

Supporting Information

Beyond Aresta's Complex: Ni- and Pd-Catalyzed Organozinc Coupling to CO₂

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Table of Contents

1. General Information	1
2. Materials	1
3. Methods	2
4. Experimental Procedures and Spectral Data	2
5. References	15

1. General Information

All manipulations were carried out using a standard Schlenk line filled with dry, oxygen-free Ar (Grade 4.8) or N₂ (Grade 5.0) and glovebox under an atmosphere of N₂ (Grade 5.0). Carboxylation experiments were conducted under a Schlenk line filled with CO₂ (Grade 4.0, <20 ppm O₂, <10 ppm H₂O).

2. Materials

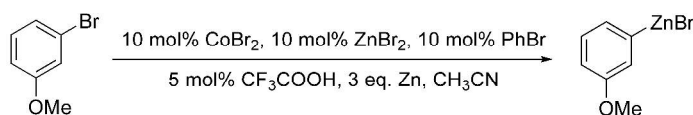
Tetrahydrofuran (THF) and diethyl ether were distilled from sodium and benzophenone under argon and degassed by three freeze-pump-thaw cycles prior to storage in the glovebox. Toluene was distilled from CaH₂ or Na and degassed prior to storage. Acetonitrile was distilled from CaH₂ and used without further purification. *N,N*-dimethylformamide (DMF) was dried by passage of anhydrous DMF through two columns of activated alumina. Bis(1,5-cyclooctadiene)nickel(0), bis(tricyclohexylphosphine)palladium(0), palladium(II) acetate, zinc bromide, tricyclohexylphosphine and diphenylzinc were purchased from Strem and used as is. Nickel(II) 2,4-pentanedionate, zinc dust (98%), cobalt(II) bromide, and all aryl and alkyl halides were available through Aldrich, Alfa-Aesar or Oakwood Chemicals and used as received. 4-bromophenyl acetate and 4-iodophenyl acetate were prepared from 4-bromophenol and 4-iodophenol, respectively.¹ Pyridine, acetic anhydride and iodine are commercially available from ACP. *d*⁸-THF and *d*⁸-toluene were purchased from Cambridge Isotope Laboratories and purified as above (Note: toluene can be transferred to a sealable Schlenk tube and degassed without distillation). Organozinc reagents were obtained from commercial sources or prepared from their corresponding aryl^{2a} or alkyl^{2b} bromides, degassed by three freeze-pump-thaw cycles, and filtered through a syringe needle equipped with a small piece of filter paper prior to use. Their concentration was evaluated by iodolytic titration either against authentic samples of their corresponding iodides by gas chromatography (GC) using dodecane as an internal standard^{2a} or by colorimetric determination.³

3. Methods

^1H -, ^{13}C -, and ^{31}P -NMR spectra were recorded on a Varian 300 or VRX-S (Unity) 400 spectrometer at ambient temperature in CDCl_3 unless otherwise noted. Data for ^1H -NMR are reported as follows: chemical shift (δ ppm), multiplicity, integration, and coupling constant (Hz). Data for ^{13}C - and ^{31}P -NMR spectra are reported in terms of chemical shift (δ ppm). All air-sensitive NMR experiments were conducted using a J-YOUNG NMR tube equipped with a Teflon stopcock. GC traces were acquired on a Perkin-Elmer AutoSystem XL Gas Chromatograph or Agilent 6890N Network GC instrument equipped with a flame-ionization detector. A Simplicity 5 column (poly(5% diphenyl/95% dimethylpolysiloxane), 30 m length, 0.32 mm inner diameter, 0.25 μm film thickness), HP-5 column (30 m length, 0.32 mm inner diameter, 0.25 μm film thickness), or ZB-FFAP column (nitroterephthalic acid modified polyethylene glycol, 30 m length, 0.25 mm inner diameter, 0.25 μm film thickness) was used for all analyses. Organic solutions were concentrated under reduced pressure on a Büchi rotary evaporator. Chromatographic purification of products was accomplished using forced-flow chromatography on Silicycle Silica-P Flash Silica Gel (40-63 μm). Thin-layer chromatography (TLC) was performed on EMD Silica Gel 60 F₂₅₄ plates (250 μm).

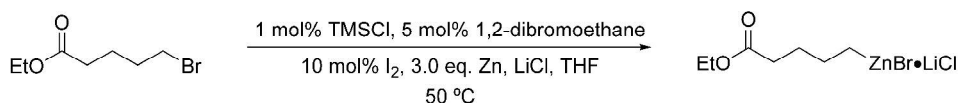
4. Experimental Procedures and Spectral Data

General Procedure A1: 3-methoxyphenylzinc bromide by Co-catalyzed zincation of 3-bromoanisole^{2a}



According to a modified procedure of Gosmini and co-workers,^{2a} a 50 mL oven-dried Schlenk flask was charged with CoBr_2 (330 mg, 1.5 mmol), ZnBr_2 (340 mg, 1.5 mmol), and Zn dust (3.25 g, 49.7 mmol). Subsequently, CH_3CN (15 mL) was added via syringe. The resulting suspension was blue in colour. Bromobenzene (160 μL , 1.5 mmol) and trifluoroacetic acid (50 μL , 0.7 mmol) were then added to produce a deep red solution within a few minutes. Within 15 min, complete consumption of the bromobenzene had taken place as judged by GC analysis. 3-bromoanisole (1.90 mL, 15.0 mmol) was syringed into the reaction vessel and the suspension was allowed to stir at rt. Upon full conversion of the aryl bromide to the organozinc species, the reaction mixture was degassed by three freeze-pump-thaw cycles. Iodolytic titration against dodecane as an internal standard revealed the concentration of 3-methoxyphenylzinc bromide to be 0.580 M.

General Procedure A2: 5-ethoxy-5-oxopentylzinc bromide-lithium chloride complex by zincation of ethyl 5-bromoveratrole^{2b}



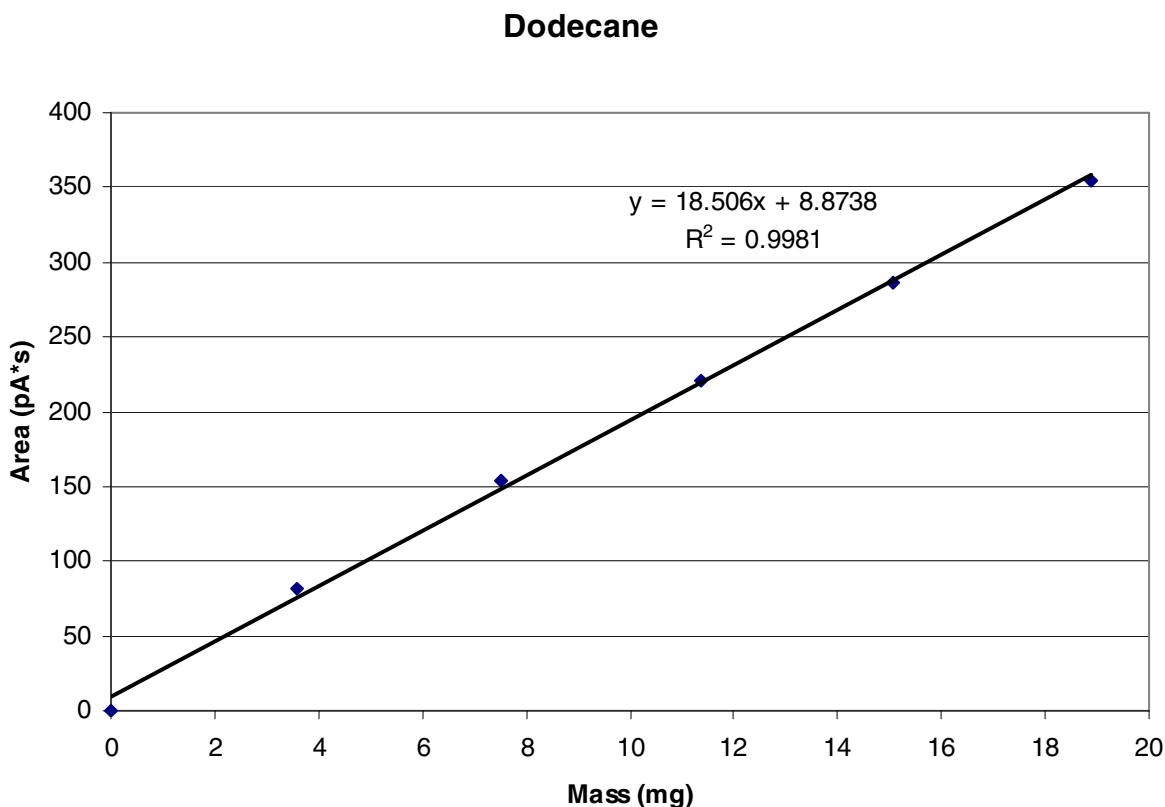
According to a modified procedure of Knochel and co-workers,^{2b} a 10 mL oven-dried Schlenk flask was charged with LiCl (339.1 mg, 8 mmol) and dried under vacuum at 150 °C for 20 min. Zn dust (1.57 g, 24 mmol) was added and the mixture was re-dried under vacuum at 150 °C for 20 min. To the solid mixture was added THF (8 mL). The resulting suspension was treated with 1,2-dibromoethane (34.5 μL , 0.4 mmol) and heated gently with a heat gun until foaming. The process was repeated twice.⁴ TMSCl (10.1 μL , 0.08 mmol) was added and the mixture was stirred for an additional 10 min. Solid I_2 (203.0 mg, 0.8

mmol) was subsequently introduced into the reaction vessel to further accelerate zincation.^{2b} Ethyl 5-bromoveratrole (1.27 mL, 8 mmol) was syringed into the reaction vessel and the suspension was heated to 50 °C. Upon >95% conversion of the alkyl bromide to the organozinc species as judged by GC analysis, the reaction mixture was degassed by three freeze-pump-thaw cycles. Iodolytic titration³ revealed the concentration of 5-ethoxy-5-oxopentylzinc bromide-lithium chloride complex to be 0.571 M.

A representative example of a calibration curve and response factor calculation is given below. Determination of the concentration of the organozinc reagent was performed immediately prior to usage in catalytic reactions.

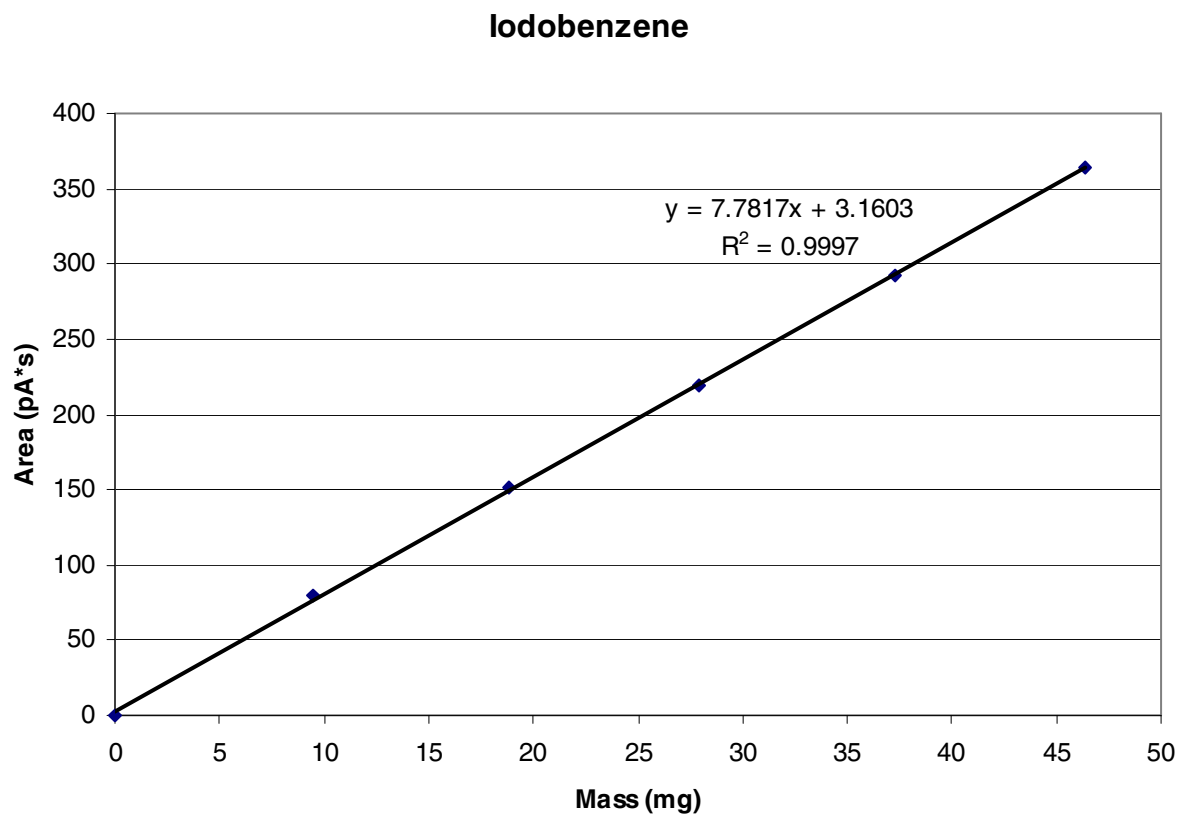
Calibration curve for internal standard (dodecane)

Mass (mg in 5 mL solvent)	Area (pA*s)
0.00	0.00000
3.58	81.39759
7.53	153.71014
11.35	220.30095
15.05	286.45884
18.88	354.66398

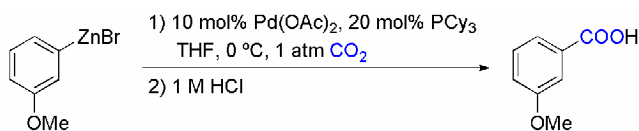


Calibration curve for iodobenzene

Mass (mg in 5 mL solvent)	Area (pA*s)
0.00	0.00000
9.43	79.94271
18.85	151.34943
27.95	219.76373
37.25	292.43249
46.40	363.94030



Dodecane		Iodobenzene		Response Factor
Amount (mmol)	Area (pA*s)	Amount (mmol)	Area (pA*s)	
0.0889	973.71112	0.0897	486.49466	0.49542
0.0889	975.18140	0.0897	487.66937	0.49586
0.0889	974.37659	0.0897	489.47055	0.49811
0.0889	948.68567	0.0897	476.77289	0.49832
0.0889	955.40955	0.0897	477.69675	0.49577
Average:				0.49670

General Procedure B: Pd-catalyzed carboxylation of 3-methoxyphenylzinc bromide

A 10 mL oven-dried Schlenk flask was charged with Pd(OAc)₂ (26.0 mg, 0.116 mmol, 0.1 eq.), PCy₃ (65.0 mg, 0.232 mmol, 0.2 eq.) and 2 mL of THF in the glovebox. The resulting pale yellow suspension was cooled to 0 °C in an ice bath and then subjected to CO₂ (15 psi). 3-methoxyphenylzinc bromide (see **General Procedure A1**) was added by syringe (2 mL, 1.160 mmol, 1 eq.), producing a pale green solution. The reaction vessel remained open to CO₂ for 1 h before it was sealed and the solution gradually became brown in colour. After 5 h, EtOAc (5 mL) was added and the suspension was concentrated to remove THF and CH₃CN to give a thick yellow paste. 1 M HCl (5 mL) and EtOAc (5 mL) were added and the aqueous layer was extracted with EtOAc (4x5 mL). The combined organic extracts were passed through a filter to remove particulates and concentrated. The resulting yellow solid was re-dissolved in 5 mL of Et₂O and extracted with 1 M NaOH (4x5 mL). Finally, the aqueous fractions were combined, acidified (pH < 2) by addition of conc. HCl and extracted with EtOAc (4x15 mL). The combined organic layers were dried over Na₂SO₄, filtered, and concentrated to give 3-methoxybenzoic acid as an off-white solid (171.2 mg, 1.125 mmol, 97%). All spectral data are in agreement with reported literature values.⁵

Note that Ni(COD)₂ is not a suitable precatalyst under these conditions. Addition of CoBr₂, ZnBr₂, and Zn individually did not inhibit reactivity (see **General Procedure A1**). The combination of these reagents presumably forms Co(I) and Co(III) species that are incompatible with Ni(0).^{2a}

Background experiments confirm no reaction at 0 °C within 3 h for all arylzinc bromides used. When the temperature was increased to 65 °C, phenylzinc bromide gave benzoic acid in 25% yield. Formation of insoluble species also occurred. Due to the robustness of Pd, we also found that phenylzinc bromide could be effectively carboxylated using a round-bottom flask equipped with a CO₂ balloon without significant loss of yields (93%).

Benzoic Acid

Prepared according to **General Procedure B** from a 0.203 M solution of phenylzinc bromide (2 mL, 0.406 mmol, 1.0 eq., Aldrich) with 10 mol% Ni(COD)₂. The product was isolated as an off-white solid (41.2 mg, 0.321 mmol, 73%). When Pd(OAc)₂ is used as the precatalyst with a 0.190 M solution of phenylzinc bromide (2 mL, 0.380 mmol, 1.0 eq., Aldrich), purification by column chromatography (5% MeOH/CH₂Cl₂) was found to be necessary to obtain the pure product (41.7 mg, 0.342 mmol, 90%). All spectral data are in agreement with reported literature values.⁶

Benzoic acid can also be prepared from diphenylzinc (219.6 mg, 1.000 mmol) with 10 mol% Ni(COD)₂. The product was isolated as a white solid (96.5 mg, 0.790 mmol, 79%).

4-methoxybenzoic acid

Prepared according to **General Procedure B** from a 0.447 M solution of 4-methoxyphenylzinc bromide (available via Co-catalyzed zincation of 4-bromoanisole^{2a}). The product was isolated as a white solid (120.6 mg, 0.793 mmol, 90%). All spectral data are in agreement with reported literature values.^{5b,6b,8}

2-methoxybenzoic acid

Prepared according to **General Procedure B** from a 0.620 M solution of 2-methoxyphenylzinc bromide (available via Co-catalyzed zincation of 2-bromoanisole^{2a}). The product was isolated as an off-white solid (151.8 mg, 0.998 mmol, 80%). All spectral data are in agreement with reported literature values.^{5b}

4-hydroxybenzoic acid

Prepared according to **General Procedure B** from a 0.106 M solution of 4-acetoxyphenylzinc bromide (available via Co-catalyzed zincation of 4-bromophenylacetate^{1,2a}). After acid-base extraction with saturated NaHCO₃, ¹H-NMR spectroscopy revealed a mixture of 4-hydroxybenzoic acid and 4-acetoxybenzoic acid. The mixture was re-dissolved in 10 mL 1 M NaOH and allowed to stir for 1 h. The aqueous layer was acidified (pH < 2) with conc. HCl and re-extracted with EtOAc (4x15 mL). Combined organic extracts were dried over Na₂SO₄, filtered, and concentrated. The product was isolated as a white solid (28.4 mg, 0.206 mmol, 97%). Due to poor solubility in CDCl₃, CD₃OD was used for analysis. All spectral data are in agreement with reported literature values.⁹

p-toluic acid

Prepared according to **General Procedure B** from a 0.552 M solution of 4-methylphenylzinc bromide (available via Co-catalyzed zincation of 4-bromotoluene^{2a}). The product was isolated as a white solid (121.7 mg, 0.894 mmol, 81%). All spectral data are in agreement with reported literature values.^{5c}

4-(trifluoromethyl)benzoic acid

Prepared according to **General Procedure B** from a 0.578 M solution of 4-trifluoromethylphenylzinc bromide (available via Co-catalyzed zincation of 4-bromobenzotrifluoride^{2a}). The product was isolated as a white solid (196.9 mg, 1.036 mmol, 90%). All spectral data are in agreement with reported literature values.^{5a}

4-chlorobenzoic acid

Prepared according to **General Procedure B** from a 0.608 M solution of 4-chlorophenylzinc bromide (available via Co-catalyzed zincation of 4-bromochlorobenzene^{2a}). The product was isolated as a white solid (168.1 mg, 1.074 mmol, 88%). All spectral data are in agreement with reported literature values.¹⁰

4-fluorobenzoic acid

Prepared according to **General Procedure B** from a 0.676 M solution of 4-fluorophenylzinc bromide (available via Co-catalyzed zincation of 4-bromofluorobenzene^{2a}). The product was isolated as a white solid (177.8 mg, 1.269 mmol, 94%). All spectral data are in agreement with reported literature values.¹¹

4-cyanobenzoic acid

Prepared according to **General Procedure B** from a 0.385 M solution of 4-cyanophenylzinc bromide (available via Co-catalyzed zincation of 4-bromobenzonitrile^{2a}). The product was isolated as a white solid (82.6 mg, 0.561 mmol, 73%). All spectral data are in agreement with reported literature values.¹²

4-acetylbenzoic acid

Prepared according to **General Procedure B** from a 0.178 M solution of 4-acetylphenylzinc bromide (available via Co-catalyzed zincation of 4-bromoacetophenone^{2a}). The product was isolated as a white solid (43.9 mg, 0.267 mmol, 75%) after acid-base extraction with saturated NaHCO₃. All spectral data are in agreement with reported literature values.¹³

Monoethylterephthalic acid

Prepared according to **General Procedure B** from a 0.539 M solution of 4-ethoxycarbonylphenylzinc bromide (available via Co-catalyzed zincation of ethyl-4-bromobenzoate^{2a}). The product was isolated as a white solid (159.5 mg, 0.821 mmol, 76%) after acid-base extraction with saturated NaHCO₃. All spectral data are in agreement with reported literature values.¹⁴

2-thienylcarboxylic acid

Prepared according to **General Procedure B** from a 0.221 M solution of 2-thienylzinc bromide (2 mL, 0.442 mmol, 1.0 eq., Aldrich). The product was isolated as an off-white solid (41.2 mg, 0.321 mmol, 73%). All spectral data are in agreement with reported literature values.^{6d,15}

Caproic acid

Prepared according to **General Procedure B** from a 0.276 M solution of pentylzinc bromide (2 mL, 0.552 mmol, 1.0 eq., Aldrich) with 5 mol% [Ni(PCy₃)₂]₂(N₂).¹⁶ The product was isolated as a colorless oil (57.6 mg, 0.496 mmol, 90%, 94% by GC). All spectral data are in agreement with reported literature values.⁷

3-phenylpropionic acid

Prepared according to **General Procedure B** from a 0.780 M solution of 2-phenylethylzinc bromide-lithium chloride complex (available via zincation of 2-(bromoethyl)-benzene,^{2b} 1 mL, 0.780 mmol, 1.0 eq.) with 5 mol% [Ni(PCy₃)₂]₂(N₂).¹⁶ The product was isolated as a viscous pale yellow oil (93.1 mg, 0.620 mmol, 80%). All spectral data are in agreement with reported literature values.¹⁷

6-chlorocaproic acid

Prepared according to **General Procedure B** from a 0.809 M solution of 5-chloropentylzinc iodide-lithium chloride complex (available via zincation of 1-chloro-5-iodopentane,^{2b} 1 mL, 0.809 mmol, 1.0 eq.) with 5 mol% [(Ni(PCy₃)₂)]₂(N₂).¹⁶ The product was isolated as a viscous yellow oil (112.0 mg, 0.744 mmol, 92%) after acid-base extraction with saturated NaHCO₃.¹⁸

5-acetoxyvaleric acid

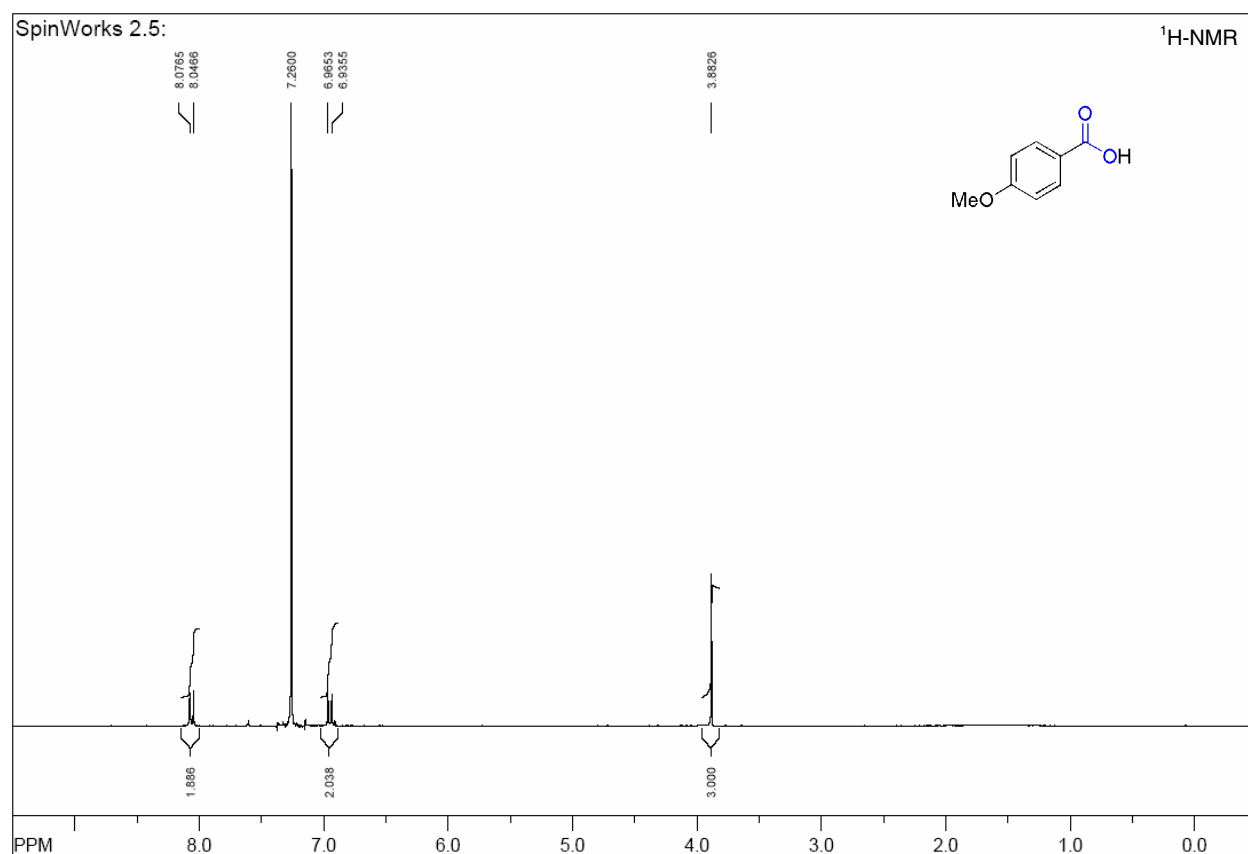
Prepared according to **General Procedure B** from a 0.811 M solution of 5-acetoxybutylzinc bromide-lithium chloride complex (available via zincation of 4-bromobutyl acetate,^{2b} 1 mL, 0.811 mmol, 1.0 eq.)

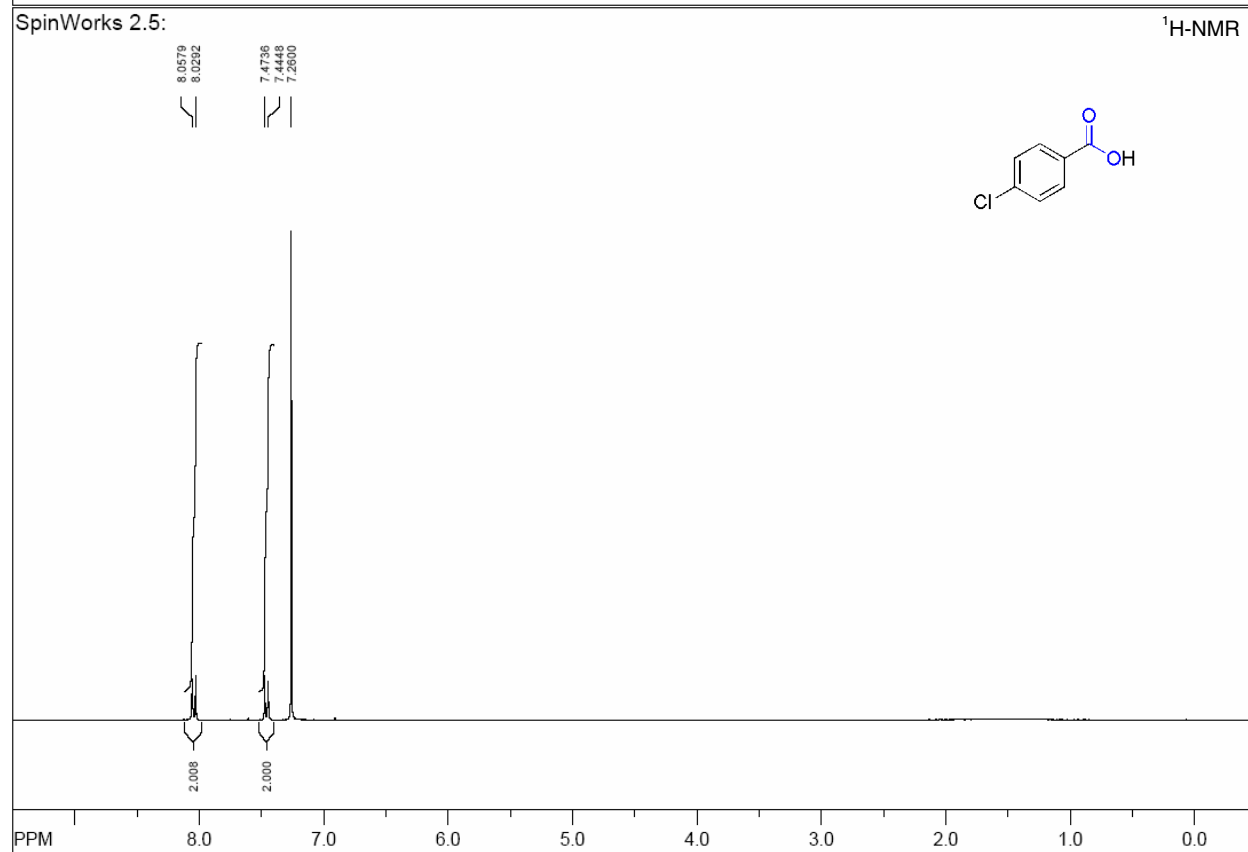
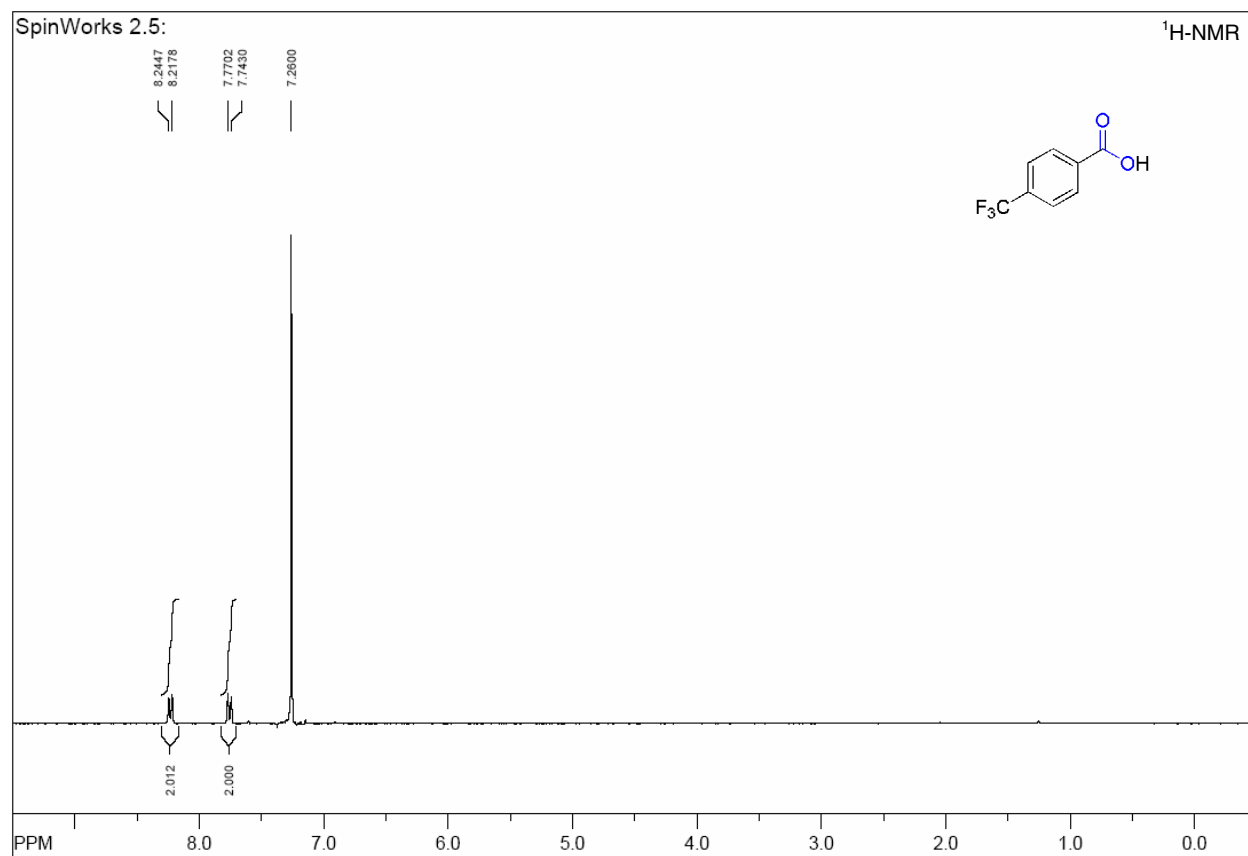
with 5 mol% $[\text{Ni}(\text{PCy}_3)_2]_2(\text{N}_2)$.¹⁶ The product was isolated as a yellow oil (96.1 mg, 0.600 mmol, 74%) after acid-base extraction with saturated NaHCO_3 . This compound has been reported in the literature.¹⁹ ^1H -NMR (300 MHz, CDCl_3) δ 4.09 (t, 2H, 6.0 Hz), 2.38 (t, 2H, 6.0 Hz), 2.05 (s, 3H), 1.72 (m, 4H).

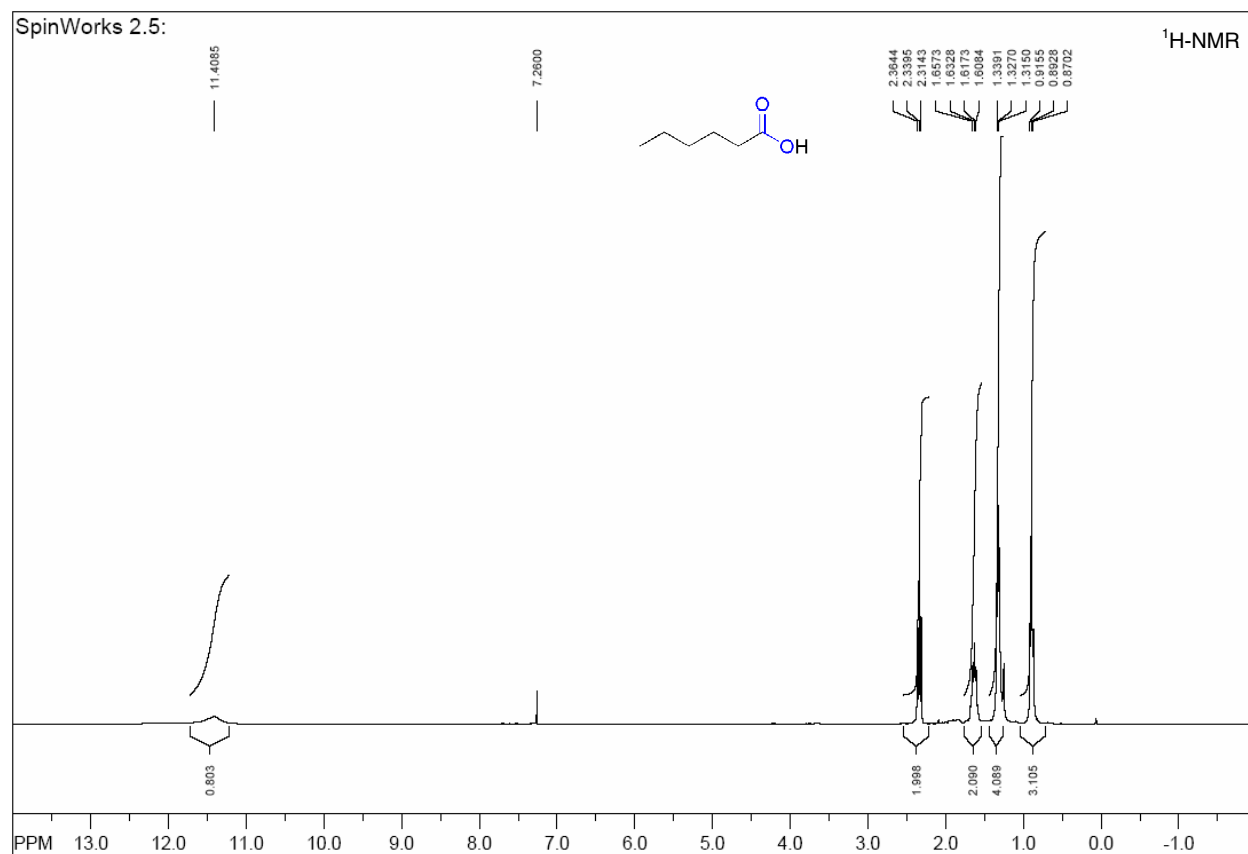
Adipic acid monoethyl ester

Prepared according to **General Procedure B** from a 0.571 M solution of 5-ethoxy-5-oxopentylzinc bromide-lithium chloride complex (available via zincation of ethyl 5-bromovalerate,^{2b} 1 mL, 0.571 mmol, 1.0 eq.) with 5 mol% $[\text{Ni}(\text{PCy}_3)_2]_2(\text{N}_2)$.¹⁶ The product was isolated as a viscous yellow oil (85.1 mg, 0.489 mmol, 86%) after acid-base extraction with saturated NaHCO_3 . All spectral data are in agreement with reported literature values.²⁰

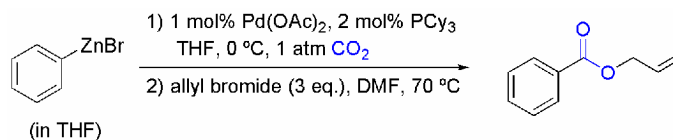
Representative NMR spectra are given to highlight the ease in purification of the product carboxylic acids via acid-base extraction (see **General Procedure B**).







General Procedure C: Allylbenzoate by carboxylation of phenylzinc bromide and direct esterification



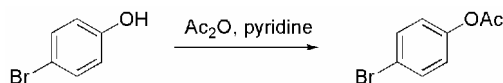
A 10 mL oven-dried Schlenk flask was charged with Pd(OAc)₂ (0.9 mg, 0.004 mmol, 0.01 eq.), PCy₃ (2.2 mg, 0.008 mmol, 0.02 eq.) and 2 mL of toluene in the glovebox. The resulting yellow suspension was cooled to 0 °C in an ice bath, and then subjected to CO₂ (15 psi). Phenylzinc bromide (0.196 M) was added by syringe (2 mL, 0.392 mmol, 1.0 eq.), producing a reddish brown solution. The reaction vessel was remained open to CO₂ for 30 min before it was sealed. After 3 h, according to the method of Ebert and co-workers,²¹ allyl bromide (101.8 μL, 1.176 mmol, 3.0 eq.) and 8 mL anhydrous DMF were added to give a yellow solution, which was heated to 70 °C for 16 h. The reaction mixture was poured into 0.1 M HCl (15 mL) and extracted with EtOAc (4x15 mL). The organic extracts were concentrated and re-dissolved in EtOAc (15 mL) and washed with distilled water (2x15 mL). The organic layer was dried over Na₂SO₄, filtered, and concentrated. The resulting residue was purified by flash column chromatography (10% EtOAc/hexanes) to give allylbenzoate as a colorless oil (45.7 mg, 0.282 mmol, 73%). All spectral data are in agreement with reported literature values.²²

Methyl benzoate

Prepared according to **General Procedure C** from a 0.196 M solution of phenylzinc bromide (2 mL, 0.392 mmol, 1.0 eq., Aldrich) and iodomethane (178.9 μL, 1.176 mmol, 3.0 eq.). The product was

isolated as a colorless oil (19.7 mg, 0.145 mmol, 37%). The low yield can be attributed to the slight volatility of the product. All spectral data are in agreement with reported literature values.²³

General Procedure D: 4-bromophenyl acetate by acetylation of 4-bromophenol¹

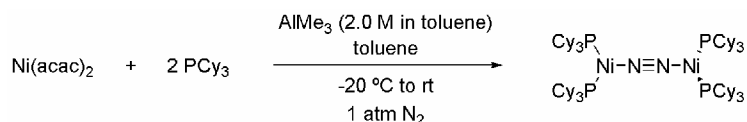


According to the procedure of Kelly and co-workers,¹ 4-bromophenol (7.83 g, 45.5 mmol) was dissolved in pyridine (50 mL). Acetic anhydride (43 mL, 455.0 mmol) was added via syringe and the mixture was stirred at rt overnight. A yellow oil resulted upon removal of volatiles. The crude mixture was purified by flash column chromatography (10% EtOAc/hexanes). The product was isolated as a colorless oil (9.50 g, 44.2 mmol, 97%). All spectral data are in agreement with reported literature values.²⁴ ¹H-NMR (300 MHz, CDCl₃) δ 7.49 (d, 2H, 8.9 Hz), 6.98 (d, 2H, 8.9 Hz), 2.29 (s, 3H).

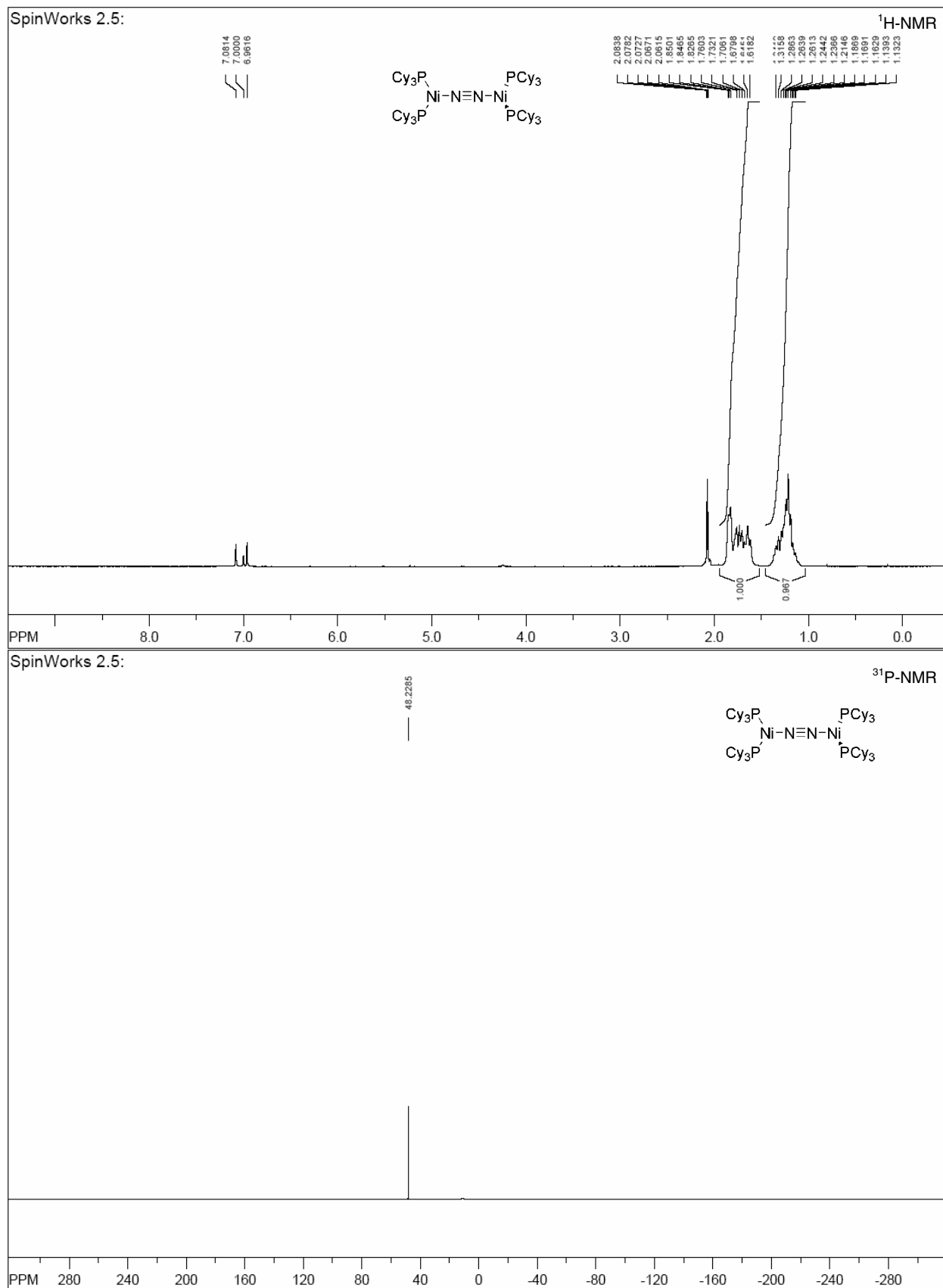
4-iodophenyl acetate¹

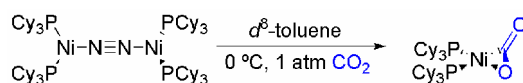
Prepared according to **General Procedure D** from 4-iodophenol (1.01 g, 4.6 mmol) in pyridine (5 mL) with acetic anhydride (4.3 mL, 45.5 mmol). The product was isolated as a colorless oil (1.16 g, 4.4 mmol, 98%). All spectral data are in agreement with reported literature values.¹ ¹H-NMR (300 MHz, CDCl₃) δ 7.68 (d, 2H, 8.9 Hz), 6.86 (d, 2H, 8.9 Hz), 2.29 (s, 3H).

Preparation of [Ni(PCy₃)₂](N₂)⁸

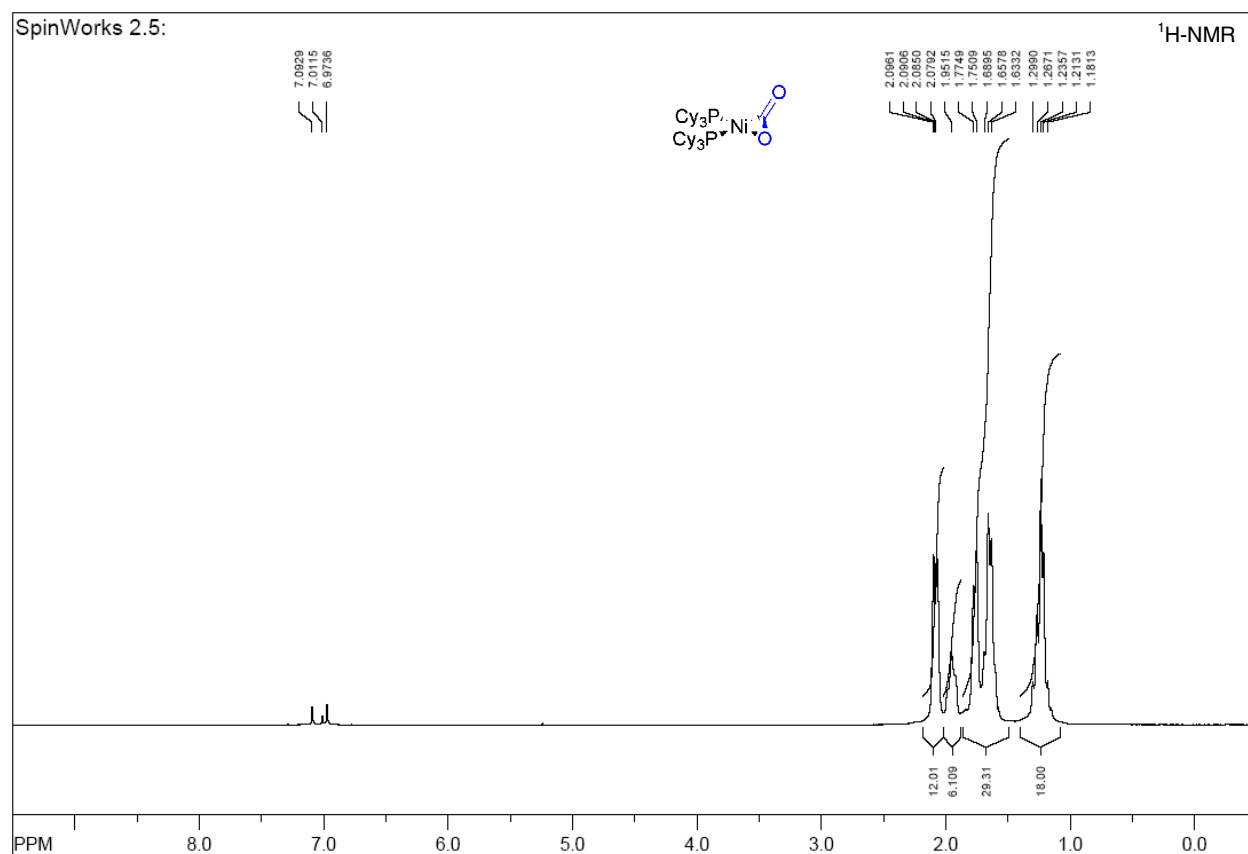


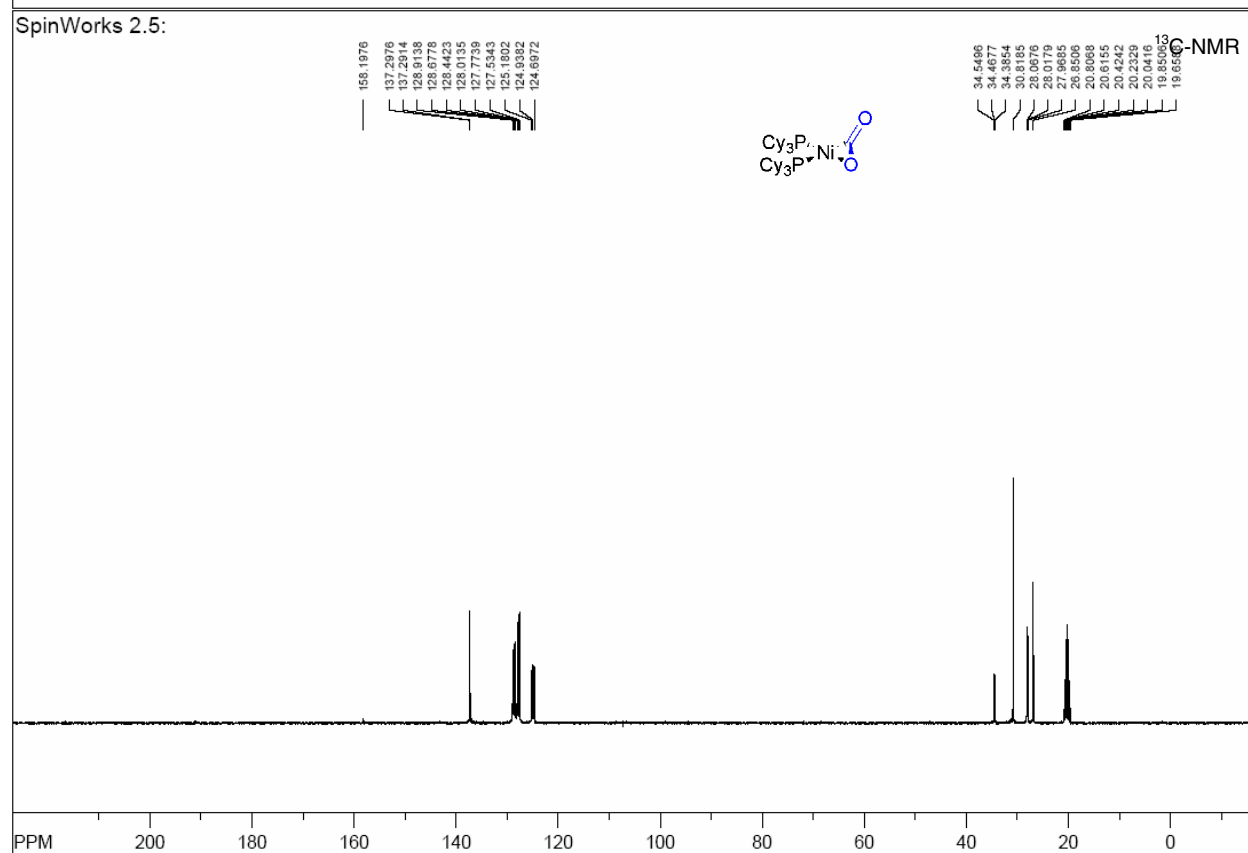
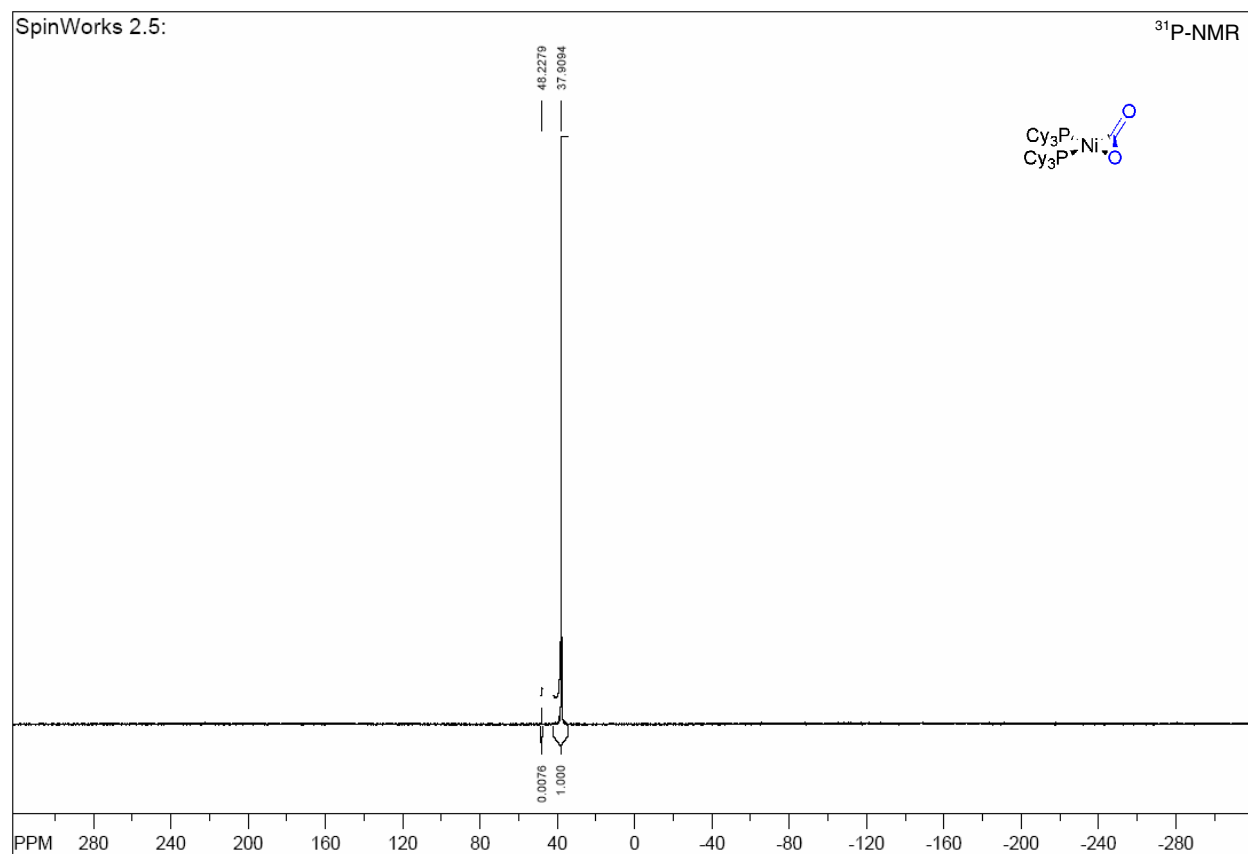
According to a modified procedure of Jolly,^{16a} Ni(acac)₂ (250 mg, 1.00 mmol, 1 eq.) and PCy₃ (560 mg, 2.00 mmol, 2 eq.) were dissolved in 1.7 mL toluene and transferred to a sealable Schlenk tube with Teflon stopcock. The turquoise solution was cooled to −20 °C using an acetone/dry ice bath and the vessel was equipped with a syringe needle immersed into the reaction mixture. Subsequently, AlMe₃ (0.6 mL, 1.10 mmol, 1.1 eq.) was added via syringe to produce a deep red/brown solution with immediate formation of precipitates. Sparging with N₂ continued for an additional 20 min at −20 °C. The flask was then sealed and allowed to reach rt overnight (15 h) with no observable change. Filtration of the mixture under N₂ and washing with cold Et₂O gave a deep red/brown solid (180 mg, 0.14 mmol, 28%) that was used without purification. The [Ni(PCy₃)₂]₂(N₂)¹⁶ complex was found to be sensitive to trace amounts of Ar. An orange/red color could be restored to the solution via sparging with N₂. All spectral data are in agreement with reported literature values.^{16b} ¹H-NMR (400 MHz, *d*⁸-toluene) δ 1.6-1.9 (m), 1.1-1.4 (m); ³¹P{H}-NMR δ 48.23 (s).



Preparation of Aresta's complex, $[\text{Ni}(\eta^2\text{-CO}_2)(\text{PCy}_3)_2]^{25}$ 

According to a modified procedure of Aresta,²⁵ $[\text{Ni}(\text{PCy}_3)_2]_2(\text{N}_2)^{16}$ (14.1 mg, 0.022 mmol) was dissolved in 1.0 mL d^8 -toluene, giving a homogeneous orange/red solution. The tube was cooled to 0 °C in an ice bath and filled with CO_2 (15 psi). The colour of the solution changed to bright yellow within a few minutes upon vigorous shaking. After 1 h, complete conversion was observed by NMR. The resulting 0.044 M solution of $\text{Ni}(\eta^2\text{-CO}_2)(\text{PCy}_3)_2$ in d^8 -toluene with <0.1% $[\text{Ni}(\text{PCy}_3)_2]_2(\text{N}_2)^{16}$. While Aresta's complex has been the subject of significant spectroscopic investigation,^{26,27} to our knowledge, no comprehensive list of relevant data peaks have been reported in the literature. ^1H -NMR (400 MHz, d^8 -toluene) δ 2.0-2.2, 1.9-2.1, 1.7-1.9, 1.6-1.8 (overlapping m, 48H), 1.1-1.4 (m, 18H); ^{13}C -NMR (100 MHz) 158.20 (s), 34.47 (t, 82.2 Hz), 30.82 (s), 28.01 (t, 49.4 Hz); $^{31}\text{P}\{^1\text{H}\}$ -NMR (162 MHz) 37.91 (s).





The ^{13}C -NMR signal at 158.20 ppm can be attributed to η^2 -bound CO_2 .²⁵ When the same conditions were applied to $\text{Pd}(\text{PCy}_3)_2$ in d^8 -THF, no changes in the ^1H - nor ^{31}P -NMR spectra were observed, in agreement with literature.²⁷ A new ^{13}C -NMR signal corresponding to dissolved CO_2 can be seen at 126.1 ppm under these conditions.

5. References

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