FeCl₂-Catalyzed Intramolecular Chloroamination Reactions

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Abstract: 2-Alkenyloxycarbonyl azides 1 and 2-alkynyloxycarbonyl azides 3 undergo in the presence of trimethylsilyl chloride and catalytic amounts of FeCl₂ an intramolecular chloroamination (aminochlorination) reaction (Procedure 1). The corresponding oxazolidinones 2 and 4 are formed in moderate to excellent yields (47–99%). The same reagent combination can be employed to convert azides 6 of γ , δ unsaturated carboxylic acids into the corresponding lactams 7. The latter reaction is best conducted as a one-pot reaction (Procedure 2) starting from the acids 5 without isolation of the corresponding azides (57-75% yield).

Key words: aminations, chloroaminations, chlorolactamizations, homogenous catalysis, iron, radical reactions



Scheme 1

Introduction

Chloroamination (aminochlorination) reactions at C-C multiple bonds have in the past been most frequently achieved starting from the corresponding N-chloroamines.³ These reactions can take place either intra-^{4,5} or intermolecularly⁶ and often follow a radical pathway. Alternatively, ionic processes are known which occur by an electrophilic halogen attack and subsequent N-C bond formation. Transition metal catalyzed chloroaminations have been reported.7 The procedures summarized in Scheme 1 encompass a unique set of reactions which allows for the transition metal catalyzed intramolecular chloroamination of three important substrate types. They employ readily accessible azides (CAUTION, see Procedures)⁸ as starting materials which in the presence of trimethylsilyl chloride (TMSCl) and an appropriate catalyst allow for an efficient addition to C–C double and triple bonds.

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Our interest in the use of azides for N-C bond formation was initiated by the observation that *tert*-butoxycarbonyl azide $(BocN_3)^8$ decomposed rapidly in various solvents upon addition of catalytic amounts of FeCl₂.9 Nitrogen evolution occurred and the resulting intermediate could be trapped by sulfides and sulfoxides, which were converted into the corresponding N-Boc protected sulfimines and sulfoximines.^{10–12} As an intermolecular transfer of the putative nitrene to alkenes was not successful¹³ we attempted intramolecular aziridination reactions. Precedence for such a reaction existed in the thermal decomposition of 2alkenyloxycarbonyl azides at 150 °C.14 The azides were shown to undergo subsequent ring opening reactions to the product of a formal chloroamination. Surprisingly, the Fe(II)-catalyzed process led directly to chloroamination products such as compound $2^{15,16}$ It could be proven that aziridines are not involved as intermediates and that the reactions proceed presumably via a N-centered radical, which can be best described as Cl₂Fe(III)NCO₂R (cf. A, Figure 1). The reaction was optimized using various chloride sources and procedure 1 emerged as a suitable method for this tethered chloroamination. It is applicable both to 2-alkenyloxycarbonyl azides 1 and to 2-alkynyloxycarbonyl azides 3.15-17



Figure 1 Postulated radical intermediates **A**, **B**, and **C** in the intramolecular chloroamination of 2-alkenyloxycarbonyl and 2-alkynyloxycarbonyl azides.

Procedure 2 was developed as an extension of the initially discovered chloroamination of alkenyloxycarbonyl azides.¹⁸ It allows for the unprecedented direct conversion of carboxylic acids **5** into halolactamization products **7**, in which the nitrogen atom is unsubstituted.¹⁸ Alternative literature procedures make use of N-substituted, secondary carboxylic amides,¹⁹ of imidates,²⁰ or of *N*-chloroamides.^{5a,c,21}

Scope and Limitations

The tethered chloroamination was extensively optimized using azide **1a** as test substrate (Scheme 1).^{13b,15b} While H_2O , THF, and MeOH proved unsuitable as solvent, reasonable conversions were achieved in EtOH, in acetone, in CH_2Cl_2 , and in acetonitrile. In acetonitrile the diastereoselectivity of the reaction was even higher (dr = 96:4) than in EtOH but larger catalyst loadings (50 mol%) were required to allow for a reasonable yield (63%). Indeed, EtOH was the only solvent in which 10 mol% of FeCl₂ proved sufficient to guarantee a complete conversion. Many attempts to replace FeCl₂ by other iron salts or iron complexes have not yet met with success.²² Significant ligand acceleration was not observed.²³ As a consequence enantioselective variants of the method have not yet been established.

Secondary allylic alcohols 1 leading to 2a-e,h (Table 1, entries 1-5, 8) reacted readily and with good to very good facial diastereoselectivity in the intramolecular chloroamination reaction. More volatile products (e.g. the oxazolidinone derived from 2-propenyloxycarbonyl azide) were difficult to isolate and yields were lower. Upon substitution of the terminal alkene carbon atom the question of stereospecifity vs. stereoconvergency was raised. For acyclic starting materials (entries 6-8) the reaction was not stereospecific. Mechanistically, a postulated radical intermediate B (Figure 1) allows for free rotation around the former C–C double bond. The same phenomenon was also observed for the corresponding acyl azides (vide infra). The threolerythro ratio can be high, however, if the radical intermediate adopts a preferred conformation (2g, entry 7). The reactions proceed under kinetic control. In cyclic systems (entries 9, 10) N-C bond formation and chlorine delivery to the intermediate radical depend on the conformation of the ring. The normal outcome is exemplified by the cyclohexyl example 2i in which *cis* addition occurred. The formation of six-membered rings has never been observed. Starting from the substrates for formation

Table 14-Chloroalkyl-Substituted Oxazolidinones 2 Obtained fromthe Corresponding 2-Alkenyloxycarbonylazides 1

Entry	Product		dr ^a	Yield (%) ^b
1		2a	91:9	72
2		2b	88:12	64
3		2c	88:12	60
4		2d	90:10	68
5		2e	94:6°	60
6		2f	d	84
7		2g	_e	76
8		2h	92:8 ^f	64
9		2i	>95:5	47
10		2j	>95:5	58

^a The diastereomeric ratio (dr) refers to the relative configuration of the stereogenic centers C-4 and C-5 of the oxazolidinones **2**. It was determined by integration of appropriate ¹H NMR signals.

^b Yield of isolated product.

^c Mixture of two 4,5-*trans*-isomers due to the additional stereogenic center at the cyclohexene ring.

^d threo/erythro = 49:51.

^e threo/erythro = >99:1.

^f threo/erythro = 65:35.

of oxazolidinones **2d**, **2h**, and **2j**, for example, five- and six-membered ring formation would have been possible but only the former reaction was observed. Any attempts to detect the postulated intermediate **B** by radical clocks have been unsuccessful.^{15b} The rate constant for the chlorine transfer was estimated as $k \ge 1.6 \cdot 10^8 \text{ s}^{-1}$. Substitution of the internal alkene carbon atom in 2-alkenyloxycarbo-

nyl azides has not been intensively studied. It appears to retard the cyclization, however, and yields were lower. 2-Methyl-2-propenyloxycarbonyl azide gave under standard reaction conditions only 22% of the reaction product.^{13b} As previously stated, any other but five-membered ring formation has never been observed. An intramolecular FeCl₂-catalyzed sulfimidation to a six-membered 2aza-4-oxa-1-thiacyclohexene was feasible, however.²⁴

A unique reaction, which can be conducted according to procedure 1, is the intramolecular chloroamination of 2-alkynylcarbonyl azides.^{15b,17} Since the reaction proceeds presumably via an alkenyl radical of type **C** (Figure 1) the reaction yields exclusively the Z-configured reaction products **4** (Table 2).

The reaction has been successfully conducted with phenyl- (entries 1-5) and butyl-substituted (entry 6) alkynes as starting materials. If R (in C) was a *tert*-butyl group the

Table 2(4-Chloromethylidene)oxazolidinones 4 Obtained from theCorresponding 2-Alkynyloxycarbonyl Azides 3

Entry	Product		Z/E^{a}	Yield (%) ^b
1		4 a	>99:1	98
2		4b	>99:1	81
3		4c	>99:1°	90
4		4d	>99:1	99
5	O = O	4e	>99:1	99
6		4f	>99:1	95
7		4g	>99:1	95

^a The Z/E ratio was determined by integration of appropriate ¹H NMR signals or by HPLC analysis of the crude product.

^b Yield of isolated product.

 $^{\rm c}$ Mixture of diastereoisomers due to the additional stereogenic center at the cyclohexene ring.

primary products rearranged and were substituted by the solvent to give products such as 4g (entry 7).

The yet least explored reaction is the chlorolactamization represented by procedure 2 in Scheme 1.¹⁸ Attempts to prepare and isolate the required acyl azides **6** by various methods were unsuccessful.²⁵ The Curtius rearrangement sets in at temperatures slightly above 0 °C and the product yields deteriorate. We eventually used a method which allows for the in situ preparation at low temperature. Still, monitoring the conversion and controlling the temperature are at times difficult. The procedure as it is now presented proved extremely convenient and has so far only been applied to a few substrates. Product yields are given in Table 3. IR spectroscopy was used to check the conversion into the intermediate acid chloride and the azide.

Table 3Iron(II)-Catalyzed Chlorolactamization of γ , δ -Unsaturated
Carboxylic Acids in a One-Pot Reaction

Entry	Product		threo/erythro ^a	Yield (%) ^b
1		7a	_	75
2		7b	>95:5	79
3		7c	90:10	75
4		7d	60:40	64
5		7e	>95:5°	57
6		7f	_	59

^a The *threolerythro* ratio was determined by integration of appropriate ¹H NMR signals or by HPLC analysis of the crude product.

^b Yield of isolated product.

^c A *trans/cis* ratio of 69:31 was determined by integration of appropriate ¹H NMR signals.

As for the 2-alkenyloxycarbonyl azides the previously discussed steps, radical addition and chlorine transfer, determine the product configuration. The radical addition step is responsible for the facial diastereoselectivity (*trans/cis* ratio) and the chlorine transfer for the degree of stereospecifity and/or stereoselectivity (*threo/erythro* ratio). Other lactams except γ -lactams have so far not been obtained.

The reaction could not be extended to 4-alkynoic acids. While the azide formation was successful a ring closure in analogy to the conversion $3 \rightarrow 4$ failed. A stereogenic center in β -position induces a moderate diastereoface differentiation (entry 5). Similar results were obtained upon replacing the methyl substituent by phenyl or other alkyl groups (*trans/cis* = 77:23 to 60:40). A substituent in α -position of the 4-alkenoic acids shut down the chlorolactamization. The corresponding azides were relatively stable but yielded only Curtius rearrangement products upon treatment with FeCl₃/TMSCl.

Procedures

Herein we describe two typical procedures for the three different substrate classes depicted in Scheme 1 and in Tables 1–3. Some of the products **7** of the chlorolactamization have not been previously described. Therefore, the analytical data for these compounds are provided in detail. For general remarks regarding the Experimental, see ref. 26.

CAUTION: All azides are potential explosives.¹¹ Appropriate safety protection and utmost care are required while preparing and handling these compounds!

Procedure 1

(±)-(4RS,5SR)-4-(Chloromethyl)-5-cyclohexyl-1,3-oxazolidin-2-one (2a)

1-Azidocarbonyloxy-1-cyclohexylprop-2-ene (**1a**; 209 mg, 1.00 mmol) was dissolved in anhyd EtOH (5 mL) and the solution was degassed with a stream of argon for 15 min at 0 °C. Trimethylsilyl chloride (163 mg, 0.19 mL, 1.50 mmol) was added to the stirred solution via syringe. Solid anhyd FeCl₂ (13 mg, 0.10 mmol) was subsequently added in one portion. The solution was allowed to warm to r.t. during 21 h. EtOAc (10 mL) was added and the resulting solution was washed with H₂O (10 mL) and brine (2 × 10 mL). The organic layer was dried (MgSO₄) and the solvent was removed in vacuo. After purification by flash chromatography [silica gel 60, pentane–*tert*-butyl methyl ether (P–TBME), 20:80], **2a**¹⁵ (156 mg, 72%) was obtained as a colorless oil. The product was a mixture of the (4*RS*,5*SR*)- and the (4*RS*,5*RS*)-isomer (dr = 91:9). The analytical data are provided for the major isomer.

Major Isomer

*R*_f 0.32 (P–TBME, 20:80); mp 115–116 °C.

¹H NMR (500 MHz, CDCl₃): $\delta = 0.90-1.40$ (m, 5 H), 1.45–1.90 (m, 6 H), 3.50 (dd, ²*J* = 11.2 Hz, ³*J* = 6.0 Hz, 1 H), 3.51 (dd, ²*J* = 11.2 Hz, ³*J* = 6.0 Hz, 1 H), 3.77 (pseudo q, ³*J* \approx ³*J* = 6.0 Hz, 1 H), 4.07 (dd, ³*J* = 4.3 Hz, ³*J* = 6.0 Hz, 1 H), 6.80 (s, 1 H).

¹³C NMR (50 MHz, CDCl₃): δ = 25.4 (t), 25.6 (t), 25.7 (t), 26.1 (t), 27.1 (t), 41.8 (d), 46.3 (t), 55.9 (d), 83.9 (d), 158.9 (s).

Oxazolidinones 4

The alkylidene oxazolidinones **4** obtained from the 2-alkynyloxycarbonyl azides **3** were not further purified as they decomposed upon attempted chromatography. They were isolated as colorless solids after work-up in analytically pure form. Typical analytical data are provided for **4a**.¹⁵

(±)-(Z)-4-(1-Chloro-1-phenylmethylidene)-5-cyclohexyl-1,3-ox-azolidin-2-one (4a) Mp 140–150 °C.

IR (KBr): 3200–3300 (br), 3120 (w), 2930 (m), 2860 (m), 1765 (vs), 1695 (m), 1445 (w), 1215 (m), 1075 (w), 1010 (w), 735 (w), 700 cm⁻¹ (w).

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¹H NMR (400 MHz, CDCl₃): δ = 0.89–1.90 (m, 11 H), 5.29 (br s, 1 H), 7.30–7.39 (m, 5 H), 7.91 (s, 1 H).

¹³C NMR (50 MHz, $CDCl_3$): $\delta = 23.9$ (t), 25.6 (t), 25.7 (t), 26.1 (t), 28.9 (t), 34.9 (d), 83.8 (d), 102.7 (s), 128.3 (d), 128.8 (s), 128.9 (d), 133.1 (d), 135.3 (s), 156.2 (s).

MS (EI, 70 eV): m/z (%) = 293 (12, [M⁺(³⁷Cl)]), 291 (32, [M⁺(³⁵Cl)]), 211 (34, [M⁺(³⁷Cl) - C₆H₁₁]), 209 (100, [M⁺(³⁵Cl) - C₆H₁₁]), 83 (38, [C₆H₁⁺]), 77 (2, [C₆H₅⁺]), 55 (52, [C₄H₉⁺]), 41 (34, [C₃H₅⁺]), 28 (75, [CO⁺]).

Procedure 2

(±)-(3aSR,7SR,7aRS)-7-Chlorohexahydro-1*H*-indol-2-(3*H*)-one (7a)

To a solution of 2-(cyclohex-2-enyl)acetic acid (5a; 141 mg, 1.0 mmol) in CH₂Cl₂ (5 mL), were added oxalyl chloride (140 mg, 94 $\mu L,\,1.10$ mmol) and DMF (one drop). The mixture was stirred at r.t. for 20 min. Dichloromethane and the excess oxalvl chloride were removed in vacuo. The remaining acid chloride was dissolved in acetone (5 mL) and a solution of NaN₃ (130 mg, 2.0 mmol) in H₂O (300 mL) was added at -15 °C. The mixture was stirred for 1.5 h at -15 °C and the solvent was removed at this temperature in vacuo. The acyl azide was dissolved in isopropanol (10 mL). A solution of FeCl₂ (25.3 mg, 0.2 mmol) and TMSCl (217 mg, 252 mL, 2.0 mmol) in isopropanol (5 mL) was added. The mixture was stirred for 5 h at -15 °C and for 8 h at r.t. After evaporation of the solvent in vacuo EtOAc (40 mL) was added. The organic layer was washed with H_2O (3 × 20 mL) and brine (2 × 20 mL) and dried (MgSO₄). After filtration, the solvent was evaporated and the crude product was purified by flash chromatography [silica gel 60, CHCl₃-P-MeOH–NH₃(aq), 60:30:10:0.5] to give lactam $7a^{18}$ (130 mg, 75%); $R_f 0.65$ [CHCl₃-P-MeOH-NH₃(aq), 60:30:10:0.5]; mp 121 °C.

IR (KBr): 3054 (m), 2970 (m), 1700 (s), 1421 (m), 1262 (s), 856 (m), 750 cm⁻¹ (s).

¹H NMR (500 MHz, CDCl₃): $\delta = 1.23-1.36$ (m, 2 H), 1.60–1.70 (m, 1 H), 1.73–1.85 (m, 2 H), 1.93–2.01 (m, 1 H), 2.05 (d, ²*J* = 16.3 Hz, 1 H), 2.35–2.45 (m, 1 H), 2.45 (dd, ²*J* = 16.3 Hz, ³*J* = 6.5 Hz, 1 H), 3.98–4.07 (m, 2 H), 5.91 (br s, 1 H).

¹³C NMR (90.6 MHz, CDCl₃): δ = 23.9 (t), 26.6 (t), 30.1 (t), 35.9 (d), 40.3 (t), 58.2 (d), 59.7 (d), 177.2 (s).

Anal. Calcd for C_8H_{12} CINO (173.64): C, 55.34; H, 6.97; N, 8.07: Found: C, 55.31; H, 6.92; N, 7.98.

(±)-(*RS*)-5-[(*RS*)-Chlorophenylmethyl)]pyrrolidin-2-one (*threo*-7b)

*R*_f 0.22 (EtOAc–Et₂O, 50:50); mp 108 °C.

IR (KBr): 3054 (w), 2921 (m), 1682 (s), 1451 (w), 1266 (s), 750 cm⁻¹ (s).

¹H NMR (360 MHz, CDCl₃): δ = 1.69–1.74 (m, 1 H), 1.94–2.05 (m, 1 H), 2.26–2.42 (m, 2 H), 4.14 (pseudo dt, ³*J* ≈ ³*J* = 8.5 Hz, ³*J* = 7.3 Hz, 1 H), 4.70 (d, ³*J* = 8.5 Hz, 1 H), 6.37 (br s, 1 H), 7.32–7.48 (m, 5 H).

¹³C NMR (90.6 MHz, CDCl₃): δ = 24.7 (t), 30.1 (t), 60.5 (d), 67.3 (d), 127.5 (d), 128.9 (d), 129.1 (d), 137.2 (s), 177.4 (s).

MS (EI, 70 eV): m/z (%) = 210 (1, [M⁺ + 1]), 174 (8, [M⁺ + 1 - Cl]), 173 (8), 125 (12), 91 (20), 84 (100, [C₄H₆NO⁺]), 56 (12), 41 (64).

Anal. Calcd for $C_{11}H_{12}$ CINO (207.06): C, 63.01; H, 5.78. Found: C, 63.03; H, 5.81.

(±)-(RS)-5-[(RS)-Chlorocyclohexylmethyl]pyrrolidin-2-one (threo-7c)

The product was a mixture of the *threo*- and the *erythro*-isomer (dr = 83:17). The analytical data are provided for the major isomer.

Major Isomer

*R*_f 0.32 (P–EtOAc–MeOH, 80:15:5); mp 115 °C.

IR (KBr): 3054 (s), 2987 (s), 1712 (w), 1422 (m), 1261 (s), 896 (m), 749 cm⁻¹ (s).

¹H NMR (360 MHz, CDCl₃): $\delta = 1.10-1.49$ (m, 5 H), 1.55–1.80 (m, 6 H), 1.81–1.91 (m, 1 H), 2.19–2.33 (m, 1 H), 2.35–2.48 (m, 2 H), 3.66 (dd, ³*J* = 8.2 Hz, ³*J* = 3.4 Hz, 1 H), 3.96 (pseudo q, ³*J* \approx 7.4 Hz, 1 H), 5.87 (br s, 1 H).

¹³C NMR (90.6 MHz, CDCl₃): δ = 25.3 (t), 25.8 (t), 26.0 (t), 26.1 (t), 26.9 (t), 30.5 (t), 31.0 (t), 40.2 (d), 57.0 (d), 73.2 (d), 176.9 (s).

MS (EI, 70 eV): m/z (%) = 215 (100, [M⁺]), 179 (70, [M⁺ – HCl]), 136 (30), 132 (24, [M⁺ – C₆H₁₁]), 108 (15).

Anal. Calcd for $C_{11}H_{18}$ CINO (215.72): C, 61.25; H, 8.41. Found: C, 61.60; H, 8.47.

(±)-(RS)-5-[(RS)-1-Chlorohexyl]pyrrolidin-2-one (7d)

The product was a mixture of the *threo*- and the *erythro*-isomer (dr = 60:40). The analytical data are provided for the major isomer.

Major Isomer

*R*_f 0.49 [CHCl₃–P–MeOH–NH₃(aq), 60:30:10:0.5]; mp 97 °C.

IR (KBr): 3054 (m), 2957 (s), 1694 (s), 1421 (m), 1264 (s), 747 $\rm cm^{-1}$ (s).

¹H NMR (360 MHz, CDCl₃): δ = 0.90 (pseudo t, *J* ≈ 6.7 Hz, 3 H), 1.19–1.45 (m, 6 H), 1.55–1.90 (m, 3 H), 2.22–2.47 (m, 3 H), 3.72–3.89 (m, 2 H), 6.54 (br s, 1 H).

¹³C NMR (90.6 MHz, CDCl₃): δ = 14.0 (q), 23.1 (t), 24.9 (t), 25.8 (t), 31.1 (t), 31.1 (t), 33.6 (t), 59.5 (d), 67.2 (d), 176.4 (s).

MS (EI, 70 eV): m/z (%) = 203 (100, [M⁺]), 168 (50, [M⁺ – Cl]), 152 (15), 136 (10), 124 (29), 110 (87).

Anal. Calcd for C₁₀H₁₈ClNO (203.11): C, 58.96; H, 8.91. Found: C, 58.98; H, 8.71.

(±)-(4RS)-5-[(RS)-Chlorophenylmethyl]-4-methylpyrrolidin-2one (*trans*-7e)

The product was obtained as a mixture of the *threo*- and the *erythro*isomer (dr = 59:41). The analytical data are provided for the major isomer.

Major Isomer

 $R_f 0.48$ (P–EtOAc–MeOH, 60:35:5); mp 95 °C.

IR (KBr): 3200 (br), 2970 (s), 1701 (s), 1265 cm⁻¹ (m).

¹H NMR (360 MHz, CDCl₃): $\delta = 0.76$ (d, ³*J* = 6.8 Hz, 3 H), 1.97 (dd, ²*J* = 17.2 Hz, ³*J* = 6.0 Hz, 1 H), 2.12–2.23 (m, 1 H), 2.57 (dd, ²*J* = 17.2 Hz, ³*J* = 9.0 Hz, 1 H), 3.68 (dd, ³*J* = 8.4 Hz, ³*J* = 4.5 Hz, 1 H), 4.71 (d, ³*J* = 8.4 Hz, 1 H), 6.30 (br s, 1 H), 7.31–7.45 (m, 5 H).

¹³C NMR (90.6 MHz, CDCl₃): δ = 20.2 (q), 32.6 (d), 38.6 (t), 67.1 (d), 67.8 (d), 127.6 (d), 129.0 (d), 129.2 (d), 137.3 (s), 176.4 (s).

MS (EI, 70 eV): m/z (%) = 223 (9, [M⁺]), 188 (32, [M⁺ – CI]), 144 (18), 131 (88), 125 (95, [PhCHCl⁺]), 117 (56), 107 (100).

HRMS: *m/z* calcd for C₁₂H₁₄ClNO: 223.0764; found: 223.0761.

(±)-5-(1-Chlorocyclohexyl)pyrrolidin-2-one (7f) $R_f 0.32$ (P–EtOAc–MeOH, 60:35:5), mp 103 °C.

¹H NMR (360 MHz, CDCl₃): $\delta = 0.98-1.14$ (m, 1 H), 1.27-1.47 (m, 2 H), 1.50-1.70 (m, 5 H), 1.73-1.83 (m, 2 H), 1.96-2.05 (m, 1 H), 2.06-2.15 (m, 1 H), 2.18-2.26 (m, 1 H), 2.28-2.38 (m, 1 H), 3.67 (dd, ³*J* = 8.2 Hz, ³*J* = 5.0 Hz, 1 H), 6.35 (br s, 1 H).

¹³C NMR (90.6 MHz, CDCl₃): δ = 21.4 (t), 22.1 (t), 25.2 (t), 30.1 (t), 34.6 (t), 35.4 (t), 64.5 (d), 178.8 (s).

MS (EI, 70 eV): m/z (%) = 201 (20, [M⁺]), 166 (100, [M⁺ – Cl]), 136 (85), 110 (78).

HRMS: *m*/*z* calcd for C₁₀H₁₆ClNO: 201.09204; found: 201.08981.

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