Electronic Supporting Information

Ruthenium Nitronate Complexes as Tunable Catalysts for Olefin Metathesis and Other Transformations

*Tomasz Wdowik, Cezary Samojłowicz, Magdalena Jawiczuk, Maura Malińska, Krzysztof Woźniak, Karol Grela**

Table of Contents

1. Equipment and chemicals used

The catalyst preparation was carried out under argon in pre-dried glassware using Schlenk techniques. The anhydrous solvents were dried by distillation over the following drying agents and were transferred under argon: THF (K/benzophenone), toluene (Na), methanol (Mg) CH_2Cl_2 (CaH_2). Analytical thin-layer chromatography (TLC) of all reactions was performed on silica gel 60 F_{254} TLC plates. Visualization was performed with standard potassium permanganate solution, vanillin spray reagent, or UV light.

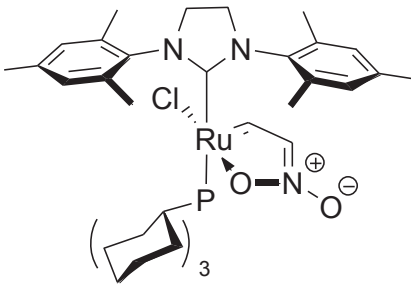
Flash columns were performed using silica gel 60 (230-400 mesh). NMR spectra were recorded with Varian (200, 400, 500 and 600 MHz) and Bruker (500 MHz) machines in $CDCl_3$; chemical shifts (δ) are given in ppm relative to TMS. Multiplicities are abbreviated as follows: singlet (s), doublet (d), triplet (t), quartet (q), pentet (p), multiplet (m).

IR spectra were recorded on a Perkin-Elmer Spectrum One FTIR spectrometer with diamond ATR accessory; wavenumbers are in cm^{-1}. MS (EI) spectra were recorded on AMD 604 Intectra GmbH spectrometer. MS (ESI) spectra were recorded on Mariner Perseptive Biosystems, Inc.

Micro-analyses were provided by Institute of Organic Chemistry, PAS, Warsaw.

2. Preparation and characterization of catalysts (refer to Scheme 1)

Synthesis of complex **7**



Complex **1b** (102 mg, 0.12 mmol) and dichloromethane (2 mL) were placed in a Schlenk flask. Next, 3-nitropropene (**5**)[i] (13.1 mg; 0.15 mmol) was added and the resulting mixture was stirred under argon at room temperature for 20 hours. From this point forth, all manipulations were carried out in air with reagent-grade solvents. The reaction mixture was concentrated under vacuum and resulting material was purified by column chromatography on

silica gel (230-400 mesh, no pre-treatment). Elution with *c*-hexane/EtOAc (9:1 v/v) removes **7** as a green band. The solvent was evaporated resulting material was dried in vacuo to afford complex **7** (52.6 mg, 55%) as a green micro-crystalline solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ = 14.27 (d, J = 3 Hz, 1H), 7.02-6.90 (m, 4H), 6.42 (d, J = 3 Hz, 1H), 3.88-3.86 (m, 2H), 3.82–3.79 (m, 2H), 2.59 (s, 3H), 2.52 (s, 3H), 2.46 (s, 3H), 2.33 (s, 3H), 2.31 (s, 3H) 1.98 (s, 3H), 1.75-1.56 (m, 21H), 1.11-1.00 (m, 9H), 0.92-0.85 (m, 3H);

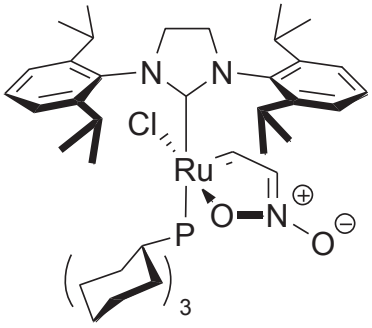
^{13}C NMR (125 MHz, $CDCl_3$) δ = 249.2, 219.3, 218.7, 138.8, 138.6, 138.4, 138.0, 137.6, 137.5, 136.3, 133.8, 130.4, 130.0, 129.9, 129.1, 128.9, 51.6, 51.2, 35.6, 35.1, 33.1, 33.0, 29.3, 28.9, 27.8, 27.7, 27.6, 27.5, 27.0, 26.5, 26.3, 26.1, 21.2, 21.1, 19.3, 18.7, 18.6, 16.9;

^{31}P NMR (202 MHz, CDCl3) δ = 34.2 (s, 1P);

IR (KBr) $\tilde{\nu}$ = 2925, 2850, 1813, 1512, 1483, 1430, 1379, 1266, 1169, 1041, 849, 743 cm^{-1}

MS (FD/FI): *m/z* calcd for $C_{41}H_{61}{}^{35}ClN_3O_2P^{102}Ru$: 795.3; found: 795.3 ($M^+$).

Synthesis of complex **8**



Complex **1c** (149 mg, 0.16 mmol) and dichloromethane (2 mL) were placed in a Schlenk flask. Next, 3-nitropropene (**5**)[i] (17.4 mg; 0.20 mmol) was added and the resulting mixture was stirred under argon at room temperature for 15 minutes. From this point forth, all manipulations were carried out in air with reagent-grade solvents. The reaction mixture was concentrated under vacuum and resulting material was purified by column chromatography on silica gel (230-400 mesh, no pre-treatment). Elution with *c*-hexane/EtOAc (9:1 v/v) removes **8** as a green band. The solvent was evaporated resulting material was dried in vacuo to afford complex **7** (93.3 mg, 66%) as a green micro-crystalline solid.

^{1}H NMR (600 MHz, $CDCl_3$) δ = 13.81 (d, J = 3 Hz, 1H), 7.36-7.10 (m, 6H), 6.29 (d, J = 3 Hz, 1H), 4.20-4.10 (m, 1H), 4.10-4.00 (m, 1H), 4.00-3.80 (m, 3H), 3.75-3.65 (m, 1H), 3.65-3.55 (m, 1H), 2.70-2.64 (m, 1H), 1.70-1.64 (m, 3H), 1.60-1.50 (m, 18H), 1.39-1.35 (m, 3H), 1.26-1.19 (m, 10H), 1.15-1.08 (m, 9H), 1,07-0.92 (m, 14H);

^{13}C NMR (150 MHz, $CDCl_3$) δ = 246.4, 222.2, 221.7, 148.64, 148.60, 148.5, 147.4, 137.5, 135.1, 130.0, 129.7, 129.0, 125.2, 124.2, 124.1, 123.9, 77.2, 77.0, 76.8, 54.0, 53.7, 33.2, 33.0, 29.6, 28.7, 28.5, 28.3, 27.9, 27.8, 27.2, 27.2, 26.9, 26.6, 26.3, 26.1, 23.4, 22.8, 22.0;

^{31}P NMR (202 MHz, $CDCl_3$) δ = 35.3 (s, 1P);

IR (KBr) $\tilde{\nu}$ = 2962, 2927, 2851, 1431, 1414, 1383, 1326, 1269, 1238, 1170, 1047, 803, 758, 734 cm^{-1};

MS (FD/FI): m/z calcd for for $C_{47}H_{73}{}^{35}ClN_3O_2P^{102}Ru$: 879.3; found: 879.3 ($M^+$).

2.1. Solid state structure of catalyst 8

The structure of **8** compound (see Figure 2) has been determined by single crystal X-ray diffraction technique.

The data were collected using the BRUKER KAPPA APEXII ULTRA controlled by APEXII software[ii], equipped with MoKα rotating anode X-ray source (λ = 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 Pantone-N oil and immediately cooled. Indexing, integration and initial scaling were performed with *SAINT*[iii] and *SADABS*[iv] software. The data collection and processing statistics are reported in tables for according structures.The crystal was positioned at 40 mm from the CCD camera. 1280 frames were measured at 0.5^{o} intervals with a counting time of 20 sec.

The structure was solved by direct methods approach using the SHELXS-97[v] program and refined with the SHELXL-97[vi]. Numerical absorption correction has been applied in the scaling procedure. After structure solution, it was found that 18% 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[vii] module SQUEEZE[viii] 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 unit cell. The number of electrons thus located was assigned to 2 molecules of dichloromethane. Applying this procedure led to significant improvement for all refinement parameters and a minimization of residuals.

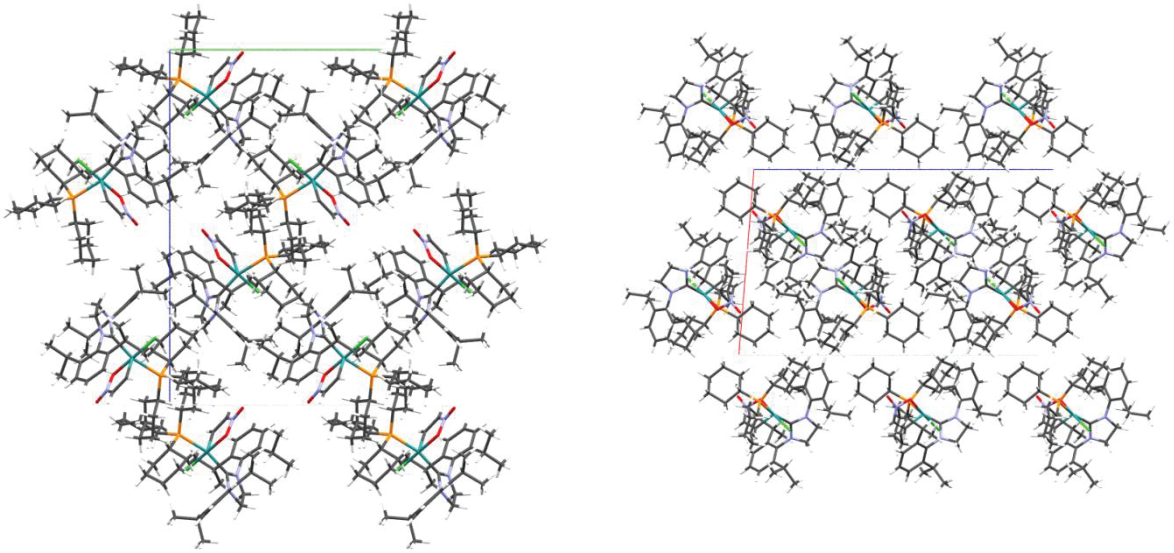
The refinement was based on F^2 for all reflections except those with negative intensities. Weighted R factors wR and all goodness-of-fit S values were based on F^2, whereas conventional R factors were based on the amplitudes, with F set to zero for negative F^2. The $F_0^2 > 2\sigma$ (F_0^2) criterion 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 solvent molecule. Scattering factors were taken from Tables 4.2.6.8 and 6.1.1.4 from the International Crystallographic Tables Vol.C[ix].

Table 1. Experimental details

	Structure **8** (CCDC = 905000)
Crystal data	
Chemical formula	$C_{47}H_{73}ClN_3O_2PRu$
M_r	879.57
Crystal system, space group	Monoclinic, $P2_1/c$
Temperature (K)	100
a, b, c (Å)	14.9004 (18), 14.2899 (13), 24.009 (2)
β (°)	94.636 (7)
V (Å^3)	5095.4 (9)
Z	4
Radiation type	Mo $K\alpha$
μ (mm^{-1})	0.43
Crystal size (mm)	0.22 × 0.10 × 0.09
Data collection	
Diffractometer	Kappa ApexII Ultra CCD diffractometer
Absorption correction	Numerical *SADABS2008*/1 - Bruker AXS area detector scaling and absorption correction
T_{min}, T_{max}	0.912, 0.963
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	117503, 9009, 5506

R_{int}	0.230
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.142, 0.325, 1.10
No. of reflections	9009
No. of parameters	497
No. of restraints	80
H-atom treatment	H-atom parameters constrained
	$w = 1/[\sigma^2(F_o^2) + (0.1126P)^2 + 70.6126P]$ where $P = (F_o^2 + 2F_c^2)/3$
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	2.57, -1.15

Computer programs: Bruker *SMART*, Bruker *SAINT*, *SHELXS97* (Sheldrick, 1990), *SHELXL97* (Sheldrick, 1997), *WinGX*, Mercury, Bruker *SHELXTL*.



(a) (b)

Figure1. Packing of molecules in crystal lattice for (a) view along the X direction (b) view along the Y direction

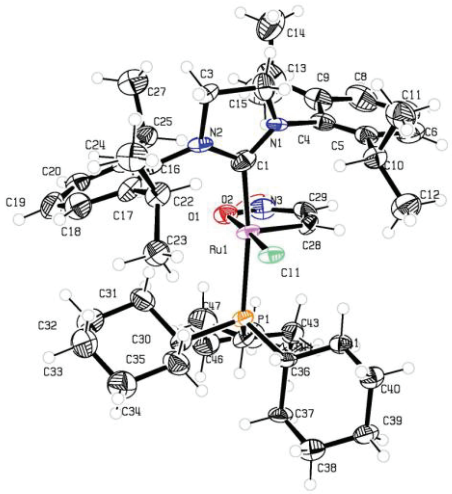


Table 2. Selected geometric parameters for structure 7 (distance [Å], angle [º])

C1—N2	1.333 (15)	C27—C28	1.555 (18)
C1—N1	1.358 (15)	C30—N3	1.299 (16)
C1—Ru1	2.069 (12)	C30—C31	1.378 (16)
C2—C3	1.487 (17)	C31—Ru1	1.878 (12)
C2—N1	1.483 (15)	C32—C33	1.531 (18)
C3—N2	1.367 (17)	C32—C37	1.544 (18)
C4—C9	1.334 (18)	C32—P1	1.861 (14)
C4—C5	1.428 (18)	C33—C34	1.53 (2)
C4—N2	1.456 (16)	C34—C35	1.51 (2)
C5—C6	1.43 (2)	C35—C36	1.49 (2)
C5—C13	1.52 (2)	C36—C37	1.54 (2)
C6—C7	1.29 (2)	C38—C39	1.511 (16)
C7—C8	1.40 (2)	C38—C43	1.544 (16)
C8—C9	1.43 (2)	C38—P1	1.847 (12)
C9—C10	1.525 (18)	C39—C40	1.522 (16)
C10—C11	1.525 (18)	C40—C41	1.526 (17)
C10—C12	1.535 (19)	C41—C42	1.506 (19)
C13—C14	1.47 (2)	C42—C43	1.521 (17)
C13—C15	1.54 (3)	C44—C45	1.52 (2)
C16—C17	1.396 (18)	C44—C49	1.544 (19)
C16—C22	1.402 (18)	C44—P1	1.836 (12)
C16—N1	1.437 (17)	C45—C46	1.52 (2)
C17—C19	1.366 (19)	C46—C47	1.51 (2)
C17—C27	1.524 (17)	C47—C48	1.47 (2)
C19—C20	1.397 (19)	C48—C49	1.561 (19)
C20—C21	1.39 (2)	N3—O2	1.269 (13)
C21—C22	1.404 (19)	N3—O1	1.330 (13)
C22—C23	1.496 (18)	O1—Ru1	2.055 (8)
C23—C24	1.528 (18)	P1—Ru1	2.406 (3)
C23—C26	1.538 (18)	Cl1—Ru1	2.374 (3)
C27—C29	1.53 (2)		
N2—C1—N1	105.4 (10)	C35—C34—C33	109.7 (13)
N2—C1—Ru1	131.5 (9)	C36—C35—C34	112.1 (14)
N1—C1—Ru1	122.3 (9)	C35—C36—C37	110.0 (13)
C3—C2—N1	98.9 (10)	C36—C37—C32	110.6 (13)
N2—C3—C2	107.1 (11)	C39—C38—C43	111.4 (10)

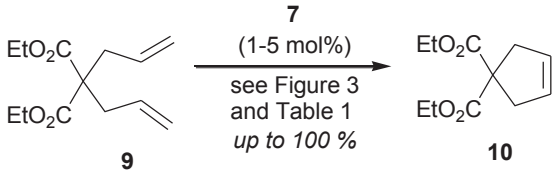
C9—C4—C5	124.0 (12)	C39—C38—P1	117.2 (8)
C9—C4—N2	119.1 (11)	C43—C38—P1	113.1 (8)
C5—C4—N2	116.6 (11)	C38—C39—C40	110.3 (10)
C4—C5—C6	114.0 (14)	C39—C40—C41	111.9 (10)
C4—C5—C13	122.0 (13)	C42—C41—C40	112.5 (11)
C6—C5—C13	123.8 (14)	C41—C42—C43	113.1 (11)
C7—C6—C5	122.2 (17)	C42—C43—C38	109.6 (10)
C6—C7—C8	124.1 (17)	C45—C44—C49	114.9 (12)
C7—C8—C9	116.1 (15)	C45—C44—P1	115.1 (9)
C4—C9—C8	119.3 (13)	C49—C44—P1	112.5 (9)
C4—C9—C10	125.2 (12)	C46—C45—C44	109.9 (13)
C8—C9—C10	115.4 (13)	C47—C46—C45	112.8 (13)
C9—C10—C11	114.0 (12)	C48—C47—C46	111.3 (13)
C9—C10—C12	110.4 (11)	C47—C48—C49	114.3 (13)
C11—C10—C12	110.0 (13)	C44—C49—C48	109.6 (12)
C14—C13—C5	111.3 (16)	C1—N1—C16	127.3 (10)
C14—C13—C15	109.8 (17)	C1—N1—C2	113.2 (10)
C5—C13—C15	110.6 (16)	C16—N1—C2	118.8 (9)
C17—C16—C22	121.8 (13)	C1—N2—C3	114.0 (11)
C17—C16—N1	120.5 (11)	C1—N2—C4	124.3 (10)
C22—C16—N1	117.7 (11)	C3—N2—C4	121.6 (10)
C19—C17—C16	119.8 (12)	O2—N3—C30	132.3 (12)
C19—C17—C27	118.5 (12)	O2—N3—O1	109.8 (10)
C16—C17—C27	121.7 (13)	C30—N3—O1	117.6 (10)
C17—C19—C20	121.8 (13)	N3—O1—Ru1	111.1 (7)
C21—C20—C19	116.5 (14)	C44—P1—C38	105.6 (5)
C20—C21—C22	124.7 (14)	C44—P1—C32	100.5 (6)
C16—C22—C21	115.2 (12)	C38—P1—C32	103.2 (5)
C16—C22—C23	123.6 (13)	C44—P1—Ru1	121.6 (4)
C21—C22—C23	121.1 (12)	C38—P1—Ru1	115.4 (4)
C22—C23—C24	109.9 (11)	C32—P1—Ru1	108.0 (4)
C22—C23—C26	111.1 (12)	C31—Ru1—O1	79.2 (4)
C24—C23—C26	109.3 (10)	C31—Ru1—C1	99.0 (5)
C29—C27—C17	114.0 (12)	O1—Ru1—C1	97.9 (4)
C29—C27—C28	107.9 (12)	C31—Ru1—Cl1	104.2 (4)
C17—C27—C28	111.0 (12)	O1—Ru1—Cl1	176.5 (3)
N3—C30—C31	115.6 (12)	C1—Ru1—Cl1	82.4 (3)
C30—C31—Ru1	116.4 (10)	C31—Ru1—P1	94.0 (3)
C33—C32—C37	108.1 (11)	O1—Ru1—P1	91.9 (2)
C33—C32—P1	110.1 (9)	C1—Ru1—P1	165.0 (3)

C37—C32—P1	115.5 (10)	Cl1—Ru1—P1	87.22 (10)
C32—C33—C34	109.2 (11)		
N1—C2—C3—N2	10.3 (13)	N2—C1—N1—C16	170.1 (11)
C9—C4—C5—C6	5.6 (19)	Ru1—C1—N1—C16	-19.1 (16)
N2—C4—C5—C6	179.8 (11)	N2—C1—N1—C2	-0.6 (14)
C9—C4—C5—C13	-169.2 (14)	Ru1—C1—N1—C2	170.1 (8)
N2—C4—C5—C13	5.0 (19)	C17—C16—N1—C1	-68.5 (16)
C4—C5—C6—C7	-4 (2)	C22—C16—N1—C1	113.2 (13)
C13—C5—C6—C7	171.0 (16)	C17—C16—N1—C2	101.8 (13)
C5—C6—C7—C8	2 (3)	C22—C16—N1—C2	-76.4 (14)
C6—C7—C8—C9	-2 (2)	C3—C2—N1—C1	-6.1 (13)
C5—C4—C9—C8	-6.1 (19)	C3—C2—N1—C16	-177.7 (10)
N2—C4—C9—C8	179.9 (11)	N1—C1—N2—C3	8.3 (14)
C5—C4—C9—C10	175.4 (11)	Ru1—C1—N2—C3	-161.3 (10)
N2—C4—C9—C10	1.4 (19)	N1—C1—N2—C4	-166.8 (11)
C7—C8—C9—C4	4.2 (19)	Ru1—C1—N2—C4	23.7 (18)
C7—C8—C9—C10	-177.2 (12)	C2—C3—N2—C1	-12.4 (15)
C4—C9—C10—C11	130.7 (14)	C2—C3—N2—C4	162.8 (11)
C8—C9—C10—C11	-47.9 (16)	C9—C4—N2—C1	-103.1 (15)
C4—C9—C10—C12	-104.8 (15)	C5—C4—N2—C1	82.4 (15)
C8—C9—C10—C12	76.6 (15)	C9—C4—N2—C3	82.2 (16)
C4—C5—C13—C14	97.1 (18)	C5—C4—N2—C3	-92.3 (15)
C6—C5—C13—C14	-77 (2)	C31—C30—N3—O2	-168.6 (12)
C4—C5—C13—C15	-140.5 (15)	C31—C30—N3—O1	4.3 (16)
C6—C5—C13—C15	45 (2)	O2—N3—O1—Ru1	171.4 (7)
C22—C16—C17—C19	-0.2 (17)	C30—N3—O1—Ru1	-3.0 (12)
N1—C16—C17—C19	-178.4 (10)	C45—C44—P1—C38	162.9 (10)
C22—C16—C17—C27	176.3 (11)	C49—C44—P1—C38	-62.9 (10)
N1—C16—C17—C27	-1.8 (17)	C45—C44—P1—C32	55.8 (12)
C16—C17—C19—C20	1.2 (19)	C49—C44—P1—C32	-170.0 (9)
C27—C17—C19—C20	-175.5 (12)	C45—C44—P1—Ru1	-63.1 (12)
C17—C19—C20—C21	2 (2)	C49—C44—P1—Ru1	71.0 (9)
C19—C20—C21—C22	-6 (2)	C39—C38—P1—C44	89.5 (10)
C17—C16—C22—C21	-3.3 (17)	C43—C38—P1—C44	-42.1 (10)
N1—C16—C22—C21	174.9 (11)	C39—C38—P1—C32	-165.4 (9)
C17—C16—C22—C23	179.7 (11)	C43—C38—P1—C32	63.0 (10)
N1—C16—C22—C23	-2.1 (17)	C39—C38—P1—Ru1	-47.8 (10)
C20—C21—C22—C16	6 (2)	C43—C38—P1—Ru1	-179.4 (7)
C20—C21—C22—C23	-176.5 (13)	C33—C32—P1—C44	-95.7 (10)

C16—C22—C23—C24	109.8 (14)	C37—C32—P1—C44	141.5 (10)
C21—C22—C23—C24	-67.0 (16)	C33—C32—P1—C38	155.3 (10)
C16—C22—C23—C26	-129.1 (13)	C37—C32—P1—C38	32.6 (11)
C21—C22—C23—C26	54.1 (16)	C33—C32—P1—Ru1	32.7 (11)
C19—C17—C27—C29	-32.4 (17)	C37—C32—P1—Ru1	-90.1 (9)
C16—C17—C27—C29	151.0 (12)	C30—C31—Ru1—O1	1.4 (8)
C19—C17—C27—C28	89.7 (15)	C30—C31—Ru1—C1	-95.0 (9)
C16—C17—C27—C28	-86.9 (15)	C30—C31—Ru1—Cl1	-179.4 (8)
N3—C30—C31—Ru1	-3.5 (14)	C30—C31—Ru1—P1	92.5 (9)
C37—C32—C33—C34	-60.8 (15)	N3—O1—Ru1—C31	0.8 (7)
P1—C32—C33—C34	172.2 (11)	N3—O1—Ru1—C1	98.5 (7)
C32—C33—C34—C35	60.5 (16)	N3—O1—Ru1—Cl1	-167 (3)
C33—C34—C35—C36	-58.8 (18)	N3—O1—Ru1—P1	-92.9 (7)
C34—C35—C36—C37	56.5 (19)	N2—C1—Ru1—C31	-17.1 (13)
C35—C36—C37—C32	-56.9 (17)	N1—C1—Ru1—C31	174.8 (10)
C33—C32—C37—C36	59.2 (15)	N2—C1—Ru1—O1	-97.4 (12)
P1—C32—C37—C36	-177.0 (10)	N1—C1—Ru1—O1	94.5 (10)
C43—C38—C39—C40	-58.4 (13)	N2—C1—Ru1—Cl1	86.1 (12)
P1—C38—C39—C40	169.2 (8)	N1—C1—Ru1—Cl1	-82.0 (10)
C38—C39—C40—C41	55.2 (14)	N2—C1—Ru1—P1	132.6 (12)
C39—C40—C41—C42	-51.9 (16)	N1—C1—Ru1—P1	-35 (2)
C40—C41—C42—C43	51.8 (15)	C44—P1—Ru1—C31	-58.4 (6)
C41—C42—C43—C38	-53.6 (14)	C38—P1—Ru1—C31	71.5 (6)
C39—C38—C43—C42	57.3 (13)	C32—P1—Ru1—C31	-173.6 (6)
P1—C38—C43—C42	-168.3 (9)	C44—P1—Ru1—O1	20.9 (6)
C49—C44—C45—C46	51.9 (16)	C38—P1—Ru1—O1	150.8 (5)
P1—C44—C45—C46	-175.0 (11)	C32—P1—Ru1—O1	-94.3 (5)
C44—C45—C46—C47	-55.0 (18)	C44—P1—Ru1—C1	151.5 (14)
C45—C46—C47—C48	57.1 (19)	C38—P1—Ru1—C1	-78.6 (14)
C46—C47—C48—C49	-54.3 (18)	C32—P1—Ru1—C1	36.3 (15)
C45—C44—C49—C48	-48.4 (15)	C44—P1—Ru1—Cl1	-162.4 (5)
P1—C44—C49—C48	177.4 (9)	C38—P1—Ru1—Cl1	-32.5 (4)
C47—C48—C49—C44	49.4 (17)	C32—P1—Ru1—Cl1	82.4 (5)

3. RCM Time-Yield Studies (refer to Table 1 and Figure 3)

Comparative RCM experiments with diene **9** (toluene, 80 °C; carbon tetrachloride, 60 °C or chloroform, 60 °C; [diene] = 0.02 M;) were performed as follows. To a stirred solution of diene **9** and *n*-dodecane (used as an internal standard) in toluene, carbon tetrachloride or chloroform placed under argon in a Schlenk tube, additive (camphorosulphonic acid, hexachloroethene, carbon tetrabromide, trimethylsilyl chloride 4-20 mol%) and catalyst (1-5 mol%) in were added in a single portion at room temperature and the reaction mixture was stirred at 80 °C (toluene) or 60 °C (carbon tetrachloride, chloroform). Aliquots taken in regular intervals, were quenched immediately with ice-cold solution of ethyl-vinyl ether (2 M in CH_2Cl_2) and analysed by GC, using HP 6890 chromatograph with HP 5 column.

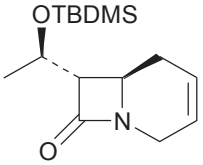


NMR data of compound **10** are consistent with literature: D. F. Taber, K. J. Frankowski, *J. Org. Chem*., **2003**, *68*, 6047-6048.

4. Preparative experiments

4.1. RCM reaction (refer to Table 2)

Synthesis of compound **13**



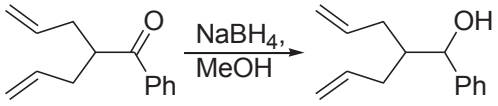
Diene **12** (343.7 mg; 0.11 mmol) and toluene (5.6 mL) were placed in a Schlenk tube. Next, hexachloroethane (10.5 mg, 0.04 mmol,) and complex **7** (8.7 mg; 0.01 mmol) were added and the resulting mixture was stirred under argon at 80 °C for 3 hours. From this point forth, all manipulations were carried out in air with reagent-grade solvents. The reaction mixture was concentrated under vacuum and resulting material was purified by column chromatography on silica gel (230-400 mesh, no per-treatment). Elution with *c*-hexane/EtOAc (9:1 v/v), solvents evaporation and drying of residue afforded **13** (301.5 mg, 96%) as a brown oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ= 5.87-5.64 (m, 2H), 4.20-4.12 (m, 1H), 4.05 (dd, *J* = 3.0, 18.2, 1H), 3.52-3.41 (m, 2H), 2.73 (dd, *J* = 1.4, 15.4 Hz, 1H), 2.46-2.35 (m, 1H), 2.20-2.07 (m, 1H), 1.23 (d, *J* = 6.2, 3H), 0.86 (s, 9H), 0.06 (s, 6H);

^{13}C NMR (62.5 MHz, $CDCl_3$) δ= 167.1, 123.9, 122.4, 66.9, 65.7, 45.9, 38.1, 28.1, 25.6, 22.8, 17.9, -4.2,-5.1;

NMR data of compound **13** are consistent with literature: A. G. M. Barrett, S. P. D. Baugh, D. C. Braddock, K. Flack, V. C. Gibson, M. R. Giles, E. L. Marshall, P. A. Procopiou, A. J. P. White, D. J. Williams, *J. Org. Chem.,* **1998**, *63*, 7893-7907.

Synthesis of compound **14**



22 **14**

To a stirred solution of ketone **22** (1 g, 5.0 mmol) in methanol (40 mL) sodium borohydride was added in portions (309.8 mg; 8.2 mmol). Resulting mixture was stirred at room temperature overnight. After that time the mixture was diluted with water and the product was extracted with ethyl acetate. The organic layers was separated and washed with water and brine, than dried over anhydrous magnesium sulfate. After evaporating solvent to dryness, crude product was obtained as a oil which was filtered through thin layer of silica gel affording colorless oil as a product **14** (861 mg, 85%)

^{1}H NMR (400 MHz, $CDCl_3$) δ= 7.38-7.24 (m, 5H), 5.88-5.71 (m, 2H), 5.11-4.98 (m, 4H), 4.71-4.67 (m, 1H), 2.23-2.17 (m, 2H) 2.16-2.06 (m, 1H), 2.01-1.86 (m, 3H);

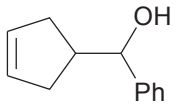
^{13}C NMR (100 MHz, $CDCl_3$) δ= 143.3, 137.0, 136.8, 128.2, 127.4, 126.4, 116.6, 116.5, 75.6, 44.7, 43.2, 32.8;

IR (film) $\tilde{\nu}$ = 3424, 3075, 2977, 2915, 1640, 1451, 1442, 1029, 1012, 996, 912, 764, 702 cm^{-1}.

HR MS (EI): calcd for $C_{14}H_{18}O$: 202.13577, found: 202.12514 (M^+)

Anal calcd for $C_{14}H_{18}O$ C: 83.12, H: 8.97; found C: 82.99, H: 9.05.

Synthesis of compound **15**



Diene **14** (262.7 mg, 1.3 mmol) and toluene (6.5 mL) were placed in a Schlenk tube. Next, hexachloroethane (12.6 mg, 0.05 mmol) and complex **7** (10.6 mg, 0.013 mmol) were added and the resulting mixture was stirred under argon at 80 °C for 3 hours. From this point forth, all manipulations were carried out in air with reagent-grade solvents. The reaction mixture was concentrated under vacuum and resulting material was purified by column chromatography on silica gel (230-400 mesh, no per-treatment). Elution with *c*-hexane/EtOAc (9:1 v/v), solvents evaporation and drying of residue afforded **15** (200.2 mg, 88%) as a oil.

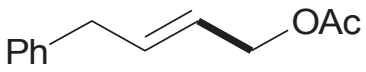
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.39-7.25 (m, 5H), 5.75-5.69 (m, 1H), 5.67-5.61 (m, 1H), 4.53 (d, J = 8 Hz, 1H), 2.76-2.63 (m, 1H), 2.59-2.39 (m, 2H), 2.25-2.13 (m, 1H), 2.10-1.98 (m, 1H), 1.94 (s, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ = 144.0, 130.0, 129.6, 128.4, 127.6, 126.5, 78.4, 44.8, 35.8, 35.4;

IR (film) $\tilde{\nu}$ = 3396, 3054, 3030, 2927, 2849, 1454, 1280, 1067, 1032, 1019, 941, 761, 700, 669, 641, 622 cm^{-1}.

Anal calcd for $C_{12}H_{14}O$ C: 82.72, H: 8.10; found C: 82.81, H: 8.22.

Synthesis of compound **18**



Allylbenzene (**16**) (108.6 mg, 0.9 mmol), diacetoxybutene (312.9 mg, 1.8 mmol) **17** and toluene (4.5 mL) were placed in a Schlenk tube. Next, hexachloroethane (17.6 mg, 0.07 mmol) and complex **7** (14.4 mg, 0.018 mmol) were added and the resulting mixture was stirred under argon at 80 °C for 24 hours. From this point forth, all manipulations were carried out in air with reagent-grade solvents. The reaction mixture was concentrated under vacuum and resulting material was purified by column chromatography on silica gel (230-400 mesh, no per-treatment). Elution with *c*-hexane/EtOAc (9:1 v/v), solvents evaporation and drying of

residue afforded **18** (114.1 mg, 65%) a brown oil as a mixture of *E* and *Z* isomer (in ratio 4:1, respectively).

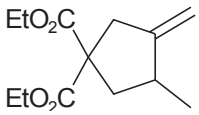
^{1}H NMR (400 MHz, $CDCl_3$) *E* isomer δ= 7.36-7.16 (m, 5H), 6.00-5.88 (m, 1H), 5.75-5.58 (m, 1H), 4.60-4.52 (m, 2H), 3.41 (d, J = 6.6 Hz, 2H), 2.07 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ= 170.8, 139.5, 134.5, 128.53, 128.50, 128.4, 128.3, 126.2, 125.2, 64.9, 38.6, 21.0.

NMR data of compound **18** are consistent with literature: W. H. Henderson , C. T. Check , N. Proust, J. P. Stambuli, *Org. Lett*., **2010**, *12*, 824–827.

4.2. Isomerization and cycloisomerization reactions (refer to Table 3)

Synthesis of compound **11**



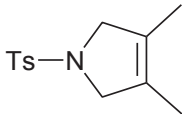
Diene **9** (73.5 mg, 0.31 mmol) and methanol (1.5 mL) were placed in a Schlenk tube. Next, complex **7** (11.7 mg, 0.015 mmol) was added and the resulting mixture was stirred under argon at 65 °C for 50 hours. GC analysis using internal standard (*n*-dodecane) performed after that time indicated yield of 82%.

^{1}H NMR (400 MHz, $CDCl_3$) δ= 4.89 (d, J = –2 Hz, 1H), 4.78 (d, J = –2 Hz, 1H), 4.28-4.08 (m, 4H), 3.10-2.88 (m, 2H), 2.68-2.46 (m, 2H), 1.80-1.68 (m, 1H), 1.30-1.20 (m, 6H), 1.09 (d, J = 6.4 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ= 172.0, 171.9, 153.4, 105.4, 61.4, 58.2, 42.1, 40.4, 37.2, 17.9, 14.0

NMR data of compound **11** are consistent with literature: N. Hayashi, I. Shibata, A. Baba, *Org. Lett.*, **2004**, *6*, 4981-4983; D. Crich, J. Hwang, S. Gastaldi, F. Recupero, D. J. Wink, *J. Org. Chem.,* **1999**, *64*, 2877-2882.

Synthesis of compound **20**

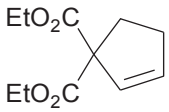


Diene **19** (77.4 mg, 0.31 mmol) and methanol (1.5 mL) were placed in a Schlenk tube. Next, complex **7** (11.9 mg, 0.015 mmol) was added and the resulting mixture was stirred under argon at 65 °C for 50 hours. GC analysis using internal standard performed (*n*-dodecane, 30 mg) after that time indicated yield of 88%.

^{1}H NMR (200 MHz, $CDCl_3$) δ= 7.71 (d, J = 8.4 Hz, 2H), 7.31 (d, J = 8.4 Hz, 2H), 3.96 (s, 4H), 2.42 (s, 3H), 1.53 (s, 6H).

NMR data of compound **20** are consistent with literature: M. Arisawa, Y. Terada, K. Takahashi, M. Nakagawa, A. Nishida, *J. Org. Chem.*, **2006**, *71*, 4255-4261.

Synthesis of compound **21**



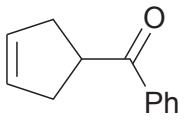
Compound **10** (54.1 mg, 0.25 mmol) and trifluoroethanol (2 mL) were placed in a Schlenk tube. Next, complex **7** (10.8 mg, 0.014 mmol) was added and the resulting mixture was stirred under argon at 70 °C for 71 hours. GC analysis using internal standard performed (*n*-dodecane, 30 mg) after that time indicated yield of 75%.

^{1}H NMR (200 MHz, $CDCl_3$) δ= 6.04-5.94 (m, 1H), 5.86-5.78 (m, 1H), 4.28-4.08 (m, 4H), 2.60-2.30 (m, 4H), 1.24 (t, J = 7.2 Hz, 6H).

NMR data of compound **21** are consistent with literature: T. S. Abram, R. Baker, C. M. Exon, V. B. Rao, *J. Chem. Soc., Perkin Trans. 1*, **1982**, 285-294.

4.3. RCM and non-metathetic process (refer to Scheme 3)

Synthesis of compound **23**



Dienone **22** (260.8 mg; 1.30 mmol) and toluene (6.5 mL) were placed in a Schlenk flask. Afterwards hexachloroethane (12.3 mg; 0.052 mmol) and complex **7** (10.3 mg; 0.013 mmol) were added and the resulting mixture was stirred under argon at 80 °C for 3 hours. From this point forth, all manipulations were carried out in air with reagent-grade solvents. The reaction mixture was concentrated under vacuum and resulting material was purified by column chromatography on silica gel (230-400 mesh, no pre-treatment). Elution with c-hexane-EtOAc (18:1), solvents evaporation and drying of residue afforded enone **23** (210.5 mg, 94%) as a colorless oil.

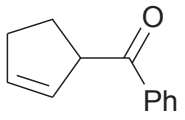
^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.02-7.94 (m, 2H), 7.60-7.42 (m, 3H), 5.74-5.64 (m, 2H); 4.12-4.02 (m, 1H); 2.85-2.65 (m, 4H).

^{13}C NMR (100 MHz, $CDCl_3$) δ = 201.4, 136.4, 132.8, 128.9, 128.5, 44.0, 36.2, 36.2.

IR (film) $\tilde{\nu}$ = 3058, 2921, 2851, 1683, 1596, 1448, 1356, 1275, 1221, 1016, 692, 674 cm^{-1}

NMR data of compound **23** are consistent with literature: T. Satoh, T. Itaya, K. Okuro, M. Miura, M. Nomura, *J. Org. Chem.,* **1995**, *60*, 7267-7271.

Synthesis of compound **24**

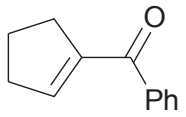


Compound **23** (51.9 mg, 0.3 mmol) and methanol (1.5 mL) were placed in a Schlenk tube. Next, complex **7** (12.0 mg, 0.015 mmol) was added and the resulting mixture was stirred under argon at 65 °C for 50 hours. From this point forth, all manipulations were carried out in air with reagent-grade solvents. The reaction mixture was concentrated under vacuum and resulting material was purified by column chromatography on silica gel (230-400 mesh, no pre-treatment). Elution with *c*-hexane-EtOAc (18:1), solvents evaporation and drying of residue afforded mixture **23** and **24** (in 1:1 ratio according to ^{1}H NMR) as a colorless oil.

^{1}H NMR (200 MHz, $CDCl_3$) δ= 8.10-7.90 (m, 2H), 7.64-7.36 (m, 3H), 6.00-5.88 (m, 1H), 5.84-5.74 (m, 1H), 4.58-4.40 (m, 1H), 2.58-2.40 (m, 2H), 2.35-2.10 (m, 2H).

NMR data of compound **24** are consistent with literature: J. L. C. Kachinsky, R. G. Salomon, *J. Org. Chem.* **1986**, *51*, 1393-1401; T. Satoh, T. Itaya, K. Okuro, M. Miura, M. Nomura, *J. Org. Chem.,* **1995**, *60*, 7267-7271.

Synthesis of compound **25**



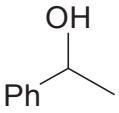
Compound **23** (34.4 mg, 0.2 mmol) and toluene (1 mL) were placed in a Schlenk tube. Next, complex **7** (8.0 mg, 0.01 mmol) and potassium bi(trimethylsilyl)amide (8.0 mg, 0.02 mmol) were added and the resulting mixture was stirred under argon at 80 °C for 65 hours. 65 °C . From this point forth, all manipulations were carried out in air with reagent-grade solvents. The reaction mixture was concentrated under vacuum and resulting material was purified by preparative thin layer chromatography on silica gel. Elution with *c*-hexane:EtOAc (9:1), solvents evaporation and drying of residue afforded enone **25** (18.1 mg, 53%) as a colorless oil.

^{1}H NMR (200 MHz, $CDCl_3$) δ= 7.78-7.66 (m, 2H), 7.58-7.34 (m, 3H), 6.58-6.48 (m, 1H), 2.84-2.68 (m, 2H), 2.68-2.55 (m, 2H), 2.00 (p, J = 7.4 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ= 194.2, 147.0, 144.5, 139.0, 131.7, 128.8, 128.1, 34.3, 31.8, 22.8.

NMR data of compound **25** are consistent with literature: C. Körner, P. Starkov, T. D. Sheppard, *J. Am. Chem. Soc.*, **2010**, *132*, 5968-5969; T. Satoh, T. Itaya, K. Okuro, M. Miura, M. Nomura, *J. Org. Chem.,* **1995**, *60*, 7267-7271.

Synthesis of compound **27**



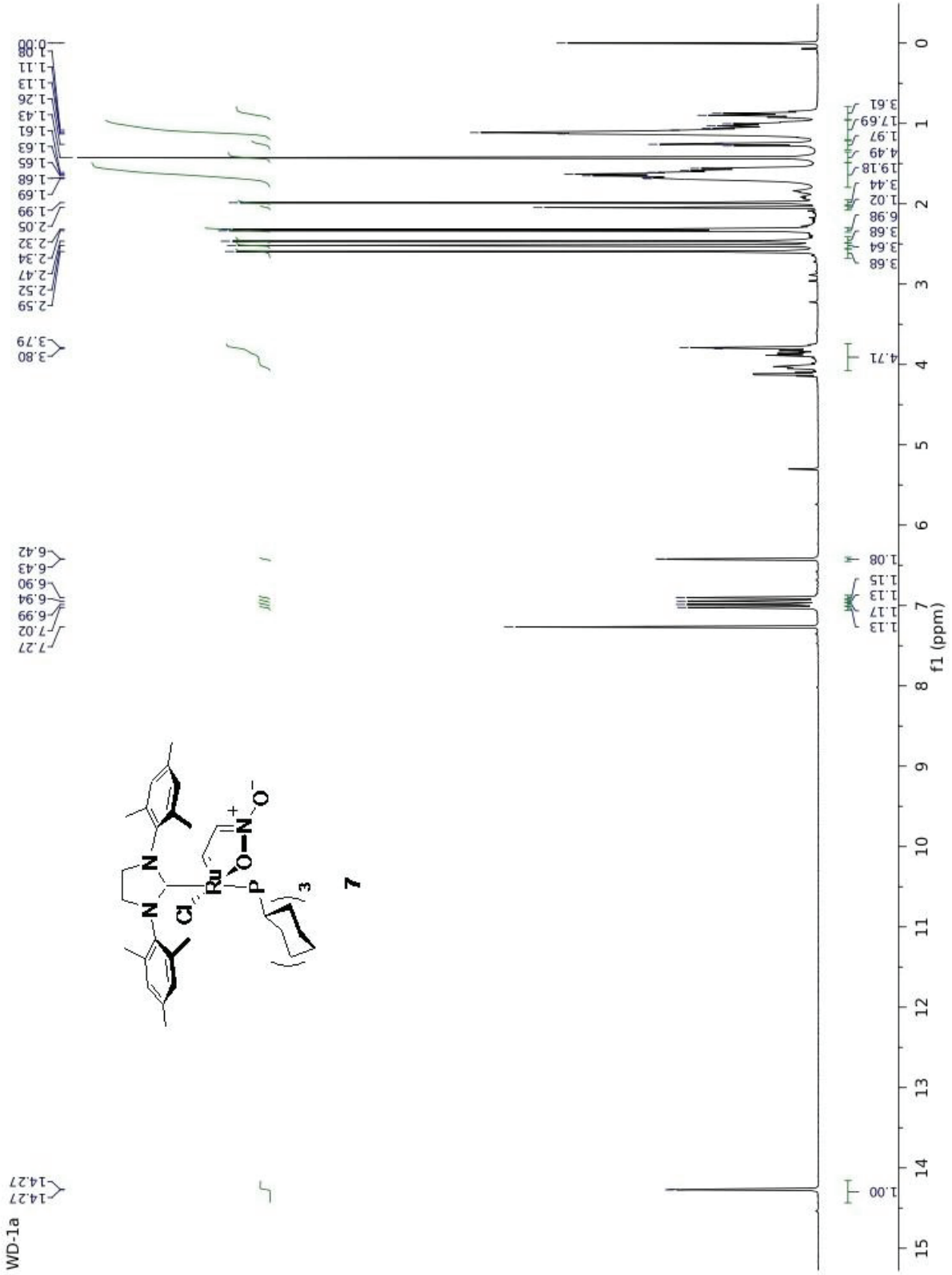
To the stirred solution of complex **7** (15.7 mg, 0.02 mmol) and sodium hydride 60% dispersion in mineral oil (2.8 mg, 0.07 mmol) in tetrahydrofuran (2.5 mL) acetophenone (**26**) (120.3 mg, 1.0 mmol) and isopropyl alcohol (2.5 mL) were added. The resulting mixture was stirred under argon at 70 °C for 5 hours. From this point forth, all manipulations were carried out in air with reagent-grade solvents. The reaction mixture was concentrated under vacuum and resulting material was purified by column chromatography on silica gel (230-400 mesh, no pre-treatment). Elution with c-hexane-EtOAc (20:1), solvents evaporation and drying of residue afforded alcohol **27** (95 mg, 78%) as a colorless oil.

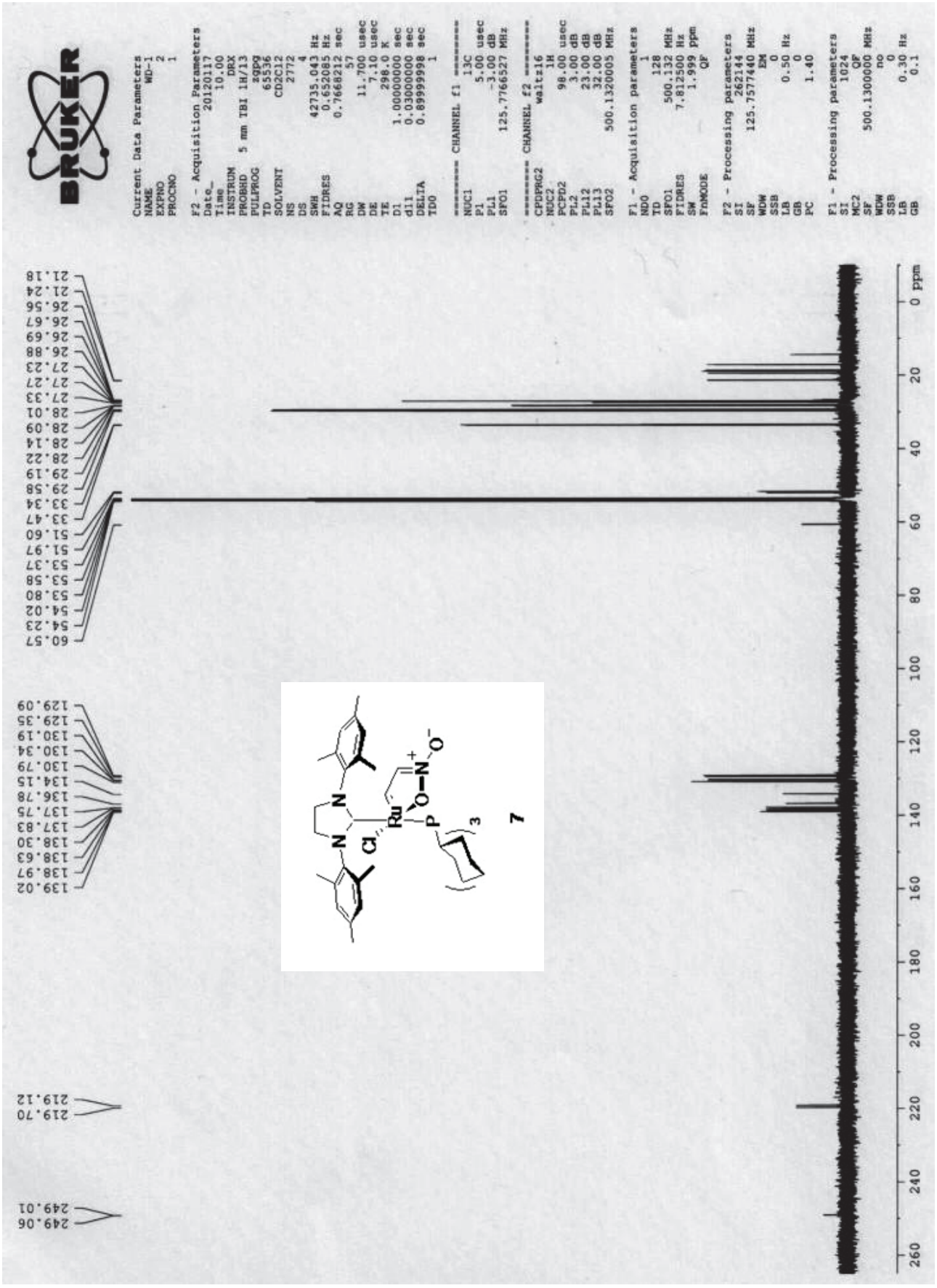
^{1}H NMR (400 MHz, $CDCl_3$) δ= 7.41-7.24 (m, 5H), 4.94-4.84 (q, J = 6.4 Hz, 1H), 2.05 (s, 1H), 1.50 (d, J =6.4 Hz, 3H).

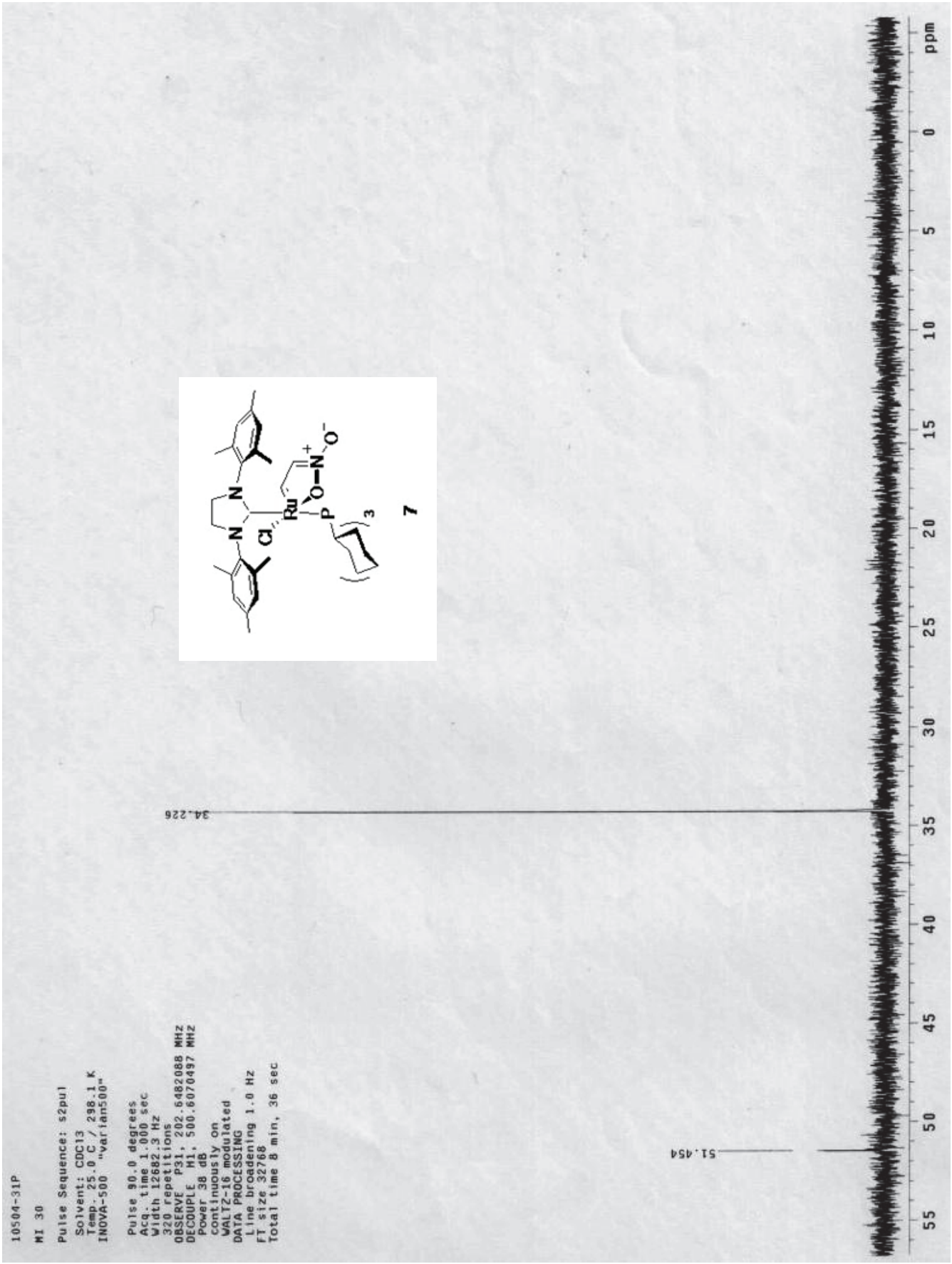
^{13}C NMR (100 MHz, $CDCl_3$) δ= 145.8, 128.4, 127.4, 125.3, 70.3, 25.1.

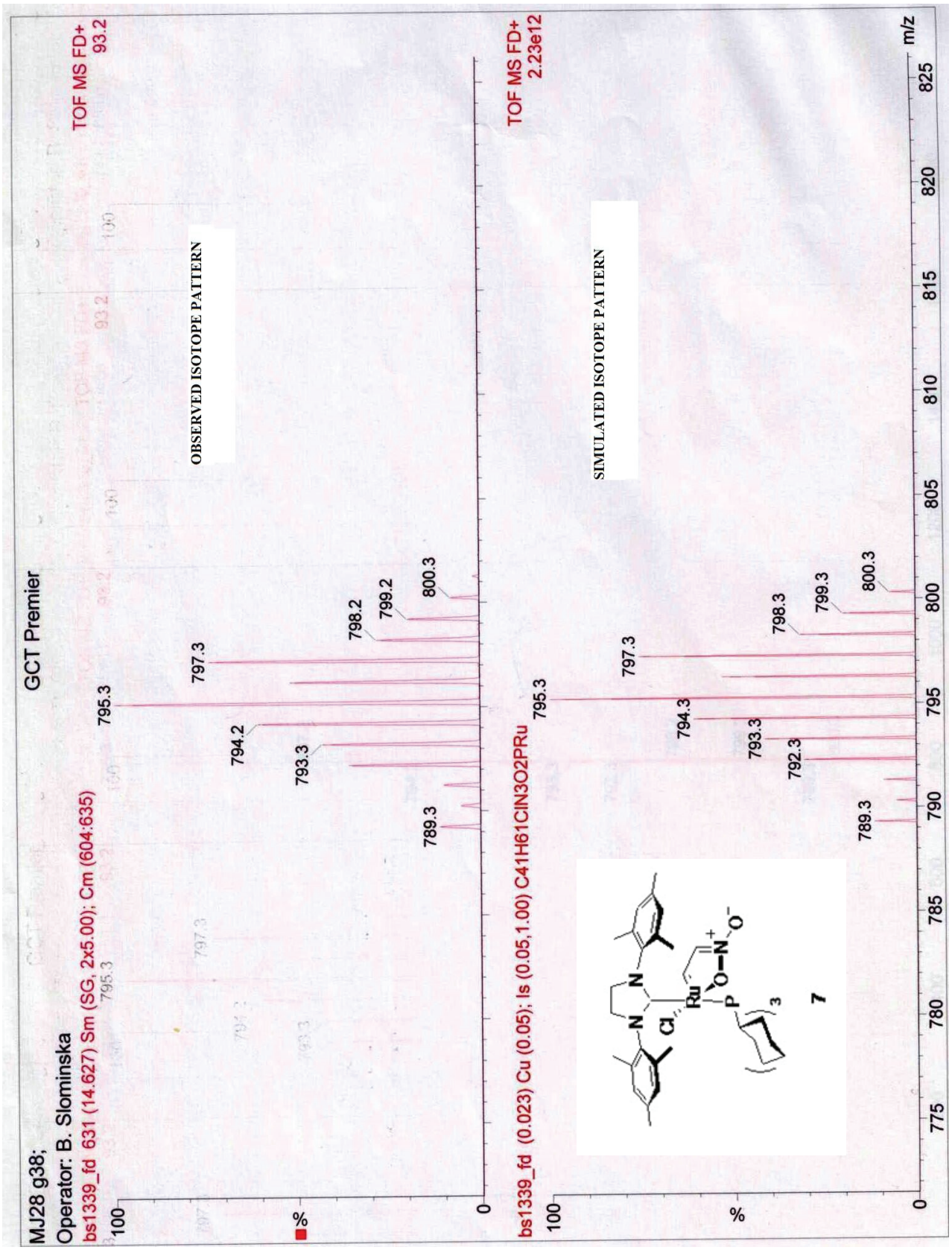
NMR data of compound **27** are consistent with literature: J. S. Yadav, B. V. S. Reddy, C. Sreelakshmi, A. B. Rao, *Synthesis,* **2009**, *11*, 1881-1885.

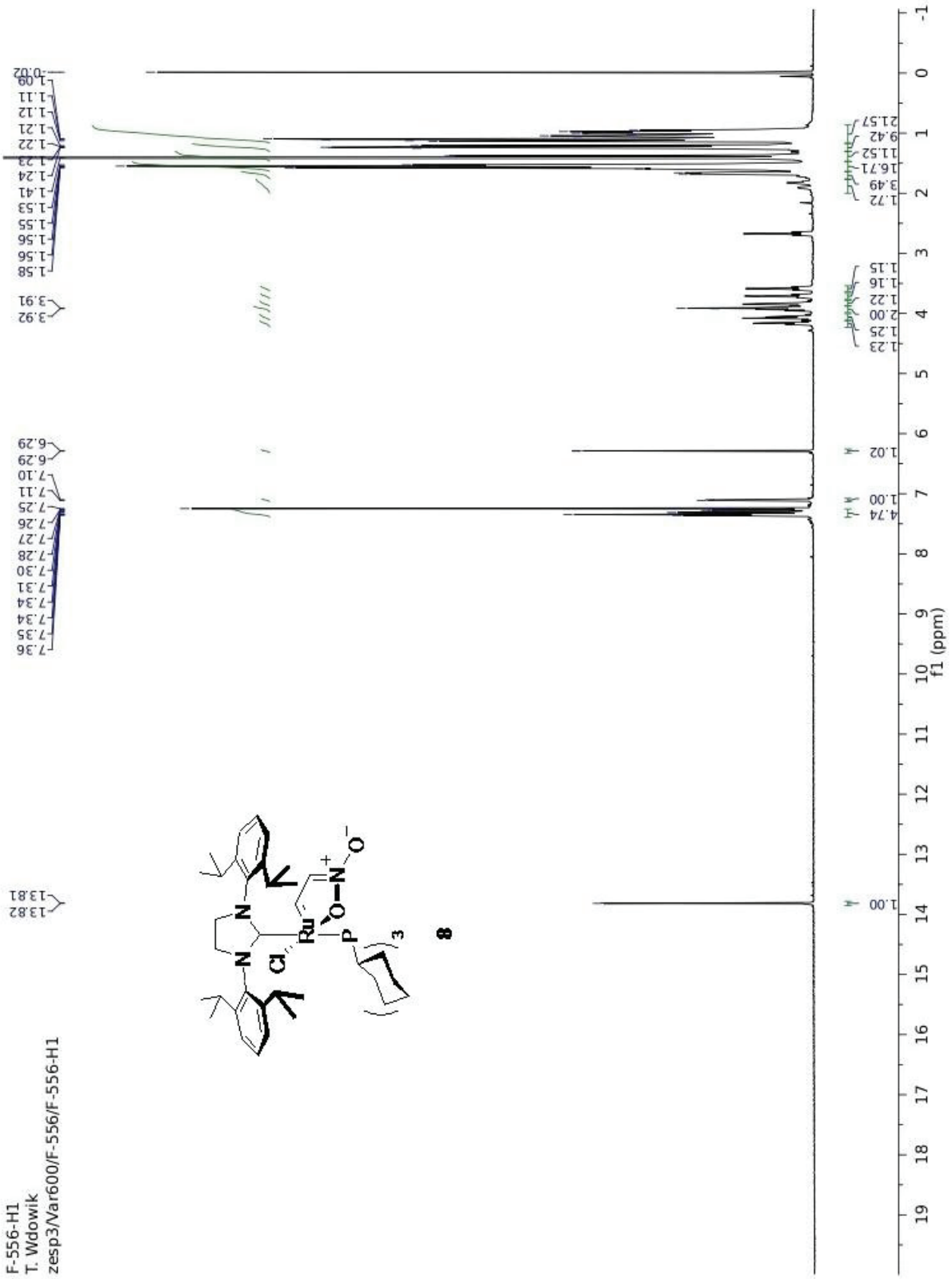
5. Spectroscopy's (NMR and MS) analysis copies

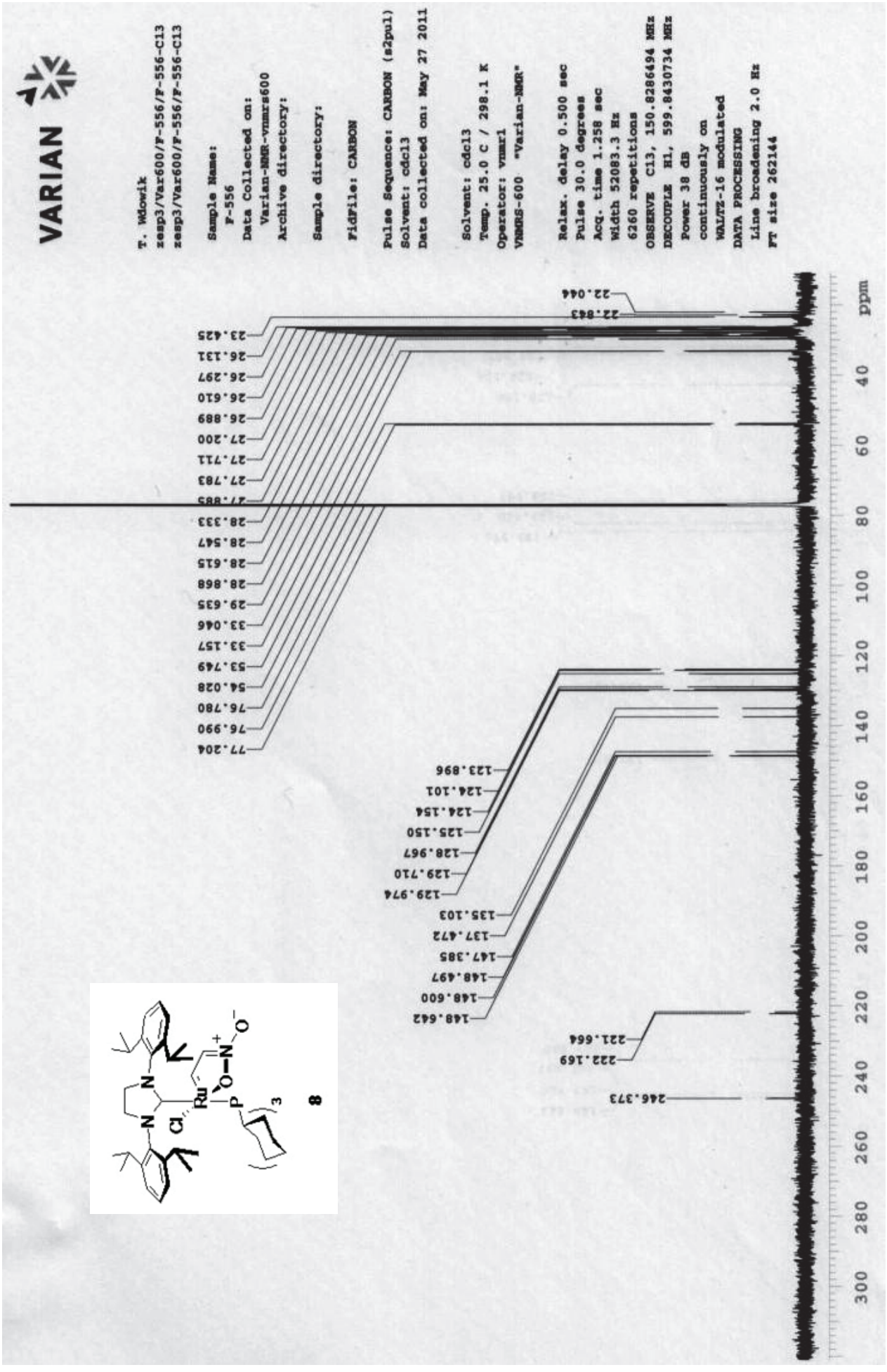


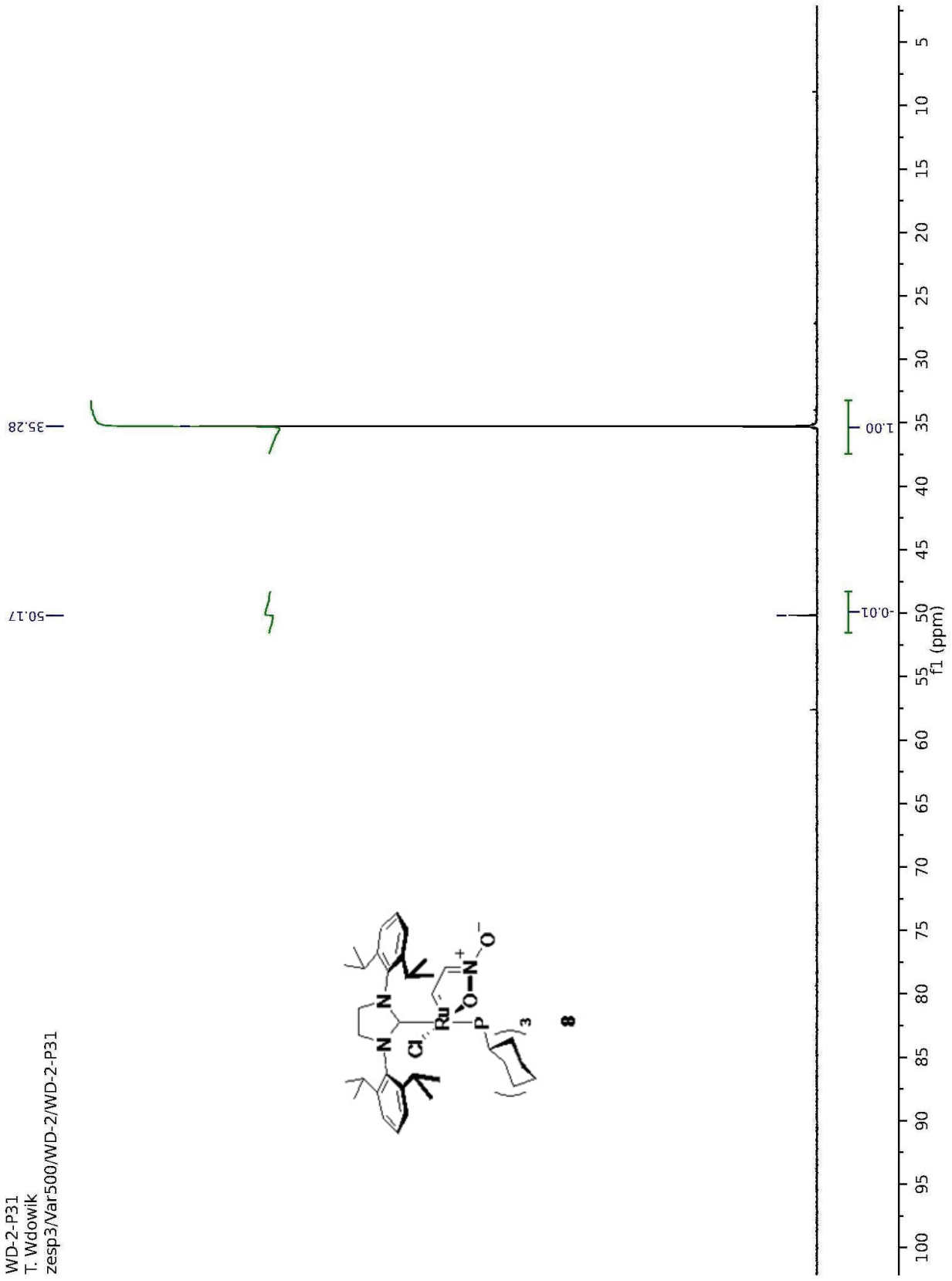

BRUKER
Current Data Parameters
NAME WD-1
EXPNO 2
PROCNO 1
F2 - Acquisition Parameters
Date_ 20120117
Time 10.00
INSTRUM DRX
PROBHD 5 mm TBI 1H/13
PULPROG zgpg
TD 65536
SOLVENT CD2Cl2
NS 2772
DS 4
SWH 42735.043 Hz
FIDRES 0.652085 Hz
AQ 0.7668212 sec
RG 57
DW 11.700 usec
DE 7.10 usec
TE 298.0 K
D1 1.00000000 sec
d11 0.03000000 sec
DELTA 0.89999998 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 5.00 usec
PL1 -3.00 dB
SFO1 125.7766527 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 98.00 usec
PL2 3.00 dB
PL12 23.00 dB
PL13 32.00 dB
SFO2 500.1320005 MHz
F1 - Acquisition parameters
NDO 1
TD 128
SFO1 500.132 MHz
FIDRES 7.812500 Hz
SW 1.999 ppm
FnMODE QF
F2 - Processing parameters
SI 262144
SF 125.7577440 MHz
WDW EM
SSB 0
LB 0.50 Hz
GB 0
PC 1.40
F1 - Processing parameters
SI 1024
MC2 QF
SF 500.1300000 MHz
WDW no
SSB 0
LB 0.30 Hz
GB 0.1
Cl
Ru
N
N
O
N
O
P
3
7
0 ppm
20
40
60
80
100
120
140
160
180
200
220
240
260

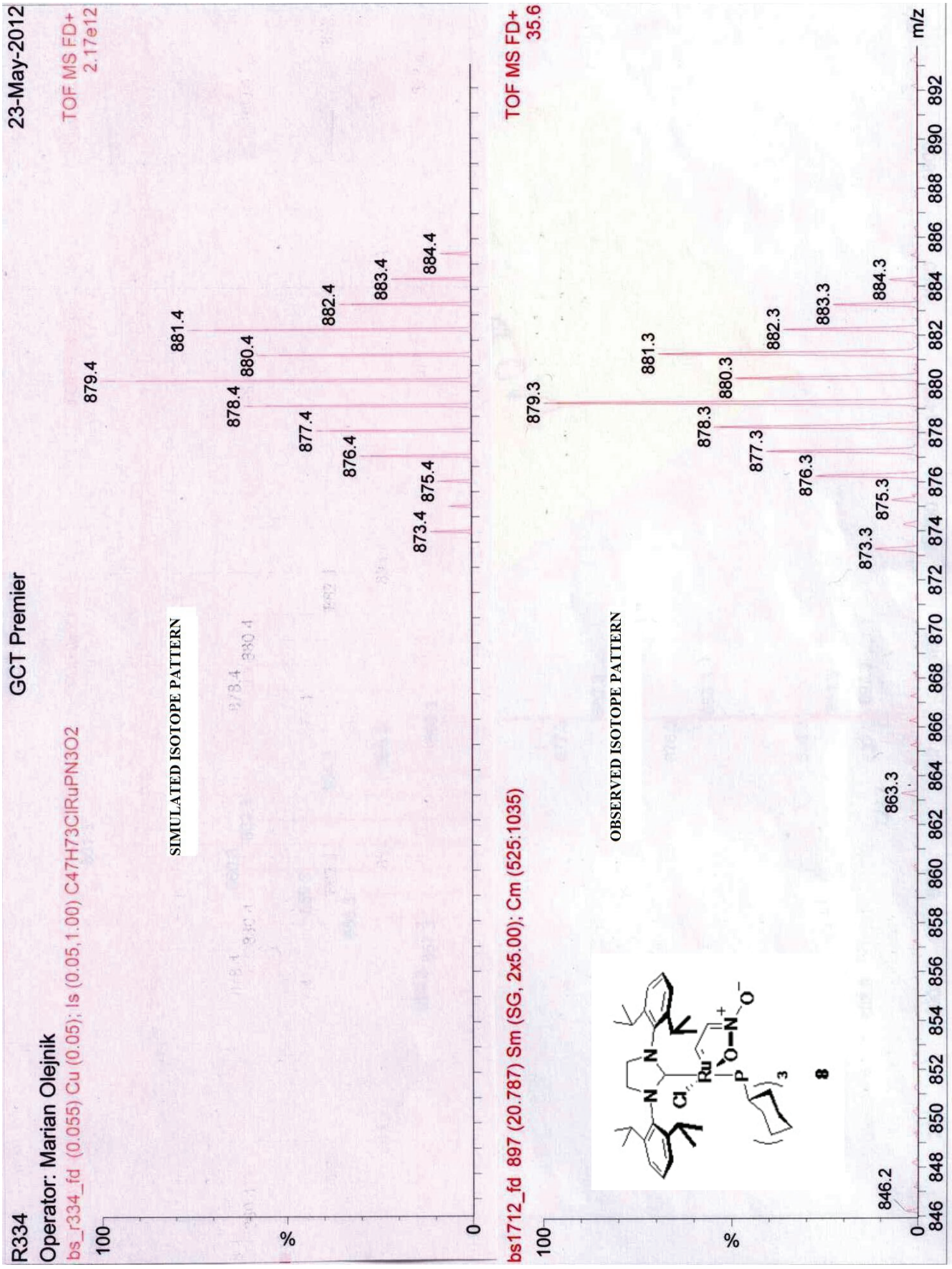

10504-31P
MI 30
Pulse Sequence: s2pul
Solvent: CDCl3
Temp. 25.0 C / 298.1 K
INOVA-500 "varian500"
Pulse 90.0 degrees
Acq. time 1.000 sec
Width 12682.3 Hz
320 repetitions
OBSERVE P31, 202.6482088 MHz
DECOUPLE H1, 500.6070497 MHz
Power 38 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 32768
Total time 8 min, 36 sec
34.226
51.454
55
50
45
40
35
30
25
20
15
10
5
0
ppm
7

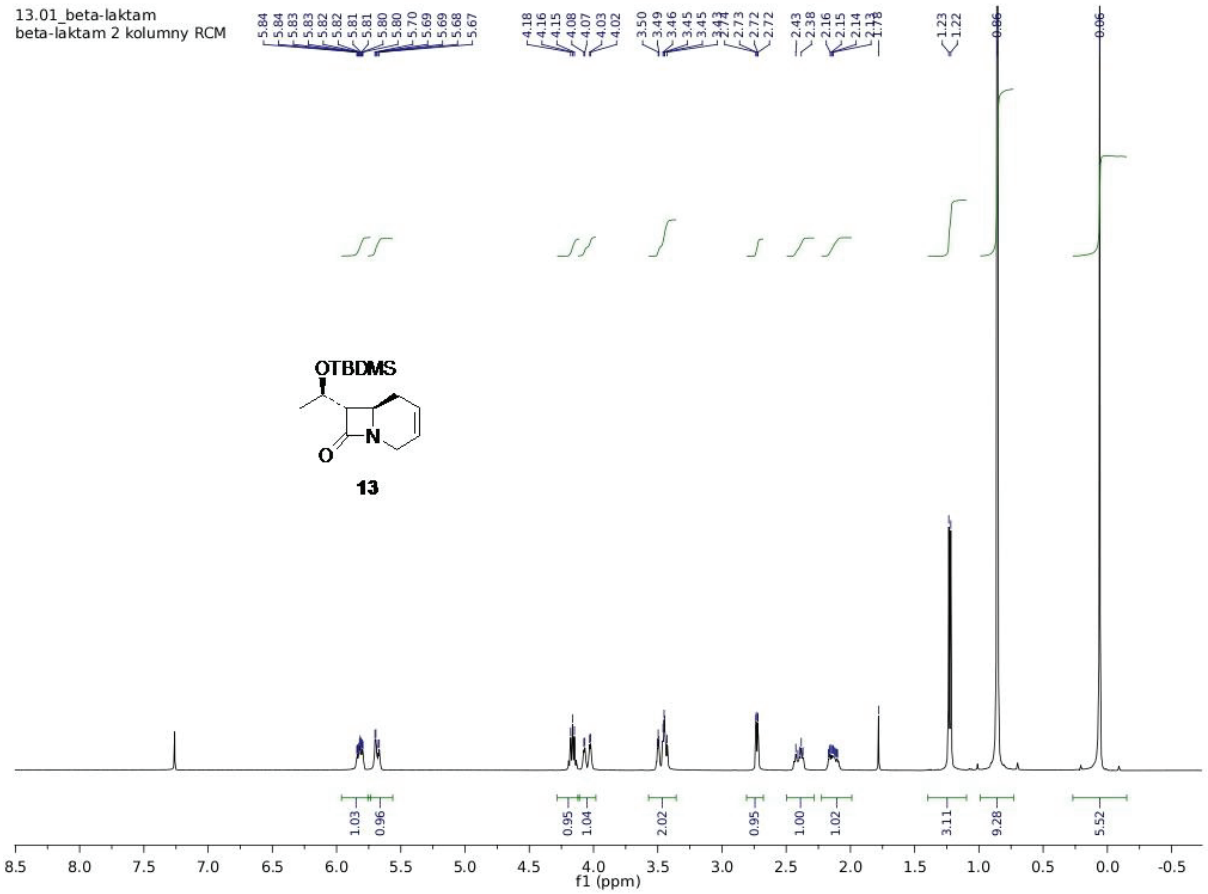

MJ28 g38;
Operator: B. Slominska
GCT Premier
bs1339_fd 631 (14.627) Sm (SG, 2x5.00); Cm (604:635)
TOF MS FD+
93.2
OBSERVED ISOTOPE PATTERN
795.3
797.3
794.2
793.3
798.2
799.2
800.3
789.3
bs1339_fd (0.023) Cu (0.05); Is (0.05,1.00) C41H61ClN3O2PRu
TOF MS FD+
2.23e12
SIMULATED ISOTOPE PATTERN
795.3
797.3
794.3
793.3
798.3
799.3
800.3
792.3
789.3
7
%
m/z
775
780
785
790
795
800
805
810
815
820
825
0
100

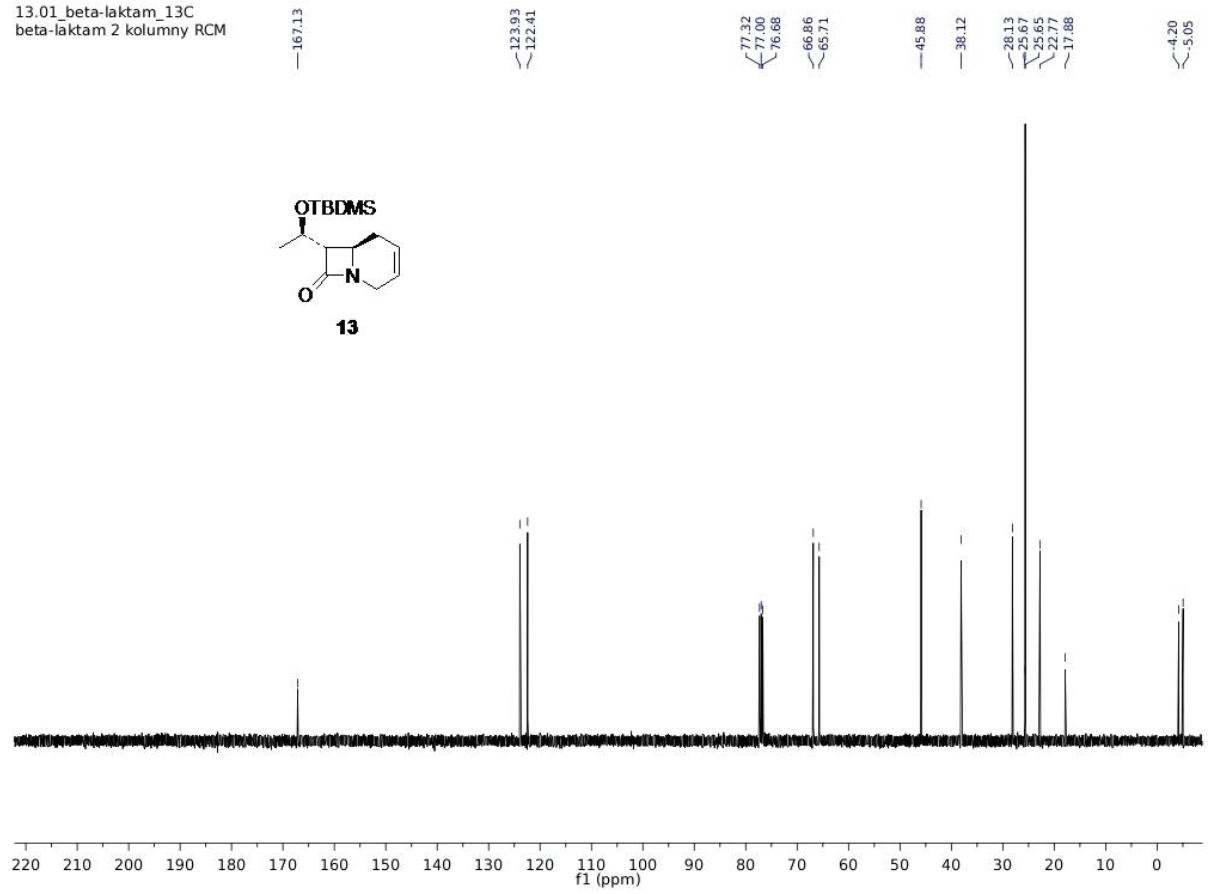

F-556-H1
T. Wdowik
zesp3/Var600/F-556/F-556-H1
f1 (ppm)
8

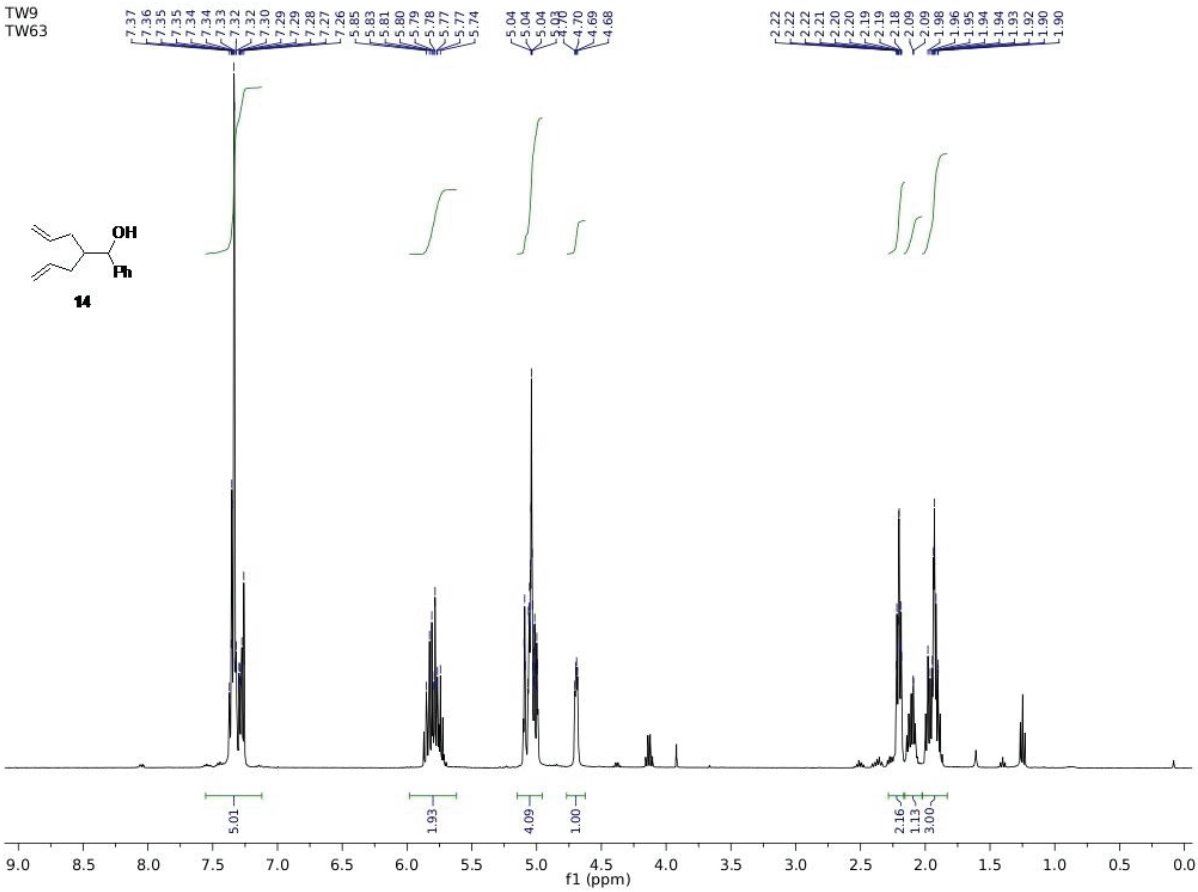


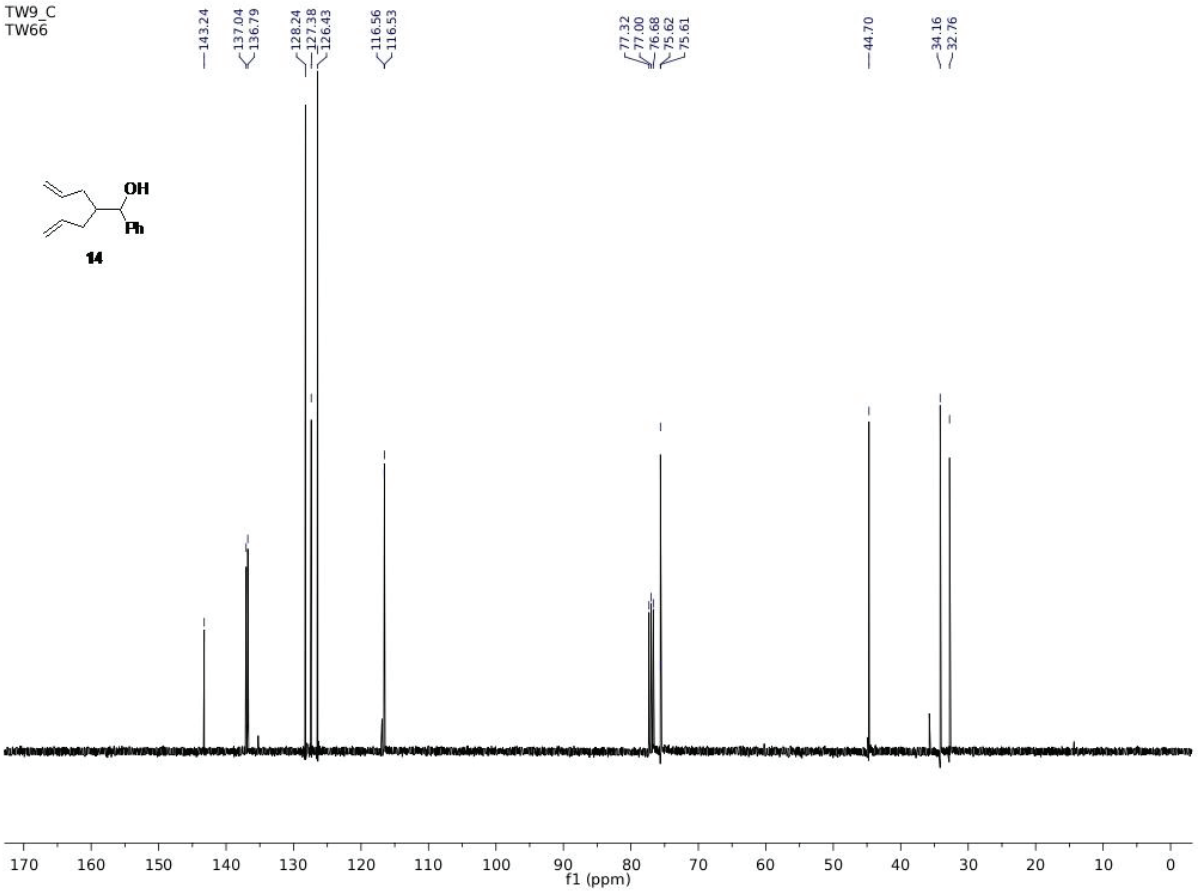

35.28
50.17
1.00
0.01
f1 (ppm)
WD-2-P31
T. Wdowik
zesp3/Var500/WD-2/WD-2-P31
8

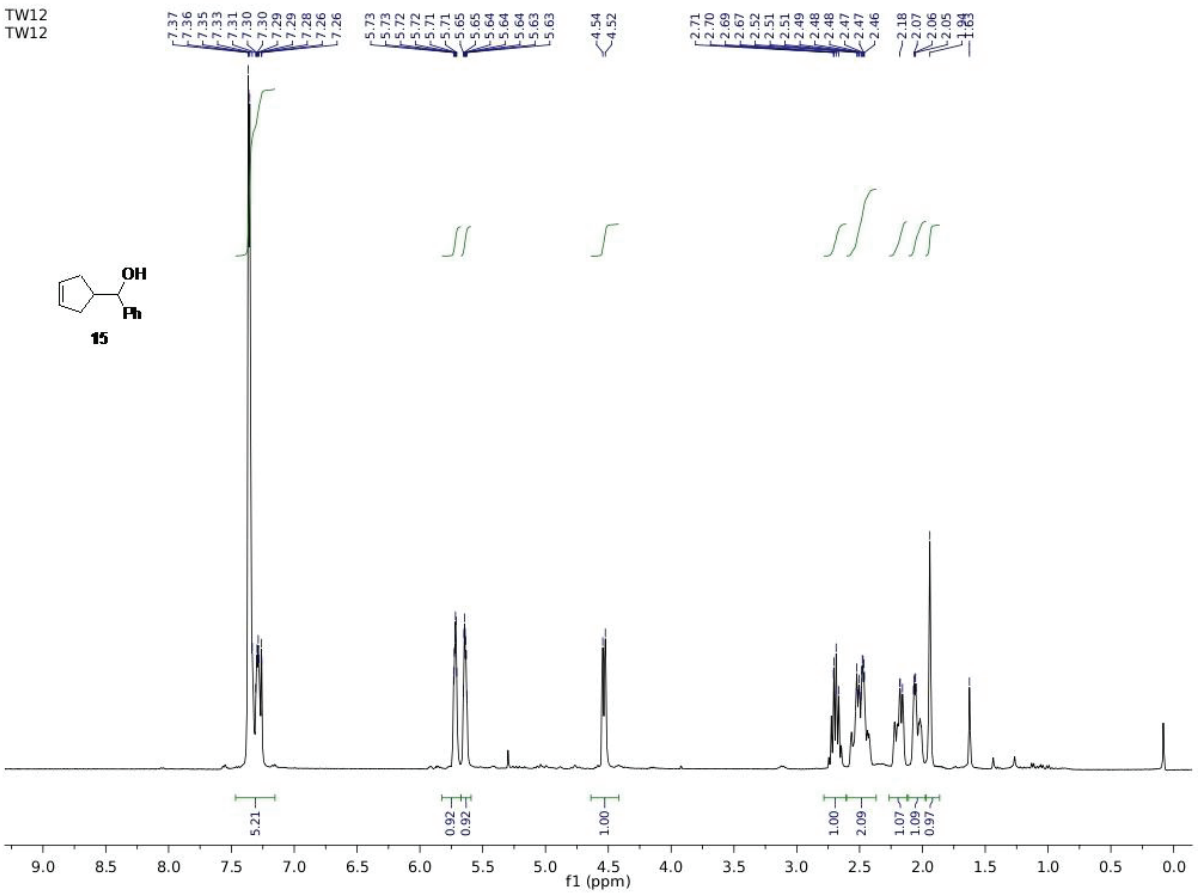

R334
GCT Premier
23-May-2012
Operator: Marian Olejnik
bs_r334_fd (0.055) Cu (0.05); Is (0.05,1.00) C47H73ClRuPN3O2
TOF MS FD+
2.17e12
SIMULATED ISOTOPE PATTERN
879.4
881.4
878.4
880.4
877.4
882.4
876.4
883.4
873.4
875.4
884.4
100
%
0
bs1712_fd 897 (20.787) Sm (SG, 2x5.00); Cm (525:1035)
TOF MS FD+
35.6
OBSERVED ISOTOPE PATTERN
879.3
881.3
878.3
880.3
877.3
882.3
876.3
883.3
873.3
875.3
884.3
863.3
846.2
100
%
0
846 848 850 852 854 856 858 860 862 864 866 868 870 872 874 876 878 880 882 884 886 888 890 892
m/z
Cl
Ru
P
O
N
3
8

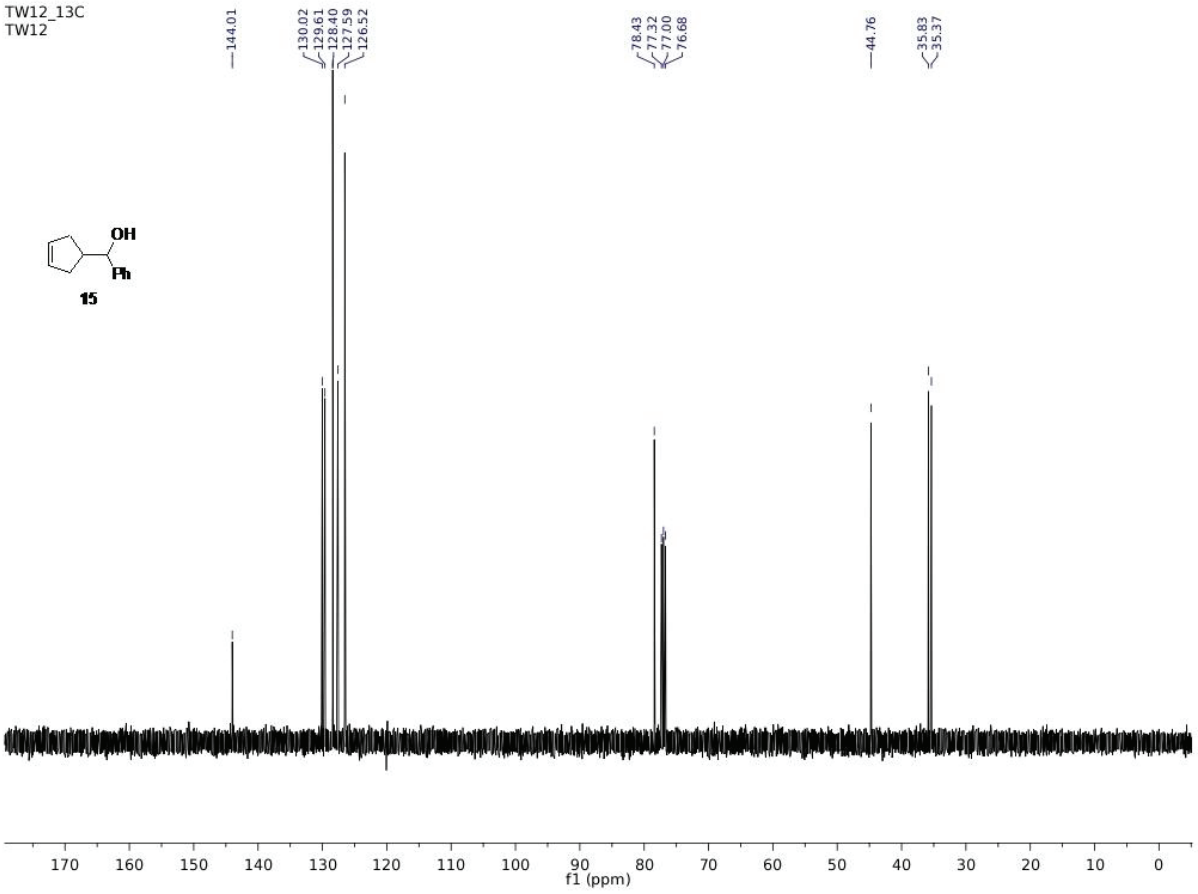

13.01_beta-laktam
beta-laktam 2 kolumny RCM
OTBDMS
N
O
13
f1 (ppm)

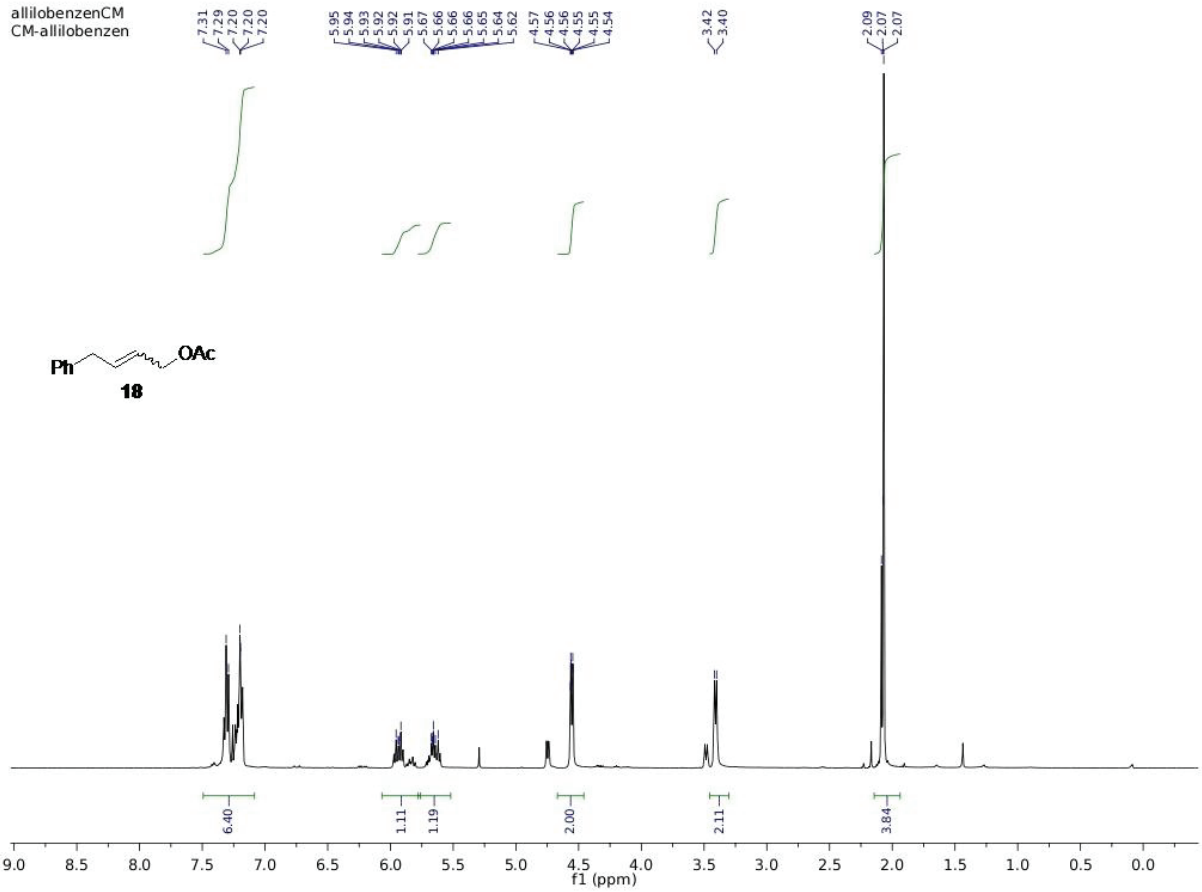

13.01_beta-laktam_13C
beta-laktam 2 kolumny RCM
OTBDMS
N
O
13
f1 (ppm)

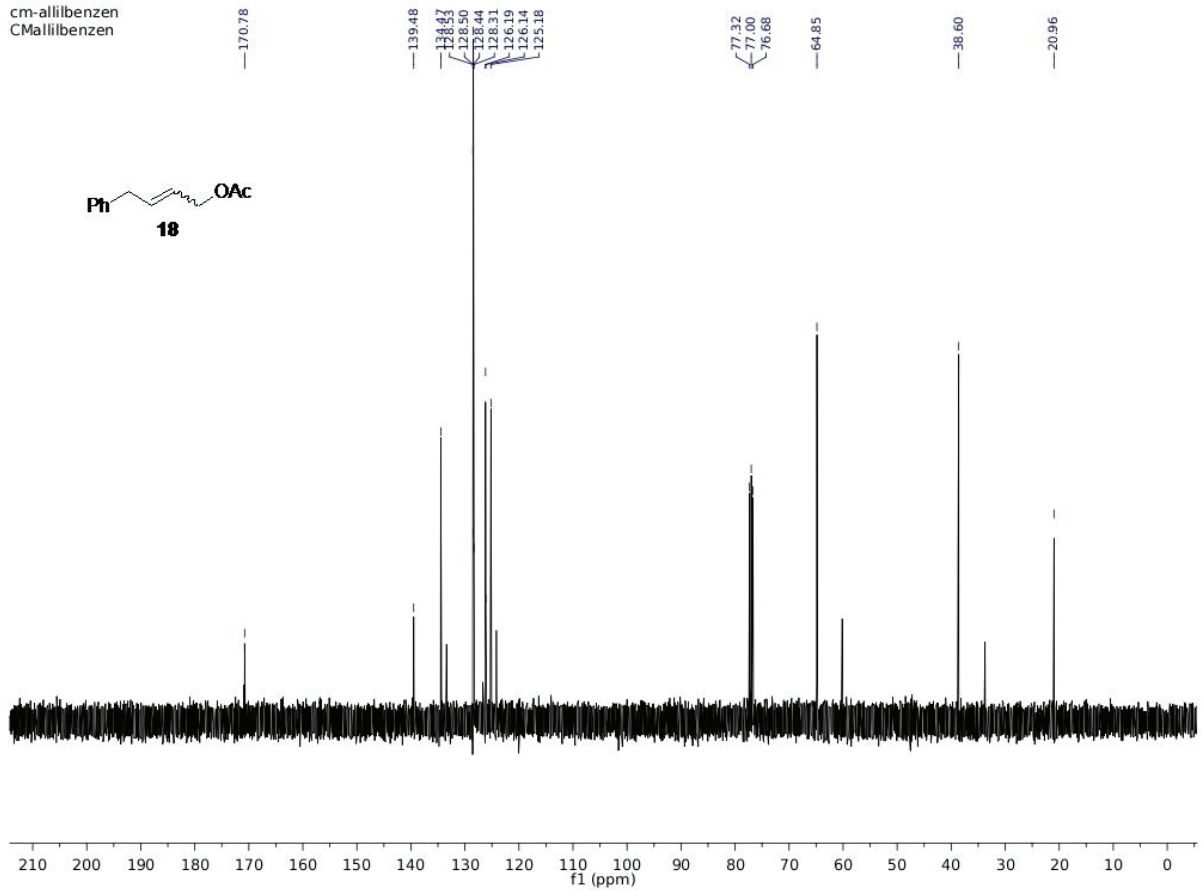

TW9
TW63
OH
Ph
14
f1 (ppm)

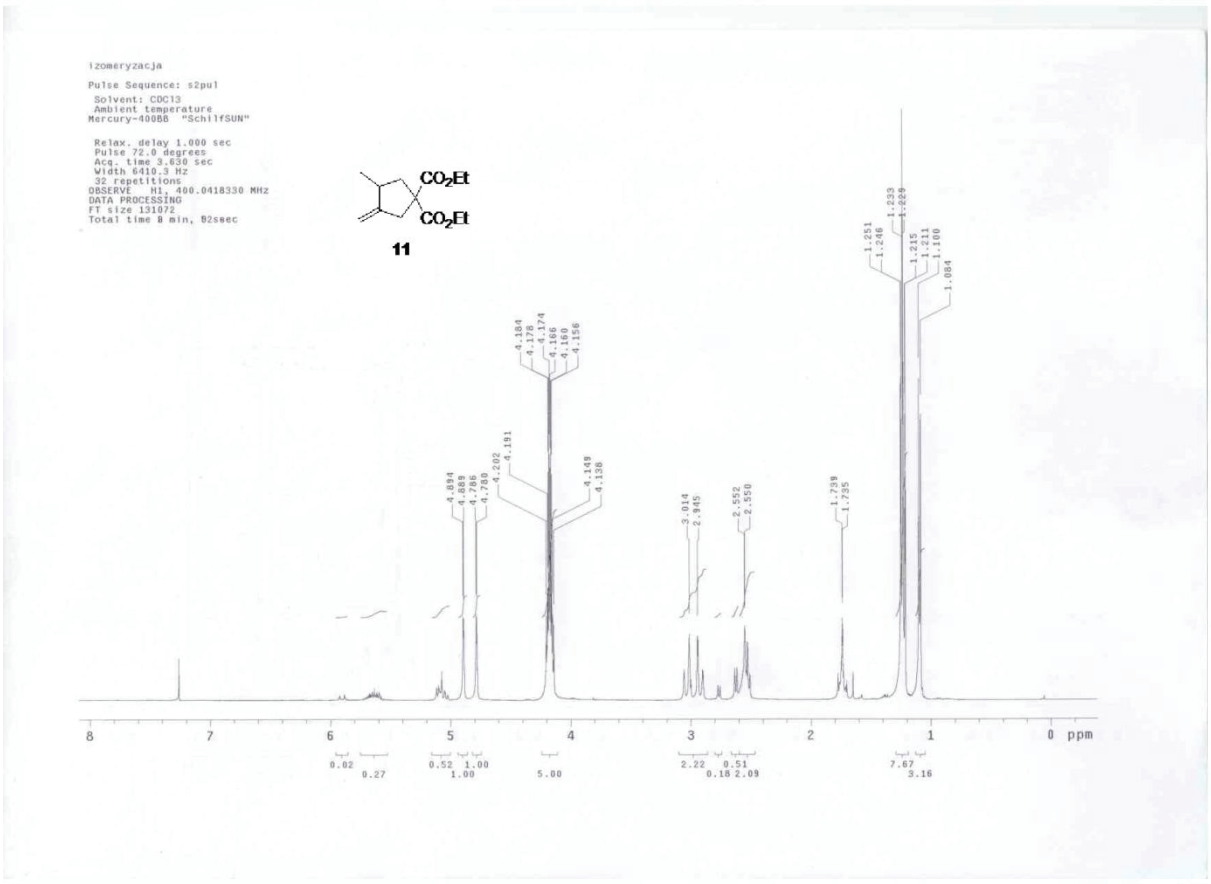

TW9_C
TW66
OH
Ph
14
f1 (ppm)

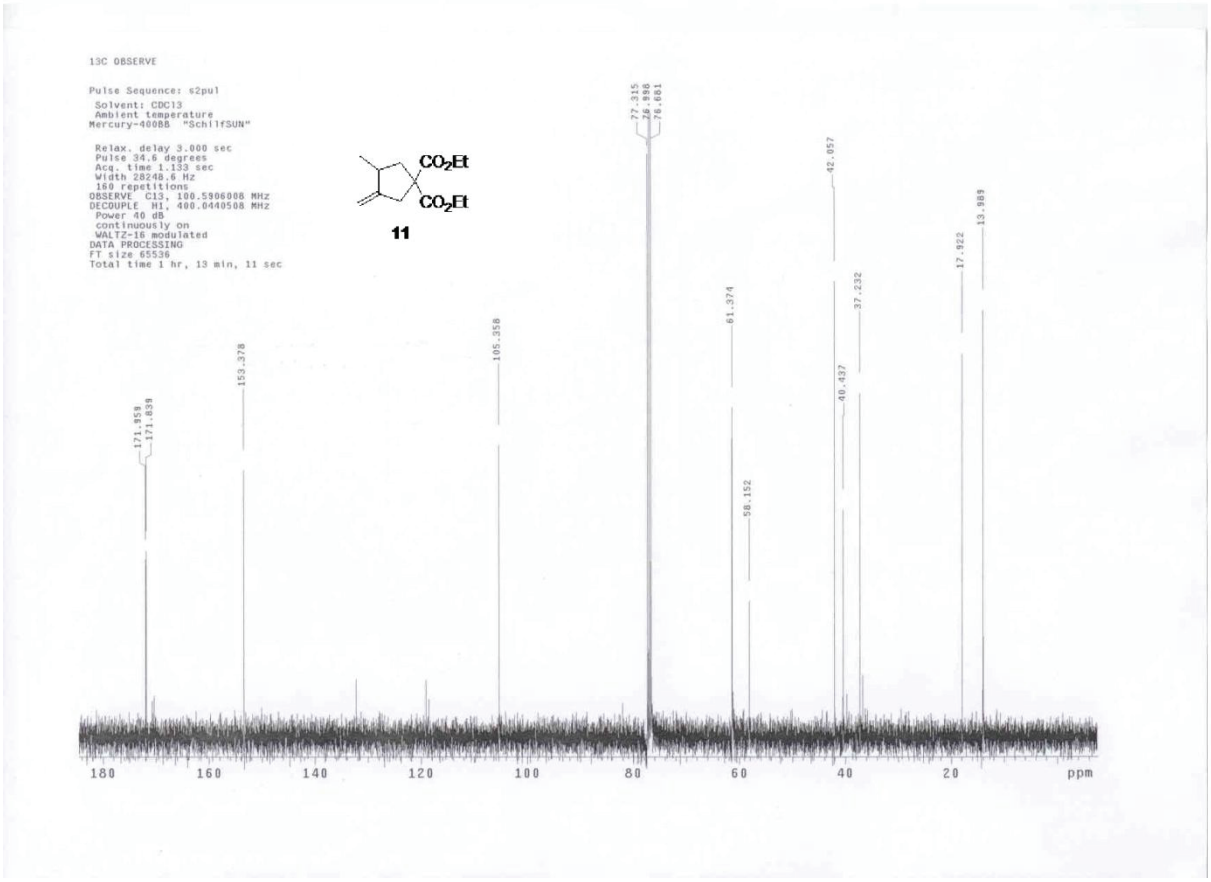

TW12
TW12
OH
Ph
15
f1 (ppm)

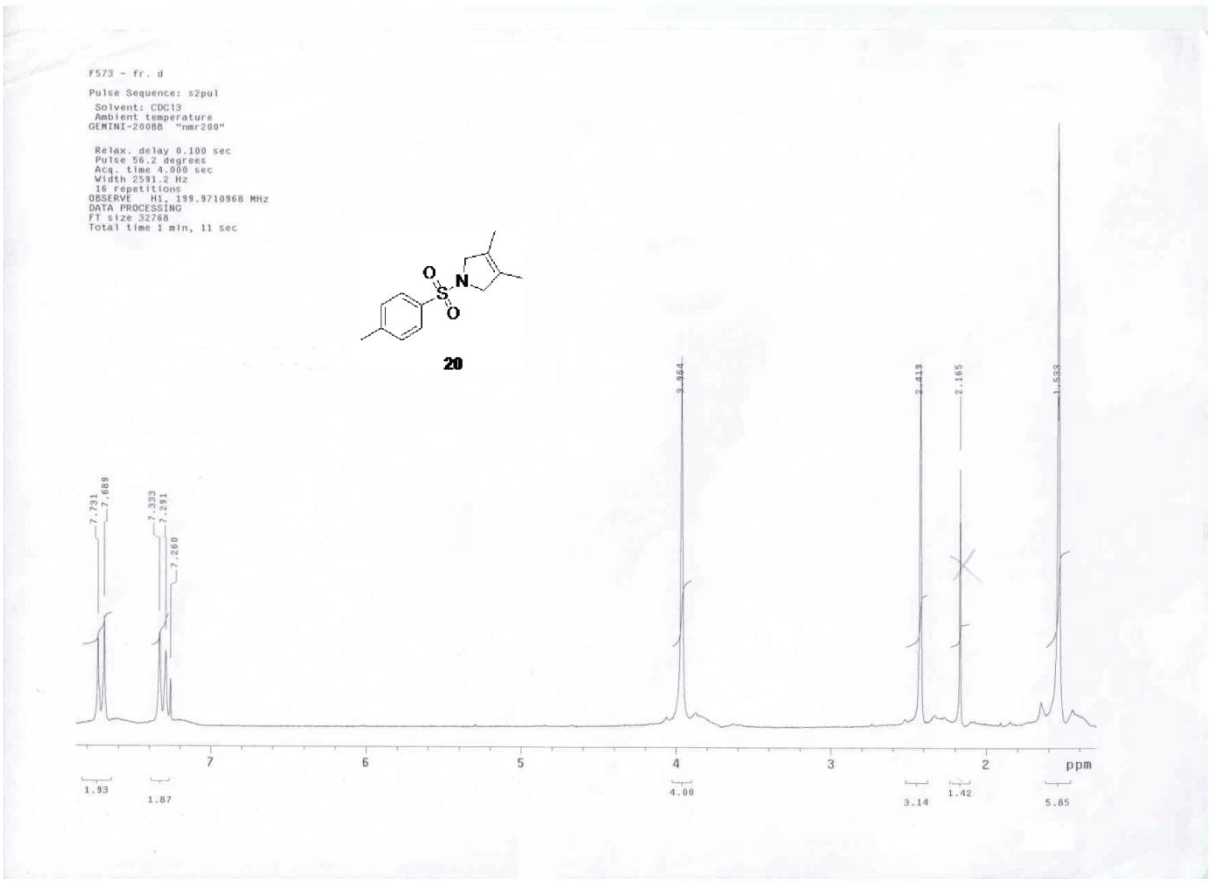

TW12_13C
TW12
OH
Ph
15
f1 (ppm)

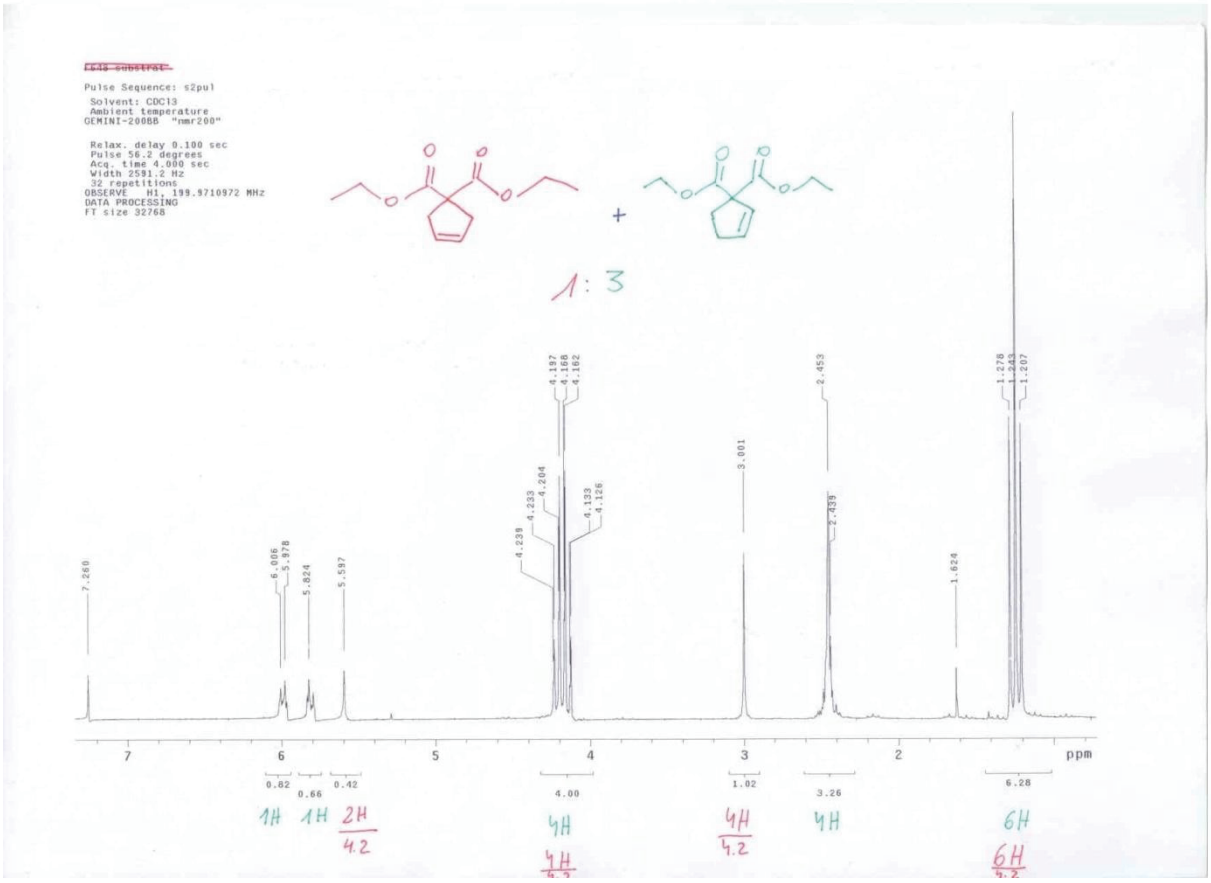

allilobenzenCM
CM-allilobenzen
Ph
OAc
18
f1 (ppm)

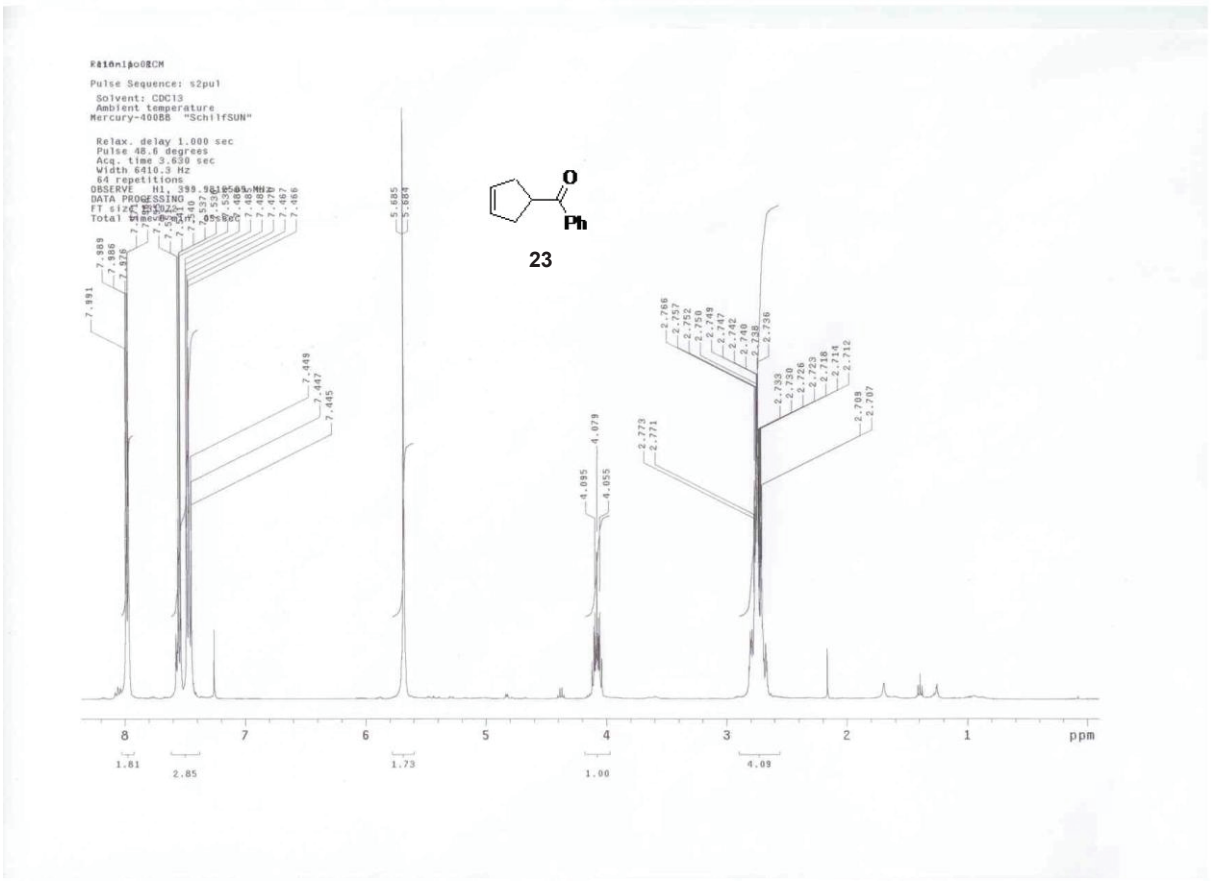

cm-allilbenzen
CMallilbenzen
Ph
OAc
18
f1 (ppm)

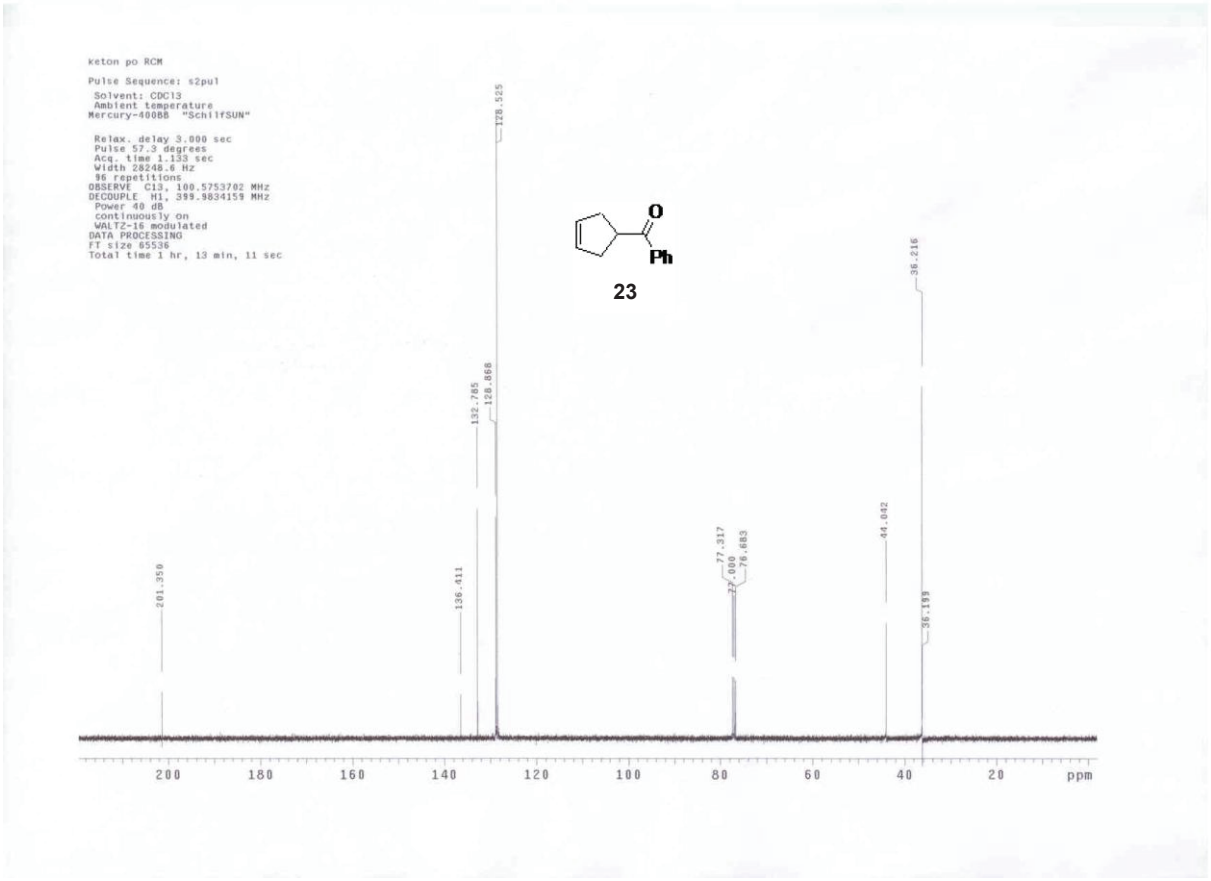

izomeryzacja
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
Mercury-400BB "SchilfSUN"
Relax. delay 1.000 sec
Pulse 72.0 degrees
Acq. time 3.630 sec
Width 6410.3 Hz
32 repetitions
OBSERVE H1, 400.0418330 MHz
DATA PROCESSING
FT size 131072
Total time 8 min, 82sec
CO2Et
CO2Et
11
8
7
6
5
4
3
2
1
0 ppm

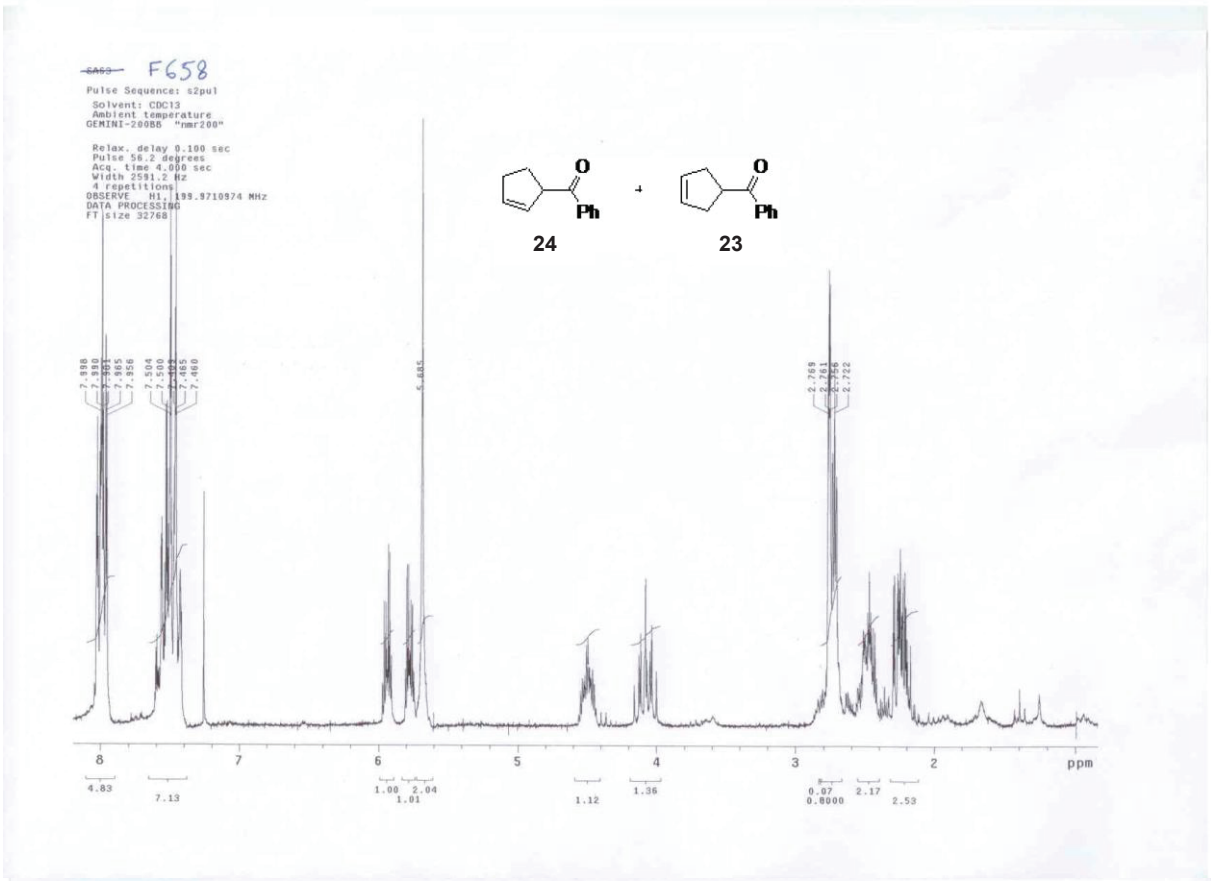

13C OBSERVE
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
Mercury-400BB "SchilfSUN"
Relax. delay 3.000 sec
Pulse 34.6 degrees
Acq. time 1.133 sec
Width 28248.6 Hz
160 repetitions
OBSERVE C13, 100.5906008 MHz
DECOUPLE H1, 400.0440508 MHz
Power 40 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
FT size 65536
Total time 1 hr, 13 min, 11 sec
CO2Et
CO2Et
11
180
160
140
120
100
80
60
40
20
ppm

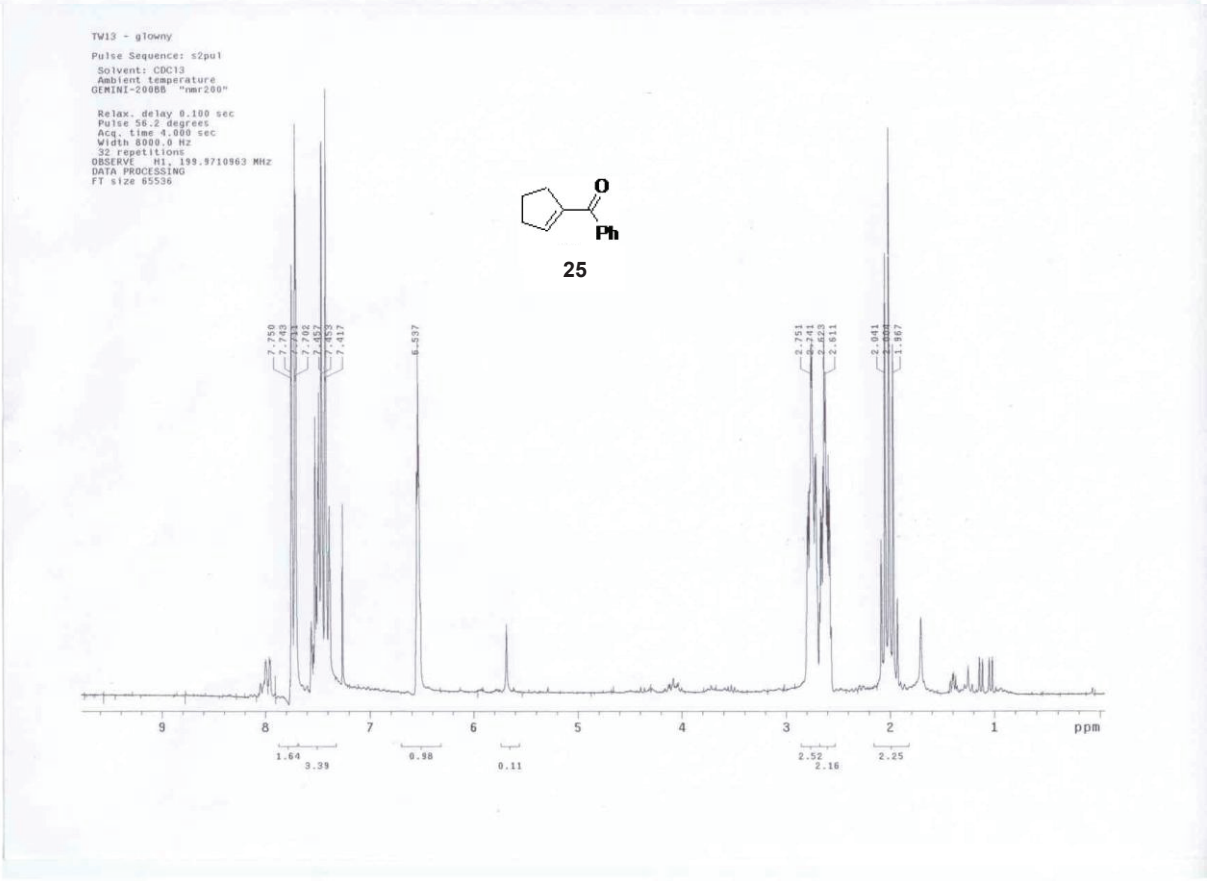

F573 - fr. d
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
GEMINI-2000B "nmr200"
Relax. delay 0.100 sec
Pulse 56.2 degrees
Acq. time 4.000 sec
Width 2591.2 Hz
16 repetitions
OBSERVE H1, 199.9710968 MHz
DATA PROCESSING
FT size 32768
Total time 1 min, 11 sec
20
7.731
7.689
7.393
7.391
7.260
3.864
2.419
2.165
1.533
ppm
1.93
1.87
4.00
3.14
1.42
5.85

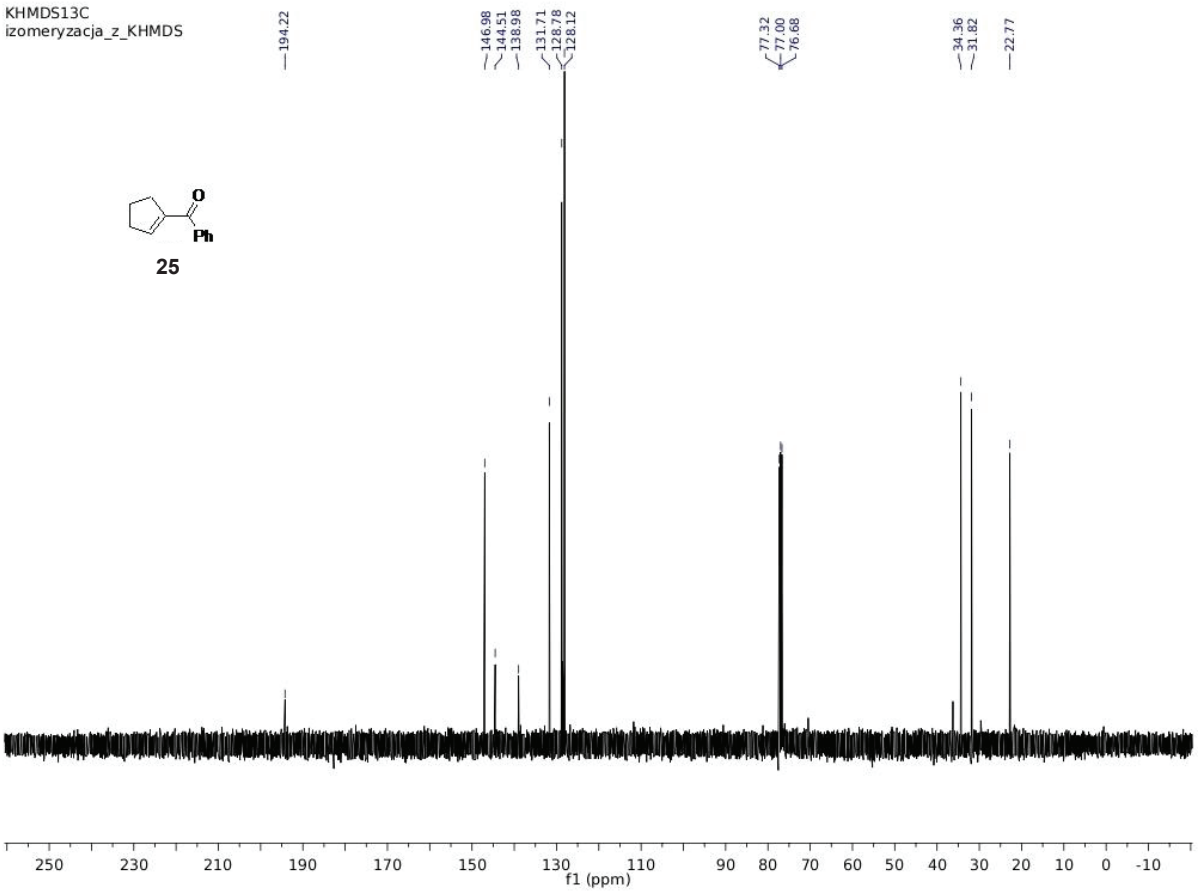

Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
GEMINI-2000B "nmr200"
Relax. delay 0.100 sec
Pulse 56.2 degrees
Acq. time 4.000 sec
Width 2591.2 Hz
32 repetitions
OBSERVE H1, 199.9710972 MHz
DATA PROCESSING
FT size 32768
+
1 : 3
7.260
6.006
5.978
5.824
5.597
4.239
4.233
4.204
4.197
4.168
4.162
4.133
4.126
3.001
2.453
2.439
1.624
1.278
1.243
1.207
ppm
0.82
0.66
0.42
4.00
1.02
3.26
6.28
1H 1H 2H/4.2
4H/4.2
4H
6H/6.2

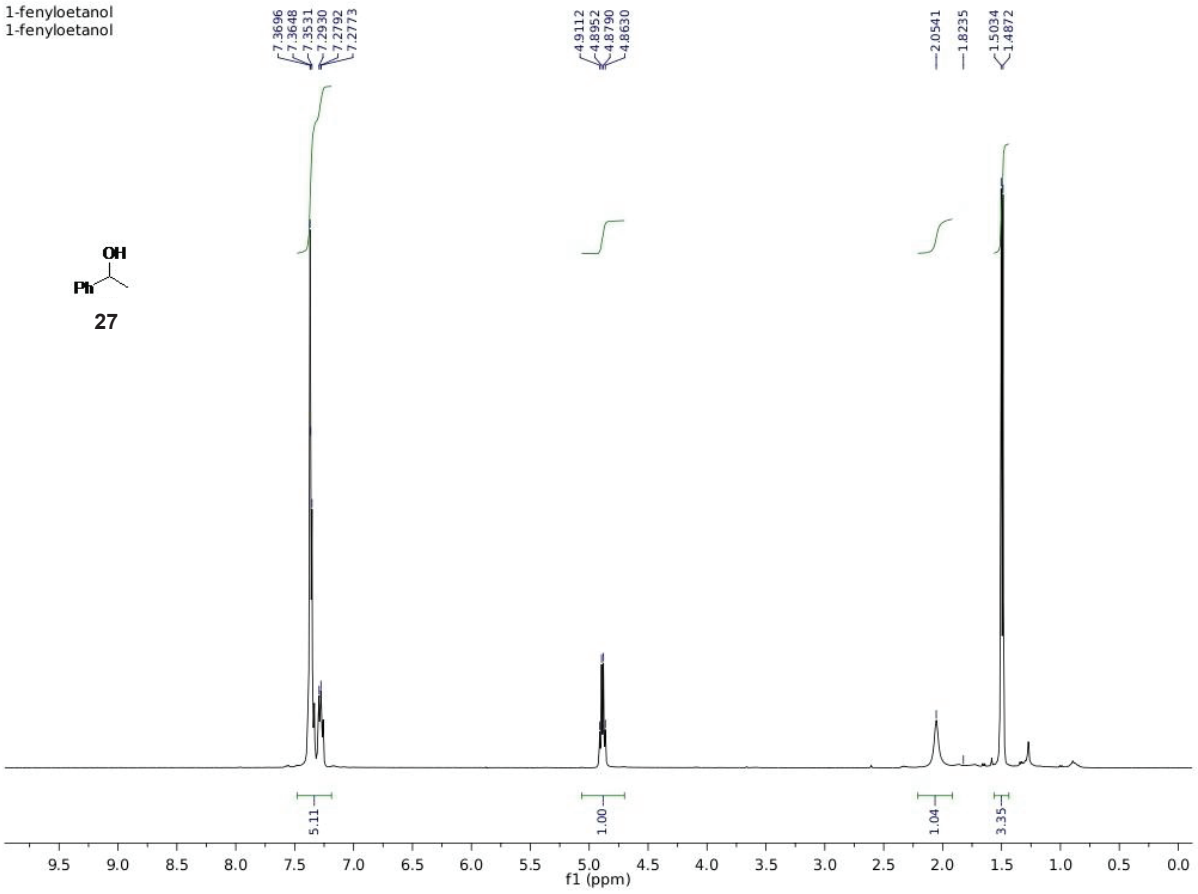

Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
Mercury-400BB "SchilfSUN"
Relax. delay 1.000 sec
Pulse 48.6 degrees
Acq. time 3.630 sec
Width 6410.3 Hz
64 repetitions
O
Ph
23
ppm

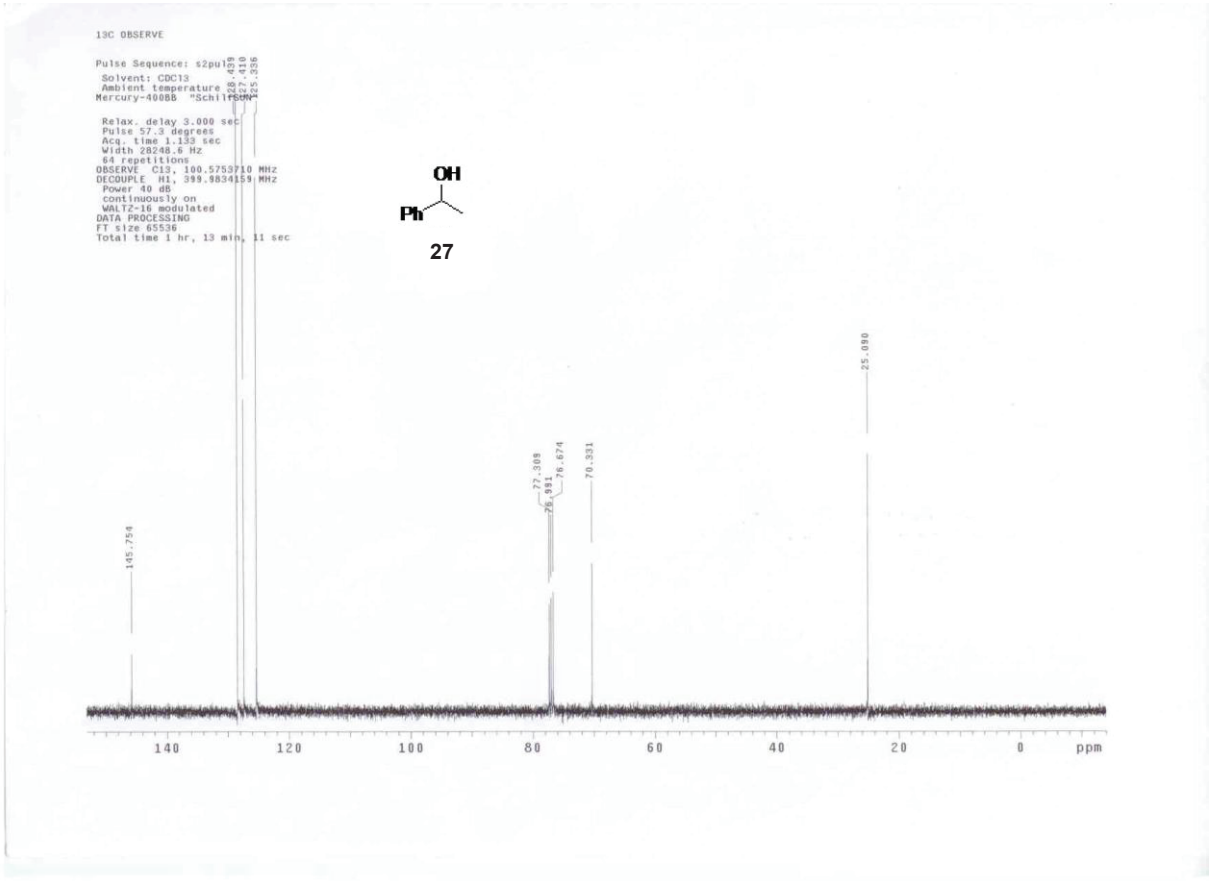

keton po RCM
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
Mercury-400BB "SchilfSUN"
Relax. delay 3.000 sec
Pulse 57.3 degrees
Acq. time 1.133 sec
Width 28248.6 Hz
96 repetitions
OBSERVE C13, 100.5753702 MHz
DECOUPLE H1, 399.9834159 MHz
Power 40 dB
continuously On
WALTZ-16 modulated
DATA PROCESSING
FT size 65536
Total time 1 hr, 13 min, 11 sec
O
Ph
23
ppm

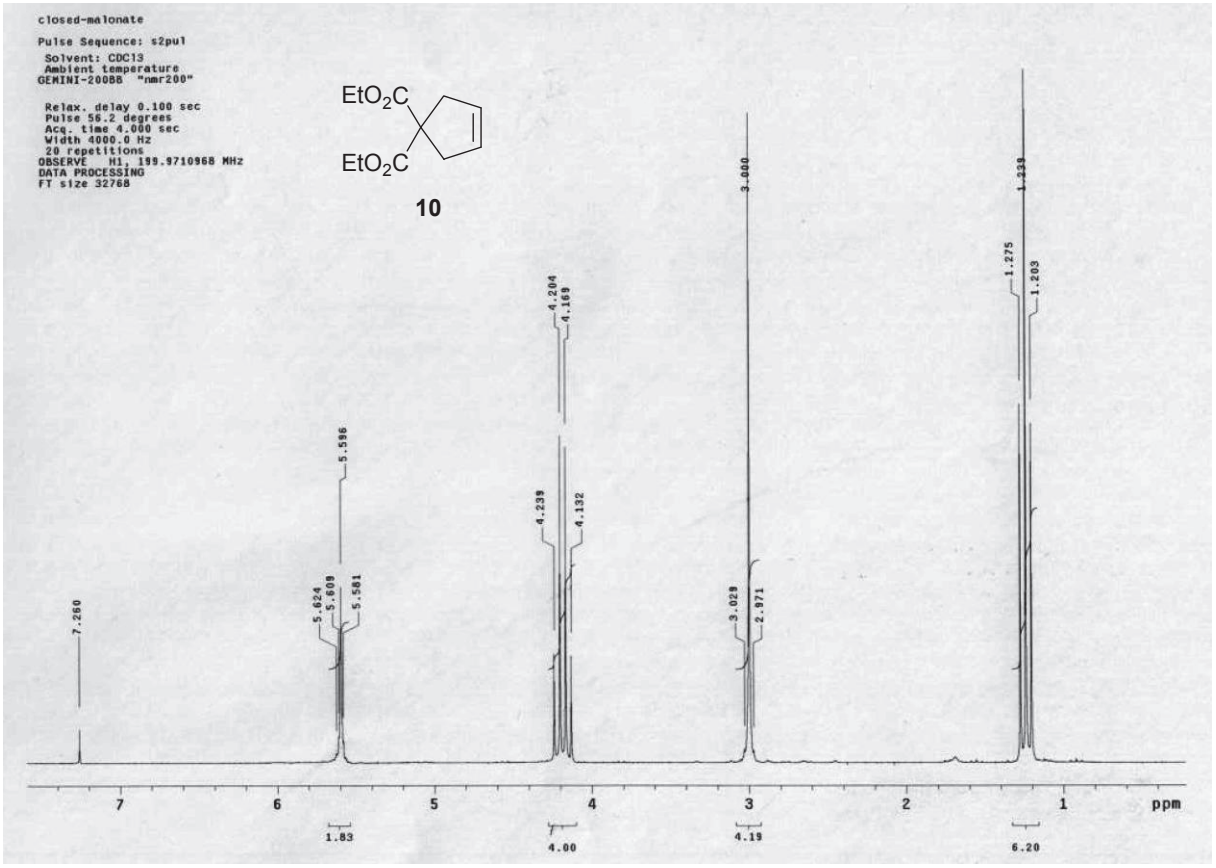

F658
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
GEMINI-200BB "nmr200"
Relax. delay 0.100 sec
Pulse 56.2 degrees
Acq. time 4.000 sec
Width 2591.2 Hz
4 repetitions
OBSERVE H1, 199.9710974 MHz
DATA PROCESSING
FT size 32768
24
23
ppm

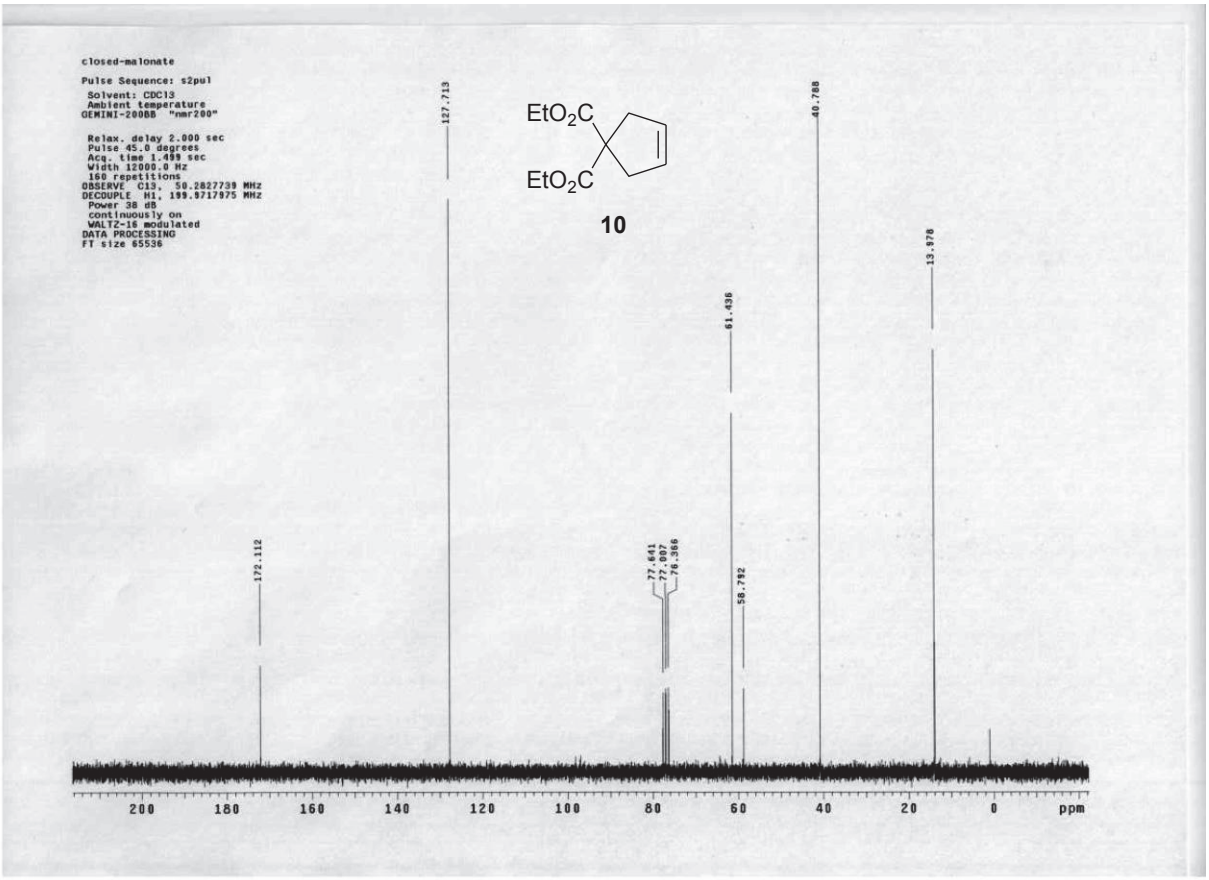

TV13 - glowny
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
GEMINI-200BB "nmr200"
Relax. delay 0.100 sec
Pulse 56.2 degrees
Acq. time 4.000 sec
Width 8000.0 Hz
32 repetitions
OBSERVE H1, 199.9710963 MHz
DATA PROCESSING
FT size 65536
25
ppm


KHMDS13C
izomeryzacja_z_KHMDS
194.22
146.98
144.51
138.98
131.71
128.78
128.12
77.32
77.00
76.68
34.36
31.82
22.77
O
Ph
25
f1 (ppm)


1-fenyloetanol
1-fenyloetanol
7.3696
7.3648
7.3531
7.2930
7.2792
7.2773
4.9112
4.8952
4.8790
4.8630
2.0541
1.8235
1.5034
1.4872
OH
Ph
27
5.11
1.00
1.04
3.35
f1 (ppm)


13C OBSERVE
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
Mercury-400BB "Schilfsun"
Relax. delay 3.000 sec
Pulse 57.3 degrees
Acq. time 1.133 sec
Width 28248.6 Hz
64 repetitions
OBSERVE C13, 100.5753710 MHz
DECOUPLE H1, 399.9834159 MHz
Power 40 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
FT size 65536
Total time 1 hr, 13 min, 11 sec
OH
Ph
27
145.754
77.309
76.981
76.674
70.331
25.080
140
120
100
80
60
40
20
0
ppm


closed-malonate
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
GEMINI-200BB "nmr200"
Relax. delay 0.100 sec
Pulse 56.2 degrees
Acq. time 4.000 sec
Width 4000.0 Hz
20 repetitions
OBSERVE H1, 199.9710968 MHz
DATA PROCESSING
FT size 32768
EtO2C
EtO2C
10
7.260
5.624
5.609
5.581
5.596
4.239
4.204
4.169
4.132
3.028
2.971
3.000
1.275
1.203
1.339
7
6
5
4
3
2
1
ppm
1.83
4.00
4.19
6.20



[i] F. G. Bordwell, J. A. Hautala, *J. Org. Chem.*, **1978**, *43*, 3116–3123

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

[iii] SAINT V7.34A Bruker Nonius 2007

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

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

[vi] Sheldrick, G. M. Acta Crystallogr. **2008**, A64, 112.

[vii] Spek, A.L. Acta Cryst. D65**, 2009**, 148-155.

[viii] Sluis, P. V. D.; Spek, A. L. Acta Crystallogr. **1990**, A46, 194.

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