Enantioselective Hydrogenation of Cyclic Imines Catalysed by Noyori-Ikariya Half-Sandwich Complexes and Their Analogues

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Table of contents:

1. Experimental

1.1 General

Reactions with oxygen- and moisture-sensitive materials were carried out under argon atmosphere using standard Schlenk techniques. Solvents were dried using activated molecular sieves (4Å).

^{1}H and ^{13}C NMR spectra were recorded on Bruker AVANCE III 400 MHz, 600 MHz and 700 MHz spectrometers with reference to the solvent residual signal as an internal standard (CD_3CN: δ_H 1.950 ppm, δ_C 118.69 and 1.39 ppm, DMSO-d_6: δ_H 2.500 ppm, δ_C 39.600 ppm, $CDCl_3$: δ_H 7.265 ppm, δ_C 77.00 ppm, CD_2Cl_2: δ_H 5.320 ppm, δ_C 54.00 ppm). ^{1}H NMR, ^{13}C NMR, COSY, gHSQCAD, gHMBCAD and 2D J-resolved spectra were measured using the manufacturers' software (Topspin 2.1 and 3.2, Bruker Biospin GmbH, Rheinstetten, Germany). The chemical shifts are given in δ scale [ppm] and coupling constants in Hz. The digital resolution enabled reporting the δ of ^{1}H to 3, coupling constants to 1, and ^{13}C to 2 decimal places. Signals assigned from 2D experiments are reported to 2 (^{1}H) and 1 (^{13}C) decimal places, respectively.

High resolution mass spectrometry measurements were carried out on LTQ Orbitrap Velos (Thermo Fisher Scientific, USA), UltrafleXtreme™ MALDI-TOF/TOF (Bruker Daltonics, Germany) and GC-MS (Agilent 7890A GC + OA-TOF Waters GCT Premier MS) spectrometers. Electrospray ionization (ESI), matrix-assisted laser desorption/ionization (MALDI), or atmospheric pressure chemical ionization (APCI) were used as an ion sources.

For imines **1**–**6**, GC analyses were carried out on a Varian CP-3800 GC equipped with a Varian 1177 autosampler, FID and and a non-polar column (Varian VF-1, 60 m × 0.25 mm × 0.25 μm). Nitrogen (99.99%) was used as the carrier gas at a flow rate of 0.5 mL/min. The injector was heated to 300 °C, the injected volume was 1 μL and split ratio 1:25. The detector was heated to 270 °C for the measurement of conversion and 250 °C for the analysis of *ee* using a pre-column derivatization method previously described by us[9e]. In the case of **7**–**12**, the conversion and ee were acquired on a Agilent 7693/7890 GC equipped with the chiral J&W CycloSilTM-B (30 m × 0.25 mm × 0.25 μm) column, Agilent 5975C Triple-Axis MSD detector and helium as the carrier gas.

IR spectra were measured on Nicolet 6700 FTIR instrument.

Crystallographic measurements were done with four circle CCD diffractometer Gemini by Oxford Diffraction, Ltd., with graphite monochromated Cu Kα radiation (λ = 1.54187 Å). The crystal structure was solved by charge flipping method using program Superflip[1] and refined with the Jana2006 program package[2] by full-matrix least squares technique on F. The molecular structure plot was prepared using ORTEP III.[3] Supramolecular interactions were viewed in Mercury.[4]

1.2 Chemicals

The following compounds were purchased from commercial sources and used as received:

(*S*,*S*)-*N*-*p*-toluenesulfonyl-1,2-diphenylethylenediamine (98 %, ABCR),
Dichloro(η^5-Cp*)rhodium(I) dimer (99 %, Strem Chemicals),
Dichloro(η^6-*p*-cymene)ruthenium(II) dimer (Sigma-Aldrich),
[RuCl(η^6-*p*-cymene)(*S*,*S*)-TsDPEN] (**A**, Sigma-Aldrich),
[RuCl(η^6-mesitylene)(*S*,*S*)-TsDPEN] (**C**, Sigma-Aldrich),
[RuCl(*S*,*S*)-Teth-TsDPEN] (**D**, Strem Chemicals),
[RuCl(*S*,*S*)-Ts-DENEB] (**E**, Strem Chemicals),
6,7-diethoxy-1-methyl-3,4-dihydroisoquinoline (**7**, Acros Organics),
7-methoxy-1-methyl-3,4-dihydro-β-carboline (harmaline, **11**, TCI).

The following known compounds were synthesized according to previously reported procedures:

6,7-dimethoxy-1-methyl-3,4-dihydroisoquinoline (**1**),[9b]
1-methyl-3,4-dihydroisoquinoline (**2**),[9b]
6-methoxy-1-methyl-3,4-dihydroisoquinoline (**3**),[9b]
7-methoxy-1-methyl-3,4-dihydroisoquinoline (**4**),[9b]
1-phenyl-3,4-dihydroisoquinoline (**5**),[9f]
1-(4-trifluoromethylphenyl)-3,4-dihydroisoquinoline (**6**),[9f]
6,7-dimethoxy-1-isopropyl-3,4-dihydroisoquinoline (**8**),[9g]
1-isopropyl-3,4-dihydroisoquinoline (**9**),[9g]
1-methyl-3,4-dihydro-β-carboline (harmalane, **10**),[9h]
3-methyl-1,2-benzoisothiazole-1,1-dioxide (**12**).[9i]

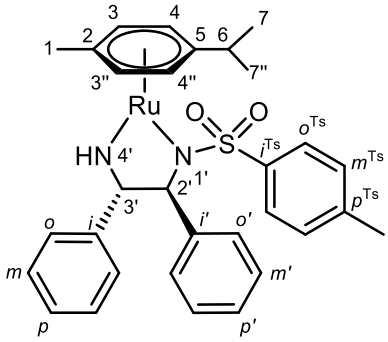
The syntheses of the following compounds are based on published procedures:

[Ru(η^6-*p*-cymene)(HN-CHPhCHPhNSO$_2$C$_6$H$_4$-*p*-CH$_3$)] (**B**),[5]
[RhCl(η^5-Cp*)(*S*,*S*)-TsDPEN] (**F**),[6a]
4-(4-methylcyclohexa-1,4-dienyl)butan-1-ol (**13a**),[7]
[(η^6-(4-(*p*-methylphenyl)butanol)RuCl$_2$]$_2$ (**14a**),[8]
4-(4-methylcyclohexa-1,4-dienyl)butane (**15a**),[7]
[RuCl(η^6-(*p*-methylphenyl)butanol)(*S*,*S*)-TsDPEN] (**G**),[6b]
[RuCl(η^6-(*p*-methylphenyl)butane)(*S*,*S*)-TsDPEN] (**H**).[6b]

1.3 Synthetic procedures

1.3.1 Synthesis of [Ru(η^6-*p*-cymene)(HN-CHPhCHPhNSO$_2$C$_6$H$_4$-*p*-CH$_3$)] (B)

[RuCl$_2$(η^6-*p*-cymene)]$_2$ (125.4 mg, 0.197 mmol), (*S*,*S*)-TsDPEN (150.0 mg, 0.409 mmol) were dissolved in dichloromethane (2.9 mL), KOH (163.8 mg, 2.920 mmol) was added and the mixture was stirred at room temperature for 5 min. The reaction mixture was washed with water (2.9 mL), dried over CaH_2 and filtered. The solvent was evaporated under reduced pressure to afford a dark purple solid. Yield: 148 mg, (61 %).



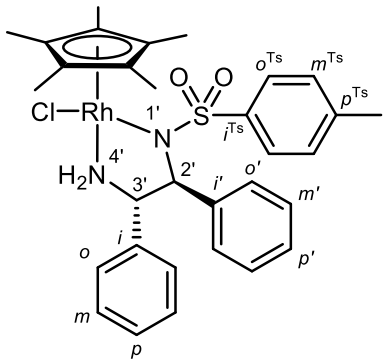
^{1}H NMR (600.23 MHz, CD_3CN, 300.0 K): δ 1.201 (3H, d, *J* = 6.9, H-7"), 1.292 (3H, d, *J* = 6.9, H-7), 2.146 (3H, s, H-1), 2.296 (3H, s, CH_3-*para*^{Ts}), 2.642 (1H, dd, *J* = 6.9, 6.9, H-6), 3.938 (1H, d, *J* = 4.9, H-3'), 4.286 (1H, s, H-2'), 5.328 (1H, d, *J* = 6.0, H-4), 5.414 (1H, d, *J* = 6.0, H-3"), 5.627 (1H, d, *J* = 6.0, H-4"), 5.768 (1H, d, *J* = 6.0, H-3), 6.945 (2H, m, H-*meta*^{TS}), 7.125 (2H, m, H-*ortho*), 7.15 (2H, m, H-*meta*), 7.17 (2H, m, H-*para*, H-*para*'), 7.211 (2H, m, H-*ortho*^{Ts}), 7.248 (2H, m, H-*meta*'), 7.443 (1H, br. s, H-4'), 7.482 (2H, m, H-*ortho*').

^{13}C NMR (150.93 MHz, CD_3CN, 300.0 K): δ 20.07 (C-1), 21.31 (CH_3-*para*^{Ts}), 23.41 (C-7"), 23.57 (C-7), 32.71 (C-6), 72.33 (C-2'), 77.00 (C-4), 80.59 (C-4"), 81.54 (C-3"), 81.96 (C-3'), 84.74 (C-3), 89.06 (C-2), 100.04 (C-5), 127.09 (C-*para*'), 127.32 (C-*ortho*^{Ts}), 127.40 (C-*ortho*), 127.65 (C-*para*), 128.06 (C-*ortho*'), 128.38 (C-*meta*'), 128.83 (C-*meta*), 129.46 (C-*meta*^{Ts}), 141.35 (C-*para*^{Ts}), 143.81 (C-*ipso*^{Ts}), 145.61 (C-*ipso*), 148.45 (C-*ipso*').

HRMS (ESI$^+$) calculated for $C_{31}H_{35}N_2O_2RuS$ [M+H]$^+$: 601.1457; found: 601.1459.

1.3.2 Synthesis of [RhCl(η^5-Cp*)(*S*,*S*)-TsDPEN] (F)

[$RhCl_2Cp^*]_2$ (154.5 mg, 0.25 mmol) and (*S*,*S*)-TsDPEN (183 mg, 0.5 mmol) were dissolved in dichloromethane (5 mL), triethylamine (139.1 µL, 101 mg, 1 mmol) was added and the solution was stirred for 20 min at room temperature. The reaction mixture was washed with water (2.5 mL), dried over $MgSO_4$ and filtered. The solvent was evaporated under reduced pressure to give an orange solid. Yield: 300 mg, 94 %. m.p. 219–220 °C (dec.).



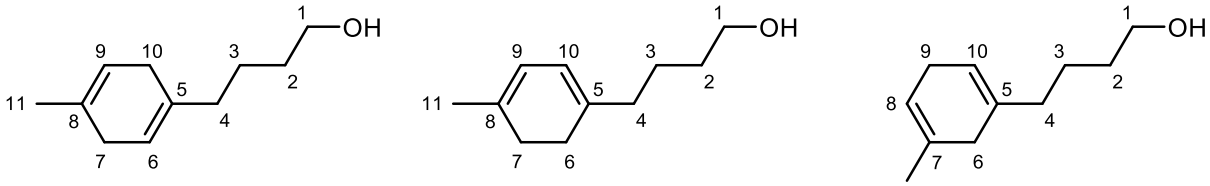
^{1}H NMR (400.00 MHz, CD_2Cl_2, 303.2 K): δ 1.817 (15H, s, CH_3^{Cp}), 2.291 (3H, s, CH_3-*para*^{Ts}), 3.447 (1H, m, H-4'), 3.713 (1H, ddd, *J* = 10.8, 13.6, 2.3, H-3'), 3.903 (1H, m, H-4'), 3.972 (1H, d, *J* = 10.8, H-2'), 6.29 (2H, m, H-*ortho*), 6.653 (2H, m, H-*ortho*'), 6.780 (2H, m, H-*meta*'), 6.85 (2H, m, H-*meta*^{Ts}), 6.86 (1H, m, H-*para*'), 7.13 (2H, m, H-*meta*), 7.14 (1H, m, H-*para*), 7.311 (2H, m, H-*ortho*^{Ts}).

^{13}C NMR (100.59 MHz, CD_2Cl_2, 303.2 K): δ 9.98 (CH_3^{Cp}), 21.42 (CH_3-*para*^{Ts}), 69.91 (C-2'), 72.14 (C-3'), 94.52 (C^{Cp}), 94.61 (C^{Cp}), 126.88 (C-*para*'), 127.58 (C-*meta*'), 127.62 (C-*ortho*), 128.32 (C-*meta*^{Ts}), 128.55 (C-*ortho*^{Ts}), 128.83 (C-*para*), 129.01 (C-*meta*), 129.35 (C-*ortho*'), 139.89 (C-*para*^{Ts}), 140.06 (C-*ipso*), 140.32 (C-*ipso*'), 142.38 (C-*ipso*^{Ts}).

HRMS (ESI$^+$) calculated for $C_{31}H_{36}N_2O_2RhS$ $[M-Cl]^+$: 603.1553; found 603.1556.

1.3.3 Synthesis of 4-(4-methylcyclohexa-1,4-dienyl)butan-1-ol (13a)

1,2-Bis(diphenylphosphino)ethane (DPPE) (102.0 mg, 0.256 mmol), $CoBr_2$ (54.3 mg, 0.248 mmol), ZnI_2 (157.6 mg, 0.494 mmol) and Zn powder (31.8 mg, 0.486 mmol) were mixed with tetrahydrofuran (33 mL) at 70 °C and the mixture was stirred for 15 min. Isoprene (1.00 g, 14.7 mmol, 1.47 mL) and 5-hexyn-1-ol (1.18 g, 12.1 mmol, 1.33 mL) were added and then further stirred for 2 hours at 70 °C. The solvent was evaporated under reduced pressure and the crude oily product was purified by flash column chromatography (hexane/EtOAc = 3:1) to afford colourless oil consisting of **13a** and side-products **13b** and **13c**. Yield: 1.86 g (93 %).



13a (74%) **13b** (19%) **13c** (7%)

13a: ^{1}H NMR (600.23 MHz, $CDCl_3$, 293.2 K): δ 1.479 (2H, m, H-3), 1.56 (2H, m, H-2), 1.663 (3H, s, H-11), 1.995 (2H, dd, J = 7.5, 7.5, H-4), 2.574 (4H, s, H-7, H-10), 3.635 (2H, dd, J = 6.4, 6.4, H-1), 5.407 (1H, s, H-9), 5.421 (1H, s, H-6).
^{13}C NMR (150.93 MHz, $CDCl_3$, 293.2 K): δ 22.98 (C-11), 23.50 (C-3), 29.81 (C-10), 31.57 (C-7), 32.35 (C-2), 36.73 (C-4), 62.83 (C-1), 118.45 (C-6), 118.57 (C-9), 131.22 (C-8), 134.60 (C-5).

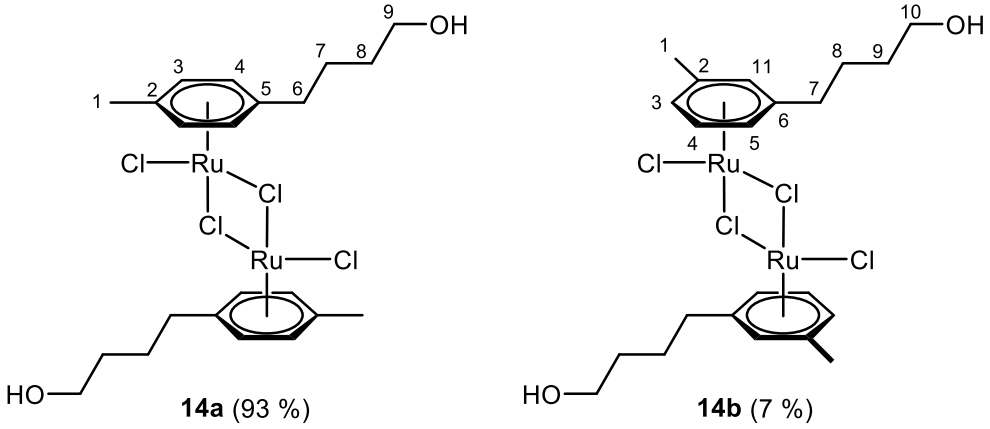
13b: ^{1}H NMR (600.23 MHz, $CDCl_3$, 293.2 K): δ 1.493 (2H, m, H-3), 1.545 (2H, m, H-2), 1.758 (3H, s, H-11), 2.076 (2H, dd, J = 7.4, 7.4, H-4), 2.093 (2H, m, H-7), 2.10 (2H, m, H-6), 3.635 (2H, dd, J = 6.4, 6.4, H-1), 5.582 (1H, d, J = 6.6, H-10), 5.590 (1H, d, J = 6.6, H-9).
^{13}C NMR (150.93 MHz, $CDCl_3$, 293.2 K): δ 22.92 (C-11), 23.73 (C-3), 26.92 (C-6), 28.66 (C-7), 32.34 (C-2), 36.61 (C-4), 62.81 (C-1), 119.02 (C-10), 119.25 (C-9), 133.01 (C-8), 135.97 (C-5).

13c: ^{1}H NMR (600.23 MHz, $CDCl_3$, 293.2 K): δ 1.543 (2H, m, H-3), 1.565 (2H, m, H-2), 1.676 (3H, s, H-11), 2.008 (2H, m, H-4), 2.472 (2H, t, J = 8.0, H-6), 2.667 (2H, br. s., H-9), 3.635 (2H, m, H-1), 5.421 (2H, m, H-8, H-10).
^{13}C NMR (150.93 MHz, $CDCl_3$, 293.2 K): δ 23.19 (C-11), 23.39 (C-3), 27.64 (C-9), 32.36 (C-2), 33.79 (C-6), 36.86 (C-4), 62.83 (C-1), 118.29, 118.48 (C-8, C-10), 131.20, 131.22 (C-5, C-7).

HRMS (ESI$^+$) calculated for $C_{11}H_{17}O$ $[M–H]^-$: 165.1279; found: 165.1277.
IR: ν_{max} = 3622, 3442, 3082, 3011, 2935, 2879, 2861, 2820, 1662, 1610, 1475, 1448, 1439, 1384, 1053, 1022 cm^{-1}.

1.3.4 Synthesis of [(η^6-(4-(*p*-tolyl)butan-1-ol)$RuCl_2$]$_2$ (14a)

Diene **13a** (1.50 g, 9.02 mmol) was dissolved in ethanol (70 mL) and $RuCl_3 \cdot xH_2O$ (387 mg, 1.48 mmol, trihydrate assumed) was added. The reaction mixture was stirred for 18 h under reflux. After the reaction, the mixture was hot-filtered to remove Ru black. The volatiles were removed on a rotary evaporator giving red-brown oil. The oil was washed with cold and degassed EtOH (3 × 3 mL) and hexane (3 × 3 mL). The resulting red-brown solid was dried in vacuum (1 Torr). Yield: 372 mg (75 %). M.p. 168–171 °C (dec.).



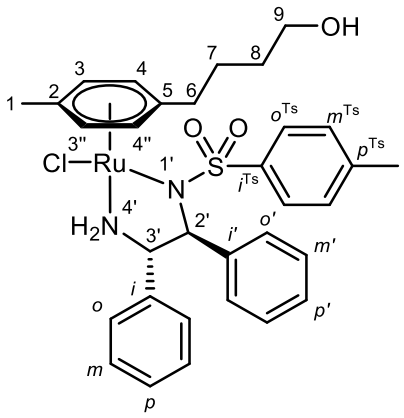
14a: ^{1}H NMR (400.00 MHz, DMSO-d_6, 303.2 K): δ 1.461 (2H, m, H-8), 1.584 (2H, m, H-7), 2.082 (3H, s, H-1), 2.383 (2H, t, J = 7.7, H-6), 3.403 (2H, t, J = 6.3, H-9), 5.751 (2H, m, H-3), 5.786 (2H, m, H-4).
^{13}C NMR (100.58 MHz, DMSO-d_6, 303.2 K): δ 17.86 (C-1), 25.89 (C-7), 31.69 (C-6), 32.00 (C-8), 60.38 (C-9), 86.93 (C-3), 87.01 (C-4), 99.62 (C-2), 101.71 (C-5).

14b: ^{1}H NMR (400.00 MHz, DMSO-d_6, 303.2 K): δ 1.565 (2H, m, H-9), 1.576 (2H, m, H-8), 2.129 (3H, s, H-1), 2.423 (2H, br. t., J = 7.6, H-7), 3.412 (2H, t, J = 6.4, H-10), 5.449 (1H, d, J = 5.7, H-3), 5.484 (1H, d, J = 5.7, H-5), 5.640 (1H, br. s., H-11), 5.964 (1H, t, J = 5.7, H-4).
^{13}C NMR (100.58 MHz, DMSO-d_6, 303.2 K): δ 18.52 (C-1), 25.64 (C-8), 32.10 (C-9), 32.47 (C-7), 60.39 (C-10), 80.19 (C-5), 81.09 (C-3), 84.18 (C-11), 88.33 (C-4), 106.58 (C-2), 109.62 (C-6).

HRMS (ESI$^+$) calculated for $C_{22}H_{32}O_2Ru_2Cl_3$ $[M-Cl]^+$: 636.9555; found 636.9556.
IR: ν_{max}=3482, 3067, 3047, 3008, 2944, 2869, 1530, 1495, 1450, 1377, 1065, 1033, 809 cm^{-1}.

1.3.5 Synthesis of [RuCl(η^6-(4-(*p*-tolyl)butan-1-ol)(*S*,*S*)-TsDPEN] (G)

Dimer **14a** (250.0 mg, 0.372 mmol) and ligand (*S*,*S*)-TsDPEN (272.5 mg, 0.744 mmol) were dissolved in dichloromethane (8.3 mL). Triethylamine (207.4 µL, 150.5 mg, 1.487 mmol) was added thereto and the solution was stirred for 1 hour at room temperature. The orange precipitate was filtered off, washed with water (3 × 2 mL) and dried in vacuum (1 Torr). Yield: 415 mg, (84 %). m.p. 205–207 °C (dec.).



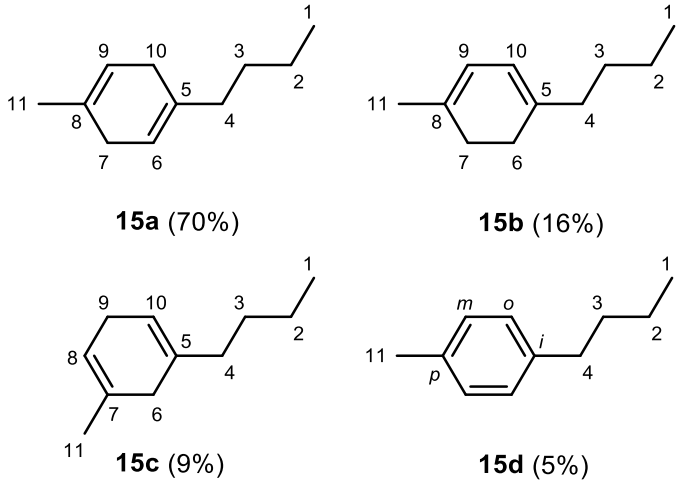
^{1}H NMR (700.13 MHz, DMSO-d_6, 303.2 K): δ 1.542 (2H, m, H-8), 1.693 (2H, m, H-7), 2.214 (3H, s, CH_3-*para*^{Ts}), 2.247 (3H, s, H-1), 2.568 (1H, m, H-6u), 2.599 (1H, m, H-6d), 3.179 (1H, dd, *J* = 10.3, 12.5, H-4'), 3.474 (2H, m, H-9), 3.557 (1H, m, H-3'), 3.708 (1H, d, *J* = 11.2, H-2'), 4.455 (1H, t, *J* = 5.1, 9-OH), 5.496 (1H, d, *J* = 5.6, H-3), 5.595 (2H, s, H-3", H-4"), 5.641 (1H, d, *J* = 5.6, H-4), 6.530 (2H, d, *J* = 7.4, H-*ortho*'), 6.673 (2H, dd, *J* = 7.4, 7.4, H-*meta*'), 6.778 (1H, t, *J* = 7.4, H-*para*'), 6.805 (2H, m, H-*ortho*), 6.819 (2H, d, *J* = 7.9, H-*meta*^{Ts}), 7.043 (2H, d, *J* = 7.9, H-*ortho*^{Ts}), 7.10 (3H, m, H-*meta*, H-*para*), 7.354 (1H, d, *J* = 7.8, H-4').

^{13}C NMR (176.06 MHz, DMSO-d_6, 303.2 K): δ 18.35 (C-1), 20.82 (CH_3-*para*^{Ts}), 26.49 (C-7), 32.11 (C-6), 32.17 (C-8), 60.48 (C-9), 68.58 (C-2'), 71.10 (C-3'), 81.95 (C-3"), 81.97 (C-4), 83.17 (C-3), 83.95 (C-4"), 95.09 (C-2), 96.65 (C-5), 125.96 (C-*para*'), 126.62 (C-*meta*', C-*ortho*^{Ts}), 127.15 (C-*ortho*), 127.56 (C-*meta*^{Ts}), 127.64 (C-*para*), 128.19 (C-*meta*), 128.93 (C-*ortho*'), 138.11 (C-*para*^{Ts}), 139.24 (C-*ipso*'), 139.90 (C-*ipso*), 143.78 (C-*ipso*^{Ts}).

HRMS (ESI$^+$) calculated for $C_{32}H_{37}N_2O_3RuS$ [M–Cl]$^+$: 631.1568; found 631.1569.
IR: ν_{max} = 3455, 3279, 3226, 3084, 3064, 3030, 2933, 2861, 1599, 1494, 1453, 1378, 1270, 1128, 1105, 1084, 1039, 821, 813, 689 cm^{-1}.
$[\alpha]^{20}_{589}$ = +66.7° (*c* 0.397, DMSO).

1.3.6 Synthesis of 4-(4-methylcyclohexa-1,4-dienyl)butane (15a)

DPPE (102.0 mg, 0.256 mmol), $CoBr_2$ (54.3 mg, 0.248 mmol), ZnI_2 (157.6 mg, 0.494 mmol) and Zn powder (31.8 mg, 0.486 mmol) were mixed with tetrahydrofuran (33 mL) at 70 °C and the mixture was stirred for 15 min. Isoprene (1.00 g, 14.7 mmol, 1.47 mL) and 1-hexyne (1.00 g, 12.1 mmol, 1.39 mL) were added and then further stirred for 2 hours at 70 °C. The solvent was evaporated under reduced pressure and the crude oily product was purified by flash column chromatography (hexane/EtOAc = 3:1) to afford colourless oil consisting of **15a–c**.[1] Yield: 1.54 g (84 %).



15a: ^{1}H NMR (600.23 MHz, $CDCl_3$, 303.2 K): δ 0.899 (3H, t, J = 7.2, H-1), 1.306 (2H, m, H-2), 1.389 (2H, m, H-3), 1.674 (3H, s, H-11), 1.968 (2H, t, J = 7.5, H-4), 2.584 (4H, m, H-7, H-10), 5.416 (1H, m, H-6), 5.421 (1H, m, H-9).
^{13}C NMR (150.93 MHz, $CDCl_3$, 303.2K): δ 14.01 (C-1), 22.44 (C-2), 23.05 (C-11), 29.70 (C-3), 29.92 (C-10), 31.61 (C-7), 36.81 (C-4), 117.97 (C-6), 118.72 (C-9), 131.28 (C-8), 135.15 (C-5).

15b: ^{1}H NMR (600.23 MHz, $CDCl_3$, 303.2 K): δ 0.899 (3H, t, J = 7.2, H-1), 1.306 (2H, m, H-2), 1.398 (2H, m, H-3), 1.767 (3H, s, H-11), 2.049 (2H, t, J = 7.6, H-4), 2.102 (4H, m, H-6, H-7), 5.578 (1H, m, H-10), 5.602 (1H, m, H-9).
^{13}C NMR (150.93 MHz, $CDCl_3$, 303.2K): δ 14.00 (C-1), 22.41 (C-2), 22.98 (C-11), 27.05 (C-6), 28.72 (C-7), 29.88 (C-3), 36.69 (C-4), 118.60 (C-10), 119.34 (C-9), 132.83 (C-8), 136.73 (C-5).

15c: ^{1}H NMR (600.23 MHz, $CDCl_3$, 303.2 K): δ 0.899 (3H, m, H-1), 1.315 (2H, m, H-2), 1.375 (2H, m, H-3) 1.687 (3H, s, H-11), 1.979 (2H, m, H-4), 2.482 (2H, t, J = 8.0, H-6), 2.678 (2H, br. s., H-9), 5.412 (2H, m, H-8, H-10).
^{13}C NMR (150.93 MHz, $CDCl_3$, 303.2K): δ 14.01 (C-1), 22.46 (C-2), 23.26 (C-11), 27.69 (C-9), 29.58 (C-3), 33.89 (C-6) 36.95 (C-4), 117.80 (C-10), 118.48 (C-8), 131.37 (C-7, C-5).

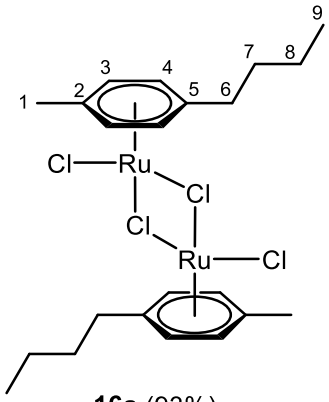
[1] Small amount (**9d**) of aromatic impurity was formed as a decomposition product, which has been assigned for the sake of completeness.

15d: ^{1}H NMR (600.23 MHz, $CDCl_3$, 303.2 K): δ 0.899 (3H, m, H-1), 1.291 (2H, m, H-2), 1.577 (2H, m, H-3), 2.318 (3H, s, H-*para*-CH_3), 2.570 (2H, t, J = 7.9, H-4), 7.074 (2H, m, H-*ortho*), 7.090 (2H, m, H-*meta*).
^{13}C NMR (150.93 MHz, $CDCl_3$, 303.2K): δ 13.96 (C-1), 20.98 (C-*para*-CH_3), 22.36 (C-2), 33.80 (C-3), 35.19 (C-4), 128.26 (C-*ortho*), 128.88 (C-*meta*), 134.91 (C-*para*), 139.81 (C-*ipso*).

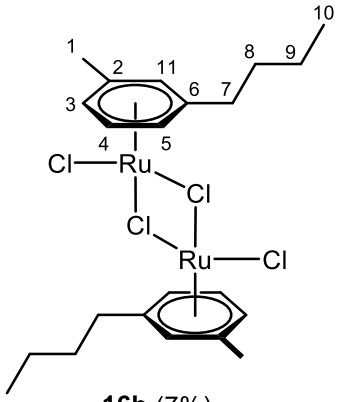
HRMS (EI) calculated for $C_{11}H_{18}$ [$M^{+\bullet}$]: 150.1409; found 150.1410.
IR: ν_{max} = 3080, 3036, 2960, 2930, 2873, 2859, 2820, 1662, 1610, 1467, 1457, 1379 cm^{-1}.

1.3.7 Synthesis of [(η^6-(1-butyl-4-methylbenzene)$RuCl_2$]$_2$ (16a)

Diene **15a** (1.547 g, 10.3 mmol) was dissolved in ethanol (80 mL) and $RuCl_3 \cdot xH_2O$ (538 mg, 2.1 mmol, trihydrate assumed) was added. The reaction mixture was stirred for 18 h under reflux. After the reaction, the mixture was hot-filtered to remove Ru black. The volatiles were removed on a rotary evaporator giving red-brown oil. The oil was washed with cold and degassed EtOH (3 × 3 mL) and hexane (3 × 3 mL). The resulting red-brown solid was dried in vacuum (1 Torr). Yield: 988 mg (75 %). M.p. 192 °C (dec.).



16a (93%)



16b (7%)

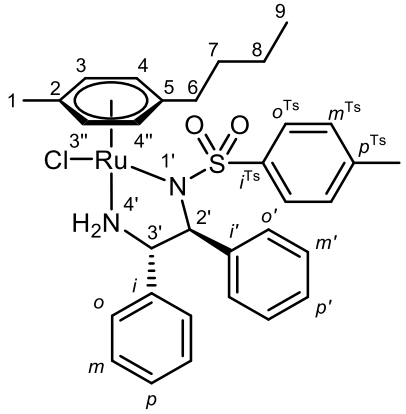
16a: ^{1}H NMR (700.13 MHz, DMSO-d_6, 303.2 K): δ 0.894 (3H, t, J = 7.3, H-9), 1.333 (2H, m, H-8), 1.539 (2H, m, H-7), 2.080 (3H, s, H-1), 2.379 (2H, t, J = 7.4, H-6), 5.745 (2H, d, J = 5.5, H-3), 5.789 (2H, d, J = 5.5, H-4).
^{13}C NMR (176.06 MHz, DMSO-d_6, 303.2K): δ 13.76 (C-9), 17.85 (C-1), 21.85 (C-8), 31.27 (C-7), 31.55 (C-6), 86.92 (C-3), 86.98 (C-4), 99.59 (C-2), 101.70 (C-5).

16b: ^{1}H NMR (700.13 MHz, DMSO-d_6, 303.2 K): δ 0.893 (3H, m, H-10), 1.347 (2H, m, H-9), 1.538 (2H, m, H-8), 2.126 (3H, s, H-1), 2.418 (2H, t, J = 7.6, H-7), 5.445 (1H, d, J = 5.2, H-3), 5.483 (1H, d, J = 5.2, H-5), 5.643 (1H, s, H-11), 5.958 (1H, t, J = 5.2, H-4).
^{13}C NMR (176.06 MHz, DMSO-d_6, 303.2K): δ 13.78 (C-10), 18.52 (C-1), 21.96 (C-9), 31.03 (C-8), 32.35 (C-7), 80.15 (C-5), 81.06 (C-3), 84.16 (C-11), 88.32 (C-4), 106.53 (C-2), 109.55 (C-6).

HRMS (MALDI) calculated for $C_{22}H_{32}Ru_2Cl_3$ $[M-Cl]^+$: 604.9651; found 604.9659.
IR: ν_{max} =3067, 3045, 3009, 2951, 2927, 2868, 2859, 1530, 1497, 1466, 1377, 1034, 811 cm^{-1}.

1.3.8 Synthesis of [RuCl(η^6-(1-butyl-4-methylbenzene)(*S*,*S*)-TsDPEN] (H)

Dimer **16a** (200.0 mg, 0.312 mmol) and ligand (*S*,*S*)-TsDPEN (228.9 mg, 0.625 mmol) were dissolved in dichloromethane (7 mL). Triethylamine (174.2 µL, 126.4 mg, 1.249 mmol) was added thereto and the solution was stirred for 1 hour at room temperature and washed with water (3 × 2 mL). Removal of solvents gave the crude product. The product was purified by flash chromatography (gradient elution from hexane to EtOAc to MeOH) and dried in vacuum (1 Torr) to give a dark orange solid. Yield: 225 mg, (56 %). m.p. 149 °C (dec.).



^{1}H NMR (600.23 MHz, $CDCl_3$, 303.2 K): δ 0.964 (3H, t, J = 7.3, H-9), 1.421 (2H, m, H-8), 1.654 (2H, m, H-7), 2.215 (3H, s, CH_3-*para*^{Ts}), 2.249 (3H, s, H-1), 2.582 (2H, m, H-6), 3.187 (1H, m, H-4'u), 3.556 (1H, m, H-3'), 3.712 (1H, d, J = 11.2, H-2'), 5.498 (1H, d, J = 5.4, H-3a), 5.592 (2H, s, H-3b, H-4b), 5.639 (1H, d, J = 5.4, H-4a), 6.534 (2H, d, J = 7.5, H-*ortho*'), 6.676 (2H, t, J = 7.5, H-*meta*'), 6.782 (1H, t, J = 7.5, H-*para*'), 6.802 (2H, m, H-*ortho*), 6.818 (2H, m, H-*meta*^{Ts}), 7.048 (2H, m, H-*ortho*^{Ts}), 7.097 (1H, m, H-*para*), 7.102 (2H, m, H-*meta*), 7.343 (1H, m, H-4'd).

^{13}C NMR (150.93 MHz, $CDCl_3$, 303.2K): δ 13.80 (C-9), 18.30 (C-1), 20.77 (CH_3-*para*^{Ts}), 21.94 (C-8), 31.92 (C-7), 31.94 (C-6), 68.56 (C-2'), 71.11 (C-3'), 81.91 (C-3b), 81.94 (C-4a), 83.17 (C-3a), 83.83 (C-4b), 95.01 (C-2), 96.68 (C-5), 125.94 (C-*para*'), 126.58 (C-*meta*'), 126.62 (C-*ortho*^{Ts}), 127.11 (C-*ortho*), 127.51 (C-*meta*^{Ts}), 127.61 (C-*para*), 128.16 (C-*meta*), 128.89 (C-*ortho*'), 138.09 (C-*para*^{Ts}), 139.27 (C-*ipso*'), 139.87 (C-*ipso*), 143.74 (C-*ipso*^{Ts}).

HRMS (ESI$^+$) calculated for $C_{32}H_{37}N_2O_2RuS$ [M–Cl]$^+$: 615.1619; found 615.1608.
IR: ν_{max} = 3275, 3219, 3085, 3061, 3029, 2956, 2927, 2871, 1599, 1534, 1494, 1466, 1378, 1269, 1132, 1129, 1085, 811, 618 cm^{-1}.
$[\alpha]^{20}_{589}$ = +28.5° (*c* 0.134, DMSO).

1.3.9 AH in batch pressure reactors – optimized setup

The substrate (44 μmol) was weighed into a GC vial and dissolved in methanol (0.5 mL). Trifluoroacetic acid (3.4 μL, 44 μmol) was added thereto, and the mixture was stirred for 5 min. The catalyst solution (0.44 μmol of catalyst; concentration 5.4 mg/1 mL in methanol) was added to the mixture and the vial was closed by a pierced square of Parafilm. The vial was placed in an autoclave, which was closed, purged (3 × 5 bar) and filled with hydrogen (15 bar).

After 6 h, the autoclave was opened and a sample of the reaction mixture (200 μL) was mixed with a saturated solution of Na_2CO_3 (1 mL). The solution was extracted with diethyl ether (3 × 1.5 mL) and the organic phase was dried over Na_2SO_4 for 1 h. The ether solution was stripped to dryness in a stream of air. The stripped residue was dissolved in acetonitrile (GC analysis) or acetonitrile-d_3 (NMR analysis).

1.3.10 ATH in an NMR spectrometer

The reactions were monitored *in situ* in an NMR spectrometer at 30 °C by following the same protocol as described in our previous publications.[9a]

Acetonitrile-d_3 (volume calculated so as to reach 730 μL of total volume of the reaction mixture), formic acid (13.1 μL, 0.347 mmol) and triethylamine (19.3 μL, 0.139 mmol) were mixed in an NMR tube. The catalyst (0.275 μmol) dissolved in acetonitrile-d_3 (conc. 5.4 mg/mL) was added to the mixture. Finally, after 5 minutes, the substrate (55 μmol) was added to the reaction mixture. The reaction was followed by ^{1}H NMR.

In the end of the kinetic experiment, a sample of the reaction mixture (200 μL) was mixed with a saturated solution of Na_2CO_3 (1 mL). The solution was extracted with diethyl ether (3 × 1.5 mL) and the organic phase was dried over Na_2SO_4 for 1 h. The ether solution was stripped to dryness in a stream of air. The stripped residue was dissolved in acetonitrile (0.8 mL) and enantioselectivity was measured by GC.[9e]

1.3.11 AH of 1 on a synthetic scale

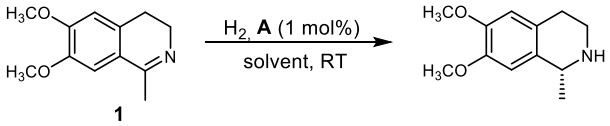
Substrate **1** (90 mg, 0.44 mmol) was weighed into a vial and dissolved in methanol (5 mL). Trifluoroacetic acid (34 μL, 0.44 mmol) was added thereto, and the mixture was stirred for 5 min. The catalyst solution (0.0044 mmol of catalyst; concentration 5.4 mg/1 mL in methanol) was added to the mixture, and the vial was closed by a pierced square of Parafilm. The vial was placed in an autoclave, which was closed, purged (3 × 5 bar) and filled with hydrogen (15 bar).

After 6 h, the autoclave was opened and the reaction mixture was alkalized with a solution of NaOH. The solution was extracted with diethyl ether (3 × 5 mL) and filtered through a plug of silica gel to remove the catalyst. The organic phase was dried over Na_2SO_4, filtered and evaporated. Pale yellow oil was obtained. Yield: 84 mg (92%). 97% *ee* and >95% purity.

2. Supplementary results

2.1 Asymmetric hydrogenation experiments

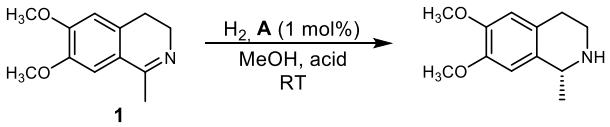
Table S1. Screening of reaction conditions in the AH of **1** with catalyst **A**.[a]



Entry	Concentration (mM)	Volume (mL)	Solvent	Conv (%)
1	44	1	acetonitrile	0
2	88	0.5	acetonitrile	0
3	176	0.25	acetonitrile	0
4	44	1	DMSO	2
5	88	0.5	DMSO	4
6	176	0.25	DMSO	3
7	44	1	MeOH	6
8	88	0.5	MeOH	10
9	176	0.25	MeOH	6

[a] Amount of substrate n = 44 µmol, catalyst loading 1 mol%, $p(H_2)$ = 15 bar, RT, 6 h.

Table S2. Screening of acid additives in the AH of **1** with catalyst **A**.[a]



Entry	Acid	Acid/Substrate[b]	Conv (%)
1	HBF_4 (48%)	1	19
2	TfOH	1	9
3	CF_3COOH	1	57
4	CF_3COOH	0.5	18
5	CF_3COOH	0.75	42
6	CF_3COOH	1.25	52
7	CF_3COOH	1.5	54

[a] Amount of substrate n = 44 µmol, concentration of substrate c = 88 mM, catalyst loading 1 mol%, $p(H_2)$ = 15 bar, RT, 6 h. [b] Molar ratio.

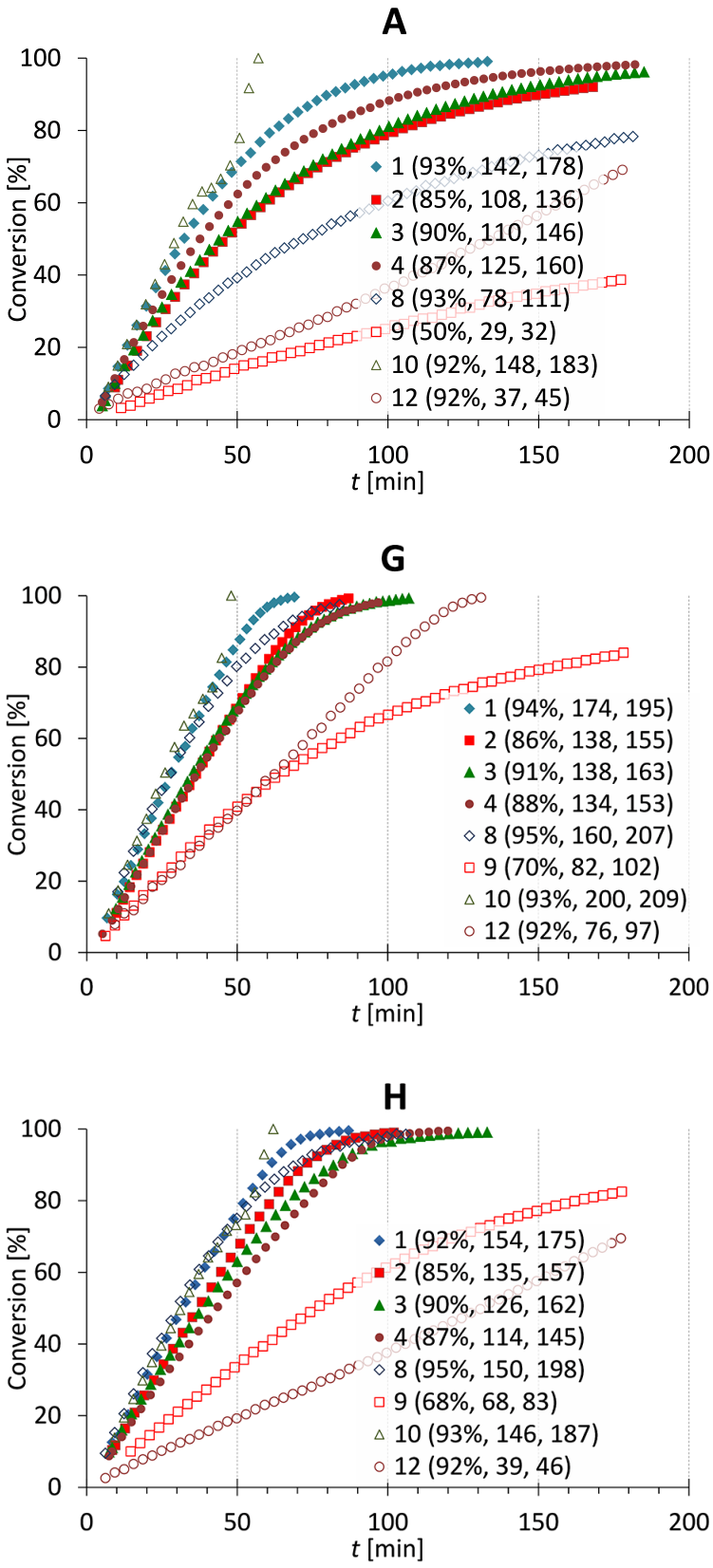
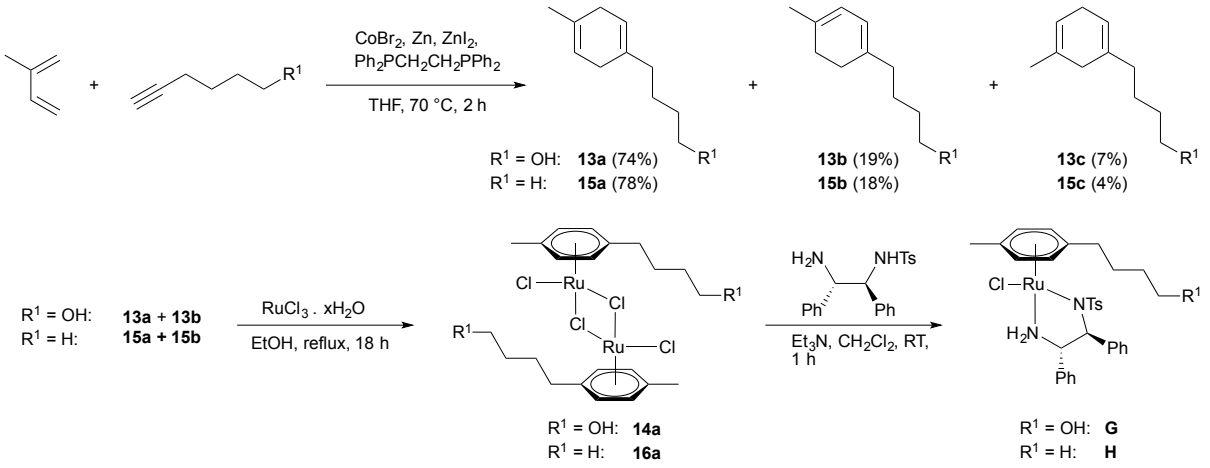


Fig. S1 ATH of imines **1**–**4**, **8**–**10** and **12** catalysed by complexes **A**, **G** and **H** using HCOOH/Et_3N (5:2) in CD_3CN at 0.5 mol% catalyst loading and a temperature of 30 °C. In parentheses: *ee*, TON after 50 min, TOF at 20% conversion in h^{-1}.

2.2 Synthesis of G and H, structural elucidation of 13a–c



Scheme S1 Synthesis of complexes **G** and **H**.

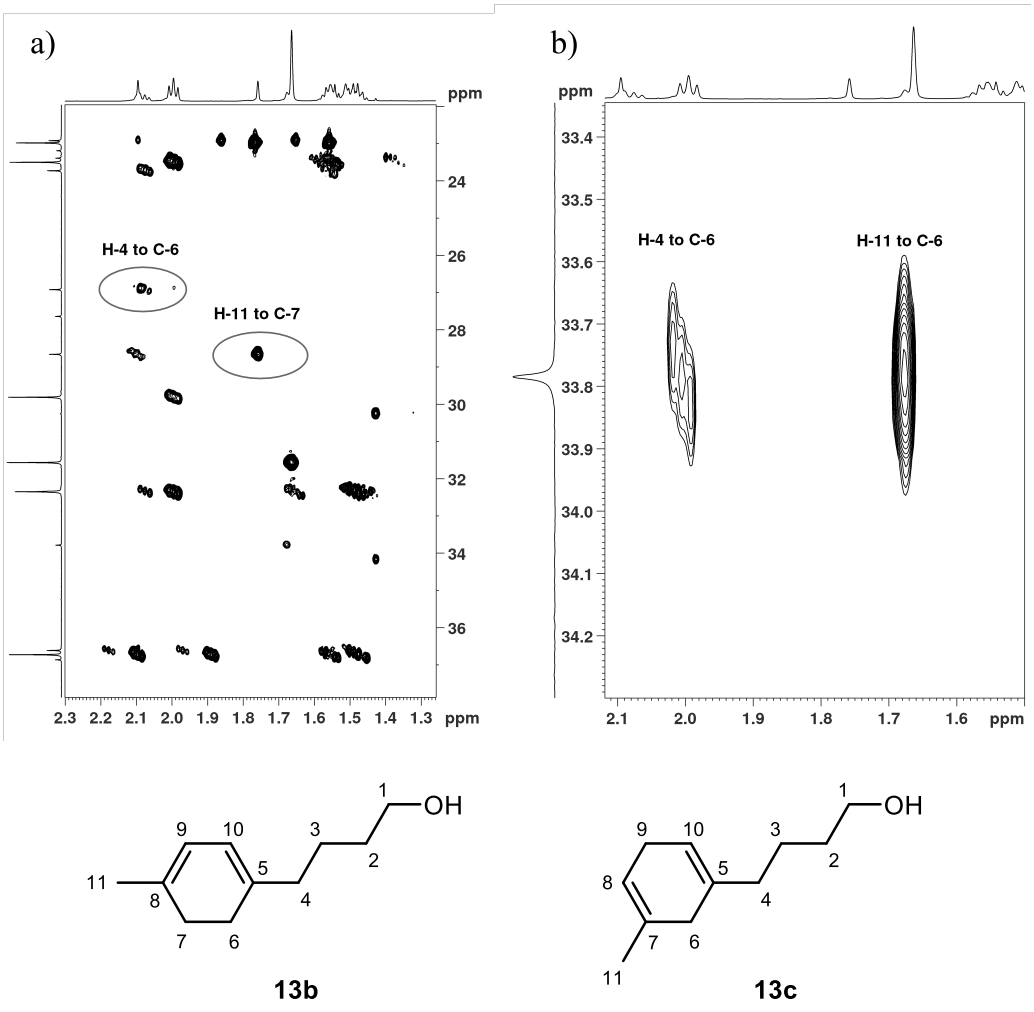


Fig. S2 Parts of a ^{1}H-^{13}C HMBC NMR spectrum of isolated mixture of **13a–c**.
a) **13b**: Correlation of methyl 11 with methylene 7, correlation between methylenes 4 and 6;
b) **13c**: Correlation of methyl 11 and methylene 4 to common methylene 6

2.3 X-ray diffraction analysis of complex G

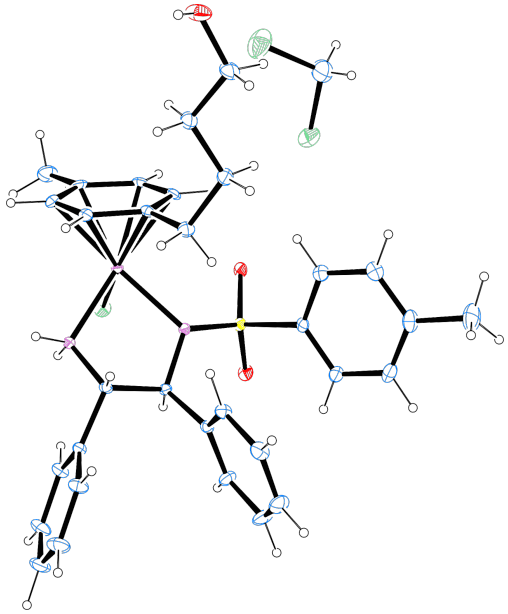


Fig. S3 Solid-state molecular structure of complex **G**

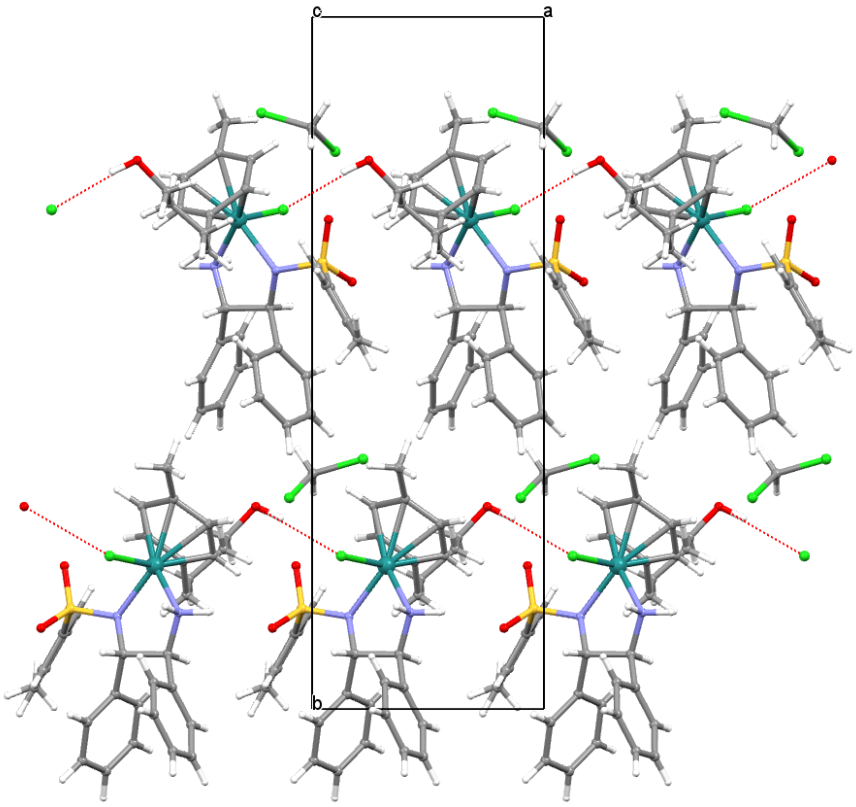


Fig. S4 The molecule of dichloromethane crystallized with **G** in an equimolar ratio. The crystal structure was held together by O-H···Cl hydrogen bonds of 2.39(5) Å between the hydroxyl group (donor) and chloride (acceptor) as evident from the packing view down the *c* axis. Such a hydrogen bond has been observed for similar compounds, although in an intramolecular manner.[10]

Table S3 Crystallographic and structure refinement for complex **G**

Empirical formula	$C_{33}H_{39}Cl_3N_2O_3RuS$
Formula weight	751.21
Crystal system, space group	monoclinic, $P2_1$
T (K)	180
a (Å)	7.77870(10)
b (Å)	22.4690(4)
c (Å)	9.7911(2)
β (deg)	104.5931(14)
V (Å^3)	1656.08(5)
Z	2
μ (mm^{-1})	6.937
Crystal size (mm)	0.38 × 0.24 × 0.18
T_{min}	0.487
T_{max}	1
Measured reflections	35936
Independent reflections	6809
Reflections with $I > 3\sigma(I)$	6754
Parameters	400
R_{int}	0.034
S	2.64
$R[F^2 > 3\sigma(F^2)]$	0.0291
$wR(F)$	0.0405
$\Delta\rho_{max}$ (e Å^{-3})	0.44
$\Delta\rho_{min}$ (e Å^{-3})	–0.91

The title compound crystallizes in the monoclinic space group $P2_1$. The molecular structure is given in Figure 1. The single-crystal structure of $C_{33}H_{39}Cl_3N_2O_3RuS$ is built up of discrete moieties of $C_{32}H_{37}Cl_2N_2O_3RuS$ and dichloromethane with the two formula units in the asymmetric unit.

The absolute structure was tested by introducing twinning and refining volume fractions. The inversion was used as a merohedral twinning operation. In this case, the volume fraction of the inversion twin is the Flack parameter.[11] This parameter refined to a final value of –0.008(7), which confirms that the above configuration is the correct absolute structure.

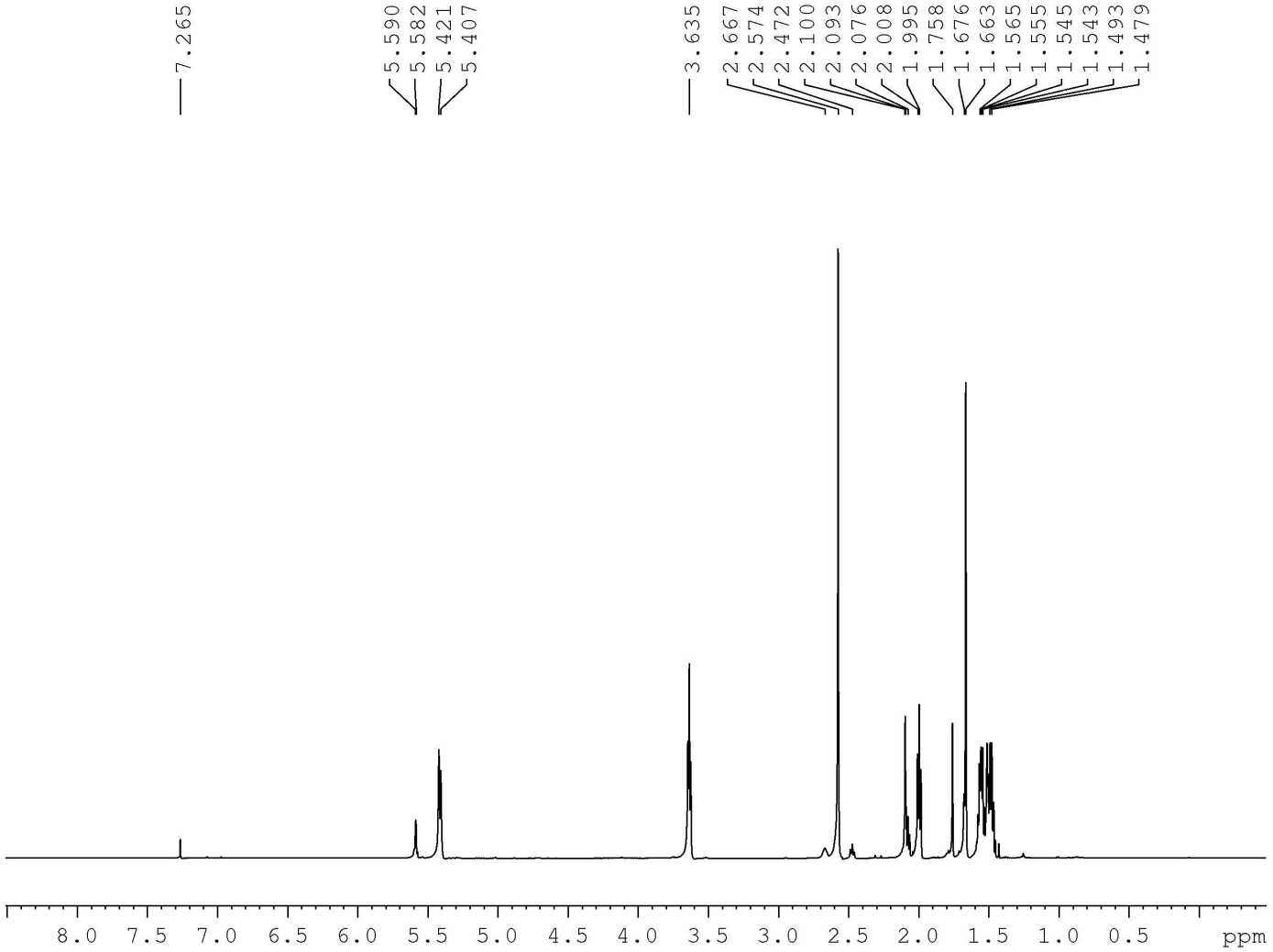
Crystallographic data (including structure factors) for the structure reported in this article has been deposited with the Cambridge Crystallographic Center, CCDC No. 1021406 Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK, fax: +44 1223 336 033, e-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk.

3. References

1. L. Palatinus and G. J. Chapuis, *Appl. Cryst.*, 2007, **40**, 786–790.
2. V. Petříček, M. Dušek and L. Palatinus (2006) *JANA2006*. Institute of Physics, Czech Academy of Sciences, Prague.
3. L. J. Farrugia, *J. Appl. Crystallogr.*, 1999, **32**, 837–838.
4. C. F. Macrae, P. R. Edgington, P. McCabe, E. Pidcock, G. P. Shields, R. Taylor, M. Towler and J. van de Streek, *J. Appl. Crystallogr.*, 2006, **39**, 453–457.
5. K.-J. Haack, S. Hashiguchi, A. Fujii, T. Ikariya and R. Noyori, *Angew. Chem. Int. Ed. Engl.*, 1997, **36**, 285–288; *Angew. Chem.*, 1997, **109**, 297–300.
6. (a) J. Mao and D. C. Baker, *Org. Lett.*, 1999, **1**, 841–843; (b) T. Wang, L.-G. Zhuo, Z. Li, F. Chen, Z. Ding, Y. He, Q.-H. Fan, J. Xiang, Z.-X. Yu and A. S. C. Chan, *J. Am. Chem. Soc.*, 2011, **133**, 9878–9891.
7. T. Touge, T. Hakamata, N. Hideki, T. Kobayashi, N. Sayo, T. Saito, Y. Kayaki and T. Ikariya, *J. Am. Chem. Soc.*, 2011, **133**, 14960–14963.
8. T. Reiner, M. Waibel, A. N. Marziale, D. Jantke, F. J. Kiefer, T. F. Fässler and J. Eppinger, *J. Org. Chem.*, 2010, **695**, 2667–2672.
9. (a) J. Václavík, J. Přech, M. Kuzma, P. Kačer and L. Červený, *Chem. Listy*, 2012, **106**, 206–210; (b) J. Václavík, J. Pecháček, B. Vilhanová, P. Šot, J. Januščák, V. Matoušek, J. Přech, S. Bártová, M. Kuzma and P. Kačer, *Catal. Lett.*, 2013, **143**, 555–562; (c) J. Václavík, P. Šot, B. Vilhanová, J. Pecháček, M. Kuzma and P. Kačer, *Molecules*, 2013, **18**, 6804–6828; (d) M. Kuzma, J. Václavík, P. Novák, J. Přech, J. Januščák, J. Červený, J. Pecháček, P. Šot, B. Vilhanová, V. Matoušek, I. I. Goncharova, M. Urbanová and P. Kačer, *Dalton Trans.*, 2013, **42**, 5174–5182; (e) J. Přech, V. Matoušek, J. Václavík, J. Pecháček, K. Syslová, P. Šot, J. Januščák, B. Vilhanová, M. Kuzma and P. Kačer, *Am. J. Anal. Chem.*, 2013, **4**, 125–133; (f) J. Přech, J. Václavík, P. Šot, J. Pecháček, B. Vilhanová, J. Januščák, K. Syslová, R. Pažout, J. Maixner, J. Zápal, M. Kuzma and P. Kačer, *Catal. Commun.*, 2013, **36**, 67–70; (g) S. Watanuki, K. Matsuura, Y. Tomura, M. Okada, T. Okazaki, M. Ohta, S. Tsukamoto, *Chem, Pharm. Bull.* 2011, **59**, 1029–1037; (h) I. Ivanov, S. Nikolova, S. Statkova-Abeghe, *Heterocycles* 2005, **65**, 2483–2492; (i) Q.-R. Zhang, J.-R. Huang, W. Zhang, L. Dong, *Org. Lett.* 2014, **16**, 1684–1687.
10. J. Čubrilo, I. Hartenbach, T. Schleid and R. F. Winter, *Zeitschrift für Anorg. und Allg. Chemie*, 2006, **632**, 400–408.
11. H. D. Flack, *Acta Crystallogr., Sect. A: Found. Cryst.*, 1983, **39**, 876–881.

4. Copies of NMR spectra

4.1 4-(4-methylcyclohexa-1,4-dienyl)butan-1-ol (13a–c)

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RG                       4.5
DW                  25.000 usec
DE                   6.50 usec
TE                   293.2 K
D1              1.00000000 sec
TD0                        1

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PL1                    4.70 dB
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SFO1           600.2360000 MHz

F2 - Processing parameters
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WDW                       no
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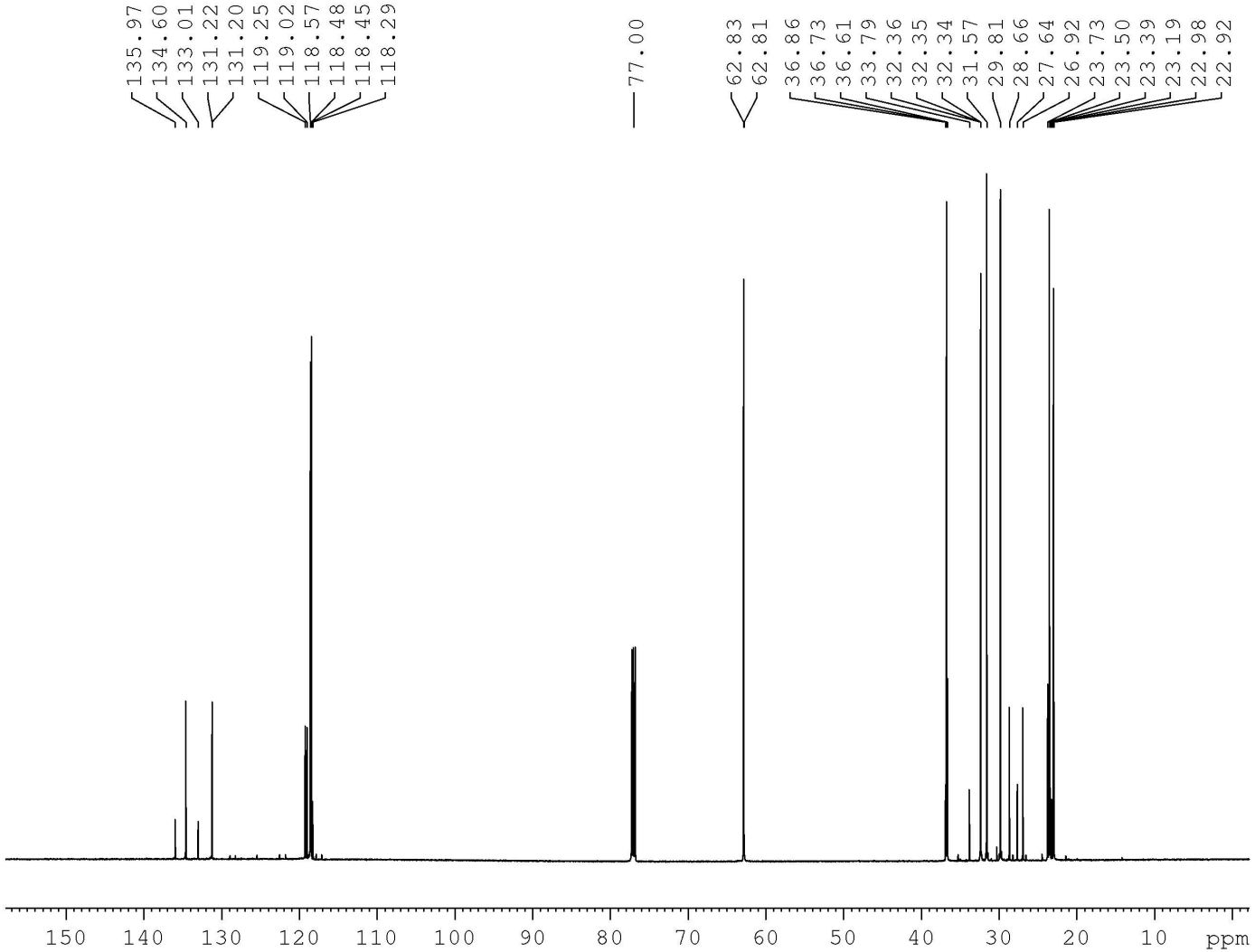
date: 8 Apr 2013

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FIDRES              0.275098 Hz
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RG                       2050
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DE                     30.00 usec
TE                     293.2 K
D1                 1.00000000 sec
D11                0.03000000 sec
L31                         1
TD0                         1

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PL1                     0.30 dB
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SFO1             150.9430463 MHz

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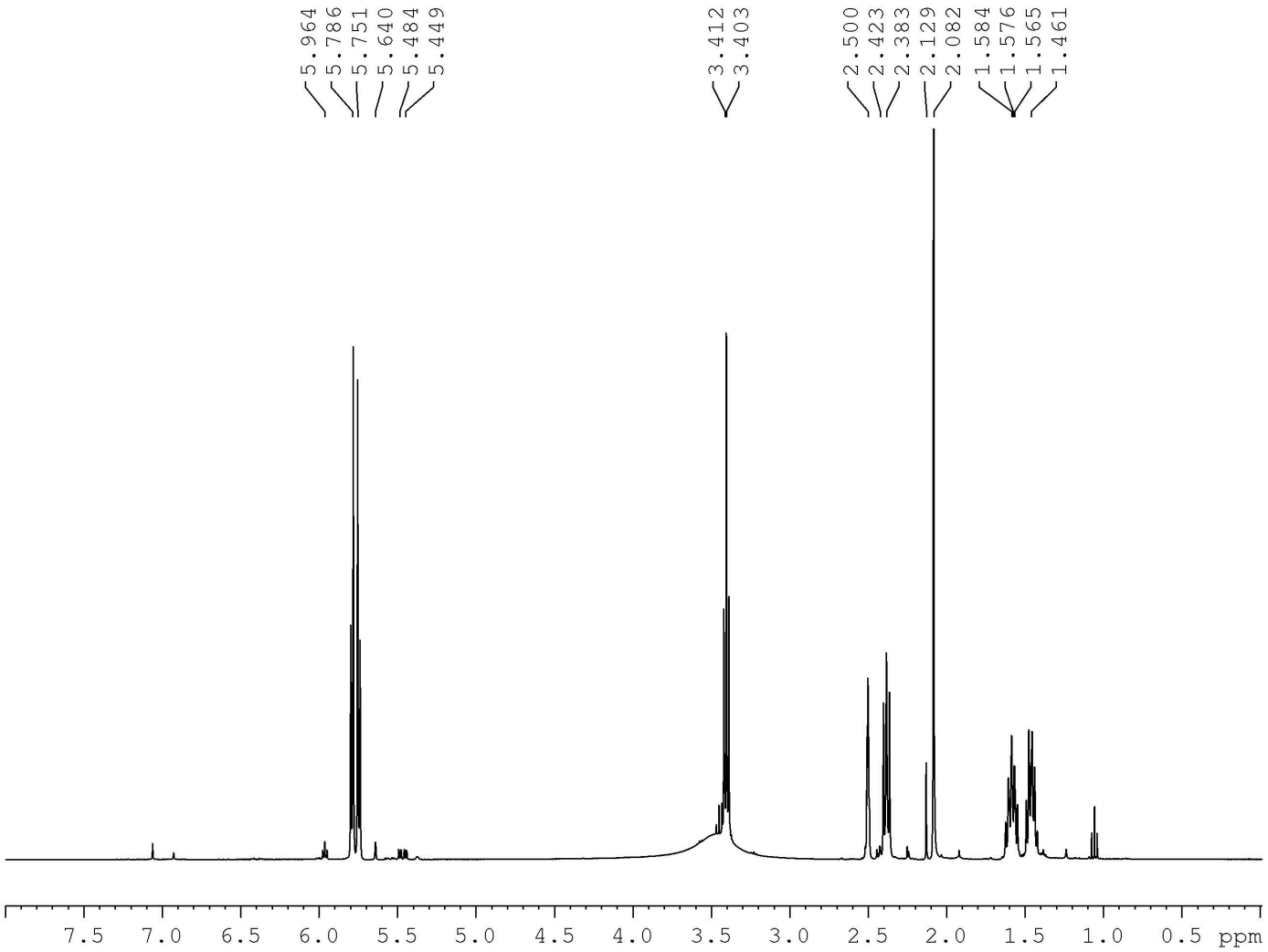
NUC2                      1H
PCPD2                  80.00 usec
PL2                     4.70 dB
PL12                   24.17 dB
PL13                   24.70 dB
PL2W               5.66006804 W
PL12W              0.06394722 W
PL13W              0.05660067 W
SFO2              600.2324009 MHz

F2 - Processing parameters
SI                      262144
SF                150.9279641 MHz
WDW                       EM
SSB          0
LB                      1.00 Hz
GB           0
PC                      1.40
```

4.2 [(η^6-(4-(*p*-methylphenyl)butanol)$RuCl_2$]$_2$ (14a,b)

BV011-3
solvent: DMSO-d6
temp: 303,2 K
date: 29 MAR 2013



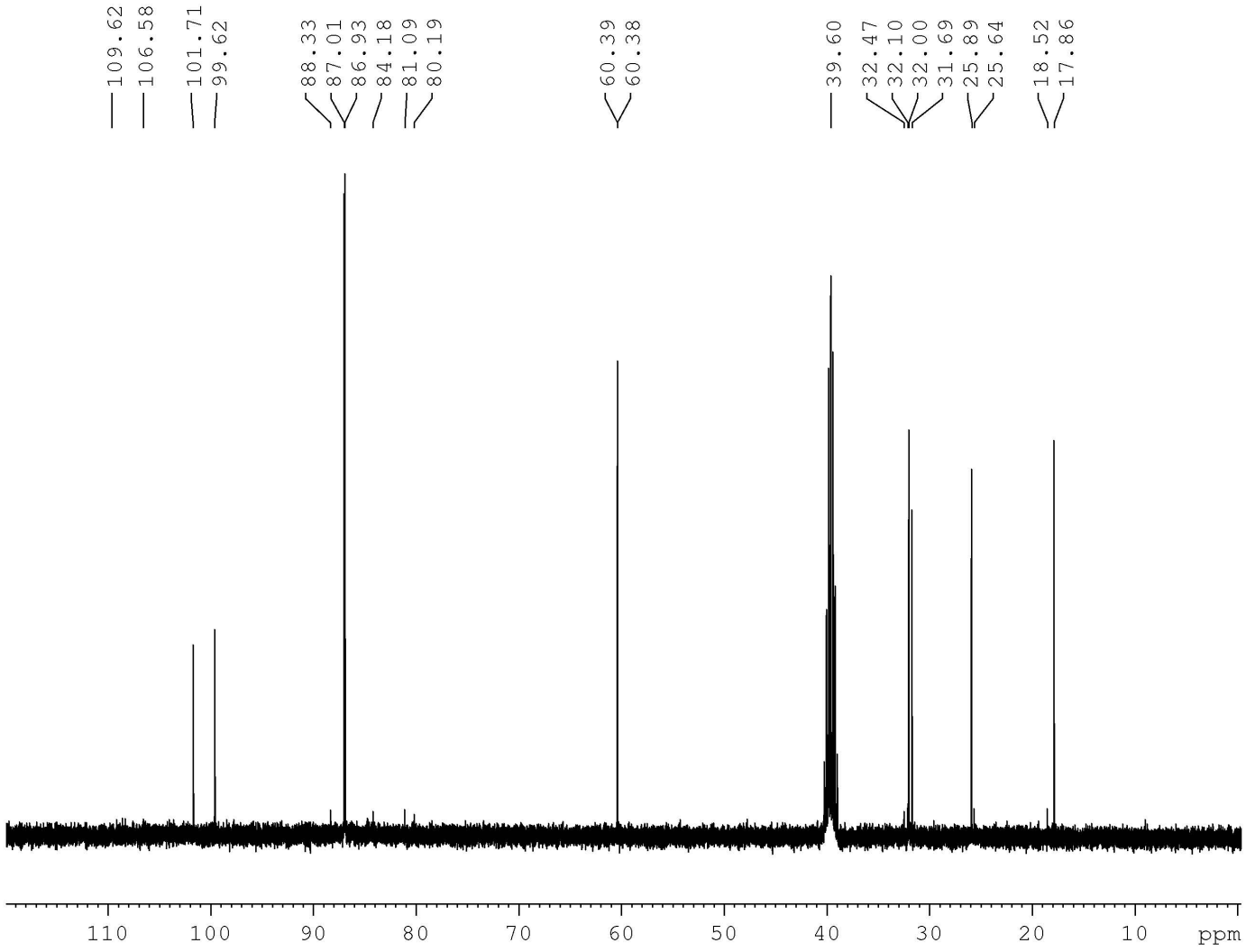

```
Current Data Parameters
NAME                  BV011-3
EXPNO                       1
PROCNO                      4

F2 - Acquisition Parameters
Date_                20130329
Time                    10.11
INSTRUM                 spect
PROBHD    5 mm BBI 1H/D-
PULPROG                    zg
TD                      65536
SOLVENT                  DMSO
NS                        128
DS                          4
SWH                  8012.820 Hz
FIDRES               0.122266 Hz
AQ                   4.0894465 sec
RG                        812
DW                     62.400 usec
DE                      6.50 usec
TE                     303.2 K
D1                1.00000000 sec
TD0                         1

======== CHANNEL f1 ========
SFO1              400.0032000 MHz
NUC1                        1H
P1                       7.00 usec
PLW1              15.10200024 W

F2 - Processing parameters
SI                      131072
SF                400.0000032 MHz
WDW                        EM
SSB       0
LB        0 Hz
GB        0
PC                       1.00
```

BV011-3
solvent: DMSO-d6
temp: 303,2 K
date: 29 MAR 2013




```
Current Data Parameters
NAME                  BV011-3
EXPNO                       2
PROCNO                      3

F2 - Acquisition Parameters
Date_               20130329
Time                   10.56
INSTRUM                spect
PROBHD    5 mm BBI 1H/D-
PULPROG                 zgpg
TD                     65536
SOLVENT                 DMSO
NS                      2304
DS                         4
SWH                25252.525 Hz
FIDRES             0.385323 Hz
AQ                 1.2976128 sec
RG                      2050
DW                    19.800 usec
DE                     6.50 usec
TE                    303.2 K
D1                 1.00000000 sec
D11                0.03000000 sec
TD0                         1

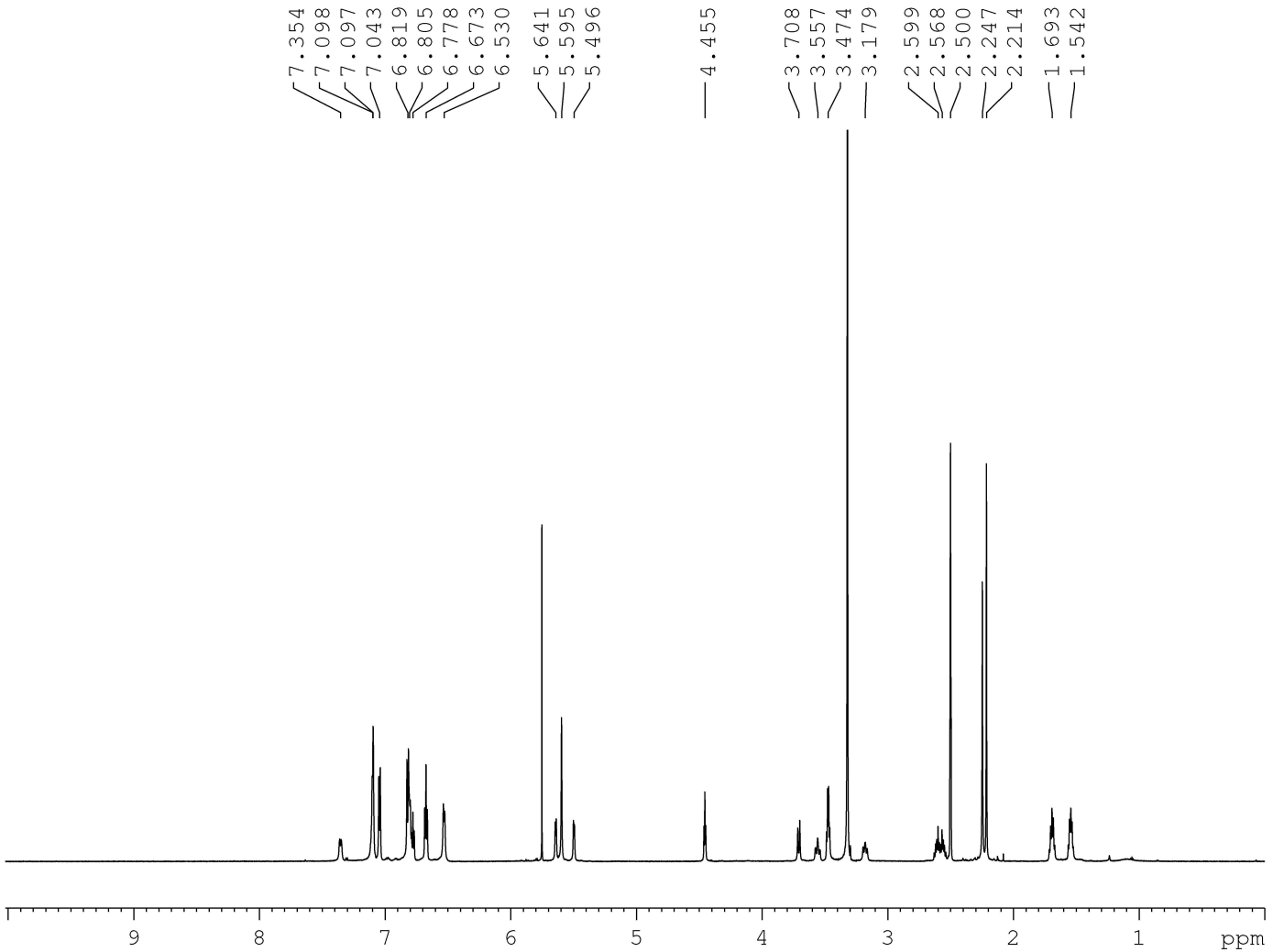
======== CHANNEL f1 ========
SFO1             100.5921496 MHz
NUC1                     13C
P1                     13.90 usec
PLW1             89.36699677 W

======== CHANNEL f2 ========
SFO2             400.0016000 MHz
NUC2                     1H
CPDPRG[2 bi_waltz65_256
PCPD2                  90.00 usec
PLW2             15.10200024 W
PLW12             0.09135900 W
PLW13             0.07400100 W

F2 - Processing parameters
SI                      131072
SF               100.5801248 MHz
WDW                       EM
SSB       0
LB        0 Hz
GB        0
PC                      1.40
```

4.3 [RuCl(η^6-(*p*-methylphenyl)butanol)(*S*,*S*)-TsDPEN] (G)

BV023-1
solvent: DMSO-d6
temp: 303,2 K
date: 9 Apr 2013



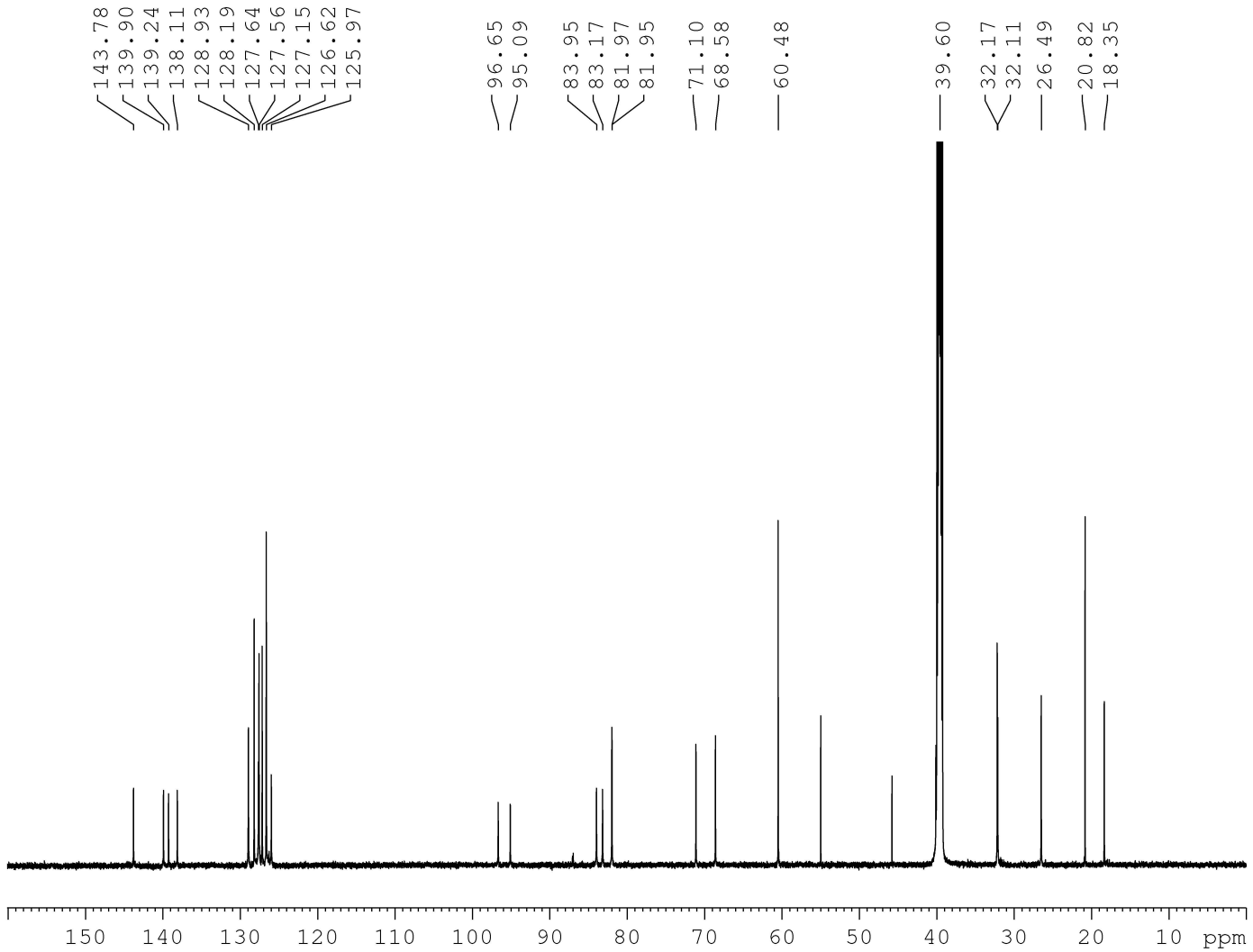

```
Current Data Parameters
NAME                  BV023-1
EXPNO                       1
PROCNO                      1

F2 - Acquisition Parameters
Date_              20130409
Time                  14.04
INSTRUM               spect
PROBHD    5 mm CPTCI 1H/
PULPROG                zg30
TD                   131072
SOLVENT                DMSO
NS                       128
DS                         4
SWH               21008.404 Hz
FIDRES             0.160281 Hz
AQ                3.1195135 sec
RG                         9
DW                   23.800 usec
DE                   21.00 usec
TE                    303.1 K
D1               1.00000000 sec
TD0                        1

======== CHANNEL f1 ========
SFO1            700.1370013 MHz
NUC1                    1H
P1                    7.10 usec
PLW1           12.00000000 W

F2 - Processing parameters
SI                    262144
SF              700.1300095 MHz
WDW                     EM
SSB       0
LB        0 Hz
GB        0
PC                    1.00
```

BV023-1
solvent: DMSO-d6
temp: 303,2 K
date: 9 Apr 2013




```
Current Data Parameters
NAME                  BV023-1
EXPNO                       2
PROCNO                      2

F2 - Acquisition Parameters
Date_                20130409
Time                    14.19
INSTRUM                spect
PROBHD    5 mm CPTCI 1H/
PULPROG                zgpg30
TD                     130892
SOLVENT                   DMSO
NS                        4096
DS                          32
SWH                 41666.668 Hz
FIDRES                0.318329 Hz
AQ                    1.5707040 sec
RG                         2050
DW                       12.000 usec
DE                       18.00 usec
TE                       303.3 K
D1                  1.00000000 sec
D11                 0.03000000 sec
TD0                         1

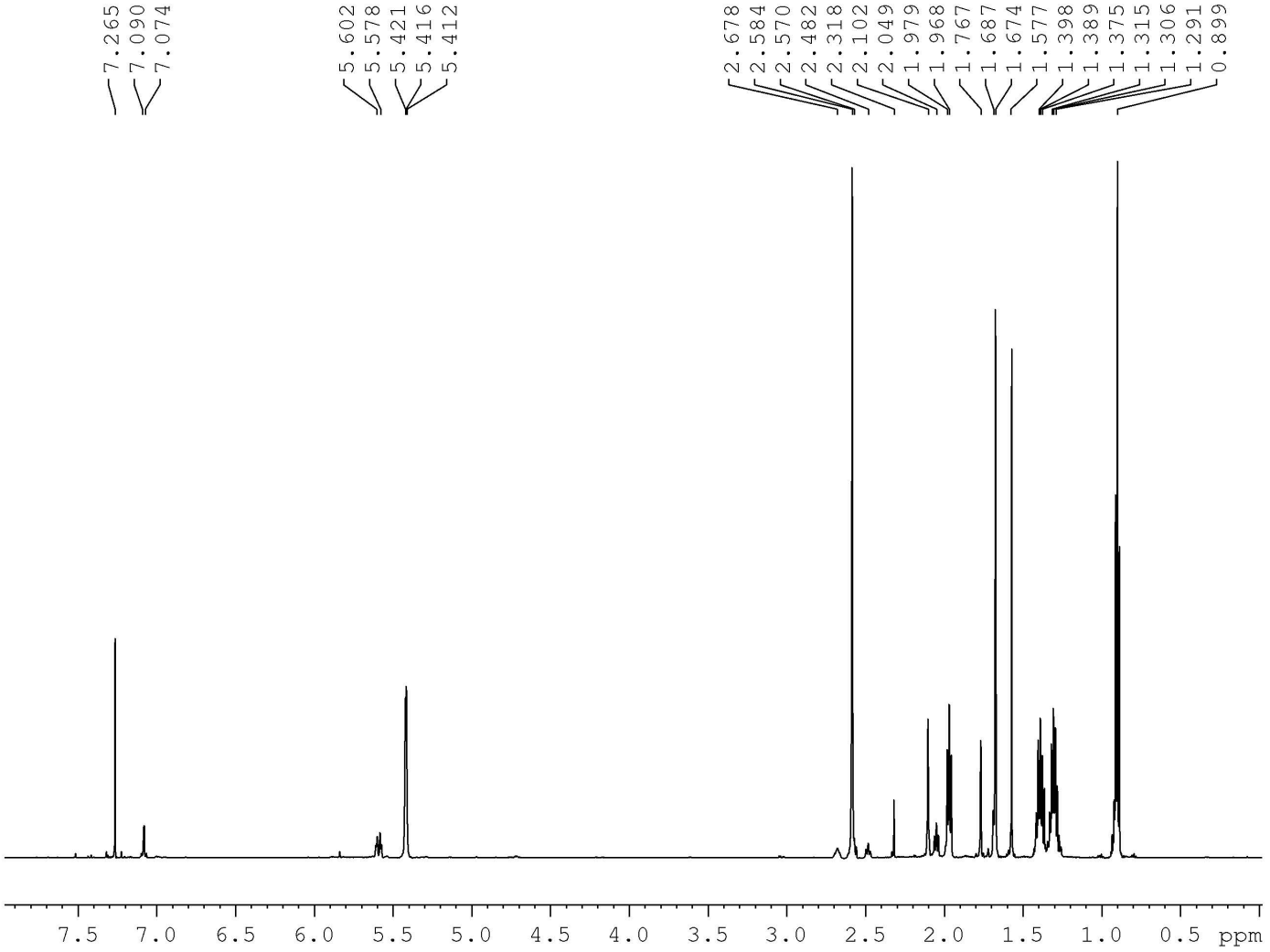
======== CHANNEL f1 ========
SFO1               176.0654325 MHz
NUC1                       13C
P1                       12.50 usec
PLW1               -1.00000000 W

======== CHANNEL f2 ========
SFO2               700.1328005 MHz
NUC2                       1H
CPDPRG[2                 mlev
PCPD2                    65.00 usec
PLW2               -1.00000000 W
PLW12              -1.00000000 W
PLW13              -1.00000000 W

F2 - Processing parameters
SI                       262144
SF                 176.0479018 MHz
WDW                        EM
SSB          0
LB                        1.00 Hz
GB           0
PC                        1.40
```

4.4 4-(4-methylcyclohexa-1,4-dienyl)butane (15a–c)

BV-D4
solvent: CDCl3
temp: 293.2 K
date : 22 Aug 2014



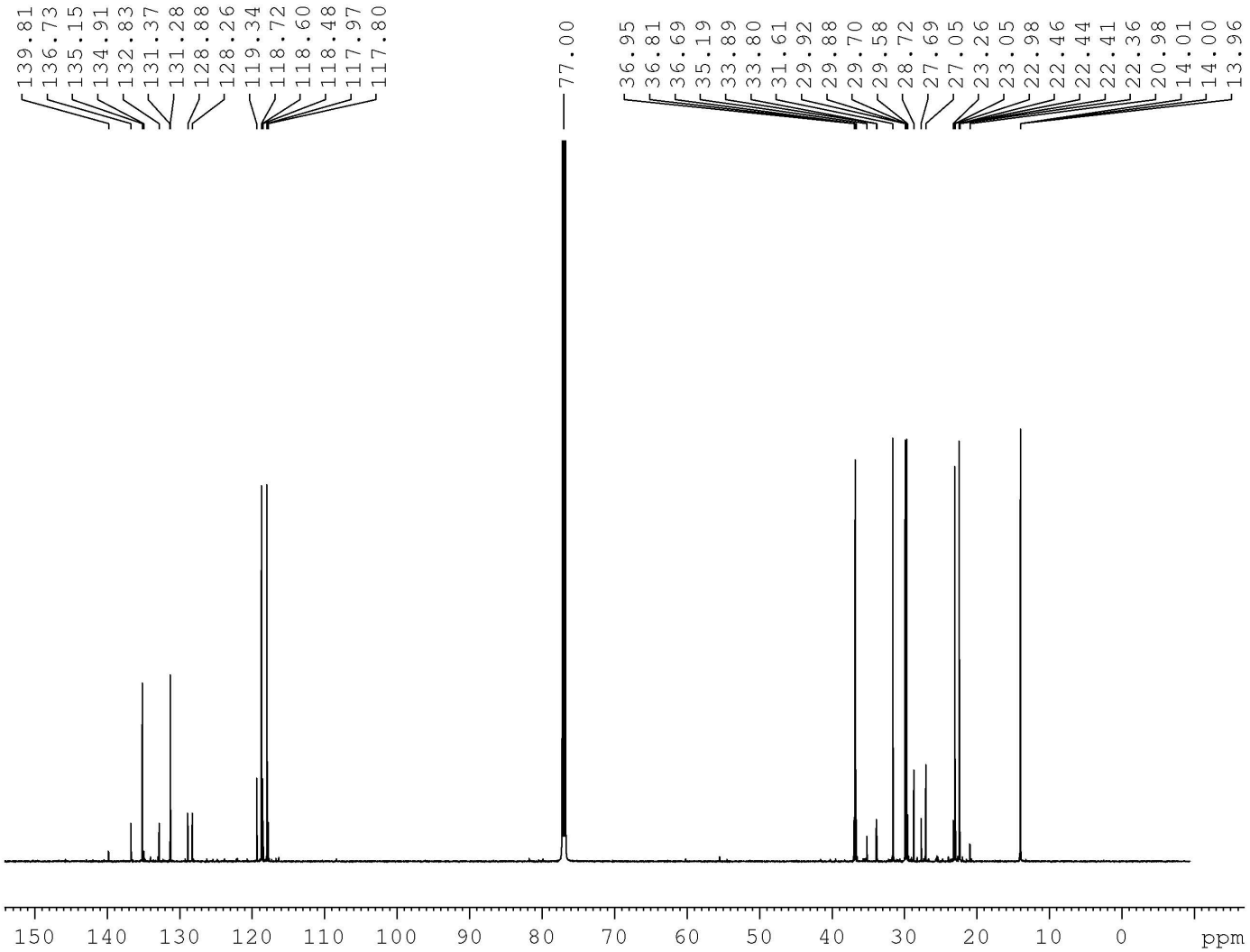

```
Current Data Parameters
NAME                  BV-D4
EXPNO                     1
PROCNO                    1

F2 - Acquisition Parameters
Date_              20140822
Time                   6.31
INSTRUM               spect
PROBHD    5 mm CPTCI 1H-
PULPROG                 zg
TD                    131072
SOLVENT               CDCl3
NS                      128
DS                        4
SWH               18028.846 Hz
FIDRES             0.137549 Hz
AQ                 3.6350634 sec
RG                        9
DW                   27.733 usec
DE                   11.49 usec
TE                   293.1 K
D1                1.00000000 sec
TD0                       1

======== CHANNEL f1 ========
SFO1            600.2360023 MHz
NUC1                    1H
P1                    8.50 usec
PLW1             5.66009998 W

F2 - Processing parameters
SI                      262144
SF              600.2300121 MHz
WDW                       EM
SSB       0
LB                    0.20 Hz
GB        0
PC                    1.00
```

BV-D4
solvent: DMSO
temp: 303.2 K
date : 22 Aug 2014




```
Current Data Parameters
NAME                  BV-D4
EXPNO                     2
PROCNO                    2

F2 - Acquisition Parameters
Date_              20140822
Time                  7.42
INSTRUM              spect
PROBHD    5 mm CPTCI 1H-
PULPROG             zgpg30
TD                  130892
SOLVENT              CDCl3
NS                    8192
DS                      64
SWH             39062.500 Hz
FIDRES           0.298433 Hz
AQ               1.6754175 sec
RG                    203
DW                 12.800 usec
DE                 30.00 usec
TE                 293.1 K
D1              1.00000000 sec
D11             0.03000000 sec
TD0                     1

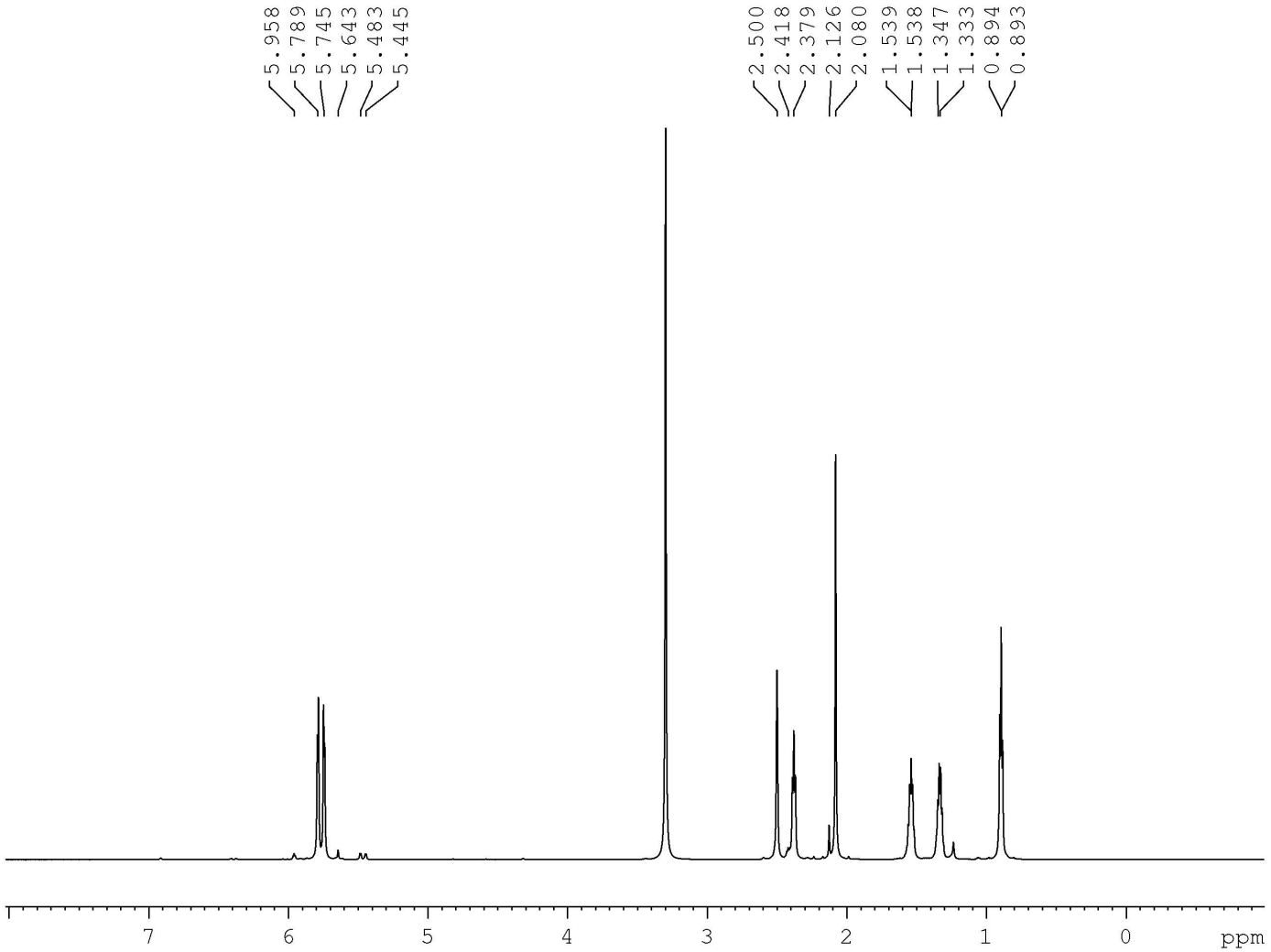
======== CHANNEL f1 ========
SFO1          150.9460654 MHz
NUC1                  13C
P1                 12.00 usec
PLW1        107.12999725 W

======== CHANNEL f2 ========
SFO2          600.2324009 MHz
NUC2                  1H
CPDPRG[2 bi_waltz65_256
PCPD2              70.00 usec
PLW2           5.66009998 W
PLW12          0.08345700 W
PLW13          0.04089400 W

F2 - Processing parameters
SI                  262144
SF            150.9279594 MHz
WDW                   EM
SSB       0
LB                 1.00 Hz
GB        0
PC                 1.40
```

4.5 [(η^6-(4-(*p*-methylphenyl)butane)$RuCl_2$]$_2$ (16a,b)

BV-037-1
solvent: DMSO
temp: 303.2 K
date : 24 Jul 2014



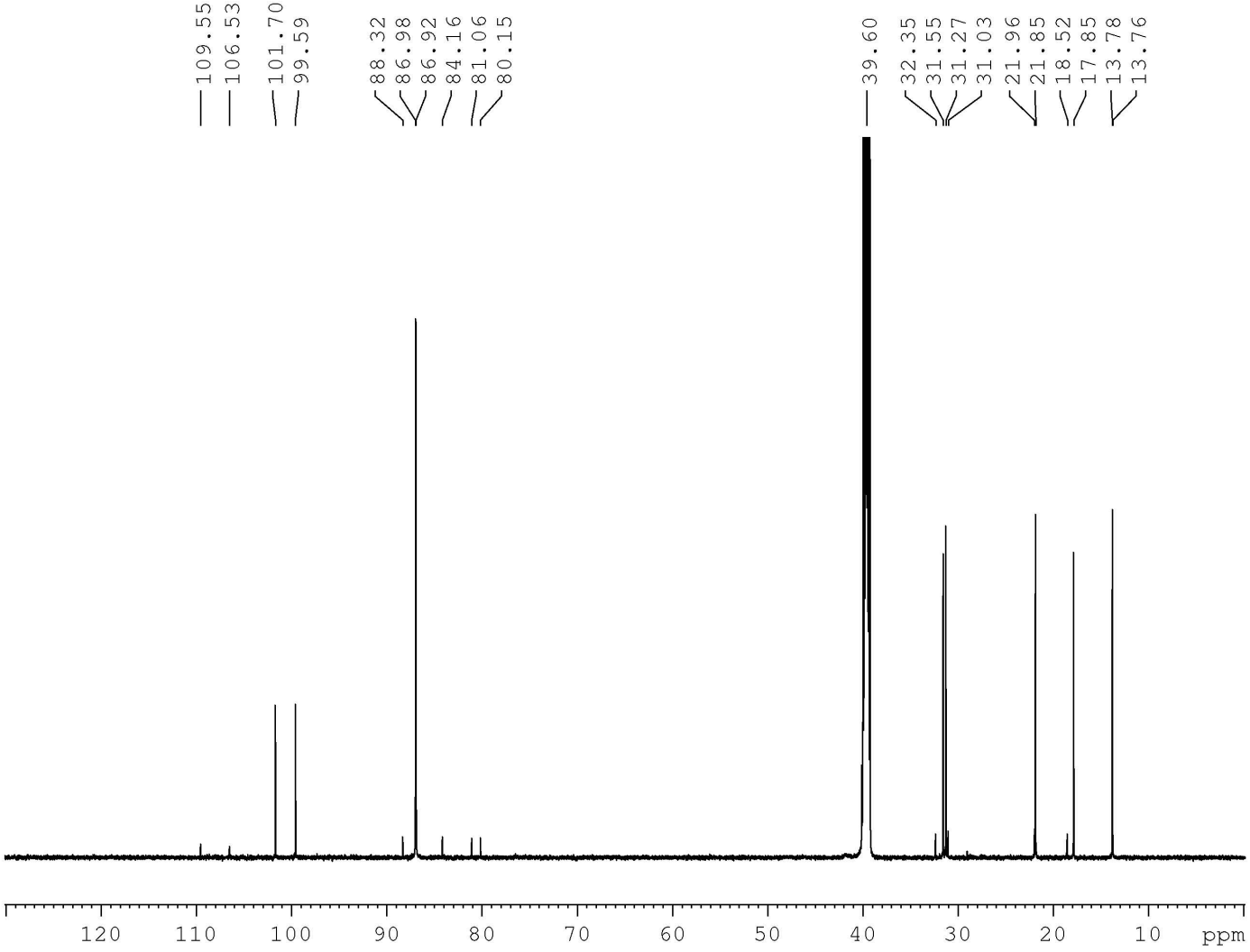

```
Current Data Parameters
NAME                  BV037-1
EXPNO                       1
PROCNO                      3

F2 - Acquisition Parameters
Date_               20140724
Time                   22.04
INSTRUM                spect
PROBHD    5 mm CPTCI 1H/
PULPROG                   zg
TD                    131072
SOLVENT                 DMSO
NS                       128
DS                         4
SWH                21008.404 Hz
FIDRES              0.160281 Hz
AQ                 3.1195135 sec
RG                         4
DW                    23.800 usec
DE                    10.00 usec
TE                     303.2 K
D1                1.00000000 sec
TD0                        1

======== CHANNEL f1 ========
SFO1             700.1370013 MHz
NUC1                     1H
P1                     7.10 usec
PLW1            12.00000000 W

F2 - Processing parameters
SI                     262144
SF               700.1300061 MHz
WDW                      EM
SSB          0
LB           0 Hz
GB           0
PC                     1.00
```

BV-037-1
solvent: DMSO
temp: 303.2 K
date : 24 Jul 2014




```
Current Data Parameters
NAME              BV037-1
EXPNO                   2
PROCNO                  4

F2 - Acquisition Parameters
Date_            20140724
Time                22.33
INSTRUM             spect
PROBHD   5 mm CPTCI 1H/
PULPROG            zgpg30
TD                 130892
SOLVENT               DMSO
NS                    2048
DS                      64
SWH             45454.547 Hz
FIDRES           0.347268 Hz
AQ               1.4398119 sec
RG                    2050
DW                 11.000 usec
DE                 30.00 usec
TE                 303.2 K
D1              1.00000000 sec
D11             0.03000000 sec
TD0                     1

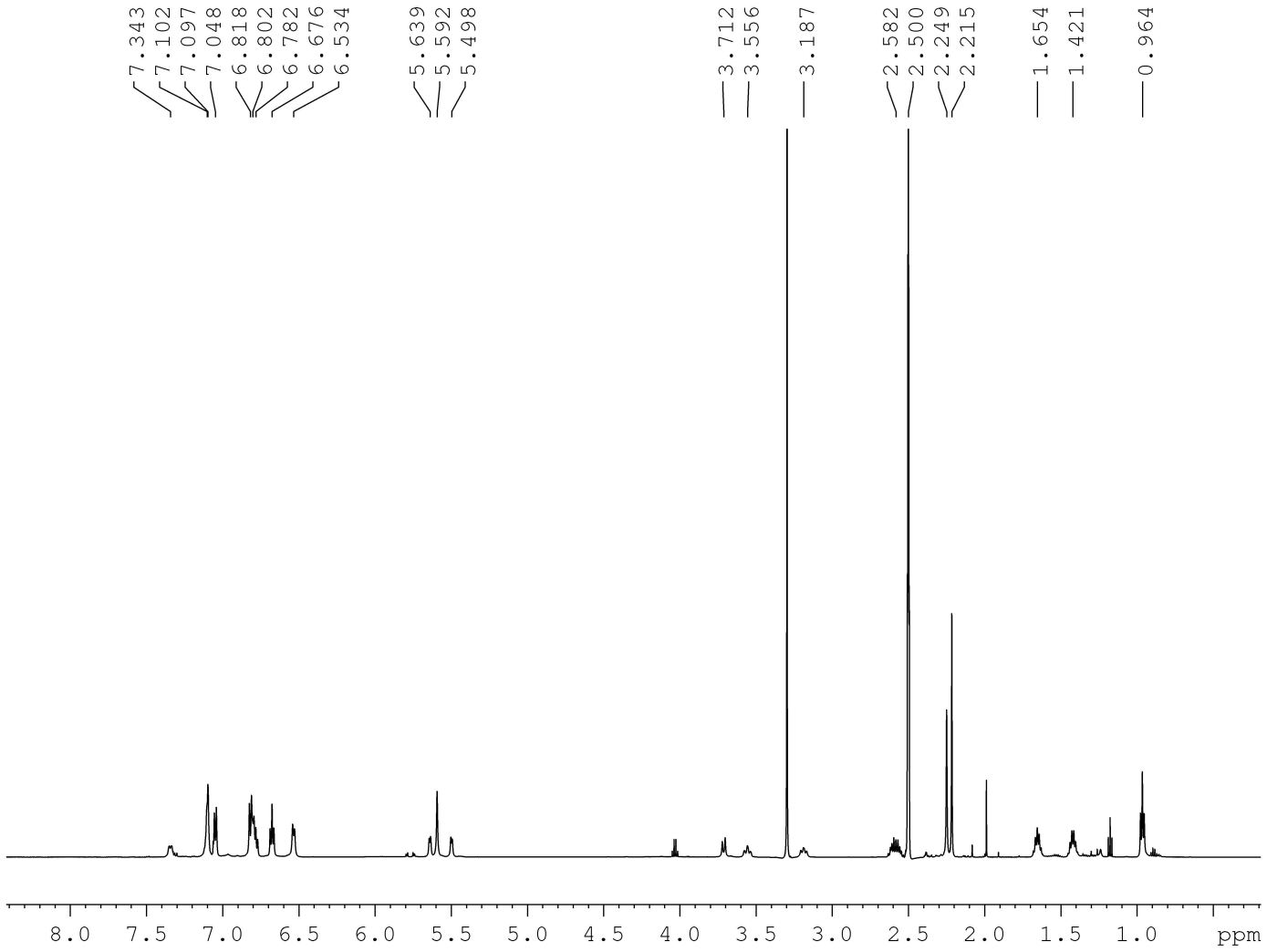
======== CHANNEL f1 ========
SFO1          176.0689543 MHz
NUC1                    13C
P1                   12.50 usec
PLW1        130.00000000 W

======== CHANNEL f2 ========
SFO2          700.1328005 MHz
NUC2                    1H
CPDPRG[2 bi_waltz65_256
PCPD2                65.00 usec
PLW2         12.00000000 W
PLW12         0.14318000 W
PLW13         0.06049200 W

F2 - Processing parameters
SI                   262144
SF            176.0479064 MHz
WDW                     EM
SSB       0
LB                    1.00 Hz
GB        0
PC                    1.40
```

4.6 [RuCl(η^6-(*p*-methylphenyl)butane)(*S*,*S*)-TsDPEN] (H)

BV038-1a
solvent: DMSO
temp: 303.2 K
date : 20 Aug 2014



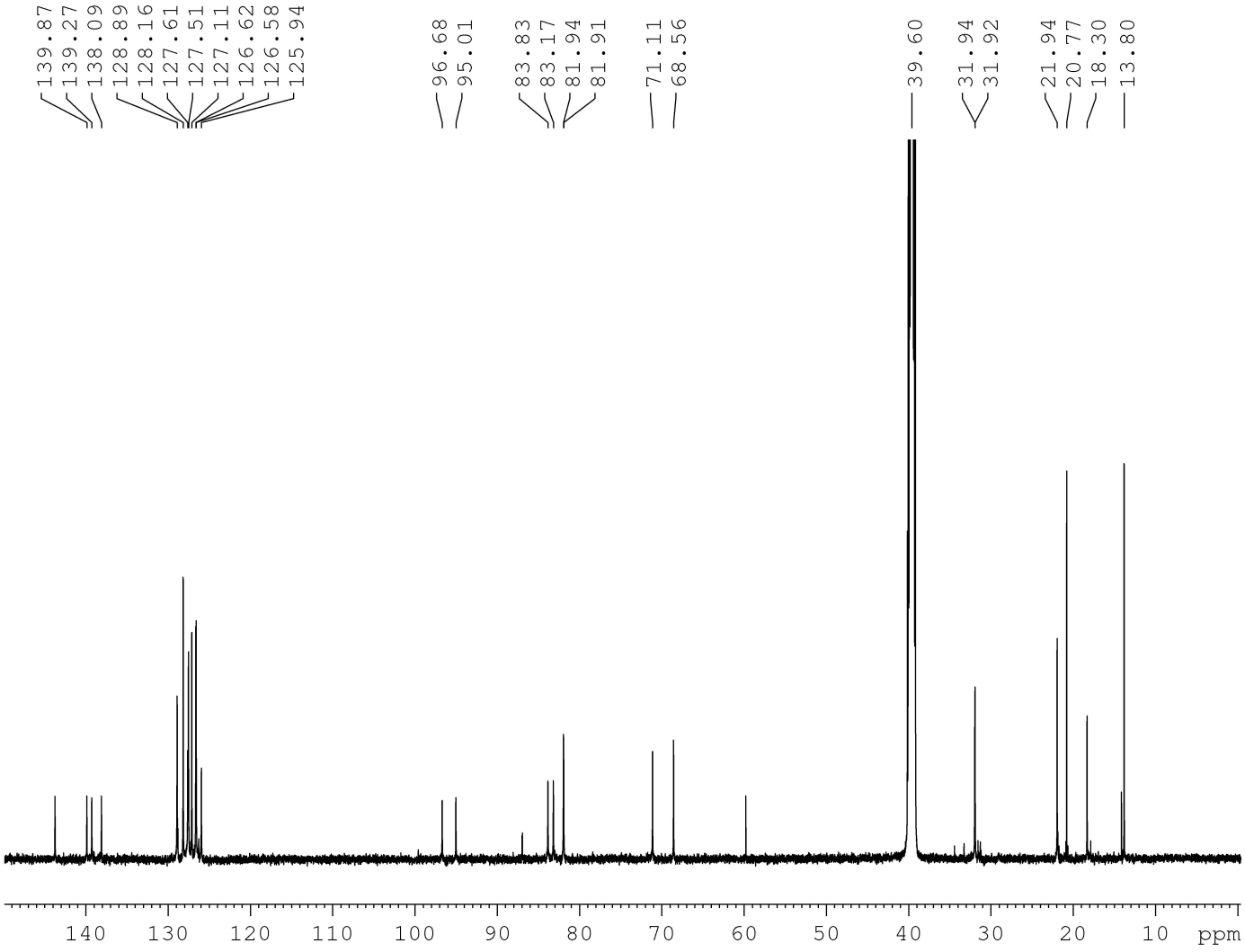

```
Current Data Parameters
NAME            BV038-1a
EXPNO                  1
PROCNO                 2

F2 - Acquisition Parameters
Date_           20140820
Time               14.27
INSTRUM            spect
PROBHD   5 mm CPTCI 1H-
PULPROG                zg
TD                131072
SOLVENT              DMSO
NS                     32
DS                      4
SWH            18028.846 Hz
FIDRES          0.137549 Hz
AQ             3.6350634 sec
RG                      9
DW                 27.733 usec
DE                  11.49 usec
TE                  303.2 K
D1           60.00000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1         600.2360023 MHz
NUC1                   1H
P1                   8.50 usec
PLW1          5.66009998 W

F2 - Processing parameters
SI                262144
SF           600.2300041 MHz
WDW                   EM
SSB       0
LB                  0.20 Hz
GB        0
PC                  1.00
```

BV038-1a
solvent: DMSO
temp: 303.2 K
date : 20 Aug 2014




```
Current Data Parameters
NAME            BV038-1a
EXPNO                  2
PROCNO                 2

F2 - Acquisition Parameters
Date_           20140820
Time               15.25
INSTRUM            spect
PROBHD   5 mm CPTCI 1H-
PULPROG           zgpg30
TD                130892
SOLVENT              DMSO
NS                    8192
DS                      64
SWH            39062.500 Hz
FIDRES          0.298433 Hz
AQ             1.6754175 sec
RG                   1620
DW                12.800 usec
DE                18.00 usec
TE                303.2 K
D1            1.00000000 sec
D11           0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1         150.9460654 MHz
NUC1                 13C
P1                12.00 usec
PLW1       107.12999725 W

======== CHANNEL f2 ========
SFO2         600.2324009 MHz
NUC2                 1H
CPDPRG[2 bi_waltz65_256
PCPD2                70.00 usec
PLW2          5.66009998 W
PLW12         0.08345700 W
PLW13         0.04089400 W

F2 - Processing parameters
SI                262144
SF           150.9280202 MHz
WDW                  EM
SSB       0
LB                1.00 Hz
GB        0
PC                1.40
```