Supporting Information

Organocatalytic C-C Bond Cleavage Approach: A Metal-Free and Peroxide-Free Facile Method for the Synthesis of Amide Derivatives

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1. General methods

All starting materials were purchased from commercial suppliers (Sigma-Aldrich, Alfa-Aesar, SD fine chemicals, Merck, HI Media, Fisher Scientific) and were used without further purification unless otherwise indicated. All reactions were performed in a 10 mL reaction vial with magnetic stirring. Solvents used in extraction and purification were distilled prior to use. Thin-layer chromatography (TLC) was performed on TLC plates purchase from Merck. Compounds were visualized with UV light (λ = 254 nm) and/or by immersion in $KMnO_4$ staining solution followed by heating. Products were purified by column chromatography on silica gel, 100 - 200 mesh. Melting points were determined in open capillary tubes on EZ-Melt automated melting point apparatus and are uncorrected. All HRMS are recoreded in EI-QTOF method and LC-MS are recorded in APCI method in acetonitrile solvent. ^{1}H (^{13}C) NMR spectra were recorded at 600 (150) MHz and 400 (100) MHz on a Brucker spectrometer using $CDCl_3$ and DMSO-d_6 as a solvent. The ^{1}H and ^{13}C chemical shifts were referenced to residual solvent signals at $\delta_{H/C}$ 7.26 /77.28 ($CDCl_3$) and $\delta_{H/C}$ 2.51 /39.50 (DMSO-d_6)relative to TMS as internal standards. Coupling constants J [Hz] were directly taken from the spectra and are not averaged. Splitting patterns are designated as s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), overlapped and br (broad).

2. Investigation of the reaction mechanism *via* mass spectrometry

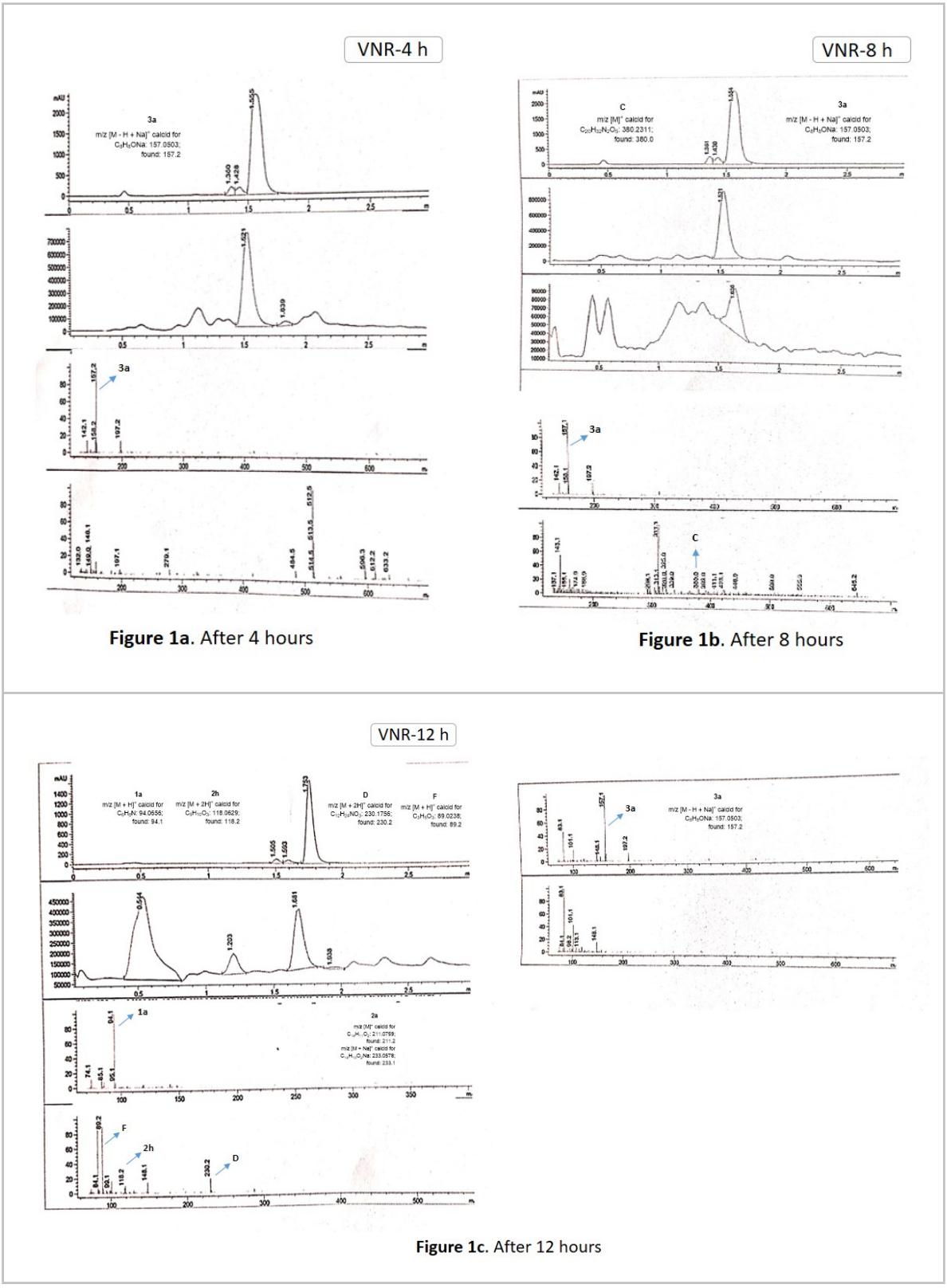


Figure 1a. After 4 hours

Figure 1b. After 8 hours

Figure 1c. After 12 hours

Figure 1. Investigation of the reaction mechanism *via* Mass Spectrometry

3. General experimental procedure for the synthesis of anilides 3a-w

A 10 mL reaction vial was charged with amines **1a-w** (1.0 mmol), 1,3-diketones **2a-e**, **h-j** (1.2 mmol), TEMPO (2,2,6,6-tetramethylpiperidin-1-yl)oxyl) (0.1 mmol, 15.6 mg), NaO^{t}Bu (2.0 mmol, 192 mg) and toluene (2.0 mL). The reaction vial was then heated at 100 °C for 16 h under air. After completion of the reaction (progress was monitored by TLC; SiO_2, Hexane/EtOAc = 7:3), the mixture was diluted with ethyl acetate (15 mL) and water (20 mL) and extracted with ethyl acetate (3 × 10 mL). The combined organic layer was washed with brine (3 × 10 mL) and dried over anhydrous Na_2SO_4. Solvent was removed under reduced pressure and the remaining residue was purified by column chromatography over silica gel using hexane / ethyl acetate = 7:3 as an eluent to obtain the desired products **3a-w** in moderate to good yields.

4. Experimental procedures and analytical data of synthesized compounds 3a-w

Synthesis of Acetanilide (**3a**); According to the general procedure, reaction between aniline (**1a**) (1.0 mmol, 93 mg) and acetylacetone (**2a**) (1.2 mmol, 120 mg) were performed using 10 mol% TEMPO (15.6 mg) and NaO^{t}Bu (2.0 mmol, 192 mg) to obtain the desired acetanilide (**3a**) in 85% (115 mg, Table 1) yield as white solid.

Acetanilide (**3a**)[1]; **White solid**; R_f = 0.30 (SiO_2, Hexane/EtOAc = 7:3); **m.p** = 110-112 °C (Lit[1] 111-113 °C); **^{1}H NMR** (600 MHz, $CDCl_3$): δ = 7.53 (brs, 1H; NH), 7.50 (d, ^3J = 9.0 Hz, 2H; 5-H and 9-H), 7.30 (t, ^3J = 8.8 Hz, 2H; 6-H and 8-H), 7.10 (t, ^3J = 6.8 Hz, 1H; 7-H), 2.16 (s, 3H; 1-H) ppm; **^{13}C NMR** (150 MHz, $CDCl_3$): δ = 168.48 (C-2), 137.94 (C-4), 129.0 (C-8 and C-6), 124.32 (C-5 and C-9), 119.95 (C-7), 24.6 (C-1) ppm; **HRMS** (EI-QTOF, $[M+H]^+$) calculated for $C_8H_{10}NO$: 136.0762; found: 136.0764.

Synthesis of *N*-(4-methylphenyl)acetamide (**3b**); According to the general procedure, reaction between *p*-toluidine (**1b**) (1.0 mmol, 107 mg) and acetylacetone (**2a**) (1.2 mmol, 120 mg) were performed using 10 mol% TEMPO (15.6 mg) and NaO^{t}Bu (2.0 mmol, 192 mg) to obtain the desired *N*-(4-methylphenyl)acetamide (**3b**) in 85% (127 mg, Scheme 2) yield as colorless solid.

***N*-(4-methylphenyl)acetamide** (**3b**)[1]; **Colorless solid**; R_f = 0.30 (SiO_2, Hexane/EtOAc = 7:3); **m.p** = 148-149 °C (Lit[1] 148-150 °C); **^{1}H NMR** (600 MHz, $CDCl_3$) δ = 7.37 (d, ^3J = 9.0 Hz, 2H; 5-H and 9-H), 7.29 (brs, 1H; NH), 7.11 (d, ^3J = 6.8 Hz, 2H; 6-H and 8-H), 2.31 (s, 3H; 10-H),

2.15 (s, 3H; 1-H) ppm; **^{13}C NMR** (150 MHz, $CDCl_3$) δ = 168.21 (C-2), 135.32 (C-7), 133.92 (C-4), 129.46 (C-6 and C-8), 120.0 (C-5 and C-9), 24.53 (C-1), 20.85 (C-10) ppm; **HRMS** (EI-QTOF, $[M+H]^+$) calculated for $C_9H_{12}NO$: 150.0919; found: 150.0916.

Synthesis of *N*-(4-isopropylphenyl)acetamide (**3c**); According to the general procedure, reaction between 4-isopropylaniline (**1c**) (1.0 mmol, 135 mg) and acetylacetone (**2a**) (1.2 mmol, 120 mg) were performed using 10 mol% TEMPO (15.6 mg) and NaO^{t}Bu (2.0 mmol, 192 mg) to obtain the desired *N*-(4-isopropylphenyl)acetamide (**3c**) in 82% (146 mg, Scheme 2) yield as colorless solid.

***N*-(4-isopropylphenyl)acetamide** (**3c**)[1]; **Colorless solid**; R_f = 0.30 (SiO_2, Hexane/EtOAc = 7:3); **m.p =** 105-107 °C (Lit[1] 104-106 °C); **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.54 (brs, 1H; NH), 7.40 (d, ^3J = 8.0 Hz, 2H; 5-H and 9-H), 7.16 (d, ^3J = 8.0 Hz, 2H; 6-H and 8-H), 2.81-2.92 (m, 1H; 10-H), 2.14 (s, 3H; 1-H), 1.22 (d, ^3J = 8.0 Hz, 6H; 11-H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 168.49 (C-2), 145.03 (C-7), 135.58 (C-4), 126.84 (C-6 and C-8), 120.22 (C-5 and C-9), 33.59 (C-10), 24.46 (C-1), 24.03 (C-11) ppm; **HRMS** (EI-QTOF, $[M+H]^+$) calculated for $C_{11}H_{16}NO$: 178.1232; found: 178.1228.

Synthesis of *N*-(4-methoxyphenyl)acetamide (**3d**); According to the general procedure, reaction between *p*-anisidine (**1d**) (1.0 mmol, 123 mg) and acetylacetone (**2a**) (1.2 mmol, 120 mg) were performed using 10 mol% TEMPO (15.6 mg) and NaO^{t}Bu (2.0 mmol, 192 mg) to obtain the desired *N*-(4-methoxyphenyl)acetamide (**3d**) in 79% (130 mg, Scheme 2) yield as colorless solid.

***N*-(4-methoxyphenyl)acetamide** (**3d**)[1]; **Colorless solid**; R_f = 0.30 (SiO_2, Hexane/EtOAc = 7:3); **m.p =** 128-130 °C (Lit[1] 127-129 °C); **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.38 (d, ^3J = 8.0 Hz, 2H; 5-H and 9-H), 7.27 (brs, 1H; NH), 6.84 (d, ^3J = 9.0, 2H; 6-H and 8-H), 3.78 (s, 3H; 10-H), 2.14 (s, 3H; 1-H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 168.29 (C-2), 156.45 (C-7), 130.93 (C-4), 121.96 (C-5 and C-9), 114.13 (C-6 and C-8), 55.49 (C-10), 24.36 (C-1) ppm; **HRMS** (EI-QTOF, $[M+H]^+$) calculated for $C_9H_{12}NO_2$: 166.0868; found: 166.0863.

Synthesis of *N*-(3,4-dimethylphenyl)acetamide (**3e**); According to the general procedure, reaction between 3,4-dimethylaniline (**1e**) (1.0 mmol, 121 mg) and acetylacetone (**2a**) (1.2 mmol, 120 mg) were performed using 10 mol% TEMPO (15.6 mg) and NaO^{t}Bu (2.0 mmol,

192 mg) to obtain the desired *N*-(3,4-dimethylphenyl)acetamide (**3e**) in 78% (127 mg, Scheme 2) yield as pale yellow solid.

***N*-(3,4-dimethylphenyl)acetamide** (**3e**)[1]; **Pale yellow solid**; R_f = 0.30 (SiO_2, Hexane/EtOAc = 7:3); **^{1}H NMR** (600 MHz, $CDCl_3$) δ = 7.48 (s, 1H; 5-H), 7.35 (d, ^3J = 6.8 Hz, 1H; 9-H), 7.26 (brs, 1H; NH), 7.14 (d, ^3J = 6.8 Hz, 1H; 8-H), 2.30 (s, 3H; 10-H), 2.28 (s, 3H; 11-H), 2.21 (s, 3H; 1-H) ppm; **HRMS** (EI-QTOF, $[M+H]^+$) calculated for $C_{10}H_{14}NO$: 164.1075; found: 164.1069.

Synthesis of *N*-(4-methoxy-2-methylphenyl)acetamide (**3f**); According to the general procedure, reaction between 4-methoxy-2-methylaniline (**1f**) (1.0 mmol, 137 mg) and acetylacetone (**2a**) (1.2 mmol, 120 mg) were performed using 10 mol% TEMPO (15.6 mg) and NaO^{t}Bu (2.0 mmol, 192 mg) to obtain the desired *N*-(4-methoxy-2-methylphenyl)acetamide (**3f**) in 71% (127 mg, Scheme 2) yield as colorless solid.

***N*-(4-methoxy-2-methylphenyl)acetamide** (**3f**)[1]; **Colorless solid**; R_f = 0.25 (SiO_2, Hexane/EtOAc = 7:3); **m.p** = 128-129 °C (Lit[1] 126-129 °C); **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.40 (d, ^3J = 8.0 Hz, 1H; 9-H), 7.03 (brs, 1H; NH), 6.72-6.70 (m, 2H; 6-H and 8-H), 3.76 (s, 3H; 11-H), 2.21 (s, 3H; 10-H), 2.16 (s, 3H; 1-H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 168.83 (C-2), 157.47 (C-7), 133.08 (C-5), 128.46 (C-4), 126.22 (C-6), 115.92 (C-8), 111.57 (C-9), 55.39 (C-11), 23.84 (C-1), 18.15 (C-10) ppm; **HRMS** (EI-QTOF, $[M+H]^+$) calculated for $C_{10}H_{14}NO_2$: 180.1025; found: 180.1020.

Synthesis of *N*-(3-chlorophenyl)acetamide (**3g**); According to the general procedure, reaction between 3-chloroaniline (**1g**) (1.0 mmol, 127.56 mg) and acetylacetone (**2a**) (1.2 mmol, 120 mg) were performed using 10 mol% TEMPO (15.6 mg) and NaO^{t}Bu (2.0 mmol, 192 mg) to obtain the desired *N*-(3-chlorophenyl)acetamide (**3g**) in 75% (127 mg, Scheme 2) yield as pale yellow solid.

***N*-(3-chlorophenyl)acetamide** (**3g**)[1]; **Pale yellow solid**; R_f = 0.30 (SiO_2, Hexane/EtOAc = 7:3); **m.p** = 76-77 °C (Lit[1] 75-78 °C); **^{1}H NMR** (600 MHz, $CDCl_3$) δ = 7.62 (s, 1H; 5-H), 7.45 (s, 1H; NH), 7.34 (dd, ^3J = 6.8 Hz, 1H; 9-H), 7.22 (t, ^3J = 8 Hz, 1H; 8-H), 7.06 (dd, ^3J = 6.8 Hz, 1H; 7-H), 2.18 (s, 3H; 1-H) ppm; **^{13}C NMR** (150 MHz, $CDCl_3$) δ = 168.41 (C-2), 139.03 (C-4), 134.6 (C-6), 129.95 (C-8), 124.29 (C-7), 119.87 (C-5), 117.71 (C-9), 24.62 (C-1) ppm; **HRMS** (EI-QTOF, $[M+H]^+$) calculated for C_8H_9ClNO: 170.0372; found: 170.0368.

Synthesis of *N*-(4-chlorophenyl)acetamide (**3h**); According to the general procedure, reaction between 4-chloroaniline (**1h**) (1.0 mmol, 127.56 mg) and acetylacetone (**2a**) (1.2 mmol, 120 mg) were performed using 10 mol% TEMPO (15.6 mg) and NaO^{t}Bu (2.0 mmol, 192 mg) to obtain the desired *N*-(4-chlorophenyl)acetamide (**3h**) in 77% (131 mg, Scheme 2) yield as brown solid.

***N*-(4-chlorophenyl)acetamide** (**3h**)[1]; **Brown solid**; R_f = 0.30 (SiO_2, Hexane/EtOAc = 70:30); **m.p** = 175-176 °C (Lit[1] 174-177 °C); **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.47 (d, ^3J = 8 Hz, 2H; 5-H and 9-H), 7.35 (s, 1H; NH), 7.29 (d, ^3J = 8 Hz, 2H; 6-H and 8-H), 2.19 (s, 3H; 1-H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 168.34 (C-2), 136.42 (C-4), 129.29 (C-7), 129.01 (C-6 and C-8), 121.08 (C-5 and C-9), 24.57 (C-1) ppm; **HRMS** (EI-QTOF, $[M+H]^+$) calculated for C_8H_9ClNO: 170.0372; found: 170.0369.

Synthesis of *N*-(3,5-dichlorophenyl)acetamide (**3i**); According to the general procedure, reaction between 3,5-dichloroaniline (**1i**) (1.0 mmol, 162 mg) and acetylacetone (**2a**) (1.2 mmol, 120 mg) were performed using 10 mol% TEMPO (15.6 mg) and NaO^{t}Bu (2.0 mmol, 192 mg) to obtain the desired *N*-(3,5-dichlorophenyl)acetamide (**3i**) in 74% (151 mg, Scheme 2) yield as pale brown solid.

***N*-(3,5-dichlorophenyl)acetamide** (**3i**)[2]; **Pale brown solid**; R_f = 0.34 (SiO_2, Hexane/EtOAc = 7:3); **m.p** = 188-190 °C (Lit[2] 189.1-189.4 °C); **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.98 (s, 1H; NH), 7.49 (s, 1H; 7-H), 7.11 (s, 2H; 5-H and 9-H), 2.20 (s, 3H; 1-H), ppm; **HRMS** (EI-QTOF, $[M+H]^+$) calculated for $C_8H_8Cl_2NO$: 203.9982; found: 203.9978.

Synthesis of *N*-(2-bromo-4-chlorophenyl)acetamide (**3j**); According to the general procedure, reaction between 2-bromo-4-chloroaniline (**1j**) (1.0 mmol, 206.47 mg) and acetylacetone (**2a**) (1.2 mmol, 120 mg) were performed using 10 mol% TEMPO (15.6 mg) and NaO^{t}Bu (2.0 mmol, 192 mg) to obtain the desired *N*-(2-bromo-4-chlorophenyl)acetamide (**3j**) in 76% (189 mg, Scheme 2) yield as colorless solid.

***N*-(2-bromo-4-chlorophenyl)acetamide** (**3j**)[1]; **Colorless solid**; R_f = 0.35 (SiO_2, Hexane/EtOAc = 7:3); **m.p** = 105-107 °C (Lit[1] 104-106 °C); **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 8.29 (d, ^3J = 8.0 Hz, 1H; 9-H), 7.56 (br s, 1H; NH), 7.53 (s, 1H; 6-H), 7.28 (dd, ^3J = 8.0 Hz, 1H; 8-H), 2.23 (s, 3H; 1-H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 168.26 (C-2), 134.49 (C-4), 131.68 (C-6 and C-7), 128.51 (C-8 and C-9), 122.52 (C-5), 24.86 (C-1) ppm; **HRMS** (EI-QTOF, $[M+H]^+$) calculated for $C_8H_8BrClNO$: 247.9477; found: 247.9474.

Synthesis of *N*-(3-bromophenyl)acetamide (**3k**); According to the general procedure, reaction between 3-bromoroaniline (**1k**) (1.0 mmol, 172 mg) and acetylacetone (**2a**) (1.2 mmol, 120 mg) were performed using 10 mol% TEMPO (15.6 mg) and NaO^{t}Bu (2.0 mmol, 192 mg) to obtain the desired *N*-(3-bromophenyl)acetamide (**3k**) in 68% (146 mg, Scheme 2) yield as white solid.

***N*-(3-bromophenyl)acetamide** (**3k**)[3]; **White solid**; R_f = 0.30 (SiO_2, Hexane/EtOAc = 7:3); **m.p** = 69-71 °C (Lit[3] 68-70 °C); **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.62 (s, 2H; 5-H and NH), 7.35 (d, ^3J = 8.0 Hz, 1H; 7-H), 7.21 (t, ^3J = 8.0 Hz, 1H; 8-H), 7.06 (d, ^3J = 8.0 Hz, 1H; 9-H), 2.17 (s, 3H; 1-H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 168.59 (C-2), 139.09 (C-4), 134.57 (C-8), 129.95 (C-7), 124.27 (C-6), 119.9 (C-5), 117.77 (C-9), 24.57 (C-1) ppm; **HRMS** (EI-QTOF, $[M+H]^+$) calculated for C_8H_9BrNO: 213.9867; found: 213.9864.

Synthesis of *N*-(4-bromophenyl)acetamide (**3l**); According to the general procedure, reaction between 4-bromoroaniline (**1l**) (1.0 mmol, 172 mg) and acetylacetone (**2a**) (1.2 mmol, 120 mg) were performed using 10 mol% TEMPO (15.6 mg) and NaO^{t}Bu (2.0 mmol, 192 mg) to obtain the desired *N*-(4-bromophenyl)acetamide (**3l**) in 70% (150 mg, Scheme 2) yield as yellowish brown solid.

***N*-(4-bromophenyl)acetamide** (**3l**)[1]; **Yellowish brown solid**; R_f = 0.30 (SiO_2, Hexane/EtOAc = 7:3); **m.p** = 169-171 °C (Lit[1] 168-171 °C); **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.38-7.43 (m, 4H; 5-H, 6-H, 8-H and 9-H), 7.32 (s, 1H; NH), 2.17 (s, 3H; 1-H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 168.35 (C-2), 136.94 (C-4), 131.97 (C-6 & C-8), 121.39 (C-5 & C-9), 116.69 (C-7), 24.61 (C-1) ppm; **HRMS** (EI-QTOF, $[M+H]^+$) calculated for C_8H_9BrNO: 213. 9867; found: 213.9865.

Synthesis of *N*-(2-bromo-5-methylphenyl)acetamide (**3m**); According to the general procedure, reaction between 2-bromo-5-methylaniline (**1m**) (1.0 mmol, 186 mg) and acetylacetone (**2a**) (1.2 mmol, 120 mg) were performed using 10 mol% TEMPO (15.6 mg) and NaO^{t}Bu (2.0 mmol, 192 mg) to obtain the desired *N*-(2-bromo-5-methylphenyl)acetamide (**3m**) in 73% (166 mg, Scheme 2) yield as white solid.

***N*-(2-bromo-5-methylphenyl)acetamide** (**3m**)[1]; **White solid**; R_f = 0.30 (SiO_2, Hexane/EtOAc = 7:3); **m.p** = 96-98 °C (Lit[1] 97-99 °C); **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 8.14 (s, 1H; NH), 7.55 (s, 1H; 9-H), 7.38 (d, ^3J = 8 Hz, 1H; 6-H), 6.78 (d, ^3J = 8 Hz, 1H; 7-H), 2.31 (s, 3H; 11-H), 2.22 (s, 3H; 1-H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 168.24 (C-2), 138.63 (C-4), 135.3 (C-

8), 131.74 (C-6), 126.12 (C-7), 122.57 (C-9), 110.0 (C-5), 24.87 (C-1), 21.31 (C-11) ppm; **HRMS** (EI-QTOF, $[M+H]^+$) calculated for $C_9H_{11}BrNO$: 228.0024; found: 228.0020.

Synthesis of *N*-(4-iodomophenyl)acetamide (**3n**); According to the general procedure, reaction between 4-iodoaniline (**1n**) (1.0 mmol, 219 mg) and acetylacetone (**2a**) (1.2 mmol, 120 mg) were performed using 10 mol% TEMPO (15.6 mg) and NaO^{t}Bu (2.0 mmol, 192 mg) to obtain the desired *N*-(4-iodomophenyl)acetamide (**3n**) in 69% (180 mg, Scheme 2) yield as yellow solid.

***N*-(4-iodomophenyl)acetamide** (**3n**)[1]; **Yellow solid**; R_f = 0.30 (SiO_2, Hexane/EtOAc = 7:3); **m.p** = 173-174 °C (Lit[1] 172-174 °C); **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.61 (d, ^3J = 8.0 Hz, 2H; 6-H and 8-H), 7.35 (s, 1H; NH), 7.29 (d, ^3J = 8.0 Hz, 2H; 5-H and 9-H), 2.17 (s, 3H; 1-H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 168.41 (C-2), 137.93 (C-4), 137.66 (C-6 and C-8), 121.68 (C-5 and C-9), 87.49 (C-7), 24.68 (C-1) ppm; **HRMS** (EI-QTOF, $[M+H]^+$) calculated for C_8H_9INO: 261.9728; found: 261.9723.

Synthesis of *N*-(4-(trifluoromethyl)phenyl)acetamide (**3o**); According to the general procedure, reaction between 4-(trifluoromethyl)aniline (**1o**) (1.0 mmol, 161 mg) and acetylacetone (**2a**) (1.2 mmol, 120 mg) were performed using 10 mol% TEMPO (15.6 mg) and NaO^{t}Bu (2.0 mmol, 192 mg) to obtain the desired *N*-(4-(trifluoromethyl)phenyl)acetamide (**3o**) in 65% (132 mg, Scheme 2) yield as white solid.

***N*-(4-(trifluoromethyl)phenyl)acetamide** (**3o**)[1]; **White solid**; R_f = 0.30 (SiO_2, Hexane/EtOAc = 7:3); **m.p** = 152-153 °C (Lit[1] 151-154 °C); **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.72 (s, 1H; NH), 7.56 (d, ^3J = 8.4 Hz, 2H;), 7.64-7.54 (m, 4H; 5-H, 6-H and 8-H 9-H), 2.20 (s, 3H; 1-H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 168.80 (C-2), 140.95 (C-4), 126.25 (q, J = 3.6 Hz, C-6 and C-8), 126.22 (q, J = 32 Hz, C-7), 122.70 (q, J = 270 Hz, C-10), 119.38 (C-5 and C-9), 24.65 (C-1) ppm; **HRMS** (EI-QTOF, $[M+H]^+$) calculated for $C_9H_9F_3NO$: 204.0636; found: 204.0632.

Synthesis of *N*-(2-nitrophenyl)acetamide (**3p**); According to the general procedure, reaction between 2-nitroaniline (**1p**) (1.0 mmol, 138 mg) and acetylacetone (**2a**) (1.2 mmol, 120 mg) were performed using 10 mol% TEMPO (15.6 mg) and NaO^{t}Bu (2.0 mmol, 192 mg) to obtain the desired *N*-(2-nitrophenyl)acetamide (**3p**) in 55% (99 mg, Scheme 2) yield as yellow solid.

***N*-(2-nitrophenyl)acetamide** (**3p**)[1]; **Yellow solid**; R_f = 0.30 (SiO_2, Hexane/EtOAc = 7:3); **m.p** = 91-93 °C (Lit[1] 90-92 °C); **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 10.31 (s, 1H; NH), 8.75 (d, ^3J = 8

Hz, 1H; 9-H), 8.20 (dd, ^3J = 8 Hz, 1H; 6-H), 7.63 (td, ^3J = 8 Hz, 1H; 8-H), 7.17 (t, ^3J = 8 Hz, 1H; 7-H), 2.29 (s, 3H; 1-H), ppm; **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 169.07 (C-2), 136.33 (C-5), 135.97 (C-4), 134.85 (C-8), 125.71 (C-6), 123.22 (C-7), 122.21 (C-9), 25.67 (C-1) ppm; **HRMS** (EI-QTOF, $[M+H]^+$) calculated for $C_8H_9N_2O_3$: 181.0613; found: 181.0609.

Synthesis of *N*-(4-nitrophenyl)acetamide (**3q**); According to the general procedure, reaction between 4-nitroaniline (**1q**) (1.0 mmol, 138 mg) and acetylacetone (**2a**) (1.2 mmol, 120 mg) were performed using 10 mol% TEMPO (15.6 mg) and NaO^{t}Bu (2.0 mmol, 192 mg) to obtain the desired *N*-(4-nitrophenyl)acetamide (**3q**) in 50% (90 mg, Scheme 2) yield as yellow solid.

***N*-(4-nitrophenyl)acetamide** (**3q**)[1]; **Yellow solid**; R_f = 0.30 (SiO_2, Hexane/EtOAc = 7:3); **m.p =** 145-147 °C (Lit[1] 146-147 °C); **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 8.20 (d, ^3J = 8 Hz, 2H; 6-H and 8-H), 7.76 (brs, 1H; NH), 7.70 (d, ^3J = 8 Hz, 2H; 5-H and 9-H), 2.23 (s, 3H; 1-H) ppm; **HRMS** (EI-QTOF, $[M+H]^+$) calculated for $C_8H_9N_2O_3$: 181.0613; found: 181.0610.

Synthesis of *N*-(4-chloro-2-nitrophenyl)acetamide (**3r**); According to the general procedure, reaction between 4-chloro-2-nitroaniline (**1r**) (1.0 mmol, 172.57 mg) and acetylacetone (**2a**) (1.2 mmol, 120 mg) were performed using 10 mol% TEMPO (15.6 mg) and NaO^{t}Bu (2.0 mmol, 192 mg) to obtain the desired *N*-(4-chloro-2-nitrophenyl)acetamide (**3r**) in 58% (125 mg, Scheme 2) yield as yellow solid.

***N*-(4-chloro-2-nitrophenyl)acetamide** (**3r**)[1]; **Yellow solid**; R_f = 0.35 (SiO_2, Hexane/EtOAc = 7:3); **m.p =** 96- 98 °C (Lit[1] 97-99 °C); **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 10.23 (brs, 1H; NH), 8.76 (d, ^3J = 8.6 Hz, 1H; 9-H), 8.18 (d, ^3J = 4 Hz, 1H; 6-H), 7.59 (dd, ^3J = 8 Hz, 1H; 8-H), 2.29 (s, 3H; 1-H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 168.97 (C-2), 136.38 (C-5), 135.9 (C-8), 133.52 (C-4), 128.36 (C-7), 125.3 (C-6), 123.41 (C-9), 25.59 (C-1) ppm; **HRMS** (EI-QTOF, $[M+H]^+$) calculated for $C_8H_8ClN_2O_3$: 215.0223; found: 215.0218.

Synthesis of 4-Acetamido-benzenesulfonamide (**3s**); According to the general procedure, reaction between sulfanilamide (**1s**) (1.0 mmol, 172 mg) and acetylacetone (**2a**) (1.2 mmol, 120 mg) were performed using 10 mol% TEMPO (15.6 mg) and NaO^{t}Bu (2.0 mmol, 192 mg) to obtain the desired 4-acetamido-benzenesulfonamide (**3s**) in 56% (120 mg, Scheme 2) yield as white crystal.

4-Acetamido-benzenesulfonamide (**3s**)[4]; **White crystal**; R_f = 0.26 (SiO_2, CH_2Cl_2/MeOH = 9.5:0.5); **m.p** = 221-222 °C (Lit[4] 223-224 °C); **^{1}H NMR** (400 MHz, DMSO-d_6) δ = 10.26 (brs, 1H; NH), 7.72 (d, ^3J = 8.0 Hz, 4H; 5-H, 6-H, 8-H and 9-H), 7.23 (s, 2H; NH_2), 2.08 (s, 3H; 1-H) ppm; **^{13}C NMR** (100 MHz, DMSO-d_6) δ = 168.97 (C-2), 142.2 (C-4), 138.07 (C-7), 126.68 (C-6 and C-8), 118.43 (C-5 and C-9), 24.12 (C-1) ppm; **HRMS** (EI-QTOF, $[M+H]^+$) calculated for $C_8H_{11}N_2O_3S$: 215.0490; found: 215.0483.

Synthesis of *N*-(2-hydroxyphenyl)acetamide (**3t**); According to the general procedure, reaction between 2-aminophenol (**1t**) (1.0 mmol, 109 mg) and acetylacetone (**2a**) (1.2 mmol, 120 mg) were performed using 10 mol% TEMPO (15.6 mg) and NaO^{t}Bu (2.0 mmol, 192 mg) to obtain the desired *N*-(2-hydroxyphenyl)acetamide (**3t**) in 78% (118 mg, Scheme 2) yield as pale yellow solid.

***N*-(2-hydroxyphenyl)acetamide** (**3t**)[5]; **Pale yellow solid**; R_f = 0.4 (SiO_2, Hexane/EtOAc = 6:4); **m.p** = 217-218 °C (Lit[5] 218-220 °C); **^{1}H NMR** (400 MHz, DMSO-d_6) δ = 9.75 (brs, 1H; NH), 9.30 (brs, 1H; OH), 7.67 (d, ^3J = 8.0 Hz, 1H; 9-H), 6.93 (t, ^3J = 7.9 Hz, 1H; 7-H), 6.84 (d, ^3J = 8.0 Hz, 1H; 6-H), 6.75 (t, ^3J = 8.0 Hz, 1H; 8-H), 2.09 (s, 3H; 1-H) ppm; **^{13}C NMR** (100 MHz, DMSO-d_6) δ = 169.49 (C-2), 148.36 (C-5), 126.89 (C-4), 125.06 (C-7), 122.78 (C-8), 119.37 (C-9), 116.38 (C-6), 24.06 (C-1) ppm; **HRMS** (EI-QTOF, $[M+H]^+$) calculated for $C_8H_{10}NO_2$: 152.0711; found: 152.0708.

Synthesis of *N*-methyl-*N*-phenylacetamide (**3u**); According to the general procedure, reaction between *N*-methylaniline (**1u**) (1.0 mmol, 107 mg) and acetylacetone (**2a**) (1.2 mmol, 120 mg) were performed using 10 mol% TEMPO (15.6 mg) and NaO^{t}Bu (2.0 mmol, 192 mg) to obtain the desired *N*-methyl-*N*-phenylacetamide (**3u**) in 63% (94 mg, Scheme 2) yield as white solid.

***N*-methyl-*N*-phenylacetamide** (**3u**)[6]; **White solid**; R_f = 0.55 (SiO_2, Hexane/EtOAc = 7:3); **m.p** = 108-110 °C (Lit[6] 108-109 °C); **^{1}H NMR** (400 MHz, DMSO-d_6): δ = 7.42 (d, ^3J = 8.0 Hz, 2H; 5-H and 9-H), 7.32 (t, ^3J = 8.0 Hz, 3H; 6-H, 7-H and 8-H), 3.13 (s, 3H; 10-H), 1.74 (s, 3H; 1-H) ppm; **HRMS** (EI-QTOF, $[M+H]^+$) calculated for $C_9H_{12}NO$: 150.0918; found: 150.0913.

Synthesis of *N*-acetyl pyrrolidine: (**3v**); According to the general procedure, reaction between pyrrolidine (**1v**) (1.0 mmol, 71 mg) and acetylacetone (**2a**) (1.2 mmol, 120 mg) were performed using 10 mol% TEMPO (15.6 mg) and NaO^{t}Bu (2.0 mmol, 192 mg) to obtain the desired *N*-acetyl pyrrolidine (**3v**) in 58% (66 mg, Scheme 2) yield as colorless liquid.

***N*-Acetyl pyrrolidine:** (**3v**)[7]; **Colorless liquid**; R_f = 0.2 (SiO_2, CH_2Cl_2/MeOH = 9.5:0.5); **^{1}H NMR** (400 MHz, DMSO-d_6): δ = 3.47-3.40 (m, 4H; 4-H and 7-H), 2.05 (s, 3H; 1-H), 1.99-1.93 (m, 4H; 5-H and 9-H), 1.90-1.83 (m, 4H; 5-H and 6-H) ppm; **^{13}C NMR** (100 MHz, DMSO-d_6) δ = 169.37 (C-2), 47.49 (C-4), 45.62 (C-7), 26.17 (C-5), 24.66 (C-6), 22.53 (C-1) ppm; **HRMS** (EI-QTOF, $[M+H]^+$) calculated for $C_6H_{12}NO$: 114.0918; found: 114.0912.

Synthesis of *N*-acetylpiperidin-4-one: (**3w**); According to the general procedure, reaction between 4-piperidinone (**1w**) (1.0 mmol, 99 mg) and acetylacetone (**2a**) (1.2 mmol, 120 mg) were performed using 10 mol% TEMPO (15.6 mg) and NaO^{t}Bu (2.0 mmol, 192 mg) to obtain the desired *N*-acetylpiperidin-4-one (**3w**) in 53% (75 mg, Scheme 2) yield as colorless liquid.

***N*-acetylpiperidin-4-one:** (**3w**)[8]; **Colorless liquid**; R_f = 0.2 (SiO_2, CH_2Cl_2/MeOH = 9.5:0.5); **^{1}H NMR** (400 MHz, DMSO-d_6): δ = 3.87 (t, *J* = 6.2 Hz, 2H; 4-H), 3.75 (t, *J* = 6.2 Hz, 2H; 8-H), 2.50-2.45 (m, 4H; 5-H and 9-H), 2.18 (s, 3H; 1-H) ppm; **^{13}C NMR** (100 MHz, DMSO-d_6) δ = 206.84 (C-6), 169.45 (C-2), 45.04 (C-4), 41.32 (C-8), 40.89 (C-5), 40.76 (C-7), 21.49 (C-1) ppm; **HRMS** (EI-QTOF, $[M+H]^+$) calculated for $C_7H_{12}NO_2$: 142.0868; found: 142.0864.

5. NMR spectral data

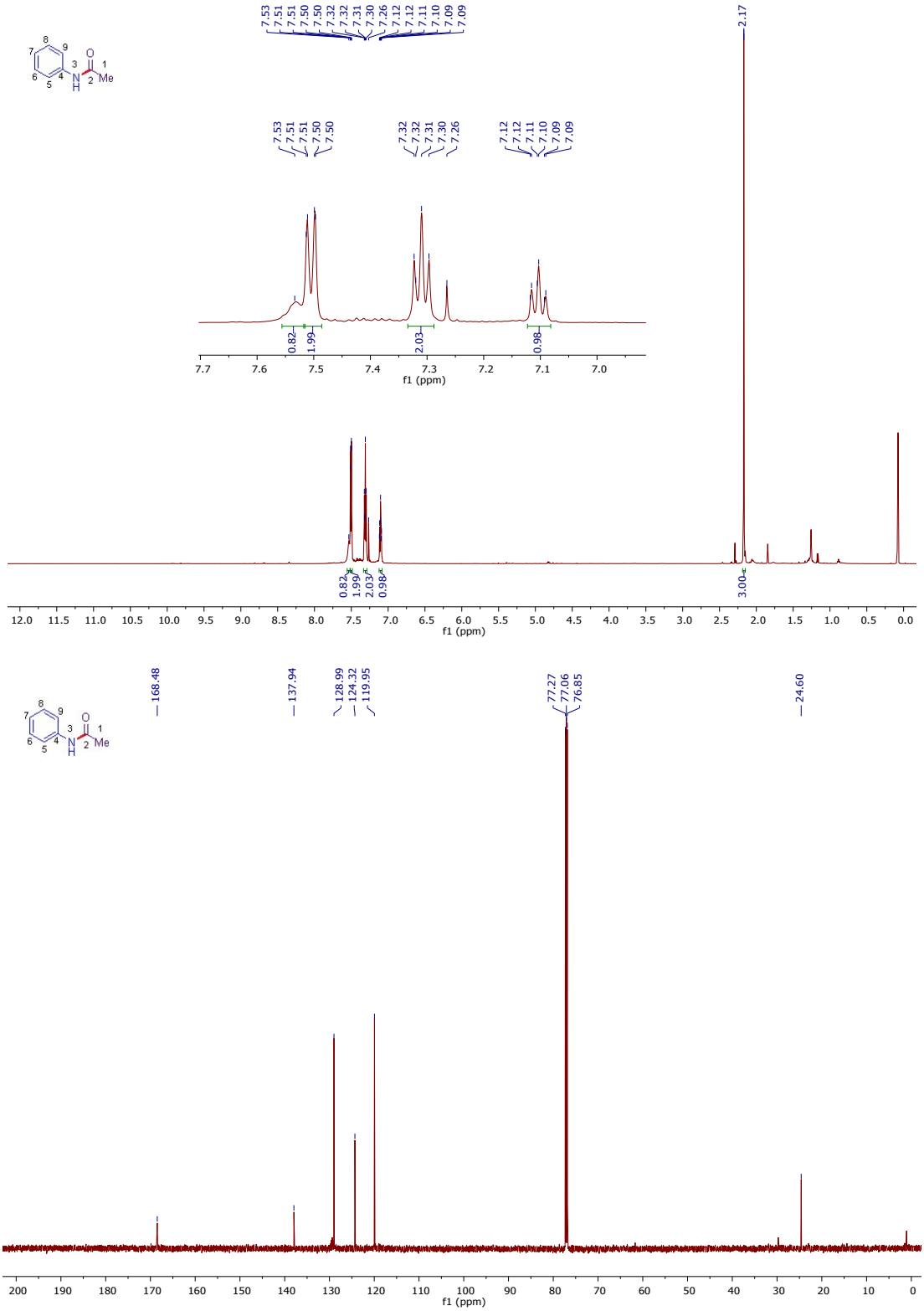


Figure 2. ^{1}H (600 MHz), ^{13}C (150 MHz) NMR spectra of **3a** in $CDCl_3$.

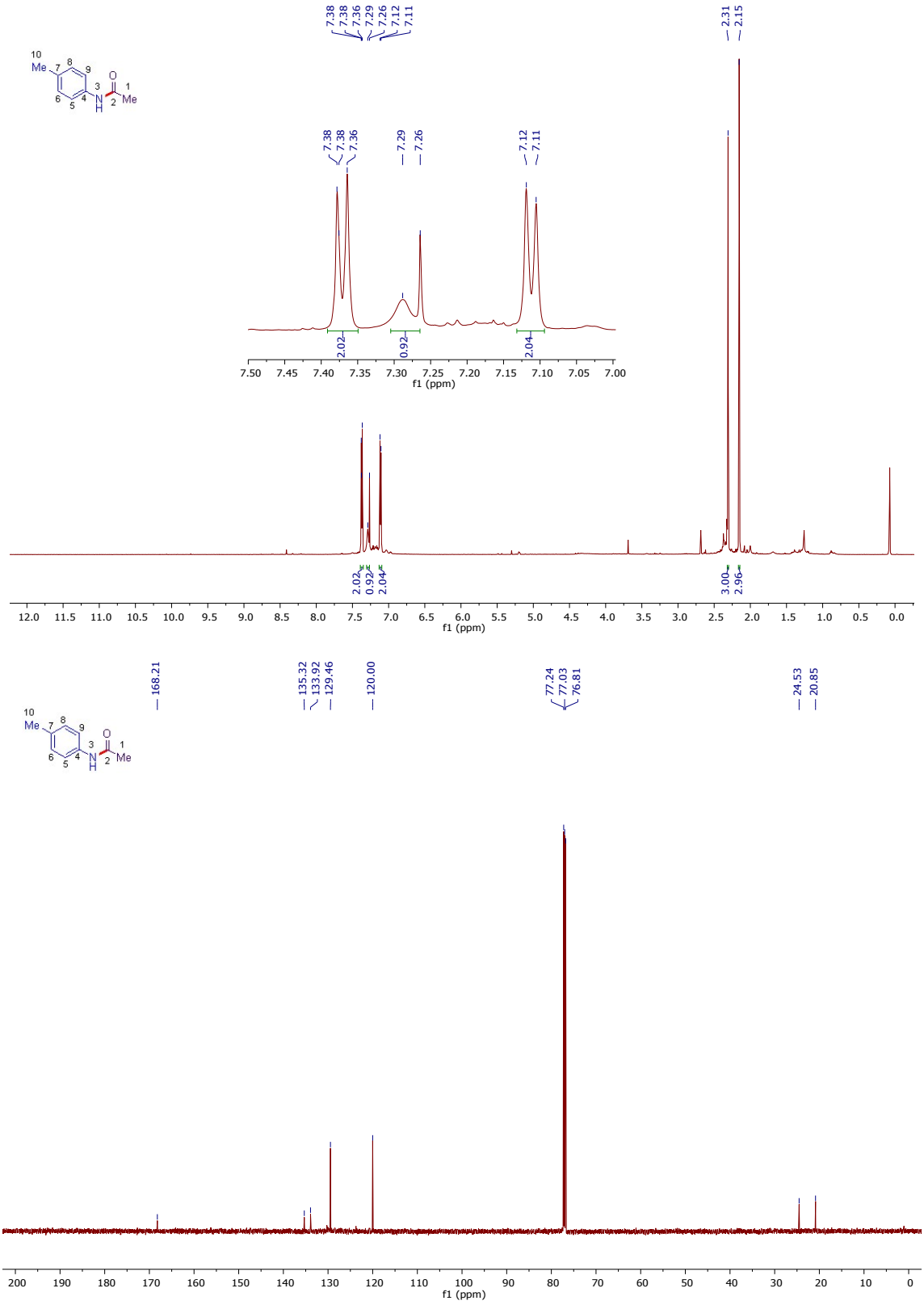


Figure 3. ^{1}H (600 MHz), ^{13}C (150 MHz) NMR spectra of **3b** in $CDCl_3$.

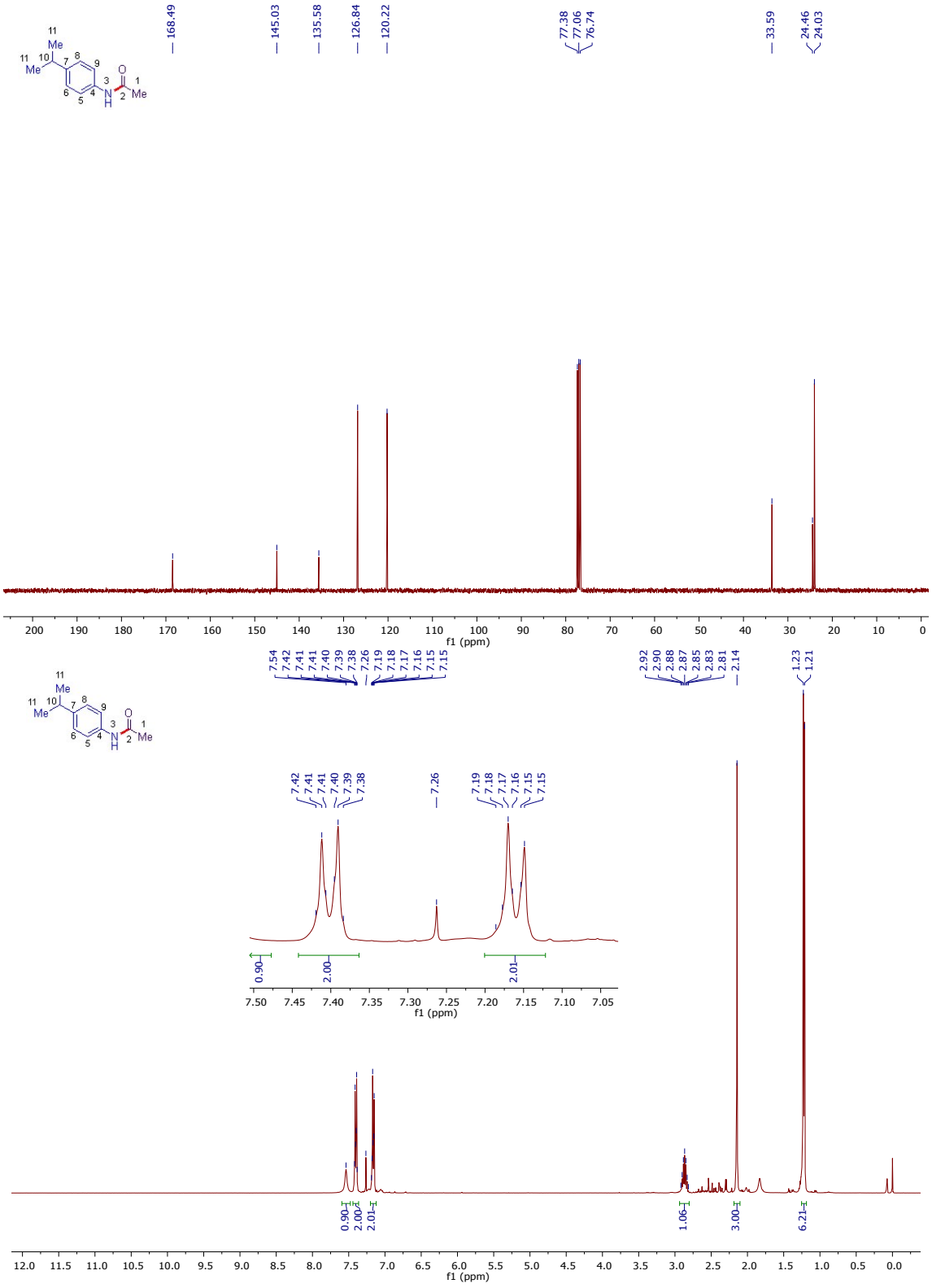


Figure 4. ^{1}H (400 MHz), ^{13}C (100 MHz) NMR spectra of **3c** in $CDCl_3$.

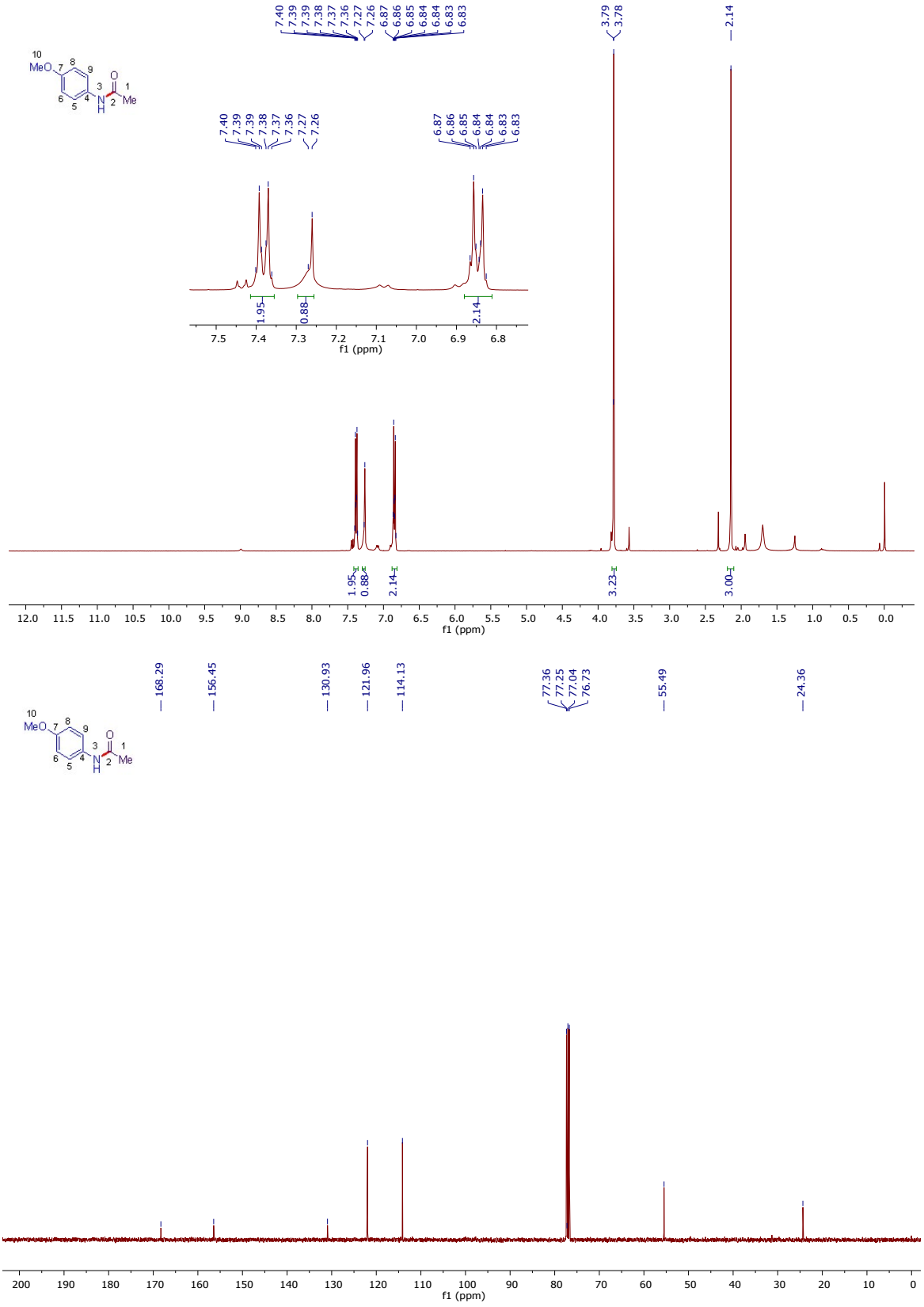


Figure 5. ^{1}H (400 MHz), ^{13}C (100 MHz) NMR spectra of **3d** in $CDCl_3$.

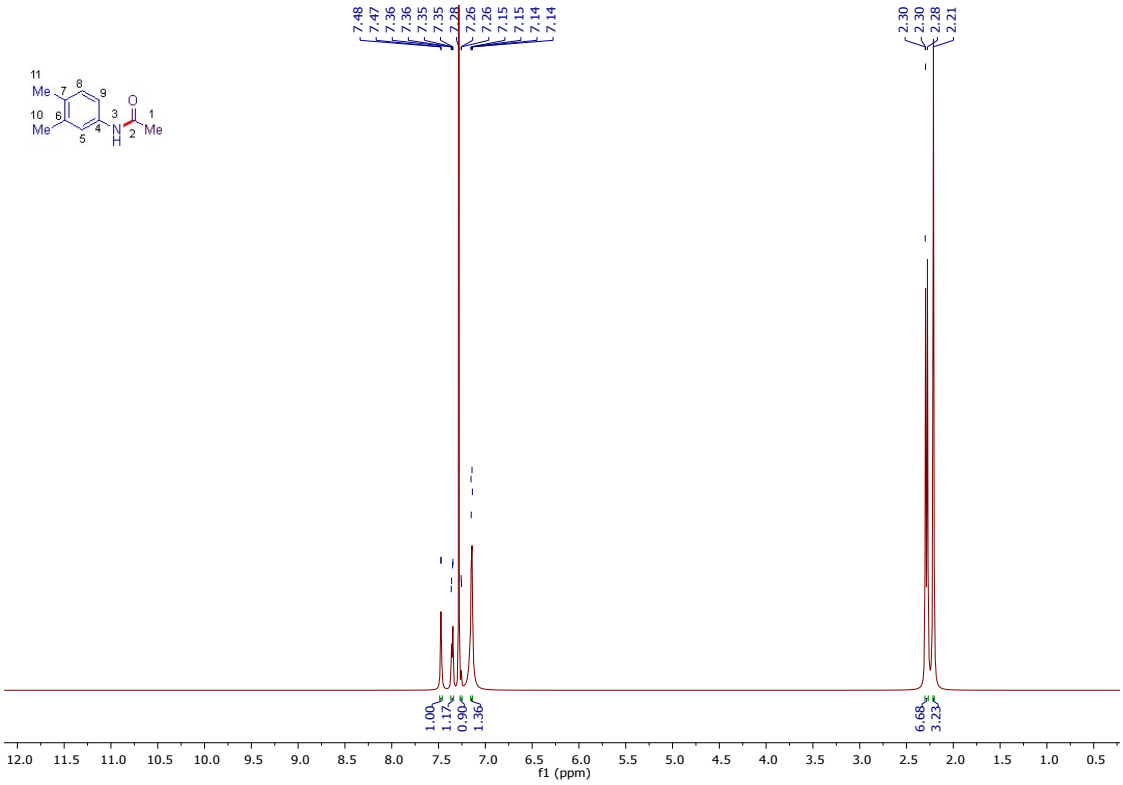
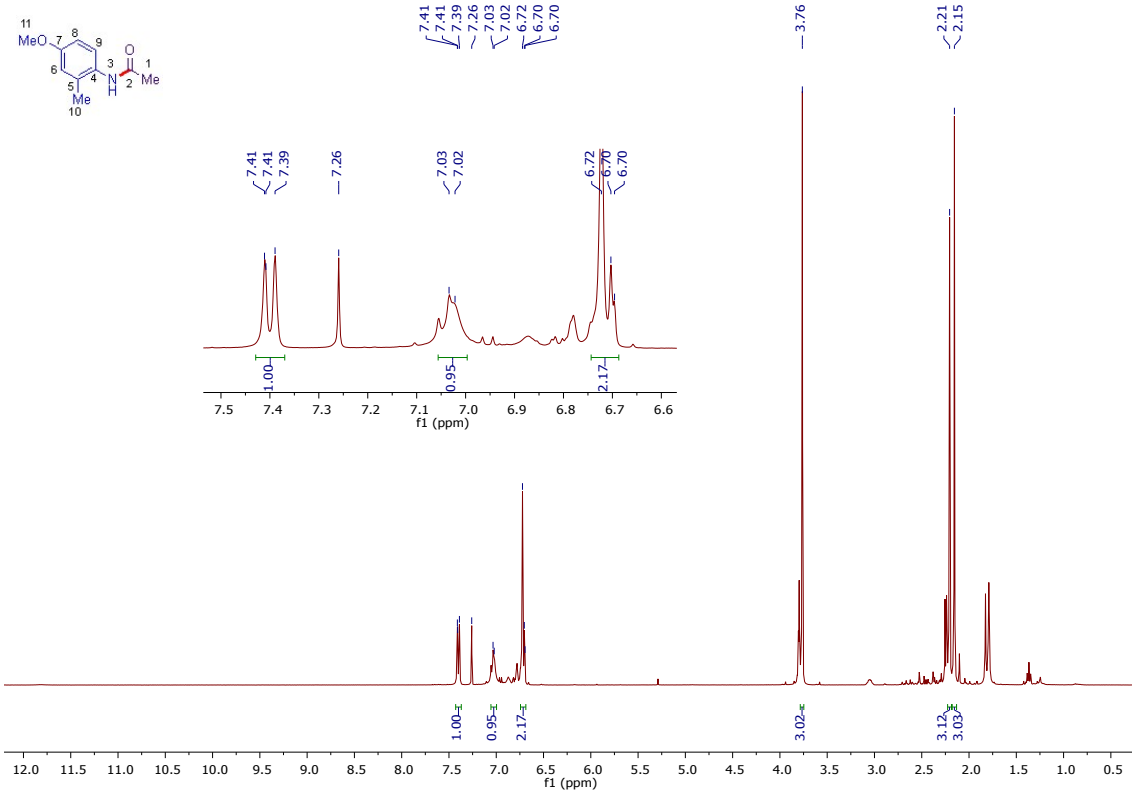


Figure 6. ^{1}H (600 MHz) NMR spectra of **3e** in $CDCl_3$.



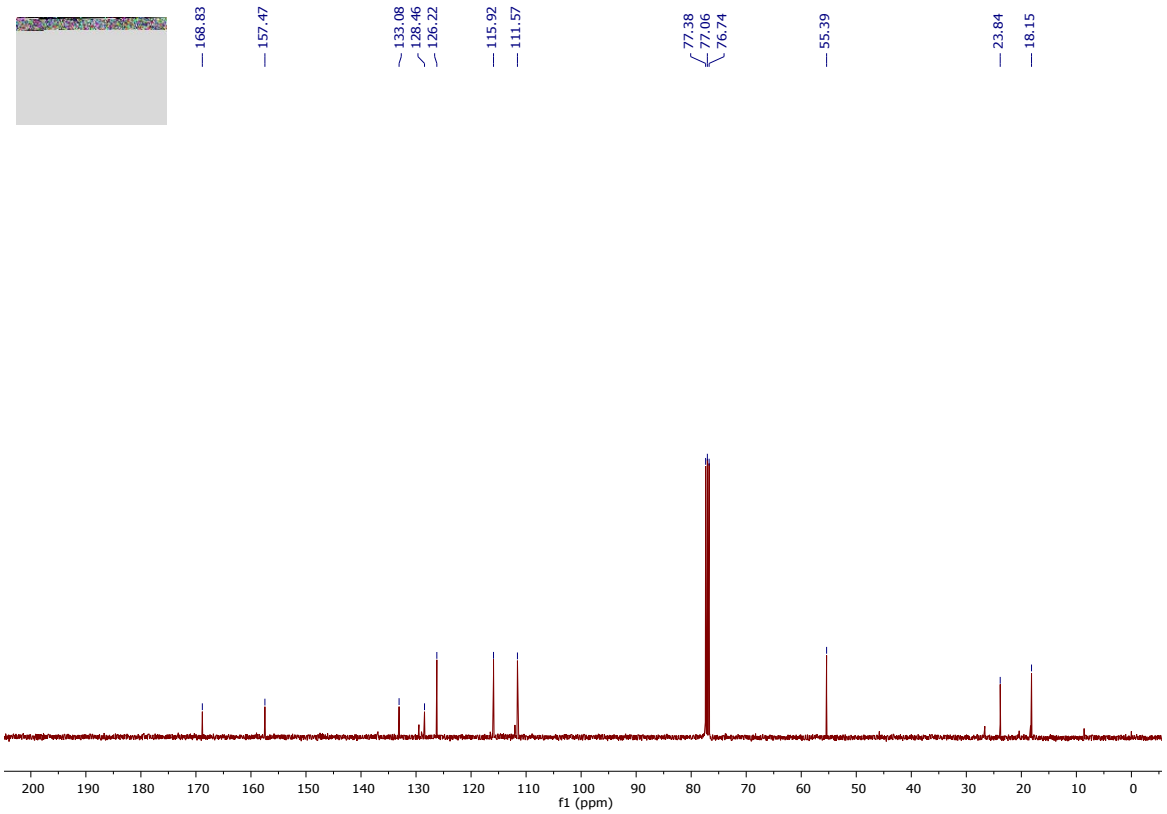
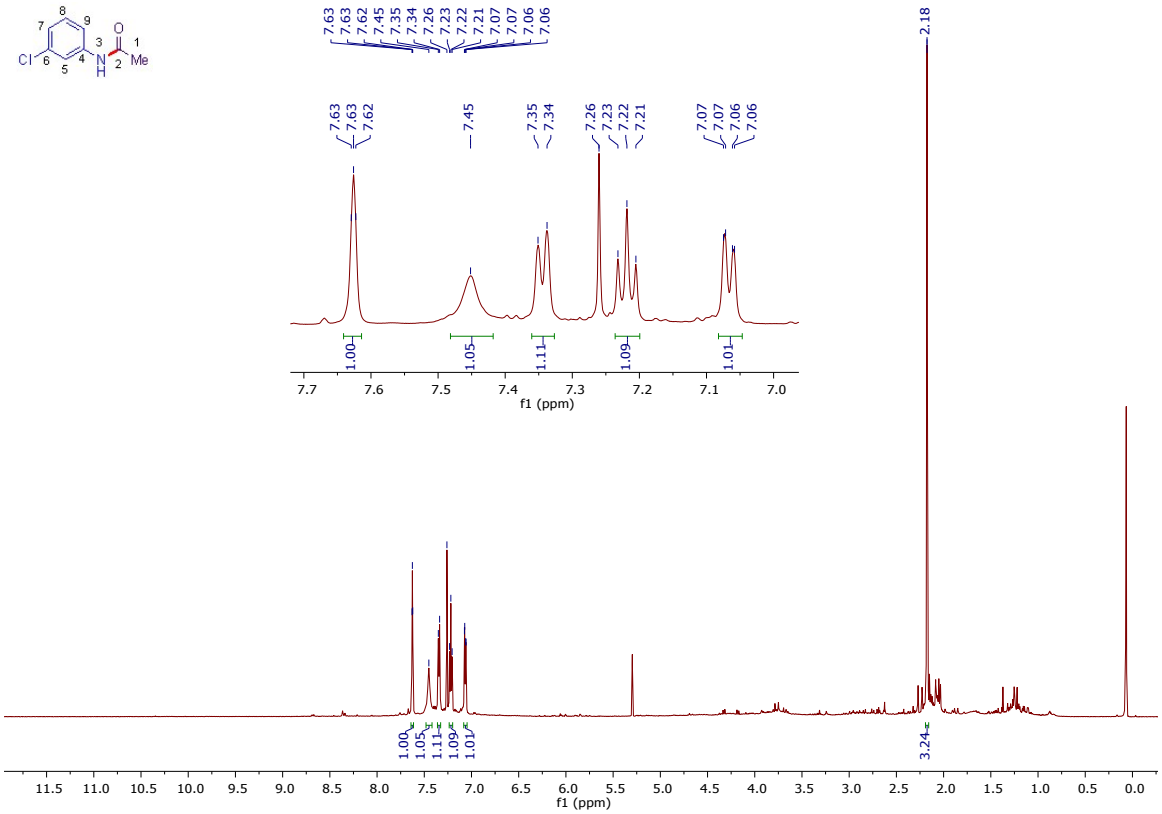


Figure 7. ^{1}H (400 MHz) and ^{13}C (100 MHz) NMR spectra of **3f** in $CDCl_3$.



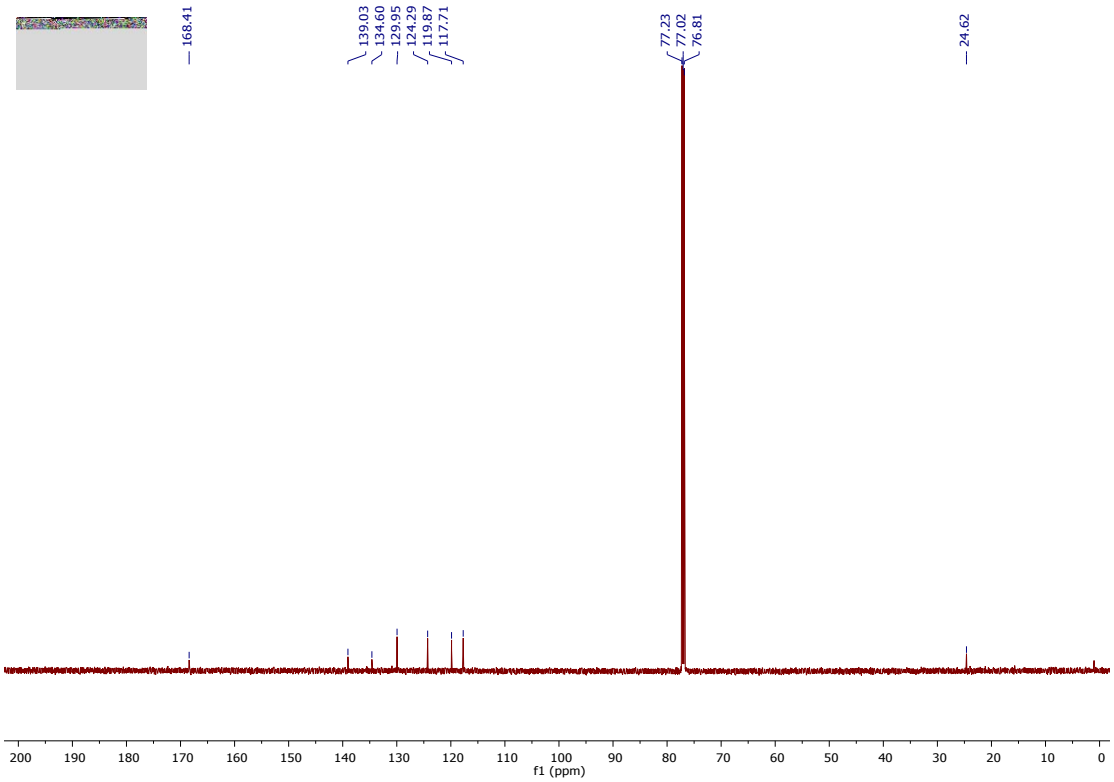
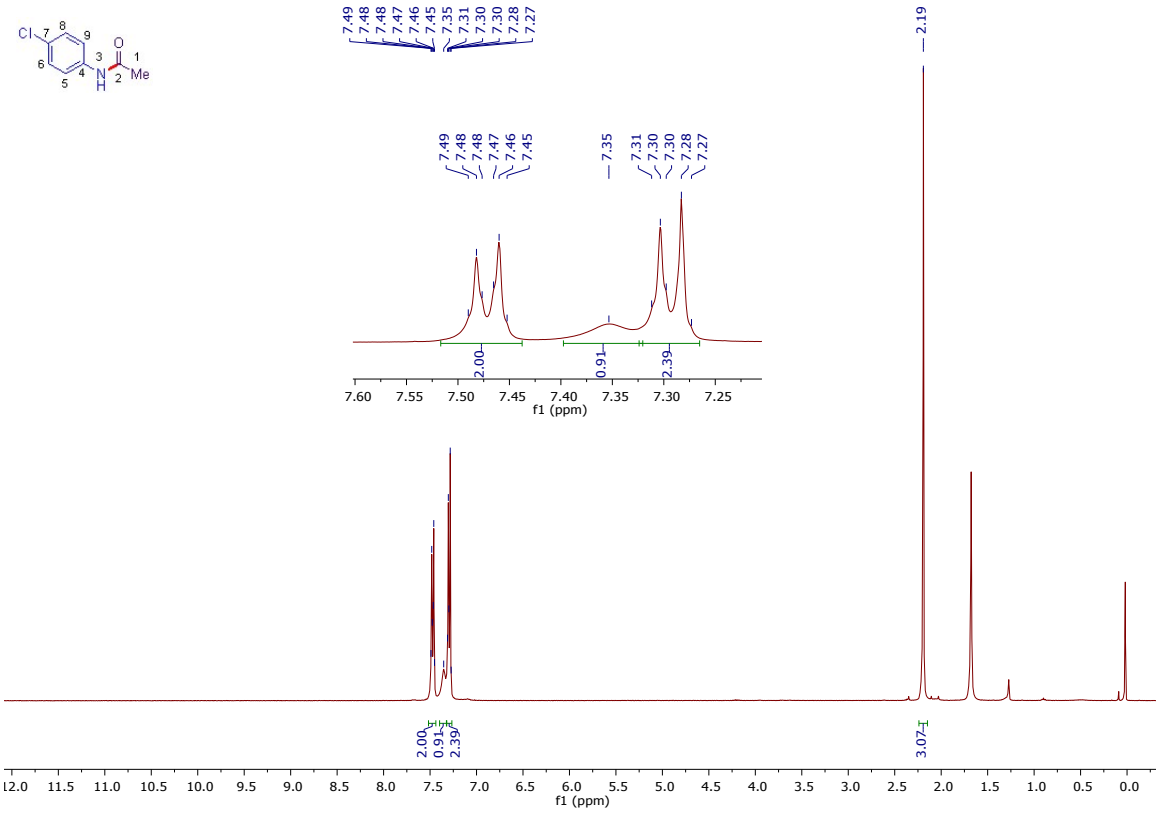


Figure 8. ^{1}H (600 MHz) and ^{13}C (150 MHz) NMR spectra of **3g** in $CDCl_3$.



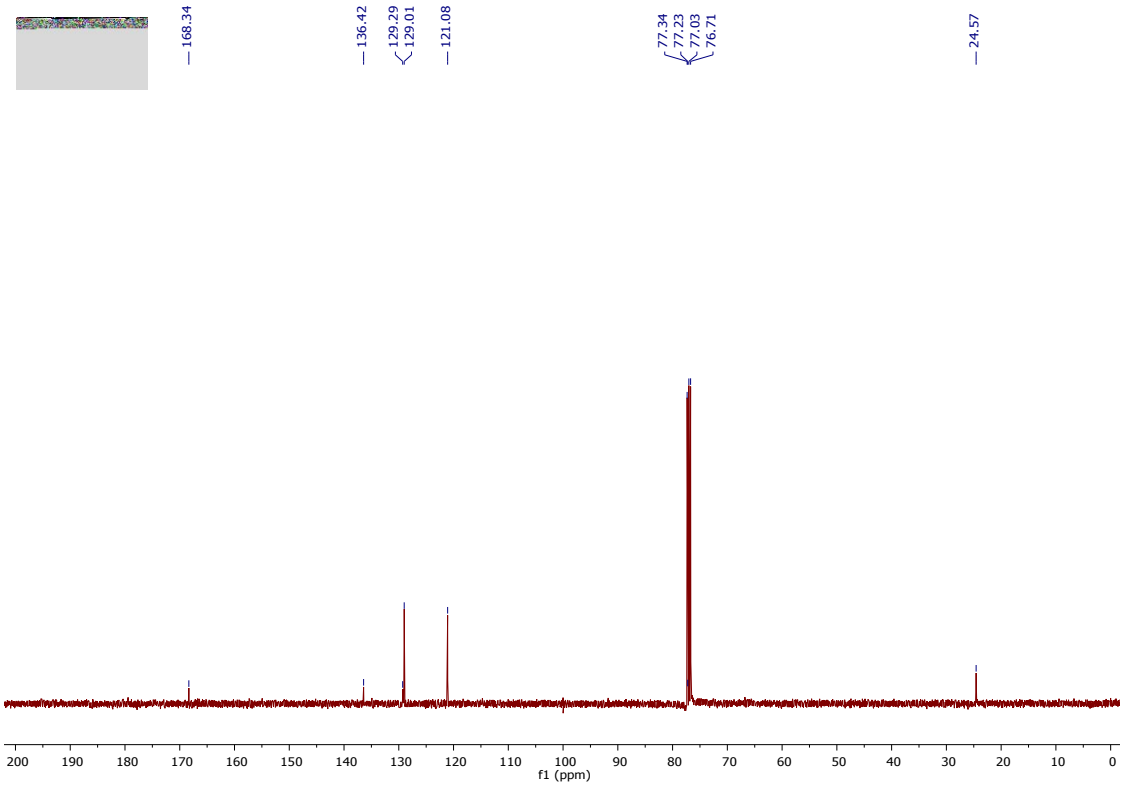


Figure 9. ^{1}H (400 MHz) and ^{13}C (100 MHz) NMR spectra of **3h** in $CDCl_3$.

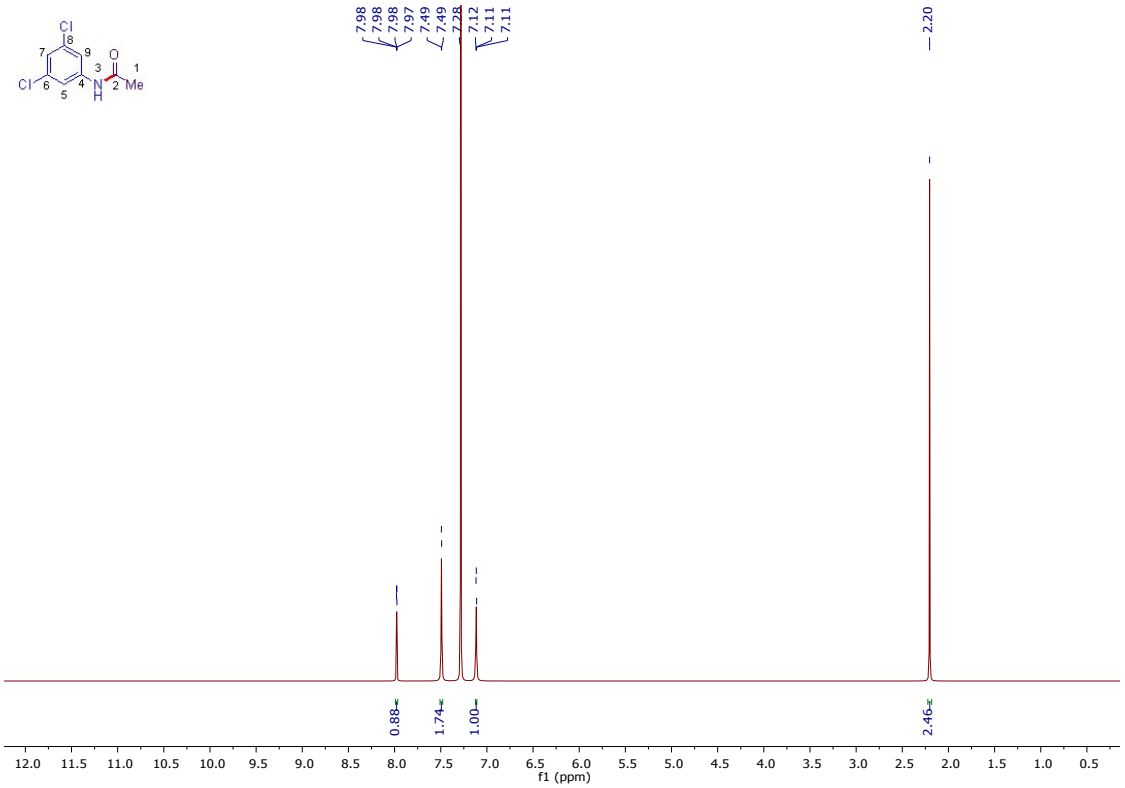


Figure 10. ^{1}H (400 MHz) NMR spectra of **3i** in $CDCl_3$.

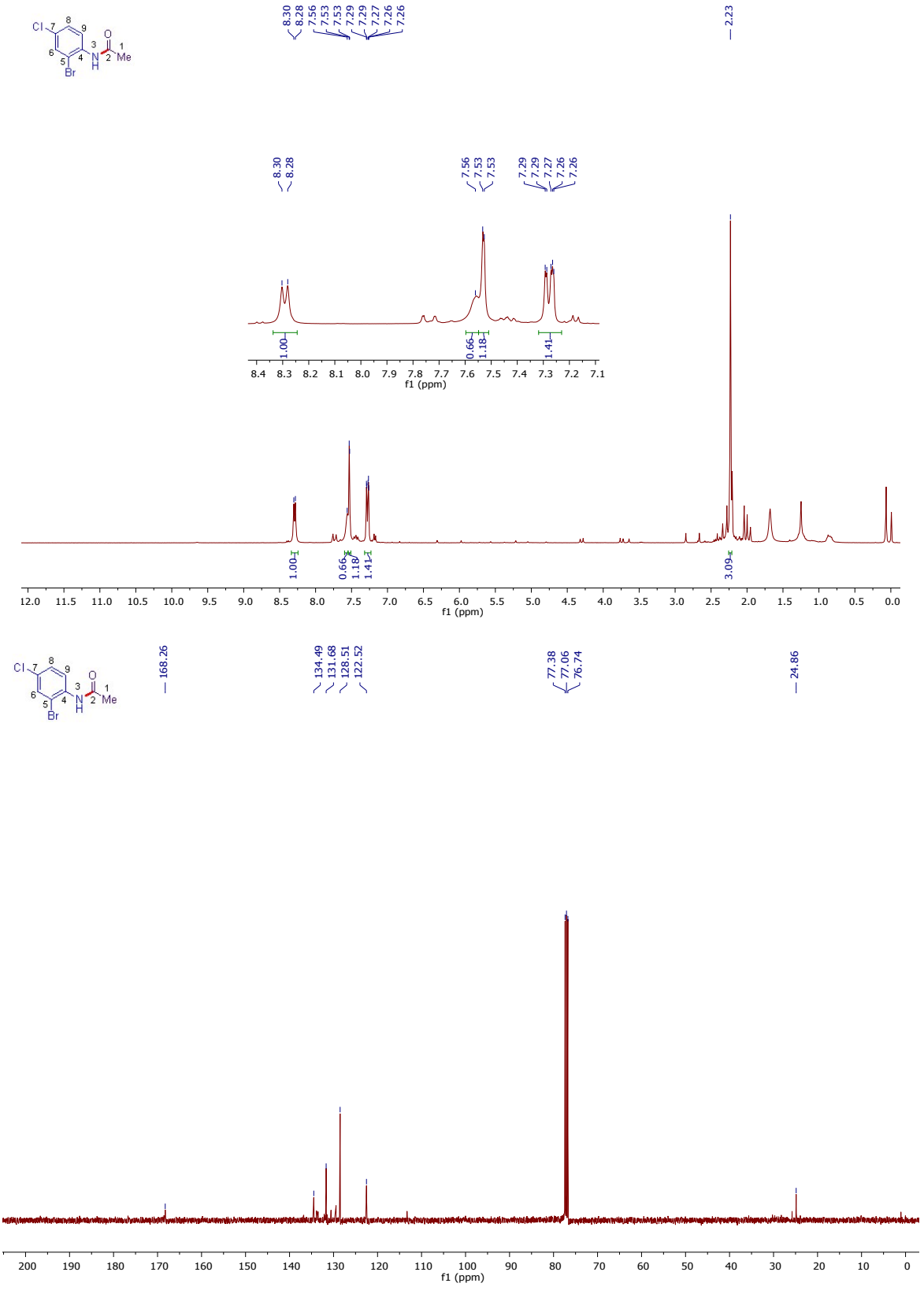


Figure 11. ^{1}H (400 MHz) and ^{13}C (100 MHz) NMR spectra of **3j** in $CDCl_3$.

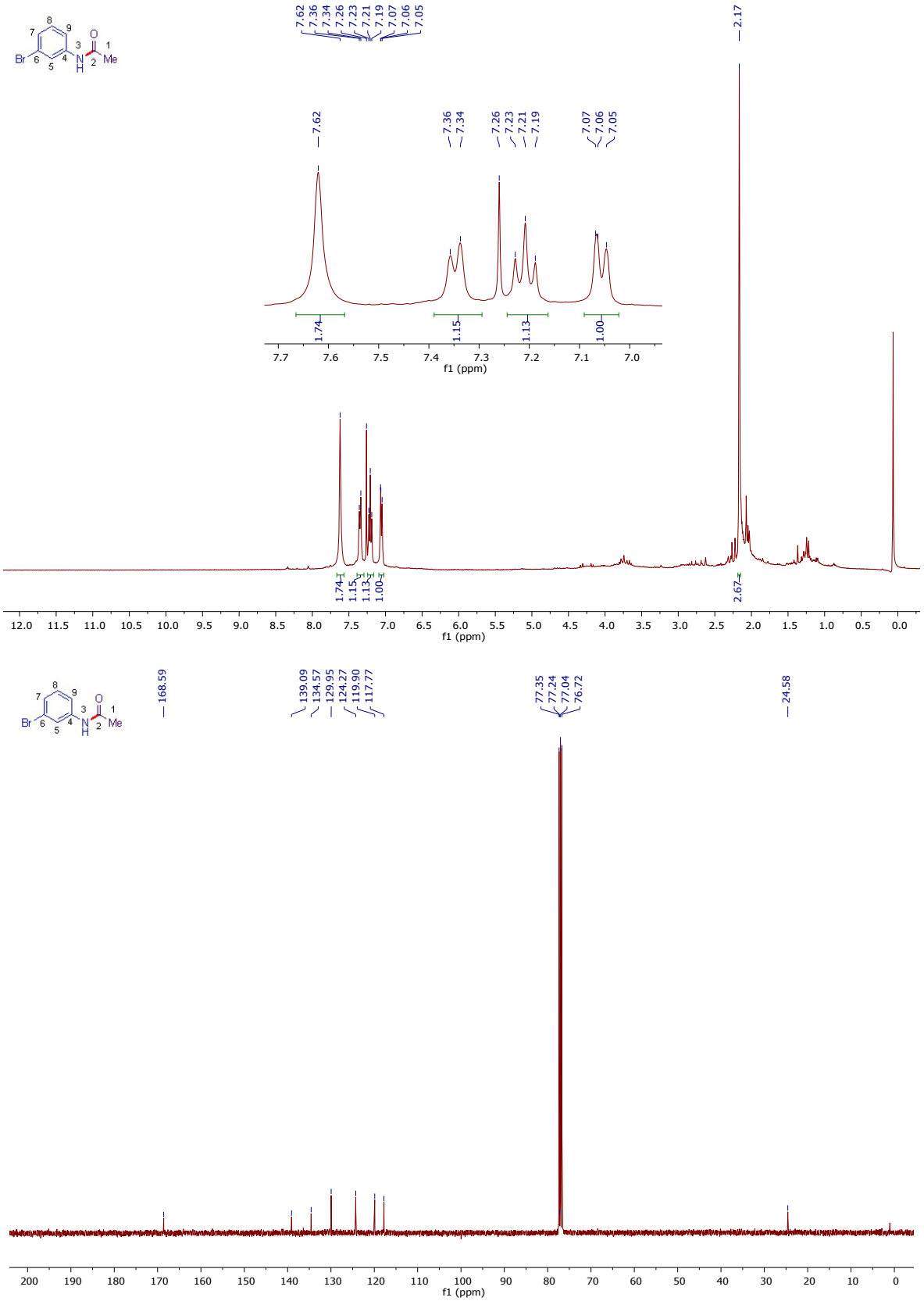


Figure 12. ^{1}H (400 MHz) and ^{13}C (100 MHz) NMR spectra of **3k** in $CDCl_3$.

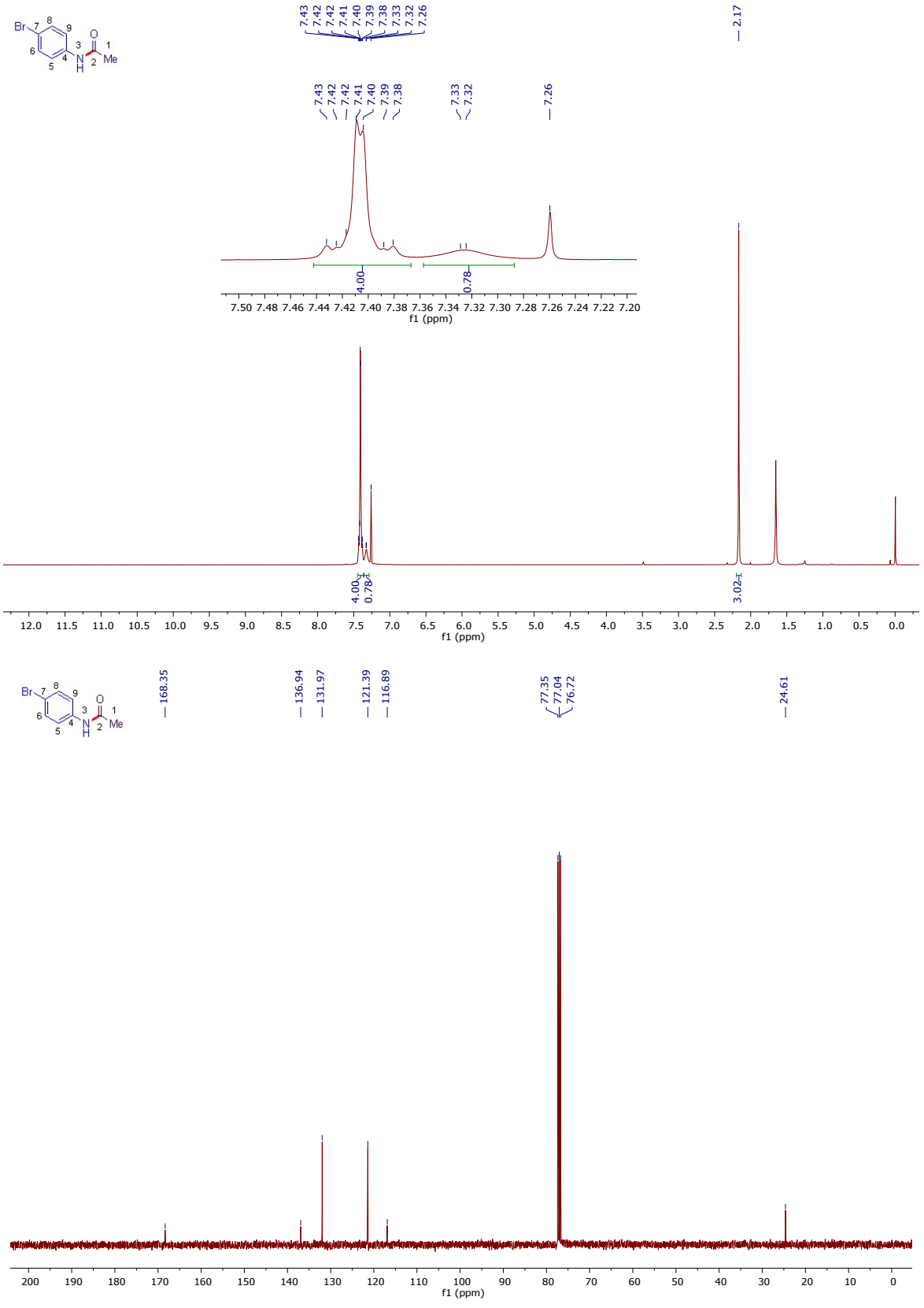


Figure 13. ^{1}H (400 MHz) and ^{13}C (100 MHz) NMR spectra of **3l** in $CDCl_3$.

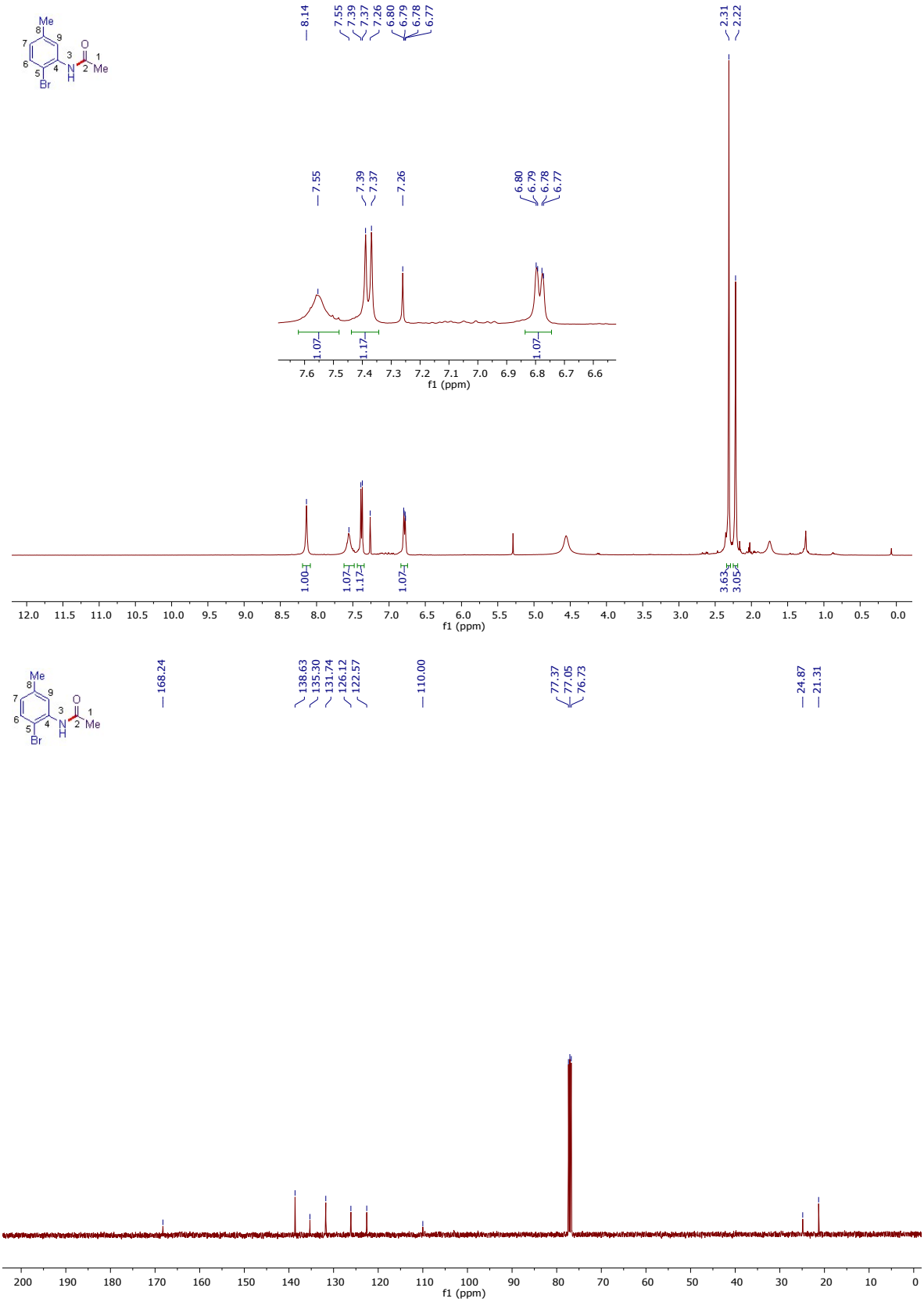


Figure 14. ^{1}H (400 MHz) and ^{13}C (100 MHz) NMR spectra of **3m** in $CDCl_3$

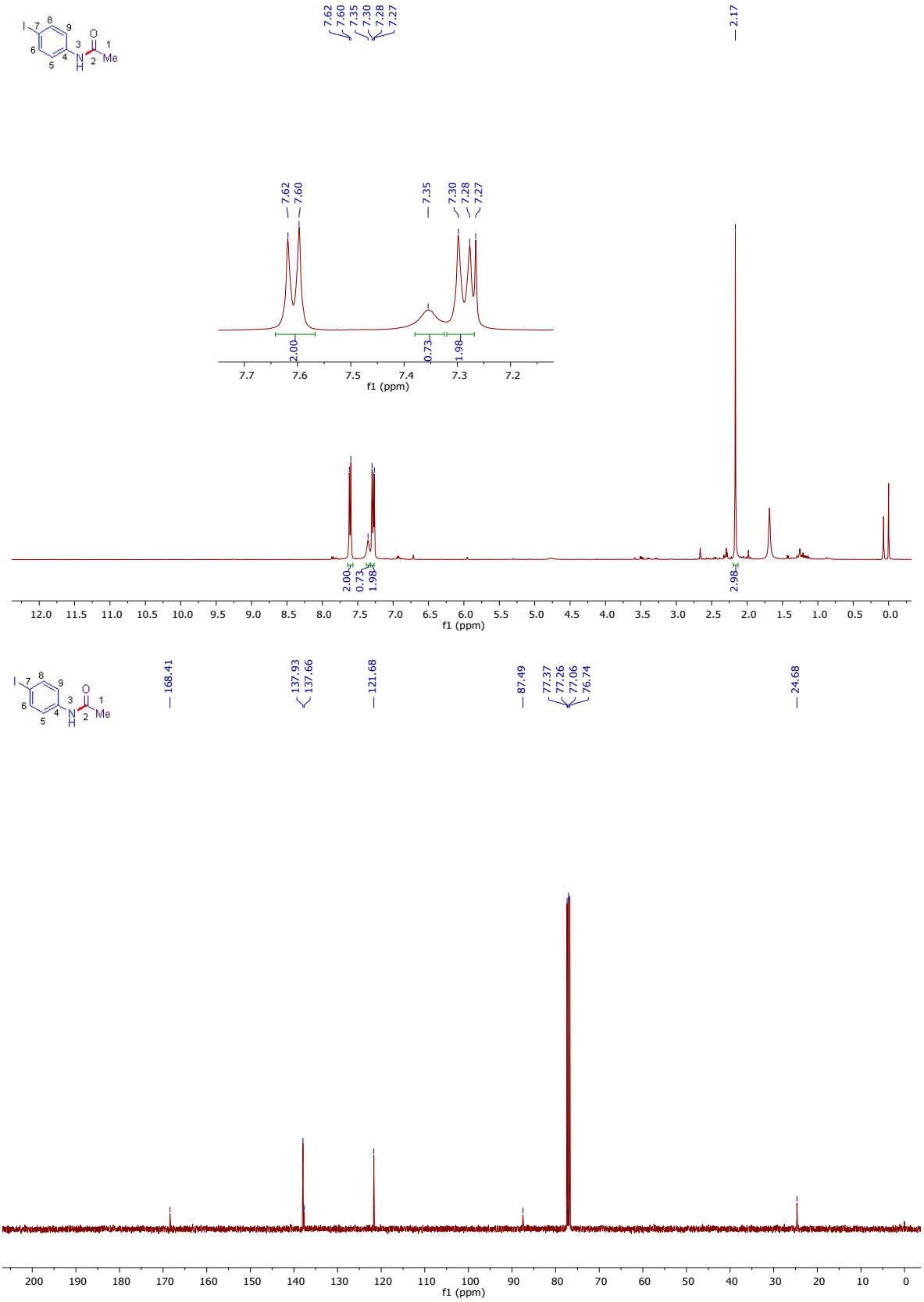


Figure 15. ^{1}H (400 MHz) and ^{13}C (100 MHz) NMR spectra of **3n** in $CDCl_3$.

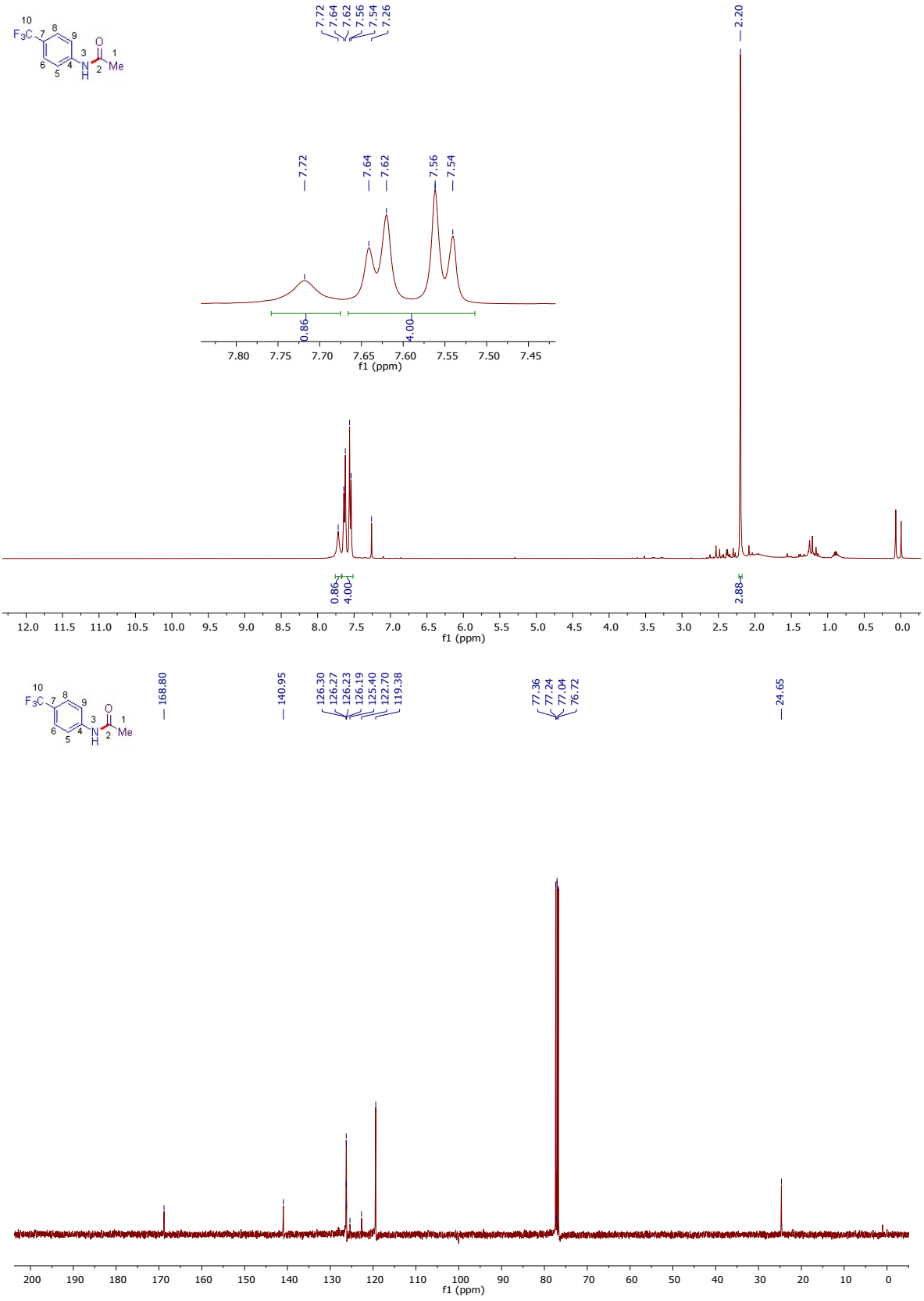
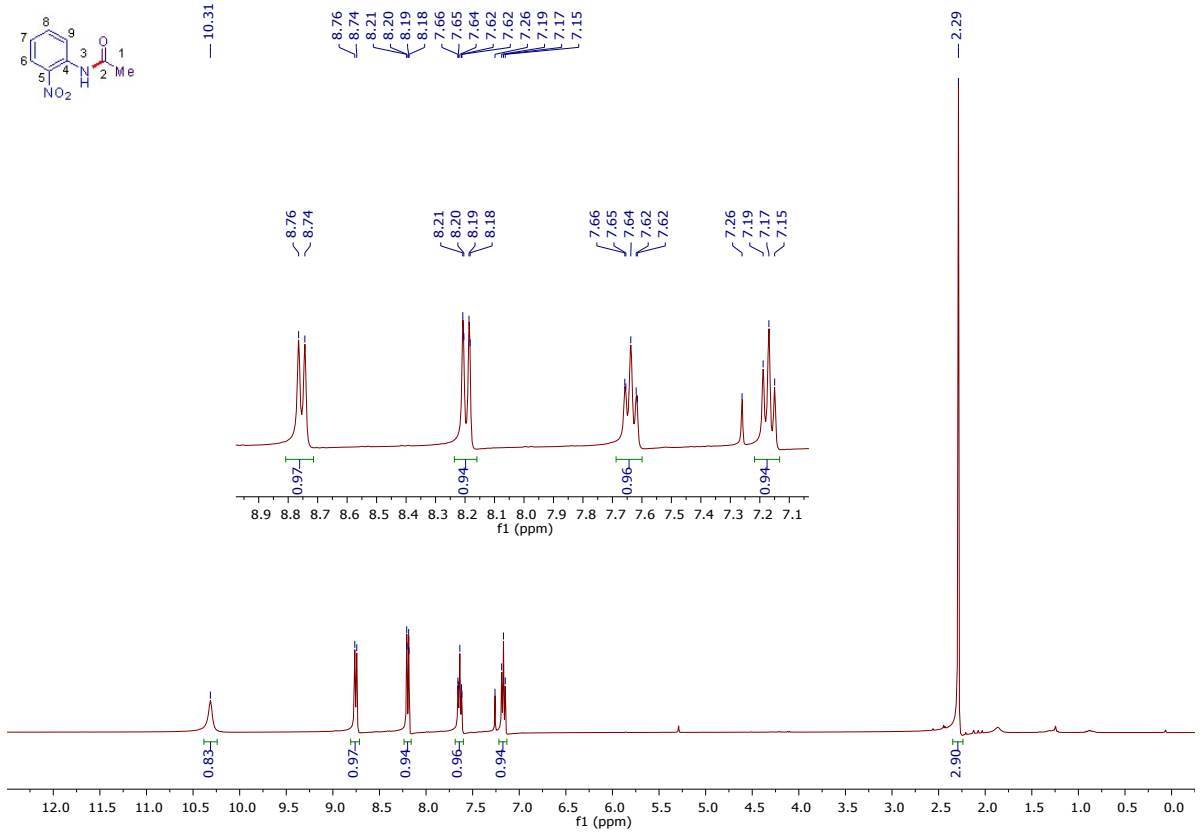


Figure 16. ^{1}H (400 MHz) and ^{13}C (100 MHz) NMR spectra of **3o** in $CDCl_3$.


10.31
8.76
8.74
8.21
8.20
8.19
8.18
7.66
7.65
7.64
7.62
7.62
7.26
7.19
7.17
7.15
2.29
0.97
0.94
0.96
0.94
f1 (ppm)
0.83
0.97
0.94
0.96
0.94
2.90
f1 (ppm)

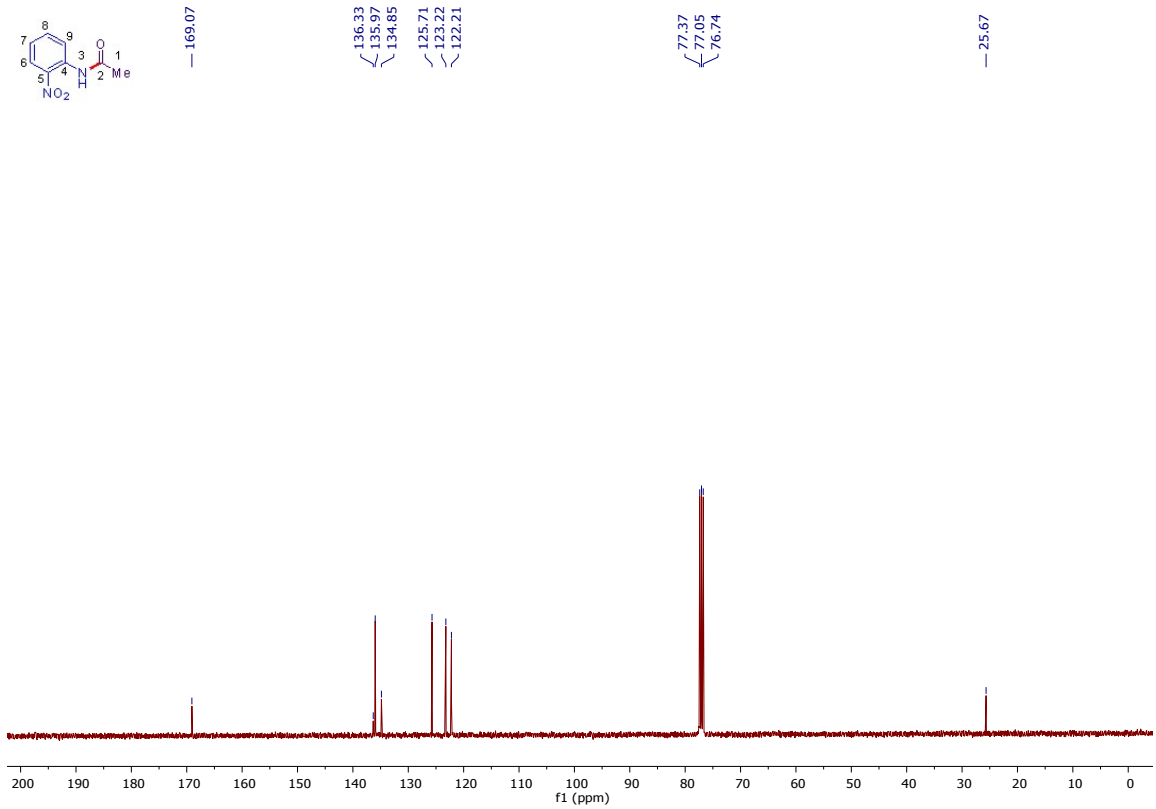

169.07
136.33
135.97
134.85
125.71
123.22
122.21
77.37
77.05
76.74
25.67
f1 (ppm)

Figure 17. ^{1}H (400 MHz) and ^{13}C (100 MHz) NMR spectra of **3p** in $CDCl_3$.

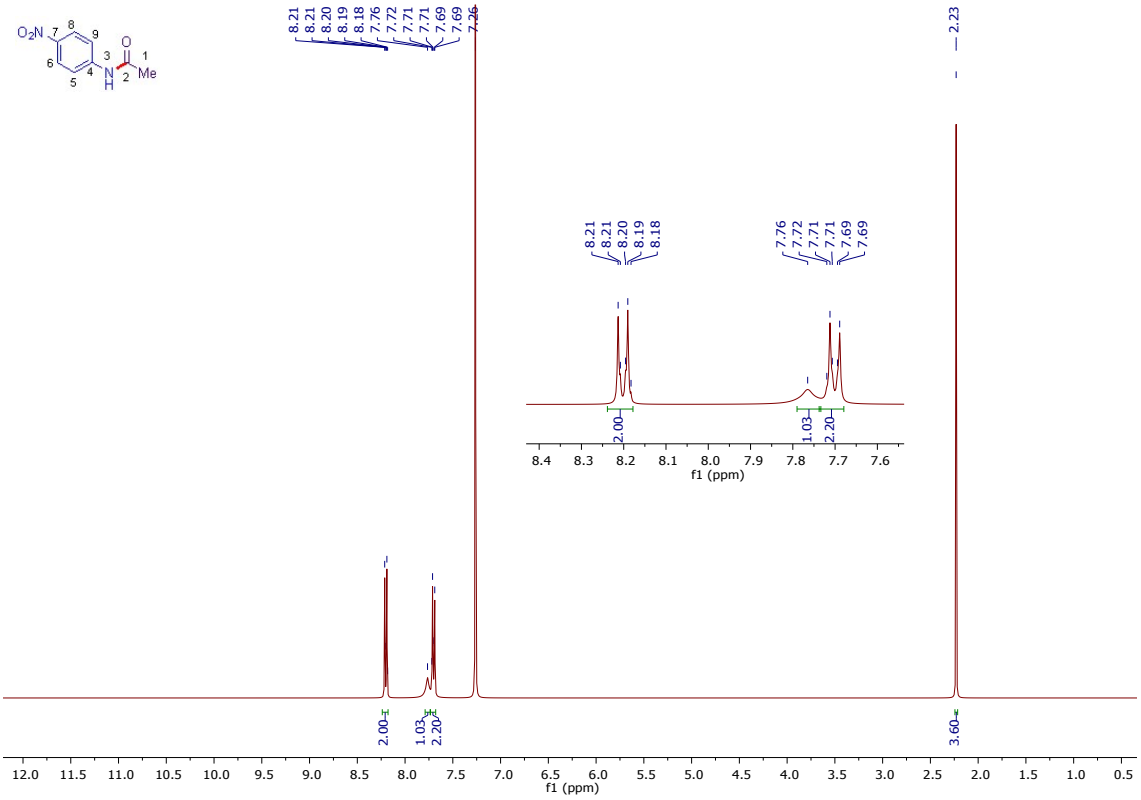


Figure 18. ^{1}H (400 MHz) NMR spectra of **3q** in $CDCl_3$.

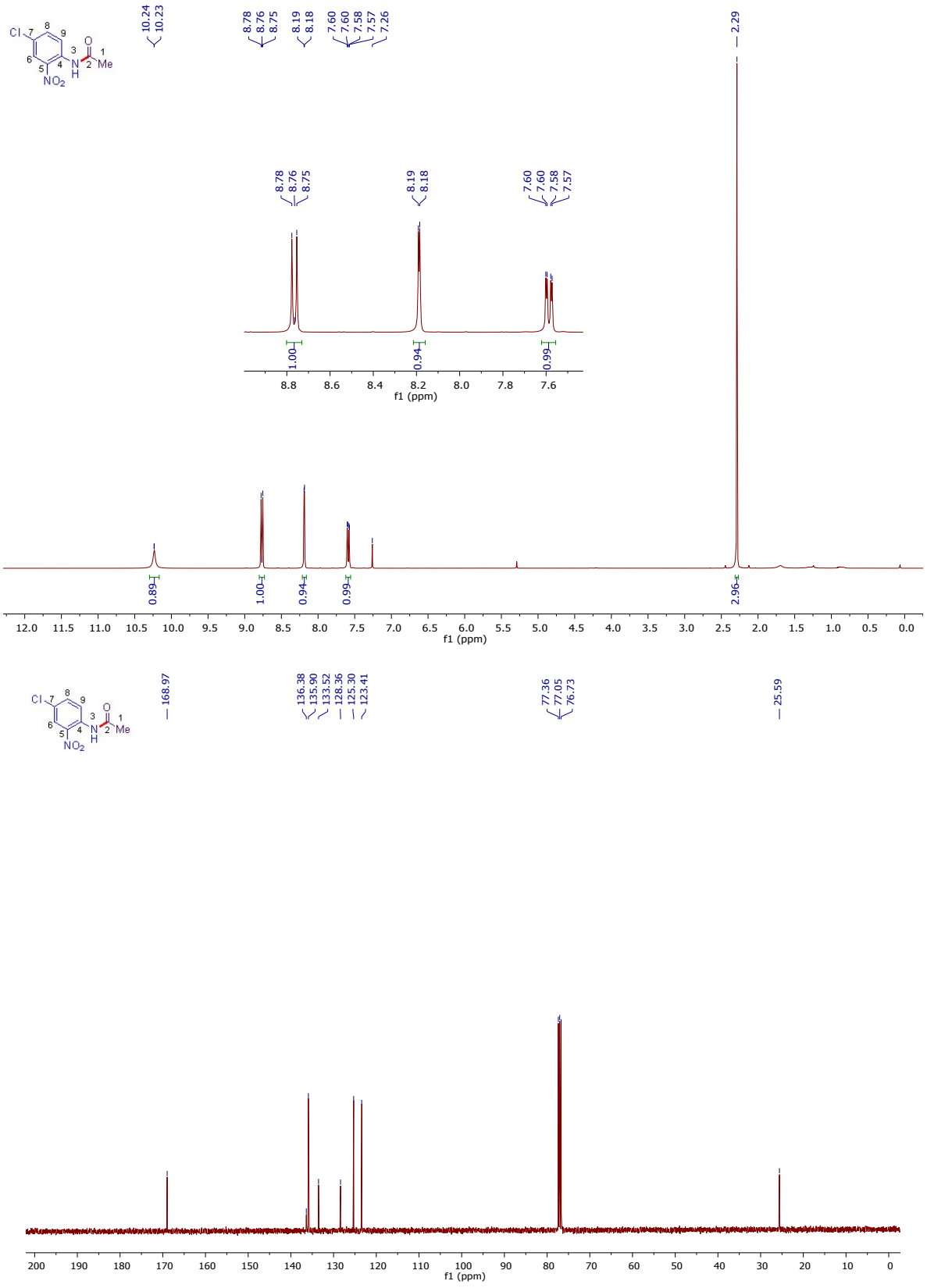
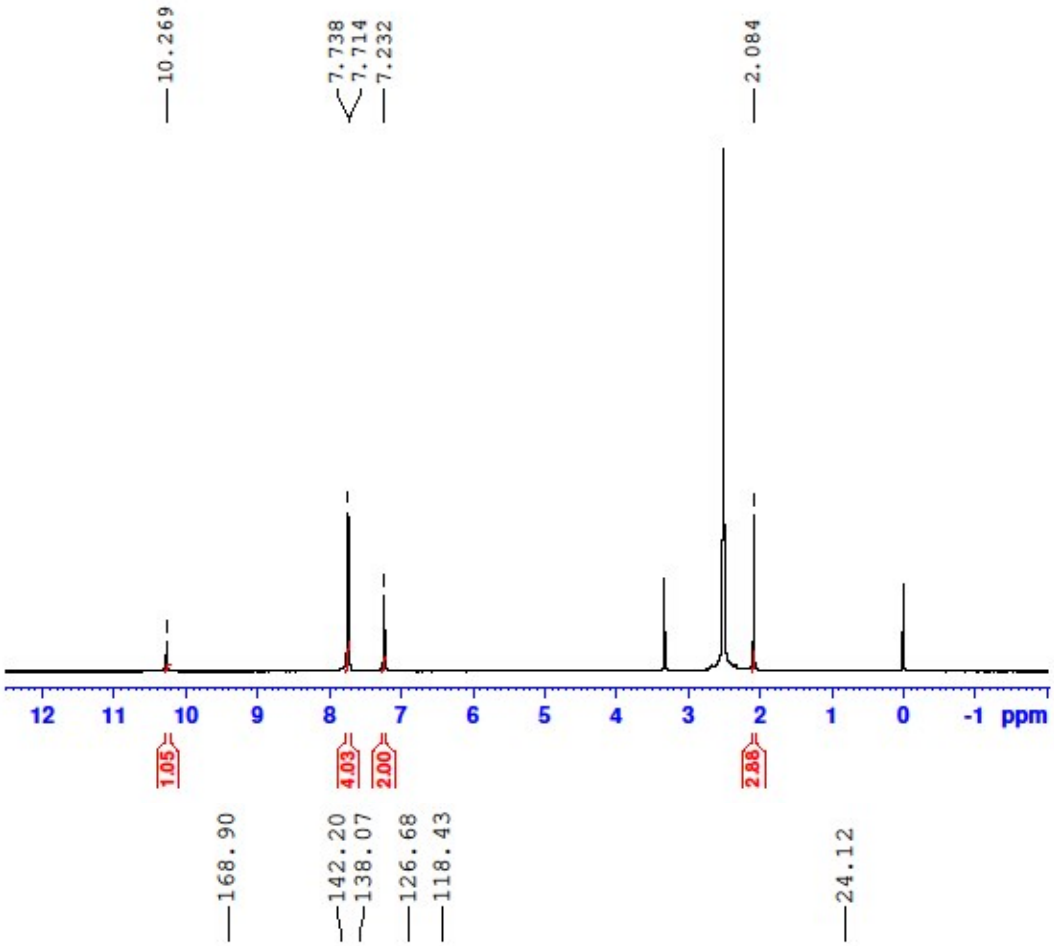


Figure 19. ^{1}H (400 MHz) and ^{13}C (100 MHz) NMR spectra of **3r** in $CDCl_3$.


10.269
7.738
7.714
7.232
2.084
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
ppm
1.05
4.03
2.00
2.86

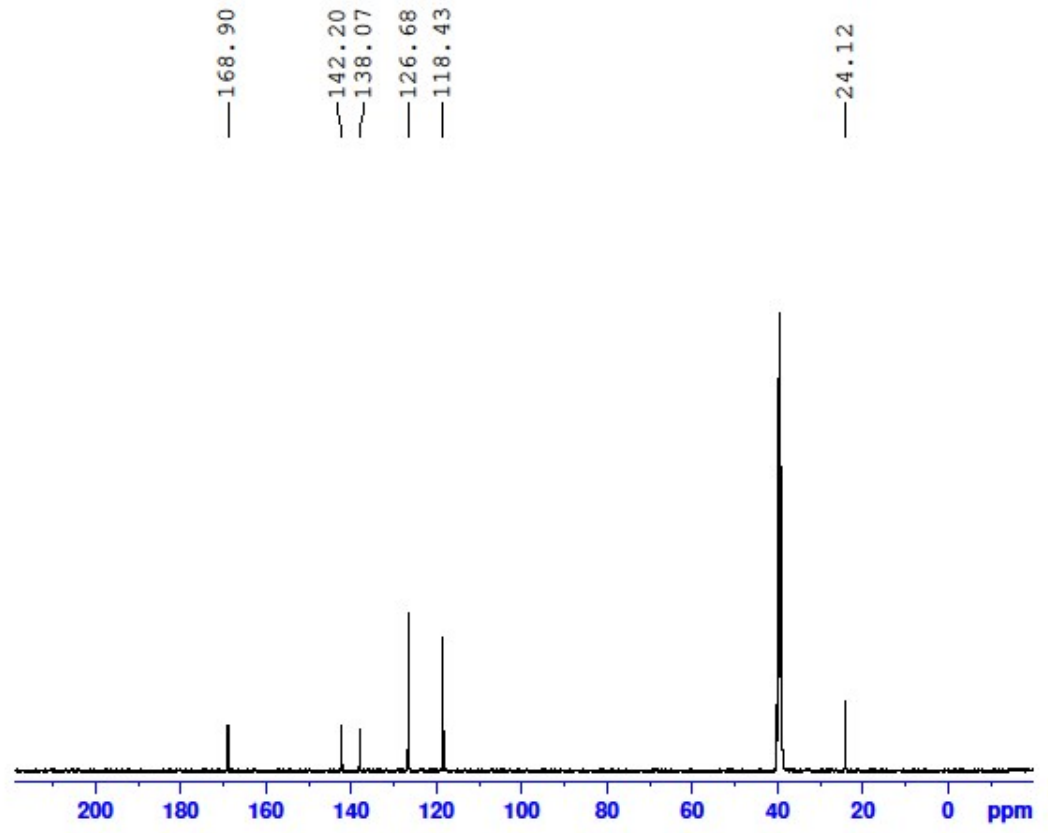
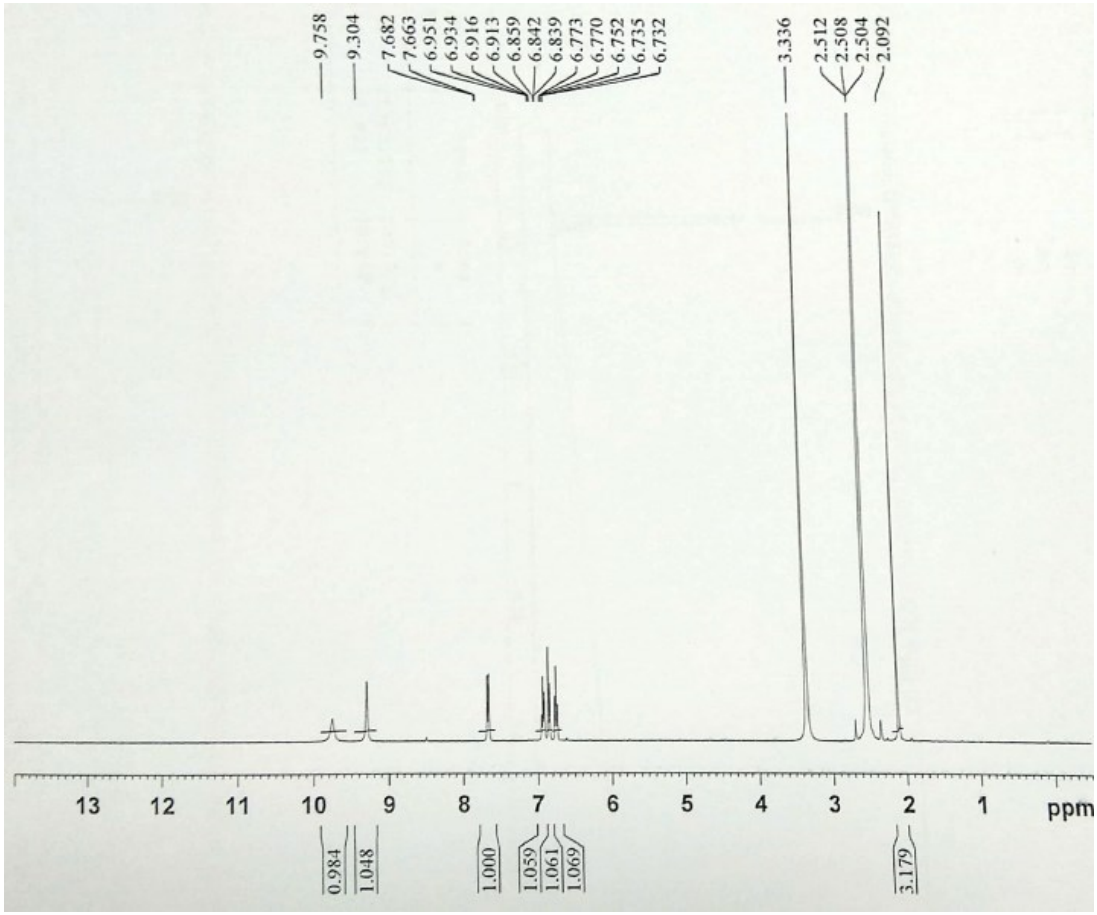

168.90
142.20
138.07
126.68
118.43
24.12
200
180
160
140
120
100
80
60
40
20
0
ppm

Figure 20. ^{1}H (400 MHz) and ^{13}C (100 MHz) NMR spectra of **3s** in DMSO-d_6.



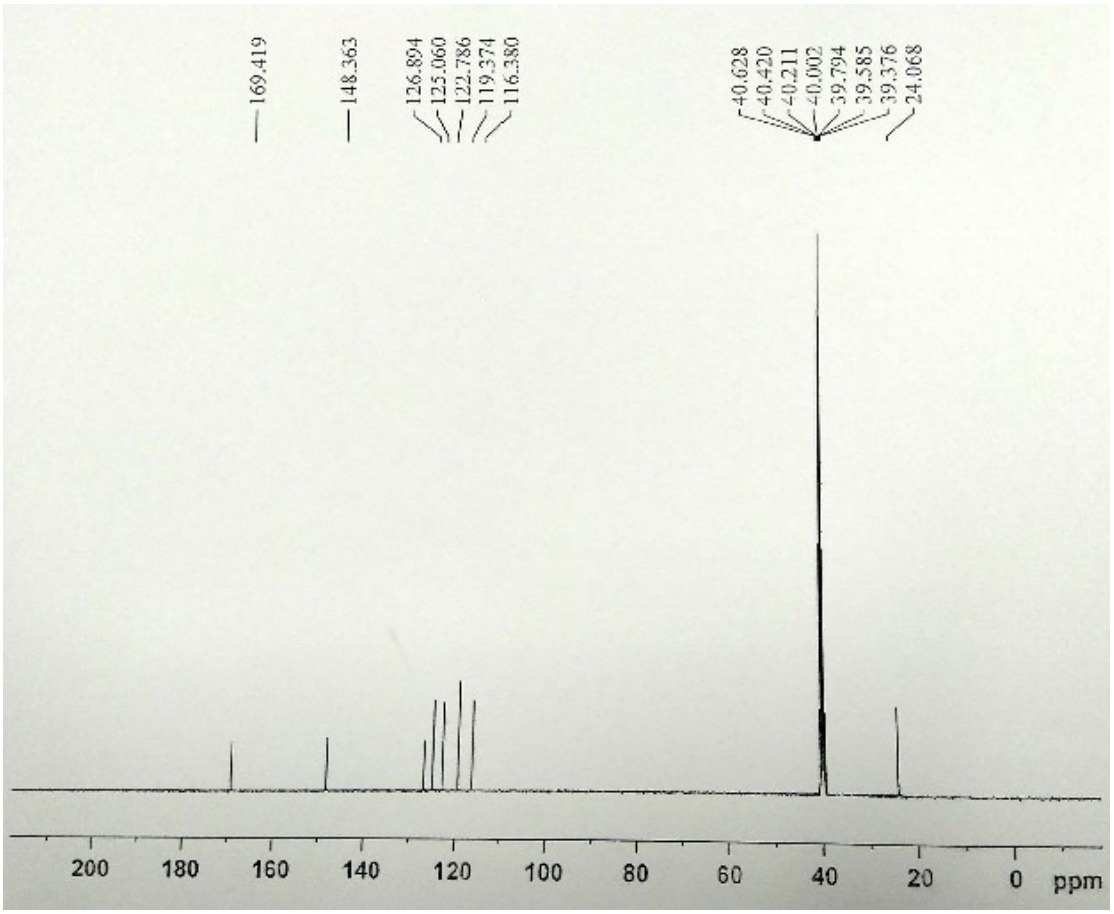


Figure 21. ^{1}H (400 MHz) and ^{13}C (100 MHz) NMR spectra of **3t** in DMSO-d_6.

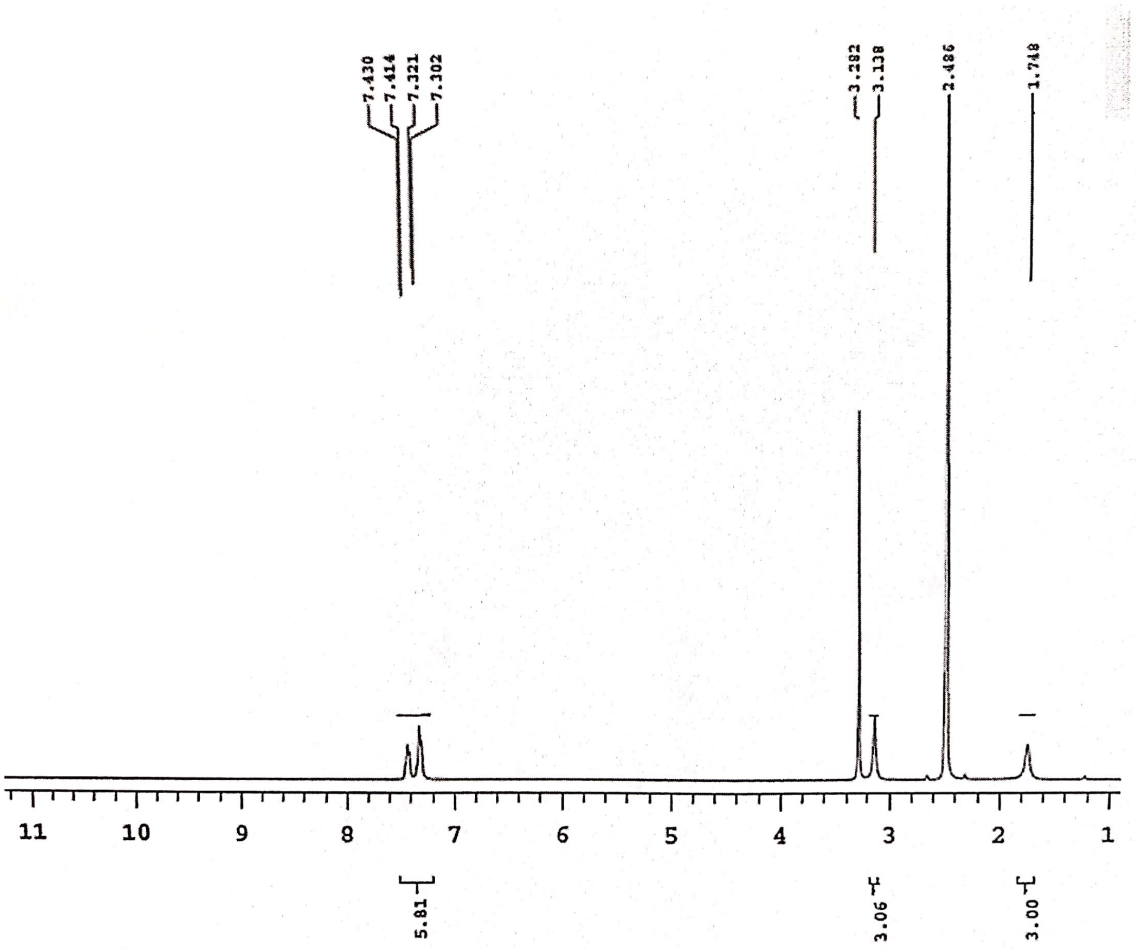
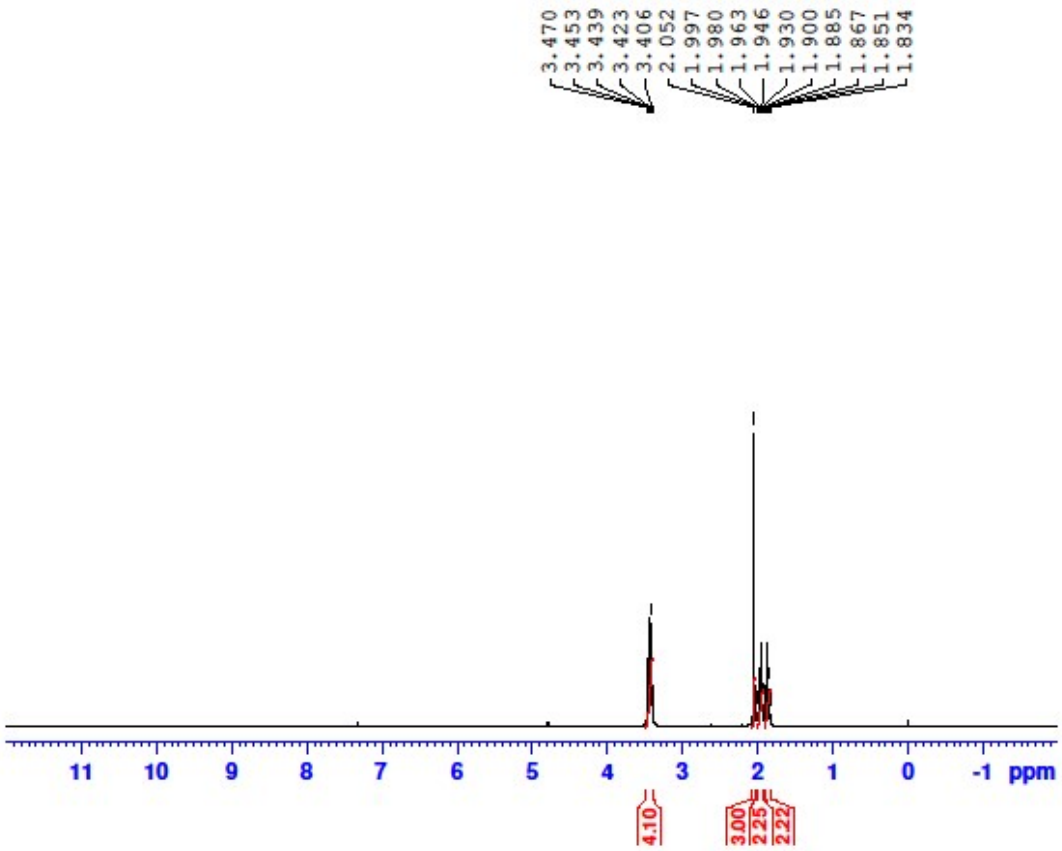


Figure 22. ^{1}H (400 MHz) NMR spectra of **3u** in DMSO-d_6.


3.470
3.453
3.439
3.423
3.406
2.052
1.997
1.980
1.963
1.946
1.930
1.900
1.885
1.867
1.851
1.834
11
10
9
8
7
6
5
4
3
2
1
0
-1
ppm
4.10
3.00
2.25
2.22

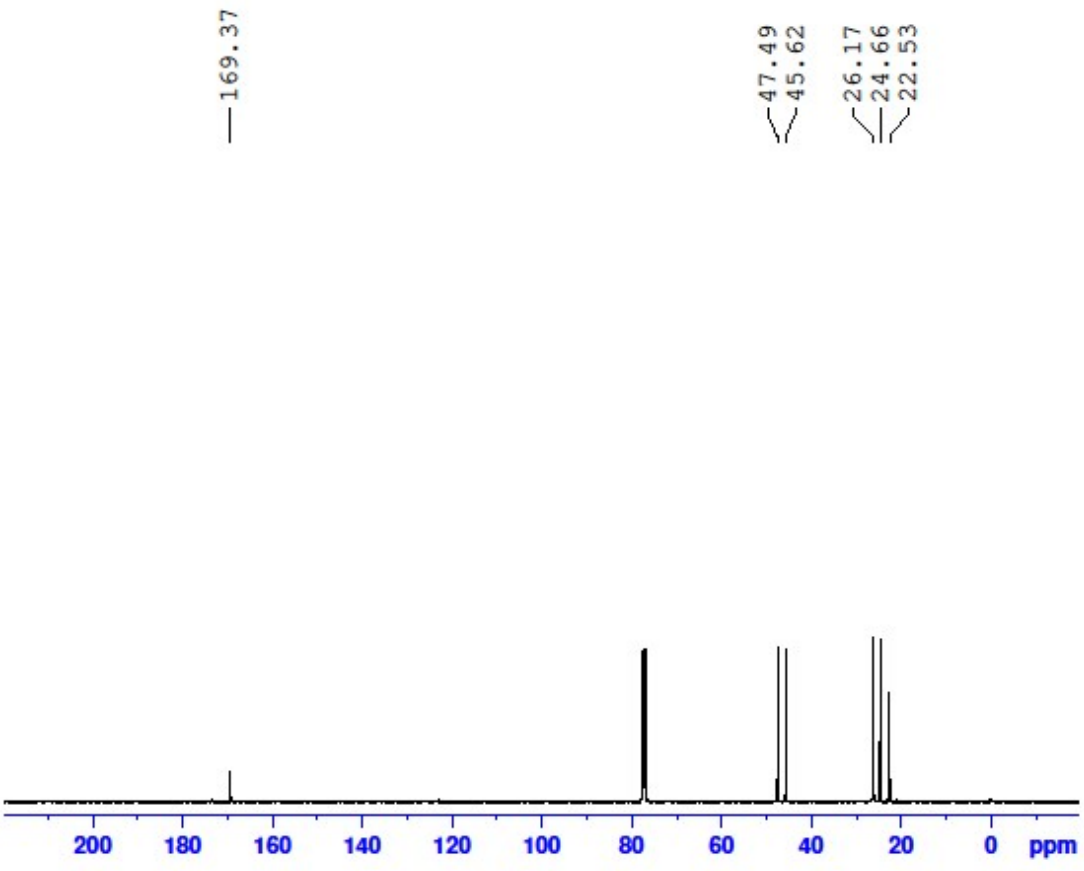
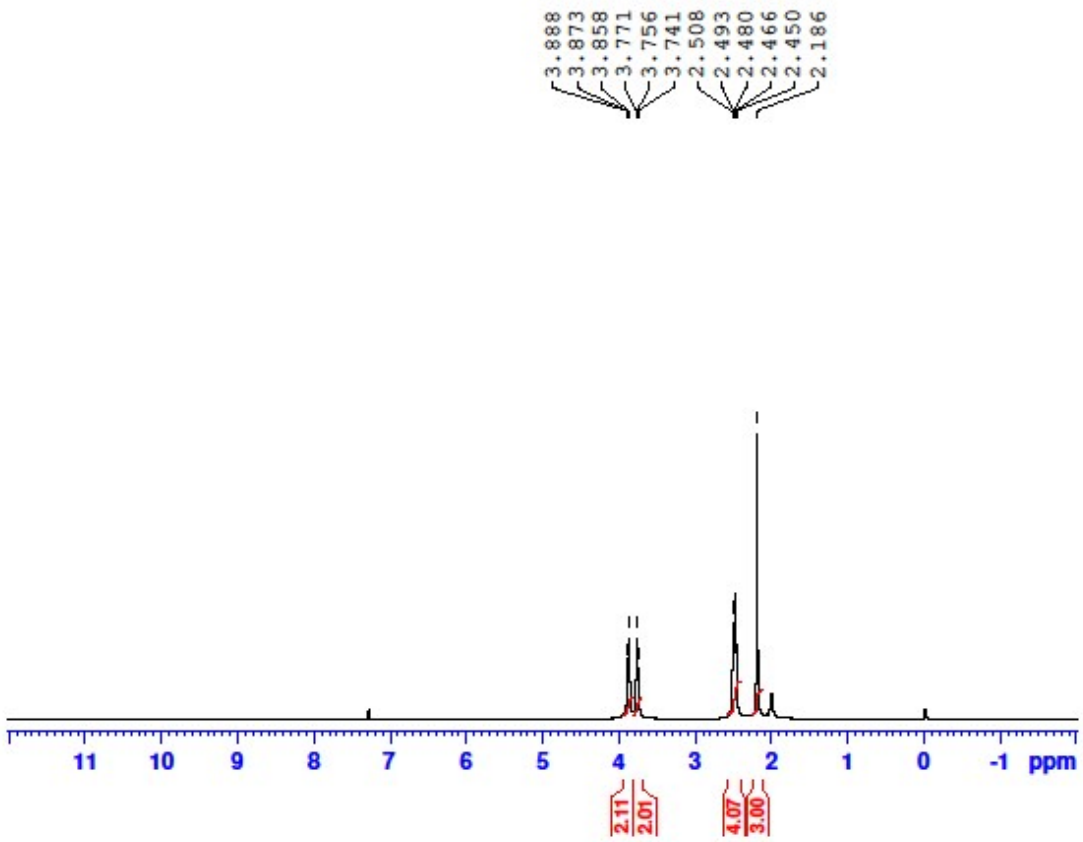


Figure 23. ^{1}H (400 MHz) and ^{13}C (100 MHz) NMR spectra of **3v** in DMSO-d_6.


3.888
3.873
3.858
3.771
3.756
3.741
2.508
2.493
2.480
2.466
2.450
2.186
11
10
9
8
7
6
5
4
3
2
1
0
-1
ppm
2.11
2.01
4.07
3.00

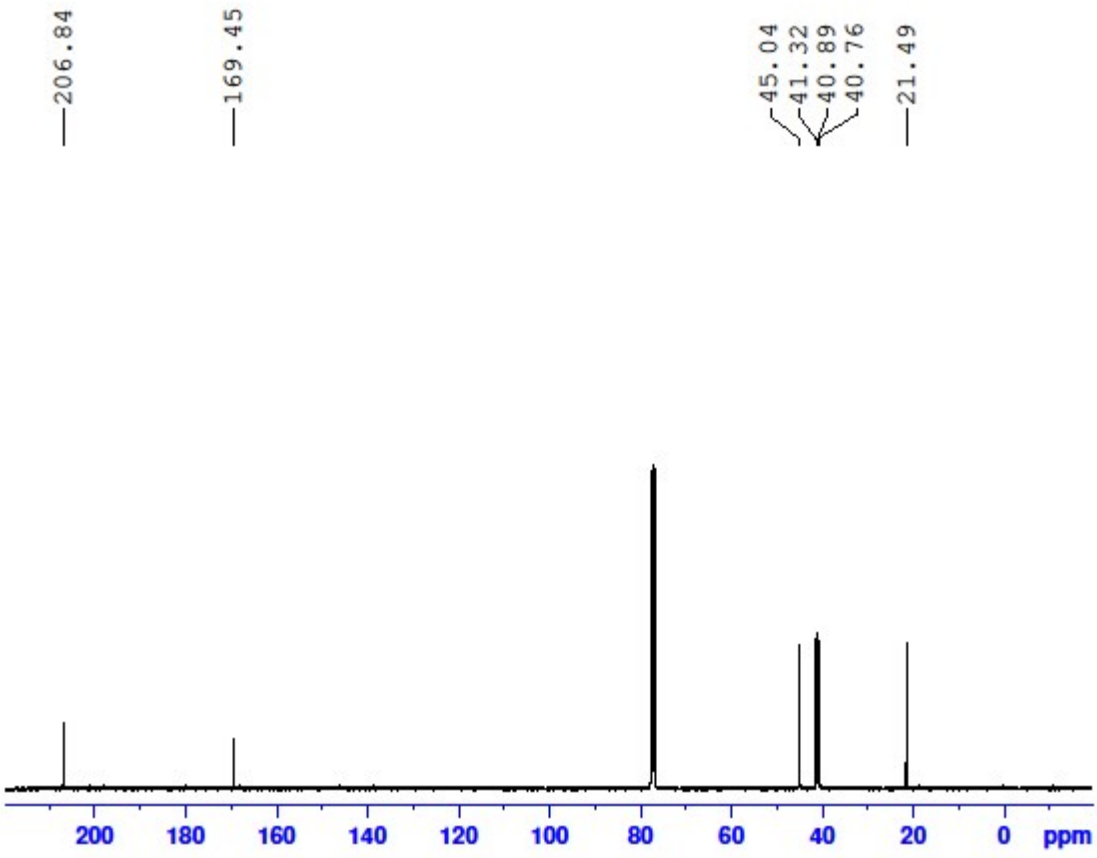


Figure 24. ^{1}H (400 MHz) and ^{13}C (100 MHz) NMR spectra of **3w** in DMSO-d_6.

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