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Facile Synthesis of Substituted Ethyl 2-(Chloromethyl)-2-hydroxy-2*H*-1-benzopyran-3-carboxylates

by **Bhimapaka China Raju***[a]), **Gannerla Saidachary**[a]), **Jaladi Ashok Kumar**[a]), and **Balasubramanian Sridhar***[b])

[a]) Organic Chemistry Division-1, Indian Institute of Chemical Technology, Hyderabad-500 607, India (phone: +914027161725; fax: +91402716512; e-mail: chinarajuiict@yahoo.co.in)

[b]) Laboratory of X-Ray Crystallography, Indian Institute of Chemical Technology, Hyderabad-500 607, India (e-mail: sshiya@yahoo.com)

Ethyl 2-(chloromethyl)-2-hydroxy-2*H*-chromene-3-carboxylates **2a**–**2j** have been synthesized by reaction of substituted salicylaldehydes with ethyl 4-chloro-3-oxobutanoate, in the presence of piperidine in CH_2Cl_2 at room temperature, in good yields.

1. Introduction. – The *Knoevenagel* condensation [1] is one of the fundamental C,C bond-forming reactions in organic chemistry. It involves the condensation of carbonyl compounds with β-keto esters in presence of a base to give coumarins and chromenes. However, the β-keto ester with a Cl substituent at C(4) has an impact on their reactivity. We studied the reactivity of substituted salicylaldehydes with ethyl 4-chloro-3-oxobutanoate in presence of various bases. The results are discussed below.

2. Results and Discussion. – In continuation of our studies on heterocyclic compounds [2] and chromenes [3], here, we report a simple, efficient, and one-pot straightforward method for the synthesis of 2,2,3-trisubstituted 2*H*-chromenes (=2*H*-1-benzopyranes) by using substituted salicylaldehydes with ethyl 4-chloro-3-oxobutanoate in the presence of piperidine in CH_2Cl_2 under mild conditions in good yields. The obtained compounds are valuable intermediates for the preparation of various bioactive heterocyclic compounds.

Typically, 1 mmol of salicylaldehyde **1a** was reacted with 1 mmol of ethyl 4-chloro-3-oxobutanoate in the presence of piperidine (30 mol-%) in CH_2Cl_2 at room temperature. The reaction was monitored by TLC (8 h) and, after column chromatography, furnished ethyl 2-(chloromethyl)-2-hydroxy-2*H*-chromene-3-carboxylate (**2a**) in 60% yield (*Scheme 1*). The effect of different solvents such as MeCN, MeOH, EtOH, $CHCl_3$, DMF, and toluene in presence of piperidine was studied, and it was found that CH_2Cl_2 was the solvent of choice in terms of yield, reaction time, and selectivity for the formation of **2a**. Regarding the optimum quantity of catalyst, we found that 30 mol-% piperidine is necessary to promote the reaction in an efficient manner. We examined the reaction under similar conditions with different bases such as pyridine, 4-(dimethylamino)pyridine (DMAP), 1,4-diazabicyclo[2.2.2]octane (DABCO), 1*H*-imidazole, Et_3N, EtN^iPr_2, EtONa in EtOH, and K_2CO_3 in acetone. However, pyridine,

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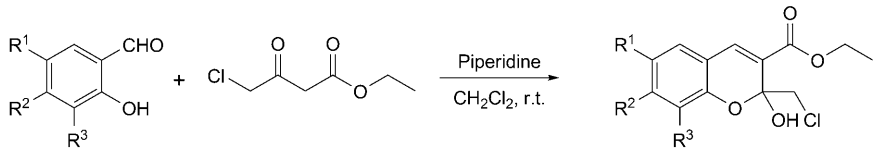
EtN^iPr_2, DABCO, and Et_3N gave lower yields of **2a**, whereas no reaction took place with other mentioned catalysts.

Scheme 1. *One-Pot Synthesis of Ethyl 2-(Chloromethyl)-2-hydroxy-2*H*-1-benzopyran-3-carboxylates*



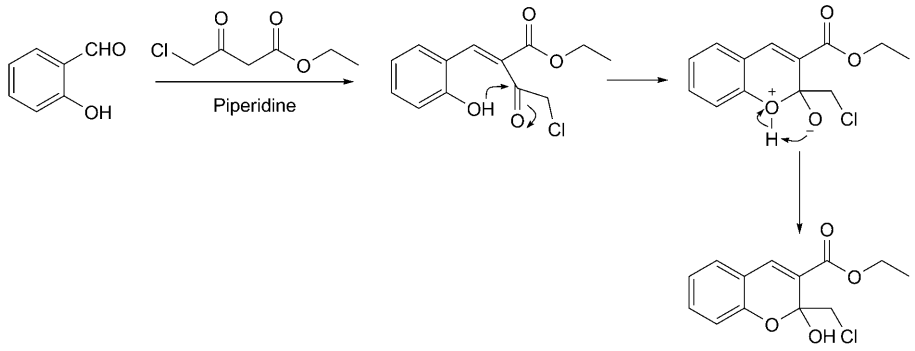
	R^1	R^2	R^3	Reaction time [h]	Product[a])	Yield [%][b])
1a	H	H	H	10	**2a**	60
1b	Br	H	H	8	**2b**	62
1c	Cl	H	H	8	**2c**	64
1d	MeO	H	H	14	**2d**	42
1e	H	CH_2=$CHCH_2O$	H	18	**2e**	42
1f	H	H	CH_2=$CHCH_2$	12	**2f**	48
1g	H	Me_2C=$CHCH_2O$	H	18	**2g**	40
1h	H	BnO	H	18	**2h**	38
1i	Ph	H	H	12	**2i**	50
1j	pyrimidin-2-yl	H	H	12	**2j**	52

[a]) All compounds were characterized by ^{1}H- and ^{13}C-NMR, IR, and MS. [b]) Yields of the isolated product.

A plausible mechanism is depicted in *Scheme 2*, according to which first the active CH_2 group reacts with the CO C-atom of salicylaldehyde to yield the corresponding *Knoevenagel* product. Then, cyclization occurs by addition of phenolic OH group to the CO group adjacent to the $ClCH_2$ group rather than to the ester CO group. This chemoselectivity may be due to the powerful inductive effect of the CH_2Cl group under basic conditions. The formation of the chromene derivative indicates that the *Knoevenagel* condensation under these conditions may give styryl intermediate in which the aromatic ring and the CH_2Cl groups are predicted to be in *cis*-configuration, thus allowing selective cyclization to give **2a** (*Scheme 2*). The IR spectrum of **2a** displayed OH absorption at 3410 cm^{-1} and the ester CO absorption at 1690 cm^{-1}. The ^{1}H-NMR spectrum of **2a** exhibited a *singlet* at δ(H) 7.68 attributed to H–C(4) of the chromene moiety. The H-atoms of the CH_2Cl group are diastereotopic, and their resonances appear, therefore, as two separate *doublet*s at δ(H) 4.04, 4.28 (each 1 H) with $J_{gem} = 11.8$ Hz. Compound **2a** was further analyzed by ^{13}C-NMR spectroscopy, where the signal of the quaternary C(2)-atom appeared at δ(C) 98.26. The signal at δ(C) 49.39 corresponds to the CH_2Cl group. The signals at δ(C) 133.12 and 136.89 are ascribed to C(3) and C(4) of the chromene moiety. Compound **2a** showed in the mass spectrum (ESI) the molecular-ion peak $[M + Na]^+$ at *m*/*z* 291 (38%) and 293 (12%). Another prominent peak appeared at *m*/*z* 251 (62%) indicating the loss of OH to give the stable benzopyrylium ion. The product **2a** was further analyzed by HR-MS with *m*/*z* 268.0507 (calc. for $C_{13}H_{13}ClO_4$: 268.0502). Compound **2a** further showed in DEPT experiments signals for two CH_2 C-atoms (δ(C) 49.39 and 61.70) and five CH C-atoms. The compound **2a** crystallized in $CHCl_3$. Its structure was, therefore, finally confirmed

by X-ray crystallography[1]) (*Fig.*) as ethyl (2-chloromethyl)-2-hydroxy-2*H*-chromene-3-carboxylate (**2a**).

Scheme 2



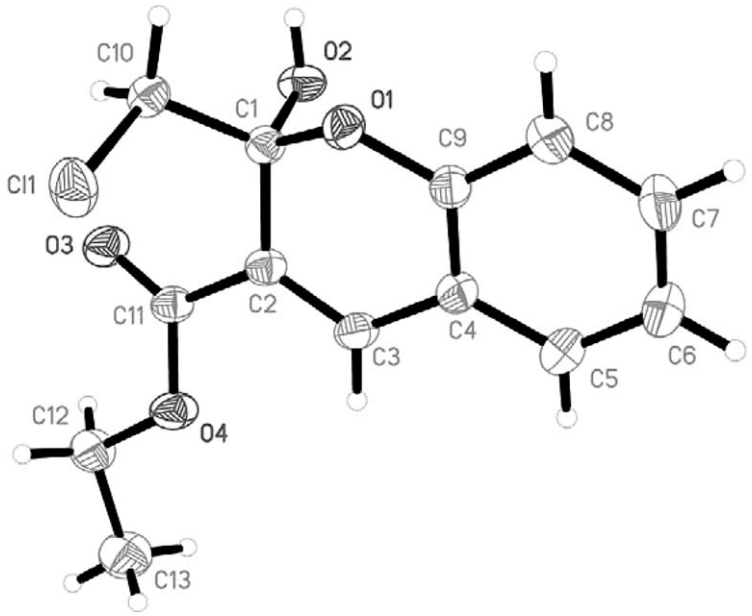


Figure. *ORTEP Diagram of compound* **2a**

[1]) Crystal data: $C_{13}H_{13}ClO_4$, M_r 268.68, orthorhombic, space group $P2_12_12_1$, $a = 7.5434(11)$, $b = 9.8585(15)$, $c = 17.342(3)$ Å, $V = 1289.7(3)$ Å^3, $Z = 4$, $D_x = 1.384$ Mg m^{-3}, $T = 294(2)$ K, $\mu = 0.299$ mm^{-1}, $F(000) = 560$, $\lambda = 0.71073$ Å. Data collection yielded 12370 reflections resulting in 2274 unique, averaged reflections, 2236 with $I > 2\sigma(I)$. Full-matrix least-squares refinement led to a final $R = 0.0231$, $wR = 0.0647$ and GOF of 1.068. Intensity data were acquired on *Bruker Smart Apex* with CCD area detector. CCDC-757819 contains the supplementary crystallographic data for this report. These data can be obtained free of charge from the *Cambridge Crystallographic Data Centre via* www.ccdc.cam.ac.uk/data_request/cif.

To evaluate the efficiency of this methodology, various substituted salicylaldehydes were reacted with ethyl 4-chloro-3-oxobutanoate having electron-withdrawing and electron-donating substituents in various positions of the benzene ring, *e.g.*, Br (**1b**), Cl (**1c**), MeO (**1d**), Ph (**1i**), and pyrimidin-2-yl (**1j**) at C(5), to form a series of new ethyl 2-(chloromethyl)-2-hydroxy-2*H*-chromene-3-carboxylates **2b**–**2j** in good yields (*Scheme 1*). Electron-withdrawing groups on the aromatic ring afforded higher yields in comparision with electron-donating groups. Compounds **1e**, **1g**, and **1h** were prepared by using 2,4-dihydroxybenzaldehyde with corresponding alkyl halides, and compound **1f** was prepared by *Claisen* rearrangement of 4-(allyloxy)-2-hydroxybenzaldehyde. Compounds **1i** and **1j** were prepared by *Suzuki* coupling [3a] of 5-bromosalicylaldehyde with phenylboronic acid and (pyrimidin-2-yl)boronic acid in the presence of $Pd(PPh_3)_4$. No 2*H*-chromene formation was observed with 2,4-dihydroxybenzaldehyde, 4-formyl-3-hydroxyphenyl acetate, and 3,5-di(*tert*-butyl)-2-hydroxybenzaldehyde.

3. Conclusions. – We have developed a new straightforward, facile, one-pot method for the synthesis of 2*H*-chromene-3-carboxylates from substituted salicylaldehydes and ethyl 4-chloro-acetoacetate. The results summarized in *Scheme 1* reflects the scope and generality of the reaction with respect to the examples described. All the new products **2a**–**2j** were characterized by their spectral data (^{1}H- and ^{13}C-NMR, IR, and MS; see *Exper. Part*).

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Experimental Part

General. Salicylaldehydes and the β-keto ester were obtained from *Sigma–Aldrich*. Solvents were also commercially available. Column chromatography (CC): silica gel (SiO_2; 60–120 mesh). M.p.: *Mettler-Temp* apparatus; uncorrected. IR Spectra: *Perkin-Elmer-1600* FT-IR spectrometer; in KBr; $\tilde{\nu}$ in cm^{-1}. ^{1}H- and ^{13}C-NMR spectra: *Bruker-Avance*-300 spectrometer; solvent $CDCl_3$; chemical shifts δ in ppm rel. to Me_4Si as internal standard, *J* in Hz. EI-MS: *7070 H* spectrometer with a direct inlet system; at 70 eV; in *m*/*z* (rel. %).

*General Procedure for Synthesis of Ethyl 2-(Chloromethyl)-2-hydroxy-2*H*-1-benzopyran-3-carboxylates.* Ethyl 4-chloro-3-oxobutanoate (1 mmol) was added to the mixture of a stirred soln. of salicylaldehyde (1 mmol) and piperidine (30 mol-%) in CH_2Cl_2 (2 ml) at r.t. during 15 min. The mixture was stirred for another 8 h at the same temp. After completion of the reaction (TLC), the crude product was subjected to CC (hexane/AcOEt 95:5) to give the pure carboxylates (*Scheme 1*).

*Ethyl 2-(Chloromethyl)-2-hydroxy-2*H*-1-benzopyran-3-carboxylate* (**2a**). Colorless solid. M.p. 113–115°. IR: 3410, 3049, 2980, 1690, 1630, 1570, 1374, 1341, 1297, 1218, 1056, 1017. ^{1}H-NMR: 1.42 (*t*, *J* = 7.2, Me); 4.04 (*d*, *J* = 11.8, 1 H, CH_2Cl); 4.28 (*d*, *J* = 11.8, 1 H, CH_2Cl); 4.32 (*q*, *J* = 7.2, CH_2O); 6.94–7.02 (*m*, 2 arom. H); 7.20–7.28 (*m*, 2 arom. H); 7.68 (*s*, 1 arom. H). ^{13}C-NMR: 14.37; 49.39; 61.70; 98.26; 116.80; 118.22; 121.93; 122.37; 129.19; 133.12; 136.89; 152.52; 165.32. LC/ESI-MS[2]): 251/253 ($[M-OH]^+$), 291/293 ($[M+Na]^+$). ESI-HR-MS: 268.0507 (M^+, $C_{13}H_{13}ClO_4^+$; calc. 268.0502).

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[2]) Operating conditions: Column *Phenomenex Luna* (C_{18}, 3000 × 3.9 mm id, 10 µl); Solvent system: gradient elution, 0–20 min, MeCN/H_2O 65:35.

*Ethyl 6-Bromo-2-(chloromethyl)-2-hydroxy-2*H*-1-benzopyran-3-carboxylate* (**2b**). Yellow solid. M.p. 90–92°. IR: 3427, 2923, 2854, 1732, 1631, 1460, 1378, 1219, 1100, 769. ^{1}H-NMR: 1.40 (*t*, *J* = 7.1, Me); 4.02 (*d*, *J* = 11.6, 1 H, CH_2Cl); 4.22 (*d*, *J* = 11.6, 1 H, CH_2Cl); 4.36 (*q*, *J* = 7.2, CH_2O); 6.90 (*d*, *J* = 8.7, 1 arom. H); 7.38–7.46 (*m*, 2 arom. H); 7.64 (*s*, 1 arom. H). ^{13}C-NMR: 14.12; 49.10; 61.69; 98.21; 114.09; 118.36; 119.73; 122.93; 131.06; 135.19; 135.28; 151.30; 164.68. LC/ESI-MS: 330/332 ($[M-OH+H]^+$), 353/355 ($[M-OH+H+Na]^+$).

*Ethyl 6-Chloro-2-(chloromethyl)-2-hydroxy-2*H*-1-benzopyran-3-carboxylate* (**2c**). Yellow oil. IR: 3422, 2925, 1709, 1634, 1479, 1274, 1213, 1051, 820. ^{1}H-NMR: 1.40 (*t*, *J* = 6.9, Me); 4.02 (*d*, *J* = 11.3, 1 H, CH_2Cl); 4.26 (*d*, *J* = 11.3, 1 H, CH_2Cl); 4.34 (*q*, *J* = 6.9, CH_2O); 6.94 (*d*, *J* = 8.5, 1 arom. H); 7.22–7.32 (*m*, 2 arom. H); 7.60 (*s*, 1 arom. H). LC-MS: 285/287 ($[M-OH]^+$), 308/310 ($[M+Na]^+$).

*Ethyl 2-(Chloromethyl)-2-hydroxy-6-methoxy-2*H*-1-benzopyran-3-carboxylate* (**2d**). Yellow liquid. IR: 3433, 2922, 2852, 1707, 1633, 1495, 1219, 1041. ^{1}H-NMR: 1.34 (*t*, *J* = 7.2, Me); 3.70 (*s*, MeO); 3.98 (*d*, *J* = 11.1, 1 H, CH_2Cl); 4.18 (*d*, *J* = 11.1, 1 H, CH_2Cl); 4.28 (*q*, *J* = 7.2, CH_2O); 6.68 (*d*, *J* = 6.7, 1 arom. H); 6.82–6.88 (*m*, 2 arom. H); 7.56 (*s*, 1 arom. H). ESI-MS: 281/283 ($[M-OH]^+$), 321/323 ($[M+Na]^+$).

*Ethyl 2-(Chloromethyl)-2-hydroxy-7-(prop-2-en-1-yloxy)-2*H*-1-benzopyran-3-carboxylate* (**2e**). Yellow liquid. IR: 3445, 2922, 2853, 1705, 1617, 1503, 1279, 1208, 1163, 930. ^{1}H-NMR: 1.38 (*t*, *J* = 7.1, Me); 4.08 (*d*, *J* = 11.6, 1 H, CH_2Cl); 4.22 (*d*, *J* = 11.6, 1 H, CH_2Cl); 4.28 (*q*, *J* = 7.2, CH_2O); 4.54 (*d*, *J* = 7.6, CH_2O); 5.26–5.32 (*dd*, *J* = 1.6, 10.3, 1 olefin. H); 5.40 (*dd*, *J* = 1.6, 15.8, 1 olef. H); 5.96–6.12 (*m*, 1 olef. H); 6.50–6.62 (*m*, 2 arom. H); 7.16 (*d*, *J* = 8.8, 1 arom. H); 7.68 (*s*, 1 arom. H). ^{13}C-NMR: 14.14; 29.61; 49.14; 61.15; 68.95; 98.34; 101.97; 109.98; 118.10; 130.01; 132.39; 136.66; 147.25; 154.01; 162.69; 165.28. ESI-MS: 307/309 ($[M-OH]^+$), 347/349 ($[M+Na]^+$).

*Ethyl 2-(Chloromethyl)-2-hydroxy-8-(prop-2-en-1-yl)-2*H*-1-benzopyran-3-carboxylate* (**2f**). Yellow liquid. IR: 3409, 2979, 2924, 1700, 1633, 1599, 1287, 1212, 1016, 913. ^{1}H-NMR: 1.34 (*t*, *J* = 7.0, Me); 3.44 (*d*, *J* = 6.6, CH_2=CH); 4.07 (*d*, *J* = 11.2, 1 H, CH_2Cl); 4.22 (*d*, *J* = 11.2, 1 H, CH_2Cl); 4.32 (*q*, *J* = 7.0, CH_2O); 5.02–5.16 (*m*, 2 olef. H); 5.92–6.08 (*m*, 1 olef. H); 6.92 (*t*, 1 arom. H); 7.10 (*d*, *J* = 7.4, 1 arom. H); 7.18 (*d*, *J* = 7.17, 1 arom. H); 7.66 (*s*, 1 arom. H). ^{13}C-NMR: 14.19; 33.59; 49.12; 61.13; 96.13; 97.92; 116.08; 117.86; 121.61; 126.97; 127.91; 133.17; 135.98; 136.86; 150.06; 164.75; 14.37; 49.39; 61.70; 98.26; 116.80; 118.22; 121.93; 122.37; 129.19; 133.12; 136.89;152.52; 165.32. ESI-MS: 291/293 ($[M-OH]^+$), 331/333 ($[M+Na]^+$).

*Ethyl 2-(Chloromethyl)-2-hydroxy-7-[(3-methylbut-2-en-1-yl)oxy]-2*H*-1-benzopyran-3-carboxylate* (**2g**). Yellow liquid. IR: 3446, 2924, 2855, 1707, 1632, 1504, 1373, 1278, 1207, 1161, 1104, 1054. ^{1}H-NMR: 1.40 (*t*, *J* = 7.2, Me); 1.78 (*s*, Me); 1.82 (*s*, Me); 4.00 (*d*, *J* = 11.1, 1 H, CH_2Cl); 4.22 (*d*, *J* = 11.1, 1 H, CH_2Cl); 4.30 (*q*, *J* = 7.2, CH_2O); 4.50 (*d*, *J* = 6.6, CH_2), 5.42–5.48 (*m*, 1 olef. H); 6.48–6.56 (*m*, 2 arom. H); 7.14 (*d*, *J* = 8.8, 1 arom. H); 7.68 (*s*, 1 arom. H). ^{13}C-NMR: 13.94, 25.49, 29.38, 48.87, 60.64, 64.64, 95.81, 97.98, 101.40, 109.80, 110.85, 116.25, 118.90, 136.25, 153.85, 162.78, 167.58. ESI-MS: 335/337 ($[M-OH]^+$), 375/377 ($[M+Na]^+$).

*Ethyl 7-(Benzyloxy)-2-(chloromethyl)-2-hydroxy-2*H*-1-benzopyran-3-carboxylate* (**2h**). Yellow liquid. IR: 3426, 2923, 1694, 1581, 1546, 1443, 1391, 1289, 1202, 1118, 991. ^{1}H-NMR: 1.42 (*t*, *J* = 7.5, Me); 4.02 (*d*, *J* = 11.3, 1 H, CH_2Cl); 4.20 (*d*, *J* = 11.3, 1 H, CH_2Cl); 4.28 (*q*, *J* = 7.5, CH_2O); 5.12 (*s*, PhCH_2); 6.62 (*m*, 2 arom. H); 7.18 (*m*, 1 arom. H); 7.32–7.44 (*m*, 5 arom. H); 7.62 (*s*, 1 arom. H). ESI-MS: 357/359 ($[M-OH]^+$), 397/399 ($[M+Na]^+$).

*Ethyl 2-(Chloromethyl)-2-hydroxy-6-phenyl-2*H*-1-benzopyran-3-carboxylate* (**2i**). Yellow solid. M.p. 112–113°. IR: 3435, 2921, 2851, 1714, 1462, 1262. ^{1}H-NMR: 1.38 (*t*, *J* = 7.1, Me); 4.00 (*d*, *J* = 11.6, 1 H, CH_2Cl), 4.30 (*q*, *J* = 7.2, CH_2O); 4.38 (*d*, *J* = 11.6, 1 H, CH_2Cl); 7.04 (*d*, *J* = 10.6, 1 arom. H); 7.26–7.54 (*m*, 7 arom. H); 7.22 (*s*, 1 atom. H); LC/MS: 327/329 ($[M-OH]^+$).

*Ethyl 2-(Chloromethyl)-2-hydroxy-6-(pyrimidin-2-yl)-2*H*-1-benzopyran-3-carboxylate* (**2j**). Colorless solid. M.p. 150–152°. IR: 3421, 2924, 2856, 1716, 1643, 1423, 1268, 1228, 1119, 1069, 1016. ^{1}H-NMR: 1.38 (*t*, *J* = 7.2, Me); 4.02 (*d*, *J* = 11.1, 1 H, CH_2Cl); 4.38 (*q*, *J* = 7.1, CH_2O); 4.54 (*d*, *J* = 11.1, 1 H, CH_2Cl); 7.16 (*d*, *J* = 7.7, 1 arom. H); 7.24 (*s*, 1 arom. H); 7.42–7.58 (*m*, 2 arom. H); 7.80 (*s*, 1 arom. H); 8.98 (*s*, 1 arom. H); 9.22 (*s*, 1 arom. H). ^{13}C-NMR: 14.08; 48.75; 61.27; 98.83; 117.70; 119.07; 123.76; 126.96; 127.69; 130.63; 135.25; 153.34; 154.17; 160.00; 164.19. ESI-MS: 347/349 ($[M+H]^+$), 369/371 ($[M+Na]^+$). HR-ESI-MS: 346.0727 (M^+, $C_{17}H_{15}ClN_2O_4^+$; calc. 346.0720).

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