

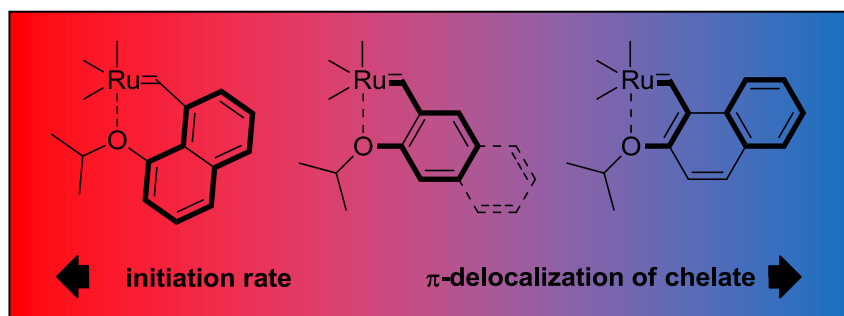
Supporting Information for:

A missing relative: Hoveyda-Grubbs metathesis catalyst bearing *peri*-substituted naphthalene framework

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submitted to *Organometallics*

Complete citation of reference 35

Gaussian 03, Revision E.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, and J. A. Pople, Gaussian, Inc., Wallingford CT, 2004.

General Informations

All synthetic manipulations were performed under argon (oxygen-free) using the Schlenk technique. Tetrahydrofuran (THF), toluene, dichloromethane, were dried by standard methods. *n*-Hexane and ethyl acetate used for column chromatography were distilled. Commercially available materials were used without further purification unless stated otherwise. Complex **12** was obtained from commercial sources, complexes **2**[10], **4a** and **4b**[9] were prepared according to literature methods. Column chromatography was performed on silica gel 60 (Aldrich, 70-230 mesh). Thin layer chromatography (TLC) was performed on Fluka aluminium backed silica plates with fluorescent UV₂₅₄ indicator. ¹H and ¹³C NMR spectra were recorded with a Bruker Avance 500 MHz spectrometer and Varian 200 MHz spectrometer. Activity profiles were recorded on a Varian 200 MHz spectrometer. Chemical shifts (δ) are given in parts per million (ppm) relative to solvent peaks CDCl₃ (7.24 ppm, and 77.0 ppm), and CH₂Cl₂ (5.32 ppm, and 53.84 ppm). Spin multiplicity were abbreviated as follows: s – singlet, d – doublet, t – triplet, sept – septet.

Abbreviations: NHC = N-heterocyclic carbene; RCM= ring-closing metathesis; ROMP = ring-opening metathesis polymerization; Cy = cyclohexyl; Ph = phenyl.

Synthesis of compound 10

Synthesis of 1,8-naphtholactam (**10**) was performed according to literature with following modifications:

An argonated three-necked round-bottom 250 ml flask was charged with 1,8-naphthalic anhydride **9** (16.89 g; 85.25 mmol), NH₂OH·HCl (5.922 g; 85.22 mmol) and pyridine (121 ml). The mixture was stirred with slight exothermic effect for few minutes. Then the mixture was heated under reflux for 10 min. Heating bath was removed, and to hot solution p-toluene sulfonyl chloride (35.58 g; 186.6 mmol) was added in portions and mixture was refluxed for 1 h. Heating bath was removed and hot mixture was poured into water (400 ml) with vigorous stirring. A formed precipitate was filtered at Schott, washer with portions of water (2×50 ml) and dried on air for 2 d. Then precipitate was washed with aqueous NaOH (2×50 ml; 0.5 M), water (2×100 ml) and transferred into 500 ml round-bottom flask. The flask was charged with water (220 ml), EtOH (65 ml), NaOH (13.35 g; 33.4 mmol), and heated under reflux for 2 h. Most of the ethanol was evaporated, and concd aqueous HCl (40 ml) was added slowly with stirring (foam is formed large amounts). Precipitate was filter at Schott, washer with water (2×50 ml) and dried at 110 °C

for 36 h. The product was placed in a flask charged with benzene (400 ml), refluxed for 1 h, and hot mixture was filtered through paper filter. Filtrate was slowly cooled to rt, while brown-orange needles of **7** were formed (7.85 g; 46.4 mmol, 54%). Second crop of crystallization from benzene (120 ml) gave yellowish powder of **10** (1.38 g; 8.2 mmol, 10%).

10, mp. 180-181.5 °C (lit.[19]: 176-180 °C). ¹H NMR (200 MHz, CDCl₃): δ 9.34 (s br, 1H), 8.09 (d, *J*=7.0 Hz, 1H), 8.02 (d, *J*=8.0 Hz, 1H), 7.71 (dd, *J*=7.0, 8.0 Hz, 1H), 7.37-7.58 (m, 2H), 7.02 (d, *J*=6.4 Hz, 1H). ¹³C NMR (50 MHz, CDCl₃): δ 170.5, 137.2, 131.2, 129.3, 128.62, 128.60, 126.7, 126.2, 124.4, 120.3, 106.7.

Synthesis of compound 11

Synthesis of 1,8-naphtholactone (**11**) was performed according to literature with following modifications:

A three-necked round-bottom 500 ml flask was charged with **10** (5.102 g; 30.16 mmol), aqueous solution of NaOH (5.02 g; 126 mmol in 250 ml H₂O) and refluxed for 17 h. Then mixture was cooled to rt, NaNO₂ was added 2.129 g; 30.9 mmol), mixture was stirred for 30 min and left in refrigerator (4 °C) overnight. A 1 l glass beaker was charged with water-ice mixture (ca. 600 ml) and concd H₂SO₄. A cold mixture from flask was added slowly to the beaker with stirring. Then mixture was warmed slowly to 70 °C within 40 min, while pale precipitate was formed. Mixture was cooled to rt, and extracted with ethyl acetate (3×150 ml). Combined organic phases were washed with water (200 ml), brine (200 ml) and dried with MgSO₄. The mixture was filtered, evaporated, and residue was separated with column chromatography (600 ml of silica, *n*-hexane : ethyl acetate 4:1 to 2:1) to obtain **11** (3.578 g; 21.03 mmol; 70%) as a pale yellow powder.

11, mp. 104.5-106.5 °C (lit.[19] 105-107.5 °C). ¹H NMR (200 MHz, CDCl₃): δ 8.13 (d, *J*=8.0 Hz, 1H), 8.11 (d, *J*=7.2 Hz, 1H), 7.78 (dd, *J*=7.2, 8.0 Hz, 1H), 7.64 (d, *J*=8.2 Hz, 1H), 7.54 (dd, *J*=7.0, 8.2 Hz, 1H), 7.13 (d, *J*=7.0 Hz, 1H). ¹³C NMR (50 MHz, CDCl₃): δ 167.1, 150.1, 132.0, 129.8, 129.5, 129.2, 126.2, 121.1, 120.8, 106.0.

Ligand exchange procedure for synthesis of 14 from 15

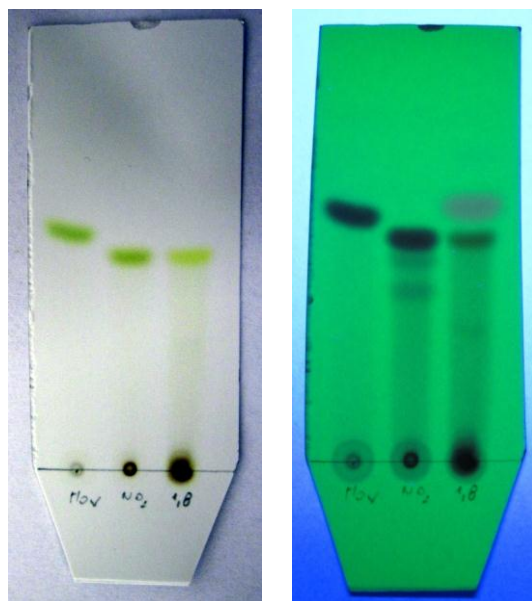
A Schlenk flask was charged with **8a** (0.127 g; 0.598 mmol), CH₂Cl₂ (30 ml), complex **15** (0.254 g; 0.299 mmol), CuCl (0.034 g; 0.35 mmol) and refluxed for 1 h under argon. Then heating bath was removed, mixture was cooled to rt, and solvent was removed *in vacuo*. Ethyl acetate (20 ml) was added, mixture was stirred and filtered at small Schott filter. The greenish precipitate was washed with portions of ethyl acetate with stirring, until it became white-grey, and filtrate was evaporated and residue dissolved in a small portion of ethyl acetate (ca. 3 ml) was placed on a top of chromatographic column (220 ml of silica; *n*-hexane : ethyl acetate 10 : 1 to 5 : 1) and eluted as a green band to obtain **14** (0.095 g; 0.14 mmol; 47%) as a dark green powder.

The same procedure using **8b** (0.136 g; 0.600 mmol), CH₂Cl₂ (29 ml), complex **15** (0.257 g; 0.302 mmol), and CuCl (0.034 g; 0.35 mmol) gave **14** (0.091 g; 0.133 mmol; 44%) as a dark green powder.

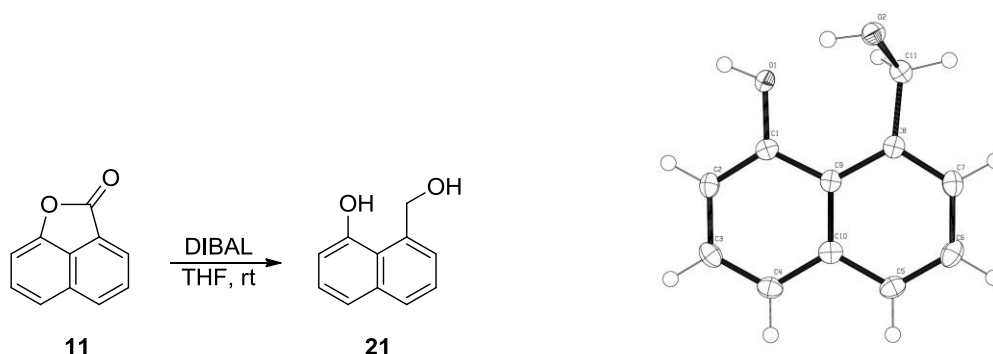
Stability of complexes 1, 2 and 14

TLC analyses of solutions of complexes **1**, **2** and **11** (from left to right on each plate) in non-degassed CD₂Cl₂ stored at room temperature for 5 days and developed in *n*-hexane : ethyl acetate 2:1 mixture. TLC

plates were illuminated by daylight (left) and UV lamp (right). Polar starting spot of complex **14** is more intensive, than for **1** and **2**, indicating a faster decomposition.



Synthesis of compound **21**

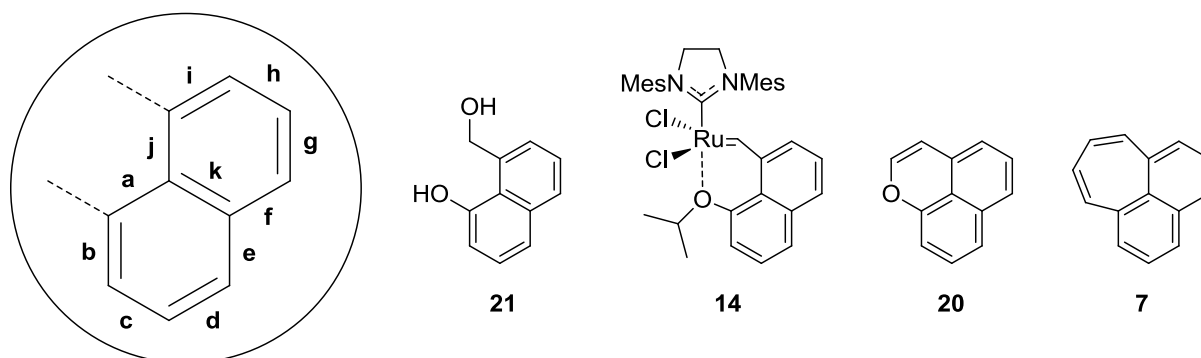


For X-ray studies intermediate compound **21** was prepared according to the following procedure:

A Schlenk flask was charged with **11** (0.339 g; 1.99 mmol), THF (10 ml) and DIBAL (4.5 ml; 2.25 mmol; 0.5 M solution in toluene) was added dropwise. Mixture was stirred overnight, then MeOH (1.5 ml) was added slowly, and mixture gelled. Ethyl acetate (10 ml) and water (20 ml) were added and flask was shaken until gel dissolved. Then water (50 ml) was added, and mixture was extracted with ethyl acetate (2×100 ml). Combined organic phases were washed with brine (50 ml) and dried with MgSO₄. The mixture was filtered, evaporated, and residue was dissolved in hot CHCl₃ (7 ml), *n*-hexane (10 ml) was added and mixture was left overnight. White cream crystals of **21** (0.116 g; 0.66 mmol; 33%) were formed and used for X-ray studies.

21, mp. 136-138 °C (lit. [R. J. Packer, D. C. C. Smith, *J. Chem. Soc. C* **1967**, 2194-2201] 144-146 °C). ¹H NMR (200 MHz, DMSO-*d*₆): δ 10.23 (s br, 1H), 7.68 (d, *J*=8.0 Hz, 1H), 7.59 (d, *J*=7.0 Hz, 1H), 7.22-7.44 (m, 3H), 6.89 (dd, *J*=1.3, 7.1 Hz, 1H), 5.50 (s br, 1H), 5.17 (s, 2H). ¹³C NMR (50 MHz, DMSO-*d*₆): δ 155.4, 139.2, 136.6, 127.8, 126.7, 126.0, 123.8, 123.1, 120.1, 110.9, 64.2.

Structural analysis of compounds 14, 15, and 21

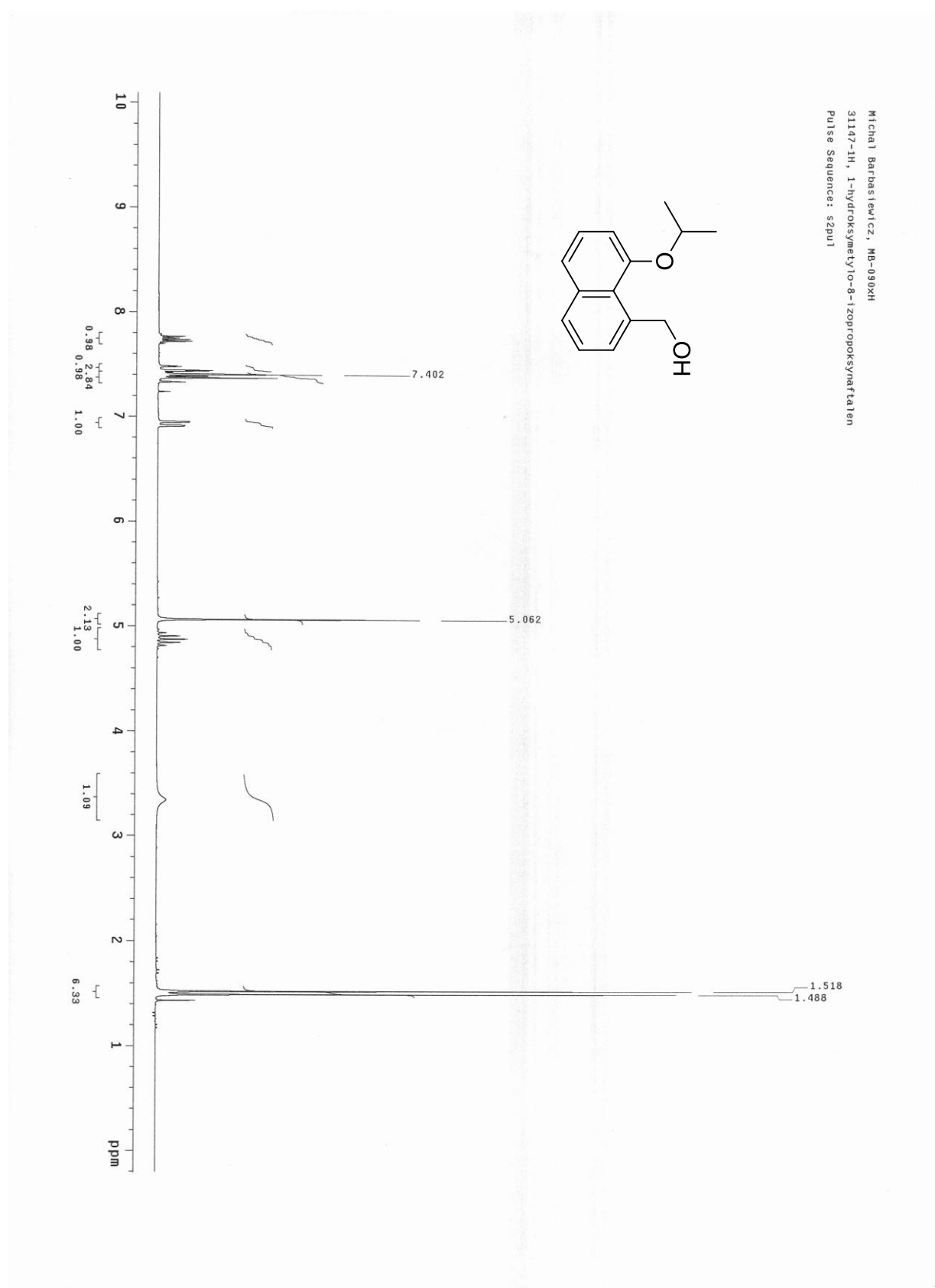


To analyze structural differences of naphthalene framework caused by formation of chelate ring in complex **14** we synthesized 8-hydroxymethyl-1-naphthol (**21**) and determined its structure with X-ray methods. Then we compared bond distances (a-k) of compounds **14** (X-ray, two molecules in asymmetric unit), **7** (calculated, and X-ray data taken from ref. [33]), **20** (calculated), and **21** (X-ray). The bond distances of naphthalene core were collected in Table (see below) and HOMA parameters (Harmonic Oscillator Model of Aromaticity, [Sobczyk, L.; Grabowski, J. S.; Krygowski, T. M.; *Chem. Rev.* **2005**, *105*, 3513-3560]) were calculated for both rings.

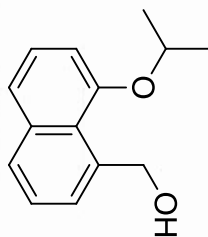
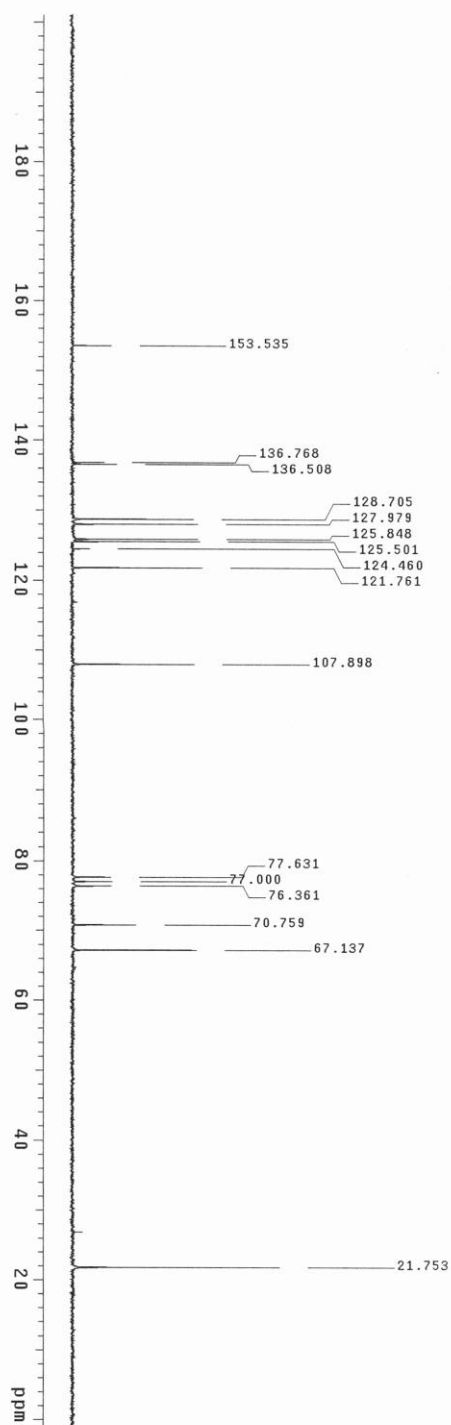
Bond	a	b	c	d	e	f	g	h	i	j	k	HOMA abcdek	HOMA fghijk
21 (X-ray)	1.430	1.366	1.401	1.364	1.409	1.421	1.358	1.401	1.375	1.435	1.427	0.79	0.74
14/1 (X-ray)	1.414	1.390	1.404	1.362	1.420	1.406	1.357	1.414	1.391	1.443	1.448	0.73	0.63
14/2 (X-ray)	1.429	1.375	1.411	1.357	1.414	1.426	1.343	1.409	1.386	1.446	1.434	0.74	0.60
20 (calcd)	1.416	1.378	1.409	1.378	1.418	1.423	1.376	1.412	1.383	1.428	1.427	0.84	0.78
7 (calcd)	1.449	1.394	1.401	1.369	1.420	1.420	1.369	1.401	1.394	1.449	1.442	0.64	0.64
7 (X-ray)	1.449	1.385	1.402	1.355	1.421	1.421	1.355	1.402	1.385	1.449	1.448	0.58	0.58

On the base of the collected data aromatic properties of naphthalene rings analyzed with HOMA model decrease in order **20** → **21** → **14** ≈ **7**.

Reproduction of ^1H NMR spectrum of compound 12.

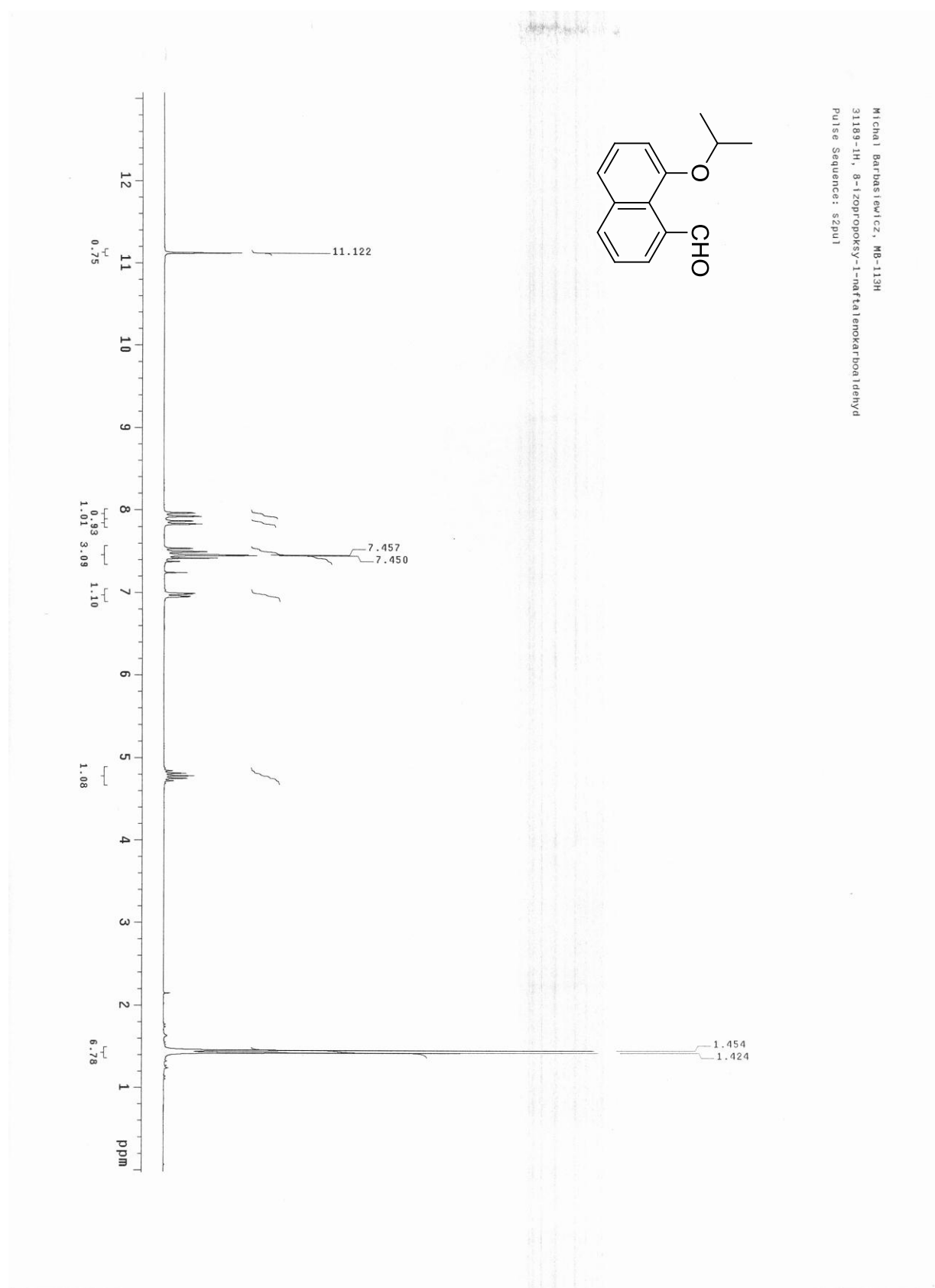


Reproduction of ^{13}C NMR spectrum of compound **12**.

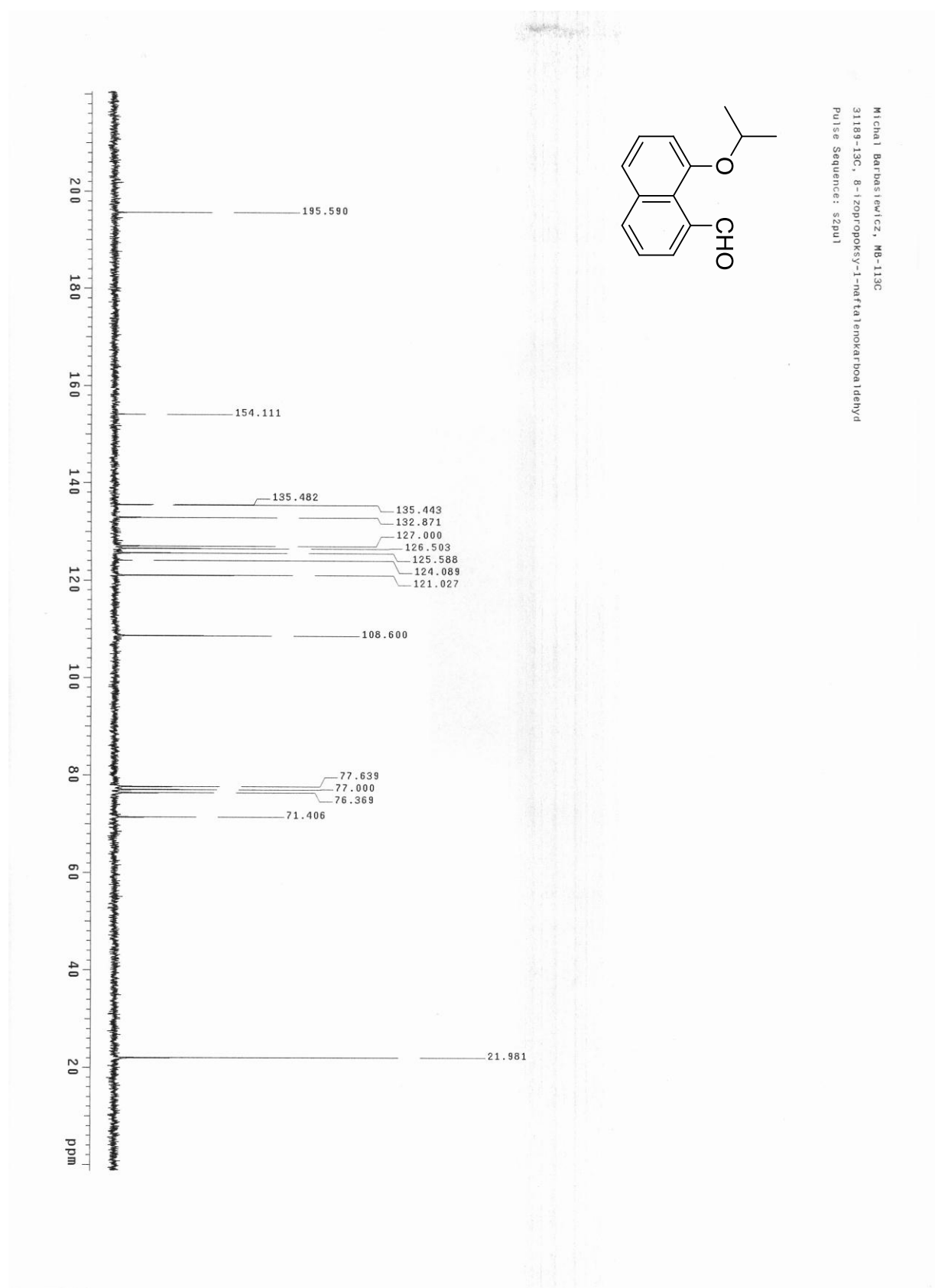


Michał Barbasiewicz, MB-030K
31147-13C, 1-hydroksymetylo-8-izopropoksynaftalen
Pulse Sequence: szpul

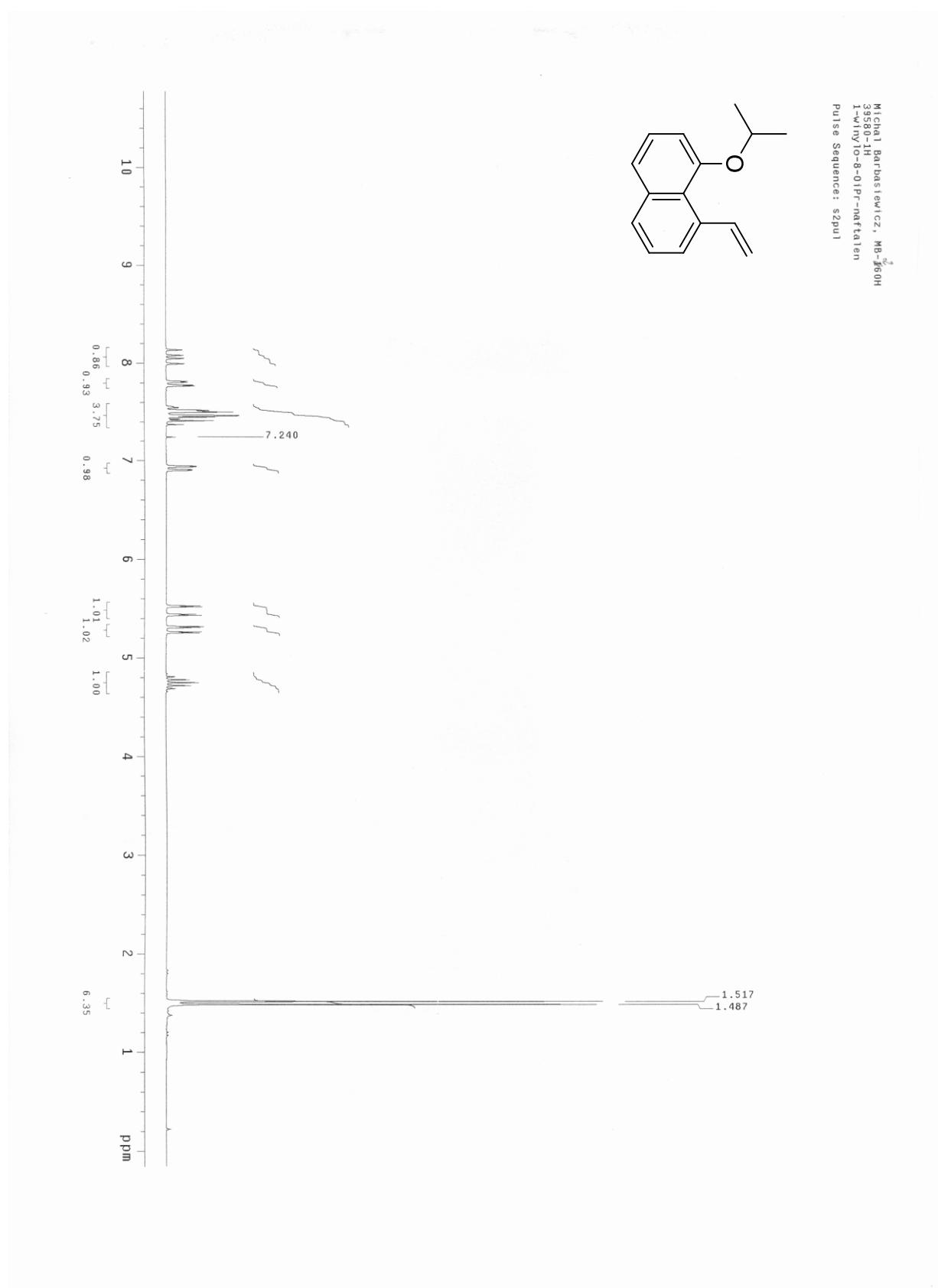
Reproduction of ^1H NMR spectrum of compound **13**.



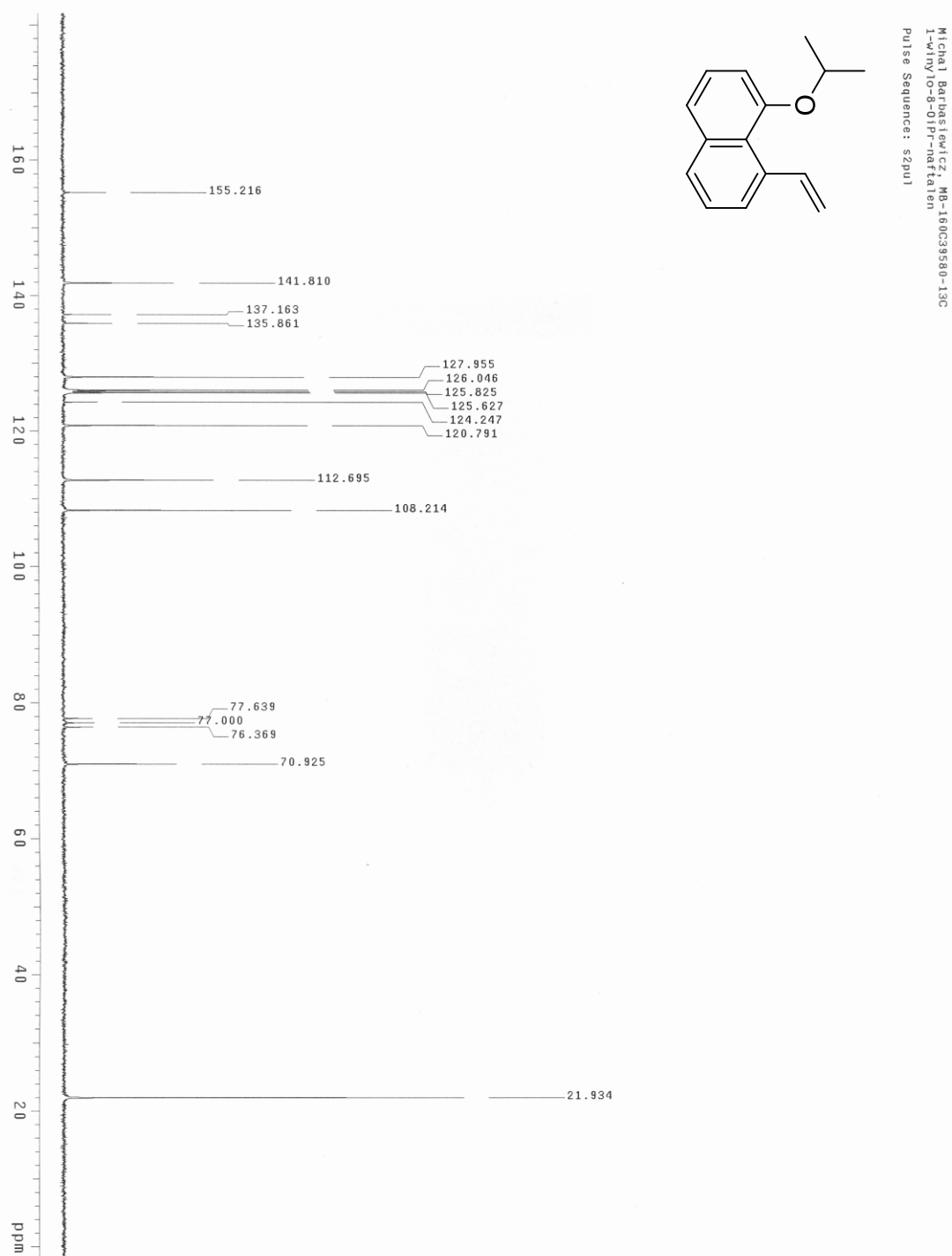
Reproduction of ^{13}C NMR spectrum of compound **13**.



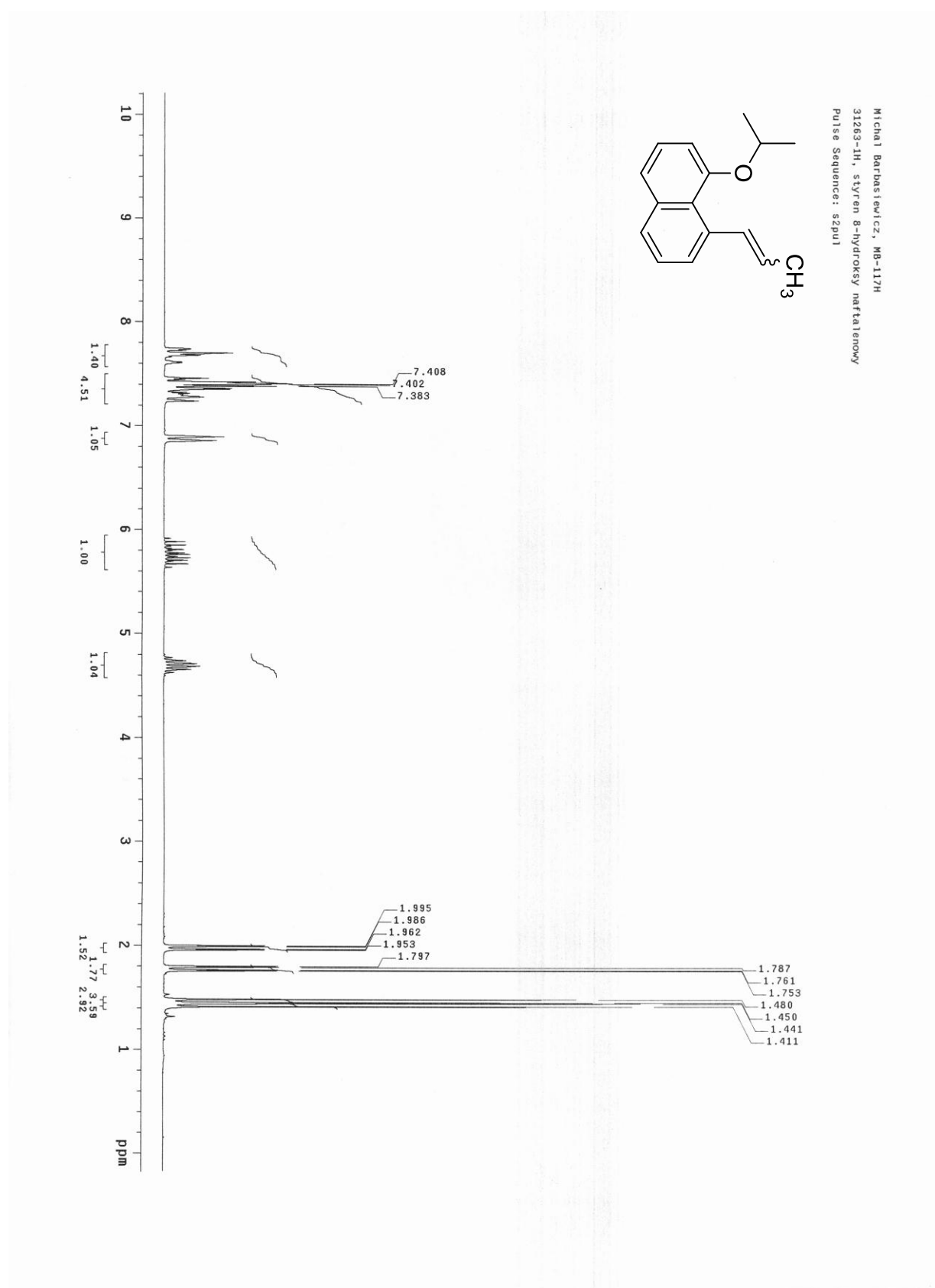
Reproduction of ^1H NMR spectrum of compound **8a**.



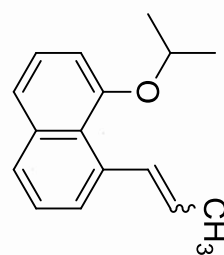
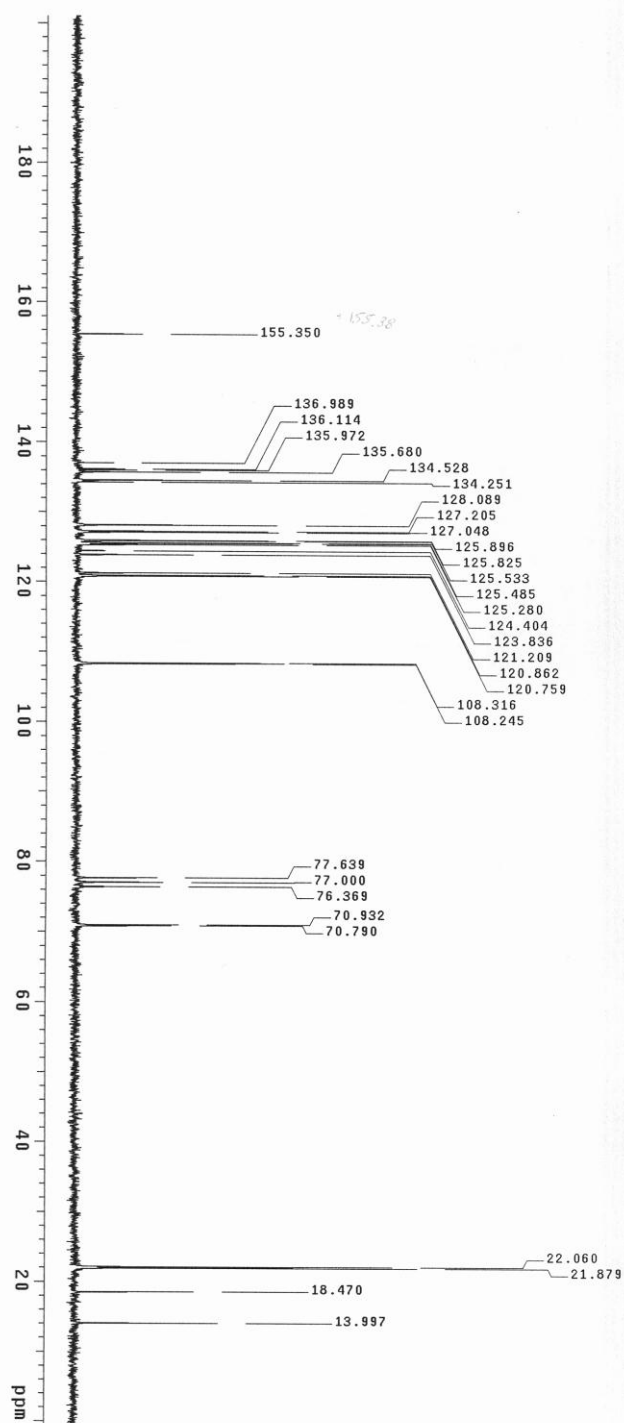
Reproduction of ^{13}C NMR spectrum of compound **8a**.



Reproduction of ^1H NMR spectrum of compound **8b**.

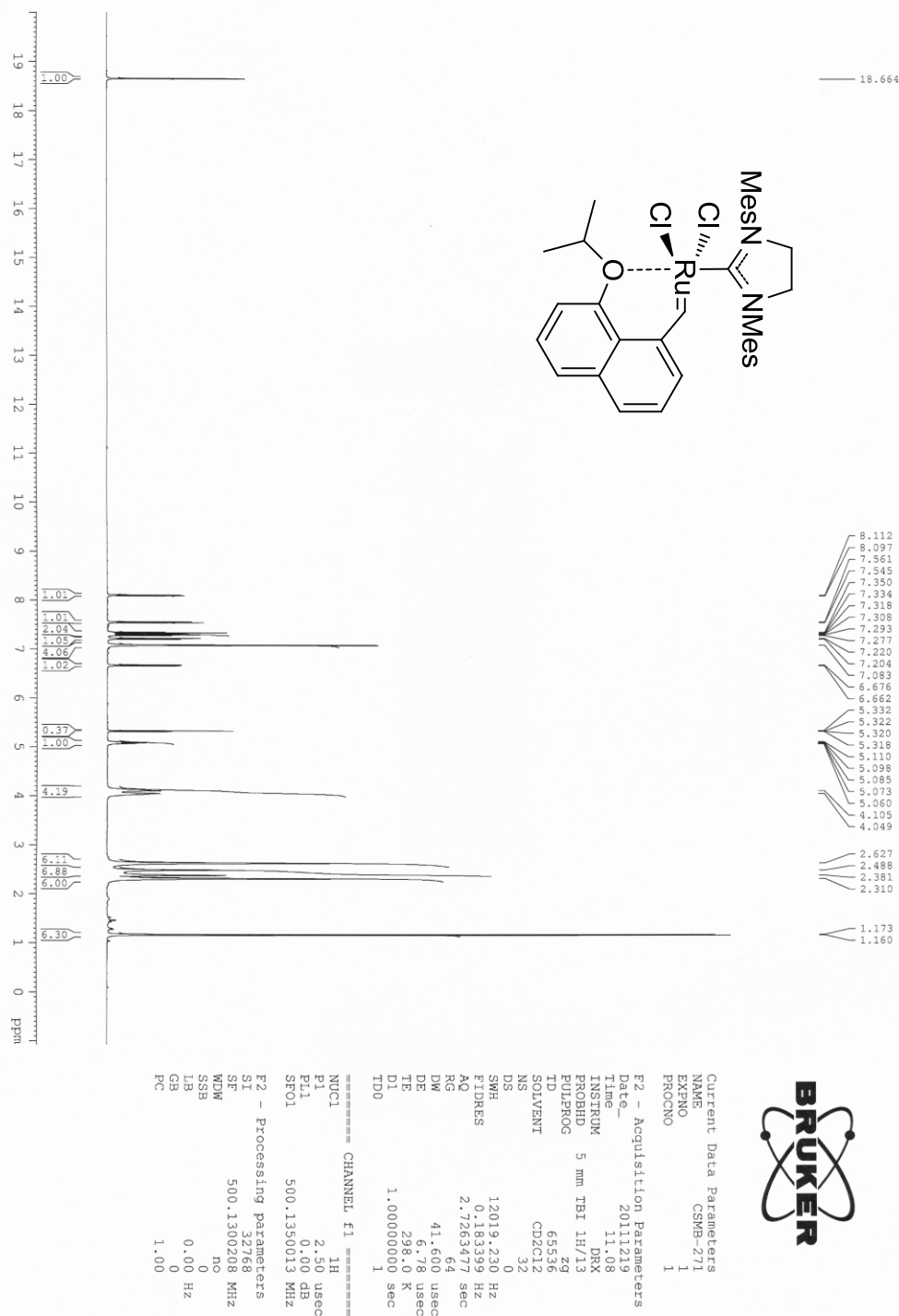


Reproduction of ^{13}C NMR spectrum of compound **8b**.

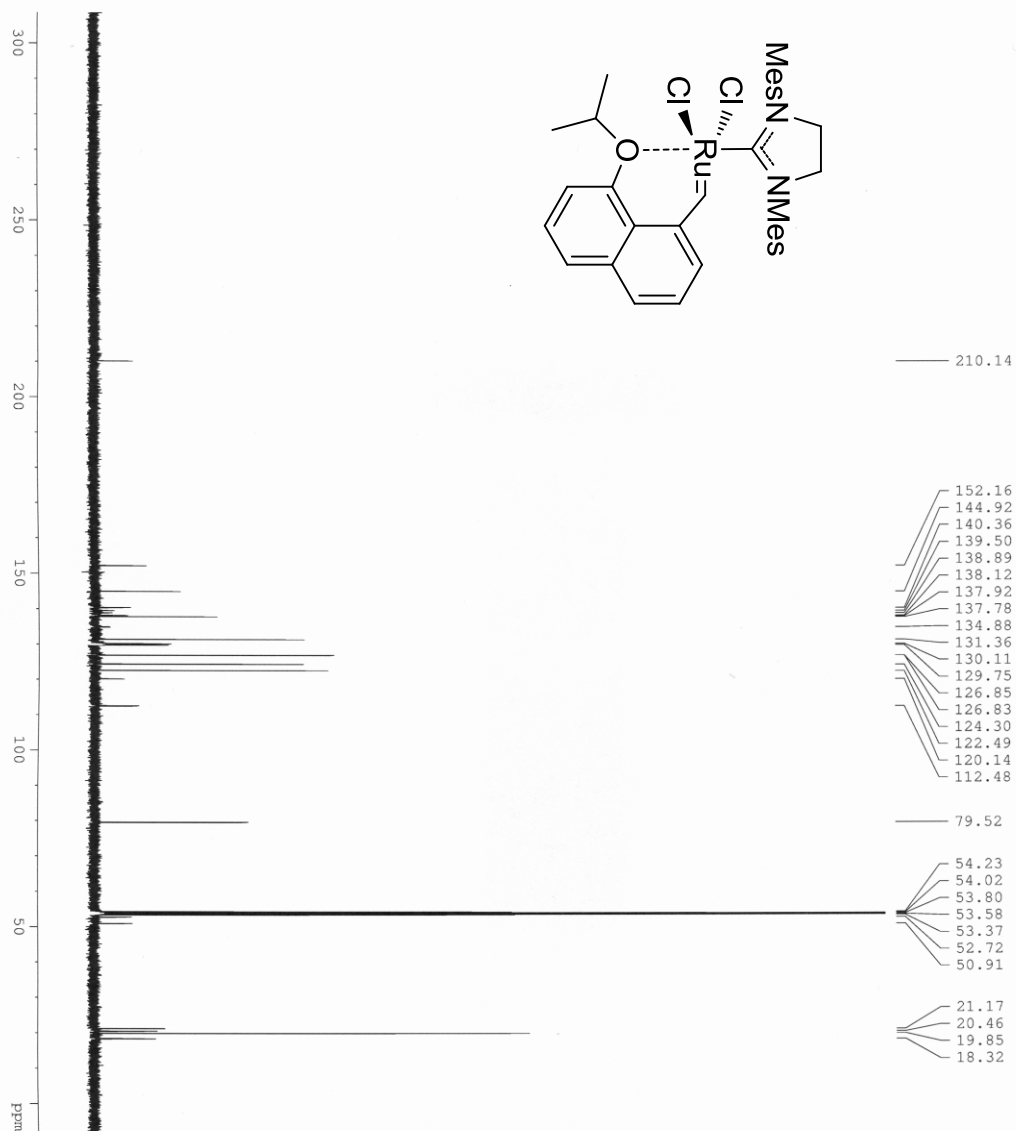


Michał Barbaśiewicz, MB-117C
31263-13C, styren 8-hydroksy nafiolenowy
Pulse Sequence: szpul

Reproduction of ^1H NMR spectrum of complex **14**.



Reproduction of ^{13}C NMR spectrum of complex **14**.



Current Data Parameters
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EXPNO 2
PROCNO 1

F2 - Acquisition Parameters
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PROBHD 5 mm TBI 1H/13
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SOLVENT CDCl₃
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DS 4
SWH 42735.043 Hz
FIDRES 0.22248 Hz
AQ 0.766212 sec
RG 57
DE 11.700 usec
TE 300.2 K
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d11 0.03000000 sec
DELTA 0.89999998 sec
TD0 1

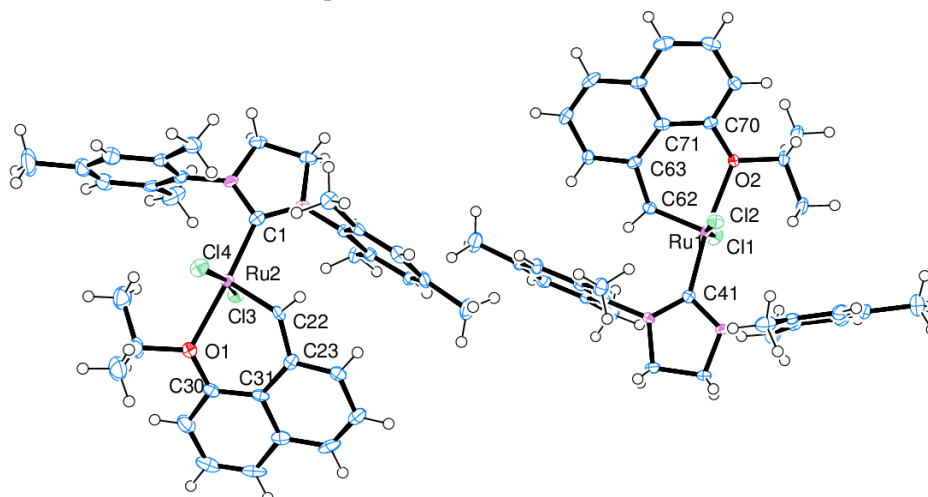
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P1 5.00 usec
PL1 -3.00 dB
SFO1 125.776527 MHz

===== CHANNEL f2 =====
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NUC2 ¹H
PCPD2 98.00 usec
PL2 3.00 dB
PL12 12.00 dB
PL11 12.00 dB
SFO2 500.132005 MHz

F1 - Acquisition parameters
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SI 12
SF 500.132 MHz
FIDRES 7.812500 Hz
SW 1.999 ppm
FMODE QF

F2 - Processing parameters
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SF 125.7577450 MHz
WDW EM
SSB 0
GB 0.50 Hz
PC 1.40

F1 - Processing parameters
SI 65536
SF 500.130000 MHz
WDW SINE
SSB 0
GB 0.30 Hz
LB 0.1



Experimental

The measurement of diffraction data was performed on a Kuma KM4CCD θ -axis diffractometer with graphite-monochromated MoK radiation and equipped with an Oxford Cryosystems nitrogen gas-flow apparatus. The crystal was positioned at 50 mm from the KM4CCD camera. 644 frames were measured at 1° intervals with a counting time of 18 sec. The data were corrected for Lorentz and polarization effects. The multi-scan absorption correction was applied. Data reduction and analysis were carried out with the Oxford Diffraction Ltd. suite of programs.[i]

The structure was solved by direct methods[ii] and refined using SHELXL.[iii] After structure solution, it was found that 12% of the total cell volume was filled with disordered solvent molecules, which could not be modeled in terms of atomic sites. From this point on, residual peaks were removed and the solvent region was refined as a diffuse contribution without specific atom positions by using the PLATON[iv] module SQUEEZE[v] which subtracts electron density from the void regions by appropriately modifying the diffraction intensities of the overall structure. An electron count over the solvent region provided an estimate for the number of solvent molecules removed from the cell. The number of electrons thus located was assigned to 1 molecule of dichloromethane. Applying this procedure led to a improvement in all refinement parameters and a minimization of residuals.

The refinement was based on F^2 for all reflections except those with very negative F^2 . Weighted R factors wR and all goodness-of-fit S values are based on F^2 . Conventional R factors are based on F with F set to zero for negative F^2 . The $F_o^2 > 2(F_o^2)$ criterion was used only for calculating R factors and is not relevant to the choice of reflections for the refinement. The R factors based on F^2 are about twice as large as those based on F. Scattering factors were taken from Tables 6.1.1.4 and 4.2.4.2 in Ref. [vi].

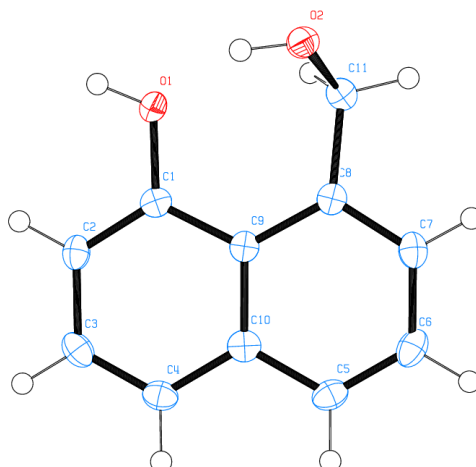
The structure of the complex **14** was refined as a racemic twin, with the final BASF 0.48(2). The orthorhombic C2/c space group was not an option, because of the lack of systematic absences of reflections for the c glide plane. The $|E^*E-1| = 0.712$ statistics suggests a non-centrosymmetric space group. The statistics strongly suggest C2 space group, which is our final choice. However, we also attempted to solve the structure with the use of direct or Patterson methods in the C2/m space group - which was unsuccessful. The solution and refinement of the structure in the C2 space group was straightforward besides of the solvent molecules. The Flack parameter refined to ca. 0.5, which suggested that space group should be centrosymmetric or the racemic twin. All attempts to change the space group to the centrosymmetric failed. There is no inversion center between the molecules in the crystal lattice. We also checked this by trying to get higher symmetry with proper symmetry checking software which also failed. And finally we refined the structure as a racemic twin. There is no A alert after a checkcif run.

-
- [i] Agilent Technology, Version 171.35.15
- [ii] Sheldrick, G. M.; *Acta Crystallogr.* **1990**, *A46*, 467-473.
- [iii] Sheldrick, G. M.; *Acta Crystallogr.* **2008**, *A64*, 112.
- [iv] Spek, A. L. PLATON, A Multipurpose Crystallographic Tool; Utrecht University, Utrecht, The Netherlands, 1998.
- [v] Sluis, P. V. D.; Spek, A. L.; *Acta Crystallogr.* **1990**, *A46*, 194.
- [vi] *International Tables for Crystallography*, Ed. A. J. C. Wilson, Kluwer, Dordrecht, **1992**, Vol. C

Table 1. Crystal data and structure refinement for **14**.

Identification code	14
Empirical formula	C ₃₅ H ₄₀ Cl ₂ N ₂ ORu
Formula weight	676.66
Temperature	100(2) K
Wavelength	0.71073 Å
Crystal system, space group	Monoclinic, C2
Unit cell dimensions	a = 37.7276(10) Å alpha = 90° b = 12.0382(3) Å beta = 108.999(3)° c = 14.8599(4) Å gamma = 90°
Volume	6381.3(3) Å ³
Z, Calculated density	8, 1.409 Mg/m ³
Absorption coefficient	0.689 mm ⁻¹
F(000)	2800
Crystal size	0.30 x 0.10 x 0.10 mm
Theta range for data collection	1.79 to 25.68°
Limiting indices	-46<=h<=43, -14<=k<=14, 0<=l<=18
Reflections collected / unique	12035 / 12035 [R(int) = 0.0000]
Completeness to theta = 25.68	100.0 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9343 and 0.8200
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	12035 / 9 / 742
Goodness-of-fit on F ²	1.202
Final R indices [I>2sigma(I)]	R1 = 0.0352, wR2 = 0.0956
R indices (all data)	R1 = 0.0388, wR2 = 0.0972
Extinction coefficient	0.00086(7)
Largest diff. peak and hole	1.185 and -0.747 e.Å ⁻³

Crystallographic Information Data of compound **21**.



Experimental

The data were collected using the BRUKER KAPPA APEXII ULTRA controlled by APEXII software[i], equipped with MoK α rotating anode X-ray source ($\lambda = 0.71073$ Å, 50.0 kV, 22.0 mA) monochromatized by multi-layer optics and APEX-II CCD detector. The experiments were carried out at 100K using the Oxford Cryostream cooling device. The crystal was mounted on Mounted CryoLoop with a droplet of Paratone-N oil and immediately cooled. Indexing, integration and initial scaling were performed with *SAINT* [ii] and *SADABS* [iii] software (Bruker, 2008). The data collection and processing statistics are reported in tables for according structures.

The crystal was positioned at 40 mm from the CCD camera. 967 frames were measured at 0.5° intervals with a counting time of 20-30 sec.

The structures were solved by direct methods approach using the SHELXS-97 [iv] program and refined with the SHELXL-97 [v]. Multi-scan absorption correction have been applied in the scaling procedure.

The refinement was based on F^2 for all reflections except those with negative intensities. Weighted R factors wR and all goodness-of-fit S values, were based on F^2 , whereas conventional R factors were based on the amplitudes, with F set to zero for negative F^2 . The $F_0^2 > 2\sigma(F_0^2)$ criterion was applied only for R factors calculation was not relevant to the choice of reflections for the refinement. The R factors based on F^2 are for all structures about twice as large as those based on F . The hydrogen atoms were located in idealized geometrical positions, except hydrogen in the solvent molecule. Scattering factors were taken from Tables 4.2.6.8 and 6.1.1.4 from the International Crystallographic Tables Vol.C [vi].

[i] APEXII-2008v1.0 Bruker Nonius 2007

[ii] SAINT V7.34A Bruker Nonius 2007

[iii] SADABS-2008/1 Bruker Nonius area detector scaling and absorption correction, 2008

[iv] G. M. Sheldrick, *Acta Crystallogr.* **1990**, A46, 467-473.

[v] G. M. Sheldrick, SHELXL93. *Program for the Refinement of Crystal Structures.*, Univ. of Göttingen, Germany.

[vi] *International Tables for Crystallography*, Ed. A. J. C. Wilson, Kluwer:Dordrecht, **1992**, Vol.C.

Table 1. Crystal data and structure refinement for **21**.

Identification code	21
Empirical formula	C ₁₁ H ₁₀ O ₂
Formula weight	174.19
Temperature	100(2) K
Wavelength	0.71073 Å
Crystal system, space group	Orthorhombic, P2 ₁ 2 ₁ 2 ₁
Unit cell dimensions	a = 4.9018(3) Å alpha = 90° b = 7.7798(5) Å beta = 90° c = 21.9948(16) Å gamma = 90°
Volume	838.77(10) Å ³
Z, Calculated density	4, 1.379 Mg/m ³
Absorption coefficient	0.094 mm ⁻¹
F(000)	368
Crystal size	0.20 x 0.20 x 0.10 mm
Theta range for data collection	1.85 to 26.40°
Limiting indices	-5 ≤ h ≤ 5, -7 ≤ k ≤ 9, -23 ≤ l ≤ 27
Reflections collected / unique	5809 / 1032 [R(int) = 0.0254]
Completeness to theta = 26.40	98.8 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9906 and 0.9814
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	1032 / 0 / 127
Goodness-of-fit on F ²	1.129
Final R indices [I > 2sigma(I)]	R1 = 0.0293, wR2 = 0.0690
R indices (all data)	R1 = 0.0365, wR2 = 0.0721
Extinction coefficient	0.014(4)
Largest diff. peak and hole	0.187 and -0.155 e.Å ⁻³