Polish J. Chem., **78**, 1871–1876 (2004)

Synthesis of Fluorinated Dialkyl 1-Aryl-4-alkoxy-5-oxo-2,5-dihydro-1*H*-pyrrole-2,3-dicarboxylates

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(Received May 31st, 2004)

Alkyl 2-(2-fluoro-anilino)-2-oxo-acetates or ethyl 2-oxo-2-(trifluoromethylanilino)-acetate undergo a multistep reaction with dialkyl acetylenedicarboxylates in the presence of triphenylphosphine to produce dialkyl l-(2-fluorophenyl)-4-alkoxy-5-oxo-2,5-dihydro-1*H*-pyrrole-2,3-dicarboxylates or dialkyl 4-ethoxy-5-oxo-1-[2-(trifluoromethyl)-phenyl]-2,5-dihydro-1*H*-pyrrole-2,3-dicarboxylates in good yields. Dynamic NMR study of dimethyl 4-ethoxy-5-oxo-1-[2-(trifluoromethyl)-phenyl]-2,5-dihydro-1*H*-pyrrole-2,3-dicarboxylate shows a fairly high energy barrier ($\Delta G^{\neq}$ = 60.9 kJ mol^{-1}) for rotation around the *N*-aryl single bond, which leads to an observable atropisomerism.

Key words: hindered rotation, rotational isomers, intramolecular *Wittig* reaction, atropisomers, triphenylphosphine

Five memberd ring lactams have successfully been used in routes to various alkaloids [1,2] and are suitable precursors for unusual γ-amino acids such as statine and its analogues [3,4]. There are also many examples of pyrroline-containing natural products with interesting pharmacological activities. Typical examples are the antitumor alkaloide Jatropham [5] and the platelet aggregation inhibitor PI-091 [6]. As part of our current studies on the development of new routes to heterocyclic and carbocyclic systems [7–11] we now report a simple one-pot synthesis of highly functionalized 3-pyrrolin-5-ones **3**. Thus, reaction of dialkyl acetylenedicarboxylates **1** with alkyl 2-arylamino-2-oxo-acetates **2** in the presence of triphenylphosphine leads to the corresponding dialkyl 1-aryl-4-alkoxy-5-oxo-2,5-dihydro-1*H*- pyrrole-2,3-dicarboxylates **3a**–**3g** in good yields (Scheme 1).

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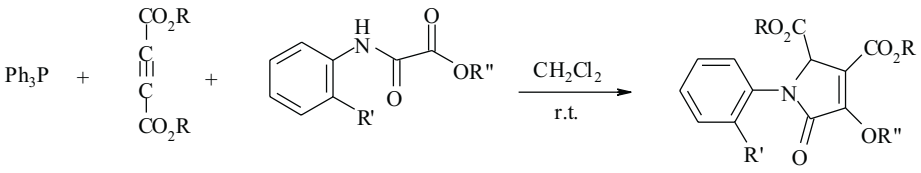
Scheme 1



1	R
a	Me
b	Et
c	^{t}Bu

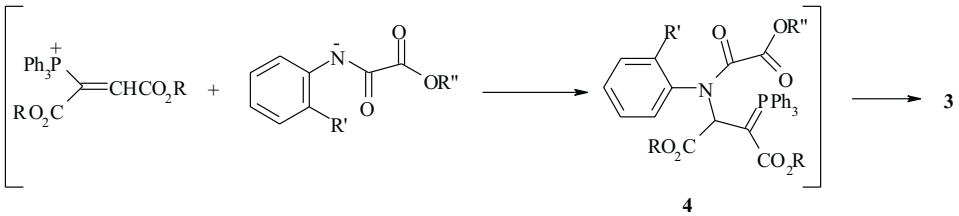
2	R'	R"
a	F	Me
b	F	Et
c	CF_3	Et

3	R	R'	R"	Yield %
a	Me	F	Me	80
b	Me	F	Et	78
c	Et	F	Et	82
d	^{t}Bu	F	Et	90
e	Me	CF_3	Et	80
f	Et	CF_3	Et	75
g	^{t}Bu	CF_3	Et	82

RESULTS AND DISCUSSION

The reaction of dialkyl acetylendicarboxylates **1** with alkyl 2-arylamino-2-oxo-acetates **2** in the presence of triphenylphosphine proceeded spontaneously at room temperature in CH_2Cl_2 and was finished within 24 h. ^{1}H, ^{13}C, and ^{19}F NMR spectra of the crude products clearly indicated the formation of dialkyl l-aryl-4-alkoxy-5-oxo-2,5-dihydro-1*H*-pyrrole-2,3-dicarboxylates **3a**–**3g**. Any product other than **3** could not be detected by NMR spectroscopy. There are known syntheses of unsaturated heterocycles employing intramolecular Wittig reaction of ylids generared from a phosphorane with a carbonyl group attached to a chain containing a heteroatom [7–12]. In investigated reactions the cyclization products apparently result from an initial addition of triphenylphosphine to the acetylenic ester followed by addition of alkyl 2-arylamino-2-oxo-acetate which finally convert into the 2,5-dihydropyrrole derivatives **3**.

Scheme 2



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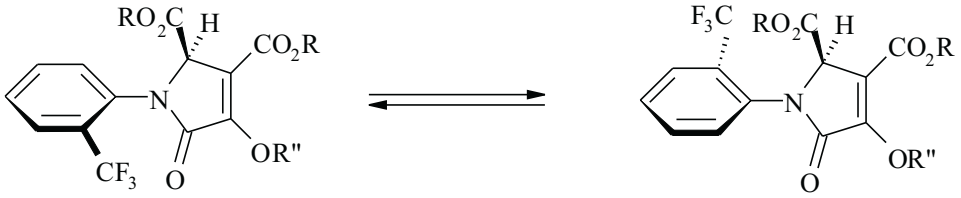
The structures of **3a**–**3g** were deduced from their elemental analyses and their IR, ^{1}H, ^{13}C, and ^{19}F NMR spectra. The mass spectra of these compounds are fairly similar, as expected, and confirm their molecular weights. Initial fragmentation involves loss from or complete loss of the side chains and scission of the heterocyclic ring system.

The ^{1}H NMR spectrum of **3a** exhibits four sharp lines for methoxy (δ = 3.45, 3.62, and 3.76 ppm) and methine (δ = 5.47 ppm) protons. The aryl moiety shows characteristic signals in the appropriate regions of the spectrum. The ^{13}C NMR spectrum of **3a** shows fifteen sharp signals in agreement with the proposed structure.

The ^{1}H NMR spectrum of **3e** reveals that one of the methoxy signals is quite broad at 298 K, while the other methoxy resonances remain sharp. The broad line sharpens at low temperature and a new weak resonance appears. The maximum exchange broadening at half peak height ($\nu_{1/2max}$) of the methoxy resonance at 298 K is 1.7 Hz. The $\nu_{1/2max}$ for a two site system with very unequal populations is given by P_B ($|\nu_A - \nu_B|$) [13,14], where P_B is the fractional population of the minor conformer that calculated to be populated to the extent of 7% at this temperature. A line-shape calculation carried out with $P_B = 7\%$, $k = 130\ s^{-1}$, and with the chemical shift differences for methoxy group at 0°C, reproduces well the observed spectrum at 25°C. The free-energy of activation ($\Delta G^{\#}$) and $\Delta G°$ for the *N*-aryl bond rotation in **3e** are then 60.9 ± 2 kJ mol^{-1} and 6.6 kJ mol^{-1}, respectively.

The observed dynamic NMR effect for **3e** can be attributed to restricted rotation around aryl-nitrogen single bond [15,16] as a result of the steric effect of the trifluoromethyl group at the ortho position (Scheme 3).

Scheme 3



The presented reaction gives a simple one-pot entry into the synthesis of polyfunctionalized 5-oxo-2,5-dihydro-1*H*-pyrrole derivatives of potential synthetic interest. Dynamic NMR effects are observed in the ^{1}H NMR spectra of **3e** and attributed to restricted rotation around the aryl-nitrogen bond.

EXPERIMENTAL

Dialkyl acetylenedicarboxylates, methyl and ethyl oxalyl chloride, and arylamine derivatives were obtained from Fluka (Buchs, Switzerland) and were used without further purification. Melting points were measured on an Electrothermal 9100 apparatus. Elemental analyses for C, H, and N were performed using a Heraeus CHN-O-Rapid analyzer. These results agreed favorably with the calculated values. Mass spectra were recorded on a Finnigan-Matt 8430 mass spectrometer operating at an ionization potential of 70 eV. ^{1}H, ^{13}C, and ^{19}F NMR spectra were measured with a Bruker DRX-500 AVANCE instrument at 500.1, 125.7, and 470.6 MHz, respectively. ^{1}H, ^{13}C, and ^{19}F NMR spectra were obtained on solution in $CDCl_3$ using TMS or $CFCl_3$ as internal standard. IR spectra were measured on a Shimadzu IR-460 spectrometer.

Methyl 2-(2-fluoroanilino)-2-oxo-acetate (2a). General procedure. To a stirred solution of 2-fluoroaniline (1.11 g, 10 mmol) in CH_2Cl_2 (20 mL) was added, dropwise, a mixture of methyl oxalyl chloride (1.22 g, 10 mmol) in CH_2Cl_2 (10 m L) and a solution of NaOH (0.40 g, 10 mmol) in water (10 ml) at 0°C over 10 min. The reaction mixture was then allowed to warm-up to room temperature and stirred for 24 h. The product was extracted three times with 20 m L of CH_2Cl_2. The organic phase was treated with anhydrous $MgSO_4$ and evaporated. The product was recrystallized from methanol to yield **2a** as colorless crystals; yield: 1.77 g (90%), mp 85–87°C. IR (KBr) $\bar{\nu}$ = 3370 (NH), 1720 and 1710 (C=O) cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 3.91 (s, 3 H, Me), 7.23-7.36 (m, 3 H, Ar), 8.10 (m, 1 H, Ar), 9.20 (br, 1 H, NH) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 53.03 (OMe), 115.37 (d, $^{2}J_{CF}$ 19.1 Hz, C–N), 123.11 (CH), 124.59 (d, $^{4}J_{CF}$ 3.5 Hz, CH), 126.42 (d, $^{3}J_{CF}$ 7.5 Hz, CH), 153.79 (d, $^{1}J_{CF}$ 245.0 Hz, CF), 154.51 and 160.76 (2 C=O) ppm. ^{19}F NMR (471 MHz, $CDCl_3$): δ = –128.95 (CF) ppm. MS: *m/z* (%) = 318 (8), 154 (19), 108 (100), 83 (46), 57 (38), 41 (27). Anal. Calcd for $C_{18}H_{23}NO_4$ (317.4): C, 68.1; H, 7.3; N, 4.4%. Found: C, 68.7; H, 7.5; N, 4.4%.

Analogously the following compounds were obtained:

Ethyl 2-(2-fluoroanilino)-2-oxo-acetate (2b). Colorless oil; yield: 1.9 g (90%). IR (KBr) $\bar{\nu}$ = 3375 (NH), 1704 and 1705 (C=O) cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.48 (t, 3 H, $^{3}J_{HH}$ 7.2 Hz, Me), 4.50 (q, 2 H, $^{3}J_{HH}$ 7.2 Hz, CH_2), 7.01–7.38 (m, 3 H, Ar), 8.25–8.40 (m, 1 H, Ar), 9.20 (br, 1 H, NH) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 13.36 (Me), 63.44 (OCH_2), 115.00 (d, $^{2}J_{CF}$ 17.8 Hz, C–N), 121.43 and 124.78 (2 CH), 125.76 (d, $^{3}J_{CF}$ = 8.1 Hz, CH), 152.70 (d, $^{1}J_{CF}$ 245.8 Hz, C-F), 154.08 and 160.50 (2 C=O) ppm.^{19}F NMR (471 MHz, $CDCl_3$): δ = –130.65 (CF) ppm.

Ethyl 2-oxo-2-[2-(trifluoromethyl)-anilino]-acetate (2c). Colorless oil; yield: 2.4 g (92%). IR (KBr) $\bar{\nu}$ = 3380 (NH), 1757, 1715 (C=O) cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.48 (t, 3 H, $^{3}J_{HH}$ 7.2 Hz, Me), 4.50 (q, 2 H, $^{3}J_{HH}$ 7.2 Hz, CH_2), 7.30–8.40 (m, 4 H, Ar), 9.35 (br, 1 H, NH) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 13.76 (Me), 64.12 (OCH_2), 120.63 (q, $^{2}J_{CF}$ 30.4 Hz, C), 123.52 and 125.83 (2 CH), 124.17 (q, $^{1}J_{CF}$ 276.2 Hz, CF_3), 126.72 (q, $^{3}J_{CF}$ 5.9 Hz, CH) 130.30 (C), 133.62 (CH), 134.32 (C–N), 154.73 and 160.88 (2 C=O) ppm.^{19}F NMR (471 MHz, $CDCl_3$): δ = –61.41 (CF_3) ppm.

Dimethyl 1-(2-fluorophenyl)-4-methoxy-5-oxo-2,5-dihydro-1*H*-pyrrol-2,3-dicarboxylate (3a). General procedure. To a stirred solution of triphenylphosphine (0.52 g, 2 mmol) and methyl 2-(2-fluoro-anilino)-2-oxo-acetate (0.39 g, 2 mmol) in CH_2Cl_2 (10 m L) was added dropwise a mixture of dimethyl acetylendicarboxylate (0.28 g, 2 mmol) in CH_2Cl_2 (4 mL) at 0°C over 10 min. The reaction mixture was then allowed to warm up to room temperature and stirred for 24 h. The solvent was removed under reduced pressure and the residue was purified by column chromatography (*n*-hexane:EtOAc, 3:1) to yield **3a** as colorless oil; yield: 0.52 g (80%). IR (KBr) $\bar{\nu}$ = 1712, 1720 (C=O) cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 3.69, 3.89, and 4.46 (3s, 9 H, 3 OCH_3), 5.37 (s, 1 H, CH), 7.25–7.43 (m, 4 H, Ar) ppm.^{13}C NMR (125 MHz, $CDCl_3$): δ = 52.18, 53.02, and 60.35 (3 OCH_3), 61.84 (d, $^{4}J_{CF}$ 3.9 Hz, OCH), 112.35 (N–C=*C*), 116.81 (d, $^{2}J_{CF}$ 19.5 Hz, CH), 122.78 (d, $^{2}J_{CF}$ 12.1 Hz, N–C), 124.81 (d, $^{3}J_{CF}$ 3.5 Hz, CH), 128.93 (CH), 130.10 (d, $^{2}J_{CF}$ 7.9 Hz, CH), 154.39 (N–*C*=C), 157.61 (d, $^{1}J_{CF}$ 251.6 Hz, CF), 162.03, 164.02, and 167.82 (3 C=O) ppm. ^{19}F NMR (471 MHz, $CDCl_3$): δ = –120.93 (CF) ppm. MS: *m/z* (%) = 323 (M^+, 25), 264 (100), 115 (40), 122 (100). Anal. Calcd for $C_{15}H_{14}FNO_6$: C, 55.73; H, 4.36; N, 4.33%. Found: C, 55.7; H, 4.4; N, 4.3%.

Analogously the following compounds were obtained:

Dimethyl 4-ethoxy-1-(2-fluorophenyl)-5-oxo-2,5-dihydro-1*H*-pyrrol-2,3-dicarboxylate (3b). Yield 78%. Colorless oil. IR (KBr) $\bar{\nu}$ = 1710 and 1720 (C=O) cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ = 1.43 (t, 3 H, $^3J_{HH}$ 6.5 Hz, CH_3), 3.60 and 3.80 (2 s, 6 H, 2 OCH_3), 4.81 (q, 2 H, $^3J_{HH}$ 6.5 Hz, CH_2), 5.29 (s, 1 H, CH), 7.15–7.35 (m, 4 H, Ar) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 15.69 (CH_3), 52.08 and 52.98 (2 OCH_3), 61.83 (d, $^4J_{CF}$ 3.5 Hz, OCH), 68.77 (OCH_2), 112.00 (N–C=*C*), 116.79 (d, $^2J_{CF}$ 20.1 Hz, CH), 123.00 (d, $^2J_{CF}$ 12.0 Hz, N–C), 124.79 (d, $^3J_{CF}$ 3.7 Hz, CH), 128.94 (CH), 130.00 (d, $^2J_{CF}$ 8.2 Hz, CH), 154.14 (N–*C*=C), 157.62 (d, $^1J_{CF}$ 250.9 Hz, CF), 162.15, 164.04, and 167.92 (3 C=O) ppm. ^{19}F NMR (471 MHz, $CDCl_3$): δ = –120.95 (CF) ppm. MS: *m/z* (%) = 338 (M^++1, 50), 337 (M^+, 30), 322 (30), 278 (80), 218 (90), 122 (100). Anal. Calcd for $C_{16}H_{16}FNO_6$: C, 56.97; H, 4.78; N, 4.15%. Found: C, 56.0; H, 4.8; N, 4.2%.

Diethyl 4-ethoxy-1-(2-fluorophenyl)-5-oxo-2,5-dihydro-1*H*-pyrrol-2,3-dicarboxylate (3c). Colorless oil; yield: 0.60 g (82%). IR (KBr) $\bar{\nu}$ = 1713 and 1715 (C=O) cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ = 0.89, 1.14, and 1.28 (3 t, 9 H, $^3J_{HH}$ 7.0 Hz, CH_3), 3.88–3.94 and 4.07–4.15 (2m, 4 H, 2 CH_2), 4.65 (q, 2 H, $^3J_{HH}$ 7.0 Hz, CH_2), 5.16 (s, 1 H, CH), 7.00–7.25 (m, 4 H, Ar) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 13.64–13.66, 13.89–13.91, and 15.39–15.41 (3m, 3 CH_3), 60.86 and 61.81 (2 OCH_2), 61.89 (d, $^4J_{CF}$ 2.9 Hz, OCH), 68.66 (OCH_2), 113.08 (N–C=*C*), 116.51 (d, $^2J_{CF}$ 20.0 Hz, CH), 122.48 (d, $^2J_{CF}$ 11.8 Hz, N–C), 124.55 (CH), 128.81 (CH), 129.74 (d, $^2J_{CF}$ 7.9 Hz, CH), 153.84 (N–*C*=C), 156.47 (d, $^1J_{CF}$ 251.5 Hz, CF), 161.33, 163.89, and 167.15 (3 C=O) ppm. ^{19}F NMR (471 MHz, $CDCl_3$): δ = –120.83 (CF) ppm. MS: *m/z* (%) = 366 (M^++1, 70), 365 (M^+, 25), 292 (75), 218 (100), 122 (75). Anal. Calcd for $C_{18}H_{20}FNO_6$: C, 59.17; H, 5.52; N, 3.83%. Found: C, 59.2; H, 5.5; N, 3.9%.

Di-*tert*-butyl 4-ethoxy-1-(2-fluorophenyl)-5-oxo-2,5-dihydro-1*H*-pyrrol-2,3-dicarboxylate (3d). Colorless oil; yield: 0.76 g (90%). IR (KBr) $\bar{\nu}$ = 1718 and 1725 (C=O) cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ = 1.18 and 1.47 (2 s, 18 H, 2 CMe_3), 1.38 (t, 3 H, $^3J_{HH}$ 7.0 Hz, CH_3), (q, 2 H, $^3J_{HH}$ 7.0 Hz, CH_2), 5.11 (s, 1 H, CH), 7.08–7.37 (m, 4 H, Ar) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 15.53 (CH_3), 27.47 and 28.06 (2 CMe_3), 63.70 (d, $^4J_{CF}$ 3.7 Hz, OCH), 68.45 (OCH_2), 82.06 and 82.62 (2 *C*Me_3), 115.10 (N–C=*C*), 116.53 (d, $^2J_{CF}$ 20.0 Hz, C-3), 123.27 (d, $^2J_{CF}$ 11.8 Hz, N–C), 124.42 (d, $^3J_{CF}$ 3.4 Hz, C-6), 128.82 (C), 129.43 (d, $^3J_{CF}$ 8.0 Hz, C), 153.55 (N–*C*=C), 157.48 (d, $^1J_{CF}$ 250.0 Hz, CF), 160.32, 164.25, and 165.92 (3 C=O) ppm. ^{19}F NMR (471 MHz, $CDCl_3$): δ = –120.23 (CF) ppm. MS: *m/z* (%) = 422 (M^++1, 50), 310 (20), 265 (20), 122 (20), 57 (100). Anal. Calcd for $C_{22}H_{28}FNO_6$: C, 62.70; H, 6.70; N, 3.32%. Found: C, 62.7; H, 6.7; N, 3.3%.

Dimethyl 4-ethoxy-5-oxo-1-[2-(trifluoromethyl)-phenyl]-2,5-dihydro-1*H*-pyrrol-2,3-dicarboxylate (3e). Colorless crystals; yield: 0.62 g (80%), mp 82–84°C. IR (KBr) $\bar{\nu}$ = 1744 and 1716 (C=O) cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ = 1.42 (t, 3 H, $^3J_{HH}$ 7.1 Hz, CH_3), 3.63 and 3.80 (2s, 6 H, 2 OMe), 4.81 (q, 2 H, $^3J_{HH}$ Hz, OCH_2), 5.11 (s, 1 H, CH), 7.24–7.77 (m, 4 H, Ar) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 15.56 (CH_3), 51.00 and 52.86 (2 OMe), 63.27 (OCH), 68.62 (OCH_2), 113.30 (N–C=*C*), 123.08 (q, $^1J_{CF}$ 271.6 Hz, CF_3), 127.67 (C–N), 129.29 (q, $^2J_{CF}$ 30.6 Hz, *C*–CF_3), 129.77, 131.57, 133.24, and 133.49 (4 C), 154.02 (N–*C*=C), 162.10, 164.90, and 168.20 (3 C=O) ppm. ^{19}F NMR (471 MHz, $CDCl_3$): δ = –61.39 (CF_3) ppm. MS: *m/z* (%) = 388 (M^++1, 15), 372 (25), 328 (50), 268 (80), 172 (100), 145 (30). Anal. Calcd for $C_{17}H_{16}F_3NO_6$: C, 52.72; H, 4.16; N, 3.62%. Found: C, 52.7; H, 4.2; N, 3.6%.

Diethyl 4-ethoxy-5-oxo-1-[2-(trifluoromethyl)-phenyl]-2,5-dihydro-1*H*-pyrrol-2,3-dicarboxylate (3f). Colorless oil; yield: 0.62 g (75%). IR (KBr) $\bar{\nu}$ = 1735 and 1721 (C=O) cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ = 1.05–1.13, 1.26–1.29, and 1.39–1.42 (3 m, 9 H, 3 CH_3), 4.05–4.18, 4.21–4.27, and 4.75–4.82 (3 m, 6 H, 3 CH_2), 5.08 (s, 1 H, CH), 7.26–7.75 (m, 4 H, Ar) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 13.89, 14.02, and 15.51 (3 CH_3), 59.51 and 61.02 (2 OCH_2), 62.06 (OCH), 68.70 (OCH_2), 113.59 (N–C=*C*), 123.10 (q, $^1J_{CF}$ 273.1 Hz, CF_3), 127.60 (C–N), 129.29 (q, $^2J_{CF}$ 38.6 Hz, *C*–CF_3), 129.66, 131.77, 133.13, and 133.57 (4 C), 153.99 (N–*C*=C), 161.53, 165.02, and 167.72 (3 C=O) ppm. ^{19}F NMR (471 MHz, $CDCl_3$): δ = –61.33 (CF_3) ppm. MS: *m/z* (%) = 416 (M^++1, 75), 415 (M^+, 25), 342 (80), 268 (100), 172 (75). Anal. Calcd for $C_{19}H_{20}F_3NO_6$: C, 54.94; H, 4.85; N, 3.37%. Found: C, 54.9; H, 4.9; N, 3.4%.

Di-*tert*-butyl 4-ethoxy-5-oxo-1-[2-(trifluoromethyl)-phenyl]-2,5-dihydro-1*H*-pyrrol-2,3-dicarboxylate (3g). Colorless crystals; yield: 0.77 g (82%), mp 94–96°C. IR (KBr) $\bar{\nu}$ = 1740, 1720 (C=O) cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.31 and 1.53 (2s, 18 H, 2 CMe_3), 1.42 (t, 3 H, $^3J_{HH}$ 7.0 Hz, CH_3), 4.78 (q, 2 H, $^3J_{HH}$ 7.0 Hz, CH_2), 4.97 (s, 1 H, CH), 7.33–7.78 (m, 4 H, Ar) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 15.56 (CH_3), 27.72 and 28.14 (2 CMe_3), 64.50 (OCH), 68.32 (OCH_2), 82.13 and 82.96 (2 *C*Me_3), 115.93 (N–C=*C*), 125.81 (q, $^1J_{CF}$ 273.1 Hz, CF_3), 127.55 (C–N), 129.35 (q, $^2J_{CF}$ 39.2 Hz, *C*–CF_3), 129.39, 132.21, 132.84, and 133.76 (4 C), 153.47 (N–*C*=C), 160.84, 165.44, and 166.40 (3 C=O) ppm. ^{19}F NMR (471 MHz, $CDCl_3$): δ = –61.19 (CF_3) ppm. MS: *m/z* (%) = 472 (M^++1, 90), 416 (15), 360 (50), 315 (75), 297 (50), 268 (75), 172 (75), 57 (100). Anal. Calcd for $C_{23}H_{28}F_3NO_6$: C, 58.99; H, 5.99; N, 2.97%. Found: C, 60.0; H, 6.0; N, 3.0%.

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