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Three-component reactions involving quinoline or isoquinoline, dialkyl acetylenedicarboxylate and β-trifluoroacetyl vinyl ethyl ether

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Dedicated to Professor Weiyuan Huang on the occasion of his 90th birthday.

ABSTRACT

The three-component reactions (TCRs) involving quinoline or isoquinoline, dialkyl acetylenedicarboxylate and β-trifluoroacetyl vinyl ethyl ether were investigated. The reaction proceeded smoothly under ambient temperature in DMSO to give the 4-trifluoroacetyl substituted benzo[c]quinolizine derivatives in moderate yields. However, under the same reaction condition, isoquinoline afforded the 2-trifluoromethyl substituted 1-oxa-(11H)-benzo[a]dihydroquinolizine or 4-trifluoroacetyl substituted benzo[a]dihydroquinolizine products. The possible reaction pathways were proposed.

1. Introduction

Multicomponent reactions (MCRs) are convergent reactions, in which three or more starting materials react and basically all or most of the atoms contribute to the newly formed product [1]. They have long been recognized as effective, economic, convenient and environmental benign, which are important synthetic strategy towards heterocycles. Among the reported MCRs, three-component reactions (TCRs) based on aza-heterocyles and dimethyl acetylenedicarboxylate (DMAD) have drawn considerable interest of organic chemists since the first example reported by Ancheson et al. [2]. The reaction proceeded via a zwitterion generated *in situ* from pyridine and DMAD. During recent years, large numbers of the three-component reactions based on quinoline or isoquinoline, DMAD and various dipolarophiles have been explored, including hexachloroacetone, C-H acids, nitromethanes, bromopyruvates, alloxanes, terminal alkynes, isocyanates, aldehydes, ketones, α,β-unsaturated ketones, and so on [3].

β-Trifluoroacetyl vinyl ethyl ether, as a fluorine-containing synthon, has been employed in the synthesis of products bearing trifluoromethyl group [4]. As part of our current studies on the chemical transformation of β-trifluoroacetyl vinyl ethyl ether, it was found a dipolarophile that could react readily with several dipoles [5]. Based on the literature works above, investigations on the three-component reactions involving quinoline or isoquinoline, dialkyl acetylenedicarboxylate and β-trifluoroacetyl vinyl ethyl ether were conducted in our laboratory. Herein, we report the results of the reactions studied.

2. Results and discussion

Initially, the reaction of equimolar β-trifluoroacetyl vinyl ethyl ether **1**, dimethyl acetylenedicarboxylate (DMAD) **2a** and quinoline **3a** was conducted in toluene at room temperature. After stirring for nearly 3d, the starting material **1** almost remained untransformed, although there was one product formed. The product was isolated from the mixture by flash chromatography as a yellow solid. According to ^{1}H NMR spectrum, it was the adduct of one molecular of quinoline with two of DMAD (Table 1, entry 1) [6]. In order to achieve the TCR, the temperature was raised to 110 °C and the desired product **4aa** was obtained in a yield of 27% (Table 1, entry 2) together with several undefined by-products. The product was determined as 1,2-dimethoxycarbonyl-4-trifluoroacetyl-(11H)-benzo[c]quinolizine by spectral methods and elemental analysis. For example, in the ^{13}C NMR spectrum, the quartet at 177.4 ppm and singlet at 164.1 ppm and 162.5 ppm were assigned to $CF_3\underline{CO}$ and two ester carbonyl group, respectively. And the singlet at −68.9 ppm in ^{19}F NMR spectrum was assigned to the

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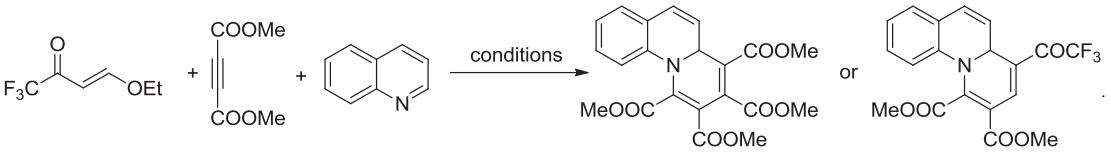
Table 1
Optimization of the reaction conditions



1a 2a 3a 4aa

Entry	Solvent	Temperature	Time (h)	Yield of **4aa** (%)[a]
1	Toluene	R. T.	72	–
2	Toluene	110 °C	10	27[b]
3	DMSO	R. T.	36	63
4	V_{DMSO}:V_{water} = 1:1	R. T.	36	Complicated
5	CH_3CN	R. T.	36	42
6	MeOH	R. T.	36	Complicated
7	Dioxane	R. T.	36	20
8	THF	R. T.	36	40
9	CH_2Cl_2	R. T.	36	Trace
10	$CHCl_3$	R. T.	36	15

[a] Determined by ^{19}F NMR spectra.
[b] Isolated yield.

trifluoroacetyl group. The mass spectrum showed a molecular ion peak at m/z = 394.2 $[M+H]^+$, which indicated that the product was generated from the coupling of the three components with an elimination of EtOH.

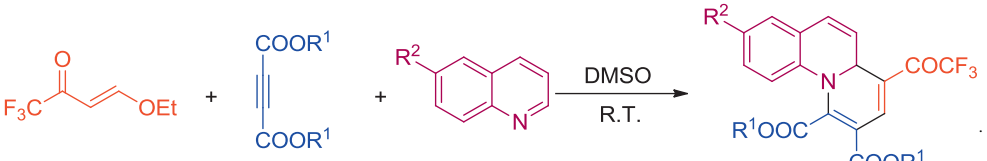
After examining the temperature carefully, it was found a paradox between the yield of **4aa** and the temperature: higher temperature gave more by-products that decreased the yield of **4aa**, but lower temperature led to little **4aa** formation. In order to solve the problem encountered, the effect of the solvents was investigated. To the best of our knowledge, more polar solvents are favorable for the dipolar reaction [7]. Several polar solvents were examined at room temperature (Table 1, entries 3–10). According to the results, DMSO was proved to be the most efficient solvent (Table 1, entry 3).

With the optimized reaction conditions in hand, several dialkyl acetylenedicarboxylates **2a–b** and quinoline derivatives **3a–c** were examined. All the reactions proceed smoothly to afford the trifluoroacetyl substituted benzo[c]quinolizine products **4** (Table 2).

It made no difference on the yields as substituent groups changed on quinolines. Furthermore, the structure of **4bb** was further confirmed by single crystal X-ray diffraction analysis (Fig. 1). As can be seen from the crystal figure, C2C3C4C5C6C7C8C9C10 atoms are coplanar, C11(C12=O1) C14C15(C16=O2)C19N1 atoms are coplanar, and the dihedral angle is 60.5°. Furthermore, the C11=C14–C15=C19-N1 cycle demonstrated the property of conjugation. The bond length of N1–C19 (1.33 Å) is even shorter than the standard bond length of C=N (1.35 Å). C19=C15 (1.38 Å), C15–C14 (1.42 Å) and C14=C11 (1.34 Å) are between the bond length of C=C (1.34 Å) and C–C (1.54 Å).

Encouraged by the results, isoquinoline **5a** was employed to react with β-trifluoroacetyl vinyl ethyl ether **1** and DMAD and a light yellow solid **6aa** was afforded. It was astonishing that the ^1H NMR and ^{19}F NMR spectra of the product **6aa** were obviously different from those of compound **4**. In the molecular structure of product **6aa**, ethoxyl group remained intact [3.76 ppm (q, 2H, J = 7.2 Hz) for $O\underline{CH_2}CH_3$ and 1.22 ppm (t, 3H, J = 7.2 Hz) for $OCH_2\underline{CH_3}$] and trifluoroacetyl group participated in the reaction [−77.1 ppm (s, CF_3) for $\underline{CF_3}(C)(C)(O)$]. Furthermore, the ^{13}C NMR of **6aa** showed a quartet at 123.9 ppm assigned to $\underline{CF_3}$ group, which was different from that of **4** (a quartet at 116.7 ppm). Instead of a quartet at about 175 ppm for $CF_3\underline{CO}$, a quartet at about 79 ppm was assigned to the quaternary carbon atom which connected to CF_3 directly. It is unusual that the CF_3CO group was attacked by the zwitterion. The reaction of 5-nitroisoquinoline **5b** with **1** and DMAD gave the same analogue product **6ab**. However,

Table 2
Reaction results of quinolines, dialkyl acetylenedicarboxylates and β-trifluoroacetyl vinyl ethyl ether



1 2a, R^1=Me; 2b, R^1=Et. 3a, R^2=H; 3b, R^2=Me; 3c, R^2=OMe. 4

Entry	**2a–b**	**3a–c**	Time (h)	Product	Yield (%)[a]
1	**2a**	**3a**	50	**4aa**	63
2		**3b**	48	**4ab**	52
3		**3c**	48	**4ac**	68
4	**2b**	**3a**	47	**4ba**	58
5		**3b**	48	**4bb**	47
6		**3c**	50	**4bc**	48

[a] Isolated yield.

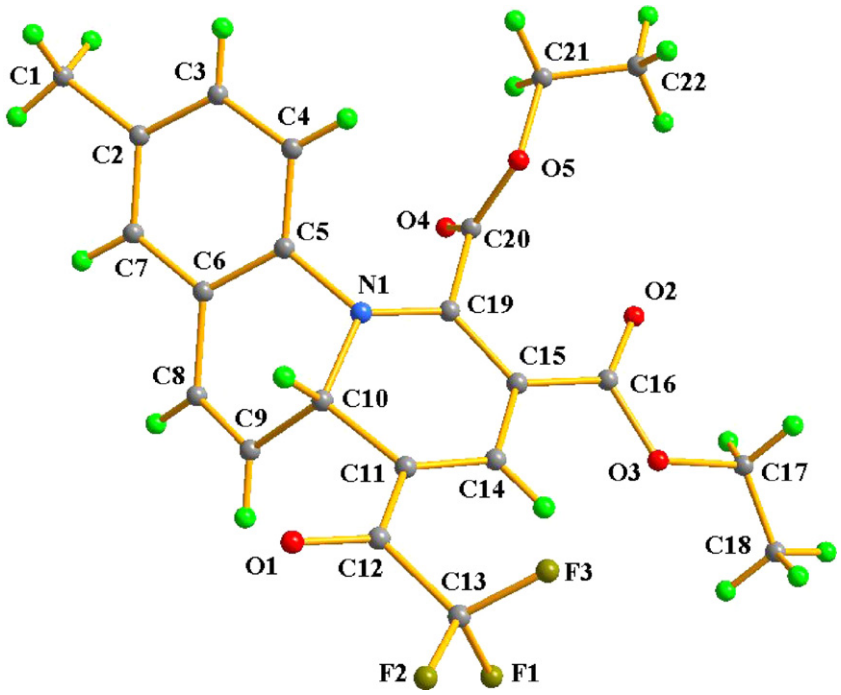
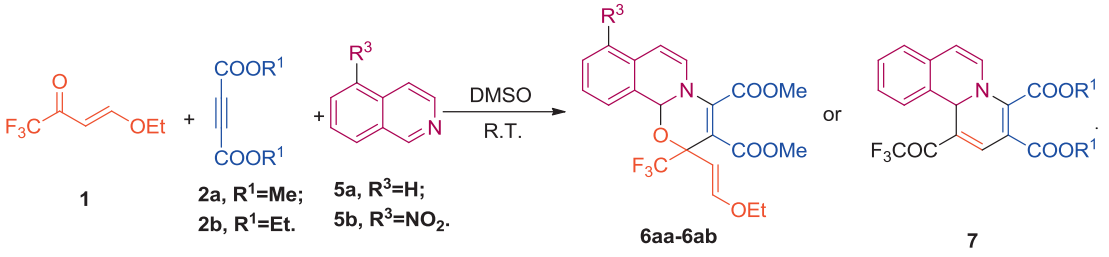


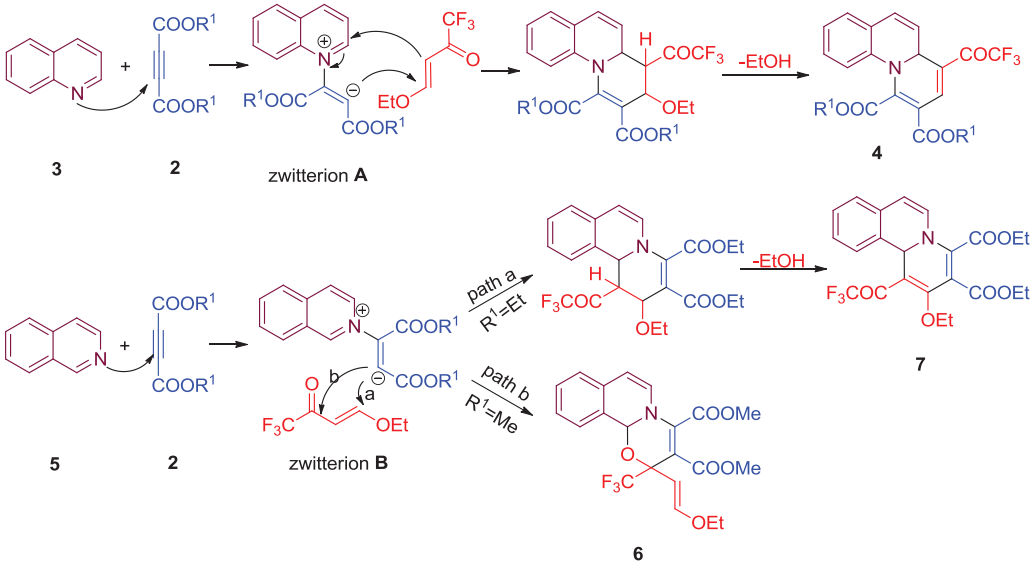
Fig. 1. Molecular structure of **4bb**.

Table 3
Reaction results of isoquinolines, dialkyl acetylenedicarboxylates and β-trifluoroacetyl vinyl ethyl ether



Entry	2a–b	5a–b	Time (h)	Product	Yield (%)[a]
1	**2a**	**5a**	60	**6aa**	63
2	**2a**	**5b**	72	**6ab**	45
3	**2b**	**5a**	63	**7**	47

[a] Isolated yield.



Scheme 1. Proposed reaction pathway.

to our astonishment, the C=C double bond involved product **7** was afforded by the reaction of **5a**, **1** and diethyl acetylenedicarboxylate **2b** in moderate yield. The results were summarized in Table 3.

The reaction pathway was proposed as shown in Scheme 1.

Zwitterion **A** was generated from dialkyl acetylenedicarboxylate **2** and quinoline **3**. The following cycloaddition with β-trifluoroacetyl vinyl ethyl ether **1** and elimination of ethanol gave the product **4**. Accordingly, when **1** was subjected to zwitterion **B**, there were two different pathways. In path a, C=C double bond was involved in the 1,4-dipolar cycloaddition, which afforded 4-trifluoroacetryl substituted benzo[a]quinolizine **7**. In the other pathway, C=O double bond was attacked by the zwitterion **B** to give the 2-trifluoromethyl substituted product **6**.

3. Conclusion

The three-component reactions of quinoline or isoquinoline, dialkyl acetylenedicarboxylate and β-trifluoroacetyl vinyl ethyl ether were investigated in DMSO under room temperature. Quinolines involved reactions afforded the corresponding 4-CF_3CO substituted benzo[c]quinolizine derivatives. But the isoquinolines involved TCRs gave 2-trifluoromethyl substituted 1-oxa-(11H)-benzo[a]dihydroquinolizine or 4-trifluoroacetyl substituted benzo[a]dihydroquinolizine products.

4. Experimental

4.1. General information

Melting points are measured on a Temp-Melt apparatus and are uncorrected. ^1H (300 MHz), ^{13}C NMR (75 MHz) and ^{19}F NMR (282 MHz) spectra were recorded on a Bruker AM-300 ultra-shield, 300 MHz, high performance digital FT-NMR spectrometer with Me_4Si and $CFCl_3$ as the internal and external standards, respectively. FT-IR spectra were obtained with a Nicolet AV-360 spectrophotometer. Low resolution mass spectra (LRMS) and high resolution mass spectra (HRMS) were obtained on a Finnigan GC–MS 4021 and a Finnigan MAT-8430 instrument using the electron impact ionization technique (70 eV) or Electrospray Ionization. Elemental analyses were performed by this institute. Single crystal X-ray structure analysis was performed on a Bruker P4 instrument. All solvents and reagents were used without further purification unless otherwise stated.

4.2. General experimental procedure

β-Trifluoroacetyl vinyl ethyl ether **1** (0.168 g, 1 mmol) and quinoline **3a** (0.129 g, 1 mmol) were solved in DMSO 5 ml. A solution of DMAD **2a** (0.142 g, 1 mmol) in DMSO 2 ml was added into the mixture dropwise. Monitored by TLC, when the reaction completed, the mixture was poured into water 20 ml and extracted by ethyl ether (30 ml × 4). The organic layer was dried over Na_2SO_4 anhydrous. After removing the solvent by a rotary evaporator, the product was isolate on silica gel (n-hexane/ethyl ether V/V = 5:1). The product was further purified by recrystallization from ethyl ether and hexane. An orange crystal was obtained in a yield of 63%.

4.2.1. 1,2-Dimethoxycarbonyl-4-trifluoroacetyl-(11H)-benzo[c]quinolizine (**4aa**)

Orange crystals, mp: 180–181 °C. FT-IR (KBr) cm^{-1}: 1742, 1715, 1620, 1481, 1438. ^1H NMR ($CDCl_3$, 300 MHz): δ 7.92 (s, 1H), 7.34–7.21 (m, 4H), 6.62 (dd, 1H, J = 2.1 Hz, 9 Hz), 5.84 (dd, 1H, J = 2.7 Hz, 9.3 Hz), 5.32 (s, 1H), 3.77 (s, 3H), 3.66 (s, 1H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 177.4 (q, J = 34.4 Hz), 164.1, 162.5, 153.0, 139.5 (q, J = 3.7 Hz), 136.1, 131.7, 130.7, 128.7, 127.6, 127.1, 125.6, 121.6, 116.7 (q, J = 288.9 Hz), 114.9, 97.7, 53.9, 53.1, 52.0. ^{19}F NMR ($CDCl_3$, 282 MHz): δ −68.95 (s, CF_3). LR-ESI-MS (m/z): 394.2 ($M+H^+$). HR-EI-MS: mass 393.0822, calcd. Mass 393.0824. Anal. Calcd. For $C_{19}H_{14}F_3NO_5$: C, 58.02; H, 3.59; N, 3.56; Found: C, 57.96; H, 3.41; N, 3.34.

4.2.2. 1,2-Dimethoxycarbonyl-4-trifluoroacetyl-8-methyl-(11H)-benzo[c]quinolizine (**4ab**)

Yellow crystals, mp: 133–135 °C. FT-IR (KBr) cm^{-1}: 2958, 1738, 1715, 1663, 1662, 1480, 1430, 1266, 1149, 1068, 848, 758, 709. ^1H NMR ($CDCl_3$, 300 MHz): δ 7.83 (s, 1H), 7.12 (d, 1H, J = 7.8 Hz), 6.98 (d, 2H, J = 7.2 Hz), 6.53 (dd, 1H, J = 2.4 Hz, 9.6 Hz), 5.79 (dd, 1H, J = 2.1 Hz, 9.0 Hz), 5.23 (s, 1H), 3.75 (s, 3H), 3.63 (s, 3H), 2.39 (s, 3H). ^{19}F NMR ($CDCl_3$, 282 MHz): δ −68.94 (s, CF_3). LR-EI-MS (m/z): 407 (100.0, M^+), 348 (37.7, M^+-COOMe), 310 (42.7, M^+-$COCF_3$), 192 (35.5). Anal. Calcd. For $C_{20}H_{16}F_3NO_5$: C, 59.07; H, 3.96; N, 3.44; Found: C, 59.20; H, 4.26; N, 3.28.

4.2.3. 1,2-Dimethoxycarbonyl-4-trifluoroacetyl-8-methoxyl-(11H)-benzo[c]quinolizine (**4ac**)

Yellow crystals, mp: 182–184 °C. FT-IR (KBr) cm^{-1}: 3121, 1737, 1714, 1661, 1621, 1572, 1482, 1431, 1268, 1152, 1016, 829, 759. ^1H NMR ($CDCl_3$, 300 MHz): δ 7.32 (s, 1H), 6.60 (1H, d, J = 7.8 Hz), 6.13 (s, 2H), 5.97 (d, 1H, J = 9.0 Hz), 5.24 (d, 1H, J = 9.0 Hz), 4.69 (s, 3H), 3.22 (s, 3H), 3.16 (s, 3H), 3.09 (s, 3H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 177.1 (q, J = 34.4 Hz), 164.1, 162.6, 159.5, 153.2, 139.5 (q, J = 4.1 Hz), 132.3, 131.8, 129.2, 125.7, 122.7, 116.8 (q, J = 288.9 Hz), 114.8, 114.4, 112.0, 97.2, 55.6, 54.4, 53.2, 52.0. ^{19}F NMR ($CDCl_3$, 282 MHz): δ −70.4 (s, CF_3). LR-EI-MS (m/z): 423 (M^+), 364 (35), 326 (32). HR-EI-MS: mass 423.0931, calcd. Mass 423.0930, formula $C_{20}H_{16}NO_6F_3$.

4.2.4. 1,2-Diethoxycarbonyl-4-trifluoroacetyl-(11H)-benzo[c]quinolizine (**4ba**)

Yellow crystals, mp: 128–131 °C. FT-IR (KBr) cm^{-1}: 3452, 2988, 1739, 1698, 1608, 1410, 1369, 1128, 834. ^1H NMR ($CDCl_3$, 300 MHz): δ 8.96 (d, 1H, J = 4.8 Hz), 7.94–7.68 (m, 5H), 7.47 (t, 1H, J = 7.5 Hz), 6.90 (s, 1H), 4.31–4.25 (m, 2H), 4.05 (q, 2H, J = 7.2 Hz,), 1.30 (t, 3H, J = 7.2 Hz,), 1.09 (t, 3H, J = 6.9 Hz,). ^{13}C NMR ($CDCl_3$, 75 MHz): δ174.2 (q, J = 29.4 Hz), 167.5, 164.9, 151.7, 138.6, 134.4 (q, J = 4.6 Hz), 134.3, 132.5, 129.2, 126.1, 121.4, 118.0 (q, J = 291.7 Hz), 115.2, 105.5, 99.7, 62.5, 61.0, 56.1, 14.5, 13.9, 13.8. ^{19}F NMR ($CDCl_3$, 282 MHz): δ −68.99 (s, CF_3). LR-ESI-MS (m/z): 422.2 ($M+H^+$). HR-EI-MS: mass 421.1139, calcd. mass 421.1137, formula $C_{21}H_{18}NO_5F_3$.

4.2.5. 1,2-Diethoxycarbonyl-4-trifluoroacetyl-8-methyl-(11H)-benzo[c]quinolizine (**4bb**)

Orange crystals, mp: 89–91 °C. FT-IR (KBr) cm^{-1}: 2987, 1742, 1719, 1657, 1609, 1479, 1296, 1067, 707, 639, 591. ^1H NMR ($CDCl_3$, 300 MHz): δ 7.94 (s, 1H), 7.18–7.12 (m, 1H), 7.01–6.98 (m, 2H), 6.55 (dd, 1H, J = 2.7 Hz, 9.6 Hz), 5.81 (dd, 1H, J = 2.7 Hz, 9.6 Hz), 5.26 (d, 1H, J = 12 Hz), 4.23–4.01 (m, 4H), 2.23 (s, 3H), 1.30–1.06 (m, 6H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 177.0 (q, J = 33.8 Hz), 163.5, 162.1, 153.2, 139.9, 138.8, 133.8, 131.7, 130.5, 128.0, 127.5, 125.6, 116.3 (q, J = 287.6 Hz), 121.7, 114.5, 97.6, 62.6, 60.7, 54.1, 21.1, 14.2, 13.5. ^{19}F NMR ($CDCl_3$, 282 MHz): δ −69.2 (s, CF_3). LR-EI-MS m/z (%): 435 (100, M^+), 362 (29), 334 (51), 192 (35). HR-EI-MS: mass 435.1292, calcd. mass 435.1294, formula $C_{22}H_{20}NO_5F_3$.

Structural parameters for **4bb** (one molecular of H_2O involved): C_{22} H_{22} F_3 N O_6, yellow block, crystal dimension 0.28 mm × 0.23 mm × 0.15 mm, monoclinic, space group P2 (1)/c, a = 19.953 (7) Å, b = 4.9688 (17) Å, c = 25.115 (9) Å, α = 90.00°, β = 110.302(5)°, γ = 90.00°, V = 2335.28 Å^3, Dc = 1.290 Mg/m^3, λ(Mo-Ka) = 0.71073 Å. CCDC reference number 731418.

*4.2.6. 1,2-Diethoxycarbonyl-4-trifluoroacetyl-8-methoxyl-(11H)-benzo[c]quinolizine (**4bc**)*

Yellow crystals, mp: 110–112 °C. FT-IR (KBr) cm^{-1}: 2985, 2936, 2909, 1741, 1716, 1653, 1603, 1420, 1304, 850, 707. ^1H NMR ($CDCl_3$, 300 MHz): δ 7.23 (d, 1H, J = 1.8 Hz), 6.49–6.48 (m, 1H), 6.00–5.98 (m, 2H), 5.84 (dd, 1H, J = 2.4 Hz, 9.6 Hz), 5.12 (dd, 1H, J = 2.4 Hz, 9.6 Hz), 4.56 (s, 1H), 3.48 (q, 2H, J = 7.2 Hz), 3.40 (q, 2H, J = 7.2 Hz), 0.56 (t, 6H, J = 7.2 Hz). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 177.2 (q, J = 40.8 Hz), 162.9, 162.1, 159.4, 153.4, 139.9, 132.5, 131.9, 129.3, 125.6, 123.1, 116.8 (q, J = 289.2 Hz), 114.2, 112.5, 111.9, 97.5, 62.6, 60.8, 55.6, 54.3, 14.3, 13.6. ^{19}F NMR ($CDCl_3$, 282 MHz): δ −70.6 (s, CF_3). LR-EI-MS (m/z): 451 (M^+, 100), 422 (4), 378 (31). HR-EI-MS: mass 451.1247, calcd. mass 451.1243, formula $C_{22}H_{20}NO_6F_3$.

*4.2.7. 2-Trifluoromethyl-2-ethoxyvinyl-3,4-dimethoxycarbonyl-(11H)-benzo[a]quinolizine (**6aa**)*

Light yellow crystals, mp: 131–133 °C. FT-IR (KBr) cm^{-1}: 2952, 1749, 1698, 1638, 1555, 1462, 1429, 921, 787, 704. ^1H NMR ($CDCl_3$, 300 MHz): δ 7.24–7.14 (m, 3H), 6.99 (d, 1H, J = 7.5 Hz), 6.82 (d, 1H, J = 12.6 Hz), 6.24 (d, 1H, J = 7.8 Hz), 5.83 (s, 1H), 5.69 (d, 1H, J = 7.5 Hz), 5.32 (d, 1H, J = 12.6 Hz), 3.82 (s, 3H), 3.76 (q, 2H, J = 7.2 Hz), 3.63 (s, 3H), 1.22 (t, 3H, J = 7.2 Hz). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 164.5, 163.5, 153.6, 146.6, 129.9, 129.8, 123.9 (q, J = 284.8 Hz), 127.4, 127.3, 125.9, 125.5, 123.6, 105.9, 105.3, 99.6, 79.7 (q, J = 31.7 Hz), 78.6, 65.4, 53.4, 52.1, 14.5. ^{19}F NMR ($CDCl_3$, 282 MHz): δ −77.1 (s, CF_3). LR-EI-MS (m/z): 439 (16, M^+), 364 (67), 298 (91), 145 (100), 129 (82). HR-EI-MS: mass 439.1242, calcd. mass 439.1243, formula $C_{21}H_{20}NO_6F_3$.

*4.2.8. 2-Trifluoromethyl-2-ethoxyvinyl-3,4-dimethoxycarbonyl-8-nitryl-(11H)-benzo[a]quinolizine (**6ab**)*

Yellow crystals, mp: 125–127 °C. FT-IR (KBr) cm^{-1}: 1738, 1649, 1528, 1438, 1470, 1185, 1115, 765, 668. ^1H NMR ($CDCl_3$, 300 MHz): δ 8.07 (d, 1H, J = 7.5 Hz), 7.63 (d, 1H, J = 7.5 Hz), 7.38 (t, 1H, J = 8.0 Hz), 6.70 (d, 1H, J = 12.6 Hz), 6.27 (s, 1H), 5.39 (d, 1H, J = 12.6 Hz), 3.92 (s, 3H), 3.81 (s, 3H), 3.78 (q, 2H, J = 7.5 Hz), 1.24 (t, 3H, J = 7.5 Hz). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 164.6, 162.0, 151.0, 144.2, 137.6, 133.7, 129.6, 127.5, 126.6, 126.4, 125.4, 124.1 (q, J = 287.9 Hz), 119.2, 97.5, 97.0, 79.7 (q, J = 3.2 Hz), 76.7 (q, J = 28.9 Hz), 65.3, 53.5, 52.7, 14.5. ^{19}F NMR ($CDCl_3$, 282 MHz): δ −75.1 (s, CF_3). LR-ESI-MS (m/z): 485.0 (M+H^+). HR-ESI-MS: formula $C_{21}H_{19}F_3N_2Na_1O_8$ (M+Na^+).

*4.2.9. 1,2-Diethoxycarbonyl-4-trifluoroacetyl-(11H)-benzo[a]quinolizine (**7**)*

Yellow crystals, mp: 145–147 °C. FT-IR (KBr) cm^{-1}: 3440, 2987, 1736, 1714, 1657, 1612, 1465, 1125, 1056, 644. ^1H NMR ($CDCl_3$, 300 MHz): δ 8.09 (d, 1H, J = 1.5 Hz), 7.28–7.25 (m, 2H), 7.18–7.15 (m, 1H), 6.75–6.72 (m, 1H), 6.57 (dd, 2H, J = 7.2 Hz, 14.4 Hz), 5.92 (1H, s), 4.41 (q, 2H, J = 7.1 Hz), 4.23 (q, 2H, J = 7.1 Hz), 1.37 (t, 3H, J = 7.2 Hz), 1.30 (t, 3H, J = 7.2 Hz). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 177.4 (q, J = 35.3 Hz), 163.4, 161.9, 149.7, 141.0 (q, J = 3.7 Hz), 130.0, 128.6, 128.4, 127.8, 125.8, 124.4, 123.4, 121.7, 116.9 (q, J = 288.5 Hz), 114.8, 97.6, 63.2, 60.9, 56.9, 14.2, 13.8. ^{19}F NMR ($CDCl_3$, 282 MHz): δ −69.3 (s, CF_3). LR-EI-MS (m/z): 421 (100, M^+), 420 (100), 348 (50.7), 320 (59.6), 178 (45.1). HR-EI-MS: mass 421.1132, calcd. mass 421.1137, formula $C_{21}H_{18}NO_5F_3$.

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