SUPPORTING INFORMATION

NiXantphos: A Deprotonatable Ligand for Room Temperature Palladium-Catalyzed Cross-Couplings of Aryl Chlorides

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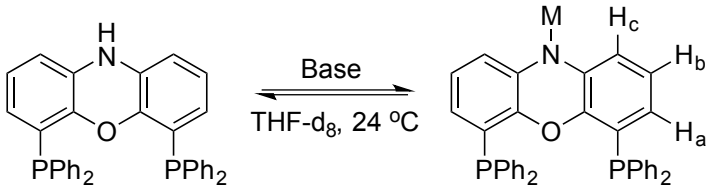
General Methods. All reactions were performed under nitrogen using oven-dried glassware and standard Schlenk or vacuum line techniques. Air- and moisture-sensitive solutions were handled under nitrogen and transferred via syringe. THF was freshly distilled from Na/benzophenone ketyl under nitrogen. Anhydrous CPME, 2-MeTHF, dioxane, and MTBE were purchased from Sigma-Aldrich and used as solvent without further purification. Unless otherwise stated, reagents were commercially available and used as purchased without further purification. Chemicals were obtained from Sigma-Aldrich, Acros, TCI America or Alfa Aesar, and solvents were purchased from Fisher Scientific. The progress of the reactions was monitored by thin-layer chromatography using Whatman Partisil K6F 250 μm precoated 60 Å silica gel plates and visualized by short-wavelength ultraviolet light as well as by treatment with ceric ammonium molybdate (CAM) stain or iodine. Silica gel (230–400 mesh, Silicycle) was used for flash chromatography. The ^{1}H NMR and ^{13}C{^{1}H} NMR spectra were obtained using a Brüker AM-500 Fourier-transform NMR spectrometer at 500 and 125 MHz, respectively. Chemical shifts are reported in units of parts per million (ppm) downfield from tetramethylsilane (TMS), and all coupling constants are reported in hertz. The ^{31}P{^{1}H} NMR spectra were obtained using a Brüker DMX-360 NMR spectrometer at 145.8 MHz, with chemical shifts reported with respect to calibration with an external standard of phosphoric acid (0 ppm). The infrared spectra were obtained with KBr plates using a Perkin-Elmer Spectrum 100 Series FTIR spectrometer. High-resolution mass spectrometry (HRMS) data were obtained on a Waters LC-TOF mass spectrometer (model LCT-XE Premier) using chemical ionization (CI) or electrospray ionization (ESI) in positive or negative mode, depending on the analyte. Melting points were determined on a Unimelt Thomas-Hoover melting point apparatus and are uncorrected.

^{1}H and ^{31}P{^{1}H} NMR Studies of NiXantphos Deprotonated by Base.



The experiments were set up inside a glovebox under a nitrogen atmosphere. NiXantphos (21.4 mg, 0.039 mmol, 1 equiv) and LiN(SiMe$_3$)$_2$ (9.8 mg, 0.059 mmol, 1.5 equiv) or KN(SiMe$_3$)$_2$ (1.5 equiv, 3 equiv, 6 equiv) were weighed in a vial, dissolved in THF-d$_8$ (0.75 mL) and transferred to a J. Young NMR tube. The solution became yellow immediately. The ^{1}H and ^{31}P{^{1}H} NMR spectra were recorded at room temperature.

NiXantphos without base: ^{1}H NMR (360 MHz, THF-d_8): δ 7.30 – 7.11 (m, 20H), 6.52 (t, *J* = 7.2 Hz, 2H), 6.32 (dd, *J* = 7.7, 1.3 Hz, 2H), 5.91 (m, 2H) ppm; ^{31}P{^{1}H} NMR (145.8 MHz, THF-d_8): δ -18.99 ppm.

NiXantphos with 1.5 equiv LiN($SiMe_3$)$_2$: ^{1}H NMR (360 MHz, THF-d_8): δ 7.28 – 7.04 (m, 20H), 6.07 (t, *J* = 7.6 Hz, 2H), 5.75 (d, *J* = 7.6 Hz, 2H), 5.22 (d, *J* = 7.9 Hz, 2H) ppm; ^{31}P{^{1}H} NMR (145.8 MHz, THF-d_8): δ -18.45 ppm.

NiXantphos with 1.5 equiv KN($SiMe_3$)$_2$: ^{1}H NMR (360 MHz, THF-d_8): δ 7.28 – 7.04 (m, 20H), 6.06 (t, *J* = 7.6 Hz, 2H), 5.73 (d, *J* = 7.6 Hz, 2H), 5.16 (d, *J* = 7.2 Hz, 2H) ppm; ^{31}P{^{1}H} NMR (145.8 MHz, THF-d_8): δ -18.69 ppm.

NiXantphos with 3 equiv KN($SiMe_3$)$_2$: ^{1}H NMR (360 MHz, THF-d_8): δ 7.27 – 7.03 (m, 20H), 6.03 (t, *J* = 7.7 Hz, 2H), 5.70 (dd, *J* = 7.6, 1.4 Hz, 2H), 5.14 (m, 2H) ppm; ^{31}P{^{1}H} NMR (145.8 MHz, THF-d_8): δ -18.69 ppm.

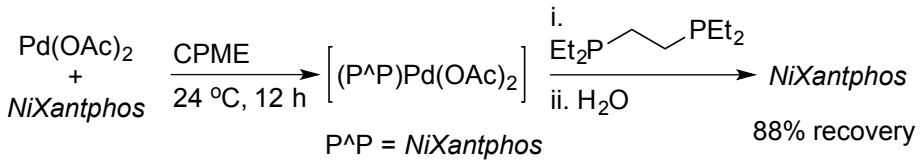
NiXantphos with 6 equiv KN($SiMe_3$)$_2$: ^{1}H NMR (360 MHz, THF-d_8): δ 7.27 – 7.03 (m, 20H), 6.04 (t, *J* = 7.6 Hz, 2H), 5.70 (dd, *J* = 7.6, 1.4 Hz, 2H), 5.15 (m, 2H) ppm; ^{31}P{^{1}H} NMR (145.8 MHz, THF-d_8): δ -18.68 ppm.

Procedure and Characterization for K−NiXantphos.

The experiments were set up inside a glovebox under a nitrogen atmosphere. To a 20 mL vial containing NiXantphos (110 mg, 0.2 mmol, 1 equiv) dissolved in 10 mL of Et_2O, a solution of KN($SiMe_3$)$_2$ (40 mg, 0.2 mmol, 1 equiv) in 2 mL of Et_2O was added slowly resulting in rapid precipitation of a yellow solid. After stirring for 2 h, the slurry was filtered through fritted filter and the solid was washed with 3 × 5 mL Et_2O. Drying under reduced pressure yielded K−NiXantphos as a yellow powder (107 mg, 91% yield). ^{1}H NMR (500 MHz, THF-d_8): δ 7.23 – 7.04 (m, 20H), 6.03 (t, *J* = 7.5 Hz, 2H), 5.70 (d, *J* = 7.5 Hz, 2H), 5.14 (d, *J* = 7.0 Hz, 2H) ppm; ^{13}C{^{1}H} NMR (125 MHz, THF-d_8): δ 150.7, 148.2, 140.2, 134.8, 128.4, 128.1, 124.5, 121.0, 118.0, 114.7 ppm; ^{31}P{^{1}H} NMR (145.8 MHz, THF-d_8): δ -18.63 ppm; IR (thin film): 1566, 1454, 1434, 1405, 742, 695 cm^{-1}. X-ray diffraction-quality single-crystals of [K(THF)$_3$−NiXantphos]$_2$ were obtained by layering a concentrated THF solution of K−NiXantphos with hexanes at –21 °C. X-ray diffraction-quality single-crystals of the reddish-orange crown ether adduct, K(THF)(18-crown-6)−NiXantphos, were obtained by vapor diffusion of pentane into a concentrated THF solution of K−NiXantphos and 18-crown-6 (1:1) at –21 °C.

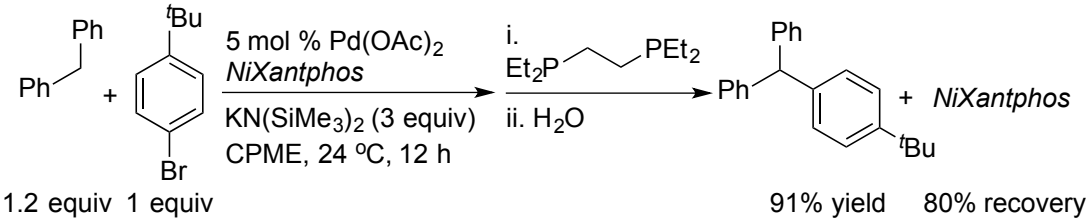
Ligand Exchange and Recovery of NiXantphos.

A. Ligand exchange and recovery process (control)



The experiments were set up inside a glovebox under a nitrogen atmosphere. A 20 mL reaction vial equipped with a stir bar was charged with $Pd(OAc)_2$ (21.0 mg, 0.094 mmol) and NiXantphos (90.4 mg, 0.164 mmol) followed by 19 mL of dry CPME. The reaction mixture was stirred for 12 h at 24 °C, resulting in coordination of NiXantphos to palladium, as judged by a singlet at 3.4 ppm in $^{31}P\{^{1}H\}$ NMR spectrum. 1,2-bis(diethylphosphino)ethane (depe, 180 μL, 0.771 mmol, depe:NiXantphos=5:1) was added into the reaction mixture. The reaction mixture was stirred for another 40 min at 24 °C. The reaction was quenched with H_2O, diluted with ethyl acetate, and filtered over a pad of silica. The pad was rinsed with additional ethyl acetate, and the solution was concentrated in vacuo. The crude material was loaded onto a silica gel column and purified by flash chromatography to afford NiXantphos (80 mg, 88% recovery).

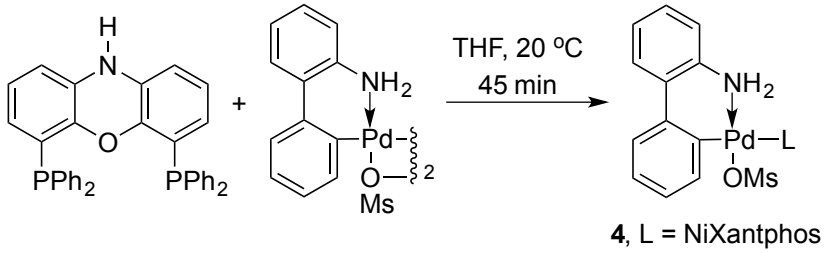
B. Cross-coupling followed by ligand exchange and recovery process



The experiments were set up inside a glovebox under a nitrogen atmosphere. An 8 mL reaction vial equipped with a stir bar was charged with $KN(SiMe_3)_2$ (329 mg, 1.65 mmol, 3 equiv). A solution of $Pd(OAc)_2$ (6.2 mg, 0.028 mmol, 5 mol %) and NiXantphos (30.0 mg, 0.054 mmol, 10 mol %) in 6 mL of dry CPME was taken up by syringe and added to the reaction vial. After stirring for 5 min at 24 °C, diphenylmethane (110 μL, 0.66 mmol, 1.2 equiv) was added to the reaction mixture followed by 1-bromo-4-*tert*-butylbenzene (95 μL, 0.55 mmol, 1 equiv). The reaction mixture was stirred for 12 h at 24 °C, before 1,2-bis(diethylphosphino)ethane (depe, 103 μL, 0.44 mmol, depe:NiXantphos=8:1) was added into the reaction mixture. The reaction mixture was stirred for another 40 min at 24 °C. The reaction was quenched with H_2O, diluted with ethyl acetate, and filtered over a pad of silica. The pad was rinsed with additional ethyl acetate, and the solution was concentrated in vacuo. The crude material was loaded

onto a silica gel column and purified by flash chromatography to afford the triarylmethane product **3aa** (91% yield) and NiXantphos (24 mg, 80% recovery).

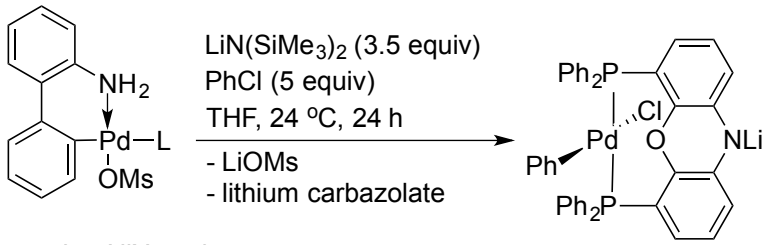
Procedure and Characterization for the Methanesulfonate Precatalyst 4.



4, L = NiXantphos

To a 50 mL flask under a nitrogen atmosphere was added degassed anhydrous THF (10.4 mL) followed by u-mesylate dimer (2.00 g, 2.84 mmol) and NiXantphos (1.04 g, 1.41 mmol). The reaction was aged for 45 minutes after which time the slurry was treated with MTBE (10 mL) and aged for an additional 30 minutes. The slurry was collected by filtration and the product washed with MTBE (2 × 5 mL). The product was dried for 13 hours by pulling N_2 through the cake (1.1 g, 85%). Note: The peaks in the NMR spectra appear broad due to the fluxional nature of the complex. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 8.99 (1H, br. s), 7.45 – 7.39 (2H, br. m), 7.27 – 7.14 (19H, m), 7.00 – 6.94 (6H, br. m), 6.81 – 6.67 (3H, br. m), 6.44 (2H, br. s), 6.25 – 6.22 (1H, br. m), 4.48 (2H, br. s), 2.64 (3H, s); ^{31}P NMR (162.0 MHz, $CDCl_3$): δ 14.27 (br. s), 3.70 (br. s).

Procedure and Characterization for Oxidative Addition of Chlorobenzene to (M−NiXantphos)Pd(0).



4, L = NiXantphos

The experiments were set up inside a glovebox under a nitrogen atmosphere. Complex **4** (9.2 mg, 0.01 mmol, 1 equiv) was added to a J. Young NMR tube followed by chlorobenzene (5.1 μL, 0.05 mmol, 5 equiv). $LiN(SiMe_3)_2$ (5.9 mg, 0.035 mmol, 3.5 equiv) was weighed in a vial, dissolved in THF (500 μL) and transferred to the NMR tube. The solution became reddish-orange immediately. The progress of the reaction was monitored by ^{31}P{^{1}H} NMR

spectroscopy. The room temperature oxidative addition of chlorobenzene reached about 75% conversion in 6 h and near completion in 24 h, as judged by a singlet at 2.6 ppm in $^{31}P\{^{1}H\}$ NMR spectrum for the oxidative addition product, (Li−NiXantphos)Pd(Ph)(Cl) (a singlet at 2.8 ppm for (K−NiXantphos)Pd(Ph)(Cl) from using $KN(SiMe_3)_2$ as base in place of $LiN(SiMe_3)_2$). The oxidative addition product was generated along with byproducts lithium mesylate and lithium carbazolate, rendering the isolation of the Pd-containing product challenging. Nevertheless, X-ray diffraction-quality single-crystals of the protonated (NiXantphos)Pd(Ph)(Cl) were obtained by vapor diffusion of pentane into a concentrated THF solution of the reaction mixture at –21 °C.

Procedure and Characterization for Pd(NiXantphos)$_2$.

The title compound was prepared according to literature procedure.[1] The experiments were set up inside a glovebox under a nitrogen atmosphere. NiXantphos (197.2 mg, 0.358 mmol) and $Pd_2(dba)_3$ (83.7 mg, 0.091 mmol) were weighed into a 40 mL reaction vial. Toluene (30 mL) was added, and the reaction mixture was stirred for 4 h. The solution was then filtered into another 40 mL vial to remove an insoluble greenish solid. This solution was concentrated to 20 mL and allowed to rest overnight so that any extra palladium black would settle. The resulting solution was filtered again and finally concentrated to dryness. The yellow solid was washed with toluene (5 × 5 mL) and hexanes (5 × 5 mL) to remove dibenzylideneacetone and excess NiXantphos, and dried under reduced pressure. The identity of the yellow solid was confirmed as Pd(NiXantphos)$_2$ by HRMS analysis, and the characteristic isotope pattern was observed. HRMS calc'd for $C_{72}H_{55}N_2O_2P_4Pd^+$ 1209.2249, observed 1209.2277 $[MH]^+$. Unfortunately, it was insoluble in common organic solvent. A similar synthetic route was reported for Pd(Xantphos)$_2$ by the Buchwald group, and its poor solubility was also noted.[1]

Procedure, Characterization and Catalytic Reactivity for (NiXantphos)Pd(4-C$_6$H$_4$CN)(Br) (5).

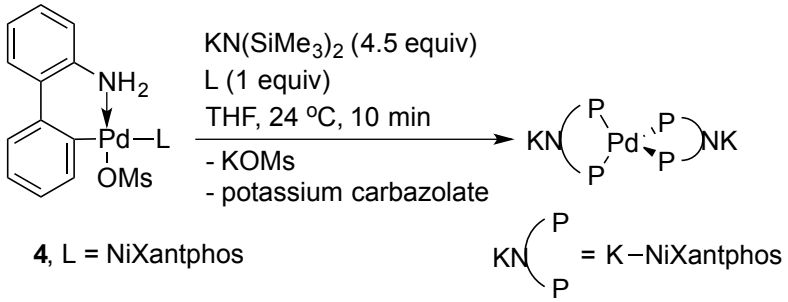
The title compound was prepared according to literature procedure.[15] The experiments were set up inside a glovebox under a nitrogen atmosphere. A solution of Pd_2dba_3 (22.9 mg, 0.025 mmol, 0.05 mmol Pd, 1 equiv Pd), NiXantphos (27.6 mg, 0.05 mmol, 1 equiv), and 4-bromobenzonitrile (45.5 mg, 0.25 mmol, 5 equiv) in dry THF (1.5 mL) was stirred at room temperature for 12 h. The reaction was filtered through fritted filter. 10 mL of pentane was then added to the residue, and the orange resulting precipitate was allowed to form upon standing for 1 day at –21 °C. The solid was then filtered, washed with 3 × 10 mL Et_2O. Drying under reduced pressure yielded **5** as an orange

powder (36.9 mg, 88% yield). ^{1}H NMR (500 MHz, CD_2Cl_2): δ 7.51 – 7.25 (m, 12H), 7.25 – 7.07 (m, 8H), 6.91 – 6.62 (m, 8H), 6.41 – 6.29 (m, 2H), 6.27 (s, 1H) ppm; ^{13}C{^{1}H} NMR (125 MHz, CD_2Cl_2): δ 169.0, 147.0, 135.6, 135.5, 135.1, 130.8, 130.6, 128.9, 128.4, 126.2, 125.1, 122.0, 120.4, 117.2, 104.6 ppm (observed complexity due to P-C splitting); ^{31}P{^{1}H} NMR (145.8 MHz, CD_2Cl_2): δ 7.2 ppm; IR (thin film): 3259, 3052, 2219, 1567, 1452, 1434, 1394, 1174, 1094, 811, 738, 692 cm^{-1}. The identity of the orange solid was confirmed as (NiXantphos)Pd(4-C_6H_4CN)(Br) by HRMS analysis, and the characteristic isotope pattern was observed. HRMS calc'd for $C_{43}H_{31}N_2OP_2Pd^+$ 759.0946, observed 759.0946 [M-Br]$^+$.

Catalytic reactivity for 5:

The reaction was performed following General Procedure I with **1a** (16.7 μL, 0.1 mmol, 1 equiv), $KN(SiMe_3)_2$ (59.8 mg, 0.30 mmol, 3 equiv) and **2a** (33.4 μL, 0.2 mmol, 2 equiv) in the presence of 5 mol % **5** in THF at 24 °C. The crude material was purified by flash chromatography on silica gel (eluted with hexanes to EtOAc:hexanes = 2:98) to give the product **3aa** (25.8 mg, 86% yield) as a white solid. Also see "**3aa – (4-*tert*-Butylphenyl)diphenylmethane**" in "Procedure and Characterization for the Pd-Catalyzed DCCP of Aryl Chlorides".

Procedure, Characterization and DOSY NMR Measurements for Pd(K−NiXantphos)$_2$.



The experiments were set up inside a glovebox under a nitrogen atmosphere. NiXantphos (5.5 mg, 0.01 mmol, 1 equiv) and complex **4** (9.2 mg, 0.01 mmol, 1 equiv) were added to a J. Young NMR tube. $KN(SiMe_3)_2$ (9.0 mg, 0.045 mmol, 4.5 equiv) was weighed in a vial, dissolved in THF (500 μL) and transferred to the NMR tube. The solution became reddish-orange immediately. The progress of the reaction was monitored by ^{31}P{^{1}H} NMR spectroscopy. The formation of Pd(K−NiXantphos)$_2$ was complete in 10 min, as judged by disappearance of **4** and appearance of a new singlet at –1.3 ppm in ^{31}P{^{1}H} NMR spectrum. The reaction mixture was set undisturbed for 12 h. X-ray diffraction-quality single-crystals of Pd[K(THF)$_2$(NiXantphos)]$_2$ were obtained under these conditions. The

crystalline product was then filtered and washed with 3 × 10 mL Et_2O. Drying under reduced pressure yielded the product as a yellow crystalline solid (9.9 mg, 63% isolated yield). ^{1}H NMR (500 MHz, THF-d_8): δ 7.03 (m, 16H), 6.84 (m, 8H), 6.67 (m, 16H), 6.06 (m, 4H), 5.76 (m, 4H), 5.48 (m, 4H) ppm; ^{31}P{^{1}H} NMR (145.8 MHz, THF-d_8): δ -1.3 ppm.

^{1}H DOSY NMR:

The NMR experiments for the determination of the self-diffusion coefficients and hydrodynamic radii were performed at 300 K on a Brüker Avance DRX 600 MHz spectrometer equipped with a 5 mm TXI probe with a z-axis gradient coil. The gradient system was calibrated with a doped water sample. Data were systematically accumulated by linearly varying the diffusion gradients from 95% to 5% for 16 gradient increment values. Data processing was accomplished with Brüker TOPSPIN 1.3 DOSY software and Brüker TOPSPIN 1.3 T1/T2 software, with representative 2D spectra processed using MestReNova v. 7.0.3. Diffusion coefficients (D_o) were obtained after fitting area data to the Stejskal-Tanner expression with the Brüker TOPSPIN 1.3 T1/T2 software and the reported D_o is an average value calculated from the different NMR responses within the same compound. Similarly, standard deviations associated with values of D_o were calculated from differences in D_o in the same sample using different NMR responses. The experiments were run in THF–d_8 (~16 mM for NiXantphos, ~2 mM for Pd[K(THF)$_2$(NiXantphos)]$_2$) with 5.0 μL tetramethylsilane (TMS) and ~1.2 mg ferrocene (Fc) used as internal standards. The hydrodynamic radii (r_H(sample)) of NiXantphos and Pd[K(THF)$_2$(NiXantphos)]$_2$ were determined following equation 1:

$$r_H(sample) = \left(\frac{D_o(reference)}{D_o(sample)} \right) \times r_H(reference) \qquad (1)$$

where D_o(reference) was the diffusion coefficient for the corresponding internal standard, D_o(sample) was the diffusion coefficient of the sample, and r_H(reference) was the hydrodynamic radii of the internal references. Equation 1 was used to minimize errors between samples due to variations in viscosity and temperature, and is derived from the Stokes-Einstein equation:[12,13]

$$D_o = \frac{kT}{6r_H\pi\eta} \qquad (2)$$

where D_o is the diffusion coefficient, k is the Boltzmann constant, T is temperature, r_H is the hydrodynamic radius, and η is the viscosity of the solution. The theoretical hydrodynamic radii ($r_{H(theo)}$) were determined from their reported crystal structures, taking the centroid of the molecule and measuring the distance to the furthest point in the molecule.

Table S1. Collected diffusion data from ^{1}H DOSY NMR experiments for **NiXantphos** and **Pd[K(THF)$_2$(NiXantphos)]$_2$**

Compound	D_o (×10^{-6} cm^2 s^{-1})			$r_{H(exp)}$ (Å)[b]	$r_{H(exp)}$ (Å)[c]	$r_{H(avg)}$ (Å)[d]	$r_{H(theo)}$ Monomer (Å)[e]	% Error
	TMS	*Fc*	*Sample*[a]					
NiXantphos	21.35	17.47	7.856(9)	6.43(8)	6.20(8)	6.32(11)	7.3295(5)	13.8
Pd[K(THF)$_2$(NiXantphos)]$_2$	21.83	17.88	6.467(54)	7.98(66)	7.71(64)	7.85(101)	8.5945(2)	8.7

a– Average of observable ^{1}H peaks corresponding to the compound. *b*– Based on $r_{H(theo)}$ for TMS. *c* – Based on $r_{H(theo)}$ for Fc. *d* – Average of $r_{H(theo)}$ for both TMS and Fc. *e* – $r_{H(theo)}$ determined from crystal structures; see Figure S1a – S1d. *f* – Standard deviation in parenthesis.

Table S2. Acquisition parameters for 2D-^{1}H DOSY

Compound	D20 (ms)	P30 (μs)	NS	D20 (ms)	P30 (μs)	NS
	Fc, TMS			Sample		
NiXantphos	60	1000	8	120	1000	8
Pd[K(THF)$_2$(NiXantphos)]$_2$	60	1000	8	140	1000	64

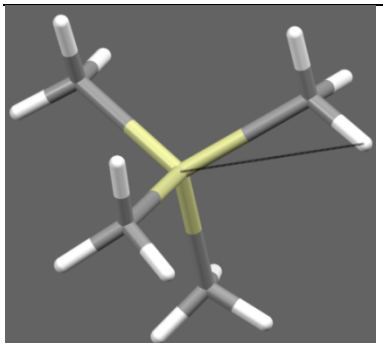


Figure S1a. Points used for determination of $r_{H(theo)}$ (2.376(6) Å) from the crystal structure of TMS (CSD ref = TIVWOL).

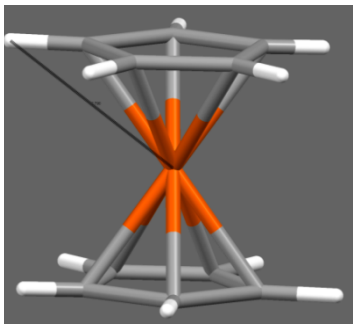


Figure S1b. Points used for determination of $r_{H(theo)}$ (2.790(2) Å) from the crystal structure of Fc (CSD ref = FEROCE).

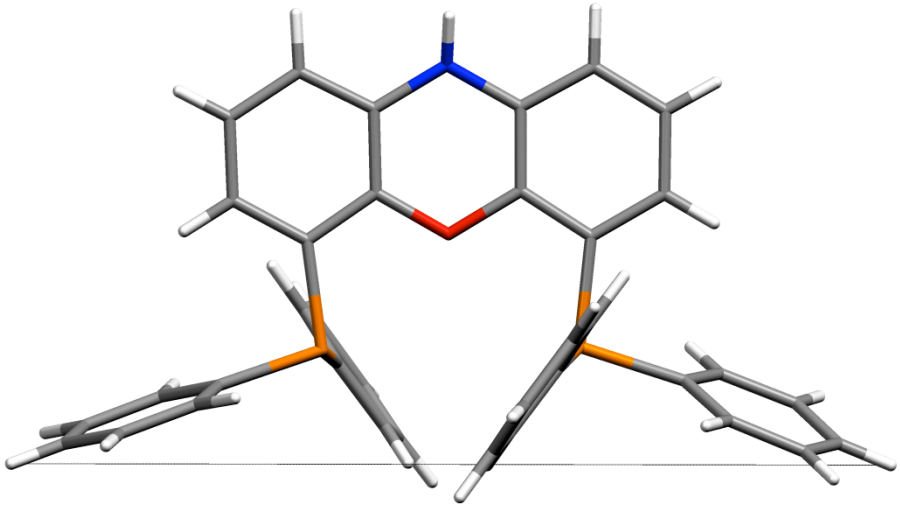


Figure S1c. Points used for determination of $r_{H(theo)}$ (7.3295(4) Å) taken from the crystal structure of **NiXantphos** (CSD ref = KIXFAZ).

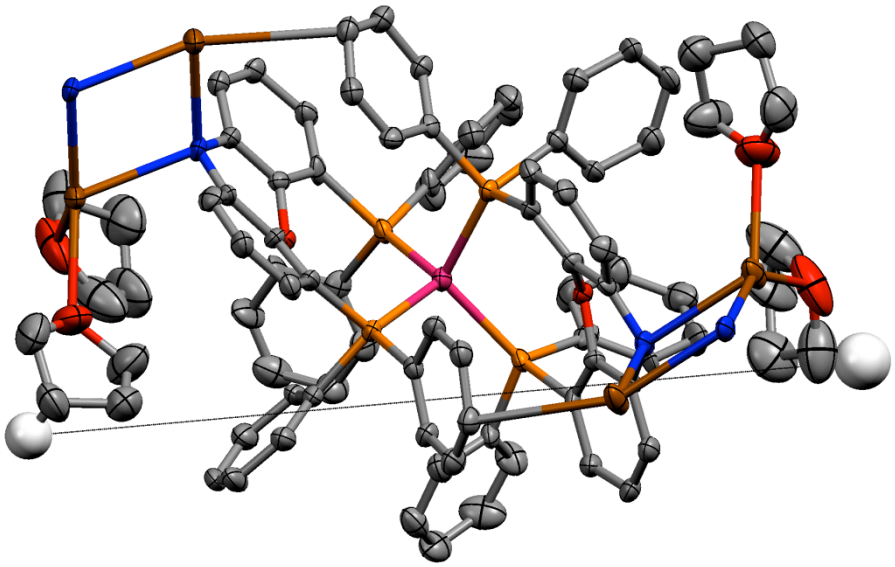


Figure S1d. Points used for determination of $r_{H(theo)}$ (8.5945(2) Å) from the crystal structure of **Pd[K(THF)$_2$(NiXantphos)]$_2$**.

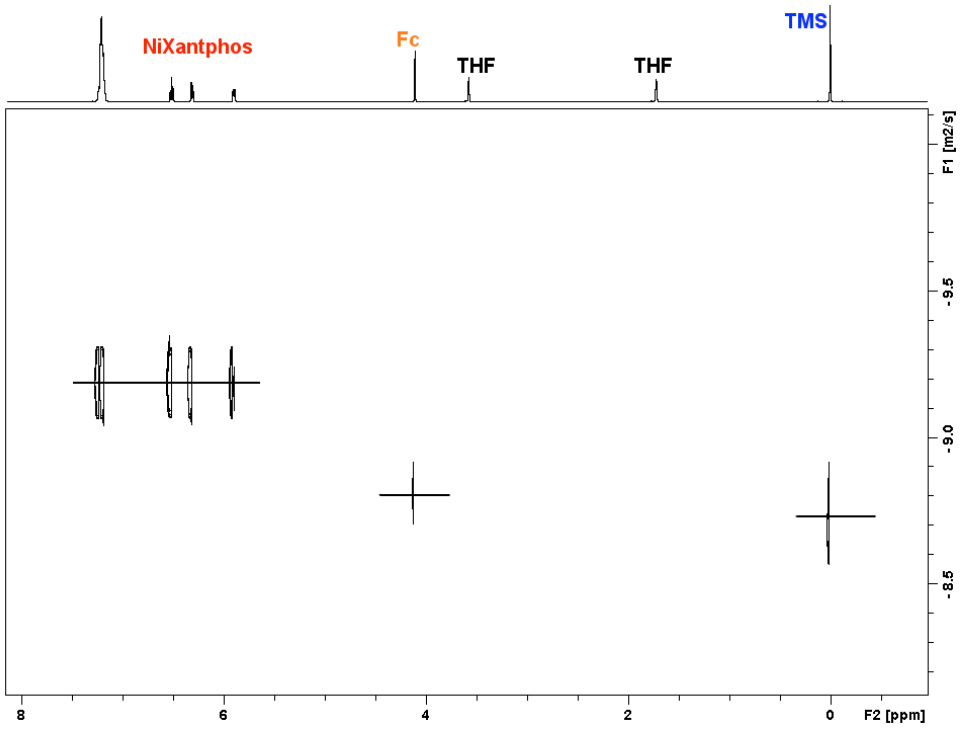


Figure S2a. 2D-^{1}H DOSY NMR spectrum of **NiXantphos** and internal references at 300 K in THF–d_8.

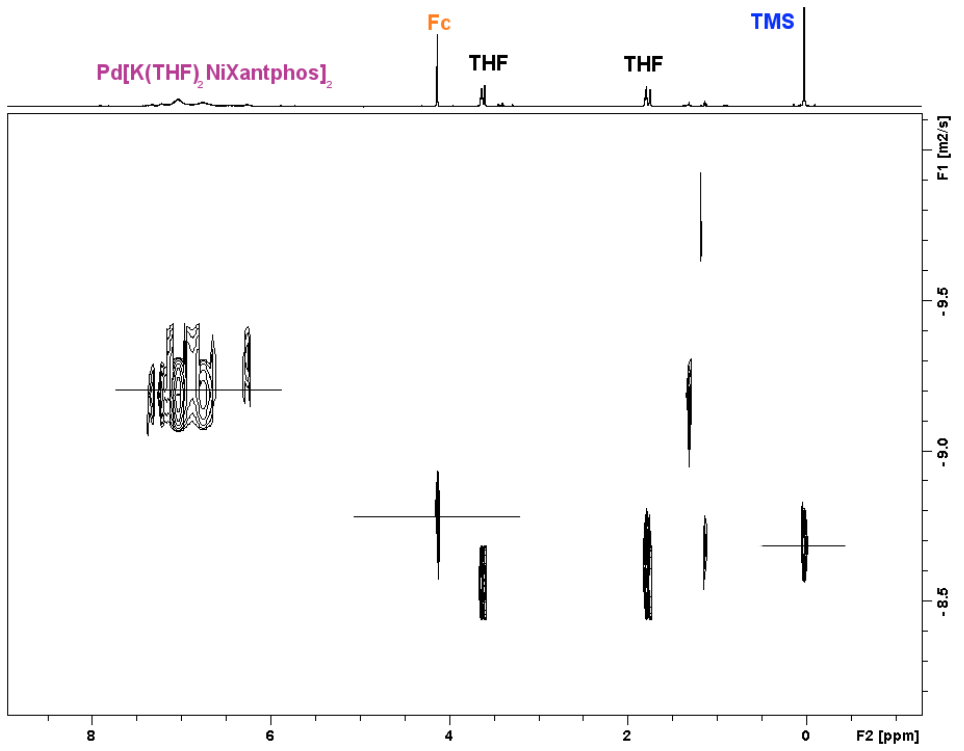


Figure S2b. 2D-^{1}H DOSY NMR spectrum of **Pd[K(THF)$_2$(NiXantphos)]$_2$** and internal references at 300 K in THF–d_8.

Identification of the Catalyst Resting State.

The experiments were set up inside a glovebox under a nitrogen atmosphere. An oven-dried 20 mL vial equipped with a stir bar was charged with complex **4** (9.2 mg, 0.01 mmol, 10 mol %) and KN(SiMe$_3$)$_2$ (59.8 mg, 0.30 mmol, 3 equiv). 0.5 mL of dry THF was taken up by syringe and added to the reaction vial, followed by diphenylmethane (**1a**, 16.7 μL, 0.1 mmol, 1 equiv) and chlorobenzene (**2b**, 20.4 μL, 0.2 mmol, 2 equiv). After stirring for 5 min at 24 °C, the orange reaction mixture was transferred to a J. Young NMR tube. The reaction mixture was monitored by ^{31}P{^{1}H} NMR spectroscopy for 12 h at 24 °C. The only species observed by ^{31}P{^{1}H} NMR spectroscopy for the DCCP reaction was Pd(K−NiXantphos)$_2$ throughout the reaction time (12 h), as judged by a singlet at −1.3 ppm in ^{31}P{^{1}H} NMR spectrum. Using 10 mol % Pd(OAc)$_2$ and 20 mol % NiXantphos as the precatalyst system gave the same dominant catalyst resting state within 10 minutes after addition of **1a**, **2b** and KN(SiMe$_3$)$_2$ at room temperature.

Countercation Effects.

To compare the catalytic reactivity using different countercations (Li, Na vs K), we carried out our DCCP reactions under standard conditions with 2-benzylpyridine (**1g**) and 1-*tert*-butyl-4-chlorobenzene (**2a**) using the following 3 bases: $LiN(SiMe_3)_2$, $NaN(SiMe_3)_2$ and $KN(SiMe_3)_2$. The reaction was performed following General Procedure I with **1g** (16.1 μL, 0.1 mmol, 1 equiv), $MN(SiMe_3)_2$ (M=Li, Na, K) (0.30 mmol, 3 equiv) and **2a** (33.4 μL, 0.2 mmol, 2 equiv) in the presence of 5 mol % Pd catalyst in THF at 24 °C. The assay yields were recorded at 2 h (average of two runs).

Base	Assay yield (%)
$LiN(SiMe_3)_2$	13.3
$NaN(SiMe_3)_2$	35.1
$KN(SiMe_3)_2$	34.2

Details on DFT Calculations.

A. Computational details. Gaussian '09 Rev. A.02 was used for all electronic structure calculations with B3LYP hybrid DFT method.[14a] The 6-31 G* basis set was employed for all atoms. The geometry optimizations were performed on gas phase structures. Frequency calculations, performed on each optimized structure, found no imaginary frequencies to confirm that the optimized structures were minima. Bonding analyses were performed using NBO 3.1.[14b]

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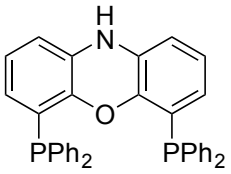
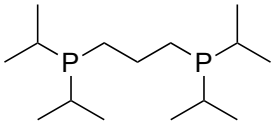
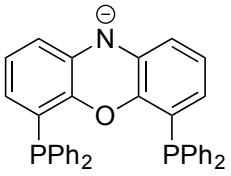
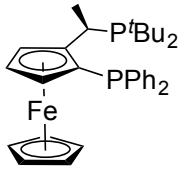
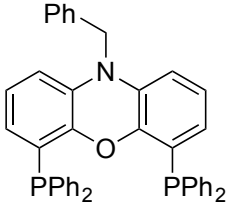
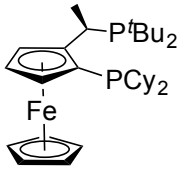
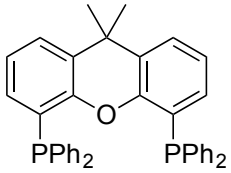
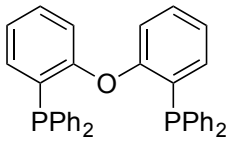
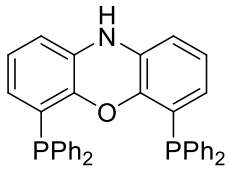
1		0.925 0.926	-0.501	6		0.842 0.848
2		0.923 0.923	-0.517	7		0.843 0.949
3		0.922 0.924	-0.499	8		0.838 0.878
4		0.930 0.930	-0.503			
5		0.918 0.926	-0.514			

B. Cartesian coordinates for phosphine ligand optimized geometries.



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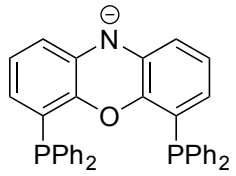

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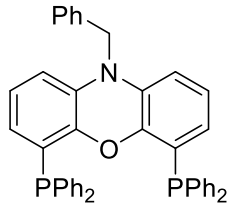

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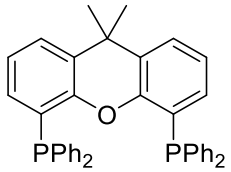

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H	2.48326800	-3.32625600	4.33098500
H	1.77796300	-4.55330900	2.28415200
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H	0.87536000	5.89910200	1.11418000
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C	-1.18545900	1.86120600	0.03162500
C	-2.45560700	3.89159700	0.08347900
C	-2.30558800	1.12017100	-0.38867600
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C	-2.72306700	-1.44821800	3.29699300
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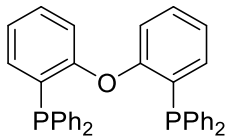

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C	4.54081800	0.30137700	-0.92519900
C	3.11028100	-2.71969900	2.06394300
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C	5.23219700	1.18437700	-0.08119600
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C	-1.50212500	-3.66232600	-2.24554200
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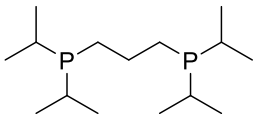

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C	3.51724000	-2.60028500	1.03982500
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C	-5.01866000	-1.50900200	-1.09188800
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C	-4.15221000	0.63831700	2.04812300
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H	-3.57161000	3.11695400	-0.34954100
H	-4.51487400	-0.39496100	2.04958500
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H	-4.86258500	1.23579200	2.63520400
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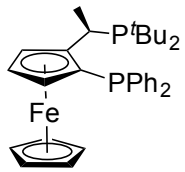

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C	1.60362300	-1.69631600	-2.70670600
H	0.96108200	-1.09680400	-3.33848800
C	1.44249700	-3.08782700	-2.43559900
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C	2.50206100	-3.49402600	-1.57147300
H	2.64822200	-4.48851000	-1.16988500
C	3.31786300	-2.35392100	-1.30570800
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H	-2.87596800	-1.92734400	3.63903200
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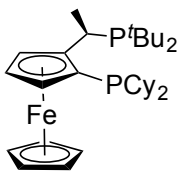

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H	0.09380700	-4.72127100	-0.18555700
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H	-1.40530500	-3.30222800	1.55258800
C	-0.57838200	-0.21885000	-0.69746300
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H	0.97580400	-0.74117000	1.44836100
C	2.09913500	-2.46614300	0.88870100
H	1.26098800	-3.11677900	1.15984500
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H	2.09076000	-0.87337000	3.34802800
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H	-4.77372600	1.08706800	3.78632000
H	-6.23791000	0.37232300	3.11649900
C	-5.14279000	1.63844700	1.72803400
H	-5.66491200	2.56328100	2.00641000
H	-5.68078000	1.22703000	0.86082300
C	-3.69776400	1.96707300	1.30931400
H	-3.19138600	2.48287100	2.13969600
H	-3.72441200	2.67346500	0.47371900

Representative Microscale High-throughput Experimentation.

General Experimental:

The experimental procedures in this work were similar to those reported.[2] Parallel synthesis was accomplished in an MBraun glovebox operating with a constant N_2-purge (oxygen typically <5 ppm). The experimental design was accomplished using Accelrys Library Studio. Screening reactions were carried out in 1 mL vials (30 mm height × 8 mm diameter) in a 96-well plate aluminum reactor block. Liquid chemicals were dosed using multi-channel or single-channel pipettors. Solid chemicals were dosed manually as solutions or slurries in appropriate solvents. Undesired additional solvent was removed using a GeneVac system located inside the glovebox. The reactions were heated and stirred on a heating block with a tumble-stirrer (V&P Scientific) using 1.98 mm diameter × 4.80 mm length parylene stir bars. The tumble stirring mechanism helped to insure uniform stirring throughout the 96-well plate. The reactions were sealed in the 96-well plate during reaction. Below each reactor vial in the aluminum 96-well plate was a 0.062 mm thick silicon-rubber gasket. Directly above the glass vial reactor tops was a Teflon perfluoroalkoxy copolymer resin sealing gasket and above that, two more 0.062 mm thick silicon-rubber gaskets. The entire assembly was compressed between an aluminum top and the reactor base with 9 evenly-placed screws.

Set up:

Experiments were set up inside a glovebox under a nitrogen atmosphere. A 96-well aluminum block containing 1 mL glass vials was predosed with $Pd(OAc)_2$ (1 μmol) and Ligand (Ligand was used in a 4:1 ratio relative to Pd for monodentate ligands and 2:1 ratio for bidentate ligands) in THF. The solvent was evacuated to dryness using a Genevac vacuum centrifuge, and $KN(SiMe_3)_2$ (30 μmol) in THF was added to the ligand/catalyst mixture. The solvent was removed on the Genevac, and a parylene stir bar was then added to each reaction vial. 1-*tert*-Butyl-4-chlorobenzene (10 μmol/reaction), diphenylmethane (12 μmol/reaction) and biphenyl (1 μmol/reaction) (used as an internal standard to measure HPLC yields) were then dosed together into each reaction vial as a solution in CPME (100 μL, 0.1 M). The 96-well plate was then sealed and stirred for 18 h at 24 °C.

Work up:

Upon opening the plate to air, 500 μL of acetonitrile was pipetted into each vial. The plate was then covered again and the vials stirred for 20 min to extract the product and to ensure good homogenization. Into a separate 96-well LC block was added 700 μL of acetonitrile, followed by 40 μL of the diluted reaction mixtures. The LC block was then sealed with a silicon-rubber storage mat, and mounted on HPLC instrument for analysis.

A complete list of 112 ligands:

	Ligand libraries (1 – 96)
1	2-Di-tert-butylphosphino-2',4',6'-triisopropylbiphenyl (*t*Bu-XPhos)
2	2-(Dicyclohexylphosphino)-2'-methylbiphenyl (MePhos)
3	2-(Di-*t*-butylphosphino)-2'-methylbiphenyl (*t*Bu-MePhos)
4	2-(Dicyclohexylphosphino)biphenyl (Cy-JohnPhos)
5	2-Di-t-butylphoshino-2'-(*N*,*N*-dimethylamino)biphenyl (*t*Bu-DavePhos)
6	Racemic-2-(di-*t*-butylphosphino)-1,1'-binaphthyl
7	1-[2-[Bis(*t*-butyl)phosphino]phenyl]-3,5-diphenyl-1H-pyrazole (TrippyPhos)
8	5-(Di-*t*-butylphosphino)-1', 3', 5'-triphenyl-1'H-[1,4']bipyrazole (BippyPhos)
9	Dicyclohexyl-[2-(*o*-tolyl)indol-1-yl]phosphane
10	Di-*t*-butyl(2,2-diphenyl-1-methyl-1-cyclopropyl)phosphine (cBRIDP [MoPhos])
11	Dicyclohexyl-(1-methyl-2,2-diphenyl-cyclopropyl)phosphane (Cy-cBRIDP)
12	Dicyclohexyl-(1-methyl-2,2-diphenyl-vinyl)phosphane (Cy-vBRIDP)
13	*N*-phenyl-2-(dicyclohexylphosphino)pyrrole (cataCXium PCy)
14	*N*-phenyl-2-(di-*t*-butylphosphino)pyrrole (cataCXium PtB)
15	Dicyclohexyl-(1-phenylindol-2-yl)phosphane (cataCXium PInCy)
16	Di-*t*-butyl-(1-phenylindol-2-yl)phosphane (cataCXium PIntB)
17	1-(2-Methoxylphenyl)-2-(dicyclohexylphosphino)pyrrole (cataCXium POMeCy)
18	Di-*t*-butyl-[1-(2-methoxyphenyl)pyrrol-2-yl]phosphane (cataCXium POMetB)
19	1-(2,4,6-Trimethylphenyl)-2-(dicyclohexylphosphino)imidazole (cataCXium PICy)
20	Di-(2-pyridyl)(dicyclohexylphosphino)amine (cataCXium KCy)
21	Di-(2-pyridyl)(diphenylphosphino)amine (cataCXium KPh)
22	(9-Butylfluoren-9-yl)-dicyclohexyl-phosphonium tetrafluoroborate (cataCXium FBu)
23	Dicyclohexyl-(9-phenethylfluoren-9-yl)phosphonium tetrafluoroborate (cataCXium FPrPh)
24	(9-Benzylfluoren-9-yl)-dicyclohexyl-phosphane; trifluoroborane; hydrofluoride (cataCXium FBn)
25	Trimethylphosphonium tetrafluoroborate
26	Trithylphosphonium tetrafluoroborate
27	Triisopropylphosphonium tetrafluoroborate

28	Tricyclohexylphosphonium tetrafluoroborate
29	Tribenzylphosphine
30	Di-*t*-butylmethylphosphonium tetrafluoroborate
31	*t*-Butyldicyclohexylphosphine
32	Di-*t*-butylcyclohexylphosphine
33	Benzyldi-1-adamantylphosphine (cataCXium ABn)
34	Di-*t*-butylneopentylphosphonium tetrafluoroborate
35	(Z)-1-*t*-butyl-2,3,6,7-tetrahydro-1H-phosphepinium tetrafluoroborate (Ellman ligand)
36	1,3,5-Triaza-7-phosphaadamantane
37	Di-*t*-butylphenylphosphonium tetrafluoroborate
38	Dicyclohexylphenylphosphine
39	(*o*-Tolyl)dicyclohexylphosphine
40	Dicyclohexyl-(2,4,6-trimethylphenyl)phosphine
41	Dicyclohexyl-(2,6-diisopropylphenyl)phosphine
42	1-Dicyclohexylphosphino-4-dimethylaminobenzene
43	1,3,5,7-Tetramethyl-8-phenyl-2,4,6-trioxa-8-phosphatricyclo[3.3.1.13,7]decane
44	2-(Dicyclohexylphosphino)benzophenone
45	2'-(Dicyclohexylphosphino)acetophenone ethylene ketal
46	1-Di-*i*-propylphosphino-2-(*N*,*N*-dimethylamino)-1H-indene
47	11-Dicyclohexylphosphino-12-phenyl-9,10-ethenoanthracene (KitPhos)
48	11-Dicyclohexylphosphino-12-(2-methoxyphenyl)-9,10-ethenoanthracene (*o*-Meo-Kitphos)
49	Triphenylphosphine
50	Tri-*o*-tolylphosphine
51	Trimesitylphosphine
52	Tri(2-furyl)phosphine
53	Tris(2-methoxyphenyl)phosphine
54	Tris(4-methoxyphenyl)phosphine
55	Tris(2,4,6-trimethoxyphenyl)phosphine

56 Tris(4-fluorophenyl)phosphine

57 Tris(pentafluorophenyl)phosphine

58 Tris[3,5-bis(trifluoromethyl)phenyl]phosphine

59 Tri(1-naphthyl)phosphine

60 1,2-Bis(diphenylphosphino)ethane monooxide

61 Cyclohexyldiphenylphosphine

62 *t*-Butyldiphenylphosphine

63 Benzyldiphenylphosphine

64 4-(Dimethylamino)phenyldiphenylphosphine

65 Diphenyl-2-pyridylphosphine

66 2-(1,1-Dimethylpropyl)-6-(diphenylphosphino)pyridine (AlpyPhos)

67 2-(Diphenylphosphino)-6-(2,4,6-triphenylphenyl)pyridine (ArpyPhos)

68 1-Diphenylphosphino-2-(*N*,*N*-dimethylamino)-1H-indene

69 2-(Diphenylphosphino)-2'-(*N*,*N*-dimethylamino)biphenyl (Ph-DavePhos)

70 Tris(2,4-di-tert-butylphenyl)phosphite

71 (1,1'-Ferrocenediyl)phenylphosphine (1,1'-(PhP)-ferrocene)

72 1,4-Bis(diphenylphosphino)butane monooxide

73 Bis(diphenylphosphino)methane

74 1,2-Bis(diphenylphosphino)ethane (dppe [diphos])

75 1,3-Bis(diphenylphosphino)propane (dppp)

76 1,4-Bis(diphenylphosphino)butane (dppb)

77 1,5-Bis(diphenylphosphino)pentane (dpppe)

78 1,8-Bis(diphenylphosphino)octane (dppo)

79 1,2-Bis(dipentafluorophenylphosphino)ethane

80 1,2-Bis(di-2-pyridylphosphino)ethane

81 1,2-Bis(diphenylphosphinomethyl)benzene

82 1,2-Bis(diphenylphosphino)benzene (dppbz)

83 1,8-Bis(diphenylphosphanyl)naphthalene

84 1,2,3,4-(Diphenylphosphinomethyl)cyclopentane (Tedicyp)

85 Bis(2-diphenylphosphinophenyl)ether (DPEPhos)

86	2,2'-Bis(diphenylphosphino)benzophenone (dpbp)
87	9,9-Dimethyl-4,5-bis(diphenylphosphino)xanthene (Xantphos)
88	4,6-Bis(diphenylphosphino)phenoxazine (NiXantphos)
89	(*S*)-(+)-2,2'-Bis(diphenylphosphino)-1,1'-binaphthyl ((*S*)-BINAP)
90	(R)-(+)-2,2'-bis(di-p-tolylphosphino)-1,1'-binaphthyl ((R)-Tol-BINAP)
91	2,2'-Bis(diphenylphosphino)-1,1'-biphenyl (Biphep)
92	3,3'-Bis(diphenylphosphino)-5,5',6,6',7,7',8,8'-octahydro[2,2']binaphthalene hemichloroform adduct (Cy-Nu-Biphep)
93	6,6'-Bis(diphenylphosphino)-1,1',3,3'-tetrahydro[5,5']biisobenzofuran (Thf-Nu-Biphep)
94	Tetramethyl 6,6'-bis(diphenylphosphino)-1,1',3,3'-tetrahydro[5,5']biindenyl-2,2',2,2'-tetracarboxylate
95	2-(Diphenylphosphino)ethylamine
96	2-[2-(Diphenylphosphino)ethyl]pyridine

1 – 24: Monodentate dialkyl biaryl phosphine ligands; **25 – 48**: Monodentate trialkyl and dialkylaryl phosphine ligands; **49 – 72**: Monodentate triaryl and diarylalkylphosphine ligands; **73 – 96**: Bidentate electron-poor phosphine ligands.

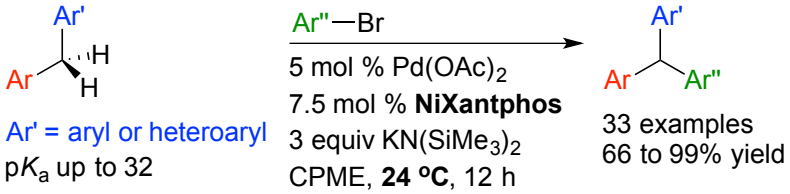
Ligand libraries (97 – 112)

97	2-Dicyclohexylphosphino-2',4',6'-tri-i-propyl-1,1'-biphenyl (XPhos)
98	2-Dicyclohexylphosphino-2',6'-dimethoxy-1,1'-biphenyl (SPhos)
99	2-(Di-*t*-butylphosphino)biphenyl (JohnPhos)
100	2-Dicyclohexylphosphino-2'-(*N*,*N*-dimethylamino)biphenyl (DavePhos)
101	2-Dicyclohexylphosphino-2',6'-di-i-propoxy-1,1'-biphenyl (RuPhos)
102	2-Di-*t*-butylphosphino-3,4,5,6-tetramethyl-2',4',6'-triisopropyl-1,1'-biphenyl (Me-4-*t*Bu-XPhos)
103	Dicyclohexyl-[3,6-dimethoxy-2-(2,4,6-triisopropylphenyl)phenyl]phosphane (BrettPhos)

104	Butyldi-1-adamantylphosphine (cataCXium A)
105	1,2,3,4,5-Pentaphenyl-1'-(di-*t*-butylphosphino)ferrocene (QPhos)
106	Tri-*t*-butylphosphonium tetrafluoroborate
107	(4-(*N*,*N*-dimethylamino)phenyl)di-*t*-butyl phosphine (AmPhos)
108	1,1'-Bis(di-*t*-butylphosphino)ferrocene (dtbpf)
109	1,1'-Bis(diphenylphosphino)ferrocene (dppf)
110	1,1'-Bis(diisopropylphosphino)ferrocene (dippf)
111	(*R*)-(+)-2,2'-Bis(diphenylphosphino)-1,1'-binaphthyl ((R)-BINAP)
112	(R)-(-)-1-[(S)-2-(Dicyclohexylphosphino)ferrocenyl]ethyldi-*t*-butylphosphine (JosiPhos SL-J009-1)

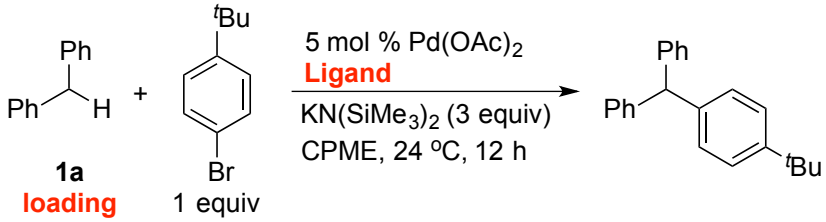
97 – 108: Monodentate phosphine ligands; **109 – 112**: Bidentate and monodentate phosphine ligands.

(1) Ligand Screening for the Cross-Coupling of Diphenylmethane with 1-Bromo-4-*tert*-butylbenzene:



NiXantphos was found to be the best ligand from the 112 ligands examined. See HTE details in reference 3.

(2) Ligand Comparison for the Cross-Coupling of Diphenylmethane with 1-Bromo-4-*tert*-butylbenzene:



Ligands examined (×7): NiXantphos, Xantphos, DPEPhos, dippp, XPhos, SPhos, PCy_3.

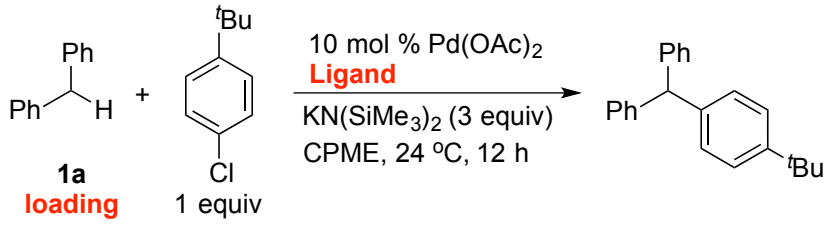
1a loadings examined (×2): 1.2 equiv, 3 equiv.

The lead hits from the screening were the combination of **1.2 equiv** of **1a** and **NiXantphos**, and the combination of **3 equiv** of **1a** and **NiXantphos**, both giving 100% assay yield of the desired DCCP product **3aa**.

1a loading

Ligand	1.2 equiv	3 equiv
NiXantphos	100	100
Xantphos	13	16
DPEPhos	3	7
dippp	0	0
XPhos	1	2
SPhos	1	2
PCy_3	3	2

(3) Ligand Comparison for the Cross-Coupling of Diphenylmethane with 1-*tert*-Butyl-4-chlorobenzene:



Ligands examined (×8): NiXantphos, *N*-Bn-NiXantphos, Xantphos, DPEPhos, dippp, XPhos, SPhos, PCy_3.

1a loadings examined (×3): 1.2 equiv, 2 equiv, 3 equiv.

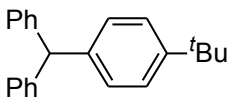
The lead hits from the screening were the combination of **1.2 equiv** of **1a** and **NiXantphos**, giving 91% assay yield of the desired DCCP product **3aa**.

	1a loading		
Ligand	1.2 equiv	2 equiv	3 equiv
NiXantphos	91	85	64
N-Bn-NiXantphos	1	2	1
Xantphos	0	0	0
DPEPhos	0	0	0
dippp	0	0	0
XPhos	1	3	2
SPhos	1	3	2
PCy_3	0	0	0

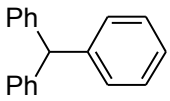
Procedure and Characterization for the Pd-Catalyzed DCCP of Aryl Chlorides.

General Procedure I: An oven-dried 10 mL reaction vial equipped with a stir bar was charged with $KN(SiMe_3)_2$ (59.8 mg, 0.30 mmol, 3 equiv) under a nitrogen atmosphere. A solution (from a stock solution) of $Pd(OAc)_2$ (0.56 mg, 0.0025 mmol, 2.5 mol %) and NiXantphos (2.76 mg, 0.0050 mmol, 5 mol %) in 0.5 mL of dry THF was taken up by syringe and added to the reaction vial. After stirring for 5 min at 24 °C, diphenylmethane (16.7 μL, 0.1 mmol, 1 equiv) was added to the reaction mixture followed by 1-*tert*-butyl-4-chlorobenzene (33.4 μL, 0.2 mmol, 2 equiv). Note that the aryl chloride in a solid form was added to the reaction vial prior to $KN(SiMe_3)_2$. The reaction mixture was stirred for 12 h at 24 °C, quenched with three drops of H_2O, diluted with 3 mL of ethyl acetate, and filtered over a pad of $MgSO_4$ and silica. The pad was rinsed with additional ethyl acetate, and the solution was concentrated in vacuo. The crude material was loaded onto a silica gel column and purified by flash chromatography.

General Procedure II: Under a nitrogen atmosphere a solution (from a stock solution) of $Pd(OAc)_2$ (1.12 mg, 0.0050 mmol, 5 mol %) and NiXantphos (5.52 mg, 0.010 mmol, 10 mol %) in 0.5 mL of dry THF was taken up by syringe and added to an oven-dried 10 mL reaction vial equipped with a stir bar. The solvent was removed under reduced pressure, and $KN(SiMe_3)_2$ (59.8 mg, 0.30 mmol, 3 equiv) was then added to the reaction vial followed by 0.5 mL of dry CPME (or 2-MeTHF). After stirring for 5 min at 24 °C, diphenylmethane (16.7 μL, 0.1 mmol, 1 equiv) was added to the reaction mixture followed by 1-*tert*-butyl-4-chlorobenzene (33.4 μL, 0.2 mmol, 2 equiv). Note that the aryl chloride in a solid form was added to the reaction vial prior to $KN(SiMe_3)_2$. The reaction mixture was stirred for 12 h at 24 °C, quenched with three drops of H_2O, diluted with 3 mL of ethyl acetate, and filtered over a pad of $MgSO_4$ and silica. The pad was rinsed with additional ethyl acetate, and the solution was concentrated in vacuo. The crude material was loaded onto a silica gel column and purified by flash chromatography.

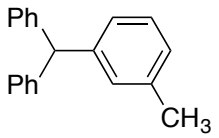


3aa – (4-*tert*-Butylphenyl)diphenylmethane: The reaction was performed following General Procedure I with **1a** (16.7 μL, 0.1 mmol, 1 equiv), $KN(SiMe_3)_2$ (59.8 mg, 0.30 mmol, 3 equiv) and **2a** (33.4 μL, 0.2 mmol, 2 equiv) in the presence of 2.5 mol % Pd catalyst in THF at 24 °C. The crude material was purified by flash chromatography on silica gel (eluted with hexanes to EtOAc:hexanes = 2:98) to give the product (24.3 mg, 81% yield) as a white solid. R_f = 0.33 (hexanes); The NMR spectral data match the previously published data.[3]

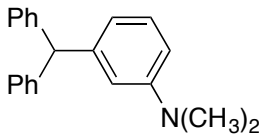


3ab – Triphenylmethane: The reaction was performed following General Procedure I with **1a** (16.7 μL, 0.1 mmol, 1 equiv), $KN(SiMe_3)_2$ (59.8 mg, 0.30 mmol, 3 equiv) and **2b** (20.4 μL, 0.2

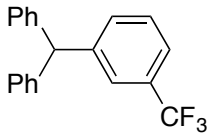
mmol, 2 equiv) in the presence of 2.5 mol % Pd catalyst in THF at 24 °C. The crude material was purified by flash chromatography on silica gel (eluted with hexanes to EtOAc:hexanes = 2:98) to give the product (23.4 mg, 96% yield) as a white solid. R_f = 0.40 (hexanes). The NMR spectral data match the previously published data.[3]



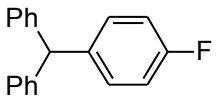
3ac – (3-Methylphenyl)diphenylmethane: The reaction was performed following General Procedure I with **1a** (16.7 μL, 0.1 mmol, 1 equiv), $KN(SiMe_3)_2$ (59.8 mg, 0.30 mmol, 3 equiv) and **2c** (23.6 μL, 0.2 mmol, 2 equiv) in the presence of 2.5 mol % Pd catalyst in THF at 24 °C. The crude material was purified by flash chromatography on silica gel (eluted with hexanes to EtOAc:hexanes = 2:98) to give the product (23.5 mg, 91% yield) as a white solid. R_f = 0.30 (hexanes); m.p. data for the title compound have been reported;[4] ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.30 – 7.25 (m, 4H), 7.22 – 7.14 (m, 3H), 7.14 – 7.09 (m, 4H), 7.02 (d, J = 7.5 Hz, 1H), 6.95 (s, 1H), 6.90 (d, J = 8.0 Hz, 1H), 5.51 (s, 1H), 2.28 (s, 3H) ppm; $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 144.2, 144.0, 138.1, 130.4, 129.7, 128.5, 128.4, 127.3, 126.7, 126.4, 57.0, 21.7 ppm; IR (thin film): 3084, 3060, 3025, 2921, 1600, 1494, 1450, 1031, 774, 748, 730, 699 cm^{-1}; HRMS calc'd for $C_{20}H_{18}^+$ 258.1409, observed 258.1404 $[M]^+$.



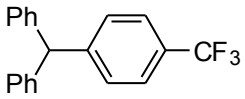
3ad – (3-Dimethylaminophenyl)diphenylmethane: The reaction was performed following General Procedure I with **1a** (16.7 μL, 0.1 mmol, 1 equiv), $KN(SiMe_3)_2$ (59.8 mg, 0.30 mmol, 3 equiv) and **2d** (27.9 μL, 0.2 mmol, 2 equiv) in the presence of 5 mol % Pd catalyst in THF at 24 °C. The crude material was purified by flash chromatography on silica gel (eluted with EtOAc:hexanes = 2:98) to give the product (27.0 mg, 94% yield) as a colorless oil. R_f = 0.30 (EtOAc:hexanes = 5:95). The NMR spectral data match the previously published data.[5]



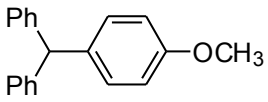
3ae – (3-Trifluoromethylphenyl)diphenylmethane: The reaction was performed following General Procedure I with **1a** (20.1 μL, 0.12 mmol, 1.2 equiv), $KN(SiMe_3)_2$ (59.8 mg, 0.30 mmol, 3 equiv) and **2e** (13.6 μL, 0.1 mmol, 1 equiv) in the presence of 5 mol % Pd catalyst in THF at 24 °C. The crude material was purified by flash chromatography on silica gel (eluted with hexanes to EtOAc:hexanes = 2:98) to give the product (25.6 mg, 82% yield) as a colorless oil. R_f = 0.30 (hexanes). The ^{1}H NMR spectrum matches the previously published report.[6] The ^{13}C NMR spectrum of the title compound was not reported before. $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 145.1, 143.2, 133.0, 130.9 (q, J = 32 Hz), 129.6, 129.0, 128.8, 126.9, 126.3 (q, J = 4 Hz), 124.4 (q, J = 273 Hz), 123.5 (q, J = 4 Hz), 56.8 ppm.



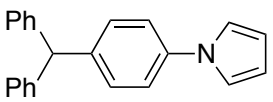
3af – (4-Fluorophenyl)diphenylmethane: The reaction was performed following General Procedure I with **1a** (16.7 μL, 0.1 mmol, 1 equiv), $KN(SiMe_3)_2$ (59.8 mg, 0.30 mmol, 3 equiv) and **2f** (21.3 μL, 0.2 mmol, 2 equiv) in the presence of 10 mol % Pd catalyst in THF at 24 °C. The crude material was purified by flash chromatography on silica gel (eluted with hexanes to EtOAc:hexanes = 2:98) to give the product (24.4 mg, 93% yield) as a white solid. R_f = 0.33 (hexanes). The NMR spectral data match the previously published data.[3]



3ag – (4-Trifluoromethylphenyl)diphenylmethane: The reaction was performed following General Procedure II with **1a** (66.9 μL, 0.40 mmol, 4 equiv), $KN(SiMe_3)_2$ (39.9 mg, 0.20 mmol, 2 equiv) and **2g** (14.0 μL, 0.1 mmol, 1 equiv) in the presence of 10 mol % Pd catalyst in CPME at 24 °C. The crude material was purified by flash chromatography on silica gel (eluted with hexanes to EtOAc:hexanes = 2:98) to give the product (27.8 mg, 89% yield) as a colorless oil. R_f = 0.33 (hexanes). The NMR spectral data match the previously published data.[3]

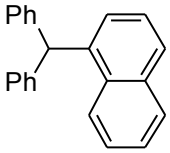


3ah – (4-Methoxyphenyl)diphenylmethane: The reaction was performed following General Procedure I with **1a** (16.7 μL, 0.1 mmol, 1 equiv), $KN(SiMe_3)_2$ (59.8 mg, 0.30 mmol, 3 equiv) and **2h** (24.5 μL, 0.2 mmol, 2 equiv) in the presence of 10 mol % Pd catalyst in THF at 80 °C. The crude material was purified by flash chromatography on silica gel (eluted with hexanes to EtOAc:hexanes = 5:95) to give the product (27.4 mg, 99% yield) as a colorless oil. R_f = 0.25 (hexanes). The NMR spectral data match the previously published data.[3]

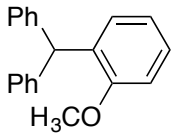


3ai – (4-(*N*-Pyrrolyl)phenyl)diphenylmethane: The reaction was performed following General Procedure I with **1a** (20.1 μL, 0.12 mmol, 1.2 equiv), $KN(SiMe_3)_2$ (59.8 mg, 0.30 mmol, 3 equiv) and **2i** (17.8 mg, 0.1 mmol, 1 equiv) in the presence of 5 mol % Pd catalyst in THF at 24 °C. The crude material was purified by flash chromatography on silica gel (eluted with hexanes to EtOAc:hexanes = 5:95) to give the product (30.9 mg, 99% yield) as a white solid. R_f = 0.40 (EtOAc:hexanes = 5:95); m.p. = 104–106 ºC; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.33 – 7.27 (m, 6H), 7.26 – 7.20 (m, 2H), 7.18 – 7.11 (m, 6H), 7.05 (t, J = 2.2 Hz, 2H), 6.32 (t, J = 2.2 Hz, 2H), 5.56 (s, 1H) ppm; $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 143.9, 141.6, 139.3, 130.7,

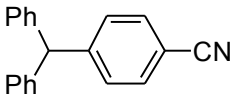
129.6, 128.6, 126.7, 120.6, 119.5, 110.5, 56.5 ppm; IR (thin film): 3025, 1519, 1491, 1329, 1070, 725, 700 cm^{-1}; HRMS calc'd for $C_{23}H_{20}N^+$ 310.1596, observed 310.1602 $[MH]^+$.



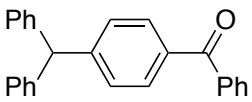
3aj – (1-Naphthyl)diphenylmethane: The reaction was performed following General Procedure II with **1a** (16.7 μL, 0.1 mmol, 1 equiv), $KN(SiMe_3)_2$ (59.8 mg, 0.30 mmol, 3 equiv) and **2j** (27.3 μL, 0.2 mmol, 2 equiv) in the presence of 10 mol % Pd catalyst in CPME at 80 °C. The crude material was purified by flash chromatography on silica gel (eluted with hexanes to EtOAc:hexanes = 3:97) to give the product (19.5 mg, 66% yield) as a white solid. R_f = 0.33 (hexanes). The NMR spectral data match the previously published data.[7]



3ak – (2-Methoxyphenyl)diphenylmethane: The reaction was performed following General Procedure II with **1a** (16.7 μL, 0.1 mmol, 1 equiv), $KN(SiMe_3)_2$ (59.8 mg, 0.30 mmol, 3 equiv) and **2k** (38.1 μL, 0.3 mmol, 3 equiv) in the presence of 5 mol % Pd catalyst in 2-MeTHF at 80 °C. The crude material was purified by flash chromatography on silica gel (eluted with hexanes to EtOAc:hexanes = 2:98) to give the product (15.3 mg, 56% yield) as a white solid. R_f = 0.40 (EtOAc:hexanes = 5:95). The NMR spectral data match the previously published data.[8]

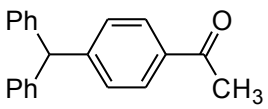


3al – (4-Cyanophenyl)diphenylmethane: The reaction was performed following General Procedure II with **1a** (20.1 μL, 0.12 mmol, 1.2 equiv), $KN(SiMe_3)_2$ (79.8 mg, 0.40 mmol, 4 equiv) and **2l** (13.8 mg, 0.1 mmol, 1 equiv) in the presence of 5 mol % Pd catalyst in 2-MeTHF at 24 °C. The crude material was purified by flash chromatography on silica gel (eluted with hexanes to EtOAc:hexanes = 2:98) to give the product (23.4 mg, 87% yield) as a colorless oil. R_f = 0.25 (hexanes). The NMR spectral data match the previously published data.[7]

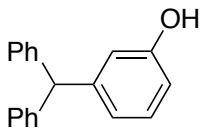


3am – 4-Benzhydrylbenzophenone: The reaction was performed following General Procedure II with **1a** (20.1 μL, 0.12 mmol, 1.2 equiv), $KN(SiMe_3)_2$ (59.8 mg, 0.30 mmol, 3 equiv) and **2m** (21.7 mg, 0.1 mmol, 1 equiv) in the presence of 5 mol % Pd catalyst in CPME at 24 °C. The crude material was purified by flash chromatography on silica gel (eluted with EtOAc:hexanes = 5:95 to 10:90) to give the product (32.9 mg, 94% yield) as a white solid. R_f = 0.25 (EtOAc:hexanes = 5:95). The ^1H NMR spectrum matches the previously published report.[9] The ^{13}C NMR spectrum of the title compound was not reported before. $^{13}C\{^1H\}$

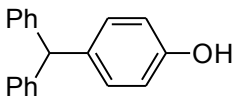
NMR (125 MHz, $CDCl_3$): δ 196.6, 149.1, 143.3, 137.9, 135.9, 132.5, 130.5, 130.2, 129.64, 129.60, 128.7, 128.4, 126.8, 57.1 ppm.



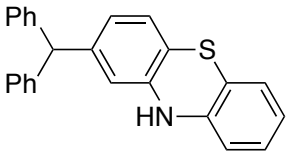
3an – (4-Acetylphenyl)diphenylmethane: The reaction was performed following General Procedure II with **1a** (50.2 μL, 0.3 mmol, 3 equiv), $KN(SiMe_3)_2$ (79.8 mg, 0.40 mmol, 4 equiv) and **2n** (13.0 μL, 0.1 mmol, 1 equiv) in the presence of 5 mol % Pd catalyst in CPME at 24 °C. The crude material was purified by flash chromatography on silica gel (eluted with hexanes to EtOAc:hexanes = 5:95) to give the product (16.9 mg, 59% yield) as a white solid. R_f = 0.33 (EtOAc:hexanes = 1:9). The NMR spectral data match the previously published data.[3]



3ao – (3-Hydroxyphenyl)diphenylmethane: The reaction was performed following General Procedure I with **1a** (50.2 μL, 0.3 mmol, 3 equiv), $KN(SiMe_3)_2$ (79.8 mg, 0.40 mmol, 4 equiv) and **2o** (10.6 μL, 0.1 mmol, 1 equiv) in the presence of 10 mol % Pd catalyst in THF at 80 °C. The crude material was purified by flash chromatography on silica gel (eluted with CH_2Cl_2) to give the product (21.9 mg, 84% yield) as a white solid. R_f = 0.35 (EtOAc:hexanes = 2:8); m.p. = 103–104 ºC; The measured m.p. data for the title compound match the previously published data;[10] ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.32 – 7.23 (m, 4H), 7.23 – 7.18 (m, 2H), 7.17 – 7.04 (m, 5H), 6.74 – 6.63 (m, 2H), 6.58 – 6.48 (m, 1H), 5.49 (s, 1H), 4.59 (s, 1H) ppm; $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 155.7, 146.1, 143.8, 129.7, 129.6, 128.5, 126.6, 122.3, 116.6, 113.5, 56.8 ppm; IR (thin film): 3400 (broad OH stretch), 3025, 1598, 1494, 1452, 698 cm^{-1}; HRMS calc'd for $C_{19}H_{16}O^+$ 260.1201, observed 260.1212 $[M]^+$.

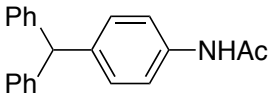


3ap – (4-Hydroxyphenyl)diphenylmethane: The reaction was performed following General Procedure I with **1a** (50.2 μL, 0.3 mmol, 3 equiv), $KN(SiMe_3)_2$ (79.8 mg, 0.40 mmol, 4 equiv) and **2p** (12.9 mg, 0.1 mmol, 1 equiv) in the presence of 10 mol % Pd catalyst in THF at 80 °C. The crude material was purified by flash chromatography on silica gel (eluted with EtOAc:hexanes = 5:95 to 1:9) to give the product (10.4 mg, 40% yield) as a white solid. R_f = 0.33 (EtOAc:hexanes = 2:8). The NMR spectral data match the previously published data.[3]

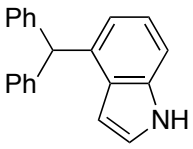


3aq – 2-Benzhydrylphenothiazine: The reaction was performed following General Procedure I with **1a** (16.7 μL, 0.1 mmol, 1 equiv), $KN(SiMe_3)_2$ (99.7 mg, 0.50 mmol, 5

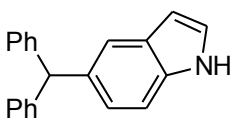
equiv) and **2q** (46.7 mg, 0.2 mmol, 2 equiv) in the presence of 5 mol % Pd catalyst in THF at 80 °C. The crude material was purified by flash chromatography on silica gel (eluted with EtOAc:hexanes = 5:95) to give the product (31.4 mg, 86% yield) as a white solid. R_f = 0.50 (EtOAc:hexanes = 1:9); m.p. = 175–178 ºC; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.31 – 7.25 (m, 4H), 7.23 – 7.18 (m, 2H), 7.13 – 7.05 (m, 4H), 6.95 (t, *J* = 7.5 Hz, 2H), 6.88 (d, *J* = 7.5 Hz, 1H), 6.79 (t, *J* = 7.5 Hz, 1H), 6.58 (dd, *J* = 7.5, 1.5 Hz, 1H), 6.46 (d, *J* = 7.5 Hz, 1H), 6.25 (d, *J* = 1.5 Hz, 1H), 5.67 (s, 1H), 5.39 (s, 1H) ppm; ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 143.9, 143.6, 141.82, 141.79, 129.6, 128.6, 127.5, 127.1, 126.8, 126.7, 124.1, 122.8, 118.5, 116.3, 115.8, 114.7, 56.4 ppm; IR (thin film): 3383 (broad NH stretch), 3024, 1567, 1462, 1431, 1305, 743, 700 cm^{-1}; HRMS calc'd for $C_{25}H_{19}NS^+$ 365.1238, observed 365.1228 $[M]^+$.



3ar – *N*-(4-Benzhydrylphenyl)acetamide: The reaction was performed following General Procedure I with **1a** (16.7 μL, 0.1 mmol, 1 equiv), $KN(SiMe_3)_2$ (99.7 mg, 0.50 mmol, 5 equiv) and **2r** (33.9 mg, 0.2 mmol, 2 equiv) in the presence of 10 mol % Pd catalyst in THF at 80 °C. The crude material was purified by flash chromatography on silica gel (eluted with EtOAc:hexanes = 3:7 to 1:1) to give the product (19.9 mg, 66% yield) as a white solid. R_f = 0.60 (EtOAc). The NMR spectral data match the previously published data.[8]

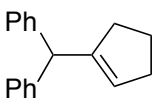


3as – 4-Benzhydryl-1*H*-indole: The reaction was performed following General Procedure II with **1a** (50.2 μL, 0.3 mmol, 3 equiv), $KN(SiMe_3)_2$ (79.8 mg, 0.40 mmol, 4 equiv) and **2s** (12.0 μL, 0.1 mmol, 1 equiv) in the presence of 10 mol % Pd catalyst in CPME at 80 °C. The crude material was purified by flash chromatography on silica gel (eluted with EtOAc:hexanes = 1:9) to give the product (15.5 mg, 55% yield) as a colorless oil. R_f = 0.12 (EtOAc:hexanes = 1:9); ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.11 (s, br, 1H), 7.30 – 7.23 (m, 5H), 7.22 – 7.15 (m, 6H), 7.12 – 7.06 (m, 2H), 6.64 (d, *J* = 7.5 Hz, 1H), 6.32 (m, 1H), 5.94 (s, 1H) ppm; ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 143.9, 136.4, 136.0, 129.7, 128.4, 127.7, 126.4, 123.9, 122.1, 120.6, 109.8, 102.0, 54.8 ppm; IR (thin film): 3419 (broad NH stretch), 3024, 1598, 1494, 1344, 1078, 753, 700 cm^{-1}; HRMS calc'd for $C_{21}H_{18}N^+$ 284.1439, observed 284.1453 $[MH]^+$.

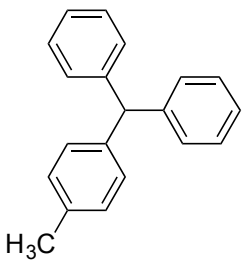


3at – 5-Benzhydryl-1*H*-indole: The reaction was performed following General Procedure I with **1a** (50.2 μL, 0.3 mmol, 3 equiv), $KN(SiMe_3)_2$ (79.8 mg, 0.40 mmol, 4 equiv) and **2t** (15.2 mg, 0.1 mmol, 1 equiv) in the presence of 10 mol % Pd catalyst in THF at 80 °C. The crude material was

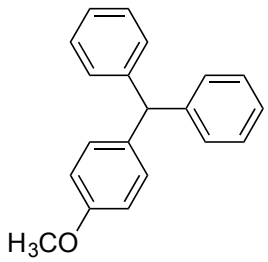
purified by flash chromatography on silica gel (eluted with hexanes to EtOAc:hexanes = 5:95 to 1:9) to give the product (16.4 mg, 58% yield) as a colorless oil. The NMR spectral data match the previously published data.[3]



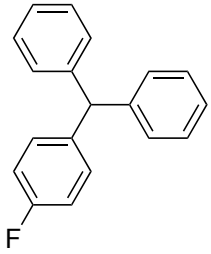
3au – 1-Benzhydrylcyclopent-1-ene: The reaction was performed following General Procedure II with **1a** (16.7 μL, 0.1 mmol, 1 equiv), $KN(SiMe_3)_2$ (59.8 mg, 0.30 mmol, 3 equiv) and **2u** (19.8 μL, 0.2 mmol, 2 equiv) in the presence of 2.5 mol % Pd catalyst in CPME at 80 °C. The crude material was purified by flash chromatography on silica gel (eluted with hexanes to EtOAc:hexanes = 0.5:99.5) to give the product (23.4 mg, 99% yield) as a colorless oil. R_f = 0.40 (hexanes); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.30 – 7.24 (m, 4H), 7.21 – 7.14 (m, 6H), 5.18 (m, 1H), 4.75 (s, 1H), 2.34 (m, 2H), 2.25 (m, 2H), 1.90 (m, 2H) ppm; $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 146.9, 143.2, 129.1, 128.6, 128.4, 126.4, 53.9, 35.2, 32.6, 24.0 ppm; IR (thin film): 3025, 2949, 2846, 1598, 1495, 1450, 1031, 744, 701 cm^{-1}; HRMS calc'd for $C_{18}H_{17}^+$ 233.1330, observed 233.1325 $[M-H]^+$.



3bb – (4-Methylphenyl)diphenylmethane: The reaction was performed following General Procedure I with **1b** (18.8 μL, 0.1 mmol, 1 equiv), $KN(SiMe_3)_2$ (59.8 mg, 0.30 mmol, 3 equiv) and **2b** (20.4 μL, 0.2 mmol, 2 equiv) in the presence of 5 mol % Pd catalyst in THF at 24 °C. The crude material was purified by flash chromatography on silica gel (eluted with hexanes to EtOAc:hexanes = 1:99) to give the product (22.4 mg, 87% yield) as a colorless oil. R_f = 0.25 (hexanes). The NMR spectral data match the previously published data.[3]

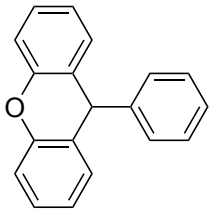


3cb – (4-Methoxyphenyl)diphenylmethane: The reaction was performed following General Procedure I with **1c** (18.9 μL, 0.1 mmol, 1 equiv), $KN(SiMe_3)_2$ (59.8 mg, 0.30 mmol, 3 equiv) and **2b** (20.4 μL, 0.2 mmol, 2 equiv) in the presence of 5 mol % Pd catalyst in THF at 24 °C. The crude material was purified by flash chromatography on silica gel (eluted with hexanes to EtOAc:hexanes = 2:98) to give the product (23.0 mg, 84% yield) as a colorless oil. R_f = 0.25 (EtOAc:hexanes = 2:98). The NMR spectral data match the previously published data.[3]

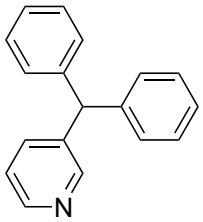


3db – (4-Fluorophenyl)diphenylmethane: The reaction was performed following General Procedure I with **1d** (18.6 μL, 0.1 mmol, 1 equiv), $KN(SiMe_3)_2$ (59.8 mg, 0.30 mmol, 3 equiv) and **2b** (20.4 μL, 0.2 mmol, 2 equiv) in the presence of 2.5 mol % Pd catalyst in THF at 24 °C.

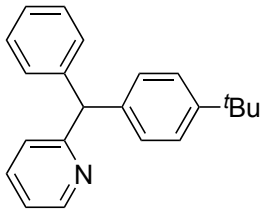
The crude material was purified by flash chromatography on silica gel (eluted with hexanes to EtOAc:hexanes = 2:98) to give the product (22.9 mg, 88% yield) as a white solid. R_f = 0.33 (hexanes). The NMR spectral data match the previously published data.[3]



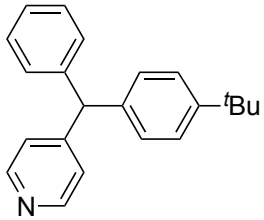
3eb – 9-Phenyl-9*H*-xanthene: The reaction was performed following General Procedure I with **1e** (18.2 mg, 0.1 mmol, 1 equiv), $KN(SiMe_3)_2$ (59.8 mg, 0.30 mmol, 3 equiv) and **2b** (20.4 μL, 0.2 mmol, 2 equiv) in the presence of 5 mol % Pd catalyst in THF at 24 °C. The crude material was purified by flash chromatography on silica gel (eluted with hexanes to EtOAc:hexanes = 5:95) to give the product (20.6 mg, 80% yield) as a white solid. R_f = 0.33 (EtOAc:hexanes = 2:98). The NMR spectral data match the previously published data.[11]



3fb – (3-Benzhydryl)pyridine: The reaction was performed following General Procedure I with **1f** (16.1 μL, 0.1 mmol, 1 equiv), $KN(SiMe_3)_2$ (59.8 mg, 0.30 mmol, 3 equiv) and **2b** (20.4 μL, 0.2 mmol, 2 equiv) in the presence of 5 mol % Pd catalyst in THF at 24 °C. The crude material was purified by flash chromatography on silica gel (eluted with EtOAc:hexanes = 2:8) to give the product (24.6 mg, 99% yield) as a white solid. R_f = 0.2 (EtOAc:hexanes = 2:98). The NMR spectral data match the previously published data.[8]



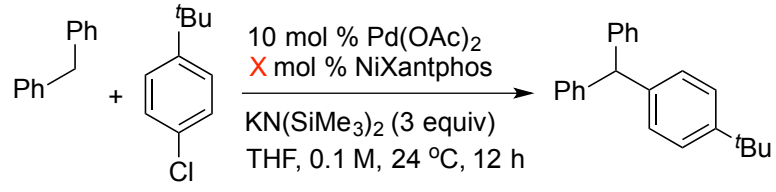
3ga – (4-*tert*-Butylphenyl)(2-pyridyl)phenylmethane: The reaction was performed following General Procedure I with **1g** (16.1 μL, 0.1 mmol, 1 equiv), $LiN(SiMe_3)_2$ (50.2 mg, 0.30 mmol, 3 equiv) and **2a** (33.4 μL, 0.2 mmol, 2 equiv) in the presence of 5 mol % Pd catalyst in THF at 24 °C. The crude material was purified by flash chromatography on silica gel (eluted with EtOAc:hexanes = 5:95 to 1:9) to give the product (23.5 mg, 78% yield) as a colorless oil. R_f = 0.30 (EtOAc:hexanes = 1:9). The NMR spectral data match the previously published data.[3]



3ha – (4-*tert*-Butylphenyl)(4-pyridyl)phenylmethane: The reaction was performed following General Procedure I with **1h** (15.9 μL, 0.095 mmol, 1 equiv), $LiN(SiMe_3)_2$ (50.2 mg, 0.30 mmol, 3 equiv) and **2a** (33.4 μL, 0.2 mmol, 2 equiv) in the presence of 5 mol % Pd catalyst in THF at 24 °C. The crude material was purified by flash

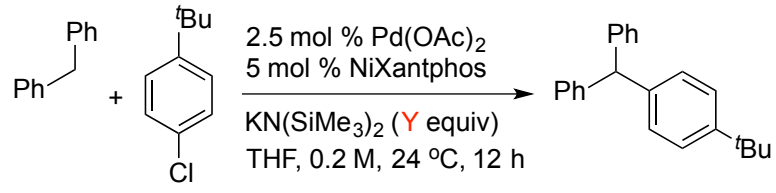
chromatography on silica gel (eluted with EtOAc:hexanes = 2:8) to give the product (21.7 mg, 76% yield) as a colorless oil. R_f = 0.20 (EtOAc:hexanes = 2:8). The NMR spectral data match the previously published data.[3]

Deviations from Standard Conditions for the Pd-Catalyzed DCCP of Aryl Chlorides.



1.2 equiv 1 equiv

X=20, Pd:L=1:2	**>95%**
X=15, Pd:L=1:1.5	67%
X=10, Pd:L=1:1	43%



1 equiv 2 equiv

Y=3	**91%**
Y=2	70%

Yield determined by ^{1}H NMR of the crude reaction mixture.

References.

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Crystal Structures.

Crystal structure of $[K(THF)_3{-}NiXantphos]_2$:

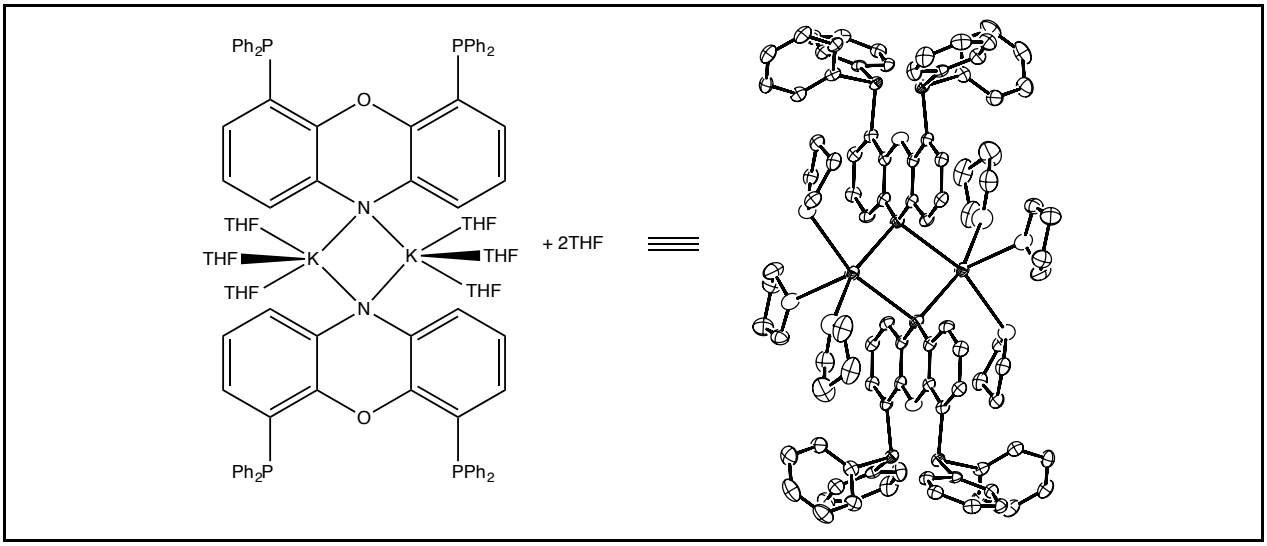


Table S3. lists cell information, data collection parameters, and refinement data.

Table S3. Summary of Structure Determination of $[K(THF)_3{-}NiXantphos]_2$

Empirical formula	$C_{52}H_{58}NP_2O_5K$
Formula weight	878.03
Temperature	100(1) K
Wavelength	0.71073 Å

Crystal system	triclinic
Space group	$P\bar{1}$
Cell constants:	
a	10.8873(6) Å
b	14.8827(9) Å
c	15.9049(9) Å
a	74.193(3)°
b	72.570(3)°
g	74.146(2)°
Volume	2313.7(2) $Å^3$
Z	2
Density (calculated)	1.260 Mg/m^3
Absorption coefficient	0.232 mm^{-1}
F(000)	932
Crystal size	0.42 x 0.15 x 0.04 mm^3
Theta range for data collection	1.78 to 25.45°
Index ranges	-13 £ h £ 13, -17 £ k £ 17, -19 £ l £ 19
Reflections collected	55008
Independent reflections	8300 [R(int) = 0.0498]
Completeness to theta = 25.45°	96.9 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7452 and 0.6170
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	8300 / 0 / 551
Goodness-of-fit on F^2	1.045
Final R indices [I>2sigma(I)]	R1 = 0.0578, wR2 = 0.1423
R indices (all data)	R1 = 0.0906, wR2 = 0.1718
Largest diff. peak and hole	0.651 and -0.474 e.$Å^{-3}$

Crystal structure of K(THF)(18-crown-6)−NiXantphos:

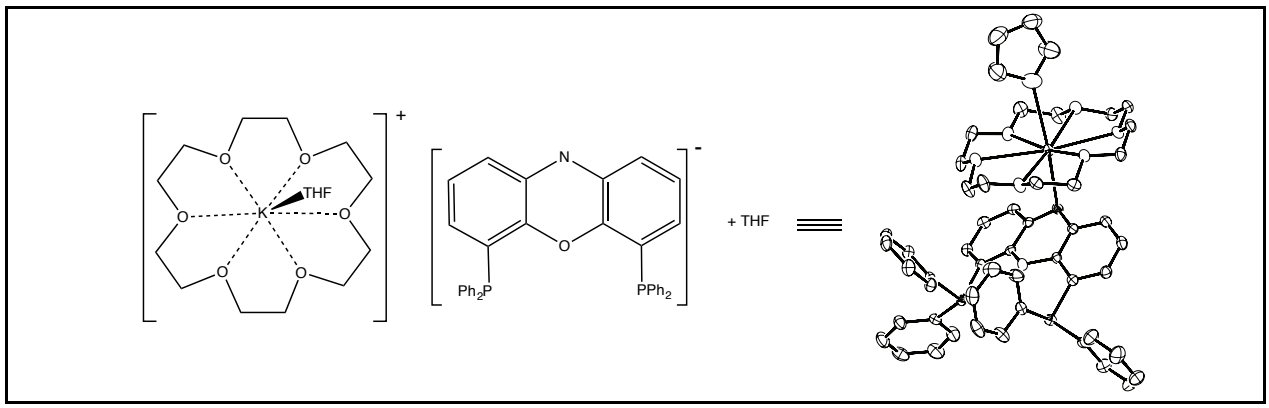


Table S4. lists cell information, data collection parameters, and refinement data.

Table S4. Summary of Structure Determination of K(THF)(18-crown-6)−NiXantphos

Empirical formula	$C_{56}H_{66}NP_2O_9K$
Formula weight	998.14
Temperature	100(1) K
Wavelength	0.71073 Å
Crystal system	monoclinic
Space group	$P2_1/n$
Cell constants:	
a	10.8453(7) Å
b	18.1426(13) Å
c	26.2160(17) Å
b	93.676(4)°
Volume	5147.7(6) $Å^3$
Z	4
Density (calculated)	1.288 Mg/m^3
Absorption coefficient	0.223 mm^{-1}
F(000)	2120
Crystal size	0.48 x 0.18 x 0.10 mm^3
Theta range for data collection	1.56 to 27.53°
Index ranges	-14 £ h £ 14, -23 £ k £ 23, -34 £ l £ 33
Reflections collected	131835
Independent reflections	11849 [R(int) = 0.0230]
Completeness to theta = 27.53°	99.8 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7456 and 0.6876
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	11849 / 70 / 632
Goodness-of-fit on F^2	1.028

Final R indices [I>2sigma(I)]	R1 = 0.0535, wR2 = 0.1391
R indices (all data)	R1 = 0.0602, wR2 = 0.1456
Largest diff. peak and hole	1.585 and -0.990 e.Å^{-3}

Crystal structure of (NiXantphos)Pd(Ph)(Cl):

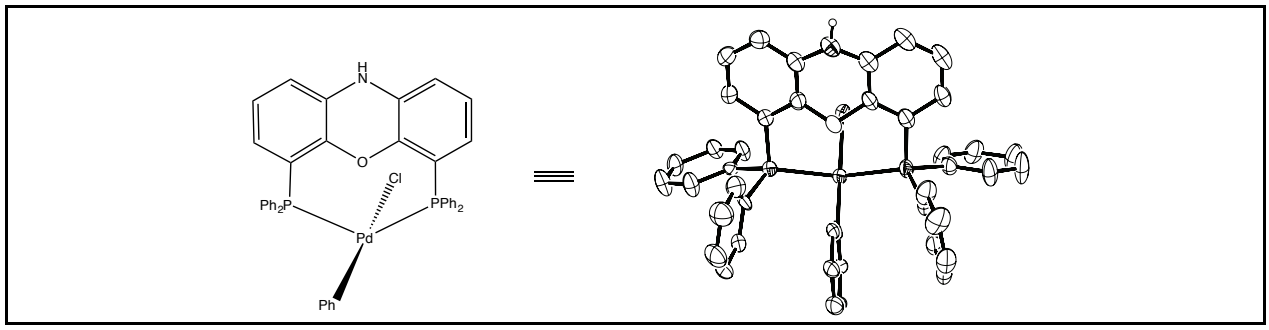


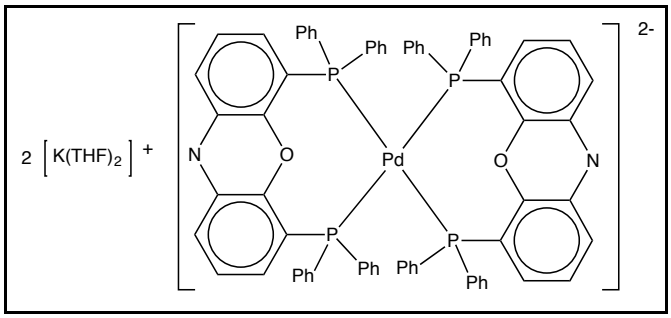
Table S5. lists cell information, data collection parameters, and refinement data.

Table S5. Summary of Structure Determination of (NiXantphos)Pd(Ph)(Cl)

Empirical formula	$C_{42}H_{32}P_2NPClPd$
Formula weight	770.48
Temperature	100(1) K
Wavelength	0.71073 Å
Crystal system	monoclinic
Space group	C2/c
Cell constants:	
a	39.5647(19) Å
b	12.2212(6) Å
c	24.1733(13) Å
b	124.594(2)°
Volume	9621.9(8) Å^3
Z	8
Density (calculated)	1.064 Mg/m^3
Absorption coefficient	0.533 mm^{-1}
F(000)	3136
Crystal size	0.14 x 0.04 x 0.02 mm^3
Theta range for data collection	1.69 to 27.59°
Index ranges	-51 £ h £ 51, -15 £ k £ 15, -31 £ l £ 31
Reflections collected	112434
Independent reflections	11102 [R(int) = 0.0703]
Completeness to theta = 27.59°	99.6 %
Absorption correction	Semi-empirical from equivalents

Max. and min. transmission	0.7456 and 0.6809
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	11102 / 570 / 528
Goodness-of-fit on F^2	1.073
Final R indices [I>2sigma(I)]	R1 = 0.0507, wR2 = 0.1313
R indices (all data)	R1 = 0.0727, wR2 = 0.1383
Largest diff. peak and hole	1.295 and -1.147 e.Å^{-3}

Crystal structure of $Pd[K(THF)_2(NiXantphos)]_2$:



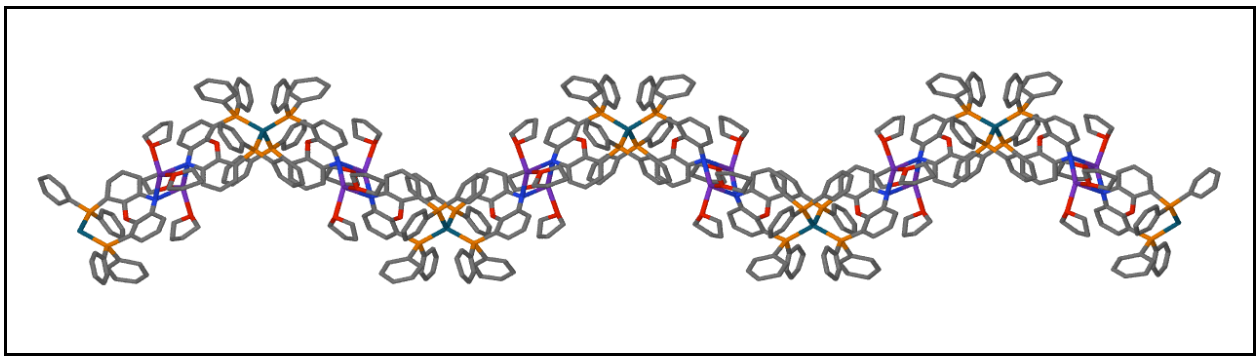


Figure S3a. Infinite chain of $Pd[K(THF)_2(NiXantphos)]_2$ complex - view is perpendicular to crystallographic 2-fold axis.

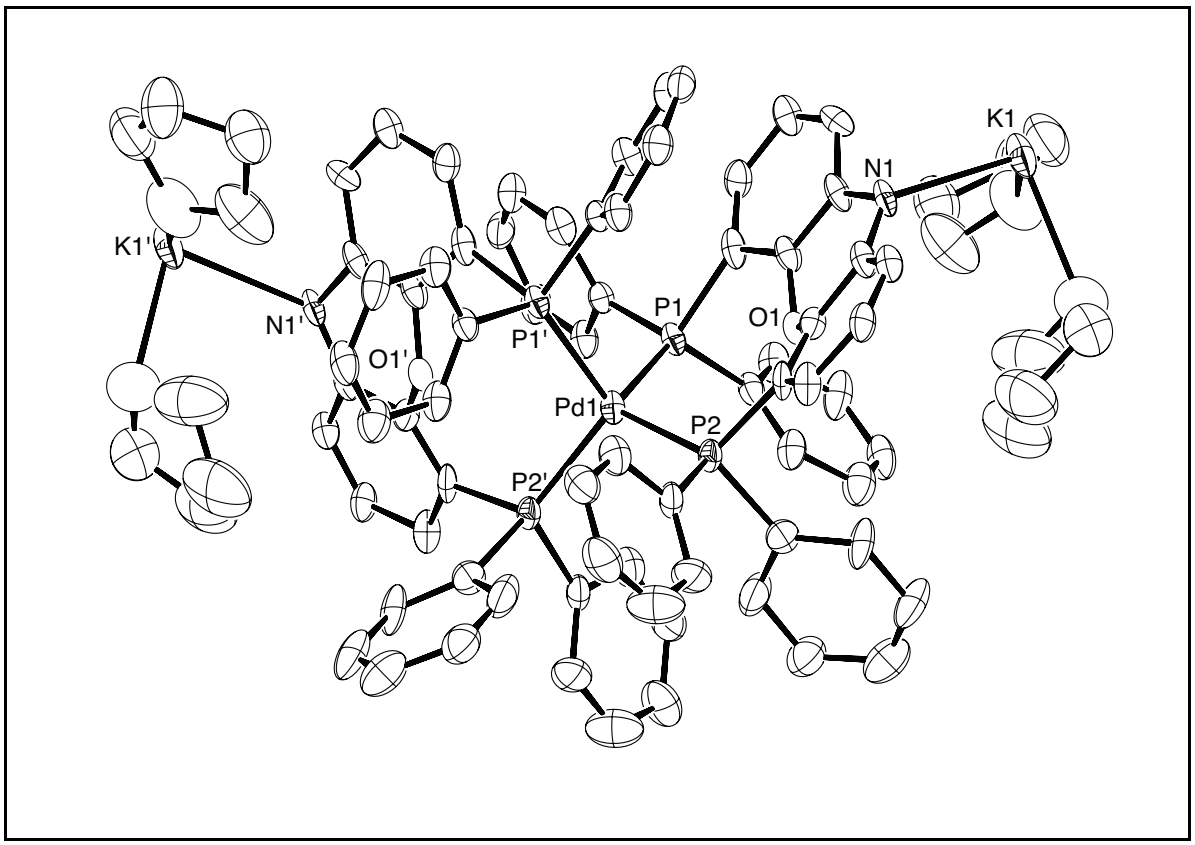


Figure S3b. ORTEP drawing of $Pd[K(THF)_2(NiXantphos)]_2$ with 30% probability thermal ellipsoids (the crystallographic 2-fold axis is vertical).

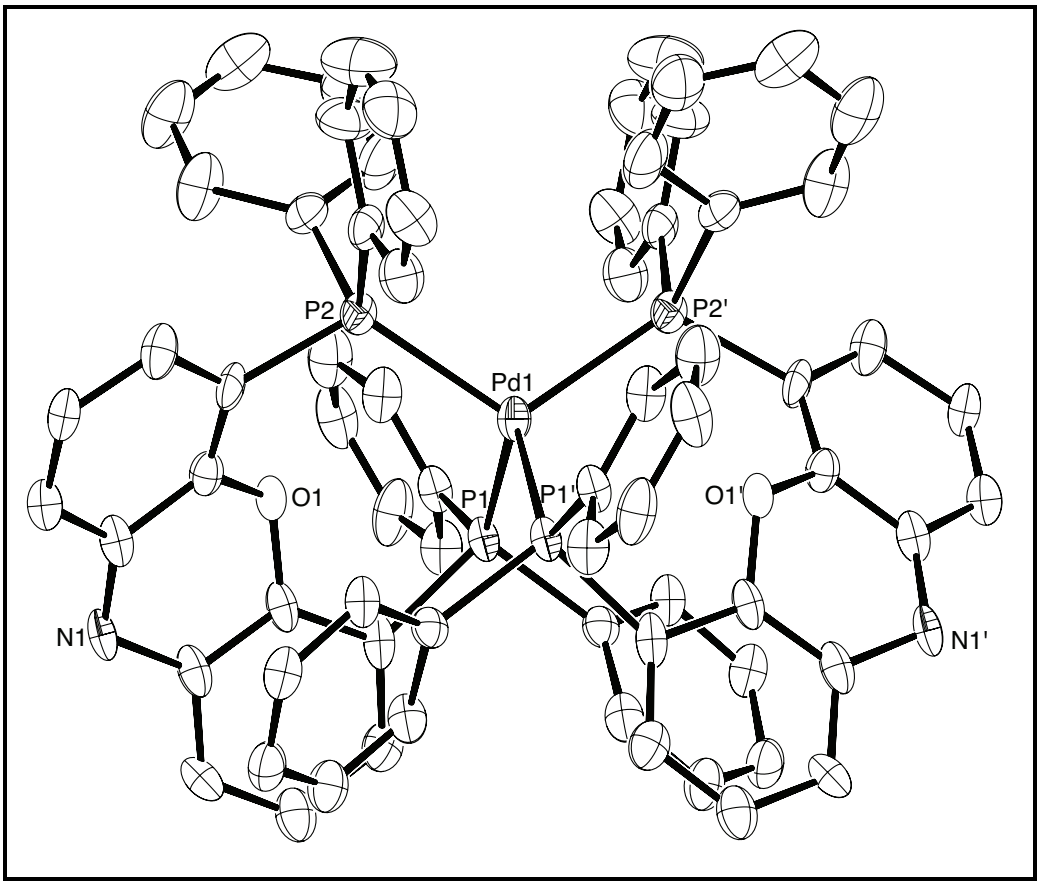


Figure S3c. ORTEP drawing of the palladium anionic complex, $Pd[(NiXantphos)]_2^{2-}$, with 30% probability thermal ellipsoids (the crystallographic 2-fold axis is vertical).

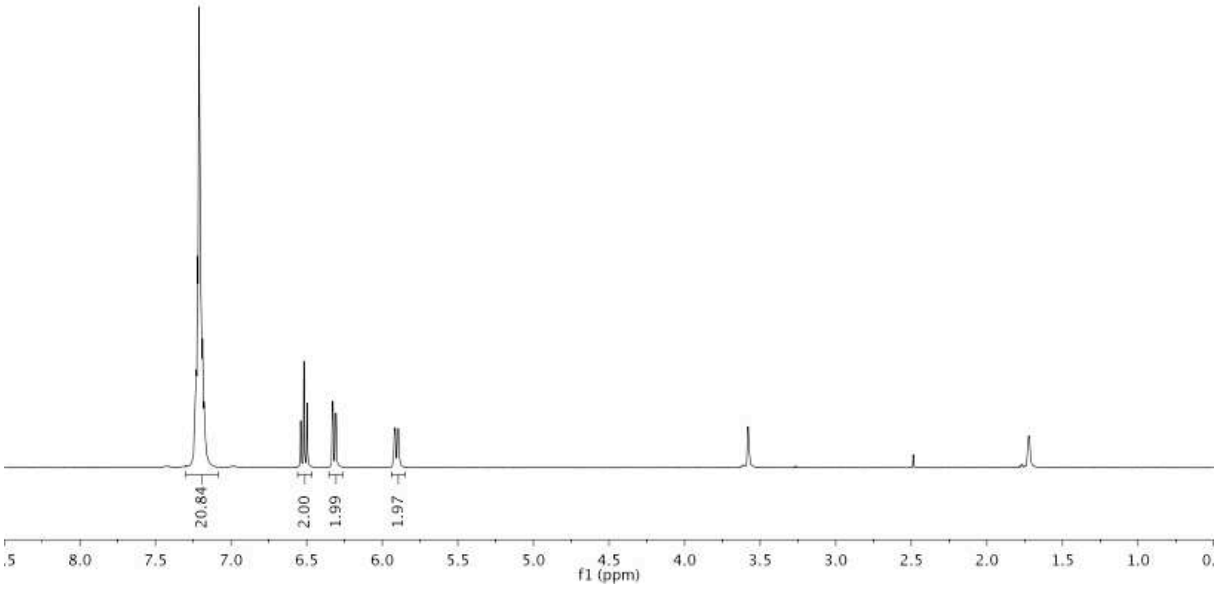
Table S6. Summary of Structure Determination of $Pd[K(THF)_2(NiXantphos)]_2$

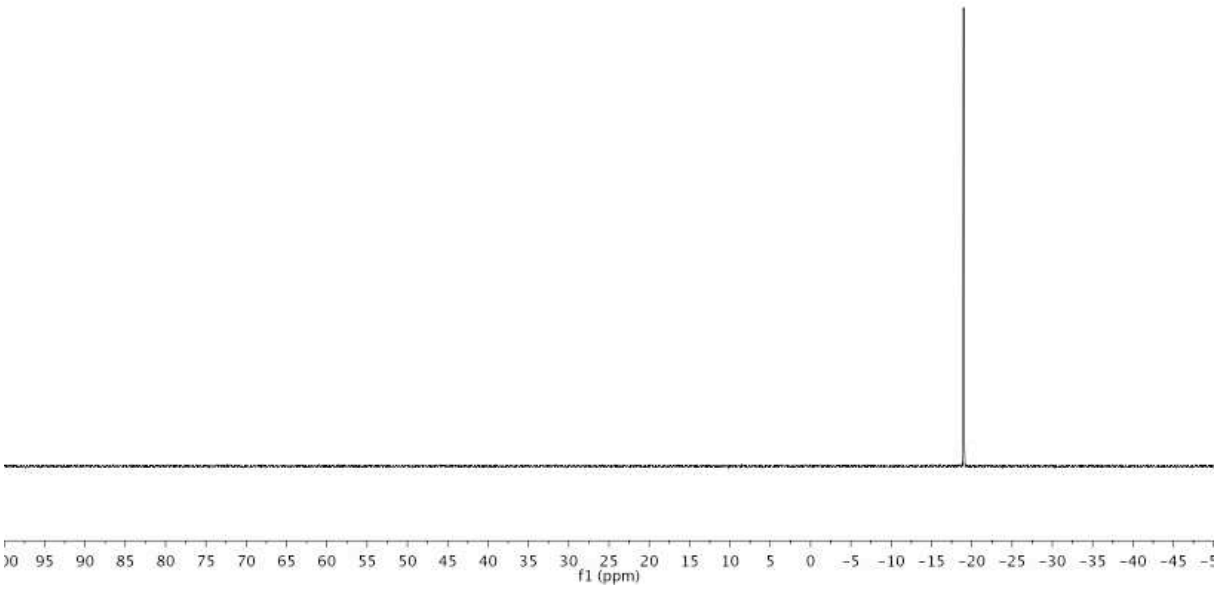
Empirical formula	$C_{88}H_{84}P_4N_2O_6K_2Pd$
Formula weight	1574.05
Temperature	100(1) K
Wavelength	0.71073 Å
Crystal system	monoclinic
Space group	C2/c
Cell constants:	
a	31.977(4) Å
b	14.9581(17) Å
c	23.583(3) Å
b	129.495(4)°
Volume	8704.6(18) $Å^3$
Z	4
Density (calculated)	1.201 Mg/m^3

Absorption coefficient	0.432 mm^{-1}
F(000)	3272
Crystal size	0.48 x 0.32 x 0.06 mm^3
Theta range for data collection	1.59 to 27.63°
Index ranges	-41 £ h £ 32, 0 £ k £ 19, 0 £ l £ 30
Reflections collected	97854
Independent reflections	10071 [R(int) = 0.1181]
Completeness to theta = 27.63°	99.3 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7456 and 0.5714
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	10071 / 127 / 475
Goodness-of-fit on F^2	1.297
Final R indices [I>2sigma(I)]	R1 = 0.1370, wR2 = 0.3553
R indices (all data)	R1 = 0.2019, wR2 = 0.3971
Largest diff. peak and hole	4.268 and -1.353 e.$Å^{-3}$

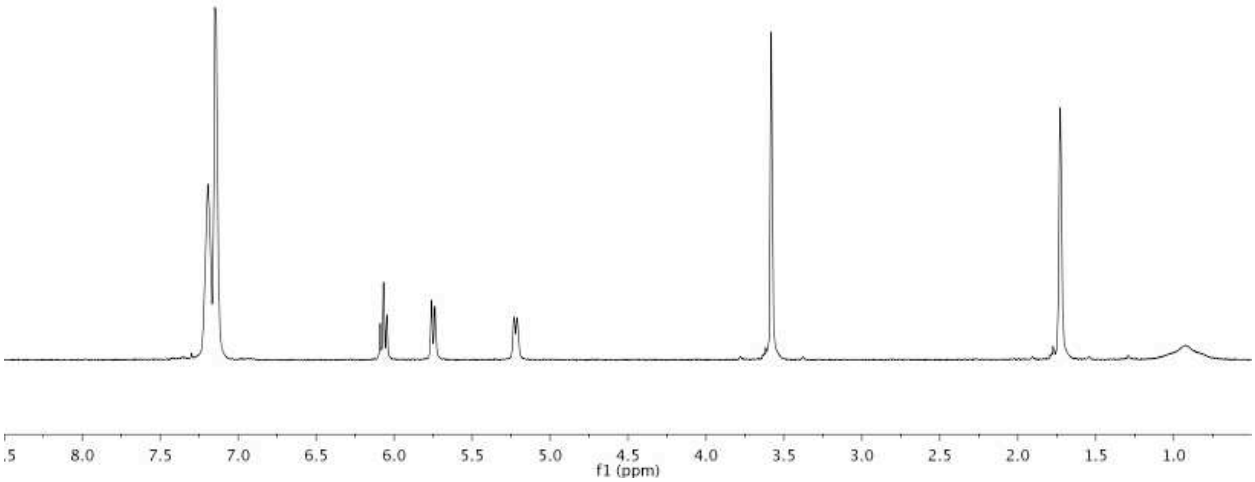
NMR Spectra.

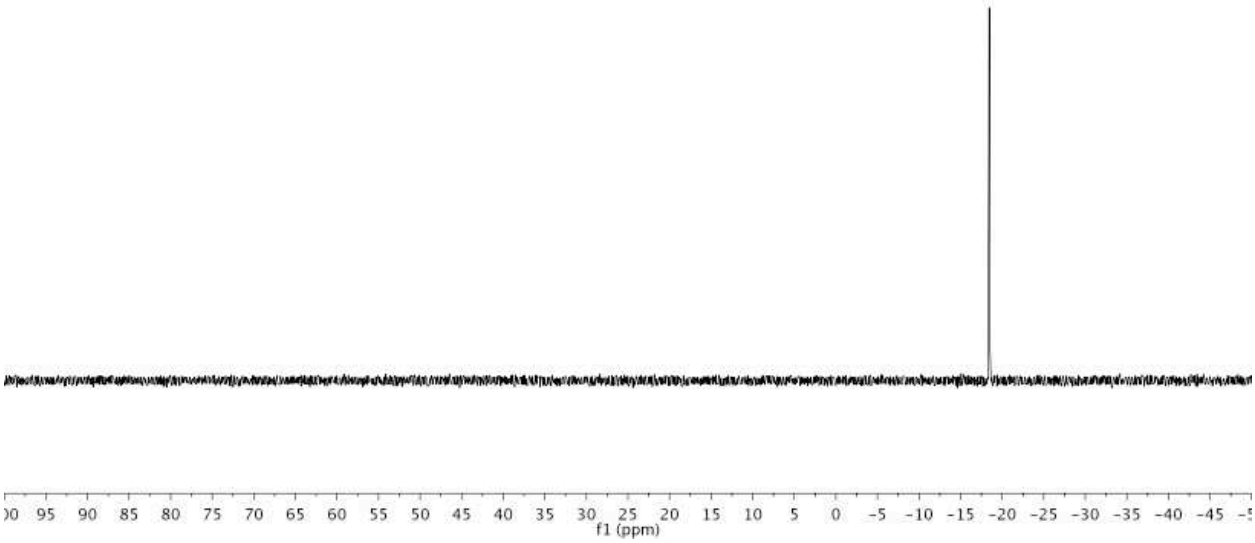
NiXantphos without base in THF-d_8



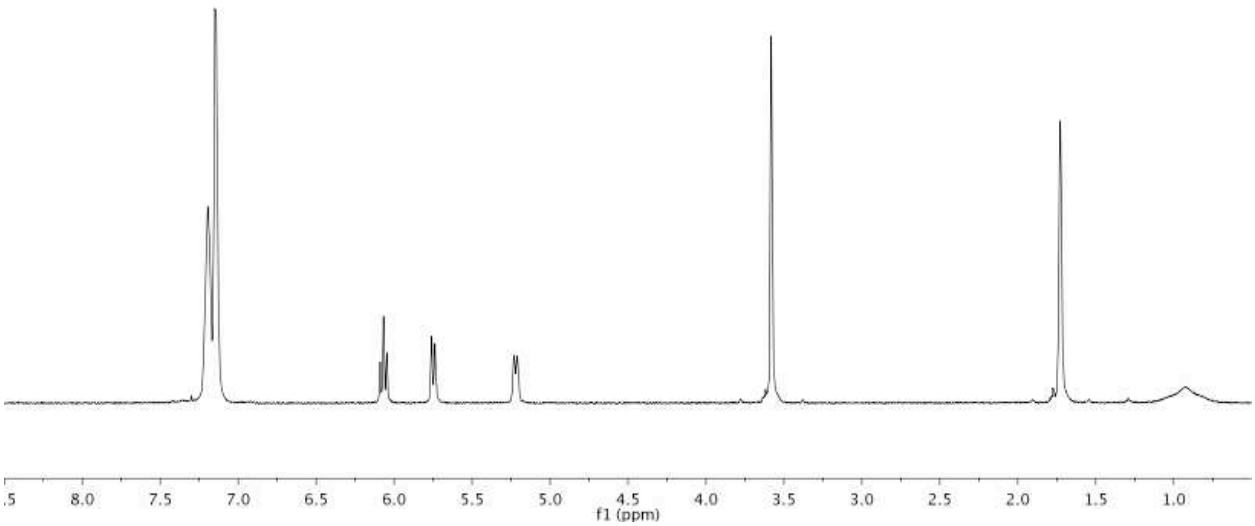


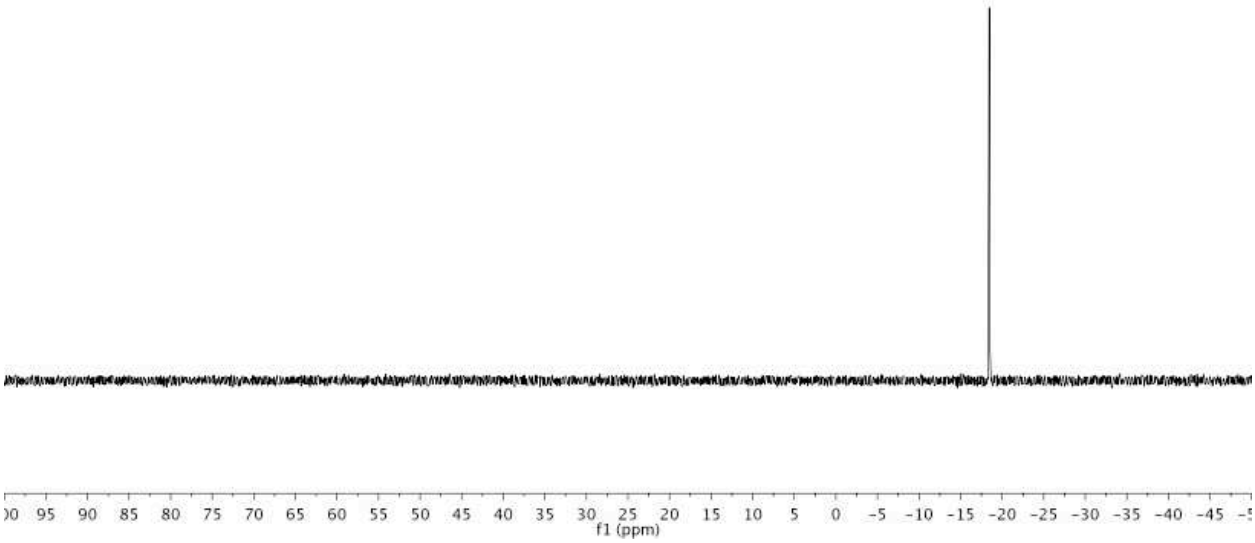
NiXantphos with 1.5 equiv $LiN(SiMe_3)_2$ in THF-d_8



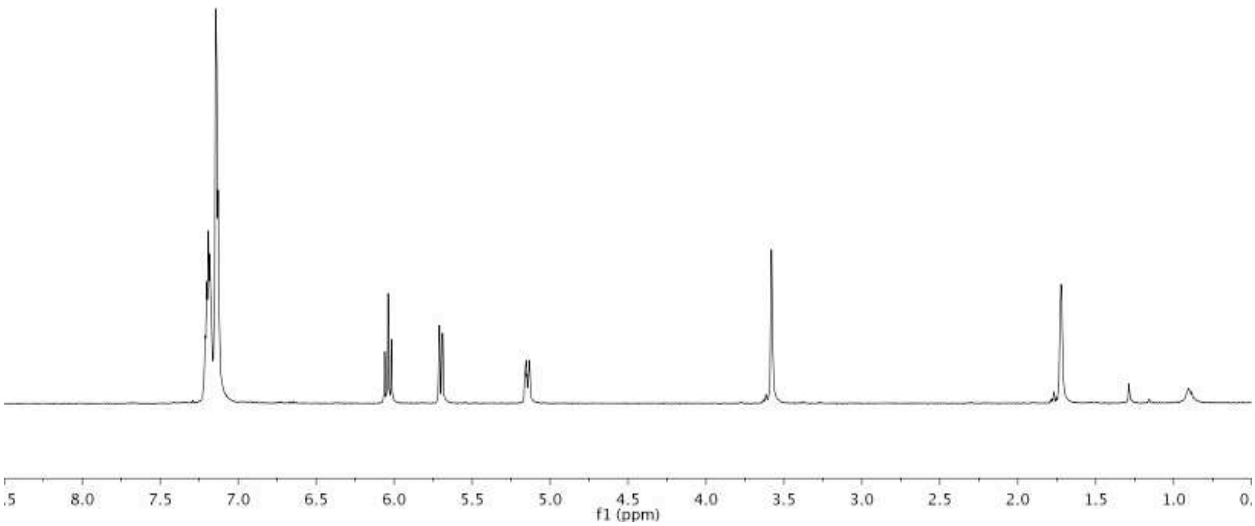


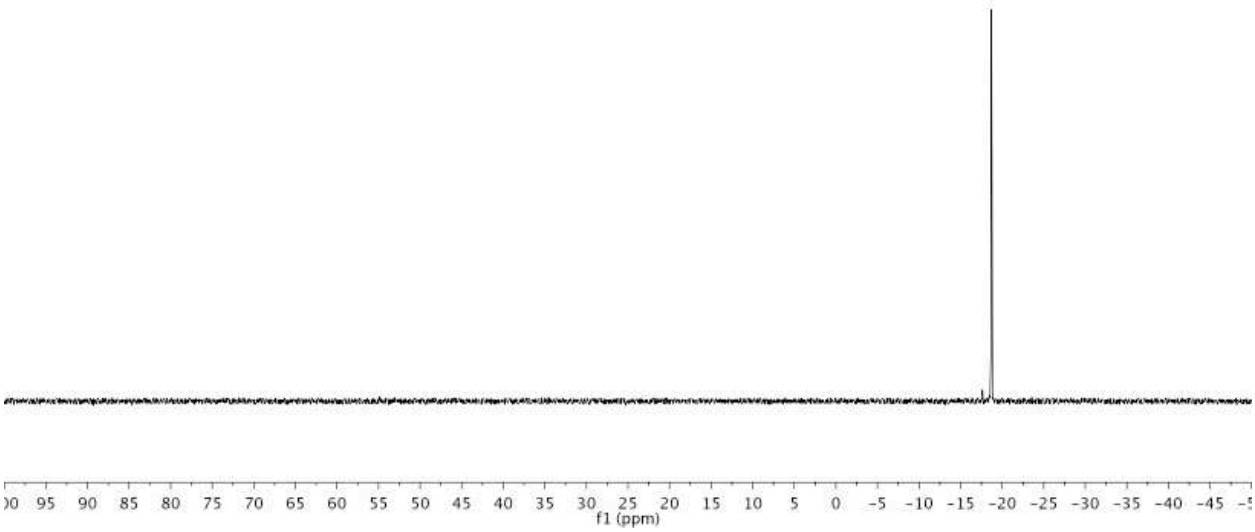
NiXantphos with 1.5 equiv $KN(SiMe_3)_2$ in THF-d_8



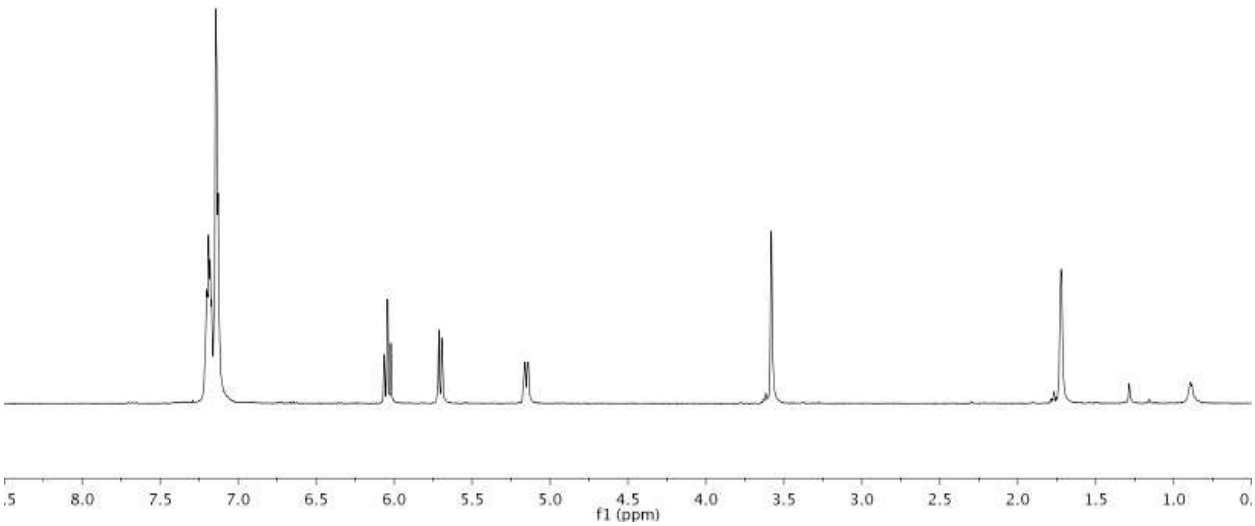


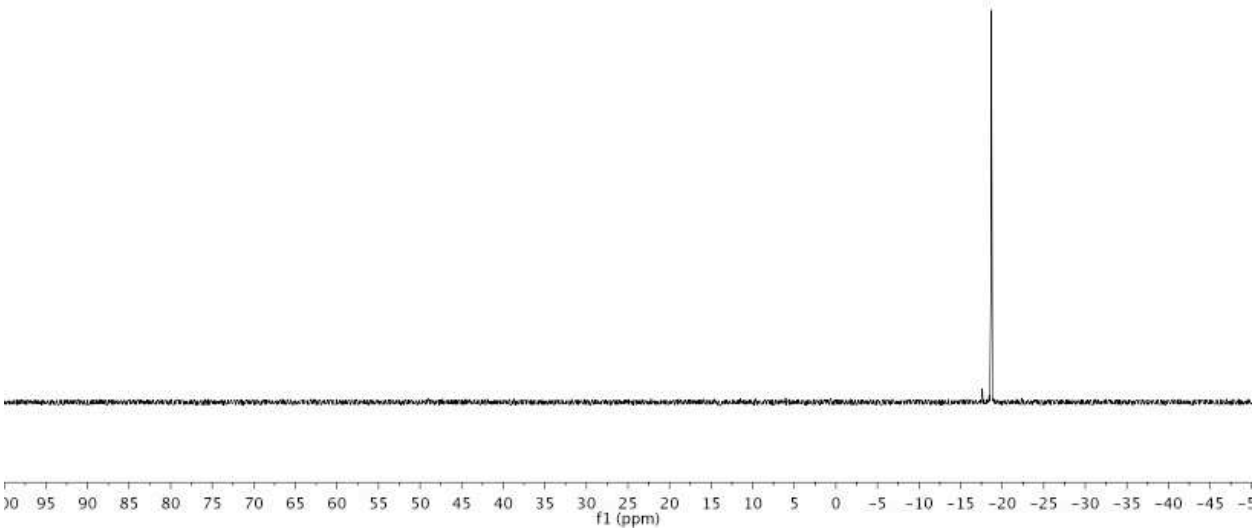
NiXantphos with 3 equiv $KN(SiMe_3)_2$ in THF-d_8



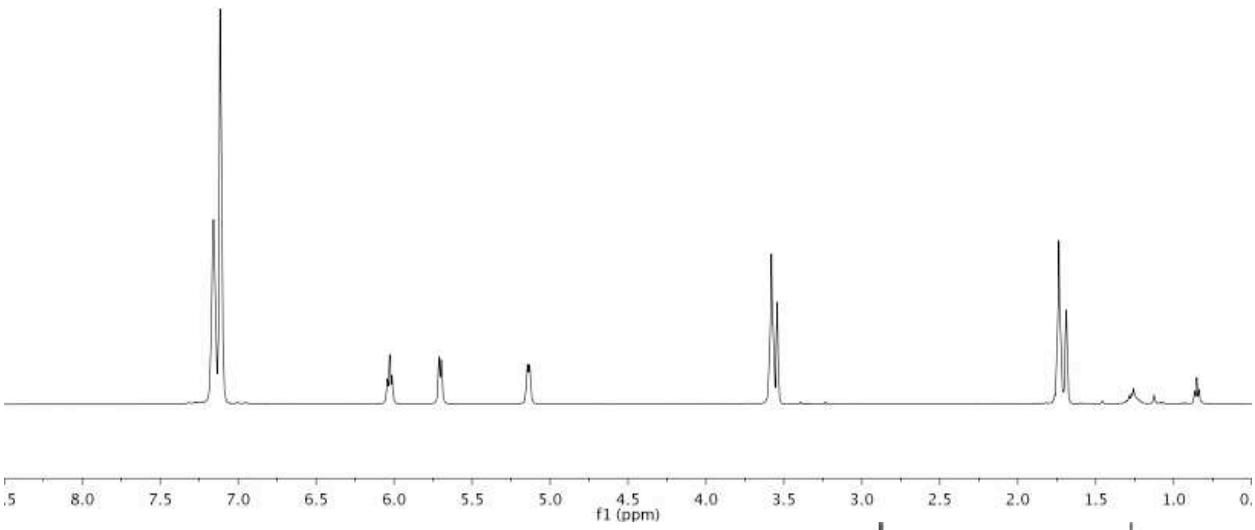


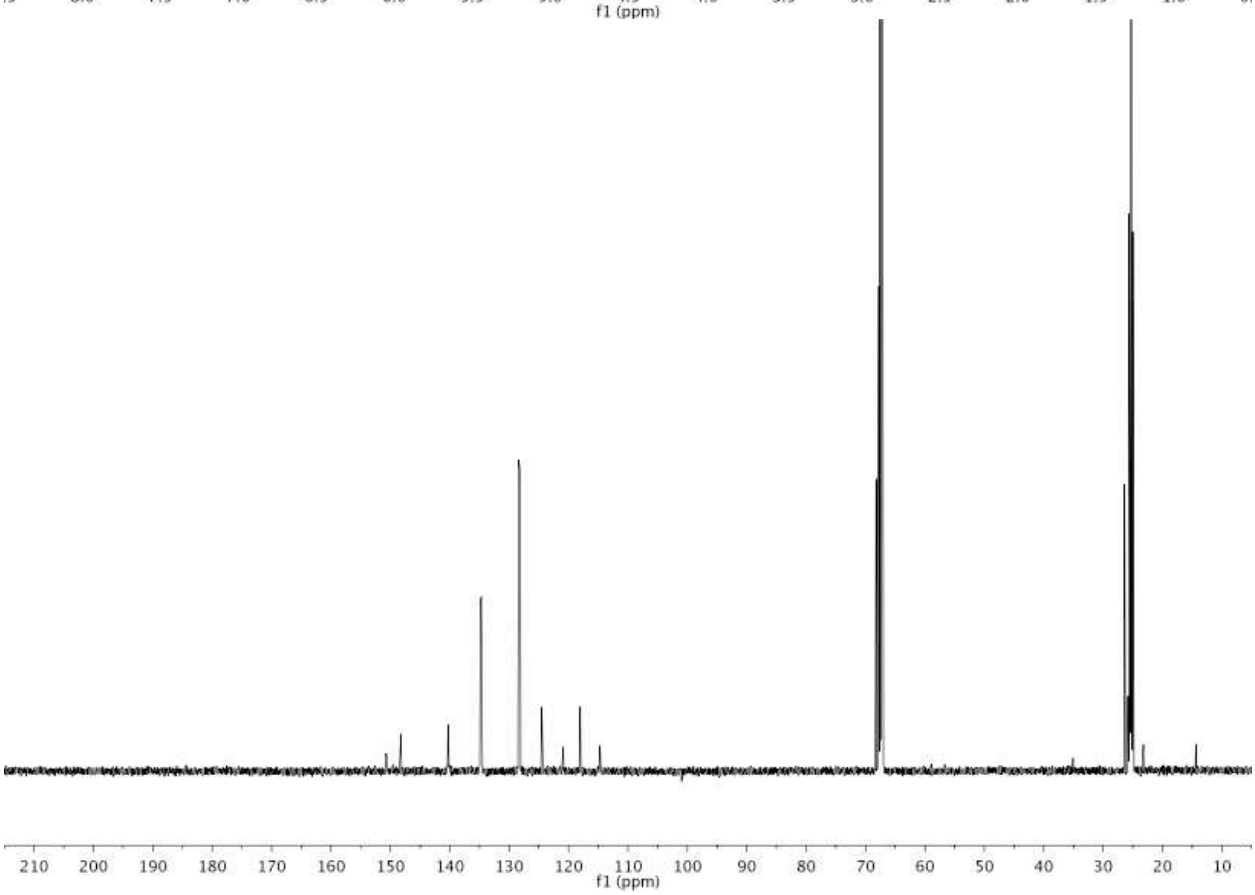
NiXantphos with 6 equiv $KN(SiMe_3)_2$ in THF-d_8

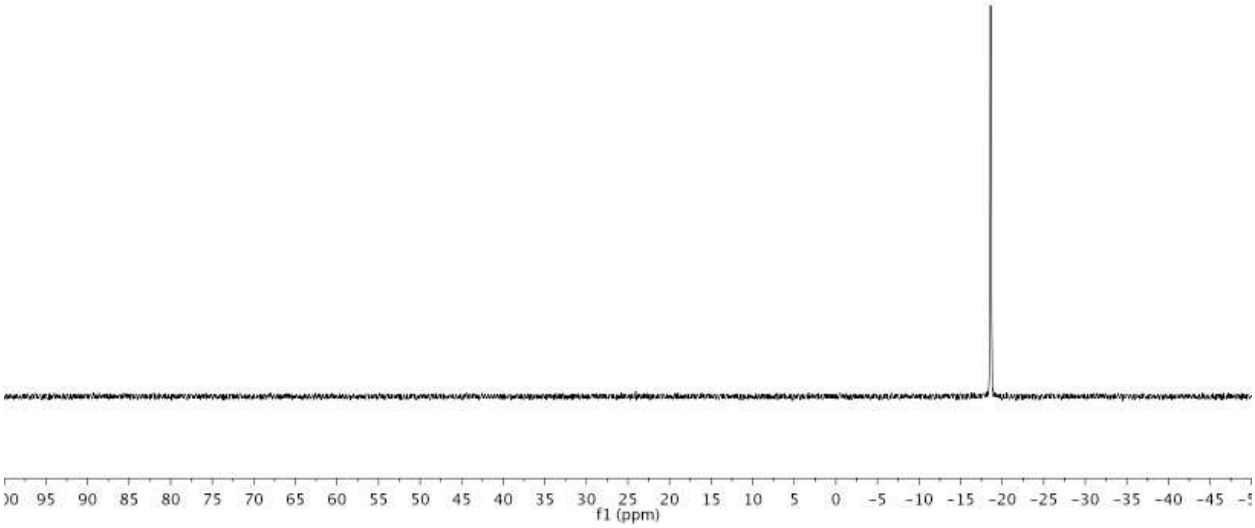




K−NiXantphos in THF-d_8



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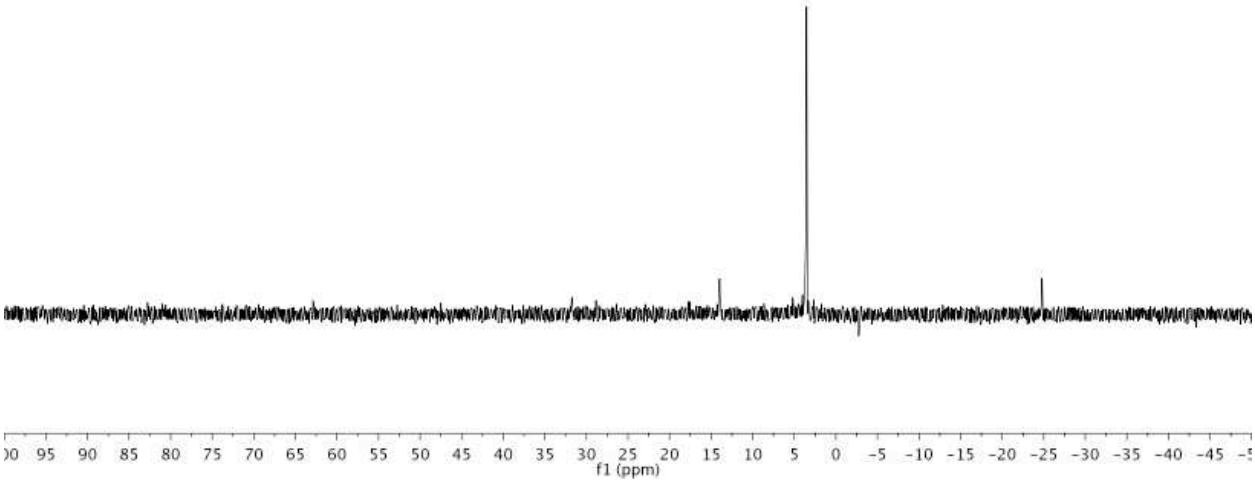
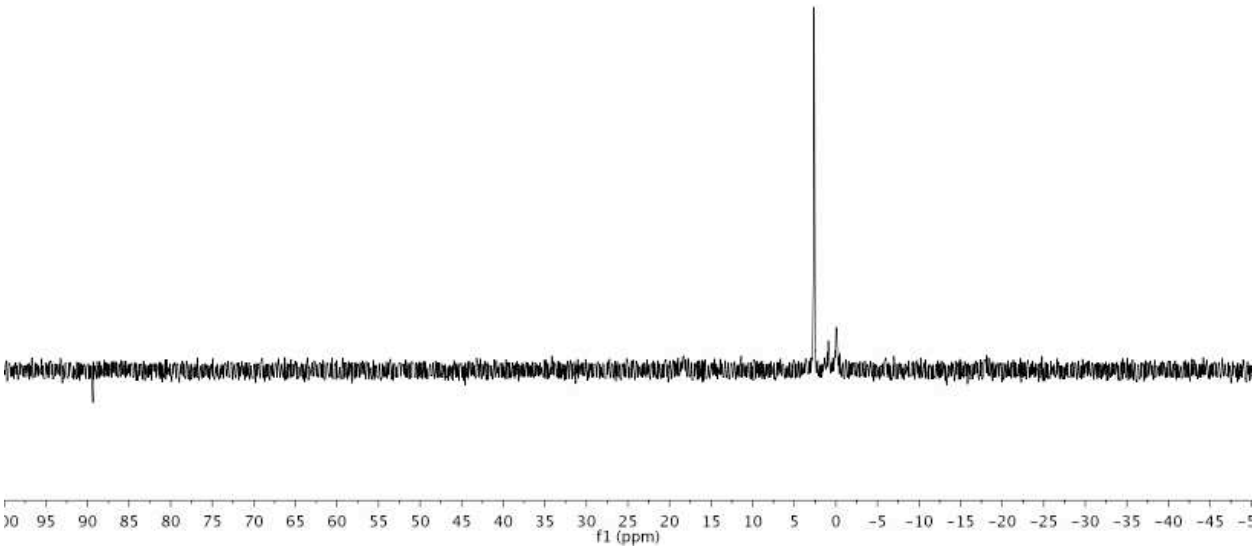
f1 (ppm)

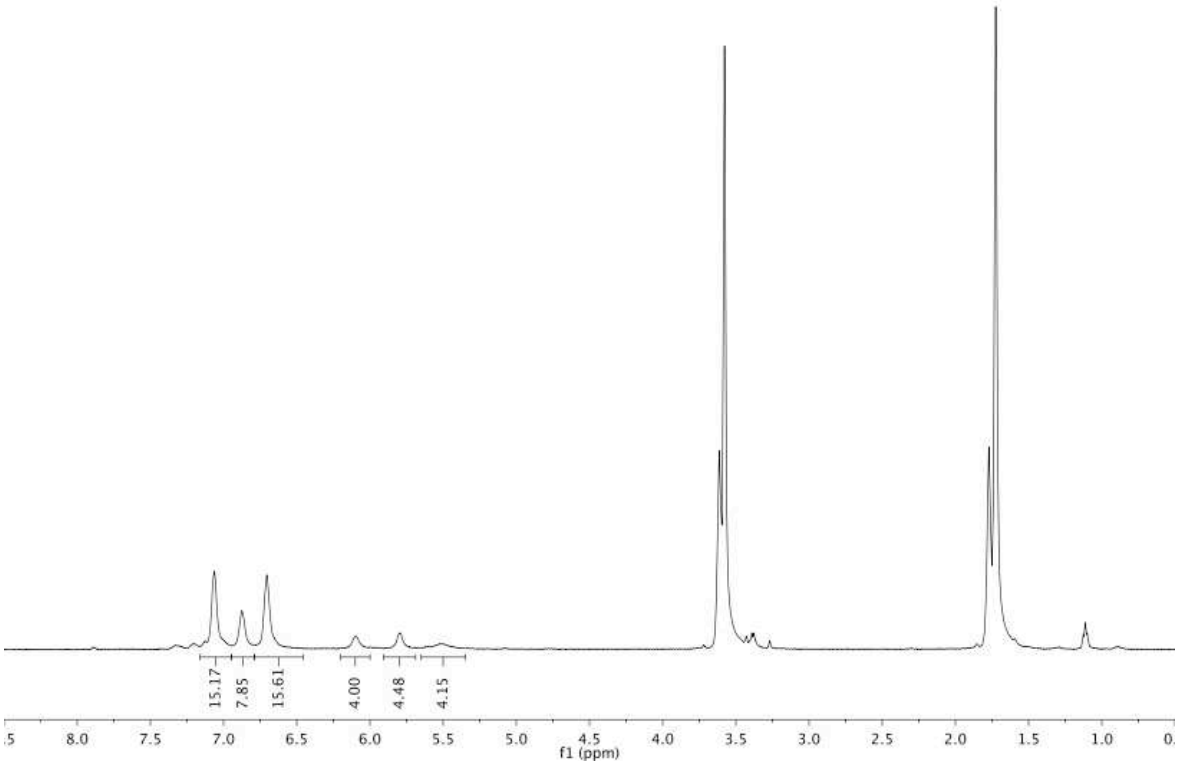
The $^{31}P\{^{1}H\}$ NMR spectrum of coordination of NiXantphos to $Pd(OAc)_2$ (1:1)



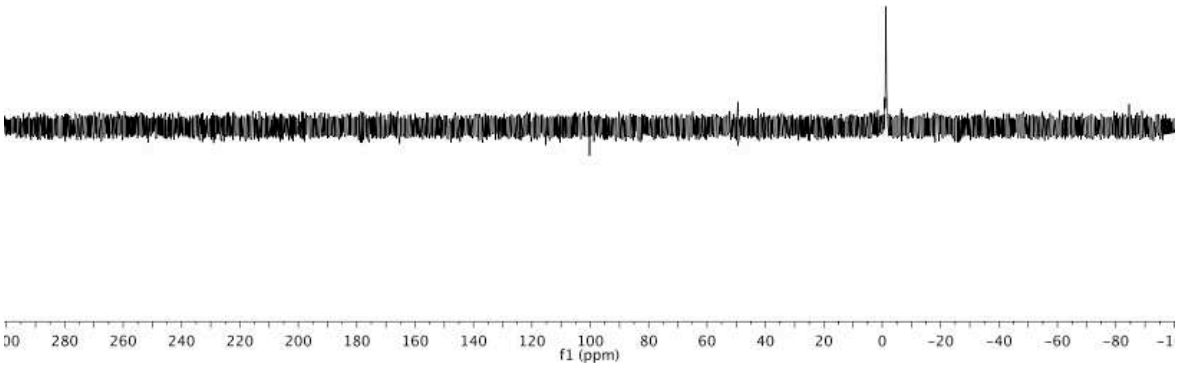
The $^{31}P\{^{1}H\}$ NMR spectrum of oxidative addition of chlorobenzene to (Li−NiXantphos)Pd(0)



The ^{1}H NMR spectrum of Pd(K−NiXantphos)$_2$

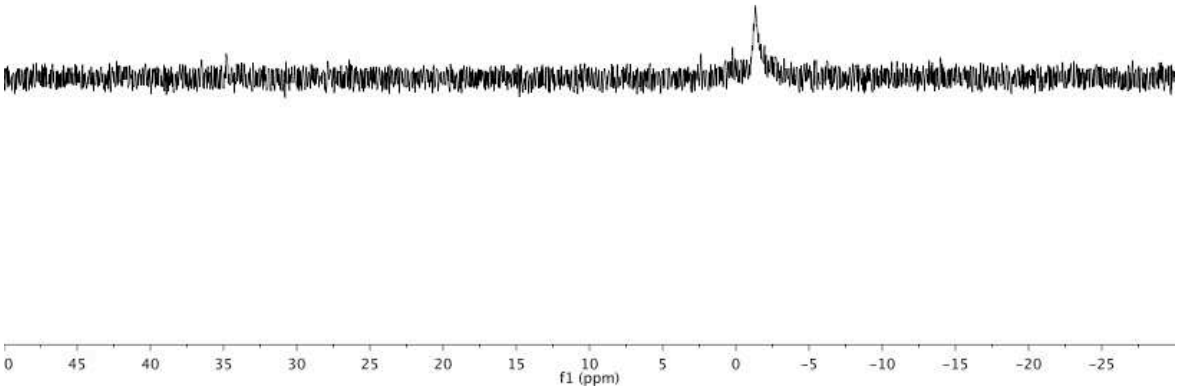


The ^{31}P{^{1}H} NMR spectrum of Pd(K−NiXantphos)$_2$

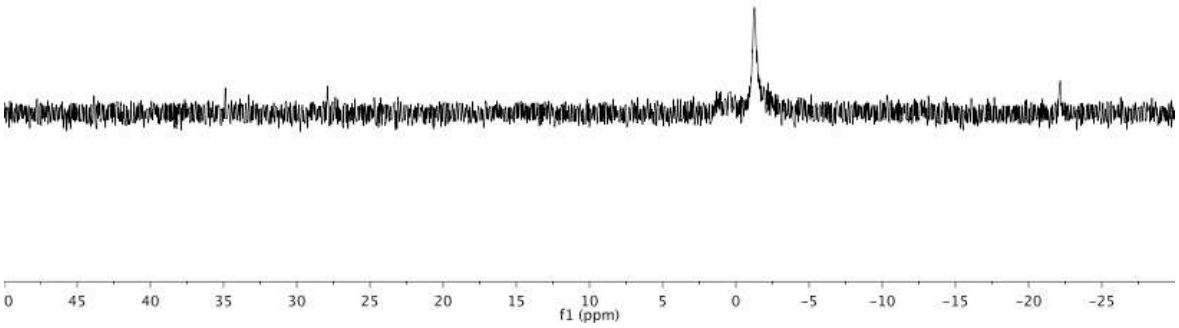


The $^{31}P\{^{1}H\}$ NMR spectrum of the catalyst resting state

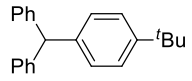
after 10 min:

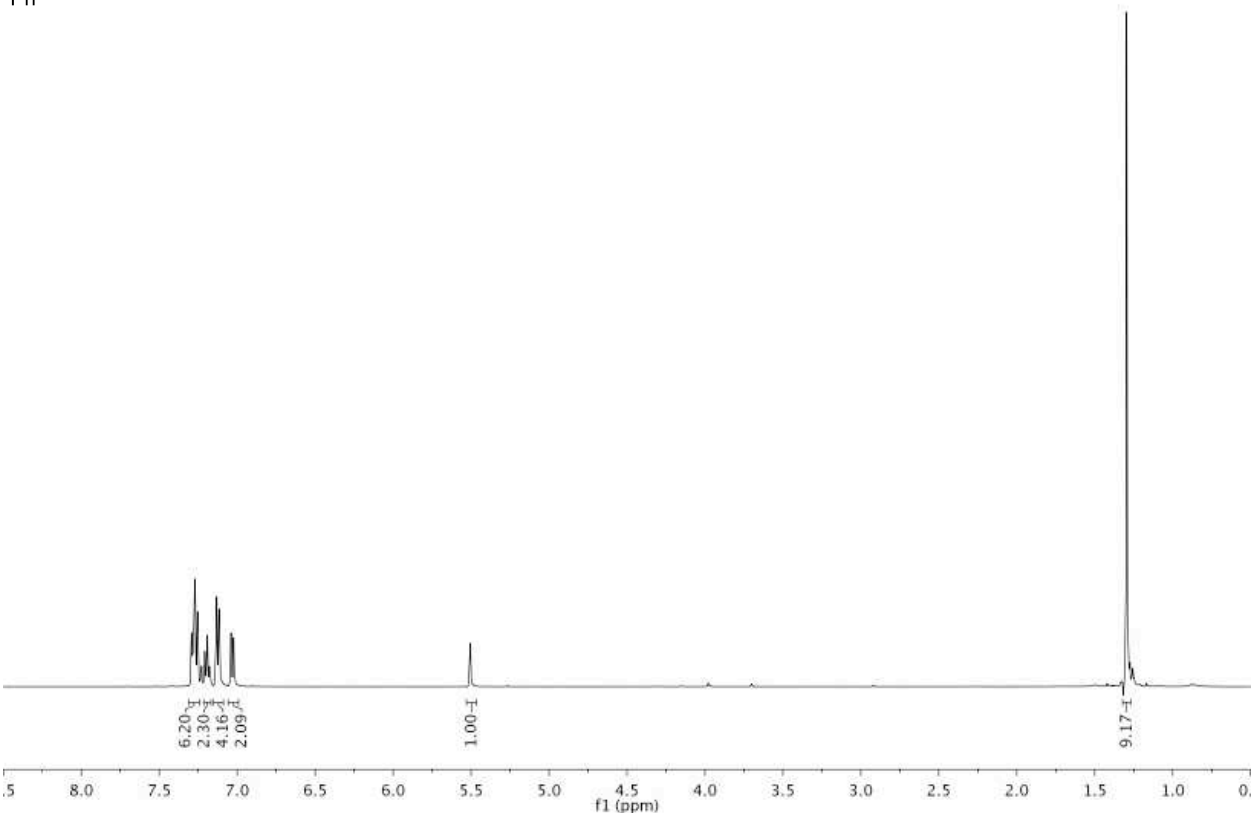


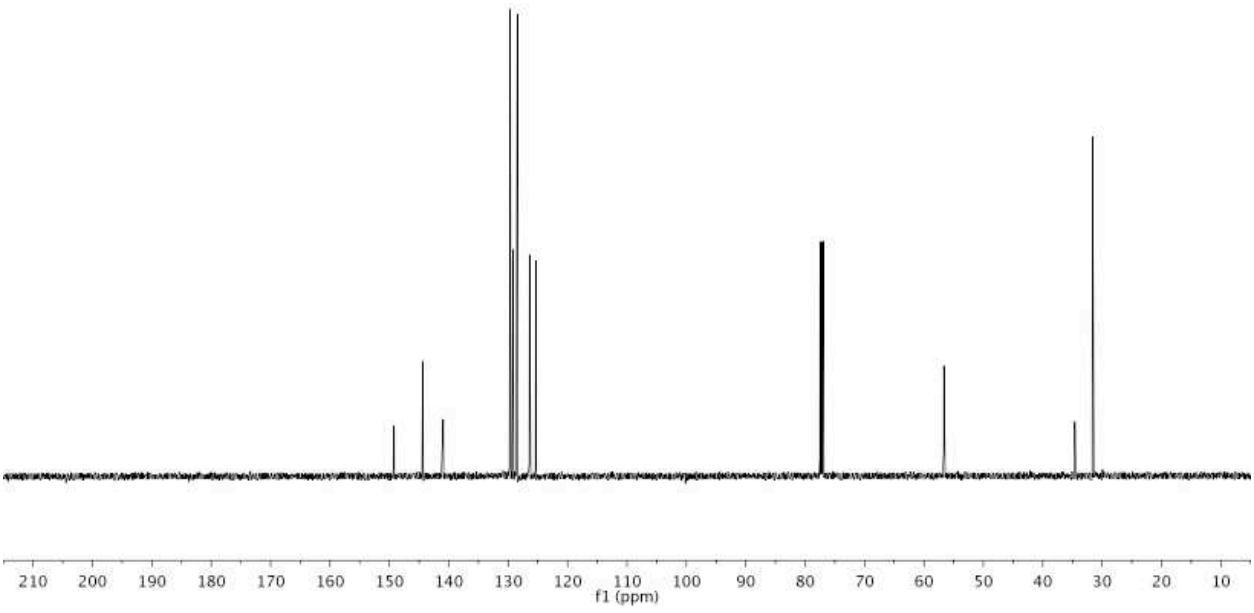
after 12 h:



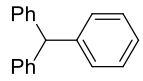
3aa – (4-*tert*-Butylphenyl)diphenylmethane

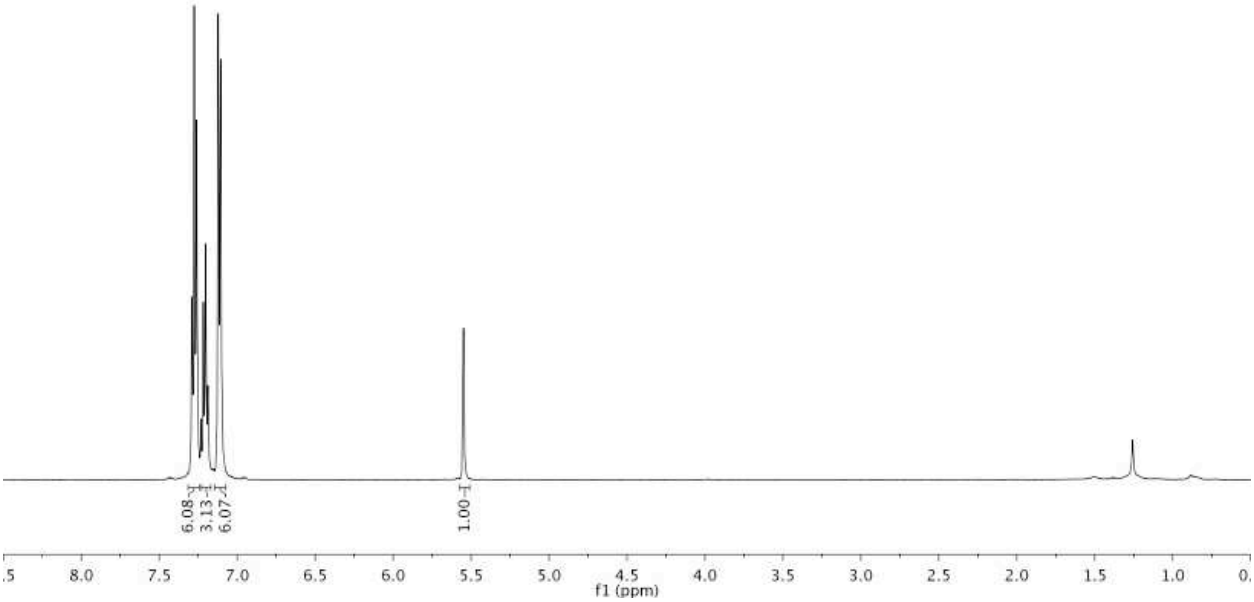


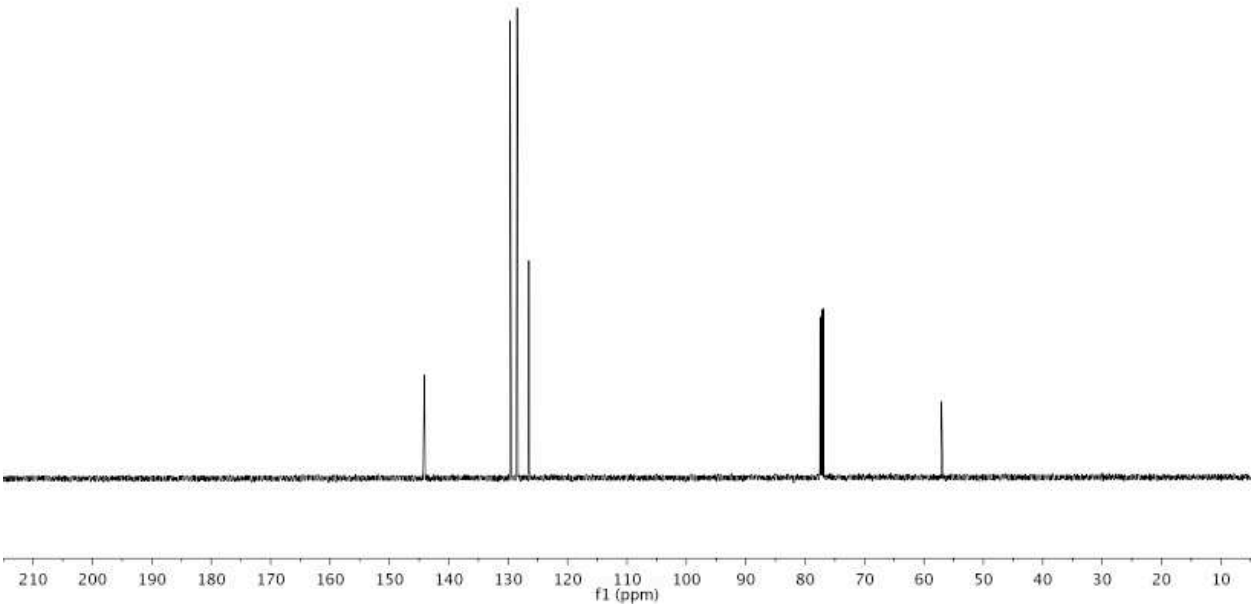




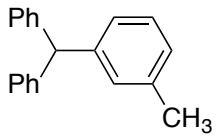
3ab – Triphenylmethane

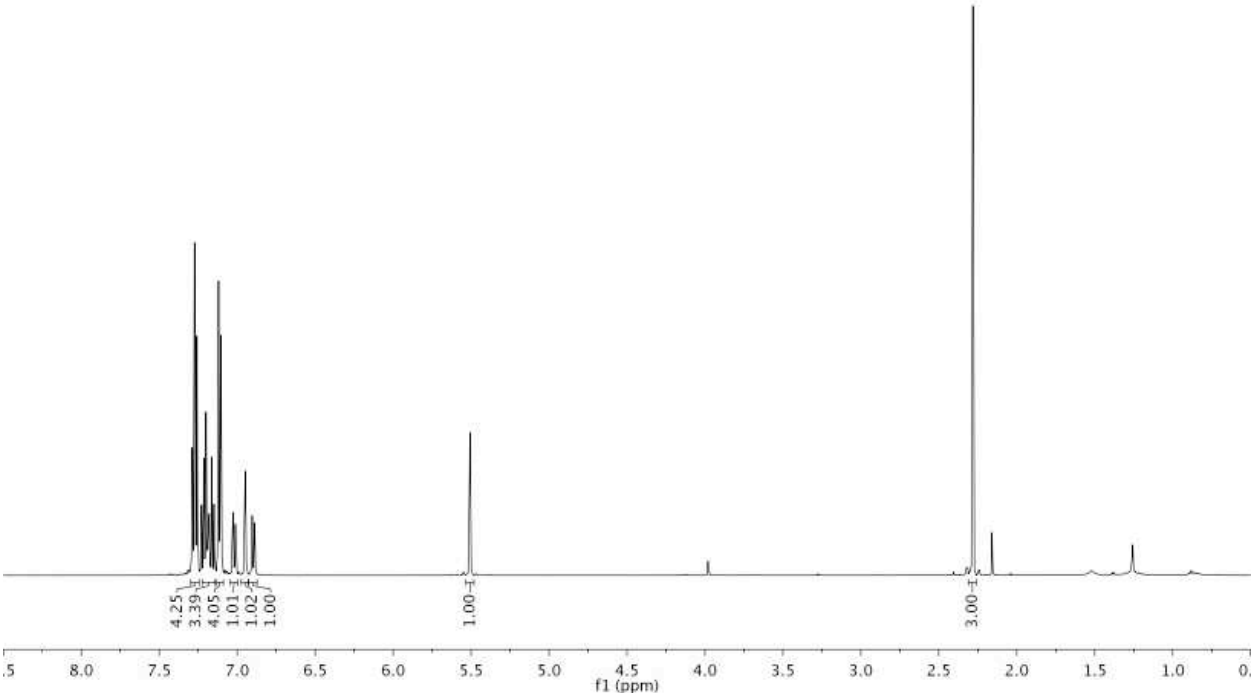


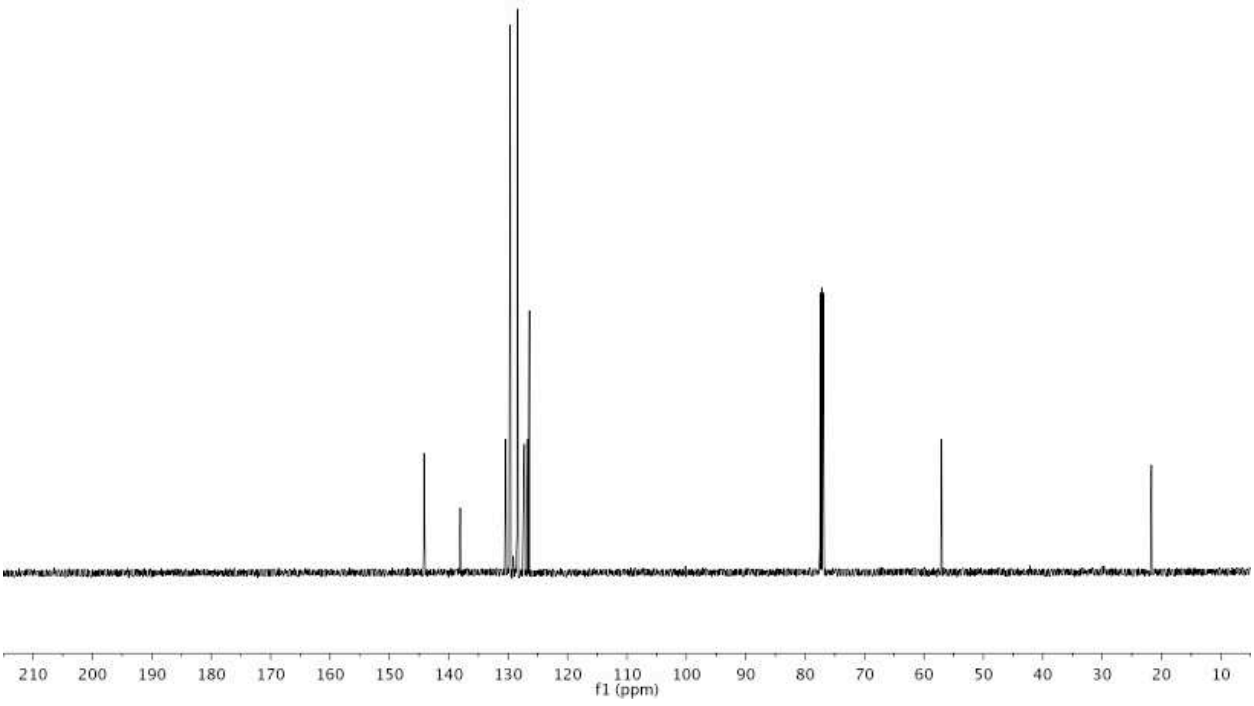




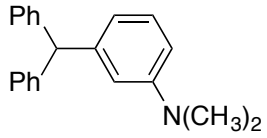
3ac – (3-Methylphenyl)diphenylmethane

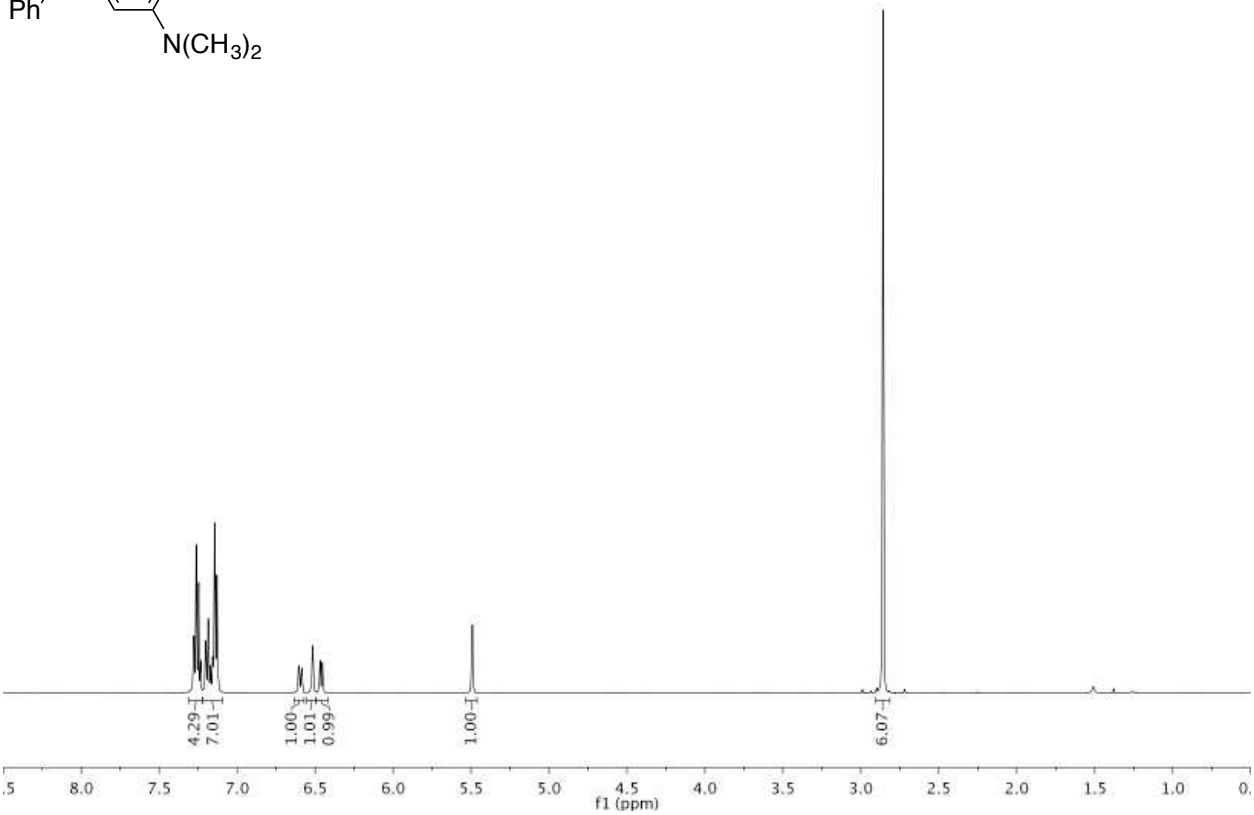


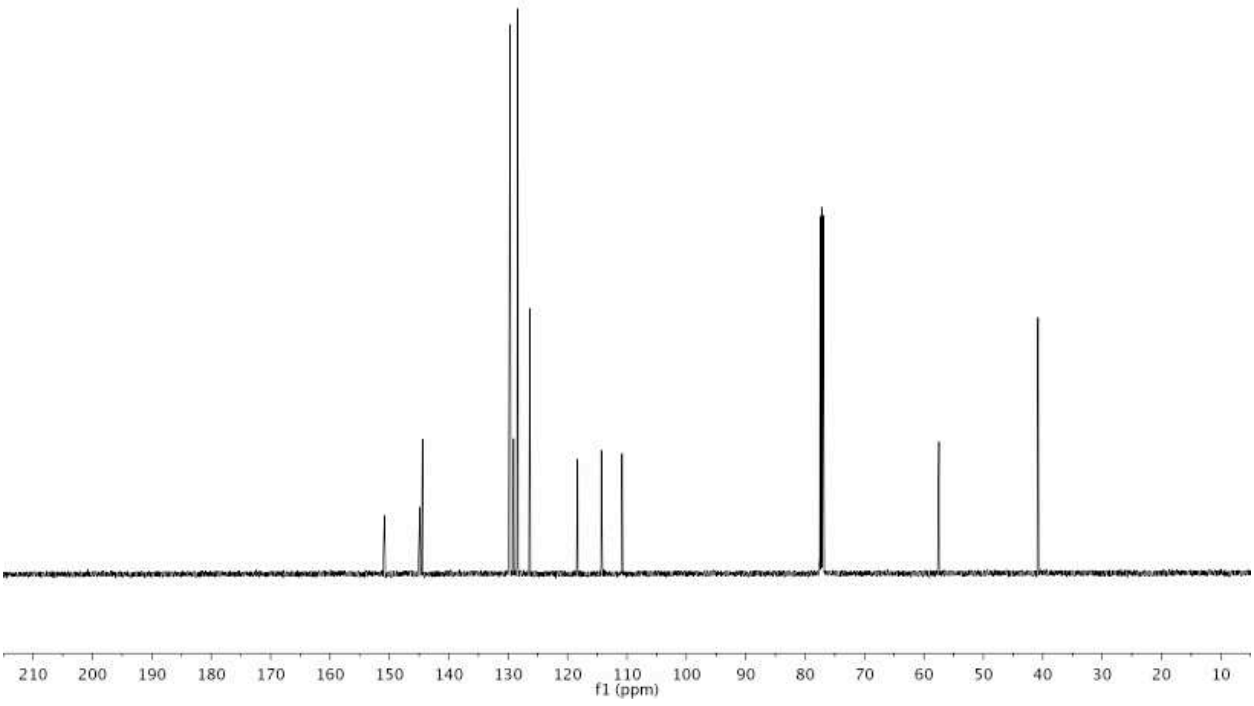




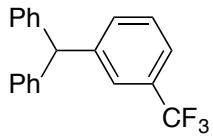
3ad – (3-Dimethylaminophenyl)diphenylmethane

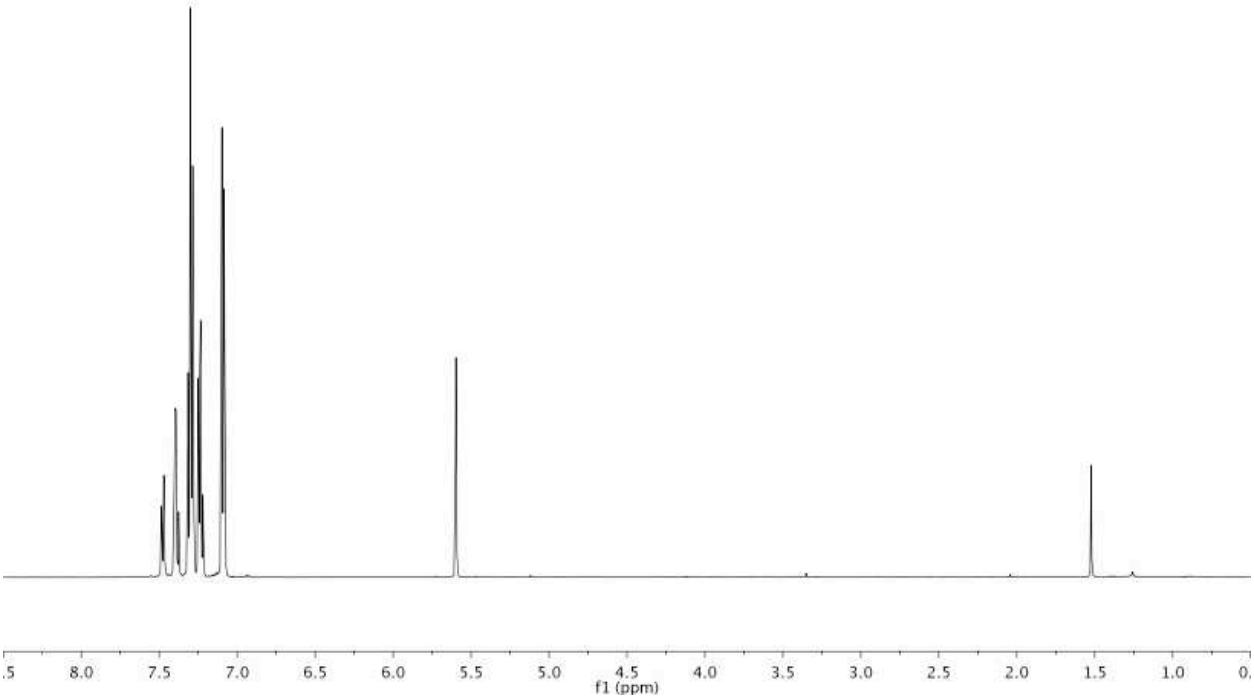


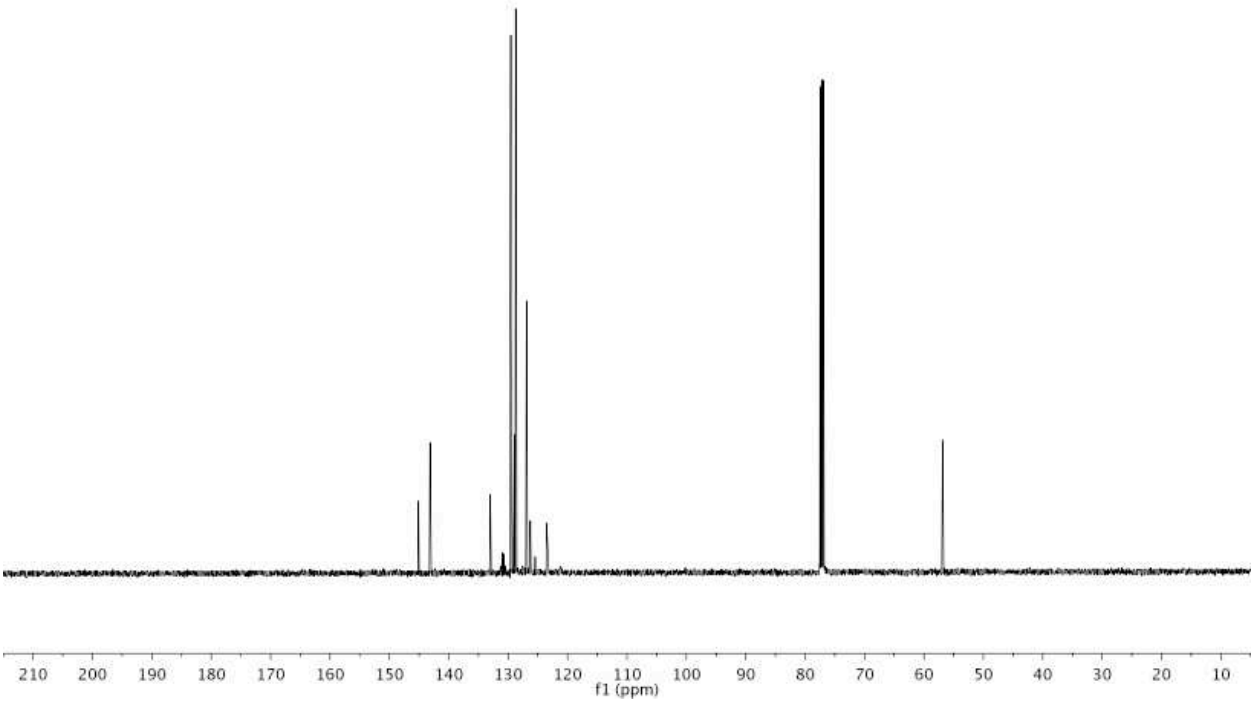




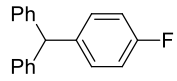
3ae – (3-Trifluoromethylphenyl)diphenylmethane

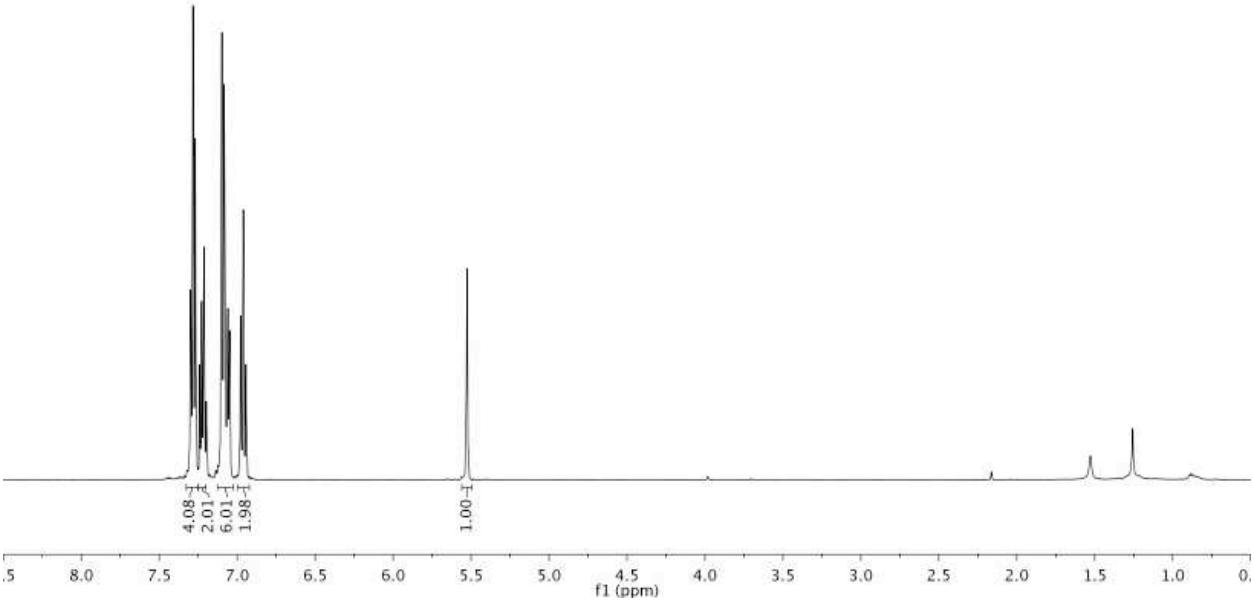


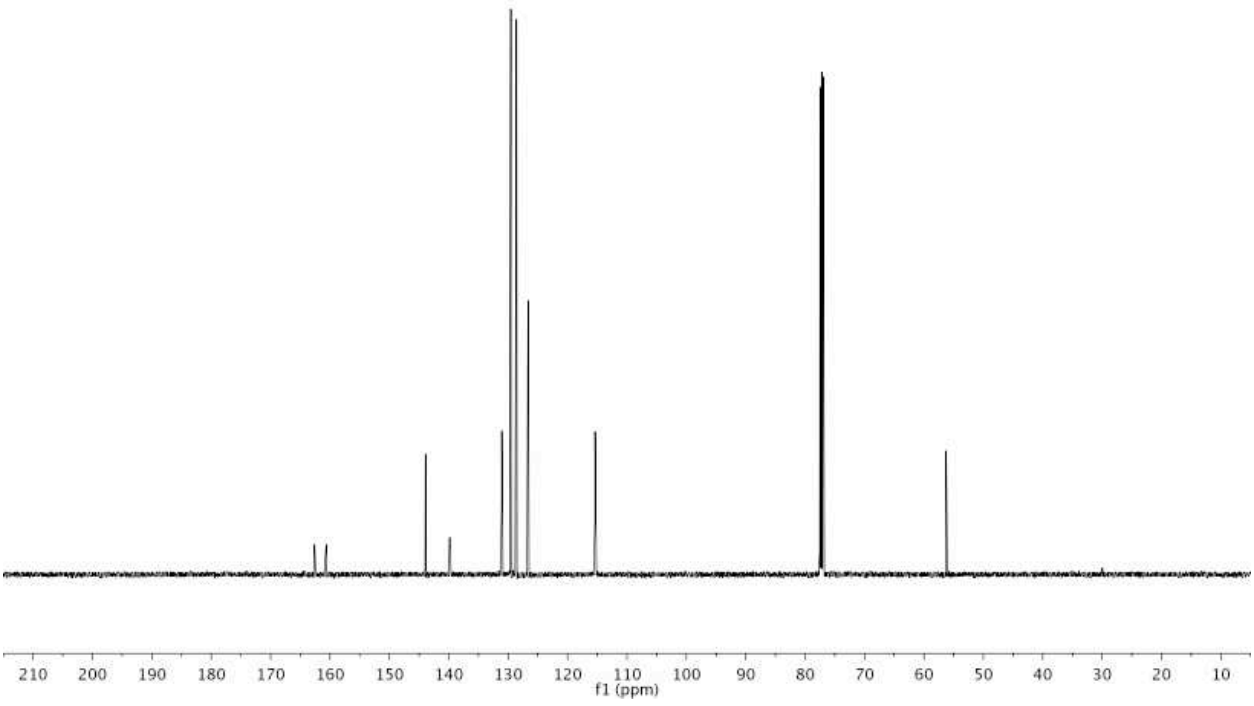




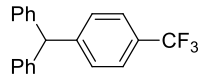
3af – (4-Fluorophenyl)diphenylmethane

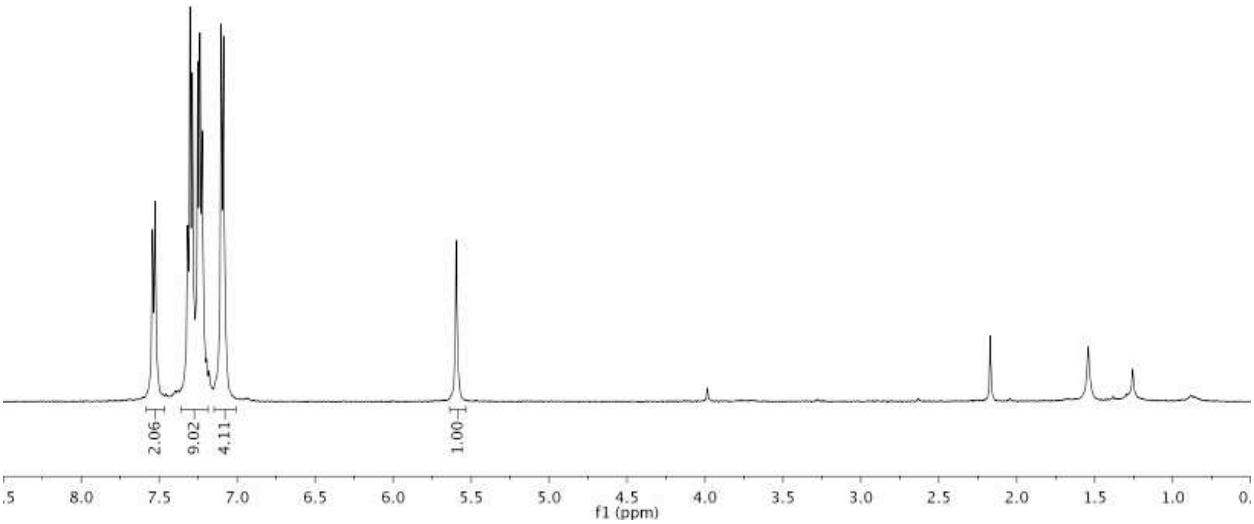


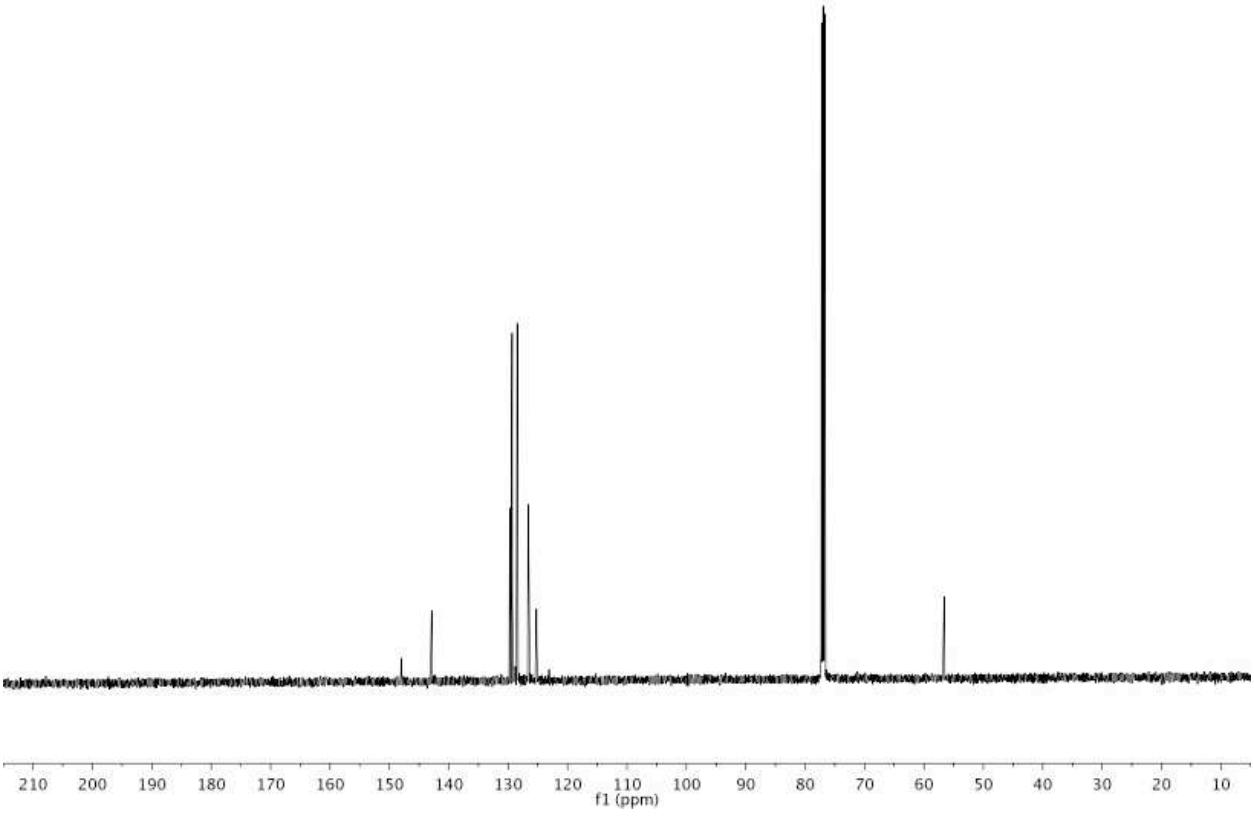




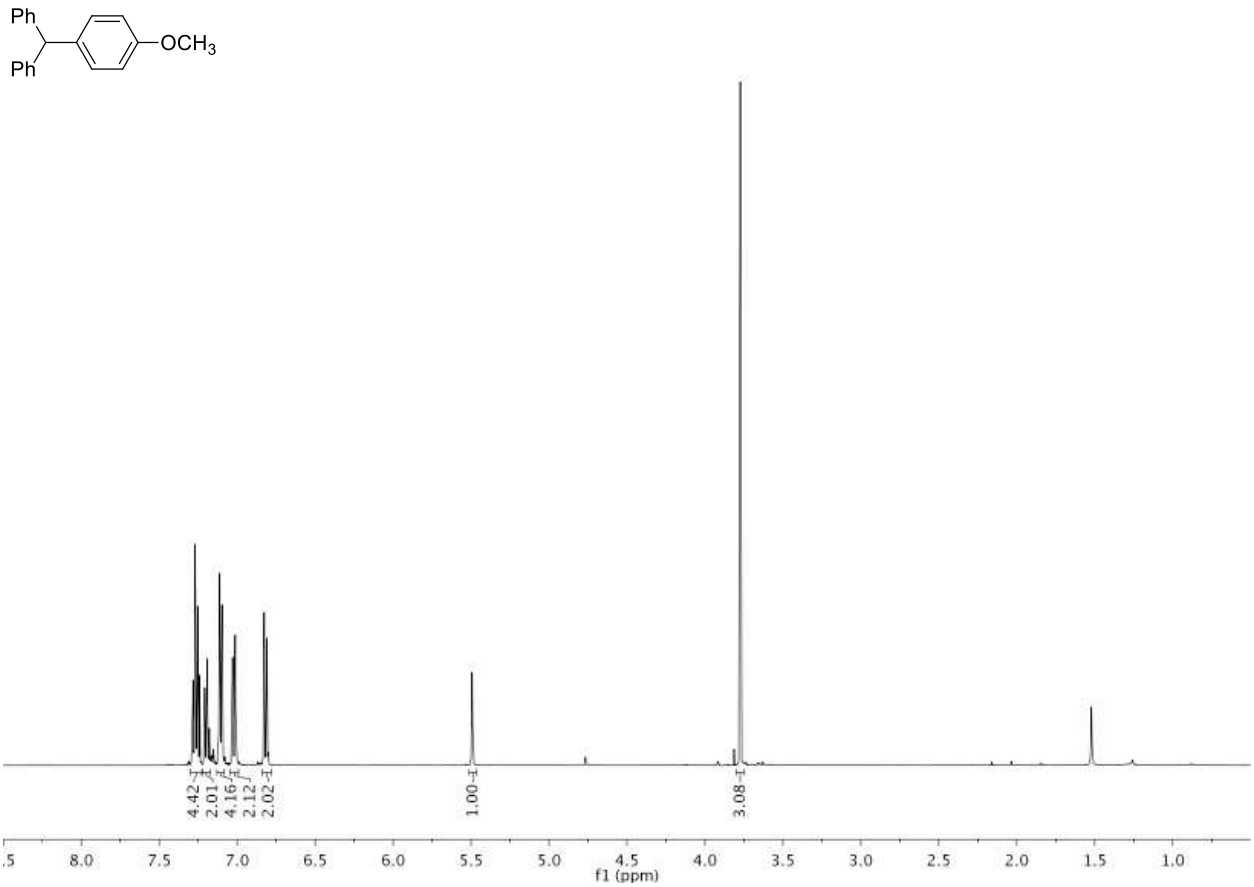
3ag – (4-Trifluoromethylphenyl)diphenylmethane

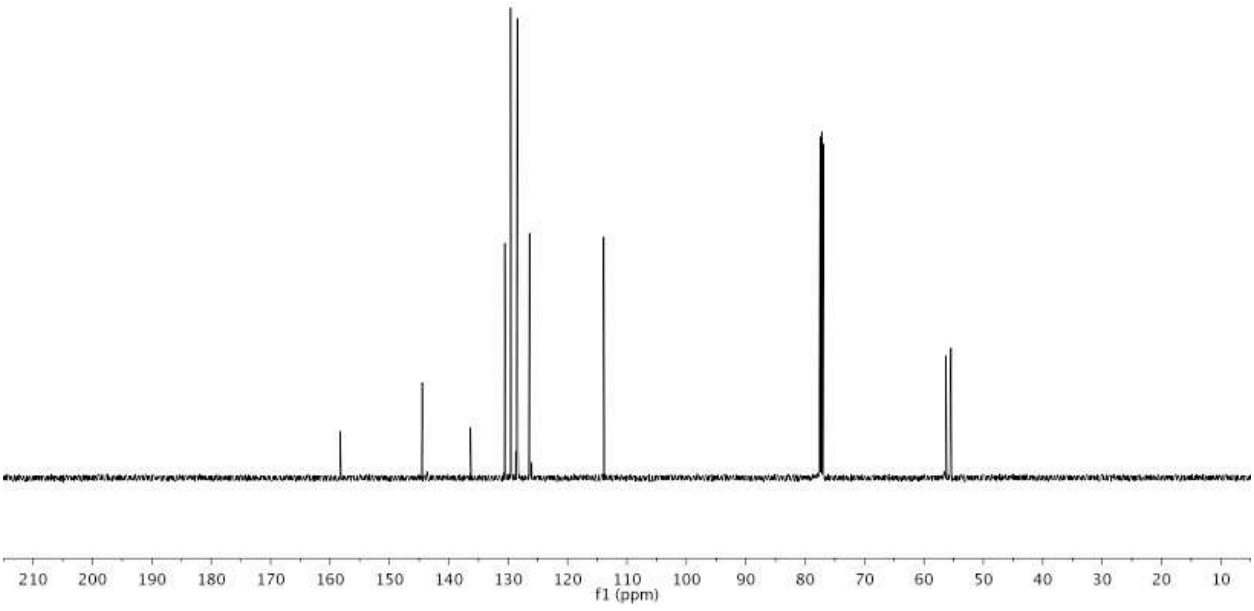




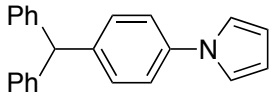


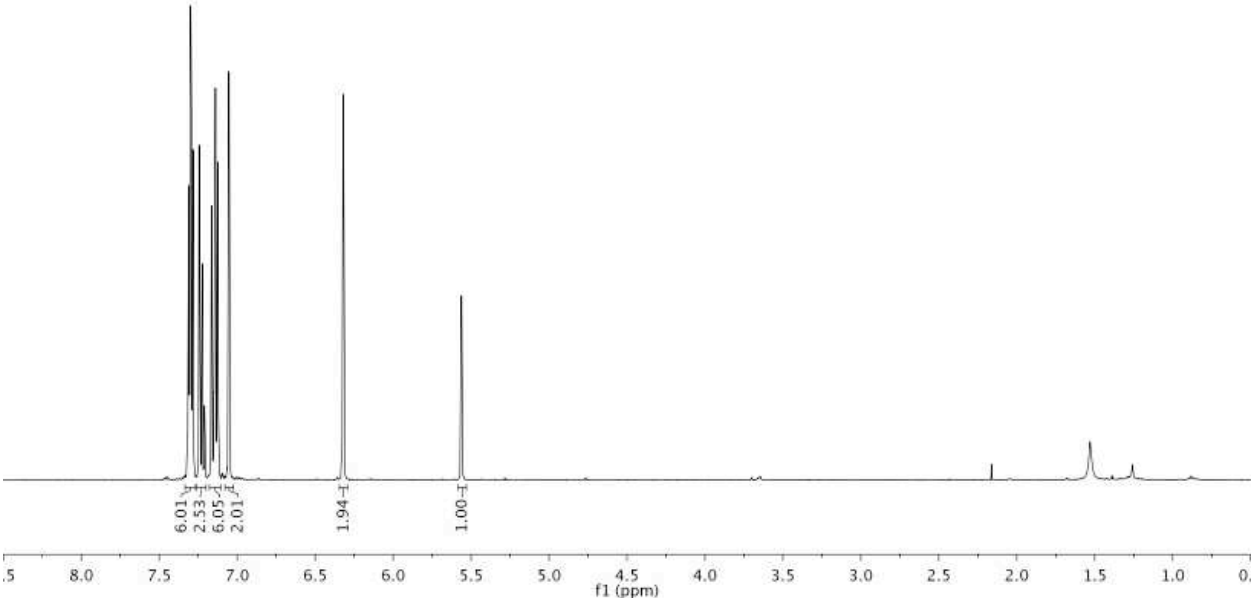
3ah – (4-Methoxyphenyl)diphenylmethane

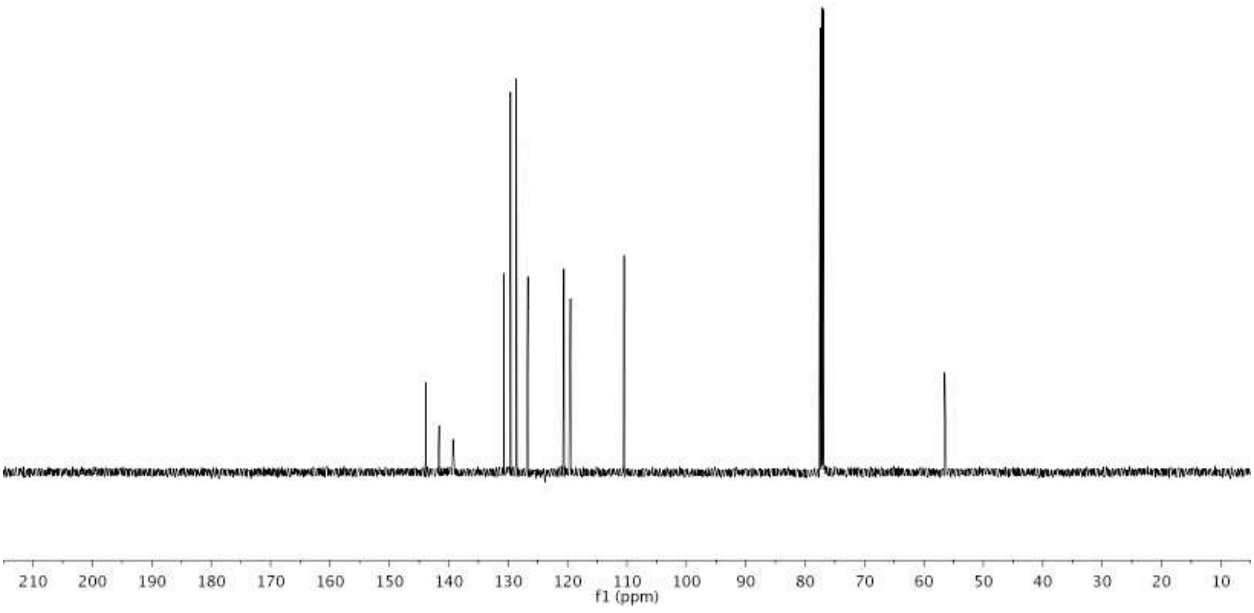




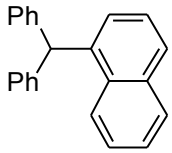
3ai – (4-(*N*-Pyrrolyl)phenyl)diphenylmethane

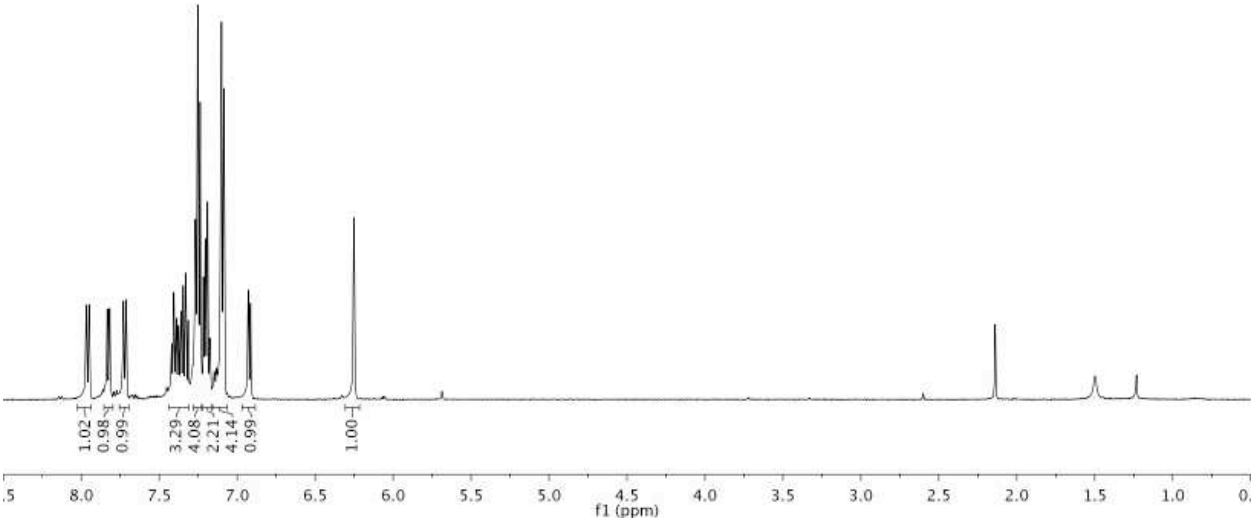


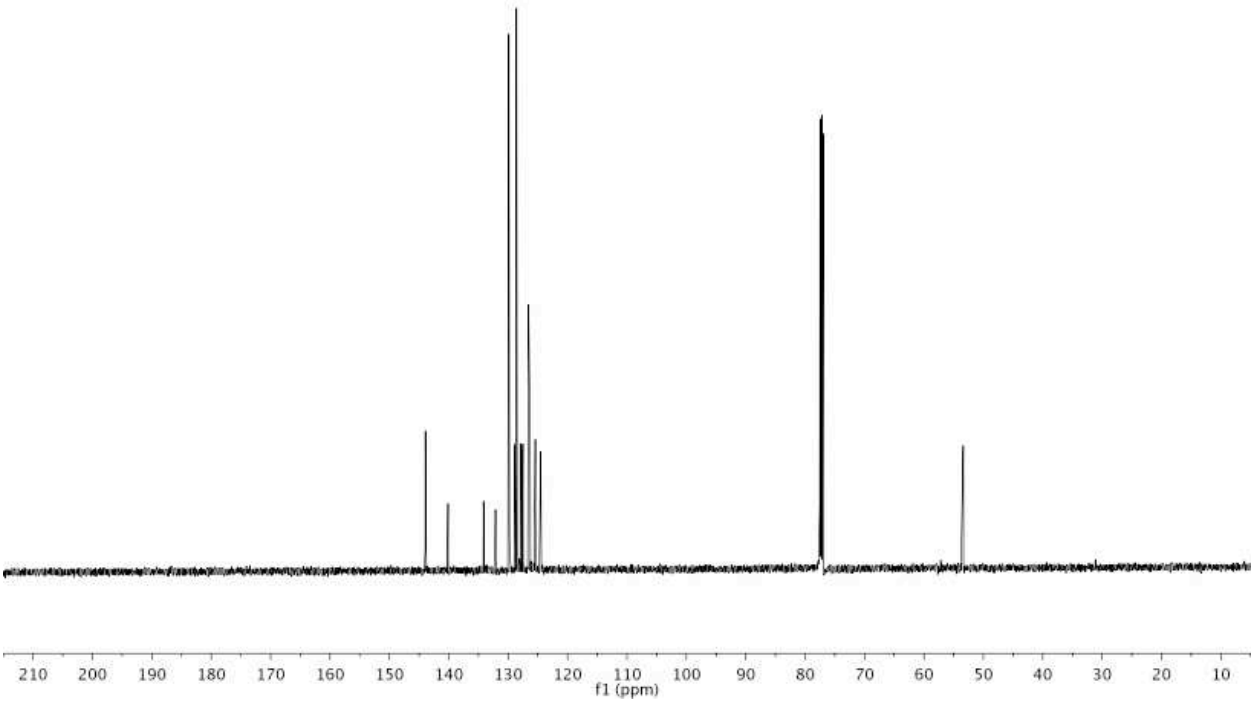




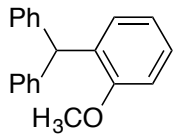
3aj – (1-Naphthyl)diphenylmethane

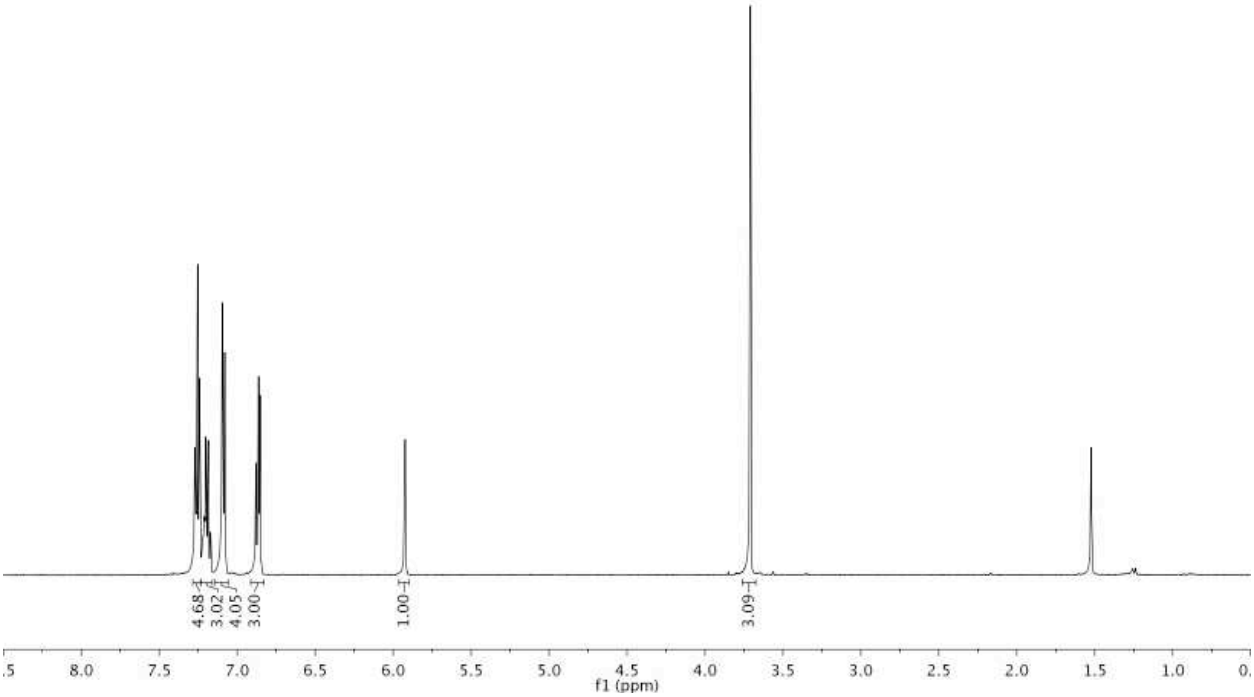


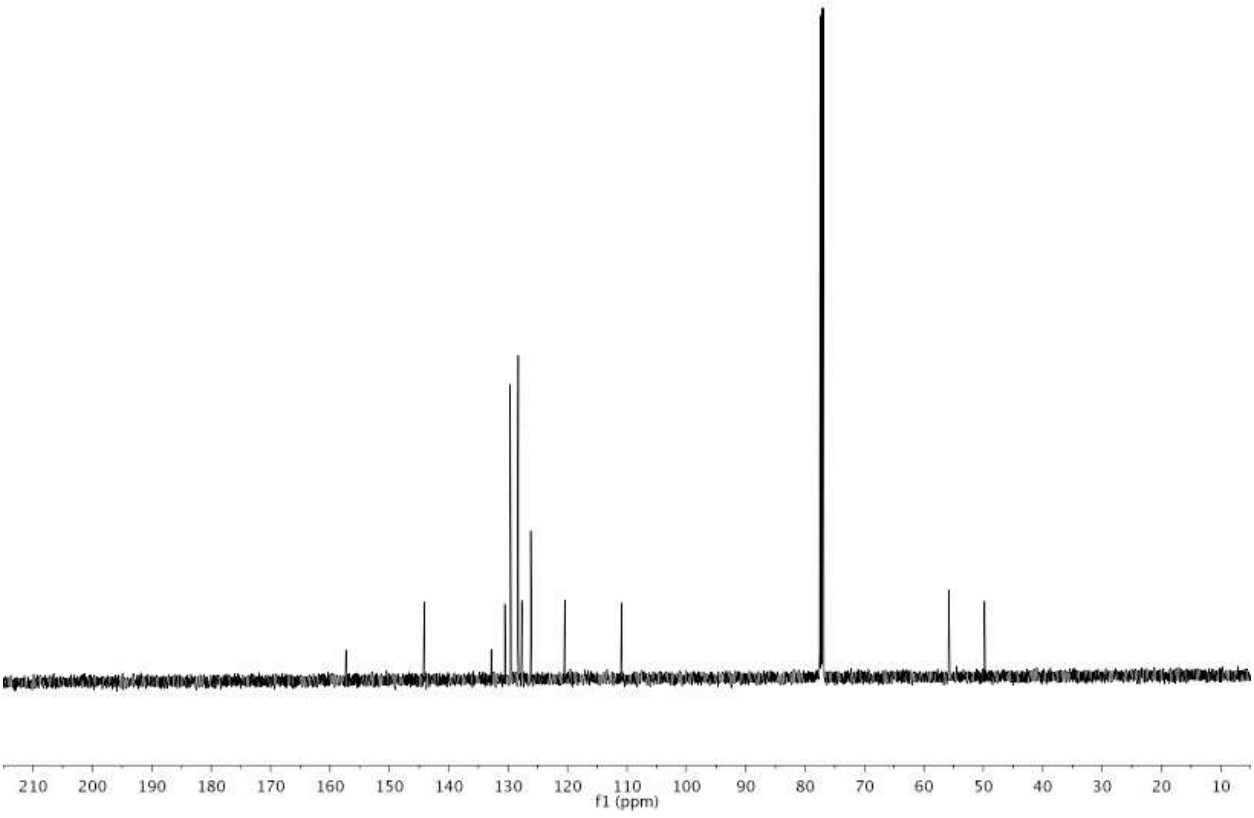




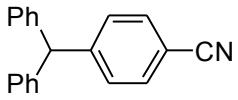
3ak – (2-Methoxyphenyl)diphenylmethane

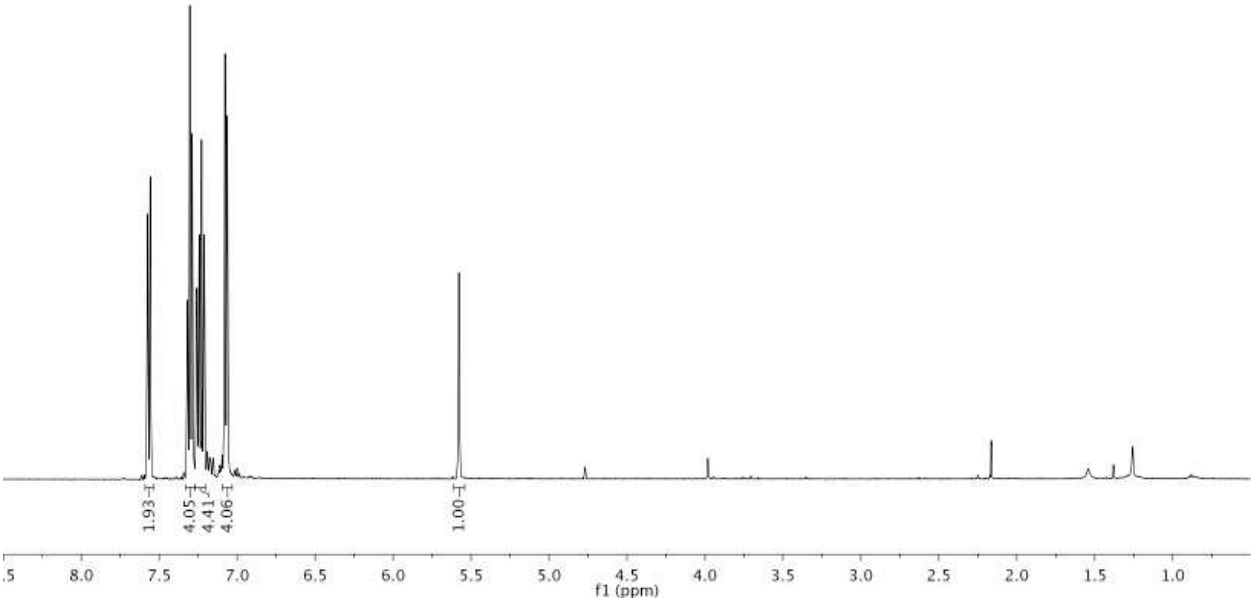


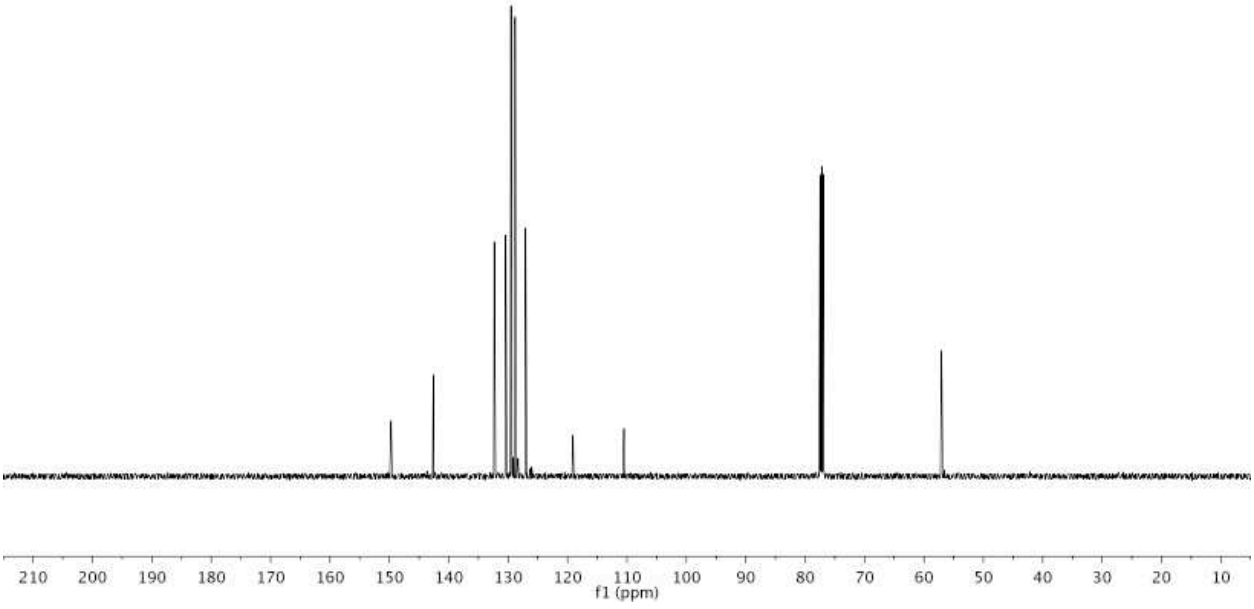




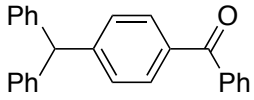
3al – (4-Cyanophenyl)diphenylmethane

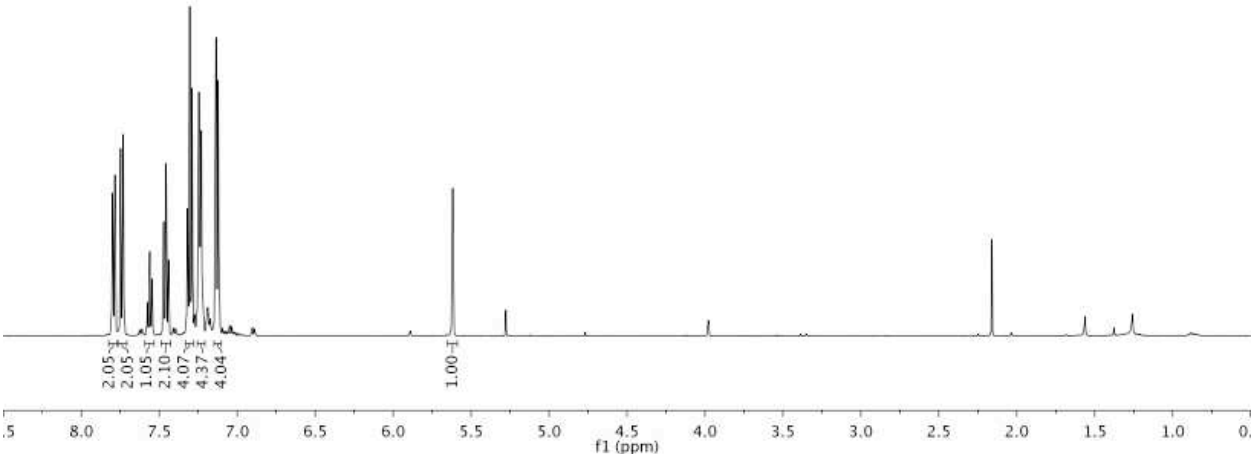


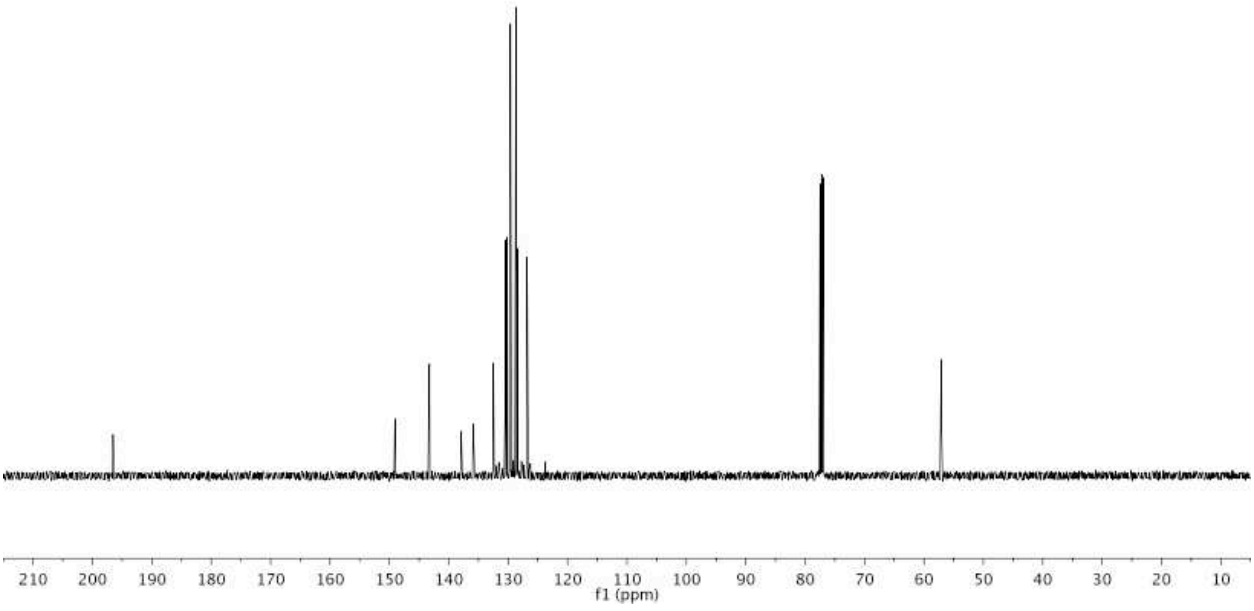




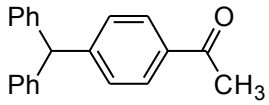
3am – 4-Benzhydrylbenzophenone

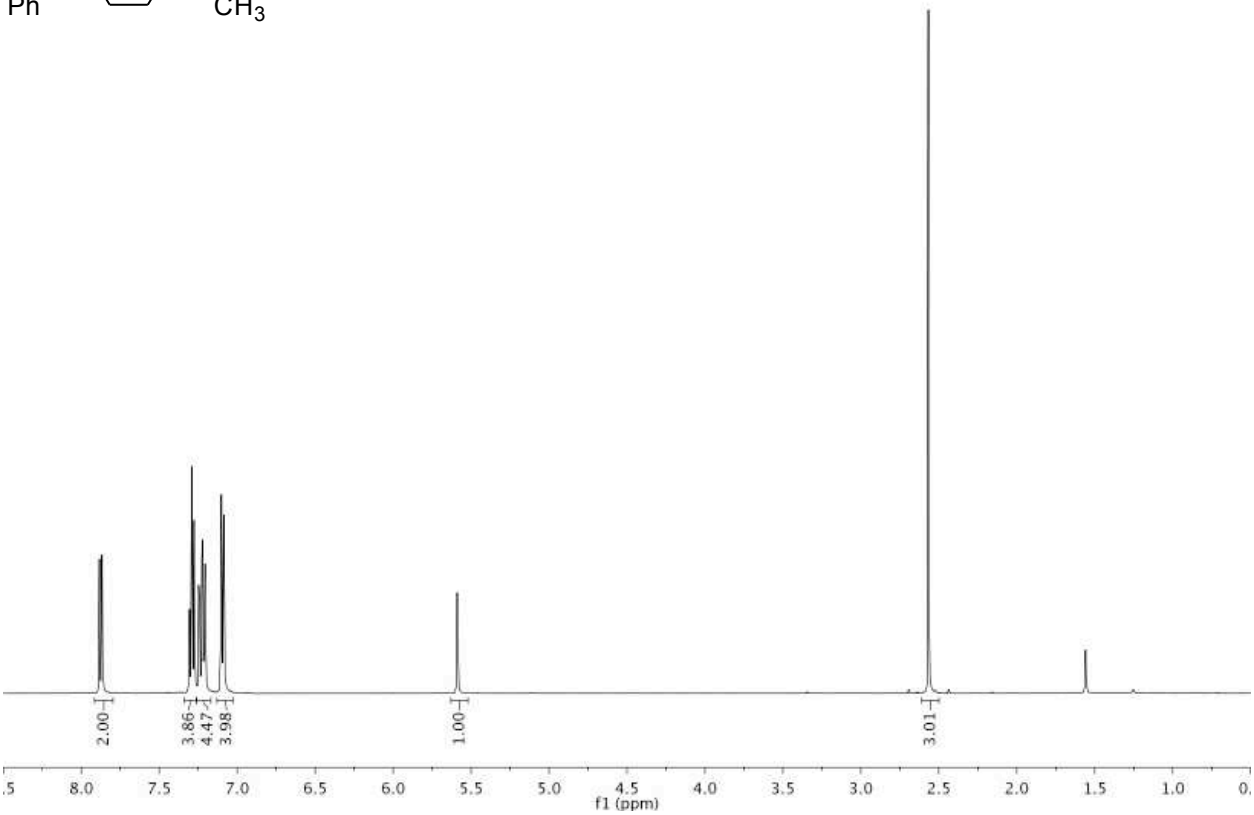


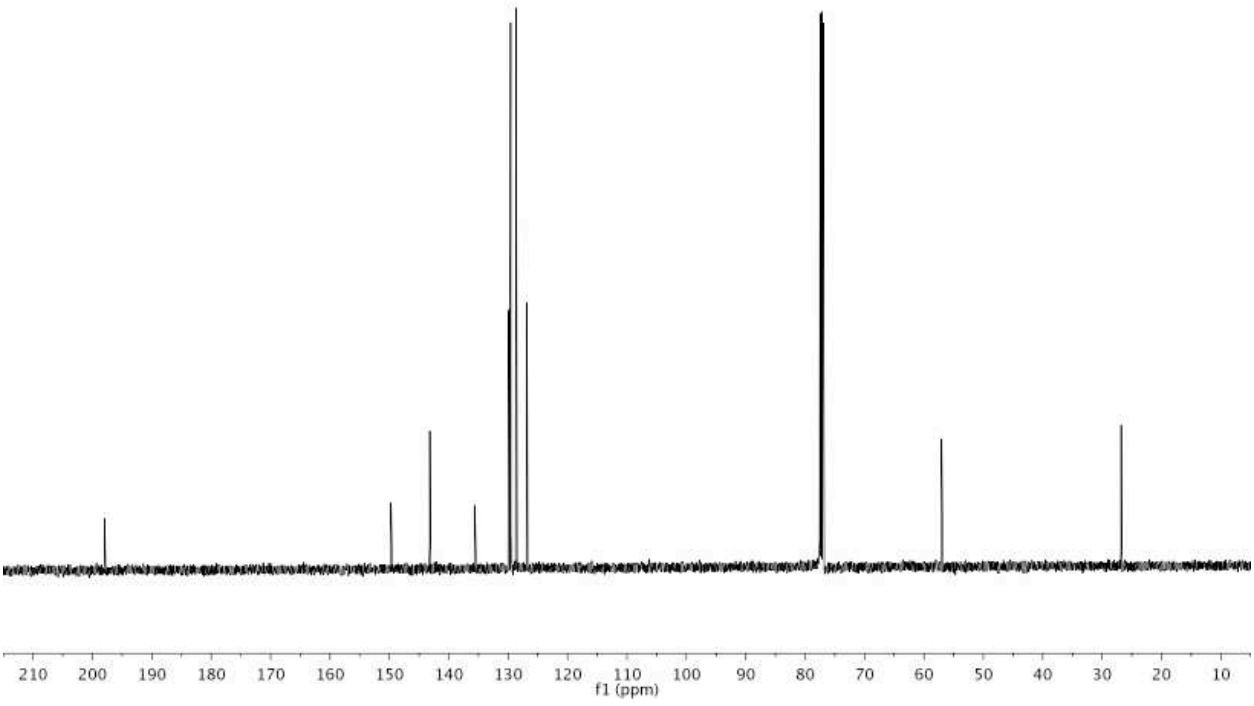




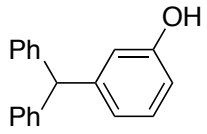
3an – (4-Acetylphenyl)diphenylmethane

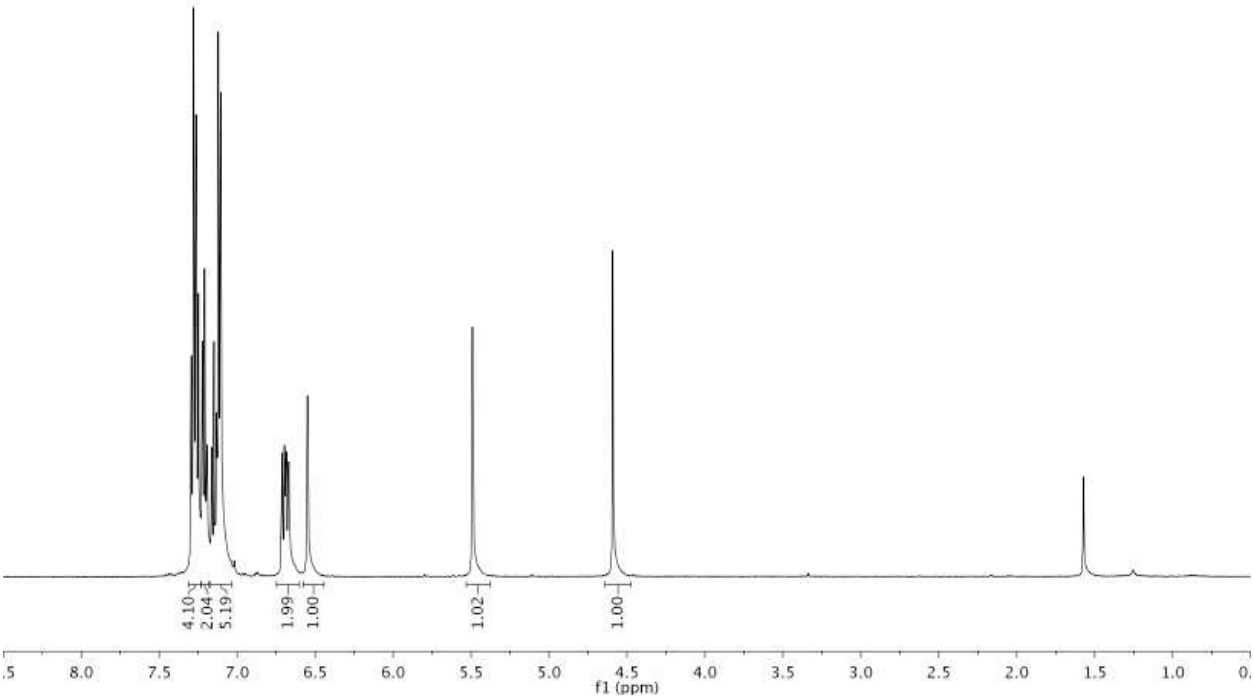


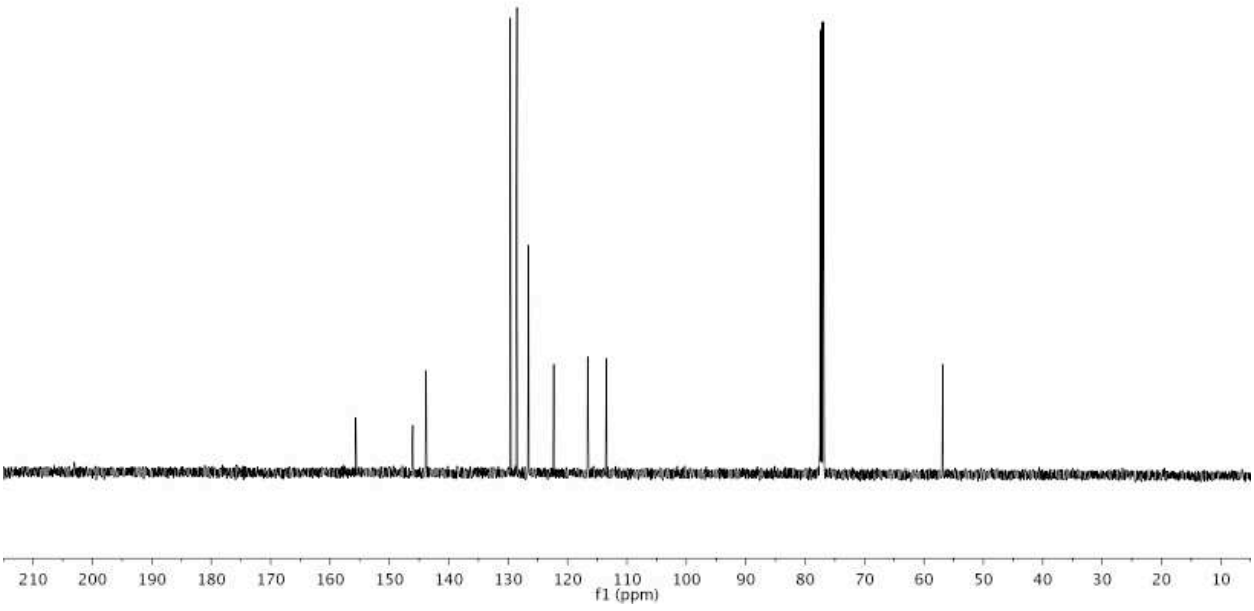




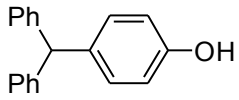
3ao – (3-Hydroxyphenyl)diphenylmethane

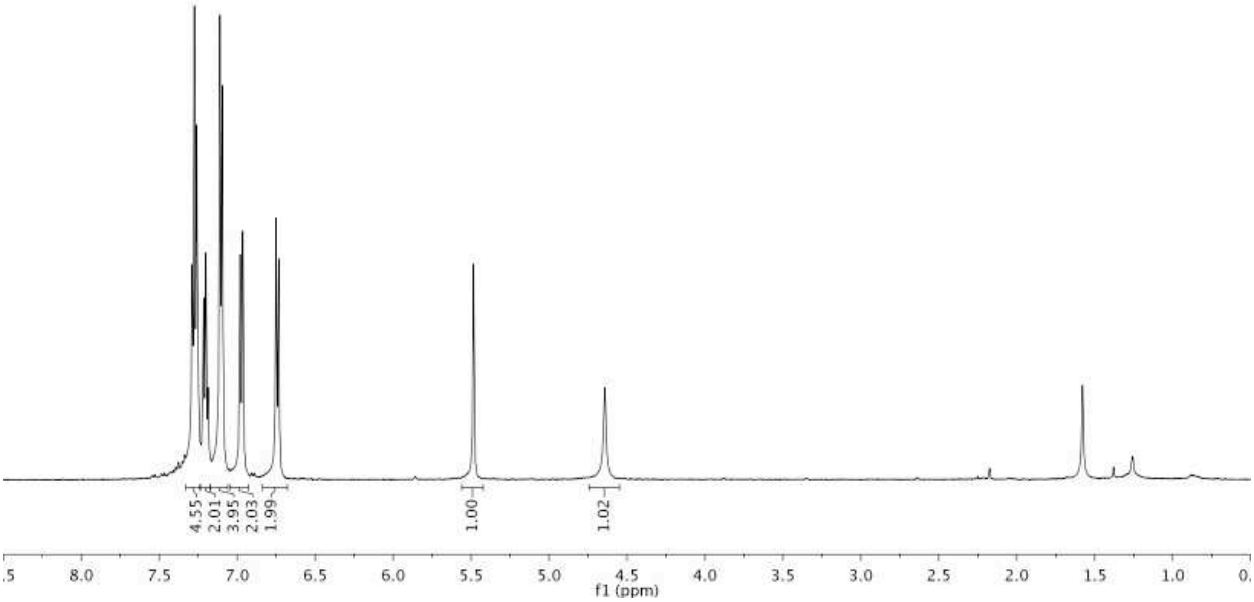


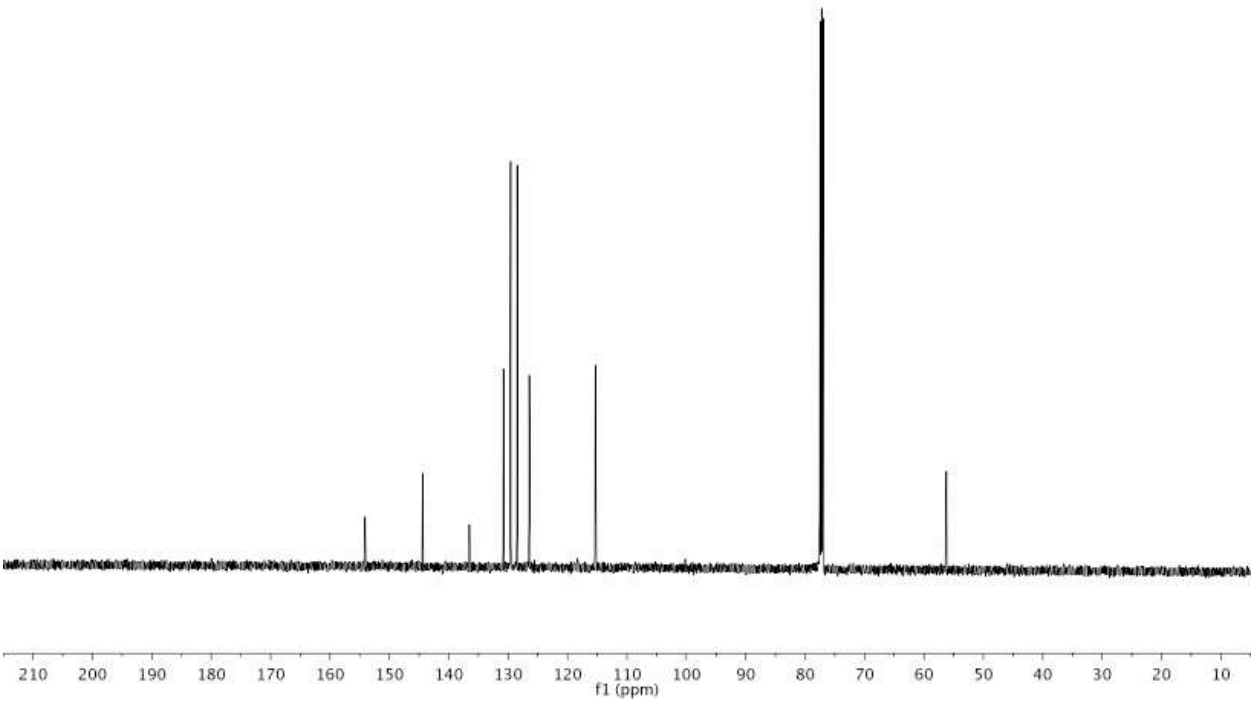




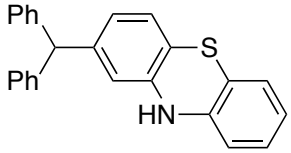
3ap – (4-Hydroxyphenyl)diphenylmethane

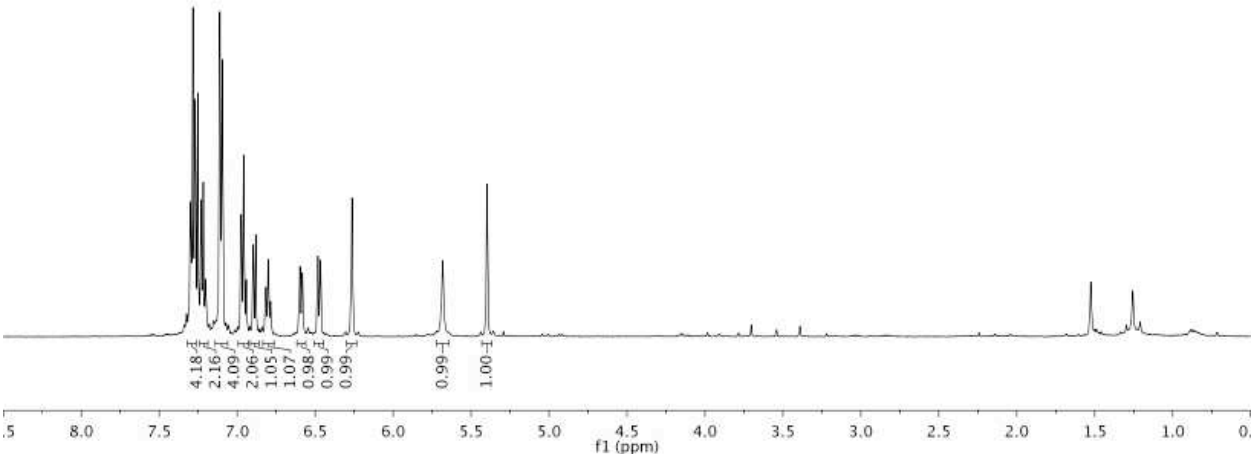


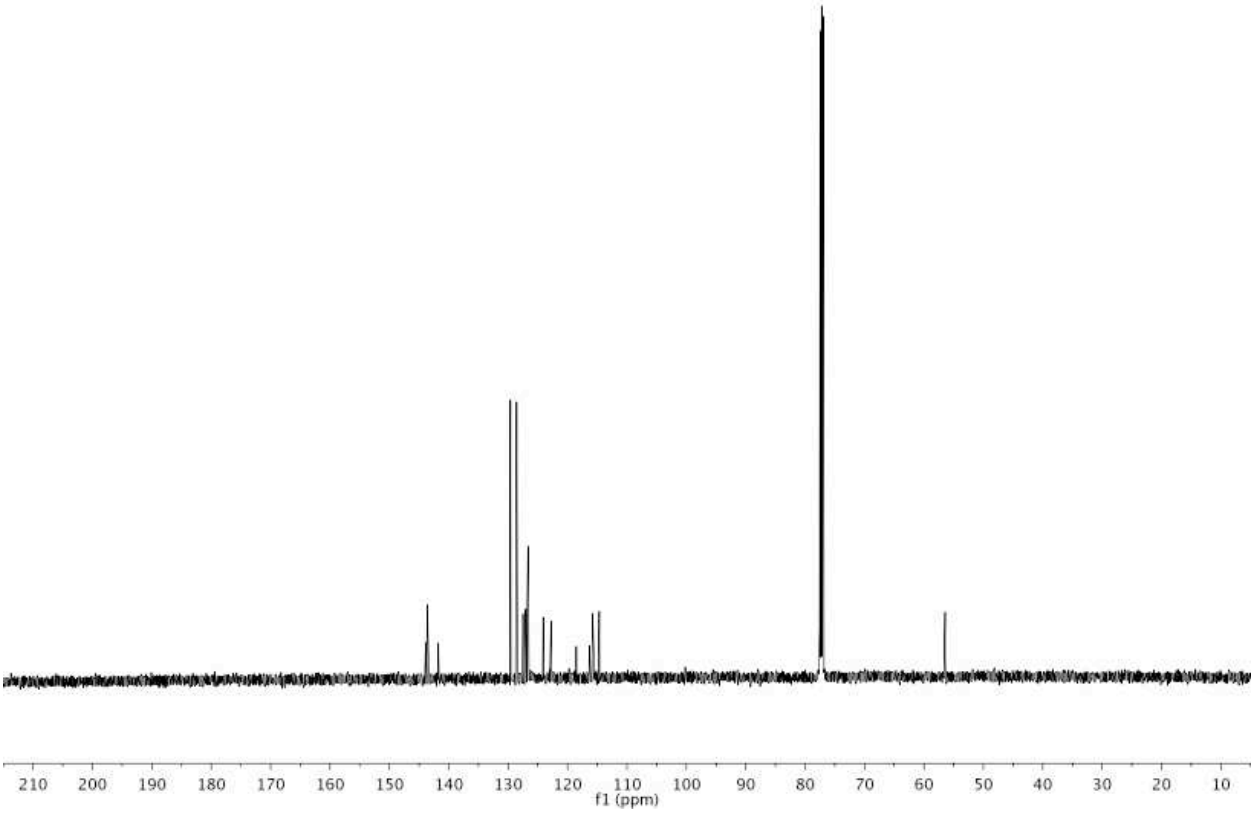




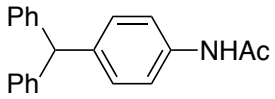
3aq – 2-Benzhydrylphenothiazine

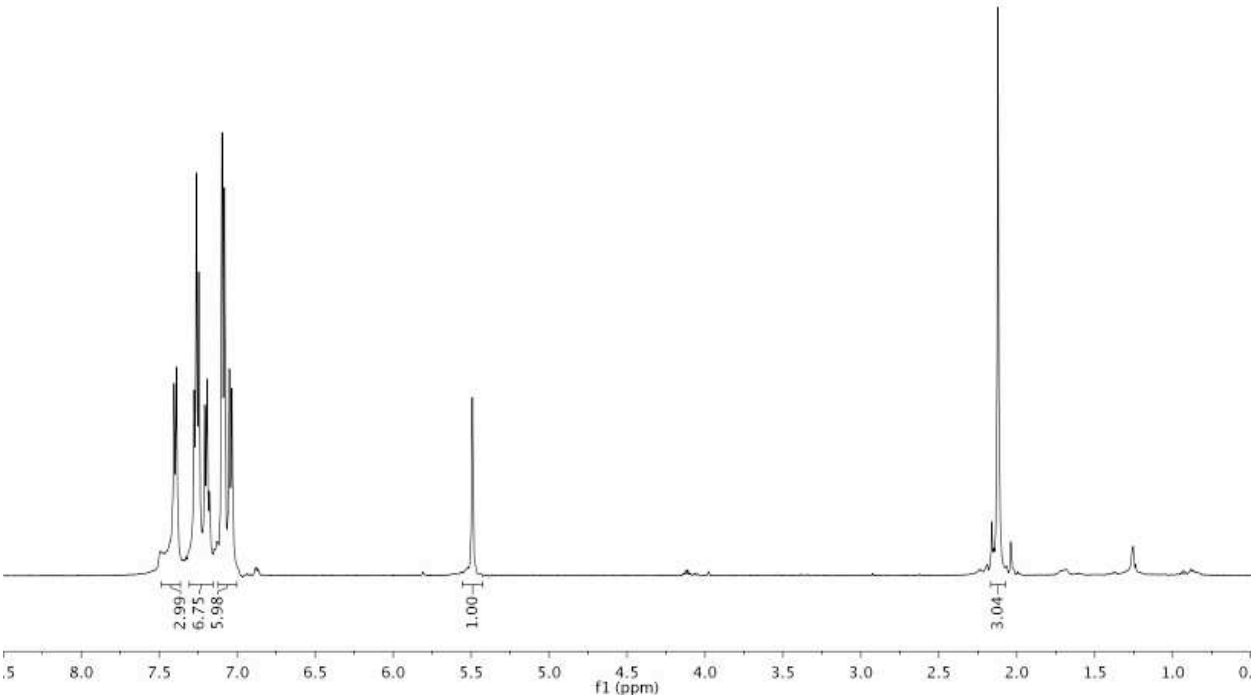


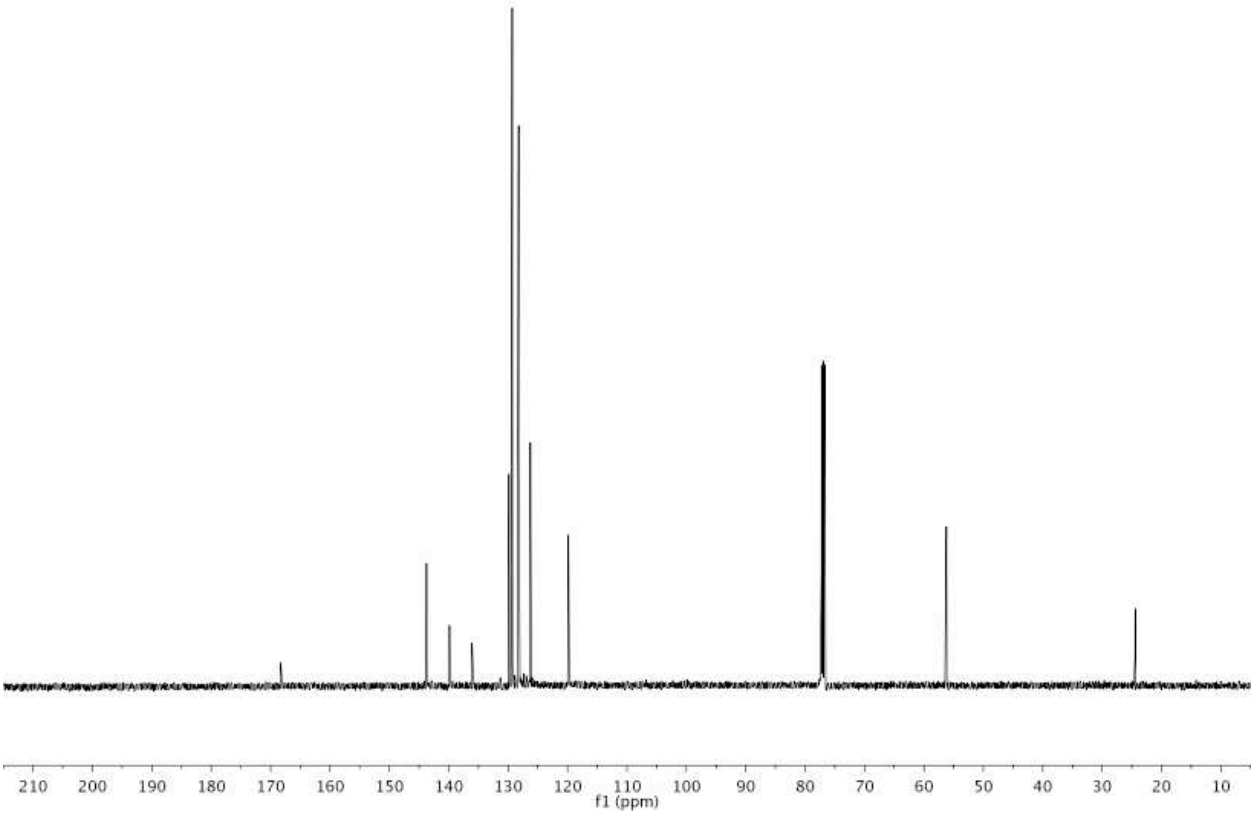




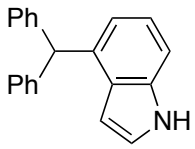
3ar – *N*-(4-Benzhydrylphenyl)acetamide

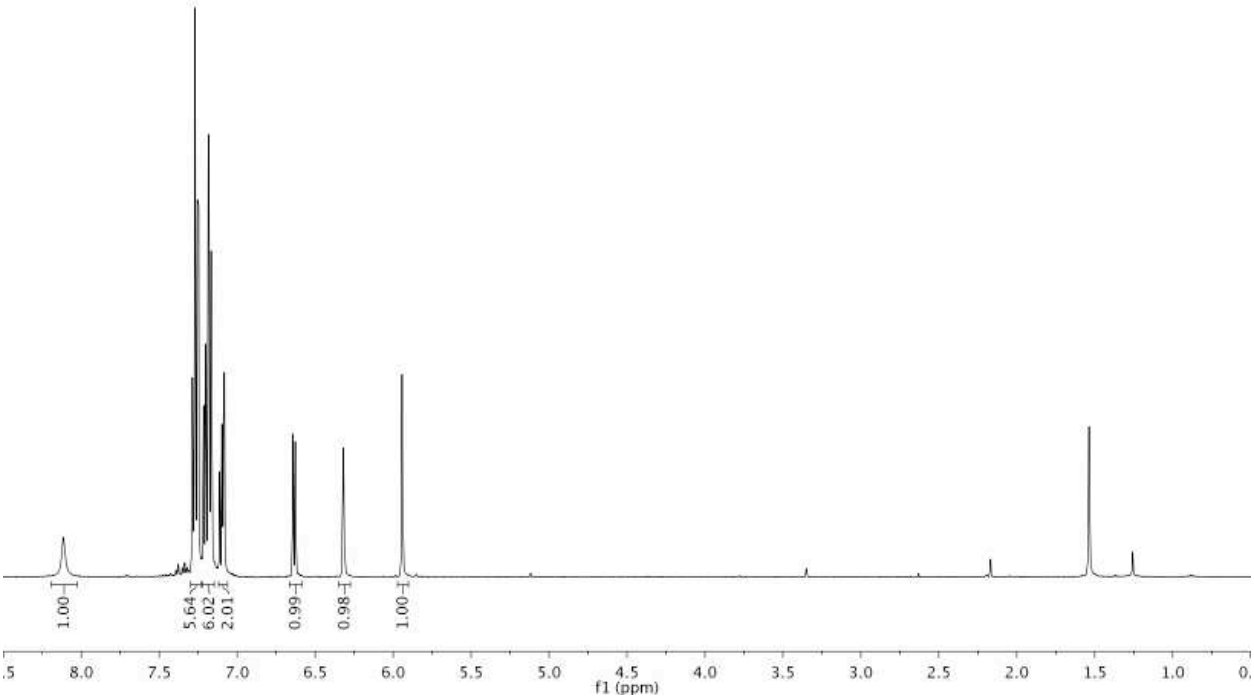


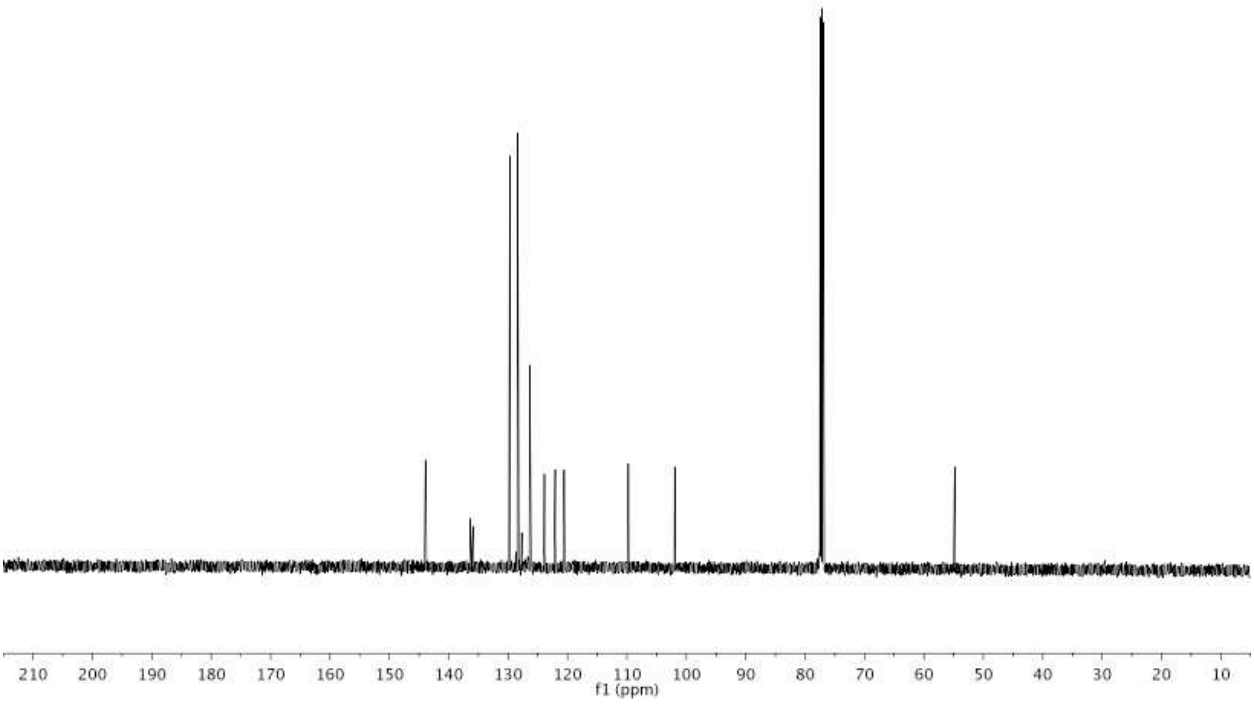




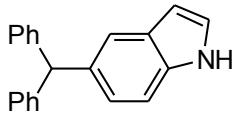
3as – 4-Benzhydryl-1*H*-indole

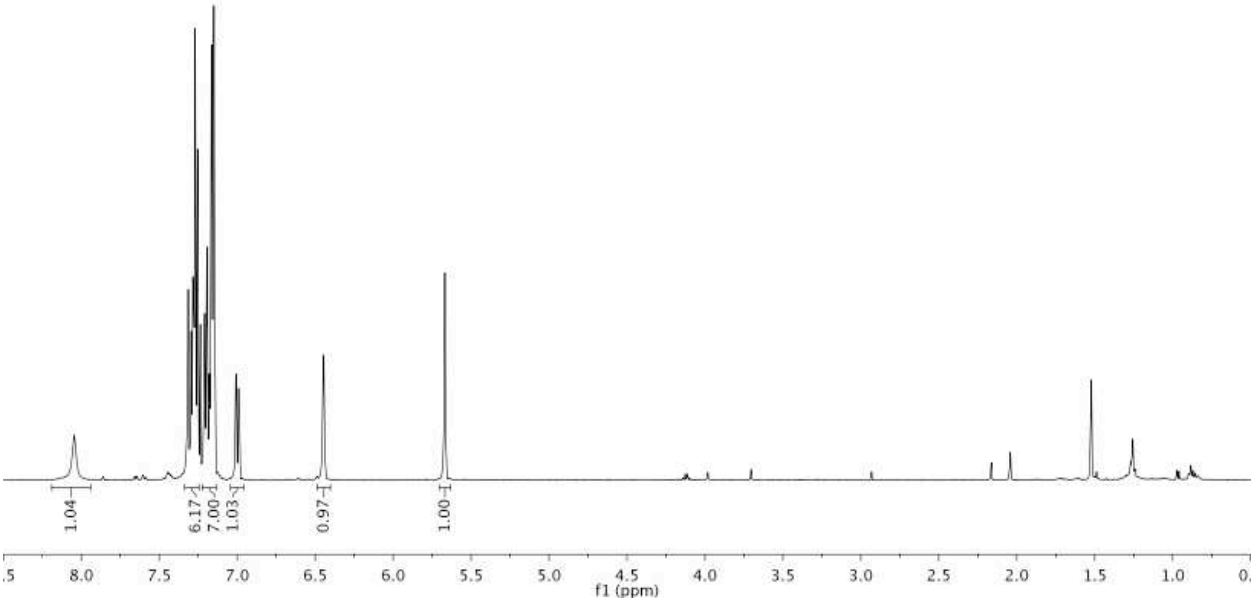


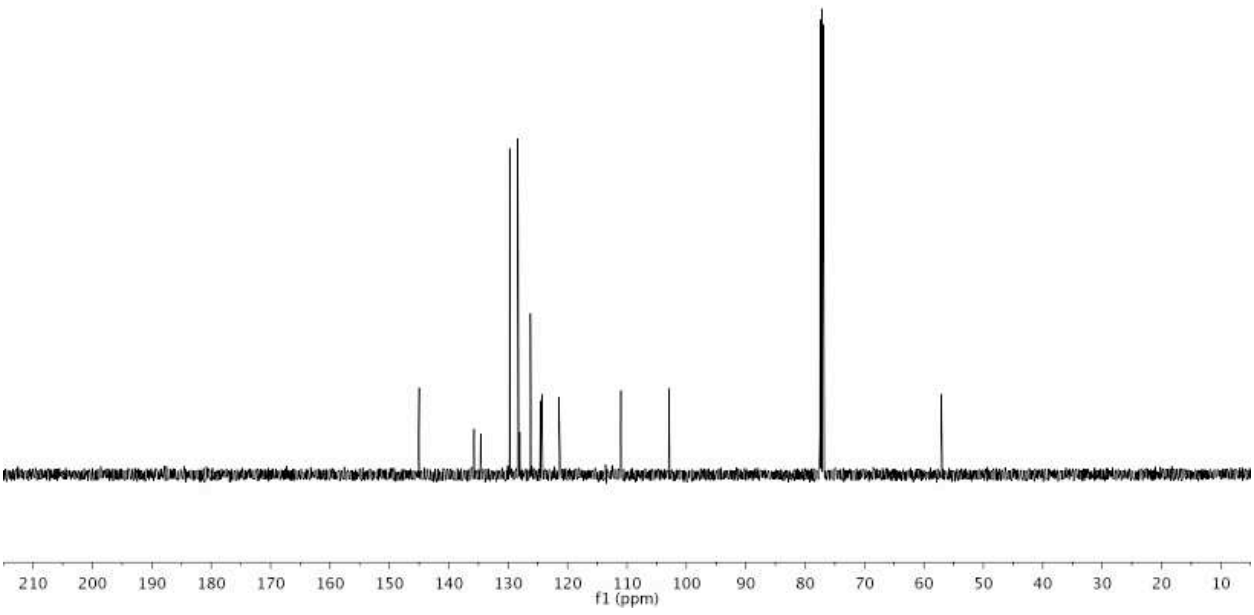




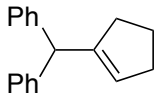
3at – 5-Benzhydryl-1*H*-indole

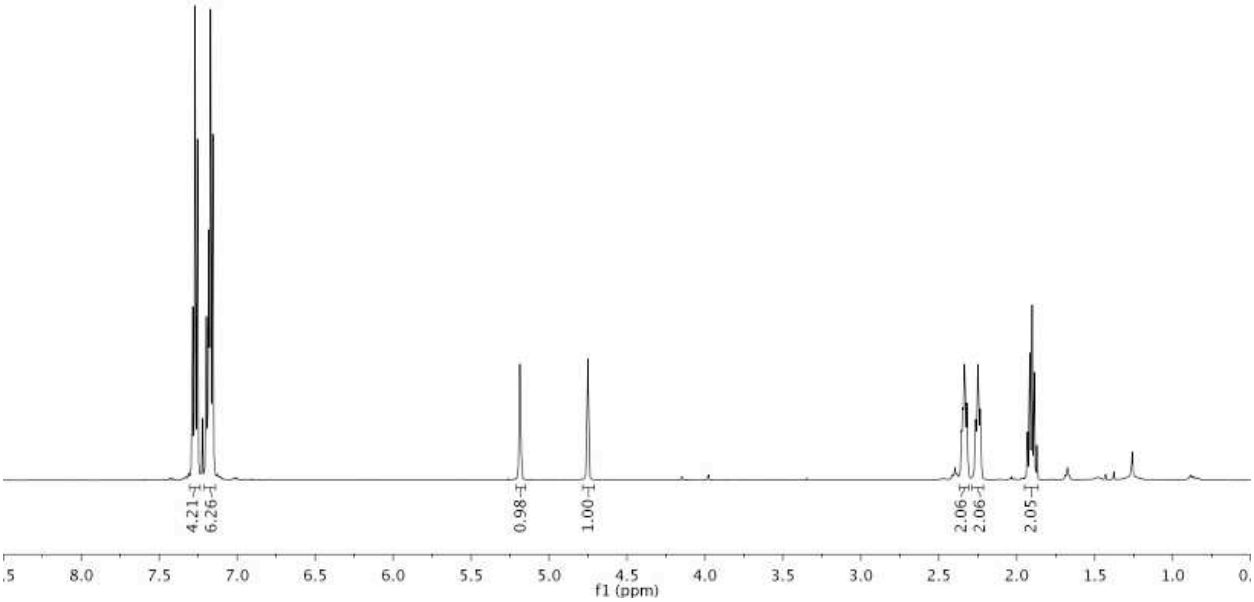


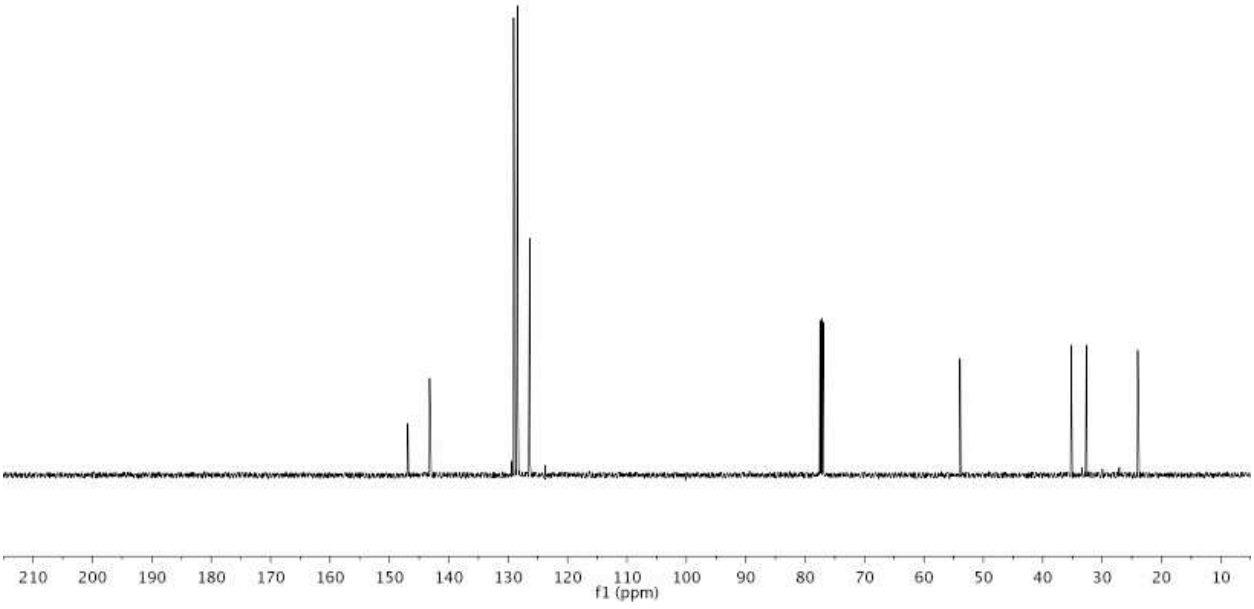




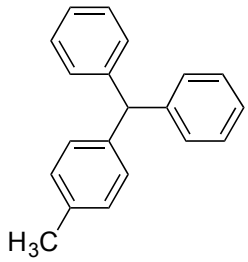
3au – 1-Benzhydrylcyclopent-1-ene

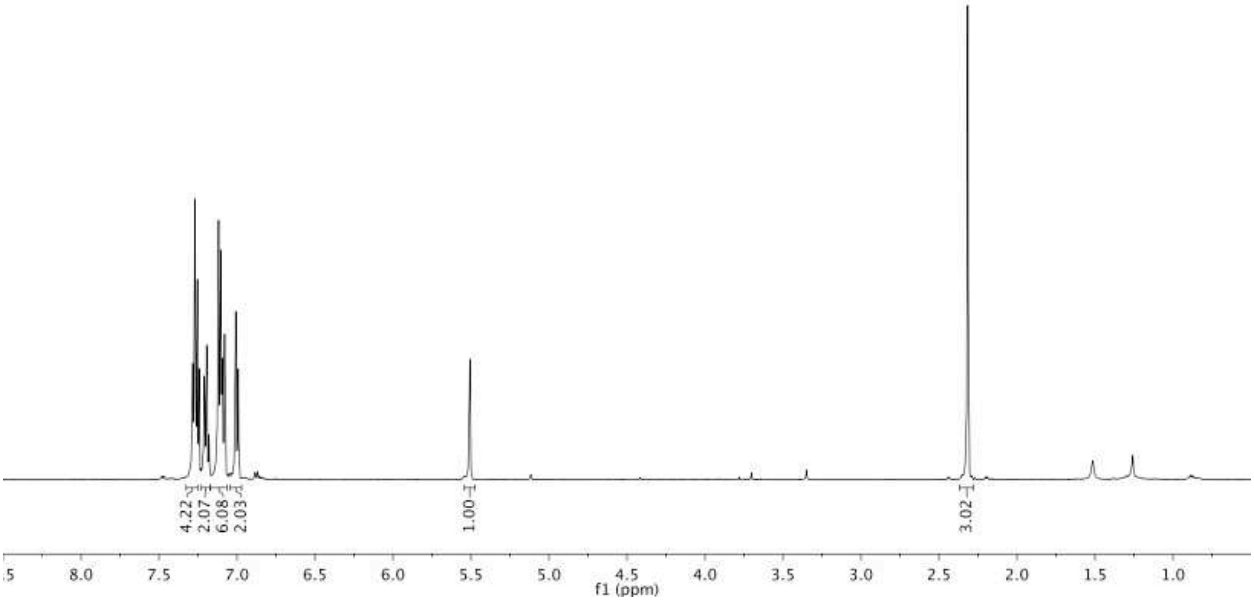


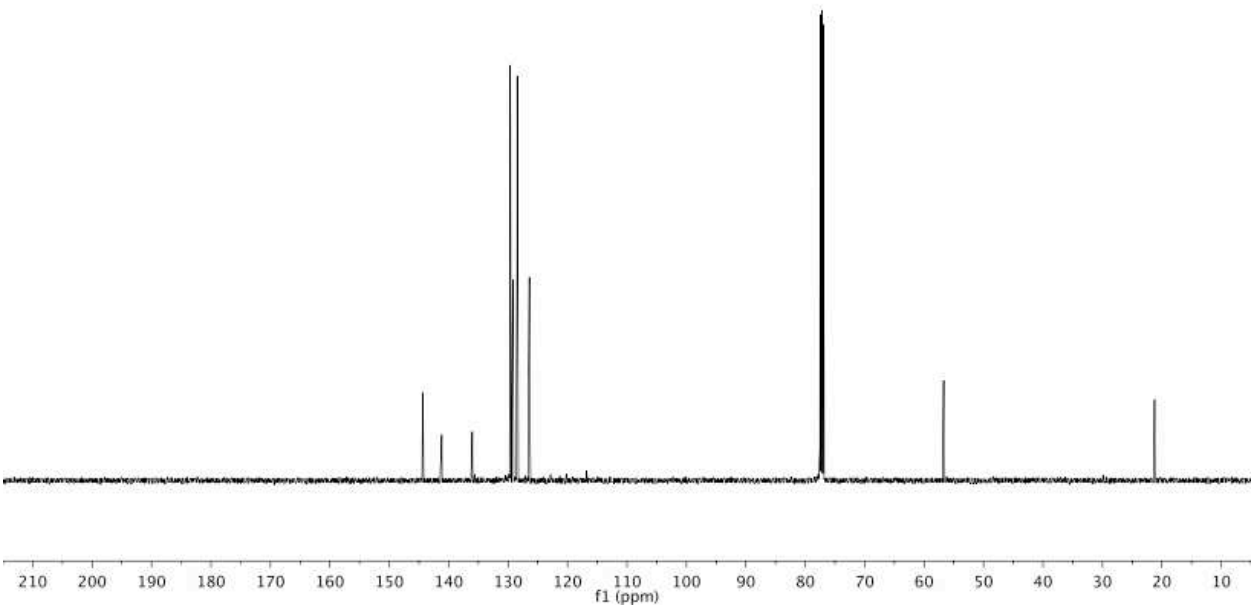




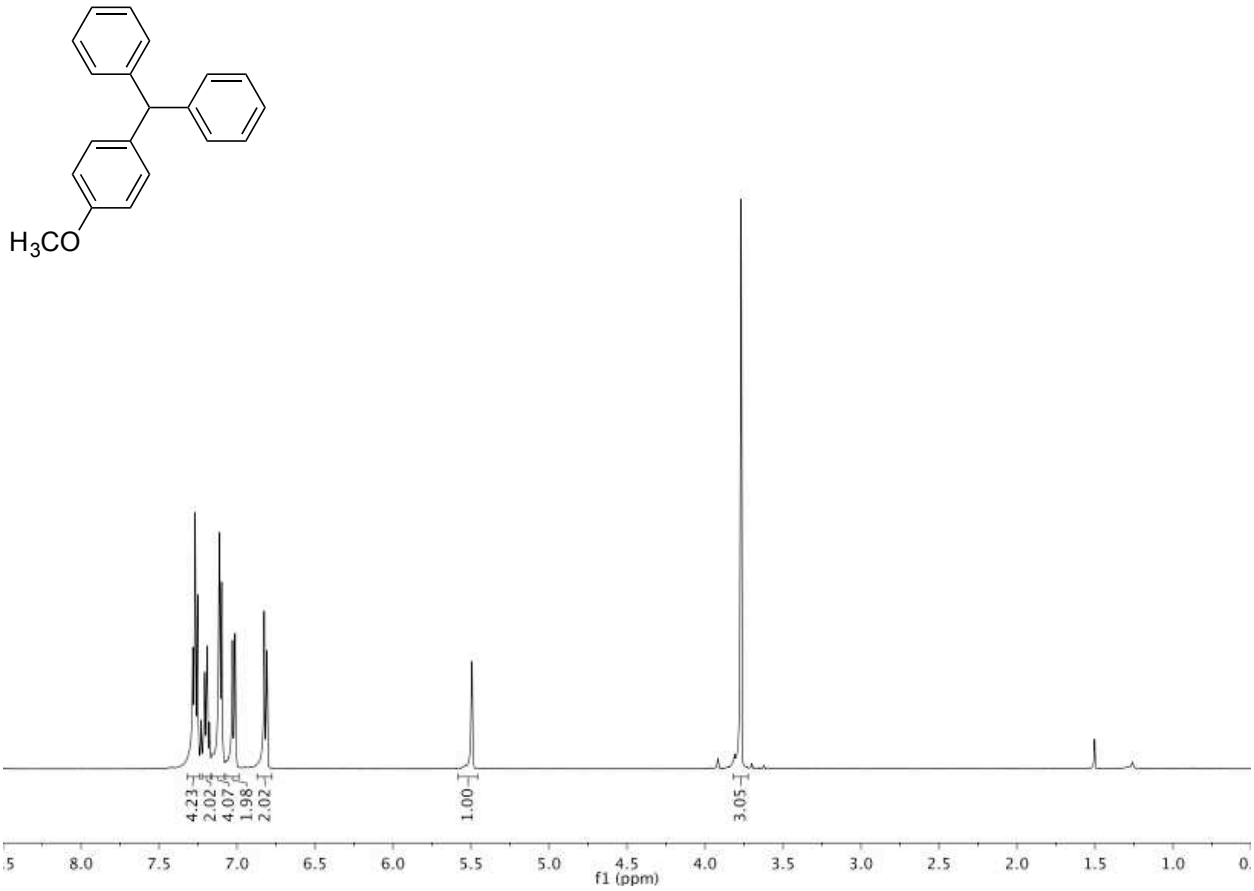
3bb – (4-Methylphenyl)diphenylmethane

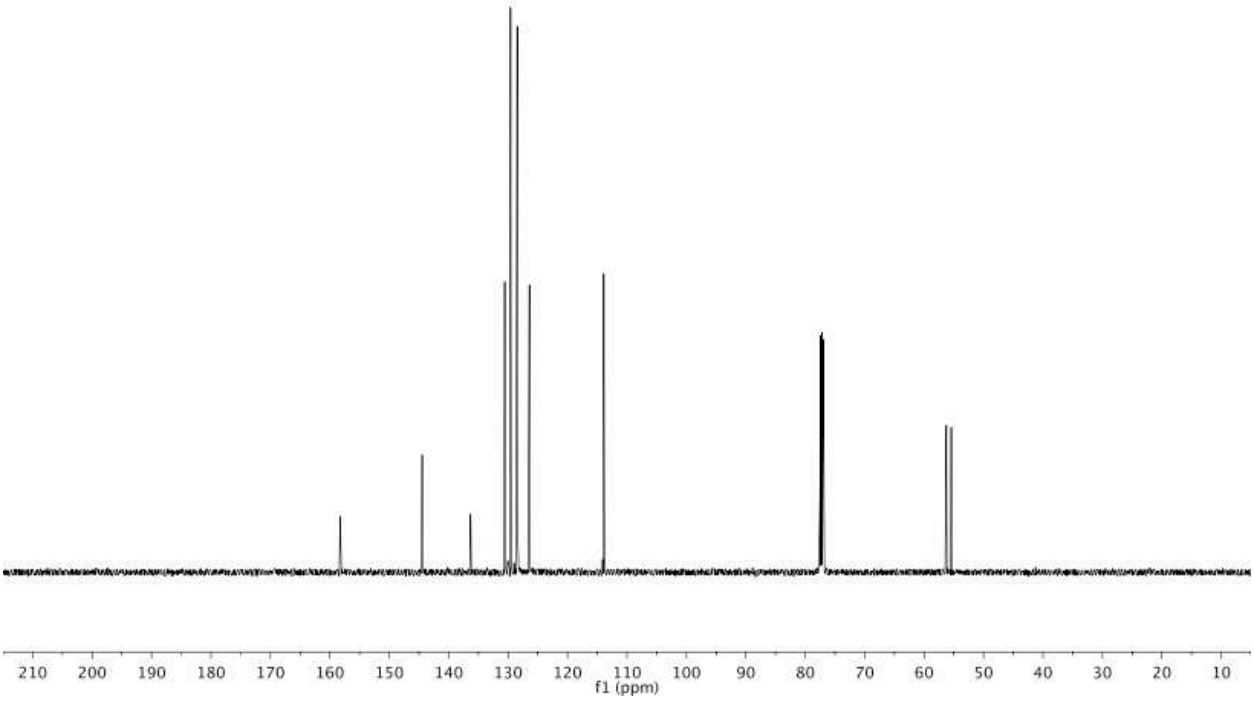




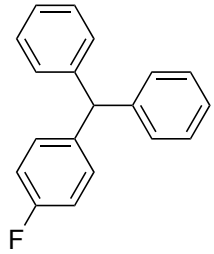


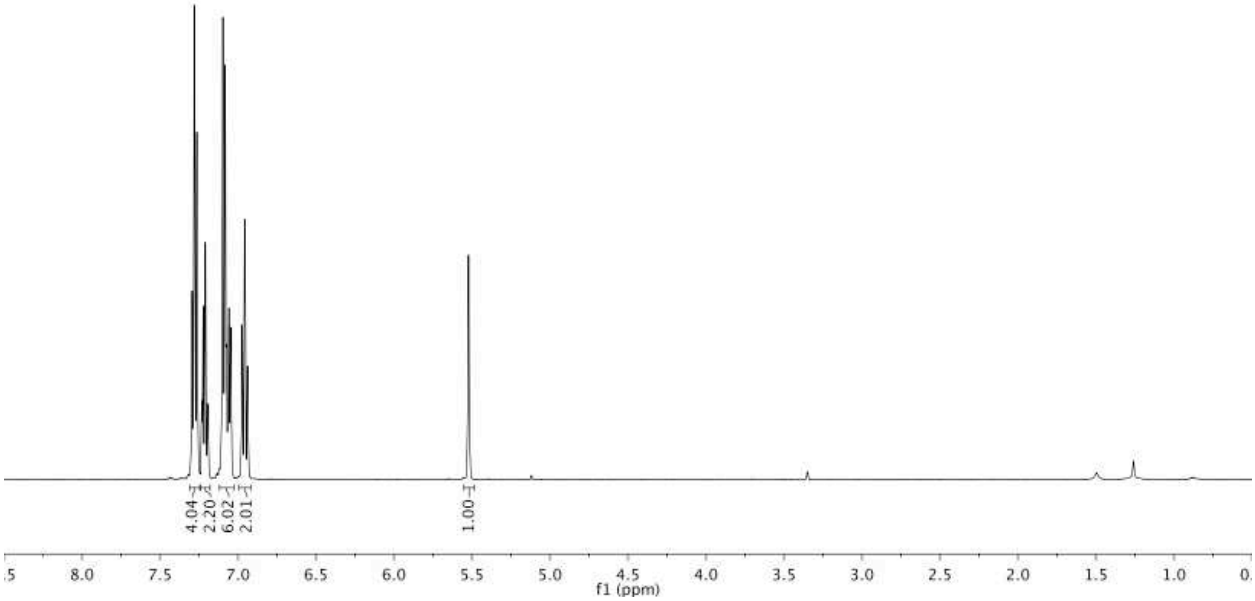
3cb – (4-Methoxyphenyl)diphenylmethane

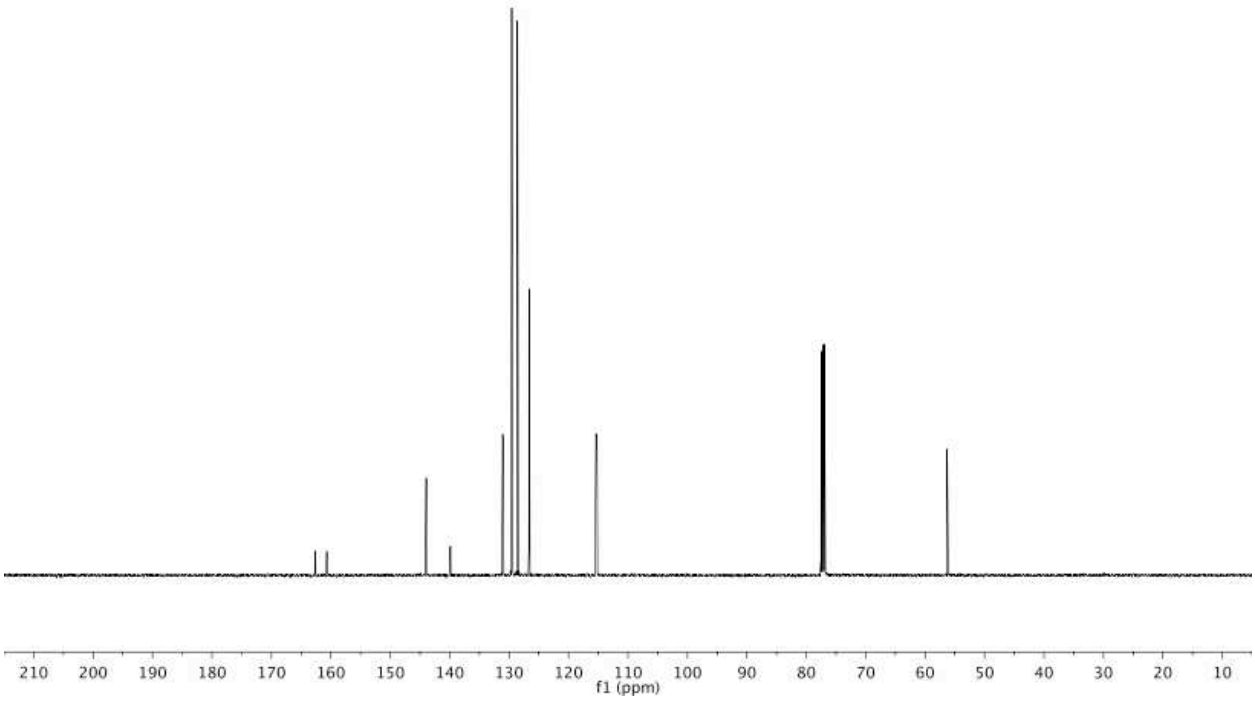




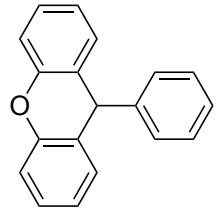
3db – (4-Fluorophenyl)diphenylmethane

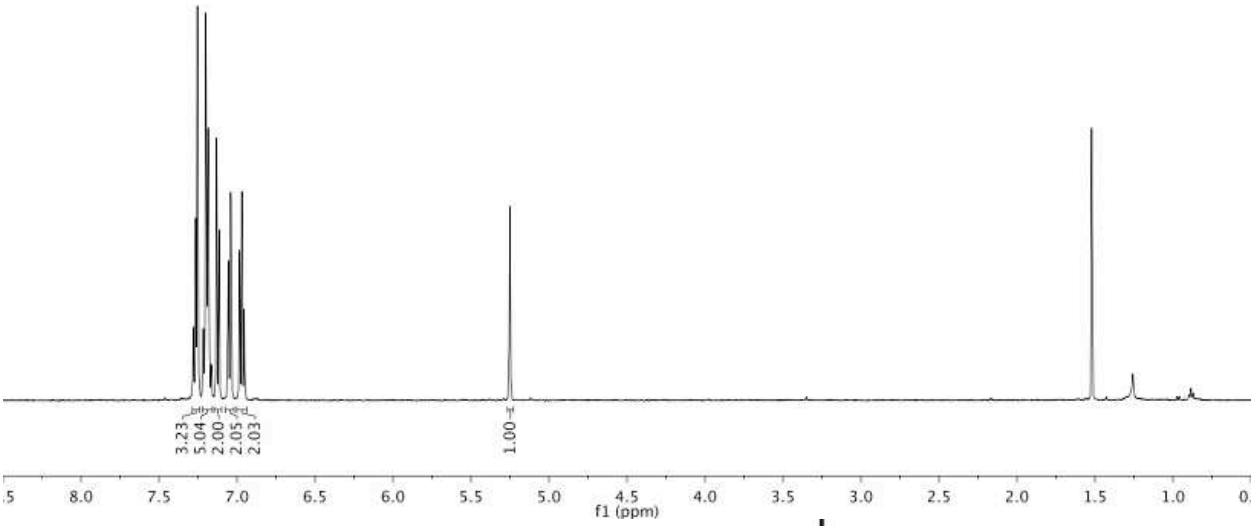


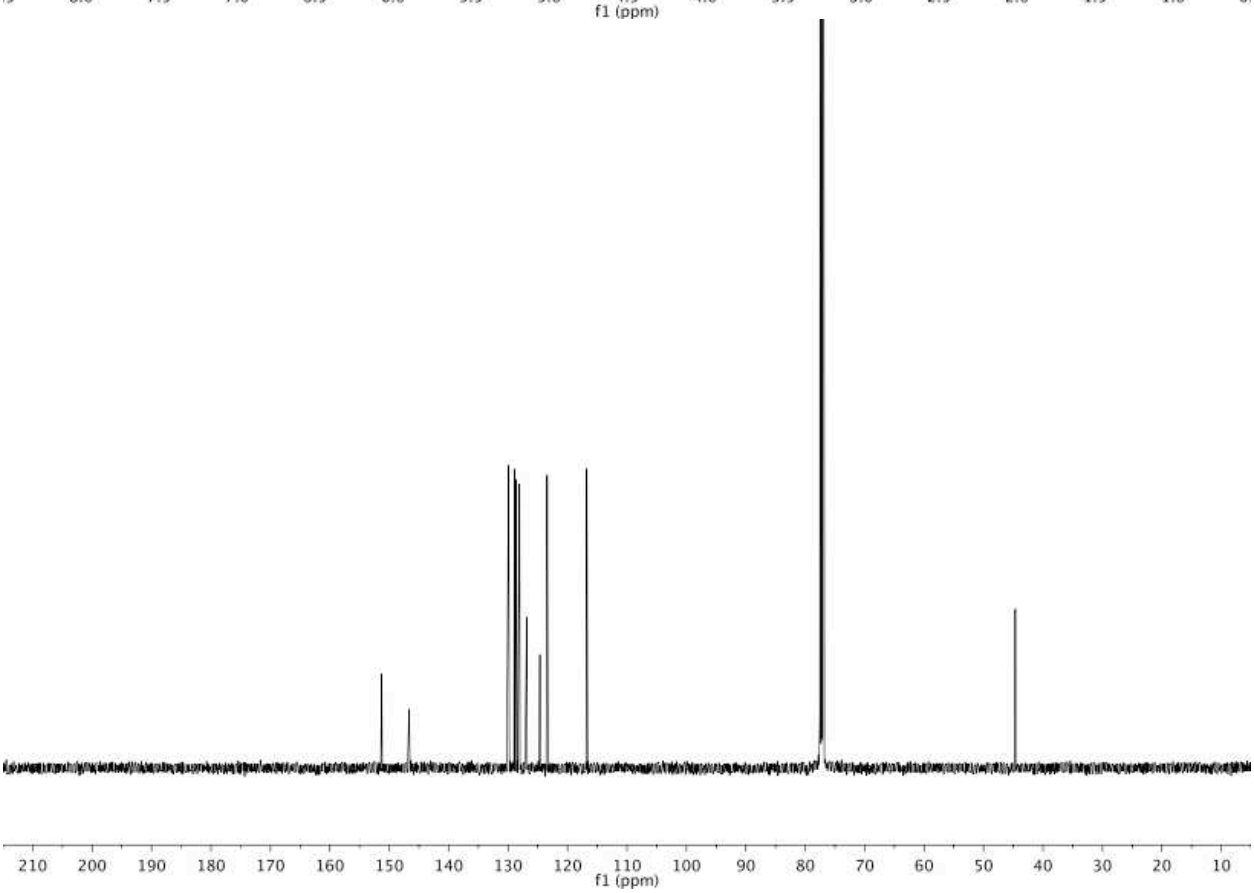




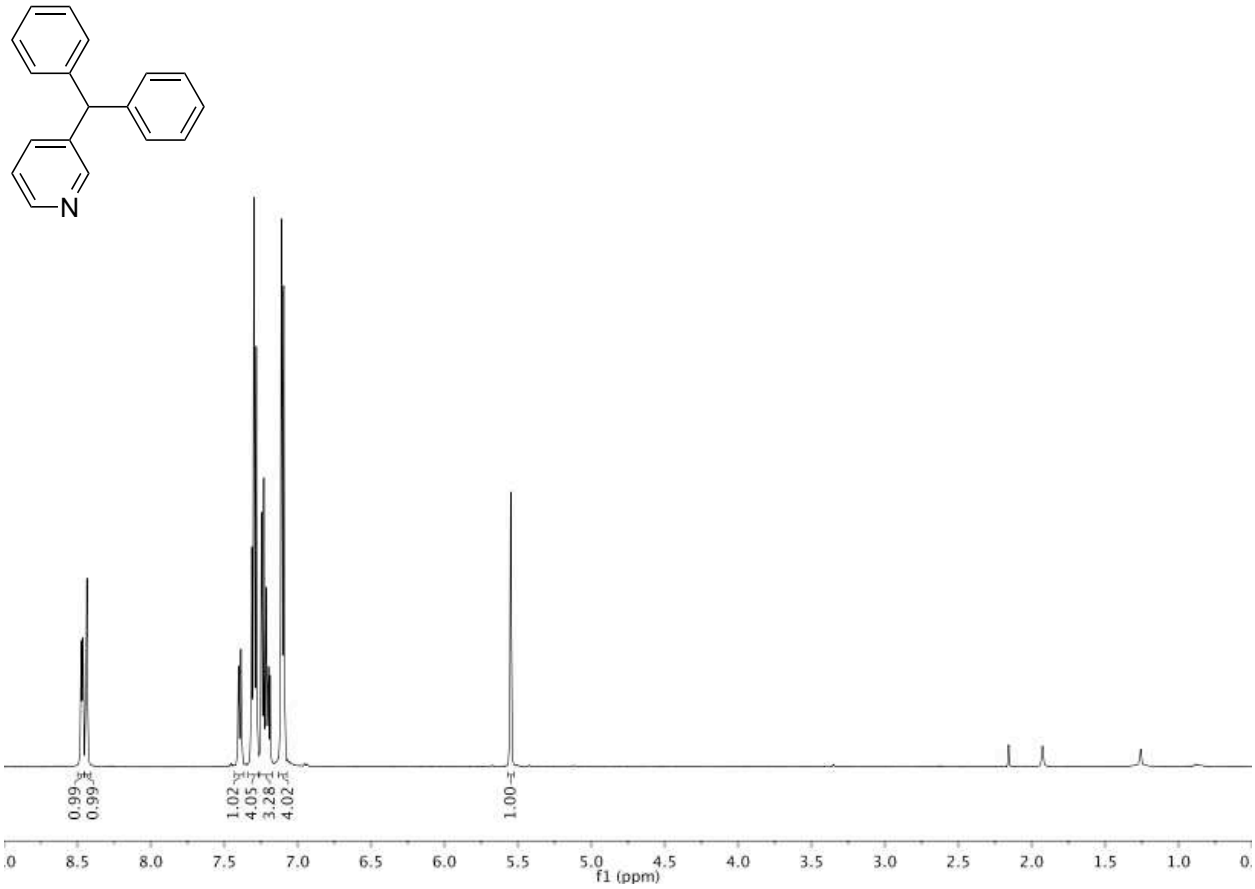
3eb – 9-Phenyl-9*H*-xanthene

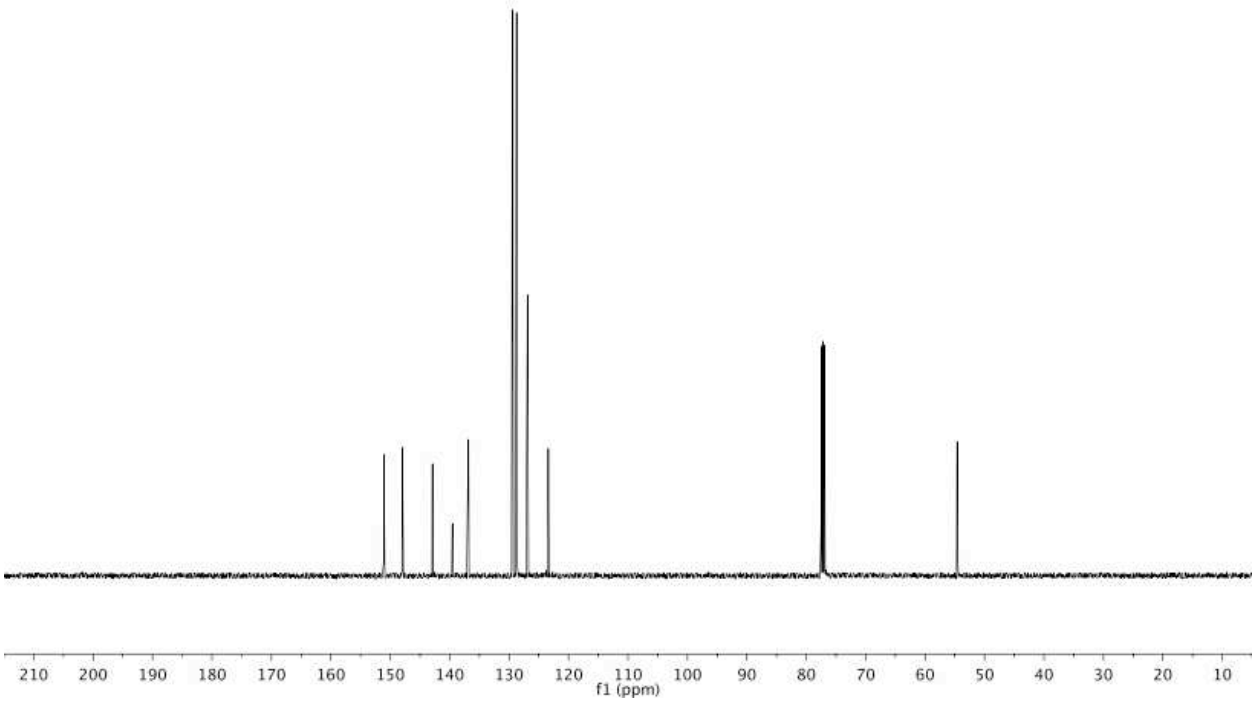




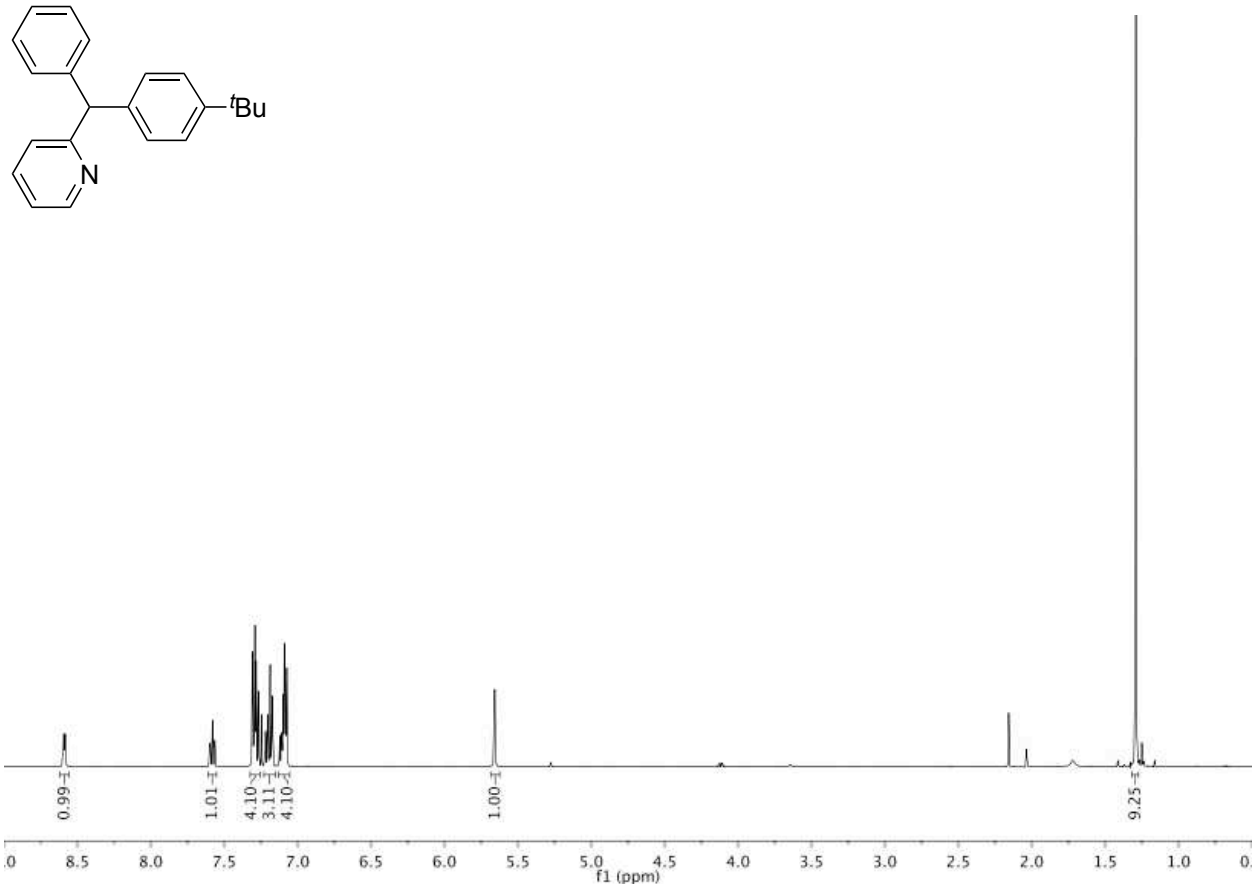


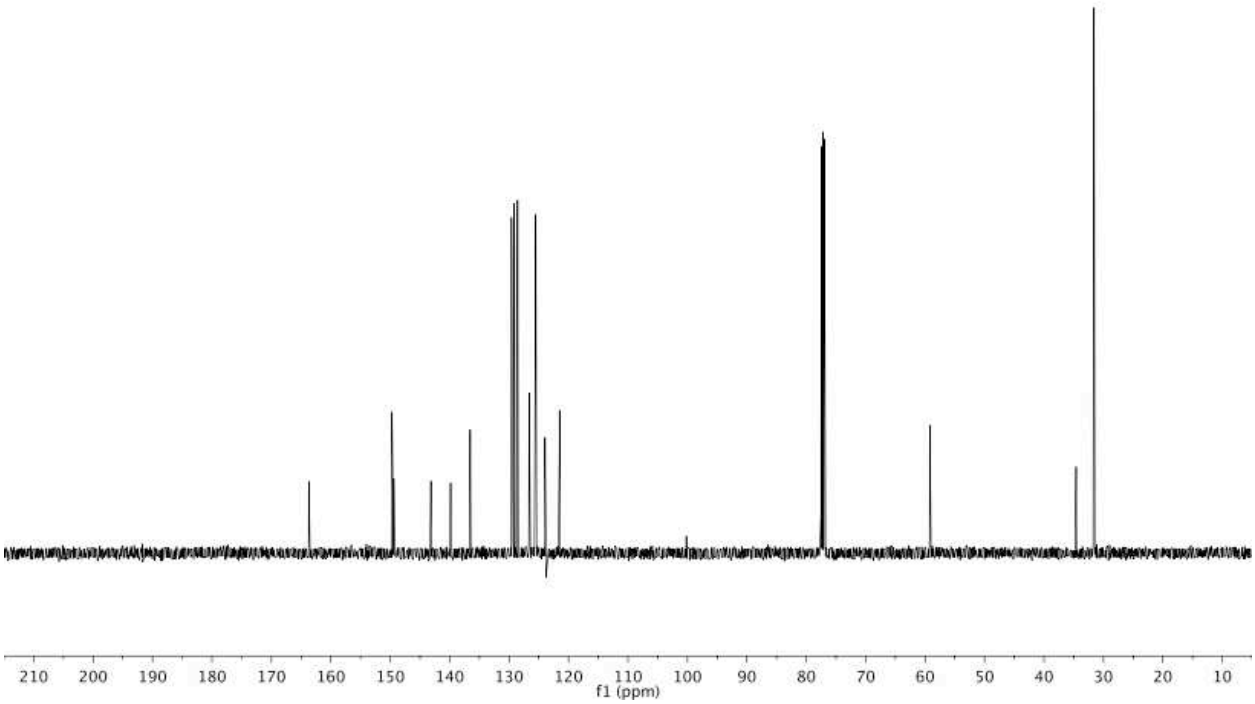
3fb – (3-Benzhydryl)pyridine



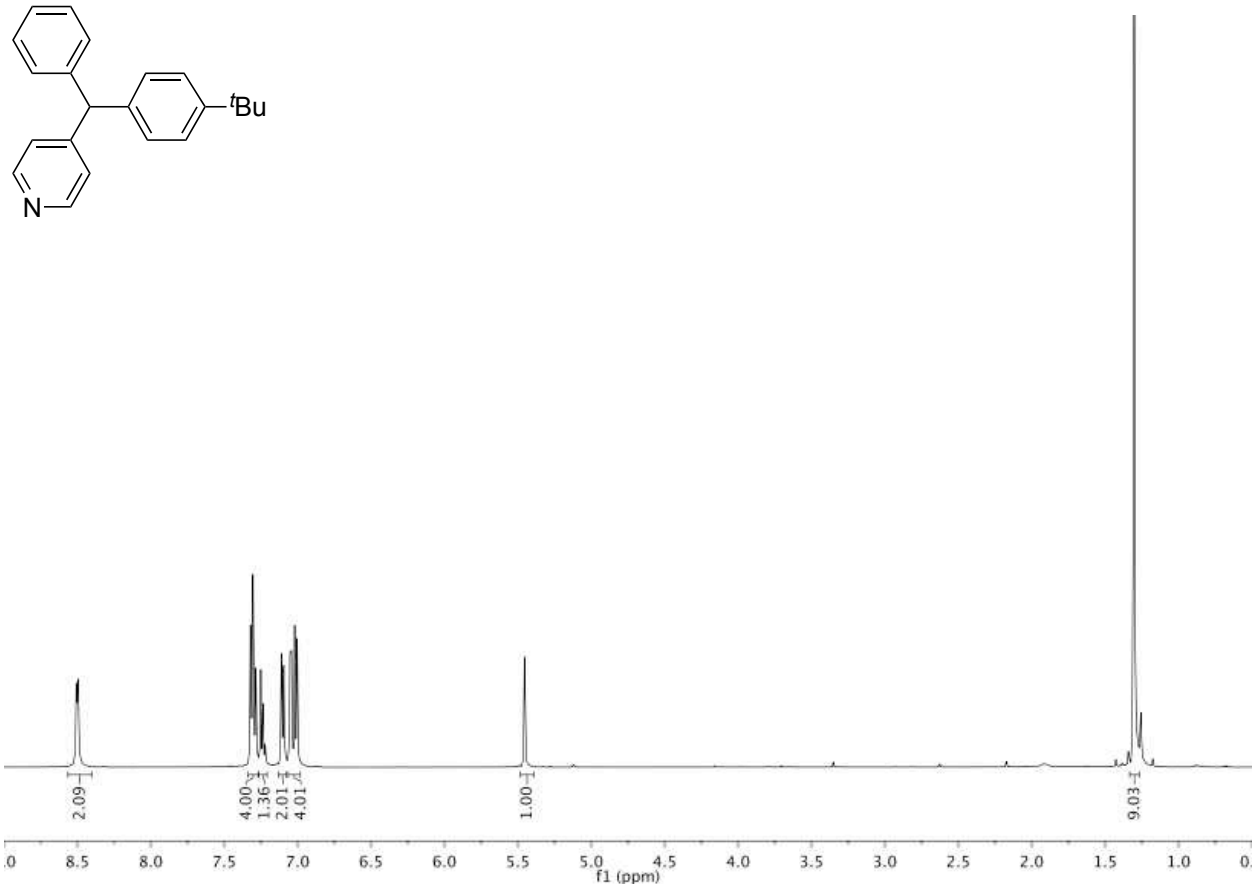


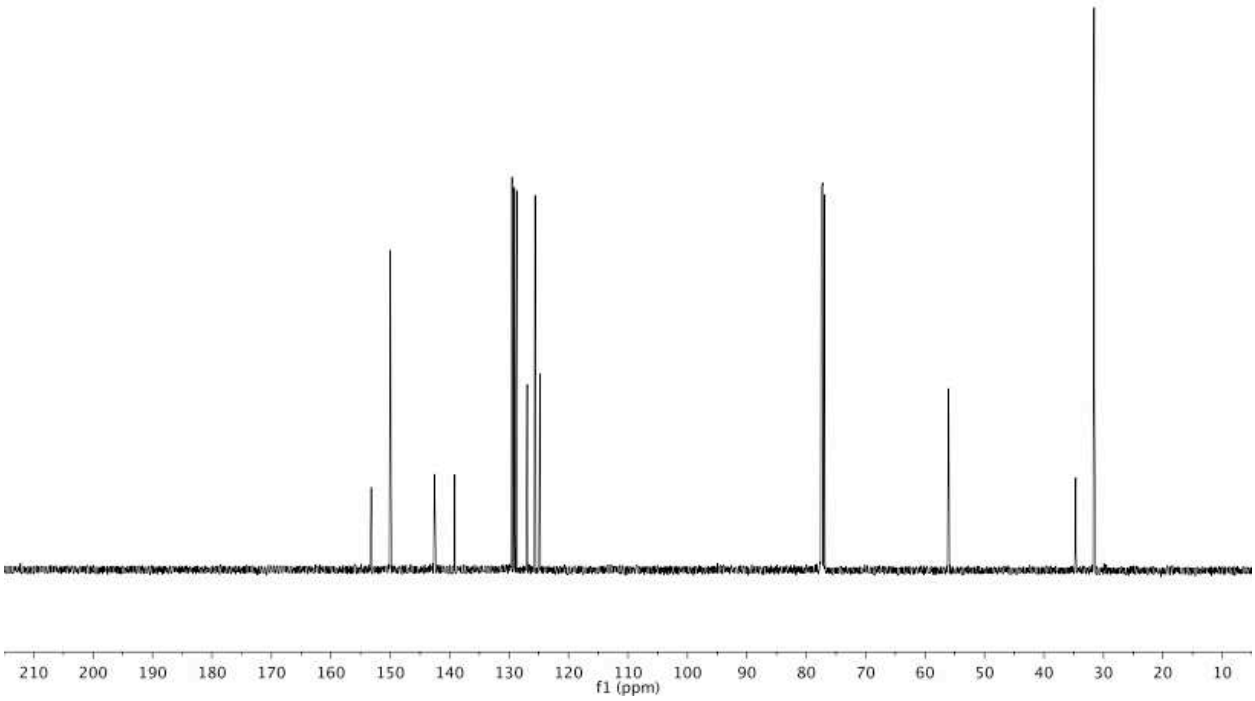
3ga – (4-*tert*-Butylphenyl)(2-pyridyl)phenylmethane



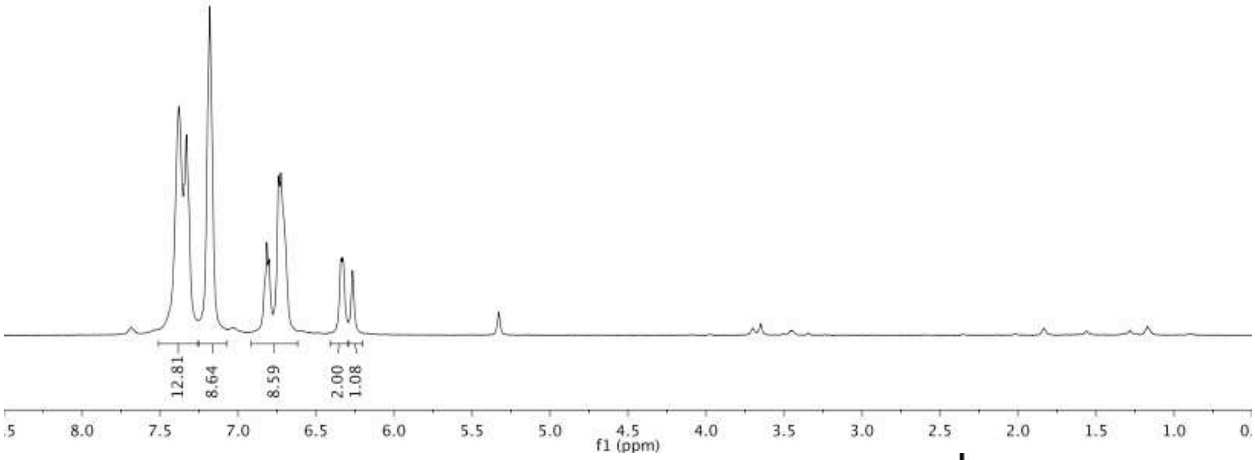


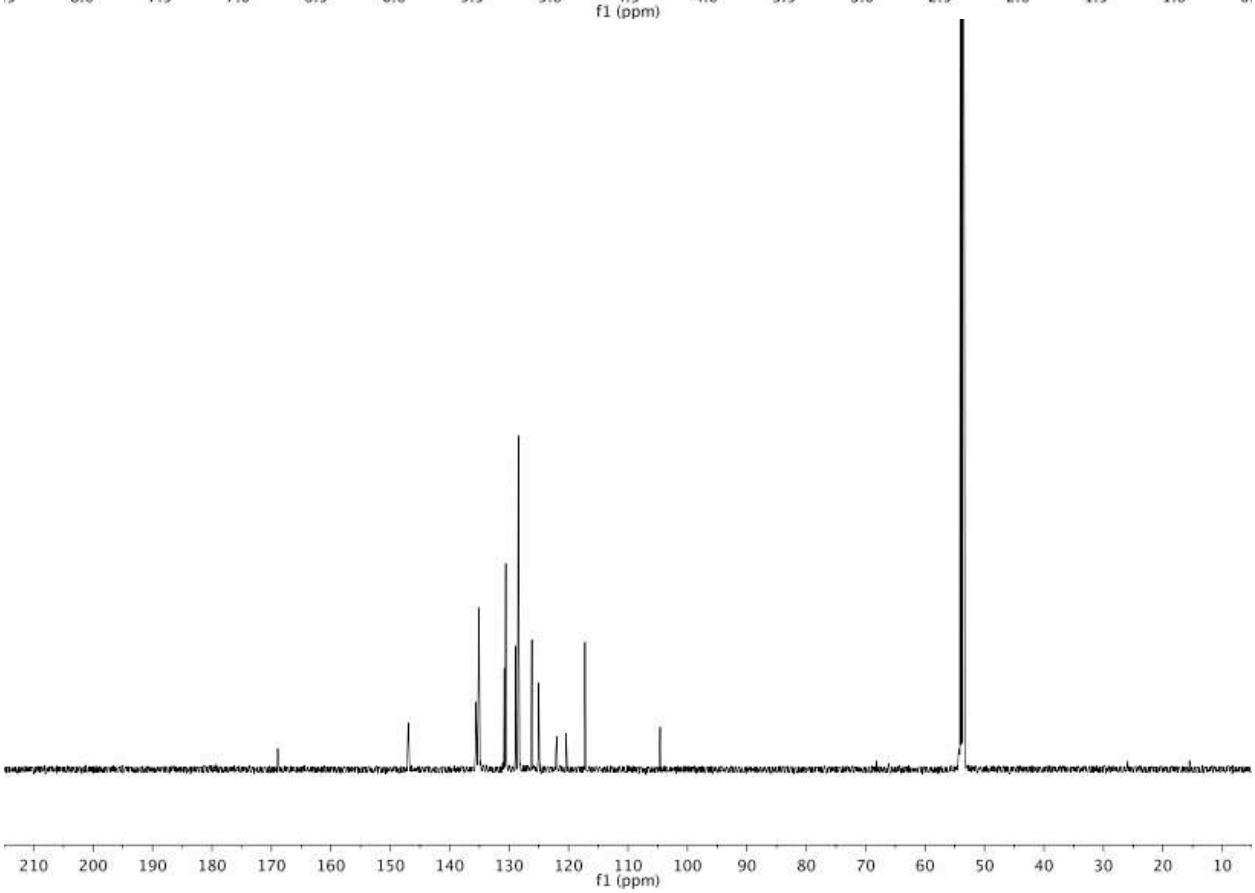
3ha – (4-*tert*-Butylphenyl)(4-pyridyl)phenylmethane

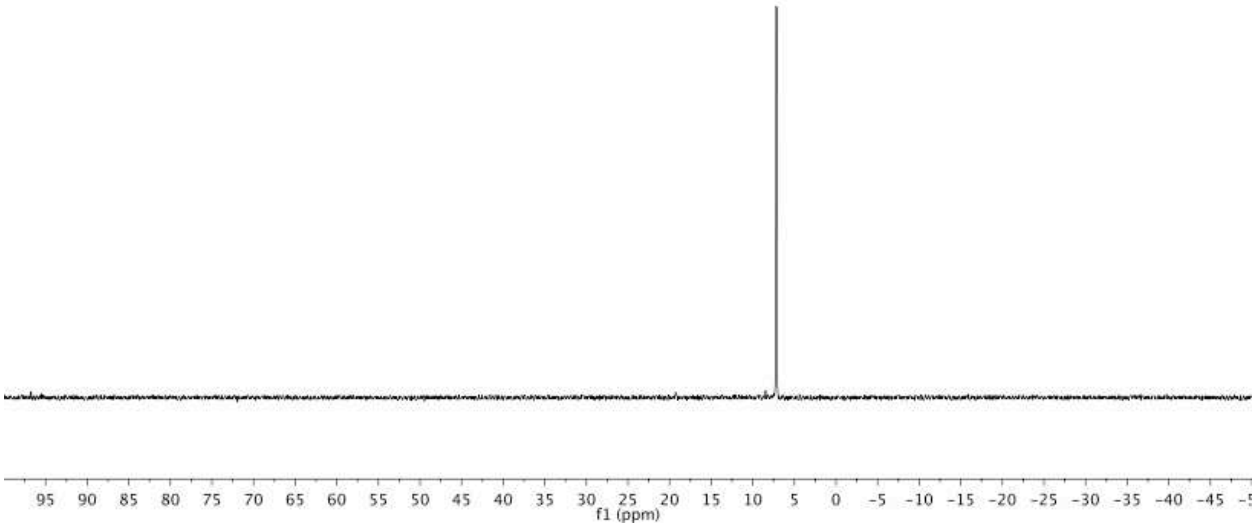




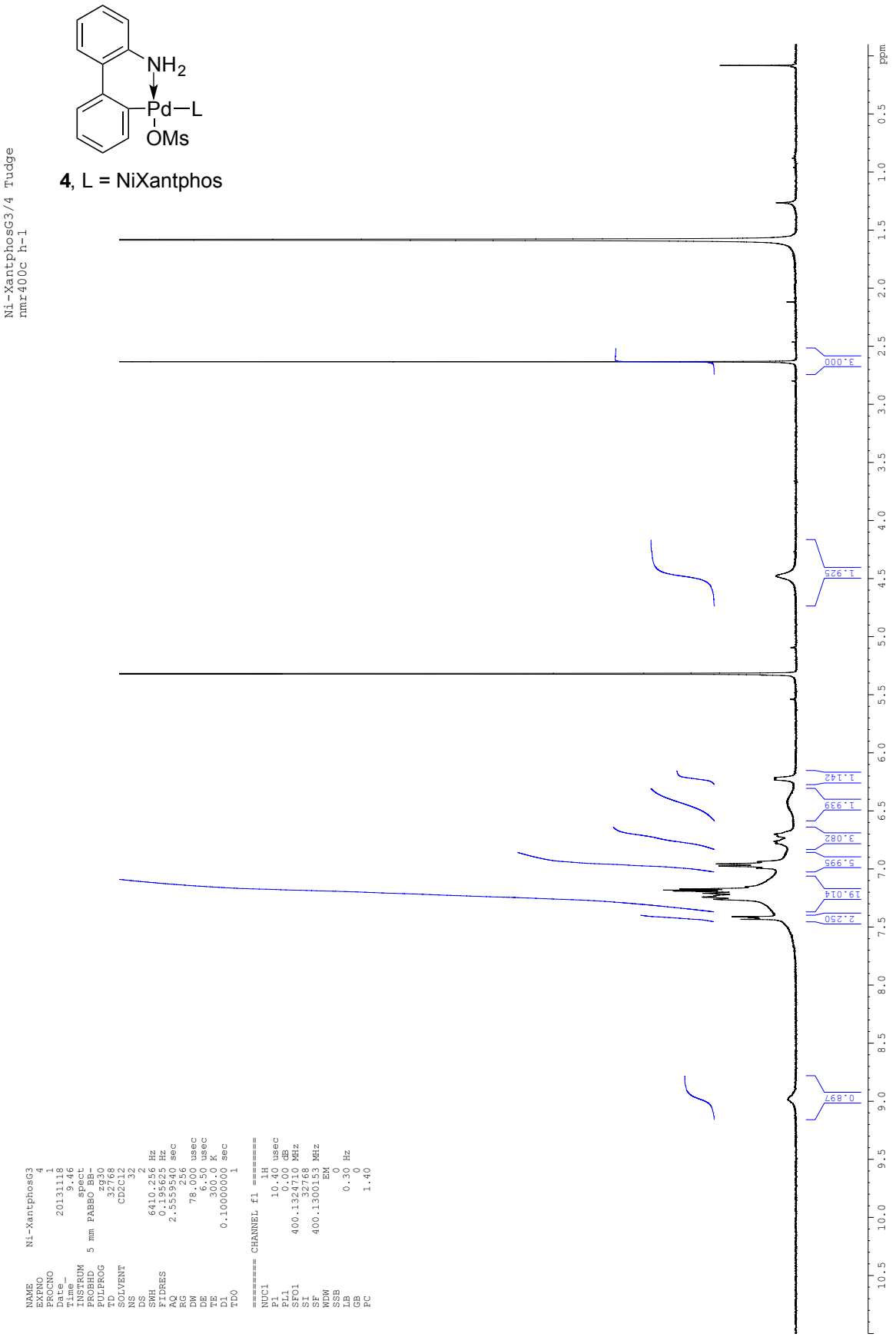
5 – (NiXantphos)Pd(4-C_6H_4CN)(Br)





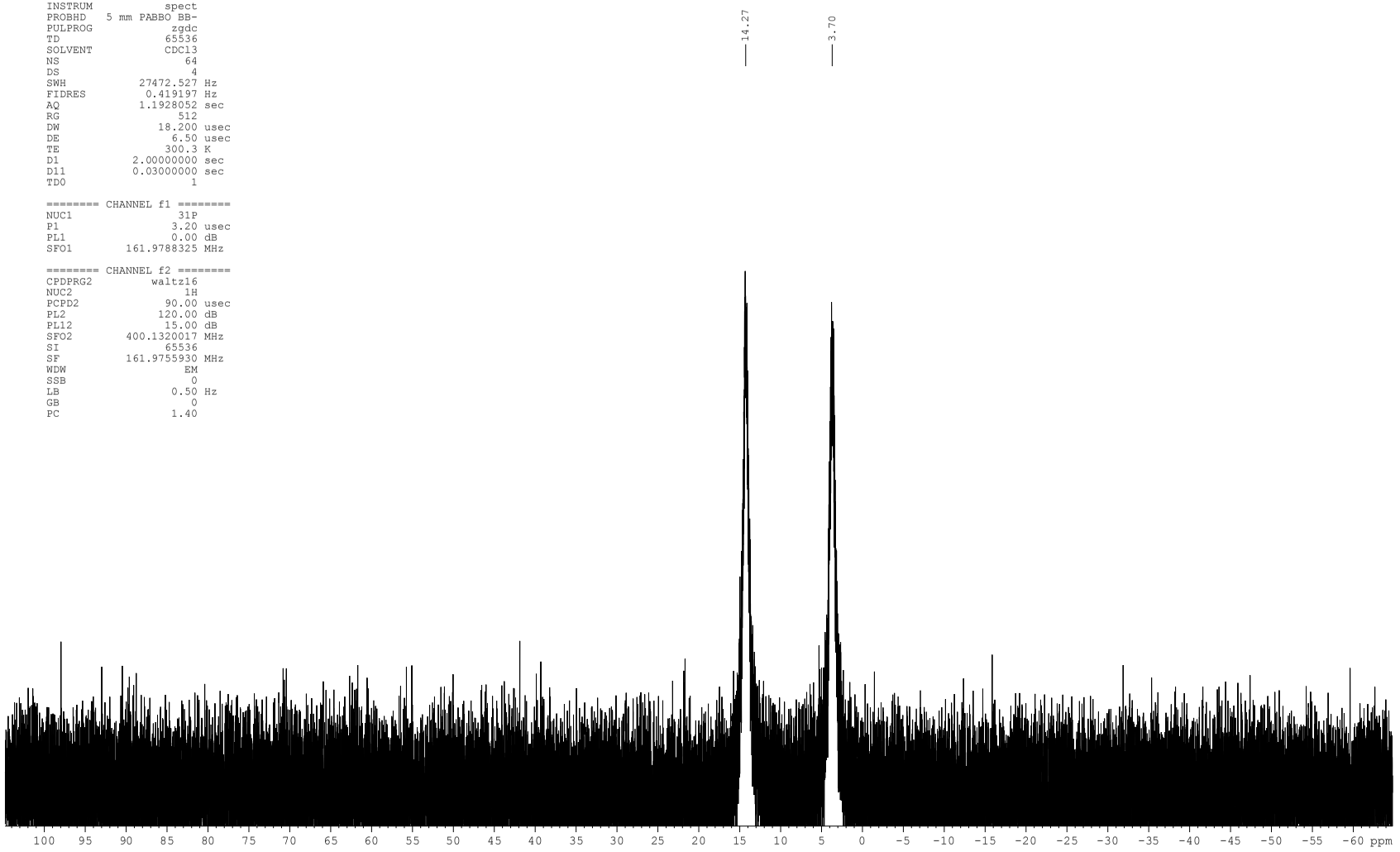

95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0 -5 -10 -15 -20 -25 -30 -35 -40 -45
f1 (ppm)

4 – the Methanesulfonate Precatalyst



Ni-XantphosG3/2 Tudge
nmr400b p-31

NAME	Ni-XantphosG3
EXPNO	2
PROCNO	1
Date_	20131115
Time	14.05
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zgdc
TD	65536
SOLVENT	CDC13
NS	64
DS	4
SWH	27472.527 Hz
FIDRES	0.419197 Hz
AQ	1.1928052 sec
RG	512
DW	18.200 usec
DE	6.50 usec
TE	300.3 K
D1	2.00000000 sec
D11	0.03000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	31P
P1	3.20 usec
PL1	0.00 dB
SFO1	161.9788325 MHz
======== CHANNEL f2 ========	
CPDPRG2	waltz16
NUC2	1H
PCPD2	90.00 usec
PL2	120.00 dB
PL12	15.00 dB
SFO2	400.1320017 MHz
SI	65536
SF	161.9755930 MHz
WDW	EM
SSB	0
LB	0.50 Hz
GB	0
PC	1.40



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