

Vilsmeier–Haack reagent-promoted formyloxylation of α -chloro-*N*-arylacetamides by formamide

Jiann-Jyh Huang,^{a,b} Shi-Han Lu,^c Yu Hsuan Chung,^{a,b} and Fung Fuh Wong*^c

^a*Department of Applied Chemistry, National Chiayi University, No. 300, Syuefu Rd., Chiayi City 60004, Taiwan*

^b*Center of Energy Research & Sensor Technology, National Chiayi University, No. 300, Syuefu Rd., Chiayi City 60004, Taiwan*

^c*School of Pharmacy, China Medical University, No. 91, Hsueh-Shih Rd., Taichung 40402, Taiwan*

*Corresponding Author. Tel.: +886 4 2205 3366 ext. 5603; Fax: +886 4 2207 8083.

E-mail address: wongfungfuh@yahoo.com.tw, ffwong@mail.cmu.edu.tw (F. F. Wong)

Keywords: Vilsmeier–Haack reagent, formyloxylation, formate ester, formamide, phosphorous bromide, α -formyloxy-*N*-arylacetamide

All chemicals were reagent grade and used as purchased. All reactions were carried out under argon or nitrogen atmosphere and monitored by TLC. Flash column chromatography was carried out on silica gel (230–400 mesh). Analytical thin-layer chromatography (TLC) was performed on precoated plates (silica gel 60 F-254) purchased from Merck Inc. Mixtures of ethyl acetate and hexanes were used as eluants. Infrared (IR) spectra were measured on a Bomem Michelson Series FT-IR spectrometer. The wavenumbers reported are referenced to the polystyrene absorption at 1601 cm⁻¹. Absorption intensities are recorded by the following abbreviations: s, strong; m, medium; w, weak. Proton NMR spectra were obtained on a Bruker (200 MHz or 500 MHz) spectrometer by use of CDCl₃ as solvent. Multiplicities are recorded by the following abbreviations: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; J, coupling constant (Hz). Carbon-13 NMR spectra were obtained on a

Bruker (50 MHz or 125 MHz) spectrometer by used of CDCl_3 as solvent. Carbon-13 chemical shifts are referenced to the center of the CDCl_3 triplet (δ 77.0 ppm). High-resolution mass spectra were obtained from a JEOL JMS-HX110 mass spectrometer.

General procedure for the formyloxylation of α -chloro-*N*-arylacetamides 1, 6a–n, 8a, 8b, and 8c with formamide in the presence of PBr_3 . α -Chloro-*N*-arylacetamides 1, 6a–n, 8a, 8b, and 8c (~1.0 mmol, 1.0 equiv) were dissolved in formamide (2.0 mL) and added with PBr_3 (3.0 equiv). The reaction mixture was heated at 80–90 °C for 4.0 h. The solution was added with saturate aqueous NaHCO_3 (15 mL) and extracted with CH_2Cl_2 (15 mL × 2). The combined organic layers were washed with saturated aqueous NaHCO_3 (15 mL), dried over MgSO_4 , filtered, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel to give the corresponding α -formyloxylated products 4, 7a–n, 9a, and 9c in 70–96% yields.

2-Oxo-2-(phenylamino)ethyl formate (4). Yield: 96%; yellow liquid; ^1H NMR (CDCl_3 , 200 MHz) δ 4.72 (s, 2 H, CH_2), 7.11–7.15 (m, 1 H, ArH), 7.25–7.33 (dd, J = 8.2, 7.8 Hz, 2 H, ArH), 7.51 (d, J = 8.2 Hz, 2 H, ArH), 8.02 (br, 1 H, NH), 8.14 (s, 1 H, O=C–H); ^{13}C NMR (CDCl_3 , 50 MHz) δ 62.36, 120.19, 125.15, 129.16, 137.04, 158.80 (NC=O), 164.11 (HC=O); IR (KBr) 3298 (br, NH), 3061, 1730 (s, C=O), 1680 (s, C=O), 1163, 759 cm^{-1} ; EIMS m/z 179 (M^+ , 43), 120 (17), 93 (100), 92 (17), 77 (24), 65 (20), 51 (6); HRMS Calcd for $\text{C}_9\text{H}_9\text{NO}_3$: 179.0582; Found: 179.0583.

2-[(2-Fluorophenyl)amino]-2-oxoethyl formate (7a). Yield: 74%; white solids; mp 43–45 °C; ^1H NMR (CDCl_3 , 200 MHz) δ 4.79 (s, 2 H, CH_2), 7.06–7.14 (m, 4 H, ArH), 8.20 (s, 1 H, O=C–H), 8.29 (br, 1 H, NH); ^{13}C NMR (CDCl_3 , 50 MHz) δ 62.31, 114.81, 115.18, 121.91, 124.75, 125.20, 125.33, 150.88, 154.97, 158.87 (NC=O), 164.29 (HC=O); IR (KBr) 3275 (br, NH), 1732 (s, C=O), 1685 (s, C=O), 1458, 1161 (C–O), 756 cm^{-1} ; EIMS m/z 197 (M^+ , 26), 111 (100), 83 (15), 110 (10), 57 (5);

HRMS Calcd for C₉H₈FNO₃: 197.0488; Found: 197.0490.

2-[(3-Fluorophenyl)amino]-2-oxoethyl formate (7b). Yield: 84%; white solids; mp 46–48 °C; ¹H NMR (CDCl₃, 200 MHz) δ 4.75 (s, 2 H, CH₂), 6.82–6.86 (m, 1 H, ArH), 7.13–7.28 (m, 2 H, ArH), 7.44 (dd, *J* = 10.7, 3.5 Hz, 1 H, ArH), 8.02 (br, 1 H, NH), 8.17 (s, 1 H, O=C–H); ¹³C NMR (CDCl₃, 50 MHz) δ 62.17, 107.44, 107.96, 111.64, 112.06, 115.40, 130.13, 130.31, 137.89, 138.10, 158.94 (NC=O), 160.41, 164.46 (HC=O), 165.29; IR (KBr) 3290 (br, NH), 1732 (s, C=O), 1681 (s, C=O), 1543, 1157 (C–O), 775 cm⁻¹; EIMS *m/z* 197 (M⁺, 40), 138 (12), 111 (100), 110 (16), 95 (16), 84 (11), 83 (19), 57 (8); HRMS Calcd for C₉H₈FNO₃: 197.0488; Found: 197.0485.

2-[(4-Fluorophenyl)amino]-2-oxoethyl formate (7c). Yield: 88%; white solids; mp 49–51 °C; ¹H NMR (CDCl₃, 200 MHz) δ 4.76 (s, 2 H, CH₂), 6.98–7.06 (m, 2 H, ArH), 7.24–7.81 (m, 2 H, ArH), 7.81 (br, 1 H, NH), 8.19 (s, 1 H, O=C–H); ¹³C NMR (CDCl₃, 125 MHz) δ 62.31, 115.80, 115.98, 122.06, 122.12, 132.51, 158.75, 158.89 (NC=O), 160.58, 164.16 (HC=O); IR (KBr) 3336 (br, NH), 2924, 1735 (s, C=O), 1681 (s, C=O), 1512, 1157 (C–O) cm⁻¹; EIMS *m/z* 197 (M⁺, 40), 138 (12), 111 (100), 110 (16), 95 (16), 84 (11), 83 (19), 57 (8); HRMS Calcd for C₉H₈FNO₃: 197.0488; Found: 197.0492.

2-[(2-Bromophenyl)amino]-2-oxoethyl formate (7d). Yield: 71%; white solids; mp 49–52 °C; ¹H NMR (CDCl₃, 200 MHz) δ 4.80 (s, 2 H, CH₂), 6.99 (dd, *J* = 7.8, 7.2 Hz, 1 H, ArH), 7.30 (dd, *J* = 7.8, 7.2 Hz, 1 H, ArH), 7.53 (dd, *J* = 7.7, 6.0 Hz, 1 H, ArH), 8.22 (s, 1 H, O=C–H), 8.32 (dd, *J* = 7.7, 6.0 Hz, 1 H, ArH), 8.43 (br, 1 H, NH); ¹³C NMR (CDCl₃, 50 MHz) δ 62.30, 113.60, 121.84, 125.89, 128.49, 132.32, 134.49, 158.76 (NC=O), 164.25 (HC=O); IR (KBr) 3375 (br, NH), 1735 (s, C=O), 1531 (s, C=O), 1438, 1157 (C–O), 582 cm⁻¹; EIMS *m/z* 259 (M⁺ + 2, 13), 257 (M⁺, 13), 173 (57), 171 (59); HRMS Calcd for C₉H₈BrNO₃: 256.9688; Found: 256.9686.

2-[(3-Bromophenyl)amino]-2-oxoethyl formate (7e). Yield: 78%; yellow liquid; ¹H

NMR (CDCl_3 , 200 MHz) δ 4.75 (s, 2 H, CH_2), 7.13–7.29 (m, 1 H, ArH), 7.41 (dd, J = 9.8, 7.5 Hz, 2 H, ArH), 7.77 (s, 1 H, ArH), 8.17 (s, 1 H, O=C–H); ^{13}C NMR (CDCl_3 , 50 MHz) δ 62.21, 118.59, 122.67, 123.06, 128.12, 130.41, 137.72, 158.81 (NC=O), 164.33 (HC=O); IR (KBr) 3305 (br, NH), 1732 (s, C=O), 1682 (s, C=O), 1423, 1161 (C–O), 590 cm^{-1} ; EIMS m/z 259 ($\text{M}^+ + 2$, 8), 257 (M^+ , 8), 231 (57), 229 (58), 200 (20), 198 (20), 173 (92), 171 (100); HRMS Calcd for $\text{C}_9\text{H}_8\text{BrNO}_3$: 256.9688; Found: 256.9686.

2-[(4-Bromophenyl)amino]-2-oxoethyl formate (7f). Yield: 89%; white solids; mp 47–50 °C; ^1H NMR (CDCl_3 , 200 MHz) δ 4.73 (s, 2 H, CH_2), 7.37–7.44 (m, 4 H, ArH), 8.03 (br, 1 H, NH) 8.15 (s, 1 H, O=C–H); ^{13}C NMR (CDCl_3 , 50 MHz) δ 62.14, 117.76, 121.71 (2 \times CH), 132.04 (2 \times CH), 135.57, 158.95 (NC=O), 164.38 (HC=O); IR (KBr) 3433 (br, NH), 1732 (s, C=O), 1689 (s, C=O), 1261, 1161 (C–O), 574 cm^{-1} ; EIMS m/z 259 ($\text{M}^+ + 2$, 16), 257 (M^+ , 16), 191 (100), 178 (25), 173 (33), 171 (33), 152 (11), 91 (17); HRMS Calcd for $\text{C}_9\text{H}_8\text{BrNO}_3$: 256.9688; Found: 256.9683.

2-Oxo-2-{[2-(trifluoromethyl)phenyl]amino}ethyl formate (7g). Yield: 70%; white solids; mp 47–49 °C; ^1H NMR (CDCl_3 , 200 MHz) δ 4.80 (s, 2 H, CH_2), 7.23–7.26 (m, 1 H, ArH), 7.57–7.63 (m, 2 H, ArH), 8.19 (s, 1 H, O=C–H), 8.20–8.24 (m, 1 H, ArH), 8.25 (br, 1 H, NH); ^{13}C NMR (CDCl_3 , 50 MHz) δ 62.19, 119.98, 120.20, 120.58, 120.87, 121.20, 124.08, 125.14, 126.27, 126.63, 133.08, 133.93, 158.62 (NC=O), 164.57 (HC=O); IR (KBr) 3433 (br, NH), 1712 (s, C=O), 1670 (s, C=O), 1319, 1114 (C–O), 767 cm^{-1} ; EIMS m/z 247 (M^+ , 32), 168 (41), 161 (100), 141 (32), 114 (11); HRMS Calcd for $\text{C}_{10}\text{H}_8\text{F}_3\text{NO}_3$: 247.0456; Found: 247.0452.

2-Oxo-2-{[3-(trifluoromethyl)phenyl]amino}ethyl formate (7h). Yield: 78%; yellow liquid; ^1H NMR (CDCl_3 , 200 MHz) δ 4.79 (s, 2 H, CH_2), 7.38–7.52 (m, 2 H, ArH), 7.78–7.84 (m, 2 H, ArH), 7.98 (br, 1 H, NH); 8.20 (s, 1 H, O=C–H); ^{13}C NMR (CDCl_3 , 50 MHz) δ 62.20, 116.79, 116.86, 121.63, 121.70, 123.18, 129.73, 130.73,

131.53, 131.82, 132.58, 132.83, 137.04, 158.78 (NC=O), 164.50 (HC=O); IR (KBr) 3425 (br, NH), 1728 (s, C=O), 1689 (s, C=O), 1161 (C–O), 1122, 698 cm⁻¹; EIMS *m/z* 247 (M⁺, 32), 161 (100), 160 (13), 145 (15), 87 (22), 55 (37), 54 (15); HRMS Calcd for C₁₀H₈F₃NO₃: 247.0456; Found: 247.0455.

2-Oxo-2-{[4-(trifluoromethyl)phenyl]amino}ethyl formate (7i). Yield: 91%; white solids; mp 50–52 °C; ¹H NMR (CDCl₃, 500 MHz) δ 4.79 (s, 2 H, CH₂), 7.59 (d, *J* = 8.5 Hz, 2 H, ArH), 7.67 (d, *J* = 8.5 Hz, 2 H, ArH), 8.20 (s, 1 H, O=C–H); ¹³C NMR (CDCl₃, 125 MHz) δ 62.32, 119.77 (2 × CH + CH), 121.43, 122.27, 122.63, 123.83, 123.07, 126.43, 126.46, 139.60, 158.67 (NC=O), 164.44 (HC=O); IR (KBr) 3441 (br, NH), 1743 (s, C=O), 1678 (s, C=O), 1539, 1165 (C–O), 740 cm⁻¹; EIMS *m/z* 247 (M⁺, 34), 161 (100), 145 (21), 142 (12), 111 (7), 87 (13); HRMS Calcd for C₁₀H₈F₃NO₃: 247.0456; Found: 247.0461.

2-Oxo-2-(*p*-tolylamino)ethyl formate (7j). Yield: 89%; white solids; mp 39–41 °C; ¹H NMR (CDCl₃, 200 MHz) δ 2.30 (s, 3 H, CH₃), 4.75 (s, 2 H, CH₂), 7.13 (d, *J* = 8.3 Hz, 2 H, ArH), 7.40 (d, *J* = 8.3 Hz, 2 H, ArH), 7.77 (br, 1 H, NH), 8.18 (s, 1 H, O=C–H); ¹³C NMR (CDCl₃, 50 MHz) δ 20.88, 62.30, 119.87, 120.30 (2 × CH), 129.62 (2 × CH), 134.92, 158.89 (NC=O), 164.14 (HC=O); IR (KBr) 3429 (br, NH), 1732 (s, C=O), 1678 (s, C=O), 1265, 1165 (C–O) cm⁻¹; EIMS *m/z* 193 (M⁺, 26), 165 (18), 134 (12), 107 (100), 106 (76), 91 (23), 77 (39), 65 (18); HRMS Calcd for C₁₀H₁₁NO₃: 193.0739; Found: 193.0735.

2-[(4-Hydroxyphenyl)amino]-2-oxoethyl formate (7k). Yield: 87%; yellow liquid; ¹H NMR (CDCl₃, 200 MHz) δ 4.77 (s, 2 H, CH₂), 7.09 (d, *J* = 8.8 Hz, 2 H, ArH), 7.55 (d, *J* = 8.8 Hz, 2 H, ArH), 7.84 (br, 1 H, NH), 8.19 (s, 1 H, O=C–H), 8.27 (s, 1 H, OH); ¹³C NMR (CDCl₃, 50 MHz) δ 62.29, 121.33 (2 × CH), 121.85 (2 × CH), 134.64, 158.77 (NC=O), 159.12, 164.22 (HC=O); IR (KBr) 3348.42 (br, NH + OH), 2920, 1728 (s, C=O), 1689 (s, C=O), 1192, 1165 (C–O) cm⁻¹; EIMS *m/z* 195 (M⁺, 40), 109

(100), 108 (33), 81 (11); HRMS Calcd for C₉H₉NO₄: 195.0532; Found: 195.0531.

2-[(4-Methoxyphenyl)amino]-2-oxoethyl formate (7l). Yield: 91%; brown solids; mp 47–48 °C; ¹H NMR (CDCl₃, 200 MHz) δ 3.77 (s, 3 H, CH₃), 4.75 (s, 2 H, CH₂), 6.86 (d, *J* = 9.0 Hz, 2 H, ArH), 7.42 (d, *J* = 9.0 Hz, 2 H, ArH), 7.78 (br, 1 H, NH), 8.18 (s, 1 H, O=C–H); ¹³C NMR (CDCl₃, 125 MHz) δ 55.47, 62.33, 114.28 (2 × CH), 122.11 (2 × CH), 129.50, 157.00, 158.85 (NC=O), 164.04 (HC=O); IR (KBr) 3309 (br, NH), 1734 (s, C=O), 1668 (s, C=O), 1247, 1149 (C–O), 835 cm⁻¹; EIMS *m/z* 209 (M⁺, 64), 123 (49), 122 (35), 113 (24), 108 (29), 91 (100), 77 (20); HRMS Calcd for C₁₀H₁₁NO₄: 209.0688; Found: 209.0687.

2-[(4-Cyanophenyl)amino]-2-oxoethyl formate (7m). Yield: 87%; white solids; mp 50–52 °C; ¹H NMR (CDCl₃, 200MHz) δ 4.79 (s, 2 H, CH₂), 7.62 (d, *J* = 9.0 Hz, 2 H, ArH), 7.70 (d, *J* = 9.0 Hz, 2 H, ArH), 8.04 (br, 1 H, NH), 8.20 (s, 1 H, O=C–H); ¹³C NMR (CDCl₃, 50 MHz) δ 62.26, 108.15, 118.52, 119.93 (2 × CH), 133.40 (2 × CH), 140.55, 158.67 (NC=O), 164.57 (HC=O); IR (KBr) 3294 (br, NH), 2225 (s, CN) 1732 (s, C=O), 1701 (s, C=O), 1315, 1161 (C–O) cm⁻¹; EIMS *m/z* 204 (M⁺, 28), 119 (12), 118 (100), 117 (14), 91 (16), 90 (17); HRMS Calcd for C₁₀H₈N₂O₃: 204.0535; Found: 204.0537.

2-[(2,5-Dimethoxyphenyl)amino]-2-oxoethyl formate (7n). Yield: 76%; white liquid; ¹H NMR (CDCl₃, 400 MHz) δ 3.72 (s, 3 H, CH₃), 3.80 (s, 3 H, CH₃), 4.73 (s, 2 H, CH₂), 6.56 (dd, *J* = 11.6, 8.8 Hz, 1 H, ArH), 6.76 (d, *J* = 9.2 Hz, 1 H), 8.02 (d, *J* = 2.8 Hz, 1 H, ArH), 8.17 (s, 1 H, O=C–H), 8.43 (br, 1 H, NH); ¹³C NMR (CDCl₃, 100 MHz) δ 55.62 (OCH₃), 56.13 (OCH₃), 62.27, 106.26 (CH), 109.02 (CH), 110.68 (CH), 126.95 (C), 142.18 (C), 153.65 (C), 158.99 (NC=O), 163.90 (HC=O); IR (KBr) 3745 (br, NH), 3251, 1770 (s, C=O), 1666 (s, C=O), 1535, 1219 (C–O) cm⁻¹; EIMS *m/z* 239 (M⁺, 70), 224 (16), 165 (11), 138 (100); HRMS Calcd for C₁₁H₁₃NO₅: 239.0794; Found: 239.0785.

2-(Naphthalen-1-ylamino)-2-oxoethyl formate (9a). Yield: 86%; white solids; mp 47–49 °C; ¹H NMR (CDCl₃, 200 MHz) δ 4.90 (s, 2 H, CH₂), 7.43–7.55 (m, 3 H, ArH), 7.71–7.90 (m, 4 H, ArH), 8.27 (s, 1 H, O=C–H); ¹³C NMR (CDCl₃, 50 MHz) δ 62.75, 120.32, 121.19, 125.69, 126.23, 126.61, 126.68, 128.87, 128.89, 130.87, 134.14, 159.02 (NC=O), 164.89 (HC=O); IR (KBr) 3248 (br, NH), 1726 (s, C=O), 1666 (s, C=O), 1217, 1163 (C–O), 767 cm⁻¹; EIMS *m/z* 229 (M⁺, 55), 179 (22), 143 (100), 115 (57), 93 (52), 77 (20); HRMS Calcd for C₁₃H₁₁NO₃: 229.0739; Found: 229.0734.

2-Oxo-2-(quinolin-8-ylamino)ethyl formate (9b). Yield: 87%; white solids; mp 46–48 °C; ¹H NMR (CDCl₃, 200 MHz) δ 4.90 (s, 2 H, CH₂), 7.47–7.56 (m, 3 H, ArH), 8.14 (d, *J* = 8.3 Hz, 1 H, ArH), 8.32 (s, 1 H, O=C–H), 8.68–8.82 (m, 2 H, ArH), 9.76 (br, 1 H, NH); ¹³C NMR (CDCl₃, 50 MHz) δ 62.61, 117.01, 121.78, 122.46, 127.29, 127.99, 136.41, 138.55, 148.56, 148.58, 159.30 (NC=O), 164.59 (HC=O); IR (KBr) 3331 (NH), 1734 (s, C=O), 1683 (s, C=O), 1153 (C–O), 788 cm⁻¹; EIMS *m/z* 230 (M⁺, 10), 172 (17), 171 (100), 144 (46), 135 (23), 91 (12); HRMS calcd for C₁₂H₁₀N₂O₃: 230.0691; Found: 230.0695.

2-Oxo-2-(Thiazolylamino)ethyl formate (9c). Yield: 71%; yellow liquid; ¹H NMR (CDCl₃, 400 MHz) δ 4.90 (s, 2 H, CH₂), 7.03 (d, *J* = 3.6 Hz, 1 H), 7.47 (d, *J* = 3.6 Hz, 1 H), 8.17 (s, 1 H, O=C–H); ¹³C NMR (CDCl₃, 100 MHz) δ 61.50, 114.39 (CH), 130.88 (C), 136.95 (CH), 159.07 (NC=O), 164.02 (HC=O); IR (KBr) 3745 (br, NH), 1728 (s, C=O), 1678 (s, C=O), 1276, 1161 (C–O) cm⁻¹; EIMS *m/z* 186 (M⁺, 20), 127 (10), 100 (100), 91 (17), 73 (9), 58 (22), 55 (13); HRMS Calcd for C₆H₆N₂O₃S: 186.0099; Found: 186.0096.

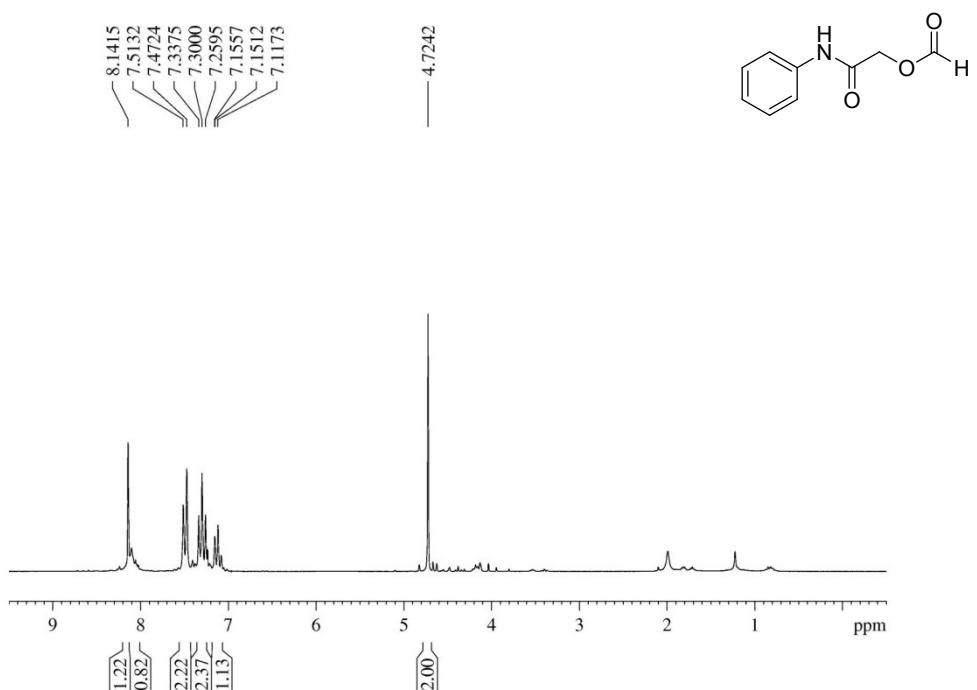


Figure ¹H NMR (CDCl₃, 200 MHz) spectrum of compound 4

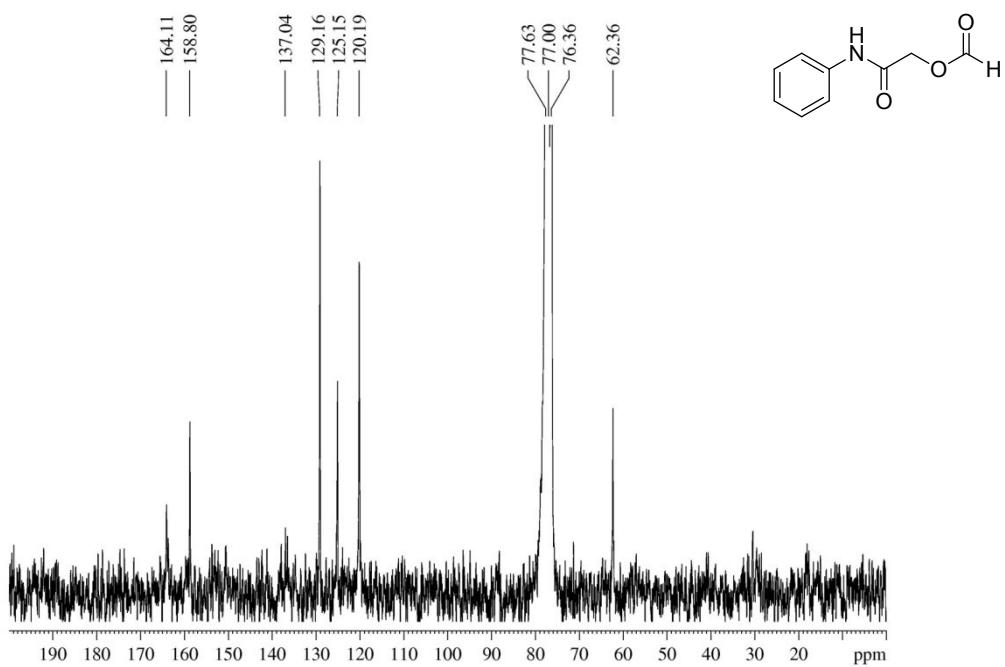


Figure ¹³C NMR (50 MHz, CDCl₃) spectrum of compound 4

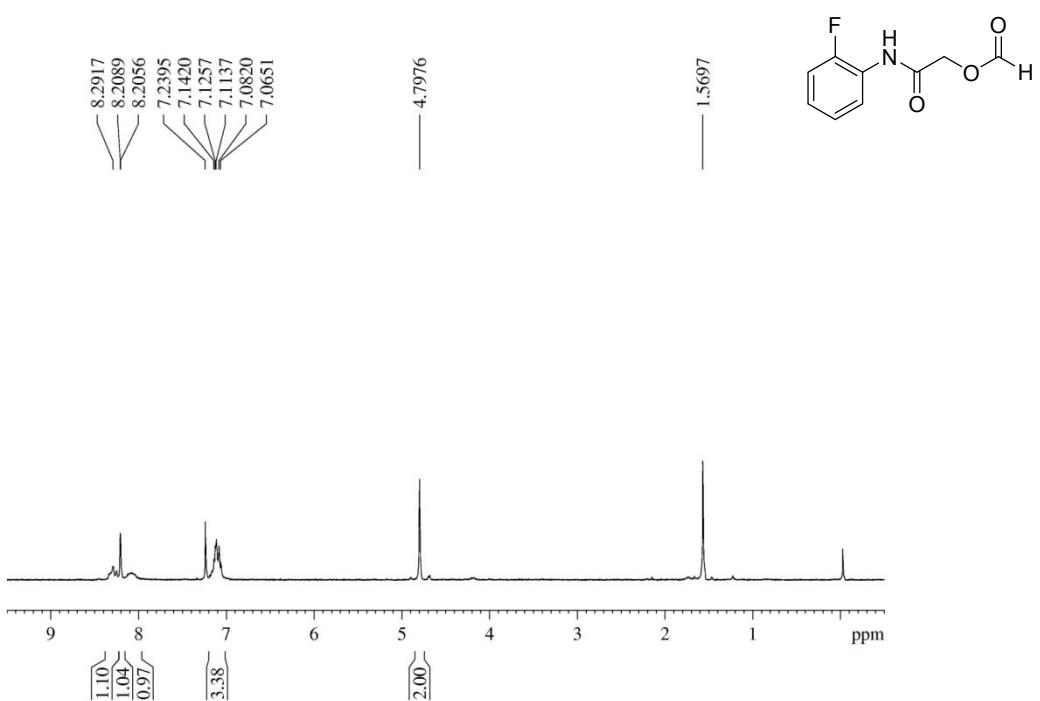


Figure ¹H NMR (CDCl₃, 200 MHz) spectrum of compound 7a

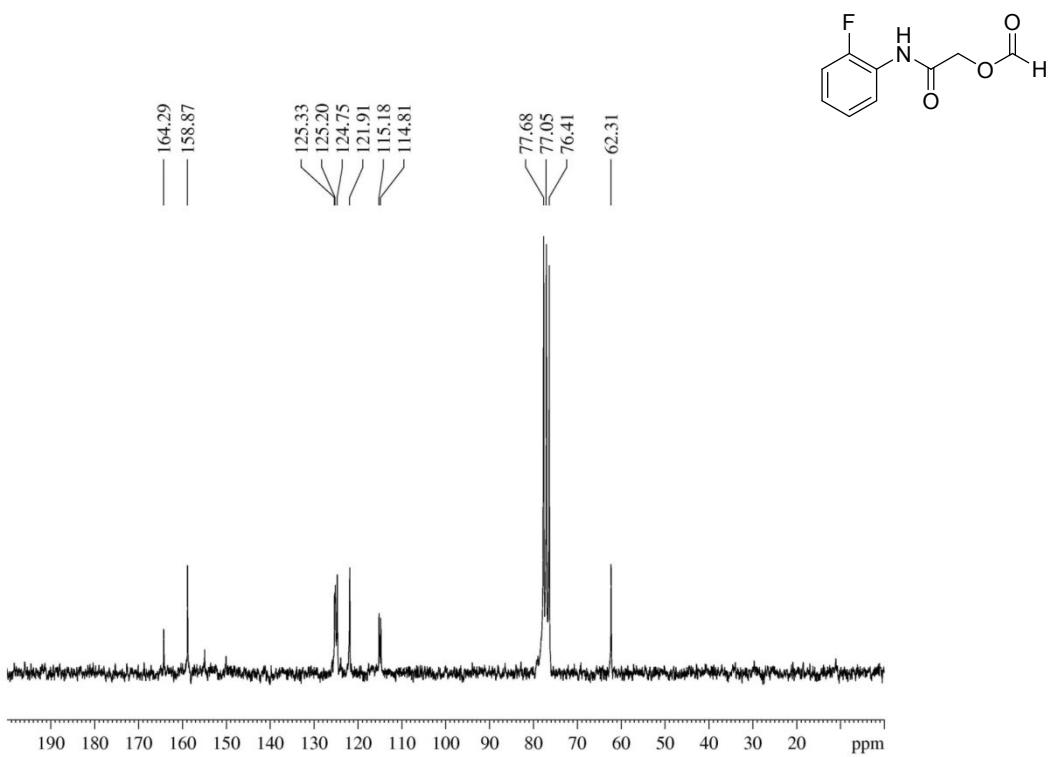


Figure ¹³C NMR (50 MHz, CDCl₃) spectrum of compound 7a

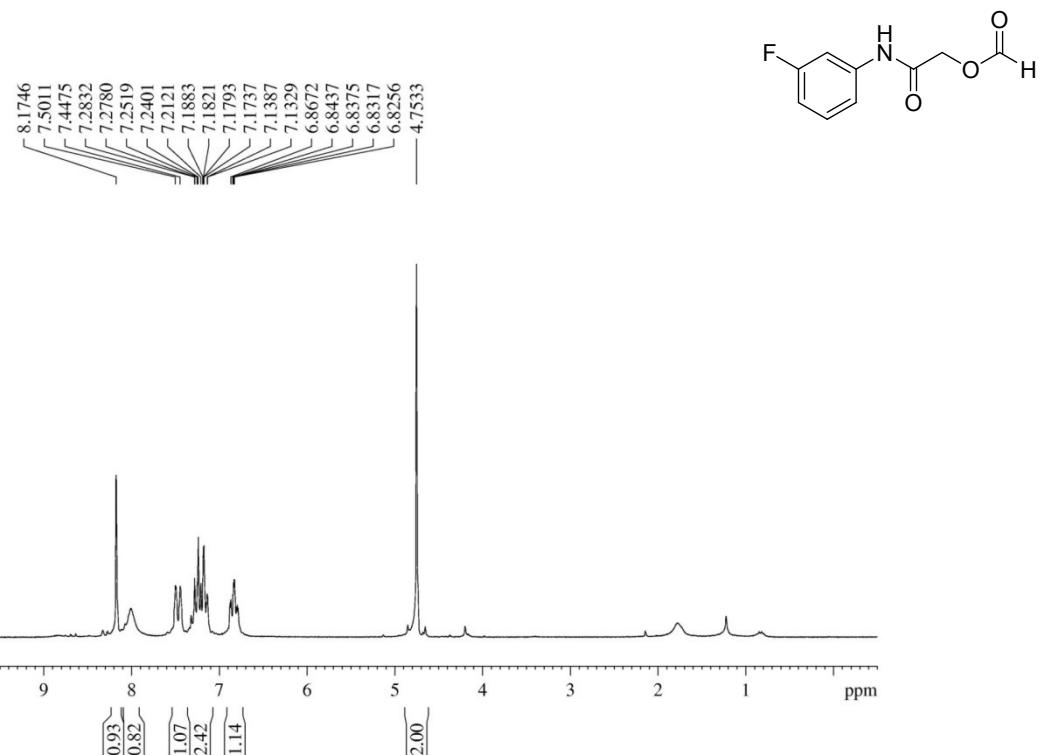


Figure ^1H NMR (CDCl_3 , 200 MHz) spectrum of compound **7b**

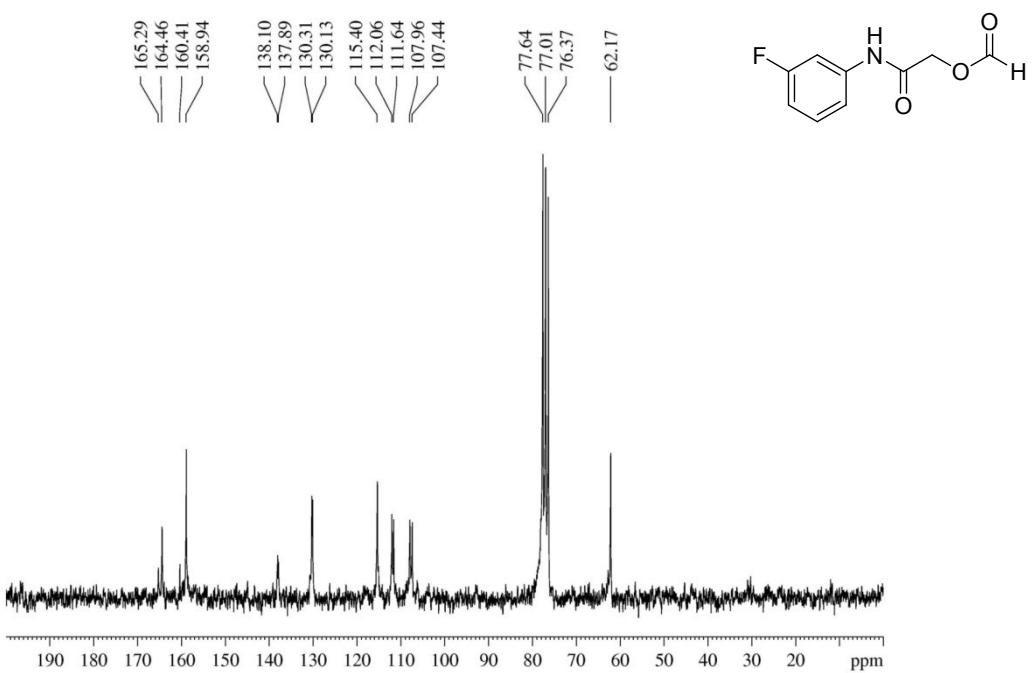


Figure ^{13}C NMR (50 MHz, CDCl_3) spectrum of compound **7b**

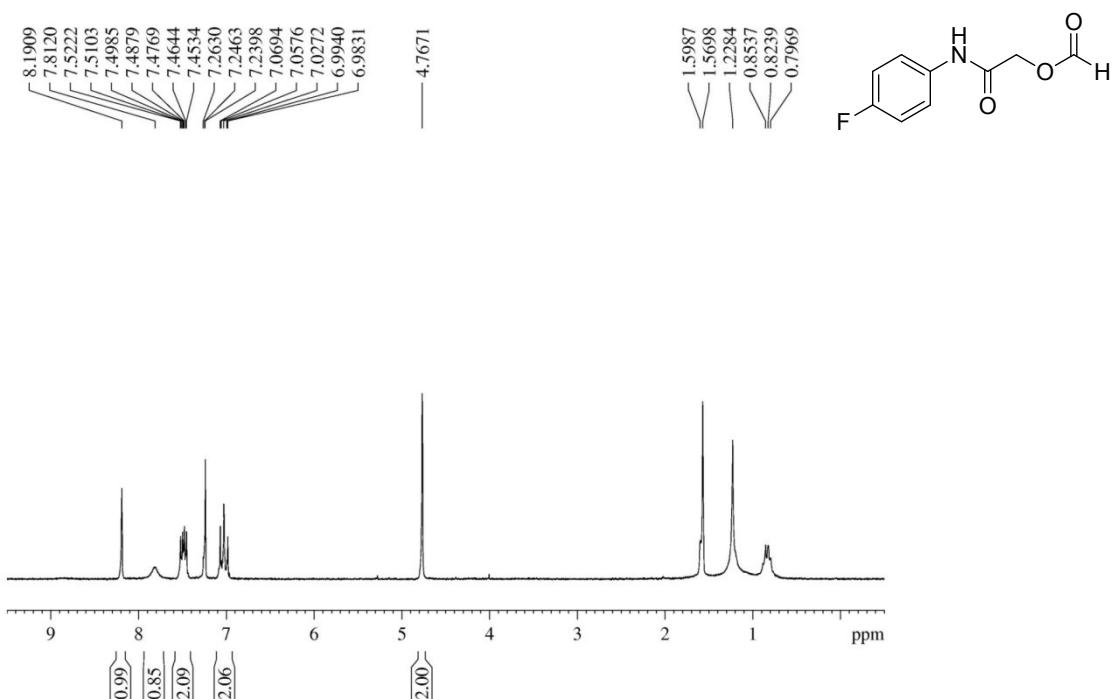


Figure ¹H NMR (CDCl₃, 200 MHz) spectrum of compound 7c

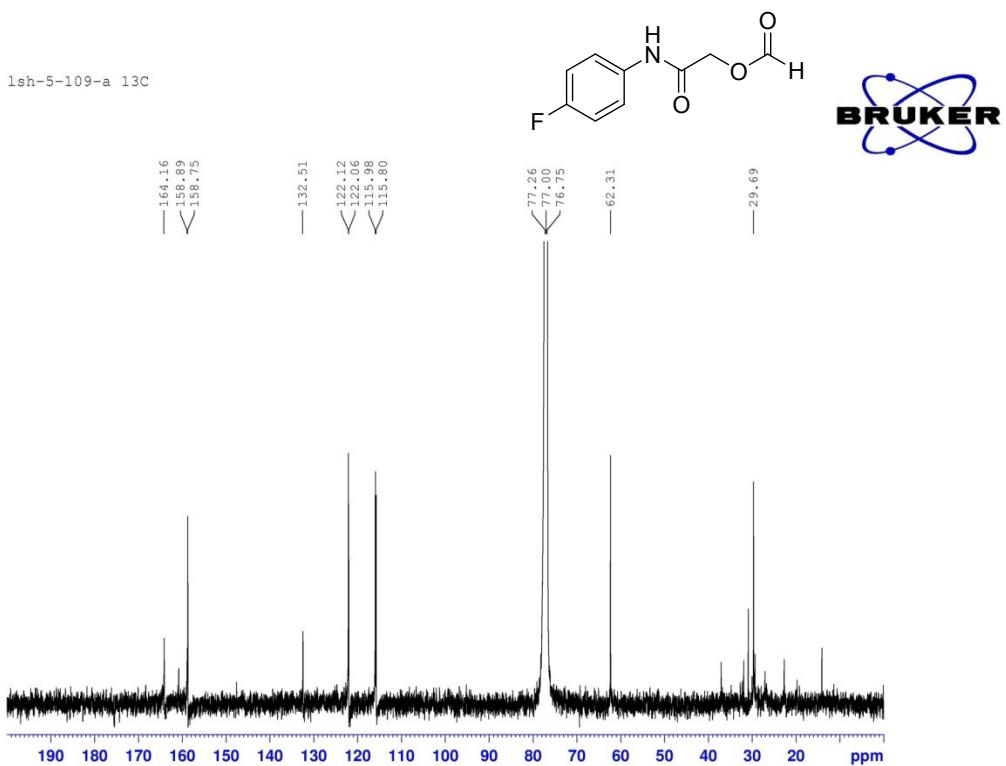


Figure ¹³C NMR (125 MHz, CDCl₃) spectrum of compound 7c

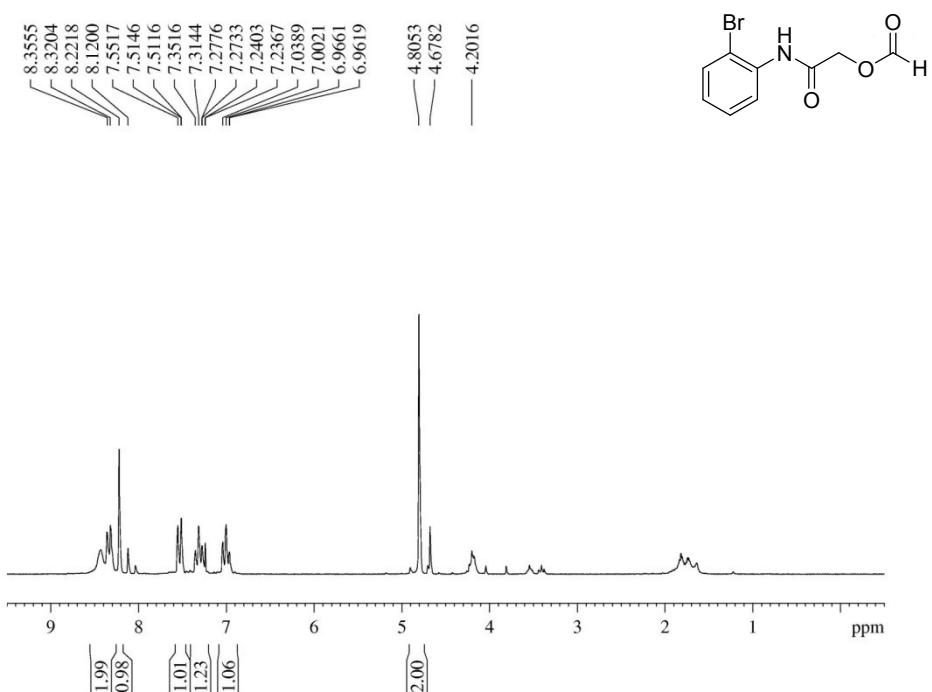


Figure ¹H NMR (50 MHz, CDCl₃) spectrum of compound 7d

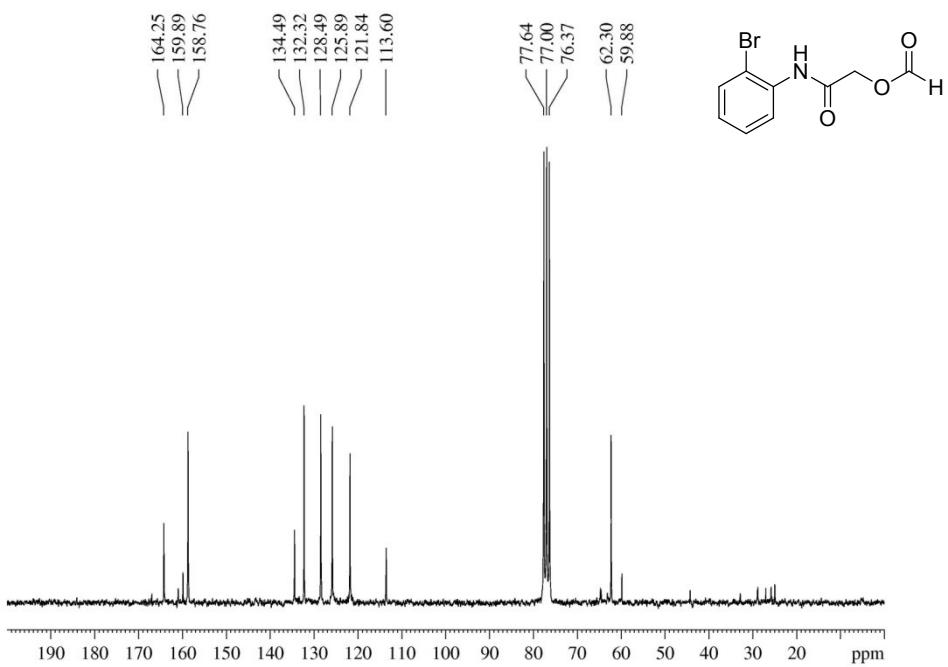


Figure ¹³C NMR (50 MHz, CDCl₃) spectrum of compound 7d

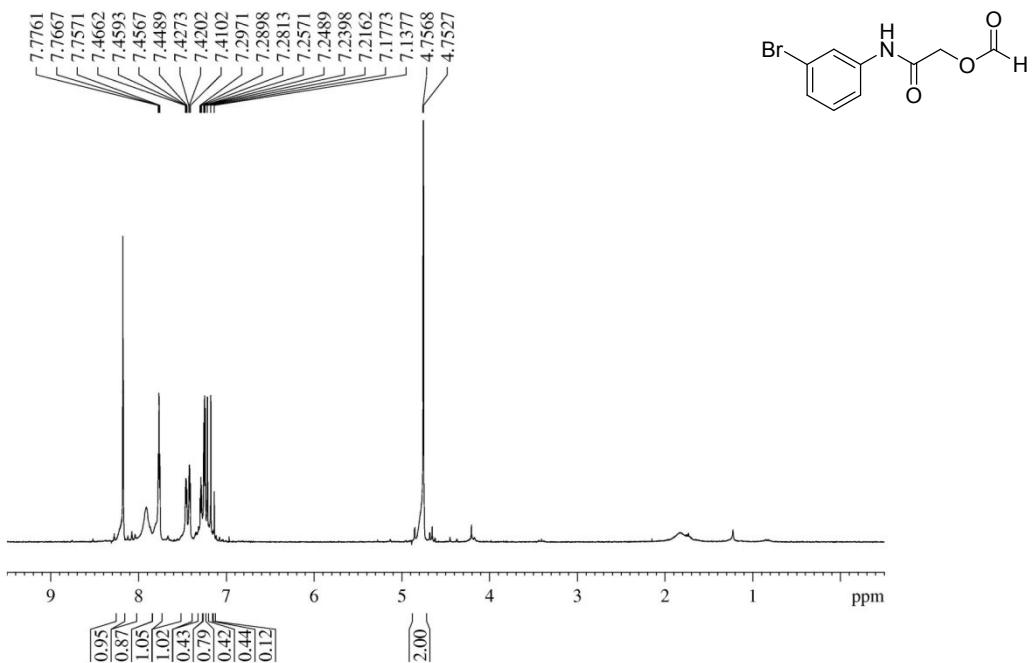


Figure ¹H NMR (CDCl₃, 200 MHz) spectrum of compound 7e

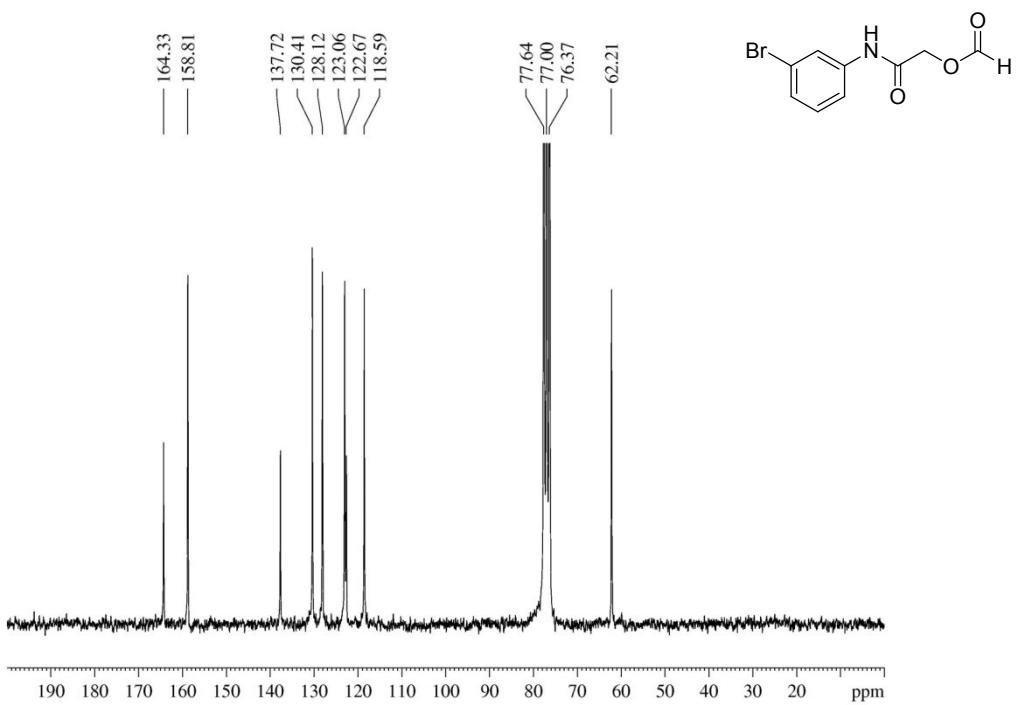


Figure ¹³C NMR (50 MHz, CDCl₃) spectrum of compound 7e

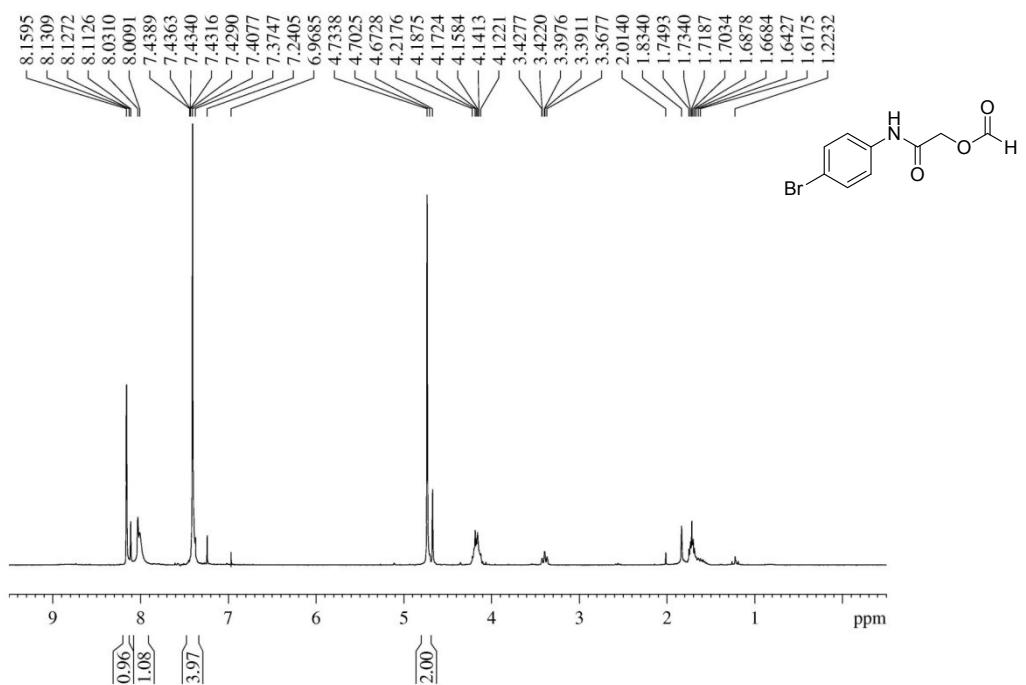


Figure ¹H NMR (CDCl₃, 200 MHz) spectrum of compound 7f

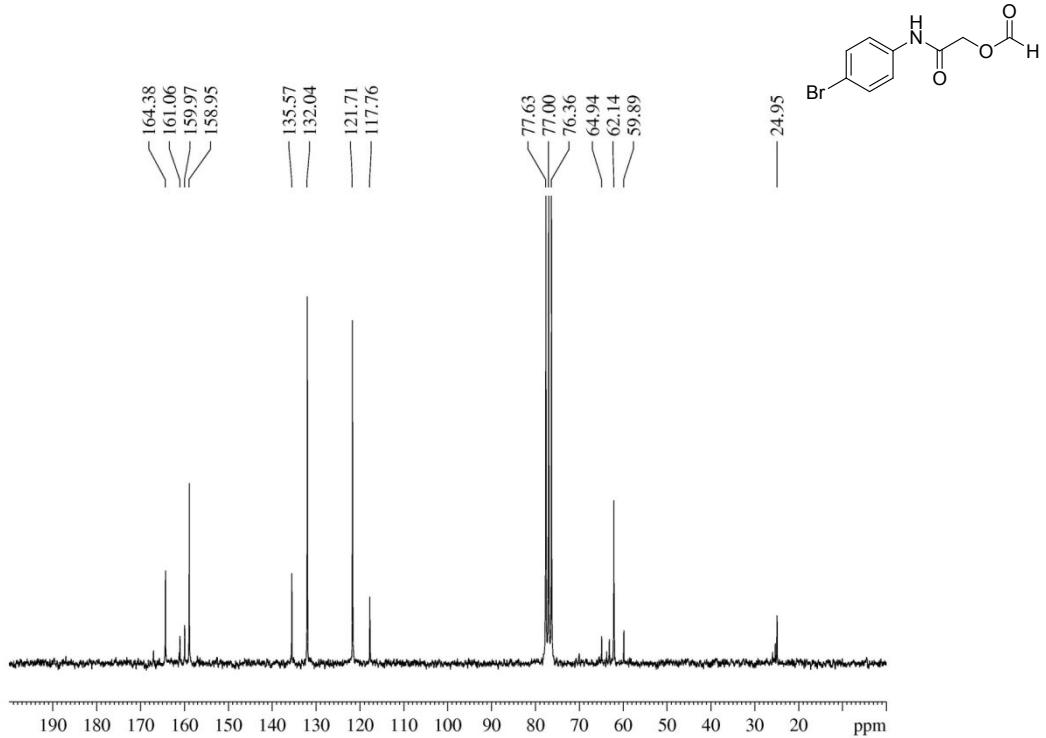


Figure ¹³C NMR (50 MHz, CDCl₃) spectrum of compound 7f

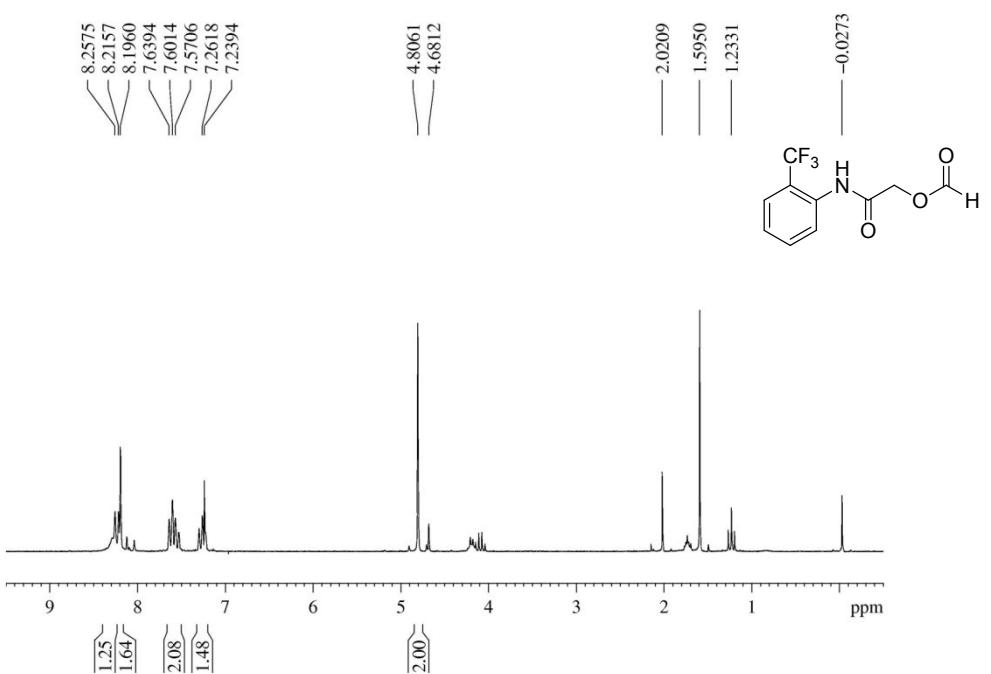


Figure ¹H NMR (CDCl₃, 200 MHz) spectrum of compound 7g

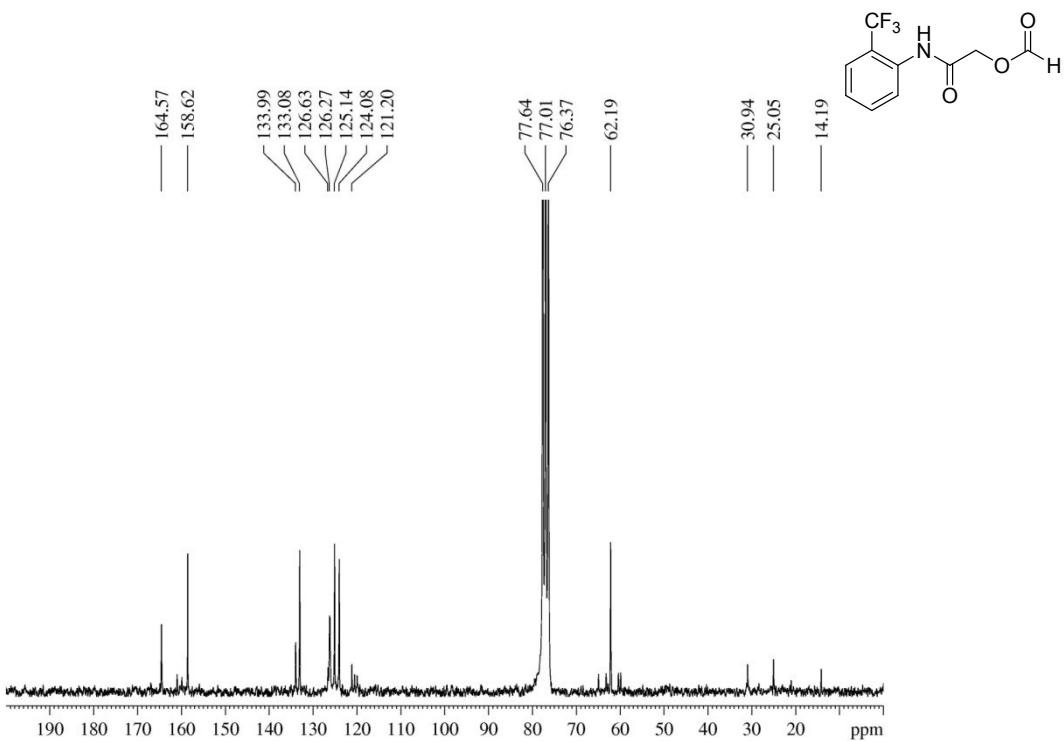


Figure ¹³C NMR (50 MHz, CDCl₃) spectrum of compound 7g

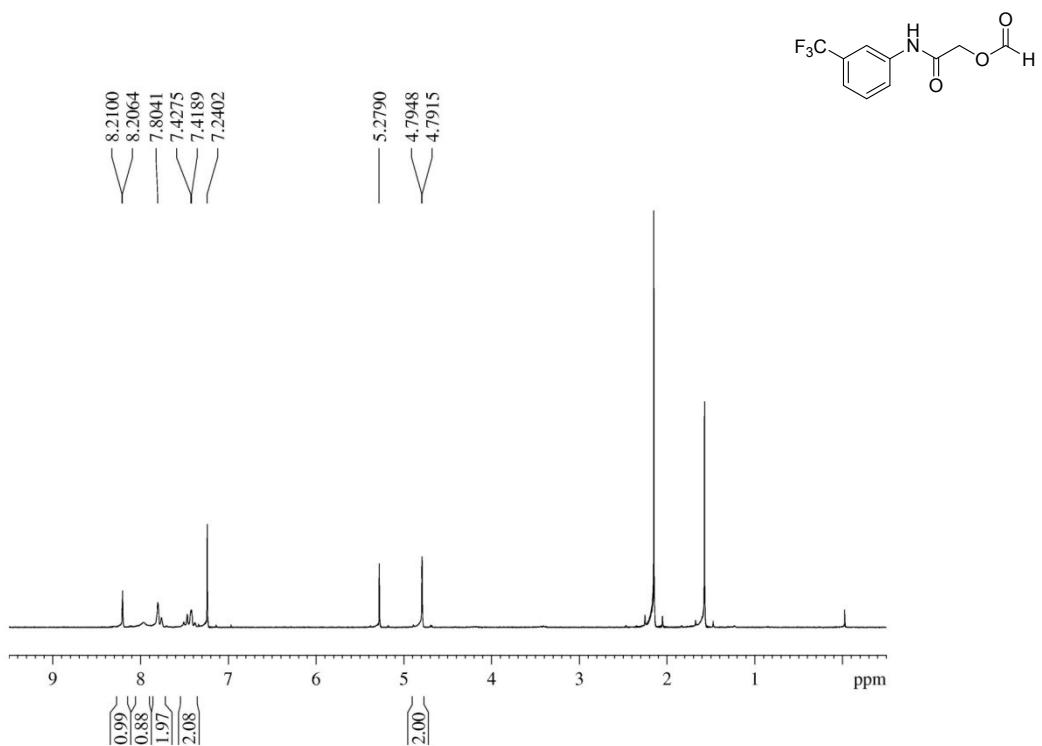


Figure ^1H NMR (CDCl_3 , 200 MHz) spectrum of compound **7h**

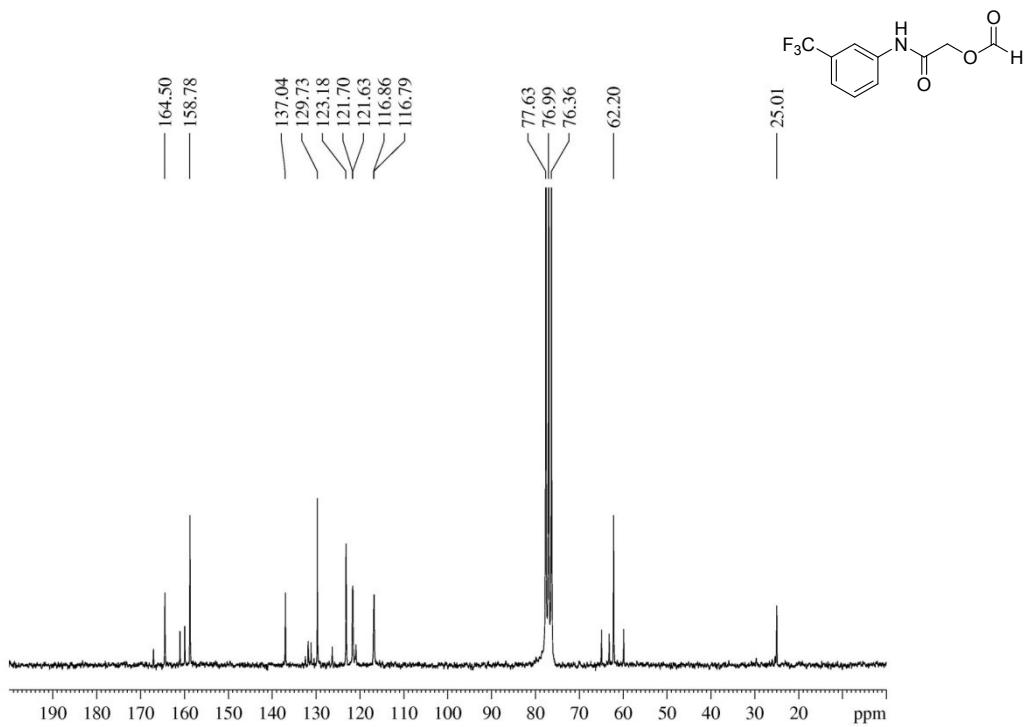


Figure ^{13}C NMR (50 MHz, CDCl_3) spectrum of compound **7h**

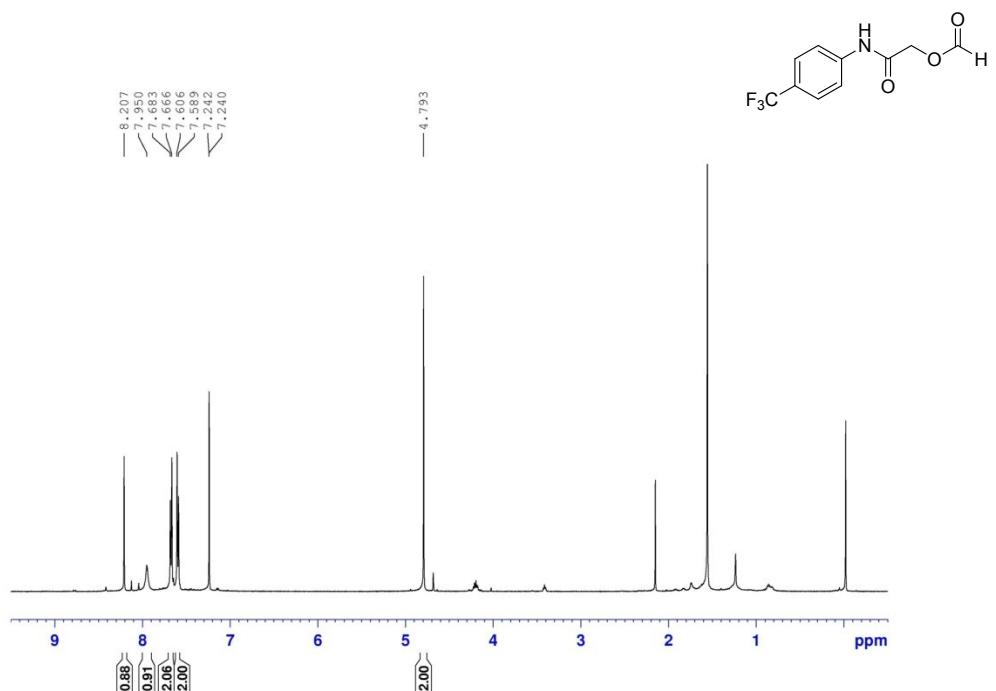


Figure ¹H NMR (CDCl₃, 500 MHz) spectrum of compound 7i

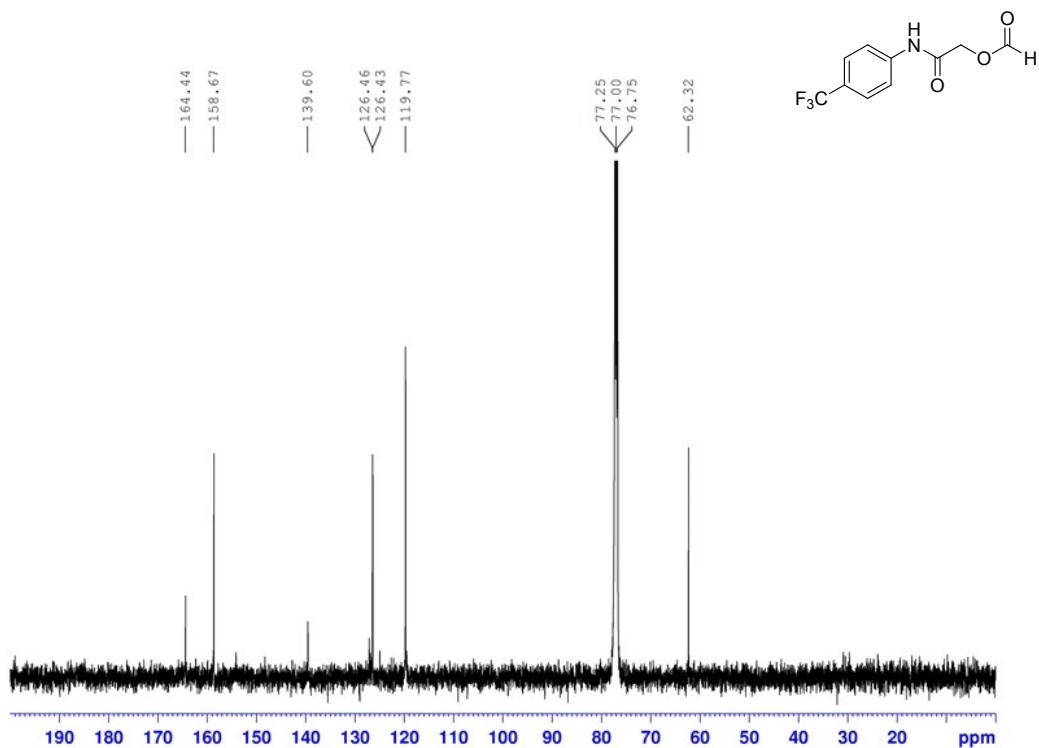


Figure ¹³C NMR (125 MHz, CDCl₃) spectrum of compound 7i

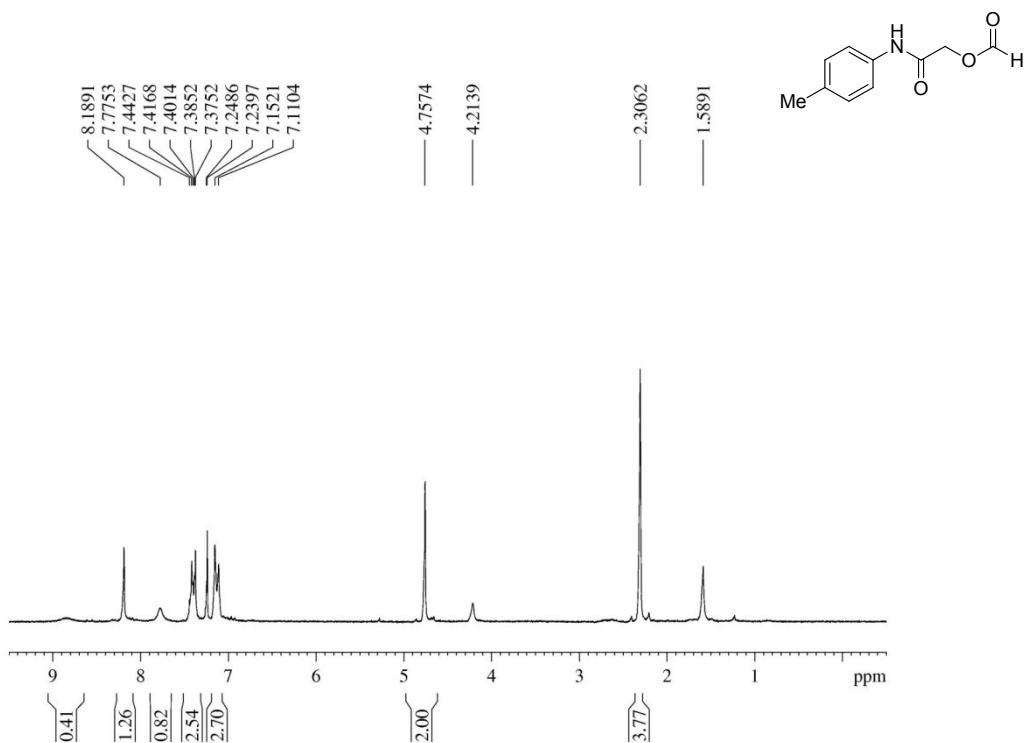


Figure ¹H NMR (CDCl₃, 200 MHz) spectrum of compound 7j

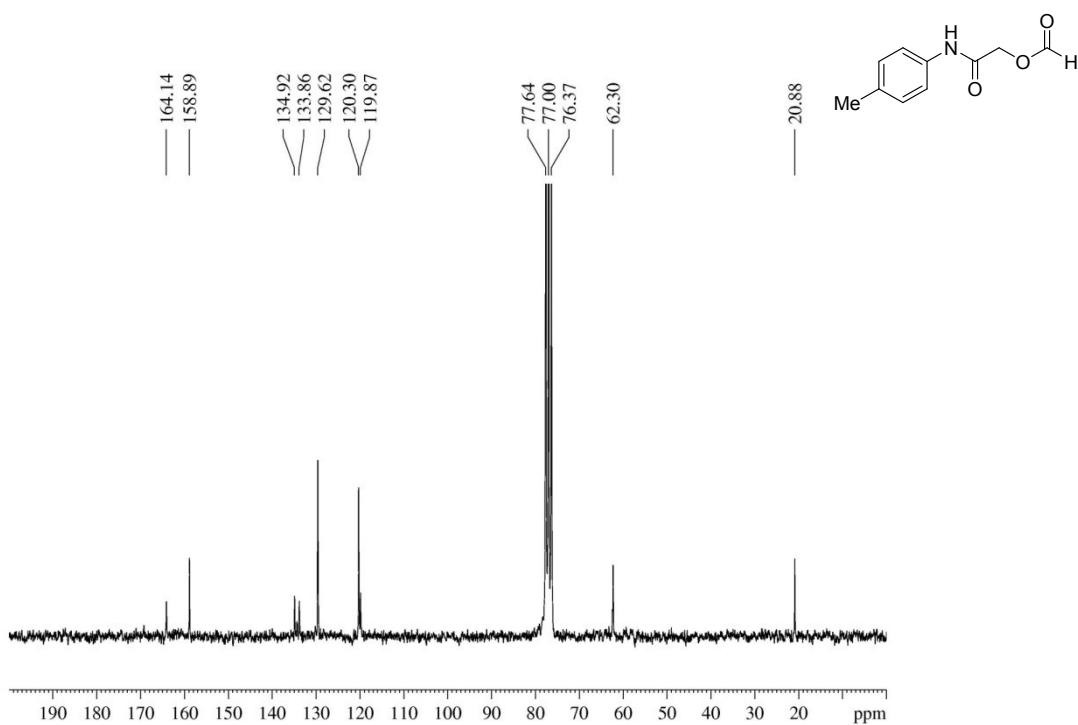


Figure ¹³C NMR (50 MHz, CDCl₃) spectrum of compound 7j

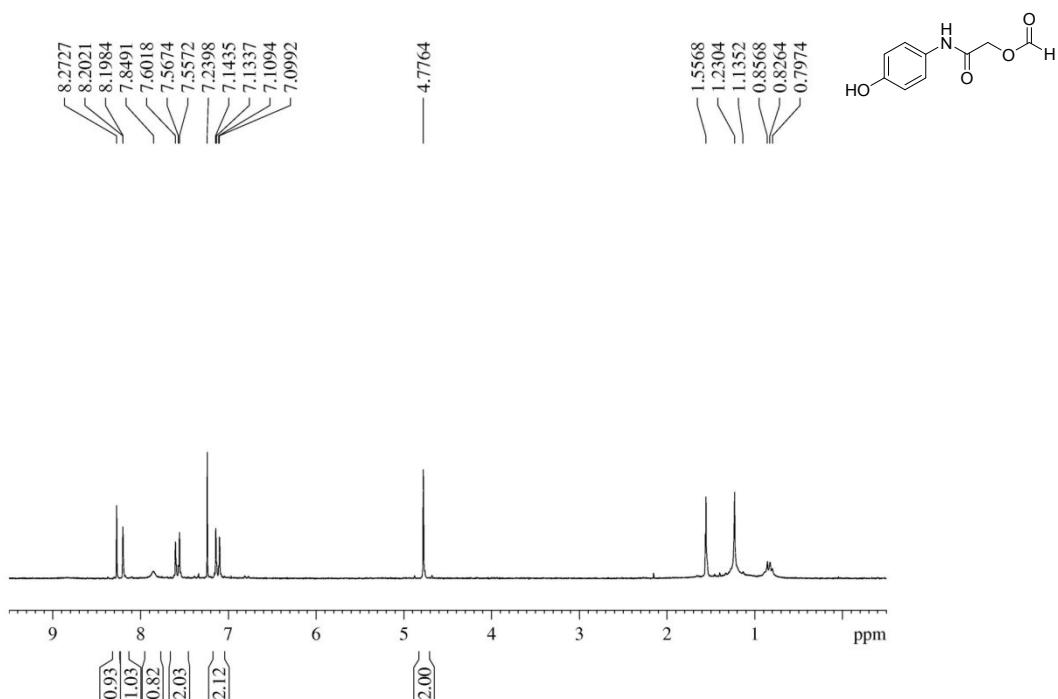


Figure ¹H NMR (CDCl₃, 200 MHz) spectrum of compound 7k

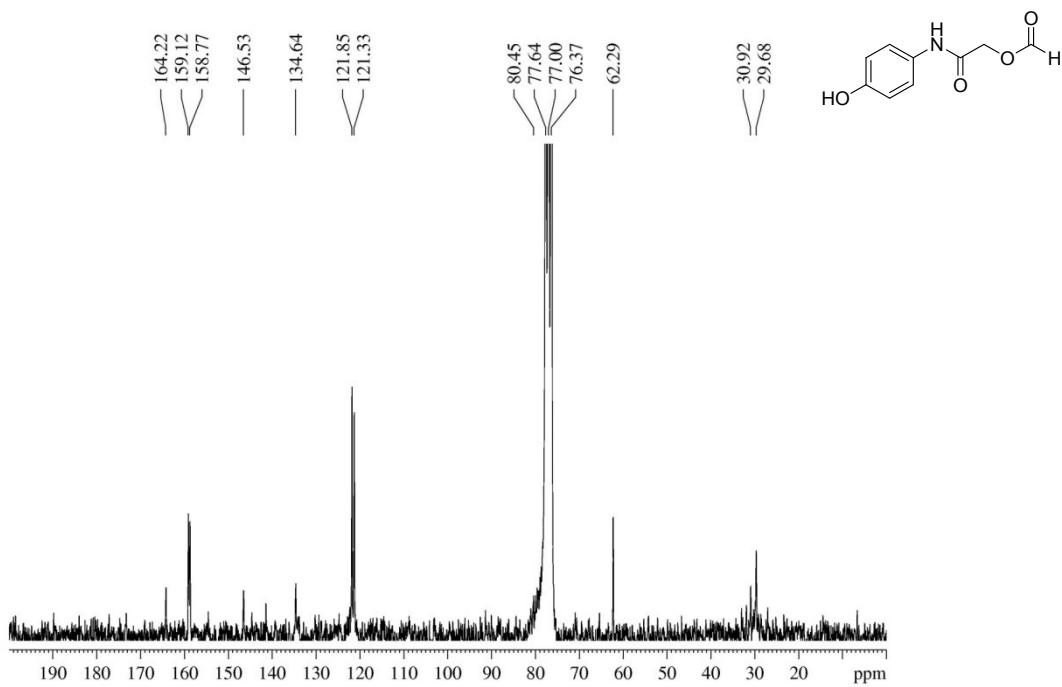


Figure ¹³C NMR (50 MHz, CDCl₃) spectrum of compound 7k

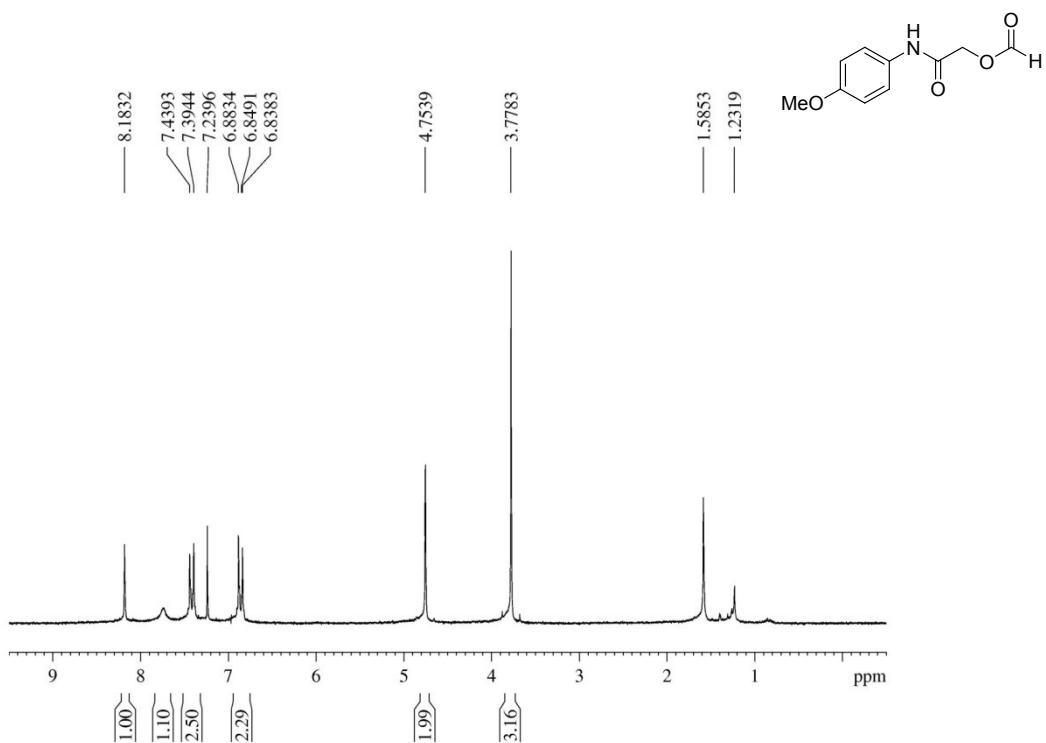


Figure ¹H NMR (CDCl₃, 200 MHz) spectrum of compound 7l

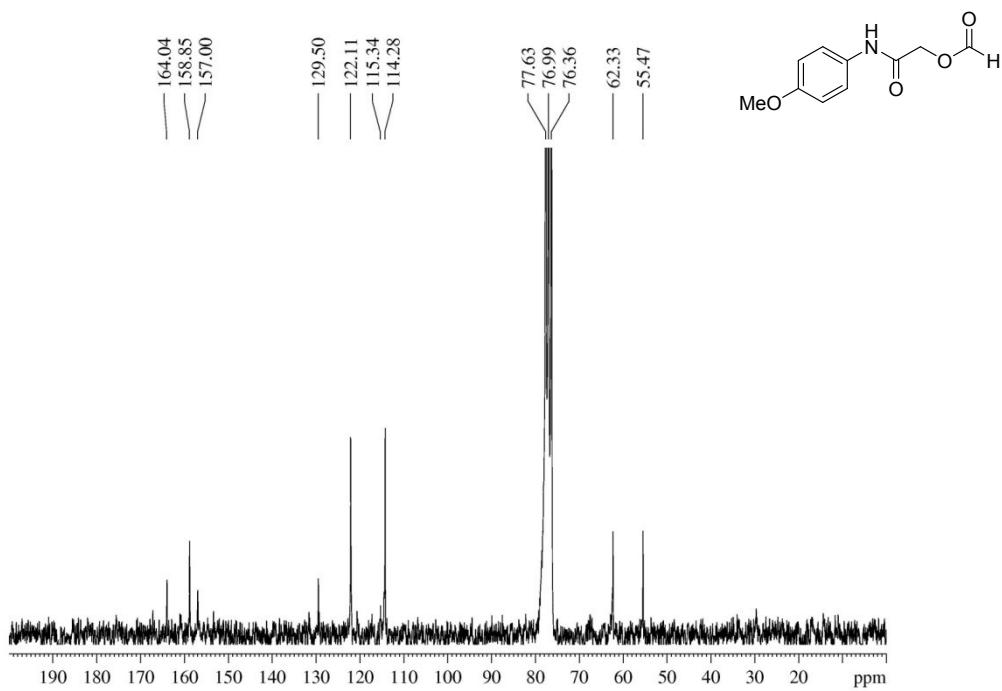


Figure ¹³C NMR (50 MHz, CDCl₃) spectrum of compound 7l

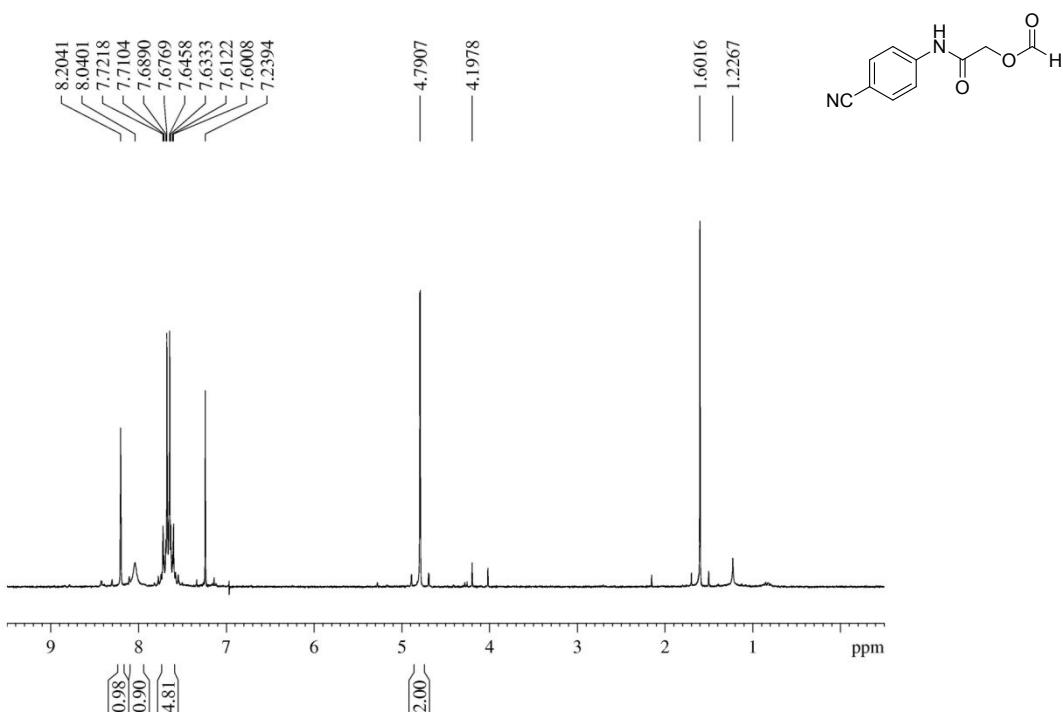


Figure ¹H NMR (CDCl₃, 200 MHz) spectrum of compound 7m

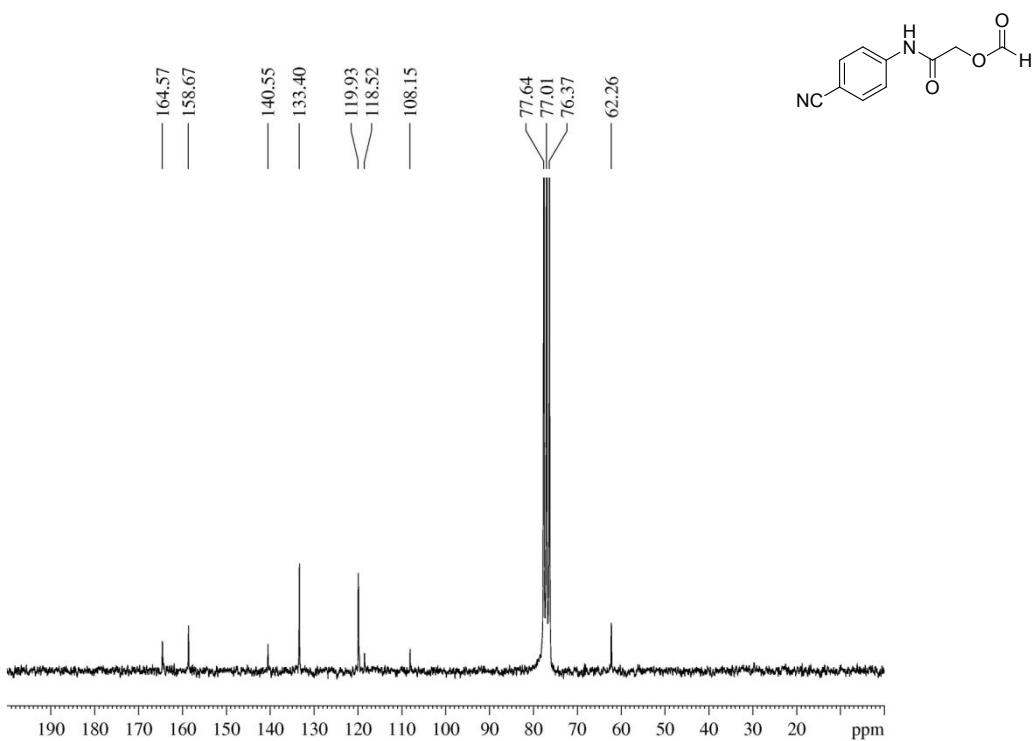


Figure ¹³C NMR (50 MHz, CDCl₃) spectrum of compound 7m

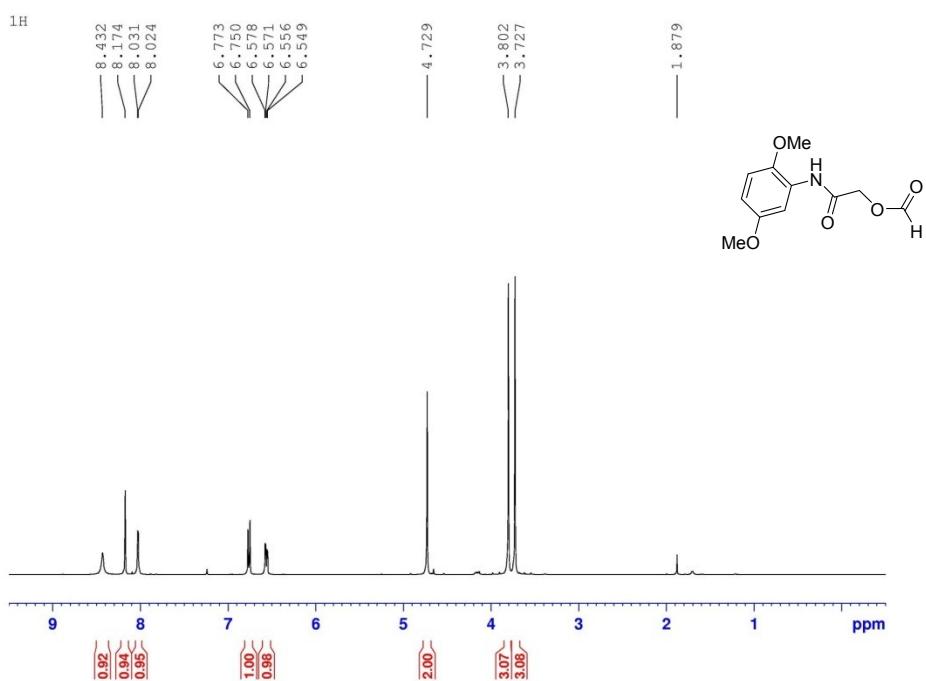


Figure ^1H NMR (CDCl_3 , 400 MHz) spectrum of compound **7n**

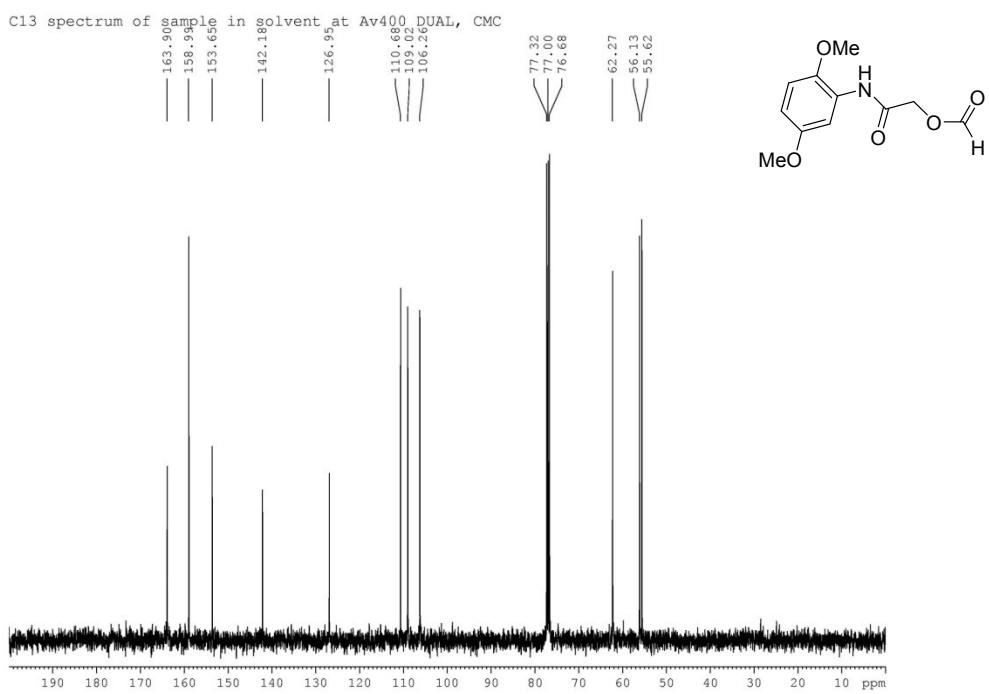


Figure ^{13}C NMR (50 MHz, CDCl_3) spectrum of compound **7n**

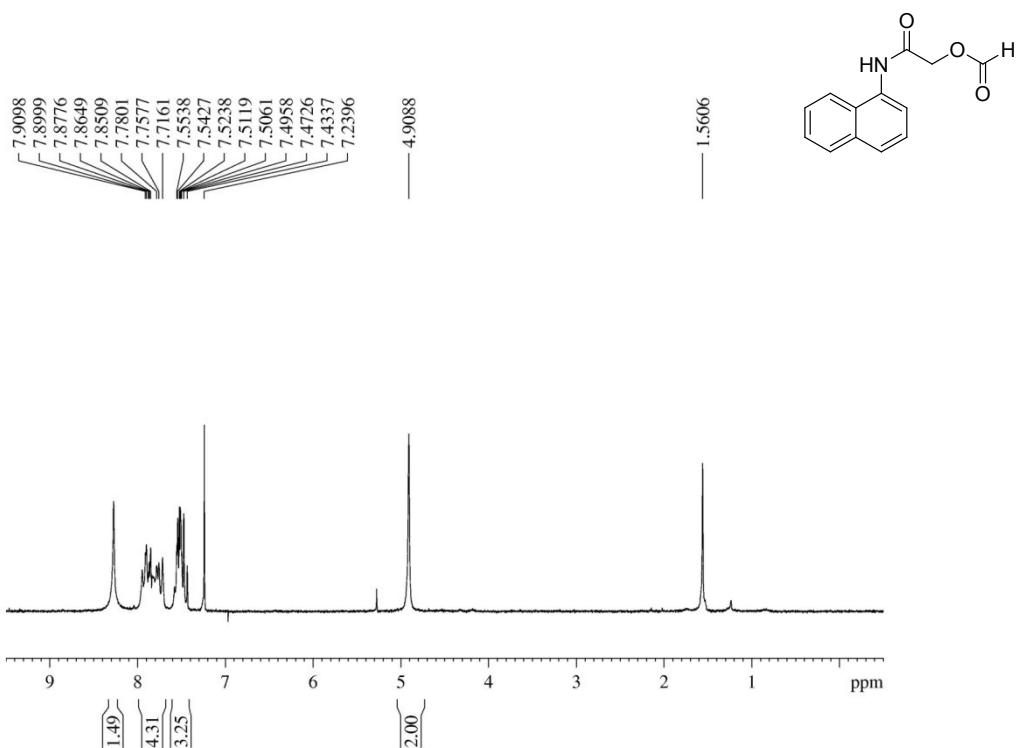


Figure ¹H NMR (CDCl_3 , 200 MHz) spectrum of compound **9a**

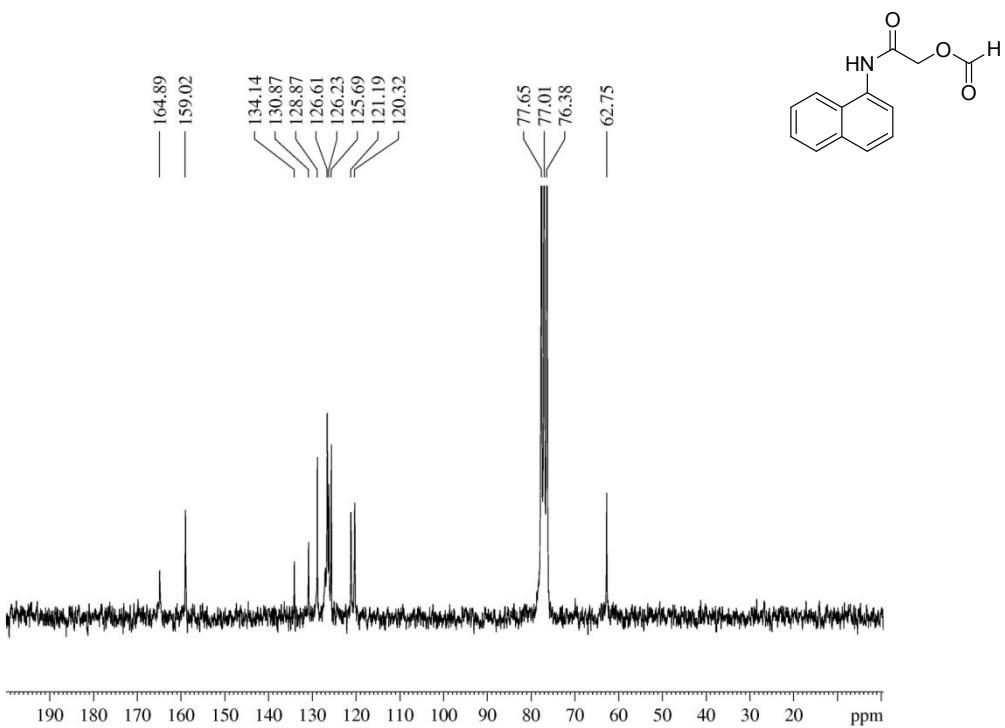


Figure ¹³C NMR (50 MHz, CDCl_3) spectrum of compound **9a**

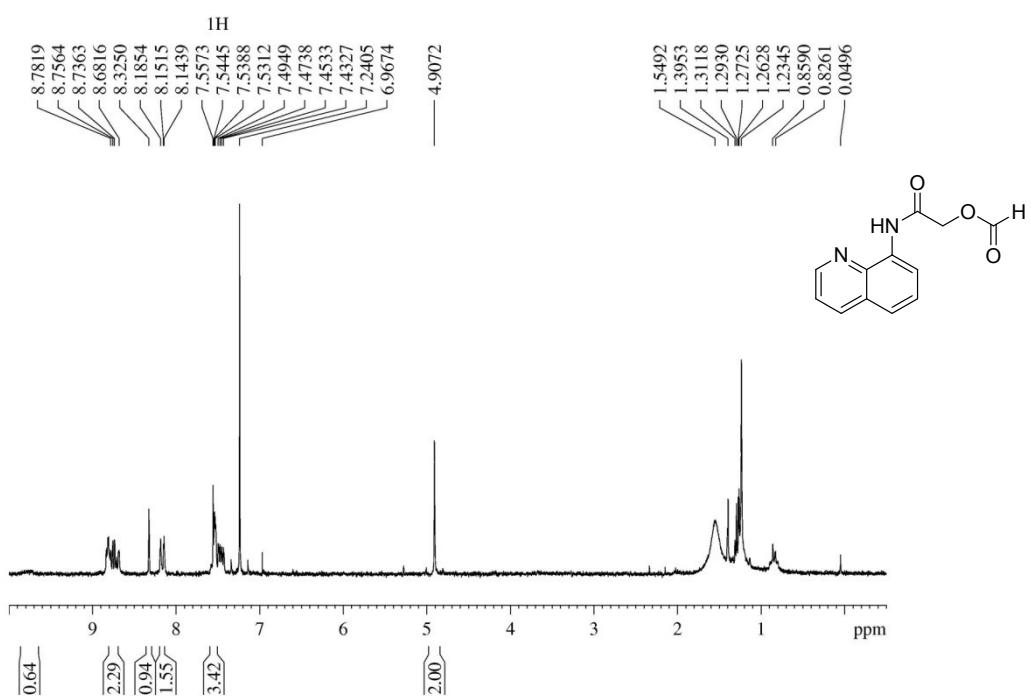


Figure ¹H NMR (CDCl_3 , 200 MHz) spectrum of compound **9b**

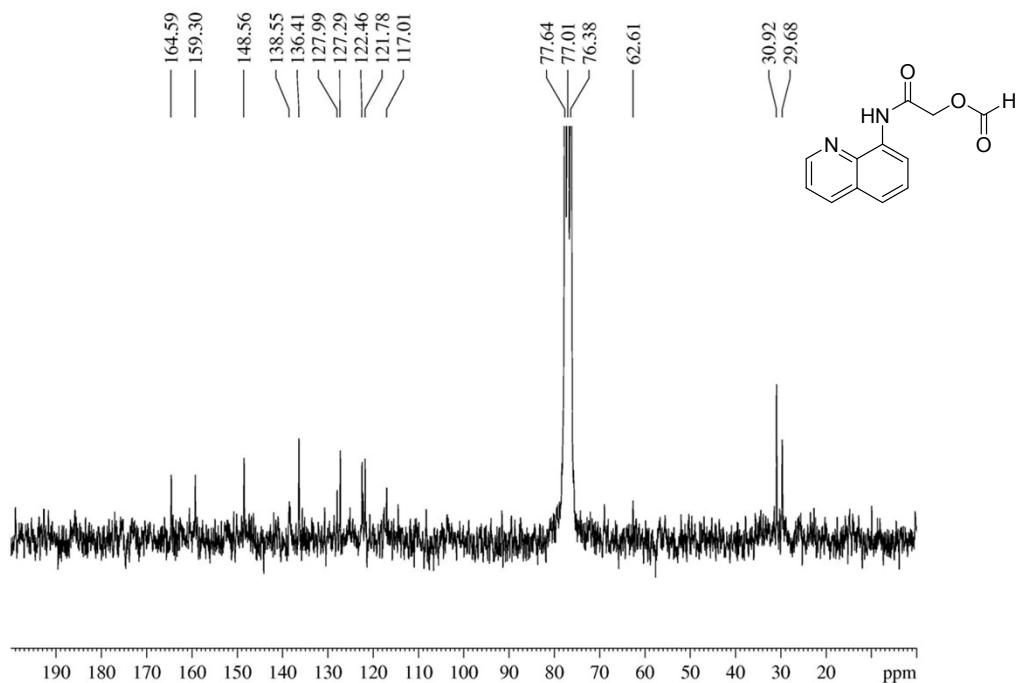


Figure ¹³C NMR (50 MHz, CDCl_3) spectrum of compound **9b**

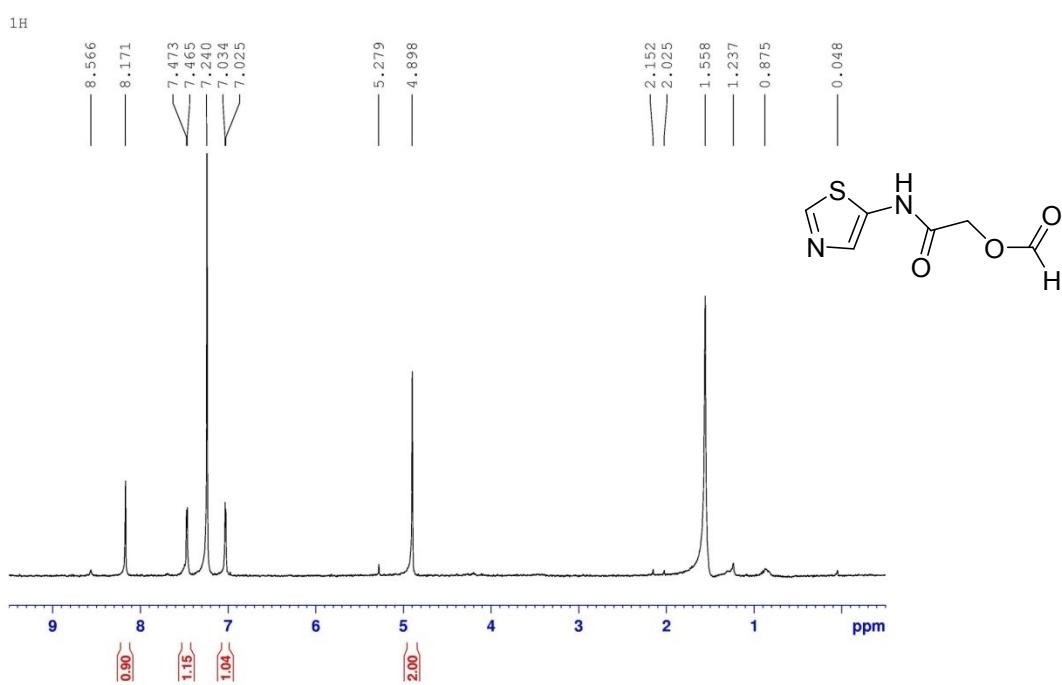


Figure ^1H NMR (CDCl_3 , 400 MHz) spectrum of compound **9c**

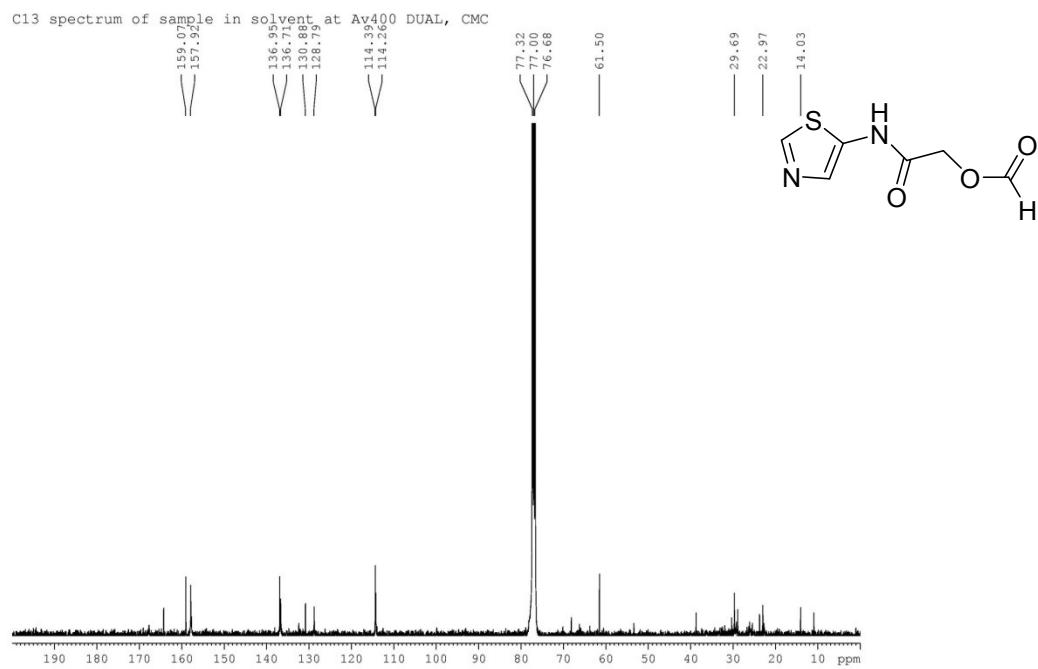


Figure ^{13}C NMR (100 MHz, CDCl_3) spectrum of compound **9c**