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Synthesis of fluorinated imines and carbodiimides from azides via aza-Wittig reaction

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Abstract

The Staudinger reaction of fluoroalkylazides were studied. A series of *N*-fluoroalkylimines were synthesized via aza-Wittig reaction of *N*-fluoroalkyliminophosphoranes. The *N*,*N*′-difluoroalkylated carbodiimide was also synthesized via the reaction of *N*-fluoroalkyliminophosphoranes with carbon dioxide or carbon disulfide.

Keywords: Fluoroalkylazide; *N*-Fluoroalkylimines; *N*-Fluoroalkyliminophosphoranes; *N*,*N*′-Difluoroalkylated carbodiimides; Staudinger reaction; Aza-Wittig reaction

1. Introduction

The Staudinger reaction between triphenylphosphines and alkyl azides [1] is useful in organic synthesis. Since the first report of the synthesis of iminophosphoranes by the reaction of a triary phosphine with organic azides [2], numerous articles have reported on the reactions and synthetic applications of these kind of compounds. They can be used to synthesis of Schift base [3], imidoyl halides [4], isocyanate and isothiocyanate [3,5], and different kind of heterocycles [6].

It has been known for some time that fluorine atom can lead to unexpected results on biological activity arising due to the special properties of the fluorine atom, such as the highest electronegativity of fluorine and high carbon–fluorine bond energy [7]. To the best our knowledge there are very few reports on the synthesis of fluorinated imine, especially for the synthesis of *N*-fluoroalkyl substituted imine. During the course of our study of the synthesis of organofluorine compounds by fluorinated building block strategy, we developed fluorinated alkylazides as the intermediates for synthesis of fluoroalkyl substituted 1,2,3-triazoles [8]. To expand the utility of these fluoroalkylazides, in this paper we would like to report the Staudinger reaction and aza-Wittig reaction of this kind of azides.

2. Results and discussion

The Staudinger reaction of fluoroalkylazide proceeded very smoothly under room temperature and the *N*-fluoroalkyliminophosphoranes **3** was precipitated as a white solid in the reaction mixture. The iminophosphoranes was obtained by direct filtration without further purification (Scheme 1).

With the iminophosphoranes **1** in hand, we then studied it's aza-Wittig reaction with carbonyl compounds. Firstly we used the reaction of **1a** and benzaldehyde as the model reaction, various conditions were studied and the results were listed in Table 1. From the table it was found that when THF was used as solvent, the imine was obtained in 53.8% yield at 50 °C after 2 days. Toluene was the best solvent, the imine could be obtained in 62.3% yield at 80 °C.

The reactions of **3** with different carbonyl compounds were explored under the optimized reaction conditions, the results are shown in Scheme 2 and Table 2.

From the table, it was found that different carbonyl compounds, e.g.: arylaldehydes (entries: 1–4 and 8–11), heterocyclic aldehydes (entries: 5, 6, 12, 13) and benzoyl

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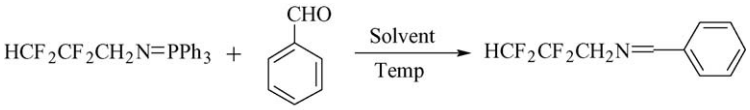
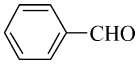
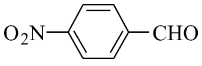
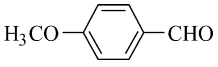
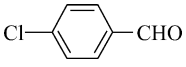
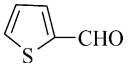
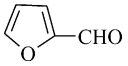
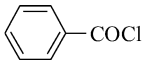
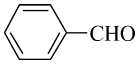
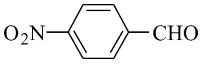
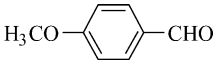
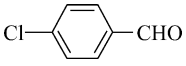
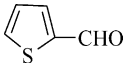
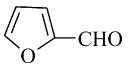
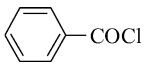
Table 1
aza-Wittig reaction under different conditions



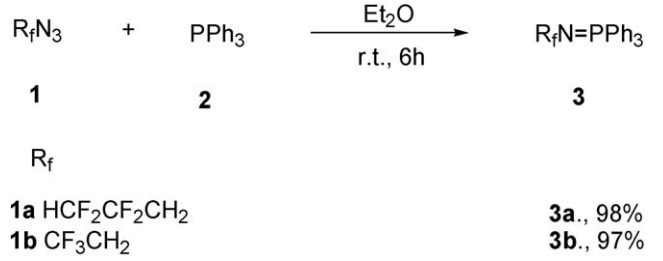
3a **4a** **5aa**

Entry	Solvent	Temperature (°C)	Time (day)	Yield (%)
1	DMSO	80	3	41.5
2	THF	50	2	53.8
3	CH_2Cl_2	r.t.	3	57.2
4	Toluene	80	3	62.3

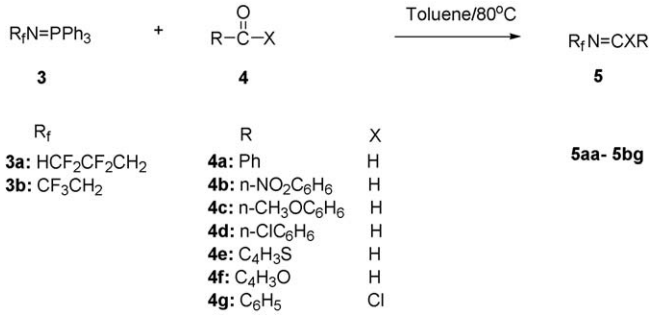
Table 2
Results of the aza-Wittig reaction

Entry	R_f	R^1	Time (day)	Product	Yield[a] (%)
1	$HCF_2CF_2CH_2$		2	**5aa**	61.0
2	$HCF_2CF_2CH_2$		2	**5ab**	78.7
3	$HCF_2CF_2CH_2$		3	**5ac**	64.4
4	$HCF_2CF_2CH_2$		2	**5ad**	65.1
5	$HCF_2CF_2CH_2$		3	**5ae**	62.3
6	$HCF_2CF_2CH_2$		3	**5af**	57.6
7	$HCF_2CF_2CH_2$		2	**5ag**	62.3
8	CF_3CH_2		2	**5ba**	41.3
9	CF_3CH_2		2	**5bb**	82.7
10	CF_3CH_2		3	**5bc**	66.2
11	CF_3CH_2		2	**5bd**	85.7
12	CF_3CH_2		4	**5be**	29.2
13	CF_3CH_2		4	**5bf**	30.3
14	CF_3CH_2		2	**5bg**	78.3

[a] Isolated yield.



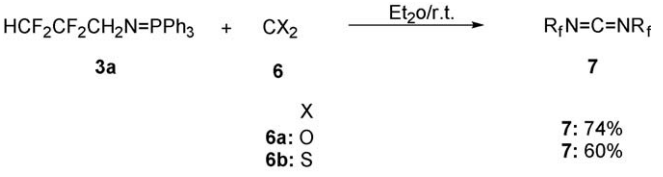
Scheme 1. The Staudinger reaction of fluoroalkylazides.



Scheme 2. The aza-Wittig reaction of *N*-fluoroalkyliminophosphoranes.

chloride (entries: 7, 14) could proceed the aza-Wittig reaction with *N*-fluoroalkyliminophosphoranes **3** smoothly in good to excellent yields. For benzoyl chloride, imidoyl chlorides were obtained as the product. Electron-withdrawing group in the benzene ring would raise the reaction yields (entries 2, 9 versus entries 3, 10). Comparing with the non-fluorinated imines, *N*-fluoroalkylimines were very unstable, they will hydrolyze during flash chromatography in a silica gel column. So all the products were purified by distillation. The imines could also be obtained in one pot reaction started from fluoroalkylazides with no effects on the yield.

This kind of *N*-fluoroalkyliminophosphoranes could also react with carbon dioxide or carbon disulfide. Not as Trabelsl's reported results [5a], in our instance, no isocyanate or isothiocyanate could be obtained, what we obtained was *N*,*N*′-difluoroalkylated carbodiimides **7**. These different results might be due to the difference of the block group between N atom and CF_2 in *N*-fluoroalkyliminophosphoranes. In the Trabelsl's report there are two CH_2 appeared in between N atom and CF_2, while in our research there was only one. The short CH_2 chain made the strong electron-withdrawing effects for the N=P bond which resulted in better reactivity for the *N*-fluoroalkyliminophosphoranes (Scheme 3).



Scheme 3. Preparation of carbodiimide.

3. Conclusion

In conclusion, a series of *N*-fluoroalkylimines were synthesis by the reaction of *N*-fluoroalkyliminophosphoranes with carbonyl compounds, which may be applied in the synthesis fluorinated organic compounds. *N*,*N*′-Difluoroalkylated carbodiimides could also be synthesized by the reaction of *N*-fluoroalkyliminophosphoranes with carbon dioxide or carbon disulfide. Further studies are currently in progress in this lab.

4. Experimental

Unless otherwise noted, solvents and reagents were commercial available and used as received. ^{1}H NMR spectra were recorded on a Brucker AM-300 (300 MHz) spectrometer with Me_4Si as internal standard. ^{19}F NMR spectra were taken on Brucker AM-300 (282 MHz) spectrometer with $CFCl_3$ as external standard, downfield shifts being designed as positive. The ^{13}C NMR spectra were measured at Brucker AM-300 (75 MHz) spectrometer with all protons decoupled, and the chemical shifts are reported in ppm downfield of $SiMe_4$. Mass spectra were taken on a HP 5989a spectrometer, and accurate mass measurements were performed on Finnigan MAT instrument, while elemental analysis were performed by this institute.

*4.1. Typical procedure for the preparation of N-fluoroalkyliminophosphoranes (**3**)*

To a solution of azide (30 mmol) in diethyl ether (20 mL), a solution of PPh_3 (30 mmol) in 30 mL Et_2O was added dropwised. After addition, the mixture was stirred at room temperature for 6 h. A white solid was precipitated in the reaction system. After filtration and dryness afford the product **3**. Without further purification, the solid can be used to following reaction.

*4.1.1. N-(2,2,3,3-Tetrafluoro-propyl)-iminophosphoranes (**3a**)*

Colorless solid; m.p.; 110–111 °C. IR (KBr) (cm^{-1}): 2825, 1143, 1098. ^{1}H NMR ($CDCl_3$) δ 3.54 (2H, q, J = 14.0 Hz, CH_2), 6.34 (1H, tt, J_1 = 6.0 Hz, J_2 = 54.0 Hz, H–C), 7.41–7.67 (15H, m, Ar). ^{19}F NMR ($CDCl_3$) δ −142.06 (2F, d, J_{FF} = 5.4 Hz), −124.79 (2F, m). MS: *m*/*z* (%) 391 (M^+, 7.00), 390 (10.00), 290 (100.00), 262 (10.00), 183 (20.00). Anal. calcd. for $C_{21}H_{18}F_4NP$: C, 64.45; H, 4.64; N, 3.58; P, 7.91. Found: C, 64.59; H, 4.72; N, 3.37; P, 8.04.

*4.1.2. N-(2,2,2-Trifluoro-ethyl)-iminophosphoranes (**3b**)*

Colorless solid; m.p.; 155–156 °C; IR (KBr) (cm^{-1}): 2840, 1439, 1130. ^{1}H NMR ($CDCl_3$) δ 3.571 (2H, qd, J_1 = 10.0 Hz, J_2 = 22.0 Hz, CH_2), 7.421–7.702 (15H, m, Ar). ^{19}F NMR ($CDCl_3$) δ −73.51 (3F, t, J = 10.0 Hz). MS: *m*/*z* (%) 359 (M^+, 23.09), 358 (49.10), 290 (100.00), 262 (22.03), 183 (34.00). Anal. calcd. for $C_{20}H_{17}F_3NP$: C, 66.85; H, 4.77; N, 3.90; P, 8.62. Found: C, 66.91; H, 4.82; N, 3.75; P, 8.60.

4.2. Typical procedure for the preparation of N,N′-difluoroalkylimines (5)

A solution of *N*-fluoroalkyliminophosphoranes **3** (10 g, 25 mmol) and carbonyl compounds **4** (2.12 g, 20 mmol) in toluene (mL) was stirred at 80 °C. The reaction was monitored by TLC. After completion (2–3 days), the solvent was removed under reduced pressure and the residue was washed with hexane (3 × 10). After removing of the solvent under reduced pressure. The residue was purified by distillation under reduced pressure to yield **5** as a colorless liquid.

4.2.1. N-(2,2,3,3-Tetrafluoro-propyl)-iminophosphoranes (3a)

Colorless solid; m.p.; 110–111 °C. IR (KBr) (cm^{-1}): 2825, 1143, 1098. ^{1}H NMR ($CDCl_3$) δ 3.54 (2H, q, J = 14.0 Hz, CH_2), 6.34 (1H, tt, J_1 = 6.0 Hz, J_2 = 54.0 Hz, H–C), 7.41–7.67 (15H, m, Ar). ^{19}F NMR ($CDCl_3$) δ −142.06 (2F, d, J_{FF} = 5.4 Hz), −124.79 (2F, m). MS: *m/z* (%) 391 (M^+, 7.00), 390 (10.00), 290 (100.00), 262 (10.00), 183 (20.00). Anal. calcd. for $C_{21}H_{18}F_4NP$: C, 64.45; H, 4.64; N, 3.58; P, 7.91. Found: C, 64.59; H, 4.72; N, 3.37; P, 8.04.

4.2.2. N-(2,2,2-Trifluoro-ethyl)-iminophosphoranes (3b)

Colorless solid; m.p.; 155–156 °C; IR (KBr) (cm^{-1}): 2840, 1439, 1130. ^{1}H NMR ($CDCl_3$) δ 3.571 (2H, qd, J_1 = 10.0 Hz, J_2 = 22.0 Hz, CH_2), 7.421–7.702 (15H, m, Ar). ^{19}F NMR ($CDCl_3$) δ −73.51 (3F, t, J = 10.0 Hz). MS: *m/z* (%) 359 (M^+, 23.09), 358 (49.10), 290 (100.00), 262 (22.03), 183 (34.00). Anal. calcd. for $C_{20}H_{17}F_3NP$: C, 66.85; H, 4.77; N, 3.90; P, 8.62. Found: C, 66.91; H, 4.82; N, 3.75; P, 8.60.

4.2.3. Benzylidene-(2,2,3,3-tetrafluoro-propyl)-amine (5aa)

Colorless liquid. b.p.; 66–68 °C, 16 mmHg. IR (KBr) (cm^{-1}): 1651, 1582, 1453, 1105, 1038, 1829, 757, 693. ^{1}H NMR ($CDCl_3$) δ 4.09 (2H, t, J = 13.6 Hz, CH_2), 6.07 (1H, tt, J_1 = 5.4 Hz, J_2 = 53.4 Hz, H–C), 7.40–7.51 (3H, m, Ar), 7.74–7.77 (2H, m, Ar), 8.34 (1H, s, H–C=). ^{19}F NMR ($CDCl_3$) δ −139.75 (2F, d, J_{FF} = 43.71 Hz), −122.25 (2F, m). MS: *m/z* (%) 219 (M^+, 12.87), 200 (3.29), 142 (0.89), 118 (72.86), 91 (100.00), 77 (13.29), 51 (27.30). Anal. calcd. for $C_{10}H_9F_4N$: C, 54.80; H, 4.14; N, 6.39. Found: C, 54.67; H, 4.07; N, 6.17.

4.2.4. (4-Nitro-benzylidene)-(2,2,3,3-tetrafluoro-propyl)-amine (5ab)

Colorless liquid. b.p.; 86–89 °C, 18 mmHg. IR (KBr) (cm^{-1}): 1650, 1604, 1527, 1352, 1188, 856, 746, 703. ^{1}H NMR ($CDCl_3$) δ 4.16 (2H, t, J = 14.1 Hz, CH_2), 6.05 (1H, tt, J_1 = 4.8 Hz, J_2 = 53.4 Hz, H–C), 7.94 (2H, d, J = 8.4 Hz, Ar), 8.29 (2H, d, J = 8.1 Hz, Ar), 8.44 (1H, s, H–C=). ^{19}F NMR ($CDCl_3$) δ −139.47 (2F, d, J_{FF} = 49.68 Hz), −122.25 (2F, m). MS: *m/z* (%) 265 (M^+, 6.16), 264 (M^+, 3.70), 248 (4.49), 217 (5.50), 163 (100.00), 117 (94.12), 51 (37.60). Anal. calcd. for $C_{10}H_8F_4N_2O_2$: C, 45.46; H, 3.05; N, 10.60. Found: C, 45.86; H, 2.92; N, 10.67.

4.2.5. (4-Methoxy-benzylidene)-(2,2,3,3-tetrafluoro-propyl)-amine (5ac)

Colorless liquid. b.p.; 73–75 °C, 17 mmHg. IR (KBr) (cm^{-1}): 1652, 1607, 1515, 1258, 1168, 1107, 1040, 831, 701, 678. ^{1}H NMR ($CDCl_3$) δ 3.86 (3H, s, CH_3), 4.06 (2H, t, J = 14.1 Hz, CH_2), 6.06 (1H, tt, J_1 = 5.7 Hz, J_2 = 53.4 Hz, H–C), 6.94 (2H, d, J = 9.0 Hz, Ar), 7.70 (2H, d, J = 8.7 Hz, Ar), 8.26 (1H, s, H–C=). ^{19}F NMR ($CDCl_3$) δ −139.62 (2F, d, J_{FF} = 5.1 Hz), −122.61 (2F, m). MS: *m/z* (%) 249 (M^+, 25.78), 230 (1.87), 148 (42.22), 121 (100.00), 51 (23.43). Anal. calcd. for $C_{11}H_{11}F_4NO$: C, 53.02; H, 4.45; N, 5.62. Found: C, 53.05; H, 5.45; N, 4.44.

4.2.6. (4-Chloro-benzylidene)-(2,2,3,3-tetrafluoro-propyl)-amine (5ad)

Colorless liquid. b.p.; 60–63 °C, 18 mmHg. IR (KBr) (cm^{-1}): 1652, 1597, 1573, 1186, 1110, 1040, 828, 749, 679. ^{1}H NMR ($CDCl_3$) δ 4.09 (2H, t, J = 12.9 Hz, CHz, CH_2), 6.05 (1H, tt, J_1 = 3.9 Hz, J_2 = 53.4 Hz, H–C), 7.42 (2H, d, J = 10.8 Hz, Ar), 7.70 (2H, d, J = 6.6 Hz, Ar), 8.30 (1H, s, H–C=). ^{19}F NMR ($CDCl_3$) δ −139.47 (2F, d, J_{FF} = 43.98 Hz), −122.25 (2F, m). MS: *m/z* (%) 253 (M^+, 13.35), 234 (2.17), 218 (1.86), 152 (73.09), 125 (100.00), 51 (32.61). Anal. calcd. for $C_{10}H_8F_4NCl$: C, 47.36; H, 3.18; N, 5.52. Found: C, 47.74; H, 3.18; N, 5.71.

4.2.7. (2,2,3,3-Tetrafluoro-propyl)-thiophen-2-ylmethylene-amine (5ae)

Colorless liquid. b.p.; 63–65 °C, 14 mmHg. IR (KBr) (cm^{-1}): 1640, 1433, 1184, 1107, 1047, 833, 763, 717. ^{1}H NMR ($CDCl_3$) δ 4.05 (2H, q, J = 12.3 Hz, CH_2), 6.04 (1H, tt, J_1 = 5.4 Hz, J_2 = 54 Hz, H–C), 7.10 (1H, q, J = 3.6 Hz, H–C=), 7.39 (1H, d, J = 3.6 Hz, H–C=), 7.48 (1H, d, J = 4.8 Hz, H–C=), 8.43 (1H, s, H–C=). ^{19}F NMR ($CDCl_3$) δ −139.84 (2F, d, J_{FF} = 45.90 Hz), −122.55 (2F, m). MS: *m/z* (%) 225 (M^+, 13.76), 206 (1.75), 124 (55.91), 110 (5.64), 97 (100.00), 51 (27.93). Anal. calcd. for $C_8H_7F_4NS$: C, 42.67; H, 3.13; N, 6.22. Found: C, 42.84; H, 3.14; N, 6.12.

4.2.8. Furan-2-ylmethylene-(2,2,3,3-tetrafluoro-propyl)-amine (5af)

Colorless liquid. b.p.; 56–60 °C, 13 mmHg. IR (KBr) (cm^{-1}): 1660, 1486, 1275, 1103, 1039, 836, 755, 695. ^{1}H NMR ($CDCl_3$) δ 4.07 (2H, q, J = 12.6 Hz, CH_2), 6.04 (1H, tt, J_1 = 5.4 Hz, J_2 = 54 Hz, H–C), 6.52 (1H, q, J = 1.5 Hz, H–C=), 6.88 (1H, d, J = 3.6 Hz, H–C=), 7.57 (1H, d, J = 0.9 Hz, H–C=), 8.140 (1H, s, H–C=). ^{19}F NMR ($CDCl_3$) δ −139.42 (2F, d, J_{FF} = 5.1 Hz), −122.22 (2F, m). MS: *m/z* (%) 209 (M^+, 13.77), 190 (2.48), 108 (100.00), 101 (2.13), 81 (88.15), 51 (42.84). Anal. calcd. for $C_8H_7F_4NO$: C, 45.94; H, 3.37; N, 6.70. Found: C, 45.90; H, 3.37; N, 6.50.

4.2.9. N-(2,2,3,3-Tetrafluoro-propyl)-benzimidoylchloride (5ag)

Colorless liquid. b.p.; 65–67 °C, 14 mmHg. IR (KBr) (cm^{-1}): 1666, 1449, 1190, 1104, 1035, 910, 833, 783, 688. ^{1}H NMR ($CDCl_3$) δ 4.16 (2H, t, J = 13.5 Hz, CH_2), 6.09 (1H, tt,

J_1 = 4.8 Hz, J_2 = 53.4 Hz, H–C), 7.25–7.54 (3H, m, Ar), 7.99–8.02 (2H, m, Ar). ^{19}F NMR ($CDCl_3$) δ −139.04 (2F, m), −121.81 (2F, m). MS: *m/z* (%) 254 (M^+, 12.09), 234 (2.20), 218 (100.00), 124 (0.63), 77 (27.14), 51 (50.40). Anal. calcd. for $C_{10}H_8F_4N_2O_2$: C, 47.36; H, 3.18; N, 5.52. Found: C, 47.42; H, 3.29; N, 5.46.

4.2.10. Benzylidene-(2,2,2-trifluoro-ethyl)-amine (**5ba**)

Colorless liquid. b.p.; 65–66 °C, 15 mmHg. IR (KBr) (cm^{-1}): 1651, 1583, 1265, 1140, 1044, 828, 756, 670. ^{1}H NMR ($CDCl_3$) δ 4.12 (2H, q, J = 9.1 Hz, CH_2), 7.40–7.51 (3H, m, Ar), 7.77–7.80 (2H, m, Ar), 8.35 (1H, s, H–C=). ^{13}C NMR ($CDCl_3$) δ 61.60, 122.74, 126.40, 128.65, 128.75, 129.03, 131.73, 135.14, 166.85. ^{19}F NMR ($CDCl_3$) δ −70.87 (3F, t, J_{FF} = 9.0 Hz). MS: *m/z* (%) 187 (M^+, 26.30), 118 (67.21), 110 (6.19), 91 (100.00), 83 (17.35), 77 (26.33), 51 (28.80). HRMS calcd. for $C_9H_8NF_3$: 187.0609; found: 187.0616.

4.2.11. (4-Nitro-benzylidene)-(2,2,2-trifluoro-ethyl)-amine (**5bb**)

Colorless liquid. b.p.; 81–83 °C, 17 mmHg. IR (KBr) (cm^{-1}): 1650, 1524, 1345, 1155, 1043, 846, 737, 670, 557. ^{1}H NMR ($CDCl_3$) δ 4.19 (2H, q, J = 7.5 Hz, CH_2), 7.98 (2H, d, J = 8.7 Hz, Ar), 8.31 (2H, t, J = 8.4 Hz, Ar), 8.45 (1H, s, H–C=). ^{19}F NMR ($CDCl_3$) δ −70.69 (3F, t, J_{FF} = 9.0 Hz). MS: *m/z* (%) 232 (M^+, 32.68), 213 (1.14), 185 (14.87), 163 (100.00), 136 (17.53), 110 (15.37), 83 (30.73). Anal. calcd. for $C_9H_7F_3N_2O_2$: C, 46.56; H, 3.04; N, 12.07. Found: C, 47.09; H, 3.20; N, 11.78.

4.2.12. (4-Methoxy-benzylidene)-(2,2,2-trifluoro-ethyl)-amine (**5bc**)

Colorless liquid. b.p.; 70–71 °C, 16 mmHg. IR (KBr) (cm^{-1}): 1650, 1606, 1515, 1259, 1141, 1110, 1049, 836, 671. ^{1}H NMR ($CDCl_3$) δ 3.86 (3H, s, CH_3), 4.08 (2H, t, J = 9.6 Hz, CH_2), 6.94 (2H, d, J = 8.1 Hz, Hz, Ar), 7.73 (2H, d, J = 8.1 Hz, Ar), 8.27 (1H, s, H–C=). ^{19}F NMR ($CDCl_3$) δ −70.96 (3F, m). MS: *m/z* (%) 217 (M^+, 63.98), 198 (1.98), 148 (41.42), 121 (100.00), 83 (11.07), 51 (18.34). Anal. calcd. for $C_{10}H_{10}F_3NO$: C, 55.30; H, 4.64; N, 6.45. Found: C, 55.47; H, 4.63; N, 6.51.

4.2.13. (4-Chloro-benzylidene)-(2,2,2-trifluoro-ethyl)-amine (**5bd**)

Colorless liquid. b.p.; 59–60 °C, 15 mmHg. IR (KBr) (cm^{-1}): 1653, 1597, 1492, 1278, 1143, 1048, 834, 670, 573. ^{1}H NMR ($CDCl_3$) δ 4.12 (2H, q, J = 8.1 Hz, CH_2), 7.42 (2H, t, J = 6.9 Hz, Ar), 7.74 (2H, t, J = 6.9 Hz, Ar), 8.31 (1H, s, H–C=). ^{19}F NMR ($CDCl_3$) δ −70.86 (3F, t, J_{FF} = 9.3 Hz). MS: *m/z* (%) 221 (M^+, 53.78), 186 (1.45), 152 (69.22), 125 (100.00), 110 (9.62), 102 (8.01), 89 (28.84), 75 (28.02), 41 (4.66). Anal. calcd. for $C_9H_7F_3NCl$: C, 48.78; H, 3.18; N, 6.32. Found: C, 48.81; H, 3.25; N, 6.19.

4.2.14. Thiophen-2-ylmethylene-(2,2,2-trifluoro-ethyl)-amine (**5be**)

Colorless liquid. b.p.; 54–57 °C, 15 mmHg. IR (KBr) (cm^{-1}): 1640, 1434, 1264, 1150, 1051, 845, 714. ^{1}H NMR ($CDCl_3$) δ 4.09 (2H, q, J = 9.0 Hz, CH_2), 7.10 (1H, t, J = 4.2 Hz, H–C=), 7.41 (1H, d, J = 3.3 Hz, H–C=), 7.49 (1H, d, J = 5.1 Hz, H–C=), 8.44 (1H, s, H–C=). ^{13}C NMR ($CDCl_3$) δ 61.24, 122.58, 127.56, 130.61, 132.28, 146.67, 159.86. ^{19}F NMR ($CDCl_3$) δ −70.86 (3F, t, J_{FF} = 9.025 Hz). MS: *m/z* (%) 193 (M^+, 45.01), 174 (0.81), 110 (14.23), 97 (100.00), 83 (26.14), 69 (21.68), 51 (7.32). HRMS calcd. for $C_7H_6NF_3NS$: 193.0173; found: 193.0175.

4.2.15. Furan-2-ylmethylene-(2,2,2-trifluoro-ethyl)-amine (**5bf**)

Colorless liquid. b.p.; 50–52 °C, 15 mmHg. IR (KBr) (cm^{-1}): 1651, 1485, 1265, 1142, 1046, 845, 754, 678. ^{1}H NMR ($CDCl_3$) δ 4.08 (2H, q, J = 9.3 Hz, CH_2), 6.52 (1H, t, J = 1.8 Hz, H–C=), 6.90 (1H, d, J = 3.3 Hz, H–C=), 7.58 (1H, s, H–C=), 8.15 (1H, s, H–C=). ^{13}C NMR ($CDCl_3$) δ 61.24, 112.14, 116.29, 122.54, 126.22, 129.89, 145.83, 150.68, 154.89. ^{19}F NMR ($CDCl_3$) δ −70.84 (3F, t, J_{FF} = 9.0 Hz). MS: *m/z* (%) 177 (M^+, 45.30), 108 (100.00), 97 (18.66), 94 (12.96), 83 (49.96), 70 (51.78), 51 (21.98). HRMS calcd. for $C_7H_6NF_3NO$: 177.0401; found: 177.0400.

4.2.16. N-(2,2,2-Trifluoro-ethyl)-benzimidoylchloride (**5bg**)

Colorless liquid. b.p.; 59–62 °C, 14 mmHg. IR (KBr) (cm^{-1}): 1668, 1582,1449, 1288, 1131, 911, 840, 767, 688. ^{1}H NMR ($CDCl_3$) δ 4.18 (2H, q, J = 9.3 Hz, CH_2), 7.41–7.53 (3H, m, Ar), 8.03–8.06 (2H, m, Ar). ^{19}F NMR ($CDCl_3$) δ −71.00 (3F, t, J_{FF} = 10.7 Hz). MS: *m/z* (%) 221 (M^+, 0.82), 186 (100.00), 146 (3.18), 104 (40.54), 89 (3.48), 77 (24.15). Anal. calcd. for $C_9H_7F_3N$: C, 48.78; H, 3.18; N, 6.32. Found: C, 48.88; H, 3.19; N, 6.30.

4.3. Preparation of N,N′-difluoroalkylated carbodiimide **7**

CO_2 gas was bubbled into a solution of **3b** (2 mmol) and Et_2O (20 mL), a white was appeared in the reaction system. The reaction was monitored by TLC. After completion, the solvent was removed under reduced pressure. The residue was purified by flash chromatography on a silicon gel column with petroleum ether/ethyl acetate (v/v = 10:1) as eluent.

4.3.1. N,N′-Difluoroalkylated carbodiimide (**7**)

Colorless liquid. IR (KBr) (cm^{-1}): 3593, 2951, 2164, 1106. ^{1}H NMR ($CDCl_3$) δ 3.80 (4H, t, J = 14.0 Hz, CH_2), 5.90 (2H, tt, J_1 = 4.0 Hz, J_2 = 53 Hz, H–C). ^{19}F NMR ($CDCl_3$) δ −137.63 (4F, d, J_{FF} = 53.0 Hz), −122.32 (4F, t, J = 14.0 Hz). MS: *m/z* (%) 270 (M^+, 7.00), 251 (9.02), 169 (100.00), 51 (25.03). Anal. calcd. for $C_7H_6F_8N_2$: C, 31.13; H, 2.24; N, 10.37. Found: C, 31.13; H, 2.34; N, 10.38.

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