Supplementary Material (ESI) for Chemical Communications

Synthesis of highly enantiomerically enriched planar chiral ruthenium complexes *via* Pd-catalysed asymmetric hydrogenolysis

Audrey Mercier, Wee Chuan Yeo, Jingyu Chou, Piyali Datta Chaudhuri, Gérald Bernardinelli and E. Peter Kündig*

Department of Organic Chemistry, University of Geneva
30 Quai Ernest Ansermet, 1211, Geneva 4, Switzerland
E-mail : Peter.Kundig@unige.ch

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1. General remarks

Solvents were purified on Al_2O_3 drying columns using a Solvtek system or by following standard procedures[1]. Reactions and manipulations involving organometallic or moisture sensitive compounds were carried out under dry nitrogen and glassware heated under vacuum prior use.

Analytical thin layer chromatography (TLC) was performed with Merck SIL G/UV_{254} plates. Column chromatography was performed in air with silicagel 60 (Fluka) or neutral alumina 50-200 micron (Acros).

Microwave reactions were performed on a Biotage Initiator, SW version 1.2 build 5637.

^{1}H-, ^{13}C-, ^{31}P-, ^{19}F-NMR spectra were recorded on Bruker ARX-500, AMX-400 or ARX-300 FT spectrometers in the solvent indicated. ^{1}H- and ^{13}C-NMR chemical shifts (δ) are quoted in parts per million (ppm) relative to the TMS scale ($CDCl_3$: $\delta_C \equiv 77.05$ ppm; residual $CHCl_3$: $\delta_H \equiv 7.26$ ppm; CD_2Cl_2: $\delta_C \equiv 53.9$ ppm; residual $CHDCl_2$: $\delta_H \equiv 5.32$ ppm; acetone-d_6: $\delta_C \equiv 28.8$ ppm; residual acetone-d_5: $\delta_H \equiv 2.05$). ^{31}P-NMR chemical shifts are referenced to H_3PO_4 as external standard. ^{19}F-NMR chemical shifts are referenced to $CFCl_3$ as external standard. Coupling constants *J* are quoted in Hz. Infrared spectra were recorded on a Perkin–Elmer Spectrum One spectrophotometer using a diamond ATR Golden Gate sampling. Electron impact (EI) HRMS mass spectra were obtained using a *Finningan MAT 95* operating at 70eV. Electrospray ionization (ESI) HRMS analyses were measured on a VG analytical 7070E instrument. Optical rotations were measured on a Perkin Elmer 241 polarimeter using a quartz cell (l = 10 cm) with a Na high-pressure lamp (λ = 589 nm). Analytical HPLC was performed using an Alligent 1100 series with a JASCO PU–980 pump and Aligent 1100 Series detection system. Melting points were determined on a Büchi 540 and are uncorrected. Elemental analysis were carried out by H. Eder, Service de Microanalyse, Section de Pharmacie, Université de Genève.

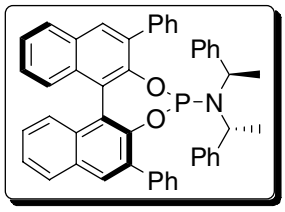
Commercially available chemicals were used as received unless otherwise stated: $RuCl_3.3H_2O$ (Pressure Chemical), Zn powder (Fluka), naphthalene (Merck), $AlCl_3$ (Acros, anhydrous powder), Al (Riedel-de Haën, fine powder), $TiCl_4$ (Acros), KPF_6 (Acros, dried under vacuum), 1-bromonaphthalene (Riedel-de Haën), NaHMDS (Aldrich,

1M in THF), 4-bromo-1-indanone (Aldrich), 2,5-dibromoaniline (Acros), $Pd(dba)_2$ (Acros), $LiBH_4$ (Acros, stored in glove-box), DABCO (Fluka, sublimed under vacuum and stored in glove-box), $Pd(OAc)_2$ (Fluka), P(*o*-tol)$_3$ (Fluka), phenylboronic acid (Fluka), K_3PO_4 (Riedel-de Haën).

$LiBH_4$ solution in DME was prepared according to a literature procedure[2] and titrated before use by injecting an aliquot into a hydrolyzing mixture of glycerine and water and measuring the hydrogen gas evolved.

Full analysis of compounds **9** and **11** were performed on racemic compounds, which were prepared using the methodology described for the corresponding dibromo-complexes.

2. Synthesis of the chiral phosphoramidite ligand



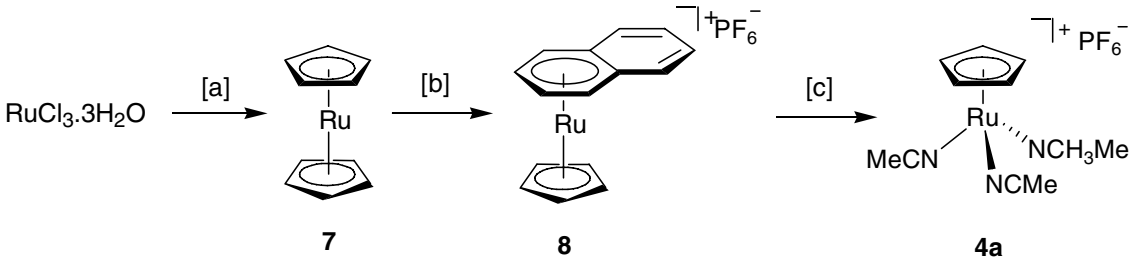
(*S*,*R*,*R*)-L*

Distilled PCl_3 (90 µL, 1.03 mmol) was added to a solution of freshly distilled Et_3N (0.84 mL, 6.03 mmol) in CH_2Cl_2 (7.5 mL) at 0 ^oC and stirred for 0.5 h at this temperature. Then, the HCl salt of the (*R*,*R*)-Whitesell amine[3,] (262 mg, 1 mmol) was added at 0 ^oC and stirred for 4 h at room temperature. (r.t.). The mixture was cooled to 0 ^oC, then diol (S)-3,3′-biphenyl-1,1′-binaphthalenyl-2,2′-diol[4] (440 mg, 1 mmol) was added and the reaction was stirred overnight at r.t. The reaction mixture was diluted with CH_2Cl_2 (50 mL) and washed with H_2O. The organic layer was dried (Na_2SO_4) and concentrated. The residue was purified by flash chromatography on silica gel (toluene/cyclohexane, 1:1) to afford ligand L* (586 mg, 85 %) as white foamy solid. mp 147-149°C. $[\alpha]_D^{25}$ = +446 (*c* = 1.0, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.04 (d, *J* = 6.8 Hz, 6 H), 4.31 (br s, 2 H), 6.71 (br s, 4 H), 6.93 (m, 4 H), 6.96-7.01 (m, 2 H), 7.24-7.35 (m, 5 H), 7.37-7.47 (m, 5 H), 7.48-7.56 (m, 4 H), 7.93-8.00 (m, 5H), 8.14 (s, 1H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 15.3, 51.7, 123.7, 124.7, 125.1, 125.95, 125.99, 126.1, 126.9, 127.2, 127.4, 127.6, 128.0, 128.1, 128.2, 128.3, 128.3, 129.0, 130.0, 130.0, 130.4, 130.4, 130.6, 131.1, 132.5, 132.6, 134.1, 135.2, 137.8, 138.1, 147.4. ^{31}P NMR (162 MHz, $CDCl_3$): δ 145.4. IR (ν_{max}/cm^{-1}): 3060, 3330, 2968, 1601, 1495, 1452, 1406, 1248, 1218, 1198, 1182, 1133, 1051, 962, 839, 751, 697. HRMS: *m/z* (ESI) calcd. for $C_{48}H_{39}O_2NP$ $[M+H]^+$: 692.2712, found: 692.2658.

3. Synthesis of compounds 4a-c

[Ru(η^5-Cp)(CH$_3$CN)$_3$][PF$_6$] (4a)



Step a: Ruthenocene [Ru(η^5-Cp)$_2$] (7)[5]

Ruthenium trichloride (5.26 g, 20.0 mmol) was dissolved in degassed ethanol (80 mL) in a 200 mL Schlenk tube. Freshly distilled cyclopentadiene (25 mL, 300 mmol, 15 eq.) was added to the dark red-black solution followed by the slow addition of finely powdered zinc (13 g, 200 mmol, 10 eq.). During this process, the reaction was cooled by an ice/water bath. The reaction mixture was stirred for 2 h at r.t., then filtered over celite, (rinsed with toluene (120 mL)). The filtrate was evaporated to dryness, then redissolved in toluene (400 mL), passed through a pad of silica gel (rinsed with toluene). The resulting clear yellow solution was evaporated to dryness and dried under vacuum to afford ruthenocene (4.46 g, 96%) as yellow crystalline solid. mp 197-200°C (ref.[5a] 199-200°C). ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.55 (s). ^{13}C NMR (100 MHz, $CDCl_3$): δ 70.1. Elemental analysis (%) calcd for $C_{10}H_{10}Ru$ (231.259): C 51.93, H 4.36; found: C 51.92, H 4.38.

Step b: [Ru(η^5-Cp)(naphthalene)][PF_6] (8)♦

To a 20 mL microwave vial equipped with a magnetic stirring bar were added: ruthenocene **7** (2.31 g, 10 mmol), naphthalene (2.56 g, 20 mmol, 2.0 eq), Al (fine powder, 135 mg, 5 mmol, 50 mol%), and $AlCl_3$ (2.70 g, 20 mmol, 2.0 eq). Then the vial was sealed, degassed, and purged with N_2. Degassed decaline (15 mL) was added followed by $TiCl_4$ (550 μL, 5 mmol, 50 mol%) was added. The mixture was stirred for 5 min. before being subjected to microwave irradiation for 15 min. at 230°C (pre-stirring 30 sec., normal absorption level). After cooling to r.t., the reaction mixture was poured into a mixture of ice and water (80 mL), 32% HCl (20 mL), 30% H_2O_2 (20 mL) and stirred vigorously for 10 min. The resulting solution was extracted with pentane (3 × 200 mL). The combined organic phases were extracted with water (2 × 100 mL). To the combined aqueous phases was added KPF_6 (2.76 g, 15 mmol, 1.5 eq.) to give a yellow precipitate and the resulting mixture was stirred for 10 min. The aqueous solution was extracted with CH_2Cl_2 (4 × 200 mL), and then the combined organic phases were dried over $MgSO_4$, filtered, concentrated under vacuum to afford 4.1 g of an orange solid. The crude product was dissolved in 60 mL of CH_2Cl_2 and filtered through a short plug of celite (4 x 5 cm). The celite was washed with CH_2Cl_2 until washings become colorless. The CH_2Cl_2 solution was concentrated to c.a. 10 mL and then poured into vigorously stirred diethyl ether (100 mL) to yield a light colored precipitate which was filtered of on a Büchner filter and washed with pentane (3 × 20 mL). The light cream-colored solid was dried in air and stored in a dark glass vial (3.7 g, 85%). mp: 155-160°C (dec.). ^{1}H NMR (400 MHz, acetone-d_6): δ 5.15 (s, 5H), 6.47-6.48 (m, 2H), 7.24-725 (m, 2H), 7.70-7.73 (m, 2H), 7.89-7.92 (m, 2H). ^{13}C NMR (100 MHz, acetone-d_6): 79.7, 83.9, 85.9, 97.2, 129.3, 131.5. ^{31}P NMR (162 MHz, acetone-d_6): δ -144.1 (sept, J = 708 Hz). MS: *m/z* (ESI) 295 $[M+H]^+$.

Step c: [Ru(η^5-Cp)(CH_3CN)$_3$][PF_6] (4a)[5b,6]

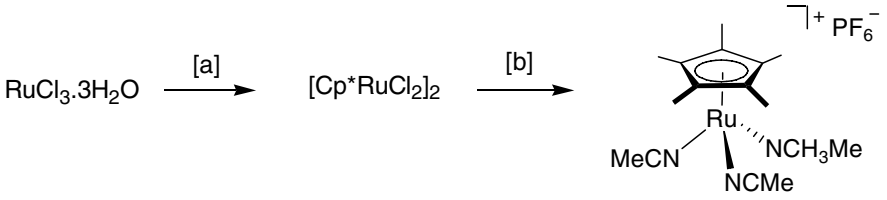
The naphthalene complex **8** (1.25 g, 2.85 mmol) was placed in a Schlenk tube equipped with a magnetic stirring bar. Dry, N_2-saturated actonitrile (13 mL) was added under N_2

♦ Caution: In the preparation of the microwave tube, care has to be exercised with the use of Al powder, which should be kept below the liquid surface. Using such precaution, five successive runs can be carried out using the same vial.

atmosphere. The yellow solution was stirred for 24 h at r.t. The resulting solution was washed with degassed hexane (3 × 18 mL) under N_2 atmosphere (naphthalene extraction). Then the acetonitrile solution was stirred for a further 24 h at r.t. followed by a second extraction by degassed hexane (4 × 18 mL) to give **4a** (1.2 g, quant.) as a yellow air-sensitive solid.

^{1}H NMR (400 MHz, acetone-d_6): δ 2.44 (s, 9 H), 4.25 (s, 5H). ^{13}C NMR (100 MHz, acetone-d_6): δ 2.4, 68.6, 125.9. IR (ν_{max}/cm^{-1}): 2282, 1412, 1032, 830, 556.

[Ru(η^5-Cp*)(CH$_3$CN)$_3$][PF$_6$] (4b)



4b

Step a: [Ru(η^5-Cp*)Cl$_2$]$_2$[7]

Ruthenium trichloride (2.30 g, 8.80 mmol) and pentamethylcyclopentadiene[8] (3.10 mL, 19.79 mmol, 2.25 eq.) were refluxed in freshly distilled and degassed ethanol (43 mL) for 3 h. The brown solid was filtered under nitrogen, and washed with degassed EtOH (2 × 9 mL), diethyl ether (2 × 9 mL), then hexane (2 × 25 mL). The dark brown solid was dried under vacuum to give [Ru(η^5-Cp*)Cl$_2$]$_2$ (2.7 g, quant). ^{1}H NMR (400 MHz, CD_2Cl_2): δ 6.06 (br s, 15H).

Step b: [Ru(η^5-Cp*)(CH$_3$CN)$_3$][PF$_6$] (4b)[9]

Zinc dust (0.085 g, 1.30 mmol) was added to a solution of [Ru(η^5-Cp*)Cl$_2$]$_2$ (0.400 g, 0.649 mmol) in dry, degassed acetonitrile (12 mL), and the mixture was stirred at r.t. for 1 h. Dry KPF_6 (0.179 g, 0.973 mmol) was added and the mixture was further stirred for 16 h at r.t.. The solvent was removed under vacuum and the residue was extracted with dry, degassed dichloromethane (25 mL), and filtered. After evaporation of volatiles, the residue was suspended in dry, degassed hexane and sonicated for a few minutes. The mixture was filtered, and the residue was washed with hexane and filtered again. The yellow solid **4b** was dried under vacuum (0.542 g, 83% yield). ^{1}H NMR (400 MHz,

CD_2Cl_2): δ 1.63 (s, 15H), 2.39 (br s, 9H). ^{13}C NMR (75 MHz, CD_2Cl_2): δ 3.8, 9.6, 80.3, 123.4.

The same procedure was used to prepare [Ru(η^5-$C_5Me_4CF_3$)(CH_3CN)$_3$][PF_6] (**4c**). 1,2,3,4-tetramethyl(trifluoromethyl)cyclopentadiene was prepared according to a literature procedure.[10]

4. Synthesis of substrates 5a-b and 6a-c

[Ru(η^5-Cp)(η^6-5,8-dibromonaphthalene)][PF_6] (5a)

[Ru(η^5-Cp)(CH_3CN)$_3$][PF_6] **4a** (3.3 g, 7.7 mmol) and 1,4-dibromonaphthalene[11] (3.31 g, 11.6 mmol) were placed in a Carrius tube, distilled and degassed CH_2ClCH_2Cl was added. The reaction mixture was heated to 80 ^{o}C and stirred for 20 h. After cooling to r.t., the reaction mixture was filtered over celite under nitrogen (washed with degassed CH_2ClCH_2Cl (3 x 10 mL)). The resulting solution was evaporated under vacuum and the residue was recrystallised with CH_2ClCH_2Cl/Hexane (30 mL/10 mL) 4 times to afford the product **5a** in 67 % yield. mp 205-207 °C (dec). ^{1}H NMR (400 MHz, CD_2Cl_2): δ 5.14 (s, 5H), 6.51 (dd, *J* = 4.4 Hz, *J* = 2.4 Hz, 2H), 7.32 (dd, *J* = 4.4 Hz, *J* = 2.4 Hz, 2H), 7.79 (s, 2H). ^{13}C NMR (100 MHz, CD_2Cl_2): δ 81.3, 84.5, 87.9, 97.9, 123.7, 135.0. ^{31}P NMR (162 MHz, CD_2Cl_2): δ -144.3 (sept, *J* = 708 Hz). IR (ν_{max}/cm^{-1}): 3121, 3089, 1603, 1523, 1471, 1415, 1345, 1237, 1171, 1109, 961, 870, 825, 780, 666. HRMS: *m/z* (ESI) calcd. for $C_{15}H_{11}Br_2Ru$ [M-PF_6]$^+$: 452.8252, found: 452.8242.

[Ru(η^5-Cp*)(η^6-5,8-dibromonaphthalene)][PF_6] (5b)

[Ru(η^5-Cp*)(CH_3CN)$_3$][PF_6] **4b** (7.5 g, 14.9 mmol) and 1,4-dibromonaphthalene[10] (6.40 g, 22.4 mmol) were stirred in dry, degassed THF (140 mL) at r.t. for 16 h. After that dry, degassed hexane (110 mL) was added and stirred for a few minutes. The precipitate was filtered and washed with 1:1 THF/hexane (100 mL). The crude product obtained was passed through a short column of neutral alumina with initially dichloromethane then 1:1 dichloromethane-acetone as eluent. Crystallisation from dichloromethane-pentane gave 4.62 g (47% yield) of complex **5b** as orange crystals. mp 251–253 ^{o}C (dec.). ^{1}H NMR

(400 MHz, CD_2Cl_2): δ 1.77 (s, 15H), 6.20 (dd, *J* = 4.6 Hz, *J* = 2.5 Hz, 2H), 6.87 (dd, *J* = 4.6 Hz, *J* = 2.5 Hz, 2H), 7.86 (s, 2H). ^{13}C NMR (100 MHz, CD_2Cl_2): δ 10.1, 85.4, 89.9, 96.5, 97.4, 122.6, 134.0. ^{31}P NMR (162 MHz, CD_2Cl_2): δ -144.1 (sept, *J* = 711 Hz). IR (ν_{max}/cm^{-1}): 3090, 2918, 1607, 1521, 1471, 1453, 1389, 1347, 1238, 1177, 1109, 1076, 1028, 985, 958, 869, 823, 740, 666. HRMS: *m/z* (ESI) calcd. for $C_{20}H_{21}Br_2Ru$ $[M\text{-}PF_6]^+$: 519.9054, found: 519.9031. Elemental analysis (%) calcd for $C_{20}H_{21}Br_2PF_6Ru$ (667.22): C 36.00, H 3.17; found C 35.99, H 3.06.

General procedure for substrates 6a-c[12]

To a cooled (0°C) solution of the corresponding indene[13] ligand in dried and degassed THF was added NaHMDS (1M in THF solution, 1 eq.). The resulting solution was stirred at 0°C for 30 min before being added to a cooled (0°C) Schlenk containing **4** (1 eq.). The mixture was stirred overnight, filtered through a short pad of silica and concentrated under vacuum. The residue was purified by flash chromatography (pentane) to afford complex **6**. Racemic complexes **11** were also prepared according to this procedure.

[Ru(η^5-Cp)(η^5-4,7-dibromoindene)] (6a)

2.4 g (92% yield) of orange crystals were obtained after flash chromatography (pentane) and crystallisation from dichloromethane / pentane, starting with 2.8 g (6.40 mmol, 1 eq.) of complex **4a**, 6.5 mL (6.40 mmol, 1 eq.) of NaHMDS solution (1M THF) and 1.80 g of 4,7-dibromoindene (6.40 mmol, 1 eq.) in 20 mL of THF. mp 152-154°C. HPLC (Daicel Chiralcel OD-H; hexane:*i*PrOH 99:1; 0.5 mL min^{-1}; λ = 254 nm): t_R = 10.2 min. ^1H NMR (400 MHz, $CDCl_3$): δ 4.33 (s, 5H), 4.69 (t, *J* = 2.3 Hz, 1H), 5.39 (d, *J* = 2.3 Hz, 2H), 6.84 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 67.9, 70.7, 73.5, 93.9, 121.0, 124.6. IR (ν_{max}/cm^{-1}): 3090, 1798, 1740, 1600, 1466, 1427, 1404, 1375, 1309, 1291, 1240, 1133, 1097, 1028, 996, 890, 833, 816, 800. HRMS: *m/z* (EI) calcd. for $C_{14}H_{10}Br_2Ru$ [M, $^{96}Ru]^+$: 431. 8225, found: 431.8220. Elemental analysis (%) calcd for $C_{14}H_{10}Br_2Ru$ (439.11): C 38.29, H 2.30; found C 38.35, H 2.27.

[Ru(η^5-Cp*)(η^5-4,7-dibromoindene)] (6b)

4.50 mg (68% yield) of orange crystals were obtained after flash chromatography on (pentane) and crystallisation from dichloromethane / pentane, starting with 3.47 mg (13.0 mmol, 1 eq.) of complex **4b**, 13.0 mL (13.0 mmol, 1 eq.) of NaHMDS solution (1M THF) and 6.40 g of 4,7-dibromoindene (13.0 mmol, 1 eq.) in 30 mL of THF. mp 170-172°C. HPLC (Pirkle Covalent; hexane:*i*PrOH 100:0; 0.5 mL min^{-1}; λ = 254 nm): t_R =. 16.1 min. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 1.67 (s, 15H), 4.52 (t, *J* = 2.5 Hz, 1H), 4.96 (d, *J* = 2.5 Hz, 2H), 6.85 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 10.4, 70.3, 77.7, 83.7, 93.9, 119.2, 122.4. IR (ν_{max}/cm^{-1}): 3078, 3040, 2965, 2897, 2852, 1737, 1592, 1498, 1471, 1441, 1377, 1372, 1328, 1297, 1127, 1029, 891, 870, 801, 783, 752, 706. HRMS: *m/z* (EI) calcd. for $C_{19}H_{20}Br_2Ru$ [M, ^{96}Ru]$^+$: 501.9007, found: 501.9000. Elemental analysis (%) calcd for $C_{19}H_{20}Br_2Ru$ (509.24): C 44.81, H 3.96; found C 44.72, H 3.89.

[Ru(η^5-$C_5Me_4CF_3$)(η^5-4,7-dibromoindene)] (6c)

Orange crystals. (31 % over 3 steps based on Ru). mp 118-119°C. HPLC (Pirkle Covalent; hexane:*i*PrOH 100:0; 0.5 mL min^{-1}; λ = 254 nm): t_R = 17.5 min. ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.53 (s, 6H), 1.83 (q, $^5J_{CF}$ = 1.0 Hz, 6H), 4.71 (t, *J* = 2.6 Hz, 1H), 5.17 (d, *J* = 2.5 Hz, 2H), 6.92 (s, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 9.1, 10.7 (q, $^5J_{CF}$ = 1.8 Hz), 71.1, 76.7 (q, $^2J_{CF}$ = 36.0 Hz), 78.0, 82.7 (q, $^3J_{CF}$ = 1.4 Hz), 86.0, 94.9, 119.4, 123.8, 127.6 (q, $^1J_{CF}$ = 270 Hz). ^{19}F NMR (470 MHz, CD_2Cl_2): δ –53.0.IR (ν_{max}/cm^{-1}): 2914, 1597, 1556, 1467, 1424, 1237, 1160, 1110, 1099, 1017, 893, 806. HRMS: *m/z* (EI) calcd. for $C_{19}H_{17}Br_2F_3Ru$ [M, ^{96}Ru]$^+$: 555.87250, found: 555.87209.

5. General procedures

a) Procedure for the desymmetrisation of 5

$[Pd(allyl)Cl]_2$[14] (1-5 mol%) and phosphoramidite ligand (*S*,*R*,*R*)-L* (4-7 mol%) were placed in a Schlenk tube and purged with N_2. Dry, degassed dichloromethane was added and the solution was stirred for 30 min at r.t. before cooling to -40 °C. Complex **5** followed by DABCO (1.5 eq.) and then dry, degassed dichloromethane was added to the

mixture. The mixture was stirred for 10 min before $LiBH_4$ in DME (1.5 eq.) solution was added dropwise over 10 min. After stirring for 3-4 h at -40 ^oC, 1 M HCl was added and stirred for 10 min at -40 ^oC before warming to r.t. The organic layer was separated and washed with 1 M HCl, water and dried ($MgSO_4$). The solvents were removed using rotary evaporator and the solid was dried under vacuum before being analyzed by ^1H NMR first without [Δ-TRISPHAT][NBu_4] (CD_2Cl_2 as solvent), then with 2 eq. of [Δ-TRISPHAT][NBu_4] ($CDCl_3$ as solvent). The crude product was dissolved in minimum amount of $CHCl_3$ and filtered through celite (to remove some of the colorless DABCO-bis(BH_3) adduct) washing with small amount of $CHCl_3$-diethyl ether. This process was repeated before recrystallisation was performed with CH_2Cl_2-diethyl ether to give yellow crystals (mixture of **9** and **10**). Such purification steps were repeated for the combined 'mother liquor' to obtain more of the products.

[Ru(η^5-Cp)(η^6-5-bromonaphthalene)][PF_6] (9a)

mp 173-174°C (dec). ^1H NMR (400 MHz, CD_2Cl_2): δ 5.09 (s, 5H), 6.35 (t, *J* = 5.8 Hz, *J* = 2.4 Hz, 2H), 6.37 (t, *J* = 5.8 Hz, 1H), 7.02 (d, *J* = 5.8 Hz, 1H), 7.26 (d, *J* = 6.0 Hz, 1H), 7.48 (dd, *J* = 8.8 Hz, *J* = 7.3 Hz , 1H), 7.77 (d, *J* = 8.8 Hz, 1H), 7.94 (d, *J* = 7.3 Hz, 1H). ^{13}C NMR (100 MHz, CD_2Cl_2): δ 80.8, 83.7, 84.8, 86.9, 87.2, 96.7, 98.9, 124.0, 129.6, 132.4, 135.3. ^{31}P NMR (162 MHz, CD_2Cl_2): δ -143.3 (sept, *J* = 709 Hz). IR (ν_{max}/cm^{-1}): 3130, 3090, 1603, 1618, 1518, 1471, 1416, 1404, 1344, 1238, 1191, 1070, 1008, 920, 911, 810, 784, 724, 656. HRMS: *m/z* (ESI) calcd. for $C_{15}H_{12}BrRu$ $[M\text{-}PF_6]^+$: 374.9154, found: 374.9125.

[Ru(η^5-Cp*)(η^6-5-bromonaphthalene)][PF_6] (9b)

mp 246-248 ^oC (decomp.). ^1H NMR (400 MHz, CD_2Cl_2): δ 1.73 (s, 15H), 6.05 (t, *J* = 6.0 Hz, 1H), 6.10 (t, *J* = 6.0 Hz, 1H), 6.51 (d, *J* = 6.0 Hz, 1H), 6.81 (d, *J* = 6.0 Hz, 1H), 7.52-7.61 (m, 2H), 8.04 (dd, *J* = 6.3 Hz, *J* = 1.8 Hz, 1H).^{13}C NMR (100 MHz, CD_2Cl_2): δ 10.0, 85.1, 85.9, 89.1, 89.4, 95.6, 96.7, 98.6, 123.0, 128.0, 131.6, 134.4. ^{31}P NMR (162 MHz, CD_2Cl_2): δ -144.1 (sept, *J* = 711 Hz). IR (ν_{max}/cm^{-1}): 3092, 2907, 1616, 1516, 1472, 1388, 1350, 1241, 1192, 1159, 1076, 1035, 952, 872, 827, 780, 723, 655. HRMS: *m/z* (ESI) calcd. For $C_{20}H_{22}BrRu$ $[M\text{-}PF_6]^+$: 442.9943, found: 442.9970.

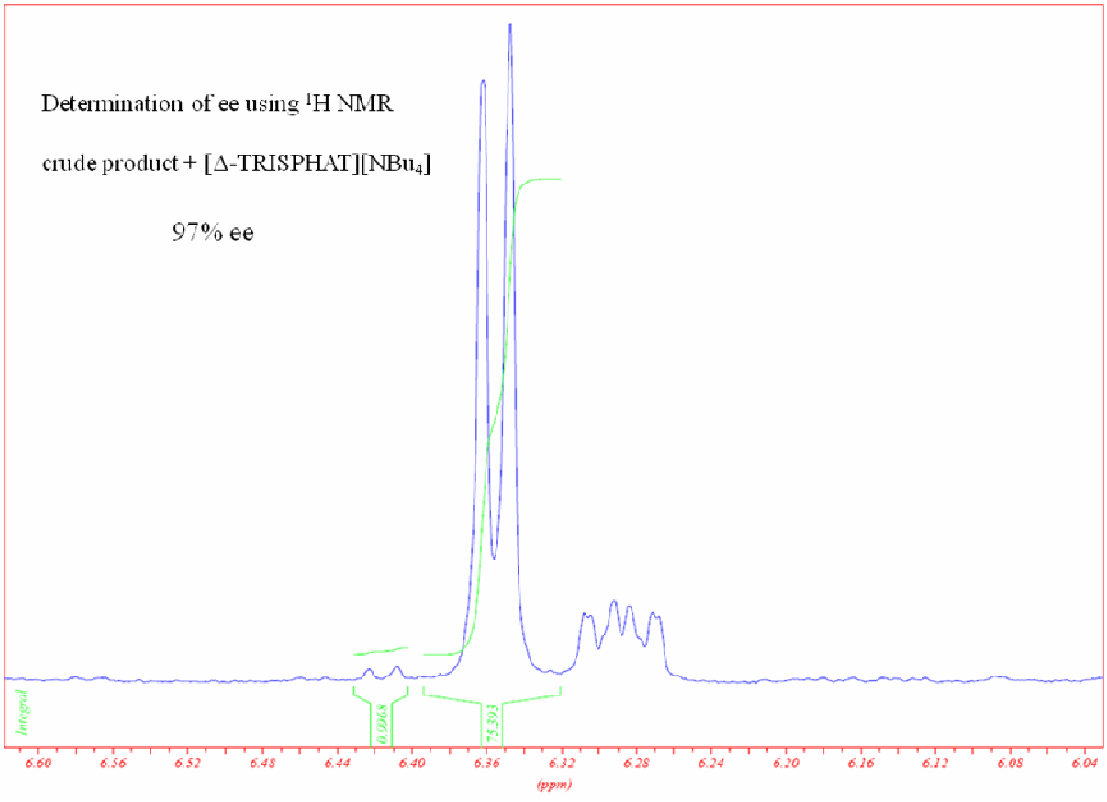
[Ru(η^5-Cp)(η^6-naphthalene)][PF$_6$] (10a)

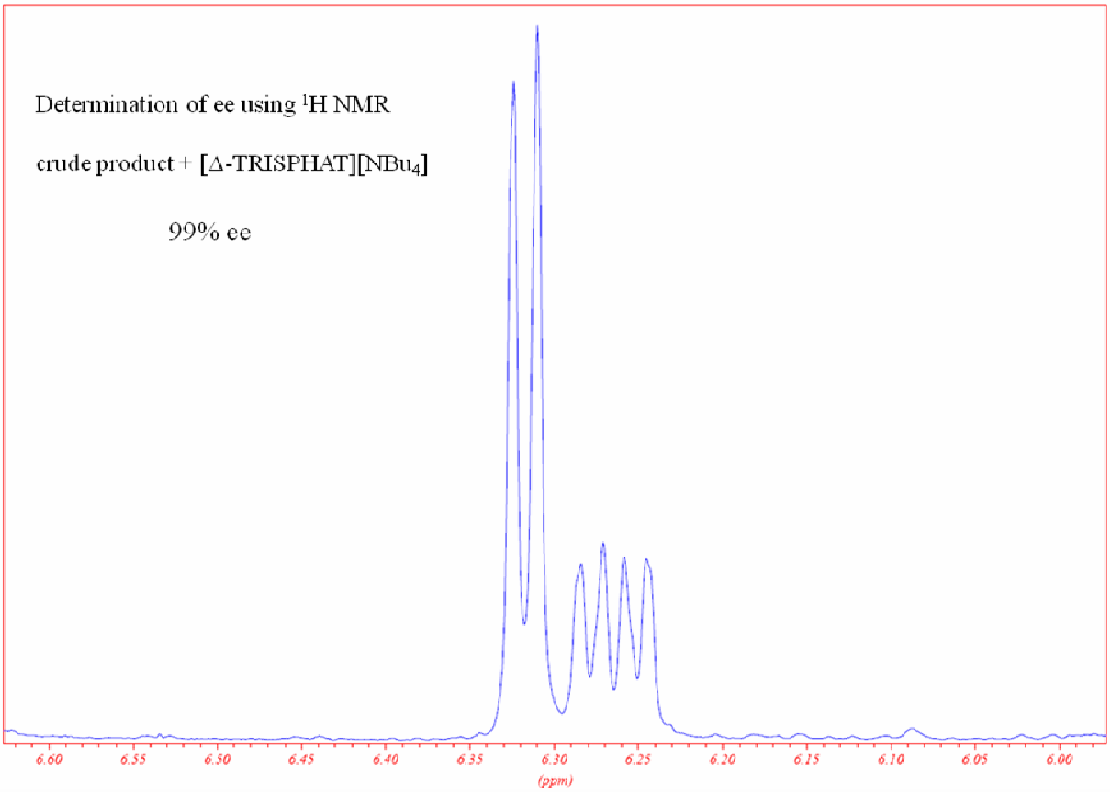
mp 155-160°C (dec.). ^{1}H NMR (400 MHz, acetone-d_6): δ 5.15 (s, 5H), 6.47-6.48 (m, 2H), 7.24-725 (m, 2H), 7.70-7.73 (m, 2H), 7.89-7.92 (m, 2H). ^{13}C NMR (100 MHz, acetone-d_6): 79.7, 83.9, 85.9, 97.2, 129.3, 131.5. ^{31}P NMR (162 MHz, acetone-d_6): δ -144.1 (sept, J = 708 Hz). MS: *m/z* (ESI) 295 $[M+H]^+$.

[Ru(η^5-Cp*)(η^6-naphthalene)][PF$_6$] (10b)

^{1}H NMR (400 MHz, CD_2Cl_2): δ 1.69 (s, 15H), 6.01 (dd, J = 4.4 Hz, J = 2.3 Hz, 2H), 6.44 (dd, J = 4.4 Hz, J = 2.3 Hz, 2H), 7.53 (dd, J = 6.7 Hz, J = 3.1 Hz, 2H), 7.74 (dd, J = 6.7 Hz, J = 3.1 Hz, 2H). ^{13}C NMR (100 MHz, CD_2Cl_2): δ 10.0, 85.7, 88.6, 94.7, 97.6, 128.0, 131.8. ^{31}P NMR (162 MHz, CD_2Cl_2): δ -144.1 (sept, J = 710 Hz).

b) Determination of *ee* of 9b in the presence of [*n*-Bu$_4$N][Δ-TRISPHAT]





c) Procedure for the microwave-assisted cross-coupling [Ru(η^5-Cp*)(η^6-5-phenylnaphthalene)][PF$_6$] ((*S*)-13b). The crystalline mixture of complexes **5b** and **10b** (90% **5b** (97% ee) and 10% **10b**, 323.3 mg, 0.50 mmol of **5b**), $Pd(OAc)_2$ (5.6 mg, 0.025 mmol, 5 mol%), P(*o*-tol)$_3$ (15.2 mg, 0.050 mmol, 10 mol%), phenylboronic acid (183 mg, 1.5 mmol, 3 eq.) and K_3PO_4 (318 mg, 1.5 mmol, 3 eq.) were placed in a 20 mL microwave vial, sealed and purged with N_2. Degassed methanol (12 mL) was added and sonicated for 2 min. before being subjected to microwave irradiation for 15 min. at 100 ^oC (pre-stirring 30 seconds, initial power ~180 W, after the temperature had reached 100 ^oC, the temperature was maintained for 15 min with power of ~30 W). The mixture was filtered through celite washing with dichloromethane. The solvents were removed using rotary evaporator. The residue was redissolved in dichloromethane (40 mL), washed with saturated $NaHCO_3$ (3 × 30 mL), then with water (2 × 40 mL) and dried ($MgSO_4$). The solvent was removed and the residue was redissolved in acetone (10 mL). KPF_6 (386 mg, 2.1 mmol) was added and stirred at r.t. for 30 min. The solvent was removed and the crude product was passed through a short column of neutral alumina eluting with initially CH_2Cl_2 and then with 2:1 CH_2Cl_2-

acetone. Crystallisation from CH_2Cl_2-diethyl ether gave 0.155 g (53% yield) of complex (*S*)-**13b** as orange crystals. mp 213-214 °C. $[\alpha]_D^{25.4}$ = +434 (*c* 0.59, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.62 (s, 15H), 6.00 (t, *J* = 6.0 Hz, 1H), 6.12 (t, *J* = 6.0 Hz, 1H), 6.41 (d, *J* = 6.0 Hz, 1H), 6.65 (d, *J* = 6.0 Hz, 1H), 7.38-7.74 (m, 8H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 10.0, 83.4, 85.8, 88.6, 89.3, 94.6, 96.8, 97.9, 128.0, 129.3, 129.6, 129.7, 130.6, 131.1, 137.5, 139.8. ^{31}P NMR (162 MHz, $CDCl_3$): δ -143.8 (sept, *J* = 713 Hz). IR (ν_{max}/cm^{-1}): 2922, 1475, 1450, 1387, 1354, 1078, 1031, 868, 831, 792, 760, 738, 705, 695, 617. HRMS: *m/z* (ESI) calcd. For $C_{26}H_{27}Ru$ $[M\text{-}PF_6]^+$: 441.1150, found: 441.1159. Elemental analysis (%) calcd for $C_{26}H_{27}PF_6Ru$ (585.53): C 53.33, H 4.65; found C 53.10, H 4.63. Enantiomeric purity was determined by ^{1}H NMR with 1.7 equivalents of [Δ-TRISPHAT][NBu_4] using $CDCl_3$ as solvent.

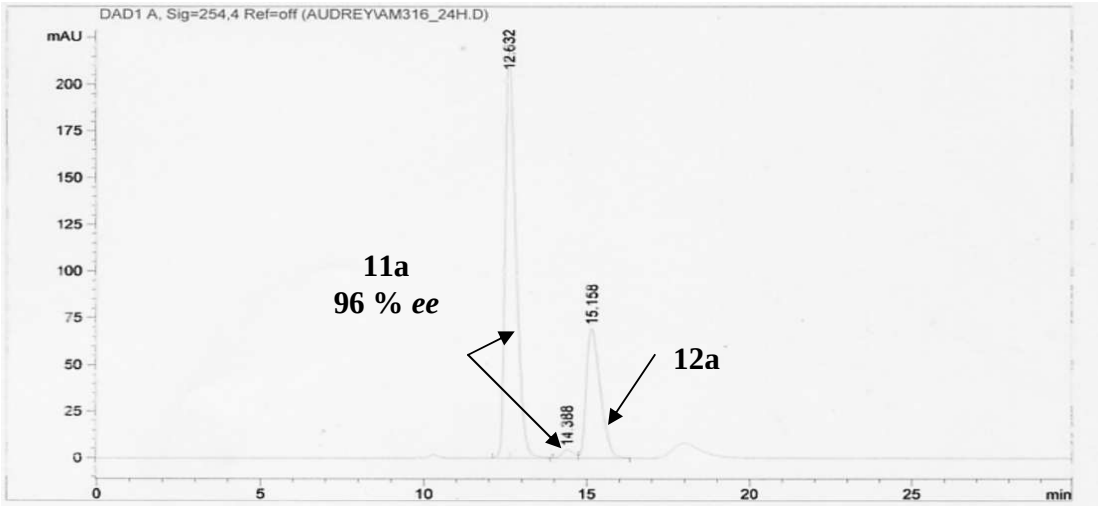
d) Procedure for the desymmetrisation of 6

$Pd(dba)_2$ (5 mol%) and phosphoramidite ligand (S_a,*R*,*R*)-L* (7 mol%) were placed in a Schlenk tube and purged with N_2. Dry, degassed toluene was added and the solution was stirred for 2 h 30 at r.t. The tube was cooled to -20°C, then complex **6** and DABCO (1.5 eq.) followed by dry, degassed toluene were added. The mixture was stirred for 5 min. before $LiBH_4$ in DME solution (1.5 eq.) was added dropwise (over 5 min.). After stirring for the time required at -20°C, the mixture was passed through a short pad of silica (pentane) and concentrated. Separation of **11** and **12** could be achieved through flash chromatography (silica gel, pentane).

[Ru(η^5-Cp)(η^5-4-bromoindene)] (11a)

mp 70-72°C. $[\alpha]_D^{25}$ = +746 (*c* = 0.61, $CHCl_3$). HPLC (Daicel Chiralcel OD-H; hexane:*i*PrOH 99:1; 0.5 mL min^{-1}; λ = 254 nm): t_{R1} = 12.6 min, t_{R2} = 14.4 min. ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.27 (s, 5H), 4.64 (t, *J* = 2.4 Hz, 1H), 5.30-5.32 (m, 2H), 6.58-6.64 (m, 1H), 6.99 (d, 1H, *J* = 6.9 Hz), 7.36 (d, *J* = 8.7 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 66.6, 67.0, 70.3, 73.0, 93.1, 121.8, 122.8, 124.5, 126.0. IR (ν_{max}/cm^{-1}): 3088, 3046, 2918, 1498, 1467, 1440, 1405, 1332, 1299, 1168, 1128, 1099, 1031, 996, 886, 849, 811, 784, 764, 709. HRMS: *m/z* (EI) calcd. for $C_{14}H_{11}BrRu$ [M, ^{96}Ru]$^+$: 353.9120, found:

353.9117. Elemental analysis (%) calcd for $C_{14}H_{11}BrRu$ (360.21): C 46.68, H 3.08; found C 46.84, H 3.01.

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Use Multiplier & Dilution Factor with ISTDs


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Totals :                  7339.52965  292.84300
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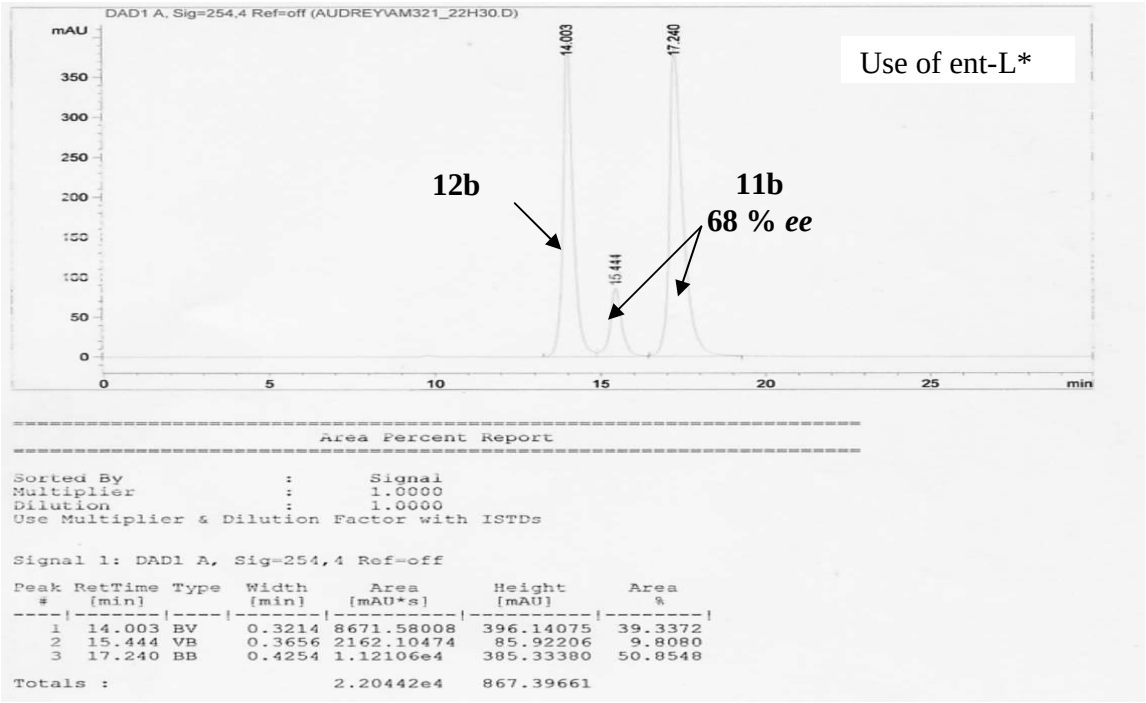
[Ru(η^5-Cp)(η^5-indene)] (12a)

mp 96-98°C. HPLC (Daicel Chiralcel OD-H; hexane:*i*PrOH 99:1; 0.5 mL min^{-1}; λ = 254 nm): t_R = 15.2. min. ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.20 (s, 5H), 4.58 (t, *J* = 2.3 Hz, 1H), 5.22 (d, *J* = 2.3Hz, 1H), 6.76 (m, 2H), 7.36 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 65.7, 69.9 , 72.6, 87.1, 122.5, 126.7. IR (ν_{max}/cm^{-1}): 3092, 3078, 3049, 3021, 2922, 1790, 1516, 1461, 1405, 1336, 1244, 1178, 1099, 1022, 1001, 988, 860, 814, 800, 737, 725. HRMS: *m/z* (EI) calcd for $C_{14}H_{12}Ru$ [M, ^{96}Ru]$^+$: 276.0015, found: 276. 0016.

[Ru(η^5-Cp*)(η^5-4-bromoindene)] (11b)

mp 127-129°C. HPLC (Pirkle Covalent; hexane:*i*PrOH 100:0; 0.5 mL min^{-1}; λ = 254 nm): t_{R1} = 15.4 min, t_{R2} = 17.2 min. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 1.63 (s, 15H), 4.47 (t, *J* = 2.5 Hz, 1H), 4.84 (dd, *J* = 2.5 Hz, *J* = 1.5 Hz, 1H), 4.86 (dd, *J* = 2.5 Hz, *J* = 0.8

Hz, 1H), 6.62 (dd, *J* = 8.6 Hz, *J* = 6.8 Hz, 1H), 7.05 (dd, *J* = 6.8 Hz, *J* = 0.8 Hz, 1H), 7.12 (dd, *J* = 8.6 Hz, *J* = 0.8 Hz 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 10.7, 69.3, 77.3, 82.9, 93.1, 93.3, 120.6, 120.9, 122.6, 124.5. IR (ν_{max}/cm^{-1}): 3040, 2964, 2896, 2851, 1739, 1600, 1498, 1471, 1441, 1378, 1371, 1327, 1287, 1167, 1126, 1029, 893, 871, 801, 783, 752, 706. HRMS: *m/z* (EI) calcd. for $C_{19}H_{21}BrRu$ [M, ^{102}Ru]$^+$: 429.9870, found: 429.9857. Elemental analysis (%) calcd for $C_{19}H_{21}BrRu$ (430.34): C 53.03, H 4.92; found C 53.00, H 4.99.



Area Percent Report

Sorted By : Signal
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Use Multiplier & Dilution Factor with ISTDs

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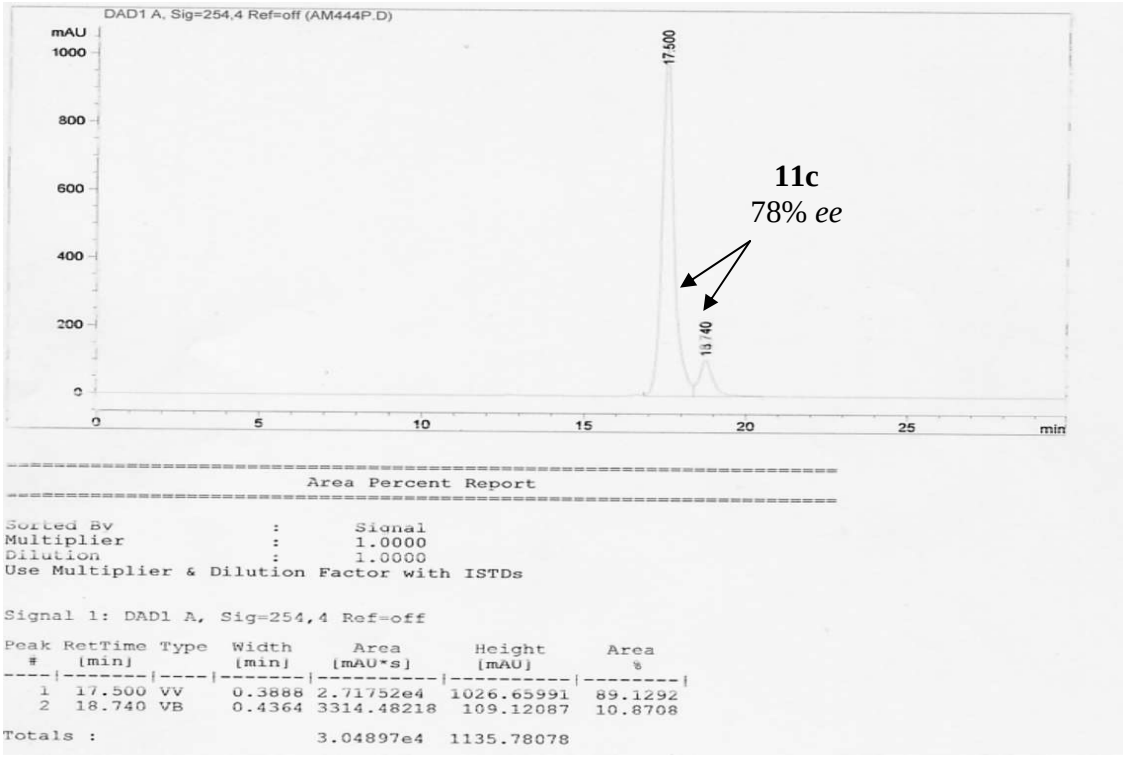
[Ru(η^5-Cp*)(η^5-indene)] (12b)

HPLC (Pirkle Covalent; hexane:*i*PrOH 100:0; 0.5 mL min^{-1}; λ = 254 nm): t_R = 14.0. min. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 1.64 (s, 15H), 4.42 (t, *J* = 2.2 Hz, 1H), 4.75 (d, *J* = 2.2 Hz, 2H), 6.82-6.85 (m, 2H), 7.09-7.12 (m, 2H). MS (ESI): *m/z* = 352 [M+H]$^+$.

[Ru(η^5-C$_5$Me$_4$CF$_3$)(η^5-4-bromoindene)] (11c)

mp 85-87°C. HPLC (Pirkle Covalent; hexane:*i*PrOH 100:0; 0.5 mL min^{-1}; λ = 254 nm): t_{R1} = 17.5 min, t_{R2} = 18.7 min. ^{11}H NMR (500 MHz, CD_2Cl_2): δ 1.53 (s, 3H), 1.61 (s, 3H), 1.65 (q, $^5J_{CF}$ = 1.1 Hz, 3H), 4.66 (t, *J* = 2.5 Hz, 1H), 5.08 (dd *J* = 1.6 Hz, *J* = 0.9 Hz, 1H), 5.10 (dd, *J* = 2.5 Hz, *J* = 1.1 Hz, 1H), 6.72 (dd, *J* = 8.7 Hz, *J* = 6.9 Hz, 1H), 7.11

(dd, J = 6.9 Hz, J < 1 Hz, 1H), 7.14 (dt, J = 8.7 Hz, J < 1Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 9.6, 10.0, 10.4 (q, $^5J_{CF}$ = 1.8 Hz), 11.2 (q, $^5J_{CF}$ = 1.9 Hz), 70.4, 76.5 (q, $^2J_{CF}$ = 35.8 Hz), 78.2, 82.2 (q, $^3J_{CF}$ = 1.4 Hz), 82.3 (q, $^3J_{CF}$ = 1.4 Hz), 86.0, 86.1, 94.5, 94.8, 120.4, 122.7, 124.3, 124.9, 128.4 (q, $^1J_{CF}$ = 270 Hz). ^{19}F NMR (470 MHz, CD_2Cl_2): δ -53.2. HRMS: *m/z* (EI) calcd. for $C_{19}H_{18}BrF_3Ru$ [M, ^{96}Ru]$^+$: 477.96198, found: 477.96134.



Area Percent Report

Sorted By : Signal
Multiplier : 1.0000
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Use Multiplier & Dilution Factor with ISTDs

Signal 1: DAD1 A, Sig=254,4 Ref=off

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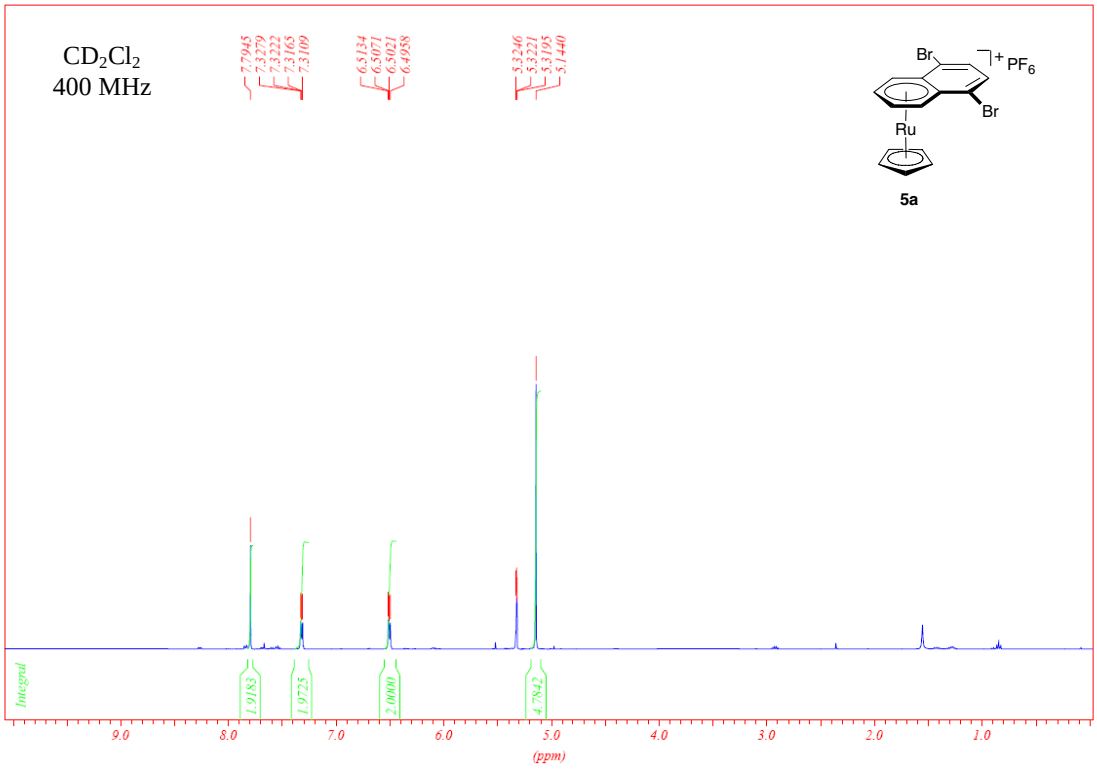
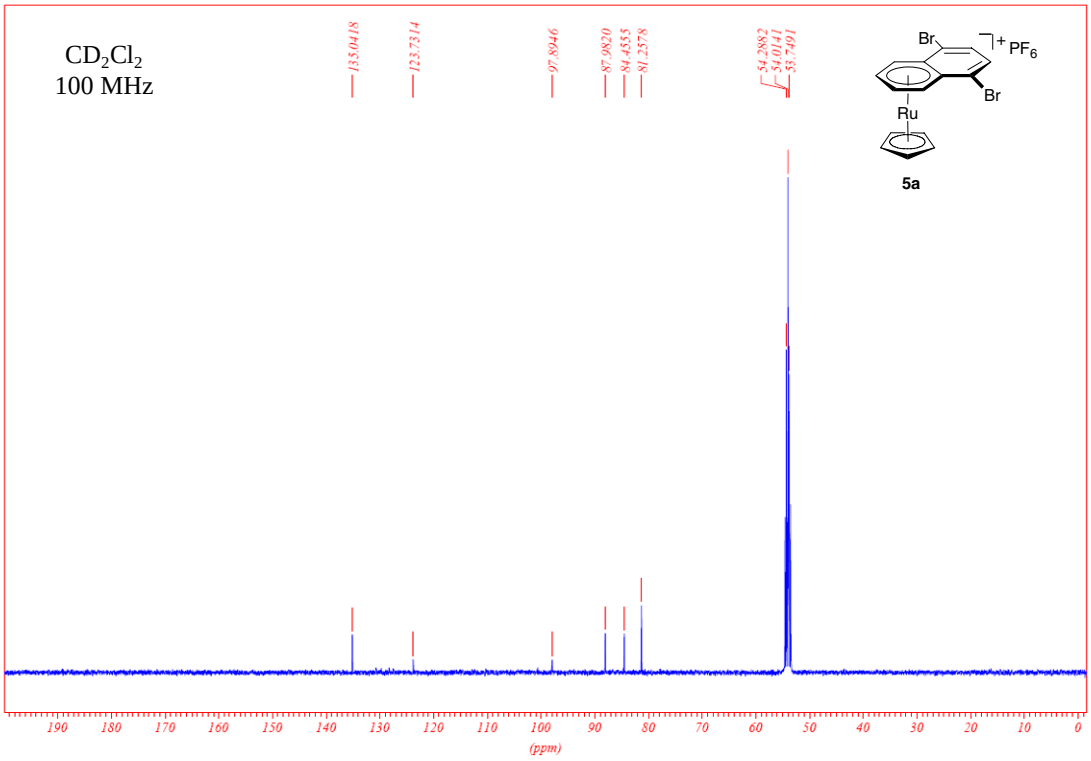
Totals :				3.04897e4	1135.78078	

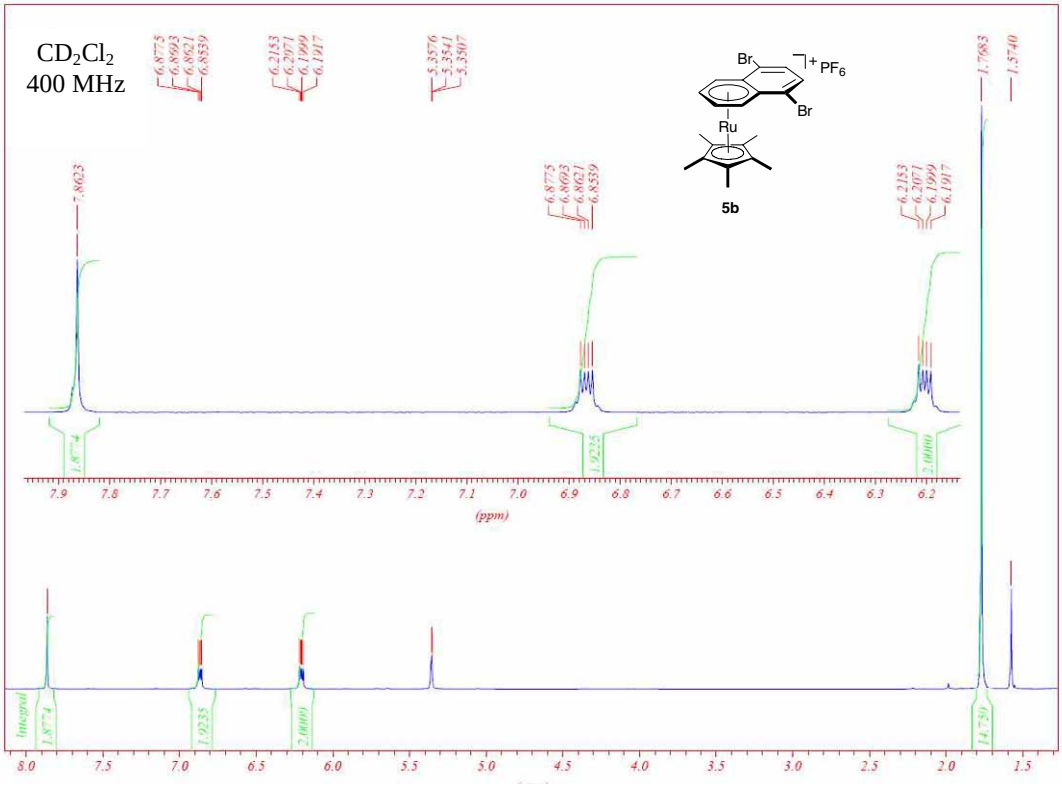
[Ru(η^5-C$_5$Me$_4$CF$_3$)(η^5-indene)] (12c)

mp 59-60°C. HPLC (Pirkle Covalent; hexane:*i*PrOH 100:0; 0.5 mL min^{-1}; λ = 254 nm): t_R = 16.6 min. ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.54 (s, 6H), 1.70 (q, $^5J_{CF}$ = 1.1 Hz, 6H), 4.58 (t, J = 2.4 Hz, 1H), 4.96 (dd, J = 2.4 Hz, J = 0.6 Hz, 2H), 6.95-6.85 (m, 2H), δ 7.17-7.06 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 10.0, 10.6 (q, $^5J_{CF}$ ≈ 2 Hz), 69.0, 75.5 (q, $^2J_{CF}$ = 35.7 Hz), 77.4, 81.2 (q, $^3J_{CF}$ = 1.4 Hz), 85.0, 93.1, 122.2, 124.9, 127.9 (q, $^1J_{CF}$ = 270 Hz). ^{19}F NMR (470 MHz, CD_2Cl_2): δ -52.9. ν_{max}/cm^{-1}: 2913, 1449, 1428, 1382, 1338, 1243, 1158, 1111, 1098, 1018, 741.

6. Spectroscopic data



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Ru
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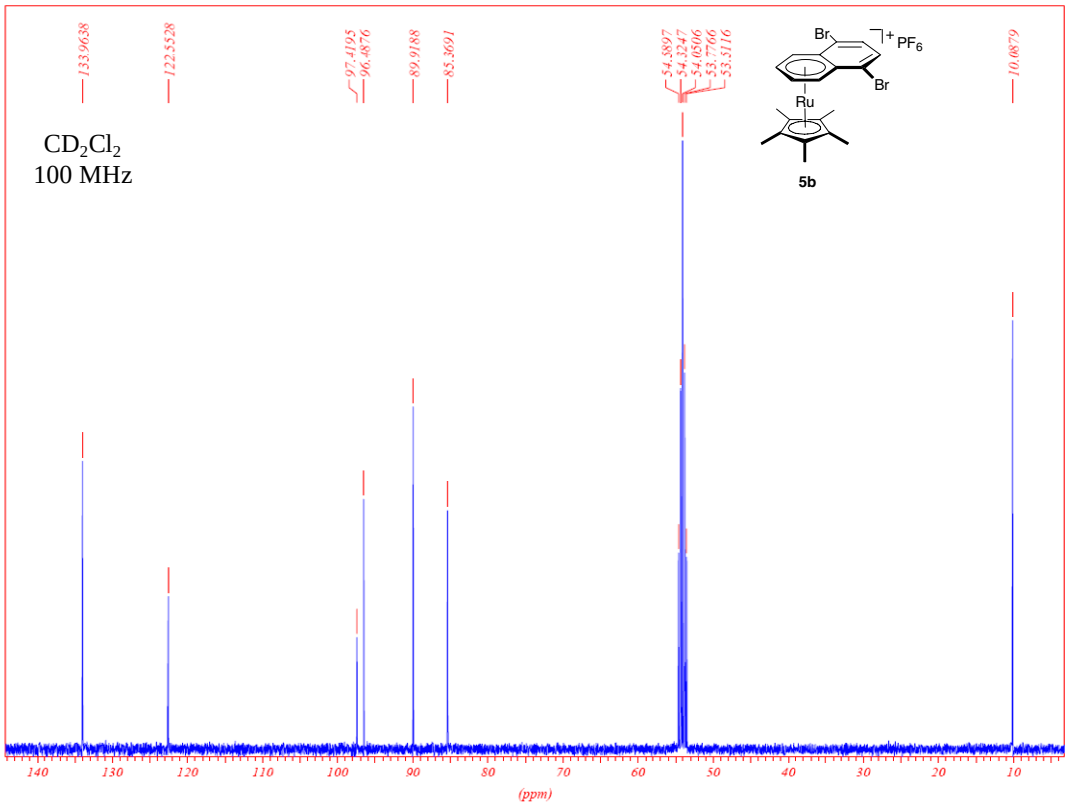
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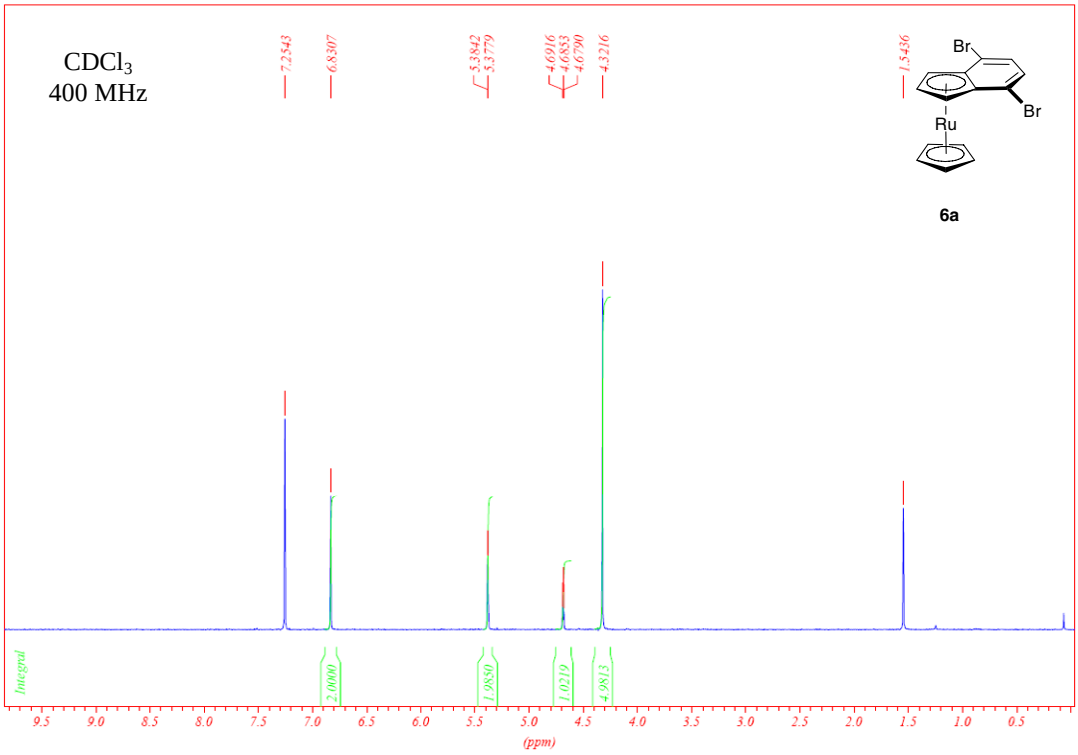
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Br
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Integral
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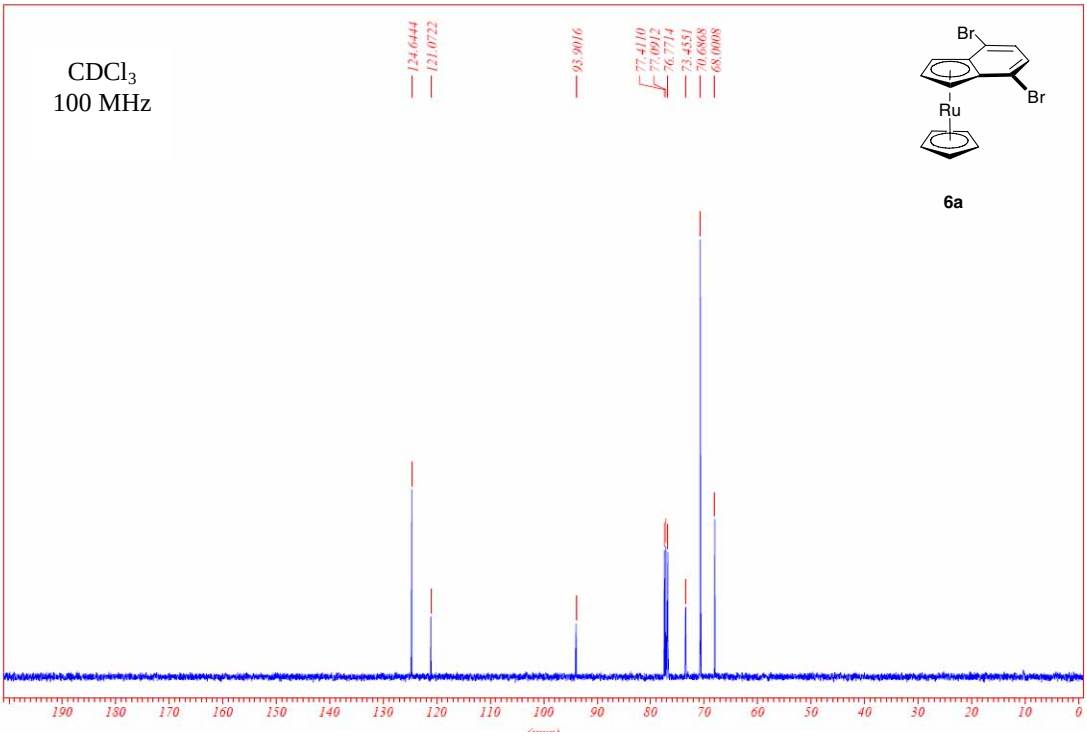
1.9850
1.0219
4.9813
(ppm)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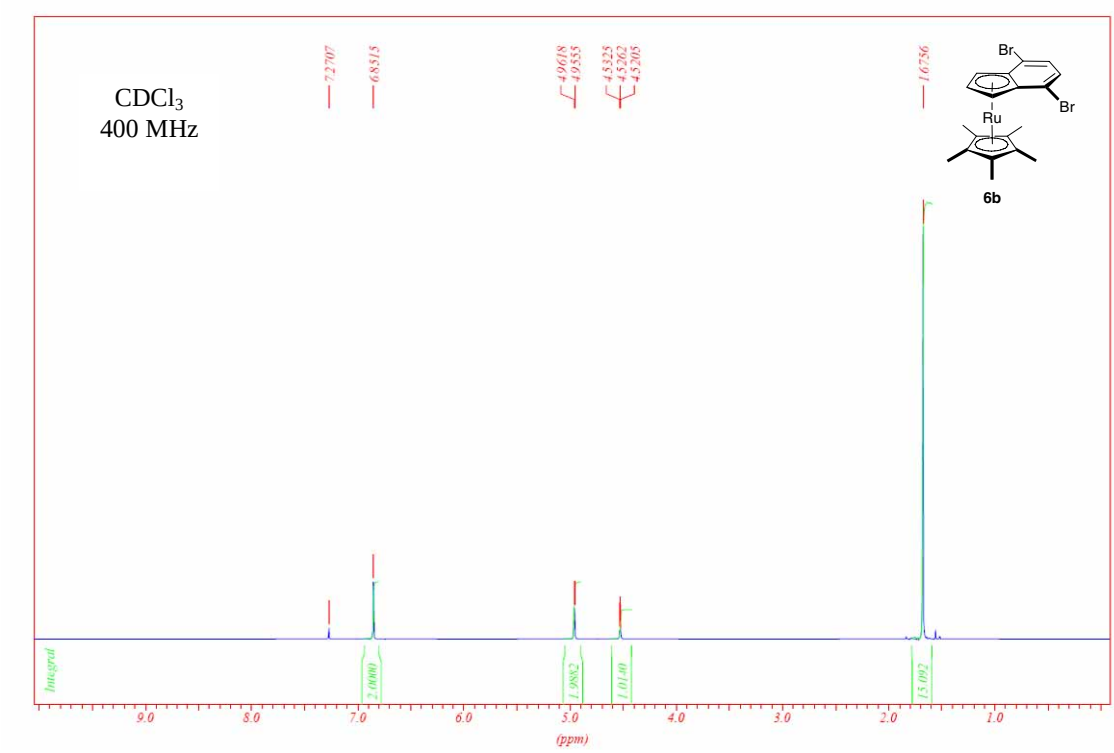
Br
Ru
6a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Ru
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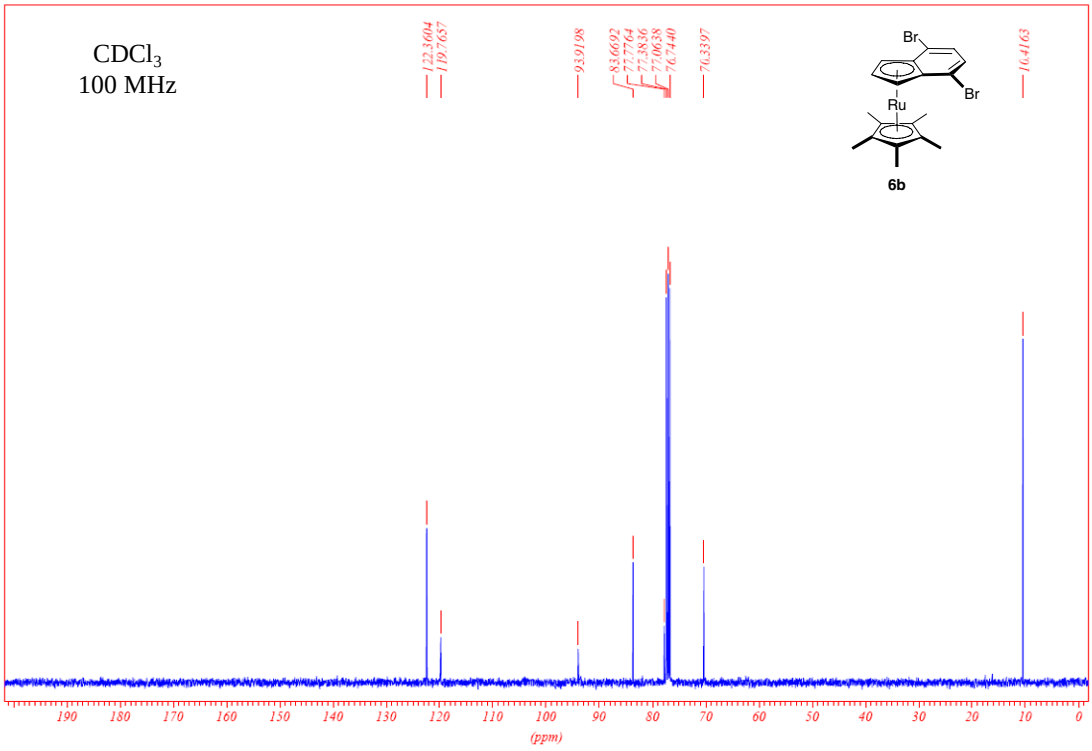
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Br
Br
Ru
6b
190
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120
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60
50
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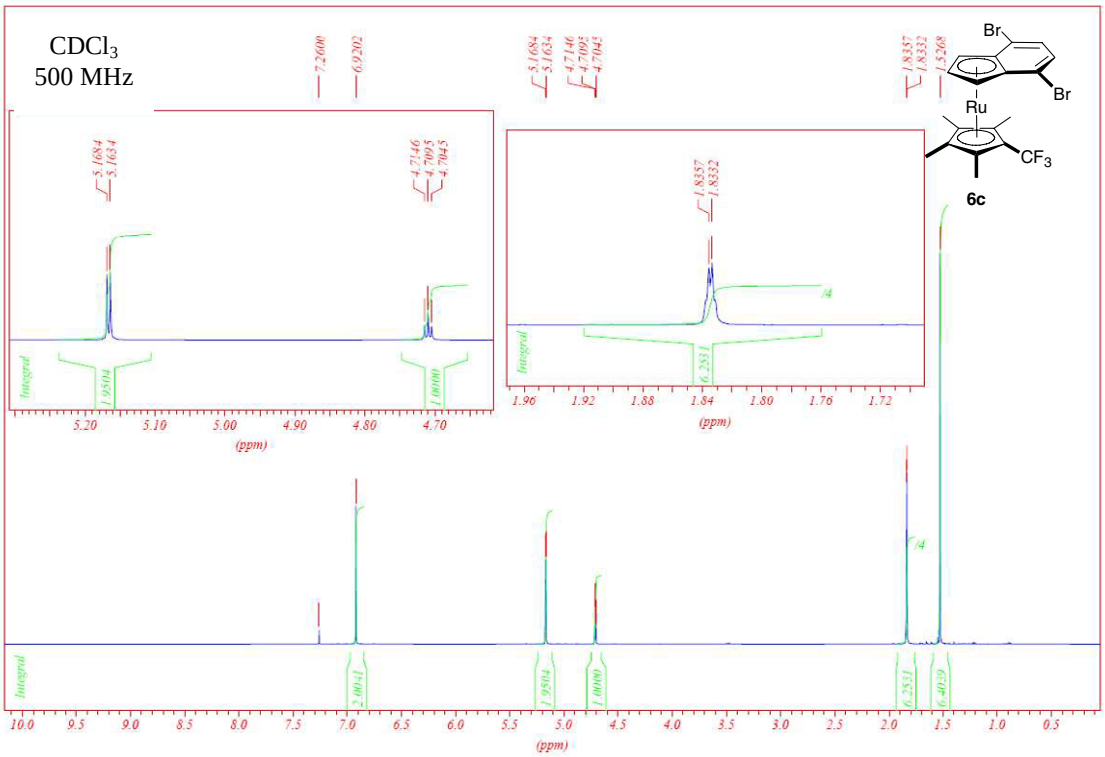
20
10
0
(ppm)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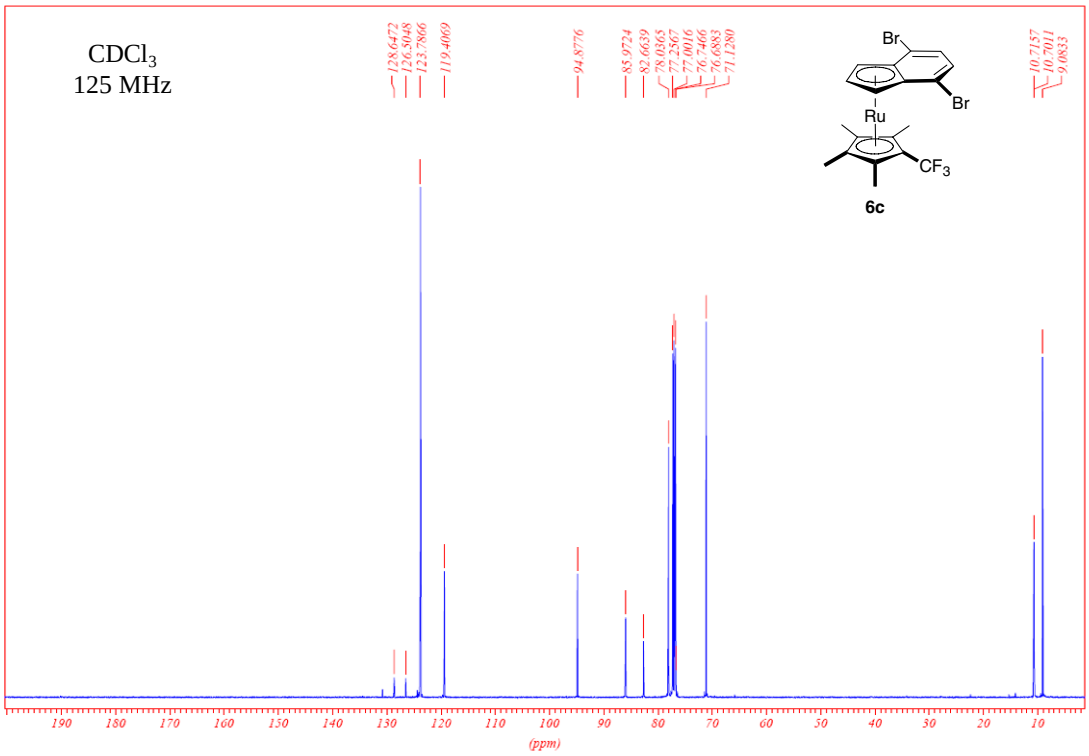
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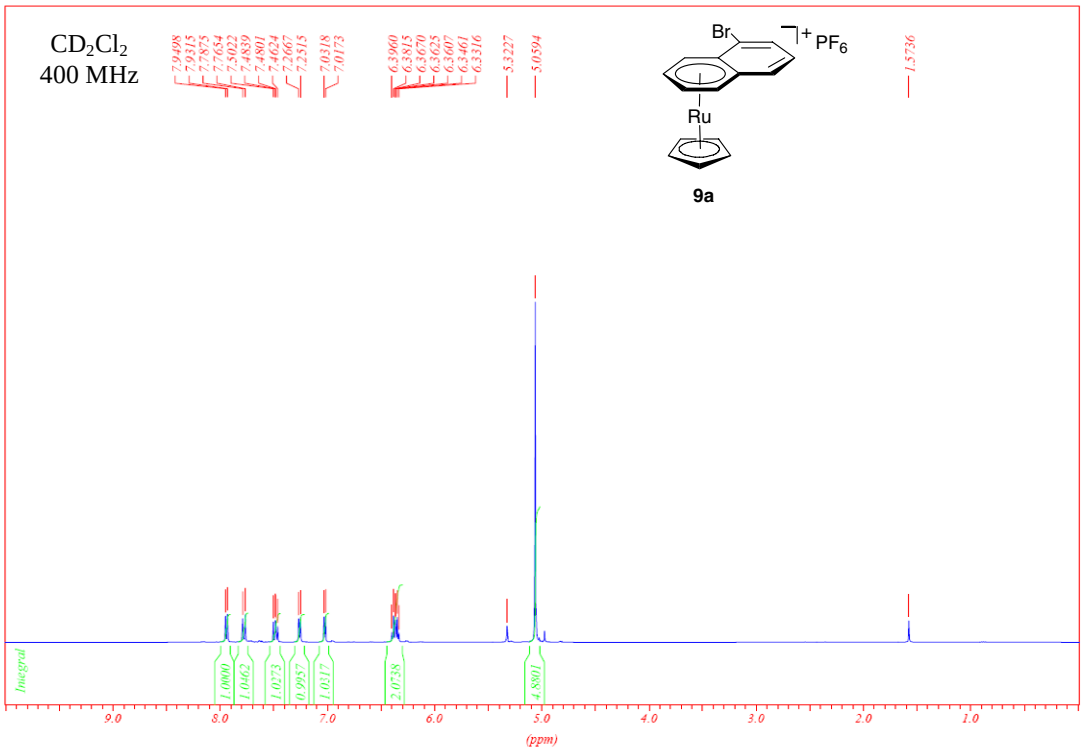
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400 MHz
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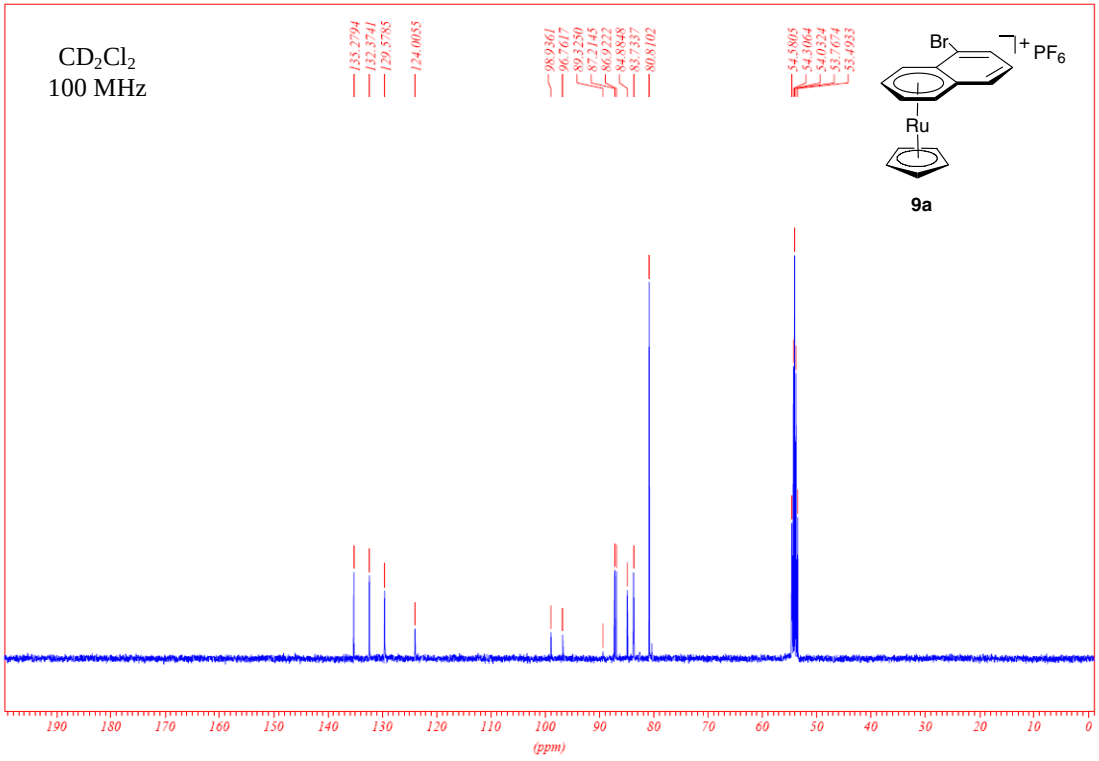
PF6
Ru
9a
Integral
(ppm)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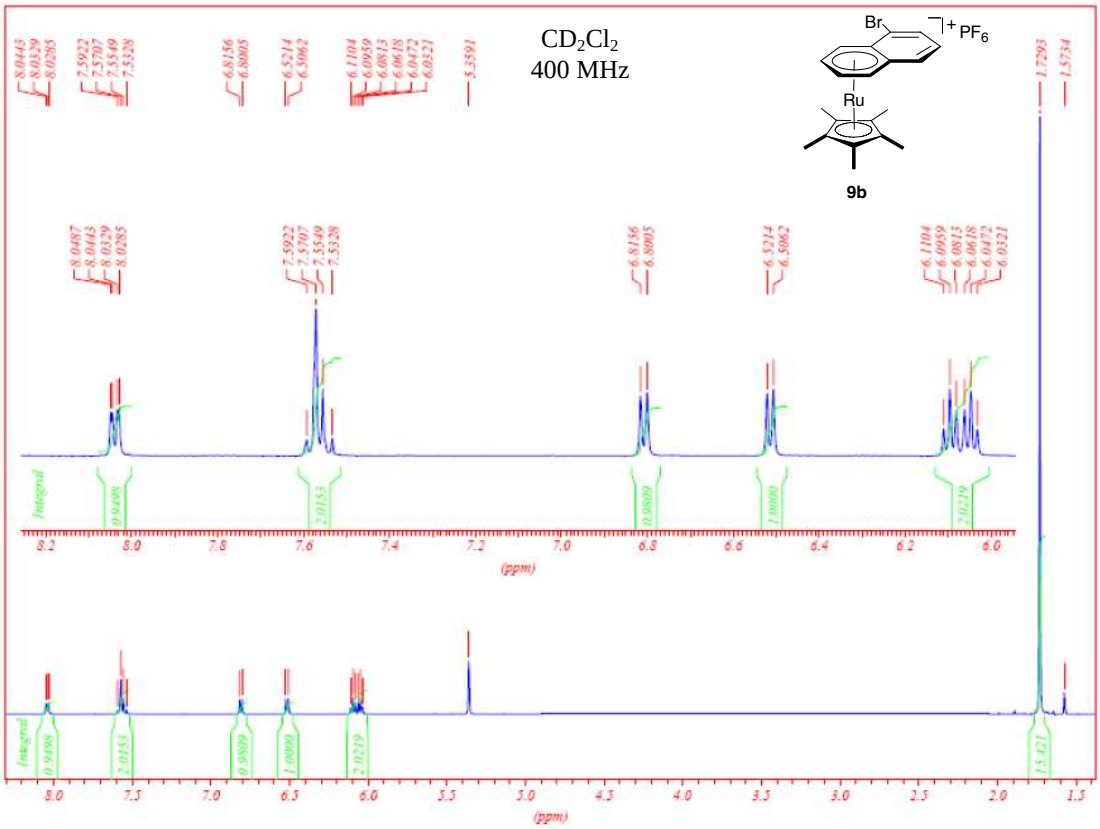
9a
(ppm)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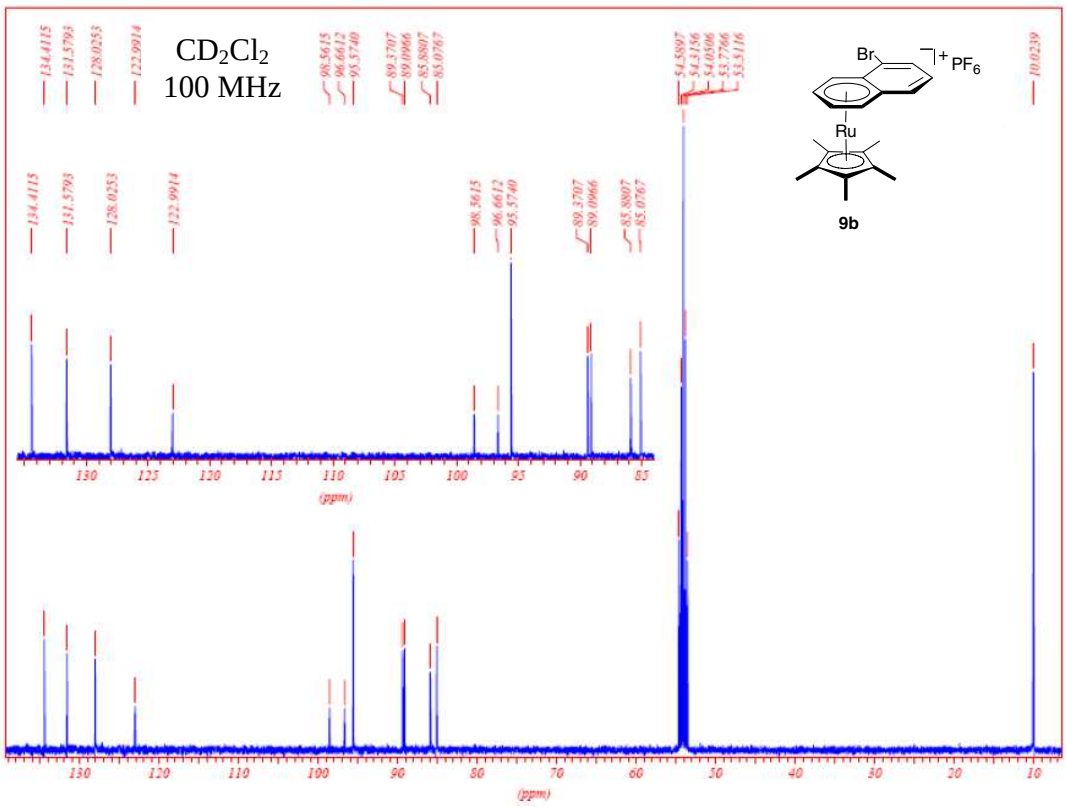
+ PF6
Ru
9b
(ppm)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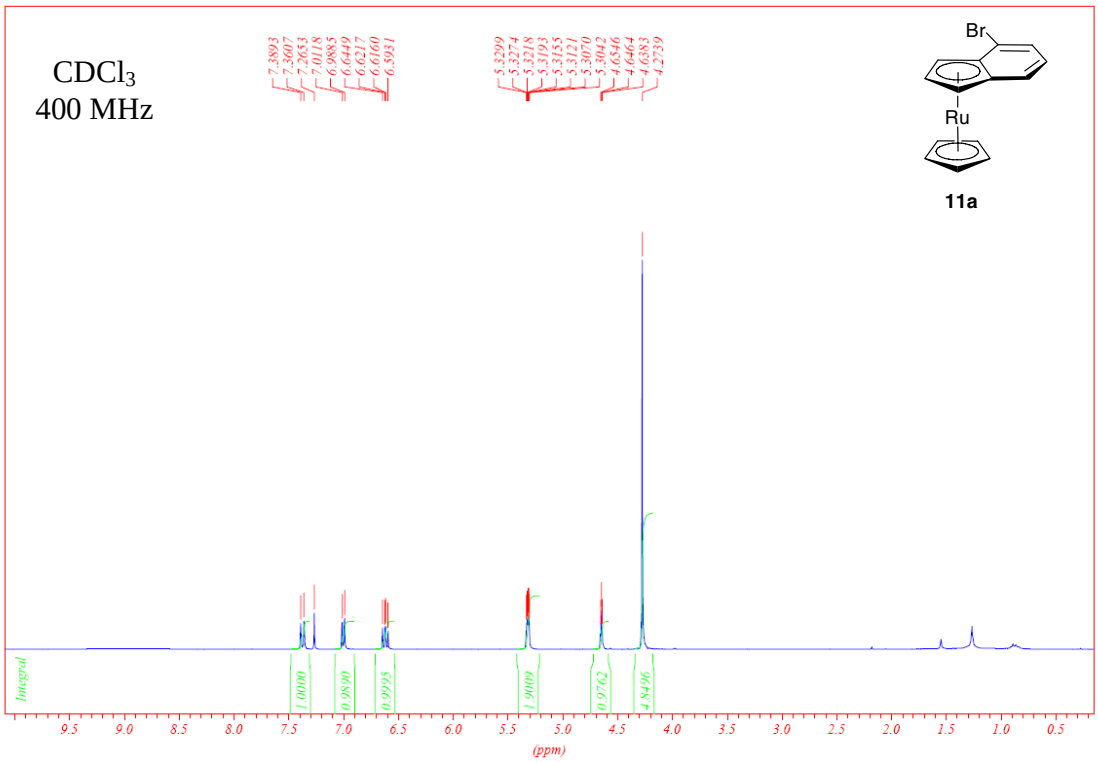
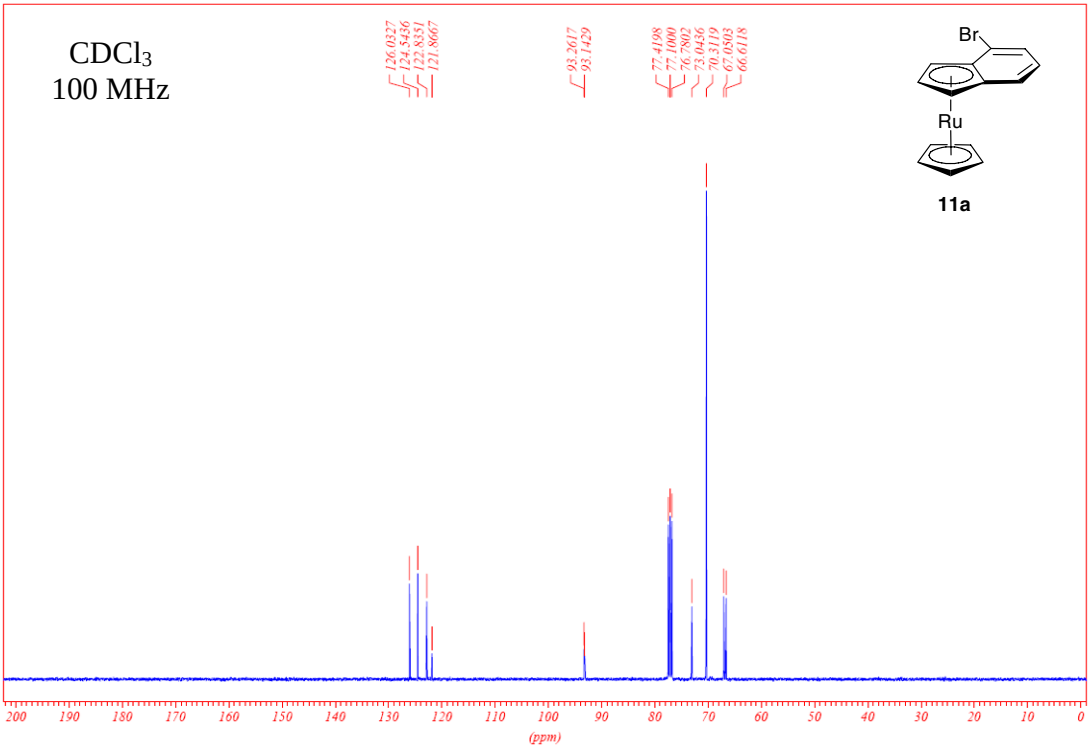
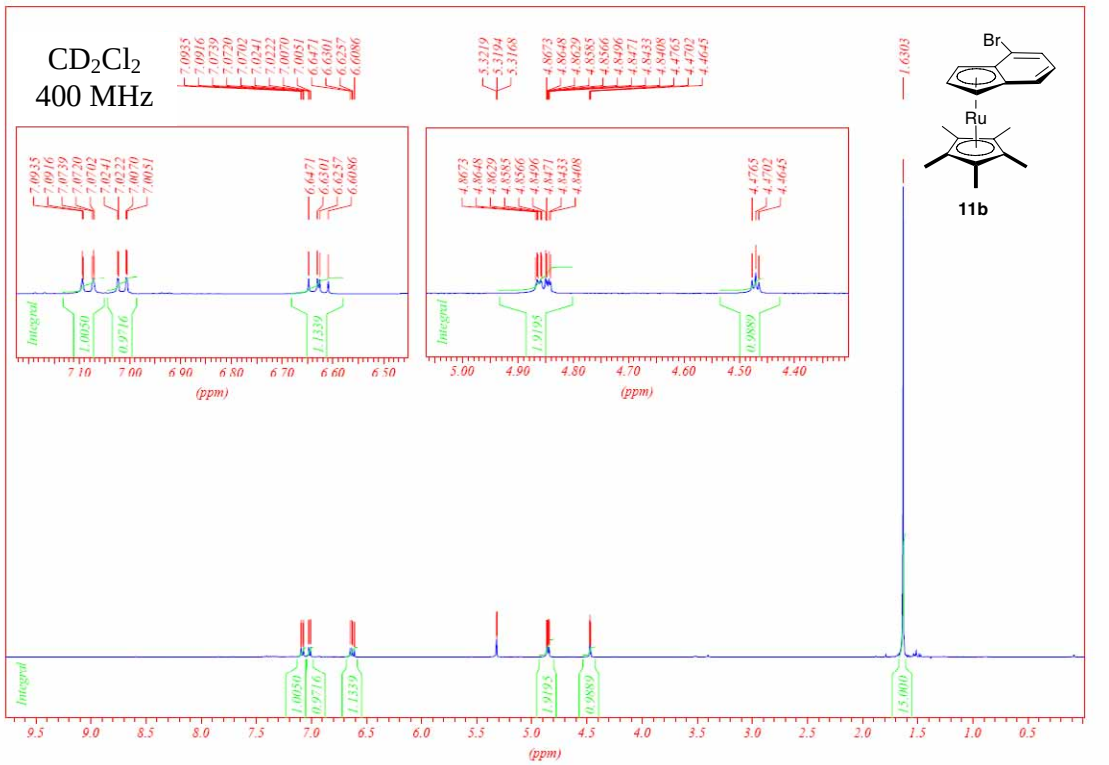
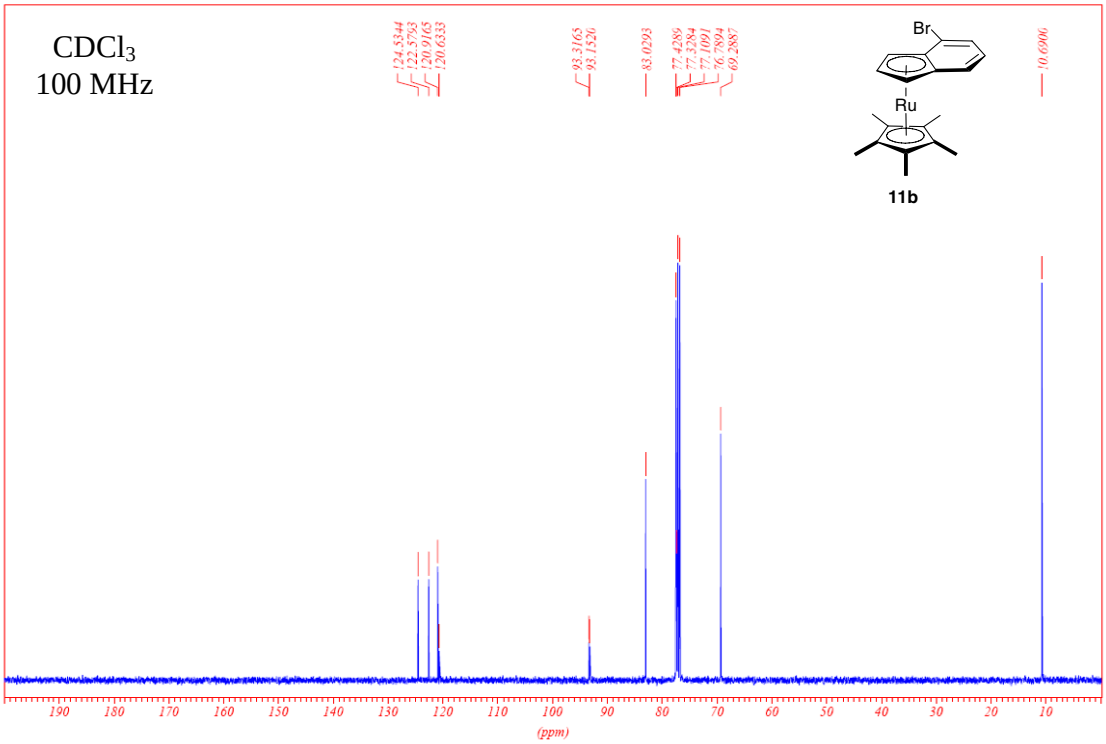
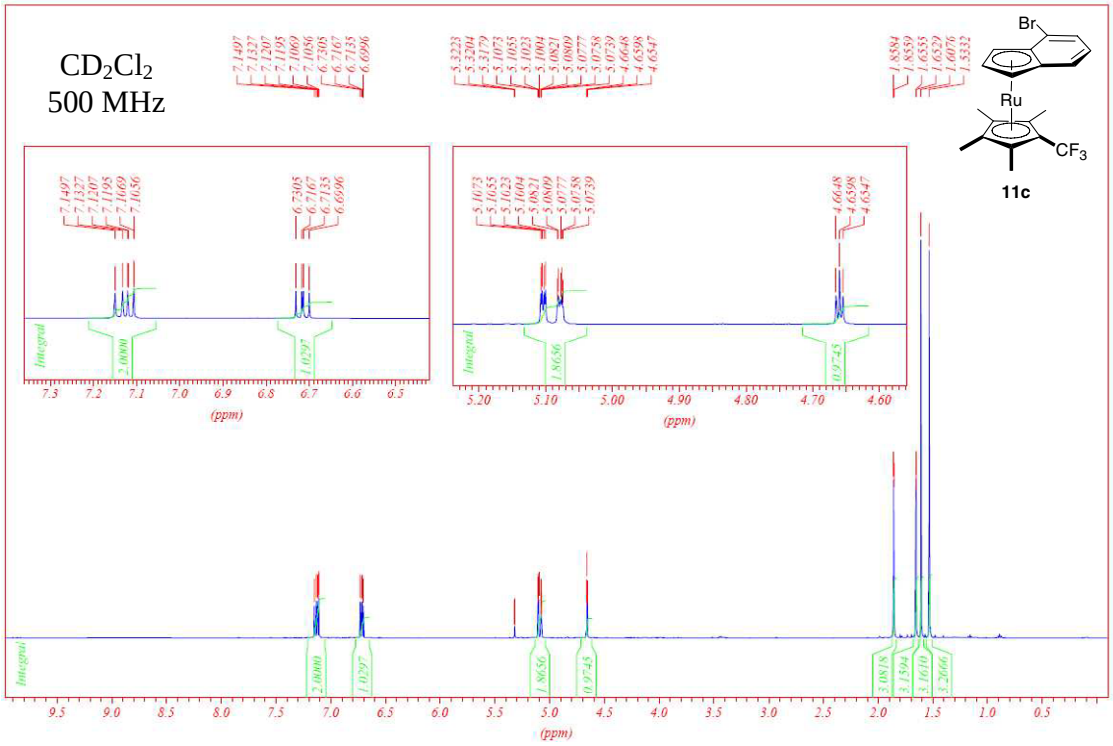
9b
(ppm)

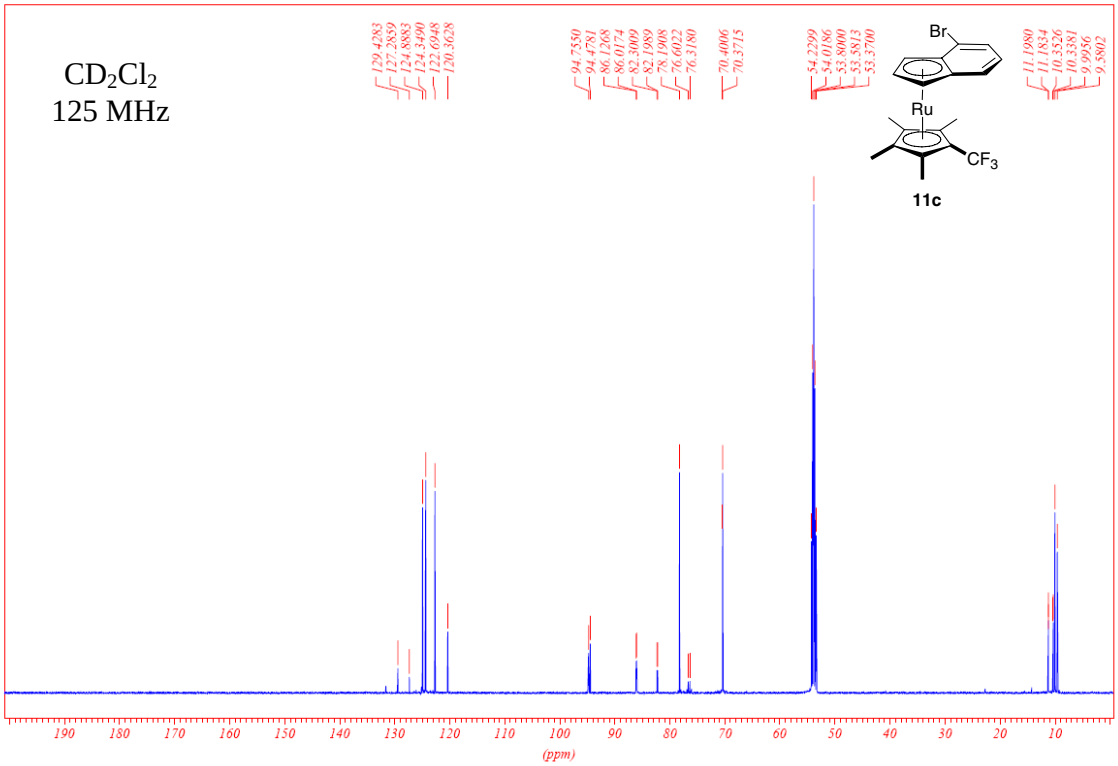

CDCl3
400 MHz
7.3893
7.3607
7.2653
7.0118
6.9885
6.6449
6.6217
6.6160
6.5931
5.3299
5.3274
5.3218
5.3193
5.3155
5.3121
5.3070
5.3042
4.6546
4.6464
4.6383
4.2739
Br
Ru
11a
Integral
1.0000
0.9830
0.9995
1.9009
0.9762
4.8496
(ppm)

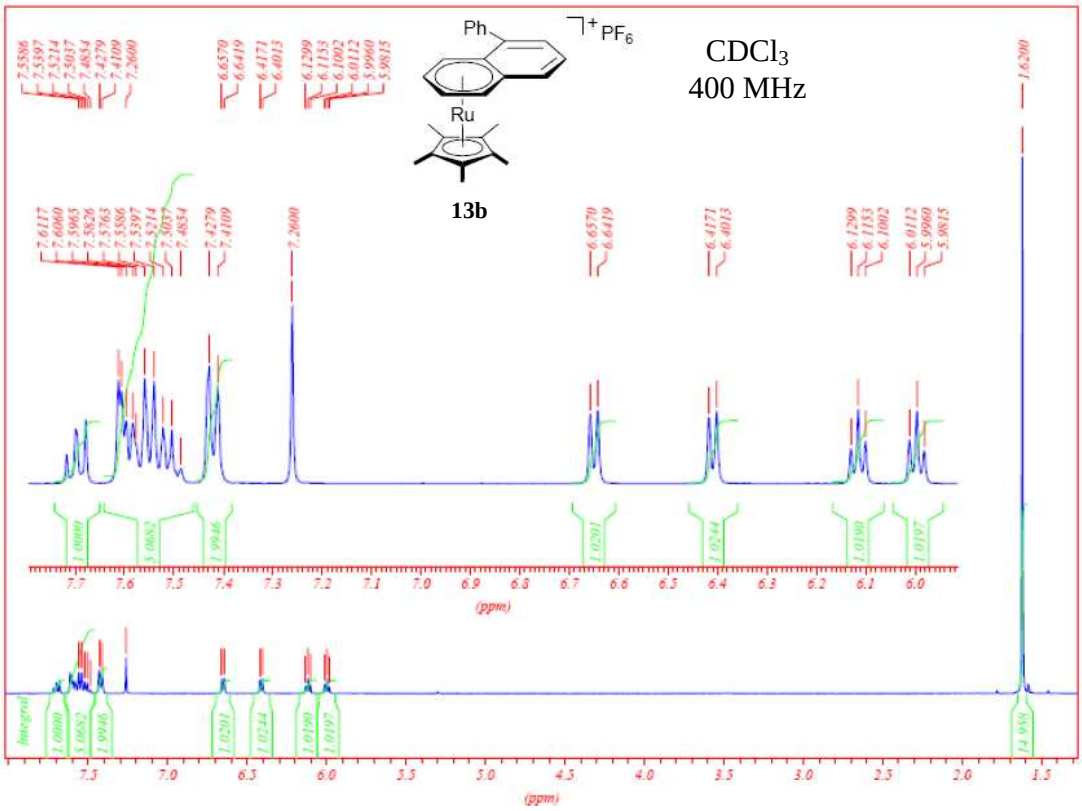

CDCl3
100 MHz
126.0327
124.5456
122.8351
121.8667
93.2617
93.1429
77.4198
77.1000
76.7802
73.0456
70.3119
67.9303
66.6118
Br
Ru
11a
(ppm)

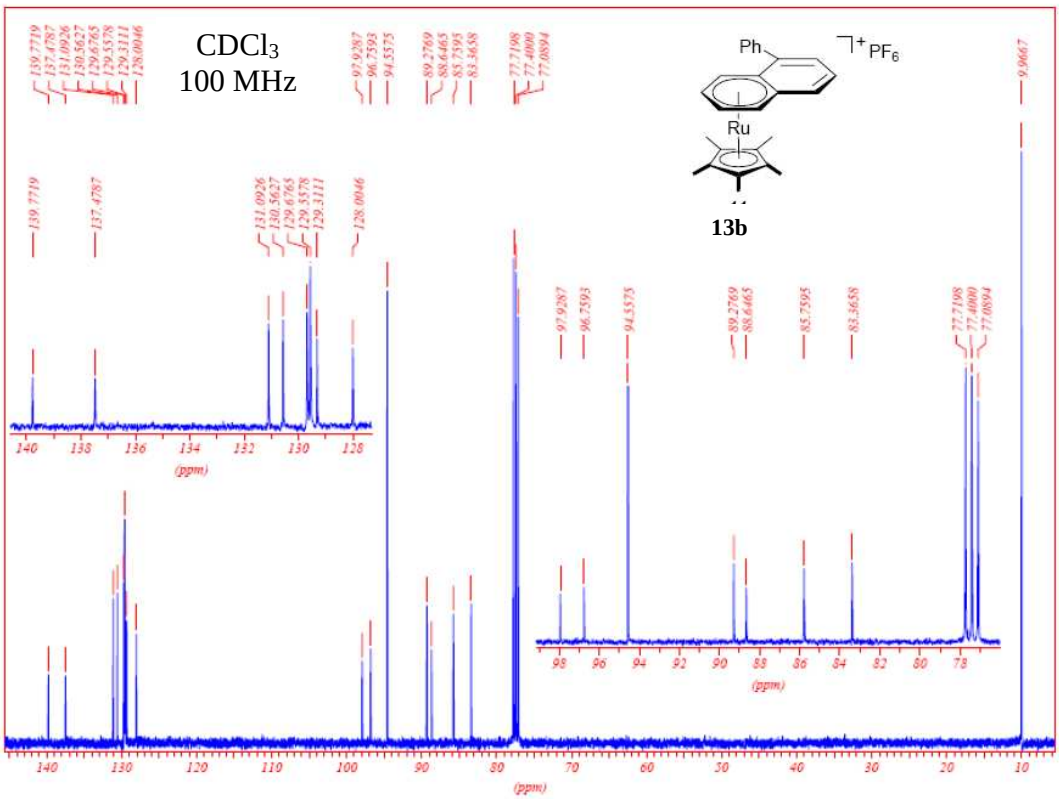

CD2Cl2
400 MHz
Br
Ru
11b
(ppm)


CDCl3
100 MHz
Br
Ru
11b
(ppm)


CD2Cl2
500 MHz
Br
Ru
CF3
11c
(ppm)


CD2Cl2
125 MHz
Br
Ru
CF3
11c
(ppm)


CDCl3
400 MHz
Ph
PF6
Ru
13b
(ppm)
integral


CDCl3
100 MHz
Ph
PF6
Ru
13b
(ppm)

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