

Enantioselective Rhodium-Catalyzed [2+2+2] Cycloadditions of Terminal Alkynes and Alkenyl Isocyanates: Mechanistic Insights Lead to a Unified Model that Rationalizes Product Selectivity

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General Methods:

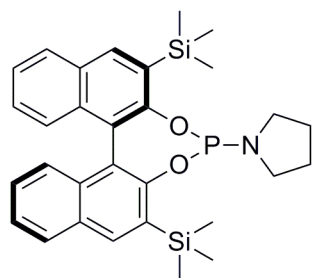
All reactions were carried out under an atmosphere of argon in oven-dried glassware with magnetic stirring. Toluene was degassed with argon and passed through one column of neutral alumina and one column of Q5 reactant. Tetrahydrofuran was degassed with argon and passed through two columns of neutral alumina. Column chromatography was performed on Silicycle Inc. silica gel 60 (230-400 mesh). Thin layer chromatography was performed on Silicycle Inc. 0.25 mm silica gel 60-F plates. Visualization was accomplished with UV light (254 nm), potassium permanganate, and/or ceric ammonium molybdate.

^1H NMR and ^{13}C NMR spectra were obtained in CDCl_3 at ambient temperature and chemical shifts are expressed in parts per million (δ , ppm). Proton chemical shifts are referenced to 7.26 ppm (CHCl_3) and carbon chemical shifts are referenced to 77.0 ppm (CDCl_3). Data reporting uses the following abbreviations: s, singlet; bs, broad singlet; d, doublet; t, triplet; m, multiplet; and J , coupling constant in Hz.

Ligands **B1** and **B3** were purchased from Aldrich Chemicals Co. and used without further purification. Ligands **T1-T3**,¹ **T8** and **T9**,² and **B4**³ were synthesized as previously reported. **A1**⁴ and **T5**⁵ were prepared according to literature procedures. Alkynes were purchased from Aldrich Chemicals Co. and used without further purification or synthesized as previously reported.¹ $[\text{Rh}(\text{C}_2\text{H}_4)_2\text{Cl}]_2$ was purchased from Strem Chemicals, Inc. and used without further purification. Isocyanates **2a-2e** and **2h-2k** were prepared as previously reported.² The synthesis of isocyanates **2f**, **2g**, and **2l-2q** are described herein.

General Procedure for Synthesis of Ligands:

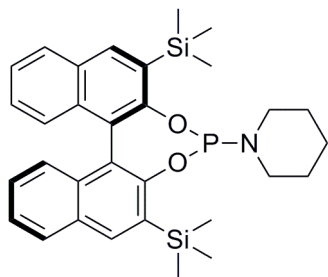
The diol (0.27 mmol) was dissolved in THF in an oven-dried round bottom flask with a magnetic stir bar. Et_3N (3.5 eq, 0.95 mmol) was added and the reaction mixture was cooled to 0 °C before dropwise addition of phosphorous trichloride (1.1 eq, 0.30 mmol). The reaction mixture was stirred for 1 h and the amine (10 eq, 2.70 mmol) was added slowly at 0 °C. The reaction was stirred overnight at 23 °C, diluted with ether, and filtered. The filtrate was concentrated in *vacuo* and the resulting crude material was purified by flash column chromatography (98:2 Hex:EtOAc) to afford the desired phosphoramidite.



$[\text{C}_{30}\text{H}_{37}\text{NO}_2\text{PSi}_2]^+$ calcd 530.2095, found 530.2104.

***O,O*-(*R*)-3,3'-bis(trimethylsilyl)-1,1'-binaphthyl-2,2'-diyl-**

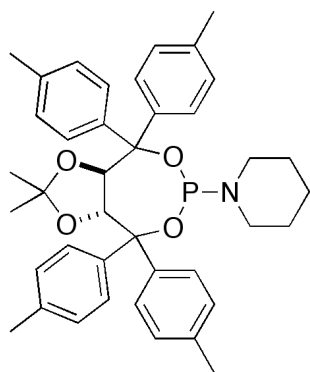
pyrrolidinephosphoramidite (B5). General procedure yielded a white solid (85%). $[\alpha]_{\text{D}}^{20} = -550.4^\circ$, $c = 0.01$ g/ml CHCl_3 . ^1H NMR (400 MHz, CDCl_3) δ 8.07 (m, 2H), 7.90 (m, 2H), 7.32 (m, 2H), 7.18 (m, 4H), 3.18 (m, 2H), 2.84 (bs, 2H), 1.65 (m, 4H), 0.45 (s, 9H), 0.44 (s, 9H). ^{13}C NMR (75 MHz, CDCl_3) δ 137.8, 136.6, 134.0, 133.7, 132.5, 132.2, 130.7, 130.1, 128.5, 128.3, 128.1, 127.5, 126.8, 126.7, 126.1, 124.2, 123.9, 123.6, 45.9, 45.7, 25.9, 25.8, 0.1, 0.0, -0.1, -0.9. ^{31}P NMR (75 MHz, CDCl_3) δ 149.82. $R_f = 0.62$ (98:2 Hex:EtOAc). IR (NaCl, Thin Film) 3534, 3053, 3032, 2960, 2899, 2858, 1578, 1388, 1255, 1086, 968, 835, 753 cm^{-1} . HRMS (ESI) m/z



$[\text{C}_{31}\text{H}_{39}\text{NO}_2\text{PSi}_2]^+$ calcd 544.2251, found 544.2263.

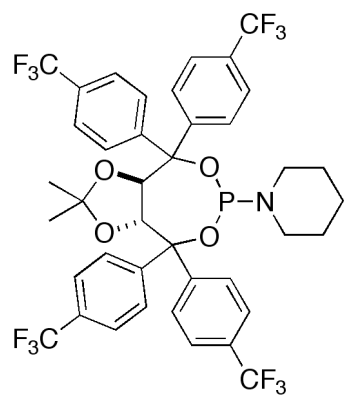
***O,O*-(*R*)-3,3'-bis(trimethylsilyl)-1,1'-binaphthyl-2,2'-diyl-**

piperidinephosphoramidite (B6). General procedure yielded a white solid (89%). $[\alpha]_{\text{D}} = -505.4^\circ$, $c = 0.01$ g/ml CHCl_3 . ^1H NMR (400 MHz, CDCl_3) δ 8.07 (m, 2H), 7.91 (m, 2H), 7.39 (m, 3H), 7.17 (m, 3H), 2.92 (m, 2H), 1.53 (m, 4H), 1.32 (m, 2H), 0.51 (s, 9H), 0.45 (s, 9H). ^{13}C NMR (75 MHz, CDCl_3) δ 153.6, 136.7, 133.9, 133.7, 132.6, 132.1, 130.7, 130.0, 128.3, 128.2, 126.8, 126.7, 126.1, 126.0, 124.3, 124.1, 30.3, 27.2, 24.8. ^{31}P NMR (75 MHz, CDCl_3) δ 146.25. $R_f = 0.40$ (98:2 Hex:EtOAc). IR (NaCl, Thin Film) 3052, 2935, 2853, 1368, 1240, 1091, 1055,



1-((3aR,8aR)-2,2-dimethyl-4,4,8,8-tetraphenyltetrahydro-[1,3]dioxolo[4,5-e][1,3,2]dioxaphosphepin-6-yl)piperidine (T6). General procedure yielded a white solid (69%). $[\alpha]_D^{20} = -95.9^\circ$, $c = 0.01\text{g/ml}$, CH_2Cl_2 . $^1\text{H NMR}$ (300 MHz, CDCl_3) δ 7.596 (d, $J = 8.25$ Hz, 2H), 7.425 (d, $J = 8.14$ Hz, 2H), 7.254 (dd, $J = 18.02, 8.16$, 4H), 7.028 (dd, $J = 7.98, 4.14$ Hz, 6H), 6.979 (d, $J = 8.19$ Hz, 2H), 5.039 (dd, $J = 8.56$ Hz, 1H), 4.645 (d, $J = 8.55$ Hz, 1H), 3.210 (m, 2H), 3.086 (m, 2H), 2.236 (d, $J = 2.34$ Hz, 9H), 2.202 (s, 3H), 1.509 (m, 6H), 1.269 (s, 3H), 0.211 (s, 3H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 144.8, 144.3, 139.6, 139.5, 136.9, 136.8, 136.7, 136.6, 129.1, 128.9, 128.8, 128.5, 128.4, 128.0, 127.2, 111.4, 83.1, 82.9, 82.7, 81.4, 81.1, 45.3, 45.1, 27.9, 27.3, 25.6, 25.5, 21.4, 21.3, 21.2. $^{31}\text{P NMR}$ (75 MHz, CDCl_3) δ 138.7.

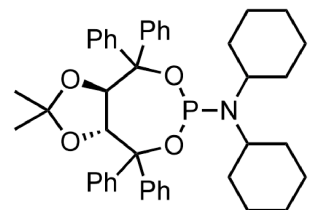
$R_f = 0.34$ (19:1 Hex:EtOAc). IR (NaCl, Thin Film) 3027, 2986, 2940, 2853, 2361, 1506, 1445, 1378, 1255, 1209, 1168, 1050, 1030, 958, 830, 738 cm^{-1} . HRMS (ESI) m/z calcd ($\text{C}_{40}\text{H}_{46}\text{NO}_4\text{P}$) $^+$ 635.3164, found 635.3174.



1-((3aR,8aR)-2,2-dimethyl-4,4,8,8-tetrakis(trifluoromethyl)phenyltetrahydro-[1,3]dioxolo[4,5-e][1,3,2]dioxaphosphepin-6-yl)piperidine (T7). General procedure yielded a white solid (51%).

$[\alpha]_D^{20} = -84.5^\circ$, $c = 0.01\text{g/ml}$ CH_2Cl_2 . $^1\text{H NMR}$ (300 MHz, CDCl_3) δ 7.88 (d, $J = 8.3$ Hz, 2H), 7.72 (d, $J = 8.3$ Hz, 2H), 7.66-7.49 (m, 13H), 5.08 (dd, $J = 8.6, 3.5$ Hz, 1H), 4.58 (d, $J = 8.6$ Hz, 1H), 3.25 (d, $J = 26.5, 6.6$ Hz, 4H), 1.71-1.57 (m, 6H), 1.37 (s, 3H), 0.31 (s, 3H). $^{13}\text{C NMR}$ (75 MHz, CDCl_3) δ 150.1, 149.3, 129.4, 129.1, 129.0, 127.6, 127.4, 126.0, 125.7, 125.6, 125.2, 124.5, 112.3, 82.5, 82.3, 82.0, 80.9, 45.4, 45.1, 27.7, 27.3, 27.2, 25.5, 25.2. $^{31}\text{P NMR}$ (75 MHz, CDCl_3) δ 138.6. $R_f = 0.44$ (19:1 Hex:EtOAc). IR (NaCl, Thin Film) 3581, 2991, 2935, 2848, 2366, 2330, 1782, 1716, 1619, 1450, 1409, 1368, 1322, 1158,

1117, 845, 728 cm^{-1} . HRMS (ESI) m/z calcd [$\text{C}_{40}\text{H}_{34}\text{F}_{12}\text{NO}_4\text{P}$] $^+$ 851.2034, found 851.2032.



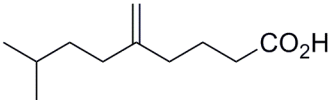
(3aR,8aR)-N,N-dicyclohexyl-2,2-dimethyl-4,4,8,8-tetraphenyltetrahydro-[1,3]dioxolo[4,5-e][1,3,2]dioxaphosphepin-6-amine (T4). General procedure yielded a white solid.

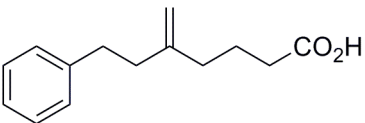
$[\alpha]_D^{20} = -60.6^\circ$, $c = 0.01\text{g/ml}$, CH_2Cl_2 . $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.80 (d, $J = 7.4$ Hz, 2H), 7.60 (d, $J = 7.6$ Hz, 2H), 7.42 (dd, $J = 7.7, 2.3$ Hz, 4H), 7.29-7.14 (m, 12H), 5.13 (dd, $J = 8.6, 3.3$ Hz, 1H), 4.60 (d, $J = 8.6$ Hz, 1H), 3.45 (s, 2H), 1.86-1.74 (m, 8H), 1.59-1.28 (m, 15H), 1.02 (d, $J = 13.1$ Hz, 2H) 0.20 (s, 3H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 147.7, 147.1, 143.0, 142.4, 129.2, 128.9, 128.8, 127.9, 127.7, 127.6, 127.5, 127.4, 127.1, 12

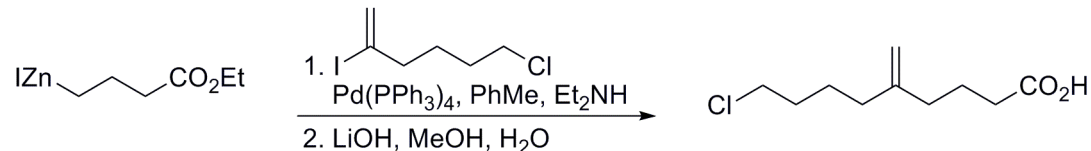
6.9, 111.2, 83.3, 83.0, 82.8, 54.0, 53.9, 35.5, 35.4, 35.2, 35.1, 27.9, 27.1, 27.0, 25.7, 25.2. $^{31}\text{P NMR}$ (75 MHz, CDCl_3) δ 141.2. $R_f = 0.30$ (19:1 Hex:EtOAc). IR (NaCl, Thin Film) 2991, 2919, 2843, 2356, 2331, 2249, 1783, 1711, 1440, 1327, 1168, 1025, 907. HRMS (ESI) m/e calcd ($\text{C}_{43}\text{H}_{50}\text{NO}_4\text{P}+\text{H}^+$) 675.3477, found 675.3472.

Synthesis of Isocyanate Precursors:

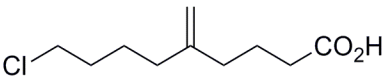
Acids **SM1** and **SM2** were synthesized as previously reported.²

 **8-Methyl-5-methylene-nonanoic acid (SM1).** General procedure yielded a clear liquid (56%). ¹H NMR (400 MHz, CDCl₃) δ 4.75 (s, 1H), 4.72 (s, 1H), 2.37 (t, *J* = 7.0 Hz, 2H), 2.04 (t, *J* = 7.0 Hz, 2H), 1.97 (t, *J* = 7.0 Hz, 2H), 1.75 (tt, *J* = 7.0, 7.0 Hz, 2H), 1.50 (sext, *J* = 7.0 Hz, 1H), 1.27 (td, *J* = 7.0, 7.0 Hz, 2H), 0.86 (d, *J* = 7.0 Hz, 6H). ¹³C NMR (100 MHz, CDCl₃) δ 180.7, 149.1, 109.6, 37.2, 35.4, 33.8, 33.7, 28.0, 22.8. *R*_f = 0.20 (Hex:EtOAc 3:1). IR (NaCl, Thin Film) 2962, 1709, 1413, 1248 cm⁻¹.

 **5-Methylene-7-phenyl-heptanoic acid (SM2).** General procedure yielded a clear liquid (60%). ¹H NMR (400 MHz, CDCl₃) δ 7.30-7.25 (m, 2H), 7.20-7.16 (m, 3H), 4.81 (s, 1H), 4.79 (s, 1H), 2.75 (t, *J* = 8.0 Hz, 2H), 2.36 (t, *J* = 7.5 Hz, 2H), 2.32 (t, *J* = 8.0 Hz, 2H), 2.11 (t, *J* = 7.5 Hz, 2H), 1.80 (tt, *J* = 8.0, 8.0 Hz, 2H). ¹³C NMR (100 MHz, CDCl₃) δ 180.5, 148.1, 142.3, 128.5, 126.1, 110.4, 37.8, 35.6, 34.5, 33.7, 22.7. *R*_f = 0.20 (Hex:EtOAc 3:1). IR (NaCl, Thin Film) 3027, 2937, 1708, 1454, 1291, 1243, 893 cm⁻¹.

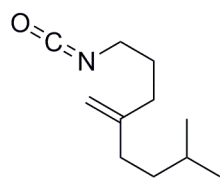


In a flame dried flask containing a suspension of zinc powder (204 mg, 3.12 mmol) in THF (0.5 mL) under Ar atmosphere, dibromoethane (23 mg, 0.12 mmol) was added. The solution was heated to 65 °C for 1 minute and cooled to room temperature. TMSCl (10 mg, 0.1 mmol) was then added, and the reaction stirred for 15 minutes. A solution of iodobutyrate (726 mg, 3.00 mmol) in THF (1.0 mL) was then added. The reaction was then stirred at 45 °C for 16 hours, cooled, and diluted with toluene/Et₂NH (10 mL/1 mL). The solution was then transferred by cannula into a flask containing palladium (116 mg, 0.1 mmol) and vinyl iodide (500 mg, 2.04 mmol). The reaction was stirred at 65 °C for 2 hours. The reaction was cooled to 23 °C, concentrated, loaded onto silica gel, and purified by flash chromatography (99:1 Hex:EtOAc). The resulting ester (0.2 M) was added to a stirring suspension of LiOH (5 eq) in MeOH:H₂O (3:1) and stirred at room temperature for 16 hours. The reaction was quenched with 1M HCl, extracted (Et₂O x 3), dried over MgSO₄, filtered, and concentrated in *vacuo*. The acid was then purified by silica gel flash chromatography (4:1 Hex:EtOAc).

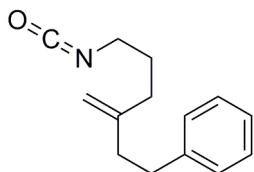
 **9-Chloro-5-methylene-nonanoic acid (SM3).** Preceding procedure yielded a clear liquid (85%). ¹H NMR (400 MHz, CDCl₃) δ 4.74 (s, 1H), 4.74 (s, 1H), 3.52 (t, *J* = 6.5 Hz, 2H), 2.34 (t, *J* = 7.0 Hz, 2H), 2.04 (t, *J* = 7.5 Hz, 2H), 2.01 (t, *J* = 7.5 Hz, 2H), 1.80-1.71 (m, 4H), 1.56 (tt, *J* = 7.5, 7.5 Hz, 2H). ¹³C NMR (100 MHz, CDCl₃) δ 179.6, 147.9, 110.4, 45.1, 35.2, 35.2, 33.5, 32.3, 25.0, 22.7. *R*_f = 0.25 (3:1 Hex:EtOAc). IR (NaCl, Thin Film) 2940, 1709, 1413, 1273 cm⁻¹.

General Procedure for Synthesis of Isocyanates:

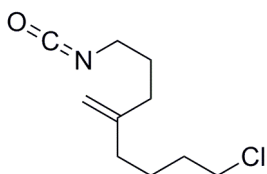
Isocyanates were synthesized as previously reported.²



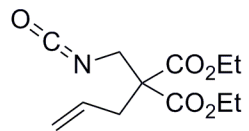
1-Isocyanato-7-methyl-4-methylene-octane (2h). General procedure yielded a clear liquid (79%). ¹H NMR (300 MHz, CDCl₃) δ 4.81 (s, 1H), 4.77 (s, 1H), 3.56 (t, *J* = 6.5 Hz, 2H), 2.16 (t, *J* = 7.5 Hz, 2H), 2.06 (t, *J* = 7.0 Hz, 2H), 1.79 (dt, *J* = 6.5, 6.5 Hz, 2H), 1.59 (sept, *J* = 6.5 Hz, 1H), 1.41-1.32 (m, 2H), 0.95 (d, *J* = 6.5 Hz, 6H). ¹³C NMR (100 MHz, CDCl₃) δ 148.5, 109.7, 42.6, 37.1, 33.9, 32.9, 29.3, 28.0, 22.7. IR (NaCl, Thin Film) 2955, 2870, 2276, 1645, 1468, 1367, 890 cm⁻¹.



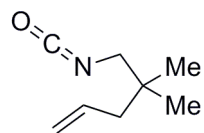
(6-Isocyanato-3-methylene-hexyl)-benzene (2i). General procedure yielded a clear liquid (56%). ¹H NMR (400 MHz, CDCl₃) δ 7.30-7.15 (m, 5H), 4.82 (s, 1H), 4.78 (s, 1H), 3.29 (t, *J* = 6.5 Hz, 2H), 2.74 (t, *J* = 7.5 Hz, 2H), 2.30 (t, *J* = 7.5 Hz, 2H), 2.13 (t, *J* = 7.0 Hz, 2H), 1.74 (tt, *J* = 7.0, 7.0 Hz, 2H). ¹³C NMR (100 MHz, CDCl₃) δ 147.6, 142.1, 128.6, 128.5, 126.1, 110.6, 42.6, 37.9, 34.5, 33.2, 29.3. IR (NaCl, Thin Film) 2941, 2277, 1645, 1496, 1454, 1355, 893 cm⁻¹.



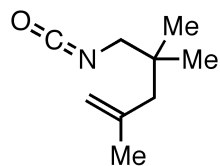
8-Chloro-1-isocyanato-4-methylene-octane (2n). General procedure yielded a clear liquid (75%). ¹H NMR (400 MHz, CDCl₃) δ 4.76 (s, 1H), 4.74 (s, 1H), 3.52 (t, *J* = 7.0 Hz, 2H), 3.29 (t, *J* = 8.0 Hz, 2H), 2.08 (t, *J* = 7.0 Hz, 2H), 2.01 (t, *J* = 7.5 Hz, 2H), 1.79-1.68 (m, 4H), 1.56 (tt, *J* = 8.0 Hz, 2H). ¹³C NMR (100 MHz, CDCl₃) δ 147.4, 110.6, 45.1, 42.7, 35.2, 32.8, 32.3, 29.3, 25.0. IR (NaCl, Thin Film) 3026, 2954, 2276, 1603, 1448, 1354, 963 cm⁻¹.



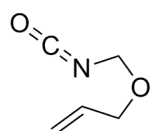
Diethyl 2-allyl-2-(isocyanomethyl)malonate (2p). General procedure yielded a clear liquid (86%). ¹H NMR (300 MHz, CDCl₃) δ 5.61 (ddt, *J* = 17.1, 9.6, 7.5 Hz, 1H), 5.20 (bd, *J* = 15.3 Hz, 1H), 5.17 (bd, *J* = 8.1 Hz, 1H), 4.25 (q, *J* = 7.2 Hz, 4H), 3.77 (s, 2H), 2.75 (d, *J* = 7.5 Hz, 2H), 1.28 (t, *J* = 7.2 Hz, 6H). ¹³C NMR (75 MHz, CDCl₃) δ 168.9, 131.3, 120.5, 62.0, 58.2, 44.8, 35.9, 14.4. IR (NaCl, Thin Film) 3083, 2976, 2930, 2259, 1737, 1440, 1368, 1224, 1091, 1004, 922 cm⁻¹.



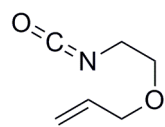
5-isocyanato-4,4-dimethylpent-1-ene (2q). General procedure yielded a clear liquid (42%). ¹H NMR (400 MHz, CDCl₃) δ 5.73 (ddt, *J* = 17.1, 10.0, 7.2 Hz, 1H), 5.06 (bd, *J* = 6.8 Hz, 1H), 5.03 (bd, *J* = 10.0 Hz, 1H), 3.05 (s, 2H), 1.99 (d, *J* = 7.6 Hz, 2H), 0.90 (s, 6H). ¹³C NMR (100 MHz, CDCl₃) δ 134.2, 118.3, 53.2, 43.8, 35.4, 24.8. IR (NaCl, Thin Film) 3078, 2950, 2930, 2264, 2131, 1711, 1629, 1469, 1342 cm⁻¹.



5-isocyanato-2,4,4-trimethylpent-1-ene (2r). General procedure yielded a colorless liquid (78%). ¹H NMR (300 MHz, CDCl₃) δ 4.90 (d, *J* = 1.0 Hz, 1H), 4.68 (d, *J* = 1.0 Hz, 1H), 3.12 (s, 2H), 2.00 (s, 2H), 1.78 (s, 3H), 0.95 (s, 6H). ¹³C NMR (75 MHz, CDCl₃) δ 142.5, 115.2, 53.5, 46.8, 36.0, 25.6, 25.4. IR (NaCl, Thin Film) 3068, 2960, 2929, 2868, 2269, 1634, 1465, 886 cm⁻¹.



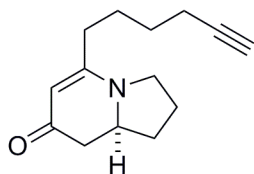
3-(isocyanatomethoxy)prop-1-ene (2s). General procedure yielded a clear liquid (36%). ¹H NMR (400 MHz, CDCl₃) δ 5.88 (ddt, *J* = 17.2, 11.6, 5.6 Hz, 1H), 5.32 (bd, *J* = 18.8 Hz, 1H), 5.24 (bd, *J* = 10.4 Hz, 1H), 4.79 (s, 2H), 4.10 (d, *J* = 8.4 Hz, 2H). ¹³C NMR (100 MHz, CDCl₃) δ 133.2, 118.8, 74.6, 70.1. IR (NaCl, Thin Film) 2863, 2254, 2136, 1731, 1183, 1055 cm⁻¹.



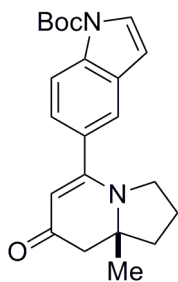
3-(2-isocyanatoethoxy)prop-1-ene (2t). General procedure yielded a clear liquid (48%). ¹H NMR (400 MHz, CDCl₃) δ 5.90 (ddt, *J* = 16.0, 10.4, 5.6 Hz, 1H), 5.28 (dd, *J* = 17.2, 1.6 Hz, 1H), 4.03 (bd, *J* = 5.6 Hz, 1H), 3.55 (t, *J* = 5.2 Hz, 2H), 3.39 (t, *J* = 5.2 Hz, 2H). ¹³C NMR (100 MHz, CDCl₃) δ 134.3, 117.7, 72.3, 69.3, 43.5. IR (NaCl, Thin Film) 2929, 2863, 2259, 2171, 1639, 1562, 1260, 1102 cm⁻¹.

General Procedure for Rhodium-Catalyzed [2+2+2] Cycloadditions:

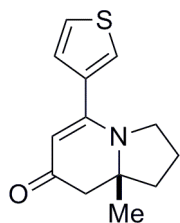
An oven-dried round bottom flask was charged with [Rh(C₂H₄)₂Cl]₂ (2.3 mg, 0.006 mmol) and ligand (0.012 mmol) and fitted with an oven-dried reflux condenser in an inert atmosphere (N₂) glove box. Upon removal from the glove box, 1 ml of toluene was added via syringe and the resulting yellow solution was stirred at ambient temperature for 15 min. To this solution, alkyne **1** (0.48 mmol) and isocyanate **2** (0.24 mmol) in 2 ml of toluene was added via syringe. An additional 4 ml of toluene was used to wash down the residue and added to the reaction mixture. The reaction mixture was heated to 110 °C in an oil bath and kept at reflux for 16 h. The reaction mixture was cooled to 23 °C, concentrated in *vacuo*, and purified by flash column chromatography (typically 20:1 EtOAc:MeOH). Evaporation of solvent afforded the analytically pure products. Absolute stereochemistry was established as previously reported.^{1,3}



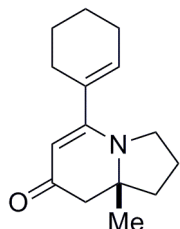
(S)-5-(hex-5-ynyl)-2,3,8,8a-tetrahydroindolizin-7(1H)-one (4y). General procedure yielded an amorphous brown solid (48%). [α]_D²⁰ = -412.7°, *c* = 0.01 g/ml CHCl₃. HPLC analysis - Chiralcel IA column, 90:10 Hex(0.5% HNEt₂):iPrOH, 1 ml/min, RT_{major} = 22.16 min, RT_{minor} = 25.88 min, 330 nm detection light, ee = 90% ee. ¹H NMR (400 MHz, CDCl₃) δ 4.93 (s, 1H), 3.72 (dddd, *J* = 5.2, 5.2, 10.4, 15.8 Hz, 1H), 3.58 (m, 1H), 3.44 (m, 1H), 2.39 (dd, *J* = 4.8, 15.9 Hz, 1H), 2.30 - 2.20 (m, 6H), 2.07 (m, 1H), 1.94 (m, 1H), 1.88 (m, 1H), 1.72 - 1.55 (m, 5H). ¹³C NMR (100 MHz, CDCl₃) δ 191.6, 163.9, 97.2, 83.7, 68.8, 59.1, 46.6, 41.2, 33.0, 32.4, 27.8, 26.0, 23.7, 18.0. R_f = 0.15 (20:1 EtOAc:MeOH). IR (NaCl, Thin Film) 2935, 2868, 1614, 1542, 1342, 1301, 1260, 1235 cm⁻¹. HRMS (ESI) *m/z* [C₁₄H₂₀NO]⁺ calcd 218.1539, found 218.1541.



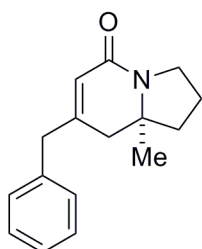
(S)-5-(8a-Methyl-7-oxo-1,2,3,7,8,8a-hexahydro-indolizin-5-yl)-indole-1-carboxylic acid tert-butyl ester (9h). General procedure yielded a clear syrup (85%). 91% ee by HPLC (Chiralcel ODH, Hex:iPrOH 85:15, 1 ml/min, RT_{major} = 12.0 min, RT_{minor} = 10.2 min). [α]_D²⁰ = +230.0°, *c* = 0.01 g/ml CHCl₃. ¹H NMR (400 MHz, CDCl₃) δ 8.12 (d, *J* = 8.0 Hz, 1H), 7.60 (d, *J* = 3.5 Hz, 1H), 7.56 (s, 1H), 7.28 (dd, *J* = 8.5, 1.5 Hz, 1H), 7.55 (d, *J* = 4.0 Hz, 1H), 5.11 (s, 1H), 3.57 (ddd, *J* = 10.5, 6.5, 6.5 Hz, 1H), 3.15 (ddd, *J* = 11.0, 7.0, 7.0 Hz, 1H), 2.68 (d, *J* = 16.0 Hz, 1H), 2.29 (d, *J* = 16.0 Hz, 1H), 2.02-1.88 (m, 4H), 1.63 (s, 9H), 1.40 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 191.9, 162.4, 149.7, 136.1, 131.4, 130.6, 127.2, 124.2, 120.9, 115.3, 107.6, 99.4, 84.4, 62.8, 50.5, 47.9, 39.9, 28.3, 24.1, 22.1. R_f = 0.26 (EtOAc). IR (NaCl, Thin Film) 2973, 2872, 1737, 1626, 1528, 1449, 1371, 1336, 1282, 1231, 1159, 1085, 768 cm⁻¹. MS (EI) *m/e* (rel intensity) 367 (100), 366 (49), 311 (80), 310 (22), 309 (13), 295 (22), 154 (15). HRMS (ESI) *m/z* [C₂₂H₂₇N₂O₃]⁺ calcd 367.2022, found 367.2013.



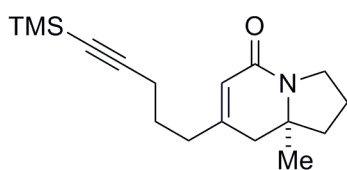
(S)-8a-Methyl-5-thiophen-3-yl-2,3,8,8a-tetrahydro-1H-indolizin-7-one (9i). General procedure yielded a clear syrup (78%). 83% *ee* by HPLC (Chiralcel ODH, Hex:*i*PrOH 85:15, 1 ml/min, RT_{major} = 16.3 min, RT_{minor} = 12.1 min). $[\alpha]_D^{20} = +280.0^\circ$, $c = 0.009$ g/ml CHCl₃. ¹H NMR (400 MHz, CDCl₃) δ 7.46 (d, $J = 3.0$ Hz, 1H), 7.32 (dd, $J = 5.0, 3.0$ Hz, 1H), 7.11 (d, $J = 5.0$ Hz, 1H), 5.15 (s, 1H), 3.61 (ddd, $J = 11.0, 6.0, 6.0$ Hz, 1H), 3.33 (ddd, $J = 11.0, 7.0, 3.5$ Hz, 1H), 2.64 (d, $J = 16.5$ Hz, 1H), 2.27 (d, $J = 16.5$ Hz, 1H), 2.00-1.82 (m, 4H), 1.36 (m, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 192.0, 156.1, 138.0, 127.4, 126.8, 126.4, 98.8, 62.9, 50.5, 47.8, 39.8, 24.2, 22.0. R_f = 0.20 (EtOAc). IR (NaCl, Thin Film) 2965, 1618, 1543, 1523, 1463, 1367, 1267 cm⁻¹. MS (EI) *m/e* (rel intensity) 234 (100), 233 (35), 218 (14), 154 (18), 138 (5), 137 (9). HRMS (ESI) *m/z* [C₁₃H₁₆NOS]⁺ calcd 234.0953, found 234.0962.



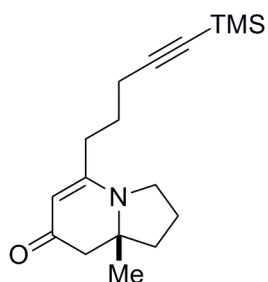
(S)-5-Cyclohex-1-enyl-8a-methyl-2,3,8,8a-tetrahydro-1H-indolizin-7-one (9p). General procedure yielded a clear syrup (84%). 91% *ee* by HPLC (Chiralcel ODH, Hex:*i*PrOH 85:15, 1 ml/min, RT_{major} = 6.8 min, RT_{minor} = 8.0 min). $[\alpha]_D^{20} = +340^\circ$, $c = 0.01$ g/ml CHCl₃. ¹H NMR (400 MHz, CDCl₃) δ 5.85 (s, 1H), 4.86 (s, 1H), 3.45 (ddd, $J = 11.0, 7.0, 7.0$ Hz, 1H), 3.32 (ddd, $J = 11.0, 6.5, 5.0$ Hz, 1H), 2.52 (d, $J = 16.5$ Hz, 1H), 2.17 (d, $J = 16.5$ Hz, 1H), 2.15-2.04 (m, 3H), 2.02-1.78 (m, 5H), 1.68-1.50 (m, 4H), 1.22 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 192.1, 164.1, 135.2, 130.4, 96.8, 62.5, 49.1, 47.7, 39.8, 27.3, 25.3, 23.9, 22.5, 21.9, 21.6. R_f = 0.30 (EtOAc). IR (NaCl, Thin Film) 2928, 2859, 1626, 1526, 1445, 1262, 1212 cm⁻¹. MS (EI) *m/e* (rel intensity) 232 (100), 231 (31), 230 (11), 216 (10), 154 (8), 136 (6). HRMS (ESI) *m/z* [C₁₅H₂₂NO]⁺ calcd 232.1701, found 232.1699.



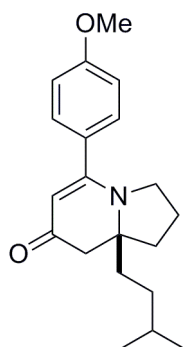
(R)-7-Benzyl-8a-methyl-2,3,8,8a-tetrahydro-1H-indolizin-5-one (8s). General procedure yielded an off white syrup (71%). 92% *ee* by HPLC (Chiralcel ODH, Hex:*i*PrOH 85:15, 1 ml/min, RT_{major} = 8.5 min, RT_{minor} = 11.0 min). $[\alpha]_D^{20} = +123.0^\circ$, $c = 0.007$ g/ml CHCl₃. ¹H NMR (400 MHz, CDCl₃) δ 7.28 (t, $J = 7.0$ Hz, 2H), 7.21 (t, $J = 7.0$ Hz, 1H), 7.13 (d, $J = 7.0$ Hz, 2H), 5.76 (t, $J = 1.0$ Hz, 1H), 3.57-3.45 (m, 2H), 3.47 (d, $J = 15.0$ Hz, 1H), 3.39 (d, $J = 15.0$ Hz, 1H), 2.27 (d, $J = 17.0$ Hz, 1H), 2.15 (d, $J = 17.0$ Hz, 1H), 1.93-1.86 (m, 3H), 1.75-1.66 (m, 1H), 1.03 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 163.4, 150.6, 137.1, 129.4, 128.8, 127.0, 120.9, 60.9, 43.7, 43.4, 41.0, 40.8, 23.6, 21.5. R_f = 0.48 (EtOAc). IR (NaCl, Thin Film) 2967, 2882, 1661, 1612, 1454, 1430 cm⁻¹. HRMS (ESI) *m/z* [C₁₆H₂₀NO]⁺ calcd 242.1539, found 242.1540.



(R)-8a-Methyl-7-(5-trimethylsilyl-pent-4-ynyl)-2,3,8,8a-tetrahydro-1H-indolizin-5-one (8ae). General procedure yielded a light yellow syrup (39%). 93% *ee* by HPLC (Chiralcel ADH, Hex:*i*PrOH 90:10, 1 ml/min, RT_{major} = 14.0 min, RT_{minor} = 11.5 min). $[\alpha]_D^{20} = +24.0^\circ$, $c = 0.01$ g/ml CHCl₃. ¹H NMR (400 MHz, CDCl₃) δ 5.70 (dd, $J = 1.5, 3.0$ Hz, 1H), 3.54-3.46 (m, 2H), 2.36 (dd, $J = 17.0, 3.0$ Hz, 1H), 2.25-2.18 (m, 5H), 2.00-1.89 (m, 3H), 1.79-1.60 (m, 3H), 1.13 (s, 3H), 0.11 (s, 9H). ¹³C NMR (100 MHz, CDCl₃) δ 163.4, 151.2, 119.9, 106.4, 85.6, 60.8, 43.7, 41.8, 40.9, 35.7, 25.8, 23.6, 21.5, 19.6, 0.3. R_f = 0.45 (EtOAc). IR (NaCl, Thin Film) 2962, 1663, 1614, 1428, 1249, 842 cm⁻¹. HRMS (ESI) *m/z* [C₁₇H₂₈NOSi]⁺ calcd 290.1935, found 290.1936.

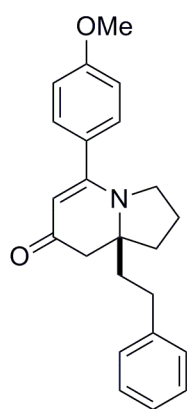


(S)-8a-Methyl-5-(5-trimethylsilyl-pent-4-ynyl)-2,3,8,8a-tetrahydro-1H-indolizin-7-one (9ae). From the same reaction above, a light yellow syrup was isolated (6%). 85% ee by HPLC (Chiralcel ADH, Hex:*i*PrOH 80:20, 1 ml/min, RT_{major} = 7.7 min, RT_{minor} = 8.6 min). $[\alpha]_D^{20} = +24.0^\circ$, $c = 0.01$ g/ml CHCl₃. ¹H NMR (400 MHz, CDCl₃) δ 4.92 (s, 1H), 3.61 (ddd, $J = 11.0, 5.0, 5.0$ Hz, 1H), 3.47 (ddd, $J = 11.0, 8.0, 8.0$ Hz, 1H), 2.49 (d, $J = 16.0$ Hz, 1H), 2.35-2.25 (m, 4H), 2.07-1.97 (m, 3H), 1.86-1.68 (m, 4H), 1.18 (s, 3H), 0.12 (s, 9H). ¹³C NMR (100 MHz, CDCl₃) δ 191.1, 162.3, 106.1, 96.2, 86.0, 63.2, 47.9, 46.6, 39.7, 32.7, 29.9, 26.4, 22.4, 20.0, 19.5, 0.3. $R_f = 0.25$ (EtOAc). IR (NaCl, Thin Film) 2959, 1626, 1536, 1485, 1249, 842 cm⁻¹. HRMS (ESI) m/z [C₁₇H₂₈NOSi]⁺ calcd 290.1935, found 290.1927.

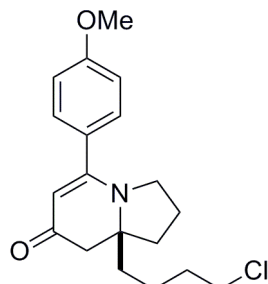


(S)-5-(4-Methoxy-phenyl)-8a-(3-methyl-butyl)-2,3,8,8a-tetrahydro-1H-indolizin-7-one (10h). General procedure yielded a light yellow solid (83%). 91% ee by HPLC (Chiralcel ODH, Hex:*i*PrOH 80:20, 1 ml/min, RT_{major} = 6.0 min, RT_{minor} = 8.4 min). $[\alpha]_D^{20} = +251.0^\circ$, $c = 0.007$ g/ml CHCl₃. ¹H NMR (400 MHz, CDCl₃) δ 7.34 (d, $J = 8.5$ Hz, 2H), 6.88 (d, $J = 8.5$ Hz, 2H), 5.09 (s, 1H), 3.81 (s, 3H), 3.49 (ddd, $J = 11.0, 7.5, 7.5$ Hz, 1H), 3.24 (ddd, $J = 11.0, 5.0, 5.0$ Hz, 1H), 2.62 (d, $J = 16.0$ Hz, 1H), 2.31 (d, $J = 16.0$ Hz, 1H), 2.10-2.02 (ddd, $J = 12.5, 8.0, 8.0$ Hz, 1H), 1.90-1.83 (m, 2H), 1.81-1.74 (m, 3H), 1.48 (sept, $J = 6.5$ Hz, 1H), 1.33-1.27 (m, 1H), 1.16-1.09 (m, 1H), 0.85 (d, $J = 7.0$ Hz, 6H). ¹³C NMR (100 MHz, CDCl₃) δ 192.1, 162.0, 161.4, 130.0, 129.4, 114.1, 99.2, 65.6, 55.6, 52.3, 45.8, 36.7, 33.4, 32.1, 28.6, 25.0, 22.8, 22.8. $R_f = 0.22$ (EtOAc). IR (NaCl, Thin Film) 2944, 1606, 1577, 1508, 1455, 1244, 1175, 1028 cm⁻¹.

HRMS (ESI) m/z [C₂₀H₂₈NO₂]⁺ calcd 314.2115, found 314.2114.

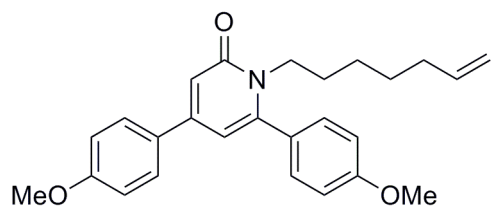


(S)-5-(4-Methoxy-phenyl)-8a-phenethyl-2,3,8,8a-tetrahydro-1H-indolizin-7-one (10i). General procedure yielded a light yellow solid (80%). 89% ee by HPLC (Chiralcel ODH, Hex:*i*PrOH 85:15, 1 ml/min, RT_{major} = 17.0 min, RT_{minor} = 22.9 min). $[\alpha]_D^{20} = +215.0^\circ$, $c = 0.009$ g/ml CHCl₃. ¹H NMR (400 MHz, CDCl₃) δ 7.31 (d, $J = 8.5$ Hz, 2H), 7.25-7.20 (m, 2H), 7.18-7.14 (m, 3H), 6.87 (d, $J = 9.0$ Hz, 2H), 5.13 (s, 1H), 3.80 (s, 2H), 3.53 (ddd, $J = 11.0, 7.5, 7.5$ Hz, 1H), 3.27 (ddd, $J = 11.0, 6.0, 5.5$ Hz, 1H), 2.74 (ddd, $J = 12.0, 12.0, 6.0$ Hz, 1H), 2.70 (d, $J = 16.0$ Hz, 1H), 2.60 (ddd, $J = 12.0, 12.0, 6.0$ Hz, 1H), 2.40 (d, $J = 16.0$ Hz, 1H), 2.22-2.05 (m, 3H), 1.87-1.84 (m, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 191.9, 162.0, 161.5, 141.7, 129.9, 129.2, 128.7, 128.5, 126.2, 114.1, 99.5, 65.4, 55.6, 52.2, 45.7, 36.9, 36.7, 31.0, 25.0. $R_f = 0.29$ (EtOAc). IR (NaCl, Thin Film) 2947, 1626, 1605, 1508, 1454, 1244, 1174, 1028 cm⁻¹. HRMS (FAB) [C₂₃H₂₆NO₂]⁺ calcd 348.1953, found 348.1943.

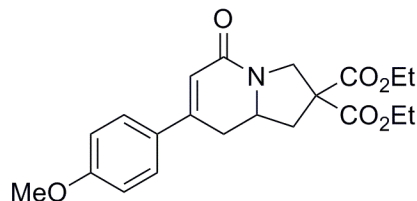


(S)-8a-(4-Chloro-butyl)-5-(4-methoxy-phenyl)-2,3,8,8a-tetrahydro-1H-indolizin-7-one (10n). General procedure yielded a light yellow solid (74%). 91% ee by HPLC (Chiralcel ODH, Hex:*i*PrOH 85:15, 1 ml/min, RT_{major} = 10.1 min, RT_{minor} = 14.0 min). $[\alpha]_D^{20} = +248.0^\circ$, $c = 0.008$ g/ml CHCl₃. ¹H NMR (400 MHz, CDCl₃) δ 7.33 (d, $J = 8.5$ Hz, 2H), 6.87 (d, $J = 8.5$ Hz, 2H), 5.08 (s, 1H), 3.80 (s, 3H), 3.55-3.46 (m, 3H), 3.24 (ddd, $J = 10.8, 5.5, 5.5$ Hz, 1H), 2.64 (d, $J = 16.5$ Hz, 1H), 2.29 (d, $J = 16.5$ Hz, 1H), 2.12-2.05 (m, 1H), 1.91-1.70 (m, 7H), 1.57-1.43 (m, 2H). ¹³C NMR (100 MHz, CDCl₃) δ 191.9, 162.1, 161.5, 129.9, 129.2, 114.1, 99.3, 65.3, 55.6, 52.3, 45.8, 45.0, 36.7, 33.6, 32.8, 25.0, 21.7. $R_f = 0.25$ (EtOAc). HRMS (ESI) m/z [C₁₉H₂₅ClNO₂]⁺ calcd 334.1568,

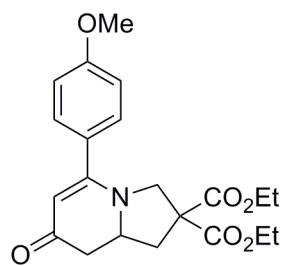
found 334.1565.



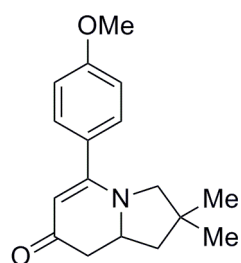
1-(hept-6-enyl)-4,6-bis(4-methoxyphenyl)-2-pyridone (7). General procedure yielded amorphous solid (62%). ^1H NMR (400 MHz, CDCl_3) δ 7.52 (d, $J = 9.2$ Hz, 2H), 7.28 (d, $J = 8.8$ Hz, 2H), 6.97 – 6.91 (m, 4H), 6.73 (d, $J = 2.0$ Hz, 1H), 6.28 (d, $J = 2.0$ Hz, 1H), 5.69 (dddd, $J = 16.8, 10.5, 6.6, 6.6$ Hz, 1H), 4.92 – 4.85 (m, 2H), 3.87 (t, $J = 8.0$ Hz, 2H), 3.85 (s, 3H), 3.81 (s, 3H), 1.90 (q, $J = 7.2$ Hz, 2H), 1.56 (m, 2H), 1.23 – 1.11 (m, 4H). ^{13}C NMR (100 MHz, CDCl_3) δ 163.8, 160.9, 160.3, 149.8, 149.5, 139.0, 130.2, 130.0, 128.4, 128.2, 114.5, 114.1, 107.8, 55.6, 45.6, 33.6, 28.7, 28.4, 26.4. $R_f = 0.54$ (EtOAc). IR (NaCl, CDCl_3) 1652, 1609, 1586, 1508, 1463, 1251, 1179, 1030 cm^{-1} . HRMS (ESI) m/z [$\text{C}_{26}\text{H}_{29}\text{NO}_3$] $^+$ calcd 403.21474, found 403.21447.



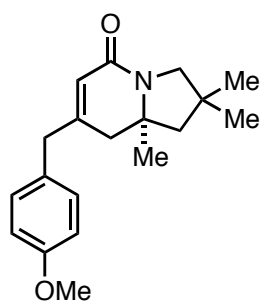
Diethyl 7-(4-methoxyphenyl)-5-oxo-8,8a-dihydroindolizine-2,2-dicarboxylate (11p). General procedure yielded a brown oil (35%). 74% ee by HPLC (Chiralcel OJH, Hex:*i*PrOH 80:20, 1 ml/min, $\text{RT}_{\text{major}} = 20.6$ min, $\text{RT}_{\text{minor}} = 24.8$ min). ^1H NMR (400 MHz, CDCl_3) δ 7.42 (d, $J = 8.8$ Hz, 2H), 6.90 (d, $J = 8.8$ Hz, 2H), 6.21 (d, $J = 2.4$ Hz, 1H), 4.23 (q, $J = 7.2$ Hz, 4H), 4.19 (d, $J = 12.8$ Hz, 1H), 4.11 (d, $J = 12.8$ Hz, 1H), 3.99 (dddd, $J = 19.2, 10.4, 4.8, 4.8$ Hz, 1H), 3.82 (s, 3H), 2.93 (dd, $J = 16.4, 4.4$ Hz, 1H), 2.83 (dd, $J = 12.8, 5.6$ Hz, 1H), 2.54 (ddd, $J = 16.4, 14.0, 2.8$ Hz, 1H), 2.27 (dd, $J = 12.8, 10.8$ Hz, 1H), 1.26 (t, $J = 7.2$ Hz, 6H). ^{13}C NMR (100 MHz, CDCl_3) δ 170.4, 169.7, 164.2, 161.0, 148.6, 129.9, 127.5, 118.4, 114.4, 62.5, 57.6, 55.6, 55.5, 50.5, 40.5, 32.9, 14.2. $R_f = 0.50$ (EtOAc). IR (NaCl, CH_2Cl_2) 2980, 2945, 2893, 1726, 1650, 1603, 1562, 1516, 1450, 1250, 1178, 1096, 1024 cm^{-1} . HRMS (ESI) m/z [$\text{C}_{21}\text{H}_{26}\text{NO}_6$] $^+$ calcd 388.1755, found 388.1737.



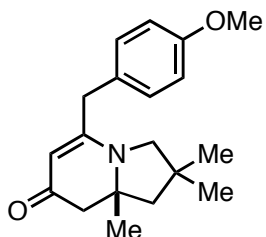
Diethyl 5-(4-methoxyphenyl)-7-oxo-8,8a-dihydroindolizine-2,2-dicarboxylate (12p). From the same reaction above, a brown oil was isolated (35%). 91% ee by HPLC (Chiralcel ADH, Hex:*i*PrOH 80:20, 1 ml/min, $\text{RT}_{\text{major}} = 8.7$ min, $\text{RT}_{\text{minor}} = 12.1$ min). $[\alpha]_{\text{D}}^{20} = +399.5^\circ$, $c = 0.018$ g/ml CHCl_3 . ^1H NMR (400 MHz, CDCl_3) δ 7.37 (d, $J = 8.8$ Hz, 2H), 6.93 (d, $J = 8.8$ Hz, 2H), 5.12 (s, 1H), 4.26 (q, $J = 7.2$ Hz, 4H), 4.23-4.09 (m, 2H), 3.84 (s, 1H), 3.67 (d, $J = 11.6$ Hz, 1H), 2.93 (dd, $J = 13.2, 6.8$ Hz, 1H), 2.55-2.42 (m, 3H), 2.35 (dd, $J = 13.2, 8.8$ Hz, 1H), 1.29 (t, $J = 7.2$ Hz, 3H), 1.23 (t, $J = 7.2$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 191.9, 169.7, 169.2, 162.2, 161.3, 129.6, 127.9, 114.2, 101.4, 62.6, 62.5, 58.8, 57.5, 55.6, 54.2, 41.6, 38.9, 14.2. $R_f = 0.17$ (EtOAc). IR (NaCl, CH_2Cl_2) 2975, 2945, 2924, 2899, 2858, 1731, 1623, 1506, 1465, 1265, 1173, 1096, 1019 cm^{-1} . HRMS (ESI) m/z [$\text{C}_{21}\text{H}_{26}\text{NO}_6$] $^+$ calcd 388.1755, found 388.1737.



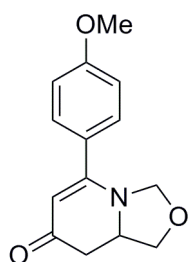
5-(4-methoxyphenyl)-2,2-dimethyl-2,3,8,8-tetrahydroindolizin-7(1H)-one (12q). General procedure yielded a brown oil (72%). 83% ee by HPLC (Chiralcel ADH, Hex:*i*PrOH 80:20, 1 ml/min, $\text{RT}_{\text{major}} = 7.8$ min, $\text{RT}_{\text{minor}} = 9.2$ min). $[\alpha]_{\text{D}}^{20} = +490.9^\circ$, $c = 0.018$ g/ml CHCl_3 . ^1H NMR (400 MHz, CDCl_3) δ 7.30 (d, $J = 8.8$ Hz, 2H), 6.92 (d, $J = 8.4$ Hz, 2H), 5.07 (s, 1H), 4.20 (m, 1H), 3.83 (s, 3H), 3.35 (d, $J = 10.8$ Hz, 1H), 3.02 (d, $J = 10.8$ Hz, 1H), 2.48 (dd, $J = 16.0, 16.0$ Hz, 1H), 2.41 (dd, $J = 16.0, 5.2$ Hz, 1H), 2.07 (dd, $J = 12.4, 6.8$ Hz, 1H), 1.61 (dd, $J = 12.4, 9.2$ Hz, 1H), 1.15 (s, 3H), 1.12 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 192.3, 162.9, 161.0, 129.5, 128.5, 114.1, 100.2, 61.6, 58.0, 55.6, 46.2, 42.1, 37.9, 26.9. $R_f = 0.17$ (EtOAc). IR (NaCl, CH_2Cl_2) 2955, 2868, 1603, 1506, 1465, 1296, 1260, 1173, 1019 cm^{-1} . HRMS (ESI) m/z [$\text{C}_{17}\text{H}_{22}\text{NO}_2$] $^+$ calcd 272.1645, found 272.1641.



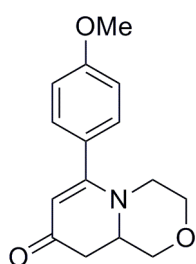
(R)-7-(4-methoxybenzyl)-2,2,8a-trimethyl-2,3,8,8a-tetrahydro-1H-indolizin-5-one (11r). General procedure yielded a clear syrup (21%). 52% ee by HPLC (Chiralcel ADH, Hex:*i*PrOH 90:10, 1 mL/min, RT_{major} = 17.6 min, RT_{minor} = 14.5 min). ¹H NMR (300 MHz, CDCl₃) δ 7.07 (d, *J* = 8.4 Hz, 2H), 6.85 (d, *J* = 8.4 Hz, 2H), 5.75 (d, *J* = 1.5 Hz, 1H), 3.79 (s, 3H), 3.71 (d, *J* = 12.1, 1H), 3.45-3.31 (ABq, 2H), 3.01 (d, *J* = 12.1 Hz, 1H), 2.37 (d, *J* = 17.0 Hz, 1H), 2.06 (d, *J* = 17.0 Hz, 1H), 1.73 (s, 2H), 1.14 (s, 3H), 1.12 (s, 3H), 1.07 (s, 3H).



(S)-5-(4-methoxybenzyl)-2,2,8a-trimethyl-2,3,8,8a-tetrahydro-1H-indolizin-7-one (12r). General procedure yielded an off white solid (44%). 94% ee by HPLC (Chiralcel ADH, Hex:*i*PrOH 90:10, 1 mL/min, RT_{major} = 17.7 min, RT_{minor} = 19.7 min). [α]_D²⁰ = 111.7°, *c* = 0.010 g/mL CHCl₃. ¹H NMR (300 MHz, CDCl₃) δ 7.10 (d, *J* = 8.8 Hz, 2H), 6.84 (d, *J* = 8.8 Hz, 2H), 4.97 (s, 1H), 3.79 (s, 3H), 3.53-3.42 (ABq, 2H), 3.19 (d, *J* = 11.0 Hz, 1H), 2.92 (d, *J* = 11.0 Hz, 1H), 2.66 (d, *J* = 16.1 Hz, 1H), 2.25 (d, *J* = 16.1 Hz, 1H), 1.74 (s, 2H), 1.24 (s, 3H), 1.07 (s, 3H), 1.05 (s, 3H). ¹³C NMR (75 MHz, CDCl₃) δ 191.8, 160.7, 158.7, 129.7, 127.9, 114.4, 98.3, 64.2, 59.5, 55.5, 53.5, 48.9, 40.2, 38.8, 29.3, 27.8, 21.8. IR (NaCl, Thin Film) 2955, 2868, 2832, 1623, 1547, 1506, 1465, 1244, 1178 cm⁻¹. MS (EI) *m/e* (rel intensity) 300 (100), 187 (75). HRMS (ESI) *m/z* [C₁₉H₂₆NO₂]⁺ calcd 300.1958, found 300.1960.



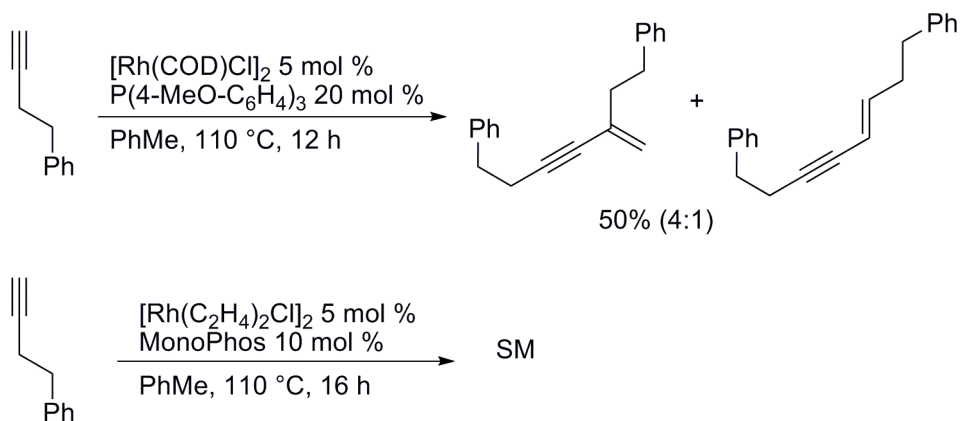
5-(4-methoxyphenyl)-8,8a-dihydro-1H-oxazolo[3,4-a]pyridine-7(3H)-one (13s). General procedure yielded a brown oil (37%). 92% ee by HPLC (Chiralcel ADH, Hex:*i*PrOH 80:20, 1 ml/min, RT_{major} = 11.4 min, RT_{minor} = 13.0 min). [α]_D²⁰ = +292.6°, *c* = 0.008 g/ml CHCl₃. ¹H NMR (400 MHz, CDCl₃) δ 7.39 (d, *J* = 7.8 Hz, 2H), 6.93 (d, *J* = 8.4 Hz, 2H), 5.23 (s, 1H), 4.95 (d, *J* = 3.3 Hz, 1H), 4.70 (d, *J* = 3.6 Hz, 1H), 4.33-4.23 (m, 2H), 3.85 (s, 3H), 3.91-3.80 (m, 1H), 2.66 (dd, *J* = 15.6, 15.6 Hz, 1H), 2.44 (dd, *J* = 16.2, 4.5 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 191.5, 162.0, 161.0, 129.6, 127.8, 114.4, 100.6, 81.8, 72.2, 55.9, 55.6, 38.9. R_f = 0.15 (EtOAc). IR (NaCl, CH₂Cl₂) 2955, 2873, 1634, 1608, 1578, 1501, 1460, 1378, 1301, 1255, 1168, 1106, 1014 cm⁻¹. HRMS (ESI) *m/z* [C₁₄H₁₆NO₃]⁺ calcd 246.1125, found 246.1113.



6-(4-methoxyphenyl)-3,4,9,9a-tetrahydropyrido[2,1-c][1,4]oxazin-8(1H)-one (13t). General procedure yielded a brown oil (41%). 96% ee by HPLC (Chiralcel ADH, Hex:*i*PrOH 80:20, 1 ml/min, RT_{major} = 9.32 min, RT_{minor} = 11.30 min). [α]_D²⁰ = -28.1°, *c* = 0.013 g/ml CHCl₃. ¹H NMR (400 MHz, CDCl₃) δ 7.21 (d, *J* = 8.8 Hz, 2H), 6.92 (d, *J* = 8.8 Hz, 2H), 5.15 (s, 1H), 3.94 (dd, *J* = 11.2, 3.2 Hz, 1H), 3.85 (m, 1H), 3.83 (s, 3H), 3.64-3.49 (m, 3H), 3.40 (ddd, *J* = 12.8, 2.0, 2.0 Hz, 1H), 2.79 (ddd, *J* = 12.0, 12.0, 3.2 Hz, 1H), 2.37 (d, *J* = 10.4 Hz, 2H). ¹³C NMR (100 MHz, CDCl₃) δ 190.8, 165.9, 160.6, 128.9, 127.8, 114.3, 104.8, 70.9, 67.0, 56.9, 55.6, 48.5, 37.7. R_f = 0.20 (EtOAc). IR (NaCl, CH₂Cl₂) 2965, 2832, 1639, 1603, 1552, 1511, 1429, 1240, 1122 cm⁻¹. HRMS (ESI) *m/z* [C₁₅H₁₈NO₃]⁺ calcd 260.1281, found 260.1276.

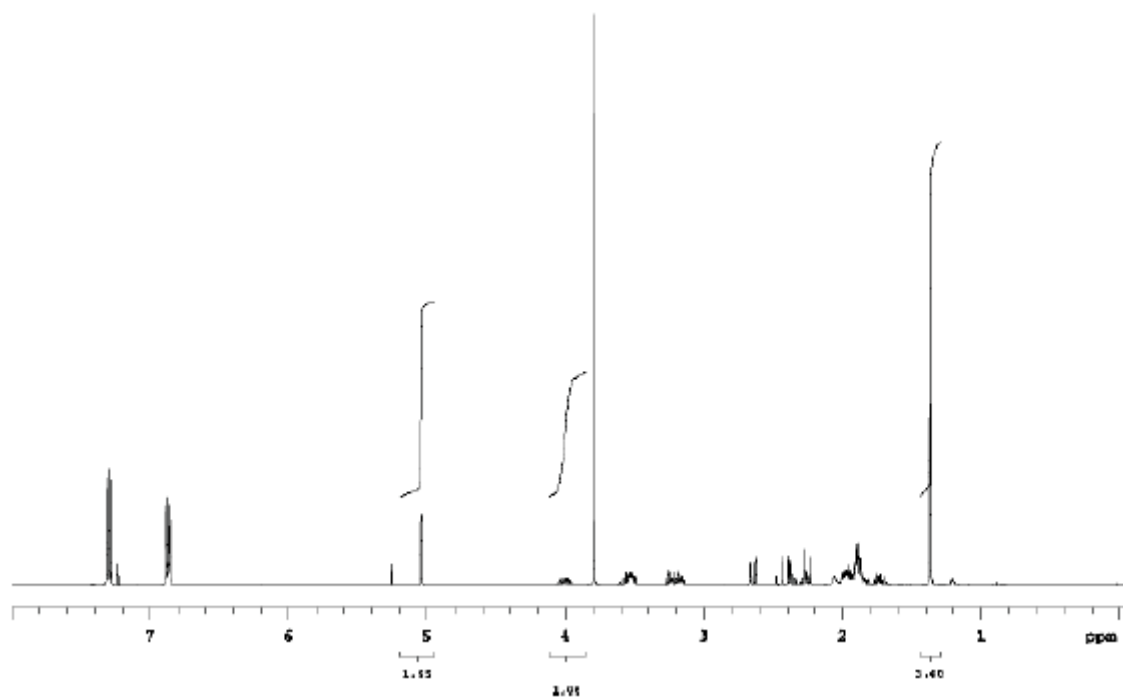
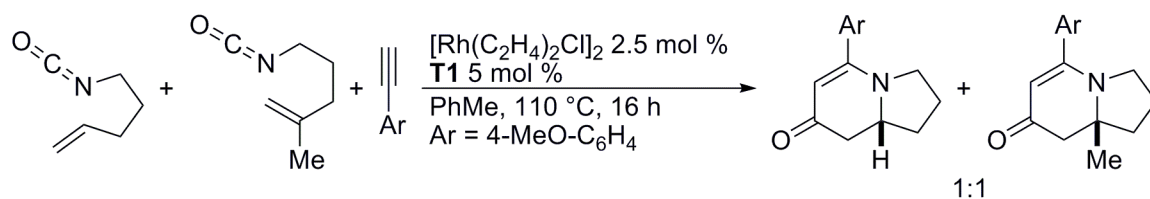
Dimerization of Terminal Alkynes:

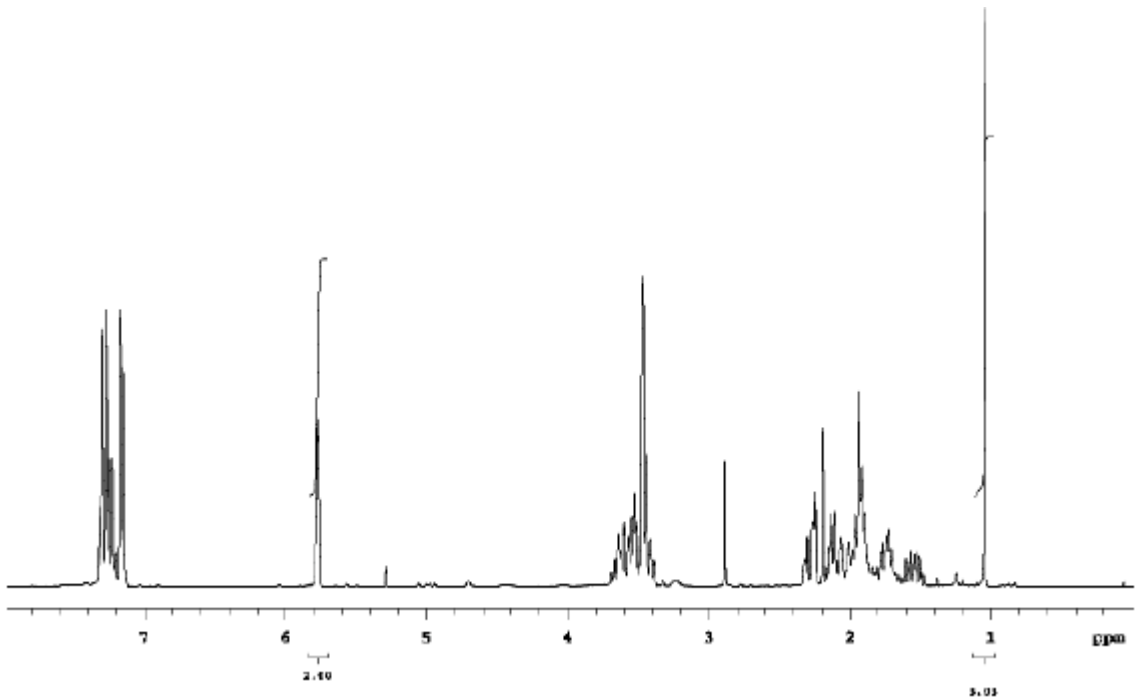
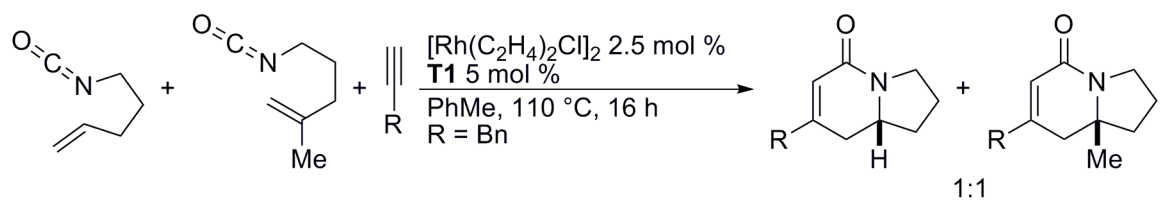
An oven-dried round bottom flask was charged with $[\text{Rh}(\text{cod})\text{Cl}]_2$ or $[\text{Rh}(\text{C}_2\text{H}_4)_2\text{Cl}]_2$ (0.012 mmol) and ligand (0.048 mmol $\text{P}(4\text{-MeO-C}_6\text{H}_4)_3$ or 0.024 mmol MonoPhos) and fitted with an oven-dried reflux condenser in an inert atmosphere (N_2) glove box. Upon removal from the glove box, 1 ml of toluene was added via syringe and the resulting yellow solution was stirred at ambient temperature for 15 min. To this solution, alkyne **1** (0.48 mmol) in 2 ml of toluene was added via syringe. An additional 4 ml of toluene was used to wash down the residue and added to the reaction mixture. The reaction mixture was heated to $110\text{ }^\circ\text{C}$ in an oil bath and kept at reflux for 12 or 16 h. The reaction mixture was cooled to $23\text{ }^\circ\text{C}$, concentrated in *vacuo*, and purified by flash column chromatography. Evaporation of solvent afforded the mixture of products.



Competition Experiments of Alkenyl Isocyanates:

An oven-dried round bottom flask was charged with $[\text{Rh}(\text{C}_2\text{H}_4)_2\text{Cl}]_2$ (2.3 mg, 0.006 mmol) and ligand (0.012 mmol) and fitted with an oven-dried reflux condenser in an inert atmosphere (N_2) glove box. Upon removal from the glove box, 1 ml of toluene was added via syringe and the resulting yellow solution was stirred at ambient temperature for 15 min. To this solution, alkyne **1** (0.24 mmol) and isocyanate **2a** and **2b** (0.24 mmol, 0.24 mmol) in 2 ml of toluene was added via syringe. An additional 4 ml of toluene was used to wash down the residue and added to the reaction mixture. The reaction mixture was heated to 110 °C in an oil bath and kept at reflux for 16 h. The reaction mixture was cooled to 23 °C, concentrated in *vacuo*, and NMR's were taken of crude reaction and can be seen below.





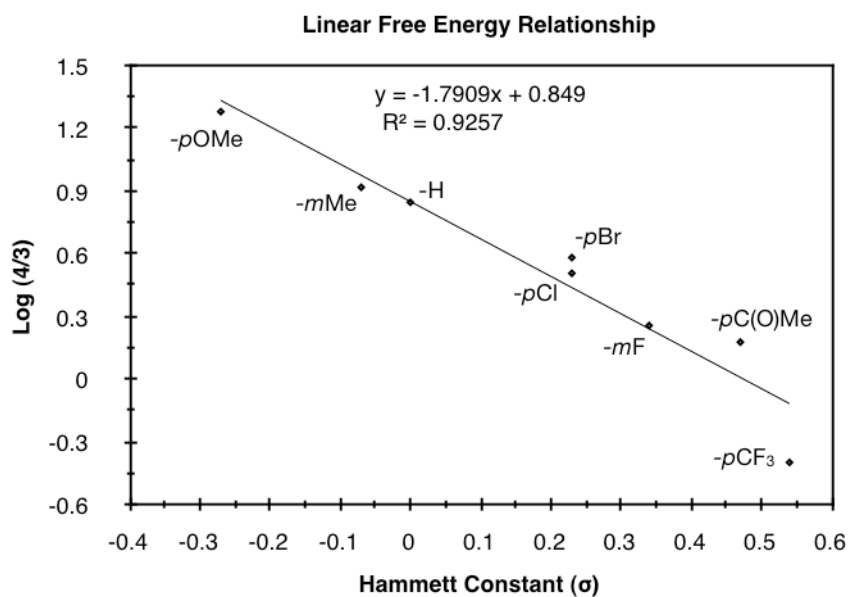
Synthesis of Rhodium(cod)chloride/phosphoramidite Complexes:

A 10 ml vial was charged with $[\text{Rh}(\text{cod})\text{Cl}]_2$ (28 mg, 0.057 mmol) and ligand (0.114 mmol) in an inert atmosphere (N_2) glove box. Upon removal from the glove box, 1 ml of CH_2Cl_2 was added via syringe and the resulting yellow solution was layered with heptanes (~2 ml). The cap was loosely sealed and the solvent was allowed to evaporated slowly, yielding X-ray quality crystals.

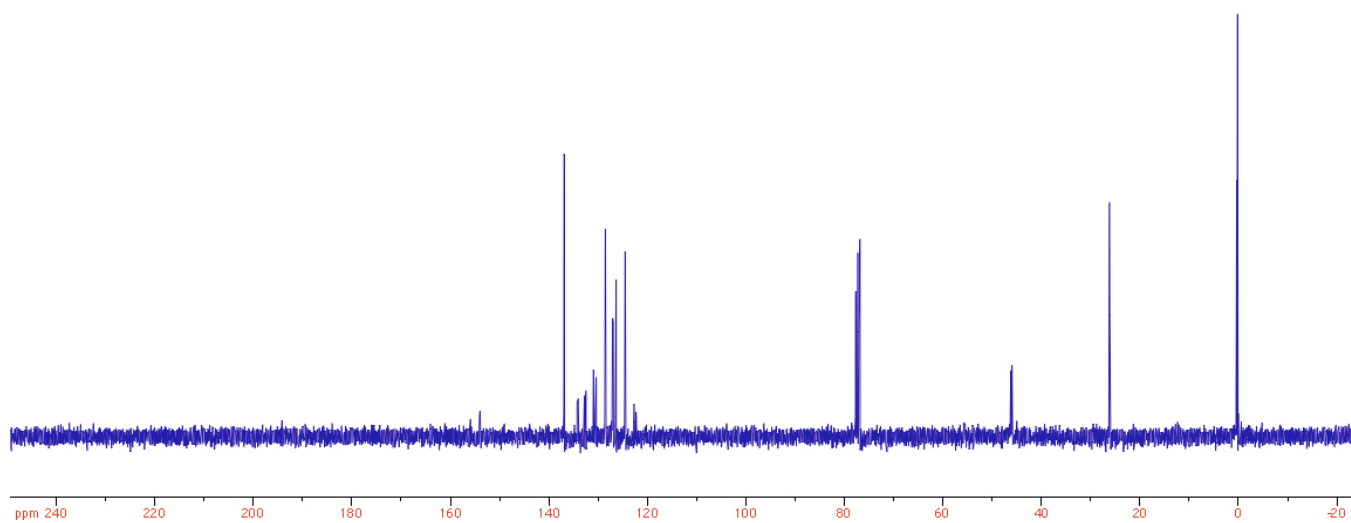
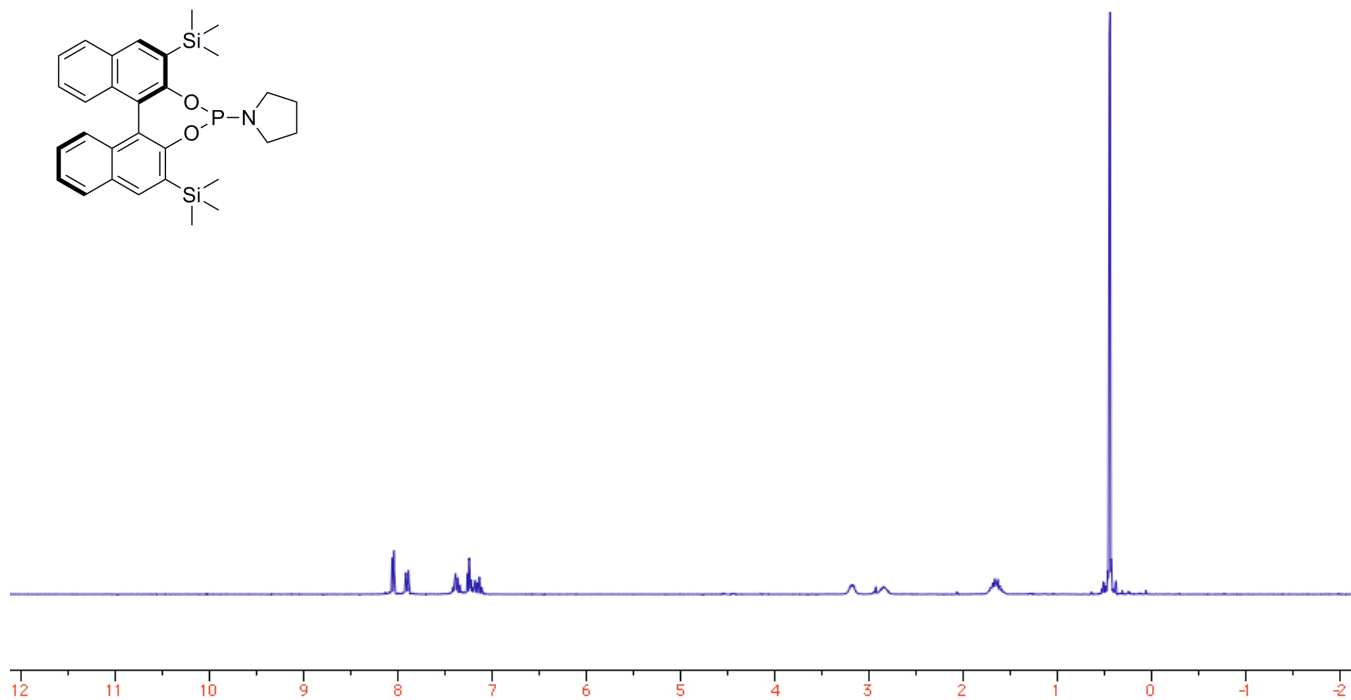
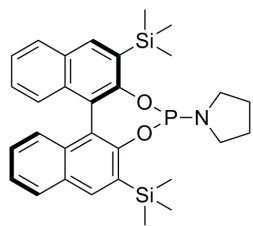
Linear Free Energy Relationship

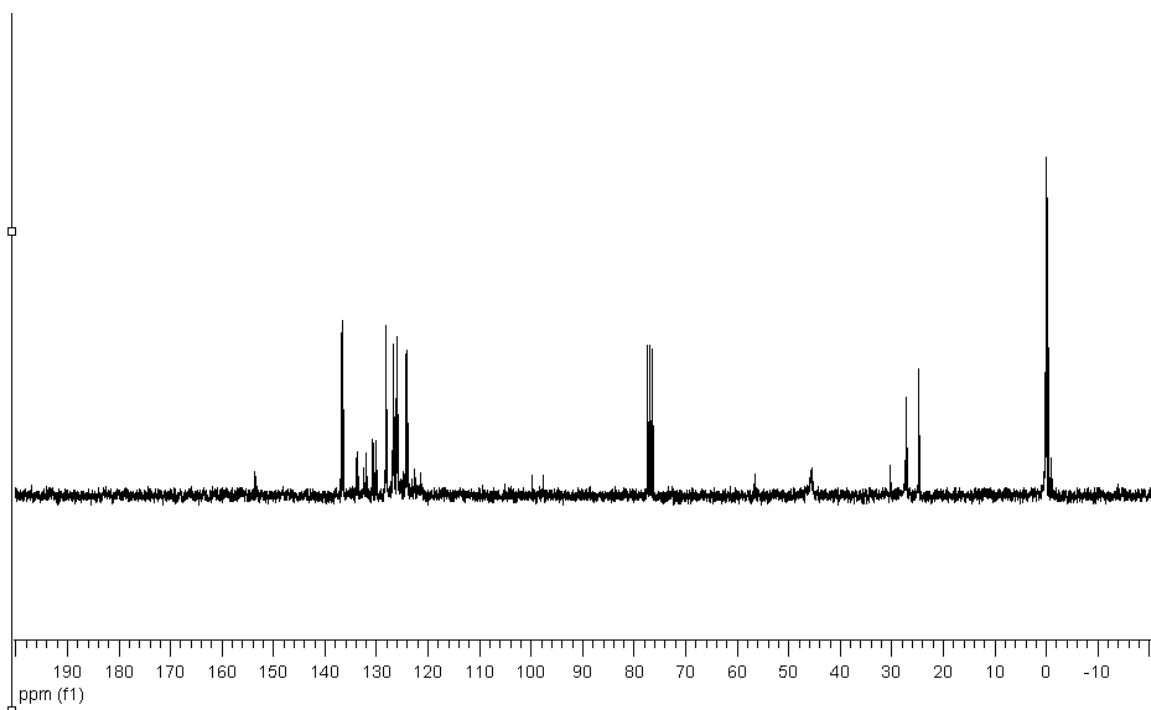
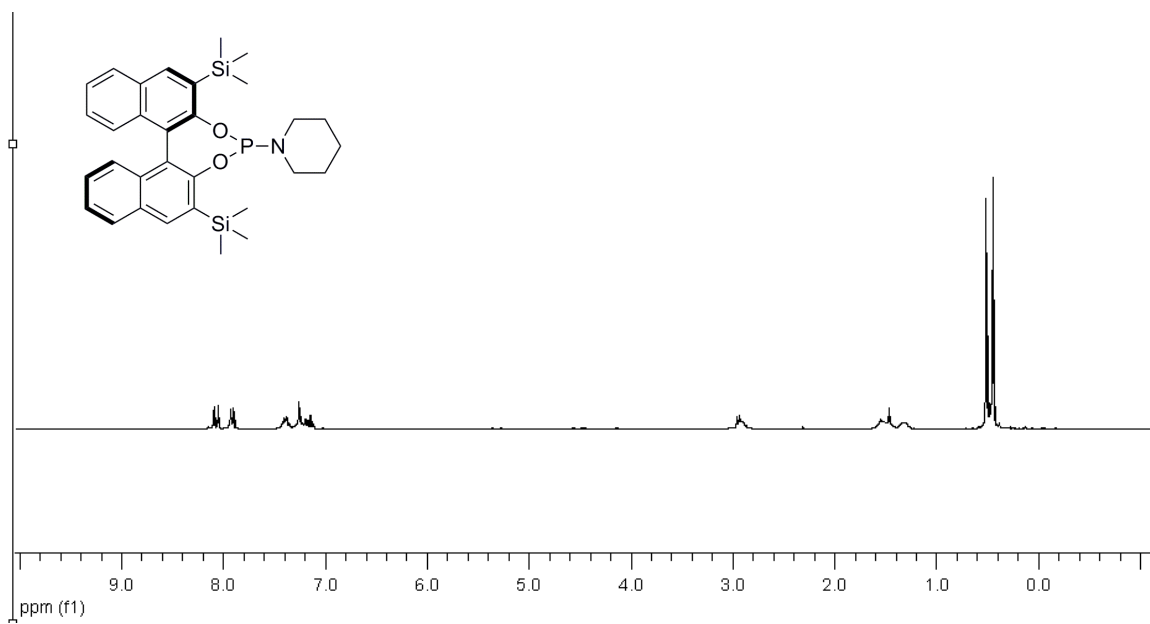
A plot of the Hammett values was made against the log of the ratio of **4/3** using Numbers software. *p*-dimethylaminophenylacetylene was not included in the plot because the sensitivity of the NMR restricted the detection of ratios as it was >20:1.

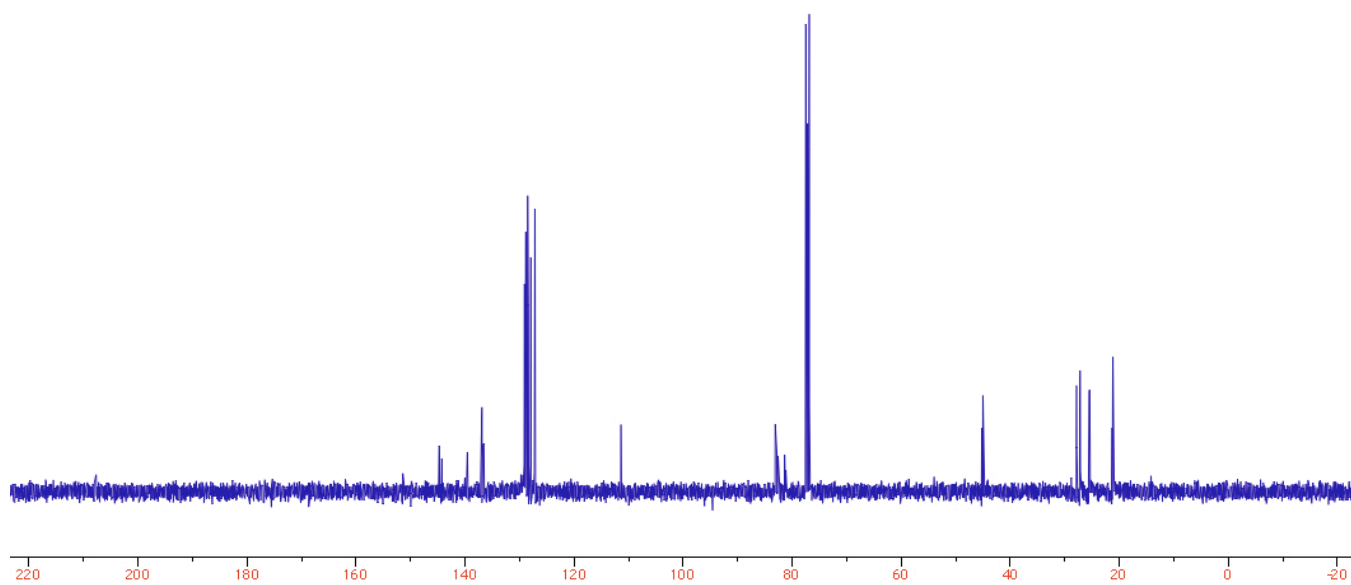
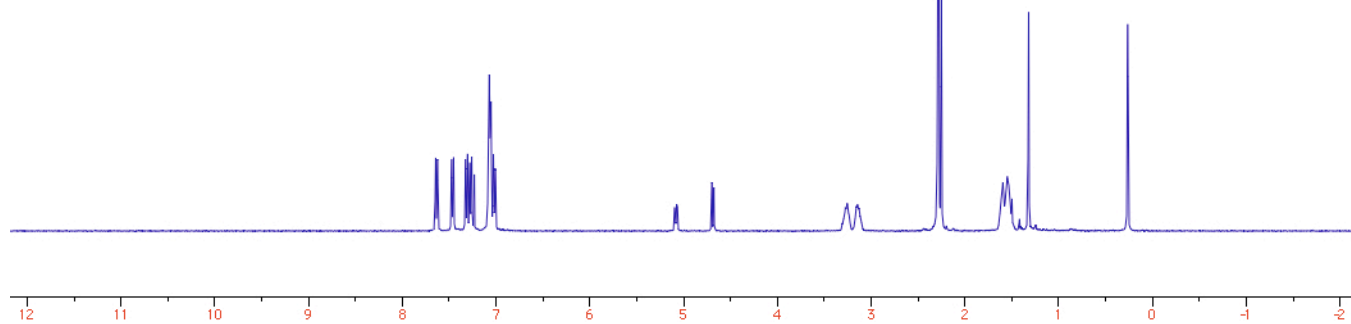
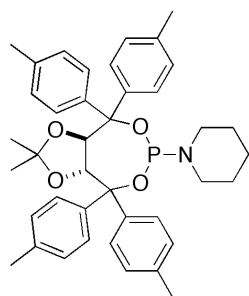
	Hammett Value	Log (4/3)	3	4
-pNMe2	-0.83	1.27875360095283	5	95
-pOMe	-0.27	1.27875360095283	5	95
-mMe	-0.07	0.916941098889173	10.8	89.2
-H	0.00	0.845098040014257	12.5	87.5
-pCl	0.23	0.580661846626732	20.8	79.2
-pBr	0.23	0.505378014283088	23.8	76.2
-mF	0.34	0.255542756812029	35.7	64.3
-pC(O)Me	0.47	0.176091259055681	40	60
-pCF3	0.54	-0.39946118179257	71.5	28.5

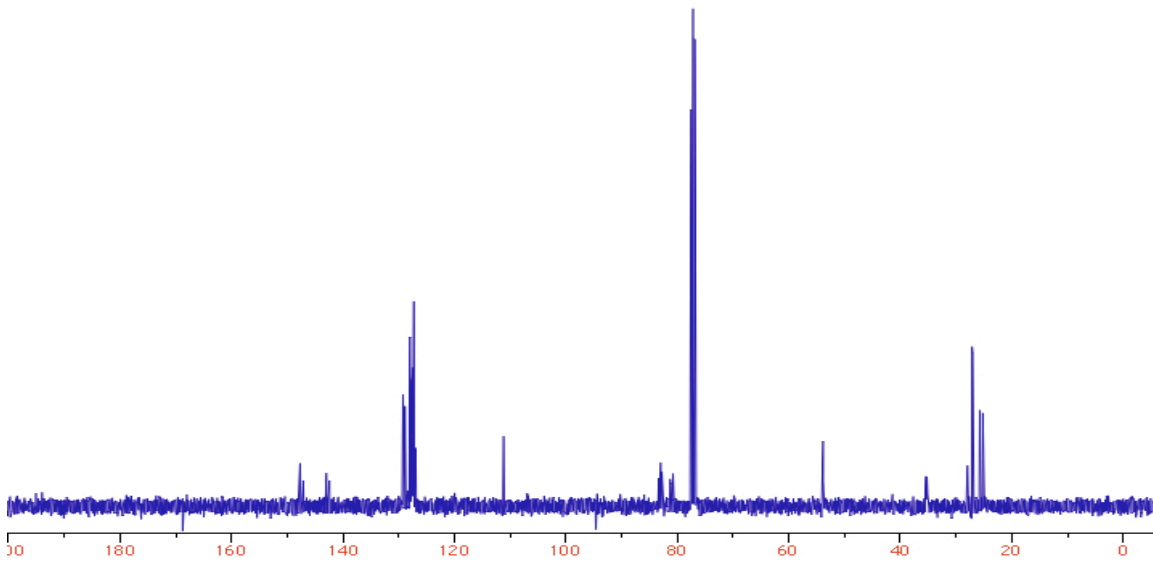
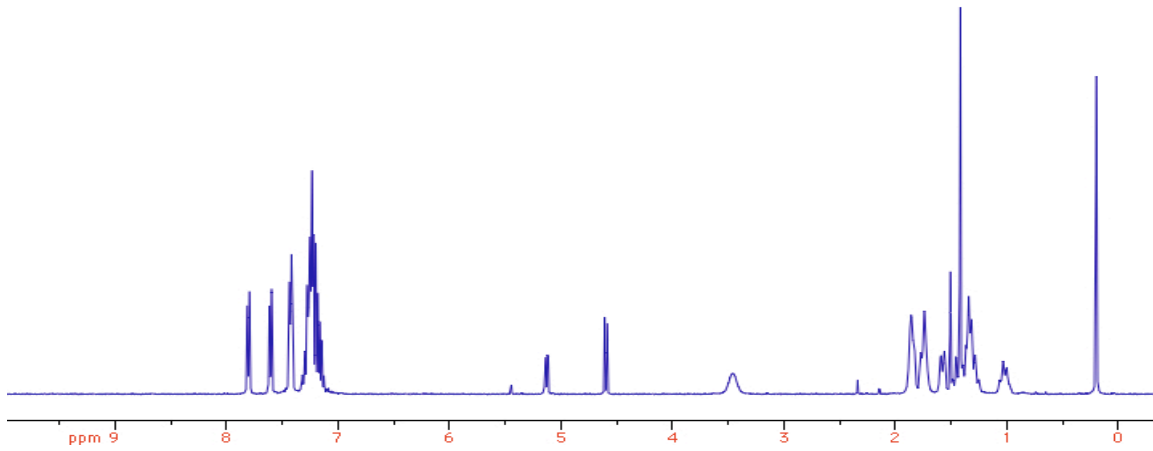
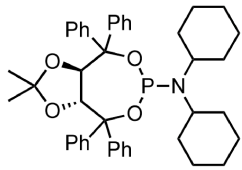


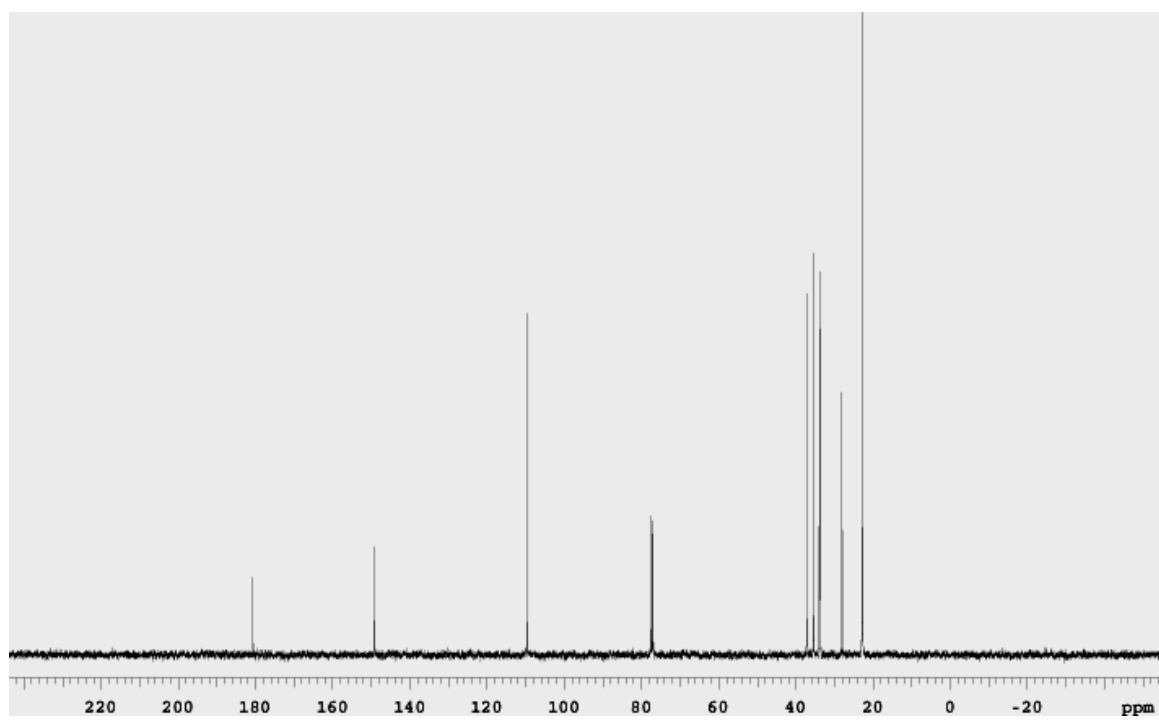
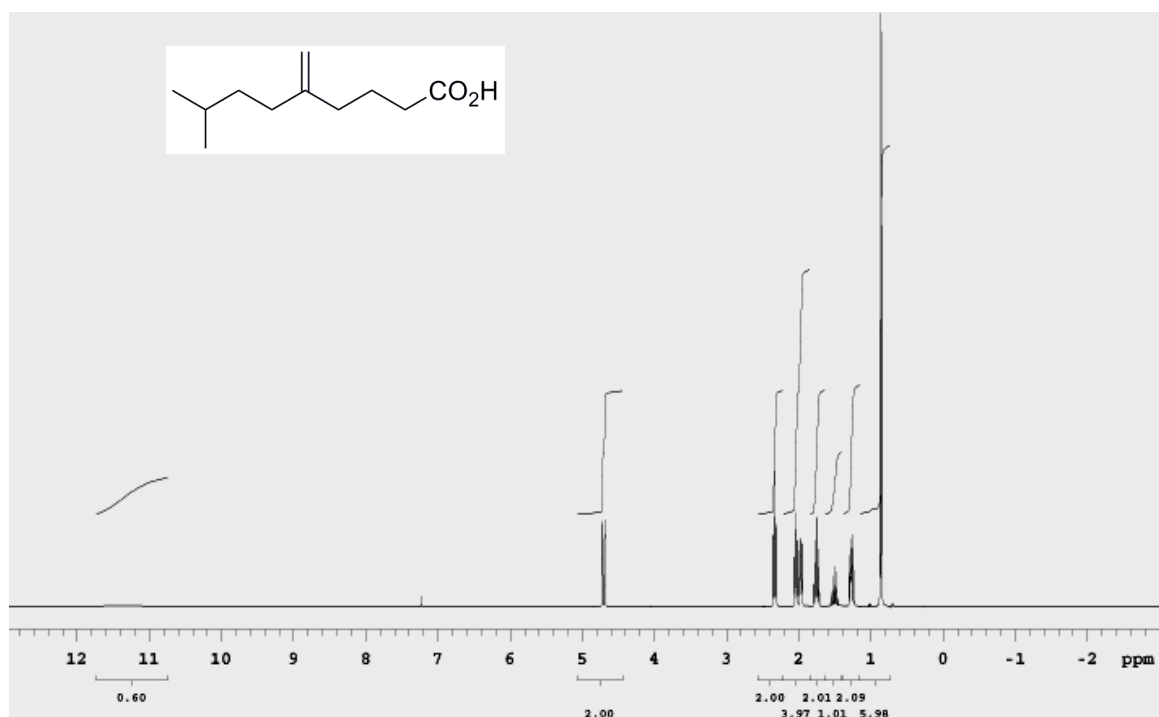
^1H NMR and ^{13}C NMR Spectra of New Compounds:

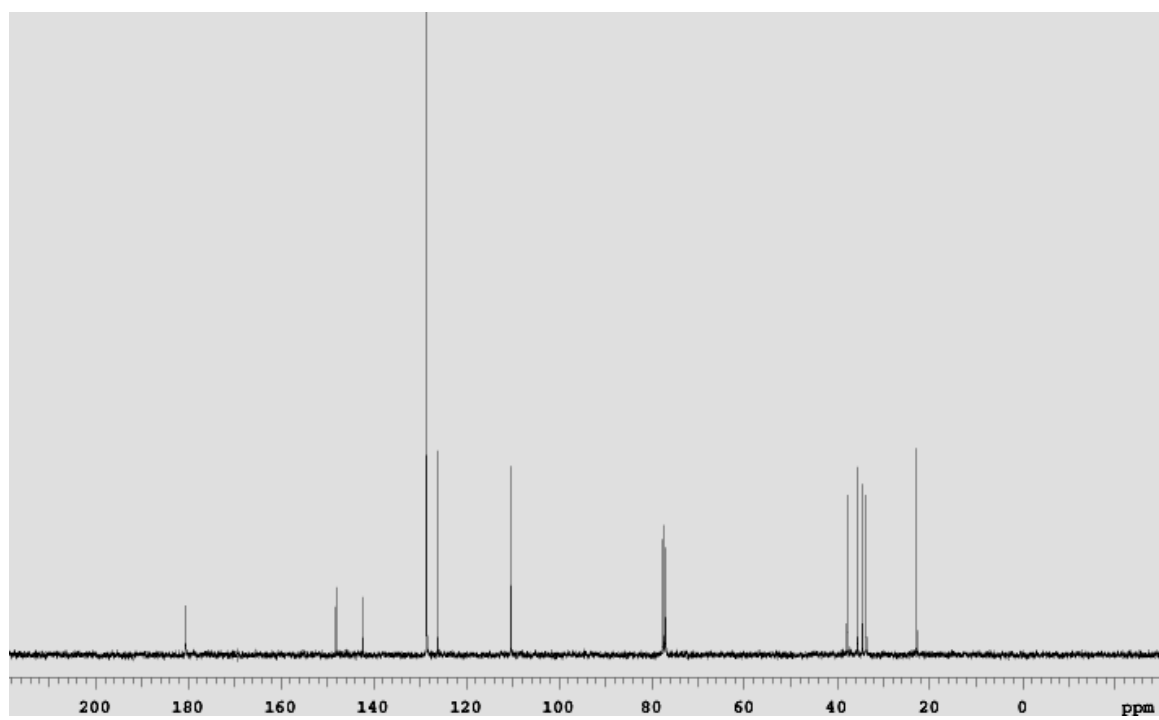
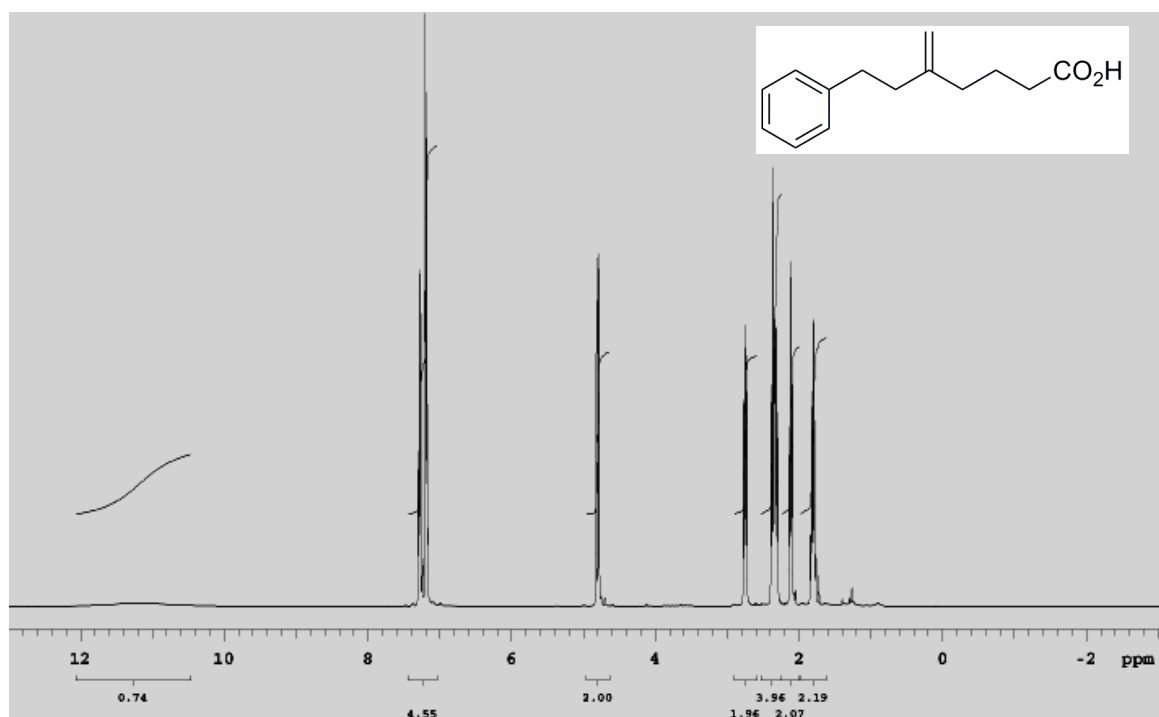


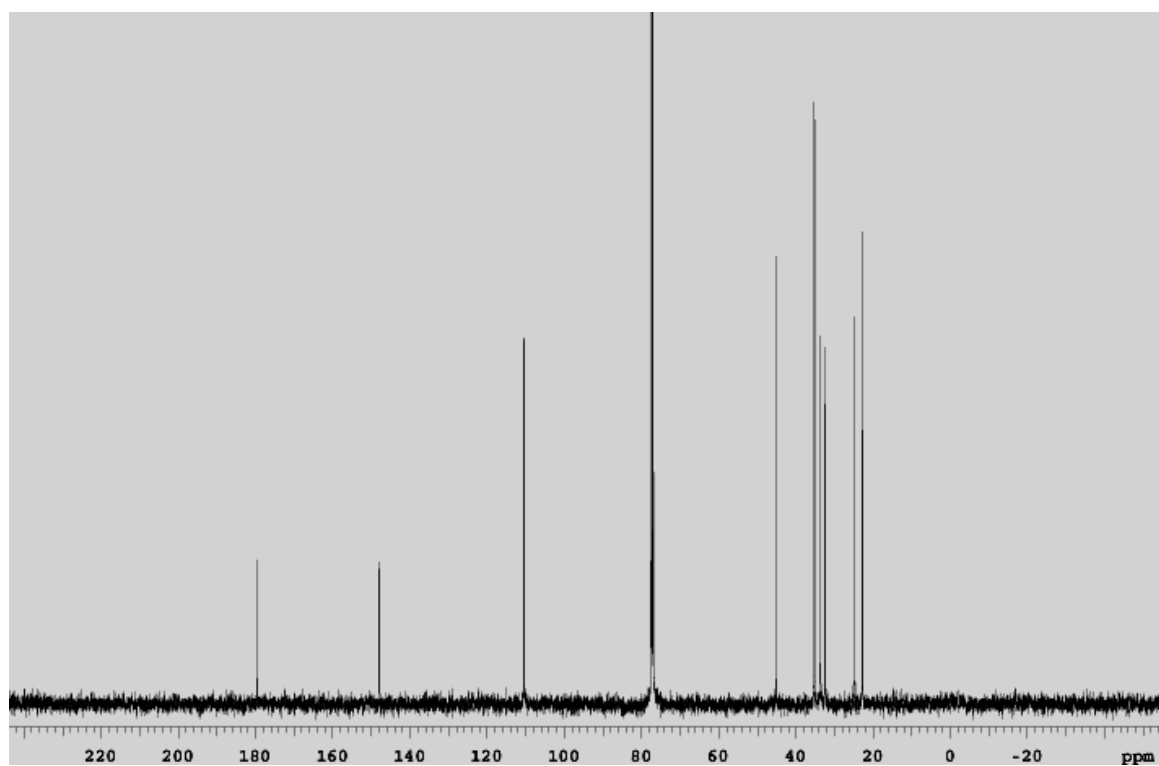
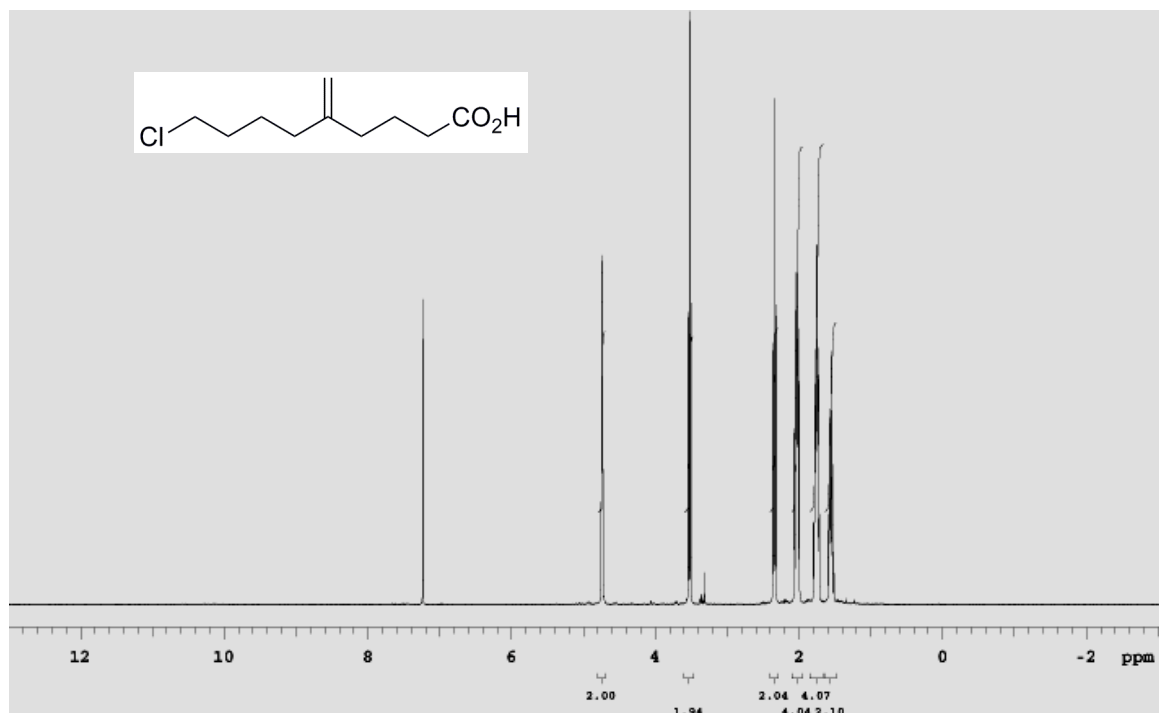


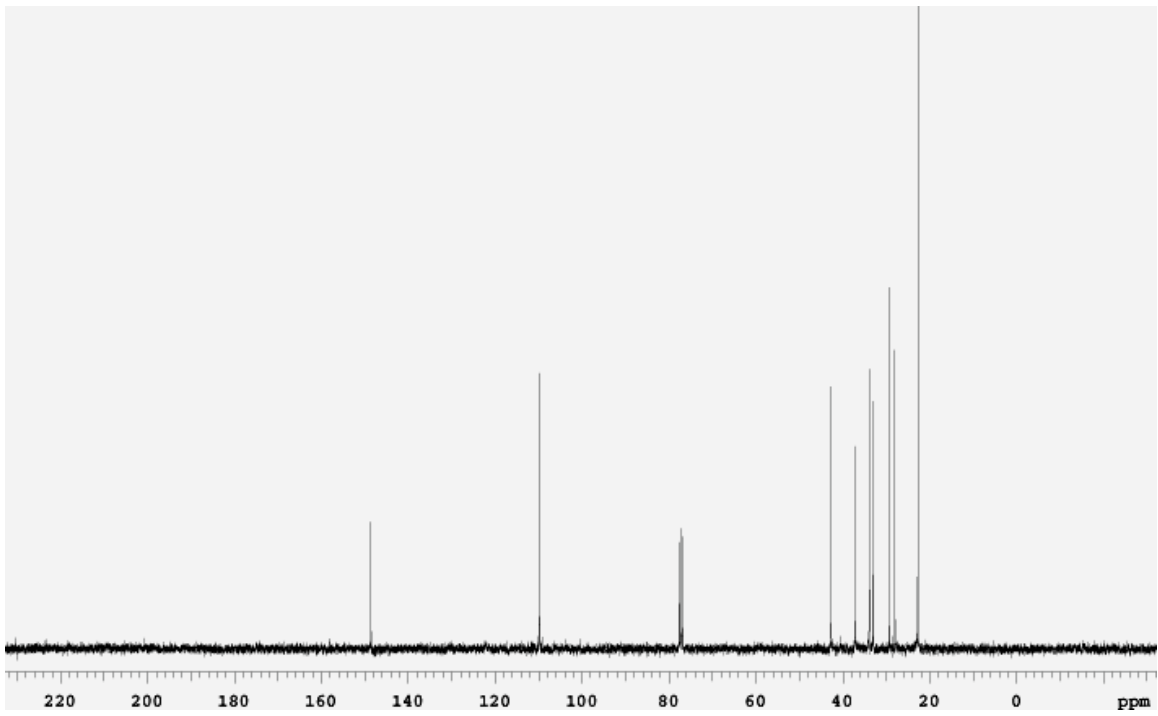
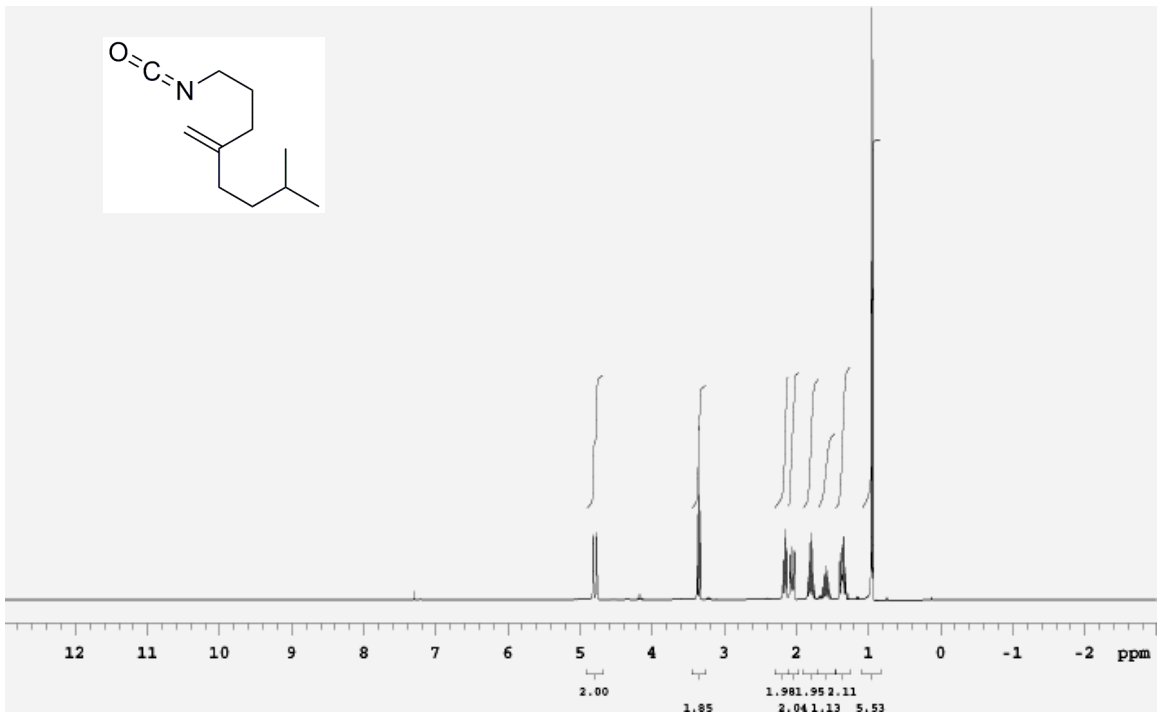
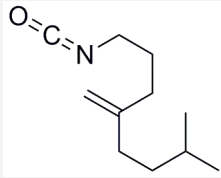


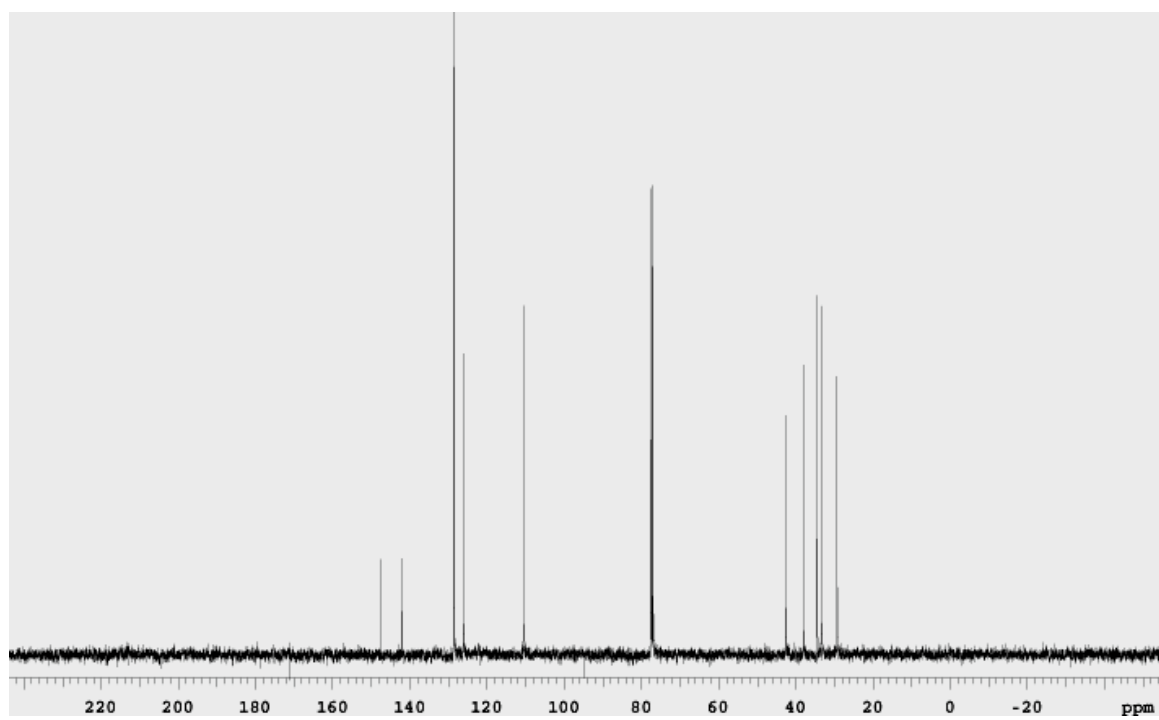
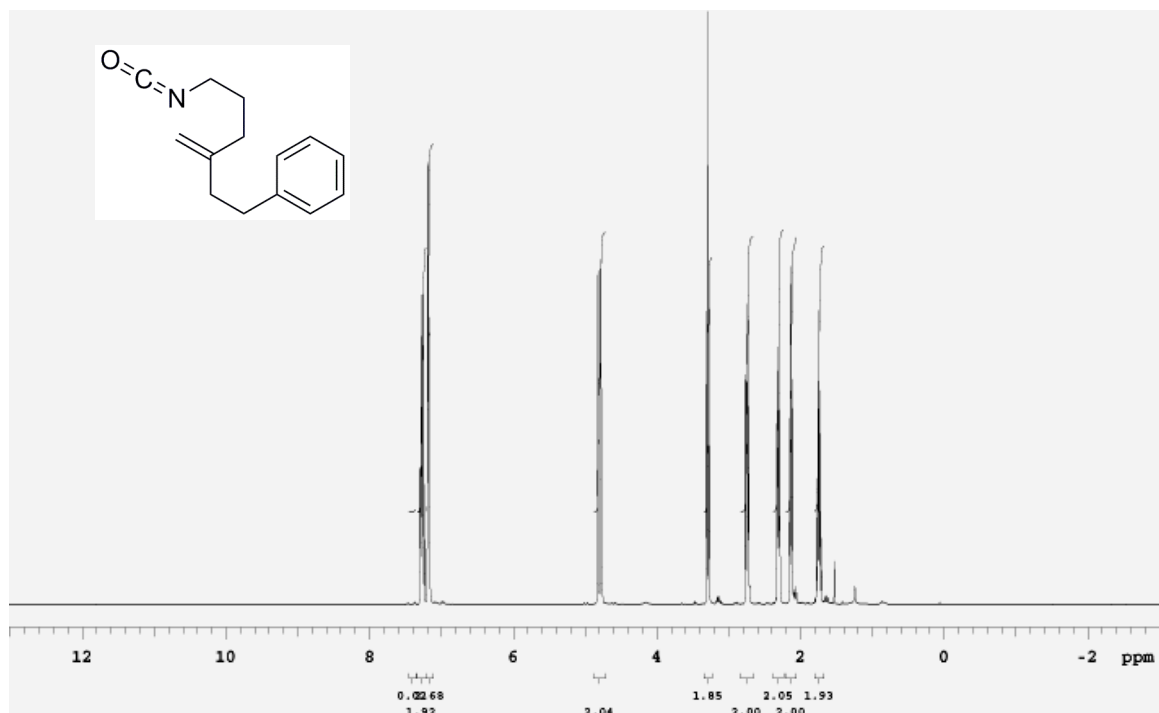


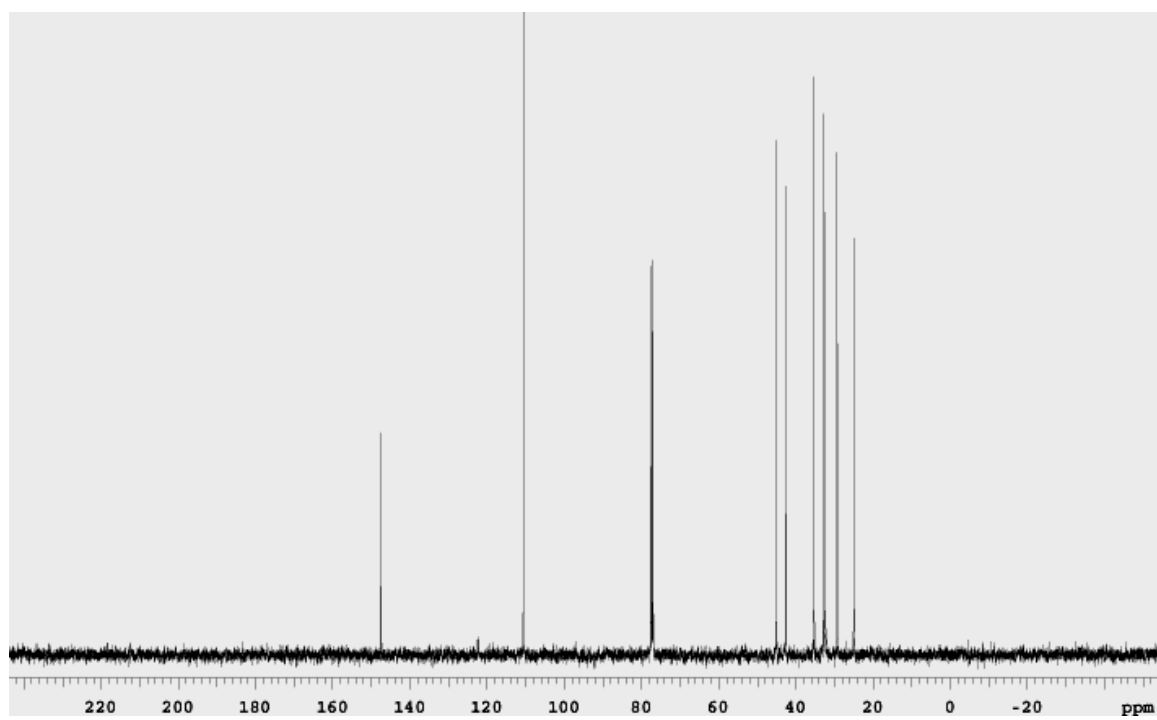
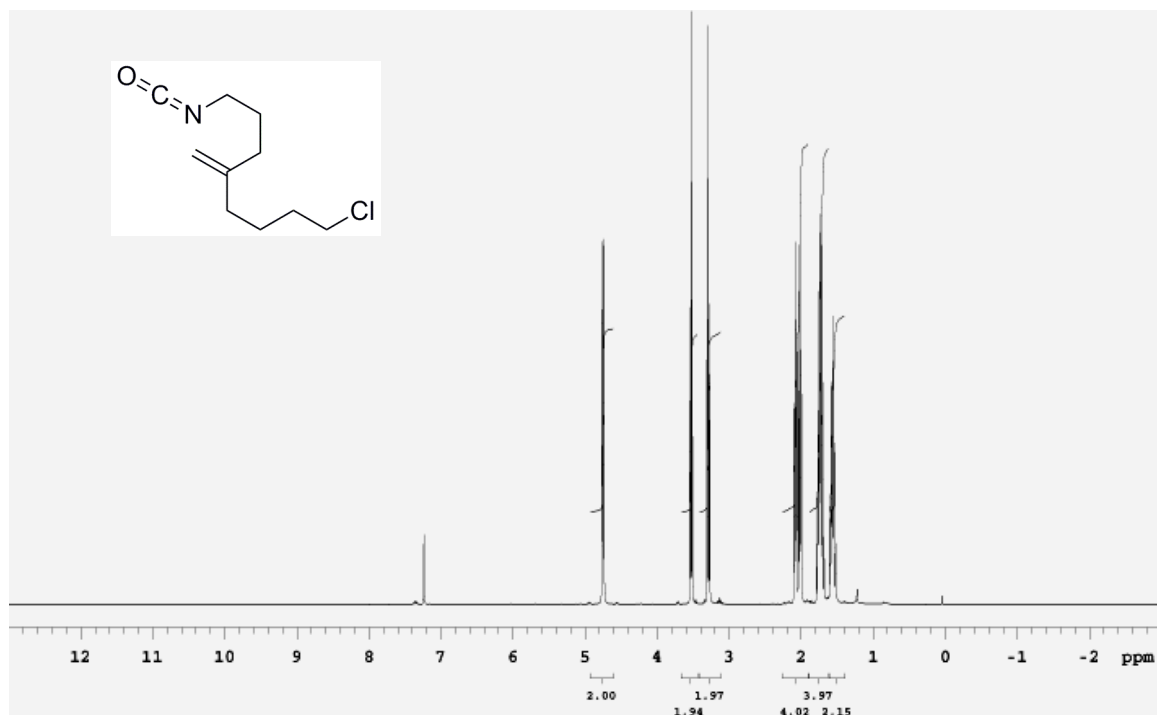




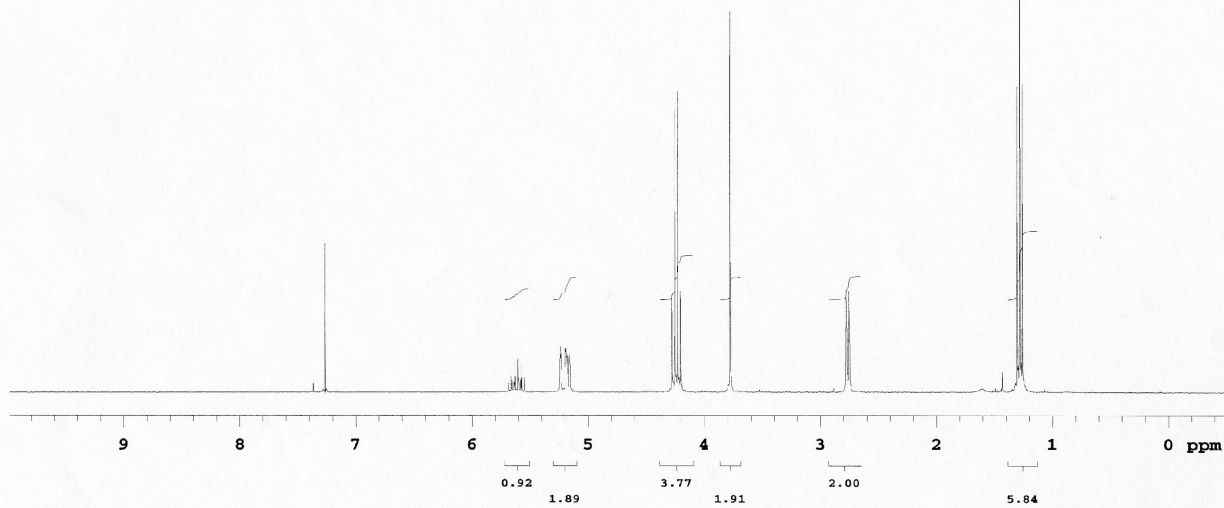
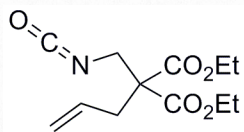




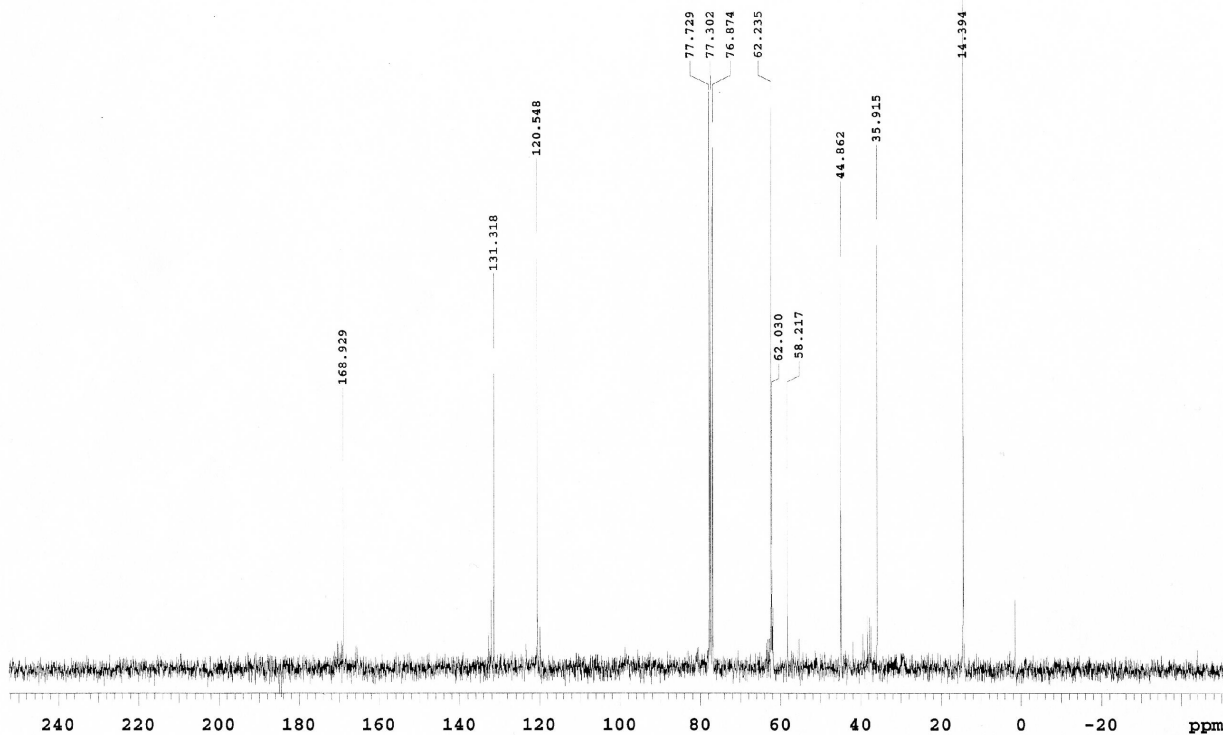




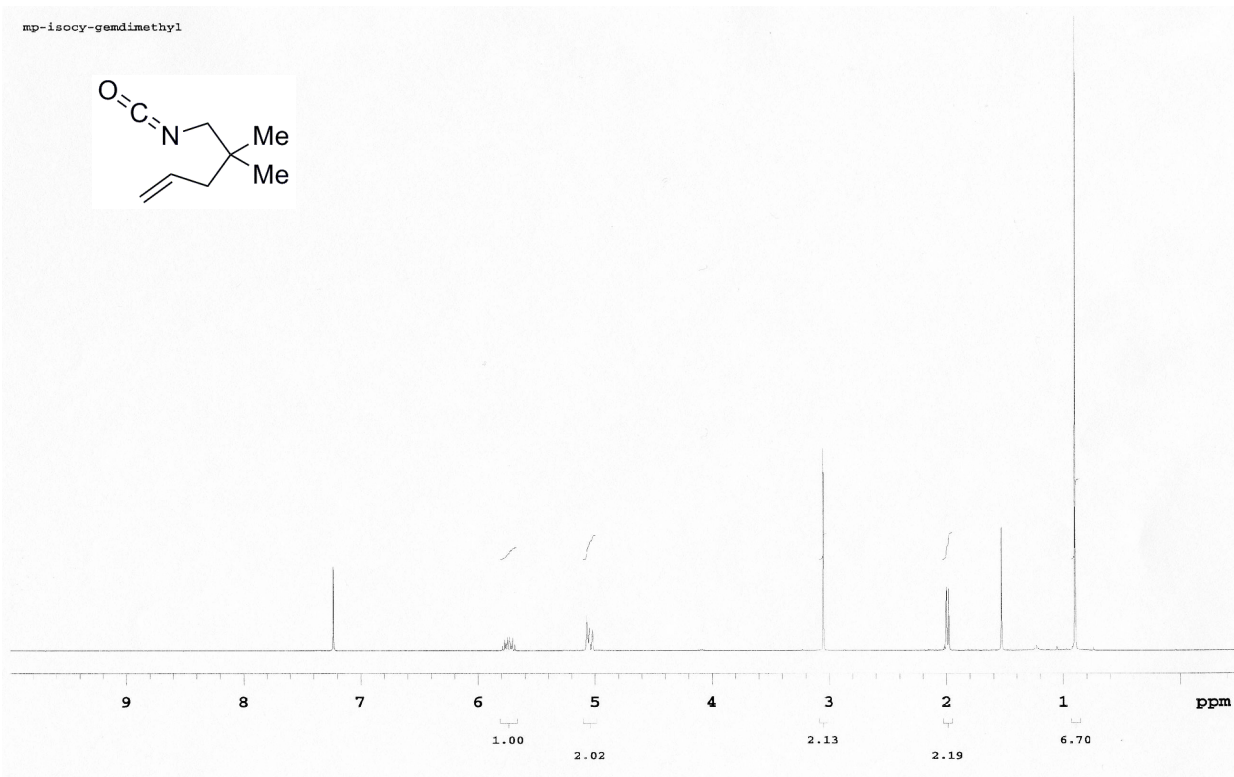
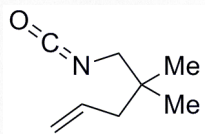
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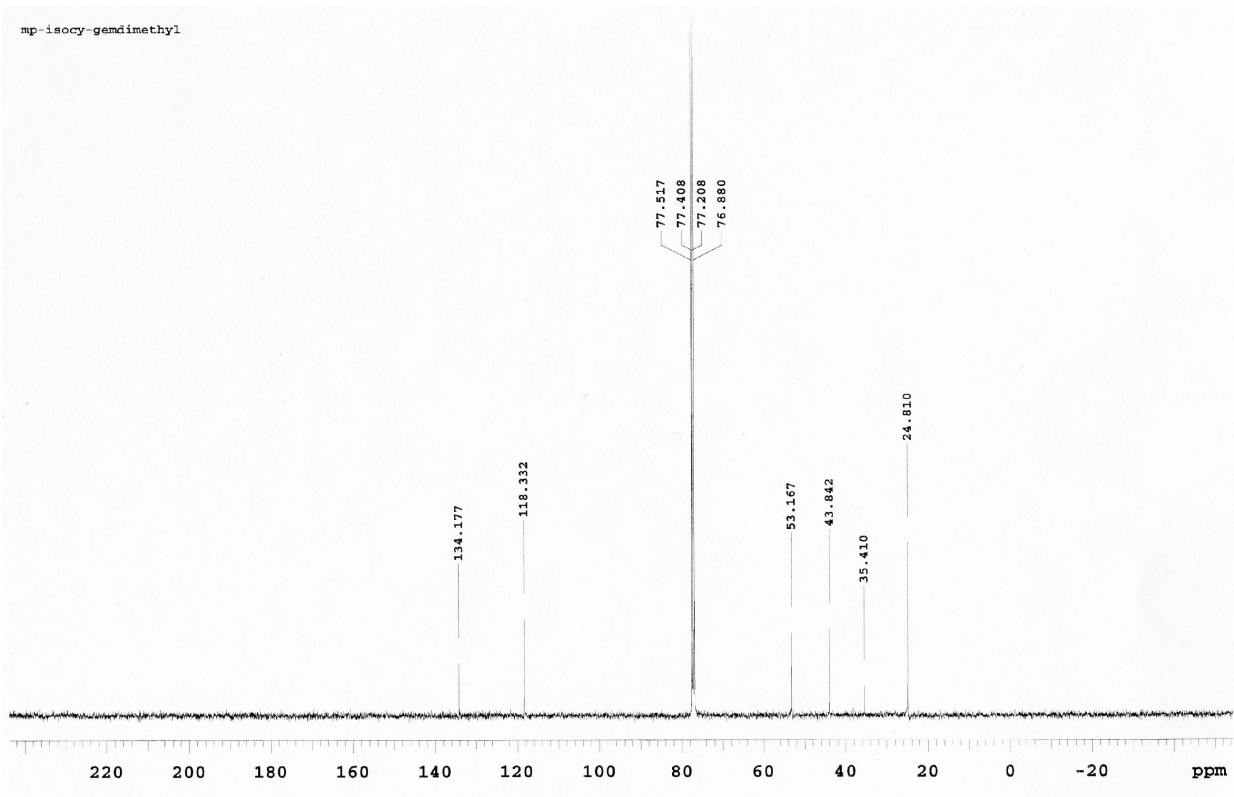
mp-109-10-7-05-carbon

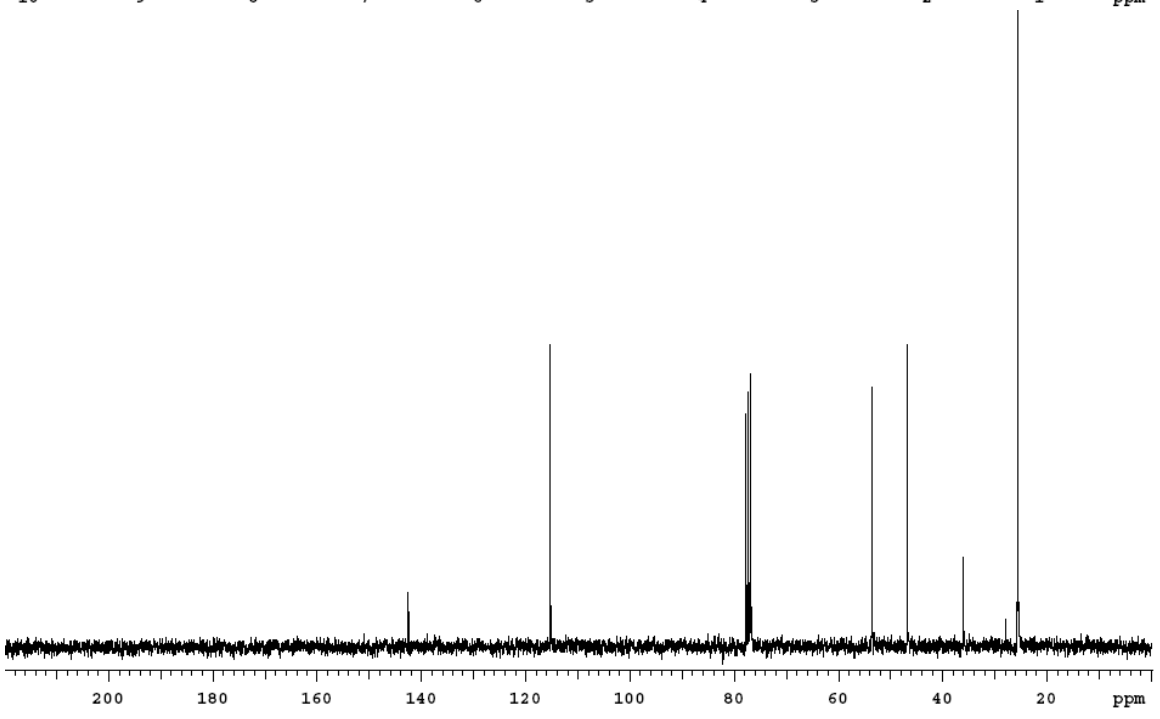
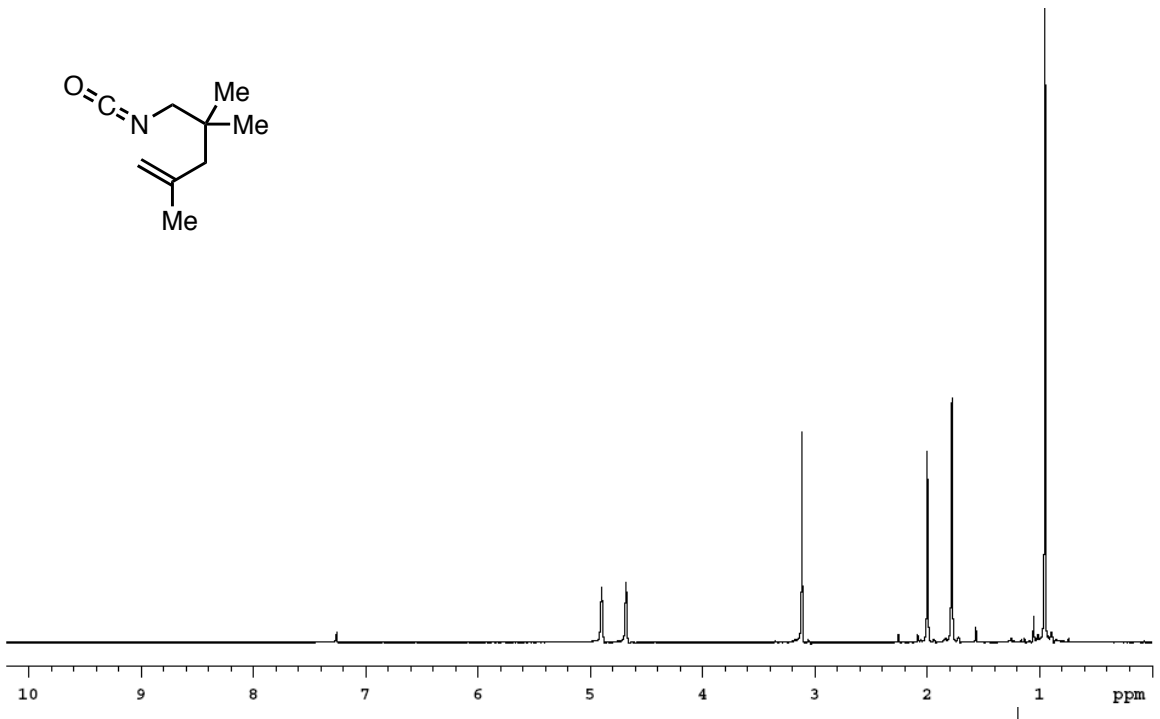
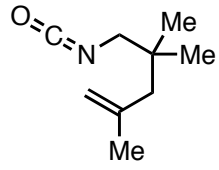


mp-isocy-gemdimethyl

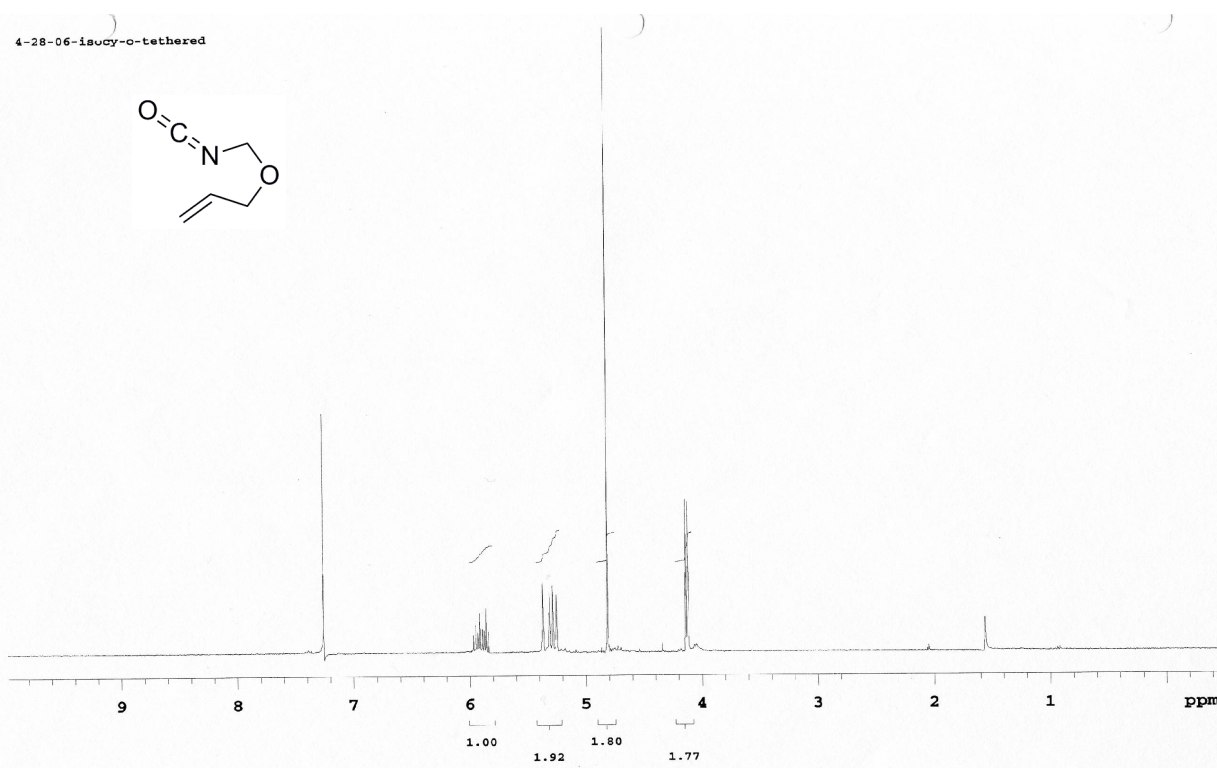
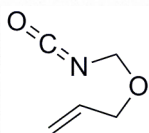


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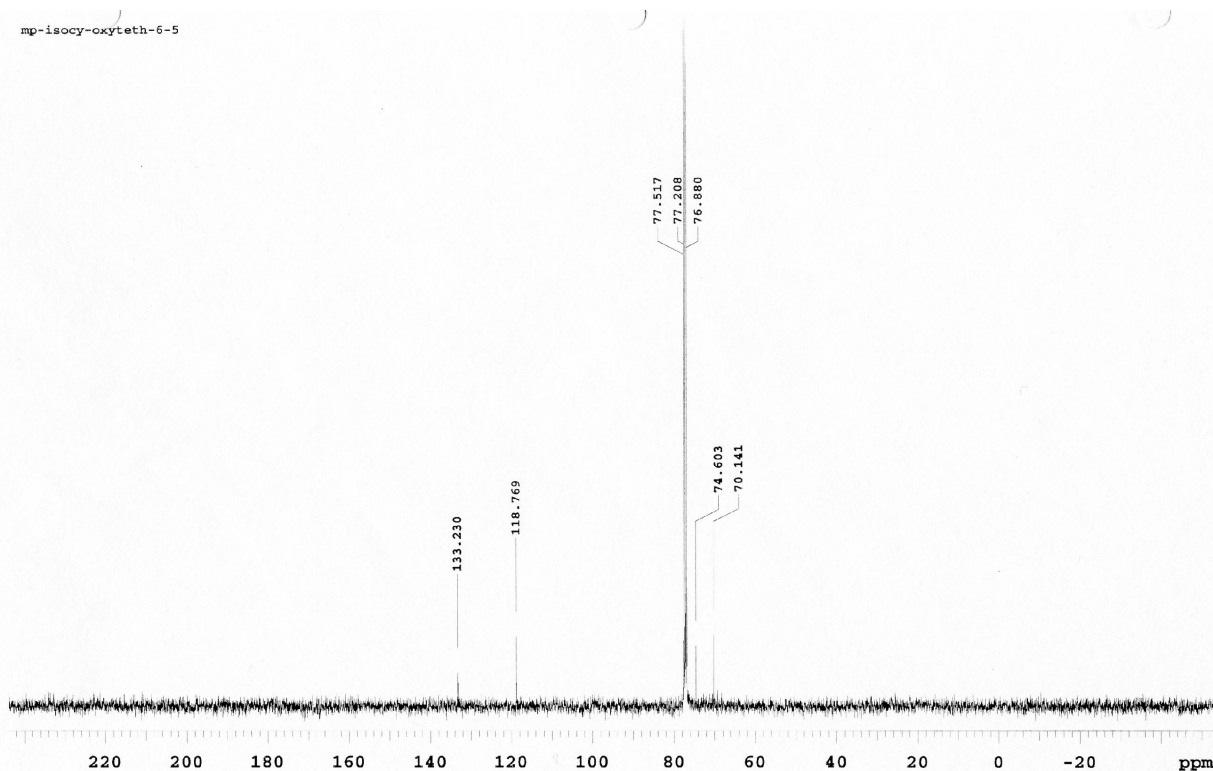




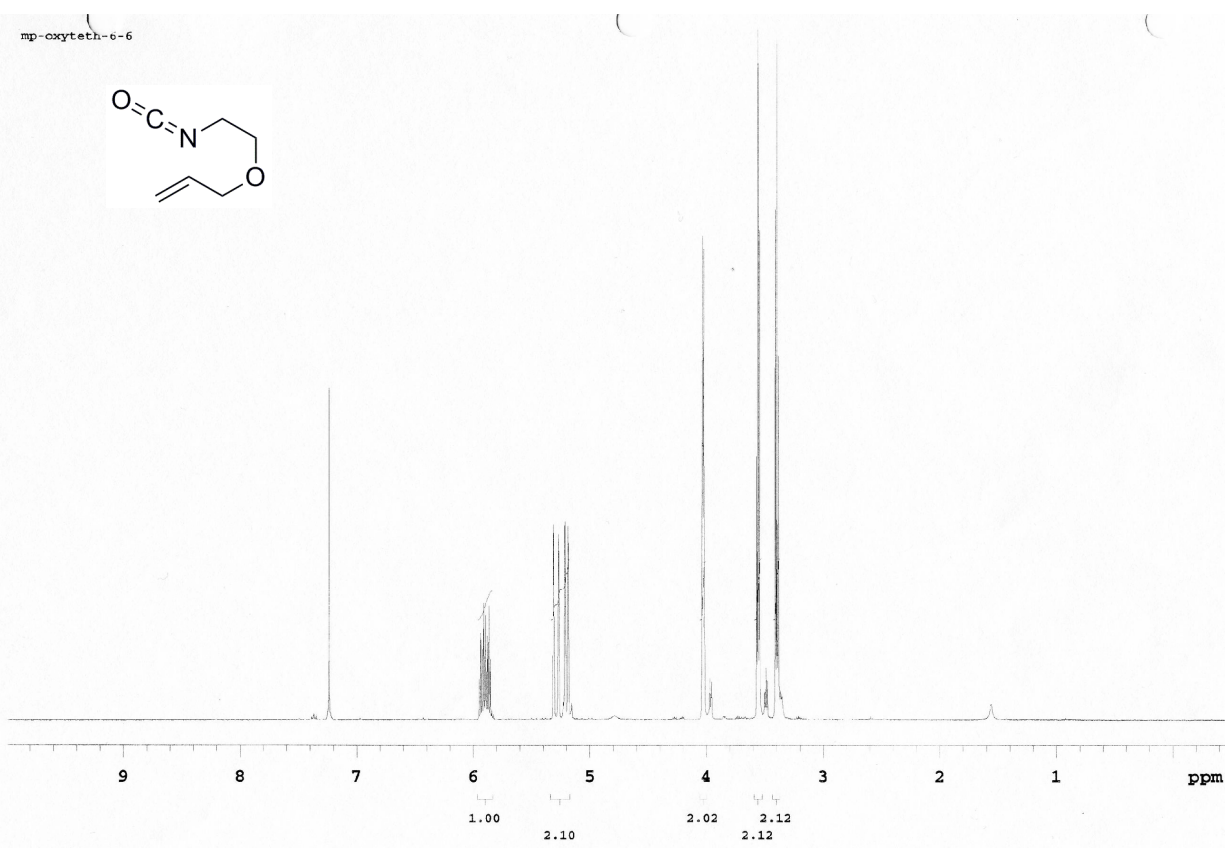
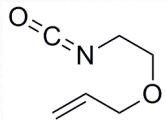
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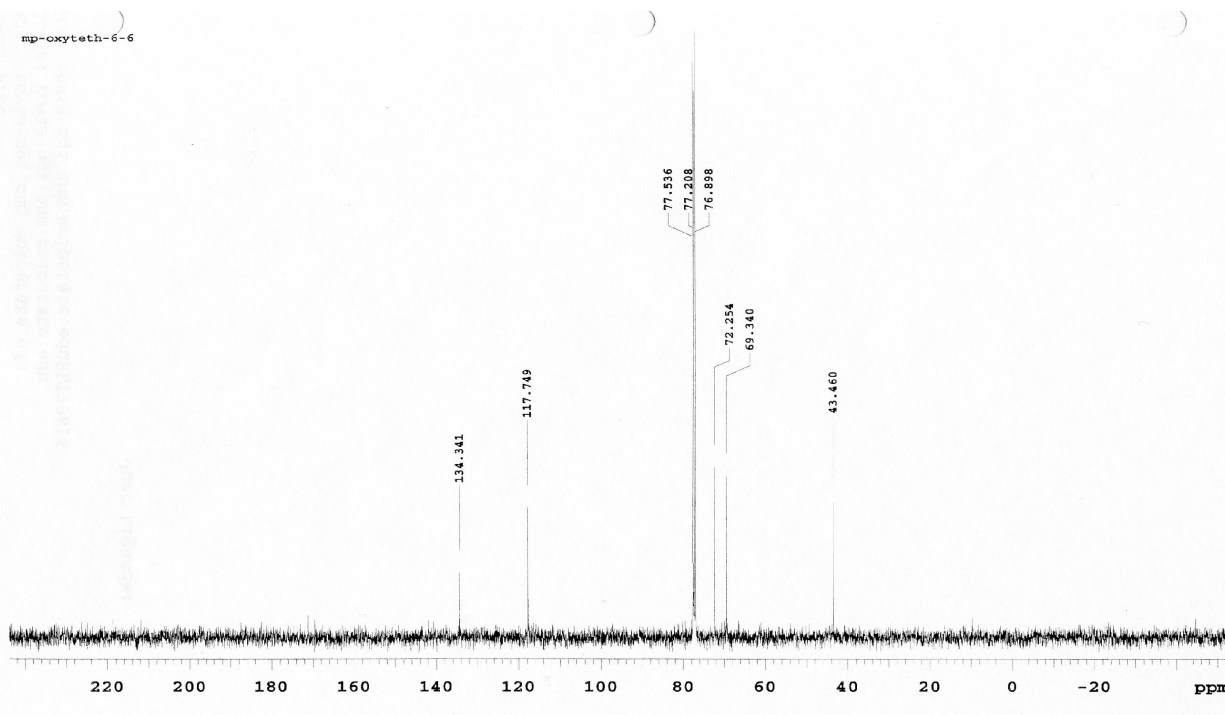
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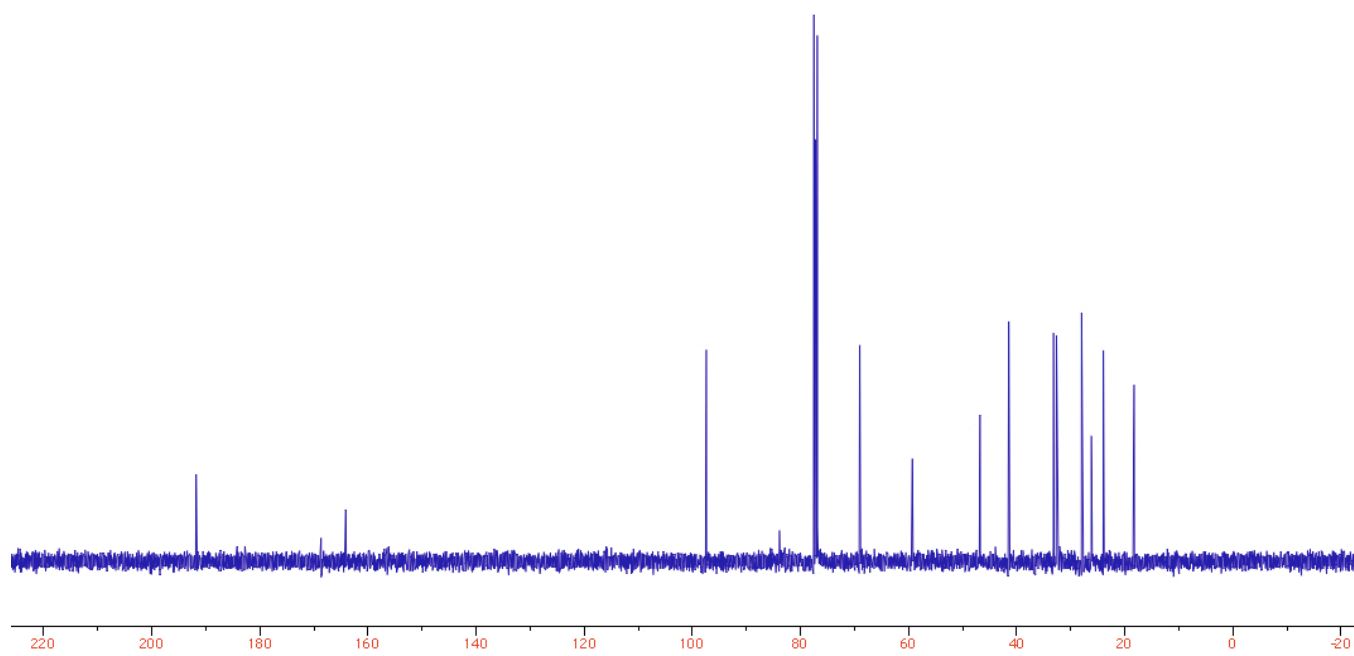
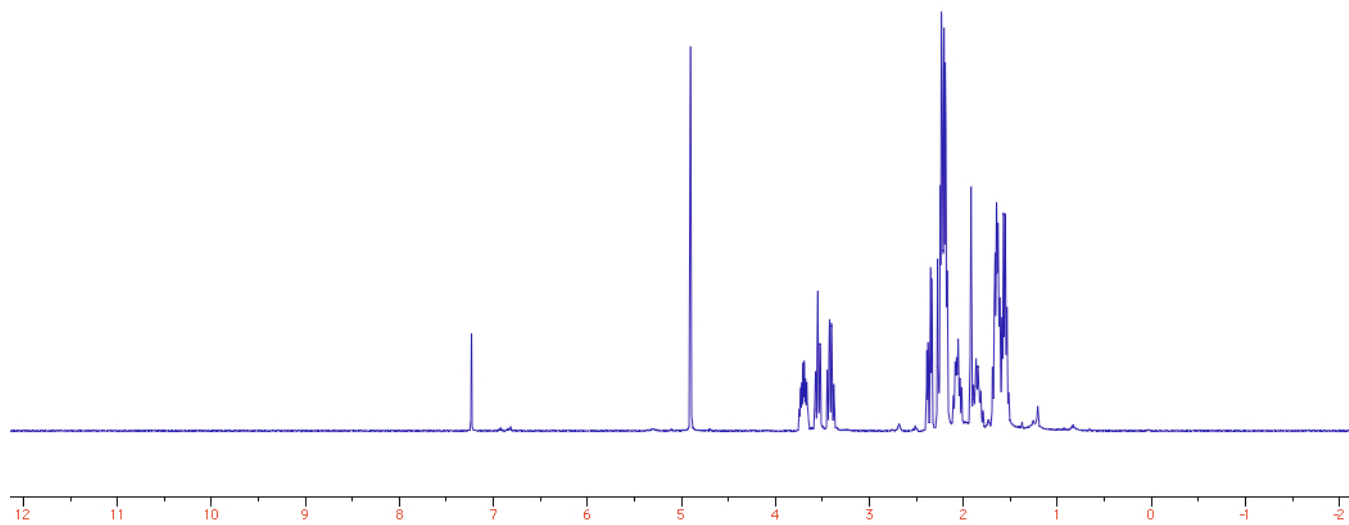
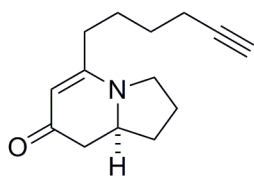


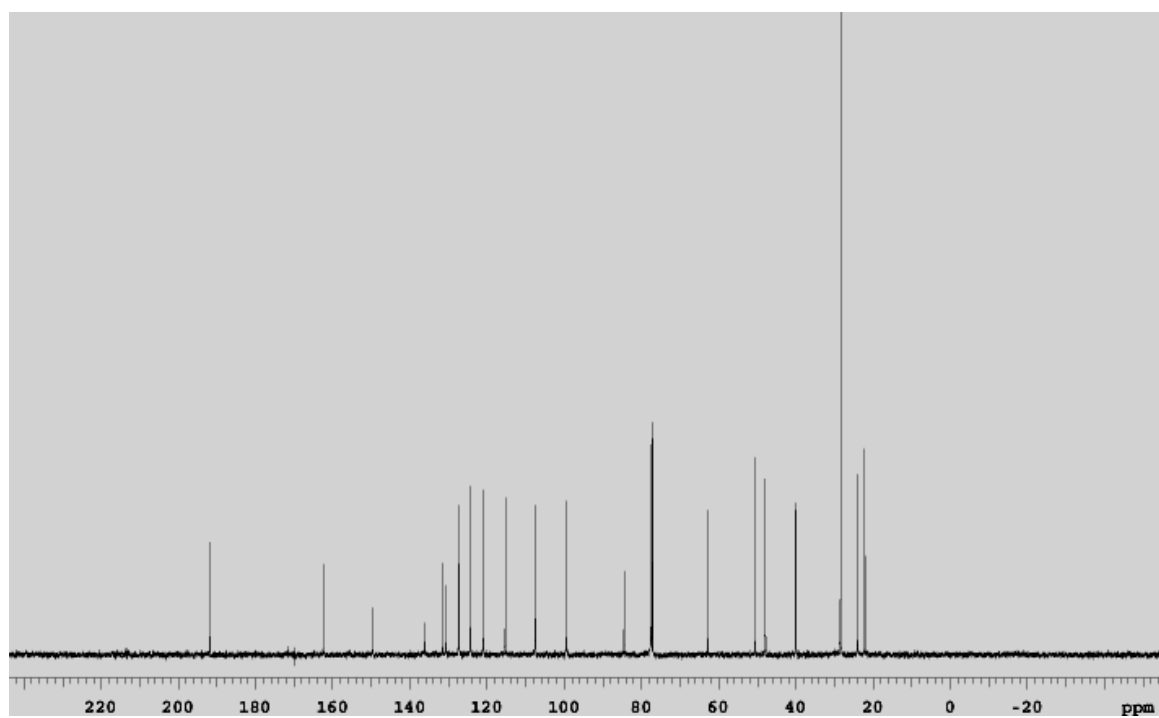
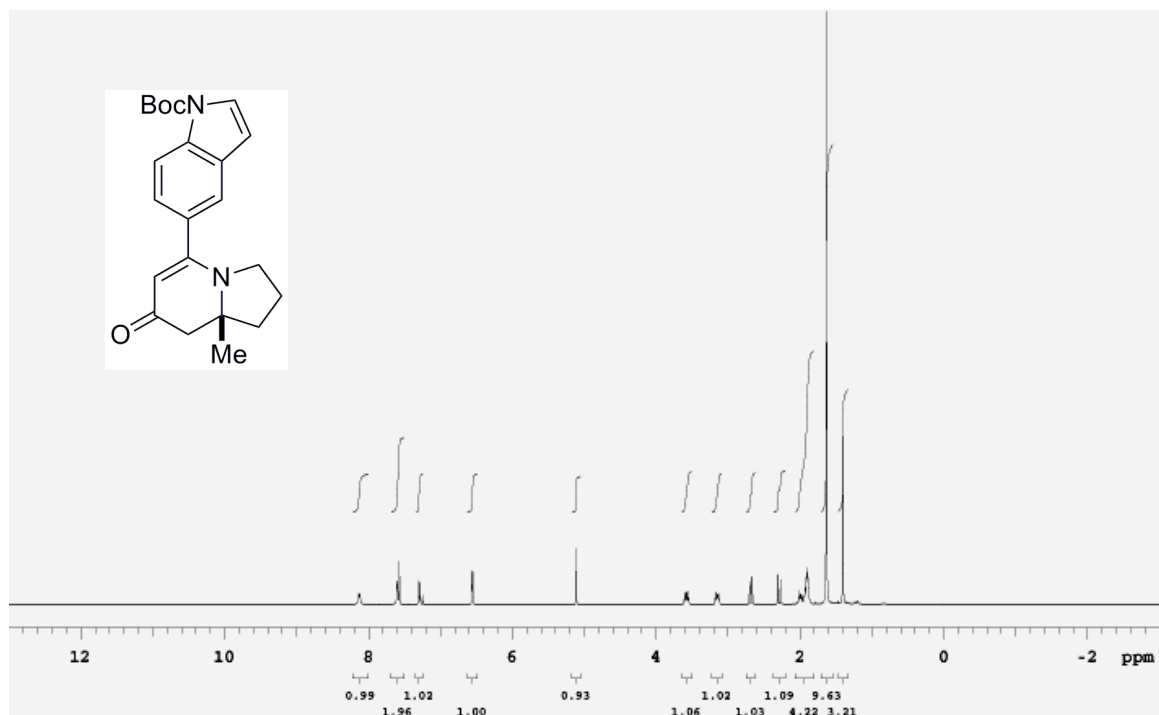
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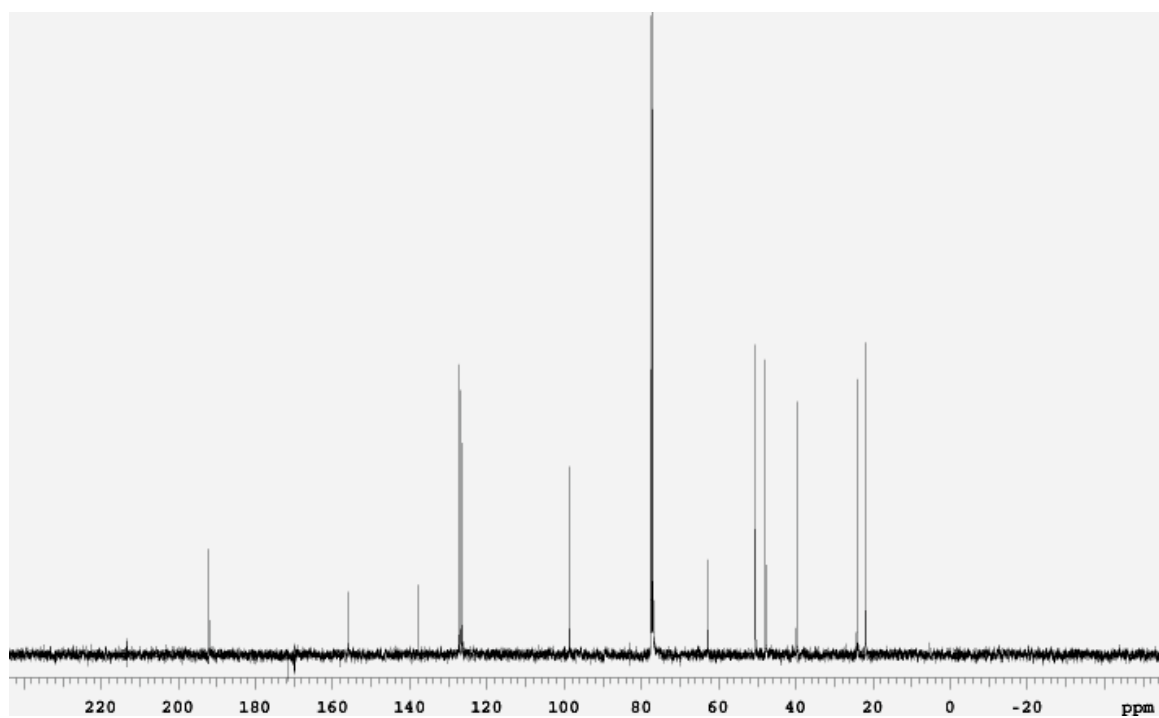
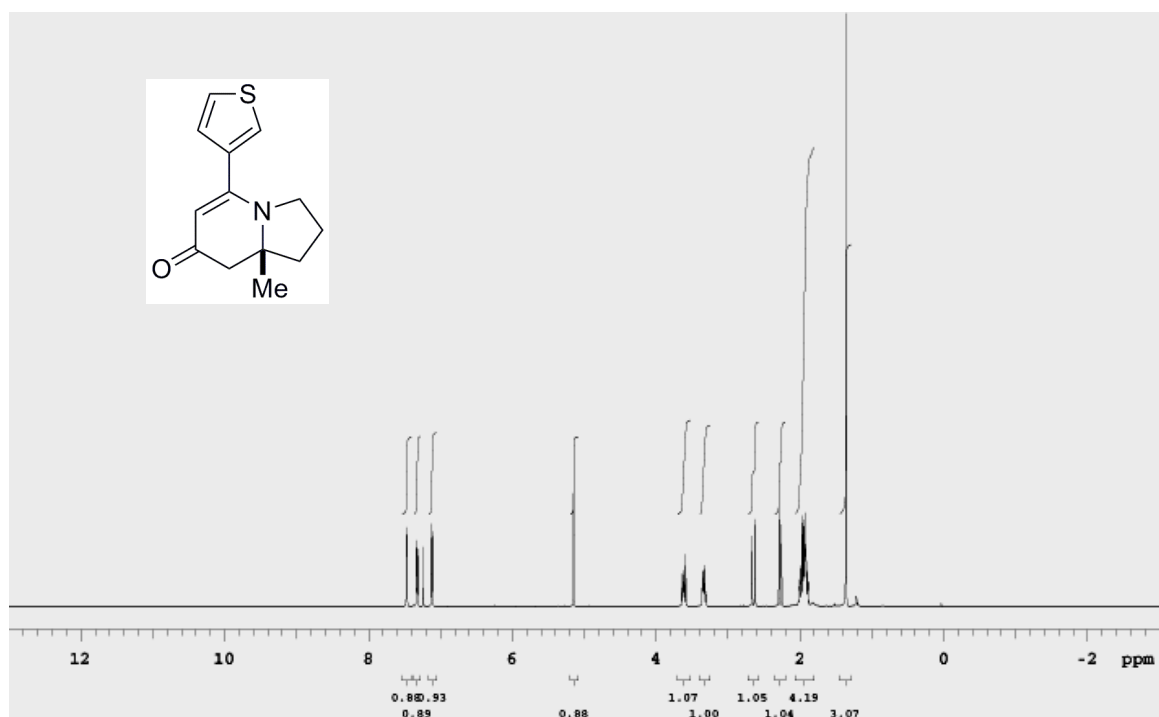
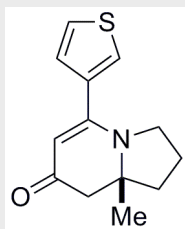


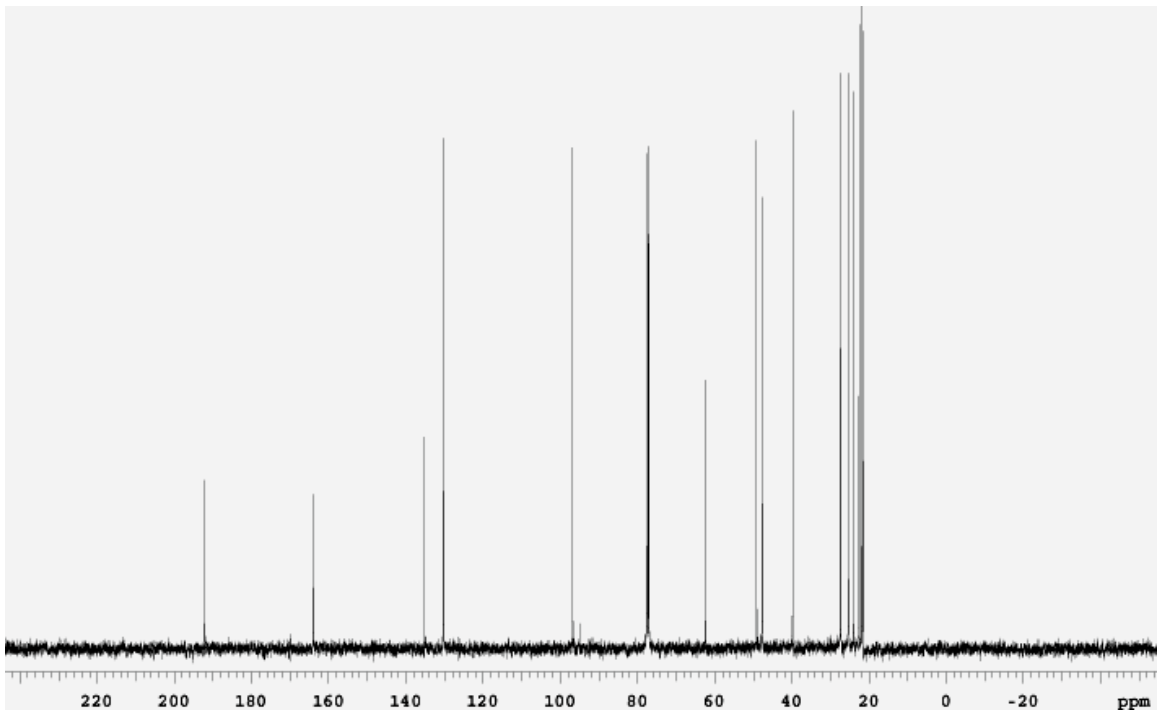
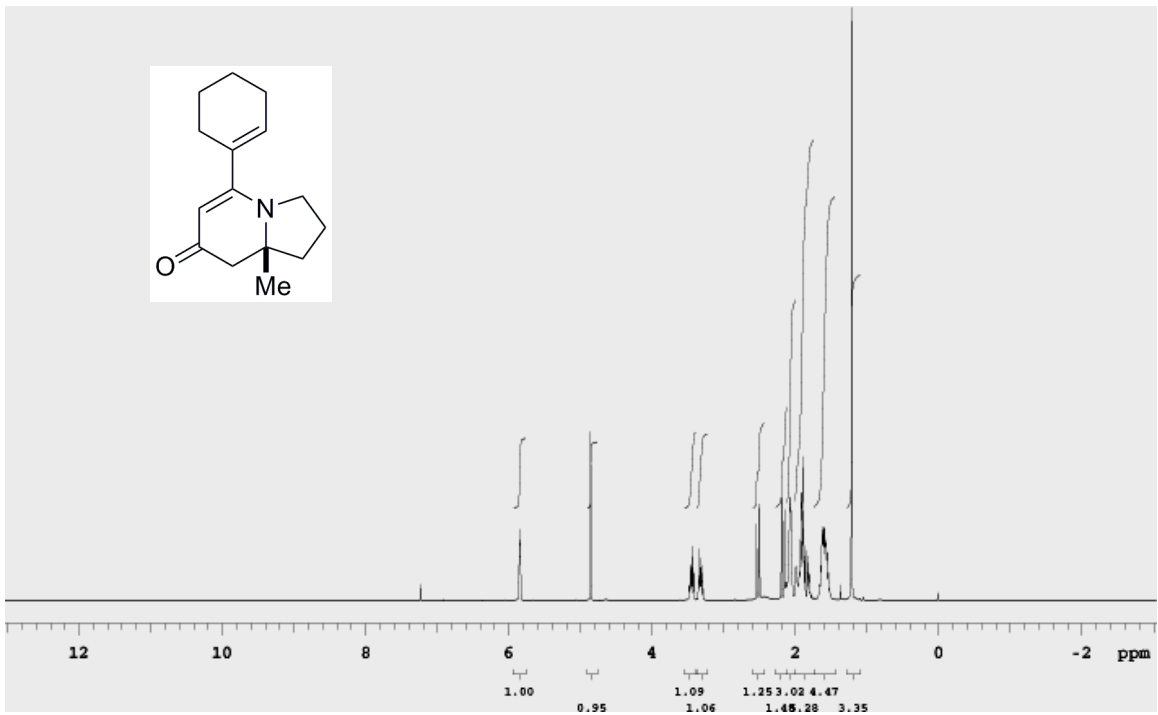
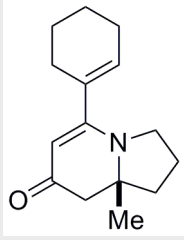
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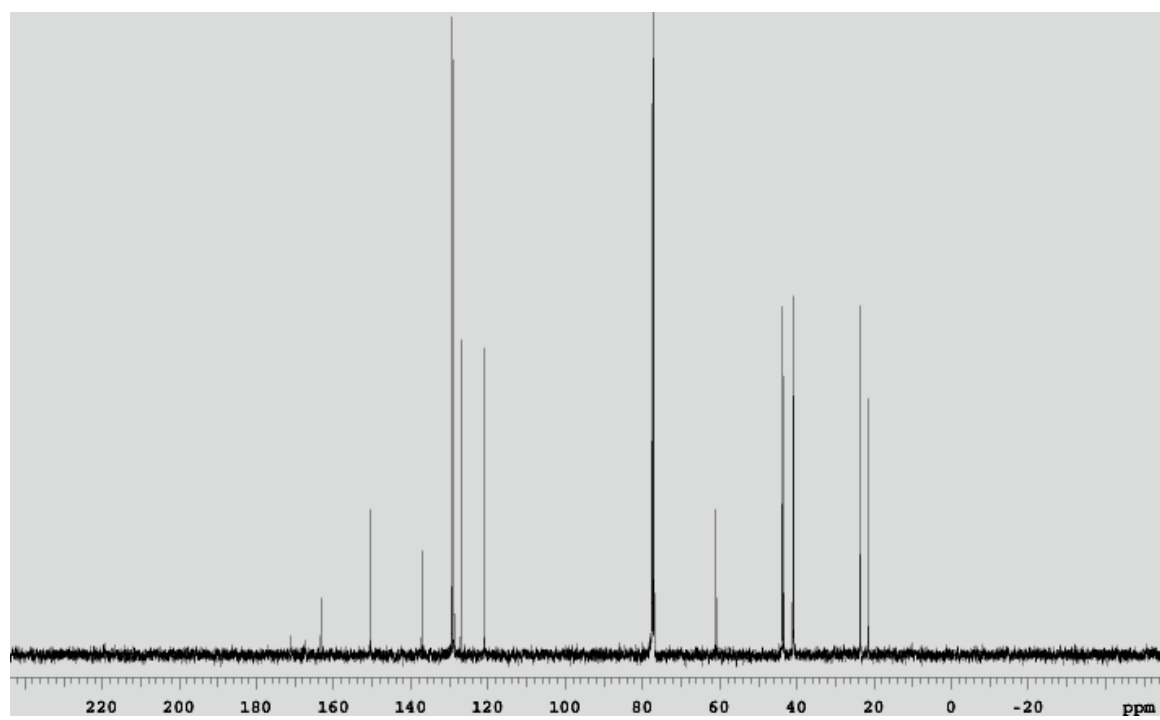
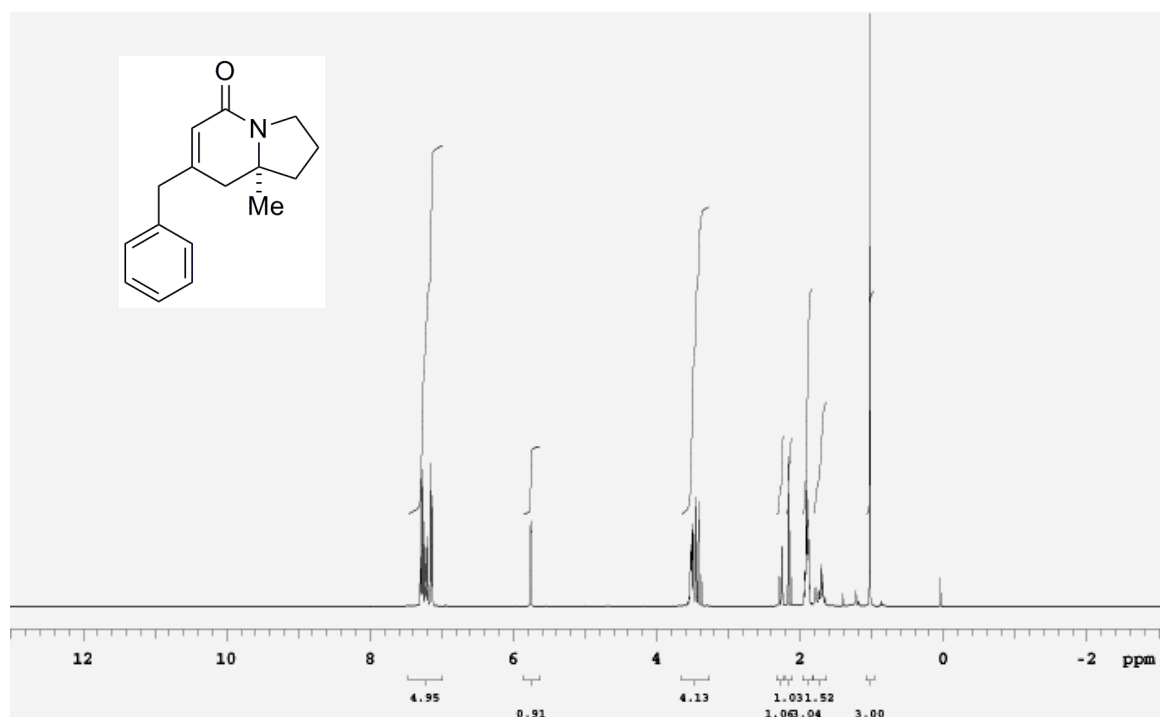


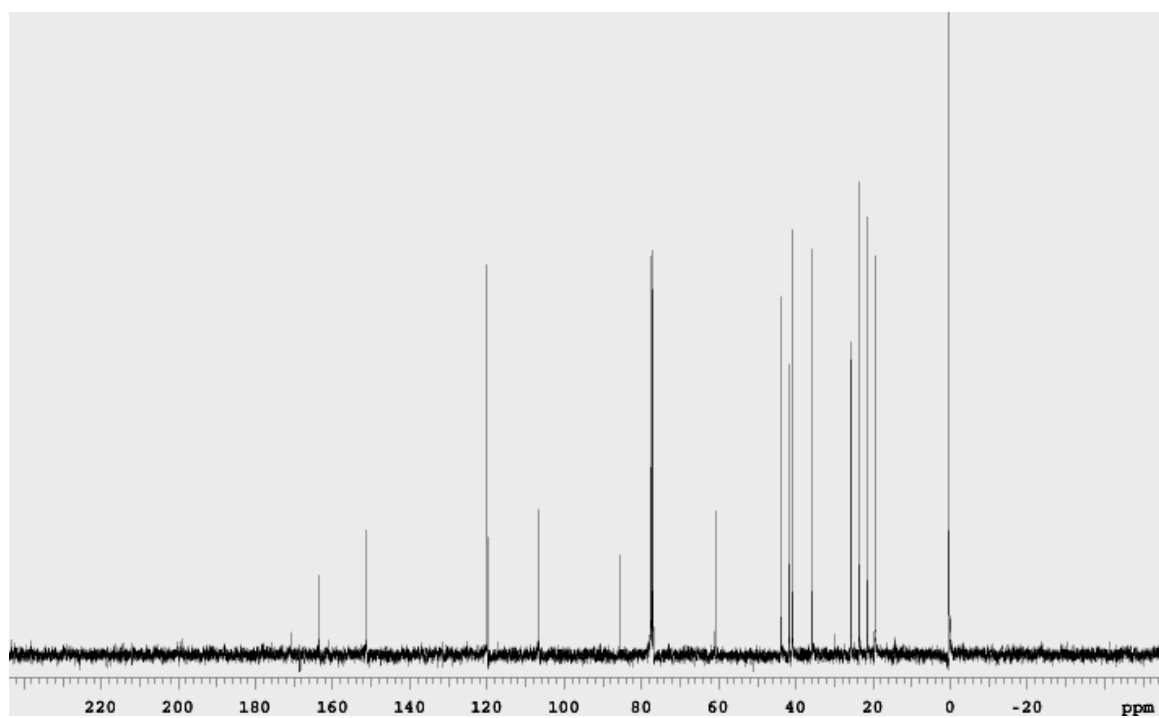
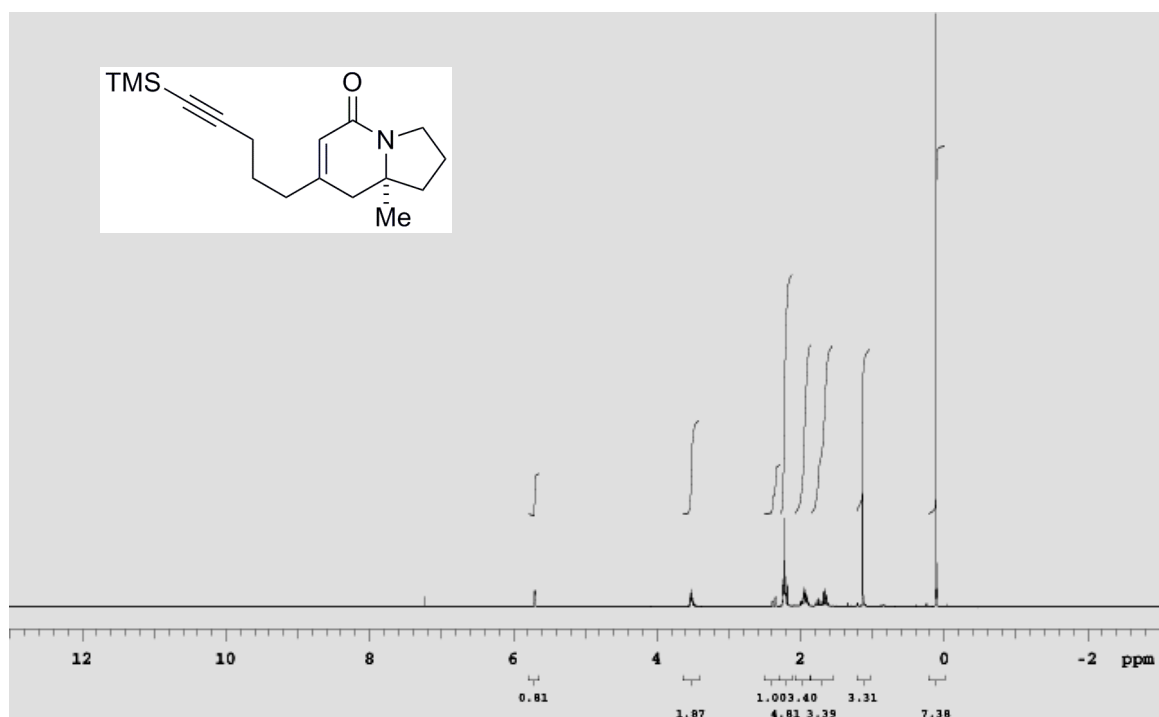


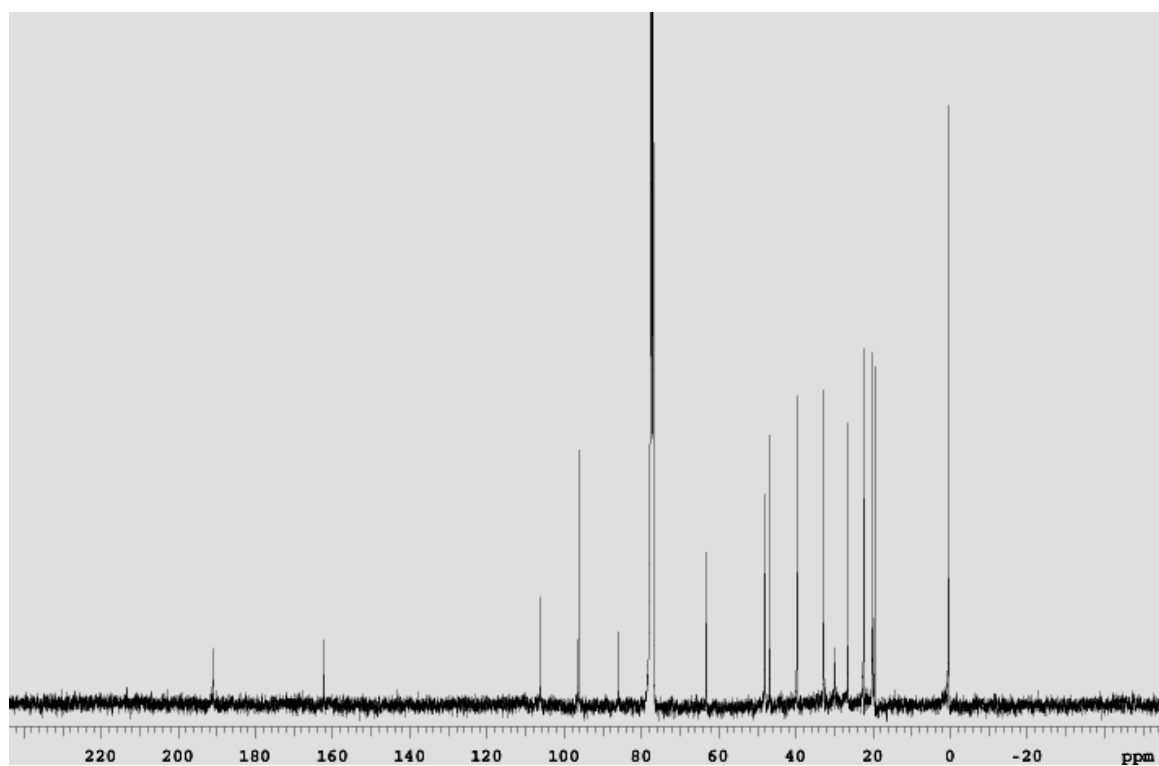
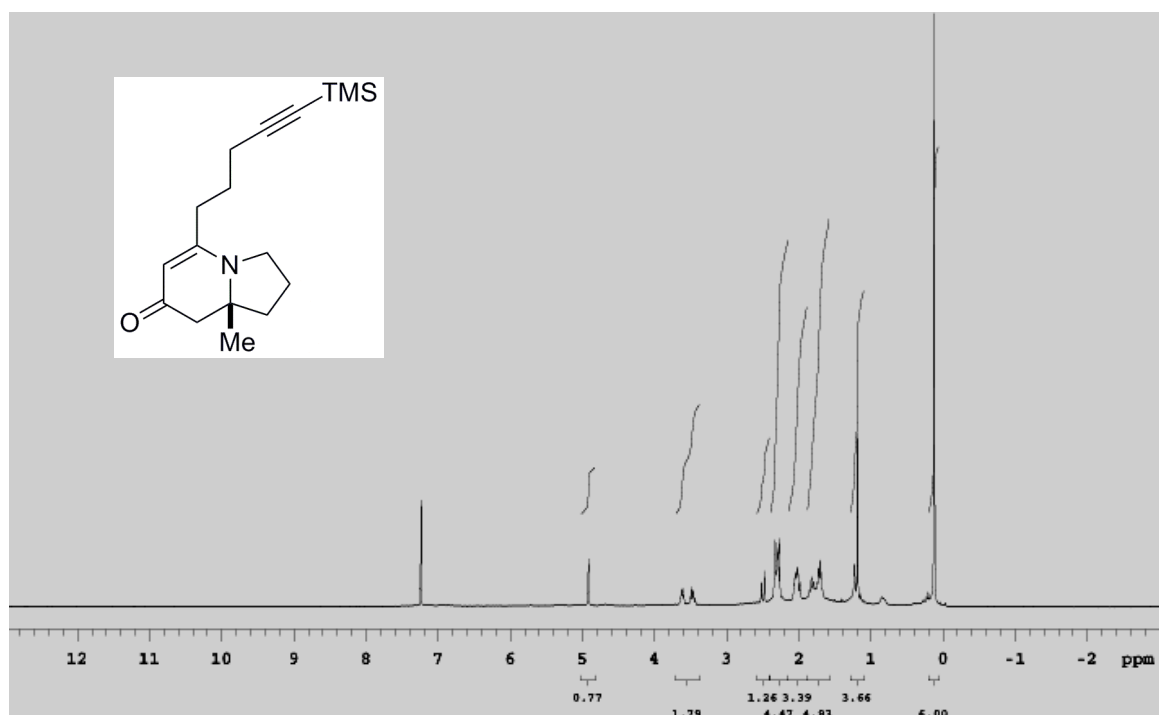


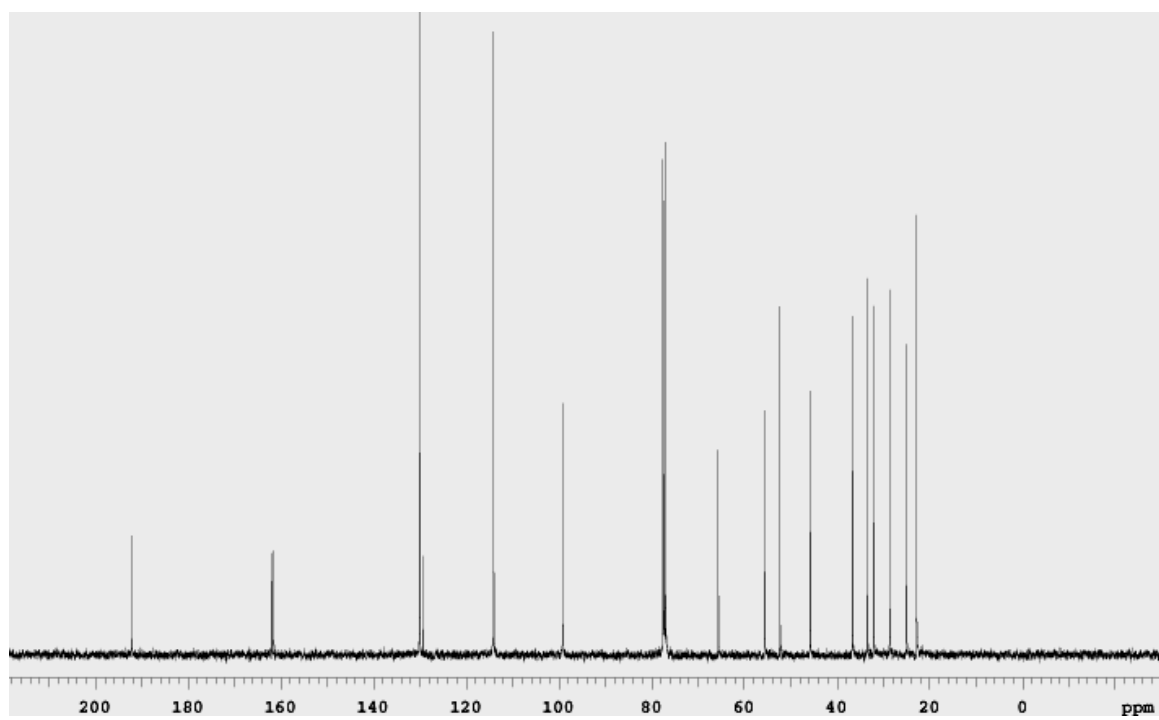
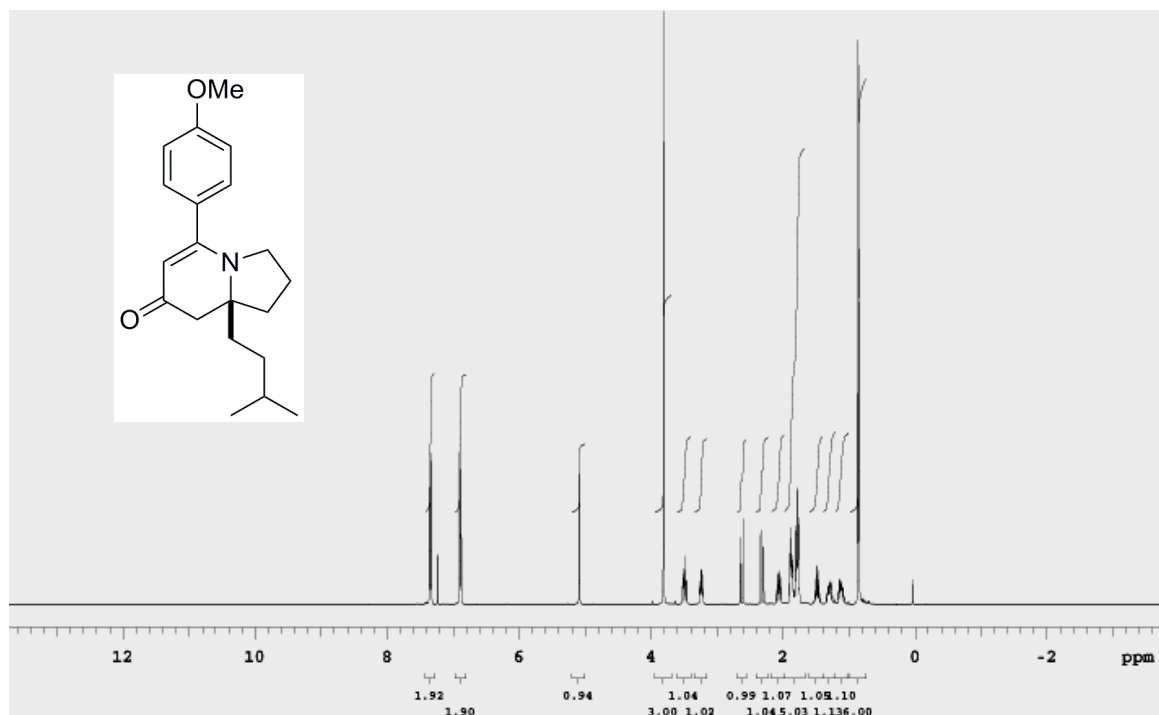


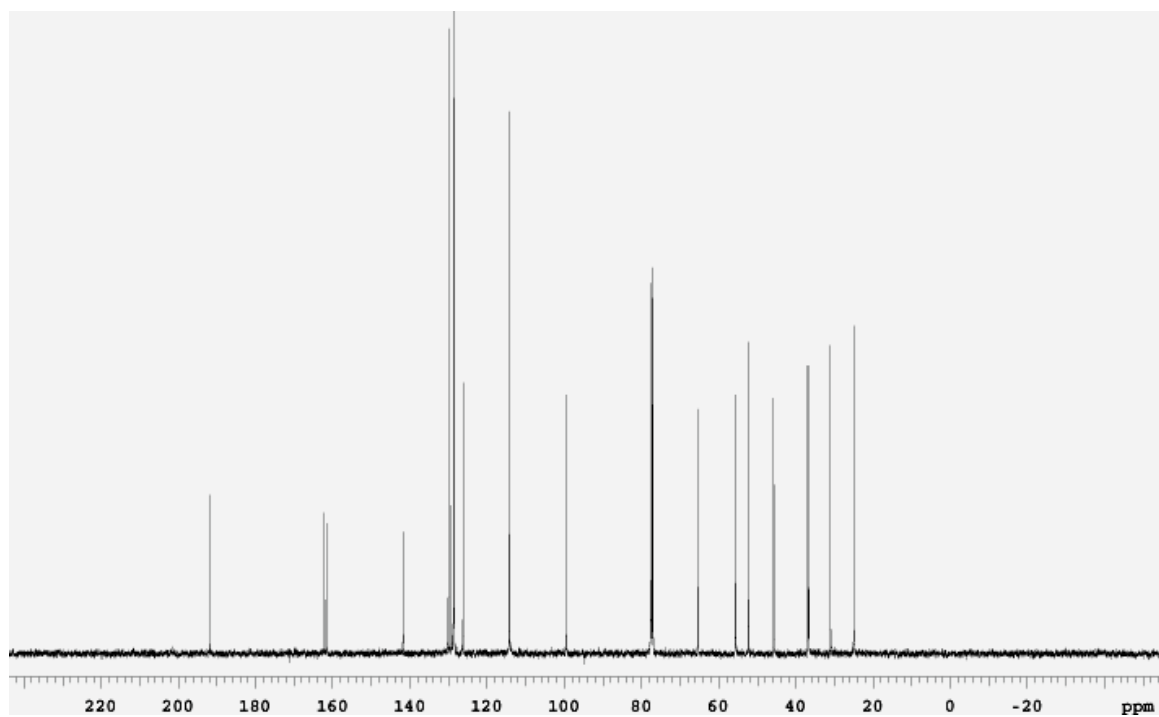
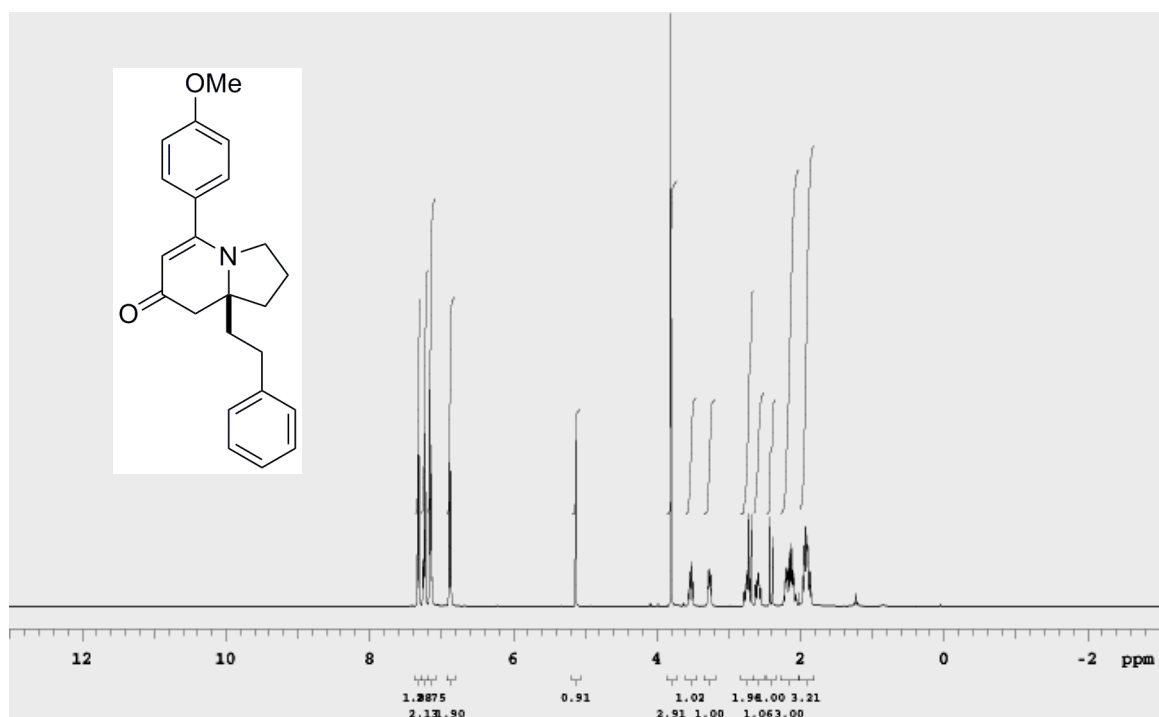


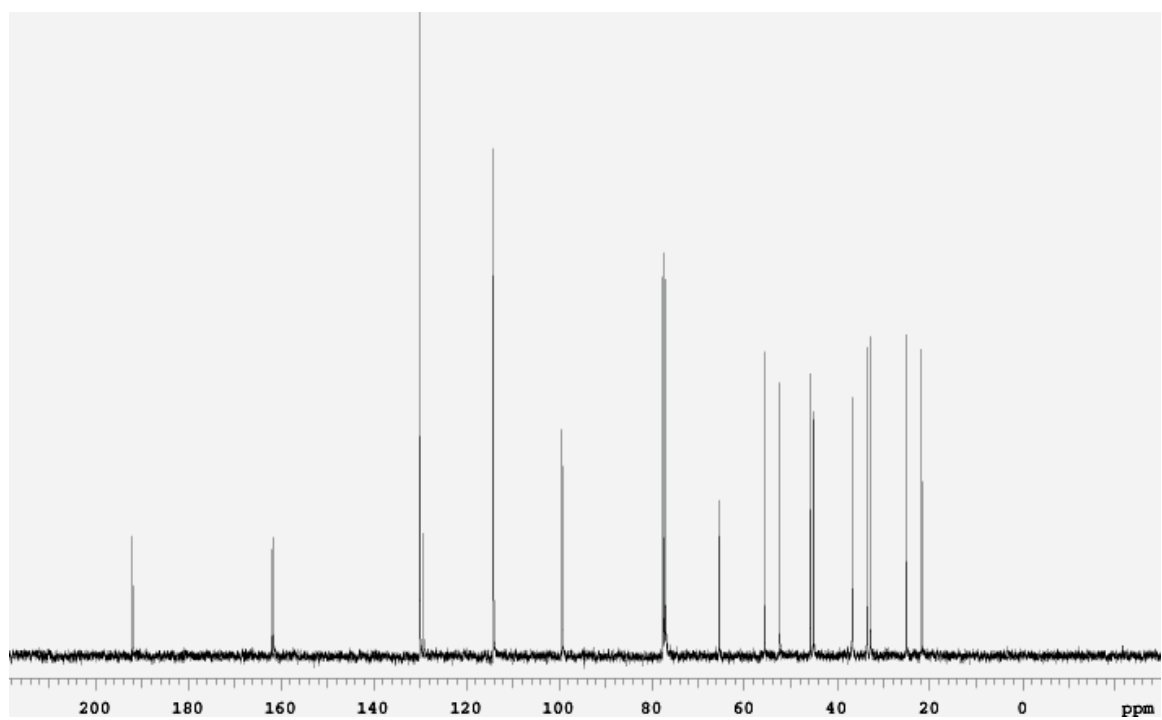
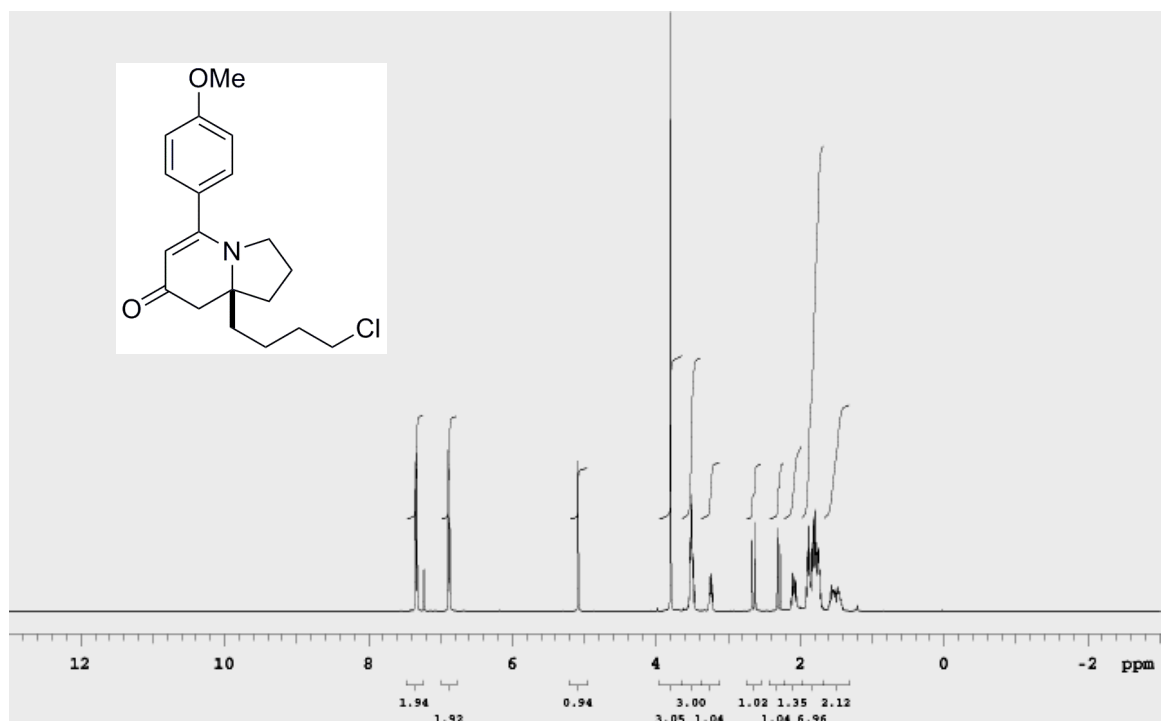


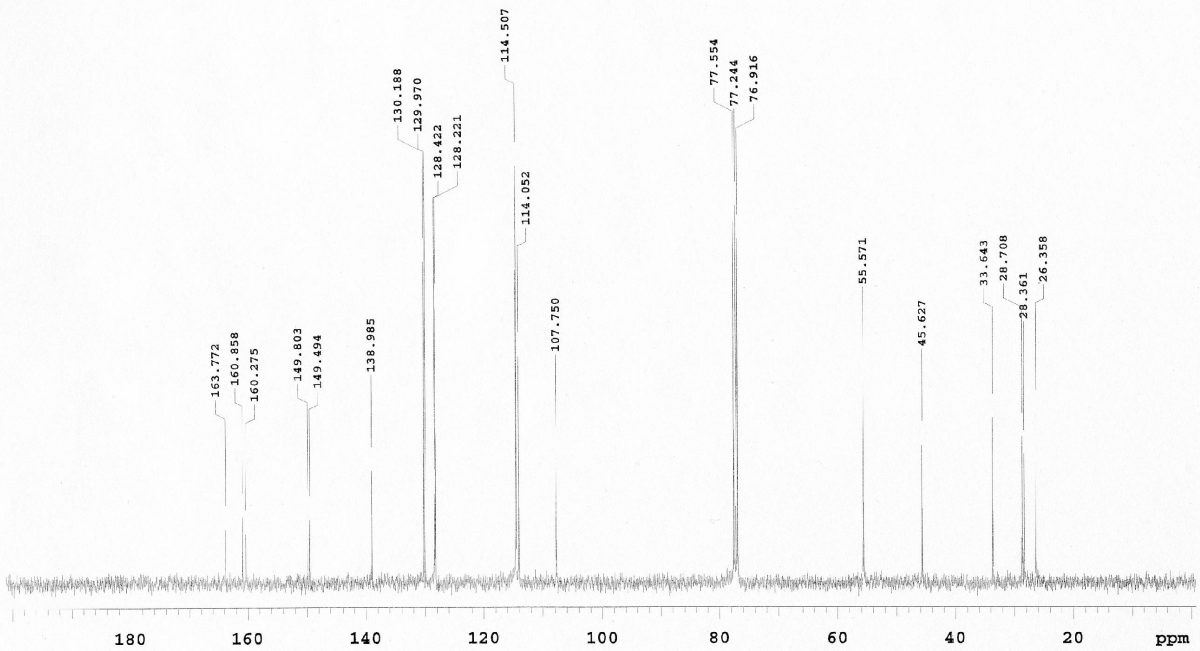
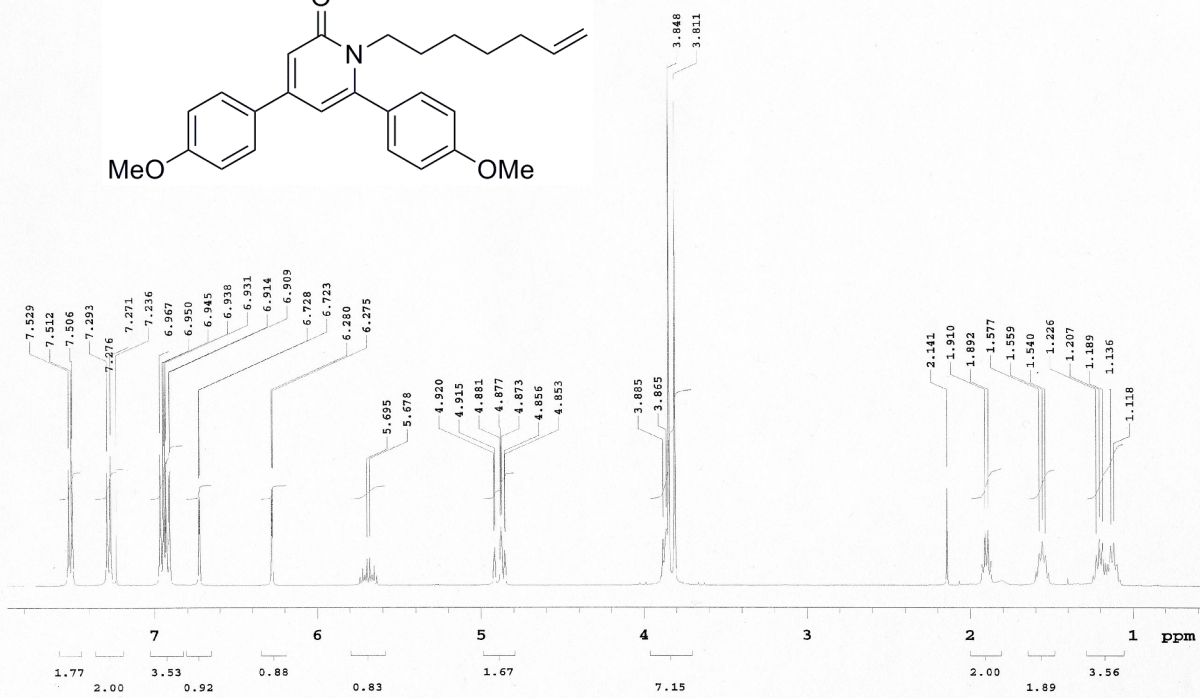
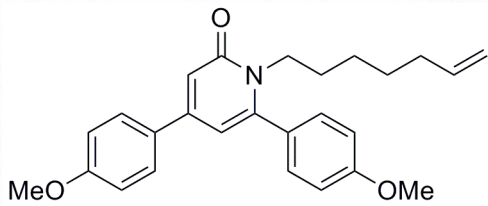




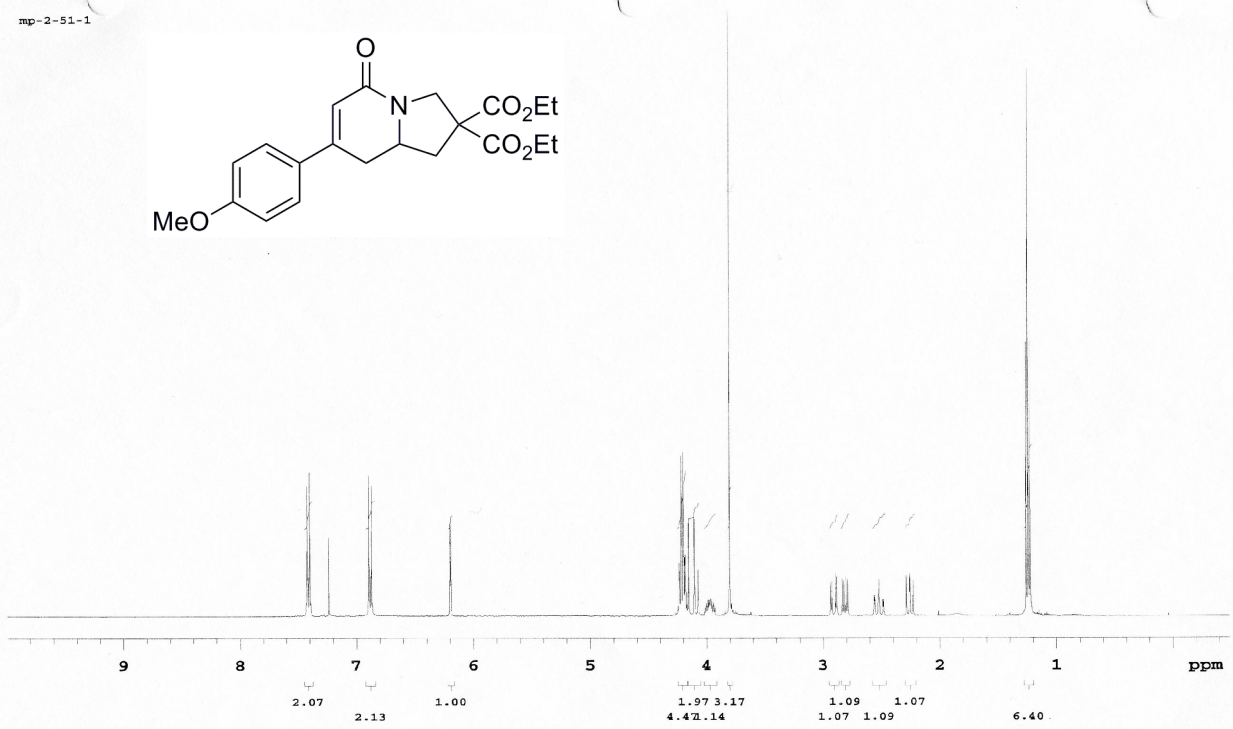
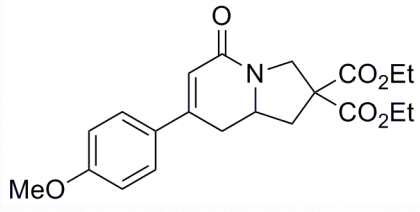




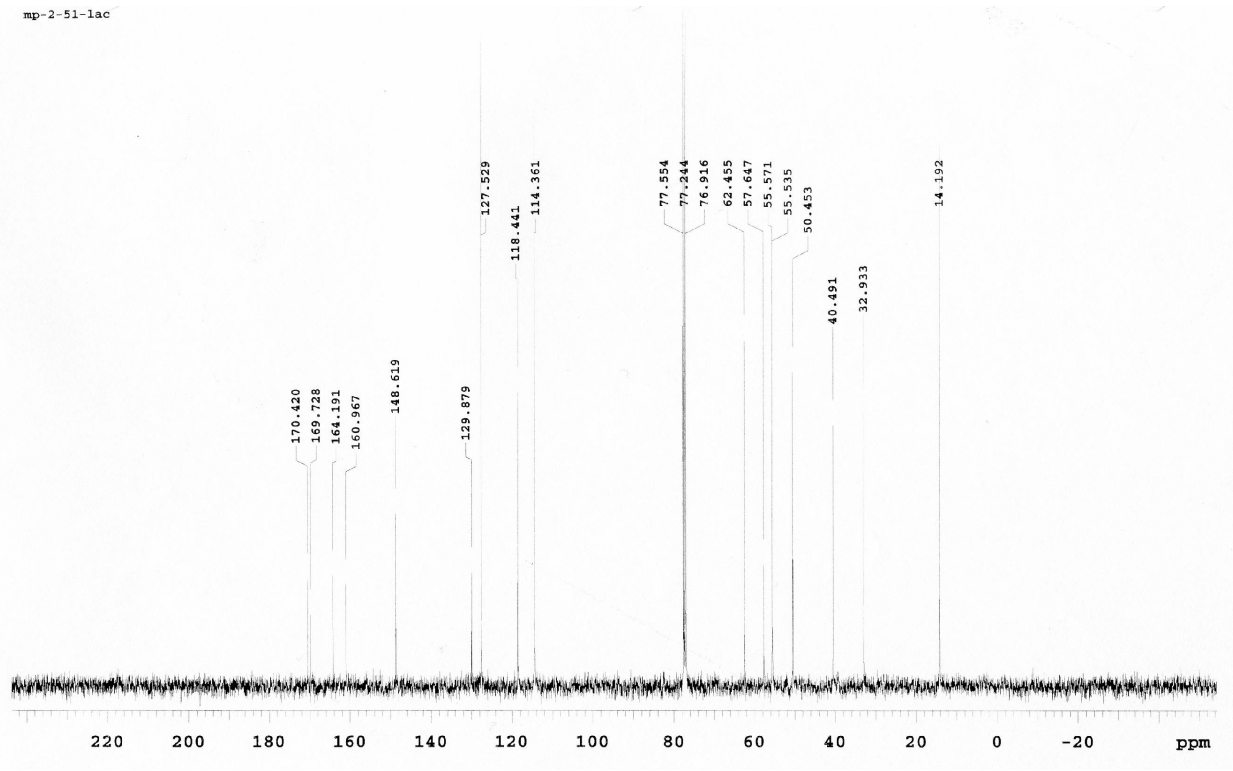




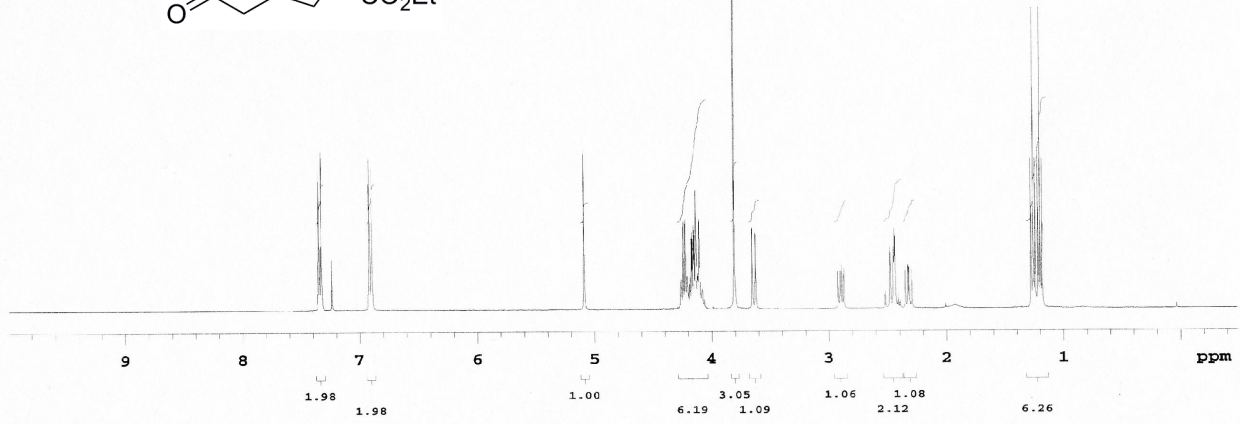
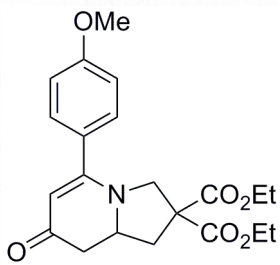
mp-2-51-1



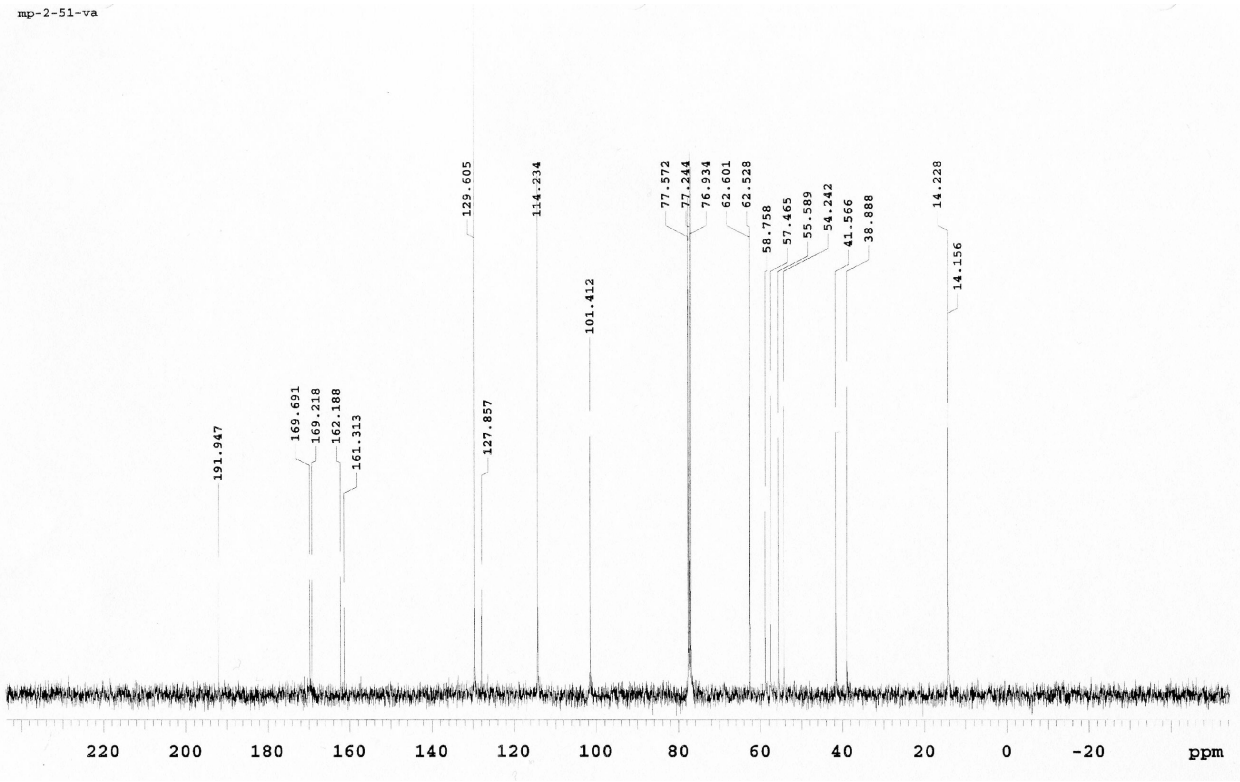
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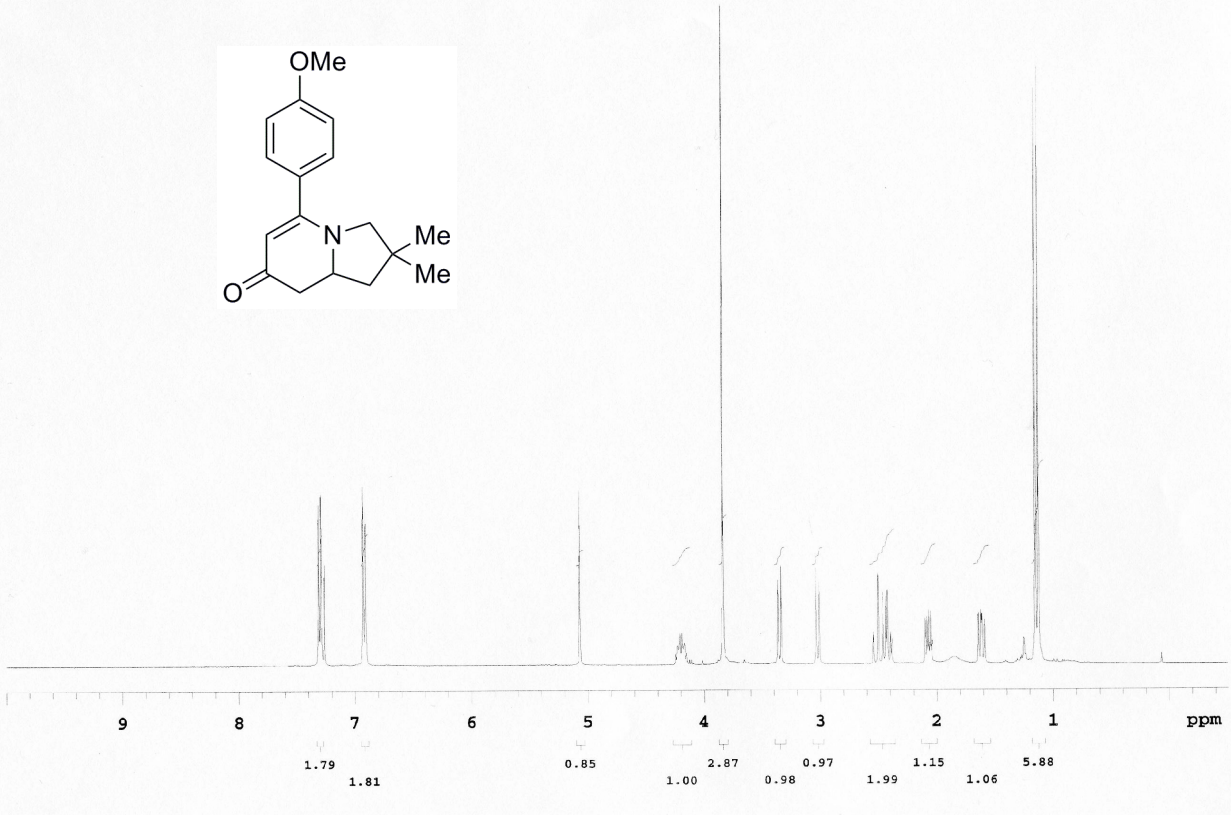
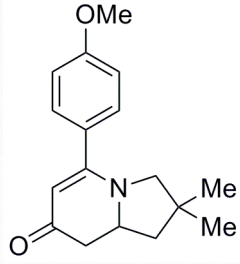
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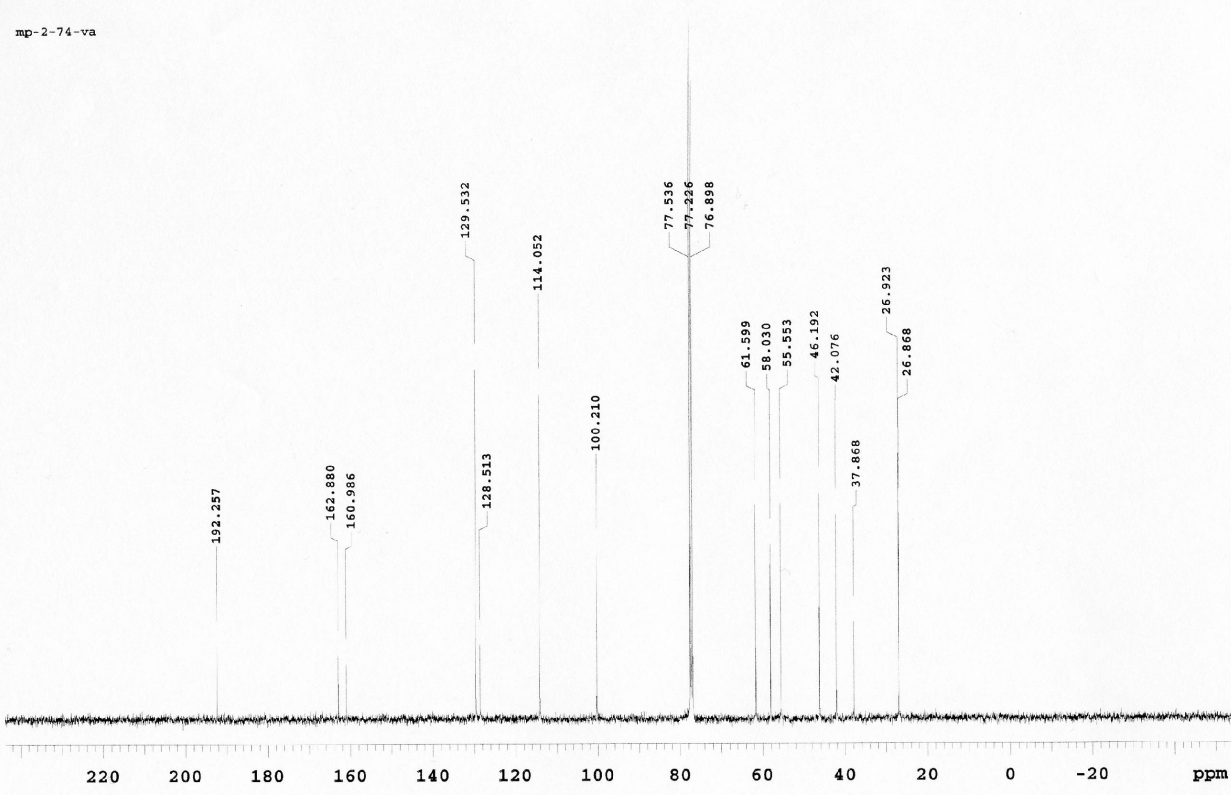
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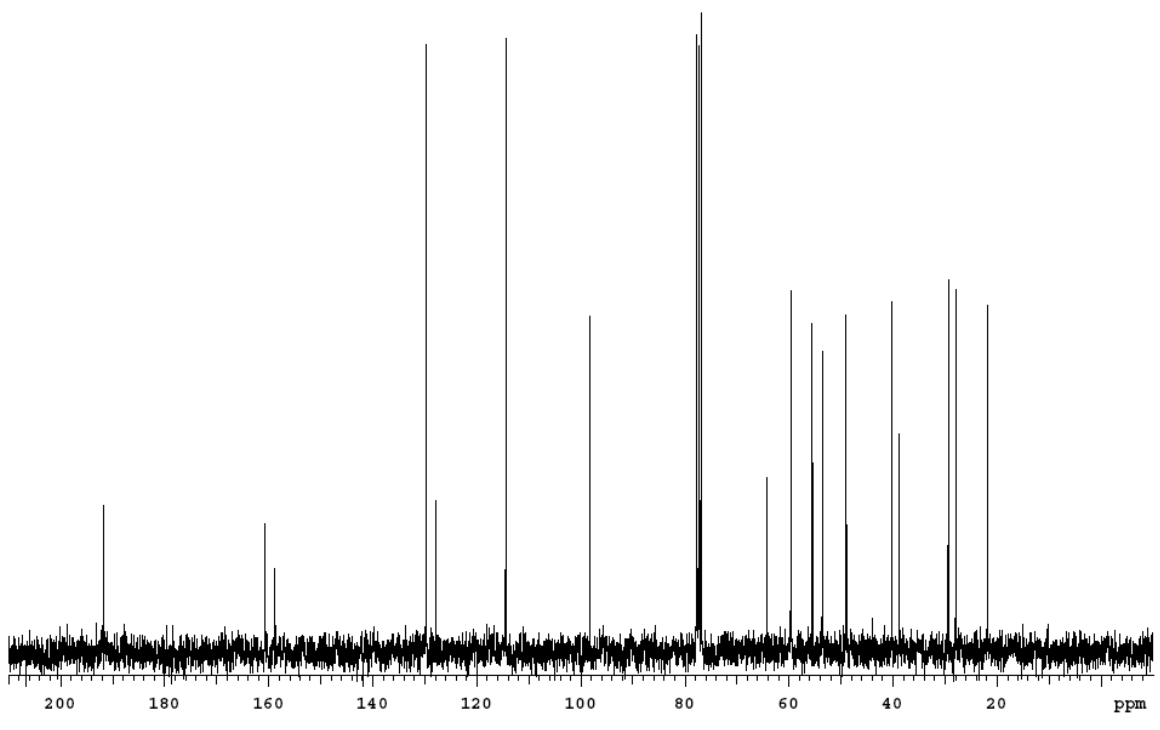
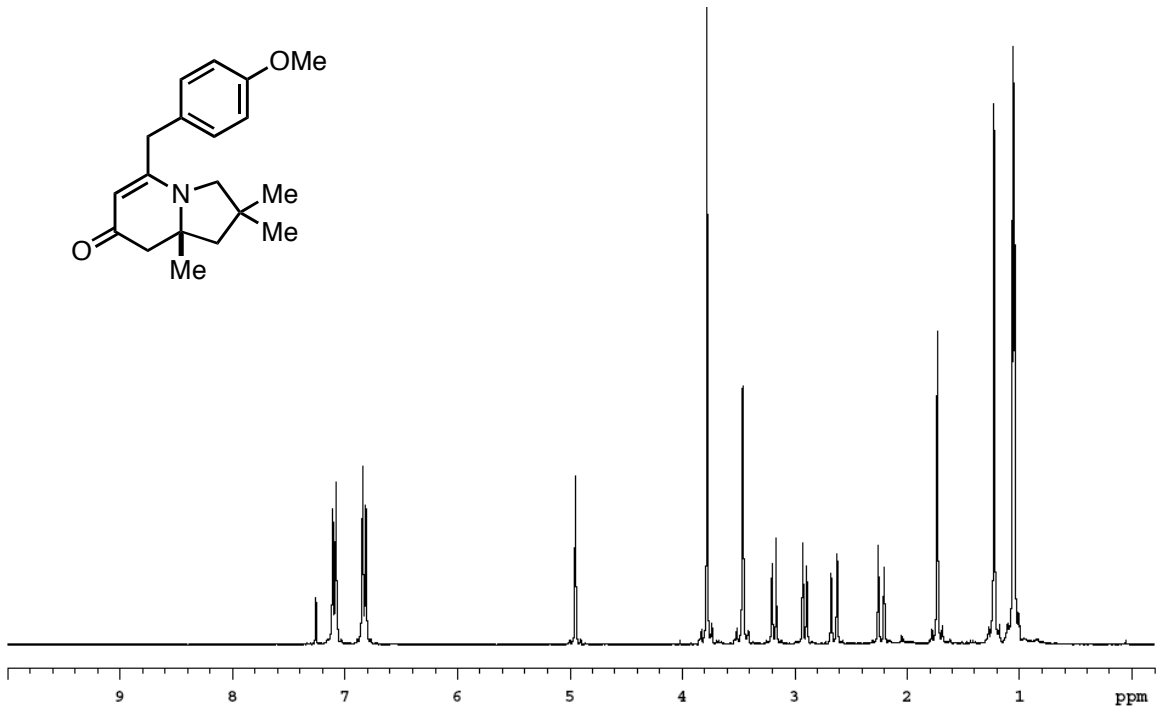
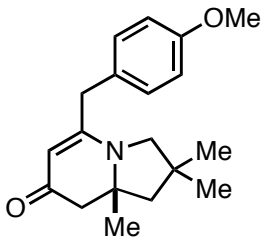


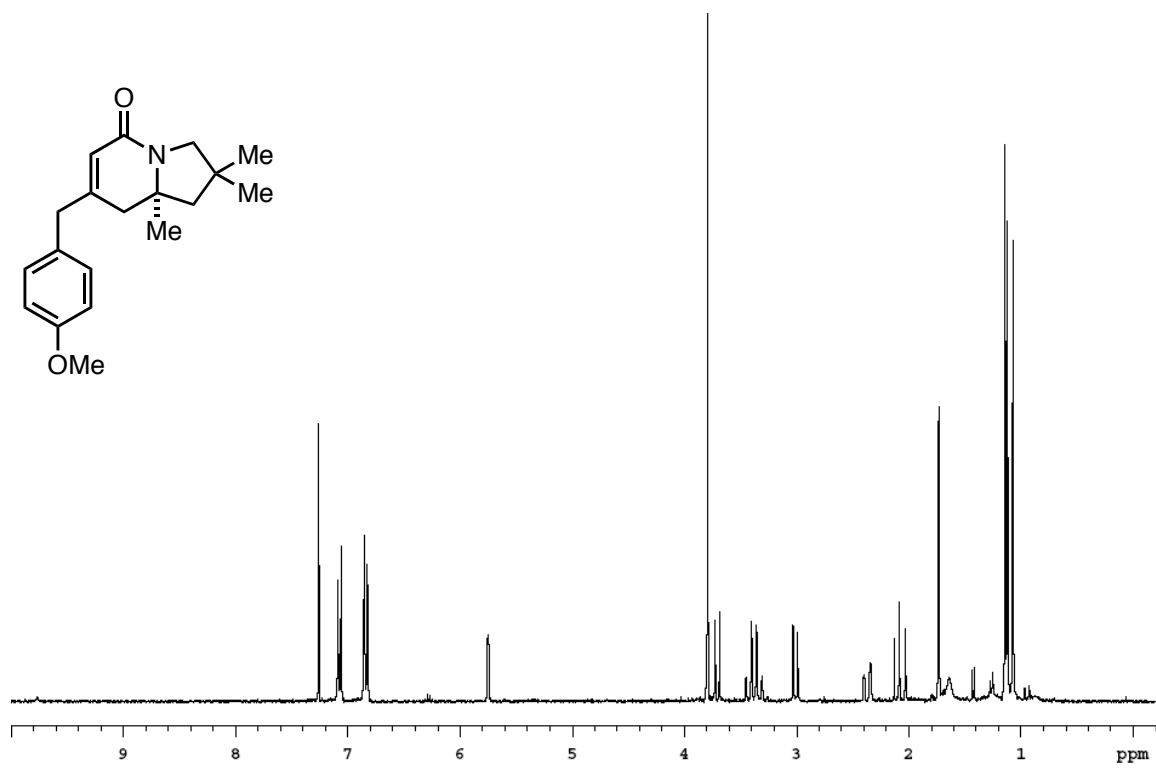
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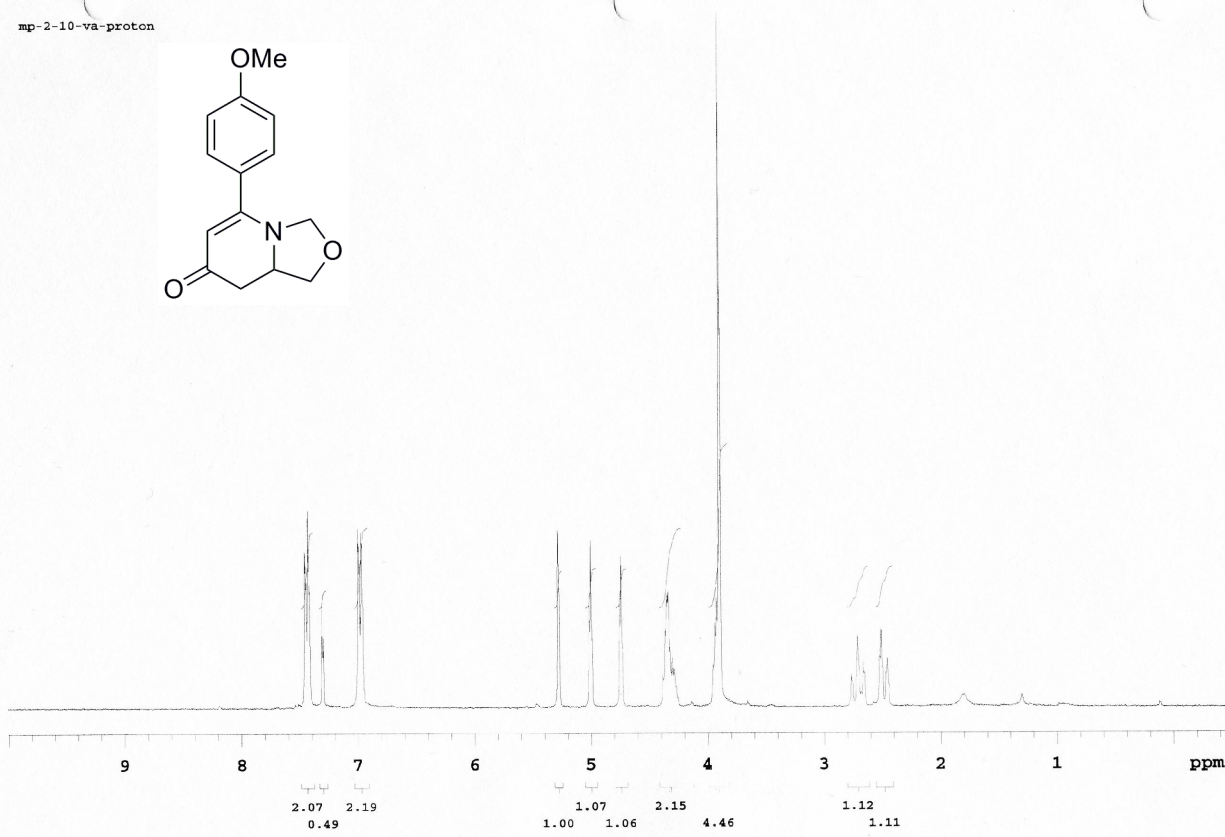
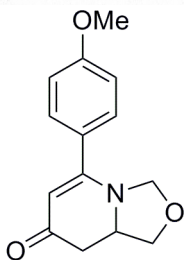
mp-2-74-va



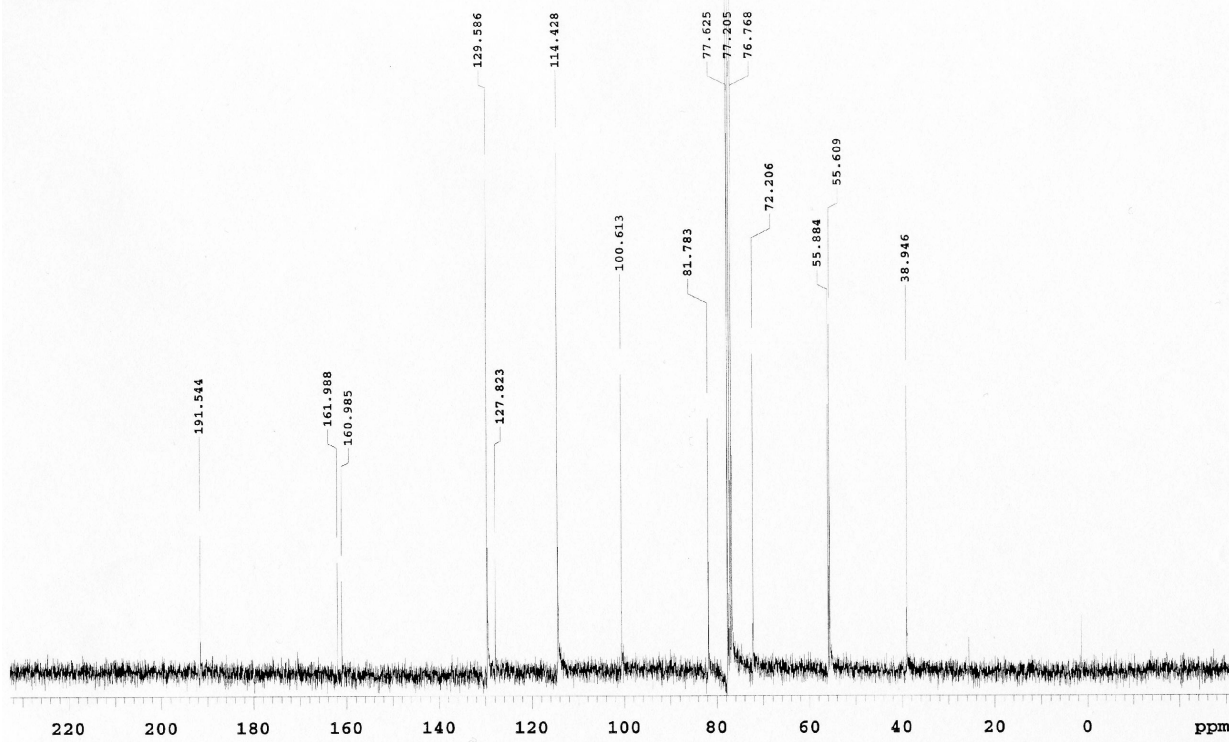


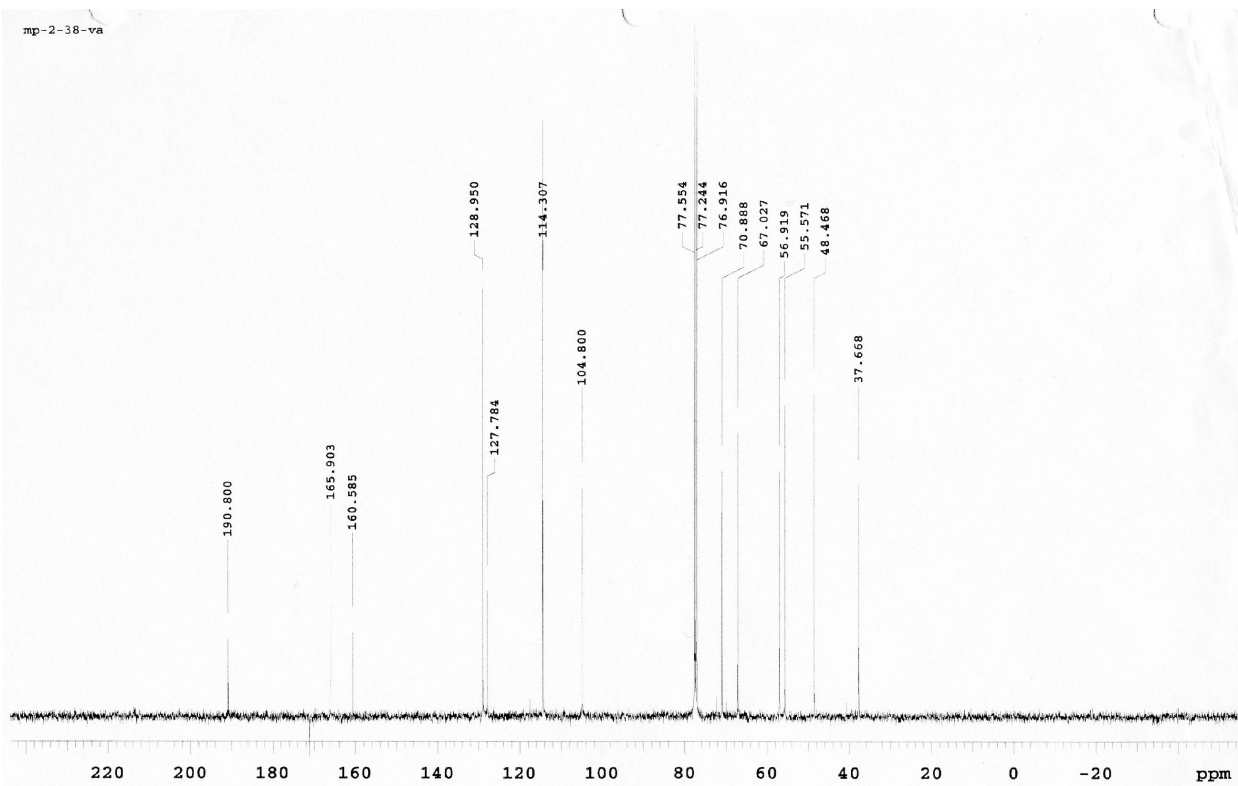
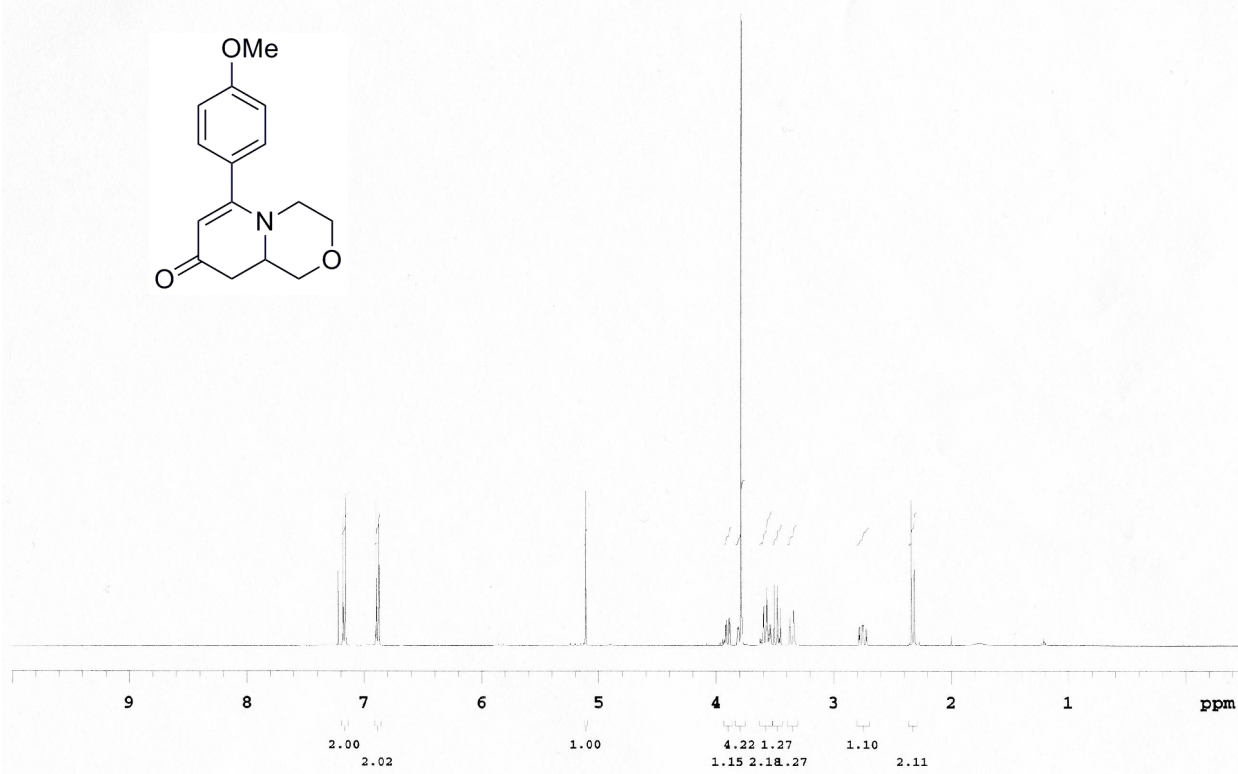
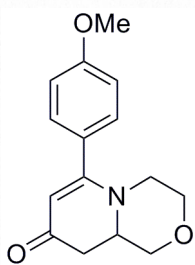


mp-2-10-va-proton



mp-2-10-va





Crystallographic Data:

All single crystals were coated in oil, transferred to a goniometer head, and mounted on a Bruker Kappa Apex CCD diffractometer under a stream of dinitrogen. All data collections were performed with Mo K α radiation and a graphite monochromator. Data sets were taken with complete coverage and fourfold redundancy at 120K. Data was integrated and corrected for absorption effects with the Apex 2 software package.⁶ Structures were solved with the SHELXTL software package.⁷ All non-hydrogen atoms were refined with anisotropic thermal parameters and hydrogen atoms placed in idealized positions. Crystal data and structure parameters are provided as CIF files. Rhodium alkene bond distances were generated in XP using cent/x and join.

Table 1. Crystal data and structure refinement for **T1**.

Identification code	rovis53_0m	
Empirical formula	C ₄₃ H ₅₀ Cl ₅ N O ₄ P Rh	
Formula weight	955.97	
Temperature	120 K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 2 ₁	
Unit cell dimensions	$a = 10.8877(3)$ Å	$\alpha = 90^\circ$
	$b = 18.0279(5)$ Å	$\beta = 91.9240(10)^\circ$
	$c = 11.1484(3)$ Å	$\gamma = 90^\circ$
Volume	2187.00(10) Å ³	
Z	2	
Density (calculated)	1.452 Mg/m ³	
Absorption coefficient	0.774 mm ⁻¹	
F(000)	984	
Crystal size	0.39 x 0.13 x 0.11 mm ³	
Theta range for data collection	1.83 to 40.55°.	
Index ranges	-19<=h<=19, -26<=k<=32, -19<=l<=20	
Reflections collected	54541	
Independent reflections	23417 [R(int) = 0.0421]	
Completeness to theta = 40.55°	98.0 %	
Absorption correction	Multi-scan	
Max. and min. transmission	0.9197 and 0.7512	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	23417 / 1 / 500	
Goodness-of-fit on F ²	1.005	
Final R indices [I>2sigma(I)]	R1 = 0.0511, wR2 = 0.1067	
R indices (all data)	R1 = 0.0786, wR2 = 0.1195	
Absolute structure parameter	-0.018(16)	
Largest diff. peak and hole	1.854 and -1.097 e.Å ⁻³	

Table 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **T1**. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	$U(\text{eq})$
C(1)	3074(3)	6207(2)	7166(3)	29(1)
C(2)	1226(2)	5493(1)	507(2)	14(1)
C(3)	2484(2)	5460(2)	292(2)	18(1)
C(4)	3092(2)	4786(2)	259(3)	23(1)
C(5)	2441(3)	4130(2)	424(3)	26(1)
C(6)	1199(3)	4155(2)	620(3)	24(1)
C(7)	585(2)	4834(1)	653(2)	19(1)
C(8)	590(2)	6245(1)	512(2)	12(1)
C(9)	402(2)	6528(1)	-775(2)	14(1)
C(10)	727(2)	7236(1)	-1124(2)	18(1)
C(11)	464(3)	7485(2)	-2298(2)	26(1)
C(12)	-134(3)	7017(2)	-3111(2)	28(1)
C(13)	-445(2)	6302(2)	-2783(2)	22(1)
C(14)	-162(2)	6053(2)	-1626(2)	18(1)
C(15)	-645(2)	6235(1)	1178(2)	13(1)
C(16)	-1006(2)	7012(1)	1583(2)	14(1)
C(17)	-2642(2)	6527(2)	462(2)	17(1)
C(18)	-3816(2)	6144(2)	798(3)	27(1)
C(19)	-2745(2)	6924(2)	-739(2)	22(1)
C(20)	-2564(2)	7261(2)	4162(3)	30(1)
C(21)	-3472(3)	6945(2)	4864(3)	38(1)
C(22)	-3436(2)	6196(2)	5135(3)	34(1)
C(23)	-2489(3)	5767(2)	4745(3)	27(1)
C(24)	-1567(2)	6084(2)	4054(2)	22(1)
C(25)	-1614(2)	6831(2)	3743(2)	16(1)
C(26)	-654(2)	7170(1)	2923(2)	13(1)
C(27)	-1118(2)	8524(2)	2479(2)	20(1)
C(28)	-497(2)	7996(2)	3178(2)	16(1)
C(29)	192(2)	8227(2)	4184(2)	20(1)
C(30)	242(3)	8973(2)	4504(3)	27(1)
C(31)	-413(3)	9495(2)	3817(3)	30(1)
C(32)	-1077(3)	9275(2)	2789(3)	26(1)

C(33)	1872(2)	5422(2)	3435(3)	23(1)
C(34)	3801(2)	6066(2)	3106(3)	22(1)
C(35)	3710(2)	9042(1)	3233(2)	19(1)
C(36)	4657(2)	8550(2)	3073(2)	20(1)
C(37)	5357(2)	8446(2)	1933(3)	23(1)
C(38)	4525(2)	8412(2)	801(2)	23(1)
C(39)	3283(2)	8043(1)	1008(2)	17(1)
C(40)	2226(2)	8450(1)	1316(2)	15(1)
C(41)	3249(2)	9587(2)	2281(2)	22(1)
C(42)	2153(2)	9276(2)	1524(2)	20(1)
C(43)	3397(4)	8641(3)	7535(5)	56(1)
Cl(1)	3137(1)	7566(1)	4920(1)	21(1)
Cl(2)	3749(1)	5357(1)	6704(1)	38(1)
Cl(3)	4118(1)	6716(1)	8085(1)	47(1)
Cl(4)	4889(2)	8948(1)	7369(2)	119(1)
Cl(5)	2367(2)	9333(1)	7852(2)	83(1)
N(1)	2454(2)	6106(1)	3050(2)	16(1)
O(1)	-2308(2)	7035(1)	1402(2)	19(1)
O(2)	-1664(2)	5988(1)	450(2)	17(1)
O(3)	1374(1)	6787(1)	1137(1)	12(1)
O(4)	493(1)	6771(1)	3220(1)	13(1)
P(1)	1779(1)	6862(1)	2553(1)	12(1)
Rh(1)	2923(1)	7898(1)	2860(1)	13(1)

Table 3. Bond lengths [\AA] and angles [$^\circ$] for **T1**.

C(1)-Cl(3)	1.763(3)	C(26)-C(28)	1.525(4)
C(1)-Cl(2)	1.784(4)	C(27)-C(28)	1.391(4)
C(2)-C(7)	1.391(3)	C(27)-C(32)	1.399(4)
C(2)-C(3)	1.400(3)	C(28)-C(29)	1.393(3)
C(2)-C(8)	1.521(3)	C(29)-C(30)	1.392(4)
C(3)-C(4)	1.385(4)	C(30)-C(31)	1.393(5)
C(4)-C(5)	1.395(4)	C(31)-C(32)	1.392(5)
C(5)-C(6)	1.378(4)	C(33)-N(1)	1.459(3)
C(6)-C(7)	1.396(4)	C(34)-N(1)	1.468(3)
C(8)-O(3)	1.460(3)	C(35)-C(36)	1.376(4)
C(8)-C(9)	1.530(3)	C(35)-C(41)	1.520(4)
C(8)-C(15)	1.558(3)	C(35)-Rh(1)	2.266(2)
C(9)-C(10)	1.384(3)	C(36)-C(37)	1.516(4)
C(9)-C(14)	1.404(3)	C(36)-Rh(1)	2.230(2)
C(10)-C(11)	1.404(3)	C(37)-C(38)	1.528(4)
C(11)-C(12)	1.385(4)	C(38)-C(39)	1.531(3)
C(12)-C(13)	1.386(4)	C(39)-C(40)	1.417(3)
C(13)-C(14)	1.390(3)	C(39)-Rh(1)	2.130(2)
C(15)-O(2)	1.424(3)	C(40)-C(42)	1.509(4)
C(15)-C(16)	1.527(3)	C(40)-Rh(1)	2.107(2)
C(16)-O(1)	1.425(3)	C(41)-C(42)	1.544(4)
C(16)-C(26)	1.556(3)	C(43)-Cl(5)	1.721(5)
C(17)-O(1)	1.429(3)	C(43)-Cl(4)	1.732(5)
C(17)-O(2)	1.442(3)	Cl(1)-Rh(1)	2.3777(6)
C(17)-C(18)	1.511(4)	N(1)-P(1)	1.637(2)
C(17)-C(19)	1.519(4)	O(3)-P(1)	1.6300(16)
C(20)-C(25)	1.386(4)	O(4)-P(1)	1.6153(16)
C(20)-C(21)	1.402(4)	P(1)-Rh(1)	2.2648(6)
C(21)-C(22)	1.383(5)	Cl(3)-C(1)-Cl(2)	110.53(16)
C(22)-C(23)	1.372(5)	C(7)-C(2)-C(3)	118.8(2)
C(23)-C(24)	1.406(4)	C(7)-C(2)-C(8)	122.0(2)
C(24)-C(25)	1.392(4)	C(3)-C(2)-C(8)	119.1(2)
C(25)-C(26)	1.537(3)	C(4)-C(3)-C(2)	120.9(2)
C(26)-O(4)	1.468(3)	C(3)-C(4)-C(5)	119.7(2)
		C(6)-C(5)-C(4)	120.0(3)

C(5)-C(6)-C(7)	120.3(3)	O(4)-C(26)-C(25)	105.20(18)
C(2)-C(7)-C(6)	120.3(2)	C(28)-C(26)-C(25)	110.54(19)
O(3)-C(8)-C(2)	109.83(17)	O(4)-C(26)-C(16)	107.92(17)
O(3)-C(8)-C(9)	106.34(17)	C(28)-C(26)-C(16)	112.29(19)
C(2)-C(8)-C(9)	109.85(18)	C(25)-C(26)-C(16)	110.36(18)
O(3)-C(8)-C(15)	106.30(17)	C(28)-C(27)-C(32)	120.9(3)
C(2)-C(8)-C(15)	113.08(18)	C(27)-C(28)-C(29)	119.0(3)
C(9)-C(8)-C(15)	111.15(17)	C(27)-C(28)-C(26)	121.0(2)
C(10)-C(9)-C(14)	118.8(2)	C(29)-C(28)-C(26)	119.8(2)
C(10)-C(9)-C(8)	123.0(2)	C(30)-C(29)-C(28)	120.7(3)
C(14)-C(9)-C(8)	118.2(2)	C(29)-C(30)-C(31)	119.8(3)
C(9)-C(10)-C(11)	120.8(2)	C(32)-C(31)-C(30)	120.1(3)
C(12)-C(11)-C(10)	119.5(3)	C(31)-C(32)-C(27)	119.4(3)
C(11)-C(12)-C(13)	120.5(2)	C(36)-C(35)-C(41)	123.8(2)
C(12)-C(13)-C(14)	119.8(2)	C(36)-C(35)-Rh(1)	70.77(15)
C(13)-C(14)-C(9)	120.5(2)	C(41)-C(35)-Rh(1)	110.26(16)
O(2)-C(15)-C(16)	104.60(17)	C(35)-C(36)-C(37)	126.1(2)
O(2)-C(15)-C(8)	113.61(18)	C(35)-C(36)-Rh(1)	73.61(14)
C(16)-C(15)-C(8)	111.45(18)	C(37)-C(36)-Rh(1)	106.97(17)
O(1)-C(16)-C(15)	104.45(18)	C(36)-C(37)-C(38)	113.4(2)
O(1)-C(16)-C(26)	110.04(18)	C(37)-C(38)-C(39)	113.3(2)
C(15)-C(16)-C(26)	113.16(18)	C(40)-C(39)-C(38)	122.7(2)
O(1)-C(17)-O(2)	105.60(17)	C(40)-C(39)-Rh(1)	69.58(13)
O(1)-C(17)-C(18)	108.0(2)	C(38)-C(39)-Rh(1)	112.99(16)
O(2)-C(17)-C(18)	108.9(2)	C(39)-C(40)-C(42)	126.5(2)
O(1)-C(17)-C(19)	110.7(2)	C(39)-C(40)-Rh(1)	71.36(13)
O(2)-C(17)-C(19)	109.98(19)	C(42)-C(40)-Rh(1)	111.08(16)
C(18)-C(17)-C(19)	113.3(2)	C(35)-C(41)-C(42)	112.2(2)
C(25)-C(20)-C(21)	120.7(3)	C(40)-C(42)-C(41)	113.5(2)
C(22)-C(21)-C(20)	120.2(3)	Cl(5)-C(43)-Cl(4)	114.2(3)
C(23)-C(22)-C(21)	119.8(3)	C(33)-N(1)-C(34)	112.9(2)
C(22)-C(23)-C(24)	120.1(3)	C(33)-N(1)-P(1)	127.56(16)
C(25)-C(24)-C(23)	120.6(3)	C(34)-N(1)-P(1)	119.52(17)
C(20)-C(25)-C(24)	118.6(2)	C(16)-O(1)-C(17)	108.22(17)
C(20)-C(25)-C(26)	120.6(2)	C(15)-O(2)-C(17)	110.19(18)
C(24)-C(25)-C(26)	120.8(2)	C(8)-O(3)-P(1)	130.68(14)
O(4)-C(26)-C(28)	110.26(17)	C(26)-O(4)-P(1)	126.17(14)

O(4)-P(1)-O(3)	103.16(8)	C(40)-Rh(1)-C(35)	81.04(9)
O(4)-P(1)-N(1)	98.40(10)	C(39)-Rh(1)-C(35)	89.20(9)
O(3)-P(1)-N(1)	111.29(10)	C(36)-Rh(1)-C(35)	35.62(9)
O(4)-P(1)-Rh(1)	119.67(7)	P(1)-Rh(1)-C(35)	168.73(7)
O(3)-P(1)-Rh(1)	110.11(6)	C(40)-Rh(1)-Cl(1)	158.25(7)
N(1)-P(1)-Rh(1)	113.35(8)	C(39)-Rh(1)-Cl(1)	162.17(6)
C(40)-Rh(1)-C(39)	39.06(9)	C(36)-Rh(1)-Cl(1)	88.55(7)
C(40)-Rh(1)-C(36)	96.83(9)	P(1)-Rh(1)-Cl(1)	88.50(2)
C(39)-Rh(1)-C(36)	81.75(9)	C(35)-Rh(1)-Cl(1)	91.57(7)
C(40)-Rh(1)-P(1)	94.83(7)		
C(39)-Rh(1)-P(1)	94.17(6)		
C(36)-Rh(1)-P(1)	155.60(7)		

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **T1**. The anisotropic displacement factor exponent takes the form: $-2p^2 [h^2 a^{*2} U^{11} + \dots + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C(1)	24(1)	34(2)	30(1)	8(1)	-1(1)	-1(1)
C(2)	15(1)	12(1)	15(1)	0(1)	1(1)	0(1)
C(3)	16(1)	19(1)	20(1)	-1(1)	5(1)	-1(1)
C(4)	17(1)	20(1)	32(1)	-4(1)	3(1)	6(1)
C(5)	30(1)	17(1)	31(1)	-2(1)	-2(1)	6(1)
C(6)	30(1)	13(1)	28(1)	-1(1)	3(1)	0(1)
C(7)	20(1)	15(1)	21(1)	0(1)	0(1)	-1(1)
C(8)	11(1)	11(1)	13(1)	0(1)	1(1)	-1(1)
C(9)	15(1)	14(1)	12(1)	0(1)	1(1)	2(1)
C(10)	24(1)	16(1)	15(1)	1(1)	0(1)	-3(1)
C(11)	34(1)	26(1)	17(1)	7(1)	-2(1)	-6(1)
C(12)	34(1)	36(2)	13(1)	4(1)	-2(1)	-6(1)
C(13)	26(1)	27(1)	13(1)	-2(1)	-3(1)	-1(1)
C(14)	19(1)	18(1)	17(1)	0(1)	-1(1)	-2(1)
C(15)	12(1)	15(1)	12(1)	0(1)	0(1)	-1(1)
C(16)	13(1)	15(1)	14(1)	1(1)	-1(1)	2(1)
C(17)	14(1)	20(1)	17(1)	-3(1)	-1(1)	0(1)
C(18)	15(1)	35(2)	31(1)	2(1)	2(1)	-2(1)
C(19)	18(1)	28(1)	19(1)	1(1)	-4(1)	2(1)
C(20)	18(1)	40(2)	32(1)	15(1)	9(1)	7(1)
C(21)	21(1)	53(2)	41(2)	17(2)	17(1)	8(1)
C(22)	15(1)	59(2)	28(1)	23(1)	2(1)	-7(1)
C(23)	31(1)	29(2)	22(1)	7(1)	1(1)	-14(1)
C(24)	24(1)	23(1)	18(1)	0(1)	5(1)	-6(1)
C(25)	12(1)	23(1)	14(1)	5(1)	1(1)	-3(1)
C(26)	11(1)	16(1)	13(1)	0(1)	1(1)	1(1)
C(27)	19(1)	20(1)	21(1)	2(1)	7(1)	3(1)
C(28)	15(1)	19(1)	16(1)	-2(1)	5(1)	-1(1)
C(29)	20(1)	22(1)	18(1)	-2(1)	3(1)	-5(1)
C(30)	31(1)	23(1)	28(1)	-9(1)	7(1)	-5(1)
C(31)	36(2)	17(1)	38(2)	-10(1)	18(1)	-3(1)
C(32)	26(1)	18(1)	34(1)	4(1)	12(1)	5(1)

C(33)	22(1)	17(1)	28(1)	10(1)	-5(1)	-3(1)
C(34)	14(1)	24(1)	28(1)	2(1)	1(1)	3(1)
C(35)	20(1)	15(1)	20(1)	-3(1)	1(1)	-5(1)
C(36)	14(1)	19(1)	26(1)	2(1)	-3(1)	-4(1)
C(37)	14(1)	23(1)	32(1)	-1(1)	3(1)	-3(1)
C(38)	19(1)	23(1)	27(1)	-2(1)	9(1)	-4(1)
C(39)	17(1)	19(1)	14(1)	0(1)	2(1)	-4(1)
C(40)	16(1)	16(1)	14(1)	0(1)	2(1)	-1(1)
C(41)	26(1)	12(1)	27(1)	-1(1)	1(1)	-2(1)
C(42)	22(1)	16(1)	23(1)	2(1)	0(1)	1(1)
C(43)	53(2)	53(3)	61(3)	-22(2)	0(2)	-1(2)
Cl(1)	23(1)	25(1)	14(1)	0(1)	-1(1)	-3(1)
Cl(2)	29(1)	36(1)	51(1)	10(1)	12(1)	0(1)
Cl(3)	43(1)	52(1)	45(1)	7(1)	-12(1)	-17(1)
Cl(4)	67(1)	161(2)	131(2)	-45(2)	11(1)	-50(1)
Cl(5)	118(1)	44(1)	90(1)	-13(1)	38(1)	11(1)
N(1)	12(1)	15(1)	20(1)	3(1)	-1(1)	0(1)
O(1)	13(1)	24(1)	17(1)	-5(1)	-2(1)	3(1)
O(2)	12(1)	19(1)	20(1)	-2(1)	-3(1)	-1(1)
O(3)	13(1)	12(1)	12(1)	0(1)	-1(1)	-3(1)
O(4)	12(1)	14(1)	14(1)	3(1)	2(1)	0(1)
P(1)	11(1)	13(1)	11(1)	1(1)	0(1)	-1(1)
Rh(1)	12(1)	13(1)	13(1)	-1(1)	1(1)	-2(1)

Table 5. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **T1**.

	x	y	z	U(eq)
H(1A)	2838	6499	6465	35
H(1B)	2339	6103	7605	35
H(3)	2917	5897	169	22
H(4)	3931	4772	129	28
H(5)	2845	3676	402	31
H(6)	767	3716	730	28
H(7)	-256	4845	774	22
H(10)	1123	7550	-575	22
H(11)	691	7960	-2527	31
H(12)	-330	7185	-3883	34
H(13)	-841	5989	-3335	26
H(14)	-349	5568	-1414	21
H(15)	-556	5913	1884	15
H(16)	-625	7384	1073	17
H(18A)	-3702	5917	1573	40
H(18B)	-4021	5769	213	40
H(18C)	-4469	6500	822	40
H(19A)	-3383	7290	-717	33
H(19B)	-2938	6571	-1362	33
H(19C)	-1978	7161	-897	33
H(20)	-2599	7763	3976	35
H(21)	-4100	7240	5148	45
H(22)	-4052	5985	5580	40
H(23)	-2456	5265	4937	33
H(24)	-921	5791	3803	26
H(27)	-1566	8375	1796	24
H(29)	625	7880	4648	24
H(30)	709	9123	5174	33
H(31)	-405	9991	4045	36
H(32)	-1491	9625	2314	31
H(33A)	2179	5012	2983	34

H(33B)	999	5459	3304	34
H(33C)	2057	5343	4274	34
H(34A)	4079	5957	3914	33
H(34B)	4136	6533	2863	33
H(34C)	4069	5682	2580	33
H(35)	3630	9214	4061	22
H(36)	5138	8438	3809	24
H(37A)	5828	7990	1996	28
H(37B)	5932	8852	1856	28
H(38A)	4944	8138	187	27
H(38B)	4385	8912	507	27
H(39)	3113	7605	508	20
H(40)	1457	8236	990	18
H(41A)	3914	9704	1755	26
H(41B)	3001	10043	2666	26
H(42A)	1398	9386	1927	24
H(42B)	2116	9526	753	24
H(43A)	3121	8394	6801	67
H(43B)	3394	8277	8176	67

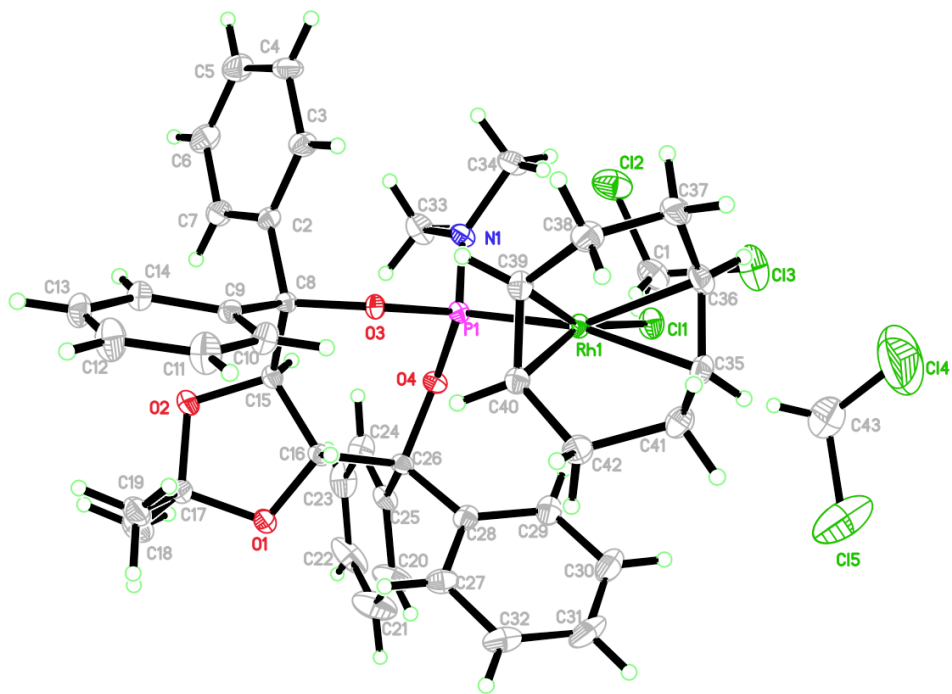


Table 6. Crystal data and structure refinement for **T2**.

Identification code	T2	
Empirical formula	C ₄₅ H ₅₂ Cl ₅ NO ₄ PRh	
Formula weight	982.01	
Temperature	120 K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2 ₁	
Unit cell dimensions	$a = 10.8926(7)$ Å	$\alpha = 90^\circ$.
	$b = 18.1189(11)$ Å	$\beta = 91.835(3)^\circ$.
	$c = 11.2230(7)$ Å	$\gamma = 90^\circ$.
Volume	2213.9(2) Å ³	
Z	2	
Density (calculated)	1.473 Mg/m ³	
Absorption coefficient	0.767 mm ⁻¹	
F(000)	1012	
Crystal size	0.32 x 0.30 x 0.26 mm ³	
Theta range for data collection	2.14 to 35.63°.	
Index ranges	-17 ≤ h ≤ 17, -29 ≤ k ≤ 29, -18 ≤ l ≤ 17	
Reflections collected	77157	
Independent reflections	20295 [R(int) = 0.0257]	
Completeness to theta = 35.63°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.8249 and 0.7898	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	20295 / 1 / 517	
Goodness-of-fit on F ²	1.018	
Final R indices [I > 2σ(I)]	R1 = 0.0232, wR2 = 0.0574	
R indices (all data)	R1 = 0.0246, wR2 = 0.0581	
Absolute structure parameter	-0.016(8)	
Largest diff. peak and hole	1.092 and -0.978 e.Å ⁻³	

Table 7. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **T2**. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	$U(\text{eq})$
C(1)	-688(1)	709(1)	7937(1)	13(1)
C(2)	-1052(1)	547(1)	6607(1)	14(1)
C(3)	-697(1)	-230(1)	6211(1)	13(1)
C(4)	541(1)	-227(1)	5541(1)	12(1)
C(5)	-2589(1)	816(1)	9192(1)	23(1)
C(6)	-1638(1)	378(1)	8768(1)	15(1)
C(7)	-1592(1)	-365(1)	9092(1)	18(1)
C(8)	-2481(1)	-667(1)	9816(1)	24(1)
C(9)	1168(1)	-978(1)	5536(1)	13(1)
C(10)	534(1)	-1632(1)	5753(1)	19(1)
C(11)	2408(1)	-1018(1)	5240(1)	16(1)
C(12)	3007(1)	-1692(1)	5198(1)	21(1)
C(13)	1139(1)	-2312(1)	5707(1)	24(1)
C(14)	-517(1)	1527(1)	8181(1)	15(1)
C(15)	-1110(1)	2061(1)	7475(1)	19(1)
C(16)	1754(1)	-987(1)	8671(1)	19(1)
C(17)	3694(1)	-502(1)	7975(1)	18(1)
C(18)	3942(1)	-1072(1)	8945(1)	24(1)
C(19)	-1039(1)	2806(1)	7778(1)	25(1)
C(20)	244(1)	2499(1)	9491(1)	26(1)
C(21)	178(1)	1753(1)	9187(1)	19(1)
C(22)	2373(1)	-2343(1)	5435(1)	24(1)
C(23)	-2683(1)	64(1)	5503(1)	17(1)
C(24)	-2777(1)	458(1)	4309(1)	21(1)
C(25)	-3867(1)	-315(1)	5834(1)	27(1)
C(26)	-3469(1)	511(1)	9928(1)	30(1)
C(27)	-3415(1)	-228(1)	10237(1)	28(1)
C(28)	-372(1)	3025(1)	8793(1)	28(1)
C(29)	-213(1)	-429(1)	3421(1)	17(1)
C(30)	348(1)	44(1)	4262(1)	13(1)
C(31)	674(1)	753(1)	3905(1)	16(1)
C(32)	416(1)	990(1)	2737(1)	22(1)

C(33)	2784(1)	-1552(1)	8874(1)	25(1)
C(34)	2212(1)	1947(1)	6321(1)	15(1)
C(35)	3278(1)	1549(1)	6034(1)	15(1)
C(36)	4523(1)	1910(1)	5841(1)	21(1)
C(37)	5339(1)	1941(1)	6985(1)	22(1)
C(38)	4626(1)	2057(1)	8100(1)	19(1)
C(39)	3669(1)	2544(1)	8237(1)	19(1)
C(40)	3218(1)	3082(1)	7284(1)	22(1)
C(41)	2140(1)	2771(1)	6521(1)	20(1)
C(42)	-179(1)	526(1)	1926(1)	24(1)
C(43)	-484(1)	-187(1)	2273(1)	21(1)
C(45)	6689(2)	7108(1)	7423(2)	40(1)
C(46)	6900(1)	4752(1)	7696(1)	26(1)
Cl(1)	3102(1)	1037(1)	9901(1)	20(1)
Cl(2)	5966(1)	5338(1)	6808(1)	46(1)
Cl(3)	6182(1)	3878(1)	7841(1)	35(1)
Cl(4)	5091(1)	7280(1)	7392(1)	58(1)
Cl(5)	7571(1)	7914(1)	7400(1)	78(1)
N(1)	2348(1)	-391(1)	8009(1)	14(1)
O(1)	445(1)	305(1)	8221(1)	13(1)
O(2)	1332(1)	315(1)	6140(1)	12(1)
O(3)	-1714(1)	-479(1)	5494(1)	16(1)
O(4)	-2352(1)	567(1)	6438(1)	19(1)
P(1)	1729(1)	384(1)	7545(1)	11(1)
Rh(1)	2890(1)	1400(1)	7862(1)	12(1)

Table 8. Bond lengths [\AA] and angles [$^\circ$] for **T2**.

C(1)-O(1)	1.4607(13)	C(23)-C(25)	1.5171(17)
C(1)-C(14)	1.5188(15)	C(23)-C(24)	1.5188(18)
C(1)-C(6)	1.5371(15)	C(26)-C(27)	1.386(2)
C(1)-C(2)	1.5594(15)	C(29)-C(43)	1.3844(17)
C(2)-O(4)	1.4228(13)	C(29)-C(30)	1.4001(15)
C(2)-C(3)	1.5291(16)	C(30)-C(31)	1.3938(16)
C(3)-O(3)	1.4210(13)	C(31)-C(32)	1.3987(16)
C(3)-C(4)	1.5655(14)	C(32)-C(42)	1.3847(19)
C(4)-O(2)	1.4569(12)	C(34)-C(35)	1.4131(16)
C(4)-C(9)	1.5214(15)	C(34)-C(41)	1.5125(17)
C(4)-C(30)	1.5260(14)	C(34)-Rh(1)	2.1071(11)
C(5)-C(26)	1.3994(19)	C(35)-C(36)	1.5270(16)
C(5)-C(6)	1.3999(17)	C(35)-Rh(1)	2.1252(11)
C(6)-C(7)	1.3947(17)	C(36)-C(37)	1.5387(19)
C(7)-C(8)	1.3959(17)	C(37)-C(38)	1.5086(19)
C(8)-C(27)	1.385(2)	C(38)-C(39)	1.3781(18)
C(9)-C(10)	1.3960(16)	C(38)-Rh(1)	2.2439(11)
C(9)-C(11)	1.4029(15)	C(39)-C(40)	1.5171(18)
C(10)-C(13)	1.4004(18)	C(39)-Rh(1)	2.2749(12)
C(11)-C(12)	1.3877(17)	C(40)-C(41)	1.5382(18)
C(12)-C(22)	1.396(2)	C(42)-C(43)	1.392(2)
C(13)-C(22)	1.389(2)	C(45)-Cl(5)	1.750(2)
C(14)-C(15)	1.3948(16)	C(45)-Cl(4)	1.769(2)
C(14)-C(21)	1.4004(16)	C(46)-Cl(2)	1.7585(16)
C(15)-C(19)	1.3941(18)	C(46)-Cl(3)	1.7756(16)
C(16)-N(1)	1.4724(15)	Cl(1)-Rh(1)	2.3842(3)
C(16)-C(33)	1.5300(18)	N(1)-P(1)	1.6355(10)
C(17)-N(1)	1.4824(14)	O(1)-P(1)	1.6184(8)
C(17)-C(18)	1.5176(18)	O(2)-P(1)	1.6263(8)
C(18)-C(33)	1.532(2)	P(1)-Rh(1)	2.2547(3)
C(19)-C(28)	1.389(2)	O(1)-C(1)-C(14)	110.61(8)
C(20)-C(28)	1.392(2)	O(1)-C(1)-C(6)	104.68(8)
C(20)-C(21)	1.3953(19)	C(14)-C(1)-C(6)	110.60(9)
C(23)-O(4)	1.4275(15)	O(1)-C(1)-C(2)	107.60(8)
C(23)-O(3)	1.4429(15)	C(14)-C(1)-C(2)	112.42(9)

C(6)-C(1)-C(2)	110.63(9)	O(4)-C(23)-O(3)	105.76(9)
O(4)-C(2)-C(3)	104.09(9)	O(4)-C(23)-C(25)	107.79(10)
O(4)-C(2)-C(1)	110.14(9)	O(3)-C(23)-C(25)	108.72(10)
C(3)-C(2)-C(1)	113.08(9)	O(4)-C(23)-C(24)	110.93(10)
O(3)-C(3)-C(2)	104.92(8)	O(3)-C(23)-C(24)	110.08(10)
O(3)-C(3)-C(4)	113.35(9)	C(25)-C(23)-C(24)	113.25(10)
C(2)-C(3)-C(4)	111.53(8)	C(27)-C(26)-C(5)	120.36(13)
O(2)-C(4)-C(9)	110.20(8)	C(8)-C(27)-C(26)	119.69(12)
O(2)-C(4)-C(30)	106.18(8)	C(19)-C(28)-C(20)	119.75(12)
C(9)-C(4)-C(30)	109.46(8)	C(43)-C(29)-C(30)	120.61(11)
O(2)-C(4)-C(3)	106.61(8)	C(31)-C(30)-C(29)	118.67(10)
C(9)-C(4)-C(3)	113.16(8)	C(31)-C(30)-C(4)	122.59(9)
C(30)-C(4)-C(3)	110.97(8)	C(29)-C(30)-C(4)	118.71(9)
C(26)-C(5)-C(6)	120.29(13)	C(30)-C(31)-C(32)	120.44(11)
C(7)-C(6)-C(5)	118.70(11)	C(42)-C(32)-C(31)	120.35(12)
C(7)-C(6)-C(1)	120.95(10)	C(16)-C(33)-C(18)	103.11(10)
C(5)-C(6)-C(1)	120.33(11)	C(35)-C(34)-C(41)	125.80(10)
C(6)-C(7)-C(8)	120.65(12)	C(35)-C(34)-Rh(1)	71.19(6)
C(27)-C(8)-C(7)	120.30(13)	C(41)-C(34)-Rh(1)	111.17(8)
C(10)-C(9)-C(11)	118.87(10)	C(34)-C(35)-C(36)	123.59(10)
C(10)-C(9)-C(4)	122.22(9)	C(34)-C(35)-Rh(1)	69.81(6)
C(11)-C(9)-C(4)	118.81(9)	C(36)-C(35)-Rh(1)	113.34(8)
C(9)-C(10)-C(13)	120.34(11)	C(35)-C(36)-C(37)	112.91(10)
C(12)-C(11)-C(9)	120.71(11)	C(38)-C(37)-C(36)	113.47(10)
C(11)-C(12)-C(22)	120.08(12)	C(39)-C(38)-C(37)	126.37(12)
C(22)-C(13)-C(10)	120.21(12)	C(39)-C(38)-Rh(1)	73.48(7)
C(15)-C(14)-C(21)	118.96(11)	C(37)-C(38)-Rh(1)	106.32(8)
C(15)-C(14)-C(1)	121.54(10)	C(38)-C(39)-C(40)	124.23(12)
C(21)-C(14)-C(1)	119.34(10)	C(38)-C(39)-Rh(1)	71.02(7)
C(19)-C(15)-C(14)	120.79(12)	C(40)-C(39)-Rh(1)	110.17(8)
N(1)-C(16)-C(33)	103.50(10)	C(39)-C(40)-C(41)	112.42(10)
N(1)-C(17)-C(18)	103.12(10)	C(34)-C(41)-C(40)	113.73(10)
C(17)-C(18)-C(33)	102.80(10)	C(32)-C(42)-C(43)	119.36(11)
C(28)-C(19)-C(15)	119.97(13)	C(29)-C(43)-C(42)	120.52(11)
C(28)-C(20)-C(21)	120.37(13)	Cl(5)-C(45)-Cl(4)	113.10(11)
C(20)-C(21)-C(14)	120.14(12)	Cl(2)-C(46)-Cl(3)	110.00(8)
C(13)-C(22)-C(12)	119.76(12)	C(16)-N(1)-C(17)	111.36(9)

C(16)-N(1)-P(1)	127.40(8)	C(34)-Rh(1)-P(1)	94.27(3)
C(17)-N(1)-P(1)	120.45(8)	C(35)-Rh(1)-P(1)	94.55(3)
C(1)-O(1)-P(1)	126.14(7)	C(38)-Rh(1)-P(1)	156.70(3)
C(4)-O(2)-P(1)	129.39(7)	C(34)-Rh(1)-C(39)	80.89(4)
C(3)-O(3)-C(23)	109.69(9)	C(35)-Rh(1)-C(39)	88.75(4)
C(2)-O(4)-C(23)	108.02(8)	C(38)-Rh(1)-C(39)	35.50(5)
O(1)-P(1)-O(2)	103.96(4)	P(1)-Rh(1)-C(39)	167.77(3)
O(1)-P(1)-N(1)	97.37(4)	C(34)-Rh(1)-Cl(1)	159.72(3)
O(2)-P(1)-N(1)	109.63(5)	C(35)-Rh(1)-Cl(1)	160.95(3)
O(1)-P(1)-Rh(1)	119.13(3)	C(38)-Rh(1)-Cl(1)	88.66(3)
O(2)-P(1)-Rh(1)	110.27(3)	P(1)-Rh(1)-Cl(1)	87.891(11)
N(1)-P(1)-Rh(1)	115.28(4)	C(39)-Rh(1)-Cl(1)	92.84(3)
C(34)-Rh(1)-C(35)	39.01(4)		
C(34)-Rh(1)-C(38)	96.89(4)		
C(35)-Rh(1)-C(38)	81.64(4)		

Symmetry transformations used to generate equivalent atoms:

Table 9. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **T2**. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U^{11} + \dots + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C(1)	11(1)	15(1)	12(1)	1(1)	1(1)	1(1)
C(2)	12(1)	16(1)	13(1)	0(1)	0(1)	1(1)
C(3)	11(1)	15(1)	13(1)	0(1)	-1(1)	-2(1)
C(4)	11(1)	12(1)	12(1)	0(1)	0(1)	-2(1)
C(5)	15(1)	32(1)	22(1)	7(1)	5(1)	5(1)
C(6)	12(1)	21(1)	12(1)	2(1)	1(1)	-2(1)
C(7)	20(1)	21(1)	15(1)	1(1)	2(1)	-6(1)
C(8)	23(1)	30(1)	18(1)	5(1)	1(1)	-11(1)
C(9)	14(1)	12(1)	13(1)	0(1)	-1(1)	0(1)
C(10)	20(1)	14(1)	24(1)	0(1)	1(1)	-2(1)
C(11)	15(1)	16(1)	18(1)	-1(1)	2(1)	2(1)
C(12)	19(1)	22(1)	22(1)	-3(1)	0(1)	7(1)
C(13)	30(1)	13(1)	29(1)	0(1)	1(1)	-1(1)
C(14)	14(1)	16(1)	16(1)	-1(1)	3(1)	0(1)
C(15)	19(1)	17(1)	21(1)	2(1)	2(1)	3(1)
C(16)	18(1)	17(1)	23(1)	7(1)	2(1)	0(1)
C(17)	12(1)	21(1)	20(1)	1(1)	0(1)	3(1)
C(18)	20(1)	24(1)	27(1)	4(1)	-6(1)	4(1)
C(19)	26(1)	16(1)	34(1)	2(1)	9(1)	5(1)
C(20)	29(1)	24(1)	25(1)	-9(1)	6(1)	-5(1)
C(21)	20(1)	20(1)	17(1)	-3(1)	2(1)	-2(1)
C(22)	30(1)	16(1)	27(1)	-2(1)	-3(1)	7(1)
C(23)	11(1)	22(1)	18(1)	0(1)	-1(1)	0(1)
C(24)	18(1)	27(1)	18(1)	1(1)	-3(1)	2(1)
C(25)	12(1)	35(1)	33(1)	5(1)	2(1)	-4(1)
C(26)	15(1)	47(1)	27(1)	12(1)	7(1)	5(1)
C(27)	14(1)	48(1)	21(1)	10(1)	1(1)	-8(1)
C(28)	33(1)	17(1)	34(1)	-7(1)	13(1)	-1(1)
C(29)	18(1)	18(1)	14(1)	-1(1)	-2(1)	-2(1)
C(30)	13(1)	14(1)	11(1)	0(1)	0(1)	0(1)
C(31)	18(1)	17(1)	13(1)	2(1)	-1(1)	-2(1)
C(32)	26(1)	22(1)	16(1)	6(1)	-2(1)	-3(1)

C(33)	23(1)	18(1)	34(1)	9(1)	-1(1)	4(1)
C(34)	16(1)	15(1)	14(1)	1(1)	-1(1)	-1(1)
C(35)	16(1)	16(1)	14(1)	0(1)	2(1)	-2(1)
C(36)	18(1)	21(1)	23(1)	0(1)	6(1)	-3(1)
C(37)	13(1)	24(1)	30(1)	0(1)	2(1)	-2(1)
C(38)	15(1)	18(1)	24(1)	0(1)	-4(1)	-4(1)
C(39)	20(1)	15(1)	21(1)	-4(1)	-2(1)	-3(1)
C(40)	24(1)	14(1)	27(1)	-1(1)	-1(1)	-1(1)
C(41)	19(1)	16(1)	24(1)	2(1)	-1(1)	2(1)
C(42)	27(1)	29(1)	14(1)	3(1)	-4(1)	-1(1)
C(43)	22(1)	26(1)	15(1)	-3(1)	-4(1)	-1(1)
C(45)	41(1)	33(1)	47(1)	6(1)	0(1)	5(1)
C(46)	20(1)	32(1)	27(1)	-5(1)	-2(1)	0(1)
Cl(1)	22(1)	25(1)	13(1)	1(1)	-2(1)	-1(1)
Cl(2)	44(1)	46(1)	47(1)	-1(1)	-12(1)	16(1)
Cl(3)	35(1)	35(1)	36(1)	-12(1)	11(1)	-8(1)
Cl(4)	40(1)	77(1)	58(1)	-25(1)	-6(1)	24(1)
Cl(5)	83(1)	39(1)	110(1)	18(1)	11(1)	-15(1)
N(1)	11(1)	16(1)	16(1)	4(1)	2(1)	1(1)
O(1)	11(1)	16(1)	13(1)	2(1)	1(1)	0(1)
O(2)	12(1)	13(1)	11(1)	0(1)	0(1)	-2(1)
O(3)	11(1)	18(1)	20(1)	-2(1)	-2(1)	-2(1)
O(4)	12(1)	27(1)	17(1)	-3(1)	-2(1)	4(1)
P(1)	10(1)	12(1)	11(1)	1(1)	0(1)	-1(1)
Rh(1)	12(1)	13(1)	12(1)	0(1)	-1(1)	-2(1)

Table 10. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **T2**.

	x	y	z	U(eq)
H(2)	-675	914	6092	16
H(3)	-609	-547	6916	15
H(5)	-2635	1313	8983	27
H(7)	-962	-662	8823	22
H(8)	-2446	-1164	10017	29
H(10)	-294	-1615	5930	23
H(11)	2832	-587	5070	20
H(12)	3832	-1711	5011	25
H(13)	713	-2745	5859	29
H(15)	-1559	1918	6795	23
H(16A)	1074	-1198	8208	23
H(16B)	1454	-808	9423	23
H(17A)	4133	-47	8146	21
H(17B)	3930	-686	7203	21
H(18A)	4042	-839	9721	29
H(18B)	4670	-1359	8787	29
H(19)	-1438	3157	7300	30
H(20)	702	2646	10163	31
H(21)	596	1405	9654	22
H(22)	2775	-2795	5411	29
H(24A)	-3468	787	4299	31
H(24B)	-2883	101	3682	31
H(24C)	-2039	735	4192	31
H(25A)	-3749	-559	6588	40
H(25B)	-4092	-671	5233	40
H(25C)	-4508	46	5889	40
H(26)	-4094	807	10211	35
H(27)	-4002	-430	10725	33
H(28)	-337	3521	9006	33
H(29)	-405	-910	3637	20
H(31)	1066	1070	4446	19

H(32)	646	1461	2505	26
H(33A)	2813	-1898	8216	30
H(33B)	2681	-1823	9609	30
H(34)	1451	1733	5983	18
H(35)	3117	1112	5538	18
H(36A)	4392	2408	5546	25
H(36B)	4948	1636	5237	25
H(37A)	5796	1483	7061	27
H(37B)	5927	2339	6914	27
H(38)	5094	1949	8840	23
H(39)	3572	2717	9056	23
H(40A)	3890	3201	6771	26
H(40B)	2960	3536	7663	26
H(41A)	1378	2883	6908	24
H(41B)	2118	3018	5753	24
H(42)	-374	689	1158	28
H(43)	-873	-503	1728	25
H(45A)	6909	6829	8137	49
H(45B)	6885	6806	6741	49
H(46A)	7038	4970	8478	32
H(46B)	7690	4691	7334	32

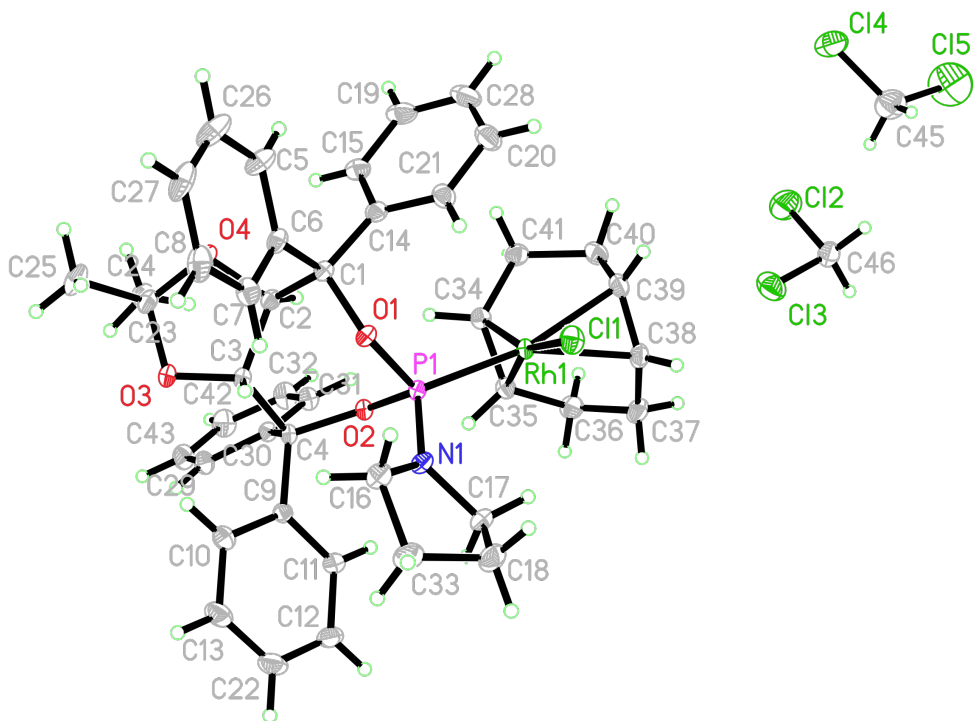


Table 11. Crystal data and structure refinement for **T8**.

Identification code	rovis73_0m	
Empirical formula	C ₅₁ H ₆₄ Cl N O ₄ P Rh	
Formula weight	924.36	
Temperature	120 K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	P 2 ₁ 2 ₁ 2 ₁	
Unit cell dimensions	$a = 15.3754(4)$ Å	$\alpha = 90^\circ$
	$b = 17.3853(4)$ Å	$\beta = 90^\circ$
	$c = 18.1214(4)$ Å	$\gamma = 90^\circ$
Volume	4844.0(2) Å ³	
Z	4	
Density (calculated)	1.268 Mg/m ³	
Absorption coefficient	0.483 mm ⁻¹	
F(000)	1944	
Crystal size	0.31 x 0.26 x 0.19 mm ³	
Theta range for data collection	2.10 to 36.43°.	
Index ranges	-25 ≤ h ≤ 25, -28 ≤ k ≤ 25, -30 ≤ l ≤ 28	
Reflections collected	52621	
Independent reflections	23450 [R(int) = 0.0546]	
Completeness to theta = 36.43°	99.5 %	
Absorption correction	Multi-Scan	
Max. and min. transmission	0.9159 and 0.8658	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	23450 / 0 / 542	
Goodness-of-fit on F ²	1.006	
Final R indices [I > 2σ(I)]	R1 = 0.0532, wR2 = 0.1024	
R indices (all data)	R1 = 0.0916, wR2 = 0.1182	
Absolute structure parameter	-0.030(17)	
Largest diff. peak and hole	1.864 and -0.936 e.Å ⁻³	

Table 12. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **T8**. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	$U(\text{eq})$
C(1)	115(2)	5573(1)	-839(1)	17(1)
C(2)	527(2)	4751(1)	-800(1)	18(1)
C(3)	120(2)	4265(1)	-177(1)	18(1)
C(4)	697(1)	4268(1)	527(1)	16(1)
C(5)	244(2)	3536(2)	-1257(2)	36(1)
C(6)	-1015(2)	5763(2)	1276(2)	23(1)
C(7)	162(2)	6373(2)	1953(2)	26(1)
C(8)	181(2)	4065(1)	1222(1)	17(1)
C(9)	-527(2)	3559(1)	1194(2)	21(1)
C(10)	-943(2)	3322(2)	1836(2)	24(1)
C(11)	-654(2)	3611(2)	2508(2)	25(1)
C(12)	33(2)	4131(2)	2553(2)	23(1)
C(13)	453(2)	4344(1)	1898(1)	19(1)
C(14)	-1687(2)	2759(2)	1810(2)	37(1)
C(15)	327(2)	4463(2)	3276(2)	33(1)
C(16)	1486(2)	3731(1)	456(1)	18(1)
C(17)	1388(2)	2939(1)	580(2)	26(1)
C(18)	2094(2)	2444(2)	503(2)	34(1)
C(19)	3008(2)	3517(2)	178(2)	33(1)
C(20)	2295(2)	4005(2)	251(2)	26(1)
C(21)	721(2)	6148(1)	-1216(1)	19(1)
C(22)	1323(2)	5918(2)	-1741(2)	24(1)
C(23)	1814(2)	6454(2)	-2126(2)	29(1)
C(24)	1704(2)	7238(2)	-1971(2)	26(1)
C(25)	1103(2)	7481(2)	-1444(2)	23(1)
C(26)	614(2)	6932(1)	-1076(1)	20(1)
C(27)	2452(2)	6205(2)	-2717(2)	45(1)
C(28)	992(2)	8326(2)	-1273(2)	33(1)
C(29)	-768(2)	5543(1)	-1231(2)	23(1)
C(30)	-1532(2)	5450(1)	-837(2)	26(1)
C(31)	-2339(2)	5401(2)	-1186(2)	35(1)
C(32)	-2349(2)	5438(2)	-1957(2)	45(1)

C(33)	-1597(3)	5526(2)	-2367(2)	39(1)
C(34)	-806(2)	5585(2)	-1996(2)	30(1)
C(35)	-3166(2)	5342(2)	-746(2)	47(1)
C(36)	-1622(3)	5568(2)	-3203(2)	60(1)
C(37)	2903(2)	2736(2)	310(2)	34(1)
C(38)	1982(3)	1595(2)	641(3)	60(1)
C(39)	-1329(2)	6069(2)	2014(2)	39(1)
C(40)	-700(2)	6709(2)	2207(2)	39(1)
C(41)	-492(4)	3227(3)	-1692(2)	115(3)
C(42)	1122(3)	3114(2)	-1364(2)	65(1)
C(43)	3898(2)	3838(2)	-40(3)	61(1)
C(44)	2693(2)	6106(2)	216(2)	29(1)
C(45)	2612(2)	6028(2)	980(2)	29(1)
C(46)	3169(2)	6399(2)	1571(2)	42(1)
C(47)	3379(2)	7236(2)	1405(2)	37(1)
C(48)	3434(2)	6544(2)	-151(2)	45(1)
C(49)	3226(2)	7394(2)	-280(2)	32(1)
C(50)	2602(2)	7729(2)	264(2)	26(1)
C(51)	2644(2)	7648(2)	1019(2)	25(1)
Cl(1)	554(1)	7756(1)	653(1)	21(1)
N(1)	-78(1)	5980(1)	1258(1)	18(1)
O(1)	-70(1)	5823(1)	-90(1)	16(1)
O(2)	1061(1)	5036(1)	596(1)	15(1)
O(3)	363(1)	4325(1)	-1449(1)	23(1)
O(4)	37(1)	3517(1)	-489(1)	23(1)
P(1)	618(1)	5885(1)	583(1)	14(1)
Rh(1)	1663(1)	6806(1)	588(1)	17(1)

Table 13. Bond lengths [Å] and angles [°] for **T8**.

C(1)-O(1)	1.454(3)	C(19)-C(43)	1.531(5)
C(1)-C(21)	1.528(3)	C(21)-C(22)	1.387(4)
C(1)-C(29)	1.533(3)	C(21)-C(26)	1.396(3)
C(1)-C(2)	1.564(3)	C(22)-C(23)	1.387(4)
C(2)-O(3)	1.413(3)	C(23)-C(24)	1.403(4)
C(2)-C(3)	1.542(3)	C(23)-C(27)	1.516(4)
C(3)-O(4)	1.425(3)	C(24)-C(25)	1.393(4)
C(3)-C(4)	1.553(3)	C(25)-C(26)	1.387(4)
C(4)-O(2)	1.454(3)	C(25)-C(28)	1.510(4)
C(4)-C(8)	1.531(3)	C(29)-C(30)	1.384(4)
C(4)-C(16)	1.536(3)	C(29)-C(34)	1.389(4)
C(5)-O(3)	1.428(3)	C(30)-C(31)	1.397(4)
C(5)-O(4)	1.428(3)	C(31)-C(32)	1.399(5)
C(5)-C(41)	1.480(5)	C(31)-C(35)	1.504(5)
C(5)-C(42)	1.548(5)	C(32)-C(33)	1.383(5)
C(6)-N(1)	1.489(3)	C(33)-C(34)	1.393(4)
C(6)-C(39)	1.517(4)	C(33)-C(36)	1.516(5)
C(7)-N(1)	1.479(3)	C(39)-C(40)	1.514(5)
C(7)-C(40)	1.520(4)	C(44)-C(45)	1.395(4)
C(8)-C(13)	1.382(3)	C(44)-C(48)	1.524(4)
C(8)-C(9)	1.400(3)	C(44)-Rh(1)	2.108(3)
C(9)-C(10)	1.391(4)	C(45)-C(46)	1.516(4)
C(10)-C(11)	1.390(4)	C(45)-Rh(1)	2.113(3)
C(10)-C(14)	1.507(4)	C(46)-C(47)	1.521(4)
C(11)-C(12)	1.392(4)	C(47)-C(51)	1.510(4)
C(12)-C(13)	1.401(4)	C(48)-C(49)	1.530(4)
C(12)-C(15)	1.501(4)	C(49)-C(50)	1.495(4)
C(16)-C(20)	1.384(4)	C(50)-C(51)	1.377(4)
C(16)-C(17)	1.402(3)	C(50)-Rh(1)	2.236(3)
C(17)-C(18)	1.392(4)	C(51)-Rh(1)	2.242(3)
C(18)-C(37)	1.387(5)	Cl(1)-Rh(1)	2.3765(6)
C(18)-C(38)	1.508(4)	N(1)-P(1)	1.633(2)
C(19)-C(37)	1.388(4)	O(1)-P(1)	1.6188(18)
C(19)-C(20)	1.392(4)	O(2)-P(1)	1.6260(15)
		P(1)-Rh(1)	2.2688(6)

O(1)-C(1)-C(21)	109.92(19)	C(8)-C(13)-C(12)	121.2(2)
O(1)-C(1)-C(29)	105.58(19)	C(20)-C(16)-C(17)	118.6(2)
C(21)-C(1)-C(29)	110.8(2)	C(20)-C(16)-C(4)	121.5(2)
O(1)-C(1)-C(2)	108.03(17)	C(17)-C(16)-C(4)	119.9(2)
C(21)-C(1)-C(2)	111.9(2)	C(18)-C(17)-C(16)	120.4(3)
C(29)-C(1)-C(2)	110.39(19)	C(37)-C(18)-C(17)	119.9(3)
O(3)-C(2)-C(3)	104.53(19)	C(37)-C(18)-C(38)	120.1(3)
O(3)-C(2)-C(1)	111.59(19)	C(17)-C(18)-C(38)	120.0(3)
C(3)-C(2)-C(1)	111.8(2)	C(37)-C(19)-C(20)	119.3(3)
O(4)-C(3)-C(2)	104.21(19)	C(37)-C(19)-C(43)	120.3(3)
O(4)-C(3)-C(4)	112.37(19)	C(20)-C(19)-C(43)	120.4(3)
C(2)-C(3)-C(4)	111.6(2)	C(16)-C(20)-C(19)	121.5(3)
O(2)-C(4)-C(8)	109.89(19)	C(22)-C(21)-C(26)	119.1(2)
O(2)-C(4)-C(16)	105.19(17)	C(22)-C(21)-C(1)	121.6(2)
C(8)-C(4)-C(16)	109.82(19)	C(26)-C(21)-C(1)	119.1(2)
O(2)-C(4)-C(3)	107.06(17)	C(23)-C(22)-C(21)	121.0(3)
C(8)-C(4)-C(3)	112.29(19)	C(22)-C(23)-C(24)	119.1(3)
C(16)-C(4)-C(3)	112.31(19)	C(22)-C(23)-C(27)	121.1(3)
O(3)-C(5)-O(4)	106.7(2)	C(24)-C(23)-C(27)	119.8(3)
O(3)-C(5)-C(41)	108.5(3)	C(25)-C(24)-C(23)	120.8(3)
O(4)-C(5)-C(41)	109.9(3)	C(26)-C(25)-C(24)	118.7(2)
O(3)-C(5)-C(42)	108.2(3)	C(26)-C(25)-C(28)	120.6(3)
O(4)-C(5)-C(42)	107.7(3)	C(24)-C(25)-C(28)	120.7(2)
C(41)-C(5)-C(42)	115.5(4)	C(25)-C(26)-C(21)	121.4(2)
N(1)-C(6)-C(39)	103.8(2)	C(30)-C(29)-C(34)	119.0(2)
N(1)-C(7)-C(40)	102.6(2)	C(30)-C(29)-C(1)	121.1(2)
C(13)-C(8)-C(9)	119.3(2)	C(34)-C(29)-C(1)	119.8(2)
C(13)-C(8)-C(4)	119.4(2)	C(29)-C(30)-C(31)	121.9(3)
C(9)-C(8)-C(4)	121.2(2)	C(30)-C(31)-C(32)	117.4(3)
C(10)-C(9)-C(8)	120.9(2)	C(30)-C(31)-C(35)	121.0(3)
C(11)-C(10)-C(9)	118.6(2)	C(32)-C(31)-C(35)	121.6(3)
C(11)-C(10)-C(14)	120.4(2)	C(33)-C(32)-C(31)	122.2(3)
C(9)-C(10)-C(14)	121.1(2)	C(32)-C(33)-C(34)	118.6(3)
C(10)-C(11)-C(12)	121.9(2)	C(32)-C(33)-C(36)	121.3(3)
C(11)-C(12)-C(13)	118.2(2)	C(34)-C(33)-C(36)	120.1(4)
C(11)-C(12)-C(15)	121.9(2)	C(29)-C(34)-C(33)	121.0(3)
C(13)-C(12)-C(15)	119.9(3)	C(18)-C(37)-C(19)	120.3(3)

C(40)-C(39)-C(6)	105.0(2)	O(1)-P(1)-O(2)	102.94(9)
C(39)-C(40)-C(7)	101.8(2)	O(1)-P(1)-N(1)	98.27(9)
C(45)-C(44)-C(48)	123.2(3)	O(2)-P(1)-N(1)	110.82(10)
C(45)-C(44)-Rh(1)	70.90(17)	O(1)-P(1)-Rh(1)	120.87(7)
C(48)-C(44)-Rh(1)	114.36(19)	O(2)-P(1)-Rh(1)	110.09(6)
C(44)-C(45)-C(46)	127.6(3)	N(1)-P(1)-Rh(1)	112.94(8)
C(44)-C(45)-Rh(1)	70.50(17)	C(44)-Rh(1)-C(45)	38.60(11)
C(46)-C(45)-Rh(1)	110.8(2)	C(44)-Rh(1)-C(50)	81.13(11)
C(45)-C(46)-C(47)	112.8(3)	C(45)-Rh(1)-C(50)	95.83(12)
C(51)-C(47)-C(46)	112.7(3)	C(44)-Rh(1)-C(51)	89.05(12)
C(44)-C(48)-C(49)	113.2(3)	C(45)-Rh(1)-C(51)	80.59(10)
C(50)-C(49)-C(48)	114.2(2)	C(50)-Rh(1)-C(51)	35.81(10)
C(51)-C(50)-C(49)	125.9(3)	C(44)-Rh(1)-P(1)	97.06(8)
C(51)-C(50)-Rh(1)	72.33(17)	C(45)-Rh(1)-P(1)	92.20(8)
C(49)-C(50)-Rh(1)	107.96(18)	C(50)-Rh(1)-P(1)	164.27(8)
C(50)-C(51)-C(47)	122.9(3)	C(51)-Rh(1)-P(1)	159.80(8)
C(50)-C(51)-Rh(1)	71.85(17)	C(44)-Rh(1)-Cl(1)	162.98(9)
C(47)-C(51)-Rh(1)	110.82(18)	C(45)-Rh(1)-Cl(1)	157.50(10)
C(7)-N(1)-C(6)	109.9(2)	C(50)-Rh(1)-Cl(1)	88.75(8)
C(7)-N(1)-P(1)	121.38(18)	C(51)-Rh(1)-Cl(1)	90.70(8)
C(6)-N(1)-P(1)	128.62(18)	P(1)-Rh(1)-Cl(1)	88.970(19)
C(1)-O(1)-P(1)	126.59(15)		
C(4)-O(2)-P(1)	132.18(13)		
C(2)-O(3)-C(5)	108.87(19)		
C(3)-O(4)-C(5)	110.29(19)		

Symmetry transformations used to generate equivalent atoms:

Table 14. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **T8**. The anisotropic displacement factor exponent takes the form: $-2p^2 [h^2 a^{*2} U^{11} + \dots + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C(1)	19(1)	16(1)	16(1)	2(1)	-2(1)	2(1)
C(2)	20(1)	18(1)	15(1)	1(1)	-1(1)	0(1)
C(3)	21(1)	15(1)	18(1)	0(1)	-2(1)	-2(1)
C(4)	19(1)	12(1)	16(1)	1(1)	0(1)	-2(1)
C(5)	62(2)	27(2)	20(1)	-5(1)	5(1)	-14(1)
C(6)	17(1)	20(1)	33(1)	3(1)	4(1)	0(1)
C(7)	28(1)	28(1)	20(1)	-2(1)	4(1)	-3(1)
C(8)	17(1)	15(1)	20(1)	4(1)	1(1)	1(1)
C(9)	24(1)	19(1)	21(1)	2(1)	-2(1)	-3(1)
C(10)	22(1)	24(1)	27(1)	5(1)	1(1)	-3(1)
C(11)	25(1)	24(1)	24(1)	11(1)	3(1)	0(1)
C(12)	25(1)	26(1)	18(1)	5(1)	1(1)	1(1)
C(13)	19(1)	19(1)	18(1)	3(1)	0(1)	-1(1)
C(14)	34(2)	39(2)	37(2)	9(1)	3(2)	-14(2)
C(15)	38(2)	41(2)	18(1)	3(1)	0(1)	-8(1)
C(16)	22(1)	18(1)	15(1)	-1(1)	-2(1)	1(1)
C(17)	30(1)	17(1)	29(1)	2(1)	2(1)	2(1)
C(18)	41(2)	20(1)	42(2)	2(1)	8(2)	8(1)
C(19)	22(1)	31(2)	45(2)	1(1)	5(1)	8(1)
C(20)	26(1)	19(1)	34(2)	1(1)	2(1)	3(1)
C(21)	21(1)	21(1)	15(1)	4(1)	-1(1)	2(1)
C(22)	27(1)	25(1)	19(1)	5(1)	2(1)	6(1)
C(23)	30(2)	35(2)	21(1)	6(1)	8(1)	5(1)
C(24)	27(1)	26(1)	26(1)	12(1)	1(1)	0(1)
C(25)	26(1)	24(1)	20(1)	4(1)	-4(1)	0(1)
C(26)	22(1)	21(1)	16(1)	3(1)	0(1)	2(1)
C(27)	47(2)	48(2)	39(2)	11(2)	25(2)	15(2)
C(28)	44(2)	23(2)	33(2)	7(1)	-1(1)	-6(1)
C(29)	25(1)	15(1)	28(1)	0(1)	-10(1)	2(1)
C(30)	20(1)	18(1)	39(2)	0(1)	-8(1)	-1(1)
C(31)	25(1)	12(1)	66(2)	-5(1)	-16(1)	3(1)
C(32)	41(2)	22(1)	72(3)	-13(2)	-38(2)	9(1)

C(33)	53(2)	25(1)	39(2)	-8(1)	-25(2)	8(2)
C(34)	36(2)	24(1)	30(2)	-2(1)	-14(1)	2(1)
C(35)	22(1)	20(1)	100(3)	1(2)	-20(2)	-4(1)
C(36)	83(3)	55(2)	41(2)	-8(2)	-39(2)	12(2)
C(37)	39(2)	26(1)	38(2)	-5(1)	2(1)	14(1)
C(38)	62(2)	21(1)	97(3)	7(2)	15(3)	12(2)
C(39)	31(2)	45(2)	39(2)	-7(2)	19(1)	-6(1)
C(40)	42(2)	42(2)	35(2)	-6(2)	12(1)	4(2)
C(41)	175(6)	133(5)	37(2)	36(3)	-47(3)	-126(5)
C(42)	111(4)	35(2)	48(2)	8(2)	32(2)	29(2)
C(43)	28(2)	46(2)	109(4)	2(2)	22(2)	6(2)
C(44)	21(1)	18(1)	46(2)	-2(1)	10(1)	1(1)
C(45)	20(1)	18(1)	49(2)	4(1)	-11(1)	-1(1)
C(46)	35(2)	33(2)	58(2)	7(2)	-18(2)	-6(1)
C(47)	36(2)	30(1)	46(2)	4(1)	-17(2)	-11(1)
C(48)	30(2)	32(2)	72(2)	-4(2)	28(2)	-2(1)
C(49)	29(2)	30(1)	37(2)	3(1)	9(1)	-6(1)
C(50)	22(1)	16(1)	40(2)	3(1)	6(1)	-7(1)
C(51)	24(1)	19(1)	31(2)	-2(1)	-2(1)	-6(1)
Cl(1)	21(1)	17(1)	25(1)	-2(1)	1(1)	2(1)
N(1)	18(1)	20(1)	17(1)	-2(1)	4(1)	-1(1)
O(1)	16(1)	17(1)	15(1)	0(1)	0(1)	1(1)
O(2)	16(1)	12(1)	18(1)	2(1)	1(1)	-1(1)
O(3)	37(1)	17(1)	15(1)	-2(1)	-4(1)	4(1)
O(4)	34(1)	16(1)	20(1)	-1(1)	-5(1)	-3(1)
P(1)	14(1)	13(1)	15(1)	1(1)	1(1)	0(1)
Rh(1)	15(1)	14(1)	21(1)	0(1)	1(1)	-1(1)

Table 15. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **T8**.

	x	y	z	U(eq)
H(2)	1155	4794	-721	21
H(3)	-458	4467	-56	21
H(6A)	-1085	5210	1248	28
H(6B)	-1329	6000	872	28
H(7A)	588	6774	1866	31
H(7B)	392	6012	2312	31
H(9)	-721	3379	740	25
H(11)	-927	3453	2940	30
H(13)	923	4680	1918	22
H(14A)	-1467	2245	1859	55
H(14B)	-1986	2808	1347	55
H(14C)	-2084	2865	2207	55
H(15A)	65	4958	3345	49
H(15B)	949	4515	3274	49
H(15C)	156	4126	3670	49
H(17)	848	2744	715	31
H(20)	2365	4528	160	32
H(22)	1399	5397	-1837	29
H(24)	2035	7601	-2223	32
H(26)	205	7089	-729	24
H(27A)	2459	5653	-2748	68
H(27B)	3023	6387	-2594	68
H(27C)	2278	6416	-3184	68
H(28A)	541	8536	-1579	50
H(28B)	1528	8591	-1368	50
H(28C)	837	8387	-763	50
H(30)	-1506	5421	-325	31
H(32)	-2879	5401	-2203	54
H(34)	-296	5654	-2264	36
H(35A)	-3464	5827	-757	71
H(35B)	-3030	5209	-245	71

H(35C)	-3532	4951	-956	71
H(36A)	-1422	6065	-3361	90
H(36B)	-2208	5490	-3370	90
H(36C)	-1253	5177	-3406	90
H(37)	3376	2406	269	41
H(38A)	2423	1315	379	90
H(38B)	1418	1435	473	90
H(38C)	2035	1493	1160	90
H(39A)	-1917	6265	1974	46
H(39B)	-1316	5668	2386	46
H(40A)	-698	6811	2733	47
H(40B)	-838	7179	1944	47
H(41A)	-986	3561	-1639	172
H(41B)	-639	2723	-1516	172
H(41C)	-330	3198	-2203	172
H(42A)	1273	3111	-1878	97
H(42B)	1072	2595	-1189	97
H(42C)	1567	3376	-1090	97
H(43A)	3937	3871	-568	91
H(43B)	4347	3503	142	91
H(43C)	3970	4341	170	91
H(44)	2501	5652	-61	34
H(45)	2369	5531	1130	34
H(46A)	3708	6113	1618	50
H(46B)	2867	6369	2040	50
H(47A)	3509	7500	1864	45
H(47B)	3895	7259	1097	45
H(48A)	3566	6303	-621	53
H(48B)	3948	6505	157	53
H(49A)	3764	7685	-262	38
H(49B)	2986	7452	-772	38
H(50)	2326	8207	100	31
H(51)	2396	8078	1298	30

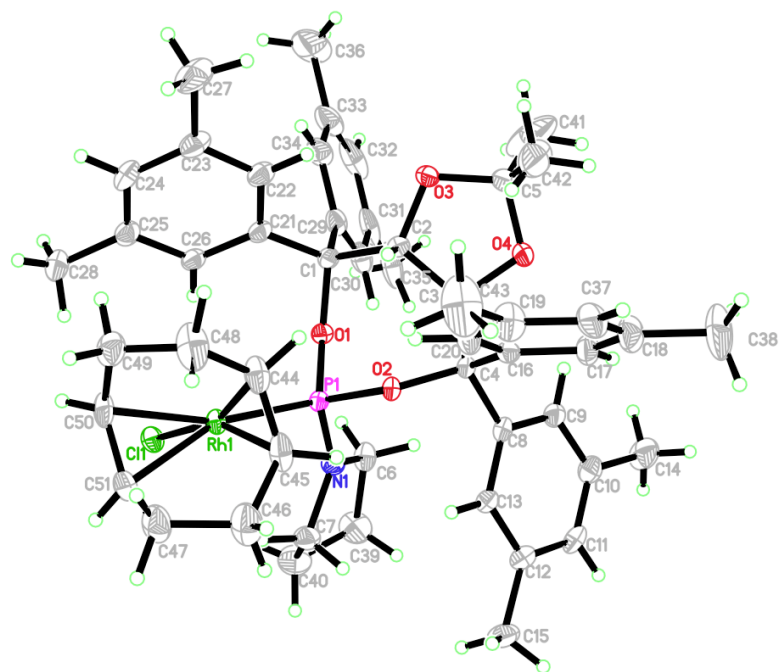


Table 16. Crystal data and structure refinement for **T9**.

Identification code	rovis36_0m	
Empirical formula	C ₅₂ H ₆₆ Cl N O ₄ P Rh	
Formula weight	938.39	
Temperature	120 K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	P 2 ₁ 2 ₁ 2 ₁	
Unit cell dimensions	$a = 15.3932(6)$ Å	$\alpha = 90^\circ$
	$b = 17.5850(7)$ Å	$\beta = 90^\circ$
	$c = 18.0197(8)$ Å	$\gamma = 90^\circ$
Volume	4877.7(3) Å ³	
Z	4	
Density (calculated)	1.278 Mg/m ³	
Absorption coefficient	0.481 mm ⁻¹	
F(000)	1976	
Crystal size	0.63 x 0.45 x 0.30 mm ³	
Theta range for data collection	2.09 to 33.49°.	
Index ranges	-21 ≤ h ≤ 23, -26 ≤ k ≤ 27, -27 ≤ l ≤ 27	
Reflections collected	138707	
Independent reflections	18942 [R(int) = 0.0541]	
Completeness to theta = 33.49°	99.3 %	
Absorption correction	Multi-scan	
Max. and min. transmission	0.8683 and 0.7527	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	18942 / 0 / 568	
Goodness-of-fit on F ²	1.029	
Final R indices [I > 2σ(I)]	R1 = 0.0333, wR2 = 0.0761	
R indices (all data)	R1 = 0.0434, wR2 = 0.0811	
Absolute structure parameter	-0.014(12)	
Largest diff. peak and hole	0.709 and -0.589 e.Å ⁻³	

Table 17. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **T9**. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
C(1)	158(1)	6132(1)	2978(1)	23(1)
C(2)	-1028(1)	5493(1)	3623(1)	21(1)
C(3)	-1684(1)	6058(1)	3313(1)	27(1)
C(4)	19(1)	5558(1)	5821(1)	16(1)
C(5)	421(1)	4739(1)	5820(1)	18(1)
C(6)	21(1)	4233(1)	5219(1)	19(1)
C(7)	611(1)	4193(1)	4521(1)	18(1)
C(8)	-607(1)	3502(1)	3843(1)	21(1)
C(9)	132(1)	3957(1)	3823(1)	18(1)
C(10)	478(1)	4166(1)	3141(1)	21(1)
C(11)	91(1)	3940(1)	2479(1)	24(1)
C(12)	-642(1)	3476(1)	2513(1)	25(1)
C(13)	1388(1)	3654(1)	4632(1)	21(1)
C(14)	1257(2)	2867(1)	4593(1)	28(1)
C(15)	-1641(1)	5510(1)	5821(1)	20(1)
C(16)	-862(1)	5565(1)	6212(1)	19(1)
C(17)	-886(1)	5604(1)	6988(1)	24(1)
C(18)	-1677(1)	5578(1)	7366(1)	28(1)
C(19)	-2443(1)	5508(1)	6967(1)	28(1)
C(20)	-109(2)	3614(1)	6349(1)	27(1)
C(21)	-1385(1)	6359(1)	2565(1)	30(1)
C(22)	-484(1)	6708(1)	2635(1)	29(1)
C(23)	-998(1)	3249(1)	3187(1)	24(1)
C(24)	2222(1)	3923(1)	4747(1)	31(1)
C(25)	1953(2)	2366(1)	4665(1)	34(1)
C(26)	-1056(2)	3632(1)	6604(1)	35(1)
C(27)	2780(2)	2655(1)	4770(1)	39(1)
C(28)	2926(2)	3425(2)	4811(2)	40(1)
C(29)	-1774(2)	2728(1)	3200(1)	38(1)
C(30)	461(2)	4190(2)	1744(1)	40(1)
C(31)	-3277(1)	5440(1)	5767(1)	32(1)
C(32)	-2438(1)	5479(1)	6191(1)	24(1)

C(33)	-1677(2)	5626(2)	8209(1)	42(1)
C(34)	809(1)	8301(1)	6194(1)	28(1)
C(35)	476(1)	6908(1)	6024(1)	18(1)
C(36)	618(1)	6146(1)	6179(1)	17(1)
C(37)	1238(1)	5939(1)	6703(1)	23(1)
C(38)	1715(1)	6499(1)	7071(1)	27(1)
C(39)	961(1)	7474(1)	6375(1)	21(1)
C(40)	2502(1)	7599(1)	4709(1)	26(1)
C(41)	2551(1)	7548(1)	3949(1)	25(1)
C(42)	3277(1)	7164(1)	3529(1)	31(1)
C(43)	3057(1)	6337(1)	3336(1)	29(1)
C(44)	2499(1)	5939(1)	3906(1)	22(1)
C(45)	2610(1)	5999(1)	4683(1)	24(1)
C(46)	3361(1)	6420(1)	5043(1)	32(1)
C(47)	3122(1)	7238(1)	5252(1)	32(1)
C(48)	1795(2)	1517(1)	4634(2)	48(1)
C(49)	2356(2)	6278(2)	7672(2)	45(1)
C(50)	3840(2)	3741(2)	4927(3)	74(1)
C(51)	411(2)	3000(1)	6718(1)	41(1)
C(52)	1574(1)	7256(1)	6899(1)	25(1)
Cl(1)	456(1)	7628(1)	4288(1)	21(1)
N(1)	-162(1)	5843(1)	3678(1)	18(1)
O(1)	-162(1)	5763(1)	5051(1)	16(1)
O(2)	981(1)	4949(1)	4424(1)	17(1)
O(3)	275(1)	4342(1)	6495(1)	23(1)
O(4)	-65(1)	3509(1)	5563(1)	24(1)
P(1)	527(1)	5784(1)	4376(1)	14(1)
Rh(1)	1566(1)	6700(1)	4344(1)	16(1)

Table 18. Bond lengths [Å] and angles [°] for **T9**.

C(1)-N(1)	1.447(2)	C(20)-O(3)	1.433(2)
C(1)-C(22)	1.545(3)	C(20)-C(51)	1.499(3)
C(2)-N(1)	1.471(2)	C(20)-C(26)	1.529(3)
C(2)-C(3)	1.523(3)	C(21)-C(22)	1.523(3)
C(3)-C(21)	1.519(3)	C(23)-C(29)	1.507(3)
C(4)-O(1)	1.4606(19)	C(24)-C(28)	1.398(3)
C(4)-C(36)	1.528(2)	C(25)-C(27)	1.384(4)
C(4)-C(16)	1.529(2)	C(25)-C(48)	1.515(3)
C(4)-C(5)	1.567(2)	C(27)-C(28)	1.375(4)
C(5)-O(3)	1.421(2)	C(28)-C(50)	1.526(4)
C(5)-C(6)	1.531(2)	C(31)-C(32)	1.502(3)
C(6)-O(4)	1.421(2)	C(34)-C(39)	1.508(3)
C(6)-C(7)	1.553(2)	C(35)-C(36)	1.387(3)
C(7)-O(2)	1.458(2)	C(35)-C(39)	1.396(2)
C(7)-C(9)	1.516(2)	C(36)-C(37)	1.390(2)
C(7)-C(13)	1.539(2)	C(37)-C(38)	1.397(3)
C(8)-C(9)	1.391(3)	C(38)-C(52)	1.384(3)
C(8)-C(23)	1.398(2)	C(38)-C(49)	1.517(3)
C(9)-C(10)	1.389(2)	C(39)-C(52)	1.389(3)
C(10)-C(11)	1.391(3)	C(40)-C(41)	1.374(3)
C(11)-C(12)	1.394(3)	C(40)-C(47)	1.506(3)
C(11)-C(30)	1.507(3)	C(40)-Rh(1)	2.2373(19)
C(12)-C(23)	1.392(3)	C(41)-C(42)	1.510(3)
C(13)-C(24)	1.384(3)	C(41)-Rh(1)	2.2430(19)
C(13)-C(14)	1.400(3)	C(42)-C(43)	1.533(3)
C(14)-C(25)	1.393(3)	C(43)-C(44)	1.510(3)
C(15)-C(16)	1.393(2)	C(44)-C(45)	1.413(3)
C(15)-C(32)	1.397(3)	C(44)-Rh(1)	2.1155(19)
C(16)-C(17)	1.400(3)	C(45)-C(46)	1.519(3)
C(17)-C(18)	1.397(3)	C(45)-Rh(1)	2.1152(19)
C(18)-C(19)	1.388(3)	C(46)-C(47)	1.532(3)
C(18)-C(33)	1.520(3)	Cl(1)-Rh(1)	2.3654(4)
C(19)-C(32)	1.401(3)	N(1)-P(1)	1.6477(15)
C(20)-O(4)	1.431(2)	O(1)-P(1)	1.6149(13)
		O(2)-P(1)	1.6283(12)
		P(1)-Rh(1)	2.2703(4)

		C(15)-C(16)-C(4)	122.06(15)
N(1)-C(1)-C(22)	111.20(15)	C(17)-C(16)-C(4)	118.87(16)
N(1)-C(2)-C(3)	110.65(15)	C(18)-C(17)-C(16)	120.60(18)
C(21)-C(3)-C(2)	110.61(16)	C(19)-C(18)-C(17)	119.41(17)
O(1)-C(4)-C(36)	110.47(13)	C(19)-C(18)-C(33)	121.51(19)
O(1)-C(4)-C(16)	105.39(13)	C(17)-C(18)-C(33)	119.1(2)
C(36)-C(4)-C(16)	109.64(13)	C(18)-C(19)-C(32)	121.05(18)
O(1)-C(4)-C(5)	107.50(12)	O(4)-C(20)-O(3)	106.10(15)
C(36)-C(4)-C(5)	112.59(14)	O(4)-C(20)-C(51)	108.68(18)
C(16)-C(4)-C(5)	110.99(14)	O(3)-C(20)-C(51)	109.99(18)
O(3)-C(5)-C(6)	104.78(13)	O(4)-C(20)-C(26)	110.15(17)
O(3)-C(5)-C(4)	112.89(13)	O(3)-C(20)-C(26)	108.71(17)
C(6)-C(5)-C(4)	112.15(14)	C(51)-C(20)-C(26)	112.99(19)
O(4)-C(6)-C(5)	104.52(13)	C(3)-C(21)-C(22)	110.09(16)
O(4)-C(6)-C(7)	111.47(14)	C(21)-C(22)-C(1)	110.59(17)
C(5)-C(6)-C(7)	111.30(14)	C(12)-C(23)-C(8)	118.50(17)
O(2)-C(7)-C(9)	109.83(13)	C(12)-C(23)-C(29)	119.99(17)
O(2)-C(7)-C(13)	105.88(14)	C(8)-C(23)-C(29)	121.49(17)
C(9)-C(7)-C(13)	108.47(13)	C(13)-C(24)-C(28)	121.2(2)
O(2)-C(7)-C(6)	106.56(13)	C(27)-C(25)-C(14)	119.2(2)
C(9)-C(7)-C(6)	113.60(14)	C(27)-C(25)-C(48)	121.0(2)
C(13)-C(7)-C(6)	112.20(14)	C(14)-C(25)-C(48)	119.8(2)
C(9)-C(8)-C(23)	120.88(17)	C(28)-C(27)-C(25)	121.3(2)
C(10)-C(9)-C(8)	119.25(16)	C(27)-C(28)-C(24)	119.0(2)
C(10)-C(9)-C(7)	118.42(16)	C(27)-C(28)-C(50)	121.1(2)
C(8)-C(9)-C(7)	122.22(16)	C(24)-C(28)-C(50)	119.8(2)
C(9)-C(10)-C(11)	121.24(17)	C(15)-C(32)-C(19)	118.71(18)
C(10)-C(11)-C(12)	118.50(17)	C(15)-C(32)-C(31)	120.98(18)
C(10)-C(11)-C(30)	120.56(18)	C(19)-C(32)-C(31)	120.28(18)
C(12)-C(11)-C(30)	120.93(17)	C(36)-C(35)-C(39)	120.92(16)
C(23)-C(12)-C(11)	121.60(17)	C(35)-C(36)-C(37)	119.84(16)
C(24)-C(13)-C(14)	118.63(18)	C(35)-C(36)-C(4)	118.26(15)
C(24)-C(13)-C(7)	122.01(16)	C(37)-C(36)-C(4)	121.60(16)
C(14)-C(13)-C(7)	119.33(18)	C(36)-C(37)-C(38)	119.96(18)
C(25)-C(14)-C(13)	120.6(2)	C(52)-C(38)-C(37)	119.33(18)
C(16)-C(15)-C(32)	121.17(16)	C(52)-C(38)-C(49)	120.58(18)
C(15)-C(16)-C(17)	119.04(16)	C(37)-C(38)-C(49)	120.1(2)

C(52)-C(39)-C(35)	118.33(17)	C(6)-O(4)-C(20)	108.63(13)
C(52)-C(39)-C(34)	121.26(16)	O(1)-P(1)-O(2)	102.74(6)
C(35)-C(39)-C(34)	120.40(17)	O(1)-P(1)-N(1)	98.83(6)
C(41)-C(40)-C(47)	125.9(2)	O(2)-P(1)-N(1)	111.92(7)
C(41)-C(40)-Rh(1)	72.37(13)	O(1)-P(1)-Rh(1)	119.87(5)
C(47)-C(40)-Rh(1)	107.56(14)	O(2)-P(1)-Rh(1)	109.79(4)
C(40)-C(41)-C(42)	124.6(2)	N(1)-P(1)-Rh(1)	112.95(6)
C(40)-C(41)-Rh(1)	71.91(12)	C(45)-Rh(1)-C(44)	39.03(7)
C(42)-C(41)-Rh(1)	111.17(14)	C(45)-Rh(1)-C(40)	80.67(8)
C(41)-C(42)-C(43)	112.04(17)	C(44)-Rh(1)-C(40)	96.82(8)
C(44)-C(43)-C(42)	114.17(17)	C(45)-Rh(1)-C(41)	88.06(8)
C(45)-C(44)-C(43)	124.86(19)	C(44)-Rh(1)-C(41)	80.98(7)
C(45)-C(44)-Rh(1)	70.48(12)	C(40)-Rh(1)-C(41)	35.72(7)
C(43)-C(44)-Rh(1)	110.32(13)	C(45)-Rh(1)-P(1)	96.58(6)
C(44)-C(45)-C(46)	123.42(19)	C(44)-Rh(1)-P(1)	92.26(6)
C(44)-C(45)-Rh(1)	70.50(12)	C(40)-Rh(1)-P(1)	161.33(6)
C(46)-C(45)-Rh(1)	114.63(14)	C(41)-Rh(1)-P(1)	162.90(6)
C(45)-C(46)-C(47)	112.35(17)	C(45)-Rh(1)-Cl(1)	164.48(6)
C(40)-C(47)-C(46)	112.80(17)	C(44)-Rh(1)-Cl(1)	155.62(6)
C(38)-C(52)-C(39)	121.59(17)	C(40)-Rh(1)-Cl(1)	89.47(6)
C(1)-N(1)-C(2)	113.37(14)	C(41)-Rh(1)-Cl(1)	90.90(6)
C(1)-N(1)-P(1)	117.90(12)	P(1)-Rh(1)-Cl(1)	88.919(14)
C(2)-N(1)-P(1)	127.45(12)		
C(4)-O(1)-P(1)	126.59(10)		
C(7)-O(2)-P(1)	131.43(10)		
C(5)-O(3)-C(20)	110.34(13)		

Symmetry transformations used to generate equivalent atoms:

Table 19. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **T9**. The anisotropic displacement factor exponent takes the form: $-2p^2 [h^2 a^{*2} U^{11} + \dots + 2 h k a^* b^* U^{12}]$

	U ¹¹	U ²²	U ³³	U ²³	U ¹³	U ¹²
C(1)	18(1)	27(1)	25(1)	-3(1)	0(1)	-3(1)
C(2)	16(1)	23(1)	23(1)	-4(1)	-2(1)	-2(1)
C(3)	19(1)	29(1)	34(1)	-9(1)	-6(1)	5(1)
C(4)	18(1)	18(1)	14(1)	-1(1)	0(1)	1(1)
C(5)	22(1)	17(1)	16(1)	-1(1)	0(1)	1(1)
C(6)	22(1)	16(1)	18(1)	0(1)	1(1)	-1(1)
C(7)	20(1)	14(1)	19(1)	-1(1)	-1(1)	1(1)
C(8)	25(1)	18(1)	21(1)	-2(1)	1(1)	-2(1)
C(9)	20(1)	16(1)	17(1)	-3(1)	0(1)	3(1)
C(10)	21(1)	24(1)	19(1)	-4(1)	2(1)	2(1)
C(11)	24(1)	28(1)	19(1)	-7(1)	2(1)	3(1)
C(12)	27(1)	27(1)	22(1)	-7(1)	-3(1)	0(1)
C(13)	28(1)	19(1)	18(1)	-1(1)	-1(1)	7(1)
C(14)	37(1)	19(1)	27(1)	-1(1)	-2(1)	7(1)
C(15)	22(1)	17(1)	23(1)	-1(1)	2(1)	0(1)
C(16)	20(1)	16(1)	21(1)	-1(1)	4(1)	0(1)
C(17)	24(1)	26(1)	22(1)	-2(1)	3(1)	-2(1)
C(18)	33(1)	25(1)	26(1)	-2(1)	11(1)	-3(1)
C(19)	26(1)	23(1)	35(1)	1(1)	13(1)	0(1)
C(20)	41(1)	20(1)	20(1)	3(1)	-4(1)	-2(1)
C(21)	29(1)	28(1)	32(1)	-2(1)	-13(1)	5(1)
C(22)	35(1)	26(1)	26(1)	3(1)	-10(1)	-1(1)
C(23)	26(1)	22(1)	25(1)	-5(1)	-2(1)	-2(1)
C(24)	25(1)	26(1)	41(1)	-1(1)	-5(1)	7(1)
C(25)	50(1)	23(1)	28(1)	0(1)	-3(1)	14(1)
C(26)	41(1)	35(1)	29(1)	3(1)	6(1)	-7(1)
C(27)	46(1)	36(1)	35(1)	0(1)	-6(1)	23(1)
C(28)	29(1)	40(1)	52(1)	1(1)	-8(1)	13(1)
C(29)	42(1)	40(1)	33(1)	-6(1)	-2(1)	-16(1)
C(30)	38(1)	61(2)	19(1)	-6(1)	3(1)	-15(1)
C(31)	20(1)	26(1)	49(1)	0(1)	3(1)	1(1)
C(32)	21(1)	15(1)	36(1)	1(1)	6(1)	1(1)

C(33)	49(2)	49(1)	28(1)	-4(1)	16(1)	-5(1)
C(34)	29(1)	23(1)	33(1)	-7(1)	0(1)	-4(1)
C(35)	16(1)	21(1)	19(1)	-4(1)	1(1)	-1(1)
C(36)	16(1)	21(1)	15(1)	-4(1)	1(1)	0(1)
C(37)	22(1)	27(1)	20(1)	-4(1)	-2(1)	4(1)
C(38)	18(1)	40(1)	23(1)	-13(1)	-3(1)	1(1)
C(39)	19(1)	22(1)	23(1)	-7(1)	2(1)	-3(1)
C(40)	18(1)	23(1)	36(1)	-6(1)	1(1)	-6(1)
C(41)	21(1)	22(1)	31(1)	1(1)	3(1)	-5(1)
C(42)	24(1)	32(1)	36(1)	-1(1)	8(1)	-5(1)
C(43)	23(1)	32(1)	31(1)	-4(1)	9(1)	-1(1)
C(44)	16(1)	21(1)	29(1)	-2(1)	0(1)	1(1)
C(45)	17(1)	26(1)	30(1)	2(1)	-4(1)	2(1)
C(46)	20(1)	41(1)	36(1)	-3(1)	-10(1)	1(1)
C(47)	21(1)	43(1)	31(1)	-8(1)	-4(1)	-5(1)
C(48)	71(2)	23(1)	49(1)	1(1)	-2(1)	16(1)
C(49)	39(1)	53(2)	43(1)	-16(1)	-23(1)	13(1)
C(50)	31(2)	57(2)	134(4)	-2(2)	-18(2)	12(1)
C(51)	58(2)	28(1)	38(1)	4(1)	-10(1)	8(1)
C(52)	20(1)	30(1)	26(1)	-13(1)	1(1)	-2(1)
Cl(1)	19(1)	19(1)	24(1)	2(1)	0(1)	1(1)
N(1)	15(1)	22(1)	16(1)	0(1)	-3(1)	-2(1)
O(1)	15(1)	17(1)	15(1)	-1(1)	-1(1)	0(1)
O(2)	17(1)	14(1)	19(1)	0(1)	1(1)	1(1)
O(3)	31(1)	21(1)	17(1)	1(1)	-1(1)	-1(1)
O(4)	38(1)	16(1)	19(1)	1(1)	4(1)	-3(1)
P(1)	14(1)	15(1)	14(1)	0(1)	-1(1)	0(1)
Rh(1)	13(1)	18(1)	19(1)	0(1)	-1(1)	-1(1)

Table 20. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **T9**.

	x	y	z	U(eq)
H(1A)	246	5704	2629	28
H(1B)	727	6383	3057	28
H(2A)	-1218	5322	4121	25
H(2B)	-998	5042	3295	25
H(3A)	-2255	5806	3257	33
H(3B)	-1754	6487	3664	33
H(5)	1061	4779	5732	22
H(6)	-566	4431	5079	22
H(8)	-849	3362	4308	26
H(10)	988	4470	3126	25
H(12)	-905	3311	2064	30
H(14)	688	2673	4516	33
H(15)	-1629	5494	5294	25
H(17)	-359	5649	7259	29
H(19)	-2981	5480	7225	34
H(21A)	-1800	6748	2385	36
H(21B)	-1372	5939	2200	36
H(22A)	-514	7168	2951	35
H(22B)	-274	6864	2138	35
H(24)	2318	4456	4783	37
H(26A)	-1370	4028	6331	52
H(26B)	-1080	3741	7136	52
H(26C)	-1326	3137	6507	52
H(27)	3256	2315	4814	47
H(29A)	-2214	2915	2851	57
H(29B)	-2020	2715	3702	57
H(29C)	-1595	2214	3055	57
H(30A)	486	3754	1406	59
H(30B)	1047	4393	1818	59
H(30C)	89	4585	1529	59
H(31A)	-3582	5927	5809	48

H(31B)	-3641	5034	5971	48
H(31C)	-3155	5334	5243	48
H(33A)	-1384	6095	8365	63
H(33B)	-1369	5186	8414	63
H(33C)	-2277	5629	8390	63
H(34A)	308	8488	6476	42
H(34B)	694	8355	5662	42
H(34C)	1325	8597	6326	42
H(35)	42	7047	5675	22
H(37)	1336	5417	6810	28
H(42A)	3812	7174	3834	37
H(42B)	3393	7449	3066	37
H(43A)	2751	6328	2853	34
H(43B)	3605	6049	3277	34
H(46A)	3860	6428	4697	39
H(46B)	3543	6143	5495	39
H(47A)	2854	7240	5752	38
H(47B)	3658	7548	5277	38
H(48A)	2230	1279	4311	71
H(48B)	1213	1418	4436	71
H(48C)	1841	1302	5134	71
H(49A)	2935	6468	7542	68
H(49B)	2375	5722	7716	68
H(49C)	2174	6499	8146	68
H(50A)	4241	3322	5030	111
H(50B)	3837	4095	5347	111
H(50C)	4027	4010	4478	111
H(51A)	161	2503	6595	62
H(51B)	398	3074	7257	62
H(51C)	1013	3022	6542	62
H(52)	1905	7636	7146	30
H(40)	2103(17)	8005(15)	4886(14)	31(7)
H(41)	2203(17)	7873(15)	3659(14)	30(7)
H(44)	2204(18)	5499(16)	3700(15)	36(7)
H(45)	2348(17)	5594(15)	4956(14)	30(6)

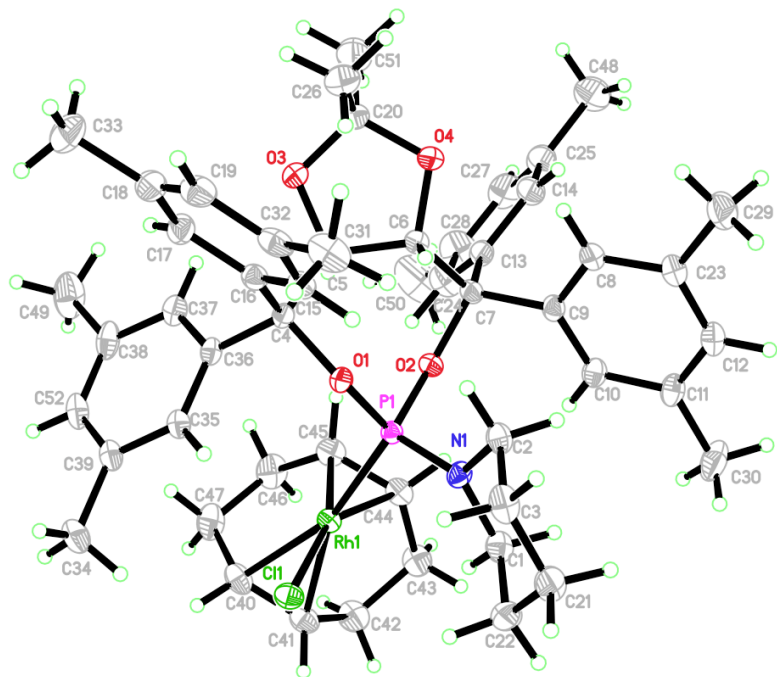


Table 21. Crystal data and structure refinement for **A1**.

Identification code	rovis41_0m	
Empirical formula	C ₃₄ H ₅₀ Cl N O ₂ P Rh	
Formula weight	674.08	
Temperature	120 K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	$a = 10.4105(5) \text{ \AA}$	$\alpha = 77.003(3)^\circ$
	$b = 10.8685(6) \text{ \AA}$	$\beta = 76.360(2)^\circ$
	$c = 16.5368(10) \text{ \AA}$	$\gamma = 64.354(2)^\circ$
Volume	1622.99(15) Å ³	
Z	2	
Density (calculated)	1.379 Mg/m ³	
Absorption coefficient	0.688 mm ⁻¹	
F(000)	708	
Crystal size	0.70 x 0.37 x 0.17 mm ³	
Theta range for data collection	2.10 to 33.37°.	
Index ranges	-16<=h<=13, -16<=k<=15, -25<=l<=25	
Reflections collected	19235	
Independent reflections	12140 [R(int) = 0.0176]	
Completeness to theta = 33.37°	96.3 %	
Absorption correction	Multi-scan	
Max. and min. transmission	0.8890 and 0.6455	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	12140 / 0 / 389	
Goodness-of-fit on F ²	1.104	
Final R indices [I>2sigma(I)]	R1 = 0.0336, wR2 = 0.0761	
R indices (all data)	R1 = 0.0410, wR2 = 0.0792	
Largest diff. peak and hole	1.056 and -0.844 e.Å ⁻³	

Table 22. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **A1**. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	$U(\text{eq})$
C(1)	2679(2)	6412(2)	4177(1)	18(1)
C(2)	3711(2)	5600(2)	3586(1)	13(1)
C(3)	3191(2)	4967(2)	3167(1)	12(1)
C(4)	1725(2)	5267(2)	3240(1)	13(1)
C(5)	1231(2)	6611(2)	4340(1)	19(1)
C(6)	728(2)	6061(2)	3855(1)	16(1)
C(7)	212(2)	7467(2)	5014(1)	29(1)
C(8)	-842(2)	6305(2)	4004(1)	22(1)
C(9)	5251(2)	5552(2)	3354(1)	17(1)
C(10)	5482(2)	6415(2)	3879(1)	23(1)
C(11)	5462(2)	6175(2)	2427(1)	24(1)
C(12)	6416(2)	4076(2)	3485(1)	23(1)
C(13)	6577(2)	718(2)	3606(1)	22(1)
C(14)	4216(2)	1871(2)	4453(1)	25(1)
C(15)	1241(2)	4796(2)	2630(1)	14(1)
C(16)	1684(2)	3384(2)	2628(1)	14(1)
C(17)	1071(2)	2863(2)	2194(1)	18(1)
C(18)	164(2)	3863(2)	1646(1)	22(1)
C(19)	-161(2)	5260(2)	1545(1)	21(1)
C(20)	342(2)	5760(2)	2065(1)	17(1)
C(21)	-45(2)	7279(2)	1987(1)	22(1)
C(22)	-1070(2)	6240(2)	893(1)	28(1)
C(23)	1264(2)	1357(2)	2277(1)	22(1)
C(24)	1991(2)	396(2)	3020(1)	27(1)
C(25)	2139(2)	773(2)	1460(2)	33(1)
C(26)	-240(2)	1330(2)	2412(2)	36(1)
C(27)	6145(2)	815(2)	289(1)	19(1)
C(28)	7404(2)	550(2)	552(1)	19(1)
C(29)	8267(2)	1418(2)	274(1)	24(1)
C(30)	7346(2)	2971(2)	255(1)	22(1)
C(31)	6010(2)	3301(2)	932(1)	16(1)
C(32)	4641(2)	3464(2)	823(1)	16(1)

C(33)	4271(2)	3234(2)	57(1)	21(1)
C(34)	5448(2)	2006(2)	-359(1)	23(1)
Cl(3)	5896(1)	-687(1)	2247(1)	21(1)
N(1)	5070(2)	1691(2)	3620(1)	16(1)
O(1)	2774(1)	2508(1)	3105(1)	14(1)
O(2)	4135(1)	4065(1)	2599(1)	12(1)
P(1)	4404(1)	2437(1)	2749(1)	12(1)
Rh(1)	5602(1)	1536(1)	1559(1)	12(1)

Table 23. Bond lengths [Å] and angles [°] for **A1**.

C(1)-C(5)	1.394(2)	C(29)-C(30)	1.536(3)
C(1)-C(2)	1.400(2)	C(30)-C(31)	1.526(2)
C(2)-C(3)	1.399(2)	C(31)-C(32)	1.409(2)
C(2)-C(9)	1.538(2)	C(31)-Rh(1)	2.1299(17)
C(3)-C(4)	1.397(2)	C(32)-C(33)	1.508(2)
C(3)-O(2)	1.3982(18)	C(32)-Rh(1)	2.1182(17)
C(4)-C(6)	1.407(2)	C(33)-C(34)	1.534(3)
C(4)-C(15)	1.492(2)	Cl(3)-Rh(1)	2.3485(4)
C(5)-C(6)	1.400(2)	N(1)-P(1)	1.6337(15)
C(5)-C(7)	1.513(2)	O(1)-P(1)	1.6333(12)
C(6)-C(8)	1.505(2)	O(2)-P(1)	1.6359(12)
C(9)-C(10)	1.533(2)	P(1)-Rh(1)	2.2451(4)
C(9)-C(11)	1.536(3)	C(5)-C(1)-C(2)	123.69(15)
C(9)-C(12)	1.540(3)	C(3)-C(2)-C(1)	114.97(14)
C(13)-N(1)	1.462(2)	C(3)-C(2)-C(9)	123.15(14)
C(14)-N(1)	1.457(2)	C(1)-C(2)-C(9)	121.57(14)
C(15)-C(16)	1.399(2)	C(4)-C(3)-O(2)	116.60(13)
C(15)-C(20)	1.403(2)	C(4)-C(3)-C(2)	122.91(14)
C(16)-C(17)	1.397(2)	O(2)-C(3)-C(2)	120.33(13)
C(16)-O(1)	1.402(2)	C(3)-C(4)-C(6)	119.67(14)
C(17)-C(18)	1.403(3)	C(3)-C(4)-C(15)	119.01(14)
C(17)-C(23)	1.538(3)	C(6)-C(4)-C(15)	121.25(14)
C(18)-C(19)	1.383(3)	C(1)-C(5)-C(6)	119.50(15)
C(19)-C(20)	1.407(2)	C(1)-C(5)-C(7)	119.57(16)
C(19)-C(22)	1.512(3)	C(6)-C(5)-C(7)	120.88(16)
C(20)-C(21)	1.503(3)	C(5)-C(6)-C(4)	118.45(15)
C(23)-C(24)	1.534(3)	C(5)-C(6)-C(8)	120.17(15)
C(23)-C(25)	1.536(3)	C(4)-C(6)-C(8)	121.37(15)
C(23)-C(26)	1.541(3)	C(10)-C(9)-C(11)	107.65(15)
C(27)-C(28)	1.369(3)	C(10)-C(9)-C(2)	111.50(14)
C(27)-C(34)	1.510(3)	C(11)-C(9)-C(2)	107.96(14)
C(27)-Rh(1)	2.2678(17)	C(10)-C(9)-C(12)	107.42(15)
C(28)-C(29)	1.501(3)	C(11)-C(9)-C(12)	109.48(15)
C(28)-Rh(1)	2.2432(17)	C(2)-C(9)-C(12)	112.70(14)
		C(16)-C(15)-C(20)	120.09(15)

C(16)-C(15)-C(4)	119.49(14)	C(31)-C(32)-Rh(1)	71.09(10)
C(20)-C(15)-C(4)	120.42(15)	C(33)-C(32)-Rh(1)	109.09(11)
C(17)-C(16)-C(15)	122.79(15)	C(32)-C(33)-C(34)	113.89(15)
C(17)-C(16)-O(1)	121.46(15)	C(27)-C(34)-C(33)	111.41(15)
C(15)-C(16)-O(1)	115.74(14)	C(14)-N(1)-C(13)	115.22(14)
C(16)-C(17)-C(18)	114.22(16)	C(14)-N(1)-P(1)	123.53(12)
C(16)-C(17)-C(23)	127.09(17)	C(13)-N(1)-P(1)	121.16(12)
C(18)-C(17)-C(23)	118.68(16)	C(16)-O(1)-P(1)	117.76(10)
C(19)-C(18)-C(17)	124.55(16)	C(3)-O(2)-P(1)	122.20(10)
C(18)-C(19)-C(20)	119.32(16)	O(1)-P(1)-N(1)	97.23(7)
C(18)-C(19)-C(22)	120.29(17)	O(1)-P(1)-O(2)	101.98(6)
C(20)-C(19)-C(22)	120.39(18)	N(1)-P(1)-O(2)	109.12(7)
C(15)-C(20)-C(19)	117.89(16)	O(1)-P(1)-Rh(1)	119.26(5)
C(15)-C(20)-C(21)	121.95(16)	N(1)-P(1)-Rh(1)	118.68(5)
C(19)-C(20)-C(21)	120.13(16)	O(2)-P(1)-Rh(1)	108.89(4)
C(24)-C(23)-C(25)	108.90(17)	C(32)-Rh(1)-C(31)	38.73(7)
C(24)-C(23)-C(17)	115.06(15)	C(32)-Rh(1)-C(28)	96.83(7)
C(25)-C(23)-C(17)	109.30(17)	C(31)-Rh(1)-C(28)	81.16(7)
C(24)-C(23)-C(26)	106.14(18)	C(32)-Rh(1)-P(1)	91.19(5)
C(25)-C(23)-C(26)	108.87(17)	C(31)-Rh(1)-P(1)	95.11(5)
C(17)-C(23)-C(26)	108.39(15)	C(28)-Rh(1)-P(1)	161.50(5)
C(28)-C(27)-C(34)	124.64(17)	C(32)-Rh(1)-C(27)	80.89(7)
C(28)-C(27)-Rh(1)	71.35(10)	C(31)-Rh(1)-C(27)	88.00(7)
C(34)-C(27)-Rh(1)	110.21(11)	C(28)-Rh(1)-C(27)	35.34(7)
C(27)-C(28)-C(29)	125.78(17)	P(1)-Rh(1)-C(27)	163.15(5)
C(27)-C(28)-Rh(1)	73.31(10)	C(32)-Rh(1)-Cl(3)	157.29(5)
C(29)-C(28)-Rh(1)	107.07(11)	C(31)-Rh(1)-Cl(3)	162.92(5)
C(28)-C(29)-C(30)	113.71(15)	C(28)-Rh(1)-Cl(3)	88.04(5)
C(31)-C(30)-C(29)	113.04(15)	P(1)-Rh(1)-Cl(3)	90.953(16)
C(32)-C(31)-C(30)	124.82(16)	C(27)-Rh(1)-Cl(3)	90.81(5)
C(32)-C(31)-Rh(1)	70.19(10)		
C(30)-C(31)-Rh(1)	113.59(11)		
C(31)-C(32)-C(33)	126.44(15)		

Symmetry transformations used to generate equivalent atoms:

Table 24. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **A1**. The anisotropic displacement factor exponent takes the form: $-2p^2 [h^2 a^{*2} U^{11} + \dots + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C(1)	19(1)	18(1)	17(1)	-7(1)	-3(1)	-7(1)
C(2)	14(1)	13(1)	14(1)	-2(1)	-3(1)	-5(1)
C(3)	12(1)	11(1)	11(1)	-3(1)	0(1)	-4(1)
C(4)	12(1)	13(1)	14(1)	-3(1)	-2(1)	-5(1)
C(5)	17(1)	18(1)	18(1)	-9(1)	2(1)	-5(1)
C(6)	12(1)	16(1)	18(1)	-5(1)	0(1)	-4(1)
C(7)	23(1)	35(1)	30(1)	-22(1)	5(1)	-8(1)
C(8)	12(1)	25(1)	27(1)	-10(1)	2(1)	-5(1)
C(9)	14(1)	20(1)	18(1)	-6(1)	-1(1)	-9(1)
C(10)	22(1)	31(1)	25(1)	-10(1)	-4(1)	-14(1)
C(11)	30(1)	29(1)	20(1)	-6(1)	2(1)	-21(1)
C(12)	15(1)	22(1)	33(1)	-7(1)	-6(1)	-5(1)
C(13)	16(1)	23(1)	21(1)	0(1)	-4(1)	-4(1)
C(14)	26(1)	28(1)	14(1)	-2(1)	-1(1)	-6(1)
C(15)	11(1)	16(1)	14(1)	-4(1)	-1(1)	-5(1)
C(16)	10(1)	17(1)	15(1)	-5(1)	0(1)	-5(1)
C(17)	14(1)	22(1)	20(1)	-11(1)	2(1)	-8(1)
C(18)	18(1)	31(1)	21(1)	-12(1)	-3(1)	-10(1)
C(19)	13(1)	31(1)	17(1)	-5(1)	-3(1)	-6(1)
C(20)	11(1)	20(1)	18(1)	-3(1)	-2(1)	-4(1)
C(21)	19(1)	18(1)	25(1)	1(1)	-7(1)	-4(1)
C(22)	21(1)	40(1)	22(1)	-4(1)	-9(1)	-8(1)
C(23)	16(1)	23(1)	33(1)	-16(1)	4(1)	-9(1)
C(24)	27(1)	20(1)	37(1)	-8(1)	2(1)	-13(1)
C(25)	29(1)	33(1)	37(1)	-23(1)	5(1)	-10(1)
C(26)	20(1)	31(1)	65(2)	-22(1)	1(1)	-14(1)
C(27)	27(1)	15(1)	15(1)	-7(1)	-1(1)	-7(1)
C(28)	20(1)	14(1)	18(1)	-5(1)	3(1)	-3(1)
C(29)	18(1)	20(1)	26(1)	-4(1)	6(1)	-5(1)
C(30)	20(1)	20(1)	23(1)	-4(1)	5(1)	-9(1)
C(31)	19(1)	12(1)	16(1)	-3(1)	1(1)	-7(1)
C(32)	18(1)	13(1)	15(1)	-2(1)	-2(1)	-3(1)

C(33)	24(1)	19(1)	18(1)	-2(1)	-7(1)	-4(1)
C(34)	32(1)	20(1)	17(1)	-5(1)	-5(1)	-8(1)
Cl(3)	22(1)	12(1)	25(1)	-1(1)	2(1)	-6(1)
N(1)	14(1)	16(1)	13(1)	-1(1)	-2(1)	-4(1)
O(1)	11(1)	14(1)	16(1)	-2(1)	0(1)	-5(1)
O(2)	12(1)	12(1)	13(1)	-4(1)	1(1)	-4(1)
P(1)	11(1)	11(1)	12(1)	-3(1)	0(1)	-4(1)
Rh(1)	12(1)	10(1)	13(1)	-3(1)	0(1)	-3(1)

Table 25. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **A1**.

	x	y	z	U(eq)
H(1)	2976	6842	4478	21
H(7A)	739	7761	5279	44
H(7B)	-220	6923	5427	44
H(7C)	-528	8260	4765	44
H(8A)	-977	5748	3683	33
H(8B)	-1408	7260	3834	33
H(8C)	-1141	6061	4591	33
H(10A)	5377	6035	4462	35
H(10B)	4779	7347	3804	35
H(10C)	6433	6403	3700	35
H(11A)	6423	6144	2266	36
H(11B)	4777	7115	2353	36
H(11C)	5319	5656	2083	36
H(12A)	6231	3656	4051	35
H(12B)	7348	4109	3385	35
H(12C)	6396	3545	3099	35
H(13A)	7027	984	3940	33
H(13B)	7074	721	3038	33
H(13C)	6619	-191	3831	33
H(14A)	3942	1106	4667	38
H(14B)	3365	2711	4419	38
H(14C)	4777	1913	4823	38
H(18)	-247	3567	1328	26
H(21A)	527	7429	2302	34
H(21B)	-1049	7738	2203	34
H(21C)	140	7640	1406	34
H(22A)	-1369	5738	620	43
H(22B)	-513	6671	483	43
H(22C)	-1905	6933	1161	43
H(24A)	1942	-481	3073	41
H(24B)	1504	796	3527	41

H(24C)	2983	272	2926	41
H(25A)	1661	1339	995	49
H(25B)	2216	-150	1498	49
H(25C)	3086	765	1378	49
H(26A)	-726	1885	1947	54
H(26B)	-793	1690	2922	54
H(26C)	-138	398	2450	54
H(29A)	8802	1246	-283	28
H(29B)	8961	1138	652	28
H(30A)	7932	3417	329	26
H(30B)	7044	3349	-292	26
H(33A)	4094	4061	-352	26
H(33B)	3384	3087	216	26
H(34A)	5027	1709	-702	28
H(34B)	6177	2291	-724	28
H(5)	3810(20)	4010(20)	1165(14)	17(5)
H(3)	7840(20)	-300(20)	836(13)	14(5)
H(2)	6040(20)	3770(20)	1363(14)	19(5)
H(4)	5750(30)	180(30)	435(16)	29(6)

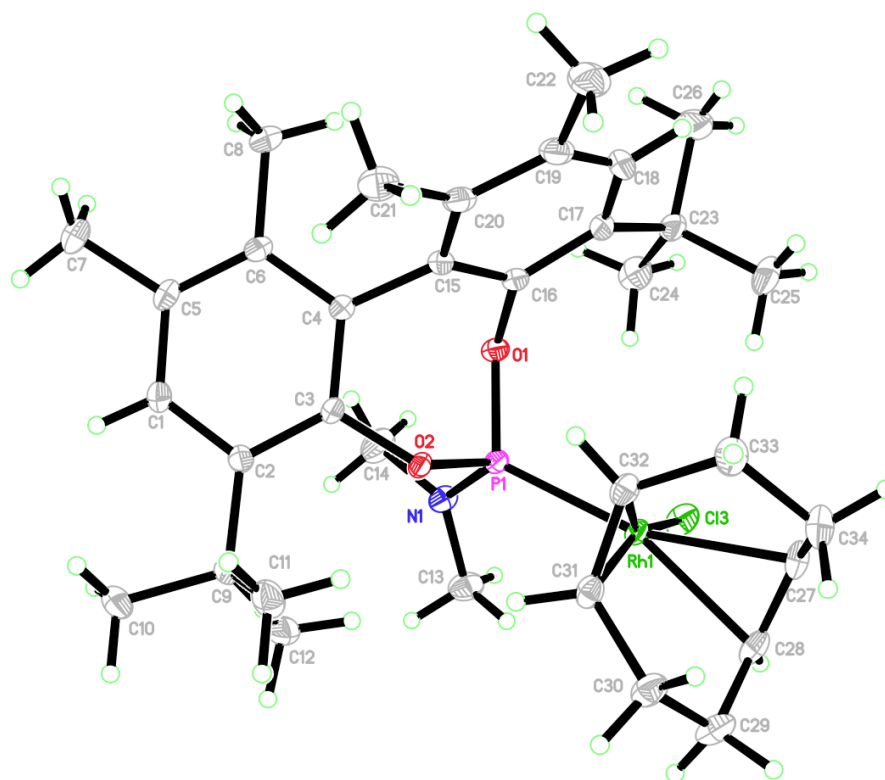


Table 26. Crystal data and structure refinement for **B4**.

Identification code	rovis45_0m	
Empirical formula	C ₃₆ H ₄₆ Cl N O ₂ P Rh Si ₂	
Formula weight	750.25	
Temperature	120 K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	P 2 ₁ 2 ₁ 2 ₁	
Unit cell dimensions	$a = 11.2417(5)$ Å	$\alpha = 90^\circ$
	$b = 14.6792(6)$ Å	$\beta = 90^\circ$
	$c = 21.3614(9)$ Å	$\gamma = 90^\circ$
Volume	3525.0(3) Å ³	
Z	4	
Density (calculated)	1.414 Mg/m ³	
Absorption coefficient	0.706 mm ⁻¹	
F(000)	1560	
Crystal size	0.23 x 0.09 x 0.07 mm ³	
Theta range for data collection	1.68 to 33.27°.	
Index ranges	-17<=h<=9, -22<=k<=13, -32<=l<=32	
Reflections collected	31400	
Independent reflections	12869 [R(int) = 0.0581]	
Completeness to theta = 33.27°	99.8 %	
Absorption correction	Multi-scan	
Max. and min. transmission	0.9535 and 0.8516	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	12869 / 0 / 422	
Goodness-of-fit on F ²	0.996	
Final R indices [I>2sigma(I)]	R1 = 0.0453, wR2 = 0.0863	
R indices (all data)	R1 = NaN, wR2 = 0.1035	
Absolute structure parameter	-0.02(2)	
Largest diff. peak and hole	0.606 and -0.511 e.Å ⁻³	

Table 27. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **B4**. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	$U(\text{eq})$
C(1)	2668(3)	9520(2)	7963(1)	13(1)
C(2)	2739(3)	9780(2)	8586(1)	13(1)
C(3)	3808(3)	9550(2)	8970(1)	14(1)
C(4)	4184(3)	8655(2)	9024(1)	14(1)
C(5)	4491(3)	10242(2)	9275(1)	16(1)
C(6)	4291(3)	11185(2)	9180(1)	21(1)
C(7)	5006(3)	11826(2)	9464(2)	25(1)
C(8)	5938(4)	11561(2)	9862(2)	28(1)
C(9)	6161(3)	10659(2)	9959(2)	25(1)
C(10)	5458(3)	9979(2)	9667(1)	18(1)
C(11)	5676(3)	9047(2)	9765(1)	20(1)
C(12)	1735(3)	9766(2)	7554(1)	14(1)
C(13)	822(3)	10266(2)	7815(1)	16(1)
C(14)	1739(3)	10247(2)	8852(1)	13(1)
C(15)	779(3)	10498(2)	8459(1)	15(1)
C(16)	5064(3)	8364(2)	9455(1)	18(1)
C(17)	-202(3)	10975(2)	8712(2)	19(1)
C(18)	-256(3)	11172(2)	9337(2)	25(1)
C(19)	660(3)	10898(2)	9735(2)	22(1)
C(20)	1644(3)	10454(2)	9501(1)	18(1)
C(21)	6948(3)	6855(3)	9421(2)	30(1)
C(22)	4290(3)	6298(2)	9382(2)	29(1)
C(23)	5371(4)	7106(3)	10556(2)	35(1)
C(24)	719(3)	10386(2)	6319(2)	29(1)
C(25)	3102(3)	9395(3)	6291(2)	28(1)
C(26)	888(4)	8363(2)	6575(2)	31(1)
C(27)	3357(3)	6739(2)	7088(2)	28(1)
C(28)	1950(3)	7068(3)	7938(2)	31(1)
C(29)	7986(3)	7731(2)	7648(2)	22(1)
C(30)	7579(3)	7587(2)	7054(2)	22(1)
C(31)	8513(3)	8598(3)	7896(2)	26(1)
C(32)	7583(3)	9197(2)	8227(2)	27(1)

C(33)	6394(3)	9198(2)	7905(2)	22(1)
C(34)	6176(3)	9175(2)	7261(2)	23(1)
C(35)	7115(3)	9224(3)	6747(2)	28(1)
C(36)	7507(3)	8280(3)	6531(2)	30(1)
Cl(1)	5810(1)	6265(1)	7811(1)	27(1)
N(1)	3063(2)	7296(2)	7631(1)	19(1)
O(1)	3630(2)	9053(1)	7708(1)	15(1)
O(2)	3651(2)	7999(1)	8639(1)	15(1)
P(2)	4043(1)	8027(1)	7902(1)	14(1)
Rh(1)	5961(1)	7841(1)	7651(1)	15(1)
Si(1)	1647(1)	9484(1)	6693(1)	18(1)
Si(3)	5400(1)	7133(1)	9681(1)	20(1)

—

Table 28. Bond lengths [Å] and angles [°] for **B4**.

C(1)-C(2)	1.387(4)	C(28)-N(1)	1.452(4)
C(1)-O(1)	1.392(3)	C(29)-C(30)	1.365(5)
C(1)-C(12)	1.411(4)	C(29)-C(31)	1.500(5)
C(2)-C(14)	1.433(4)	C(29)-Rh(1)	2.282(3)
C(2)-C(3)	1.494(4)	C(30)-C(36)	1.513(5)
C(3)-C(4)	1.385(4)	C(30)-Rh(1)	2.252(3)
C(3)-C(5)	1.430(4)	C(31)-C(32)	1.539(5)
C(4)-O(2)	1.402(3)	C(32)-C(33)	1.503(5)
C(4)-C(16)	1.417(4)	C(33)-C(34)	1.396(5)
C(5)-C(6)	1.417(4)	C(33)-Rh(1)	2.120(3)
C(5)-C(10)	1.426(4)	C(34)-C(35)	1.525(5)
C(6)-C(7)	1.378(5)	C(34)-Rh(1)	2.141(3)
C(7)-C(8)	1.404(5)	C(35)-C(36)	1.525(5)
C(8)-C(9)	1.363(5)	Cl(1)-Rh(1)	2.3455(8)
C(9)-C(10)	1.417(4)	N(1)-P(2)	1.643(3)
C(10)-C(11)	1.406(4)	O(1)-P(2)	1.630(2)
C(11)-C(16)	1.385(4)	O(2)-P(2)	1.634(2)
C(12)-C(13)	1.380(4)	P(2)-Rh(1)	2.2388(9)
C(12)-Si(1)	1.888(3)		
C(13)-C(15)	1.418(4)		
C(14)-C(15)	1.415(4)		
C(14)-C(20)	1.424(4)		
C(15)-C(17)	1.414(4)		
C(16)-Si(3)	1.907(3)		
C(17)-C(18)	1.367(5)		
C(18)-C(19)	1.394(5)		
C(19)-C(20)	1.377(4)		
C(21)-Si(3)	1.872(4)		
C(22)-Si(3)	1.863(4)		
C(23)-Si(3)	1.870(3)		
C(24)-Si(1)	1.866(4)		
C(25)-Si(1)	1.852(4)		
C(26)-Si(1)	1.871(4)		
C(27)-N(1)	1.457(4)		

		C(18)-C(17)-C(15)	120.8(3)
C(2)-C(1)-O(1)	117.8(3)	C(17)-C(18)-C(19)	120.1(3)
C(2)-C(1)-C(12)	124.5(3)	C(20)-C(19)-C(18)	120.6(3)
O(1)-C(1)-C(12)	117.5(2)	C(19)-C(20)-C(14)	120.9(3)
C(1)-C(2)-C(14)	117.8(3)	C(30)-C(29)-C(31)	126.2(3)
C(1)-C(2)-C(3)	120.7(3)	C(30)-C(29)-Rh(1)	71.30(19)
C(14)-C(2)-C(3)	121.5(2)	C(31)-C(29)-Rh(1)	109.4(2)
C(4)-C(3)-C(5)	118.2(3)	C(29)-C(30)-C(36)	126.9(3)
C(4)-C(3)-C(2)	120.4(3)	C(29)-C(30)-Rh(1)	73.67(19)
C(5)-C(3)-C(2)	121.4(3)	C(36)-C(30)-Rh(1)	105.3(2)
C(3)-C(4)-O(2)	118.1(3)	C(29)-C(31)-C(32)	112.3(3)
C(3)-C(4)-C(16)	123.6(3)	C(33)-C(32)-C(31)	113.2(3)
O(2)-C(4)-C(16)	118.2(3)	C(34)-C(33)-C(32)	127.3(3)
C(6)-C(5)-C(10)	118.0(3)	C(34)-C(33)-Rh(1)	71.7(2)
C(6)-C(5)-C(3)	123.0(3)	C(32)-C(33)-Rh(1)	108.7(2)
C(10)-C(5)-C(3)	118.9(3)	C(33)-C(34)-C(35)	125.9(3)
C(7)-C(6)-C(5)	120.7(3)	C(33)-C(34)-Rh(1)	70.0(2)
C(6)-C(7)-C(8)	120.8(3)	C(35)-C(34)-Rh(1)	113.6(2)
C(9)-C(8)-C(7)	119.9(3)	C(36)-C(35)-C(34)	112.0(3)
C(8)-C(9)-C(10)	121.0(3)	C(30)-C(36)-C(35)	113.7(3)
C(11)-C(10)-C(9)	121.5(3)	C(28)-N(1)-C(27)	115.2(3)
C(11)-C(10)-C(5)	119.0(3)	C(28)-N(1)-P(2)	124.7(2)
C(9)-C(10)-C(5)	119.5(3)	C(27)-N(1)-P(2)	119.7(2)
C(16)-C(11)-C(10)	123.2(3)	C(1)-O(1)-P(2)	125.26(19)
C(13)-C(12)-C(1)	116.0(3)	C(4)-O(2)-P(2)	115.68(17)
C(13)-C(12)-Si(1)	118.1(2)	O(1)-P(2)-O(2)	101.02(11)
C(1)-C(12)-Si(1)	125.8(2)	O(1)-P(2)-N(1)	108.82(13)
C(12)-C(13)-C(15)	123.0(3)	O(2)-P(2)-N(1)	98.22(12)
C(15)-C(14)-C(20)	117.7(3)	O(1)-P(2)-Rh(1)	108.99(8)
C(15)-C(14)-C(2)	119.2(2)	O(2)-P(2)-Rh(1)	119.14(8)
C(20)-C(14)-C(2)	123.1(3)	N(1)-P(2)-Rh(1)	118.83(10)
C(17)-C(15)-C(14)	119.8(3)	C(33)-Rh(1)-C(34)	38.25(13)
C(17)-C(15)-C(13)	121.1(3)	C(33)-Rh(1)-P(2)	92.62(10)
C(14)-C(15)-C(13)	119.1(3)	C(34)-Rh(1)-P(2)	95.22(10)
C(11)-C(16)-C(4)	116.0(3)	C(33)-Rh(1)-C(30)	96.59(14)
C(11)-C(16)-Si(3)	117.8(2)	C(34)-Rh(1)-C(30)	80.79(13)
C(4)-C(16)-Si(3)	126.0(2)	P(2)-Rh(1)-C(30)	159.00(9)

C(33)-Rh(1)-C(29)	80.71(13)
C(34)-Rh(1)-C(29)	87.19(13)
P(2)-Rh(1)-C(29)	165.96(9)
C(30)-Rh(1)-C(29)	35.02(12)
C(33)-Rh(1)-Cl(1)	154.96(10)
C(34)-Rh(1)-Cl(1)	165.24(10)
P(2)-Rh(1)-Cl(1)	90.89(3)
C(30)-Rh(1)-Cl(1)	88.71(9)
C(29)-Rh(1)-Cl(1)	90.14(9)
C(25)-Si(1)-C(24)	110.21(17)
C(25)-Si(1)-C(26)	106.13(18)
C(24)-Si(1)-C(26)	108.07(18)
C(25)-Si(1)-C(12)	114.94(15)
C(24)-Si(1)-C(12)	106.95(15)
C(26)-Si(1)-C(12)	110.39(15)
C(22)-Si(3)-C(23)	108.46(19)
C(22)-Si(3)-C(21)	112.20(17)
C(23)-Si(3)-C(21)	107.93(18)
C(22)-Si(3)-C(16)	113.88(15)
C(23)-Si(3)-C(16)	105.61(16)
C(21)-Si(3)-C(16)	108.39(16)

Symmetry transformations used to generate equivalent atoms:

Table 29. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **B4**. The anisotropic displacement factor exponent takes the form: $-2p^2 [h^2 a^{*2} U^{11} + \dots + 2 h k a^* b^* U^{12}]$

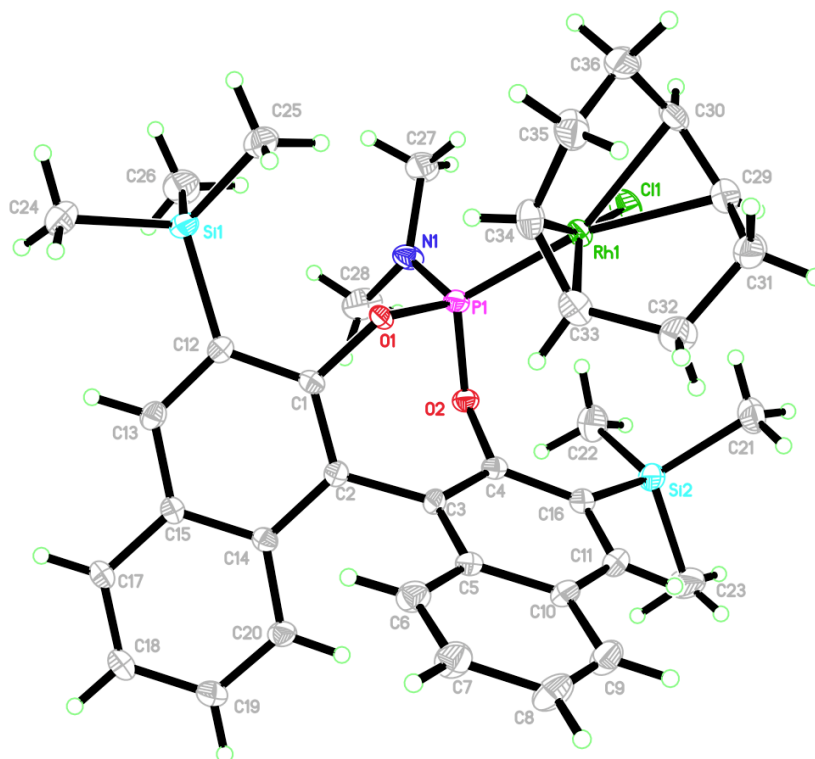
	U ¹¹	U ²²	U ³³	U ²³	U ¹³	U ¹²
C(1)	14(1)	11(1)	14(1)	-1(1)	3(1)	1(1)
C(2)	14(1)	12(1)	14(1)	0(1)	-1(1)	-1(1)
C(3)	14(2)	16(1)	12(1)	2(1)	-1(1)	2(1)
C(4)	15(2)	15(1)	12(1)	-1(1)	2(1)	0(1)
C(5)	18(2)	18(1)	13(1)	-3(1)	0(1)	3(1)
C(6)	26(2)	17(1)	20(1)	-1(1)	-2(1)	0(1)
C(7)	31(2)	18(2)	27(2)	-2(1)	-6(1)	-1(1)
C(8)	32(2)	25(2)	26(2)	-4(1)	-10(2)	-10(2)
C(9)	25(2)	27(2)	22(1)	-2(1)	-8(1)	-2(1)
C(10)	19(2)	20(2)	14(1)	-2(1)	-3(1)	-1(1)
C(11)	20(2)	24(2)	18(1)	-3(1)	-5(1)	3(1)
C(12)	14(1)	14(1)	14(1)	1(1)	-1(1)	-2(1)
C(13)	15(2)	16(1)	17(1)	-1(1)	-4(1)	-2(1)
C(14)	15(1)	11(1)	14(1)	1(1)	2(1)	1(1)
C(15)	14(2)	14(1)	17(1)	0(1)	0(1)	1(1)
C(16)	18(2)	23(2)	14(1)	-2(1)	-1(1)	5(1)
C(17)	18(2)	18(2)	21(1)	-3(1)	0(1)	6(1)
C(18)	24(2)	25(2)	26(2)	-4(1)	0(1)	11(2)
C(19)	24(2)	26(2)	17(1)	-3(1)	3(1)	5(1)
C(20)	24(2)	15(1)	14(1)	0(1)	-1(1)	2(1)
C(21)	24(2)	30(2)	35(2)	-3(2)	-4(2)	9(2)
C(22)	30(2)	22(2)	34(2)	6(2)	-3(2)	2(2)
C(23)	54(2)	33(2)	19(1)	3(2)	-5(2)	13(2)
C(24)	33(2)	34(2)	21(2)	-1(1)	-7(2)	5(2)
C(25)	24(2)	43(2)	18(1)	0(2)	0(1)	1(2)
C(26)	32(2)	29(2)	32(2)	-8(2)	-3(2)	-3(2)
C(27)	28(2)	28(2)	29(2)	-16(2)	-5(2)	0(2)
C(28)	26(2)	41(2)	26(2)	-4(2)	4(1)	-16(2)
C(29)	19(1)	23(2)	25(1)	2(2)	0(1)	1(1)
C(30)	15(2)	25(2)	24(2)	-6(1)	4(1)	3(1)
C(31)	19(2)	35(2)	24(2)	-2(2)	-2(1)	-3(2)
C(32)	25(2)	28(2)	29(2)	-6(2)	0(2)	-6(2)

C(33)	19(2)	15(2)	32(2)	-3(1)	3(1)	-4(1)
C(34)	20(2)	17(1)	31(2)	5(1)	-2(1)	2(1)
C(35)	22(2)	35(2)	29(2)	10(2)	3(2)	1(2)
C(36)	22(2)	47(2)	20(2)	1(2)	4(1)	-2(2)
Cl(1)	26(1)	15(1)	38(1)	-2(1)	2(1)	2(1)
N(1)	17(1)	21(1)	20(1)	-7(1)	3(1)	-4(1)
O(1)	14(1)	17(1)	13(1)	0(1)	2(1)	5(1)
O(2)	18(1)	15(1)	13(1)	-2(1)	0(1)	1(1)
P(2)	14(1)	15(1)	14(1)	-2(1)	1(1)	0(1)
Rh(1)	14(1)	14(1)	19(1)	-2(1)	1(1)	1(1)
Si(1)	18(1)	23(1)	14(1)	-3(1)	-2(1)	0(1)
Si(3)	23(1)	19(1)	18(1)	1(1)	-2(1)	6(1)

Table 30. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **B4**.

	x	y	z	U(eq)
H(6)	3669	11374	8924	25
H(7)	4870	12442	9391	30
H(8)	6403	11999	10059	33
H(9)	6783	10487	10220	30
H(11)	6260	8881	10052	25
H(13)	206	10460	7557	19
H(17)	-818	11158	8450	23
H(18)	-904	11489	9497	30
H(19)	607	11016	10162	27
H(20)	2254	10286	9771	21
H(21A)	6980	6848	8972	44
H(21B)	7171	6268	9579	44
H(21C)	7488	7308	9578	44
H(22A)	3502	6509	9476	43
H(22B)	4417	5718	9579	43
H(22C)	4377	6235	8937	43
H(23A)	5537	6499	10698	53
H(23B)	4600	7290	10701	53
H(23C)	5962	7516	10717	53
H(24A)	765	10328	5872	44
H(24B)	1006	10975	6442	44
H(24C)	-93	10318	6450	44
H(25A)	3546	9946	6355	43
H(25B)	2976	9304	5851	43
H(25C)	3539	8888	6459	43
H(26A)	1386	7882	6730	46
H(26B)	742	8272	6136	46
H(26C)	146	8360	6797	46
H(27A)	2769	6827	6768	43
H(27B)	3374	6109	7208	43
H(27C)	4124	6913	6931	43

H(28A)	2039	6504	8161	47
H(28B)	1334	7005	7630	47
H(28C)	1741	7542	8227	47
H(31A)	8860	8938	7552	32
H(31B)	9144	8452	8188	32
H(32A)	7481	8982	8653	33
H(32B)	7878	9818	8247	33
H(35A)	6795	9557	6393	34
H(35B)	7802	9555	6902	34
H(36A)	6951	8062	6218	36
H(36B)	8281	8329	6334	36
H(29)	8080(30)	7230(20)	7882(15)	16(8)
H(30)	7440(30)	7020(20)	6941(14)	8(8)
H(33)	5790(40)	9430(30)	8163(18)	31(11)
H(34)	5530(30)	9340(30)	7133(17)	20(10)



¹ Yu, R. T.; Rovis, T. *J. Am. Chem. Soc.* **2006**, *128*, 12370-12371.

² Lee, E. E.; Rovis, T. *Org. Lett.* **2008**, *10*, 1231-1234.

³ Yu, R. T.; Lee, E. E.; Malik, G.; Rovis, T. *Angew. Chem. Int. Ed.* **2009**, *48*, 2379-2382.

⁴ Giacomina, F.; Meetsma, A.; Panella, L.; Lefort, L.; de Vries, A. H. M.; de Vries, J.G. *Angew. Chem. Int. Ed.* **2007**, *46*, 1497-1500.

⁵ Yu, R. T.; Rovis, T. *J. Am. Chem. Soc.* **2008**, *130*, 3262-3263.

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⁷ Sheldrick, G. (1997) *SHELXL-97 Program for Crystal Structure Refinement*, Institut für Anorganische Chemie der Universität, Göttingen, Germany.