Face to face activation of a phenylselenium borane with α,β-unsaturated carbonyl substrates: facile synthesis of C-Se bonds

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Contents

1. Instrumentation and chemicals

All reactions and manipulations were carried out under argon atmosphere using Schlenk-type techniques and oven-dried (120 ºC) glassware, which was cooled in a stream of argon. Solvents were dried using a solvent purification system (Pure SOLV system-4). Substrates were purchased from Sigma-Aldrich and Strem Chemicals, and used as received. The reagent phenylselenium pinacolborane (**1**) was fully synthesized and stored in the glovebox.

Deuterated chloroform ($CDCl_3$) was used as solvent for routine NMR measurements. NMR spectra were obtained using a Varian Mercury 400 spectrometer. ^{1}H NMR and $^{13}C\{^{1}H\}$ NMR chemical shifts (δ) are reported in ppm relative to tetramethylsilane, referenced to the chemical shift of residual solvents resonances. $^{11}B\{^{1}H\}$ NMR chemical shifts are reported in ppm (δ) relative to $BF_3{\cdot}OEt_2$ (δ $^{11}B\{^{1}H\}$ = 0.00 ppm) as the external reference. Coupling constants (*J*) are given in Hz, and the multiplicity of the NMR signals is described as singlet (s), doublet (d), triplet (t), quartet (q) and multiplet (m).

Electron impact (EI) (70 EV) was recorded with a Kratos MS50 spectrometer. Accurate mass determinations were carried out in a liquid cromatograph TOF.

2. Synthesis of 4,4,5,5-tetramethyl-2-(phenylselanyl)-1,3,2-dioxaborolane, PhSeBpin (1)

To a toluene (10 mL) solution of benzeneselenol (2.22 g, 14.13 mmol) and pinacolborane (1.85 g, 14.45 mmol) was added a $RhCl(PPh_3)_3$ (3 mg, 0.0035 mmol, 0.02 mol%) as a solid. The reaction was allowed to proceed for 18 h, at which point solvent was removed under vacuum to give an off-white solid. The solid was dissolved in hexane (4 mL) and stored at -30 ^oC. The resulting precipitate was collected by suction filtration to afford **1** as an off-white solid. Yield: 3.55 g (89%); mp 55-57 ^oC. Spectroscopic NMR data in $CDCl_3$: ^1H δ: 7.58 (m, 2H, Ar), 7.25-7.20 (ov m, 3H, Ar), 1.32 (s, 12H, pin); ^{11}B δ: 33 (br); $^{13}C\{^1H\}$ δ: 134.5, 129.0, 126.8, 124.9, 85.7, 24.7. Anal. Calcd. for $C_{12}H_{17}BO_2Se$ (283.03): C, 50.92; H, 6.05. Found: C, 51.23; H, 6.11.

3. Crystal data and structure refinement 4,4,5,5-tetramethyl-2-(phenylselanyl)-1,3,2-dioxaborolane, PhSeBpin (1)

Crystals of **1** were grown from a saturated Et_2O solution stored at -30 ^oC. Single crystals were coated with Paratone-N oil, mounted using a polyimide MicroMount and frozen in the cold nitrogen stream of the goniometer. A hemisphere of data was collected on a Bruker AXS P4/SMART 1000 diffractometer using ω and ϕ scans with a scan width of 0.3^o and 20 s exposure time. The detector distance was 5 cm. The data were reduced (SAINT)[1] and corrected for absorption (SADABS).[2] The structure was solved by direct methods and refined by full-matrix least squares on F^2(SHELXTL).[3] All non-hydrogen atoms were refined using anisotropic displacement parameters. Hydrogen atoms were found in Fourier difference maps and refined using isotropic displacement parameters.

Table 1. Crystal data and structure refinement for STG1.

Identification code	SW100891	
Empirical formula	C12 H17 B O2 Se	
Formula weight	283.03	
Temperature	213(1) K	
Wavelength	0.71073 Å	
Diffractometer used	Bruker AXS P4/SMART 1000	
Detector distance	5 cm	
Monochromator used	Graphite	
Crystal size	0.30 x 0.25 x 0.15 mm^3	
Colour and habit	Colourless, irregular	
Crystal system	Orthorhombic	
Space group	Pbca	
Unit cell dimensions	a = 12.6814(12) Å	$\alpha = 90°$
	b = 13.1877(13) Å	$\beta = 90°$
	c = 16.1788(16) Å	$\gamma = 90°$
Volume	2705.7(5) $Å^3$	
Z	8	
Density (calculated)	1.390 Mg/m^3	
Absorption coefficient	2.759 mm^{-1}	
F(000)	1152	
Theta range for data collection	2.52 to 27.50°	
Completeness to theta = 25.00°	100.0 %	
Scan type	ω and ϕ	
Scan range	0.3°	
Exposure time	20s	

Index ranges	$-16 \le h \le 16, -17 \le k \le 17, -20 \le l \le 20$
Standard reflections	50 frames at beginning and end of data collection
Crystal stability	no decay
Reflections collected	17722
Independent reflections	3075 [R(int) = 0.0404]
Solution	Direct methods
Hydrogen atoms	Calculated positions, riding model
Absorption correction	SADABS
Max. and min. transmission	0.6824 and 0.4916
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3075 / 0 / 149
Goodness-of-fit on F^2	1.027
Final R indices [I>2sigma(I)]	R1 = 0.0331, wR2 = 0.0712
R indices (all data)	R1 = 0.0630, wR2 = 0.0840
Largest/mean shift/esd	0.000/0.000
Largest diff. peak and hole	0.673 and -0.509 e.Å^{-3}

$wR2 = (\sum[w(F_o^2-F_c^2)^2]/\sum[wF_o^4])^{1/2}$

$R1 = \sum \big| |F_o| - |F_c| \big| / \sum |F_o|$

$Weight = 1 / [\sigma^2(F_o^2) + (0.0316 * P)^2 + (1.8528 * P)]$

where $P = (\max(F_o^2, 0) + 2 * F_c^2)/3$

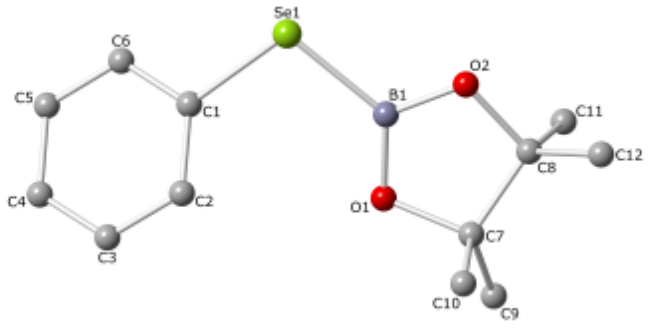


Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3)

for STG1. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Se(1)	4525(1)	2070(1)	4727(1)	50(1)
B(1)	5228(2)	1690(2)	3701(2)	38(1)
O(1)	4946(2)	932(1)	3187(1)	45(1)
O(2)	6072(2)	2236(1)	3457(1)	52(1)
C(1)	3413(2)	1088(2)	4832(1)	39(1)
C(2)	3494(2)	92(2)	4566(2)	48(1)
C(3)	2667(3)	-567(2)	4698(2)	54(1)
C(4)	1770(2)	-255(2)	5099(2)	50(1)
C(5)	1698(2)	735(2)	5375(2)	48(1)
C(6)	2513(2)	1404(2)	5238(2)	42(1)
C(7)	5797(2)	858(2)	2567(2)	44(1)
C(8)	6320(2)	1918(2)	2612(2)	46(1)
C(9)	5295(3)	606(3)	1748(2)	82(1)
C(10)	6503(3)	5(2)	2857(2)	75(1)
C(11)	5796(3)	2696(3)	2049(2)	85(1)
C(12)	7500(3)	1929(3)	2506(3)	82(1)

Table 3. Bond lengths [Å] and angles [°] for STG1.

Se(1)-C(1)	1.923(3)
Se(1)-B(1)	1.950(3)
B(1)-O(2)	1.349(4)
B(1)-O(1)	1.349(3)
O(1)-C(7)	1.476(3)
O(2)-C(8)	1.464(3)
C(1)-C(6)	1.381(4)
C(1)-C(2)	1.385(3)
C(2)-C(3)	1.379(4)
C(2)-H(2)	0.9400
C(3)-C(4)	1.373(4)
C(3)-H(3)	0.9400
C(4)-C(5)	1.383(4)
C(4)-H(4)	0.9400
C(5)-C(6)	1.376(4)
C(5)-H(5)	0.9400
C(6)-H(6)	0.9400
C(7)-C(9)	1.507(4)
C(7)-C(10)	1.512(4)
C(7)-C(8)	1.549(4)
C(8)-C(12)	1.507(4)
C(8)-C(11)	1.524(4)
C(9)-H(9A)	0.9700
C(9)-H(9B)	0.9700
C(9)-H(9C)	0.9700
C(10)-H(10A)	0.9700
C(10)-H(10B)	0.9700
C(10)-H(10C)	0.9700
C(11)-H(11A)	0.9700

C(11)-H(11B)	0.9700
C(11)-H(11C)	0.9700
C(12)-H(12A)	0.9700
C(12)-H(12B)	0.9700
C(12)-H(12C)	0.9700

C(1)-Se(1)-B(1)	103.69(12)
O(2)-B(1)-O(1)	115.2(2)
O(2)-B(1)-Se(1)	118.3(2)
O(1)-B(1)-Se(1)	126.5(2)
B(1)-O(1)-C(7)	105.9(2)
B(1)-O(2)-C(8)	106.9(2)
C(6)-C(1)-C(2)	119.7(3)
C(6)-C(1)-Se(1)	116.40(19)
C(2)-C(1)-Se(1)	123.8(2)
C(3)-C(2)-C(1)	119.5(3)
C(3)-C(2)-H(2)	120.3
C(1)-C(2)-H(2)	120.3
C(4)-C(3)-C(2)	121.0(3)
C(4)-C(3)-H(3)	119.5
C(2)-C(3)-H(3)	119.5
C(3)-C(4)-C(5)	119.3(3)
C(3)-C(4)-H(4)	120.4
C(5)-C(4)-H(4)	120.4
C(6)-C(5)-C(4)	120.2(3)
C(6)-C(5)-H(5)	119.9
C(4)-C(5)-H(5)	119.9
C(5)-C(6)-C(1)	120.3(2)
C(5)-C(6)-H(6)	119.9
C(1)-C(6)-H(6)	119.9
O(1)-C(7)-C(9)	107.6(2)

O(1)-C(7)-C(10)	105.8(2)
C(9)-C(7)-C(10)	111.1(3)
O(1)-C(7)-C(8)	102.79(19)
C(9)-C(7)-C(8)	114.9(3)
C(10)-C(7)-C(8)	113.8(2)
O(2)-C(8)-C(12)	108.5(3)
O(2)-C(8)-C(11)	105.7(2)
C(12)-C(8)-C(11)	111.0(3)
O(2)-C(8)-C(7)	102.1(2)
C(12)-C(8)-C(7)	115.3(3)
C(11)-C(8)-C(7)	113.1(3)
C(7)-C(9)-H(9A)	109.5
C(7)-C(9)-H(9B)	109.5
H(9A)-C(9)-H(9B)	109.5
C(7)-C(9)-H(9C)	109.5
H(9A)-C(9)-H(9C)	109.5
H(9B)-C(9)-H(9C)	109.5
C(7)-C(10)-H(10A)	109.5
C(7)-C(10)-H(10B)	109.5
H(10A)-C(10)-H(10B)	109.5
C(7)-C(10)-H(10C)	109.5
H(10A)-C(10)-H(10C)	109.5
H(10B)-C(10)-H(10C)	109.5
C(8)-C(11)-H(11A)	109.5
C(8)-C(11)-H(11B)	109.5
H(11A)-C(11)-H(11B)	109.5
C(8)-C(11)-H(11C)	109.5
H(11A)-C(11)-H(11C)	109.5
H(11B)-C(11)-H(11C)	109.5
C(8)-C(12)-H(12A)	109.5
C(8)-C(12)-H(12B)	109.5

H(12A)-C(12)-H(12B)	109.5
C(8)-C(12)-H(12C)	109.5
H(12A)-C(12)-H(12C)	109.5
H(12B)-C(12)-H(12C)	109.5

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for STG1. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Se(1)	58(1)	45(1)	48(1)	-15(1)	15(1)	-5(1)
B(1)	37(2)	42(2)	35(2)	-2(1)	-1(1)	3(1)
O(1)	47(1)	53(1)	35(1)	-8(1)	4(1)	-10(1)
O(2)	48(1)	54(1)	53(1)	-16(1)	10(1)	-13(1)
C(1)	48(2)	39(1)	29(1)	2(1)	6(1)	4(1)
C(2)	60(2)	39(1)	46(2)	-2(1)	18(1)	7(1)
C(3)	78(2)	37(2)	46(2)	0(1)	14(2)	-2(2)
C(4)	55(2)	51(2)	43(2)	7(1)	3(1)	-6(1)
C(5)	47(2)	52(2)	45(2)	5(1)	8(1)	8(1)
C(6)	53(2)	36(1)	38(1)	2(1)	7(1)	8(1)
C(7)	43(2)	55(2)	34(1)	-9(1)	1(1)	0(1)
C(8)	43(2)	54(2)	41(2)	-2(1)	9(1)	-1(1)
C(9)	82(3)	122(3)	41(2)	-24(2)	5(2)	-26(2)
C(10)	88(3)	57(2)	79(2)	-3(2)	12(2)	18(2)
C(11)	97(3)	79(3)	80(3)	32(2)	13(2)	8(2)
C(12)	46(2)	99(3)	101(3)	-22(2)	25(2)	-16(2)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for STG1.

	x	y	z	U(eq)
H(2)	4109	-133	4298	58
H(3)	2719	-1240	4511	65
H(4)	1210	-710	5185	60
H(5)	1091	952	5657	58
H(6)	2457	2078	5421	51
H(9A)	4961	-55	1782	123
H(9B)	5831	596	1321	123
H(9C)	4768	1114	1616	123
H(10A)	6828	191	3379	112
H(10B)	7048	-117	2448	112
H(10C)	6087	-605	2931	112
H(11A)	5038	2674	2128	128
H(11B)	5961	2540	1478	128
H(11C)	6055	3368	2183	128
H(12A)	7752	2623	2517	123
H(12B)	7683	1620	1982	123
H(12C)	7826	1550	2953	123

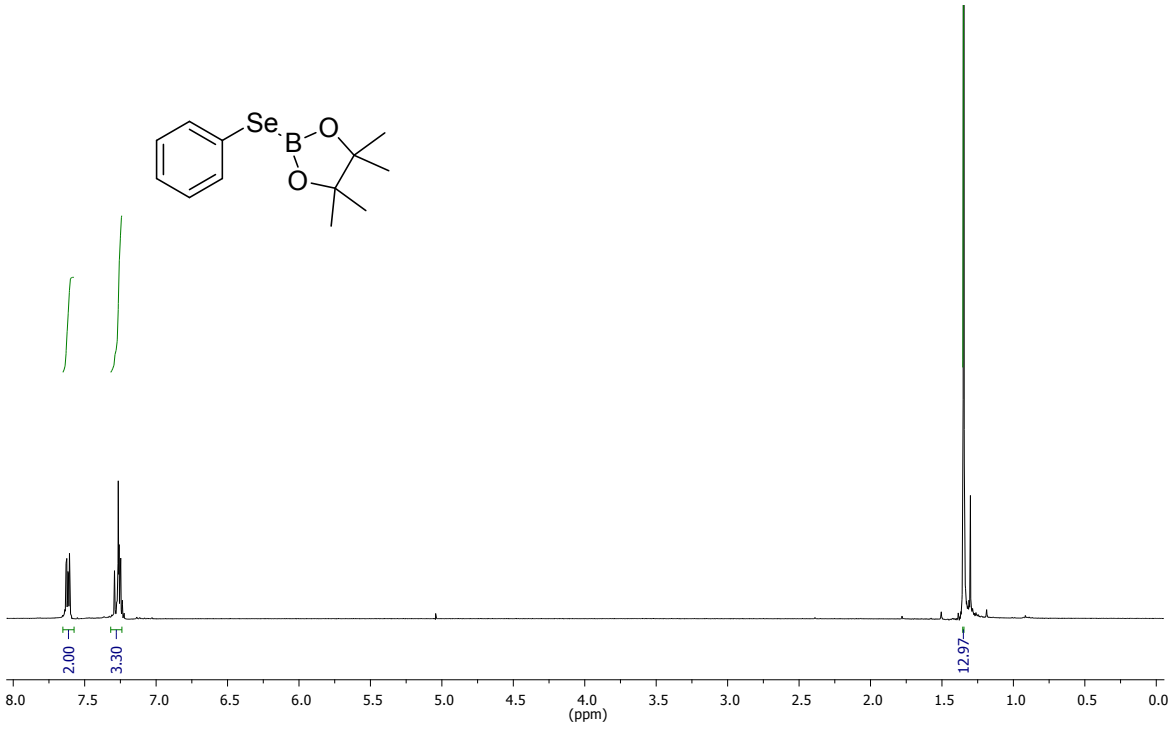
4. ^{1}H NMR, ^{11}B NMR, ^{13}B NMR spectra of 4,4,5,5-tetramethyl-2-(phenylselanyl)-1,3,2-dioxaborolane, PhSeBpin (1)

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.58 (m, 2H, Ar), 7.25-7.20 (ov m, 3H, Ar), 1.32 (s, 12H, pin).

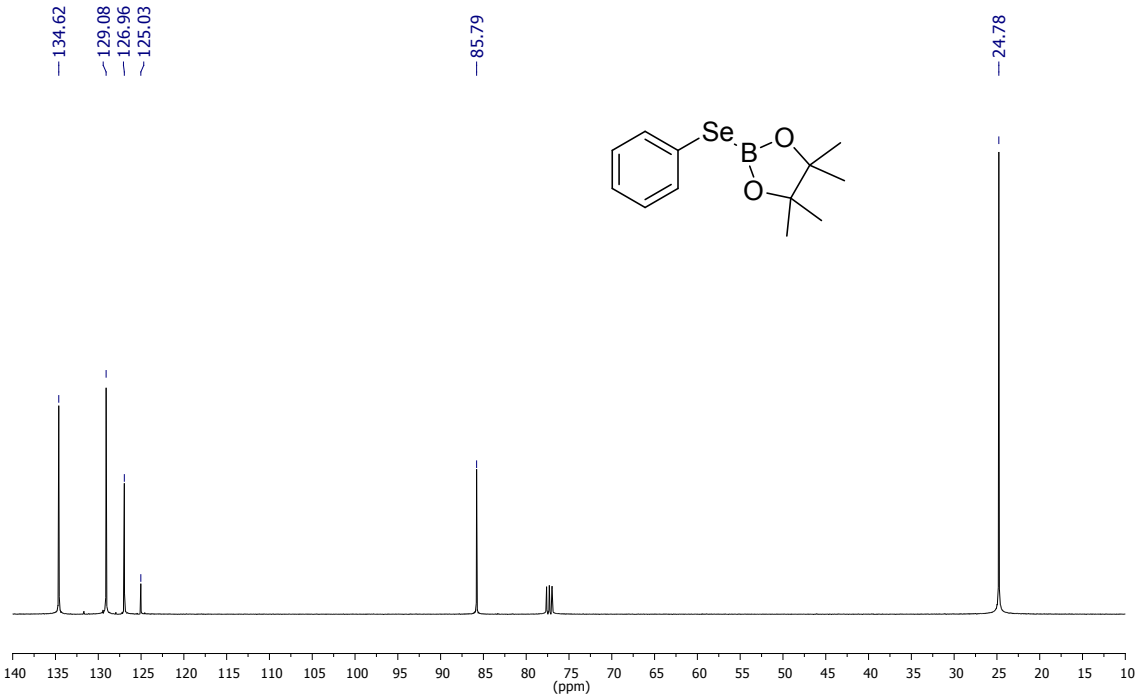
^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$) δ (ppm): 134.6, 129.0, 126.9, 125.0, 85.7, 24.7.

^{11}B NMR (128 MHz, $CDCl_3$) δ (ppm): 32.82.

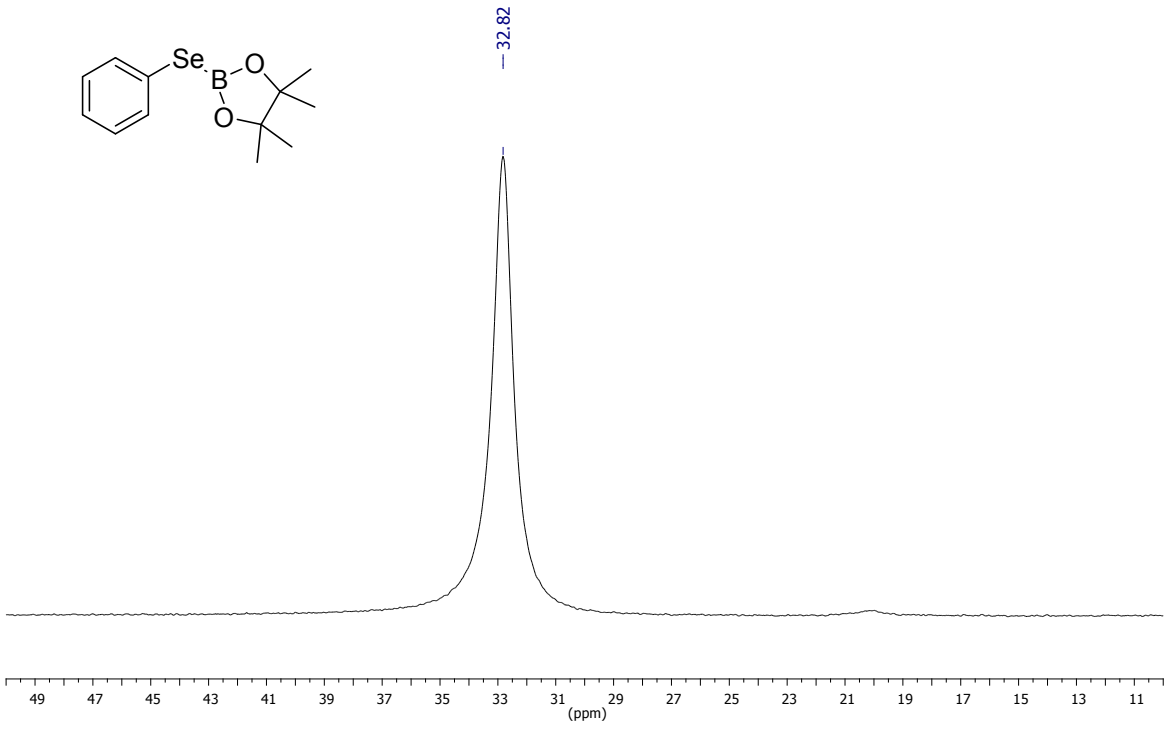
^{1}H NMR



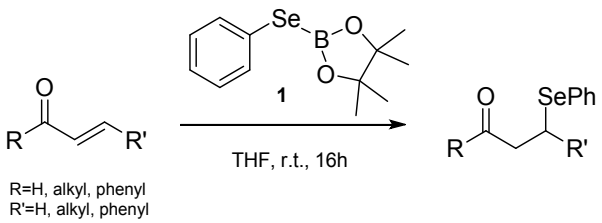
^{13}C NMR



^{11}B NMR



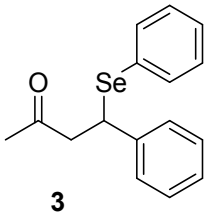
5. General procedures for the β-selenation of α,β-unsaturated ketones and aldehydes



PhSeBpin (**1**) (30 mg, 0.11 mmol, 1.1 eq.) was weighed and transferred into an oven-dried Schlenk tube inside the glovebox. The corresponding substrate (0.10 mmol) was introduced in the Schlenk tube under argon and dry THF (2 mL) was added. The mixture was stirred for 16 hours at room temperature. An aliquot of 0.2 mL was taken from the solution and gently concentrated on a rotary evaporator at r.t, and analyzed by ^{1}H NMR spectroscopy. Conversion was determined by correlation of the integrals of the protons of the product and the substrate. The product β-(phenylseleno) substituted ketone was purified by flash chromatography using a silica gel column, and the mixture of petroleum ether and ethyl acetate adequate for each case.

6. Characterization of β-(phenylseleno) substituted ketones and aldehydes

4-phenyl-4-phenylseleno-2-butanone (3)



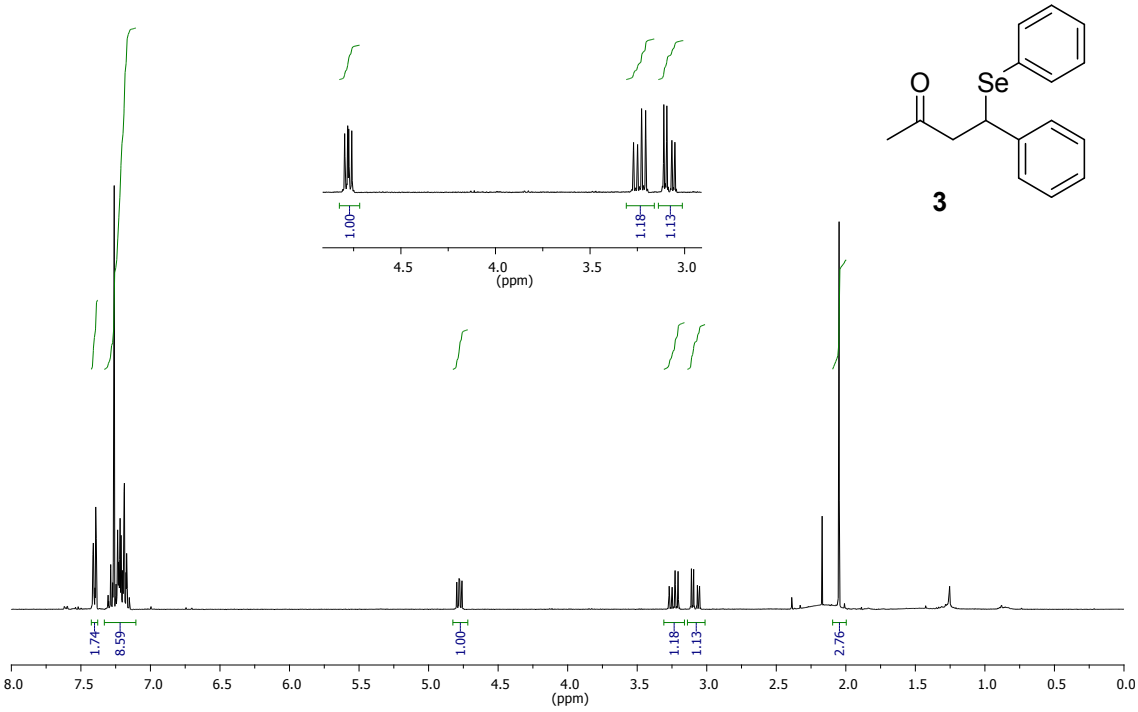
3

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.46 – 7.34 (m, 2H), 7.32 – 7.11 (m, 8H), 4.80 – 4.76 (dd, *J*=8.6, 6.4 Hz, 1H), 3.26 – 3.20 (dd, *J*=17.1, 8.6 Hz, 1H), 3.12 – 3.04 (dd, *J*=17.1, 6.4 Hz, 1H), 2.05 (s, 3H).

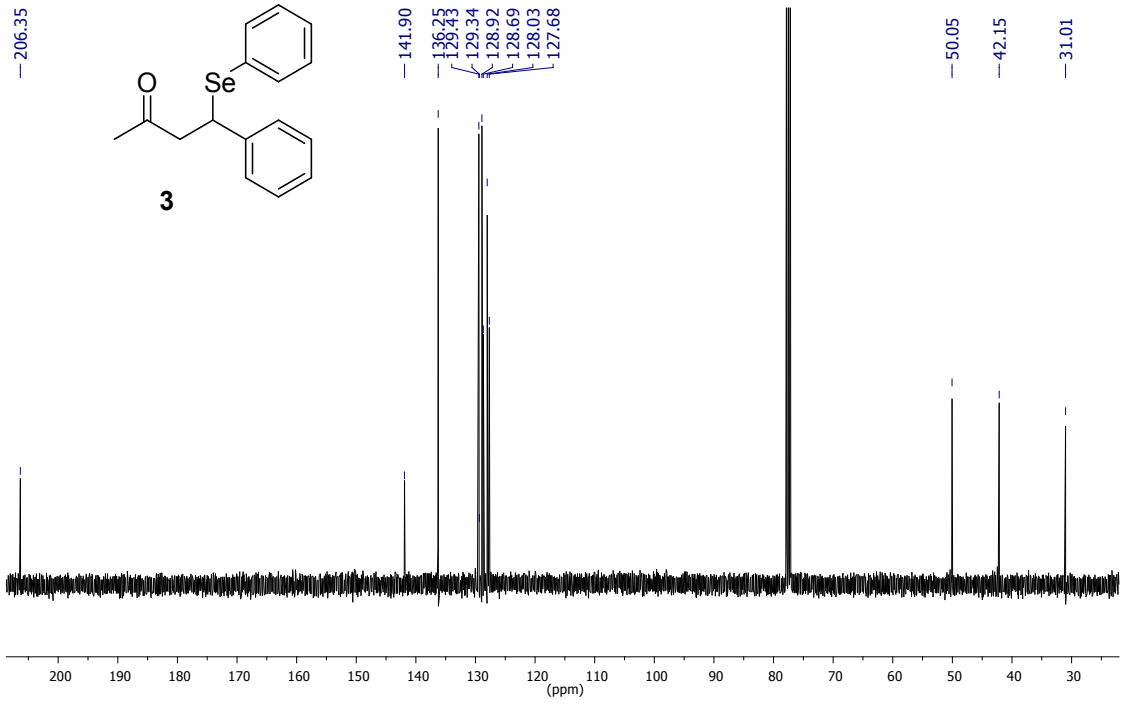
^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 206.3, 141.9, 136.2, 129.4, 129.3, 128.9, 128.6, 128.0, 127.6, 50.0, 42.1, 31.0.

MS(70eV) m/z= 304.04 $[M]^+$. MS(TOF): 305.0421$[M+H]^+$.

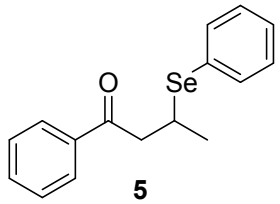
^{1}H NMR



^{13}C NMR


206.35
141.90
136.25
129.43
129.34
128.92
128.69
128.03
127.68
50.05
42.15
31.01
O
Se
3
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
(ppm)

1-phenyl-3-phenylseleno-1-butanone (5)



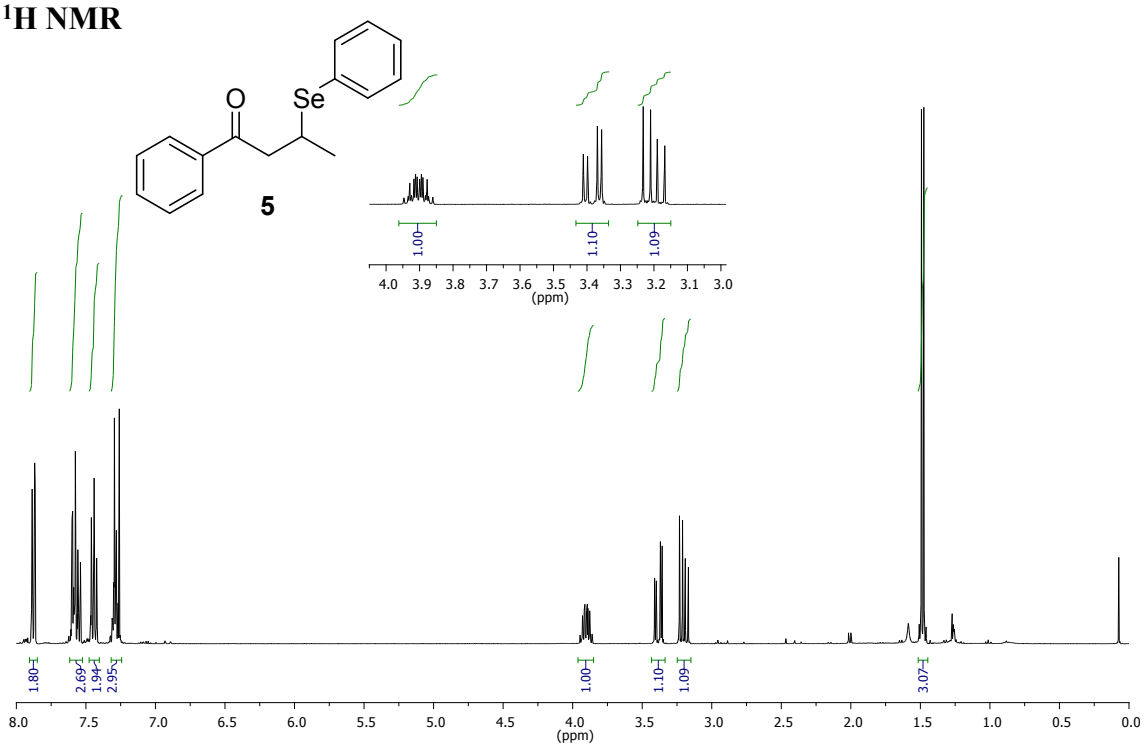
5

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.92 – 7.83 (m, 2H), 7.60 – 7.54 (m, 3H), 7.49 – 7.37 (m, 2H), 7.30 – 7.25 (m, 3H), 3.95 – 3.86 (m, 1H), 3.41 – 3.36 (dd, *J*=16.8, 5.0 Hz, 1H), 3.12 – 3.04 (dd, *J*=16.8, 10.1Hz, 1H), 2.04 (s, 3H).

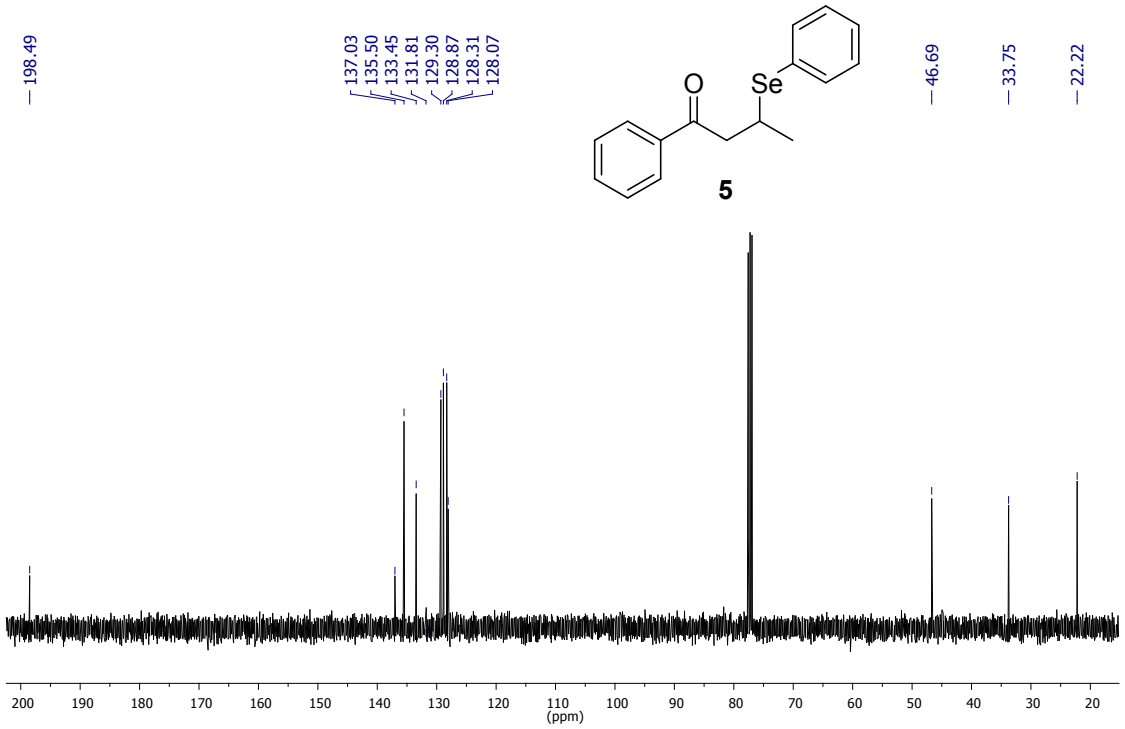
^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 198.4, 137.0, 135.5, 133.4, 131.8, 129.3, 128.8, 128.3, 128.0, 46.6, 33.7, 22.2

MS(70eV) m/z= 304.06 $[M]^+$. MS(TOF): 305.0381$[M+H]^+$.

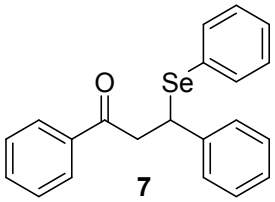
^{1}H NMR



^{13}C NMR


198.49
137.03
135.50
133.45
131.81
129.30
128.87
128.31
128.07
46.69
33.75
22.22
O
Se
5
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
(ppm)

1,3-bisphenyl-3-phenylseleno-1-propanone (7)



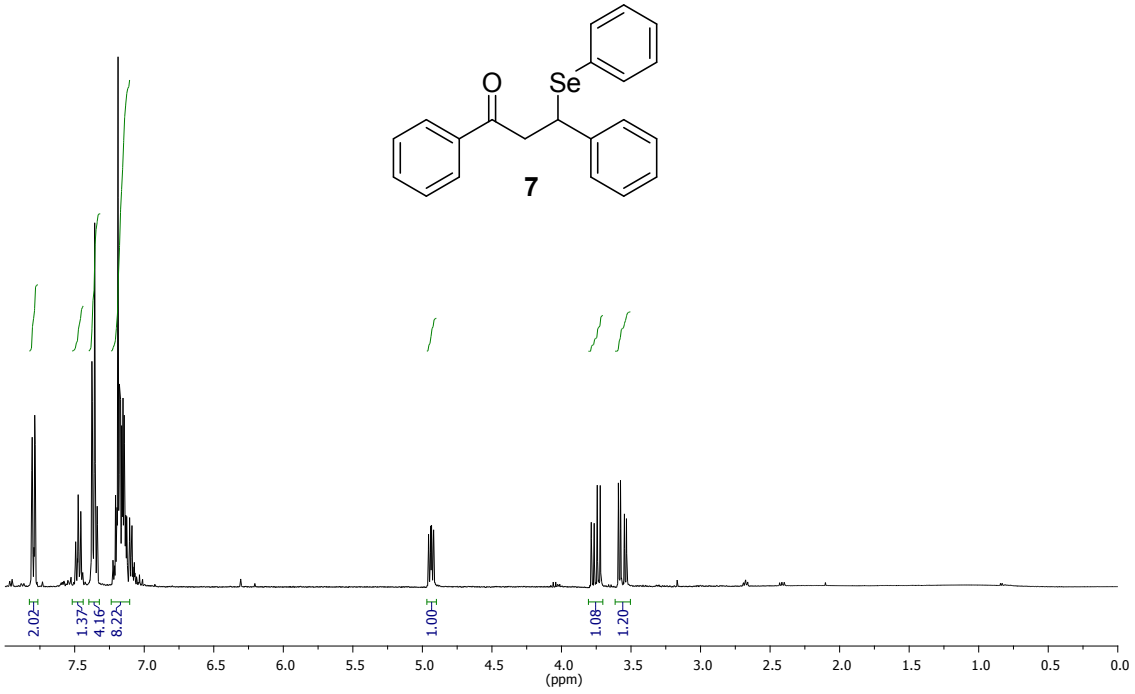
7

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.85 – 7.74 (m, 2H), 7.53 – 7.41 (m, 1H), 7.41 – 7.29 (m, 4H), 7.26 – 7.04 (m, 8H), 4.94 – 4.90 (dd, *J* = 8.6, 6.0 Hz, 1H), 3.75 (dd, *J* = 17.3, 8.6 Hz, 1H), 3.56 (dd, *J* = 17.3, 6.0 Hz, 1H).

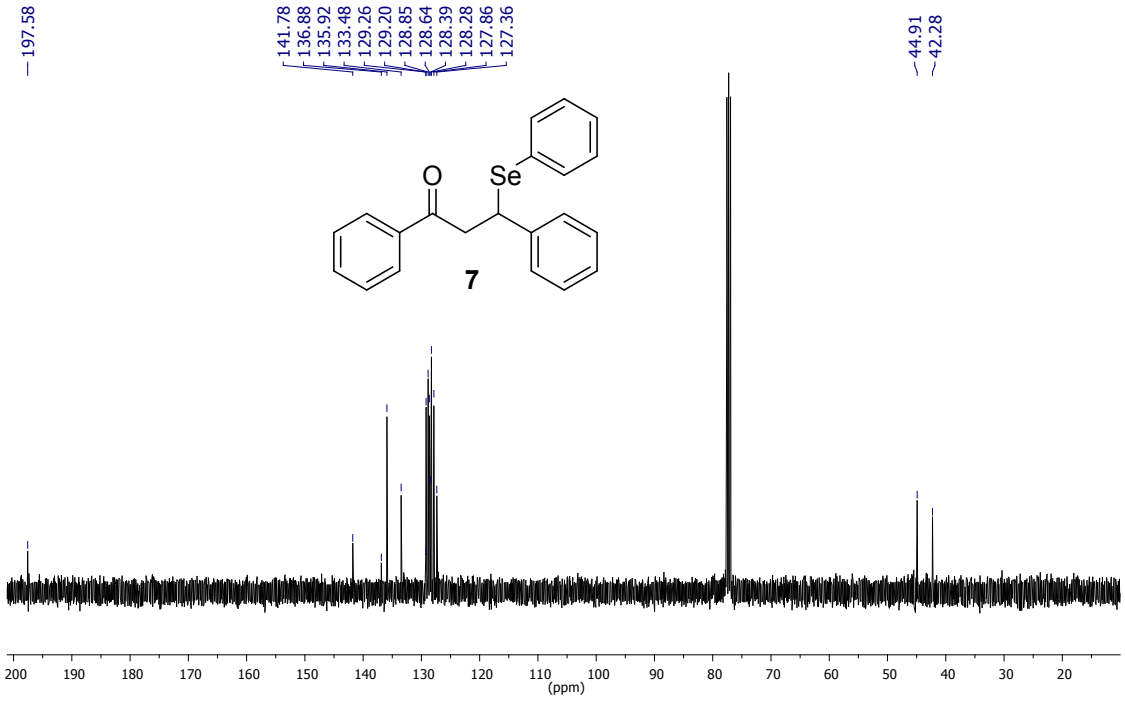
^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 197.5, 141.7, 136.8, 135.9, 133.4, 129.2, 129.2, 128.8, 128.6, 128.3, 128.2, 127.8, 127.3, 44.9, 42.2

MS(70eV) m/z= 366.05 $[M]^+$. MS(TOF): 367.0368$[M+H]^+$.

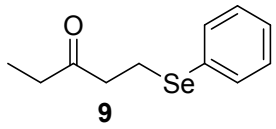
^{1}H NMR



^{13}C NMR


197.58
141.78
136.88
135.92
133.48
129.26
129.20
128.85
128.64
128.39
128.28
127.86
127.36
44.91
42.28
O
Se
7
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
(ppm)

5-phenylseleno-3-pentanone (9)



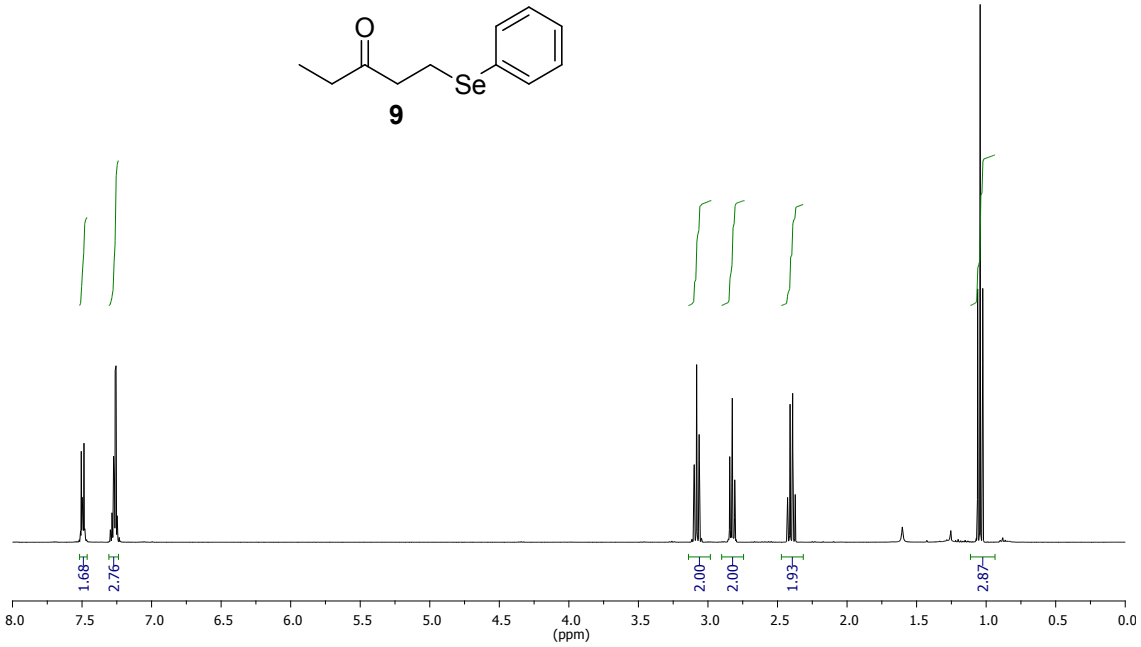
9

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.55 – 7.43 (m, 2H), 7.31 – 7.17 (m, 3H), 3.08 (t, *J* = 7.5 Hz, 2H), 2.89 – 2.77 (t, *J* = 7.5 Hz, 2H), 2.40 (q, *J* = 7.3 Hz, 2H), 1.04 (t, *J* = 7.3 Hz, 3H).

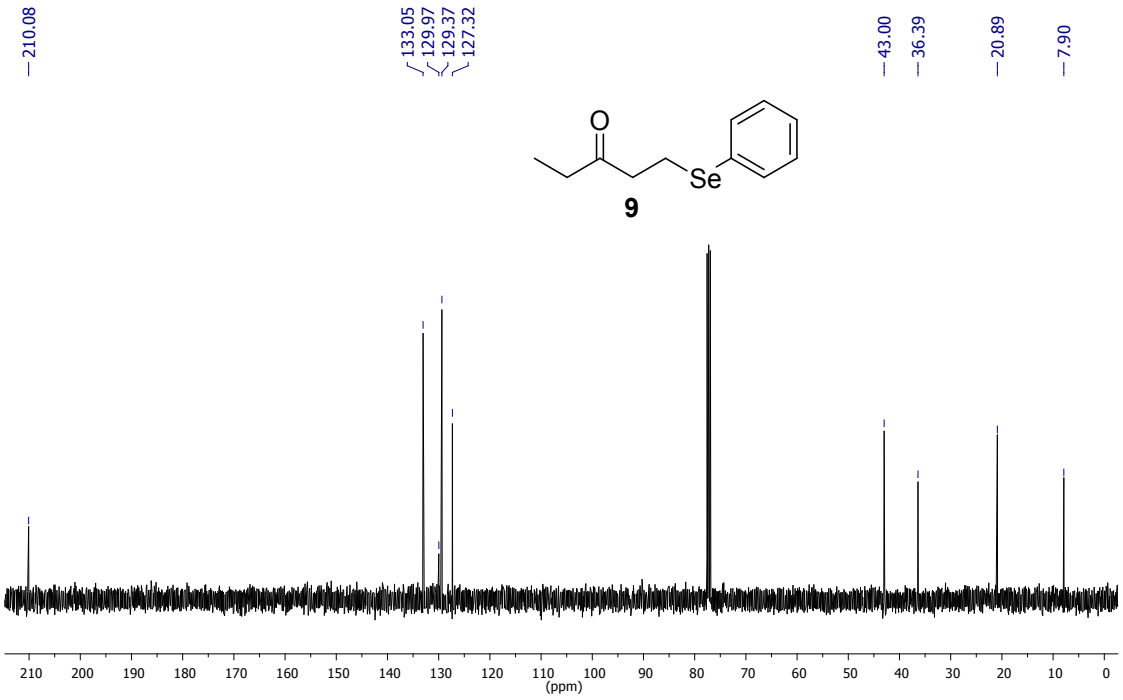
^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 210.0, 135.0, 129.9, 129.3, 127.3, 43.0, 36.3, 20.8, 7.9.

MS(70eV) m/z= 242.02 $[M]^+$. MS(TOF): 243.0731$[M+H]^+$.

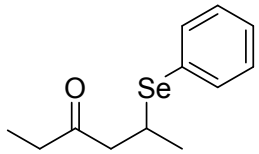
^{1}H NMR



^{13}C NMR


210.08
133.05
129.97
129.37
127.32
43.00
36.39
20.89
7.90
O
Se
9
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
(ppm)

5-phenylseleno-3-hexanone (11)



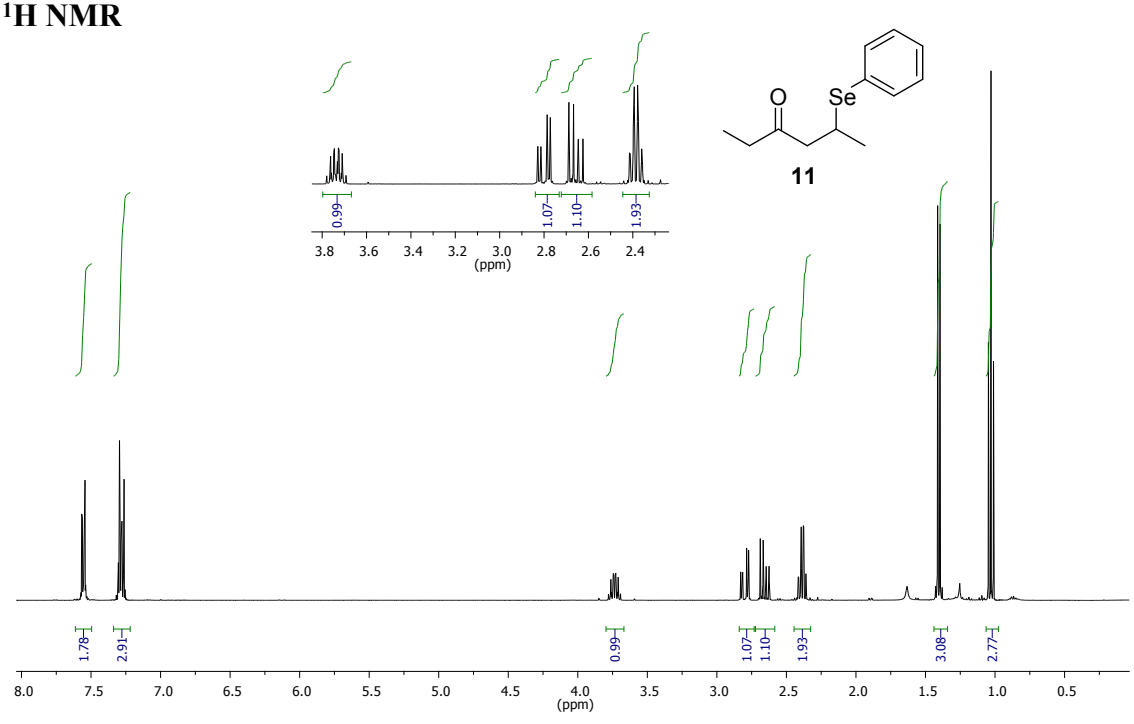
11

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.61 – 7.51 (m, 2H), 7.35 – 7.21 (m, 3H), 3.81 – 3.65 (m, 1H), 2.80 (dd, *J* = 16.9, 5.7 Hz, 1H), 2.66 (dd, *J* = 16.9, 8.4 Hz, 1H), 2.47 – 2.29 (q, *J* = 7.3 Hz, 2H), 1.40 (d, *J* = 6.9 Hz, 3H), 1.03 (t, *J* = 7.3 Hz, 3H).

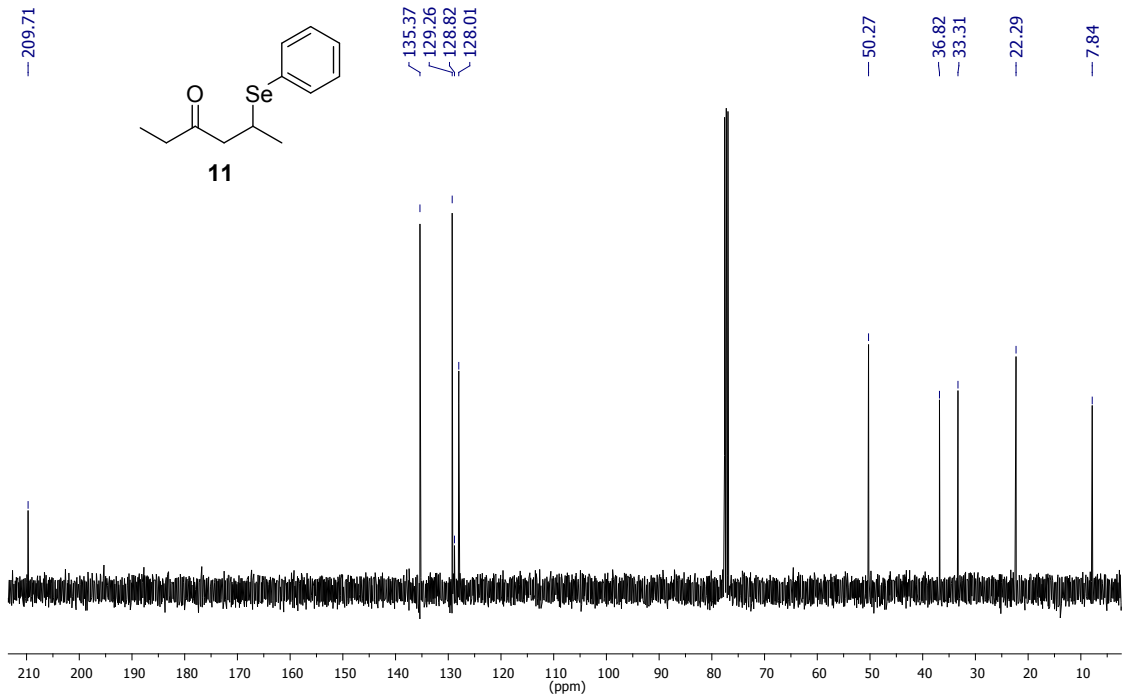
^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 209.7, 135.3, 129.2, 128.8, 128.0, 50.2, 36.8, 33.3, 22.2, 7.8.

MS(70eV) m/z= 256.04 $[M]^+$. MS(TOF): 257.0854$[M+H]^+$.

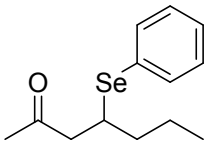
^{1}H NMR



^{13}C NMR


209.71
135.37
129.26
128.82
128.01
50.27
36.82
33.31
22.29
7.84
O
Se
11
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
(ppm)

4-phenylseleno-2-heptanone (13)



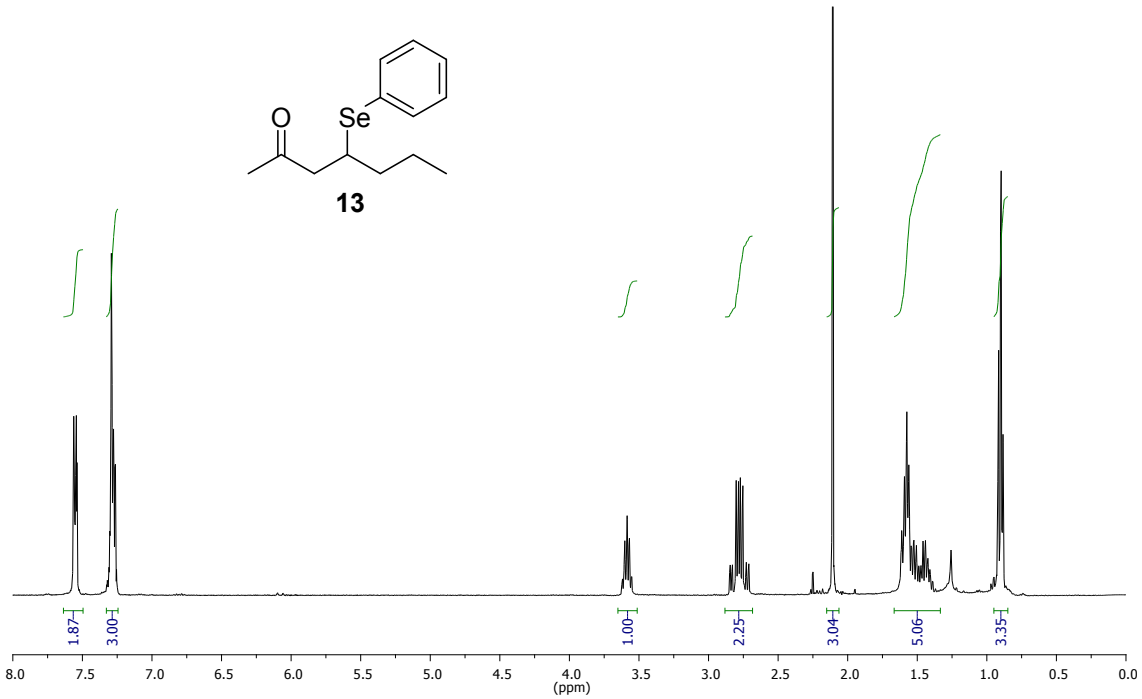
13

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.62 – 7.48 (m, 2H), 7.28 (m, 3H), 3.67 – 3.49 (m, 1H), 2.78 (dd, *J* = 17.3, 6.9, 1H), 2.75 (dd, *J* = 17.3, 6.0, 1H), 2.11 (s, 3H), 1.66 – 1.33 (m, 4H), 0.96 – 0.81 (t, *J* = 7.3, 3H).

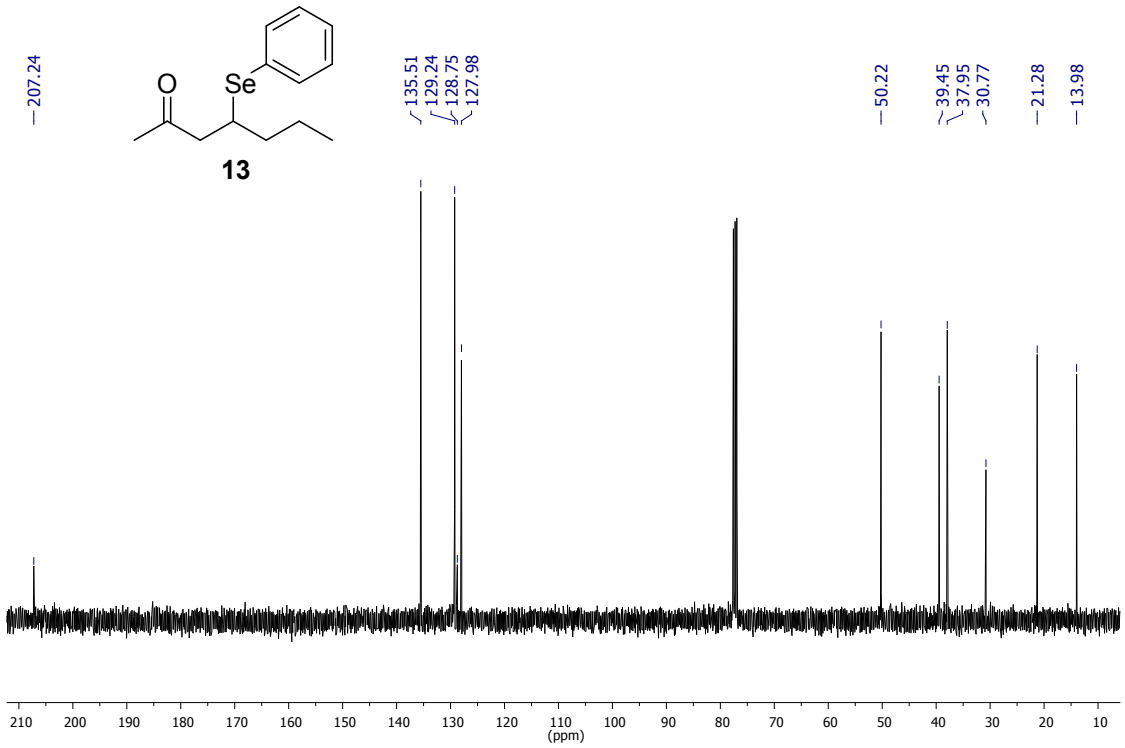
^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 207.2, 135.5, 129.2, 128.7, 127.9, 50.2, 39.4, 37.9, 30.7, 21.2, 13.9.

MS(70eV) m/z= 270.05 $[M]^+$. MS(TOF): 271.0467$[M+H]^+$.

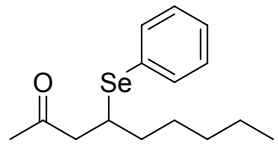
^{1}H NMR



^{13}C NMR


207.24
O
Se
13
135.51
129.24
128.75
127.98
50.22
39.45
37.95
30.77
21.28
13.98
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
(ppm)

4-phenylseleno-2-nonanone (15)



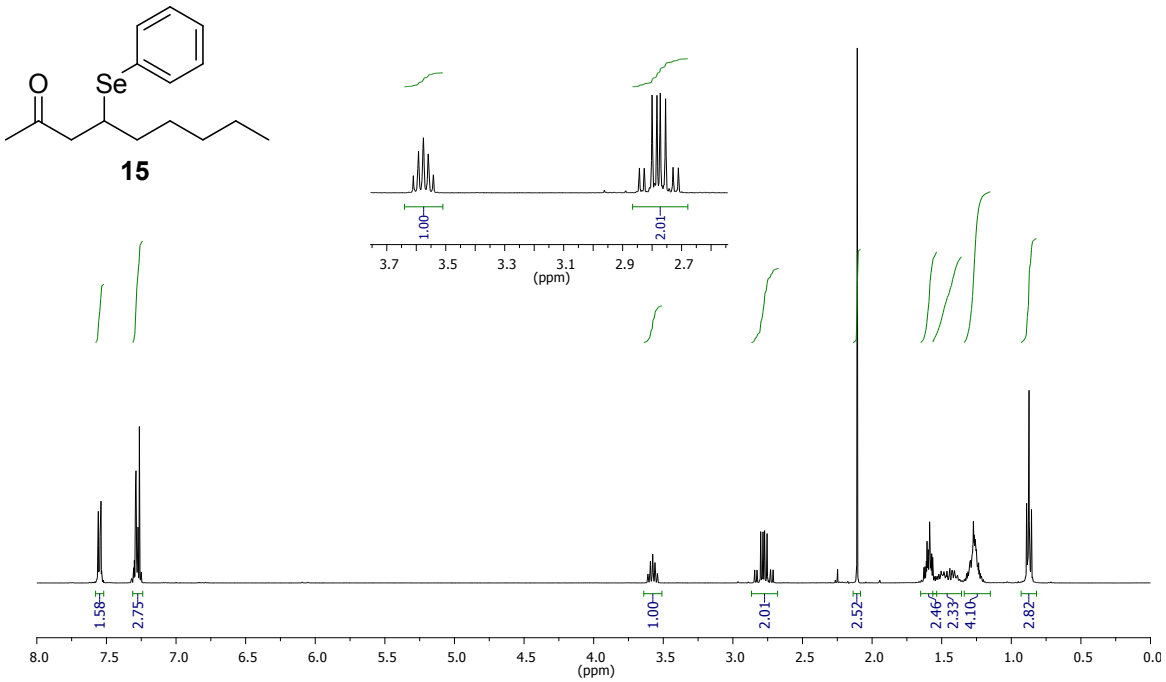
15

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.59 – 7.50 (m, 2H), 7.34 – 7.21 (m, 3H), 3.64 – 3.50 (m, 1H), 2.78 (dd, *J* = 17.3, 6.9 Hz, 1H), 2.69 (dd, *J* = 17.3, 6.3 Hz, 1H), 2.11 (s, 3H), 1.66 – 1.56 (m, 2H), 1.56 – 1.34 (m, 2H), 1.34 – 1.18 (m, 4H), 0.94 – 0.78 (t, *J* = 7.3 Hz, 3H).

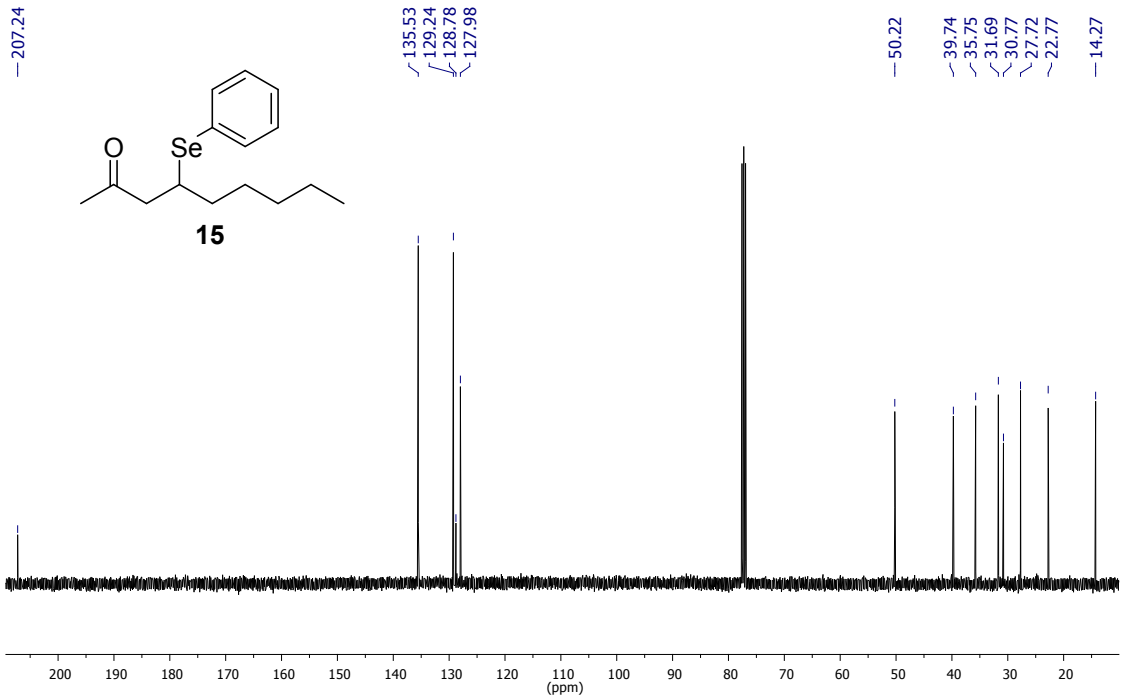
^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 207.2, 135.5, 129.2, 128.7, 127.9, 50.2, 39.7, 35.7, 31.6, 30.7, 27.7, 22.7, 14.2.

MS(70eV) m/z= 298.08 $[M]^+$. MS(TOF): 299.0734$[M+H]^+$.

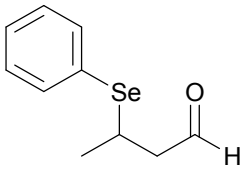
^{1}H NMR



^{13}C NMR


207.24
135.53
129.24
128.78
127.98
50.22
39.74
35.75
31.69
30.77
27.72
22.77
14.27
O
Se
15
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
(ppm)

3-phenylseleno-1-butanal (19)



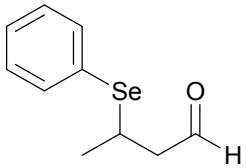
19

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 9.72 (t, *J* = 1.7 Hz, 1H), 7.64 – 7.49 (m, 2H), 7.38 – 7.28 (m, 3H), 3.79 – 3.62 (m, 1H), 2.75 (dd, *J* = 17.6, 5.6 Hz, 1H), 2.60 (dd, *J* = 17.6, 8.7 Hz, 1H), 1.52 – 1.42 (d, *J* = 3.3 Hz, 3H).

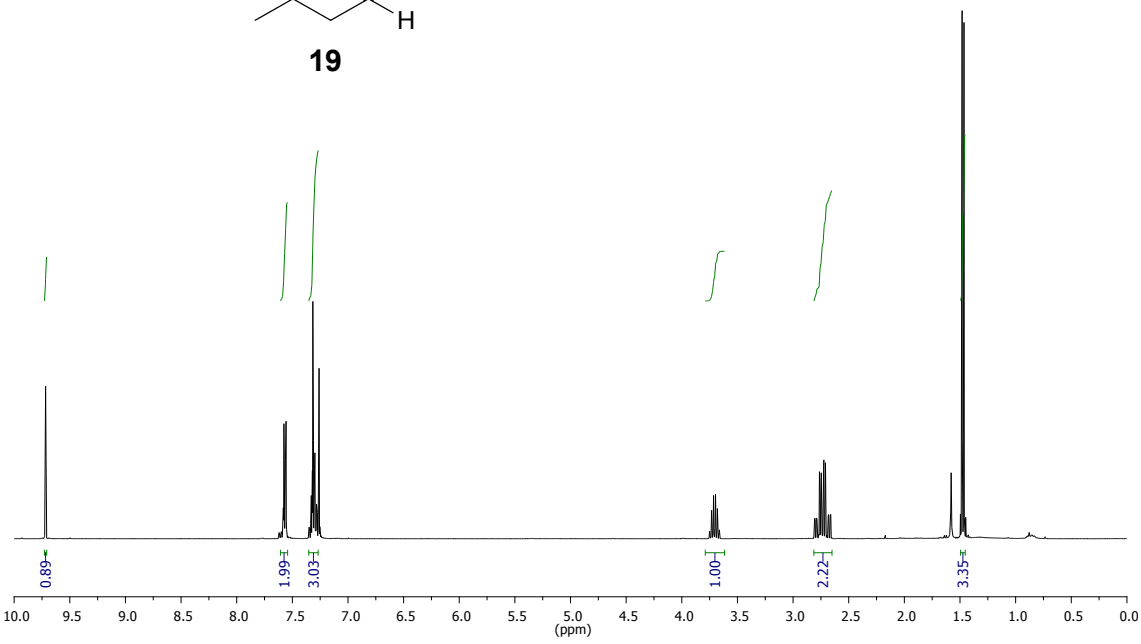
^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 200.9, 135.8, 129.3, 128.3, 128.0, 51.1, 31.9, 22.3.

MS(70eV) m/z= 240.01 $[M]^+$. MS(TOF): 241.0998$[M+H]^+$.

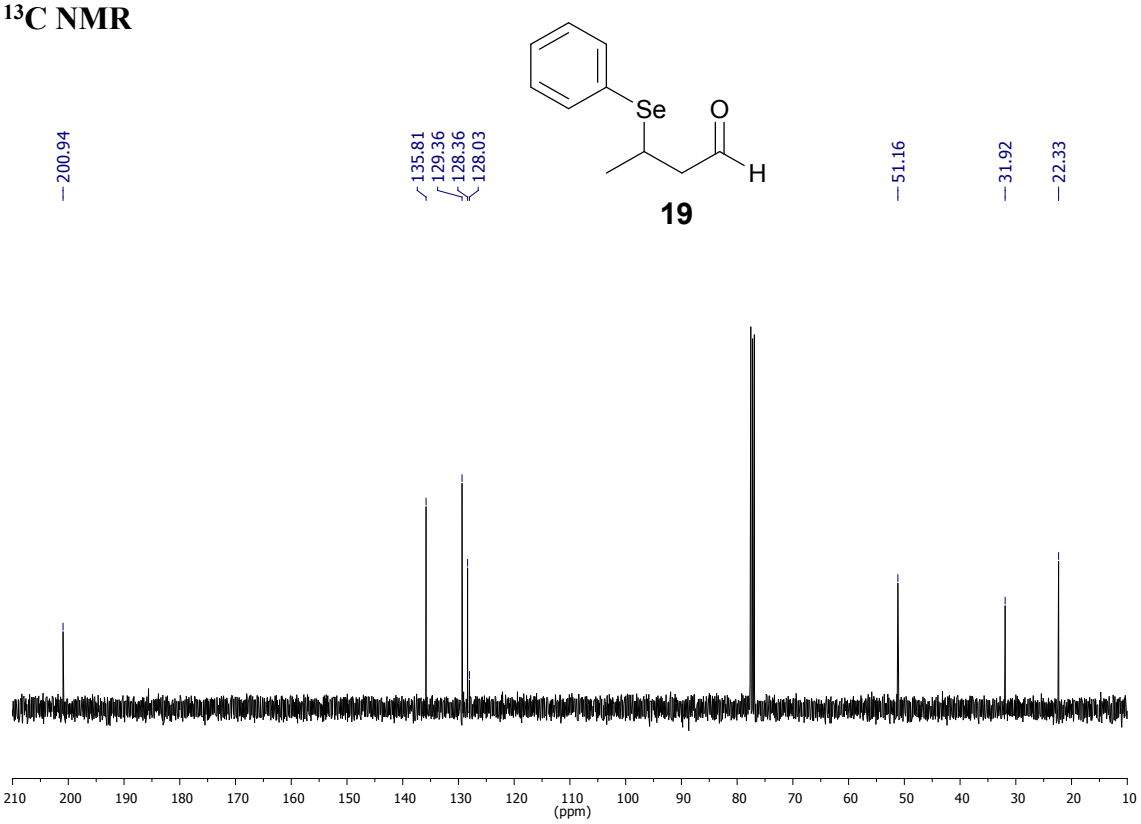
^{1}H NMR



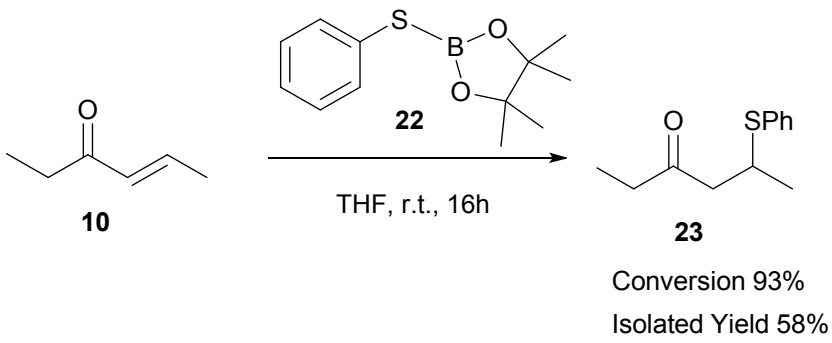
19



^{13}C NMR


200.94
135.81
129.36
128.36
128.03
51.16
31.92
22.33
Se
O
H
19
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
(ppm)

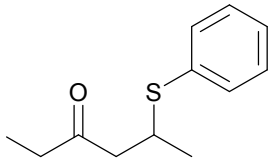
7. General procedure for the synthesis of 5-phenylsulfanyl-hexan-3-one (23)



PhSBpin (**22**) (0.11 mmol, 1.1 eq.) was weighted and transferred into an oven-dried Schlenk tube inside the glovebox. 4-Hexen-3-one (0.10 mmol) was introduced in the Schlenk tube under argon and dry THF (2 mL) was added. The mixture was stirred for 16 hours at room temperature. An aliquot of 0.2 mL was taken from the solution and gently concentrated on a rotary evaporator at r.t, and analyzed by ^{1}H NMR spectroscopy. Conversion was determined by correlation of the integrals of the protons of the product and the substrate. The product β-(phenylsulfanyl) substituted ketone was purified by flash chromatography using a silica gel column, and the mixture of petroleum ether and ethyl acetate (1:1).

8. Characterization of 5-phenylsulfanyl-hexan-3-one (23)

5-phenylsulfanyl-hexan-3-one (23)



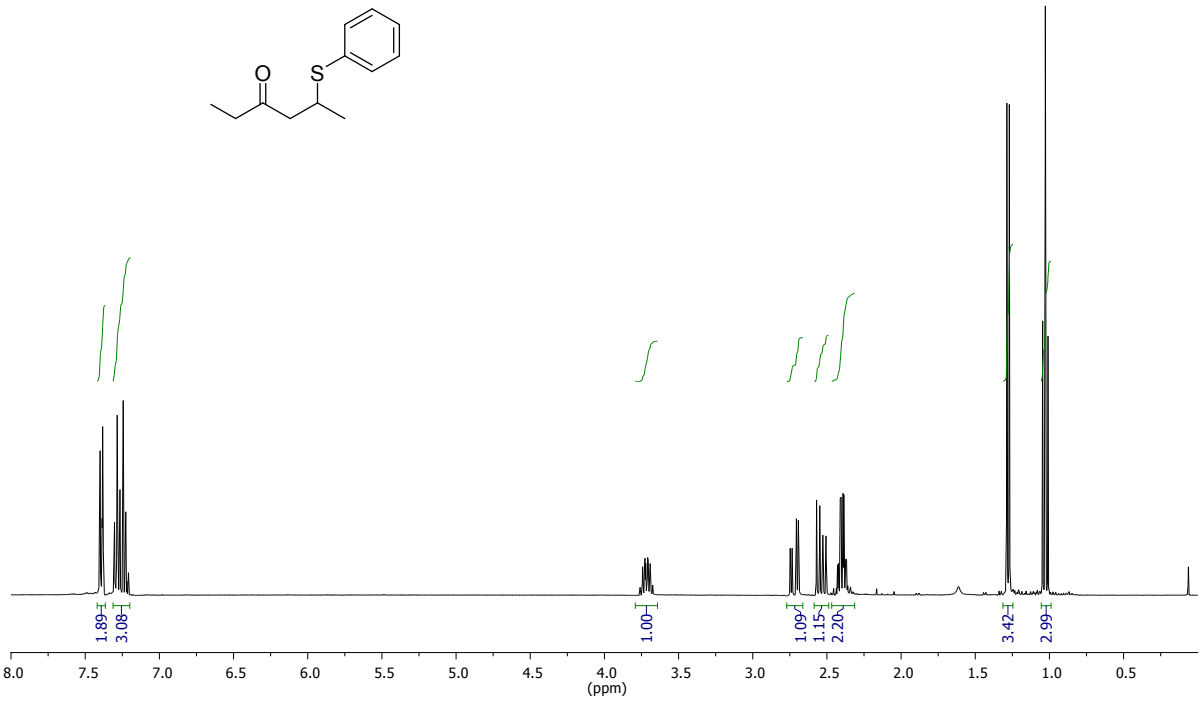
23

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.46 – 7.35 (m, 2H), 7.35 – 7.16 (m, 3H), 3.81 – 3.62 (m, 1H), 2.72 (dd, *J* = 16.8, 5.2 Hz, 1H), 2.54 (dd, *J* = 16.8, 8.5 Hz, 1H), 2.46 – 2.29 (q, *J* = 8.5 Hz, 2H), 1.28 (d, *J* = 6.7 Hz, 3H), 1.03 (t, *J* = 8.5 Hz, 3H).

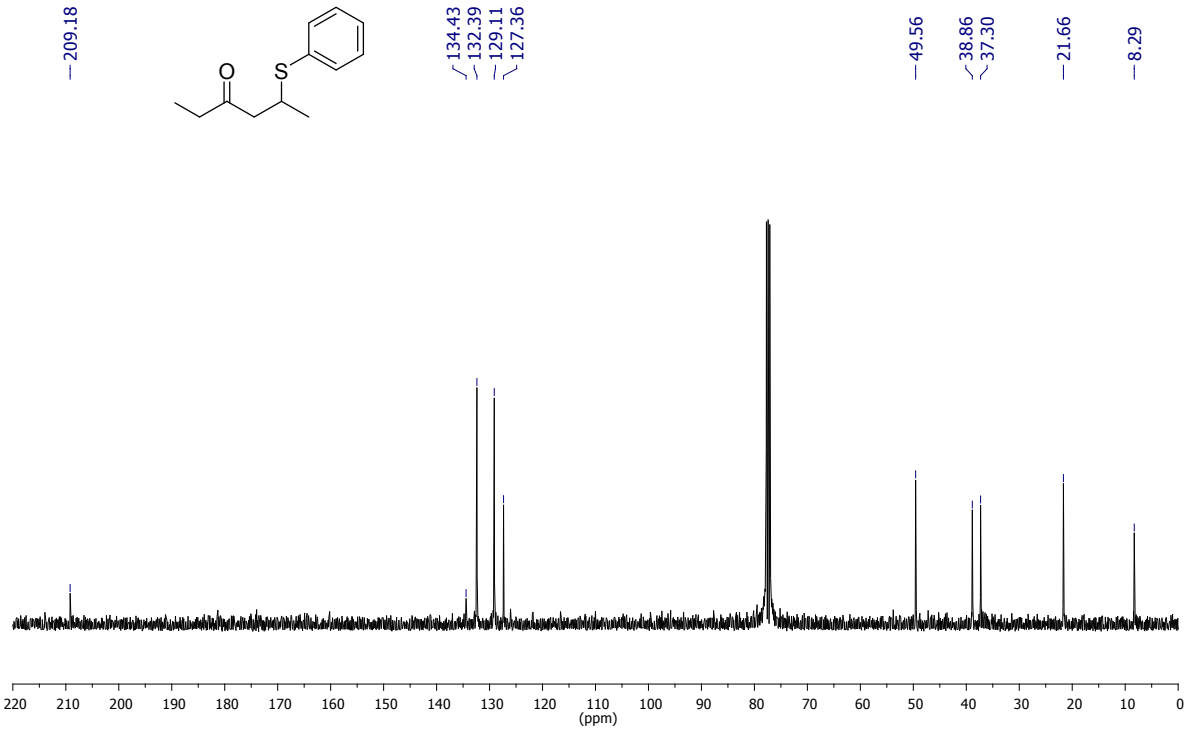
^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 209.2, 134.4, 132.4, 129.1, 127.4, 49.6, 38.9, 37.3, 21.7, 8.3.

MS(70eV) m/z= 208.09 $[M]^+$. MS(TOF): 209.0173$[M+H]^+$.

^{1}H NMR



^{13}C NMR


209.18
134.43
132.39
129.11
127.36
49.56
38.86
37.30
21.66
8.29
O
S
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
(ppm)

9. Computational details

All calculations were performed by using the Gaussian 09 package[4] with the hybrid M06-2X functional.[5] The standard 6–311G(d,p) basis set was used to describe the H, C, B, O, S and Se atoms. Full geometry optimizations were performed without constrains. The nature of the stationary points encountered was characterized either as minima or transition states by means of harmonic vibrational frequencies analysis. The zero-point, thermal, and entropy corrections were evaluated to compute enthalpies and Gibbs free energies (T=298 K, p=1 bar). Nuclear Magnetic Resonance isotropic chemical shifts[6] were computed doing single point calculations using the same functional and cc-pVTZ as basis set.[7] Hydrogens have been omitted for clarity in the graphic representation of the geometries.

10. Computed ^{11}B NMR shifts

All NMR shifts (δ) are in ppm and computed in M06-2X and cc-pVTZ as a basis set.

	$BF_3{\cdot}Et_2O$ (ref.)	PinBSePh	PinBSPh
δ	104.1	64.8	68.4
δ_{ref} - δ	-	39.3	35.7

11. Computed energies and relevant distances for the considered species

All energies are in kcal·mol^{-1} and all distances are in Å.

Reagents and substrates:

	PinBSePh	PinBSPh	PinBOPh	3-Penten-2-one (*cis*)	3-Penten-2-one (*trans*)
$\mathcal{E}_0$	**-1910382.37**	**-653254.22**	**-450606.03**	**-169740.72**	**-169740.33**
$\mathcal{E}_{ZPE}$	172.70	173.32	175.02	74.22	74.14
E_{tot}	182.76	183.11	184.43	78.81	78.77
H_{corr}	183.35	183.70	185.03	79.40	79.36
G_{corr}	145.02	146.54	148.46	54.65	54.44
$\mathcal{E}_0+\mathcal{E}_{ZPE}$	-1910209.67	-653080.90	-450431.01	-169666.50	-169666.19
$\mathcal{E}_0+E_{tot}$	-1910199.61	-653071.11	-450421.59	-169661.92	-169661.56
$\mathcal{E}_0+H_{cor}$	-1910199.02	-653070.52	-450421.00	-169661.32	-169660.97
$\mathcal{E}_0+G_{cor}$ (G^o)	**-1910237.35**	**-653107.69**	**-450457.56**	**-169686.07**	**-169685.88**
B-X	1.953	1.816	1.358		
B-O_1					
O_1-C_2				1.208	1.209
C_2-C_3				1.493	1.487
C_3-C_4				1.332	1.332

PinBSePh + 3-Penten-2-one (*cis*) reaction:

	TS 1	I1	TS2 1_2	I2 1_2	TS2 1_4	I2 1_4
$\mathcal{E}_0$	**-2080128.11**	**-2080128.89**	**-2080117.99**	**-2080147.88**	**-2080122.97**	**-2080154.84**
$\mathcal{E}_{ZPE}$	247.36	247.44	247.43	248.65	247.60	249.72
E_{tot}	262.24	262.57	262.18	263.61	262.04	264.36
H_{corr}	262.84	263.17	262.77	264.20	262.64	264.95
G_{corr}	214.69	214.52	213.86	214.16	215.81	216.37
$\mathcal{E}_0+\mathcal{E}_{ZPE}$	-2079880.75	-2079881.44	-2079870.56	-2079899.23	-2079875.37	-2079905.12
$\mathcal{E}_0+E_{tot}$	-2079865.87	-2079866.31	-2079855.81	-2079884.27	-2079860.93	-2079890.47
$\mathcal{E}_0+H_{cor}$	-2079865.27	-2079865.72	-2079855.22	-2079883.68	-2079860.33	-2079889.88
$\mathcal{E}_0+G_{cor}$ (G^o)	**-2079913.42**	**-2079914.37**	**-2079904.13**	**-2079933.72**	**-2079907.16**	**-2079938.47**
B-X	2.039	2.089	2.223		2.170	3.553
B-O_1	1.899	1.619	1.539	1.357	1.551	1.361
O_1-C_2	1.234	1.244	1.282	1.416	1.281	1.380
C_2-C_3	1.460	1.466	1.454	1.504	1.408	1.332
C_3-C_4	1.339	1.337	1.340	1.328	1.369	1.494
Se-C_x			2.735	2.007	2.922	2.002
Imag. Freq.	-141.52		-189.38		-118.88	

PinBSPh + 3-Penten-2-one (*cis*) reaction:

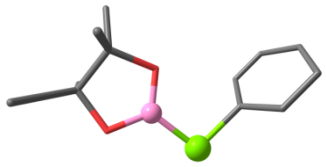
	TS 1	I1	TS2 1_2	I2 1_2	TS2 1_4	I2 1_4
$\mathcal{E}_0$	**-823000.00**	**-823000.22**	**-822989.50**	**-823018.68**	**-822997.82**	**-823025.19**
$\mathcal{E}_{ZPE}$	248.09	248.00	247.68	249.47	248.27	250.31
E_{tot}	262.59	262.91	262.20	264.09	262.49	264.72
H_{corr}	263.18	263.50	262.79	264.68	263.08	265.32
G_{corr}	216.40	215.60	215.43	215.89	217.05	217.29
$\mathcal{E}_0+\mathcal{E}_{ZPE}$	-822751.91	-822752.22	-822741.82	-822769.21	-822749.55	-822774.88
$\mathcal{E}_0+E_{tot}$	-822737.41	-822737.31	-822727.30	-822754.59	-822735.33	-822760.46
$\mathcal{E}_0+H_{cor}$	-822736.81	-822736.72	-822726.71	-822754.00	-822734.73	-822759.87
$\mathcal{E}_0+G_{cor}$ (G^o)	**-822783.59**	**-822784.61**	**-822774.07**	**-822802.80**	**-822780.77**	**-822807.89**
B-X	1.902	1.943	2.038		2.018	3.429
B-O_1	1.851	1.661	1.549	1.357	1.541	1.361
O_1-C_2	1.236	1.247	1.290	1.418	1.278	1.380
C_2-C_3	1.459	1.447	1.450	1.508	1.402	1.331
C_3-C_4	1.339	1.343	1.340	1.328	1.376	1.499
Se-C_x			2.610	1.857	2.619	1.857
Imag. Freq.	-111.85		-253.4		-178.76	

PinBOPh + 3-Penten-2-one (*cis*) reaction:

	TS2 1_2	I2 1_2	TS2 1_4	I2 1_4
$\mathcal{E}_0$	**-620332.65**	**-620352.84**	**-620337.32**	**-620352.24**
$\mathcal{E}_{ZPE}$	250.16	251.71	250.46	252.52
E_{tot}	263.90	265.80	264.10	266.56
H_{corr}	264.49	266.40	264.70	267.15
G_{corr}	219.05	218.94	219.84	218.93
$\mathcal{E}_0+\mathcal{E}_{ZPE}$	-620082.48	-620101.12	-620086.86	-620099.72
$\mathcal{E}_0+E_{tot}$	-620068.75	-620087.03	-620073.22	-620085.68
$\mathcal{E}_0+H_{cor}$	-620068.16	-620086.44	-620072.63	-620085.09
$\mathcal{E}_0+G_{cor}$ (G^o)	**-620113.59**	**-620133.90**	**-620117.49**	**-620133.31**
B-X	1.555		1.538	
B-O_1	1.545	1.353	1.539	1.359
O_1-C_2	1.304	1.417	1.292	1.386
C_2-C_3	1.468	1.508	1.381	1.328
C_3-C_4	1.334	1.324	1.402	1.500
Se-C_x	1.886	1.420	1.964	1.430
Imag. Freq.	-235.6		-324.39	

12. Structures, Gibbs free energies and imaginary frequencies of the involved species

PhSeBpin (1)



$\mathcal{E}_0$: -1910382.37 kcal·mol^{-1}

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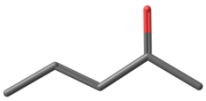
33

 C          0.554747    2.247224    0.819014
 C         -0.161282    1.915983   -0.529795
 C         -0.408443    2.324705    1.998856
 C          1.459662    3.464733    0.777890
 C         -1.564687    2.478655   -0.662522
 C          0.680578    2.269970   -1.751865
 B          0.764383    0.054212    0.341722
 O          1.372872    1.064177    1.026088
 O         -0.240698    0.468278   -0.482432
 C          2.439028   -1.806400    1.948643
 C          3.490380   -0.897025    2.041242
 C          2.266723   -2.776311    2.933345
 C          4.355880   -0.954940    3.127298
 C          3.146307   -2.836554    4.009246
 C          4.190584   -1.925343    4.110455
 H          4.872891   -1.970195    4.950666
 H          0.172356    2.337910    2.922074
 H         -1.021201    3.227547    1.954315
 H         -1.065727    1.452740    2.020190
 H          0.881763    4.359210    0.530191
 H          1.917197    3.610480    1.757738
 H          2.253590    3.342391    0.042177
 H         -1.544797    3.570231   -0.603578
 H         -1.978165    2.193517   -1.631115
 H         -2.221501    2.093456    0.116233
 H          0.220400    1.820664   -2.632941
 H          0.737263    3.350665   -1.897463
 H          1.693407    1.872596   -1.655501
 H          3.623214   -0.143624    1.276074
 H          1.444687   -3.478364    2.860978
 H          5.168987   -0.242146    3.199317
 H          3.008268   -3.594562    4.771326
 Se         1.244913   -1.836757    0.432747
```

3-Penten-2-one (*cis*)



$\mathcal{E}_0$: -169740.72 kcal·mol^{-1}

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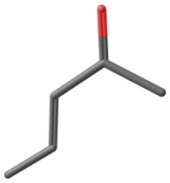
14

 C         1.722668    0.948079    0.838061
 C         3.208677    0.872300    0.571407
 H         3.495896   -0.163656    0.371323
 H         3.463441    1.500169   -0.279435
 H         3.762101    1.196992    1.456685
 C         1.222546    0.135466    1.986029
 H         1.945038   -0.446295    2.552423
 C        -0.070846    0.126695    2.302265
 H        -0.730242    0.735429    1.686466
 C        -0.680361   -0.647204    3.423888
 H        -1.429029   -1.346769    3.041410
 H         0.070293   -1.208637    3.981163
 H        -1.200559    0.023991    4.112869
 O         0.986111    1.625030    0.160928
```

3-Penten-2-one (*trans*)

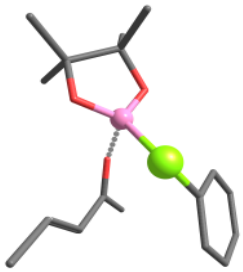


$\mathcal{E}_0$: -169740.33 kcal·mol^{-1}

```
14

 C         1.770630    0.996883    0.843293
 C         3.244755    0.892036    0.507812
 H         3.521745   -0.147452    0.317743
 H         3.439630    1.490237   -0.379258
 H         3.855956    1.253961    1.337574
 C         1.250068    0.270298    2.031244
 H         0.184234    0.399574    2.198350
 C         1.988734   -0.482288    2.845623
 H         3.053418   -0.589850    2.648651
 C         1.462137   -1.211368    4.040356
 H         1.974080   -0.880966    4.948321
 H         0.391370   -1.048677    4.164442
 H         1.644867   -2.285295    3.946120
 O         1.018535    1.656161    0.164709
```

TS1 (Se)



$\mathcal{E}_0$: -2080128.11 kcal·mol^{-1}
Imaginary frequency: -141.52 cm^{-1}

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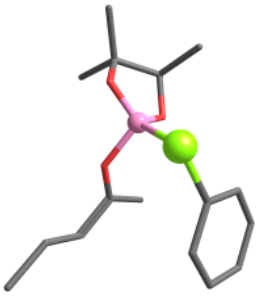
47

 B       -3.133519   -1.691884    4.639207
 Se      -3.538443   -3.509443    5.468658
 C       -3.165556   -3.973264    2.159871
 O       -1.614167   -2.055602    3.559630
 C       -1.089204   -3.040073    3.031832
 C       -1.852892   -4.105342    2.389138
 C        0.403864   -3.178145    3.070810
 C       -0.800287   -3.196668    6.384384
 C       -1.742170   -4.074564    5.839616
 C       -1.369358   -5.386401    5.544512
 C       -4.030656   -5.029690    1.566274
 C        0.860497   -4.952772    6.358163
 C       -0.074899   -5.825651    5.814323
 C        0.492774   -3.636944    6.635574
 O       -4.142570   -1.238785    3.798941
 O       -2.584296   -0.660191    5.389817
 C       -3.402535    0.503033    5.165381
 C       -4.445472    0.545467    6.280563
 C       -4.033785    0.201450    3.767614
 C       -3.108630    0.579907    2.613020
 C       -2.523961    1.741606    5.209215
 C       -5.419081    0.786518    3.555511
 H       -1.316643   -5.009449    2.117883
 H        0.644909   -4.009214    3.744416
 H        0.797339   -3.422564    2.081960
 H        0.851873   -2.265006    3.455612
 H       -2.095835   -6.061587    5.106295
 H       -4.815850   -5.289847    2.282577
 H       -4.532451   -4.656009    0.669704
 H       -3.644196   -3.032415    2.421784
 H       -1.086311   -2.172488    6.595130
 H        0.199679   -6.850934    5.593446
 H       -3.467515   -5.928498    1.314074
 H        1.216803   -2.949250    7.057542
 H       -3.925556    0.541931    7.239836
 H       -5.089248   -0.335807    6.241325
```

H	-5.065509	1.442987	6.219925
H	-3.500634	0.139873	1.693661
H	-3.059881	1.663864	2.485667
H	-2.102319	0.193731	2.780369
H	-1.681415	1.647708	4.525257
H	-2.133042	1.872400	6.219829
H	-3.101307	2.632305	4.945422
H	-5.771805	0.533679	2.553827
H	-6.128266	0.387731	4.280027
H	-5.392626	1.876044	3.645548
H	1.867638	-5.293341	6.567056

I1 (Se)



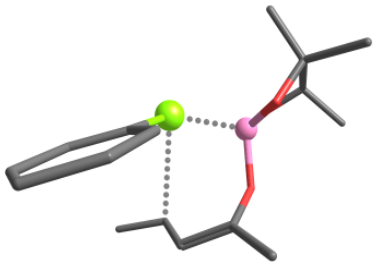
$\mathcal{E}_0$: -2080128.89 kcal·mol^{-1}

47

B	-2.829339	-1.067915	4.803532
Se	-1.785127	-2.368748	6.061542
C	-3.197327	-4.436767	2.237559
O	-2.961441	-2.020795	3.500903
C	-2.237010	-2.208997	2.507179
C	-2.421513	-3.457005	1.761118
C	-1.219016	-1.239984	2.008110
C	0.614655	-1.309259	4.841392
C	-0.219549	-2.425973	4.948633
C	0.087606	-3.575922	4.216637
C	-3.411070	-5.752132	1.572515
C	2.031931	-2.492718	3.285077
C	1.210199	-3.609620	3.391595
C	1.729980	-1.343274	4.013408
O	-4.114904	-0.813901	5.309101
O	-2.202920	0.151573	4.440052
C	-3.003260	1.208196	4.992427
C	-2.482123	1.513906	6.395659
C	-4.421230	0.555023	5.014649
C	-5.102687	0.607697	3.646636
C	-2.879754	2.433555	4.101747
C	-5.350299	1.091206	6.090597
H	-1.868208	-3.566627	0.834088
H	-1.161870	-0.358952	2.639114
H	-0.247546	-1.742339	1.956231
H	-1.499009	-0.967716	0.984780
H	-0.557808	-4.442832	4.299426

H	-3.088628	-6.562648	2.232201
H	-4.476890	-5.909405	1.384684
H	-3.697055	-4.262085	3.188233
H	0.370498	-0.415989	5.402855
H	1.442596	-4.511232	2.835936
H	-2.870046	-5.825755	0.629223
H	2.370222	-0.471539	3.940252
H	-1.420114	1.758192	6.326246
H	-2.588736	0.642968	7.045094
H	-3.005820	2.362095	6.842902
H	-5.966667	-0.058705	3.663475
H	-5.440707	1.617460	3.401705
H	-4.421208	0.266204	2.863638
H	-3.104403	2.190384	3.063080
H	-1.859566	2.819595	4.152079
H	-3.560359	3.221777	4.435557
H	-6.314708	0.584038	6.023486
H	-4.938664	0.911222	7.083128
H	-5.515344	2.164680	5.960542
H	2.907737	-2.518290	2.647181

TS2 1_4 (Se)



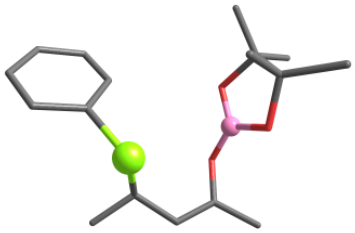
$\mathcal{E}_0$: -2080122.97 kcal·mol^{-1}
Imaginary frequency: -118.88 cm^{-1}

47

B	-2.600434	-1.043156	4.206173
Se	-3.688537	-2.396497	5.507990
C	-4.260418	-3.824600	3.023965
O	-2.576003	-1.762213	2.831640
C	-2.099352	-2.923158	2.575210
C	-2.951952	-4.038774	2.681734
C	-0.657234	-3.018830	2.205210
C	-1.115236	-3.740326	5.466840
C	-2.484292	-3.865503	5.711427
C	-3.004310	-5.121254	6.047404
C	-5.197597	-4.922356	3.381696
C	-0.813189	-6.111059	5.836658
C	-2.174920	-6.232314	6.110228
C	-0.290257	-4.863273	5.525149
O	-3.361861	0.133304	4.155549
O	-1.270142	-0.752490	4.603916
C	-1.269942	0.601022	5.085098

C	-1.547872	0.576830	6.587477
C	-2.444296	1.231631	4.268413
C	-2.018585	1.632037	2.855736
C	0.093011	1.214986	4.809803
C	-3.145403	2.387855	4.960840
H	-2.526619	-5.035626	2.662579
H	-0.081633	-2.381864	2.880455
H	-0.295392	-4.045354	2.229800
H	-0.538653	-2.615505	1.194232
H	-4.064114	-5.221533	6.255344
H	-5.869942	-4.601113	4.178505
H	-5.816907	-5.168137	2.511230
H	-4.668399	-2.831314	2.882669
H	-0.698226	-2.763250	5.254697
H	-2.591776	-7.197930	6.373284
H	-4.661376	-5.818876	3.695332
H	0.771278	-4.751874	5.333047
H	-0.813824	-0.074758	7.066039
H	-2.541519	0.175919	6.794877
H	-1.467727	1.575231	7.024188
H	-2.916137	1.855362	2.276419
H	-1.374955	2.515109	2.860998
H	-1.492544	0.809137	2.366913
H	0.376238	1.087691	3.765256
H	0.845542	0.727692	5.433110
H	0.089723	2.282158	5.049215
H	-3.941434	2.766851	4.317143
H	-3.590597	2.065939	5.901628
H	-2.443420	3.203252	5.157371
H	-0.168271	-6.980401	5.881748

I2 1_4 (Se)



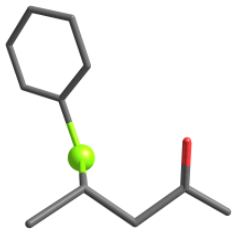
$\mathcal{E}_0$: -2080154.84 kcal·mol^{-1}

47

C	-1.659267	-1.790550	2.538789
O	-2.565735	-0.891412	3.061335
C	-1.710099	-3.052171	2.962373
C	-2.653675	-3.492017	4.034402
C	-2.963629	-4.979094	4.012350
C	-0.738849	-1.231912	1.505073
Se	-1.842287	-2.947505	5.782051
C	-3.467730	-2.941164	6.814787
C	-3.748945	-3.982832	7.697234
C	-4.365414	-1.880009	6.678166
C	-4.924437	-3.964428	8.441903

C	-5.543155	-1.873845	7.418512
C	-5.822470	-2.912318	8.301727
B	-2.201478	0.074071	3.948627
O	-3.145261	0.801558	4.625863
O	-0.914336	0.465686	4.205255
C	-2.451761	1.932150	5.198931
C	-0.981283	1.402499	5.307675
C	-2.589805	3.085399	4.208719
C	-3.101016	2.285195	6.525193
C	0.090365	2.461062	5.114204
C	-0.735270	0.619144	6.592235
H	-3.567143	-2.899143	3.987248
H	-3.616859	-5.250891	4.843484
H	-0.108002	-0.460814	1.954738
H	-0.105909	-2.013670	1.087134
H	-1.317469	-0.769624	0.701350
H	-1.022116	-3.777374	2.541779
H	-3.467762	-5.239748	3.076796
H	-2.046373	-5.566975	4.089294
H	-3.047148	-4.802303	7.796610
H	-4.141482	-1.064784	5.996457
H	-5.138812	-4.775143	9.128274
H	-6.241138	-1.052279	7.307476
H	-2.143711	4.002666	4.598732
H	-3.650274	3.261183	4.022978
H	-2.111523	2.840259	3.257664
H	-3.155833	1.416891	7.181438
H	-2.538155	3.075505	7.029062
H	-4.115237	2.646894	6.346623
H	0.024938	2.915785	4.126266
H	-0.006660	3.242967	5.872213
H	1.075011	2.002229	5.218710
H	-0.683125	1.287281	7.454800
H	-1.520839	-0.120320	6.757778
H	0.211695	0.084757	6.499859
H	-6.738579	-2.901096	8.880318

P 1_4 (Se)



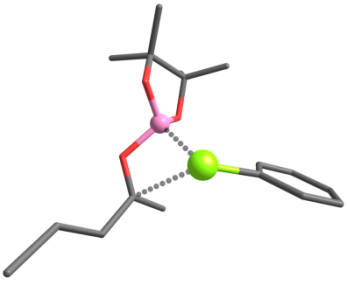
$\mathcal{E}_0$: -1822463.15 kcal·mol^{-1}

27

C	-0.922804	3.511158	1.100375
C	-1.384897	2.211666	1.741931
H	-0.749116	1.403179	1.381415
O	1.300832	2.654431	0.999657
C	0.593730	3.629829	1.023506

Se	-0.996690	2.308230	3.689264
C	-0.382257	0.498787	3.910215
C	-1.055518	-0.361780	4.773514
C	0.750480	0.060430	3.223257
C	-0.593617	-1.662836	4.952311
H	-1.939179	-0.015946	5.296295
C	1.193318	-1.245796	3.394004
H	1.272857	0.740780	2.558881
C	0.526778	-2.107235	4.260711
H	-1.118373	-2.330050	5.625907
H	2.069977	-1.586537	2.855722
H	0.881333	-3.122029	4.395898
H	-1.285896	3.558515	0.063536
C	-2.852563	1.905530	1.486725
H	-3.035591	1.801012	0.412223
H	-3.141928	0.975484	1.977712
H	-3.492684	2.704093	1.868972
C	1.152685	5.029037	0.961019
H	1.042936	5.484482	1.950098
H	2.205723	4.999679	0.689187
H	0.588347	5.642717	0.254960
H	-1.344292	4.386538	1.605980

TS2 1_2 (Se)



$\mathcal{E}_0$: - 2080117.99 kcal·mol^{-1}
Imaginary frequency: -189.38 cm^{-1}

47

B	1.030956	1.279475	-0.024564
Se	0.074069	-0.388957	-1.139479
C	3.593566	-1.874669	0.387098
O	2.013831	0.356548	0.717193
C	1.554454	-0.767470	1.128720
C	2.399071	-1.942257	0.989592
C	0.379699	-0.841023	2.046920
C	-2.410448	0.364380	0.215067
C	-1.813771	-0.370852	-0.812332
C	-2.615373	-1.180379	-1.624889
C	4.522621	-3.024986	0.216571
C	-4.576587	-0.525862	-0.383473
C	-3.984594	-1.258106	-1.408353
C	-3.784782	0.285792	0.420396
O	1.704344	2.122931	-0.915361
O	0.195501	2.031646	0.828909
C	0.127785	3.359261	0.272292

C	1.506112	3.466001	-0.453783
H	2.022764	-2.872825	1.401211
H	-0.235919	0.051455	1.981400
H	-0.210628	-1.737010	1.857938
H	0.792765	-0.905915	3.063081
H	-2.158249	-1.744764	-2.429490
H	4.718088	-3.189955	-0.847096
H	5.488307	-2.805962	0.680984
H	3.901543	-0.910659	-0.010843
H	-1.802269	1.013425	0.830732
H	-4.592024	-1.889970	-2.046245
H	4.120867	-3.941707	0.647930
H	-4.236913	0.865134	1.217682
H	-5.645460	-0.584348	-0.217154
C	-1.043766	3.418354	-0.706853
H	-0.911113	2.691723	-1.512538
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H	-1.145608	4.415461	-1.141027
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H	-1.060619	4.208558	1.847450
C	1.523582	4.403224	-1.649245
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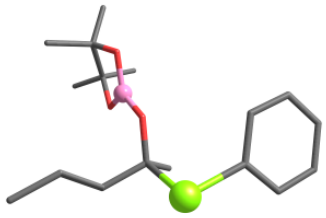
H	2.528181	4.428999	-2.075398
H	0.834758	4.060429	-2.420592
C	2.643450	3.805447	0.509698
H	3.591432	3.646728	-0.007044
H	2.595598	4.844957	0.843103
H	2.616644	3.150721	1.383774

I2 1_2 (Se)



$\mathcal{E}_0$: -2080147.88 kcal·mol^{-1}

47

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H	-0.462414	4.318472	-1.093247
H	0.749817	4.231602	0.206935
H	0.252891	2.752584	-0.635674
O	-1.578502	4.741455	1.362226
C	-2.559825	7.250562	-0.992498
C	-3.224085	7.710347	0.346802

C	-1.211869	3.518672	0.750439
Se	-0.606265	2.313245	2.236733
C	1.034916	3.226457	2.647407
C	0.997524	4.492021	3.234086
C	2.260261	2.629897	2.354770
C	2.185763	5.158951	3.511484
H	0.040150	4.946548	3.456690
C	3.445672	3.295637	2.651079
H	2.281813	1.650374	1.892165
C	3.409496	4.561473	3.224774
H	2.153959	6.144452	3.961116
H	4.396420	2.826417	2.426931
B	-2.078578	5.795746	0.668704
O	-2.210424	5.879833	-0.696864
O	-2.517552	6.918612	1.323295
C	-3.477441	7.275797	-2.201674
H	-3.853728	8.287639	-2.374943
H	-2.923133	6.958922	-3.086812
H	-4.321763	6.600770	-2.067336
C	-4.696414	7.315479	0.432438
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C	-1.259497	7.993258	-1.286238
H	-0.742517	7.486307	-2.102694
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H	-0.604911	7.993791	-0.411689
C	-3.043261	9.181150	0.676172
H	-3.486665	9.805995	-0.103761
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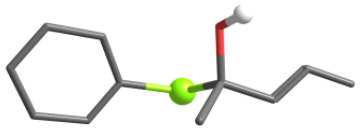
H	4.332953	5.081310	3.450720
H	-2.148692	2.014429	-0.548306
H	-4.523125	1.573155	-0.821196
H	-5.424491	1.850741	0.678991
H	-3.868934	3.827276	1.212598

P 1_2 (Se)



$\mathcal{E}_0$: -1822448.09 kcal·mol^{-1}

27

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H	-0.546370	3.747926	-1.298873
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O	-1.506657	4.349315	1.159196

C	-1.124175	3.077693	0.661428
Se	-0.335086	2.101268	2.217251
C	1.081881	3.345280	2.599288
C	0.790506	4.585237	3.167852
C	2.403426	2.997213	2.323082
C	1.822162	5.473303	3.449759
H	-0.239502	4.846076	3.372402
C	3.432281	3.885935	2.620305
H	2.620248	2.034794	1.874972
C	3.142248	5.124422	3.180954
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H	3.943754	5.816962	3.409209
H	-3.151248	2.369246	1.026851
H	-4.532715	0.953036	-0.358923
H	-4.203014	1.163967	-2.088000
H	-1.721849	1.508592	-1.541638
H	-1.854107	4.849888	0.412400

H2O

$\mathcal{E}_0$: -47949.42 kcal·mol^{-1}

3			
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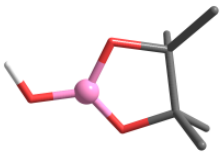
H	0.638614	-0.501093	0.000000
H	-0.596681	0.371941	0.000000

PinBOH



$\mathcal{E}_0$: -305652.89 kcal·mol^{-1}

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C	-2.237441	-0.612269	1.316117
H	-3.305738	-0.419520	1.208271
H	-2.098050	-1.632344	1.679827
H	-1.837108	0.083078	2.057423
C	-2.105264	-1.390474	-1.059456
H	-1.795043	-2.408472	-0.808640
H	-3.195838	-1.352978	-1.058569
H	-1.756627	-1.149793	-2.063055
C	0.591752	-1.244554	1.137107
H	0.343491	-2.291917	0.945235
H	1.678404	-1.142931	1.130152
H	0.228755	-0.969847	2.126777
C	0.677873	-0.591849	-1.278272

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H         1.732721   -0.329061   -1.184526
H         0.602554   -1.637103   -1.585006
H         0.234343    0.034313   -2.055688
O         0.225949    1.029516    0.416820
O        -1.888687    0.936146   -0.468029
B        -0.861513    1.736710   -0.045454
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H        -0.098935    3.484098    0.210520


1.64471900
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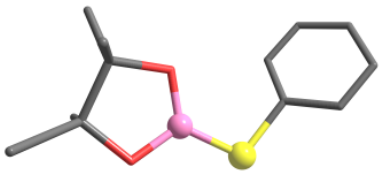
PinBSPh



$\mathcal{E}_0$: -653254.22 kcal·mol^{-1}

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33

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C         1.352024    3.384042    0.792618
C        -1.518035    2.321840   -0.873198
C         0.803077    2.201660   -1.807825
B         0.820078   -0.045083    0.248412
O         1.351887    0.976783    0.981083
O        -0.146098    0.349801   -0.632507
H        -0.025535    2.152359    2.818818
H        -1.187995    3.015671    1.791817
H        -1.162769    1.240029    1.816972
H         0.753189    4.259373    0.527028
H         1.736033    3.523488    1.804345
H         2.198339    3.314940    0.110343
H        -1.534749    3.412195   -0.794057
H        -1.857455    2.043646   -1.872162
H        -2.212807    1.902950   -0.146380
H         0.424009    1.752311   -2.726671
H         0.831914    3.286075   -1.932750
H         1.819818    1.838392   -1.642627
S         1.304610   -1.792005    0.346337
C         2.424082   -1.804535    1.744859
C         3.491491   -0.914368    1.847001
C         2.249790   -2.792720    2.711479
C         4.363999   -1.004032    2.924010
C         3.136307   -2.885887    3.778717
C         4.192881   -1.990305    3.890278
H         3.626712   -0.148688    1.094685
H         1.418635   -3.482439    2.627151
H         5.187046   -0.303697    3.002843
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H         4.880425   -2.060170    4.724422
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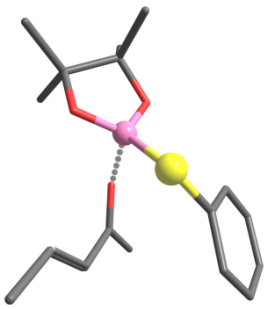
TS1 (S)



$\mathcal{E}_0$: -823000.00 kcal·mol^{-1}
Imaginary frequency: -111.85 cm^{-1}

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 C       -0.814529   -3.091040    6.344308
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 C        0.456043   -3.573170    6.627291
 O       -4.099730   -1.231623    3.768835
 O       -2.527426   -0.617318    5.335536
 C       -3.395022    0.512656    5.146099
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 H        0.800428   -3.446441    2.023237
 H        0.877169   -2.187974    3.305870
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 H        1.189210   -2.910434    7.072551
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 H       -5.031790   -0.409895    6.231005
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 H       -3.525966    0.189372    1.673095
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H	-1.730074	1.737039	4.503466
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H	-3.184939	2.656151	4.951310
H	-5.800250	0.504330	2.567496
H	-6.128168	0.325202	4.296166
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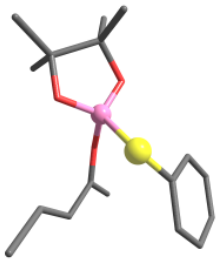
I1 (S)



$\mathcal{E}_0$: -823000.22 kcal·mol^{-1}

47

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C	0.485456	-3.601244	6.619100
O	-3.962003	-1.199055	3.645114
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H	0.661814	-3.905172	3.741241
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H	0.017423	-6.799526	5.593692
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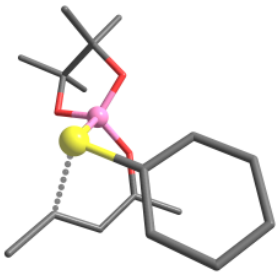
TS2 1_4 (S)



$\mathcal{E}_0$: -822997.82 kcal·mol^{-1}
Imaginary frequency: -178.76 cm^{-1}

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H	-1.046278	1.484531	7.120851

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H	-1.012437	-6.425632	5.723549
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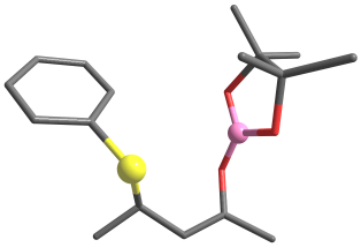
I2 1_4 (S)



$\mathcal{E}_0$: -823025.19 kcal·mol^{-1}

47

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C	-3.417992	-2.863787	6.680583
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C	-5.477864	-1.812226	7.365630
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C	-3.176150	2.215488	6.511155
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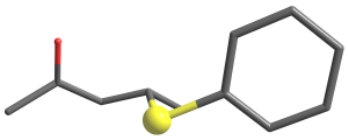
C	-0.843897	0.508167	6.609820
H	-3.613807	-2.858499	3.927925
H	-3.687577	-5.170711	4.880265
H	-0.087302	-0.496894	1.928880
H	-0.082829	-2.066540	1.092448
H	-1.275437	-0.818957	0.658488
H	-1.040967	-3.789324	2.580105
H	-3.480831	-5.226479	3.120654
H	-2.091244	-5.510232	4.190517
H	-2.879986	-4.651754	7.734035
H	-4.192921	-1.052626	5.811837
H	-4.879659	-4.598738	9.204594
H	-6.202743	-1.013871	7.257583
H	-2.114887	3.978502	4.680961
H	-3.615624	3.289637	4.029530
H	-2.060281	2.862458	3.301643
H	-3.269470	1.326136	7.134123
H	-2.618410	2.977786	7.061719
H	-4.176898	2.601565	6.308969
H	0.049279	2.864700	4.247312
H	-0.042542	3.138468	6.000097
H	1.039885	1.897662	5.348167
H	-0.810223	1.148538	7.494146
H	-1.649715	-0.218647	6.725733
H	0.094856	-0.042801	6.534310
H	-6.543914	-2.781125	8.961721

P 1_4 (S)



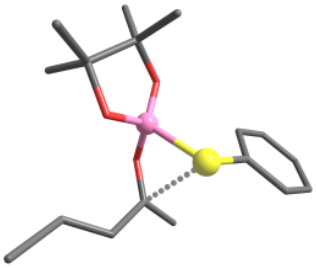
$\mathcal{E}_0$: -56533.74 kcal·mol^{-1}

27

C	-0.920018	3.555599	1.124137
C	-1.301809	2.190085	1.676104
H	-0.651071	1.447694	1.212739
O	1.324276	2.782851	0.878178
C	0.587096	3.729809	0.981149
S	-0.873057	2.181365	3.469380
C	-0.436463	0.461942	3.666374
C	-1.205758	-0.364294	4.482441
C	0.693845	-0.046329	3.023000
C	-0.844746	-1.697183	4.656691
H	-2.082762	0.040667	4.973015
C	1.037718	-1.381582	3.188046

H	1.289268	0.611087	2.397389
C	0.272800	-2.207757	4.007930
H	-1.444265	-2.336665	5.293892
H	1.913082	-1.775729	2.685604
H	0.549353	-3.246845	4.140332
H	-1.344149	3.680696	0.118555
C	-2.764773	1.836540	1.453736
H	-2.987133	1.787977	0.383484
H	-2.991945	0.864846	1.895981
H	-3.419234	2.581492	1.912183
C	1.095484	5.149955	0.958954
H	1.025006	5.555549	1.972777
H	2.132754	5.170084	0.631408
H	0.474923	5.776212	0.313704
H	-1.336799	4.366722	1.731091

TS2 1_2 (S)



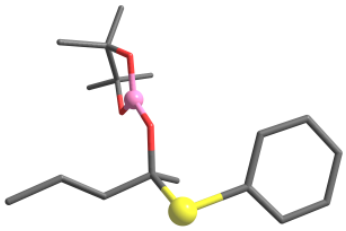
$\mathcal{E}_0$: -822989.50 kcal·mol^{-1}
Imaginary frequency: -253.4 cm^{-1}

47

B	0.770831	1.052828	0.020891
S	-0.357520	-0.033460	-1.282733
C	3.150698	-1.213542	0.049481
O	0.854801	0.011968	1.165589
C	0.819080	-1.202501	0.732922
C	1.939557	-1.787356	0.021573
C	-0.229559	-2.100384	1.289989
C	-2.377026	0.627798	0.536936
C	-1.969590	-0.151810	-0.550673
C	-2.851526	-1.105346	-1.074013
C	4.360580	-1.760631	-0.622319
C	-4.507004	-0.520261	0.579113
C	-4.107572	-1.287477	-0.511760
C	-3.638488	0.435313	1.093083
O	1.977571	1.323789	-0.672764
O	0.241624	2.251288	0.533072
C	0.937543	3.329870	-0.102512
C	2.331695	2.684982	-0.383657
H	1.770892	-2.736578	-0.474736
H	-1.149501	-1.548522	1.478492
H	-0.412451	-2.951416	0.634829
H	0.154260	-2.474077	2.247335

H	-2.542092	-1.703253	-1.924095
H	4.718335	-1.033930	-1.358492
H	5.170388	-1.906227	0.097598
H	3.256669	-0.278642	0.588423
H	-1.711262	1.380403	0.938277
H	-4.777557	-2.030834	-0.928314
H	4.157927	-2.703775	-1.129699
H	-3.941101	1.044813	1.936999
H	-5.487014	-0.662864	1.018415
C	0.194228	3.691465	-1.387926
H	-0.844455	3.914797	-1.136557
H	0.633729	4.566653	-1.872361
H	0.201172	2.853222	-2.087356
C	0.968131	4.516277	0.847204
H	1.605613	5.311787	0.451116
H	-0.041656	4.913554	0.965716
H	1.336080	4.219830	1.829094
C	3.071288	3.265750	-1.576713
H	3.251536	4.335293	-1.435602
H	4.037134	2.768286	-1.688252
H	2.503715	3.118767	-2.494911
C	3.227260	2.687380	0.856121
H	4.104985	2.067929	0.655794
H	3.571438	3.693239	1.106988
H	2.693611	2.271607	1.714395

I2 1_2 (S)



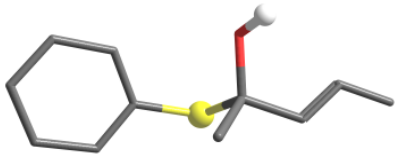
$\mathcal{E}_0$: -823018.68 kcal·mol^{-1}

47

C	-2.342097	2.717692	0.257140
C	-3.608127	2.946751	0.584308
C	-4.777126	2.199294	0.020988
H	-3.825242	3.723744	1.314957
H	-5.464748	2.879781	-0.489287
C	-0.071759	3.687351	-0.206902
H	-0.480107	4.252640	-1.045073
H	0.755940	4.244137	0.235245
H	0.302185	2.726933	-0.564354
O	-1.560869	4.693631	1.426198
C	-2.623908	7.145940	-0.952050
C	-3.288988	7.606353	0.386480
C	-1.166781	3.467538	0.831647
S	-0.571284	2.376308	2.210754
C	0.959647	3.185197	2.641962
C	0.943177	4.425045	3.283337

C	2.176604	2.569338	2.351908
C	2.141102	5.048250	3.612241
H	-0.008671	4.889666	3.507400
C	3.371714	3.190144	2.699460
H	2.179324	1.607670	1.852576
C	3.355368	4.431944	3.324391
H	2.125335	6.012981	4.105503
H	4.314766	2.705292	2.476523
B	-2.094055	5.724296	0.723459
O	-2.240147	5.787741	-0.642087
O	-2.555841	6.844673	1.367124
C	-3.550802	7.134324	-2.154345
H	-3.952753	8.134674	-2.336556
H	-2.995639	6.820250	-3.039959
H	-4.377609	6.440866	-2.005519
C	-4.750477	7.176682	0.487838
H	-5.085692	7.323967	1.515499
H	-5.388177	7.762027	-0.178017
H	-4.860019	6.118092	0.238520
C	-1.343443	7.914964	-1.264594
H	-0.821288	7.410355	-2.079209
H	-1.559379	8.940938	-1.570004
H	-0.682894	7.939651	-0.394935
C	-3.142114	9.085344	0.695538
H	-3.606712	9.688649	-0.089080
H	-3.638627	9.308583	1.641289
H	-2.093567	9.366578	0.784904
H	4.286554	4.917699	3.590753
H	-2.086330	1.930487	-0.447592
H	-4.454942	1.438034	-0.690871
H	-5.343245	1.709937	0.818063

P 1_2 (S)



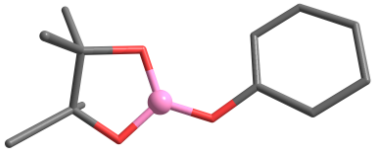
$\mathcal{E}_0$: -565318.76 kcal·mol^{-1}

27

C	-2.464297	2.477089	0.234403
C	-3.748912	2.664665	0.514614
C	-4.858722	1.777661	0.040747
H	-5.597849	2.345783	-0.530411
C	-0.348468	3.659996	-0.380068
H	-0.855599	4.166419	-1.207971
H	0.450367	4.303313	-0.009620
H	0.084331	2.732775	-0.758277
O	-1.857063	4.594113	1.255884
C	-1.360170	3.379925	0.726563
S	-0.597870	2.459924	2.136115
C	0.863652	3.442942	2.426888
C	0.755100	4.725301	2.968145

C	2.120332	2.919971	2.124828
C	1.900619	5.481303	3.185814
H	-0.227047	5.117000	3.199492
C	3.263992	3.675513	2.360820
H	2.194654	1.924527	1.703163
C	3.155053	4.958120	2.886264
H	1.813499	6.478414	3.601272
H	4.238909	3.263469	2.128641
H	4.046033	5.547636	3.067068
H	-2.146346	1.630156	-0.369591
H	-4.482054	0.969862	-0.588240
H	-5.384726	1.335335	0.891152
H	-4.017306	3.509046	1.144437
H	-2.197955	5.107209	0.514442

PinBOPh



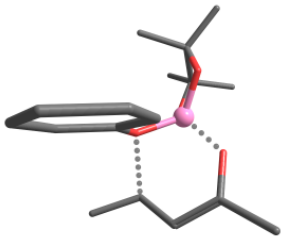
$\mathcal{E}_0$: -450606.03 kcal·mol^{-1}

33

C	0.492267	2.246680	0.627284
C	-0.082256	1.606975	-0.680275
C	-0.553630	2.373006	1.730820
C	1.222257	3.561988	0.426854
C	-1.532407	1.950121	-0.971575
C	0.790632	1.879801	-1.902075
B	1.008234	0.051410	0.533753
O	1.440342	1.242501	1.061339
O	0.016356	0.195737	-0.397101
C	2.370106	-1.486959	1.849359
C	3.385950	-0.623392	2.247743
C	2.247951	-2.748140	2.424404
C	4.270542	-1.034318	3.239817
C	3.138404	-3.145126	3.411661
C	4.153815	-2.288860	3.826246
H	-0.046268	2.616075	2.665489
H	-1.276602	3.160194	1.507386
H	-1.090457	1.431533	1.866101
H	0.544637	4.312305	0.010879
H	1.588933	3.925624	1.388220
H	2.072525	3.444160	-0.243548
H	-1.652901	3.029031	-1.101836
H	-1.842246	1.455264	-1.893411
H	-2.186549	1.614562	-0.167753
H	0.458738	1.234588	-2.716631
H	0.715758	2.920555	-2.224138
H	1.837948	1.652319	-1.690475
H	3.472859	0.354720	1.795265
H	1.450920	-3.396075	2.081980
H	5.060790	-0.362137	3.552646

H	3.037394	-4.127398	3.857866
O	1.467807	-1.184151	0.860750
H	4.848318	-2.598282	4.597302

TS2 1_4 (O)



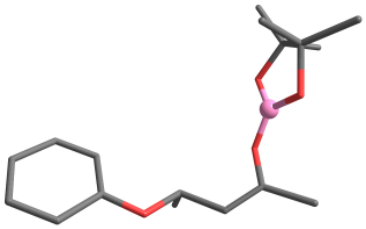
$\mathcal{E}_0$: -620337.32 kcal·mol^{-1}
Imaginary frequency: -324.39 cm^{-1}

47

B	-1.821022	-0.593253	3.906081
C	-1.443138	-2.279032	2.034544
O	-1.294029	-1.105958	2.554397
C	-2.427724	-3.155141	2.448675
C	-3.389917	-2.678949	3.350528
C	-4.272861	-3.612069	4.102091
H	-3.785327	-1.679034	3.197912
H	-4.723858	-3.111151	4.957719
O	-2.959326	0.249778	3.757806
O	-0.775663	0.129821	4.528246
C	-2.550139	1.573342	4.118207
C	-1.376816	1.290509	5.109507
C	-3.731927	2.309659	4.727253
C	-2.072163	2.284719	2.852170
C	-0.331943	2.390983	5.193062
C	-1.878789	0.923200	6.507315
H	-2.265119	1.795009	7.040862
H	-0.783841	3.331757	5.520297
H	0.148813	2.543119	4.227013
H	0.435571	2.108151	5.916277
H	-1.044722	0.503655	7.073280
H	-2.664162	0.166763	6.444093
H	-4.176032	1.731969	5.537611
H	-3.422369	3.285131	5.113118
H	-1.815497	3.328788	3.047942
H	-4.494883	2.469992	3.962508
H	-2.875449	2.253527	2.113576
H	-1.201328	1.774191	2.435516
C	-0.416848	-2.640016	1.008476
H	-0.588144	-3.632897	0.596939
H	-0.452935	-1.899969	0.205998
H	0.578118	-2.587232	1.455880
C	-1.365147	-2.652724	5.303793
C	-0.038938	-2.746139	4.880225
C	-1.822405	-3.456440	6.349335
C	-0.962775	-4.358346	6.960069
C	0.359335	-4.462618	6.537486
C	0.813609	-3.648732	5.506797

H	0.330710	-2.081458	4.110987
H	-2.847587	-3.342829	6.680367
H	-1.323732	-4.974521	7.774992
H	1.846367	-3.709810	5.184312
H	1.031803	-5.163682	7.016186
H	-2.339541	-4.210345	2.226039
H	-5.079504	-3.927594	3.431578
H	-3.728957	-4.499274	4.429440
O	-2.272382	-1.819539	4.717395

I2 1_4 (O)



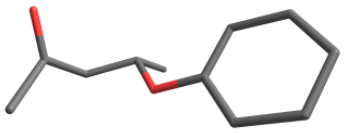
$\mathcal{E}_0$: -620352.24 kcal·mol^{-1}

47

C	-1.310750	-1.775377	3.369922
O	-2.142213	-0.666886	3.326857
C	-1.756693	-2.872668	3.969568
C	-3.101790	-2.961516	4.627596
C	-4.182913	-3.374762	3.631958
H	-3.344159	-1.990455	5.069128
H	-5.146574	-3.520134	4.123500
C	-0.012299	-1.637104	2.641444
H	0.604014	-0.865213	3.105687
H	0.528761	-2.582156	2.648964
H	-0.200316	-1.343945	1.604905
H	-1.153874	-3.772671	3.960259
H	-4.284969	-2.601771	2.868281
H	-3.893828	-4.311135	3.150860
O	-2.972197	-3.936987	5.664858
C	-3.893668	-3.967756	6.661933
C	-3.732079	-4.990669	7.601620
C	-4.946441	-3.063226	6.807647
C	-4.605655	-5.102539	8.669755
H	-2.908359	-5.680382	7.466411
C	-5.816389	-3.188392	7.888847
H	-5.106274	-2.267538	6.093399
C	-5.657374	-4.200539	8.823105
H	-4.465195	-5.900075	9.389991
H	-6.629765	-2.479402	7.990233
H	-6.340892	-4.289844	9.657830
B	-1.781853	0.546635	3.821762
O	-2.672895	1.582028	3.881757
O	-0.538901	0.861293	4.311094
C	-1.913729	2.757102	4.240035
C	-0.674600	2.141079	4.972737
C	-1.538768	3.460369	2.938547

C	-2.778203	3.658285	5.103491
C	0.616285	2.922213	4.808304
C	-0.945200	1.849783	6.445740
H	-1.014570	4.399361	3.127736
H	-2.453316	3.674583	2.383800
H	-0.903887	2.822779	2.319078
H	-3.176495	3.119349	5.962052
H	-2.200408	4.516014	5.458114
H	-3.616965	4.028639	4.511911
H	0.905480	2.992892	3.760374
H	0.505057	3.931209	5.214194
H	1.417495	2.419459	5.352682
H	-0.993054	2.769600	7.032183
H	-1.884731	1.306407	6.568951
H	-0.136938	1.227695	6.832606

P 1_4 (O)

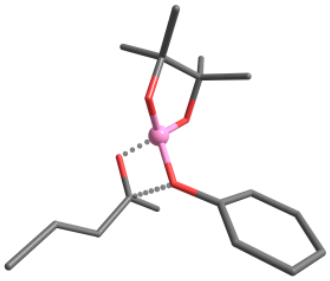


$\mathcal{E}_0$: -362665.40 kcal·mol^{-1}

27

C	-1.068976	3.476727	0.961800
C	-1.124582	1.967674	1.166164
H	-0.321713	1.525481	0.566923
O	1.249468	3.667832	0.522870
C	0.344257	3.965833	1.259219
O	-0.841728	1.779197	2.555207
C	-0.504506	0.540010	3.013287
C	-0.445137	0.409326	4.402258
C	-0.209177	-0.554803	2.202449
C	-0.090551	-0.801435	4.973152
H	-0.683492	1.274776	5.008364
C	0.144748	-1.766736	2.791580
H	-0.245346	-0.480054	1.124233
C	0.206403	-1.901191	4.170609
H	-0.047347	-0.888573	6.052418
H	0.375055	-2.611900	2.153625
H	0.481642	-2.848019	4.617379
H	-1.297102	3.704256	-0.081888
C	-2.479171	1.379717	0.804386
H	-2.679117	1.520062	-0.259719
H	-2.520433	0.312526	1.026558
H	-3.262357	1.879888	1.378184
C	0.542301	4.770531	2.516494
H	0.196653	4.170194	3.362720
H	1.592435	5.029213	2.634403
H	-0.070079	5.675785	2.484982
H	-1.809695	3.953896	1.608264

TS2 1_2 (O)



$\mathcal{E}_0$: -620332.65 kcal·mol^{-1}
Imaginary frequency: -235.6 cm^{-1}

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47

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 O         0.366702   -0.131554   -0.189477
 C         2.983216   -2.286451   -0.178976
 O         2.197780    0.096689    0.997474
 C         1.431491   -0.949580    1.135602
 C         1.878660   -2.226338    0.566438
 C         0.459692   -0.996710    2.273542
 C        -1.898321    0.477865    0.395714
 C        -0.975886   -0.177774   -0.420820
 C        -1.412493   -0.965435   -1.485376
 C         3.535885   -3.530501   -0.787090
 C        -3.698299   -0.435147   -0.935835
 C        -2.771157   -1.092797   -1.739298
 C        -3.256150    0.347451    0.125293
 O         1.847920    1.741861   -0.827105
 O         0.627896    2.008320    1.112129
 C         0.720373    3.295772    0.487540
 C         1.964217    3.114063   -0.442641
 H         1.284162   -3.107980    0.785360
 H         0.980072   -1.451010    3.122896
 H         0.153024    0.013232    2.541903
 H        -0.406920   -1.613187    2.026541
 H        -0.667445   -1.456473   -2.099426
 H         3.595780   -3.421699   -1.873631
 H         4.555494   -3.704980   -0.432605
 H         3.515962   -1.354181   -0.351440
 H        -1.538856    1.094845    1.207978
 H        -3.106203   -1.702526   -2.570046
 H         2.926869   -4.403909   -0.552542
 H        -3.973676    0.862752    0.752987
 H        -4.758169   -0.531423   -1.137060
 C        -0.560126    3.544749   -0.309228
 H        -1.418208    3.467454    0.361959
 H        -0.562985    4.540901   -0.758170
 H        -0.678041    2.800199   -1.100086
 C         0.883985    4.355272    1.565664
 H         1.071141    5.336210    1.119490
 H        -0.031557    4.417486    2.157763
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H	1.707092	4.105123	2.234011
C	1.958416	3.980124	-1.691214
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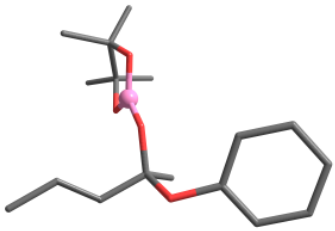
H	2.866965	3.790529	-2.266000
H	1.100760	3.747007	-2.321416
C	3.280854	3.282561	0.317524
H	4.093975	2.933519	-0.321456
H	3.465946	4.326320	0.582338
H	3.279127	2.678592	1.227818

I2 1_2 (O)



$\mathcal{E}_0$: -620352.84 kcal·mol^{-1}

47

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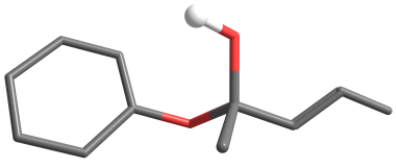
C	-3.436695	2.799043	0.560854
C	-4.501308	1.842560	0.118101
H	-3.775237	3.725081	1.018635
H	-5.152899	2.305190	-0.628305
C	-0.080420	3.831886	-0.261927
H	-0.630634	4.239524	-1.108066
H	0.670335	4.553027	0.068082
H	0.424972	2.912792	-0.563499
O	-1.565975	4.713871	1.441090
C	-2.743080	7.091632	-0.949958
C	-3.226006	7.672770	0.418862
C	-1.044716	3.522057	0.879844
O	-0.382918	2.832303	1.929436
C	0.789792	3.369636	2.414428
C	0.795466	4.533761	3.179428
C	1.973743	2.681616	2.169614
C	2.001291	5.010422	3.681864
H	-0.139282	5.041075	3.373714
C	3.172146	3.161641	2.684656
H	1.933253	1.770255	1.585034
C	3.190661	4.332030	3.435898
H	2.007400	5.915353	4.278175
H	4.092350	2.621633	2.495494
B	-2.118260	5.732983	0.743084
O	-2.420432	5.727428	-0.598699
O	-2.447850	6.911301	1.363799
C	-3.791265	7.085465	-2.047525
H	-4.133559	8.103009	-2.254523
H	-3.359144	6.676172	-2.962216
H	-4.648688	6.473098	-1.771170
C	-4.695500	7.367189	0.698246
H	-4.905765	7.595087	1.744143

H	-5.355720	7.965870	0.067169
H	-4.911387	6.309628	0.527369
C	-1.451899	7.741692	-1.440333
H	-1.057862	7.154240	-2.271349
H	-1.623827	8.763383	-1.785341
H	-0.701671	7.761353	-0.646219
C	-2.941089	9.150659	0.618998
H	-3.435485	9.743680	-0.155200
H	-3.324240	9.466066	1.590852
H	-1.871165	9.354261	0.593038
H	4.124856	4.707832	3.835489
H	-1.768752	1.650982	0.010325
H	-4.068758	0.939389	-0.314346
H	-5.133994	1.552546	0.961209

P 1_2 (O)



$\mathcal{E}_0$: -362654.77 kcal·mol^{-1}

27

C	-2.386892	2.438201	0.479280
C	-3.664245	2.783971	0.410485
C	-4.796640	1.811967	0.279303
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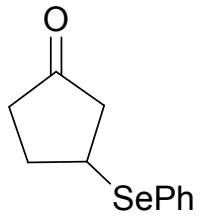
C	-0.458282	3.508902	-0.707149
H	-1.111908	3.880174	-1.496640
H	0.393177	4.186516	-0.595237
H	-0.081157	2.524668	-0.988181
O	-1.761677	4.667644	0.951922
C	-1.251228	3.417029	0.594042
O	-0.419340	2.871659	1.637808
C	0.659232	3.623139	2.029625
C	0.489461	4.702334	2.895548
C	1.934546	3.265032	1.599051
C	1.599732	5.427552	3.315299
H	-0.509208	4.938818	3.240094
C	3.038637	3.991371	2.028834
H	2.040448	2.409958	0.942000
C	2.874354	5.078143	2.882014
H	1.467440	6.261919	3.993904
H	4.029992	3.706641	1.696900
H	3.736585	5.642465	3.215622
H	-2.076731	1.397258	0.447981
H	-4.436102	0.783073	0.239420
H	-5.484369	1.903893	1.124253
H	-3.913918	3.840073	0.461613
H	-1.075734	5.327813	0.811497

13. Characterization of 3-phenylseleno-1-cyclopentanone and 3-phenylseleno-1-cyclohexanone

3-phenylseleno-1-cyclopentanone

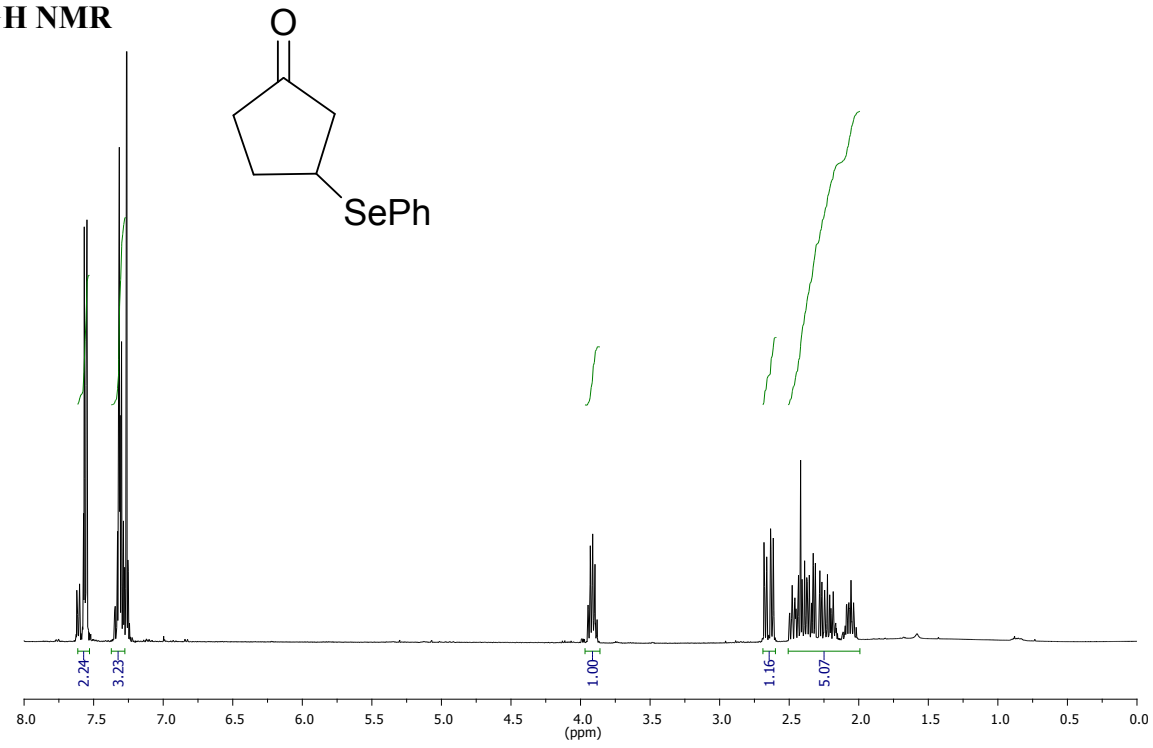


Isolated Yeld: 44%

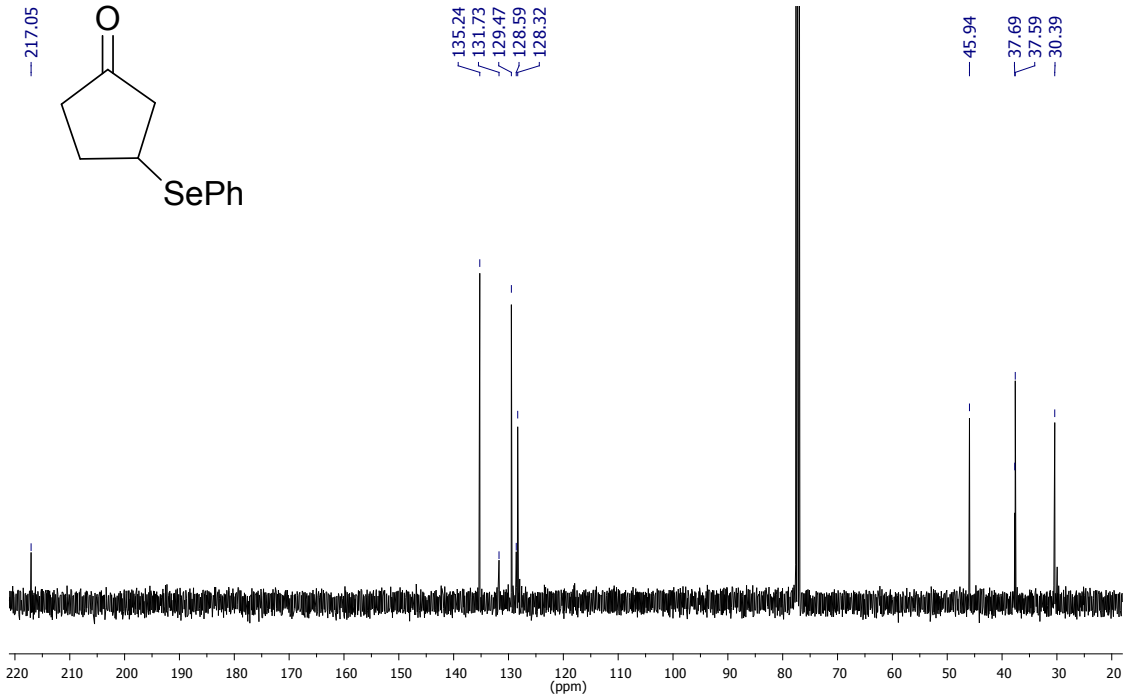
^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.66 – 7.48 (m, 2H), 7.36 – 7.19 (m, 3H), 3.90 (m, 1H), 2.74 – 2.57 (dd, *J*= 18.8, 7.6 Hz, 1H), 2.51 – 2.14 (m, 4H), 2.14 – 1.97 (m, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 217.0, 135.2, 131.7, 129.4, 128.5, 128.3, 45.9, 37.6, 37.5, 30.3.

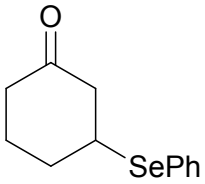
^{1}H NMR



^{13}C NMR


217.05
135.24
131.73
129.47
128.59
128.32
45.94
37.69
37.59
30.39
O
SePh
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
(ppm)

3-phenylseleno-1-cyclohexanone

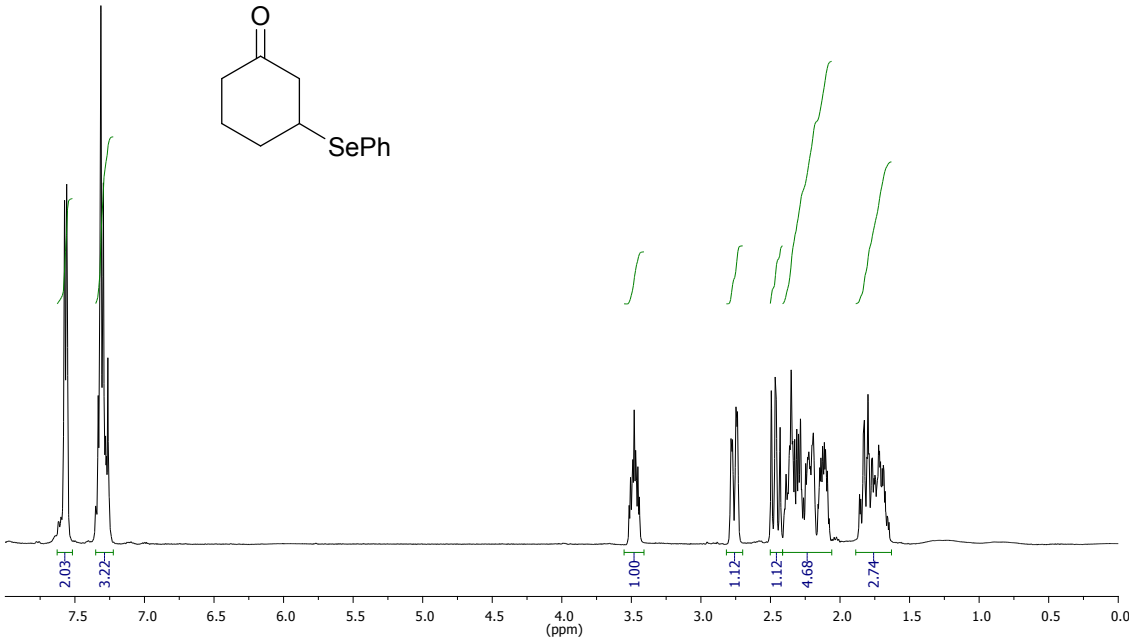


Isolated Yeld: 65%

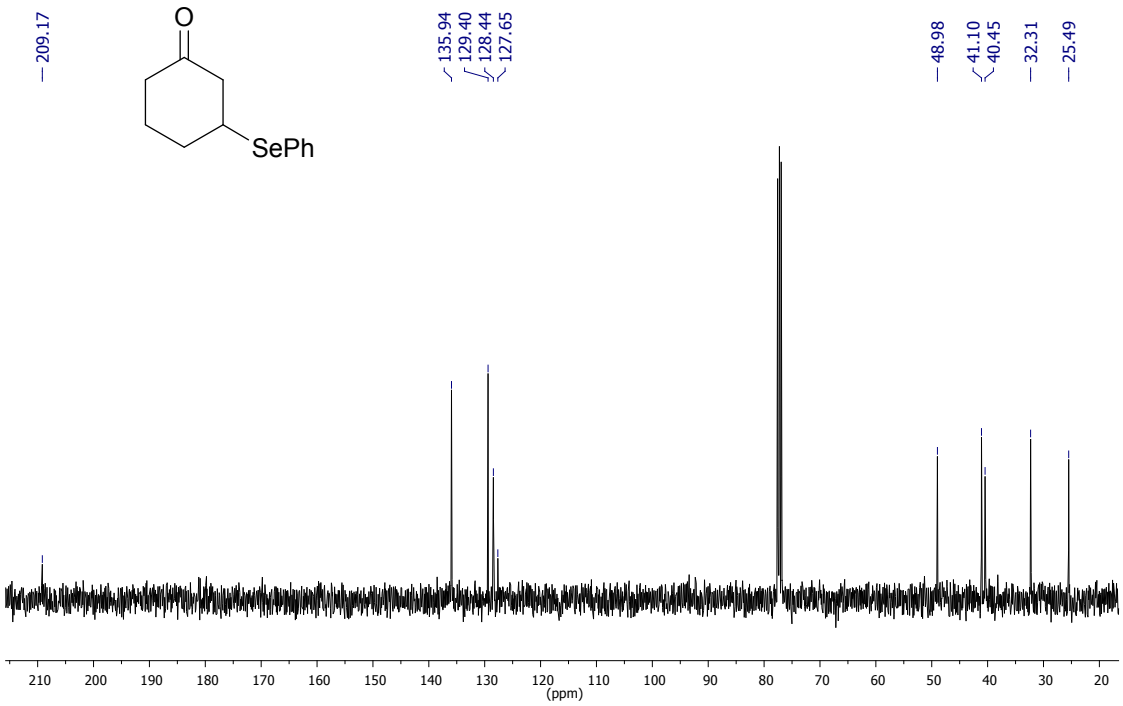
^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.69 – 7.51 (m, 2H), 7.29 (m, 3H), 3.54 – 3.39 (m, 1H), 2.84 – 2.70 (dd, *J* = 14.2, 8.9 Hz, 1H), 2.46 (dd, *J* = 14.2, 11.2 Hz, 1H), 2.41 – 2.05 (m, 4H), 1.90 – 1.61 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 209.1, 135.9, 129.4, 128.4, 127.6, 48.9, 41.1, 40.4, 32.3, 25.4

^{1}H NMR



^{13}C NMR


209.17
135.94
129.40
128.44
127.65
48.98
41.10
40.45
32.31
25.49
O
SePh
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20
(ppm)

14.References

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