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Stereoselective preparation of 1,2,4-oxadiazole derivatives substituted by pentafluorophenyl by 1,3-dipolar cycloaddition reaction

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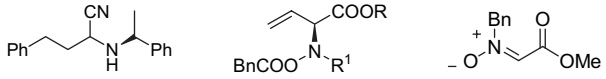
Abstract—1,3-Dipolar cycloaddition reactions of chiral imines obtained from optically active amino acids with nitrile oxides afforded 1,2,4-oxadiazole derivatives in moderate to good yields with good stereoselectivity. Investigation on the effect of bases suggested that triethylamine was prone to afford better stereoselectivity, while $NaHCO_3$ was prone to increase the reaction rates and yields.

1. Introduction

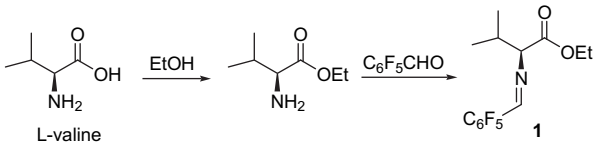
1,3-Diploar cycloaddition (1,3-DC) reaction for the synthesis of five-membered heterocycles is a classic reaction in organic chemistry, due to a high degree of site-, regio-, and stereoselectivity.[1] Therefore, these reactions are widely used for the preparation of molecules with significance for both academia and industry. In recent years, the development of new stereoselective version has been a major challenge. The stereochemistry of the 1,3-DC reaction can be controlled either by the appropriate substrates or choosing a metal complex as a catalyst.[2] Compared with the utilization of a metal catalyst, it is straightforward to employ the chiral substrate in the reaction system. Generally, the most commonly used chiral dipoles or philodipoles were derived from optically active amino acids or their derivatives.[3]



Nitrile oxides are known to be remarkably active dipoles in 1,3-DC reactions, and have been extensively investigated for their synthetic application and for elucidation of the reaction mechanism of 1,3-DC reaction.[4] Generally, the 1,3-DC reaction of nitrile oxides with philodipoles can afford two regioisomers, each as a pair of enantiomers in which the relative configuration between the 4- and 5-substituents is determined by the geometry of the phliodipoles. Due to the potential versatility of this reaction for the construction of chiral compounds,[5] the demand for asymmetric versions of this reaction has increased over the last 20 years. Thus, several publications on asymmetric 1,3-DC reactions of nitrile oxides with alkenes have appeared.[6] However, to the best of our knowledge, only a few applications of imino-1,3-DC reaction were reported;[7] furthermore, no literature has reported the reaction of optically active imine in the reaction. As a continuation of our research interests in chemical transformation of fluorine-containing imine,[8] we report herein the 1,3-DC reaction of chiral imine **1** prepared from perfluorobenzaldehyde and (*S*)-ethyl 2-amino-3-methylbutanoate with nitrile oxides in the presence of triethylamine or $NaHCO_3$. It was favorable that the reaction can afford the corresponding five-membered heterocycles with good stereoselectivity.

2. Results and discussion

Compound **1** can be conveniently prepared by the dehydration reaction of perfluorobenzaldehyde with (*S*)-ethyl 2-amino-3-methylbutanoate (Scheme 1).[9] Compared with unfluorinated imine, pentafluorophenyl reinforced the stability of **1** to react with nitrile oxides.



Scheme 1.

Keywords: 1,3-Dipolar cycloaddition; Nitrile oxides; Pentafluorophenyl-containing imine; Stereoselectivity.
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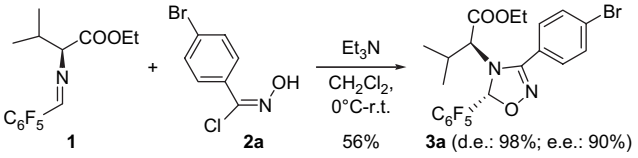
Nitrile oxides are almost always generated in situ in order to avoid dimerization. Generally, triethylamine (TEA) was utilized prevalently to prepare nitrile oxides in situ from benzohydroximinoyl chlorides.[10] On the other hand, $NaHCO_3$ could be employed in some 1,3-DC reactions as an alternative to TEA.[11] In this work, we compared base effects in the 1,3-DC reaction of optically active imine with nitrile oxides. First, we investigated the 1,3-DC reaction of **1** and *p*-bromophenyl nitrile oxide in the presence of TEA and the expected oxadiazole derivative **3a** was isolated in a moderate yield and with good diastereoselectivity and enantioselectivity (Scheme 2). Furthermore, the X-ray single crystal diffraction analysis was carried out to get more stereochemistry information (Fig. 1).



Scheme 2.

Based on the same reaction conditions, a series of structurally diversified nitrile oxides were used in the reaction and all results are summarized in Table 1. Just like **2a**, other substituted-phenyl nitrile oxides reacted with optically active imine in the presence of TEA (Table 1, entries 2–5). The aliphatic nitrile oxide **2f** also afforded the oxadiazole derivative in considerable yield. It showed that all the yields were not satisfactory and it was attributed to the slow and uncontrollable decomposition of the imine, because pentafluorobenzaldehyde and valinoethylate were detected in the reaction mixture. It was worthy to note that no product was isolated when a strong electron-withdrawing group such as NO_2 was present (Table 1, entry 7).

Compared with TEA, $NaHCO_3$ shortened the reaction time obviously from 3 days to 1 day as well as improved the yield (Table 2, entries 1–5). In addition, it was worthy to note that nitrile oxide containing the strong electron-withdrawing group such as nitryl could also afford the 1,2,4-oxadiazole

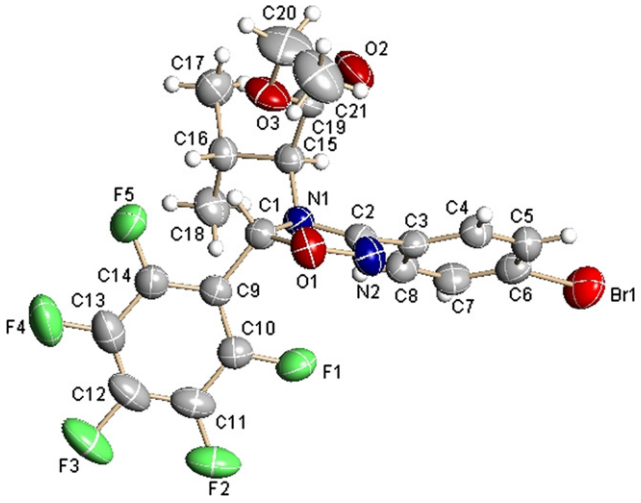
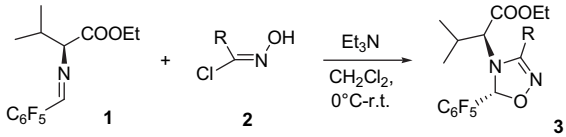


Figure 1. Molecular structure of **3a**.

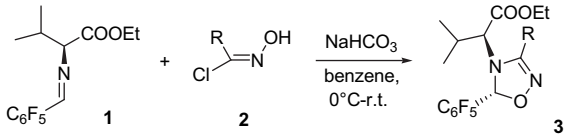
Table 1. Results of 1,3-DC reaction of **1** in the presence of TEA



Entry	**2** (R=)	Time (d)	Yield[a] **3** (%)	de[b] (%)	ee[c] (%)
1	**2a** (*p*-C_6H_4Br)	2	**3a** (56)	98	90
2	**2b** (*o*-C_6H_4Cl)	3	**3b** (44)	95	78
3	**2c** (*p*-C_6H_4F)	3	**3c** (45)	99	78
4	**2d** (*o*-C_6H_4F)	2	**3d** (54)	96	68
5	**2e** (*p*-C_6H_4Me)	2	**3e** (42)	91	86
6	**2f** ($CH{=}CHC_6H_5$)	2	**3f** (57)	90	77
7	**2g** (*m*-$C_6H_4NO_2$)	3	No[d]	—	—

[a] Isolated yield.
[b] ^1H NMR.
[c] Chiral HPLC.
[d] No product was isolated.

Table 2. Results of 1,3-DC reaction of **1** in the presence of $NaHCO_3$



Entry	**2** (R=)	Time (d)	Yield[a] **3** (%)	de[b] (%)	ee[c] (%)
1	**2a** (*p*-C_6H_4Br)	1	**3a** (90)	97	57
2	**2b** (*o*-C_6H_4Cl)	1	**3b** (78)	92	54
3	**2c** (*p*-C_6H_4F)	1	**3c** (84)	97	55
4	**2d** (*o*-C_6H_4F)	1	**3d** (74)	95	55
5	**2e** (*p*-C_6H_4Me)	1	**3e** (54)	99	59
6	**2g** (*m*-$C_6H_4NO_2$)	1	**3g** (69)	89	[d]

[a] Isolated yield.
[b] ^1H NMR.
[c] Chiral HPLC.
[d] Due to the limitation of the apparatus the ee value cannot be detected.

product in the presence of $NaHCO_3$ (Table 2, entry 6). However, lower enantioselectivity was observed in all cases, which could be attributed to the greater racemization of imine in the presence of $NaHCO_3$. On the other hand, the value of de in both tables indicated that the ratio of the diastereoisomers was not influenced by the experimental conditions.

3. Conclusion

We have demonstrated a new version of enantioselective 1,3-DC reaction of pentafluorophenyl-substituted imines and nitrile oxides. When TEA was utilized as the base, the 1,2,4-oxadiazole derivatives were isolated in moderate yields with good enantioselectivity. On the other hand, if $NaHCO_3$ was employed, higher yields were obtained even with nitrile oxides substituted by strong electron-withdrawing group; furthermore, the mild reaction conditions, ease of manipulation, straightforward procedure, and considerable yield of useful products make this transformation potentially useful in organic synthesis.

4. Experimental

4.1. General

Melting points were measured on a Temp-Melt. apparatus and are uncorrected. ^{1}H, ^{13}C, and ^{19}F NMR spectra were recorded on Bruker AM-300 or AM-400 instruments with Me_4Si and $CFCl_3$ as the internal 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, respectively, using the electron impact ionization technique (70 eV). Single crystal X-ray structure analysis was performed on a Bruker P4 instrument.

4.2. Preparation of compound 1

(*S*)-Ethyl 2-amino-3-methylbutanoate (50 mmol) and pentafluorobenzaldehyde (50 mmol) were refluxed in EtOH (10 ml) for 20 h. Then TLC analysis showed that the reaction was over and the product was purified by column chromatography on silica gel to give compound **1** (92%).

4.2.1. (*S*,*E*)-Ethyl 3-methyl-2-(perfluorobenzylideneamino)butanoate 1. Yellow oil. ^{1}H NMR ($CDCl_3$): δ 8.27 (1H, s, CH═), 4.16 (2H, dd, $^3J_{HH}$=14, 7 Hz, CH_2), 3.64 (1H, d, $^3J_{HH}$=7 Hz, CH), 2.37–2.34 (1H, m, CH), 1.22 (3H, t, $^3J_{HH}$=7 Hz, CH_3), 0.90 (6H, t, $^3J_{HH}$=6 Hz, CH_3). ^{19}F NMR ($CDCl_3$): −142.00 to −142.11 (2F, m), −150.61 (1F, t, $^2J_{FF}$=20 Hz), −161.70 to −161.90 (2F, m).

4.3. Experimental procedure

Method a: Et_3N (0.5 mmol) in 1 mL of CH_2Cl_2 was added slowly to the mixture of **1** (0.3 mmol) and nitrile oxide **2a** (0.3 mmol) in 2 mL CH_2Cl_2 at 0 °C. Then the mixture was warmed to room temperature. TLC analysis was used to monitor the reaction. After 2 days, the reaction was completed. After general work-up, the residue was purified by column chromatography on silica gel to give the product **3a** in a yield of 56%. *Method b*: the mixture of **1** (0.3 mmol) and nitrile oxide **2a** (0.3 mmol) in 2 mL of benzene was added slowly into the mixture of $NaHCO_3$ (0.6 mmol) in 1 mL benzene at 0 °C. Then the mixture was warmed to room temperature. TLC analysis was used to monitor the reaction. After 1 day, the reaction was over completely. After general work-up, the residue was purified by column chromatography on silica gel to give the product **3a** in a yield of 90%.

4.3.1. (*S*)-Ethyl-2-((*R*)-3-(4-bromophenyl)-5-(perfluorophenyl)-1,2,4-oxadiazol-4(5*H*)-yl)-3-methylbutanoate 3a. Mp: 56–57 °C. ^{1}H NMR ($CDCl_3$): δ 7.56 (2H, d, $^3J_{HH}$=8 Hz, Ph), 7.40 (2H, d, $^3J_{HH}$=8 Hz, Ph), 7.19 (1H, s, CH), 4.21–4.05 (2H, m, CH_2), 3.42 (1H, d, $^3J_{HH}$=11 Hz, CH), 1.89–1.85 (1H, m, CH), 1.19 (3H, t, $^3J_{HH}$=7 Hz, CH_3), 0.809 (3H, d, $^3J_{HH}$=6 Hz, CH_3), 0.76 (3H, d, $^3J_{HH}$= 6 Hz, CH_3). ^{19}F NMR ($CDCl_3$): −142.72 to −142.82 (2F, m), −151.5 (1F, t, $^2J_{FF}$=20 Hz), −160.42 to −160.61 (2F, m). ^{13}C NMR ($CDCl_3$): δ 169.36 (C═O), 156.53 (C═N), 132.49 (Ph), 129.85 (Ph), 125.64 (Ph), 123.49 (Ph), 85.69, 66.52, 61.52, 29.71 (CH), 19.46 (CH_3), 19.30 (CH_3), 14.22 (CH_3). MS [ESI] (*m*/*z*, %): 521.2 (M^++H). IR (cm^{-1}): 2967, 1734, 1522, 1506, 1153, 1003. HRMS calcd for $C_{21}H_{19}BrN_2O_3F_5$: 521.0499; found: 521.0494.

X-ray data of compound ***3a***: $C_{21}H_{19}BrF_5N_2O_3$: FW=521.28; temperature 293(2) K; monoclinic, *P*2(1)/*c*; wavelength 0.71 Å; a=11.934(3) Å, b=12.730(3) Å, c=15.089(14) Å, α=90.00°, β=108.035(4)°, γ=90.00°; V=2179.7(9) Å; Z=4, Dc=1.589 mg/m^3; absorption coefficient 1.954 mm^{-1}; F (000)=1048; 1.79<θ<27.00; reflections collected 12,234; absorption correction empirical; transmission 1.000_{max}−0.5946_{min}; final R indices R_1=0.0511, wR_2=0.0867. The CCDC number is 612390.

4.3.2. (*S*)-Ethyl-2-((*R*)-3-(2-chlorophenyl)-5-(perfluorophenyl)-1,2,4-oxadiazol-4(5*H*)-yl)-3-methylbutanoate 3b. Mp: 73–75 °C. ^{1}H NMR ($CDCl_3$): δ 7.59 (1H, s, Ph), 7.53–7.40 (3H, m, Ph), 7.29 (1H, s, CH), 4.30–4.14 (2H, m, CH_2), 3.52 (1H, d, $^3J_{HH}$=11 Hz, CH), 1.99–1.92 (1H, m, CH), 1.34 (3H, t, $^3J_{HH}$=7 Hz, CH_3), 0.89 (3H, d, $^3J_{HH}$=7 Hz, CH_3), 0.84 (3H, d, $^3J_{HH}$=7 Hz, CH_3). ^{19}F NMR ($CDCl_3$): −142.6 to −142.79 (2F, m), −151.45 (1F, t, $^2J_{FF}$=20 Hz), −160.35 to −160.54 (2F, m). ^{13}C NMR ($CDCl_3$): δ 169.34 (C═O), 156.22 (C═N), 135.16 (Ph), 131.26 (Ph), 130.45 (Ph), 128.48 (Ph), 126.45 (Ph), 126.34 (Ph), 85.79, 66.44, 61.54, 29.69 (CH), 19.44 (CH_3), 19.28 (CH_3), 14.19 (CH_3). MS [ESI] (*m*/*z*, %): 477.2 (M^++H). IR (cm^{-1}): 2970, 1735, 1653, 1523, 1508, 1004. HRMS calcd for $C_{21}H_{18}ClN_2O_3F_5$: (M^++H) 477.1008; found: 477.0999.

4.3.3. (*S*)-Ethyl-2-((*R*)-3-(4-fluorophenyl)-5-(perfluorophenyl)-1,2,4-oxadiazol-4(5*H*)-yl)-3-methylbutanoate 3c. Mp: 109–111 °C. ^{1}H NMR ($CDCl_3$): δ 7.60 (2H, t, $^3J_{HH}$=6 Hz, Ph), 7.298 (1H, s, CH), 7.19 (2H, d, $^3J_{HH}$=6 Hz, Ph), 4.29–4.14 (2H, m, CH_2), 3.51 (1H, d, $^3J_{HH}$=11 Hz, CH), 1.99–1.92 (1H, m, CH), 1.26 (3H, t, $^3J_{HH}$=7 Hz, CH_3), 0.89 (3H, d, $^3J_{HH}$=7 Hz, CH_3), 0.84 (3H, d, $^3J_{HH}$= 7 Hz, CH_3). ^{19}F NMR ($CDCl_3$): −108.09 (1F), −142.76 to −143.92 (2F, m), −151.73 (1F, t, $^2J_{FF}$=20 Hz), −160.51 to −160.70 (2F, m). ^{13}C NMR ($CDCl_3$): δ 169.43 (C═O), 156.45 (C═N), 130.56 (Ph), 130.47 (Ph), 116.56 (Ph), 116.33 (Ph), 85.57, 66.40, 61.49, 29.72 (CH), 19.46 (CH_3), 19.30 (CH_3), 14.21 (CH_3). MS [ESI] (*m*/*z*, %): 461.2 (M^++H). IR (cm^{-1}): 2973, 1735, 1605, 1523, 1508, 1003. HRMS calcd for $C_{21}H_{18}N_2O_3F_6$: (M^++H) 461.1298; found: 461.1294.

4.3.4. (*S*)-Ethyl-2-((*R*)-3-(2-fluorophenyl)-5-(perfluorophenyl)-1,2,4-oxadiazol-4(5*H*)-yl)-3-methylbutanoate 3d. Oil. ^{1}H NMR ($CDCl_3$): δ 7.56–7.54 (2H, m, Ph), 7.35 (1H, s, CH), 7.29–7.21 (2H, m, Ph), 4.24–4.18 (2H, m, CH_2), 3.38 (1H, d, $^3J_{HH}$=11 Hz, CH), 1.96–1.84 (1H, m, CH), 1.27 (3H, t, $^3J_{HH}$=7 Hz, CH_3), 0.85 (3H, d, $^3J_{HH}$= 7 Hz, CH_3), 0.75 (3H, d, $^3J_{HH}$=7 Hz, CH_3). ^{19}F NMR ($CDCl_3$): −111.16 (1F), −142.59 to −142.66 (2F, m), −151.76 (1F, t, $^2J_{FF}$=20 Hz), −160.69 to −160.91 (2F, m). ^{13}C NMR ($CDCl_3$): δ 169.59 (C═O), 158.99 (C═N), 133.36 (Ph), 133.02 (Ph), 131.25 (Ph), 124.90 (Ph), 116.79 (Ph), 116.58 (Ph), 85.59, 66.22, 61.45, 29.59 (CH), 19.44 (CH_3), 19.01 (CH_3), 14.09 (CH_3). MS [ESI] (*m*/*z*, %): 461.2 (M^++H). IR (cm^{-1}): 2972, 1734, 1522, 1508, 1003.

HRMS calcd for $C_{21}H_{18}N_2O_3F_6$: (M^++H) 461.1302; found: 461.1294.

4.3.5. (*R*)-Ethyl-3-methyl-2-((*R*)-5-(perfluorophenyl)-3-*p*-tolyl-1,2,4-oxadiazol-4(5*H*)-yl)butanoate 3e. Mp: 72–73 °C. ^{1}H NMR ($CDCl_3$): δ 7.42 (2H, d, $^3J_{HH}$=7 Hz, Ph), 7.28 (2H, d, $^3J_{HH}$=7 Hz, Ph), 7.27 (1H, s, CH), 4.26–4.14 (2H, m, CH_2), 3.56 (1H, d, $^3J_{HH}$=10 Hz, CH), 2.42 (3H, s, CH_3), 1.96–1.92 (1H, m, CH), 1.28 (3H, t, $^3J_{HH}$=7 Hz, CH_3), 0.87 (3H, d, $^3J_{HH}$=7 Hz, CH_3), 0.84 (3H, d, $^3J_{HH}$=7 Hz, CH_3). ^{19}F NMR ($CDCl_3$): −142.63 to −142.73 (2F, m), −151.99 (1F, t, $^2J_{FF}$=20 Hz), −160.68 to −160.86 (2F, m). ^{13}C NMR ($CDCl_3$): 169.62 (C=O), 157.30 (C=N), 141.48 (Ph), 129.94 (Ph), 128.37 (Ph), 121.48 (Ph), 85.42, 66.31, 61.39, 29.74 (CH), 21.54 (CH_3), 19.50 (CH_3), 19.31 (CH_3), 14.23 (CH_3). MS [ESI] (*m*/*z*, %): 457.2 (M^++H). IR (cm^{-1}): 2966, 1733, 1522, 1507, 1154. HRMS calcd for $C_{22}H_{21}N_2O_3F_5$: 456.1472; found: 456.1465.

4.3.6. (*S*)-Ethyl-3-methyl-2-((*R*)-5-(perfluorophenyl)-3-((*E*)-styryl)-1,2,4-oxadiazol-4(5*H*)-yl)butanoate 3f. Mp: 59–61 °C. ^{1}H NMR ($CDCl_3$): δ 7.50 (2H, d, $^3J_{HH}$=6 Hz, Ph), 7.42–7.30 (3H, m, Ph), 7.25 (1H, s, CH), 7.24 (1H, d, $^3J_{HH}$=11 Hz, CH=), 6.56 (1H, d, $^3J_{HH}$=11 Hz, CH=), 4.24–4.19 (2H, m, CH_2), 3.69 (1H, d, $^3J_{HH}$=10 Hz, CH), 2.09–1.98 (1H, m, CH), 1.27 (3H, t, $^3J_{HH}$=7 Hz, CH_3), 0.96 (3H, d, $^3J_{HH}$=7 Hz, CH_3), 0.86 (3H, d, $^3J_{HH}$=7 Hz, CH_3). ^{19}F NMR ($CDCl_3$): −142.54 to −142.67 (2F, m), −151.81 (1F, t, $^2J_{FF}$=20 Hz), −160.72 to −160.91 (2F, m). ^{13}C NMR ($CDCl_3$): δ 169.65 (C=O), 155.08 (C=N), 138.75 (Ph), 138.57, 135.13 (Ph), 129.68 (Ph), 129.57 (Ph), 128.88 (Ph), 127.37, 110.04, 86.07, 66.41, 61.48, 29.86 (CH), 19.55 (CH_3), 19.29 (CH_3), 14.15 (CH_3). MS [ESI] (*m*/*z*, %): 469.2 (M^++H). IR (cm^{-1}): 2970, 1735, 1653, 1522, 1508, 1003. HRMS calcd for $C_{23}H_{21}N_2O_3F_5$: (M^++H) 469.1559; found: 469.1545.

4.3.7. (*S*)-Ethyl-3-methyl-2-((*R*)-3-(3-nitrophenyl)-5-(perfluorophenyl)-1,2,4-oxadiazol-4(5*H*)-yl)butanoate 3g. Mp: 87–89 °C. ^{1}H NMR ($CDCl_3$): δ 8.46 (1H, s, Ph), 8.41 (1H, d, $^3J_{HH}$=8 Hz, Ph), 7.98 (1H, d, $^3J_{HH}$=7 Hz, Ph), 7.75 (1H, d, $^3J_{HH}$=7 Hz, Ph), 7.34 (1H, s, CH), 4.32–4.18 (2H, m, CH_2), 3.50 (1H, d, $^3J_{HH}$=11 Hz, CH), 2.02–1.98 (1H, m, CH), 1.27 (3H, t, $^3J_{HH}$=7 Hz, CH_3), 0.96–0.86 (6H, m, CH_3). ^{19}F NMR ($CDCl_3$): −142.75 to −142.85 (2F, m), −151.03 (1F, t, $^2J_{FF}$=20 Hz), −160.08 to −160.26 (2F, m). ^{13}C NMR ($CDCl_3$): δ 169.03 (C=O), 155.59 (C=N), 148.64 (Ph), 133.91 (Ph), 130.44 (Ph), 126.51 (Ph), 125.96 (Ph), 123.25 (Ph), 86.08, 66.67, 61.72, 29.67 (CH), 19.40 (CH_3), 19.26 (CH_3), 14.18 (CH_3). MS [ESI] (*m*/*z*, %): 488 (M^++H). IR (cm^{-1}): 2970, 1736, 1730, 1523, 1508, 1350, 1003. HRMS calcd for $C_{20}H_{18}N_3O_5F_5$: 487.1167; found: 487.1174.

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