(Trifluoroacetimidoyl)lithiums and Their Reaction with Electrophiles

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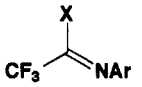
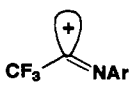
N-Aryltrifluoroacetimidoyl iodides have been lithiated with *n*-butyllithium in ether. Because of the highly ionic nature of a carbon–lithium bond, the imidoyl carbanions are only stable below –60 °C. The reaction temperature, solvent, and steric bulkiness of the *N*-aryl substituents greatly affected alkylation. [*N*-(2,6-dimethylphenyl)trifluoroacetimidoyl]lithium in ether is stable enough to be alkylated and silylated on the imino carbon with electrophiles such as acyl chlorides, aldehydes, ketones, chloroformate, and trimethylsilyl chloride.

Trifluoromethylated compounds are receiving increasing attention in the medicinal, agricultural, and material sciences.[1] The generation of reagents for the trifluoromethylation and fluorination of particular functional groups, in order to prepare trifluoromethyl compounds, is an area of active investigation.[2] The preparation and application of trifluoromethylated synthetic blocks is another approach to the same goal. Promising synthetic blocks must be readily available and multifunctional. *N*-Aryltrifluoroacetimidoyl halides (1, X = Cl; 2, X = Br; 3, X = I) are among the most useful trifluoromethylated synthetic blocks. The halogen of 1–3 can be replaced with various nucleophiles, and the carbon–nitrogen double bond can be used for further functionalization en route to target nitrogen compounds.



1 X = Cl
2 X = Br
3 X = I

Clemence first reported in a patent the reaction of 1 with carbon nucleophiles as a step leading to the syntheses of trifluoromethylated quinoline compounds.[3] Reactions of 1 with carbon and nitrogen nucleophiles were also described by Tanaka[4] and ourselves.[5] The recent development of one-pot syntheses[6] of 1 and 2 has prompted us to further study the chemistry of 1–3. Reactions of 1 with nucleophiles have been described in which 1 behaves as carbocation equivalent 4. However, no reports of the



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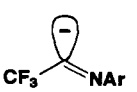

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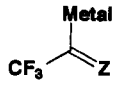
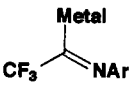


6 Z = CF_2 or CH_2
7 Z = O or NR



8 Metal = Li
9 Metal = Pd

chemistry of imidoyl carbanions have appeared. To determine the full utility of synthetic blocks 1–3, we found it essential to understand their metalation and reactions with electrophiles, in which they act as the carbanion equivalent 5.

Trifluoromethylated vinyl metals 6 have been demonstrated in which the lithium,[7] zinc,[8] silver,[9] and palladium[10] species have been prepared and alkylated with electrophiles specifically at the carbon attached to the metal. However, the organometals 7 in which the metal is attached to the carbon–heteroatom double bond are not known. Recently, we communicated that the imidoylpalladiums 9 are stable even at 60 °C and alkynylated, alkenylated,[11] and carbonylated[12] specifically at the imino carbon. The high covalency of a carbon–palladium bond tends[13] to fix the palladium on the imino carbon. Because of the electronegativity difference between carbon and a heteroatom, the electron density of the carbon–heteroatom double bond localizes on the heteroatom. This implies that in the case of a more ionic bond, such as a carbon–lithium bond, it is questionable whether lithium is located on the imidoyl carbon of 8. In fact, benzoyllithium is in equilibrium with its carbene species.[14] Therefore, it is important to control the reactivity of 8 so as to alkylate

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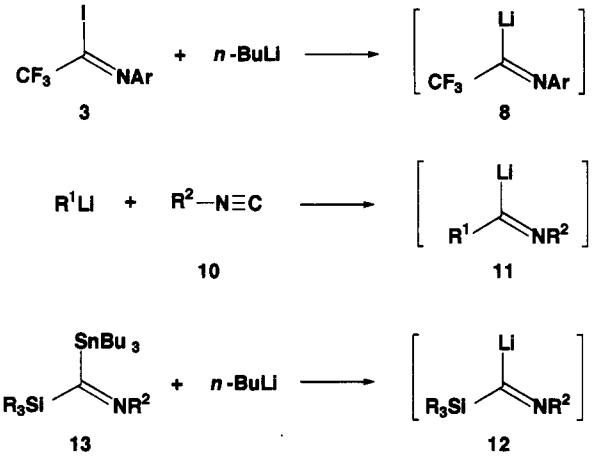
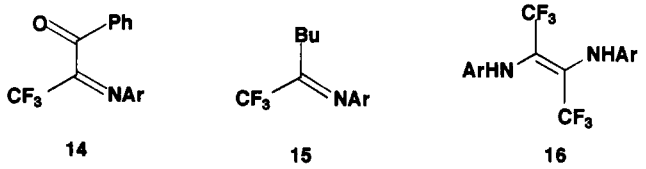
with electrophiles on the imino carbon. This paper describes the generation and chemical properties of the imidoyl lithium 8.[15]



Results and Discussion

Nonfluorinated (acylimidoyl)lithium species 11 and 12 have been prepared by the addition of alkyllithiums to isonitriles[16] and by the lithium–tin exchange reaction[17] of [(2,6-xylylimino)(trialkylsilyl)methyl]stannanes (13). We have tried iodine–lithium exchange between the iodide 3 and *n*-BuLi. Thus, treatment of the iodide 3 with *n*-BuLi in ether at −78 °C cleanly generated the lithium species 8, which was trapped with benzoyl chloride to give 14. In contrast, butylation (substitution of chlorine with a butyl group) proceeded exclusively upon reacting the imidoyl chloride 1 with *n*-BuLi under the same conditions. The same reaction of the bromide 2 gave a mixture of 14 and 15. Iodine–lithium exchange of the iodide 3 is much faster than nucleophilic butylation on the imino carbon, whereas butylation on the imino carbon of the chloride 1 to give 15 is faster than the chlorine–lithium exchange.



The effects of reaction temperature, *N*-aryl substituent, and solvent on benzoylation of the imidoyllithium are summarized in Table 1. The solvent effect was drastic. Ether promoted the benzoylation, but the ethereal solvents THF and DME failed. No 14 was obtained, and the dimer 16 was the major isolable product in THF.

The benzoylation was also markedly affected by the reaction temperature. In particular, the temperature effect is pronounced for 4-substituted compounds. The lithium species of the 4-methoxy compound was benzoylated at −78 °C to give the desired adduct in only 32% yield. At −100 °C, the yield increased to 65%. However, at −60 °C the yield was very poor (6%). The yield decreased sharply with increasing temperature. The same behavior was observed for the 4-methyl compound. The 2-methoxy compound showed the same trend with temperature (Figure 1), but the effect was moderate compared to that of the 4-methoxy compound. The lithium species from the highly substituted 2,6-dimethyl compound is relatively stable in the temperature range of −100 to −60 °C and benzoylated on the imino carbon. The temperature effect clearly reveals that the imino form 8 of the lithium species is stable at around −100 °C regardless of the ring substituents, but it collapses and then dimerizes with increasing temperature. This is particularly pronounced for the 4-substituted compounds.

Substituents on the aryl ring were found to play an important role in the stability of the imidoyllithium. The position of the substituent on the aryl ring rather than its electronic properties most affected benzoylation. Ortho substitution enhanced benzoylation. Comparisons of 2-methoxyphenyl compound **3e** with 4-methoxyphenyl compound **3f** and 2-ethylphenyl compound **3d** with 4-methylphenyl compound **3g** reveal the ortho substitution effect. Particularly noteworthy is the fact that the 2,6-dimethylphenyl group (entry 5 in Table 1) greatly promotes the reaction relative to 3,5-dimethyl and 3,4-dimethylphenyl groups (entries 6 and 7), in spite of the large steric factor presented by the 2,6-dimethyl substituents. In contrast, the corresponding palladium species 9 (Ar = 2,6-dimethylphenyl) reacts with carbon monoxide more slowly than the 4-methylphenyl species 9.[12] This suggests that the

Table 1. Effects of Temperature, Solvent, and Substituent on the Reaction of 3 with Benzoyl Chloride[a]

					yield of 14[b] (%)	
entry	3	Ar	solvent		−78 °C	−100 °C
1	**3a**	2,6-$Me_2C_6H_3$	hexane	**14a**	trace	
2			toluene	**14a**	19	
3			THF	**14a**	0[c]	
4			DME	**14a**	trace	
5			ether	**14a**	62	65
6	**3b**	3,5-$Me_2C_6H_3$	ether	**14b**	36	68
7	**3c**	3,4-$Me_2C_6H_3$	ether	**14c**	33	56
8	**3d**	2-EtC_6H_4	ether	**14d**	43	61
9	**3e**	2-$MeOC_6H_4$	ether	**14e**	55	72
10	**3f**	4-$MeOC_6H_4$	ether	**14f**	32	65
11	**3g**	4-MeC_6H_4	ether	**14g**	*d*	57
12	**3h**	4-ClC_6H_4	ether	**14h**	23	47

[a] **3** (0.31 mmol), *n*-BuLi (1.2 equiv), benzoyl chloride (1.5 equiv) in dry ether (1.5 mL), −78 to −55 °C or −100 to −75 °C. [b] Isolated yield based on **3**. [c] Dimerized product **16** (50% yield) was mainly obtained. [d] A complex mixture of products was obtained, and **14g** could not be isolated.

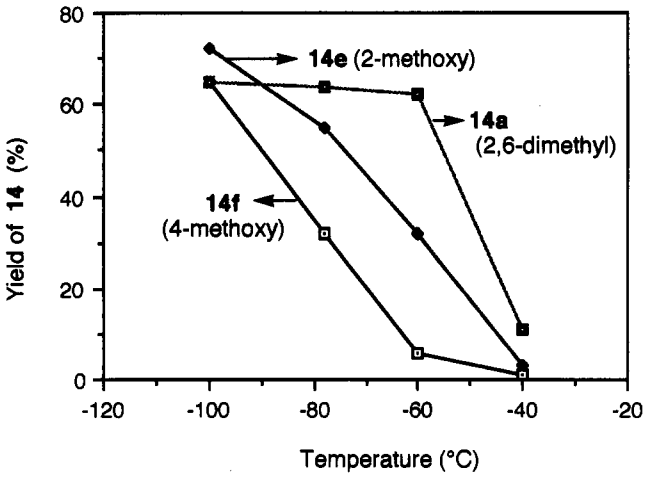


Figure 1. Effect on the reaction temperature to the yields of 14 in benzoylation of 3.

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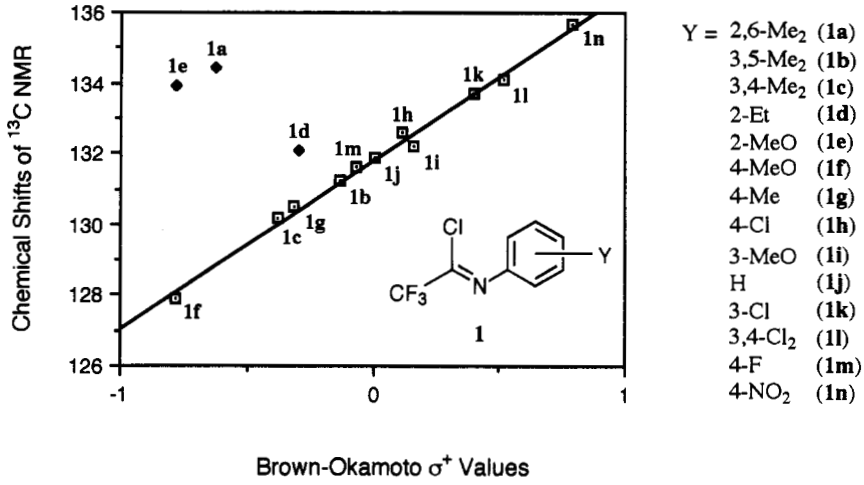
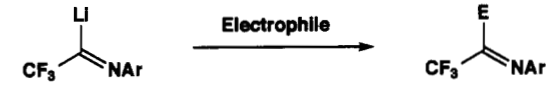


Figure 2. Plot of the ^{13}C-chemical shifts of the imino carbon of **1** versus Brown–Okamoto σ^+ values.

steric effect is more important for the stability of the imidoyllithium than is an electronic effect.

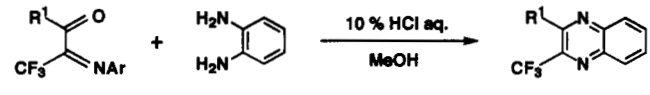
To demonstrate the steric effect, the substituent effect on the ^{13}C NMR chemical shift of the imino sp^2 carbon of **1** was examined in detail. The ^{13}C NMR chemical shifts of the imino sp^2 carbons of **1** are significantly changed by the substituents. The chemical shifts were plotted against Brown–Okamoto σ^+ values,[18] affording a clean, straight line as shown in Figure 2.[19] The good correlation of the chemical shifts with the σ^+ values suggests that the electronic effect of para substituents such as methoxyl and methyl groups is transmitted through resonance to the imino carbon and also that the π-orbital of the C=N bond of the imino group of **1** is coplanar with those of the aryl group. Although there is a linear correlation of the electronic effect with the chemical shifts for para and meta substituents, there exists no such correlation for ortho substituents. The points for the chemical shifts of the 2-methoxy, 2-ethyl, and 2,6-dimethyl compounds significantly deviated from the correlation line. In particular, the deviation of the 2,6-dimethyl compound exceeded the others even though the chemical shifts of the related 3,5-dimethyl and 3,4-dimethyl compounds correlated well with the σ^+ values of the substituents. The large downfield chemical shift of the 2,6-dimethyl compound's resonance reveals that the 2,6-dimethylphenyl group apparently behaves as an electron-withdrawing group even though a methyl group is electron-donating. This fact can be reasonably explained by the noncoplanarity between the π-bond of the C=N bond and that of the aryl ring for 2-substituted compounds and in particular for a 2,6-disubstituted one. Therefore, this noncoplanarity would reflect the stability of the lithium species. The C=N bond of 2,6-dimethyllithium species **8** (Ar = 2,6-dimethylphenyl) would not be conjugated with the aryl ring, leading to fixation of lithium on the imino carbon and to preferencial alkylation on the carbon, by electrophiles.

Nucleophilic reactions of lithium species **8** with various electrophiles were examined to determine the scope and the limitation of the present reaction. Reaction with both aromatic and aliphatic acid chlorides gave the imino ketones in good yields (entries 1–3 in Table 2). Reactions with aromatic aldehydes proceeded efficiently, affording the imino alcohols **22**, **23**, and **24** in excellent yields (entries 4–6) regardless of the electronic nature of the ring substituents. The lithium species **8** also reacted well with hexanal (74%) and α,β-unsaturated aldehydes to give the 1,2-addition products (**26** and **27**). Ketones are less reactive electrophiles and thus reacted more slowly than aldehydes to give adducts in moderate yields along with dimer **16** and some unidentified compounds. The reaction of **3a** with ethyl chloroformate provided the ethoxycarbonylated product **32** in 69% yield. Formylation of **3a** with *N,N*-dimethylformamide did occur but the yield was poor (26%). Nucleophilic ring opening of propylene oxide with **3a** occurred but took longer and yielded only 20% of the desired alcohol. Silylation and stannylation of **3a** with the corresponding silyl chloride and stannyl chloride provided the desired iminosilane and stannane in reasonable yields (entries 12 and 13). Judging from the electrophiles so far examined, the reactive electrophiles are useful in the reaction with **3** because **8** is rather unstable under the reaction conditions. It is recommended that the lithium species are handled at below –60 °C as shown in Figure 1.



8 **20 – 34**

The trifluoroacetimidoyl group is a synthetic equivalent of a trifluoroacetyl group. Thus, α-keto (**14a**, **20**, and **21**) and α-formyl (**33**) imidoyl compounds were transformed to the 2-(trifluoromethyl)-3-substituted quinoxalines[20] **35–38** in quantitative (from **14a** and **20**), 61% (from **3a**),[21] and 26% (from **3a**)[21] yields, respectively, by treatment with 1,2-phenylenediamine in methanol in the presence of 10% hydrochloric acid.



14a	$R^1 = C_6H_5$	Ar = 2,6-dimethylphenyl	**35**
20	$R^1 = 3\text{-}ClC_6H_4$		**36**
21	$R^1 = n\text{-}C_5H_{11}$		**37**
33	$R^1 = H$		**38**

Experimental Section

^{1}H, ^{13}C, and ^{19}F NMR spectra were obtainted in $CDCl_3$ and DMSO-d_6 as indicated. Chemical shifts for ^{1}H and ^{13}C NMR spectra are reported in δ (ppm) downfield form TMS. ^{19}F NMR spectra was obtained using C_6F_6 as an internal standard.

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(19) Chemical shifts of the compounds **1e–1n** were obtained from ref 6.

Table 2. Reaction of 3a (Ar = 2,6-Dimethylphenyl) with Electrophiles[a]

entry	electrophile	E of product	yield[b] (%)
1	PhCOCl	PhCO–	**14a** (62)
2	3-ClC_6H_4COCl	3-ClC_6H_4CO–	**20** (61)
3	*n*-$C_5H_{11}COCl$	*n*-$C_5H_{11}CO$–	**21** (61)[c]
4	PhCHO	PhCH(OH)–	**22** (89)
5	4-ClC_6H_4CHO	4-$ClC_6H_4CH(OH)$–	**23** (81)
6	4-$MeOC_6H_4CHO$	4-$MeOC_6H_4CH(OH)$–	**24** (81)
7	*n*-$C_5H_{11}CHO$	*n*-$C_5H_{11}CH(OH)$–	**25** (74)
8	PhCH=CHCHO	PhCH=CHCH(OH)–	**26** (48)
9	CH_3CH=CHCHO	CH_3CH=CHCH(OH)–	**27** (54)
10	PhCOMe	PhCMe(OH)–	**28** (39)
11			**29** (40)
12	Me_3SiCl	Me_3Si–	**30** (84)
13	*n*-Bu_3SnCl	*n*-Bu_3Sn–	**31** (60)
14	$ClCO_2Et$	EtOCO–	**32** (69)
15	Me_2NCHO	HCO–	**33** (26)[c,d]
16		$CH_3CH(OH)CH_2$–	**34** (20)[e]

[a] **3a** (0.31 mmol), *n*-BuLi (1.2 equiv), electrophile (1.5 equiv) in dry ether (1.5 mL), −78 to −55 °C. [b] Isolated yield based on **3a**. [c] Yield as the derivatives **37** and **38**. Both **21** and **33** are unstable under the conditions of purification through silica gel. [d] Electrophile (10 equiv) was employed. [e] Electrophile (3 equiv) was employed.

Reaction of 2,2,2-Trifluoroacetimidoyl Iodide 3a with Electrophiles. To a solution of *N*-(2,6-dimethylphenyl)-2,2,2-trifluoroacetimidoyl iodide (**3a**) (0.1 g, 0.31 mmol) in dry ether (1 mL) was added dropwise *n*-butyllithium (0.15 mL of 2.5 M hexane solution, 0.37 mmol) under nitrogen at −78 °C, and the solution was stirred for 3 min. Then, benzoyl chloride (0.067 g, 0.46 mmol) dissolved in dry ether (0.5 mL) was added dropwise to the solution. The mixture was stirred for 15 min, while the temperature was allowed to reach −55 °C. The reaction mixture was quenched with water. The ether layer was dried over anhydrous magnesium sulfate, and the solvent was evaporated. The residue was chromatographed over silica gel to give **14a** (0.058 g, 62% yield).

14a: IR (neat) 1680 cm^{-1}; ^{19}F NMR (188 MHz, $CDCl_3$) δ 93.75 (s, 3F, CF_3). Anal. Calcd for $C_{17}H_{14}F_3NO$: C, 66.88; H, 4.62; N, 4.59. Found: C, 67.16; H, 4.45; N, 4.86.

14b: IR (neat) 1676, 1598 cm^{-1}; ^{19}F NMR (188 MHz, $CDCl_3$) δ 93.18 (s, 3F, CF_3). Anal. Calcd for $C_{17}H_{14}F_3NO$: C, 66.88; H, 4.62; N, 4.59. Found: C, 67.14; H, 4.83; N, 4.61.

14c: yellow crystals; mp 60–61 °C. IR (Nujol) 1670 cm^{-1}; ^{19}F NMR (188 MHz, $CDCl_3$) δ 93.35 (s, 3F, CF_3). Anal. Calcd for $C_{17}H_{14}F_3NO$: C, 66.88; H, 4.62; N, 4.59. Found: C, 67.13; H, 4.85; N, 4.29.

14d: IR (neat) 1678 cm^{-1}; ^{19}F NMR (188 MHz, $CDCl_3$), δ 93.48 (s, 3F, CF_3). Anal. Calcd for $C_{17}H_{14}F_3NO$: C, 66.88; H, 4.62; N, 4.59. Found: C, 66.75; H, 4.67; N, 4.61.

14e: IR (neat) 1678, 1596 cm^{-1}; ^{19}F NMR (188 MHz, $CDCl_3$) δ 93.45 (s, 3F, CF_3). Anal. Calcd for $C_{16}H_{12}F_3NO_2$: C, 62.54; H, 3.94; N, 4.56. Found: C, 62.42; H, 4.03; N, 4.85.

14f: IR (neat) 1676, 1598 cm^{-1}; ^{19}F NMR (188 MHz, $CDCl_3$) δ 93.52 (s, 3F, CF_3). Anal. Calcd for $C_{16}H_{12}F_3NO_2$: C, 62.54; H, 3.94; N, 4.56. Found: C, 62.25; H, 4.00; N, 4.70.

14g: yellow crystals; mp 58–59 °C; IR (neat) 1674, 1596 cm^{-1}; ^{19}F NMR (188 MHz, $CDCl_3$) δ 93.26 (s, 3F, CF_3). Anal. Calcd for $C_{16}H_{12}F_3NO$: C, 65.97; H, 4.15; N, 4.81. Found: C, 66.18; H, 4.35; N, 4.64.

14h: IR (neat) 1678 cm^{-1}; ^{19}F NMR (188 MHz, $CDCl_3$) δ 93.16 (s, 3F, CF_3). Anal. Calcd for $C_{15}H_9ClF_3NO$: C, 57.80; H, 2.91; N, 4.50. Found: C, 57.73; H, 3.19; N, 4.20.

16b. Anal. Calcd for $C_{20}H_{20}F_6N_2$: C, 59.70; H, 5.01; N, 6.96. Found: C, 59.97; H, 5.14; N, 6.85.

20: IR (neat) 1684 cm^{-1}; ^{19}F NMR (188 MHz, $CDCl_3$) δ 93.74 (s, 3F, CF_3). Anal. Calcd for $C_{17}H_{13}ClF_3NO$: C, 60.10; H, 3.86; N, 4.12. Found: C, 60.17; H, 3.95; N, 4.35.

22: IR (neat) 3420, 1688 cm^{-1}; ^{19}F NMR (188 MHz, $CDCl_3$) δ 95.42 (s, 3F, CF_3). Anal. Calcd for $C_{17}H_{16}F_3NO$: C, 66.44; H, 5.25; N, 4.56. Found: C, 66.52; H, 5.26; N, 4.72.

23: IR (neat) 3348, 1680 cm^{-1}; ^{19}F NMR (188 MHz, $CDCl_3$) δ 95.52 (s, 3F, CF_3). Anal. Calcd for $C_{17}H_{15}ClF_3NO$: C, 59.74; H, 4.42; N, 4.10. Found: C, 59.85, H, 4.35, N, 4.37.

24: IR (neat) 3432, 1690, 1614 cm^{-1}; ^{19}F NMR (188 MHz, $CDCl_3$) δ 95.14 (s, 3F, CF_3). Anal. Calcd for $C_{18}H_{18}F_3NO$: C, 64.09; H, 5.38; N, 4.15. Found: C, 64.14; H, 5.46; N, 4.15.

25: (as acetate) IR (neat) 1754, 1688 cm^{-1}; ^{19}F NMR (188 MHz, 80 °C, DMSO-d_6) δ 95.16 (s, 3F, CF_3). Anal. Calcd for $C_{18}H_{24}F_3NO_2$: C, 62.96; H, 7.04; N, 4.08. Found: C, 63.11; H, 7.20; N, 3.94.

26: IR (neat) 3416, 1684 cm^{-1}; ^{19}F NMR (188 MHz, DMSO-d_6) δ 96.37 (s, 3F, CF_3). Anal. Calcd for $C_{19}H_{18}F_3NO$: C, 68.46; H, 5.44; N, 4.02. Found: C, 68.39; H, 5.55; N, 4.02.

27: colorless crystals; mp 69–70 °C; IR (Nujol) 3428, 1682 cm^{-1}; ^{19}F NMR (188 MHz, DMSO-d_6) δ 96.55 (s, 3F, CF_3). Anal. Calcd for $C_{14}H_{16}F_3NO$: C, 61.98; H, 5.94; N, 5.16. Found: C, 62.32; H, 6.12; N, 5.41.

28: colorless crystals; mp 79–80 °C; IR (neat) 3420, 1690, 1596 cm^{-1}; ^{19}F NMR (188 MHz, $CDCl_3$) δ 98.66 (s, 3F, CF_3). Anal. Calcd for $C_{18}H_{18}F_3NO$: C, 67.28; H, 5.64; N, 4.36. Found: C, 67.28; H, 5.67; N, 4.30.

29: IR (neat) 3444, 1684 cm^{-1}; ^{19}F NMR (188 MHz, $CDCl_3$) δ 98.53 (s, 3F, CF_3). Anal. Calcd for $C_{16}H_{20}F_3NO$: C, 64.20; H, 6.73; N, 4.68. Found: C, 64.27; H, 6.90; N, 4.68.

30: ^{19}F NMR (188 MHz, $CDCl_3$) δ 93.36 (s, 3F, CF_3). Anal. Calcd for $C_{13}H_{18}F_3NSi$: C, 57.11; H, 6.64; N, 5.13. Found: C, 57.40; H, 6.72; N, 5.34.

31: ^{19}F NMR (188 MHz, $CDCl_3$) δ 92.29 (s, 3F, CF_3). Anal. Calcd for $C_{22}H_{36}F_3NSn$: C, 53.90; H, 7.40; N, 2.86. Found: C, 54.14; H, 7.57; N, 3.00.

32: IR (neat) 1750 cm^{-1}; ^{19}F NMR (188 MHz, $CDCl_3$) δ 92.26 (s, 3F, CF_3); ^{13}C NMR (126 MHz, $CDCl_3$) 13.41, 17.46 (2C), 62.64, 117.97 (q, J_{CF} = 297.2 Hz, CF_3), 124.54, 124.97, 127.70, 127.77 (2C), 145.11, 150.89 (q, J_{CCF} = 36.5 Hz, C), 158.70. Anal. Calcd for $C_{13}H_{14}F_3NO_2$: C, 57.14; H, 5.16; N, 5.13. Found: C, 57.40; H, 5.25; N, 5.33.

34: IR (neat) 3456, 1684 cm^{-1}; ^{19}F NMR (188 MHz, DMSO-d_6) δ 93.17 (s, 3F, CF_3). Anal. Calcd for $C_{13}H_{16}F_3NO$: C, 60.22; H, 6.22; N, 5.40. Found: C, 60.45; H, 6.39; N, 5.33.

Preparation of 2-Phenyl-3-(trifluoromethyl)quinoxaline (35). To a mixture of **14a** (0.050g, 0.164 mmol) and 1,2-phenylenediamine (0.018 g, 0.164 mmol) in MeOH (2.5 mL) was added 10% HCl (aq) (0.5 mL), and then the mixture was stirred for 36 h at room temperature. The reaction mixture was extracted with hexane. The hexane layer was dried over anhydrous magnesium sulfate and concentrated under reduced pressure. Chromatography of the residue over silica gel gave **35** (0.046 g, quant).

35: colorless crystals; mp 115–116 °C; ^{19}F NMR (188 MHz, $CDCl_3$) δ 100.07 (s, 3F, CF_3). Anal. Calcd for $C_{15}H_9F_3N_2$: C, 65.69; H, 3.31; N, 10.22. Found: C, 65.83; H, 3.32; N, 9.92.

36: colorless crystals; mp 122–123 °C; ^{19}F NMR (188 MHz, $CDCl_3$) δ 100.03 (s, 3F, CF_3). Anal. Calcd for $C_{15}H_8ClF_3N_2$: C, 58.36; H, 2.61; N, 9.08. Found: C, 58.46; H, 2.52, N, 9.10.

37: colorless crystals; mp 29–30 °C; ^{19}F NMR (188 MHz, $CDCl_3$) δ 96.83 (s, 3F, CF_3). Anal. Calcd for $C_{14}H_{15}F_3N_2$: C, 62.67; H, 5.64; N, 10.44. Found: C, 62.69; H, 5.60; N, 10.60.

38: colorless crystals; mp 60–61 °C; ^{19}F NMR (188 MHz, $CDCl_3$) δ 94.75 (s, 3F, CF_3). Anal. Calcd for $C_9H_5F_3N_2$: C, 54.55; H, 2.53, N, 14.14. Found: C, 54.80; H, 2.59; N, 13.95.

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(21) Compounds **21** and **33** were too unstable to isolate so that the transformations of **21** and **33** were performed without their isolation. Therefore, the total yields from **3a** are indicated.