Supporting Information

Mechanistic Interrogation of Co/Ni-Dual Catalyzed Hydroarylation

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Materials

1,3-Dimethyl-3,4,5,6-tetrahydro-2(1H)-pyrimidinone (DMPU) was purchased from Oakwood Chemicals and distilled under vacuum over calcium hydride (10 % w/v). DMPU was degassed by sparging with argon or *via* three freeze-pump-thaw cycles, before it was stored under inert atmosphere in a Schlenk flask. Tetrahydrofuran (THF) was purchased from Sigma-Aldrich and degassed *via* three freeze-pump-thaw cycles. Pentane, hexanes, dichloromethane (DCM), toluene (PhMe), ethyl acetate (EtOAc) and diethyl ether were purchased from Fisher Chemicals and used without further purification. 1-fluoro-2,4,6-trimethylpyridinium tetrafluoroborate and 4-phenyl-1-butene, 4-iodobenzotrifluoride, decane and cobalt(II) acetate tetrahydrate, nickel bromide diglyme ($NiBr_2$·diglyme) and $Ni(COD)_2$ were purchased from TCI, Combi-blocks, Acros, Sigma-Aldrich and Strem chemicals, respectively, and used without further purification. Cobalt(Salen$^{t\text{-Bu},t\text{-Bu}}$) (referred to as Co(II)(salen)) and cobalt(Salen$^{t\text{-Bu},t\text{-Bu}}$)Cl (referred to as **Co(III)Cl**),[1] Ph(*i*-PrO)SiH_2,[2] (3-bromobutyl)benzene,[3] methyl (triphenylphosphoranylidene)acetate,[4] and acetylferrocenium tetrafluoroborate ($AcFcBF_4$)[5] were prepared according to established literature procedures. All other reagents were purchased at the highest commercial quality and used without further purification, unless otherwise stated.

Methods

All reactions were carried out under a positive pressure of argon unless otherwise stated. Reactions were monitored by thin layer chromatography (TLC) using pre-coated silica gel plates from EDM Chemicals (TLC Silica gel 60 F254, 250 um thickness). Flash column chromatography was performed over Silica gel 60 (particle size 0.04-0.063 mm) from EDM Chemicals. ^1H NMR spectra were recorded on Bruker AV-399, Bruker AV-400, Bruker AV-500 or Bruker AV-600 (equipped with cryoprobe) spectrometers and are reported in parts per million (ppm) relative to residual solvent peaks (7.26 ppm for $CDCl_3$, 7.16 ppm for C_6D_6, 2.50 for DMSO-d_6, 2.05 for acetone-d_6). NMR data are denoted with apparent multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, hept = heptet and combinations thereof. Quantitative ^1H NMR was taken using five times the T1 relaxation time. Stoichiometric reactions with organocobalt complexes were run in the dark and/or wrapped in aluminum foil. GC/MS analysis was performed on Agilent 7820A/5975 GC/MSD system with helium as a carrier gas. Unless otherwise specified, GC runs were performed using the following method: GC/MS; HP-5MS UI; 139 KPa; flow rate 2 mL/min; inlet temperature 200 °C; column temperature 50 °C for 0 min, then 20 °C/min to 280 °C, then hold 2 min. GC/FID analysis was conducted on an Agilent 7820A GC/FID system with nitrogen as a carrier gas and with air and hydrogen as combustion gasses. Three methods were used for GC/FID analysis: GC/FID; HP-5MS UI, Part # 190915-577UI; (A) inlet temperature 250 °C; column temperature 50 °C for 0 min, then 20 °C/min to 280 °C, then held for 2 min (B) inlet temperature 250 °C; column temperature 110 °C for 5 min, then 15 °C/min to 155 °C, then held for 6 min, then 25 °C/min to 280 °C (C) inlet temperature 250 °C; column temperature 60 °C for 0 min, then 15 °C/min to 165 °C, then held for 5 min, then 20 °C/min to 280 °C.

Kinetics: Reaction set-up and data analysis

The Co(II)(salen) (18.1 mg, 300 μmol) and 1-fluoro-2,4,6-trimethylpyridinium tetrafluoroborate (17.0 mg, 750 μmol) were transferred to an oven-dried reaction vial equipped with a Teflon-lined stir bar. The atmosphere was evacuated and backfilled with nitrogen on a Schlenk line before switched to an argon-filled balloon. DMPU (0.30 mL) was added, and reaction mixture was sonicated if undissolved solid remained on the walls of the reaction vessel. To the reaction vial was added 4-phenyl-1-butene (29 μL, 0.195 mmol, 1.3 equiv), decane (29 μL, 0.150 mmol, 1.0 equiv) and 4-iodobenzotrifluoride (22 μL, 0.150 mmol, 1.0 equiv) and the mixture was placed in a water bath. After slow addition of Ph(*i*-PrO)SiH_2 (54 μL, 0.300 mmol, 2.0 equiv), the stopwatch was started. The first aliquot of the reaction mixture was taken after two minutes. The reaction was stirred for an additional three minutes before dtbbpy$NiBr_2$* (40 μL, 0.19M in DMPU) was added (this is the zero timepoint). The solution was left in the water bath and timepoints were taken at 5, 10, 15, 20, 30, 40, 50, 60 and 90 minutes. To quench each sample, an aliquot was immediately transferred to ethyl acetate (2 mL) and further quenched with addition of 1M HCl (1 mL). The ethyl acetate layer was washed with 2M aqueous lithium chloride (1 mL), dried over Na_2SO_4, filtered and the product composition analyzed by GC-FID (Method A).

**dtbbpy$NiBr_2$ precatalyst solution*: $NiBr_2$·diglyme (8.0 mg, 22 μmol), 4,4'-di-*tert*-butyl-2,2'-dipyridyl (6.0 mg, 22 μmol) were measured out into a 1-dram vial with a PTFE/silicone septa screw cap. The atmosphere was evacuated/backfilled with nitrogen and switched to an argon balloon. DMPU (120 μL) was added and the mixture was sonicated for thirty minutes until a dark green solution was formed.

In order to characterize the product, the organic layer was concentrated and the product isolated by preparatory TLC (Rf = 0.55 in 100% hexanes, UV).

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.56 (d, *J* = 8.0 Hz, 2H), 7.31 (d, *J* = 8.0 Hz, 3H), 7.28 – 7.25 (m, 2H), 7.20 – 7.16 (m, 1H), 7.14 – 7.10 (m, 2H), 2.83 – 2.75 (m, 1H), 2.57 – 2.47 (m, 2H), 1.97 – 1.90 (m, 2H), 1.29 (d, *J* = 6.9 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 151.38, 142.03, 128.35, 128.32, 128.32 (q, *J* = 32.2 Hz), 127.06, 125.81, 125.36 (q, *J* = 3.7 Hz), 39.67, 39.40, 33.77, 22.28.

^{19}F NMR (376 MHz, $CDCl_3$): δ -62.51.

LRMS (EI, 70 eV) – *m/z* (M^+) calcd. for $C_{17}H_{17}F_3$: 278.13. Found *m/z* (%) 278.1 (25), 173.0 (19), 133.0 (16), 105.1 (69), 92.1 (100), 77 (15).

Different Excess Experiments: Olefin, Iodoarene, Silane and Oxidant (NFTPB)

The experiments were run changing the initial concentration of the substrate in question. The data were plotted against the standard conditions. Because no variation in rate (product concentration vs. time) was observed, the olefin, iodoarene and silane were judged to be *zero order*. The oxidant displayed an induction period, but the same rate at lower loading (20 mol %), so was judged to not be involved in the rate-determining step. A deleterious effect on the yield and rate was observed when a higher loading (75 mol %) oxidant was used. All concentrations are listed as moles/liter (M). See Figure 2 and Figure 4 in main text.

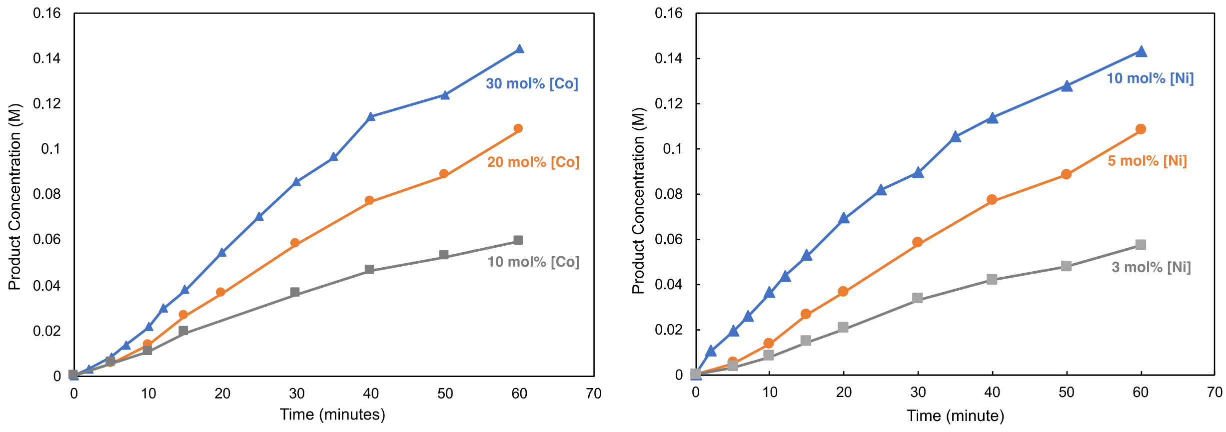
Experiment	[Co]	[Ni]	[NFTPB]	[olefin]	[iodoarene]	[silane]
Standard conditions	0.0638	0.0160	0.1596	0.4150	0.3191	0.6383
Excess iodoarene	0.0638	0.0160	0.1596	0.4150	**0.2340**	0.6383
Excess olefin	0.0638	0.0160	0.1596	**0.3191**	0.3191	0.6383
Excess silane	0.0638	0.0160	0.1596	0.4150	0.3191	**0.4894**
Excess NFTPB (20 mol %)	0.0638	0.0160	**0.0638**	0.4150	0.3191	0.6383
Excess NFTPB (75 mol %)	0.0638	0.0160	**0.2447**	0.4150	0.3191	0.6383

Different Excess Experiments: Cobalt and Nickel

The experiments were run at three different initial concentrations of the precatalyst in question. The product concentration was plotted as a function of time. All concentrations are listed as moles/liter (M).

Experiment	[Co]	[Ni]	[NFTPB]	[olefin]	[iodoarene]	[silane]
Standard conditions	0.0638	0.0160	0.1596	0.4150	0.3191	0.6383
10 mol % Co(II)(salen)	**0.0319**	0.0160	0.1596	0.4150	0.3191	0.6383
30 mol % Co(II)(salen)	**0.0957**	0.0160	0.1596	0.4150	0.3191	0.6383
3 mol % dtbbpyNiBr$_2$	0.0638	**0.0096**	0.1596	0.4150	0.3191	0.6383
10 mol % dtbbpyNiBr$_2$	0.0638	**0.0319**	0.1596	0.4150	0.3191	0.6383

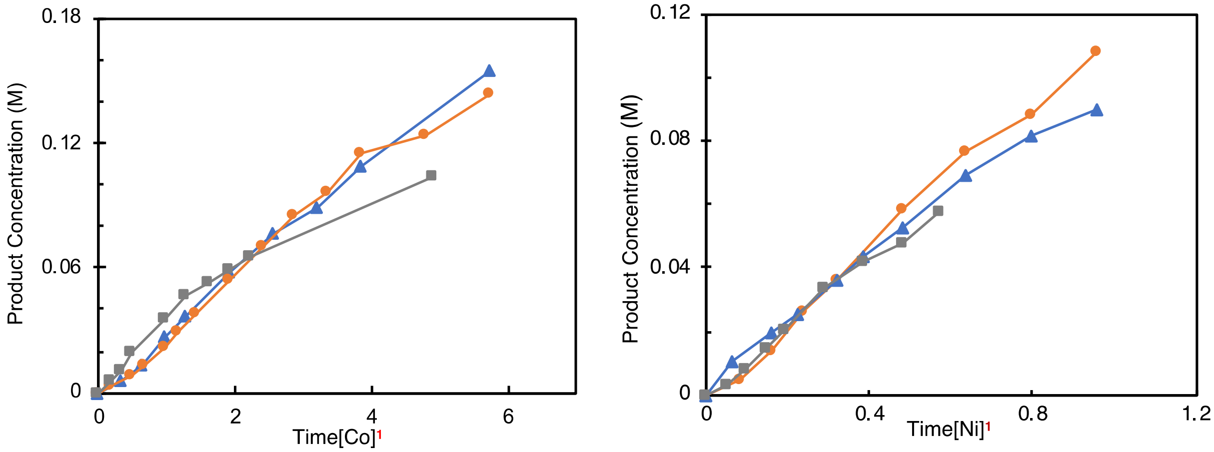
Figure S1. **Plot of product concentration versus time for different catalyst loadings.**



Kinetics: Reaction order for cobalt and nickel catalysts by the Burés method[6]

In order to obtain a graphical rate law, we chose to use a normalized time scale. The product concentration is plotted as a function of time*[catalyst concentration]^n, in which n is the order of the reaction. The value at which all of concentration profiles overlay reflects the order of the catalyst. For both cobalt and nickel, $n = 1$. See Figure 3 in main text or Figure S2.

Figure S2. **Burés graphical rate analysis for cobalt and nickel.**



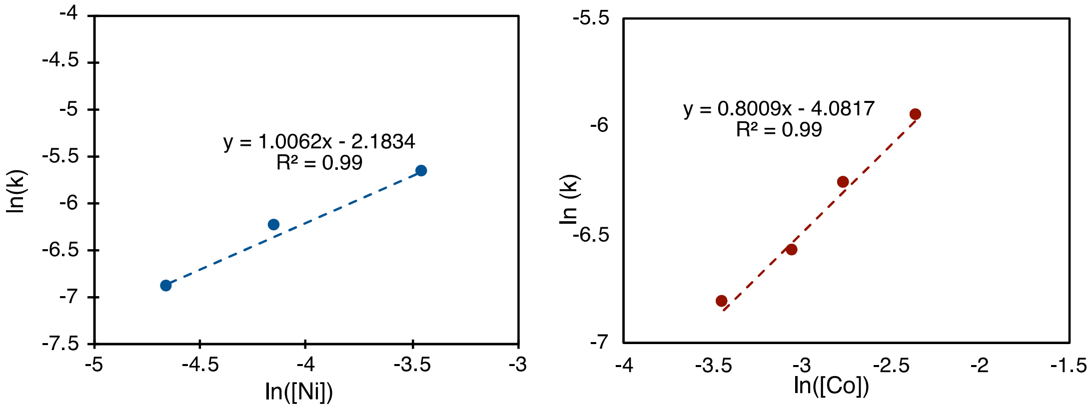
Kinetics: Reaction order for cobalt and nickel catalysts using initial rates

The initial rates of [Co] 10, 20 and 30% and for [Ni] for 3, 5, 10% catalyst loading were obtained by fitting the data with linear least squares analysis. The data was plotted as a function of ln(concentration) versus ln(rate constant). The slope of the fitted line was taken to be the order of the reaction (m = 1.0 for Ni, m = 0.8 for Co). In the case of cobalt loading, the catalyst order was shown to be 0.8. While this is a non-integer value, the corroboration with Burés graphical rate analysis led us to establish that the reaction was pseudo-first order in cobalt.

Experiment	[Co] (M)	ln([Co])	Initial rate const. (k)	ln(k)
10 mol % (salen)Co	0.0319	-3.44	0.0011	-6.81
15 mol % (salen)Co	0.0478	-3.04	0.0014	-6.57
20 mol % (salen)Co	0.0638	-2.75	0.0019	-6.27
30 mol % (salen)Co	0.0957	-2.35	0.0026	-5.95

Experiment	[Ni] (M)	ln([Ni])	Initial rate const. (k)	ln(k)
3 mol % dtbbpyNiBr$_2$	0.00957	-4.65	0.0010	-6.91
5 mol % dtbbpyNiBr$_2$	0.0160	-4.14	0.0019	-6.27
10 mol % dtbbpyNiBr$_2$	0.0319	-3.44	0.0034	-5.68

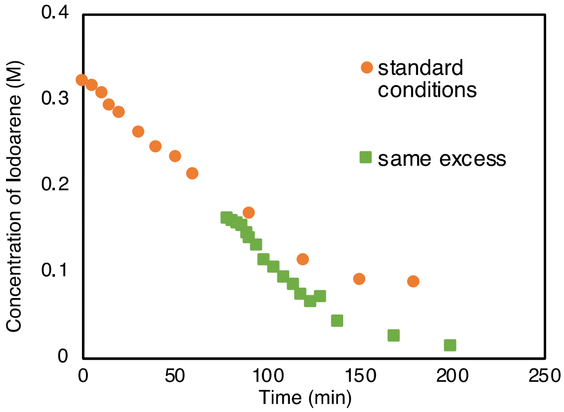
Figure S3. **Initial Rates analysis of nickel and cobalt.**



Kinetics: Same excess experiment:[7] The reaction was run under otherwise standard conditions, but with half the concentration of olefin and iododarene. The data was plotted as concentration of iodoarene starting material versus time with a normalized time profile for the same excess conditions. The halfway point of the reaction using standard concentrations was determined to be 79 minutes. Because the rate of the same excess experiment overlaps with the standard conditions, there is no product inhibition. Catalyst deactivation under standard concentration conditions is observed at high conversions of starting material after 125 minutes. Therefore, we used the data before 125 minutes for our graphical rate law analysis.

Experiment	[Co]	[Ni]	$[F^+]$	[olefin]	[iodoarene]	[silane]
Standard conditions	0.0638	0.0160	0.1596	0.4150	0.3191	0.6383
Same Excess	0.0638	0.0160	0.1596	**0.2074**	**0.1596**	0.6383

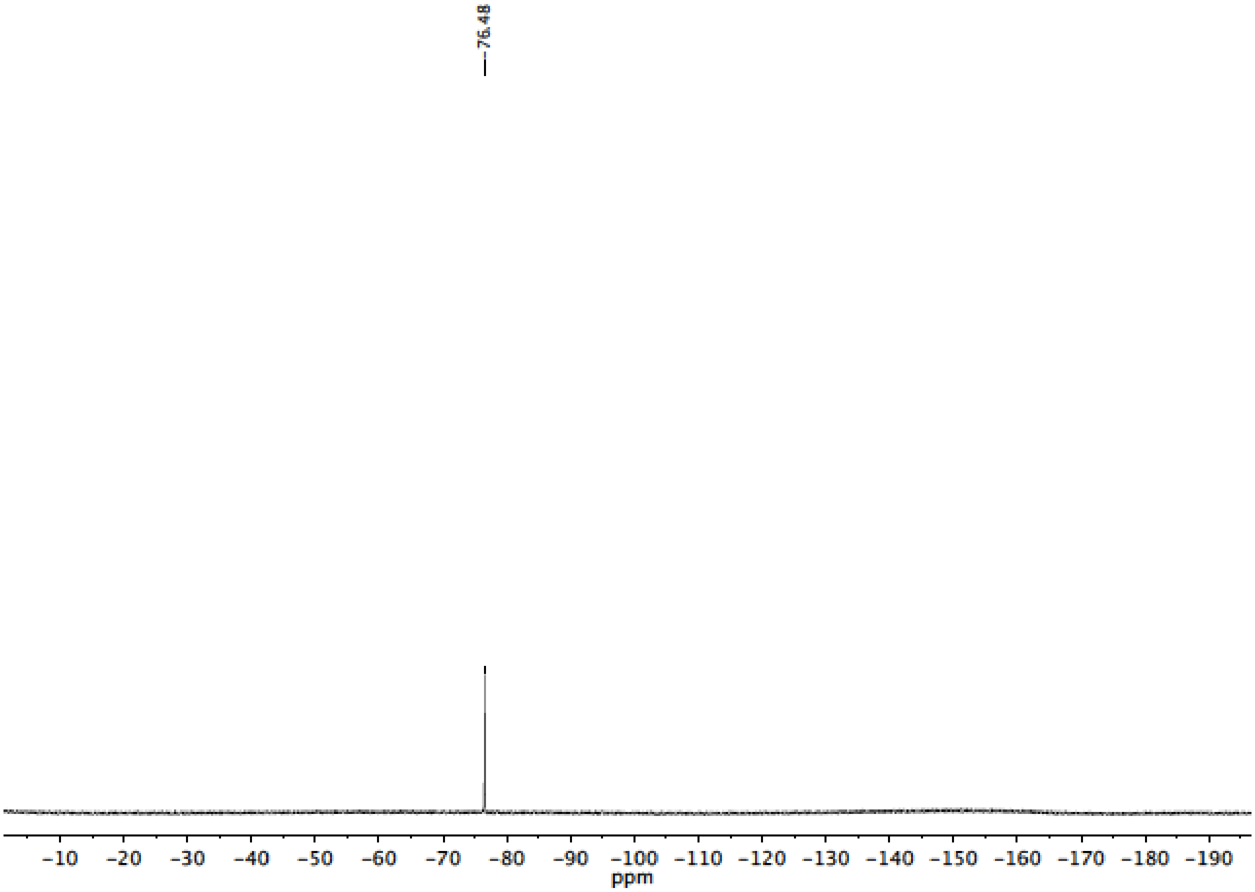
Figure S4. **Same Excess Experiment.**

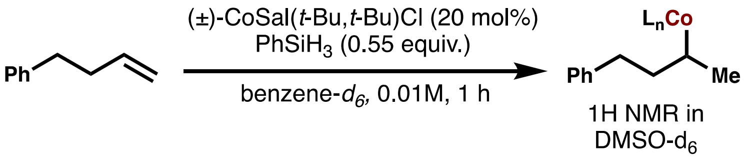


Oxidation of Co(II)(salen) with 1-fluoro-2,4,6-trimethylpyridinium triflate:

The Co(II)(salen) (2.3 mg, 3.8 μmol) and 1-fluoro-2,4,6-trimethylpyridinium triflate (0.55 mg, 2.4 μmol) were transferred to a flame-dried NMR tube capped with a septum and sealed with parafilm. The atmosphere was evacuated and backfilled with nitrogen on a Schlenk line and then the mixture was dissolved with 0.5 ml of C_6D_6 previously degassed with argon. DMPU (5 μL) was added, and the tube was shaken for 10 min at room temperature. The reaction continued for one hour before ^{1}H NMR acquisition. A pentane layer was added to the NMR tube to aid crystallization. See Figure 9 in the main text. Only one peak was observed in the ^{19}F NMR at δ –76.5 ppm corresponding to the triflate counteranion.[8]

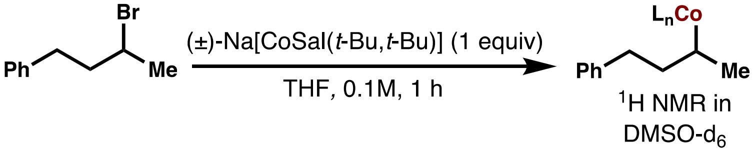
Figure S5. **^{19}F NMR of Co^{II}(Salen$^{t\text{-Bu},t\text{-Bu}}$) oxidation product**





Organocobalt formation via MHAT

To an oven-dried reaction vial charged with a stir bar was added, $Co^{III}(Salen^{t\text{-}Bu,t\text{-}Bu})Cl$ (2.0 mg, 3.1 µmol, 0.21 equiv) and 1,3,5-trimethoxybenzene (1.5 mg, 8.9 µmol, 0.61 equiv). The vial was capped with a PTFE/silicone septa screw cap and the atmosphere was evacuated and backfilled with nitrogen three times. The reaction was topped with an argon balloon, before benzene-d_6 (0.15 mL) was added, followed by 1-phenyl-4-butene (2.2 µL, 1.5 µmol, 1.0 equiv). A 10 µL aliquot was diluted into d_6-DMSO (0.5 mL) and an initial ^{1}H NMR was taken (t_0). Phenylsilane (1.0 µL, 8.1 µmol, 0.55 equiv) was added and the RM was allowed to stir for one hour at ambient temperature. Another 10 µL aliquot was diluted into d_6-DMSO (0.5 mL) for ^{1}H NMR acquisition.



Organocobalt formation via S_N2

An oven-dried, 1-dram vial was charged with $[Co(Salen^{t\text{-}Bu,t\text{-}Bu})(pyridine)_2]Br$[9] (17.6 mg, 0.0209 mmol, 1 equiv) Na/Hg amalgam (approx. 20% by wt, 10.0 mg, 4.2 equiv) and a stir bar. The vial was brought into an inert-atmosphere glovebox before tetrahydrofuran (0.20 mL) was added. The reaction was allowed to stir at ambient temperature until a dark green solution was formed. The solution was transferred to a separate 1-dram vial before (3-bromobutyl)benzene (3.6 µL, 0.021 mmol, 1.0 equiv) was added. The brown reaction mixture was stirred at ambient temperature for 15 minutes. An aliquot of the reaction mixture was transferred to a 1-dram vial and solvent was removed by evaporation. The remaining solid was taken up in d_6-DMSO and transferred to a 5 mm NMR tube and the cap was wrapped in parafilm. The NMR tube was removed from the glovebox and a ^{1}H NMR was taken.

Figure S6. Observation of organocobalt formation via ^{1}H NMR

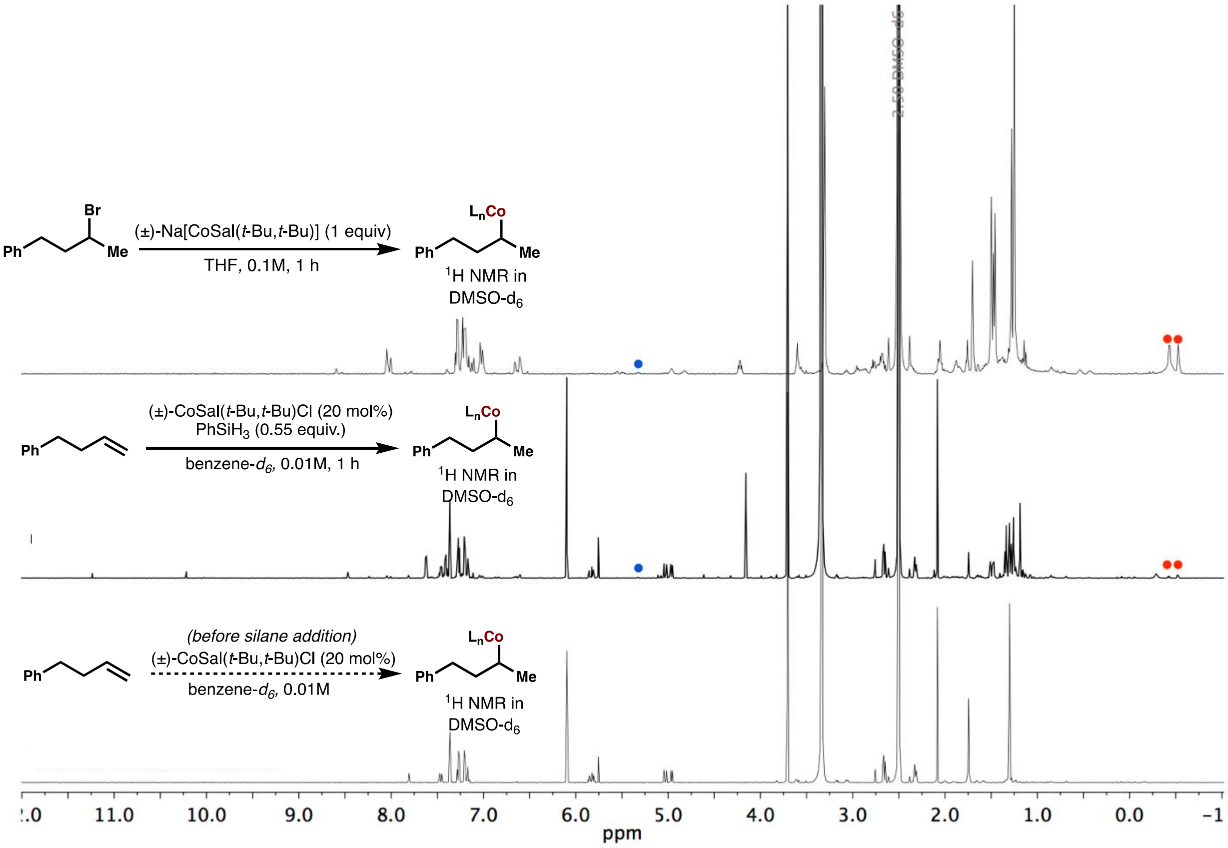


Figure S7. **Observation of organocobalt formation via ^{1}H NMR – upfield zoom.**

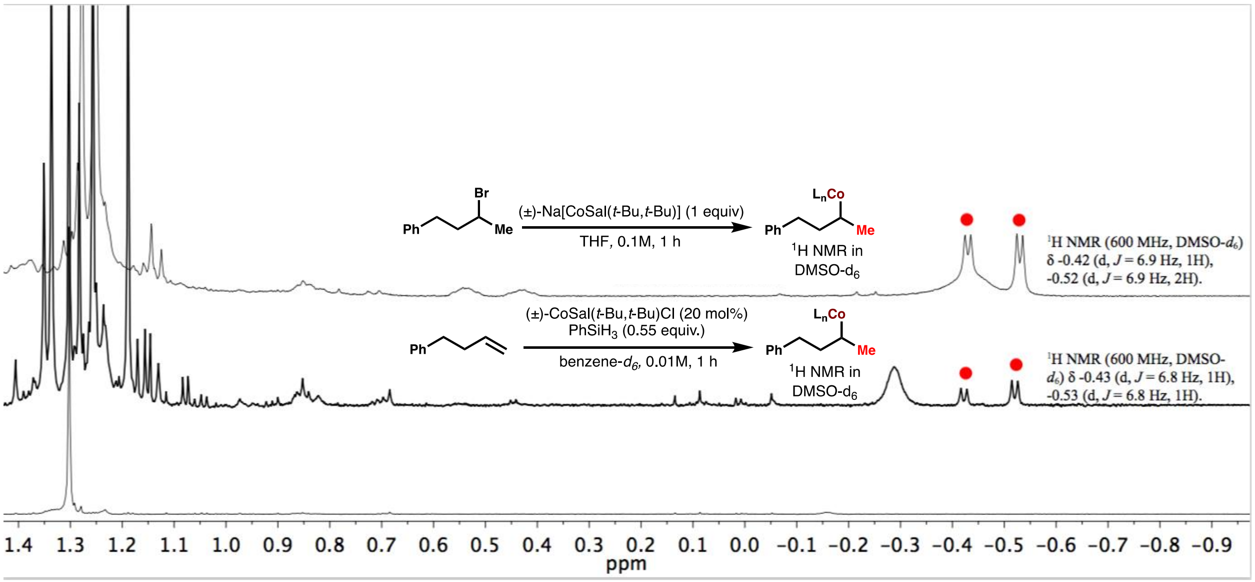
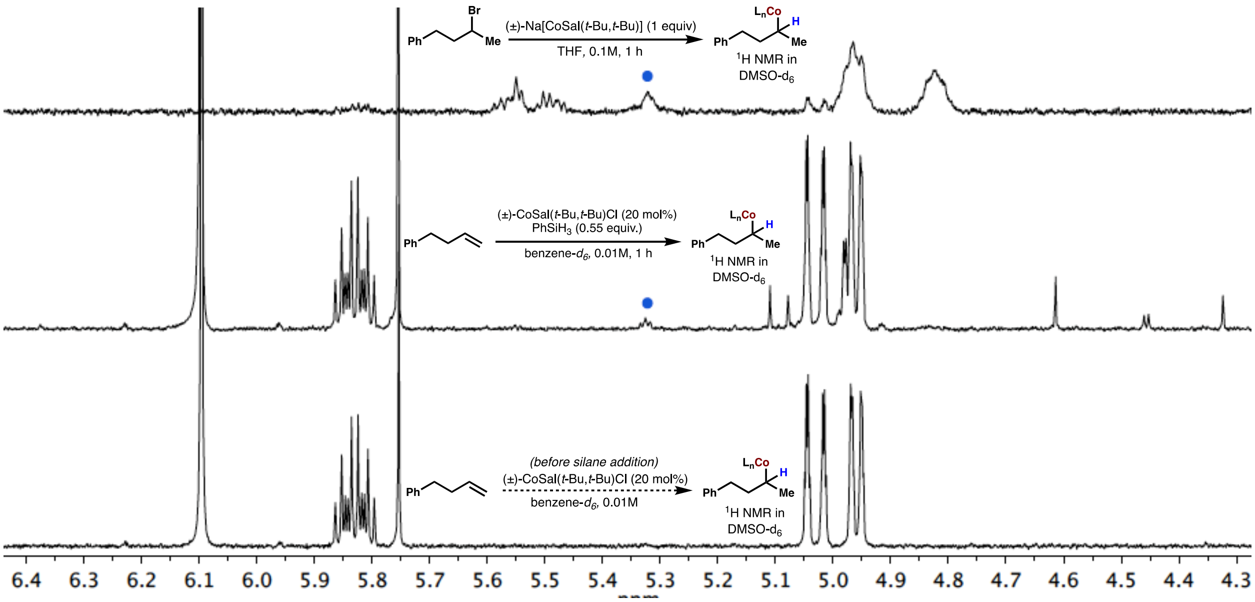
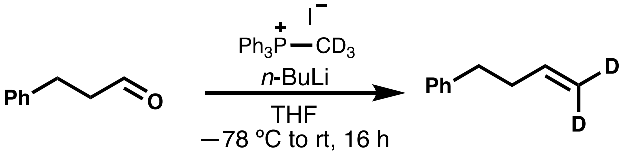


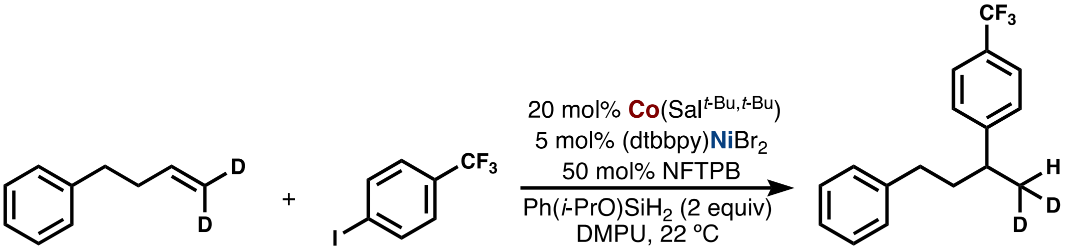
Figure S8. **Observation of organocobalt formation via ^{1}H NMR – midfield zoom.**



Hydroarylation with d_2-alkene



(But-3-en-1-yl-4,4-d_2)benzene.[10] (Methyl-d_3)triphenylphosphonium iodide[11] (768 mg, 1.89 mmol) was measured out into a 25-mL, flame-dried round bottom flask charged with a stir bar. The atmosphere was evacuated and backfilled with nitrogen three times. Tetrahydrofuran (9.5 mL) was added and the reaction mixture was cooled to –78 °C before *n*-butyllithium (0.73 mL, 2.6 M in tetrahydrofuran, 1.89 mmol) was added. The reaction mixture was allowed to warm to 0 °C and to stir for one hour before it was cooled to –78 °C. A solution of 3-phenylpropanal (254 mg, 1.89 mmol) in tetrahydrofuran (2 mL) was added and the reaction mixture was allowed to warm to ambient temperature. The reaction was stirred overnight, at which point it was filtered and concentrated. Pentane was added and the suspension was filtered again. The filtrate was concentrated and purified via silica gel chromatography to yield a clear oil (64.0 mg, 0.480 mmol, 25%). A quantitative ^{1}H NMR showed that the product contained 73% d_2-4-phenyl-1-butene, 27% (*E*)/(*Z*)-d_1-4-phenyl-1-butene. The spectral data matched the literature. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.32-7.27 (m, 2H), 7.23 – 7.16 (m, 3H), 5.91 – 5.81 (m, 1H), 5.04 (dt, *J* = 17.0, 1.6 Hz, 0.19 H, d_1-product), 4.97 (dd, *J* = 10.2, 1.3 Hz, 0.08 H, d_1-product), 2.75 – 2.68 (m, 2H), 2.45 – 2.33 (m, 2H). LRMS (EI, 70eV) – m/z (M^+) calcd. for $C_{10}H_{10}D_2$: 134.11. Found *m/z* (%) 134.1 (21), 91.1 (100), 65.1 (14).

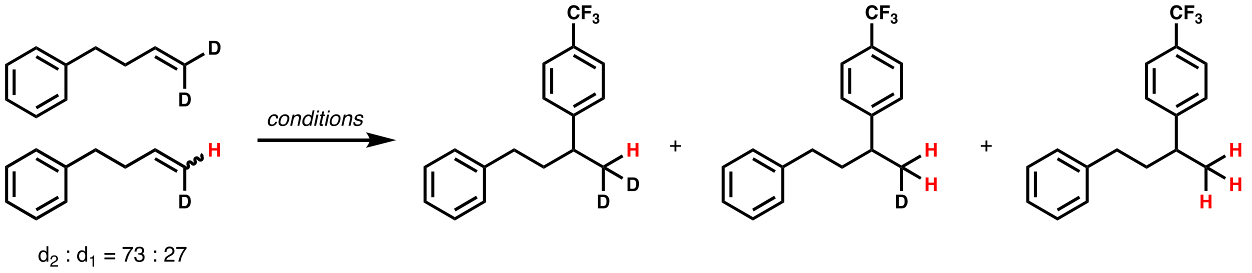


Hydroarylation with d_2-4-phenyl-1-butene. The hydroarylation was carried out according to the standard procedure. To a reaction vial charged with a stir bar was added (but-3-en-1-yl-4,4-d_2)benzene (22.0 mg, 0.164 mmol), Co(II)(salen) (18.0 mg, 30.0 μmol) and 1-fluoro-2,4,6-trimethylpyridinium tetrafluoroborate (17.0 mg, 75.0 μmol). The vial was sealed with a PTFE/silicone septa screw cap and atmosphere was evacuated and backfilled with argon. DMPU (0.3 mL) was added, followed by 1-iodo-4-benzotrifluoride (22 μL, 0.15 mmol) and the reaction was stirred for approximately five minutes until all solids went into solution. The reaction vessel was placed in a water bath before isopropoxy(phenyl)silane (54 μL, 0.30 mmol) was added slowly. The reaction was stirred for two minutes before a solution of dtbbpy$NiBr_2$* (40 μL, 0.19 M in DMPU) was added to the reaction mixture. After 16 hours, the reaction mixture was quenched by addition of 2M HCl and extracted into ethyl acetate. The product was purified via silica gel column chromatography to yield a clear oil (R_f = 0.65 in hexanes, 10.1 mg, 24%). The extent of H/D exchange was evaluated by quantitative ^{1}H NMR.

**dtbbpyNiBr$_2$ precatalyst solution*: $NiBr_2$·diglyme (8.0 mg, 22 μmol), 4,4'-di-*tert*-butyl-2,2'-dipyridyl (6.0 mg, 22 μmol) were measured out into a 1-dram vial with a PTFE/silicone septa screw cap. The atmosphere was evacuated/backfilled with nitrogen and switched to an argon balloon. DMPU (120 μL) was added and the mixture was sonicated for thirty minutes until a dark green solution was formed.

Product Characterization:
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.57 (d, *J* = 8.0 Hz, 2H), 7.34 – 7.25 (m, 3H), 7.23 – 7.16 (m, 2H), 7.12 (d, *J* = 8.0 Hz, 2H), 2.81 – 2.75 (m, 1H), 2.58 – 2.45 (m, 2H), 1.98 – 1.89 (m, 2H), 1.31 – 1.23 (m, **1.44H**).
^{13}C NMR (151 MHz, $CDCl_3$) δ 151.52, 142.18, 128.49, 128.46, 128.46 (q, *J* = 32.4 Hz), 125.95, 125.50 (q, *J* = 3.8 Hz), 124.50 (q, *J* = 271.8 Hz), 39.77, 39.40, 33.92, 22.29 – 21.38 (m).
LRMS (EI, 70 eV) – *m/z* (M^+) calcd. for $C_{17}H_{15}D_2F_3$: 280.14. Found *m/z* (%) 280.2 (27), 175.1 (22), 159.0 (12), 105.1 (59), 92.1 (100), 77.1 (12).

Calculating percent D/H scrambling:



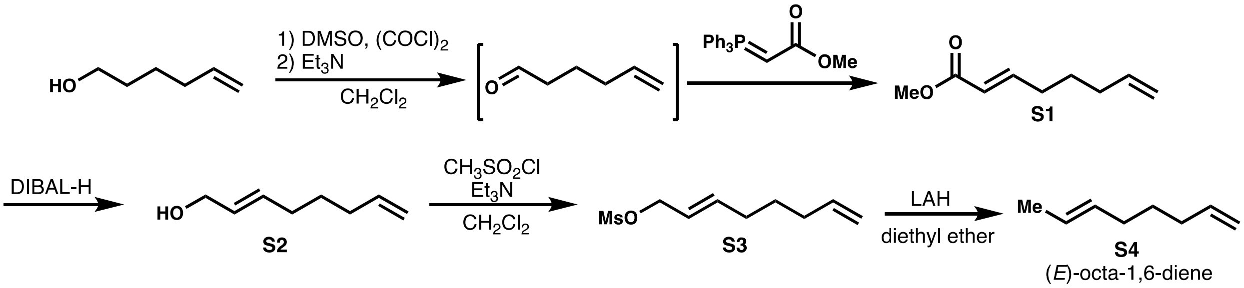
The starting alkene was found to have a 73:27 ratio of d_2-alkene to (*E*)/(*Z*)-d_1-alkene. If there were no H/D exchange, the integration of the methyl protons would be equivalent to 1.27.
(0.73∗1) + (0.27∗2) = **1.27**

In the ^{1}H NMR, the integration is 1.44.

1.44 /1.27 = 1.13 – there is 13% increase in hydrogen relative to what we would expect had there been no H/D exchange.

Radical Clock Experiment:

Synthesis of (*E*)-1,6-octadiene

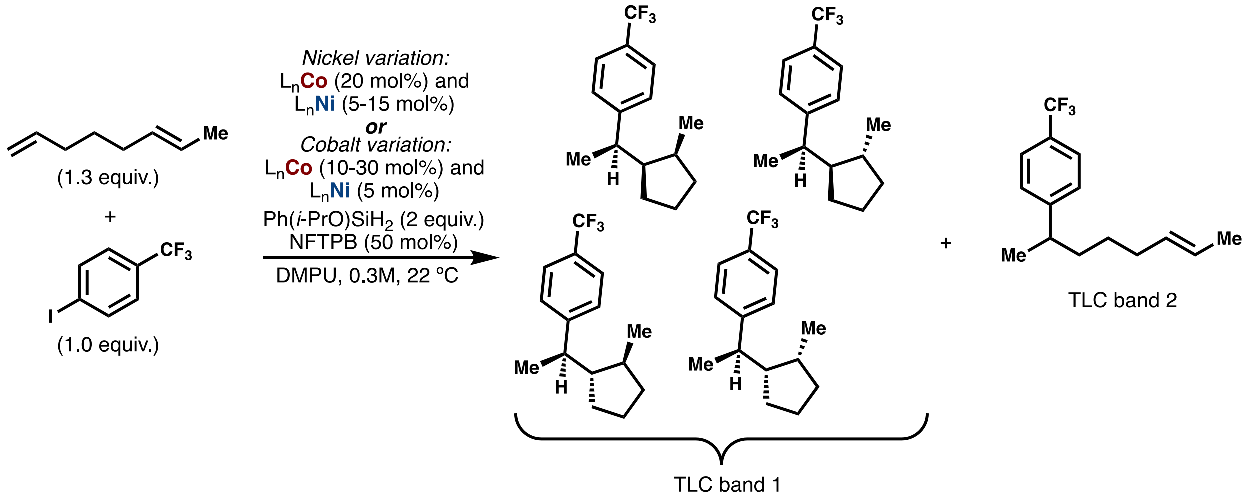


Methyl (*E*)-octa-2,7-dienoate (S1). Methyl (*E*)-octa-2,7-dienoate was prepared according to the literature.[12] A flame-dried, 500-mL round-bottom flask was charged with a stir bar and dichloromethane and the atmosphere replaced with nitrogen. Oxalyl chloride (5.2 mL, 60 mmol, 1.2 equiv) was added and the solution was cooled to –78 ºC in a dry ice/acetone bath for ten minutes before dimethyl sulfoxide (4.3 mL, 60 mmol, 1.2 equiv) was added. After 15 minutes, hex-5-en-1-ol (6.0 mL, 50 mmol, 1.0 equiv,) was added and the reaction mixture was stirred for one hour at –78 ºC. To the reaction mixture, was added triethylamine (24 mL, 170 mmol, 3.4 equiv) and the reaction mixture was warmed to room temperature over 3 hours. The yellow suspension was filtered to remove white precipitate and transferred to a flame-dried 500-mL round-bottom flask. The yellow solution was put under a nitrogen atmosphere and cooled to 0 ºC in an ice bath before methyl 2-(triphenylphosphoranylidene)acetate (28.1 g, 61.0 mmol, 1.2 equiv) was added. The reaction mixture was allowed to warm to room temperature and stirred overnight. After addition of water (200 mL) and diethyl ether (350 mL), the reaction mixture was transferred to a separatory funnel. The organic layer was separated and washed with water (200 mL) and brine (100 mL), dried over Na_2SO_4, filtered, and concentrated to a yellow solid. The yellow solid was dissolved in 5% diethyl ether in pentane (50 mL), filtered to remove solids, and concentrated. Methyl (*E*)-octa-2,7-dienoate was isolated via silica gel chromatography (2% ethyl acetate in hexanes) as an oil (4.15 g, 48%). The spectral data matches the literature. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.97 (dt, *J* = 15.7, 7.0 Hz, 1H), 5.88 – 5.69 (m, 2H), 5.08 – 4.92 (m, 2H), 2.22 (qd, *J* = 7.1, 1.6 Hz, 2H), 2.15 – 2.01 (m, 2H), 1.64 – 1.49 (m, 2H).

(*E*)-octa-2,7-dien-1-ol (S2).[13] To a flame-dried, 500-mL round-bottom flask under a nitrogen atmosphere was added a solution of methyl (E)-octa-2,7-dienoate (4.15 g, 26.9 mmol, 1.0 equiv) in dichloromethane (100 mL). The solution was cooled to –78 ºC before a solution of diisobutylaluminum hydride in dichloromethane (60 mL, 53.8 mmol, 0.89 M) was added slowly. After one hour, an additional portion of diisobutylaluminum hydride in dichloromethane (15 mL, 13.5 mmol, 0.89 M) was added, and the reaction was stirred for two hours at 0 ºC until full conversion observed by TLC. The reaction mixture was cooled to –78 ºC before ethyl acetate (80 mL) was added, followed by slow addition of 1M HCl (160 mL). The reaction was allowed to warm to ambient temperature, diluted with dichloromethane (75 mL) and transferred to a separatory funnel. The organic layer was separated and saved, and the aqueous layer was extracted with dichloromethane (2 x 75 mL). The combined organic layer was dried over Na_2SO_4, filtered and concentrated to a yellow oil. The crude product was used in the next step without purification (3.35 g). ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.80 (ddt, *J* = 16.9, 10.2, 6.7 Hz, 1H), 5.74 – 5.58 (m, 2H), 4.98-5.04 (m, 1H), 4.93-4.98 (m, 1H), 4.02-4.07 (m, 2H), 2.02-2.12 (m, 4H), 1.44-1.54 (m, 2H).

(*E*)-octa-1,6-diene (S4). The following procedure was adapted from the literature.[14] The crude product (**S2**) (*E*)-octa-2,7-dien-1-ol (3.35 g) from the previous step was transferred to a 500-mL flame-dried round-bottom flask charged with a stir bar and dichloromethane (125 mL). The solution was cooled to 0 ºC in an ice water bath before triethylamine (20.3 mL, 146 mmol, 5.5 equiv) and methanesulfonyl chloride (11.3 mL, 146 mmol, 5.5 equiv) were added. The reaction mixture was allowed to stir overnight. After complete conversion observed by TLC, the reaction was poured into ice water and extracted into hexanes. The organic layer was successively washed with 5% aqueous HCl, saturated aqueous $NaHCO_3$ and brine and dried over Na_2SO_4. After filtration, the solvent was removed *in vacuo* and the crude product (**S3**) carried forward immediately without purification. The mesylate was dissolved in diethyl ether (100 mL) in a 500-mL round-bottom flask under a nitrogen atmosphere and cooled to –78 ºC in a dry ice/acetone bath. A solution of lithium aluminum hydride in diethyl ether (7.7 mL, 31 mmol, 4.0 M) was added slowly and the reaction mixture was allowed to warm to ambient temperature over a period of two hours. After full conversion observed by TLC, the reaction mixture was cooled to 0 ºC and quenched by sequential slow addition of water (1.2 mL), 15% aqueous sodium hydroxide (1.2 mL) and water (3.6 mL). The resultant suspension was allowed to warm to room temperature and stirred for 15 minutes before anhydrous magnesium sulfate was added. The reaction mixture was stirred for an additional 15 minutes before filtration to remove salts. The solvent was removed by distillation and the crude product was purified via silica gel chromatography to remove impurities (100% pentane, Rf~0.99, $KMnO_4$). The chromatography solvent was removed by distillation to yield (*E*)-octa-1,6-diene as a clear oil (584 mg, 20% yield over three steps). The spectral data matched that of the literature.[15] ^1H NMR (400 MHz, $CDCl_3$): δ 5.81 (ddt, *J* = 16.9, 10.2, 6.7 Hz, 1H), 5.49 – 5.36 (m, 2H), 5.04-4.96 (m, 1H), 4.96-4.91 (m, 1H), 2.09 – 1.95 (m, 4H), 1.67 – 1.63 (m, 3H), 1.49-1.39 (m, 2H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 139.09, 131.32, 125.14, 114.49, 33.39, 32.16, 28.96, 18.08. LRMS (EI, 70 eV) – *m/z* (M^+) calcd. for C_8H_{14}: 110.1. Found *m/z* (%) 110.1 (2), 95.1 (19), 81.1 (53), 68.1 (100), 55.1 (54).

Hydroarylation with (*E*)-1,6-octadiene



An oven-dried screw-cap glass reaction tube was charged with a solution of Co(II)(salen) in dichloromethane (*see chart*). Dichloromethane was removed via a steady stream of nitrogen and the reaction vial was placed in a 240 ºC oven for twenty minutes to ensure dryness. To each vial was added 1-fluoro-2,4,6-trimethylpyridinium tetrafluoroborate (5.7 mg, 0.025 mmol) and a stir bar. The reaction tube was sealed with a PTFE/silicone septa screw cap and wrapped with parafilm. The atmosphere was evacuated and backfilled with nitrogen three times and subsequently switched to an argon balloon. DMPU (100 µL) was added, followed by 4-iodobenzotrifluoride (7.5 µL, 0.053 mmol), decane (10 µL, 0.053 mmol) and (*E*)-octa-1,6-diene (10 µL, 0.067 mmol). The dark green reaction mixture was allowed to stir for approximately fifteen minutes at ambient temperature. The reaction vessel was placed in a water bath, before the appropriate nickel solution (20 µL) was added followed immediately by addition of Ph(*i*-PrO)SiH_2 (18 µL, 0.097 mmol). Once gas evolution subsided, the dark red solution was taken out of the water bath. The argon balloon was removed and the reaction vessel was sealed with a layer of parafilm and electrical tape. The reaction was allowed to proceed for exactly six hours.

The reaction mixture was quenched by addition of 2M hydrochloric acid (1 mL) and extracted into ethyl acetate (2.5 mL). Product composition was measured by GC-FID (method B). **U**/**R** ratios were averaged over four independent trials.

Co(II)(salen) solution: To a reaction vial was added Co(II)(salen) (62.0 mg, 0.103 mmol) and dichloromethane (6.2 mL) to form a 10 mg/mL stock solution.

mol % (*for a 50 µmol scale reaction*)	**10**	**15**	**20**	**25**	**30**
mass (mg)	3.1	4.6	6.2	7.7	9.2
volume stock solution (µL)	310	460	620	770	920

dtbbpyNiBr₂ solution: A 1-dram vial was charged with nickel bromide diglyme and 4,4'-di-tert-butyl-2,2'-dipyridyl (*see chart*). The atmosphere was evacuated/backfilled with nitrogen three times, before switched to an argon balloon. DMPU (250 µL) was added and the mixture was sonicated for thirty minutes until a dark green solution was formed. To each reaction mixture was added 20 µL of the appropriate solution.

mol % (*for a 50 µmol scale reaction*)	**5**	**7.5**	**10**	**12.5**	**15**
amount dtbbpy ligand (mg)	6.8	10.3	13.7	17.1	20.5
amount $NiBr_2$·diglyme (mg)	9.0	13.4	18.0	22.4	27.0

Separation and identification of unrearranged and rearranged hydroarylation products:

Crude material from several experiments was combined before isolation. The combined products were isolated by preparatory TLC (silica) (Rf = 0.8—0.82 in 100% hexanes, UV). The combined products were further separated via preparatory TLC on silver nitrate impregnated silica to yield two bands containing four rearranged diastereomeric products and the unrearranged product, respectively (Rf = 0.85 and 0.70, respectively). The peak fractions were identified by GC-MS, GC-FID and ^{1}H NMR.

Rearranged products 1-4 *m/z* (M^+) calcd. for $C_{15}H_{19}F_3$: 256.14

peak 1 - MS (EI, 70 eV): m/z (%) 256.1 (1), 173.0 (10), 159.0 (9), 133.0 (12), 83.1 (100), 67.1 (8), 55.1 (38).

peak 2 - MS (EI, 70 eV): m/z (%) 256.2 (1), 173.1 (10), 159.1 (9), 133.0 (13), 83.1 (100), 67 (8), 55.1 (38).

peak 3 - MS (EI, 70 eV): m/z (%) 256.1 (1), 173.1 (10), 159.0 (10), 133.0 (12), 83.1 (100), 55.1 (35).

peak 4 - MS (EI, 70 eV): m/z (%) 256.1 (1), 173.1 (11), 159.0 (9), 133.0 (13), 83.1 (100), 55.1 (36).

Unrearranged product

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.53 (d, *J* = 8.0 Hz, 2H), 7.31 – 7.26 (m, 2H), 5.43 – 5.34 (m, 2H), 2.79 – 2.62 (m, 1H), 2.00 – 1.89 (m, 2H), 1.65 – 1.54 (m, 4H), 1.40 – 1.27 (m, 3H), 1.24 (d, *J* = 6.9 Hz, 3H).

^{19}F NMR (376 MHz, $CDCl_3$): δ -62.53.

m/z (M^+) calcd. for $C_{15}H_{19}F_3$: 256.14. MS (EI, 70 eV): m/z (%) 256.1 (6), 199.1 (17), 187.1 (14), 173.1 (33), 159.0 (15), 153.1 (12), 133 (17), 55.1 (16)

Figure S9. **Independence of radical clock substrate cyclization on nickel concentration**

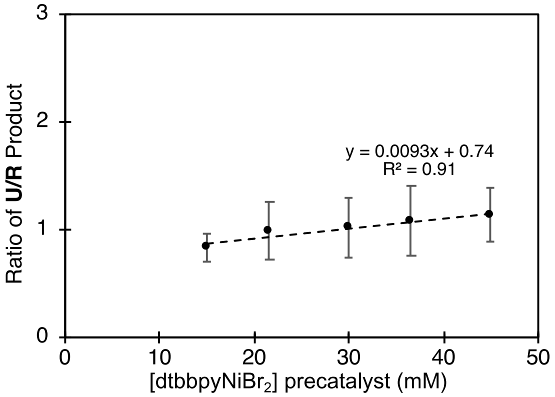
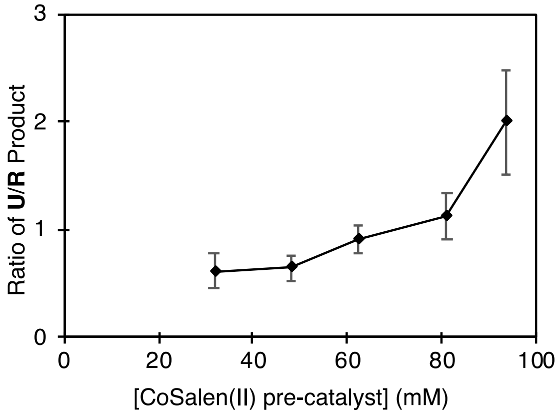
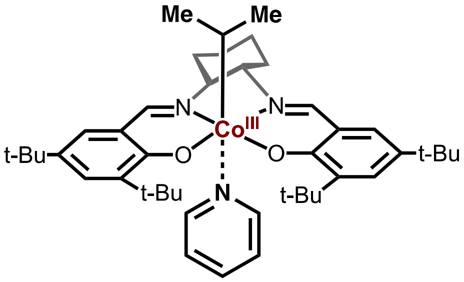


Figure 10. **Dependence of radical clock substrate cyclization on cobalt concentration.**

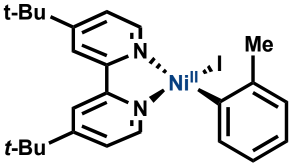


Stoichiometric Experiments



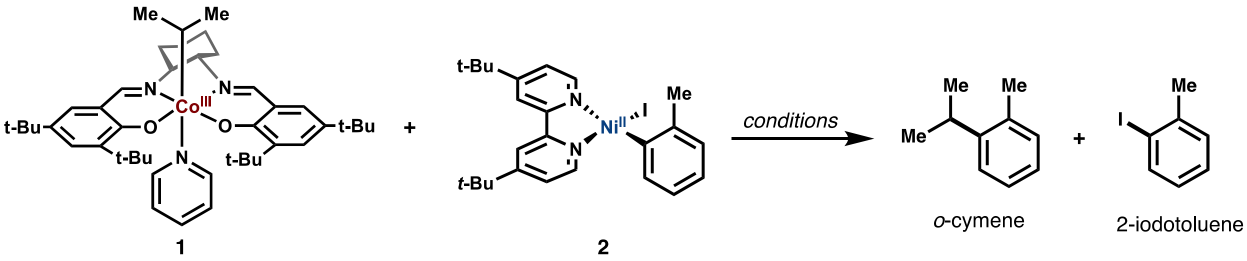
(*i*-Pr)Co^{III}(Salen$^{t\text{-Bu},t\text{-Bu}}$)(pyr) (1). The synthesis of **1** was based on literature precedent for the synthesis of primary alkyl CoSalen complexes.[16] An oven-dried, 1-dram vial was charged with Co(II)(salen) (121.1 mg, 0.201 mmol), Na/Hg amalgam (approx. 20% by wt, 110.0 mg, 0.97 mmol) and a stir bar. The vial was brought into an inert-atmosphere glovebox and tetrahydrofuran (2.0 mL) and pyridine (33 µL, 0.41 mmol) were added. The red suspension was stirred at ambient temperature for approximately two hours, until a dark green solution formed. An aliquot (1.7 mL, 0.17 mmol, 0.1 M in tetrahydrofuran) of the green solution was transferred to a separate 1-dram vial and cooled in a –35 °C freezer for one hour. The vial was removed from the freezer and wrapped in aluminum foil before 2-bromopropane (18 µL, 0.19 mmol, 1.1 equiv) was added (the glovebox lights were turned off at this point). The brown reaction mixture was allowed to warm to ambient temperature over thirty minutes before used in the next reaction.

To take a ^{1}H NMR, approximately 20 µL was transferred to a 1-dram vial. The solvent was evaporated to leave a brown solid that was subsequently taken up in *d*$_6$-benzene and transferred to a 5 mm NMR tube. The tube was capped and wrapped in parafilm before it was removed from the box. ^{1}H NMR (600 MHz, Benzene-*d*$_6$) δ 7.75 (d, *J* = 2.7 Hz, 1H), 7.73 (d, *J* = 2.7 Hz, 1H), 7.60 (d, *J* = 1.7 Hz, 1H), 7.47 (d, *J* = 1.7 Hz, 1H), 7.18 (d, *J* = 2.6 Hz, 1H), 7.11 (d, *J* = 2.6 Hz, 1H), 5.11 (hept, *J* = 6.8 Hz, 1H), 2.61 – 2.54 (m, 1H), 2.42 – 2.36 (m, 1H), 2.11 – 2.06 (m, 1H), 2.03 (s, 9H), 1.98 (s, 9H), 1.97 – 1.93 (m, 1H), 1.87 – 1.75 (m, 4H), 1.42 (s, 9H), 1.41 (s, 9H), -0.28 (d, *J* = 6.7 Hz, 3H), -0.33 (d, *J* = 6.7 Hz, 3H).



dtbbpyNi(*o*-Tol)I (2). The synthesis of **2** was adapted from the literature.[17] A 20-mL scintillation vial charged with a Teflon-lined stir bar and 4,4'-di-*tert*-butyl-2,2'-dipyridyl (82.1 mg, 0.306 mmol) was brought into an inert atmosphere glovebox. Ni(cod)$_2$ (79.9 mg, 0.290 mmol) was added followed by tetrahydrofuran (3 mL). The dark purple solution was stirred for two days at ambient temperature inside the glovebox (overnight stirring is sufficient). Upon addition of 2-iodotoluene (48 µL, 0.38 mmol), the reaction mixture turned a dark red. After three hours of stirring, the solution was filtered through a Celite plug into a 25-mL Schlenk tube. The Schlenk tube was removed from the glovebox and the solvent removed *in vacuo* on a Schlenk line. The resulting orange solid was triturated under an inert atmosphere with copious amounts of pentane (until supernatant ran clear) and dried under vacuum for one hour. The air-sensitive orange solid was brought back into the glovebox and stored in a –35 °C freezer. The complex was used within two days (120 mg, 76%). ^{1}H NMR (400 MHz, acetone-*d*$_6$) δ 9.57 (d, *J* = 5.9 Hz, 1H), 8.40 (dd, *J* =

13.0, 2.0 Hz, 2H), 7.66 (dd, *J* = 6.0, 2.0 Hz, 1H), 7.57 (dd, *J* = 7.4, 1.3 Hz, 1H), 7.39 (dd, *J* = 6.1, 2.1 Hz, 1H), 6.84 (d, *J* = 6.2 Hz, 1H), 6.79 – 6.74 (m, 1H), 6.73 – 6.67 (m, 1H), 6.64 (dd, *J* = 7.2, 1.4 Hz, 1H), 2.96 (s, 3H), 1.43 (s, 9H), 1.37 (s, 9H).



Stoichiometric Transmetalation Experiment

***1** + **2** only* -

An oven-dried 1-dram vial was charged with a Teflon-lined stir bar and 1,3,5-trimethoxybenzene (1.8 mg, 0.011 mmol). The reaction vial was brought into an argon-filled glovebox and dtbbpyNi(*o*-Tol)I (**2**) (5.5 mg, 0.010 mmol) was added. Addition of DMPU (100 µL) was followed immediately by addition of **1** (0.10 mL, 0.010 mmol, 0.1 M in tetrahydrofuran). The reaction vial was wrapped in aluminum foil and allowed to stir at ambient temperature. After 18 hours, the reaction vial was removed from the box, quenched with degassed 2M HCl and diluted with ethyl acetate. The organic layer was separated, dried over sodium sulfate and product composition was measured by GC-FID (method C). Yields reflect average of two independent trials. See Scheme 6 in main text.

***1** + **2** + oxidant* –

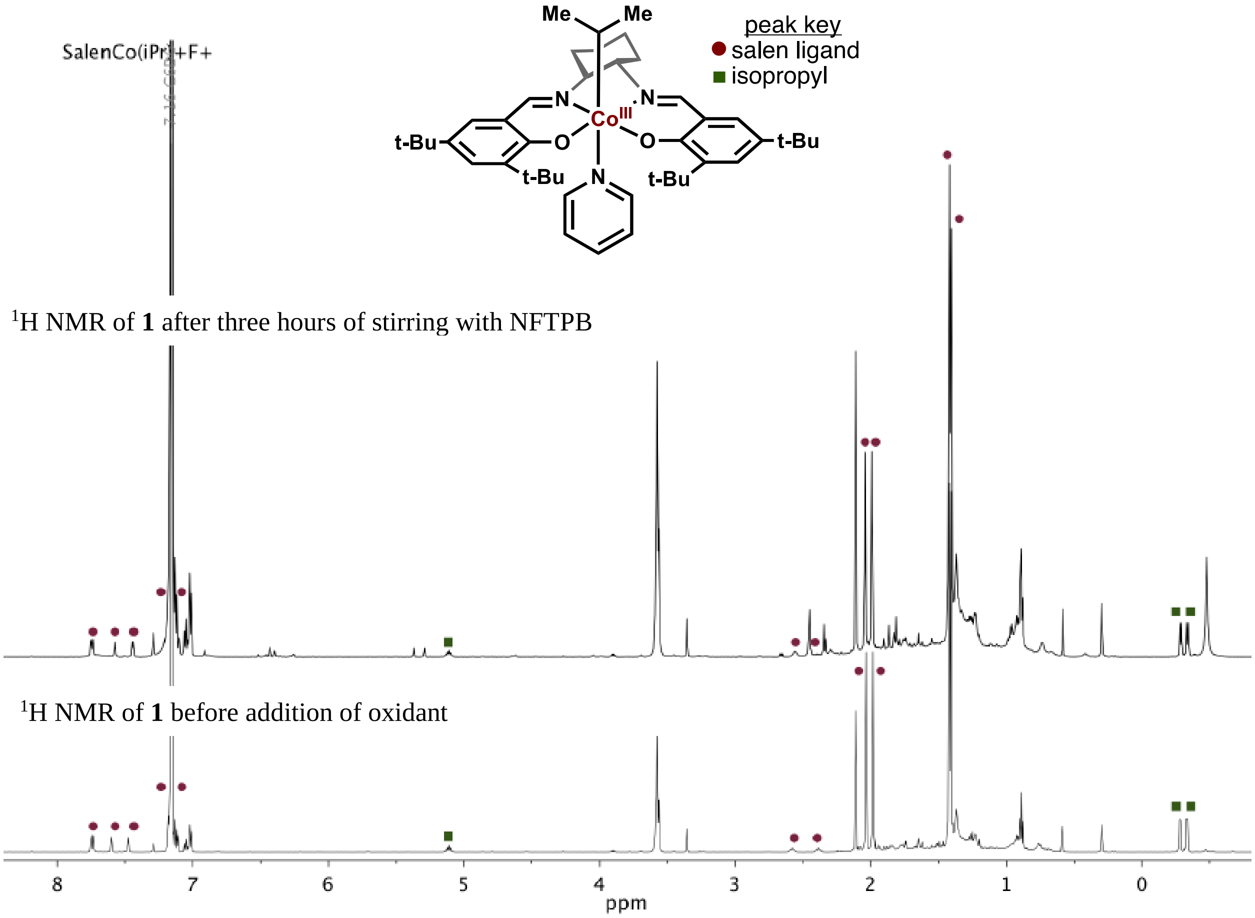
An oven-dried 1-dram vial was charged with a Teflon-lined stir bar, 1,3,5-trimethoxybenzene (1.8 mg, 0.011 mmol) and oxidant (*see chart*). The reaction vial was brought into an argon-filled glovebox and dtbbpyNi(*o*-Tol)I (**2**) (5.5 mg, 0.010 mmol) was added. DMPU (100 µL) was added and the reaction mixture was stirred for three hours at ambient temperature, a solution of **1** (0.10 mL, 0.010 mmol, 0.1 M in tetrahydrofuran) was added. The reaction vial was wrapped in aluminum foil and allowed to stir at ambient temperature for 18 hours. After removal from the glovebox, the reaction mixture was quenched by addition of degassed 2M HCl and diluted with ethyl acetate. The organic layer was separated, dried over sodium sulfate and product composition was measured by GC-FID (method C). The products, *o*-cymene and 2-iodotoluene, were identified by matching retention times with authentic material (GC-MS/GC-FID). 2,2'-dimethyl-1,1'-biphenyl was identified by GC-MS only. Yields reflect average of two independent trials. See Table 1 in main text.

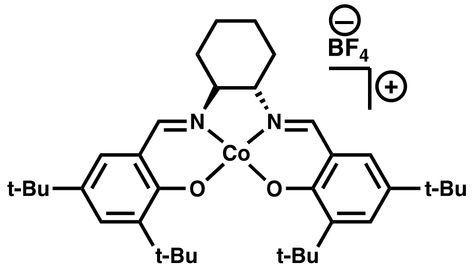
oxidant	equivalents	mass	mmol
NFTPB	1.0	2.3 mg	0.010 mmol
$AcFcBF_4$	1.0	3.1 mg	0.010 mmol
$AcFcBF_4$	2.0	6.2 mg	0.020 mmol

Reaction of **1** with NFTPB:

A solution of **1** (0.1 M in tetrahydrofuran) was prepared as detailed above. To a separate 1-dram vial equipped with a stir bar was added 1-fluoro-2,4,6-trimethylpyridinium tetrafluoroborate (4.5 mg, 0.020 mmol, 1.0 equiv) and brought into the glovebox. A solution of **1** (0.20 mL, 0.020 mmol, 1.0 equiv, 0.1 M in tetrahydrofuran) was added to this vial and the reaction mixture was stirred for three hours at ambient temperature. A small aliquot of the reaction mixture was removed and transferred to a separate vial. The solvent was evaporated to leave a brown solid that was subsequently taken up in d_6-benzene and transferred to a 5 mm NMR tube. The tube was capped, wrapped in parafilm and removed from the glovebox for ^{1}H NMR acquisition.

Figure S11. **^{1}H NMR of (*i*-Pr)Co^{III}(Salen$^{t\text{-Bu},t\text{-Bu}}$)(pyr) before and after reaction with NFTPB**





(±)-*N*,*N′*-bis(3,5-di-tert-butylsalicylidene)-1,2-cyclohexanediaminato cobalt(III) tetrafluoroborate ($Co(III)BF_4$). This procedure was adapted from the literature.[18] A 20-mL scintillation vial was charged with Co(II)(salen) (252 mg, 0.417 mmol). Dichloromethane (5 mL) was added, followed by addition of $AgBF_4$ (92.1 mg, 0.459 mmol). The reaction was wrapped in aluminum foil and carried out in the dark. After three hours stirring at room temperature, the dark green reaction mixture was filtered through Celite and concentrated. The resulting solid was taken up in pentane (30 mL) and collected on a fritted filter. The dark green solid was washed with additional pentane (50 mL) until the filtrate ran clear. After two hours drying under vacuum, the solid was used without further purification (239 mg, 81%). One molecule of water coordination is assumed in yield calculations. The compound was characterized by ^1H and ^{19}F NMR in dilute DMSO-d_6. In accordance with the literature, the compound exists as a *C2*-symmetric species with two axial DMSO-d_6 ligands.[1] The tetrafluoroborate anion appears in the ^{19}F NMR as two unsymmetrical peaks.

^1H NMR (400 MHz, DMSO-d_6) δ 7.82 (s, 2H), 7.48 (d, J = 2.5 Hz, 2H), 7.45 (d, J = 2.6 Hz, 2H), 3.61 (d, J = 8.0 Hz, 2H), 3.08 (d, J = 11.8 Hz, 2H), 2.05-1.85 (m, 2H), 1.75 (s, 18H), 1.72-1.56 (m, 4H), 1.31 (s, 18H).

^{19}F NMR (376 MHz, DMSO-d_6) δ -150.56, -150.61.

General Procedure for hydroarylation with [Co]X precatalyst:

An oven-dried reaction vial was charged with a stir bar and **[Co]X** precatalyst (*see chart*, Table 2 in main text) and any additives (*see chart*). The vial was sealed with a PTFE/silicone septa screw cap and the atmosphere was evacuated/backfilled with nitrogen three times. The vial was switched to an argon balloon, before DMPU (100 μL), decane (10 μL, 0.051 mmol), 4-phenyl-1-butene (10 μL, 0.067 mmol), and 4-iodobenzotrifluoride (7.5 μL, 0.051 mmol) were added. After five minutes of stirring, isopropoxy(phenyl)silane (18 μL, 0.10 mmol) was added and the reaction mixture was stirred for approximately three minutes before addition of **L**$NiBr_2$ (20 μL, 0.13M solution in DMPU).* The argon balloon was removed and the reaction wrapped in parafilm and electrical tape. The reaction was allowed to stir for 6-12 hours before quenched with 2M HCl and diluted with ethyl acetate. The crude product composition was measured by GC-FID. Yields reflect average of two independent trials. See Table 2 in main text.

additive/[Co]X	equivalents	mg	mmol
$Co(III)BF_4$	0.2	7.2 mg	10 μmol
Co(III)Cl	0.2	6.7 mg	10 μmol
Mn^{0**}	2	5.6 mg	100 μmol
NFTPB	0.3	3.5 mg	15 μmol

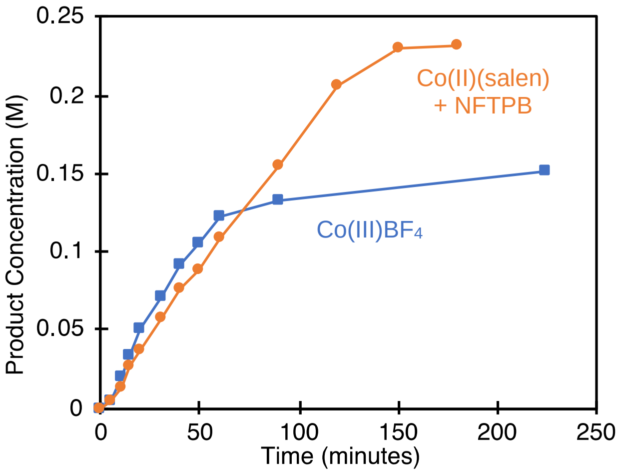
*dmbpyNiBr$_2$ – To an oven-dried 1-dram vial was added nickel bromide diglyme (18.0 mg, 0.051 mmol) and 4,4'-dimethoxy-2,2'-dipyridyl (11.0 mg, 0.051 mmol). The vial was evacuated/backfilled with nitrogen and switched to an argon balloon. DMPU (400 μL) was added and the vial was sonicated for approximately 20 minutes, or until a dark green solution resulted.

*dtbbpyNiBr$_2$ – To an oven-dried 1-dram vial was added nickel bromide diglyme (18.0 mg, 0.051 mmol) and 4,4'-di-*tert*-butyl-2,2'-dipyridyl (13.7 mg, 0.051 mmol). The vial was evacuated/backfilled with nitrogen and switched to an argon balloon. DMPU (400 μL) was added and the vial was sonicated for approximately 20 minutes, or until a dark green solution resulted.

**When setting up the Mn^0 reactions, stirring was started *after* silane addition as competitive reduction of the Co(III)BF$_4$ precatalyst occurred during the reaction set-up otherwise (as evidenced by appearance of red solid).

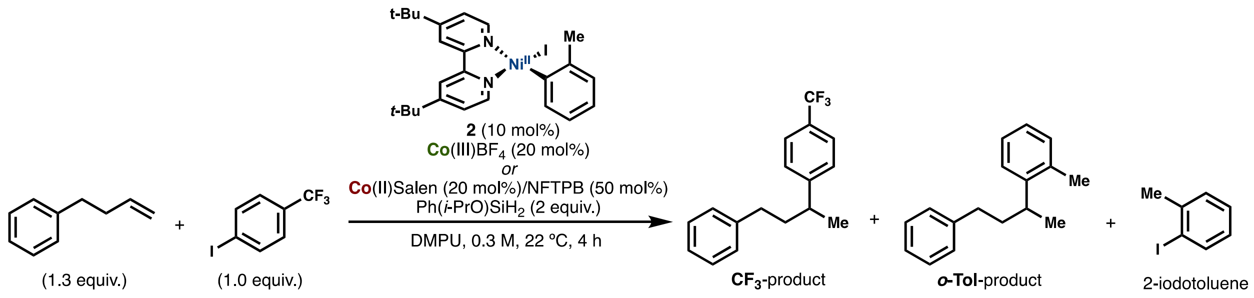
Kinetic profile of reaction when using Co(III)BF$_4$ precatalyst:
The kinetics were run according to the procedure outlined for the standard procedure, but **[Co]BF$_4$** (20.7 mg, 0.292 mmol) was used in place of Co(II)(salen) and 1-fluoro-2,4,6-trimethylpyridinium tetrafluoroborate.

***Figure S12.* Kinetic monitoring of (●) Co(II)(salen) + NFTPB (standard conditions) and (■) precatalyst Co(III)BF$_4$.**



The rates of both reactions overlay providing further evidence that NFTPB is not involved in the rate-determining transmetalation step. Interestingly, the **Co(III)BF$_4$** reaction stops abruptly, which could be due to catalyst deactivation.

Hydroarylation using dtbbpyNi(*o*-Tol)(I) (2) (10 mol %) as precatalyst:

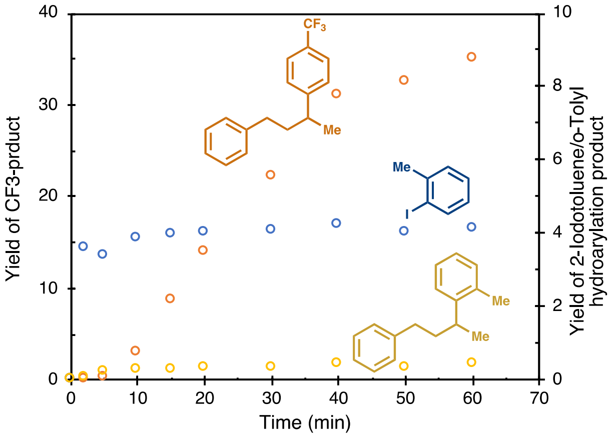


The dtbbpyNi(*o*-Tol)I complex (**2**) (30.0 mg, 55.0 μmol) was measured out into a 1-dram vial in an inert-atmosphere glovebox. The vial was capped with a PTFE/silicone septa screw cap and wrapped in parafilm before removed from the glovebox. An oven-dried reaction vial was charged with the cobalt precatalyst (*see chart*) and a Teflon-lined stir bar. The vial was sealed and evacuated/backfilled with nitrogen (three times). DMPU was added (200 μL) followed by addition of decane (20 μL, 0.10 mmol), 4-phenyl-1-butene (20 μL, 0.13 mmol), and 4-iodobenzotrifluoride (15 μL, 0.10 mmol). To the reaction mixture was added isopropoxy(phenyl)silane (38 μL, 0.20 mmol). Concurrently, DMPU (135 μL) was added to the nickel complex and the vial was briefly shaken to dissolve the complex. Five minutes after initial silane addition, the nickel solution was added to the reaction (25 μL, 10.2 μmol, 0.41 M in DMPU). The reaction was stopped after 12 hours and worked up as previously described. Yields reflect average of two independent trials.

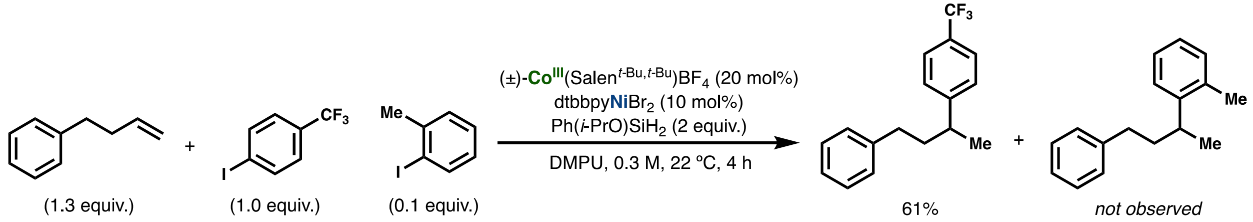
			Yield (%)		
Precatalyst	mmol	mg	**CF_3**-product	***o*-Tol**-product	2-iodotoluene
SalenCo(II)+NFTPB			68	1.7	5
Co(II)	0.021	12.3			
NFTPB	0.051	11.6			
Co(III)BF_4	0.021	14.5	49	0.3	5

***Figure S13.* Kinetic Profile of CF_3-product, o-Tol-product, and 2-iodotoluene formation**

Aliquots were taken after nickel precatalyst addition. Yields were obtained by GC-FID compared to an internal standard (decane).



Hydroarylation run with 0.1 equiv of 2-iodotoluene:



The reaction was run according to the standard conditions detailed above. A reaction vial was charged with **Co(III)BF$_4$** (14.0 mg, 0.020 mmol) and a Teflon-lined stir bar. The vial was sealed and evacuated/backfilled with nitrogen (three times). DMPU was added (200 μL) followed by addition of decane (20 μL, 0.10 mmol), 4-phenyl-1-butene (20 μL, 0.13 mmol), 4-iodobenzotrifluoride (15 μL, 0.10 mmol), and 2-iodotoluene (1.3 μL, 0.010 mmol). After five minutes of stirring, isopropoxy(phenyl)silane (36 μL, 0.20 mmol) was added and the reaction mixture was stirred for approximately three minutes before addition of dtbbpyNiBr$_2$ (20 μL, 0.26 M solution in DMPU). The argon balloon was removed and the reaction wrapped in parafilm and electrical tape. The reaction was allowed to stir for 6 hours before quenched with 2M HCl and diluted with ethyl acetate. The crude product composition was measured by GC-FID. No *o*-tolyl hydroarylation product was observed by GC-FID or GC-MS.

Catalytic hydroarylation – additional arene scope.

A reaction vial was charged with **Co(III)BF$_4$** (14.0 mg, 0.020 mmol) and a Teflon-lined stir bar. The vial was sealed and evacuated and backfilled with nitrogen three times. DMPU was added (200 μL) followed by addition of decane (20 μL, 0.10 mmol), 4-phenyl-1-butene (20 μL, 0.13 mmol), and aryl halide (*see chart*, 0.10 mmol). After five minutes of stirring, isopropoxy(phenyl)silane (38 μL, 0.21 mmol) was added and the reaction mixture was stirred for approximately three minutes before addition of dtbbpyNiBr$_2$ (20 μL, 0.13M solution in DMPU). The argon balloon was removed and the reaction cap wrapped in parafilm and electrical tape. The reaction was allowed to stir for 6 hours before quenched with 2M HCl and diluted with ethyl acetate. Product yields were measured by GC-FID using decane as an internal standard. Yields reflect average of two independent trials.

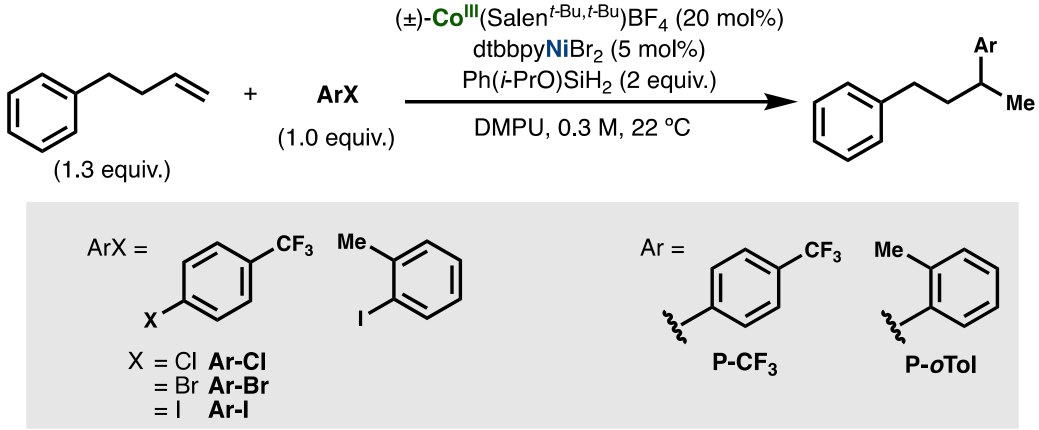


Table 1. **Additional aryl halide scope of hydroarylation.**

entry	ArX	μL added	Product	Yield (%)
1	**Ar-I**	15	**P-CF$_3$**	53
2	**Ar-Br**	14	**P-CF$_3$**	39
3	**Ar-Cl**	14	**P-CF$_3$**	7
4	2-iodotoluene	13	**P-*o*Tol***	25

*Characterization of **P-*o*-Tol**: The product was isolated by preparatory TLC using 100% pentane (R_f – 0.65, 100% pentane).

^{1}H NMR (600 MHz, CDCl$_3$): δ 7.28 – 7.07 (m, 9H), 2.98 (h, *J* = 7.0 Hz, 1H), 2.63 – 2.50 (m, 2H), 2.24 (s, 3H), 2.00 – 1.93 (m, 1H), 1.92 – 1.85 (m, 1H), 1.24 (d, *J* = 6.9 Hz, 3H).

^{13}C NMR (151 MHz, CDCl$_3$): δ 145.36, 142.51, 135.44, 130.25, 128.34, 128.26, 126.23, 125.65, 125.52, 125.19, 39.28, 33.91, 25.56, 21.72, 19.49.

LRMS (EI, 70 eV) – *m/z* (M$^+$) calcd. for $C_{17}H_{20}$: 224.16. Found *m/z* (%) 224.1 (24), 120.1 (34), 119.1 (100), 117.1 (16), 105.1 (33), 91.1 (37), 77.1 (10).

Figure S14. **GC-FID of typical hydroarylation reaction**

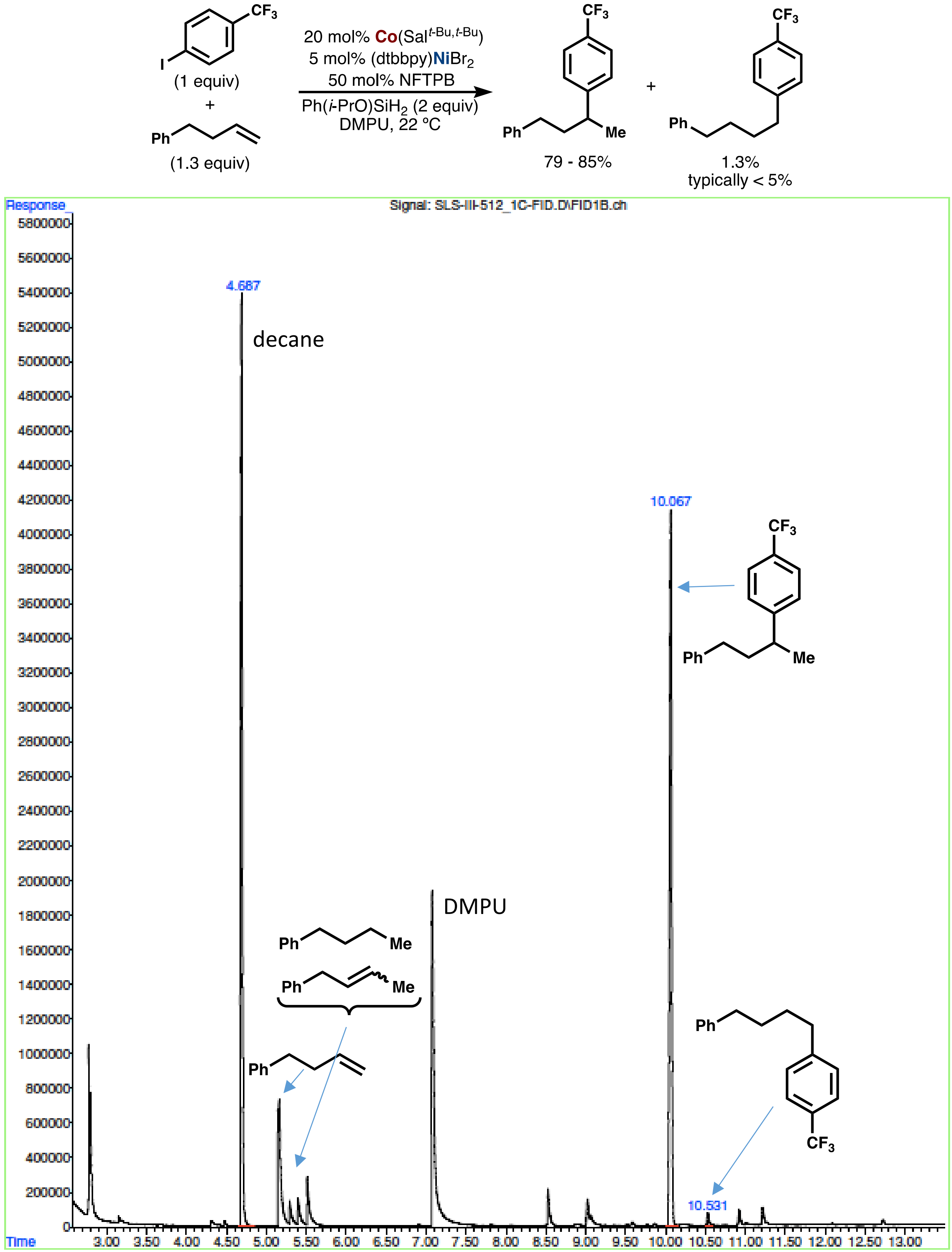


Figure S15**. ^{1}H NMR of 1-(4-phenylbutan-2-yl)-4-(trifluoromethyl)benzene**

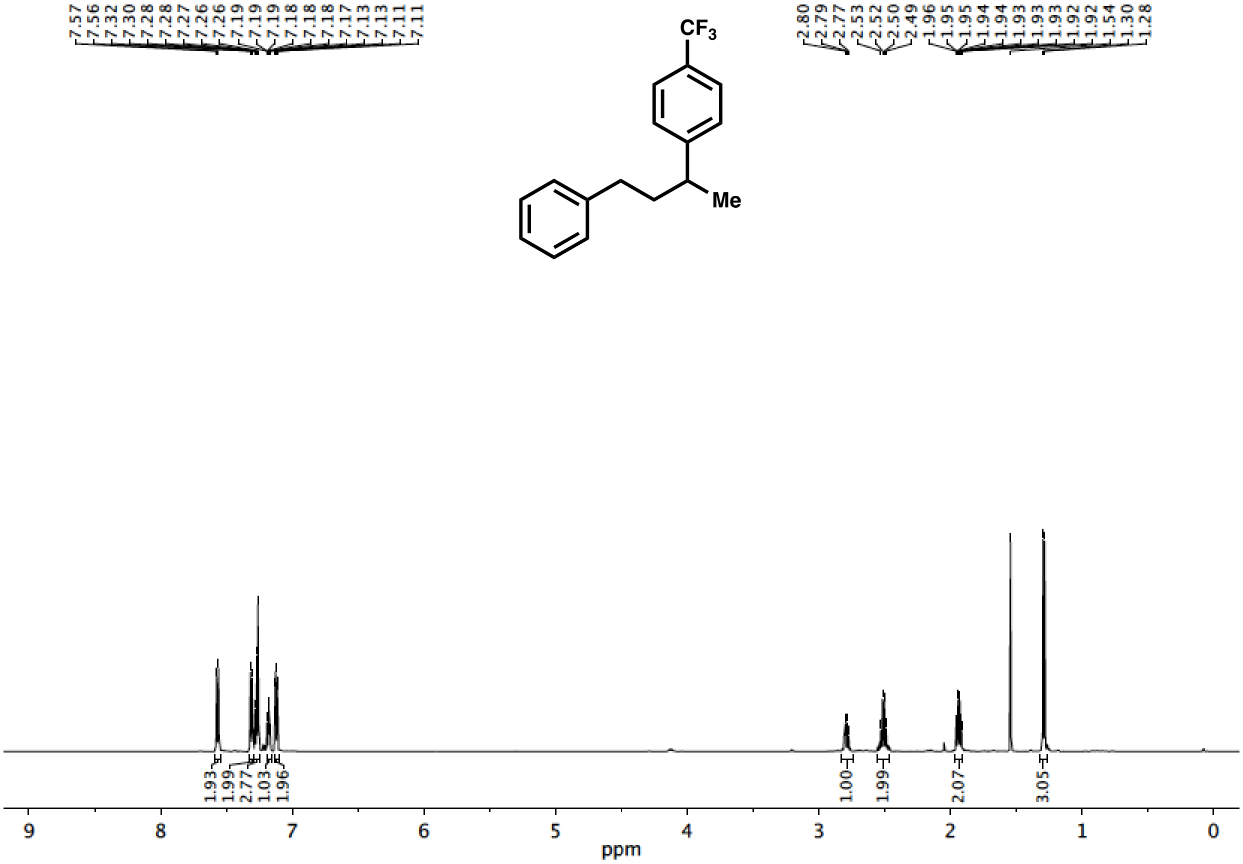


Figure S16. **^{13}C NMR of 1-(4-phenylbutan-2-yl)-4-(trifluoromethyl)benzene**

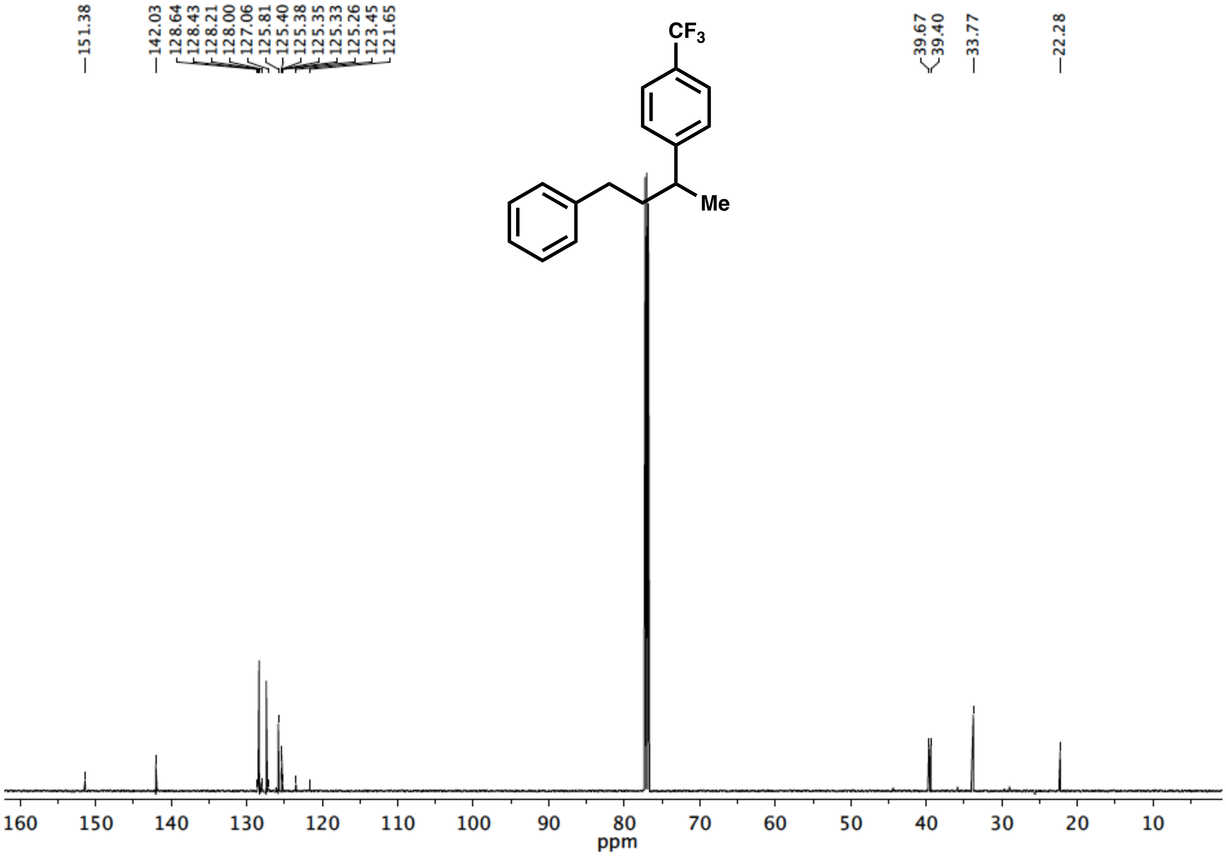


Figure S17. **^{19}F NMR of 1-(4-phenylbutan-2-yl)-4-(trifluoromethyl)benzene**

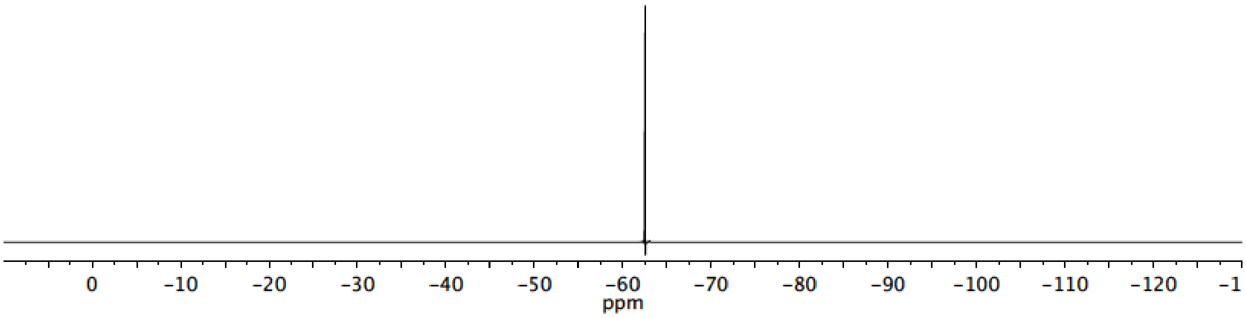


Figure S18. **^{1}H NMR of 1-methyl-2-(4-phenylbutan-2-yl)benzene**

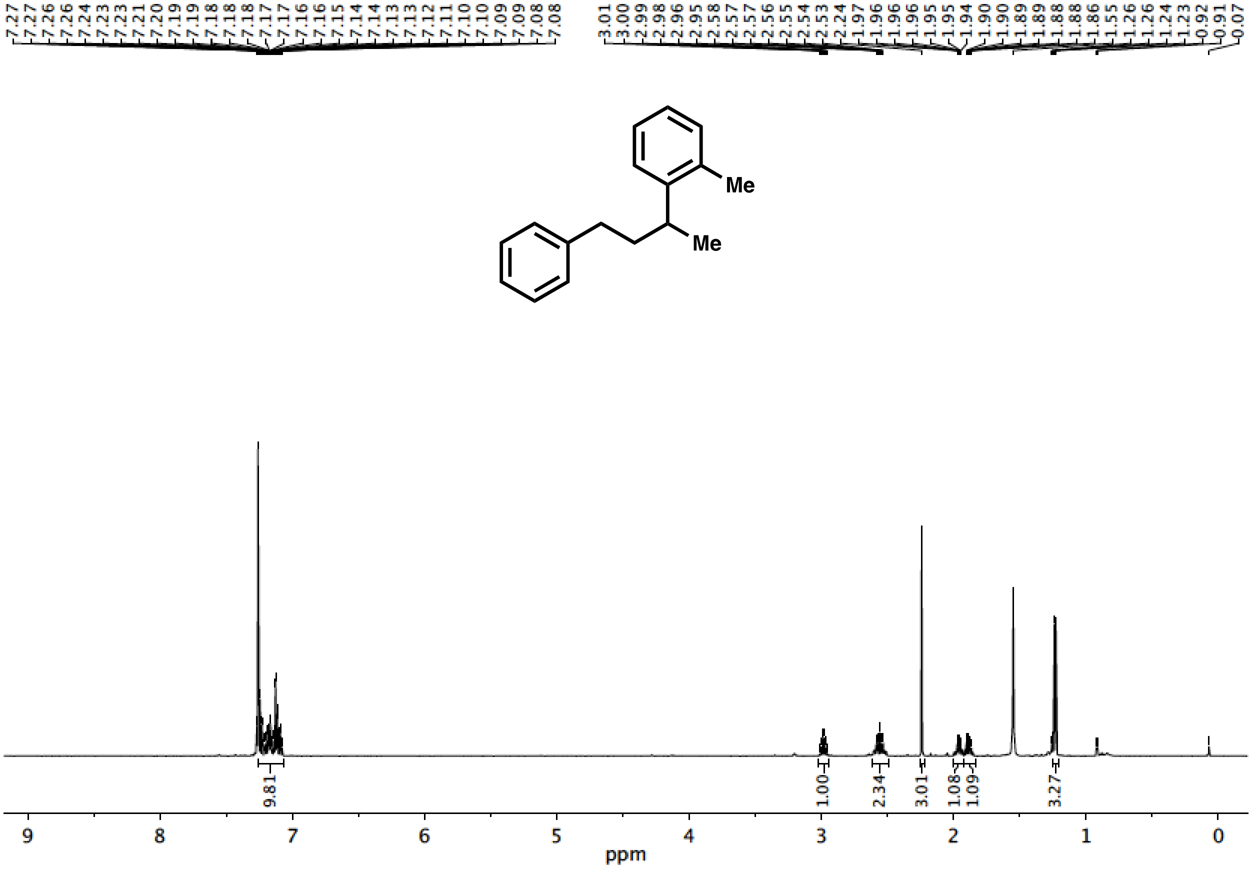


Figure S19. **^{13}C NMR of 1-methyl-2-(4-phenylbutan-2-yl)benzene**

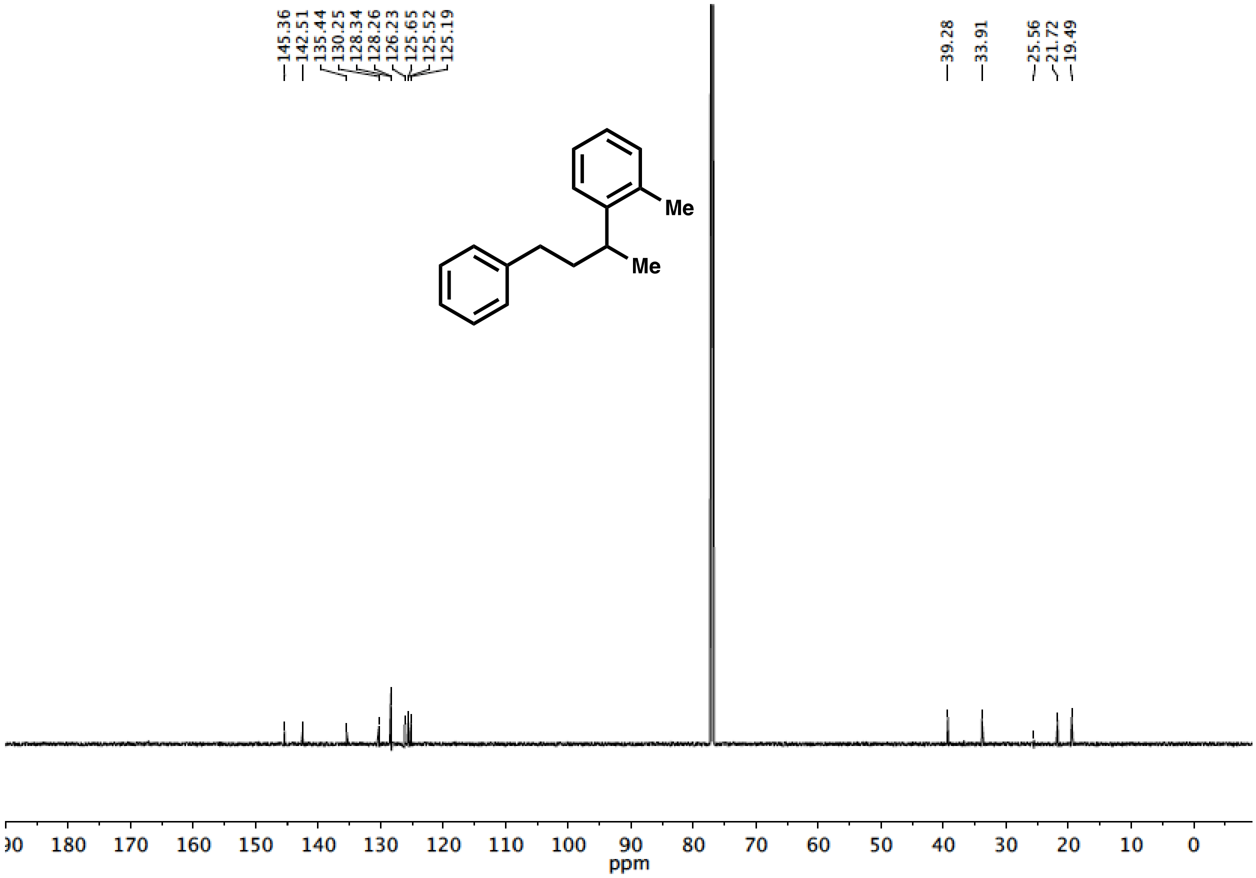


***Figure S20*. ^{1}H NMR of (but-3-en-1-yl-4,4-d_2)benzene**

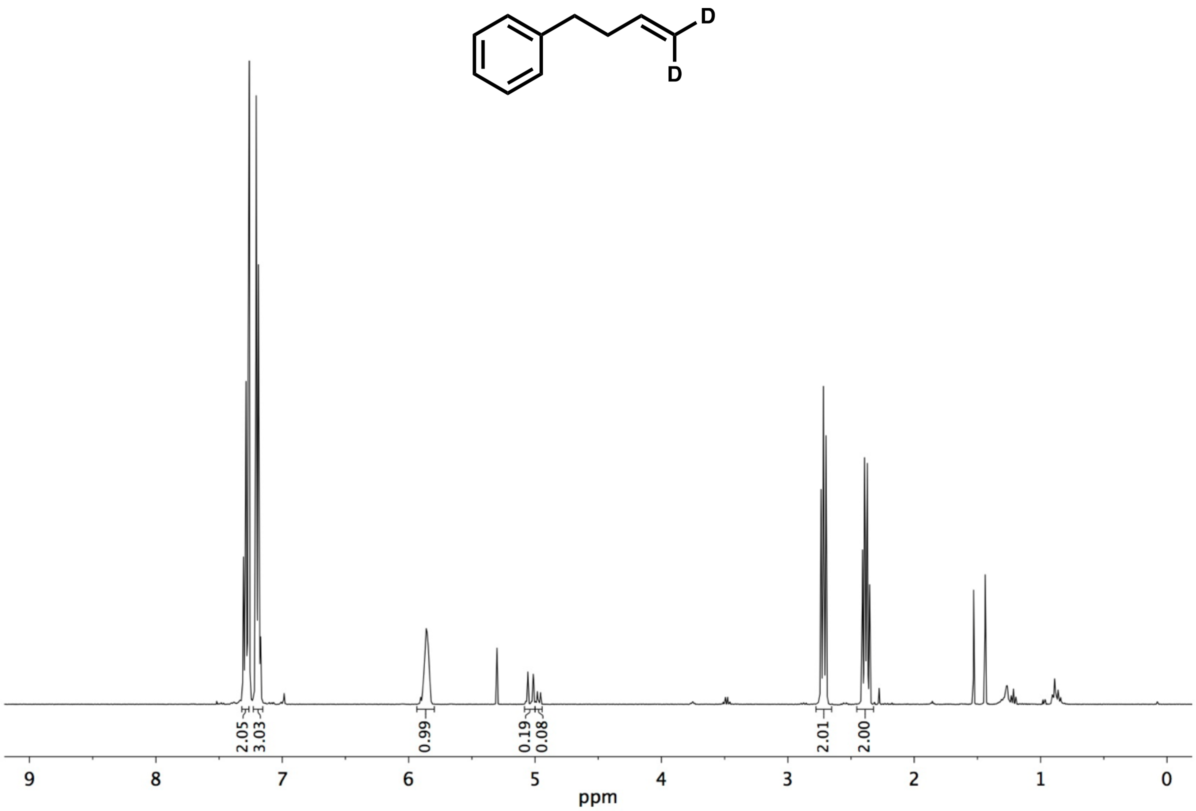


Figure S21. **^{1}H NMR of 1-(4-phenylbutan-2-yl-1,1-*d_2*)-4-(trifluoromethyl)benzene**

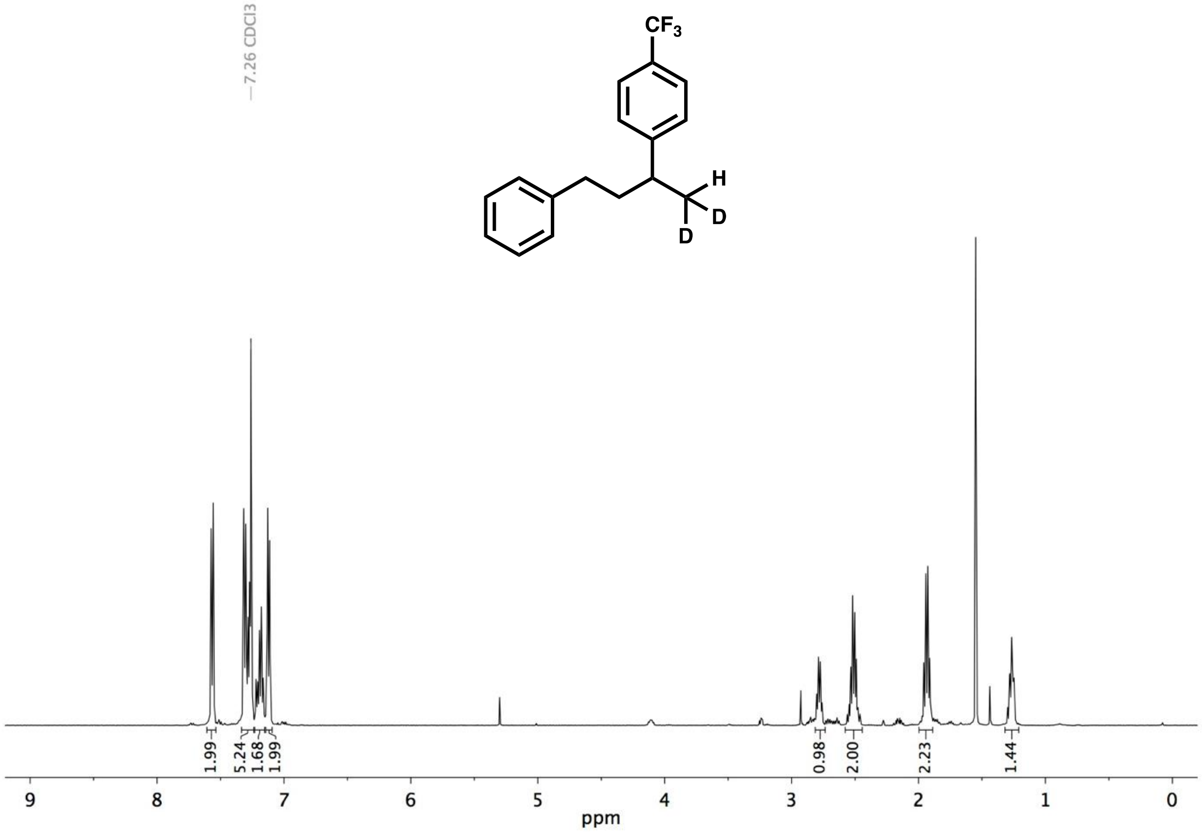


Figure S22. **^{13}C NMR of 1-(4-phenylbutan-2-yl-1,1-*d*$_2$)-4-(trifluoromethyl)benzene**

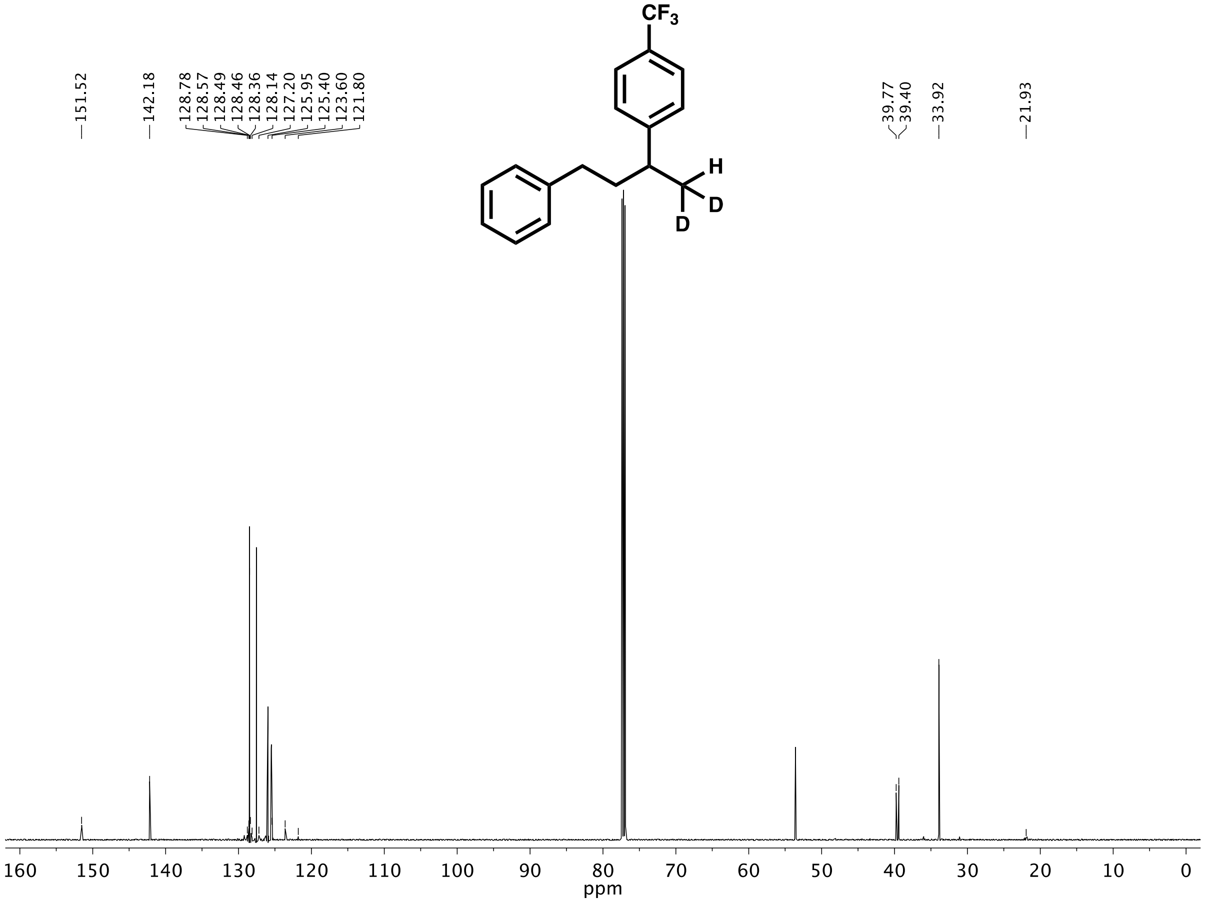
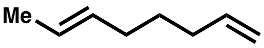


Figure S23. **^{1}H NMR of (*E*)-1,6-octadiene**



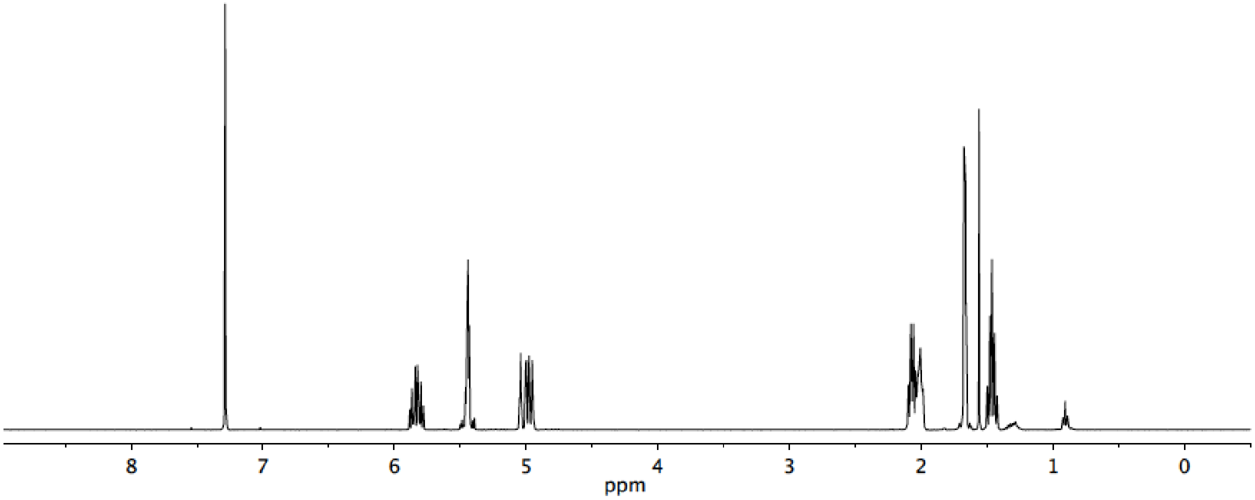


Figure S24. **^{13}C NMR of (*E*)-1,6-octadiene**

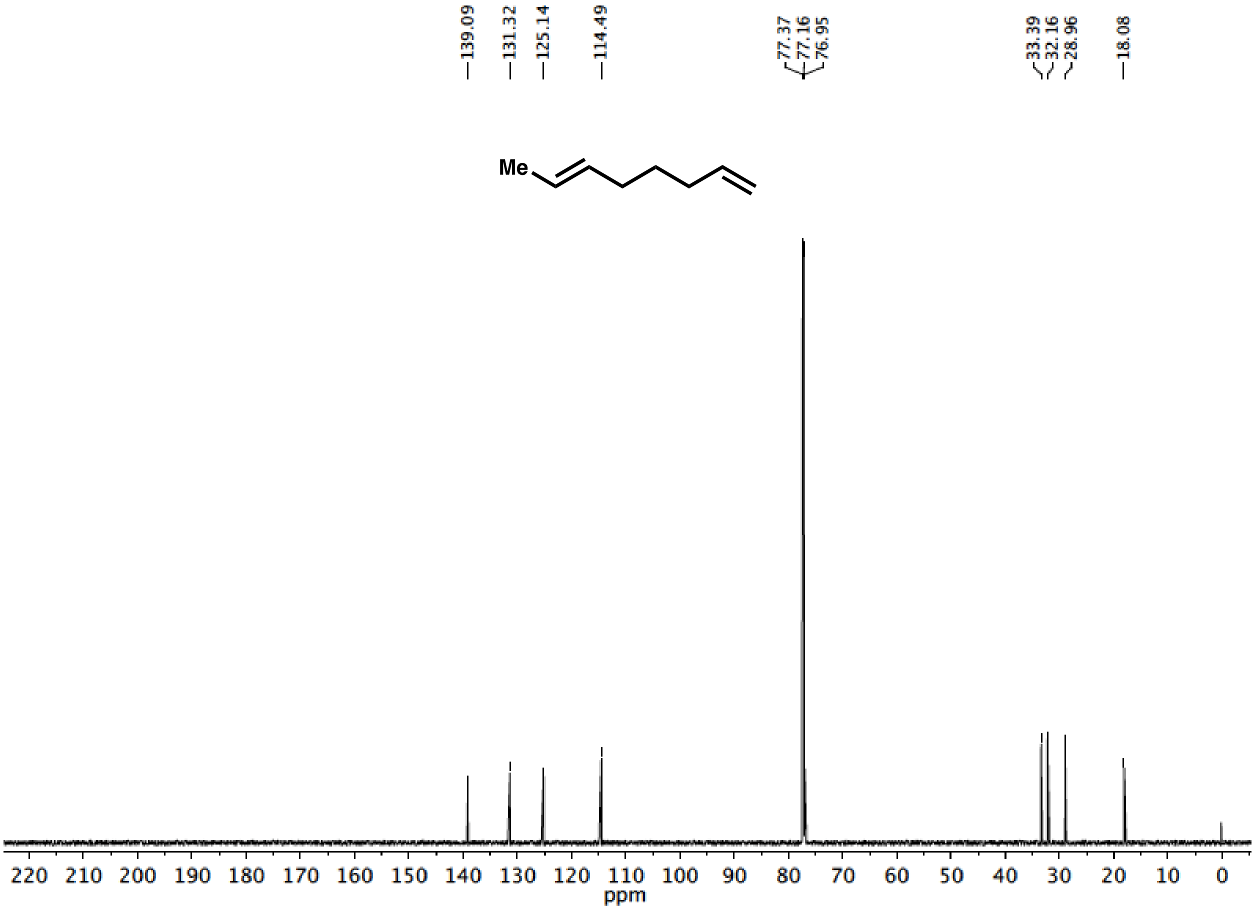


***Figure S25*. GC-MS trace of radical clock hydroarylation products.**

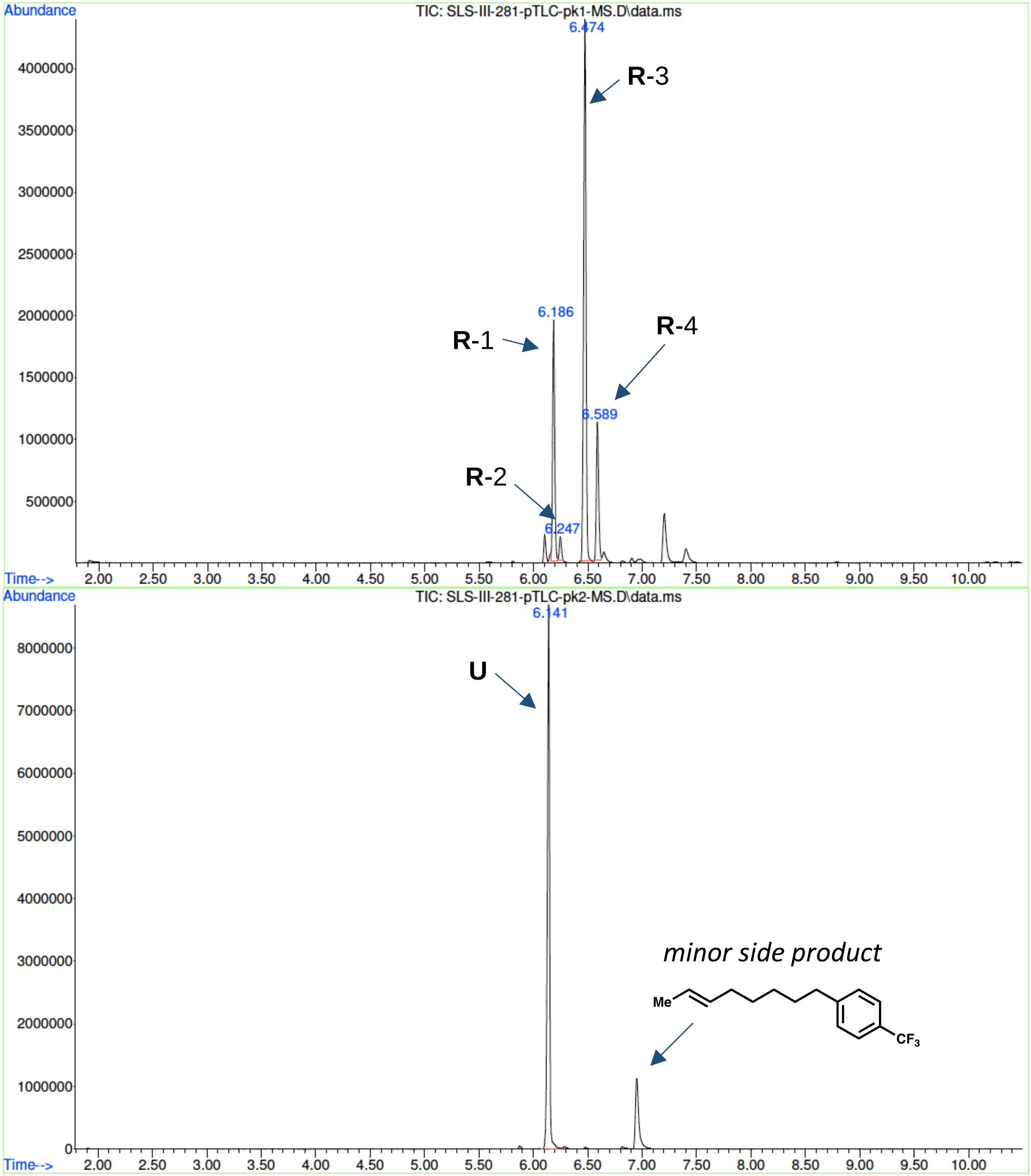
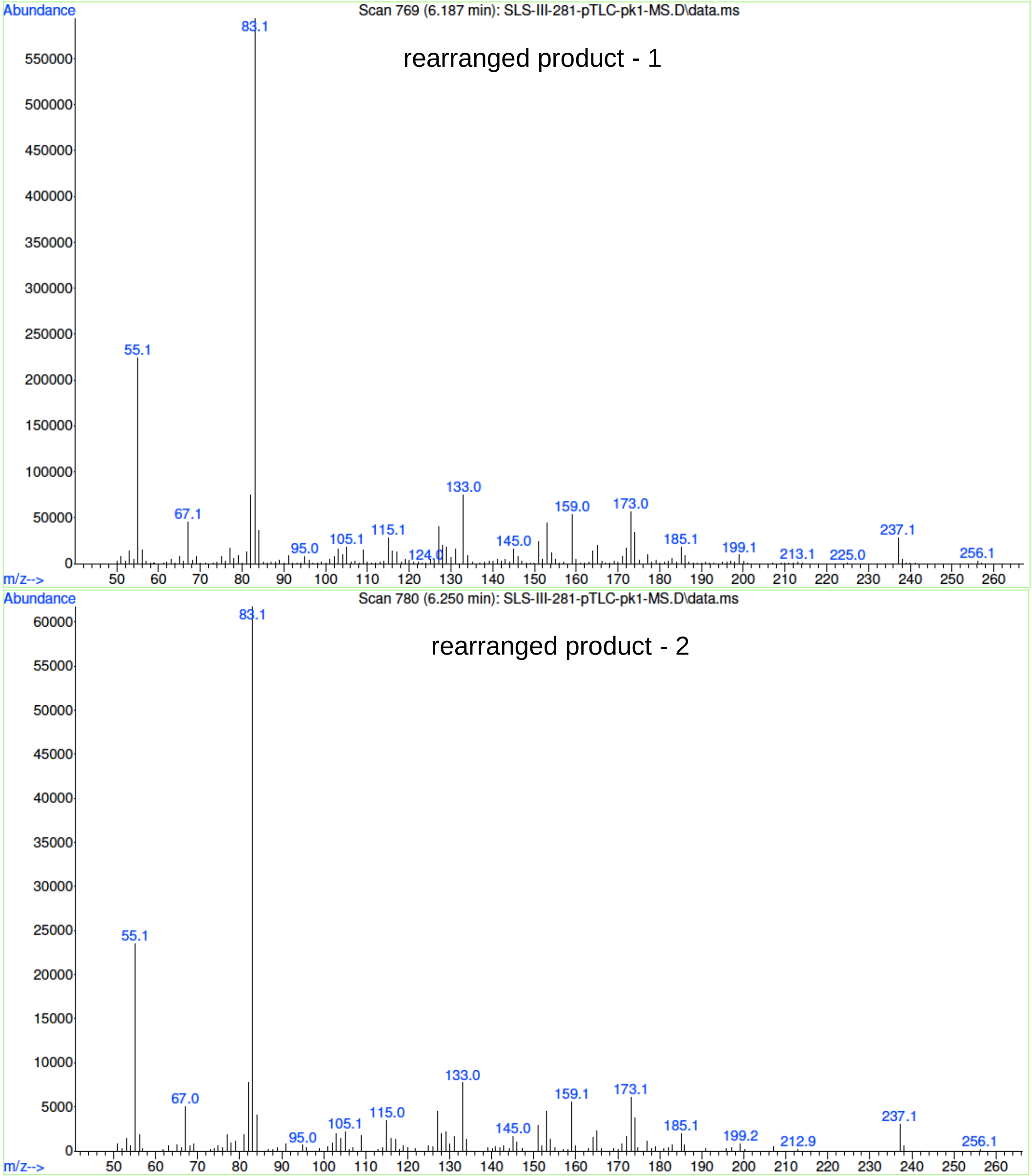
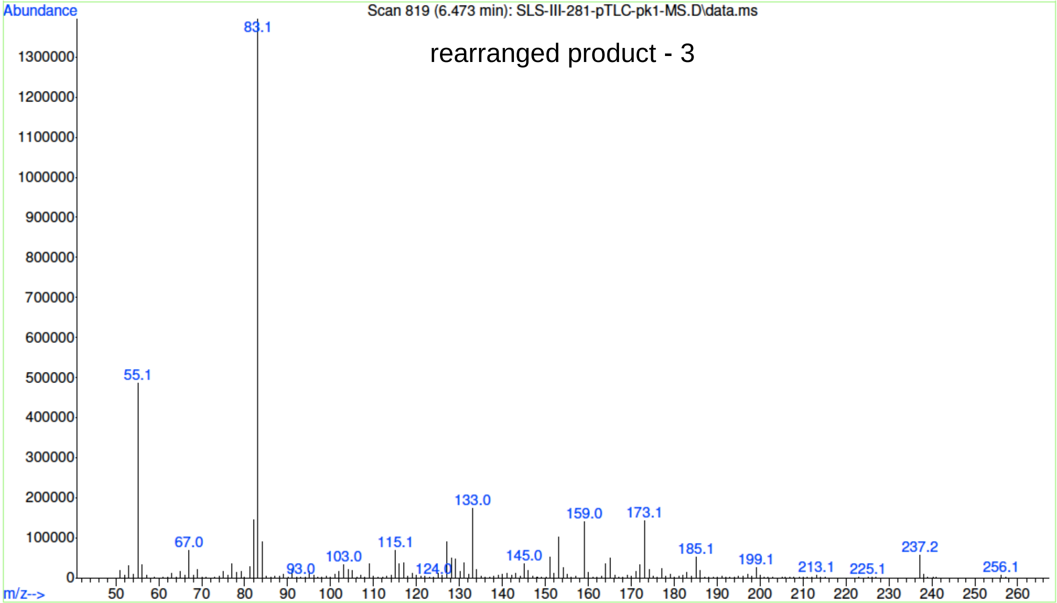
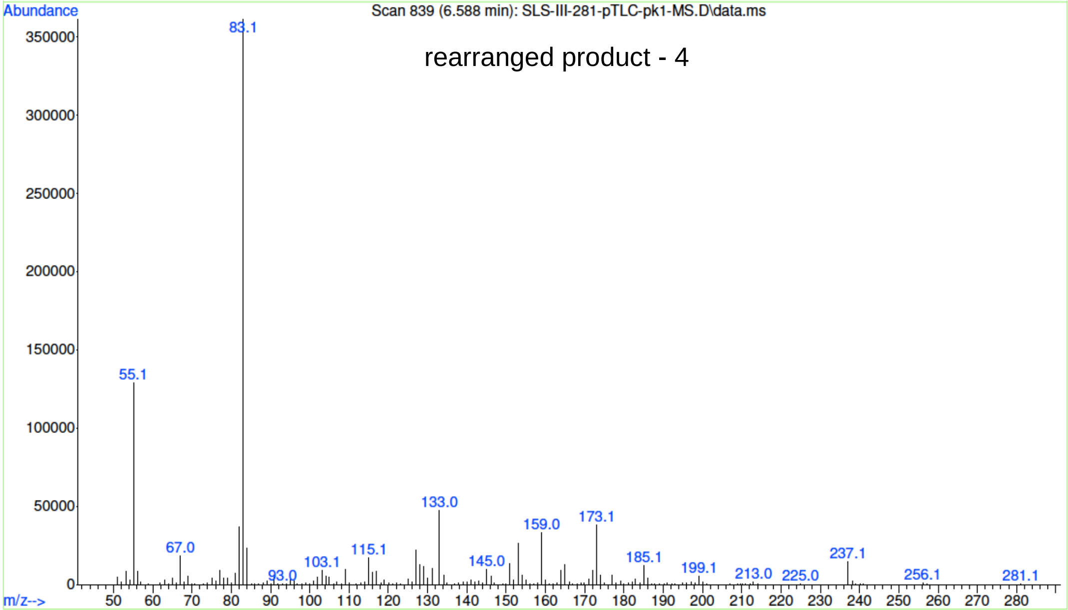
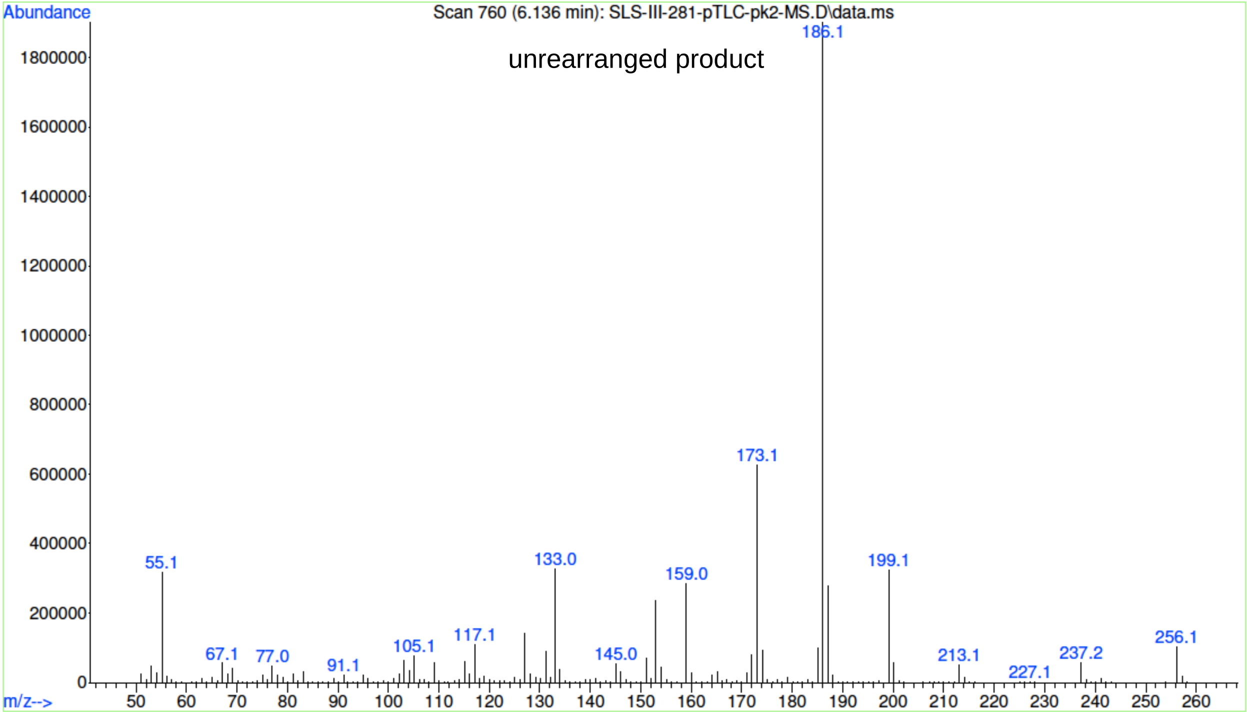


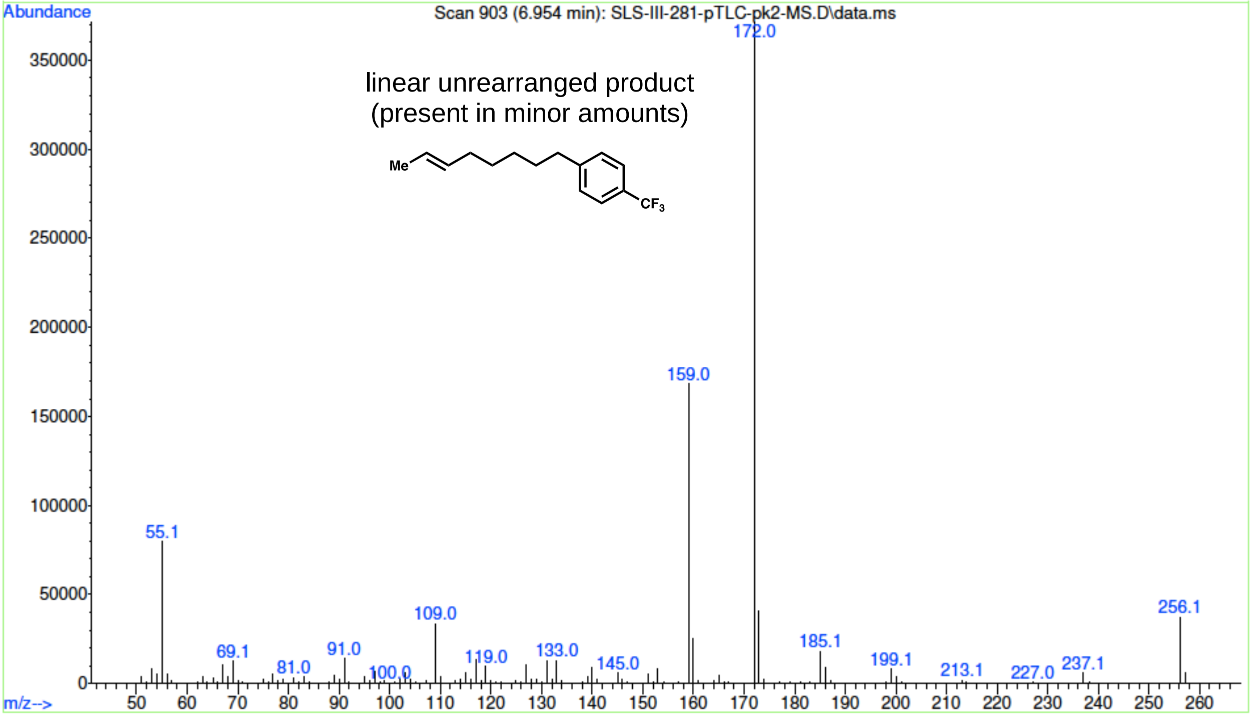
***Figure S26*. MS-TIC of radical clock hydroarylation products.**




Abundance
Scan 819 (6.473 min): SLS-III-281-pTLC-pk1-MS.D\data.ms
rearranged product - 3
1300000
1200000
1100000
1000000
900000
800000
700000
600000
500000
400000
300000
200000
100000
0
83.1
55.1
67.0
93.0
103.0
115.1
124.0
133.0
145.0
159.0
173.1
185.1
199.1
213.1
225.1
237.2
256.1
m/z-->
50 60 70 80 90 100 110 120 130 140 150 160 170 180 190 200 210 220 230 240 250 260


Abundance
Scan 839 (6.588 min): SLS-III-281-pTLC-pk1-MS.D\data.ms
rearranged product - 4
350000
300000
250000
200000
150000
100000
50000
0
83.1
55.1
67.0
93.0
103.1
115.1
133.0
145.0
159.0
173.1
185.1
199.1
213.0
225.0
237.1
256.1
281.1
m/z-->
50 60 70 80 90 100 110 120 130 140 150 160 170 180 190 200 210 220 230 240 250 260 270 280





The linear hydroarylation product was observed during isolation of the unrearranged and rearranged products and identified based on mass splitting alone. It was present in minor amounts during the radical clock experiments. As it arises via a different mechanistic pathway (nickel-only catalyzed), it was not included in the **U**/**R** ratio.

Figure S27. **^{1}H NMR of combined rearranged diastereomers**

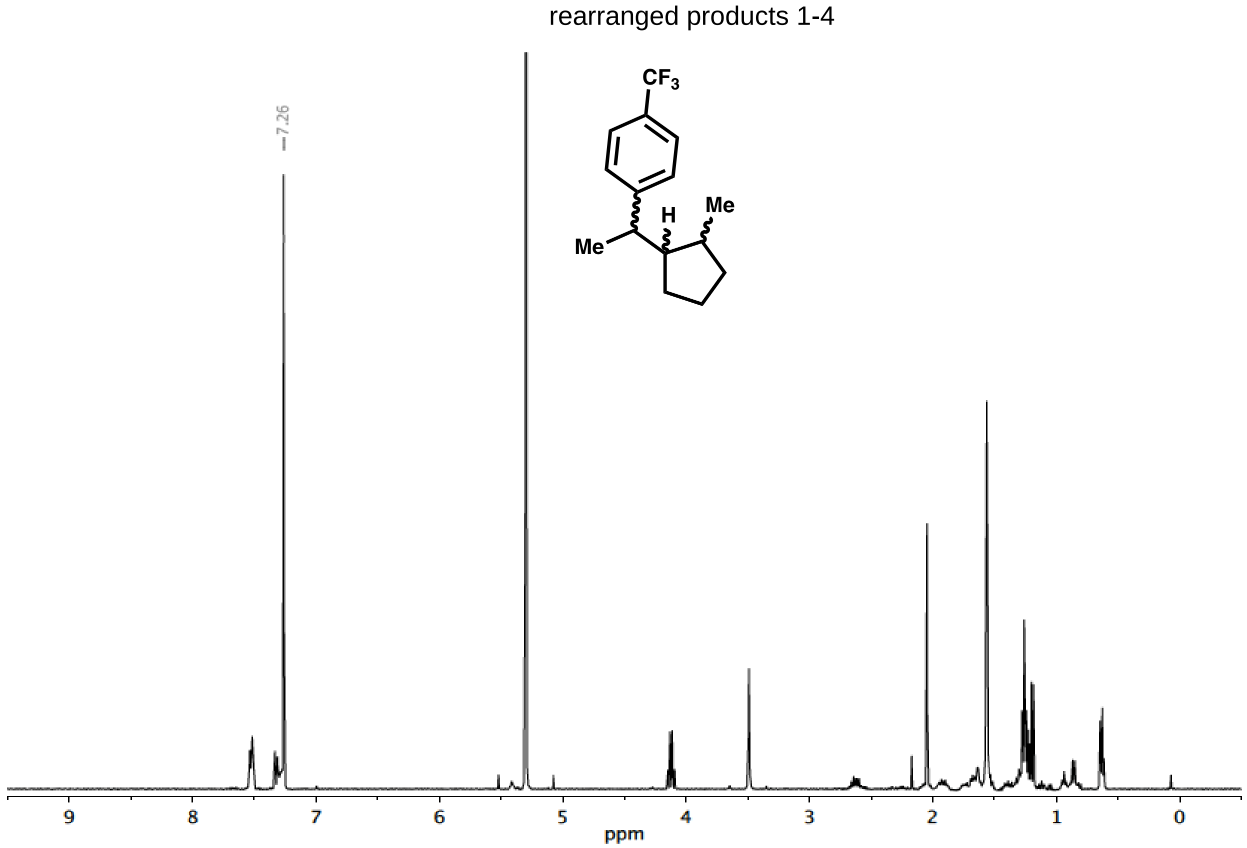


Figure S**28.^{19}F NMR of combined rearranged diastereomers**

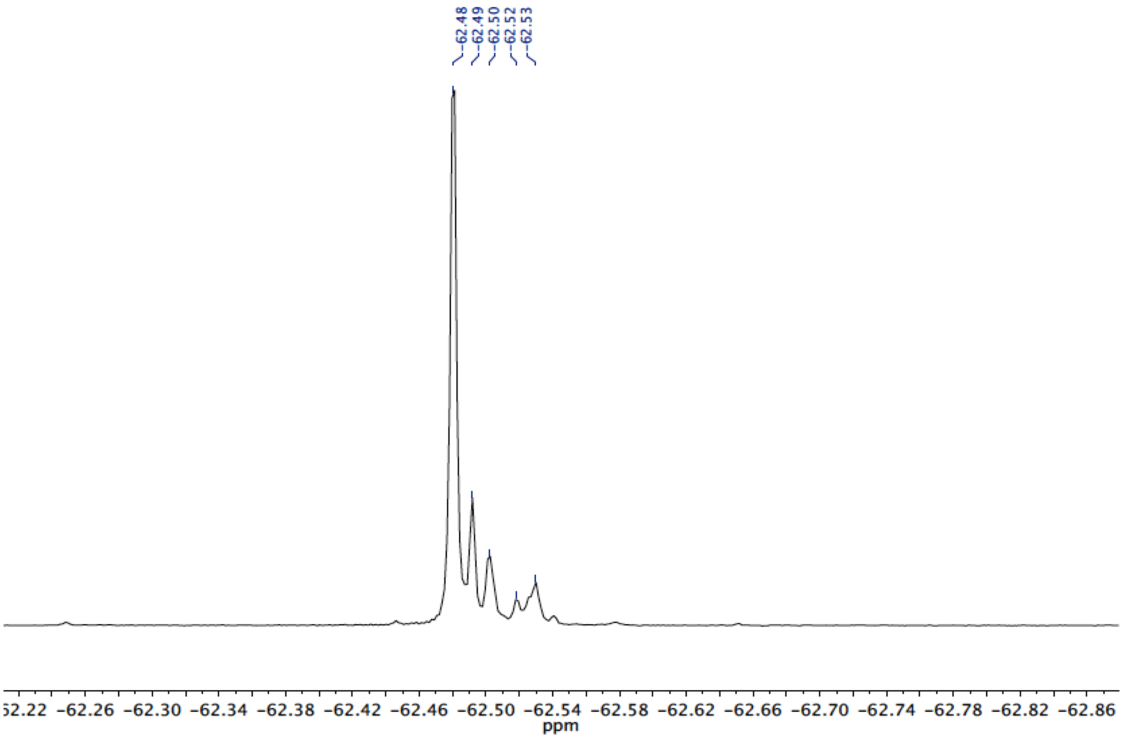


Figure S29. **^{1}H NMR of unrearranged product (and minor linear, unrearranged product)**

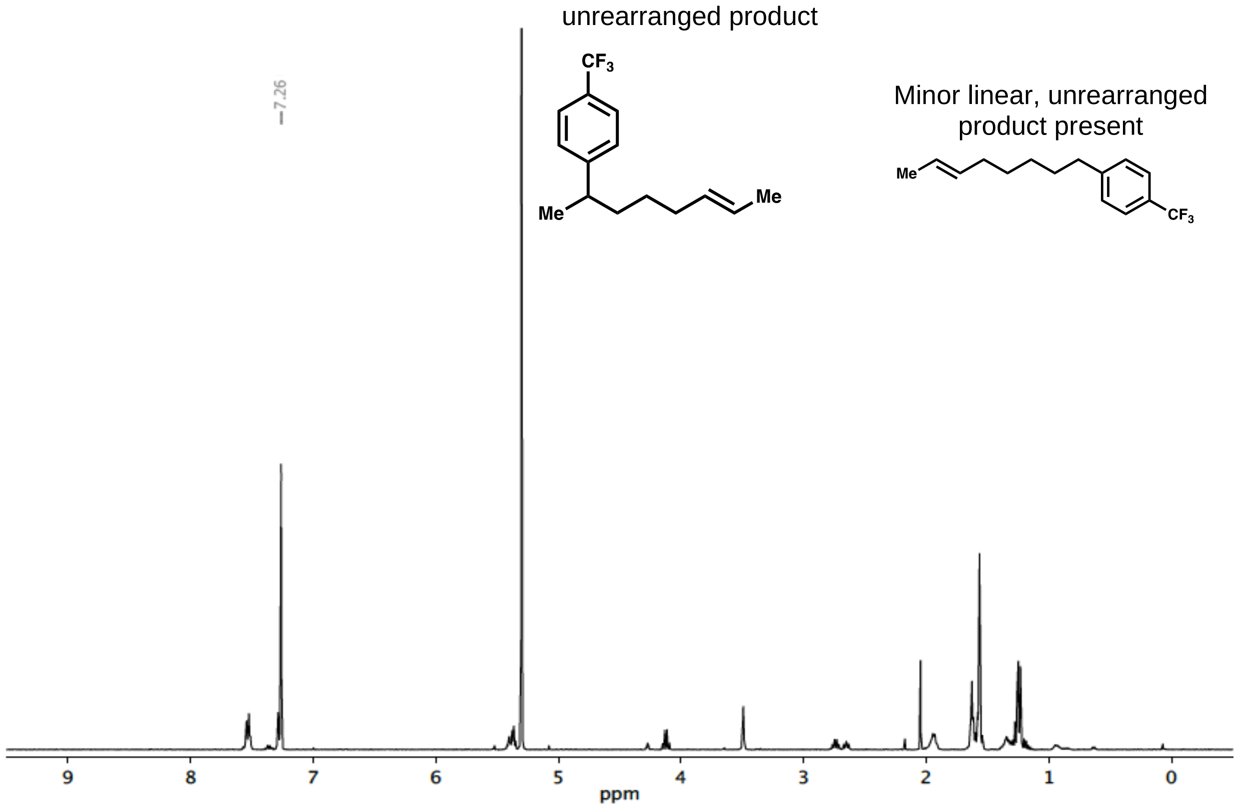


Figure S30. **19F NMR of unrearranged product (and minor linear, unrearranged product)**

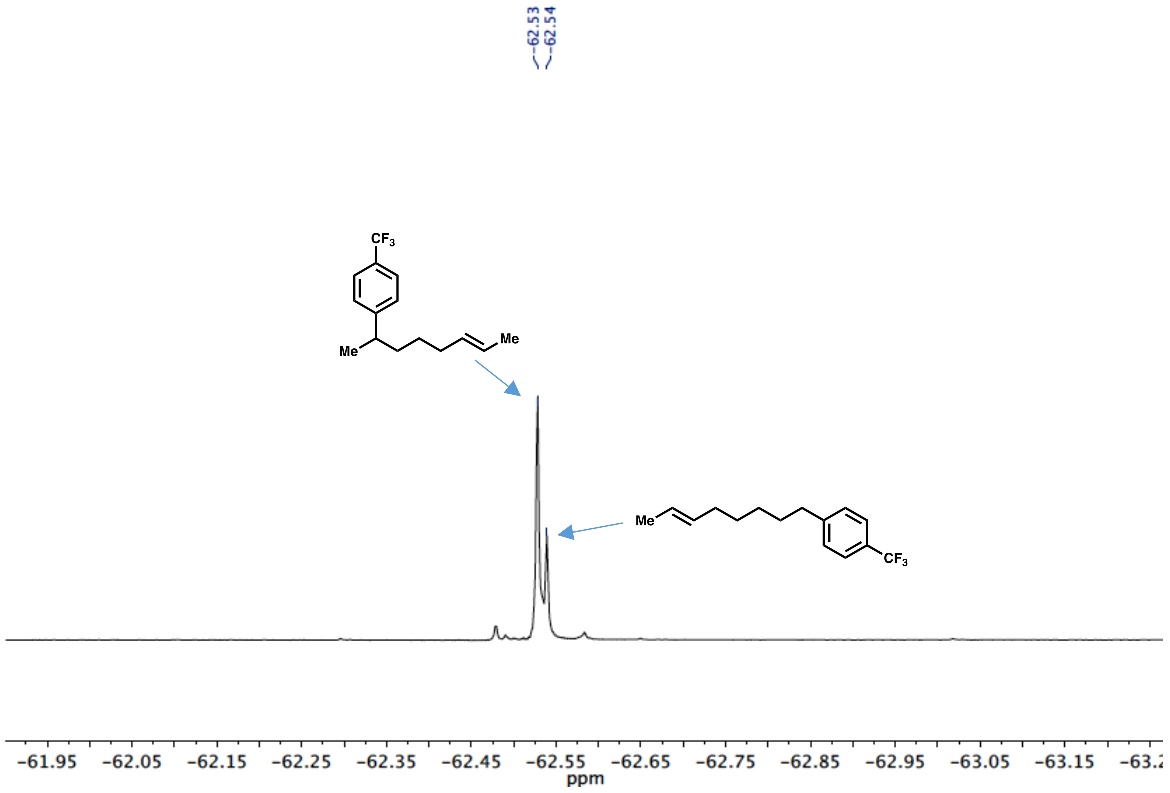


***Figure S31*. Representative GC-FID trace of radical clock cyclization experiment (20 mol % CoSalen/10% dtbbpyNiBr$_2$)**

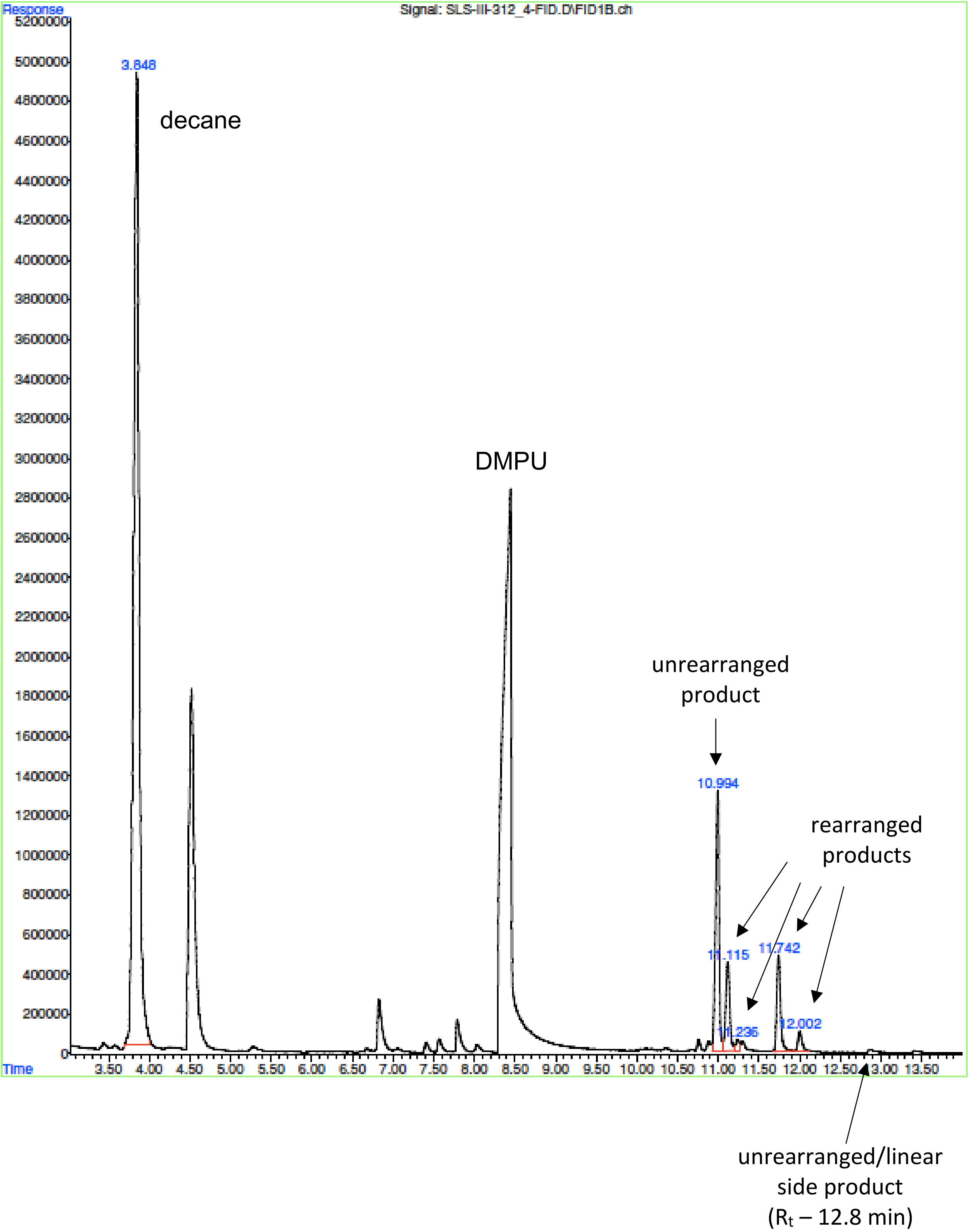


***Figure S32.* ^{1}H NMR of SalenCo(*i*-Pr)(pyridine) (1)**

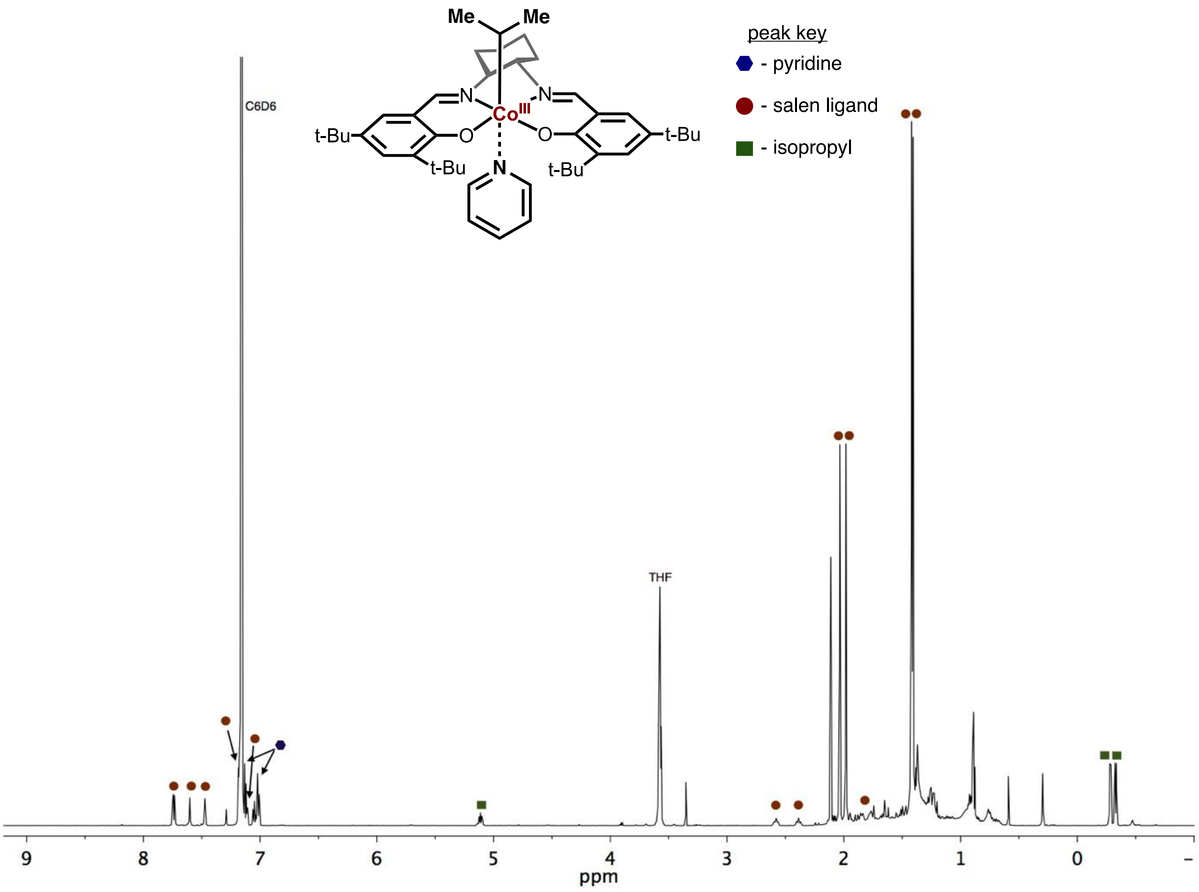


***Figure S33*. ^{1}H NMR of dtbbpyNi(*o*-Tol)I (2)**

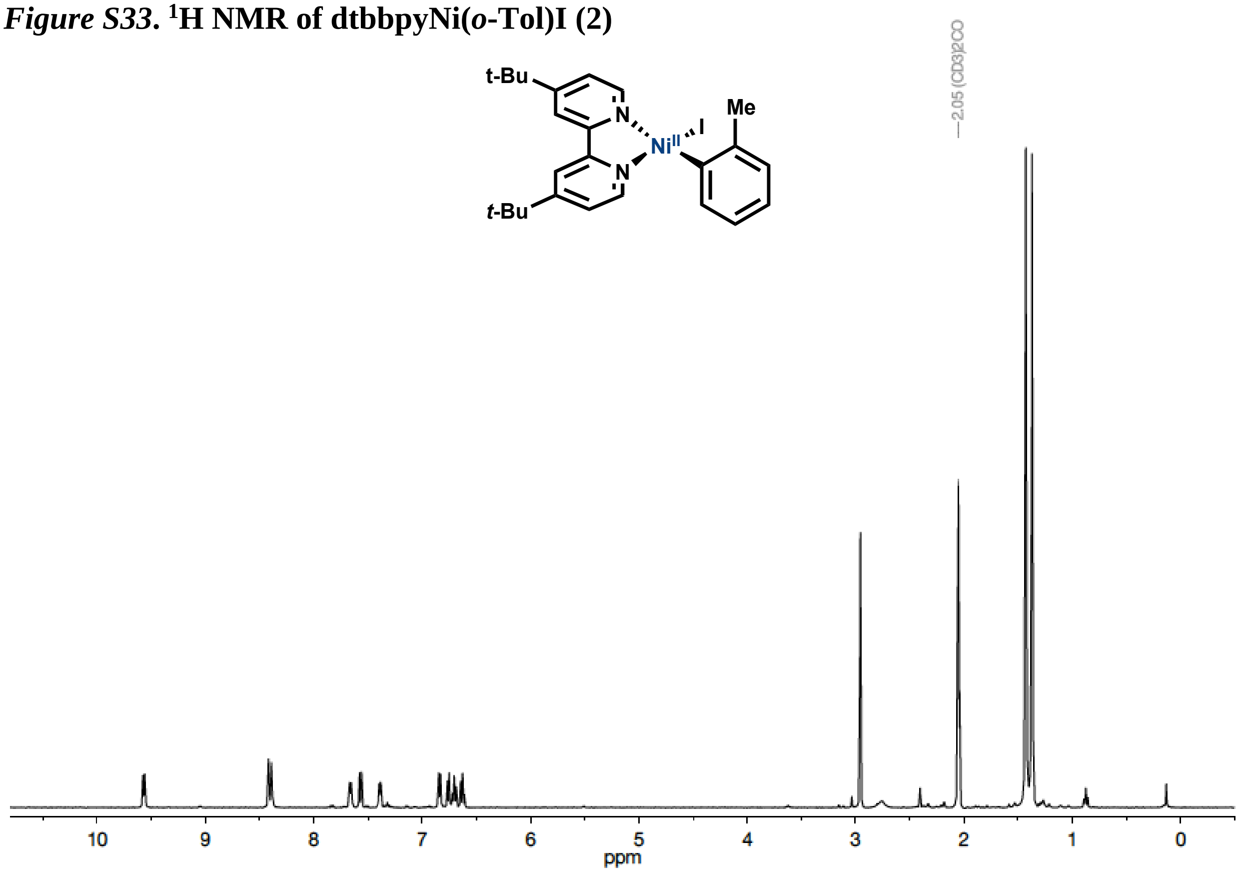


***Figure S34*. GC-FID of stoichiometric experiment – 1 + 2** only

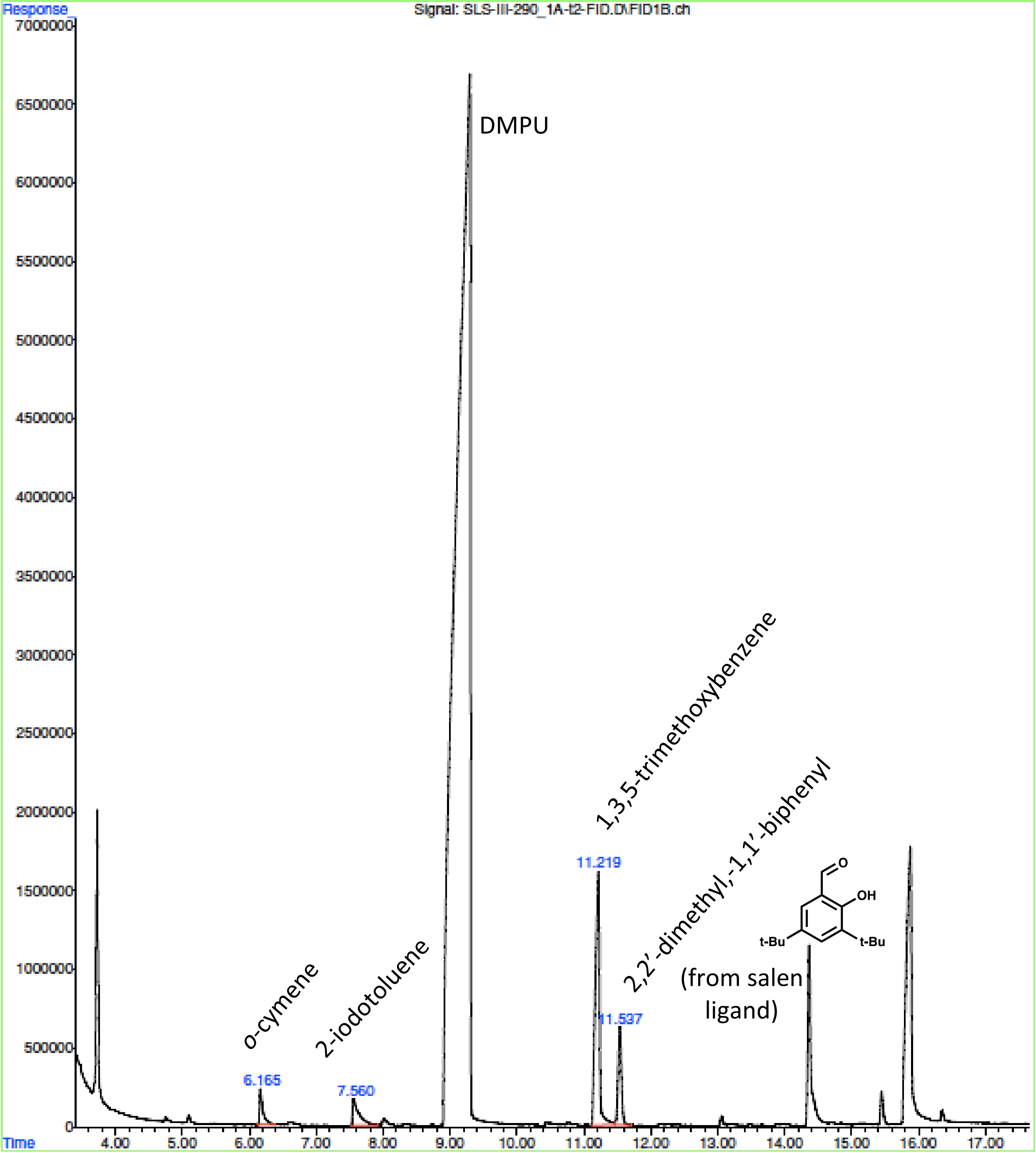


***Figure S35*. GC-FID of stoichiometric experiment with oxidant. No added oxidant (Table 1, entry 1).**

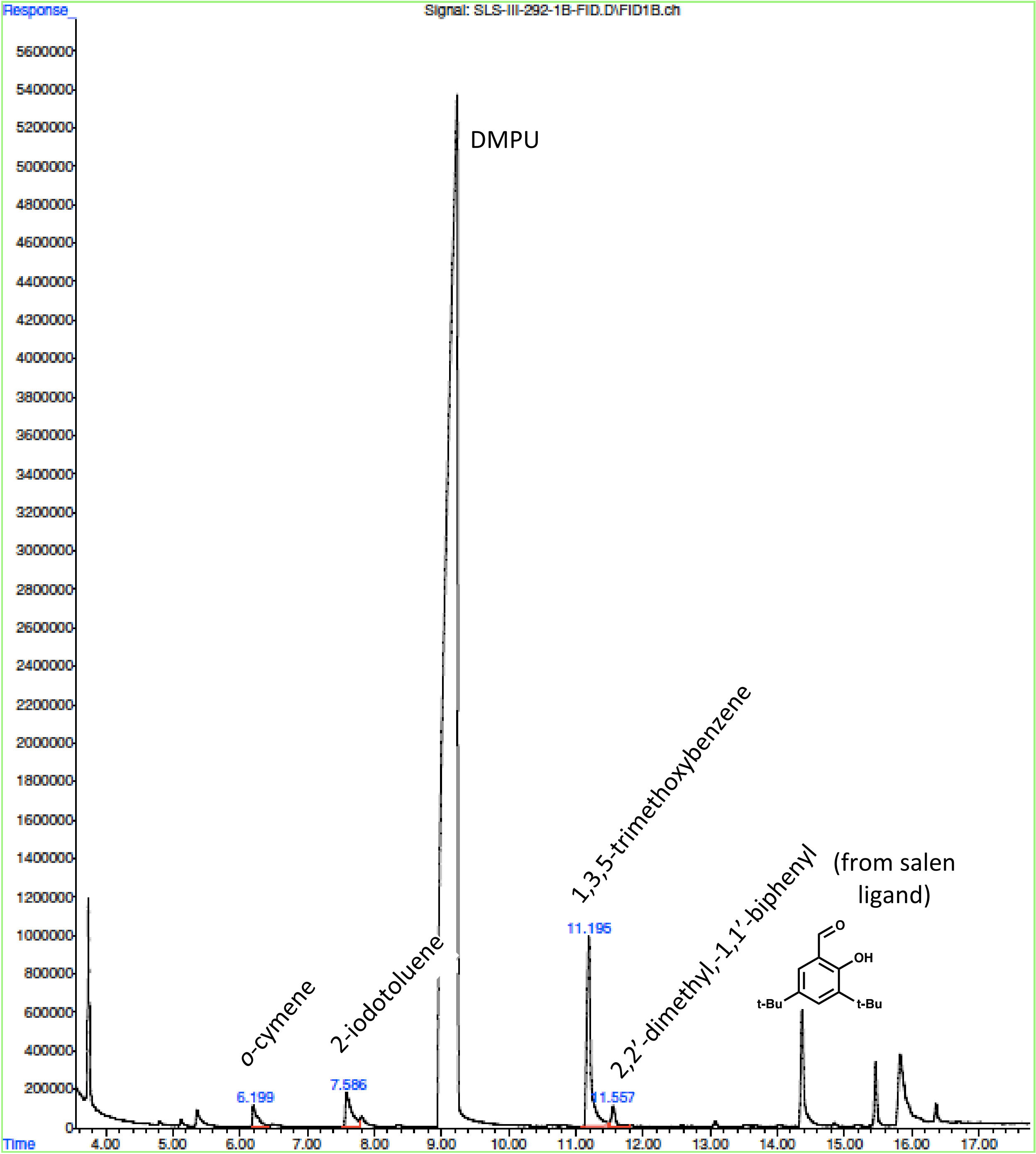


***Figure S36*. GC-FID of stoichiometric experiment with NFTPB (1 equiv) (Table 1, entry 2).**

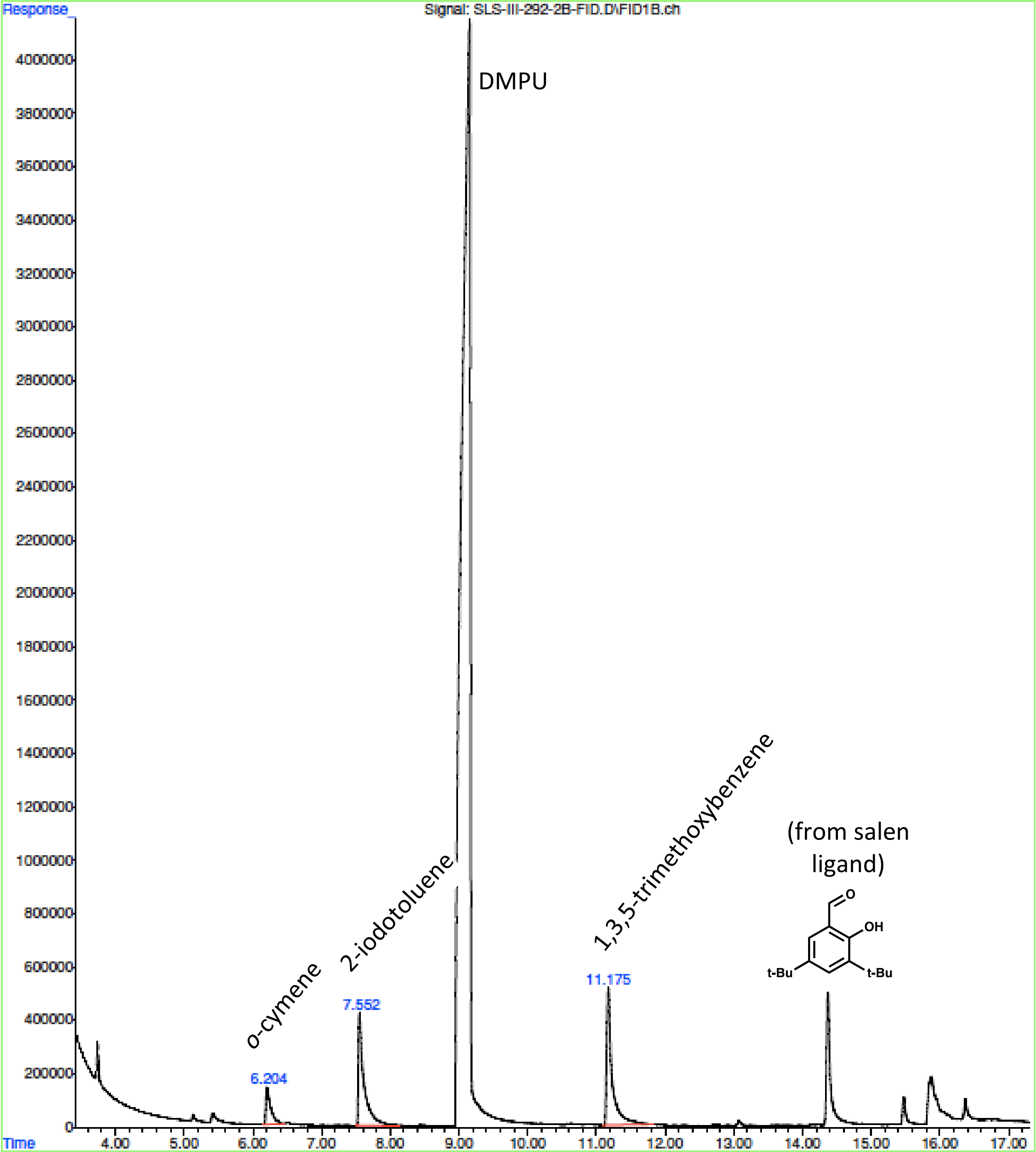


***Figure S37*. GC-FID of stoichiometric experiment with AcFcBF$_4$ (1 equiv) (Table 1, entry 3).**

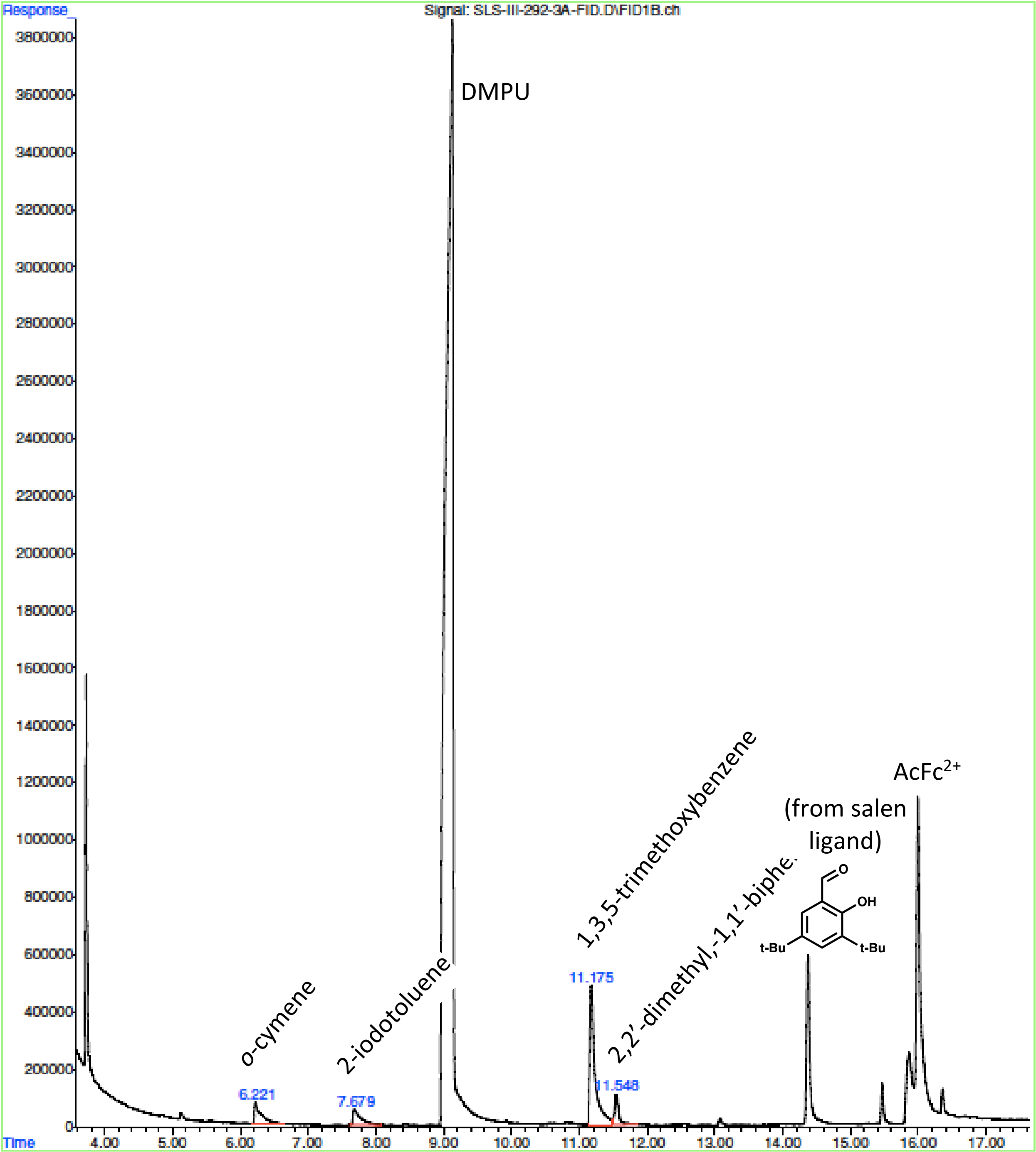


Figure S38 **GC-FID of stoichiometric experiment with AcFcBF₄ (2 equiv) (Table 1, entry 4).**

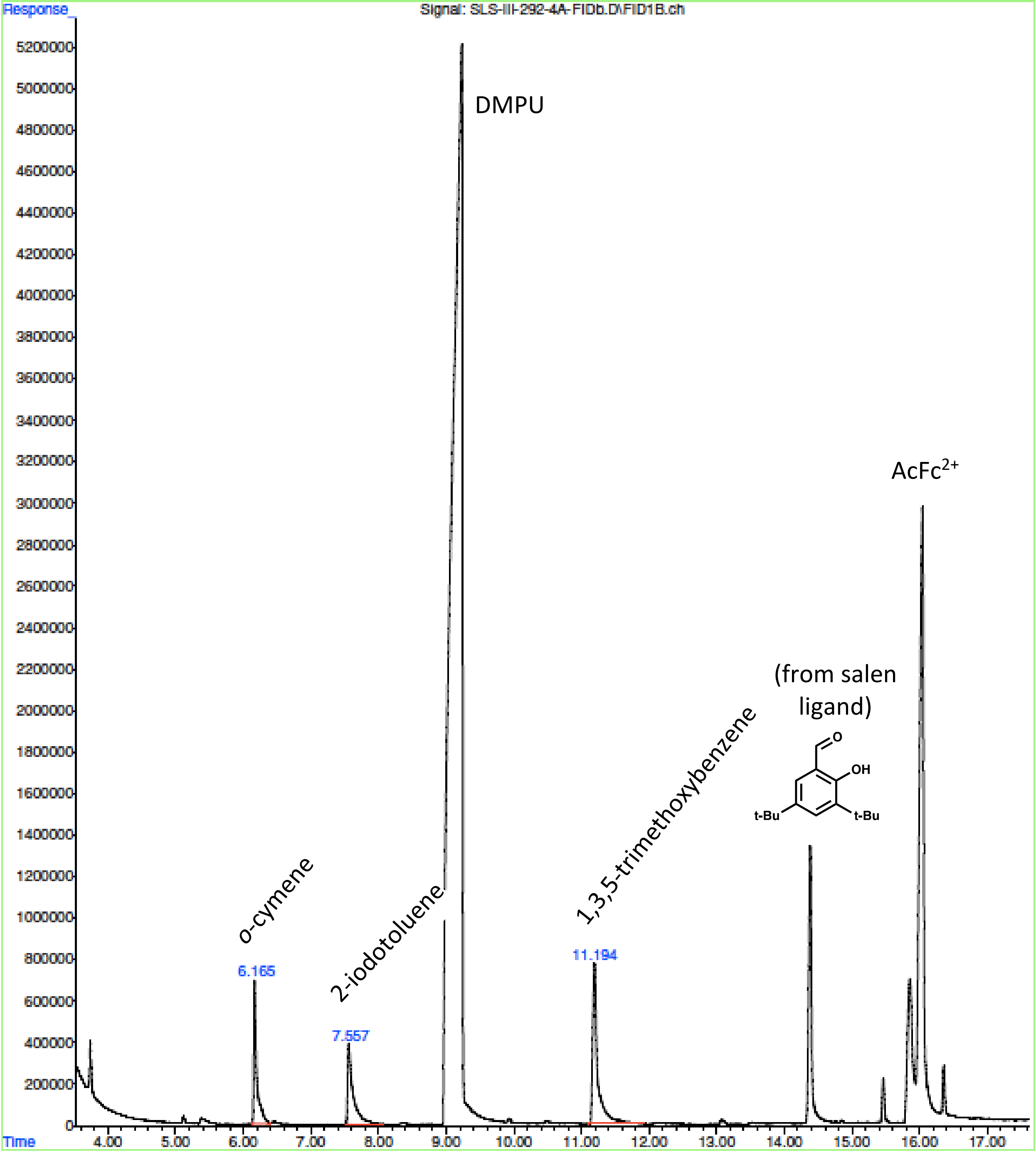
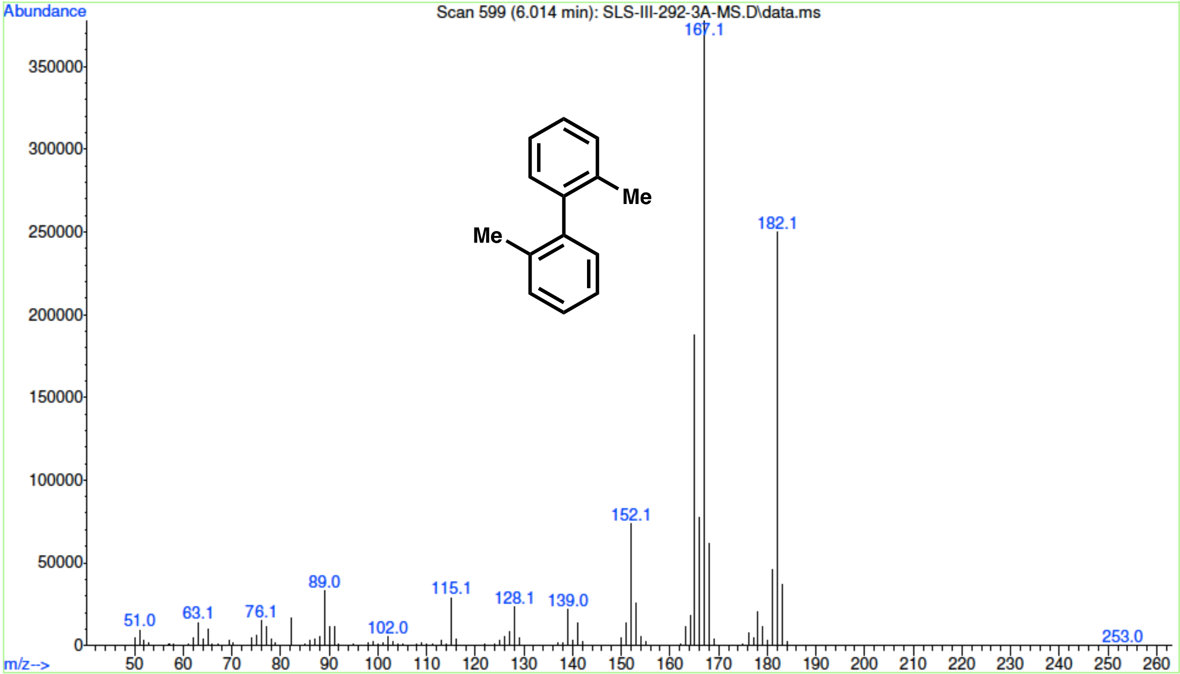


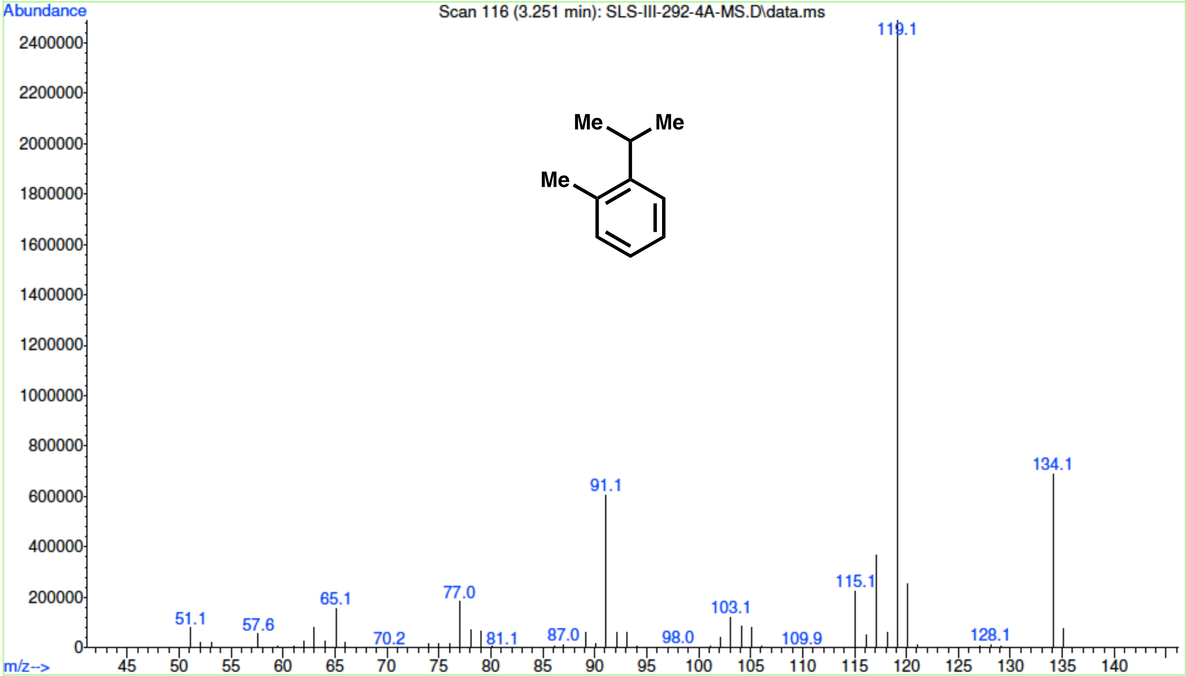
***Figure S39*. MS-TIC of 2,2’-dimethyl-1,1’-biphenyl and *o*-cymene**

2,2’-dimethyl-1,1’-biphenyl -



LRMS (EI, 70eV) – m/z (M^+) calcd. for $C_{14}H_{14}$: 182.11. Found *m/z* (%) 182.1 (66), 167.1 (100), 152.1 (19), 89.0 (9).

***o*-cymene** -



LRMS (EI, 70eV) – m/z (M^+) calcd. for $C_{10}H_{14}$: 134.11. Found *m/z* (%) 134.1 (28), 119.1 (100), 117.1 (15), 115.1 (9), 91.1 (24), 77.0 (7), 65.1 (6).

Figure S40. **^{1}H NMR of Co(III)BF$_4$**

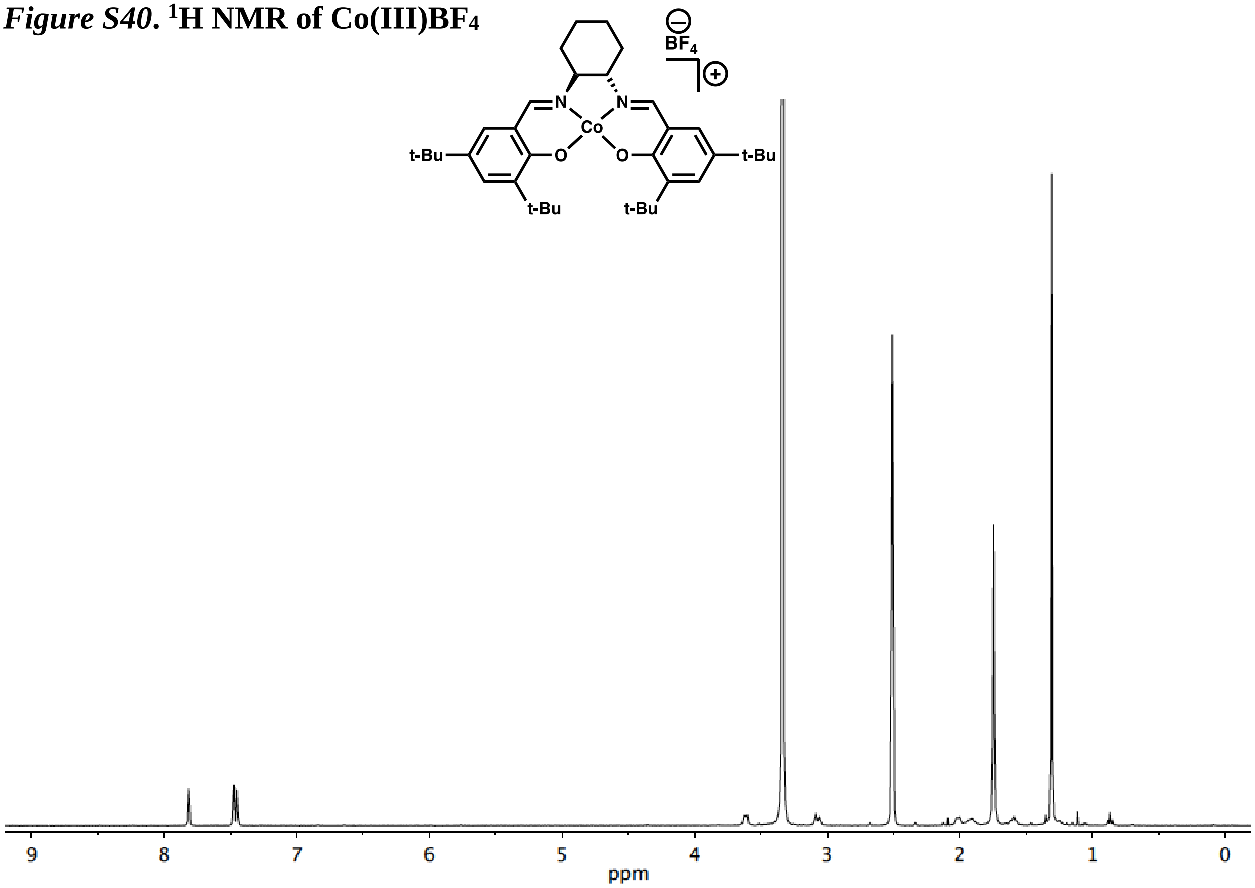


Figure S41. **^{19}F NMR of Co(III)BF$_4$**

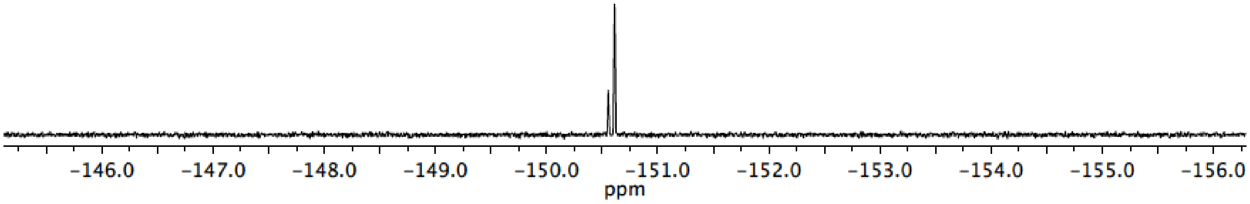
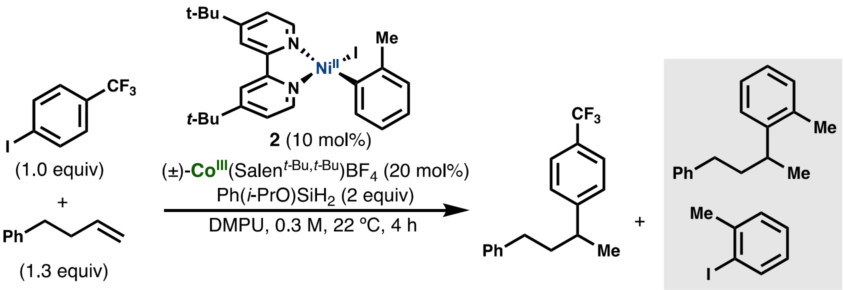


***Figure S42*. GC-FID of hydroarylation using dtbbpyNi(*o*-Tol) (2) (10 mol %) as precatalyst**



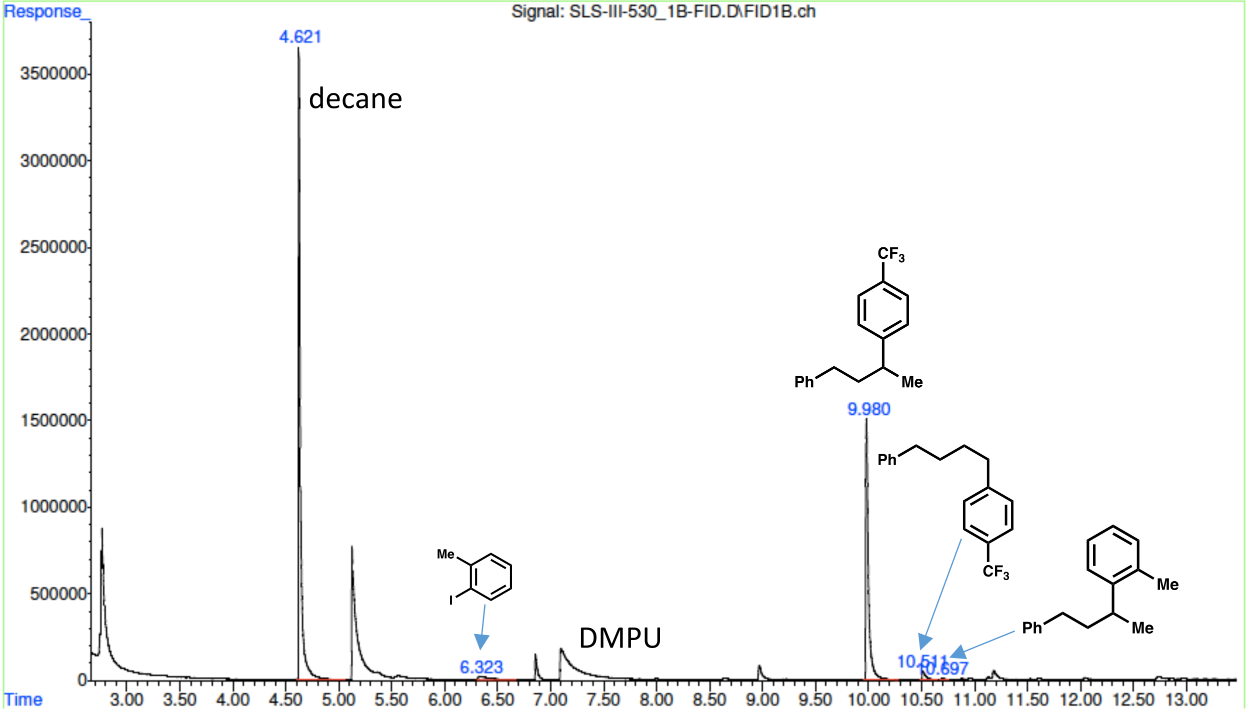
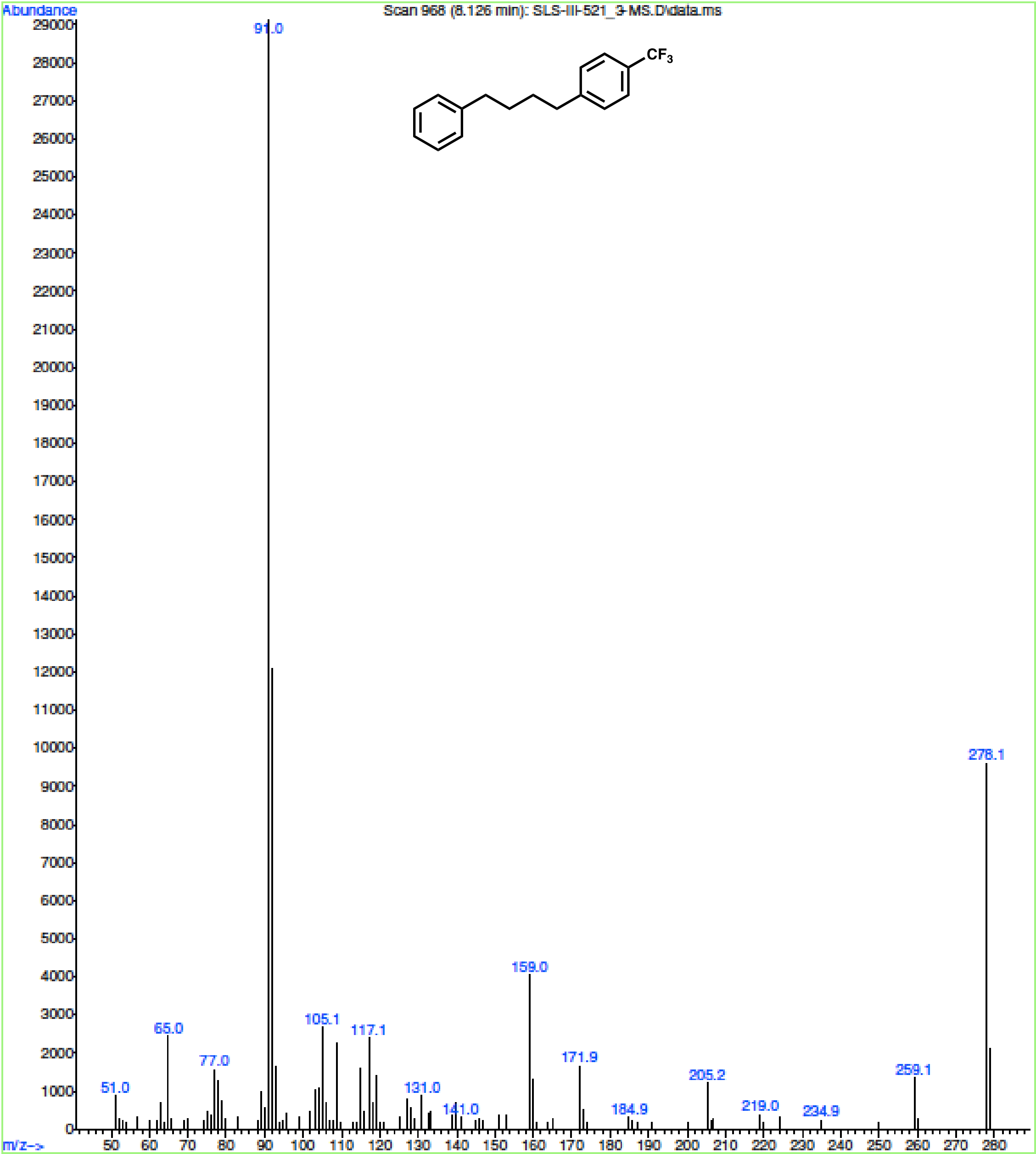


***Figure S43*. MS-TIC of linear hydroarylation product (minor side product).**

The linear hydroarylation product was identified by GC-MS splitting fragmentation. The retention time was verified by independent synthesis.[19]
LRMS (EI, 70eV) – m/z (M^+) calcd. for $C_{17}H_{17}F_3$: 278.13. Found *m/z* (%) 278.1 (33), 159.0 (14), 105.1 (9), 91.0 (100).



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