Supplementary information

Mechanistic Investigation of *Anti*-Elimination in (*Z*)-1,2-bis(arylseleno)-1-alkenes and their Sulfur Analogs

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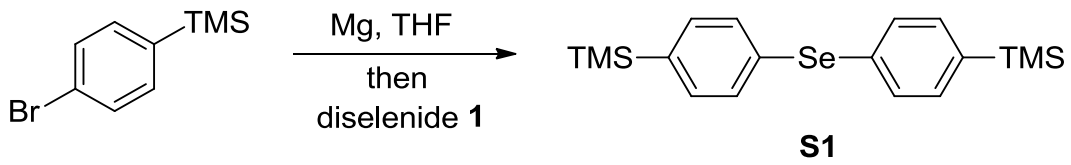
Contents:

Procedure for synthesis of bis(4-trimethylsilylphenyl)selenide (S1)



S1

1-Bromo-4-trimethylsilylbenzene (195 μL, 1.0 mmol) was added to a suspension of Mg (36 mg, 1.5 mmol) and trace amount of I_2 in anhydrous tetrahydrofuran (6 mL) at room temperature, and the mixture was stirred at the same temperature for 2.5 h. Then, diselenide **1** (225 mg, 0.5 mmol) was added to the reaction mixture and vigorously stirred for 3 h at 60 °C. The reaction was cooled and filtered through a celite pad. The filtrate was poured into cold a saturated aqueous solution of NH_4Cl (20 mL) and the mixture was extracted with EtOAc (20 mL×3). The organic layer was washed with brine (20 mL×2), dried over magnesium sulfate, and concentrated under vacuum. The residue was dissolved in ether (40 mL), treated with a solution of $NaBH_4$ (80 mg, 2.1 mmol) in methanol (2 mL), washed with 2N aqueous solution of KOH (20 mL). These treatment and washing were continued until the disappearance of the color of organic layer. The organic layer was dried over magnesium sulfate and concentrated under vacuum. The residue was purified by silica gel preparative thin layer chromatography (hexane) to give **S1** (146 mg, 77%).

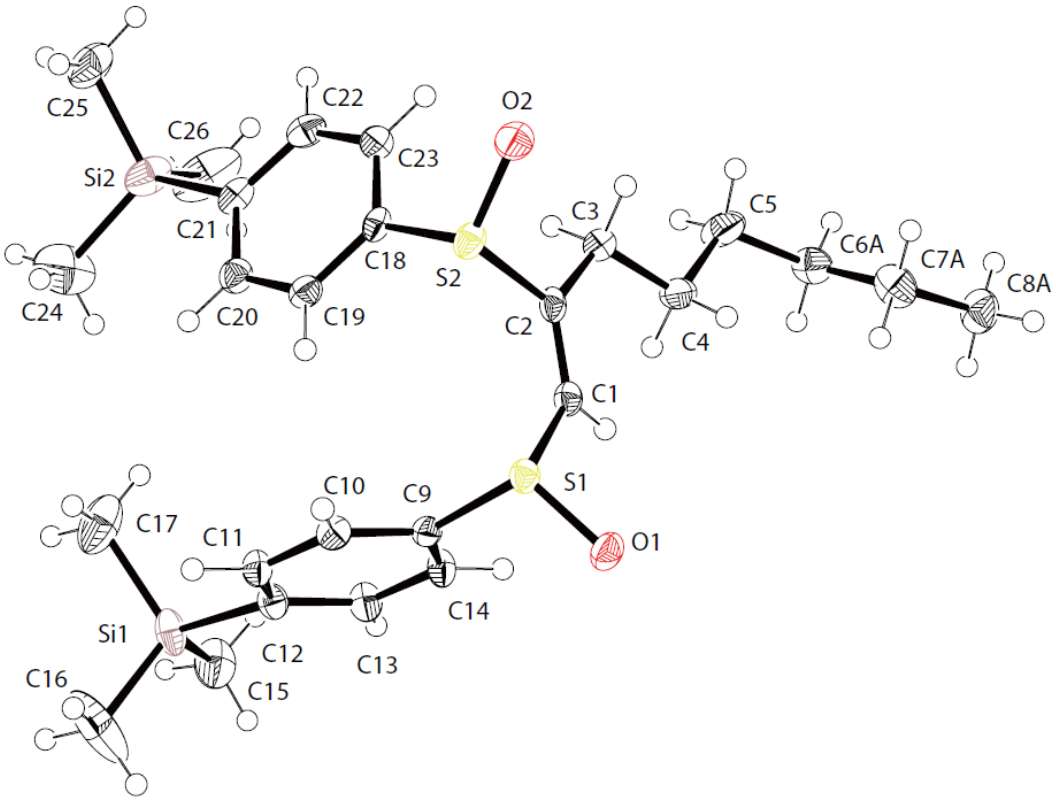
^{1}H NMR (400 MHz, $CDCl_3$) δ: 0.25 (18H, s, Si-$(CH_3)_3$), 7.41 (4H, d, *J* = 8.1 Hz, Ar−H), 7.44 (4H, d, *J* = 8.1 Hz, Ar−H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ: −1.2, 131.9, 132.2, 134.2, 139.5; MS (EI) *m/z*: 378 (M^+, 100), 363 (91), 214 (9), 73 (52); HR-MS (EI) *m/z*: 378.0740 (Calcd for $C_{18}H_{27}SeSi_2$: 378.0738); *Anal*: Found: C, 54.79; H, 6.40 (Calcd for $C_{18}H_{26}OSeSi_2$: C, 54.94; H, 6.66%).

Crystal data and structure refinement for compound 15

Empirical formula	C_{26} H_{40} O_2 S_2 Si_2	
Formula weight	504.88	
Temperature	100 K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P -1	
Unit cell dimensions	a = 11.205(3) Å	a= 108.312(3)°.
	b = 11.346(3) Å	b= 90.218(3)°.
	c = 13.093(4) Å	g = 112.482(3)°.
Volume	1445.6(7) $Å^3$	
Z	2	
Density (calculated)	1.160 Mg/m^3	
Absorption coefficient	0.287 mm^{-1}	
F(000)	544	
Crystal size	0.140 x 0.100 x 0.080 mm^3	
Theta range for data collection	1.655 to 26.811°.	
Index ranges	-13<=h<=14, -14<=k<=14, -16<=l<=16	
Reflections collected	14519	
Independent reflections	5515 [R(int) = 0.0315]	
Completeness to theta = 25.242°	98.9 %	
Absorption correction	None	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5515 / 0 / 325	
Goodness-of-fit on F^2	1.033	
Final R indices [I>2sigma(I)]	R1 = 0.0411, wR2 = 0.0986	
R indices (all data)	R1 = 0.0554, wR2 = 0.1064	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.859 and -0.529 $e.Å^{-3}$	

ORTEP Diagram of the compound 15

conformer A



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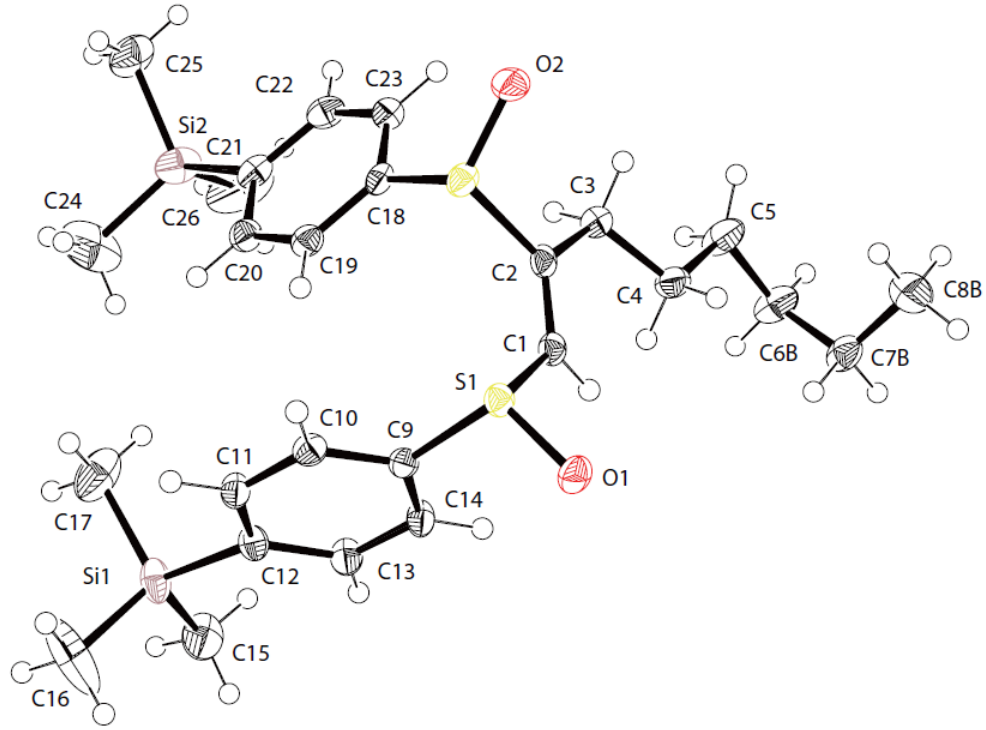
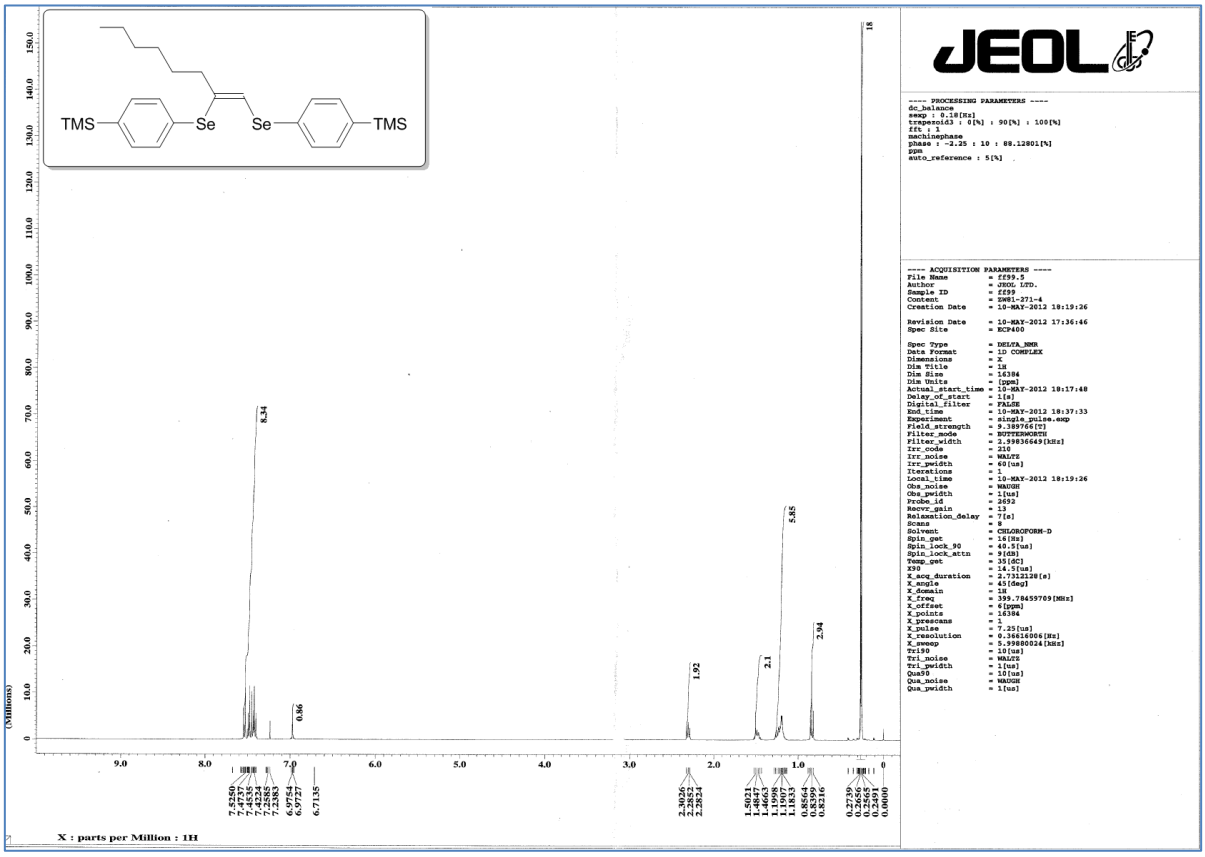
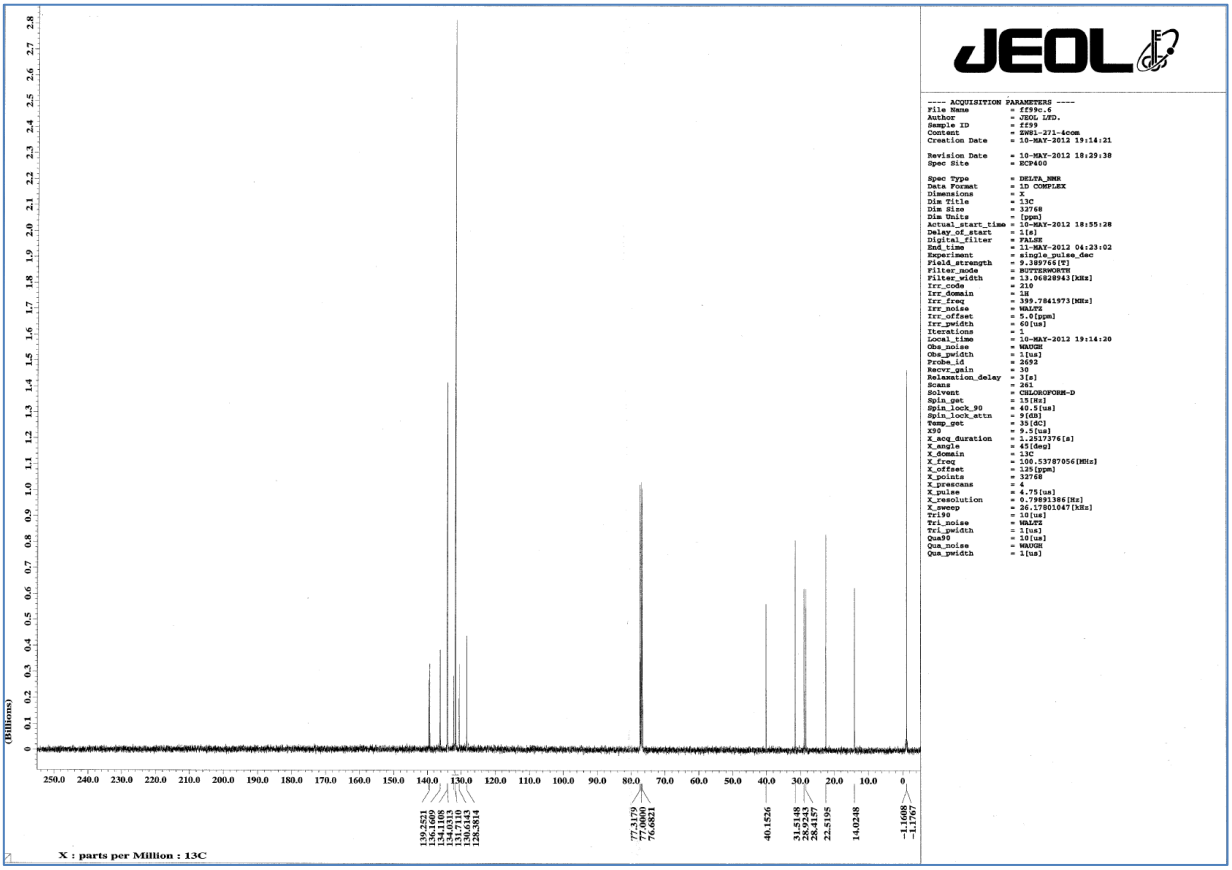
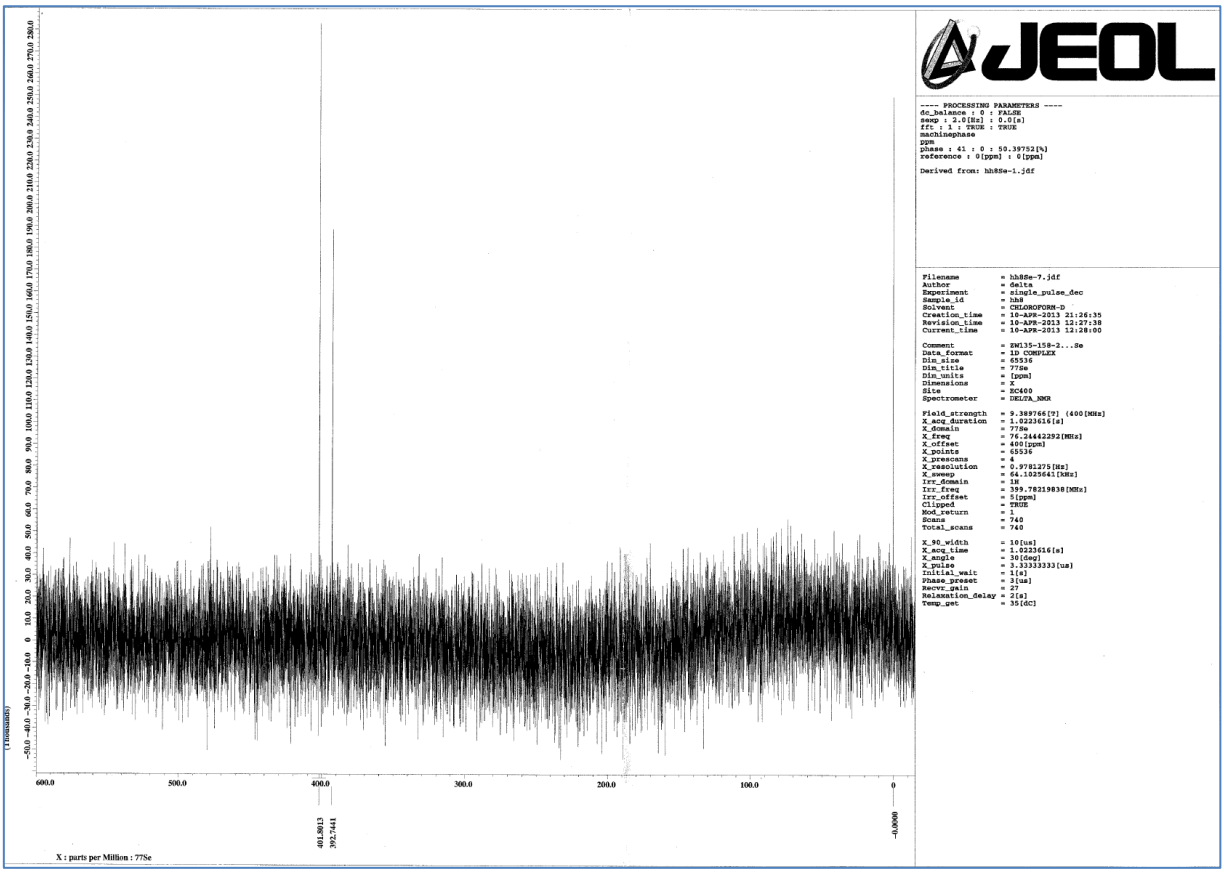


^{1}H, ^{13}C and ^{77}Se NMR of 3a



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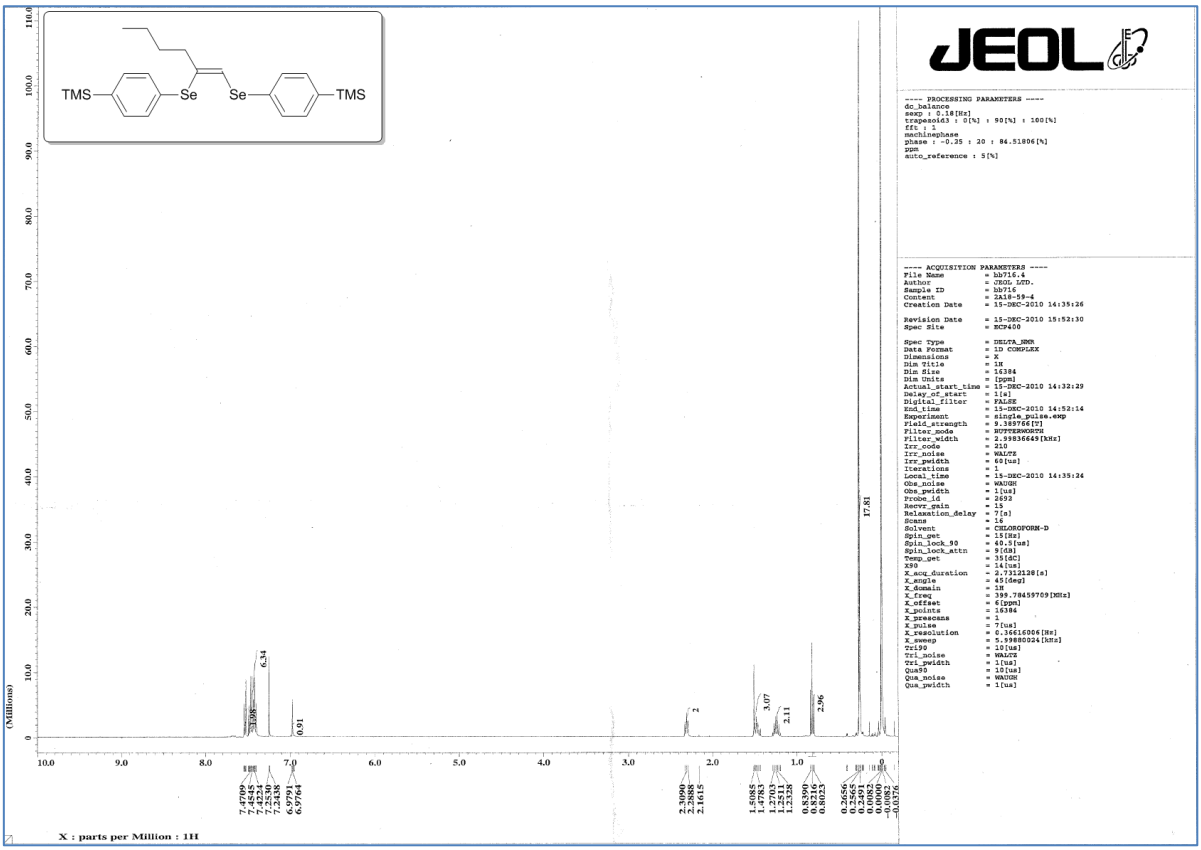
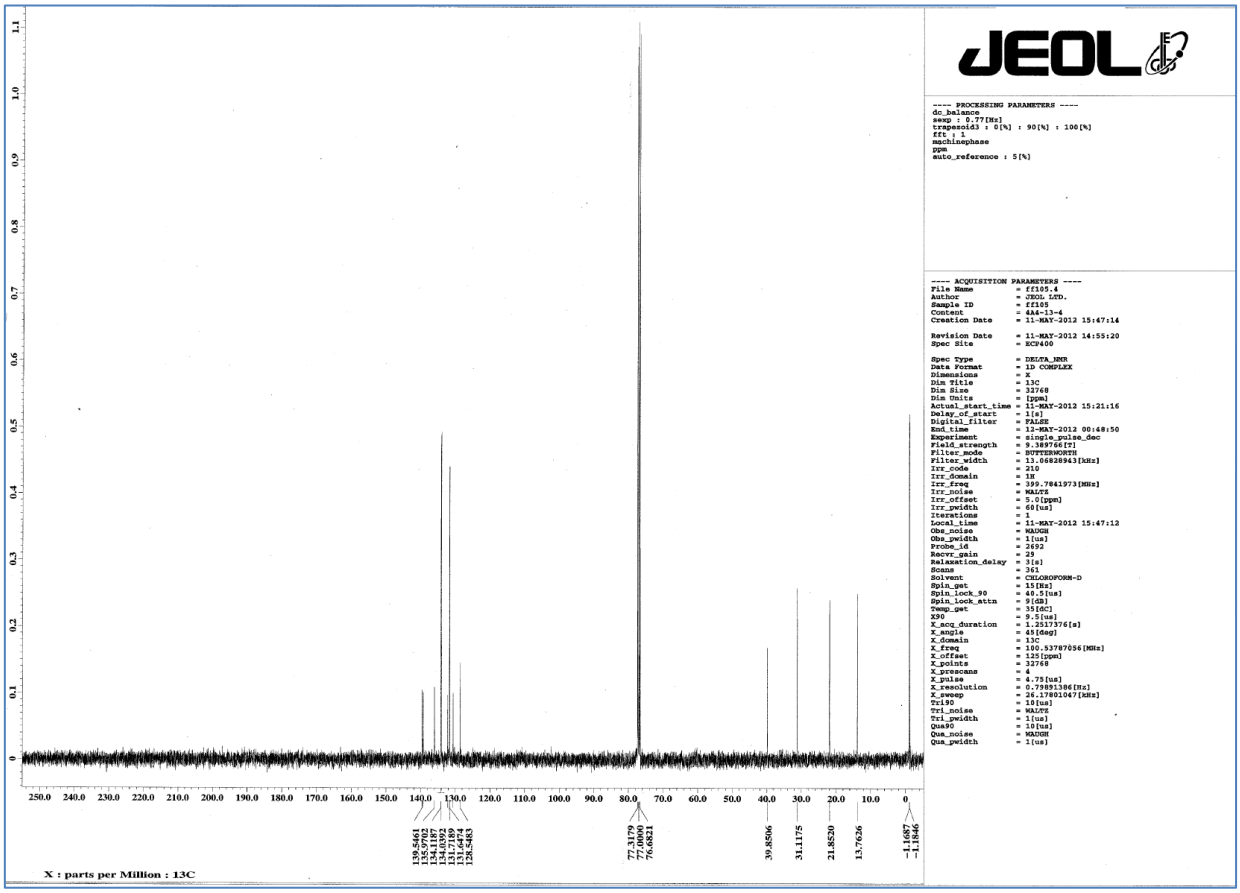
^{1}H and ^{13}C NMR of 3b





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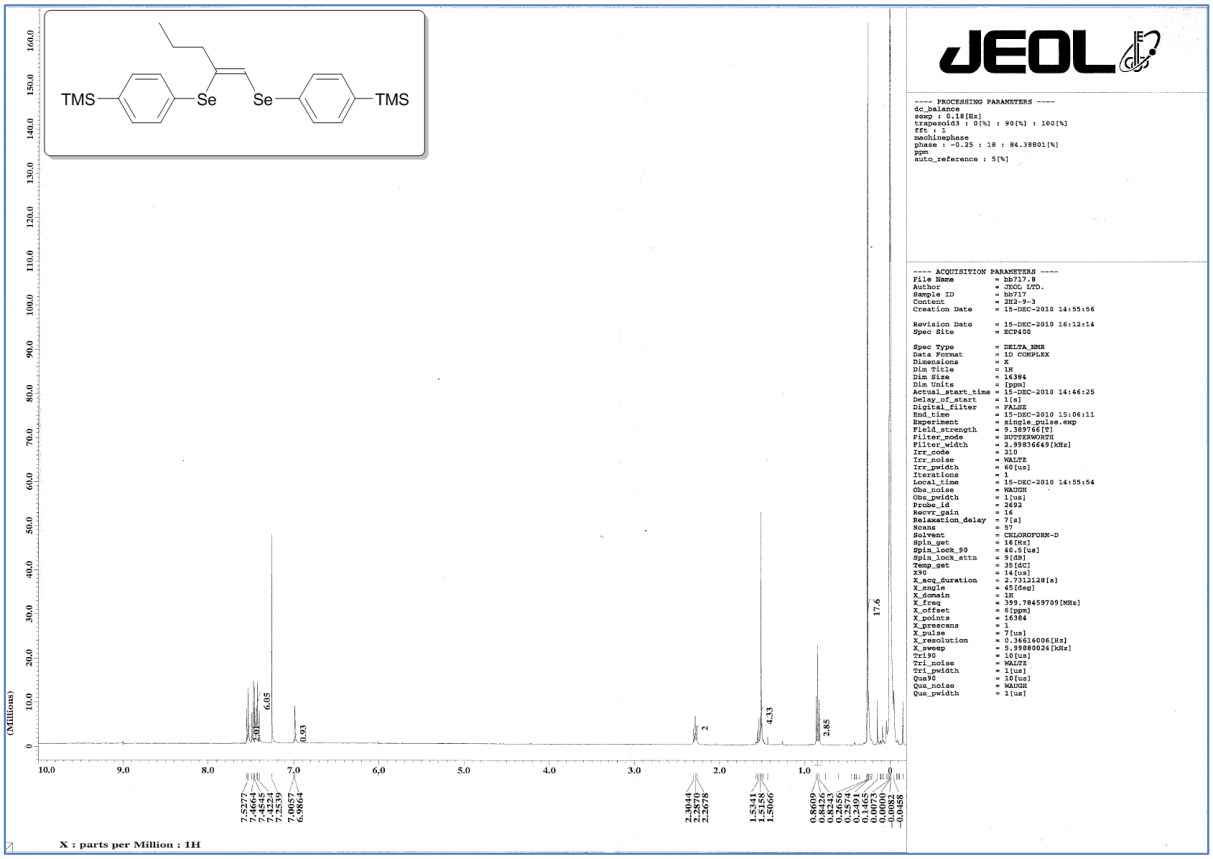
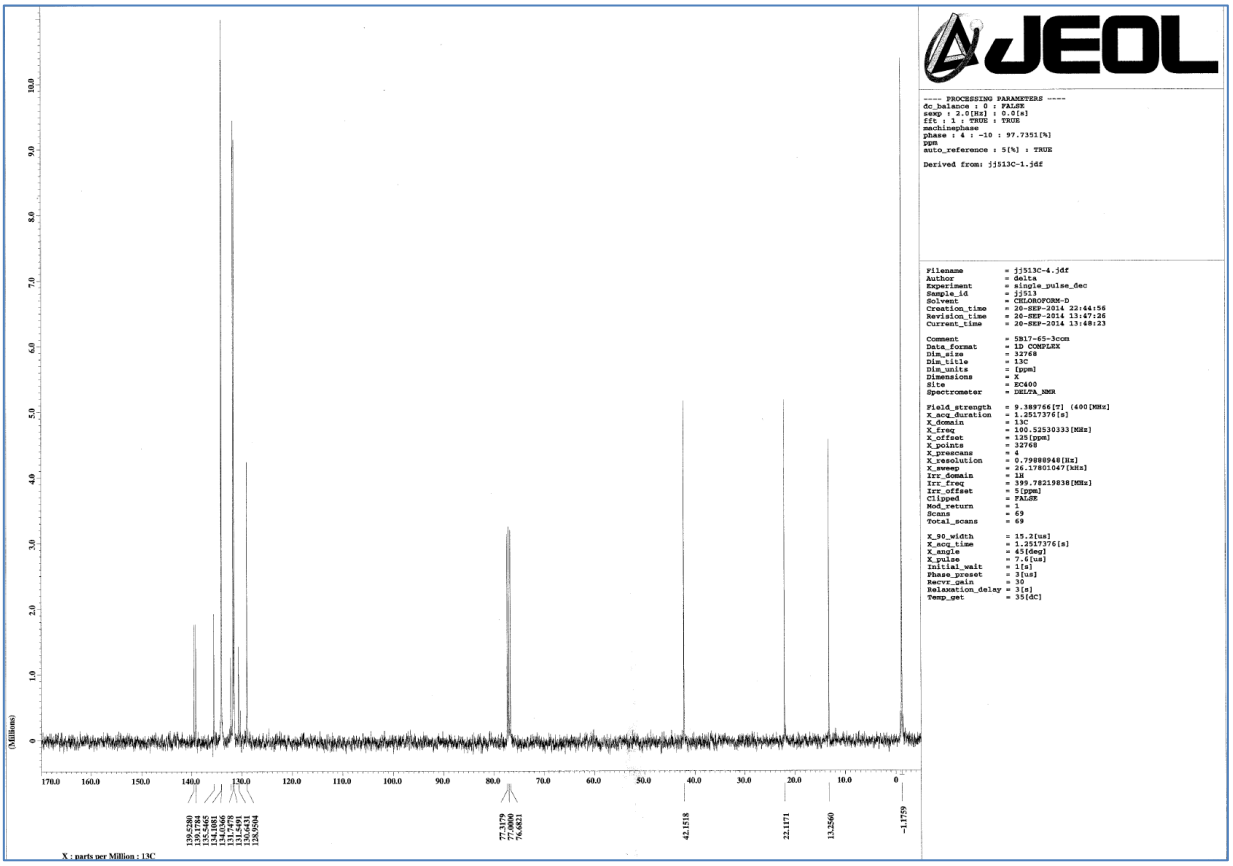
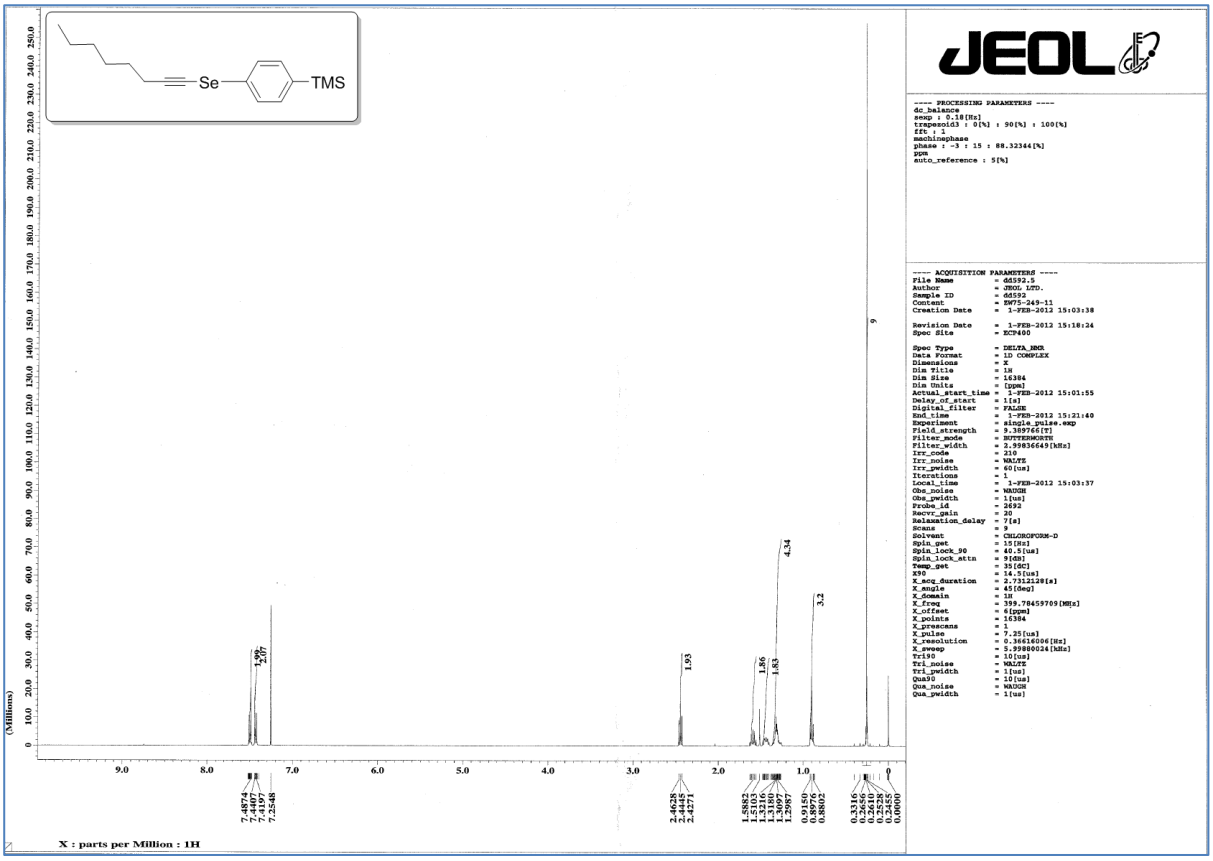
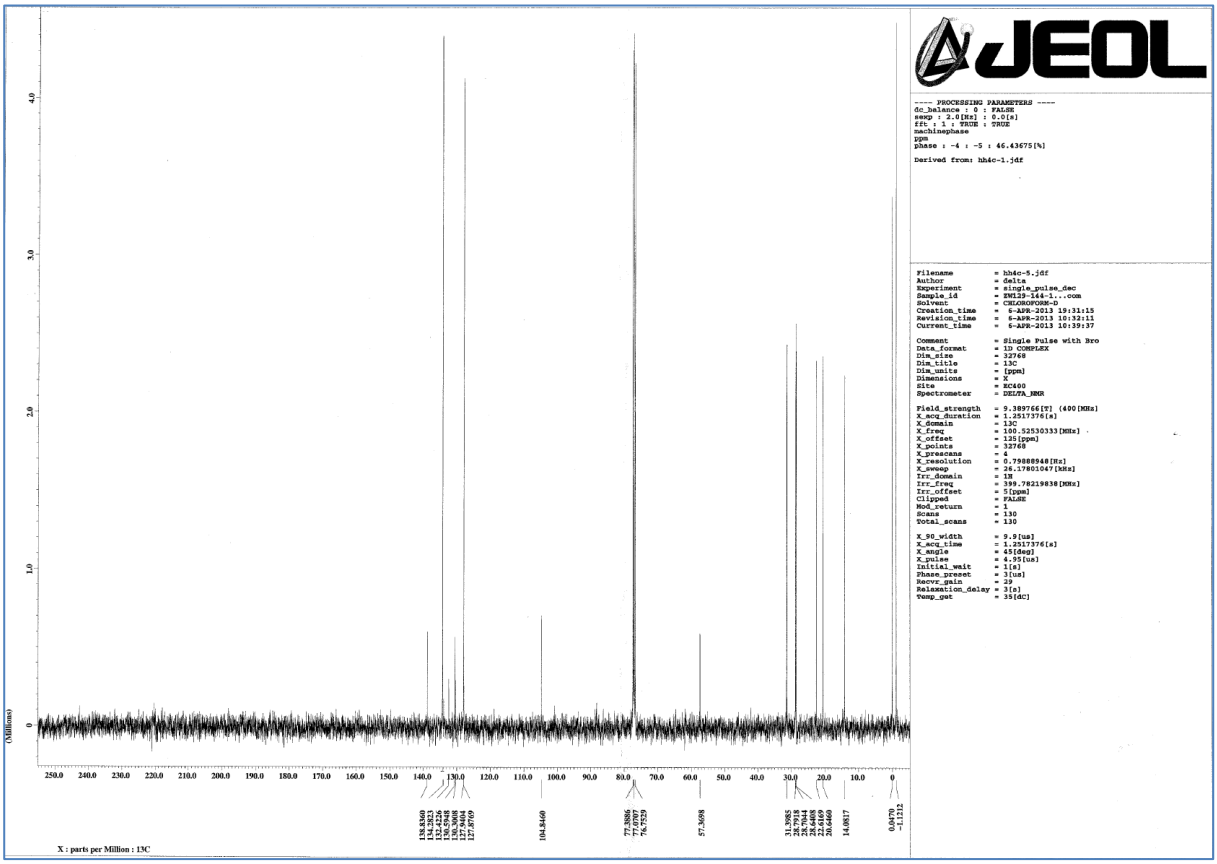
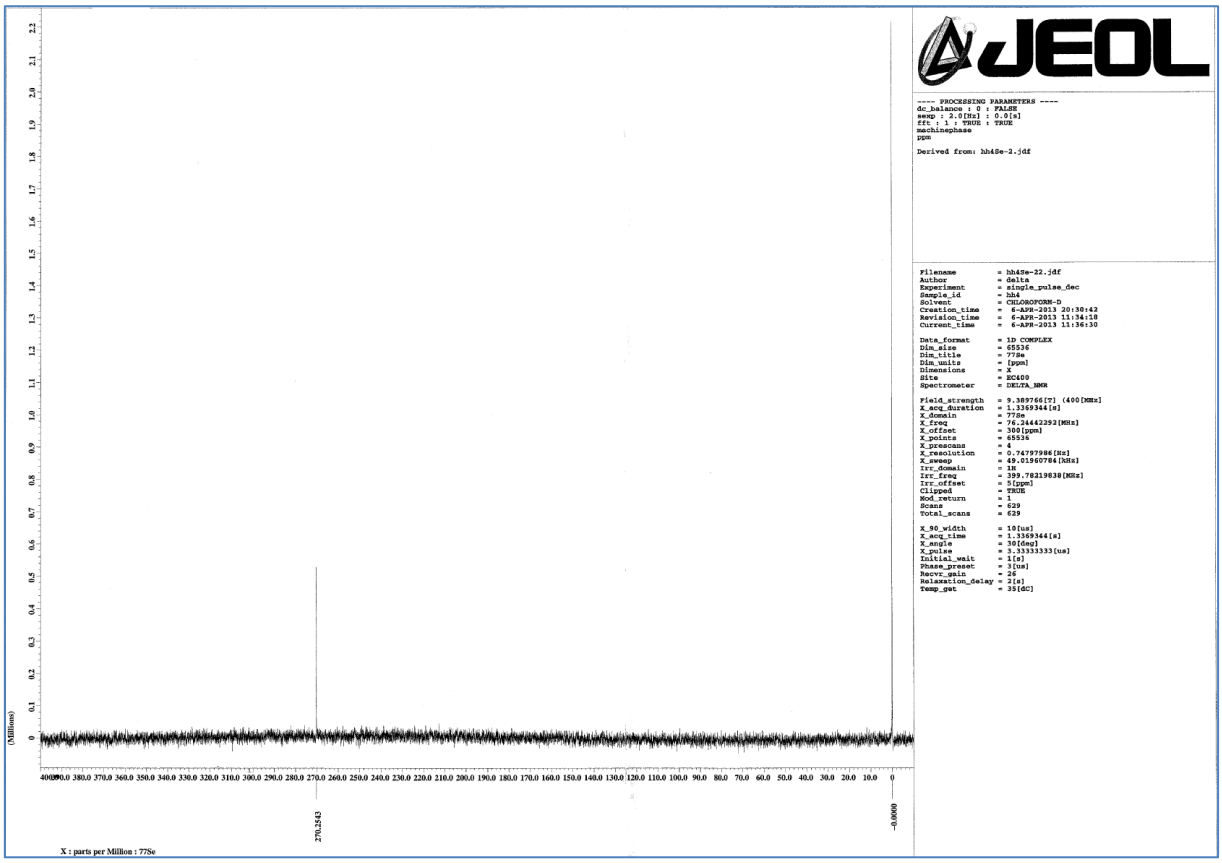




^{1}H, ^{13}C and ^{77}Se NMR of 4a



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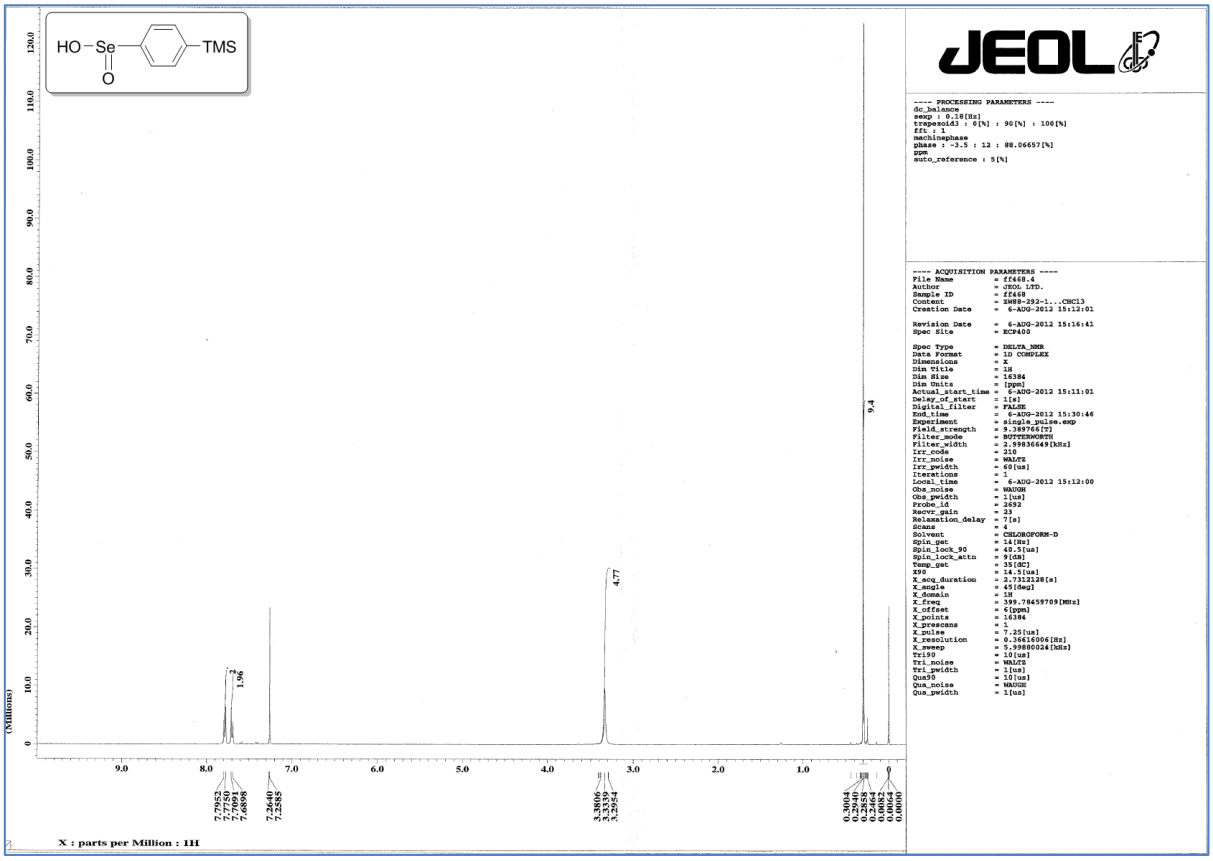
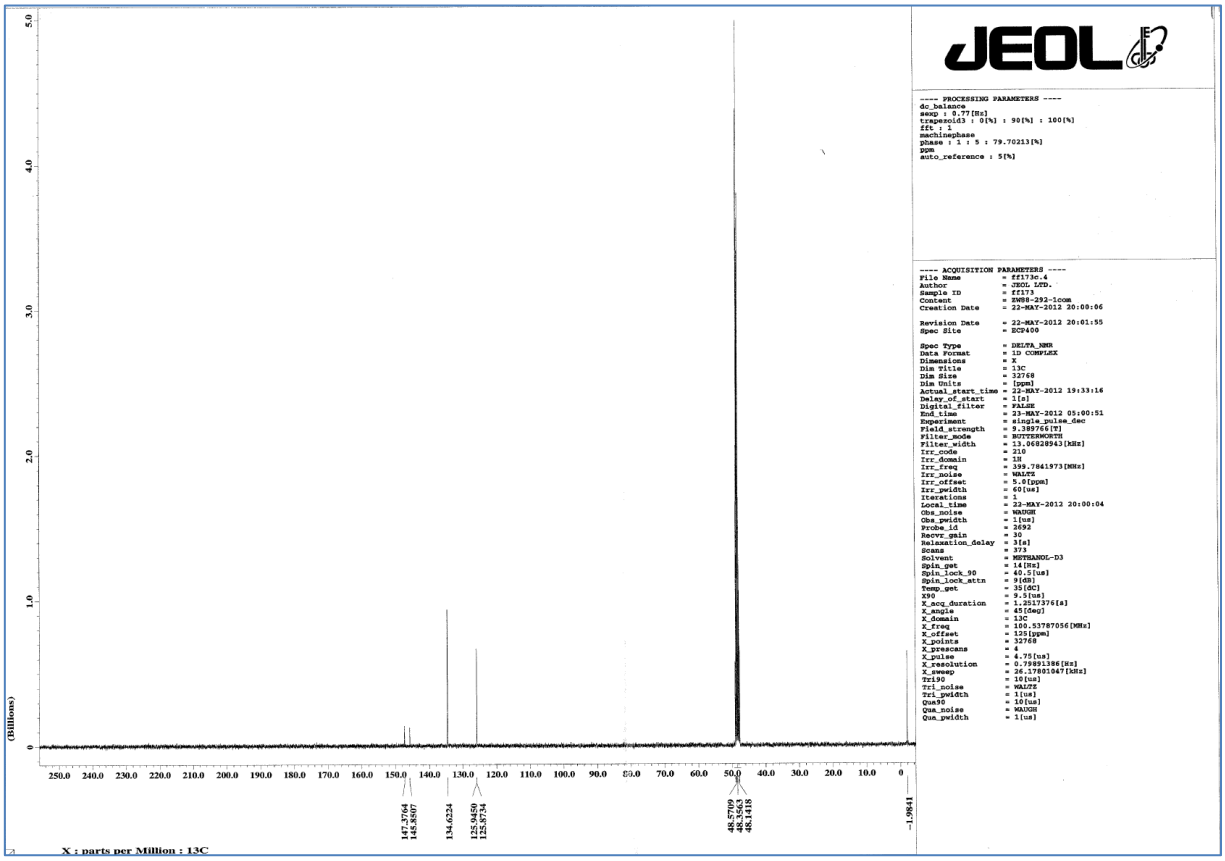
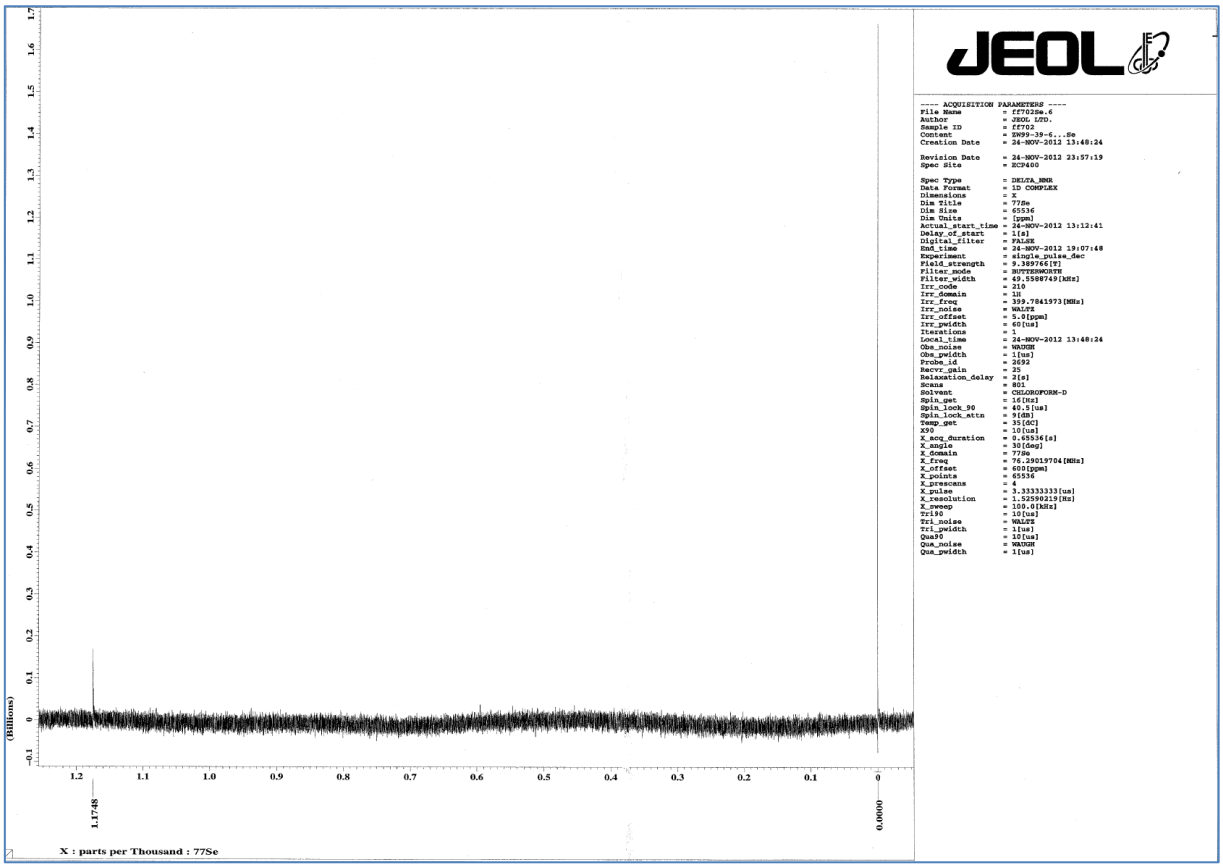
^{1}H, ^{13}C and ^{77}Se NMR of 5







JEOL

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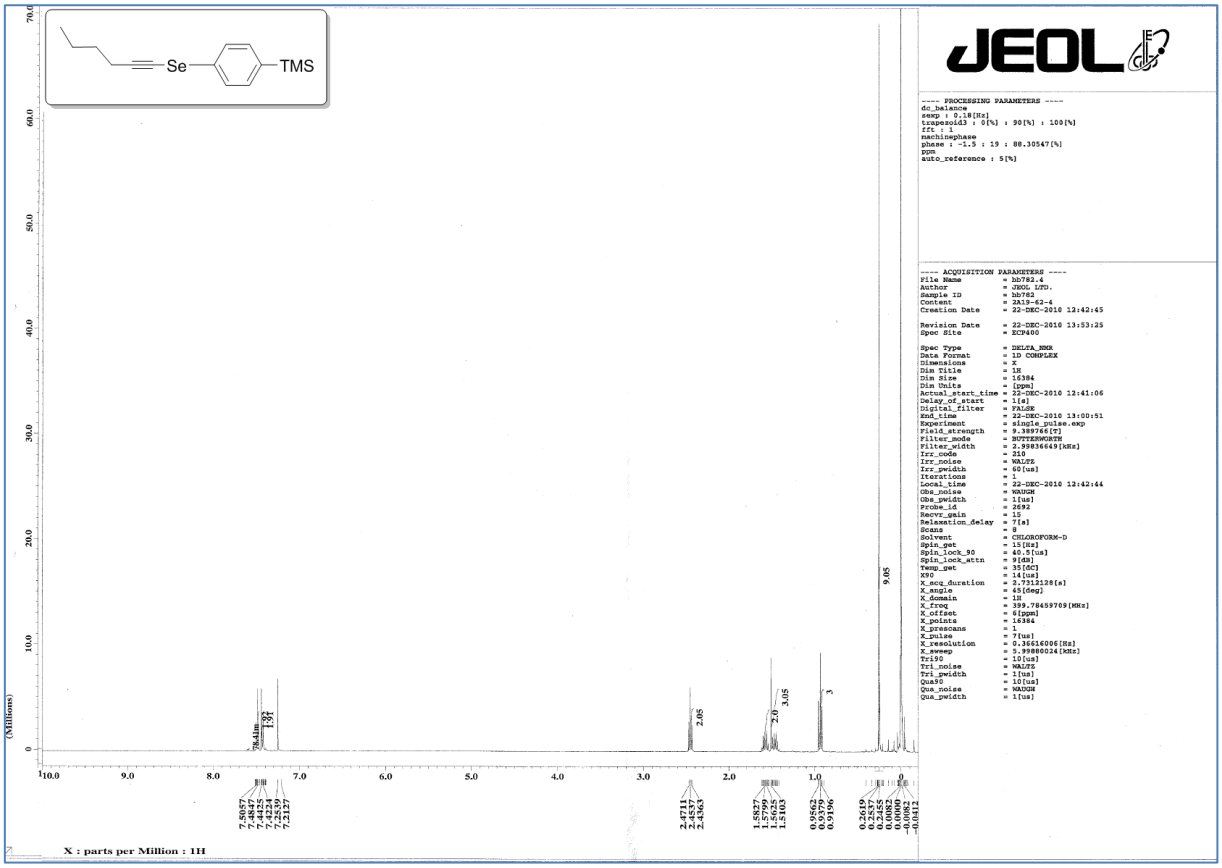
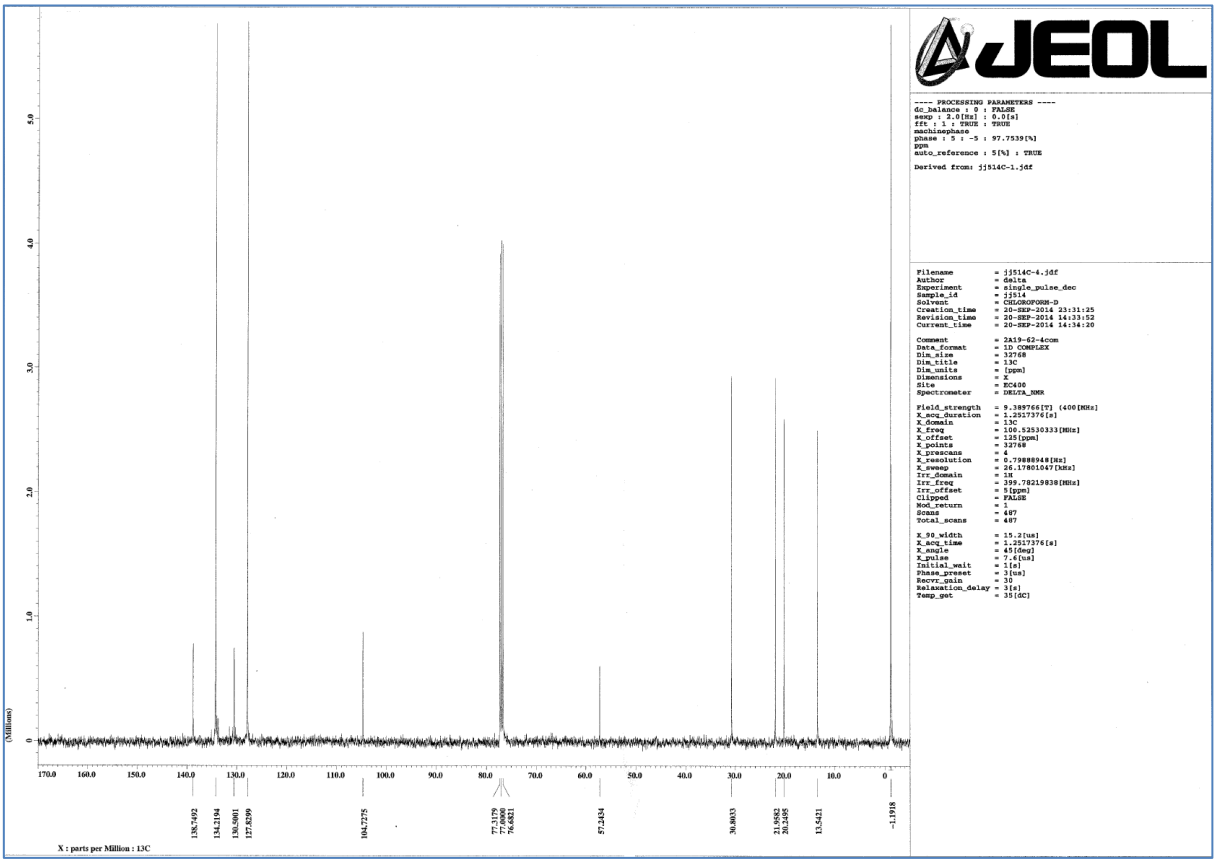
^{1}H and ^{13}C NMR of 4b





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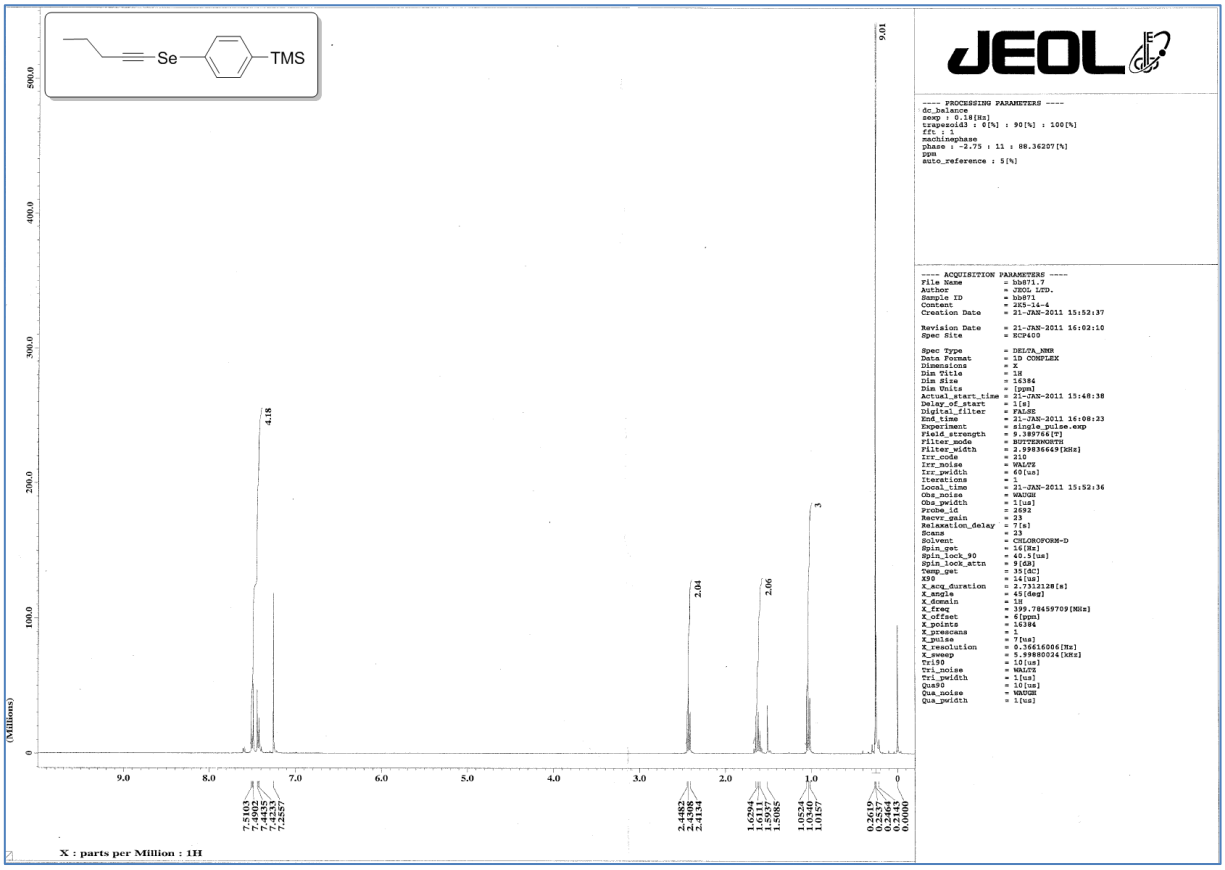
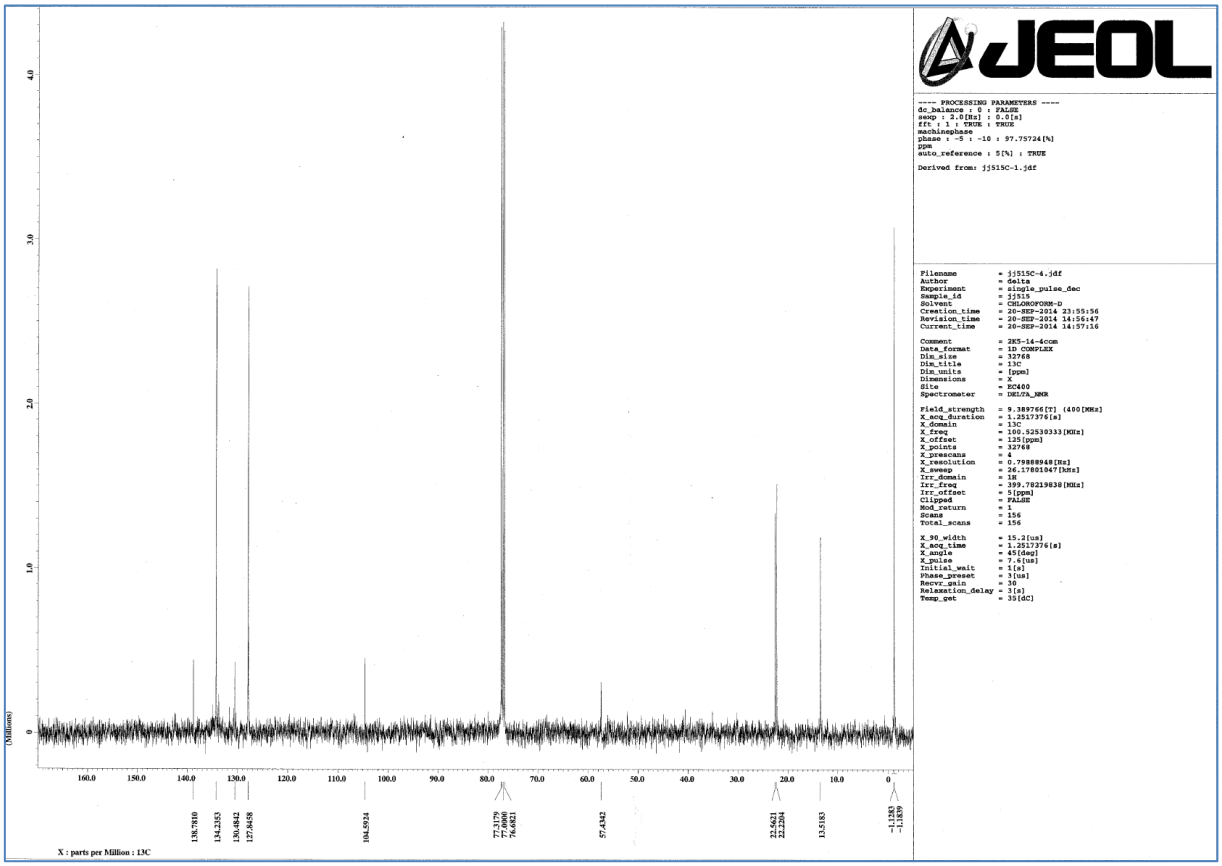
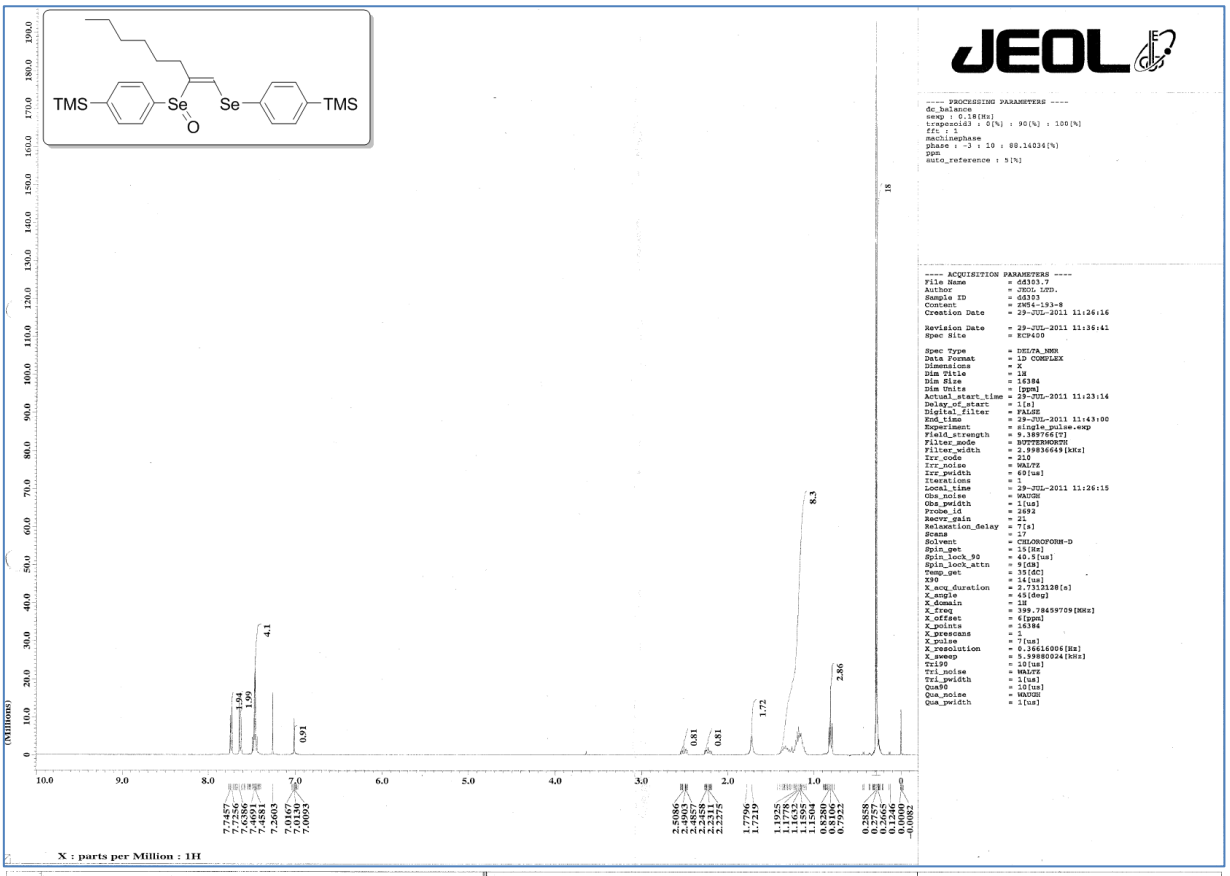
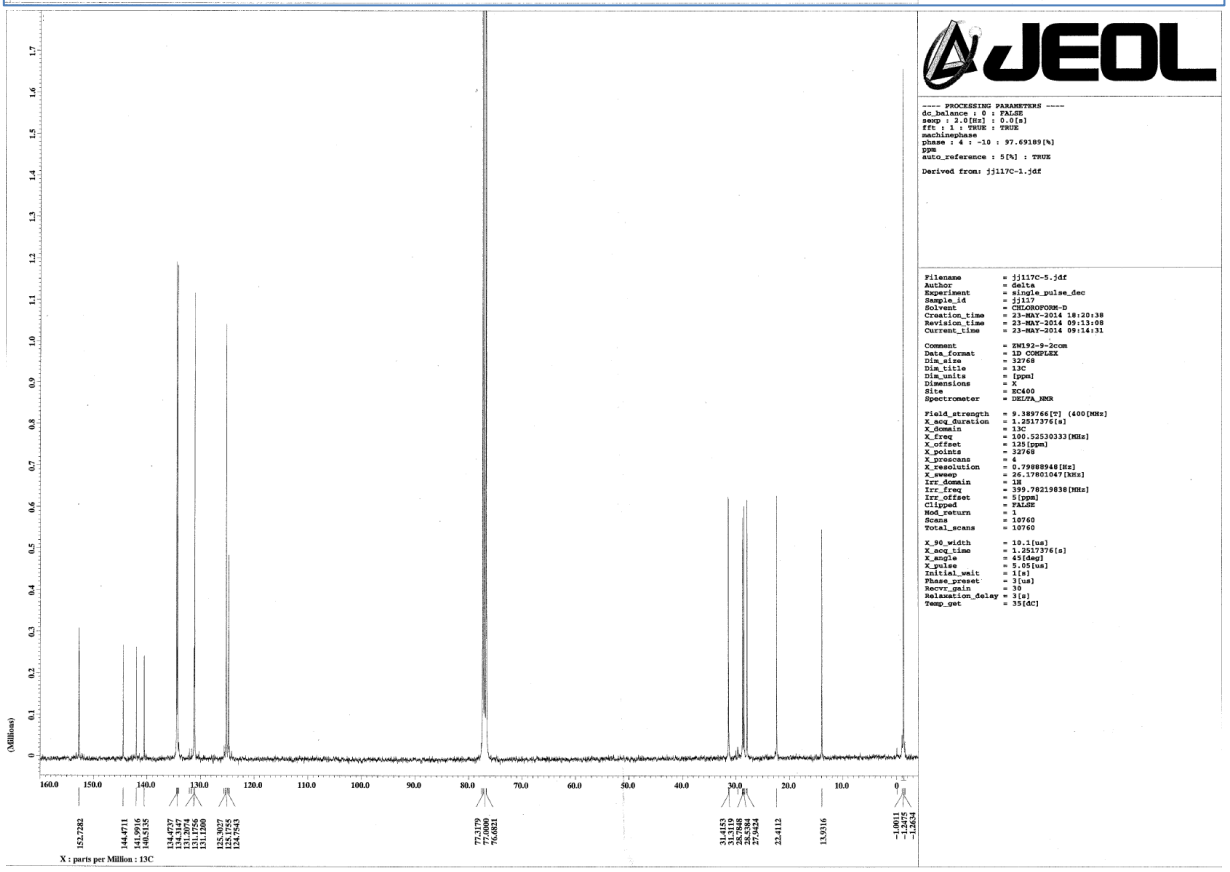
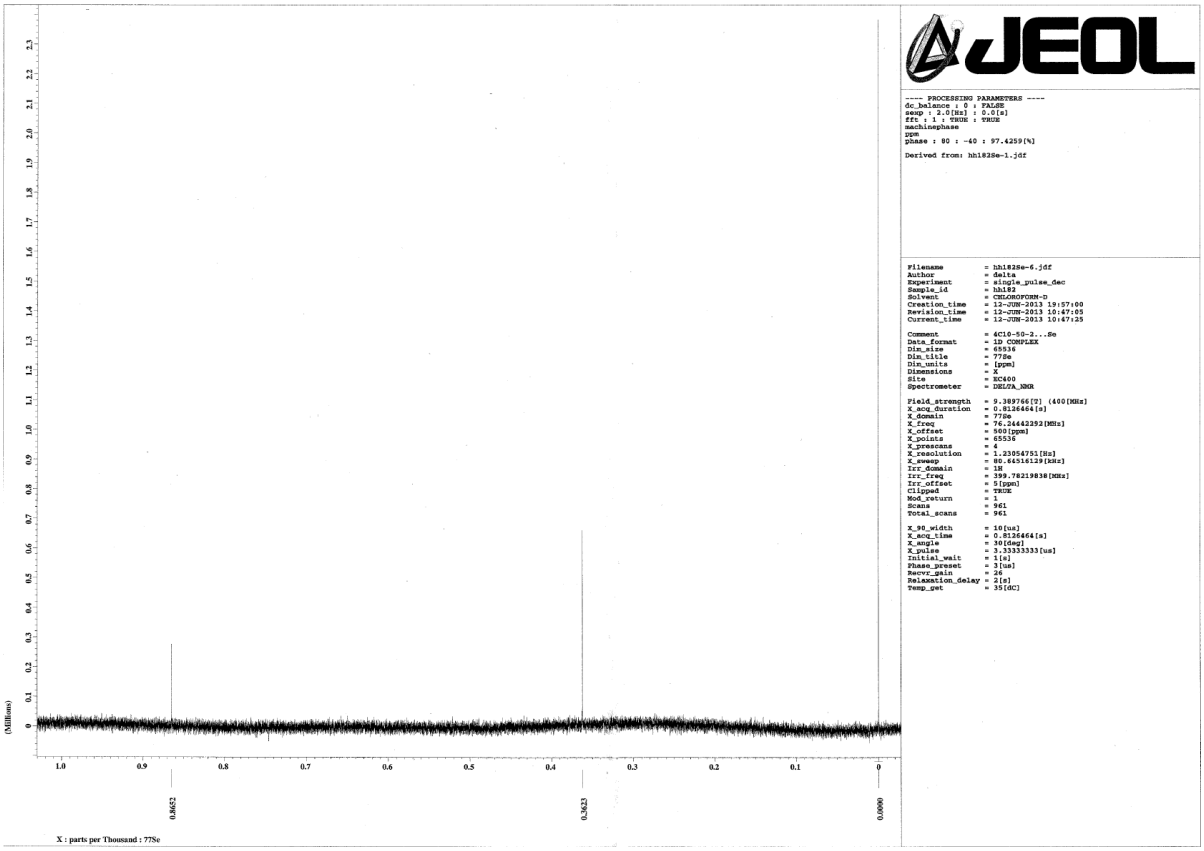




^{1}H, ^{13}C and ^{77}Se NMR of 6





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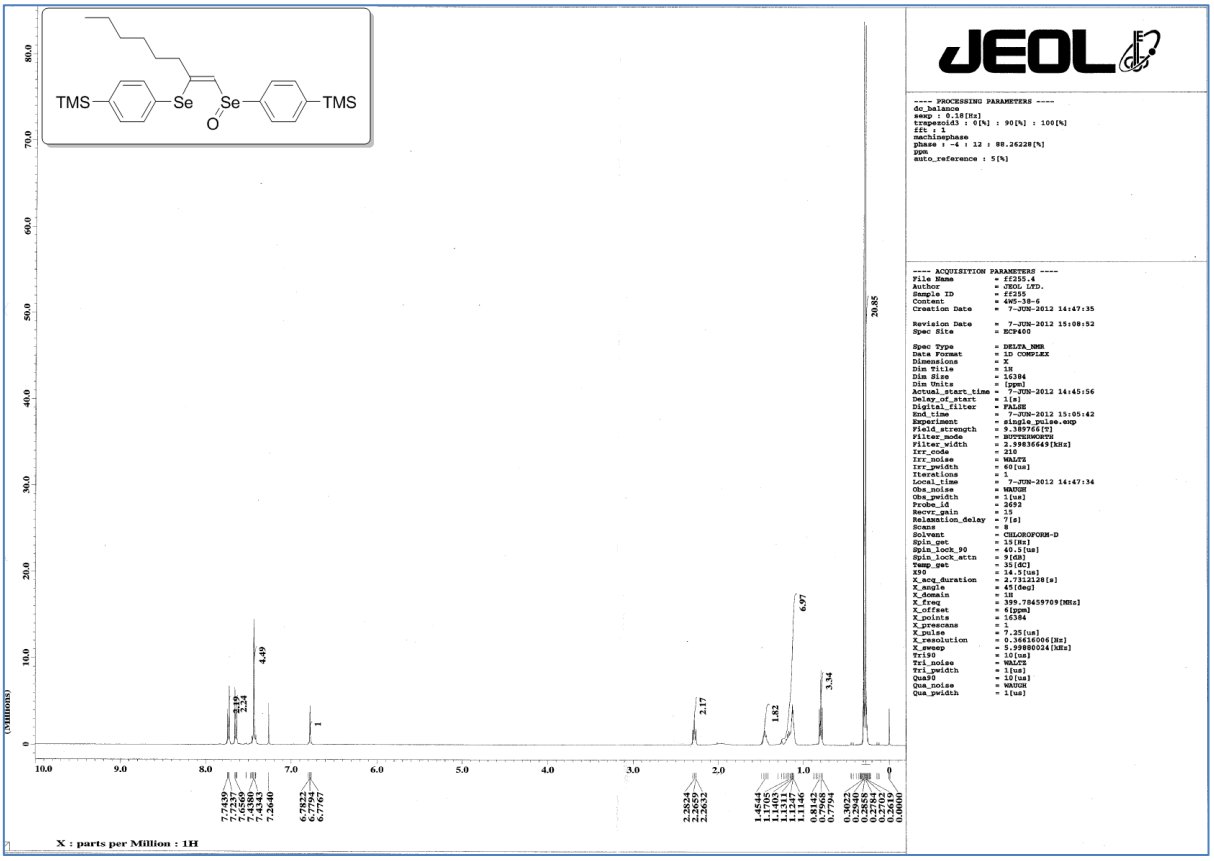
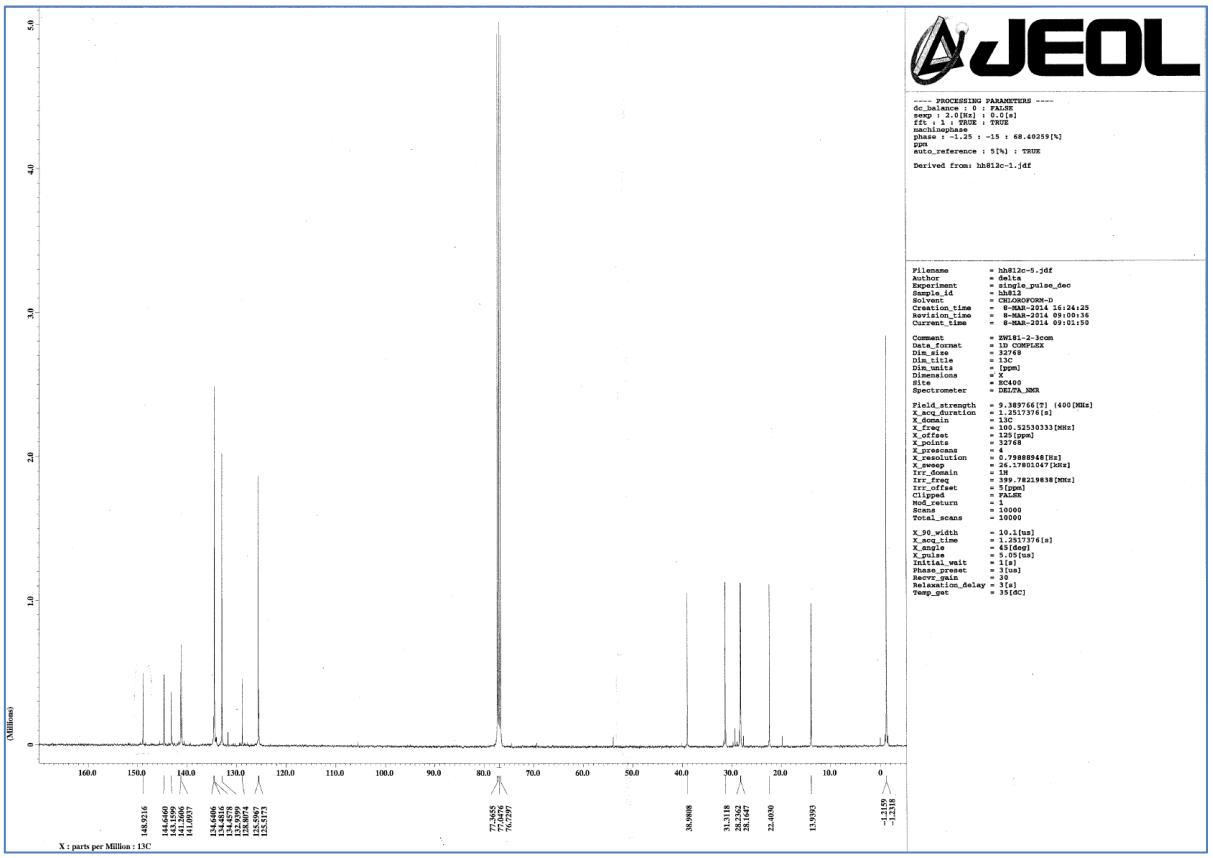
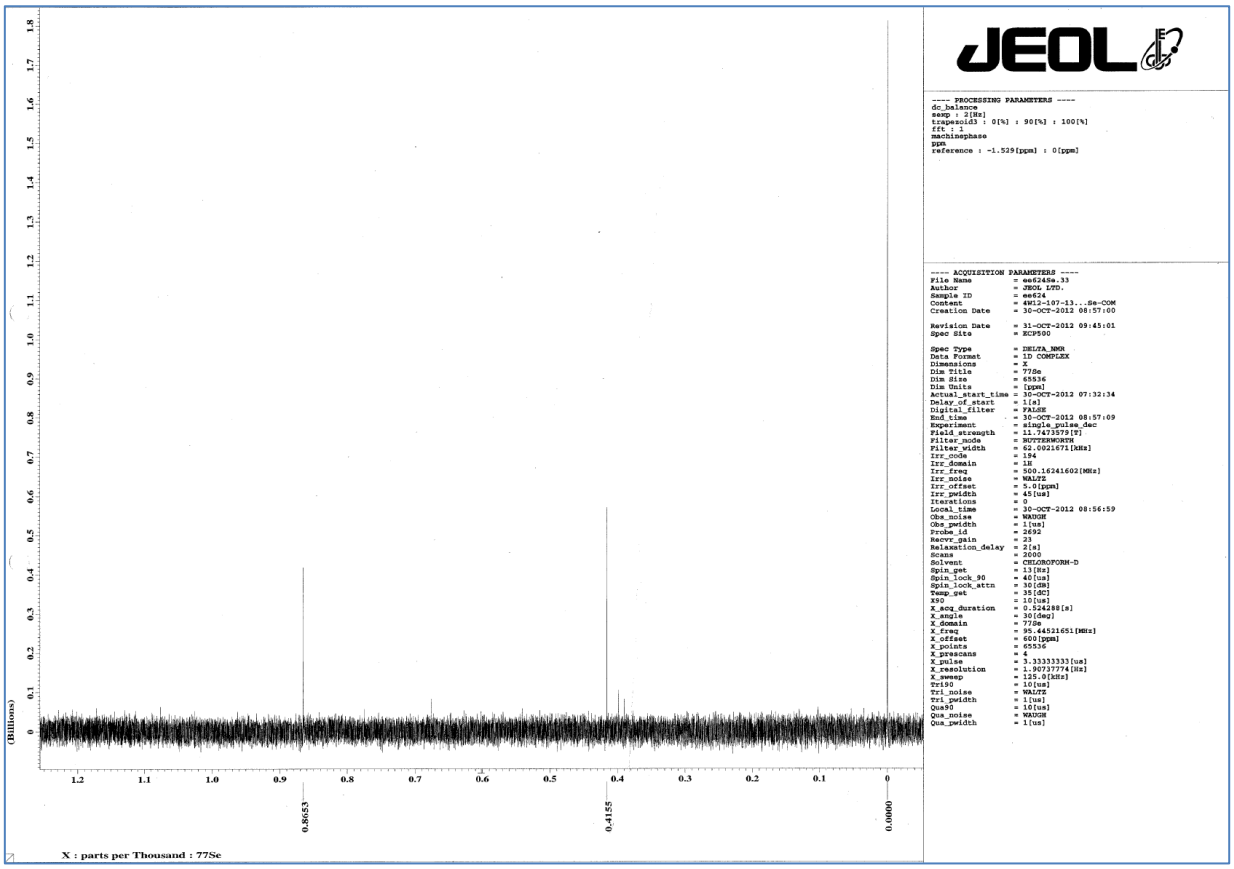
^{1}H, ^{13}C and ^{77}Se NMR of 7







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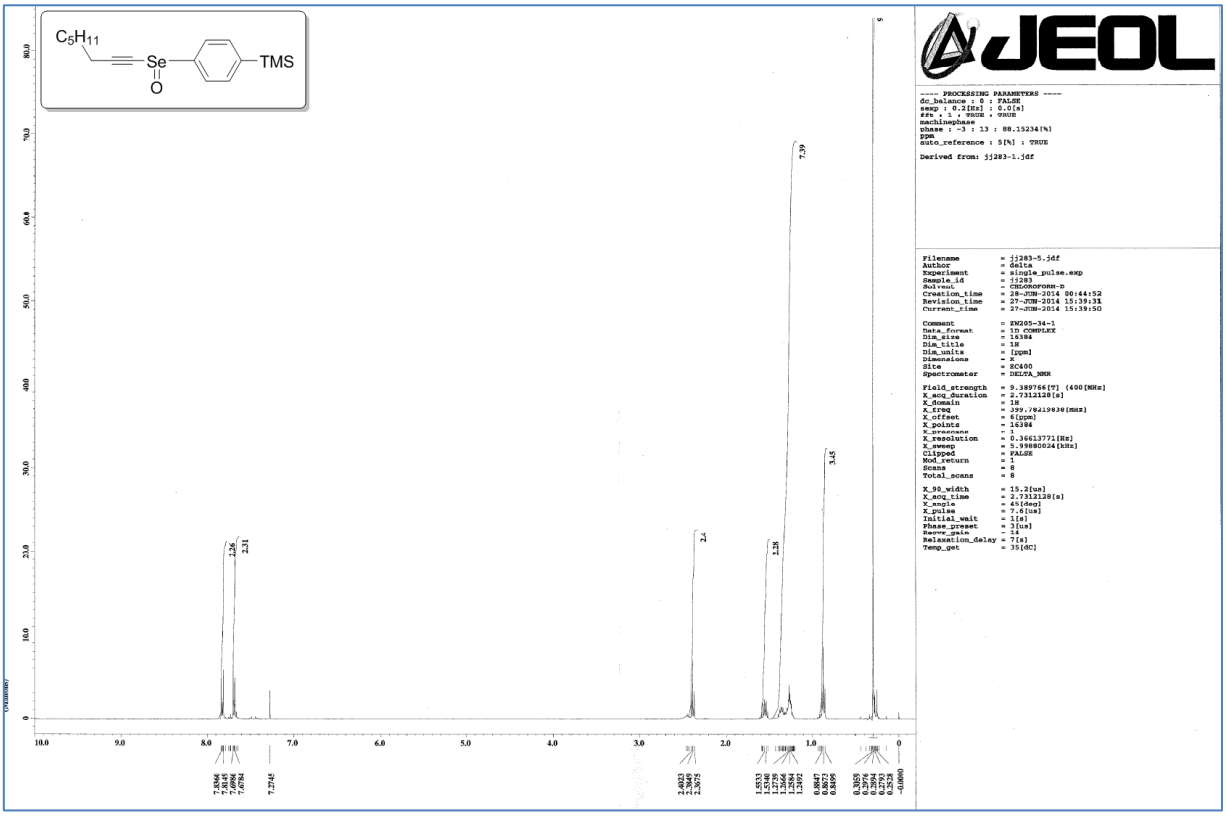
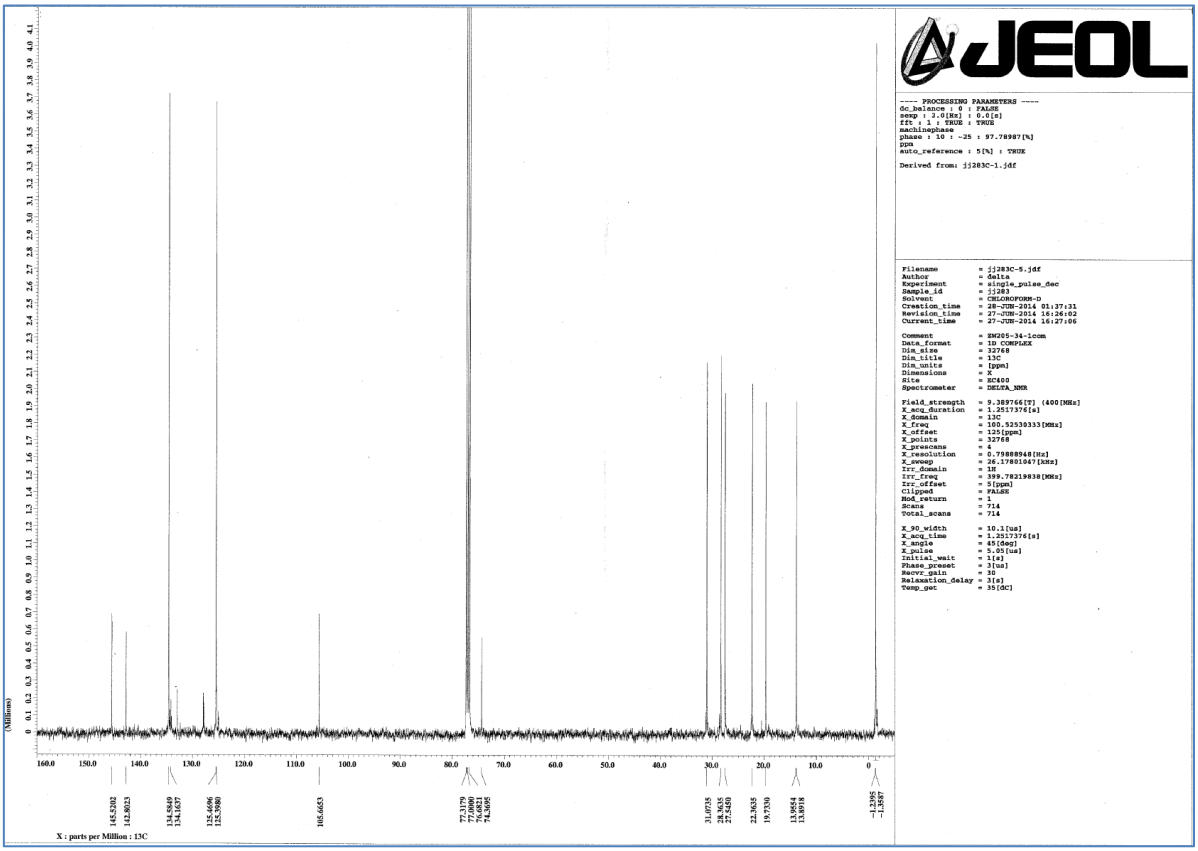
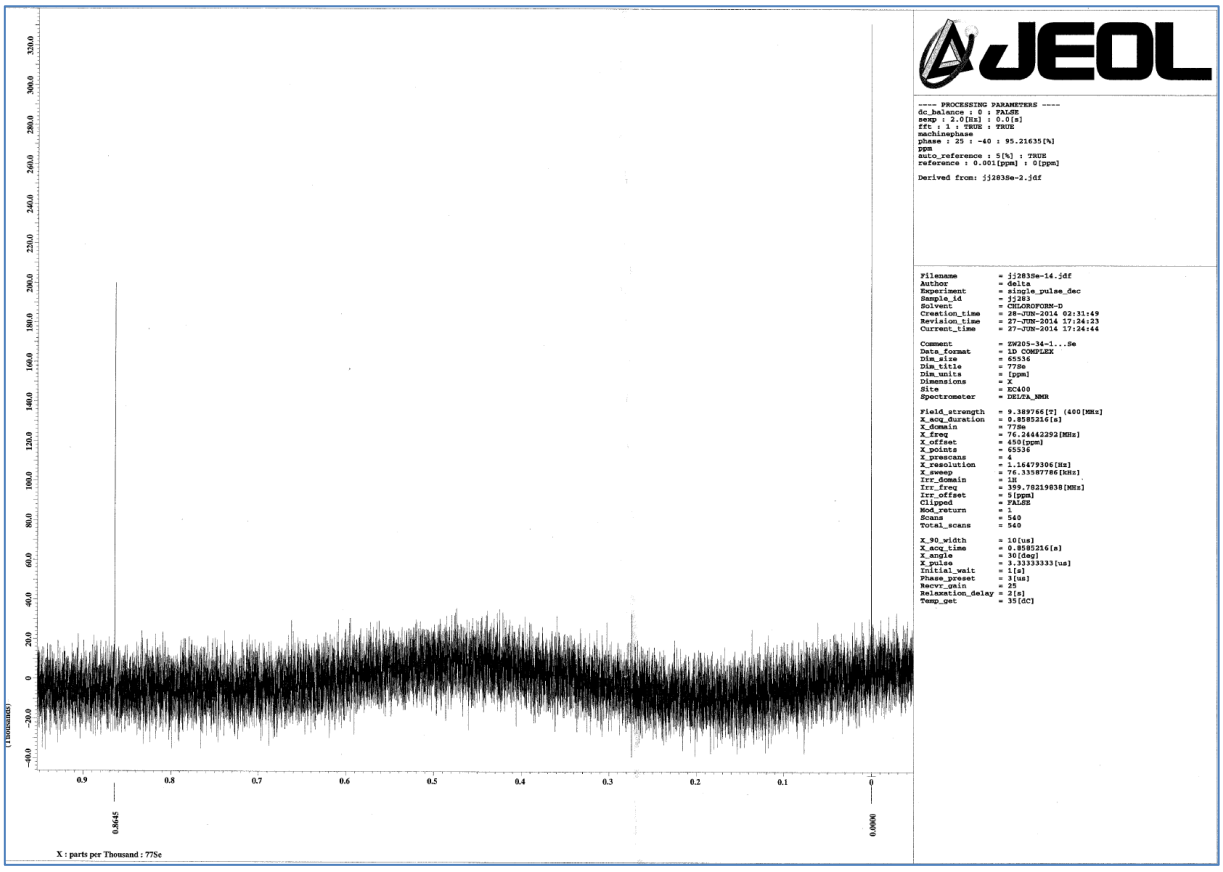
Qua_pwidth	= 1[us]

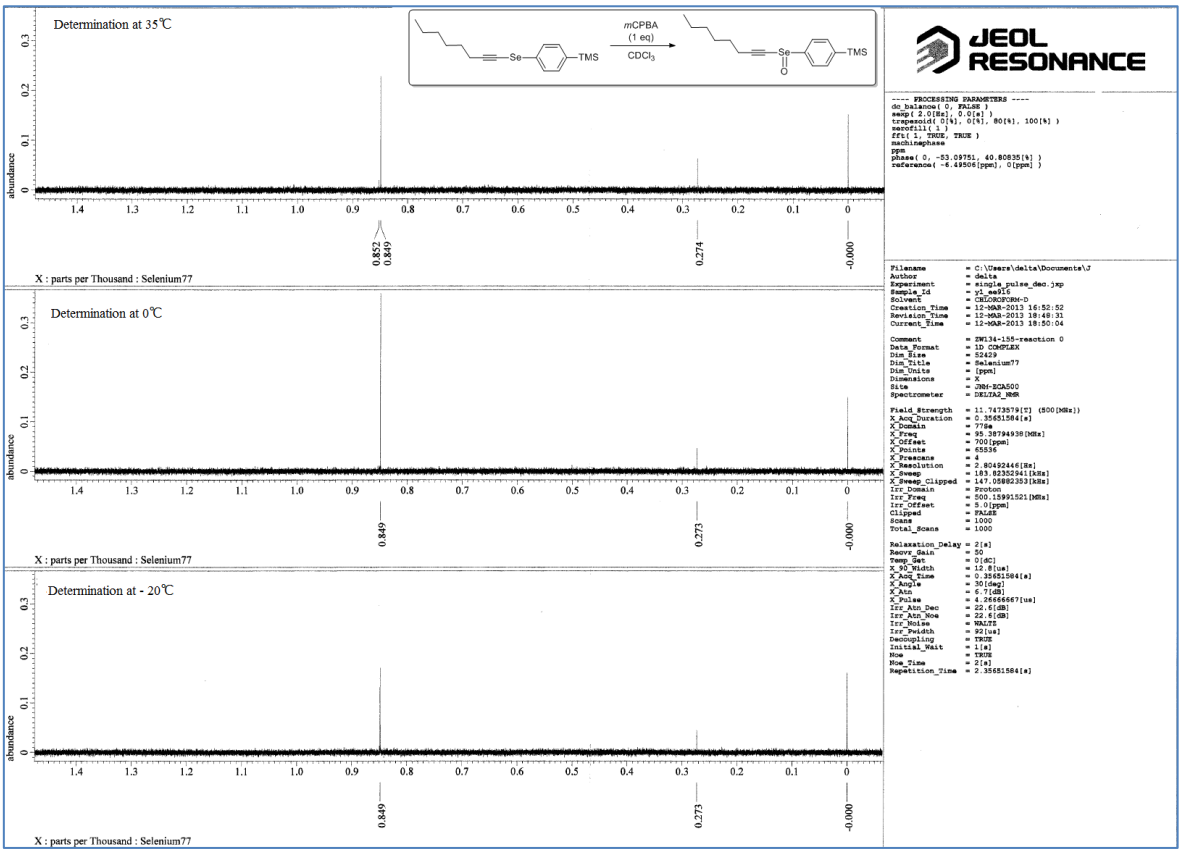
^{1}H, ^{13}C and ^{77}Se NMR of 8a



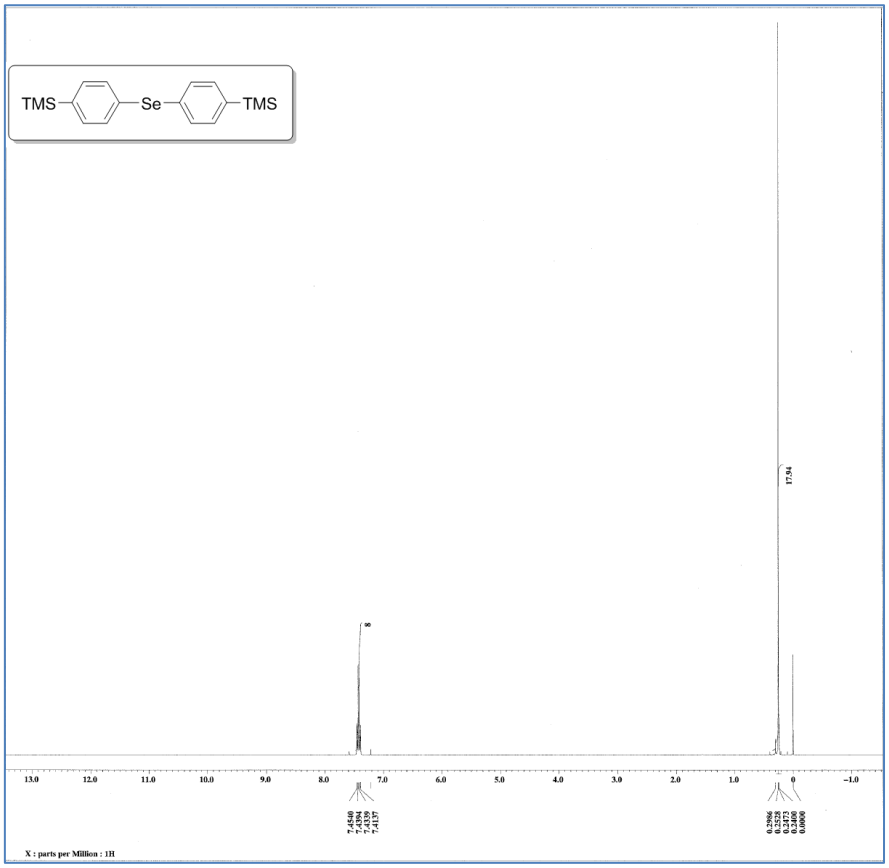


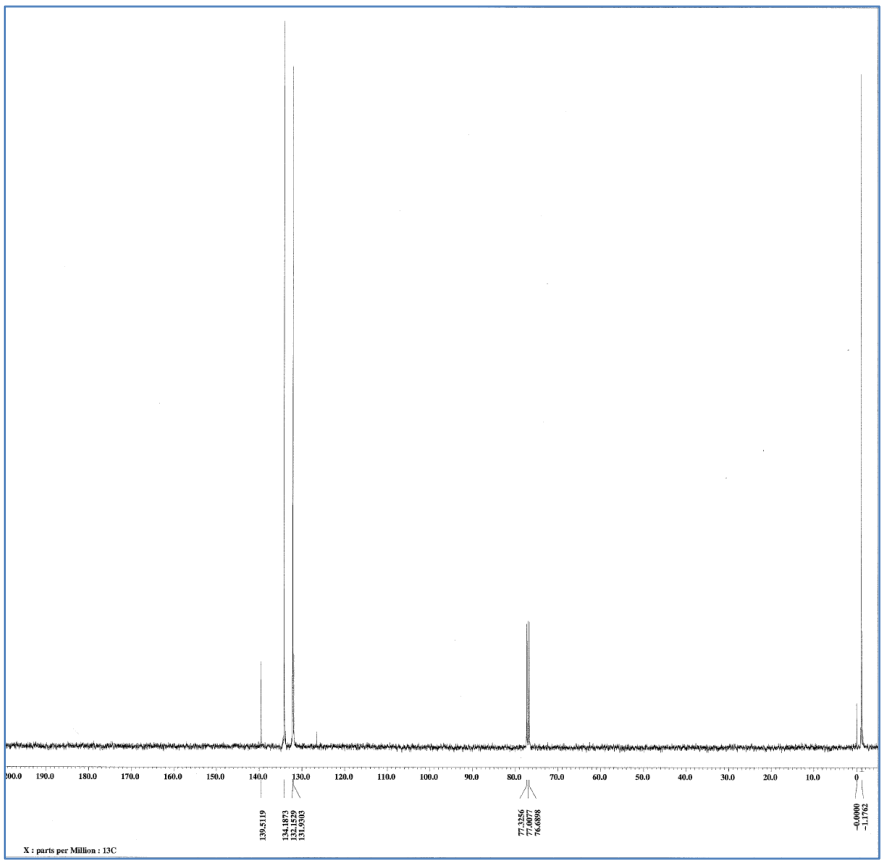

JEOL
---- PROCESSING PARAMETERS ----
dc_balance : 0 : FALSE
zexp : 2.0[Hz] : 0.0[s]
fft : 1 : TRUE : TRUE
zachinsphase
phase : 25 : -40 : 95.21635[%]
ppm
auto_reference : 5[%] : TRUE
reference : 0.001[ppm] : 0[ppm]
Derived from: jj2838e-2.jdf
Filename = jj2838e-14.jdf
Author = delta
Experiment = single_pulse_dec
Sample_id = jj283
Solvent = CHLOROFORM-D
Creation_time = 26-JUN-2014 02:31:49
Revision_time = 27-JUN-2014 17:24:23
Current_time = 27-JUN-2014 17:24:44
Comment = ZW205-34-1...Se
Data_format = 1D COMPLEX
Dim_size = 65536
Dim_title = 77Se
Dim_units = [ppm]
Dimensions = X
Site = EC400
Spectrometer = DELTA_NMR
Field_strength = 9.389766[T] (400[MHz]
X_acq_duration = 0.8585216[s]
X_domain = 77Se
X_freq = 76.24442292[MHz]
X_offset = 650[ppm]
X_points = 65536
X_prescans = 4
X_resolution = 1.16479306[Hz]
X_sweep = 76.33587786[kHz]
Irr_domain = 1H
Irr_freq = 399.78219838[MHz]
Irr_offset = 5[ppm]
Clipped = FALSE
Mod_return = 1
Scans = 540
Total_scans = 540
X_90_width = 10[us]
X_acq_time = 0.8585216[s]
X_angle = 30[deg]
X_pulse = 3.33333333[us]
Initial_wait = 1[s]
Phase_preset = 3[us]
Recvr_gain = 25
Relaxation_delay = 2[s]
Temp_get = 35[dC]
0.8645
0.0000
X : parts per Thousand : 77Se

^{77}Se NMR of reaction mixture of 8a

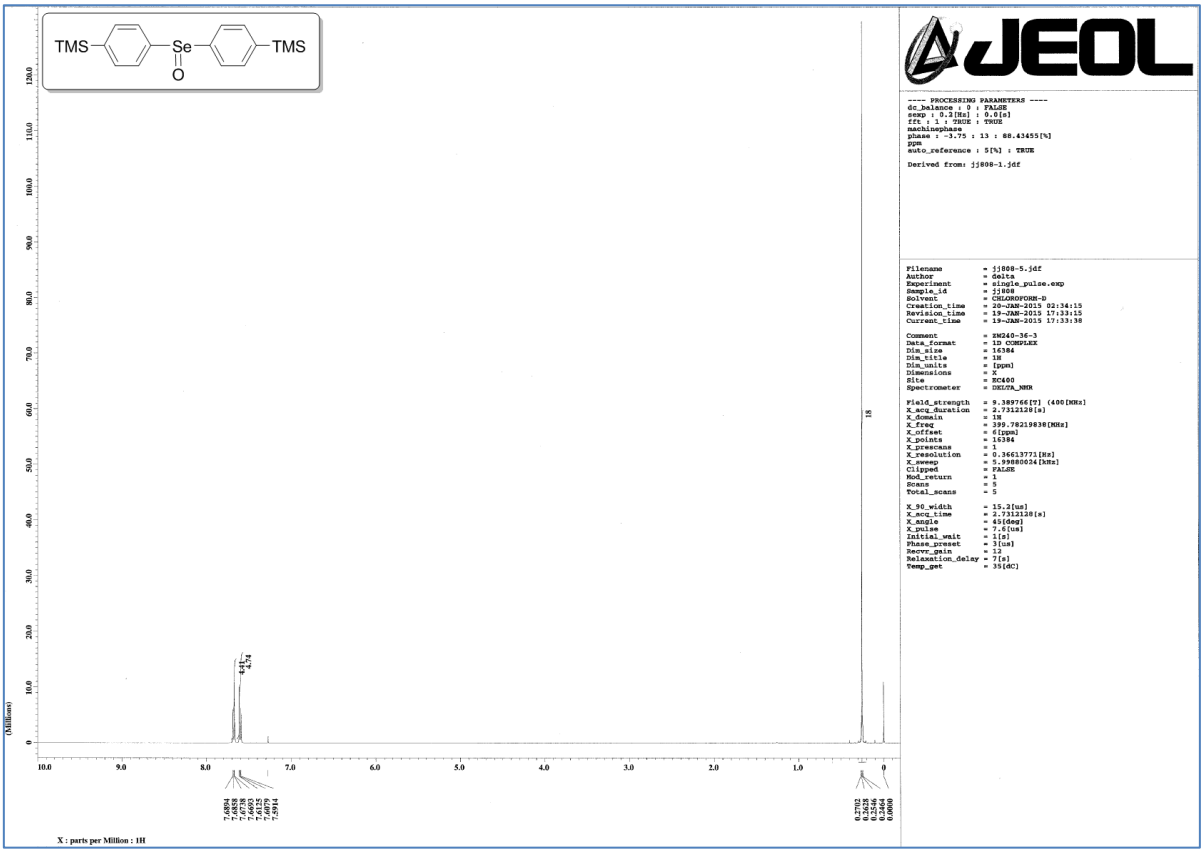


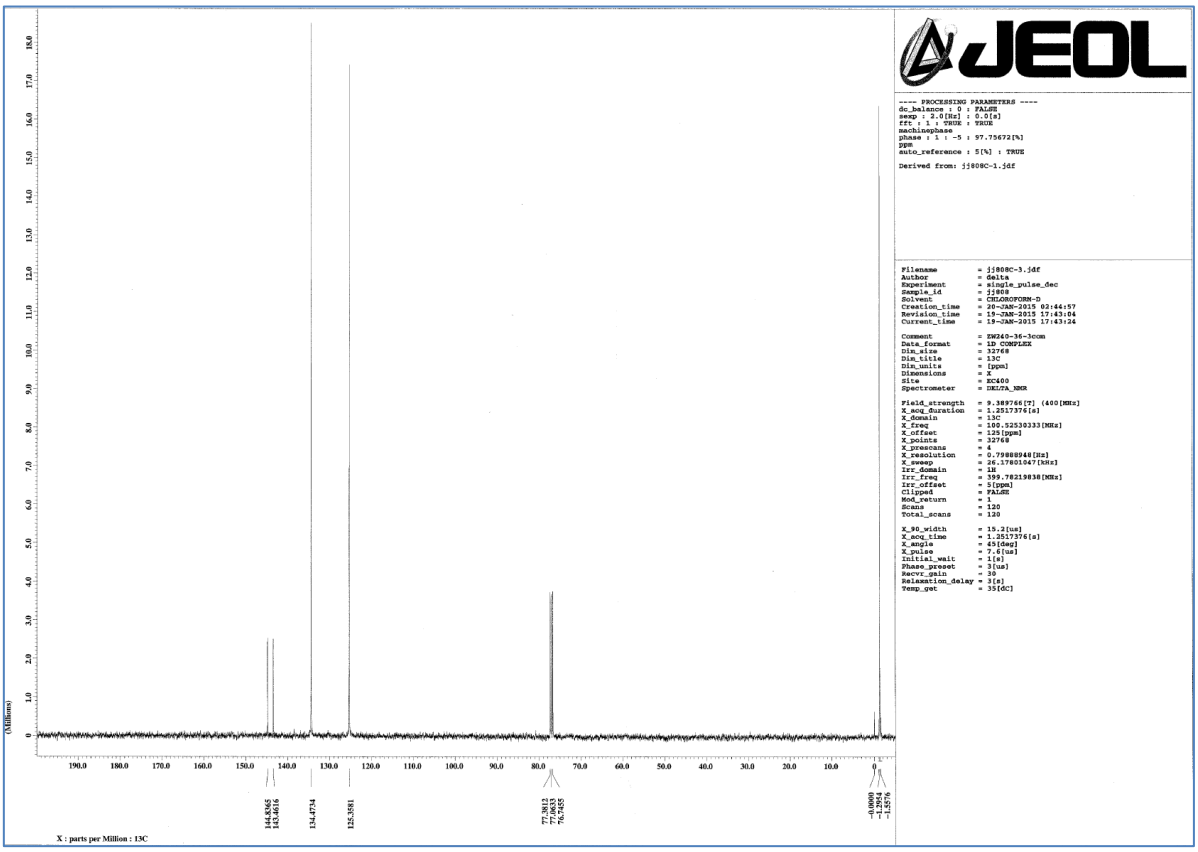
^{1}H and ^{13}C NMR of S1

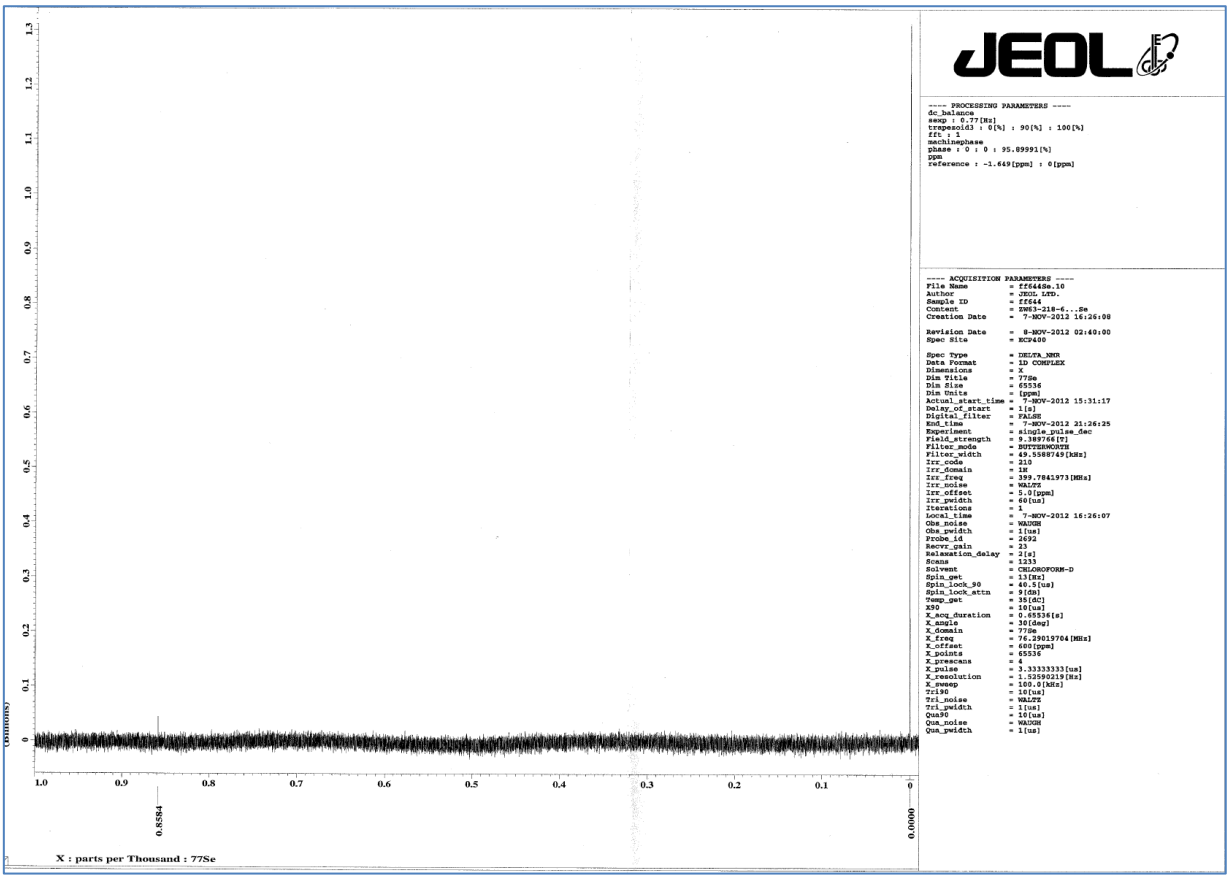




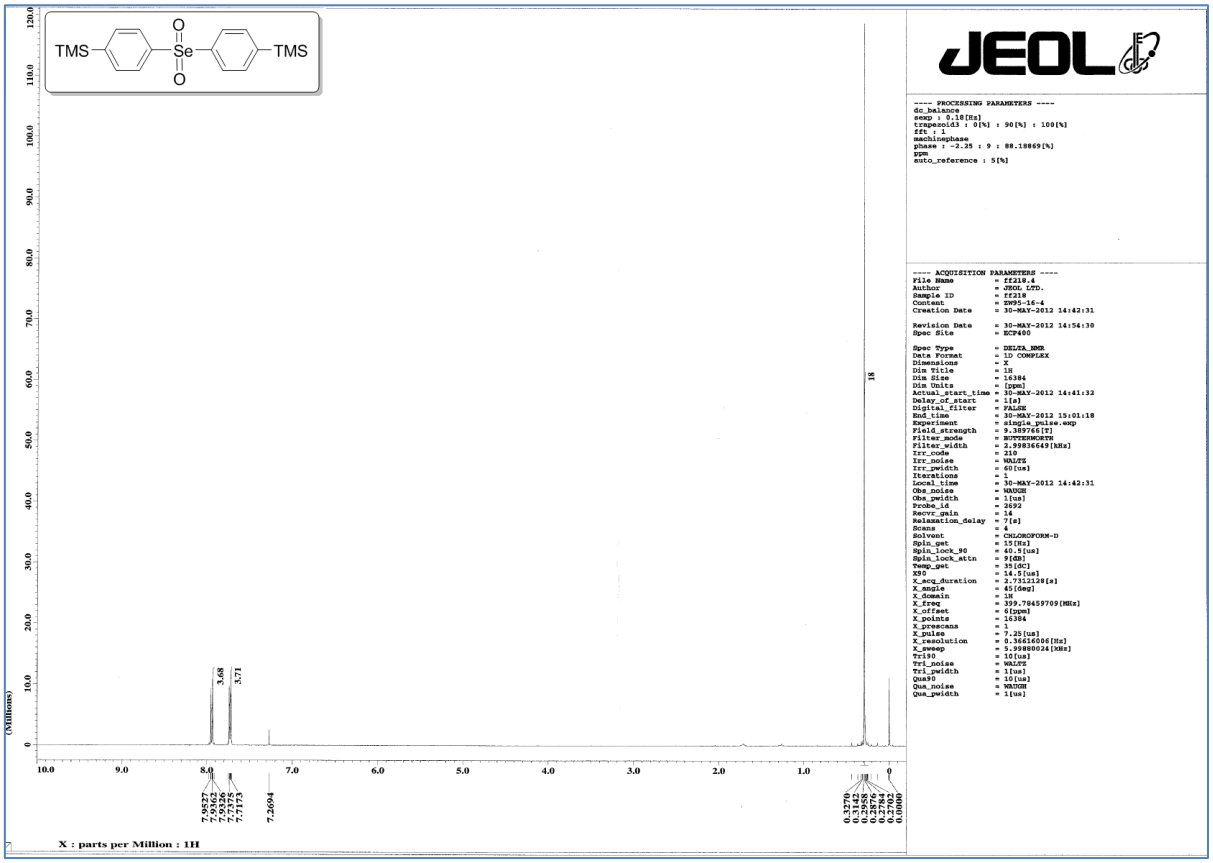
^{1}H, ^{13}C and ^{77}Se NMR of 9

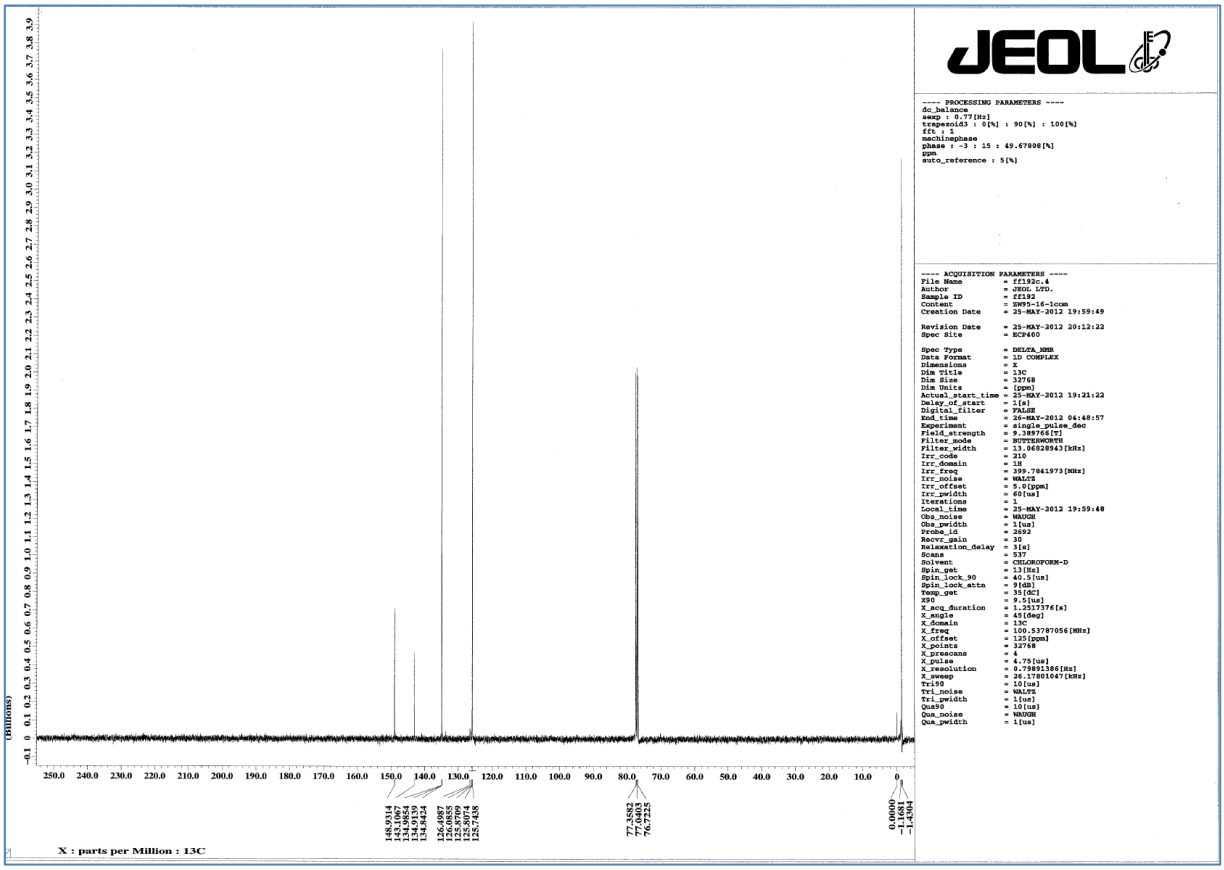


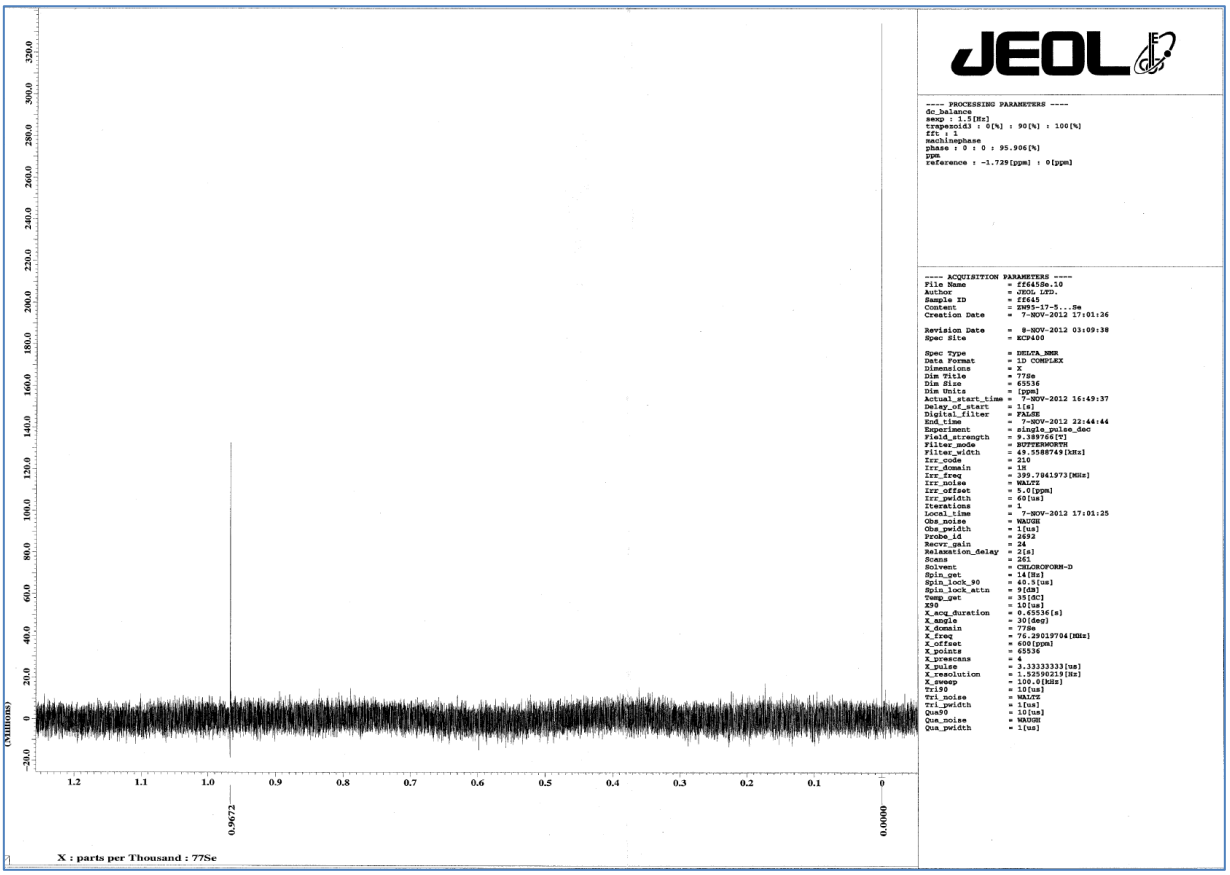



JEOL
---- PROCESSING PARAMETERS ----
dc_balance
exp : 0.77[Hz]
trapezoid3 : 0[%] : 90[%] : 100[%]
fft : 1
machinephase
phase : 0 : 0 : 95.89991[%]
ppm
reference : -1.649[ppm] : 0[ppm]
---- ACQUISITION PARAMETERS ----
File Name = ff644Se.10
Author = JEOL LTD.
Sample ID = ff644
Content = SW53-218-4...Se
Creation Date = 7-NOV-2012 16:26:08
Revision Date = 8-NOV-2012 02:40:00
Spec Site = ECP400
Spec Type = DELTA_NMR
Data Format = 1D COMPLEX
Dimensions = X
Dim Title = 77Se
Dim Size = 65536
Dim Units = [ppm]
Actual_start_time = 7-NOV-2012 15:31:17
Delay_of_start = 1[s]
Digital_filter = FALSE
End_time = 7-NOV-2012 21:26:25
Experiment = single_pulse_dec
Field_strength = 9.389766[T]
Filter_mode = BUTTERWORTH
Filter_width = 49.5588749[kHz]
Irr_code = 210
Irr_domain = 1H
Irr_freq = 399.7841973[MHz]
Irr_noise = WALTZ
Irr_offset = 5.0[ppm]
Irr_pwidth = 60[us]
Iterations = 1
Local_time = 7-NOV-2012 16:26:07
Obs_noise = WALTZ
Obs_pwidth = 1[us]
Probe_id = 2692
Recvr_gain = 23
Relaxation_delay = 2[s]
Scans = 1233
Solvent = CHLOROFORM-D
Spin_set = 13[Hz]
Spin_lock_90 = 49.5[us]
Spin_lock_attn = 9[dB]
Temp_set = 35[DC]
X90 = 10[us]
X_acq_duration = 0.65536[s]
X_angle = 30[deg]
X_domain = 77Se
X_freq = 76.29019704[MHz]
X_offset = 600[ppm]
X_points = 65536
X_prescans = 4
X_pulse = 3.33333333[us]
X_resolution = 1.52590219[Hz]
X_sweep = 100.0[kHz]
Tri90 = 10[us]
Tri_noise = WALTZ
Tri_pwidth = 1[us]
Qua90 = 10[us]
Qua_noise = WALTZ
Qua_pwidth = 1[us]
(Normal)
1.3
1.2
1.1
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
0.8584
0.0000
X : parts per Thousand : 77Se

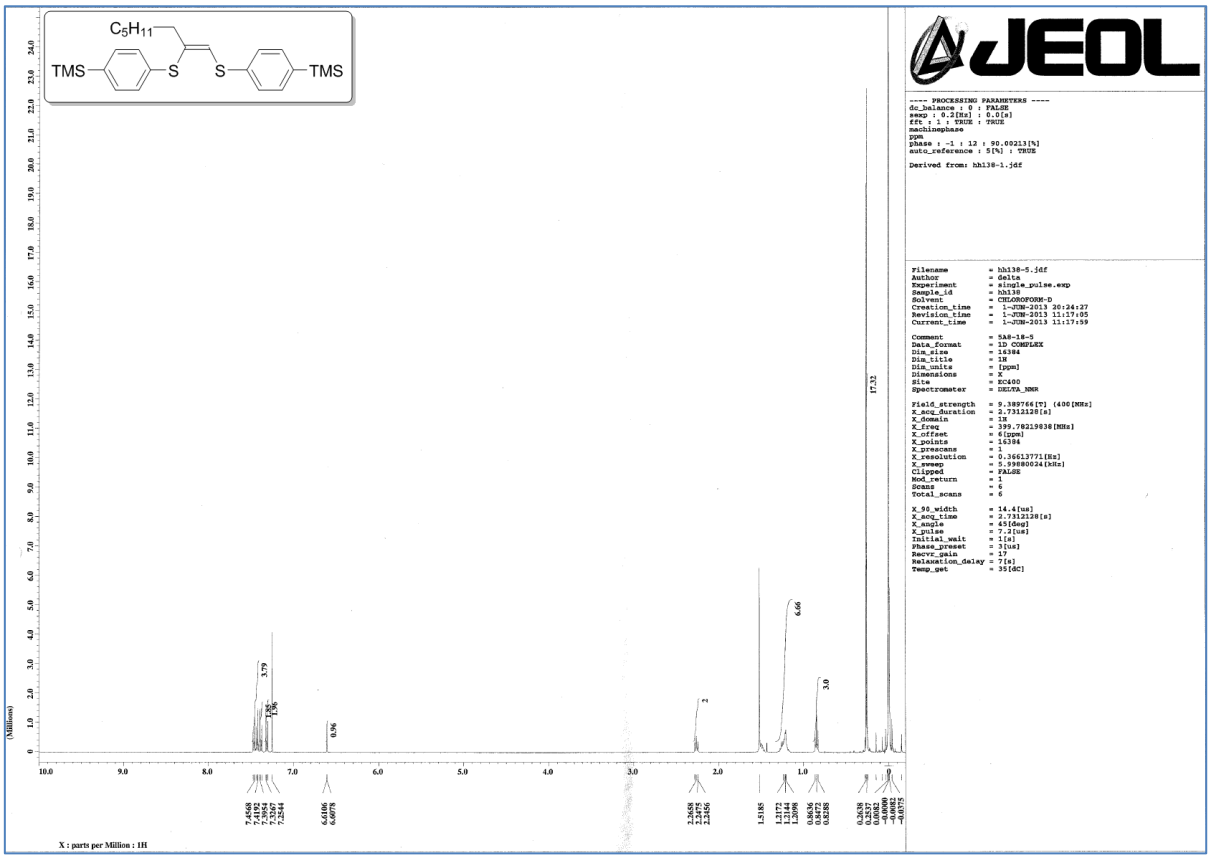
^{1}H, ^{13}C and ^{77}Se NMR of 10

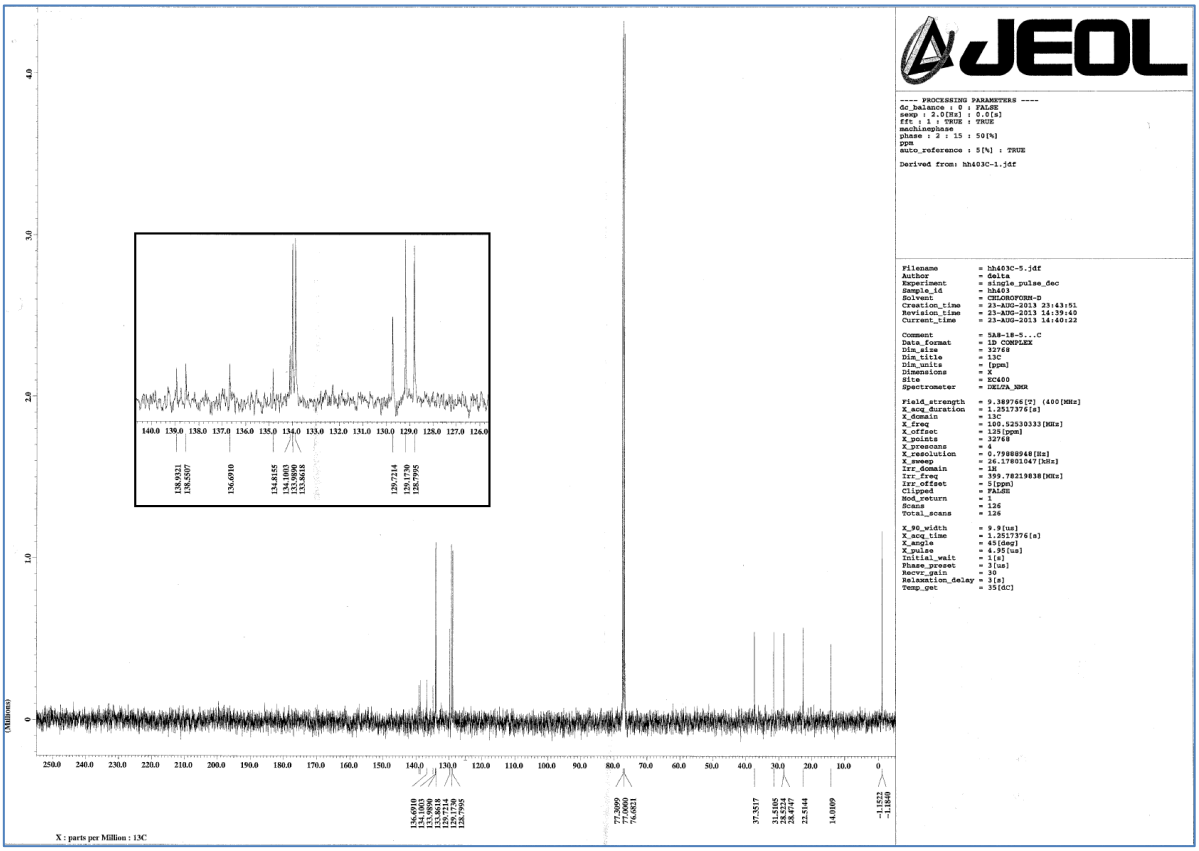




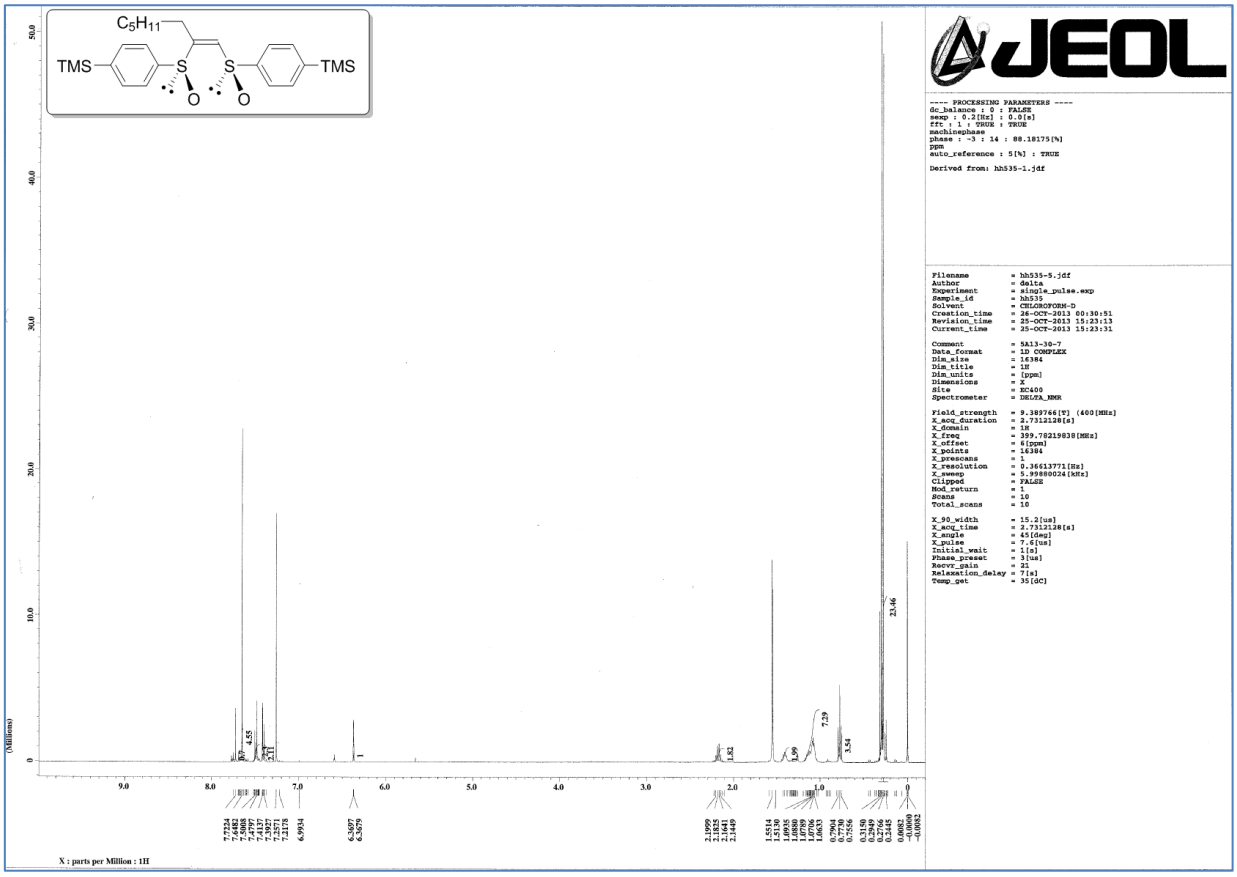

JEOL
---- PROCESSING PARAMETERS ----
dc_balance
sexp : 1.5[Hz]
trapezoid1 : 0[%] : 90[%] : 100[%]
fft : 1
machinephase
phase : 0 : 0 : 95.906[%]
ppm
reference : -1.729[ppm] : 0[ppm]
---- ACQUISITION PARAMETERS ----
File Name = ff645de.10
Author = JEOL LTD.
Sample ID = ff645
Content = EN95-17-5...Se
Creation Date = 7-NOV-2012 17:01:36
Revision Date = 8-NOV-2012 03:09:38
Spec Site = ECP400
Spec Type = DELTA_NMR
Data Format = 1D COMPLEX
Dimensions = X
Dim Title = 77Se
Dim Size = 65536
Dim Units = [ppm]
Actual_start_time = 7-NOV-2012 16:49:37
Delay_of_start = 1[s]
Digital_filter = FALSE
End_time = 7-NOV-2012 22:44:44
Experiment = single_pulse_dec
Field_strength = 9.389766[T]
Filter_mode = BUTTERWORTH
Filter_width = 49.5588749[kHz]
Irr_code = 210
Irr_domain = 1H
Irr_freq = 399.7841973[MHz]
Irr_noise = WALTZ
Irr_offset = 5.0[ppm]
Irr_pwidth = 60[us]
Iterations = 1
Local_time = 7-NOV-2012 17:01:25
Obs_noise = WAUGH
Obs_pwidth = 1[us]
Probe_id = 2692
Recvr_gain = 24
Relaxation_delay = 2[s]
Scans = 261
Solvent = CHLOROFORM-D
Spin_get = 14[Hz]
Spin_lock_90 = 40.5[us]
Spin_lock_attn = 9[dB]
Temp_get = 35[SC]
X90 = 10[us]
X_acq_duration = 0.65536[s]
X_angle = 30[deg]
X_domain = 77Se
X_freq = 76.29019704[MHz]
X_offset = 600[ppm]
X_points = 65536
X_prescans = 4
X_pulse = 3.33333333[us]
X_resolution = 1.52590219[Hz]
X_sweep = 100.0[kHz]
Tri90 = 10[us]
Tri_noise = WALTZ
tri_pwidth = 1[us]
Qua90 = 10[us]
Qua_noise = WAUGH
Qua_pwidth = 1[us]
(Millions)
320.0
300.0
280.0
260.0
240.0
220.0
200.0
180.0
160.0
140.0
120.0
100.0
80.0
60.0
40.0
20.0
0
-20.0
1.2
1.1
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
0.9672
0.0000
X : parts per Thousand : 77Se

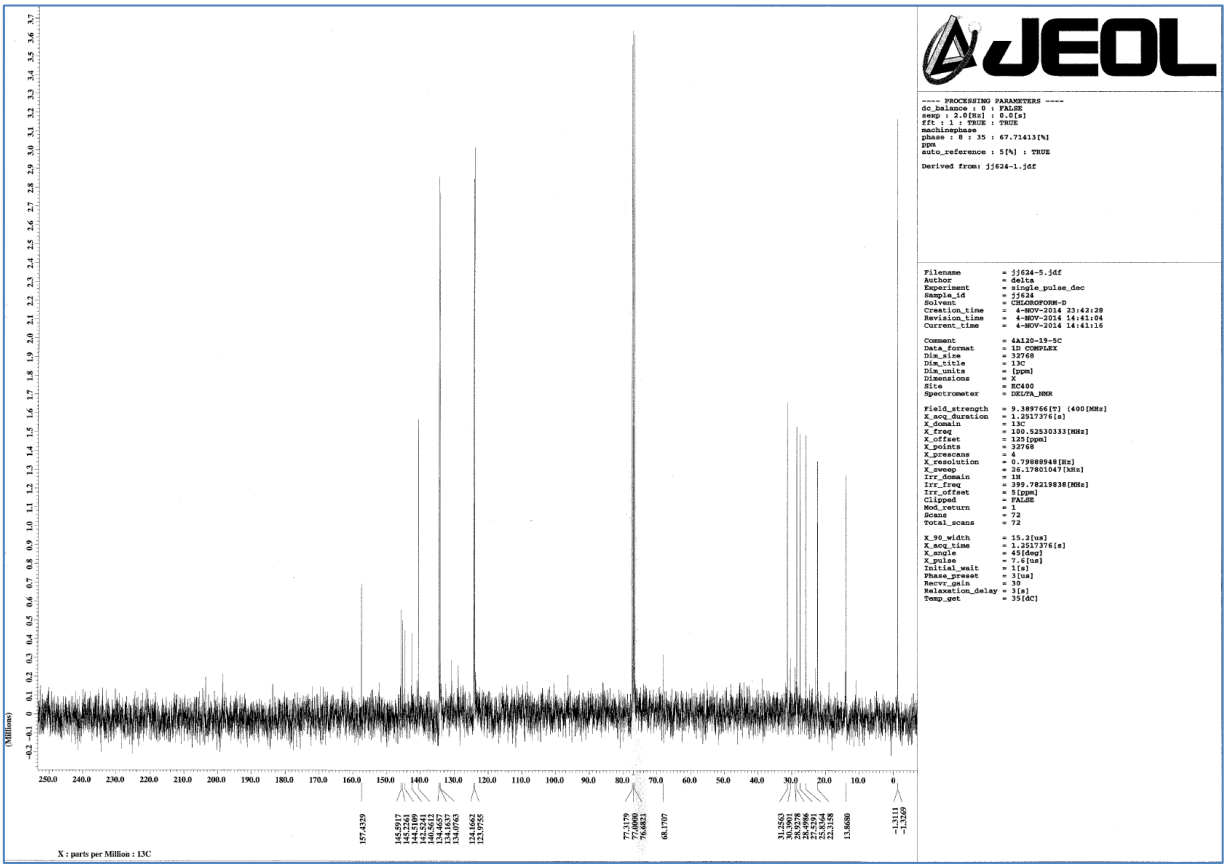
^{1}H and ^{13}C NMR of 14



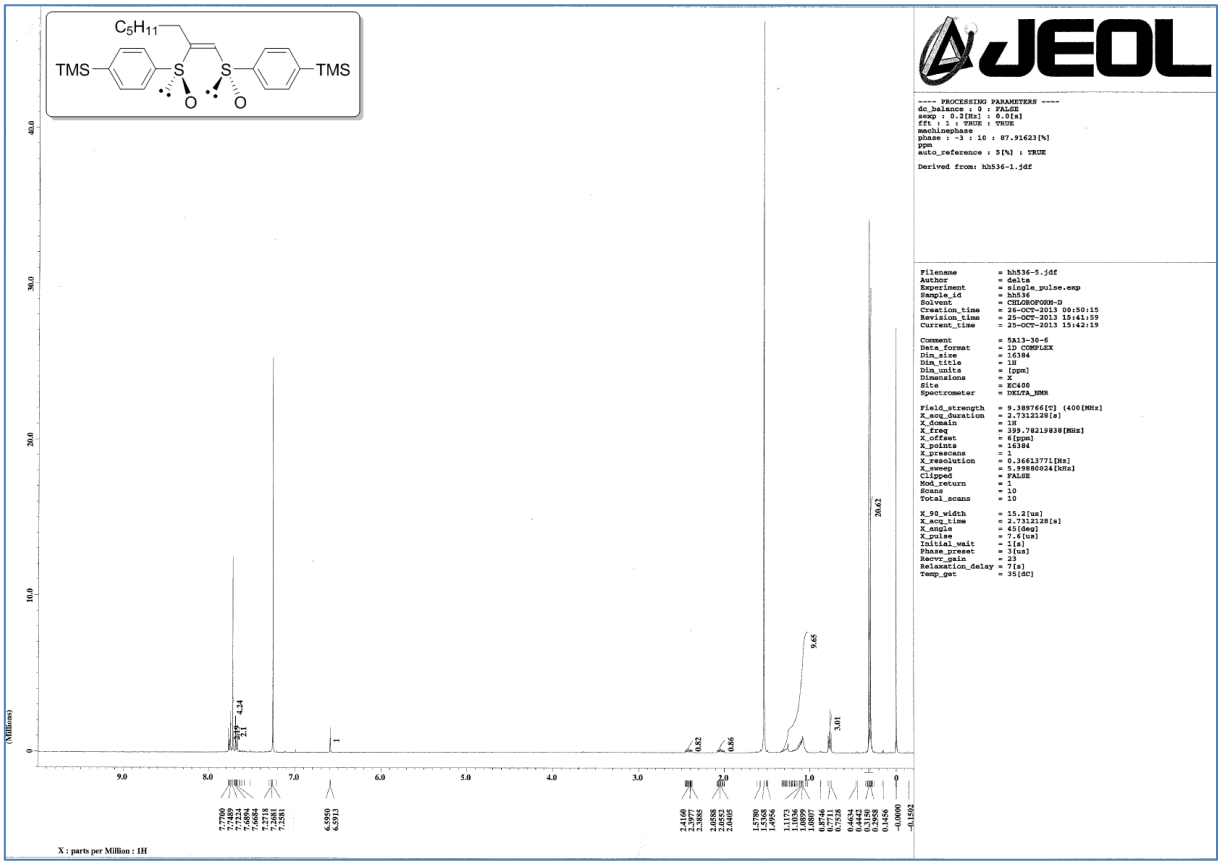


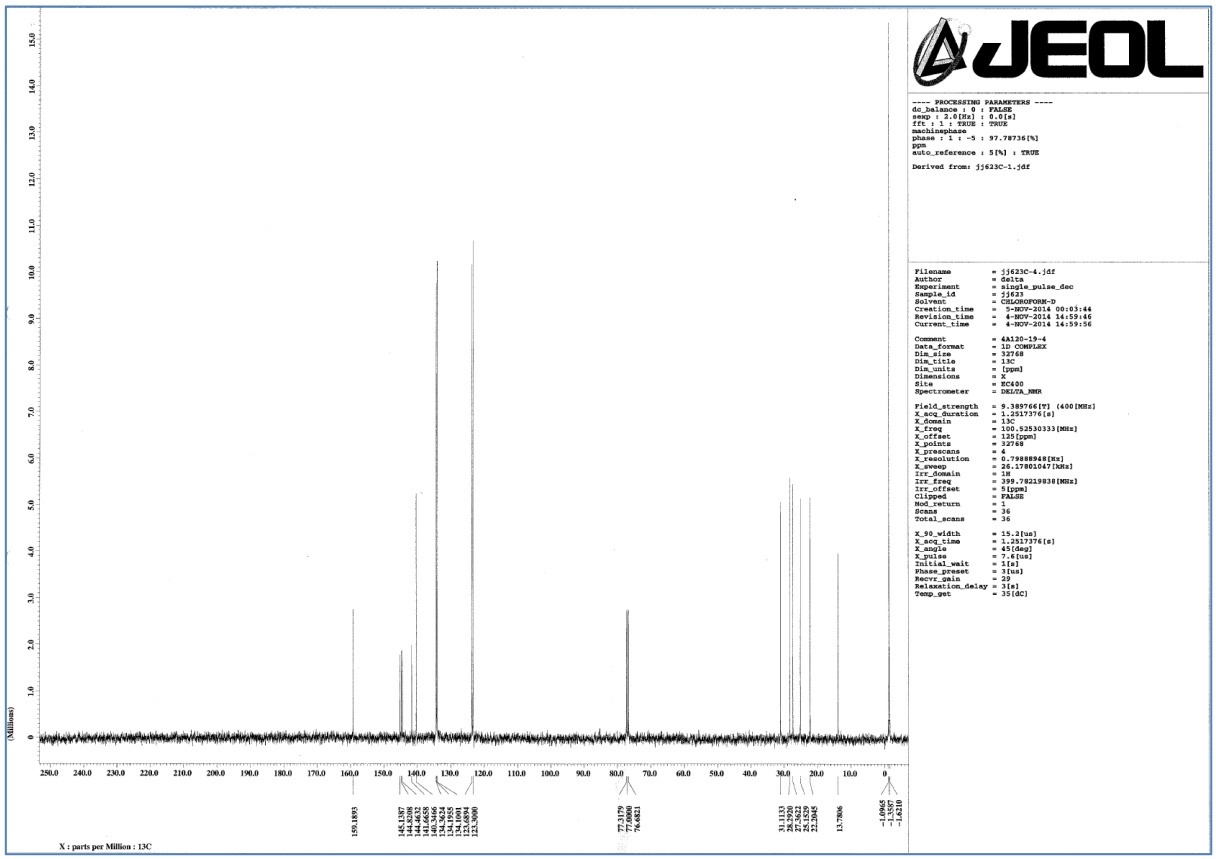
^{1}H and ^{13}C NMR of 15



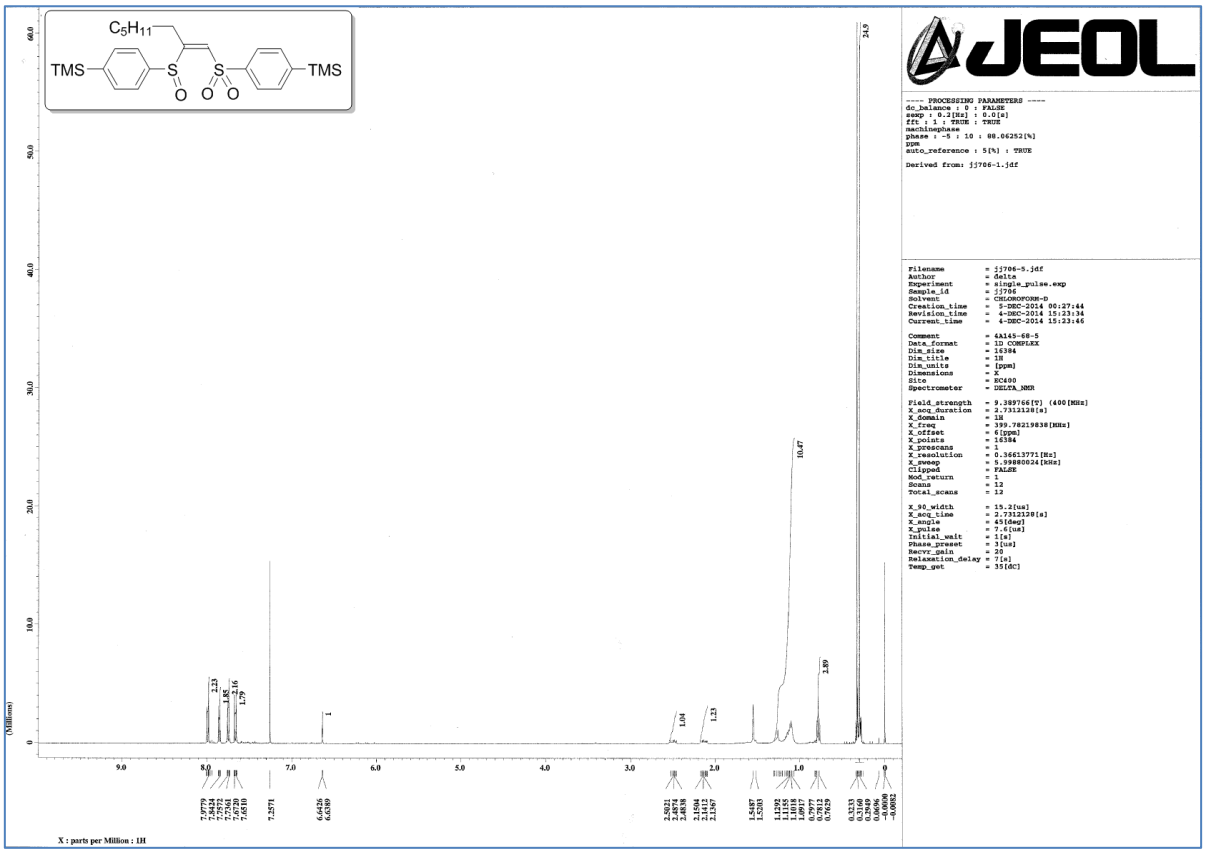


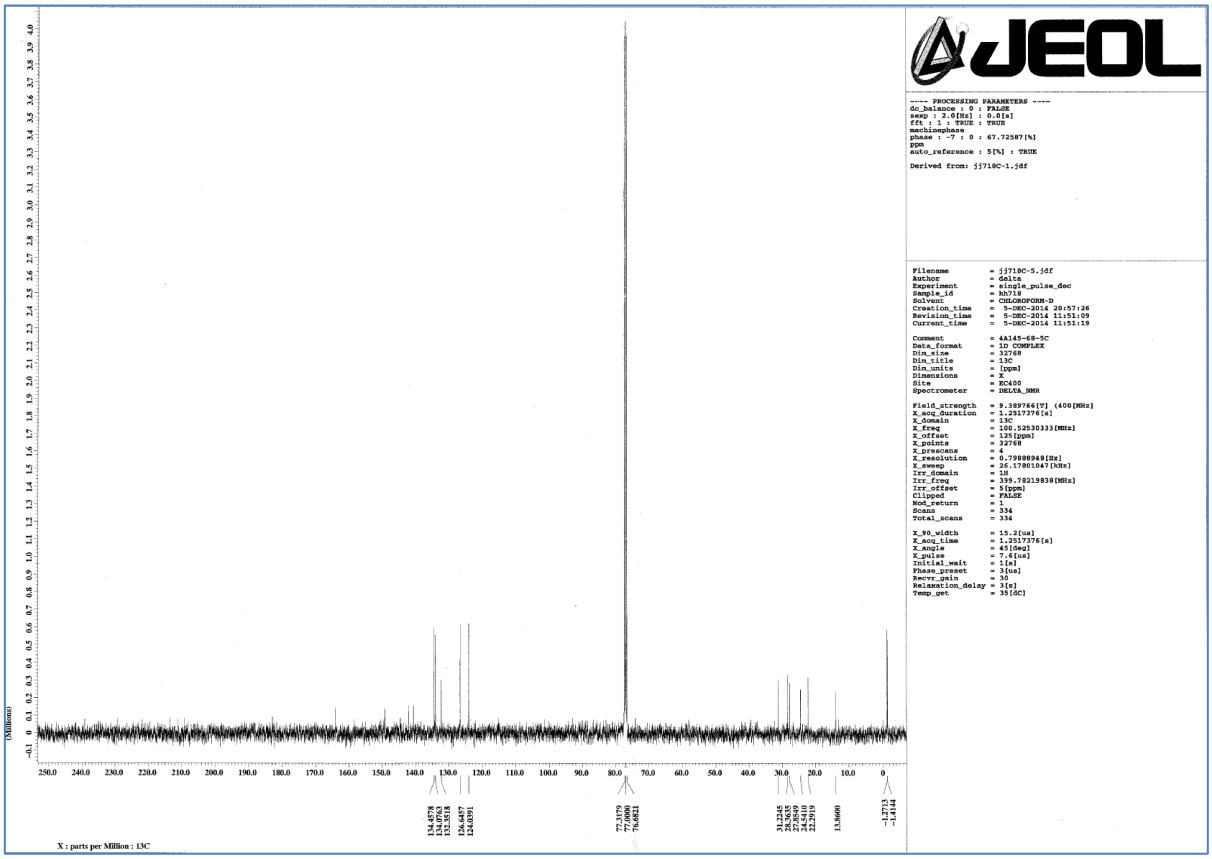
^{1}H and ^{13}C NMR of 15’





^{1}H and ^{13}C NMR of 16





^{1}H and ^{13}C NMR of 17