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BF_3-promoted cyclization reaction of imines and salicylaldehyde with silyl enol ethers: unexpected formation of dioxaspiro compounds

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ABSTRACT

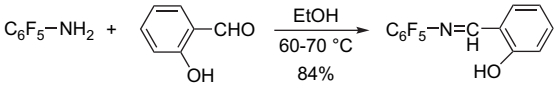
Unexpected spiro cyclic products were formed from the reaction of imines and salicylaldehyde with silyl enol ethers in the presence of $BF_3 \cdot OEt_2$. Different kinds of dioxaspiro products were afforded depending on the nature of starting materials. Furthermore, salicylaldehyde could also react directly with several silyl enol ethers, giving three products with different spiro cyclic structure under the same reaction conditions.

1. Introduction

β-Amino carbonyls are key structural units in biologically relevant compounds such as β-lactams and β-amino acids, and were efficiently synthesized by addition reaction of silyl enolates to imines promoted by Lewis acid.[1] In these reactions, equimolar amount of Lewis acid is usually required as a promoter due to stronger basicity of nitrogen in the imines. Since the less reactivity of imines comparing to corresponding ketone moiety, nucleophilic addition to imines have been less extensively studied.[2] Recently, several Mannich-type reactions involving addition of enolate reagents to *N*-aryl imines,[3] *N*-acyl imines,[4] and *N*-phosphinoyl imines[5] have been reported in the literatures. Nevertheless, the use of imines derived from salicylaldehyde and aniline as electrophiles is limited mainly due to the presence of an unprotected active hydroxyl group. To the best of our knowledge, only few precedents concerning the reaction of silyl enolates with salicyl imines bearing a protected hydroxyl group were reported, affording usual addition–elimination products.[6] More recently, we have described an unusual formation of spiro or fused cyclic compounds from the reaction of fluorine-containing push–pull alkene with silyl enol ethers in the presence of $BF_3 \cdot OEt_2$.[7] To expand this reaction, herein, we wish to report a novel $BF_3 \cdot OEt_2$-promoted cyclization reaction from imines and salicylaldehyde with silyl enol ethers, different kinds of dioxaspiro compounds could be generated in this way.

2. Results and discussion

Imine **1** was easily prepared from the direct condensation of salicylaldehyde and pentafluoroaniline with good yield (Scheme 1).

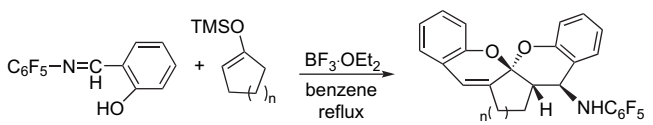


1

Scheme 1. Preparation of imine **1**.

Generally, hydroxyl is considered as an active functional group, which could easily react with catalysts such as $TiCl_4$ and $BF_3 \cdot OEt_2$, and need to be protected before conducting the reaction. However, we were pleased to find that imine **1** could react directly with five-membered silyl enol ether **2a** in benzene under reflux and afford an unexpected spiro cyclic product **3a** in 42% yield (Table 1, entry 1). From its ^1H and ^{19}F NMR spectra, it was clear that a pentafluorophenylamino moiety was still contained in the molecular structure. The spiro structure was further confirmed by X-ray single crystal diffraction analysis (Fig. 1). There exists a strong intramolecular hydrogen bonding between N1–H2 and O2 ($d_{N1-H2\cdots O2}$= 2.211 Å, $\angle_{N1-H2-O2}$=137.0°) together with a weak intramolecular hydrogen bonding ($d_{N1-H2\cdots F1}$=2.303 Å, $\angle_{N1-H2-F1}$= 106.9°) between N1–H2 and F1. Furthermore, the torsion angle

Table 1
Reaction results of imine **1** with silyl enol ether **2**[a]



1 **2** **3**

Entry	*n*	**2**	Time (d)	Product **3**	Yield[a] (%)
1	1	**2a**	3	**3a**	42
2	3	**2c**	2	**3c**	58

[a] Isolated yield.

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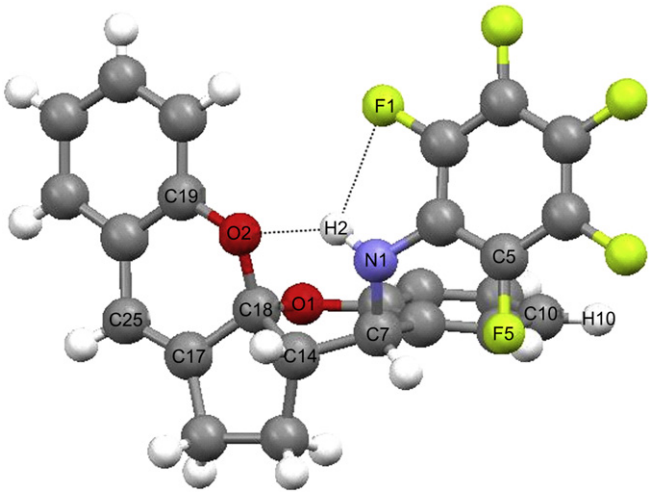


Figure 1. Molecular structure of **3a** ($d_{N1-H2\cdots O2}$=2.211 Å, $\angle_{N1-H2-O2}$=137.0°; $d_{N1-H2\cdots F1}$=2.303 Å, $\angle_{N1-H2-F1}$=106.9°).

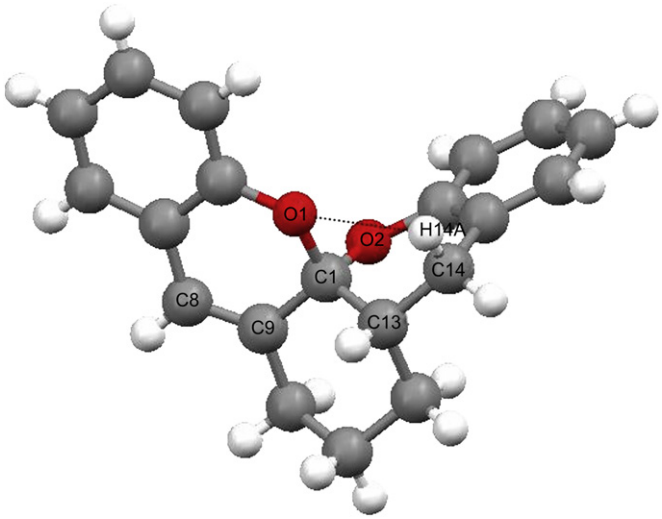
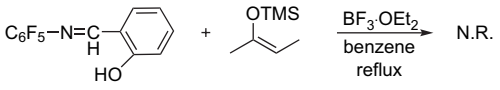


Figure 2. Molecular structure of **4** (C8–C9=1.330 Å, C13–C14=1.526 Å).

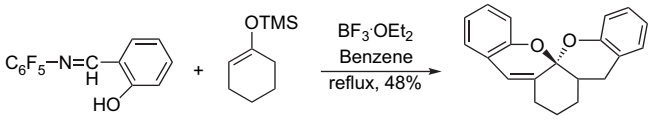
of $\angle_{N1-C7-C14-H14}$ is only 42°, and the pentafluorophenylamino group and H14 adopts a *syn*-configuration. It should be noted that product **3a** is very stable even being heated to 200 °C for 24 h without any elimination of pentafluoroamido group and ring-opening reaction happened. We envisioned that the stability of this configuration could be attributed from the intramolecular hydrogen bonding effect. Subsequently, treatment of seven-membered silyl enol ether **2c** with **1** also successfully afforded a similar spiro cyclic product **3c** in 58% yield (Table 1, entry 2), whereas no reaction was observed between **1** and open-chained trimethyl(pent-2-en-3-yloxy)silane **2d** under the same reaction conditions (Scheme 2).



1 2d

Scheme 2. Reaction of **1** with open-chained trimethyl(pent-2-en-3-yloxy)silane.

Unexpectedly, when six-membered silyl enol ether **2b** was employed to react with **1** under the same reaction conditions, a spiro cyclic product **4** was isolated without pentafluoroaniline moiety attached (Scheme 3). The molecular structure was finally confirmed by X-ray single crystal diffraction analysis with a saturated carbon–carbon bond (C_{13}–C_{14}=1.526 Å) (Fig. 2).



1 2b 4

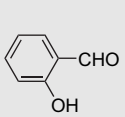
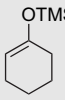
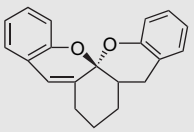
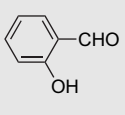
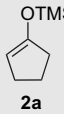
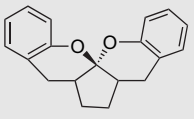
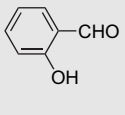
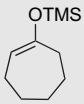
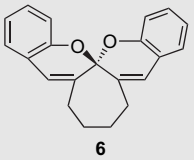
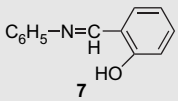
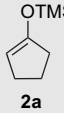
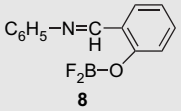
Scheme 3. Preparation of spiro compound **4**.

To investigate the plausible reaction pathway, the reaction of salicylaldehyde with **2b** was conducted and found that the same spiro cyclic product **4** was obtained in 68% yield under the same reaction conditions (Table 2, entry 1), which implied that the reaction might undergo a salicylaldehyde intermediate. Thus, we hypothesized that imine **1** decomposed gradually during the reaction to give salicylaldehyde, which reacted with silyl enol ether **2b** subsequently to afford the final product **4**.

Consequently, other two silyl enol ethers **2a** and **2c** were employed to investigate the reaction of salicylaldehyde (Table 2, entries 2 and 3). Compound **5** containing two saturated C–C bonds was isolated from the reaction of salicylaldehyde and five-membered **2a**. In its ^{1}H NMR spectrum, eight phenyl H signals were distributed in low field and another eight aliphatic H signals distributed in high field (Table 2, entry 2). In addition, compound **5** was found to possess an absolute symmetrical configuration from the ^{13}C NMR spectrum, and three C signals (41.52, 31.47, and 28.22 ppm) were assigned to six aliphatic carbon atoms. However, the normal addition–elimination product **6** was given in good yield from seven-membered **2c** (Table 2, entry 3). Furthermore, a hydrocarbonic analogue of imine **1** was studied and found that the difluoroboryl derivative **8** was formed in almost quantitative yield instead of spiro cyclic compound **3** (Table 2, entry 4).

The plausible mechanism for the formation of **3** was proposed according to our former work on fluorinated push–pull alkene with silyl enolates (Scheme 3).[7] Imine **1** underwent a similar $BF_3\cdot Et_2O$-catalyzed nucleophilic addition reaction with silyl enol ethers to

Table 2
Reaction of salicylaldehyde with silyl enol ethers **2a**–**c**[a]

Entry	Reactant	Silyl enol ether	Product	Yield[b] (%)
1				68
2				34
3				67
4				96

[a] Reaction condition: $BF_3\cdot OEt_2$, benzene, reflux.
[b] Isolated yields.

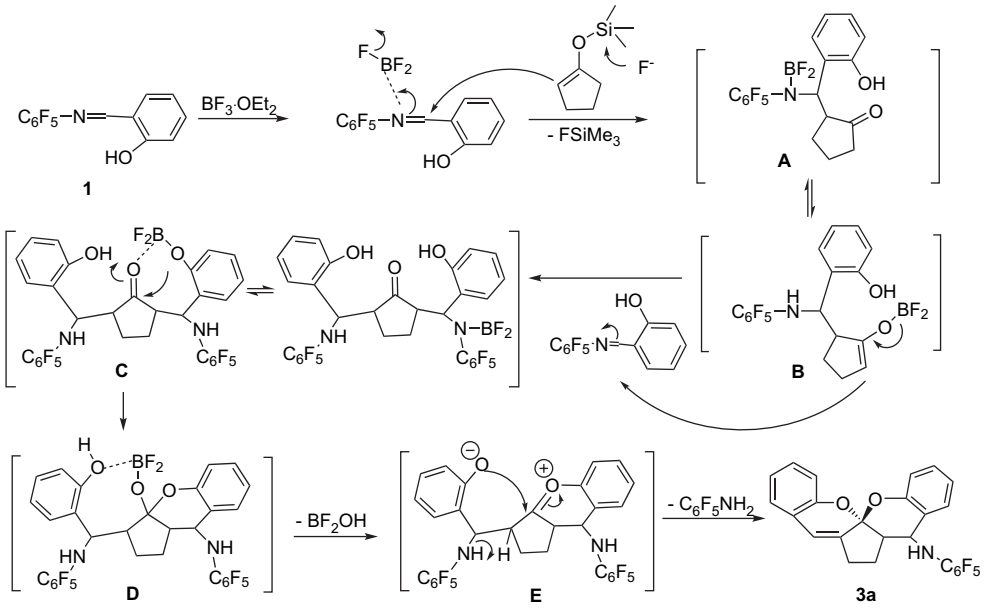


Figure 3. Plausible mechanism for the formation of **3**.

give intermediate **A**, which is in equilibrium with an intermediate **B**. The formed intermediate **B** was then attacked by another **1** to form neutral intermediate **C**, which could undergo further cyclization reaction to form a ketal intermediate **D**, which could continually eliminate a molecule of pentafluoroaniline and BF_2OH followed by second cyclization reaction to give the final spiro product **3a**. However, the detailed mechanism for the formation of compounds **4** and **5** is not clear at this time. Studies aimed at elucidating the mechanism of this transformation are under investigation in our laboratory and will be reported in due course (Fig. 3).

3. Conclusion

We have reported an unexpected formation of dioxaspiro compounds from imines and salicylaldehyde with silyl enol ethers in the presence of $BF_3{\cdot}OEt_2$. Fluorine-containing spiro products were given from the reaction of fluorine-containing imines with five- and seven-membered silyl enol ethers, however, pentafluoroaniline-emitted product was resulted when six-membered silyl enol ether was employed. The normal addition–elimination product was afforded from salicylaldehyde and seven-membered silyl enol ether, whereas two unique spiro cyclic products were obtained, respectively, from five- and six-membered silyl enol ethers.

4. Experimental

4.1. General

Melting points are measured on a Temp-Melt. apparatus and are uncorrected. ^1H, ^{13}C, and ^{19}F NMR spectra were recorded on Bruker AM-300 instruments with Me_4Si and $CFCl_3$ as the internal and external standards, respectively. FTIR spectra were obtained with a Nicolet AV-360 spectrophotometer. Low resolution mass spectra (LRMS) or high resolution mass spectra (HRMS) were obtained on a Finnigan GC–MS 4021 or a Finnigan MAT-8430 instrument using the electron impact ionization technique (70 eV1), respectively. Elemental analyses were performed by this institute. Single crystal X-ray structure analysis was performed on a Bruker P4 instrument.

4.2. Preparation of imine 1

Pentafluoroaniline (1.83 g, 10 mmol) was added into a 50 mL flask containing salicylaldehyde (1.22 g, 10 mmol) and the mixture was heated to reflux overnight. The reaction mixture was purified by recrystallization (hexane/AcOEt) to give the product 2-((perfluorophenylimino)methyl)phenol **1** as a white solid.

4.3. General experimental procedures for reaction of imine 1 with silyl enol ethers

$BF_3{\cdot}Et_2O$ (1.2 mmol) was added dropwise to the mixture of **1** (0.287 g, 1 mmol) and silyl enol ethers (1.2 mmol) in CH_2Cl_2 (5 mL) at 0 °C. Then the mixture was warmed to room temperature slowly. After appropriate time TLC analysis showed that the reaction was over. Water (10 mL) was added to quench the reaction, extracted with CH_2Cl_2 (3×10 mL), and then the organic layer was dried over Na_2SO_4. The residue was purified by column chromatography on silica gel (AcOEt/hexane=1:200) to give the corresponding products **3**.

*4.3.1. Cyclobuta[1,2-b]-2H-chromene-[1,5-b]-N-(perfluorophenyl)-3,4-dihydro-2H-chromen-4-amine **3a***

White solid, mp: 211–214 °C. Yield: 42%. IR (KBr): 3381, 1523, 1485, 999 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 7.31 (1H, d, $^3J_{HH}$=6 Hz, Ph), 7.26–7.18 (3H, m, Ph), 7.02 (2H, t, $^3J_{HH}$=6 Hz, Ph), 6.93 (1H, d, $^3J_{HH}$=8 Hz, Ph), 6.79 (1H, d, $^3J_{HH}$=8 Hz, Ph), 6.55 (1H, s, CH), 4.83 (1H, d, $^3J_{HH}$=11 Hz, NH), 4.72 (1H, d, $^3J_{HH}$=11 Hz, CH), 2.91–2.84 (1H, m, CH_2), 2.75–2.65 (2H, m, CH_2), 2.03–1.98 (1H, m, CH_2), 1.57–1.48 (1H, m, CH_2). ^{13}C NMR (75 MHz, $CDCl_3$): δ 24.2 (C_{21}), 25.7 (C_{20}), 45.1 (C11), 50.9 (C_{12}), 101.4 (C_9), 116.7 (C_{19}), 117.1 (C_{23}), 119.2 (C_1), 120.9 (C_{24}), 121.9 (C_3), 122.2 (C_{28}), 122.5 (C_{18}), 126.7 (C_{13}), 126.8 (C_{25}), 128.5 (C_2), 128.9 (C_{27}), 130.1 (C_6), 130.6 (C_{16}), 135.0 (C_{26}), 135.8 (C_8), 150.1 (C_4), 150.4 (C_{14}). ^{19}F NMR (282 MHz, $CDCl_3$): δ −153.68 to −154.21 (2F, m), −164.73 to −164.82 (2F, m), −170.32 to −170.47 (1F, m). EIMS *m/z* (relative intensity): 287 ($C_6F_4NHCHC_6H_4OH^+$, 6.86), 196 ($C_6F_5NHC^+$, 1.65), 170 ($C_6H_4C_5H_7O^+$, 100). Anal. Calcd for $C_{25}H_{16}F_5NO_2$: C, 65.65; H, 3.53; N, 3.06. Found: C, 65.61; H, 3.55; N, 2.93.

*X-ray data of **3a*** (CCDC no. 653590): $C_{25}H_{16}F_5NO_2$; FW=457.39; temperature 293 K; monoclinic, *P*2(1)/*c*; wavelength 0.71 Å;

a=11.826(3) Å, b=25.095(7) Å, c=6.8451(19) Å, α=90°, β=103.303(5)°, γ=90°; V=1977.0(9) Å^3; Z=4, D_c=1.537 mg/m^3; absorption coefficient 0.129 mm^{-1}; F(000)=936; size 0.298×0.112×0.087 mm; $1.62<\theta<26.49$; reflections collected 11,035; empirical absorption correction; transmission $1.00_{max}-0.823_{min}$; goodness of fit on F^2 0.838; final R indices R_1=0.1472, wR_2=0.0816.

4.3.2. Cyclohepta-[1,2-b]-2H-chromene-[1,7-b]-N-(perfluoro-phenyl)-3,4-dihydro-2H-chromen-4-amine ***3c***

White solid, mp: 185–187 °C. Yield: 58%. IR (KBr): 3389, 2931, 1518, 1487, 932 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.20–7.09 (3H, m, Ph), 7.03–6.96 (2H, m, Ph), 6.90–6.72 (2H, m, Ph), 6.71–6.69 (1H, m, Ph), 6.56 (1H, s, CH), 5.64 (1H, d, $^3J_{HH}$=11 Hz, NH), 4.84 (1H, dd, $^3J_{HH}$=6, 11 Hz, CH), 2.76–2.71 (1H, m, CH), 2.59–2.57 (1H, m, CH_2), 2.50–2.46 (1H, m, CH_2), 2.16–1.96 (4H, m, CH_2), 1.56–1.47 (2H, m, CH_2). ^{13}C NMR (75 M, $CDCl_3$): δ 26.4, 30.5, 32.2, 32.5, 48.7, 54.0, 101.7, 116.3, 116.4, 117.5, 121.6, 122.1, 121.8–122.5, 122.5, 124.2, 126.4–126.5, 126.8, 128.6, 129.1, 129.5–130.3, 149.9, 151.2. ^{19}F NMR (282 MHz, $CDCl_3$): δ −157.76 (2F, d, $^3J_{HH}$=23 Hz), −164.41 (2F, d, $^3J_{HH}$=23 Hz), −171.47 (1F, t, $^3J_{HH}$=23 Hz). EIMS m/z (relative intensity): 287 ($C_6F_4NHCHC_6H_4OH^+$, 15.09), 198 ($C_6H_4C_8H_9O^+$, 100). Anal. Calcd for $C_{27}H_{20}F_5NO_2$: C, 66.80; H, 4.15; N, 2.89. Found: C, 66.81; H, 4.04; N, 2.72.

4.4. General experimental procedures for reaction of salicylaldehyde with silyl enol ethers

$BF_3\cdot Et_2O$ (1.2 mmol) was added dropwise to the mixture of salicylaldehyde (0.122 g 1 mmol) and silyl enol ethers (1.2 mmol) in CH_2Cl_2 (5 mL) at 0 °C. Then the temperature was slowly warmed to room temperature. After appropriate time TLC analysis showed that the reaction was over. Water (10 mL) was added to quench the reaction, extracted with CH_2Cl_2 (3×10 mL), and then the organic layer was dried over Na_2SO_4. The residue was purified by column chromatography on silica gel (AcOEt/hexane=1:200) to give the corresponding products.

4.4.1. 5a,6,7,8-Tetrahydro-5H-chromeno[3,2-d]xanthene ***4***

White solid, mp: 129–131 °C. Yield: 65%. IR (KBr): 2934, 1486, 1456, 1226, 946 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.13–7.06 (4H, m, Ph), 6.93–6.88 (2H, m, Ph), 6.88–6.74 (2H, m, Ph), 6.43 (1H, s, CH=), 3.59 (1H, J=6 Hz, CH), 2.60–2.38 (4H, m, CH_2), 1.66–1.50 (m, 4H, CH_2). ^{13}C NMR (75 MHz, $CDCl_3$): δ 25.0 (C_{21}), 27.3 (C_{22}), 29.0 (C_{20}), 31.5 (C_{12}), 38.9 (C_{11}), 97.7 (C_9), 116.0 (C_{19}), 116.9 (C_{17}), 120.4 (C_{13}), 120.6 (C_2), 121.0 (C_{17}), 121.5 (C_6), 126.0 (C_{18}), 127.3 (C_1), 128.3 (C_5), 129.5 (C_{16}), 133.4 (C_8), 150.9 (C_3), 151.3 (C_{14}). EIMS m/z (relative intensity): 290 (M^+, 31.47), 184 ($C_6H_4C_8H_9O^+$, 100), 77 ($C_6H_5^+$, 10.03). Anal. Calcd for $C_{20}H_{18}O_2$: C, 82.73; H, 6.25. Found: C, 82.75; H, 6.26.

X-ray data of ***4*** (CCDC no. 653589): $C_{20}H_{18}O_2$; FW=290.34; temperature 293 K; triclinic, P-1; wavelength 0.71 Å; a=11.1837(14) Å, b=11.3076(14) Å, c=14.3656(17) Å, α=71.829(2)°, β=89.714(2)°, γ=62.197(2)°; V=1505.3(3) Å^3; Z=4, D_c=1.281 mg/m^3; absorption coefficient 0.081 mm^{-1}; F(000)=616; size 0.506×0.375×0.314 mm; $1.51<\theta<27.00$; reflections collected 8899; absorption correction empirical; transmission $1.00_{max}-0.604_{min}$; goodness of fit on F^2 0.810; final R indices R_1=0.0489, wR_2=0.1037.

4.4.2. Cyclobuta[1,2-b]-2,3,4,5-tetrahydro-2H-chromene-[1,5-b]-3,4-dihydro-2H-chromene ***5***

White solid, mp: 151–152 °C. Yield: 34%. IR (KBr): 2953, 1484, 1457, 1043, 755 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.23–7.11 (4H, m, Ph), 6.95 (2H, t, $^3J_{HH}$=7 Hz, Ph), 6.80 (2H, d, $^3J_{HH}$=7 Hz, Ph), 3.04–2.97 (2H, m, CH_2), 2.64–2.48 (4H, m, CH_2), 2.02–1.97 (2H, m, CH_2), 1.37–1.25 (2H, m, CH_2). ^{13}C NMR (75 MHz, $CDCl_3$): δ 153.15 (C_{10}), 128.55 (C_6), 127.42 (C_8), 123.77 (C_1), 121.66 (C_5), 117.42 (C_7), 109.12 (C_9), 41.52 (C_2), 28.22 (C_4), 27.75 (C_3). EIMS m/z (relative intensity): 278 (M^+, 48.45), 250 ($M^+-C_2H_4$, 0.73), 171 ($M^+-C_7H_7O^+$, 100), 107 ($C_7H_7O^+$, 21.71), 77 ($C_6H_5^+$, 17.80). HRMS for $C_{19}H_{18}O_2$ (%): calcd 278.1307, found 278.1305.

4.4.3. Cyclohepta-[1,2-b]-2H-chromene-[1,7-b]-2H-chromen-4-amine ***6***

White solid, mp: 207–208 °C. Yield: 67%. IR (KBr): 2920, 1486, 1226, 926, 754 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.13 (4H, t, $^3J_{HH}$=7 Hz, Ph), 6.96 (2H, t, $^3J_{HH}$=7 Hz, Ph), 6.79 (2H, d, $^3J_{HH}$=7 Hz, Ph), 6.67 (2H, s, CH=), 2.57 (2H, dd, $^3J_{HH}$=5, 12 Hz, CH_2), 2.40 (2H, t, $^3J_{HH}$=12 Hz, CH_2), 2.05 (2H, t, $^3J_{HH}$=5 Hz, CH_2), 1.53 (2H, t, $^3J_{HH}$=9 Hz, CH_2). ^{13}C NMR (75 MHz, $CDCl_3$): δ 32.3, 33.6, 100.8, 116.4, 120.9, 121.8, 123.6, 126.2, 128.8, 135.4, 149.8. EIMS m/z (relative intensity): 302 (M^+, 100), 285 (M^+-OH, 73.04), 273 ($M^+-C_2H_5^+$, 43.74), 195 ($M^+-C_7H_7O$, 11.97), 107 (C_7H_7O, 8.90), 77 ($C_6H_5^+$, 7.98). Anal. Calcd for $C_{20}H_{18}O_2$: C, 83.42; H, 6.00. Found C, 83.44; H, 6.00.

4.5. Typical procedures for reaction of imine 7[9] with silyl enol ether 2a

$BF_3\cdot Et_2O$ (1.2 mmol) was added dropwise to the mixture of **7** (0.197 g, 1 mmol) and **2a** (1.2 mmol) in CH_2Cl_2 (5 mL) at 0 °C. Then the mixture was slowly warmed to room temperature. After one day TLC analysis showed that the reaction was complete. Water (10 mL) was added to quench the reaction, extracted with CH_2Cl_2 (3×10 mL), and then the organic layer was dried over Na_2SO_4. The residue was purified by column chromatography on silica gel (hexane/AcOEt=200:1) to give the corresponding product **8** in 96% yield.

4.5.1. (E)-N-(2-(Difluoroboryloxy)benzylidene)benzenamine ***8***[10]

Red solid, mp: 230–232 °C. Yield: 92%. ^{1}H NMR ($CDCl_3$): δ 9.16 (1H, s, CH), 7.80 (1H, d, $^3J_{HH}$=7 Hz, Ph), 7.73 (1H, t, $^3J_{HH}$=7 Hz, Ph), 7.63 (2H, d, $^3J_{HH}$=7 Hz, Ph), 7.58–7.49 (3H, m, Ph), 7.14–7.07 (2H, m, Ph). ^{19}F NMR ($CDCl_3$): δ −148.08 (s). MS (m/z, %): 245 (M^+, 7.92), 198 (M^++H-BF_3, 2.22), 105 ($C_6H_5N{=}CH_2^+$, 3.17). IR (KBr): 3048, 1624, 1553, 1385, 1317, 760 cm^{-1}.

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