Supporting Information to

Air-Stable Nickel Precatalysts for Fast and Quantitative Cross-Coupling of Aryl Sulfamates with Aryl Neopentylglycolboronates at Room Temperature

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1. Materials

Tricyclohexylphosphine, $NiCl_2 \cdot 6H_2O$, 1,5-cyclooctadiene, sodium, pyridine, 4-iodobenzoic acid, borane-dimethylsulfide complex, 2-methoxyphenol, anthracene, potassium phosphate tribasic trihydrate, potassium phosphate anhydrous, and Mg turnings were used as received from commercial sources. THF, and toluene were distilled from sodium and benzophenone. Hexanes were distilled from sodium. Triethylamine was distilled from calcium hydride. Methanol was distilled from Mg turnings. Triphenyl phosphine was recrystallized from hexanes. 9-Chloroanthracene,[1] 9-chlorophenanthrene, 5-chloro-dihydroacenaphthene,[2] methyl 4-(5,5-dimethyl-1,3,2-dioxaborinan-2-yl)benzoate,[3] 1-naphthyl 4-methylbenzenesulfonate, 2-naphthyl 4-methylbenzenesulfonate, 1-naphthyl methanesulfonate, 1-naphthyl methanesulfonate and 2-methoxyphenyl dimethylsulfamate were synthesized according to literature procedures.[4] $Ni^{II}Cl$(1-Naphthyl)$(PPh_3)_2$, and $Ni^{II}Br$(1-Naphthyl)$(PPh_3)_2$ were synthesized according to a literature procedure.[5] C_6D_6 was distilled from sodium and benzophenone and kept inside a nitrogen filled glove box. Chlorobenzene was dried over P_2O_5 for 4 h and then distilled from molecular sieves (0.3 nm) under N_2. Phenanthrene and acenaphthene were recrystallized from ethanol. Solvents for column chromatography were used as received from commercial sources. 1-Naphthol and 2-naphthol were sublimed prior use in the synthesis of their mesylates and tosylates.

2. Instrumentation

^1H NMR and ^{13}C NMR spectra were recorded at 500 or 360 MHz on a Bruker DRX (500 MHz) or Bruker DMX (360 MHz). All NMR spectra were measured at 25°C in the indicated deuterated solvents. Proton and carbon chemical shifts (δ) are reported in ppm and coupling constants (J) are reported in Hertz (Hz). The resonance multiplicities in the ^1H NMR spectra are described as "s" (singlet), "d" (doublet), "t" (triplet), "quint" (quintuplet) and "m" (multiplet) and broad resonances are indicated by "br". Residual protic solvent of $CDCl_3$ (^1H, 7.27 ppm; ^{13}C, 77.16 ppm (central resonance of the triplet)), and tetramethylsilane (TMS) were used as the internal reference. ^{31}P NMR (203 MHz) spectra were recorded using H_3PO_4 in D_2O as external standard. A GC coupled with an FID detector and column HP 19091J-413 (5%-phenyl)-methylpolysiloxane 30m length 0.32mm internal diameter was used to follow the reaction conversions and to assess purity of final compounds complementary to the NMR technique. The crude reaction mixtures were diluted with distilled THF. Evolution of the reaction, when indicated, was monitored by analytical thin-layer chromatography using silica gel 60 F254 pre-coated plates (E. Merck). Compounds were visualized by 254 nm light. Purifications by flash column chromatography were performed using flash silica gel from Silicycle (60 Å, 40-63 μm)

with the indicated eluent. The purity of the products was determined by a combination of thin-layer chromatography (TLC) on silica gel coated aluminum plates (with F253 indicator; layer thickness, 200 μm; particle size, 2-25 μm; pore size, 60 Å). Detection was done by UV absorbance at 254 nm. Accurate mass measurements (HRMS) were performed on a high-resolution double focusing chemical ionization mass spectrometer (Mass Spectrometry Facility, University of Pennsylvania). Dechlorinated $[M-Cl]^+$, protonated molecular ions $[M+nH]^{n+}$ or sodium adducts $[M+Na]^+$ were used for empirical formula confirmation. LC/MS were performed with a Waters LCT Premier XE LC/MS system and a Waters GC-TOF Premier. The LCT Premier was equipped with a high-resolution orthogonal time-of-flight (oa-TOF) analyzer using ESI^+ ionization condition. Dechlorinated $[M-Cl]^+$, $[M-OTs]^+$, protonated molecular ions $[M+nH]^{n+}$ or sodium adducts $[M+Na]^+$ were used for empirical formula confirmation. Elemental analyses were performed at M-H-W Laboratories in Phoenix, AZ.

3. List of Abbreviations

COD	1, 5-cyclooctadiene
dppe	1, 2-bis(diphenylphosphino)ethane
dppf	1, 1'-bis(diphenylphosphino)ferrocene
dppp	1, 3-dis(diphenylphosphino)propane
PCy_3	tricyclohexylphosphine
PPh_3	triphenylphosphine
THF	tetrahydrofuran
Tol	toluene

4. Experiments

4.1 Syntheses of Coupling Reagents

Synthesis of 2-Methoxyphenyl dimethylsulfamate (1). 2-Methoxyphenyl dimethylsulfamate was synthesized according to a literature procedure.[6] A flame-dried round bottom flask was charged with a stirring bar and sodium hydride (0.864 g, 36 mmol, 1.2 equiv). The flask was degassed by evacuation for 5 min, backfilled with nitrogen for 1 min for three cycles. 2-Methoxyphenol (3.724 g, 30 mmol, 1 equiv) in dry THF (20 mL) was added dropwise *via*

syringe. The flask was cooled in an ice bath for 10 min. *N*,*N*-dimethyl sulfamoyl chloride (3.54 mL, 33 mol, 1.1 equiv) in dry THF (20 mL) was added dropwise to the solution. The solution was warmed to room temperature and reacted for 1 h. The crude was quenched by addition of deionized water (20 mL). Ethyl acetate (30 mL) was added to extract the organic phase. The aqueous phase was back extracted with DCM (20 mL) twice. The organic phases were combined, dried over $MgSO_4$ and then filtered. The filtrate was concentrated on a rotary evaporator and purified by silica gel column chromatography with 40% ethyl ether in hexanes as eluent. The off-white solid was recrystallized from methanol to give a white solid. Yield (5.49 g, 23.73 mmol, 79%), m. p. 47-48.5 ºC. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.37 (d, *J* = 8.0 Hz, 1H, Ar*H*), 7.23 (t, *J* = 7.9 Hz, 1H, Ar*H*), 6.96 (dd, *J* = 13.5, 6.0 Hz, 2H, 2Ar*H*), 3.90 (s, 3H, OCH_3), 2.97 (d, *J* = 1.3 Hz, 6H, N(CH_3)$_2$). ^{13}C NMR (126 MHz, $CDCl_3$) δ 151.7(Ar*C*), 139.5(Ar*C*), 127.7(Ar*C*), 123.9(Ar*C*), 121.0(Ar*C*), 113.0(Ar*C*), 56.1(O*C*H$_3$), 38.8 (N(*C*H$_3$)$_2$). ^{1}H and ^{13}C NMR spectra match with literature data.[7]

Synthesis of Methyl 4-(5,5-dimethyl-1,3,2-dioxaborinan-2-yl)benzoate (2). Methyl 4-(5,5-dimethyl-1,3,2-dioxaborinan-2-yl)benzoate was synthesized according to a literature procedure.[8]

Preparation of Neopentylglycolborane

Neopentylglycol (recrystallized from DCM, 1. 25 g, 12 mmol) and a stirring bar were added to a 50 mL round bottom flask. The flask was evacuated for 5 min and then refilled with N_2 three times. Toluene (distilled, 6 mL) was added *via* syringe. The flask was cooled to 0 ºC in an ice/water bath for 10 min. Borane dimethyl sulfide complex (1.14 mL, 12 mmol) was added dropwise *via* a syringe. The reaction was kept at 0 ºC for 0. 5 h then 23 ºC for 1.5 h until the bubbling ceased.

Neopentylglycolborylation of Methyl 4-Iodobenzoate

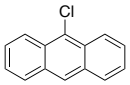
A 50 mL round bottom flask was charged with a stirring bar, methyl 4-iodobenzoate (1. 572 g, 6 mmol), $NiCl_2$(dppp) (163 mg, 0. 3 mmol, 0.05 equiv), PPh_3 (157 mg, 0.6 mmol, 0.1 equiv). The flask was degassed for 10 min and refilled with nitrogen. The process was repeated two more times. Then, toluene (distilled, 6 mL) was added *via* syringe. The reaction was left stirring for 5 min. Et_3N (dry, 2.5 mL, 18 mmol, 3 equiv) was added *via* a syringe. The neopentylglycolborane prepared in step 1 was transferred to the flask *via* a syringe right after the addition of Et_3N. The flask was heated to 100 ºC for 1 h. Then the reaction mixture was cooled to 23 ºC, quenched by addition of saturated ammonium chloride solution (20 mL) and ethyl acetate (20 mL). The

organic phase was washed with saturated ammonium chloride solution (20 mL) twice. The aqueous phase was combined and extracted with ethyl acetate (25 mL) three times. The organic phase was collected, combined and dried over brine and then anhydrous $MgSO_4$. The solution was filtered and the filtrate was concentrated under vacuum. The crude product was purified by silica gel column chromatography with DCM/hexanes mixture, gradient from DCM/hexanes = 7:3 to DCM to DCM/ethyl acetate = 17:3 to obtain a white solid. The white solid was recrystallized from methanol to give a colorless flat crystal, m.p. 113-115.5 ºC, 1.35 g, 91%. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.01 (d, *J* = 8.4 Hz, 2Ar*H*), 7.87 (d, *J* = 8.3 Hz, 2Ar*H*), 3.93 (s, 3COOCH_3), 3.79 (s, 4H, 2(OCH_2)), 1.04 (s, 6H, 2CH_3). ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.2(*C*OOCH$_3$), 133.7(Ar*C*), 131.7(Ar*C*), 128.4(Ar*C*), 72.3(O*C*H$_2$), 52.0(COO*C*H$_3$), 31.8(*C*(CH$_2$O)$_2$(CH$_3$)$_2$), 21.8(*C*H$_3$). ^{1}H and ^{13}C NMR spectra match with literature data.[9]

4.2 Syntheses of Precatalysts

4.2.1 Syntheses of Precursors for Precatalysts

Synthesis of 9-Chloroanthracene. 9-Chloroanthracene was synthesized according to a literature procedure.[1] A 250 mL round bottom flask was charged with a stirring bar, anthracene (3.56 g, 20 mmol, 1 equiv), $CuCl_2$ (anhydrous, dried in a 180 ºC oven for 24 h prior to use, 5.44 g, 40 mmol, 2 equiv) and chlorobenzene (100 mL). The reaction mixture was heated in a silicone oil bath from 23 ºC to 150 ºC in 30 min and was allowed to cool in the oil bath to 23 ºC in approximately 1 h. The solid cuprous chloride was removed by filtration. The filtrate was passed through 40 g basic alumina column to remove the copper residue. The column was eluted with chlorobenzene (50 mL), hexanes (100 mL) and dichloromethane (100 mL). The solution was collected and concentrated first in a rotary evaporator. Subsequently the chlorobenzene was removed by vacuum distillation. The solid was purified by silica gel column chromatography with hexanes. The first portion (R_f = 0.7) was 9,10-dichloroanthracene, the second portion (R_f = 0.6) was 9-chloroanthracene and the last portion was anthracene (R_f = 0.5). 9-Chloroanthracene was recrystallized from ethanol prior to being used.

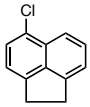


9-Chloroanthracene. Lemon yellow needle crystals (1.465 g, 70%) were obtained by recrystallization from ethanol. m.p. 108-109 ºC, lit.[1] 104-106 ºC. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.52 (d, J = 8.8, 2H, 2Ar*H*-1), 8.41 (s, 1H, Ar*H*-10), 8.02 (d, J = 8.4, 2H, 2Ar*H*-4), 7.74 – 7.59

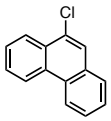
(m, 2H, 2Ar*H*-2), 7.59 – 7.50 (m, 2H, 2Ar*H*-3). ^{13}C NMR (126 MHz, $CDCl_3$) δ 128.7 (2Ar*C*CCl), 127.0 (Ar*C*Cl), 126.2 (2Ar*C*), 125.8 (Ar*C*H), 124.9 (Ar*C*H). M. p. matches with literature data.[1]

Chlorination of Phenanthrene and 1, 2-Dihydroacenaphthene.

9-Chlorophenanthrene and 5-chloro-dihydroacenaphthene were synthesized according to a literature procedure.[2] $CuCl_2$ on basic alumina was prepared by dissolving $CuCl_2$ (10g) in water and adding it to basic alumina (20 g). The solid was dried in a rotary evaporator and then at 180 ºC for 24 h prior to use. A round bottom flask was charged with a stirring bar, 1,2-dihydroacenaphthene (1.386 g, 9 mmol), $CuCl_2/Al_2O_3$ (22 g) and chlorobenzene (90 mL). The mixture was heated to 130 ºC for 2 h. The mixture was filtered, washed with 10 mL chlorobenzene, and concentrated by vacuum distillation. An orange solid (972.6 mg, 57%) was obtained after purification by silica gel column chromatography with hexanes.



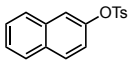
5-Chloro-dihydroacenaphthene. An orange solid (972.6 mg, 57%) was obtained after purification by silica gel column chromatography with hexanes. m. p. 71 ºC, lit.[10] 70. 5 ºC. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.86 (d, J = 8.3, 1H, Ar*H*-6), 7.66 – 7.54 (m, 1H, Ar*H*-7), 7.49 (d, J = 7.3, 1H, Ar*H*-8), 7.35 (d, J = 6.8, 1H, Ar*H*-4), 7.18 (d, J = 7.3, 1H, Ar*H*-3), 3.56 – 3.40 (m, 2H, ArCH_2-2), 3.40 – 3.26 (m, 2H, ArCH_2-1). ^{13}C NMR (126 MHz, $CDCl_3$) δ 150.6 (Ar*C*-CH_2), 146.2 (Ar*C*-CH_2), 145.2 (Ar*C*), 140.3 (Ar*C*), 129.5 (Ar*C*Cl), 128.9 (Ar*C*H), 127.4 (Ar*C*H), 126.9 (Ar*C*H), 120.2 (Ar*C*H), 119.6 (Ar*C*H), 119.4 (Ar*C*H), 30.8 (Ar*C*H_2), 29.9 (Ar*C*H_2). m. p. matches with literature data.[10]



9-Chlorophenanthrene.[2] A round bottom flask was charged with a stirring bar, phenanthrene (1.604 g, 9 mmol), $CuCl_2/Al_2O_3$ (22 g) and chlorobenzene (90 mL). The reaction mixture was heated to 130 ºC for 2 h. The mixture was lifted out of the oil bath, cooled to 23 ºC, filtered, washed with 10 mL chlorobenzene, and concentrated by vacuum distillation. An off-white solid (1.3844 g, 72.3%) was obtained after purification by silica gel column chromatography with hexanes. m. p. 49 ºC. The solid was recrystallized from aqueous ethanol (95% ethanol in water) two times to give white needle-like crystals (0.374 g, 27.6%) with m. p. 51-52 ºC. lit. 51-52 ºC.[2] ^{1}H NMR matches with literature data.[2] ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.72 (d, J = 8.0, 1H, Ar*H*-5), 8.67 (d, J = 8.4, 1H Ar*H*-4), 8.41 (d, J = 8.6, 1H, Ar*H*-8), 7.89 (s, 1H, Ar*H*-10), 7.82 (d, J =

7.7, 1H, Ar*H*-1), 7.79 – 7.70 (m, 2H, 2Ar*H*-3, 6), 7.67 (t, J = 7.5, 1H, Ar*H*-7), 7.62 (t, J = 7.4, 1H, Ar*H*-2). ^{13}C NMR (126 MHz, $CDCl_3$) δ 131.7 (Ar*C*), 131.3 (Ar*C*), 130.5 (Ar*C*-Cl), 129.4 (Ar*C*), 129.3 (Ar*C*), 127.8 (Ar*C*H), 127.3 (Ar*C*H), 127.2 (Ar*C*H), 127.2 (Ar*C*H), 126.8 (Ar*C*H), 126.4 (Ar*C*H), 125.2 (Ar*C*H), 122.8 (Ar*C*H), 122.6 (Ar*C*H).

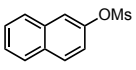
1-Naphthyl 4-methylbenzenesulfonate. Under nitrogen, to an oven dried round bottom flask charged with a stirring bar was added the sublimed 1-naphthol (3.0 g, 2.08 x 10^{-2} mol), toluenesulfonyl chloride (5.95 g, 3.12 x10^{-2} mol) and freshly distilled dichloromethane (20mL). The flask was cooled for 10 min in an ice water bath. Anhydrous pyridine (25 mL, 0.31 mol) was added. The reaction was allowed to proceed with stirring in the ice water bath for 4 h after which the ice water bath was removed and the reaction was allowed to warm to room temperature and stirring was continued until complete consumption of the starting material was observed by TLC. The reaction was quenched by addition of water (40 mL) and the organic phase was separated. The aqueous phase was further extracted with dichloromethane (3 x 20mL) and all the organic layers were combined and washed successively with 15% HCl (2 x 20 mL) and Brine (3 x 20mL) then dried over anhydrous $MgSO_4$. Following filtration the solvent was removed under reduced pressure and purified by silica gel column chromatography with dichloromethane to yield a pale yellow crystal (4.37 g, 70%). Recrystalization from methanol gives white crystals, m.p. 87 ºC. lit.[11] 89-91 ºC. If 1-naphthol used in this synthesis is not sublimed, the resulting tosylate crystals are pale yellow. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.93 (dd, *J* = 8.6, 1.2 Hz, 1H), 7.81 (dd, *J* = 12.5, 8.0 Hz, 3H), 7.75 (d, *J* = 8.3 Hz, 1H), 7.46 (dt, *J* = 21.4, 6.9 Hz, 2H), 7.38 (t, *J* = 7.9 Hz, 1H), 7.29 (d, *J* = 8.1 Hz, 2H), 7.23 (dd, *J* = 7.6, 1.1 Hz, 1H), 2.43 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 145.7, 145.3, 134.6, 132.7, 129.7, 128.4, 127.6, 127.2, 127.0, 126.6, 126.6, 125.0, 121.7, 118.3, 21.6.



2-Naphthyl 4-methylbenzenesulfonate. Under nitrogen, to an oven dried round bottom flask charged with a stirring bar was added the sublimed 2-naphthol (5.48 g, 3.8 x 10^{-2} mol), toluenesulfonyl chloride (8.68 g, 4.56 x10^{-2} mol) and freshly distilled dichloromethane (31mL). The flask was cooled for 10 min in an ice water bath. Anhydrous pyridine (15g, 0.19 mol) was added. The reaction was allowed to proceed with stirring in the ice water bath for 4 h after which the ice water bath was removed and the reaction was allowed to warm to room temperature and stirring was continued until complete consumption of the starting material was observed by TLC.

The reaction was quenched by addition of water (40 mL) and the organic phase was separated. The aqueous phase was further extracted with dichloromethane (3 x 20mL) and all organic layers were combined and washed successively with 15% HCl (2 x 20 mL) and Brine (3 x 20mL) then dried over anhydrous $MgSO_4$. Following filtration the solvent was removed under reduced pressure and purified by silica gel column chromatography with dichloromethane to yield pale yellow crystals (5.6 g, 80%). Recrystalization from methanol gives white crystals, m.p. 125 ºC. lit.[11] 119-120 ºC. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.82 (d, *J* = 9.0 Hz, 1H), 7.75 (t, *J* = 8.8 Hz, 4H), 7.54 - 7.44 (m, 3H), 7.31 (d, *J* = 8.1 Hz, 2H), 7.11 (dd, *J* = 8.9, 2.1 Hz, 1H), 2.45 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 147.1, 145.3, 133.4, 132.4, 131. 8, 129.7, 129.6, 128.5, 127.8, 127.6, 126.7, 126.3, 121.1, 119.9, 21.6.

1-Naphthyl methanesulfonate. A flame-dried 50mL round bottom flask was charged with a stirring bar, sublimed 1-naphthol (2.88 g, 20 mmol, 1 equiv), and DMAP (244 mg, 2 mmol, 0.1 equiv). The flask was sealed with a rubber septum and then purged with nitrogen for 10 min. Dichloromethane (20 ml) was added *via* syringe followed by pyridine (8 mL, 100 mmol, 5 equiv). The flask was placed in a 0°C ice bath and stirred for 10 min. Methanesulfonylchloride (2.4 mL, 30 mmol, 1.5 equiv) was added dropwise *via* syringe. The reaction was allowed to run for 1h and then the ice bath was removed. After 10 hours, the reaction was quenched by addition of 10 mL of 1M HCl. The contents of the flask were transferred to a 125 mL separatory funnel and then washed three times with 10 mL of 1M HCl. The organic layer was dried by washing two times with 15 mL brine solution and then stirred over anhydrous $MgSO_4$. The solution was filtered and then the solvent was removed on a rotary evaporator. Column chromatography on silica gel with dichloromethane yielded a solid that was recrystallized from methanol to obtain colorless crystals. Yield (4.08g, 92%), m.p. 36.5°C, lit.[11] 35-36 ºC.^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.16 - 8.11 (m, 1H), 7.89 (d, *J* = 8.1 Hz, 1H), 7.81 (dd, *J* = 8.1, 1.1 Hz, 1H), 7.62 - 7.51 (m, 3H), 7.47 (td, *J* = 7.9, 1.0 Hz, 1H), 3.20 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 145.4, 135.0, 128.2, 127.5, 127.4, 127.1, 125.5, 121.5, 118.5, 38.1.



2-Naphthyl methanesulfonate. A flame-dried 50mL round bottom flask was charged with a stirring bar, sublimed 2-naphthol (2.88 g, 20 mmol, 1 equiv), and DMAP (244 mg, 2

mmol, 0.1 equiv). The flask was sealed with a rubber septum and then purged with nitrogen for 10 minutes. Dichloromethane (20 ml) was added *via* syringe followed by pyridine (8 mL, 100 mmol, 5 equiv). The flask was placed in a 0°C ice bath and stirred for 10 min. Methanesulfonylchloride (2.4 mL, 30 mmol, 1.5 equiv) was added dropwise *via* syringe. The reaction was allowed to run for 1 h and then the ice bath was removed. After 10 h, the reaction was quenched by addition of 10 mL of 1M HCl. The contents of the flask were transferred to a 125 mL separatory funnel and then washed three times with 10 mL of 1 M HCl. The organic layer was dried by washing two times with 15 mL brine solution and then stirred over anhydrous $MgSO_4$. The solution was filtered and then the solvent was removed on a rotary evaporator. Column chromatography on silica gel with dichloromethane yielded a solid that was recrystallized from MeOH to obtain colorless crystals. Yield (3.20g, 72%) m. p. 105-106.5 ºC, lit.[11] 101-102 ºC. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.93 - 7.83 (m, 3H), 7.78 (s, 1H), 7.55 (p, *J* = 6.8 Hz, 2H), 7.42 (d, *J* = 9.0 Hz, 1H), 3.19 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 146.8, 133.5, 132.0, 130.2, 127.8, 127.8, 127.1, 126.5, 120.7, 119.3, 37.3.

Ni(COD)$_2$. Ni(COD)$_2$ was synthesized *via* a modified literature procedure.[12] $NiCl_2$(pyridine)$_4$ (20.58 g) was prepared by refluxing of $NiCl_2(H_2O)_6$ (10.8 g) in pyridine (125 mL) for 3 h. The bright blue solid was collected by vacuum filtration, and then allowed to air dry. A 250 mL round bottom flask was charged with a stirring bar and $NiCl_2$(pyridine)$_4$ (8.92 g, 20 mmol). The flask was evacuated (10 min) and refilled with nitrogen three times. 1,5-Cyclooctadiene (7.4 mL, 60 mmol) and THF (12 mL, distilled immediately before addition) were introduced *via* syringes. The mixture was left stirring for 5 min. Na (in small pieces, 0.92 g) was added quickly. The solution was cooled down to – 78 ºC for 10 min. The flask was evacuated (15 s), refilled with nitrogen (1 min) and the procedure was repeated two more times. The mixture was warmed to 23 ºC and kept stirring vigorously at 23 ºC for 3 h. MeOH (24 mL, distilled from Mg turnings under nitrogen immediately before addition) was added to induce the precipitation of Ni(COD)$_2$. Stirring was halted, and the yellow precipitate was allowed to settle. After all sodium was consumed, the black upper layer was removed by syringe. MeOH (12 mL) was added again to rinse the crystals, and the upper layer was removed by syringe. The procedure was repeated 4 more times until the upper layer was clear. The Ni(COD)$_2$ (3.3 g, 70%, yellow solid) was dried overnight under vacuum for 12 h. Ni(COD)$_2$ (1 g) was dissolved in toluene (distilled within 1 day of use) at 23 ºC inside the glove box, and then the solution was filtered through celite inside the glove box. The

filtrate was kept in a screw cap vial (20 mL) at – 78 ºC for 12 h until a bright yellow solid formed in the bottom of the vial. The bright yellow crystals (350 mg) were washed with ethyl ether (distilled right before use) two times, hexanes (distilled right before use) two times and dried under vacuum for 2 h. The NMR tube was prepared inside a nitrogen filled glove box with C_6D_6. ^{1}H NMR (500 MHz, C_6D_6) δ 4.40 (s, 4H, 4C*H*), 2.17 (s, 8H, 4CH_2). ^{13}C NMR (126 MHz, C_6D_6) δ 89.7 (4*C*H), 30.9 (4*C*H_2). ^{1}H NMR matches with literature data.[12]

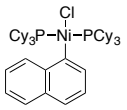
4.2.2 Syntheses of Precatalysts

General Procedure for the Synthesis of $Ni^{II}X(Aryl)(PCy_3)_2$. Nickel sigma complexes used as precatalysts were synthesized according to a literature procedure.[13] All nickel sigma complexes were synthesized and purified in a nitrogen filled glove box.

General Procedure for the Synthesis of $Ni^{II}Cl(Aryl)(PCy_3)_2$.

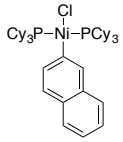
Oxidative Addition of Aryl Cchlorides to $Ni(COD)_2$. In a nitrogen filled glove box, a stirring bar, $Ni(COD)_2$ (100 mg, 0.36 mmol), PCy_3 (300 mg, 1.07 mmol), and THF (1 mL) were added to a 20 mL vial. The solution was left stirring for 1 min, and then 9-chloroanthracene (76 mg, 0.36 mmol) was added. The reaction was left stirring inside a glove box with inert atmosphere for 6 h. At this time the oxidative addition reaction was complete as demonstrated by NMR. The reaction mixture was filtered through a membrane (0.22 μm) inside the glovebox, the solid was collected, washed 5 times with distilled hexanes (2 mL), then dried for 12 h under vacuum. Yield: 200 mg, 70%.

Ligand exchange. $Ni^{II}Cl(1\text{-naphthyl})(PPh_3)_2$ (0.2 mmol, 149 mg), PCy_3 (0.6 mmol, 148 mg) and 10 mL EtOH (anhydrous) were added to a Schlenk tube inside the glovebox with a stirring bar. The tube was sealed, brought outside the glovebox, and then heated to 80 ºC for 2 h. The reaction mixture was then cooled to 23 ºC. The Schlenk tube was brought inside the glove box. After filtration, the solid was washed with ethyl ether three times inside the glovebox. The solid was recrystallized from a DCM/hexanes = 2:8 mixture to yield a yellow solid (106 mg, 68%).

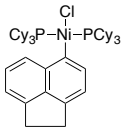


(**6**) The reaction was carried out following the general procedure from 1-chloronaphthalene (50 μL, 0.36 mmol). Yield: by oxidative addition, from 1-chloronaphthalene (50 μL, 0.36 mmol), $Ni(COD)_2$ (100 mg, 0.36 mmol), 200mg, 70%; by ligand exchange method, from $Ni^{II}Cl(1\text{-naphthyl})(PPh_3)_2$ (0.2 mmol, 149 mg), PCy_3 (0.6 mmol, 148 mg), yield 106 mg, 68%. Yellow solid, m.p. 190.4 ºC (decompose). ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.18 (d, J = 8.6, 1H), 7.50 (d, J = 8.4, 1H), 7.47 – 7.42 (m, 1H), 7.40 (s, 1H), 7.23 (d, J = 7.6, 2H), 7.05 – 6.97 (m,

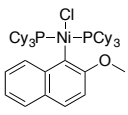
1H), 2.10-0.72 (br, 76H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 153.8, 141.6, 136.7, 135.1, 132.5, 127.8, 124.5, 124.3, 122.4, 121.4, 33.4, 30.2, 29.4, 28.1, 28.0, 27.7, 26.6. ^{31}P NMR (203 MHz, $CDCl_3$) δ 10.66. $[M-Cl]^+$ calcd for $C_{46}H_{73}NiP_2$, 745.4541, HRMS found 745. 4360.



(**7**) The reaction was carried out following the general procedure from 2-naphthyl chloride (59 mg, 0.36 mmol, 1 equiv), with $Ni(COD)_2$ (100 mg, 0.36 mmol, 1 equiv). Yield: 147 mg, 52%. Yellow solid, m.p. 147-148 ºC (decompose). ^{1}H NMR (500 MHz, C_6D_6) δ 8.22 (d, J = 7.8, 1H), 8.18 (s, 1H), 7.77 (d, J = 7.4, 2H), 7.71 (d, J = 7.9, 1H), 7.52 (d, J = 7.8, 1H), 7.46 – 7.36 (m, 2H), 7.31 (s, 1H), 1.07-2.26 (br, 66 H). ^{31}P NMR (203 MHz, C_6D_6) δ 12.36. ^{13}C NMR (126 MHz, C_6D_6) δ 137.8, 137.6, 132.6, 130.3, 128.5, 128.2, 125.2, 125.0, 123.2, 122.9, 33.9, 30.1, 27.8, 26.6. ^{1}H and ^{31}P NMR spectra match literature data.[14] The catalyst was also recrystallized from toluene/hexanes = 1:10 mixture. In an oven dried screw cap vial were added $Ni^{II}Cl(2\text{-Naphthyl})(PCy_3)_2$ (100.1 mg), the catalyst was dissolved in 4 mL boiling toluene/hexanes = 1:10 mixture. The dark red solution was filtered through a 0.22 μm membrane filter and cooled in -10 ºC freezer for 4 h. The solid was collected, washed with cold hexanes and dried in vacuum. Yield: 77.8 mg. The ^{1}H, ^{31}P NMR spectra as well as kinetic results are identical with that of the non-recrystalized precatalyst.

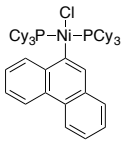


(**12**) The reaction was carried out following the general procedure from 5-chloro-1,2-dihydroacenaphthene (68.6 mg, 0.36 mmol). Yield: 110mg, 39%. Yellow-brown solid, m.p. 151-153 ºC (decompose). ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.92 (d, J = 7.0, 1H), 7.75 (d, J = 6.5, 2H), 7.32 (d, J = 6.4, 2H), 3.33 (s, 2H), 3.31 (s, 2H), 2.48-0.91 (br, 66H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 146.1, 141.0, 139.4, 138.4, 137.6, 129.9, 129.2, 125.4, 119.1, 118.5, 34.0, 30.8, 30.0, 28.4, 28.1, 27.1. ^{31}P NMR (203 MHz, $CDCl_3$) δ 11.69. $[M-Cl]^+$ calcd for $C_{48}H_{75}NiP_2$, 771.470, LC/MS found 771.500. Anal. calcd for $C_{48}H_{75}ClNiP_2$: C, 71.33; H, 9.35. Found: C 71.63 H, 8.97.



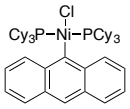
(**13**)In a nitrogen filled glove box, 1-chloro-2methoxynaphthalene (154 mg, 0.8 mmol, 1.1 equiv), $Ni(COD)_2$ (200 mg, 0.72 mmol, 1 equiv) and PCy_3 (610 mg, 2.16 mmol, 3 equiv) were added to a 20 mL vial charged with a stirring bar. THF (distilled, 1 mL) was added via syringe. The solution was left stirring for 18 h, transferred to a Schlenk flask and brought outside the glove box. The dark red solution was concentrated under reduced pressure and brought inside

the glove box. Distilled hexanes (1 mL) were added to induce precipitation. The precipitation was collected and washed with distilled hexanes (0.5 mL) five times. The pink solid was collected and dried under vacuum for 6 h. Then, the pink solid (150 mg) was transferred to a 4 mL vial. Dichloromethane/hexanes 1:7 solution was heated until boiling and added to the solid until the solid was fully dissolved. (In the case of slow solvation, a maximum of 4 mL of mixed solvent was added and the vial was sealed and heated until homogenous.) The solution was filtered while still hot to generate a red solution. The red solution was left in a -10 ºC freezer for 12 h to produce a pink solid. The pink solid was collected, washed with distilled hexanes (0.5 mL) three times and dried under vacuum to give the COD free catalyst. (57.8 mg, yield: 10%) m.p. 193 ºC. ^{1}H NMR (500 MHz, Benzene-d_6) δ 10.70 (d, J = 8.4 Hz, 1H), 7.81-7.68 (m, 2H), 7.51 (d, J = 8.7 Hz, 1H), 7.35 (d, J = 7.6 Hz, 1H), 6.71 (d, J = 8.5 Hz, 1H), 3.72 (s, 3H), 2.38 (s, 6H), 2.06 (s, 6H), 1.86 (m, 18H), 1.75-1.59 (m, 18H), 1.26 (s, 12H), 1.07 - 0.90 (m, 12H). ^{31}P NMR (203 MHz, C_6D_6) δ 11.76. ^{13}C NMR (126 MHz, C_6D_6) δ 159. 7, 143.7, 134.2, 128.8, 128.2, 124.3, 123.2, 122.5, 109.1, 53.2, 36.0, 34.6, 34.0, 30.4, 28.2, 28.0, 26.7, 25.3, 20.5, 11.3. $[M\text{-}Cl]^+$ calcd for $C_{47}H_{75}ONiP_2$, 775.4647, HRMS found 775.4639.



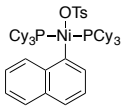
(**14**) In a nitrogen filled glove box, 9-chlorophenanthrene (61 mg, 0.29 mmol, 1.1 equiv), $Ni(COD)_2$ (70 mg, 0.26 mmol, 1 equiv) and PCy_3 (280 mg, 0.78 mmol, 3 equiv) were added to a 20 mL vial charged with a stirring bar. THF (distilled, 0.5 mL) was added via a syringe. The solution was left stirring for 6 h. The solid was collected, washed with hexanes (1 mL) five times. The yellow solid was dried under vacuum for 6 h to remove the solvent. Then, the yellow solid (97 mg) was transferred to a 4 mL vial. Dichloromethane/hexanes 1:5 solution was heated until boiling and added to the solid until the solid was fully dissolved. (In the case of slow solvation, maximum of 4 mL of mixed solvent was added and the vial was sealed and heated till homogenous) The solution was filtered while still hot to generate a red solution. The red solution was concentrated under reduced pressure to produce a yellow solid. The yellow solid was washed 3 times with distilled hexanes to remove the COD. The yellow solid was collected and dried under vacuum for 12 h. (59.2 mg, yield: 27.4%) Yellow solid, m.p. 158 ºC (decompose). ^{1}H NMR (500 MHz, $CDCl_3$) δ 11.13 (d, J = 8.0 Hz, 1H), 8.61 (dd, J = 31.5, 8.3 Hz, 2H), 7.99 (s, 1H), 7.91 (t, J = 7.4 Hz, 1H), 7.75 (d, J = 7.9 Hz, 1H), 7.61 (t, J = 7.5 Hz, 1H), 7.51 (t, J = 7.4 Hz, 1H), 7.46-7.38 (m, 1H), 4.38 (s, 1.2 H, CH_2Cl_2), 2.55-0.72 (m, 80H). ^{13}C NMR (91 MHz, $CDCl_3$) δ 141.2, 137.4, 136.1, 135.1, 132.2, 128.5, 127.1, 126.3, 125.6, 125.4, 123.9,

122.6, 122.5, 34.7, 33.8, 30.5, 29.7, 28.1, 27.8, 26.7. ^{31}P NMR (203 MHz, $CDCl_3$) δ 9.75. $[M\text{-}Cl]^+$ calcd for $C_{50}H_{75}NiP_2$, 795.470, LC-MS found 795.509. Anal. calcd for $C_{50}H_{75}NiClP_2(CH_2Cl_2)_{0.55}$: C, 69.08; H, 8.73. Found: C 68.69 H, 8.48. The ratio between CH_2Cl_2 and the nickel complex was determined by ^{1}H NMR.



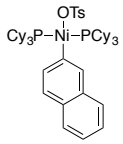
(**15**) The reaction was carried out following the general procedure, from 9-chloroanthracene (77 mg, 0.36 mmol). Yield: 248 mg, 82%. Orange solid, m.p. 170 ºC (decompose). ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.21 (d, J = 7.6, 2H), 7.79 (s, 1H), 7.73 (d, J = 7.2, 2H), 7.48 – 7.39 (m, 2H), 7.39 – 7.31 (m, 2H), 1.92 – 0.50 (br, 68H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 140.0, 136.3, 130.6, 128.6, 124.6, 121.4, 121.4, 121.0, 77.4, 77.2, 76.9, 34.1, 34.0, 34.0, 30.1, 28.1, 26.6. ^{31}P NMR (146 MHz, $CDCl_3$) δ 8.82. $[M\text{-}Cl]^+$ calcd for $C_{50}H_{75}NiP_2$, 795.4697, HRMS found 795.4698.

General Procedure for the Synthesis of $Ni^{II}OTs(Aryl)(PCy_3)_2$ or $Ni^{II}OMs(Aryl)(PCy_3)_2$. A stirring bar, $Ni(COD)_2$ (100 mg, 0.36 mmol), PCy_3 (300 mg, 1.07 mmol), and 1 mL THF were added to a 20 mL vial. The solution was left stirring for 1 min, and then 1-naphthyl 4-methylbenzenesulfonate (107 mg, 0.36 mmol) was added. The reaction was left stirring inside a glove box with inert atmosphere for 6 h - until the oxidative addition reaction was complete as demonstrated by NMR. The reaction mixture was dissolved in THF, filtered through a 22 μm membrane and collected. The filtrate was collected in a 50 mL Schlenk flask and dried under vacuum outside the glove box. The side arm of the flask was degassed prior to application of the vacuum. Once the filtrate had dried, the flask was brought inside the glove box and the residue was washed with hexanes 5 times. The solid was collected and dried under vacuum overnight.

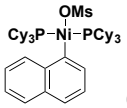


(**8**) The reaction was carried out following the general procedure from 1-naphthyl 4-methylbenzenesulfonate (108.5 mg, 0. 36 mmol), $Ni(COD)_2$ (100 mg, 0.36 mmol). Yield: 212 mg, 64%. The catalyst contained a small amount of $Ni^{II}OTs(2\text{-Naphthyl})(PCy_3)_2$, as indicated by a small peak in ^{31}P NMR. Yellow solid, m.p. 149 ºC. ^{1}H NMR (500 MHz, C_6D_6) δ 10.86 (d, J = 15.3, 1H), 8.18 (d, J = 7.9, 2H), 7.77 (d, J = 6.9, 2H), 7.56 (d, J = 8.0, 1H), 7.48 – 7.35 (m, 2H), 7.31 (d, J = 7.6, 1H), 7.11 (t, J = 7.5, 1H), 7.02 (d, J = 7.8, 2H), 2.51-2.13 (br, 6H), 2.13 (s, 3H), 2.13 – 0.80 (br, 60H). ^{31}P NMR (203 MHz, C_6D_6) δ 11.04. ^{13}C NMR (126 MHz, C_6D_6) δ 143.4, 141.3, 139.4, 136.5, 135.4, 132.5, 128.3, 128.2, 128.0, 127.1, 125.3, 123.7, 123.5, 122.2, 34.0, 31.6, 30.6, 30.0, 27.7, 26.5, 22.7, 20.7. $[M+H]^+$ calcd for $C_{53}H_{81}NiO_3P_2S$, 917.473, LC/MS found

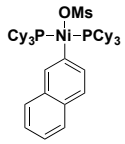
917.057. $[M\text{-}OTs]^+$ calcd for $C_{46}H_{73}NiP_2$, 745.4541, HRMS found 745.4539, $[M\text{-}OTs + MeCN]^+$ calcd for $C_{48}H_{76}NNiP_2$, 786.4806, HRMS found 786.4839.



(**9**) The reaction was carried out following the general procedure from 2-naphthyl 4-methylbenzenesulfonate (108. 5 mg, 0. 36 mmol), with $Ni(COD)_2$ (100 mg, 0.36 mmol). Yield: 182 mg, 55%. Yellow solid, m.p. 112-113 ºC. ^{1}H NMR (500 MHz, C_6D_6) δ 8.40 (d, J = 7.0, 1H), 8.07 (d, J = 6.5, 2H), 7.79 (s, 1H), 7.59 (dd, J = 21.9, 7.6, 2H), 7.32 (d, J = 4.7, 1H), 7.26 (t, J = 7.3, 1H), 6.92 (d, J = 6.9, 2H), 2.35-1.99 (br, 11H), 1.99 (s, 3H), 1.99-0.83 (br, 63H). ^{31}P NMR (203 MHz, C_6D_6) δ 10.99. ^{13}C NMR (126 MHz, $CDCl_3$) δ 143.4, 139.5, 137.1, 136.9, 132.4, 130.6, 128.4, 128.0, 127.0, 125.3, 125.0, 123.6, 122.7, 34.1, 31.6, 30.2, 29.9, 27.5, 26.5, 20.7. $[M\text{-}OTs]^+$ calcd for $C_{46}H_{73}NiP_2$, 745.454, LC/MS found 745. 611. $[M+MeCN+Na]^+$ calcd for $C_{55}H_{83}NNaNiO_3P_2S$, 980.482, LC/MS found 980.470. $[M\text{-}OTs]^+$ calcd for $C_{46}H_{73}NiP_2$, 745.4541, HRMS found 745.4555.



(**10**) The reaction was carried out following the general procedure from 1-naphthyl methylsulfonate (163 mg, 0. 72 mmol), with $Ni(COD)_2$ (200 mg, 0.72 mmol). Yield: 482 mg, 79%. Yellow solid, m.p. 139-143 ºC. The catalyst had small amount of impurity after 24 h of drying under vacuum by ^{31}P NMR. The crude was used for reactivity tests. ^{1}H NMR (500 MHz, Benzene-d_6) δ 10.96 (d, J = 8.7 Hz, 1H), 7.74 (s, 1H), 7.64 (s, 1H), 7.54 (s, 1H), 7.39 (d, J = 9.3 Hz, 1H), 7.10 (s, 1H), 3.67 (s, 2.8H), 2.87 (s, 3H), 1.10 (s, 77H). ^{31}P NMR (203 MHz, Benzene-d_6) δ 10.01, 9.67. ^{13}C NMR (126 MHz, C_6D6) δ 141.27, 136.29, 135.12, 132.30, 128.19, 127.17, 125.24, 123.85, 123.60, 122.16, 67.46, 40.34, 33.84, 31.40, 31.30, 30.53, 29.84, 27.80, 27.68, 26.55, 25.46. Anal. calcd for $C_{47}H_{76}NiO_3P_2S(C_4H_8O)_{0.7}(C_6H_{14})_{0.5}$: C, 67.85; H, 9.48. Found: C 67.67; H, 9.16. The ratio of THF and hexanes to the nickel complex was determined by ^{1}H NMR spectroscopy.



(**11**) The reaction was carried out following the general procedure from 2-naphthyl methylsulfonate (163 mg, 0. 72 mmol), with $Ni(COD)_2$ (200 mg, 0.72 mmol). Yield: 458 mg, 75%. Yellow solid, m. p. 123 ºC. ^{1}H NMR (500 MHz, Benzene-d_6) δ 8.41 (s, 1H), 7.74 (s, 1H), 7.66 – 7.44 (m, 2H), 7.26 (m, 2H), 3.57 (s, 3H, THF), 2.74 (s, 3H), 1.73-1.13 (m, 74H). ^{31}P NMR (203 MHz, Benzene-d_6) δ 9.84. ^{13}C NMR (126 MHz, Benzene-d_6) δ 136.6, 136.5, 132.5, 128.2,

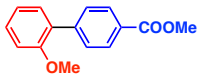
128.0, 126.3, 125.9, 125.3, 125.0, 123.6, 122.7, 34.6, 33.8, 30.2, 30.0, 29.8, 27.6, 26.5, 25.5. Anal. calcd for $C_{47}H_{76}NiO_3P_2S(C_4H_8O)_{0.7}$: C, 67.09; H, 9.15. Found: C 66.99; H, 8.90. The ratio of THF to the nickel complex was determined by ^{1}H NMR spectroscopy.

4.3 General Procedure for Kinetic Experiments

Sampling Kinetic Experiment Without Additional PCy_3. In an oven dried test tube (15 mm x 85 mm) charged with a stirring bar (5/8'' x 5/16'') were added 2-methoxyphenyl dimethylsulfamate (69.40 ± 0.10 mg, 0. 3 mmol, 1 equiv), methyl 4-(5,5-dimethyl-1,3,2-dioxaborinan-2-yl)benzoate (78.15 + 0.10 mg, 0.315 mmol, 1.05 equiv), $Ni^{II}Cl(1\text{-Naphthyl})(PCy_3)_2$ (11.73 ± 0.0510 mg, 0.015 mmol, 5% catalyst loading) and $K_3PO_4(H_2O)_n$ (191.00 ± 1.00 mg, ~ 9 mmol, ~ 3 equiv). The test tube was brought into a nitrogen filled glove box (moisture level < 10 ppm) through three degassing cycles. Distilled THF (1 mL) was added inside the glove box and the test tube was sealed by a rubber septum and left stirring for 60 min. A sample was taken by syringe and transferred outside the glove box. The sample was diluted by distilled THF (0.2 mL) and filtered through a short column of silica gel. The filtrate was concentrated and the GC analysis was carried out.

Sampling Kinetic Experiment with Additional PCy_3 (10%). Inside a nitrogen filled glove box, a 20 mL vial was charged with a stirring bar, PCy_3 (37.1 mg) and distilled THF (4.5 mL). The vial was screw closed and kept stirring. The solution was prepared prior to the kinetic experiments and kept inside the glove box for less than 4 h to prevent the oxidation of PCy_3 and evaporation of THF. Outside the glove box, in an oven dried test tube (15 mm x 85 mm) charged with a stirring bar (5/8'' x 5/16'') were added 2-methoxyphenyl dimethylsulfamate (69.40 ± 0.10 mg, 0. 3 mmol, 1 equiv), methyl 4-(5,5-dimethyl-1,3,2-dioxaborinan-2-yl)benzoate (78.15 + 0.10 mg, 0.315 mmol, 1.05 equiv), $Ni^{II}Cl(1\text{-Naphthyl})(PCy_3)_2$ (11.73 ± 0.050 mg, 0.015 mmol, 5% catalyst loading) and $K_3PO_4(H_2O)_n$ (191.00 ± 1.00 mg, ~ 9 mmol, ~ 3 equiv). The test tube was brought into a nitrogen filled glove box (moisture level < 10 ppm) through three degassing cycles. PCy_3 in THF (1 mL) was added inside the glove box. The test tube was sealed by a rubber septum and left stirring for 60 min. A sample was taken by syringe and transferred outside the glove box. The sample was diluted by distilled THF (0.2 mL) and filtered through a short column of silica gel. The filtrate was concentrated and the GC analysis was carried out. The results are summarized in Table SI 1-8. The product was isolated by silica gel column chromatography with 10% ethyl acetate in hexanes.

Sampling Kinetic Experiments with as Received THF. As received, wet THF was used from a commercial source (Fisher certified grade), containing ~0.025% butylated hydroxytoluene, about five months after opening and purged by N_2 for 30 min prior to use. In an oven dried test tube (15 mm x 85 mm) charged with a stirring bar (5/8'' x 5/16'') were added 2-methoxyphenyl dimethylsulfamate (69.40 ± 0.10 mg, 0. 3 mmol, 1 equiv), methyl 4-(5,5-dimethyl-1,3,2-dioxaborinan-2-yl)benzoate (78.15 + 0.10 mg, 0.315 mmol, 1.05 equiv), $Ni^{II}Cl$(1-Naphthyl)$(PCy_3)_2$ (11.73± 0.10 mg, 0.015 mmol, 5% catalyst loading) and $K_3PO_4(H_2O)_n$ (191.00 ± 1.00 mg, ~ 9 mmol, ~ 3 equiv). The test tube was brought into a nitrogen filled glove box (moisture level < 10 ppm) through three degassing cycles. Wet THF (1 mL) was added inside the glove box and the test tube was sealed by a rubber septum and left stirring for 60 min. A sample was taken by syringe and transferred outside the glove box. The sample was diluted by distilled THF (0.2 mL) and filtered through a short column of silica gel. The filtrate was concentrated and the GC analysis was carried out.



3: Isolated after kinetics experiments. Purified by silica gel column chromatography with hexanes to 10% ethyl acetate in hexanes gradient. White solid, m.p. 47.5-49 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.79 (d, J = 7.6, 1H), 7.50 (t, J = 7.5, 1H), 7.37 (t, J = 8.3, 2H), 7.25 (d, J = 8.6, 2H), 6.94 (d, J = 8.5, 2H), 3.85 (s, 3H), 3.67 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 169.5, 159.1, 131.3, 131.0, 130.9, 129.9, 129.6, 127.0, 113.7. Spectroscopy data matches with literature data.[9]

Isolated yields are listed in Table SI 9. ^{1}H and ^{13}C NMR spectra are listed in section 5.

Sample Procedures for Drying $K_3PO_4(H_2O)_n$ and Measuring Water Content:

Measuring Water Content in $K_3PO_4(H_2O)_n$ by Weight Loss:

In a tared round bottom flask (47.6791 g, average of three measurements within instrumental error) fitted with an adapter were added $K_3PO_4(H_2O)_n$ (48.9636 g for flask and base). The round bottom flask was heated by a Fischer burner until the visible water was evaporated. The flask was then connected to vacuum and flame dried until constant mass (flask + base: 48.6924 g, average of three measurements within instrumental error). The value of n is determined by the following equation:

$$n = \frac{mole\ (H_2O)}{mole\ (K_3PO_4)} = \frac{m(H_2O)/M_w(H_2O)}{m(K_3PO_4)/M_w(K_3PO_4)} = \frac{\frac{(48.9636-48.6924)g}{18.02g/mol}}{\frac{(48.6924-47.6791)g}{212.27g/mol}} = 3.2$$

The water content determination is more accurate with large amount of base. To minimize error induced by dehydration of glassware, water content determination with smaller round bottom flask (25 mL) are more accurate compared to large ones (250 mL) when the water content of base is determined.

Drying $K_3PO_4(H_2O)_n$ to Predetermined n:

The amount of weight loss desired is calculated from following equation:

$$m(mass\ loss) = m_1 \frac{18.02(n_1 - n_2)}{(212.27 + 18.02 \times n_1)}$$

where: m_1 is the mass of the $K_3PO_4(H_2O)n_1$ from commercial source;

n_1 is the water content determined by weight loss in commercial source

n_2 is the desired water content.

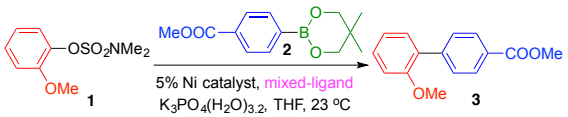
Drying procedure for base with n = 3.2:

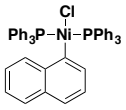
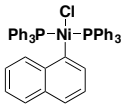
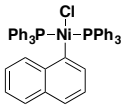
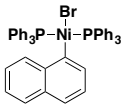
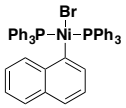
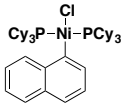
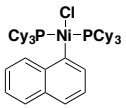
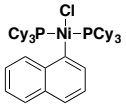
From the equation above, for 23.8093 g of $K_3PO_4(H_2O)_7$, the desired weight loss was calculated to be 4.9 g. In a tared round bottom flask (250 mL) fitted with an adapter were added a stirring bar, $K_3PO_4(H_2O)_7$ (23.8093 g, hydrous, tribasic from commercial source) were added and dried at 40 ºC under vacuum. After 6 h, the mass of the flask with the base was weighed and 4.8841 g water was lost. The base was ground and the exact amount of water was then verified to be 3.2 by the method above.

Kinetics experiments were carried out with bases dried by these procedures and the results are provided in Table SI 2.

4.4 Supporting Data for Kinetic Experiments

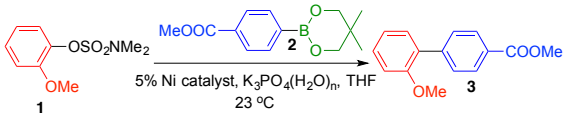
Table SI 1. Supporting Data for Table 1[a]

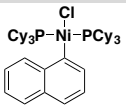
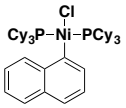
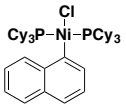
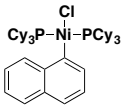
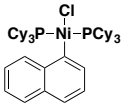
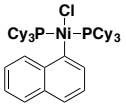
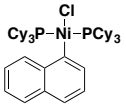
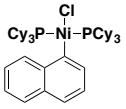
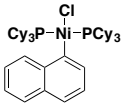
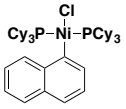


entry	catalyst	mixed-ligand (%)	time (h)	convn/yield (%)	compound number
1	$Ni(COD)_2$	PPh_3 (10)	90	6.9	
2	$Ni(COD)_2$	PCy_3 (10)	1	71/71	**3a**
3	$Ni(COD)_2$	PCy_3 (20)	1	92/89	**3b**
4		PCy_3 (10)	1	61	
			24	95	
			48	96	
			70	100/96	**3c**
5		PCy_3 (15)	48	99	
			56	100	
6		PCy_3 (20)	24	100/95	**3d**
7		PCy_3 (10)	48	96	
			70	100/94	**3e**
8		PCy_3 (15)	48	99	
			57	100	
9			0.7	98	
			0.9	100	
10		COD (10)	1	44	
			2	57/50	**3f**
11		PPh_3 (10)	1	53	
			2	60/48	**3g**

[a]Conversion by GC, isolated yield, both as percentages.

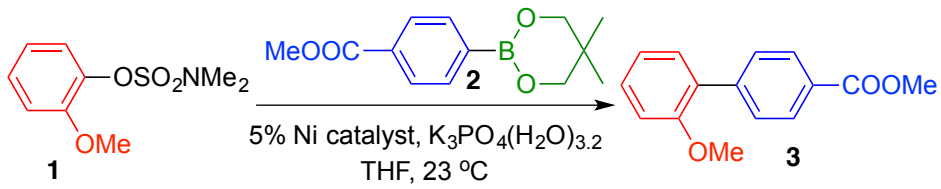
Table SI 2. Supporting Data for Table 2

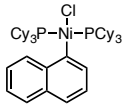
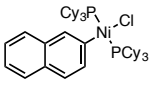
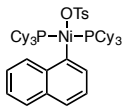
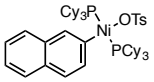
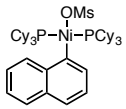
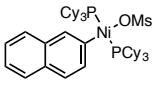


entry	catalyst	THF	n	time (min)	convn (%)
1		dry	1.0	70 270 990 1620	16 45 92 100
2		dry	3.0	60	100
3		dry	3.1	50 60 70	97 98 99
4		dry	3.2	42 52	97 100
5		dry	3.7	40 50 60 52	92 95 98 100
6		dry	4.7	70 80 90	97 99 99
7		dry	7.0	60 90 168	94 97 99
8		dry	2.8	38 58 78 116	75 85 95 98
9		dry	3.2	50 60	99 100/95 (**3h**)
10		As received	1.0	58 78 116	85 95 98
11		As received	3.2	50 70 120 160	94 96 99 100
12		As received	7.0	60 120 180	93 98 99

[a]Conversion by GC, isolated yield, both as percentages.

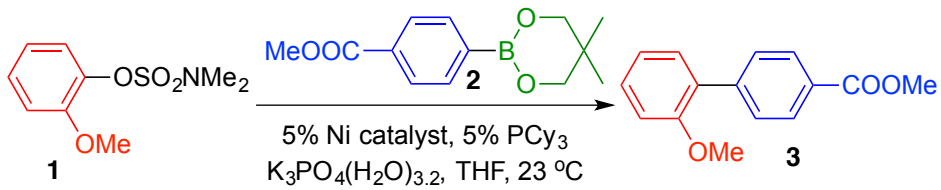
Table SI 3. Supporting Data for Table 3 with 0% PCy_3

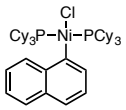
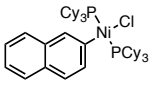
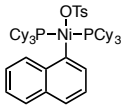
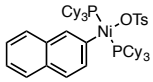
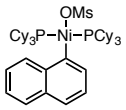
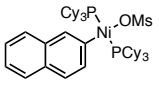


entry	catalyst	time (min)	convn/ yield (%)	time (min)	convn/ yield (%)	time (min)	convn/ yield (%)
1		42	98	50	94	50	97
		52	100	60	100	60	98
		-	-	70	100	70	99
2		50	99	40	98	50	98
		60	100	50	99	60	99
		70	100/95 (**3h**)	60	100	70	99
3		47	97	50	100	50	100
		57	100	60	100	60	100
		-	-	70	100	70	100
4		47	98.0	50	99	50	98
		57	100	60	100	60	99
		-	-	70	100	70	100
5		50	99	50	98	50	97
		60	99	60	99	60	98
		70	100/91 (**3i**)	70	99	70	99
6		42	99	40	95	40	96
		52	100/95 (**3j**)	50	96	50	99
		62	100	60	98	60	100

[a]Conversion by GC as percentages. Reactions were duplicated by three different chemists.

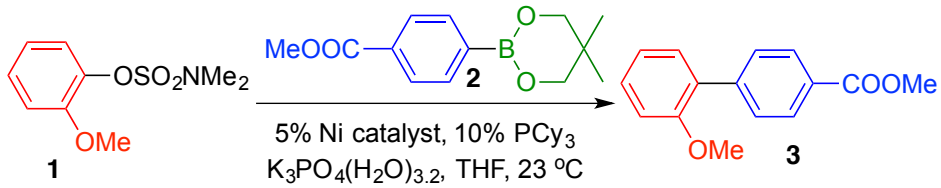
Table SI 4. Supporting Data for Table 3 with 5% PCy_3

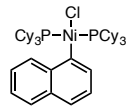
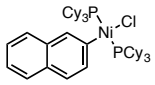
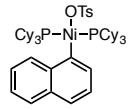
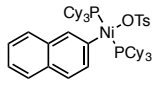
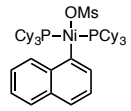
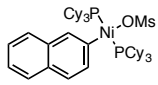


entry	catalyst	time(min)	convn(%)	time(min)	convn(%)
1		30	97	40	96
		40	99	50	97
		-	-	60	99
2		37	99	40	99
		47	100	50	99
		-	-	60	100
3		43	98	40	100
		53	100	50	100
		-	-	60	100
4		-	-	40	99
		-	-	50	100
		-	-	60	100
5		-	-	40	96
		-	-	50	97
		-	-	60	99
6		-	-	40	99
		-	-	50	99
		-	-	60	100

[a]Conversion by GC as percentages. Reactions were duplicated by two different chemists.

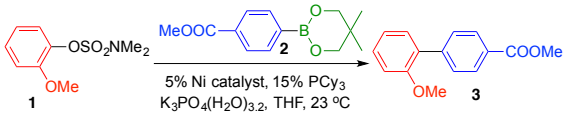
Table SI 5. Supporting Data for Table 3 with 10% PCy_3

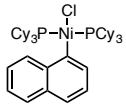
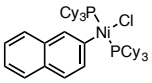
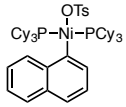
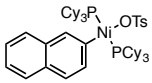


entry	catalyst	time (min)	convn/ yield (%)	time (min)	convn(%)	time (min)	convn(%)
1		38	99	40	98	40	99
		48	100	50	100	50	99
		-	-	60	100	60	100
2		37	99	40	97	40	99
		47	100	50	99	60	100
		-	-	60	100	-	-
3		40	94	40	94	40	100
		50	100	50	99	50	100
		-	-	60	100	60	100
4		42	97	40	96	40	100
		53	100	50	99	50	100
		-	-	60	100	60	100
5		40	100/98 (**3k**)	40	97	40	100
		50	100	50	98	50	100
		-	-	60	99	60	100
6		40	98	40	95	40	100
		50	100	50	96	50	100
		-	-	60	98	60	100

[a]Conversion by GC, isolated yields, both as percentages. Reactions were duplicated by three different chemists.

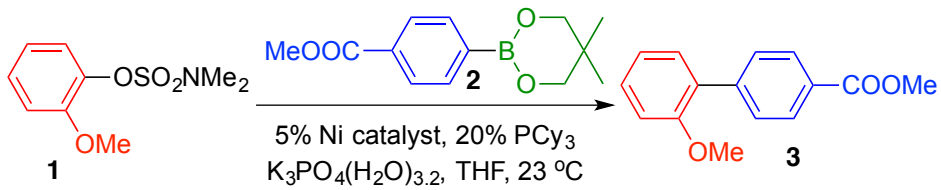
Table SI 6. Supporting Data for Table 3 with 15% PCy_3

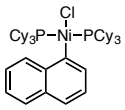
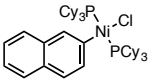
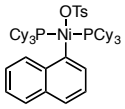
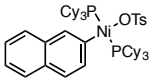
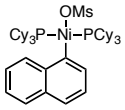
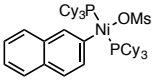


entry	catalyst	time(min)	convn(%)
1		30	99
		40	100
2		34	98
		44	100
3		57	100
		67	100
4		45	97
		55	100
		65	100

[a]Conversion by GC as percentages.

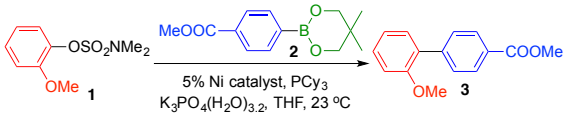
Table SI 7. Supporting Data for Table 3 with 20% PCy_3

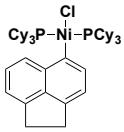
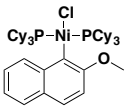
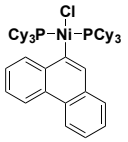
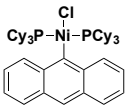


entry	catalyst	time(min)	convn(%)	time(min)	convn(%)
1		40	97/97 (**3l**)	40	97
		50	99	50	97
		-	-	60	97
2		50	99	40	98
		60	100	50	98
		-	-	60	99
3		40	100/99 (**3m**)		
		50	100		
4		40	100		
		50	100/96 (**3n**)		
5		40	100	30	100
		50	100/98 (**3o**)	40	100
6		30	100	30	100
		40	100	40	100

[a]Conversion by GC as percentages. Reactions were duplicated by two different chemists.

Table SI 8. Supporting Data for Table 4



entry	catalyst	PCy_3	time (min)	convn (%)
1		0	40	97
			50	99
			70	99/95 (**3p**)
		10	50	97
			60	98
			70	99
		20	30	95
			40	99
			50	100
2		0	40	85
			60	95
			70	97
3		0	60	97
			70	99
		10	80	99
			50	98
			60	99
			70	100
		20	40	96
			50	98
			60	99
4		0	40	97
			50	99
			60	100
		10	50	99
			60	100
			70	100
		20	40	96
			50	97
			60	99

[a]Conversion was determined by GC as percentages.

Table SI 9. Isolated Yields and Spectroscopy Data for Kinetics Experiments

entry	compound number	isolated yield (mg)	isolated yield (%)
1	**3a**	51.41	71
2	**3b**	64.45	89
3	**3c**	69.80	96
4	**3d**	68.97	95
5	**3e**	68.32	94
6	**3f**	36.56	50
7	**3g**	34.59	48
8	**3h**	69.19	95
9	**3i**	70.52	91
10	**3j**	68.79	95
11	**3k**	71.09	98
12	**3l**	70.52	97
13	**3m**	72.11	99
14	**3n**	69.42	96
15	**3o**	71.06	98
16	**3p**	69.28	95

4.5 Experiments to Study the Activation of Precatalyst 6

Procedure for Monitoring the Activation of Precatalyst 6 by ^{1}H NMR

In an oven dried screw cap vial (4 mL) charged with a stirring bar were added methyl 4-(5,5-dimethyl-1,3,2-dioxaborinan-2-yl)benzoate (78.15 mg, 0.315 mmol, 1.05 equiv), and $K_3PO_4(H_2O)_n$ (191.02 mg, ~ 9 mmol, ~ 3 equiv), in a separate oven dried screw cap vial (4 mL) was added $Ni^{II}Cl(1\text{-Naphthyl})(PCy_3)_2$ (11.72 mg, 0.015 mmol, 5% catalyst loading). The vials were brought into a nitrogen filled glove box (moisture level < 10 ppm) through three degassing cycles (5 min each). Distilled THF (1 mL) was added inside the glove box to the second vial to dissolve $Ni^{II}Cl(1\text{-naphthyl})(PCy_3)_2$ and the solution was transferred to the first vial. The vial was capped and left stirring for 5 min. A sample (100 μL) was taken and injected into an NMR tube. The tube was brought outside the glove box. C_6D_6 (0.5 mL) was added outside the glove box and ^{1}H NMR was carried out right away. The spectra are shown in Figure SI 1.

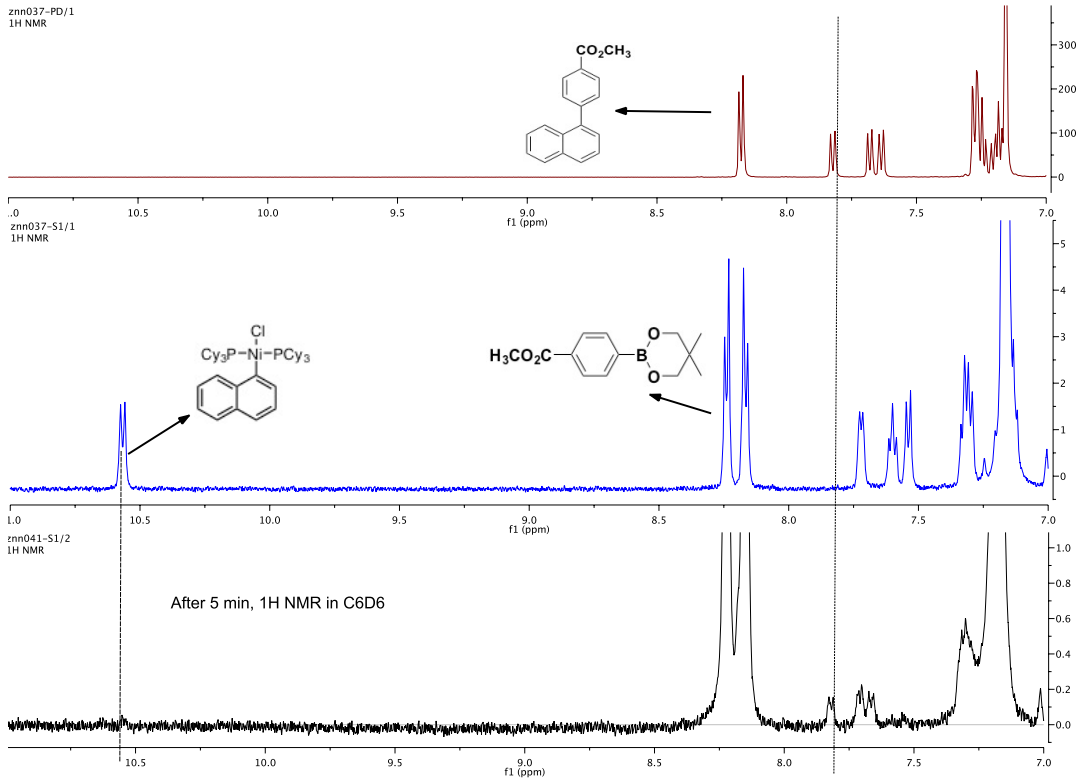


Figure SI 1. Activation of precatalyst **6** monitored by ^{1}H NMR in C_6D_6.

Procedure for Model Reaction of Activation of Precatalyst 6

In an oven dried screw cap vial (4 mL) charged with a stirring bar were added methyl 4-(5,5-dimethyl-1,3,2-dioxaborinan-2-yl)benzoate (49.60 mg, 0.2 mmol, 2 equiv), $Ni^{II}Cl(1\text{-naphthyl})(PCy_3)_2$ (78.31 mg, 0.1 mmol) and $K_3PO_4(H_2O)_n$ (63.62 mg, ~ 0.3 mmol, ~ 3 equiv). The vial was brought into a nitrogen filled glove box (moisture level < 10 ppm) through three degassing cycles. Distilled THF (1 mL) was added inside the glove box, the vial was capped, and then left stirring for 12 h. The reaction mixture was dissolved in DCM, filtered and concentrated. The crude product was purified by silica gel column chromatography with DCM/hexanes = 1:1 eluent twice. Methyl 4-(naphthalen-1-yl)benzoate (**16**) was isolated to yield: 21.4 mg, 88%. White solid, m.p. 70 ºC. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.17 (dd, *J* = 8.3, 2.4 Hz, 2H), 7.90 (dd, *J* = 13.8, 8.2 Hz, 2H), 7.84 (d, *J* = 8.4 Hz, 1H), 7.63 - 7.48 (m, 4H), 7.44 (dd, *J* = 12.8, 7.2 Hz, 2H), 3.97 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.2, 145.7, 139.3, 133.9, 131.38, 130.3, 129.7, 129.2, 128.5, 128.4, 127.1, 126.5, 126.1, 125.8, 125.5, 52.3. NMR spectra match with literature data.[15]

5. Characterization of the Reaction Products

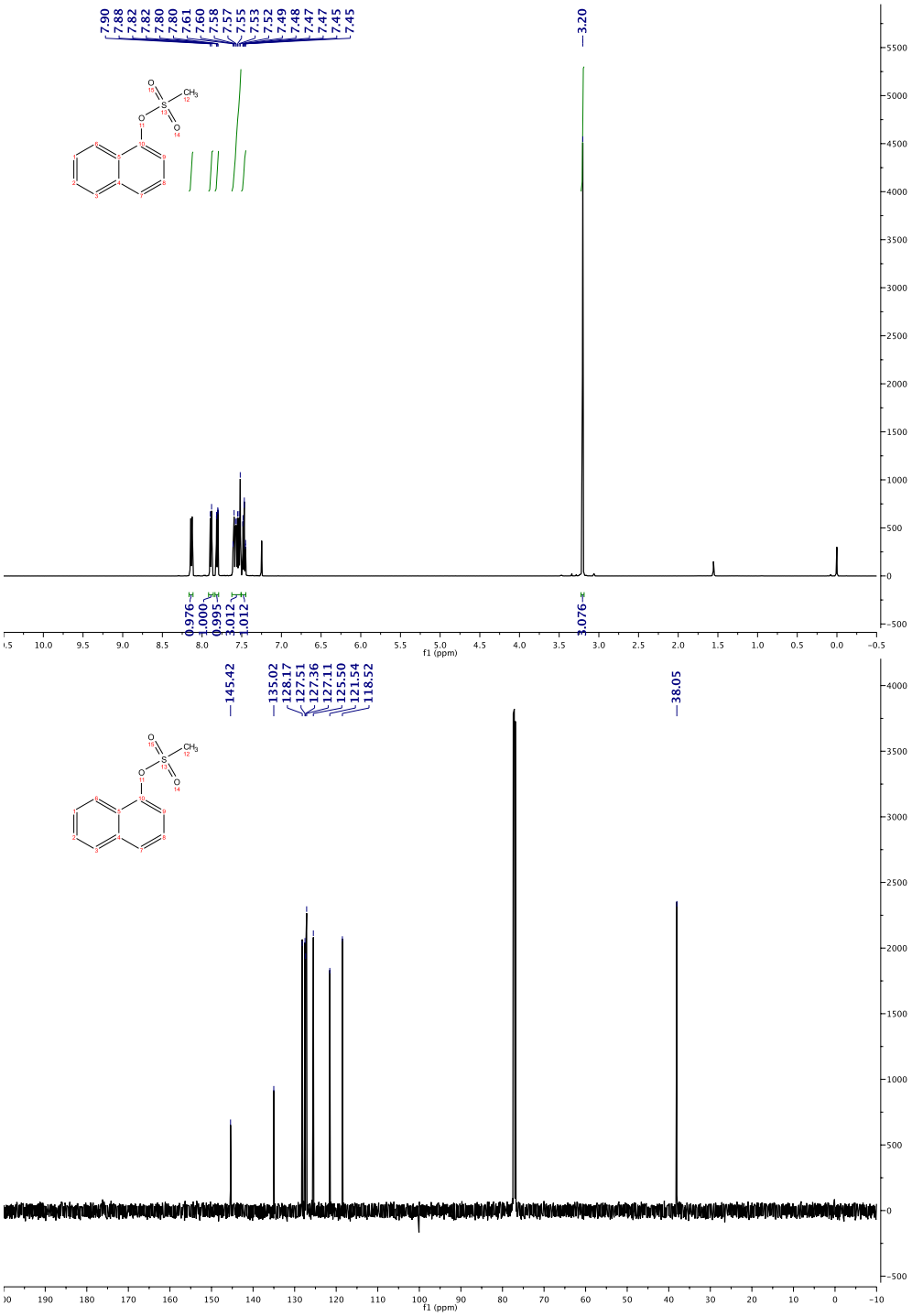


Figure SI 2. ^{1}H NMR (top, 500 MHz), and ^{13}C NMR (bottom, 125 MHz) spectra of 1-naphthyl methanesulfonate in $CDCl_3$.

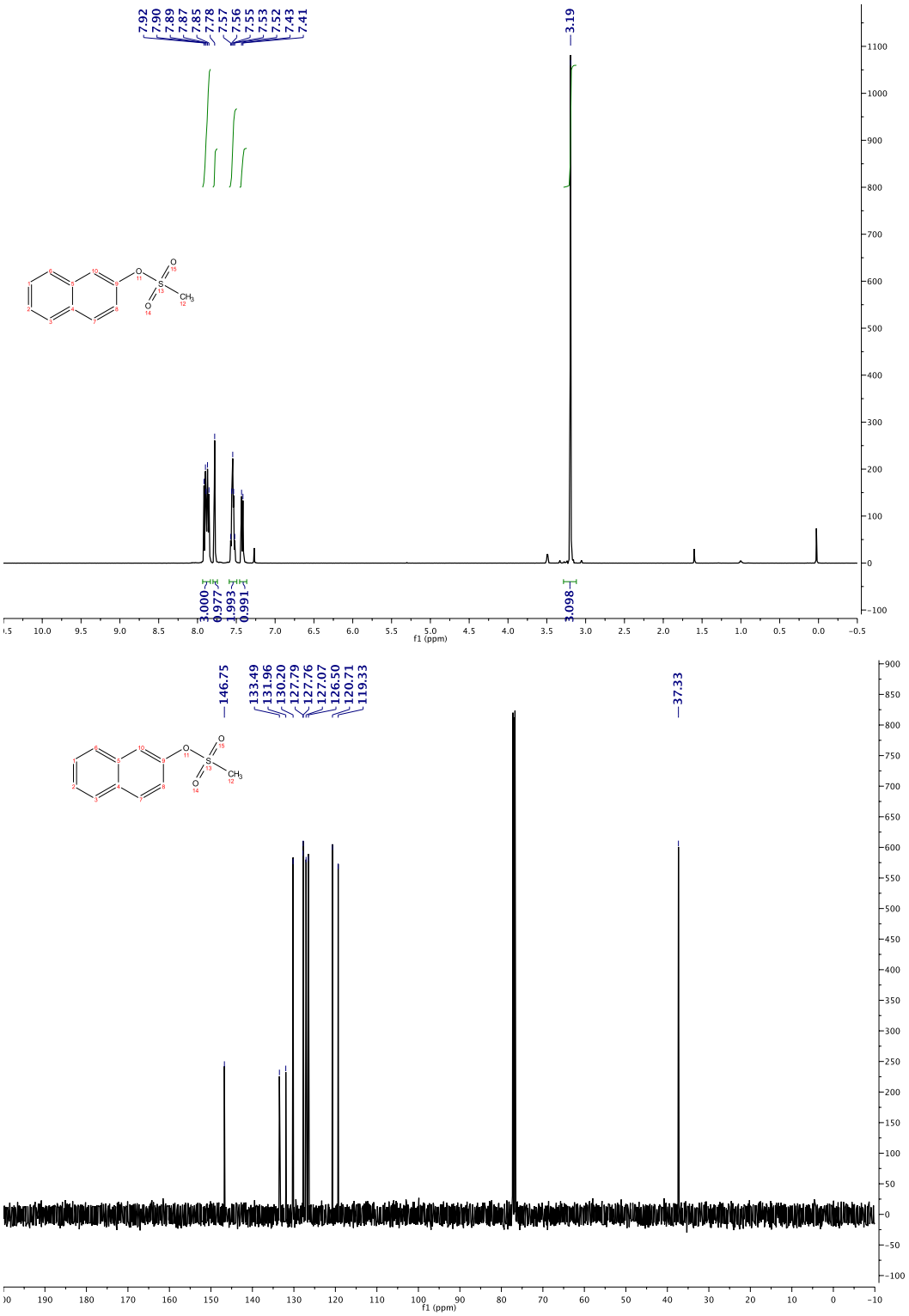


Figure SI 3. ^{1}H NMR (top, 500 MHz), and ^{13}C NMR (bottom, 125 MHz) spectra of 2-naphthyl methanesulfonate in $CDCl_3$.

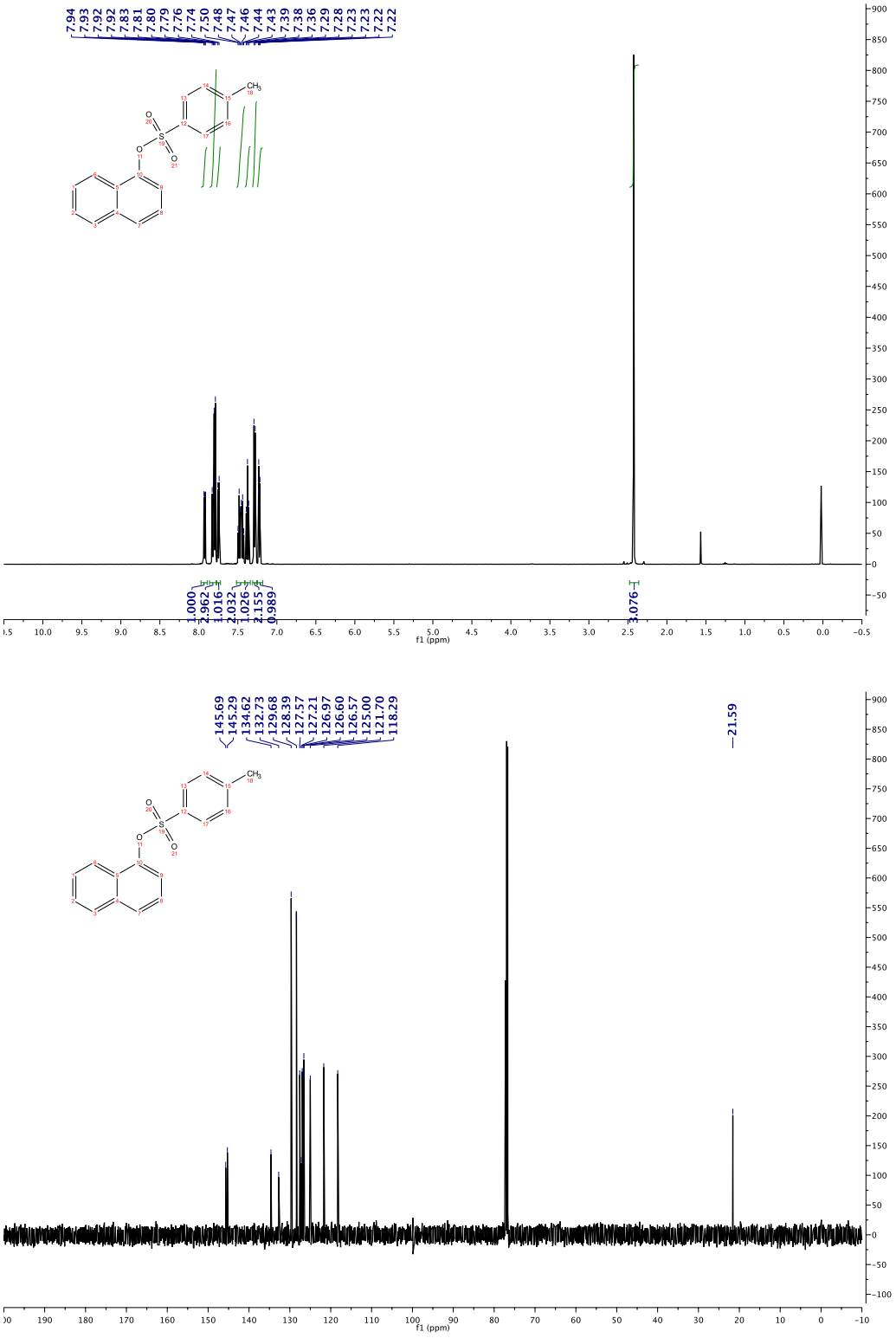


Figure SI 4. ^{1}H NMR (top, 500 MHz), and ^{13}C NMR (bottom, 125 MHz) spectra of 1-naphthyl 4-methylbenzenesulfonate in $CDCl_3$.

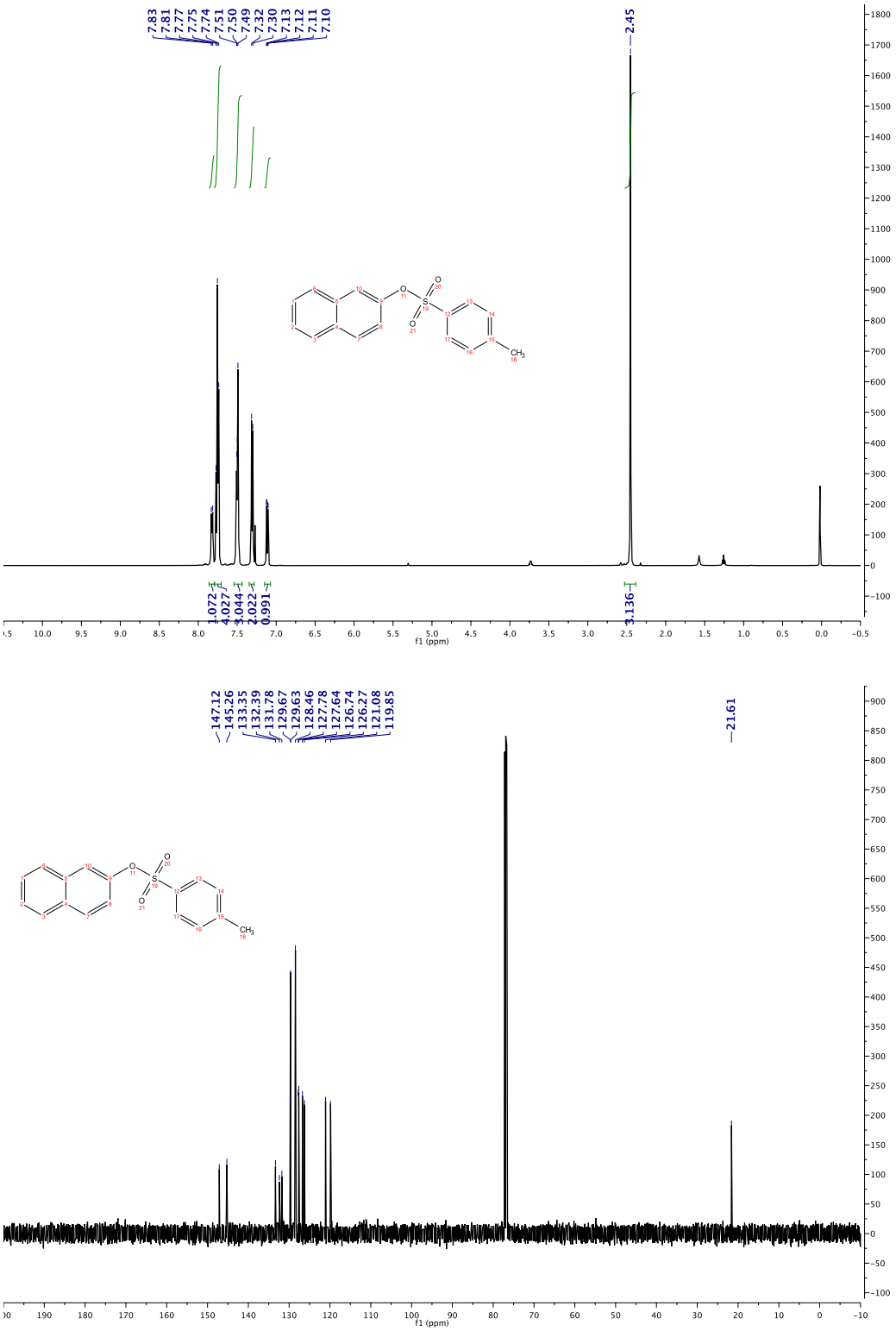


Figure SI 5. ^{1}H NMR (top, 500 MHz), and ^{13}C NMR (bottom, 125 MHz) spectra of 2-naphthyl 4-methylbenzenesulfonate in $CDCl_3$.

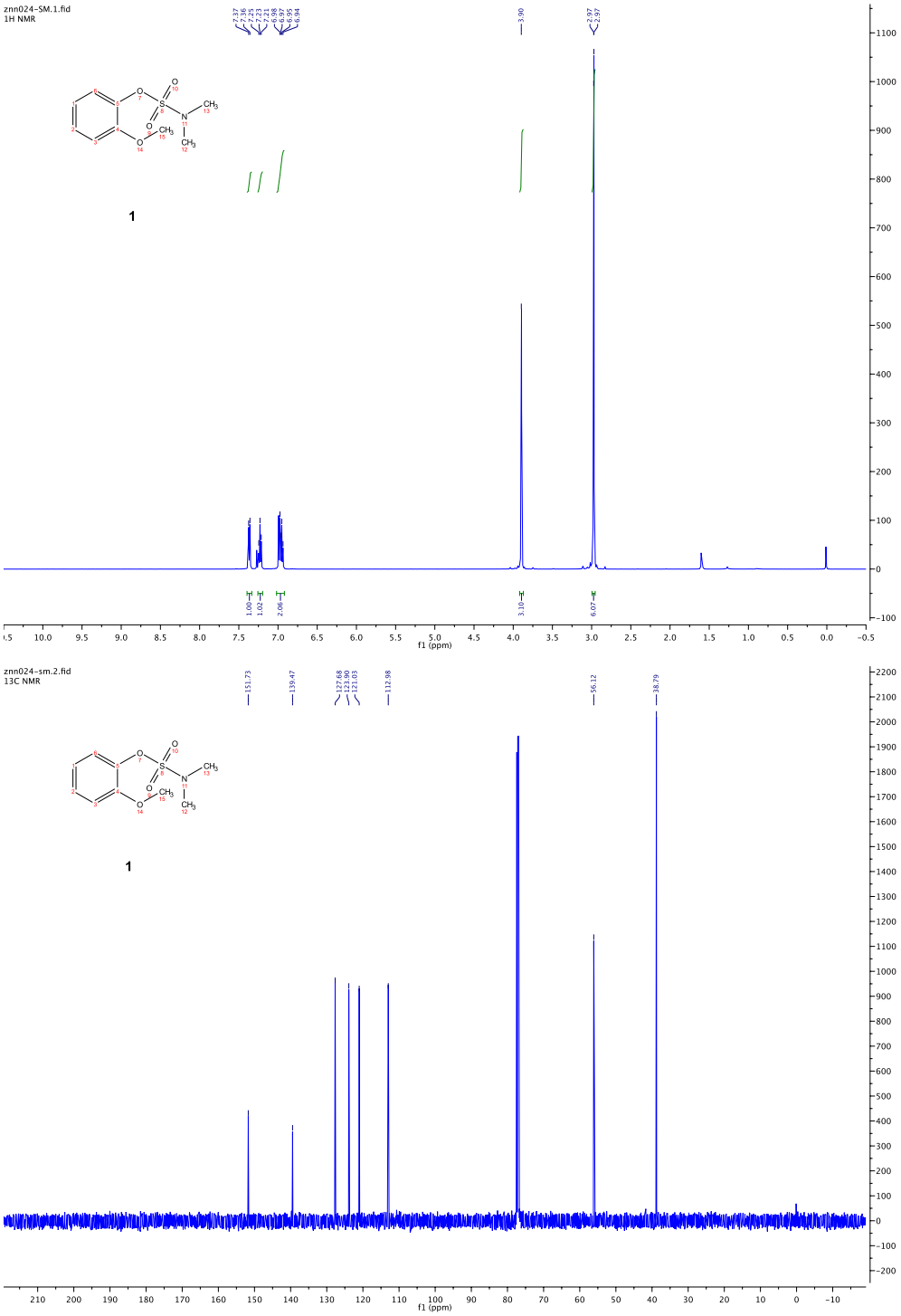


Figure SI 6. ^{1}H NMR (top, 500 MHz), and ^{13}C NMR (bottom, 125 MHz) spectra of 2-methoxyphenyl dimethylsulfamate in $CDCl_3$.

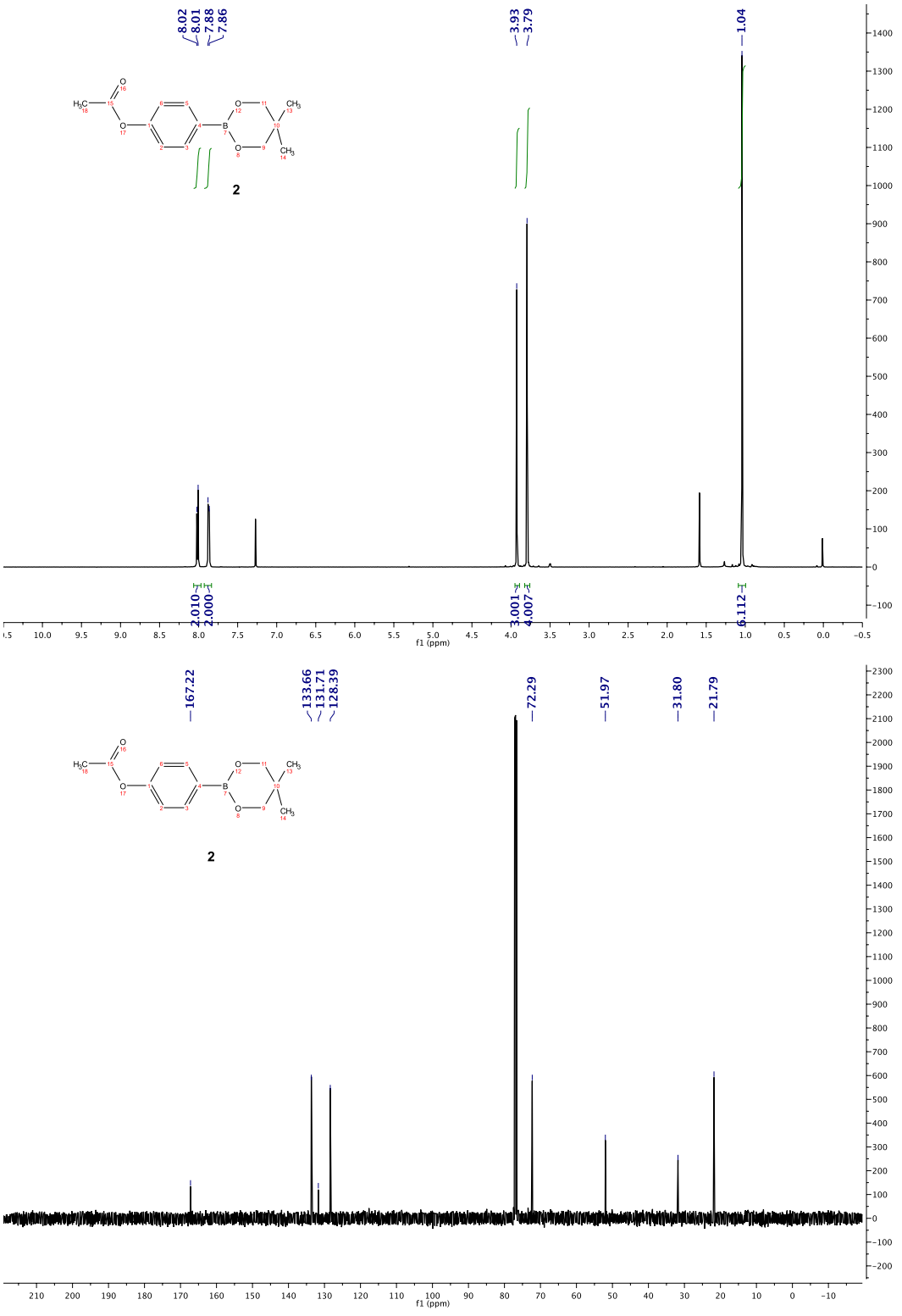


Figure SI 7. ^{1}H NMR (top, 500 MHz), and ^{13}C NMR (bottom, 125 MHz) spectra of 4-(5,5-dimethyl-1,3,2-dioxaborinan-2-yl)phenyl acetate in $CDCl_3$.

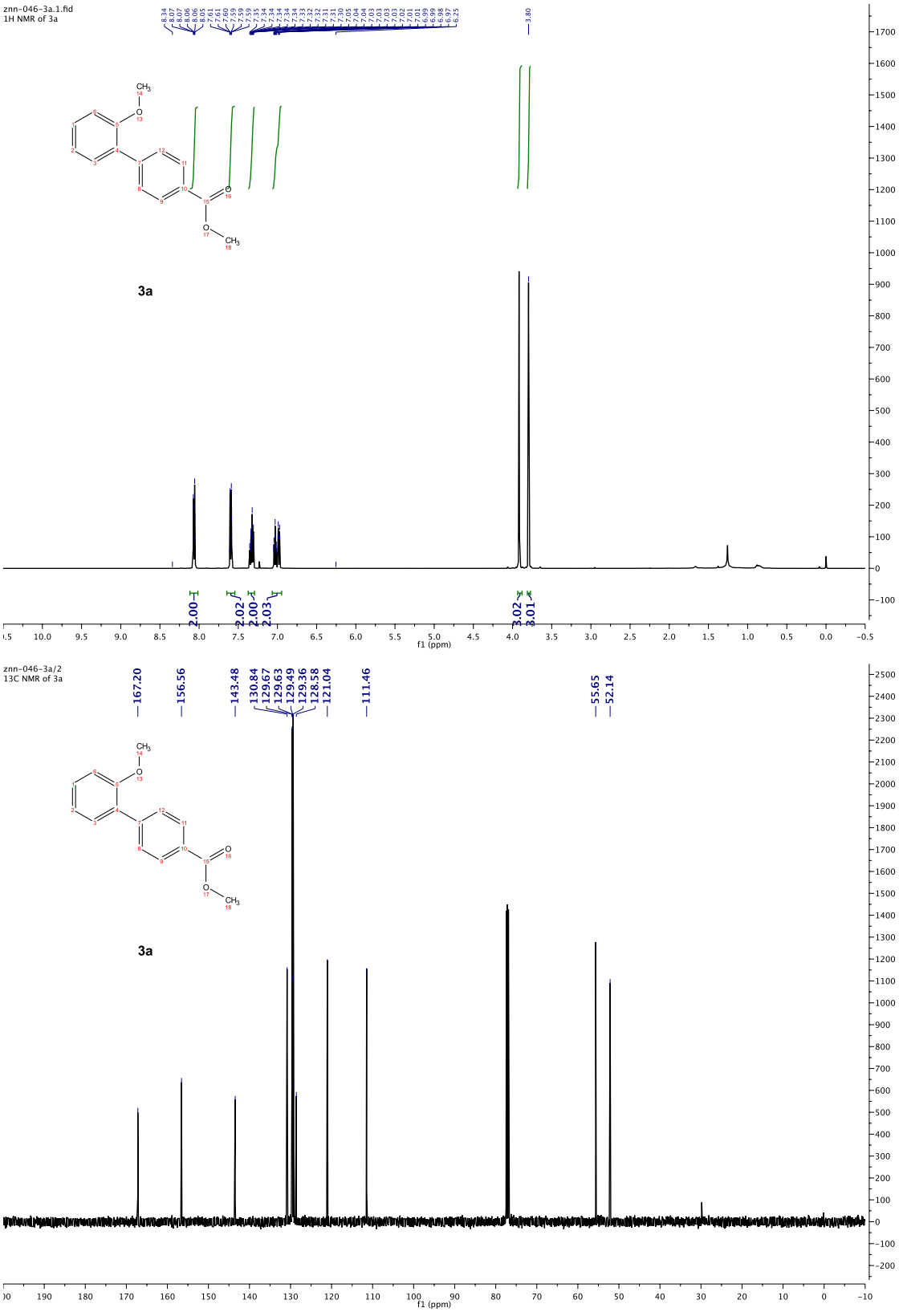


Figure SI 8. ^{1}H NMR (top, 500 MHz), and ^{13}C NMR (bottom, 125 MHz) spectra of **3a** in $CDCl_3$.

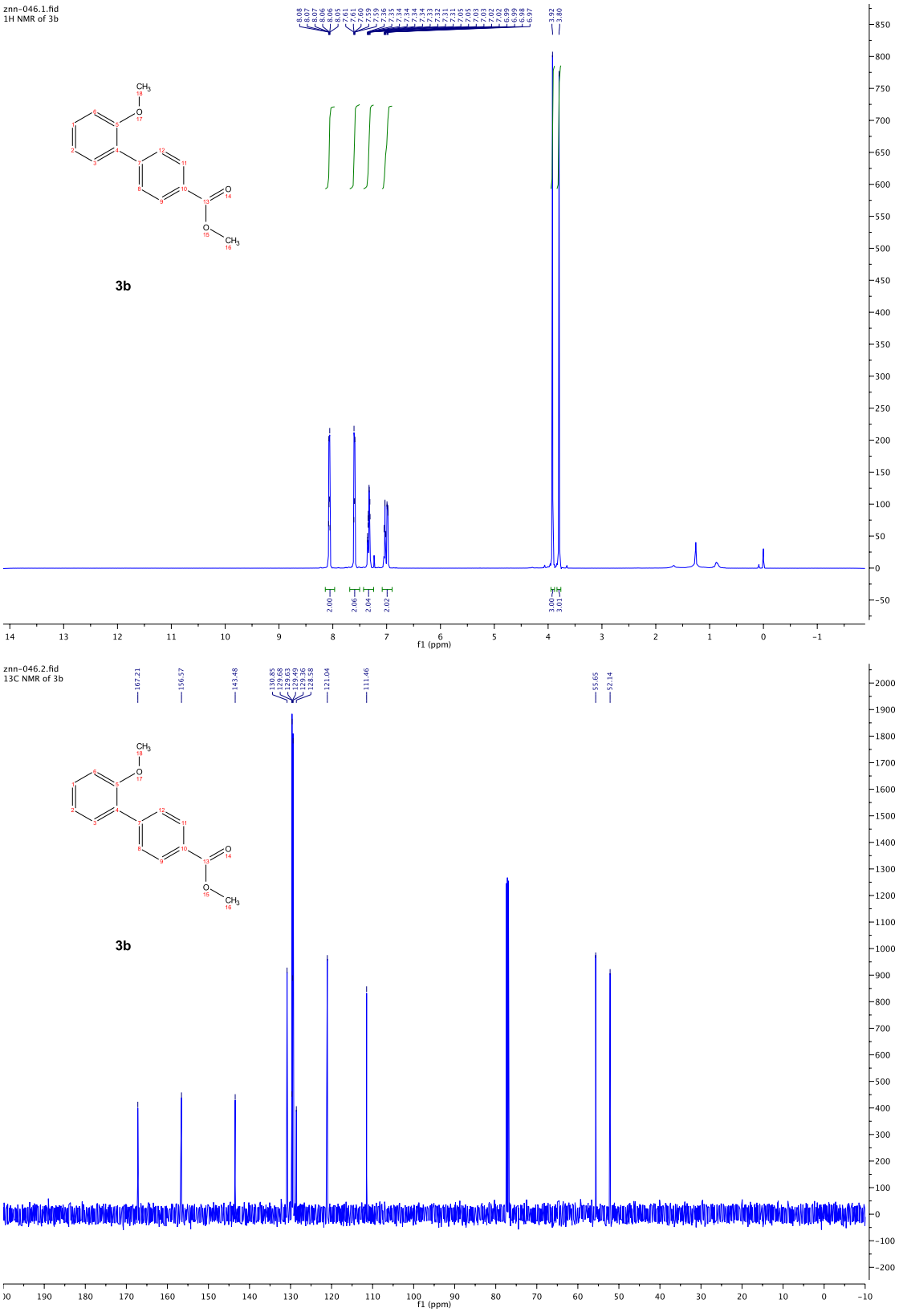


Figure SI 9. ^{1}H NMR (top, 500 MHz), and ^{13}C NMR (bottom, 125 MHz) spectra of **3b** in $CDCl_3$.

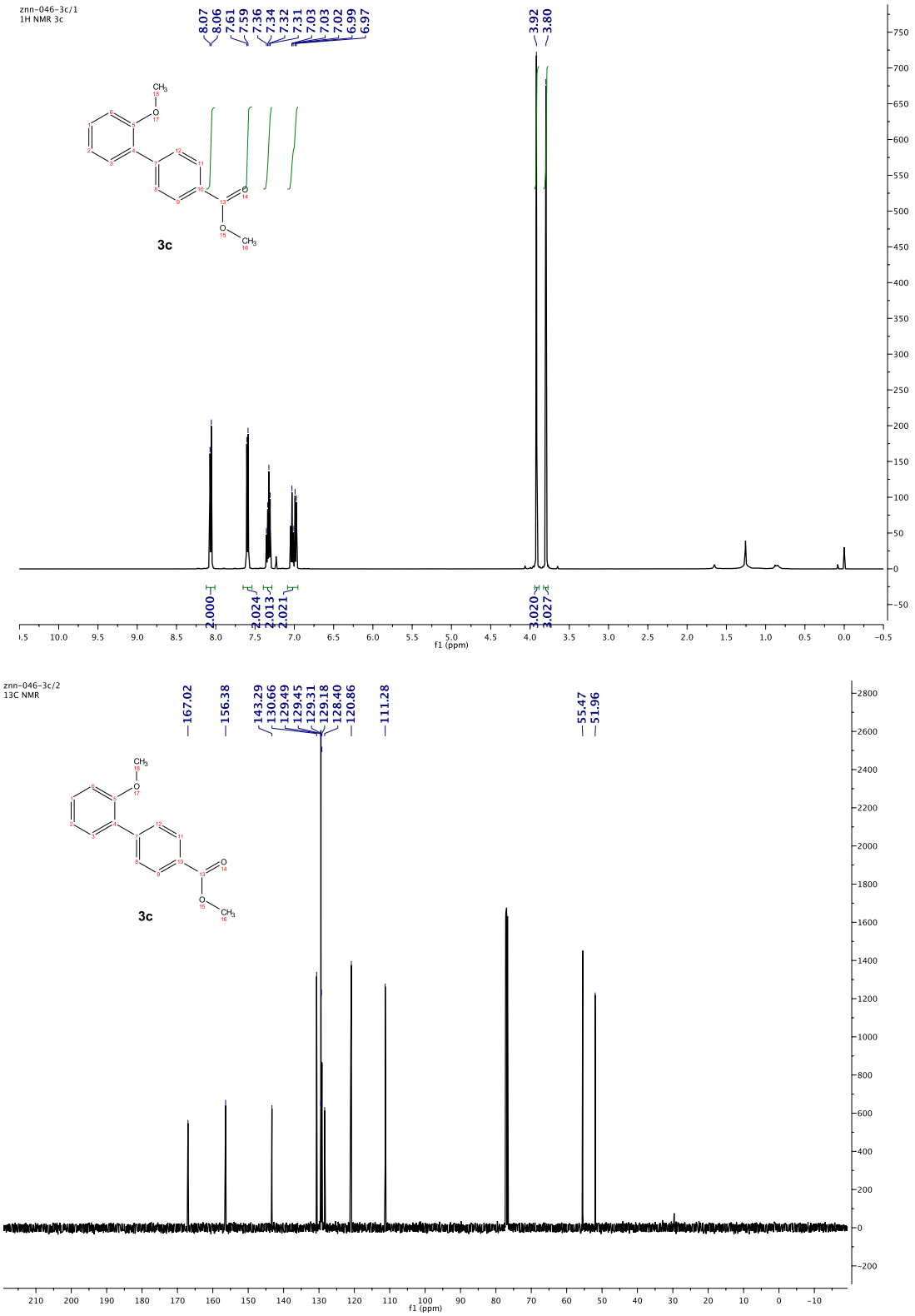


Figure SI 10. ^{1}H NMR (top, 500 MHz), and ^{13}C NMR (bottom, 125 MHz) spectra of **3c** in $CDCl_3$.

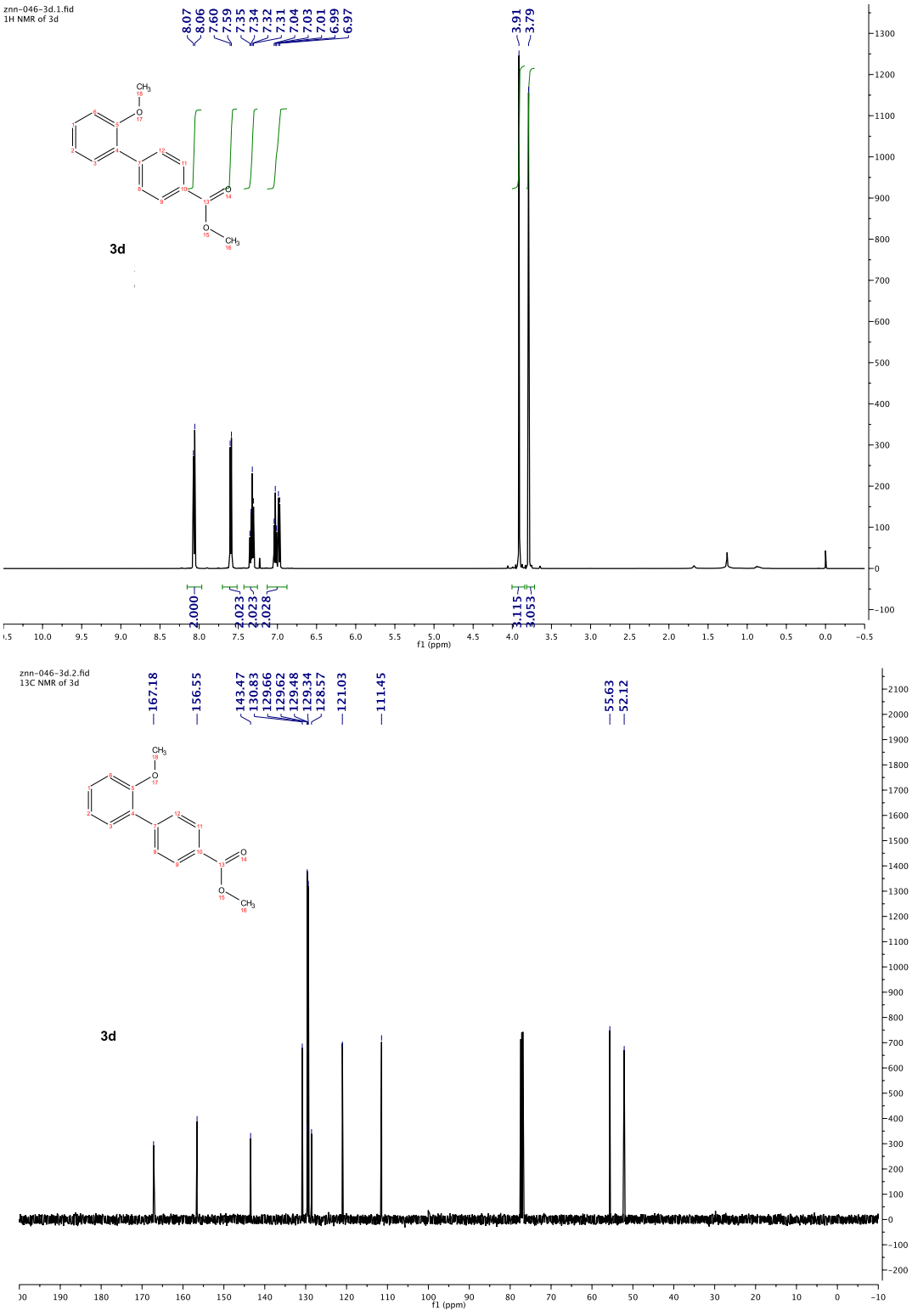


Figure SI 11. ^{1}H NMR (top, 500 MHz), and ^{13}C NMR (bottom, 125 MHz) spectra of **3d** in $CDCl_3$.

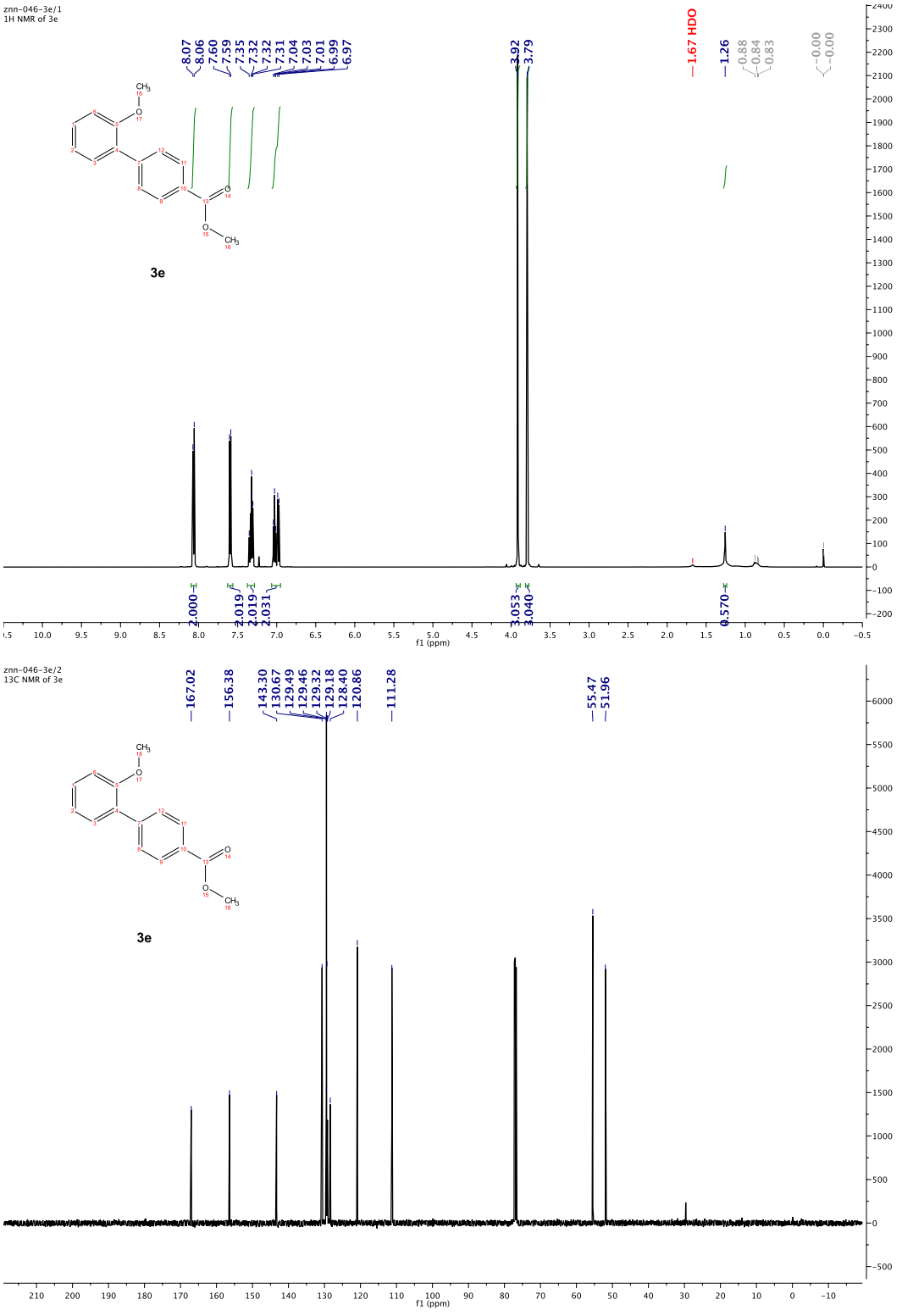


Figure SI 12. ^{1}H NMR (top, 500 MHz), and ^{13}C NMR (bottom, 125 MHz) spectra of **3e** in $CDCl_3$.

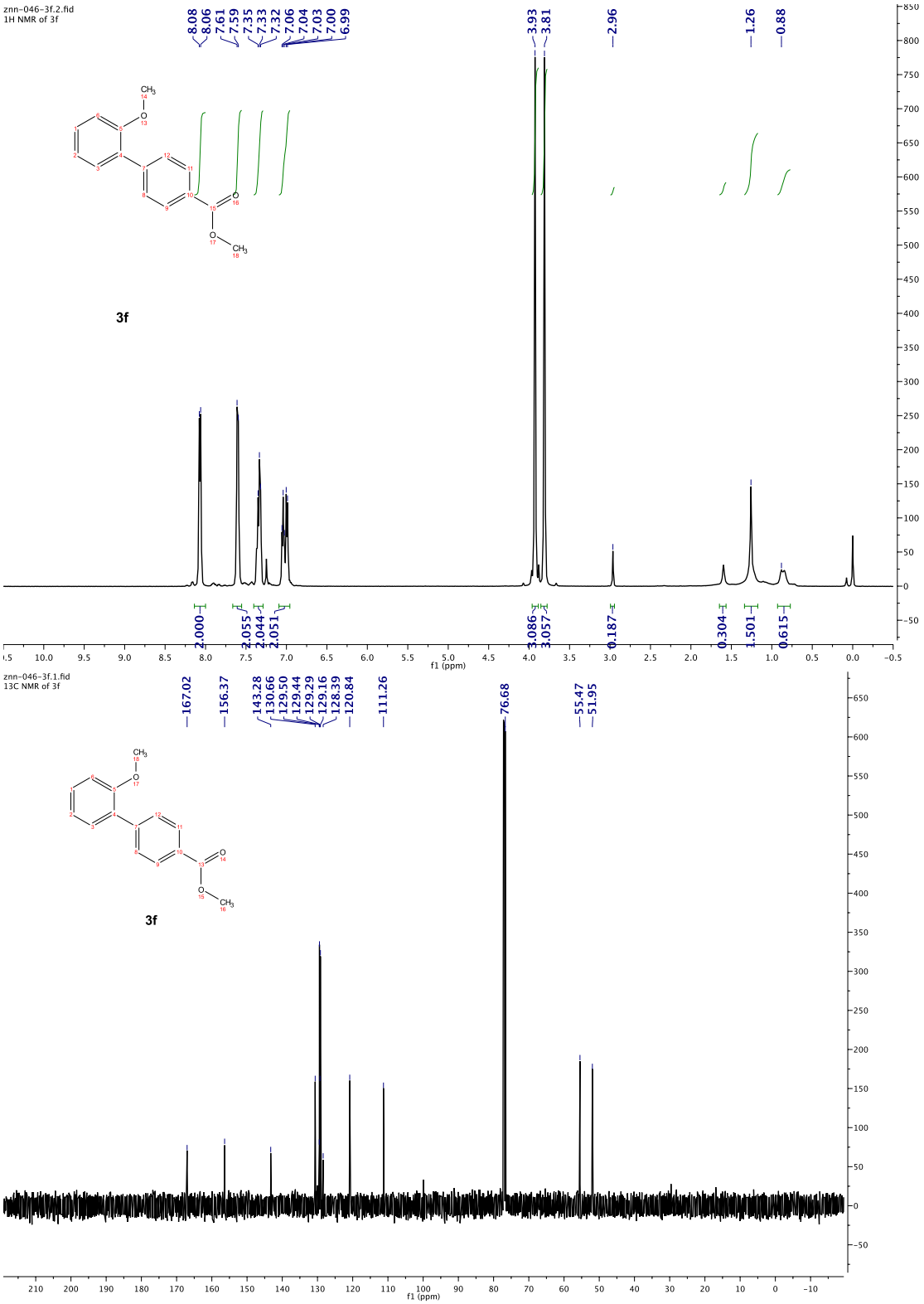


Figure SI 13. ^{1}H NMR (top, 500 MHz), and ^{13}C NMR (bottom, 125 MHz) spectra of **3f** in $CDCl_3$.

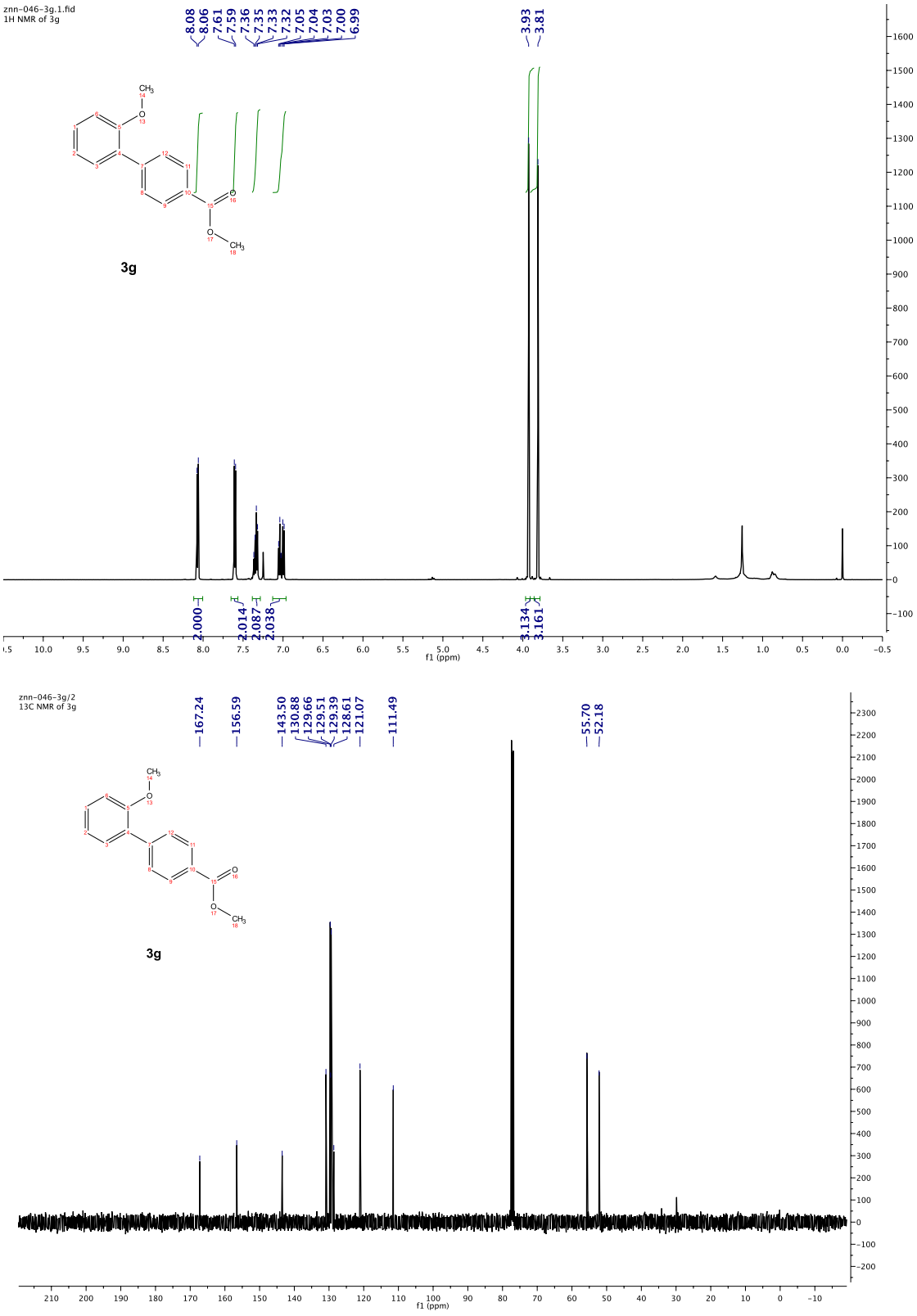


Figure SI 14. ^{1}H NMR (top, 500 MHz), and ^{13}C NMR (bottom, 125 MHz) spectra of **3g** in $CDCl_3$.

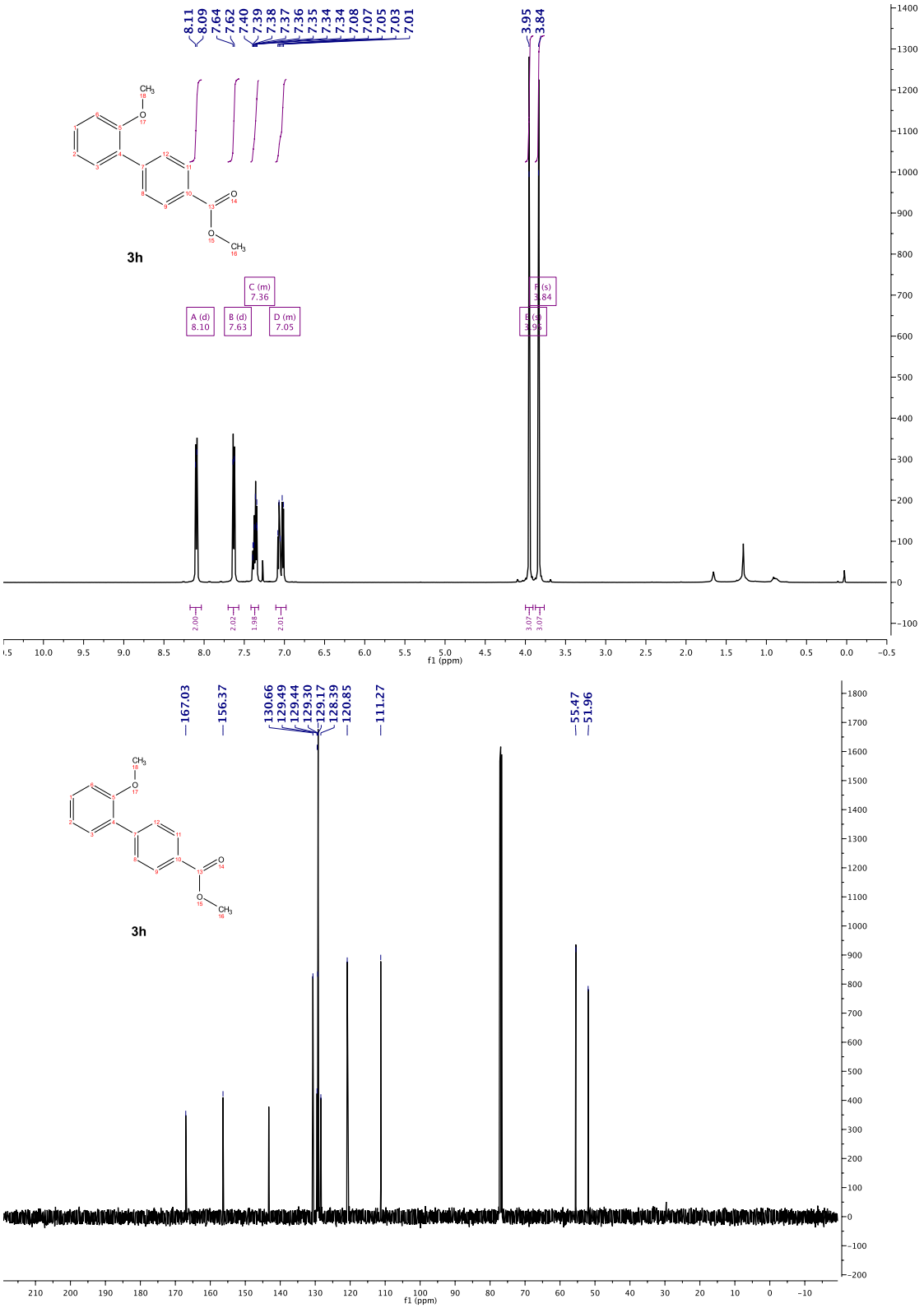


Figure SI 15. ^{1}H NMR (top, 500 MHz), and ^{13}C NMR (bottom, 125 MHz) spectra of **3h** in $CDCl_3$.

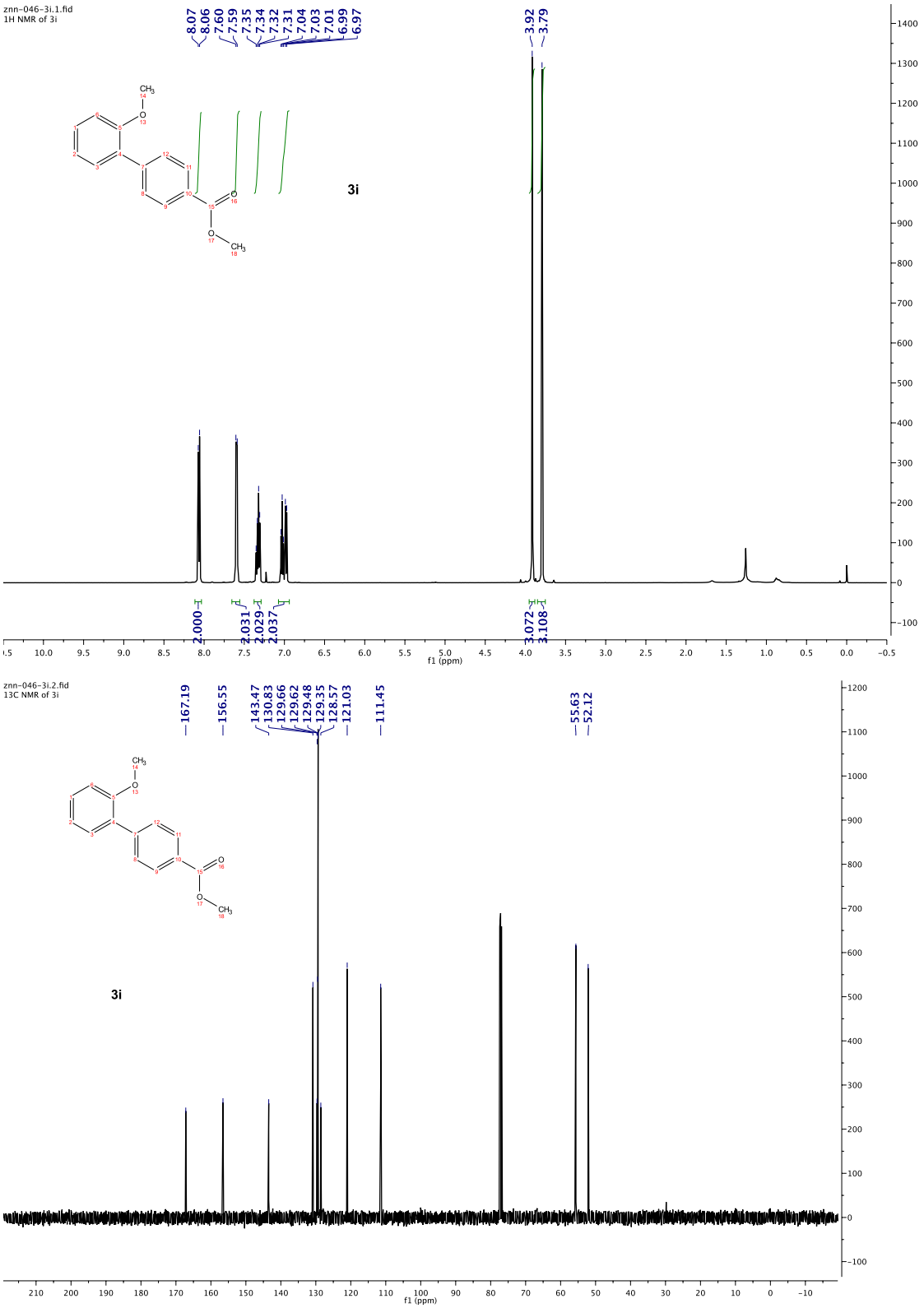


Figure SI 16. ^{1}H NMR (top, 500 MHz), and ^{13}C NMR (bottom, 125 MHz) spectra of **3i** in $CDCl_3$.

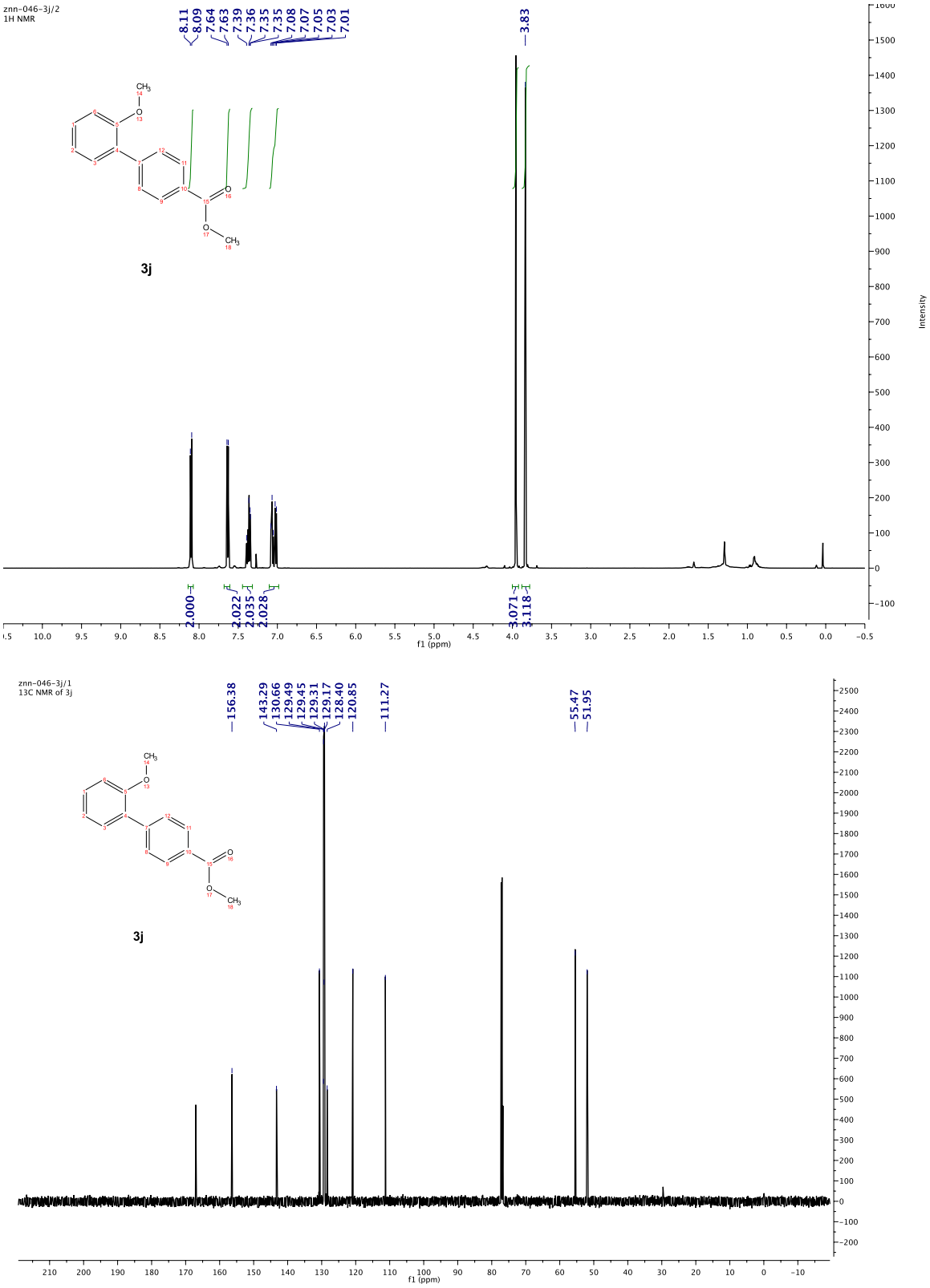


Figure SI 17. ^{1}H NMR (top, 500 MHz), and ^{13}C NMR (bottom, 125 MHz) spectra of **3j** in $CDCl_3$.

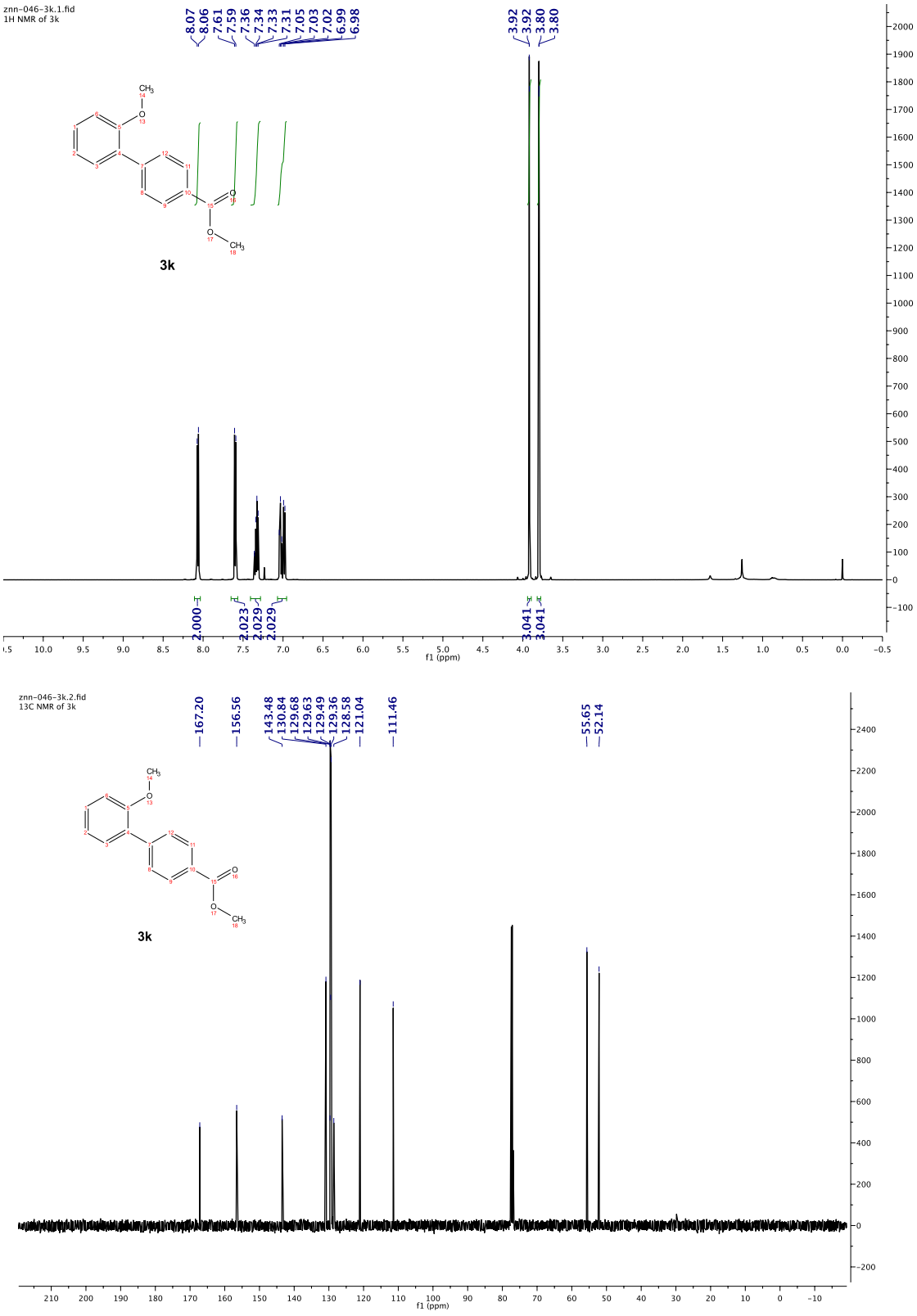


Figure SI 18. ^{1}H NMR (top, 500 MHz), and ^{13}C NMR (bottom, 125 MHz) spectra of **3k** in $CDCl_3$.

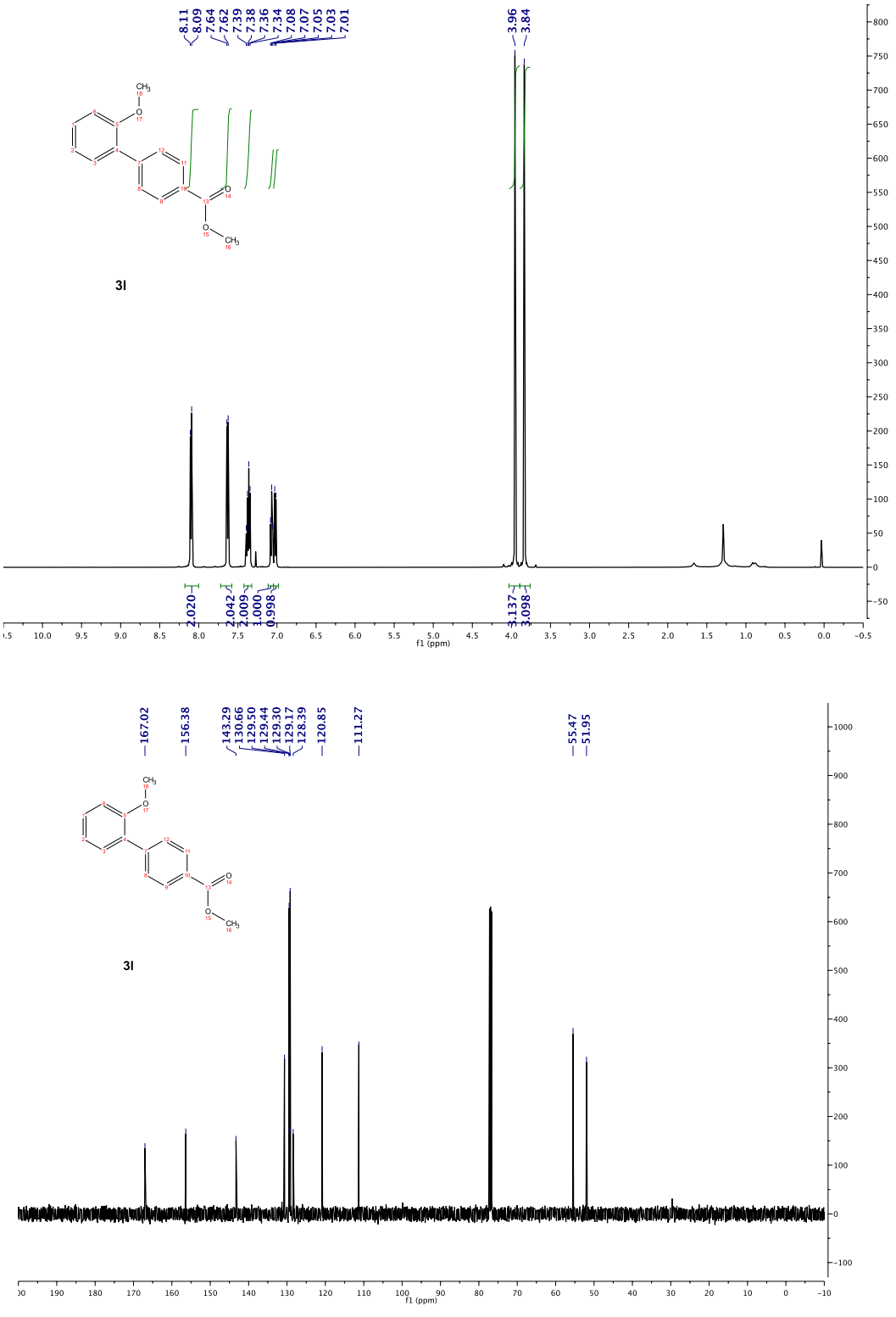


Figure SI 19. ^{1}H NMR (top, 500 MHz), and ^{13}C NMR (bottom, 125 MHz) spectra of **3l** in $CDCl_3$.

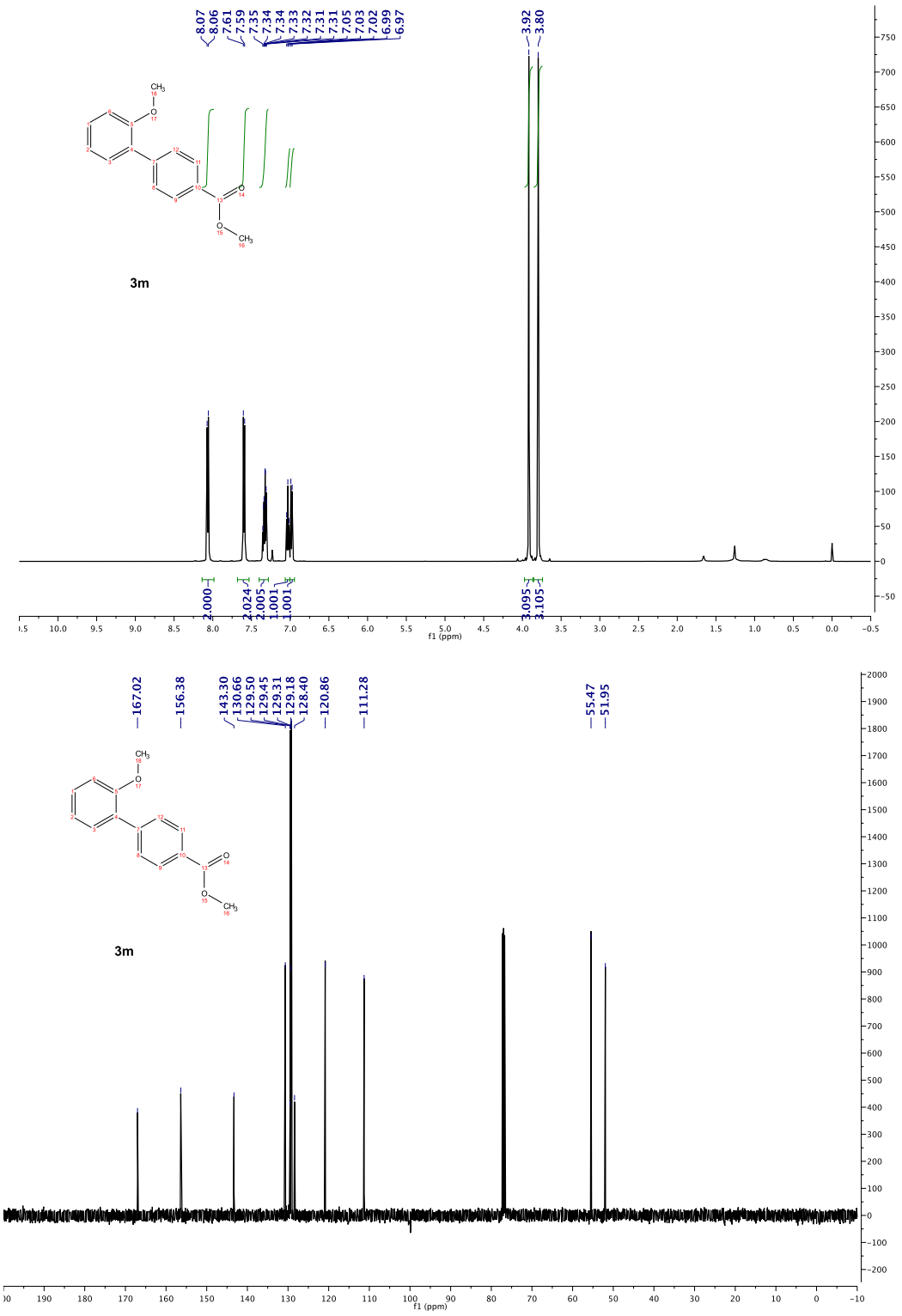


Figure SI 20. ^{1}H NMR (top, 500 MHz), and ^{13}C NMR (bottom, 125 MHz) spectra of **3m** in $CDCl_3$.

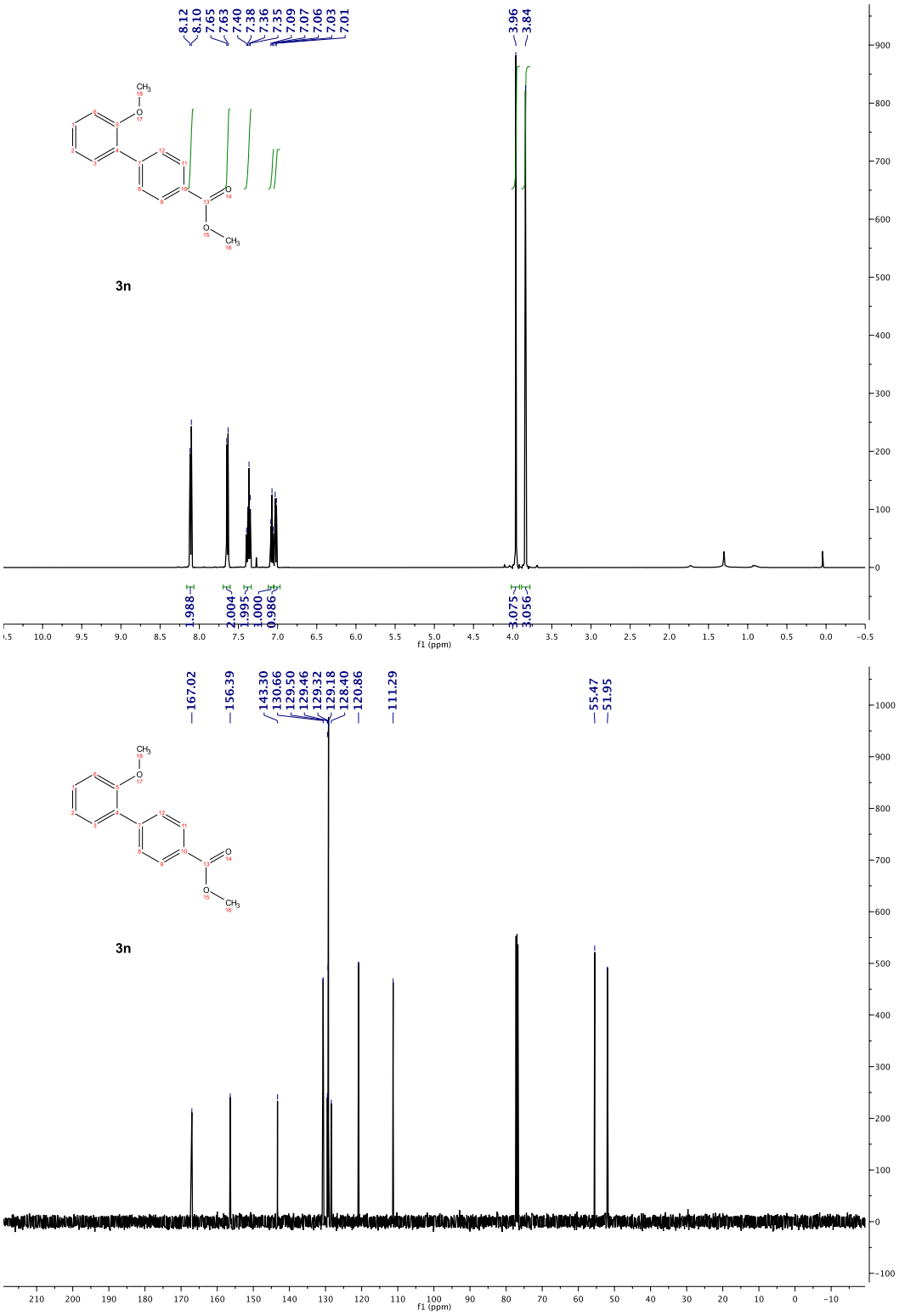


Figure SI 21. ^{1}H NMR (top, 500 MHz), and ^{13}C NMR (bottom, 125 MHz) spectra of **3n** in $CDCl_3$.

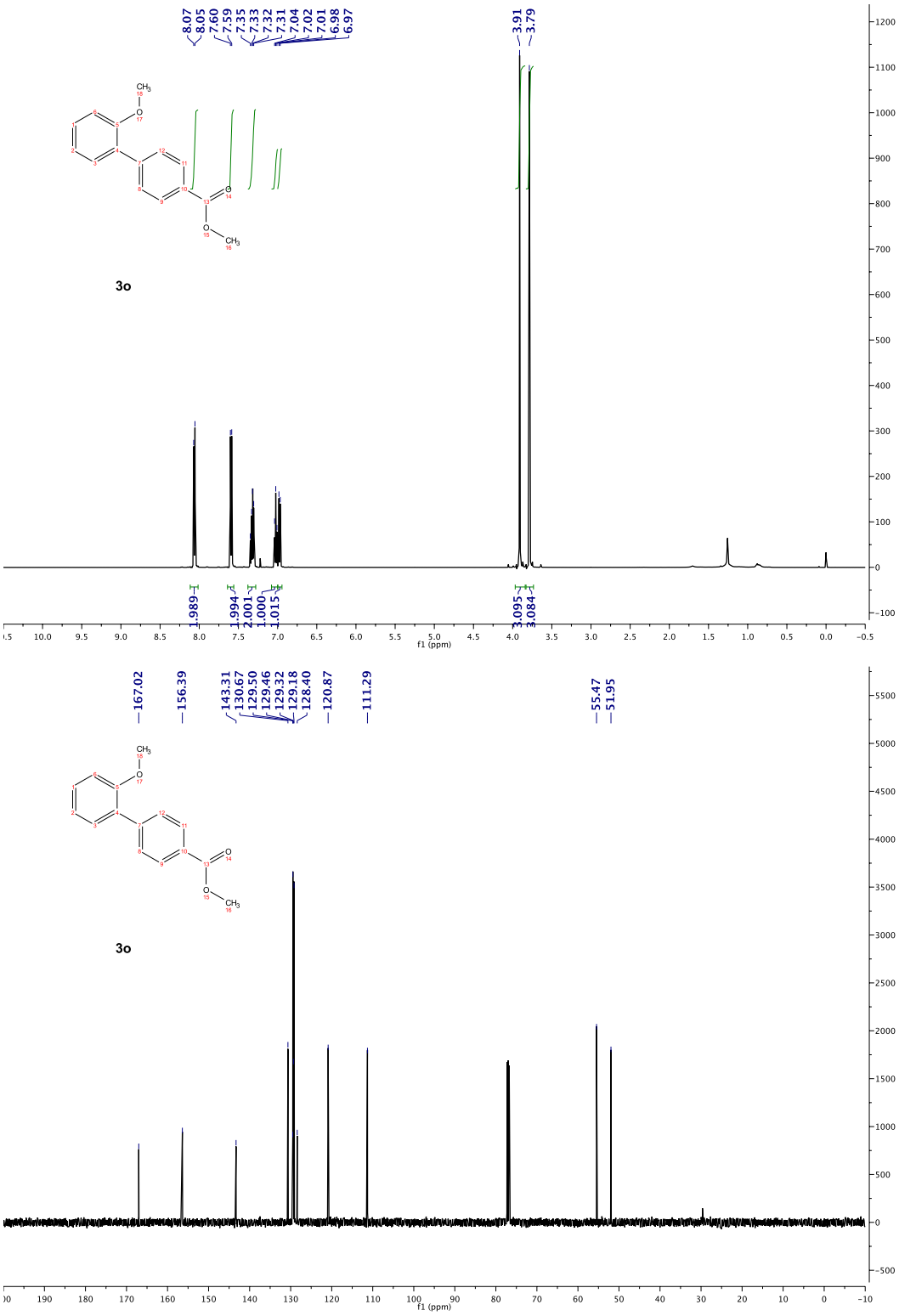


Figure SI 22. ^{1}H NMR (top, 500 MHz), and ^{13}C NMR (bottom, 125 MHz) spectra of **3o** in $CDCl_3$.

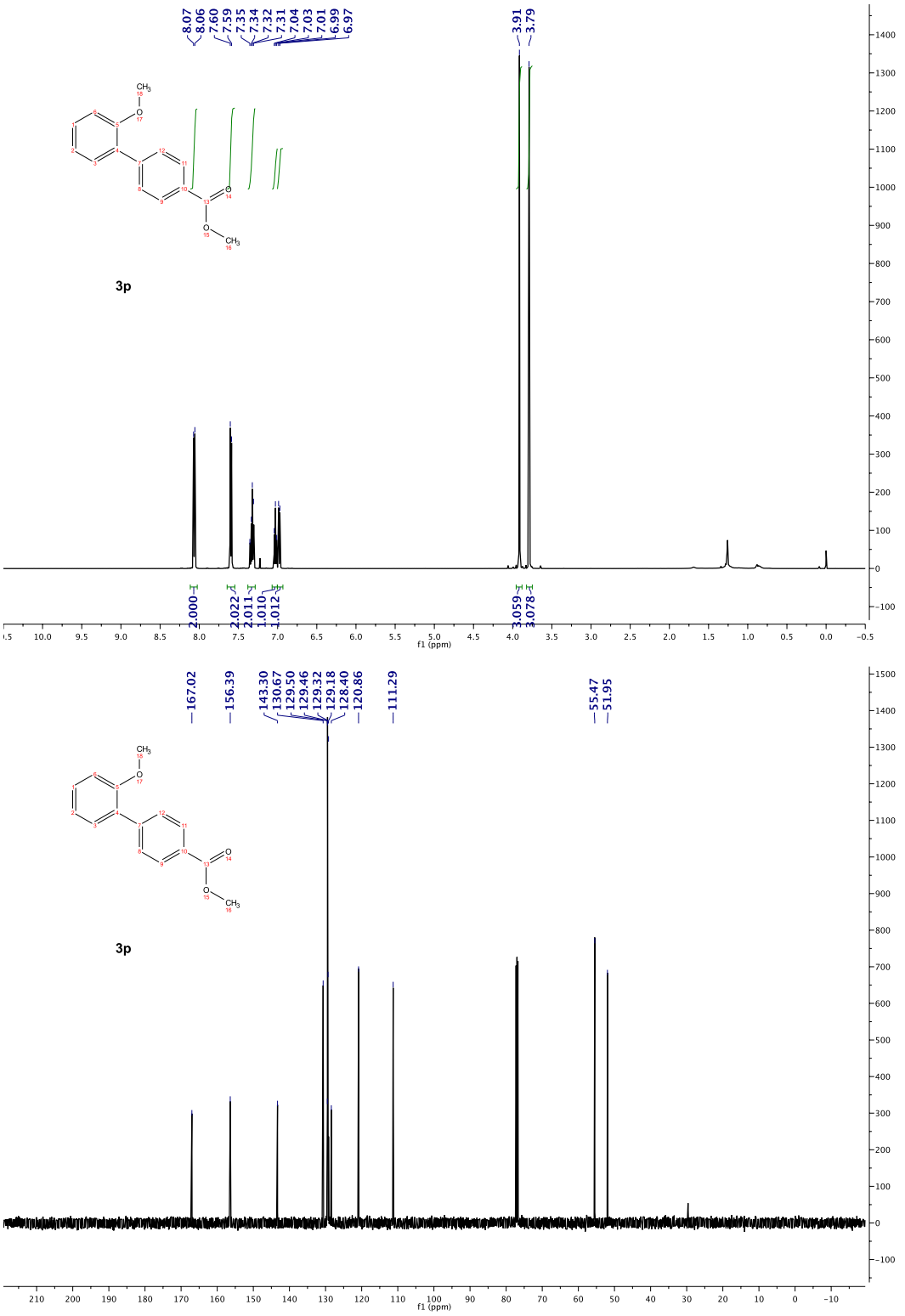
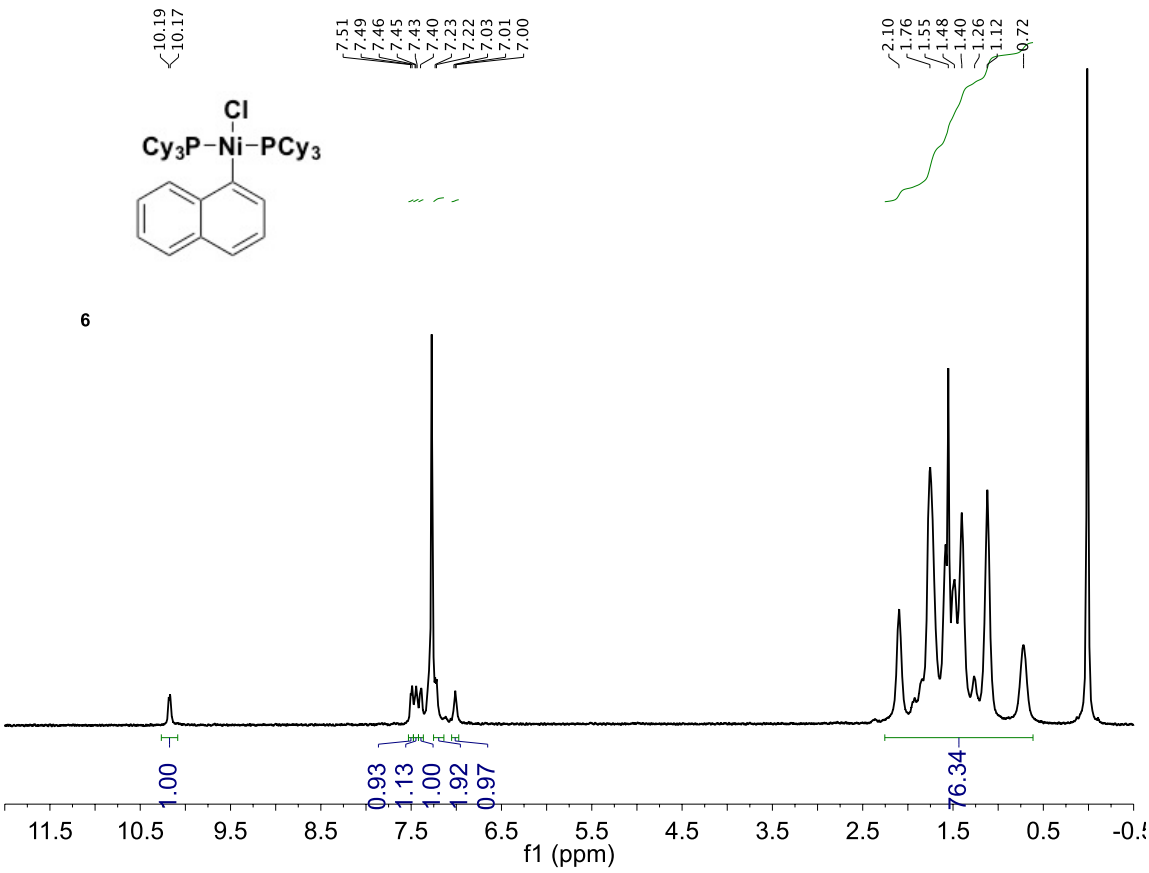
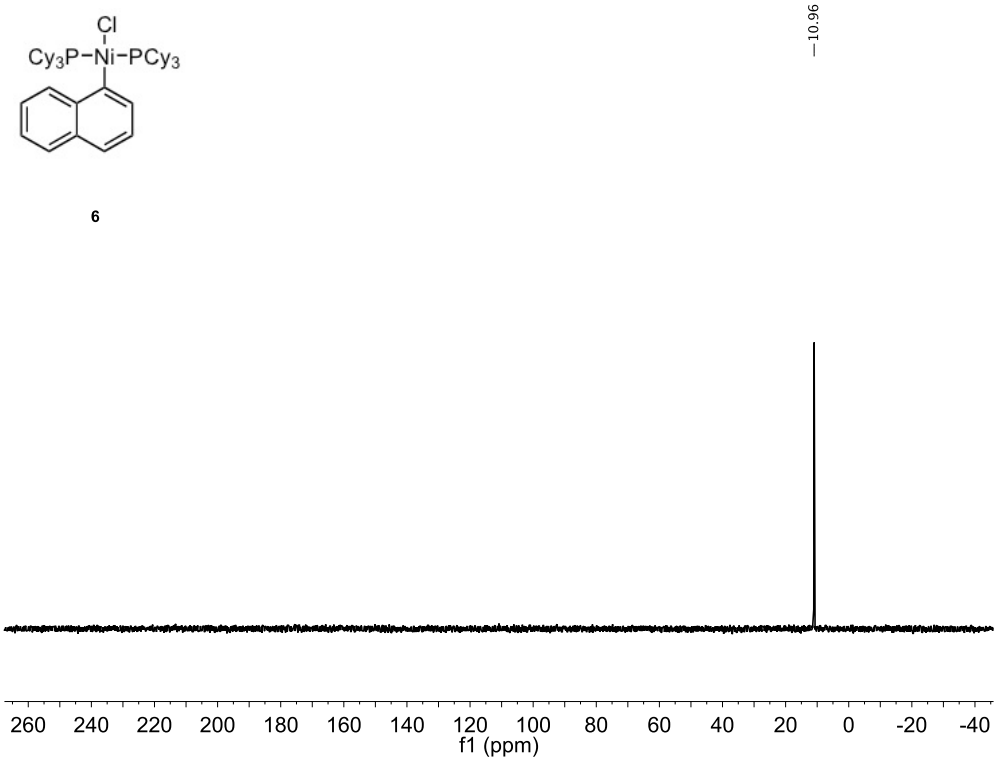


Figure SI 23. ^{1}H NMR (top, 500 MHz), and ^{13}C NMR (bottom, 125 MHz) spectra of **3p** in $CDCl_3$.


10.19
10.17
7.51
7.49
7.46
7.45
7.43
7.40
7.23
7.22
7.03
7.01
7.00
2.10
1.76
1.55
1.48
1.40
1.26
1.12
0.72
Cl
Cy3P–Ni–PCy3
6
1.00
0.93
1.13
1.00
1.92
0.97
76.34
11.5
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
f1 (ppm)


10.96
Cl
Cy3P–Ni–PCy3
6
260
240
220
200
180
160
140
120
100
80
60
40
20
0
-20
-40
f1 (ppm)

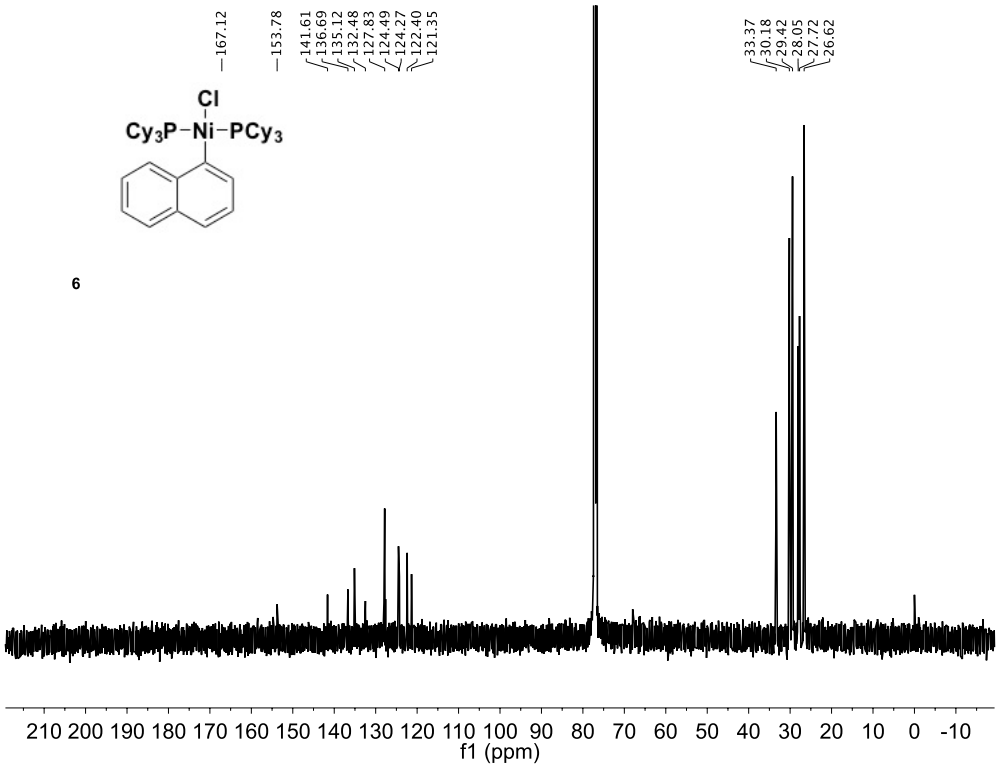
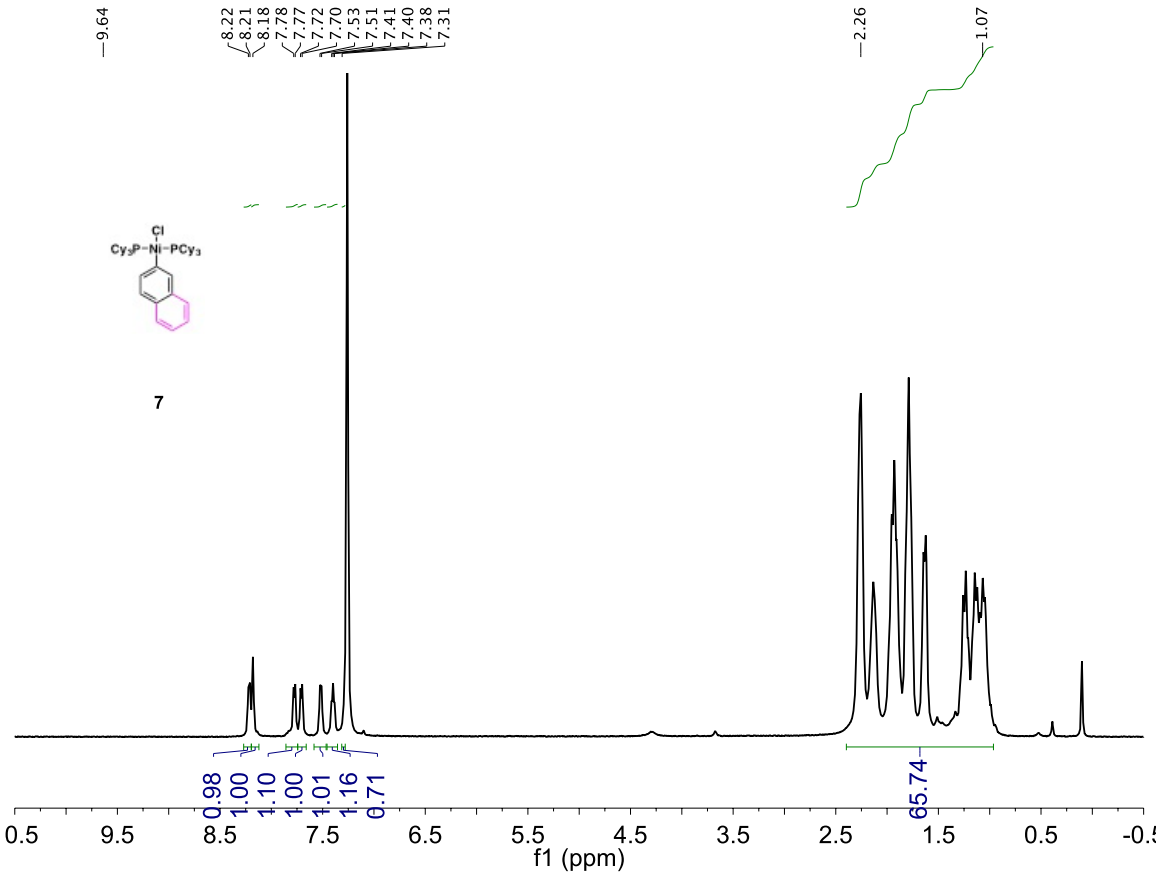
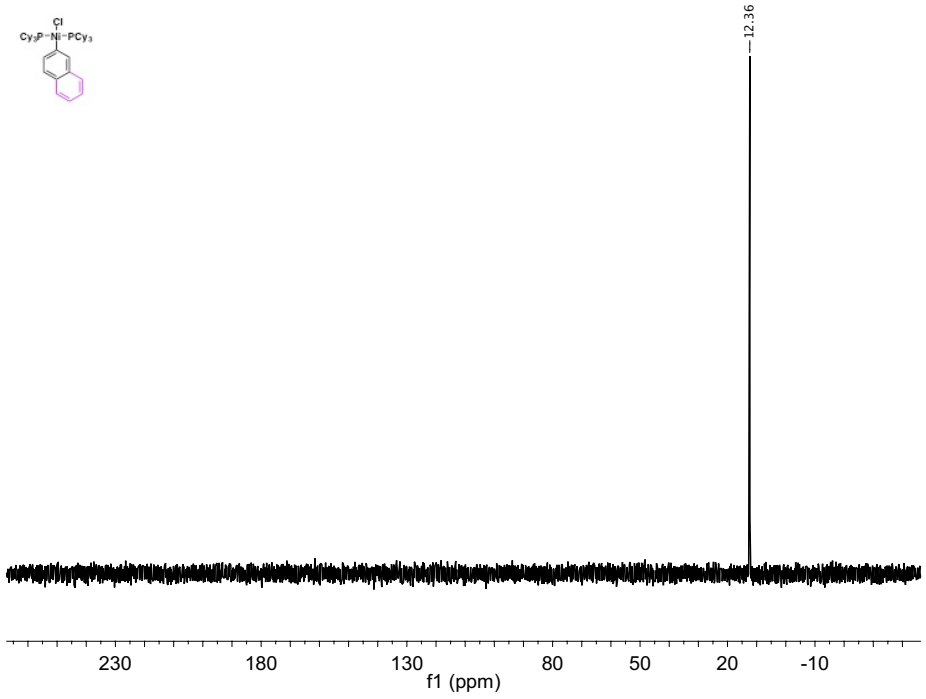


Figure SI 24. ^{1}H NMR (top, 500 MHz), ^{31}P NMR (middle, 203 MHz) and ^{13}C NMR (bottom, 125 MHz) spectra of $Ni^{II}Cl(1\text{-naphthyl})(PCy_3)_2$ in C_6D_6.


9.64
8.22
8.21
8.18
7.78
7.77
7.72
7.70
7.53
7.51
7.41
7.40
7.38
7.31
2.26
1.07
Cl
Cy3P–Ni–PCy3
7
0.98
1.00
1.10
1.00
1.01
1.16
0.71
65.74
0.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5
f1 (ppm)


Cl
Cy3P–Ni–PCy3
12.36
230
180
130
80
50
20
-10
f1 (ppm)

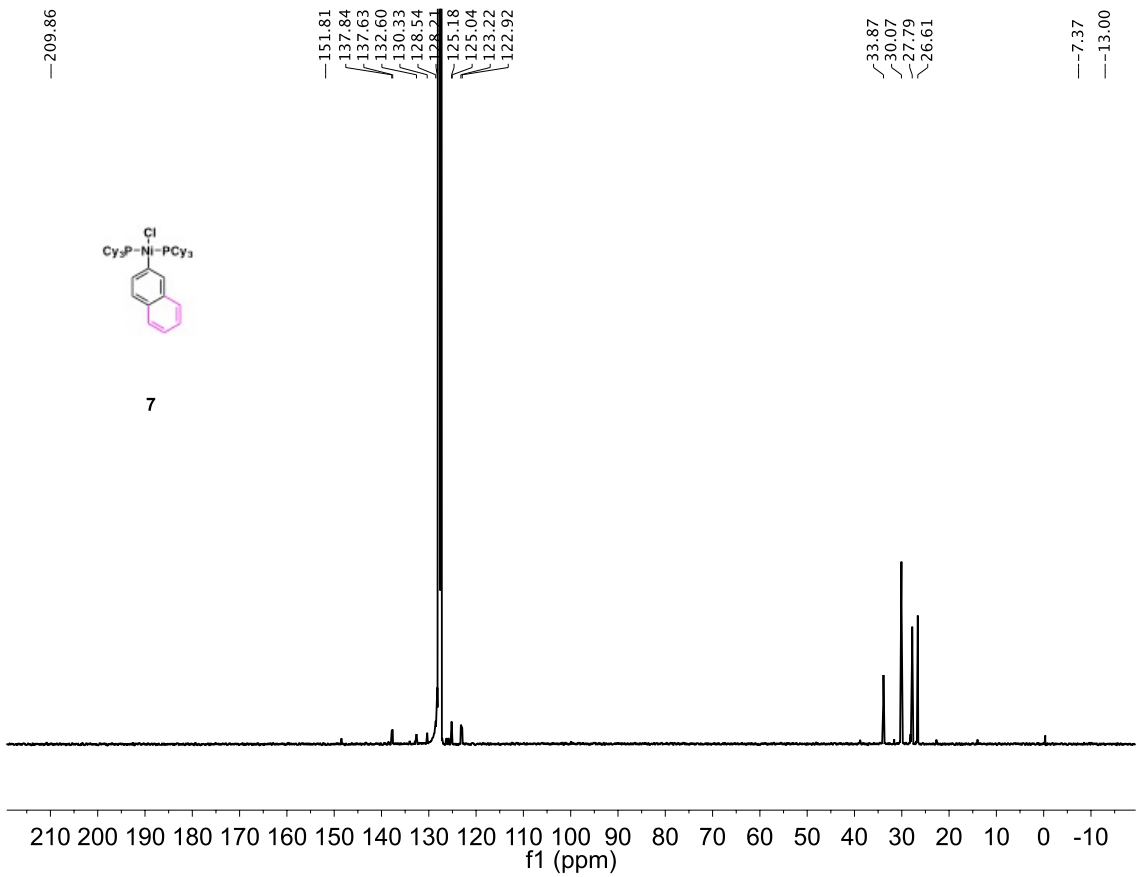
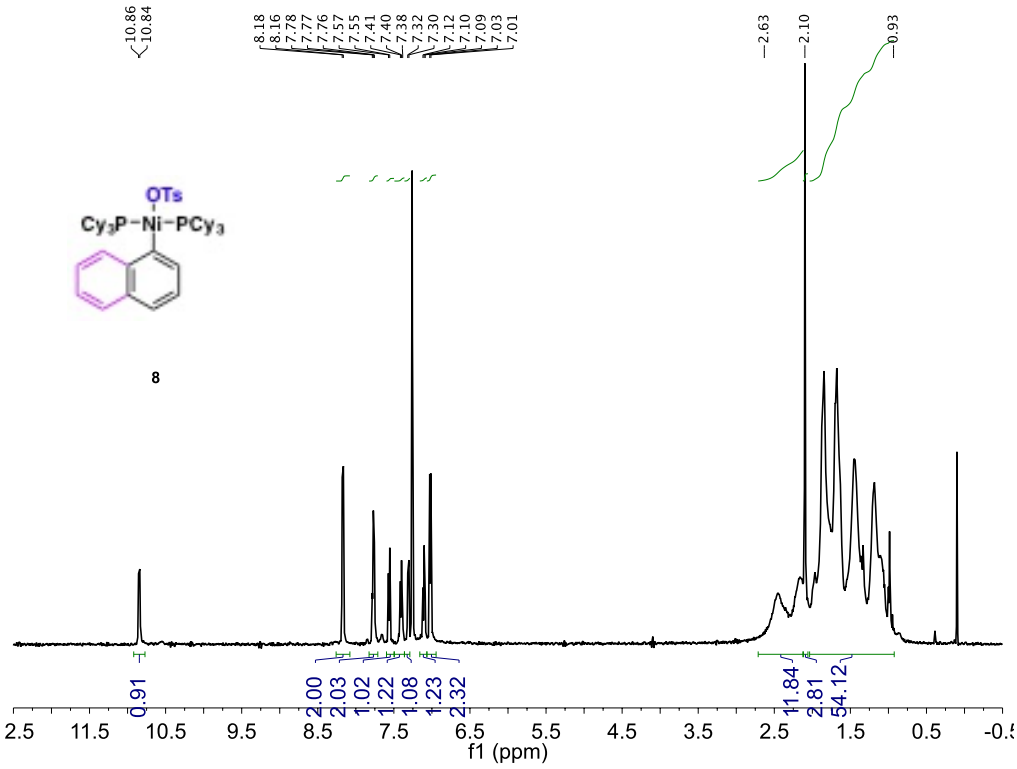
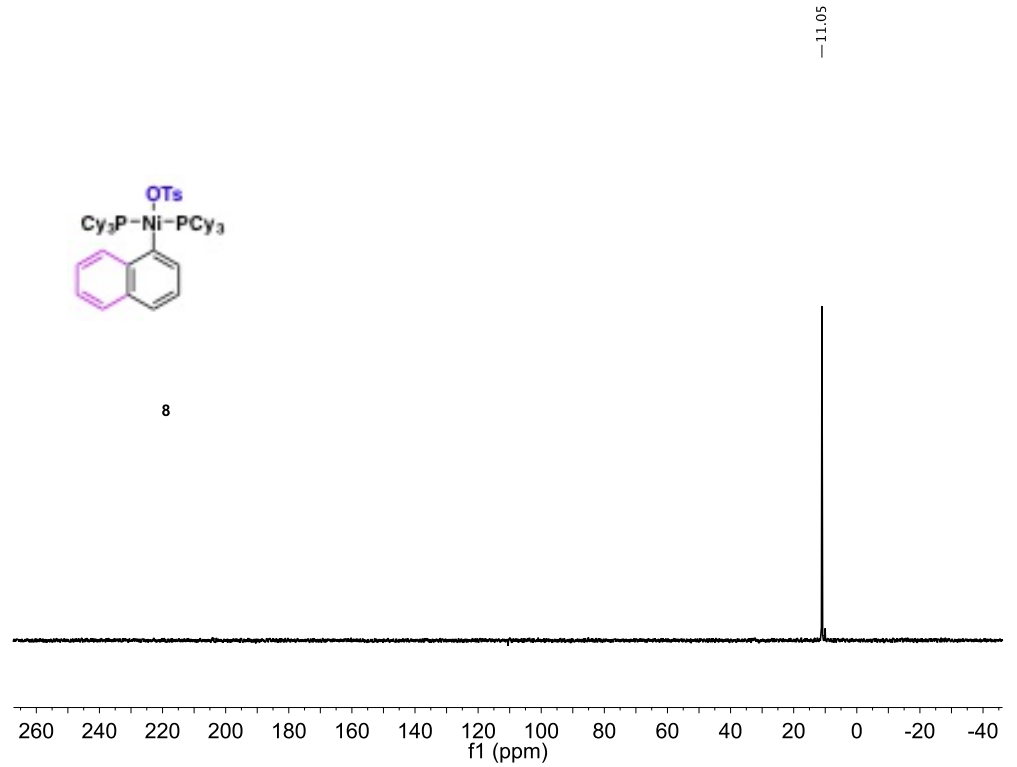


Figure SI 25. ^{1}H NMR (top, 500 MHz), ^{31}P NMR (middle, 203 MHz) and ^{13}C NMR (bottom, 125 MHz) spectra of $Ni^{II}Cl(2\text{-naphthyl})(PCy_3)_2$ in C_6D_6.


10.86
10.84
8.18
8.16
7.78
7.77
7.76
7.57
7.55
7.41
7.40
7.38
7.32
7.30
7.12
7.10
7.09
7.03
7.01
2.63
2.10
0.93
OTs
Cy3P–Ni–PCy3
8
0.91
2.00
2.03
1.02
1.22
1.08
1.23
2.32
11.84
2.81
54.12
2.5 11.5 10.5 9.5 8.5 7.5 6.5 5.5 4.5 3.5 2.5 1.5 0.5
f1 (ppm)


11.05
OTs
Cy3P–Ni–PCy3
8
260 240 220 200 180 160 140 120 100 80 60 40 20 0 -20 -40
f1 (ppm)

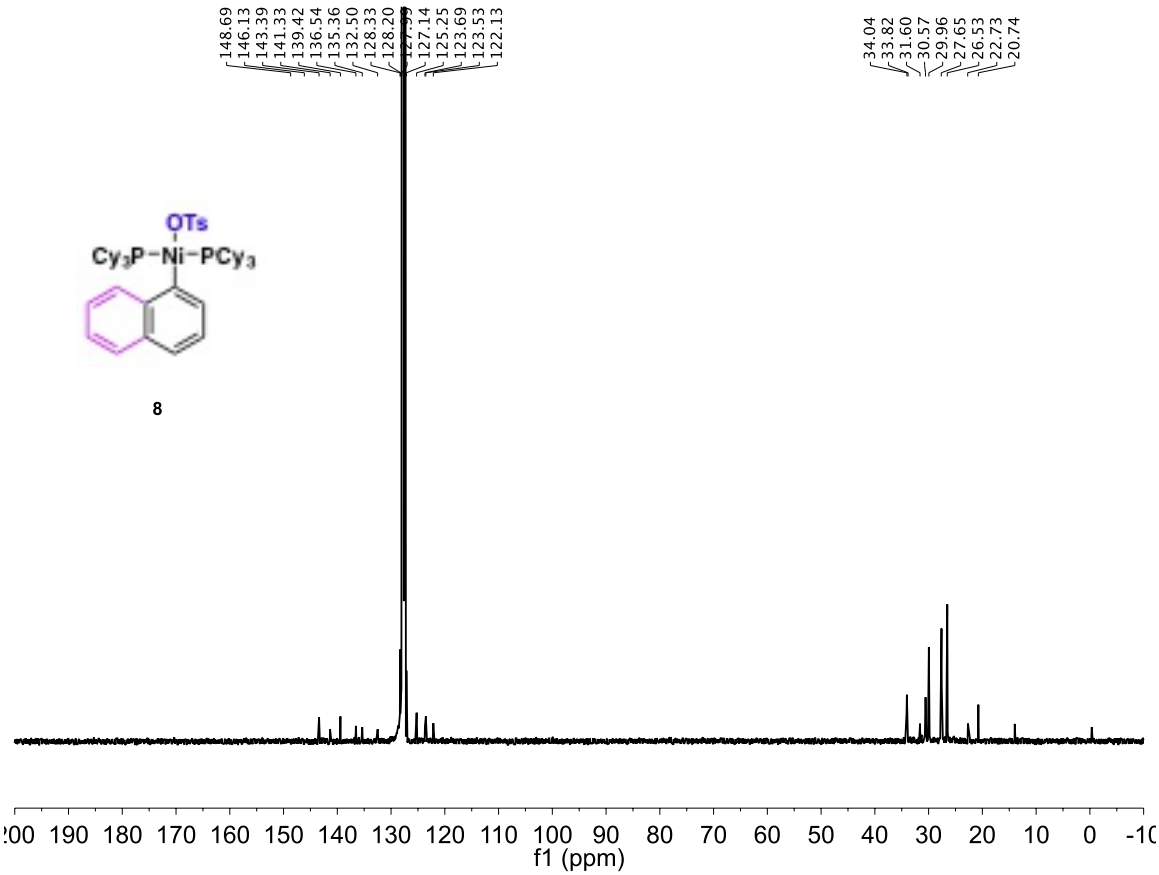
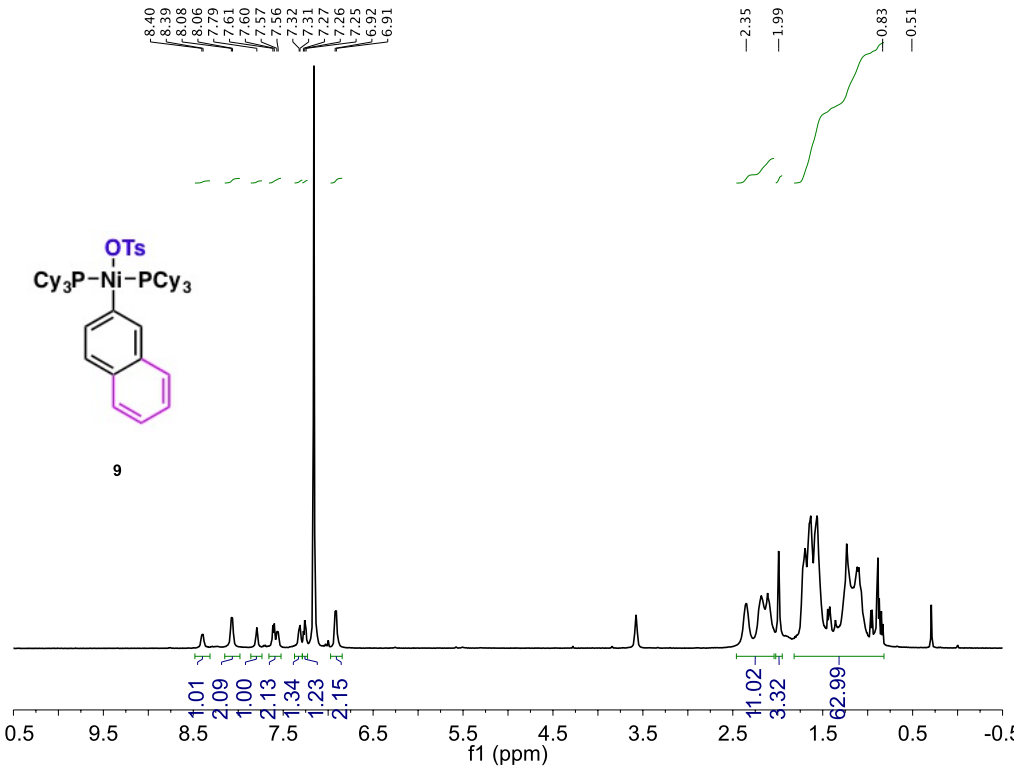
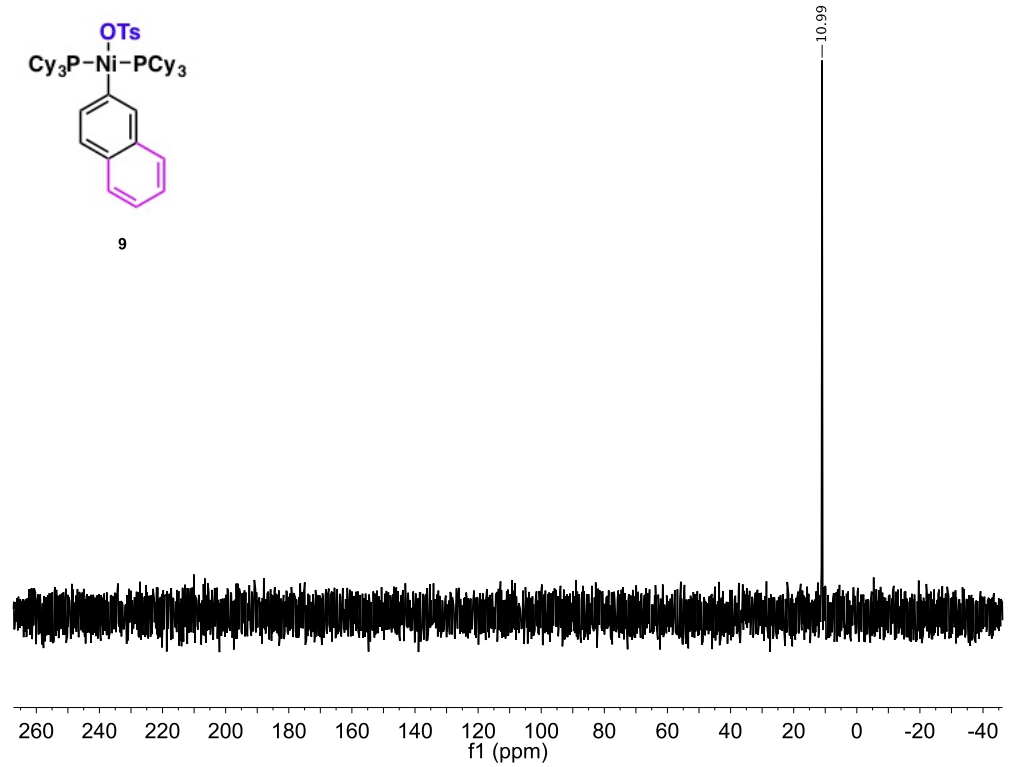


Figure SI 26. ^{1}H NMR (top, 500 MHz), ^{31}P NMR (middle, 203 MHz) and ^{13}C NMR (bottom, 125 MHz) spectra of $Ni^{II}OTs(1\text{-naphthyl})(PCy_3)_2$ in C_6D_6.


8.40
8.39
8.08
8.06
7.79
7.61
7.60
7.57
7.56
7.32
7.31
7.27
7.26
7.25
6.92
6.91
2.35
1.99
0.83
0.51
OTs
Cy3P–Ni–PCy3
9
1.01
2.09
1.00
2.13
1.34
1.23
2.15
11.02
3.32
62.99
0.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
f1 (ppm)


OTs
Cy3P–Ni–PCy3
9
10.99
260
240
220
200
180
160
140
120
100
80
60
40
20
0
-20
-40
f1 (ppm)

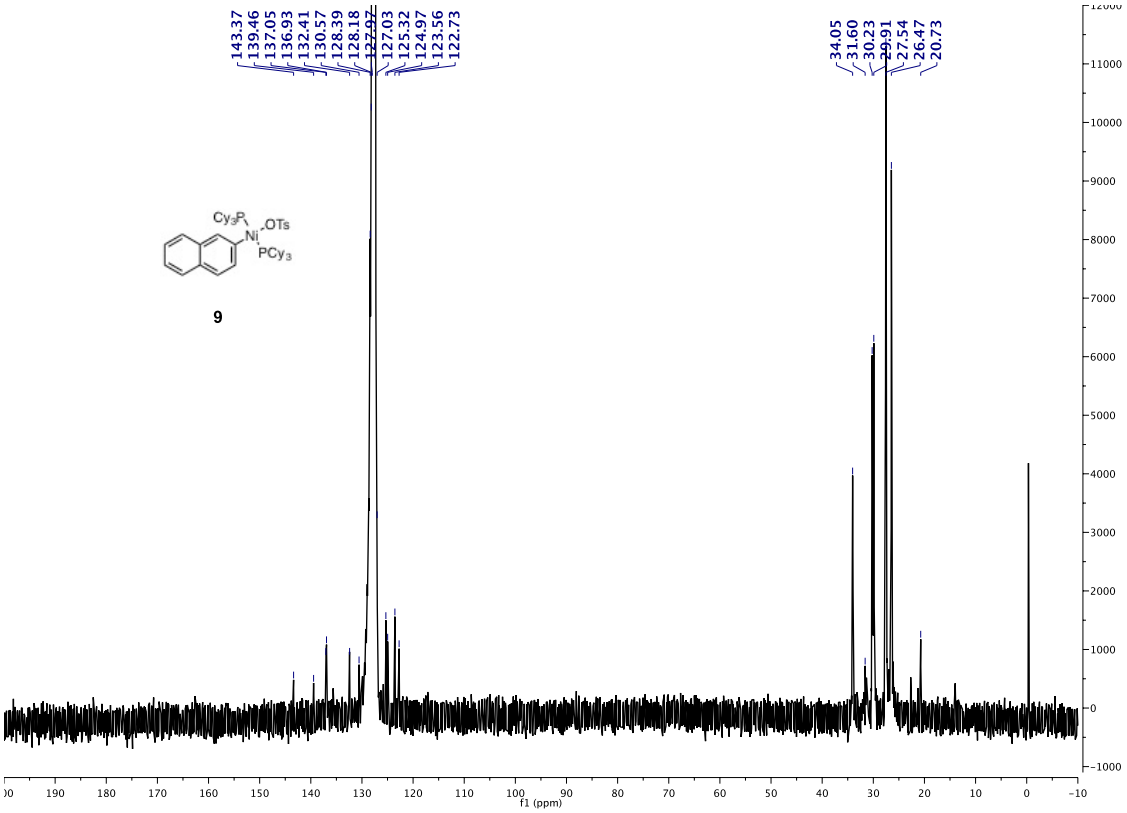
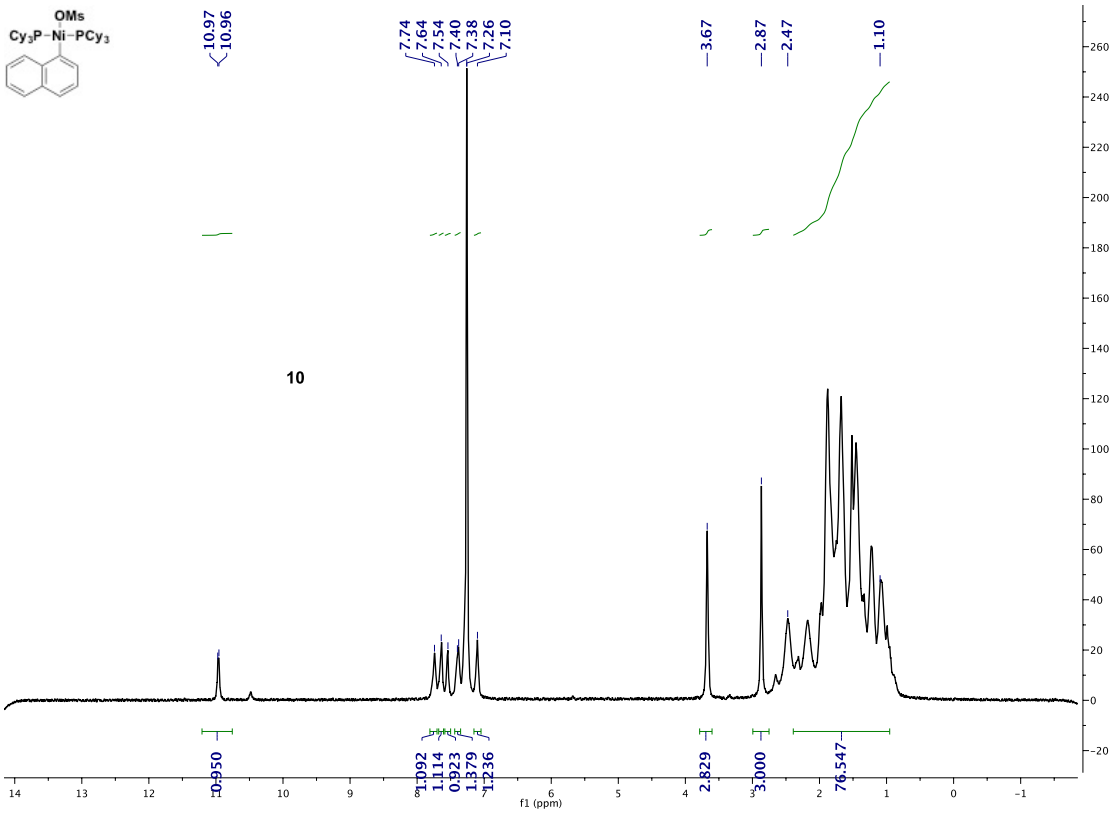
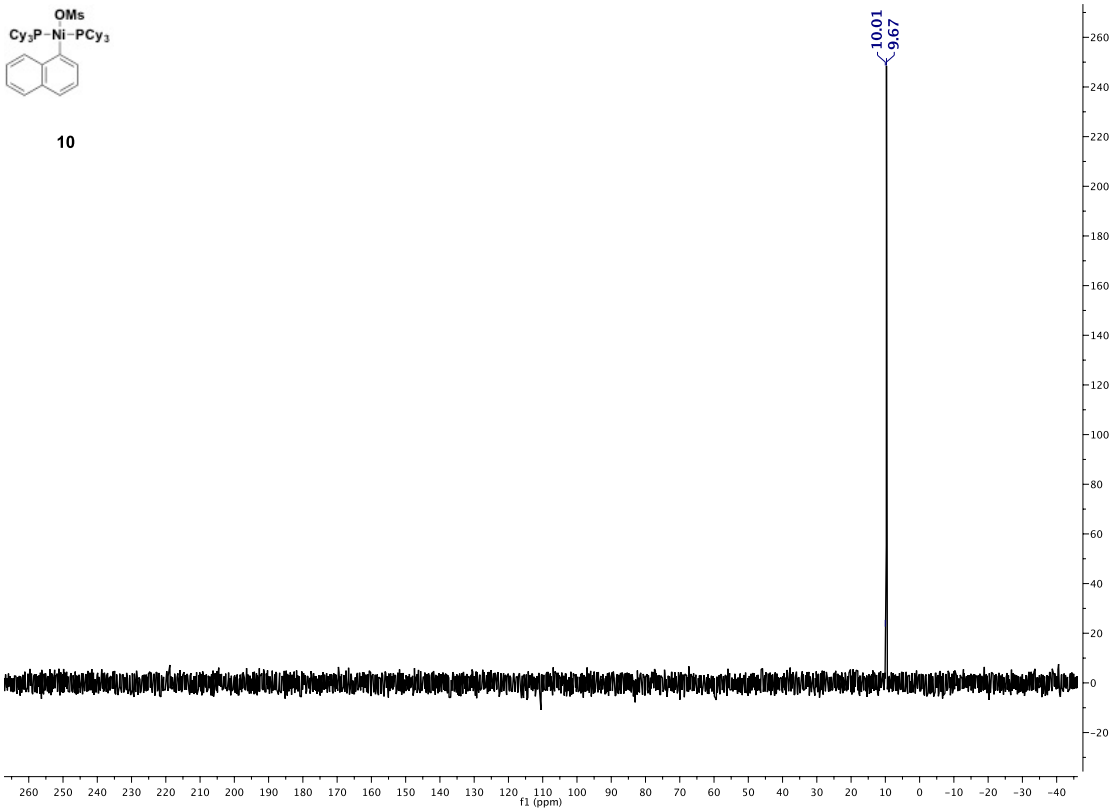


Figure SI 27. ^{1}H NMR (top, 500 MHz), ^{31}P NMR (middle, 203 MHz) and ^{13}C NMR (bottom, 126 MHz) spectra of $Ni^{II}OTs(2\text{-naphthyl})(PCy_3)_2$ in C_6D_6.


OMs
Cy3P–Ni–PCy3
10.97
10.96
7.74
7.64
7.54
7.40
7.38
7.26
7.10
3.67
2.87
2.47
1.10
10
0.950
1.092
1.114
0.923
1.379
1.236
2.829
3.000
76.547
f1 (ppm)


OMs
Cy3P–Ni–PCy3
10
10.01
9.67
f1 (ppm)

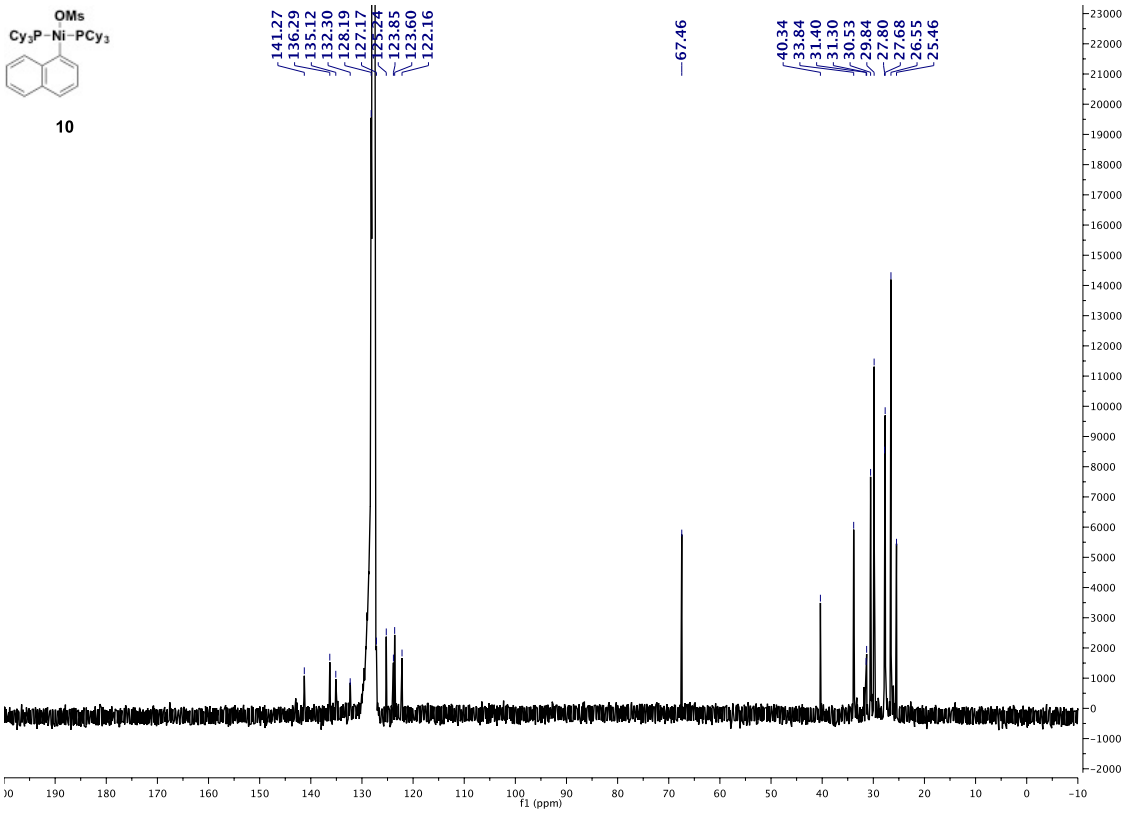
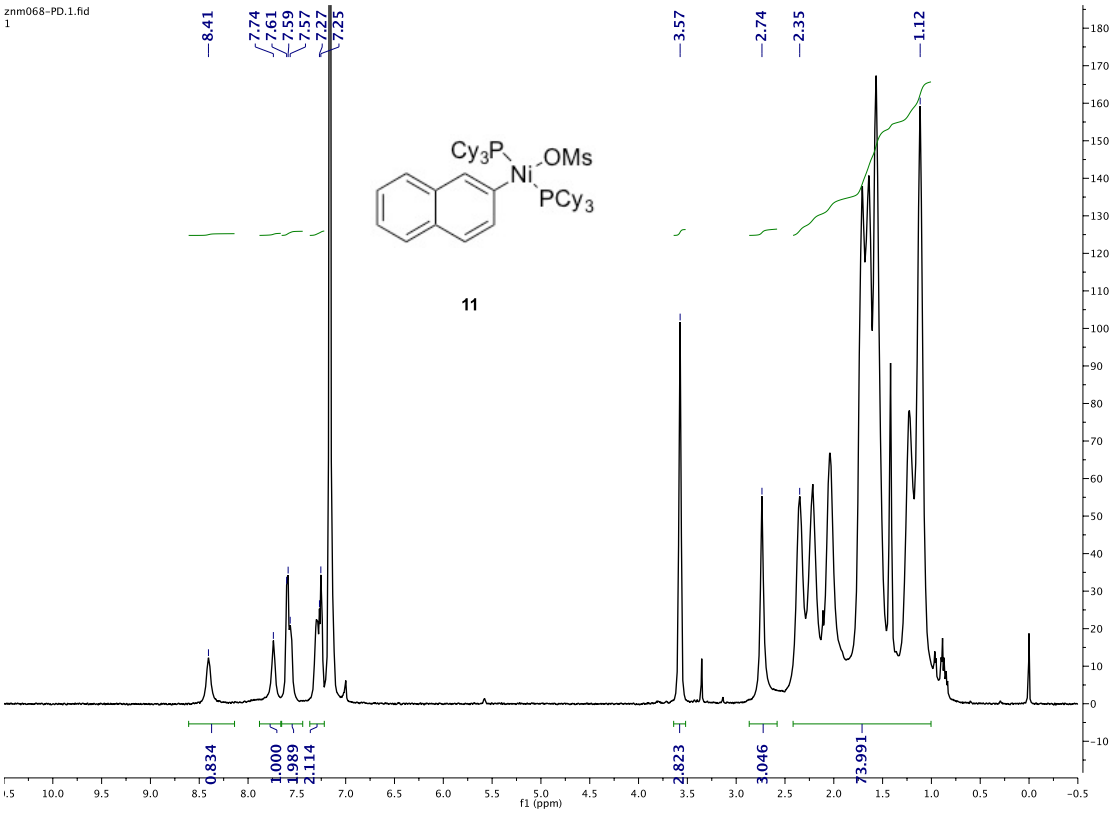
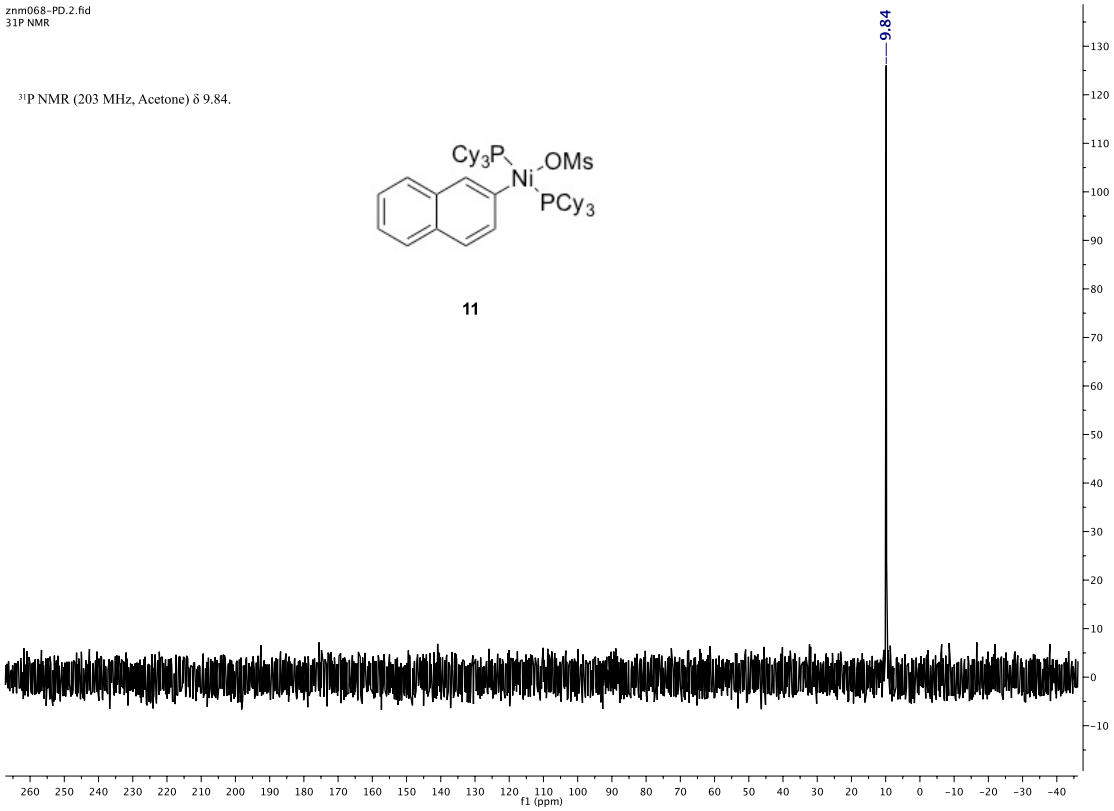


Figure SI 28. ^{1}H NMR (top, 500 MHz), and ^{31}P NMR (bottom, 203 MHz) spectra of $Ni^{II}OMs(1\text{-naphthyl})(PCy_3)_2$ in C_6D_6.





^{31}P NMR (203 MHz, Acetone) δ 9.84.

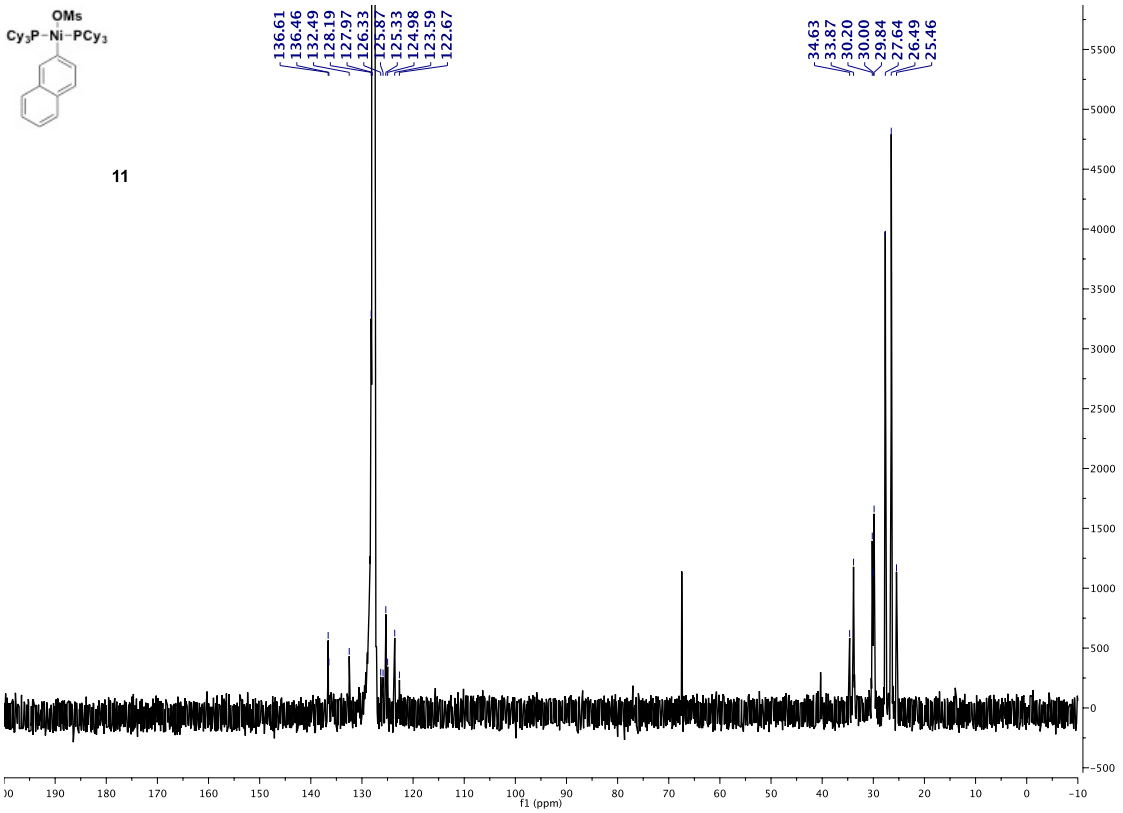
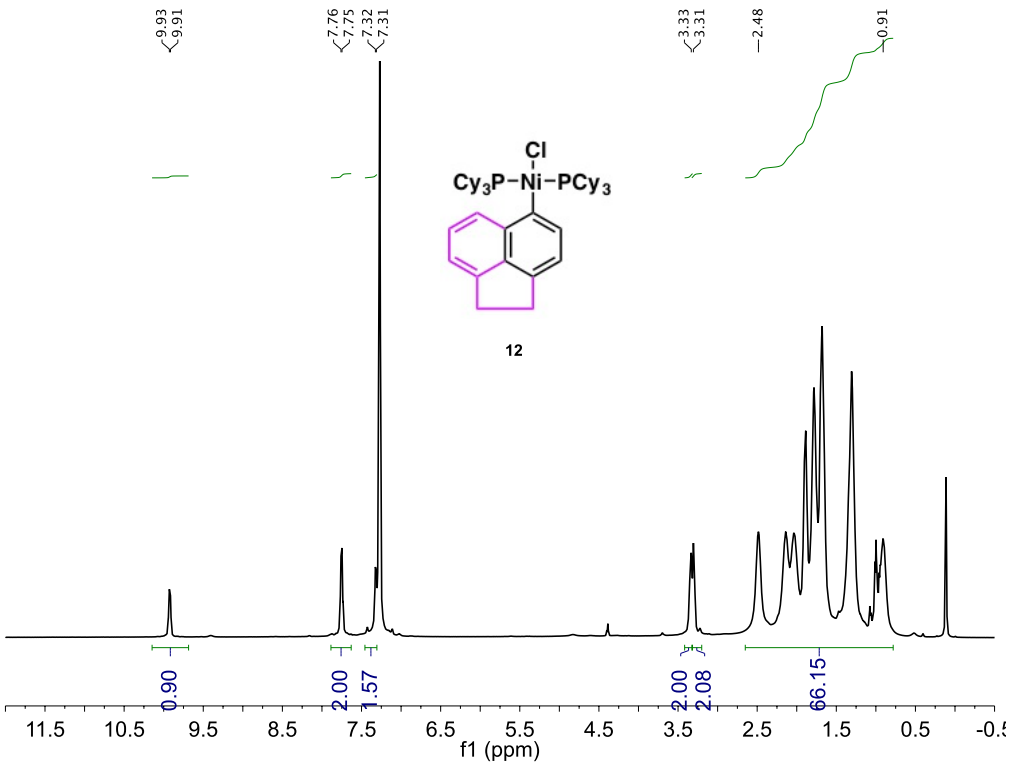
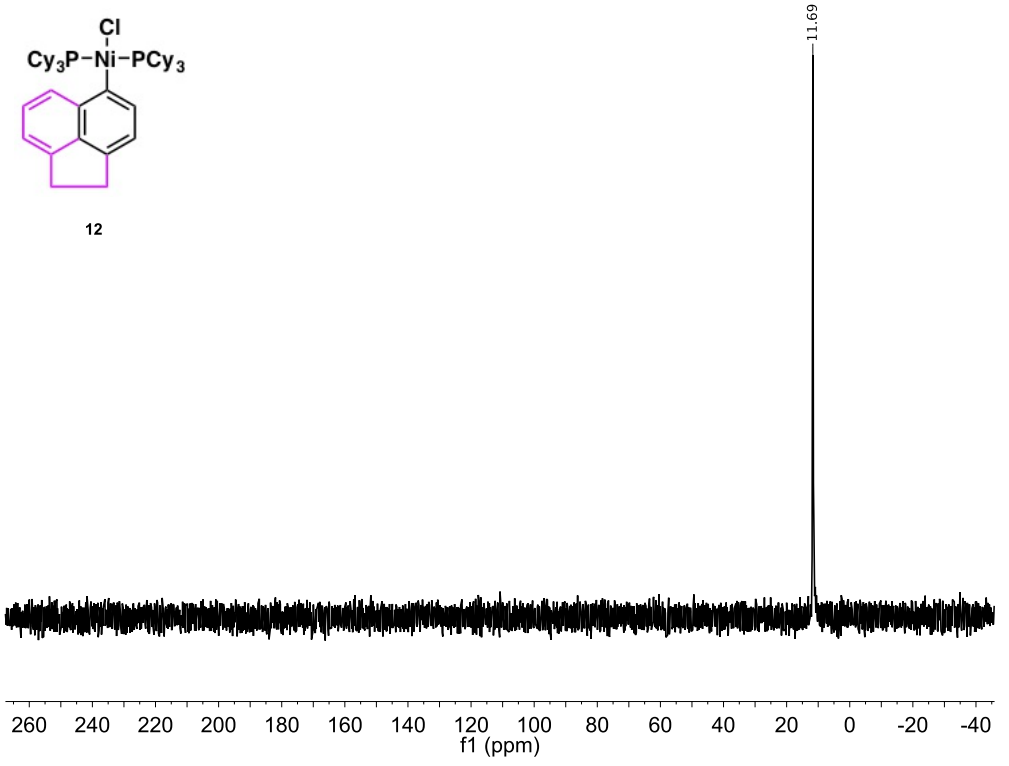


Figure SI 29. ^{1}H NMR (top, 500 MHz), and ^{31}P NMR (bottom, 203 MHz) spectra of $Ni^{II}OMs(2\text{-naphthyl})(PCy_3)_2$ in C_6D_6.


9.93
9.91
7.76
7.75
7.32
7.31
3.33
3.31
2.48
0.91
Cl
Cy3P–Ni–PCy3
12
0.90
2.00
1.57
2.00
2.08
66.15
11.5
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
f1 (ppm)


Cl
Cy3P–Ni–PCy3
12
11.69
260
240
220
200
180
160
140
120
100
80
60
40
20
0
-20
-40
f1 (ppm)

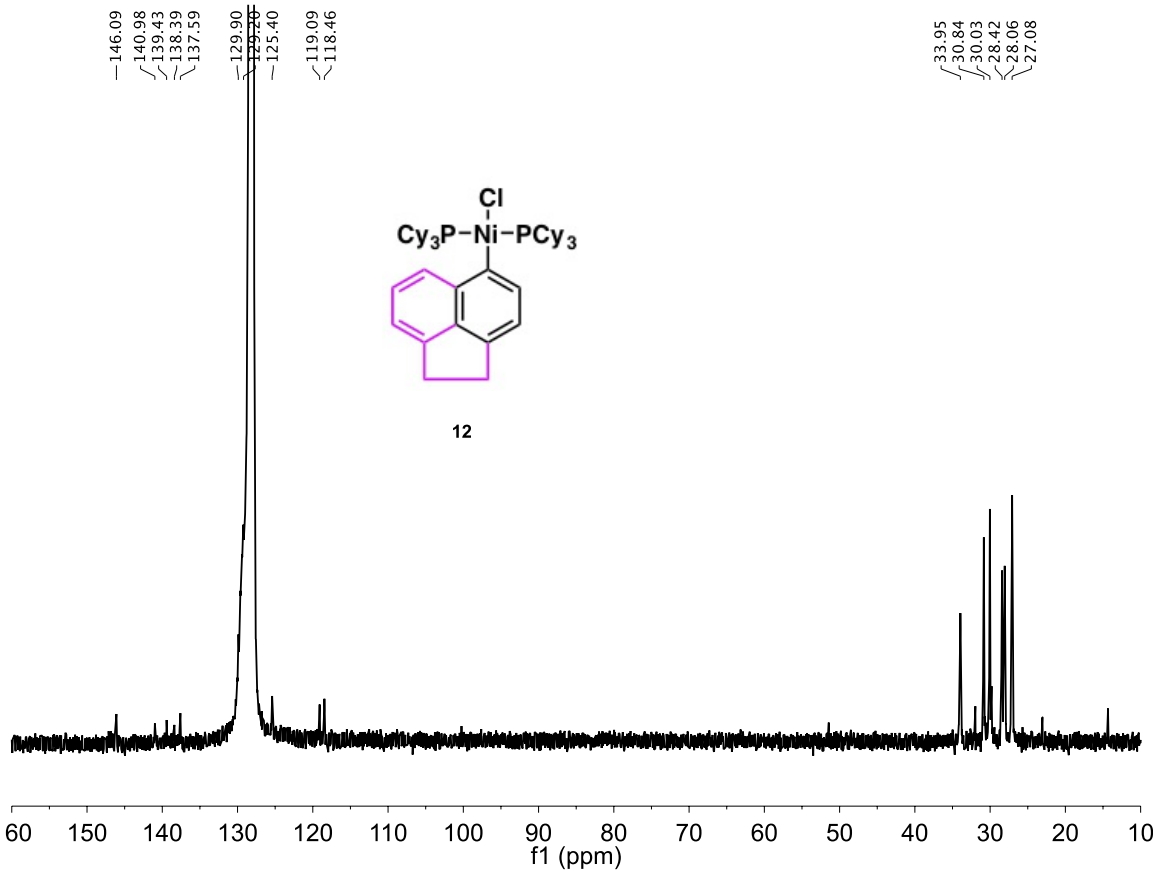
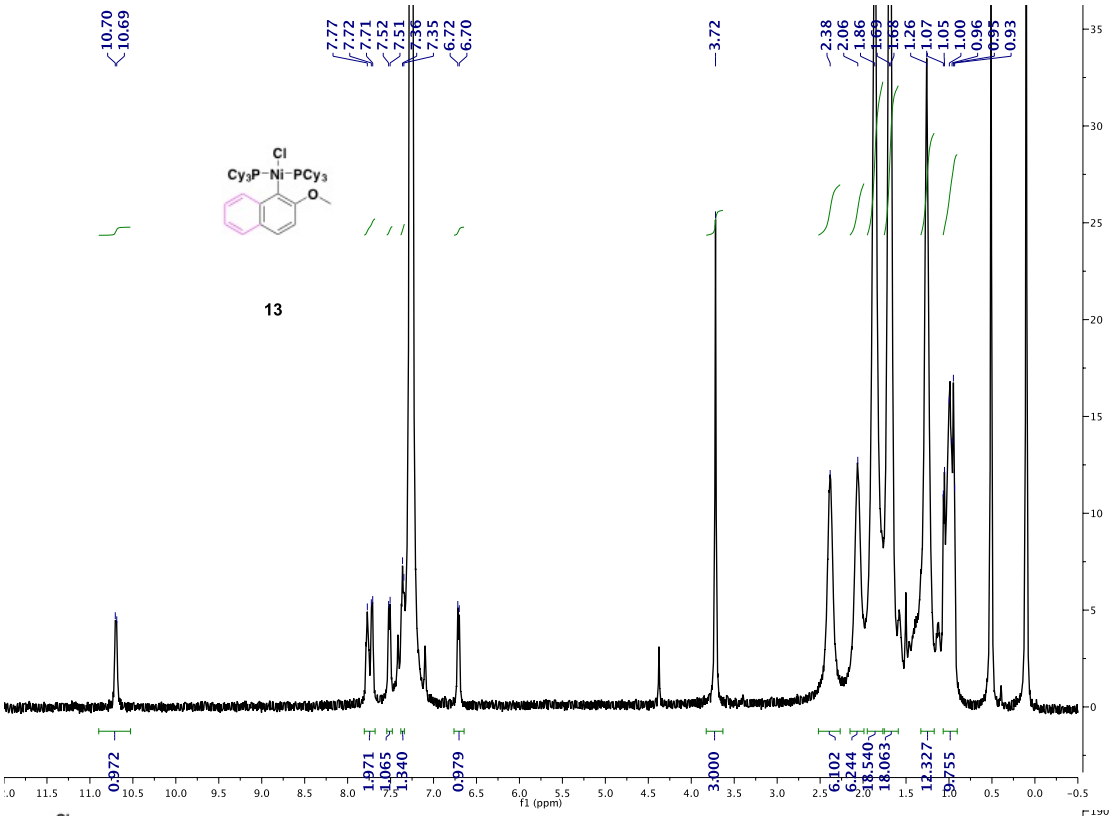
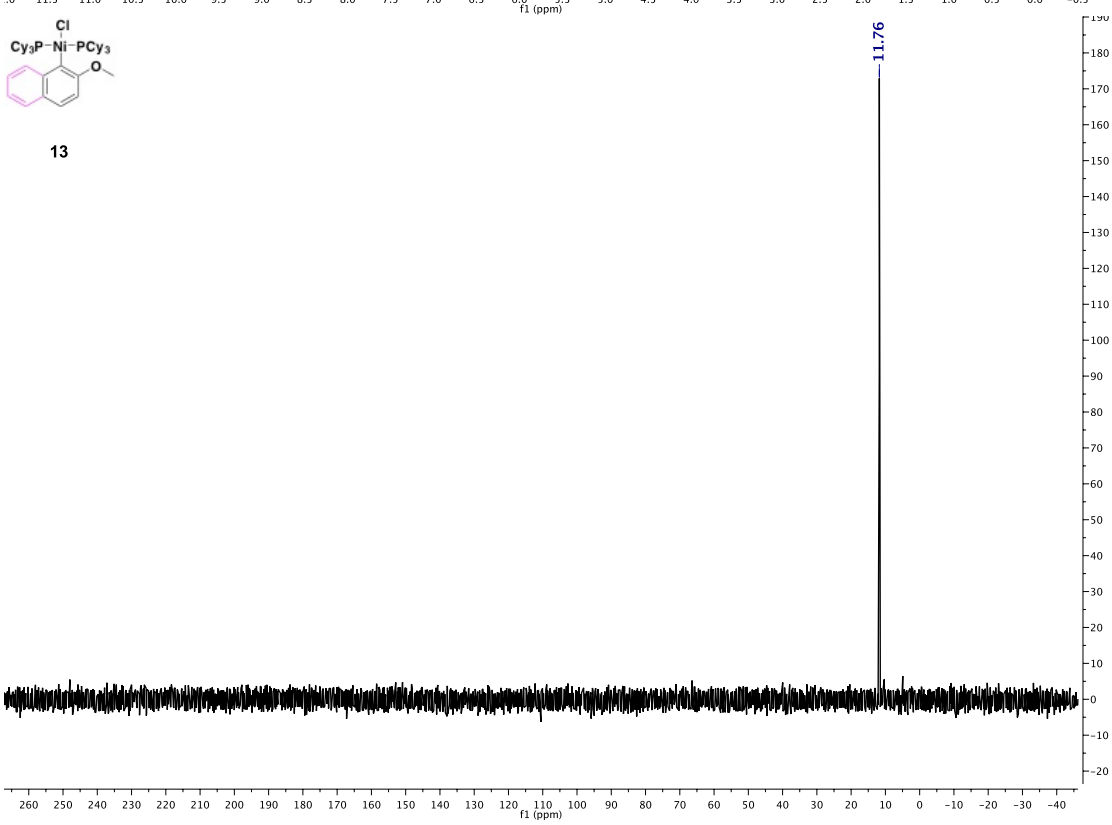


Figure SI 30. ^{1}H NMR (top, 500 MHz), ^{31}P NMR (middle, 203 MHz) and ^{13}C NMR (bottom, 125 MHz) spectra of $Ni^{II}Cl(5\text{-acenaphthyl})(PCy_3)_2$ in $CDCl_3$.


10.70
10.69
7.77
7.72
7.71
7.52
7.51
7.36
7.35
6.72
6.70
3.72
2.38
2.06
1.86
1.69
1.68
1.26
1.07
1.05
1.00
0.96
0.95
0.93
Cl
Cy3P–Ni–PCy3
O
13
0.972
1.971
1.065
1.340
0.979
3.000
6.102
6.244
18.540
18.063
12.327
9.755
f1 (ppm)


Cl
Cy3P–Ni–PCy3
O
13
11.76
f1 (ppm)

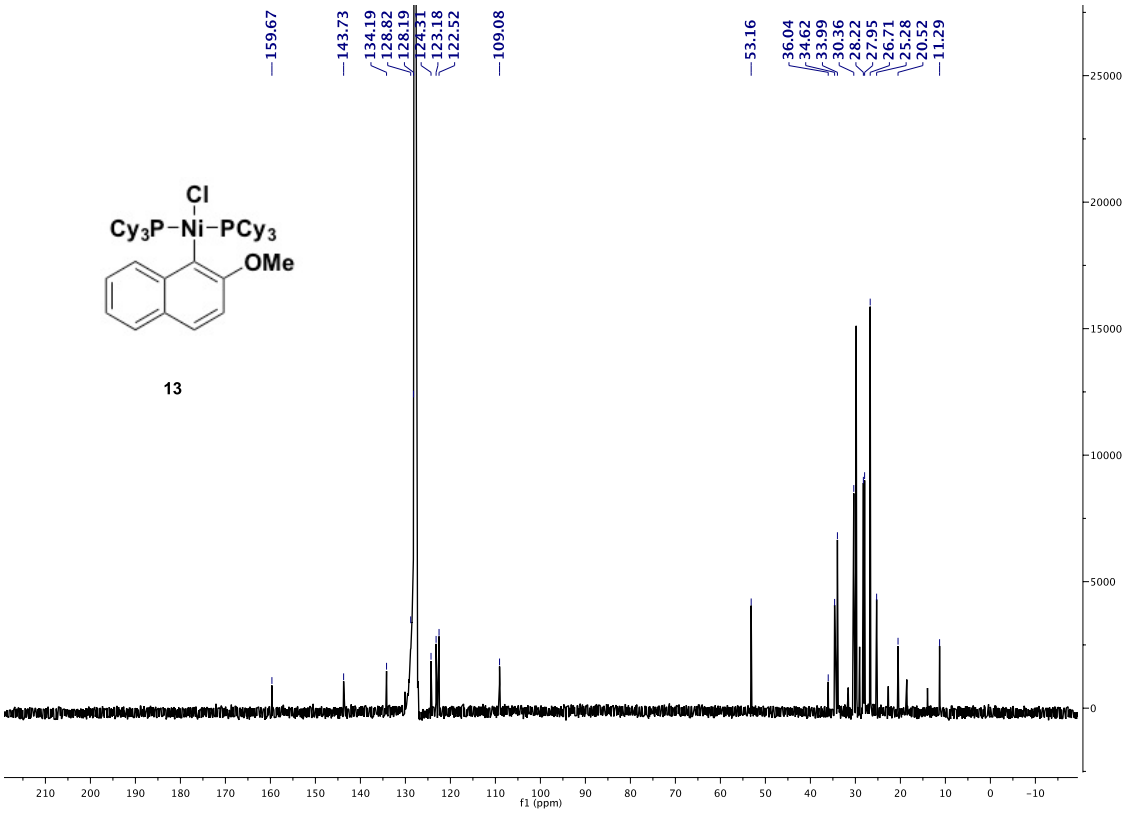
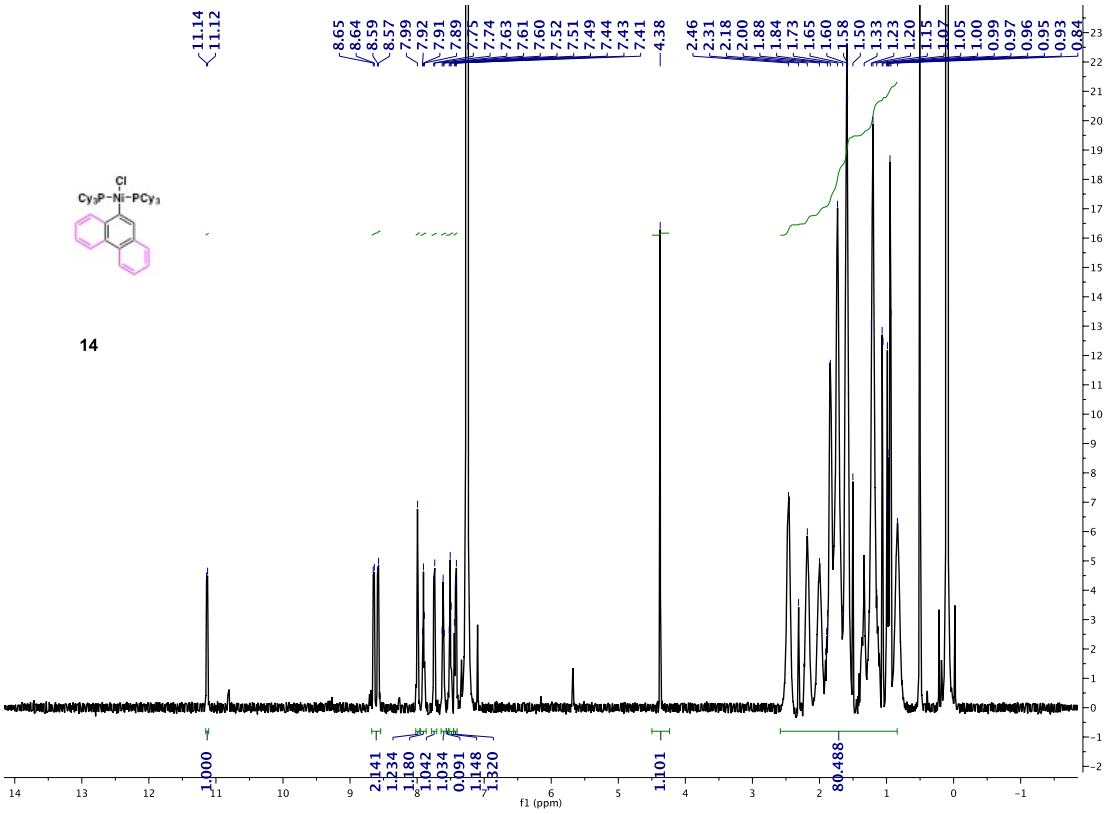


Figure SI 31. ^{1}H NMR (top, 360 MHz), ^{31}P NMR (middle, 203 MHz) and ^{13}C NMR (bottom, 91 MHz) spectra of $Ni^{II}Cl(2\text{-}OMeNaphthyl)(PCy_3)_2$ in C_6D_6.


11.14
11.12
8.65
8.64
8.59
8.57
7.99
7.92
7.91
7.89
7.75
7.74
7.63
7.61
7.60
7.52
7.51
7.49
7.44
7.43
7.41
4.38
2.46
2.31
2.18
2.00
1.88
1.84
1.73
1.65
1.60
1.58
1.50
1.33
1.23
1.20
1.15
1.07
1.05
1.00
0.99
0.97
0.96
0.95
0.93
0.84
1.000
2.141
1.234
1.180
1.042
1.034
0.091
1.148
1.320
1.101
80.488
f1 (ppm)


Cl
Cy3P–Ni–PCy3

14

f1 (ppm)

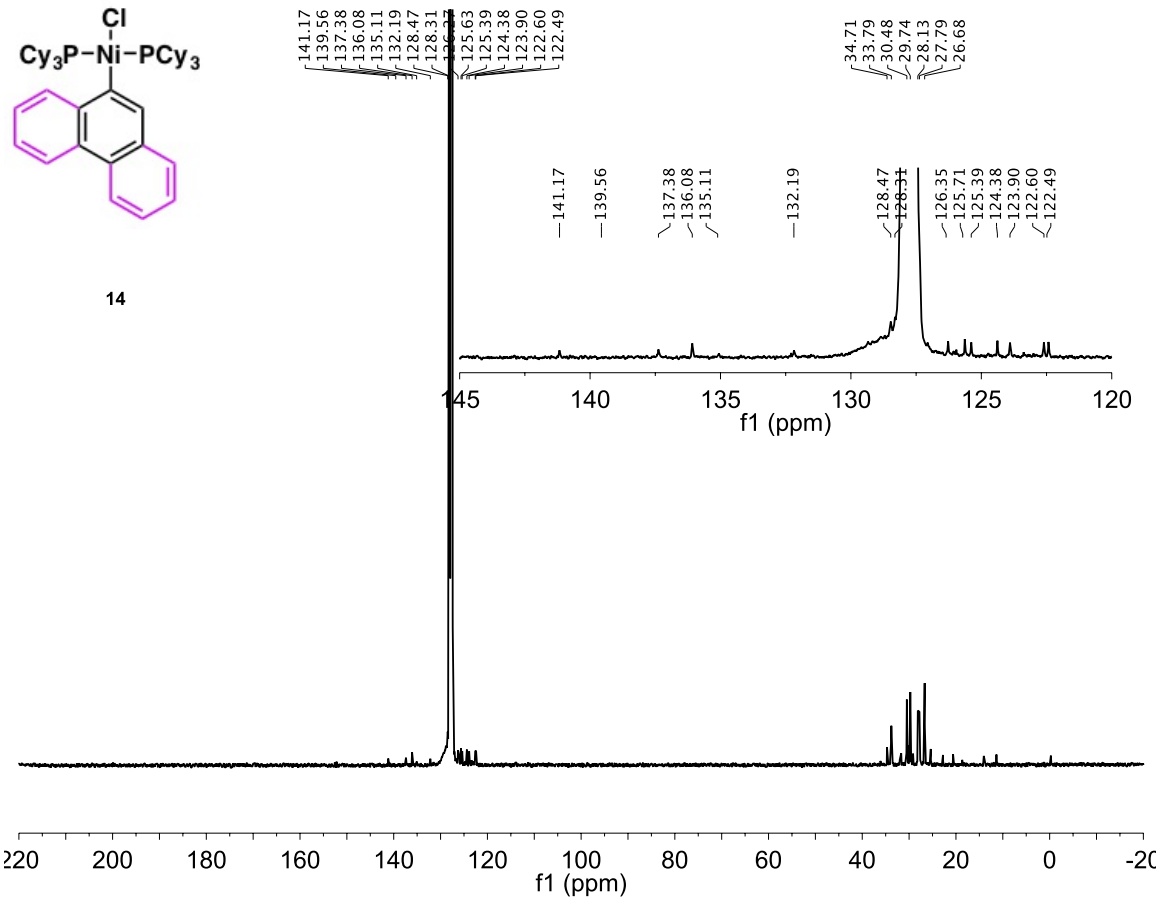
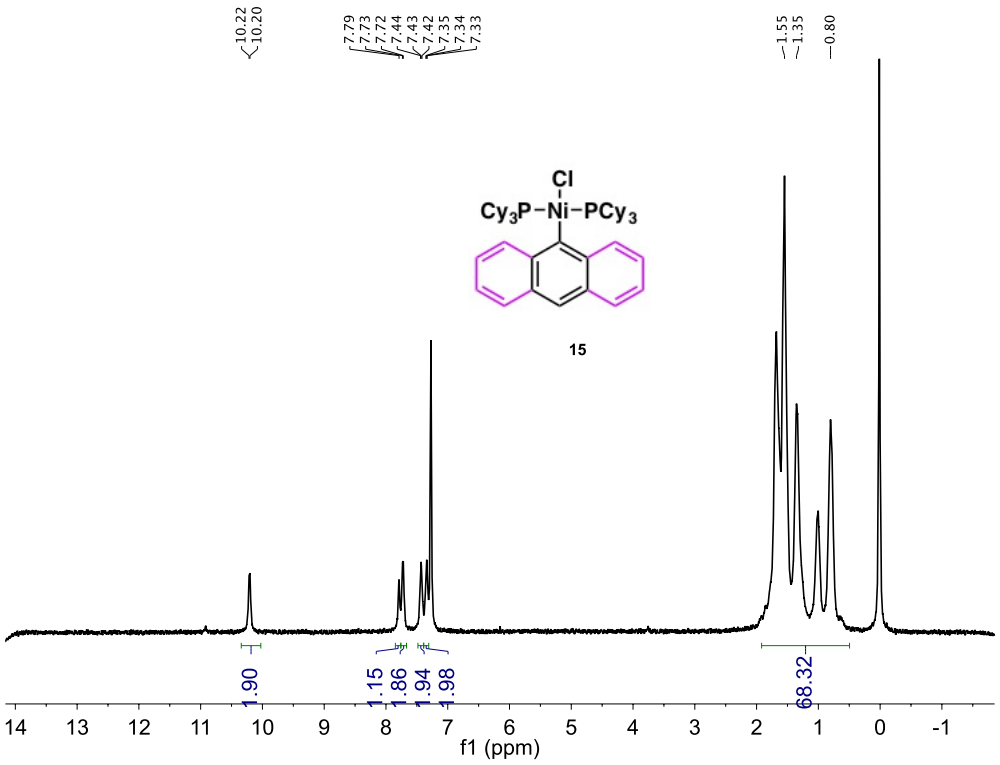


Figure SI 32. ^{1}H NMR (top, 360 MHz), ^{31}P NMR (middle, 203 MHz) and ^{13}C NMR (bottom, 91 MHz) spectra of $Ni^{II}Cl$(9-phenathrenyl)$(PCy_3)_2$ in C_6D_6 and $CDCl_3$.


10.22
10.20
7.79
7.73
7.72
7.44
7.43
7.42
7.35
7.34
7.33
1.55
1.35
0.80
Cl
Cy3P–Ni–PCy3
15
1.90
1.15
1.86
1.94
1.98
68.32
14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1
f1 (ppm)

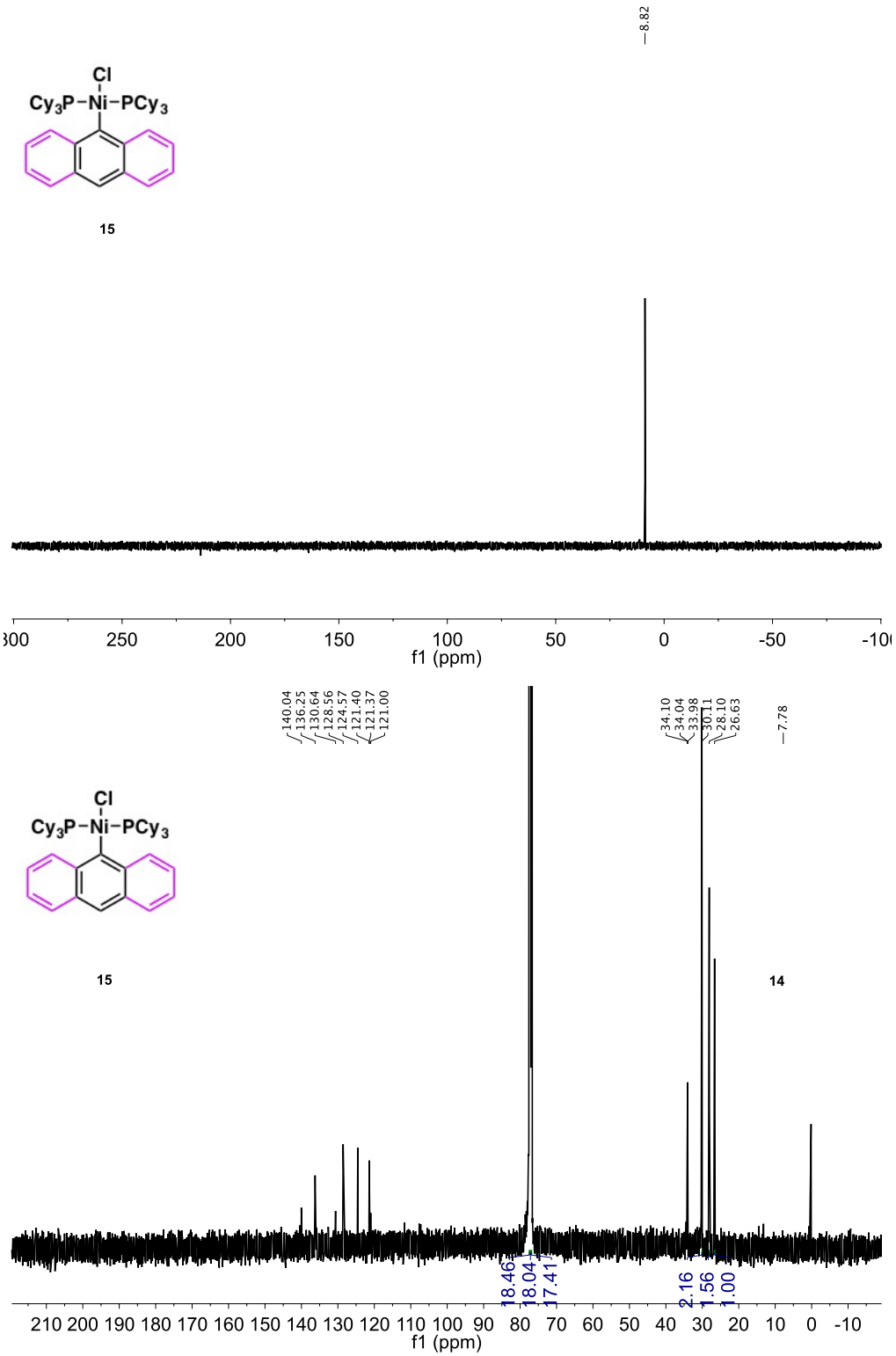


Figure SI 33. ^{1}H NMR (top, 500 MHz), ^{31}P NMR (middle, 203 MHz) and ^{13}C NMR (bottom, 125 MHz) spectra of $Ni^{II}Cl(9\text{-anthracyl})(PCy_3)_2$ in $CDCl_3$.

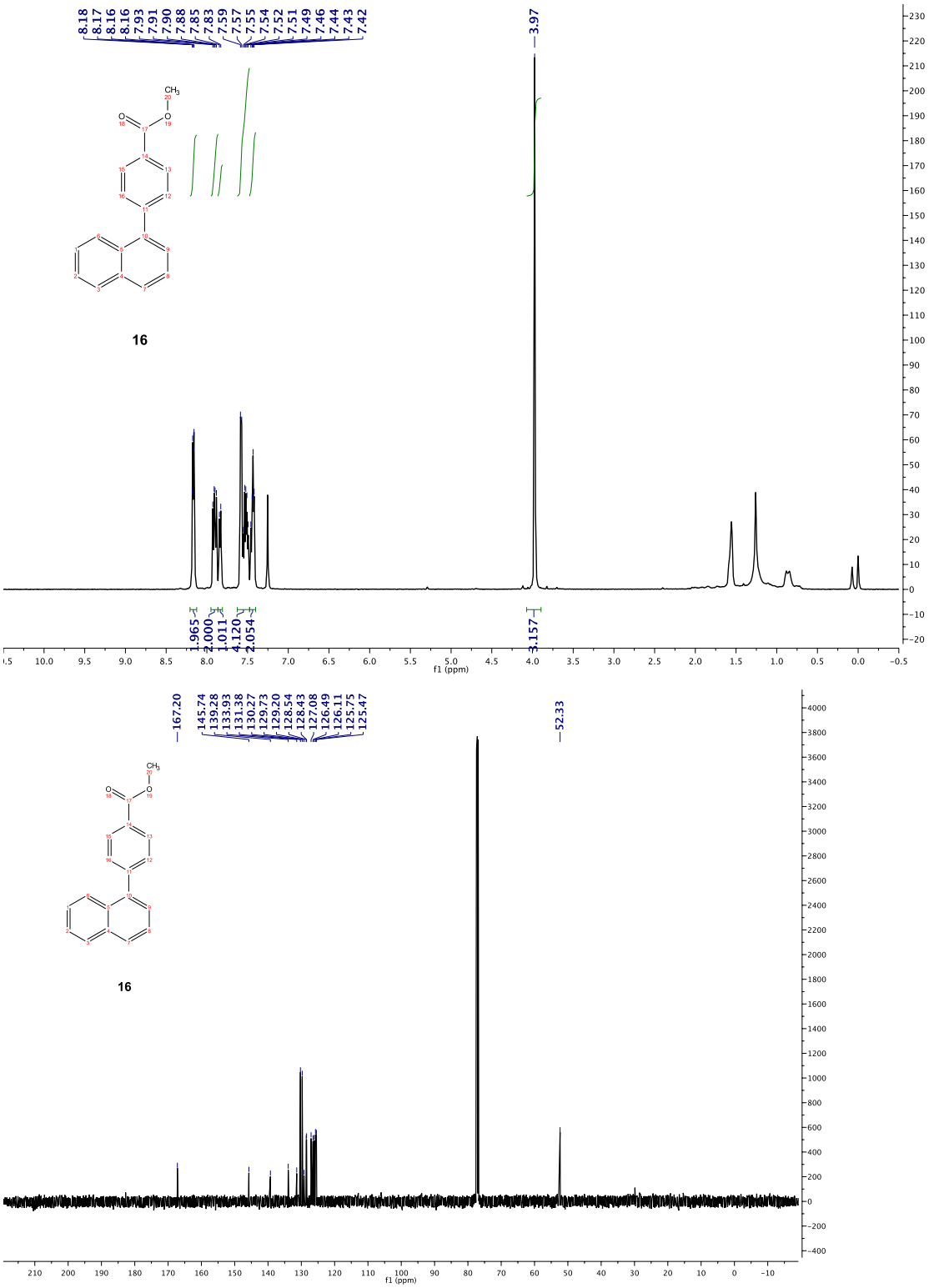


Figure SI 34. ^{1}H NMR (top, 500 MHz), ^{31}P NMR (middle, 203 MHz) and ^{13}C NMR (bottom, 125 MHz) spectra of methyl 4-(naphthalen-1-yl)benzoate in $CDCl_3$.

6. References

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