4
SWH 5882.353 Hz
FIDRES 5.744485 Hz
AQ 0.1740800 sec
RG 16
DW 85.000 usec
DE 13.61 usec
TE 298.0 K
D0 0.00006972 sec
D1 2.00000000 sec
D8 0.30000001 sec
D16 0.00020000 sec
IN0 0.00017000 sec
TDav 1
SFO1 600.1328206 MHz
NUC1 1H
P1 12.00 usec
P2 24.00 usec
PLW1 19.40099907 W
GPNAM[1] SMSQ10.100
GPZ1 40.00 %
P16 1000.00 usec

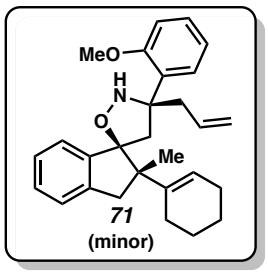
======== F1 INDIRECT DIMEN
td1 256
sw_F1 9.801752

F1 - Acquisition parameters
TD 256
SFO1 600.1328 MHz
FIDRES 45.955883 Hz
SW 9.802 ppm
FnMODE TPPI

F2 - Processing parameters
SI 1024
SF 600.1300057 MHz
WDW QSINE
SSB 2
LB 0 Hz
GB 0
PC 1.00

F1 - Processing parameters
SI 1024
MC2 TPPI
SF 600.1300069 MHz
WDW QSINE
SSB 2
LB 0 Hz
GB 0

Purified product, 1H NMR

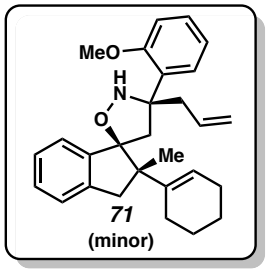


Current Data Parameters
NAME ASB-2023-090
EXPNO 40
PROCNO 1

F2 - Acquisition Parameters
Date_ 20230614
Time 18.34 h
INSTRUM av500
PROBHD Z119248_0002 (
PULPROG zg30
TD 65536
SOLVENT DMSO
NS 8
DS 0
SWH 10000.000 Hz
FIDRES 0.305176 Hz
AQ 3.2767999 sec
RG 12.14
DW 50.000 usec
DE 10.00 usec
TE 298.0 K
D1 2.00000000 sec
TD0 1
SFO1 500.1330008 MHz
NUC1 1H
P1 10.00 usec
PLW1 13.50000000 W

F2 - Processing parameters
SI 65536
SF 500.1300047 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

Purified product, 13C NMR

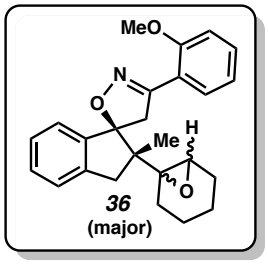


Current Data Parameters
NAME ASB-2023-090
EXPNO 50
PROCNO 1

F2 - Acquisition Parameters
Date_ 20230614
Time 18.39 h
INSTRUM av500
PROBHD Z119248_0002 (
PULPROG zgpg30
TD 65536
SOLVENT DMSO
NS 45
DS 2
SWH 31250.000 Hz
FIDRES 0.953674 Hz
AQ 1.0485760 sec
RG 204.54
DW 16.000 usec
DE 28.00 usec
TE 298.0 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
SFO1 125.7722511 MHz
NUC1 13C
P1 10.50 usec
PLW1 23.00000000 W
SFO2 500.1330008 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 80.00 usec
PLW2 13.50000000 W
PLW12 0.21094000 W
PLW13 0.10610000 W

F2 - Processing parameters
SI 131072
SF 125.7578455 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

Purified product, 1H NMR

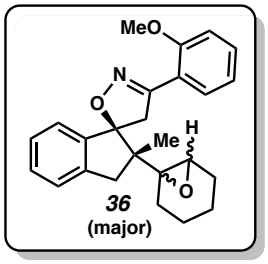


Current Data Parameters
NAME ASB-2023-065
EXPNO 10
PROCNO 1

F2 - Acquisition Parameters
Date_ 20230416
Time 19.02 h
INSTRUM Avance
PROBHD Z168773_0038 (
PULPROG zg30
TD 81920
SOLVENT CDCl3
NS 8
DS 0
SWH 11904.762 Hz
FIDRES 0.290644 Hz
AQ 3.4406400 sec
RG 101
DW 42.000 usec
DE 13.70 usec
TE 298.0 K
D1 1.00000000 sec
TD0 1
SFO1 600.1337058 MHz
NUC1 1H
P0 4.00 usec
P1 12.00 usec
PLW1 19.40099907 W

F2 - Processing parameters
SI 65536
SF 600.1300154 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

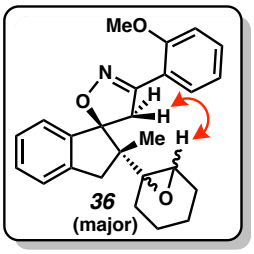
Purified product, 13C NMR



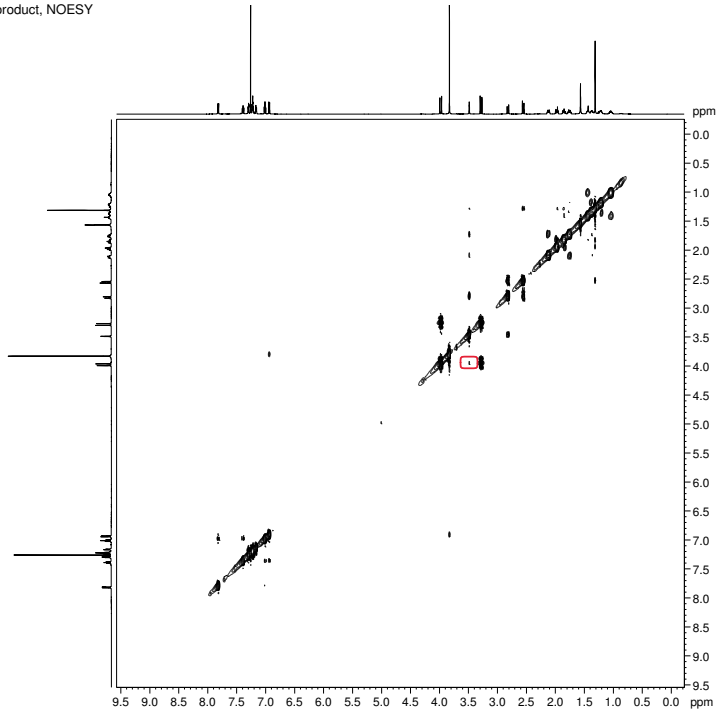
Current Data Parameters
NAME ASB-2023-065
EXPNO 13
PROCNO 1

F2 - Acquisition Parameters
Date_ 20230417
Time 1.26 h
INSTRUM Avance
PROBHD Z168773_0038 (
PULPROG zgpg30
TD 131072
SOLVENT CDCl3
NS 256
DS 0
SWH 35714.285 Hz
FIDRES 0.544957 Hz
AQ 1.8350080 sec
RG 101
DW 14.000 usec
DE 18.00 usec
TE 298.0 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
SFO1 150.9178988 MHz
NUC1 13C
P0 3.33 usec
P1 10.00 usec
PLW1 86.29599762 W
SFO2 600.1324005 MHz
NUC2 1H
CPDPRG[2 waltz65
PCPD2 80.00 usec
PLW2 19.40099907 W
PLW12 0.43652001 W
PLW13 0.21922000 W

F2 - Processing parameters
SI 65536
SF 150.9027888 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40



Purified product, NOESY

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Current Data Parameters
NAME        ASB-2023-065
EXPNO              12
PROCNO              1

F2 - Acquisition Parameters
Date_         20230417
Time          1.10 h
INSTRUM         Avance
PROBHD   Z168773_0038 (
PULPROG      noesygpph
TD               2048
SOLVENT         CDCl3
NS                 20
DS                  4
SWH          5882.353 Hz
FIDRES       5.744485 Hz
AQ           0.1740800 sec
RG                 16
DW             85.000 usec
DE             13.61 usec
TE             298.0 K
D0           0.00006972 sec
D1           2.00000000 sec
D8           0.30000001 sec
D16          0.00020000 sec
IN0          0.00017000 sec
TDav               1
SFO1         600.1328206 MHz
NUC1               1H
P1             12.00 usec
P2             24.00 usec
PLW1        19.40099907 W
GPNAM[1]    SMSQ10.100
GPZ1           40.00 %
P16          1000.00 usec

======== F1 INDIRECT DIMEN
td1    256
sw_F1    9.801752

F1 - Acquisition parameters
TD               256
SFO1         600.1328 MHz
FIDRES       45.955883 Hz
SW             9.802 ppm
FnMODE           TPPI

F2 - Processing parameters
SI               1024
SF         600.1300158 MHz
WDW              QSINE
SSB                2
LB              0 Hz
GB                 0
PC              1.00

F1 - Processing parameters
SI               1024
MC2              TPPI
SF         600.1300335 MHz
WDW              QSINE
SSB                2
LB              0 Hz
GB                 0
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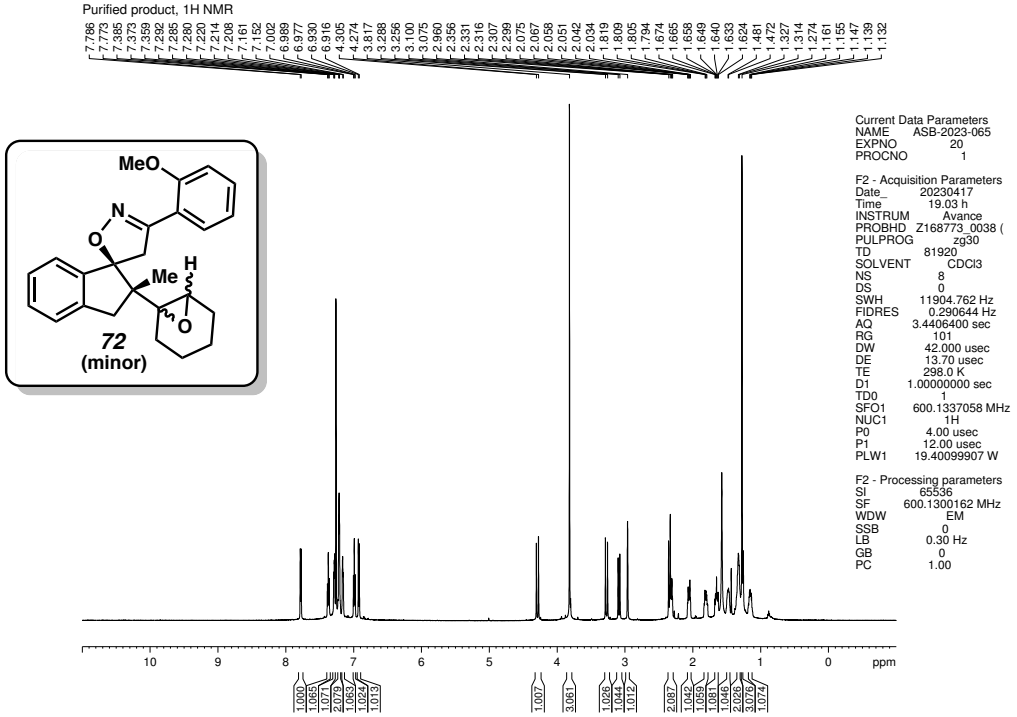
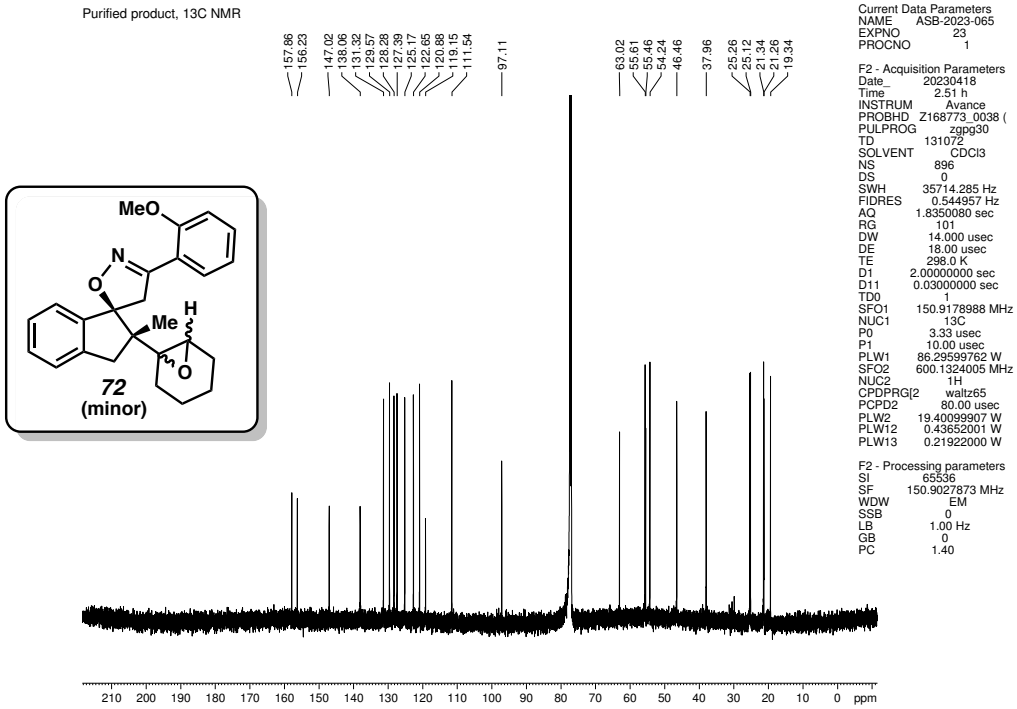
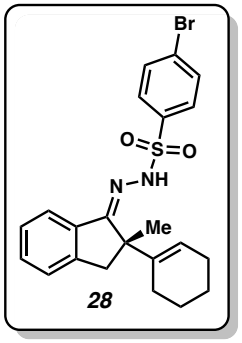
Purified product, 1H NMR



Purified product, 13C NMR



Purified product, 1H NMR



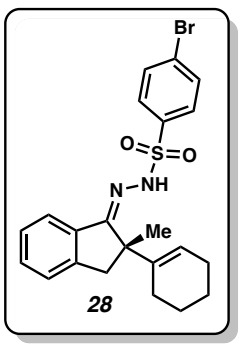
Current Data Parameters
NAME Heck
EXPNO 40
PROCNO 1

F2 - Acquisition Parameters
Date_ 20230414
Time 12.52
INSTRUM av300
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 8
DS 0
SWH 5995.204 Hz
FIDRES 0.091480 Hz
AQ 5.4657025 sec
RG 812.7
DW 83.400 usec
DE 6.00 usec
TE 300.0 K
D1 2.00000000 sec
TD0 1

======== CHANNEL f1 ======
NUC1 1H
P1 15.00 usec
PL1 0 dB
PL1W 9.31909847 W
SFO1 300.1318008 MHz

F2 - Processing parameters
SI 65536
SF 300.1300131 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.40

Purified product, 13C NMR



Current Data Parameters
NAME DJN-2023-057-C-NM
EXPNO 12
PROCNO 1

F2 - Acquisition Parameters
Date_ 20230509
Time 17.15 h
INSTRUM av500
PROBHD Z119248_0002 (
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 64
DS 2
SWH 31250.000 Hz
FIDRES 0.953674 Hz
AQ 1.0485760 sec
RG 204.54
DW 16.000 usec
DE 28.00 usec
TE 298.0 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
SFO1 125.7722511 MHz
NUC1 13C
P1 10.50 usec
PLW1 23.00000000 W
SFO2 500.1330008 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 80.00 usec
PLW2 13.50000000 W
PLW12 0.21094000 W
PLW13 0.10610000 W

F2 - Processing parameters
SI 131072
SF 125.7577725 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

References

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