Rh(III)-Catalyzed Decarboxylative Coupling of Acrylic Acids with Unsaturated Oxime Esters: Carboxylic Acids Serve as Traceless Activators

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Supporting Information

General Methods

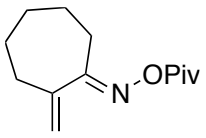
All reactions were carried out in oven-dried glassware under an atmosphere of argon with magnetic stirring. Reagent grade silver acetate and silver tosylate and ACS grade acetic acid were purchased from Sigma-Aldrich Co. and used without further purification. ACS grade potassium persulfate was purchased from Mallinckrodt Chemicals and used as received. 1,1,1,3,3,3-Hexafluoro-2-propanol was distilled from 3Å molecular sieves and dichloroethane was distilled from calcium hydride under an atmosphere of argon. Cinnamic acid (**2h**) was purchased from Alfa Aesar and used without further purification. Crotonic acid (**2a**) and acrylic acid (**2n**) were distilled under reduced pressure prior to use. Methoxycinnamic acids **2i** and **2j** were recrystallized from methanol prior to use. Alkyl acrylic acids[1] **2b**, **2c**, **2d**, **2e**, **2f**, and **2g** and aryl acrylic acids[2] **2k**, **2l**, and **2m** were synthesized according to literature procedure. $[RhCp^*Cl_2]_2$,[3] $RhCp^*(OAc)_2$[4] and $[RhCp^{CF_3}Cl_2]_2$[5] were prepared as previously reported. Column chromatography was performed on Silicycle® Silica*Flash*® P60 (230-400 mesh). Thin layer chromatography was performed on Silicycle® 250μm silica gel 60A plates. Visualization was accomplished with UV light (254 nm) or potassium permanganate.

^1H NMR and ^{13}C NMR spectra were collected at ambient temperature in $CDCl_3$ or CD_2Cl_2 on a Varian 400 MHz. Chemical shifts are expressed as parts per million (δ, ppm) and are referenced to 7.26 ($CHCl_3$) or 5.29 (CH_2Cl_2) for ^1H NMR and 77.0 ($CDCl_3$) or 53.5 (CD_2Cl_2) for ^{13}C NMR. Signal data uses the following abbreviations: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet and *J* = coupling constant. Mass spectra were obtained on an Agilent Technologies 6130 Quadropole Mass Spec (LRMS). Infrared spectra were collected on a Bruker Tensor 27 FT-IR spectrometer or a Nicolet SX-60 FT-IR spectrometer.

General Procedure for Oxime Ester Synthesis

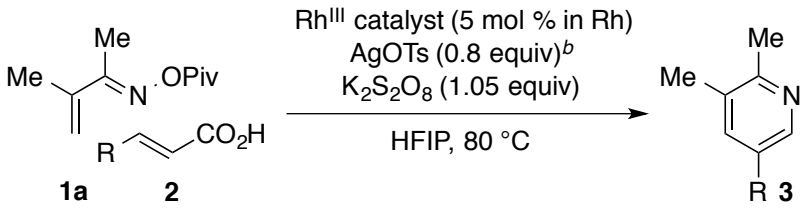
O-Pivaloyl oxime esters **1** were generated from the corresponding α,β-unsaturated ketones according to the following representative procedure, adapted from the literature.[6] Hydroxylamine hydrochloride (347 mg, 1.4 equiv) and Na_2CO_3 (742 mg, 1.4 equiv) were added to the enone (5 mmol) in 15 mL MeOH and the mixture was stirred at 65 °C for 1 hour (or room temperature for 3 hours in the case of **1b**). The solvent was removed *in vacuo* and the resulting residue was dissolved in 10 mL DCM and cooled to 0 °C. After the addition of Et_3N (1.74 mL, 2.5 equiv), a solution of pivaloyl chloride (1.23 mL, 2.0 equiv) in 5 mL DCM was added dropwise at 0 °C. The mixture was stirred at room temperature overnight and quenched with water. The aqueous layer was extracted with DCM three times and the combined organic layers were washed with saturated $NaHCO_3$ and brine, dried over $MgSO_4$, filtered and concentrated *in vacuo*. The crude product was purified by flash column chromatography.

Compounds **1a**, **1b** and **1c** were characterized in our previous report.[7]

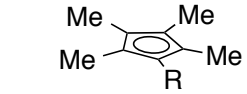


(*E*)-2-methylenecycloheptanone *O*-pivaloyl oxime (1d). Colorless liquid. R_f = 0.15 (10:1 hexanes/EtOAc). ^1H NMR (400 MHz, $CDCl_3$) δ 5.48 (d, *J* = 1.6 Hz, 1H), 5.06 (d, *J* = 1.6 Hz, 1H), 2.64 (m, 2H), 2.38 (m, 2H), 1.64 (m, 6H), 1.28 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.0, 170.9, 144.3, 117.2, 38.8, 34.9, 30.6, 29.4, 28.9, 27.3, 25.3. IR (NaCl, thin film) ν 2928, 1755, 1479, 1270, 1099, 1026, 882 cm^{-1}. LRMS (ESI) *m/z* [M+H] calcd 447.3, found 447.6.

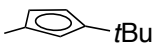
Catalyst Optimization



entry	R	catalyst	yield **3** (%)[c]
1	Me	$RhCp^*(OAc)_2$	80
2	Ph[d]	$RhCp^*(OAc)_2$	15
3	(*m*-OMe)C_6H_4	$RhCp^*(OAc)_2$	50
4	(*p*-OMe)C_6H_4	$RhCp^*(OAc)_2$	45
5	2-furyl	$RhCp^*(OAc)_2$	15
6	(*m*-OMe)C_6H_4	$[RhCp^*Cl_2]_2$	45
7	(*m*-OMe)C_6H_4	$[RhCp^tCl_2]_2$	15
8	(*m*-OMe)C_6H_4	$[RhCp^{PMP}Cl_2]_2$	25
9	(*m*-OMe)C_6H_4	$[RhCp^{pCF_3}Cl_2]_2$	35
10	(*m*-OMe)C_6H_4	$[RhCp^{CF_3}Cl_2]_2$	70
11	Me	$[RhCp^{CF_3}Cl_2]_2$	75



Cp^*: R = Me
Cp^{PMP}: R = (*p*-MeO)C_6H_4
Cp^{pCF_3}: R = (*p*-CF_3)C_6H_4
Cp^{CF_3}: R = CF_3

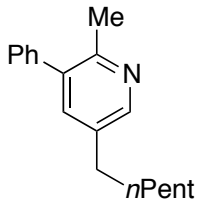
Cp^t: 

[a]1.2 equiv **2**, 0.3 M solution. [b]0.9 equiv AgOTs with $[RhCp^xCl_2]_2$ catalysts. [c]Determined by ^1H NMR. [d]With (*Z*)-cinnamic acid.

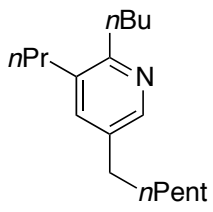
General Procedure for Pyridine Synthesis

A 0.5 dram vial was charged with oxime ester **1** (0.21 mmol), AgOTs (52.7 mg, 0.9 equiv) and $K_2S_2O_8$ (59.6 mg, 1.05 equiv) and a solution of $[RhCp^{CF_3}Cl_2]_2$ (3.8 mg, 0.025 equiv) and alkene **2** (0.252 mmol, 1.2 equiv) in 0.7 mL HFIP was added. The vial was flushed with argon, sealed and heated at 58 °C in an aluminum heating block for 12 hours. In the event that an observable amount of **1** remained after 12 hours, the mixture was heated at 100 °C until it was consumed (this serves to decompose **1** and simplifies purification). The mixture was diluted with DCM and washed with 1M NaOH. The aqueous layer was extracted twice with DCM and the combined organic layers were dried over $MgSO_4$, filtered and concentrated *in vacuo*. The residue was dissolved in EtOAc and passed through a short plug of silica to provide analytically pure product.

Compounds **3ab** and **3ae** were characterized in our previous report.[7] Compounds **3ak** and **3ai** were characterized by Ellman and coworkers.[8] Compound **3bn** was characterized by Craig and coworkers.[9]

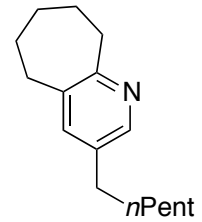


5-hexyl-2-methyl-3-phenylpyridine (3bb). Yellow orange viscous liquid. R_f = 0.42 (3:1 hexanes/EtOAc). ^1H NMR (400 MHz, $CDCl_3$) δ 8.32 (d, *J* = 2.0 Hz, 1H), 7.45-7.31 (m, 6H), 2.61 (t, *J* = 7.6 Hz, 2H), 2.47 (s, 3H), 1.62 (m, 2H), 1.37-1.26 (m, 6H), 0.88 (t, *J* = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.9, 147.8, 140.1, 137.3, 136.5, 135.3, 129.0, 128.3, 127.3, 32.5, 31.6, 31.4, 28.8, 22.8, 22.5, 14.0. IR (NaCl, thin film) ν 2928, 2857, 1459, 1183, 1027, 909, 702 cm^{-1}. LRMS (ESI + APCI) *m/z* [M+H] calcd 254.2, found 254.7.

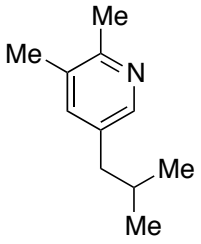


2-Butyl-5-hexyl-3-propylpyridine (3cb). Yellow viscous liquid. R_f = 0.61 (3:1 hexanes/EtOAc). ^1H NMR (400 MHz, $CDCl_3$) δ 8.17 (d, *J* = 2.0 Hz, 1H), 7.21 (d, *J* = 1.6 Hz, 1H), 2.74 (m, 2H), 2.54 (m, 4H), 1.69-1.53 (m, 6H), 1.41 (m, 2H), 1.34-1.25 (m, 6H), 0.96 (m, 6H), 0.87 (t, *J* = 6.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.4, 146.4, 136.9, 135.1, 134.7, 34.2, 34.2, 32.6, 32.0, 31.6, 31.2, 28.9, 23.9, 22.9,

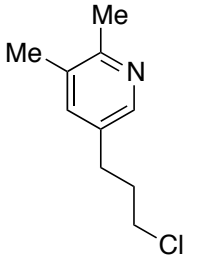
22.6, 14.0, 14.0. IR (NaCl, thin film) ν 2959, 1562, 1459, 1378, 1287, 1183, 1102 cm^{-1}. LRMS (ESI + APCI) *m*/*z* [M+H] calcd 262.3, found 262.8.



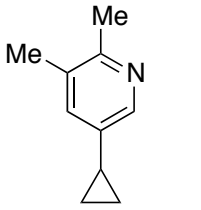
3-Hexyl-6,7,8,9-tetrahydro-5*H*-cyclohepta[*b*]pyridine (3db). Yellow viscous liquid. R_f = 0.38 (3:1 hexanes/EtOAc). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (d, *J* = 1.6 Hz, 1H), 7.18 (d, *J* = 2.0 Hz, 1H), 2.99 (m, 2H), 2.73 (m, 2H), 2.52 (t, *J* = 7.6 Hz, 2H), 1.85 (m, 2H), 1.70-1.54 (m, 6H), 1.34-1.25 (m, 6H), 0.87 (t, *J* = 6.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.3, 145.5, 137.7, 136.8, 135.4, 38.7, 35.3, 32.5, 31.6, 31.1, 28.9, 28.0, 26.5, 22.6, 14.0. IR (NaCl, thin film) ν 2926, 2855, 1468, 1287, 1182, 958 cm^{-1}. LRMS (ESI + APCI) *m*/*z* [M+H] calcd 232.2, found 232.7.



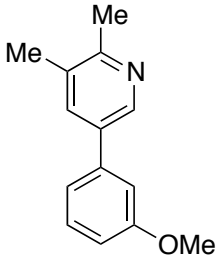
5-Isobutyl-2,3-dimethylpyridine (3ac). Pale yellow viscous liquid. R_f = 0.33 (1:1 hexanes/EtOAc). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (d, *J* = 1.6 Hz, 1H), 7.19 (d, *J* = 1.2 Hz, 1H), 2.46 (s, 3H), 2.40 (d, *J* = 7.2 Hz, 2H), 2.25 (s, 3H), 1.82 (m, 1H), 0.89 (d, *J* = 6.8 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.2, 146.7, 138.0, 134.2, 130.8, 41.8, 30.0, 22.2, 21.9, 19.1. IR (NaCl, thin film) ν 2957, 2870, 1475, 1412, 1214, 1001, 900, 723 cm^{-1}. LRMS (ESI + APCI) *m*/*z* [M+H] calcd 164.1, found 164.5.



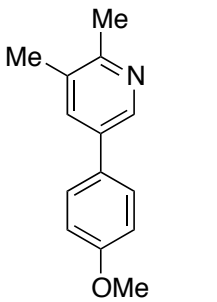
5-(3-Chloropropyl)-2,3-dimethylpyridine (3ad). Pale yellow viscous liquid. R_f = 0.25 (1:1 hexanes/EtOAc). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (s, 1H), 7.24 (s, 1H), 3.51 (t, *J* = 6.4 Hz, 2H), 2.71 (t, *J* = 7.2 Hz, 2H), 2.46 (s, 3H), 2.25 (s, 3H), 2.05 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.8, 146.1, 137.5, 133.3, 131.2, 43.9, 33.7, 29.3, 22.0, 19.1. IR (NaCl, thin film) ν 2922, 1476, 1444, 1413, 1286, 1213, 1182, 731, 706 cm^{-1}. LRMS (ESI + APCI) *m*/*z* [M+H] calcd 184.1, found 184.5.



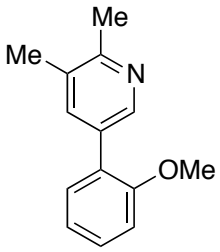
5-Cyclopropyl-2,3-dimethylpyridine (3af). Pale yellow viscous liquid. R_f = 0.34 (1:1 hexanes/EtOAc). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (s, 1H), 7.04 (s, 1H), 2.44 (s, 3H), 2.22 (s, 3H), 1.82 (m, 1H), 0.96 (m, 2H), 0.65 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.7, 144.3, 136.8, 134.4, 131.1, 21.6, 19.1, 12.5, 8.6. IR (NaCl, thin film) ν 2922, 1480, 1460, 1286, 1224, 1183, 1101, 1020, 989, 729 cm^{-1}. LRMS (ESI + APCI) *m*/*z* [M+H] calcd 148.1, found 148.4.



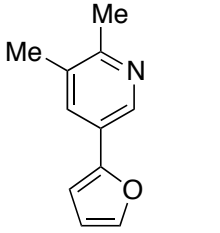
5-(3-Methoxyphenyl)-2,3-dimethylpyridine (3ai). Yellow viscous liquid. R_f = 0.37 (1:1 hexanes/EtOAc). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.55 (d, *J* = 2.0 Hz, 1H), 7.59 (d, *J* = 2.0 Hz, 1H), 7.36 (t, *J* = 8.0 Hz, 1H), 7.14 (d, *J* = 7.6 Hz, 1H), 7.08 (t, *J* = 2.4 Hz, 1H), 6.91 (dd, *J* = 8.0 Hz, 2.4 Hz, 1H), 3.86 (s, 3H), 2.54 (s, 3H), 2.34 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.0, 154.0, 144.6, 139.4, 135.7, 134.1, 131.3, 130.0, 119.4, 113.0, 112.7, 55.3, 22.2, 19.2. IR (NaCl, thin film) ν 2941, 1583, 1471, 1387, 1285, 1219, 1046, 870, 827, 781, 730, 697 cm^{-1}. LRMS (ESI + APCI) *m*/*z* [M+H] calcd 214.1, found 214.6.



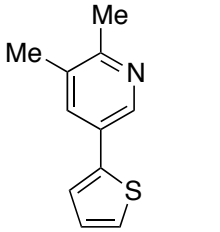
5-(4-Methoxyphenyl)-2,3-dimethylpyridine (3aj). Yellow orange viscous liquid. R_f = 0.34 (1:1 hexanes/EtOAc). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.51 (s, 1H), 7.56 (s, 1H), 7.49 (d, *J* = 8.0 Hz, 2H), 6.99 (d, *J* = 8.4 Hz, 2H), 3.85 (s, 3H), 2.53 (s, 3H), 2.33 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.4, 155.2, 144.3, 135.3, 134.0, 131.2, 130.4, 128.0, 114.4, 55.3, 22.1, 19.2. IR (NaCl, thin film) ν 2936, 1610, 1516, 1470, 1387, 1287, 1249, 1180, 1112, 1033, 830 cm^{-1}. LRMS (ESI + APCI) *m*/*z* [M+H] calcd 214.1, found 214.1.



5-(2-Methoxyphenyl)-2,3-dimethylpyridine (3ak). Yellow viscous liquid. R_f = 0.37 (1:1 hexanes/EtOAc). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.48 (d, *J* = 1.6 Hz, 1H), 7.58 (d, *J* = 1.2 Hz, 1H), 7.36-7.28 (m, 2H), 7.04 (t, *J* = 7.6 Hz, 1H), 6.99 (d, *J* = 8.0 Hz, 1H), 3.81 (s, 3H), 2.54 (s, 3H), 2.32 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.6, 155.3, 146.7, 138.0, 131.8, 130.5, 129.1, 127.2, 120.9, 111.2, 55.5, 22.2, 19.2. IR (NaCl, thin film) ν 2941, 1598, 1498, 1471, 1392, 1242, 1122, 1026, 754 cm^{-1}. LRMS (ESI + APCI) *m*/*z* [M+H] calcd 214.1, found 214.6.

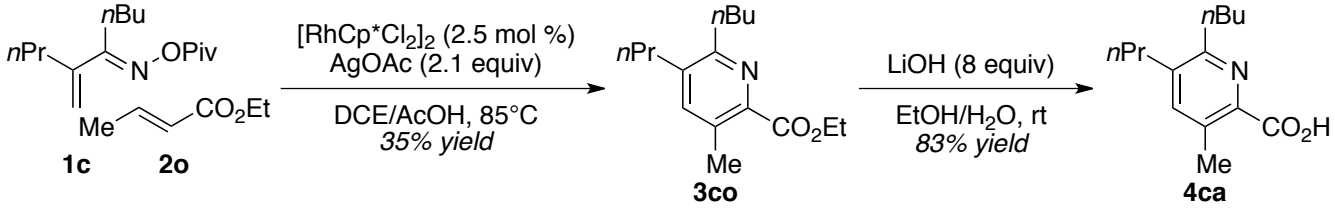


5-(Furan-2-yl)-2,3-dimethylpyridine (3al). Yellow orange viscous liquid. R_f = 0.48 (1:1 hexanes/EtOAc). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.64 (d, *J* = 2.0 Hz, 1H), 7.71 (d, *J* = 1.2 Hz, 1H), 7.49 (d, *J* = 1.6 Hz, 1H), 6.68 (d, *J* = 3.2 Hz, 1H), 6.48 (dd, *J* = 3.2 Hz, 1.6 Hz, 1H), 2.53 (s, 3H), 2.33 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.4, 151.1, 142.6, 141.3, 132.6, 131.7, 125.0, 111.7, 105.8, 21.9, 19.1. IR (NaCl, thin film) ν 2922, 1684, 1596, 1401, 1143, 1017, 885, 735 cm^{-1}. LRMS (ESI + APCI) *m*/*z* [M+H] calcd 174.1, found 174.5.



2,3-Dimethyl-5-(thiophen-2-yl)pyridine (3am). Yellow orange viscous liquid. R_f = 0.51 (1:1 hexanes/EtOAc). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.59 (d, *J* = 2.0 Hz, 1H), 7.62 (d, *J* = 1.2 Hz, 1H), 7.31 (m, 2H), 7.10 (m, 1H), 2.52 (s, 3H), 2.33 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.8, 143.0, 140.5, 134.7, 131.7, 128.3, 128.1, 125.4, 123.7, 21.9, 19.1. IR (NaCl, thin film) ν 2920, 1474, 1402, 1231, 895, 843, 697 cm^{-1}. LRMS (ESI + APCI) *m*/*z* [M+H] calcd 190.1, found 190.1.

Preparation of Compound 4ca

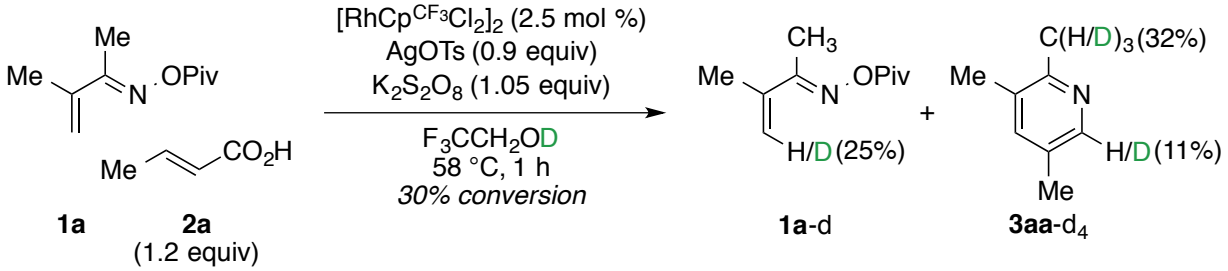


Ethyl 6-butyl-3-methyl-5-propylpicolinate (3co). An oven-dried 20 mL vial was charged with $[RhCp^*Cl_2]_2$ (27.8 mg, 0.025 equiv) and AgOAc (631 mg, 2.1 equiv) and a solution of **1c** (456 mg, 1.8 mmol) and **2o** (0.27 mL, 1.2 equiv) in 0.7 mL 2:1 DCE/AcOH was added. The vial was flushed with argon, sealed and heated at 85 °C in a sand bath for 14 hours. The solids were filtered and the mixture was diluted with DCM and washed with 15% Na_2CO_3. The aqueous layer was extracted twice with DCM and the combined organic layers were dried over $MgSO_4$, filtered and concentrated *in vacuo*. The crude product was purified by flash column chromatography (5:1 hexanes/EtOAc) to afford **3co** (168 mg, 35% yield) as a colorless liquid. R_f = 0.35 (5:1 hexanes/EtOAc). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 (s, 1H), 4.42 (q, *J* = 7.2 Hz, 2H), 2.79 (m, 2H), 2.58 (m, 2H), 2.45 (s, 3H), 1.69-1.55 (m, 4H), 1.46-1.36 (m, 5H), 0.95 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.0, 157.9, 145.2, 140.0, 137.9, 131.3, 61.3, 34.3, 34.0, 31.8, 23.6, 22.8, 19.2, 14.3, 14.0. IR (NaCl, thin film) ν 2960, 2873, 1719, 1456, 1366, 1309, 1244, 1150, 1058 cm^{-1}. LRMS (ESI + APCI) *m*/*z* [M+H] calcd 264.2, found 264.7.

6-Butyl-3-methyl-5-propylpicolinic acid (4ca). A solution of pyridine **3co** (146 mg, 0.55 mmol) in 7.4 mL EtOH was added to LiOH (106 mg, 8 equiv) in 3.7 mL H_2O and the mixture was stirred at room temperature overnight. The solution was acidified with 3M HCl and extracted with EtOAc. The organ-

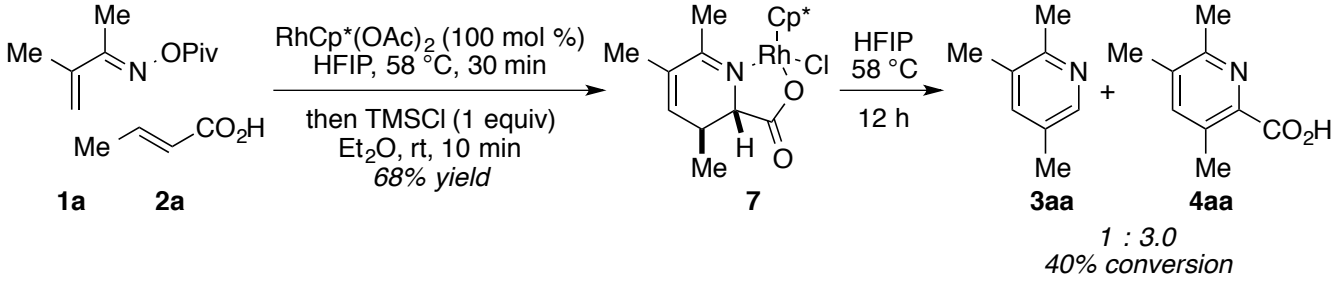
ic layer was washed with H_2O and brine, dried over $MgSO_4$, filtered and concentrated *in vacuo* to provide **4ca** (107 mg, 83% yield) as a colorless liquid. R_f = 0.24 (1:1 hexanes/EtOAc). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (s, 1H), 2.78 (m, 2H), 2.68 (s, 3H), 2.63 (m, 2H), 1.74-1.59 (m, 4H), 1.41 (m, 2H), 0.98 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.7, 156.3, 142.0, 140.8, 139.8, 134.3, 33.8, 33.2, 30.9, 23.4, 22.6, 19.4, 14.0, 14.0. IR (NaCl, thin film) ν 3420, 2960, 2873, 1763, 1639, 1460, 1363 cm^{-1}. LRMS (ESI + APCI) *m/z* [M+H] calcd 236.2, found 236.7.

Deuterium Incorporation Study



An isotope experiment was performed according to the procedure described above with 2,2,2-trifluoroethanol-d_1 (purchased from Sigma-Aldrich Co. and used as received) as the solvent for one hour. Deuterium incorporation was determined by integration of the ^{1}H NMR spectrum collected with first relaxation delay (d1) = 25 seconds of the reaction mixture.

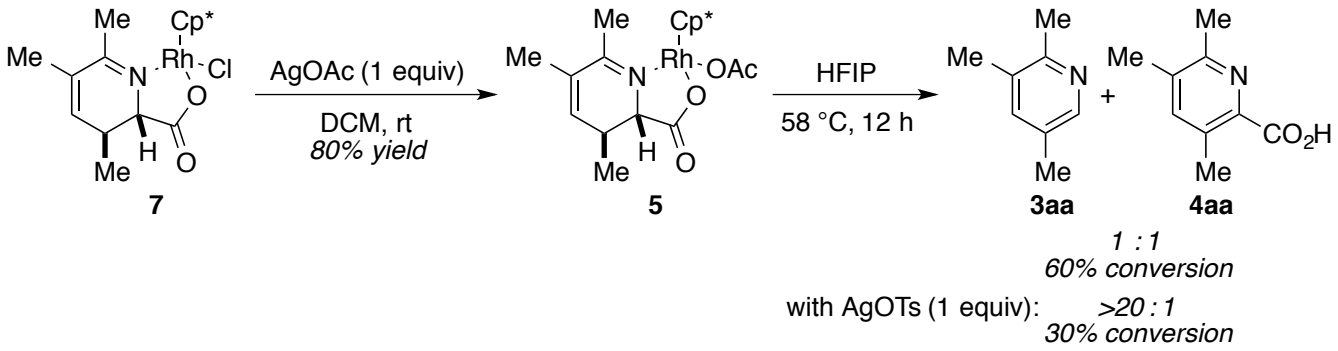
Preparation and Reactions of Rhodium Complexes 5 and 7



A 0.5 dram vial was charged with RhCp*$(OAc)_2$ (0.054 mmol, 100 mol %) and a solution of oxime ester **1a** (0.054 mmol) and crotonic acid **2a** (0.054 mmol, 1 equiv) in 0.18 mL HFIP was added. The vial was flushed with argon, sealed and heated at 58 °C in an aluminum heating block for 30 minutes. The mixture was transferred to a 1 dram vial, the solvents were removed and a solution of TMSCl (0.054 mmol, 1 equiv) in 1 mL Et_2O was added. After 10 minutes stirring at room temperature, the heterogeneous mixture was filtered and the solid rinsed with Et_2O. The solid was dissolved in DCM, the solution was filtered and the filtrate was concentrated to give **7** (16.2 mg, 68% yield) as an orange solid. A 0.5 dram vial was charged with a solution of complex **7** (7.5 mg, 0.017 mmol) in 0.06 mL HFIP, flushed with argon and heated for 24 hours in an aluminum heating block. The solvent was removed and the reaction mixture analyzed by ^{1}H NMR.

Slow evaporation of a concentrated solution of **7** in DCM afforded prismatic orange crystals suitable for X-ray diffraction analysis.

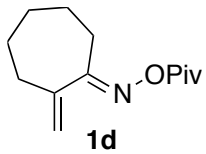
Rhodium chloride complex 7. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.88 (bs, 1H), 3.59 (dq, *J* = 16.0 Hz, 2.4 Hz, 1H), 2.71-2.61 (m, 1H), 2.52 (d, *J* = 2.4 Hz, 3H), 1.89 (dd, *J* = 2.4 Hz, 1.6 Hz, 3H), 1.66 (s, 15H), 1.34 (d, *J* = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.8, 172.0, 141.7, 127.4, 93.5 (d, *J* = 8.6 Hz), 70.3, 31.5, 26.9, 21.3, 19.3, 9.1. IR (thin film) ν 2922, 1639, 1587, 1448, 1323, 1089, 1025, 921, 809, 726 cm^{-1}. LRMS (ESI + APCI) *m/z* [M-Cl] calcd 404.1, found 404.3.



A 1 dram vial was charged with **7** (29.7 mg, 0.068 mmol) and AgOAc (0.068, 1 equiv) and 1.4 mL DCM was added. The vial was flushed with argon, sealed, wrapped in aluminum foil and stirred at room temperature overnight. The heterogeneous mixture was filtered and the filtrate concentrated to give **5** (25.0 mg, 80% yield) as an orange solid. A 0.5 dram vial was charged with a solution of complex **5** (12.7 mg, 0.027 mmol) in 0.09 mL HFIP, flushed with argon and heated for 24 hours in an aluminum heating block. The solvent was removed and the reaction mixture analyzed by ^{1}H NMR. Alternatively, a 0.5 dram vial was charged with AgOTs (0.029 mmol, 1 equiv) and a solution of **7** (13.4 mg, 0.029 mmol) in 0.1 mL HFIP was added. The vial was flushed with argon, sealed and heated at 58 °C in an aluminum heating block for 24 hours. The solvent was removed and the reaction mixture analyzed by ^{1}H NMR.

Rhodium acetate complex 5. ^{1}H NMR (400 MHz, CD_2Cl_2) δ 5.84 (bs, 1H), 3.40 (dq, J = 15.6 Hz, 2.4 Hz, 1H), 2.55-2.43 (m, 1H), 2.49 (d, J = 2.8 Hz, 3H), 1.87 (dd, J = 2.4 Hz, 1.6 Hz, 3H), 1.83 (s, 3H), 1.57 (s, 15H), 1.27 (d, J = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, CD_2Cl_2) δ 176.8, 176.6, 171.4, 141.2, 127.8, 92.8 (d, J = 8.8 Hz), 70.1, 31.6, 26.5, 24.3, 21.1, 19.1, 9.0. IR (thin film) ν 2922, 1640, 1613, 1448, 1359, 1315, 1160, 1090, 1026, 809, 727, 666 cm^{-1}. LRMS (ESI + APCI) *m/z* [M-OAc] calcd 404.1, found 404.1.

^{1}H NMR and ^{13}C NMR Spectra of New Compounds



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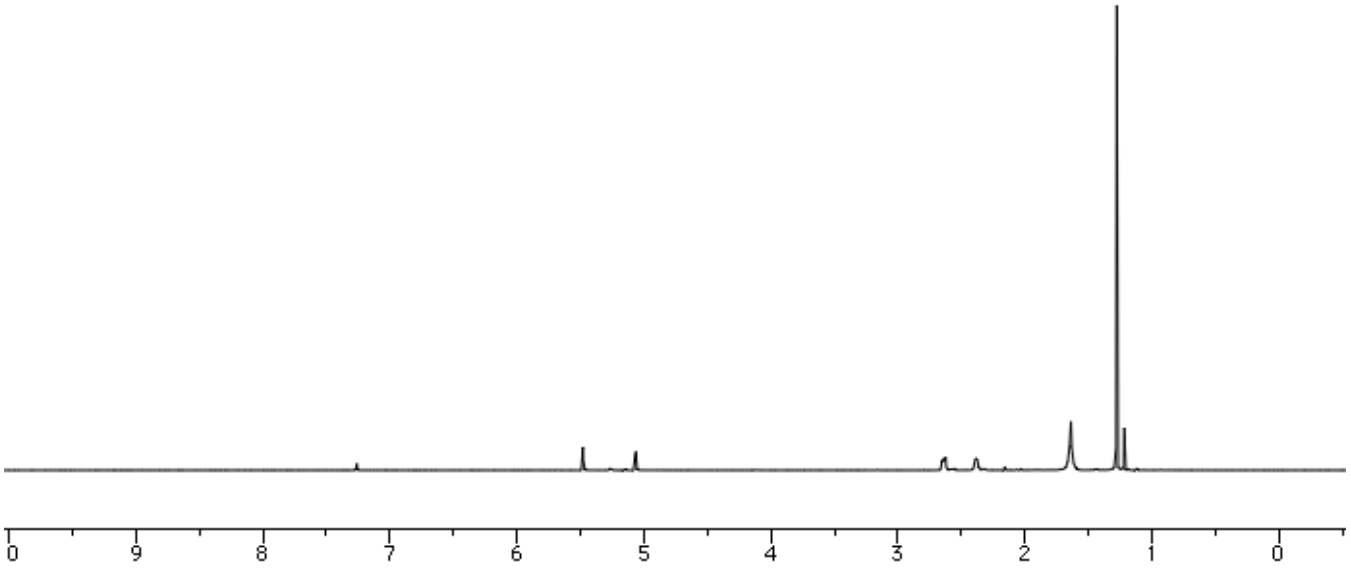

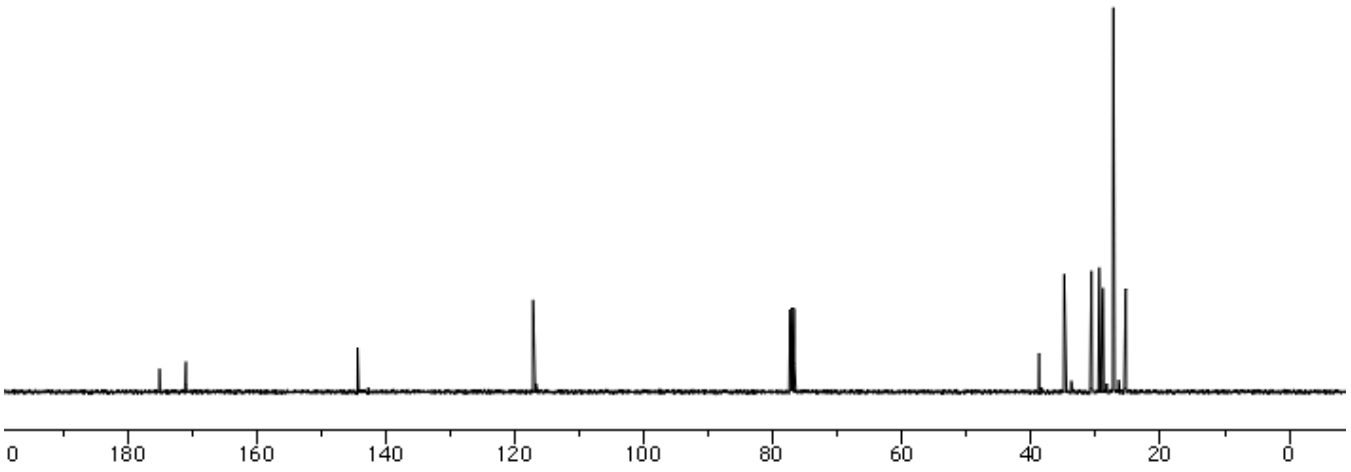

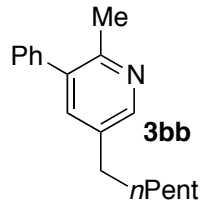

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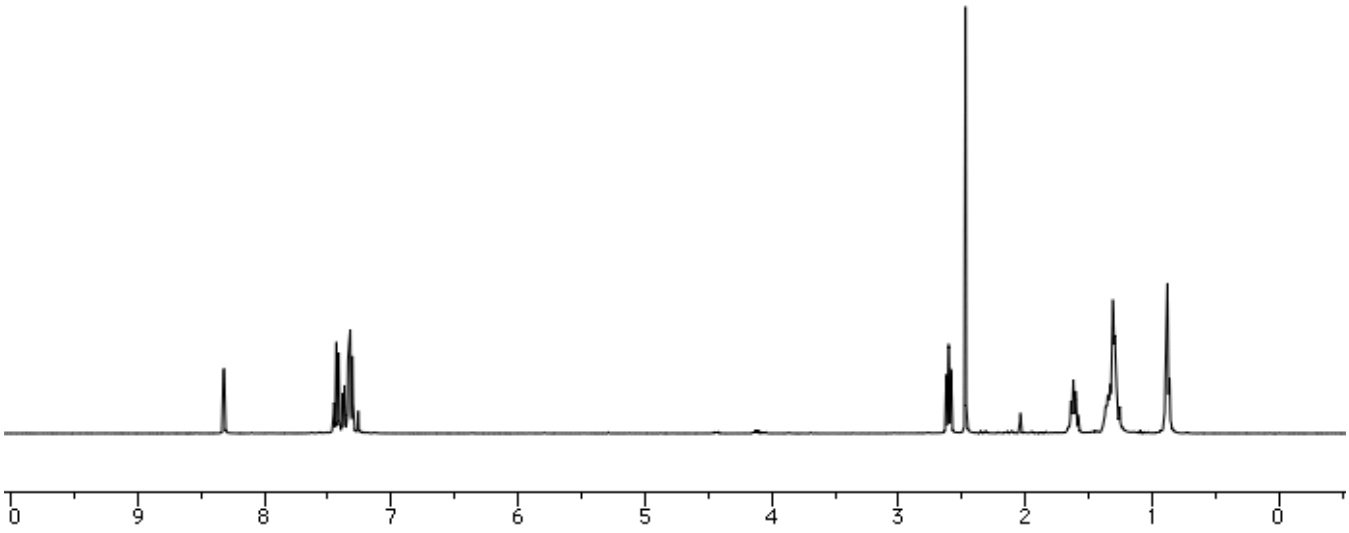

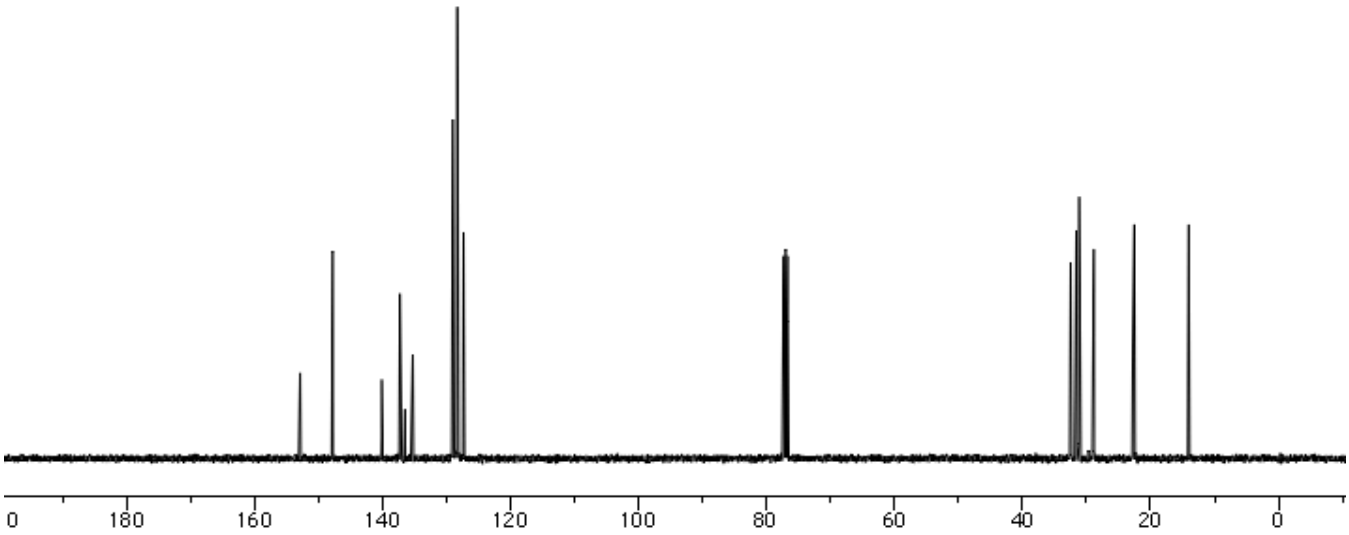

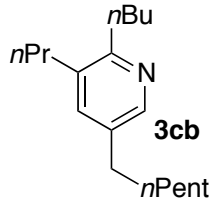

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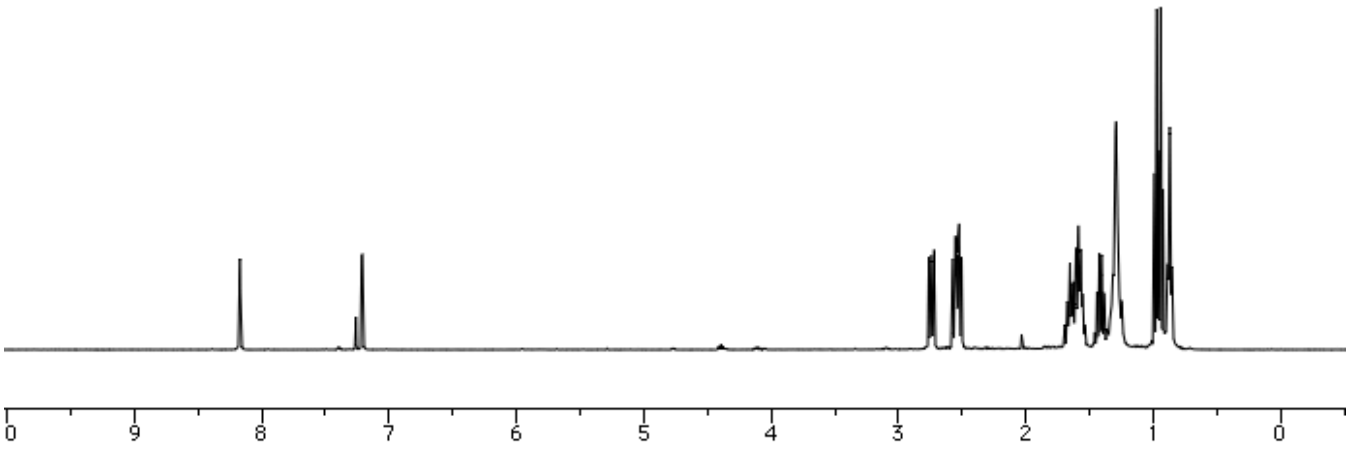

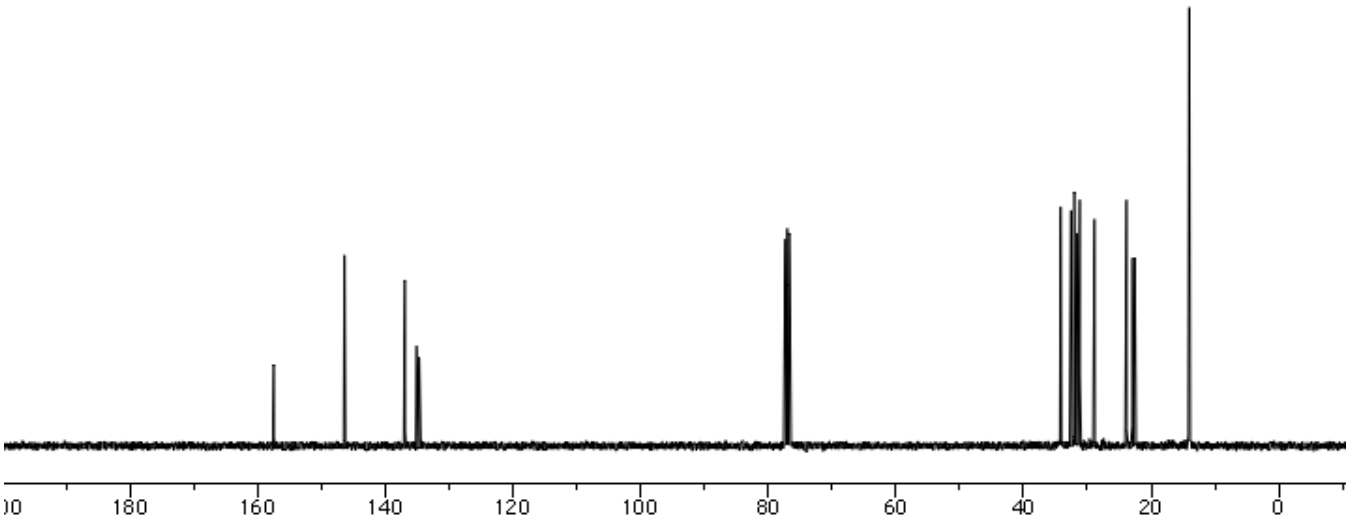

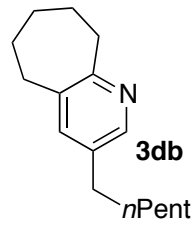
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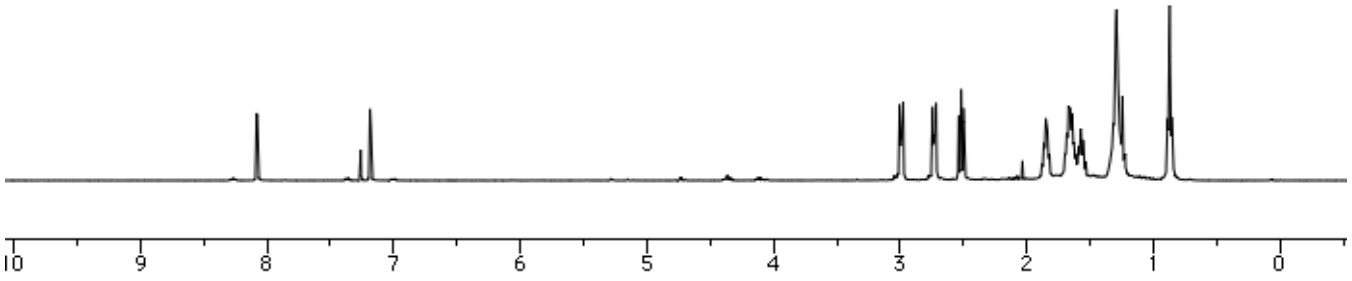
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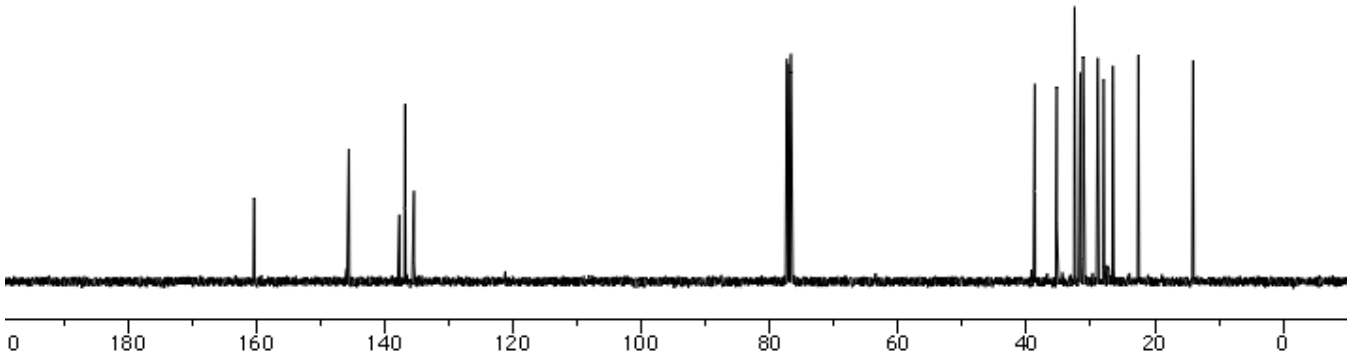
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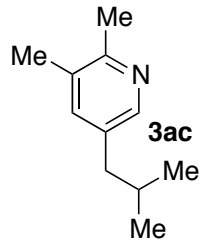

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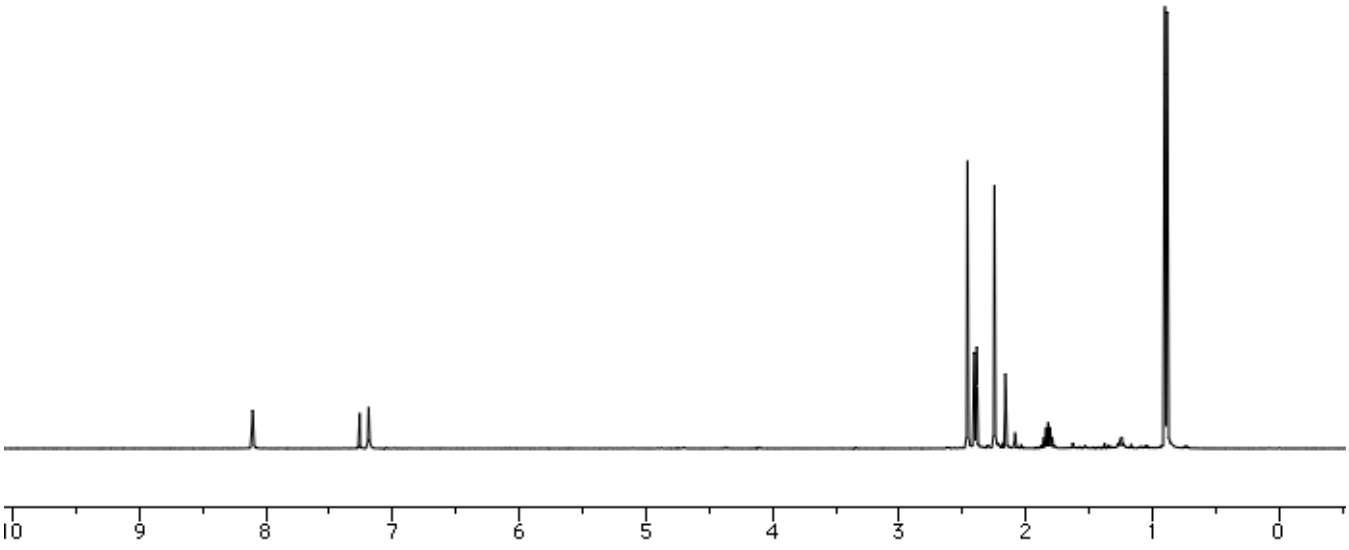

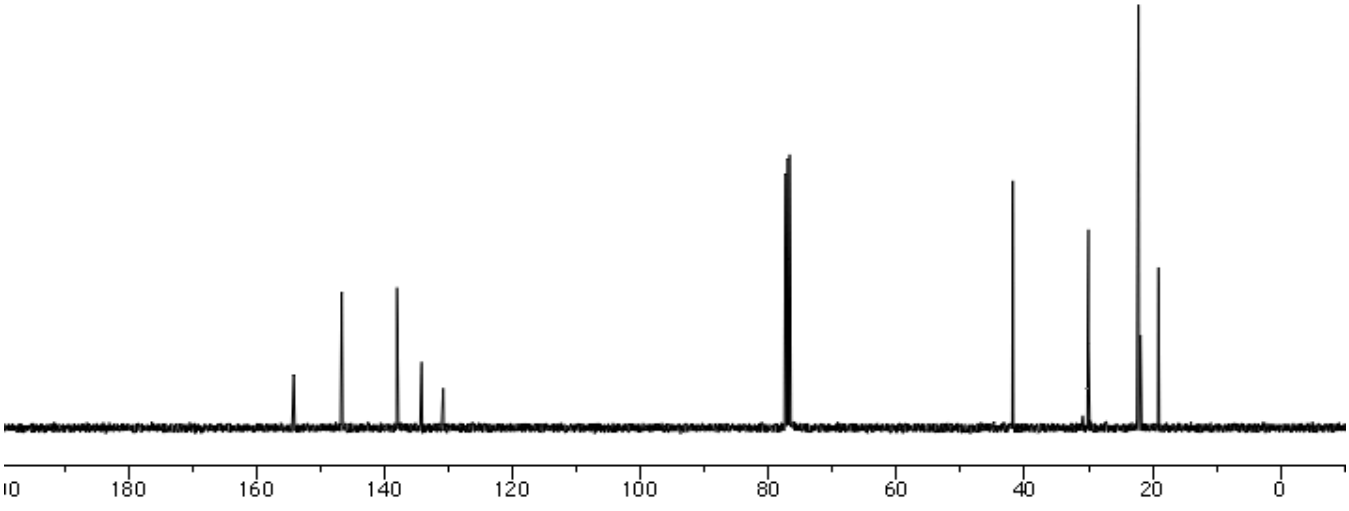

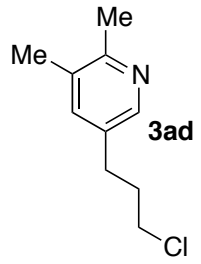

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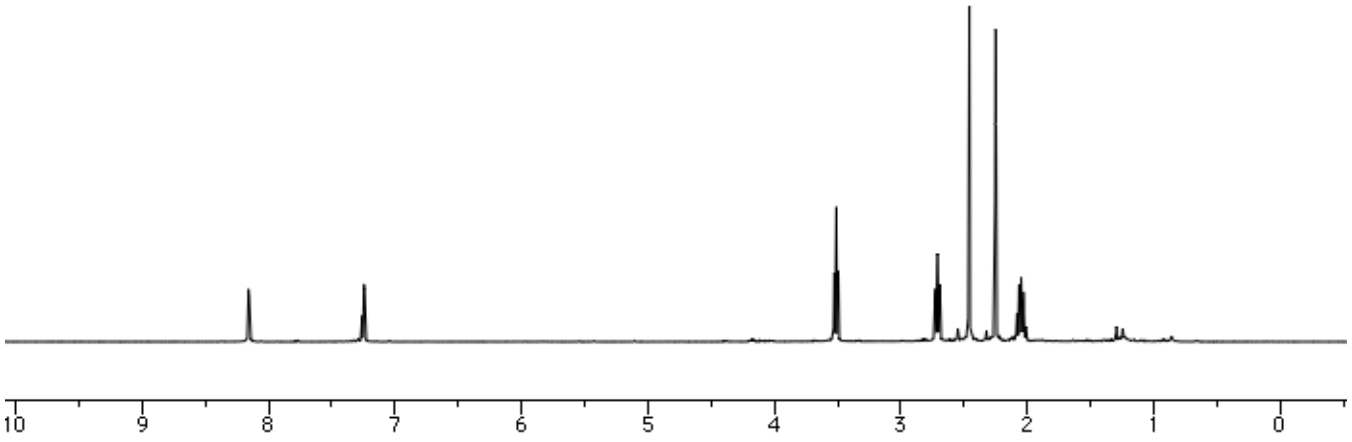

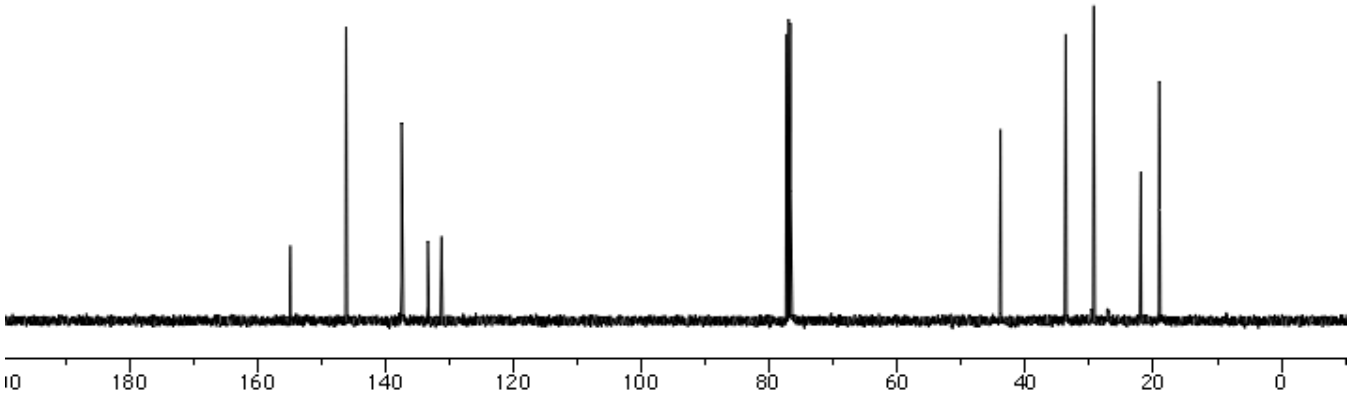

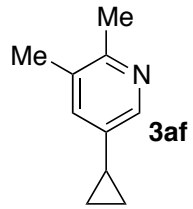

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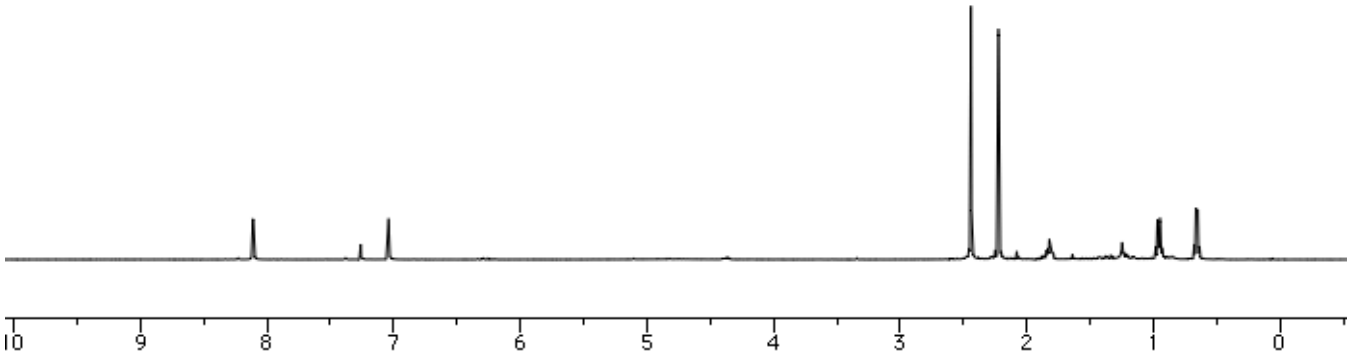

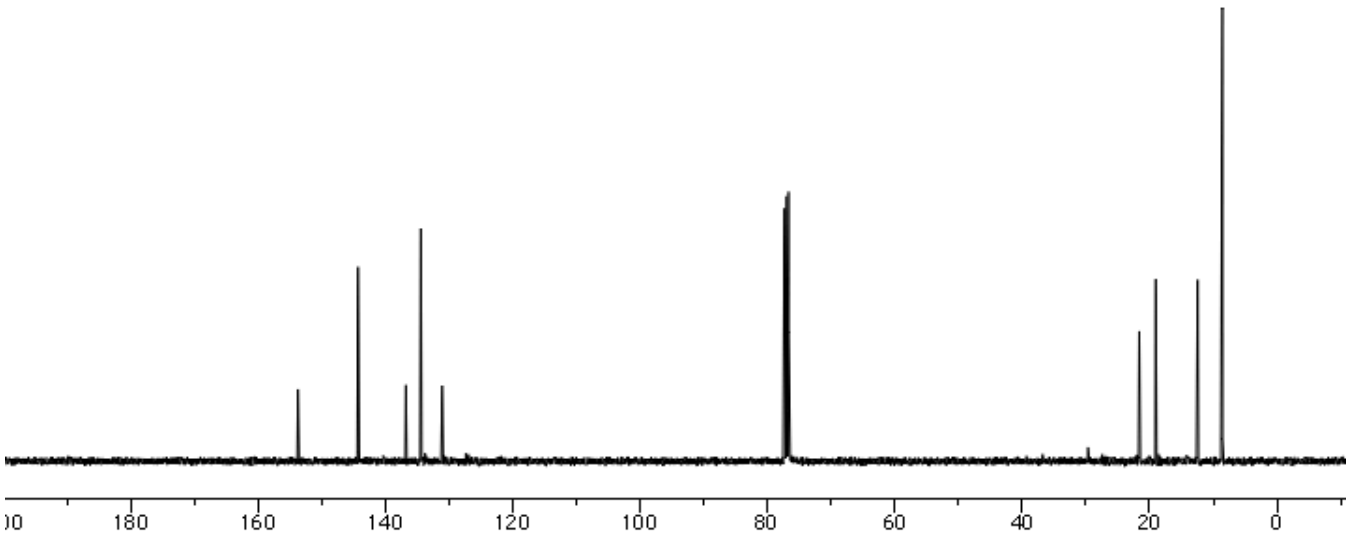

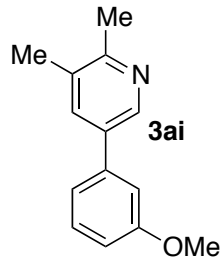

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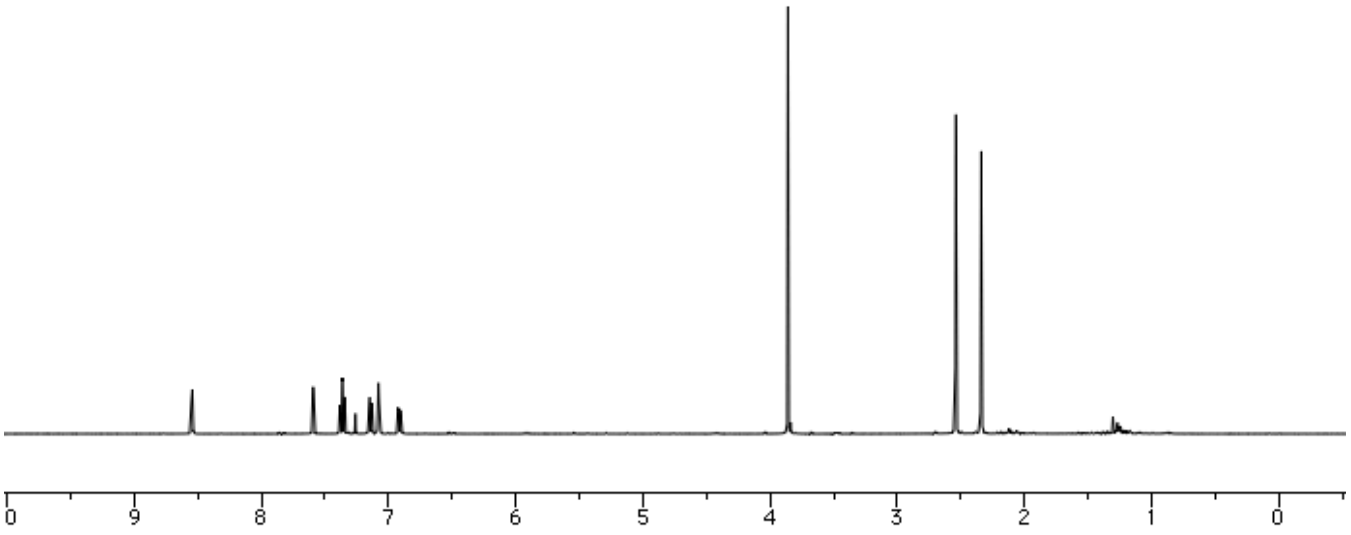

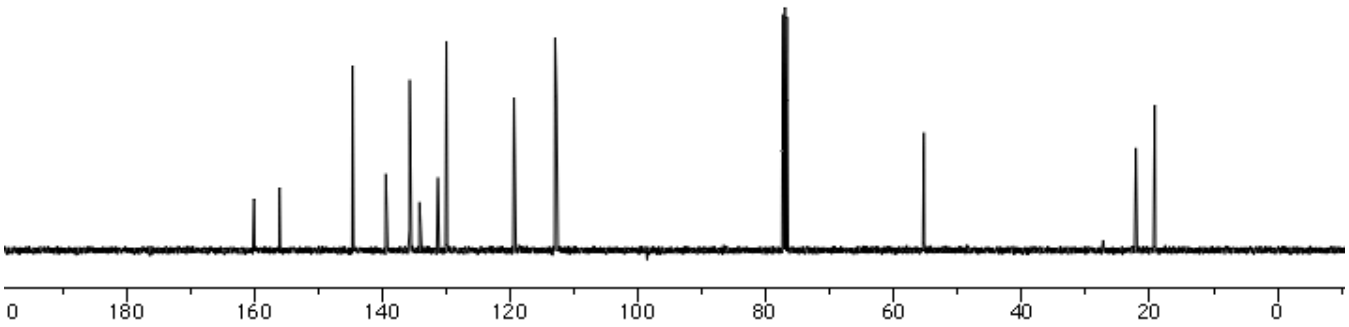

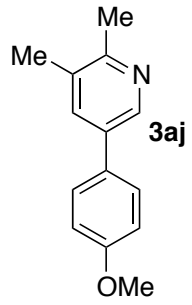

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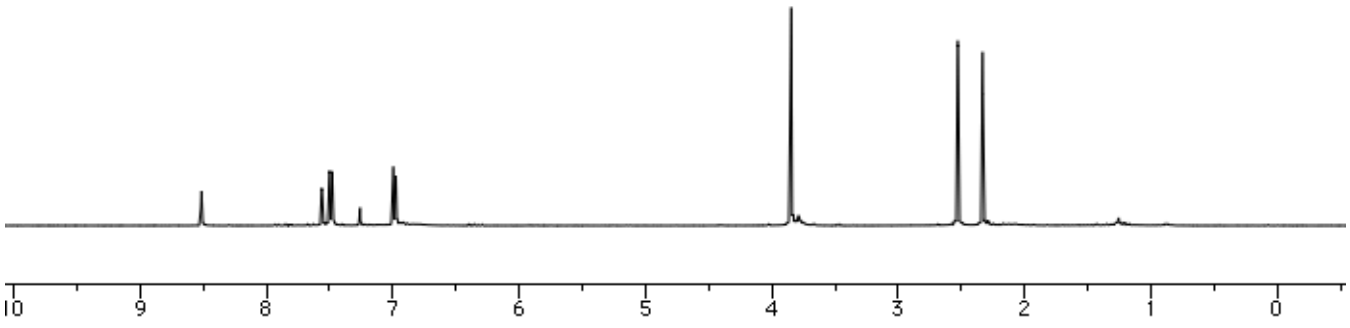

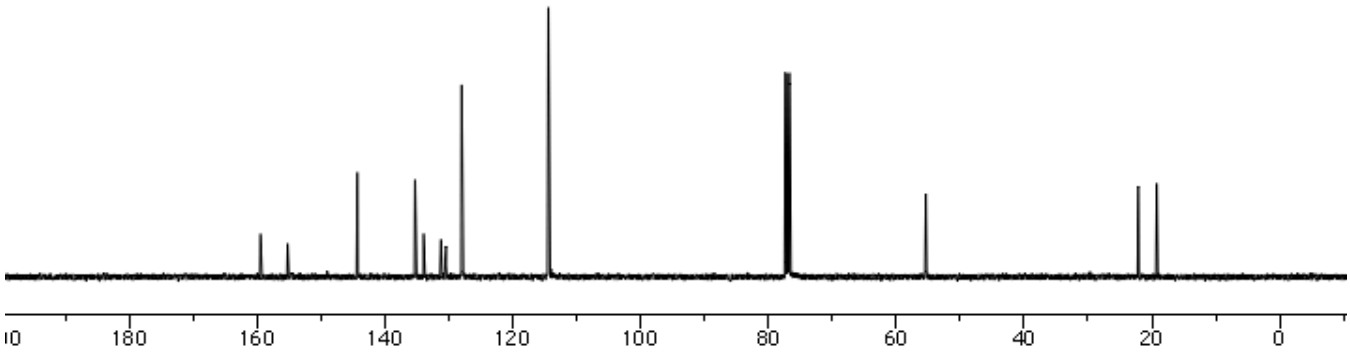

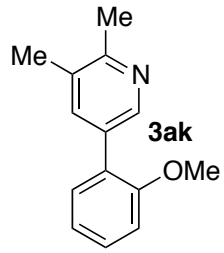

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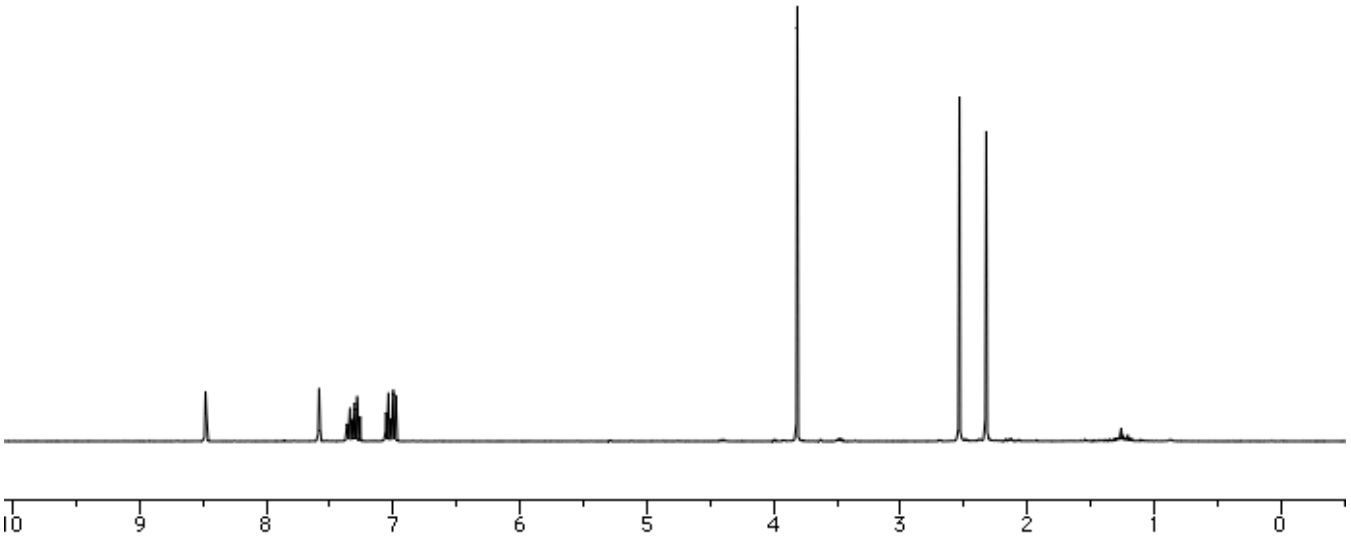

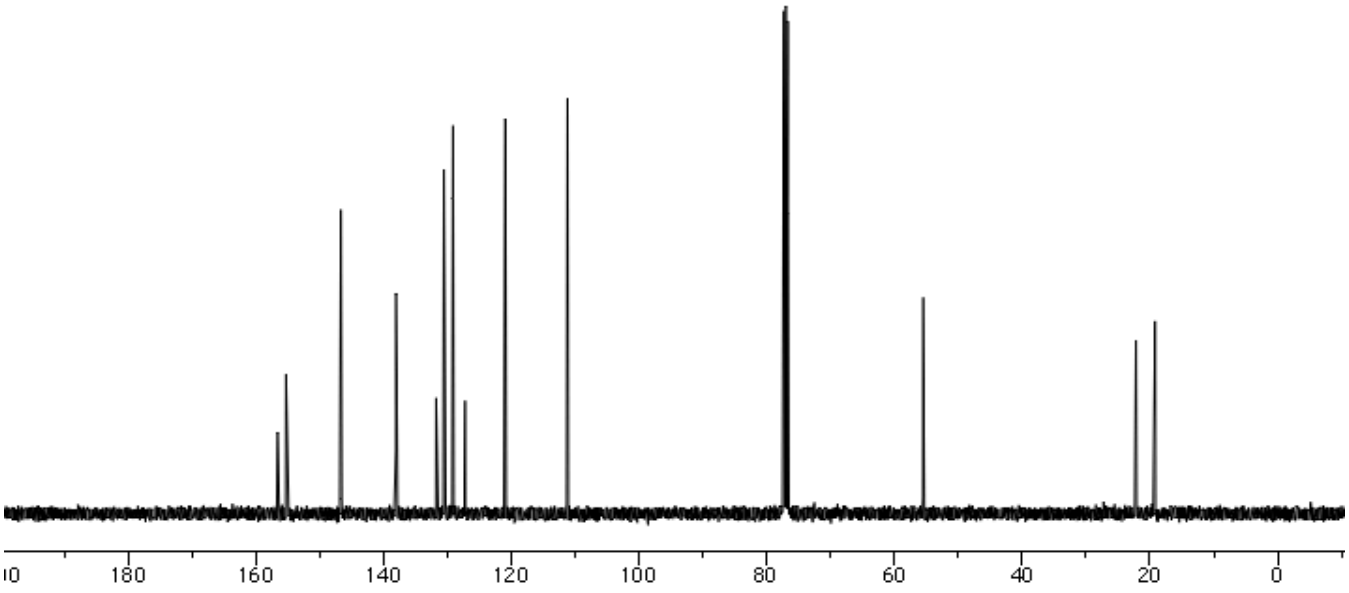

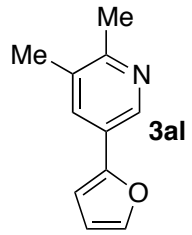

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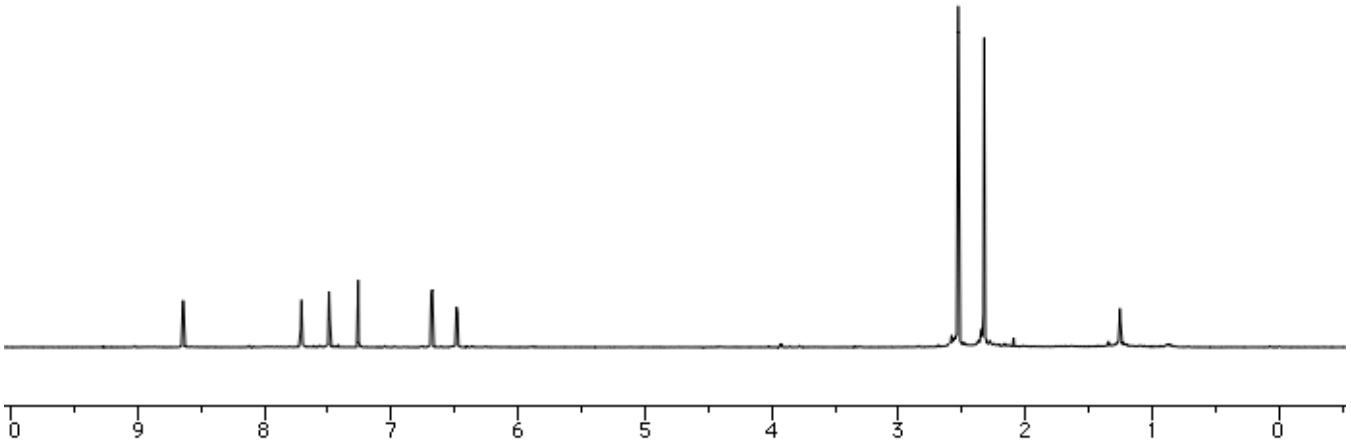

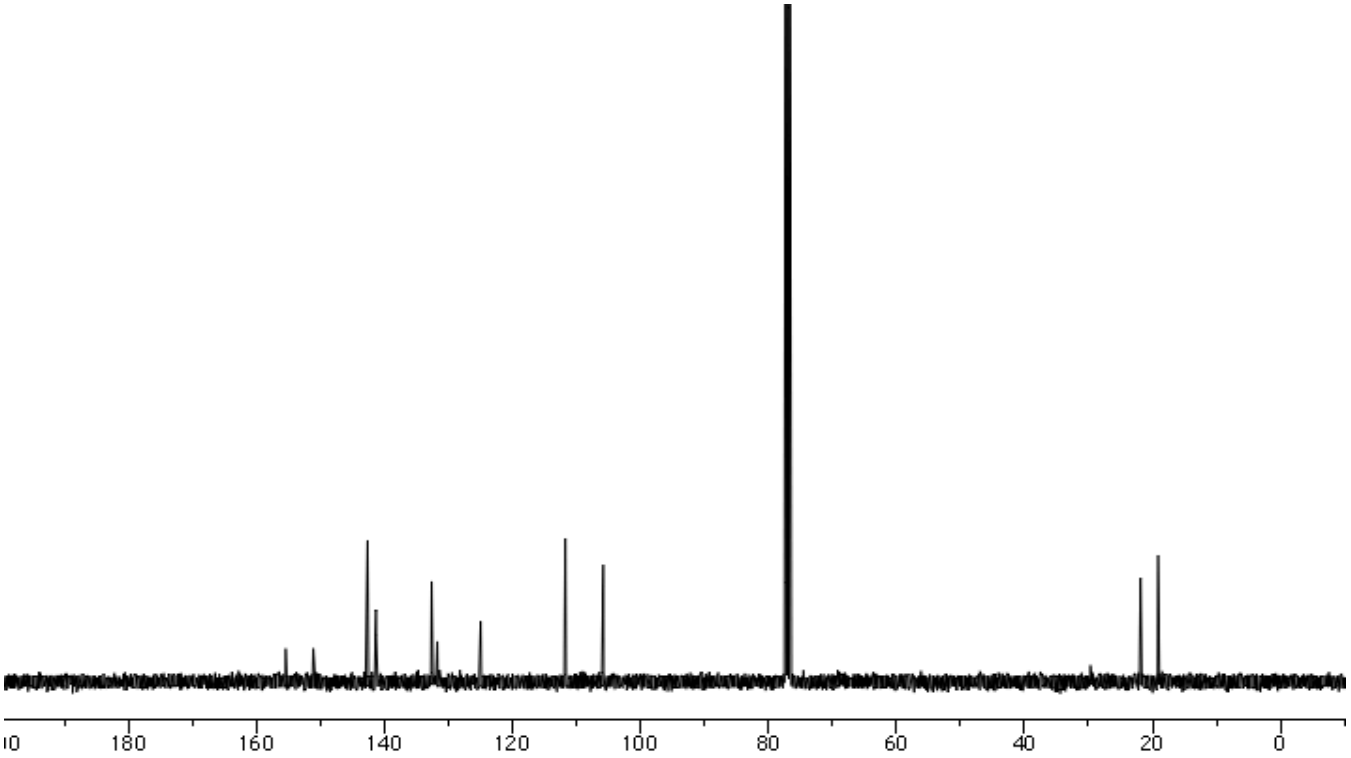

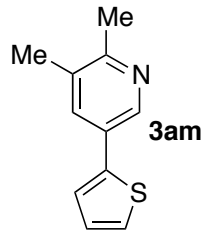

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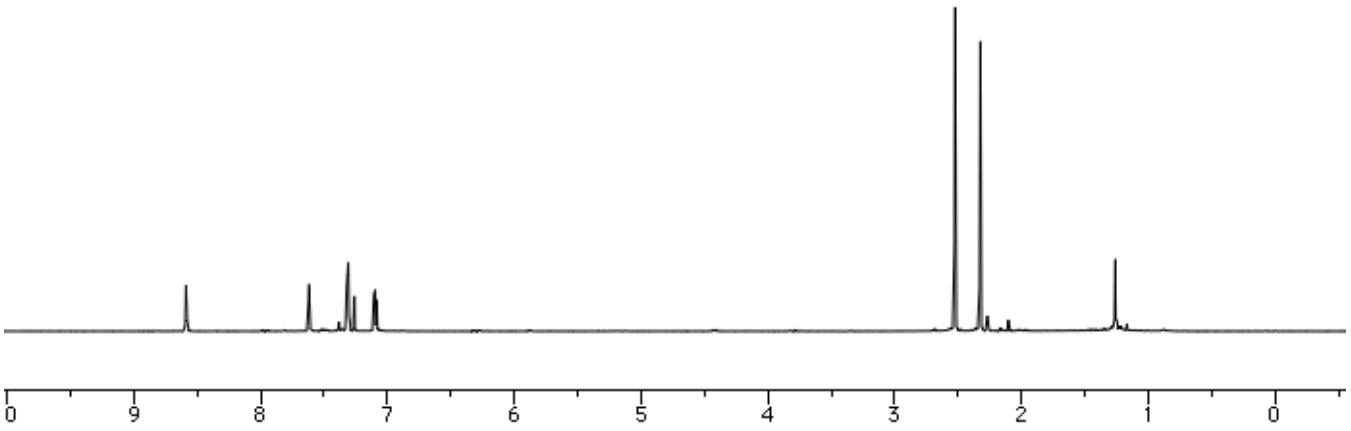

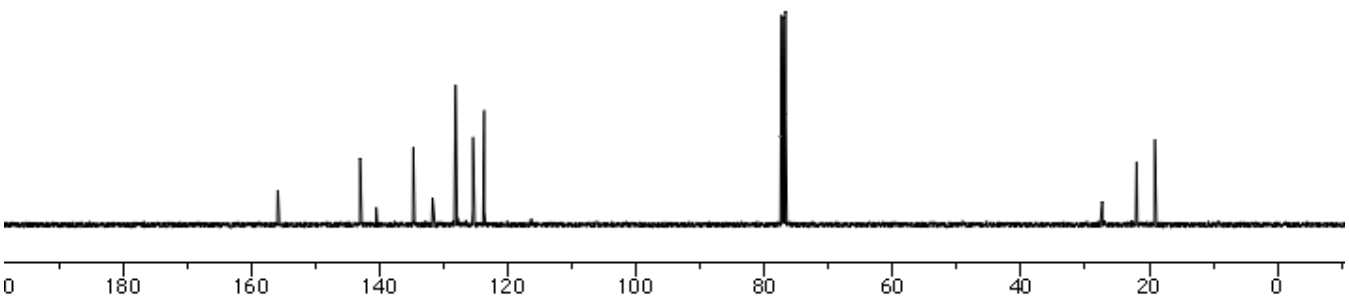

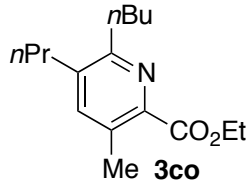
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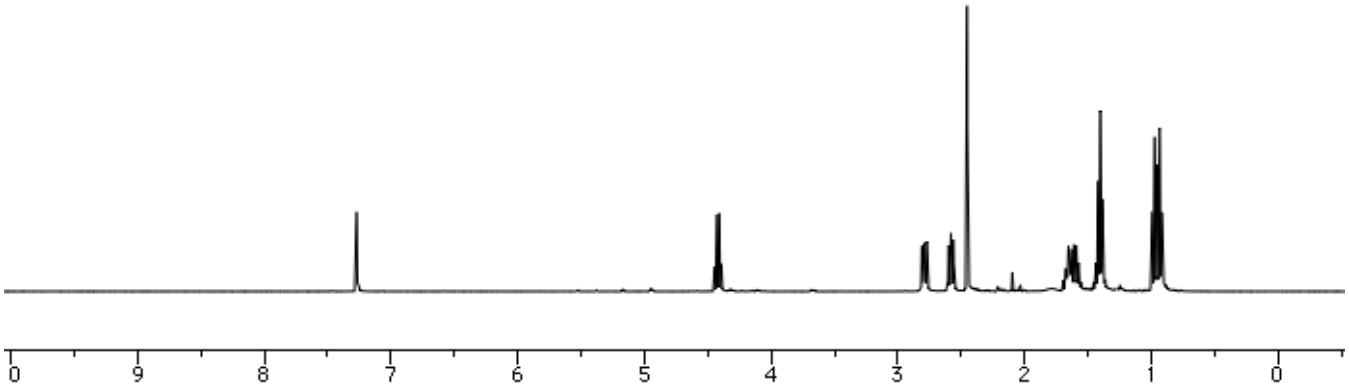
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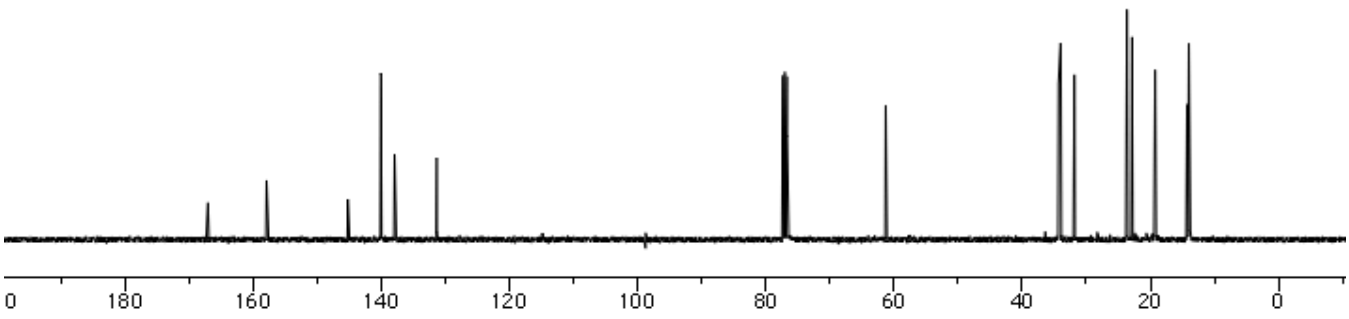
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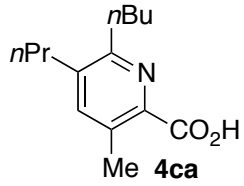

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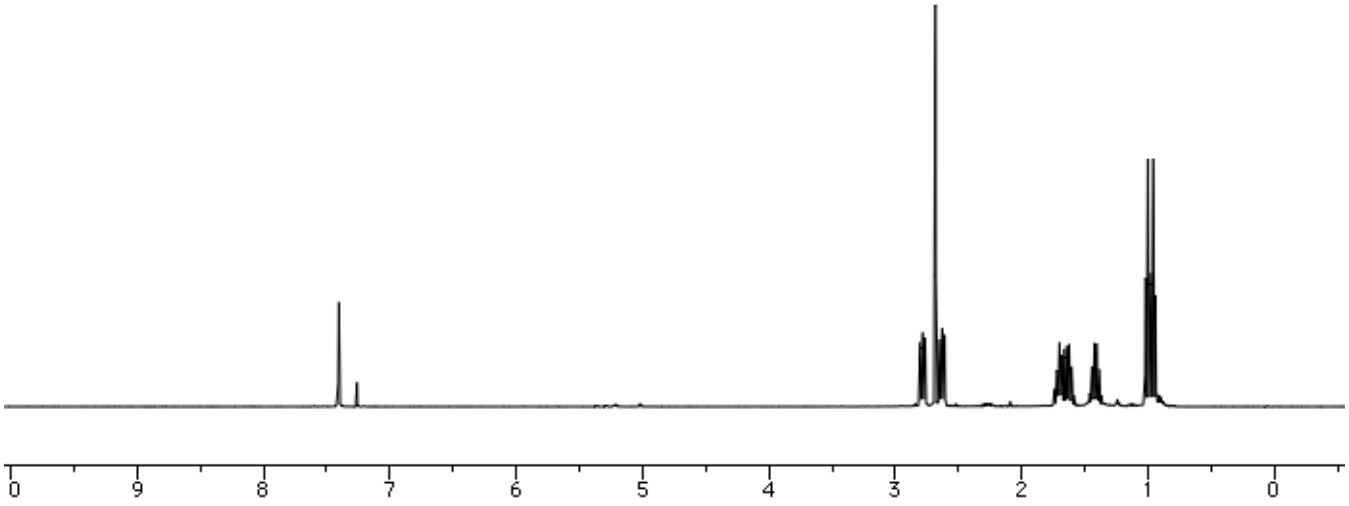

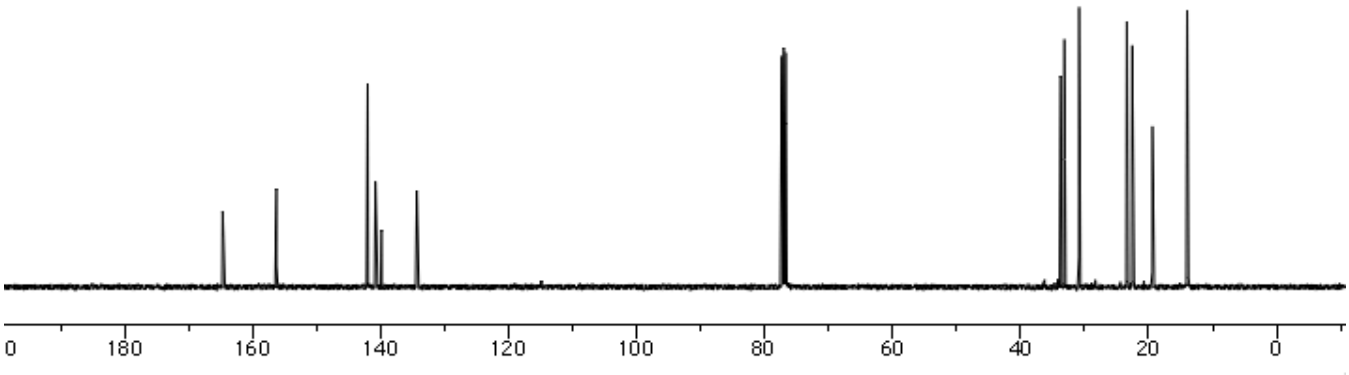

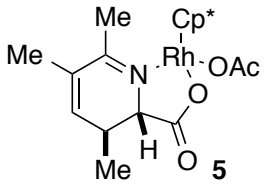
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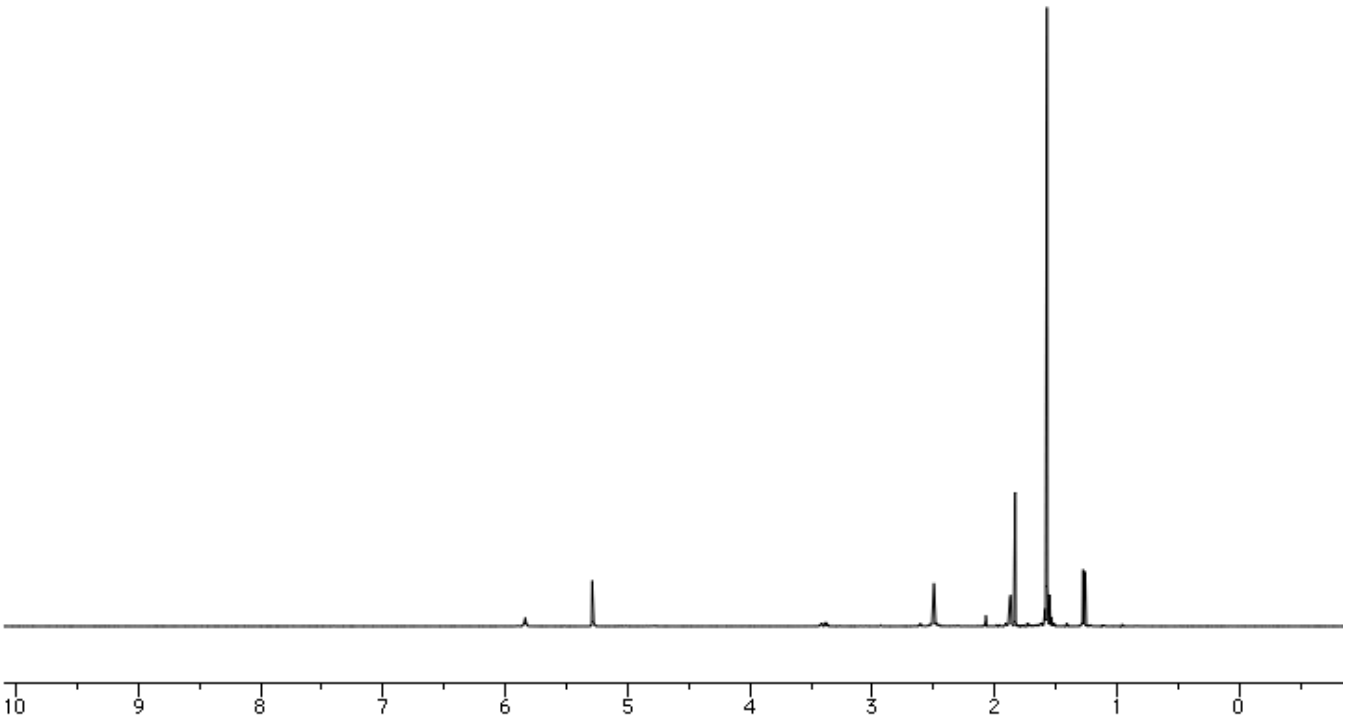
N
O
H
O
Me

5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4
3
2
1
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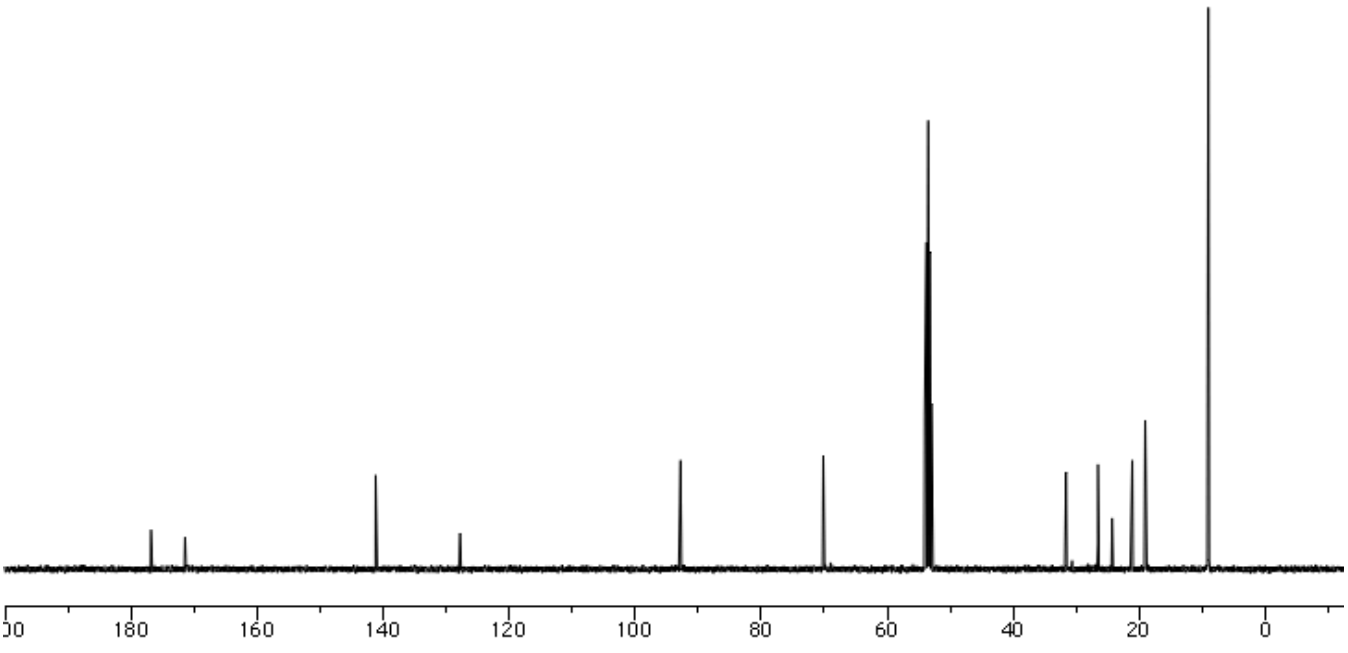
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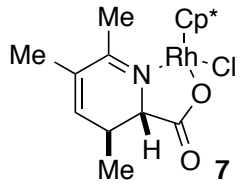
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N
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Cl
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H
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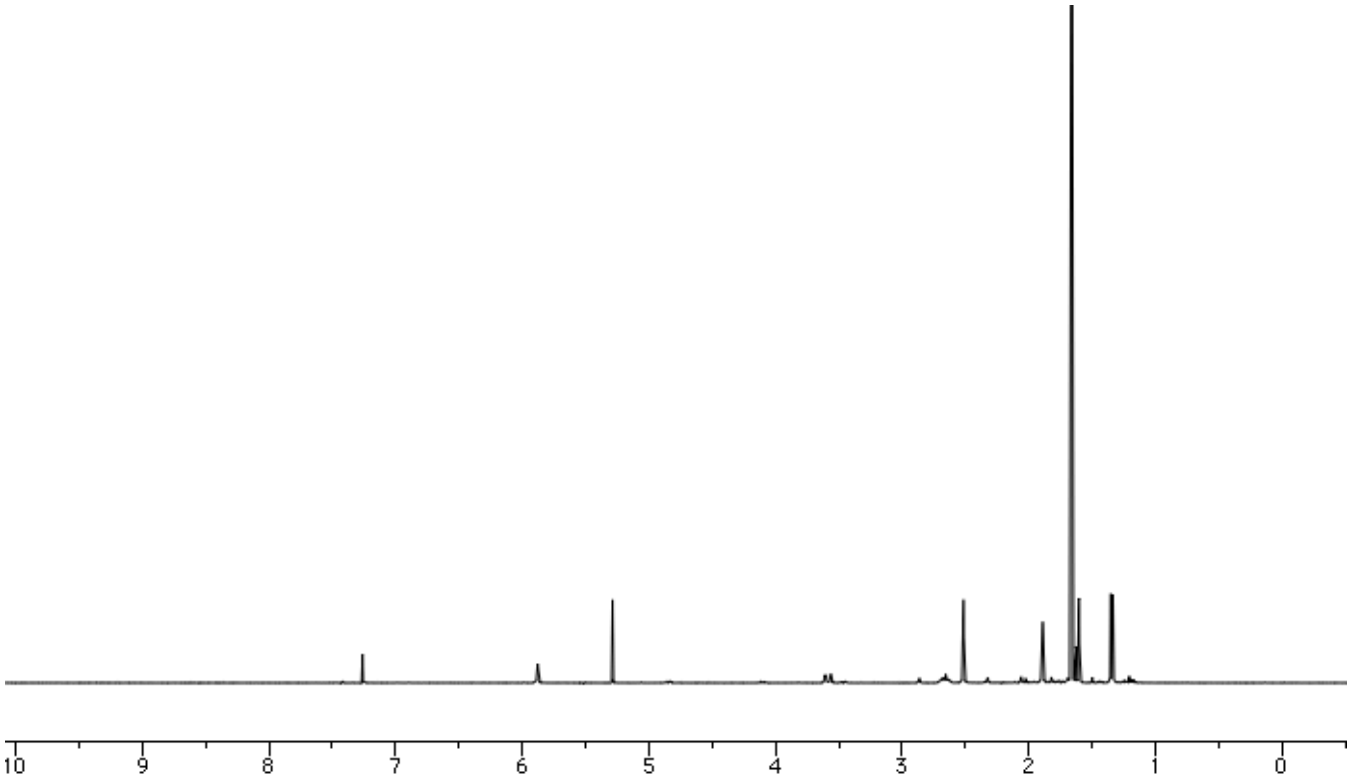
Me

7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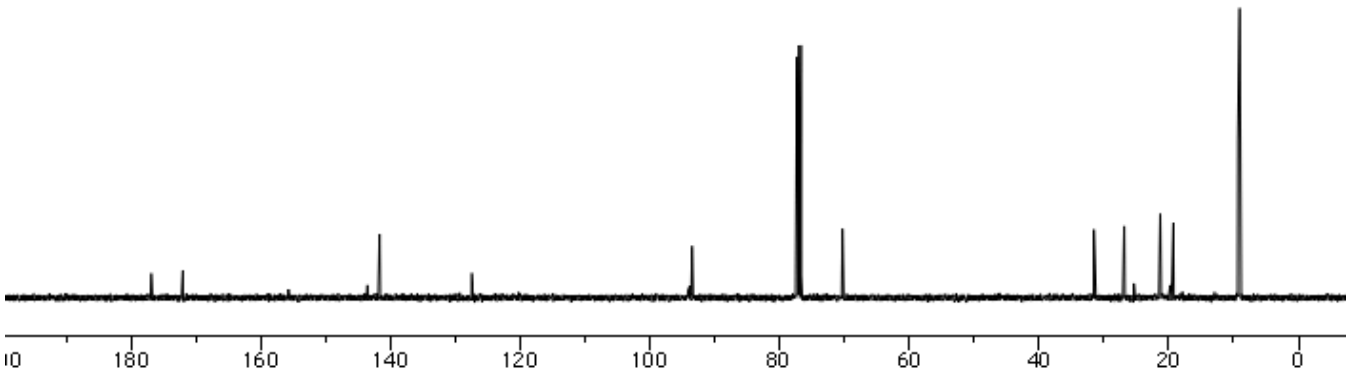
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Crystallographic Data for Rhodium Complex 7

Prismatic orange crystals were obtained after slow evaporation of a concentrated solution of **7** in DCM in loosely sealed vial. A single crystal was coated in Paratone-N oil and mounted under a stream of nitrogen. X-ray diffraction data was collected on a Bruker Kappa Apex II CCD diffractometer with Mo Kα radiation (λ = 0.71073 Å) and a graphite monochromator. Data integration and Lorentz and polarization corrections were accomplished with Bruker APEX2 software and semiempirical absorption corrections were applied using SCALE with the aid of numerical face indexing.[11] The crystal structure was solved with SHELXTL software.[12] The thermal parameters of all non-hydrogen atoms were refined anisotropically and hydrogen atoms were added in idealized positions. All crystallographic data is provided in a CIF file included in the Supporting Information.

Table S1. Crystal data and structure refinement for **7**.

Identification code	rovis178	
Empirical formula	$C_{19}H_{27}NO_2RhCl$	
Formula weight	439.78	
Temperature	120(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/n$	
Unit cell dimensions	a = 10.0060(6) Å	α= 90°.
	b = 12.4200(6) Å	β= 106.763(3)°.
	c = 15.5420(12) Å	γ = 90°.
Volume	1849.4(2) Å^3	
Z	4	
Density (calculated)	1.579 Mg/m^3	
Absorption coefficient	1.079 mm^{-1}	
F(000)	904	
Crystal size	0.35 x 0.13 x 0.11 mm^3	
Theta range for data collection	2.14 to 26.41°.	
Index ranges	-12<=h<=12, -15<=k<=15, -19<=l<=19	
Reflections collected	60907	
Independent reflections	3791 [R(int) = 0.0479]	
Completeness to theta = 26.41°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.8887 and 0.7039	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3791 / 0 / 225	
Goodness-of-fit on F^2	1.056	
Final R indices [I>2sigma(I)]	R1 = 0.0201, wR2 = 0.0439	
R indices (all data)	R1 = 0.0282, wR2 = 0.0477	
Largest diff. peak and hole	0.441 and -0.325 e.Å^{-3}	

Table S2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **7**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Rh(1)	5817(1)	2969(1)	2469(1)	12(1)
C(1)	8845(2)	3809(2)	3093(1)	15(1)
C(2)	10154(2)	4189(2)	2928(1)	18(1)
C(3)	10348(2)	4010(2)	2130(2)	20(1)
C(4)	9311(2)	3467(2)	1366(1)	19(1)
C(5)	7866(2)	3434(2)	1514(1)	16(1)
C(6)	8750(2)	3865(2)	4034(1)	22(1)
C(7)	11201(2)	4768(2)	3674(2)	25(1)
C(8)	9231(2)	4020(2)	478(2)	27(1)
C(9)	6980(2)	2484(2)	1021(1)	19(1)
N(1)	7809(2)	3456(1)	2452(1)	14(1)
O(1)	7174(2)	2132(1)	329(1)	30(1)
O(2)	6066(1)	2111(1)	1378(1)	19(1)
C(10)	3796(2)	2905(2)	2710(1)	16(1)
C(11)	3635(2)	3255(2)	1814(1)	17(1)
C(12)	4431(2)	4230(2)	1847(1)	17(1)
C(13)	5038(2)	4501(2)	2778(1)	18(1)
C(14)	4677(2)	3680(2)	3312(1)	16(1)
C(15)	3146(2)	1944(2)	3008(2)	23(1)
C(16)	2850(2)	2698(2)	969(1)	24(1)
C(17)	4479(2)	4901(2)	1056(2)	28(1)
C(18)	5867(2)	5496(2)	3098(2)	27(1)
C(19)	5035(2)	3620(2)	4316(1)	23(1)
Cl(1)	6832(1)	1481(1)	3429(1)	21(1)

Table S3. Bond lengths [Å] and angles [°] for **7**.

Rh(1)-O(2)	2.0779(14)
Rh(1)-N(1)	2.0904(16)
Rh(1)-C(12)	2.1299(19)
Rh(1)-C(11)	2.1556(19)
Rh(1)-C(14)	2.1592(19)
Rh(1)-C(13)	2.162(2)
Rh(1)-C(10)	2.1618(19)
Rh(1)-Cl(1)	2.4089(5)
C(1)-N(1)	1.290(3)
C(1)-C(2)	1.483(3)
C(1)-C(6)	1.495(3)
C(2)-C(3)	1.328(3)
C(2)-C(7)	1.501(3)
C(3)-C(4)	1.493(3)
C(4)-C(8)	1.523(3)
C(4)-C(5)	1.529(3)
C(5)-N(1)	1.475(2)
C(5)-C(9)	1.540(3)
C(9)-O(1)	1.228(2)
C(9)-O(2)	1.285(2)
C(10)-C(11)	1.424(3)
C(10)-C(14)	1.450(3)
C(10)-C(15)	1.495(3)
C(11)-C(12)	1.442(3)
C(11)-C(16)	1.491(3)
C(12)-C(13)	1.439(3)
C(12)-C(17)	1.498(3)
C(13)-C(14)	1.426(3)
C(13)-C(18)	1.493(3)
C(14)-C(19)	1.499(3)

O(2)-Rh(1)-N(1)	78.40(6)
O(2)-Rh(1)-C(12)	102.84(7)
N(1)-Rh(1)-C(12)	106.29(7)
O(2)-Rh(1)-C(11)	92.42(7)
N(1)-Rh(1)-C(11)	141.83(7)
C(12)-Rh(1)-C(11)	39.32(8)

O(2)-Rh(1)-C(14)	156.05(7)
N(1)-Rh(1)-C(14)	124.22(7)
C(12)-Rh(1)-C(14)	65.56(8)
C(11)-Rh(1)-C(14)	65.11(7)
O(2)-Rh(1)-C(13)	140.23(7)
N(1)-Rh(1)-C(13)	98.92(7)
C(12)-Rh(1)-C(13)	39.17(8)
C(11)-Rh(1)-C(13)	65.11(8)
C(14)-Rh(1)-C(13)	38.53(8)
O(2)-Rh(1)-C(10)	117.45(7)
N(1)-Rh(1)-C(10)	162.92(7)
C(12)-Rh(1)-C(10)	65.58(8)
C(11)-Rh(1)-C(10)	38.51(7)
C(14)-Rh(1)-C(10)	39.21(7)
C(13)-Rh(1)-C(10)	65.06(8)
O(2)-Rh(1)-Cl(1)	89.06(4)
N(1)-Rh(1)-Cl(1)	89.77(5)
C(12)-Rh(1)-Cl(1)	161.53(5)
C(11)-Rh(1)-Cl(1)	127.42(6)
C(14)-Rh(1)-Cl(1)	98.04(6)
C(13)-Rh(1)-Cl(1)	130.71(6)
C(10)-Rh(1)-Cl(1)	96.47(6)
N(1)-C(1)-C(2)	121.91(18)
N(1)-C(1)-C(6)	120.53(17)
C(2)-C(1)-C(6)	117.55(17)
C(3)-C(2)-C(1)	118.79(19)
C(3)-C(2)-C(7)	122.93(19)
C(1)-C(2)-C(7)	118.27(18)
C(2)-C(3)-C(4)	124.29(18)
C(3)-C(4)-C(8)	111.16(18)
C(3)-C(4)-C(5)	111.31(17)
C(8)-C(4)-C(5)	110.06(17)
N(1)-C(5)-C(4)	117.08(16)
N(1)-C(5)-C(9)	108.98(16)
C(4)-C(5)-C(9)	112.34(16)
O(1)-C(9)-O(2)	124.2(2)
O(1)-C(9)-C(5)	119.67(19)
O(2)-C(9)-C(5)	116.14(17)
C(1)-N(1)-C(5)	121.20(16)

C(1)-N(1)-Rh(1)	130.20(13)
C(5)-N(1)-Rh(1)	108.39(12)
C(9)-O(2)-Rh(1)	115.78(13)
C(11)-C(10)-C(14)	107.79(18)
C(11)-C(10)-C(15)	127.55(19)
C(14)-C(10)-C(15)	124.61(18)
C(11)-C(10)-Rh(1)	70.51(11)
C(14)-C(10)-Rh(1)	70.30(11)
C(15)-C(10)-Rh(1)	126.52(14)
C(10)-C(11)-C(12)	108.40(17)
C(10)-C(11)-C(16)	127.02(19)
C(12)-C(11)-C(16)	124.51(19)
C(10)-C(11)-Rh(1)	70.98(11)
C(12)-C(11)-Rh(1)	69.38(11)
C(16)-C(11)-Rh(1)	122.98(14)
C(13)-C(12)-C(11)	107.51(17)
C(13)-C(12)-C(17)	126.2(2)
C(11)-C(12)-C(17)	125.94(19)
C(13)-C(12)-Rh(1)	71.61(11)
C(11)-C(12)-Rh(1)	71.30(11)
C(17)-C(12)-Rh(1)	127.64(14)
C(14)-C(13)-C(12)	108.32(18)
C(14)-C(13)-C(18)	127.46(19)
C(12)-C(13)-C(18)	124.21(19)
C(14)-C(13)-Rh(1)	70.63(11)
C(12)-C(13)-Rh(1)	69.22(11)
C(18)-C(13)-Rh(1)	126.99(14)
C(13)-C(14)-C(10)	107.91(17)
C(13)-C(14)-C(19)	128.08(19)
C(10)-C(14)-C(19)	123.90(19)
C(13)-C(14)-Rh(1)	70.83(11)
C(10)-C(14)-Rh(1)	70.49(11)
C(19)-C(14)-Rh(1)	127.04(14)

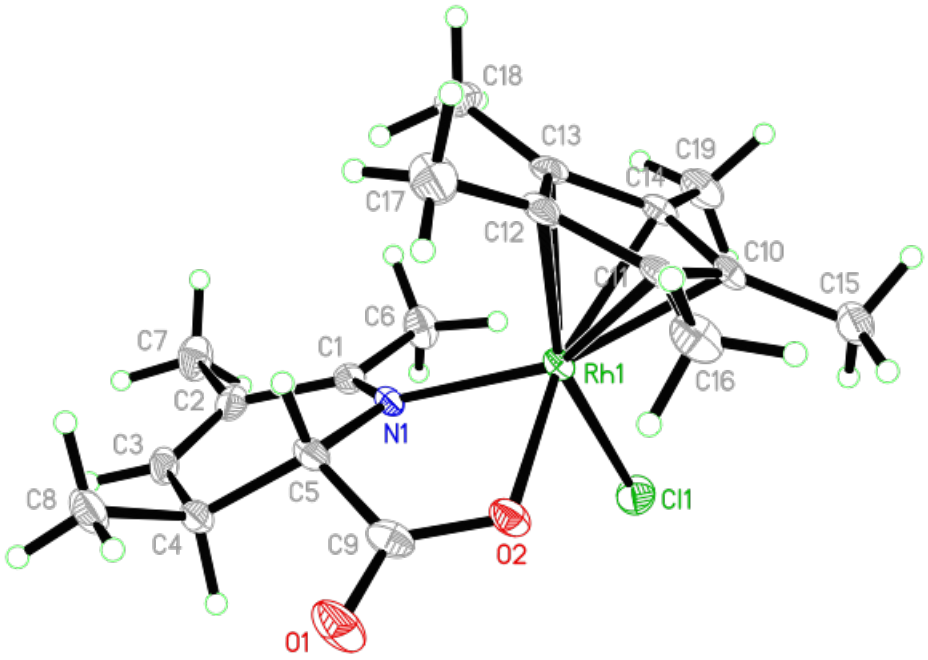
Symmetry transformations used to generate equivalent atoms:

Table S4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for **7**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ...\ + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Rh(1)	10(1)	15(1)	11(1)	0(1)	3(1)	1(1)
C(1)	14(1)	15(1)	17(1)	3(1)	4(1)	2(1)
C(2)	13(1)	16(1)	24(1)	7(1)	4(1)	2(1)
C(3)	14(1)	18(1)	28(1)	7(1)	10(1)	2(1)
C(4)	20(1)	18(1)	23(1)	3(1)	12(1)	3(1)
C(5)	16(1)	19(1)	16(1)	1(1)	7(1)	4(1)
C(6)	18(1)	31(1)	17(1)	-2(1)	5(1)	-5(1)
C(7)	16(1)	29(1)	29(1)	4(1)	3(1)	-5(1)
C(8)	31(1)	31(1)	26(1)	6(1)	20(1)	7(1)
C(9)	16(1)	24(1)	16(1)	-1(1)	3(1)	7(1)
N(1)	13(1)	15(1)	13(1)	1(1)	6(1)	2(1)
O(1)	30(1)	44(1)	20(1)	-13(1)	12(1)	-3(1)
O(2)	16(1)	23(1)	18(1)	-7(1)	6(1)	0(1)
C(10)	10(1)	21(1)	18(1)	-1(1)	6(1)	3(1)
C(11)	10(1)	23(1)	16(1)	-1(1)	3(1)	6(1)
C(12)	13(1)	20(1)	18(1)	3(1)	6(1)	6(1)
C(13)	14(1)	17(1)	22(1)	-2(1)	6(1)	5(1)
C(14)	14(1)	20(1)	17(1)	-3(1)	6(1)	3(1)
C(15)	20(1)	26(1)	26(1)	-1(1)	10(1)	-2(1)
C(16)	18(1)	35(1)	17(1)	-3(1)	1(1)	4(1)
C(17)	26(1)	33(1)	27(1)	13(1)	10(1)	9(1)
C(18)	27(1)	16(1)	38(1)	-4(1)	9(1)	1(1)
C(19)	22(1)	34(1)	14(1)	-3(1)	6(1)	4(1)
Cl(1)	20(1)	19(1)	24(1)	6(1)	6(1)	3(1)

Table S5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for **7**.

	x	y	z	U(eq)
H(3)	11202	4242	2040	24
H(4)	9628	2709	1332	23
H(5)	7376	4100	1226	19
H(6A)	8771	4620	4222	33
H(6B)	9541	3480	4436	33
H(6C)	7875	3532	4062	33
H(7A)	12021	4952	3479	38
H(7B)	11484	4301	4204	38
H(7C)	10781	5428	3825	38
H(8A)	8949	4772	503	40
H(8B)	8543	3649	-11	40
H(8C)	10147	3993	369	40
H(15A)	2657	1515	2482	35
H(15B)	2481	2181	3324	35
H(15C)	3875	1504	3412	35
H(16A)	3503	2297	726	36
H(16B)	2354	3232	528	36
H(16C)	2175	2197	1098	36
H(17A)	3694	5407	910	42
H(17B)	4418	4433	539	42
H(17C)	5359	5304	1202	42
H(18A)	5245	6123	2979	41
H(18B)	6577	5580	2781	41
H(18C)	6324	5440	3746	41
H(19A)	5751	4158	4583	35
H(19B)	5391	2900	4518	35
H(19C)	4198	3763	4505	35



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(10) The analogous reaction with $[RhCp^*Cl_2]_2$ was also performed and only starting material was observed.

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