Direct Conversion of Carbonyl Compounds into Organic Halides: Indium (III) Hydroxide-Catalyzed Deoxygenative Halogenation Using Chlorodimethylsilane

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Supporting Information

General. IR spectra were recorded as thin films or as solids in KBr pellets on a HORIBA FT-720 spectrophotometer. ^1H and ^{13}C spectra were obtained with a 270 and 67.9 MHz spectrometer, respectively, with TMS as internal standard. Mass spectra were recorded on a JEOL JMS-DS303 spectrometer. GLC analyses were performed on a Shimadzu GC-14A with FID using a 15 m $\times$ 3 mm capillary column packed with TC-WAX (0.25 μm). Column chromatography was performed on silica gel (MERK C60). Bulb-to-bulb distillation (Kugelrohr) was accomplished in a Sibata GTO-250RS at the oven temperature and pressure indicated. Yields were determined by GLC or ^1H NMR using internal standards.

Materials. Chloroform (stabilized with 2-methyl-2-butene) was used without purification. All catalysts in Table 1, carbonyl compounds **1a-r**, HSiEt_3 , Me_3SiCl , HSiMe_2Cl (**2b**), allylchlorodimethylsilane (**2d**), and LiI were commercially available. The silyl ether **7** was prepared and the experimental details are described below (This preparation method was not optimized.).

4'-Chlorobenzyl chlorodimethylsilyl ether (7). To a solution of Me_2SiCl_2 (8.34 g, 65 mmol) and pyridine (4.79 g, 63 mmol) in benzene (100 mL) was slowly added a solution of 4'-chlorobenzyl alcohol (7.13 g, 50 mmol) in chloroform (25 mL) at ambient temperature for 30 min. Removal of the resultant pyridinium salt by the continuous filtration and evaporation of solvents gave a crude mixture. The resultant mixture was distilled to give the pure product as a colorless liquid (11.11 g, 94%): bp 60 $^\circ\text{C}$ / 0.2 mmHg; ^1H NMR (270 MHz, CDCl_3) δ 7.13-7.04 (m, 5H,

aroma), 4.58 (s, 2H, CH₂), 0.29 (s, 6H, Si-Me₂); ¹³C NMR (67.9 MHz, CDCl₃) δ 137.82 (Ar-1'), 133.16 (C-4'), 128.46 (C-3', 5'), 128.09 (C-2', 6'), 64.36 (CH₂), 2.11 (Si-C).

(+)-1-Phenylethyl chlorodimethylsilyl ether. To a solution of Me₂SiCl₂ (6.78 g, 52.5 mmol) and pyridine (40 mL) in benzene (50 mL) was slowly added a solution of (*R*)-(+)-1-phenylethanol (4.82 g, 39.5 mmol) in benzene (20 mL) at ambient temperature for 25 min. The mixture was stirred in refluxing benzene for 3.5 h. Removal of the resultant pyridinium salt by the filtration and successive evaporation of solvents gave a crude mixture. The residual oil was distilled to give the pure product as a colorless liquid (4.00 g, 47%): bp 32 °C/ 0.072 mmHg; ¹H NMR (270 MHz, CDCl₃) δ 7.36-7.21 (m, 5H, aroma), 5.10 (q, *J* = 6.35 Hz, 1H, CH), 1.50 (d, *J* = 6.35 Hz, 3H, CH₃), 0.50 (s, 3H, Si-CH₃), 0.32 (s, 3H, Si-CH₃); ¹³C NMR (67.9 MHz, CDCl₃) δ 144.84 (Ph), 128.23 (Ph), 127.23 (Ph), 125.36 (Ph), 71.72 (C-1), 26.19 (C-2), 2.79 (Si-C), 2.53 (Si-C); [α]_D = +66.69° (*c* = 8.895, chloroform).

General Procedure for Deoxygenative Chlorination of Carbonyls (eq 1, Table 1, and Table 2). To a mixture of the catalyst (0.1 mmol) and carbonyls (2.0 mmol) in chloroform (4.0 mL) was added chlorodimethylsilane (**2b**, 2.4 mmol) under nitrogen. The reaction mixture was stirred under the reaction conditions noted in the text. The resulting mixture was poured into EtOAc (50 mL) and washed by aqueous NaHCO₃ (50 mL). The organic layer was dried over MgSO₄ and concentrated *in vacuo*. The procedures of further purification for new compounds are shown in the Product data section.

Chlorination of the enantio-pure chlorosilylether (reference 6). To a suspension of In(OH)₃ (0.15 mmol) in chloroform (6.0 mL) was added (+)-1-phenylethyl chlorodimethylsilyl ether (3.0 mmol) under nitrogen. The reaction mixture was stirred under nitrogen for 1 h. The resulting mixture was poured into EtOAc (50 mL) and washed by aqueous NaHCO₃ (50 mL). The organic layer was dried over MgSO₄ and concentrated *in vacuo*. The product was purified by column chromatography (SiO₂), and followed by distillation (yield = 80%, 0.88%ee (major; (*R*)-(+)-1-chlorophenylethane). Optical purity was calculated based on the literature (Holcomb, H. L.; Nakanishi, S.; Flood, T. C. *Organometallics* **1996**, *15*, 4228-4234).

Product data. The spectral data of the products **3a-e**, **3m-n**, **4b**, **5** and **6** are in excellent agreement with the samples which were commercially available. Spectral data for the products, **3f-j**, **3o-r**, **8**, **9b** and **9s** are shown below.

1-Chloro-1-(4-Chlorophenyl)ethane (3f). According to the general procedure, this compound was prepared from HSiMe₂Cl (**2b**), *p*-chloroacetophenone (**1f**), and In(OH)₃ in chloroform to give the product as a colorless liquid after distillation: bp 58 °C/ 0.11 mmHg; ¹H NMR (270 MHz, CDCl₃) δ 7.40-7.27 (m, 5H, aroma), 5.05 (q, *J* = 6.8 Hz, 1H, CH), 1.82 (d, *J* = 6.8 Hz, 3H, CH₃); ¹³C NMR (67.9 MHz, CDCl₃) δ 141.29 (C-4'), 133.95 (C-1'), 128.77 (C-2', 6'), 127.90 (C-3', 5'), 57.76 (C-1), 26.44 (C-2); IR (neat) 1095 (Ar-Cl), 825 cm⁻¹ (C-Cl); MS

(EI, 70 eV) 178 ($M^+ + 4$, 2), 176 ($M^+ + 2$, 13), 174 (M^+ , 20), 139 ($M^+ - \text{Cl}$, 100), 103 ($M^+ - \text{Cl} - \text{Cl}$, 63), 77 (Ph, 22); HRMS (EI, 70 eV) calculated for ($\text{C}_8\text{H}_8\text{Cl}_2$) 174.0003 (M^+) found for m/z 174.0000.

4-(1-Chloroethyl)benzonitrile (3g). According to the general procedure, this compound was prepared from HSiMe_2Cl (**2b**), *p*-acetylbenzonitrile (**1g**), and $\text{In}(\text{OH})_3$ in chloroform to give the product as a colorless liquid after distillation: bp 85 °C/ 0.11 mmHg; ^1H NMR (270 MHz, CDCl_3) δ 7.65 (d, $J = 8.4$ Hz, 2H, 3'5'-H), 7.53 (d, $J = 8.4$ Hz, 2H, 2'6'-H), 5.08 (q, $J = 6.8$ Hz, 1H, 1-H), 1.84 (d, $J = 6.8$ Hz, 3H, 2-H); ^{13}C NMR (67.9 MHz, CDCl_3) δ 147.71 (C-1'), 132.49, 127.30 (C-2', C-3'), 118.41 (CN), 112.04 (C-4'), 57.18 (C-1), 26.29 (C-2); MS (EI, 70 eV) 167 ($M^+ + 2$, 10), 165 (M^+ , 27), 150 ($M^+ - \text{Me}$, 13), 130 ($M^+ - \text{Cl}$, 100), 77 (Ph, 7); HRMS (EI, 70 eV) calculated for ($\text{C}_9\text{H}_8\text{NCl}$) 165.0345 (M^+) found for m/z 165.0354. Analysis; calculated for $\text{C}_9\text{H}_8\text{NCl}$: C, 65.27 H, 4.87 N, 8.46 Cl, 21.41; found: C, 65.30 H, 4.97 N, 8.50 Cl, 20.96.

4-(1-Chloroethyl)benzoic acid ethyl ester (3h). According to the general procedure, this compound was prepared from HSiMe_2Cl (**2b**), *p*-acetylbenzoic acid methyl ester (**1h**), and $\text{In}(\text{OH})_3$ in chloroform to give the product as a colorless liquid after distillation: bp 82 °C/0.11 mmHg; ^1H NMR (270 MHz, CDCl_3) δ 8.04 (d, $J = 8.54$ Hz, 2H, 2'6'-H), 7.49 (d, $J = 8.54$ Hz, 2H, 3'5'-H), 5.11 (q, $J = 6.84$ Hz, 1H, CH), 4.38 (q, $J = 7.08$ Hz, 2H, esterCH₂), 1.85 (d, $J = 6.84$ Hz, 3H, CH₃), 1.39 (t, $J = 7.08$ Hz, 3H, esterCH₃); ^{13}C NMR (67.9 MHz, CDCl_3) δ 166.07 (s, C=O), 147.43 (s, Ar), 130.28 (s, Ar), 129.90 (d, Ar), 126.46 (d, Ar), 61.02 (t, esterCH₂), 57.78 (d, CH), 26.39 (q, CH₃), 14.29 (q, esterCH₃); IR (neat) 1720 cm^{-1} (C=O); MS (EI, 70 eV) 214 ($M^+ + 2$, 6), 212 (M^+ , 17), 177 ($M^+ - \text{Cl}$, 100), 167 ($M^+ - \text{OEt}$, 45), 149 ($M^+ - \text{C}_2\text{H}_4\text{Cl}$, 21), 139 ($M^+ - \text{COOEt}$, 8), 91 (Bn, 4), 77 (Ph, 13); HRMS (EI, 70 eV) calculated for ($\text{C}_{11}\text{H}_{13}\text{O}_2\text{Cl}$) 212.0604 (M^+) found for m/z 212.0601.

4-(1-Chloroethyl)benzoic acid (3i). According to the general procedure, this compound was prepared from HSiMe_2Cl (**2b**), *p*-acetylbenzoic acid (**1i**), and $\text{In}(\text{OH})_3$ in chloroform to give the product as a white solid after recrystallization: ^1H NMR (270 MHz, $\text{DMSO}-d_6$) δ 7.89 (d, $J = 8.37$, 2H, 3'5'-H), 7.45 (d, $J = 8.37$, 2H, 2'6'-H), 4.78 (q, $J = 6.48$, 1H, CH), 1.32 (d, $J = 6.48$, 3H, Me); ^{13}C NMR (67.9 MHz, $\text{DMSO}-d_6$) δ 167.74 (C=O), 148.13 (C-1'), 131.44 (C-4'), 130.59 (C-3'5'), 127.80 (C-2'6'), 59.14 (CH), 26.87 (Me); MS (EI, 70 eV) 186 ($M^+ + 2$, 8), 184 (M^+ , 21), 171 ($M^+ + 2 - \text{Me}$, 2), 169 ($M^+ - \text{Me}$, 7), 149 ($M^+ - \text{Cl}$, 100), 141 ($M^+ + 2 - \text{COOH}$, 5), 139 ($M^+ - \text{COOH}$, 4), 131 ($M^+ - \text{CH}_2\text{CHCl}$, 22); HRMS (EI, 70 eV) calculated for ($\text{C}_9\text{H}_9\text{O}_2\text{Cl}$) 184.0291 (M^+) found for m/z 184.0293.

1-(1-Chloroethyl)-4-methylbenzene (3j). According to the general procedure, this compound was prepared from HSiMe_2Cl (**2b**), *p*-methylacetophenone (**1j**), and $\text{In}(\text{OH})_3$ in chloroform to give the product as a colorless liquid after distillation: bp 35 °C/ 0.3 mmHg; ^1H

NMR (270 MHz, CDCl₃) δ 7.31 (d, J = 8.10 Hz, 2H, 2'6'-H), 7.16 (d, J = 8.10 Hz, 2H, 3'5'-H), 5.08 (t, J = 6.81 Hz, 1H, CH), 2.35 (s, 3H, 4'-Me), 1.84 (d, J = 6.81 Hz, 3H, 2-Me); ¹³C NMR (67.9 MHz, CDCl₃) δ 134.84 (Ar), 138.04 (Ar), 129.22 (C-3'5'), 126.35 (C-2'6'), 58.81 (CH), 26.48 (C-2), 21.17 (C-4'); IR (neat) 809 cm⁻¹ (Ar); MS (EI, 70 eV) 156 (M⁺ + 2, 8), 154 (M⁺, 22), 141 (M⁺ + 2 - Me, 2), 139 (M⁺ - Me, 7), 119 (M⁺ - Cl, 100), 91 (C₇H₇⁺, 30); HRMS (EI, 70 eV) calculated for (C₉H₁₁Cl) 154.0549 (M⁺) found for m/z 154.0511.

β -Chlorobenzenepropanoic acid ethyl ester (3o). According to the general procedure, this compound was prepared from HSiMe₂Cl (**2b**), ethylbenzoylacetate (**1o**), and In(OH)₃ in chloroform to give the product as a colorless liquid after distillation: bp 80 °C/ 0.11 mmHg; ¹H NMR (270 MHz, CDCl₃) δ 7.43-7.31 (m, 5H, aroma), 5.35 (dd, J = 5.81 Hz, 8.91 Hz, 1H, 3-H), 4.16 (q, J = 6.83 Hz, 2H, 1'-H), 3.17 (dd, J = 8.91 Hz, 15.66 Hz, 1H, 2-H^A), 3.02 (dd, J = 5.81 Hz, 15.66 Hz, 3H, 2-H^B), 1.23 (t, J = 6.83 Hz, 3H, 2'-H); ¹³C NMR (67.9 MHz, CDCl₃) δ 169.52 (s, C=O), 140.24 (s, *ipso*-Ph), 128.75 (d, Ph), 128.68 (d, Ph), 126.89 (d, Ph), 61.00 (t, C-1'), 58.08 (d, C-3), 44.87 (t, C-2), 14.08 (q, C-2'); IR (neat) 1740 cm⁻¹ (C=O); MS (EI, 70 eV) 214 (M⁺ + 2, 20), 212 (M⁺, 57), 183 (M⁺ - C₂H₅, 37), 167 (M⁺ - OEt, 19), 91 (Bn, 11), 77 (Ph, 29); HRMS (EI, 70 eV) calculated for (C₁₁H₁₃O₂Cl) 212.0604 (M⁺) found for m/z 212.0613.

1-(2-Bromo-1-chloroethyl)-4-chlorobenzene (3p). According to the general procedure, this compound was prepared from HSiMe₂Cl (**2b**), *p*-chlorophenacyl bromide (**1p**), and In(OH)₃ in chloroform to give the product as a colorless liquid after distillation: bp 70 °C/ 0.11 mmHg; ¹H NMR (270 MHz, CDCl₃) δ 7.41-7.24 (m, 4H, aroma), 5.02 (dd, J = 5.94 Hz, 9.18 Hz, 1H, 1-H), 3.89 (dd, J = 5.94 Hz, 10.26 Hz, 1H, 2-H^A), 3.77 (dd, J = 9.18 Hz, 10.26 Hz, 1H, 2-H^B); ¹³C NMR (67.9 MHz, CDCl₃) δ 136.84 (*para*-Ph), 135.02 (*ipso*-Ph), 129.01 (*meta*-Ph), 128.74 (*ortho*-Ph), 60.19 (C-1), 35.52 (C-2); MS (EI, 70 eV) 258 (M⁺ + 6, 2), 256 (M⁺ + 4, 16), 254 (M⁺ + 2, 33), 252 (M⁺, 20), 217 (M⁺ - Cl, 71), 173 (M⁺ - Br, 6), 159 (M⁺ - CH₂Br, 93), 138 (M⁺ - Cl - Br, 100), 77 (Ph, 18); HRMS (EI, 70 eV) calculated for (C₈H₇Cl₂Br) 251.9108 (M⁺) found for m/z 251.9126, 251.9097. Analysis; calculated for C₈H₇Cl₂Br: C, 37.84 H, 2.78 Cl, 31.46 Br, 27.92 found: C, 37.93 H, 2.82.

(1-Chloro-2-methoxyethyl)benzene (3q). According to the general procedure, this compound was prepared from HSiMe₂Cl (**2b**), 2-methoxyacetophenone (**1q**), and In(OH)₃ in chloroform to give the product as a colorless liquid after distillation: bp 109 °C/ 31 mmHg; ¹H NMR (270 MHz, CDCl₃) δ 7.44-7.33 (m, 5H, aroma), 5.01 (dd, J = 7.32 Hz, 5.86 Hz, 1H, 1-H), 3.83 (dd, J = 7.32 Hz, 10.75 Hz, 1H, 2-H^A), 3.77 (dd, J = 5.86 Hz, 10.75 Hz, 1H, 2-H^B), 3.41 (s, 3H, CH₃); ¹³C NMR (67.9 MHz, CDCl₃) δ 138.58 (*ipso*-Ph), 128.65 (Ph), 127.38 (Ph), 97.20 (C-2), 60.79, 59.08; IR (neat) 1126 (C-O-C); MS (EI, 70 eV) 172 (M⁺ + 2, 7), 170 (M⁺,

22), 138 ($M^+ - \text{CH}_3\text{OH}$, 10), 125 ($M^+ - \text{CH}_2\text{OCH}_3$, 39), 91 (Bn, 14), 77 (Ph, 7); HRMS (EI, 70 eV) calculated for ($\text{C}_9\text{H}_{11}\text{OCl}$) 170.0498 (M^+) found for m/z 170.0495.

(3-Chloro-1-butynyl)benzene (3r). According to the general procedure, this compound was prepared from HSiMe_2Cl (**2b**), 4-phenyl-3-butyn-2-one (**1r**), and $\text{In}(\text{OH})_3$ in chloroform to give the product as a colorless liquid after distillation: bp 60 °C/ 0.11 mmHg; ^1H NMR (270 MHz, CDCl_3) δ 7.45-7.29 (m, 5H, aroma), 4.89 (q, $J = 6.75$ Hz, 1H, CH), 1.84 (d, $J = 6.75$ Hz, 3H, Me); ^{13}C NMR (67.9 MHz, CDCl_3) δ 131.76 (*ortho*-Ph), 128.72 (*para*-Ph), 128.28 (*meta*-Ph), 122.06 (*ipso*-Ph), 88.29 (C-2), 85.28 (C-1), 44.05 (CH), 26.59 (Me); MS (EI, 70 eV) 166 ($M^+ + 2$, 10), 164 (M^+ , 28), 151 ($M^+ + 2 - \text{Me}$, 2), 149 ($M^+ - \text{Me}$, 5), 129 ($M^+ - \text{Cl}$, 100), 77 (Ph^+ , 8); HRMS (EI, 70 eV) calculated for ($\text{C}_{10}\text{H}_9\text{Cl}$) 164.0393 (M^+) found for m/z 164.0401.

(3-Iodobutyl)benzene (8). To a mixture of the $\text{In}(\text{OH})_3$ (0.1 mmol), LiI (3.0 mmol), and chlorodimethylsilane (**2b**, 2.4 mmol) in chloroform (4.0 mL) was added benzylacetone (**1m**, 2.0 mmol) under nitrogen. The reaction mixture was stirred for 11 h. The resulting mixture was poured into EtOAc (30 mL) and washed by aqueous NaHCO_3 (30 mL). The organic layer was dried over MgSO_4 and concentrated *in vacuo*. The product **8** was obtained as a pale purple liquid by silica gel column chromatography followed by distillation: bp 70 °C/ 0.11 mmHg; ^1H NMR (270 MHz, CDCl_3) δ 7.31-7.16 (m, 5H, aroma), 4.09 (ddq, $J = 4.39, 9.28, 6.83$ Hz, 1H, CH), 2.83 (ddd, $J = 5.37, 9.28, 13.67$ Hz, 1H, 1- H^{A}), 2.68 (ddd, $J = 5.37, 8.79, 13.67$ Hz, 1H, 1- H^{B}), 2.14 (ddt, $J = 9.28, 18.06, 5.37$ Hz, 1H, 2- H^{A}), 1.93 (d, $J = 6.83$ Hz, 3H, Me), 1.84 (dddd, $J = 4.39, 8.79, 9.28, 18.06$ Hz, 1H, 2- H^{B}); ^{13}C NMR (67.9 MHz, CDCl_3) δ 140.66 (*ipso*-Ph), 128.45 (*meta*-Ph), 128.42 (*ortho*-Ph), 126.05 (*para*-Ph), 44.32 (C-2), 35.78 (C-1), 29.63, 28.95; IR (neat) 1604 (Ph), 748 (Ph), 702 cm^{-1} (Ph); MS (EI, 70 eV) 260 (M^+ , 8), 133 ($M^+ - \text{I}$, 54), 91 (C_7H_7^+ , 100), 77 (Ph^+ , 2); HRMS (EI, 70 eV) calculated for ($\text{C}_{10}\text{H}_{13}\text{I}$) 260.0062 (M^+) found for m/z 260.0079. Analysis; calculated for $\text{C}_{10}\text{H}_{13}\text{I}$: C, 46.17 H, 5.04 I, 48.79 found: C, 45.92 H, 5.17 I, 48.58.

2-(4-Nitro-phenyl)-2-chloro-pent-4-ene (9b). To a mixture of the $\text{In}(\text{OH})_3$ (0.1 mmol) and *p*-nitrobenzacetophenone (**1b**, 2.0 mmol) in chloroform (4.0 mL) was added allylchlorodimethylsilane (**2d**, 2.4 mmol) under nitrogen. The reaction mixture was stirred for 1 h at 0 °C. The resulting mixture was poured into EtOAc (30 mL) and washed by aqueous NaHCO_3 (30 mL). The organic layer was dried over MgSO_4 and concentrated *in vacuo*. The product **9b** was obtained as a pale yellow liquid by silica gel column chromatography followed by distillation: bp 102 °C/ 0.3 mmHg; ^1H NMR (270 MHz, CDCl_3) δ 8.20 (d, $J = 9.16$ Hz, 2H, 3'5'-H), 7.71 (d, $J = 9.16$ Hz, 2H, 2'6'-H), 5.68 (dddd, $J = 6.85, 13.34, 14.16, 14.16$ Hz, 1H, 4-H), 5.13 (dd, $J = 1.80, 6.85$ Hz, 1H, 5- H^{trans}), 5.08 (dd, $J = 1.80, 13.34$ Hz, 1H, 5- H^{cis}), 2.94 (dd, $J = 6.59, 14.16$ Hz, 1H, 3- H^{A}), 2.87 (dd, $J = 6.59, 14.16$ Hz, 1H, 3- H^{B}), 1.98 (s, 3H, 1-H); ^{13}C NMR (67.9 MHz, CDCl_3) δ 151.65 (Ar), 146.95 (Ar), 132.14 (C-4), 127.21 (C-2'6'), 123.29 (C-

3'5'), 119.81 (C-5), 70.86 (C-2), 50.58 (C-3), 30.99 (C-1); IR (neat) 1604 (Ar), 1523 (NO₂), 1350 (NO₂), 856 cm⁻¹ (C-Cl); MS (EI, 70 eV) 227 (M⁺ + 2, trace), 225 (M⁺, 5), 186 (M⁺ + 2 – allyl, 43), 184 (M⁺ – allyl, 100); HRMS (EI, 70 eV) calculated for (C₁₁H₁₂ClNO₂) 225.0557 (M⁺) found for *m/z* 225.0543.

1-(1-Chlorobut-3-enyl)-4-nitrobenzene (9s). To a mixture of In(OH)₃ (0.1 mmol) and *p*-nitrobenzaldehyde (**1s**, 2.0 mmol) in chloroform (4.0 mL) was added allylchlorodimethylsilane (**2d**, 2.4 mmol) under nitrogen. The reaction mixture was stirred for 1.5 h at 60 °C. The resulting mixture was poured into EtOAc (30 mL) and washed by aqueous NaHCO₃ (30 mL). The organic layer was dried over MgSO₄ and concentrated *in vacuo*. The product **9s** was obtained as a pale yellow liquid by silica gel column chromatography followed by distillation: bp 105 °C/0.3 mmHg; ¹H NMR (270 MHz, CDCl₃) δ 8.27 (d, *J* = 8.92 Hz, 2H, 3'5'-H), 7.57 (d, *J* = 8.92 Hz, 2H, 2'6'-H), 5.73 (dddd, *J* = 6.84, 10.26, 11.35, 18.19 Hz, 1H, 3-H), 5.13 (dd, *J* = 1.46, 10.26 Hz, 1H, 4-H^{cis}) 5.12 (dd, *J* = 1.46, 18.19 Hz, 1H, 4-H^{trans}), 4.96 (dd, *J* = 7.33, 7.33 Hz, 1H, 1-H), 2.93-2.74 (m, 2H, 2-H); ¹³C NMR (67.9 MHz, CDCl₃) δ 147.92 (Ar), 147.51 (Ar), 132.60 (C-3), 128.00 (C-2'6'), 123.76 (C-3'5'), 119.17 (C-4), 60.74 (C-1), 43.88 (C-2); IR (neat) 1643 (C=C), 1604 (Ar), 1527 (NO₂), 1349 cm⁻¹ (NO₂); MS (EI, 70 eV) 213 (M⁺ + 2, 11), 211 (M⁺, 31), 172 (M⁺ + 2 – allyl, 38), 170 (M⁺ – allyl, 100); HRMS (EI, 70 eV) calculated for (C₁₀H₁₀ClNO₂) 211.0400 (M⁺) found for *m/z* 211.0407. Analysis; calculated for C₁₀H₁₀ClNO₂: C, 56.75 H, 4.75 N, 6.62 O, 15.12 Cl, 16.75 found: C, 56.65 H, 4.81 N, 6.64 Cl, 16.48.