Supplementary Material

Design of bis-NHC Ru-complexes featuring diarylmethylene N-substituents for olefin metathesis

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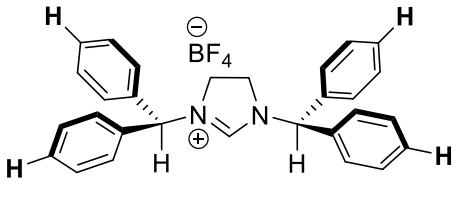
General Information

General. All reactions were carried out under an atmosphere of argon using standard Schlenk techniques. Toluene, diethyl ether, dichloromethane and tetrahydrofuran were purified using MBraun Solvent Purification Systems. All commercial chemicals were used as received unless otherwise noted. The 1 M solution of hydrogen chloride in ethanol and 0.5 M solution of potassium bis(trimethylsilyl)amid in toluene were purchased from Acros Organics with AcroSeal packaging. NMR spectra were recorded on a Bruker ARX400 spectrometer (^{1}H (400 MHz), ^{13}C (101 MHz), ^{19}F (376 MHz) and ^{11}B (128 MHz)) with complete proton decoupling for ^{13}C. Chemical shifts are reported in parts per million with the solvent resonance as the internal standard ($CDCl_3$, ^{1}H: δ 7.26 ppm, ^{13}C: δ 77.16 ppm; DMSO, ^{1}H: δ 2.50 ppm, ^{13}C: δ 39.52 ppm). Coupling constants are reported in Hertz (Hz). Abbreviations are used as follows: s = singlet, d = doublet, t = triplet, dd = double doublet, td = triple doublet, q = quartet, m = multiplet. High Resolution Mass Spectrometry (HRMS) were recorded on a Waters QTof-I spectrometer using electrospray ionization at the Centre Régional de Mesures Physiques de l'Ouest (CRMPO), Université de Rennes 1. Melting points were measured on a Stuart Melting Point Apparatus SMP3 and are uncorrected.

Synthesis of Imidazolinium Salts

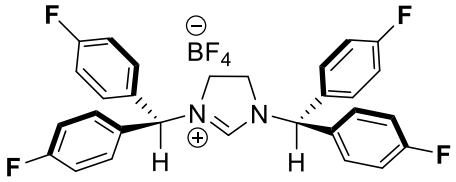
General procedure for synthesis of imidazolinium salts: Ethylene diamine (1 equiv), diarylketone (2 or 3 equiv), sodium cyanoborohydride (3 equiv) and ethanol (3 mL/mmol) were added in a round-bottom flask. The pH of the solution was adjusted at 5-6 with a 1 M solution of HCl.EtOH and the mixture was refluxed overnight. After cooling to room temperature, the solvent was evaporated and the crude mixture was dissolved in DCM and washed with a saturated solution of $NaHCO_3$. The crude product was purified by flash chromatography (DCM/acetone as eluent) and used for the next step. Then, the diamine (1 equiv), NH_4BF_4 (1 equiv) and triethylorthoformate (1 mL/mmol of diamine) were heated at 120 °C during 2 h under an argon atmosphere. The volatiles were removed under vacuum and the corresponding imidazolinium salt was purified by precipitation with diethyl ether or by flash chromatography on silica gel (DCM/acetone).



$C_{29}H_{27}BF_4N_2$
490,35 g.mol^{-1}

1H-1,3-dibenzhydryl-4,5-dihydroimidazolinium tetrafluoroborate (3a)
Following the general procedure for the synthesis of symmetric imidazolinium salts, with benzophenone (3.681 g, 20.2 mmol) and ethylenediamine (680 µL, 10.2 mmol), the desired product was isolated as a white solid (2.2983 g, 46% yield) after purification by chromatography on silica gel (DCM/acetone 98/2).
mp = 205 °C
^{1}H NMR (400 MHz, *DMSO-d$_6$*): δ ppm) 8.22 (s, 1H), 7.45-7.34 (m, 20H), 6.25 (s, 2H), 3.85 (s, 4H)
^{13}C NMR (101 MHz, *DMSO-d$_6$*): δ ppm) 158.1, 136.7, 129.0, 128.6, 128.2, 64.8, 48.0
^{19}F NMR (376 MHz, *DMSO-d$_6$*): δ ppm) -148.2, -148.3
^{11}B NMR (128 MHz, *DMSO-d$_6$*): δ ppm) 1.2
HRMS (ESI) : m/z : M^+ ($C_{29}H_{27}N_2$) calc.: 403.21742; found: 403.2173 (1 ppm).

1H-1,3-bis[di-(4-fluorophenyl)methyl]-4,5-dihydroimidazolinium tetrafluoroborate (3b)



$C_{29}H_{23}BF_8N_2$
562,31 g.mol^{-1}

Following the general procedure for the synthesis of symmetric imidazolinium salts with 4,4' difluorobenzophenone (3.298 g, 15.1 mmol) and ethylenediamine (350 µL, 5.2 mmol), the desired product was isolated as a white solid (1.259 g, 45% yield) after precipitation.
mp = 194 °C

^{1}H NMR (400 MHz, *DMSO-d$_6$*): δ ppm) 8.17 (s, 1H), 7.40-7.36 (m, 8H), 7.29-7.24 (m, 8H), 6.22 (s, 2H), 3.80 (s, 4H)

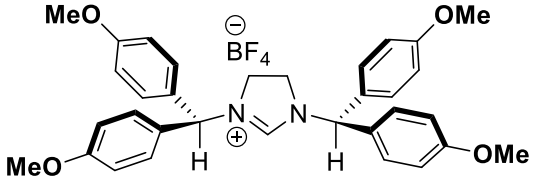
^{13}C NMR (101 MHz, *DMSO-d$_6$*): δ ppm) 162.1 (d, *J* = 246.6 Hz), 158.2, 132.8 (d, *J* = 3.1 Hz), 130.5 (d, *J* = 8.5 Hz), 115.9 (d, *J* = 21.7 Hz), 63.4, 47.8

^{19}F NMR (376 MHz, *DMSO-d$_6$*): δ ppm) -148.3, -148.2, -113.3

^{11}B NMR (128 MHz, *DMSO-d$_6$*): δ ppm) -1.3

HRMS (ESI) : m/z : M^+ ($C_{29}H_{23}N_2F_4$) calc.: 475.17974; found: 475.1794 (1 ppm).

1H-1,3-bis[di(4-methoxyphenyl)methyl]-4,5-dihydroimidazolinium tetrafluoroborate (3c)



$C_{33}H_{35}BF_4N_2O_4$
610,46 g.mol^{-1}

Following the general procedure for the synthesis of symmetric imidazolinium salts with 4,4'-dimethoxybenzophenone (3.677 g, 15.2 mmol) and ethylenediamine (330 µL, 4.9 mmol), the desired product was isolated as a white solid (0.570 g, 19% yield) after purification by chromatography on silica gel (DCM/acetone 100/0 to 95/5).
mp = 57 °C

^{1}H NMR (400 MHz, *DMSO-d$_6$*): δ ppm) 8.04 (s, 1H), 7.23-7.20 (m, 8H), 6.97-6.94 (m, 8H), 6.07 (s, 2H), 3.77 (s, 4H), 3.73 (s, 12H)

^{13}C NMR (101 MHz, *DMSO-d$_6$*): δ ppm) 159.2, 157.5, 129.5, 128.8, 114.4, 63.9, 55.2, 47.7

^{19}F NMR (376 MHz, *DMSO-d$_6$*): δ ppm) -148.3, -148.2

^{11}B NMR (128 MHz, *DMSO-d$_6$*): δ ppm) -1.3

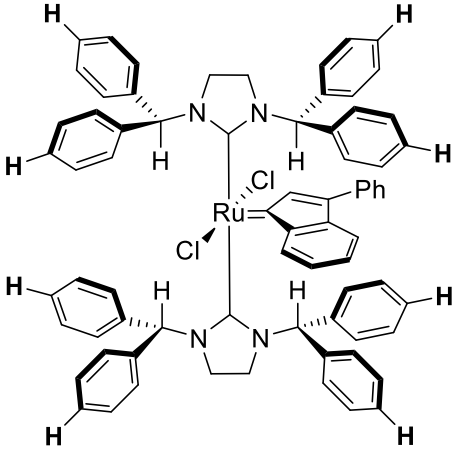
HRMS (ESI) : m/z : M^+ ($C_{33}H_{35}N_2O_4$) calc.: 523.25913; found: 523.2595 (1 ppm).

Synthesis of bis-carbene complexes

General procedure for synthesis of bis-carbene complexes:

In the glovebox, to a suspension of imidazolinium salt (4 equiv) in toluene (1 mL/mmol of Ru) was added a 0.5 M solution of potassium bis(trimethylsilyl)amide in toluene (4 equiv). After 5 minutes of stirring, dichloro-(3-phenyl-1H-inden-1-ylidene)bis(tricyclohexylphosphine)ruthenium(II) or M1 (1 equiv) was added and the mixture was stirred at 60 °C outside of the glovebox during 3 h. The crude mixture was purified by flash chromatography using a mixture of Pentane/Et_2O solvent (9/1 to 7/3).

Dichloro-bis(1,3-dibenzhydryl-4,5-dihydroimidazol-2-ylidene)-(3-phenyl-1H-inden-1-ylidene) ruthenium(II) (Ru-11a)



$C_{73}H_{62}Cl_2N_4Ru$
1167,31 g.mol^{-1}

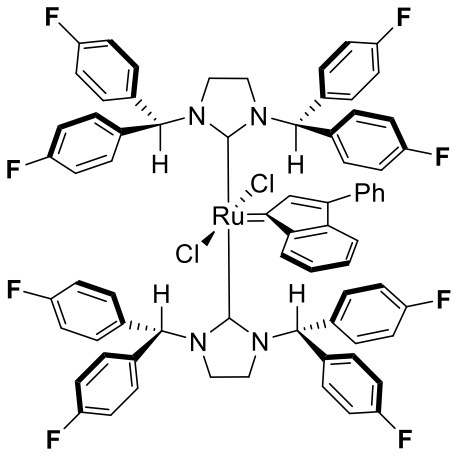
Following the general procedure for the synthesis of bis-carbene complexes with **3a** (301.7 mg, 0.61 mmol), KHMDS solution (1.23 mL, 0.61 mmol) and M1 (141.3 mg, 0.15 mmol), the desired product was obtained as a red solid (132 mg, 73% yield).

^{1}H NMR (400 MHz, *$CDCl_3$*): δ ppm) 8.66 (dd, *J* = 7.5, 1.2 Hz, 1H), 7.77 (s, 2H), 7.41-7.32 (m, 3H), 7.31-7.18 (m, 22H), 7.17-7.12 (m, 2H), 7.09-6.93 (m, 16H), 6.91-6.83 (m, 1H), 6.84-6.77 (m, 4H), 6.77-6.72 (m, 1H), 5.85 (s, 2H), 3.51-3.34 (m, 4H), 3.28-3.17 (m, 4H)

^{13}C NMR (101 MHz, *$CDCl_3$*): δ ppm) 296.5, 214.4, 142.3, 140.8, 140.2, 140.0, 139.4, 138.6,138.5, 138.2, 135.9, 130.3, 130.2, 129.3, 129.2, 128.8, 128.2, 127.9, 127.8, 127.6 127.5, 127.3, 126.9, 126.7, 117.2, 65.5, 64.4, 46.3, 45.6

HRMS (ESI): m/z: M^+ ($C_{73}H_{62}N_4{}^{35}Cl_2{}^{102}Ru$) calc.: 1166.33895; found: 1166.3400 (1 ppm).

Dichloro-bis(1,3-[di-(4-fluorophenyl)methyl]-4,5-dihydroimidazol-2-ylidene)-(3-phenyl-1H-inden-1-ylidene) ruthenium(II) (Ru-11b)



$C_{73}H_{54}Cl_2F_8N_4Ru$
1311,22 g.mol^{-1}

Following the general procedure for the synthesis of bis-carbene complexes with **3b** (104.3 mg, 0.18 mmol), KHMDS solution (0.36 mL, 1.18 mmol) and M1 (39.1 mg, 0.04 mmol), the desired product was obtained as a red solid (48.5 mg, 88% yield).

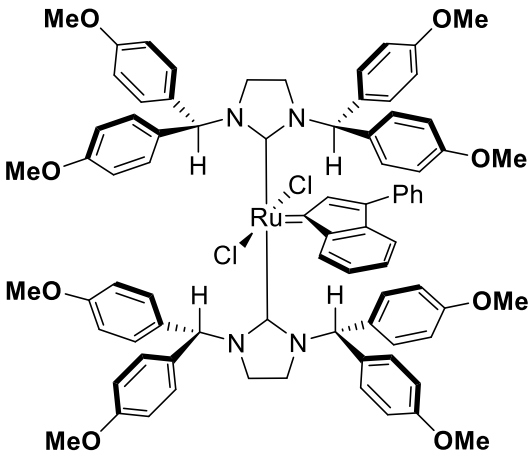
^{1}H NMR (400 MHz, *CDCl$_3$*): δ ppm) 8.54 (dd, *J* = 7.5, 1.1 Hz, 1H), 7.58 (s, 2H), 7.46-7.41 (m, 1H), 7.32-7.28 (m, 2H), 7.25-7.12 (m, 12H), 7.07 (td, *J* = 7.4, 1.2 Hz, 1H), 6.98-6.90 (m, 12H), 6.80 (dd, *J* = 7.4, 1.0 Hz, 1H), 6.73-6.63 (m, 12H), 5.72 (s, 2H), 3.40-3.35 (m, 4H), 3.20-3.15 (m, 4H)

^{13}C NMR (101 MHz, *CDCl$_3$*): δ ppm) 297.1, 214.6, 163.1, 163.0, 161.4 (d, *J* = 248.3 Hz), 160.7, 160.6, 142.3, 141.3, 140.0, 138.1, 135.2, 135.1, 135.1, 134.5 (d, *J* = 3.0 Hz), 133.7 (d, *J* = 3.4 Hz), 133.6 (d, *J* = 3.2 Hz), 131.8 (d, *J* = 7.1 Hz), 131.7 (d, *J* = 7.2 Hz), 130.7 (d, *J* = 2.8 Hz), 130.6 (d, *J* = 2.6 Hz), 129.5, 129.2, 129.0, 128.7, 128.4, 126.9, 117.6, 115.1, 115.0, 114.9, 114.8, 114.7, 114.6, 64.4, 63.3, 46.0, 45.3

^{19}F NMR (376 MHz, *CDCl$_3$*): δ ppm) -114.3, -114.3, -115.1, -115.7

HRMS (ESI): m/z: M^+ ($C_{73}H_{54}N_4F_8{}^{35}Cl_2{}^{102}Ru$) calc.: 1310.26358; found: 1310.2648 (1 ppm)

Dichloro-bis(1,3-[di-(4-methoxyphenyl)methyl]-4,5-dihydroimidazol-2-ylidene)-(3-phenyl-1H-inden-1-ylidene) ruthenium(II) (Ru-11c)



$C_{81}H_{78}Cl_2N_4O_8Ru$
1407,51 g.mol^{-1}

Following the general procedure for the synthesis of bis-carbene complexes with **3c** (349.3 mg, 0.57 mmol), KHMDS solution (1.15 mL, 0.57 mmol) and M1 (132 mg, 0.14 mmol), the desired product was obtained as a red solid (50.4 mg, 25% yield).

^{1}H NMR (400 MHz, *CDCl$_3$*): δ ppm) 8.66 (d, *J* = 7.6 Hz, 1H), 7.50 (s, 2H), 7.38-7.27 (m, 4H), 7.19-7.07 (m, 10H), 6.99-6.93 (m, 1H), 6.92-6.81 (m, 6H), 6.79-6.69 (m, 12H), 6.55-6.48 (m, 8H), 5.70 (s, 2H), 3.79-3.77 (m, 12H), 3.71 (s, 6H), 3.57 (s, 6H), 3.43-3.37 (m, 4H), 3.23-3.10 (m, 4H)

^{13}C NMR (101 MHz, *CDCl$_3$*): δ ppm) 294.9, 214.1, 158.8, 158.3, 158.2, 142.8, 140.3, 139.6, 138.3, 136.1, 132.1, 131.8, 131.5, 130.8, 130.3, 129.1, 128.3, 128.2, 127.4, 127.1, 117.0, 113.2, 113.1, 113.0, 64.5, 63.4, 55.3, 55.2, 55.1, 55.0, 45.9, 45.2

HRMS (ESI): m/z: M^+ ($C_{81}H_{78}N_4O_8{}^{35}Cl_2{}^{102}Ru$) calc.: 1406.42347; found: 1406.4244 (1 ppm).

General procedure stability studies of synthesised Ru-complexes

In a glovebox, a NMR tube was charged with Ru complex (0.005 mmol), anthracene (0.005 mmol) as the internal standard, and toluene-d_8 (0.5 mL). The tube was sealed and shaken vigorously. A ^{1}H NMR spectrum was recorded for reference at time = 0. The tube was then placed in an oil bath set at 60 °C. Degradation was monitored by observing the disappearance of the most downfield signal ($\delta = 8.66$ ppm for **Ru-11a**, $\delta = 8.54$ ppm for **Ru-11b**, $\delta = 8.66$ ppm for **Ru-11c**) by ^{1}H NMR.

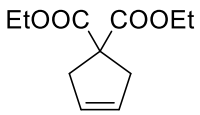
General Procedure for kinetic studies

Diethyl allyl(methallyl)-malonate (51 mg, 0.2 mmol), mesitylene (9.2 µL, 0.066 mmol) as the internal standard and toluene (1.8 mL) were added in a Schlenk tube under argon. The solution was equilibrated at 80 °C before the catalyst addition (0.2 mL of a 0.01 M solution of catalyst, 1 mol%). Aliquots were taken and the conversion was calculated from ^{1}H NMR spectra by comparing the characteristic signal for allylic proton to the internal standard.

Metathesis Reactions

General Procedure for Metathesis Reactions: To a Schlenk apparatus was filled the substrate (0.3 mmol) and toluene (3 mL, c = 0.1 M) under argon, the precatalyst (0.003 mmol) was added. The media was heated at 80 °C and the progress of the reaction was monitored by TLC until complete conversion or until the catalyst death was observed. The solvent was removed under vacuum and trimethoxybenzene (0.1 mmol) was added in the mixture as internal standard to determine the conversion by ^{1}H NMR. Then the crude residue was purified by column chromatography to yield the pure product.

Diethyl cyclopent-3-ene-1,1-dicarboxylate (7)



$C_{11}H_{16}O_4$
212,25 g.mol^{-1}

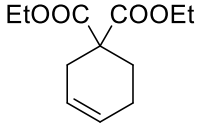
Following the general procedure for metathesis reactions with the desired precatalyst (0.003 mmol) and diethyl 2,2-diallylmalonate (72.1 mg, 0.3 mmol), the desired product was obtained after purification on silica gel (Pentane/Et_2O: 9/1) as a colorless oil (49.2 mg, 77% yield with **Ru-11a** after 5 h reaction and 53.2 mg, 83% yield with **Ru-11b** after 5 h reaction).

^{1}H NMR (400 MHz, *$CDCl_3$*): δ ppm) 5.63-5.57 (m, 2H), 4.19 (q, *J* = 7.1 Hz, 4H), 3.01 (s, 4H), 1.24 (t, *J* = 7.1 Hz, 6H).

^{13}C NMR (101 MHz, *$CDCl_3$*): δ ppm) 172.4, 127.9, 61.7, 59.0, 41.0, 14.2.

Analytical data for this compound were consistent with the previously reported data[1]

Diethyl cyclohex-3-ene-1,1-dicarboxylate (9)



$C_{12}H_{18}O_4$
226,27 g.mol^{-1}

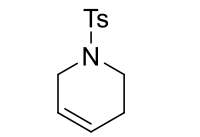
Following the general procedure for metathesis reactions with the desired precatalyst (0.003 mmol) and diethyl 2-allyl-2-(but-3-en-1-yl)malonate (76.3 mg, 0.3 mmol), the desired product was obtained after purification on silica gel (Pentane/Et_2O: 9/1) as a colorless oil (60.3 mg, 89% yield with **Ru-11a** after 3 h reaction and 62.1 mg, 97% yield with **Ru-11b** after 3 h reaction).

^{1}H NMR (400 MHz, *$CDCl_3$*): δ ppm) 5.70-5.62 (m, 2H), 4.24-4.12 (m, 4H), 2.57-2.52 (m, 2H), 2.16-2.05 (m, 4H), 1.23 (t, *J* = 7.1 Hz, 6H).

^{13}C NMR (101 MHz, *$CDCl_3$*): δ ppm) 171.6, 126.1, 124.0, 61.3, 52.9, 30.4, 27.3, 22.3, 14.1.

Analytical data for this compound were consistent with the previously reported data[1]

1-tosyl-1,2,3,6-tetrahydropyridine (11)



$C_{12}H_{15}NO_2S$
237,32 g.mol^{-1}

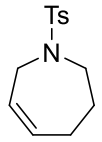
Following the general procedure for metathesis reactions with the desired precatalyst (0.003 mmol) and *N*-allyl-*N*-(but-3-en-1-yl)-4-methylbenzenesulfonamide (79.6 mg, 0.3 mmol), the desired product was obtained after purification on silica gel (Pentane/Et_2O: 8/2) as a white solid (58.2 mg, 82% yield with **Ru-11a** after 5 h reaction and 55.0 mg, 77% yield with **Ru-11b** after 5 h reaction).

^{1}H NMR (400 MHz, *$CDCl_3$*): δ ppm) 7.71-7.64 (m, 2H), 7.35-7.29 (m, 2H), 5.79-5.72 (m, 1H), 5.66-5.57 (m, 1H), 3.57 (dt, *J* = 5.2, 2.8 Hz, 2H), 3.17 (t, *J* = 5.7 Hz, 2H), 2.43 (s, 3H), 2.26-2.17 (m, 2H).

^{13}C NMR (101 MHz, *$CDCl_3$*): δ ppm) 143.5, 133.4, 129.6, 127.7, 125.1, 122.8, 44.8, 42.6, 25.3, 21.5.

Analytical data for this compound were consistent with the previously reported data[1]

1-tosyl-2,3,4,7-tetrahydro-1H-azepine (13)



$C_{13}H_{17}NO_2S$
251,34 g.mol^{-1}

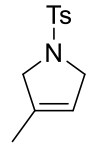
Following the general procedure for metathesis reactions with the desired precatalyst (0.003 mmol) and *N*-allyl-4-methyl-*N*-(pent-4-en-1-yl)benzenesulfonamide (83.8 mg, 0.3 mmol), the desired product was obtained after purification on silica gel (Pentane/Et_2O: 8/2) as a white solid (61.0 mg, 86% yield with **Ru-11a** after 5 h reaction and 65.3 mg, 92% yield with **Ru-11b** after 4 h reaction).

^{1}H NMR (400 MHz, *CDCl$_3$*): δ ppm) 7.72-7.62 (m, 2H), 7.35-7.26 (m, 2H), 5.82-5.71 (m, 1H), 5.69-5.59 (m, 1H), 3.84-3.80 (m, 2H), 3.38-3.34 (m, 2H), 2.41 (s, 3H), 2.22-2.13 (m, 2H), 1.83-1.74 (m, 2H).

^{13}C NMR (101 MHz, *CDCl$_3$*): δ ppm) 143.0, 136.3, 132.9, 129.5, 127.2, 126.6, 49.6, 46.4, 26.8, 21.5.

Analytical data for this compound were consistent with the previously reported data[1]

3-methyl-1-tosyl-2,5-dihydro-1H-pyrrole (15)



$C_{12}H_{15}NO_2S$
237,32 g.mol^{-1}

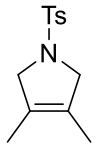
Following the general procedure for metathesis reactions with the desired precatalyst (0.003 mmol) and *N*-allyl-4-methyl-*N*-(2-methylallyl)benzenesulfonamide (79.6 mg, 0.3 mmol), the desired product was obtained after purification on silica gel (Pentane/Et_2O: 9/1) as a colorless oil (59.1 mg, 83% yield with **Ru-11a** after 5 h reaction and 61.2 mg, 86% yield with **Ru-11b** after 5 h reaction).

^{1}H NMR (400 MHz, *CDCl$_3$*): δ (ppm) 7.74-7.69 (m, 2H), 7.36-7.29 (m, 2H), 5.27-5.23 (m, 1H), 4.09-4.05 (m, 2H), 3.99-3.94 (m, 2H), 2.43 (s, 3H), 1.68-1.64 (m, 3H).

^{13}C NMR (101 MHz, *CDCl$_3$*): δ (ppm) 143.5, 135.2, 134.5, 129.9, 127.6, 119.2, 57.8, 55.3, 21.7, 14.2.

Analytical data for this compound were consistent with the previously reported data[1]

3-methyl-1-tosyl-2,5-dihydro-1H-pyrrole (17)



$C_{13}H_{17}NO_2S$
251,34 g.mol^{-1}

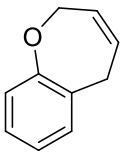
Following the general procedure for the metathesis reactions with the desired precatalyst (0.003 mmol) and 4-methyl-*N,N*-bis(2-methylallyl)benzenesulfonamide (83.8 mg, 0.3 mmol), the desired product was obtained as a after purification on silica gel (Pentane/Et_2O: 9/1) colorless oil (55.1 mg, 72% yield with **Ru-11a** after 5 h reaction and 52.3 mg, 69% yield with **Ru-11b** after 5 h reaction).

^{1}H NMR (400 MHz, *CDCl$_3$*): δ (ppm) 7.74-7.69 (m, 2H), 7.34-7.29 (m, 2H), 3.97 (s, 4H), 2.42 (s, 3H), 1.54 (s, 6H).

^{13}C NMR (101 MHz, *CDCl$_3$*): δ (ppm) 143.4, 134.4, 129.8, 127.6, 126.3, 59.0, 21.7, 11.3.

Analytical data for this compound were consistent with the previously reported data[1]

3-methyl-1-tosyl-2,5-dihydro-1H-pyrrole (19)



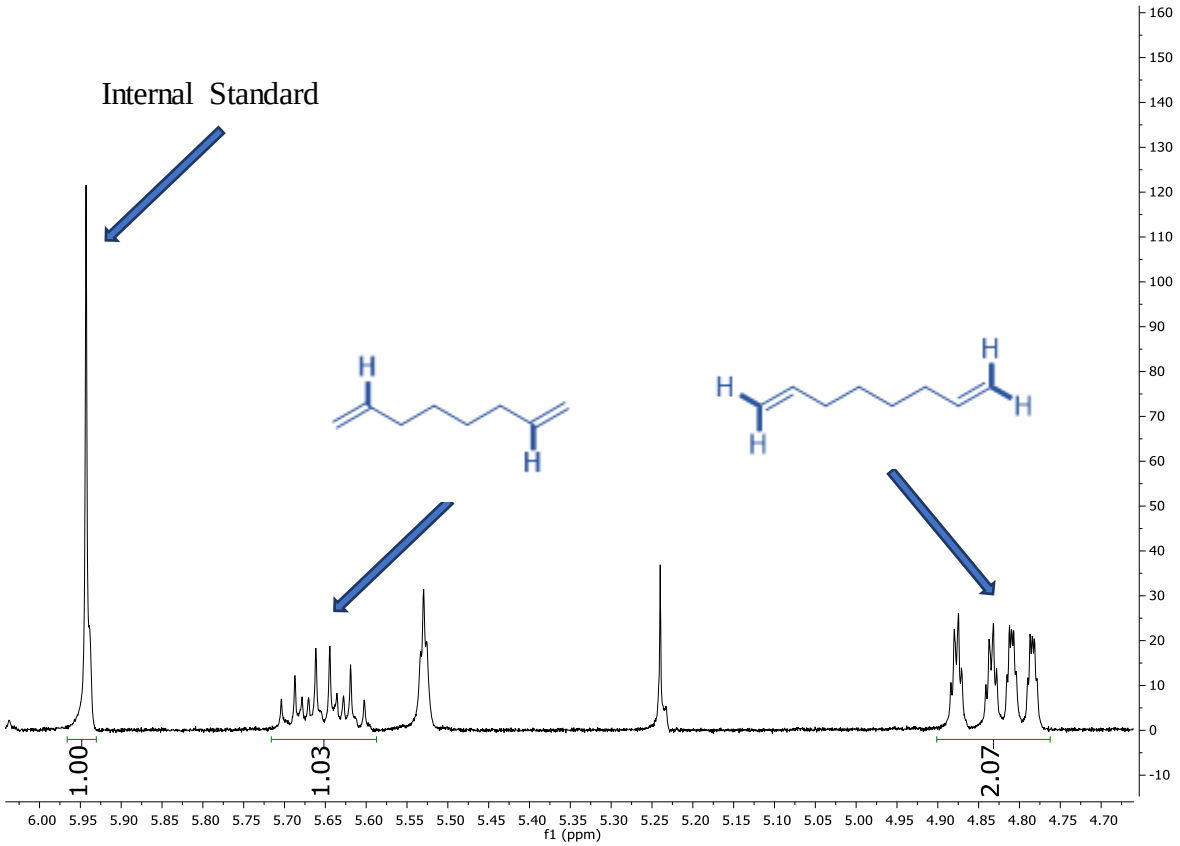
$C_{10}H_{10}O$
146,19 g.mol^{-1}

Following the general procedure for the metathesis reactions with the desired precatalyst (0.003 mmol) and 1-allyl-2-(allyloxy)benzene (52.2 mg, 0.3 mmol), the desired product was obtained after purification on silica gel (Pentane/Et_2O: 9/1) as a colorless oil (38.0 mg, 87% yield with **Ru-11a** after 5 h reaction and 39.0 mg, 88% yield with **Ru-11b** after 5 h reaction).
^{1}H NMR (400 MHz, *CDCl$_3$*): δ (ppm) 7.20 (ddd, *J* = 7.9, 7.3, 1.8 Hz, 1H), 7.13-7.00 (m, 3H), 5.86 (m, 1H), 5.51-5.45 (m, 1H), 4.62-4.58 (m, 2H), 3.52-3.48 (m, 2H).
^{13}C NMR (101 MHz, *CDCl$_3$*): δ (ppm) 158.9, 136.3, 128.9, 128.0, 127.5, 125.9, 124.2, 121.6, 71.4, 31.9.
Analytical data for this compound were consistent with the previously reported data[1]

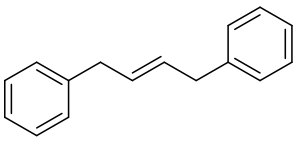
Cyclohexene (21)

C_6H_{10}
82,15 g.mol^{-1}

Following the general procedure at 60 °C instead of 80 °C for the metathesis reactions with the desired precatalyst (0.003 mmol) and 1,7-octadiene (52.3 mg, 0.3 mmol) in Toluene-*d$_8$*, conversion was determined by ^{1}H-NMR comparing internal standard peak with internal olefin peak on the starting material. (>98% with **Ru-11a** and with **Ru-11b** after 5 h reaction)
Example of ^{1}H-NMR spectra at 49% conversion :



1,4-diphenylbut-2-ene (23)



$C_{16}H_{16}$
208,30 g.mol^{-1}

Following the general procedure for the metathesis reactions with the desired precatalyst (0.003 mmol) and allylbenzene (70.9 mg, 0.6 mmol), the desired product was obtained after purification on silica gel (Pentane) as a white solid (33.7 mg, 55% yield with **Ru-11a** after 5 h reaction and 44.5 mg, 71% yield with **Ru-11b** after 5 h reaction).

^{1}H NMR (400 MHz, *$CDCl_3$*): δ (ppm) 7.33-7.27 (m, 4H), 7.25-7.17 (m, 6H), 5.68 (ddd, *J* = 5.3, 3.7, 1.6 Hz, 2H), 3.41-3.36 (m, 4H).

^{13}C NMR (101 MHz, *$CDCl_3$*): δ (ppm) 140.7, 130.4, 128.5, 128.4, 126.0, 39.0.

E/Z ratio: 9/1

Analytical data for this compound were consistent with the previously reported data[2]

References :

[1] Hervé Clavier, Steven P. Nolan, *Chem. Eur. J.* **2007**, *13,* 8029 – 8036

[2] Levente Ondi, Gergely M. Nagy, Janos B. Czirok, Agota Bucsai, Georg E. Frater, *Org. Process Res. Dev.* **2016**, *20*, 1709-1716

NMR spectra of synthesised compounds

NHC Precursors

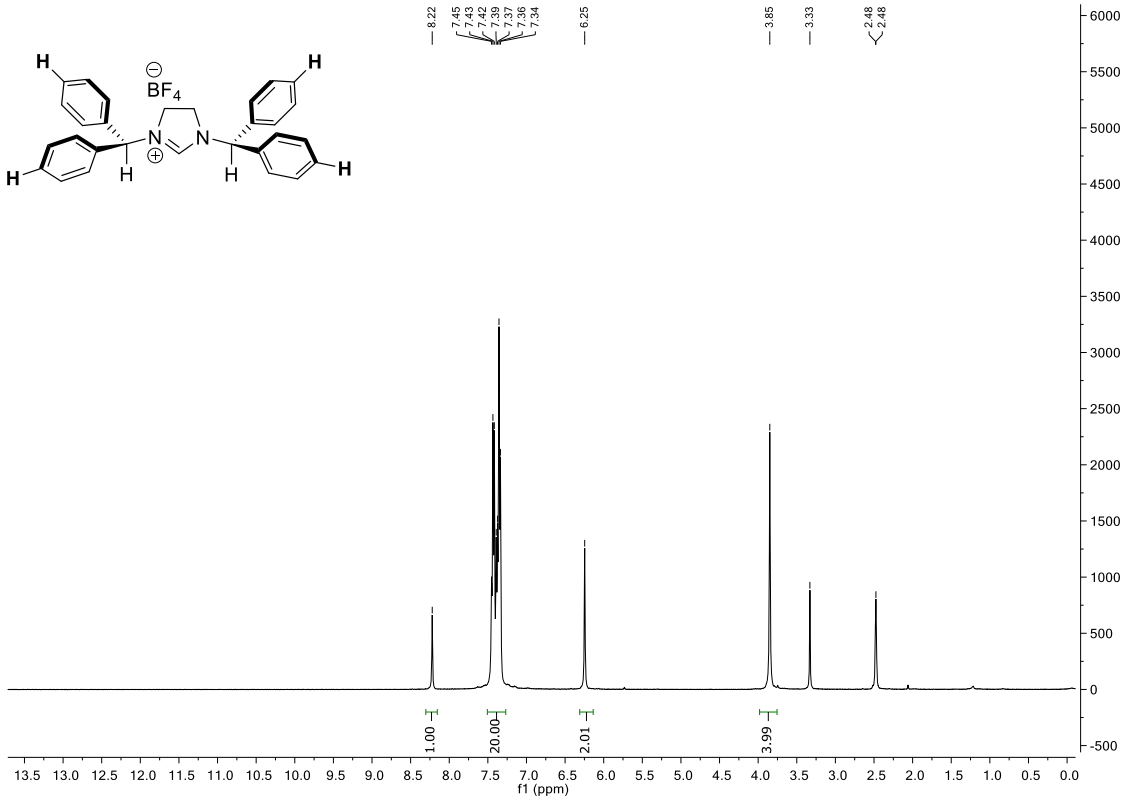


Figure S1: ^{1}H NMR (400 MHz, *DMSO-d_6*) of **3a**

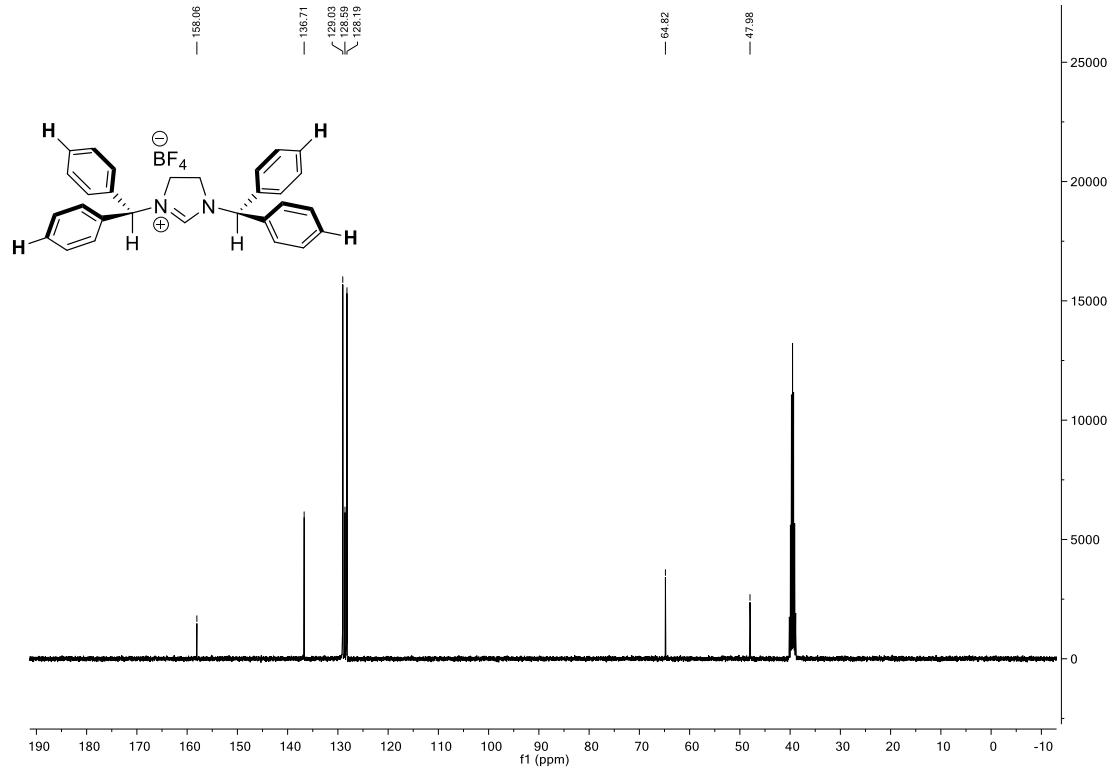


Figure S2: ^{13}C NMR (101 MHz, *DMSO-d_6*) of **3a**

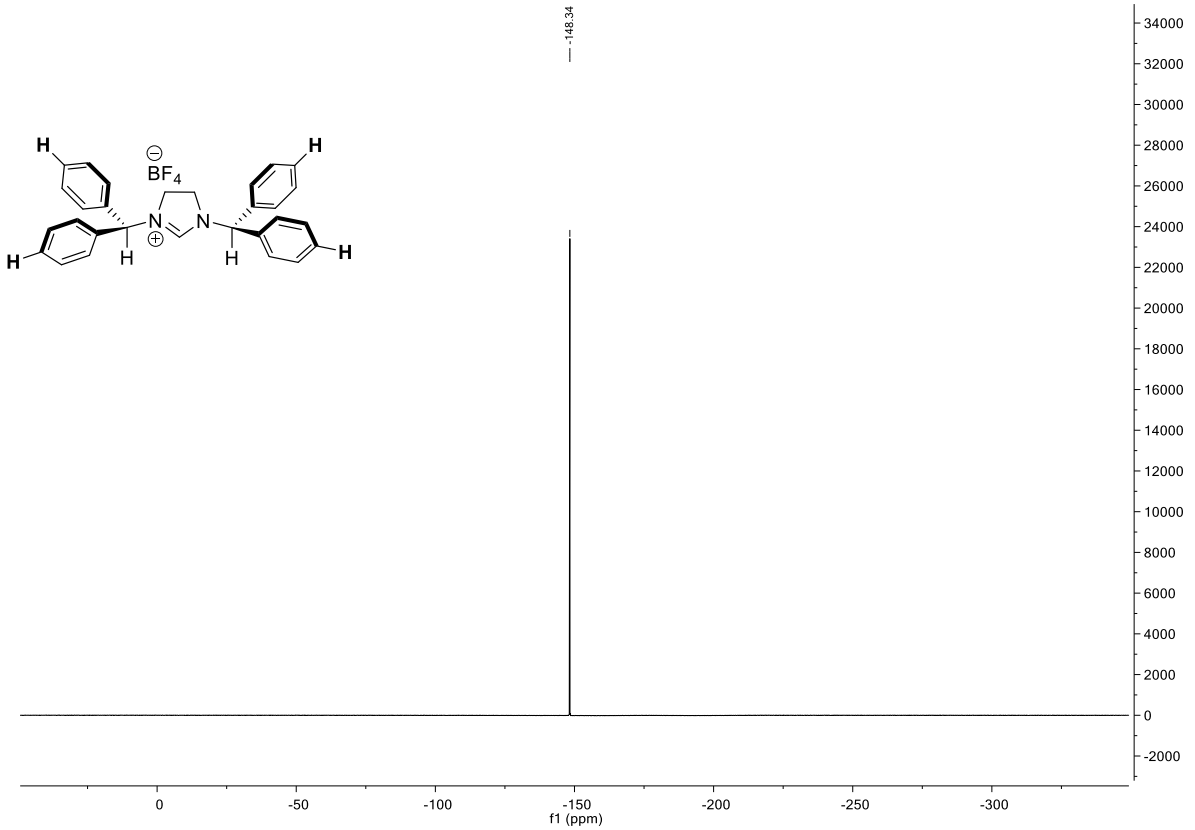


Figure S3: ^{19}F NMR (376 MHz, *DMSO-d*$_6$) of **3a**

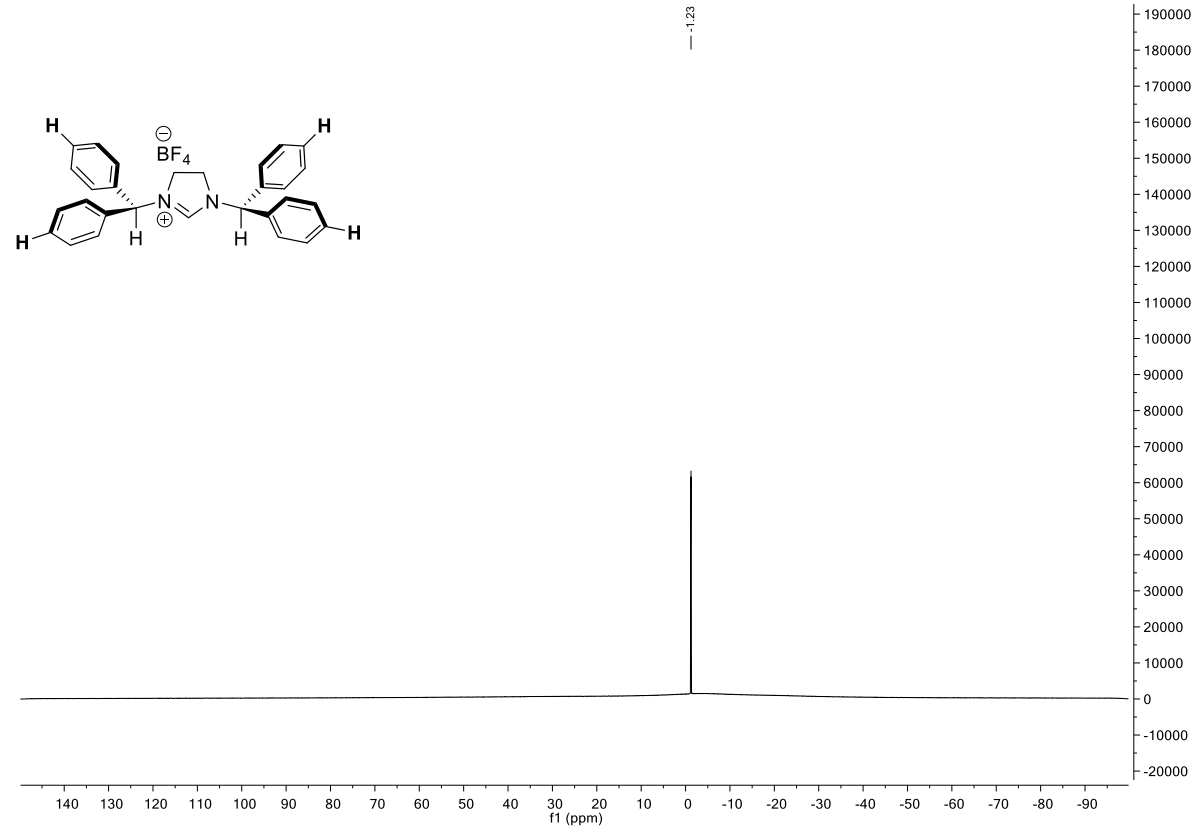


Figure S4: ^{11}B NMR (128 MHz, *DMSO-d*$_6$) of **3a**

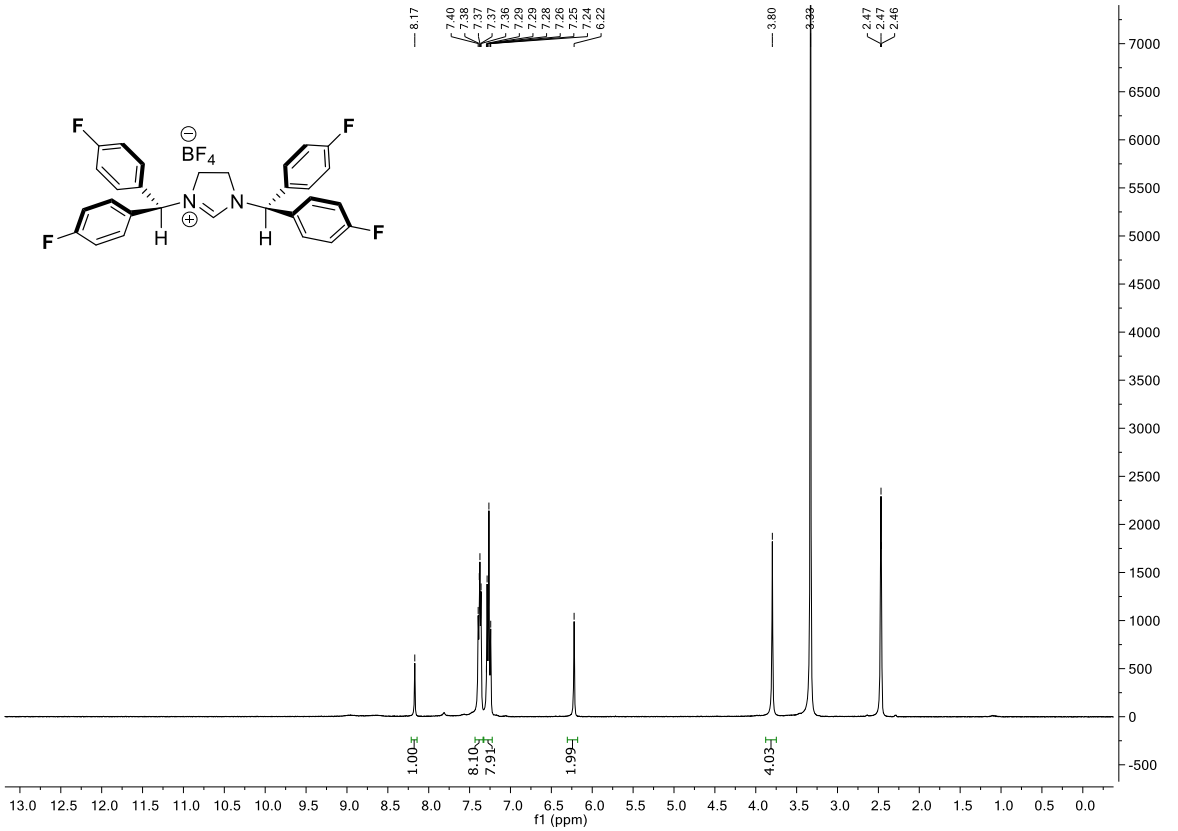


Figure S5: ^{1}H NMR (400 MHz, *DMSO-d*$_6$) of **3b**

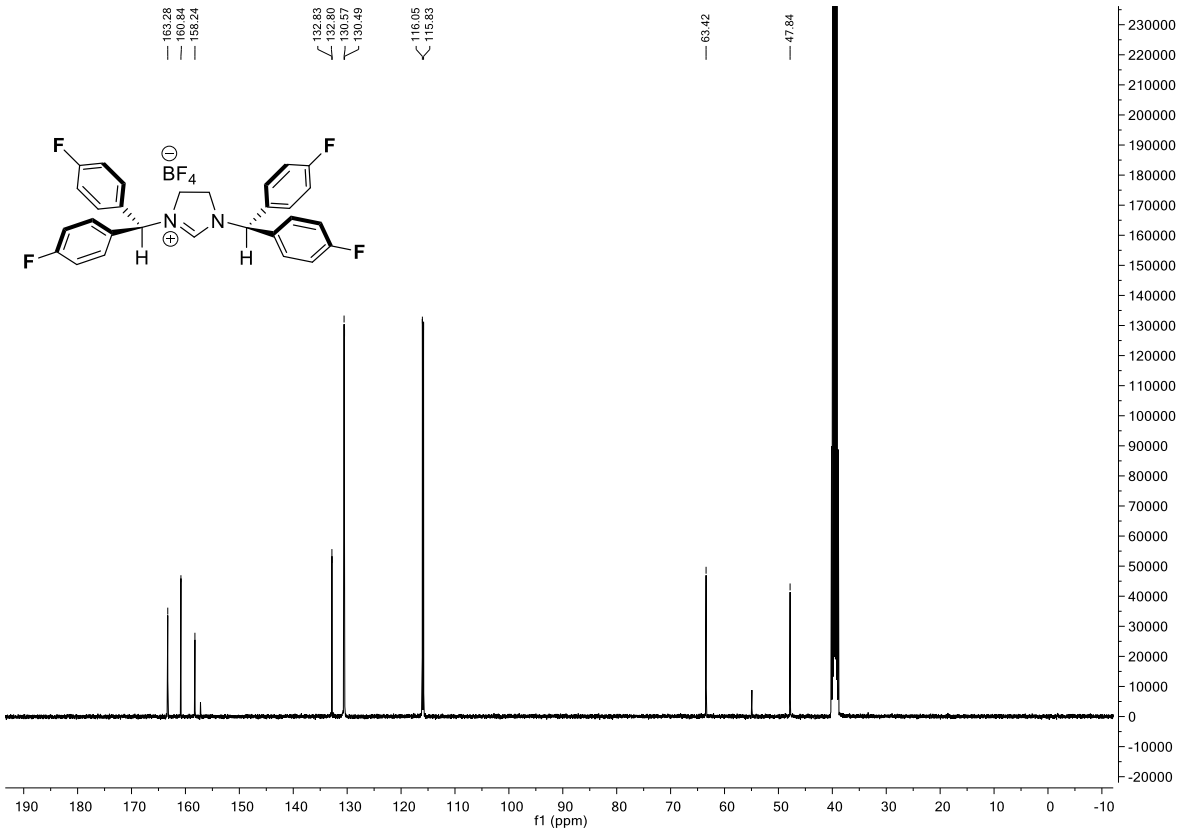


Figure S6: ^{13}C NMR (101 MHz, *DMSO-d*$_6$) of **3b**

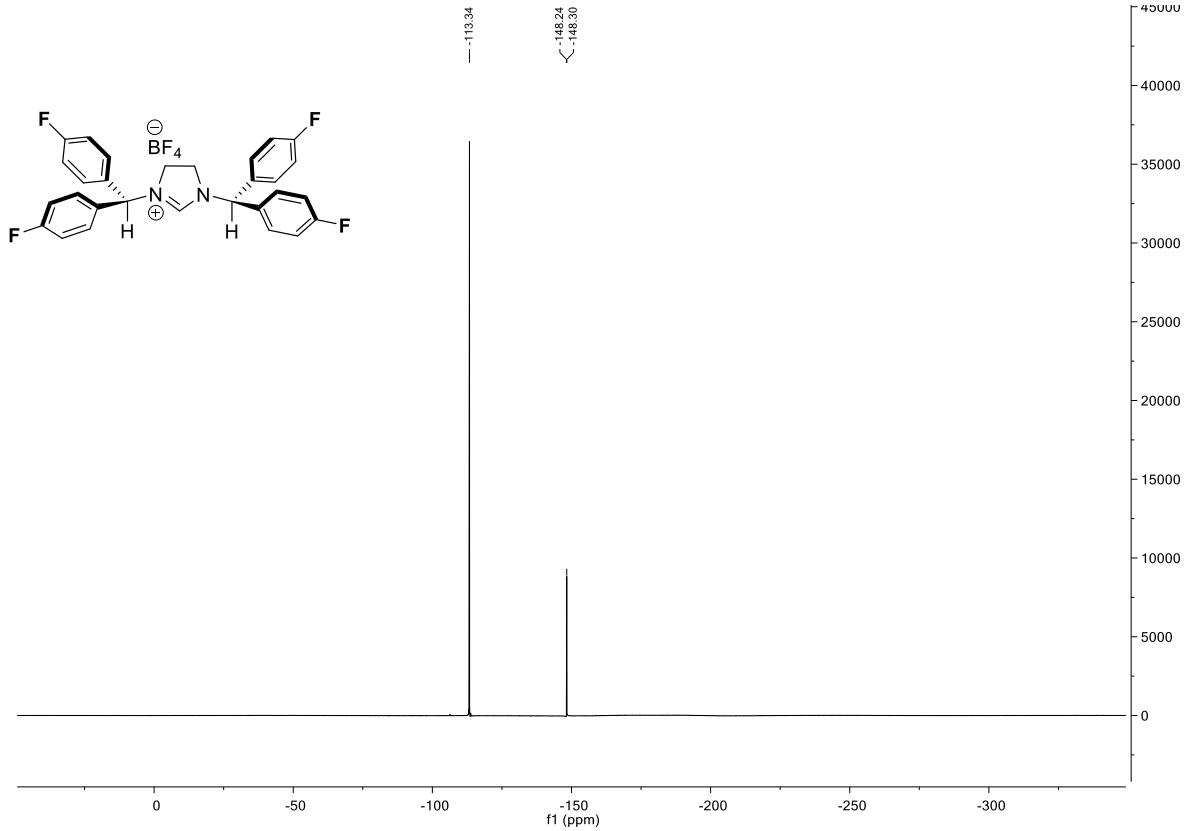


Figure S7: ^{19}F NMR (376 MHz, *DMSO-d*$_6$) of **3b**

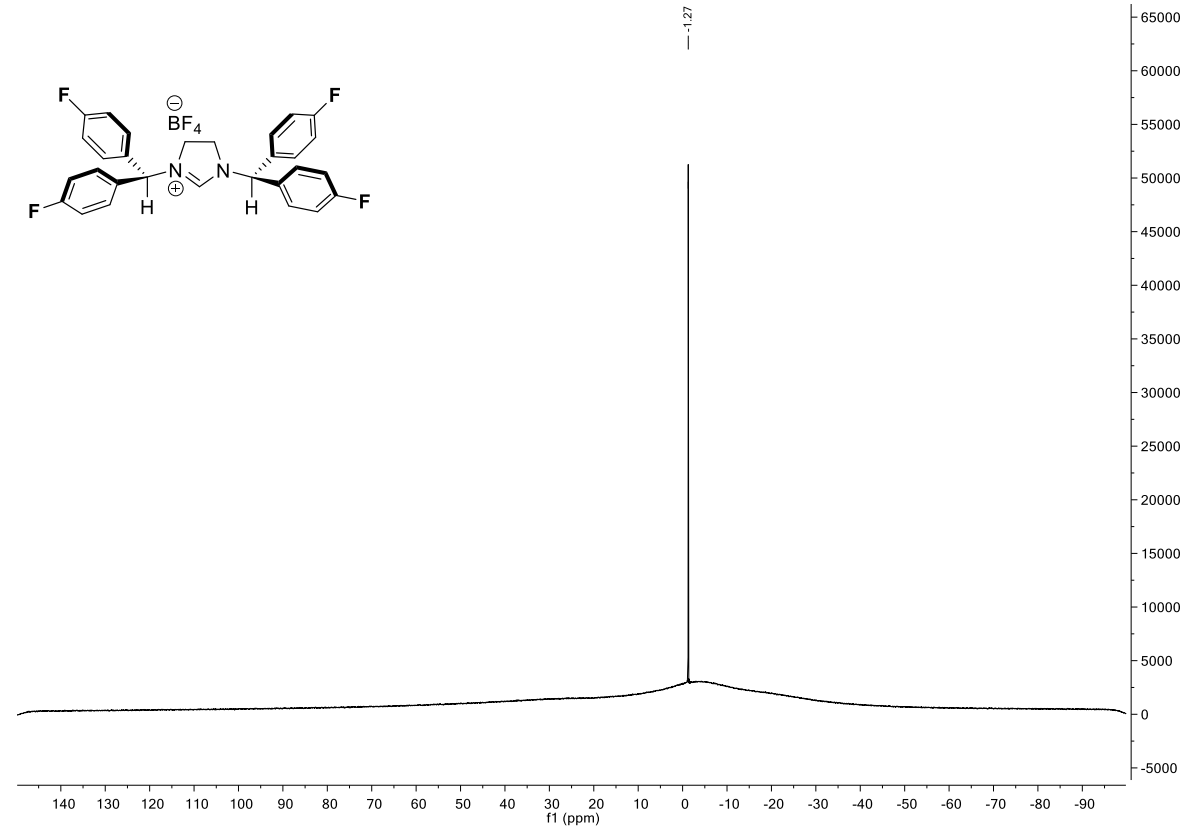


Figure S8: ^{11}B NMR (128 MHz, *DMSO-d*$_6$) of **3b**

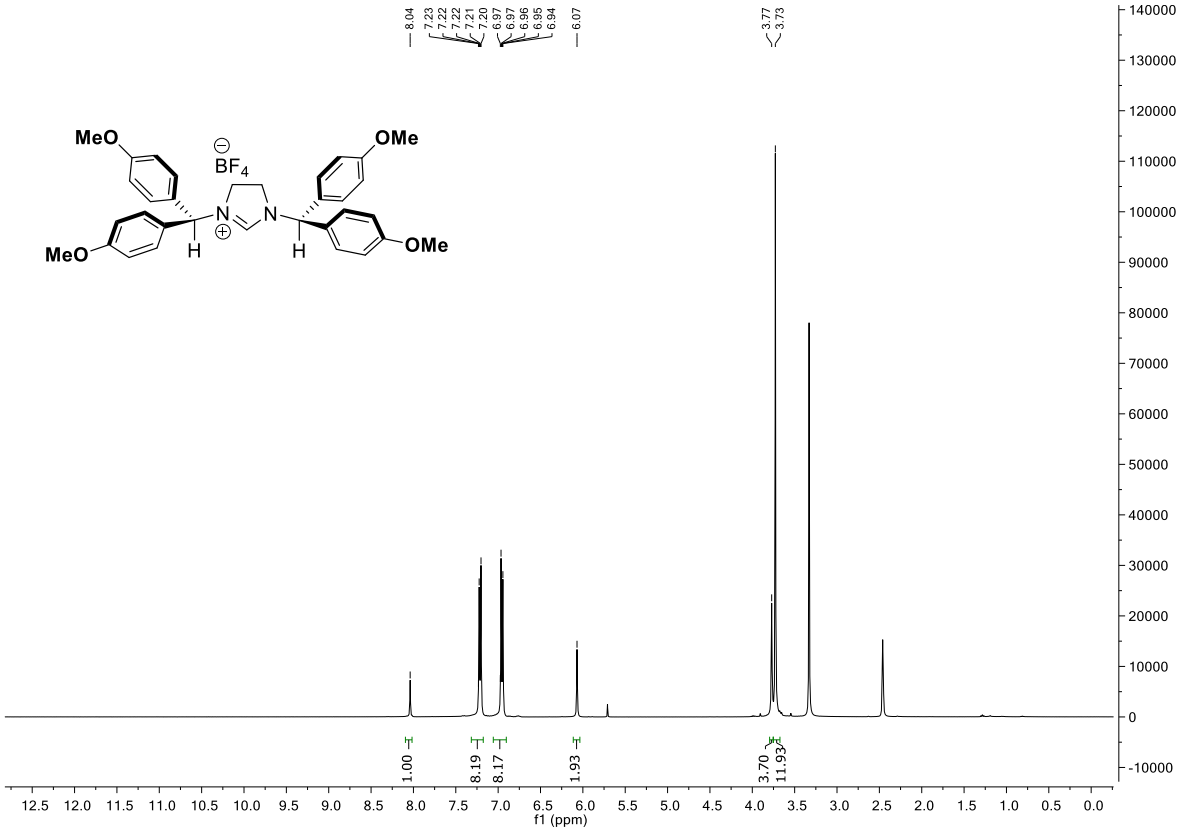


Figure S9: ^{1}H NMR (400 MHz, *DMSO-d*$_6$) of **3c**

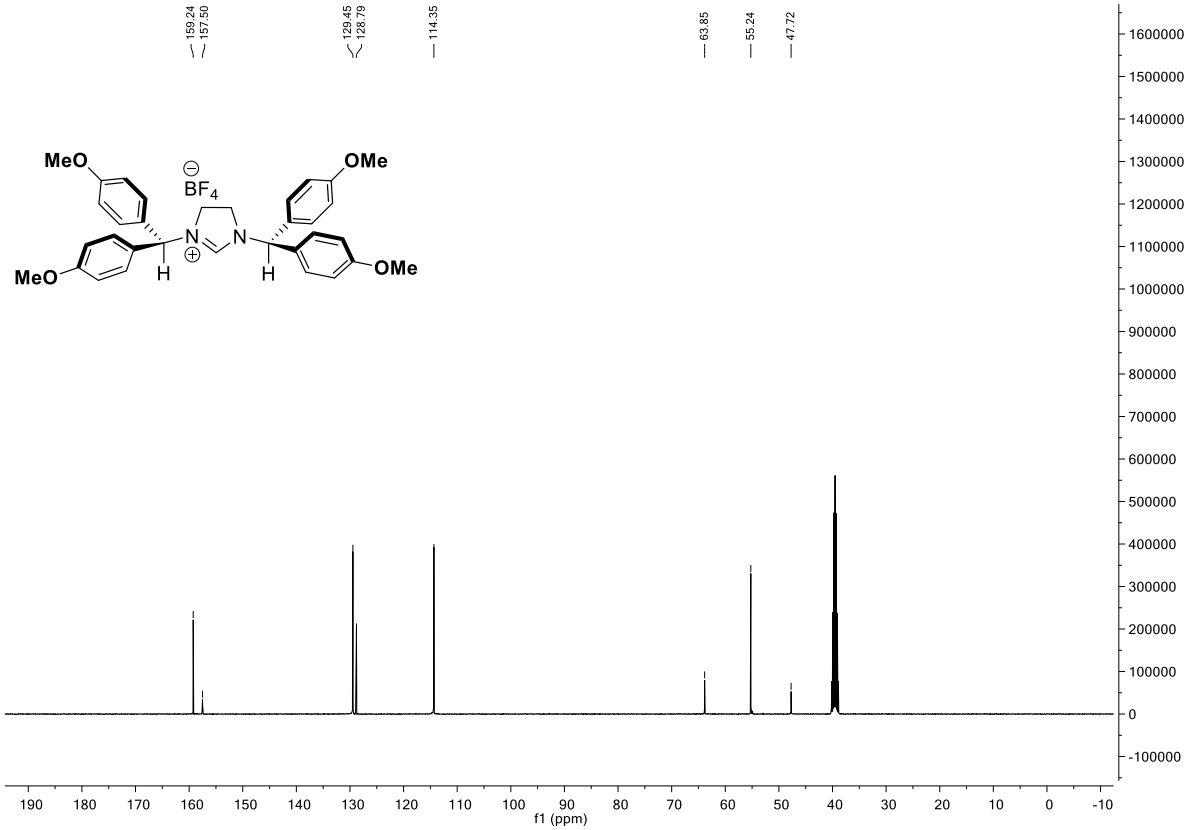


Figure S10: ^{13}C NMR (101 MHz, *DMSO-d*$_6$) of **3c**

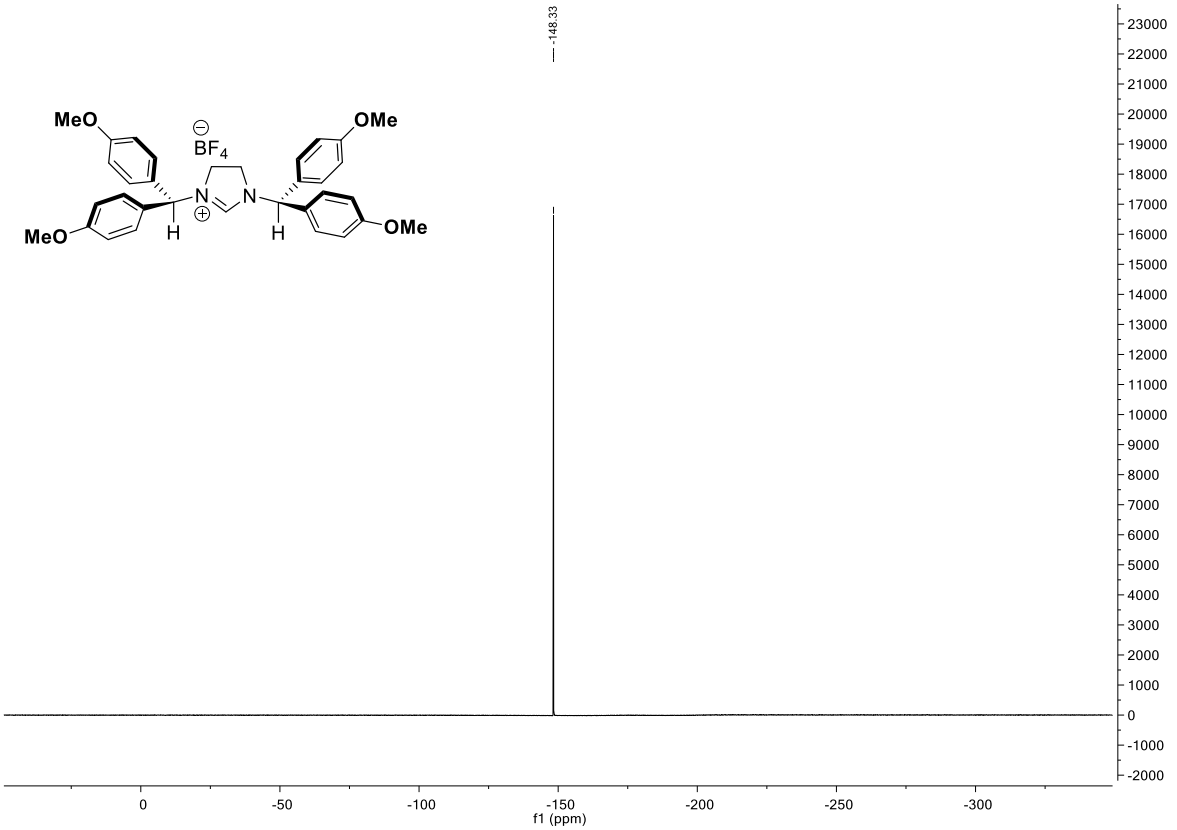


Figure S11: ^{19}F NMR (376 MHz, *DMSO-d*$_6$) of **3c**

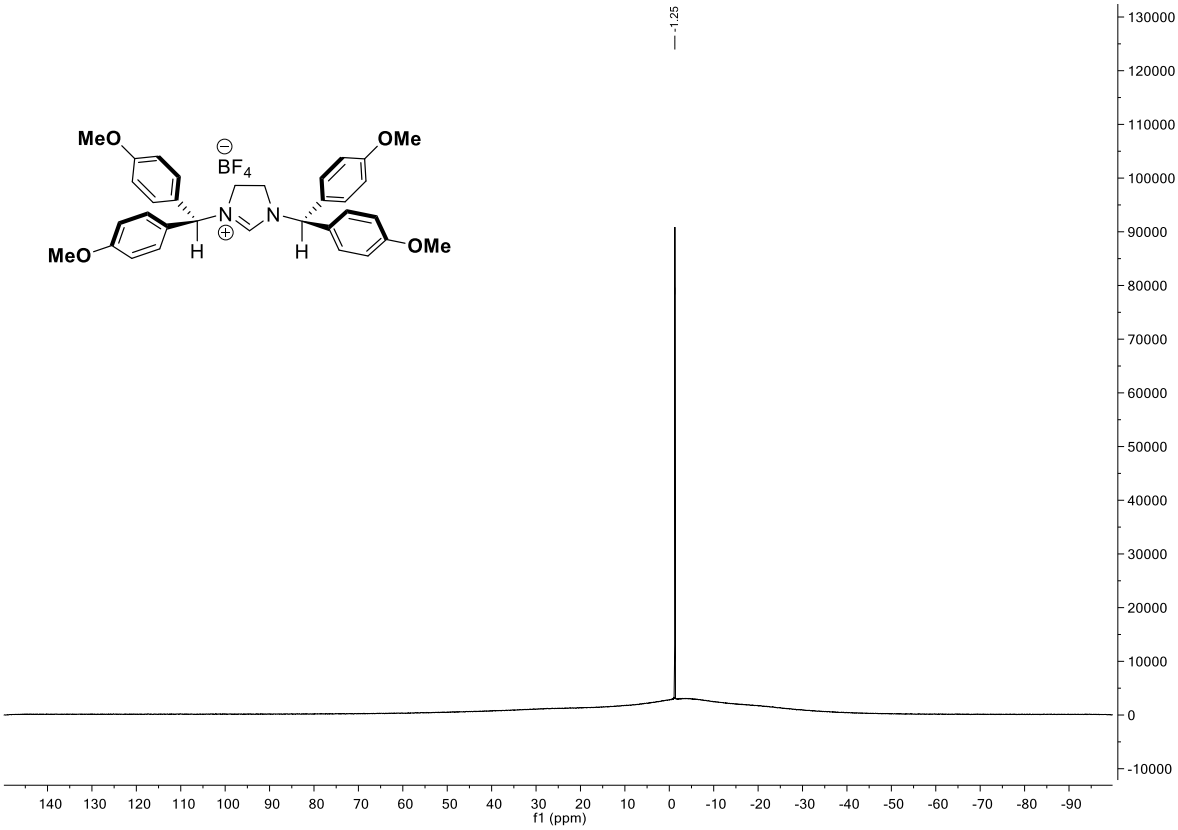


Figure S12: ^{11}B NMR (128 MHz, *DMSO-d*$_6$) of **3c**

Ruthenium Complexes

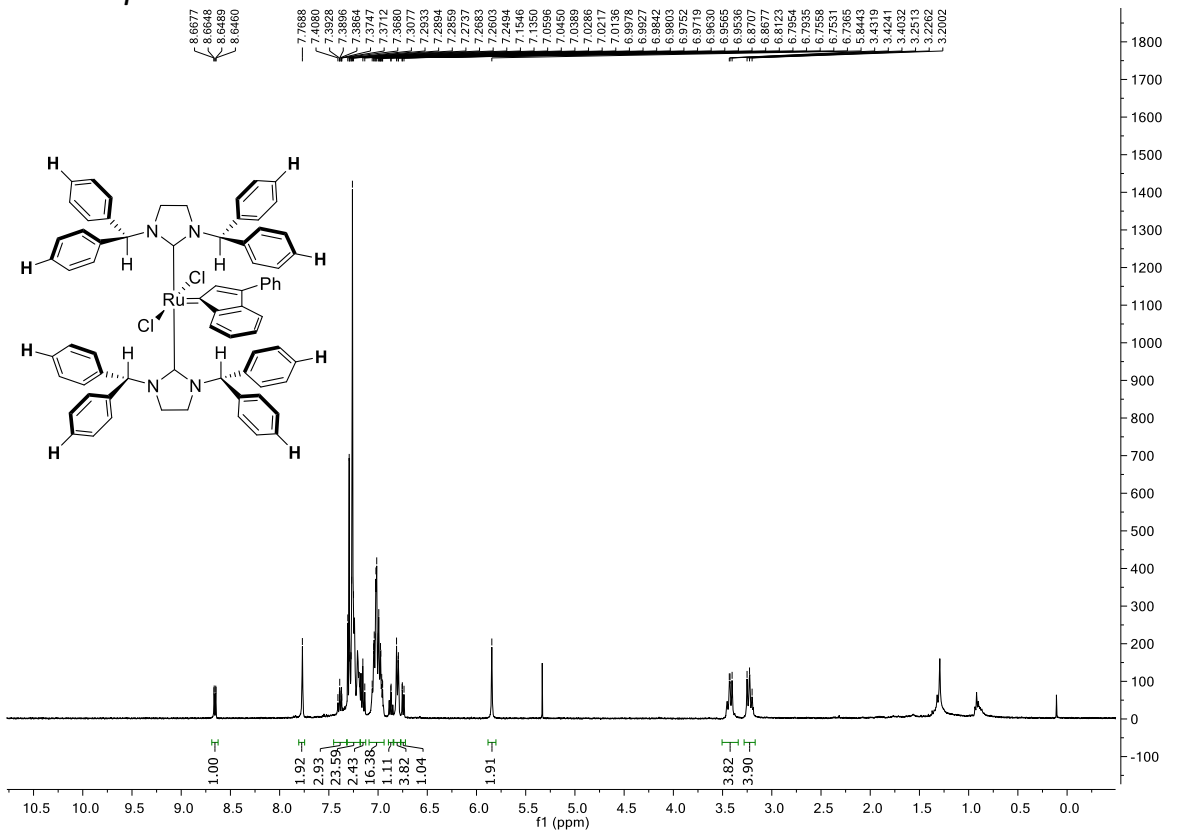


Figure S13: ^{1}H NMR (400 MHz, *CDCl*$_3$) of **Ru-11a**

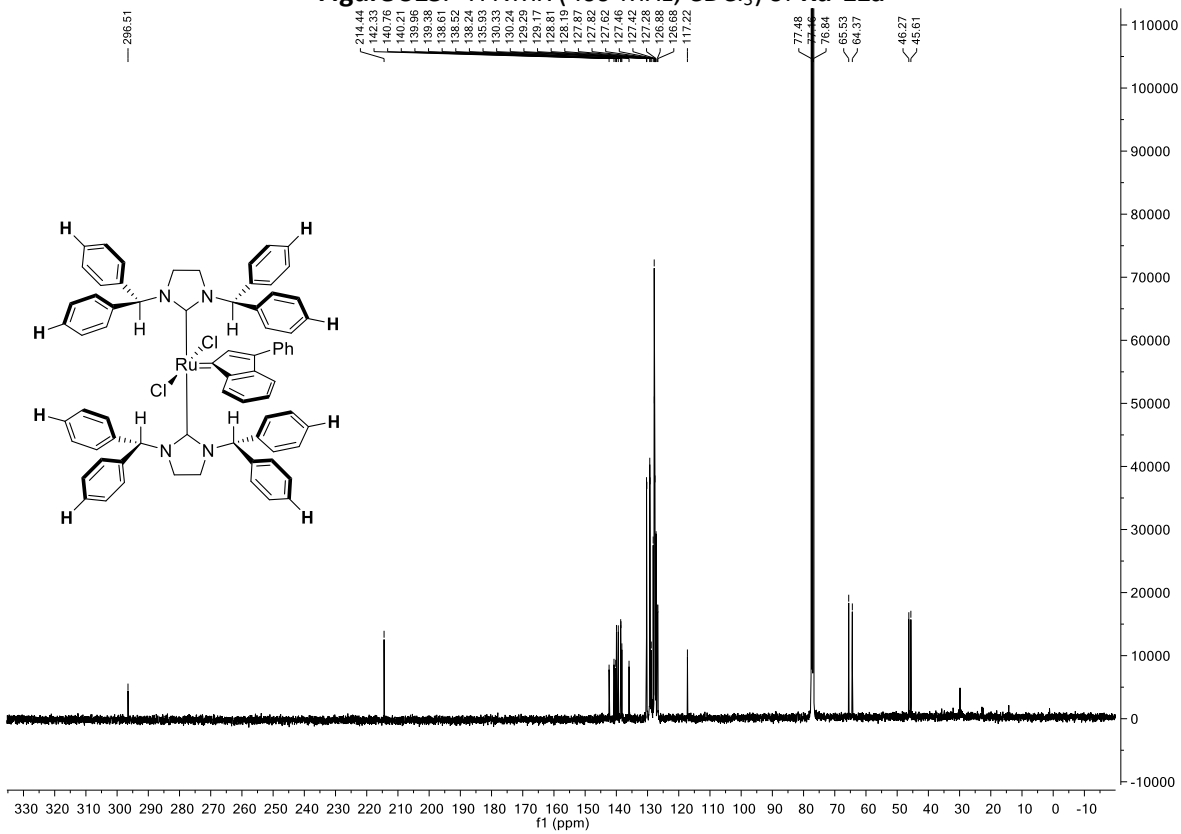


Figure S14: ^{13}C NMR (101 MHz, *CDCl*$_3$) of **Ru-11a**

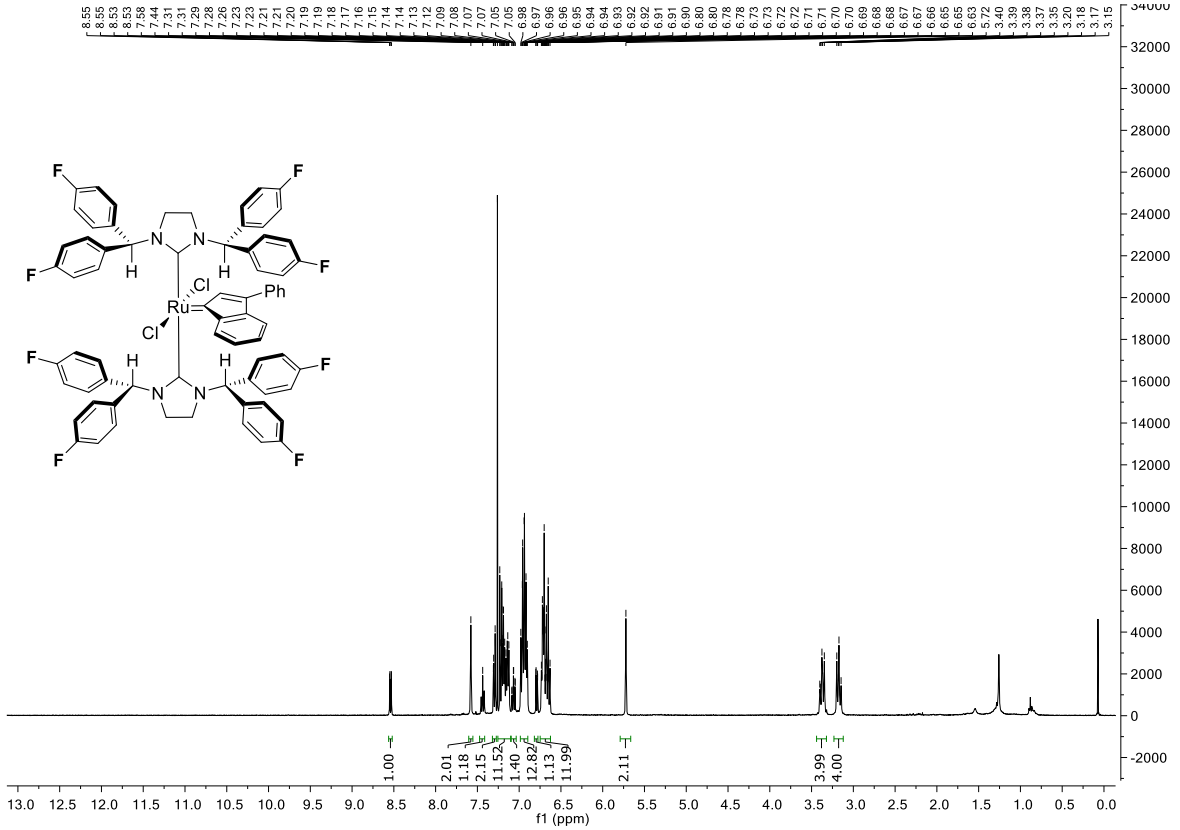


Figure S15: ^{1}H NMR (400 MHz, *CDCl$_3$*) of **Ru-11b**

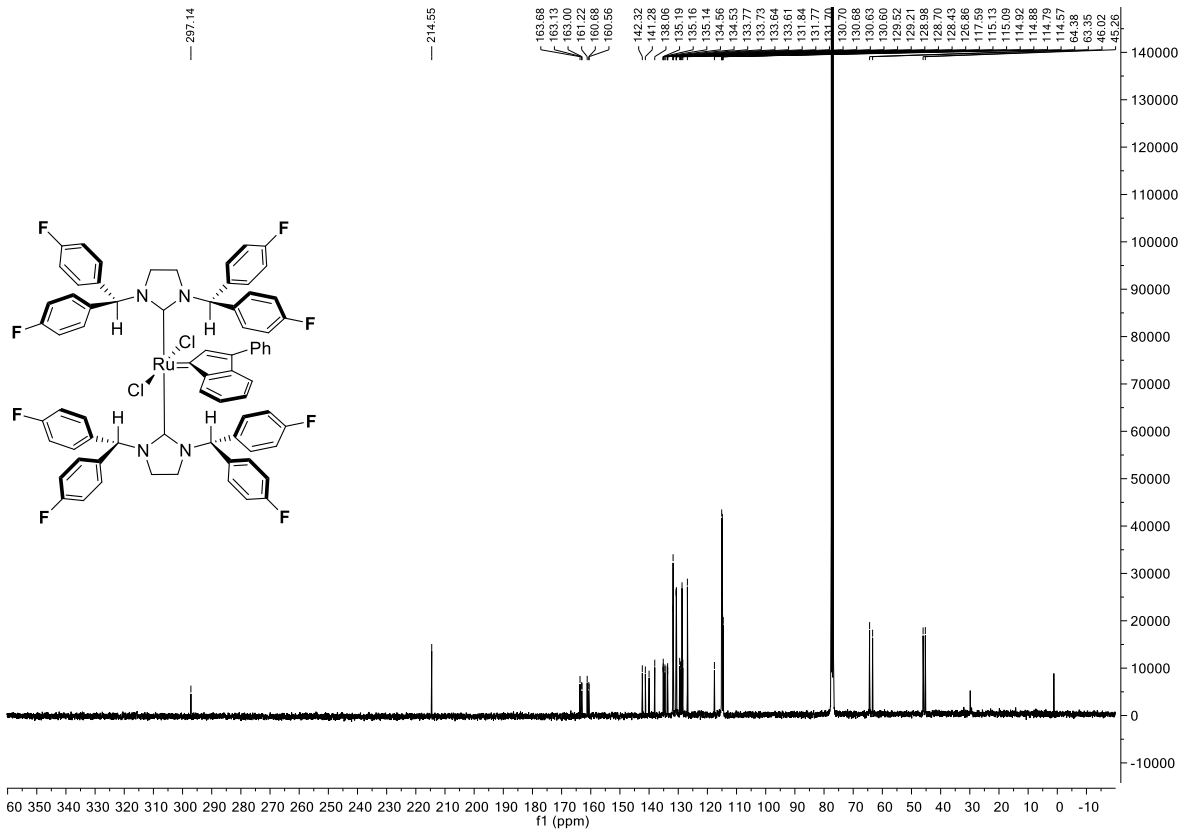


Figure S16: ^{13}C NMR (101 MHz, *CDCl$_3$*) of **Ru-11b**

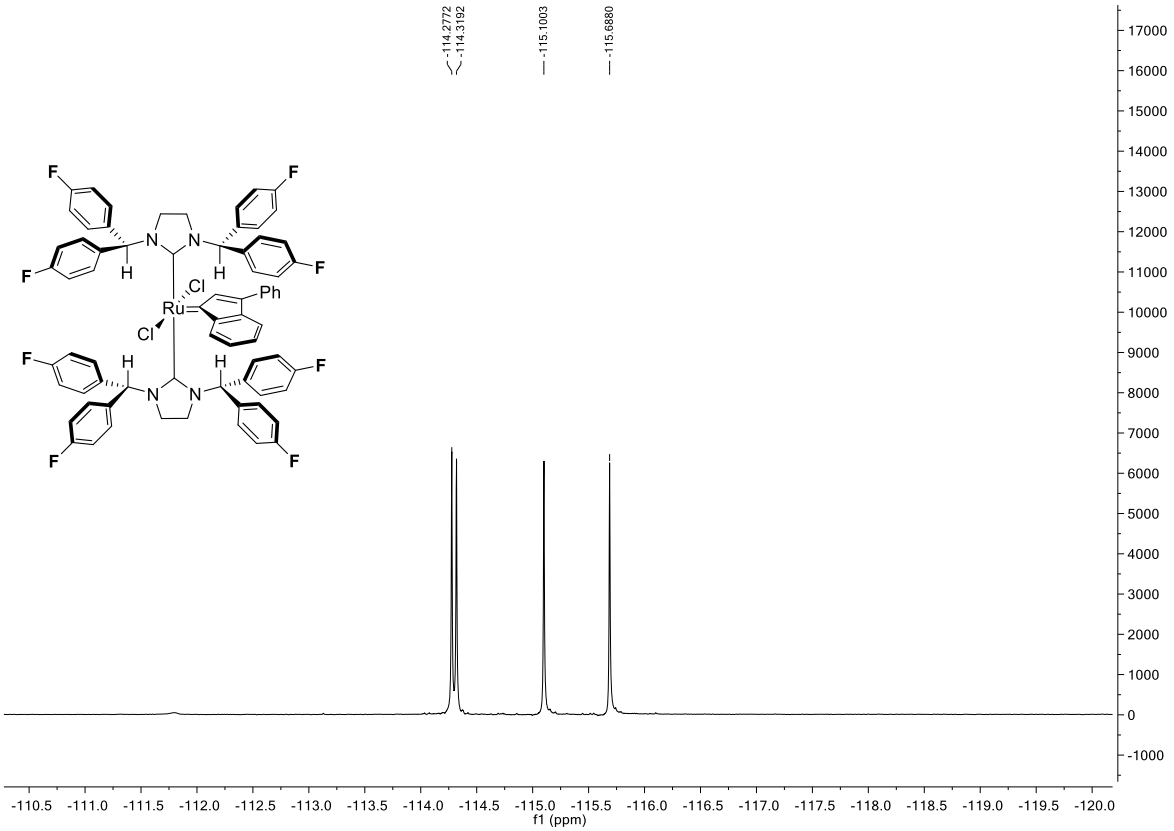


Figure S17: ^{19}F NMR (376 MHz, *CDCl*$_3$) of **Ru-11b**

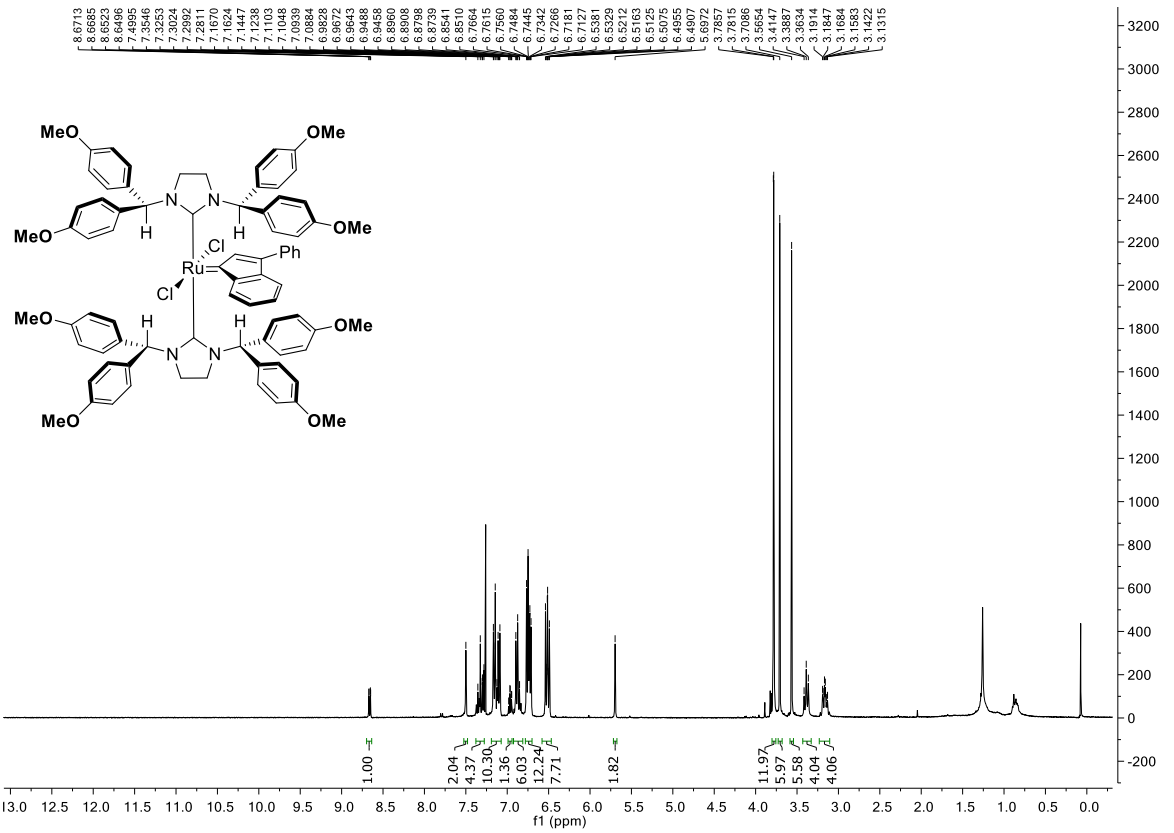


Figure S18: ^{1}H NMR (400 MHz, *CDCl*$_3$) of **Ru-11c**

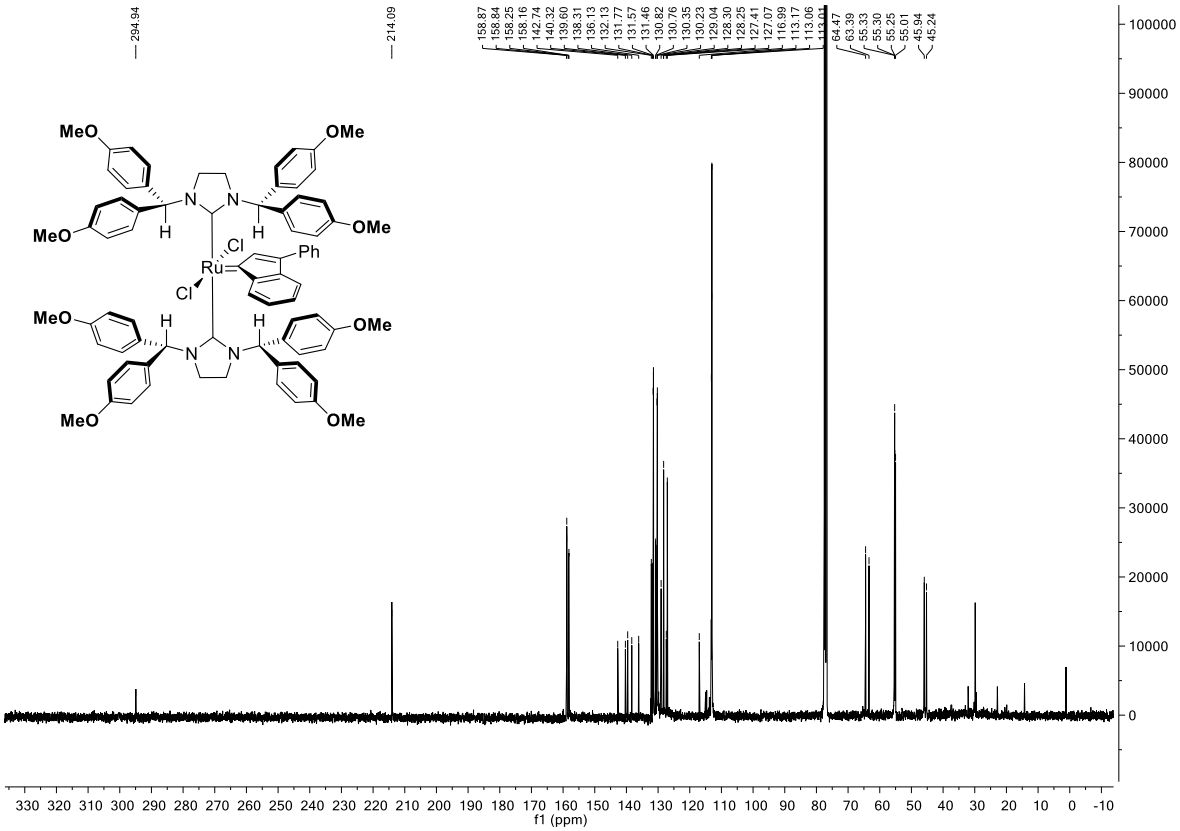


Figure S19: ^{13}C NMR (101 MHz, *CDCl$_3$*) of **Ru-11c**

Metathesis products

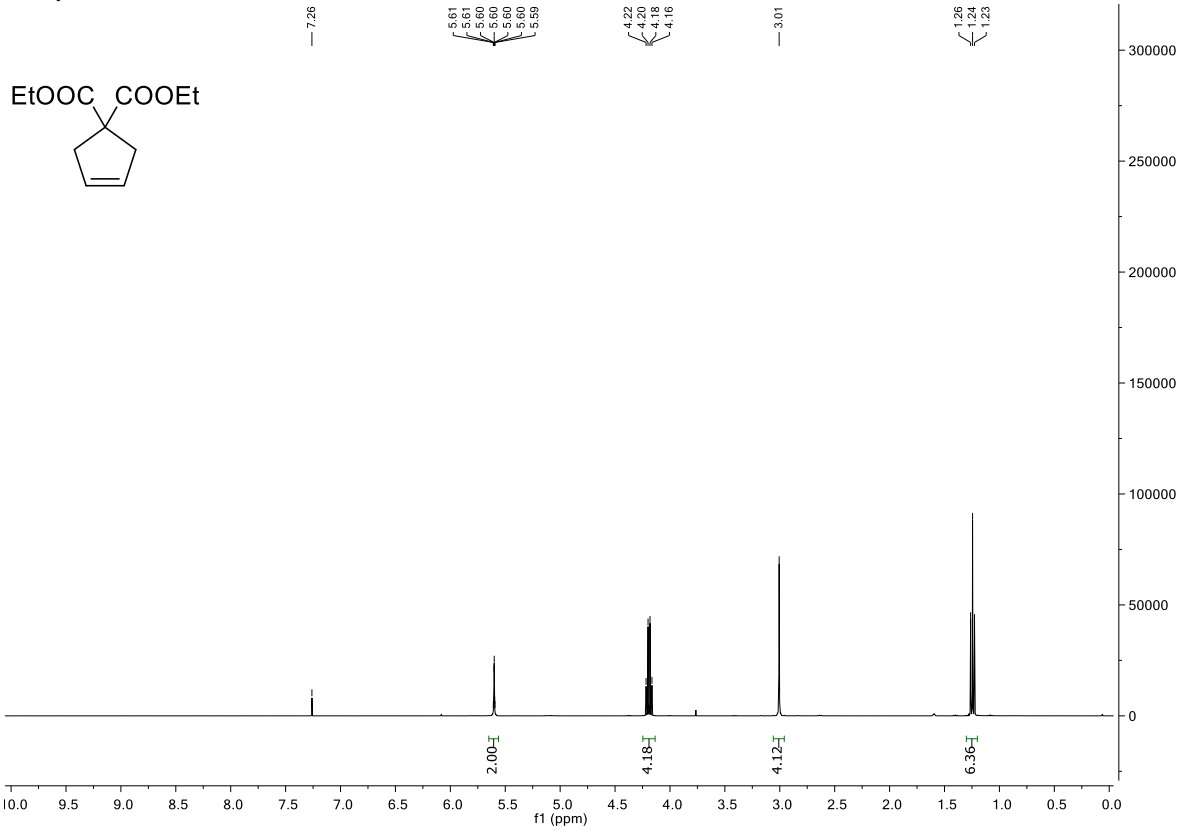


Figure S20: ^{1}H NMR (400 MHz, *CDCl$_3$*) of **7**

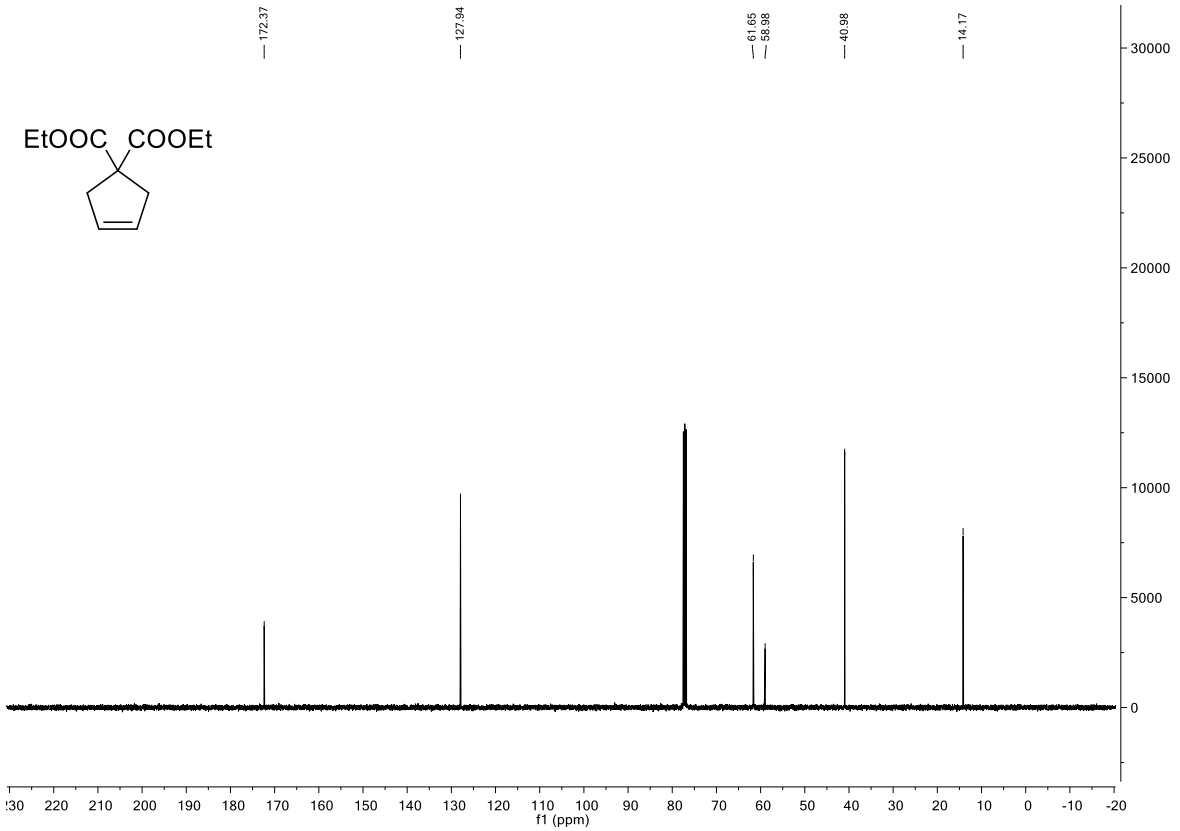


Figure S21: ^{13}C NMR (101 MHz, *CDCl*$_3$) of **7**

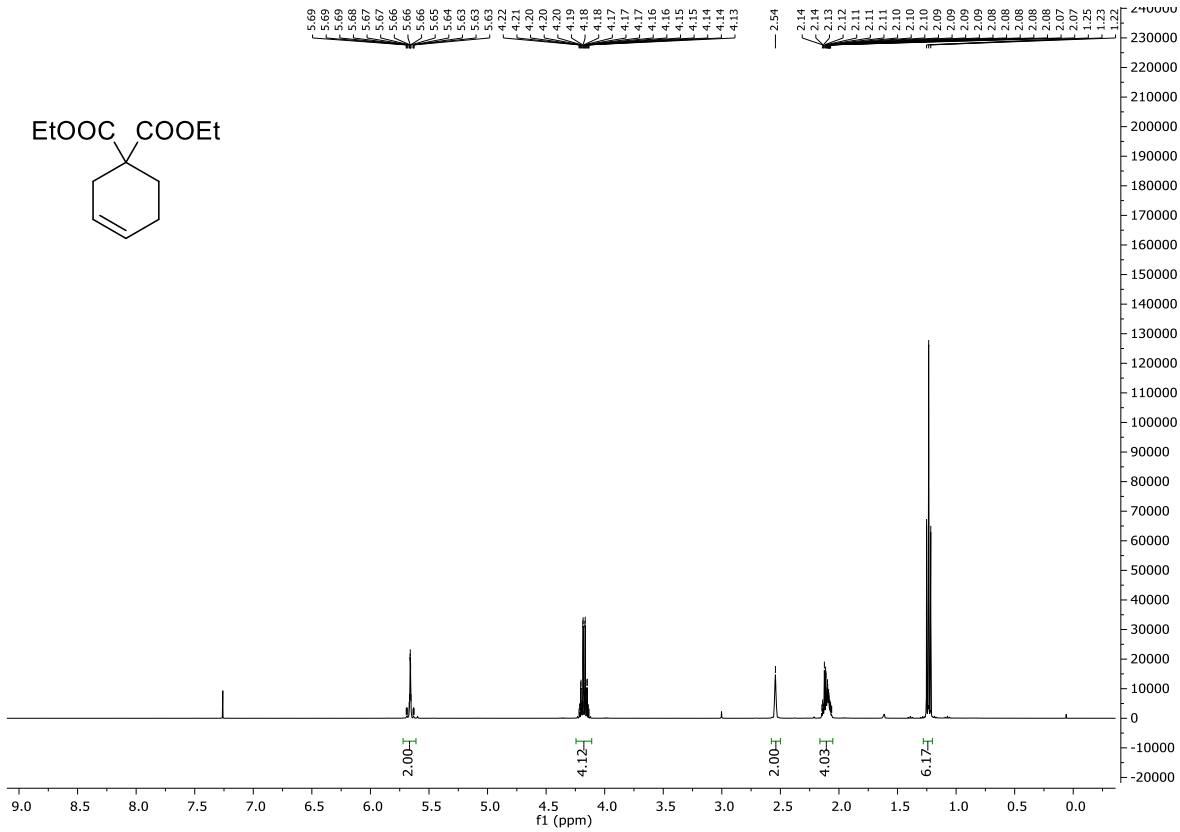


Figure S22: ^{1}H NMR (400 MHz, *CDCl*$_3$) of **9**

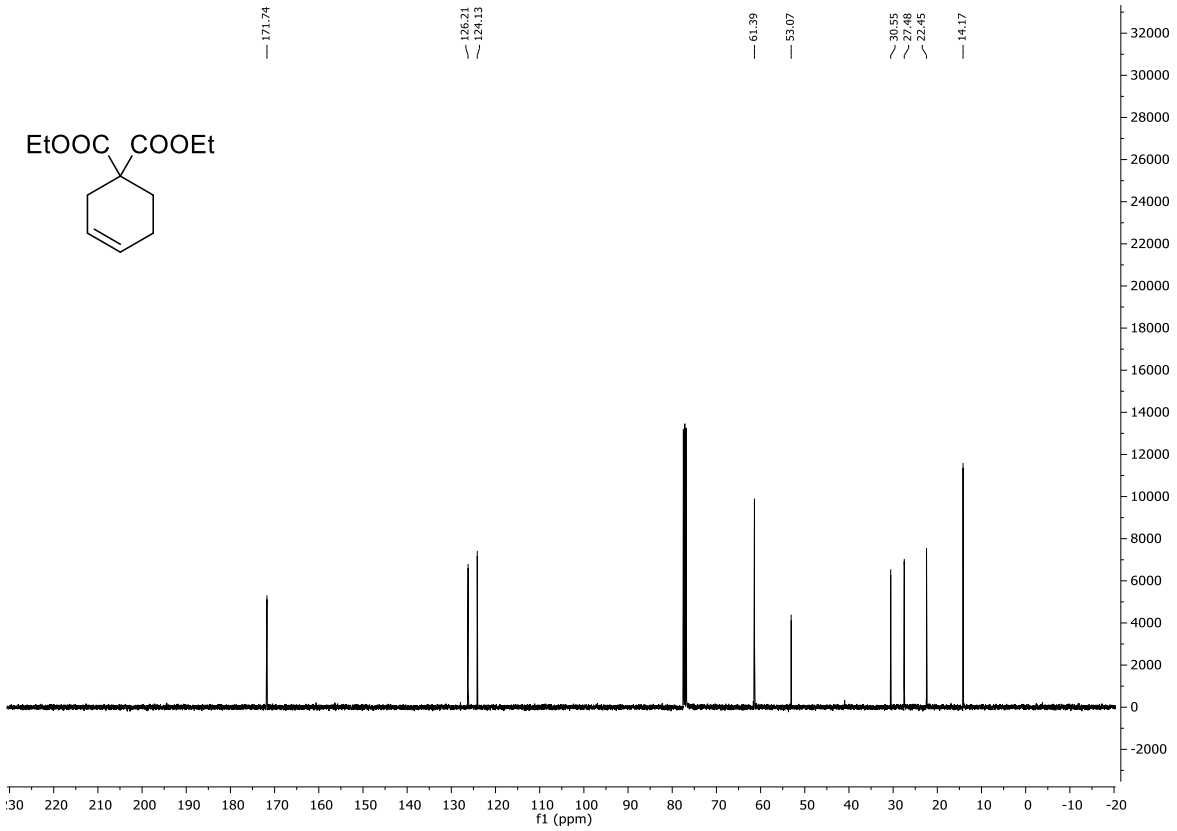


Figure S23: ^{13}C NMR (101 MHz, *CDCl*$_3$) of **9**

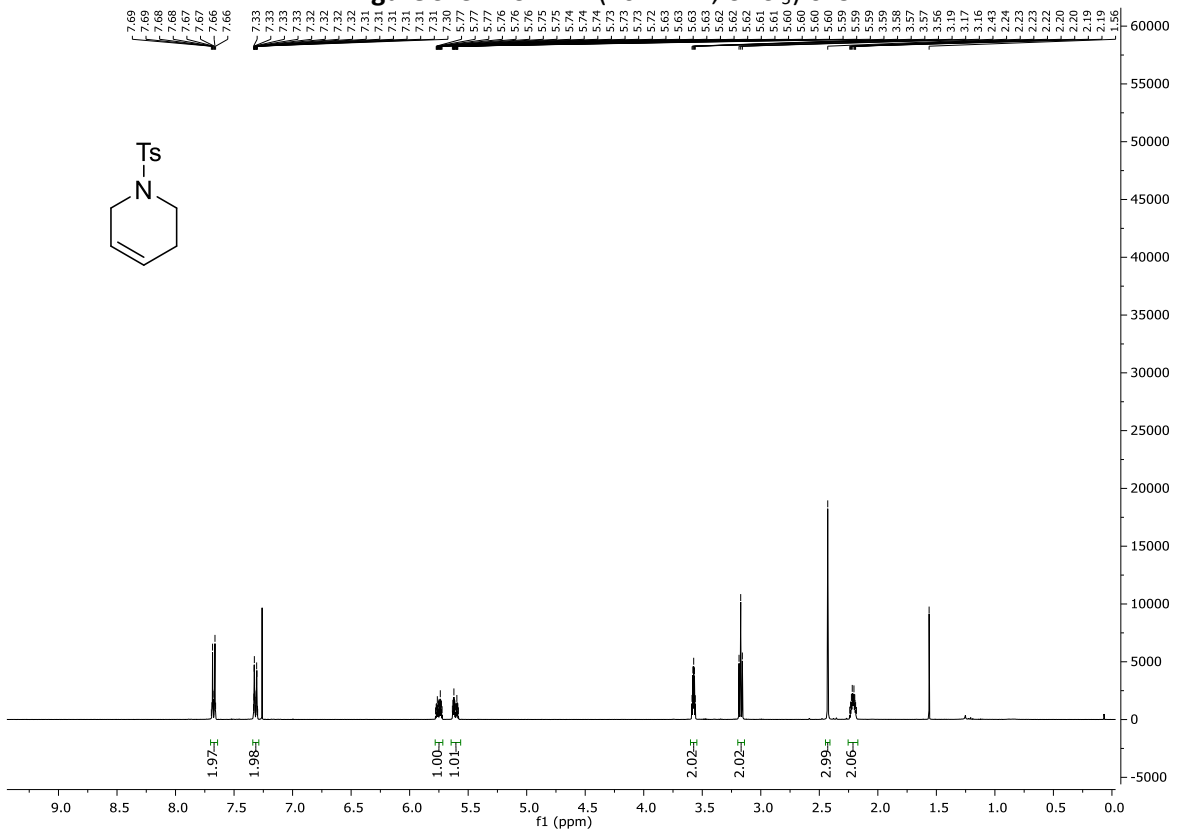


Figure S24: ^{1}H NMR (400 MHz, $CDCl_3$) of **11**

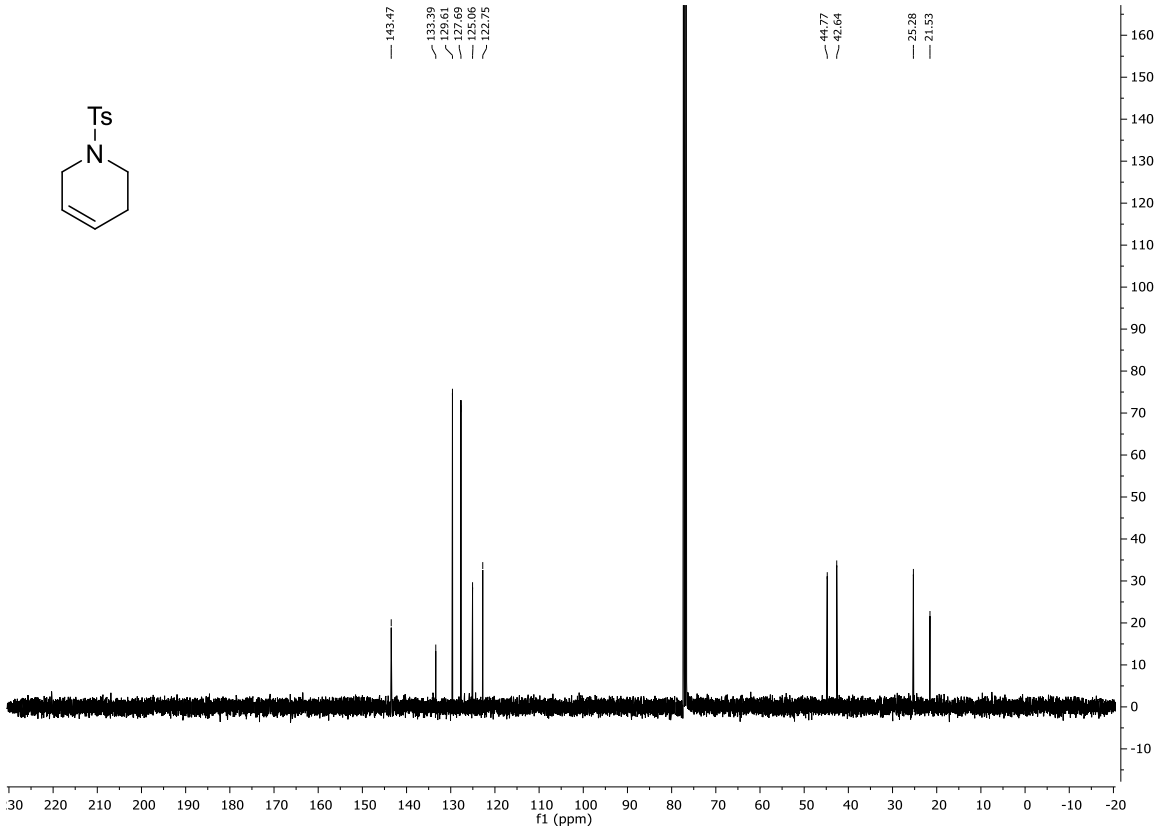


Figure S25: ^{13}C NMR (101 MHz, $CDCl_3$) of **11**

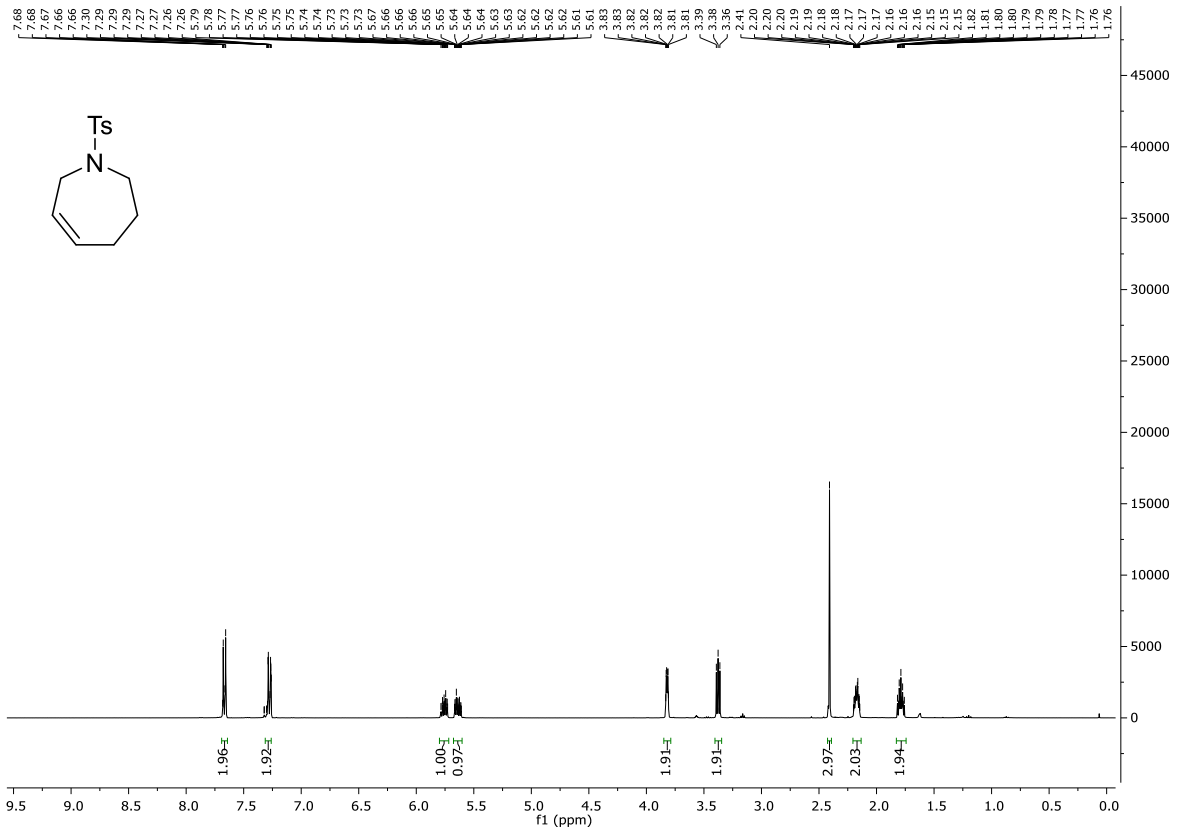


Figure S26: ^{1}H NMR (400 MHz, $CDCl_3$) of **13**

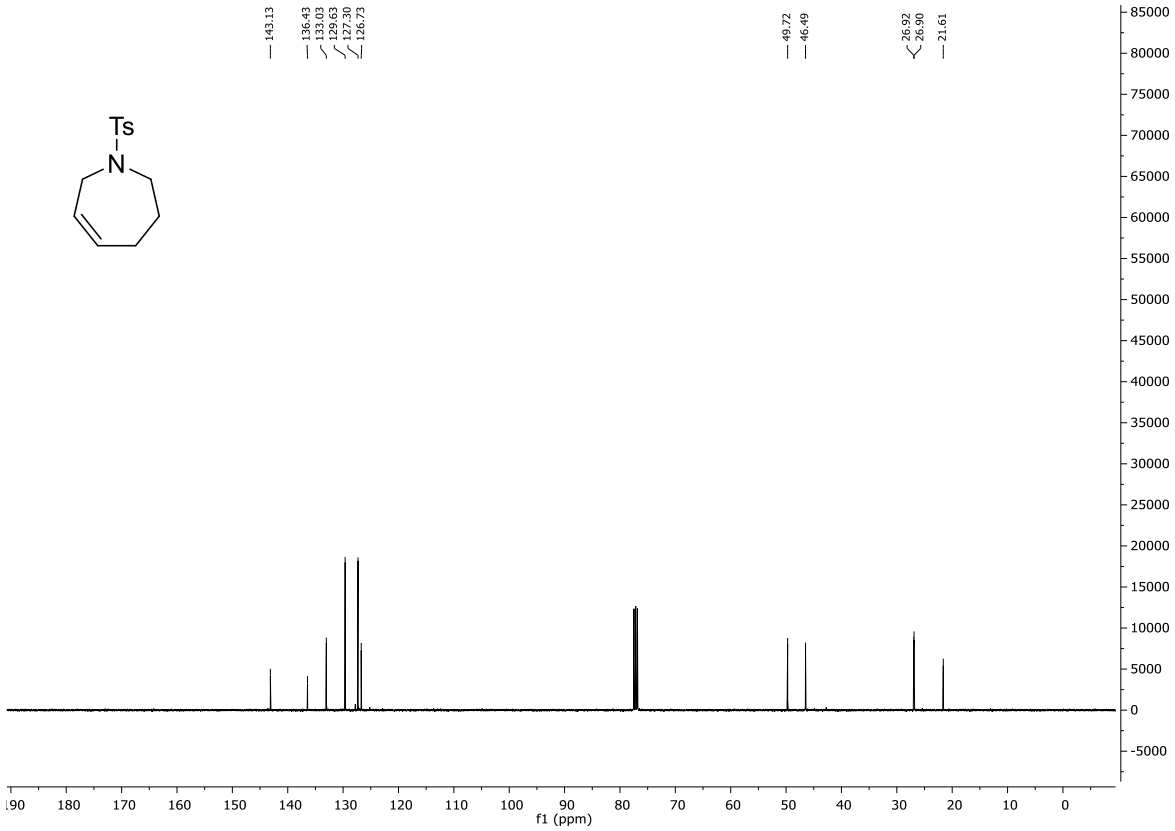


Figure S27: ^{13}C NMR (101 MHz, $CDCl_3$) of **13**

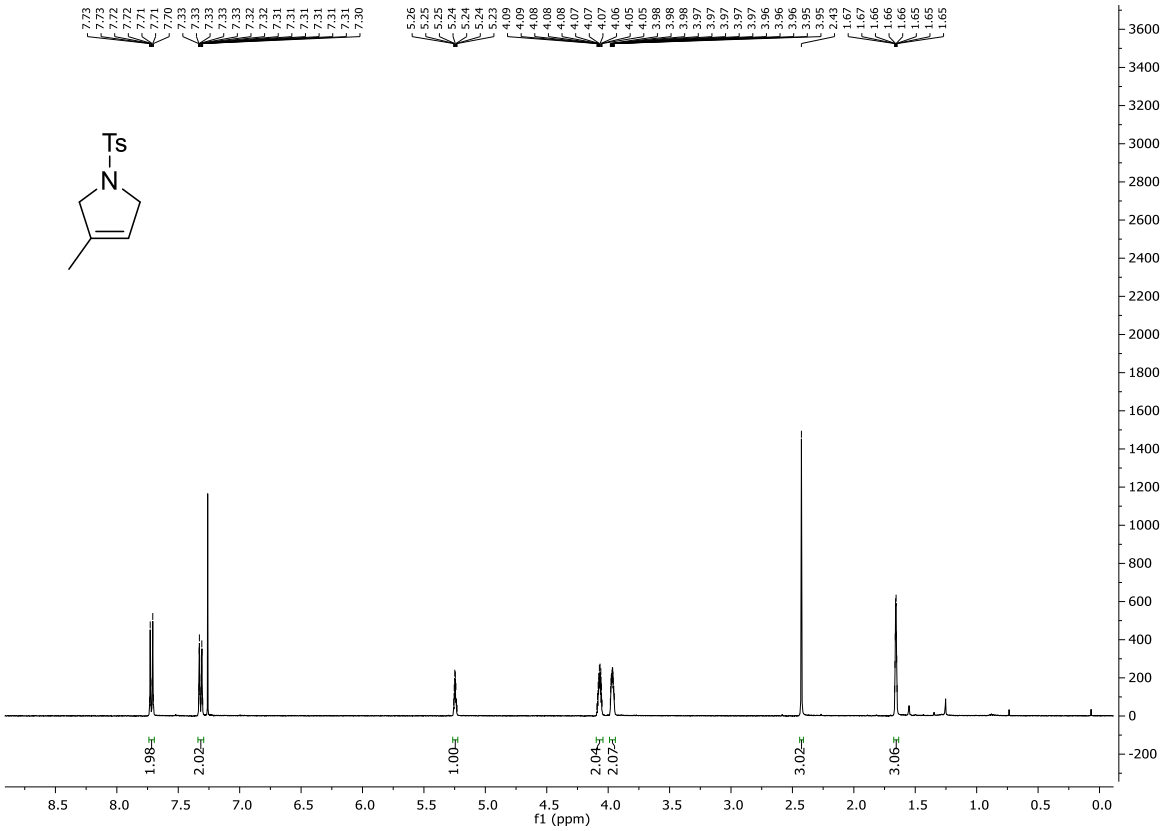


Figure S28: ^{1}H NMR (400 MHz, *CDCl*$_3$) of **15**

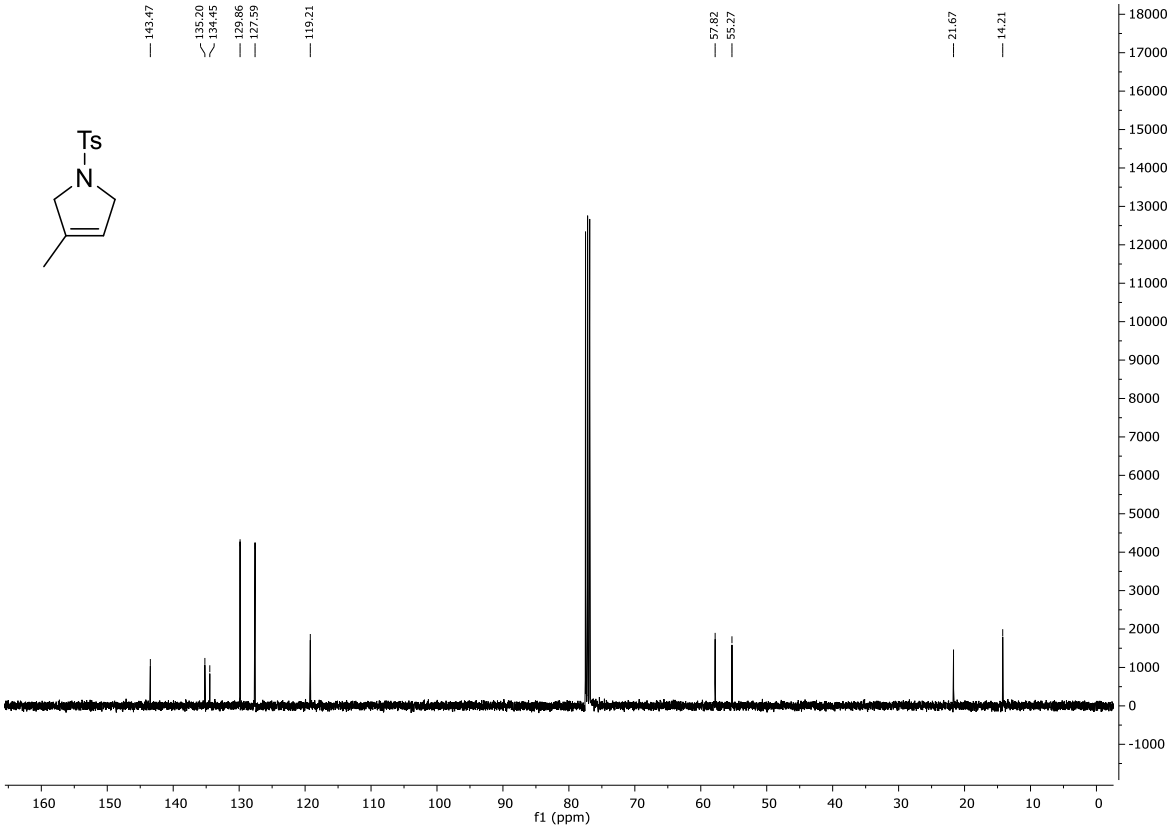


Figure S29: ^{13}C NMR (101 MHz, *CDCl*$_3$) of **15**

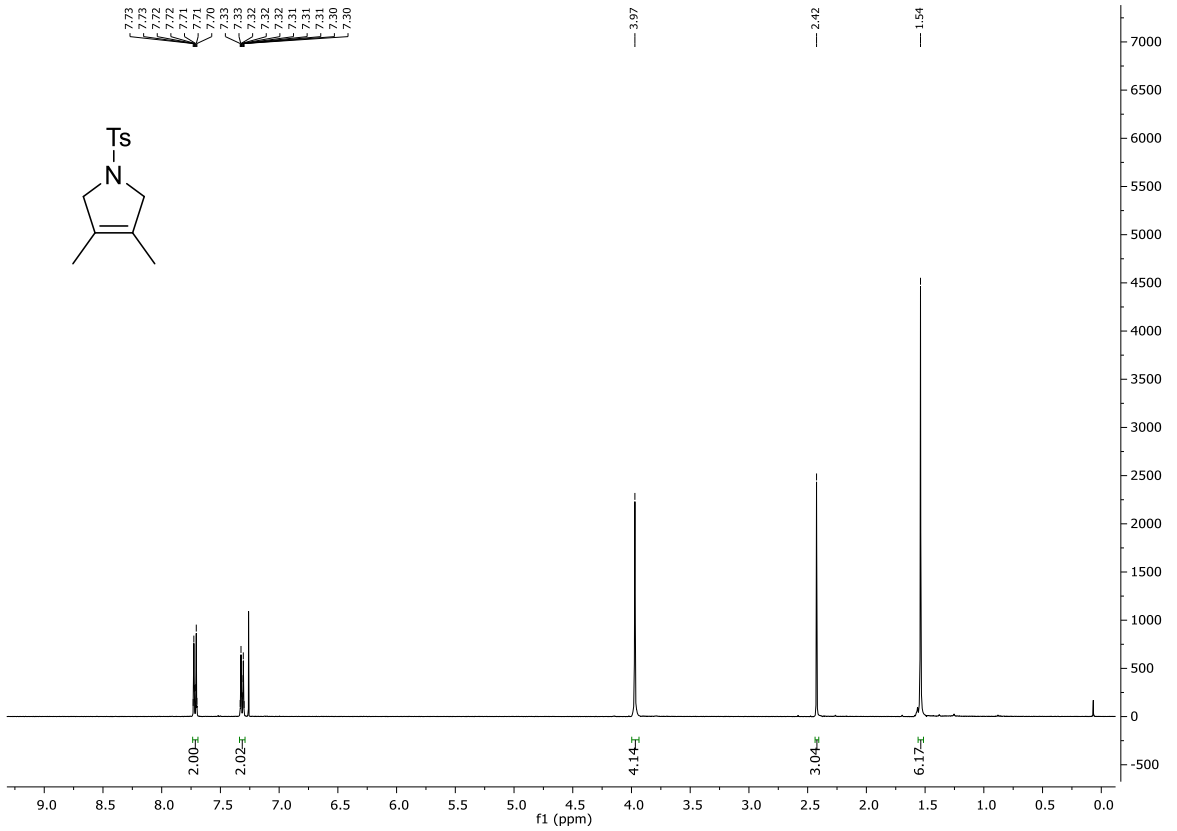


Figure S30: ^{1}H NMR (400 MHz, *CDCl*$_3$) of **17**

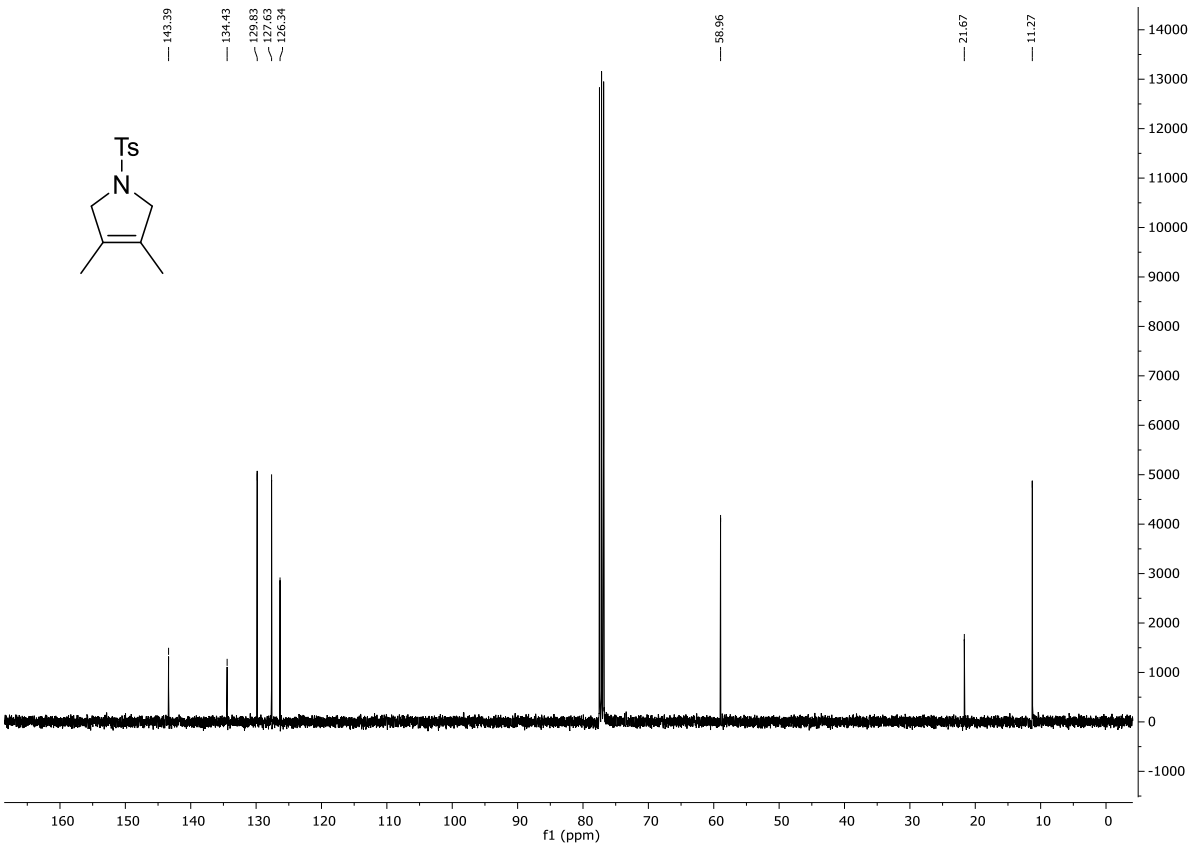


Figure S31: ^{13}C NMR (101 MHz, *CDCl*$_3$) of **17**

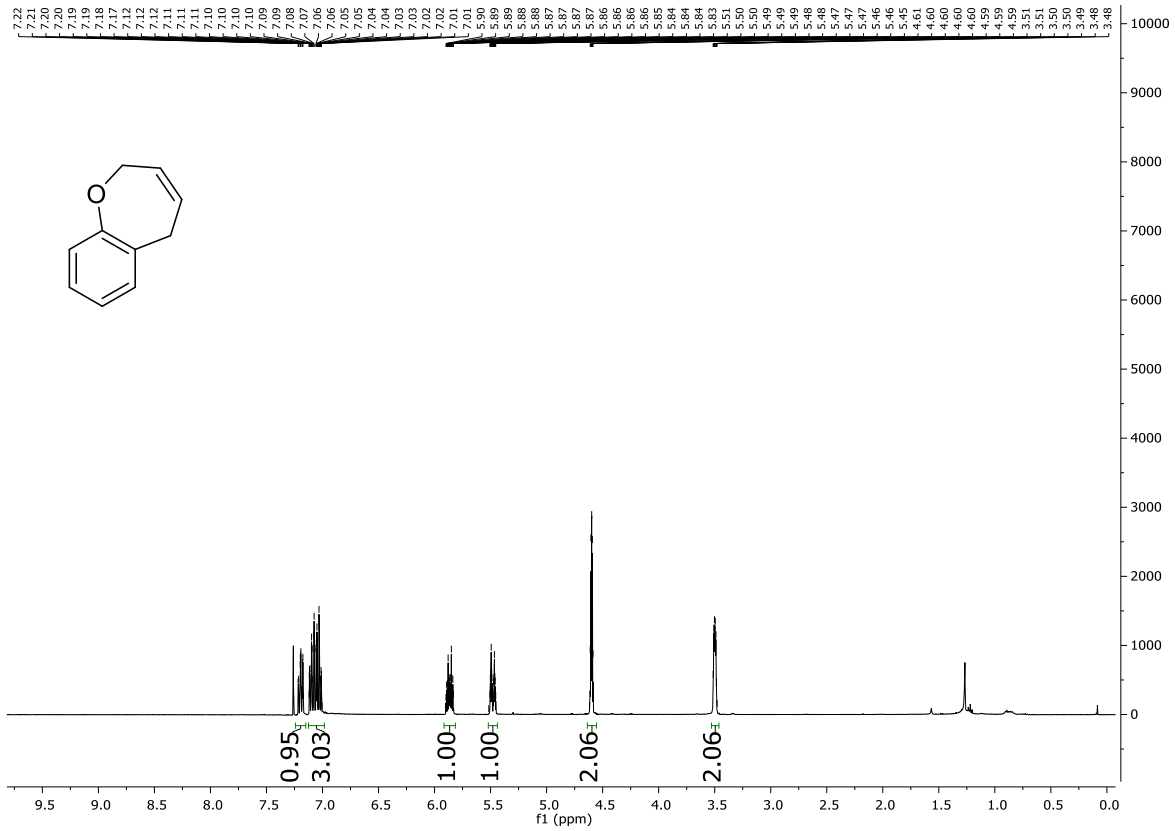


Figure S32: ^{1}H NMR (400 MHz, *CDCl$_3$*) of **17**

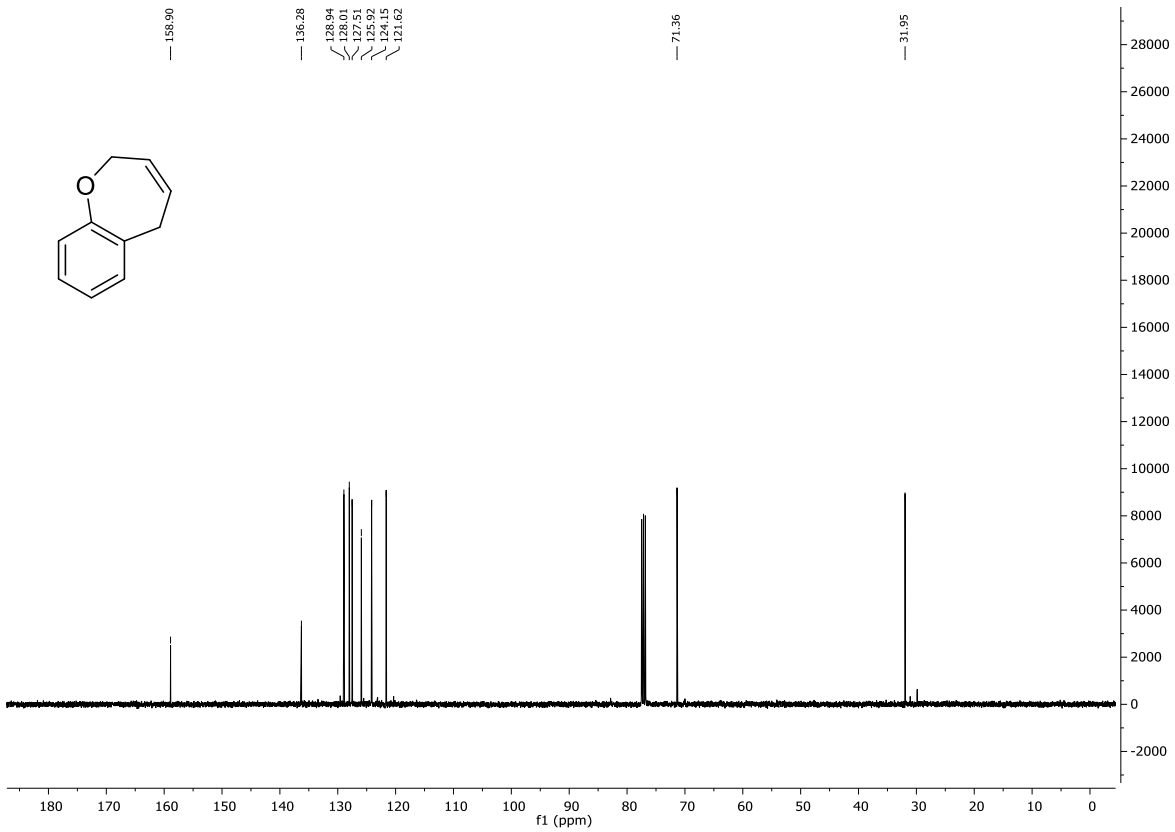


Figure S33: ^{13}C NMR (101 MHz, *CDCl$_3$*) of **17**

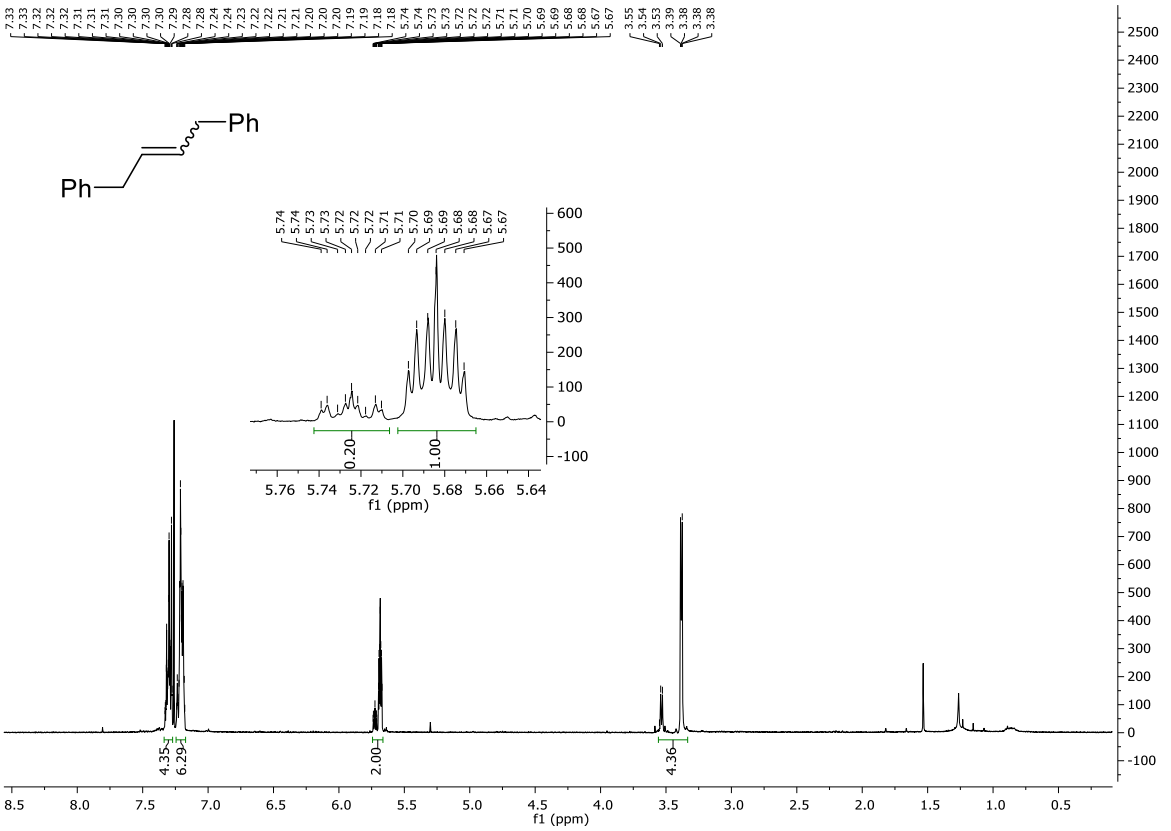


Figure S34: ^{1}H NMR (400 MHz, *CDCl*$_3$) of **23**

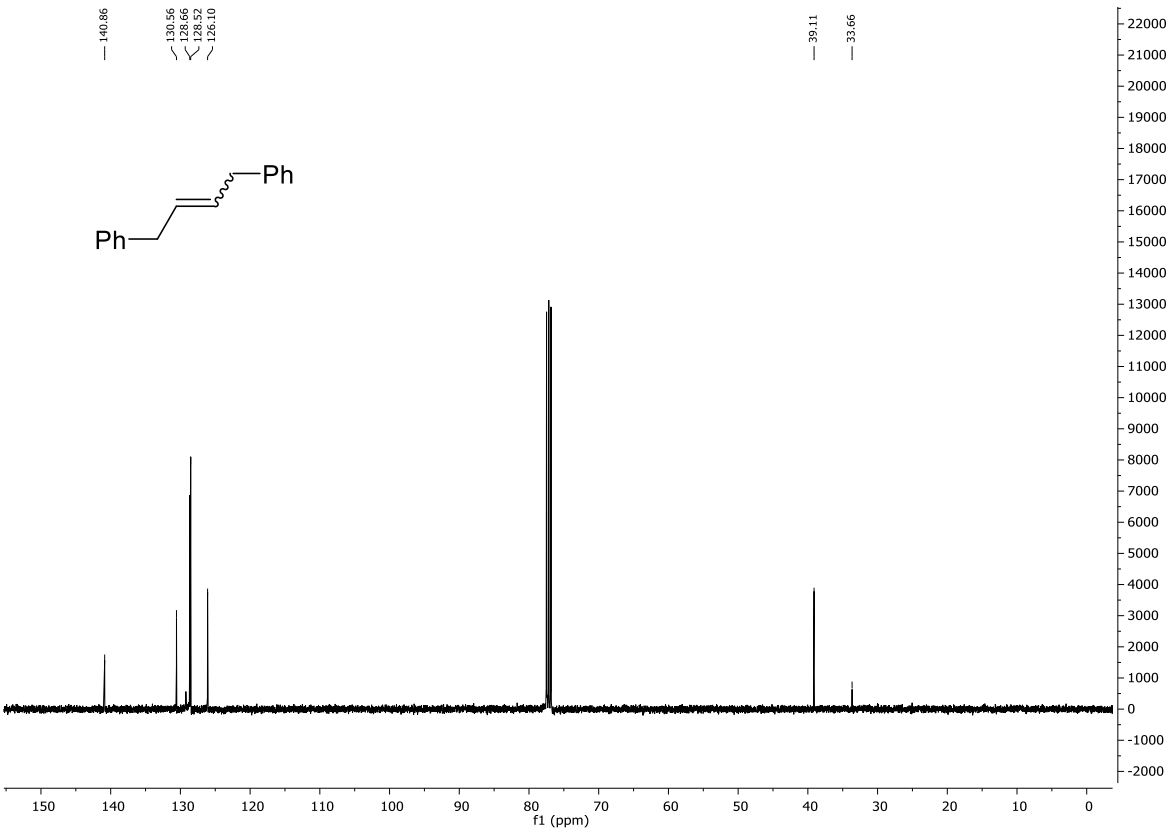
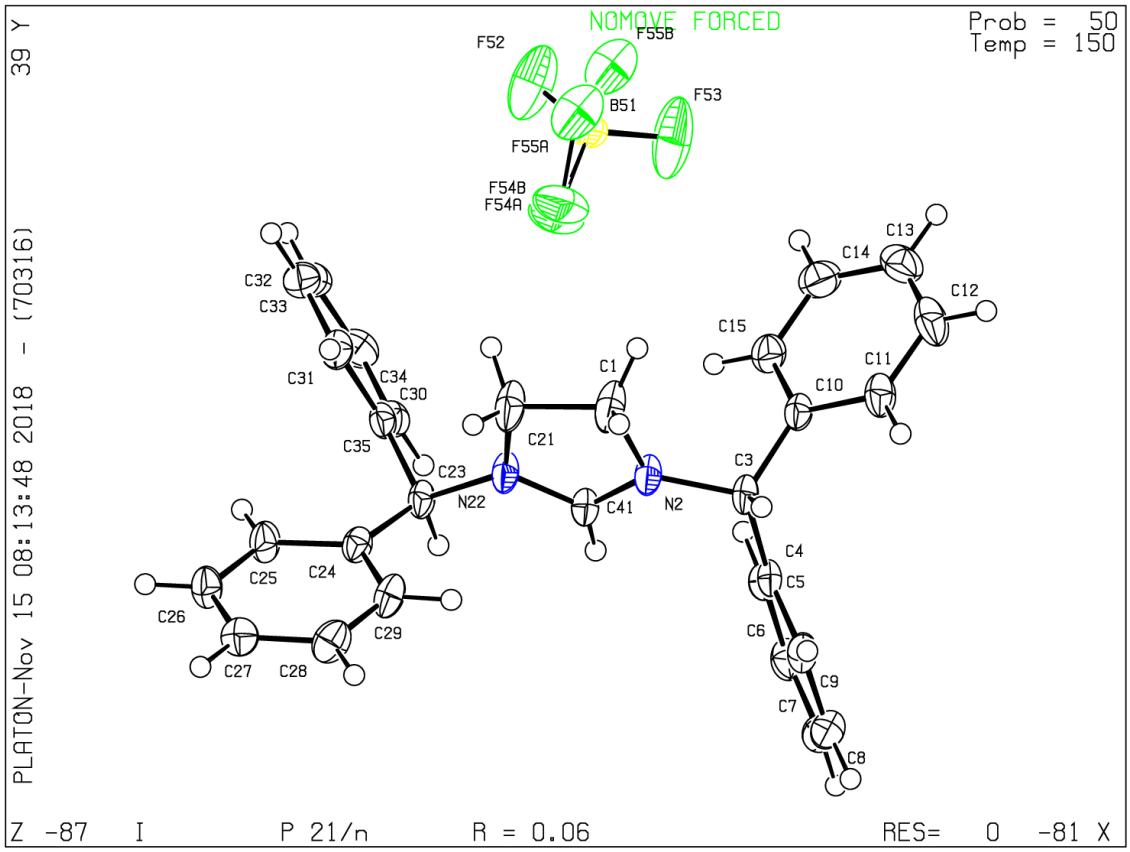


Figure S35: ^{13}C NMR (101 MHz, *CDCl*$_3$) of **23**

X-ray crystallographic data

X-ray for Ru-11b

- ORTEP for 3a; CCDC n°1891522



Structural data

Empirical formula	C29 H27 B F4 N2
Formula weight	490.33 g/mol
Temperature	150 K
Wavelength	0.71073 Å
Crystal system, space group	monoclinic, P 21/n
Unit cell dimensions	a = 8.8913(9) Å, b = 11.1221(13) Å, c = 24.600(3) Å, alpha = 90 °, beta = 95.261(4) °, gamma = 90 °
Volume	2422.5(5) Å3
Z, Calculated density	4, 1.344 g.cm-3
Absorption coefficient	0.099 mm-1
F(000)	1024
Crystal size	0.280 x 0.190 x 0.120 mm
Crystal color	colourless
Theta range for data collection	2.998 to 27.479 °
h_min, h_max	-10, 11
k_min, k_max	-12, 14
l_min, l_max	-31, 31

Reflections collected / unique	23143 / 5542 [R(int) = 0.0318]
Reflections [I>2sigma(I)]	4737
Completeness to theta_max	0.996
Absorption correction type	multi-scan
Max. and min. transmission	0.988 , 0.772
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	5542 / 0 / 332
Goodness-of-fit	1.027
Final R indices [I>2sigma(I)]	R1 = 0.0609, wR2 = 0.1514
R indices (all data)	R1 = 0.0705, wR2 = 0.1602
Largest diff. peak and hole	0.734 and -0.626 e.Å-3

Fractional coordinates, site occupancy (%) and equivalent isotropic displacement parameters (Å^2). U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

Atom	x	y	z	occ.	U(eq)
C1	0.5392(2)	0.4192(3)	0.70232(8)	1	0.0420(6)
H1A	0.609033	0.354273	0.712404	1	0.050
H1B	0.585818	0.495123	0.713666	1	0.050
N2	0.39409(17)	0.40204(15)	0.72645(6)	1	0.0278(3)
C3	0.3915(2)	0.39463(16)	0.78630(6)	1	0.0250(4)
H3	0.446313	0.465043	0.801684	1	0.030
C4	0.2327(2)	0.40187(16)	0.80428(6)	1	0.0240(4)
C5	0.1266(2)	0.31016(17)	0.79396(7)	1	0.0268(4)
H5	0.151873	0.241826	0.775002	1	0.032
C6	-0.0167(2)	0.32056(19)	0.81192(8)	1	0.0336(4)
H6	-0.087739	0.260083	0.804236	1	0.040
C7	-0.0538(2)	0.4212(2)	0.84131(8)	1	0.0381(5)
H7	-0.149572	0.428172	0.853326	1	0.046
C8	0.0519(3)	0.5112(2)	0.85272(8)	1	0.0380(5)
H8	0.027690	0.577929	0.872956	1	0.046
C9	0.1940(2)	0.50189(17)	0.83398(7)	1	0.0301(4)
H9	0.264061	0.563161	0.841359	1	0.036
C10	0.47809(19)	0.28454(17)	0.80839(7)	1	0.0251(4)
C11	0.5621(2)	0.29350(19)	0.85872(7)	1	0.0316(4)
H11	0.565708	0.365991	0.877634	1	0.038
C12	0.6406(2)	0.1946(2)	0.88078(9)	1	0.0418(5)
H12	0.696273	0.200975	0.914557	1	0.050
C13	0.6365(2)	0.0865(2)	0.85282(10)	1	0.0420(5)
H13	0.688935	0.020289	0.867863	1	0.050
C14	0.5543(2)	0.0771(2)	0.80243(9)	1	0.0393(5)
H14	0.552146	0.004829	0.783375	1	0.047
C15	0.4750(2)	0.17605(19)	0.78041(8)	1	0.0334(4)
H15	0.419425	0.169515	0.746633	1	0.040
C21	0.4910(2)	0.4184(3)	0.64067(8)	1	0.0436(6)
H21A	0.513681	0.494595	0.624029	1	0.052
H21B	0.540634	0.354226	0.622500	1	0.052
N22	0.32688(17)	0.39820(15)	0.63839(6)	1	0.0283(3)
C23	0.22495(19)	0.39402(17)	0.58739(6)	1	0.0249(4)
H23	0.122732	0.381803	0.598251	1	0.030
C24	0.22375(19)	0.51503(17)	0.55808(7)	1	0.0247(4)
C25	0.1919(2)	0.52139(17)	0.50164(7)	1	0.0308(4)
H25	0.176499	0.451084	0.481436	1	0.037

C26	0.1830(2)	0.63196(18)	0.47536(8)	1	0.0327(4)
H26	0.163091	0.635010	0.437609	1	0.039
C27	0.2033(2)	0.73755(18)	0.50474(8)	1	0.0318(4)
H27	0.197535	0.811345	0.486897	1	0.038
C28	0.2323(2)	0.73256(19)	0.56093(8)	1	0.0360(4)
H28	0.245464	0.803178	0.581048	1	0.043
C29	0.2418(2)	0.62198(18)	0.58724(7)	1	0.0324(4)
H29	0.260555	0.619398	0.625037	1	0.039
C30	0.26050(19)	0.28517(16)	0.55327(7)	1	0.0247(4)
C31	0.3855(2)	0.28136(18)	0.52252(7)	1	0.0295(4)
H31	0.451008	0.346624	0.522940	1	0.035
C32	0.4121(2)	0.1808(2)	0.49147(8)	1	0.0343(4)
H32	0.495224	0.179146	0.471129	1	0.041
C33	0.3154(2)	0.08246(19)	0.49054(9)	1	0.0355(4)
H33	0.332867	0.015553	0.469337	1	0.043
C34	0.1932(2)	0.08486(18)	0.52127(9)	1	0.0344(4)
H34	0.129216	0.018739	0.521294	1	0.041
C35	0.1654(2)	0.18563(17)	0.55222(7)	1	0.0284(4)
H35	0.082179	0.186554	0.572495	1	0.034
C41	0.2834(2)	0.39065(16)	0.68784(7)	1	0.0241(4)
H41	0.183512	0.378374	0.694803	1	0.029
B51	0.8720(2)	0.1845(2)	0.66431(9)	1	0.0302(4)
F52	0.8644(2)	0.10494(16)	0.62170(6)	1	0.0733(6)
F53	0.8432(3)	0.13283(17)	0.71147(6)	1	0.0839(7)
F54A	0.8308(5)	0.3083(4)	0.65756(16)	0.5	0.0743(9)
F54B	0.7381(5)	0.2433(4)	0.65038(16)	0.5	0.0743(9)
F55A	0.9861(4)	0.2618(3)	0.66155(15)	0.5	0.0562(7)
F55B	1.0337(4)	0.1988(3)	0.67632(15)	0.5	0.0562(7)

Anisotropic displacement parameters (Å^2) The anisotropic displacement factor exponent takes the form: -2pi^2 [h^2 a*^2 U11> + ... + 2 h k a* b* U12].

Atom	U11	U22	U33	U23	U13	U12
C1	0.0273(9)	0.0799(17)	0.0188(8)	0.0004(9)	0.0020(7)	-0.0170(10)
N2	0.0236(7)	0.0435(9)	0.0160(7)	0.0022(6)	0.0008(5)	-0.0070(6)
C3	0.0277(9)	0.0318(9)	0.0149(7)	-0.0001(6)	-0.0010(6)	-0.0073(7)
C4	0.0286(9)	0.0289(9)	0.0143(7)	0.0044(6)	0.0003(6)	-0.0018(7)
C5	0.0299(9)	0.0289(9)	0.0215(8)	0.0032(7)	0.0018(6)	-0.0024(7)
C6	0.0306(10)	0.0423(11)	0.0278(9)	0.0070(8)	0.0023(7)	-0.0046(8)
C7	0.0337(10)	0.0511(13)	0.0306(10)	0.0079(9)	0.0090(8)	0.0071(9)
C8	0.0485(12)	0.0395(11)	0.0272(9)	0.0014(8)	0.0092(8)	0.0090(9)
C9	0.0391(10)	0.0305(9)	0.0206(8)	0.0016(7)	0.0016(7)	-0.0016(8)

C10	0.0213(8)	0.0367(9)	0.0173(7)	0.0008(7)	0.0006(6)	-0.0046(7)
C11	0.0297(9)	0.0420(11)	0.0221(8)	0.0014(7)	-0.0033(7)	-0.0088(8)
C12	0.0329(10)	0.0584(14)	0.0316(10)	0.0119(9)	-0.0101(8)	-0.0058(9)
C13	0.0276(10)	0.0508(13)	0.0480(12)	0.0159(10)	0.0053(9)	0.0069(9)
C14	0.0372(11)	0.0411(11)	0.0409(11)	-0.0021(9)	0.0104(9)	0.0045(9)
C15	0.0327(10)	0.0417(11)	0.0250(9)	-0.0056(8)	-0.0017(7)	0.0015(8)
C21	0.0234(9)	0.0877(18)	0.0194(9)	0.0040(10)	0.0005(7)	-0.0133(10)
N22	0.0232(7)	0.0457(9)	0.0157(7)	0.0016(6)	0.0001(5)	-0.0085(6)
C23	0.0226(8)	0.0359(9)	0.0155(7)	-0.0006(6)	-0.0020(6)	-0.0063(7)
C24	0.0217(8)	0.0329(9)	0.0195(8)	-0.0025(7)	0.0013(6)	-0.0047(7)
C25	0.0408(10)	0.0308(9)	0.0198(8)	-0.0038(7)	-0.0034(7)	-0.0030(8)
C26	0.0401(11)	0.0355(10)	0.0215(8)	-0.0002(7)	-0.0023(7)	-0.0019(8)
C27	0.0312(9)	0.0316(10)	0.0328(10)	0.0010(8)	0.0037(7)	-0.0030(7)
C28	0.0437(11)	0.0328(10)	0.0318(10)	-0.0093(8)	0.0054(8)	-0.0069(8)
C29	0.0391(10)	0.0390(10)	0.0194(8)	-0.0061(7)	0.0039(7)	-0.0087(8)
C30	0.0233(8)	0.0323(9)	0.0175(7)	0.0033(6)	-0.0030(6)	-0.0011(7)
C31	0.0259(9)	0.0388(10)	0.0236(8)	0.0021(7)	0.0012(7)	-0.0048(7)
C32	0.0276(9)	0.0446(11)	0.0312(9)	0.0014(8)	0.0051(7)	0.0043(8)
C33	0.0347(10)	0.0339(10)	0.0372(10)	-0.0026(8)	-0.0009(8)	0.0078(8)
C34	0.0304(10)	0.0306(10)	0.0409(11)	0.0020(8)	-0.0026(8)	-0.0014(8)
C35	0.0226(8)	0.0349(10)	0.0270(9)	0.0039(7)	-0.0002(7)	-0.0011(7)
C41	0.0261(8)	0.0285(8)	0.0176(7)	0.0022(6)	0.0013(6)	-0.0057(7)
B51	0.0301(10)	0.0306(10)	0.0313(10)	0.0074(8)	0.0099(8)	0.0043(8)
F52	0.0991(14)	0.0777(12)	0.0453(8)	-0.0194(8)	0.0190(8)	-0.0507(10)
F53	0.1435(19)	0.0729(12)	0.0377(8)	0.0100(8)	0.0208(10)	-0.0454(12)
F54A	0.075(2)	0.069(2)	0.0801(16)	0.0201(16)	0.0177(17)	0.0438(14)
F54B	0.075(2)	0.069(2)	0.0801(16)	0.0201(16)	0.0177(17)	0.0438(14)
F55A	0.0457(16)	0.070(2)	0.0547(16)	-0.0176(14)	0.0122(12)	-0.0235(13)
F55B	0.0457(16)	0.070(2)	0.0547(16)	-0.0176(14)	0.0122(12)	-0.0235(13)

Bond lengths [Å]

C1 - N2	= 1.481(2)
C1 - C21	= 1.538(3)
C1 - H1A	= 0.9700
C1 - H1B	= 0.9700
N2 - C41	= 1.310(2)
N2 - C3	= 1.477(2)
C3 - C10	= 1.520(3)
C3 - C4	= 1.520(2)
C3 - H3	= 0.9800
C4 - C9	= 1.391(3)
C4 - C5	= 1.397(2)
C5 - C6	= 1.391(3)

C5 - H5 = 0.9300
C6 - C7 = 1.389(3)
C6 - H6 = 0.9300
C7 - C8 = 1.383(3)
C7 - H7 = 0.9300
C8 - C9 = 1.388(3)
C8 - H8 = 0.9300
C9 - H9 = 0.9300
C10 - C15 = 1.388(3)
C10 - C11 = 1.390(2)
C11 - C12 = 1.386(3)
C11 - H11 = 0.9300
C12 - C13 = 1.384(4)
C12 - H12 = 0.9300
C13 - C14 = 1.384(3)
C13 - H13 = 0.9300
C14 - C15 = 1.390(3)
C14 - H14 = 0.9300
C15 - H15 = 0.9300
C21 - N22 = 1.472(2)
C21 - H21A = 0.9700
C21 - H21B = 0.9700
N22 - C41 = 1.312(2)
N22 - C23 = 1.479(2)
C23 - C30 = 1.523(3)
C23 - C24 = 1.527(3)
C23 - H23 = 0.9800
C24 - C29 = 1.391(3)
C24 - C25 = 1.393(2)
C25 - C26 = 1.388(3)
C25 - H25 = 0.9300
C26 - C27 = 1.382(3)
C26 - H26 = 0.9300
C27 - C28 = 1.384(3)
C27 - H27 = 0.9300
C28 - C29 = 1.389(3)
C28 - H28 = 0.9300
C29 - H29 = 0.9300
C30 - C35 = 1.392(3)
C30 - C31 = 1.401(2)
C31 - C32 = 1.387(3)
C31 - H31 = 0.9300
C32 - C33 = 1.390(3)
C32 - H32 = 0.9300

C33 - C34 = 1.379(3)
C33 - H33 = 0.9300
C34 - C35 = 1.390(3)
C34 - H34 = 0.9300
C35 - H35 = 0.9300
C41 - H41 = 0.9300
B51 - F55A = 1.336(4)
B51 - F53 = 1.340(2)
B51 - F52 = 1.369(3)
B51 - F54B = 1.374(4)
B51 - F54A = 1.431(4)
B51 - F55B = 1.450(4)
F54A - F54B = 1.099(5)
F54A - F55A = 1.469(5)
F55A - F55B = 0.880(4)

Angles [deg]

N2 - C1 - C21 = 102.72(15)
N2 - C1 - H1A = 111.20
C21 - C1 - H1A = 111.20
N2 - C1 - H1B = 111.20
C21 - C1 - H1B = 111.20
H1A - C1 - H1B = 109.10
C41 - N2 - C3 = 129.65(15)
C41 - N2 - C1 = 110.25(14)
C3 - N2 - C1 = 120.04(14)
N2 - C3 - C10 = 110.34(14)
N2 - C3 - C4 = 112.78(14)
C10 - C3 - C4 = 113.09(14)
N2 - C3 - H3 = 106.70
C10 - C3 - H3 = 106.70
C4 - C3 - H3 = 106.70
C9 - C4 - C5 = 118.94(17)
C9 - C4 - C3 = 118.44(16)
C5 - C4 - C3 = 122.57(16)
C6 - C5 - C4 = 120.30(18)
C6 - C5 - H5 = 119.80
C4 - C5 - H5 = 119.80
C7 - C6 - C5 = 120.02(19)
C7 - C6 - H6 = 120.00
C5 - C6 - H6 = 120.00
C8 - C7 - C6 = 119.97(19)
C8 - C7 - H7 = 120.00
C6 - C7 - H7 = 120.00
C7 - C8 - C9 = 120.05(19)

C7 - C8 - H8 = 120.00
C9 - C8 - H8 = 120.00
C8 - C9 - C4 = 120.70(19)
C8 - C9 - H9 = 119.70
C4 - C9 - H9 = 119.70
C15 - C10 - C11 = 119.24(18)
C15 - C10 - C3 = 122.46(15)
C11 - C10 - C3 = 118.30(17)
C12 - C11 - C10 = 120.14(19)
C12 - C11 - H11 = 119.90
C10 - C11 - H11 = 119.90
C13 - C12 - C11 = 120.35(19)
C13 - C12 - H12 = 119.80
C11 - C12 - H12 = 119.80
C14 - C13 - C12 = 119.90(2)
C14 - C13 - H13 = 120.10
C12 - C13 - H13 = 120.10
C13 - C14 - C15 = 119.80(2)
C13 - C14 - H14 = 120.10
C15 - C14 - H14 = 120.10
C10 - C15 - C14 = 120.59(18)
C10 - C15 - H15 = 119.70
C14 - C15 - H15 = 119.70
N22 - C21 - C1 = 102.95(15)
N22 - C21 - H21A = 111.20
C1 - C21 - H21A = 111.20
N22 - C21 - H21B = 111.20
C1 - C21 - H21B = 111.20
H21A - C21 - H21B = 109.10
C41 - N22 - C21 = 110.46(15)
C41 - N22 - C23 = 125.06(15)
C21 - N22 - C23 = 124.40(14)
N22 - C23 - C30 = 110.51(15)
N22 - C23 - C24 = 110.49(14)
C30 - C23 - C24 = 115.68(14)
N22 - C23 - H23 = 106.50
C30 - C23 - H23 = 106.50
C24 - C23 - H23 = 106.50
C29 - C24 - C25 = 118.29(17)
C29 - C24 - C23 = 120.99(15)
C25 - C24 - C23 = 120.50(16)
C26 - C25 - C24 = 120.46(17)
C26 - C25 - H25 = 119.80
C24 - C25 - H25 = 119.80

C27 - C26 - C25 = 120.66(17)
C27 - C26 - H26 = 119.70
C25 - C26 - H26 = 119.70
C26 - C27 - C28 = 119.46(18)
C26 - C27 - H27 = 120.30
C28 - C27 - H27 = 120.30
C27 - C28 - C29 = 119.92(18)
C27 - C28 - H28 = 120.00
C29 - C28 - H28 = 120.00
C28 - C29 - C24 = 121.19(17)
C28 - C29 - H29 = 119.40
C24 - C29 - H29 = 119.40
C35 - C30 - C31 = 118.44(17)
C35 - C30 - C23 = 119.11(16)
C31 - C30 - C23 = 122.45(16)
C32 - C31 - C30 = 120.36(18)
C32 - C31 - H31 = 119.80
C30 - C31 - H31 = 119.80
C31 - C32 - C33 = 120.47(18)
C31 - C32 - H32 = 119.80
C33 - C32 - H32 = 119.80
C34 - C33 - C32 = 119.52(19)
C34 - C33 - H33 = 120.20
C32 - C33 - H33 = 120.20
C33 - C34 - C35 = 120.29(19)
C33 - C34 - H34 = 119.90
C35 - C34 - H34 = 119.90
C34 - C35 - C30 = 120.91(17)
C34 - C35 - H35 = 119.50
C30 - C35 - H35 = 119.50
N2 - C41 - N22 = 113.61(16)
N2 - C41 - H41 = 123.20
N22 - C41 - H41 = 123.20
F55A - B51 - F53 = 121.80(3)
F55A - B51 - F52 = 111.20(2)
F53 - B51 - F52 = 112.69(19)
F55A - B51 - F54B = 109.00(3)
F53 - B51 - F54B = 100.90(2)
F52 - B51 - F54B = 97.80(3)
F55A - B51 - F54A = 64.00(3)
F53 - B51 - F54A = 116.50(2)
F52 - B51 - F54A = 122.60(2)
F54B - B51 - F54A = 46.10(2)
F55A - B51 - F55B = 36.56(19)

F53 - B51 - F55B = 97.80(2)
F52 - B51 - F55B = 101.90(2)
F54B - B51 - F55B = 145.00(3)
F54A - B51 - F55B = 99.00(3)
F54B - F54A - B51 = 64.20(3)
F54B - F54A - F55A = 117.80(4)
B51 - F54A - F55A = 54.90(2)
F54A - F54B - B51 = 69.70(3)
F55B - F55A - B51 = 78.80(4)
F55B - F55A - F54A = 136.20(5)
B51 - F55A - F54A = 61.10(2)
F55A - F55B - B51 = 64.70(4)

Torsion angles [deg]

C21 - C1 - N2 - C41 = 1.20(3)
C21 - C1 - N2 - C3 = 178.57(18)
C41 - N2 - C3 - C10 = 113.00(2)
C1 - N2 - C3 - C10 = -63.80(2)
C41 - N2 - C3 - C4 = -14.60(3)
C1 - N2 - C3 - C4 = 168.63(18)
N2 - C3 - C4 - C9 = -113.38(17)
C10 - C3 - C4 - C9 = 120.54(17)
N2 - C3 - C4 - C5 = 69.10(2)
C10 - C3 - C4 - C5 = -56.90(2)
C9 - C4 - C5 - C6 = 1.70(3)
C3 - C4 - C5 - C6 = 179.18(16)
C4 - C5 - C6 - C7 = -1.50(3)
C5 - C6 - C7 - C8 = 0.00(3)
C6 - C7 - C8 - C9 = 1.10(3)
C7 - C8 - C9 - C4 = -0.90(3)
C5 - C4 - C9 - C8 = -0.60(3)
C3 - C4 - C9 - C8 = -178.13(16)
N2 - C3 - C10 - C15 = -37.10(2)
C4 - C3 - C10 - C15 = 90.20(2)
N2 - C3 - C10 - C11 = 143.43(16)
C4 - C3 - C10 - C11 = -89.21(19)
C15 - C10 - C11 - C12 = -0.60(3)
C3 - C10 - C11 - C12 = 178.86(17)
C10 - C11 - C12 - C13 = 0.30(3)
C11 - C12 - C13 - C14 = 0.30(3)
C12 - C13 - C14 - C15 = -0.60(3)
C11 - C10 - C15 - C14 = 0.30(3)
C3 - C10 - C15 - C14 = -179.14(17)
C13 - C14 - C15 - C10 = 0.30(3)
N2 - C1 - C21 - N22 = -1.30(3)
C1 - C21 - N22 - C41 = 1.00(3)
C1 - C21 - N22 - C23 = 177.83(19)
C41 - N22 - C23 - C30 = -117.36(19)
C21 - N22 - C23 - C30 = 66.30(2)
C41 - N22 - C23 - C24 = 113.31(19)
C21 - N22 - C23 - C24 = -63.00(2)
N22 - C23 - C24 - C29 = -32.50(2)
C30 - C23 - C24 - C29 = -158.99(17)
N22 - C23 - C24 - C25 = 152.92(17)
C30 - C23 - C24 - C25 = 26.40(2)
C29 - C24 - C25 - C26 = 1.80(3)
C23 - C24 - C25 - C26 = 176.58(18)

C24 - C25 - C26 - C27 = -0.90(3)
C25 - C26 - C27 - C28 = -0.20(3)
C26 - C27 - C28 - C29 = 0.40(3)
C27 - C28 - C29 - C24 = 0.50(3)
C25 - C24 - C29 - C28 = -1.60(3)
C23 - C24 - C29 - C28 = -176.34(18)
N22 - C23 - C30 - C35 = 103.72(18)
C24 - C23 - C30 - C35 = -129.78(17)
N22 - C23 - C30 - C31 = -76.50(2)
C24 - C23 - C30 - C31 = 49.90(2)
C35 - C30 - C31 - C32 = 0.60(3)
C23 - C30 - C31 - C32 = -179.11(16)
C30 - C31 - C32 - C33 = -0.10(3)
C31 - C32 - C33 - C34 = -0.70(3)
C32 - C33 - C34 - C35 = 1.10(3)
C33 - C34 - C35 - C30 = -0.60(3)
C31 - C30 - C35 - C34 = -0.20(3)
C23 - C30 - C35 - C34 = 179.51(16)
C3 - N2 - C41 - N22 = -177.65(18)
C1 - N2 - C41 - N22 = -0.60(2)
C21 - N22 - C41 - N2 = -0.30(2)
C23 - N22 - C41 - N2 = -177.10(17)
F55A - B51 - F54A - F54B = 166.40(4)
F53 - B51 - F54A - F54B = -79.30(4)
F52 - B51 - F54A - F54B = 66.90(4)
F55B - B51 - F54A - F54B = 177.30(3)
F53 - B51 - F54A - F55A = 114.30(3)
F52 - B51 - F54A - F55A = -99.60(3)
F54B - B51 - F54A - F55A = -166.40(4)
F55B - B51 - F54A - F55A = 10.90(3)
F55A - F54A - F54B - B51 = 12.50(4)
F55A - B51 - F54B - F54A = -12.90(4)
F53 - B51 - F54B - F54A = 116.40(3)
F52 - B51 - F54B - F54A = -128.60(3)
F55B - B51 - F54B - F54A = -4.70(6)
F53 - B51 - F55A - F55B = 55.40(5)
F52 - B51 - F55A - F55B = -81.20(4)
F54B - B51 - F55A - F55B = 172.10(4)
F54A - B51 - F55A - F55B = 161.80(5)
F53 - B51 - F55A - F54A = -106.40(3)
F52 - B51 - F55A - F54A = 117.00(3)
F54B - B51 - F55A - F54A = 10.30(3)
F55B - B51 - F55A - F54A = -161.80(5)
F54B - F54A - F55A - F55B = -40.10(9)

B51 - F54A - F55A - F55B = -26.30(7)
F54B - F54A - F55A - B51 = -13.80(4)
F54A - F55A - F55B - B51 = 23.30(6)
F53 - B51 - F55B - F55A = -135.00(4)
F52 - B51 - F55B - F55A = 109.70(4)
F54B - B51 - F55B - F55A = -13.10(7)
F54A - B51 - F55B - F55A = -16.50(4)