Supporting Information

Chelate-Assisted Oxidative Coupling Reaction of Arylamides and Unactivated Alkenes: Mechanistic Evidence for Vinyl C–H Bond Activation Promoted by an Electrophilic Ruthenium-Hydride Catalyst

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General Information. All operations were carried out in an inert-atmosphere glove box or by using standard high vacuum and Schlenk techniques unless otherwise noted. Tetrahydrofuran, benzene, toluene, chlorobenzene and Et_2O were distilled from purple solutions of sodium and benzophenone. Dichloromethane and *n*-hexanes were distilled over CaH_2. The NMR solvents were dried from activated molecular sieves (4 Å). The ^{1}H, ^{2}H, ^{13}C and ^{31}P NMR spectra were recorded on a Varian 300 or 400 MHz FT-NMR spectrometer. Mass spectra were recorded from a Agilent 6850 GC/MS spectrometer. The conversion of organic products was measured from a Hewlett-Packard HP 6890 GC spectrometer. FT-IR spectra were recorded on Perkin Elmer Spectrum 100. Elemental analysis was performed at the Midwest Microlab, Indianapolis, IN.

General Procedure for Catalyst Survey. In a glove box, catalyst (25 μmol, 5 mol %), *N,N*-dimethylbenzamide (75 mg, 0.5 mmol) and cyclopentene (170 mg, 2.5 mmol) were dissolved in CH_2Cl_2 (2 mL) in a 25 mL Schlenk tube equipped with a Teflon screw cap stopcock and a magnetic stirring bar. The tube was brought out of the box, and was stirred for 5 h in an oil bath set at 80 °C. After the tube was cooled to room temperature, the solution was filtered through a short silica plug (hexanes/EtOAc = 2:1) in air, and the filtrate was analyzed by GC.

Table S1. Catalyst Survey for the Coupling reaction of *N,N*-Dimethylbenzamide and Cyclopentene.[a]

entry	catalyst	additive	**2a**:**3a**	yield[b]
1	**1**		88:12	52
2	**1**	$HBF_4{\cdot}OEt_2$	80:20	48
3	$[RuH(CO)(PCy_3)]_4(O)(OH)_2$	$HBF_4{\cdot}OEt_2$	84:16	52
4	$RuHCl(CO)(PCy_3)_2$	$HBF_4{\cdot}OEt_2$		0
5	$RuH_2(CO)(PPh_3)_3$	$HBF_4{\cdot}OEt_2$		0
6	$RuCl_2(PPh_3)_3$	$HBF_4{\cdot}OEt_2$		0
7	$RuCl_3{\cdot}3H_2O$	$HBF_4{\cdot}OEt_2$		0
8	$RuH_2(CO)(PPh_3)_3$	$HBF_4{\cdot}OEt_2$		0
9	$Ru_3(CO)_{12}$	NH_4PF_6		0

10[c]	$[RuH(CO)(PCy_3)_2(S)_2]^+BF_4^-$		0
11	$Re(CO)_3(THF)_2Br$	$HBF_4 \cdot OEt_2$	0
12	$Au(PPh_3)_3Cl$	$HBF_4 \cdot OEt_2$	0
13	$HBF_4 \cdot OEt_2$		0
14	$Cy_3PH^+BF_4^-$		0

[a]Reaction conditions: *N,N*-dimethylbenzamide (75 mg, 0.5 mmol), cyclopentene (170 mg, 2.5 mmol), catalyst (5 mol %), CH_2Cl_2 (2 mL), 80 °C, 5 h. [b]The conversion of *N,N*-dimethylbenzamide as determined by GC. [c]S = CH_3CN.

Representative Procedure of the Catalytic Reaction. In a glove box, complex **1** (15 mg, 25 μmol), an arylamide (0.5 mmol) and an alkene (2.5 mmol) were dissolved in CH_2Cl_2 (2 mL) in a 25 mL Schlenk tube equipped with a Teflon screw cap stopcock and a magnetic stirring bar. The tube was brought out of the box, and was stirred for 5 h in an oil bath set at 80 °C (chlorobenzene was used for the reaction temperature at 100-130 °C). After the tube was cooled to room temperature, the solution was filtered through a short silica plug (hexanes/EtOAc = 2:1) in air, and the filtrate was analyzed by GC. Typically, the product mixture of **2** and **3** was not separable by column chromatography, and was subjected to the hydrogenation reaction to obtain isolated yield of the products. The treatment of the crude product mixture with H_2 (1 atm) in the presence of **1** (15 mg, 5 mol %) in chlorobenzene at 110 °C for 2 h led to the clean formation of the hydrogenated product **3**. Analytically pure organic product was isolated after a column chromatography on silica gel (hexanes/EtOAc).

$[(C_{10}H_7CONMe_2)RuH(CO)(PCy_3)]^+BF_4^-$ (5). In a glove box, $\{[(PCy_3)(CO)RuH]_4(\mu_4\text{-}O)(\mu_3\text{-}OH)(\mu_2\text{-}OH)\}$, (200 mg, 0.12 mmol) and *N,N*-dimethyl-2-naphthamide were dissolved in CH_2Cl_2 (5 mL) in a 25 mL Schlenk tube equipped with a Teflon screw cap stopcock and a magnetic stirring bar. The tube was brought out of the box, and $HBF_4 \cdot OEt_2$ (64 μL, 0.48 mmol) was added under N_2 stream. The color of the solution was changed from dark red to green immediately. After stirring for 1 h at room temperature, the solvent was removed under vacuum,

and the residue was crashed by adding hexanes (10 mL). Filtering the resulting solid through a fritted funnel and recrystallization from CH_2Cl_2/hexanes yielded the product as a light green powder (210 mg, ca. 60% yield, estimated purity by ^1H NMR ~80%; contained 2 other minor isomers (~20%)).

Spectroscopic data for the major isomer of **5**: ^1H NMR (CD_2Cl_2, 400 MHz) δ 7.9-7.4 (m, 7H, Ar), 3.2 and 3.0 (s, 3H, $N(CH_3)_2$), 2.0-1.2 (m, PCy_3), -21.7 (br, Ru-H); $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 100.5 MHz) δ 197.6 (d, J_{CP} = 18.2 Hz, Ru-CO), 178.7 ($CON(CH_3)_2$), 134.8, 132.9, 129.6, 129.2, 128.9, 128.4, 128.0 and 123.9 (Ar), 38.9 ($N(CH_3)_2$), 38.6 (CH), 35.1 ($N(CH_3)_2$), 32.1, 30.9, 30.4, 29.9, 28.0, 26.8, 26.2 (CH_2); $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 161.8 MHz) δ 74.4 (PCy_3); IR (CD_2Cl_2) ν_{CO} = 1930, 1585 cm^{-1}.

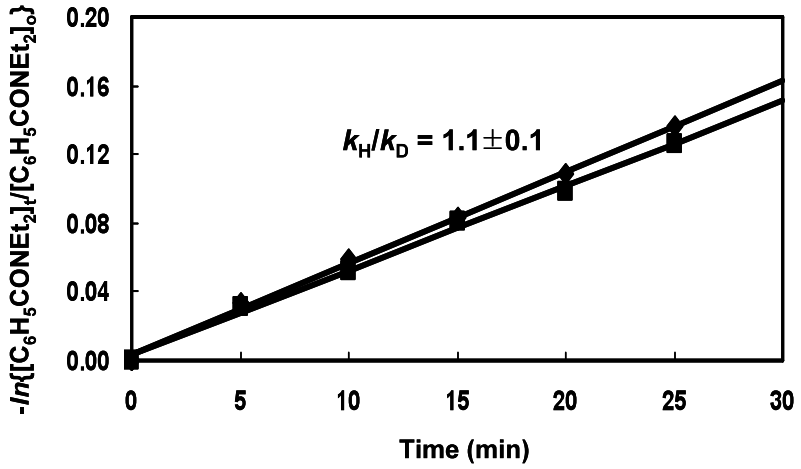
$[(C_{15}H_{13}CONMe_2)RuH(CO)(PCy_3)]^+BF_4^-$ (6). In a glove box, complex **5** (100 mg, 0.14 mmol) and cyclopentene (100 mg, 1.5 mmol) were dissolved in CH_2Cl_2 (5 mL) in a 25 mL Schlenk tube equipped with a Teflon screw cap stopcock and a magnetic stirring bar. The color of the solution was changed from green to orange immediately. After stirring for 1 h at room temperature, the solvent was removed under vacuum, and *n*-hexanes (10 mL) was added to the residue. The resulting solid was filtered through a fritted funnel and recrystallized from CH_2Cl_2/hexanes to yield the product as a pale yellow powder (90 mg, 82% yield). Single crystals of **6** suitable for X-ray crystallography were obtained from CH_2Cl_2/*n*-pentane solution.

For **6**: ^1H NMR (CD_2Cl_2, 400.0 MHz) δ 8.45 (s, 1H, Ar), 8.06 (m, 1H, Ar), 7.94 (m, 2H, Ar), 7.72 (m, 2H, Ar), 5.5 (s, CC*H*CH_2) 3.4 (s, 3H, $N(CH_3)_2$), 3.3 (m, 1H, CH_2), 3.2 (s, 3H, $N(CH_3)_2$), 3.1 (m, 1H, CH_2), 2.8 (m, 2H, CH_2), 2.0-1.8 (br, 6H, PCy_3), 1.8 (m, 2H, CH_2), 1.8-0.6 (br, 27H, PCy_3), -19.6 (d, J_{PH} = 21.8 Hz, Ru-H); $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 100.5 MHz) δ 201.2 (d, J_{CP} = 15.4 Hz, Ru-CO), 174.3 ($CON(CH_3)_2$), 136.4, 135.2, 132.4, 130.7, 130.5, 130.3, 129.4, 129.2, 128.3 and 117.8 (Ar), 115.5 (d, J_{CP} = 5.1 Hz, Ru-C), 104.7 (d, J_{CP} = 11.6 Hz, Ru-C), 42.4 ($N(CH_3)_2$), 37.6 and 37.5 (CH_2), 37.3 ($N(CH_3)_2$), 34.6 and 34.4 (CH), 30.4, 30.0, 28.1, 28.0, 27.9, 27.8, 26.4 and 21.0 (CH_2); $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 161.8 MHz) δ 65.4 (PCy_3); IR (CD_2Cl_2) ν_{CO}

= 1948, 1600 cm^{-1}; Anal. Calcd for $C_{38}H_{55}BCl_2F_4NO_2PRu$: C, 53.85; H, 6.54. Found: C, 53.51; H, 6.48.

Deuterium Isotope Effect Study. In a glove box, complex **1** (17 mg, 30 μmol), *N*,*N*-diethylbenzamide (177 mg, 1.0 mmol) or *N*,*N*-diethylbenzamide-d_5 (182 mg, 1.0 mmol) and cyclopentene (0.09 g, 5 mmol) were dissolved in CH_2Cl_2 (5.0 mL) in a 25 mL Schlenk tube equipped with a Teflon screw cap stopcock and a magnetic stirring bar. After stirring at room temperature for 10 min, an equal amount of the solution (1.4 mL) was divided and placed into 5 different Schlenk tubes. The tubes were brought out of the box, and were stirred for 25 min in an oil bath set at 80 °C. Each reaction tube was taken out from the oil bath in 5 min intervals, and was immediately cooled in a dry ice/acetone bath. After filtering through a small silica gel column (hexanes/EtOAc = 2:1), the solution was analyzed by GC. The k_{obs} was determined from a first-order plot of *ln*[**2e** + **3e**] vs time as measured by the appearance of the products **2e** and **3e** by GC (Figure S1).

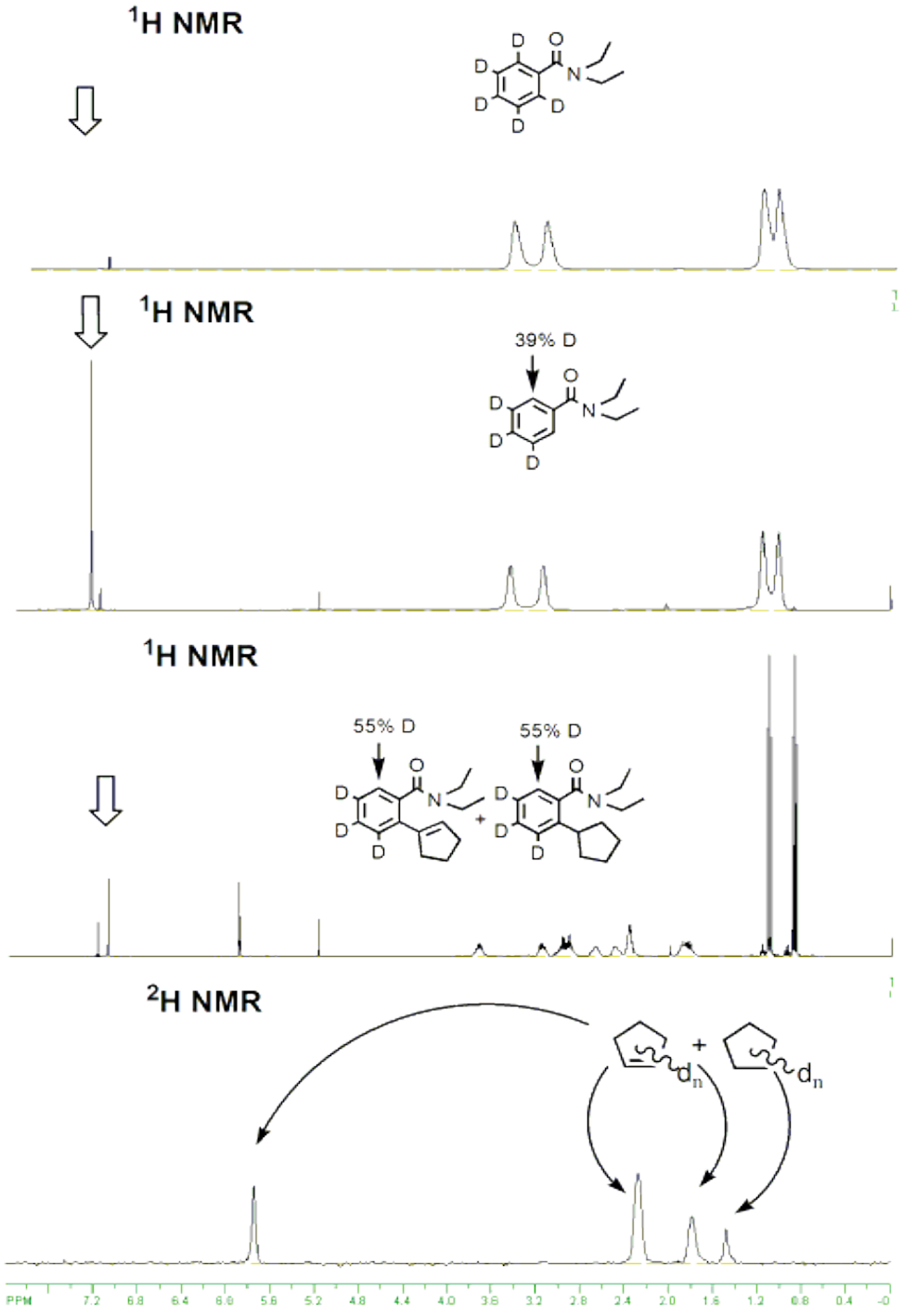
Figure S1. First-Order Plot of $-ln[C_6H_5CONEt_2]_t/[C_6H_5CONEt_2]_0$ vs Time for the Coupling Reaction.



◆ $C_6H_5CONEt_2$, ■ $C_6D_5CONEt_2$

Deuterium Labeling Study. In a glove box, complex **1** (15 mg, 25 μmol), *N*,*N*-diethylbenzamide-d_5 (91 mg, 0.50 mmol) and cyclopentene (0.17 g, 2.5 mmol) were dissolved in CH_2Cl_2 (2 mL) in a 25 mL Schlenk tube equipped with a Teflon screw cap stopcock and a magnetic stirring bar. The tube was brought out of the box, and was stirred for 1 h in an oil bath set at 80 °C. The tube was immediately cooled and was open to air. After filtering through a short silica gel column (hexanes/EtOAc = 2:1), the conversion was determined by GC. Both unreacted cyclopentene-d_n and cyclopentane-d_n were collected separately via a vacuum transfer. The product mixture of **2e**-d_n and **3e**-d_n and unreacted *N*,*N*-diethylbenzamide-d_n was separated by a column chromatography on silica gel (hexanes/EtOAc), and each was analyzed by both ^{1}H and ^{2}H NMR (Figure S2).

Figure S2. ^{1}H and ^{2}H NMR Spectra of the Coupling Reaction of *N*,*N*-Diethylbenzamide-d_5 and Cyclopentene.



Carbon Isotope Effect Study. In a glove box, complex **1** (0.23 g, 0.4 mmol), *N,N*-diethylbenzamide (1.4 g, 8.0 mmol) and cyclopentene (2.72 g, 0.04 mol) were dissolved in CH_2Cl_2 (32 mL) in a 100 mL Schlenk tube equipped with a Teflon screw cap stopcock and a magnetic stirring bar. The tube was brought out of the box, and was stirred in an oil bath at 80 °C for 5 h. The tube was allowed to cool to room temperature and was open to air. After filtering through a small silica column (hexanes/EtOAc = 2:1), the conversion was determined by GC (78%, 80% and 82% conversion). Unreacted *N,N*-diethylbenzamide was separated by a column chromatography on silica gel (hexanes/EtOAc) for $^{13}C\{^1H\}$ NMR analysis.

The ^{13}C NMR analysis of the recovered and virgin samples of *N,N*-diethylbenzamide was performed by following Singleton's ^{13}C NMR method (ref. 9 in the main text). The NMR sample of virgin and recovered *N,N*-diethylbenzamide was prepared identically by dissolving *N,N*-diethylbenzamide (100 mg) in DMSO-d_8 (0.5 mL) in a 5 mm high precision NMR tube. The $^{13}C\{^1H\}$ NMR spectra were recorded with H-decoupling and 45 degree pulses. A 60 s delay between pulses was imposed to minimize T_1 variations (d1 = 60 s, at = 5.0 s, np = 245098, nt = 706). The data are summarized in Table S2.

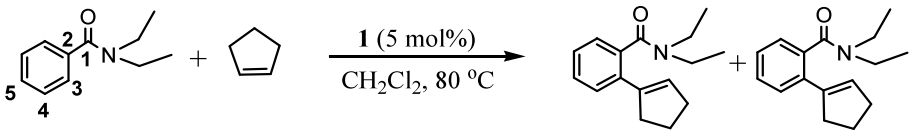


Table S2. Average ^{13}C Integration of the Recovered and Virgin Samples of *N,N*-Diethylbenzamide.

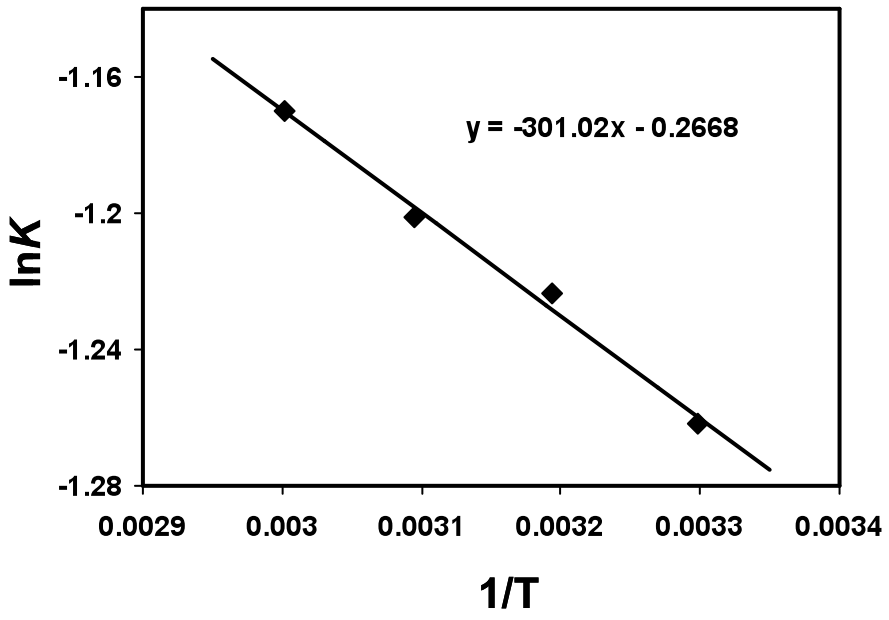
C #	virgin	recovered (78 % conv.)	recovered/virgin	change (%)
1	1.034	1.041	1.007	0.70
2(ref)	1.000	1.000	1.000	0.00
3	**1.975**	**2.020**	**1.023**	**2.27**
4	1.986	1.985	0.999	-0.10
5	0.956	0.954	0.998	-0.20

C #	virgin	recovered (80 % conv.)	recovered/virgin	change (%)
1	1.034	1.041	1.007	0.70
2(ref)	1.000	1.000	1.000	0.00
3	**1.975**	**2.024**	**1.023**	**2.48**
4	1.986	1.984	0.999	-0.10
5	0.956	0.957	1.001	0.10

C #	virgin	recovered (82 % conv.)	recovered/virgin	change (%)
1	1.034	1.041	1.007	0.70
2(ref)	1.000	1.000	1.000	0.00
3	**1.975**	**2.023**	**1.024**	**2.43**
4	1.986	1.988	1.001	0.10
5	0.956	0.953	0.997	-0.30

VT NMR Study for the Reaction of 1 with *N,N*-dimethyl-2-naphthamide. In a glove box, complex **1** (50 mg, 87 μmol) and *N,N*-dimethyl-2-naphthamide (17 mg, 87 μmol) were dissolved in CD_2Cl_2 (0.5 mL) in a heavy-walled J-Young NMR tube. The tube was allowed to equilibrate for 30 min before the NMR analysis. The sample tube was inserted into the NMR probe. The equilibrium constants were determined from the phosphorus integration of **1** and **5** by ^{31}P NMR in the temperature range 30 to 60 °C (10 °C intervals). The sample was allowed to equilibrate for 10-15 min at each temperature prior to the data acquisition. The van't Hoff plots led to the thermodynamic values for $\Delta H° = 0.6 \pm 0.1$ kcal/mol and $\Delta S° = -0.5 \pm 0.1$ e.u. (Figure S3).

Figure S3. van't Hoff Plot of ln*K* vs 1/T



Characterization Data of Organic Products

For **3a**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23, 7.09 and 7.01 (Ar), 3.04 (s, 3H, $N(CH_3)_2$), 2.90 (m, ArCH), 2.72 (s, 3H, $N(CH_3)_2$), 2.0-1.4 (br, 8H, CH_2); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 171.7 (CO), 142.8, 136.4, 128.9, 126.3, 125.7 and 125.4 (Ar), 42.3 (ArCH), 38.9 ($N(CH_3)_2$), 35.4 (CH_2), 34.5 (CH_2), 34.4 ($N(CH_3)_2$), 25.7 (CH_2); GC-MS *m*/*z* = 217 (M^+); Anal. Calcd for $C_{14}H_{19}NO$: C, 77.38; H, 8.81. Found: C, 77.49; H, 8.70.

For **3b**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.96, 6.77 and 6.64 (Ar), 3.70 (s, 3H, OCH_3), 3.02 (s, 3H, $N(CH_3)_2$), 2.92 (m, ArCH), 2.74 (s, 3H, $N(CH_3)_2$), 1.9-1.4 (br, 8H, CH_2); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 171.6 (CO), 159.8, 144.8, 129.0, 126.8, 112.0 and 110.6 (Ar), 55.0 (OCH_3), 42.3 (ArCH), 38.9 ($N(CH_3)_2$), 35.0 (CH_2), 34.5 ($N(CH_3)_2$), 34.4 (CH_2), 25.6 (CH_2); GC-MS *m*/*z* = 247 (M^+); Anal. Calcd for $C_{15}H_{21}NO_2$: C, 72.84; H, 8.56. Found: C, 72.68; H, 8.55.

For **3c**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23, 7.07 and 6.98 (Ar), 3.02 (s, 3H, $N(CH_3)_2$), 2.91 (m, ArCH), 2.72 (s, 3H, $N(CH_3)_2$), 2.0-1.4 (br, 8H, CH_2); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 170.5 (CO), 145.5, 134.8, 134.6, 126.9, 126.6 and 125.8 (Ar), 42.1 (ArCH), 38.7 ($N(CH_3)_2$, 35.2 (CH_2), 34.4 ($N(CH_3)_2$), 34.3 (CH_2), 25.6 (CH_2); GC-MS *m*/*z* = 251 (M^+); Anal. Calcd for $C_{14}H_{18}ClNO$: C, 66.79; H, 7.21. Found: C, 66.83; H, 7.30.

For **3d**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21, 7.05 and 6.98 (Ar), 6.28 (d, *J* = 3.9 Hz NH), 3.18 (m, ArCH), 2.71 (d, *J* = 4.9, Hz, $NHCH_3$), 2.0-1.4 (br, 8H, CH_2); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 171.5 (CO), 144.3, 140.0, 129.7, 126.41, 126.40 and 125.4 (Ar), 41.8 (ArCH), 35.1 ($CHCH_2$), 26.5 (NCH_3), 25.8 (CH_2); GC-MS *m*/*z* = 203 (M^+); Anal. Calcd for $C_{13}H_{17}NO$: C, 76.81; H, 8.43. Found: C, 76.58; H, 8.18.

For **3e**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23, 7.07 and 7.02 (Ar), 3.68 (m, H, $N(CH_2CH_3)_2$), 3.37 (m, H, $N(CH_2CH_3)_2$), 3.03 (m, 2H, $N(CH_2CH_3)_2$), 2.92 (m, ArCH), 2.0-1.4 (br, 8H, CH_2),

1.15 (t, J = 6.8 Hz, CH_2CH_3), 0.93 (t, J = 6.8 Hz, CH_2CH_3); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 170.9 (CO), 142.6, 136.8, 128.7, 126.1, 125.5, and 125.1 (Ar), 42.7 ($N(CH_2CH_3)_2$), 42.2 (ArCH), 38.4 ($N(CH_2CH_3)_2$), 35.5 (CH_2), 34.4 (CH_2), 25.8 (CH_2), 25.6 (CH_2), 13.8 ($N(CH_2CH_3)_2$), 12.6 ($N(CH_2CH_3)_2$); GC-MS m/z = 245 (M^+); Anal. Calcd for $C_{16}H_{22}NO$: C, 78.32; H, 9.45. Found: C, 78.10; H, 9.23.

For **3f**: ^1H NMR (400 MHz, $CDCl_3$) δ 7.3-7.1 (Ar), 6.97 (m, 1H, Ar), 6.35 (br, NH), 4.38 (m, 2H, $NHCH_2Ar$), 3.17 (m, ArCH), 1.9-1.3 (br, 8H, CH_2); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 170.5 (CO), 144.2, 138.3, 136.8, 129.8, 128.6, 127.7, 127.4, 126.5, 126.4 and 125.4 (Ar), 43.6 (CH_2Ar), 41.8 (ArCH), 35.1 (CH_2), 25.7 (CH_2); GC-MS m/z = 279 (M^+); Anal. Calcd for $C_{19}H_{21}NO$: C, 81.68; H, 7.58. Found: C, 81.72; H, 7.38.

For **3g**: ^1H NMR (400 MHz, $CDCl_3$) δ 7.66 (s, NH), 7.48, 7.28 and 7.05 (Ar), 3.30 (m, ArCH), 1.98 (br, 2H, CH_2), 1.7-1.5 (br, 6H, CH_2); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 168.8 (CO), 144.8, 138.2, 137.1, 130.4, 129.2, 126.9, 126.5, 125.7, 124.5 and 119.9 (Ar), 42.0 (ArCH), 35.3 (CH_2), 25.9 (CH_2); GC-MS m/z = 265 (M^+); Anal. Calcd for $C_{18}H_{19}NO_2$: C, 81.47; H, 7.22. Found: C, 81.61; H, 7.11.

For **3h**: ^1H NMR (400 MHz, $CDCl_3$) δ 7.45 (Ar), 7.35 (br, NH), 7.33, 7.15 and 6.84 (Ar), 3.73 (s, OCH_3), 3.34 (m, ArCH), 2.05 (br, 2H, CH_2), 1.8-1.5 (br, 6H, CH_2); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 168.7 (CO), 156.7, 144.9, 137.2, 131.3, 130.4, 127.0, 126.5, 125.8, 121.8 and 114.4 (Ar), 55.5 (OCH_3), 42.0 (ArCH), 35.4 (CH_2), 26.0 (CH_2); GC-MS m/z = 295 (M^+); Anal. Calcd for $C_{19}H_{21}NO_2$: C, 77.26; H, 7.17. Found: C, 77.05; H, 7.02.

For **3i**: ^1H NMR (400 MHz, $CDCl_3$) δ 7.87 (s, NH), 7.39, 7.29 and 7.16 (Ar), 7.05 (m, 1H, Ar), 3.25 (m, ArCH), 1.94 (br, 2H, CH_2), 1.7-1.5 (br, 6H, CH_2); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 169.1 (CO), 144.7, 136.8, 136.6, 130.4, 129.3, 129.0, 126.9, 126.4, 125.7 and 121.3

(Ar), 42.0 (ArCH), 35.2 (CH_2), 25.9 (CH_2); GC-MS *m/z* = 299 (M^+); Anal. Calcd for $C_{18}H_{18}ClNO$: C, 72.11; H, 6.05. Found: C, 71.84; H, 6.10.

For **3j**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.2-7.1 and 7.01 (Ar), 6.17 (br, NH), 4.45 (d, *J* = 6.0 Hz, NHC*H*$_2$Ar), 2.95 (m, ArCH), 1.73 (m, 2H, CH_2), 1.6-1.3 (m, 10H, CH_2); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 170.5 (CO), 147.6, 138.5, 135.5, 130.0, 128.8, 128.0, 127.6, 126.9, 126.4 and 125.4 (Ar), 43.8 (*C*H_2Ar), 42.3 (ArCH), 36.9 (CH_2), 27.8 (CH_2), 27.4 (CH_2); GC-MS *m/z* = 307 (M^+); Anal. Calcd for $C_{18}H_{21}NO$: C, 82.04; H, 8.20. Found: C, 82.01; H, 7.99.

For **3k**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27, 7.10 and 7.03 (Ar), 3.07 (s, 3H, $N(CH_3)_2$), 2.77 (s, 3H, $N(CH_3)_2$), 2.74 (m, ArCH), 1.8-1.5 (br, 14H, CH_2); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 171.7 (CO), 146.4, 135.3, 128.9, 126.9, 125.6 and 125.4 (Ar), 40.0 (ArCH), 38.8 ($N(CH_3)_2$), 35.3 (CH_2), 34.5 ($N(CH_3)_2$), 26.8 (CH_2), 26.7 (CH_2), 26.6 (CH_2), 26.5 (CH_2), 25.6 (CH_2); GC-MS *m/z* = 259 (M^+); Anal. Calcd for $C_{17}H_{25}NO$: C, 78.72; H, 9.71. Found: C, 78.67; H, 9.67.

For **3l**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.3-7.0 (Ar), 3.02 (s, 3H, $N(CH_3)_2$), 2.71 (s, 3H, $N(CH_3)_2$), 2.41 (br, C*H*$_2$CH$(CH_3)_2$), 1.81 (m, CH_2C*H*$(CH_3)_2$), 0.80 (d, *J* = 6.7 Hz, 6H, CH_3); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 171.4 (CO), 138.0, 136.6, 130.1, 128.5, 126.0, and 125.8 (Ar), 42.2 (*C*H_2CH$(CH_3)_2$), 38.7 ($N(CH_3)_2$), 34.5 ($N(CH_3)_2$), 29.3 (CH_2*C*H$(CH_3)_2$), 22.6 (CH_2CH(*C*$H_3)_2$); GC-MS *m/z* = 205 (M^+); Anal. Calcd for $C_{13}H_{19}NO$: C, 76.06; H, 9.33. Found: C, 75.82; H, 9.34.

For **3m**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.3-7.0 (Ar), 3.12 (br, C*H*$_2$CH(CH_3)Ph), 3.01 (br, 3H, $N(CH_3)_2$), 2.77 (t, *J* = 6.5 Hz, CH_2C*H*(CH_3)Ph), 2.65 (br, 3H, $N(CH_3)_2$), 1.21 (d, *J* = 6.5 Hz, CH_2CHC*H*$_3$(Ph)); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 171.0 (CO), 146.6, 137.2, 136.3, 130.2, 128.3, 128.1, 126.8, 126.0, 125.9 and 125.8 (Ar), 41.9 (*C*H_2CHCH_3(Ph)), 40.8 (CH_2*C*HCH_3(Ph)),

38.3 ($N(CH_3)_2$), 343 ($N(CH_3)_2$), 21.4 (CH_3); GC-MS *m/z* = 267 (M^+); Anal. Calcd for $C_{18}H_{21}NO$: C, 80.86; H, 7.92. Found: C, 80.57; H, 7.90.

For **3n**: ^1H NMR (400 MHz, $CDCl_3$) δ 7.2-7.0 (Ar), 3.04 (s, 3H, $N(CH_3)_2$), 2.73 (s, 3H, $N(CH_3)_2$), 2.47 (br, CH_2), 1.5-1.3 (br, CH_2), 0.82 (s, $C(CH_3)_3$); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 171.4 (CO), 139.6, 136.4, 129.5, 128.8, 125.9, and 125.8 (Ar), 45.7 ($CH_2CH_2C(CH_3)_2$), 38.8 ($N(CH_3)_2$), 34.5 ($N(CH_3)_2$), 30.5 ($CH_2CH_2C(CH_3)_3$), 29.2 ($CH_2CH_2C(CH_3)_3$), 28.4 ($CH_2CH_2C(CH_3)_2$); GC-MS *m/z* = 233 (M^+); Anal. Calcd for $C_{15}H_{23}NO$: C, 77.21; H, 9.93. Found: C, 76.97; H, 10.08.

For **3o**: ^1H NMR (400 MHz, $CDCl_3$) δ 7.63, 7.57 and 7.26 (Ar), 3.04 (s, 3H, $N(CH_3)_2$), 2.68 (s, 3H, $N(CH_3)_2$), 2.47 (br, $CH_2CH(CH_3)_2$), 1.86 (m, $CH_2CH(CH_3)_2$), 0.81 (d, J = 6.6 Hz, $CH_2CH(CH_3)_2$); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 170.9 (CO), 135.4, 135.0, 132.9, 131.1, 128.4, 127.3, 127.0, 126.3, 125.5 and 125.2 (Ar), 42.3 ($CH_2CH(CH_3)_2$), 38.5 ($N(CH_3)_2$), 34.3 ($N(CH_3)_2$), 28.8 (CH_2), 22.4 (CH_3); GC-MS *m/z* = 257 (M^+); Anal. Calcd for $C_{17}H_{21}NO$: C, 79.96; H, 8.29. Found: C, 79.41; H, 8.11.

For **3p**: ^1H NMR (400 MHz, $CDCl_3$) δ 7.62, 7.54 and 7.25 (Ar), 2.99 (s, 3H, $N(CH_3)_2$), 2.66 (s, 3H, $N(CH_3)_2$), 2.57 (br, CH_2), 1.5-1.3 (br, CH_2), 0.84 (s, $C(CH_3)_3$); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 171.0 (CO), 137.2, 135.2, 133.4, 131.1, 127.7, 127.5, 127.1, 126.4, 125.6 and 125.2 (Ar), 45.6 ($CH_2CH_2C(CH_3)_3$), 38.7 ($N(CH_3)_2$), 34.4 ($N(CH_3)_2$), 29.1 ($CH_2CH_2C(CH_3)_3$), 28.3 ($CH_2CH_2C(CH_3)_3$), 28.4 ($CH_2CH_2C(CH_3)_3$); GC-MS *m/z* = 283 (M^+); Anal. Calcd for $C_{19}H_{25}NO$: C, 80.52; H, 8.89. Found: C, 79.92; H, 8.63.

For **3q**: ^1H NMR (400 MHz, $CDCl_3$) δ 7.69, 7.53 and 7.36 (Ar), 3.09 (s, 3H, $N(CH_3)_2$), 3.05 (m, ArCH), 2.77 (s, 3H, $N(CH_3)_2$), 2.2-1.6 (br, 8H, CH_2); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 171.8 (CO), 140.9, 135.7, 133.7, 131.5, 127.7, 127.6, 126.6, 125.9, 125.1 and 125.0 (Ar), 42.5

(ArCH), 39.3 ($N(CH_3)_2$), 34.9 (CH_2), 34.8 ($N(CH_3)_2$), 34.7 (CH_2), 25.7 (CH_3); GC-MS *m/z* = 267 (M^+); Anal. Calcd for $C_{18}H_{21}NO$: C, 80.86; H, 7.92. Found: C, 79.90; H, 7.90.

For **3r**: ^1H NMR (400 MHz, $CDCl_3$) δ 7.37, 7.18 and 7.01 (Ar), 6.22 (t, *J* = 5.6 Hz, NH), 4.52 (d, *J* = 6.0 Hz, NHCH_2Ar), 2.44 (d, *J* = 7.8 Hz, CH_2CH$(CH_3)_2$), 1.89 (m, $CH_2CH(CH_3)_2$), 0.84 (d, J = 6.4 Hz, $CH_2CH(CH_3)_2$); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 169.9 (CO), 138.3, 138.0, 137.8, 128.7, 128.5, 128.1, 127.6 and 127.3 (Ar), 43.8 (CH_2Ar), 42.4 (CH_2CHCH_2), 29.7 (CH_2), 22.6 (CH_3); GC-MS *m/z* = 267 (M^+); Anal. Calcd for $C_{18}H_{21}NO$: C, 80.86; H, 7.92. Found: C, 80.72; H, 8.08.

For **3s**: ^1H NMR (400 MHz, $CDCl_3$) δ 7.28, 7.19 and 7.12 (Ar), 6.33 (t, *J* = 4.9 Hz, NH), 4.54 (d, *J* = 5.9 Hz, NHCH_2Ar), 2.71 (m, C$H_2CH_2C(CH_3)_3$), 1.42 (m, C$H_2CH_2C(CH_3)_3$), 0.94 (s, $CH_2CH_2C(CH_3)_3$); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 170.1 (CO), 1417, 138.4, 136.4, 130.2, 129.9, 128.8, 128.0, 127.6, 126.9 and 125.7 (Ar), 46.6 ($CH_2CH_2C(CH_3)_3$) 43.9 (CH_2Ar), 30.7 ($CH_2CH_2C(CH_3)_3$), 29.3 ($CH_2CH_2C(CH_3)_3$), 28.7 ($CH_2CH_2C(CH_3)_3$); GC-MS *m/z* = 295 (M^+); Anal. Calcd for $C_{20}H_{25}NO$: C, 81.31; H, 8.53. Found: C, 81.09; H, 8.26.

For **3t**: ^1H NMR (400 MHz, $CDCl_3$) δ 7.58, 7.32 and 7.19 (Ar), 2.74 (d, *J* = 7.1 Hz, 2H, ArCH_2), 2.53 (s, 3H, C(O)CH_3), 1.80 (m, 1H, C$H(CH_3)_2$), 0.86 (d, *J* = 6.6 Hz, 6H, $CH(CH_3)_2$); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 202.4 (*C*O), 141.5, 138.4, 132.1, 131.0, 129.0 and 125.8 (Ar), 42.8 (ArCH_2), 30.3 ($CH(CH_3)_2$), 30.1 (C(O)CH_3), 22.6 ($CH(CH_3)_2$); GC-MS *m/z* = 176 (M^+); The ^1H and ^{13}C NMR spectral data are in good agreement with the literature data.[1]

For **3u**: ^1H NMR (400 MHz, $CDCl_3$) δ 7.60, 7.08 and 7.04 (Ar), 2.78 (d, *J* = 7.0 Hz, 2H, ArCH_2), 2.57 (s, 3H, C(O)CH_3), 2.38 (s, 3H, $ArCH_3$) 1.81 (m, 1H, C$H(CH_3)_2$), 0.92 (d, *J* = 6.6 Hz, 6H, $CH(CH_3)_2$); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 202.0 (*C*O), 142.3, 141.7, 135.6, 133.2, 130.0 and 126.6 (Ar), 43.1 (ArCH_2), 30.5 ($CH(CH_3)_2$), 30.1 (C(O)CH_3), 22.8 ($CH(CH_3)_2$), 21.7

($ArCH_3$); GC-MS *m/z* = 190 (M^+); The ^1H and ^{13}C NMR spectral data are in good agreement with the literature data.[2]

For **3v**: ^1H NMR (400 MHz, $CDCl_3$) δ 7.94, 7.52, 7.45 and 7.35 (Ar), 2.88 (q, *J* = 7.3 Hz, 2H, C(O)CH_2CH$_3$), 2.69 (d, *J* = 7.2 Hz, 2H, ArCH_2), 1.80 (m, 1H, $CH_2CH(CH_3)_2$), 1.18 (t, *J* = 7.3 Hz, 3H, (CO)CH_2CH_3), 0.88 (d, *J* = 7.2 Hz, 6H, $CH_2CH(CH_3)_2$); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 206.3 (*C*O), 141.1, 139.3, 132.0, 130.7, 128.1 and 125.8 (Ar), 42.7 (Ar*C*H_2), 35.6 (C(O)*C*H_2CH_3), 30.4 ($CH_2CH(CH_3)_2$), 28.2 (C(O)(CH_2CH_3), 22.7 ($CH_2CH(CH_3)_2$); GC-MS *m/z* = 190 (M^+); The ^1H and ^{13}C NMR spectral data are in good agreement with the literature data.[3]

For **3w**: ^1H NMR (400 MHz, $CDCl_3$) δ 7.71, 7.58, 7.44 and 7.26 (Ar), 2.56 (d, *J* = 7.4 Hz, 2H, ArCH_2), 1.79 (m, 1H, $CH_2CH(CH_3)_2$), 0.80 (d, *J* = 6.6 Hz, 6H, $CH_2CH(CH_3)_2$); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 199.0 (*C*O), 140.9, 139.0, 138.1, 133.3, 131.1, 130.4, 130.1, 128.8, 128.6 and 125.4 (Ar), 42.5 (Ar*C*H_2), 30.4 ($CH_2CH(CH_3)_2$), 22.7 ($CH_2CH(CH_3)_2$; GC-MS *m/z* = 238 (M^+); The ^1H and ^{13}C NMR spectral data are in good agreement with the literature data.[4]

For **4t**: ^1H NMR (300 MHz, $CDCl_3$) δ 8.15, 7.06, 7.68 and 7.36 (Ar), 2.86 and 2.68 (s, 3H, $ArCH_3$); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 135.2, 134.2, 134.1, 131.1, 129.1, 128.1, 125.8, 125.5, 125.0 and 124.1 (Ar), 21.8 and 19.4 ($ArCH_3$); GC-MS *m/z* = 156 (M^+); The ^1H and ^{13}C NMR spectral data are in good agreement with the literature data.[5]

For **4u**: ^1H NMR (400 MHz, $CDCl_3$) δ 7.95, 7.62, 7.55, 7.42 and 7.22 (Ar), 2.80, 2.66 and 2.62 (s, 3H, $ArCH_3$); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 135.2, 134.3, 134.0, 129.3, 128.3, 127.2, 127.1, 124.9 and 124.0 (Ar), 21.8, 21.7 and 19.4 ($ArCH_3$); GC-MS *m/z* = 170 (M^+); The ^1H and ^{13}C NMR spectral data are in good agreement with the literature data.[6]

For **4v**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09, 7.85, 7.57, 7.53 and 7.28 (Ar), 3.17 (q, J = 7.5 Hz, 2H, CH_2CH$_3$), 2.58 (s, 3H, ArCH$_3$), 1.47 (t, J = 7.5 Hz, 3H, CH$_2$CH_3); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 140.2, 135.3, 134.3, 130.2, 128.3, 127.4, 125.7, 125.5, 125.0 and 123.7 (Ar), 26.0 (CH$_2$CH$_3$), 21.9 (ArCH$_3$), 15.3 (CH$_2$$CH_3$); GC-MS *m/z* = 170 ($M^+$); The ^{1}H and ^{13}C NMR spectral data are in good agreement with the literature data.[7]

For **4w**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99, 7.92, 7.74, 7.64-7.44 and 7.41 (Ar), 2.65 (s, 3H, ArCH$_3$); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 141.0, 140.3, 135.1, 134.3, 130.2, 130.1, 129.4, 128.4, 127.8, 127.4, 126.8, 126.0 and 125.3 (Ar), 21.8 (ArCH$_3$); GC-MS *m/z* = 218 (M^+); The ^{1}H and ^{13}C NMR spectral data are in good agreement with the literature data.[8]

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Table S3. Crystal data and structure refinement for **6**.

Empirical formula	$C_{38}\ H_{55}\ B\ Cl_2\ F_4\ N\ O_2\ P\ Ru$
Formula weight	847.58
Temperature	100(2) K
Wavelength	0.7107 Å
Crystal system	Triclinic
Space group	P-1
Unit cell dimensions	a = 10.23664(13) Å
	α = 100.1596(12)°
	b = 12.0713(2) Å
	β = 102.3207(11)°.
	c = 16.7295(2) Å
	γ = 103.8371(12)°.
Volume	1903.84(5) $Å^3$
Z	2
Density (calculated)	1.479 Mg/m^3
Absorption coefficient	0.649 mm^{-1}
F(000)	880
Crystal size	0.4281 x 0.2686 x 0.1765 mm^3
Theta range for data collection	3.38 to 37.83°
Index ranges	$-17 \le h \le 17$, $-20 \le k \le 20$, $-28 \le l \le 28$
Reflections collected	95037
Independent reflections	19744 [R(int) = 0.0279]
Absorption correction	Numerical
Max. and min. transmission	0.915 and 0.811
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	19744 / 0 / 487
Goodness-of-fit on F^2	1.004
Final R indices [I>2sigma(I)]	R1 = 0.0214, wR2 = 0.0609
R indices (all data)	R1 = 0.0270, wR2 = 0.0625
Largest diff. peak and hole	0.692 and -0.496 $e.Å^{-3}$

Table S4. Atomic Coordinates (Å × 10^4) and Equivalent Isotropic Displacement Parameters (Å^2 × 10^3) for **6**. Ueq is defined as 1/3 of of the trace of the orthogonalized Uij tensor.

Atom	*x*	*y*	*z*	U(eq)
Ru1	10291.87(5)	721.72(5)	3115.42(3)	8.96(2)
P1	10266.8(19)	2396.33(16)	4043.74(11)	9.64(3)
O1	13385.2(6)	1341.3(7)	3736.3(5)	25.22(14)
O2	8055.3(5)	264.3(5)	2707.3(3)	11.74(9)
N1	6205.9(6)	-629.3(6)	1578.7(4)	12.83(10)
C1	10625.3(7)	1010.4(6)	1048.9(5)	12.43(11)
C2	9784.1(7)	343.3(6)	1447.1(4)	10.64(10)
C3	8407.9(7)	485.6(6)	1386.3(4)	10.56(10)
C4	7955.4(7)	1249.6(6)	952.2(4)	11.94(11)
C5	8385.2(8)	2767.1(7)	144.3(5)	14.34(12)
C6	9262(8)	3428.6(7)	-222.9(5)	16.22(13)
C7	10603(9)	3290(7)	-188.7(5)	17.06(13)
C8	11060.2(8)	2501.9(7)	215.8(5)	15.81(13)
C9	10178(7)	1806.3(6)	604.2(5)	12.35(11)
C10	8821.7(7)	1935.1(6)	555.9(4)	11.92(11)
C11	10339.5(7)	-454.6(6)	1904.2(4)	10.79(11)
C12	9692.2(7)	-1210.2(6)	2332.8(5)	11.87(11)
C13	10524.8(8)	-2031.6(7)	2570.4(5)	15.17(12)
C14	11969.8(8)	-1478.4(7)	2453.1(5)	16.38(13)
C15	11725.5(8)	-674(7)	1849(5)	13.48(12)
C16	7524.1(7)	0.5(6)	1917.8(4)	10.48(10)
C17	5557.4(8)	-1077.7(7)	674.7(5)	18.65(14)
C18	5285.1(8)	-915.8(8)	2115.8(5)	17.61(13)
C19	12184.8(8)	1105(7)	3491.5(5)	15.09(12)

C21	12949.5(9)	3768.9(7)	5172.3(5)	19.39(14)
C22	13804.6(10)	4242.5(8)	6099(6)	23.78(17)
C23	14013.9(9)	3244.7(8)	6513(5)	19.91(15)
C24	12613.7(9)	2373.1(8)	6426.8(5)	19.85(15)
C25	11763(8)	1906.4(7)	5505.6(5)	15.91(13)
C26	8528.8(7)	2192.8(6)	4252.5(4)	11.36(11)
C27	8116.6(8)	1124.7(7)	4625.2(5)	14.36(12)
C28	6595.9(8)	875.3(7)	4664.4(6)	17.6(13)
C29	6350.1(8)	1950.6(7)	5172.9(5)	16.74(13)
C30	6780.2(8)	3020.2(7)	4816.2(5)	16.75(13)
C31	8309.7(8)	3274.4(7)	4785.5(5)	15.81(13)
C32	10533.5(8)	3673.1(6)	3559.2(4)	12.15(11)
C33	9218.9(8)	3642(7)	2896.2(5)	16.47(13)
C34	9483(10)	4714.4(8)	2516.4(6)	20.93(15)
C35	10739.4(10)	4834.2(7)	2146.9(5)	19.43(14)
C36	12036.9(9)	4830.8(8)	2792.3(5)	20.18(15)
C37	11748.3(8)	3738.7(7)	3146.7(5)	16.79(13)
Cl1	3685.9(7)	5662.2(13)	988.6(5)	27.52(12)
Cl2	6706.7(8)	6231.9(17)	1298.1(4)	32.99(17)
C38	5140(5)	5087(3)	1176(2)	25.2(4)
Cl1A	3733(4)	5439(5)	1004(3)	27.52(12)
Cl2A	6610(4)	5909(6)	1279(3)	32.99(17)
C38A	5130(3)	4950(2)	1069(14)	25.2(4)
F1	5730(2)	2729.4(19)	1179.3(19)	27(3)
F2	3993(3)	1131(2)	1173.3(14)	31(3)
F3	4151(4)	2873(2)	1968.5(17)	38.7(4)

B1	4954(11)	2203(9)	1684(6)	21.2(6)
F1A	5899(11)	2864(8)	1384(6)	27(3)
F2A	4290(9)	1158(11)	1204(7)	31(3)
F3A	4556(11)	3067(9)	2120(7)	38.7(4)
F4A	5763(11)	2159(9)	2419(7)	37.1(3)
B1A	5010(5)	2150(5)	1750(3)	21.2(6)

Table S5. Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for **6**. The Anisotropic displacement factor exponent takes the form: -2π2[h2a*2U 11+...+2hka×b×U12]

Atom	U11	U22	U33	U23	U13	U12
Ru1	7.99(2)	9.07(2)	9.59(2)	2.26(2)	2.05(2)	2.26(2)
P1	10.13(7)	8.49(7)	9.6(7)	2.38(5)	1.92(6)	1.88(5)
O1	11.2(2)	31.8(3)	26.8(3)	-1.1(3)	1.1(2)	4.8(2)
O2	10.3(2)	14(2)	10.4(2)	2.18(16)	2.51(16)	3.29(17)
N1	8.9(2)	14.5(3)	13.4(2)	3.6(2)	1.85(19)	0.93(19)
C1	11.1(3)	13.3(3)	14(3)	4(2)	4.8(2)	3.6(2)
C2	10(3)	10.7(3)	10.9(3)	1.8(2)	2.8(2)	2.8(2)
C3	9.1(2)	11.2(3)	10.9(3)	2.4(2)	2.9(2)	2.2(2)
C4	10.2(3)	13.1(3)	12.5(3)	3.6(2)	2.8(2)	3(2)
C5	14.5(3)	14.2(3)	14.5(3)	5(2)	3.2(2)	3.8(2)
C6	18.5(3)	14(3)	15.9(3)	6(2)	3.6(3)	3.5(2)
C7	18.1(3)	16(3)	17.6(3)	6.9(3)	6.8(3)	2.1(3)
C8	14.3(3)	16.6(3)	17.8(3)	6.3(2)	6.8(2)	3(2)
C9	12.4(3)	12.6(3)	12.6(3)	3.7(2)	4.5(2)	2.9(2)
C10	12.5(3)	11.6(3)	11.2(3)	2.8(2)	2.8(2)	2.8(2)
C11	10.6(3)	10.9(3)	11.2(3)	2.5(2)	3.3(2)	3.5(2)
C12	11.7(3)	10.3(3)	14(3)	2.7(2)	4.4(2)	3.2(2)
C13	16.1(3)	13.1(3)	19.5(3)	6.4(2)	6.6(3)	6.5(2)
C14	14.2(3)	16.9(3)	22(3)	8(3)	6.4(3)	8(2)
C15	12.3(3)	14.2(3)	16.7(3)	4.6(2)	6.5(2)	5.8(2)
C16	9.1(2)	10.6(3)	11.9(3)	3(2)	2.7(2)	3(2)
C17	15.3(3)	18.8(3)	15.4(3)	4.2(3)	-2.5(3)	-1.2(3)
C18	10.5(3)	21.9(3)	21.5(3)	8.9(3)	6.1(3)	2.4(2)
C19	13.5(3)	15.9(3)	14.4(3)	1.2(2)	3.1(2)	3.8(2)

C21	17.4(3)	17.4(3)	17.1(3)	5.9(3)	-1.4(3)	-2.4(3)
C22	22(4)	18.7(4)	19.9(4)	1.4(3)	-4.9(3)	-2.2(3)
C23	16(3)	27(4)	13.6(3)	3.7(3)	0.4(3)	4.6(3)
C24	17.5(3)	27.4(4)	14.3(3)	8.9(3)	2.1(3)	4.9(3)
C25	15.1(3)	15.9(3)	14.9(3)	6.5(2)	0.3(2)	2.3(2)
C26	12.3(3)	10.1(3)	11.7(3)	2.2(2)	4(2)	2.8(2)
C27	15.8(3)	13.4(3)	17.2(3)	6.2(2)	7.6(2)	5.4(2)
C28	16.5(3)	14.4(3)	24.3(4)	5.2(3)	10.5(3)	3.9(2)
C29	15.9(3)	18.7(3)	17.8(3)	4.2(3)	8.1(3)	6.1(3)
C30	17.4(3)	15.2(3)	20(3)	3.4(3)	7.7(3)	7.4(3)
C31	16.8(3)	11.6(3)	18.7(3)	0.6(2)	7.1(3)	3.5(2)
C32	14.4(3)	9.9(3)	11.3(3)	3.4(2)	2.5(2)	2.1(2)
C33	16.5(3)	15.7(3)	16.8(3)	7.1(2)	1.2(2)	4.2(2)
C34	26.9(4)	19.1(3)	21.6(4)	11.9(3)	7(3)	10(3)
C35	29.3(4)	15.7(3)	15.1(3)	7.5(3)	6.9(3)	6.3(3)
C36	23.1(4)	18.4(3)	18(3)	8.3(3)	6.8(3)	0(3)
C37	16.8(3)	18.6(3)	17.1(3)	8.5(3)	6.5(3)	4.3(3)
Cl1	17.71(10)	27.5(3)	35.94(13)	11.29(19)	1.82(9)	5.9(16)
Cl2	18.41(13)	41.7(5)	33.29(13)	0.5(2)	8.56(11)	3(2)
C38	34.2(5)	19(10)	24.5(11)	3.8(7)	8(8)	12.3(8)
Cl1A	17.71(10)	27.5(3)	35.94(13)	11.29(19)	1.82(9)	5.9(16)
Cl2A	18.41(13)	41.7(5)	33.29(13)	0.5(2)	8.56(11)	3(2)
C38A	34.2(5)	19(10)	24.5(11)	3.8(7)	8(8)	12.3(8)
F1	29.3(6)	23.3(5)	36.5(9)	11.8(6)	18.6(7)	10.2(4)
F2	20(7)	36.7(4)	29.2(4)	7.4(3)	5.6(6)	-3.8(6)
F3	37.7(10)	39.2(7)	54.6(9)	14.4(6)	29.4(8)	21.7(7)

B1	19.9(11)	23.8(12)	25.1(18)	10.3(9)	8.3(12)	10.6(6)
F1A	29.3(6)	23.3(5)	36.5(9)	11.8(6)	18.6(7)	10.2(4)
F2A	20(7)	36.7(4)	29.2(4)	7.4(3)	5.6(6)	-3.8(6)
F3A	37.7(10)	39.2(7)	54.6(9)	14.4(6)	29.4(8)	21.7(7)
F4A	33.6(4)	33.8(9)	39.8(6)	13.7(6)	-4.1(4)	10.8(5)
B1A	19.9(11)	23.8(12)	25.1(18)	10.3(9)	8.3(12)	10.6(6)

Table S6. Bond Lengths for **6.**

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Ru1	P1	2.33092(19)	C20	C21	1.5383(11)
Ru1	O2	2.1467(5)	C20	C25	1.5330(11)
Ru1	C11	2.2771(7)	C21	C22	1.5380(12)
Ru1	C12	2.3291(7)	C22	C23	1.5267(13)
Ru1	C19	1.8202(8)	C23	C24	1.5228(12)
P1	C20	1.8607(7)	C24	C25	1.5287(11)
P1	C26	1.8531(7)	C26	C27	1.5378(10)
P1	C32	1.8549(7)	C26	C31	1.5378(10)
O1	C19	1.1555(10)	C27	C28	1.5312(11)
O2	C16	1.2664(8)	C28	C29	1.5264(11)
N1	C16	1.3233(9)	C29	C30	1.5262(12)
N1	C17	1.4599(10)	C30	C31	1.5357(11)
N1	C18	1.4598(10)	C32	C33	1.5384(11)
C1	C2	1.3914(10)	C32	C37	1.5387(11)
C1	C9	1.4155(10)	C33	C34	1.5325(11)
C2	C3	1.4440(10)	C34	C35	1.5294(13)
C2	C11	1.4737(10)	C35	C36	1.5238(13)
C3	C4	1.3745(10)	C36	C37	1.5300(11)
C3	C16	1.4919(10)	Cl1	C38	1.780(4)
C4	C10	1.4158(10)	Cl2	C38	1.796(5)
C5	C6	1.3733(11)	Cl1A	C38A	1.66(3)
C5	C10	1.4176(11)	Cl2A	C38A	1.60(3)
C6	C7	1.4126(12)	F1	B1	1.407(10)
C7	C8	1.3737(12)	F2	B1	1.419(12)

C9	C10	1.4206(10)	F4	B1	1.423(7)
C11	C12	1.3891(10)	F1A	B1A	1.41(5)
C11	C15	1.5227(10)	F2A	B1A	1.31(6)
C12	C13	1.5054(10)	F3A	B1A	1.40(5)
C13	C14	1.5396(11)	F4A	B1A	1.21(4)
C14	C15	1.5430(11)			

Table S7. Bond Angles for **6.**

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
O1	C19	Ru1	179.29(8)	C19	Ru1	C11	90.42(3)
O2	Ru1	P1	88.448(15)	C19	Ru1	C12	103.01(3)
O2	Ru1	C11	90.78(2)	C20	P1	Ru1	119.81(2)
O2	Ru1	C12	77.39(2)	C21	C20	P1	116.23(5)
O2	C16	N1	121.21(6)	C22	C21	C20	110.36(7)
O2	C16	C3	117.74(6)	C23	C22	C21	111.34(7)
N1	C16	C3	120.94(6)	C23	C24	C25	111.48(7)
C1	C2	C3	117.19(6)	C24	C23	C22	110.59(7)
C1	C2	C11	118.80(6)	C24	C25	C20	110.85(7)
C1	C9	C8	121.82(7)	C25	C20	P1	112.79(5)
C1	C9	C10	119.40(6)	C25	C20	C21	109.17(6)
C2	C1	C9	122.41(7)	C26	P1	Ru1	110.10(2)
C2	C3	C16	121.75(6)	C26	P1	C20	104.56(3)
C2	C11	Ru1	87.69(4)	C26	P1	C32	105.76(3)
C2	C11	C15	120.94(6)	C27	C26	P1	112.41(5)
C3	C2	C11	124.01(6)	C28	C27	C26	110.81(6)
C3	C4	C10	121.46(7)	C29	C28	C27	111.01(7)
C4	C3	C2	121.09(6)	C29	C30	C31	111.23(7)
C4	C3	C16	116.16(6)	C30	C29	C28	110.85(6)
C4	C10	C5	121.61(7)	C30	C31	C26	109.94(6)
C4	C10	C9	118.46(7)	C31	C26	P1	115.91(5)
C5	C6	C7	120.34(7)	C31	C26	C27	109.80(6)
C5	C10	C9	119.89(7)	C32	P1	Ru1	110.29(2)
C6	C5	C10	119.98(7)	C32	P1	C20	105.32(3)

C8	C7	C6	120.92(7)	C33	C32	C37	108.91(6)
C10	C9	C8	118.78(7)	C34	C33	C32	110.93(7)
C11	Ru1	P1	159.351(19)	C35	C34	C33	112.25(7)
C11	Ru1	C12	35.08(2)	C35	C36	C37	110.68(7)
C11	C12	Ru1	70.41(4)	C36	C35	C34	111.29(7)
C11	C12	C13	111.56(6)	C36	C37	C32	111.24(7)
C11	C15	C14	104.66(6)	C37	C32	P1	110.76(5)
C12	Ru1	P1	161.466(19)	Cl1	C38	Cl2	109.0(2)
C12	C11	Ru1	74.50(4)	Cl2A	C38A	Cl1A	117.5(14)
C12	C11	C2	128.97(6)	F1	B1	F2	108.0(7)
C12	C11	C15	109.57(6)	F1	B1	F4	110.0(7)
C12	C13	C14	104.09(6)	F2	B1	F4	106.3(6)
C13	C12	Ru1	121.33(5)	F3	B1	F1	112.1(6)
C13	C14	C15	105.49(6)	F3	B1	F2	105.6(7)
C15	C11	Ru1	117.74(5)	F3	B1	F4	114.3(7)
C16	O2	Ru1	115.84(4)	F2A	B1A	F1A	110(4)
C16	N1	C17	124.61(6)	F2A	B1A	F3A	130(4)
C16	N1	C18	120.23(6)	F3A	B1A	F1A	94(3)
C18	N1	C17	115.17(6)	F4A	B1A	F1A	104(4)
C19	Ru1	P1	90.82(2)	F4A	B1A	F2A	121(3)
C19	Ru1	O2	178.35(3)	F4A	B1A	F3A	92(4)

Table S8. Torsion Angles for **6.**

A	B	C	D	Angle(°)
Ru1	P1	C20	C21	88.41(6)
Ru1	P1	C20	C25	-38.75(6)
Ru1	P1	C26	C27	58.49(5)
Ru1	P1	C26	C31	-174.09(5)
Ru1	P1	C32	C33	76.06(6)
Ru1	P1	C32	C37	-46.22(5)
Ru1	O2	C16	N1	158.89(5)
Ru1	O2	C16	C3	-24.80(8)
Ru1	C11	C12	C13	-116.93(6)
Ru1	C11	C15	C14	71.18(7)
Ru1	C12	C13	C14	-64.52(7)
P1	Ru1	O2	C16	130.47(5)
P1	Ru1	C11	C2	-22.50(8)
P1	Ru1	C11	C12	-154.14(4)
P1	Ru1	C11	C15	101.57(6)
P1	Ru1	C12	C11	151.06(5)
P1	Ru1	C12	C13	-105.05(7)
P1	Ru1	C19	O1	93(8)
P1	C20	C21	C22	172.90(6)
P1	C20	C25	C24	-170.88(5)
P1	C26	C27	C28	-171.45(5)
P1	C26	C31	C30	173.25(5)
P1	C32	C33	C34	179.69(5)
P1	C32	C37	C36	-176.50(5)

O2	Ru1	P1	C26	21.27(3)
O2	Ru1	P1	C32	-95.06(3)
O2	Ru1	C11	C2	65.16(4)
O2	Ru1	C11	C12	-66.47(4)
O2	Ru1	C11	C15	-170.77(5)
O2	Ru1	C12	C11	110.04(4)
O2	Ru1	C12	C13	-146.06(6)
O2	Ru1	C19	O1	29(8)
C1	C2	C3	C4	0.01(10)
C1	C2	C3	C16	-168.04(6)
C1	C2	C11	Ru1	113.21(6)
C1	C2	C11	C12	-178.92(7)
C1	C2	C11	C15	-8.05(10)
C1	C9	C10	C4	-0.50(10)
C1	C9	C10	C5	177.21(7)
C2	C1	C9	C8	178.59(7)
C2	C1	C9	C10	-0.16(11)
C2	C3	C4	C10	-0.68(11)
C2	C3	C16	O2	52.71(9)
C2	C3	C16	N1	-130.98(7)
C2	C11	C12	Ru1	-73.85(7)
C2	C11	C12	C13	169.22(7)
C2	C11	C15	C14	176.37(6)
C3	C2	C11	Ru1	-66.52(7)
C3	C2	C11	C12	1.35(11)
C3	C2	C11	C15	172.22(6)

C3	C4	C10	C9	0.92(10)
C4	C3	C16	O2	-115.90(7)
C4	C3	C16	N1	60.42(9)
C5	C6	C7	C8	-0.51(12)
C6	C5	C10	C4	179.06(7)
C6	C5	C10	C9	1.42(11)
C6	C7	C8	C9	0.34(12)
C7	C8	C9	C1	-178.05(7)
C7	C8	C9	C10	0.70(11)
C8	C9	C10	C4	-179.28(7)
C8	C9	C10	C5	-1.57(11)
C9	C1	C2	C3	0.41(10)
C9	C1	C2	C11	-179.34(6)
C10	C5	C6	C7	-0.37(12)
C11	Ru1	P1	C20	-129.42(6)
C11	Ru1	P1	C26	109.36(6)
C11	Ru1	P1	C32	-6.97(6)
C11	Ru1	O2	C16	-28.89(5)
C11	Ru1	C12	C13	103.89(7)
C11	Ru1	C19	O1	-108(8)
C11	C2	C3	C4	179.74(6)
C11	C2	C3	C16	11.69(10)
C11	C12	C13	C14	15.03(8)
C12	Ru1	P1	C20	102.65(7)
C12	Ru1	P1	C26	-18.56(7)
C12	Ru1	P1	C32	-134.90(6)

C12	Ru1	C11	C2	131.63(6)
C12	Ru1	C11	C15	-104.30(7)
C12	Ru1	C19	O1	-75(8)
C12	C11	C15	C14	-11.15(8)
C12	C13	C14	C15	-21.09(8)
C13	C14	C15	C11	19.85(8)
C15	C11	C12	Ru1	114.46(5)
C15	C11	C12	C13	-2.47(8)
C16	C3	C4	C10	168.01(6)
C17	N1	C16	O2	-173.05(7)
C17	N1	C16	C3	10.77(11)
C18	N1	C16	O2	7.37(11)
C18	N1	C16	C3	-168.81(7)
C19	Ru1	P1	C20	-36.03(4)
C19	Ru1	P1	C26	-157.25(4)
C19	Ru1	P1	C32	86.42(4)
C19	Ru1	O2	C16	-165.7(10)
C19	Ru1	C11	C2	-115.96(4)
C19	Ru1	C11	C12	112.40(5)
C19	Ru1	C11	C15	8.10(6)
C19	Ru1	C12	C11	-71.60(5)
C19	Ru1	C12	C13	32.30(6)
C20	P1	C26	C27	-71.46(6)
C20	P1	C26	C31	55.96(6)
C20	P1	C32	C33	-153.33(5)
C20	P1	C32	C37	84.39(6)

C21	C20	C25	C24	58.30(9)
C21	C22	C23	C24	-55.39(10)
C22	C23	C24	C25	55.31(10)
C23	C24	C25	C20	-57.47(9)
C25	C20	C21	C22	-58.17(9)
C26	P1	C20	C21	-147.67(6)
C26	P1	C20	C25	85.17(6)
C26	P1	C32	C33	-42.95(6)
C26	P1	C32	C37	-165.23(5)
C26	C27	C28	C29	-56.80(9)
C27	C26	C31	C30	-58.04(8)
C27	C28	C29	C30	55.66(9)
C28	C29	C30	C31	-56.39(9)
C29	C30	C31	C26	57.71(9)
C31	C26	C27	C28	57.94(8)
C32	P1	C20	C21	-36.43(7)
C32	P1	C20	C25	-163.59(5)
C32	P1	C26	C27	177.62(5)
C32	P1	C26	C31	-54.95(6)
C32	C33	C34	C35	55.25(9)
C33	C32	C37	C36	59.04(8)
C33	C34	C35	C36	-53.65(10)
C34	C35	C36	C37	54.59(9)
C35	C36	C37	C32	-58.26(9)
C37	C32	C33	C34	-57.00(8)

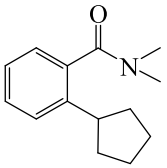
Table S9. Hydrogen Atom Coordinates (Å × 10^4) and Isotropic Displacement Parameters (Å^2 × 10^3) for **6.**

Atom	*x*	*y*	*z*	U(eq)
H1	10341(13)	146(11)	3835(8)	27(3)
H1A	11533	929	1077	15
H4	7041	1319	917	14
H5	7487	2867	122	17
H6	8965	3982	-501	19
H7	11197	3748	-449	20
H8	11967	2421	236	19
H13B	10093	-2830	2198	18
H13A	10596	-2079	3162	18
H14A	12355	-2094	2206	20
H14B	12629	-1017	3000	20
H15A	12487	73	2029	16
H15B	11672	-1066	1266	16
H17C	6270	-913	368	28
H17B	4840	-693	499	28
H17A	5127	-1928	551	28
H18C	5781	-522	2705	26
H18A	4999	-1768	2055	26
H18B	4457	-650	1948	26
H20	11079	3364	5475	16
H21A	13470	3356	4849	23
H21B	12804	4432	4926	23
H22A	14726	4771	6129	29

H23B	14596	2835	6243	24
H23A	14511	3572	7117	24
H24B	12078	2763	6753	24
H24A	12774	1707	6665	24
H25B	10850	1362	5473	19
H25A	12264	1463	5187	19
H26	7841	2008	3690	14
H27B	8240	427	4273	17
H27A	8736	1278	5199	17
H28B	5972	654	4085	21
H28A	6365	206	4927	21
H29B	5349	1784	5159	20
H29A	6897	2121	5767	20
H30A	6654	3714	5172	20
H30B	6171	2878	4241	20
H31A	8928	3471	5364	19
H31B	8555	3957	4537	19
H32	10781	4404	4016	15
H33A	8944	2915	2443	20
H33B	8441	3630	3162	20
H34B	8642	4646	2067	25
H34A	9645	5433	2959	25
H35B	10523	4175	1648	23
H35A	10925	5576	1959	23
H36B	12326	5545	3258	24
H36A	12811	4844	2523	24

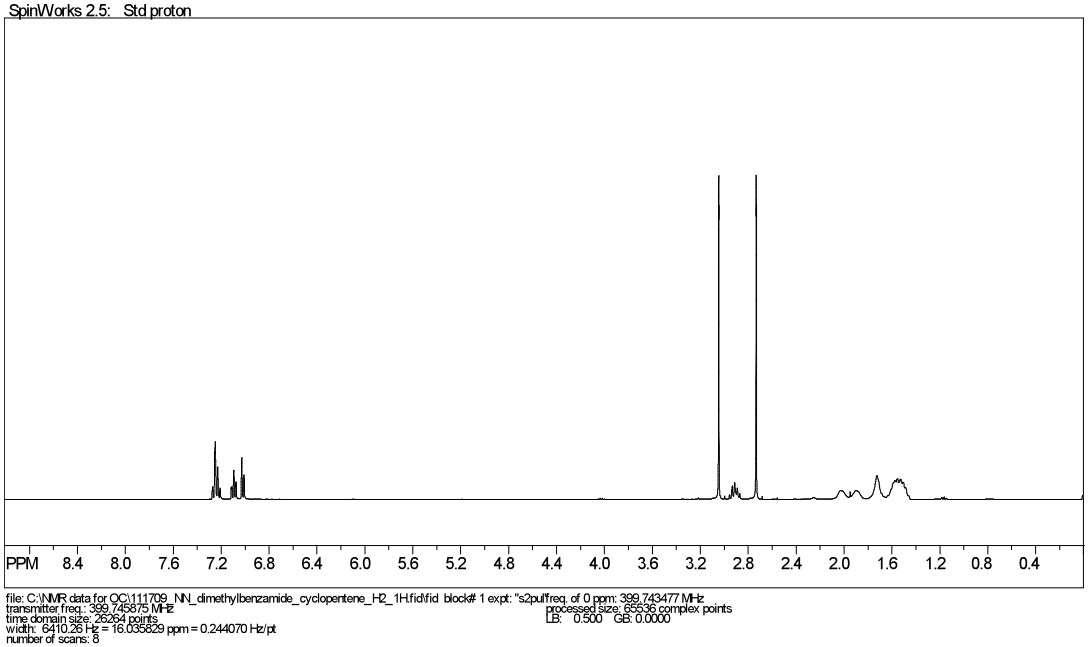
H37B	11517	3027	2686	20
H38B	5026	4427	697	30
H38A	5199	4787	1693	30
H38C	5160	4500	1508	30
H38D	4991	4399	527	30
H12	8760(11)	-1412(9)	2318(7)	11(2)

The ^{1}H and ^{13}C NMR Spectra of Selected Organic Products

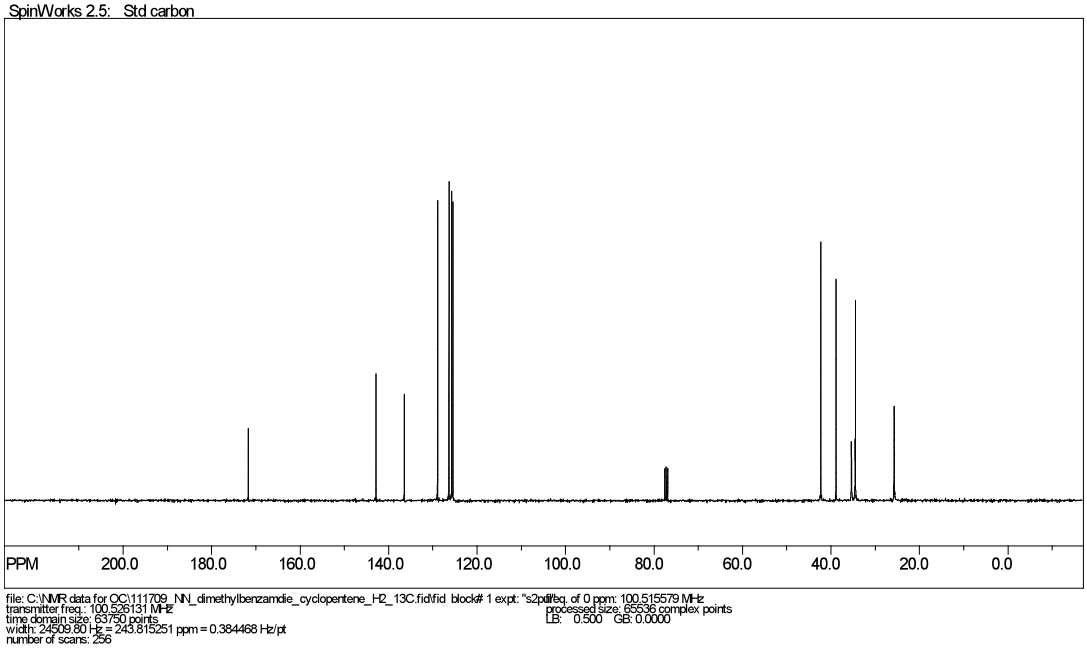


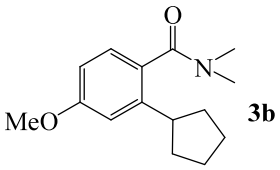
3a

^{1}H NMR (400 MHz, $CDCl_3$)



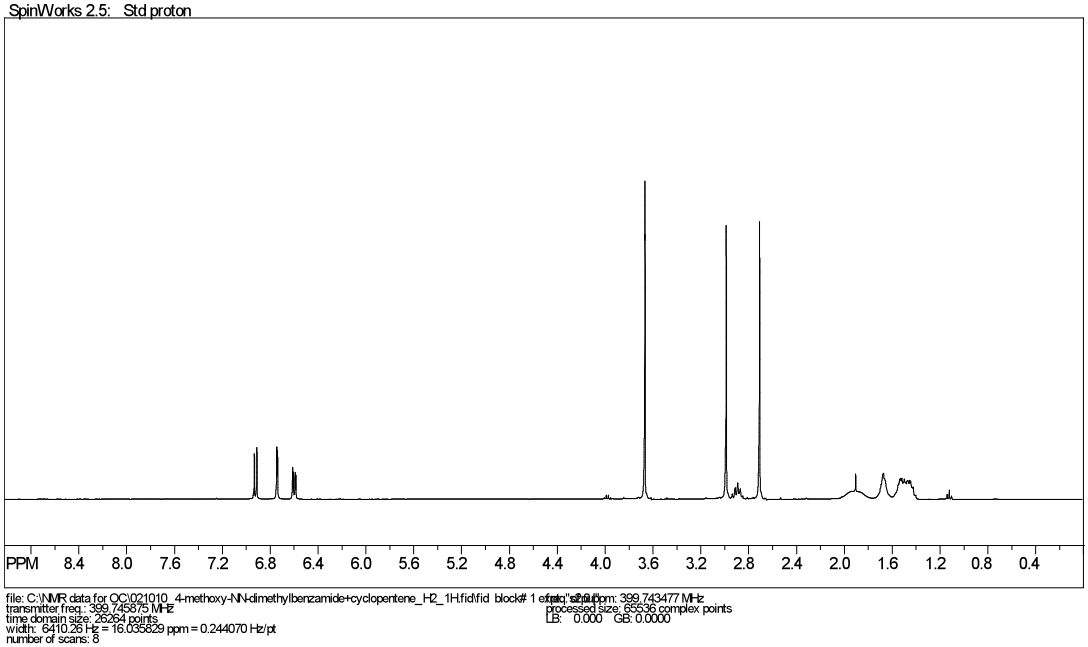
$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)



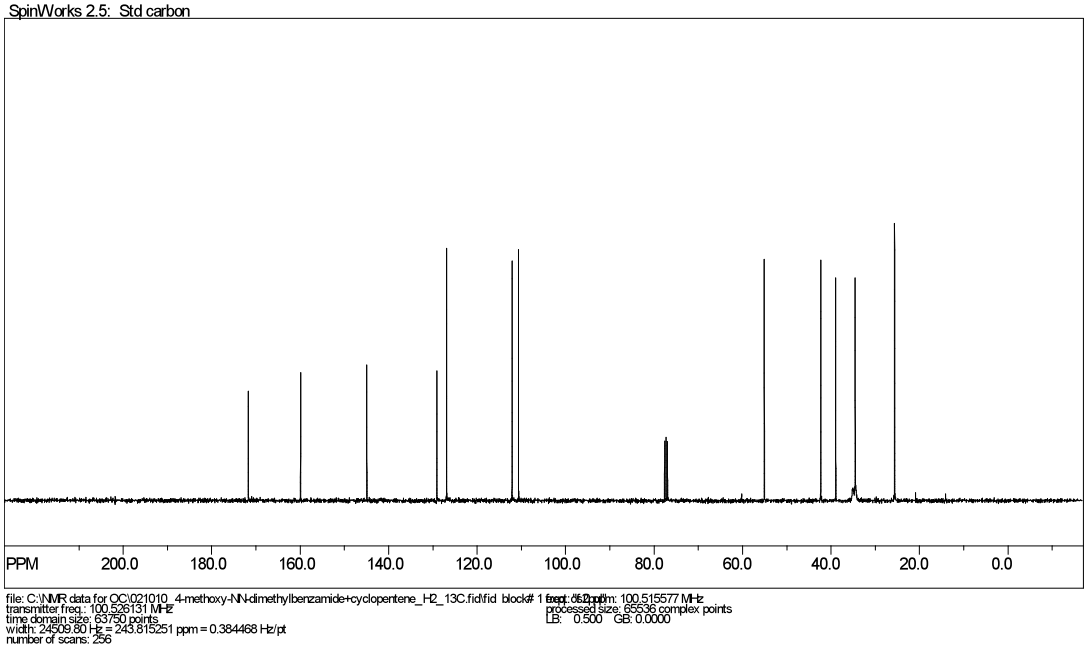


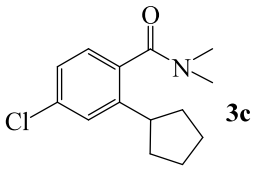
3b

^{1}H NMR (400 MHz, $CDCl_3$)



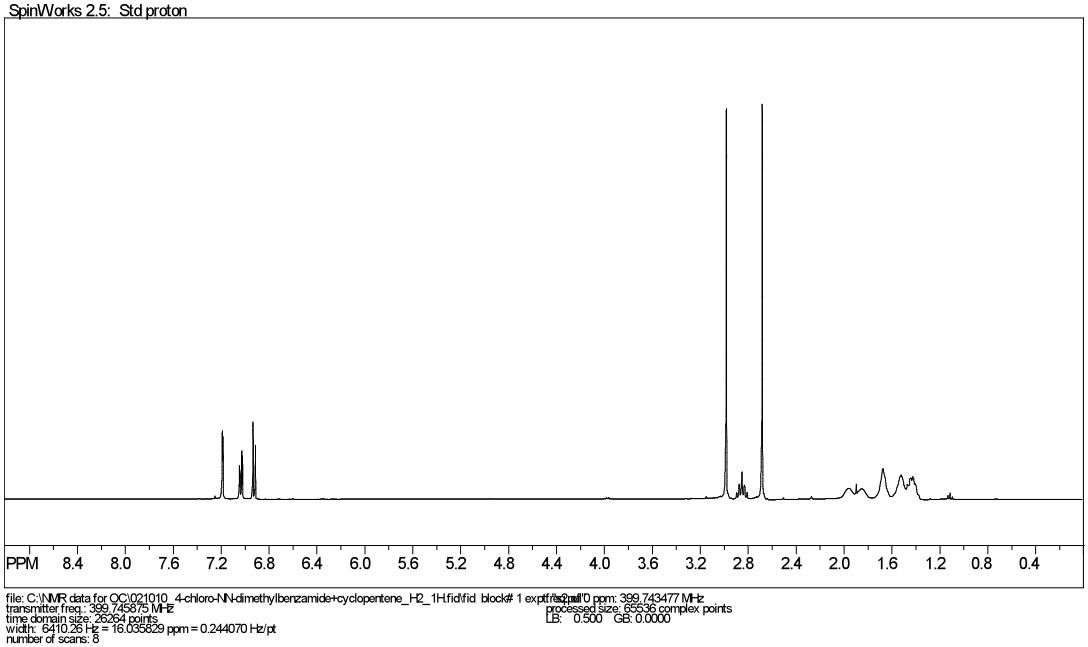
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)



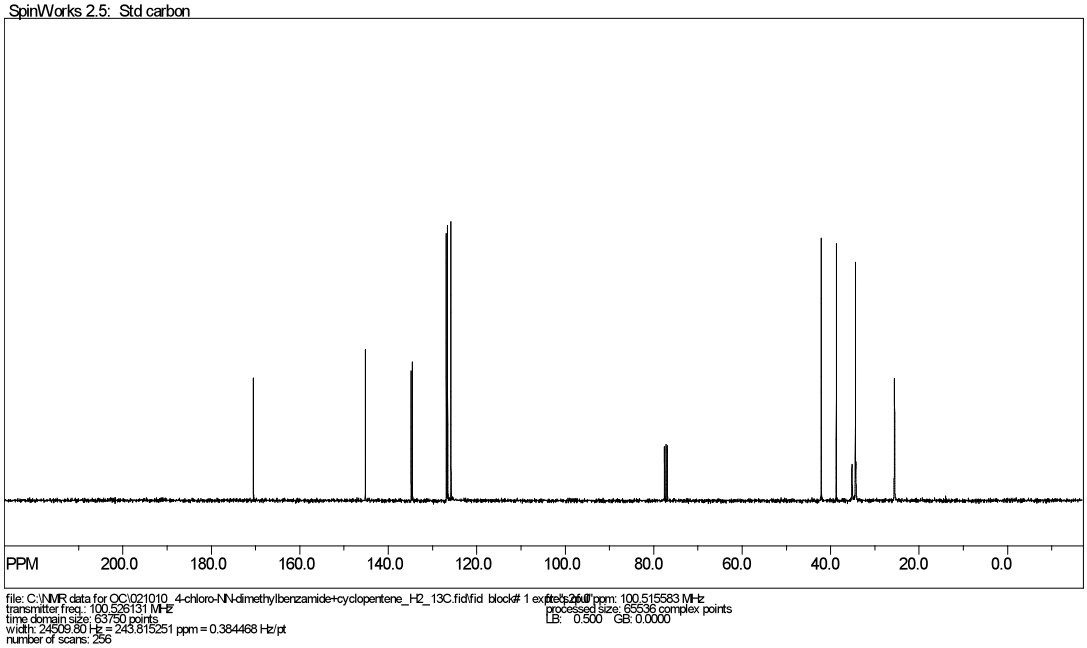


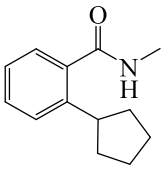
3c

^{1}H NMR (400 MHz, $CDCl_3$)



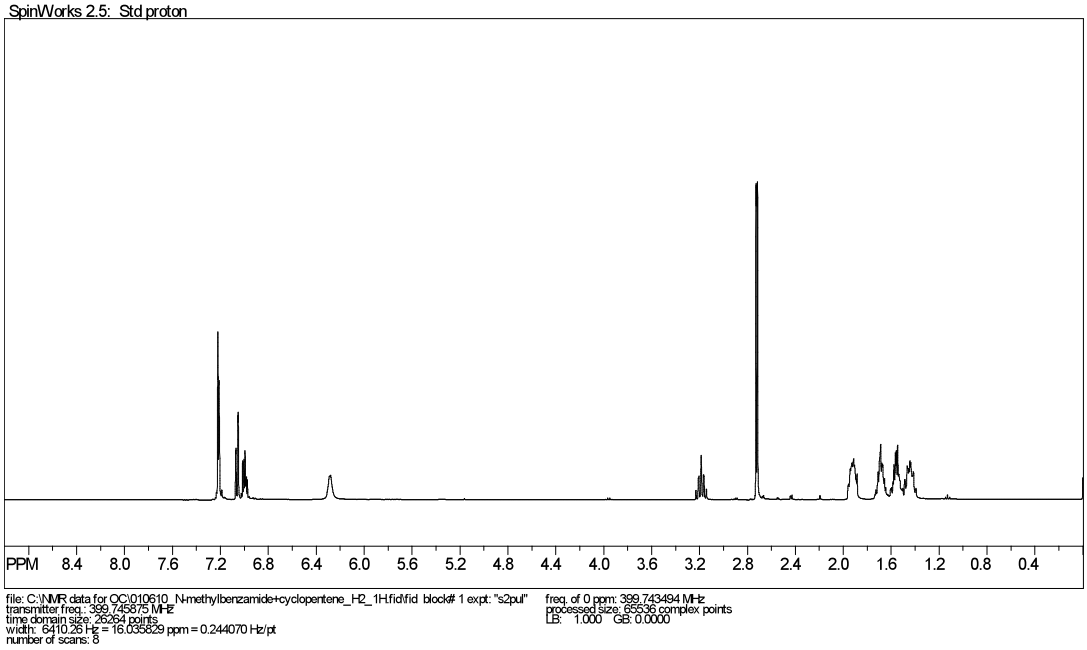
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)



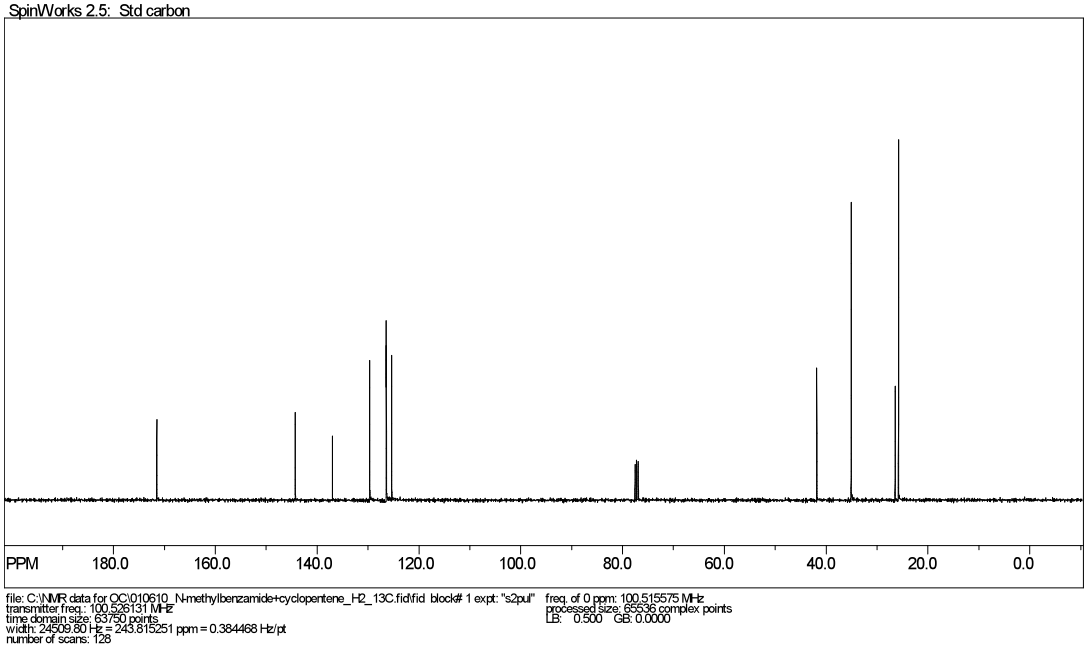


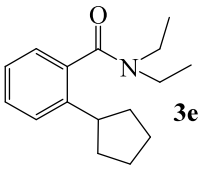
3d

^{1}H NMR (400 MHz, $CDCl_3$)



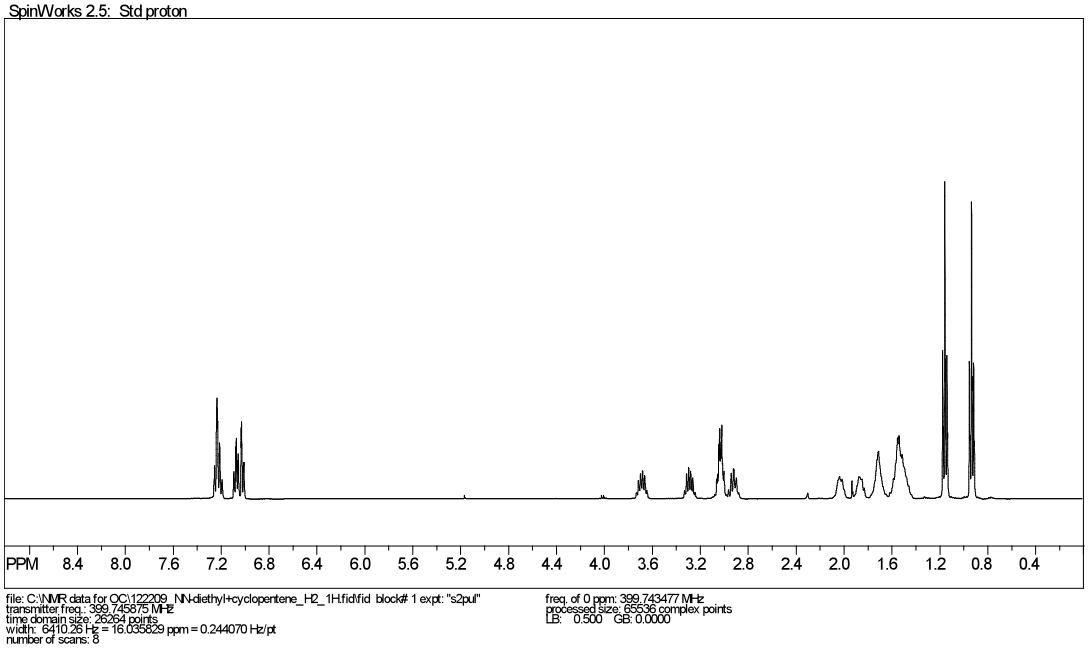
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)



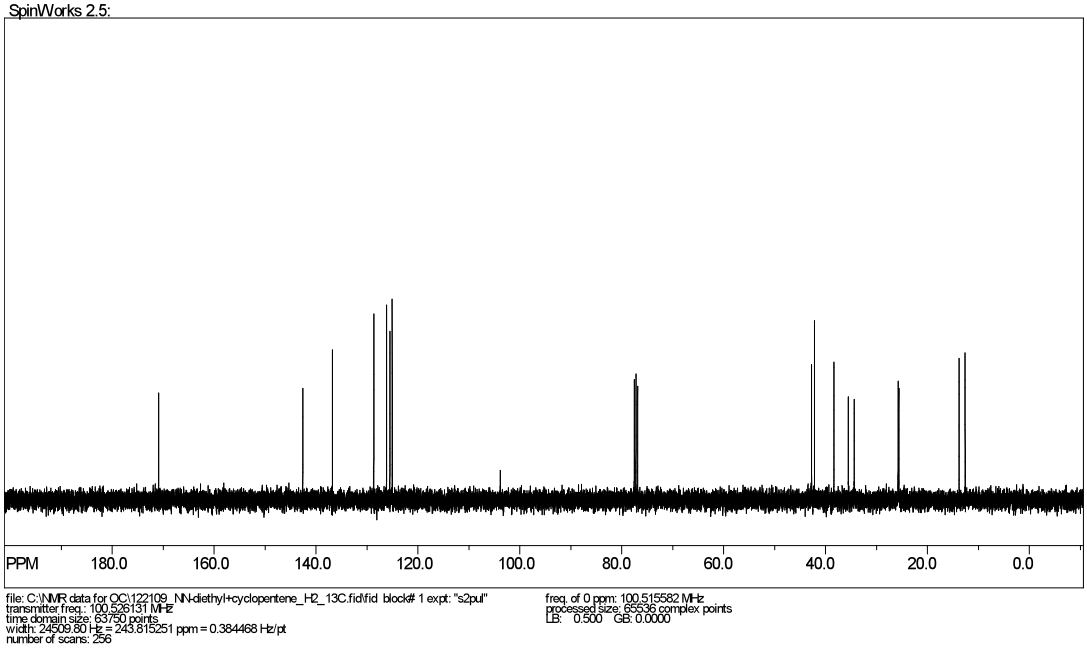


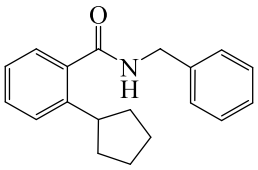
3e

^{1}H NMR (400 MHz, $CDCl_3$)



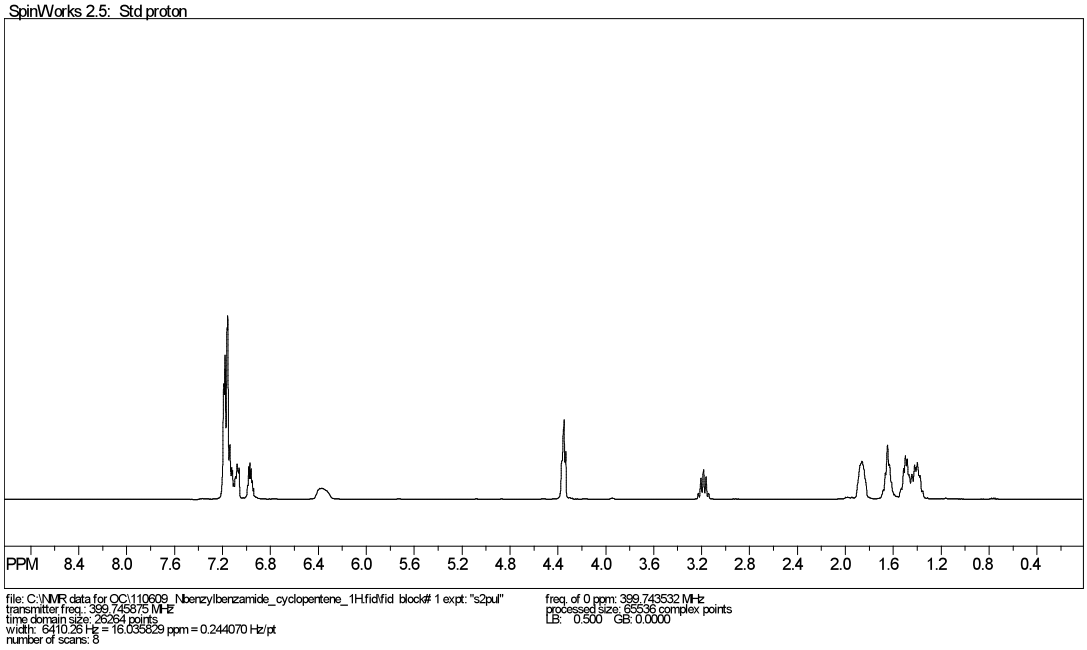
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)



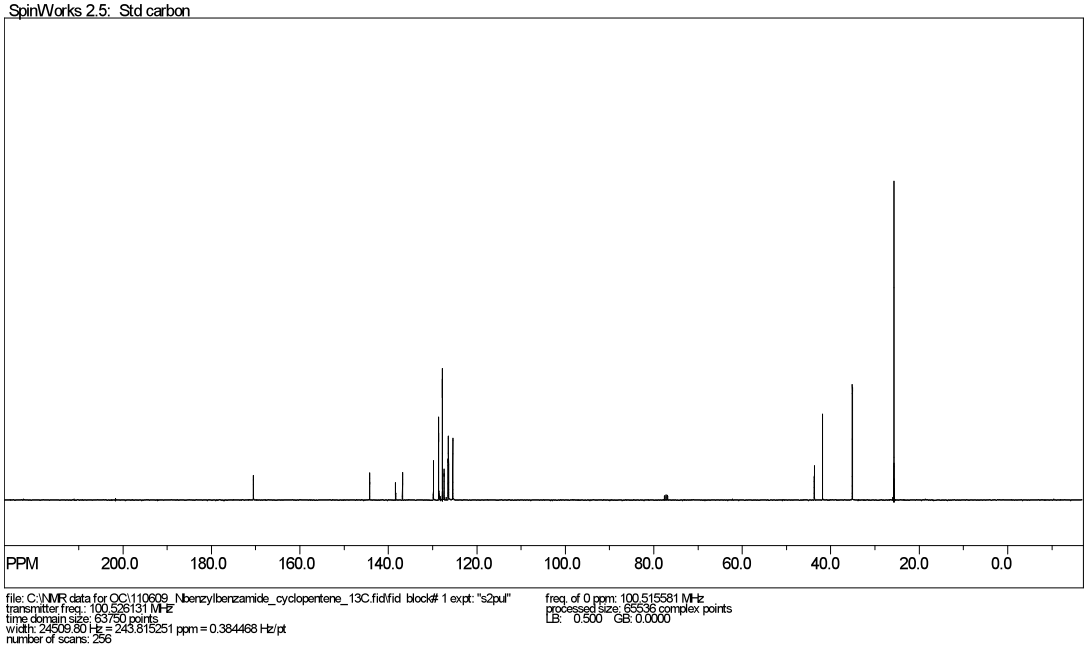


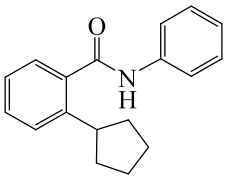
3f

^{1}H NMR (400 MHz, $CDCl_3$)



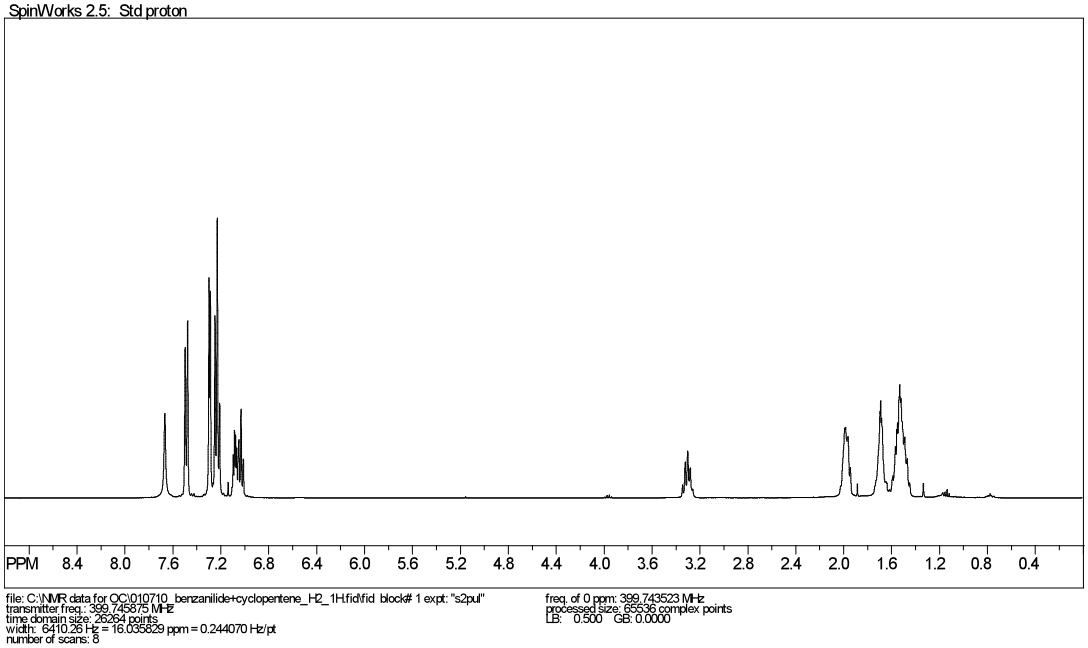
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)



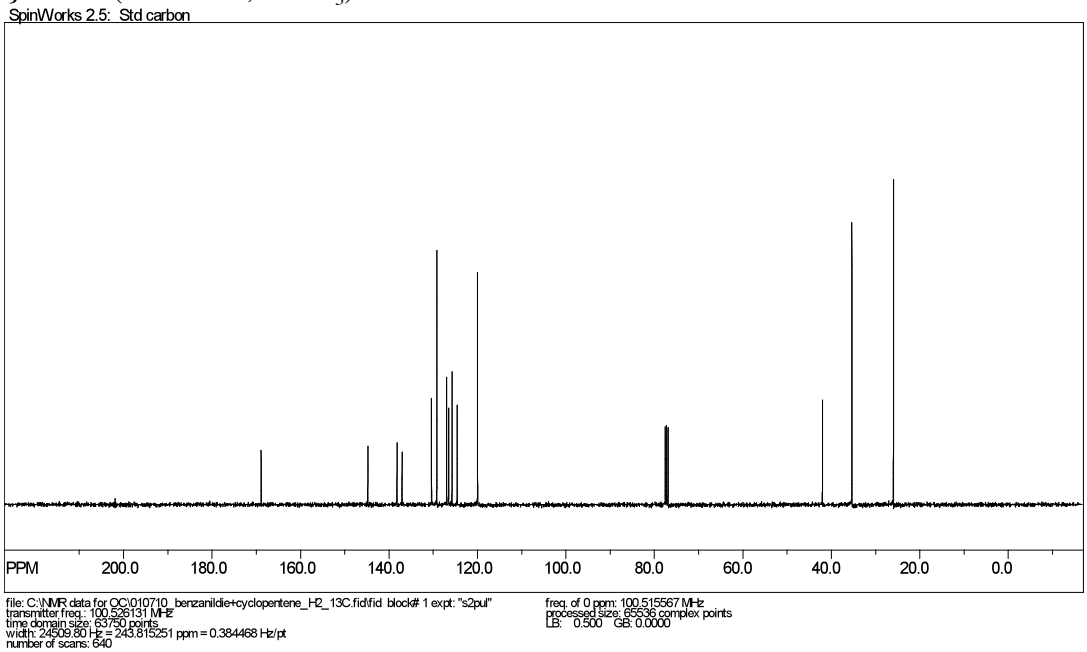


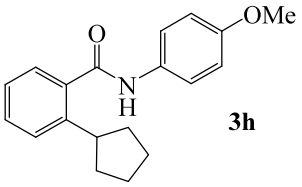
3g

^{1}H NMR (400 MHz, $CDCl_3$)



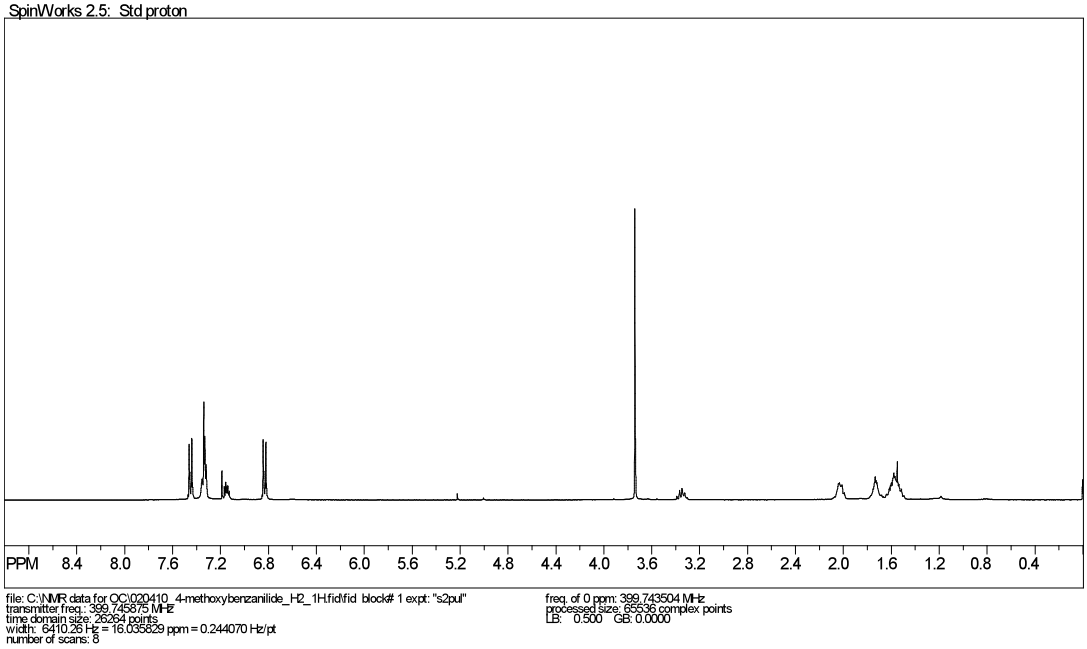
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)



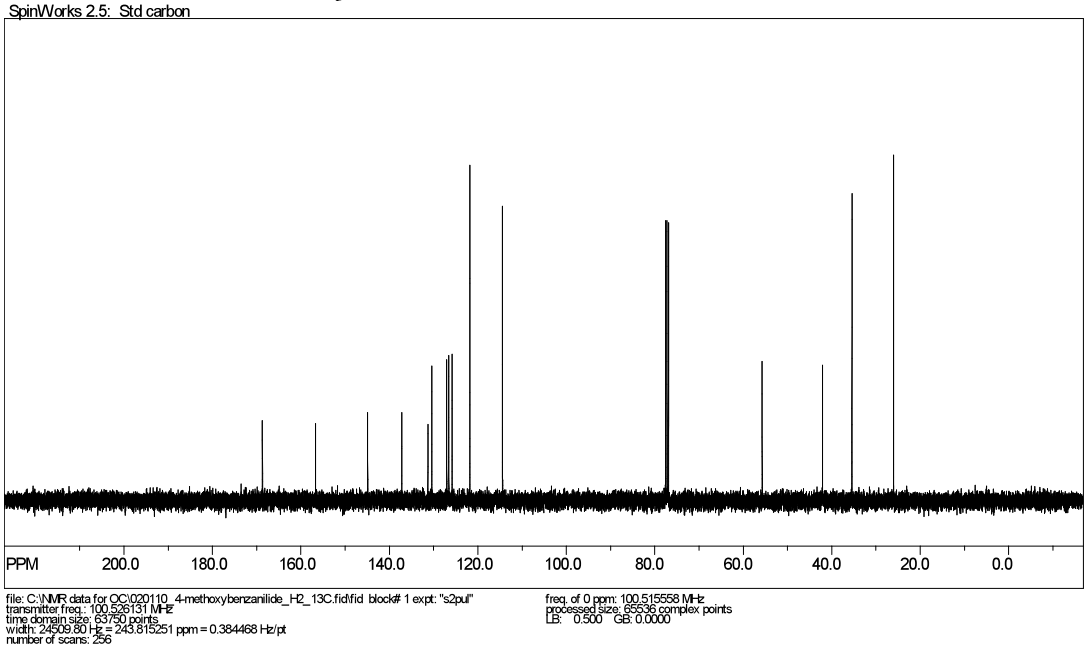


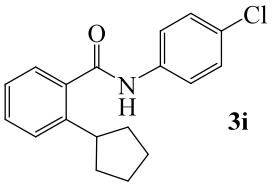
3h

^{1}H NMR (400 MHz, $CDCl_3$)



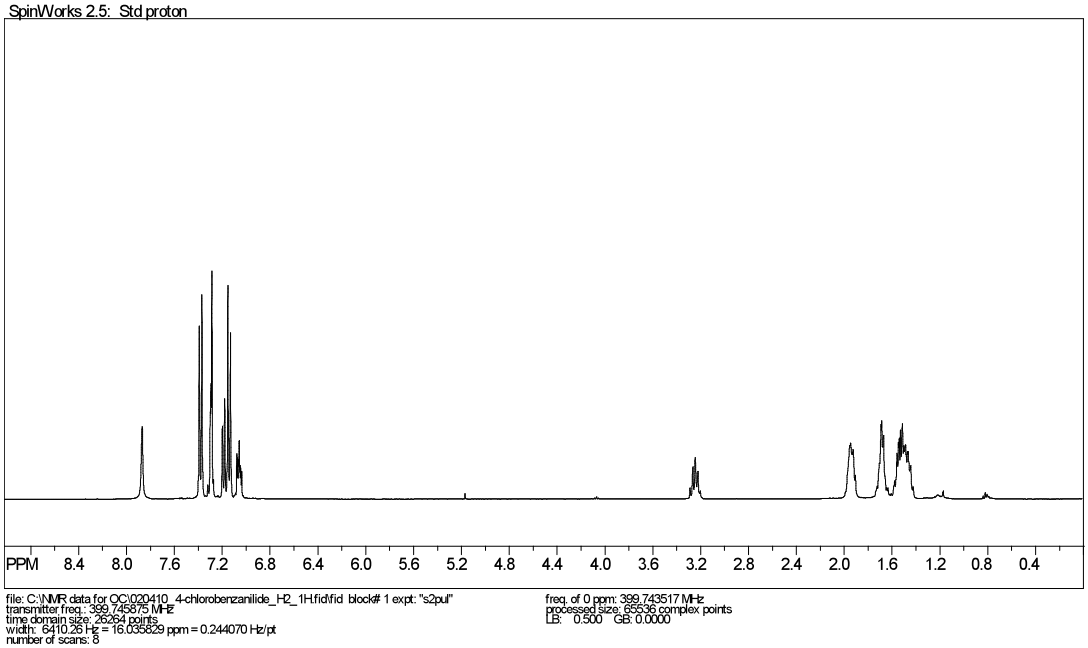
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)



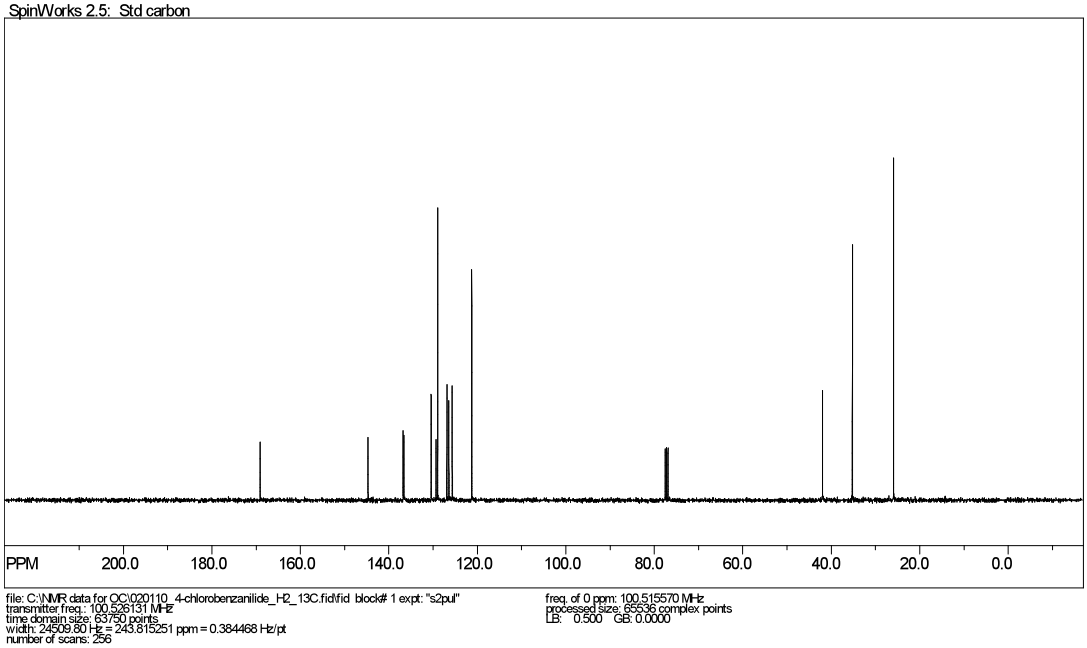


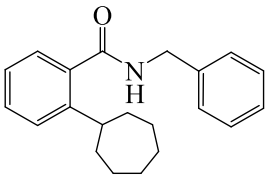
3i

^{1}H NMR (400 MHz, $CDCl_3$)



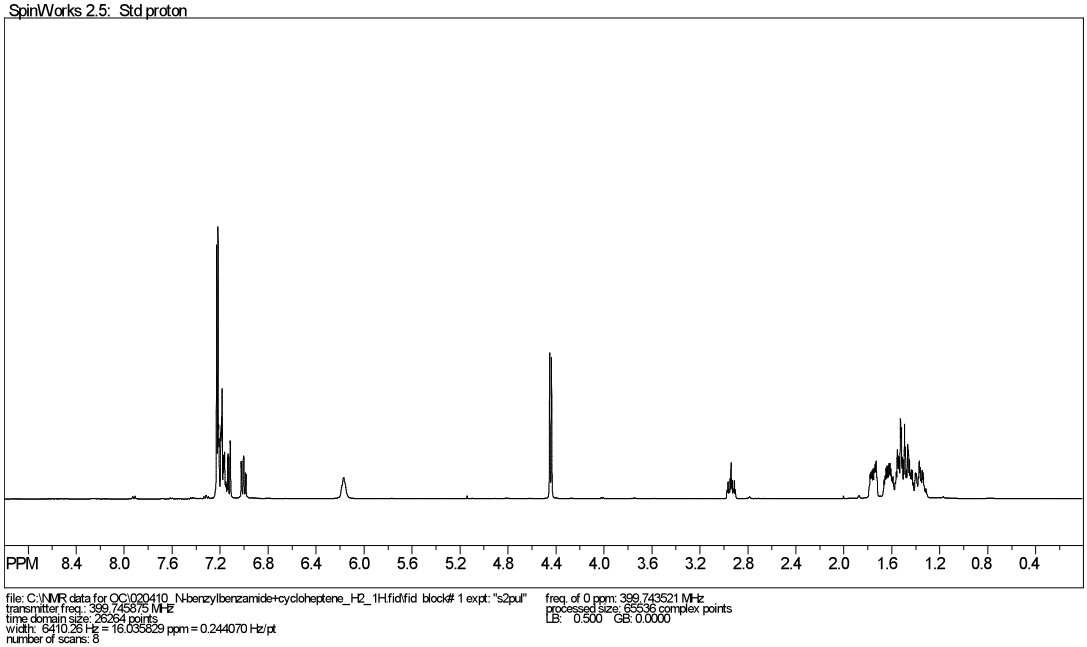
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)



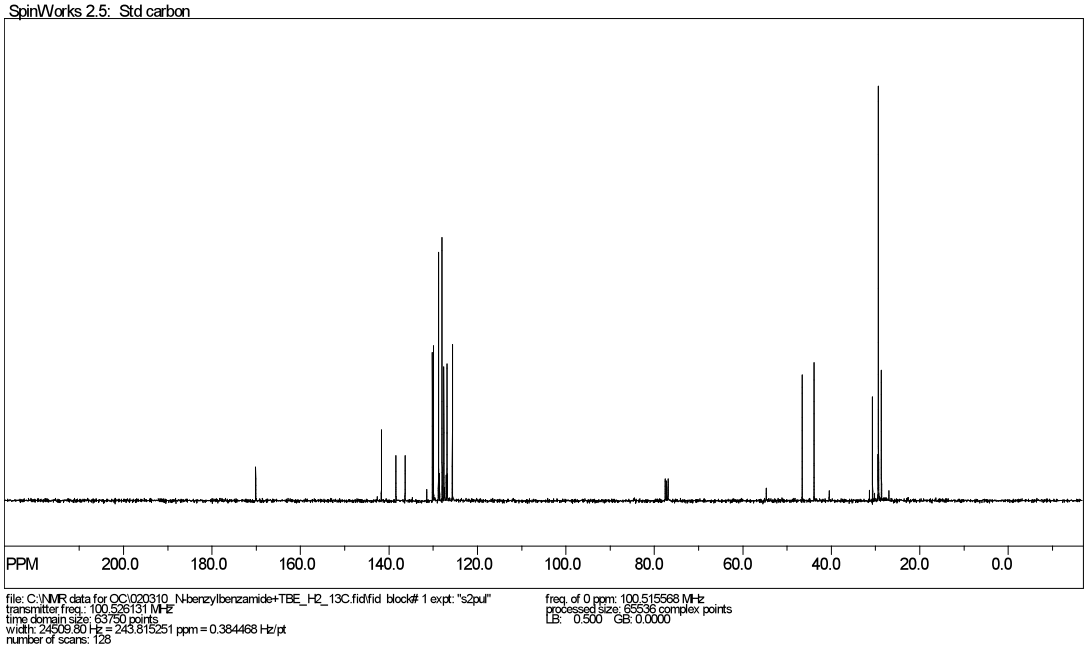


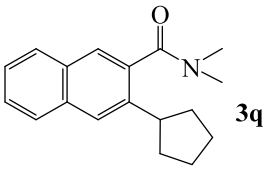
3j

^{1}H NMR (400 MHz, $CDCl_3$)



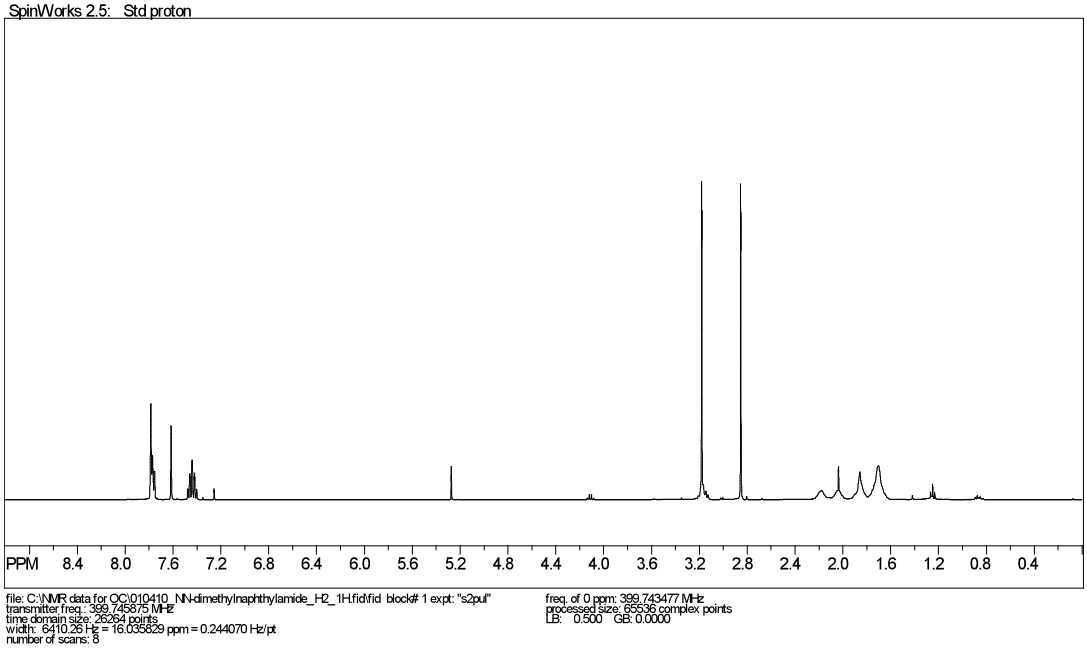
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)



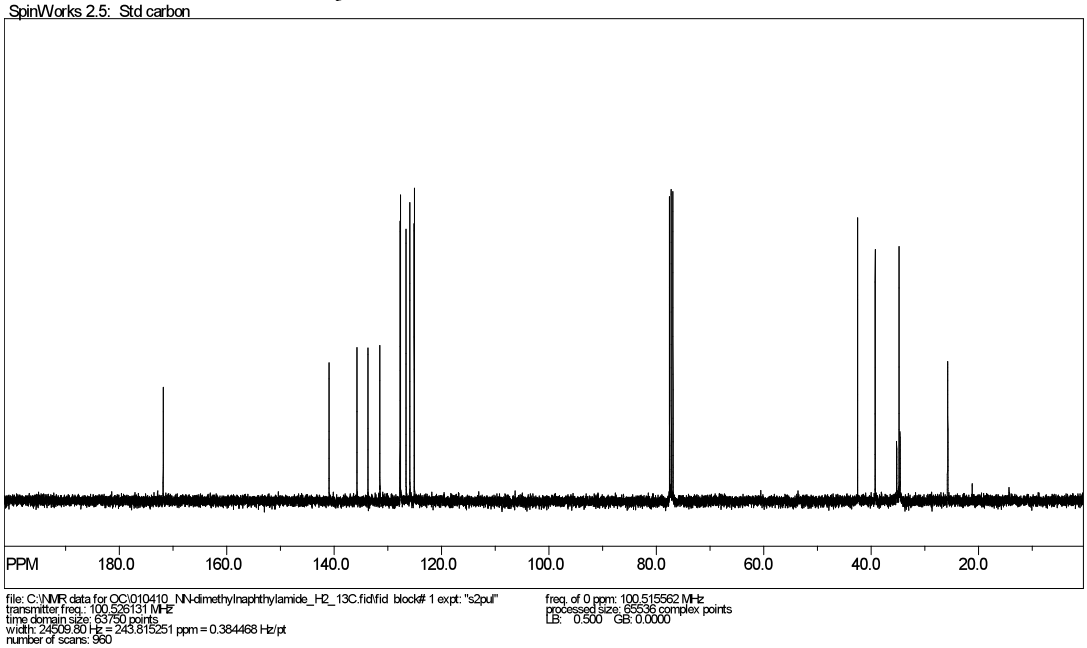


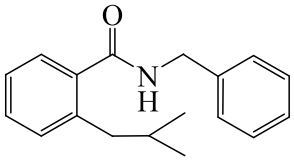
3q

^{1}H NMR (400 MHz, $CDCl_3$)



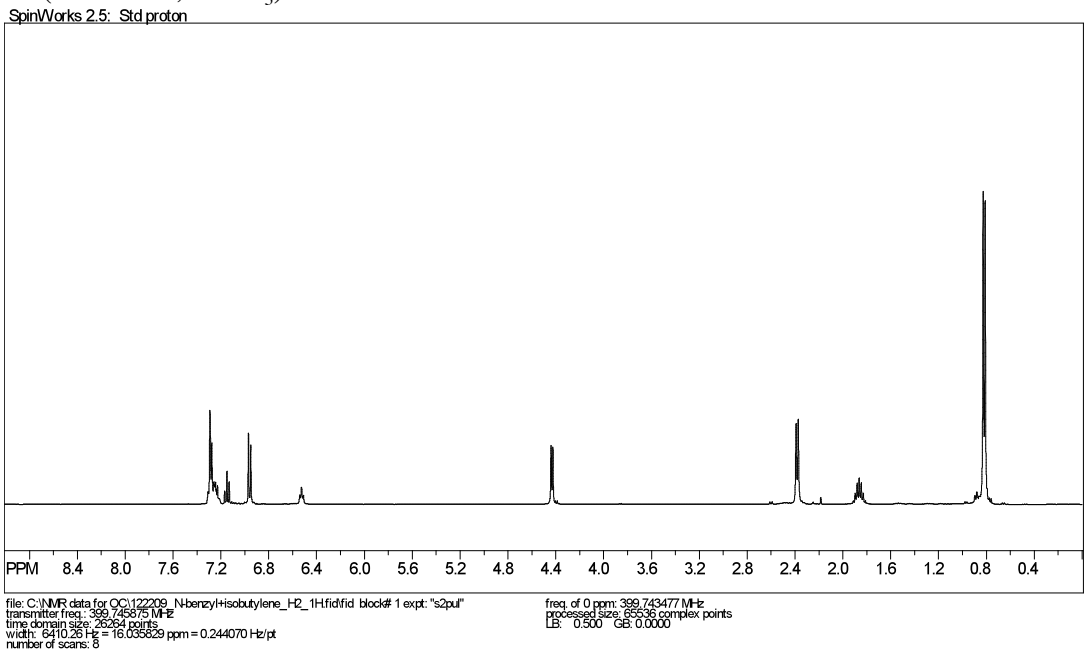
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)



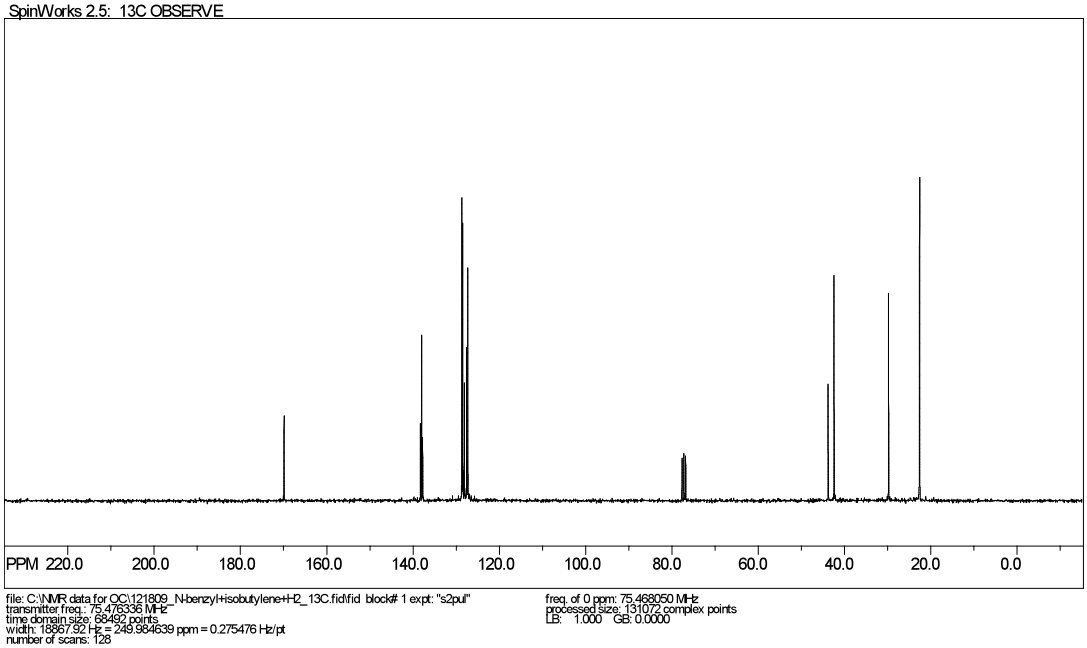


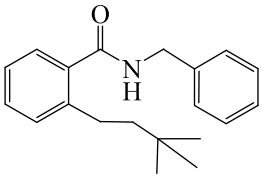
3r

^{1}H NMR (400 MHz, $CDCl_3$)



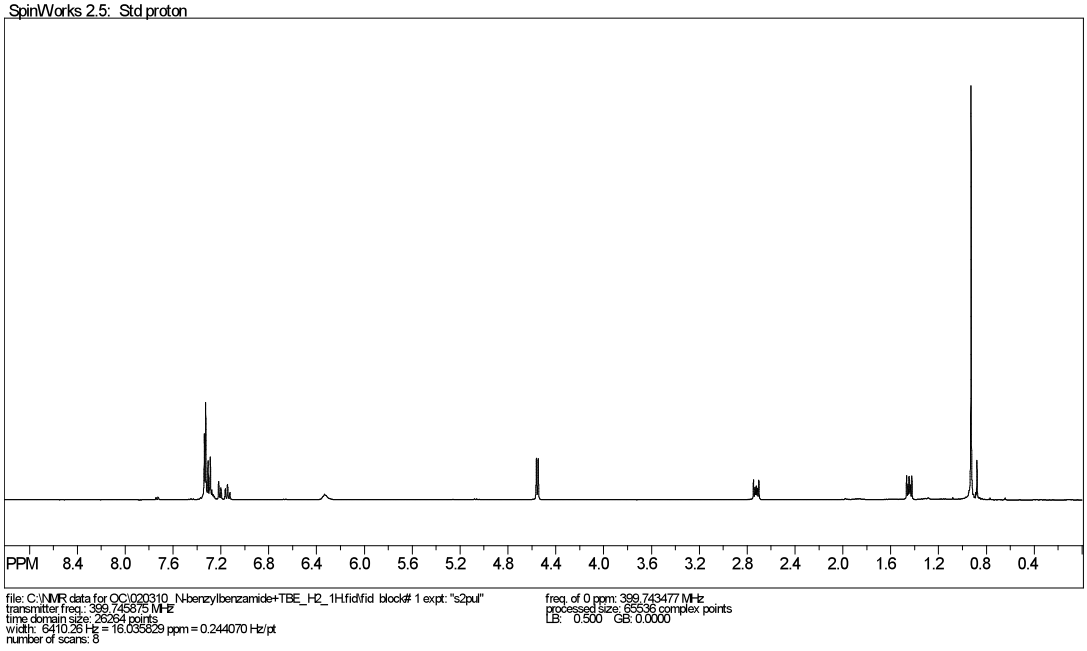
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)



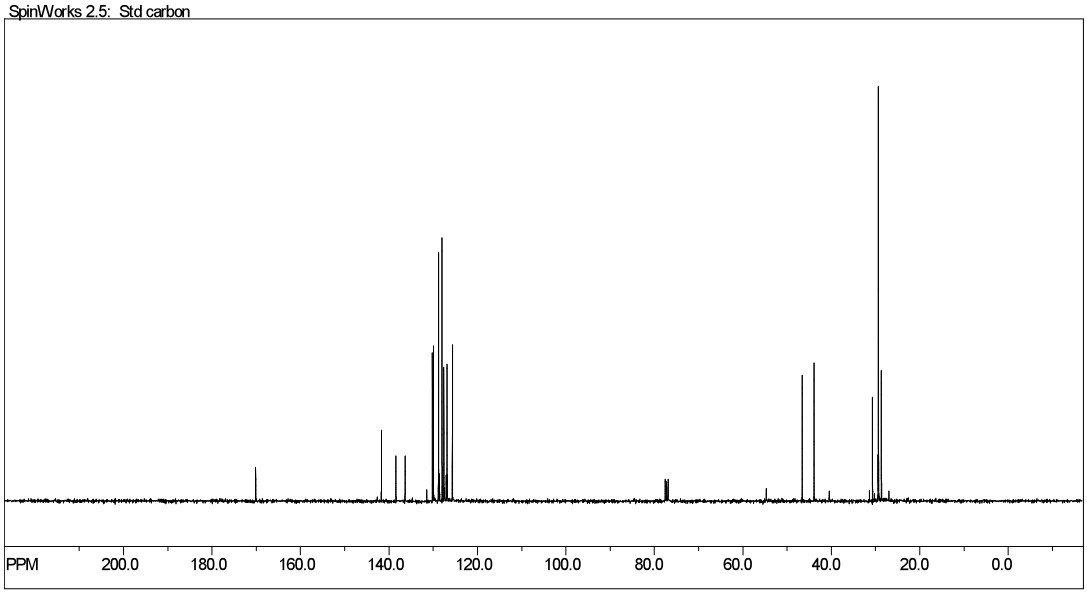


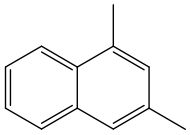
3s

^{1}H NMR (400 MHz, $CDCl_3$)



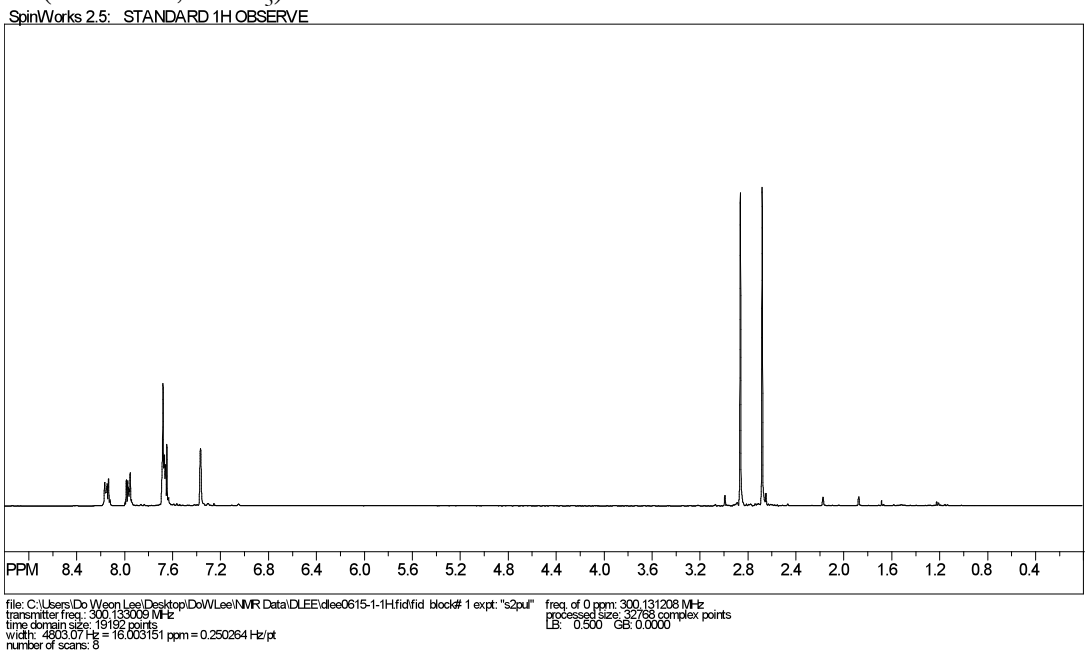
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)



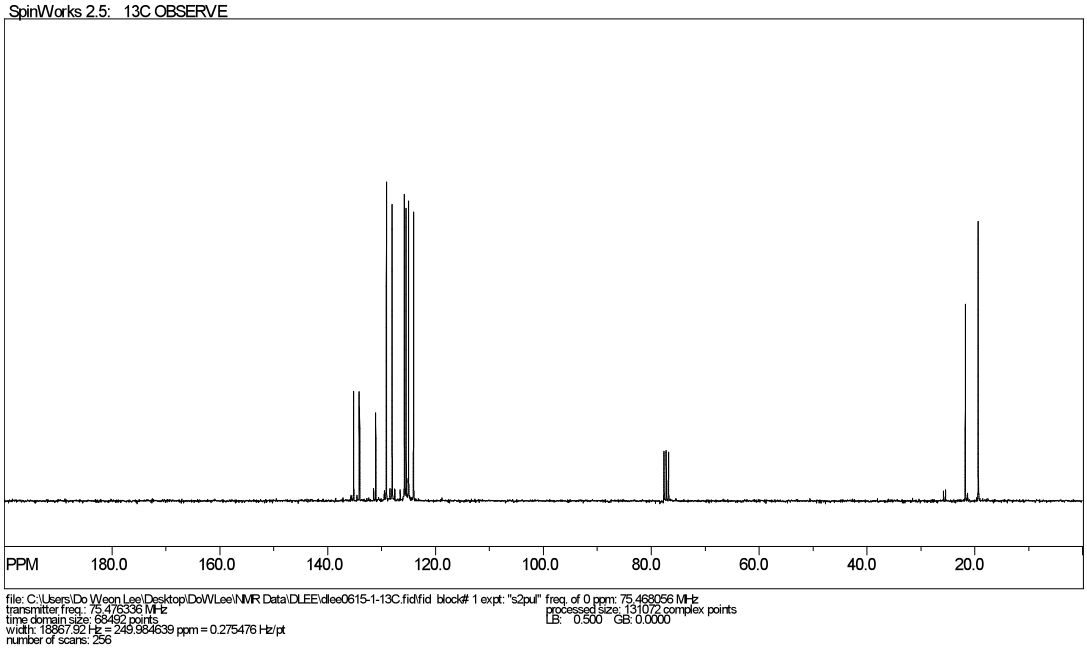


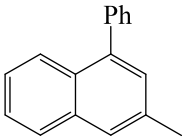
4t

^{1}H NMR (300 MHz, $CDCl_3$)



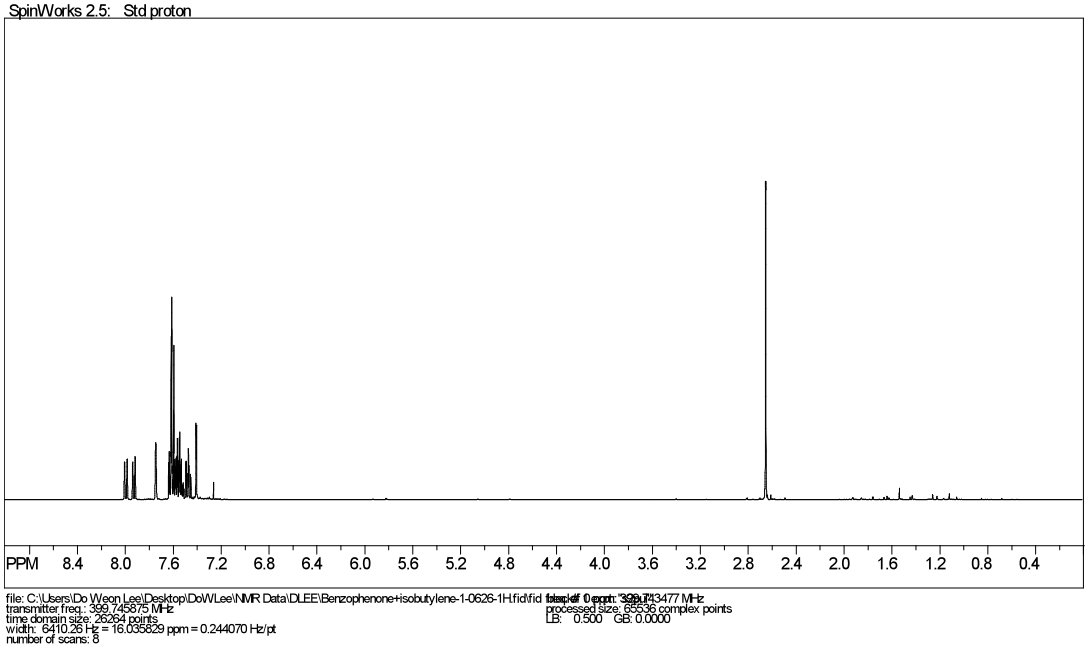
^{13}C{^{1}H} NMR (76 MHz, $CDCl_3$)





4w

^{1}H NMR (400 MHz, $CDCl_3$)



$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)