Synthesis of BF_2 complex of 3-methylthio enaminones

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Abstract

Novel BF_2 complex of 3-methylthio enaminones or 3-methylthio enaminoketonatoboron difluorides have been synthesized *via* reactions of 3-methylthio enaminones with $BF_3{\cdot}Et_2O$ in the presence of Et_3N in good to excellent yields.

Keywords: 3-Methylthio enaminones, ketene *N,S*-acetals, BF_2 complexes, synthesis.

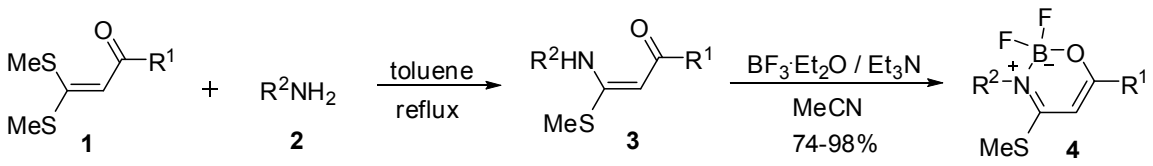
Introduction

Enaminones are useful synthetic intermediates that combine the ambident nucleophilicity of enamines with the ambident electrophilicity of enones, and their chemistry has received considerable attention continuously since their first appearance.[1] Enaminones have proved to be versatile building blocks in organic synthesis,[2] especially for the preparation of various heterocycles as potential agrochemicals or intermediates in dye and pharmaceutical industries.[3] While their early use has been limited to serving as synthetic intermediates in organic synthesis, recent exploration on enaminones' applications in pharmaceutical development has made impressive progress.[4] The therapeutic potential of these compounds has been realized in a number of areas, such as candidate agents as potential anticonvulsants and as potential modulators of multidrug resistance (MDR).[4a] 3-Methylthio enaminones or ketene *N,S*-acetals,[5] a special class of enaminones with a 3-methylthio substitution at the β-position, have attracted our attention due to the polyfunctional feature of these molecules. Because the MeS group is a good leaving group and could be subjected to a number of chemical transformations, the exploration on the synthetic utilities of 3-methylthio enaminones might result in the synthesis of a variety of novel nitrogen-containing heterocycles. In order to explore the chemical reactivity of 3-methylthio enaminones, especially the region-selectivity of these bis-nucleophiles, we decided to

make the BF_2 complex of 3-methylthio enaminones and examine their chemical reactivity. While the synthesis of BF_2 complexes of enaminones and their applications in organic synthesis have been reported before,[6] the synthesis and applications of the BF_2 complexes of 3-methylthio enaminones are yet to be explored. Due to the availability of a large number of enaminones, this might be resulted in the build-up of novel heterocyclic libraries of BF_2 complexes which could be valuable entities for pharmaceutical and agrochemical applications.

Results and Discussion

3-Methylthio enaminones **3** have been synthesized via the reactions of ketene *S,S*-acetals **1** with various aryl substituents and the corresponding amines **2** according to the reported methods.[8-13] The amino group and the carbonyl group of compound **3** are in *Z*-configuration due to the strong intramolecular hydrogen bonding between these two groups. Treatment of **3** with excess amount of $BF_3{\cdot}Et_2O$ (5 equiv) in the presence of Et_3N followed by crystallization, afforded BF_2 complex **4** in good to excellent yields (74–98%). The reaction was conducted in the presence of Et_3N at room temperature for about 30 min (Scheme 1). The results are summarized in Table 1.



Scheme 1. Synthesis of BF_2 complex from 3-methylthio enaminone.

As shown in Table 1, the reaction is barely affected by electronic and steric factors of the substitutions. All 3-methylthio enaminones, either with electron-donating or electron-withdrawing aryl groups underwent the reaction smoothly affording the desired products in high yields. Cyclohexyl substituent slightly decreased the yield of the reaction probably due to the steric effect (Table 1, entries 17, 18, 19). In the case of enaminone **3e** which bears a fully substituted aryl group, the reaction had to be performed at 50ºCC for 8h. in order to complete the reaction. Steric hindrance might be the cause of this observation (Table 1, entry 5).

All BF_2 complexes were fully characterized by their spectral data. To take compound **4f** as an example, in its IR spectrum, there was no signal which could be assigned to C=O group; its ^{1}H-NMR spectrum did not display the characteristic peak of NH group; and its ^{13}C NMR spectrum displayed two characteristic signals at δ 174.0 and 166.8 for the two tertiary carbon of BF_2 complex at C-3 and C-1. These evidences, together with the mass spectrum and element analysis, indicated that the transformation of the enaminone structure to the iminium-enol structure and the involvement of the *N,O*-atoms of the 3-methylthio enaminones in the formation

of the six-member ring BF_2 complex. The structure of BF_2 complex **4f** was further proved by the single crystal X-ray analysis (Figure 1).[7]

Table 1. Synthesis of BF_2 complex **4a–s**

Entry	Reactant	R^1	R^2	Product	Time (h)[a]	Yield (%)[b]	m.p. (ºC)
1	**3a**	Ph	*n*-Pr	**4a**	0.5	88	134–135
2	**3b**	*p*-CH_3-Ph	*n*-Pr	**4b**	0.5	95	126–127
3	**3c**	*p*-Cl-Ph	*n*-Pr	**4c**	0.5	98	138–139
4	**3d**	*p*-CH_3O-Ph	*n*-Pr	**4d**	0.5	87	132–133
5	**3e**	4-*t*-butyl-2,6-dimethyl-3,5-dinitrophenyl	*n*-Pr	**4e**	8 [c]	89	146–147
6	**3f**	*p*-phenyl-Ph	*n*-Pr	**4f**	0.5	90	141–142
7	**3g**	*p*-F-Ph	*n*-Pr	**4g**	0.5	92	138–139
8	**3h**	*p*-CF_3-Ph	*n*-Pr	**4h**	0.5	88	105–106
9	**3i**	Ph	Ph	**4i**	0.5	91	192–194
10	**3j**	Ph	*i*-Pr	**4j**	0.5	96	132–134
11	**3k**	Ph	*n*-Bu	**4k**	0.5	90	101–102
12	**3l**	Ph	$CH_2CH=CH_2$	**4l**	0.5	86	135–137
13	**3m**	Ph	cyclohexyl	**4m**	0.5	93	144–145
14	**3n**	*p*-CH_3-Ph	Ph	**4n**	0.5	90	202–203
15	**3o**	*p*-Cl-Ph	Ph	**4o**	0.5	91	189–190
16	**3p**	*p*-F-Ph	Ph	**4p**	0.5	93	178–179
17	**3q**	*p*-CH_3-Ph	cyclohexyl	**4q**	0.5	85	155–156
18	**3r**	*p*-Cl-Ph	cyclohexyl	**4r**	0.5	83	173–174
19	**3s**	*p*-CH_3O-Ph	cyclohexyl	**4s**	0.5	74	137–139

[a]Monitored by TLC analysis. [b]Isolated yields by crystallization of the crude product from petroleum ether and ethyl acetate at room temperature. [c]The reaction was performed at 50ºC for 8 h.

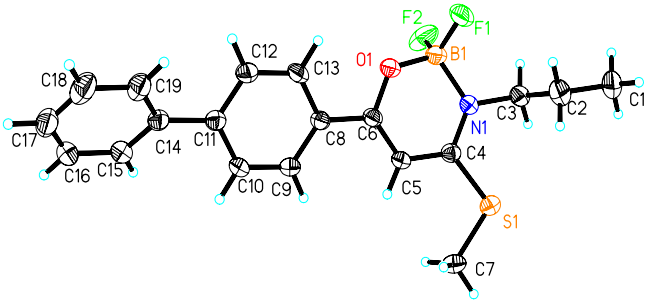


Figure 1. X-ray structure of **4f**.

Conclusions

In summary, novel BF_2 complex of 3-methylthio enaminones have been synthesized efficiently *via* the reactions of 3-methylthio enaminones with $BF_3{\cdot}Et_2O$ in the presence of Et_3N in good to excellent yields. These novel compounds will be helpful for us to better understand the chemical reactivity of enaminones and might be valuable in pharmaceutical and agrochemical applications.

Experimental Section

General. Melting points were determined using an electrothermal melting point apparatus and were uncorrected. IR spectra were recorded on a JASCO FT/IR-480 spectrometer using KBr pellets. ^{1}H NMR (300 MHz) and ^{13}C NMR (75 MHz) were recorded on a Bruker AV300 magnetic resonance spectrometer in $CDCl_3$ solution. Chemical shifts (δ) are reported in ppm with tetramethylsilane as internal standard. High resolution mass spectra (HRMS) were recorded on an APEXII FT-ICR spectrometer with EI mode. Elemental analysis was performed at the Center for Instrumental Analysis of ICCAS.

General procedure for the synthesis of 3-methylthio enaminone

A solution of ketene *S*,*S*-acetals **1** (1.0 equiv) and corresponding amines **2** (2.0–5.0 equiv) in toluence (30 mL) was heated to reflux. When TLC indicated the completion of the reaction, the resulting reaction mixture was concentrated *in vacuo*. The residue was purified by column chromatography (silica gel, AcOEt-petroleum ether: v/v=1/15–1/8) affording the desired ketene *N*,*S*-acetals **3**.

(*E*)-3-(Methylthio)-1-phenyl-3-(propylamino)prop-2-en-1-one (3a). The known compound **3a** was made according to the reported method. [8] Reaction of *S*,*S*-acetal **1** (R^1 = Ph, 1.12 g, 5.0 mmol) and *n*-propylamine (25.0 mmol) generated the product **3a** (965 mg, 82%) as a yellow oil. FT-IR (film/cm^{-1}): 3059w, 2963m, 2930m, 2873m, 1560s, 1496s, 1471s, 1436s, 1273s, 721s, 641s; ^{1}H NMR (300 MHz, $CDCl_3$): δ 11.92 (s, 1H, NH), 7.87–7.83 (m, 2H, PhH), 7.38–7.33 (m, 3H, PhH), 5.61 (s, 1H, =CH), 3.31–2.25 (m, 2H, $NHCH_2$), 2.34 (s, 3H, SCH_3), 1.69–1.62 (m, 2H, CH_2), 1.01 (t, J = 7.4 Hz, 3H, CH_3) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 184.8, 169.6, 140.7, 130.3, 128.1, 126.8, 86.0, 45.6, 22.8, 14.1, 11.4 ppm.

(*E*)-3-(Methylthio)-3-(propylamino)-1-*p*-tolylprop-2-en-1-one (3b). The known compound **3b** was made according to the reported method.[9] Reaction of *S*,*S*-acetal **1** (R^1 = *p*-CH_3-Ph, 2.38 g, 10.0 mmol) and *n*-propylamine (50.0 mmol) generated the product **3b** (1.94 g, 78%) as a yellow solid. m.p. 36–38ºC (EtOAc); FT-IR (film/cm^{-1}): 3024w, 2963m, 2928m, 2873m, 1566s, 1472s, 1272s, 1078m, 767s, 705m; ^{1}H NMR (300 MHz, $CDCl_3$): δ 11.88 (s, 1H, NH), 7.76 (d, J = 7.1 Hz, 2H, PhH), 7.17 (d, J = 6.7 Hz, 2H, PhH), 5.61 (s, 1H, =CH), 3.28–3.22 (m, 2H, $NHC\underline{H}_2$), 2.36–2.33 (m, 6H, SCH_3, $PhCH_3$), 1.70–1.65 (m, 2H, CH_2), 1.02 (t, J = 7.2 Hz, 3H, CH_3) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 184.8, 169.3, 140.6, 138.0, 128.9, 126.9, 85.8, 45.7, 22.9, 21.3,

14.1, 11.5 ppm; LRMS (ESI, positive) *m/z* 250.2 $[M+H]^+$; Anal.calcd for $C_{14}H_{19}NOS$: C, 67.43; H, 7.68; N, 5.62. Found: C, 67.14; H, 7.68; N, 5.66.

(*E*)-1-(4-Chlorophenyl)-3-(methylthio)-3-(propylamino)prop-2-en-1-one (3c). The known compound **3c** was made according to the reported method.[10] Reaction of *S*,*S*-acetal **1** (R^1 = *p*-Cl-Ph, 2.59 g, 10.0 mmol) and *n*-propylamine (50.0 mmol) generated the product **3c** (2.28 g, 84%) as a slightly yellow solid. m.p. 69–71ºC (EtOAc); FT-IR (film/cm^{-1}): 2963m, 2930m, 2873w, 1559s, 1471s, 1272s, 1091s, 1011m, 846m, 763s; ^{1}H NMR (300 MHz, $CDCl_3$): δ 11.88(s, 1H, NH), 7.80 (d, *J* = 8.5 Hz, 2H, PhH), 7.38 (d, *J* = 8.5Hz, 2H, PhH), 5.59 (s, 1H, =CH), 3.39–3.32 (m, 2H, NHC$\underline{H}_2$), 2.47 (s, 3H, SCH_3), 1.76–1.64 (m, 2H, CH_2), 1.06 (t, *J* = 7.4 Hz, 3H, CH_3) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 183.6, 170.0, 139.2, 136.4, 128.4, 128.3, 85.8, 45.8, 22.8, 14.3, 11.5 ppm; LRMS (ESI, positive) *m/z* 270.1 $[M+H]^+$; Anal.calcd for $C_{13}H_{16}ClNOS$: C, 57.87; H, 5.98; N, 5.19. Found: C, 57.69; H, 5.94; N, 5.20.

(*E*)-1-(4-Methoxyphenyl)-3-(methylthio)-3-(propylamino)prop-2-en-1-one (3d). The known compound **3d** was made according to the reported method.[9] Reaction of *S*,*S*-acetal **1** (R^1 = *p*-CH_3O-Ph, 717 mg, 2.8 mmol) and *n*-propylamine (14.0 mmol) generated the product **3d** (636 mg, 85%) as a slightly yellow solid. m.p. 42–44ºC (EtOAc); FT-IR (film/cm^{-1}): 2962m, 2931m, 2873w, 1565s, 1472s, 1251s, 1169s, 1031m, 771m; ^{1}H NMR (300 MHz, $CDCl_3$): δ 11.82 (s, 1H, NH), 7.84 (d, *J* = 8.8 Hz, 2H, PhH), 6.88 (d, *J* = 8.8 Hz, 2H, PhH), 5.59 (s, 1H, =CH), 3.76–3.70 (s, 3H, OCH_3), 3.33–3.26 (m, 2H, NHC$\underline{H}_2$), 2.38 (s, 3H, SCH_3), 1.71–1.63 (m, 2H, CH_2), 1.02 (t, *J* = 7.4 Hz, 3H, CH_3) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 184.2, 168.9, 161.5, 133.2, 128.6, 113.3, 85.5, 55.2, 45.6, 22.9, 14.1, 11.4 ppm; LRMS (ESI, positive) *m/z* 266.2 $[M+H]^+$; Anal.calcd for $C_{14}H_{19}NO_2S$: C, 63.36; H, 7.22; N, 5.28. Found: C, 63.21; H, 7.19; N, 5.38.

(*E*)-1-(4-*tert*-Butyl-2,6-dimethyl-3,5-dinitrophenyl)-3-(methylthio)-3-(propylamino) prop-2-en-1-one (3e). Using the general procedure, reaction of *S*,*S*-acetal **1** (R^1 = 4-*t*-butyl-2,6-dimethyl-3,5-dinitrophenyl, 2.04 g, 5.0 mmol) and *n*-propylamine (25.0 mmol) generated the product **3e** (1.85 g, 89%) as a white solid. m.p. 42–44ºC (EtOAc); FT-IR (film/cm^{-1}): 2967m, 2931m, 2875w, 1539s, 1474s, 1352s, 1275s; ^{1}H NMR (300 MHz, $CDCl_3$): δ 11.62 (s, 1H, NH), 4.98 (s, 1H, =CH), 3.41–3.34 (m, 2H, NHC$\underline{H}_2$), 2.36 (s, 3H, SCH_3), 2.17 (s, 6H, 2PhCH_3), 1.79–1.71 (m, 2H, CH_2), 1.44 (s, 9H, 3CH_3), 1.06 (t, *J*= 7.4 Hz, 3H, CH_3) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 185.3, 171.3, 150.2, 144.3, 130.2, 128.2, 89.8, 46.0, 37.1, 30.3, 22.6, 15.2, 14.2, 11.3 ppm; LRMS (ESI, positive) *m/z* 410.4 $[M+H]^+$; Anal.calcd for $C_{19}H_{27}N_3O_5S$: C, 55.73; H, 6.65; N, 10.26. Found: C, 55.62; H, 6.74; N, 9.91.

(*E*)-3-(Methylthio)-1-(4-phenylphenyl)-3-(propylamino)prop-2-en-1-one (3f). Using the general procedure, reaction of *S*,*S*-acetal **1** (1.54 g, 5.1 mmol) and *n*-propylamine (R^1 = *p*-phenyl-Ph, 25.5 mmol) generated the product **3f** (1.15 g, 72%) as a yellow oil. FT-IR (film/cm^{-1}): 3029w, 2962w, 2929w, 2872w, 1559s, 1471s, 1276s, 749s, 698m; ^{1}H NMR (300 MHz, $CDCl_3$): δ 11.97 (t, *J* = 4.8 Hz, 1H, NH), 7.94–7.92(m, 2H, PhH), 7.61–7.56 (m, 4H, PhH), 7.40–7.23 (m, 3H, PhH), 5.65 (s, 1H, =CH), 3.30–3.24 (m, 2H, NHC$\underline{H}_2$), 2.33 (s, 3H, SCH_3), 1.69–1.62 (m, 2H, CH_2), 1.01 (t, *J* = 7.3 Hz, 3H, CH_3) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 184.4, 169.6,

143.0, 140.4, 139.6, 128.9, 127.7, 127.5, 127.1, 126.9, 86.2, 45.8, 22.9, 14.2, 11.6 ppm; HRMS (EI) Calcd for $C_{19}H_{21}NOS$ $[M]^+$ 311.1344, Found 311.1347.

(E)-1-(4-Fluorophenyl)-3-(methylthio)-3-(propylamino)prop-2-en-1-one (3g). Using the general procedure, reaction of *S*,*S*-acetal **1** (R^1 = *p*-F-Ph, 1.33 g, 5.5 mmol) and *n*-propylamine (27.5 mmol) generated the product **3g** (1.27 g, 92%) as a yellow oil. FT-IR (film/cm^{-1}): 2964m, 2931m, 2874w, 1569s, 1474s, 1273s, 1231s, 1153s, 849m, 768s, 595s; ^{1}H NMR (300 MHz, $CDCl_3$): δ 11.87 (s, 1H, NH), 7.88–7.83 (m, 2H, PhH), 7.06–7.00 (m, 2H, PhH), 5.56 (s, 1H, =CH), 3.32–3.25 (m, 2H, NHC$\underline{H}_2$), 2.37 (s, 3H, SCH_3), 1.70–1.63 (m, 2H, CH_2), 1.02 (t, J = 7.4 Hz, 3H, CH_3) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 183.2, 169.6, 165.5 (d, $^1J_{C\text{-}F}$ = 247.5 Hz, 1C, C-F), 136.8 (d, $^4J_{C\text{-}F}$ = 3.0 Hz, 1C), 129.0 (d, $^3J_{C\text{-}F}$ = 8.5 Hz, 2C), 114.8 (d, $^2J_{C\text{-}F}$ = 21.0 Hz, 2C), 85.5, 45.6, 22.7, 13.9, 11.3 ppm; HRMS (EI) Calcd for $C_{13}H_{16}FNOS$ $[M]^+$ 253.0937, Found 253.0939.

(E)-1-(4-(Trifluoromethyl)phenyl)-3-(methylthio)-3-(propylamino)prop-2-en-1-one (3h). Using the general procedure, reaction of *S*,*S*-acetal **1** (R^1 = *p*-CF_3-Ph, 1.57 g, 5.4 mmol) and *n*-propylamine (25.0 mmol) generated the product **3h** (1.45 g, 89%) as a yellow solid. m.p. 43–44ºC (EtOAc); FT-IR (film/cm^{-1}): 2966w, 2933w, 2876w, 1566s, 1478s, 1324s, 1124s, 1015m; ^{1}H NMR (300 MHz, $CDCl_3$): δ 12.00 (s, 1H, NH), 7.96 (d, J = 8.1 Hz, 2H, PhH), 7.64 (d, J = 8.1 Hz, 2H, PhH), 5.62 (s, 1H, =CH), 3.35–3.28 (m, 2H, NHC$\underline{H}_2$), 2.41 (s, 3H, SCH_3), 1.73–1.66 (m, 2H, CH_2), 1.04 (t, J = 7.4 Hz, 3H, CH_3) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 182.8, 170.5, 144.0, 131.6 (q, $^2J_{C\text{-}F}$ = 30.0 Hz, 1C, $\underline{C}CF_3$), 124.0 (q, $^1J_{C\text{-}F}$ = 270.0 Hz, 1C, $\underline{C}F_3$), 127.1, 125.0 (q, $^3J_{C\text{-}F}$ = 5.6 Hz, 2C), 86.0, 45.7, 22.6, 13.9, 11.2 ppm; LRMS (ESI, positive) *m/z* 304.1 $[M+H]^+$; Anal.calcd for $C_{14}H_{16}F_3NOS$: C, 55.43; H, 5.32; N, 4.62. Found: C, 55.53; H, 5.33; N, 4.83.

(*E*)-3-(Methylthio)-1-phenyl-3-(phenylamino)prop-2-en-1-one (3i). The known compound **3i** was made according to the reported method.[11] Reaction of *S*,*S*-acetal **1** (R^1 = Ph, 1.12 g, 5.0 mmol) and aniline (15.0 mmol) generated the product **3i** (942 mg, 70%) as a yellow solid. m.p. 55–56ºC (EtOAc); FT-IR (film/cm^{-1}): 3060m, 2925s, 1557vs, 1466s, 1431s, 1298s, 1261s, 729s, 692s; ^{1}H NMR (300 MHz, $CDCl_3$): δ 13.58 (s, 1H, NH), 7.92–7.89 (m, 2H, PhH), 7.41–7.17 (m, 8H, PhH), 5.86 (s, 1H, =CH), 2.32 (s, 3H, SCH_3) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 186.1, 167.6, 140.3, 138.3, 131.0, 129.1, 128.4, 127.2, 126.4, 125.2, 88.9, 14.8 ppm; LRMS (ESI, positive) *m/z* 270.2 $[M+H]^+$; Anal.calcd for $C_{16}H_{15}NOS$: C, 71.34; H, 5.61; N, 5.20. Found: C, 71.17; H, 5.68; N, 5.34. [lit [4]: m.p. 56–57ºC; ^{1}H NMR: δ 8.0–8.3 (m, 2H), 7.4–7.8 (m, 8H), 6.11 (s, 1H, H-2), 2.50 (s, 3H, SCH_3) ppm.]

(*E*)-3-(Isopropylamino)-3-(methylthio)-1-phenylprop-2-en-1-one (3j). The known compound **3j** was made according to the reported method.[8] Reaction of *S*,*S*-acetal **1** (R^1 = Ph, 1.07 g, 4.8 mmol) and isopropylamine (24.0 mmol) generated the product **3j** (974 mg, 87%) as a yellow oil. FT-IR (film/cm^{-1}): 3058w, 2970m, 2927w, 2871w, 1565s, 1469s, 1279s, 1155m, 722s, 641m; ^{1}H NMR (300 MHz, $CDCl_3$): δ 11.91 (d, J = 8.1 Hz, 1H, NH), 7.87–7.84 (m, 2H, PhH), 7.37–7.33 (m, 3H, PhH), 5.59 (s, 1H, =CH), 3.91–3.84 (m, 1H, NHC$\underline{H}$), 2.34 (s, 3H, SCH_3), 1.27 (t, J =

6.3 Hz, 6H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 184.7, 168.1, 140.7, 130.3, 128.1, 126.8, 85.8, 46.0, 23.2, 14.1 ppm. (lit[8]: no data reported)

(*E*)-3-(Butylamino)-3-(methylthio)-1-phenylprop-2-en-1-one (3k). The known compound **3k** was made according to the reported method.[12] Reaction of *S*,*S*-acetal **1** (R^1 = Ph, 1.05 g, 4.7 mmol) and *n*-butylamine (23.5 mmol) generated the product **3k** (906 mg, 78%) as a yellow oil. FT-IR (film/cm^{-1}): 3058w, 2957s, 2929s, 2871m, 1559vs, 1471s, 1275s, 1066m, 721s, 641m; ^{1}H NMR (300 MHz, $CDCl_3$): δ 11.91 (s, 1H, NH), 7.87–7.84 (m, 2H, PhH), 7.36–7.34 (m, 3H, PhH), 5.61 (s, 1H, =CH), 3.34–3.27 (m, 2H, NHC$\underline{H}_2$), 2.33 (s, 3H, SCH_3), 1.66–1.56 (m, 2H, CH_2), 1.45–1.38 (m, 2H, CH_2), 0.95 (t, J = 7.2 Hz, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 184.7, 169.5, 140.7, 130.3, 128.1, 126.8, 85.9, 43.6, 31.5, 20.0, 14.1, 13.7 ppm. (lit [12]: no data reported)

(E)-3-(Allylamino)-3-(methylthio)-1-phenylprop-2-en-1-one (3l). Using the general procedure, reaction of *S*,*S*-acetal **1** (R^1 = Ph, 1.16 g, 5.2 mmol) and allylamine (26.0 mmol) generated the product **3l** (1.04 g, 86%) as a red oil. FT-IR (film/cm^{-1}): 3060m, 2925m, 1560vs, 1471s, 1271vs, 726s, 688m; ^{1}H NMR (300 MHz, $CDCl_3$): δ 11.96 (s, 1H, NH), 7.88–7.85 (m, 2H, PhH), 7.36–7.32 (m, 3H, PhH), 5.87–5.80 (m, 1H, CH_2=C$\underline{H}$CH_2), 5.65 (s, 1H, =CH), 5.31–5.14 (m, 2H, =CH_2), 3.94–3.91 (m, 2H, NHC$\underline{H}_2$), 2.31 (s, 3H, SCH_3) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 185.0, 169.5, 140.6, 132.9, 130.5, 128.2, 126.9, 116.8, 86.6, 46.0, 14.2 ppm; HRMS (EI) Calcd for $C_{13}H_{15}NOS$ $[M]^+$ 233.0874, Found 233.0878.

(*E*)-3-(Cyclohexylamino)-3-(methylthio)-1-phenylprop-2-en-1-one (3m). The known compound **3m** was made according to the reported method.[13] Reaction of *S*,*S*-acetal **1** (R^1 = Ph, 1.31 g, 5.9 mmol) and cyclohexylamine (11.8 mmol) generated the product **3m** (1.45 g, 90%) as a yellow solid. m.p. 96–97ºC (EtOAc); FT-IR (film/cm^{-1}): 3060w, 2931s, 2852m, 1557s, 1469s, 1283s, 1066m, 722s, 643m; ^{1}H NMR (300 MHz, $CDCl_3$): δ 12.01 (d, J = 8.4 Hz, 1H, NH), 7.86–7.83 (m, 2H, PhH), 7.38–7.34 (m, 3H, PhH), 5.61 (s, 1H, =CH), 3.62–3.58 (m, 1H, NHC$\underline{H}$), 2.40 (s, 3H, SCH_3), 1.99–1.96 (m, 2H), 1.78–1.75 (m, 2H), 1.58–1.28 (m, 6H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 184.8, 168.0, 140.8, 130.3, 128.2, 126.8, 85.9, 52.8, 33.1, 25.4, 24.3, 14.2 ppm; LRMS (ESI, positive) *m/z* 276.2 $[M+H]^+$; Anal.calcd for $C_{16}H_{21}NOS$: C, 69.78; H, 7.69; N, 5.09. Found: C, 69.72; H, 7.65; N, 5.38. (lit [13]: no data reported)

(*E*)-3-(Methylthio)-3-(phenylamino)-1-*p*-tolylprop-2-en-1-one (3n). The known compound **3n** was made according to the reported method.[11] Reaction of *S*,*S*-acetal **1** (R_1= *p*-CH_3-Ph, 1.11 g, 4.7 mmol) and aniline (14.2 mmol) generated the product **3n** (608 mg, 60%) as a yellow oil. FT-IR (film/cm^{-1}): 3028w, 2923w, 1557vs, 1468s, 1261s, 758s, 693m; ^{1}H NMR (300 MHz, $CDCl_3$): δ 13.54 (s, 1H, NH), 7.83 (d, J = 8.1 Hz, 2H, PhH), 7.33–7.28 (m, 4H, PhH), 7.22–7.20 (m, 3H, PhH), 5.86 (s, 1H, =CH), 2.36 (s, 6H, $PhCH_3$, SCH_3) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 186.0, 167.1, 141.4, 138.4, 137.5, 129.1, 129.1, 127.2, 126.3, 125.3, 125.2, 88.8, 21.5, 14.8 ppm. [lit [11]: ^{1}H NMR (100 MHz, $CDCl_3$): δ 13.48 (s, 1H, NH), 7.81 (d, J = 8.3 Hz, 2H, PhH), 7.37–7.25 (m, 7H, PhH), 5.88 (s, 1H, 2-H), 2.43 (s, 6H, $PhCH_3$, SCH_3) ppm.]

(*E*)-1-(4-Chlorophenyl)-3-(methylthio)-3-(phenylamino)prop-2-en-1-one (3o). The known compound **3o** was made according to the reported method.[11] Reaction of *S*,*S*-acetal **1** (R^1 = *p*-Cl-

Ph, 2.02 g, 7.8 mmol) and aniline (23.4 mmol) generated the product **3o** (1.71 g, 72%) as a yellow solid. m.p. 83–84ºC (EtOAc); FT-IR (film/cm^{-1}): 3061w, 2925w, 1557s, 1466s, 1300s, 1260s, 1092s, 1012s, 839m, 760s, 693m; ^{1}H NMR (300 MHz, $CDCl_3$): δ 13.56 (s, 1H, NH), 7.83–7.80 (m, 2H, PhH), 7.36–7.18 (m, 7H, PhH), 5.78 (s, 1H, =CH), 2.32 (s, 3H, SCH_3) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 184.4, 168.0, 138.6, 138.1, 137.0, 129.1, 128.6, 126.5, 125.1, 88.5, 14.8 ppm; LRMS (ESI, positive) *m/z* 304.1 $[M+H]^+$; Anal.calcd for $C_{16}H_{14}ClNOS$: C, 63.25; H, 4.64; N, 4.61. Found: C, 63.31; H, 4.68; N, 4.91. [lit [4]: m.p. 84ºC; ^{1}H NMR (100 MHz, $CDCl_3$): δ 13.42 (s, 1H, NH), 7.92 (d, J = 8.9 Hz, 2H, PhH), 7.52–7.23 (m, 7H, PhH), 6.21 (s, 1H, 2-H), 2.52 (s, 3H, SCH_3) ppm.]

(*E*)-1-(4-Fluorophenyl)-3-(methylthio)-3-(phenylamino)prop-2-en-1-one (3p). Using the general procedure, reaction of *S*,*S*-acetal **1** (R^1 = *p*-F-Ph, 1.27 g, 5.3 mmol) and aniline (15.9 mmol) generated the product **3p** (1.16 g, 76%) as a yellow solid. m.p. 70–71ºC (EtOAc); FT-IR (film/cm^{-1}): 3062w, 2925w, 1557s, 1468s, 1259s, 1155s, 848m, 767m, 693m; ^{1}H NMR (300 MHz, $CDCl_3$): δ 13.49 (s, 1H, NH), 7.93–7.88 (m, 2H, PhH), 7.37–7.19 (m, 5H, PhH), 7.10–7.05 (m, 2H, PhH), 5.81 (s, 1H, =CH), 2.37 (s, 3H, SCH_3) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 184.6, 167.7, 166.2 and 164.6 (d, $^1J_{C\text{-}F}$ = 249.8 Hz, 1C, C-F), 138.2, 136.4 (d, $^4J_{C\text{-}F}$ = 3.0 Hz, 1C), 129.3 (d, $^3J_{C\text{-}F}$ = 9.0 Hz, 2C), 129.1, 126.5, 125.2, 115.3 (d, $^2J_{C\text{-}F}$ = 21.8 Hz, 2C), 88.4, 11.7 ppm; LRMS (ESI, positive) *m/z* 288.1 $[M+H]^+$; Anal.calcd for $C_{16}H_{14}FNOS$: C, 66.88; H, 4.91; N, 4.87. Found: C, 67.08; H, 4.93; N, 5.07.

(*E*)-3-(Cyclohexylamino)-3-(methylthio)-1-*p*-tolylprop-2-en-1-one (3q). The known compound **3q** was made according to the reported method.[13] Reaction of *S*,*S*-acetal **1** (R^1 = *p*-CH_3-Ph, 1.04 g, 4.4 mmol) and cyclohexylamine (8.8 mmol) generated the product **3q** (1.26 g, 85%) as a yellow oil. FT-IR (film/cm^{-1}): 2930s, 2853m, 1559vs, 1470s, 1268s, 1080m, 755m; ^{1}H NMR (300 MHz, $CDCl_3$): δ 12.00 (d, J = 8.4 Hz, 1H, NH), 7.77–7.74 (m, 2H, PhH), 7.17–7.14 (m, 2H, PhH), 5.59 (s, 1H, =CH), 3.61–3.57 (m, 1H, NHC<u>H</u>), 2.36 (s, 3H, $PhCH_3$), 2.32 (s, 3H, SCH_3), 1.98–1.94 (m, 2H), 1.76–1.74 (m, 2H), 1.57–1.25 (m, 6H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 184.7, 167.7, 140.5, 138.0, 130.3, 128.8, 126.8, 85.7, 52.7, 33.2, 25.4, 24.3, 21.3, 14.2 ppm. (lit [13]: no data reported)

(*E*)-1-(4-Chlorophenyl)-3-(cyclohexylamino)-3-(methylthio)prop-2-en-1-one (3r). The known compound **3r** was made according to the reported method.[13] Reaction of *S*,*S*-acetal **1** (R^1 = *p*-Cl-Ph, 1.58 g, 6.1 mmol) and cyclohexylamine (12.2 mmol) generated the product **3r** (1.88 g, 98%) as a yellow oil. FT-IR (film/cm^{-1}): 2931s, 2853m, 1558s, 1470s, 1288s, 1091s, 1012m, 845m, 763m; ^{1}H NMR (300 MHz, $CDCl_3$): δ 12.02 (d, J = 8.7 Hz, 1H, NH), 7.79–7.76 (m, 2H, PhH), 7.37–7.31 (m, 2H, PhH), 5.54 (s, 1H, =CH), 3.62–3.57 (m, 1H, NHC<u>H</u>), 2.38 (s, 3H, SCH_3), 1.97–1.94 (m, 2H), 1.76–1.74 (m, 2H), 1.57–1.25 (m, 6H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 183.0, 168.4, 139.1, 136.2, 128.2, 128.2, 85.6, 52.8, 33.0, 25.3, 24.2, 14.1 ppm; HRMS (EI) Calcd for $C_{16}H_{20}ClNOS$ $[M]^+$ 309.0954, Found 309.0958. (lit [13]: no data reported)

(*E*)-3-(Cyclohexylamino)-1-(4-methoxyphenyl)-3-(methylthio)prop-2-en-1-one (3s). The known compound **3s** was made according to the reported method.[13] Reaction of *S*,*S*-acetal **1** (R^1 = *p*-CH_3O-Ph, 1.20 g, 4.7 mmol) and cyclohexylamine (9.4 mmol) generated the product **3s**

(1.23 g, 88%) as a white solid. m.p. 76–78ºC (EtOAc); FT-IR (film/cm^{-1}): 2930m, 2852m, 1560s, 1470s, 1252s, 1169m, 1031m; ^{1}H NMR (300 MHz, $CDCl_3$): δ 11.96 (d, J = 8.4 Hz, 1H, NH), 7.84 (d, J = 9.0 Hz, 2H, PhH), 6.87 (d, J = 9.0 Hz, 2H, PhH), 5.58 (s, 1H, =CH), 3.74 (s, 3H, OCH_3), 3.60–3.58 (m, 1H, NHCH), 2.38 (s, 3H, SCH_3), 1.97–1.94 (m, 2H), 1.76–1.74 (m, 2H), 1.56–1.30 (m, 6H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 184.0, 167.3, 161.5, 133.2, 128.5, 113.3, 85.3, 55.1, 52.6, 33.1, 25.4, 24.2, 14.1 ppm; LRMS (ESI, positive) *m/z* 306.2 $[M+H]^+$; Anal.calcd for $C_{17}H_{23}NO_2S$: C, 66.85; H, 7.59; N, 4.59. Found: C, 66.68; H, 7.60; N, 4.72. (lit [13]: no data reported)

General procedure for the synthesis of BF_2 complex from N,S-acetal

To a stirring mixture of ketene *N*,*S*-acetal **3** (1.0 equiv) and Et_3N (3.0 equiv) in dry MeCN (20 mL) was added $BF_3{\cdot}Et_2O$ (5.0 equiv) at room temperature. The reaction was monitored by TLC and after TLC indicated the completion of the reaction, the reaction mixture was quenched by addition of saturated aq. $NaHCO_3$ (30 mL) and extracted with CH_2Cl_2 (3×20mL). The combined organic layers were dried over Na_2SO_4, filtered and concentrated. The resulting precipitates were crystallized from a mixture of ethyl acetate and petroleum ether (v/v=1/5–1/10) to afford pure BF_2 complexes **4**.

1-Difluoroboronyloxyl-3-methylthio-1-phenyl-3-(*N*-propylimino)-1-propene (4a). Following the general procedure, reaction of *N*,*S*-acetal **3a** (300 mg, 1.28 mmol) yielded the product **4a** (323 mg, 88%) as a white solid. m.p. 134–135ºC (EtOAc); FT-IR (film/cm^{-1}): 2962w, 2930w, 2874w, 1597m, 1574m, 1521s, 1500m, 1459m, 1101s, 1022s, 750s, 686m; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.89–7.86 (m, 2H, PhH), 7.36–7.39 (m, 3H, PhH), 6.07 (s, 1H, =CH), 3.60 (t, J = 5.6 Hz, 2H, NCH_2), 2.60 (s, 3H, SCH_3), 1.83–1.76 (m, 2H, CH_2), 0.99 (t, J = 7.4 Hz, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 174.1, 167.1, 133.6, 132.0, 128.6, 127.2, 89.8, 49.4, 21.9, 14.8, 11.5 ppm; LRMS (ESI, negative) *m/z* 268.2 $[M-15]^-$; Anal.calcd for $C_{13}H_{16}BF_2NOS$: C, 55.14; H, 5.70; N, 4.95. Found: C, 55.23; H, 5.82; N, 4.95.

1-Difluoroboronyloxyl-3-methylthio-3-(*N*-propylimino)-1-*p*-tolyl-1-propene (4b). Following the general procedure, reaction of *N*,*S*-acetal **3b** (350 mg, 1.41 mmol) yielded the product **4b** (402 mg, 95%) as a white solid. m.p. 126–127ºC (EtOAc); FT-IR (film/cm^{-1}): 2975w, 2874w, 1559m, 1519s, 1499s, 1469m, 1102m, 1012s, 766s; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.78–7.75 (m, 2H, PhH), 7.21–7.19 (m, 2H, PhH), 6.03 (s, 1H, =CH), 3.59 (t, J = 5.6 Hz, 2H, NCH_2), 2.59 (s, 3H, $PhCH_3$), 2.37 (s, 3H, SCH_3), 1.82–1.75 (m, 2H, CH_2), 0.98 (t, J = 7.4 Hz, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 173.9, 167.3, 142.7, 130.8, 129.4, 127.2, 89.3, 49.4, 22.0, 21.5, 14.8, 11.5 ppm; LRMS (ESI, negative) *m/z* 282.1 $[M-15]^-$; Anal.calcd for $C_{14}H_{18}BF_2NOS$: C, 56.58; H, 6.11; N, 4.71. Found: C, 56.53; H, 6.17; N, 4.83.

1-(4-Chlorophenyl)-1-difluoroboronyloxyl-3-methylthio-3-(*N*-propylimino)-1-propene (4c). Following the general procedure, reaction of *N*,*S*-acetal **3c** (322 mg, 1.20 mmol) yielded the product **4c** (375 mg, 98%) as a white solid. m.p. 138–139ºC (EtOAc); FT-IR (film/cm^{-1}): 3018w, 2960w, 2879w, 1599s, 1566m, 1521s, 1487m, 1087s, 1023s, 769m; ^{1}H NMR (300 MHz,

$CDCl_3$): δ 7.81–7.78 (m, 2H, PhH), 7.38–7.35 (m, 2H, PhH), 6.04 (s, 1H, =CH), 3.60 (t, J = 5.5 Hz, 2H, NCH_2), 2.61 (s, 3H, SCH_3), 1.82–1.75 (m, 2H, CH_2), 0.99 (t, J = 7.4 Hz, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 174.2, 165.7, 138.2, 132.0, 128.9, 128.4, 89.9, 49.5, 21.9, 14.8, 11.4 ppm; LRMS (ESI, negative) *m/z* 302.1 $[M-15]^-$; Anal.calcd for $C_{13}H_{15}BClF_2NOS$: C, 49.16; H, 4.76; N, 4.41. Found: C, 49.25; H, 4.85; N, 4.31.

1-Difluoroboronyloxyl-1-(4-methoxyphenyl)-3-methylthio-3-(*N*-propylimino)-1-propene (4d). Following the general procedure, reaction of *N*,*S*-acetal **3d** (330 mg, 1.25 mmol) yielded the product **4d** (340 mg, 87%) as a yellow solid. m.p. 132–133ºC (EtOAc); FT-IR (film/cm^{-1}): 2967w, 2836w, 1590s, 1521s, 1498s, 1467m, 1256s, 1100s, 1024s; ^1H NMR (300 MHz, $CDCl_3$): δ 7.86–7.83 (m, 2H, PhH), 6.92–6.89 (m, 2H, PhH), 5.98 (s, 1H, =CH), 3.84 (s, 3H, OCH_3), 3.59 (t, J = 6.2 Hz, 2H, NCH_2), 2.59 (s, 3H, SCH_3), 1.83–1.75 (m, 2H, CH_2), 0.99 (t, J = 7.4 Hz, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 173.6, 167.0, 162.9, 129.1, 125.8, 114.0, 88.6, 55.4, 49.3, 22.0, 14.8, 11.5 ppm; LRMS (ESI, negative) *m/z* 298.2 $[M-15]^-$; Anal.calcd for $C_{14}H_{18}BF_2NO_2S$: C, 53.69; H, 5.79; N, 4.47. Found: C, 53.93; H, 5.90; N, 4.35.

1-(4-*tert*-Butyl-2,6-dimethyl-3,5-dinitrophenyl)-1-difluoroboronyloxyl-3-methylthio-3-(*N*-propylimino)-1-propene (4e). Following the general procedure, reaction of *N*,*S*-acetal **3e** (334 mg, 0.82 mmol) yielded the product **4e** (332 mg, 89%) as a white solid. m.p. 146–147ºC (EtOAc); FT-IR (film/cm^{-1}): 2973m, 2935w, 2878w, 1603s, 1539s, 1353s, 1120s, 1045s; ^1H NMR (300 MHz, $CDCl_3$): δ 5.63 (s, 1H, =CH), 3.84 (s, 3H, OCH_3), 3.67 (t, J = 7.6 Hz, 2H, NCH_2), 2.56 (s, 3H, SCH_3), 2.20–2.17 (m, 6H, $PhCH_3$), 1.87–1.79 (m, 2H, CH_2), 1.45–1.42 (m, 9H, $3CH_3$), 1.03 (t, J = 7.4 Hz, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 174.4, 166.1, 150.3, 136.7, 132.6, 130.5, 96.0, 50.0, 37.5, 30.3, 21.7, 15.5, 14.9, 11.4 ppm; LRMS (ESI, negative) *m/z* 442.2 $[M-15]^-$; Anal.calcd for $C_{19}H_{26}BF_2N_3O_5S$: C, 49.90; H, 5.73; N, 9.19. Found: C, 49.98; H, 5.81; N, 9.03.

1-Difluoroboronyloxyl-3-methylthio-1-(4-phenylphenyl)-3-(*N*-propylimino)-1-propene (4f). Following the general procedure, reaction of *N*,*S*-acetal **3f** (377 mg, 1.21 mmol) yielded the product **4f** (395 mg, 91%) as a yellow solid. m.p. 141–142ºC (EtOAc); FT-IR (film/cm^{-1}): 3033w, 2966m, 2932w, 2874w, 1590s, 1507s, 1103s, 1035s, 758s, 698m; ^1H NMR (300 MHz, $CDCl_3$): δ 7.95–7.93 (m, 2H, PhH), 7.64–7.58 (m, 4H, PhH), 7.46–7.24 (m, 3H, PhH), 6.10 (s, 1H, =CH), 3.61 (t, J = 6.7 Hz, 2H, NCH_2), 2.60 (s, 3H, SCH_3), 1.84–1.76 (m, 2H, CH_2), 0.99 (t, J = 7.4 Hz, 3H, CH_3) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 174.0, 166.8, 144.7, 139.8, 132.3, 129.0, 128.2, 127.7, 127.2, 127.1, 89.7, 49.5, 22.0, 14.8, 11.5 ppm; LRMS (ESI, positive) *m/z* 339.9 $[M-19]^+$; Anal.calcd for $C_{19}H_{20}BF_2NOS$: C, 63.52; H, 5.61; N, 3.90. Found: C, 63.45; H, 5.63; N, 4.07.

1-Difluoroboronyloxyl-1-(4-fluorophenyl)-3-methylthio-3-(*N*-propylimino)-1-propene (4g). Following the general procedure, reaction of *N*,*S*-acetal **3g** (373 mg, 1.47 mmol) yielded the product **4g** (405 mg, 90%) as a white solid. m.p. 138–139ºC (EtOAc); FT-IR (film/cm^{-1}): 2961w, 2873w, 1605m, 1581s, 1528s, 1501s, 1456m, 1098s, 1036s, 769m; ^1H NMR (300 MHz, $CDCl_3$): δ 7.89–7.84 (m, 2H, PhH), 7.10–7.04 (m, 2H, PhH), 6.03 (s, 1H, =CH), 3.56 (d, J = 6.2 Hz, 2H, NCH_2), 2.60 (s, 3H, SCH_3), 1.81–1.74 (m, 2H, CH_2), 0.98 (t, J = 7.4 Hz, 3H, CH_3) ppm; ^{13}C

NMR (75 MHz, $CDCl_3$): δ 174.3, 165.7, 165.0 (d, $^1J_{C\text{-}F}$ = 252.0Hz, 1C, C-F), 129.7, 129.5 (d, $^3J_{C\text{-}F}$ = 9.0Hz, 2C), 115.8 (d, $^2J_{C\text{-}F}$ = 21.8Hz, 2C), 89.6, 49.3, 21.9, 14.7, 11.4 ppm; LRMS (ESI, negative) *m/z* 286.2 $[M\text{-}15]^-$; Anal.calcd for $C_{13}H_{15}BF_3NOS$: C, 51.85; H, 5.02; N, 4.65. Found: C, 52.03; H, 5.17; N, 4.68.

1-Difluoroboronyloxyl-1-(4-(trifluoromethyl)phenyl)-3-methylthio-3-(*N*-propylimino)-1-propene (4h). Following the general procedure, reaction of *N*,*S*-acetal **3h** (325 mg, 1.07 mmol) yielded the product **4h** (351 mg, 92%) as a white solid. m.p. 105–106ºC (EtOAc); FT-IR (film/cm^{-1}): 2972w, 2938w, 2880w, 1601s, 1574s, 1526s, 1510s, 1324s, 1128s, 1067s, 854m, 779m; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.97–7.95 (m, 2H, PhH), 7.65–7.62 (m, 2H, PhH), 6.16 (s, 1H, =CH), 3.60 (t, J = 7.0 Hz, 2H, NCH_2), 2.64 (s, 3H, SCH_3), 1.82–1.74 (m, 2H, CH_2), 0.99 (t, J = 7.4 Hz, 3H, CH_3) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 174.6, 164.8, 136.9, 133.1 (q, $^2J_{C\text{-}F}$ = 32.2Hz, *C*CF_3), 127.4, 125.5 (q, $^3J_{C\text{-}F}$ = 3.8Hz, *CH*CCF_3), 120.1 (q, $^1J_{C\text{-}F}$ = 270.8Hz, CF_3), 90.9, 49.6, 21.7, 14.7, 11.3 ppm; LRMS (ESI, negative) *m/z* 336.1 $[M\text{-}15]^-$; Anal.calcd for $C_{14}H_{15}BF_5NOS$: C, 47.89; H, 4.31; N, 3.99. Found: C, 47.79; H, 4.37; N, 4.11.

1-Difluoroboronyloxyl-3-methylthio-1-phenyl-3-(*N*-phenylimino)-1-propene (4i). Following the general procedure, reaction of *N*,*S*-acetal **3i** (346 mg, 1.29 mmol) yielded the known product **4i** (362 mg, 88%) as a white solid. m.p. 194–196ºC (EtOAc); FT-IR (film/cm^{-1}): 3061w, 1590m, 1563s, 1454s, 1112s, 1048m, 757s, 706m; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.98–7.95 (m, 2H, PhH), 7.53–7.39 (m, 6H, PhH), 7.31–7.24 (m, 2H, PhH), 6.24 (s, 1H, =CH), 2.47 (s, 3H, SCH_3) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 177.2, 169.2, 139.7, 133.5, 132.5, 129.3, 128.8, 128.8, 127.5, 127.0, 89.9, 15.4 ppm; HRMS (EI) *m/z* Calcd for $C_{16}H_{14}BF_2NOS$ $[M]^+$ 317.0857, Found 317.0862. [lit [4]: m.p. 196ºC; H NMR (100 MHz, $CDCl_3$): δ 7.93–8.04 (m, 2H, PhH), 7.25–7.58 (m, 8H, PhH), 6.24 (s, 1H, 3-H), 2.52 (s, 3H, SCH_3) ppm.]

1-Difluoroboronyloxyl-3-(*N*-isopropylimino)-3-methylthio-1-phenyl-1-propene (4j). Following the general procedure, reaction of *N*,*S*-acetal **3j** (339 mg, 1.44 mmol) yielded the product **4j** (400 mg, 96%) as a white solid. m.p. 132–134ºC (EtOAc); FT-IR (film/cm^{-1}): 2978w, 2938w, 2874w, 1594s, 1569s, 1489s, 1308m, 1101s, 1005s, 753m, 688m; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.89–7.86 (m, 2H, PhH), 7.50–7.38 (m, 3H, PhH), 6.08 (s, 1H, =CH), 4.34–4.28 (m, 1H, NCH), 2.60 (s, 3H, SCH_3), 1.48 (d, J = 6.6 Hz, 6H, $2CH_3$) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 173.3, 166.6, 133.5, 131.9, 128.6, 127.2, 89.9, 52.9, 21.1, 21.1, 15.3 ppm; LRMS (ESI, positive) *m/z* 264.2 $[M\text{-}19]^+$; Anal.calcd for $C_{13}H_{16}BF_2NOS$: C, 55.14; H, 5.70; N, 4.95. Found: C, 54.88; H, 5.73; N, 5.05.

3-(*N*-Butylimino)-1-difluoroboronyloxyl-3-methylthio-1-phenyl-1-propene (4k). Following the general procedure, reaction of *N*,*S*-acetal **3k** (373 mg, 1.50 mmol) yielded the product **4k** (399 mg, 90%) as a white solid. m.p. 101–102ºC (EtOAc); FT-IR (film/cm^{-1}): 2962m 2934m, 2872m, 1596s, 1571s, 1520s, 1492s, 1316m, 1101s, 1032s, 751s, 687m; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.89–7.85 (m, 2H, PhH), 7.47–7.38 (m, 3H, PhH), 6.07 (s, 1H, =CH), 3.63 (t, J = 5.7 Hz, 2H, NCH_2), 2.59 (s, 3H, SCH_3), 1.80–1.69 (m, 2H, CH_2), 1.42–1.35 (m, 2H, CH_2), 0.98 (t, J = 7.4 Hz, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 174.0, 167.0, 133.6, 132.0, 128.6, 127.1,

89.8, 47.7, 30.5, 20.4, 14.8, 13.7 ppm; LRMS (ESI, positive) *m/z* 278.2 $[M-19]^+$; Anal.calcd for $C_{14}H_{18}BF_2NOS$: C, 56.58; H, 6.11; N, 4.71. Found: C, 56.53; H, 6.21; N, 4.63.

3-(*N*-Allylimino)-1-difluoroboronyloxyl-3-methylthio-1-phenyl-1-propene (4l). Following the general procedure, reaction of *N*,*S*-acetal **3l** (365 mg, 1.57 mmol) yielded the product **4l** (378 mg, 86%) as a yellow solid. m.p. 135–137ºC (EtOAc); FT-IR (film/cm^{-1}): 1595s, 1571s, 1517s, 1500m, 1490s, 1312m, 1102s, 1048s, 749m, 687m; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.90–7.87 (m, 2H, PhH), 7.48–7.38 (m, 3H, PhH), 6.07 (s, 1H, =CH), 5.91–5.80 (m, 1H, =CH), 5.31–5.23 (m, 2H, $=CH_2$), 4.27 (s, 2H, NCH_2), 2.59 (s, 3H, SCH_3) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 175.3, 167.5, 133.4, 132.1, 131.5, 128.7, 127.2, 118.8, 89.9, 49.6, 14.9 ppm; LRMS (ESI, negative) *m/z* 266.2 $[M-15]^-$; Anal.calcd for $C_{13}H_{14}BF_2NOS$: C, 55.54; H, 5.02; N, 4.98. Found: C, 55.59; H, 4.99; N, 5.10.

3-(*N*-Cyclohexylimino)-1-difluoroboronyloxyl-3-methylthio-1-phenyl-1-propene (4m). Following the general procedure, reaction of *N*,*S*-acetal **3m** (325 mg, 1.18 mmol) yielded the product **4m** (354 mg, 93%) as a slightly yellow solid. m.p. 144–145ºC (EtOAc); FT-IR (film/cm^{-1}): 3064m, 2933s, 2855m, 1594s, 1568s, 1505s, 1489s, 1309m, 1104s, 1025s, 990s, 752s, 688m; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.89–7.86 (m, 2H, PhH), 7.47–7.37 (m, 3H, PhH), 6.07 (s, 1H, =CH), 3.86–3.85 (m, 1H, NCH), 2.59 (s, 3H, SCH_3), 2.00–1.84 (m, 6H), 1.67–1.66 (m, 1H), 1.32–1.24 (m, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 173.3, 166.5, 133.5, 131.9, 128.6, 127.1, 89.8, 61.6, 31.1, 26.1, 25.2, 15.3 ppm; LRMS (ESI, positive) *m/z* 304.1 $[M-19]^+$; Anal.calcd for $C_{16}H_{20}BF_2NOS$: C, 59.46; H, 6.24; N, 4.33. Found: C, 59.29; H, 6.30; N, 4.37.

1-Difluoroboronyloxyl-3-methylthio-3-(*N*-phenylimino)-1-*p*-tolyl-1-propene (4n). Following the general procedure, reaction of *N*,*S*-acetal **3n** (325 mg, 1.15 mmol) yielded the known product **4n** (342 mg, 90%) as a white solid. m.p. 210–211ºC (EtOAc); FT-IR (film/cm^{-1}): 1585m, 1558s, 1491s, 1111s, 1038s, 755s, 695m; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.88 (d, J = 8.3 Hz, 2H, PhH), 7.44–7.39 (m, 3H, PhH), 7.31–7.24 (m, 4H, PhH), 6.21 (s, 1H, =CH), 2.48 (s, 3H, SCH_3), 2.41 (s, 3H, $PhCH_3$) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 176.9, 169.4, 143.4, 139.8, 130.6, 129.5, 129.3, 128.7, 127.6, 127.1, 89.4, 21.6, 15.3 ppm; HRMS (EI) *m/z* Calcd for $C_{17}H_{16}BF_2NOS$ $[M]^+$ 331.1014, Found 331.1018. [lit [4]: m.p. 212ºC; ^{1}H NMR (100 MHz, $CDCl_3$): δ 7.87 (d, J = 8.4 Hz, 2H, PhH), 7.35 (d, J = 8.4 Hz, 2H, PhH), 7.48–7.21 (m, 5H, PhH), 6.20 (s, 1H, 3-H), 2.49 (s, 3H, SCH_3), 2.42 (s, 3H, 4-Me) ppm.]

1-(4-Chlorophenyl)-1-difluoroboronyloxyl-3-methylthio-3-(*N*-phenylimino)-1-propene (4o). Following the general procedure, reaction of *N*,*S*-acetal **3o** (369 mg, 1.22 mmol) yielded the known product **4o** (389 mg, 98%) as a white solid. m.p. 184–185ºC (EtOAc); FT-IR (film/cm^{-1}): 1586s, 1557s, 1502s, 1482s, 1115m, 1043m, 764m, 696m; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.90 (d, J = 8.6 Hz, 2H, PhH), 7.47–7.40 (m, 5H, PhH), 7.29–7.24 (m, 2H, PhH), 6.21 (s, 1H, =CH), 2.46 (s, 3H, SCH_3) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 177.5, 167.7, 139.6, 138.8, 131.9, 129.3, 129.1, 128.8, 126.9, 90.0, 15.3 ppm; LRMS (ESI, positive) *m/z* 332.0 $[M-19]^+$; Anal.calcd for $C_{16}H_{13}BClF_2NOS$: C, 54.66; H, 3.73; N, 3.98. Found: C, 54.68; H, 3.77; N, 4.18. [lit [4]: m.p. 184ºC; ^{1}H NMR (100 MHz, $CDCl_3$): δ 7.90 (d, J = 8.8 Hz, 2H, PhH), 7.42 (d, J = 8.8 Hz, 2H, PhH), 7.52–7.22 (m, 5H, PhH), 6.20 (s, 1H, 3-H), 2.50 (s, 3H, SCH_3) ppm.)

1-Difluoroboronyloxyl-1-(4-fluorophenyl)-3-methylthio-3-(*N*-phenylimino)-1-propene (4p). Following the general procedure, reaction of *N*,*S*-acetal **3p** (349 mg, 1.22 mmol) yielded the product **4p** (379 mg, 93%) as a white solid. m.p. 178–179ºC (EtOAc); FT-IR (film/cm^{-1}): 1602s, 1568s, 1490s, 1114m, 1042m, 757m, 696m; ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.01–7.97 (m, 2H, PhH), 7.46–7.41 (m, 3H, PhH), 7.32–7.29 (m, 2H, PhH), 7.18 (t, J = 8.6 Hz, 2H, PhH), 6.19 (s, 1H, =CH), 2.50 (s, 3H, SCH_3) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 177.2, 168.0, 165.4 (d, $^1J_{C\text{-}F}$ = 252.8 Hz, 1C, C-F), 139.6, 129.9 (d, $^3J_{C\text{-}F}$ = 9.0 Hz, 2C), 129.6, 129.3, 128.8, 126.9, 116.0 (d, $^2J_{C\text{-}F}$ = 21.8 Hz, 2C), 89.5, 15.4 ppm; LRMS (ESI, positive) *m/z* 316.1 [M-19]$^+$; Anal.calcd for $C_{16}H_{13}BF_3NOS$: C, 57.34; H, 3.91; N, 4.18. Found: C, 57.42; H, 4.02; N, 4.31.

3-(*N*-Cyclohexylimino)-1-difluoroboronyloxyl-3-methylthio-1-*p*-tolyl-1-propene (4q). Following the general procedure, reaction of *N*,*S*-acetal **3q** (435 mg, 1.51 mmol) yielded the product **4q** (431 mg, 85%) as a slightly yellow solid. m.p. 155–156ºC (EtOAc); FT-IR (film/cm^{-1}): 2932m, 2855m, 1590s, 1564s, 1496s, 1489s, 1308m, 1101s, 1005s, 753s, 688m; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.78 (d, J = 8.2 Hz, 2H, PhH), 7.20 (d, J = 8.1 Hz, 2H, PhH), 6.03 (s, 1H, =CH), 3.84–3.83 (m, 1H, NCH), 2.57 (s, 3H, SCH_3), 2.36 (s, 3H, $PhCH_3$), 1.99–1.83 (m, 6H), 1.67–1.65 (m, 1H), 1.26–1.23 (m, 3H) ppm; ^{13}C NMR(75 MHz, $CDCl_3$): δ 173.2, 166.6, 142.6, 130.7, 129.3, 127.2, 89.3, 61.5, 31.1, 26.1, 25.2, 21.5, 15.3 ppm; HRMS (EI) *m/z* Calcd for $C_{17}H_{22}BF_2NOS$ [M]$^+$ 337.1483, Found 337.1488.

1-(4-Chlorophenyl)-3-(*N*-cyclohexylimino)-1-difluoroboronyloxyl-3-methylthio-1-propene (4r). Following the general procedure, reaction of *N*,*S*-acetal **3r** (376 mg, 1.22 mmol) yielded the product **4r** (361 mg, 83%) as a white solid. m.p. 173–174ºC (EtOAc); FT-IR (film/cm^{-1}): 2933w, 2855w, 1594s, 1560s, 1485s, 1437s, 1102m, 1024m, 989m; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.74–7.80 (m, 2H, PhH), 7.41–7.26 (m, 2H, PhH), 6.04 (s, 1H, =CH), 3.86–3.79 (m, 1H, NCH), 2.62 (s, 3H, SCH_3), 2.01–1.86 (m, 6H), 1.68–1.59 (m, 1H), 1.28–1.25 (m, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 173.2, 165.4, 138.1, 132.0, 128.9, 128.5, 89.9, 61.9, 31.0, 26.1, 25.1, 15.4 ppm; LRMS (ESI, negative) *m/z* 342.0 [M-15]$^-$; Anal.calcd for $C_{16}H_{19}BClF_2NOS$: C, 53.73; H, 5.35; N, 3.92. Found: C, 53.55; H, 5.20; N, 3.89.

3-(*N*-Cyclohexylimino)-1-difluoroboronyloxyl-1-(4-methoxyphenyl)-3-methylthio-1-propene (4s). Following the general procedure, reaction of *N*,*S*-acetal **3s** (375 mg, 1.23 mmol) yielded the product **4s** (321 mg, 74%) as a slightly yellow solid. m.p. 137–139ºC (EtOAc); FT-IR (film/cm^{-1}): 2934m, 2854m, 1589s, 1566s, 1490s, 1259s, 1179s, 1107s, 990s, 841m, 768m; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.85 (dd, J_1 = 7.0 Hz, J_2 = 2.0 Hz, 2H, PhH), 6.91 (dd, J_1 = 7.0 Hz, J_2 = 1.9 Hz, 2H, PhH), 5.98 (s, 1H, =CH), 3.83 (s, 4H, NCH, OCH_3), 2.58 (s, 3H, SCH_3), 1.96–1.84 (m, 6H), 1.67 (m, 1H), 1.29–1.24 (m, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 172.9, 166.4, 162.8, 129.1, 125.8, 114.0, 88.6, 61.4, 55.4, 31.1, 26.1, 25.2, 15.3 ppm; LRMS (ESI, positive) *m/z* 334.1 [M-19]$^+$; Anal.calcd for $C_{17}H_{22}BF_2NO_2S$: C, 57.80; H, 6.28; N, 3.97. Found: C, 57.83; H, 6.42; N, 4.02.

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