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Efficient synthesis of new 1-alkyl(aryl)-5-(3,3,3-trihalo-2-oxopropylidene)-1*H*-pyrrol-2(5*H*)-ones

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ABSTRACT

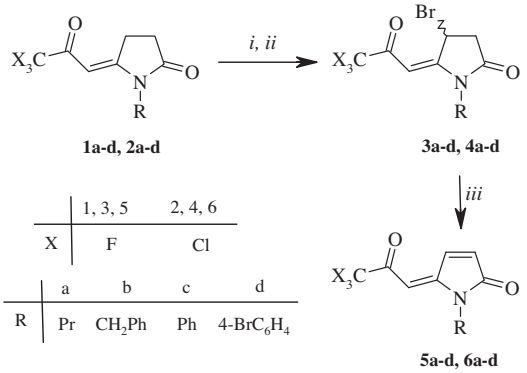
The synthesis of 1-alkyl(aryl)-5-(3,3,3-trihalo-2-oxopropylidene)-1*H*-pyrrol-2(5*H*)-ones **5, 6a–d** from 1-alkyl(aryl)-4-bromo-5-(3,3,3-trihalo-2-oxopropylidene)-1*H*-pyrrolidin-2-ones **3, 4a–d** is reported. The 1-alkyl(aryl)-4-bromo-5-(3,3,3-trihalo-2-oxopropylidene)-1*H*-pyrrolidin-2-ones **3, 4a–d** were obtained from regiospecific bromination of 1-alkyl(aryl)-5-(3,3,3-trihalo-2-oxopropylidene)-1*H*-pyrrolidin-2-ones **1, 2a–d** with molecular bromine. The NMR and X-ray diffraction data showed that 1-alkyl(aryl)-5-(3,3,3-trihalo-2-oxopropylidene)-1*H*-pyrrolidin-2-ones were brominated at 4-position in the pyrrolidin-2-one ring.

Our continuing interest in 1,3-dielectrophilic compounds has led us to study a new aspect of the application of the acetal acylation method for producing methyl 4-methoxy-6-oxo-7,7,7-trihalo-4-heptenoates **1** and **2**.[1] These 1,3-dielectrophilic precursors have proved to be important building blocks for regiospecific synthesis of heterocyclic compounds bearing trihalomethyl group with important pharmacological and synthetic applications.[2] Recently, the synthesis of 5-bromo-1,1,1-trichloro-(fluoro)-4-methoxy pent-3-en-2-ones, obtained from bromination of the parent enones, has been developed, in analytical purity and good yields.[3]

On the other hand, the importance of the pyrrole ring has continued to stimulate a great deal of interest in the development of new methodologies for its synthesis.[4–8] Pyrrolin-2-ones are biologically active compounds, which are important structural units in alkaloids, nucleosides, antineoplastic agents or immunosuppressants.[9–12] In 3-pyrrolin-2-ones, the α,β-unsaturated lactam moiety can be utilized as a Michael acceptor for a variety of nucleophiles, including carbon and nitrogen nucleophiles. In addition pyrrolidin-2-ones can be utilized as precursors for a variety of heterocycles, including 3-(3-azolyl)propanoates and 3-(3-azolyl)propanamides.[2,13]

Herein, we wish to report an efficient approach for the synthesis of 1-alkyl(aryl)-4-bromo-5-(3,3,3-trihalo-2-oxopropylidene)-1*H*-pyrrolidin-2-ones (**3a–d, 4a–d**) from the corresponding 1-alkyl (aryl)-5-(3,3,3-trihalo-2-oxopropylidene)-1*H*-pyrrolidin-2-ones (**1a–d**, **2a–d**), and their subsequent dehydrobromination with triethylamine to the 1-alkyl(aryl)-5-(3,3,3-trihalo-2-oxopropylidene)-1*H*-pyrrol-2(5*H*)-ones (**5a–d, 6a–d**). The starting 1-alkyl (aryl)-5-(3,3,3-trihalo-2-oxopropylidene)-1*H*-pyrrolidin-2-ones (**1a–d**, **2a–d**) were prepared from the corresponding methyl 4-methoxy-6-oxo-7,7,7-trihalo-4-heptenoates reacting with primary alkyl and aryl amines.[1]

The precursors **1a–d** and **2a–d** have two obvious nucleophilic sites, 1-position at propylidene chain and 3-position at pyrrolidin-2-one ring. However, we observed that the electrophilic bromine, from molecular bromine, reacted exclusively at 4-position in pyrrolidin-2-one ring, the reactive nucleophilic site under used conditions (Scheme 1). The monobromination was instantaneous without acid catalysis, as soon as the bromine was added to pyrr-



Scheme 1. Reagents and conditions: (i) Br_2, CH_2Cl_2, 25 °C, 4 h; (ii) pyridine, 0–25 °C, 30 min; (iii) Et_3N, CH_2Cl_2, 25 °C, 15 min.

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olidin-2-ne solution, the red coloration was lost and the HBr was released. The ^{1}H NMR data have demonstrated that the brominated products **3** and **4** are pure. The unambiguous ^{1}H and ^{13}C NMR chemical shift assignments of compounds **3a–d** and **4a–d** were obtained with the help of 2D and DEPT 135 NMR experiments. The structure of **3d** was elucidated by an X-ray crystallographic analysis (Fig. 1).[14] Given the novelty of the NMR assignment for brominated 5-(3,3,3-trifluoro-2-oxopropylidene)-1*H*-pyrrolidin-2-ones we are pleased that these assignments could be validated by X-ray crystallographic result.

Compounds **3a–d** and **4a–d** show ^{1}H chemical shifts of the diastereotopic methylene hydrogens (H-3) as a characteristic ABX system, a doublet at 3.1 ppm with a geminal coupling constant at ^2J = 19 Hz from hydrogen cis to the bromine atom and a double doublet at 3.32 ppm with a vicinal coupling constant at ^3J = 7 Hz and a geminal coupling constant at ^2J = 19 Hz from hydrogen trans to bromine. The signal from the H-4 was a doublet at the range of 5.75–5.90 ppm with ^3J = 7 Hz. The signal characteristic of vinylic hydrogen at the propylidene moiety was observed as a singlet at 5.6–5.8 ppm. The ^{13}C NMR spectra showed the signals of the propylidene moiety at characteristic regions, CF_3 at 117 ppm as a quartet with J_{CF} = 292 Hz or CCl_3 as a low intense signal at 96 ppm, C-sp^2 at 91–94 ppm and carbonyl at the range of 177–178 ppm as a quartet with J_{CF} = 35 Hz for **3a–d**, and carbonyl at 178–180 ppm for **4a–d**. Brominated carbon was observed at a range of 36 ppm in lower field than signal for C-3 at range 40 ppm.

A proposed mechanism for bromination of **1a–d** and **2a–d** could involve a tautomerization as showed in Scheme 2.

The compounds **5a–d** and **6a–d** show ^{1}H chemical shifts of the vinylic hydrogens, H-3 as a doublet at 8.2 ppm with a cis coupling constant at ^3J = 6 Hz, and H-4 as a doublet of doublets at 6.5 ppm with a cis coupling constant at ^3J = 6 Hz and a coupling constant ^4J = 1 Hz from hydrogen at the propylidene moiety H-6. The signal from vinylic hydrogen H-6 was observed as a tin doublet with ^4J = 1 Hz, for trifluorinated derivatives at 5.9 ppm and for trichlorinated derivatives at 6.3 ppm. The ^{13}C NMR spectra showed the signals of the propylidene moiety at characteristic regions, CF_3 at

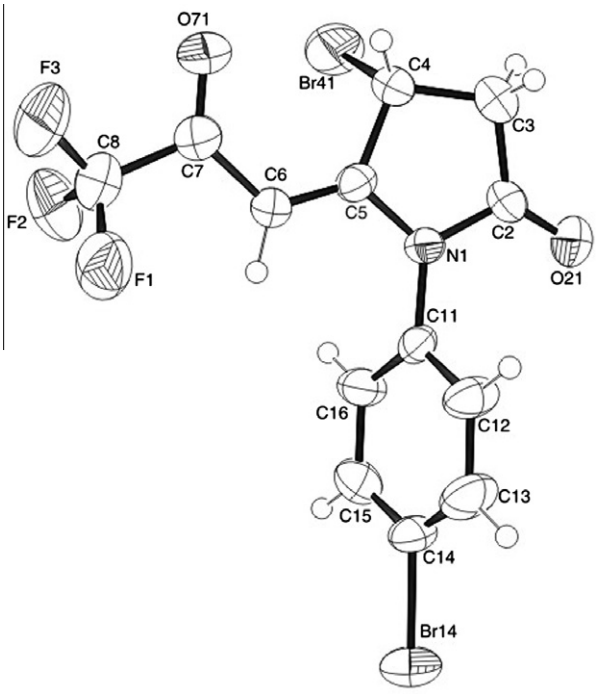
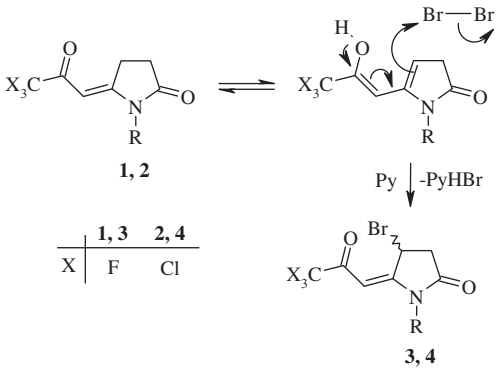


Figure 1. X-ray molecular structure of compound **6a** in representation of atoms via thermal ellipsoids at 50% probability level.

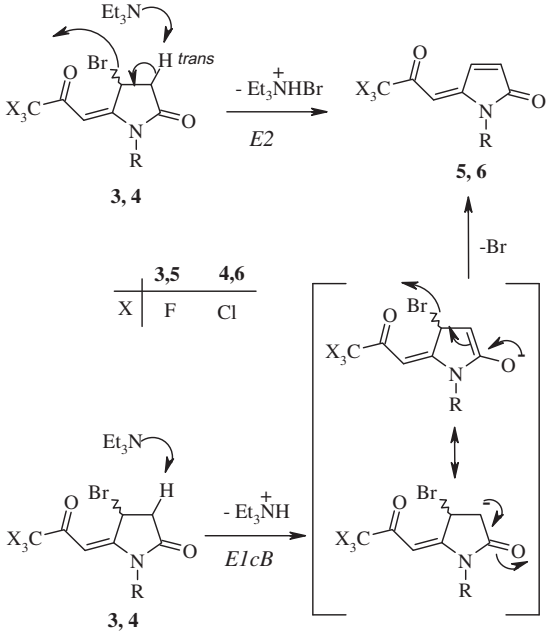


Scheme 2.

116 ppm as a quartet with J_{CF} = 291 Hz or CCl_3 as a low intense signal at 96.5 ppm, C-6 at 96–98 ppm and carbonyl C-7 at the range of 179–180 ppm as a quartet with J_{CF} = 35 Hz for **5a–d**, and as a short singlet at 178–180 ppm **6a–d**. Carbons C-3 and C-4 from the pyrrolone ring were observed, respectively, at the range of 136 and 128 ppm, typical chemical shifts for vinylic C-sp^2.

The HBr elimination from **3** and **4** with triethylamine furnished 1-alkyl(aryl)-5-(3,3,3-trihalo-2-oxopropylidene)-1*H*-pyrrol-2(5*H*)-ones **5** and **6** in a short reaction time (15 min) in quantitative yield. The structure of the synthesized products has been confirmed by mass spectrometry and ^{1}H and ^{13}C NMR spectroscopy. The mechanism involves two possibilities including classical E2 elimination, with Et_3N attack to trans bromine hydrogen and concerted output of the bromide, or E1cB elimination with amide enolate formation followed for bromide elimination. It still remains unknown, but investigations are currently in progress (Scheme 3).

In conclusion, we report a convenient synthesis of a new series of 1-alkyl(aryl)-4-bromo-5-(3,3,3-trihalo-2-oxopropylidene)-1*H*-pyrrolidin-2-ones and 1-alkyl(aryl)-5-(3,3,3-tri halo-2-oxopropylidene)-1*H*-pyrrol-2(5*H*)-ones. 1-Alkyl (aryl)-4-bromo-5-(3,3,3-trihalo-2-oxopropylidene)-1*H*-pyr rolidin-2-ones were regiospecifically brominated with molecular bromine under mild conditions furnishing good yields of products which were dehydrobrominated under alkaline conditions using Et_3N. This approach shows a clear advantage over the methods reported in the literature where the



Scheme 3.

synthesis of functionalized 5-propylidene-1*H*-pyrrolidin-2-one derivatives was obtained in several reaction steps, or using expensive reagents.[6–12,15]

All common reagents and solvents were used as obtained from commercial suppliers without further purification. All melting points were determined on a Reichert Thermovar apparatus and are uncorrected. ^{1}H and ^{13}C NMR spectra were acquired on a Bruker DPX 400spectrometer (^{1}H at 400.13 MHz and ^{13}C at 100.63 MHz), 5 mm sample tubes, 298 K, digital resolution ±0.01 ppm, in $CDCl_3$, and TMS as internal reference.

The general procedure for 1-alkyl(aryl)-4-bromo-5-(3,3,3-trihalo-2-oxopropylidene)-1*H*-pyrrolidin-2-ones (**3a–d, 4a–d**) with molecular bromine: to a stirred solution of 1-alkyl(aryl)-5-(3,3,3-trihalo-2-oxopropylidene)-1*H*-pyrroli din-2-one (2 mmol) in methylene chloride (5 mL) was added dropwise a solution of molecular bromine in methylene chloride. The mixture was stirred for 4 h at room temperature. Then the mixture was cooled in ice bath, at −4 °C, and to which was added a solution with pyridine (2 mmol) in methylene chloride. The resulting solution was stirred for 30 min. Then, it was washed with water (3 × 15 mL), and the organic layer was dried over Na_2SO_4. The solvent was evaporated to give pure products **3a–d** and **4a–d**. Products were fully characterized by elemental analysis and NMR data.[16]

The general procedure for 1-alkyl(aryl)-5-(3,3,3-trihalo-2-oxopropylidene)-1*H*-pyrrol-2(5*H*)-ones (**5a–d**, **6a–d**): to a stirred solution of 1-alkyl(aryl)-4-bromo-5-(3,3,3-trihalo-2-oxopropylidene)-1*H*-pyrrolidin-2-one (2 mmol) in methylene chloride (5 mL) at 0 °C was dropwise added a solution of triethylamine (2.1 mmol) in methylene chloride (5 mL). The mixture was stirred for 15 min. Then the mixture was washed with water (3 × 15 mL), and the organic layer was dried over $MgSO_4$. The solvent was evaporated to give pure products **5a–d** and **6a–d**. Products were fully characterized by elemental analysis and NMR data.[17]

Acknowledgments

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Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2010.07.073.

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16. For **3a**: 86%, red-brown oil, ^{1}H NMR δ 5.85 (s, 1H, H-6), 5.78 (d, 1H, J_{HH} = 7 Hz, H-4), 3.75 (m, 1H, H-9), 3.52 (m, 1H, H-9), 3.26 (dd, 1H, J_{HH} = 19 and 7 Hz, H-3), 3.03 (d, 1H, J_{HH} = 19 Hz, H-3), 1.69 (sx, 2H, J_{HH} = 7 Hz, H-10), 0.99 (t, 3H, J_{HH} = 7 Hz, H-11). ^{13}C NMR δ 177.7 (q, J_{CF} = 35 Hz, C-7), 173 (C-5), 165.6 (C-2), 116.1 (q, J_{CF} = 291 Hz, C-8), 91.5 (C-6), 42.4 (C-9), 39.7 (C-3), 36 (C-4), 19.4 (C-10), 11 (C-11). MS *m/z* (%) 315(M^++2, 10), 313 (M^+, 8), 244 (39), 234 (100), 204 (15), 108 (35). Compound **3b**: 91%, red oil, ^{1}H NMR δ 7.38–7.23 (m, 5H, Ph), 5.81 (s, 1H, H-6), 5.75 (d, 1H, J_{HH} = 7 Hz, H-4), 4.95 (d, 1H, J_{HH} = 16 Hz, H-9), 4.71 (d, 1H, J_{HH} = 16 Hz, H-9), 3.32 (dd, 1H, J_{HH} = 19 and 7 Hz, H-3), 3.09 (d, 1H, J_{HH} = 19 Hz, H-3). ^{13}C NMR δ 177.6 (q, J_{CF} = 35 Hz, C-7), 172.9 (C-5), 164.7 (C-2), 133, 129, 128.3, 127 (Ph), 115.9 (q, J_{CF} = 291 Hz, C-8), 92.8 (C-6), 44.4 (C-9), 39.7 (C-3), 35.9 (C-4). MS *m/z* (%) 364(M^++2, <5), 362 (M^+, <5), 292 (9), 282 (100), 204 (15), 91 (67). Compound **3c**: 90%, white solid, mp 77–79 °C, ^{1}H NMR δ 7.61–7.24 (m, 5H, Ph), 5.89 (d, 1H, J_{HH} = 7 Hz, H-4), 5.66 (d, 1H, H-6), 3.44 (dd, 1H, J_{HH} = 19 and 7 Hz, H-3), 3.16 (d, 1H, J_{HH} = 19 Hz, H-3). ^{13}C NMR δ 178.2 (q, J_{CF} = 35 Hz, C-7), 172.3 (C-5), 166.4 (C-2), 132.4, 130.2, 130, 126.9 (Ph), 115.9 (q, J_{CF} = 291 Hz, C-8), 93.3 (C-6), 40.1 (C-3), 36.2 (C-3). MS *m/z* (%) 349(M^++2, <5), 347 (M^+, <5), 278 (9), 268 (16), 198 (75), 170 (38), 144 (22), 77 (100). Compound **3d**: 80%, yellow solid, mp 139–141 °C, ^{1}H NMR δ 7.72 (m, 2H, Ar), 7.15 (m, 2H, Ar), 5.89 (d, 1H, J_{HH} = 7 Hz, H-4), 5.67 (d, 1H, H-6), 3.43 (dd, 1H, J_{HH} = 19 and 7 Hz, H-3), 3.17 (d, 1H, J_{HH} = 19 Hz, H-3). ^{13}C NMR δ 178 (q, J_{CF} = 35 Hz, C-7), 172 (C-5), 165.9 (C-2), 133.5, 131.3, 128.5, 120.1 (Ar), 115.8 (q, J_{CF} = 291 Hz, C-8), 93.2 (C-6), 40 (C-4), 36.1 (C-3). Compound **4a**: 79%, brown oil, ^{1}H NMR δ 6.15 (s, 1H, H-6), 5.83 (d, 1H, J_{HH} = 7 Hz, H-4), 3.78 (m, 1H, H-9), 3.53 (m, 1H, H-9), 3.26 (dd, 1H, J_{HH} = 19 and 7 Hz, H-3), 3.03 (d, 1H, J_{HH} = 19 Hz, H-3), 1.70 (sx, 2H, J_{HH} = 7 Hz, H-10), 0.99 (t, 3H, J_{HH} = 7 Hz, H-11). ^{13}C NMR δ 178.7 (C-7), 172.8 (C-5), 164.3 (C-2), 96.9 (C-8), 91.4 (C-6), 42.3 (C-9), 39.9 (C-3), 35.9 (C-4), 19.5 (C-10), 11.1 (C-11). MS *m/z* (%) 364(M^++2, <5), 362 (M^+, <5), 246 (100), 244 (90), 204 (13), 202 (10), 164 (55), 122 (58), 80 (20), 78 (18). Compound **4b**: 97%, brown oil, ^{1}H NMR δ 7.37–7.25 (m, 5H, Ph), 6.11 (s, 1H, H-6), 5.79 (d, 1H, J_{HH} = 7 Hz, H-4), 4.98 (d, 1H, J_{HH} = 16 Hz, H-9), 4.74 (d, 1H, J_{HH} = 16 Hz, H-9), 3.33 (dd, 1H, J_{HH} = 19 and 7 Hz, H-3), 3.11 (d, 1H, J_{HH} = 19 Hz, H-3). ^{13}C NMR δ 178.5 (C-7), 172.8 (C-5), 163.1 (C-2), 133.3, 129, 128.3, 127.3 (Ph), 96.7 (C-8), 93.1 (C-6), 44.5 (C-9), 40 (C-3), 35.7 (C-4). Compound **4c**: 89%, yellow solid, mp 118–120 °C, ^{1}H NMR δ 7.60–7.27 (m, 5H, Ph), 5.99 (d, 1H, H-6), 5.95 (d, 1H, J_{HH} = 7 Hz, H-4), 3.47 (dd, 1H, J_{HH} = 19 and 7 Hz, H-3), 3.17 (d, 1H, J_{HH} = 19 Hz, H-3). ^{13}C NMR δ 179 (C-7), 172.1 (C-5), 165.2 (C-2), 132.7, 130.1, 129.8, 126.9 (Ph), 96.6 (q, J_{CF} = 291 Hz, C-8), 93.3 (C-6), 40.4 (C-3), 36.2 (C-4). Compound **4d**: 91%, yellow solid, mp 146–148 °C, ^{1}H NMR δ 7.75 (m, 2H, Ar), 7.14 (m, 2H, Ar), 5.99 (d, 1H, H-6), 5.94 (d, 1H, J_{HH} = 7 Hz, H-4), 3.46 (dd, 1H, J_{HH} = 19 and 7 Hz, H-3), 3.17 (d, 1H, J_{HH} = 19 Hz, H-3). ^{13}C NMR δ 178.9 (q, J_{CF} = 35 Hz, C-7), 171.8 (C-5), 164.5 (C-2), 133.4, 131.7, 128.5, 123.9 (Ar), 96.5 (C-8), 93.4 (C-6), 40.3 (C-4), 36 (C-3).
17. For **5a**: 92%, yellow oil, ^{1}H NMR δ 8.06 (d, 1H, J_{HH} = 6 Hz, H-3), 6.38 (dd, 1H, $^3J_{HH}$ = 6 Hz, $^4J_{HH}$ = 1 Hz, H-4), 5.94 (s, 1H, H-6), 3.53 (t, 2H, $^3J_{HH}$ = 7 Hz, H-9), 1.56 (sx, 2H, J_{HH} = 7 Hz, H-10), 0.87 (t, 3H, $^3J_{HH}$ = 7 Hz, H-11). ^{13}C NMR δ 179.2 (q, J_{CF} = 35 Hz, C-7), 170.2 (C-2), 156.1 (C-5), 136.4 (C-3), 128.7 (C-4), 116.0 (q, J_{CF} = 291 Hz, C-8), 95.7 (C-6), 41.2 (C-9), 21.5 (C-10), 11.2 (C-11). MS *m/z* (%) 233 (M^+, 32), 164 (100), 136 (30). Compound **5b**: 87%, yellow oil, ^{1}H NMR δ 8.13 (d, 1H, $^3J_{HH}$ = 6 Hz, H-3), 7.37–7.18 (m, 5H, Ph), 6.52 (dd, 1H, $^3J_{HH}$ = 6 Hz, $^4J_{HH}$ = 1 Hz, H-4), 5.99 (s, 1H, H-6), 4.83 (s, 2H, H-9). ^{13}C NMR δ 179.1 (q, J_{CF} = 35 Hz, C-7), 170 (C-2), 155.4 (C-5), 136.7 (C-3), 134.9, 129, 128.7, 128.1, 127 (Ph), 115.8 (q, J_{CF} = 291 Hz, C-8), 96.9 (C-6), 43.2 (C-9). MS *m/z* (%) 281(M^+, 100), 212 (13), 184 (30), 91 (69). Compound **5c**: 94%, white solid, mp 98–99 °C, ^{1}H NMR δ 8.28 (d, 1H, $^3J_{HH}$ = 6 Hz, H-3), 7.6–7.21 (m, 5H, Ph), 6.58 (dd, 1H, $^3J_{HH}$ = 6 Hz, $^4J_{HH}$ = 1 Hz, H-4), 5.95 (s, 1H, H-6). ^{13}C NMR δ 179.4 (q, J_{CF} = 36 Hz, C-7), 169.3 (C-2), 156.5 (C-5), 136.5 (C-3), 132.2, 129.9, 129.3, 128.6, 123.4 (Ph), 115.8 (q, J_{CF} = 291 Hz, C-8), 97.3 (C-6). MS *m/z* (%) 267 (M^+, 39), 198 (100), 170 (51), 144 (9), 77 (28). Compound **5d**: 94%, yellow oil. ^{1}H NMR δ 8.28 (d, 1H, $^3J_{HH}$ = 6 Hz, H-3), 7.71 (m, 2H, Ar), 7.12 (m, 2H, Ar), 6.58 (dd, 1H, $^3J_{HH}$ = 6 Hz, $^4J_{HH}$ = 1 Hz, H-4), 5.94 (d, 1H, H-6). ^{13}C NMR δ 179.4 (q, J_{CF} = 36 Hz, C-7), 169 (C-2), 156 (C-5), 136.7 (C-3), 133.2, 131.2, 129.4 (Ar), 128.6 (C-4), 123.4 (Ar), 115.7 (q, J_{CF} = 291 Hz, C-8), 97.4 (C-6). MS *m/z* (%) 347 (M^++2, 25), 345 (M^+, 25), 276 (58), 248 (9), 169 (100). Compound **6a**: 89%, white solid, mp 52–53 °C. ^{1}H NMR δ 8.18 (d, 1H, $^3J_{HH}$ = 6 Hz, H-3), 6.43 (dd, 1H, $^3J_{HH}$ = 6 Hz, $^4J_{HH}$ = 1 Hz, H-4), 6.37 (d, 1H, $^4J_{HH}$ = 1 Hz, H-6), 3.64 (t, 2H, $^3J_{HH}$ = 7 Hz, H-9), 1.65 (sx, 2H, $^3J_{HH}$ = 7 Hz, H-10), 0.95 (t, 3H, J_{HH} = 7 Hz, H-11). ^{13}C NMR δ 179.4 (C-7), 170 (C-2), 155.3 (C-5), 135.9 (C-3), 128.2 (C-4), 96.7 (C-6), 96 (C-8), 41 (C-9), 21.6 (C-10), 11.2 (C-11). MS *m/z* (%) 281 (M^+, <5), 164 (100), 145 (14), 122 (31). Compound **6b**: 93%, white solid, mp 92–94 °C. ^{1}H NMR δ 8.17 (d, 1H, $^3J_{HH}$ = 6 Hz, H-3), 7.38–7.20 (m, 5H, Ph), 6.5 (dd, 1H, $^3J_{HH}$ = 6 Hz, $^4J_{HH}$ = 1 Hz, H-4), 6.33 (s, 1H, H-6), 4.86 (s, 2H, H-9). ^{13}C NMR δ 179.3 (C-7), 169.9 (C-2), 154.5 (C-5), 136.2 (C-3), 135.3, 128.9, 128.1, 128, 127.2 (Ph), 97.6 (C-6), 96.5 (C-8), 43.3 (C-9). MS *m/z* (%) 331 (M^++2, 12), 329 (M^+, 13), 294 (46), 212 (59), 184 (5), 91 (100). Compound **6c**: 88%, white solid, mp 130–132 °C, ^{1}H NMR δ 8.33 (d, 1H, $^3J_{HH}$ = 6 Hz, H-3), 7.56–7.26 (m, 5H, Ph), 6.56 (dd, 1H, $^3J_{HH}$ = 6 Hz, $^4J_{HH}$ = 1 Hz, H-4), 6.31 (d, 1H, $^4J_{HH}$ = 1 Hz, H-6). ^{13}C NMR δ 179.7 (C-7), 169.3 (C-2), 155.8 (C-5), 136.1 (C-3), 132.5, 129.8 (Ph), 129 (C-4), 128.1, 127.7 (Ph), 97.9 (C-6), 96.4 (C-8). MS *m/z* (%) 317 (M^++2, <5), 315 (M^+, <5), 198 (100), 170 (23), 144 (9), 77 (28). Compound **6d**: 86%, yellow solid, mp 127–130 °C, ^{1}H NMR δ 8.33 (d, 1H, $^3J_{HH}$ = 6 Hz, H-3), 7.69 (m, 2H, Ar), 7.15 (m, 2H, Ar), 6.56 (dd, 1H, $^3J_{HH}$ = 6 Hz, $^4J_{HH}$ = 1 Hz, H-4), 6.31 (d, 1H, H-6). ^{13}C NMR δ 179.6 (C-7), 169 (C-2), 155.2 (C-5), 136.3 (C-3), 133.1, 131.5, 129.3 (Ar), 128.1 (C-4), 123.1 (Ar), 98 (C-8), 96.3 (C-6). MS *m/z* (%) 395 (M^++2, <5), 393 (M^+, <5), 276 (100), 248 (8), 169 (30).