Reaction of α-Oxoketene Dithioacetals with Arylamines in the Presence of BF_3–OEt_2 for the Synthesis of Ketene *S,N*-Acetals

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Reaction of α-oxoketene dithioacetals with arylamines was accelerated with a catalytic amount of BF_3–OEt_2 to give the corresponding α-oxoketene *S,N*-acetals selectively in good yields.

Keywords α-oxoketene dithioacetal; α-oxoketene *S,N*-acetal; Lewis acid; BF_3–OEt_2; enaminoketone

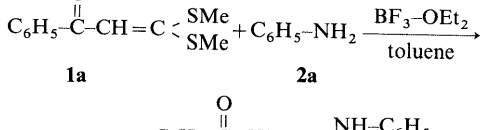
Ketene dithioacetals have become established electrophilic intermediates in synthetic organic methodology. Enaminoketones are also useful intermediates for the synthesis of a variety of compounds,[1-10] in particular, α-oxoketene *S,N*-acetals are good reagents for the synthesis of heterocycles.[3,4] Generally, the best method for the preparation of α-oxoketene *S,N*-acetals involves reaction of an enolate anion with isothiocyanate followed by *S*-alkylation.[2] Also, the reaction of α-oxoketene dithioacetals, which are easily prepared by the reaction of acetophenone derivatives with carbon disulfide in the presence of a base and an alkylating reagent, with aliphatic amines gives the corresponding ketene *S,N*-acetals and *N,N*-aminals. But the reactions of α-oxoketene dithioacetals with aromatic amines did not give good results.[5] The reaction of 3,3-bis(methylthio)-1-phenyl-2-propen-1-one (**1a**) with aniline under heating at 150 °C gives a mixture of the corresponding ketenes *S,N*-acetal and *N,N*-aminal in poor yield.[5]

Various Lewis acids have been used to accelerate a variety of C–C bond-forming reaction.[11-13] Our own interest in this field has inolved the use of Lewis acid to promote the reaction of α-oxoketene dithiacetals with aromatic amines as an efficient route to α-oxoketene *S,N*-acetals. During the course of our studies on the potential usefulness of ketene dithioacetals, we found that α-oxoketene dithioacetals become highly active in the presence of boron trifluoride etherate (BF_3–OEt_2).

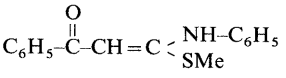
In the first place, the reaction of **1a** with aniline (**2a**) was taken as a model, and several combinations of BF_3–OEt_2 and **2a** were examined (Table I). A mixture of **1a** and 1 molar eq of **2a** was heated under reflux in toluene in the presence of 10% molar eq of BF_3–OEt_2 to give the corresponding displacement product, (*E*)-3-methylthio-1-phenyl-3-phenylaminoprop-2-en-1-one (**3a**), in 40% yield (Table I, entry 1). It should be noted that effective catalysis can be attained in this reaction by using a suitable combination of the Lewis acid and amine, and the yields were improved when 10% molar eq of BF_3–OEt_2 and 1.5 molar eq of aniline were used (entry 2). On the other hand, the reaction of **1a** and two eq of **2a** without Lewis acid under refluxing in toluene for 2 h gave no **3a** (entry 6).

As shown in Table II, a variety of aromatic amines (**2**) smoothly reacted with **1a** to give the corresponding α-oxoketene *S,N*-acetals in good yields. In general, the

TABLE I. Reaction of α-Oxoketene Dithioacetal (**1a**) with Aniline in the Presence of BF_3–Et_2O; Effect of Amount of Aniline and BF_3–OEt_2[a]



1a **2a**

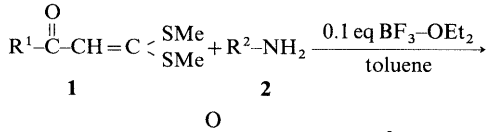


3a

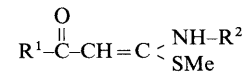
Entry	**1a** :	**2a** :	BF_3–OEt_2[b]	Yield (%)[c]
1	1.0	1.0	0.1	40
2	1.0	1.5	0.1	91
3	1.0	2.0	0.1	81
4	1.0	1.2	0.2	60
5	1.0	2.5	0.2	68
6	1.0	2.0	0	0

a) All reactions were carried out under reflux for 2 h in toluene. *b*) Molar ratio. *c*) Isolated yield.

TABLE II. Reaction of α-Oxoketene Dithioacetals with Arylamines in the Presence of a Catalytic Amount of BF_3–OEt_2[a]



1 **2**

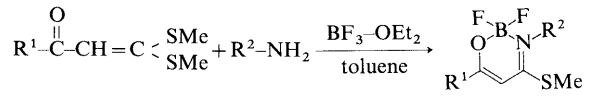


3

Entry	R^1	R^2	Product	Yield (%)[b]
1	C_6H_5 (**1a**)	C_6H_5 (**2a**)	**3a**	90
2	C_6H_5 (**1a**)	C_6H_4–Me(4) (**2b**)	**3b**	84
3	C_6H_5 (**1a**)	C_6H_4–Cl(4) (**2c**)	**3c**	94
4	C_6H_5 (**1a**)	C_6H_4–Cl(2) (**2d**)	**3d**	88
5	C_6H_5 (**1a**)	C_6H_4–Br(4) (**2e**)	**3e**	77
6	C_6H_5 (**1a**)	C_6H_4–Br(2) (**2f**)	**3f**	62
7	C_6H_4–Me(4) (**1b**)	C_6H_5 (**2a**)	**3g**	85
8	C_6H_4–OMe(4) (**1c**)	C_6H_5 (**2a**)	**3h**	84
9	C_6H_4–Cl(4) (**1d**)	C_6H_5 (**2a**)	**3i**	94
10	C_6H_4–Br(4) (**1e**)	C_6H_5 (**2a**)	**3j**	80
11	2-Thienyl (**1f**)	C_6H_5 (**2a**)	**3k**	80
12	2-Furyl (**1g**)	C_6H_5 (**2a**)	**3l**	85
13	C_6H_4–Cl(4) (**1d**)	C_6H_4–Cl(4) (**2c**)	**3m**	98
14	C_6H_4–Cl(4) (**1d**)	C_6H_4–Cl(2) (**2d**)	**3n**	98
15	C_6H_4–Cl(4) (**1d**)	C_6H_3–Cl_2(2,3) (**2g**)	**3o**	79

a) All reactions were carried out in the presence of 10 mol% of BF_3–OEt_2 under reflux for 2 h in toluene. *b*) Isolated yield.

TABLE III. Reaction of α-Oxoketene Dithioacetals with Arylamines in the Presence of BF_3–OEt_2[a]



1 2 4

Entry	R^1	R^2	Product	Yield (%)[b]
1	C_6H_5 (**1a**)	C_6H_5 (**2a**)	**4a**	95
2	C_6H_5 (**1a**)	C_6H_4–Cl(4) (**2c**)	**4b**	95
3	C_6H_5 (**1a**)	C_6H_4–Cl(2) (**2d**)	**4c**	98
4	C_6H_5 (**1a**)	C_6H_4–Br(4) (**2e**)	**4d**	89
5	C_6H_5 (**1a**)	C_6H_4–Br(2) (**2f**)	**4e**	82
6	C_6H_5 (**1a**)	C_6H_3–Cl_2(3,4) (**2h**)	**4f**	88
7	C_6H_4–Me(4) (**1b**)	C_6H_5 (**2a**)	**4g**	98
8	C_6H_4–OMe(4) (**1c**)	C_6H_5 (**2a**)	**4h**	97
9	C_6H_4–Cl(4) (**1d**)	C_6H_5 (**2a**)	**4i**	90
10	C_6H_4–Br(4) (**1e**)	C_6H_5 (**2a**)	**4j**	99
11	2-Thienyl (**1f**)	C_6H_5 (**2a**)	**4k**	95
12	2-Furyl (**1g**)	C_6H_5 (**2a**)	**4l**	90

a) All reactions were carried out under reflux for 2 h in toluene. **1**:**2**:BF_3–OEt_2 = 1:2.75:1. b) Isolated yield.

reactions of *o*-substituted aromatic amines with ketene dithioacetals gave poor results. *o*-Substituted aryl amines (entries 4 and 6) reacted with **1a** to give the corresponding *S,N*-acetals, no other product being detected in the reaction mixture. A variety of α-oxoketene dithioacetals (**1b**—**g**) also reacted with **2a**, **c**, **d** and **g** in the presence of a catalytic amount of BF_3–OEt_2 to give ketene *S,N*-acetals (**3g**—**o**) in good yields (entries 7—15). The geometrical configuration of **3** was established by the infrared (IR) spectra.[9] Absorption bands assignable to hydrogen-bonded carbonyls were present in the IR spectra.

When a stoichiometric amount of BF_3–OEt_2 was used, borate complexes (**4a**—**l**) were obtained in excellent yields as shown in Table III. The products are very stable crystals which can be recrystallized from methanol to give the pure compounds. For the preparation of these complexes, 2.75-fold molar excess of amine was required.

In conclusion, Lewis acid-promoted displacement reaction of α-oxoketene dithioacetals with aromatic amines was found to be an efficient and useful method of synthesis of α-oxoketene *S,N*-acetals. This reaction may be applied to the preparation of various ketene *S,N*-acetals bearing acyl groups and alkoxycarbonyl groups.

Experimental

All melting points were determined in a capillary tube and are uncorrected. Infrared (IR) spectra were recorded in potassium bromide pellets on a JASCO IRA-2 spectrometer and ultraviolet (UV) absorption spectra were determined in 95% ethanol on a Hitachi EP-S2 spectrometer. Nuclear magnetic resonance (NMR) spectra were obtained on JNM-PS-100 (100 MHz) and JNM-FX-90Q (90 MHz) spectrometer with tetramethylsilane as an internal standard. Mass spectra (MS) were recorded on a JEOL01SG mass spectrometer.

Synthesis of α-Oxoketene *S,N*-Acetals A solution of 1.0 mmol of an α-oxoketene dithioacetal (**1**), 1.5 mmol of an aromatic amine (**2**), 0.1 mmol of BF_3–OEt_2 in 8 ml of dry toluene was refluxed for 2 h. After cooling, the reaction mixture was washed with 10 ml of 10% hydrochloric acid and 20 ml of water, then dried over anhydrous sodium sulfate. The organic layer was chromatographed on an alumina (20 g) column using toluene as an eluent. The solvent was evaporated to leave the corresponding almost pure α-oxoketene *S,N*-acetal (**3a**—**o**), which was recrystallized from an appropriate solvent.

(*E*)-3-Methylthio-1-phenyl-3-(phenylamino)prop-2-en-1-one (3a) Pale yellow needles, mp 58 °C [lit. 5, mp 58 °C], yield 91%. ^{1}H-NMR ($CDCl_3$) δ: 2.44 (3H, s, SMe), 5.89 (1H, s, 2-H), 7.22—7.51 (8H, m, phenyl-H), 7.85—7.96 (2H, m, phenyl-H).

(*E*)-3-(4-Methylphenyl)amino-3-methylthio-1-phenylprop-2-en-1-one (3b) Yield 84%. An analytical sample was recrystallized from methanol to give pale yellow needles, mp 117 °C. IR ν_{max}^{KBr} cm^{-1}: 3000 (NH), 1595, 1560, 1463. UV λ_{max}^{EtOH} nm (log ε): 250 (4.10), 358 (4.41). ^{1}H-NMR ($CDCl_3$) δ: 2.36 (3H, s, 4-Me), 2.42 (3H, s, SMe), 5.86 (1H, s, 2-H), 7.18 (5H, s, phenyl-H), 7.35—7.51 (3H, m, phenyl-H), 7.84—7.95 (2H, m, phenyl-H), 13.37 (1H, br s, NH). *Anal.* Calcd for $C_{17}H_{17}NOS$: C, 72.05; H, 6.05; N, 4.94; S, 11.31. Found: C, 72.05; H, 6.03; N, 5.02; S, 12.15.

(*E*)-3-(4-Chlorophenyl)amino-3-methylthio-1-phenylprop-2-en-1-one (3c) Yield 94%. An analytical sample was recrystallized from methanol to give pale yellow needles, mp 120 °C [lit. 5, mp 116—117 °C]. IR ν_{max}^{KBr} cm^{-1}: 3050 (NH), 1620, 1560, 1530,1462. UV λ_{max}^{EtOH} nm (log ε): 255 (4.11), 359 (4.44). ^{1}H-NMR ($CDCl_3$) δ: 2.45 (3H, s, SMe), 5.89 (1H, s, 2-H), 7.19—7.50 (7H, m, phenyl-H), 7.83—7.95 (2H, m, phenyl-H), 13.47 (1H, br s, NH).

(*E*)-3-(2-Chlorophenyl)amino-3-methylthio-1-phenylprop-2-en-1-one (3d) Yield 98%. An analytical sample was recrystallized from ethanol to give pale yellow prisms, mp 135 °C. IR ν_{max}^{KBr} cm^{-1}: 3055 (NH), 1590, 1560, 1485. UV λ_{max}^{EtOH} nm (log ε): 250 (3.95), 352 (4.39). ^{1}H-NMR ($CDCl_3$) δ: 2.44 (3H, s, SMe), 5.95 (1H, s, 2-H), 7.15—7.57 (7H, m, phenyl-H), 7.83—7.98 (2H, m, phenyl-H), 13.42 (1H, br s, NH). *Anal.* Calcd for $C_{16}H_{14}ClNOS$: C, 63.26; H, 4.67; N, 4.61; S, 10.55. Found: C, 63.22; H, 4.65; N, 4.58; S, 10.58.

(*E*)-3-(4-Bromophenyl)amino-3-methylthio-1-phenylprop-2-en-1-one (3e) Yield 77%. An analytical sample was recrystallized from ethanol to give pale yellow needles, mp 120 °C. IR ν_{max}^{KBr} cm^{-1}: 3050 (NH), 1582, 1550, 1460. UV λ_{max}^{EtOH} nm (log ε): 262 (4.18), 360 (4.45). ^{1}H-NMR ($CDCl_3$) δ: 2.45 (3H, s, SMe), 5.85 (1H, s, 2-H), 7.19 (2H, d, J=8.8 Hz, phenyl-H), 7.49 (2H, d, J=8.8 Hz, phenyl-H), 7.27—7.54 (3H, m, phenyl-H), 7.84—7.95 (2H, m, phenyl-H), 13.46 (1H, br s, NH). *Anal.* Cacld for $C_{16}H_{14}BrNOS$: C, 55.18; H, 4.05; N, 4.02; S, 9.21. Found: C, 55.10; H, 4.01; N, 4.00; S, 9.11.

(*E*)-3-(2-Bromophenyl)amino-3-methylthio-1-phenylprop-2-en-1-one (3f) Yield 62%. An analytical sample was recrystallized from methanol to give pale yellow needles, mp 115 °C. IR ν_{max}^{KBr} cm^{-1}: 3055 (NH), 1590, 1560, 1483. UV λ_{max}^{EtOH} nm (log ε): 250 (4.02), 349 (4.42). ^{1}H-NMR ($CDCl_3$) δ: 2.44 (3H, s, SMe), 5.80 (1H, s, 2-H), 7.02—7.70 (7H, m, phenyl-H), 7.88—7.94 (2H, m, phenyl-H), 13.37 (1H, br s, NH). *Anal.* Calcd for $C_{16}H_{14}BrNOS$: C, 55.18; H, 4.05; N, 4.02; S, 9.21. Found: C, 55.15; H, 4.01; N, 4.08; S, 9.32.

(*E*)-1-(4-Methylphenyl)-3-methylthio-3-(phenylamino)prop-2-en-1-one (3g) Yield 85%. An analytical sample was purified on an alumina column using toluene as an eluent to give a pale yellow oil. IR ν_{max}^{KBr} cm^{-1}: 3025 (NH), 1590, 1550, 1465. ^{1}H-NMR ($CDCl_3$) δ: 2.40 (3H, s, 4-Me or SMe), 2.43 (3H, s, SMe or 4-Me), 5.88 (1H, s, 2-H), 7.25—7.37 (7H, m, phenyl-H), 7.81 (2H, d, J=8.3 Hz, phenyl-H), 13.48 (1H, br s, NH). *Anal.* Calcd for $C_{17}H_{17}NOS$: C, 72.05; H, 6.05; N, 4.94; S, 11.31. Found: C, 72.02; H, 6.11; N, 4.76; S, 11.45.

(*E*)-3-Methylthio-3-phenylamino-1-(4-methoxyphenyl)prop-2-en-1-one (3h) Yield 84%. An analytical sample was recrystallized from methanol to give pale yellow prisms, mp 75 °C [lit. 5, mp 66—67 °C]. IR ν_{max}^{KBr} cm^{-1}: 1590, 1560, 1540, 1465, 1250. UV λ_{max}^{EtOH} nm (log ε): 220 (4.14), 276 (4.10), 360 (4.51). ^{1}H-NMR ($CDCl_3$) δ: 2.43 (3H, s, SMe), 3.86 (3H, s, OMe), 5.86 (1H, s, 2-H), 6.93 (2H, d, J=9.0 Hz, phenyl-H), 7.19—7.38 (5H, m, phenyl-H), 7.89 (2H, d, J=9.0 Hz, phenyl-H), 13.42 (1H, br s, NH).

(*E*)-1-(4-Chlorophenyl)-3-methylthio-3-(phenylamino)prop-2-en-1-one (3i) Yield 94%. Pale yellow prisms, mp 84 °C. IR ν_{max}^{KBr} cm^{-1}: 1580, 1555, 1500, 1480, 1104. ^{1}H-NMR ($CDCl_3$) δ: 2.52 (3H, s, SMe), 6.21 (1H, s, 2-H), 7.23—7.52 (7H, m, phenyl-H), 7.92 (2H, d, J=8.9 Hz, phenyl-H), 13.42 (1H, br s, NH). *Anal.* Calcd for $C_{16}H_{14}ClNOS$: C, 63.26; H, 4.67; N, 4.61; S, 10.55. Found: C, 62.96; H, 4.67; N, 4.61; S, 10.57.

(*E*)-1-(4-Bromophenyl)-3-methylthio-3-(phenylamino)prop-2-en-1-one (3j) Yield 81%. Pale yellow prisms, mp 89 °C [lit. 5, mp 85—86 °C]. IR ν_{max}^{KBr} cm^{-1}: 3330 (NH), 1570 (CO). ^{1}H-NMR ($CDCl_3$) δ: 2.48 (3H, s, SMe), 6.01 (1H, s, 2-H), 7.20—7.70 (3H, m, phenyl-H), 7.80 (4H, m, phenyl-H), 8.33 (2H, m, phenyl-H), 13.40 (1H, br s, NH).

(*E*)-3-Methylthio-3-phenylamino-1-thien-2-ylprop-2-en-1-one (3k) Yield 80%. An analytical sample was recrystallized from isopropanol to give yellow prisms, mp 77 °C. IR ν_{max}^{KBr} cm^{-1}: 1550, 1515, 1470. UV λ_{max}^{EtOH} nm (log ε): 266 (4.09), 366 (4.45). ^{1}H-NMR ($CDCl_3$) δ: 2.43 (3H, s, SMe), 5.77 (1H, s, 2-H), 7.08 (1H, dd, J=3.7, 5.0 Hz, 4′-H), 7.20—7.40 (5H, m, phenyl-H), 7.48 (1H, dd, J=1.1, 5.0 Hz, 5′-H), 7.61 (1H, dd, J=1.1, 3.7 Hz,

3′-H), 13.08 (1H, br s, NH). *Anal.* Calcd for $C_{14}H_{13}NOS$: C, 61.06; H, 4.76; N, 5.09; S, 23.29. Found: C, 60.90; H, 4.73; N, 5.11; S, 23.61.

(*E*)-1-(2-Furyl)-3-methylthio-3-(phenylamino)prop-2-en-1-one (3l) Yield 85%. An analytical sample was recrystallized from isopropanol to give pale yellow prisms, mp 98 °C. IR ν_{max}^{KBr} cm^{-1}: 3100 (NH), 1562, 1530, 1490. UV λ_{max}^{EtOH} nm (log ε): 278 (4.08), 368 (4.50). ^{1}H-NMR ($CDCl_3$) δ: 2.44 (3H, s, SMe), 5.87 (1H, s, 2-H), 6.50 (1H, dd, J=1.7, 3.4 Hz, 4′-H), 7.07 (1H, dd, J=0.8, 3.4 Hz, 5′-H), 7.15—7.40 (5H, m, phenyl-H), 7.49 (1H, dd, J=0.8, 1.7 Hz, 3′-H), 13.08 (1H, br s, NH). *Anal.* Calcd for $C_{14}H_{13}NO_2S$: C, 64.84; H, 5.05; N, 5.40; S, 12.36. Found: C, 64.85; H, 5.06; N, 5.36; S, 12.20.

(*E*)-1-(4-Chlorophenyl)-3-(4-chlorophenyl)amino-3-(methylthio)prop-2-en-1-one (3m) Yield 98%. An analytical sample was recrystallized from ethanol to give pale yellow needles, mp 147 °C. IR ν_{max}^{KBr} cm^{-1}: 1585, 1545, 1460. UV λ_{max}^{EtOH} nm (log ε): 260 (4.20), 360 (4.46). ^{1}H-NMR ($CDCl_3$) δ: 2.45 (3H, s, SMe), 5.83 (1H, s, 2-H), 7.17—7.37 (4H, m, phenyl-H), 7.39 (2H, d, J=8.8 Hz, phenyl-H), 7.83 (2H, d, J=8.8 Hz, phenyl-H), 13.44 (1H, br s, NH). *Anal.* Calcd for $C_{16}H_{13}Cl_2NOS$: C, 56.81; H, 3.87; Cl, 20.97; N, 4.14; S, 9.46. Found: C, 56.75; H, 3.90; Cl, 20.90; N, 4.24; S, 9.27.

(*E*)-1-(4-Chlorophenyl)-3-(2-chlorophenyl)amino-3-(methylthio)prop-2-en-1-one (3n) Yield 98%. An analytical sample was recrystallized from isopropanol to give pale yellow needles, mp 94 °C. IR ν_{max}^{KBr} cm^{-1}: 1590, 1562, 1530, 1455. UV λ_{max}^{EtOH} nm (log ε): 260 (4.16), 357 (4.42). ^{1}H-NMR ($CDCl_3$) δ: 2.45 (3H, s, SMe), 5.89 (1H, s, 2-H), 7.17—7.56 (4H, m, phenyl-H), 7.39 (2H, d, J=8.8 Hz, phenyl-H), 7.86 (2H, d, J=8.8 Hz, phenyl-H), 13.37 (1H, br s, NH). *Anal.* Calcd for $C_{16}H_{13}Cl_2NOS$: C, 56.81; H, 3.87; Cl, 20.97; N, 4.14; S, 9.46. Found: C, 56.85; H, 3.96; Cl, 20.92; N, 4.97; S, 9.58.

(*E*)-1-(4-Chlorophenyl)-3-(2,3-dichlorophenyl)amino-3-(methylthio)prop-2-en-1-one (3o) Yield 79%. An analytical sample was recrystallized from ethanol to give pale yellow needles, mp 142 °C. IR ν_{max}^{KBr} cm^{-1}: 3060 (NH), 1595, 1560, 1535, 1470. UV λ_{max}^{EtOH} nm (log ε): 250 (4.18), 355 (4.55). ^{1}H-NMR ($CDCl_3$) δ: 2.46 (3H, s, SMe), 5.97 (1H, s, 2-H), 7.08—7.53 (6H, m, phenyl-H), 7.87—7.97 (2H, m, phenyl-H), 13.44 (1H, br s, NH). *Anal.* Calcd for $C_{16}H_{13}Cl_2NOS$: C, 56.81; H, 3.87; Cl, 20.97; N, 4.14; S, 9.46. Found: C, 56.65; H, 3.93; Cl, 20.69; N, 4.10; S, 9.70.

(*Z*,*Z*)-4-(Difluoroboryl)oxy-2-methylthio-1,4-diphenyl-1-aza-1,3-butadiene (4a) A solution of 0.448 g (2 mmol) of **1a**, 0.466 g (5 mmol) of aniline (**2a**), 0.644 g (4 mmol) of BF_3–OEt_2 in 30 ml of dry toluene was refluxed for 2 h. After removal of the solvent, the residue was washed with 3 ml of isopropanol and recrystallized from methanol to give 0.603 g (95%) of colorless needles, mp 196 °C. IR ν_{max}^{KBr} cm^{-1}: 1590, 1562, 1502, 1482. UV λ_{max}^{EtOH} nm (log ε): 252 (3.82), 340 (4.48). ^{1}H-NMR ($CDCl_3$) δ: 2.52 (3H, s, SMe), 6.24 (1H, s, 3-H), 7.25—7.58 (8H, m, phenyl-H), 7.93—8.04 (2H, m, phenyl-H). MS *m/z*: 317 (M^+, 50), 270 (91), 105 (100), 77 (46), 51 (15). *Anal.* Calcd for $C_{16}H_{14}BF_2NOS$; C, 60.59; H, 4.45; N, 4.42; S, 10.11. Found: C, 60.57; H, 4.62; N, 4.30; S, 10.38.

(*Z*,*Z*)-1-(4-Chlorophenyl)-4-(difluoroboryl)oxy-2-methylthio-4-phenyl-1-aza-1,3-butadiene (4b) This compound was synthesized from **1a** and 4-chloroaniline (**2c**) in 95% yield in a manner similar to that described for the preparation of **4a**. An analytical sample was recrystallized from methanol to give colorless needles, mp 214 °C. IR ν_{max}^{KBr} cm^{-1}: 1592, 1582, 1503, 1485. UV λ_{max}^{EtOH} nm (log ε): 253 (3.79), 344 (4.50). ^{1}H-NMR ($CDCl_3$) δ: 2.53 (3H, s, SMe), 6.24 (1H, s, 3-H), 7.19—7.65 (7H, m, phenyl-H), 7.88—8.02 (2H, m, phenyl-H). *Anal.* Calcd for $C_{16}H_{13}BClF_2NOS$: C, 54.66; H, 3.72; Cl, 10.08; N, 3.98; S, 9.12. Found: C, 54.50; H, 3.82; Cl, 10.05; N, 4.01; S, 9.14.

(*Z*,*Z*)-4-(2-Chlorophenyl)-4-(difluoroboryl)oxy-2-methylthio-1-phenyl-1-aza-1,3-butadiene (4c) This compound was synthesized from **1a** and 2-chloroaniline (**2d**) in 95% yield in a manner similar to that described for the preparation of **4a**. An analytical sample was recrystallized from methanol to give colorless needles, mp 169 °C. IR ν_{max}^{KBr} cm^{-1}: 1590, 1578, 1502, 1490. UV λ_{max}^{EtOH} nm (log ε): 255 (3.74), 344 (4.50). ^{1}H-NMR ($CDCl_3$) δ: 2.57 (3H, s, SMe), 6.28 (1H, s, 3-H), 7.33—7.58 (7H, m, phenyl-H), 7.94—8.05 (2H, m, phenyl-H). *Anal.* Calcd for $C_{17}H_{16}BClF_2NO_2S$: C, 54.66; H, 3.72; Cl, 10.08; N, 3.98; S, 9.12. Found: C, 54.55; H, 3.83; Cl, 10.11; N, 4.01; S, 9.14.

(*Z*,*Z*)-4-(4-Bromophenyl)-4-(difluoroboryl)oxy-2-methylthio-1-phenyl-1-aza-1,3-butadiene (4d) This compound was synthesized from **1a** and 4-bromoaniline (**2e**) in 89% yield in a manner similar to that described for the preparation of **4a**. An analytical sample was recrystallized from methanol to give colorless needles, mp 201 °C. IR ν_{max}^{KBr} cm^{-1}: 1594, 1582, 1502, 1485. UV λ_{max}^{EtOH} nm (log ε): 250 (3.83), 345 (4.52). ^{1}H-NMR ($CDCl_3$) δ: 2.53 (3H, s, SMe), 6.24 (1H, s, 3-H), 7.18 (2H, d, J=8.8 Hz, phenyl-H), 7.39—7.65 (3H, m, phenyl-H), 7.57 (2H, d, J=8.8 Hz, phenyl-H), 7.65—8.02 (2H, m, phenyl-H). *Anal.* Calcd for $C_{17}H_{16}BBrF_2NOS$: C, 48.52; H, 3.31; N, 3.54; S. 8.10. Found: C, 48.46; H, 3.35; N, 3.54; S, 8.12.

(*Z*,*Z*)-1-(2-Bromophenyl)-4-(difluoroboryl)oxy-2-methylthio-4-phenyl-1-aza-1,3-butadiene (4e) This compound was synthesized from **1a** and 2-bromoaniline (**2f**) in 82% yield in a manner similar to that described for the preparation of **4a**. An analytical sample was recrystallized from methanol to give colorless needles, mp 188 °C. IR ν_{max}^{KBr} cm^{-1}: 1590, 1550, 1502, 1484. UV λ_{max}^{EtOH} nm (log ε): 255 (3.75), 345 (4.49). ^{1}H-NMR ($CDCl_3$) δ: 2.57 (3H, s, SMe), 6.29 (1H, s, 3-H), 7.16—7.73 (7H, m, phenyl-H), 7.93—8.06 (2H, m, phenyl-H). *Anal.* Calcd for $C_{16}H_{13}BBrF_2NOS$: C, 48.52; H, 3.31; N, 3.54; S, 8.10. Found: C, 48.51; H, 3.32; N, 3.54; S, 8.17.

(*Z*,*Z*)-4-(3,4-Dichlorophenyl)-4-(difluoroboryl)oxy-2-methylthio-1-phenyl-1-aza-1,3-butadiene (4f) This compound was synthesized from **1a** and 3,4-dichloroaniline (**2h**) in 88% yield in a manner similar to that described for the preparation of **4a**. An analytical sample was recrystallized from methanol to give colorless needles, mp 201 °C. IR ν_{max}^{KBr} cm^{-1}: 1590, 1578, 1500, 1482. UV λ_{max}^{EtOH} nm (log ε): 250 (3.85), 340 (4.50). ^{1}H-NMR ($CDCl_3$) δ: 2.55 (3H, s, SMe), 6.25 (1H, s, 3-H), 7.16 (1H, dd, J=2.4, 8.5 Hz, phenyl-H), 7.91—8.02 (2H, m, phenyl-H). *Anal.* Calcd for $C_{16}H_{12}BCl_2F_2NOS$: C, 49.65; H, 3.39; N, 3.62; S, 8.28. Found: C, 49.86; H, 3.20; N, 3.66; S, 8.31.

(*Z*,*Z*)-4-(Difluoroboryl)oxy-4-(4-methylphenyl)-2-methylthio-1-phenyl-1-aza-1,3-butadiene (4g) This compound was synthesized from **1b** and aniline in 98% yield in a manner similar to that described for the preparation of **4a**. An analytical sample was recrystallized from methanol to give colorless needles, mp 212 °C. IR ν_{max}^{KBr} cm^{-1}: 1580, 1555, 1500, 1480. ^{1}H-NMR ($CDCl_3$) δ: 2.42 (3H, s, 4-Me), 2.49 (3H, s, SMe), 6.20 (1H, s, 3-H), 7.21—7.48 (5H, m, phenyl-H), 7.35 (2H, d, J=8.4 Hz, phenyl-H), 7.87 (2H, d, J=8.4 Hz, phenyl-H). *Anal.* Calcd for $C_{17}H_{16}BF_2NOS$: C, 61.65; H, 4.87; N, 4.23; S, 9.68. Found: C, 61.59; H, 5.00; N, 4.23; S, 9.82.

(*Z*,*Z*)-4-(Difluoroboryl)oxy-2-methylthio-4-(4-methoxyphenyl)-1-phenyl-1-aza-1,3-butadiene (4h) This compound was synthesized from **1c** and aniline in 98% yield in a manner similar to that described for the preparation of **4a**. An analytical sample was recrystallized from methanol to give colorless needles, mp 220 °C. IR ν_{max}^{KBr} cm^{-1}: 1602, 1590, 1560, 1490. UV (EtOH, insufficient solubility) λ_{max} nm: 238, 277, 358; λ_{min} nm: 250, 296. ^{1}H-NMR ($CDCl_3$) δ: 2.50 (3H, s, SMe), 3.88 (3H, s, OMe), 6.15 (1H, s, 3-H), 6.96 (2H, d, J=9.0 Hz, phenyl-H), 7.23—7.48 (5H, m, phenyl-H), 7.95 (2H, d, J=9.0 Hz, phenyl-H). *Anal.* Calcd for $C_{17}H_{16}BF_2NO_2S$: C, 58.81; H, 4.64; N, 4.03; S, 9.24. Found: C, 58.46; H, 4.67; N, 4.04; S, 9.34.

(*Z*,*Z*)-4-(4-Chlorophenyl)-4-(difluoroboryl)oxy-2-methylthio-1-phenyl-1-aza-1,3-butadiene (4i) This compound was synthesized from **1d** and aniline in 98% yield in a manner similar to that described for the preparation of **4a**. An analytical sample was recrystallized from methanol to give colorless needles, mp 184 °C. IR ν_{max}^{KBr} cm^{-1}: 1580, 1555, 1500, 1480. UV λ_{max}^{EtOH} nm (log ε): 260 (3.81), 344 (4.39). ^{1}H-NMR ($CDCl_3$) δ: 2.50 (3H, s, SMe), 3.88 (3H, s, OMe), 6.20 (1H, s, 3-H), 7.22—7.52 (5H, m, phenyl-H), 7.42 (2H, d, J=8.8 Hz, phenyl-H), 7.90 (2H, d, J=8.8 Hz, phenyl-H). *Anal.* Calcd for $C_{17}H_{16}BClF_2NO_2S$: C, 54.66; H, 3.72; N, 3.98; S, 9.12; Cl, 10.08. Found: C, 54.48; H, 3.90; N, 3.94; S, 9.11; Cl, 10.15.

(*Z*,*Z*)-4-(4-Bromophenyl)-4-(difluoroboryl)oxy-2-methylthio-1-phenyl-1-aza-1,3-butadiene (4j) This compound was synthesized from **1e** and aniline in 98% yield in a manner similar to that described for the preparation of **4a**. An analytical sample was recrystallized from methanol to give colorless needles, mp 195 °C. IR ν_{max}^{KBr} cm^{-1}: 1590, 1558, 1500, 1480. UV λ_{max}^{EtOH} nm (log ε): 263 (3.84), 345 (4.51). ^{1}H-NMR ($CDCl_3$) δ: 2.52 (3H, s, SMe), 6.20 (1H, s, 3-H), 7.23—7.49 (5H, m, phenyl-H), 7.59 (2H, d, J=8.8 Hz, phenyl-H), 7.84 (2H, d, J=8.8 Hz, phenyl-H). *Anal.* Calcd for $C_{17}H_{16}BBrF_2NO_2S$: C, 48.52; H, 3.31; N, 3.54; S, 8.10. Found: C, 48.46; H, 3.37; N, 3.52; S, 8.15.

(*Z*,*Z*)-4-(Difluoroboryl)oxy-2-methylthio-1-phenyl-4-(2-thienyl)-1-aza-1,3-butadiene (4k) This compound was synthesized from **1f** and aniline in 98% yield in a manner similar to that described for the preparation of **4a**. An analytical sample was recrystallized from methanol to give colorless needles, mp 182 °C. IR ν_{max}^{KBr} cm^{-1}: 1570, 1512, 1485. UV λ_{max}^{EtOH} nm (log ε): 270 (3.84), 366 (4.53). ^{1}H-NMR ($CDCl_3$) δ: 2.48 (3H, s, SMe), 6.08 (1H, s, 3-H), 7.14 (1H, dd, J=1.3, 5.0 Hz, 4′-H), 7.22—7.52 (5H, m, phenyl-H), 7.59 (1H, dd, J=1.3, 5.0 Hz, 5′-H), 7.80 (1H, d, J=1.3, 3.8 Hz, 3′-H). *Anal.* Calcd for $C_{14}H_{12}BF_2NOS_2$: C, 52.03; H, 3.74; N, 4.33; S, 19.84. Found: C, 51.90; H, 3.86; N, 4.42; S, 20.08.

(*Z*,*Z*)-4-(Difluoroboryl)oxy-4-(2-furyl)-2-methylthio-1-phenyl-1-aza-1,3-butadiene (4l) This compound was synthesized from **1g** and aniline in 98% yield in a manner similar to that described for the preparation of **4a**. An analytical sample was recrystallized from methanol to give colorless needles, mp 221 °C. IR ν_{max}^{KBr} cm^{-1}: 1608, 1542, 1500. UV λ_{max}^{EtOH} nm (log ε):

277 (3.75), 357 (4.58). ^{1}H-NMR ($CDCl_3$) δ: 2.50 (3H, s, SMe), 6.20 (1H, s, 3-H), 6.59 (1H, dd, J=1.8, 3.5 Hz, 4′-H), 7.22—7.52 (6H, m, phenyl-H, 5′-H)), 7.58 (1H, dd, J=0.7, 1.5 Hz, 3′-H). *Anal.* Calcd for $C_{14}H_{12}BF_2NO_2S$: C, 54.75; H, 3.94; N, 4.56; S, 10.44. Found: C, 54.80; H, 3.99; N, 4.70; S, 10.61.

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