Trichloroacetonitrile as a Source of Positive Chlorine Ion for Trapping *Huisgen*'s Zwitterions

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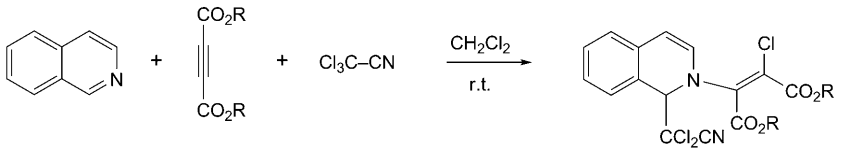
The zwitterionic 1:1 intermediates generated by addition of N-heterocycles to activated acetylenes are trapped by trichloroacetonitrile to afford 1,2- or 1,4-disubstituted N-heterocycles in moderate to good yields under mild reaction conditions.

Introduction. – Activated nitriles are highly reactive reagents that have found application in organic synthesis [1]. Among them, trichloroacetonitrile is a unique compound in which both the cyano group and the trichloromethyl group acquire high reactivities as a result of their mutual effect [2]. In spite of extensive applications of trichloroacetonitrile in organic synthesis [3][4], there has been no published report on its use as a source of positive chlorine ion.

The fascinating chemistry that stems from the addition of nucleophiles to activated acetylenic compounds has evoked considerable interest. Usually, the addition of nucleophiles devoid of an acidic H-atom leads to a zwitterionic 1:1 intermediate (*Huisgen*'s zwitterion) that can undergo further transformations culminating in a stabilized product [5]. Nucleophiles such as Ph_3P [6], pyridine [7], amines [8], and isocyanides [9] can invoke zwitterion formation. In addition, there are several recent reports on trapping of these zwitterions *via* [4 + 2] cycloadditions [10–12], hexachloroacetone [13], and some heterocyclic ketones [14–16].

Results and Discussion. – As part of our current studies on the development of new routes in heterocyclic synthesis [17–20], we report the results of our studies involving trapping of *Huisgen*'s zwitterions derived from isoquinoline (**1**) and acetylenic esters **2** with trichloroacetonitrile (**3**), which constitutes a synthesis of dialkyl 2-chloro-3-{1-[dichloro(cyano)methyl]isoquinolin-2(1*H*)-yl}maleates **4** in good yields (*Scheme 1*).

Scheme 1

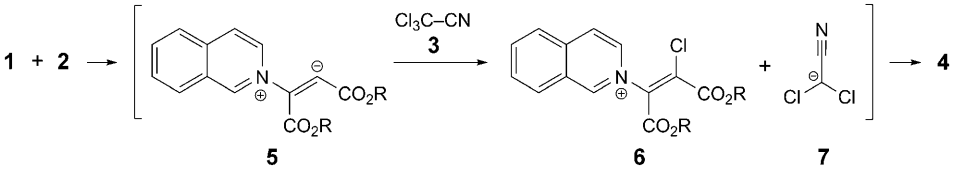


1 **2a** R = Me, **2b** R = Et, **3** → **4a** R = Me (90%), **4b** R = Et (80%)

Compounds **4a** and **4b** were obtained as a single geometrical isomer. The structures of compounds **4** were deduced from their IR and ^{1}H- and ^{13}C-NMR spectra. For example, the ^{1}H-NMR spectrum of **4a** showed signals for two MeO groups (δ(H) 3.85 and 3.86), a CH group (δ(H) 5.39), and two olefinic H-atoms (δ(H) 5.98 and 6.59), together with characteristic signals for the aromatic H-atoms. The ^{1}H-decoupled ^{13}C-NMR spectrum of **4a** exhibited 17 distinct resonances in agreement with the proposed structure. The IR spectrum of **4a** displayed characteristic absorptions for ester C=O, CN, and C–Cl groups. The mass spectrum of **4a** showed the molecular-ion peak at *m*/*z* 415. The (*Z*)-configuration (maleate) was assigned in analogy to the products of the addition of secondary amines to **2** [21]. The NMR spectra of **4b** were similar to those for **4a**, except for the alkyl moieties, which exhibited characteristic resonances in appropriate regions of the spectrum.

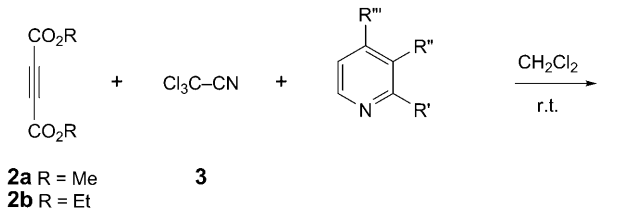
Although the mechanistic details of the reaction are not known, a plausible rationalization may be advanced to explain the product formation. Presumably, the zwitterionic intermediate **5**, formed from **1** and **2**, is chlorinated by **3** to furnish intermediate **6**, which is attacked by **7** to give **4** (*Scheme 2*).

Scheme 2



Under similar conditions, the reaction of pyridine derivatives **8a**–**8e** with acetylenic esters **2** led to dialkyl 2-chloro-3-{4-[dichloro(cyano)methyl]pyridin-1(4*H*)-yl}maleates **9a**–**9f** in good yields (*Scheme 3*). Compounds **9** were again fully characterized with their elemental analyses and their IR, and ^{1}H- and ^{13}C-NMR spectra.

Scheme 3

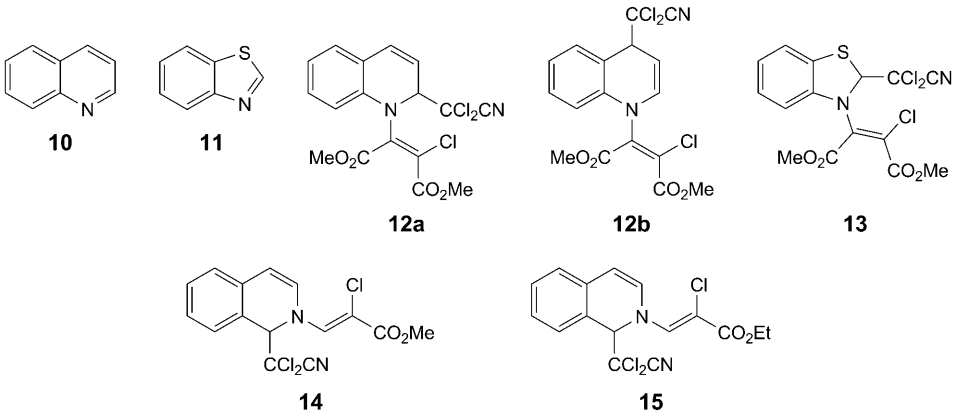


	R'	R''	R'''
8a	H	H	H
8b	H	Me	H
8c	H	H	Me
8d	Me	H	H
8e	Cl	H	H

	R	R'	R''	R'''	Yield [%]
9a	Me	H	H	H	85
9b	Et	H	H	H	72
9c	Me	H	Me	H	90
9d	Me	H	H	Me	80
9e	Me	Me	H	H	89
9f	Me	Cl	H	H	82

To extend our knowledge of this transformation, we performed the reaction between **2a** and quinoline (**10**) or benzothiazole (**11**) in the presence of **3**. These reactions led to two structural isomers **12a** and **12b**, in nearly 1:1 ratio, and to

compound **13**, respectively. We were not able to separate the isomeric compounds **12**, thus, the spectroscopic data of the mixture is given. Also we performed the reaction between **1**, alkyl propiolates (= alkyl prop-2-ynoates), and **3**. These reactions led to compounds **14** and **15**. The ^{1}H-NMR spectra of **14** and **15** exhibited a C=CH H-atom signal at δ(H) *ca.* 7.1, which is in agreement with the (*Z*)-configuration [22] for the olefinic moiety in these compounds.



In conclusion, the zwitterionic 1:1 intermediates generated by addition of N-heterocycles to acetylenic esters are trapped by **3** to produce 1,2- or 1,4-disubstituted N-heterocycles. The present procedure has the advantage that the reactants can be mixed without any prior activation or modification, and the reaction is performed under neutral conditions. With this, we report for the first time that **3** can act as a source of positive chlorine ion in trapping *Huisgen*'s zwitterions.

Experimental Part

General. Compounds **1**–**3**, **8**, **10**, **11**, and alkyl propiolates were obtained from *Merck* and used without further purification. M.p.: *Electrothermal-9100* apparatus; uncorrected. IR Spectra: *Shimadzu-IR-460* spectrometer; 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 **4**, **9**, and **12**–**15**. *General Procedure.* To a stirred soln. of **3** (0.145 g, 1 mmol) and **2** (1 mmol) was added dropwise N-heterocycle (1 mmol) at r.t. After completion of the reaction (0.5–1 h), as indicated by TLC (AcOEt/hexane 1:5), the solvent was evaporated, and the residue was purified by column chromatography (SiO_2 (230–240 mesh; *Merck*), AcOEt/hexane 1:8): pure product.

*Dimethyl (2Z)-2-Chloro-3-{1-[dichloro(cyano)methyl]isoquinolin-2(1*H*)-yl}but-2-enedioate* (**4a**): Yield 0.37 g (90%). Yellow powder. M.p. 114–115°. IR (KBr): 2959, 2250 (CN), 1737 (C=O), 1720 (C=O), 1579, 1480, 1275, 1219, 1068, 780. ^{1}H-NMR: 3.85 (*s*, MeO); 3.86 (*s*, MeO); 5.39 (*d*, ^4J = 0.8, CH); 5.98 (*d*, ^3J = 7.7, CH); 6.59 (*dd*, ^3J = 7.7, ^4J = 0.8, CH); 7.22 (*dd*, ^3J = 7.6, ^4J = 1.0, CH); 7.30 (*td*, ^3J = 6.5, ^4J = 1.0, CH); 7.39 (*dd*, ^3J = 7.6, ^4J = 1.0, CH); 7.42 (*td*, ^3J = 6.5, ^4J = 1.0, CH). ^{13}C-NMR: 53.4 (MeO); 53.5 (MeO); 70.7 (CH); 71.9 (C); 107.8 (CH); 114.8 (C); 120.0 (C); 121.0 (CH); 125.1 (CH); 126.7 (CH); 128.9 (CH); 129.9 (CH); 130.3 (C); 131.6 (C); 142.8 (C); 163.1 (COO); 163.3 (COO). EI-MS: 415 (2, M^+), 379 (10), 306 (100), 275 (12), 189 (8), 154 (24), 129 (20), 43 (25). Anal. calc. for $C_{17}H_{13}Cl_3N_2O_4$ (413.99): C 49.12, H 3.15, N 6.74; found: C 49.39, H 3.31, N 6.52.

*Diethyl (2Z)-2-Chloro-3-{1-[dichloro(cyano)methyl]isoquinolin-2(1*H*)-yl}but-2-enedioate* (**4b**): Yield 0.35 g (80%). Dark yellow oil. IR (KBr): 2985, 2245 (CN), 1715 (C=O), 1655 (C=O), 1599, 1452, 1272, 1199, 1015, 747. ^{1}H-NMR: 1.24 (*t*, ^3J = 7.1, Me); 1.31 (*t*, ^3J = 7.1, Me); 4.25–4.35 (*m*, 2 CH_2O); 5.37 (*s*, CH); 5.95 (*d*, ^3J = 7.7, CH); 6.59 (*dd*, ^3J = 7.7, ^4J = 0.8, CH); 7.21 (*dd*, ^3J = 7.7, ^4J = 0.8, CH); 7.30 (*td*, ^3J = 7.5, ^4J = 0.9, CH); 7.39 (*dd*, ^3J = 7.5, ^4J = 0.9, CH); 7.42 (*td*, ^3J = 7.7, ^4J = 0.9, CH). ^{13}C-NMR: 13.7 (Me); 13.8 (Me); 64.6 (CH_2O); 65.0 (CH_2O); 70.9 (CH), 71.9 (C); 107.4 (CH); 114.9 (C); 120.0 (C); 121.0 (CH); 124.9 (CH); 126.6 (CH); 129.2 (CH); 129.9 (CH); 130.2 (C); 131.7 (C); 142.3 (C); 162.4 (COO); 162.9 (COO). EI-MS: 443 (5, M^+), 407 (13), 334 (100), 290 (22), 180 (11), 156 (28), 129 (16), 43 (35). Anal. calc. for $C_{19}H_{17}Cl_3N_2O_4$ (442.03): C 51.43, H 3.86, N 6.31; found: C 51.74, H 3.89, N 6.38.

*Dimethyl (2Z)-2-Chloro-3-{4-[dichloro(cyano)methyl]pyridin-1(4*H*)-yl}but-2-enedioate* (**9a**): Yield 0.31 g (85%). Yellow oil. IR (KBr): 2952, 2252 (CN), 1734 (C=O), 1684 (C=O), 1591, 1437, 1263, 1171, 1002, 744. ^{1}H-NMR: 3.84 (*s*, MeO); 3.86 (*s*, MeO); 3.96 (*t*, ^3J = 4.5, CH); 5.09 (*td*, ^3J = 8.1, 4.5, 2 CH); 6.42 (*d*, ^3J = 8.1, 2 CH). ^{13}C-NMR: 49.3 (CH); 53.5 (MeO); 53.6 (MeO); 73.4 (C); 98.2 (2 CH); 114.7 (C); 119.0 (C); 131.7 (2 CH); 139.0 (C); 162.9 (COO); 163.0 (COO). EI-MS: 366 (30, M^+), 295 (18), 265 (28), 237 (24), 203 (21), 178 (25), 94 (78), 50 (100). Anal. calc. for $C_{13}H_{11}Cl_3N_2O_4$ (363.98): C 42.71, H 3.03, N 7.66; found: C 43.04, H 3.13, N 7.82.

*Diethyl (2Z)-2-Chloro-3-{4-[dichloro(cyano)methyl]pyridin-1(4*H*)-yl}but-2-enedioate* (**9b**): Yield 0.27 g (72%). Yellow oil. IR (KBr): 2981, 2240 (CN), 1730 (C=O), 1632 (C=O), 1594, 1450, 1380, 1253, 1014, 751. ^{1}H-NMR: 1.27 (*t*, ^3J = 7.1, Me); 1.32 (*t*, ^3J = 7.1, Me); 3.96 (*t*, ^3J = 4.4, CH); 4.26–4.34 (*m*, 2 CH_2O); 5.07 (*td*, ^3J = 8.1, 4.4, 2 CH); 6.42 (*d*, ^3J = 8.1, 2 CH). ^{13}C-NMR: 13.8 (Me); 13.9 (Me); 49.4 (CH); 62.9 (CH_2O); 63.0 (CH_2O); 73.5 (C); 97.9 (2 CH); 114.8 (C); 119.1 (C); 131.8 (2 CH); 138.7 (C); 162.4 (COO); 162.5 (COO). EI-MS: 378 (35, M^+), 309 (60), 277 (30), 250 (23), 219 (19), 191 (28), 93 (72), 50 (100). Anal. calc. for $C_{15}H_{15}Cl_3N_2O_4$ (392.01): C 45.77, H 3.84, N 7.12; found: C 46.10, H 3.91, N 7.24.

*Dimethyl (2Z)-2-Chloro-3-{4-[dichloro(cyano)methyl]-3-methylpyridin-1(4*H*)-yl}but-2-enedioate* (**9c**): Yield 0.34 g (90%). Yellow oil. IR (KBr): 2925, 2243 (CN), 1740 (C=O), 1638 (C=O), 1627, 1582, 1436, 1260, 1075, 793. ^{1}H-NMR: 2.01 (*s*, Me); 3.83 (*s*, MeO); 3.84 (*s*, MeO); 3.87 (*d*, ^3J = 5.3, CH); 5.07 (*dd*, ^3J = 7.7, 5.3, CH); 6.30 (^4J = 1.1, CH); 6.46 (*dd*, ^3J = 7.3, ^4J = 1.1, CH). ^{13}C-NMR: 22.6 (Me); 53.4 (CH); 53.5 (MeO); 53.6 (MeO); 73.1 (C); 97.7 (CH); 108.3 (C); 115.4 (C); 115.8 (C); 128.6 (CH); 131.1 (CH); 140.1 (C); 163.1 (COO); 163.2 (COO). EI-MS: 379 (35, M^+), 309 (60), 279 (30), 251 (23), 219 (19), 191 (28), 93 (72), 50 (100). Anal. calc. for $C_{14}H_{13}Cl_3N_2O_4$ (377.99): C 44.29, H 3.45, N 7.38; found: C 44.02, H 3.65, N 7.56.

*Dimethyl (2Z)-2-Chloro-3-{4-[dichloro(cyano)methyl]-4-methylpyridin-1(4*H*)-yl}but-2-enedioate* (**9d**): Yield 0.30 g (80%). White powder. M.p. 117–118° (dec.). IR (KBr): 2956, 2243 (CN), 1738 (C=O), 1718 (C=O), 1683, 1623, 1588, 1438, 1073, 799. ^{1}H-NMR: 1.51 (*s*, Me); 3.83 (*s*, MeO); 3.86 (*s*, MeO); 4.90 (*d*, ^3J = 6.6, 2 CH); 6.35 (*d*, ^3J = 6.6, 2 CH). ^{13}C-NMR: 26.1 (Me), 48.2 (C); 53.4 (MeO); 53.5 (MeO); 76.2 (C); 103.2 (2 CH); 114.8 (C); 117.7 (C); 129.6 (2 CH); 139.3 (C); 162.9 (COO); 163.1 (COO). EI-MS: 379 (35, M^+), 309 (60), 279 (30), 251 (23), 219 (19), 191 (28), 93 (72), 50 (100). Anal. calc. for $C_{14}H_{13}Cl_3N_2O_4$ (377.99): C 44.29, H 3.45, N 7.38; found: C 44.02, H 3.65, N 7.56.

*Dimethyl (2Z)-2-Chloro-3-{4-[dichloro(cyano)methyl]-2-methylpyridin-1(4*H*)-yl}but-2-enedioate* (**9e**): Yield 0.34 g (89%). Yellow oil. IR (KBr): 2925, 2243 (CN), 1742 (C=O), 1638 (C=O), 1612, 1456, 1436, 1230, 1066, 753. ^{1}H-NMR: 1.81 (*s*, Me); 3.87 (*s*, MeO); 3.88 (*s*, MeO); 3.95 (*dd*, ^3J = 4.1, 3.6, CH); 4.78 (br. *s*, CH); 4.92–4.95 (*m*, CH); 6.16 (*d*, ^3J = 8.0, CH). ^{13}C-NMR: 29.7 (Me); 51.2 (CH); 53.3 (MeO); 53.6 (MeO); 74.0 (C); 94.6 (CH); 95.9 (CH); 105.3 (C); 115.1 (C); 133.2 (CH); 134.4 (C); 139.0 (C); 162.6 (COO); 162.8 (COO). EI-MS: 379 (35, M^+), 309 (60), 279 (30), 251 (23), 219 (19), 191 (28), 93 (72), 50 (100). Anal. calc. for $C_{14}H_{13}Cl_3N_2O_4$ (377.99): C 44.29, H 3.45, N 7.38; found: C 44.02, H 3.65, N 7.56.

*Dimethyl (2Z)-2-Chloro-3-{2-chloro-4-[dichloro(cyano)methyl]pyridin-1(4*H*)-yl}but-2-enedioate* (**9f**): Yield 0.33 g (82%). Dark yellow oil. IR (KBr): 2955, 2244 (CN), 1741 (C=O), 1674 (C=O), 1617, 1436, 1320, 1274, 1074, 750. ^{1}H-NMR: 3.85 (*s*, MeO); 3.90 (*s*, MeO); 4.09 (*t*, ^3J = 4.5, CH); 5.02 (*ddd*, ^3J = 8.0, 4.5 ^4J = 2.0, CH); 5.12 (*dd*, ^3J = 4.5, 2.3, CH); 6.21 (*d*, ^3J = 8, CH). ^{13}C-NMR: 52.5 (CH); 53.4 (MeO); 53.7 (MeO); 73.2 (C); 94.9 (CH); 96.8 (CH); 106.2 (C); 114.6 (C); 132.7 (C); 133.3 (CH); 139.2 (C); 161.9 (COO); 162.5 (COO). EI-MS: 400 (40, M^+), 329 (52), 298 (8), 271 (14), 237 (24), 212 (31), 93

(65), 50 (100). Anal. calc. for $C_{13}H_{10}Cl_4N_2O_4$ (397.94): C 39.03, H 2.52, N 7.00; found: C 39.37, H 2.58, N 7.16.

Dimethyl (2Z)-2-Chloro-3-{2-[dichloro(cyano)methyl]quinolin-1(2H)-yl}but-2-enedioate (**12a**) *and Dimethyl (2Z)-2-Chloro-3-{4-[dichloro(cyano)methyl]quinolin-1(4H)-yl}but-2-enedioate* (**12b**): Yield 0.36 g (88%). Yellow oil. IR (KBr): 2954, 2239 (CN), 1740 (C=O), 1659 (C=O), 1602, 1490, 1274, 1092, 1051, 750. ^{1}H-NMR: 3.73 (*s*, MeO); 3.82 (*s*, MeO); 3.88 (*s*, MeO); 3.91 (*s*, MeO); 4.49 (*d*, $^3J = 5.2$, CH); 5.01 (*dd*, $^3J = 5.6$, 5.5, CH); 5.15 (*dd*, $^3J = 7.9$, 5.2, CH); 6.02 (*dd*, $^3J = 9.7$, 5.5, CH); 6.53 (*d*, $^3J = 7.9$, CH); 6.71–6.77 (*m*, 2 CH); 6.90–6.94 (*m*, 2 CH); 7.10–7.12 (*m*, 2 CH); 7.16 (*td*, $^3J = 7.3$, $^4J = 1.5$, CH); 7.30 (*td*, $^3J = 8.4$, $^4J = 1.4$, CH); 7.53 (*dd*, $^3J = 7.7$, $^4J = 1.1$, CH). ^{13}C-NMR: 52.3 (MeO); 53.1 (MeO); 53.3 (MeO); 53.6 (MeO); 65.7 (C); 69.4 (CH); 71.6 (C); 74.0 (C); 94.5 (2 CH); 114.2 (C); 114.7 (C); 115.0 (C); 116.3 (C); 122.0 (CH); 122.6 (CH); 123.3 (CH); 127.4 (C); 128.0 (CH); 129.6 (CH); 129.7 (CH); 129.8 (CH); 131.5 (CH); 132.0 (CH); 133.8 (2 CH); 134.4 (C); 138.3 (C); 138.9 (C); 139.3 (C); 162.7 (COO); 162.8 (COO); 163.1 (COO); 163.6 (COO). EI-MS: 415 (1, M^+), 379 (10), 306 (100), 275 (7), 189 (5), 154 (12), 129 (15), 50 (35). Anal. calc. for $C_{17}H_{13}Cl_3N_2O_4$ (413.99): C 49.12, H 3.15, N 6.74; found: C 49.42, H 3.27, N 6.52.

Dimethyl (2Z)-2-Chloro-3-{2-[dichloro(cyano)methyl]benzothiazol-3(2H)-yl}but-2-enedioate (**13**): Yield 0.33 g (79%). Orange oil. IR (KBr): 2254, (CN), 1733 (C=O), 1612 (C=O), 1471, 1261, 1201, 1098, 1040, 748. ^{1}H-NMR: 3.83 (*s*, MeO); 3.92 (*s*, MeO); 5.28 (*s*, CH); 6.54 (*d*, $^3J = 7.9$, CH); 6.94 (*t*, $^3J = 7.6$, CH); 7.05 (*t*, $^3J = 7.8$, CH); 7.15 (*d*, $^3J = 7.5$, CH). ^{13}C-NMR: 53.4 (MeO); 53.5 (MeO); 71.9 (C); 79.6 (CH); 111.4 (CH); 113.5 (C); 118.6 (C); 121.5 (CH); 123.2 (CH); 126.1 (CH); 133.8 (C); 138.3 (C); 142.3 (C); 161.9 (COO); 162.8 (COO). EI-MS: 421 (1, M^+), 384 (7), 312 (100), 281 (10), 251 (22), 194 (23), 135 (16), 94 (28), 77 (32), 39 (21). Anal. calc. for $C_{15}H_{11}Cl_3N_2O_4S$ (419.95): C 42.70, H 2.63, N 6.60; found: C 42.50, H 2.74, N 6.47.

Methyl (2Z)-2-Chloro-3-{1-[dichloro(cyano)methyl]isoquinolin-2(1H)-yl}prop-2-enoate (**14**): Yield 0.32 g (89%). Orange oil. IR (KBr): 2959, 2250 (CN), 1743 (C=O), 1438, 1322, 1276, 1234, 1076, 765. ^{1}H-NMR: 3.81 (*s*, MeO); 5.85 (*s*, CH); 6.15 (*d*, $^3J = 7.7$, CH); 7.22–7.27 (*m*, 2 CH); 7.34 (*t*, $^3J = 7.7$, CH); 7.44–7.47 (*m*, 2 CH); 7.71 (*s*, CH). ^{13}C-NMR: 52.9 (MeO); 70.7 (CH); 71.4 (C); 111.7 (CH); 114.7 (C); 122.4 (C); 125.6 (CH); 127.1 (CH); 127.4 (CH); 129.7 (CH); 129.9 (CH); 130.6 (CH); 131.4 (C); 141.3 (C); 164.8 (COO). EI-MS: 358 (2, M^+), 321 (18), 248 (100), 218 (26), 190 (13), 156 (29), 129 (24), 43 (33). Anal. calc. for $C_{15}H_{11}Cl_3N_2O_2$ (357): C 50.24, H 3.37, N 7.81; found: C 50.56, H 3.51, N 7.60.

Ethyl (2Z)-2-Chloro-3-{1-[dichloro(cyano)methyl]isoquinolin-2(1H)-yl}prop-2-enoate (**15**): Yield 0.26 g (70%). Orange oil. IR (KBr): 2924, 2248 (CN), 1732 (C=O), 1558, 1376, 1256, 1170, 1029, 753. ^{1}H-NMR: 1.25 (*t*, $^3J = 7.1$, Me); 4.24 ($^3J = 7.1$, CH_2O); 5.86 (*s*, CH); 6.13 (*d*, $^3J = 7.6$ Hz, CH); 7.22–7.26 (*m*, 2 CH); 7.32 (*t*, $^3J = 7.4$, CH); 7.42–7.45 (*m*, 2 CH); 7.70 (*s*, CH). ^{13}C-NMR: 14.3 (Me); 62.1 (CH_2O); 70.6 (CH); 71.4 (C); 111.5 (CH); 114.9 (C); 122.8 (C); 125.0 (CH); 127.3 (CH); 127.5 (CH); 129.2 (CH); 129.8 (CH); 130.4 (CH); 131.7 (C); 141.1 (C); 164.8 (COO). EI-MS: 371 (4, M^+), 335 (16), 262 (100), 218 (21), 190 (12), 156 (23), 129 (15), 43 (31). Anal. calc. for $C_{16}H_{13}Cl_3N_2O_2$ (370): C 51.71, H 3.53, N 7.54; found: C 51.42, H 3.64, N 7.32.

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