Dramatic Effects of Boryl Substituents on Thermal Ring-Closing Reaction of Vinylallenes

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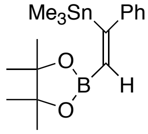
Supporting Information

General. All reactions were carried out under a nitrogen atmosphere. Column chromatography was performed with silica gel 60 N (Kanto). Preparative thin-layer chromatography was performed with silica gel 60 PF_{254} (Merck). ^{1}H and ^{13}C NMR spectra were recorded on a Varian Gemini 2000 (^{1}H at 300.07 Hz and ^{13}C at 75.46 Hz) spectrometer. ^{11}B NMR spectra were recorded on a Varian Mercury 400 (^{11}B at 128.48 Hz). Proton chemical shifts are referenced to residual $CHCl_3$. Carbon chemical shifts are referenced to $CDCl_3$. Boron chemical shifts are referenced to external standard $BF_3{\cdot}OEt_2$. High resolution mass spectra were recorded on a JEOL JMS-SX102A spectrometer.

Materials. Unless otherwise noted, all chemicals and anhydrous solvents were obtained from commercial suppliers and used as received. Bis(diethylamido)(trimethylstannyl)borane[1] and 1-(trimethylsilyl)penta-1,4-diyne[2] were prepared according to the literature procedures.

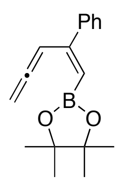
Preparation and Ring-Closing Reaction of Boryl-Substituted Vinylallenes



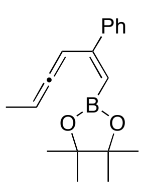
(Z)-1-Phenyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1-(trimethylstannyl)ethene (1): To a benzene solution (10 mL) of $Pd(PPh_3)_4$ (346 mg, 0.30 mmol) were added bis(diethylamido)(trimethylstannyl)borane (3.18 g, 10.0 mmol) and phenylacetylene (1.13 g, 10.0 mmol) at room temperature, and the

(1) Nöth, H.; Schwerthöffer, R. *Chem. Ber.* **1981**, *114*, 3056.
(2) Ashe, A. J., III; Chan, W.-T.; Smith, T. W.; Taba, K. M. *J. Org. Chem.* **1981**, *46*, 881.

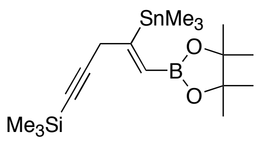
mixture was stirred for 1 h. To the mixture was added pinacol (1.18 g, 10.0 mmol), and the mixture was stirred for 1 h at room temperature. The reaction mixture was passed through a plug of Florisil® (ether) and concentrated. The residue was subjected to column chromatography on silica gel (ether) to afford **1** (3.83 g, 97%). **1a:** ^{1}H NMR δ 0.18 (s, $^{2}J_{Sn-H}$ = 54.9, 53.1 Hz, 9H), 1.30 (s, 12H), 6.28 (s, $^{3}J_{Sn-H}$ = 153.0, 146.4 Hz, 1H), 7.02-7.08 (m, 2H), 7.13–7.21 (m, 1H), 7.24–7.31 (m, 2H); ^{13}C NMR δ –5.5 ($^{1}J_{Sn-C}$ = 353.7, 338.7 Hz), 24.9, 83.5, 126.09 (J = 18.6 Hz), 126.12, 127.8, 133.3 (br), 149.1, 176.0; HRMS (EI) calcd for $C_{16}H_{24}BO_2Sn$ (M^+ – Me) 379.0891, found 379.0891.



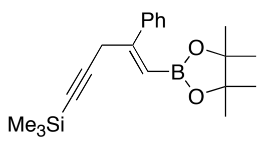
(*E*)-4-Phenyl-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)penta-1,2,4-triene (2a): To a DMF solution (5.5 mL) of $PhCH_2PdCl(PPh_3)_2$ (59.7 mg, 0.078 mmol) and CuI (23.7 mg, 0.12 mmol) were added propargyl bromide (2.65 g, 22.5 mmol) and **1** (1.76 g, 4.5 mmol), and the mixture was stirred for 1 h at room temperature then for 18 h at 35 °C. To the mixture was added saturated KF aqueous solution, and the mixture was extracted with ether, passed through a plug of Florisil® (ether), and concentrated. The residue was subjected to column chromatography on silica gel (hexane:AcOEt = 40:3) to afford **2a** (542 mg, 45%). **2a:** ^{1}H NMR δ 1.34 (s, 12H), 4.84 (dd, J = 6.8, 2.0 Hz, 2H), 5.45-5.47 (m, 1H), 7.16 (t, J = 6.8 Hz, 1H), 7.28-7.40 (m, 5H); ^{13}C NMR δ 24.9, 77.3, 83.2, 94.5, 118.8 (br), 127.5, 127.8, 127.9, 142.1, 156.1, 212.9; ^{11}B NMR δ 29.3; HRMS (EI) calcd for $C_{17}H_{21}O_2B$ 268.1635, found 268.1640.



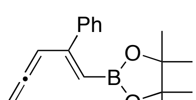
(*E*)-2-Phenyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexa-1,3,4-triene (2b): According to the procedure analogous to that described for **2a**, **2b** (59 mg, 11%) was prepared from **1** (784 mg, 2.0 mmol) and 3-chloro-1-butyne (352 mg, 4.0 mmol). **2b:** ^{1}H NMR δ 1.32 (s, 12H), 1.62 (dd, J = 7.2, 3.3 Hz, 3H), 5.15 (ddq, J = 6.3, 1.4, 7.1 Hz, 1H), 5.42 (dd, J = 1.2, 0.6 Hz, 1H), 7.05 (d sext, J = 0.6, 3.2 Hz, 1H), 7.26-7.36 (m, 5H); ^{13}C NMR δ 13.5, 24.9, 83.1, 87.7, 94.6, 118.4 (br), 127.5, 127.7, 127.9, 142.5, 157.3, 209.8; HRMS (EI) calcd for $C_{18}H_{23}O_2B$ 282.1791, found 282.1793.



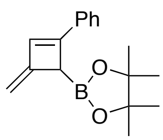
(*Z*)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-5-(trimethylsilyl)-2-(trimethylstannyl)pent-1-en-4-yne (3): According to the procedure analogous to that described for **1**, **3** (2.23 g, 52%) was prepared from bis(diethylamido)(trimethylstannyl)borane (3.19 g, 10 mmol) and 1-(trimethylsilyl)penta-1,4-diyne (1.62 g, 12.0 mmol). **3:** ^{1}H NMR δ 0.15 (s, 9H), 0.20 (s, $^{2}J_{Sn-H}$ = 55.8, 53.4 Hz, 9H), 1.25 (s, 12H), 3.29 (d, J = 1.7 Hz, $^{3}J_{Sn-H}$ = 34.2 Hz, 2H), 6.39 (t, J = 1.7 Hz, $^{3}J_{Sn-H}$ = 149.3 Hz, 1H); ^{13}C NMR δ –6.4 ($^{1}J_{Sn-C}$ = 353.7, 338.6 Hz), 0.1, 24.8, 35.2, 83.3, 88.7, 103.9, 130.9 (br), 169.3; HRMS (EI) calcd for $C_{16}H_{30}BO_2SiSn$ (M^+ – Me) 413.1130, found 413.1129.



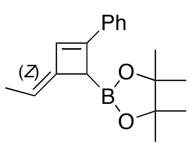
(*Z*)-2-Phenyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-5-(trimethylsilyl)pent-1-en-4-yne (3´): To a DMF solution (2.0 mL) of $PhCH_2PdCl(PPh_3)_2$ (37 mg, 0.050 mmol) and CuI (19 mg, 0.10 mmol) were added iodobenzene (244 mg, 1.2 mmol) and **3** (4.27 g, 1.0 mmol), and the mixture was stirred for 1 h at room temperature and then for 3 h at 90 °C. The reaction mixture was passed through a plug of Florisil® and concentrated. The residue was subjected to column chromatography on silica gel (hexane:AcOEt = 9:1) to afford **3´** (82 mg, 24%). **3´:** ^{1}H NMR δ 0.16 (s, 9H), 1.12 (s, 12H), 3.38 (d, J = 1.7 Hz, 2H), 5.91 (t, J = 1.7 Hz, 1H), 7.22-7.31 (m, 5H); ^{13}C NMR δ 0.1, 24.6, 31.2, 83.1, 88.7, 103.1, 117.6 (br), 127.5, 127.6, 127.7, 141.9, 154.5; HRMS (EI) calcd for $C_{20}H_{29}BO_2Si$ 340.2030, found 340.2030.



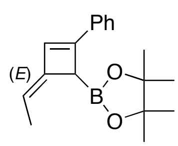
(*Z*)-4-Phenyl-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)penta-1,2,4-triene (4): To a MeOH solution (1.0 mL) of **3´** (47.4 mg, 0.14 mmol) was added MeOH solution (1.0 mL) of NaOH (40 mg, 1.0 mmol), and the mixture was stirred for 24 h at room temperature. To the mixture were added saturated NH_4Cl aqueous solution and brine, and the mixture was extracted with ether, dried over Na_2SO_4, and concentrated. The residue was subjected to flash chromatography on silica gel (hexane:AcOEt = 9:1) followed by HPLC purification (hexane:AcOEt = 20:1) to afford **4** (6 mg, 16%). **4:** ^{1}H NMR δ 1.10 (s, 12H), 4.81 (dd, J = 6.5, 1.4 Hz, 2H), 5.58 (d, J = 0.6 Hz, 1H), 6.11 (dt, J = 0.6, 6.5 Hz, 1H), 7.21-7.30 (m, 5H); ^{13}C NMR δ 24.6, 78.0, 99.2, 127.1, 127.4, 128.9, 139.8, 154.3, 211.8; [11]B NMR δ 29.4.



3-Methylene-1-phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclobutene (5a). A xylene solution (5.0 mL) of **2a** (156 mg, 0.58 mol) was heated for 3 h at 140 °C. After evaporating the solvent, the residue was subjected to flash chromatography on silica gel (hexane:AcOEt = 9:1) to afford **5a** (150 mg, 96%). **5a:** [1]H NMR δ 1.22 (s, 6H), 1.24 (s, 6H), 3.19 (s, 1H), 4.58 (s, 1H), 4.84 (d, J = 1.5 Hz, 1H), 6.61 (s, 1H), 7.22-7.38 (m, 3H), 7.41-7.46 (m, 2H), [13]C NMR δ 24.5, 24.7, 35.7 (br), 83.5, 99.3, 125.6, 126.5, 128.2, 128.3, 133.7, 144.8, 151.6; HRMS (EI) calcd for $C_{17}H_{21}O_2B$ 268.1635, found 268.1636.



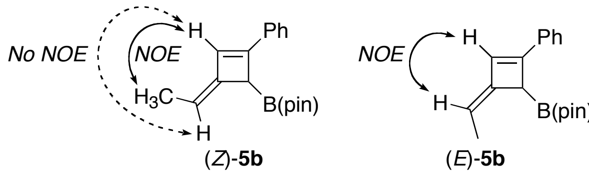
major

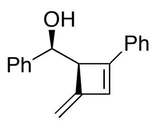


minor

(*Z*)- and (*E*)-3-Etylidene-1-phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclobutene (5b): [1]H NMR δ 1.21 (s, 12H, major and minor), 1.238 (s, 6H, major), 1.243 (s, 6H, minor), 1.72 (d, *J* = 6.9 Hz, 3H, minor), 1.79 (d, *J* = 6.9 Hz, 1H, major), 3.13 (s, 1H, major), 3.18 (s, 1H, minor), 4.96 (q, *J* = 6.9 Hz, 1H, major), 5.30 (dq, *J* = 1.5, 6.9 Hz, 1H, minor), 6.60 (d, *J* = 1.5 Hz, 1H, minor), 6.79 (d, *J* = 1.2 Hz, 1H, major), 7.19-7.45 (m, 5H); [13]C NMR δ 13.8, 14.4, 24.48, 24.54, 24.65, 24.71, 33.8 (br), 83.4, 83.5, 109.9, 110.2, 124.5, 125.2, 125.3, 126.4, 127.8, 127.9, 128.2, 134.2, 136.9, 138.1, 147.7, 149.7 [some signals are overlapping]; HRMS (EI) calcd for $C_{18}H_{23}O_2B$ 282.1791, found 282.1794.

Stereochemical Assignment of 5b. The two isomers, (*Z*)- and (*E*)-**5b**, were subjected to NOE experiments. No NOE between the cyclobutene vinyl proton (δ 6.79) and the ethylidene vinyl proton (δ 4.96) was observed for (*Z*)-**5b**, whereas NOE between the cyclobutene vinyl proton and the ethylidene methyl proton (δ 1.79) was observed. On the other hand, an NOE between the cyclobutene vinyl proton (δ 6.60) and the ethylidene vinyl proton (δ 5.30) was observed for (*E*)-**5b**.





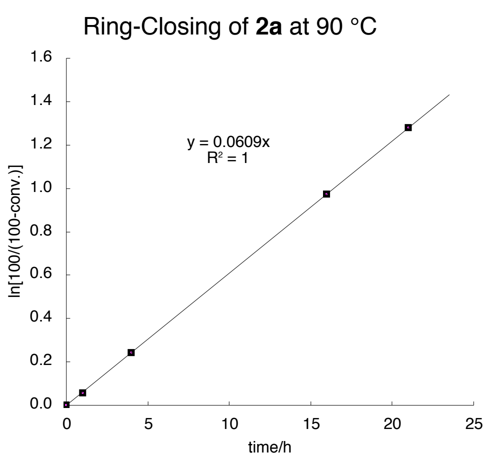
(4-Methylene-2-phenylcyclobut-2-enyl)phenylmethanol (13). A xylene solution (2.0 mL) of vinylallene **2a** (132 mg, 0.49 mmol) was heated for 5 h at 140 °C to afford **5a**. To the solution was added benzaldehyde (72 mg, 0.68 mmol) at room temperature, and the mixture was heated for 48 h at 80 °C. The reaction mixture was acidified with 0.1 N HCl (5 mL), extracted with ether, dried over $MgSO_4$, and concentrated. The residue was subjected to column chromatography on silica gel (hexane:ether = 3:1) to give **13** as a diastereomeric mixture (87 mg, 71%, 17:1 by ^{1}H NMR). **13:** ^{1}H NMR δ 2.10 (d, J = 4.8 Hz, 1H), 4.07 (dt, J = 4.5, 1.2 Hz, 1H), 4.40 (s, 1H), 4.76 (d, J = 1.5 Hz, 1H), 5.15 (t, J = 4.7 Hz, 1H), 6.63 (d, J = 0.6 Hz, 1H), 7.25-7.42 (m, 10H); ^{13}C NMR δ 55.5, 73.1, 99.9, 126.0, 126.1, 127.3, 128.0, 128.4, 128.6, 130.7, 133.0, 142.7, 145.0, 152.2; HRMS (EI) calcd for $C_{18}H_{16}O$ 248.1201, found 248.1200. For the minor diastereomer: ^{1}H NMR δ 4.02 (d, J = 6.9 Hz, 1H), 4.18 (s, 1H), 4.68 (d, J = 1.2 Hz, 1H), 4.95 (d, J = 7.2 Hz, 1H), 6.60 (s, 1H), the remaining signals were not resolved.

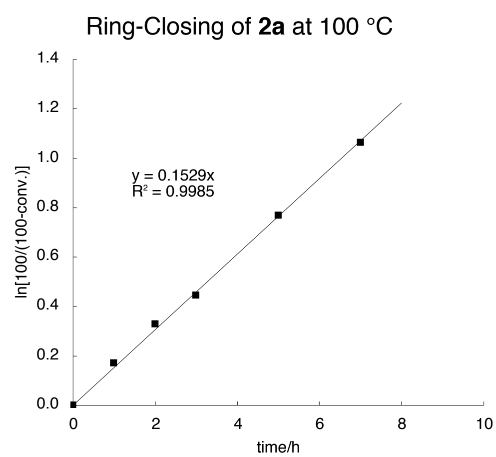
Kinetic Studies on Ring-Closing Reactions of Boryl-Substituted Vinylallenes 2a, 2b, and 4

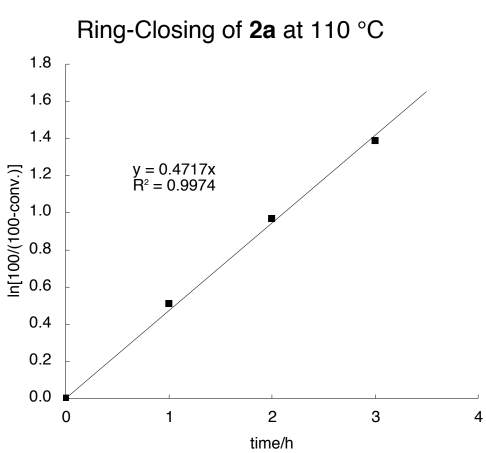
Rate Measurements: The ring-closing reactions of **2a**, **2b**, and **4** were monitored using ^{1}H NMR spectroscopy. The boryl-substituted vinylallene was dissolved in benzene-d_6 or *o*-xylene-d_{10}. The solution in an NMR tube was heated in a temperature-controlled oil bath at the specified temperature. The reaction was intercepted at intervals, and the ^{1}H NMR spectrum was recorded. The conversion was determined on the basis of the ^{1}H NMR integrations of the allenic (vinylic) protons of the reactants and products. The %conversion versus time data were subjected to least-squares analysis.

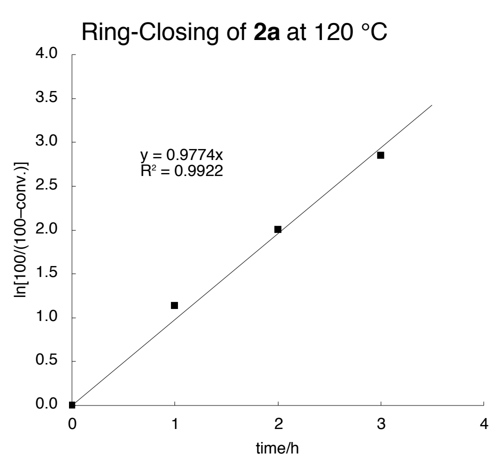
Ring-Closing Reaction of 2a

90 °C		100 °C		110 °C		120 °C	
time/h	conv./%	time/h	conv./%	time/h	conv./%	time/h	conv./%
0	0.0	0	0.0	0	0.0	0	0.0
1	5.5	1	15.8	1	39.9	1	67.9
4	21.4	2	28.1	2	62.0	2	86.5
16	62.2	3	35.9	3	75.0	3	94.2
21	72.2	5	53.6				
		7	65.5				

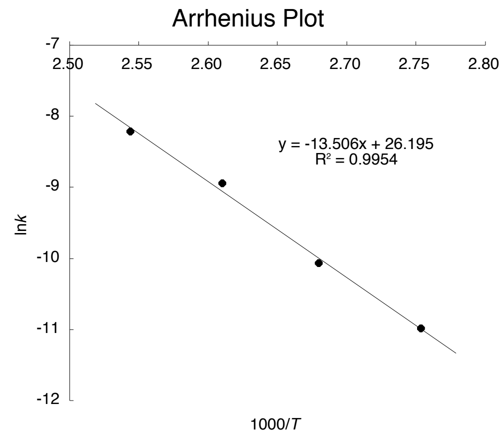








T (°C)	k (s^{-1})	1000/T (K^{-1})	ln$k$
90	1.69×10^{-5}	2.75	–11.0
100	4.25×10^{-5}	2.68	–10.1
110	1.31×10^{-4}	2.61	–8.94
120	2.72×10^{-4}	2.54	–8.21

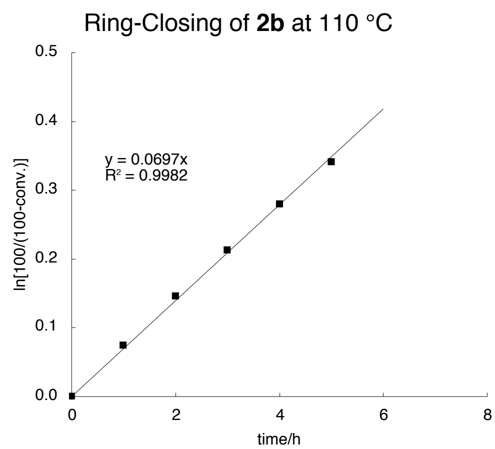


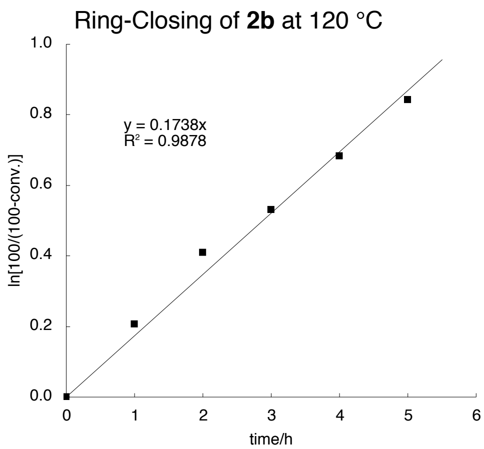
ln$A$ = 26.2; $A = 10^{11.4}$ s^{-1}

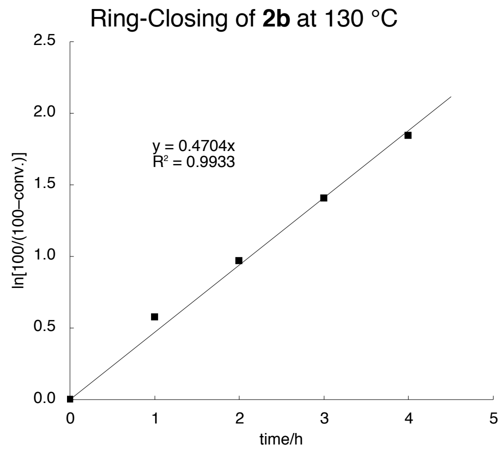
E_a = 1000R×13.5 = 26.8 kcal/mol

Ring-Closing Reaction of 2b

110 °C		120 °C		130 °C	
time/h	conv./%	time/h	conv./%	time/h	conv./%
0	0.0	0	0.0	0	0.0
1	7.2	1	18.6	1	42.9
2	13.6	2	33.6	2	62.0
3	19.2	3	41.2	3	75.5
4	24.4	4	49.5	4	84.2
5	28.9	5	56.9		



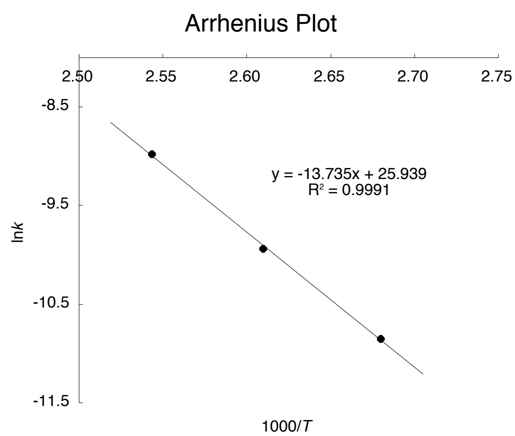




T (°C)	k (s^{-1})	1000/T (K^{-1})	ln$k$
110	1.94×10^{-5}	2.61	–10.9
120	4.83×10^{-5}	2.54	–9.94
130	1.31×10^{-4}	2.48	–8.94

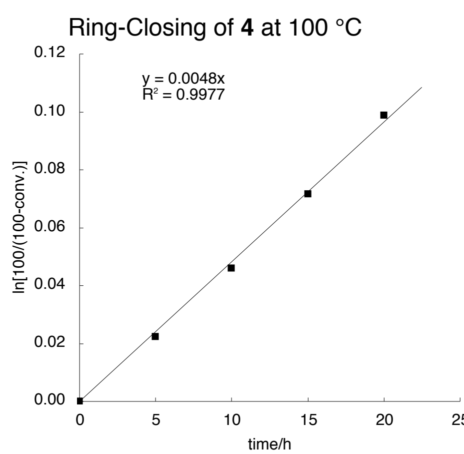
$\ln A = 27.6$; $A = 10^{12.0}\ s^{-1}$

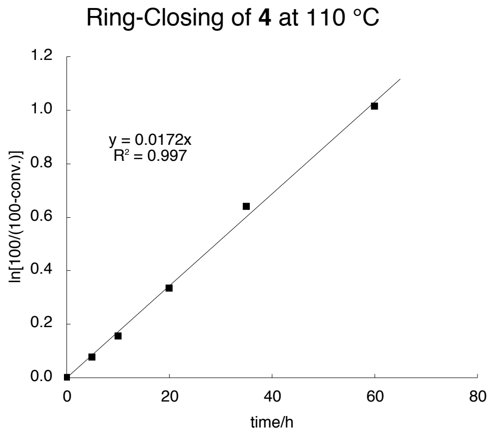
$E_a = 1000R\times14.7 = 29.3$ kcal/mol

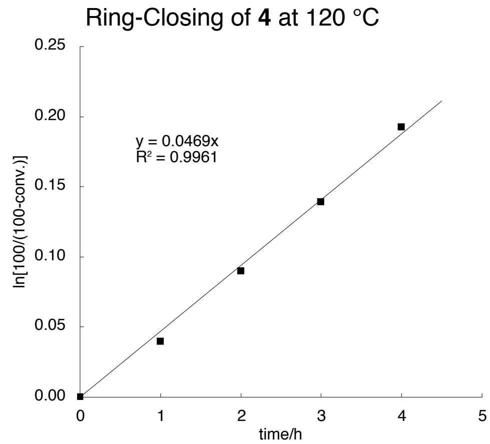


Ring-Closing Reaction of 4

100 °C		110 °C		120 °C	
time/h	conv./%	time/h	conv./%	time/h	conv./%
0	0.0	0	0.0	0	0.0
5	2.2	5	7.4	1	3.9
10	4.5	10	14.4	2	8.6
15	6.9	20	28.4	3	13.0
20	9.4	35	47.3	4	17.5
		60	63.7	5	22.1



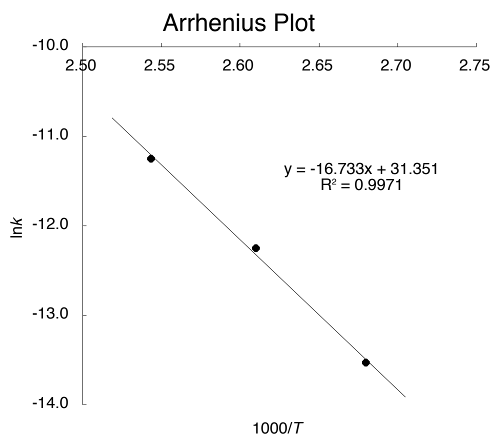




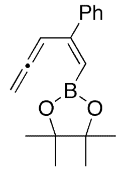
T (°C)	k (s^{-1})	$1000/T$ (K^{-1})	ln$k$
100	1.33×10^{-6}	2.68	–13.5
110	4.78×10^{-6}	2.61	–12.3
120	1.30×10^{-5}	2.54	–11.2

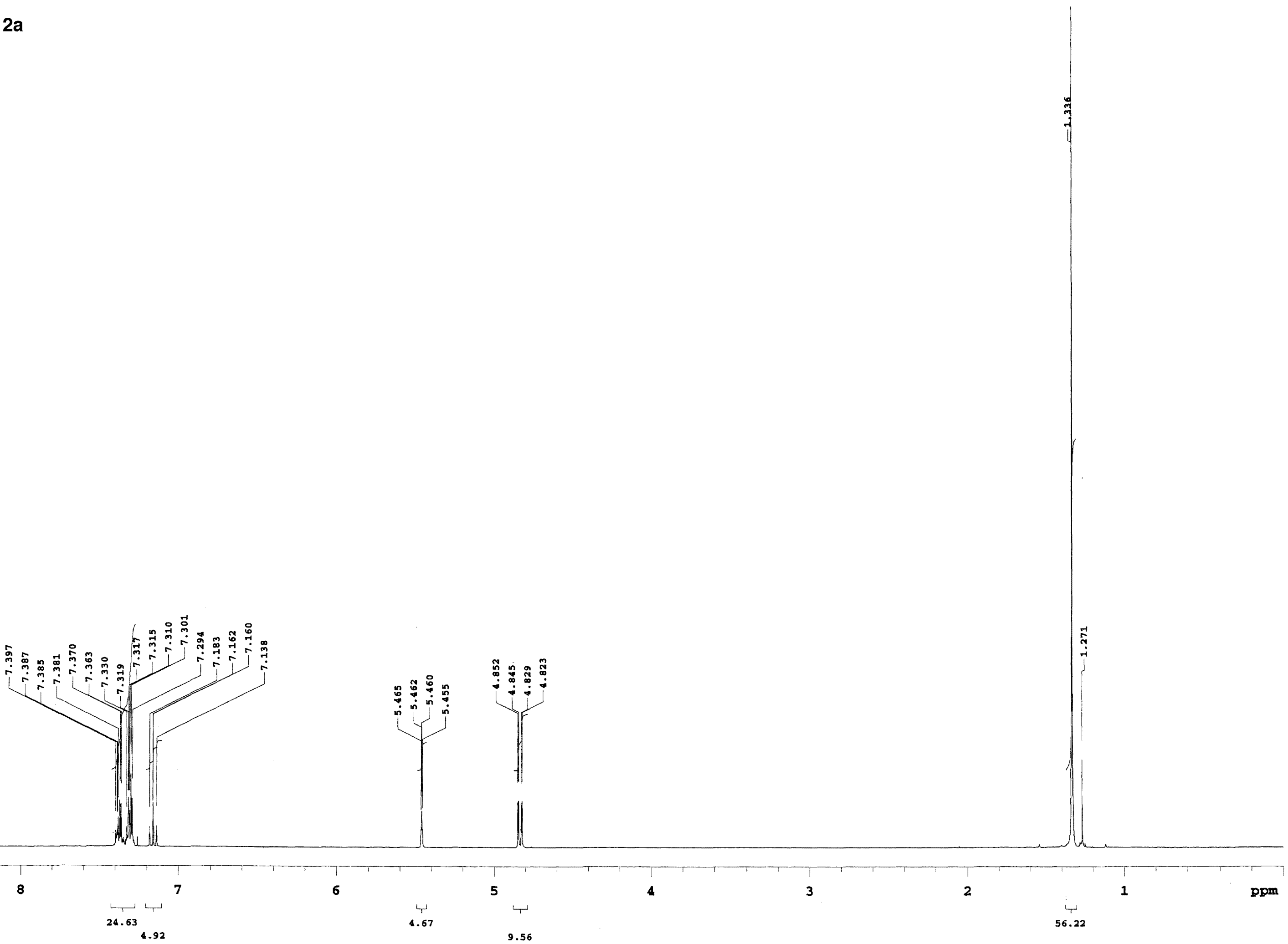
$\ln A = 31.4$; $A = 10^{13.6}$ s^{-1}

$E_a = 1000R\times16.7 = 33.2$ kcal/mol

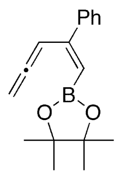


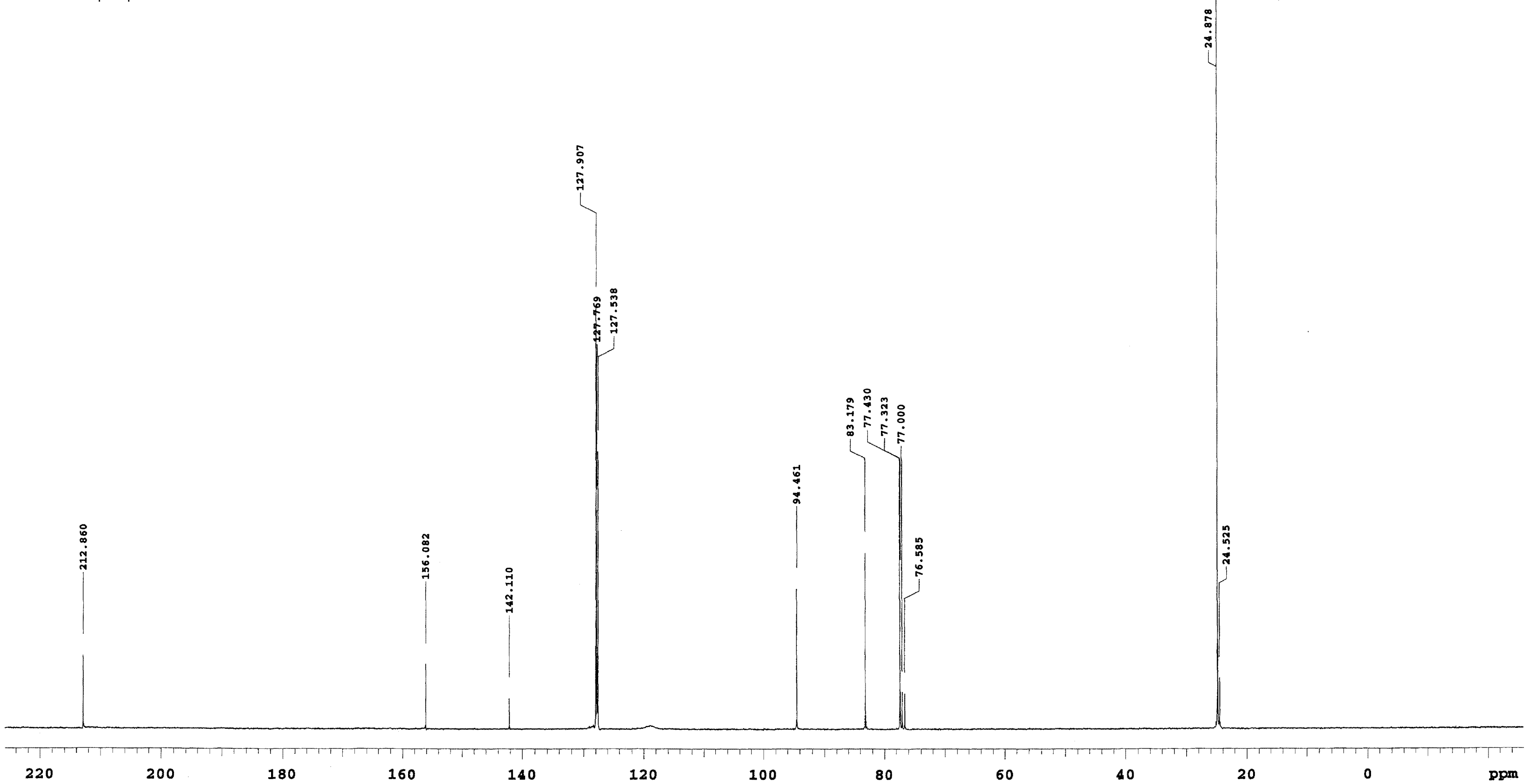
^{1}H spectrum of **2a**



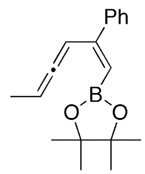


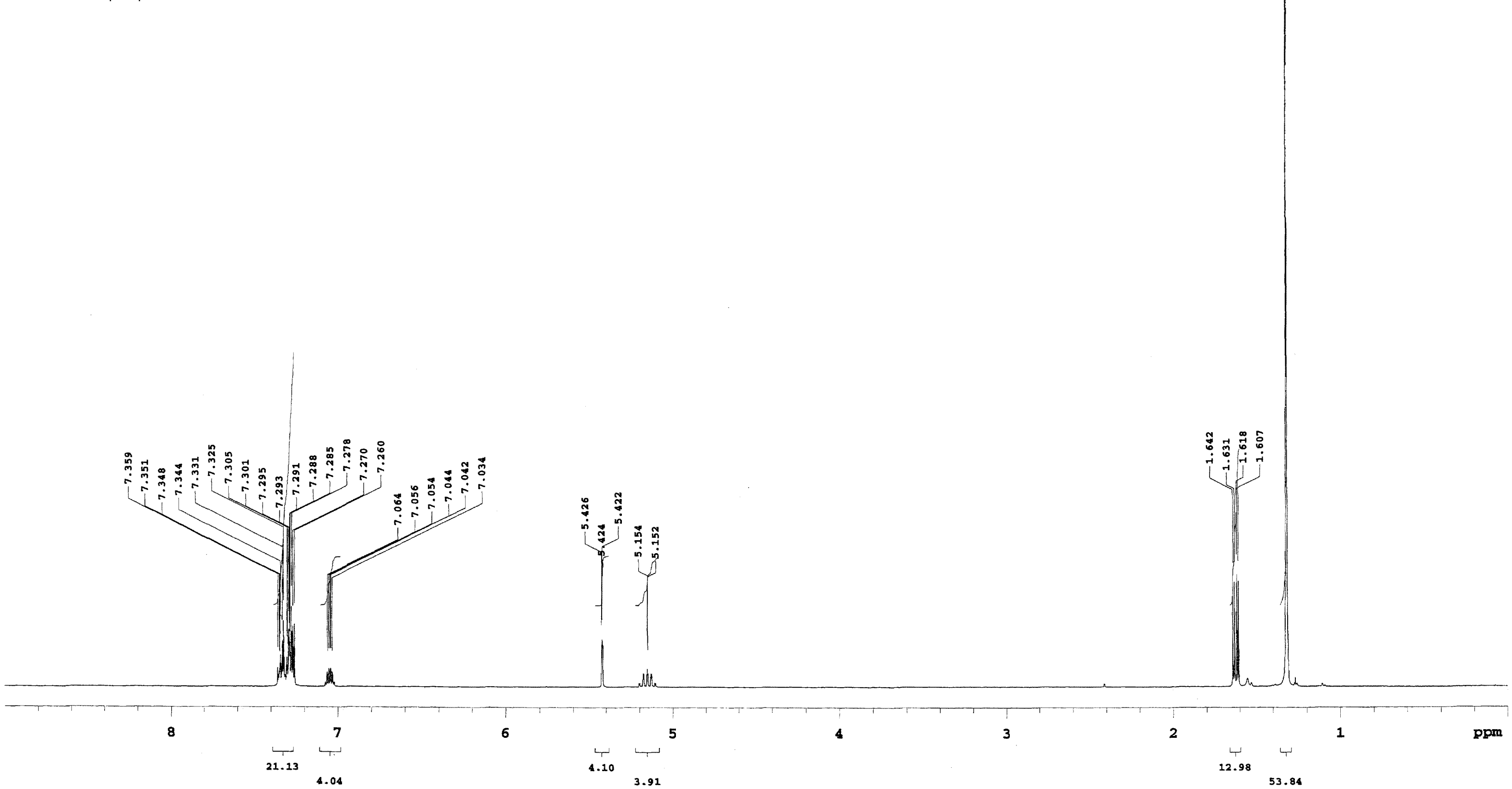
^{13}C spectrum of **2a**



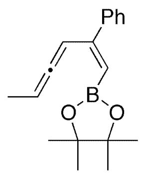


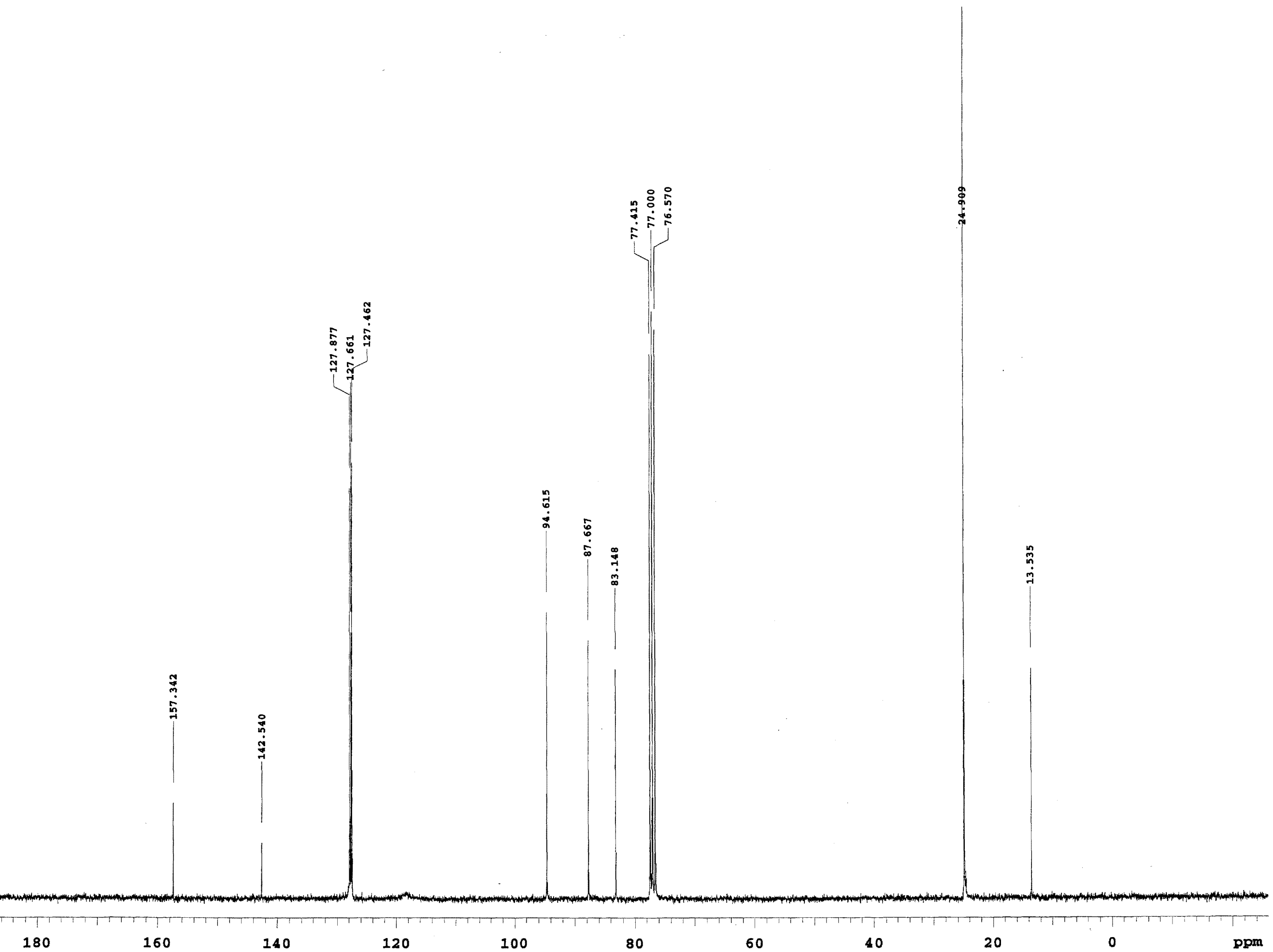
[1]H spectrum of **2b**



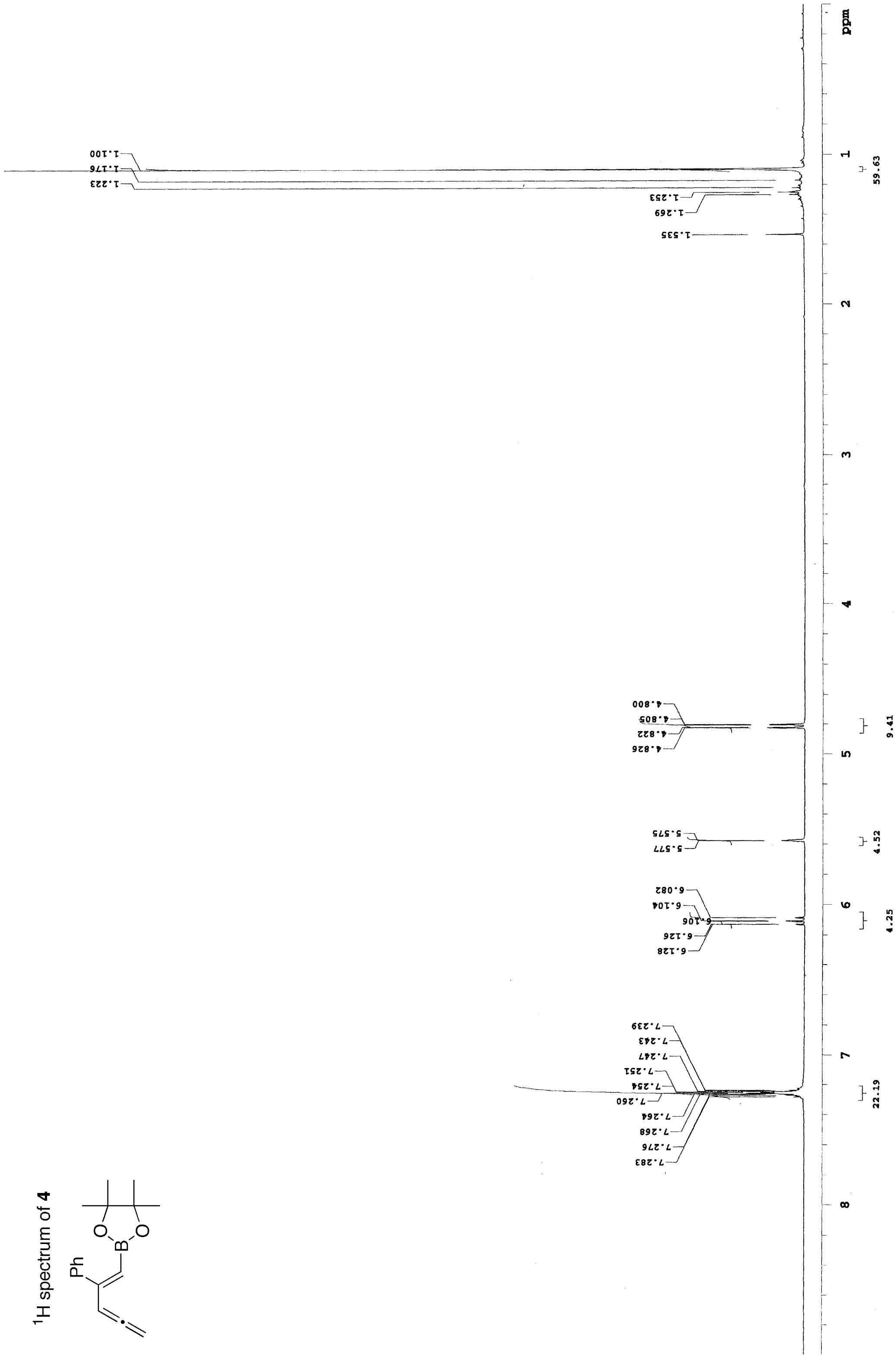


^{13}C spectrum of **2b**

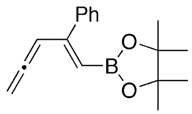


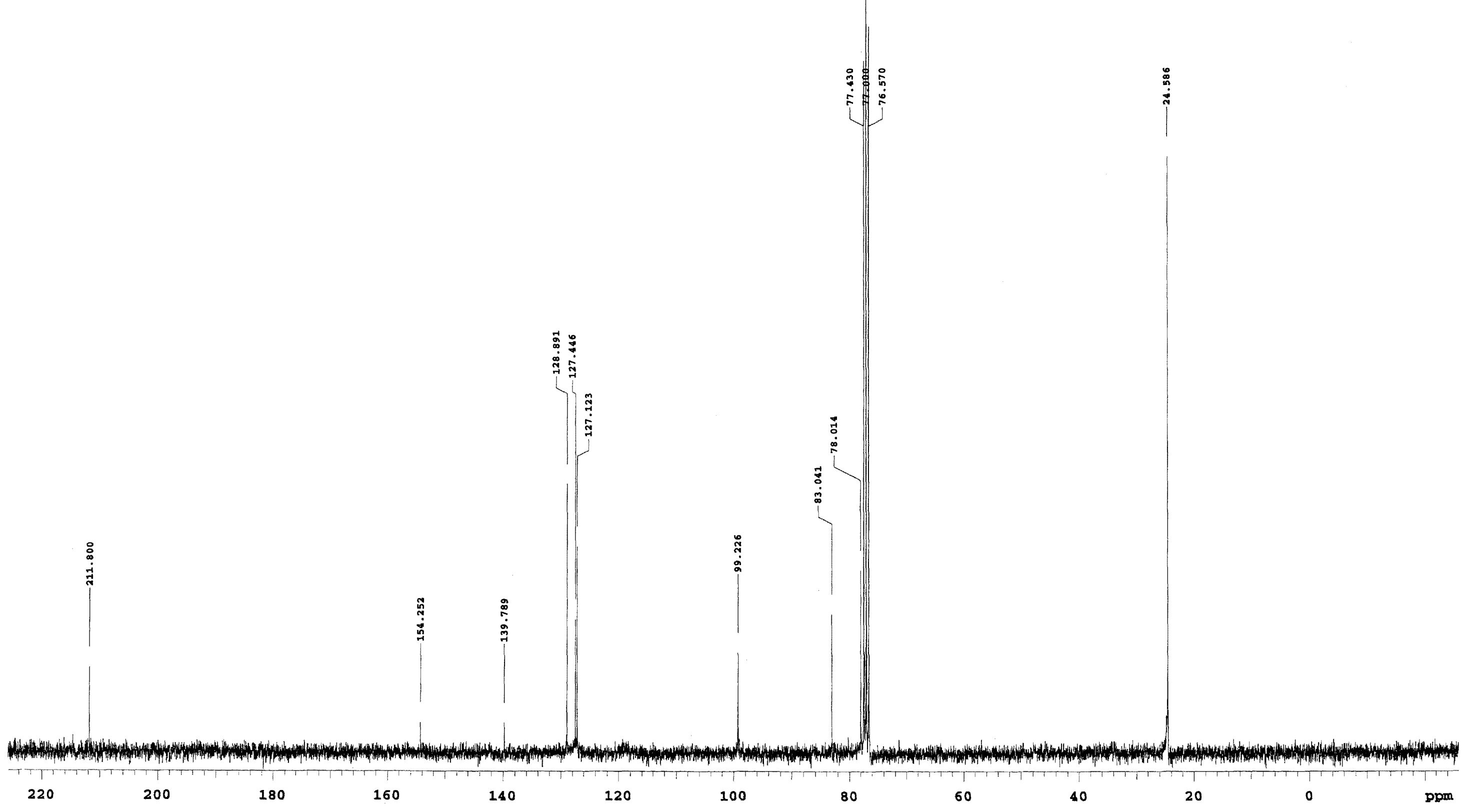


^{1}H spectrum of **4**

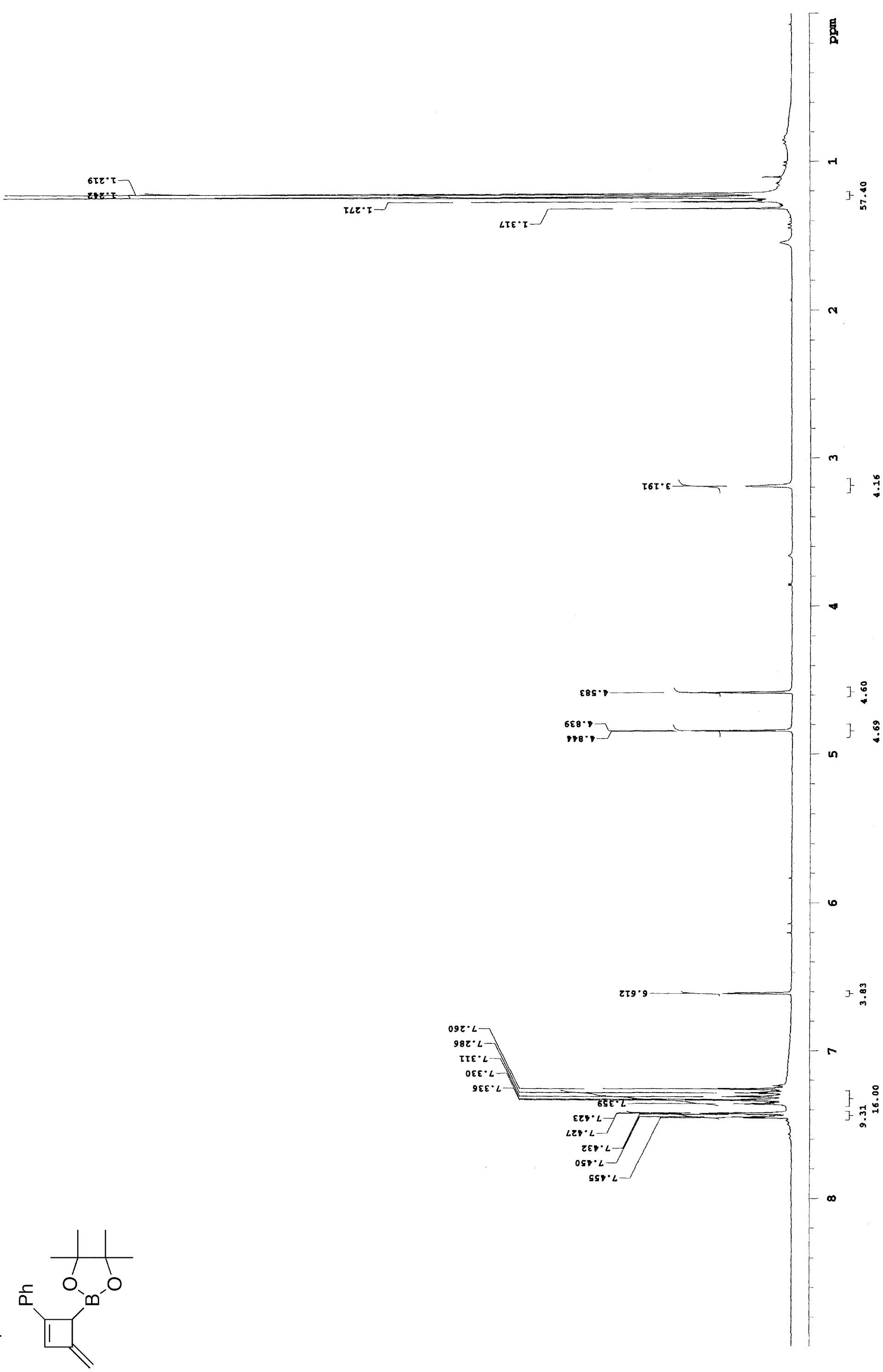


^{13}C spectrum of **4**

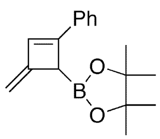


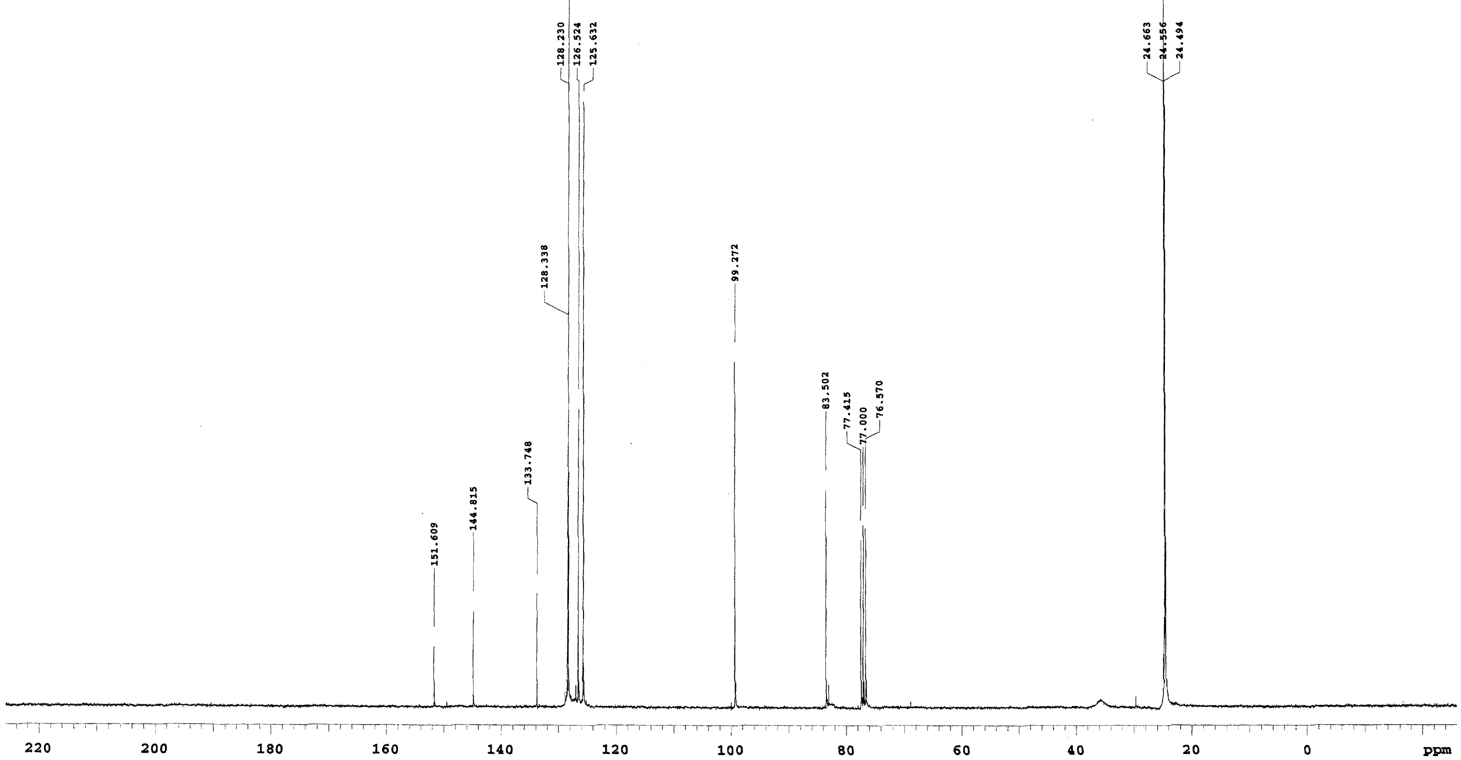


^1H spectrum of **5a**

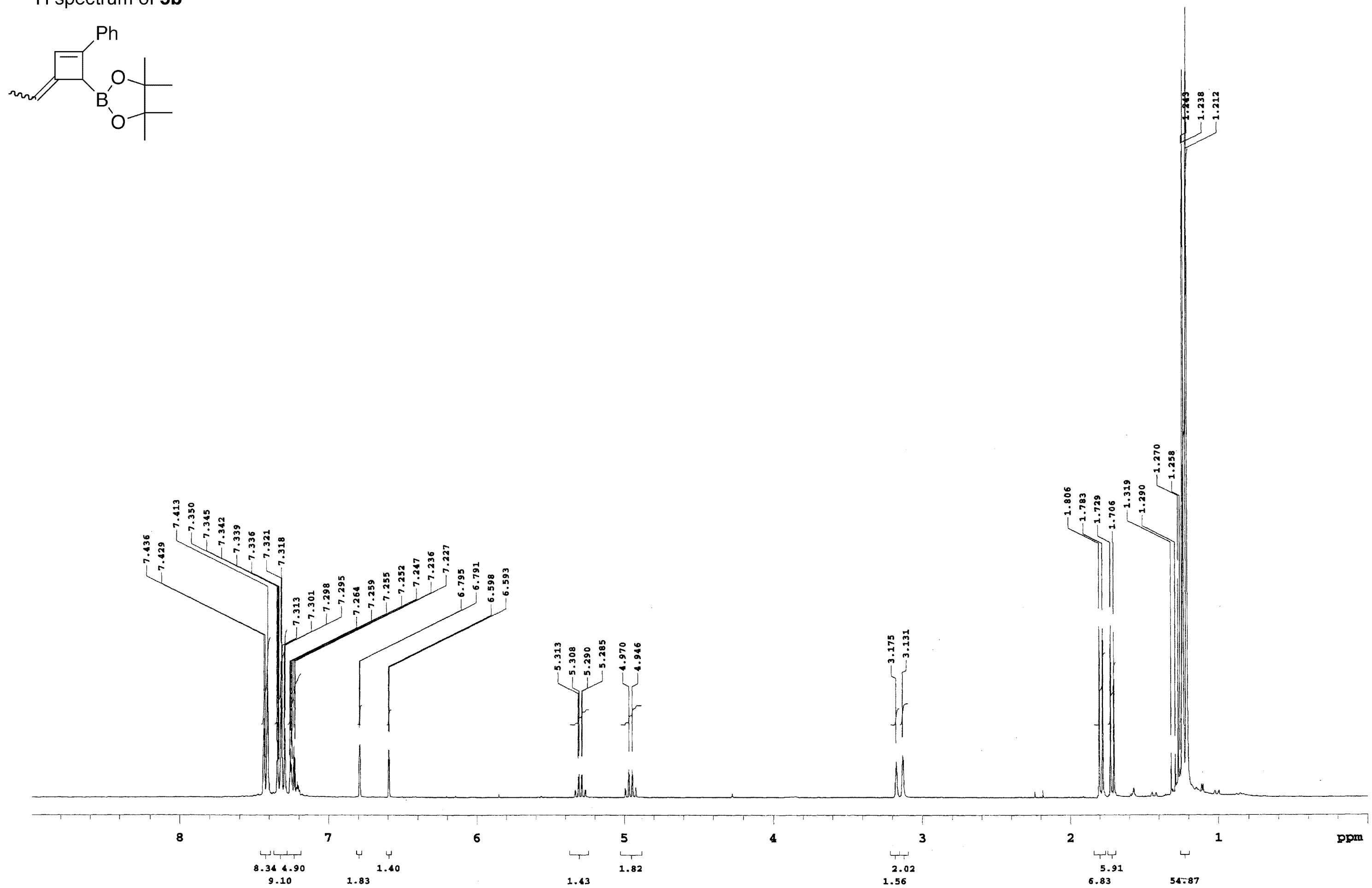


^{13}C spectrum of **5a**

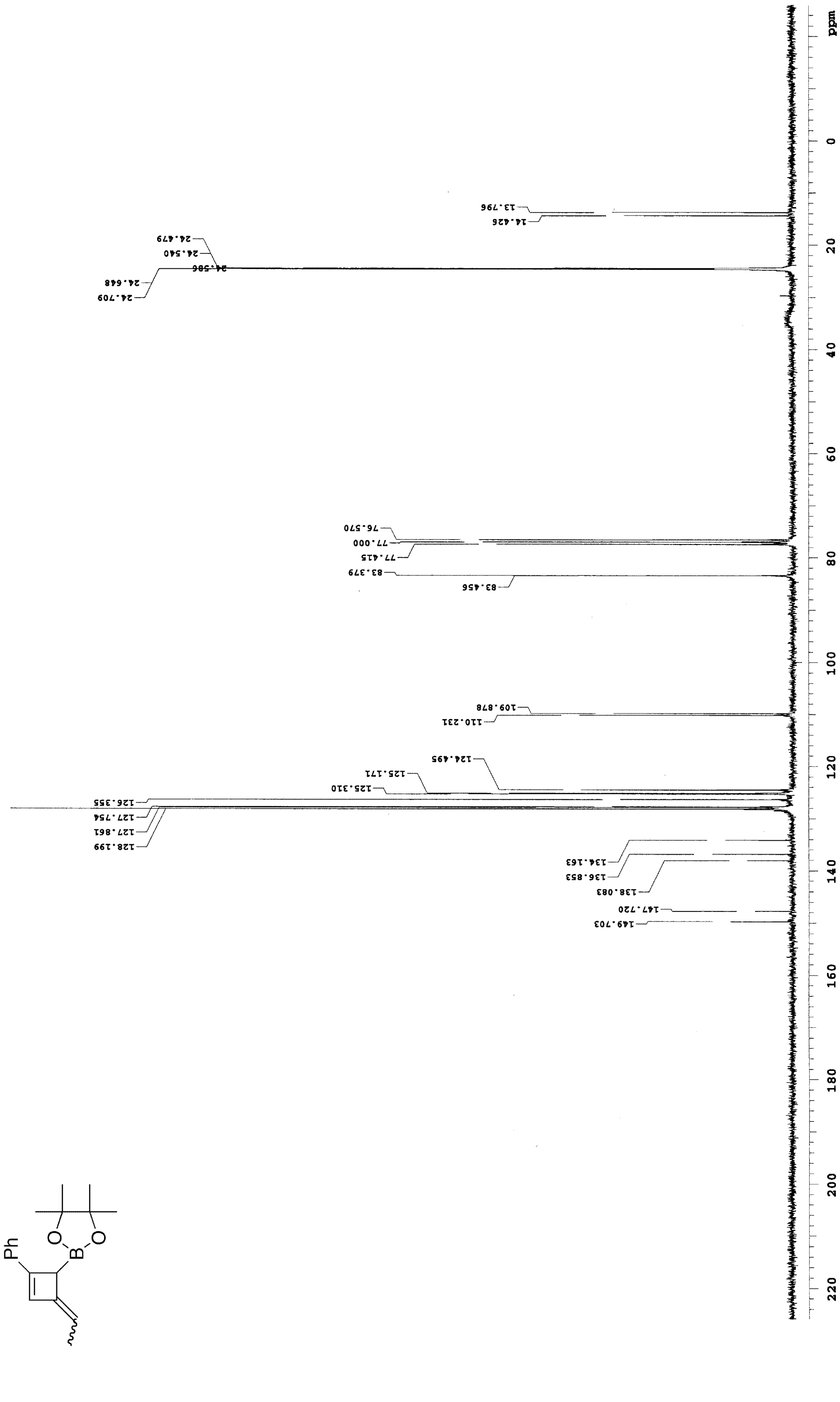




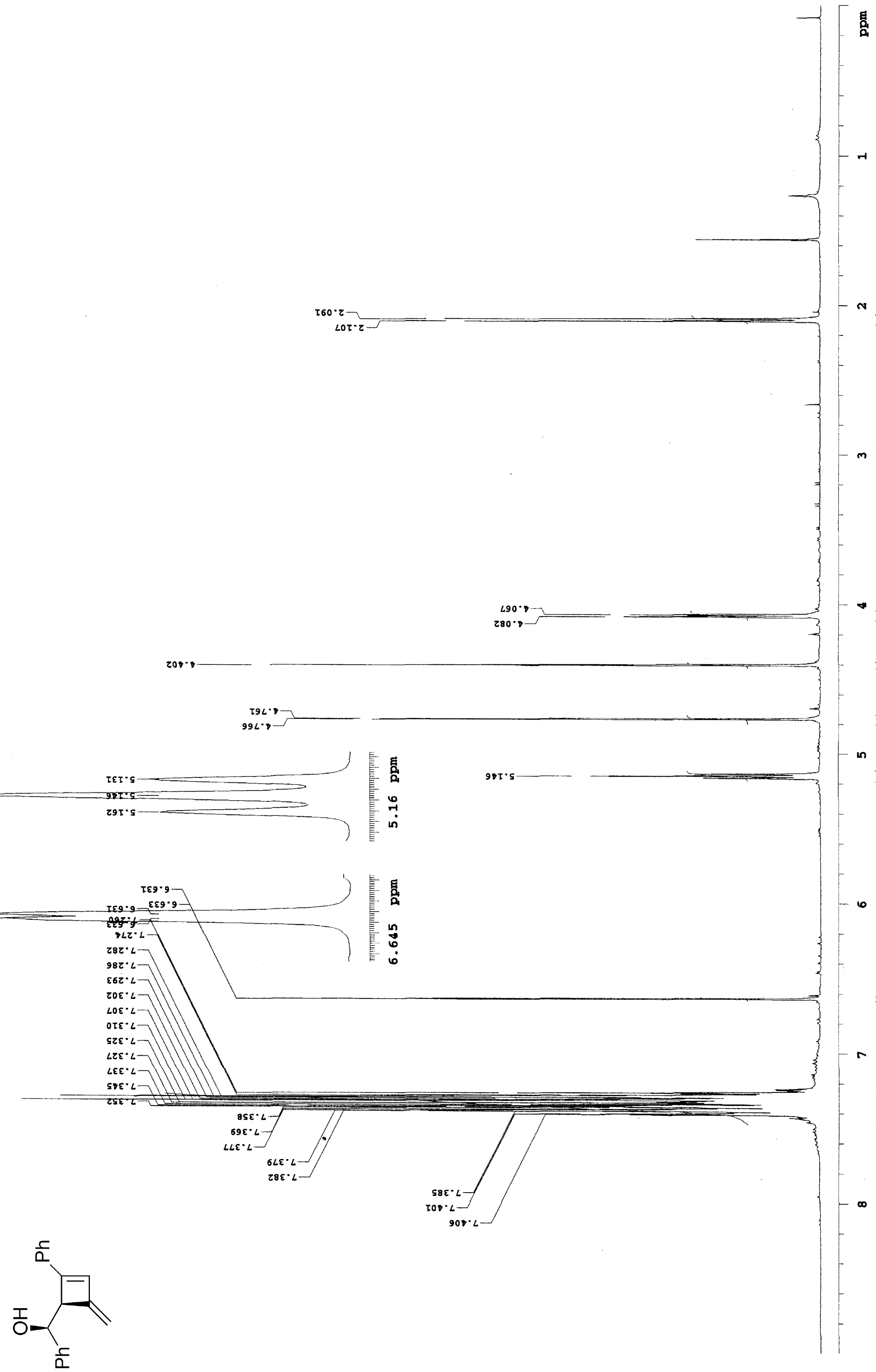
[1]H spectrum of **5b**



^{13}C spectrum of **5b**



^{1}H spectrum of **13**



^{13}C spectrum of **13**