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Acidic Hierarchical Zeolite ZSM-5 Supported Ru Catalyst with High Activity and Selectivity in Seleno-functionalization of Alkenes

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1. Figures

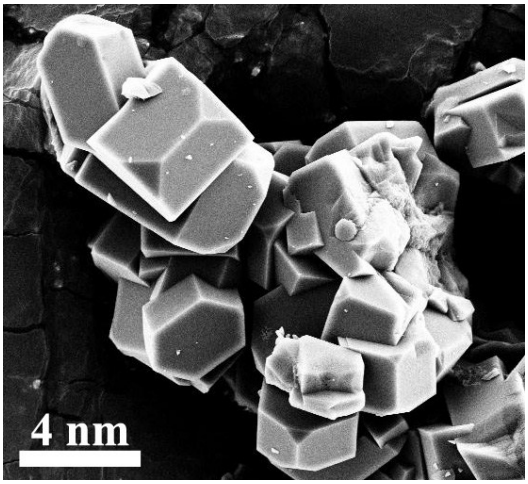


Fig. S1 SEM image of the microporous zeolite ZSM-5

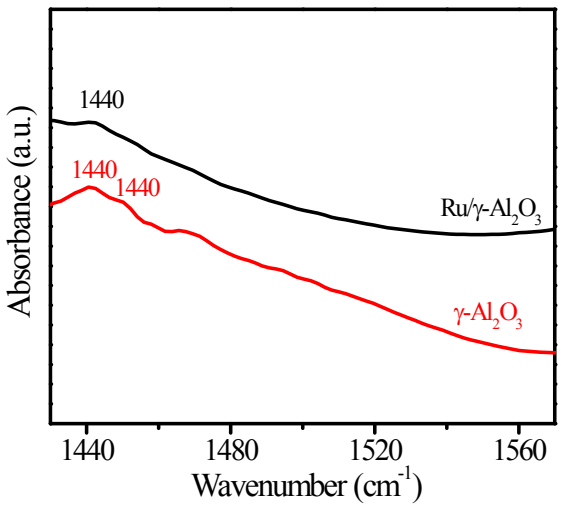


Fig. S2 Py-IR spectra of the γ-Al_2O_3 and Ru/γ-Al_2O_3 samples.

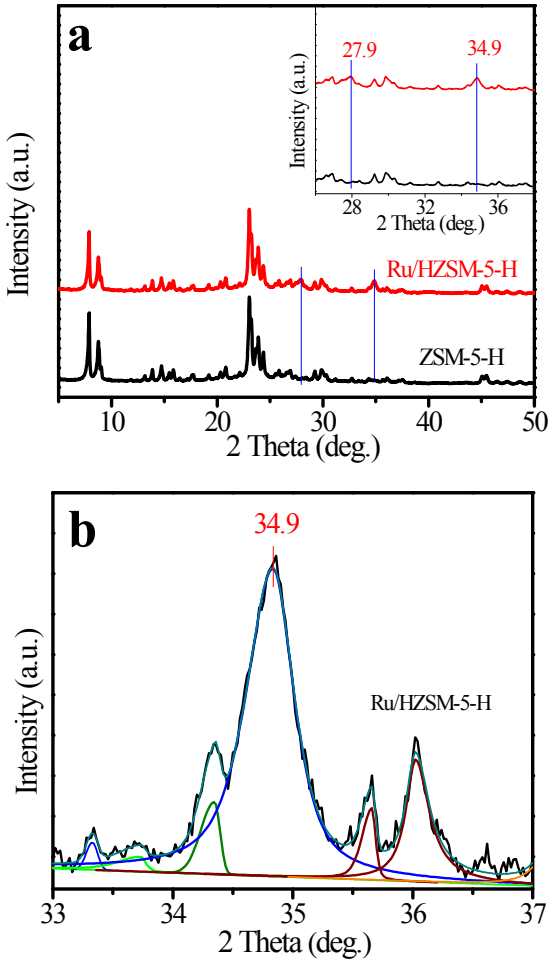


Fig. S3 (a) XRD patterns of ZSM-5-H and Ru/HZSM-5-H samples, and (b) the peak fitting of XRD patterns of Ru/HZSM-5-H between diffraction peaks at 2θ=33-37°.

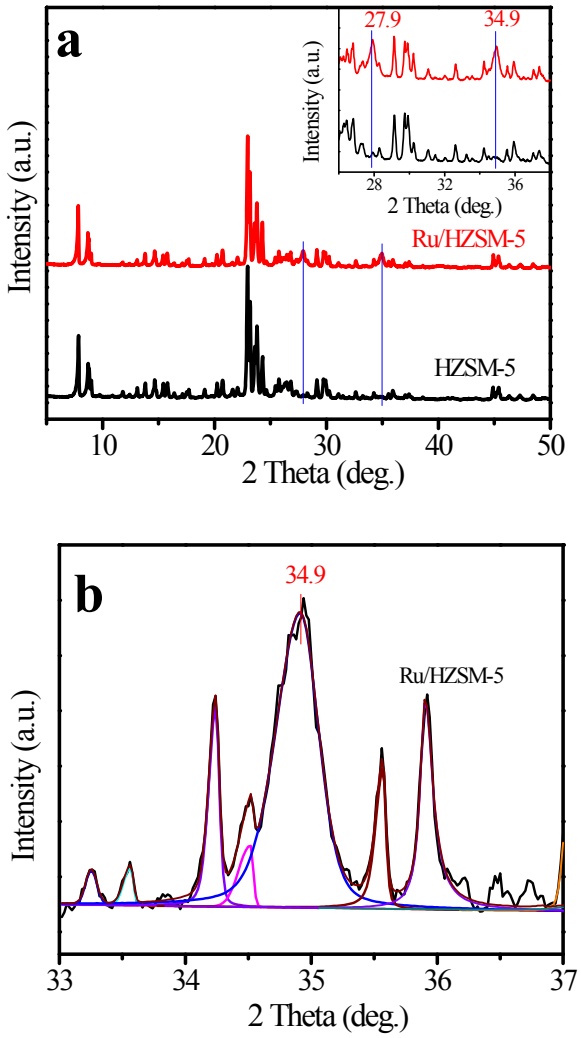


Fig. S4 XRD patterns of ZSM-5 and Ru/HZSM-5 samples, and (b) the peak fitting of XRD patterns of Ru/HZSM-5-H between diffraction peaks at 2θ=33-37°

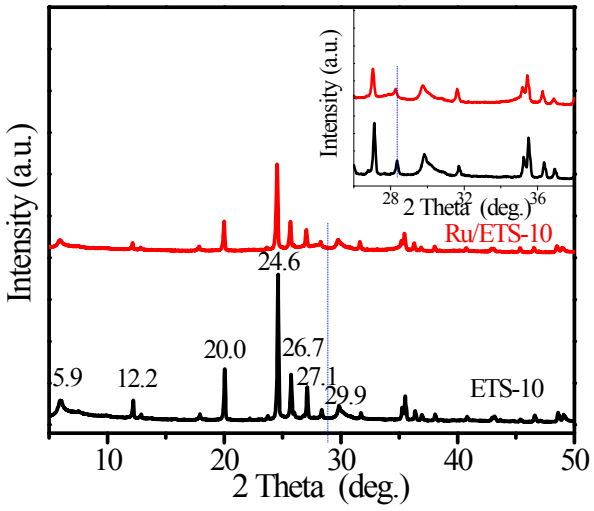


Fig. S5 XRD patterns of ETS-10 and Ru/ETS-10 samples.

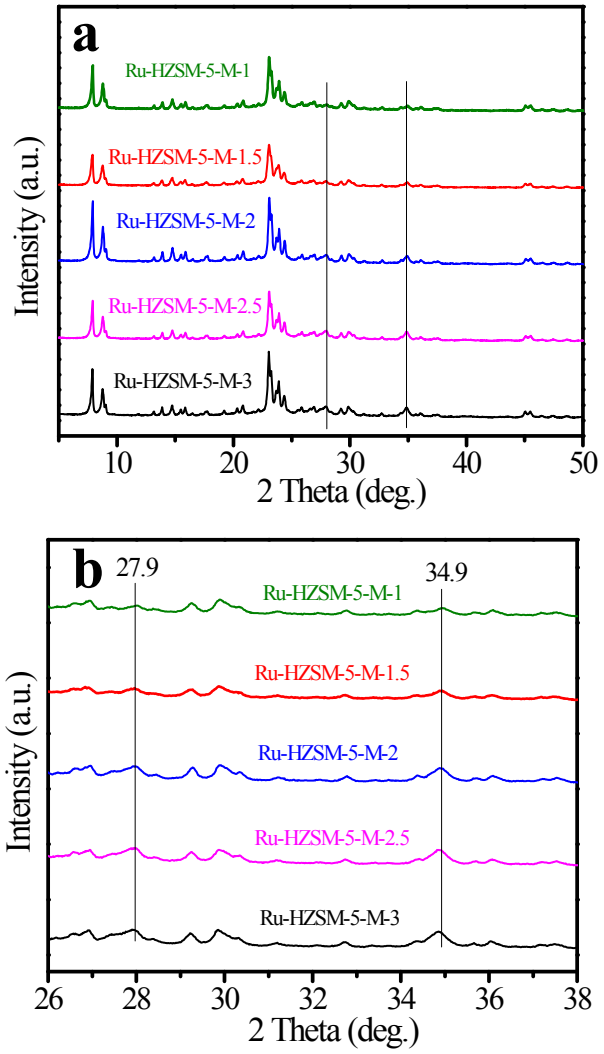


Fig. S6. XRD patterns of the HZSM-5-H supported Ru catalysts.

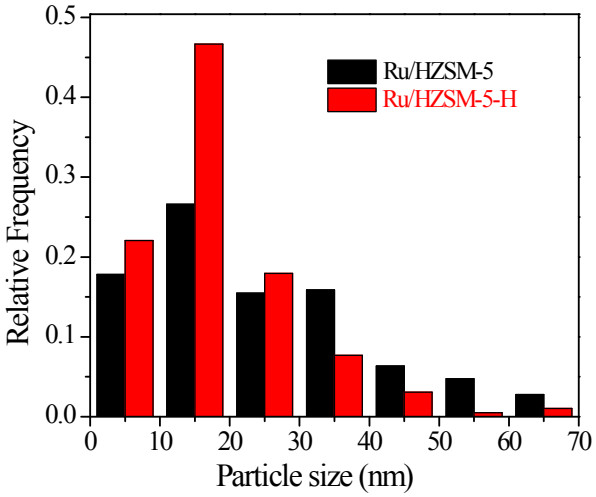


Fig. S7 The size distributions of the RuO_2 particles on the Ru/HZSM-5-H and Ru/HZSM-5 catalysts.

Discussion: The size distributions of the RuO_2 in the catalyst were also obtained by statistical analyses from at least 20 images of 150-200 RuO_2 particles from different regions of each catalyst. The average RuO_2 particle size ($D_{aver.}$) was also calculated according to following equation:

$$D_{aver.} = \frac{\sum_{i=1}^{n} d_i}{n_i}$$

where n_i is the number of the RuO_2 particles and d_i is the size of each RuO_2 particle. **Fig. S5** shows the size distributions of the RuO_2 particle size distribution on the Ru/HZSM-5 and Ru/HZSM-5-H sample. The particle size of RuO_2 on mainly ranges from 1 to 40 nm, while that on Ru/HZSM-5-H samples are mainly 1-30 nm. Based on the data in **Fig. S5**, the average RuO_2 particle size ($D_{aver.}$) was calculated, the $D_{aver.}$ is 17.9 nm on the Ru/HZSM-5-H, while that is 23.3 nm on Ru/HZSM-5 catalyst.

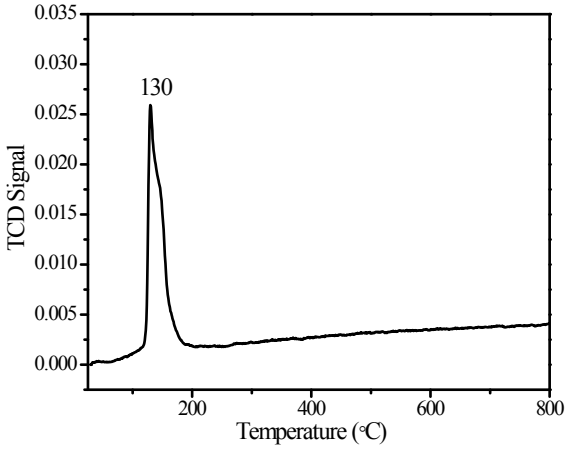


Fig. S8. H_2-TPR profile of the calcined Ru/HZSM-5-H catalyst.

Discussion: H_2-TPR profile shows one reduction peak at 130 °C, which should be attributed to the reduction of Ru species.

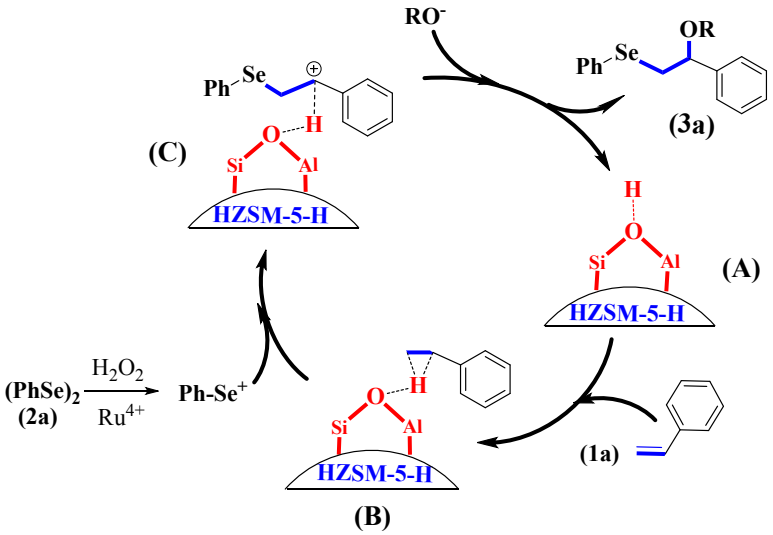


Fig. S9. Possible reaction mechanism on Ru/HZSM-5-H catalyst.

Discussion: The seleno-functionalization of styrene with hydroxyl, alkoxy and carbethoxy nucleophilic reagents on Ru/HZSM-5-H is illustrated in **Fig. S8**. Firstly, the C=C bond in styrene (**1a**) could be activated through the C=C bond interacting with H^+ site on Ru/HZSM-5-H catalyst to form an intermediate **B**. Simultaneously, the Ru^{4+} species facilitate the transformation from diaryl diselenides (**2a**) to electrophilic selenium species under the H_2O_2 oxidizing agent, and electrophilic selenium species attack the activated C=C bond in styrene to form intermediate **C.** Finally, the nucleophilic reagents react with intermediate **C** to generate the final target product **3a**.

2. Tables

Table S1. Texture parameters of all catalyst samples.

Sample	S_{BET} (m^2/g)[a]	S_{ext} (m^2/g)[b]	V_{mic} (cm^3/g)[c]	V_{meso} (cm^3/g)[d]	Si/Al(Ti)
ZSM-5-H	460	208	0.11	0.47	36
ZSM-5	392	45	0.12	0.03	30
HZSM-5-H	408	167	0.08	0.45	35
HZSM-5	376	43	0.11	0.03	31
ETS-10	316	18	0.09	0.03	7
γ-Al_2O_3	354	311	-	0.88	-
Ru/HZSM-5-H	392	162	0.08	0.40	-
Ru/HZSM-5	343	37	0.11	0.03	-
Ru/ETS-10	305	22	0.11	0.03	-
Ru/γ-Al_2O_3	359	332	0.02	0.83	-

[a]BET surface area. [b]External surface area, including mesoporous surface area. [c]Microporous volume. [d]Mesoporous volume.

Table S2 Total acidities and the acidic sites distributions of the supports and catalysts

Catalyst	Weak acidic sites (μmol/g)[a]	Medium acidic sites (μmol/g)[b]	Strong acidic sites (μmol/g)[c]	Total acidic sites (μmol/g)[d]
γ-Al_2O_3	317	163	-	480
HZSM-5-H	227	153	120	500
HZSM-5	287	164	129	580
Ru/γ-Al_2O_3	-	-	-	340
Ru/HZSM-5-H	-	-	-	420
Ru/HZSM-5	-	-	-	480

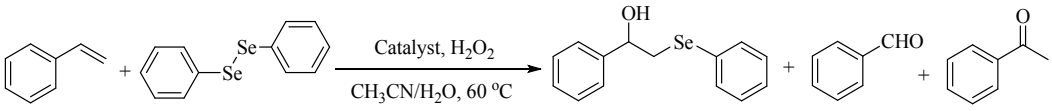
[a] Weak acidic sites estimated from the relative area of the deconvoluted peak.

[b] Medium acidic sites estimated from the relative area of the deconvoluted peak.

[c] Strong acidic sites estimated from the relative area of the deconvoluted peak.

[d] Total acidic site determined by titration technique.

Table S3. Hydroxyselenation of styrene with diaryl diselenide over a series of catalysts.

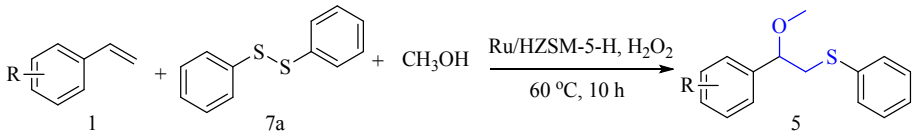


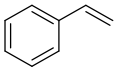
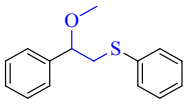
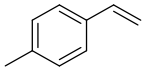
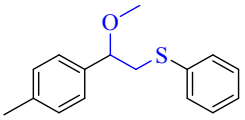
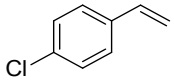
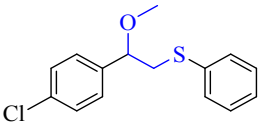
1a **2a** **3a** **3a'** **3a''**

Entry	Catalyst	Conversion (%)	Selectivity (%)		
			3a	**3a′**	**3a″**
1	Ru/HZSM-5-H-1	70	85	8	7
2	Ru/HZSM-5-H-1.5	73	86	8	6
3	Ru/HZSM-5-H-2	90	80	5	15
4	Ru/HZSM-5-H-2.5	92	90	6	11
5	Ru/HZSM-5-H-3	94	94	4	2

[a]Reaction conditions: catalysts (25 mg), styrene **1a** (1.0 mmol), diaryl diselenides **2a** (0.6 mmol), H_2O_2 (1.5 mmol, 30% aqueous solution), acetonitrile (1 mL) and H_2O (1 mL) were placed in a sealed tube (10 mL). The reaction was proceeded at 60 °C for 7 h.

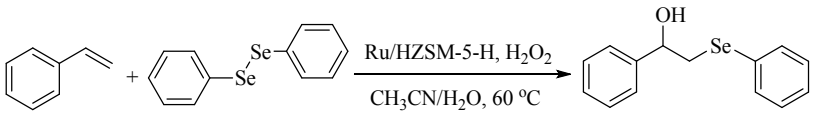
Table S4. Alkoxysulfennylation of styrenes with diaryl disulfides in the presence of methanol over Ru/HZSM-5-H catalyst.[a]



Entry	Alkenes	Products	Conv. (%)
1		 **5a**	75 (83)
2		 **5b**	82 (88)
3		 **5c**	88 (84)

[a]Reaction condition: 25 mg solid catalyst, styrene (1.0 mmol), diaryl disulfides (0.6 mmol), H_2O_2 (1.5 mmol), methanol (2.0 mL), 60 °C for 10 h. The data out of parenthesis is conversion, and in parenthesis is selectivity.

Table S5. The reusability of the catalyst. [a]

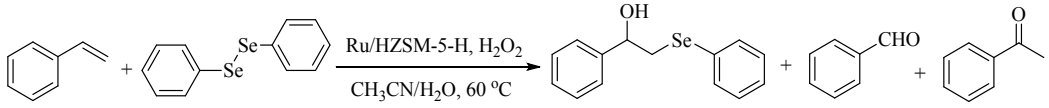


1a **2a** **3a**

Entry	Recycle	Conversion (%)	Selectivity (%)
1	Run 1	94	95
2	Run 2	94	94
3	Run 3	92	93
4	Run 4	90	92
5	Run 5	89	91
6	Run 6	90	90
7	Run 7	90	91

[a] Reaction condition: 25 mg solid catalyst, styrene (1.0 mmol), diaryl diselenides (0.6 mmol), H_2O_2 (1.5 mmol), H_2O (1.0 mL), CH_3CN (1.0 mL), reaction time of 7 h. The yield was analyzed by LC. The spend catalyst was carefully collected, washed with acetonitrile 10 times, and dried at 120 °C for 10 h, and followed by calcination at 450 °C in air for next recycle.

Table S6. Hydroxyselenation of styrene with diaryl diselenide over Ru/HZSM-5-H catalyst.[a]

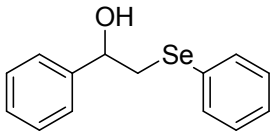


1a **2a** **3a** **3a'** **3a''**

Entry	Catalyst	Conv. (%)[b]	Selectivity (%)[c]			Error bars	
			3a	**3a′**	**3a″**	Conv.	Selectivity
1	Ru/HZSM-5-H	94	95	2	3	0.41	0.48
2	Ru/HZSM-5-H	93	93	4	3		
3	Ru/HZSM-5-H	95	93	3	3		
4	Ru/HZSM-5-H	94	94	4	2		

[a]Reaction condition: 25 mg solid catalyst, styrene **1a** (1.0 mmol), diaryl diselenides **2a** (0.6 mmol), H_2O_2 (1.5 mmol), H_2O (1.0 mL), CH_3CN (1.0 mL), 7 h.

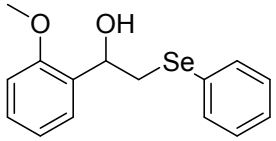
3. Analytical data



(3a) 1-phenyl-2-(phenylselanyl)ethanol

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45-7.38 (m, 2H), 7.24-7.10 (m, 8H), 4.63 (dt, *J* = 3.2, 6.4 Hz, 1H), 3.18 (dd, *J* = 4.0, 12.8 Hz, 1H), 3.04 (dd, *J* = 9.6, 12.8 Hz,1H), 2.86 (d, *J* = 2.4 Hz, 1H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 142.3, 132.9, 132.8, 129.1, 128 .4, 127.8, 127.2, 125.7, 72.1, 38.2.

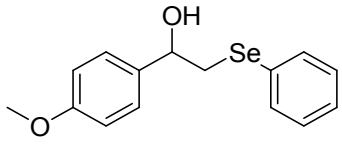


(3b) 1-(2-methoxyphenyl)-2-(phenylselanyl)ethanol

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45-7.38 (m, 2H), 7.33 (d, *J* = 7.6 Hz, 1H), 7.18-7.08 (m, 4H), 6.87

(t, *J* = 7.6 Hz, 1H), 6.72 (d, *J* = 8.0 Hz, 1H), 4.98-4.90 (m, 1H), 3.66 (s, 3H), 3.35 (dd, *J* = 4.0, 12.8 Hz, 1H), 3.07-2.95 (m, 2H);

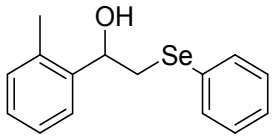
^{13}C NMR (100 MHz, $CDCl_3$) δ 155.9, 132.1, 130.3, 129.8, 128.8,128.5, 126.6, 126.5, 120.6, 110.1, 68.7, 55.0, 35.8.



(3c) 1-(4-methoxyphenyl)-2-(phenylselanyl)ethanol

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.58-7.49 (m, 2H), 7.31-7.22 (m, 5H), 6.90-6.82 (m, 2H), 4.73 (dt, *J* = 3.3, 6.6 Hz, 1H), 3.79 (s, 3H), 3.30 (dd, *J* = 3.9, 12.9 Hz, 1H), 3.17 (dd, *J* = 9.3, 12.6 Hz, 1H);

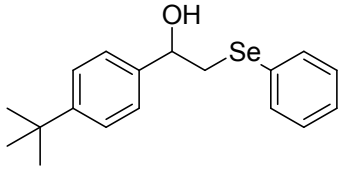
^{13}C NMR (100 MHz, $CDCl_3$) δ 159.2, 134.5, 133.0, 129.2, 128.1, 127.3, 127.0, 113.8, 71.8, 55.2, 38.3.



(3d) 2-(phenylselanyl)-1-(o-tolyl)ethanol

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60-7.54 (m, 2H), 7.52 (d, *J*=7.6 Hz, 1H), 7.31-7.22 (m, 3H), 7.21 (t, *J* = 7.6 Hz, 1H), 7.16 (d, *J* = 7.6 Hz, 1H), 7.09 (d, *J* = 7.6 Hz, 1H), 4.92 (dt, *J* = 2.4, 4.8 Hz, 1H), 3.25 (dd, *J* =2.8, 12.8 Hz, 1H), 3.04 (dd, J= 10.0, 12.8 Hz, 1H), 2.80 (d, *J* = 2.4 Hz, 1H), 2.11 (s, 3H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 140.3, 134.3, 133.4, 130.3, 129.1, 128.8, 127.57, 127.52, 126.3, 125.0, 68.6, 37.4, 18.7.

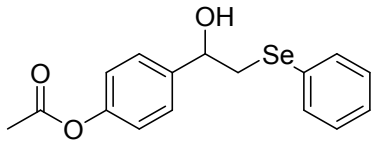


(3e) 1-(4-(tert-butyl)phenyl)-2-(phenylselanyl)ethanol

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55-7.48 (m, 2H), 7.36 (d, *J* = 8.0 Hz, 2H), 7.29-7.21 (m, 5H), 4.75

(dt, *J* = 3.2, 6.4 Hz, 1H), 3.31 (dd, *J* = 3.6, 12.8 Hz, 1H), 3.18 (dd, *J* = 9.6, 12.8 Hz, 1H), 2.77 (d, *J* = 2.8 Hz, 1H), 1.30 (s, 9H);

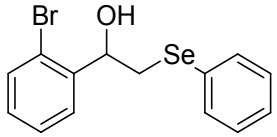
^{13}C NMR (100 MHz, $CDCl_3$) δ 150.8, 139.4, 132.9, 129.2, 129.1, 127.2, 125.5, 125.4, 72.0, 38.2, 34.5, 31.2.



(3f) 4-(1-hydroxy-2-(phenylselanyl)ethyl)phenyl acetate

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48-7.40 (m, 2H), 7.26 (d, *J* = 8.4 Hz, 2H), 7.21-7.15 (m, 3H), 6.97 (d, *J* = 8.8 Hz, 2H), 4.65 (d, *J* = 7.2 Hz, 1H), 3.20 (dd, *J* = 3.6, 12.8 Hz, 1H), 3.04 (dd, J = 9.2, 12.8 Hz, 1H), 2.86 (s, 1H);

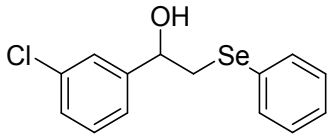
^{13}C NMR (100 MHz, $CDCl_3$) δ 169.4, 150.0, 140.0, 133.0, 129.2, 128.9, 127.3, 126.8, 121.5, 71.6, 38.2, 21.0.



(3g) 1-(2-bromophenyl)-2-(phenylselanyl)ethanol

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55-7.46 (m, 3H), 7.38 (dd, *J* = 1.2, 8.0 Hz, 1H), 7.35-7.13 (m, 4H), 7.04-7.98 (m, 1H), 4.97 (dt, *J* = 2.8, 5.6 Hz, 1H), 3.48-3.49 (m, 1H), 2.96 (d, *J* = 3.2 Hz, 1H), 2.84 (dd, *J* = 5.6, 8.8 Hz, 1H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 1412, 133.4, 133.3, 132.5, 129.0, 128.5, 127.7, 127.4, 127.2, 121,5, 70.7, 36.6.

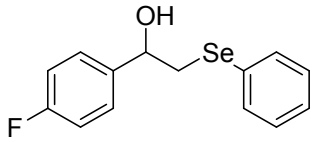


(3h) 1-(3-chlorophenyl)-2-(phenylselanyl)ethanol

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49-7.41 (m, 2H), 7.27-7.08 (m, 7H), 4.62 (dt, *J* = 3.2, 6.4 Hz, 1H),

3.20 (dd, *J* = 3.6, 12.8 Hz, 1H), 3.04-2.92 (m, 1H), 2.85 (d, *J* = 2.8 Hz, 1H);

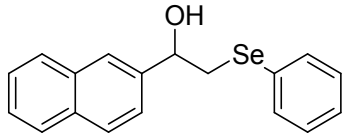
^{13}C NMR (100 MHz, $CDCl_3$) δ 144.4, 134.3, 133.2, 129.7, 129.3, 128.6, 127.9, 127.5, 125.9, 123.9, 71.4, 38.3.



(3i) 1-(4-fluorophenyl)-2-(phenylselanyl)ethanol

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47-7.39 (m, 2H), 7.23-7.14 (m, 5H), 6.92 (t, *J* = 8.4 Hz, 2H), 4.66-4.55 (m,1H), 3.17 (dd, *J* = 4.0, 12.8 Hz, 1H), 3.02 (dd, *J* = 9.6, 12.8 Hz, 1H), 2.87 (d, *J* = 2.4 Hz, 1H);

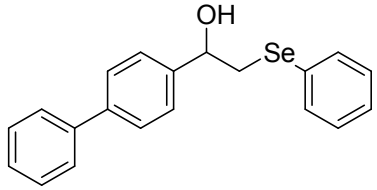
^{13}C NMR (100 MHz, $CDCl_3$) δ 163.4 (d, *J* = 244.4 Hz), 138.1 (d, *J* = 3.0 Hz), 133.0, 129.2, 128.8, 127.48, 127.42 (d, *J* = 2.7 Hz), 115.3 (d, *J* = 21.2 Hz), 71.4, 38.3.



(3j) 1-(naphthalen-2-yl)-2-(phenylselanyl)ethanol

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.85-7.76 (m, 4H), 7.60-7.52 (m, 2H), 7.51-7.40 (m, 3H), 7.31-7.23 (m, 3H), 4.93 (dt, *J* = 3.3, 6.3 Hz, 1H), 3.41 (dd, *J* = 3.6, 12.9 Hz, 1H), 3.24 (dd, *J* = 9.6, 12.9 Hz, 1H), 2.95 (d, *J* = 3.6 Hz, 1H);

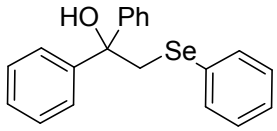
^{13}C NMR (125 MHz, $CDCl_3$) δ 139.7, 133.2, 133.1, 133.0, 129.2, 129.0, 128.3, 127.9, 127.6, 127.4, 126.2, 125.9, 124.6, 123.7, 72.2, 38.4.



(3k) 1-([1,1'-biphenyl]-4-yl)-2-(phenylselanyl)ethanol

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60-7.49i (m, 6H), 7.46-7.30 (m, 5H), 7.29-7.21 (m, 3H), 4.83-4.73 (m, 1H), 3.34 (dd, *J* = 3.6, 12.8 Hz, 1H), 3.19 (dd, *J* = 9.6, 12.8 Hz, 1H), 2.88 (d, *J* = 2.4 Hz, 1H);

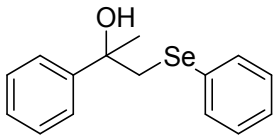
^{13}C NMR (100 MHz, $CDCl_3$) δ 141.4, 140.7, 140.6, 133.1, 129.2, 129.0, 128.7, 127.3, 127.29, 127.23, 127.0, 126.2, 71.9, 38.3.



(3l) 1,1-diphenyl-2-(phenylselanyl)ethanol

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53-7.46 (m, 2H), 7.44 (d, *J* = 7.2 Hz, 4H), 7.31 (t, J = 5.4 Hz, 4H), 7.25-7.17 (m, 5H), 3.86 (s, 2H), 3.57 (s, 1H);

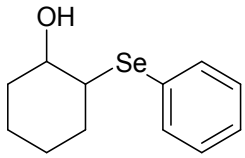
^{13}C NMR (100 MHz, $CDCl_3$) δ 145.3, 133.0, 130.7, 129.1, 128.2, 127.3, 127.2, 125.9, 75.5, 44.6.



(3m) 2-phenyl-1-(phenylselanyl)propan-2-ol

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38-7.30 (m, 4H), 7.24-7.16 (m, 2H), 7.16-7.06 (m, 4H), 3.50 (d, *J* = 12.4 Hz, 1H), 3.24 (d, *J* = 12.4 Hz, 1H), 2.84 (s, 1H), 1.52 (s, 3H);

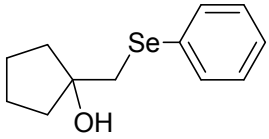
^{13}C NMR (100 MHz, $CDCl_3$) δ 146.3, 132.7, 130.4, 129.0, 128.1, 126.98, 126.96, 124.6, 73.5, 45.0, 29.7.



(3n) 2-(phenylselanyl)cyclohexanol

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62-7.56 (m, 2H), 7.36-7.24 (m, 3H), 3.35 (td, *J* = 4.0, 10.0 Hz, 1H), 2.96-2.83 (m, 2H), 2.24-2.07 (m, 2H), 1.77-1.56 (m, 2H), 1.48-1.13 (m, 5H);

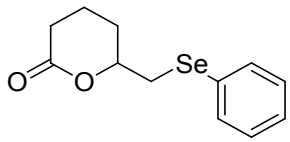
^{13}C NMR (100 MHz, $CDCl_3$) δ 136.1, 128.9, 128.1, 126.5, 72.1, 53.5, 33.8, 33.3, 26.8, 24.4.



(3o) 1-((phenylselanyl)methyl)cyclopentanol

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50-7.44 (m, 2H), 7.19-7.10 (m, 3H), 3.17 (t, *J* = 5.6 Hz, 2H), 2.26 (s, 1H), 1.81-1.59 (m, 4H), 1.58-1.43 (m, 4H);

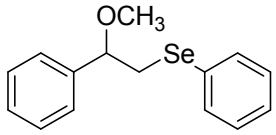
^{13}C NMR (100 MHz, $CDCl_3$) δ 132.5, 130.7, 129.0, 126.8, 81.5, 42.0, 39.6, 23.9.



(3p) 6-((phenylselanyl)methyl)tetrahydro-2H-pyran-2-one

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47-7.39 (m, 2H), 7.23-7.15 (m, 3H), 4.23-4.29 (m, 1H), 3.19 (dd, *J* = 4.8, 12.8 Hz, 1H), 2.96 (dd, *J* = 7.6, 12.8 Hz, 1H), 2.55-2.42 (m, 1H), 2.41-2.26 (m, 1H), 2.11-2.01 (m, 1H), 1.88-1.64 (m, 2H), 1.56-1.41 (m, 1H);

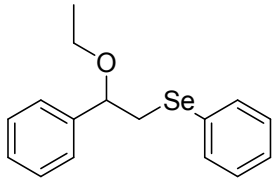
^{13}C NMR (100 MHz, $CDCl_3$) δ 170.9, 132.6, 129.2, 129.1, 127.2, 79.6, 32.0, 29.2, 27.1, 18.2.



(4a) (2-methoxy-2-phenylethyl)(phenyl)selane

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52-7.43 (m, 2H), 7.40-7.27 (m, 5H), 7.25-7.21 (m, 3H), 4.36 (dd, *J* = 4.8, 8.4 Hz, 1H), 3.34 (dd, *J* = 8.4, 12.0 Hz, 1H), 3.24 (s, 3H), 3.12 (dd, *J* = 5.2, 12.4 Hz, 1H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 140.8, 132.5, 130.6, 128.9, 128.5, 128.0, 126.7, 126.6, 83.1, 57.0, 35.3.

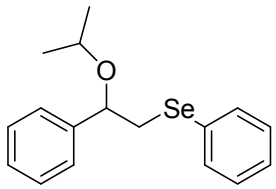


(4b) (2-ethoxy-2-phenylethyl)(phenyl)selane

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53-7.43 (m, 2H), 7.38-7.27 (m, 5H), 7.24-7.17 (m, 2H), 4.48 (dd, *J* = 5.2, 8.4 Hz, 1H), 3.47-3.29 (m, 3H), 3.11 (dd, *J* = 5.2, 12.0 Hz, 1H), 1.19 (t, *J* = 7.2 Hz, 3H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 141.6, 132.4, 130.8, 128.9, 128.4, 127.9, 126.6, 126.5, 81.3, 64.6,

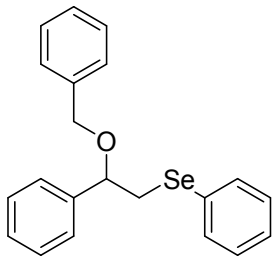
35.5, 15.2.



(4c) (2-isopropoxy-2-phenylethyl)(phenyl)selane

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (d, *J* = 7.6 Hz, 2H), 7.37-7.27 (m, 5H), 7.25-7.17 (m, 3H), 4.59 (dd, *J* = 4.8, 8.4 Hz, 1H), 3.55-3.45 (m, 1H), 3.32 (dd, *J* = 8.8, 12.0 Hz, 1H), 3.09 (dd, *J* = 4.8, 12.0 Hz, 1H), 1.17 (d, *J* = 6.0, 3H), 1.08 (d, *J* = 6.0 Hz, 3H);

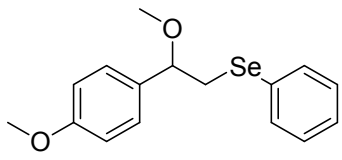
^{13}C NMR (75 MHz, $CDCl_3$) δ 142.4, 132.2, 131.0, 128.9, 128.4, 127.7, 126.58, 126.52, 78.6, 69.7, 35.9, 23.2, 21.2.



(4d) (2-(benzyloxy)-2-phenylethyl)(phenyl)selane

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48-7.38 (m, 2H), 7.38-7.26 (m, 10H), 7.25-7.14 (m, 3H), 4.63-4.52 (m, 1H), 4.50 (d, *J* = 11.6, 1H), 4.31 (d, *J* = 12.0 Hz, 1H), 3.42 (dd, *J* = 8.4, 12.0 Hz, 1Hz), 3.14 (dd, *J* = 5.2, 12.4 Hz, 1H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 141.0, 138.0, 132.4, 130.7, 128.9, 128.5, 128.3, 128.1, 127.8, 127.5, 126.8, 126.6, 80.7, 70.7, 35.4.

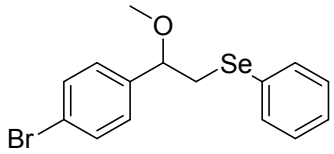


(4e) (2-methoxy-2-(4-methoxyphenyl)ethyl)(phenyl)selane

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.51-7.43 (m, 2H), 7.27-7.18 (m, 5H), 6.92-6.83 (m, 2H), 4.34-4.25 (dd, *J* = 5.4, 8.4 Hz, 1H), 3.80 (s, 3H), 3.36 (dd, *J* = 8.4, 12.3 Hz, 1H), 3.21 (s, 3H), 3.11 (dd, *J* =

5.4, 12.3 Hz, 1H);

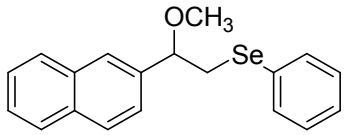
^{13}C NMR (100 MHz, $CDCl_3$) δ 159.4, 132.8, 132.5, 130.7, 128.9, 127.8, 126.7, 113.8, 82.7, 56.7, 55.2, 35.3.



(4f) (2-(4-bromophenyl)-2-methoxyethyl)(phenyl)selane

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.50-7.41 (m, 4H), 7.25-7.21 (m, 3H), 7.19-7.15 (m, 2H), 4.32 (dd, *J* = 5.4, 8.1 Hz, 1H), 3.31 (dd, *J* = 8.1, 12.3 Hz, 1H), 3.22 (s, 3H), 3.08 (dd, *J* = 5.7, 12.6 Hz, 1H);

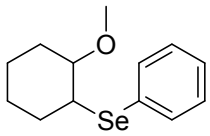
^{13}C NMR (100 MHz, $CDCl_3$) δ 139.8, 132.6, 131.6, 130.2, 129.0, 128.4, 126.9, 121.9, 82.5, 57.0, 35.0.



(4g) (2-methoxy-2-(naphthalen-2-yl)ethyl)(phenyl)selane

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, *J* = 7.6 Hz, 3H), 7.73 (s, 1H), 7.54-7.38 (m, 5H), 7.24-7.15 (m, 3H), 4.55-4.46 (m, 1H), 3.47-3.34 (m, 1H), 3.27 (s, 3H), 3.20 (dd, *J* = 5.2, 12.4 Hz, 1H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 138.2, 133.2, 133.1, 132.6, 130.5, 128.9, 128.5, 127.8, 127.7, 126.8, 126.2, 126.1, 126.0, 124.0, 83.3, 57.0, 35.1.



(4h) (2-methoxycyclohexyl)benzene

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64-7.54 (m, 2H), 7.34-7.19 (m, 3H), 3.37 (s, 3H), 3.32-3.11 (m, 2H), 2.21-2.07 (m, 1H), 2.05-1.92 (m, 1H), 1.79-1.67 (m, 1H), 1.67-1.55 (m, 2H), 1.55-1.40 (m 1H), 1.31-1.22 (m, 2H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 135.3, 128.9, 128.8, 127.4, 82.2, 56.4, 47.4, 32.1, 30.3, 25.7, 23.4,

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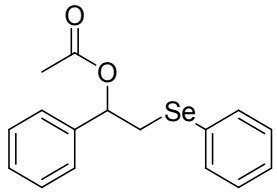
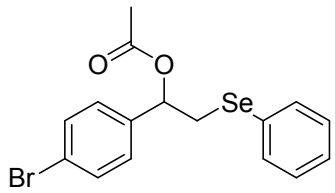


(4i) 1-phenyl-2-(phenylselanyl)ethyl acetate

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53-7.44 (m, 2H), 7.35-7.19 (m, 8H), 5.94 (dd, *J* = 6.0, 8.0 Hz, 1H), 3.39 (dd, *J* = 8.0, 12.8 Hz, 1H), 3.24 (dd, *J* = 5.6, 12.8 Hz, 1H), 2.0 (s, 3H);

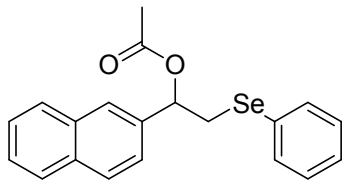
^{13}C NMR (100 MHz, $CDCl_3$) δ 169.9, 139.3, 133.0, 129.7, 129.0, 128.5, 128.3, 127.2, 126.5, 75.1, 33.3, 21.0.



(4j) 1-(4-bromophenyl)-2-(phenylselanyl)ethyl acetate

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.49-7.39 (m, 4H), 7.28-7.20 (m, 3H), 7.20-7.12 (m, 2H), 5.87 (dd, *J* = 6.3, 7.5 Hz, 1H), 3.36 (dd, *J* = 7.5, 12.9 Hz, 1H), 3.20 (dd, *J* = 6.3, 12.9 Hz, 1H), 1.99 (s,3H);

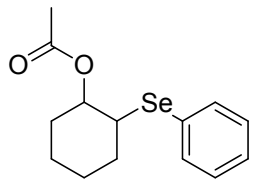
^{13}C NMR (75 MHz, $CDCl_3$) δ 169.8, 138.2, 133.0, 131.5, 129.0, 128.3,127.2, 126.3, 122.2, 74.5, 32.9, 20.9.



(4k) 1-(naphthalen-2-yl)-2-(phenylselanyl)ethyl acetate

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88-7.72 (m, 4H), 7.55-7.37 (m, 5H), 7.25-7.17 (m, 3H), 6.11 (dd, *J* = 6.4, 7.6 Hz, 1H), 3.48 (dd, *J* = 8.0, 12.8 Hz, 1H), 3.33 (dd, *J* = 5.6, 12.8 Hz, 1H), 2.03 (s, 3H);

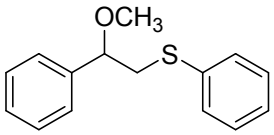
^{13}C NMR (100 MHz, $CDCl_3$) δ 170.0, 136.6, 133.2, 133.1, 133.0, 129.7, 129.0, 128.4, 128.0, 127.6, 127.2, 126.3, 126.2, 126.0, 124.0, 75.4, 33.2, 21.0.



(4l) 2-(phenylselanyl)cyclohexyl acetate

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.62-7.48 (m, 2H), 7.32-7.19 (m, 3H), 4.91-4.73 (m, 1H), 3.27-3.07 (m, 1H), 2.22-1.98 (m, 2H), 1.94 (d, *J* = 4.8 Hz, 2H), 1.80-1.16 (m, 7H);

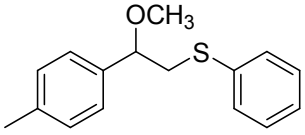
^{13}C NMR (75 MHz, $CDCl_3$) δ 170.2, 134.9, 128.8, 128.4, 127.4, 75.3, 46.0, 32.2, 31.7, 25.7, 23.5, 21.0.



(5a) (2-methoxy-2-phenylethyl)(phenyl)sulfane

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.40-7.28 (m, 8H), 7.26-7.23 (m, 1H), 7.20-7.13 (m, 1H), 4.31 (dd, *J* = 4.8, 8.1 Hz, 1H), 3.35 (dd, *J* = 8.1, 13.2 Hz, 1H), 3.24 (s, 3H), 3.16 (dd, *J* = 5.1, 13.2 Hz, 1H);

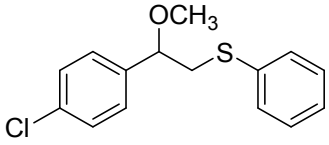
^{13}C NMR (75 MHz, $CDCl_3$) δ 140.4, 136.4, 129.2, 128.8, 128.5, 128.1, 126.7, 125.9, 82.4, 57.0, 41.4.



(5b) (2-methoxy-2-(p-tolyl)ethyl)(phenyl)sulfane

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.37-7.29 (m, 2H), 7.28-7.10 (m, 7H), 4.28 (dd, *J* = 4.8, 8.1 Hz, 1H), 3.34 (dd, *J* = 8.1, 13.2 Hz, 1H), 3.22 (s, 3H), 3.14 (dd, *J* = 5.1, 13.2 Hz, 1H), 2.34 (s, 3H);

^{13}C NMR (75 MHz, $CDCl_3$) δ 137.8, 137.3, 136.5, 129.18, 129.15, 128.7, 126.6, 125.8, 82.1, 56.8, 41.3, 21.1.

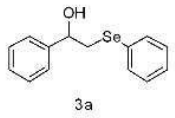


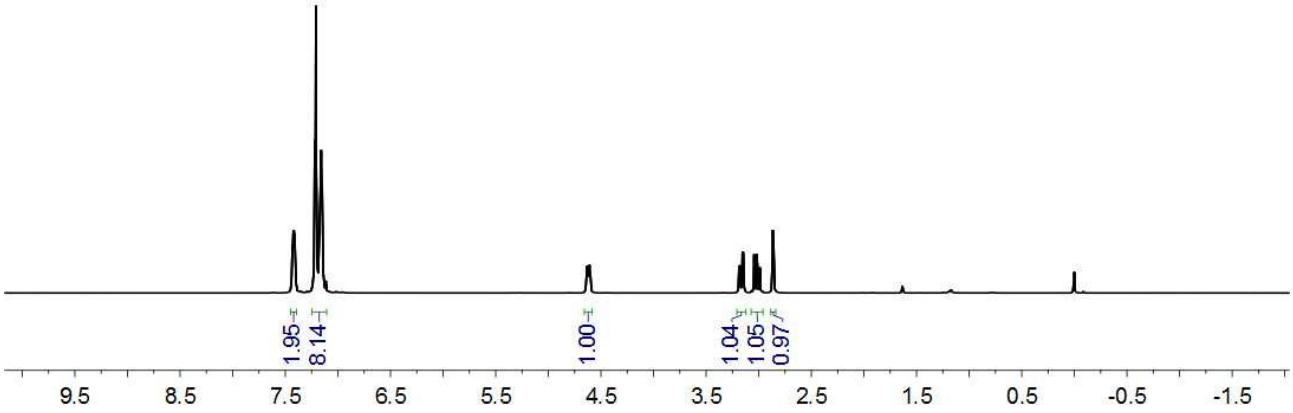
(5c) (2-(4-chlorophenyl)-2-methoxyethyl)(phenyl)sulfane

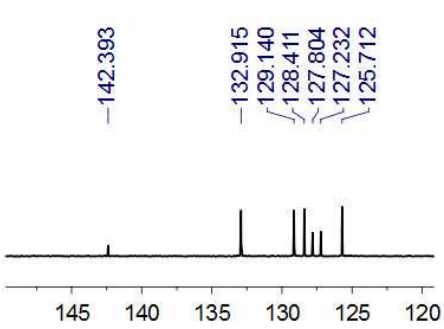
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.35-7.14 (m, 9H), 4.28, (dd, *J* = 5.4, 7.8 Hz, 1H), 3.33 (dd, *J* = 7.5, 13.2 Hz, 1H), 3.23 (s, 3H), 3.11 (dd, *J* = 5.4, 13.5 Hz, 1H);

^{13}C NMR (75 MHz, $CDCl_3$) δ 138.9, 136.1, 133.8, 129.4, 128.9, 128.7, 128.1, 126.1, 81.8, 57.0, 41.3.

4. Spectral of these compounds



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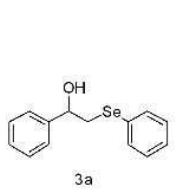
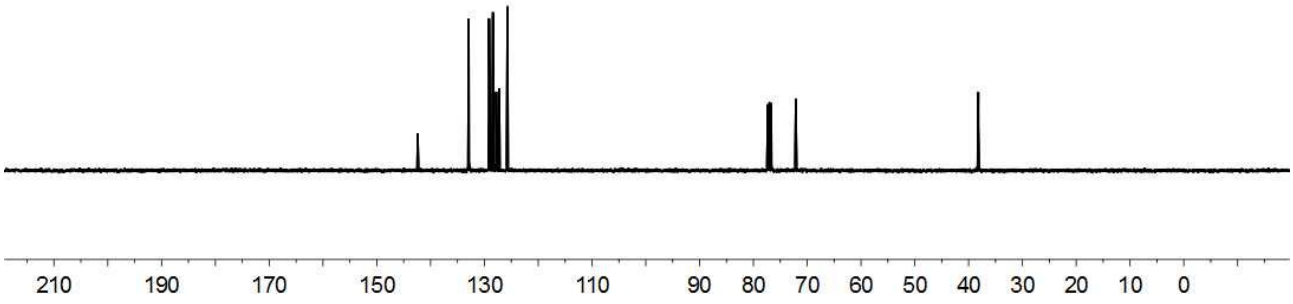
128.411
127.804
127.232
125.712
145
140
135
130
125
120


72.119
38.201
OH
Se

3a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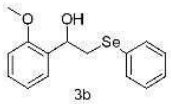
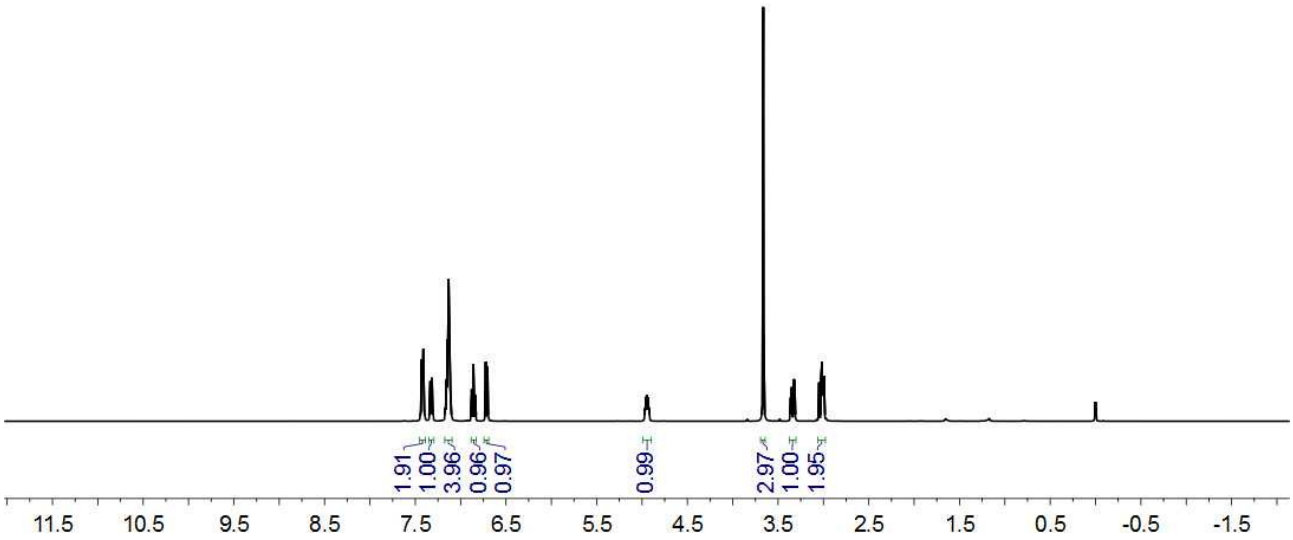
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0


O
OH
Se

3b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0.99
2.97
1.00
1.95
11.5
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
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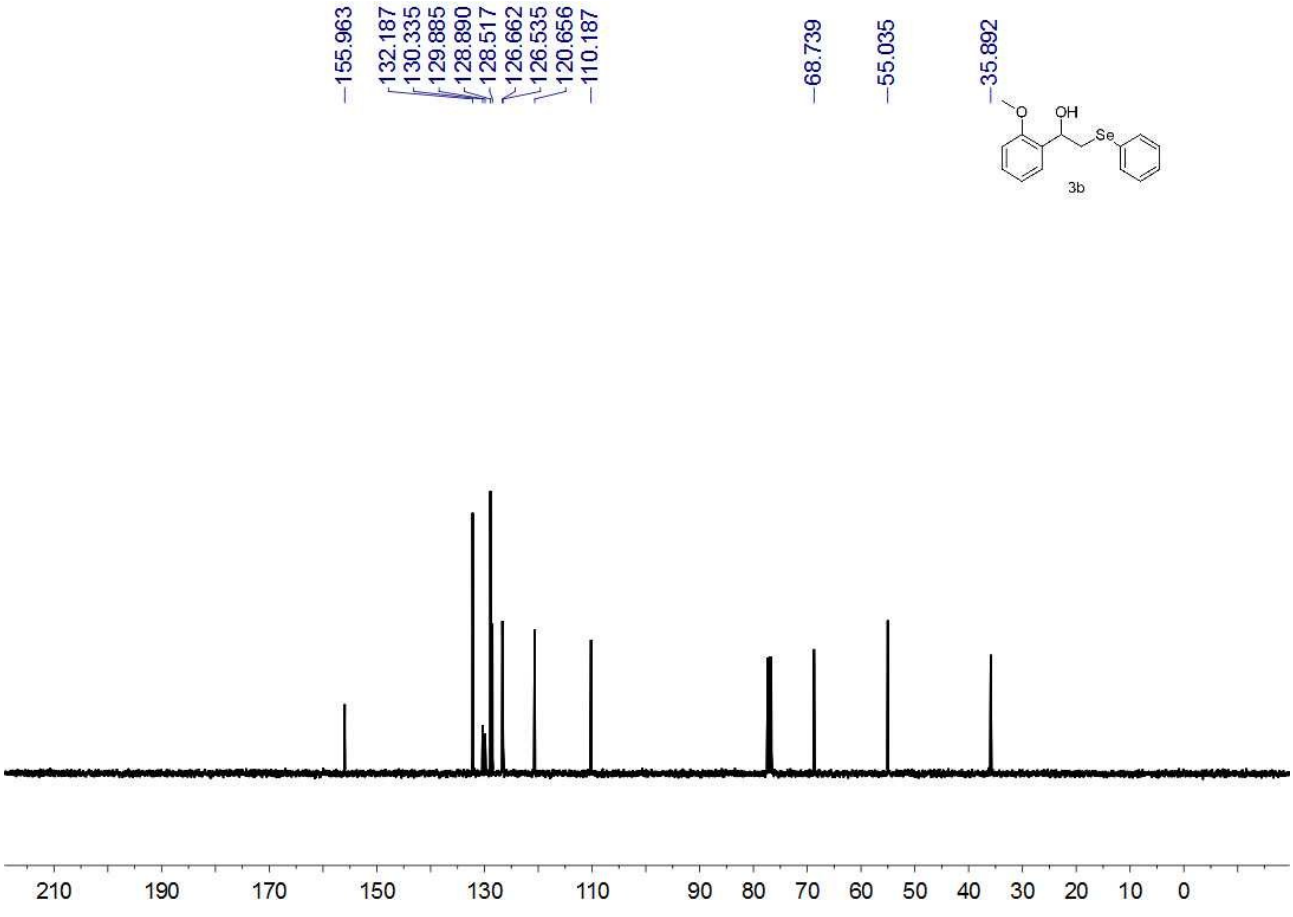
-1.5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128.890
128.517
126.662
126.535
120.656
110.187
68.739
55.035
35.892
O
OH
Se
3b
210
190
170
150
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110
90
80
70
60
50
40
30
20
10
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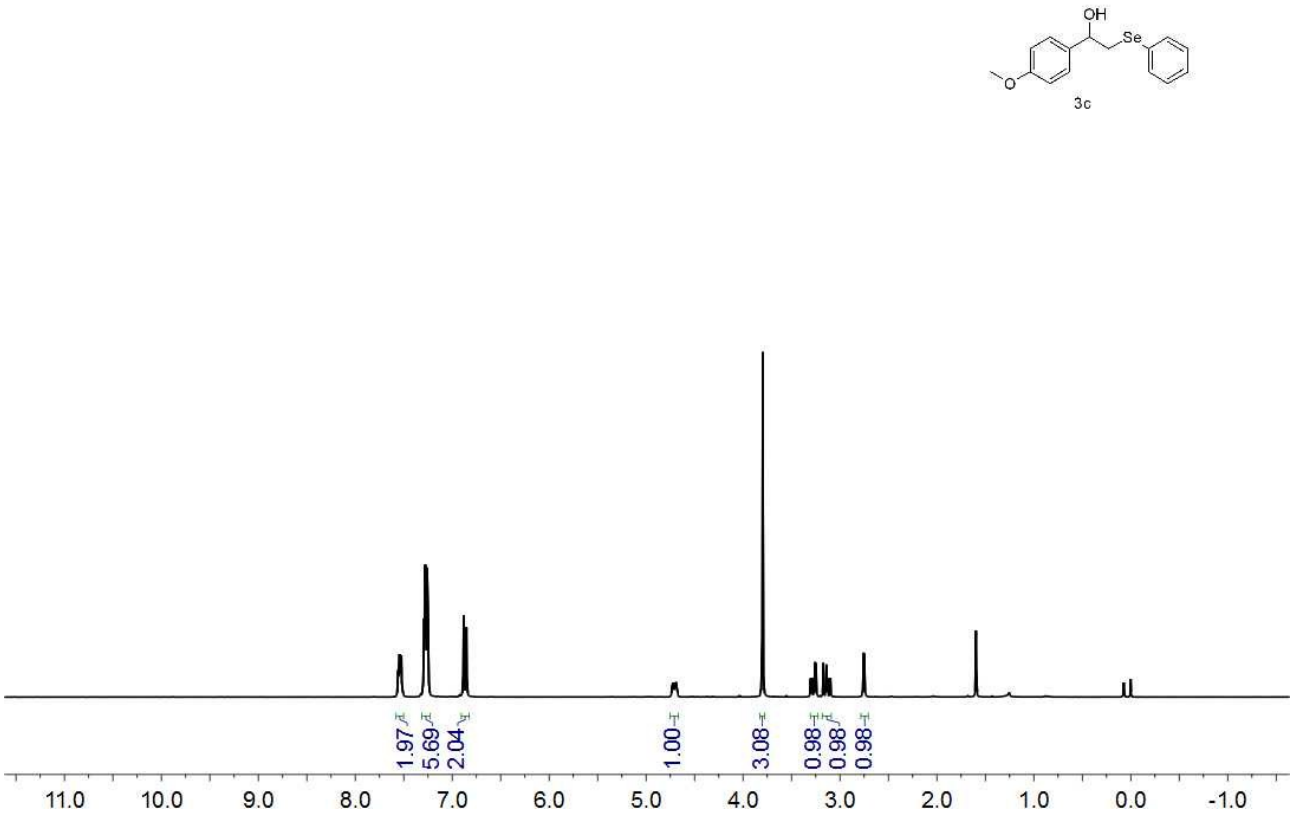
OH
Se
O
3c
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5.69
2.04
1.00
3.08
0.98
0.98
0.98
11.0
10.0
9.0
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7.0
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3.0
2.0
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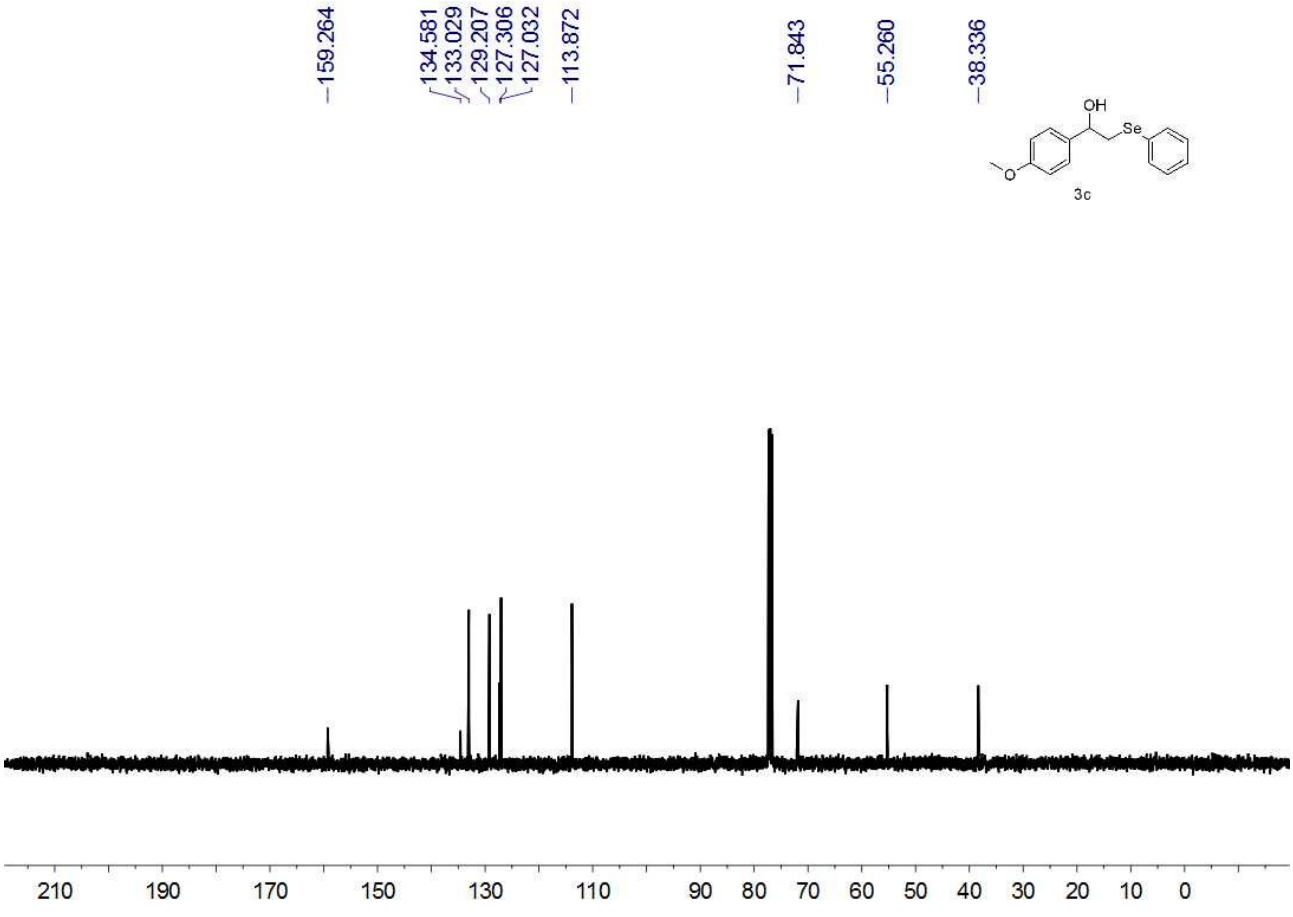
-1.0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133.029
129.207
127.306
127.032
113.872
71.843
55.260
38.336
OH
Se
O
3c
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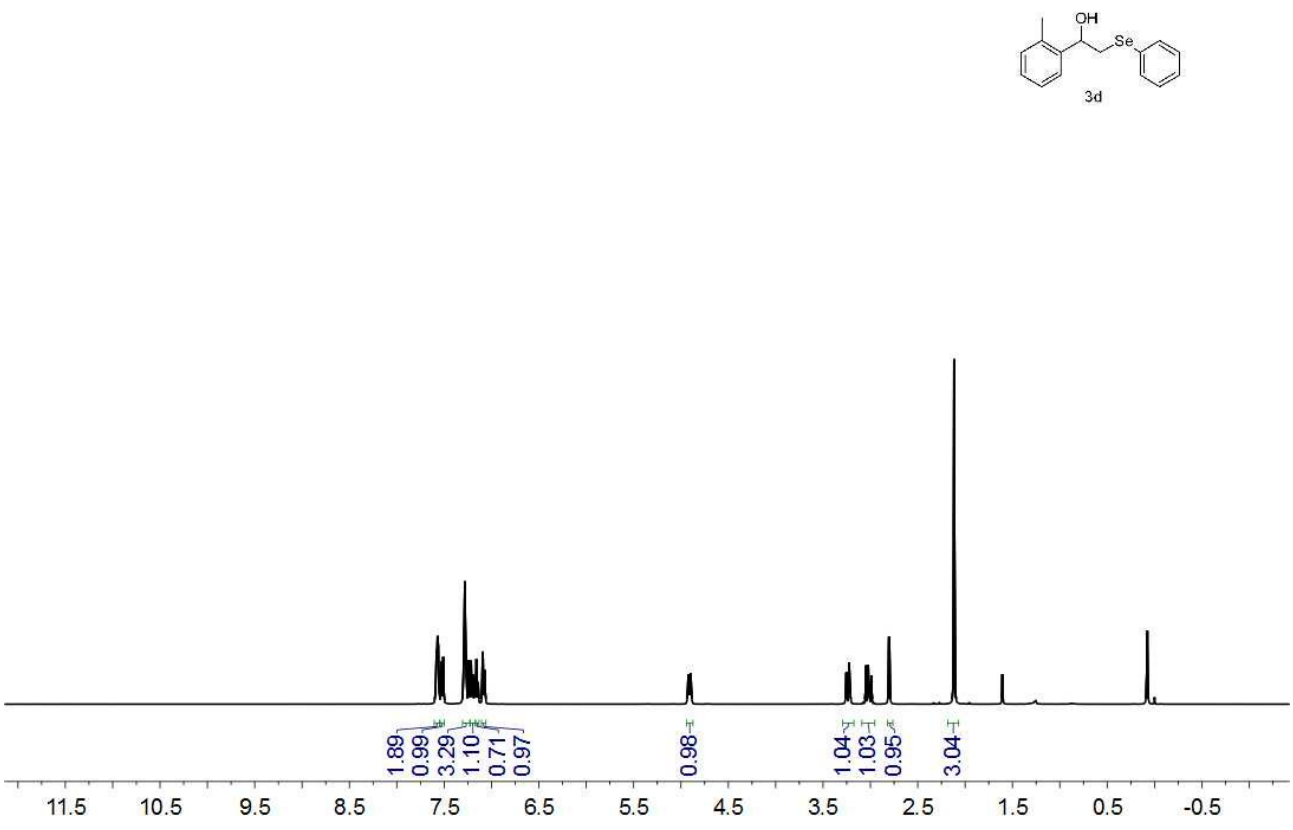
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0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Se
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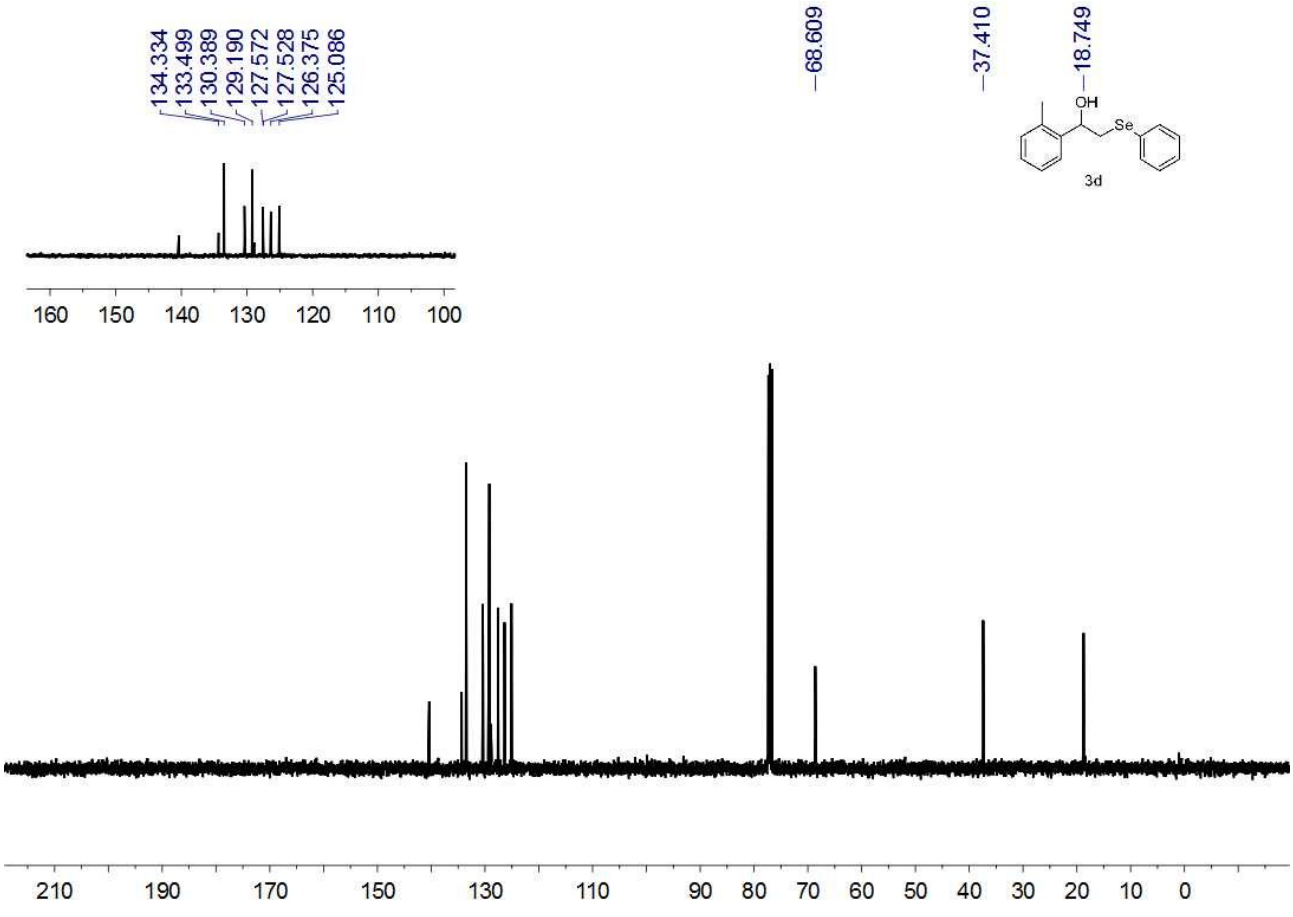
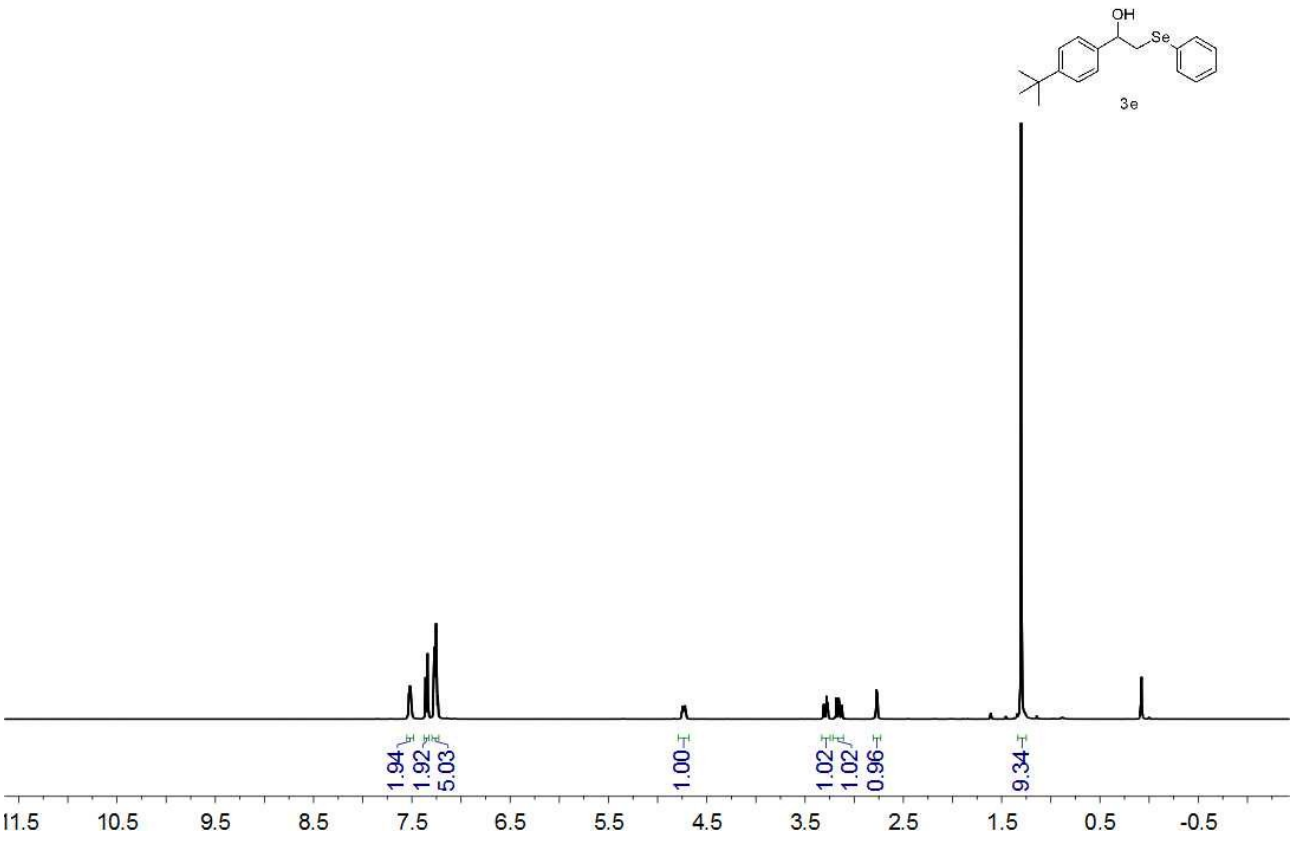
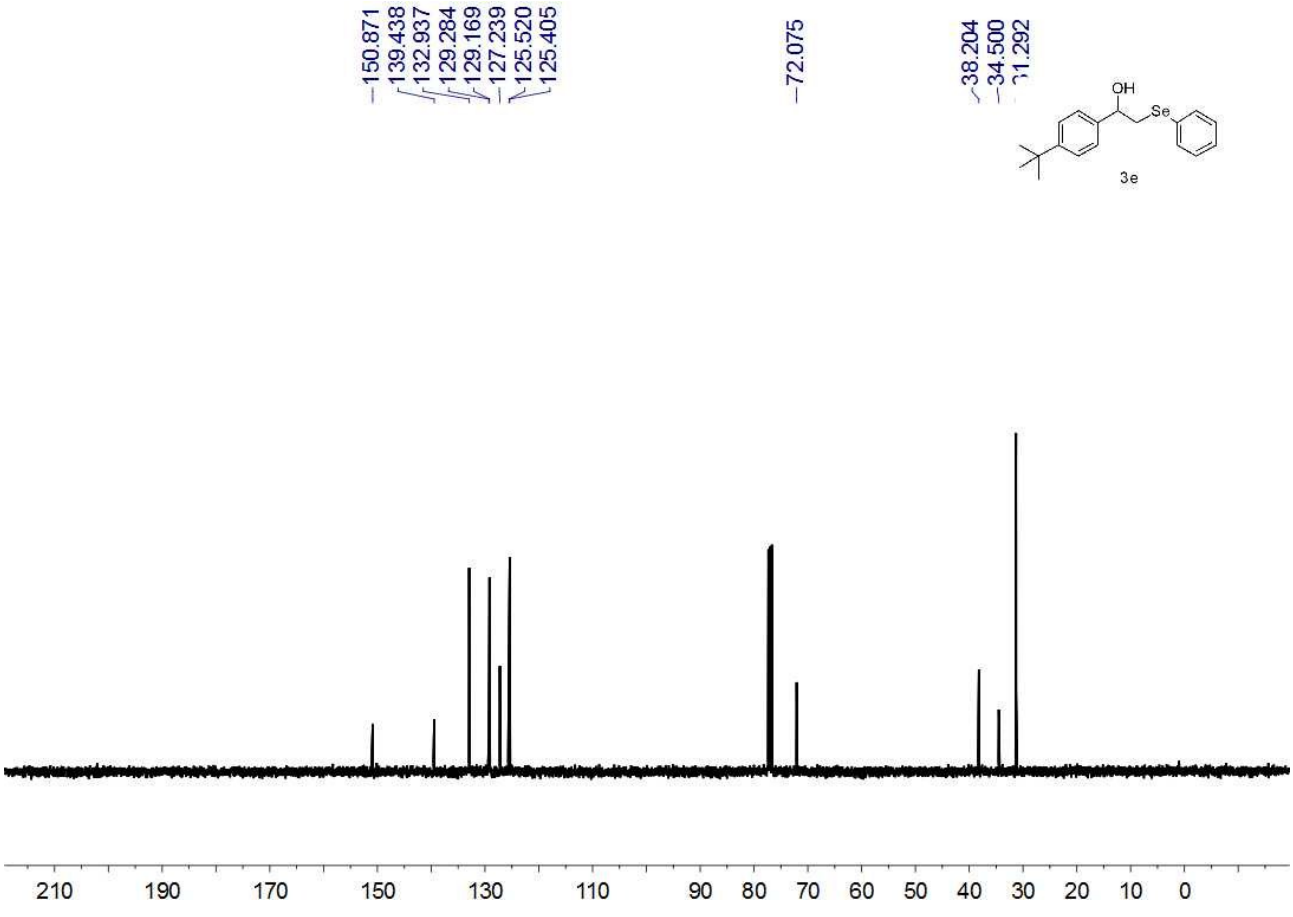
0.99
3.29
1.10
0.71
0.97
0.98
1.04
1.03
0.95
3.04
11.5
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5


134.334
133.499
130.389
129.190
127.572
127.528
126.375
125.086
68.609
37.410
18.749
OH
Se
3d
160 150 140 130 120 110 100
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0


OH
Se
3e
1.94
1.92
5.03
1.00
1.02
1.02
0.96
9.34
11.5 10.5 9.5 8.5 7.5 6.5 5.5 4.5 3.5 2.5 1.5 0.5 -0.5


150.871
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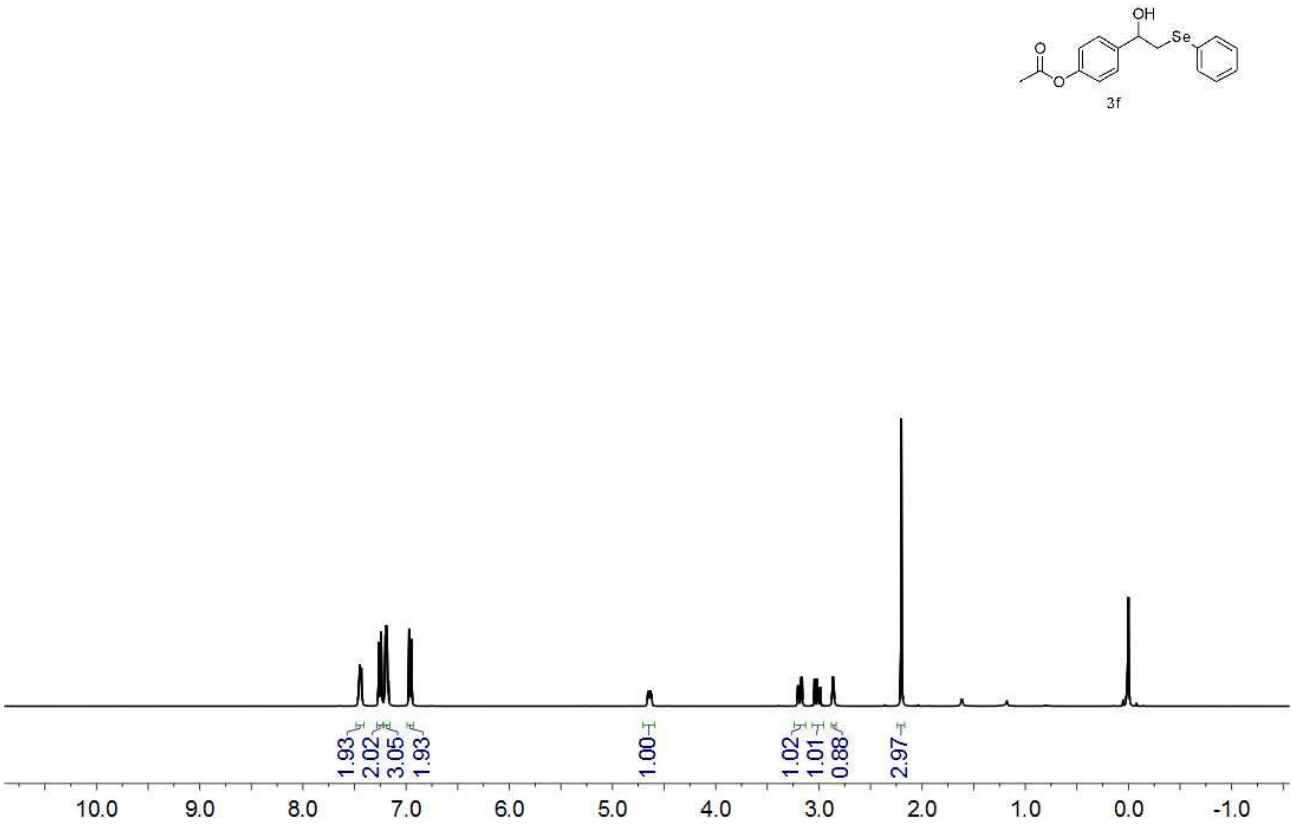
132.937
129.284
129.169
127.239
125.520
125.405
72.075
38.204
34.500
31.292
OH
Se
3e
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0


OH
Se
O
O
3f
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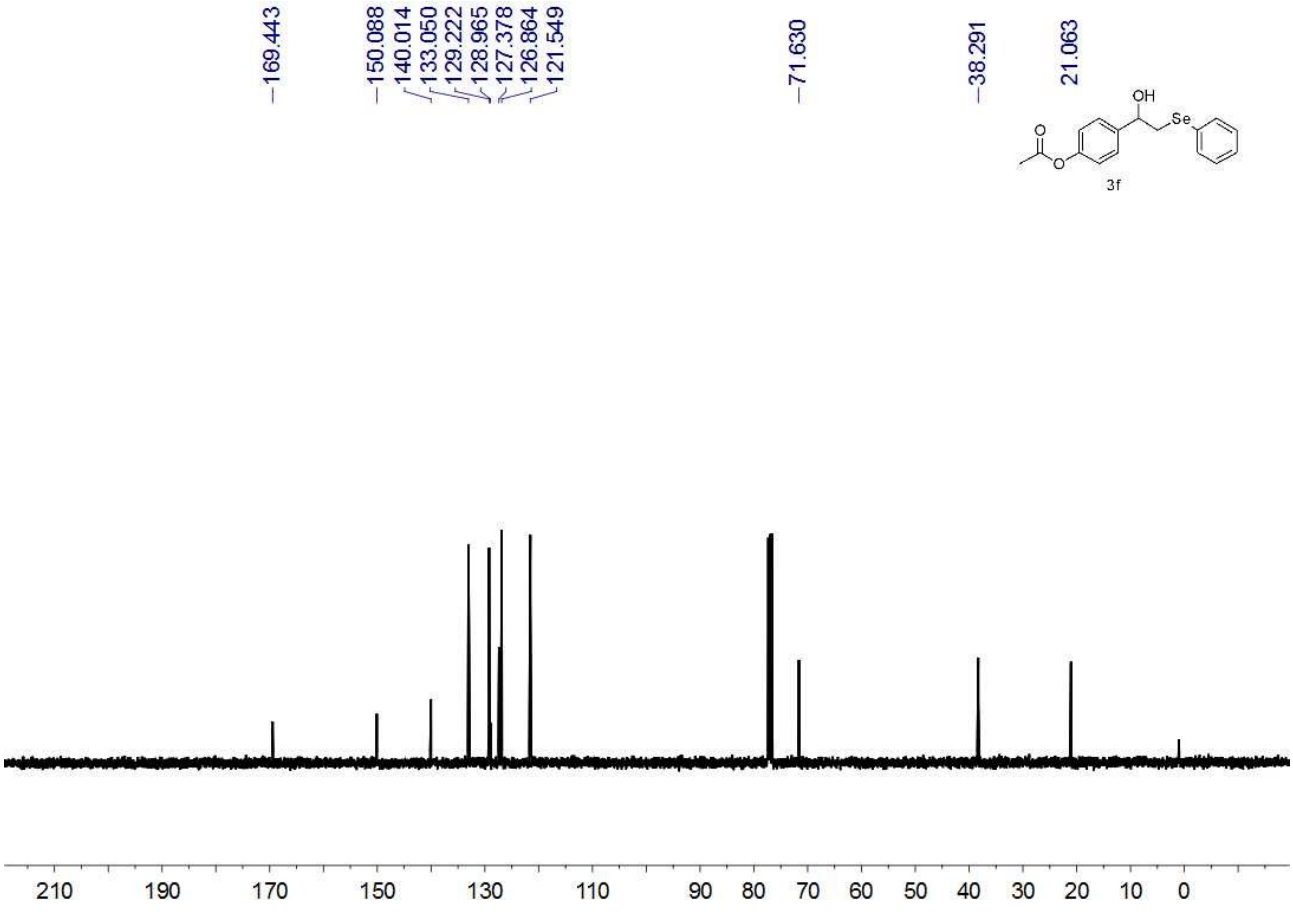
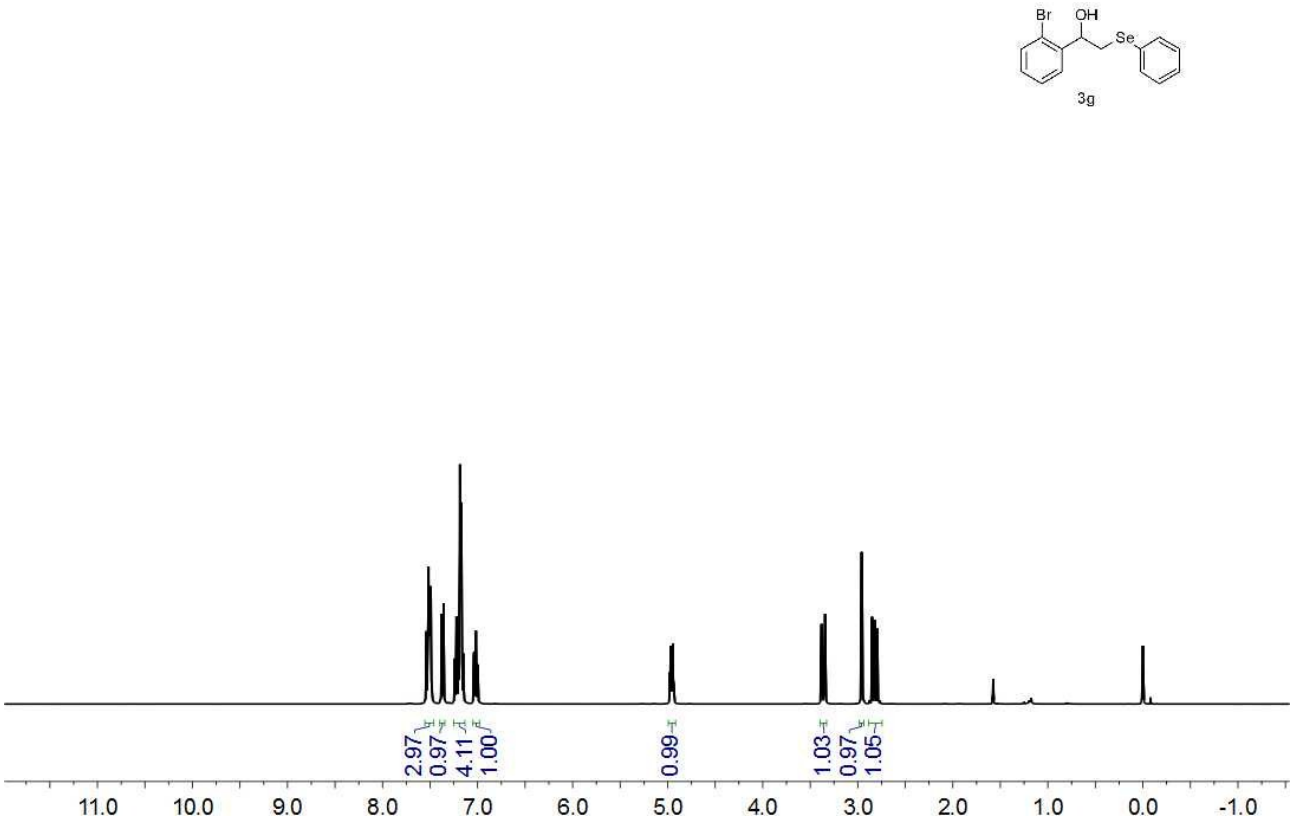
2.02
3.05
1.93
1.00
1.02
1.01
0.88
2.97
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0


169.443
150.088
140.014
133.050
129.222
128.965
127.378
126.864
121.549
71.630
38.291
21.063
OH
Se
O
O
3f
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0


Br
OH
Se
3g
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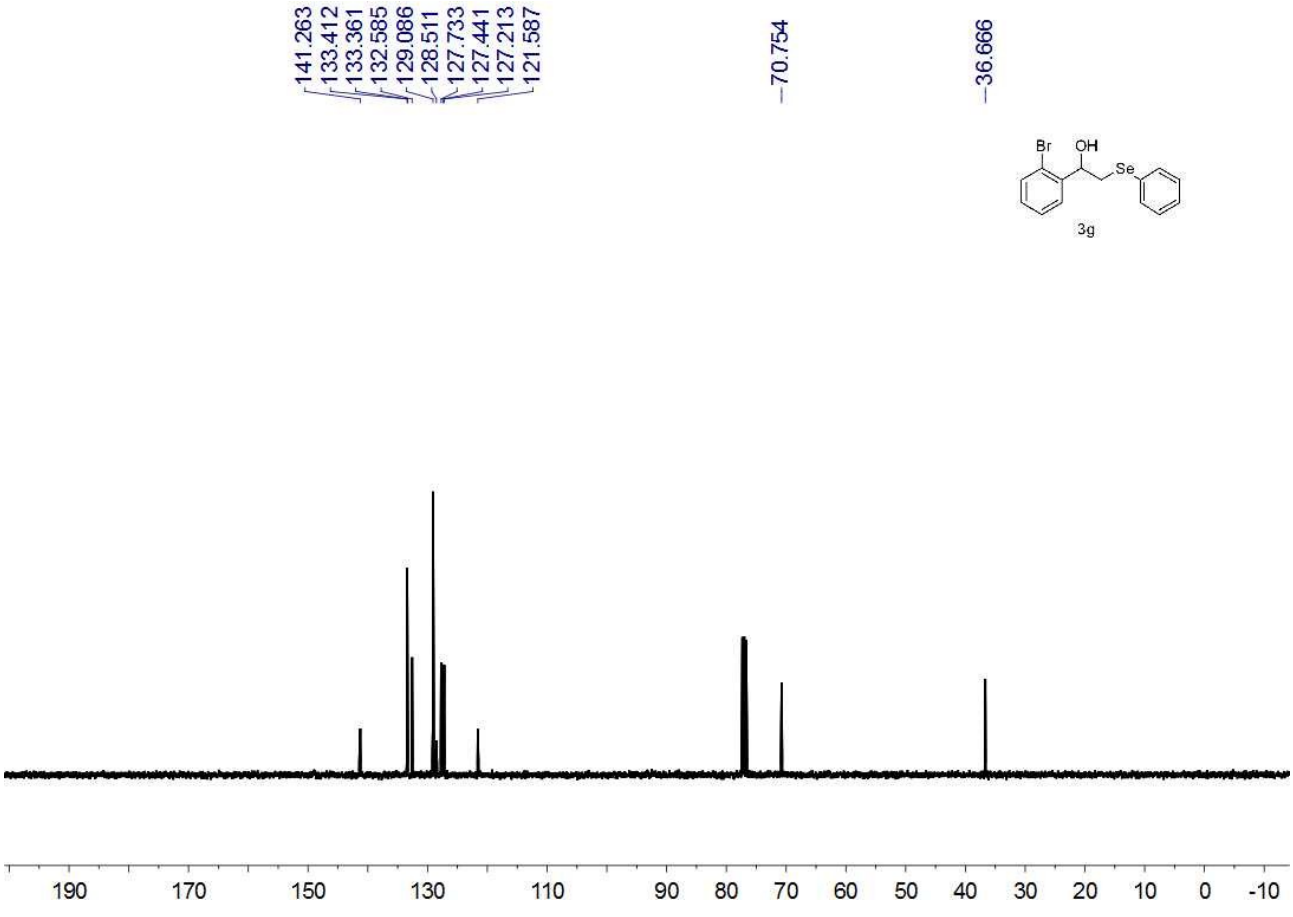
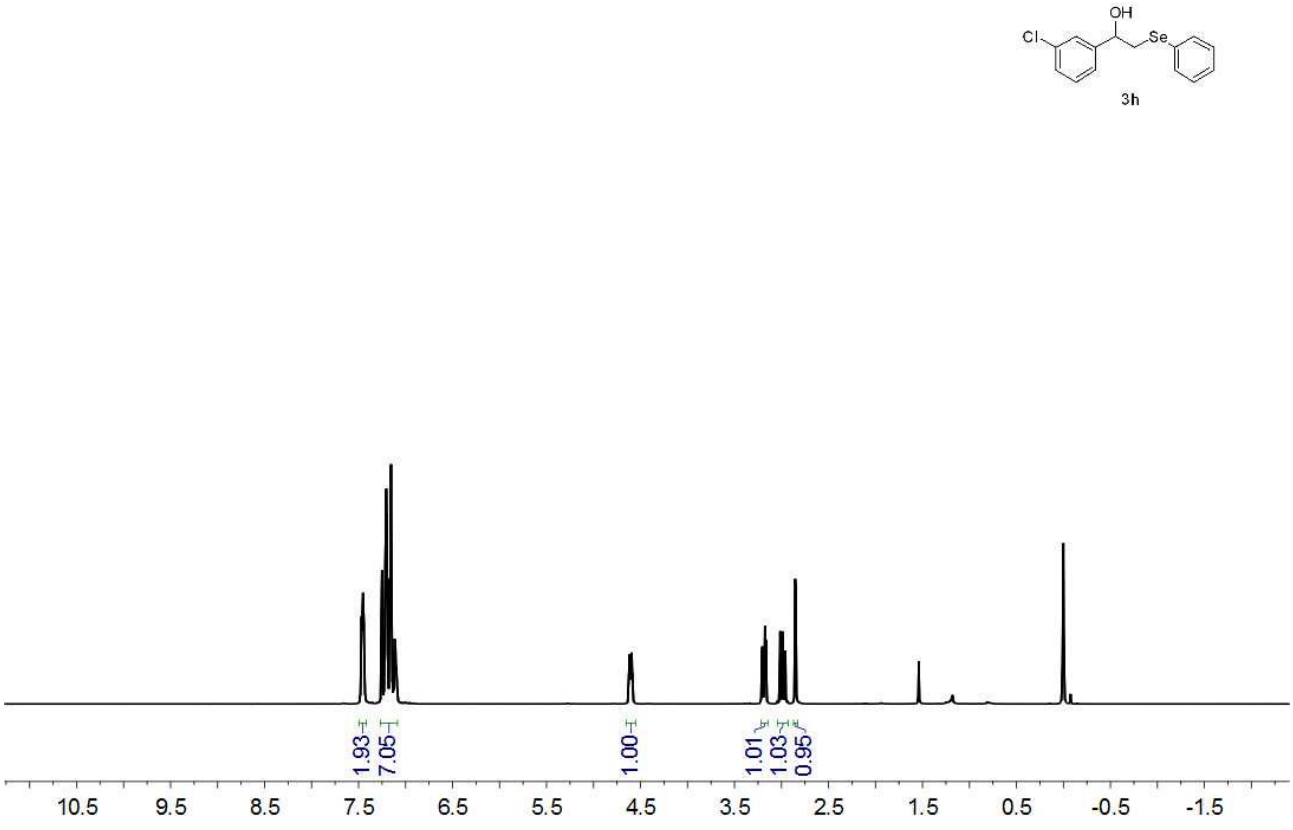
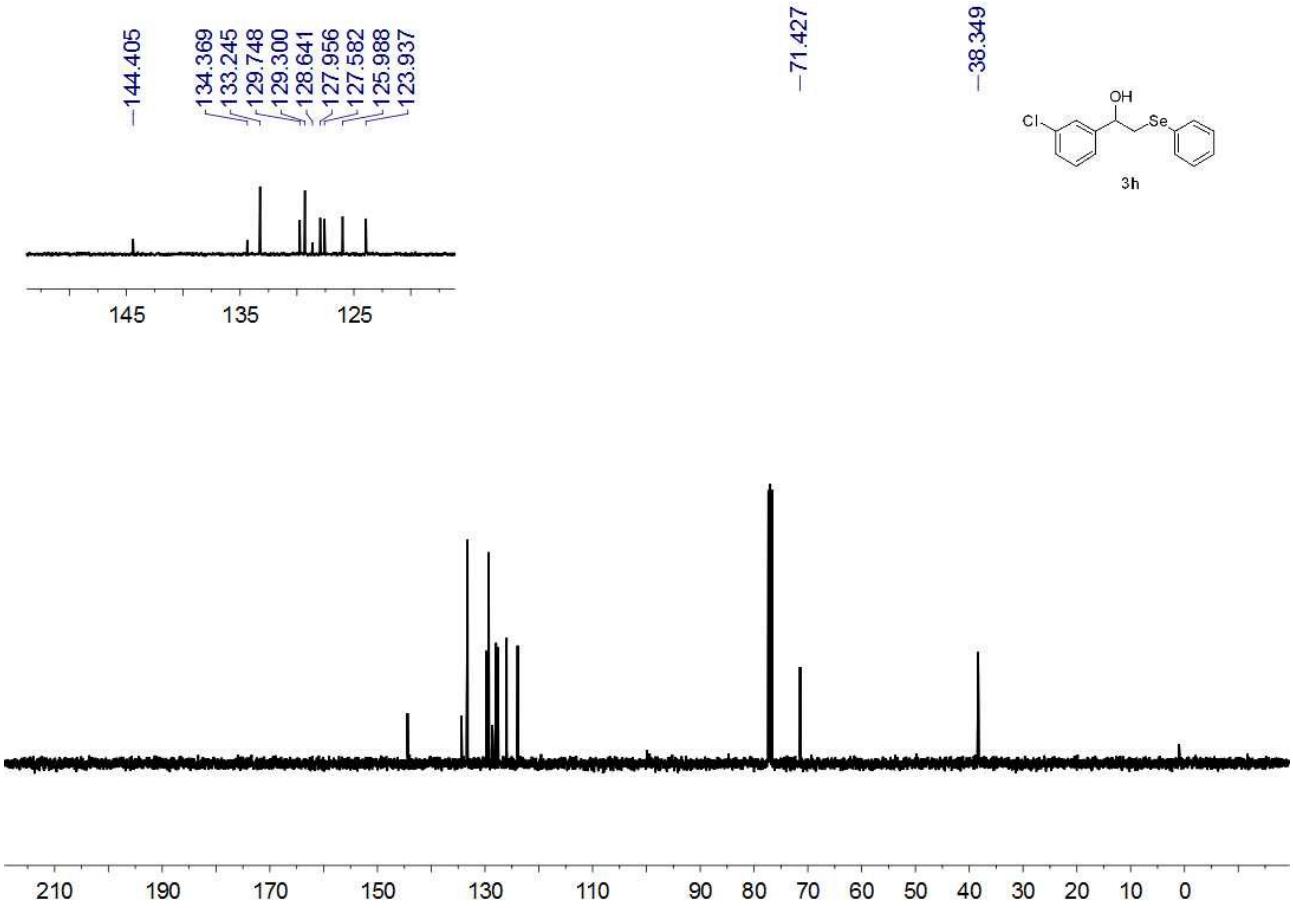
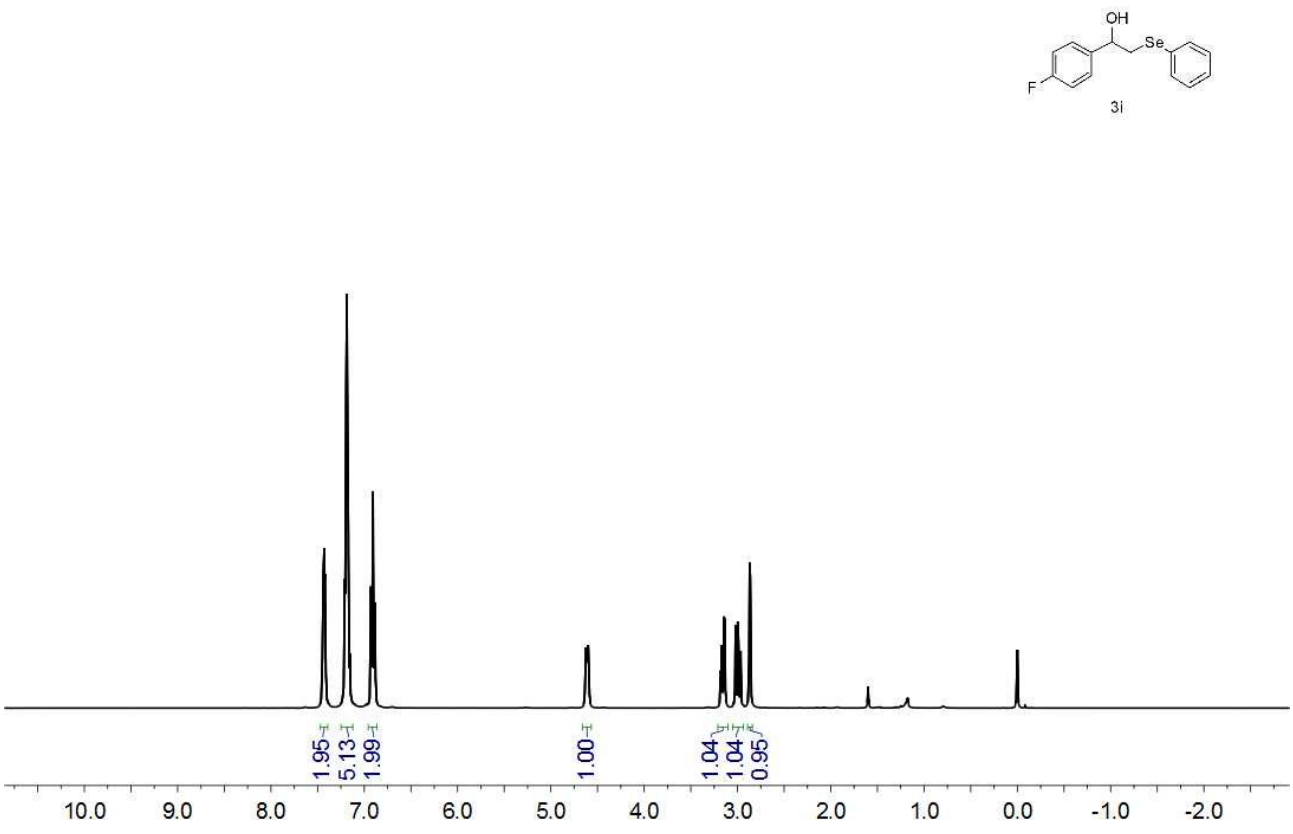
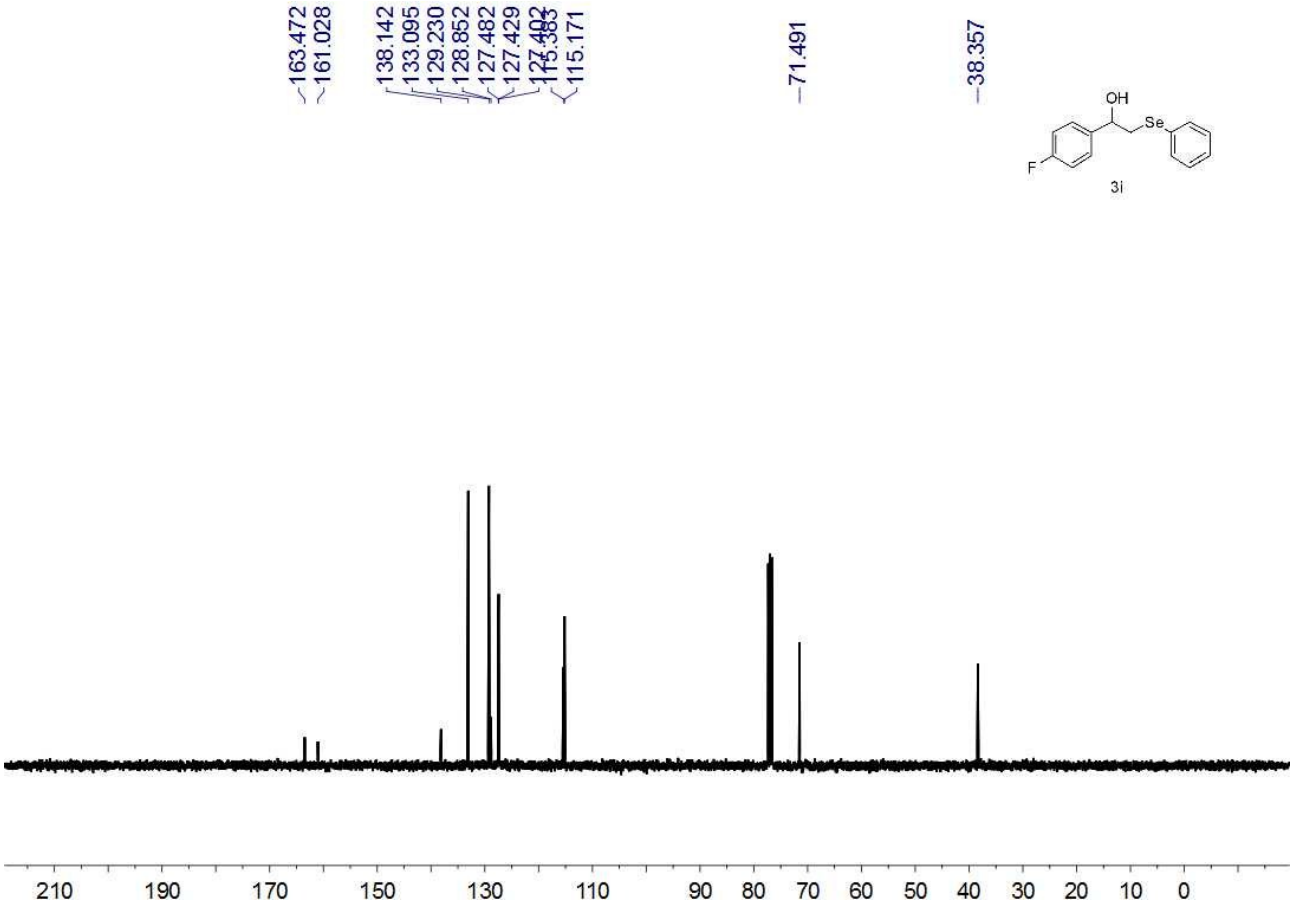
0.97
4.11
1.00
0.99
1.03
0.97
1.05
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0


141.263
133.412
133.361
132.585
129.086
128.511
127.733
127.441
127.213
121.587
70.754
36.666
Br
OH
Se
3g
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10


OH
Cl
Se
3h
1.93
7.05
1.00
1.01
1.03
0.95
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5
-1.5


144.405
134.369
133.245
129.748
129.300
128.641
127.956
127.582
125.988
123.937
71.427
38.349
OH
Cl
Se
3h
145
135
125
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0


OH
Se
F
3i
1.95
5.13
1.99
1.00
1.04
1.04
0.95
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
-2.0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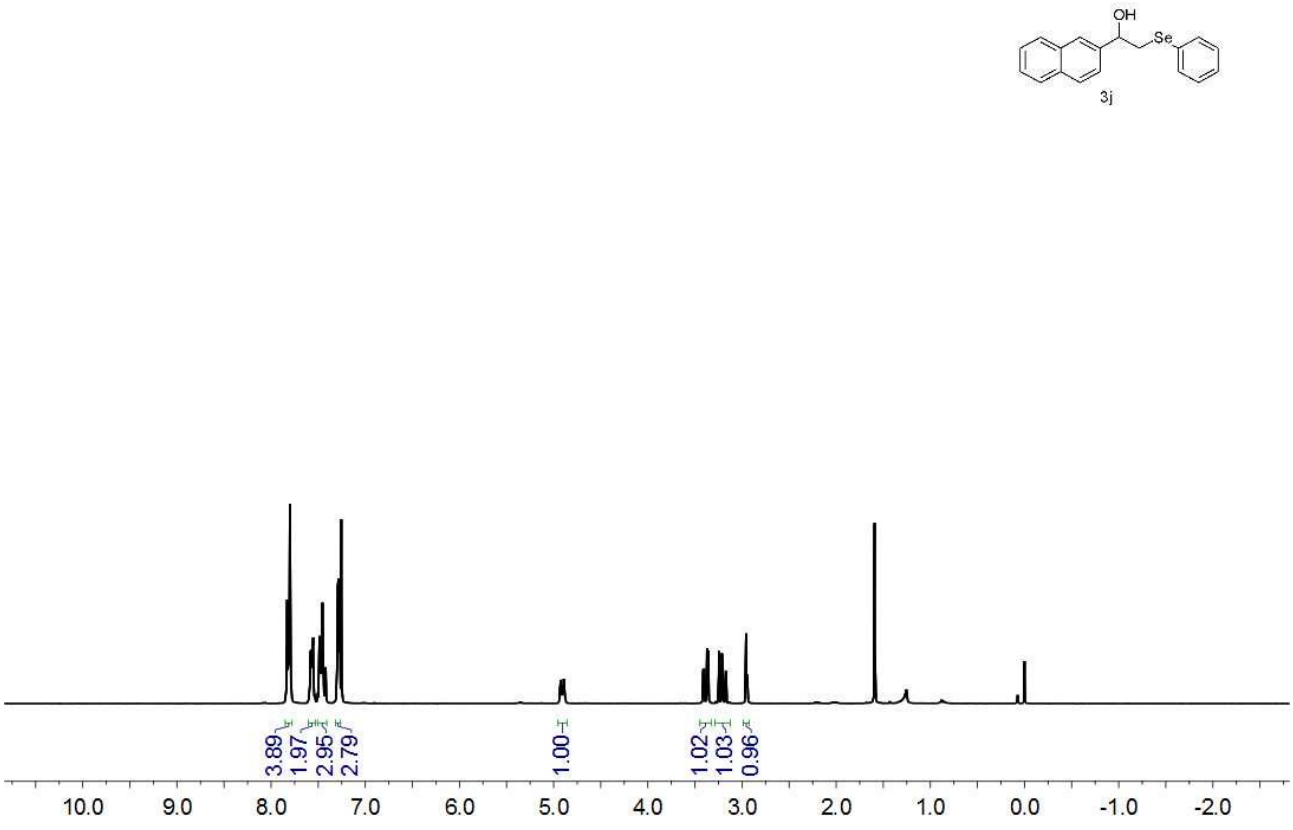
128.852
127.482
127.429
115.383
115.171
71.491
38.357
OH
Se
F
3i
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0


OH
Se
3j
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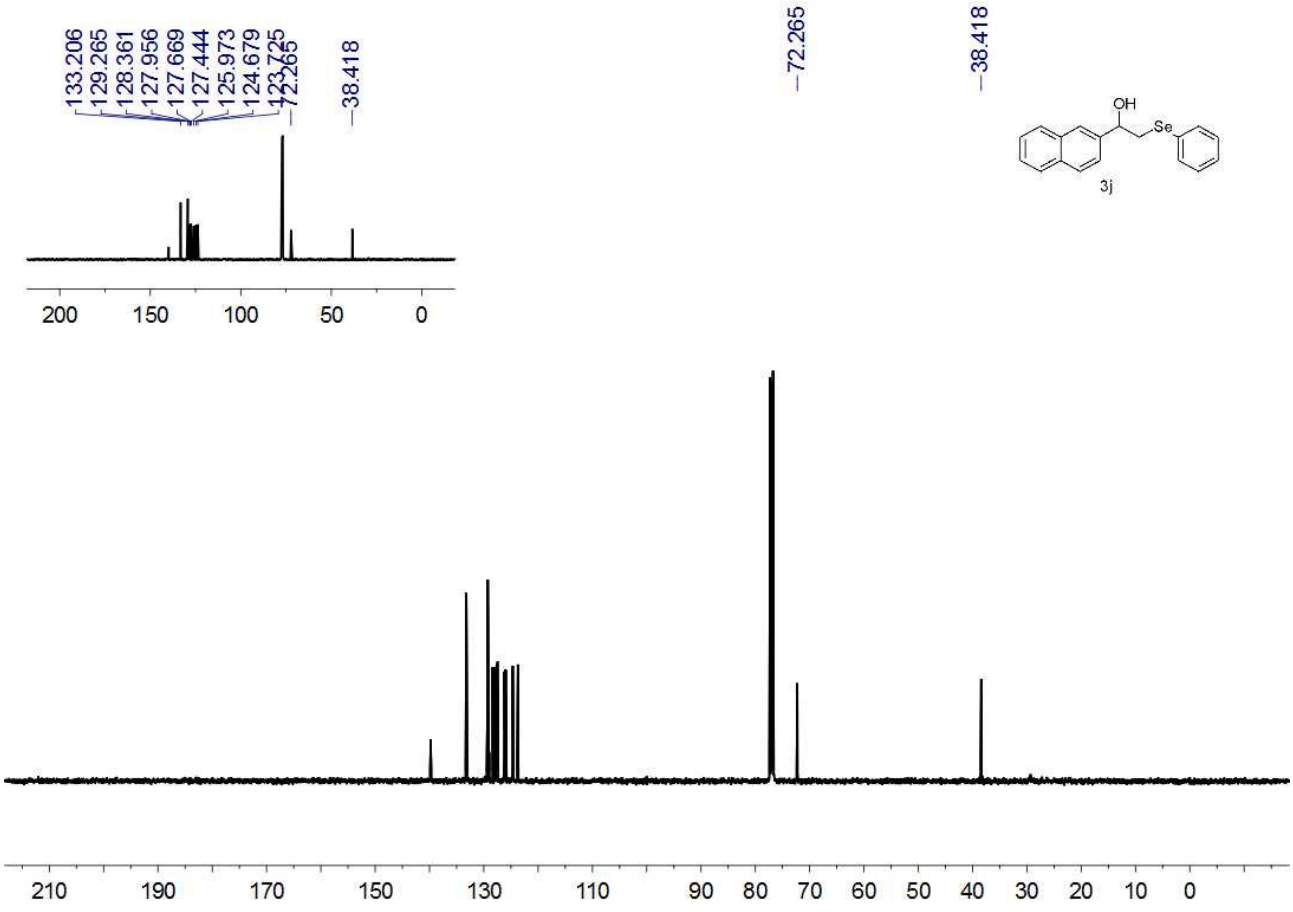
1.97
2.95
2.79
1.00
1.02
1.03
0.96
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
-2.0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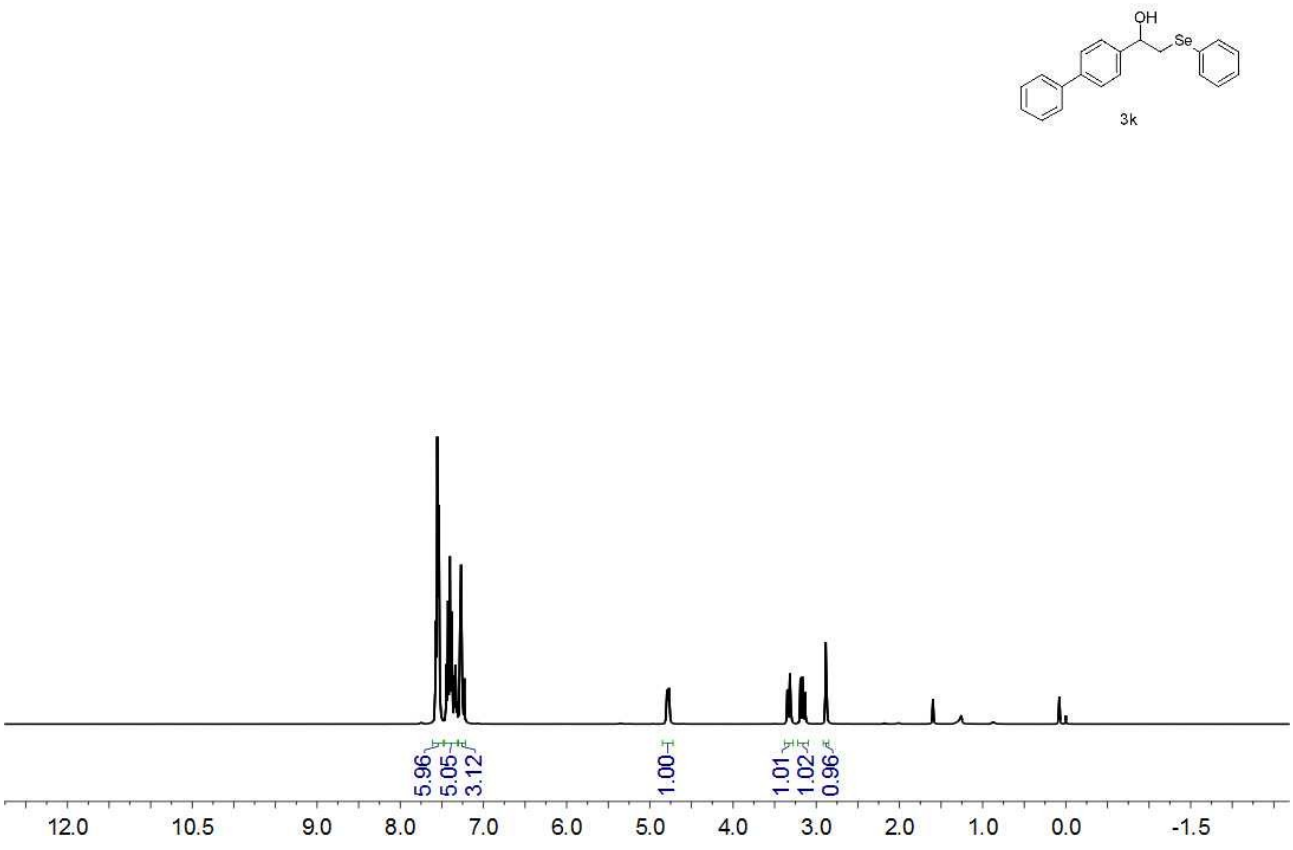
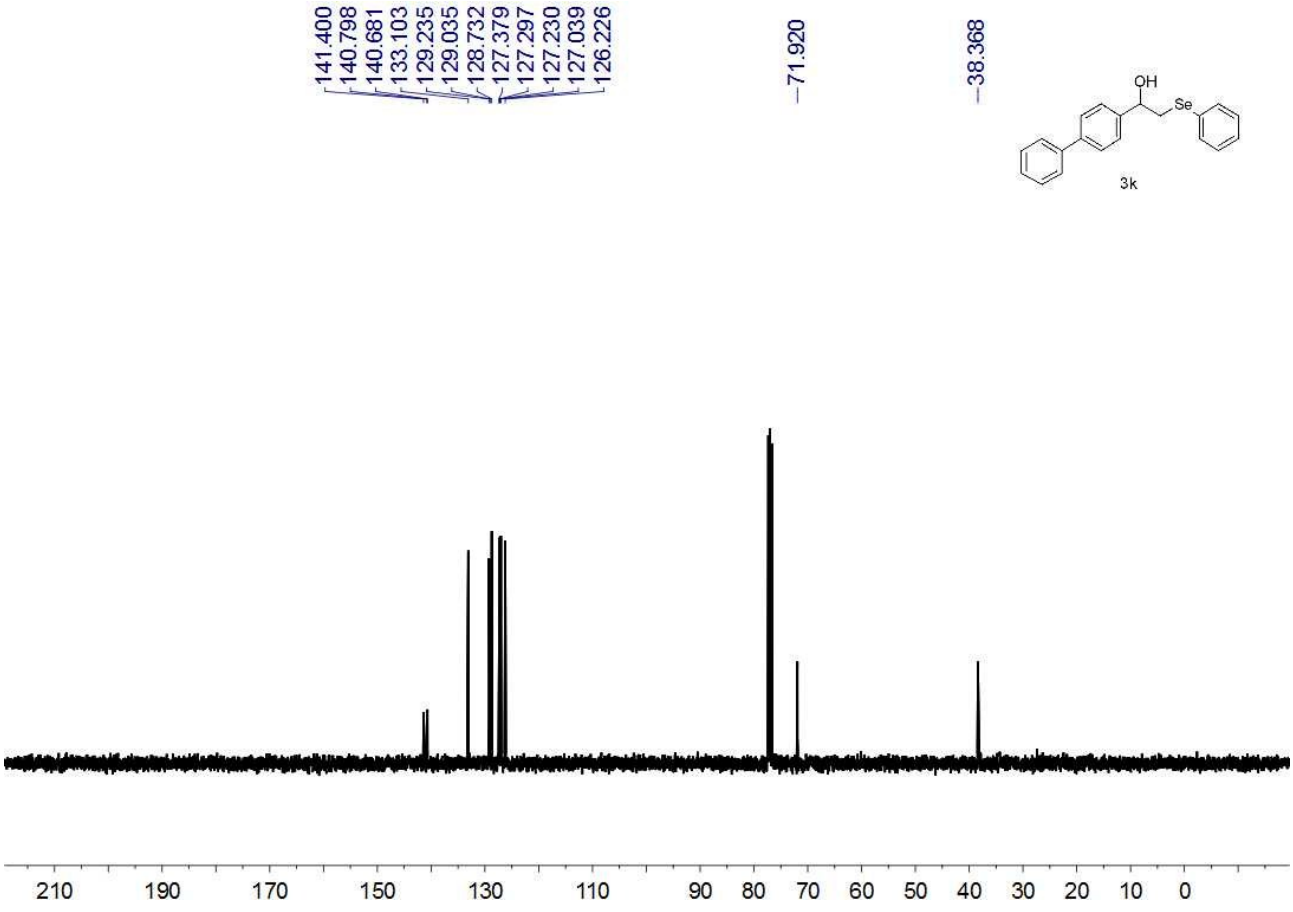
127.956
127.669
127.444
125.973
124.679
123.725
72.265
38.418
72.265
38.418
OH
Se
3j
200
150
100
50
0
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0


OH
Se
3k
5.96
5.05
3.12
1.00
1.01
1.02
0.96
12.0
10.5
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.5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140.681
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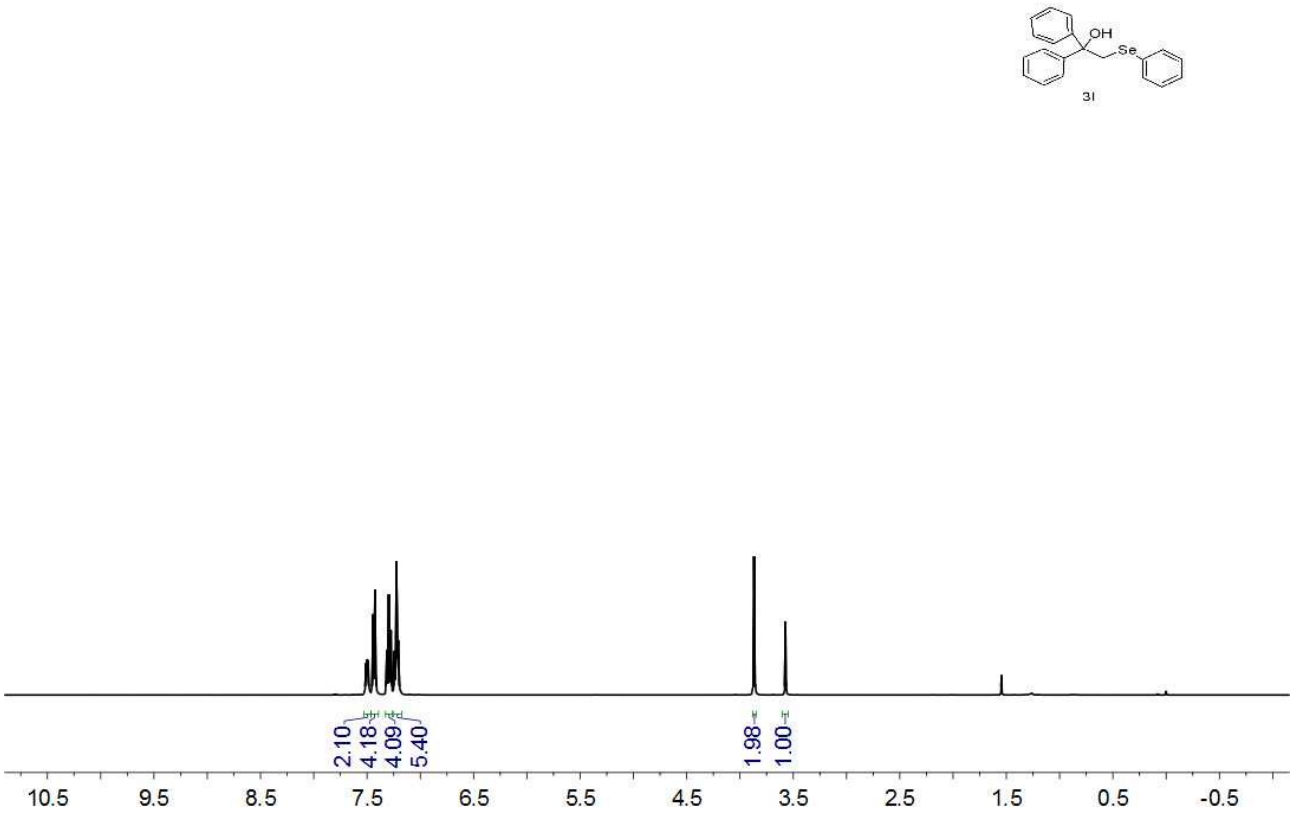
129.235
129.035
128.732
127.379
127.297
127.230
127.039
126.226
71.920
38.368
OH
Se
3k
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0


OH
Se
3l
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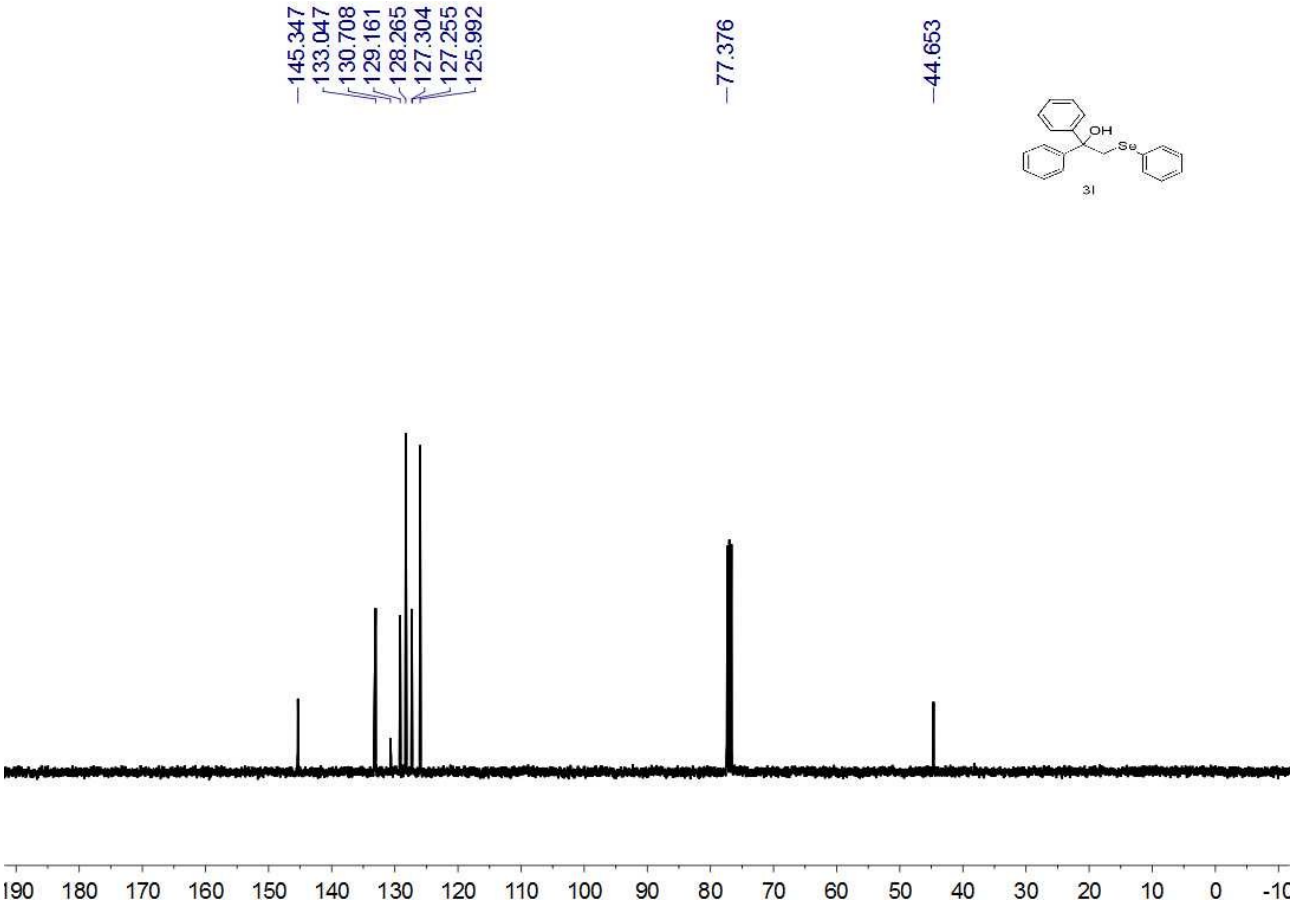
4.18
4.09
5.40
1.98
1.00
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5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129.161
128.265
127.304
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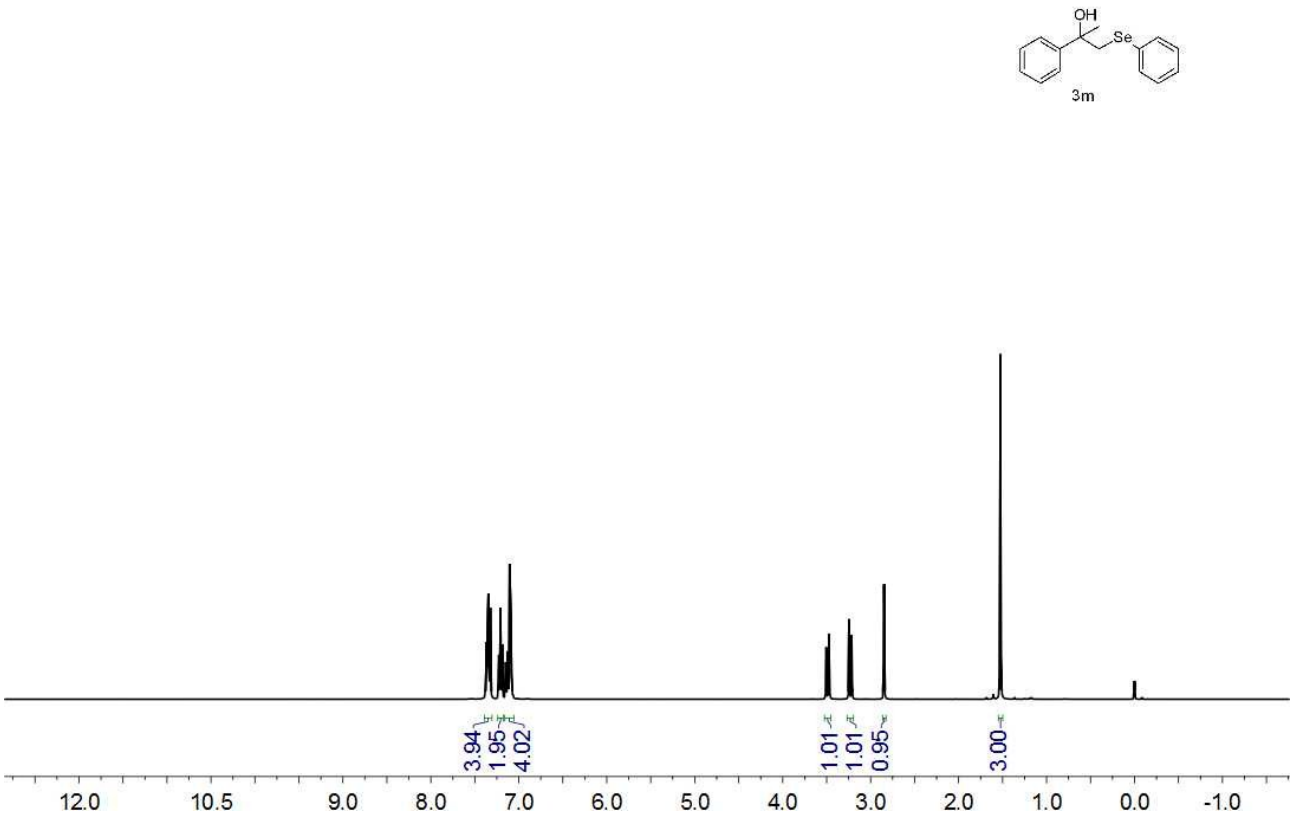
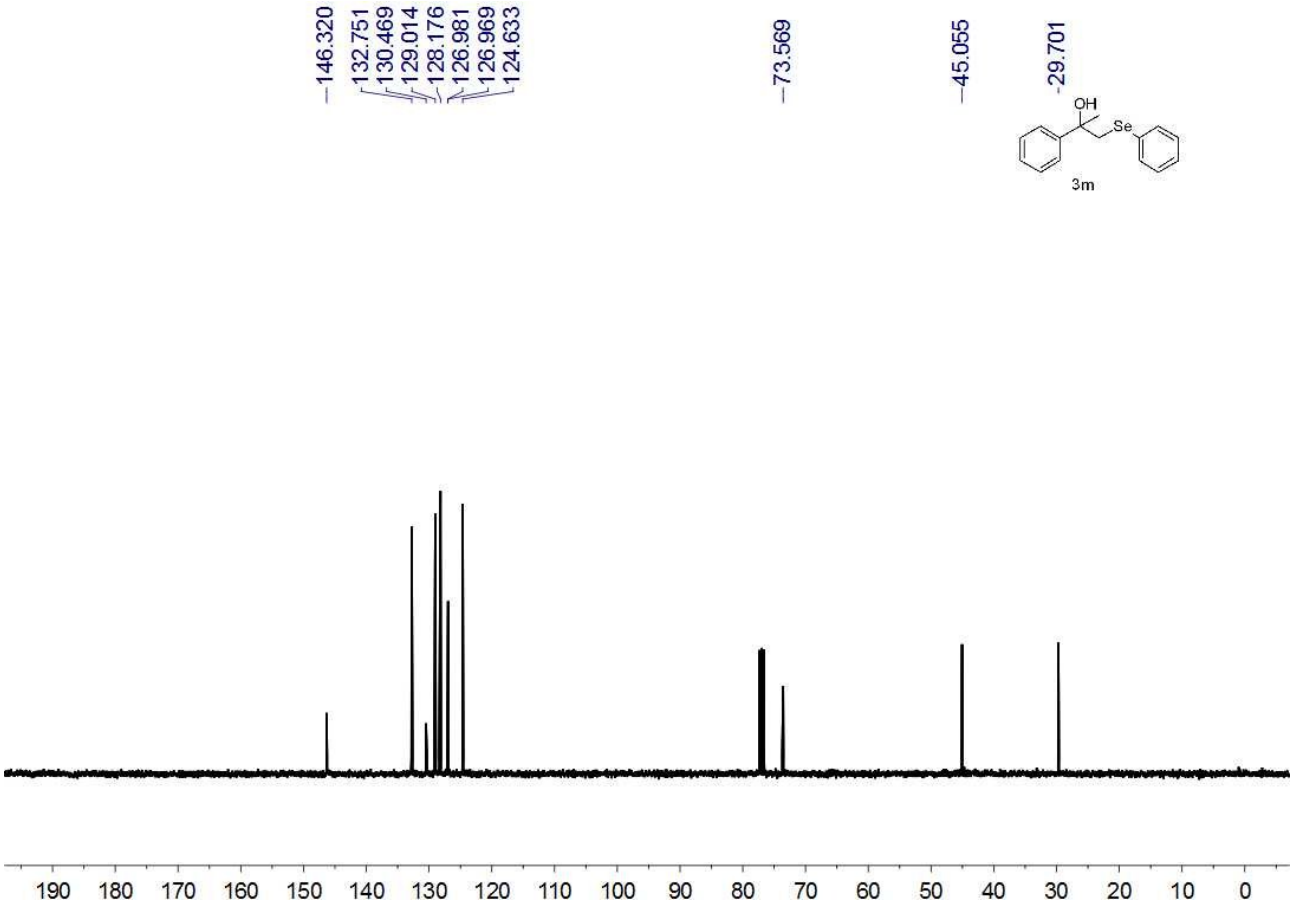
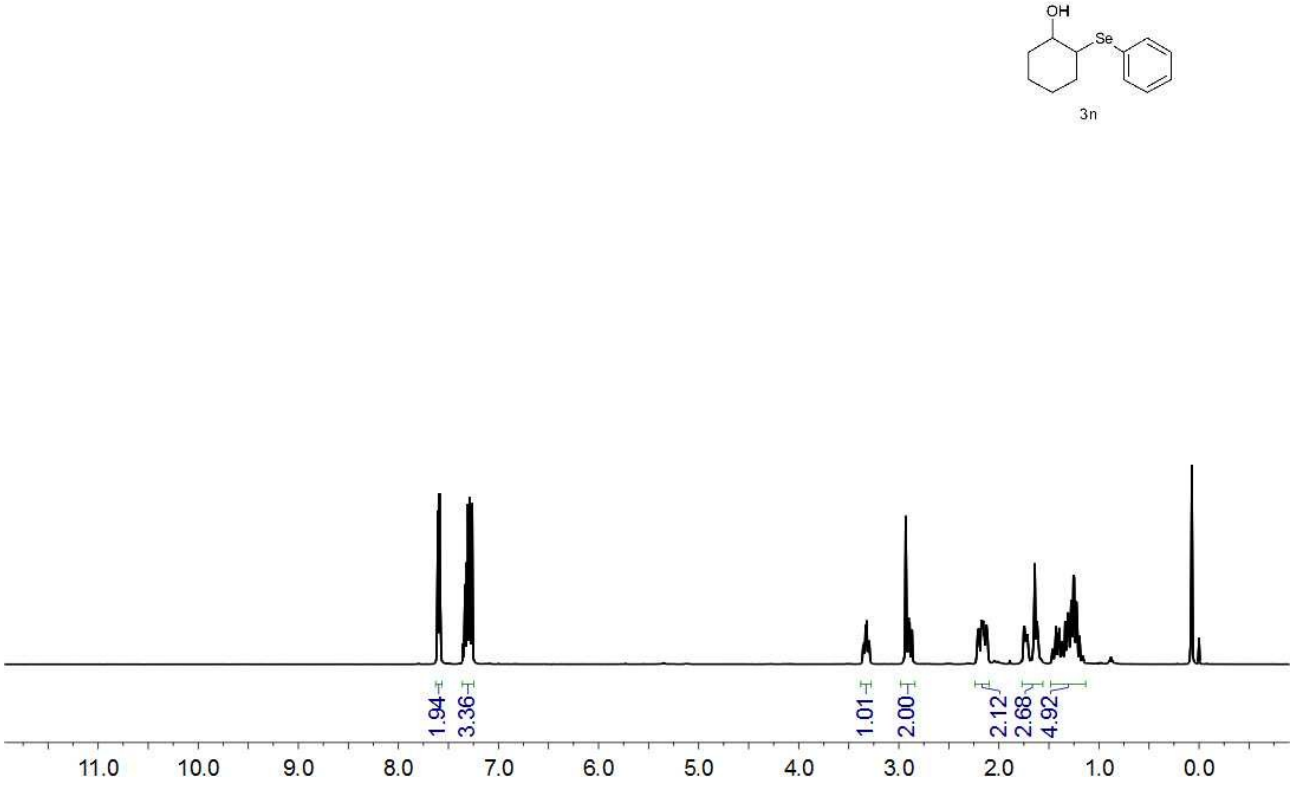
125.992
77.376
44.653
OH
Se
3l
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10


OH
Se
3m
3.94
1.95
4.02
1.01
1.01
0.95
3.00
12.0 10.5 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0 -1.0


146.320
132.751
130.469
129.014
128.176
126.981
126.969
124.633
73.569
45.055
29.701
OH
Se
3m
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0


OH
Se
3n
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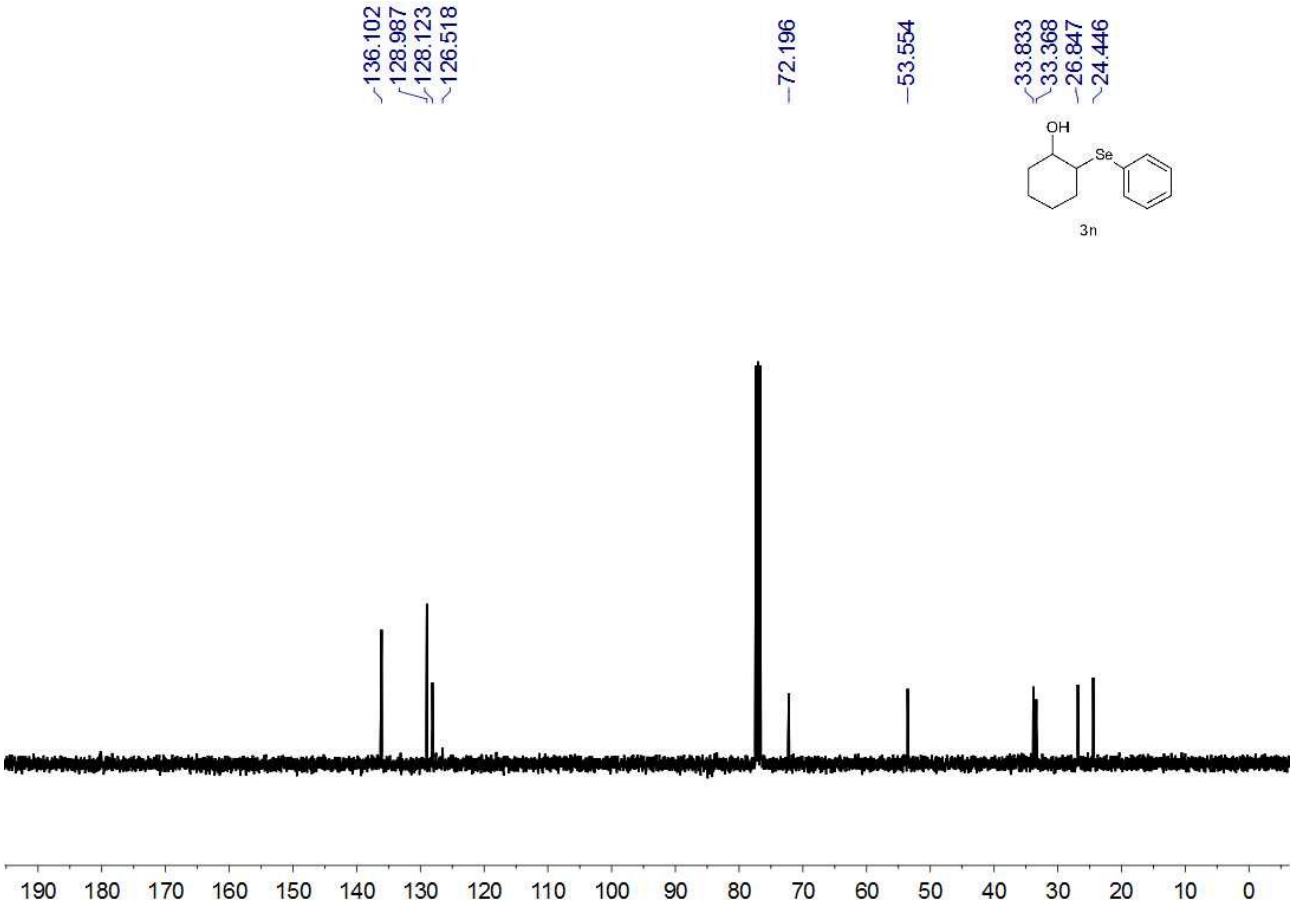
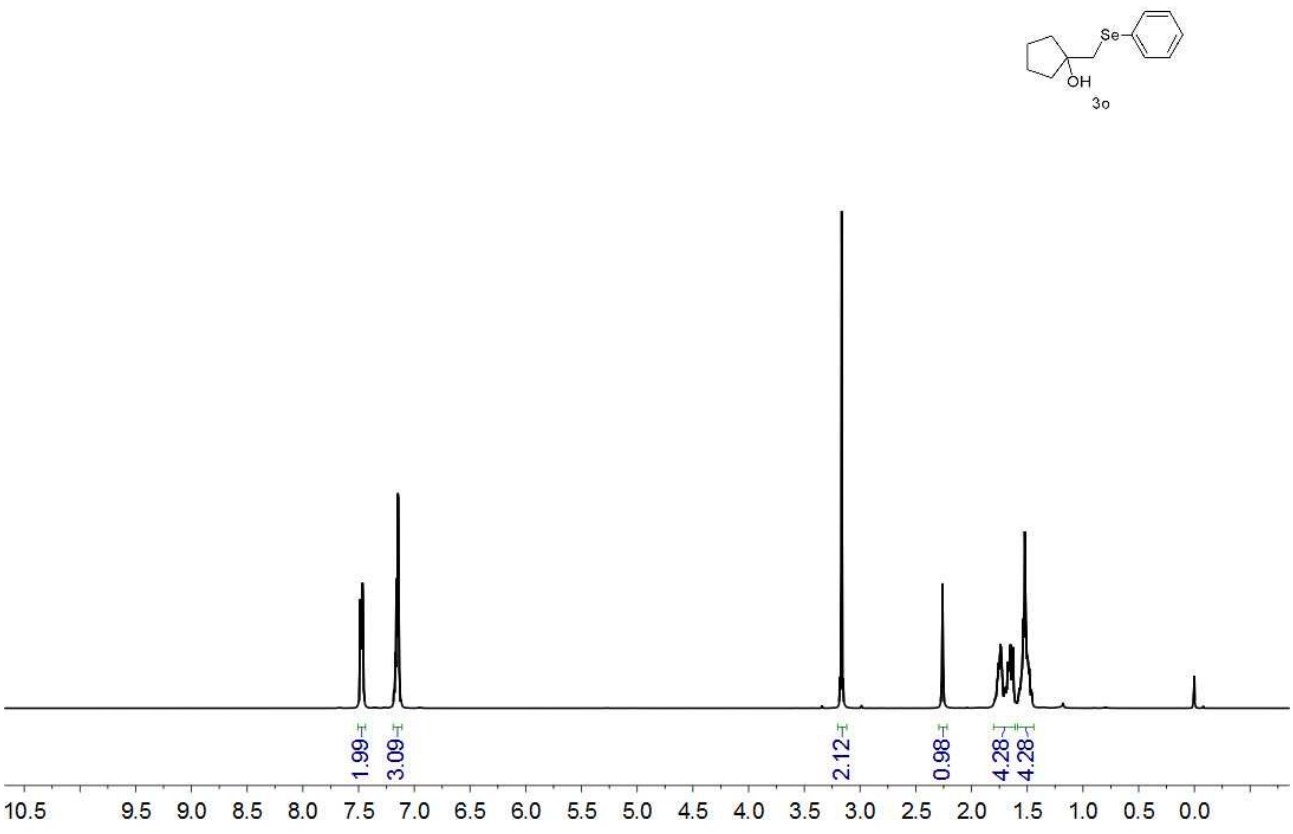
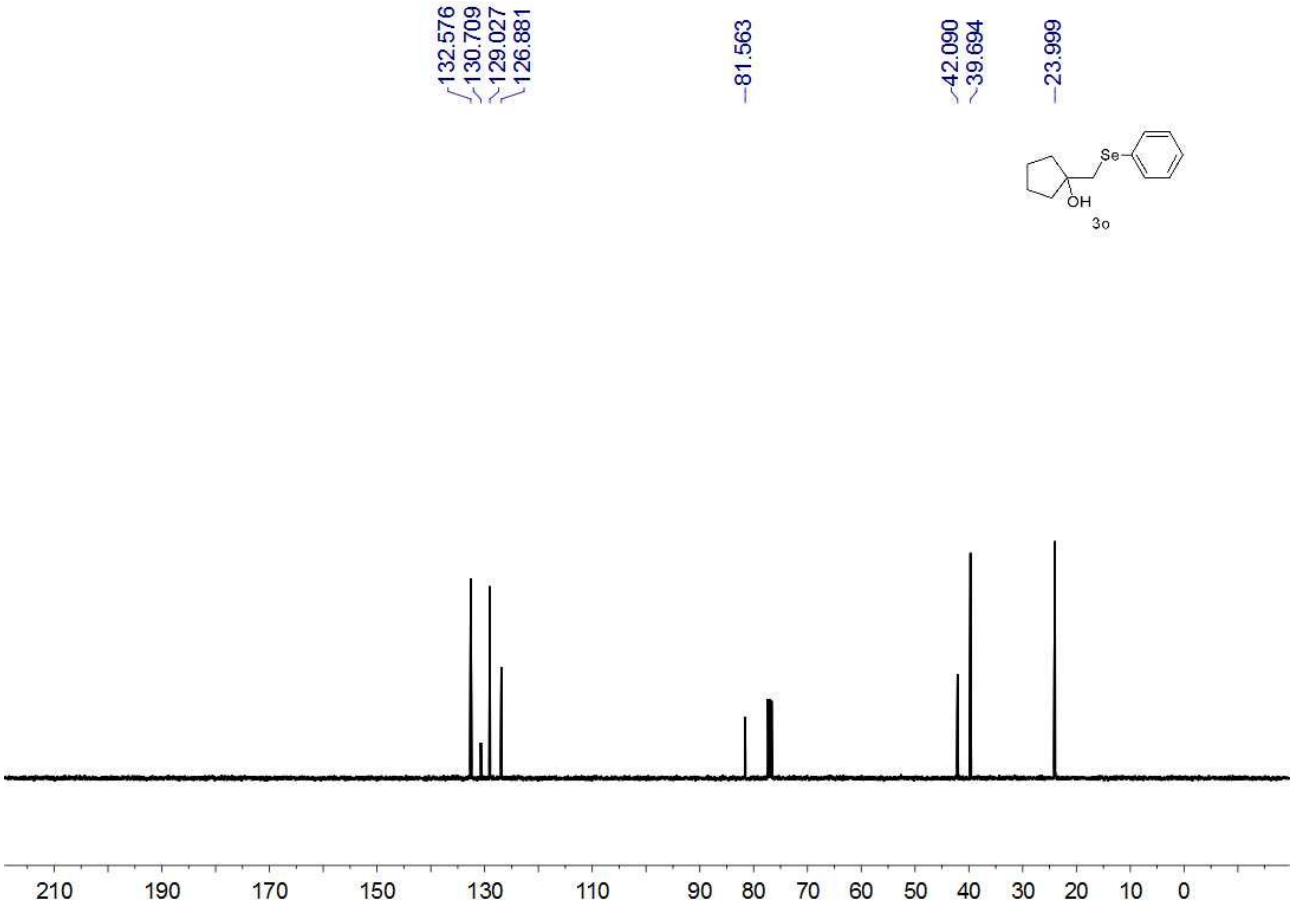
3.36
1.01
2.00
2.12
2.68
4.92
11.0 10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0


136.102
128.987
128.123
126.518
72.196
53.554
33.833
33.368
26.847
24.446
OH
Se
3n
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0


Se
OH
3o
1.99
3.09
2.12
0.98
4.28
4.28
10.5 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0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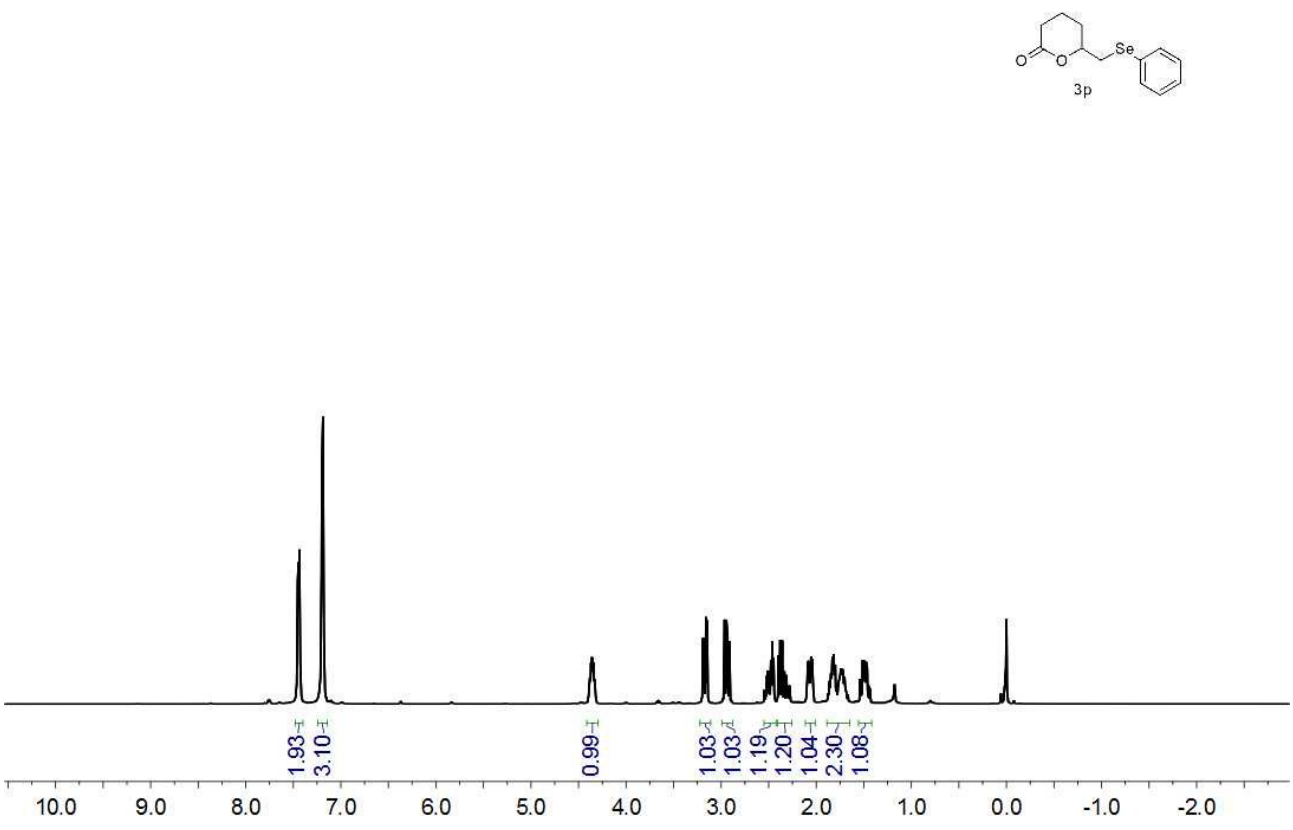
129.027
126.881
81.563
42.090
39.694
23.999
Se
OH
3o
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0


O
O
Se
3p
1.93
3.10
0.99
1.03
1.03
1.19
1.20
1.04
2.30
1.08
10.0
9.0
8.0
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4.0
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1.0
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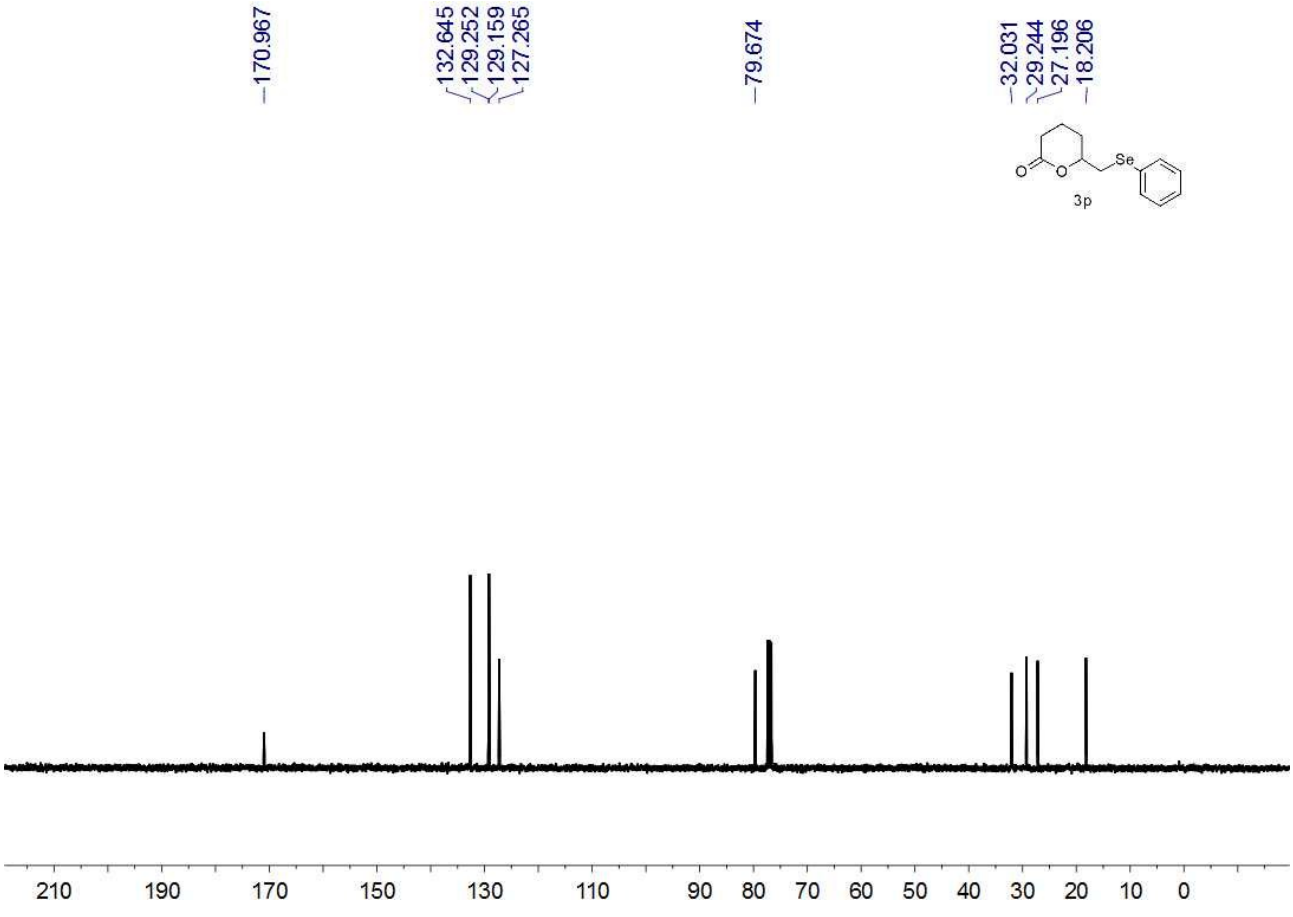
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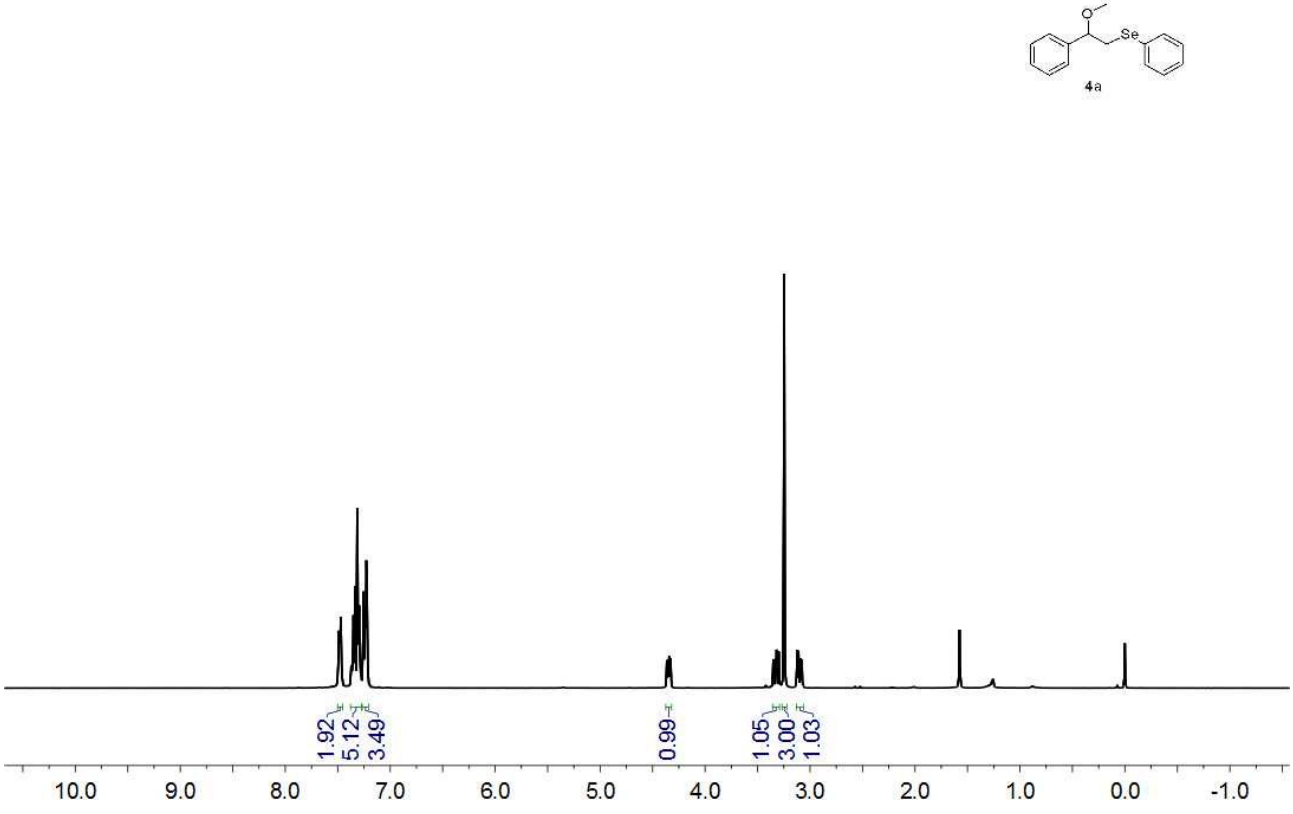
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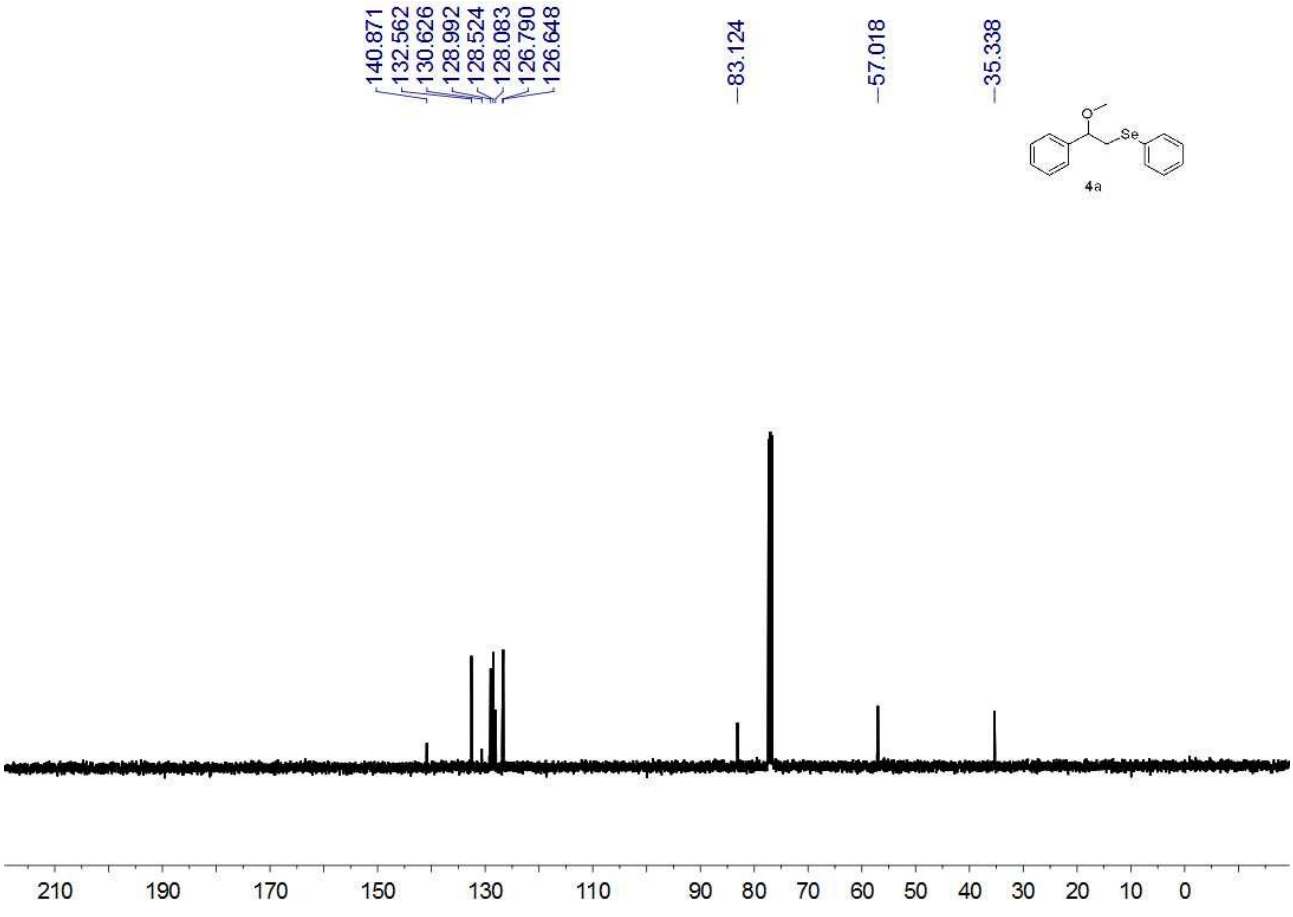
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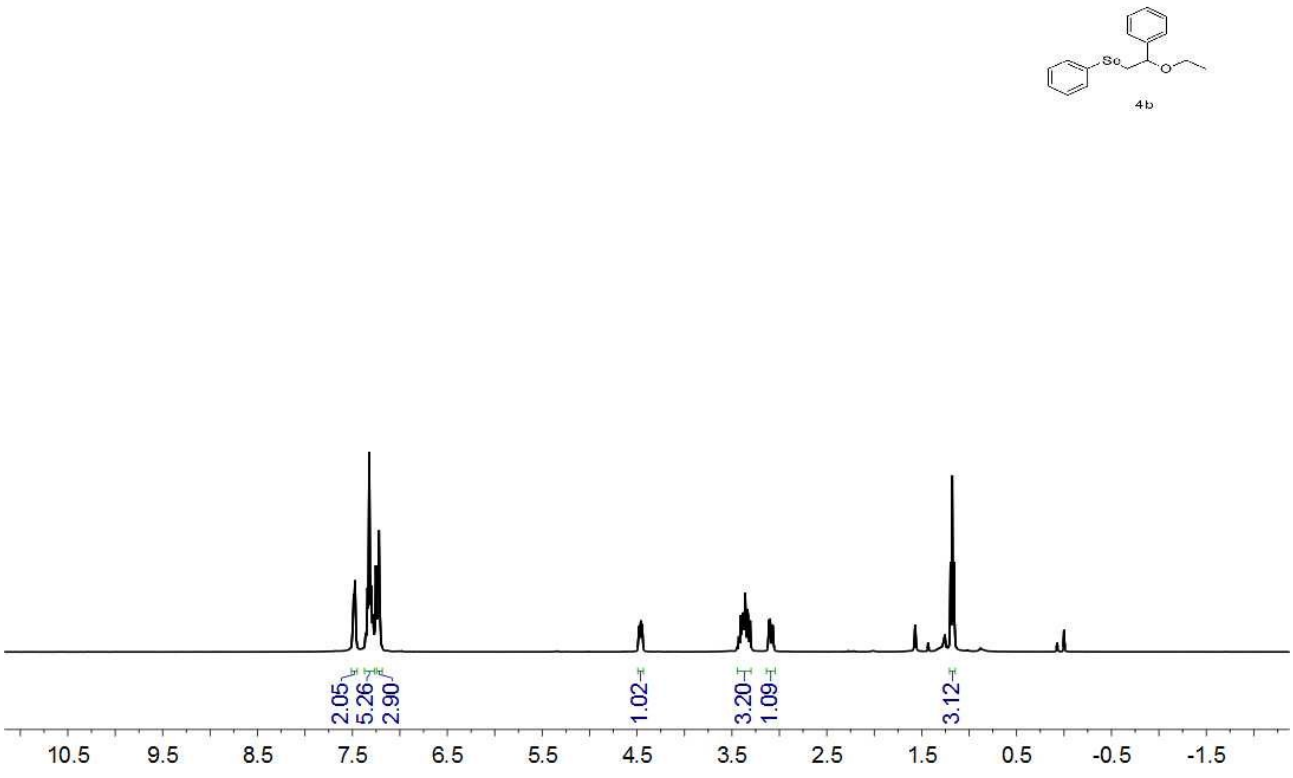
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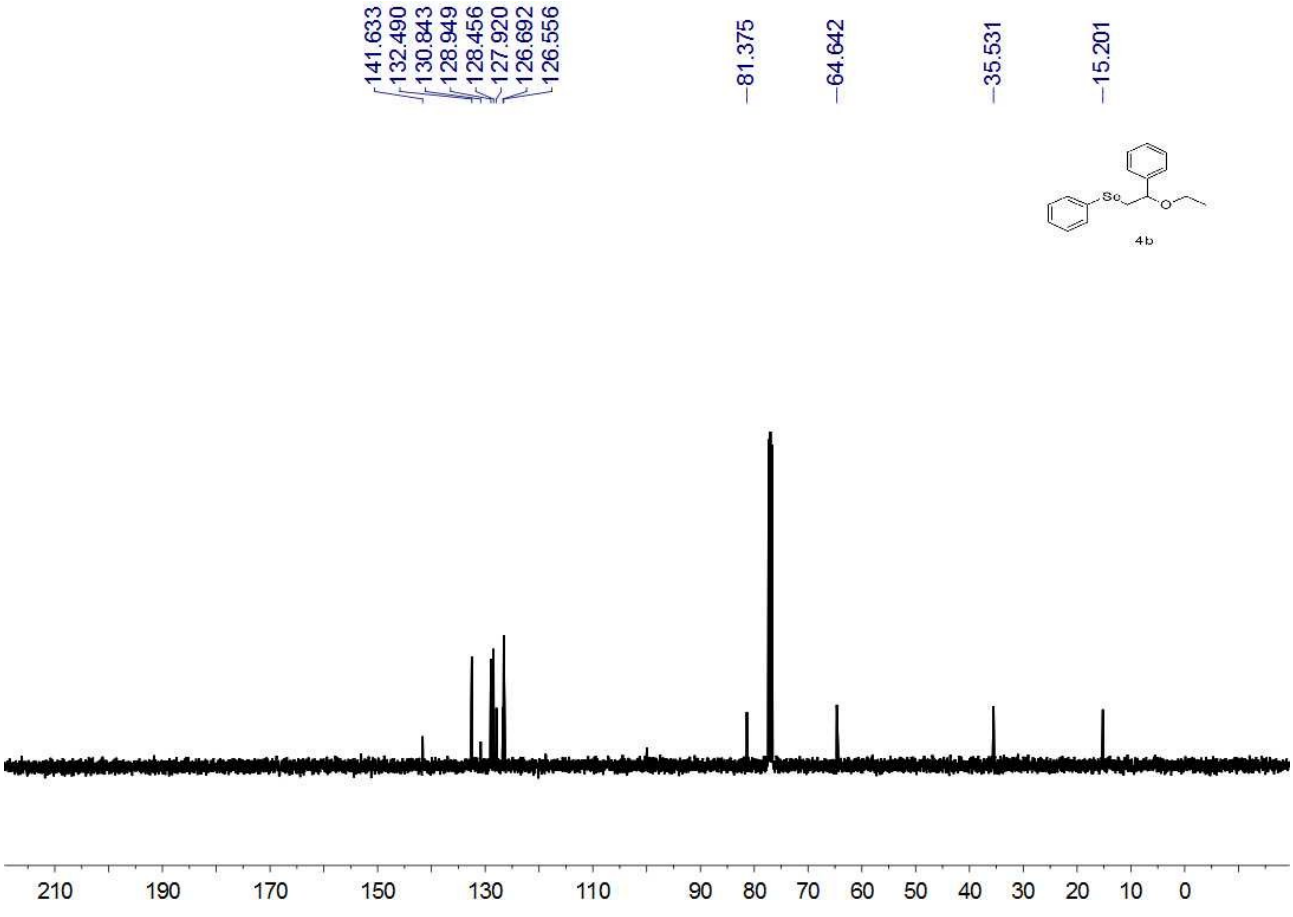
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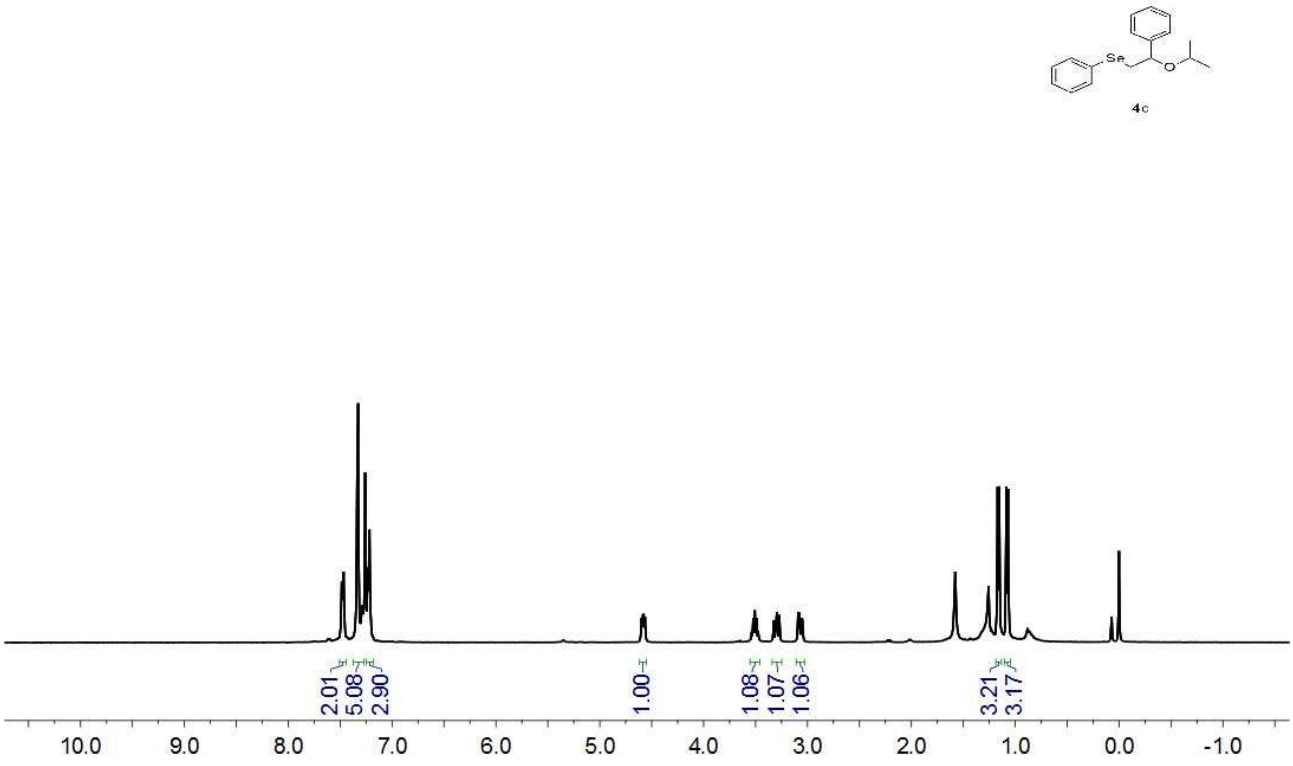
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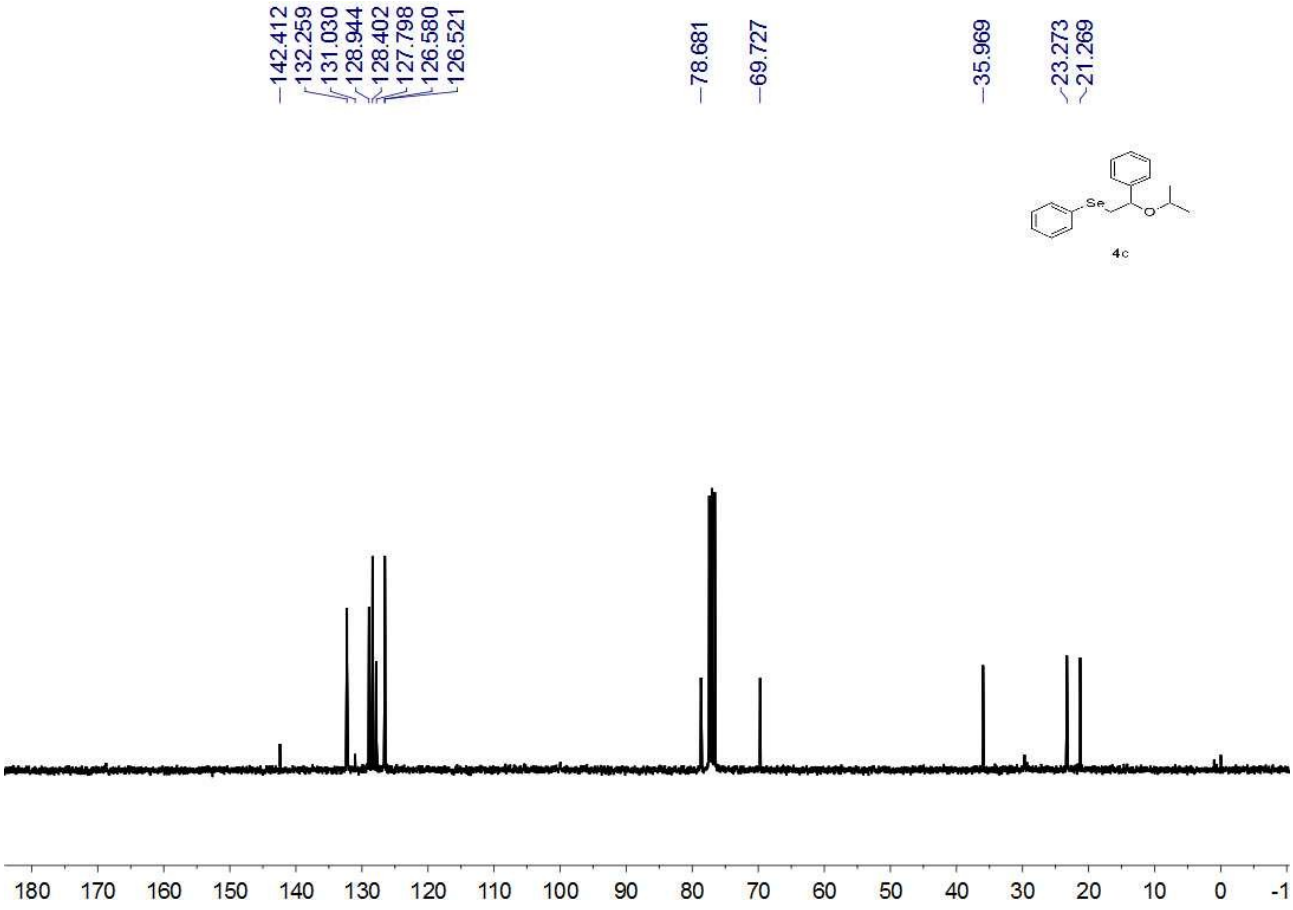
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4c
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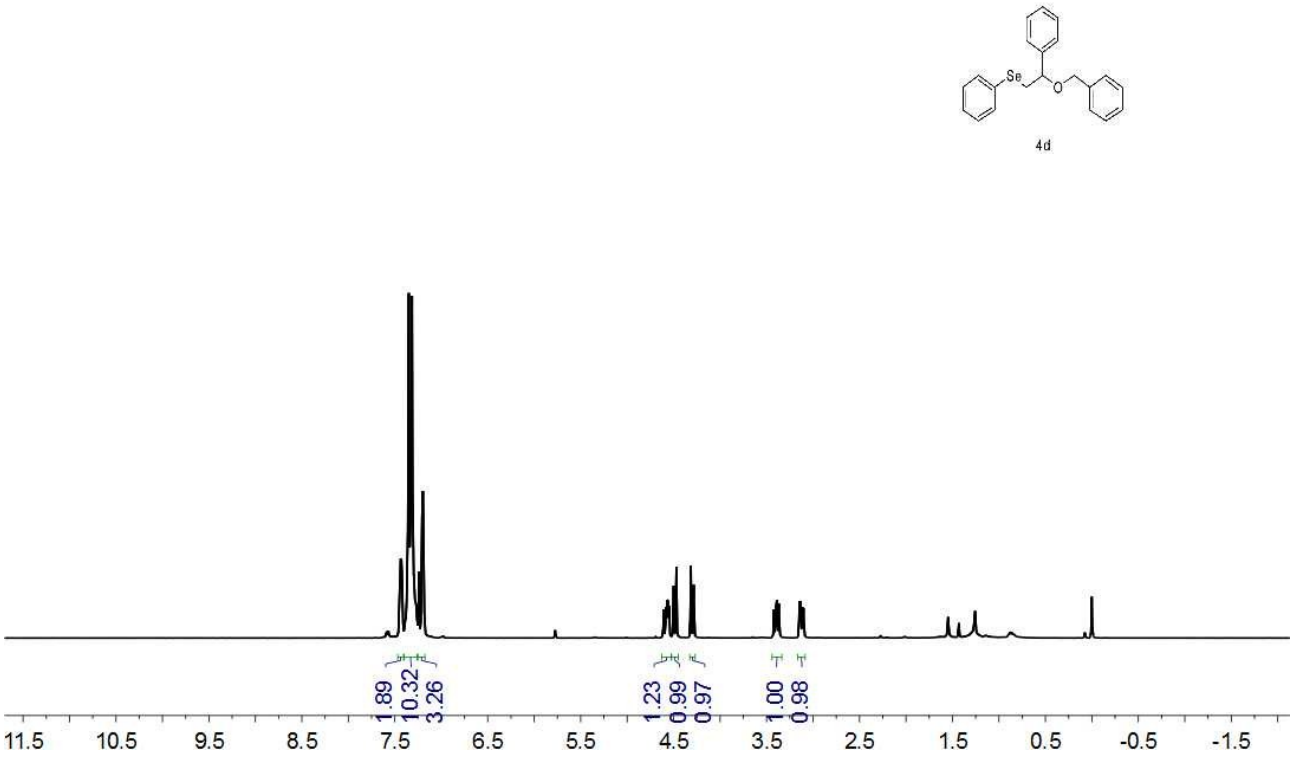
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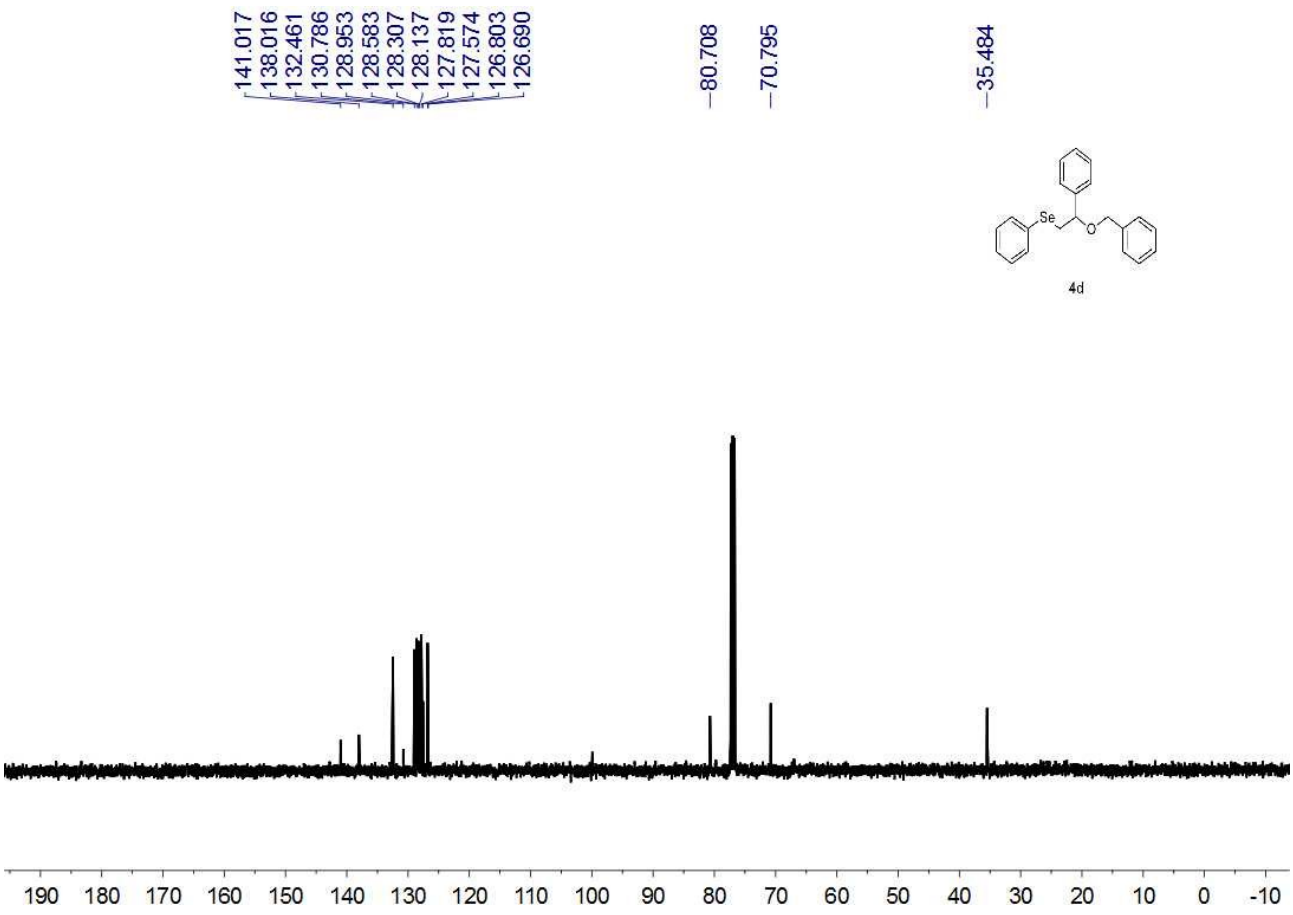
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127.574
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70.795
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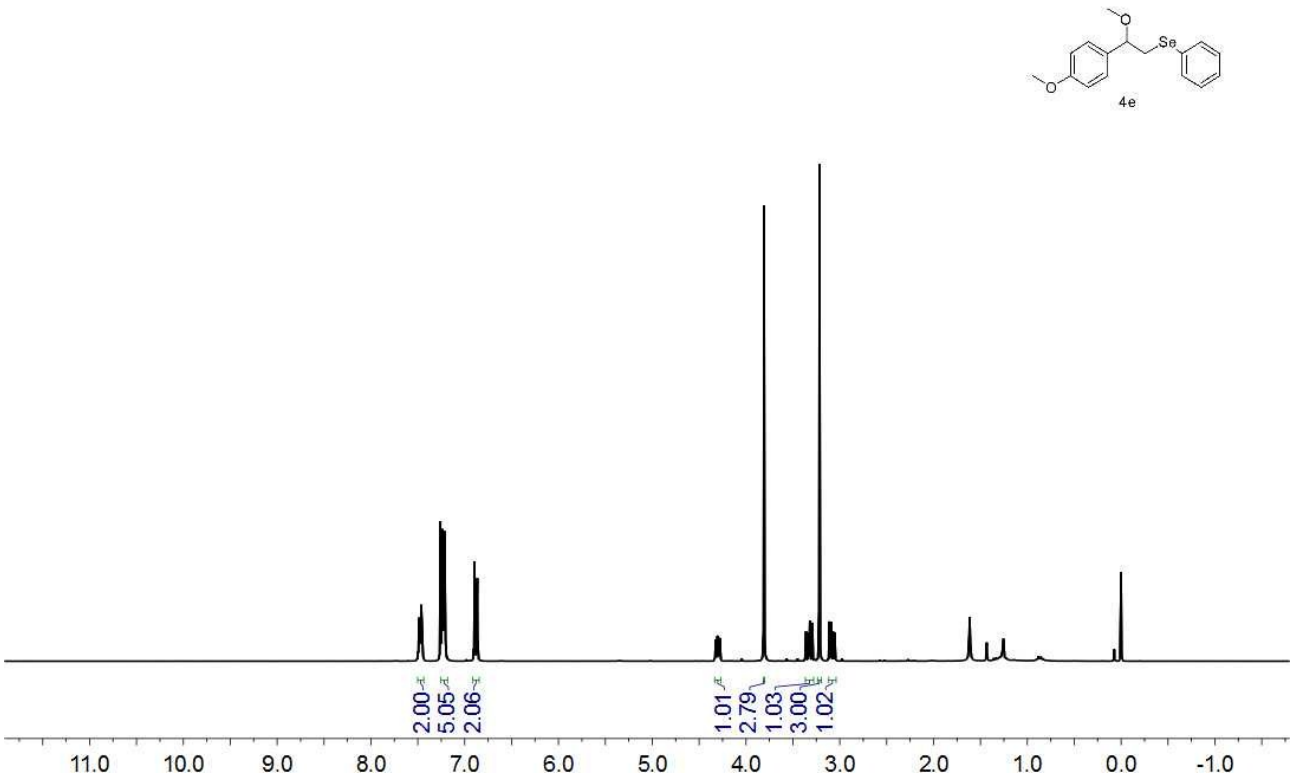
O
4d
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10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Se
O
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5.05
2.06
1.01
2.79
1.03
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1.02
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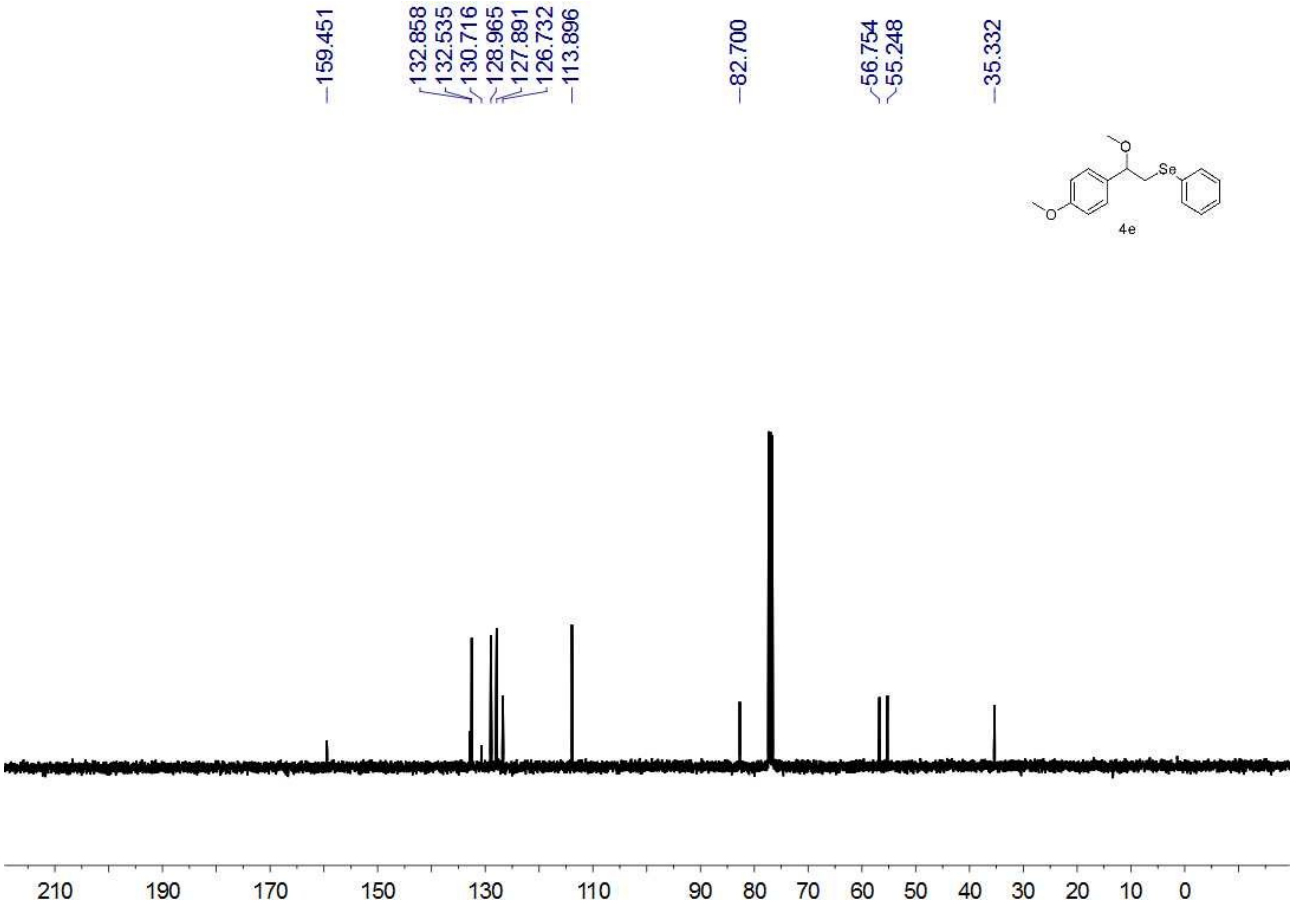
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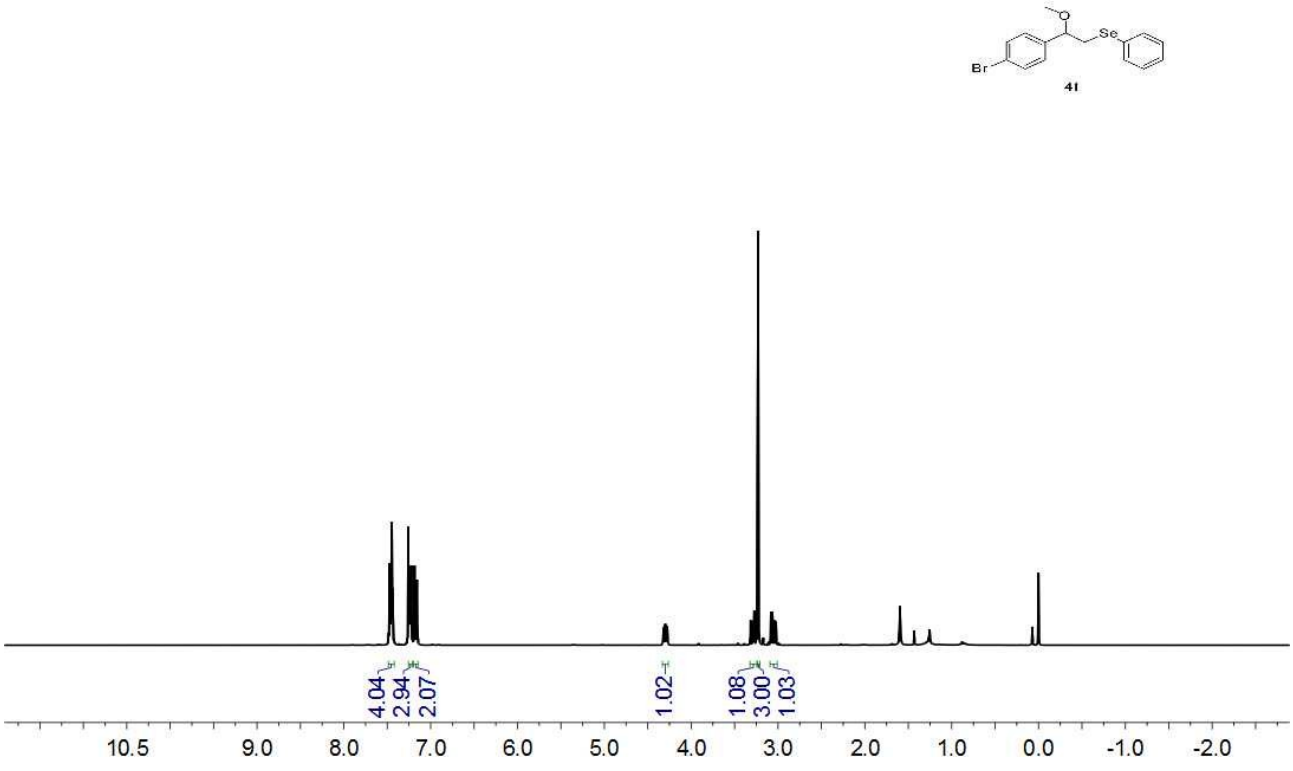
Br
Se
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2.07
1.02
1.08
3.00
1.03
10.5
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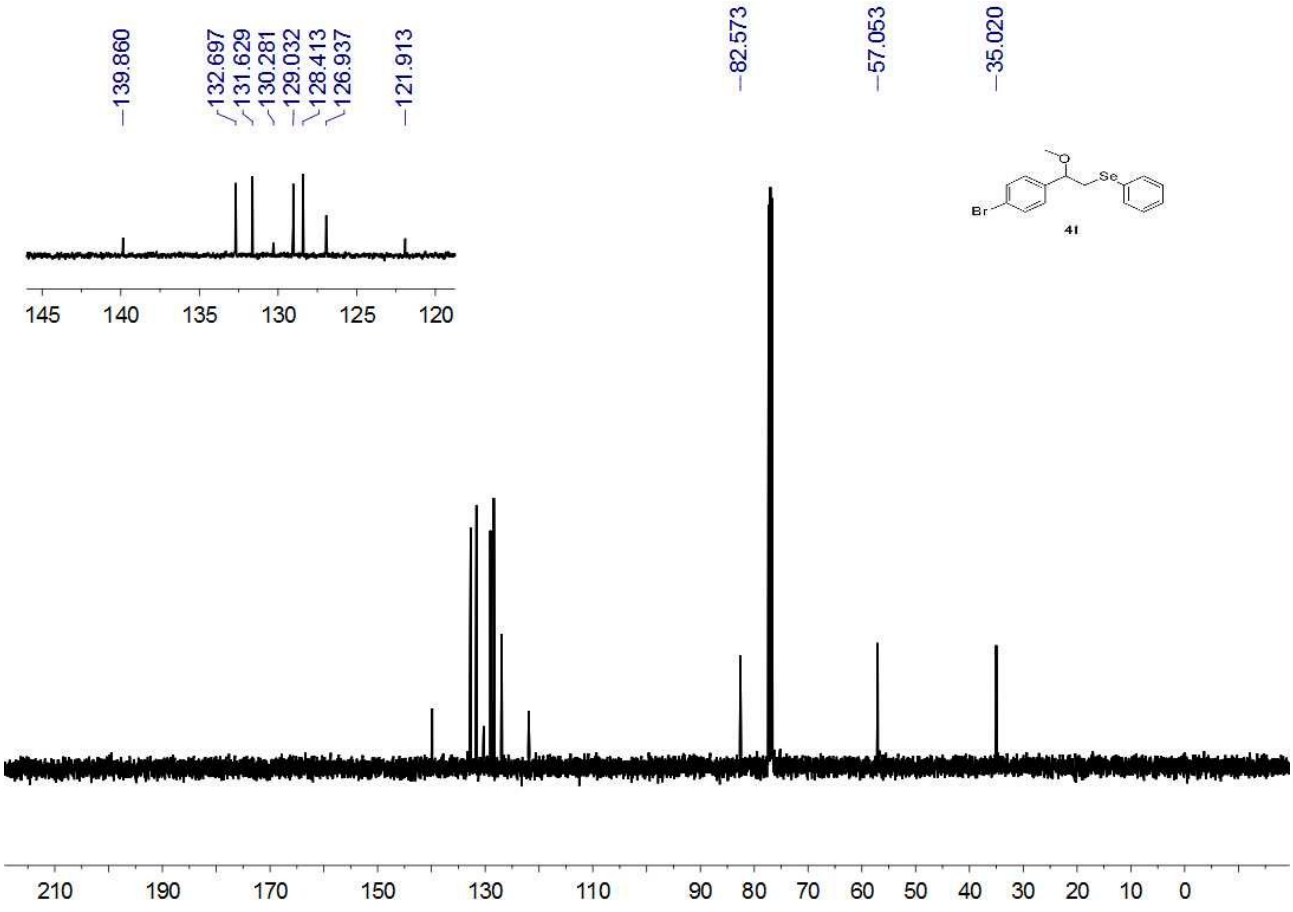
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Se
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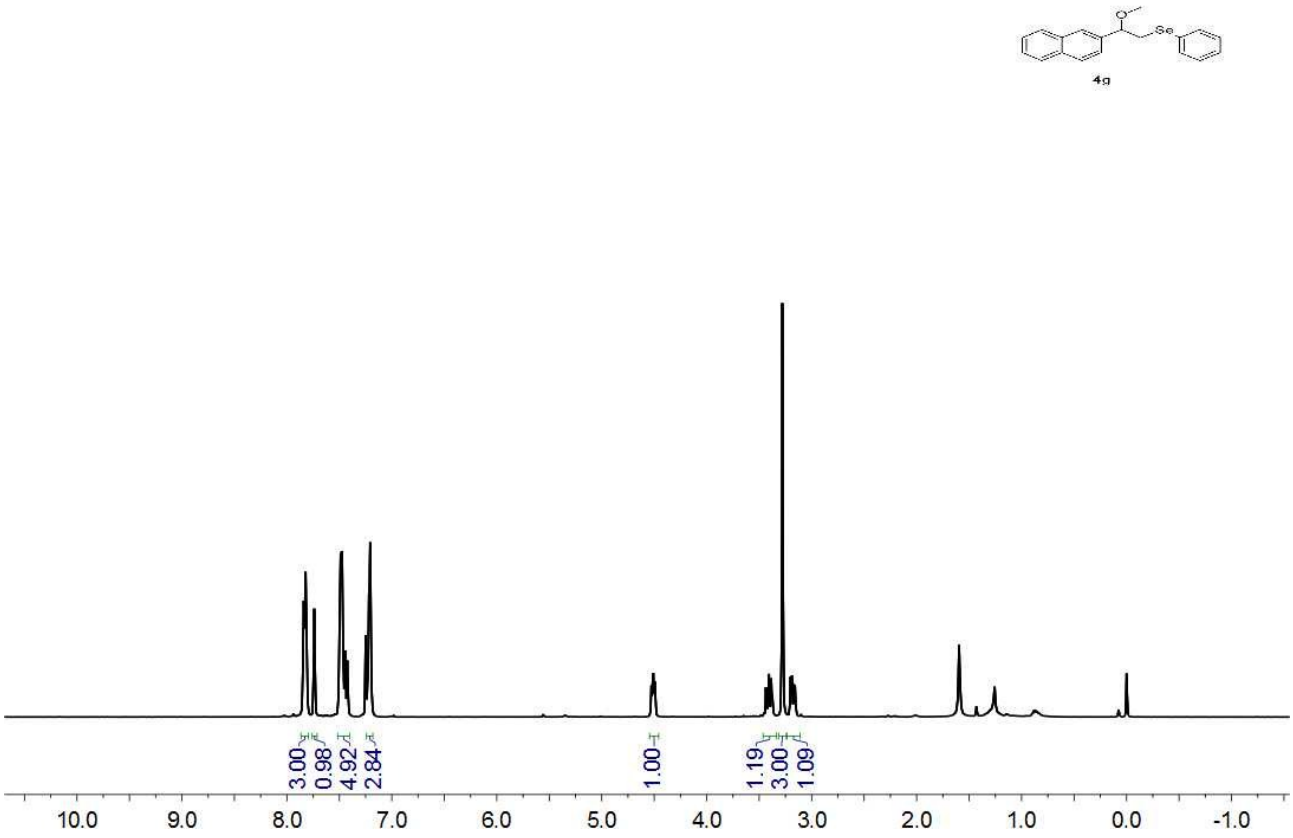
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2.84
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3.00
1.09
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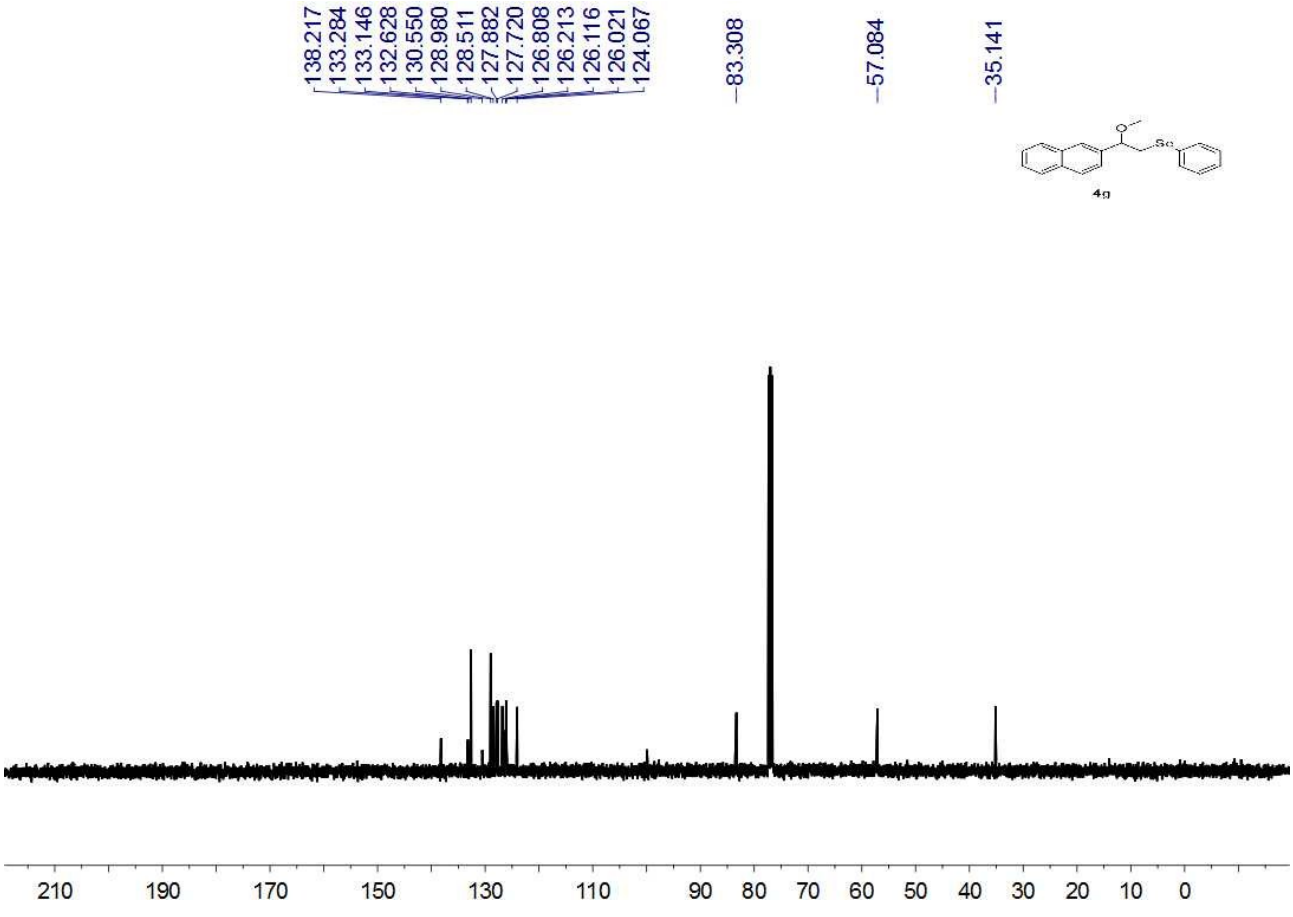
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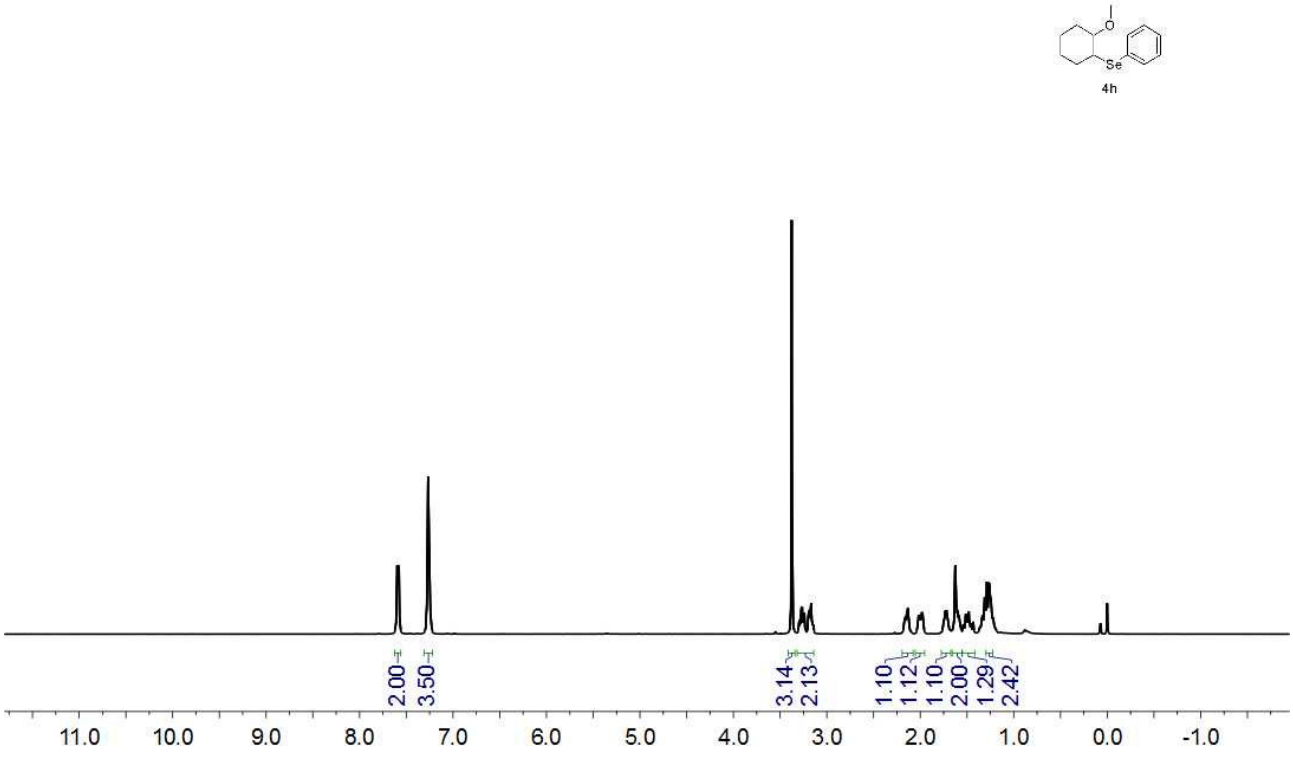
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1.10
2.00
1.29
2.42
11.0
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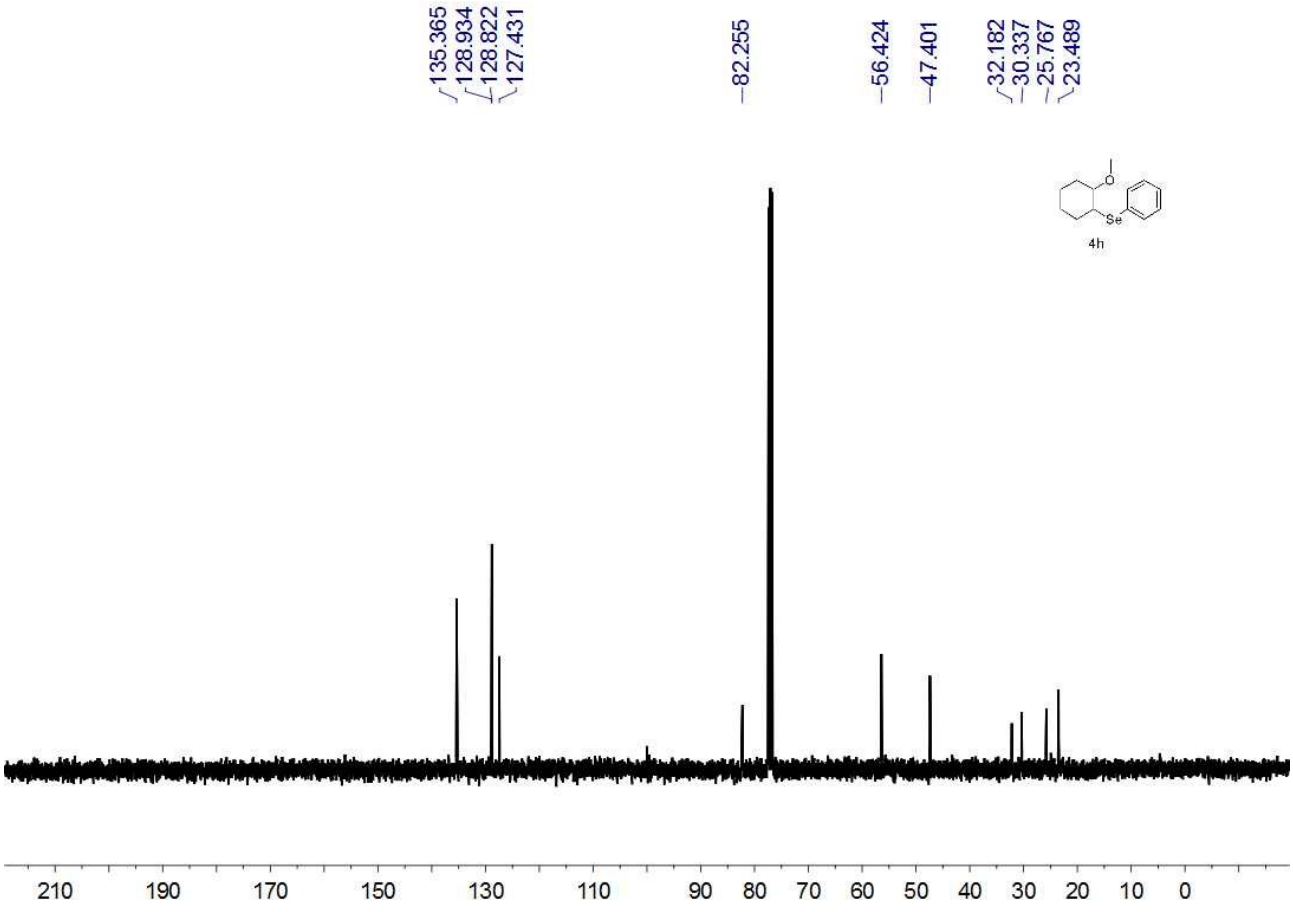
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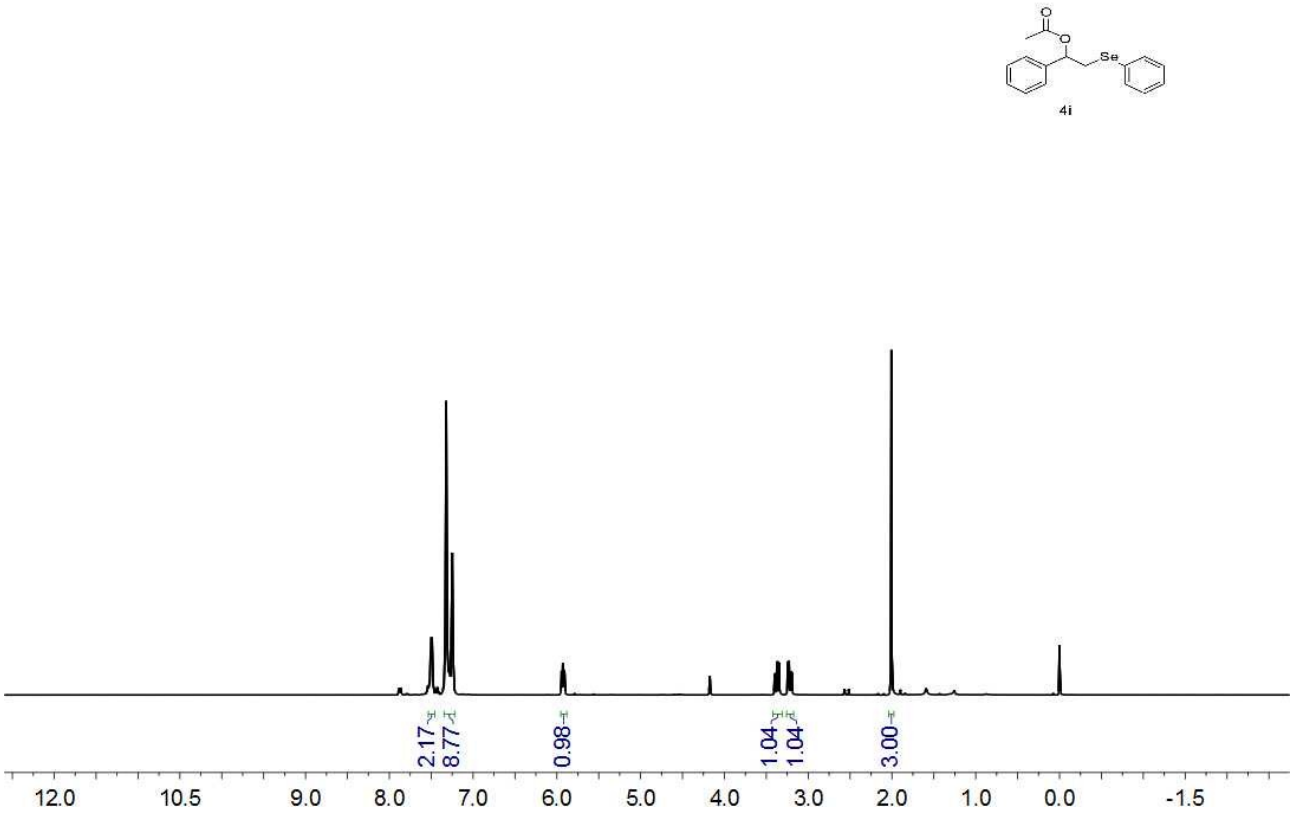
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O
Se
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1.04
1.04
3.00
12.0
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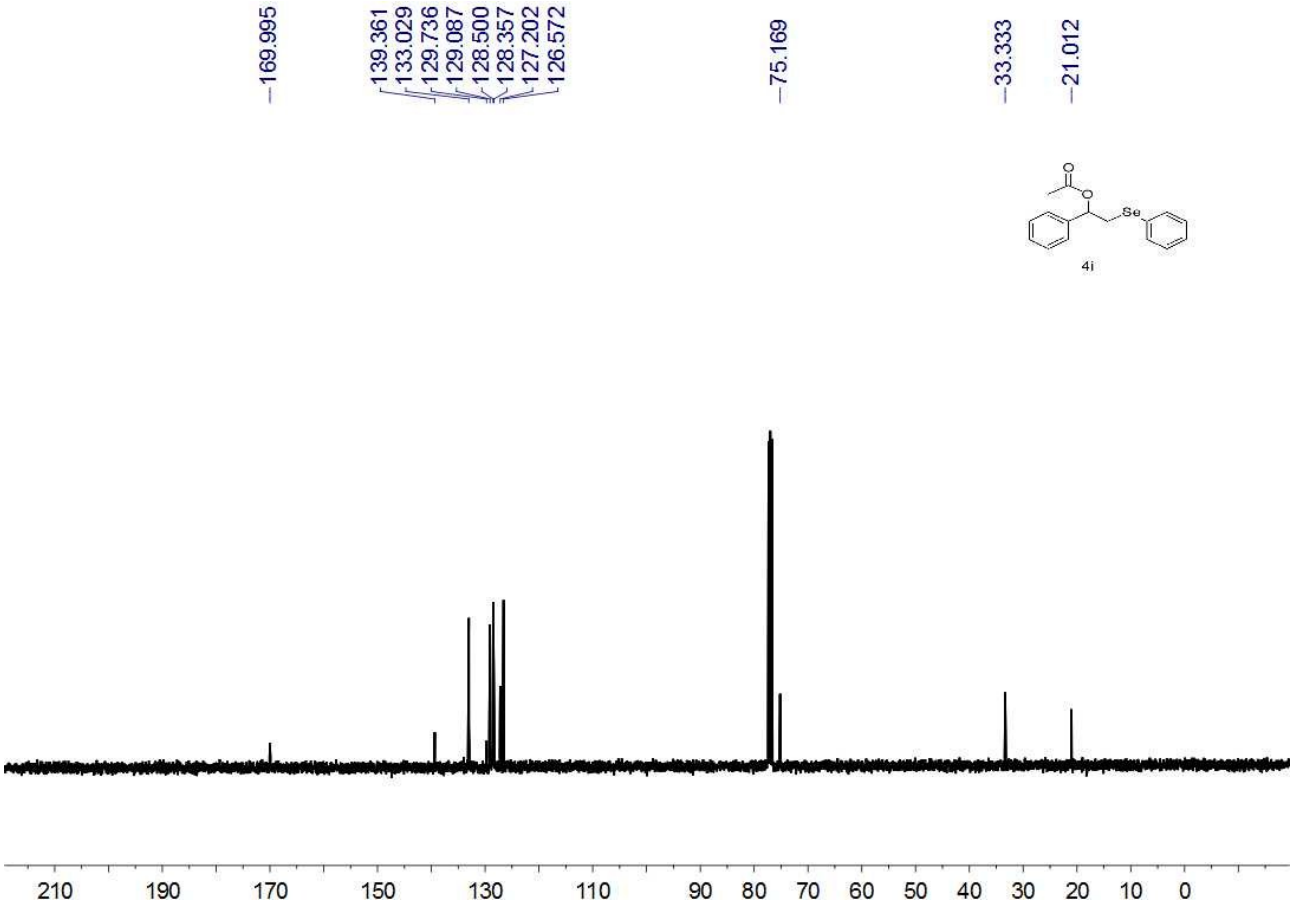
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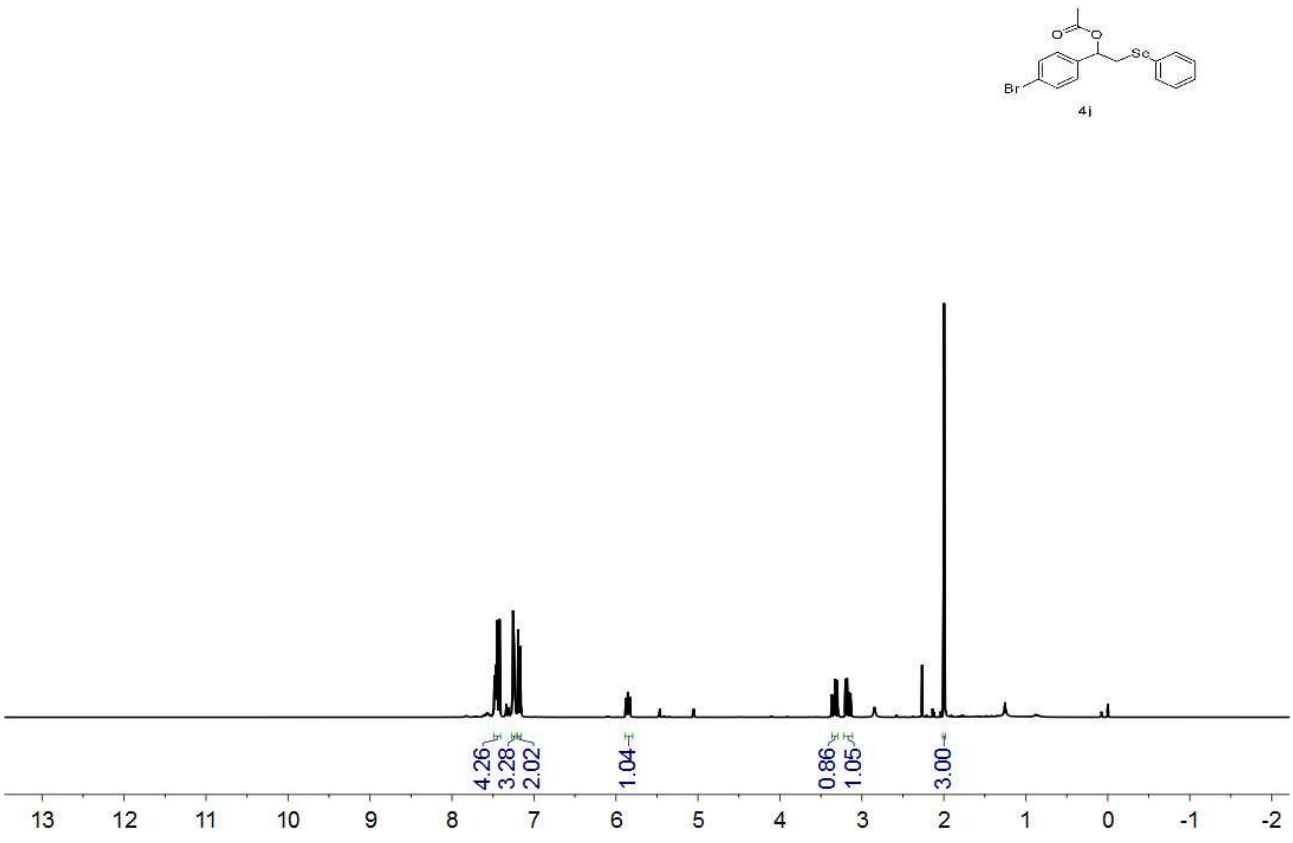
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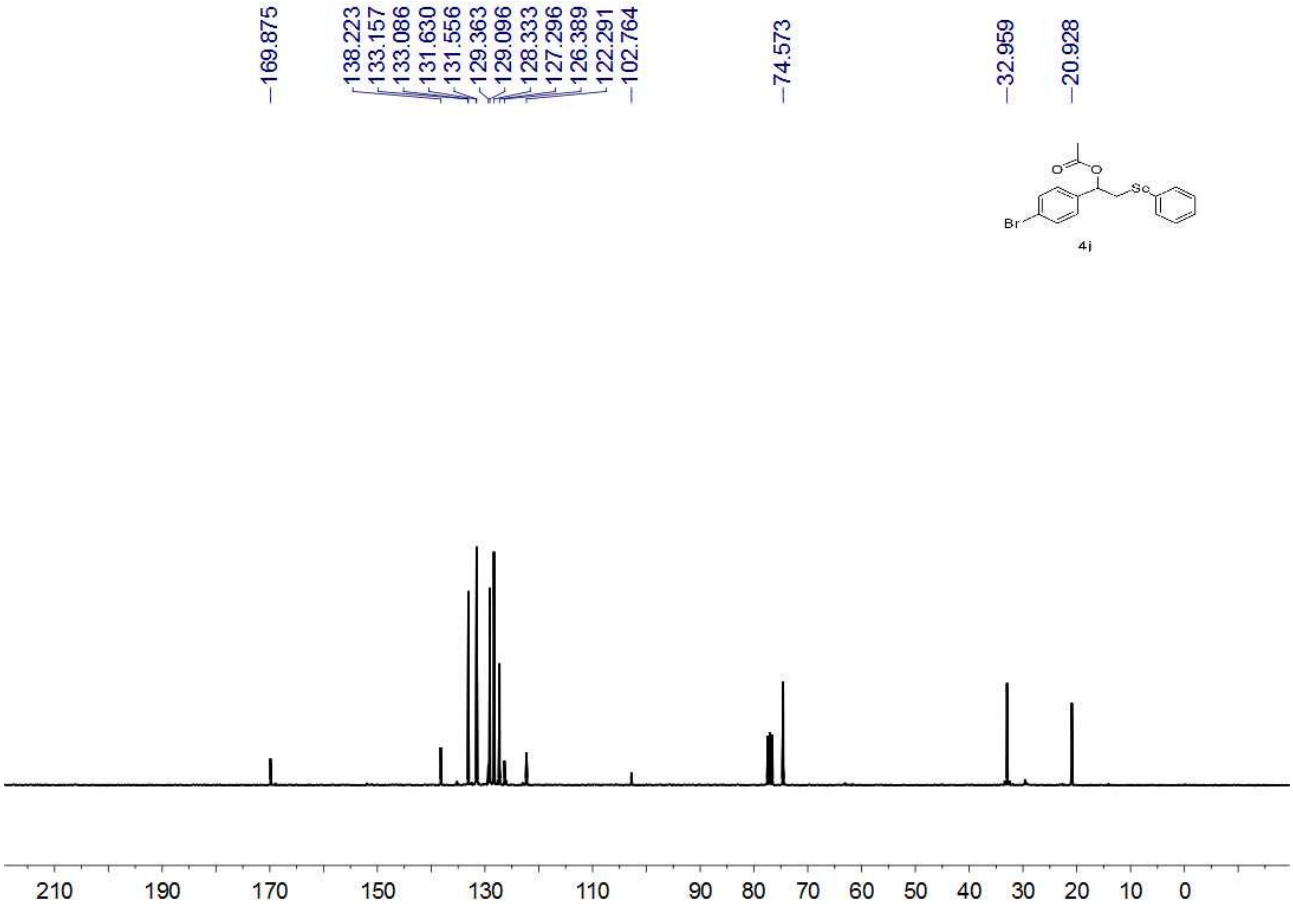
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74.573
32.959
20.928
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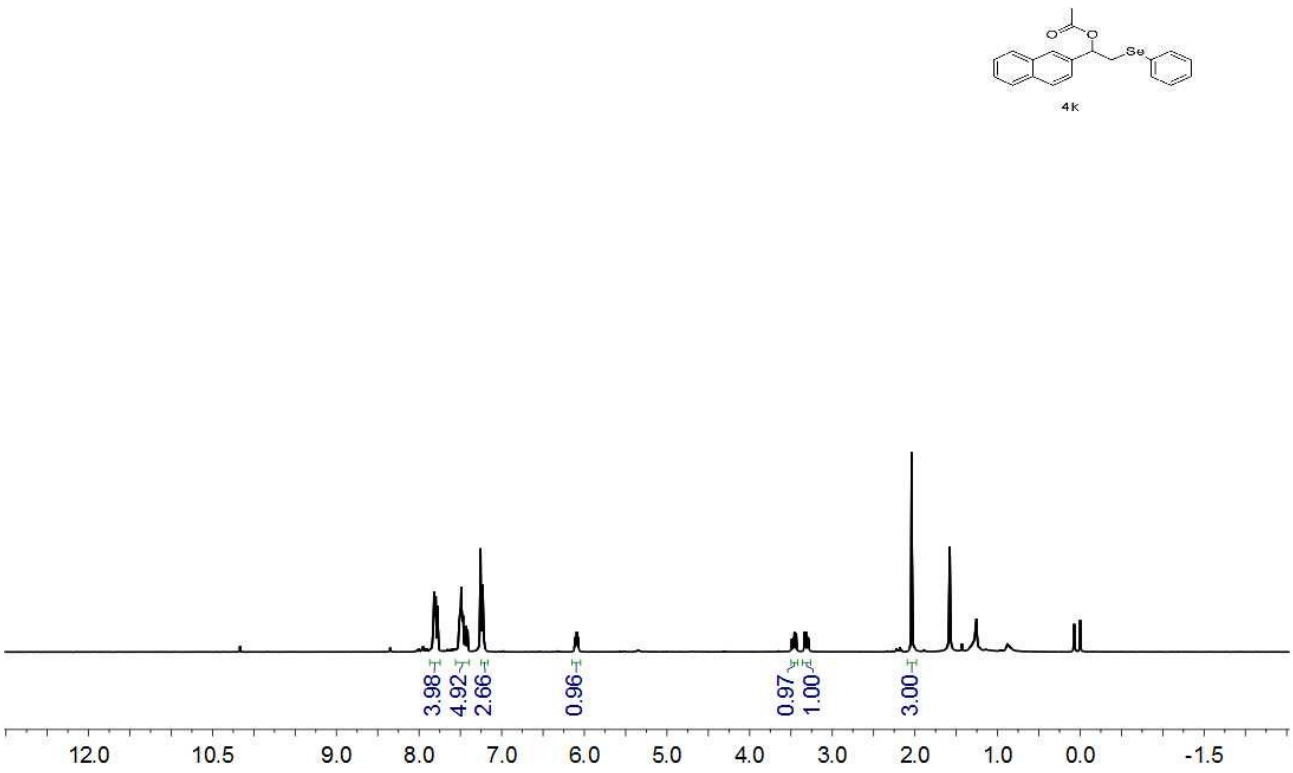
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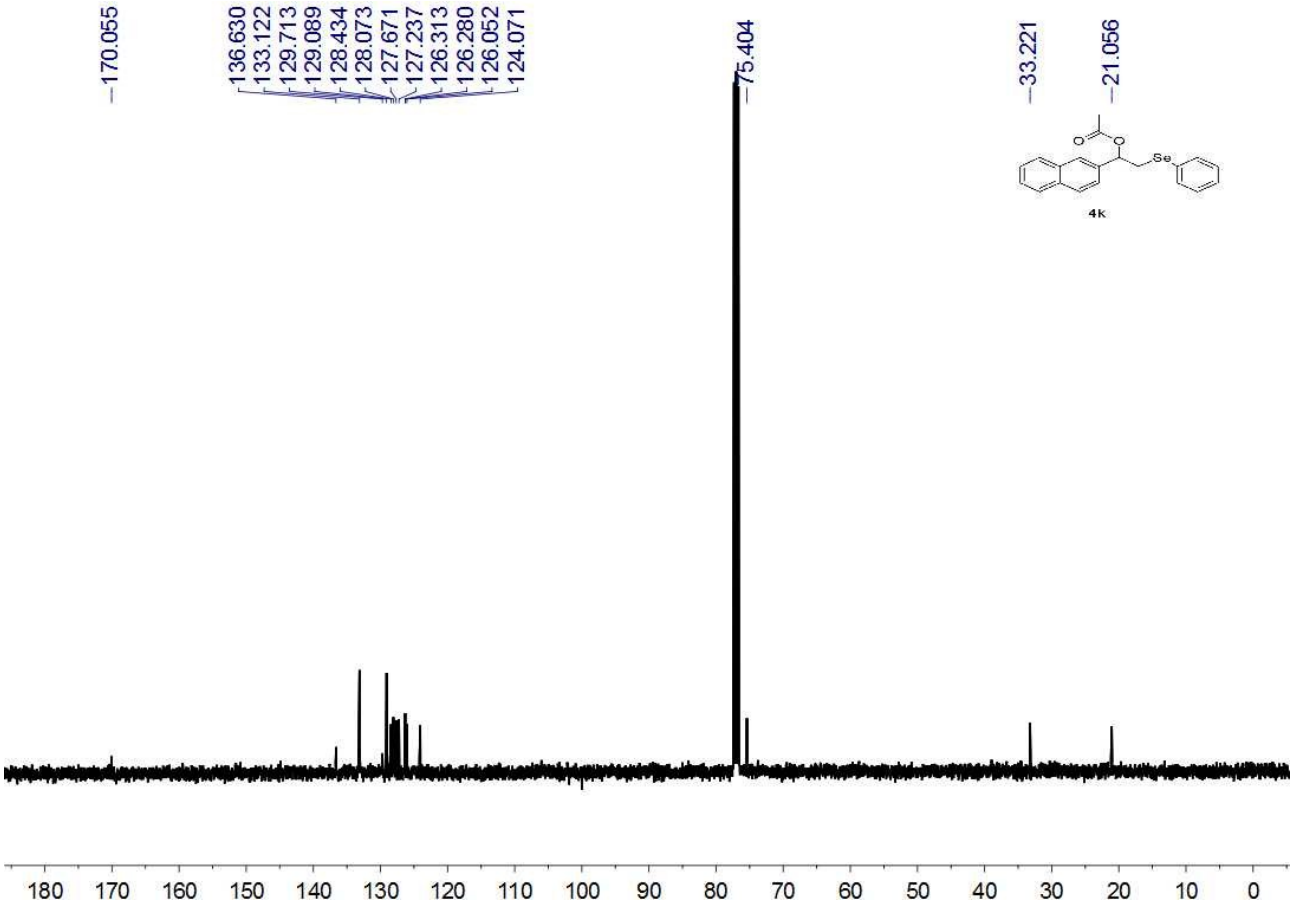
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124.071
75.404
33.221
21.056
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4k
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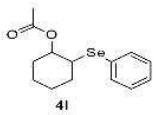
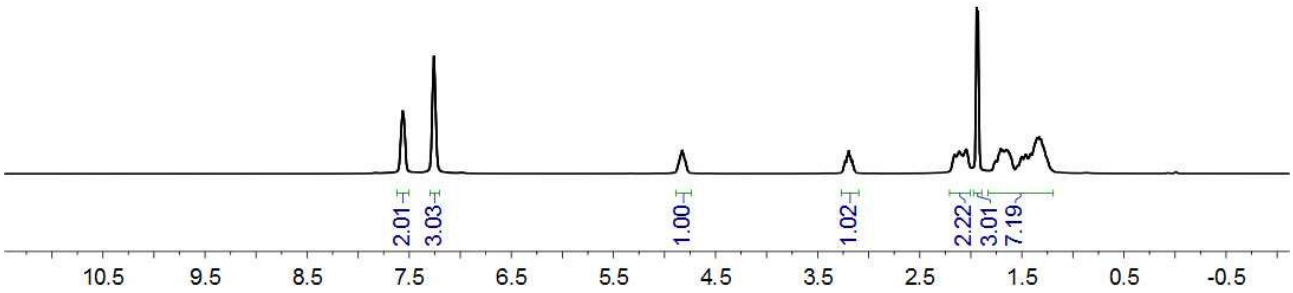

Se
4l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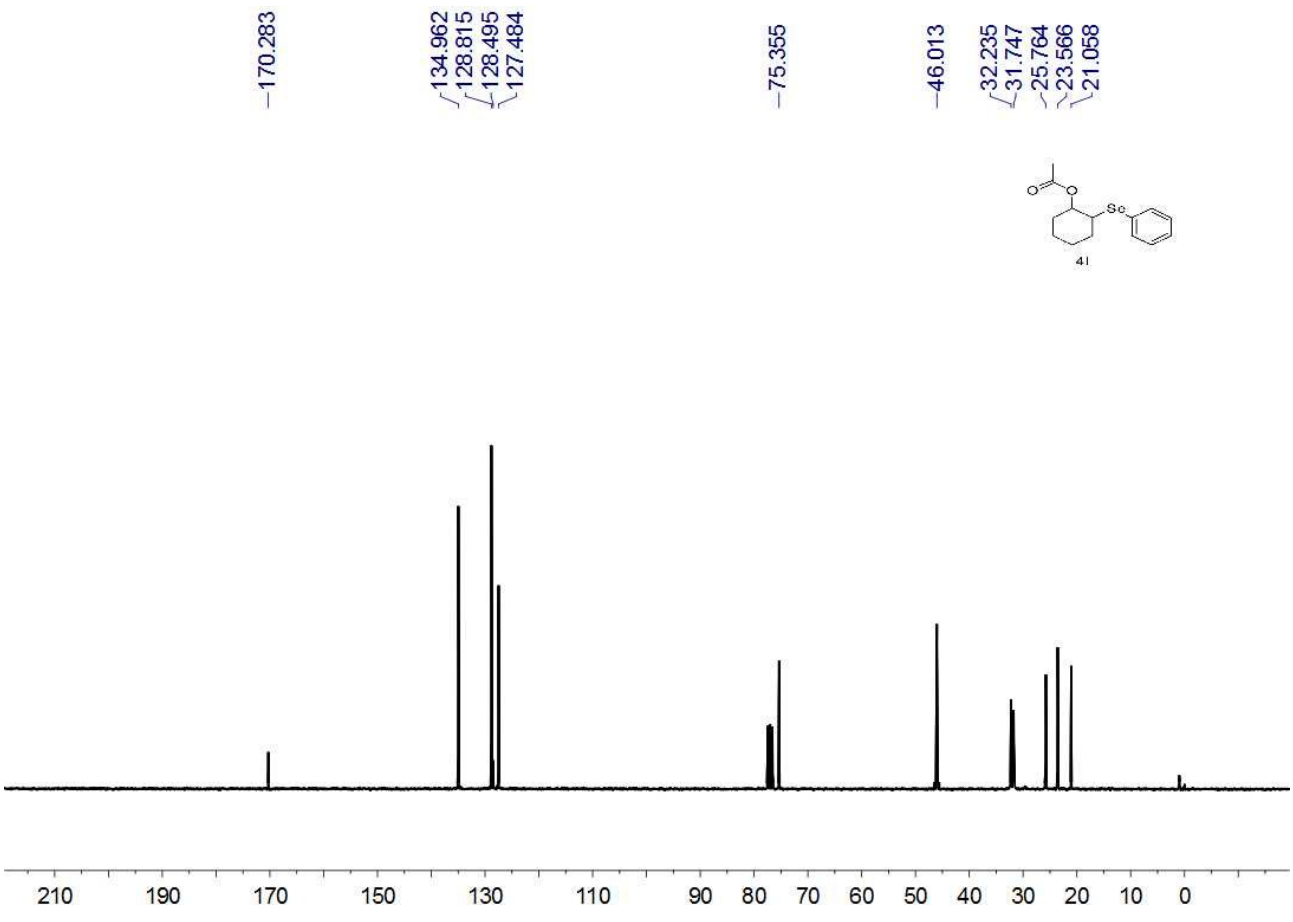
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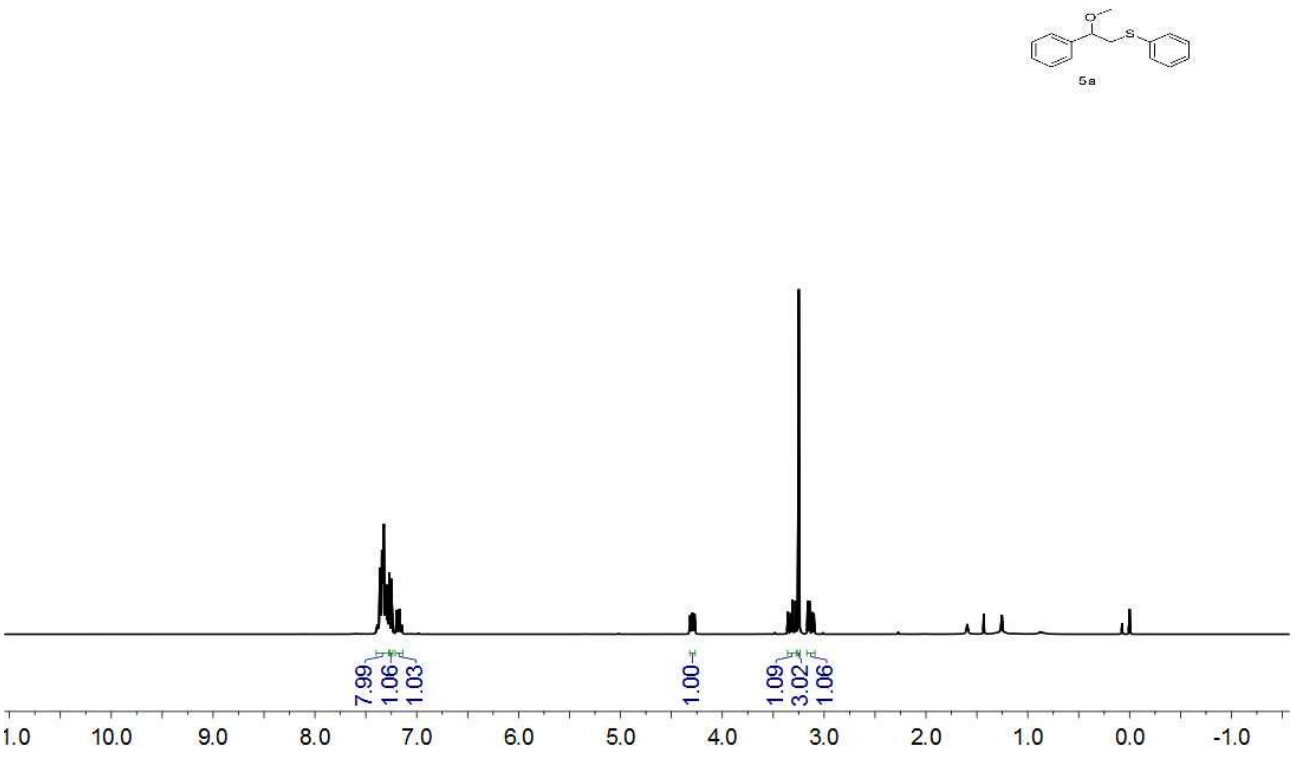
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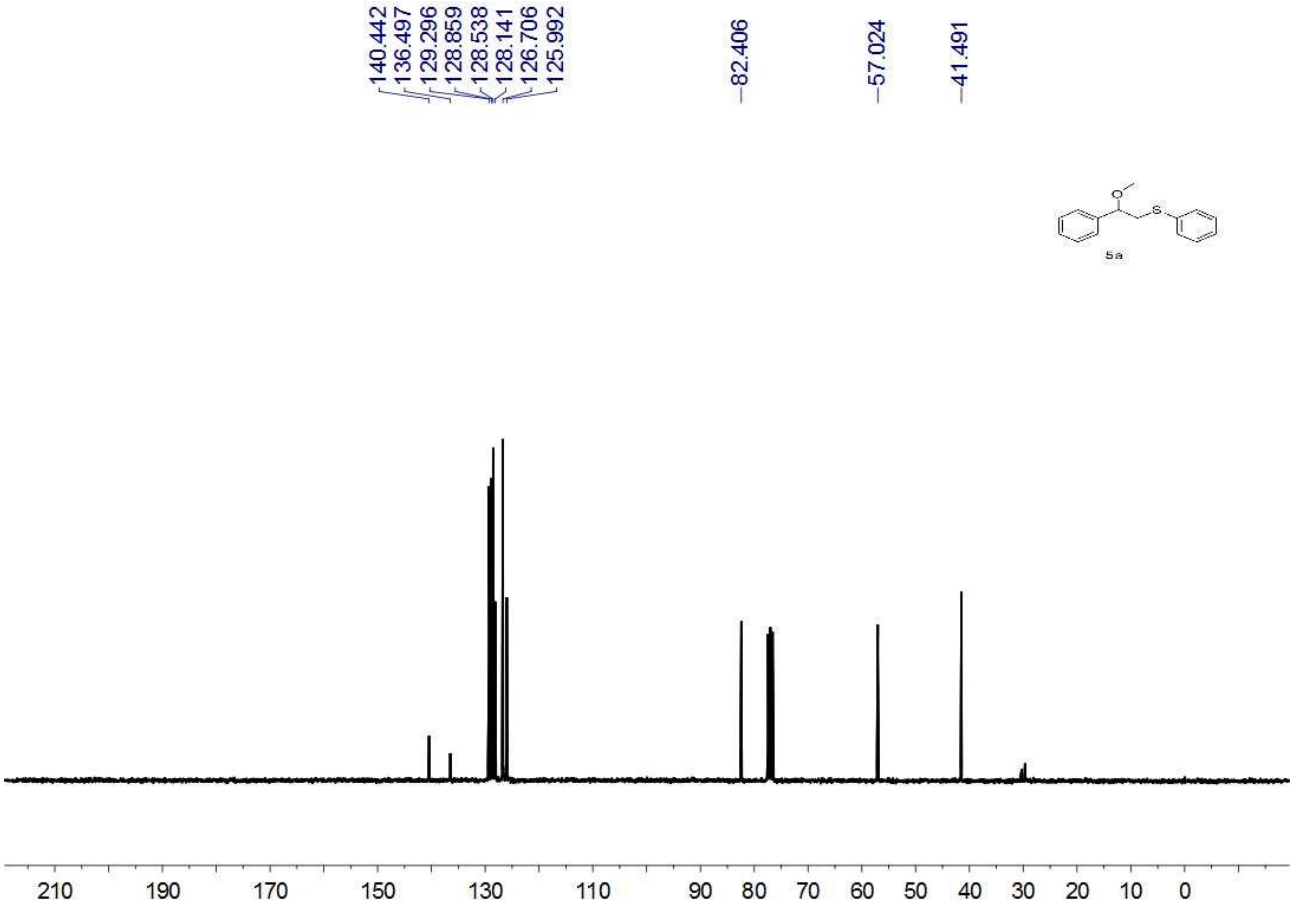
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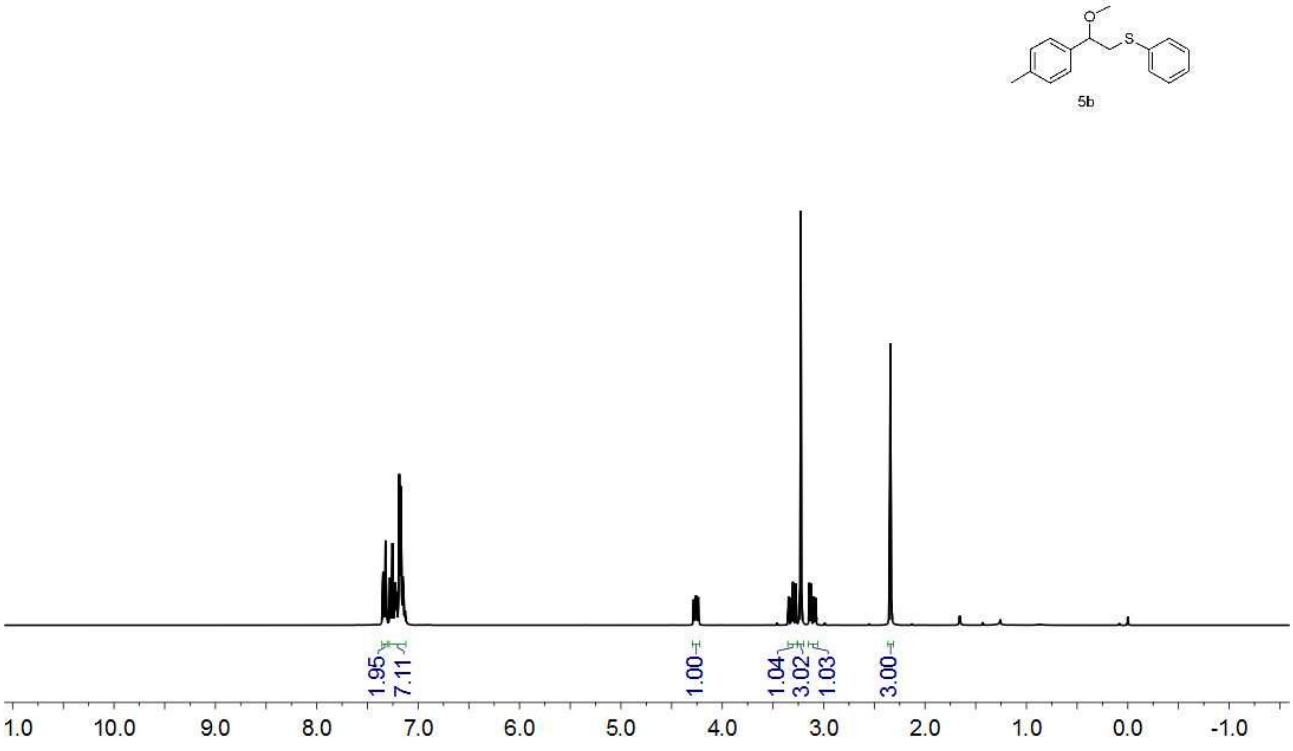
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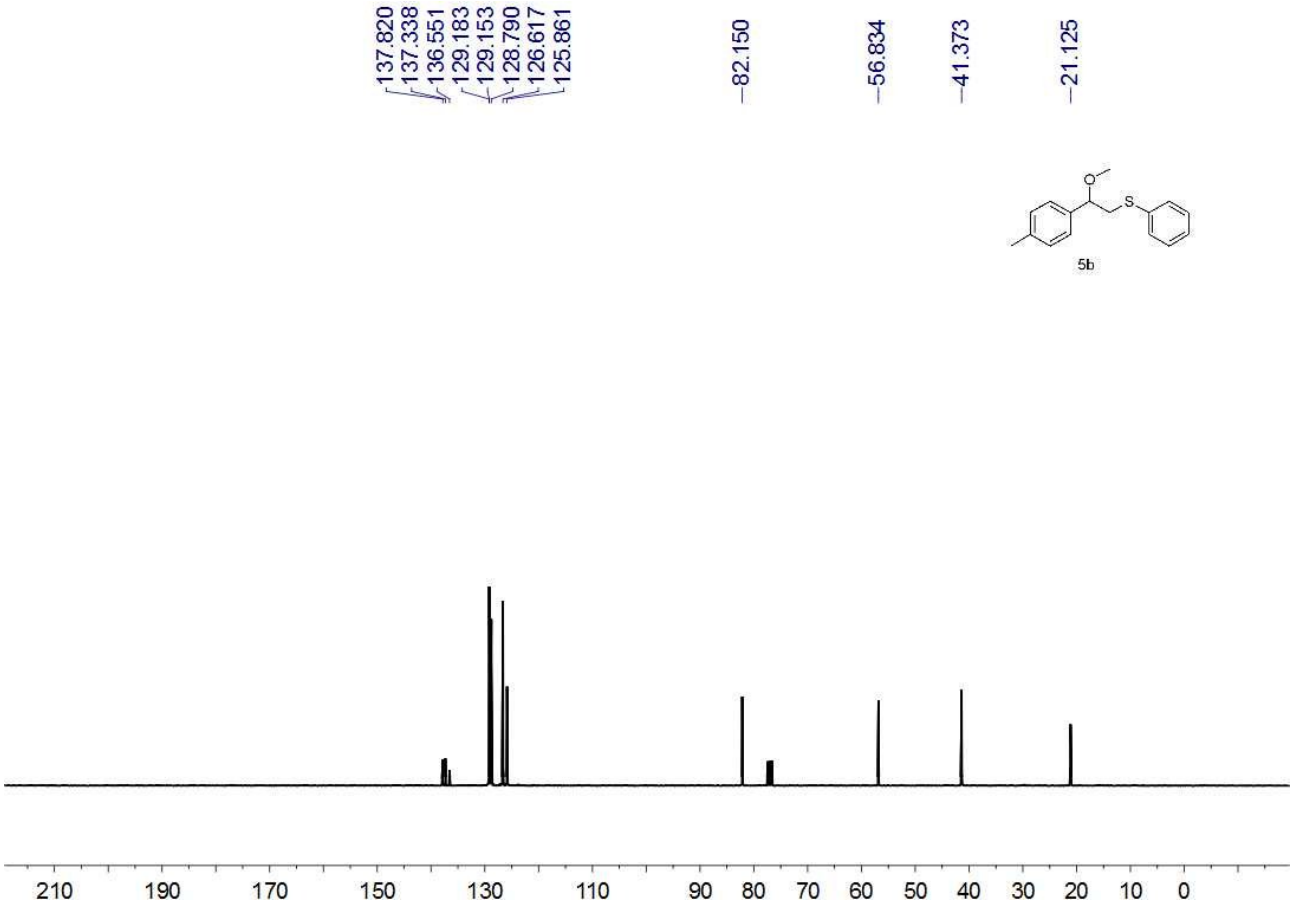
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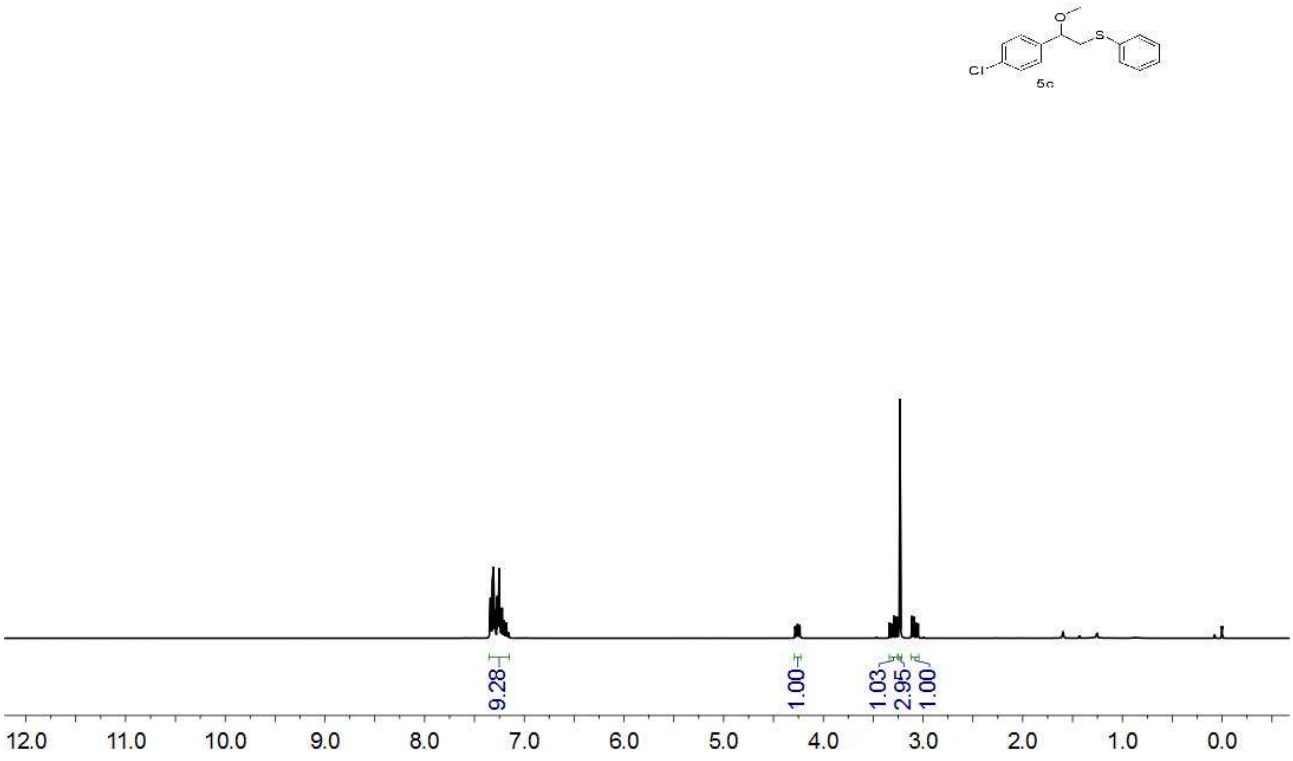
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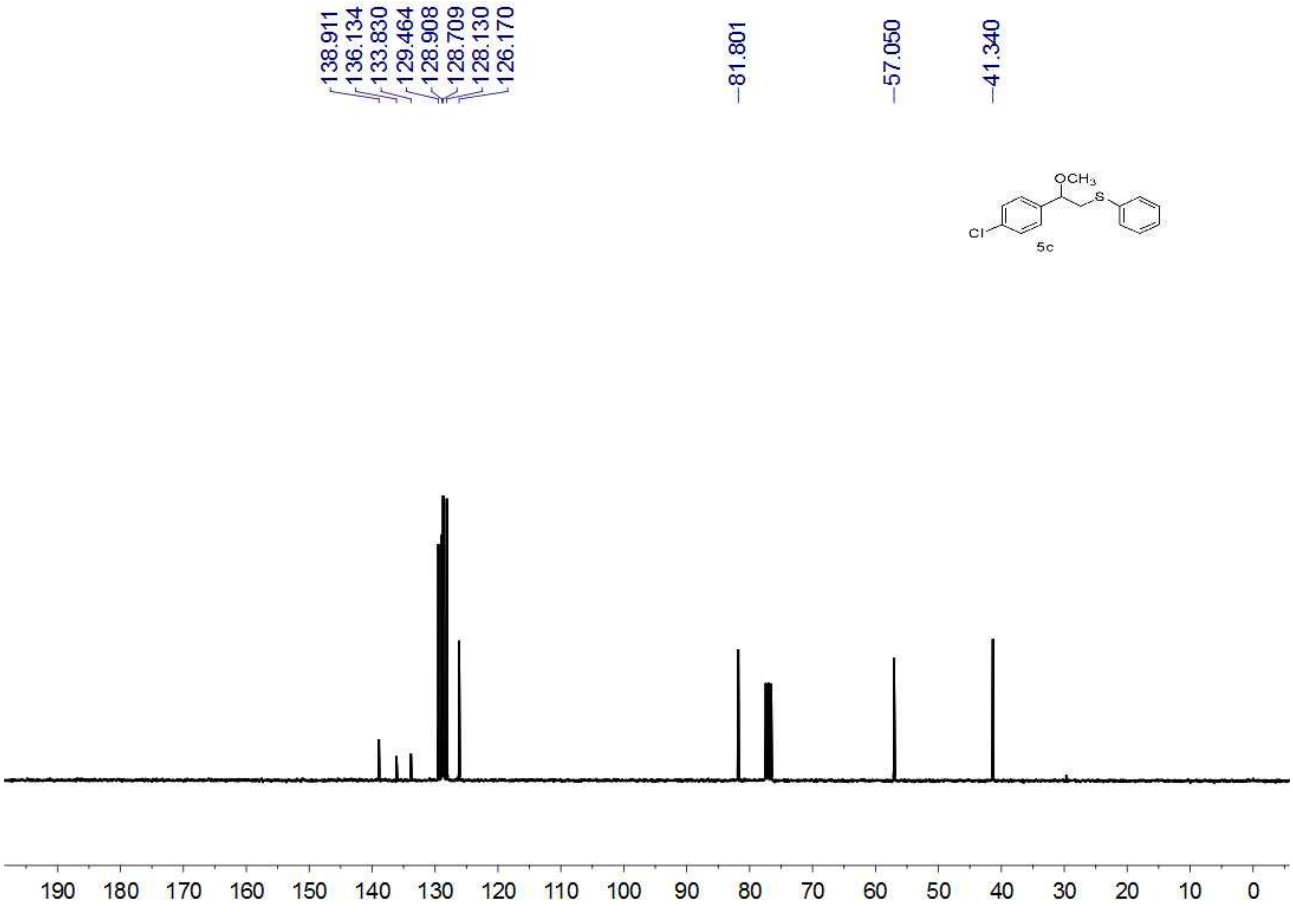
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OCH3
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Cl
5c
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