Potassium Thiocyanate-Promoted One-Pot Synthesis of (1,3-Diaryl-2,5-dioxoimidazolidin-4-ylidene)acetates from Aryl Isocyanates and Alkyl Propiolates

Short Communication

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The reaction of aryl isocyanates and alkyl propiolates (= alkyl prop-2-ynoates) in the presence of potassium thiocyanate (KSCN) led to geometric isomers of alkyl 2-(1,3-diaryl-2,5-dioxoimidazolidin-4-ylidene)acetates in moderate-to-good yields.

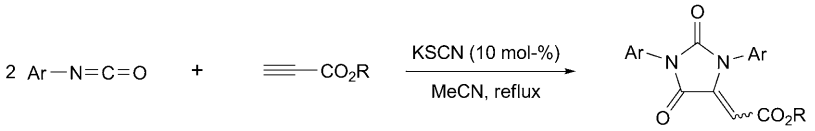
Introduction. – Hydantoins, a class of cyclic imides, have been shown to possess a wide range of pharmacological properties [1–3]. *C(5)*-Unsaturated hydantoins are important as biological and pharmaceutical intermediates and as precursors to *C(5)*-substituted hydantoins and their subsequent α-amino acids [4–6]. Classic methods for preparing these compounds are *i*) base- or acid-catalyzed condensations of 5-unsubstituted hydantoins with aldehydes, and unhindered or activated ketones [4][5] and *ii*) reactions of aldehydes, certain ketones, and α-dicarbonyl compounds with diethyl hydantoinyl-5-phosphonate in the presence of a base [6]. Recently, three-component synthesis of 1-alkyl-3-(arylsulfonyl)-5-methylidenehydantoins has been reported [7][8]. 1,3-Diaryl-5-arylidenehydantoins have been obtained by the reaction of terminal alkynes with isocyanates in the presence of a catalytic amount of a manganese complex, $MnBr(CO)_5$, rhenium complex, $Re_2(CO)_{10}$, or an iron complex, $Fe(CO)_5$ [9][10].

As part of our current studies on the development of new routes to heterocyclic systems [11–13], we now report a straightforward synthesis of alkyl 2-(2,5-dioxo-1,3-diarylimidazolidin-4-ylidene)acetates (**3**) from aryl isocyanates and alkyl propiolates in the presence of KSCN in good-to-moderate yields (*Scheme 1*).

Results and Discussion. – The reaction of **1** and **2** in the presence of 10 mol-% KSCN in MeCN at reflux temperature led to a mixture of geometric isomers of alkyl 2-(1,3-diaryl-2,5-dioxoimidazolidin-4-ylidene)acetates (**3**) in 55–73% yields.

The structures of compounds **3a**–**3g** were deduced from their IR, and ^{1}H- and ^{13}C-NMR spectra. For example, the ^{1}H-NMR spectrum of (*Z*)-**3a** exhibited two *singlet*s (δ(H) 3.22 and 6.22) for the MeO and olefinic groups, along with *multiplet*s (δ(H) 7.34–7.54) for the Ph groups. The MeO and olefinic groups of (*E*)-**3a** also showed two *singlet*s (δ(H) 3.83 and 5.66). The ^{1}H-decoupled ^{13}C-NMR spectra of (*Z*)-**3a** and (*E*)-**3a** exhibited, in each case, 14 distinct resonances that confirm the proposed structures. The ^{1}H- and ^{13}C-NMR spectra of **3b**–**3g** were similar to those of **3a** except for the aryl

Scheme 1



1a Ar = Ph
1b Ar = 3-Cl-4-Me–C_6H_3
1c Ar = 4-Cl–C_6H_4

2a R = Me
2b R = Et
2c R = ^{t}Bu

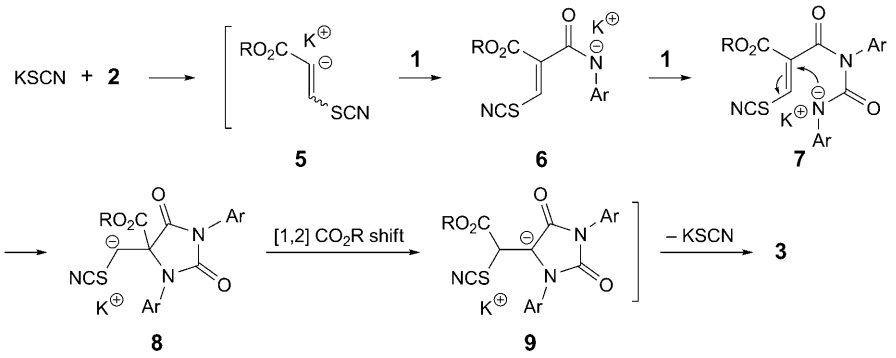
	Ar	R	Yield [%] (*Z*/*E*)
3a	Ph	Me	47:20
3b	Ph	Et	45:18
3c	3-Cl-4-Me–C_6H_3	Me	40:25
3d	3-Cl-4-Me–C_6H_3	Et	38:25
3e	4-Cl–C_6H_4	Me	50:22
3f	4-Cl–C_6H_4	Et	48:25
3g	4-Cl–C_6H_4	^{t}Bu	30:25

and alkoxy residues, which showed characteristic resonances in appropriate regions of the spectrum.

Assignment of the (*Z*)- and (*E*)-configuration to the C=C bond in (*Z*)-**3a** and (*E*)-**3a** is based on the chemical shift of the olefinic H-atoms [14]. The IR spectra of these compounds are in agreement with the proposed structure. The mass spectra of these compounds displayed molecular-ion peaks at the appropriate *m*/*z* values and were fairly identical in each pair of geometric isomers.

A tentative mechanism for the formation of **3** is proposed in *Scheme 2*. It is conceivable that the reaction involves the initial formation of anionic intermediate **5** from KSCN and **2** [15], which reacts with **1** to produce **6**. Intermediate **6** reacts with another molecule of aryl isothiocyanate **1** to produce **7**. Cyclization of this intermediate, followed by [1,2] shift of the ester group and subsequently loss of KSCN, leads to geometric isomers of **3** through intermediates **8** and **9** (*Scheme 2*).

Scheme 2



In conclusion, we have described the use of KSCN in a synthesis of geometrical isomers of alkyl 2-(2,5-dioxo-1,3-diphenylimidazolidin-4-ylidene)acetates (**3**) from aryl isocyanates and alkyl propiolates. Simple mixing of the starting materials, use of KSCN as a recoverable and inexpensive catalyst, and potential diversity of this type of reaction are the advantages of this procedure.

Experimental Part

General. Compounds **1**, **2**, and KSCN were obtained from *Merck* and used without further purification. Column chromatography (CC): silica gel (SiO_2; 230–400 mesh; *Merck*). M.p.: *Electrothermal-9100* apparatus. IR Spectra: *Shimadzu IR-460* spectrometer; $\tilde{\nu}$ in cm^{-1}. ^{1}H- and ^{13}C-NMR spectra: *Bruker DRX-500 Avance* instrument; in $CDCl_3$ at 500.1 and 125.7 MHz, resp.; δ in ppm, J in Hz. MS: *Finnigan-MAT-8430* mass spectrometer, at 70 eV; in m/z (rel. %). Elemental analyses (C, H, N): *Heraeus CHN-O-Rapid* analyzer.

Compounds **3**: *General Procedure.* To a stirred soln. of **1** (4.2 mmol) and **2** (2 mmol) in MeCN (7 ml) was added KSCN (0.02 g, 0.2 mmol) at r.t. The mixture was refluxed for *ca.* 2 h (as indicated by TLC), and then the solvent was evaporated, and the brown residue, dissolved in CH_2Cl_2 (5 ml), was purified by CC and KSCN was filtered. Separation of the products was achieved by CC (SiO_2; hexane/AcOEt 4 :1).

*Methyl (*Z*)-(2,5-Dioxo-1,3-diphenylimidazolidin-4-ylidene)acetate* ((*Z*)-**3a**). Yield: 0.30 g (47%). Pale yellow crystals. M.p. 173–175°. IR (KBr): 1787, 1739, 1704 (CO–NR–CO, COO), 1654 (C=C), 1592, 1492, 1452, 1396, 1259, 1206, 1170, 1120, 960, 874, 827, 768. ^{1}H-NMR: 3.22 (*s*, MeO); 6.22 (*s*, CH); 7.34–7.36 (*m*, 2 CH); 7.41–7.44 (*m*, 2 CH); 7.48–7.54 (*m*, 6 CH). ^{13}C-NMR: 51.7 (MeO); 100.6 (CH); 125.8 (2 CH); 126.6 (2 CH); 128.5 (CH); 128.6 (CH); 129.2 (2 CH); 129.3 (2 CH); 131.6 (C); 134.6 (C); 135.0 (C); 152.9 (C=O); 161.5 (C=O); 163.8 (C=O). EI-MS: 323 (8, $[M+1]^+$), 322 (5, M^+), 321 (20), 263 (18), 175 (52), 144 (100), 119 (70), 77 (22), 51 (19). Anal. calc. for $C_{18}H_{14}N_2O_4$ (322.32): C 67.07, H 4.38, N 8.69; found: C 67.11, H 4.39, N 8.72.

*Methyl (*E*)-2-(2,5-Dioxo-1,3-diphenylimidazolidin-4-ylidene)acetate* ((*E*)-**3a**). Yield: 0.13 g (20%). Pale yellow crystals. M.p. 199–201°. IR (KBr): 1777, 1730, 1703 (CO–N–CO, COO), 1661 (C=C), 1589, 1490, 1450, 1406, 1295, 1257, 1214, 1179, 1148, 934, 882, 855, 811, 768. ^{1}H-NMR: 3.83 (*s*, MeO); 5.66 (*s*, CH); 7.39–7.44 (*m*, 3 CH); 7.49–7.51 (*m*, 5 CH); 7.55–7.58 (*m*, 2 CH). ^{13}C-NMR: 52.5 (MeO); 103.7 (CH); 126.0 (2 CH); 127.6 (2 CH); 128.5 (CH); 129.1 (2 CH); 129.5 (CH); 130.1 (2 CH); 132.1 (C); 135.1 (C); 136.3 (C); 151.7 (C=O); 158.7 (C=O); 164.7 (C=O). EI-MS: 323 (8, $[M+1]^+$), 322 (5, M^+), 321 (20), 263 (18), 175 (52), 144 (100), 119 (70), 77 (22), 51 (19). Anal. calc. for $C_{18}H_{14}N_2O_4$ (322.32): C 67.07, H 4.38, N 8.69; found: C 67.10, H 4.39, N 8.71.

*Ethyl (*Z*)-2-(2,5-Dioxo-1,3-diphenylimidazolidin-4-ylidene)acetate* ((*Z*)-**3b**). Yield: 0.30 g (45%). Pale yellow crystals. M.p. 115–117°. IR (KBr): 1783, 1737, 1708 (CO–N–CO, COO), 1665 (C=C), 1592, 1490, 1455, 1393, 1249, 1208, 1170, 1106, 1029, 963, 857, 822, 769, 691. ^{1}H-NMR: 1.00 (*t*, $^3J=7.2$, Me); 3.69 (*q*, $^3J=7.2$, CH_2O); 6.24 (*s*, CH); 7.35–7.37 (*m*, 2 CH); 7.42–7.44 (*m*, 2 CH); 7.47–7.51 (*m*, 6 CH). ^{13}C-NMR: 13.8 (Me); 61.1 (CH_2O); 101.2 (CH); 125.9 (2 CH); 126.4 (2 CH); 128.5 (CH); 128.6 (CH); 129.2 (2 CH); 129.3 (2 CH); 131.0 (C); 134.6 (C); 134.7 (C); 152.9 (C=O); 161.6 (C=O); 163.5 (C=O). EI-MS: 337 (8, $[M+1]^+$), 336 (4, M^+), 335 (15), 263 (20), 189 (35), 144 (100), 119 (75), 77 (27), 51 (25). Anal. calc. for $C_{19}H_{16}N_2O_4$ (336.34): C 67.85, H 4.79, N 8.33; found: C 67.79, H 4.75, N 8.30.

*Ethyl (*E*)-2-(2,5-Dioxo-1,3-diphenylimidazolidin-4-ylidene)acetate* ((*E*)-**3b**). Yield: 0.12 g (18%). Pale yellow crystals. M.p. 117–119°. IR (KBr): 1779, 1735, 1707 (CO–N–CO, COO), 1663 (C=C), 1590, 1491, 1450, 1402, 1297, 1253, 1211, 1158, 1113, 1033, 975, 926, 862, 810, 769, 710. ^{1}H-NMR: 1.33 (*t*, $^3J=7.2$, Me); 4.30 (*q*, $^3J=7.2$, CH_2O); 5.67 (*s*, CH); 7.40–7.43 (*m*, 2 CH); 7.48–7.51 (*m*, 5 CH); 7.55–7.58 (*m*, 3 CH). ^{13}C-NMR: 14.0 (Me); 61.8 (CH_2O); 104.3 (CH); 126.1 (2 CH); 127.6 (2 CH); 128.6 (CH); 129.2 (2 CH); 129.4 (CH); 130.1 (2 CH); 131.4 (C); 131.9 (C); 136.0 (C); 151.7 (C=O); 158.7 (C=O); 164.3 (C=O). EI-MS: 337 (8, $[M+1]^+$), 336 (4, M^+), 335 (15), 263 (20), 189 (35), 144 (100), 119 (75), 77 (27), 51 (25). Anal. calc. for $C_{19}H_{16}N_2O_4$ (336.34): C 67.85, H 4.79, N 8.33; found: C 67.79, H 4.80, N 8.35.

*Methyl (*Z*)-2-[1,3-Bis(3-chloro-4-methylphenyl)-2,5-dioxoimidazolidin-4-ylidene]acetate* ((*Z*)-**3c**). Yield: 0.34 g (40%). Pale yellow crystals. M.p. 156–158°. IR (KBr): 1785, 1733, 1701 (CO–N–CO, COO), 1670 (C=C), 1494, 1433, 1390, 1309, 1268, 1229, 1207, 1162, 1119, 1049, 867, 815. ^{1}H-NMR: 2.42 (*s*, Me); 2.43 (*s*, Me); 3.36 (*s*, MeO); 6.23 (*s*, CH); 7.15 (*dd*, $^3J=8.1$, $^4J=2.2$, CH); 7.30–7.37 (*m*, 4 CH); 7.53 (*d*, $^4J=2.0$, CH). ^{13}C-NMR: 19.8 (Me); 19.9 (Me); 51.9 (MeO); 101.0 (CH); 123.9 (CH); 124.8 (CH); 126.3 (CH); 127.2 (CH); 129.4 (C); 131.2 (CH); 131.3 (CH); 132.9 (C); 134.6 (C); 134.7 (C); 134.8 (C); 136.9 (C); 137.0 (C); 152.5 (C=O); 161.1 (C=O); 163.6 (C=O). EI-MS: 422 (4, $[M+3]^+$) 421 (6, $[M+2]^+$), 420 (10, $[M+1]^+$), 419 (6, M^+), 418 (19), 360 (15), 223 (48), 192 (100), 165 (75), 132 (65), 89 (50). Anal. calc. for $C_{20}H_{16}Cl_2N_2O_4$ (419.26): C 57.30, H 3.85, N 6.68; found: C 57.41, H 3.79, N 6.72.

*Methyl (*E*)-2-[1,3-Bis(3-chloro-4-methylphenyl)-2,5-dioxoimidazolidin-4-ylidene]acetate* ((*E*)-**3c**). Yield: 0.21 g (25%). Pale yellow crystals. M.p. 222–224°. IR (KBr): 1779, 1732, 1707 (CO–N–CO, COO), 1655 (C=C), 1571, 1492, 1411, 1397, 1296, 1262, 1207, 1180, 1098, 1051, 813, 753. ^{1}H-NMR: 2.42 (*s*, 2 Me); 3.84 (*s*, MeO); 5.66 (*s*, CH); 7.18–7.20 (*m*, 2 CH); 7.26–7.36 (*m*, 3 CH); 7.39–7.42 (*m*, CH). ^{13}C-NMR: 19.9 (2 Me); 52.6 (MeO); 104.3 (CH); 124.1 (CH); 125.7 (CH); 126.5 (CH); 126.6 (CH); 128.2 (C); 129.0 (CH); 131.2 (C); 131.4 (CH); 131.8 (C); 132.2 (C); 134.9 (C); 137.9 (C); 148.2 (C); 151.2 (C=O); 158.3 (C=O); 164.4 (C=O). EI-MS: 422 (4, $[M+3]^+$) 421 (7, $[M+2]^+$), 420 (10, $[M+1]^+$), 419 (6, M^+), 418 (19), 360 (15), 223 (48), 192 (100), 165 (75), 132 (65), 89 (50). Anal. calc. for $C_{20}H_{16}Cl_2N_2O_4$ (419.26): C 57.30, H 3.85, N 6.68; found: C 57.35, H 3.81, N 6.74.

*Ethyl (*Z*)-2-[1,3-Bis(3-chloro-4-methylphenyl)-2,5-dioxoimidazolidin-4-ylidene]acetate* ((*Z*)-**3d**). Yield: 0.33 g (38%). Pale yellow crystals. M.p. 168–170°. IR (KBr): 1786, 1734, 1702 (CO–N–CO, COO), 1671 (C=C), 1493, 1457, 1392, 1310, 1287, 1224, 1204, 1162, 1119, 1093, 1070, 869, 817. ^{1}H-NMR: 1.01 (*t*, $^3J=7.1$, Me); 2.42 (*s*, Me); 2.43 (*s*, Me); 3.81 (*q*, $^3J=7.1$, CH_2O); 6.24 (*s*, CH); 7.16 (*dd*, $^3J=8.1$, $^4J=2.0$, CH); 7.30–7.37 (*m*, 4 CH); 7.52 (*d*, $^4J=1.9$, CH). ^{13}C-NMR: 13.8 (Me); 19.8 (2 Me); 61.4 (CH_2O); 101.6 (CH); 123.9 (CH); 124.8 (CH); 126.3 (CH); 127.0 (CH); 129.4 (C); 131.2 (CH); 131.3 (CH); 132.9 (C); 134.2 (C); 134.6 (C); 134.8 (C); 136.9 (C); 137.0 (C); 152.5 (C=O); 161.1 (C=O); 163.2 (C=O). EI-MS: 436 (3, $[M+3]^+$), 435 (4, $[M+2]^+$), 434 (12, $[M+1]^+$), 433 (7, M^+), 432 (20), 360 (12), 237 (41), 192 (100), 165 (82), 132 (51), 89 (49). Anal. calc. for $C_{21}H_{18}Cl_2N_2O_4$ (433.28): C 58.21, H 4.19, N 6.47; found: C 58.08, H 4.25, N 6.43.

*Ethyl (*E*)-2-[1,3-Bis(3-chloro-4-methylphenyl)-2,5-dioxoimidazolidin-4-ylidene]acetate* ((*E*)-**3d**). Yield: 0.22 g (25%). Pale yellow crystals. M.p. 141–143°. IR (KBr): 1782, 1734, 1708 (CO–N–CO, COO), 1666 (C=C), 1496, 1409, 1303, 1268, 1198, 1179, 1144, 1097, 1049, 1025, 809, 764, 693. ^{1}H-NMR: 1.32 (*t*, $^3J=7.2$, Me); 2.41 (*s*, Me); 2.45 (*s*, Me); 4.30 (*q*, $^3J=7.2$, CH_2O); 5.66 (*s*, CH); 7.20 (*dd*, $^3J=8.1$, $^4J=2.1$, CH); 7.30 (*dd*, $^3J=8.2$, $^4J=2.0$, CH); 7.34–7.42 (*m*, 3 CH); 7.52 (*d*, $^4J=1.9$, CH). ^{13}C-NMR: 14.0 (Me); 19.8 (Me); 19.9 (Me); 61.9 (CH_2O); 100.0 (CH); 124.1 (CH); 125.8 (CH); 126.6 (CH); 128.2 (CH); 129.3 (C); 130.3 (C); 131.2 (CH); 132.1 (CH); 134.7 (C); 135.6 (C); 135.7 (C); 136.9 (C); 138.1 (C); 153.7 (C=O); 158.3 (C=O); 164.0 (C=O). EI-MS: 436 (3, $[M+3]^+$), 435 (4, $[M+2]^+$), 434 (12, $[M+1]^+$), 433 (7, M^+), 432 (20), 360 (12), 237 (41), 192 (100), 165 (82), 132 (51), 89 (49). Anal. calc. for $C_{21}H_{18}Cl_2N_2O_4$ (433.28): C 58.21, H 4.19, N 6.47; found: C 58.14, H 4.26, N 6.45.

*Methyl (*Z*)-[1,3-Bis(4-chlorophenyl)-2,5-dioxoimidazolidin-4-ylidene]acetate* ((*Z*)-**3e**). Yield: 0.39 g (50%). Pale yellow crystals. M.p. 182–184°. IR (KBr): 1784, 1730, 1710 (CO–N–CO, COO), 1671 (C=C), 1491, 1435, 1407, 1306, 1271, 1220, 1200, 1158, 1119, 1112, 1087, 962, 824, 803. ^{1}H-NMR: 3.35 (*s*, MeO); 6.25 (*s*, CH); 7.27–7.29 (*m*, 2 CH); 7.44–7.52 (*m*, 6 CH). ^{13}C-NMR: 51.9 (MeO); 101.1 (CH); 126.9 (2 CH); 127.9 (2 CH); 129.3 (C); 129.4 (2 CH); 129.5 (2 CH); 132.9 (C); 134.5 (C); 134.6 (C); 134.7 (C); 152.4 (C=O); 161.1 (C=O); 163.5 (C=O). EI-MS: 394 (3, $[M+3]^+$), 393 (5, $[M+2]^+$), 392 (15, $[M+1]^+$), 391 (6, M^+), 390 (28), 332 (18), 209 (62), 178 (100), 153 (72), 125 (26), 90 (15). Anal. calc. for $C_{18}H_{12}Cl_2N_2O_4$ (391.21): C 55.26, H 3.09, N 7.16; found: C 55.32, H 3.10, N 7.15.

*Methyl (*E*)-[1,3-Bis(4-chlorophenyl)-2,5-dioxoimidazolidin-4-ylidene]acetate* ((*E*)-**3e**). Yield: 0.17 g (22%). Pale yellow crystals. M.p. 184–186°. IR (KBr): 1781, 1737, 1711 (CO–N–CO, COO), 1657 (C=C), 1490, 1413, 1402, 1340, 1312, 1272, 1247, 1191, 1157, 1137, 1088, 1014, 942, 898, 851, 845, 818. ^{1}H-NMR: 3.83 (*s*, MeO); 5.64 (*s*, CH); 7.32 (*d*, $^3J=8.3$, 2 CH); 7.44–7.47 (*m*, 4 CH); 7.53 (*d*, $^3J=8.3$, 2 CH). ^{13}C-NMR: 52.7 (MeO); 104.3 (CH); 127.1 (2 CH); 128.9 (2 CH); 129.3 (C); 129.4 (2 CH); 130.2 (C); 130.5 (2 CH); 134.5 (C); 135.6 (C); 135.7 (C); 151.2 (C=O); 158.2 (C=O); 164.3 (C=O). EI-MS: 394 (3, $[M+3]^+$), 393 (4, $[M+2]^+$), 392 (14, $[M+1]^+$), 391 (6, M^+), 390 (28), 332 (18), 209 (62), 178 (100), 153 (72), 125 (26), 90 (15). Anal. calc. for $C_{18}H_{12}Cl_2N_2O_4$ (391.21): C 55.26, H 3.09, N 7.16; found: C 55.30, H 3.09, N 7.15.

*Ethyl (*Z*)-[1,3-Bis(4-chlorophenyl)-2,5-dioxoimidazolidin-4-ylidene]acetate* ((*Z*)-**3f**). Yield: 0.39 g (48%). Pale yellow crystals. M.p. 164–166°. IR (KBr): 1793, 1735, 1706 (CO–N–CO, COO), 1667 (C=C), 1490, 1456, 1428, 1394, 1365, 1305, 1217, 1155, 1121, 1088, 1025, 976, 941, 828, 803. ^{1}H-NMR: 1.07 (*t*, $^3J=7.2$, Me); 3.81 (*q*, $^3J=7.2$, CH_2O); 6.26 (*s*, CH); 7.27–7.30 (*m*, 2 CH); 7.44–7.50 (*m*, 6 CH). ^{13}C-NMR: 13.8 (Me); 61.3 (CH_2O); 101.7 (CH); 126.9 (2 CH); 127.8 (2 CH); 128.9 (C); 129.4 (2 CH); 129.5 (2 CH); 132.9 (C); 134.3 (C); 134.6 (C); 134.7 (C); 152.4 (C=O); 161.1 (C=O); 163.5 (C=O). EI-MS: 408 (2, $[M+3]^+$), 407 (3, $[M+2]^+$), 406 (10, $[M+1]^+$), 405 (5, M^+), 404 (18), 332 (22), 223 (55),

178 (100), 153 (65), 125 (20), 90 (10). Anal. calc. for $C_{19}H_{14}Cl_2N_2O_4$ (405.24): C 56.32, H 3.48, N 6.91; found: C 56.41, H 3.50, N 7.01.

*Ethyl (*E*)-[1,3-Bis(4-chlorophenyl)-2,5-dioxoimidazolidin-4-ylidene]acetate* ((*E*)-**3f**). Yield: 0.20 g (25%). Pale yellow crystals. M.p. 203–205°. IR (KBr): 1782, 1737, 1708 (CO–N–CO, COO), 1662 (C=C), 1490, 1468, 1396, 1366, 1310, 1301, 1266, 1221, 1185, 1146, 1087, 1015, 918, 869, 832, 802, 765. ^{1}H-NMR: 1.32 (*t*, ^3J = 7.1, Me); 4.30 (*q*, ^3J = 7.1, CH_2O); 5.66 (*s*, CH); 7.34 (*d*, ^3J = 8.5, 2 CH); 7.44–7.50 (*m*, 4 CH); 7.53 (*d*, ^3J = 8.5, 2 CH). ^{13}C-NMR: 14.0 (Me); 61.9 (CH_2O); 104.9 (CH); 127.1 (2 CH); 128.9 (2 CH); 129.3 (C); 129.4 (2 CH); 130.3 (C); 130.4 (2 CH); 134.5 (C); 135.4 (C); 135.6 (C); 151.2 (C=O); 158.2 (C=O); 163.8 (C=O). EI-MS: 408 (4, $[M+3]^+$), 407 (5, $[M+2]^+$), 406 (12, $[M+1]^+$), 405 (7, M^+), 404 (18), 332 (24), 223 (56), 178 (100), 153 (65), 125 (20), 90 (11). Anal. calc. for $C_{19}H_{14}Cl_2N_2O_4$ (405.24): C 56.32, H 3.48, N 6.91; found: C 56.40, H 3.50, N 6.95.

tert-*Butyl (*Z*)-[1,3-Bis(4-chlorophenyl)-2,5-dioxoimidazolidin-4-ylidene]acetate* ((*Z*)-**3g**). Yield: 0.26 g (30%). Pale yellow crystals. M.p. 186–188°. IR (KBr): 1762, 1736, 1705 (CO–N–CO, COO), 1681 (C=C), 1490, 1451, 1401, 1365, 1316, 1290, 1237, 1195, 1148, 1089, 1013, 961, 830, 807. ^{1}H-NMR: 1.25 (*s*, ^{t}Bu); 6.22 (*s*, CH); 7.27–7.31 (*m*, 2 CH); 7.42–7.47 (*m*, 6 CH). ^{13}C-NMR: 27.8 (Me_3C); 82.5 (Me_3C); 103.8 (CH); 126.9 (2 CH); 127.8 (2 CH); 129.3 (C); 129.5 (2 CH); 129.6 (2 CH); 131.9 (C); 133.4 (C); 134.4 (C); 134.5 (C); 152.5 (C=O); 161.3 (C=O); 164.7 (C=O). EI-MS: 436 (2, $[M+3]^+$), 435 (5, $[M+2]^+$), 434 (8, $[M+1]^+$), 433 (6, M^+), 432 (15), 332 (15), 251 (32), 178 (81), 153 (27), 125 (11), 90 (5), 57 (100). Anal. calc. for $C_{21}H_{18}Cl_2N_2O_4$ (433.29): C 58.21, H 4.19, N 6.47; found: C 58.30, H 4.16, N 6.50.

tert-*Butyl (*E*)-[1,3-Bis(4-chlorophenyl)-2,5-dioxoimidazolidin-4-ylidene]acetate* ((*E*)-**3g**). Yield: 0.22 g (25%). Pale yellow crystals. M.p. 177–179°. IR (KBr): 1780, 1734, 1707 (CO–N–CO, COO), 1666 (C=C), 1454, 1400, 1365, 1314, 1291, 1268, 1220, 1156, 1090, 1014, 983, 915, 868, 819, 759. ^{1}H-NMR: 1.54 (*s*, ^{t}Bu); 5.64 (*s*, CH); 7.35 (*d*, ^3J = 8.5, 2 CH); 7.44–7.50 (*m*, 4 CH); 7.52 (*d*, ^3J = 8.5, 2 CH). ^{13}C-NMR: 27.9 (Me_3C); 82.6 (Me_3C); 106.6 (CH); 127.2 (2 CH); 128.9 (2 CH); 129.4 (2 CH); 129.5 (C); 130.4 (2 CH); 130.5 (C); 134.2 (C); 134.4 (C); 135.4 (C); 152.5 (C=O); 158.4 (C=O); 163.0 (C=O). EI-MS: 436 (3, $[M+3]^+$), 435 (5, $[M+2]^+$), 434 (8, $[M+1]^+$), 433 (6, M^+), 432 (15), 332 (15), 251 (32), 178 (80), 153 (27), 125 (14), 90 (5), 57 (100). Anal. calc. for $C_{21}H_{18}Cl_2N_2O_4$ (433.29): C 58.21, H 4.19, N 6.47; found: C 58.27, H 4.15, N 6.52.

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