Supporting Information to

[Ru(triphos)(CH$_3$CN)$_3$](OTf)$_2$ as a homogeneous catalyst for the hydrogenation of biomass derived 2,5-hexanedione and 2,5-dimethylfuran in aqueous acidic medium.

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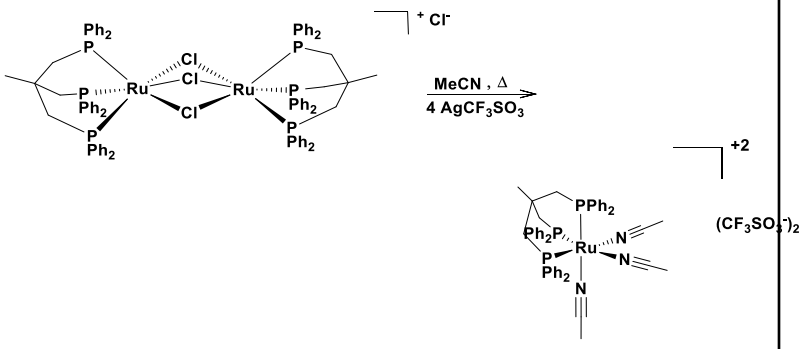
Contents:

Compound Name: $[Ru(MeCN)_3(triphos)](CF_3SO_3)_2$ (**1**)

MW: 1147.11 $gmol^{-1}$

Synthesis and Structure:



Appearance:

White powder

Lit. and/or notebook # and page: Rhodes, L. F.; Sorato, C.; Venanzi, L. M.; Bachechi, F. Inorganic Chemistry 1988, 27, 604.

First made on date: June 8, 2015
El-IV-59

Made by:
Elnaz Latifi

^{1}H NMR (400 MHz, CD_3CN): δ = 7.32 (m, 18H) , 7.21 (m, 12H), 2.56 (br, 6H), 2.19 (s, 9H), 1.70 (br, 3H).

^{31}P{^{1}H} NMR(161.923 MHz, CD_3CN): δ =28.56 (s).

^{13}C NMR (100.580 MHz, CD_3CN): δ =132.8 (C), 132.7 (CH), 131.4 (CH), 129.5 (CH), 120.6 (C), 38.7 (C), 36.8 (CH_3), 31.8 (CH_2), 1.8 (CH_3).

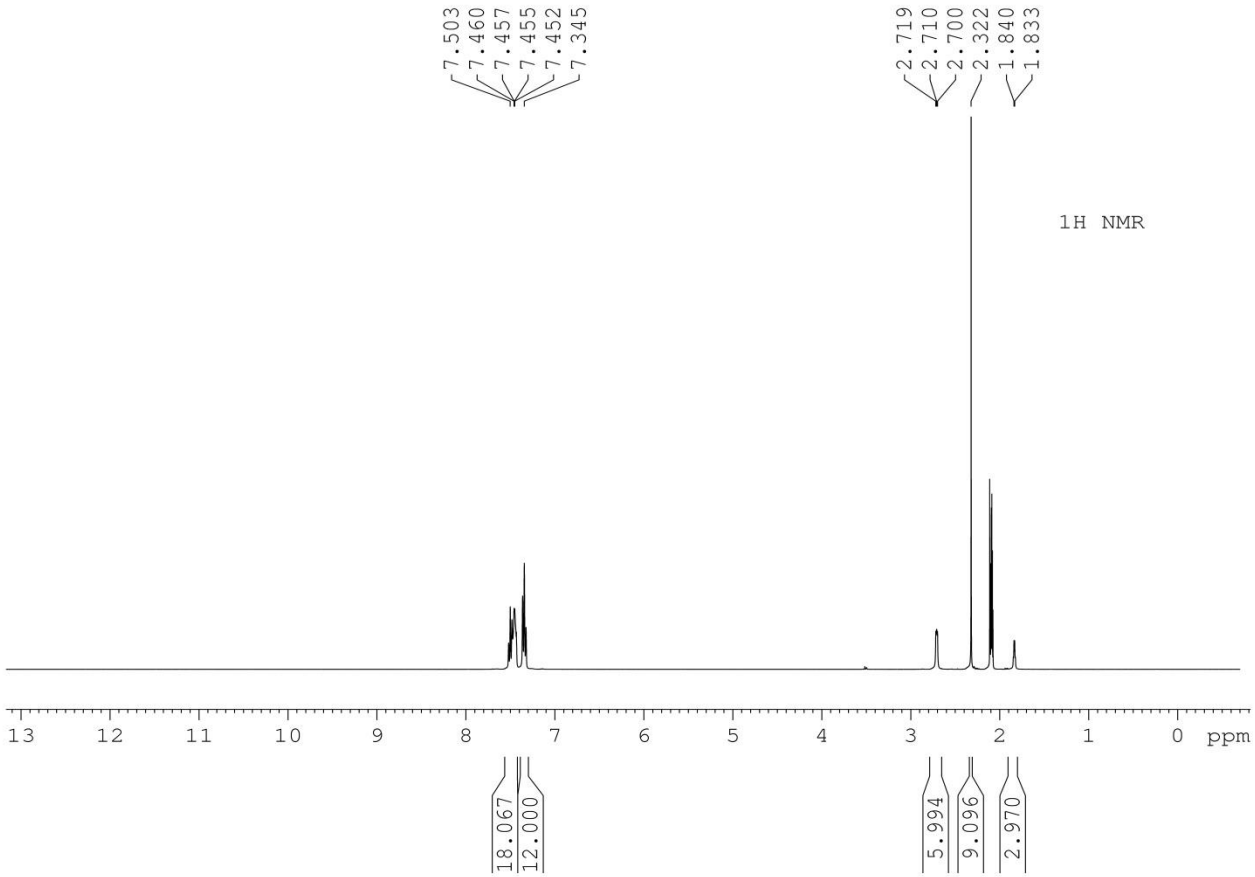


Figure S1: ^{1}H-NMR of [Ru(MeCN)$_3$(triphos)](CF$_3$SO$_3$)$_2$ (**1**) in CD$_3$CN

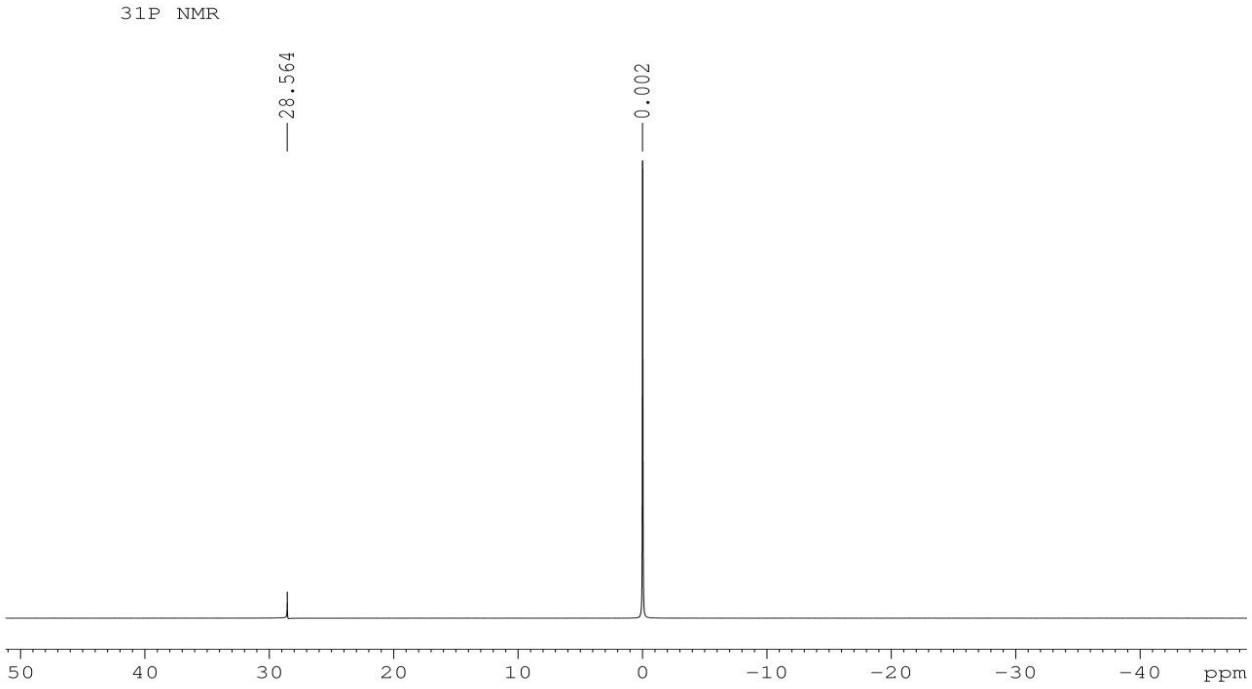


Figure S2: ^{31}P-NMR of [Ru(MeCN)$_3$(triphos)] (CF_3SO_3)$_2$ (**1**) in CD_3CN with phosphoric acid as an internal standard.

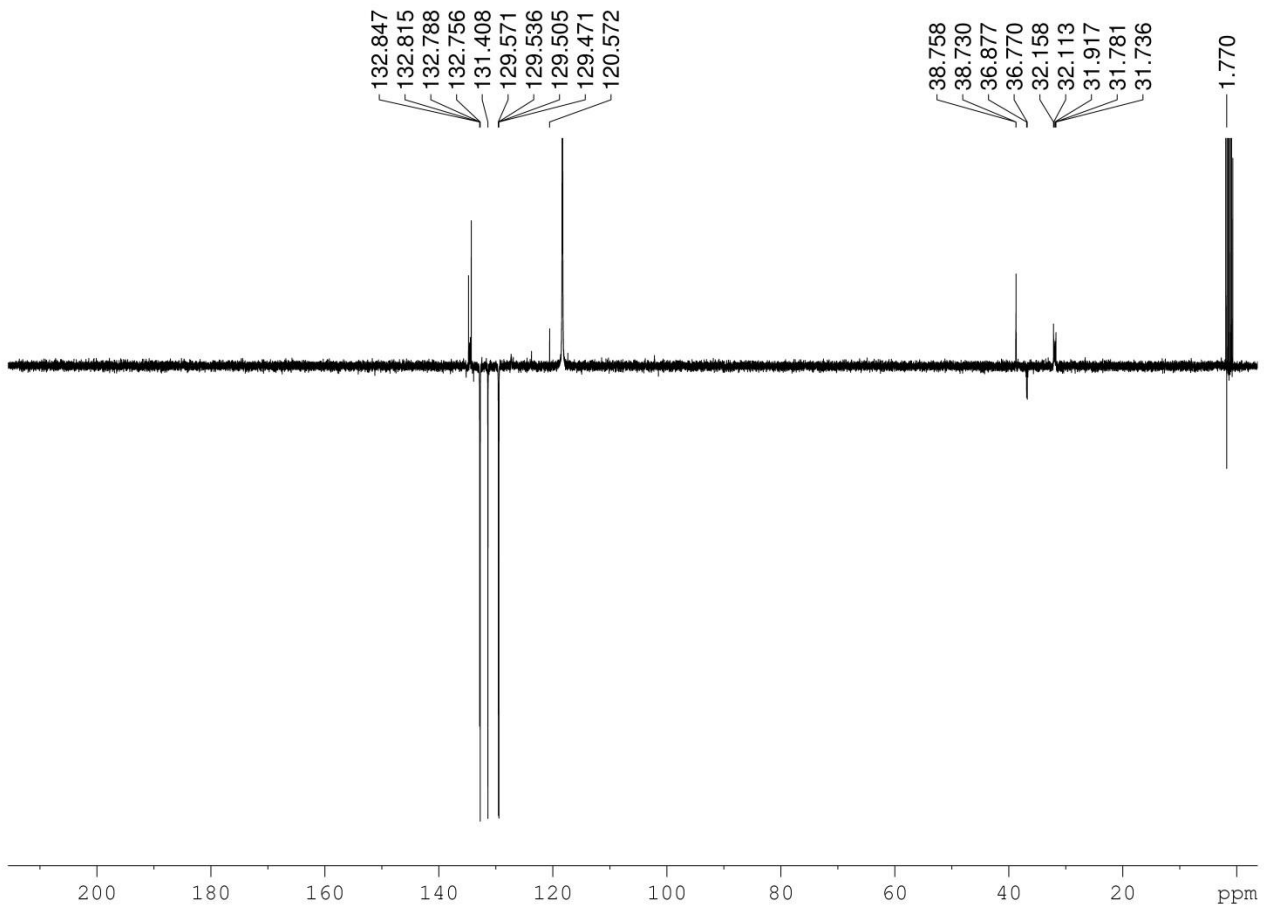
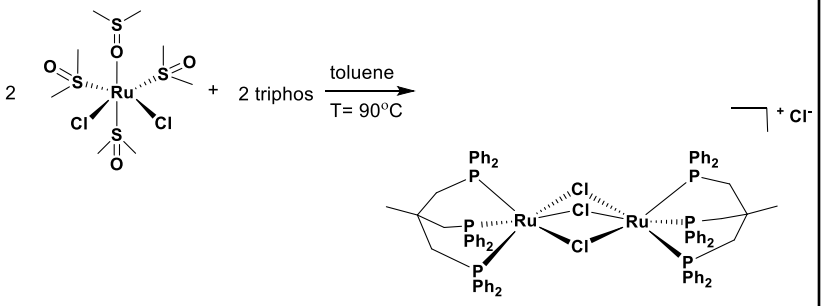


Figure S3: ^{13}C-NMR of [Ru(MeCN)$_3$(triphos)](CF$_3$SO$_3$)$_2$ (**1**) in CD$_3$CN

Compound Name: $[Ru_2(\mu\text{-}Cl)_3(triphos)_2]Cl$

MW: 1607.1 $gmol^{-1}$

Synthesis and Structure:



Appearance:

Pale yellow powder

Lit. and/or notebook # and page: Rhodes, L. F.; Sorato, C.; Venanzi, L. M.; Bachechi, F. Inorganic Chemistry 1988, 27, 604.

First made on date: June 4, 2015

Made by:
Elnaz Latifi

^{1}H NMR (400 MHz, CD_2Cl_2): δ = 7.4 (br t, 24H) , 7.2 (t, 12H), 6.8 (t, 24H), 2.43 (br s, 12H), 1.6 (br q, 6H).

^{31}P{^{1}H} NMR(161.923 MHz, CD_2Cl_2): δ =36.25 (s).

^{13}C NMR (100.580 MHz, CD_2Cl_2): δ =149.4 (C), 146.0 (CH), 142.0 (CH), 140.0 (CH), 51.3 (C), 50.2 (CH_3), 47.9 (CH_2).

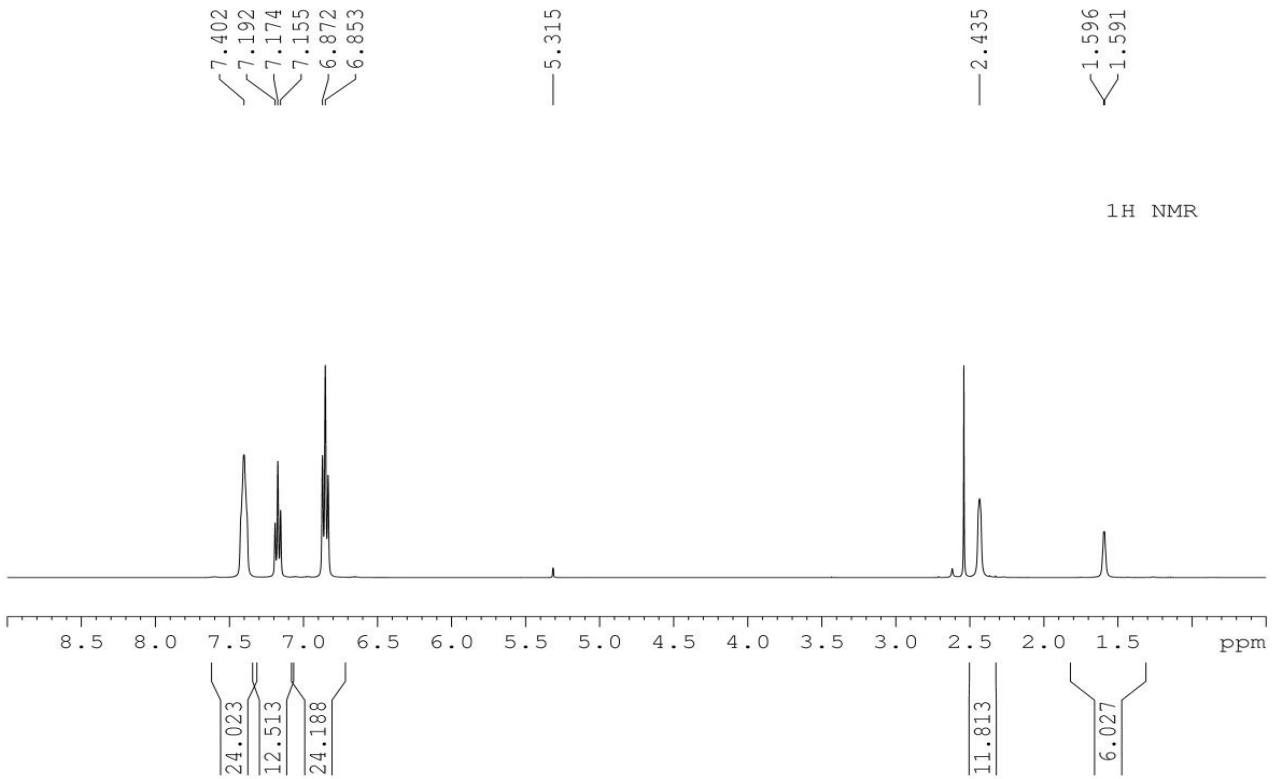


Figure S4: ^{1}H-NMR of $[Ru_2(\mu\text{-}Cl)_3(triphos)_2]Cl$ in CD_2Cl_2

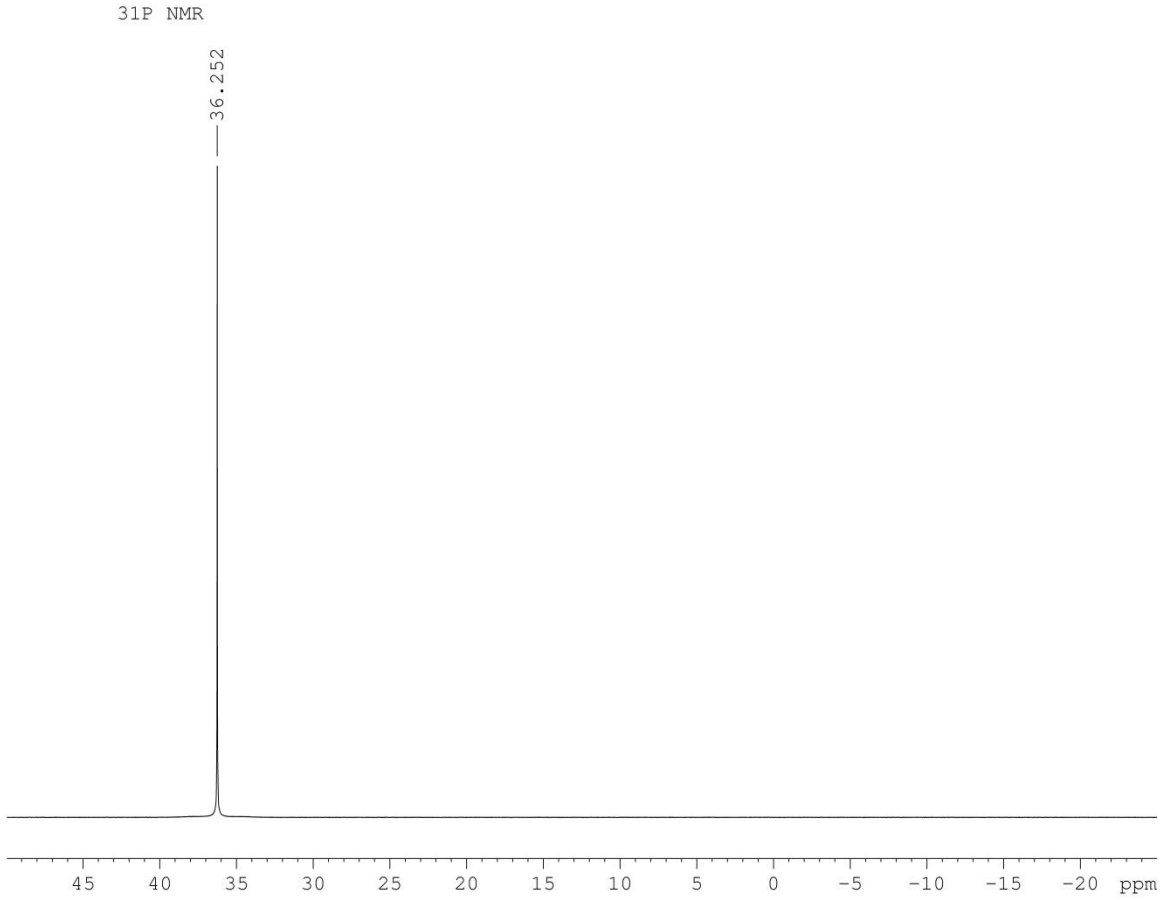


Figure S5: ^{31}P-NMR of $[Ru_2(\mu\text{-}Cl)_3(triphos)_2]Cl$ in CD_2Cl_2

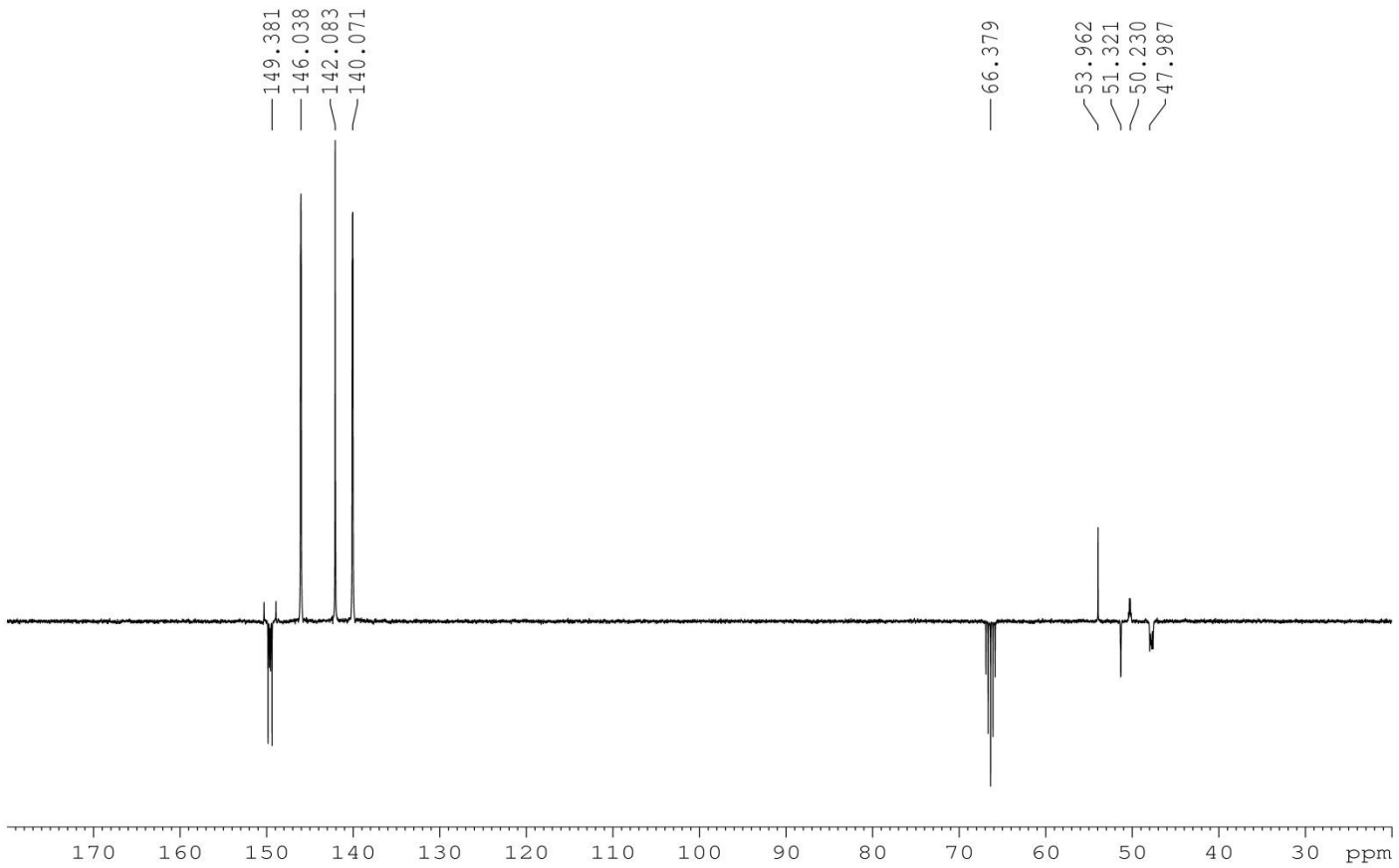
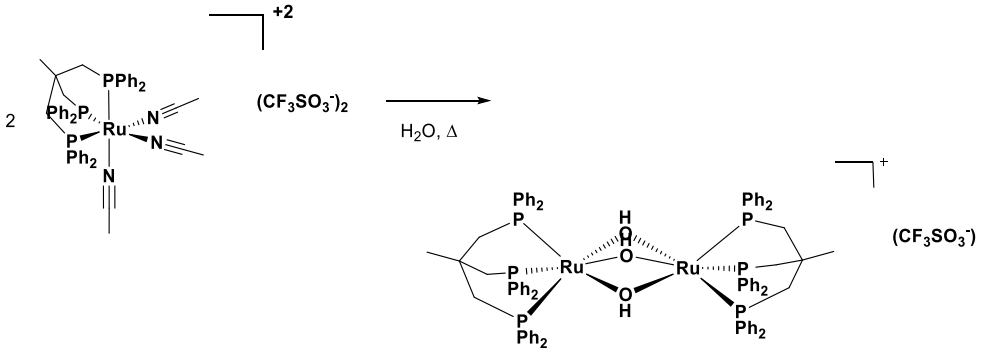


Figure S6: ^{13}C-NMR of $[Ru_2(\mu\text{-}Cl)_3(triphos)_2]Cl$ in CD_2Cl_2

Compound Name: $[Ru_2(\mu\text{-}OH)_3(triphos)_2](CF_3SO_3)$ (**2**)

MW: 1667.25 $gmol^{-1}$

Synthesis and Structure:



Appearance:

Orange powder
El-V-61

First made on date:
16th June 2016

El-IV-61

Made by:
Elnaz Latifi

^{1}H NMR (400 MHz, CD_3OD): δ = 7.44 (br t, 24H) , 7.19 (t, 12H), 6.82 (t, 24H), 2.47 (br s, 12H), 1.62 (br q, 6H).

^{31}P{^{1}H} NMR(161.923 MHz, CD_3OD): δ = 41.5 (s).

^{13}C NMR (100.580 MHz, CD_3OD): δ =140 (C), 134.9 (CH), 130.7 (CH), 129.7 (CH), 40 (C), 38.6 (CH_3), 36.0 (CH_2).

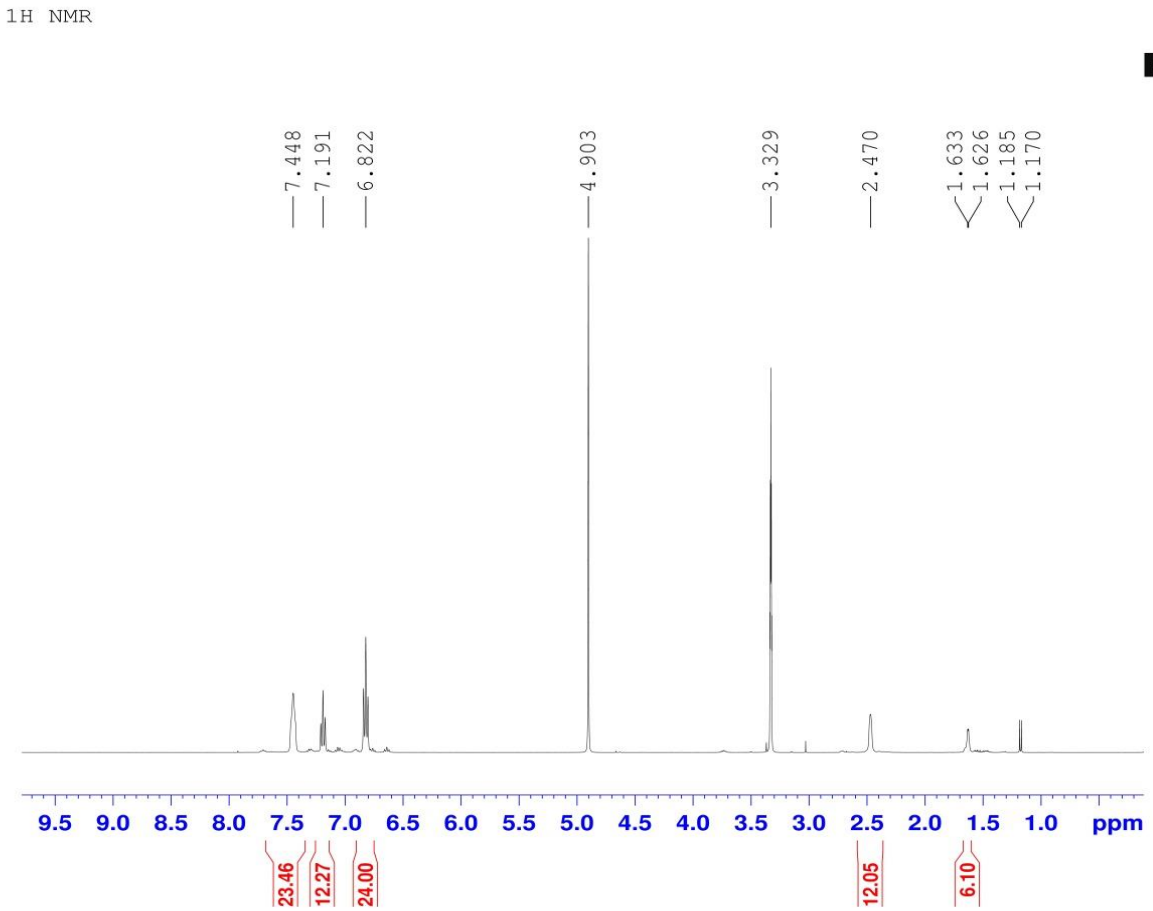


Figure S7: ^{1}H-NMR of $[Ru_2(\mu\text{-}OH)_3(triphos)_2](CF_3SO_3)$ (**2**) in CD_3OD

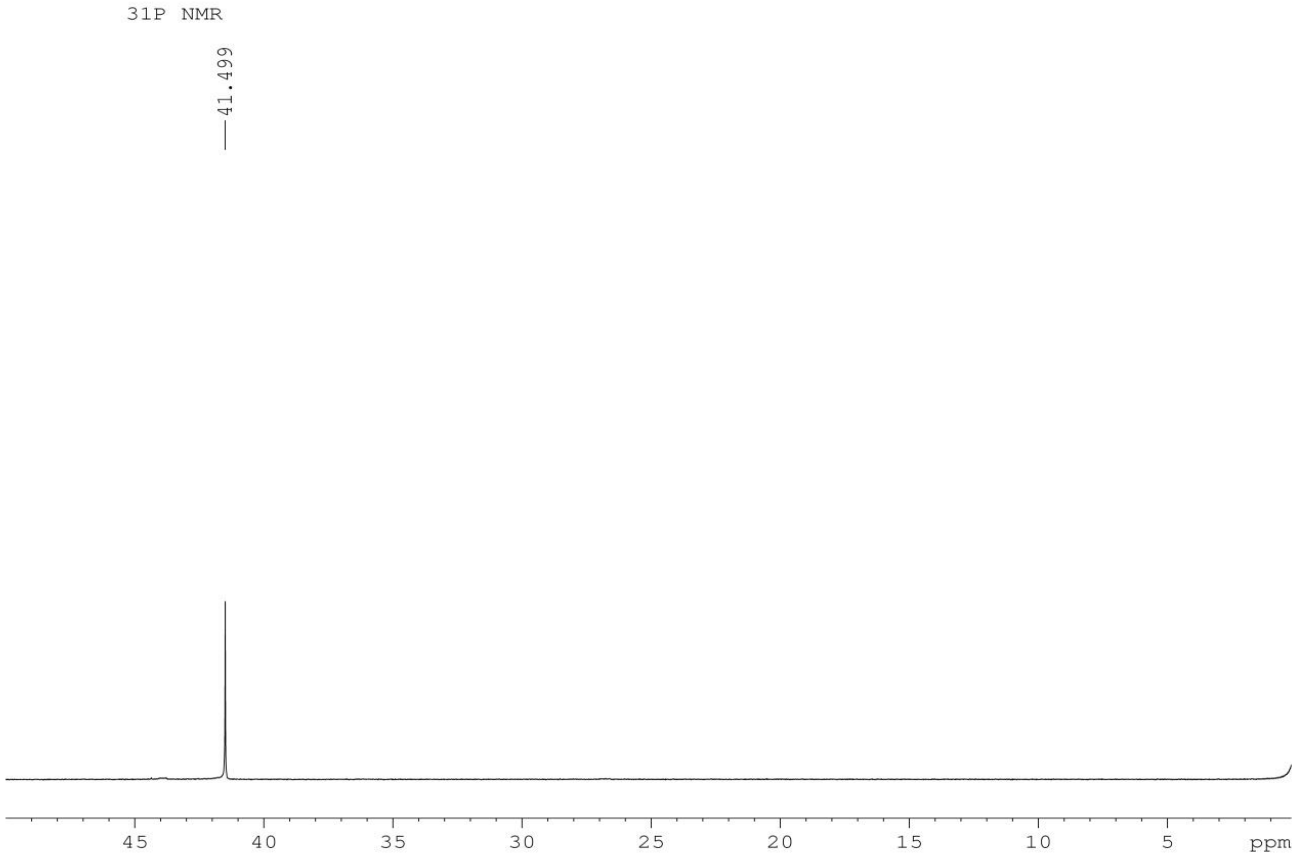


Figure S8: ^{31}P-NMR of $[Ru_2(\mu\text{-}OH)_3(triphos)_2](CF_3SO_3)$ (**2**) in CD_3OD

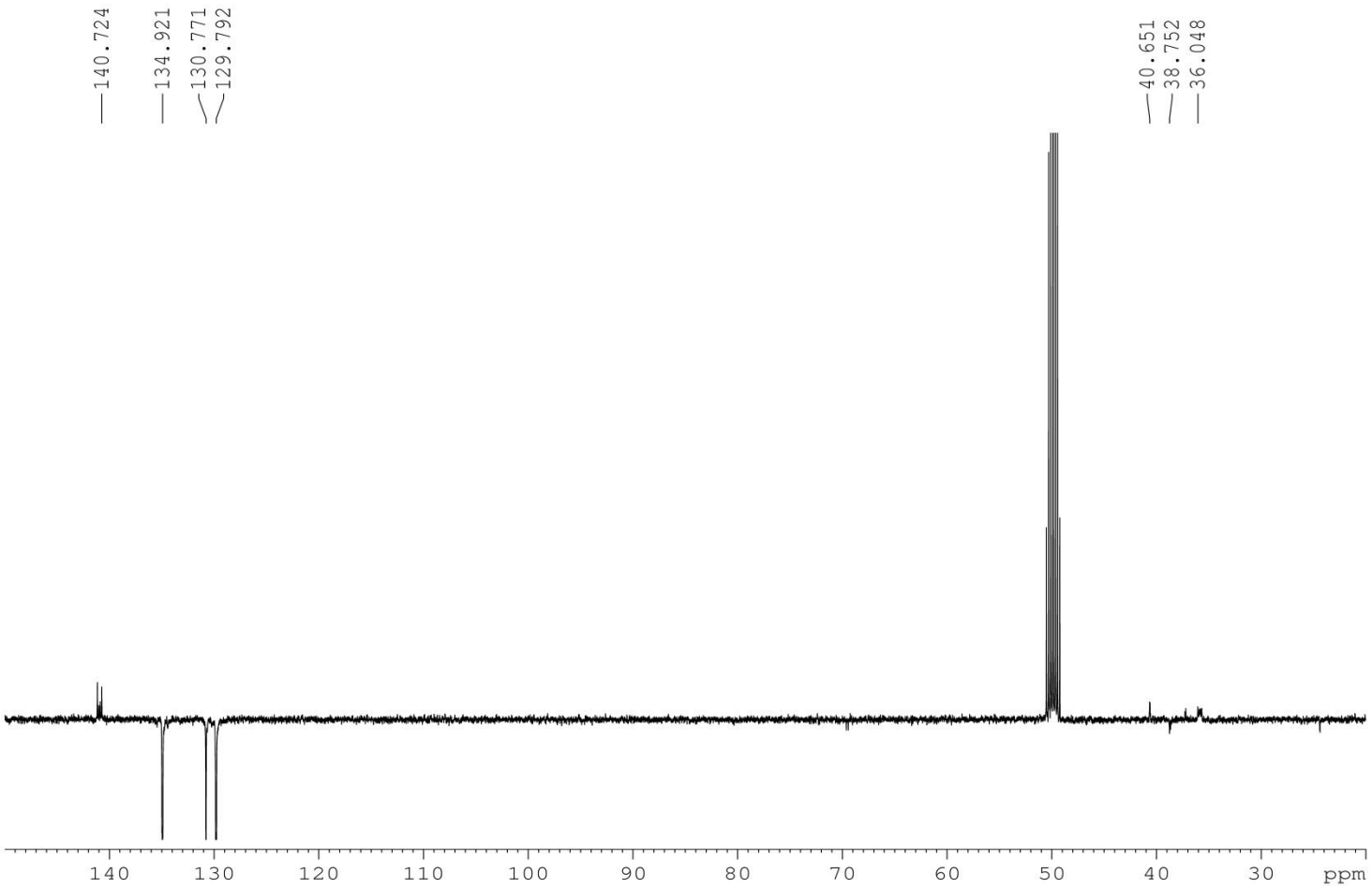


Figure S9: ^{13}C-NMR of $[Ru_2(\mu\text{-}OH)_3(triphos)_2](CF_3SO_3)$ (**2**) in CD_3OD

High-Res ESI-MS of dimer **2** (MeOH solution, +-ve ionization mode) only yields MS spectra of the Ru(triphos) fragment in association with H_2O/H_3O^+ or OTf^-:

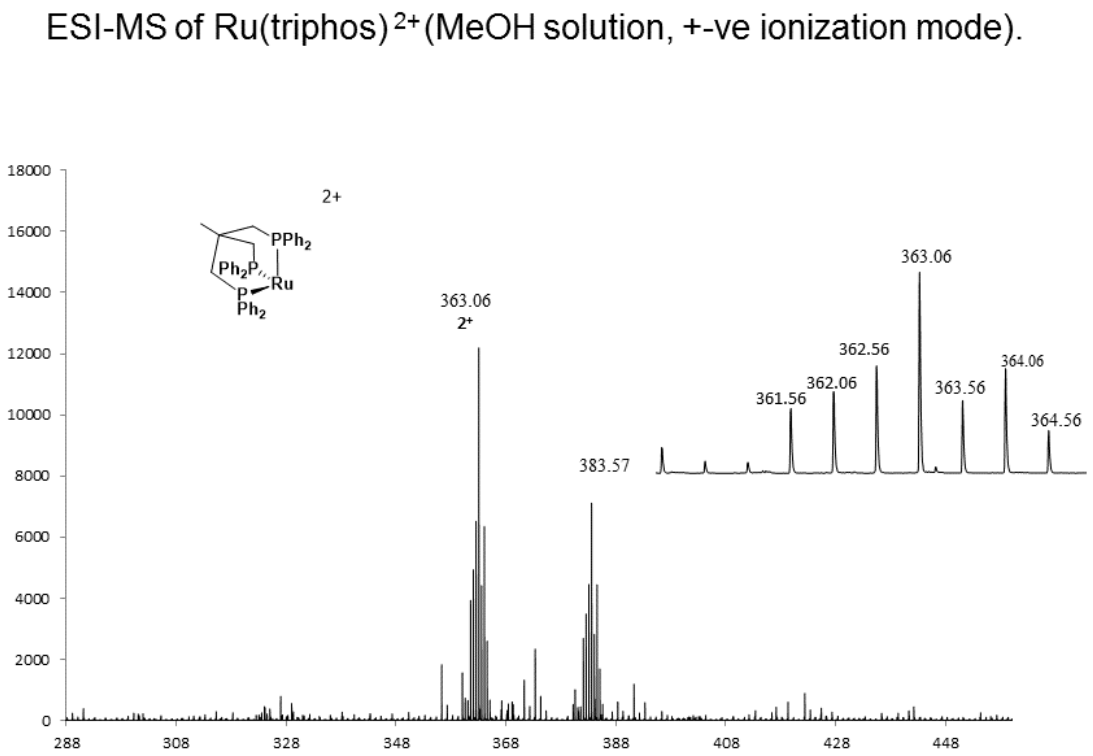


Figure S10: ESI-MS of **2**

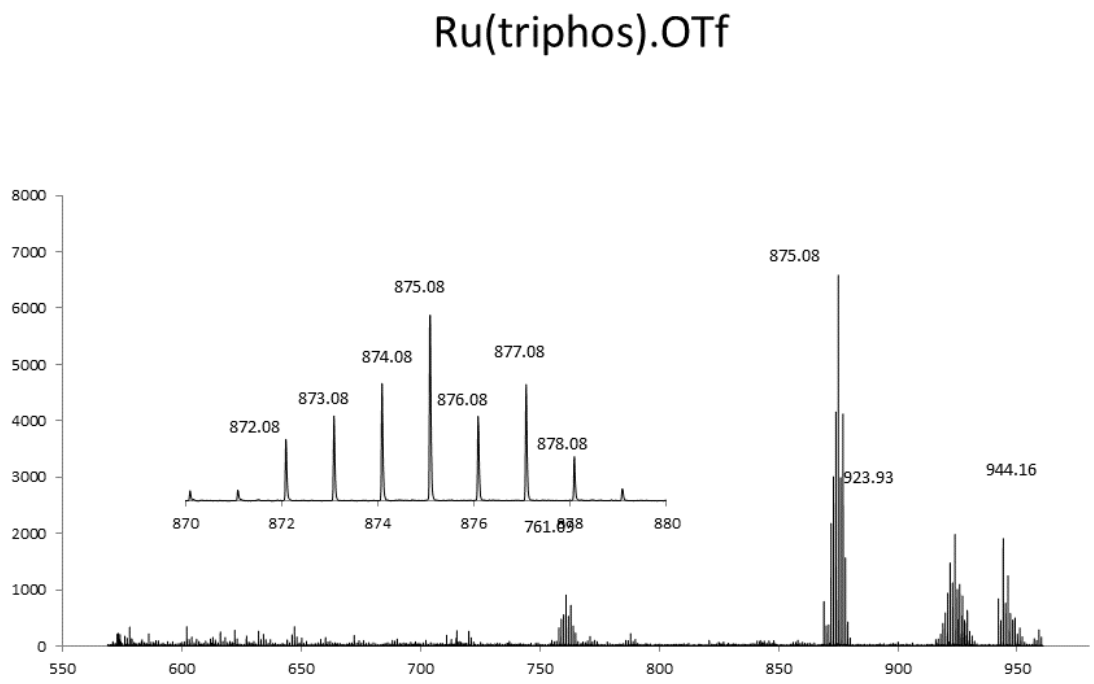


Figure S11: ESI-MS of **2**.

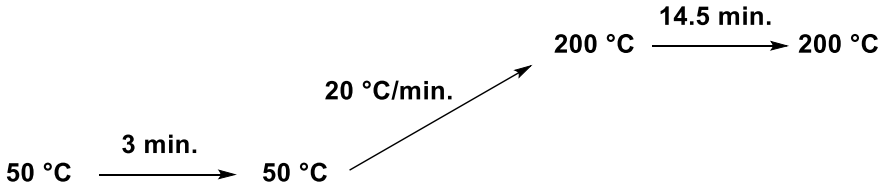
GC method for all analyses:

30 m × 0.25 mm Stabilwax-da (acid-deactivated polyethylene glycol)

Constant Flow Rate: 1 mL/min.

Injector: 200 °C FID Detector: 250 °C

Oven temperature program:



Note: Observed retention times given below may differ depending on column age and history !!!

Sample GC trace and retention times for 2,5-hexanedione reactions

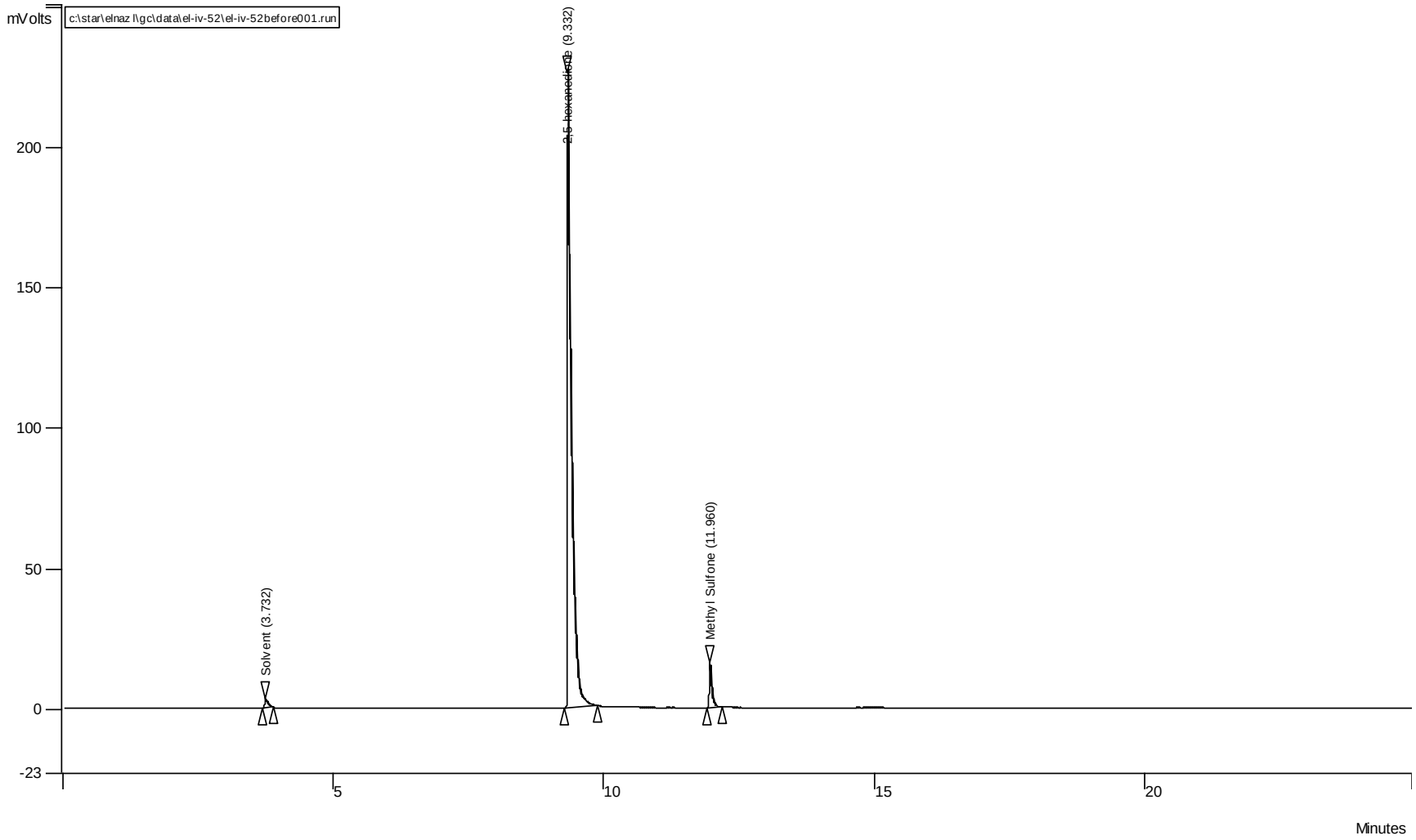


Figure S12: Reaction mixture of 2,5-hexanedione before run.

```
Title       :
Run File    : c:\star\elnaz l\gc\data\el-iv-52\el-iv-52before001.run
Method File : c:\star\elnaz l\methods\2,5-hexanedione polar elnaz june 26 2015.mth
Sample ID   : El-IV-52before
Injection Date: 6/30/15 12:56 PM    Calculation Date: 7/1/15 9:19 AM
Operator    : Schlaf Group          Detector Type: 3800 (1 Volt)
Workstation:                        Bus Address  : 45
Instrument : 3800_DualFID           Sample Rate  : 10.00 Hz
Channel    : Middle = FID           Run Time     : 24.977 min
** Star Chromatography Workstation Version 6.00 ** 00479-7088-C69-21B5 **
Run Mode        : Analysis
Peak Measurement: Peak Area
Calculation Type: Internal Standard
```

Peak No.	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)	Rel. Ret. Time	Sep. Code	Width 1/2 (sec)	Status Codes
1	Solvent	no result	3.732	-0.006	13655	0.312	BB	3.9	C*
2	2,5-hexanedione	1009.1528	9.332	-0.002	1153878	0.780	BB	4.1	
3	Methyl Sulfo	INT STD	11.960	0.005	52573	1.000	BB	2.7	SR
	Totals:	1009.1528		-0.003	1220106				

```
Status Codes:
R - Reference peak
* - No result could be calculated; check calibration curve
C - Out of calibration range
S - Internal Standard peak
Total Unidentified Counts :          0 counts
Detected Peaks: 3           Rejected Peaks: 0      Identified Peaks: 3
Standard Peak Amount:
Methyl Sulfone    Amount = 100
Multiplier: 1          Divisor: 1          Unidentified Peak Factor: 0
Baseline Offset: 89 microVolts          LSB:     1 microVolts
Noise (used): 30 microVolts - monitored before this run
Vial: 40       Injection Number: 1     Volume: 1.0  uL     Position: 2
********************************************************************************
```

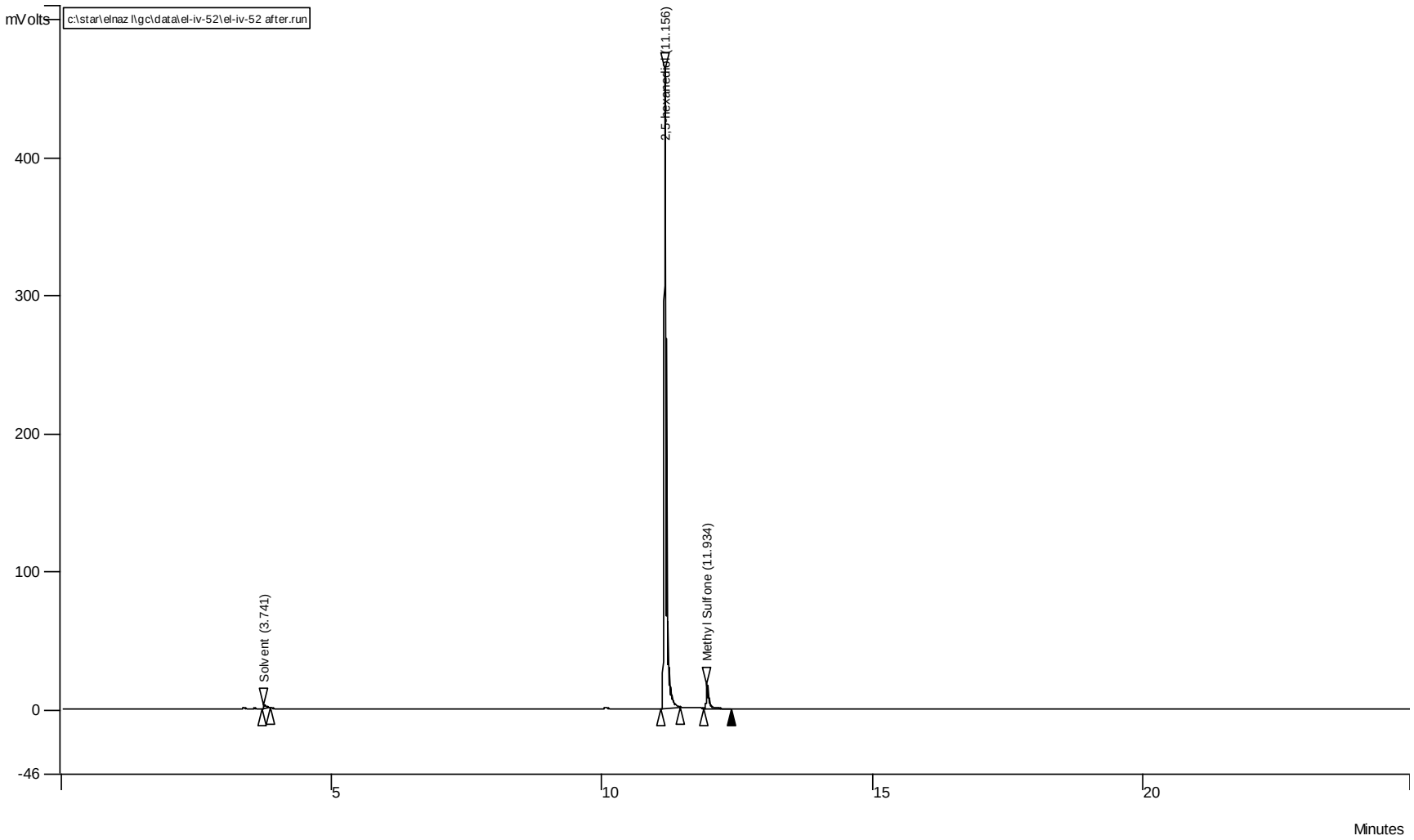


Figure S13: Reaction mixture of 2,5-hexanedione after run.

```
Title       :
Run File    : c:\star\elnaz l\gc\data\el-iv-52\el-iv-52 after.run
Method File : c:\star\elnaz l\methods\2,5-hexanedione polar elnaz june 26 2015.mth
Sample ID   : El-IV-52 after
Injection Date: 6/30/15 1:25 PM    Calculation Date: 7/1/15 9:20 AM
Operator    : Schlaf Group          Detector Type: 3800 (1 Volt)
Workstation:                        Bus Address  : 45
Instrument : 3800_DualFID           Sample Rate  : 10.00 Hz
Channel    : Middle = FID           Run Time     : 24.975 min
** Star Chromatography Workstation Version 6.00 ** 00479-7088-C69-21B5 **
Run Mode        : Analysis
Peak Measurement: Peak Area
Calculation Type: Internal Standard
```

Peak No.	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)	Rel. Ret. Time	Sep. Code	Width 1/2 (sec)	Status Codes
1	Solvent	no result	3.741	0.010	9309	0.313	BB	0.0	C*
2	2,5-hexanediol	1021.3284	11.156	0.017	1222625	0.935	BB	2.1	
3	Methyl Sulfo	INT STD	11.934	-0.021	55041	1.000	BB	2.5	USR
	Totals:	1021.3284		0.006	1286975				

```
Vial: 41       Injection Number: 1     Volume: 1.0  uL     Position: 2
********************************************************************************
```

Sample GC trace and retention times for 2,5-dimethylfuran reactions

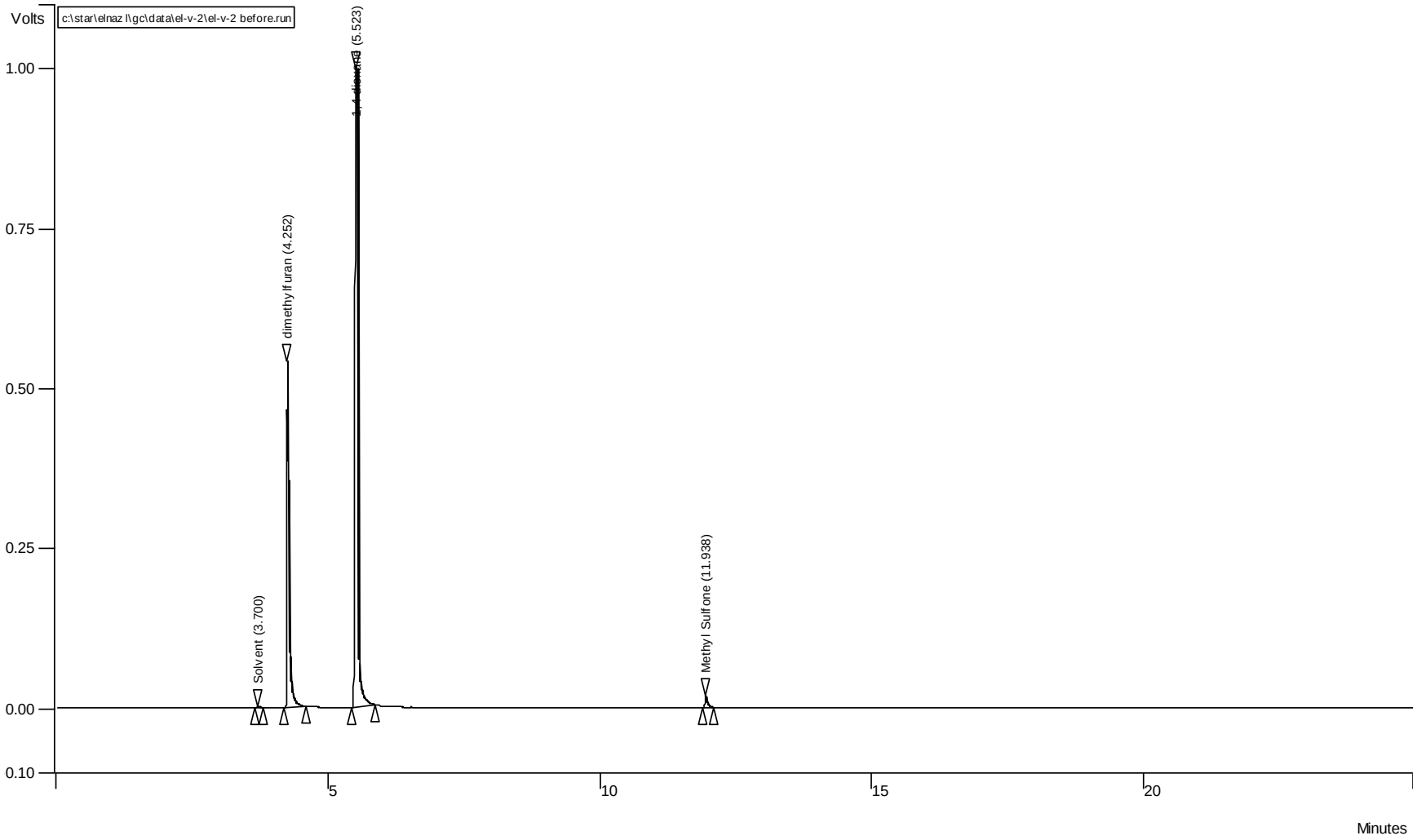


Figure S14: Reaction mixture of 2,5-dimethylfuran before run.

Title :

Run File : c:\star\elnaz l\gc\data\el-v-2\el-v-2 before.run
Method File : c:\windows\temp\~2,5-dimethylfuran polar elnaz sept 24 2015.tmp
Sample ID : El-V-2 before
Injection Date: 9/24/15 3:58 PM Calculation Date: 9/24/15 5:02 PM
Operator : Schlaf Group Detector Type: 3800 (1 Volt)
Workstation: Bus Address : 45
Instrument : 3800_DualFID Sample Rate : 10.00 Hz
Channel : Middle = FID Run Time : 24.975 min
** Star Chromatography Workstation Version 6.00 ** 00479-7088-C69-21B5 **
Run Mode : Analysis
Peak Measurement: Peak Area
Calculation Type: Internal Standard

Peak No.	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)	Rel. Ret. Time	Sep. Code	Width 1/2 (sec)	Status Codes
1	Solvent	no result	3.700	0.008	7209	0.310	BB	3.0	C*
2	2,5-dimethylfuran	1063.0715	4.252	-0.004	1543417	0.356	BB	2.4	C
3	1,4-dioxane	no result	5.523	-0.009	4444740	0.463	BB	4.1	C*
4	Methyl Sulfo	INT STD	11.938	-0.007	58657	1.000	BB	2.6	SR
	Totals:	1063.0715		-0.012	6054023				

Status Codes:
R - Reference peak
* - No result could be calculated; check calibration curve
C - Out of calibration range
S - Internal Standard peak
Total Unidentified Counts : 0 counts
Detected Peaks: 4 Rejected Peaks: 0 Identified Peaks: 4
Standard Peak Amount:
Methyl Sulfone Amount = 100
Multiplier: 1 Divisor: 1 Unidentified Peak Factor: 0

```
Baseline Offset: -4 microVolts          LSB:     1 microVolts
Noise (used): 39 microVolts - monitored before this run
Vial: 0        Injection Number: 1     Volume: 1.0  uL     Position: 2
********************************************************************************
```

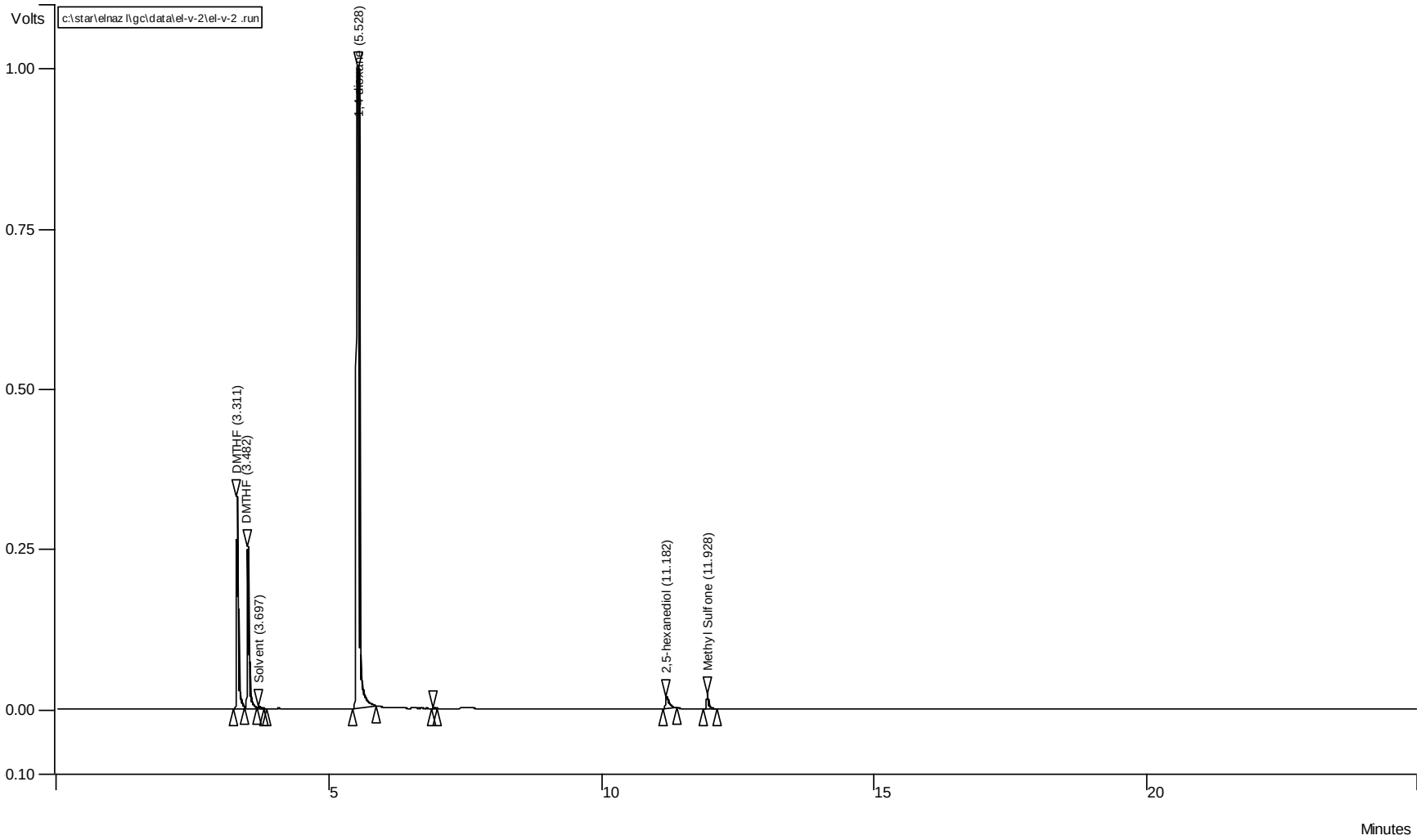


Figure S15: Reaction mixture of 2,5-dimethylfuran after run.

Title :
Run File : c:\star\elnaz l\gc\data\el-v-2\el-v-2 .run
Method File : c:\windows\temp\~2,5-dimethylfuran polar elnaz sept 24 2015.tmp
Sample ID : El-V-2
Injection Date: 9/24/15 4:27 PM Calculation Date: 10/26/15 9:03 AM
Operator : Schlaf Group Detector Type: 3800 (1 Volt)
Workstation: Bus Address : 45
Instrument : 3800_DualFID Sample Rate : 10.00 Hz
Channel : Middle = FID Run Time : 24.975 min
** Star Chromatography Workstation Version 6.00 ** 00479-7088-C69-21B5 **
Run Mode : Analysis
Peak Measurement: Peak Area
Calculation Type: Internal Standard

Peak No.	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)	Rel. Ret. Time	Sep. Code	Width 1/2 (sec)	Status Codes
1	DMTHF	504.2209	3.311	-0.003	746991	0.278	BV	1.9	
2	DMTHF	399.5470	3.482	-0.030	591919	0.292	GR	0.0	
3	Solvent	no result	3.697	0.008	6157	0.310	TS	0.0	C*
4	1,4-dioxane	no result	5.528	-0.001	4348537	0.463	BB	4.0	C*
5	2,5-hexanediol	58.0343	11.182	0.054	85977	0.937	BB	4.0	
6	Methyl Sulfo	INT STD	11.928	-0.017	59855	1.000	BB	2.2	SR
	Totals:	961.8022		0.011	5839436				

Status Codes:
R - Reference peak
* - No result could be calculated; check calibration curve
C - Out of calibration range
S - Internal Standard peak
Total Unidentified Counts : 0 counts
Detected Peaks: 7 Rejected Peaks: 1 Identified Peaks: 6
Standard Peak Amount:
Methyl Sulfone Amount = 100

```
Multiplier: 1          Divisor: 1          Unidentified Peak Factor: 0
Baseline Offset: -61 microVolts          LSB:     1 microVolts
Noise (used): 52 microVolts - monitored before this run
Vial: 1        Injection Number: 1     Volume: 1.0  uL     Position: 2
********************************************************************************
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Images of high-pressure reactor set-up and glass tube insert used for kinetic studies.

Figure S16: Overall Reactor set-up at the University of Guelph High-Pressure Hydrogenation Facility.

Figure S17: Reactor body with insert NMR glass tube (side view).

Figure S18: Reactor body with insert NMR glass tube (top view).