

Supporting Information:

Manganese-Catalyzed Direct C-C Coupling of α -C-H bonds of Amides and Ester with Alcohols via Hydrogen Autotransfer

Ekambaram Balaraman^{*a} Jagannath Rana,^{b,c} Virendrakumar Gupta^{*d}

^a Department of Chemical Sciences, Indian Institute of Science Education and Research – Tirupati (IISER-T), Tirupati 517507, India.

^b Organic Chemistry Division, CSIR-National Chemical Laboratory (CSIR-NCL), Dr. Homi Bhabha Road, Pune 411008, India.

^c Academy of Scientific and Innovative Research (AcSIR), Ghaziabad - 201002, India.

^d Polymer Synthesis & Catalysis, Reliance Research & Development Centre, Reliance Industries Limited, Ghansoli 400701, Navi Mumbai, India.

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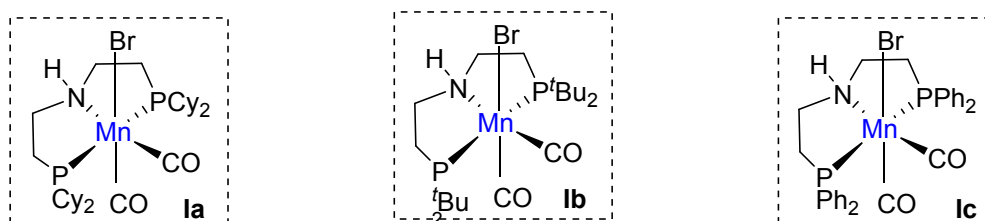
1 Experimental Section

1a. General Information

All catalytic experiments were carried out using standard Schlenk techniques. Unless otherwise stated reaction were conducted in flame-dried glassware under an atmosphere of nitrogen and commercially obtained reagent were used as received. All solvents were reagent grade or better. Toluene was refluxed over sodium/benzophenone, followed by distilled under argon atmosphere and stored over sodium. Chemicals used in catalysis reactions were used without additional purification. Thin layer chromatography (TLC) was performed using silica gel precoated aluminium foil which was visualized with visualized with UV light at 254 nm or under iodine. Column chromatography was performed with SiO₂ (Silicycle Siliaflash F60 (230-400 mesh). ¹H NMR (500, 200 MHz), ¹³C NMR (126, 50 MHz) spectra were recorded on the NMR spectrometer. Deuterated chloroform was used as the solvent, and chemical shift values (δ) are reported in parts per million relative to the residual signals of this solvent [δ 7.27 for ¹H (chloroform-d), δ 77.2 for ¹³C{¹H} (chloroform-d). Abbreviations used in the NMR follow-up experiments: s, singlet; d, doublet; dd, doublet of doublet; t, triplet; tt, triplet of triplet; td, triplet of doublet; q, quartet; br, broad; m, multiplet. GC analysis was carried out using a HP-5 column (30 m, 0.25 mm, 0.25 μ). Mass spectra were obtained on a GCMS-QP 5000 instruments with ionization voltages of 70 eV. High resolution mass spectra (HRMS) were obtained on a High-resolution mass spectra (HRMS) were obtained by fast atom bombardment (FAB) using a double focusing magnetic sector mass spectrometer and electron impact (EI) ionization technique (magnetic sector-electric sector double focusing mass analyzer).

1b. Complexes used for the present study

In a three-necked round-bottom flask (100 mL) under an argon atmosphere, $\text{Mn}(\text{CO})_5\text{Br}$ (1.0 equivalents) was added in toluene. After that, PNP pincer ligand (1.05 equivalents) was added drop by drop *via* syringe at room temperature. After stirring, the reaction mixture was heated to 100 °C for 20 h. During that time the reaction mixture became an orange solution. After cooling down to room temperature and removing the solvent at reduced pressure, led to a yellow solid. Washing this solid with heptane (2 x 10 mL) and drying under high vacuum provided the corresponding manganese complexes. The synthetic procedure for the complex was followed from this literature, matches the data with literature value. [M. Peña-López, P. Piehl, S. Elangovan, H. Neumann, M. Beller, *Angew. Chem. Int. Ed.* 2016, **55**, 14967.]



1c. General experimental procedure for Mn-catalyzed C-alkylation of amides

In a 10 mL oven dried sealed tube, alcohol **2** (0.5 mmol, 1 equiv), and amide **1** (1.0 mmol, 2 equiv), manganese complex [Mn]-**Ia** (0.5 mol%), KO^tBu (0.6 mmol, 1.2 equiv) were added under an argon atmosphere in toluene (1.0 mL). The flask was sealed with a teflon plug under an argon atmosphere, and the solution stirred at 110 °C for 16 hours. Then the reaction mixture was cooled to room temperature, and the reaction mixture was quenched with water (20 mL) and extracted with dichloromethane (2 x 20 mL). The entire organic layer was combined, washed with brine (20 mL) and then dried over Na₂SO₄. After concentration under reduced pressure, residue was purified by 250-400 mesh silica-gel column chromatography using ethyl acetate/petroleum ether (1:3) to afford the pure product **3**.

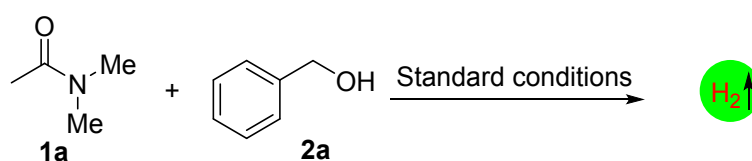
1d. General experimental procedure for Mn-catalyzed C-alkylation of *tert*-butyl acetate

In a 10 mL oven dried sealed tube, alcohol **2** (0.5 mmol, 1 equiv), and *tert*-butyl acetate **1a'** (1.0 mmol, 2 equiv), manganese complex [Mn]-**1a** (0.5 mol%), KO^tBu (0.6 mmol, 1.2 equiv) were added under an argon atmosphere in toluene (1.0 mL). The flask was sealed with a teflon plug under an argon atmosphere, and the solution stirred at 80 °C for 12 hours. Then the reaction mixture was cooled to room temperature, and the reaction mixture was quenched with water (20 mL) and extracted with dichloromethane (2 x 20 mL). The entire organic layer was combined, washed with brine (20 mL) and then dried over Na₂SO₄. After concentration under reduced pressure, residue was purified by 250-400 mesh silica-gel column chromatography using ethyl acetate/petroleum ether (1:3) to afford the pure product **5**.

2. Mechanistic investigations

2a. Detection of H₂ gas liberation

The evolution of H₂ gas during the alkylation process was qualitatively observed using GC analysis which reveals the reaction takes place *via* Mn-catalyzed auto hydrogen transfer pathway.



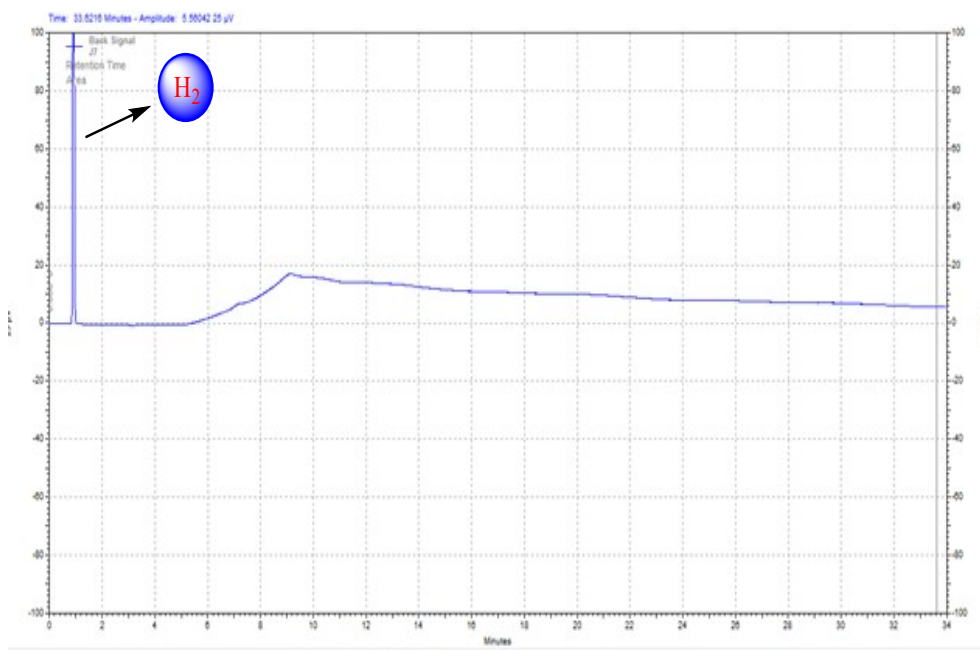
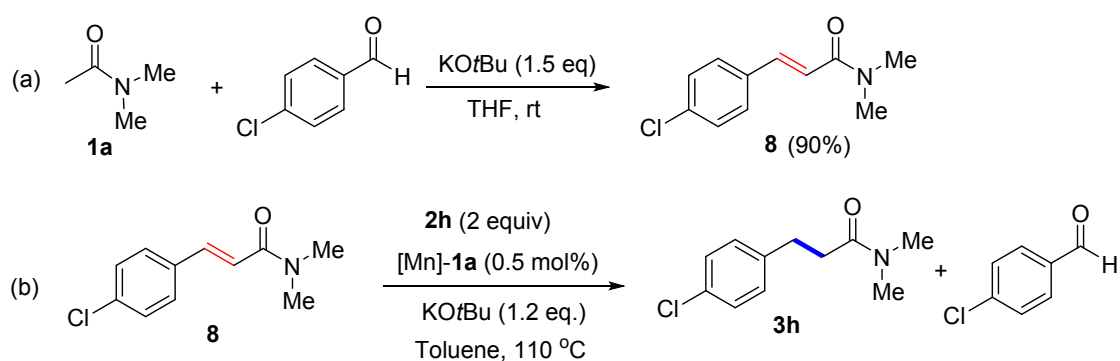


Figure S1. GC analysis.

2b. Intermediate Determination

An α,β -unsaturated amide **8** was applied under standard catalytic conditions in the presence of benzyl alcohol **2h** as hydrogen donor. The GC analysis of crude mixture showed the formation of α -alkylated amide and the corresponding dehydrogenated product (aldehyde) of **2h** which confirmed the formation of enone (**8**) as a key intermediate in the catalytic process.



2c. Deuterium experiment

a) To a 15 mL clean and oven-dried screw cap reaction tube, **1a** or **8** (1.0 mmol) and **2h-[d]** (96%) (0.5 mmol) were added under standard reaction conditions. Then the reaction was performed under standard condition for 16 h. The percentage of deuterium incorporation in the product was calculated based on HRMS analysis.

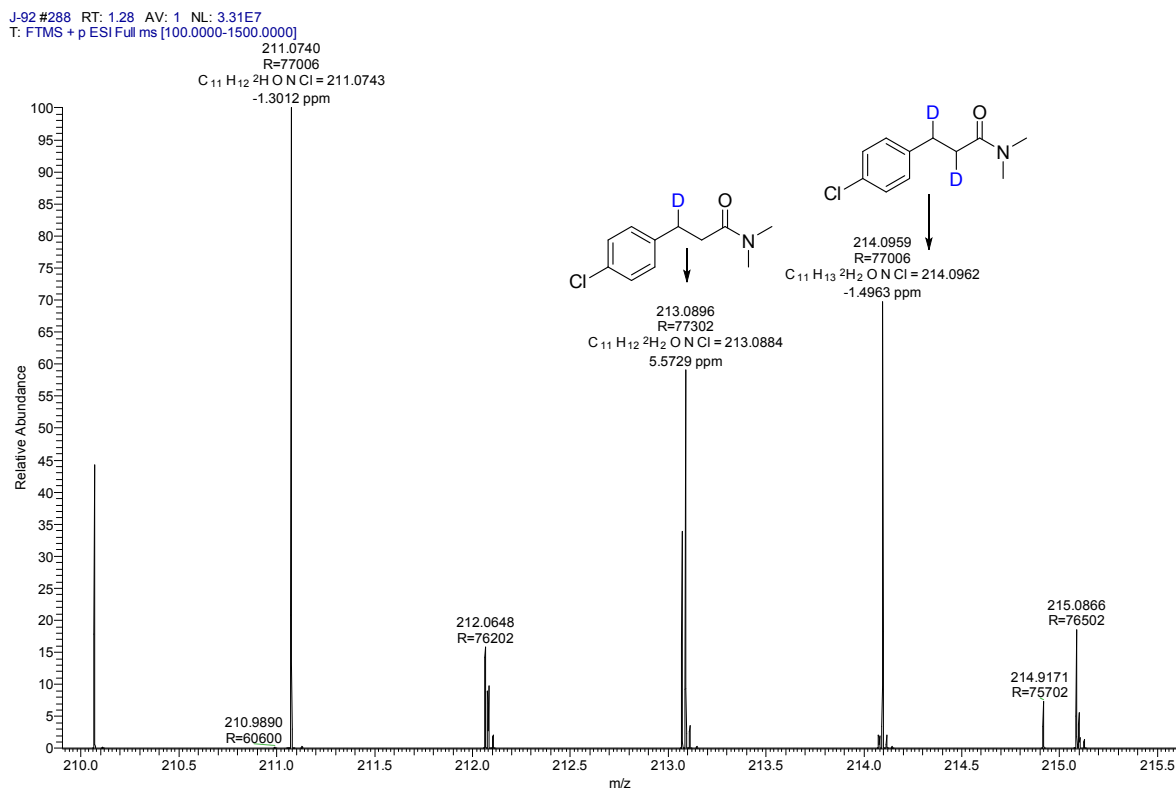
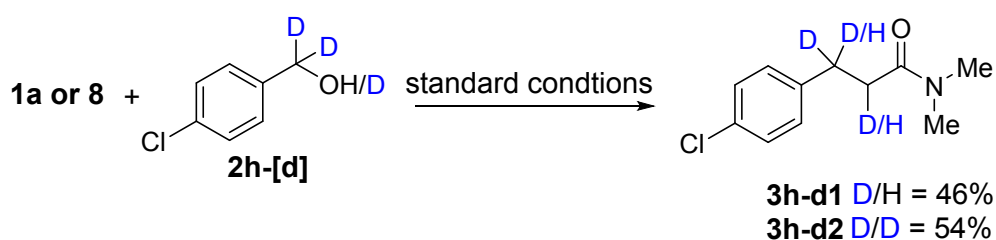


Figure S2. HRMS data for deuterium incorporation.

2d. Parallel and competition experiments

To a 15 mL clean and oven-dried screw cap reaction tube, **1a** (1.0 mmol) and **2h** (0.5 mmol), **2h-[d]** (96%) (0.5 mmol) were added under standard reaction conditions. Then the reaction was carried out for 16 h. The percentage of deuterium incorporation in the product was calculated based on HRMS analysis.

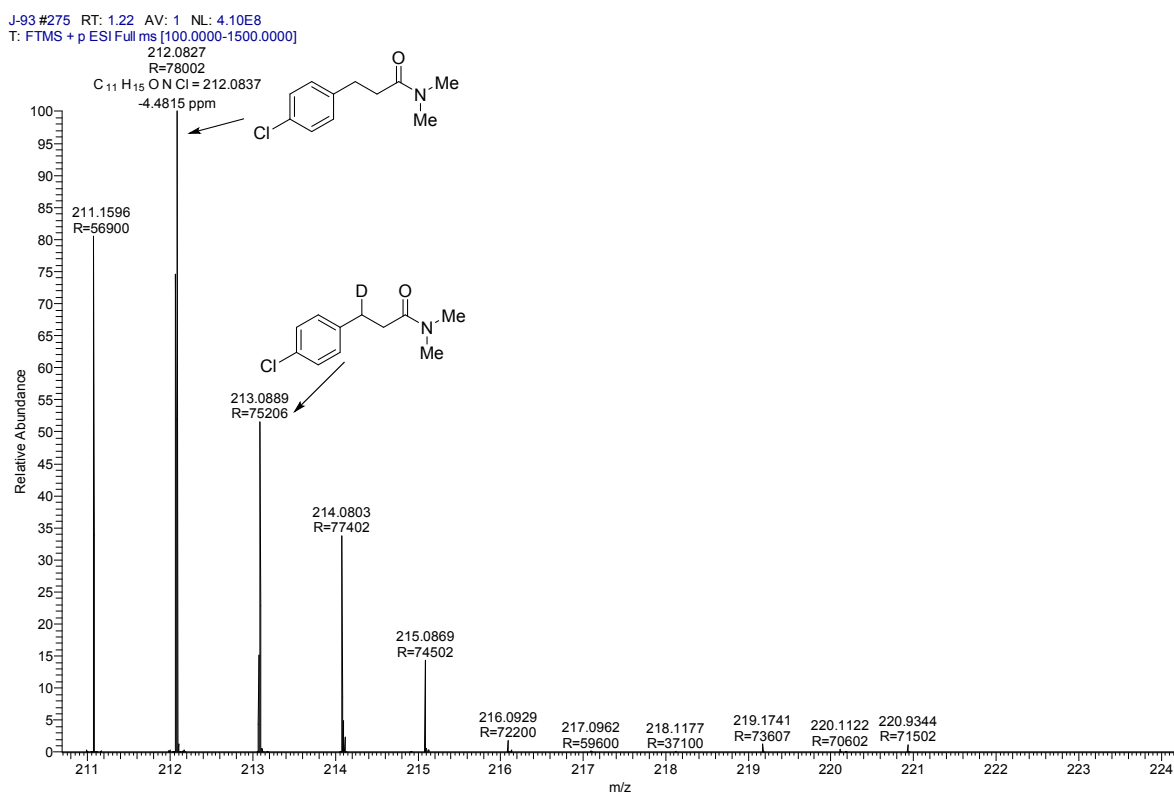
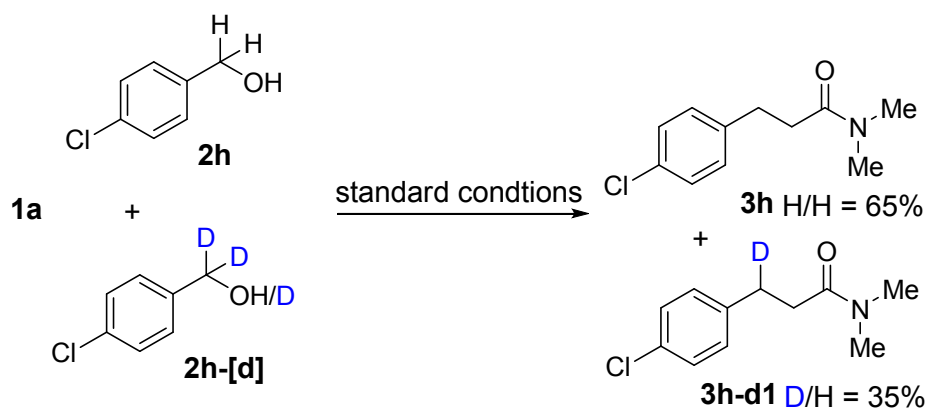
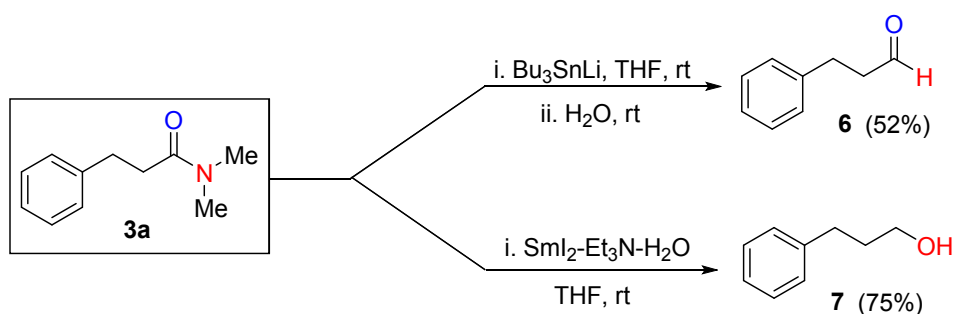


Figure S3. HRMS data for deuterium incorporation.

2e. Homogeneous nature of Mn-catalysis

In a 10 mL oven dried sealed tube, **2b** (0.5 mmol, 1 equiv), **1a** (1.0 mmol, 2 equiv), manganese complex **[Mn]-1a** (0.5 mol%), KO^tBu (0.6 mmol, 1.2 equiv), and Hg (1 drop) were added under an argon atmosphere in toluene (1.0 mL). The flask was sealed with a teflon plug under an argon atmosphere, and the solution stirred at 110 °C for 16 hours. Then the reaction mixture was cooled to room temperature, and the reaction mixture was quenched with water (20 mL) and extracted with dichloromethane (2 x 20 mL). The entire organic layer was combined, washed with brine (20 mL) and then dried over Na₂SO₄. After concentration under reduced pressure, residue was purified by 250-400 mesh silica-gel column chromatography using ethyl acetate/petroleum ether (1:3) to afford C-alkylated amide (**3b**) in 71% isolated yield.

3. Diversification of C-alkylated amides



3.1. α -alkylated amide to aldehyde

To a 15 mL clean, oven-dried screw cap reaction tube was added **3a** (0.1 mmol) and Bu₃SnLi (320 mol%) in THF under argon atmosphere at 0°C. Then the reaction was stirring at room temperature for 48 h. After that the reaction mixture was quenched with water and extracted with dichloromethane (3 x 5 mL). The resultant organic layer was dried over anhydrous Na₂SO₄ and the solvent was evaporated under reduced pressure. The crude mixture was purified by silica gel column chromatography (230-400 mesh size) using petroleum-ether/ethyl acetate as an eluting system.

3.2. α -alkylated amide to alcohol

To a 15 mL clean, oven-dried screw cap reaction tube was added **3a** (0.1 mmol) and samarium(II) iodide (THF solution, 8 equiv) followed by Et₃N (72 equiv) and H₂O (72 equiv) under argon atmosphere, resulted the formation of a dark brown color of the SmI₂-Et₃N-H₂O complex. Then the reaction mixture was stirred for 24 h at room temperature. After the completion of reaction the reaction mixture was diluted with CH₂Cl₂ and NaOH (1N) solution. The aqueous layer was extracted with CH₂Cl₂ (3 x 30 mL) and the combined organic layers were dried over Na₂SO₄, and concentrated. The crude mixture was purified by silica gel column chromatography (230-400 mesh size) using petroleum-ether/ethyl acetate as an eluting system.

4. Characterization Data of Compounds

N,N-dimethyl-3-phenylpropanamide (**3a**)

The general procedure was followed to afford the title compound as colourless liquid, isolated yield: 82%, 72 mg; ¹H NMR (200 MHz, CDCl₃) δ 7.39-7.33 (m, 2H), 7.31-7.25 (m, 3H), 3.07-2.98 (m, 8H), 2.69 (t, J = 6.7 Hz, 2H); ¹³C NMR (50 MHz, CDCl₃) δ 172.1, 141.4, 128.4, 128.3, 126.0, 37.0, 35.3, 35.2, 31.3. HRMS (EI) m/z Calcd for C₁₁H₁₆NO [M+H]⁺: 178.1226; Found: 178.1233.

N,N-dimethyl-3-(*p*-tolyl)propanamide (**3b**)

The general procedure was followed to afford the title compound as colourless oil, isolated yield: 85%, 81 mg; ¹H NMR (200 MHz, CDCl₃) δ 7.22-7.03 (m, 4H), 3.04-2.86 (m, 8H), 2.60 (t, J = 6.7 Hz, 2H), 2.33(s, 3H); ¹³C NMR (50 MHz, CDCl₃) δ 172.3, 138.4, 135.5, 129.0, 128.2, 37.1, 35.4 (2), 30.9, 20.9; HRMS (EI) m/z Calcd for C₁₂H₁₈NO [M+H]⁺: 192.1383; Found: 192.1384.

***N,N*-dimethyl-3-(*m*-tolyl)propanamide (3c)**

The general procedure was followed to afford the title compound as colourless oil, isolated yield: 78%, 74 mg; ¹H NMR (200 MHz, CDCl₃) δ = 7.18 (t, *J* = 8.1 Hz, 1H), 7.04-7.01 (m, 3H), 2.95-2.90 (m, 8H), 2.61 (t, *J* = 7.3 Hz, 2H), 2.34 (s, 3H); ¹³C NMR (50 MHz, CDCl₃) δ = 172.2, 141.3, 137.9, 129.1, 128.3, 126.7, 125.3, 37.1, 35.3, 35.3, 31.2, 21.3; HRMS (EI): *m/z* Calcd for C₁₂H₁₈NO [M+H]⁺: 192.1383; Found: 192.1384.

***N,N*-dimethyl-3-(*o*-tolyl)propanamide (3d)**

The general procedure was followed to afford the title compound as colourless oil, isolated yield: 70%, 67 mg; ¹H NMR (500 MHz, CDCl₃) δ 7.20-7.07 (m, 4H), 3.00-2.90 (m, 8H), 2.57 (t, *J* = 6.7 Hz, 2H), 2.34(s, 3H); ¹³C NMR (126 MHz, CDCl₃) δ 172.3, 139.5, 135.9, 130.2, 128.7, 126.2, 126.0, 37.1, 35.4, 33.8, 28.7, 19.3; HRMS (EI): *m/z* Calcd for C₁₂H₁₈NO [M+H]⁺: 192.1383; Found: 192.1384.

3-(4-methoxyphenyl)-*N,N*-dimethylpropanamide (3e)

The general procedure was followed to afford the title compound as colourless oil, isolated yield: 88%, 91 mg; ¹H NMR (200 MHz, CDCl₃) δ 7.20-7.06 (td, *J* = 8.6, 2.1 Hz, 2H), 6.89-6.76 (td, *J* = 8.6, 2.1 Hz, 2H), 3.78 (s, 3H), 2.98-2.84 (m, 8H), 2.58 (t, *J* = 6.6 Hz, 2H); ¹³C NMR(50 MHz, CDCl₃) δ 172.2, 157.8, 133.4, 129.2, 113.7, 55.1, 37.0, 35.4, 35.3, 30.3; HRMS (EI): *m/z* Calcd for C₁₂H₁₈NO₂[M+H]⁺: 208.1332; Found: 208.1331.

3-(3-methoxyphenyl)-*N,N*-dimethylpropanamide (3f)

The general procedure was followed to afford the title compound as colorless oil, isolated yield: 72%, 74mg; ¹H NMR (200 MHz, CDCl₃) δ 7.23-7.03 (m, 1H), 6.84-6.58 (m, 3H), 3.71 (s, 3H), 3.04-2.72 (m, 8H), 2.53 (t, *J* = 6.7 Hz, 2H); ¹³C NMR (50 MHz, CDCl₃) δ 172.3,

159.6, 143.0, 129.4, 120.7, 114.1, 111.3, 55.1, 37.1, 35.4, 35.1, 31.3; HRMS (EI): m/z Calcd for $C_{12}H_{18}NO_2[M+H]^+$: 208.1332; Found: 208.1331.

***N,N*-dimethyl-3-(4-(methylthio)phenyl)propanamide (3g)**

The general procedure was followed to afford the title compound as colourless sticky liquid, isolated yield: 78%, 87 mg; 1H NMR (200 MHz, $CDCl_3$) δ = 7.23-7.12 (m, 4H), 2.97-2.89 (m, 8H), 2.59 (t, J = 8.3 Hz, 2H), 2.46 (s, 3H); ^{13}C NMR (50 MHz, $CDCl_3$) δ = 172.2, 138.5, 135.7, 128.9, 127.1, 37.2, 35.5, 35.1, 30.7, 16.2. HRMS(EI): m/z Calcd for $C_{12}H_{17}NOS$ $[M+H]^+$: 224.1031; Found: 224.1029.

3-(4-chlorophenyl)-*N,N*-dimethylpropanamide (3h)

The general procedure was followed to afford the title compound as colourless oil, isolated yield: 65%, 68 mg; 1H NMR (500 MHz, $CDCl_3$) δ 7.38-7.34 (m, 2H), 7.31-7.28 (m, 2H), 3.06-2.97 (m, 8H), 2.69 (t, J = 6.6 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 172.2, 141.5, 128.5, 128.4, 126.1, 37.2, 35.4, 35.3, 33.4; HRMS (EI): m/z Calcd for $C_{11}H_{15}NOCl$ $[M+H]^+$: 212.0837; Found: 212.0837.

3-(4-fluorophenyl)-*N,N*-dimethylpropanamide (3i)

The general procedure was followed to afford the title compound as colourless sticky liquid. Yield: 62%, 60 mg; 1H NMR (500 MHz, $CDCl_3$) δ = 7.19-7.16 (m, 2H), 6.96 (t, J = 8.8 Hz, 2H), 2.96-2.91 (m, 8H), 2.59 (t, J = 8.0 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ = 172.0, 162.3, 160.4, 137.0, 129.7, 128.4, 126.1, 115.2, 115.0, 37.1, 35.4, 35.2, 30.5.

3-(3,4-dimethoxyphenyl)-*N,N*-dimethylpropanamide (3j)

The general procedure was followed to afford the title compound as a colorless oil, isolated yield: 80%, 95 mg; 1H NMR (500 MHz, $CDCl_3$) δ 6.81-6.71 (m, 3H), 3.86 (s, 3H), 3.84 (s,

3H), 2.96-2.84 (m, 8H), 2.59 (t, $J = 6.8$ Hz, 2H); ^{13}C NMR (126 MHz, CDCl_3) δ 172.2, 148.7, 147.2, 134.0, 120.0, 111.7, 111.1, 55.8, 55.7, 37.1, 35.4, 35.3, 30.9; HRMS (EI): m/z Calcd for $\text{C}_{13}\text{H}_{20}\text{NO}_3$ $[\text{M}+\text{H}]^+$: 238.1438; Found: 238.1439.

***N,N*-dimethyl-3-(naphthalen-2-yl)propanamide (3k)**

The general procedure was followed to afford the title compound as colourless oil, isolated yield: 76%, 86 mg; ^1H NMR (500 MHz, CDCl_3) δ 7.84-7.76 (m, 3H), 7.67 (m, 1H), 7.49-7.41 (m, 2H), 7.40-7.35 (m, 1H), 3.15 (t, $J = 8.4$ Hz, 2H), 2.97 (s, 3H), 2.94 (s, 3H), 2.71 (t, $J = 7.4$ Hz, 2H); ^{13}C NMR (126 MHz, CDCl_3) δ 172.1, 138.9, 133.6, 132.0, 127.9, 127.6, 127.4, 127.2, 126.4, 125.9, 125.2, 37.2, 35.4, 35.2, 31.5; HRMS (EI): m/z Calcd for $\text{C}_{15}\text{H}_{18}\text{NO}$ $[\text{M}+\text{H}]^+$: 228.1383; Found: 228.1384.

***N,N*-dimethyloctanamide (3l)**

The general procedure was followed to afford the title compound as colourless oil, isolated yield: 56%, 48 mg; ^1H NMR (200 MHz, CDCl_3) δ 2.98 (s, 3H), 2.91 (s, 3H), 2.28 (t, $J = 7.1$ Hz, 2H), 1.69-1.48 (m, 2H), 1.32-1.19 (m, 8H), 0.89-0.80 (m, 3H); ^{13}C NMR (50 MHz, CDCl_3) δ 173.3, 37.2, 35.2, 33.4, 31.6, 29.4, 29.0, 25.1, 22.5, 13.9; HRMS (EI): m/z Calcd for $\text{C}_{10}\text{H}_{22}\text{NO}$ $[\text{M}+\text{H}]^+$: 172.1696; Found: 172.1697.

3-cyclopropyl-*N,N*-dimethylpropanamide (3m)

The general procedure was followed to afford the title compound as a colorless oil, isolated yield: 52%, 37 mg; ^1H NMR (500 MHz, CDCl_3) δ 3.03 (s, 3H), 2.94 (s, 3H), 2.42 (t, $J = 7.4$ Hz, 2H), 1.52 (q, $J = 7.6$ Hz, 2H), 0.73 (m, 1H), 0.48-0.34 (m, 2H), 0.10-0.02 (m, 2H); ^{13}C NMR (126 MHz, CDCl_3) δ 173.1, 37.3, 35.3, 33.3, 30.4, 10.7, 4.5; HRMS (EI): m/z Calcd for $\text{C}_8\text{H}_{16}\text{NO}$ $[\text{M}+\text{H}]^+$: 142.1226; Found: 142.1228.

3-(furan-2-yl)-*N,N*-dimethylpropanamide (3n)

The general procedure was followed to afford the title compound as colourless oil, isolated yield: 75%, 62 mg; ¹H NMR (500 MHz, CDCl₃) δ 7.31 (m, 1H), 6.30-6.25 (m, 1H), 6.06-6.00 (m, 1H), 3.02-2.94 (m, 8H), 2.66 (t, *J* = 8.7 Hz, 2H); ¹³C NMR (126 MHz, CDCl₃) δ 171.8, 154.9, 140.9, 110.2, 105.2, 37.1, 35.4, 31.8, 23.7; HRMS (EI): *m/z* Calcd for C₉H₁₄O₂N [M+H]⁺: 168.1019; Found: 168.1027.

1-(pyrrolidin-1-yl)-3-(*p*-tolyl)propan-1-one (4a)

The general procedure was followed to afford the title compound as colourless oil, isolated yield: 65%, 70 mg; ¹H NMR (500 MHz, CDCl₃) δ 7.11 (s, 4H), 3.67-3.57 (m, 4H), 3.52 (t, *J* = 5.0 Hz, 2H), 3.36 (t, *J* = 4.4 Hz, 2H), 2.94 (t, *J* = 8.2 Hz, 2H), 2.60 (t, *J* = 7.6 Hz, 2H), 2.32 (s, 3H); ¹³C NMR (126 MHz, CDCl₃) δ 170.9, 137.9, 135.7, 129.2, 128.3, 66.8, 66.4, 45.9, 41.9, 34.9, 30.9, 20.9; HRMS (EI): *m/z* Calcd for C₁₄H₂₀NO [M+H]⁺: 218.1539; Found: 218.1545.

1-(piperidin-1-yl)-3-(*p*-tolyl)propan-1-one (4b)

The general procedure was followed to afford the title compound as colourless oil, isolated yield: 74%, 85 mg; ¹H NMR (500 MHz, CDCl₃) δ 7.16-7.06 (m, 4H), 3.56 (t, *J* = 6.7 Hz, 2H), 3.35 (t, *J* = 5.7 Hz, 2H), 2.93 (t, *J* = 8.3 Hz, 2H), 2.60 (t, *J* = 7.7 Hz, 2H), 2.32 (s, 3H), 1.65-1.58 (m, 2H), 1.56-1.45 (m, 4H); ¹³C NMR (126 MHz, CDCl₃) δ 170.5, 138.4, 135.5, 129.1, 128.3, 46.6, 42.7, 35.4, 31.1, 26.4, 25.5, 24.5, 20.9; HRMS (EI): *m/z* Calcd for C₁₅H₂₂NO [M+H]⁺: 232.1696; Found: 232.1697.

1-morpholino-3-(*p*-tolyl)propan-1-one (4c)

The general procedure was followed to afford the title compound as colourless oil, isolated yield: 54%, 69 mg; ¹H NMR (500 MHz, CDCl₃) δ 7.13-7.09 (m, 4H), 3.47 (t, *J* = 6.7 Hz,

2H), 3.30 (t, $J = 6.9$ Hz, 2H), 2.95 (t, $J = 8.5$ Hz, 2H), 2.54 (t, $J = 8.5$ Hz, 2H), 2.32 (s, 3H), 1.89 (m, 2H), 1.82 (m, 2H); ^{13}C NMR (126 MHz, CDCl_3) δ 170.9, 138.4, 135.5, 129.0, 128.3, 46.5, 45.6, 36.9, 30.7, 26.0, 24.3, 20.9. HRMS (EI): m/z Calcd for $\text{C}_{14}\text{H}_{19}\text{NO}_2\text{Na}$ $[\text{M}+\text{Na}]^+$: 256.1308; Found: 256.1306.

***N*-methyl-*N*-phenyl-3-*p*-tolylpropanamide (4d)**

The general procedure was followed to afford the title compound as colourless oil, isolated yield: 72%, 91 mg; ^1H NMR (200 MHz, CDCl_3) $\delta = 7.38$ -7.33 (m, 3H), 7.07-6.94 (m, 5H), 3.26 (s, 3H), 2.88 (t, $J = 8.2$ Hz, 2H), 2.36 (t, $J = 7.9$ Hz, 2H), 2.30 (s, 3H). ^{13}C NMR (50 MHz, CDCl_3) $\delta = 172.3$, 143.9, 138.1, 135.4, 129.7, 128.9, 128.2, 127.7, 127.3, 37.3, 36.1, 31.3, 20.9. HRMS(EI): m/z Calcd for $\text{C}_{17}\text{H}_{19}\text{NO}$ $[\text{M}+\text{H}]^+$: 254.1467; Found: 254.1466.

1-methyl-3-(4-methylbenzyl)piperidin-2-one (4e)

The general procedure was followed to afford the title compound as colourless oil, isolated yield: 48%, 52mg; ^1H NMR (500 MHz, CDCl_3) δ 7.15-7.04 (m, 4H), 3.49-3.33 (m, 1H), 3.31-3.13 (m, 2H), 2.95 (s, 3H), 2.68-2.45 (m, 2H), 2.31(s, 3H), 1.90-1.57 (m, 3H), 1.53-1.36 (m, 1H); ^{13}C NMR (126 MHz, CDCl_3) δ 172.0, 137.0, 135.4, 129.0, 128.9, 50.1, 43.3, 37.3, 34.9, 25.7, 21.3, 20.9; HRMS (EI): m/z Calcd for $\text{C}_{14}\text{H}_{20}\text{NO}$ $[\text{M}+\text{H}]^+$: 218.1539; Found: 218.1545.

3-(4-methylbenzyl)piperidin-2-one (4f)

The general procedure was followed to afford the title compound as colourless oil. Here we got *N*-alkylation product rather than *C*-alkylation product. Isolated yield: 35%, 36 mg; ^1H NMR (200 MHz, CDCl_3) $\delta = 7.18$ -7.09 (m, 4H), 4.56 (s, 2H), 3.18 (t, $J = 4.4$ Hz, 2H), 2.46 (t, $J = 6.3$ Hz, 2H), 2.33 (s, 3H), 1.78-1.75 (m, 4H); ^{13}C NMR (50 MHz, CDCl_3) $\delta = 169.7$,

136.9, 134.2, 129.2, 128.0, 49.7, 47.0, 32.3, 23.1, 21.3, 21.0; HRMS (EI): m/z Calcd for C₁₃H₁₈NO [M+H]⁺: 204.1383; Found: 204.1386.

***tert*-butyl 3-(4-methoxyphenyl)propanoate (5a)**

The general procedure was followed to afford the title compound as colorless sticky liquid. Isolated yield: 72%, 85 mg; ¹HNMR (200 MHz, CDCl₃) δ = 7.13 (d, *J* = 8.5 Hz, 2H), 6.83 (d, *J* = 8.7 Hz, 2H), 3.79 (s, 3H), 2.86 (t, *J* = 8.1 Hz, 2H), 2.51 (t, *J* = 7.3 Hz, 2H), 1.43 (s, 9H); ¹³CNMR (50 MHz, CDCl₃) δ = 172.4, 157.9, 132.8, 129.2, 113.8, 80.2, 55.2, 37.4, 30.2, 28.1. (Known compound: Deibl, N.; Kempe, R. *J. Am. Chem. Soc.* **2016**, *138*, 10786-10789).

***tert*-butyl 3-*p*-tolylpropanoate (5b)**

The general procedure was followed to afford the title compound as colorless sticky liquid. Isolated yield: 65%, 71 mg; ¹HNMR (400 MHz, CDCl₃) δ = 7.12-7.10 (m, 4H), 2.90 (t, *J* = 7.9 Hz, 2H), 2.54 (t, *J* = 7.9 Hz, 2H), 2.34 (s, 3H), 1.45 (s, 9H); ¹³CNMR (100 MHz, CDCl₃) δ = 172.3, 137.7, 135.5, 129.0, 128.1, 80.2, 37.2, 30.7, 28.0, 20.9. (Known compound: Deibl, N.; Kempe, R. *J. Am. Chem. Soc.* **2016**, *138*, 10786-10789).

***tert*-butyl 3-*o*-tolylpropanoate (5c)**

The general procedure was followed to afford the title compound as colorless sticky liquid. Isolated yield: 54%, 59 mg; ¹HNMR (400 MHz, CDCl₃) δ = 7.16-7.14 (m, 4H), 2.91 (t, *J* = 7.9 Hz, 2H), 2.51 (t, *J* = 8.5 Hz, 2H), 2.34 (s, 3H), 1.45 (s, 9H); ¹³CNMR (100 MHz, CDCl₃) δ = 172.4, 138.9, 135.9, 130.2, 128.5, 126.2, 125.9, 80.3, 35.7, 28.4, 28.1, 19.3. (Known compound: Deibl, N.; Kempe, R. *J. Am. Chem. Soc.* **2016**, *138*, 10786-10789).

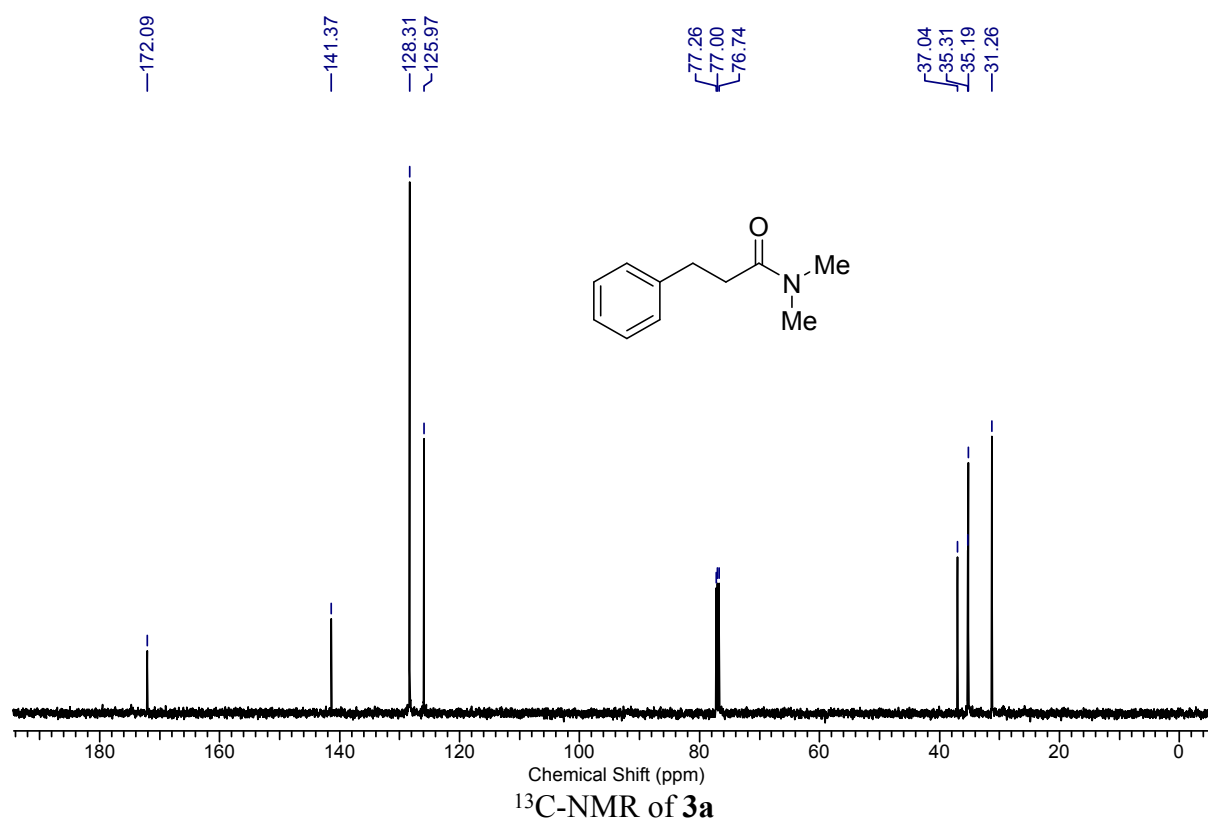
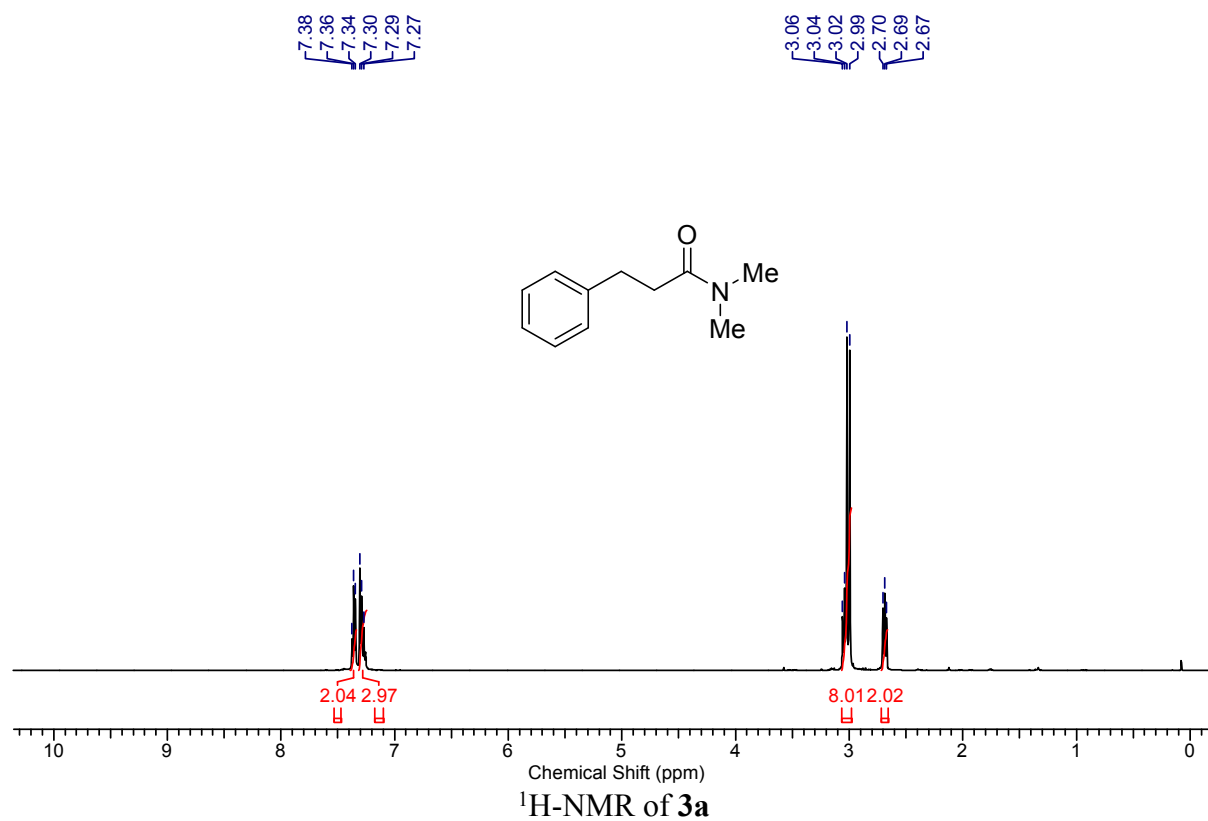
3-phenylpropanal (6)

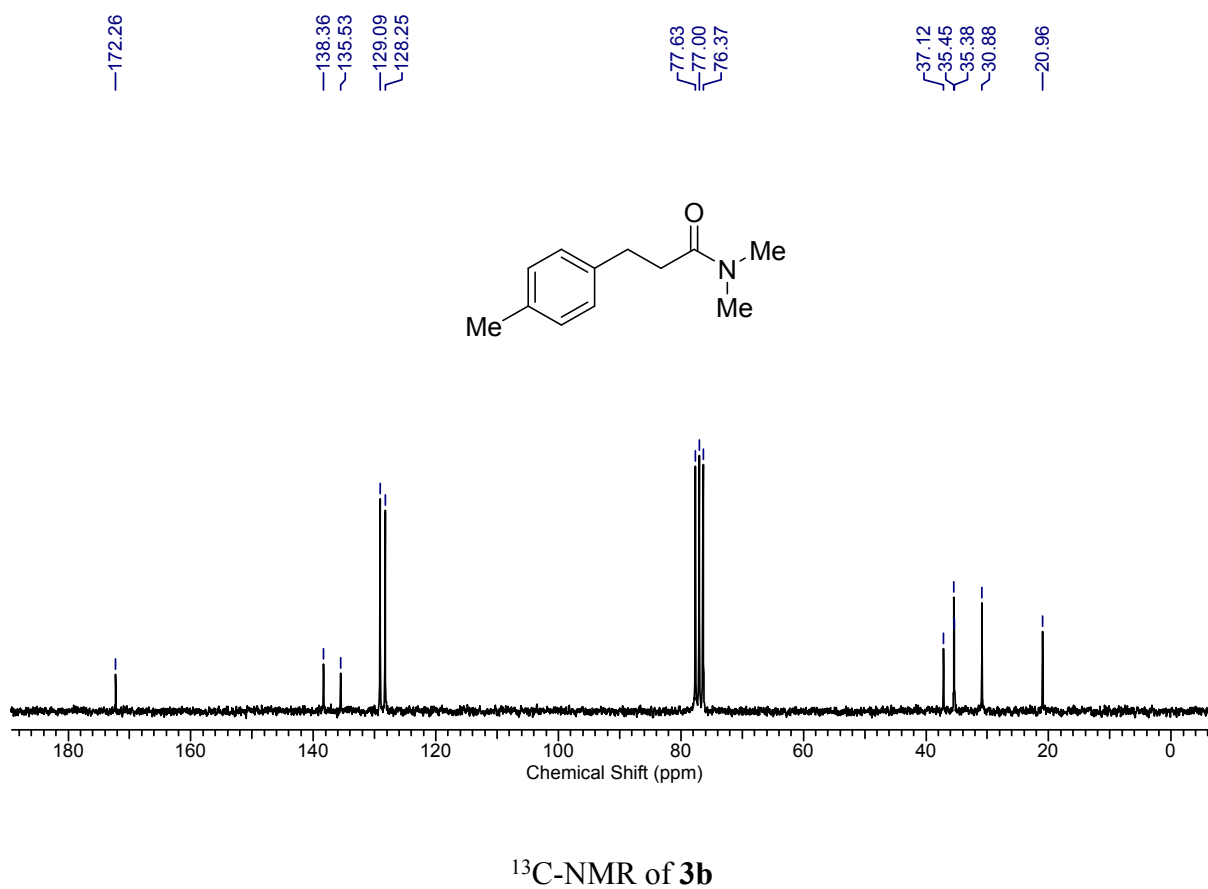
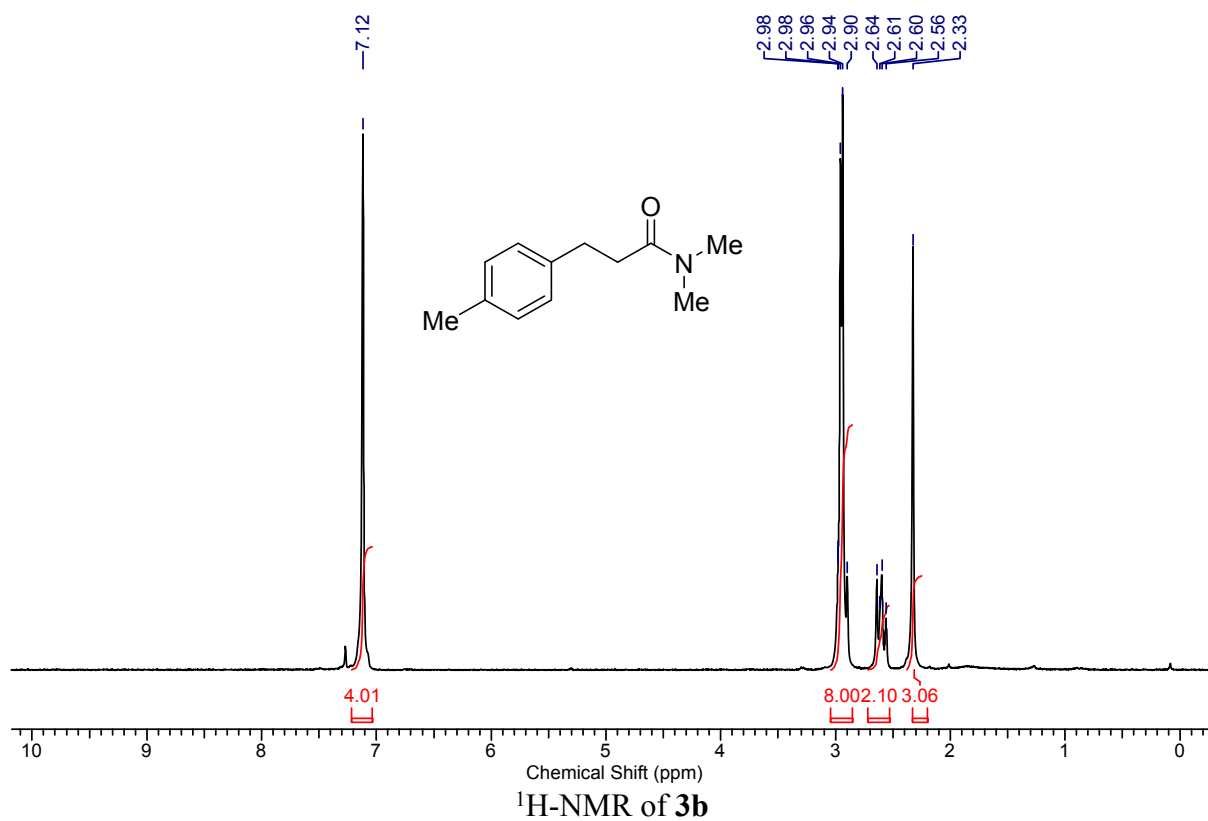
Colourless liquid, 35 mg, 52% yield; ^1H NMR (500 MHz, CDCl_3) δ 9.89 (s, 1H), 7.41-7.33 (m, 2H), 7.30-7.24 (m, 3H), 3.04 (t, $J = 6.4$ Hz, 2H), 2.85 (t, $J = 7.4$ Hz, 2H); ^{13}C NMR (126 MHz, CDCl_3) δ 200.8, 139.5, 127.8, 127.5, 125.5, 44.5, 27.3; HRMS (EI) m/z Calcd for $\text{C}_9\text{H}_{10}\text{ONa}$ $[\text{M}+\text{Na}]^+$: 157.0624; Found: 157.0626.

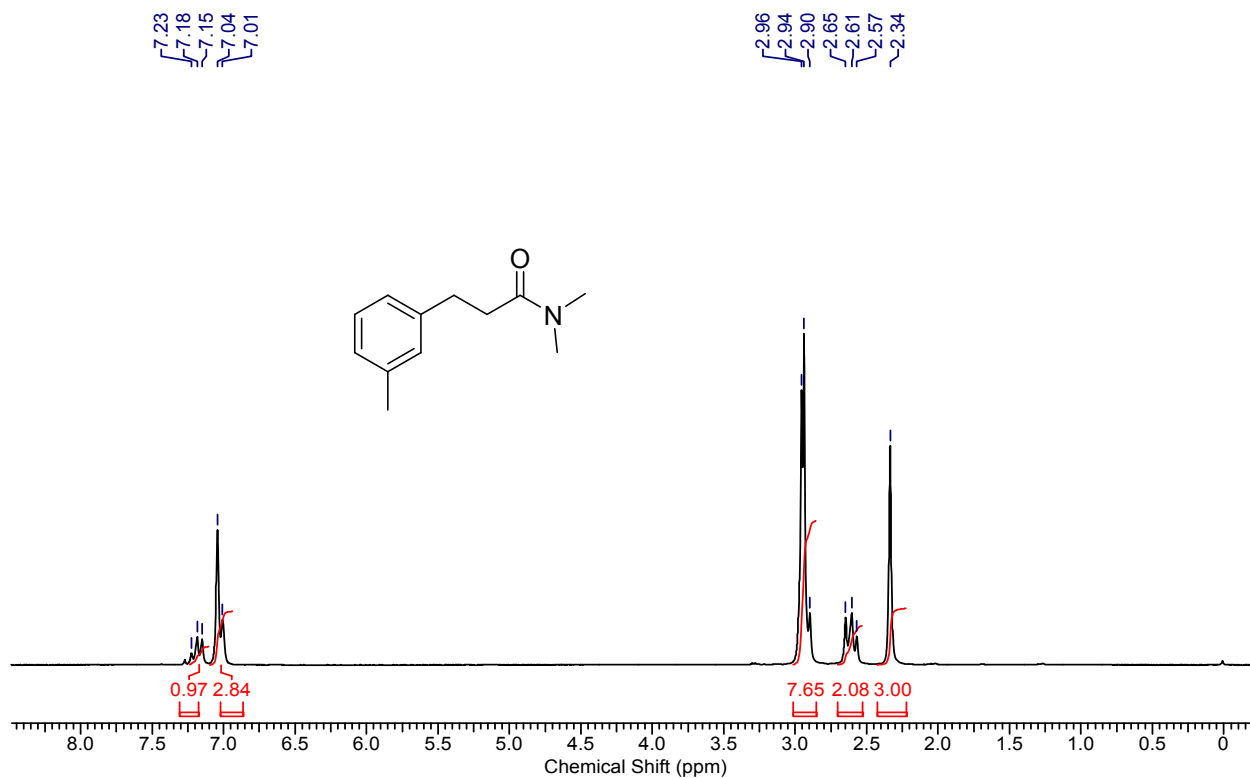
3-phenylpropan-1-ol (7)

Colourless liquid, 51 mg, 75% yield; ^1H NMR (500 MHz, CDCl_3) δ 7.42-7.34 (m, 2H), 7.33-7.22 (m, 3H), 3.73 (t, $J = 6.4$ Hz, 2H), 2.79 (t, $J = 7.4$ Hz, 2H), 2.42 (brs, 1H), 1.97 (p, $J = 6.7$ Hz, 2H); ^{13}C NMR (126 MHz, CDCl_3) δ 141.7, 128.3, 128.2, 125.7, 61.9, 34.1, 31.9; HRMS (EI) m/z Calcd for $\text{C}_9\text{H}_{12}\text{ONa}$ $[\text{M}+\text{Na}]^+$: 159.0780; Found: 159.0783.

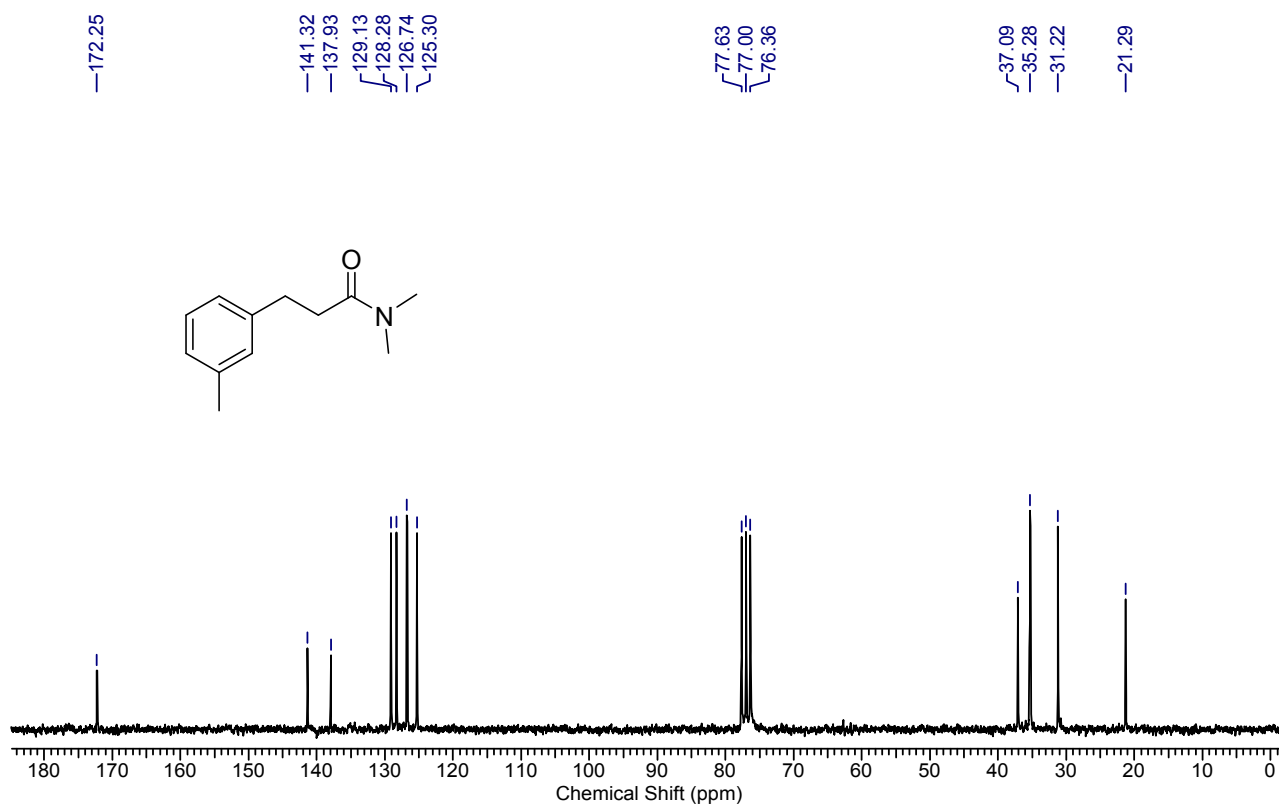
5. Copy of ^1H & ^{13}C NMR



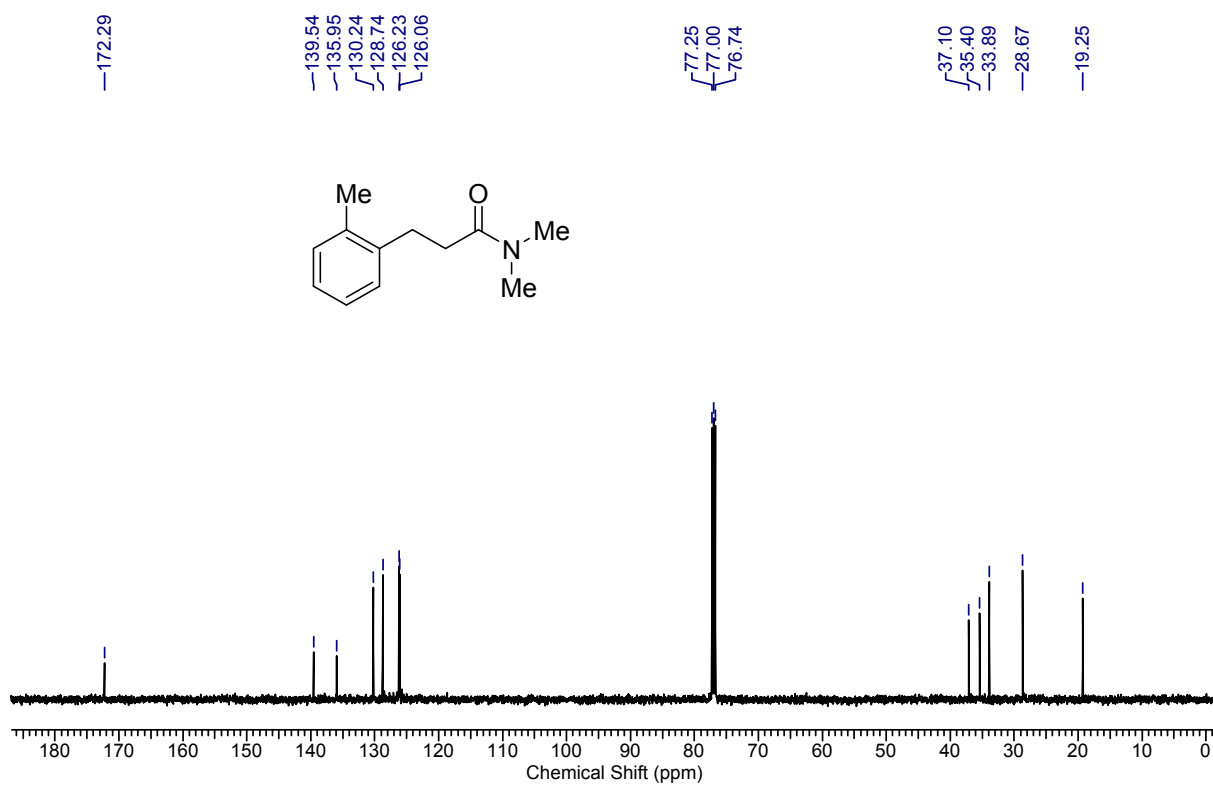
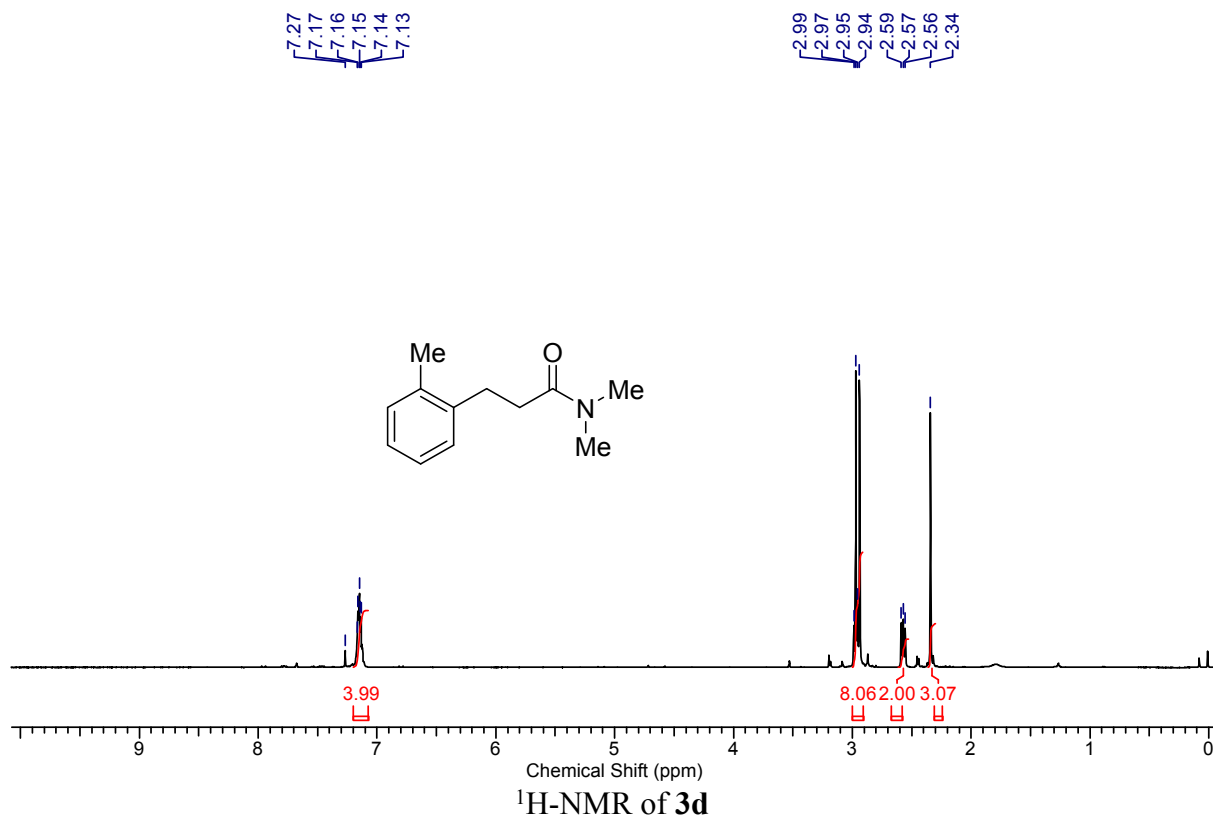


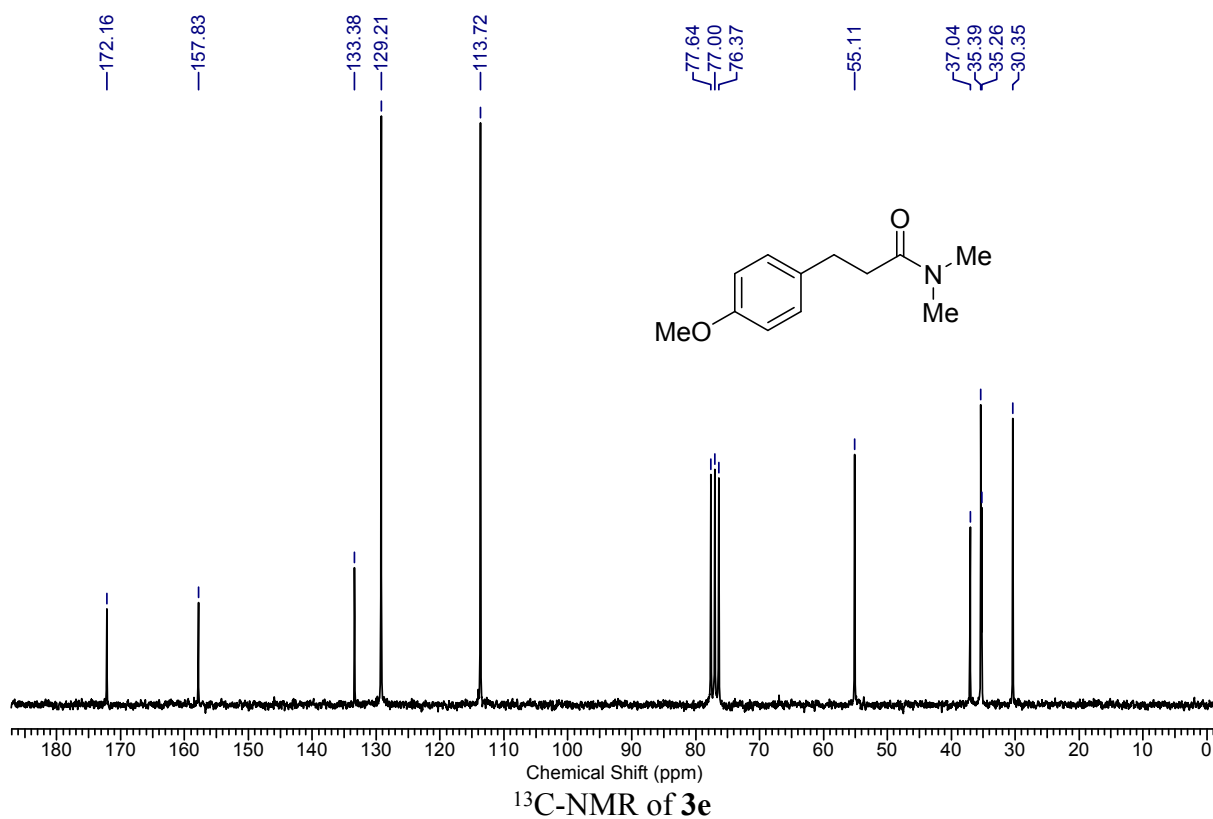
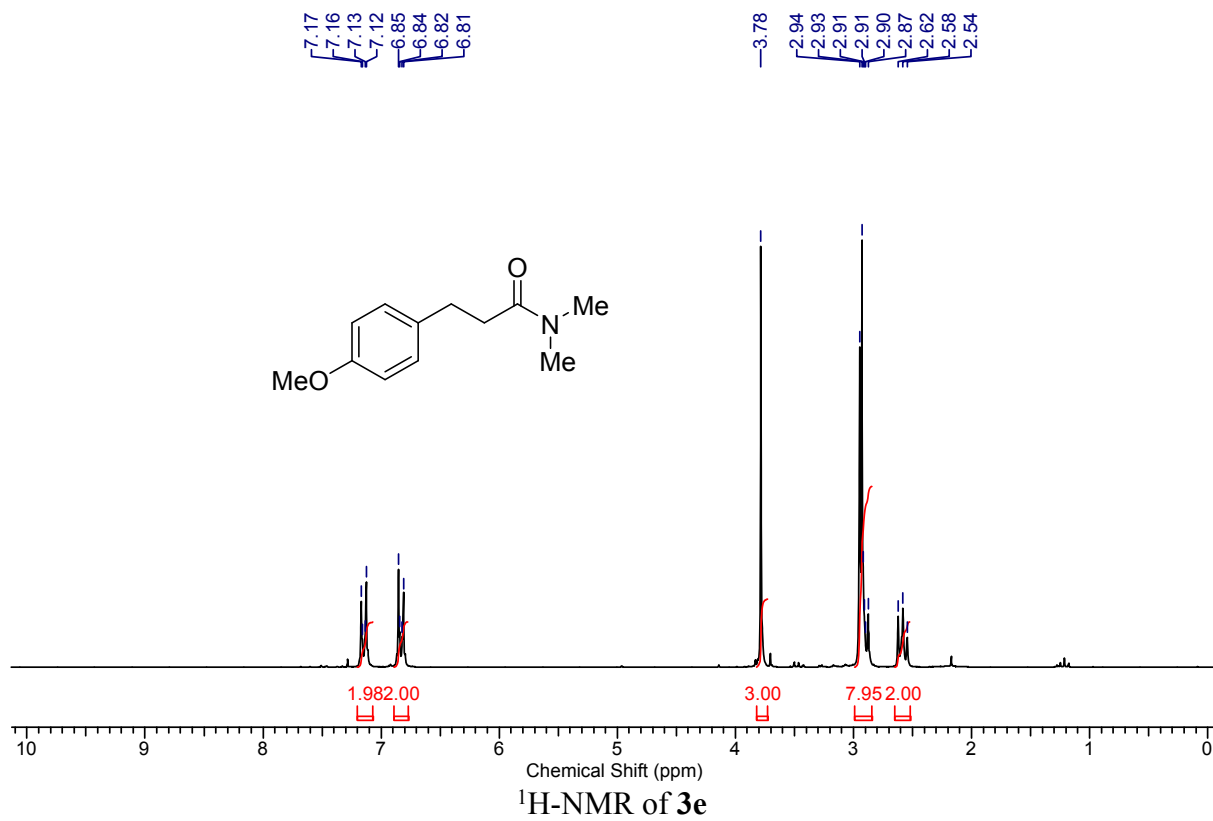


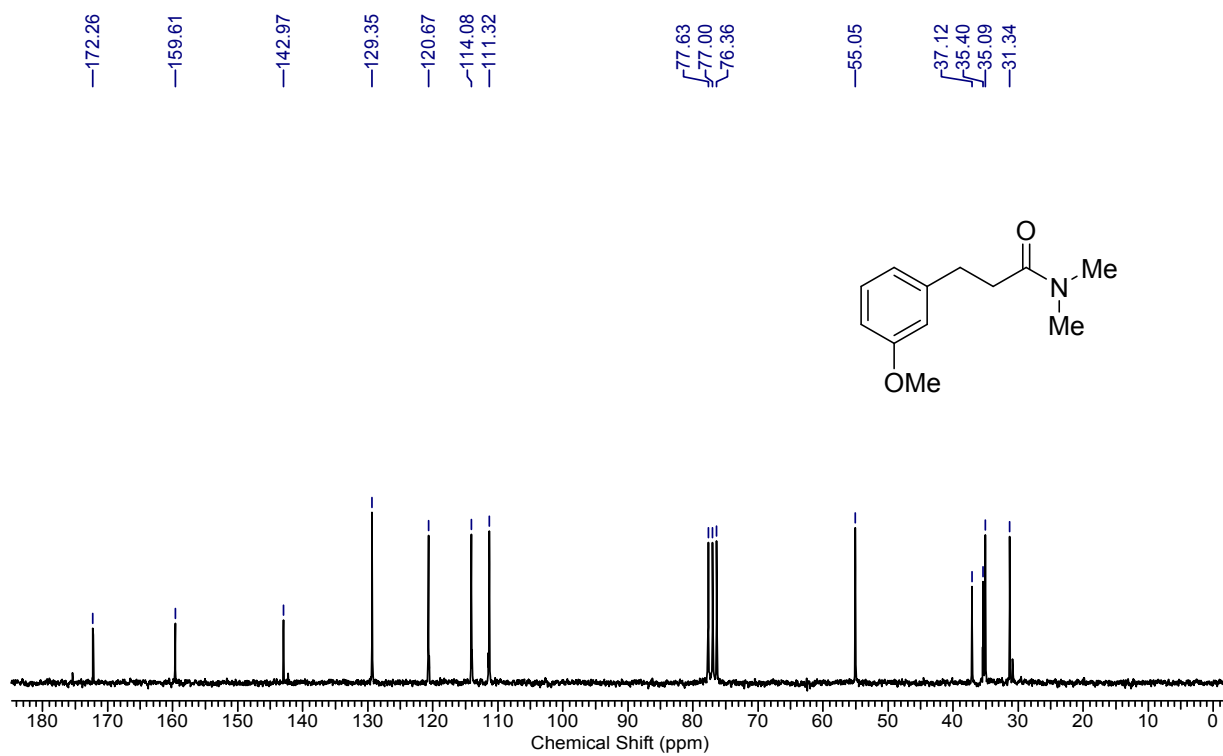
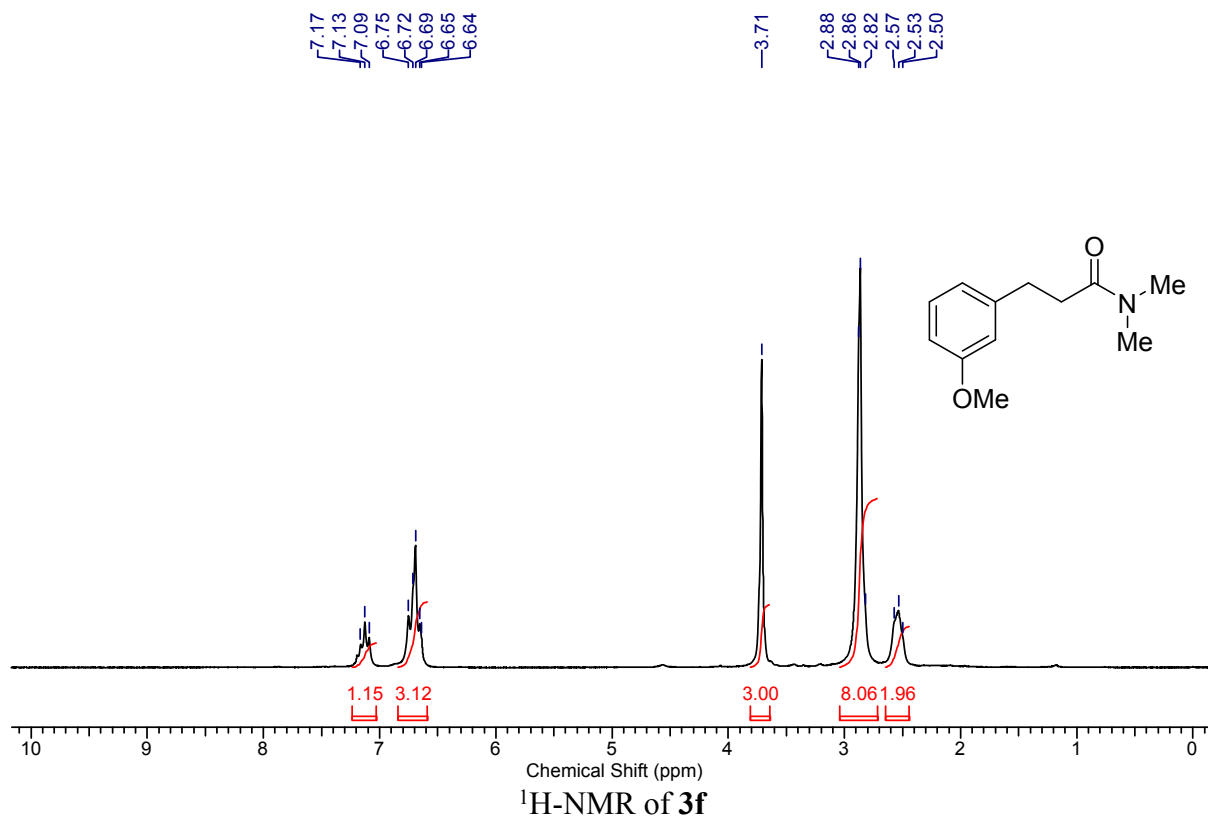
¹H-NMR of **3c**

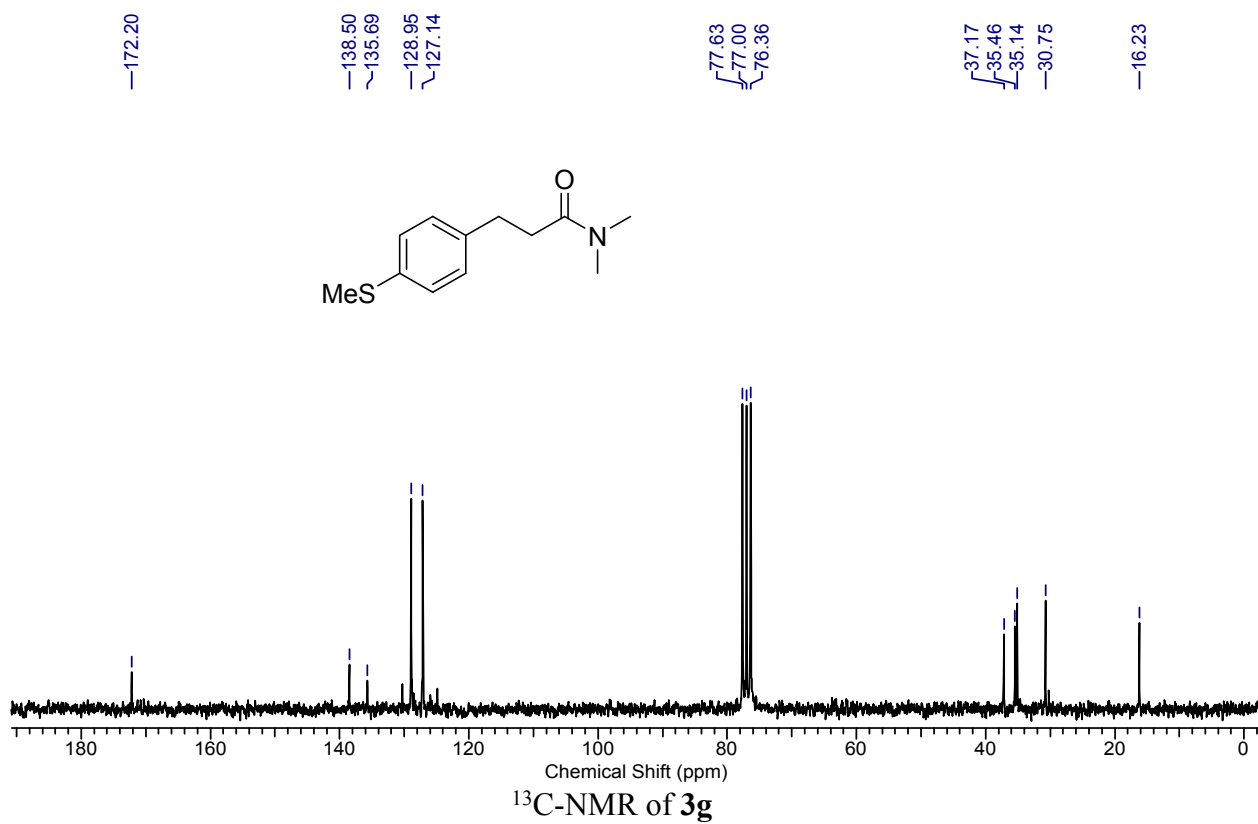
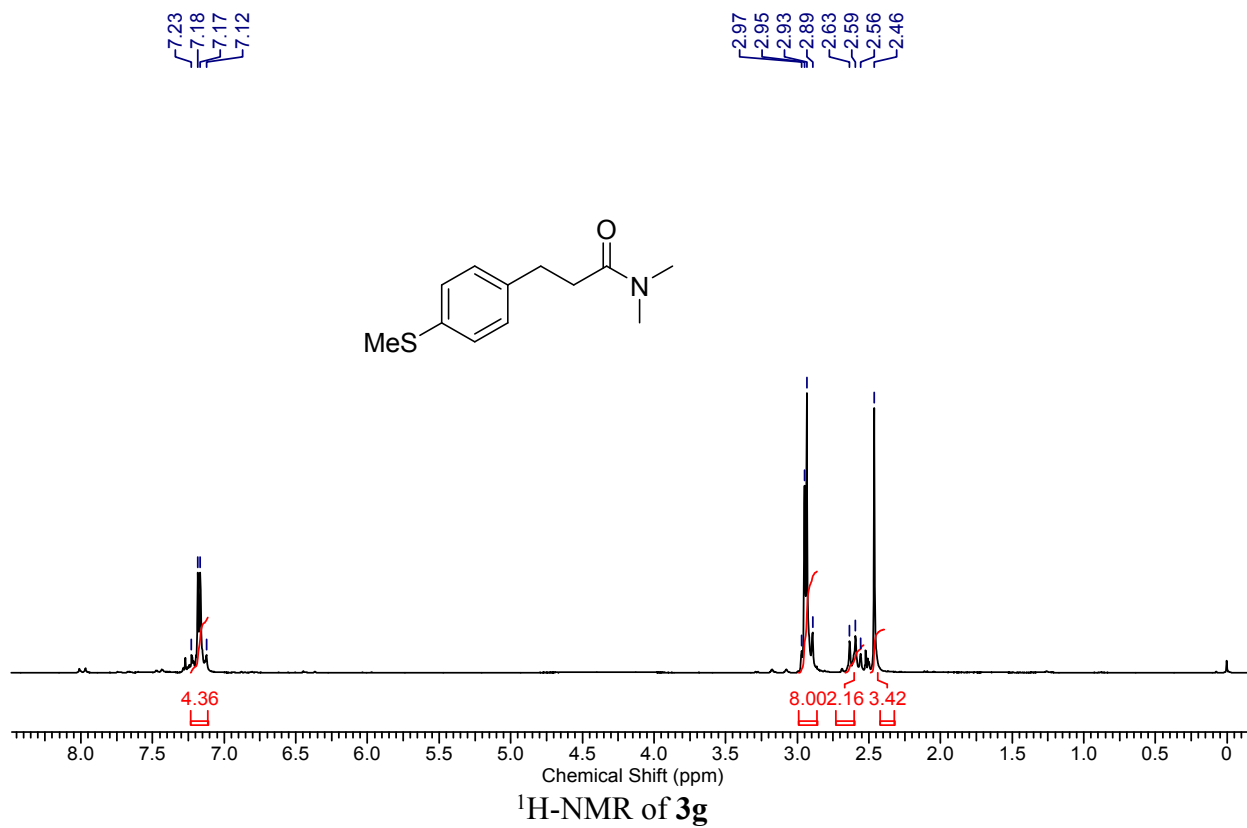


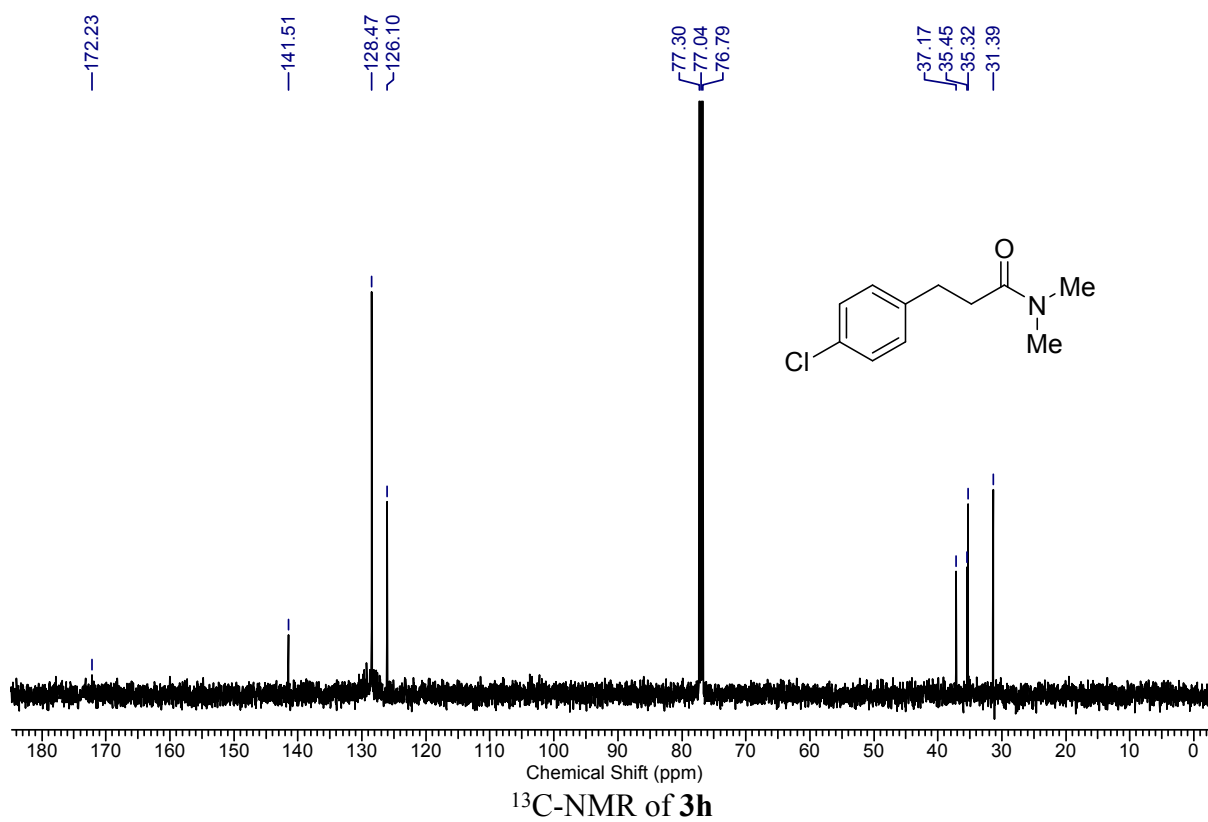
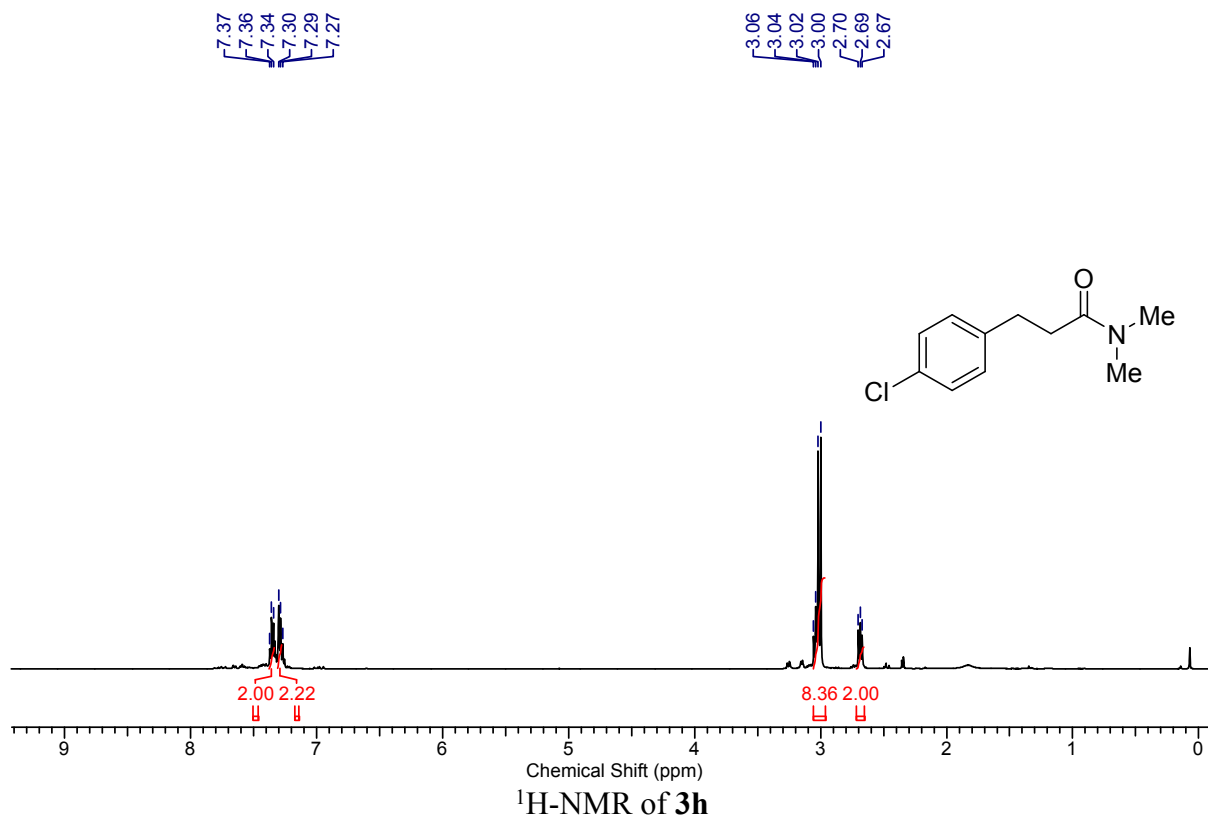
¹³C-NMR of **3c**

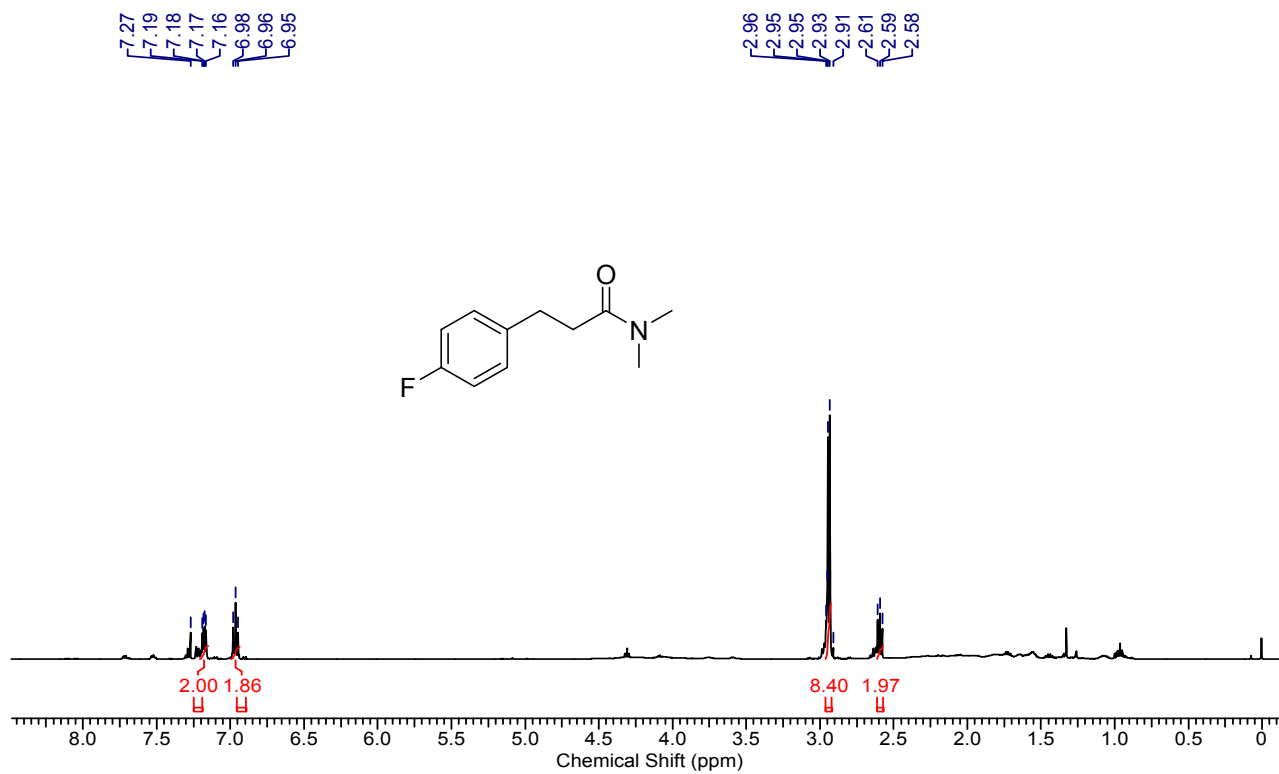




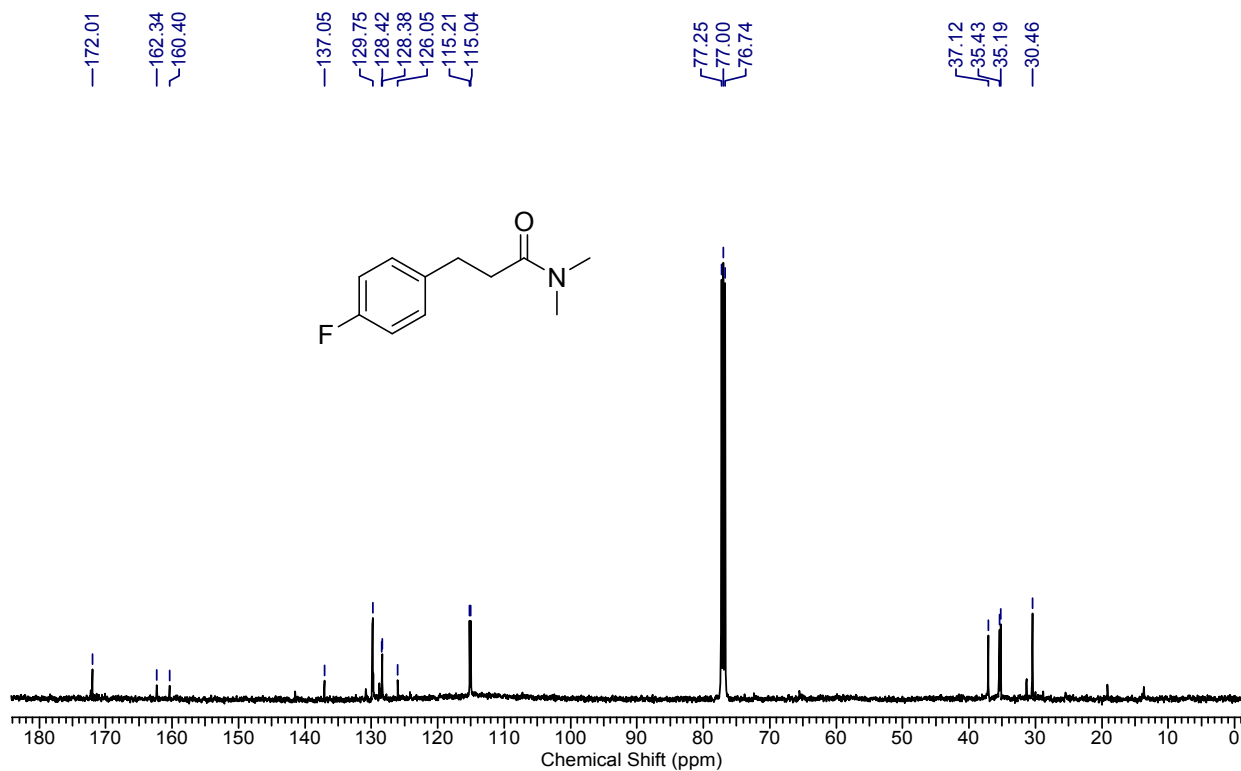




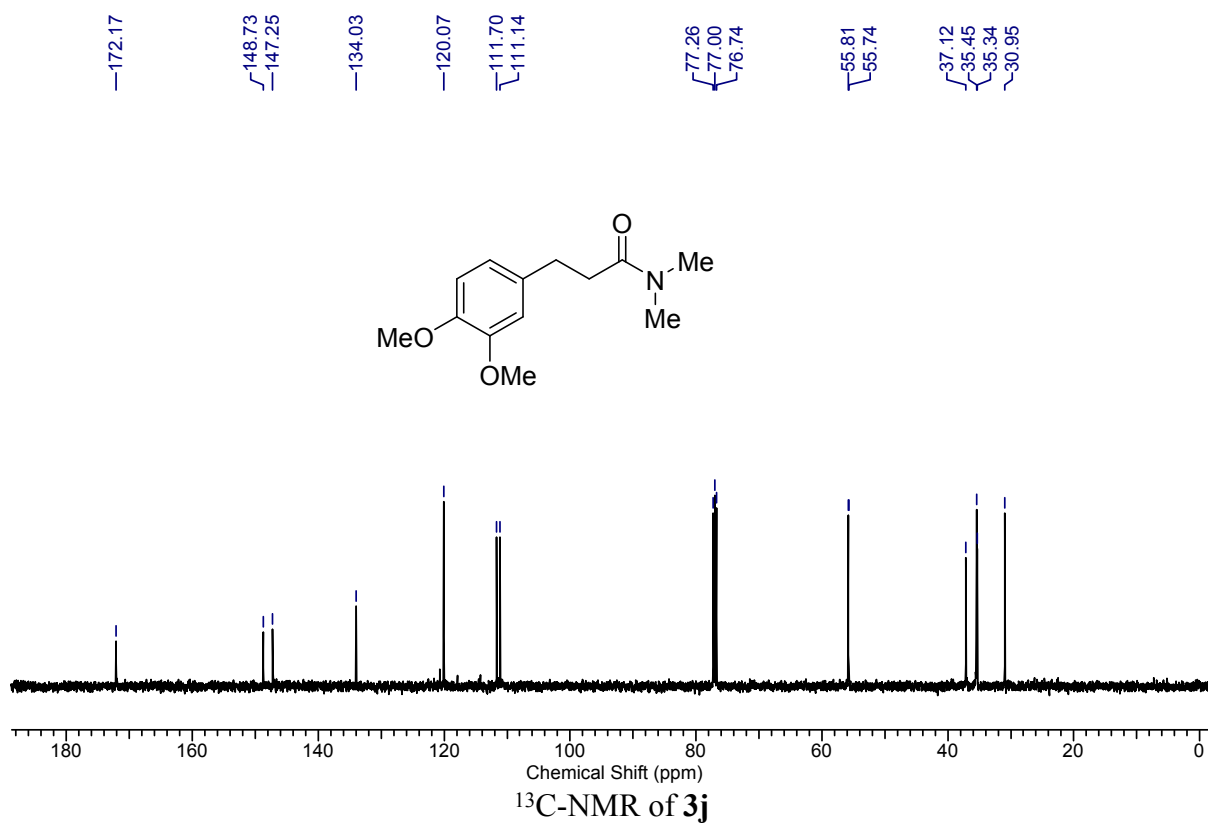
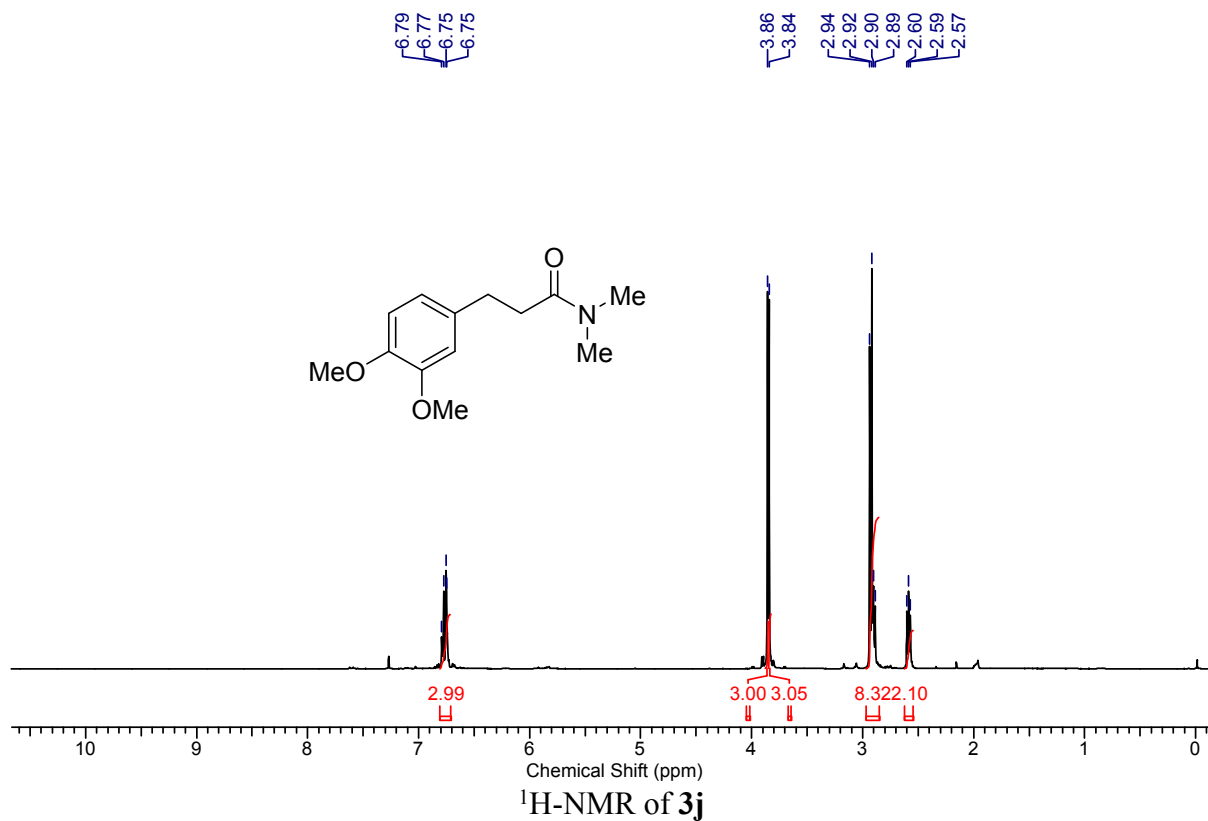


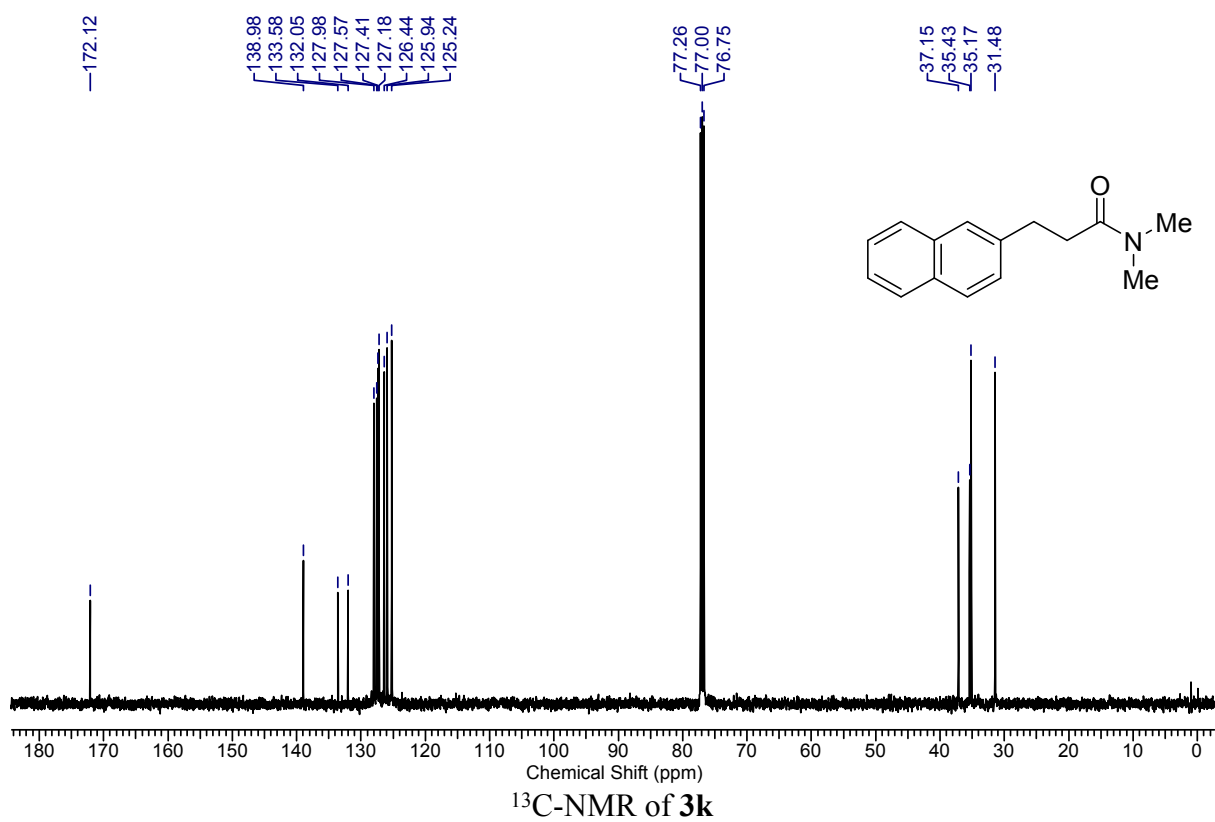
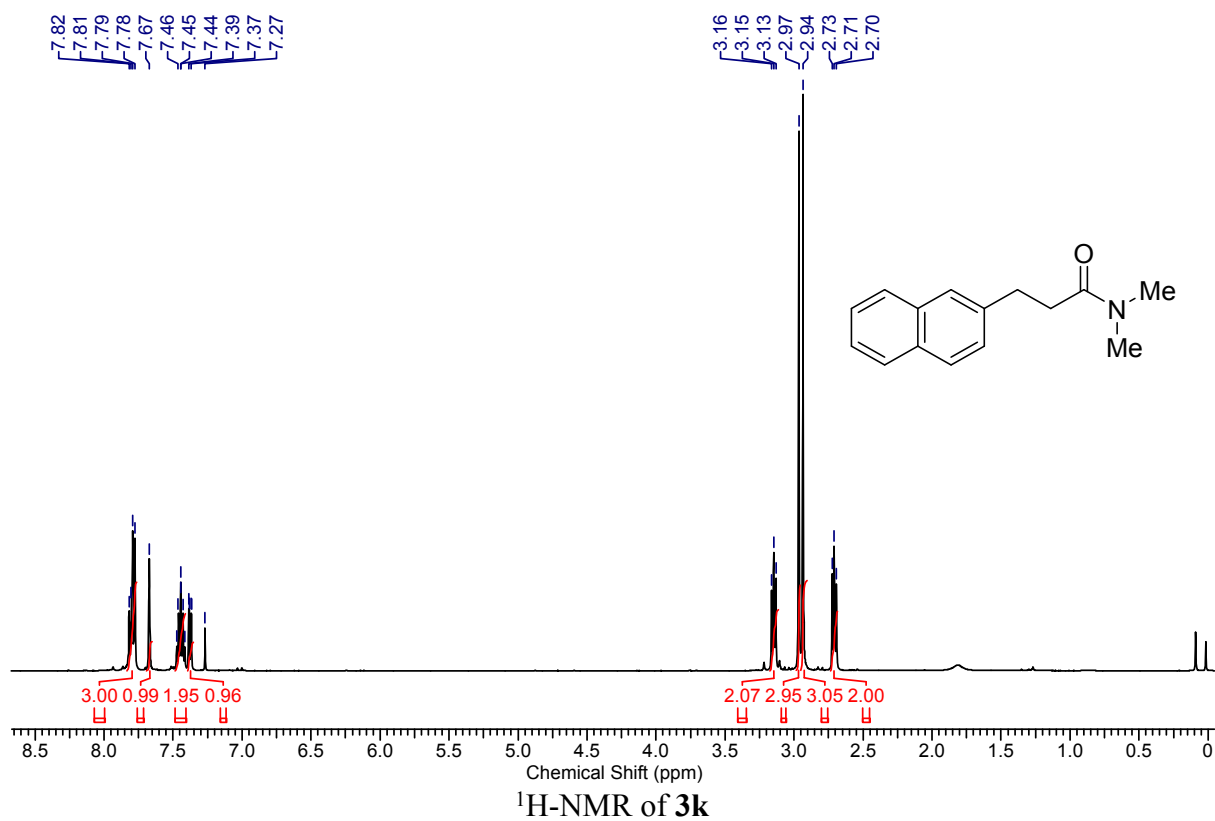


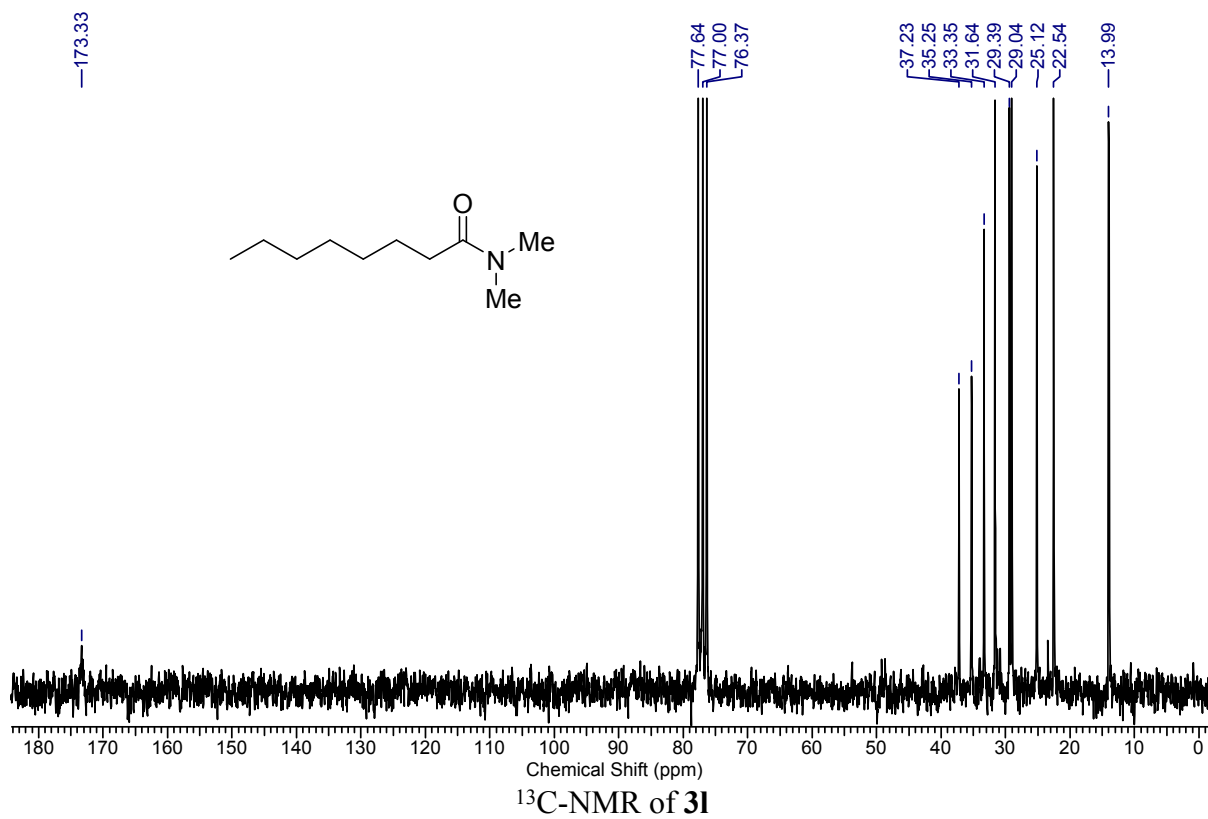
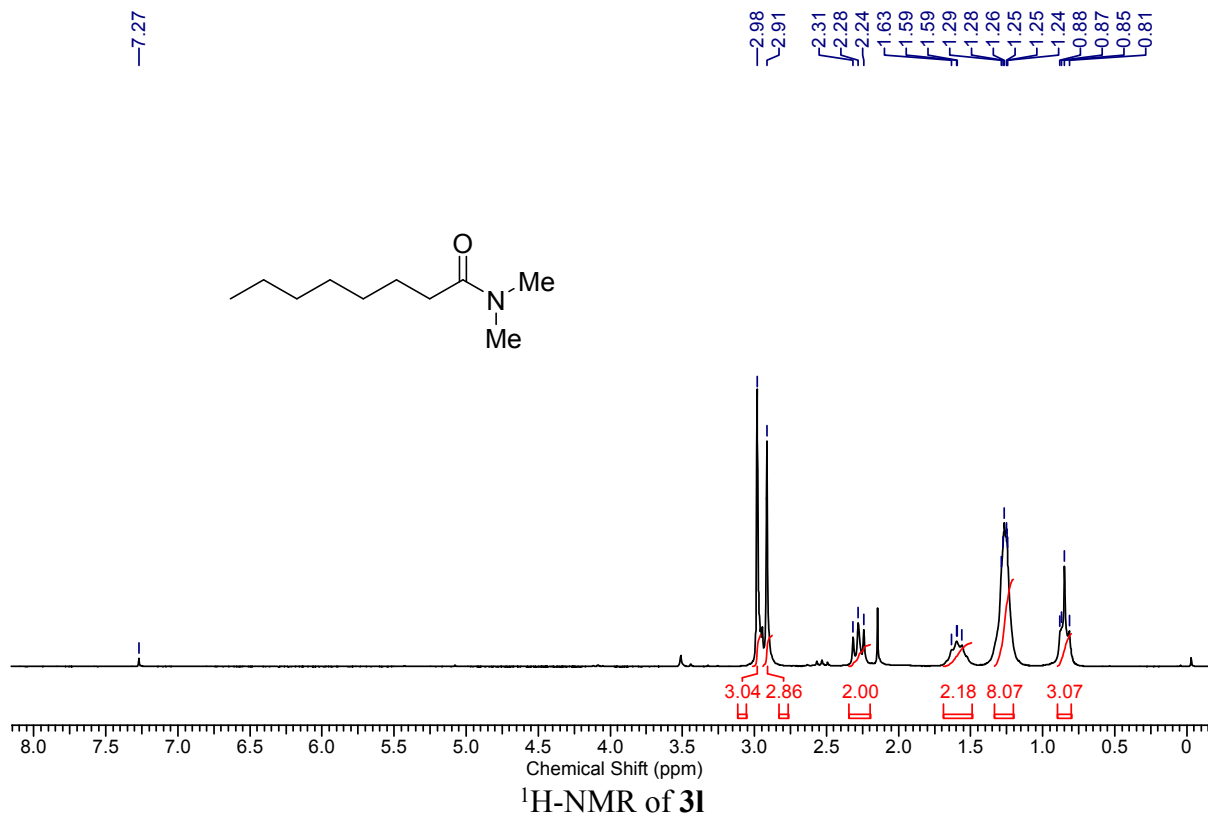
¹H-NMR of **3i**

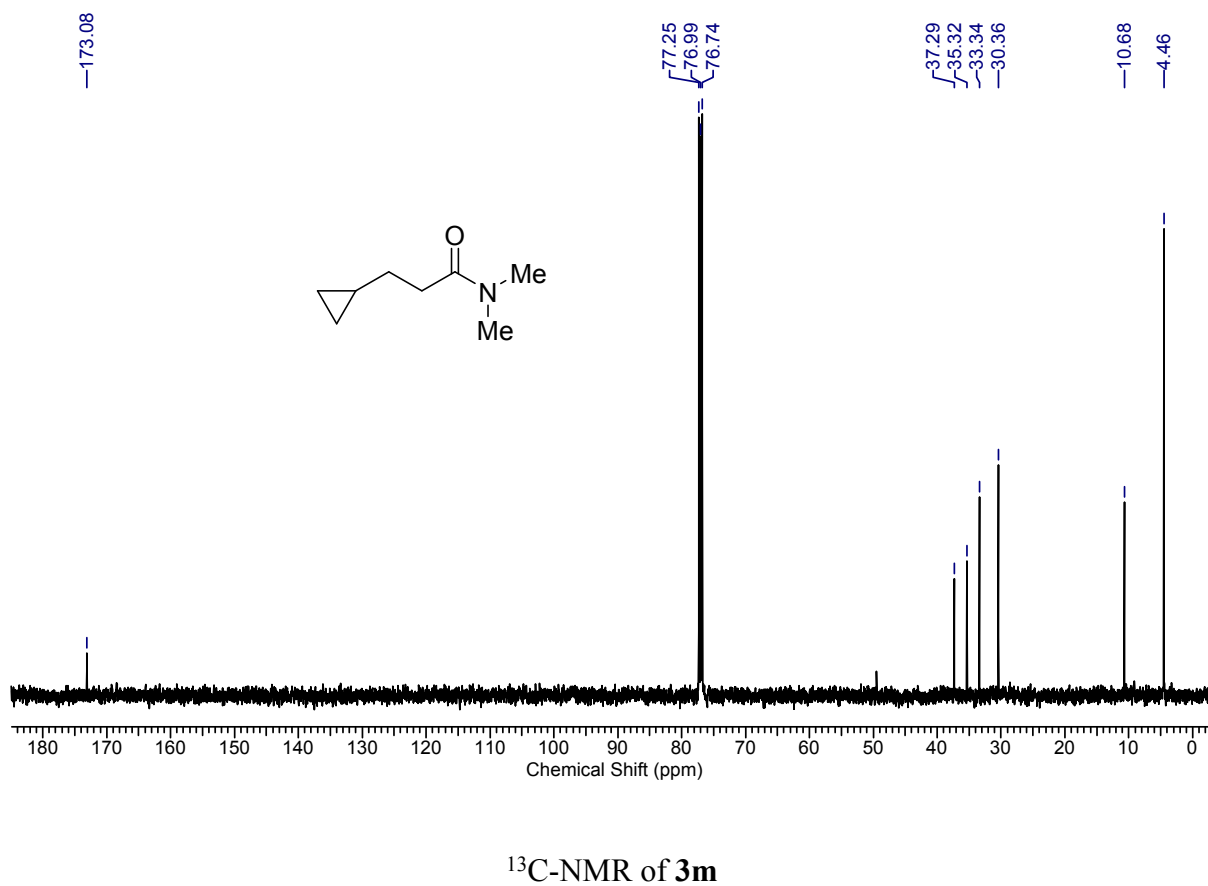
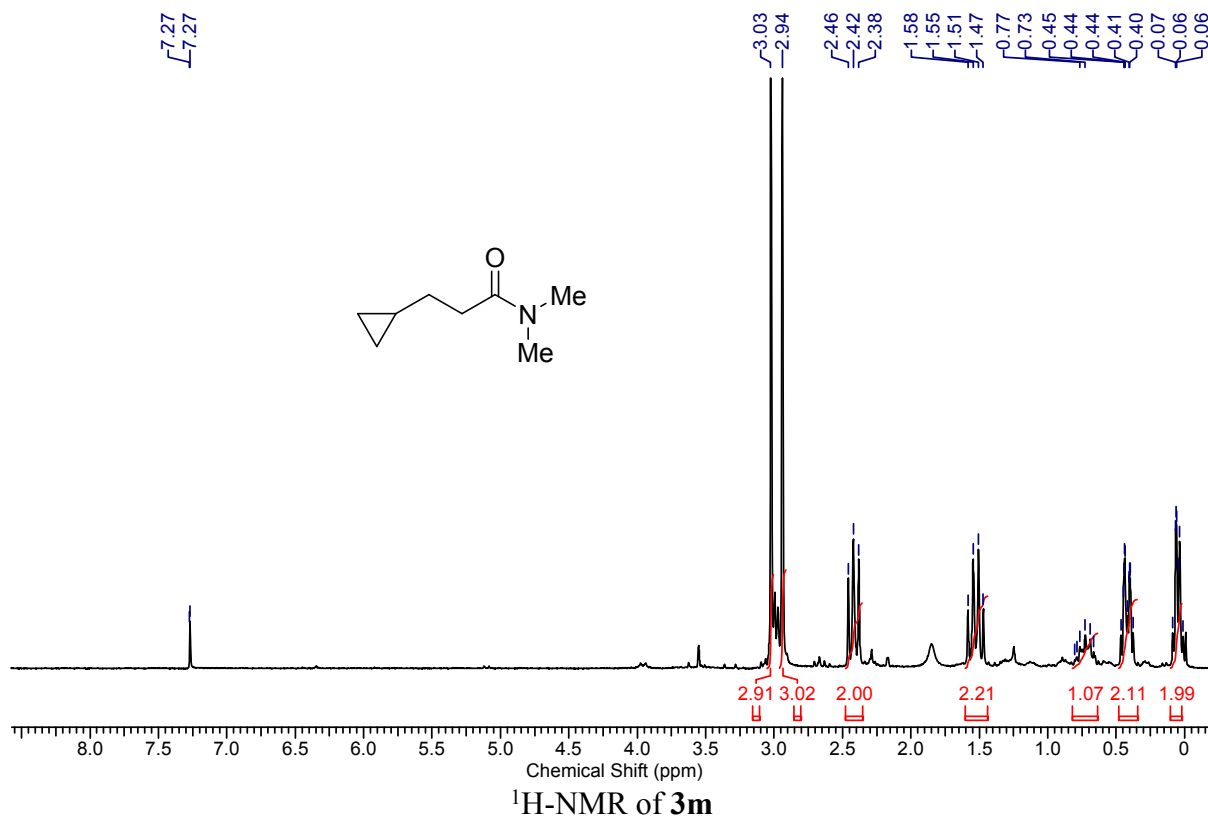


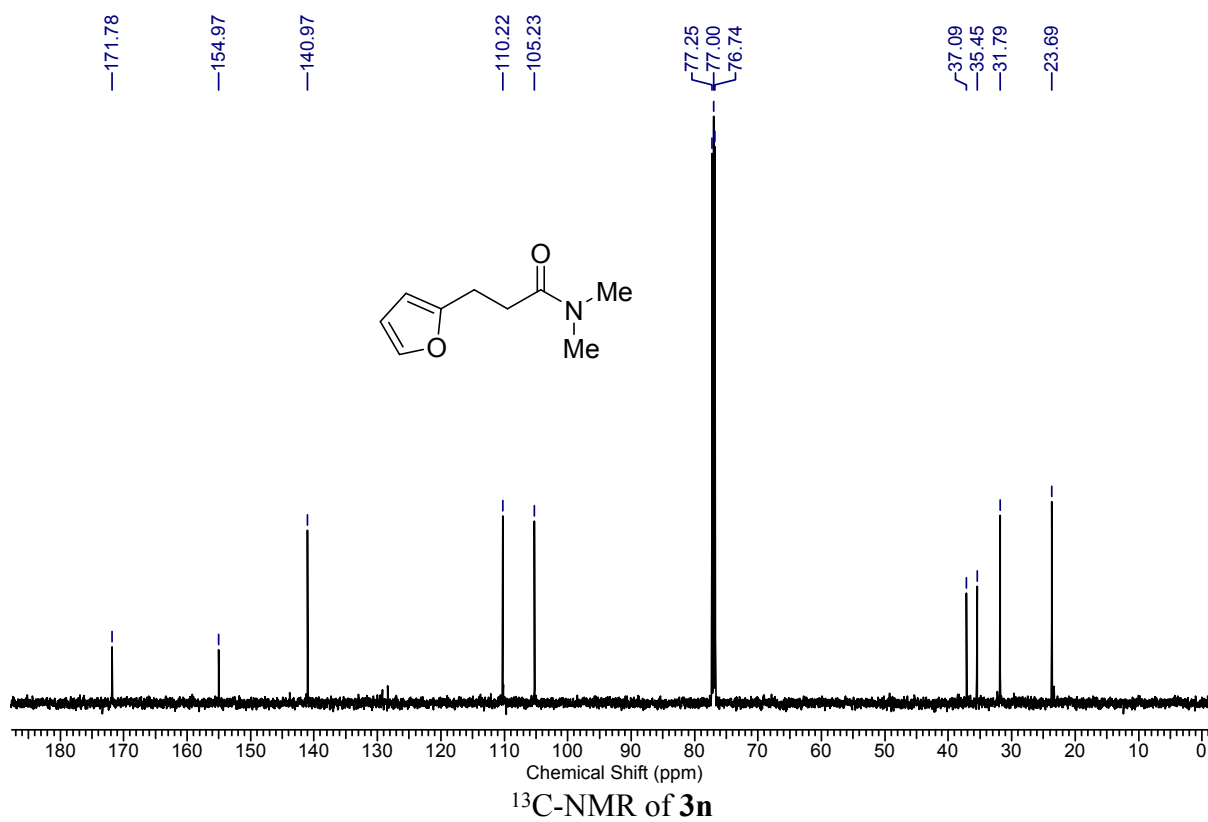
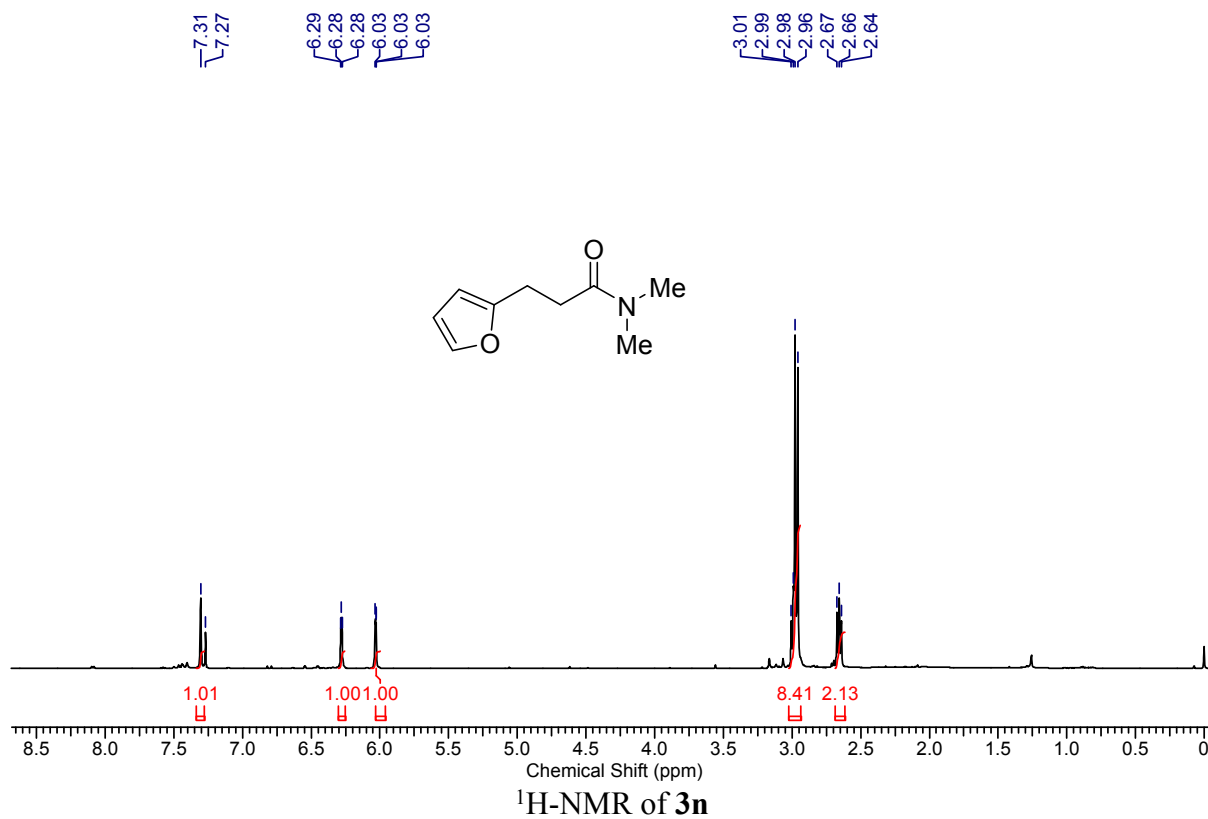
¹³C-NMR of **3i**

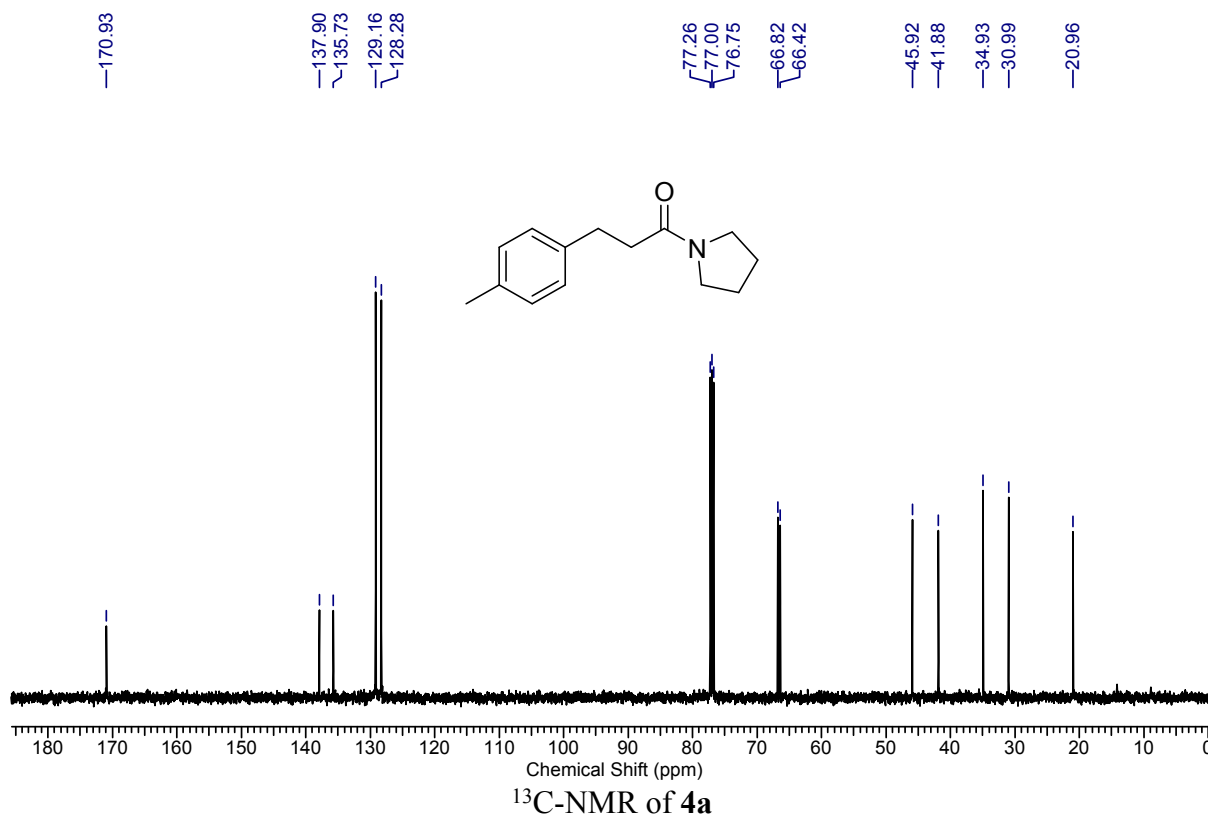
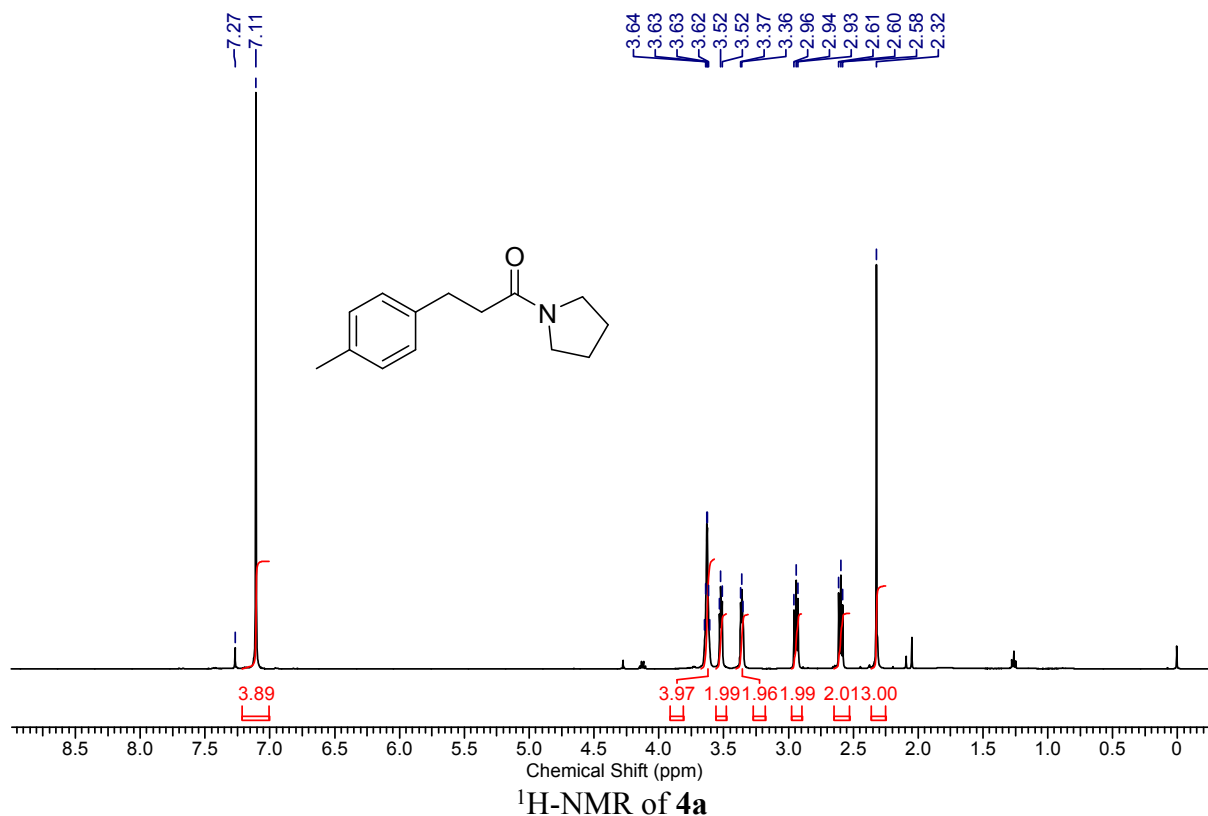


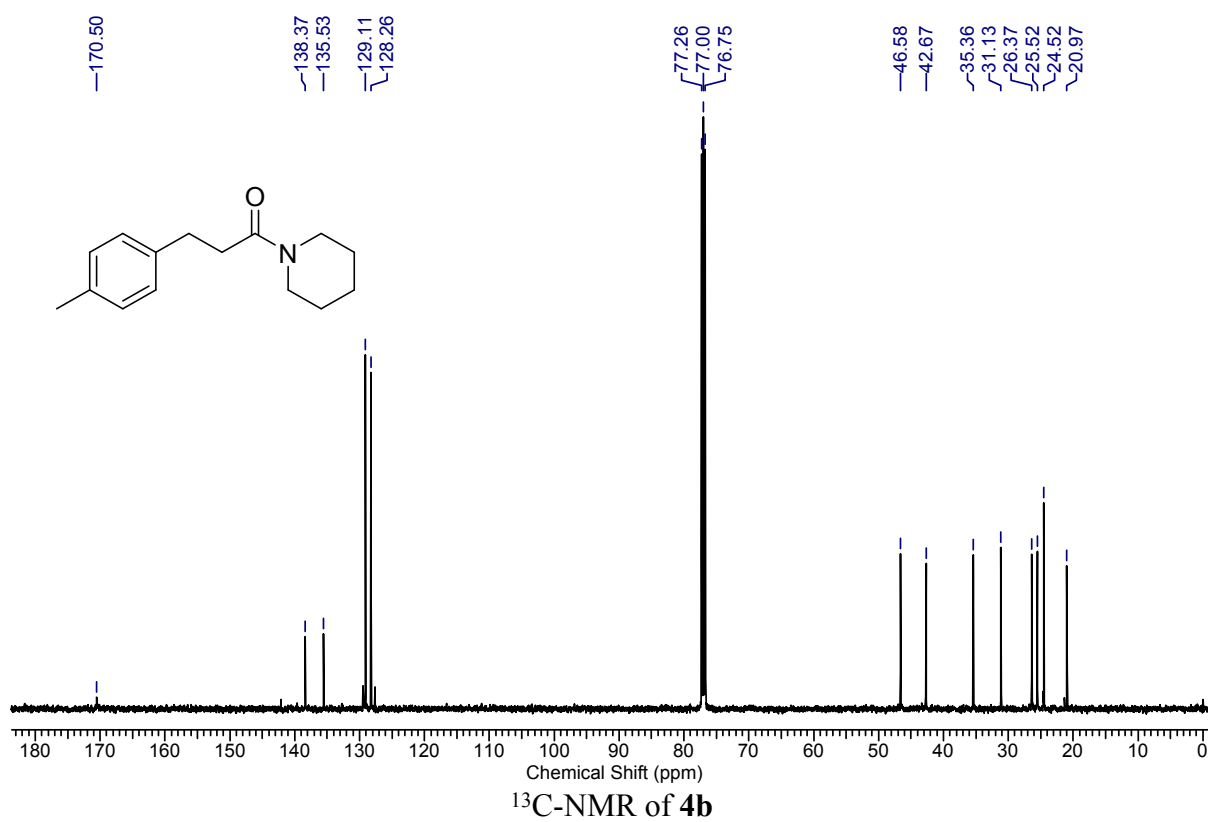
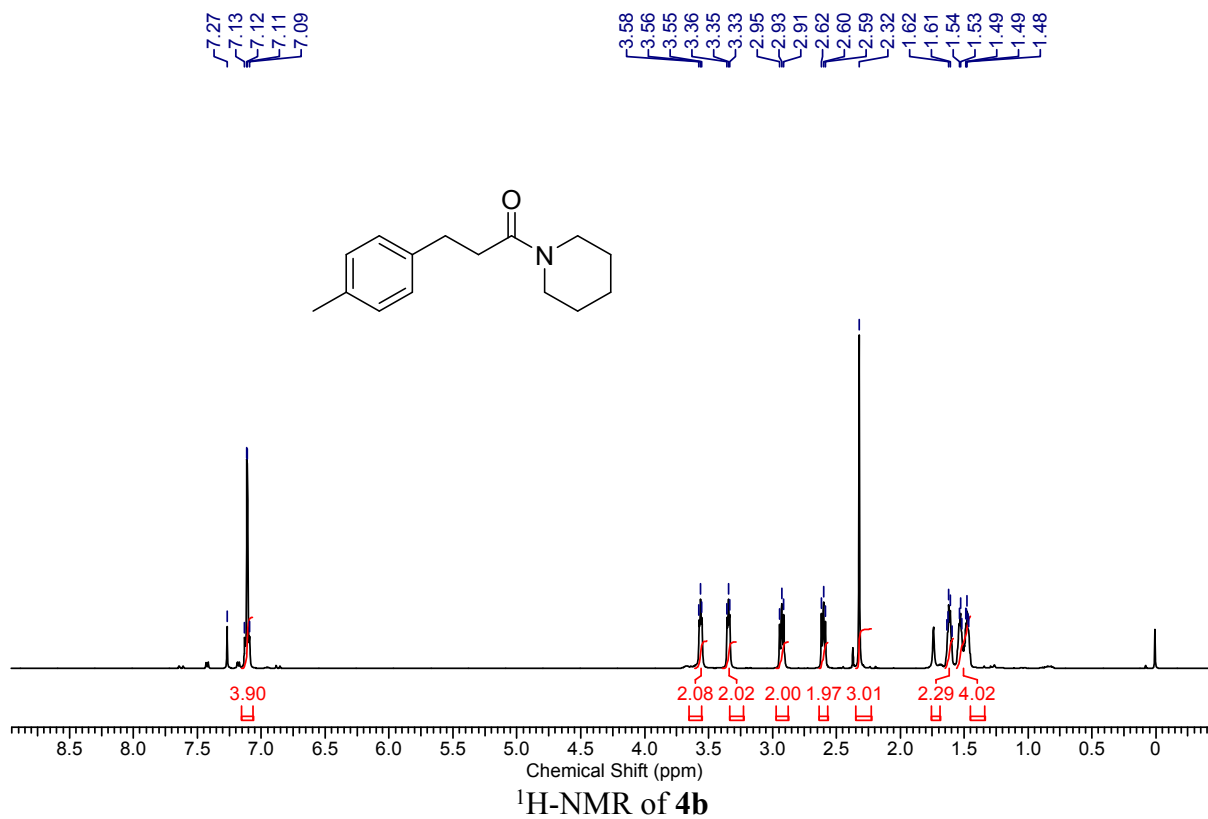


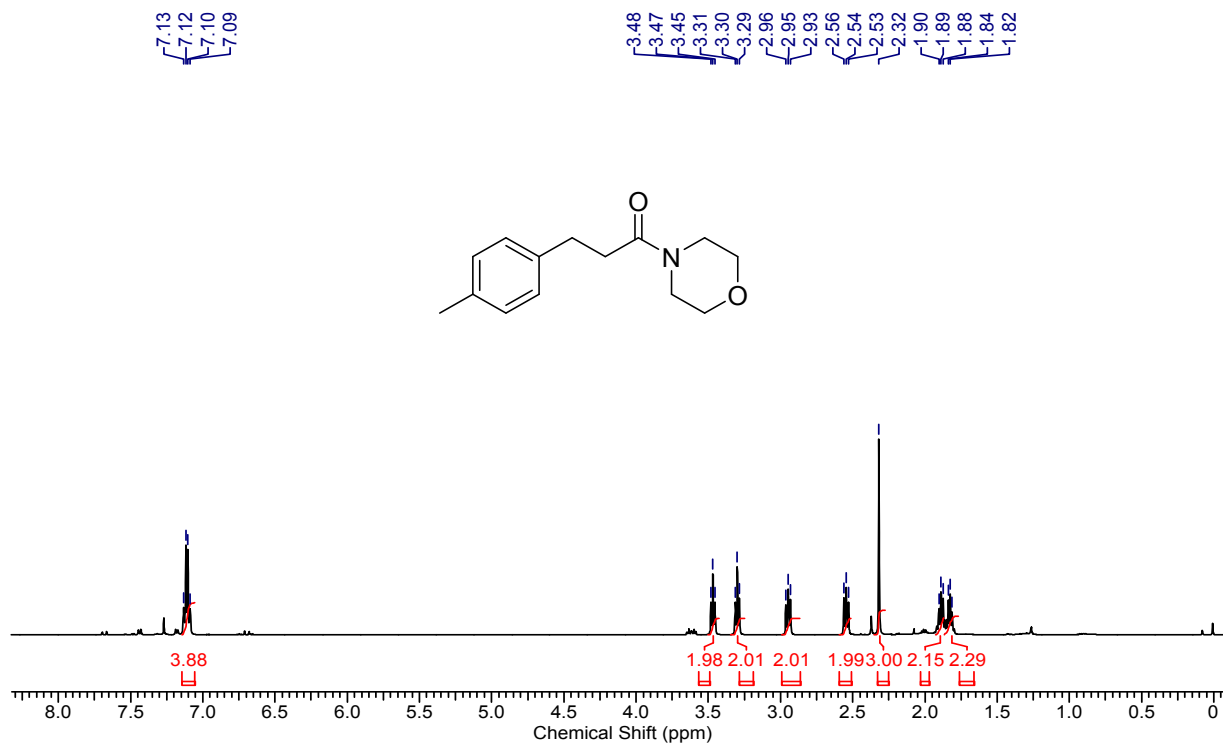




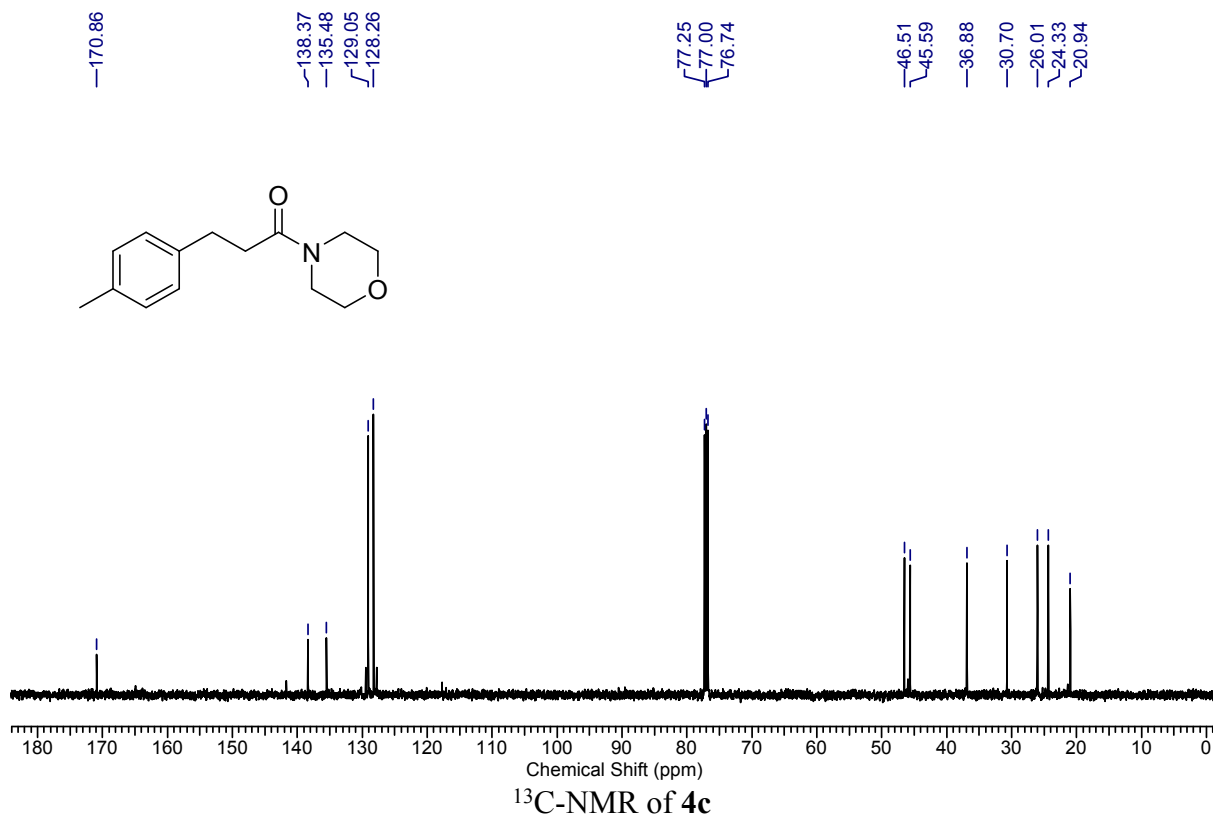




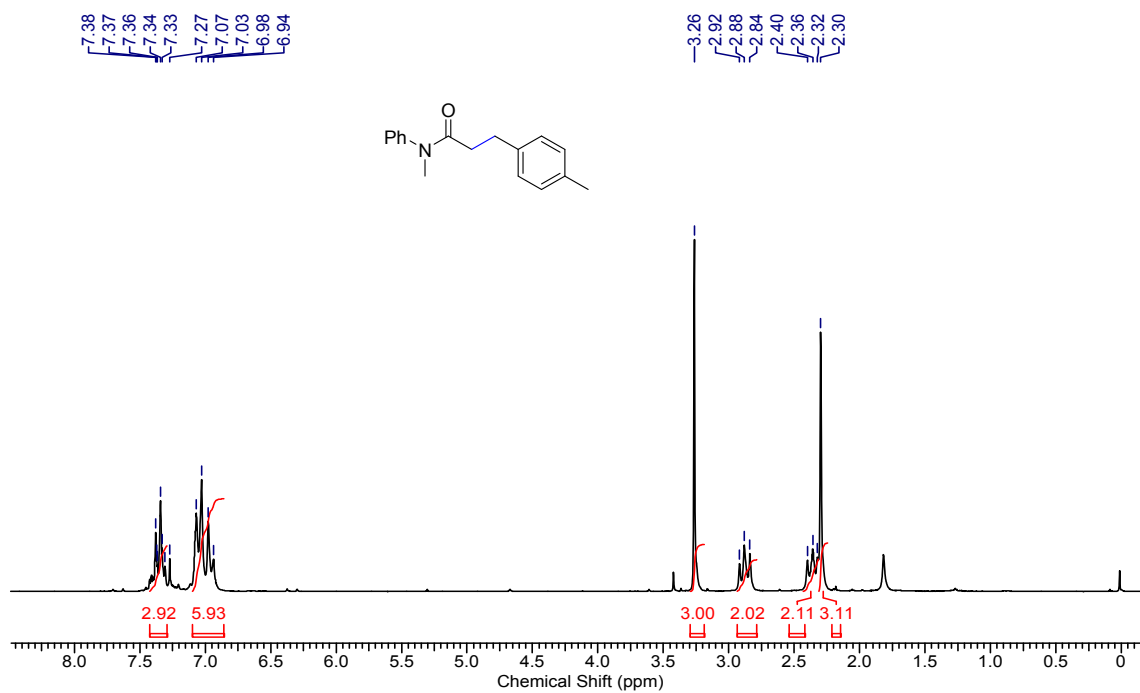




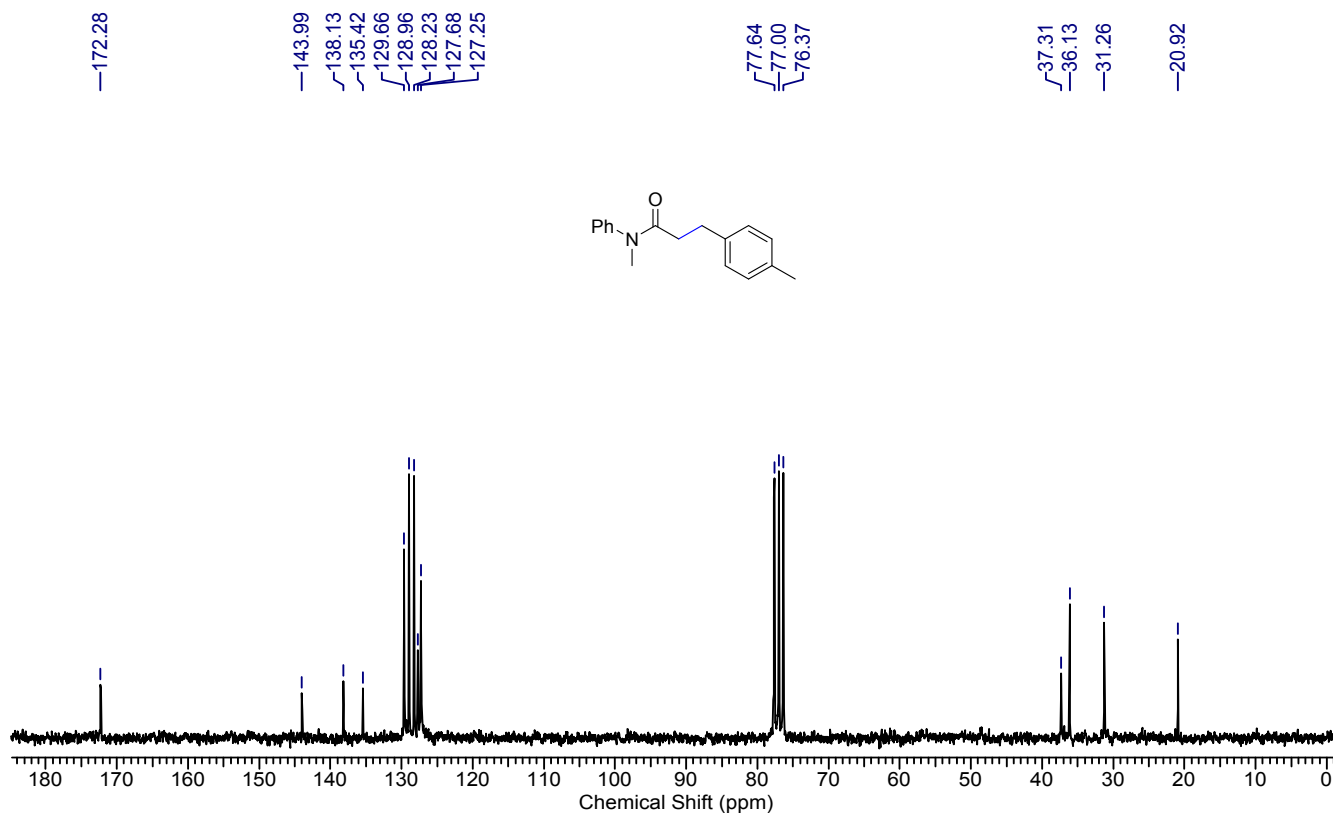
¹H-NMR of 4c



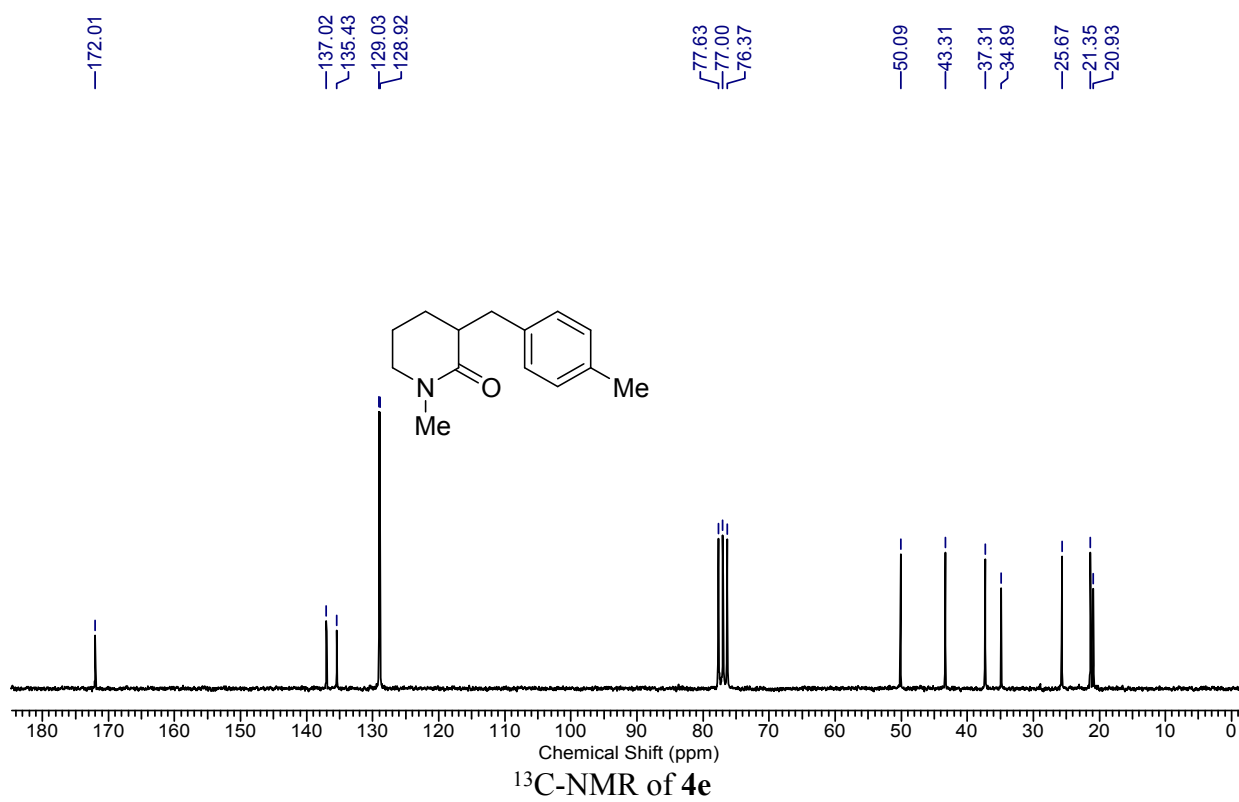
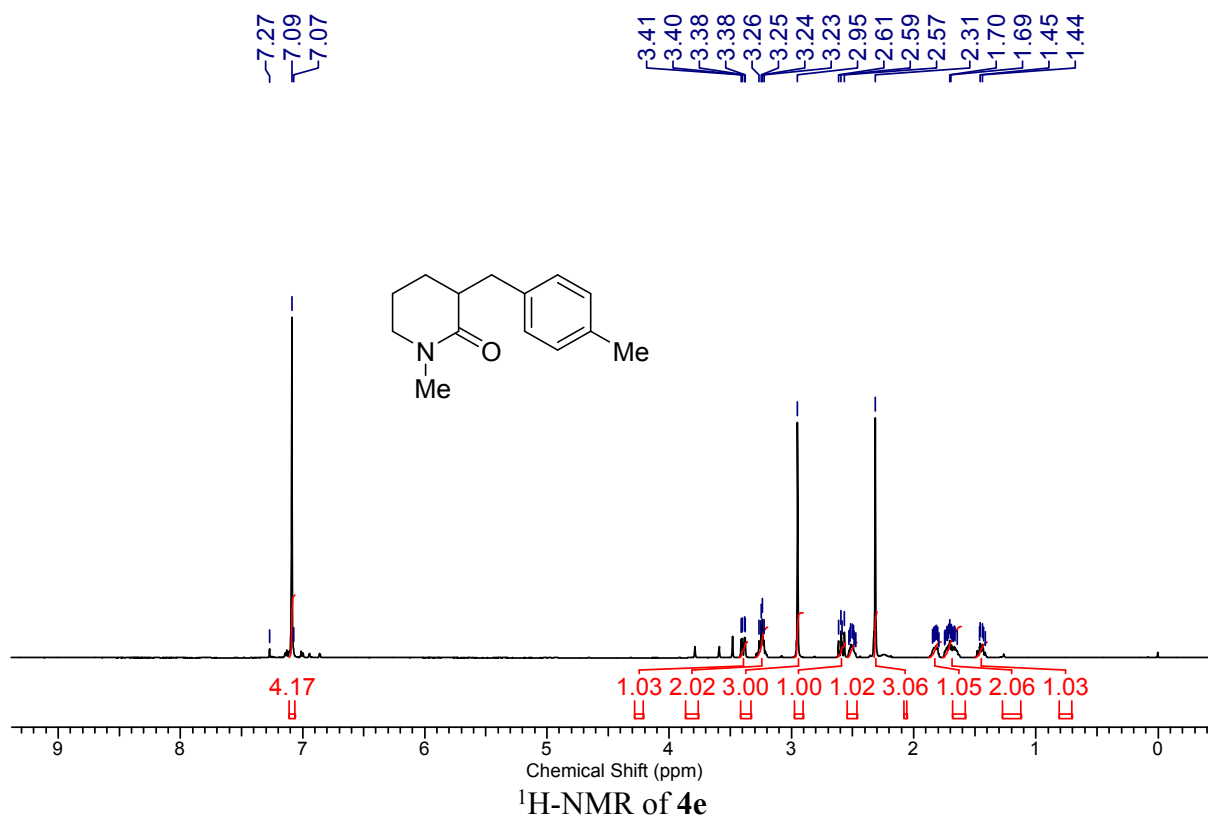
¹³C-NMR of 4c

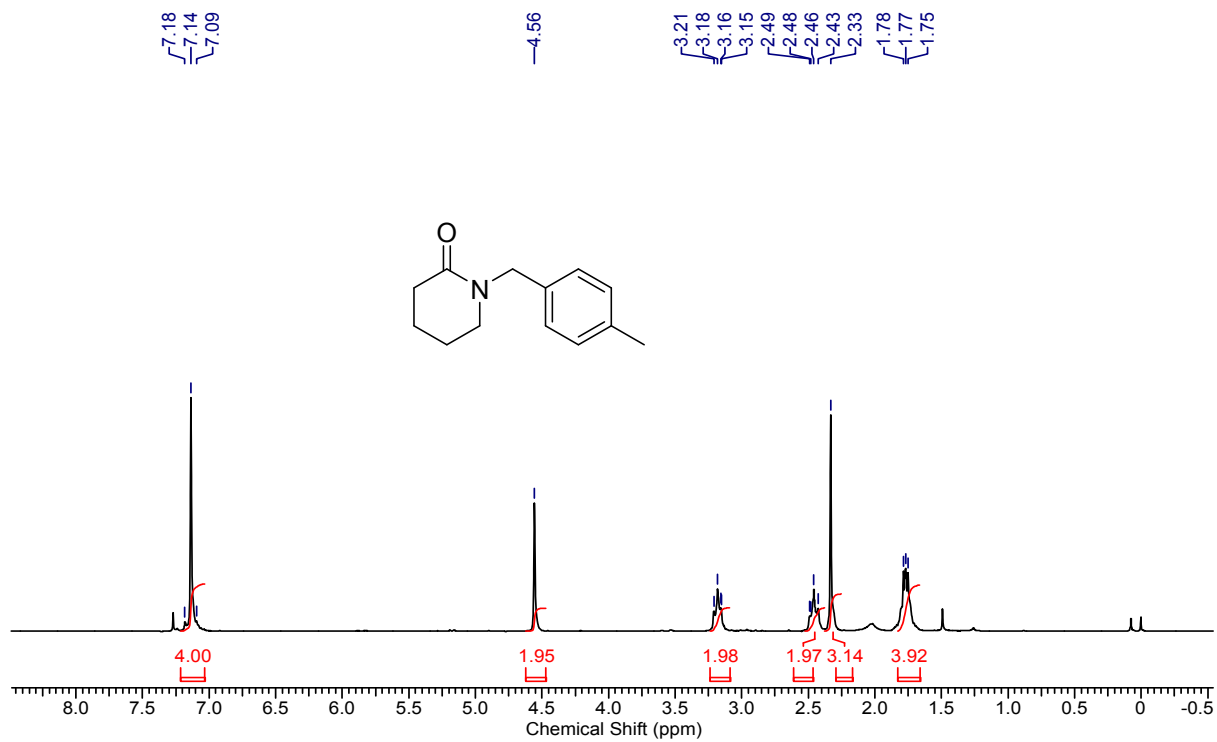


¹H NMR of **4d**

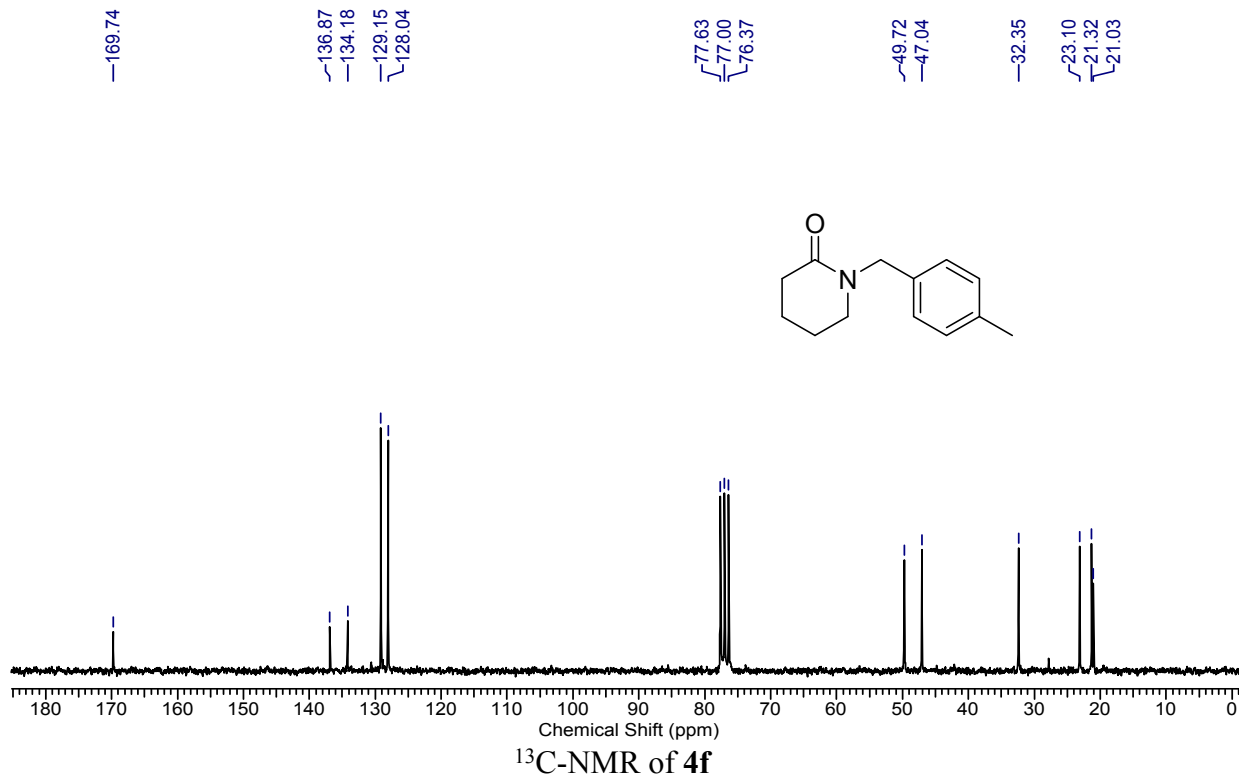


¹³C NMR of **4d**

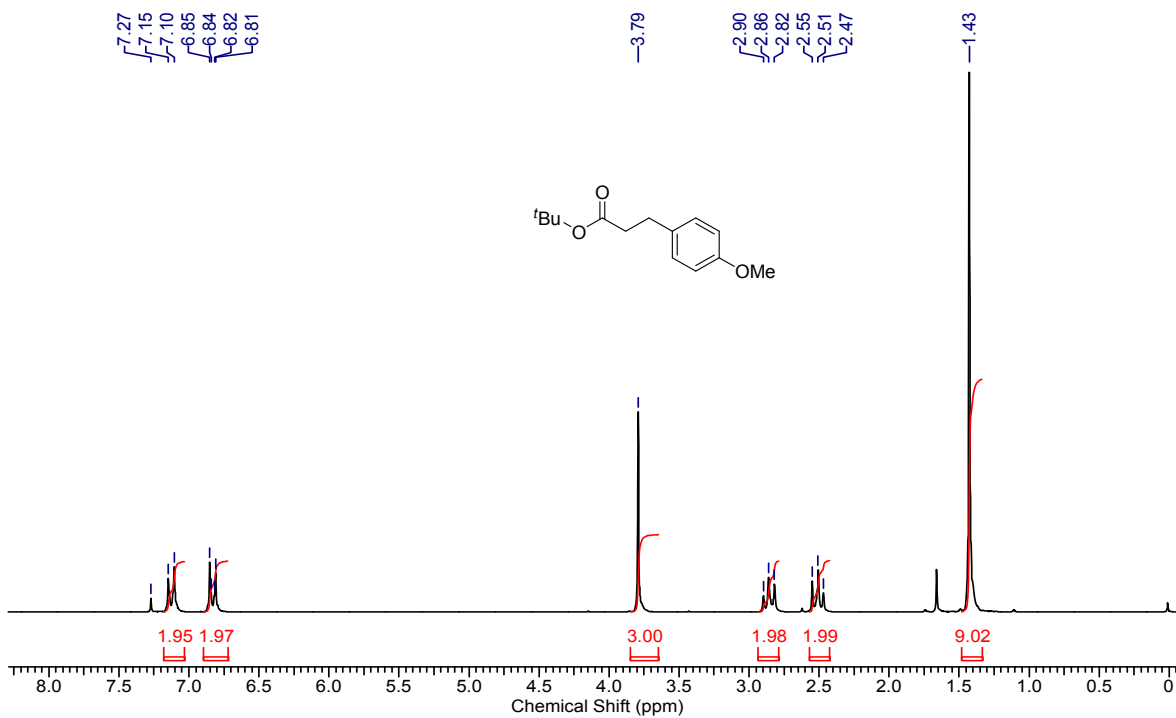




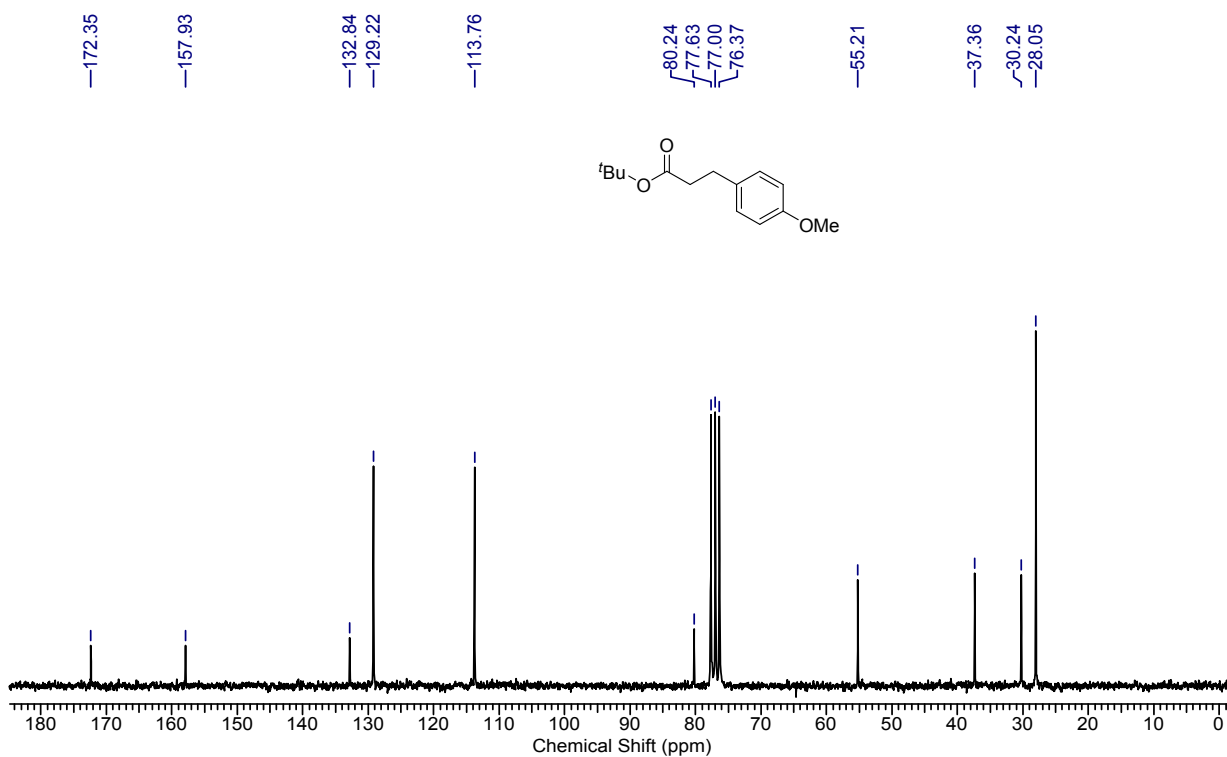
¹H-NMR of 4f



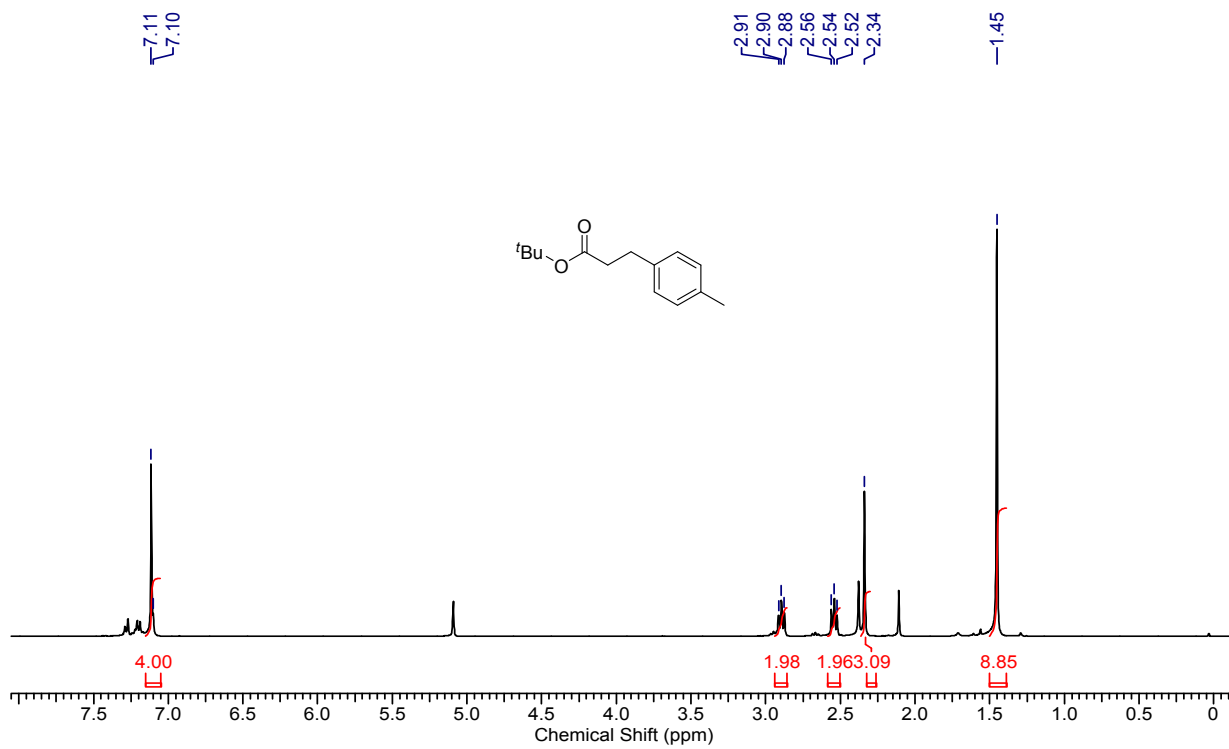
¹³C-NMR of 4f



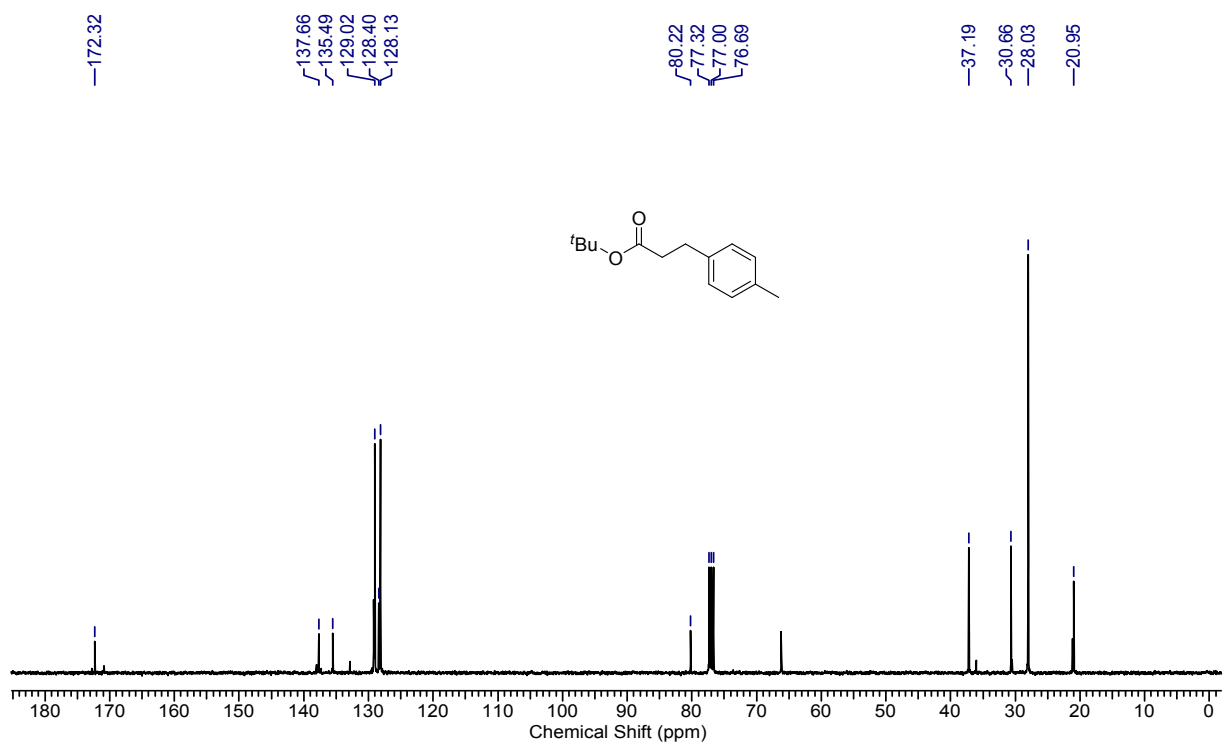
¹H-NMR of 5a



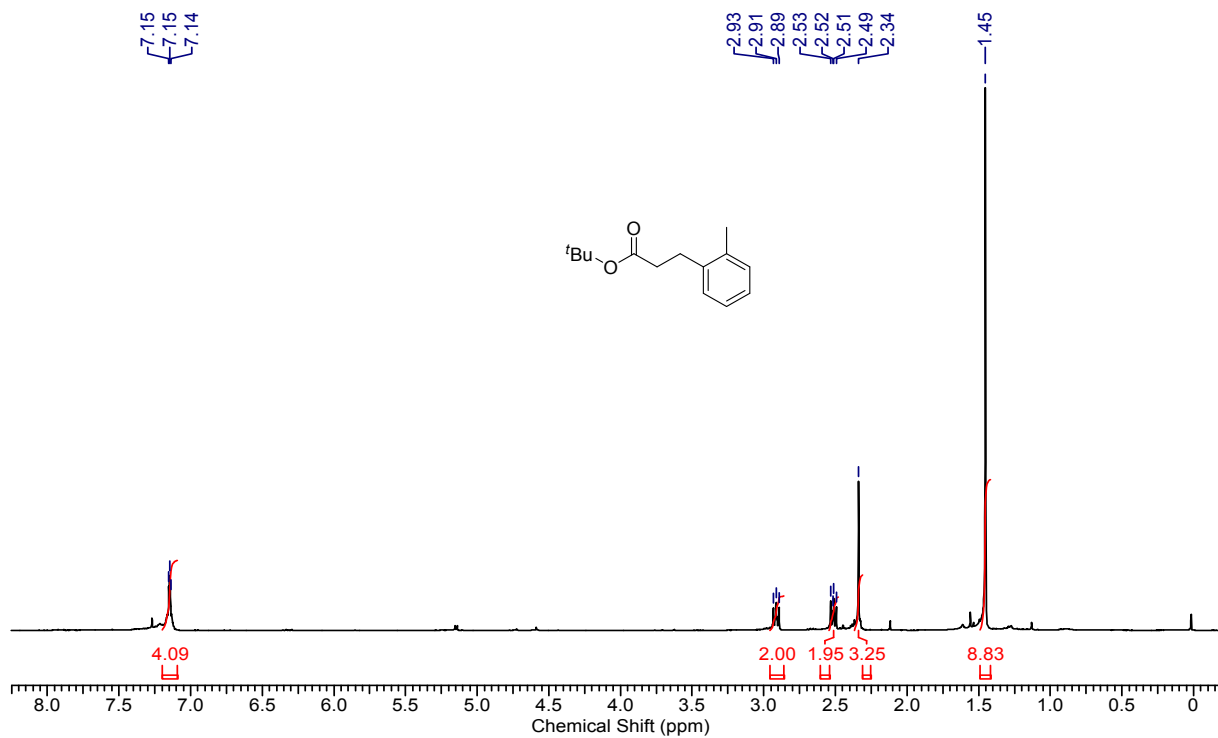
¹³C-NMR of 5a



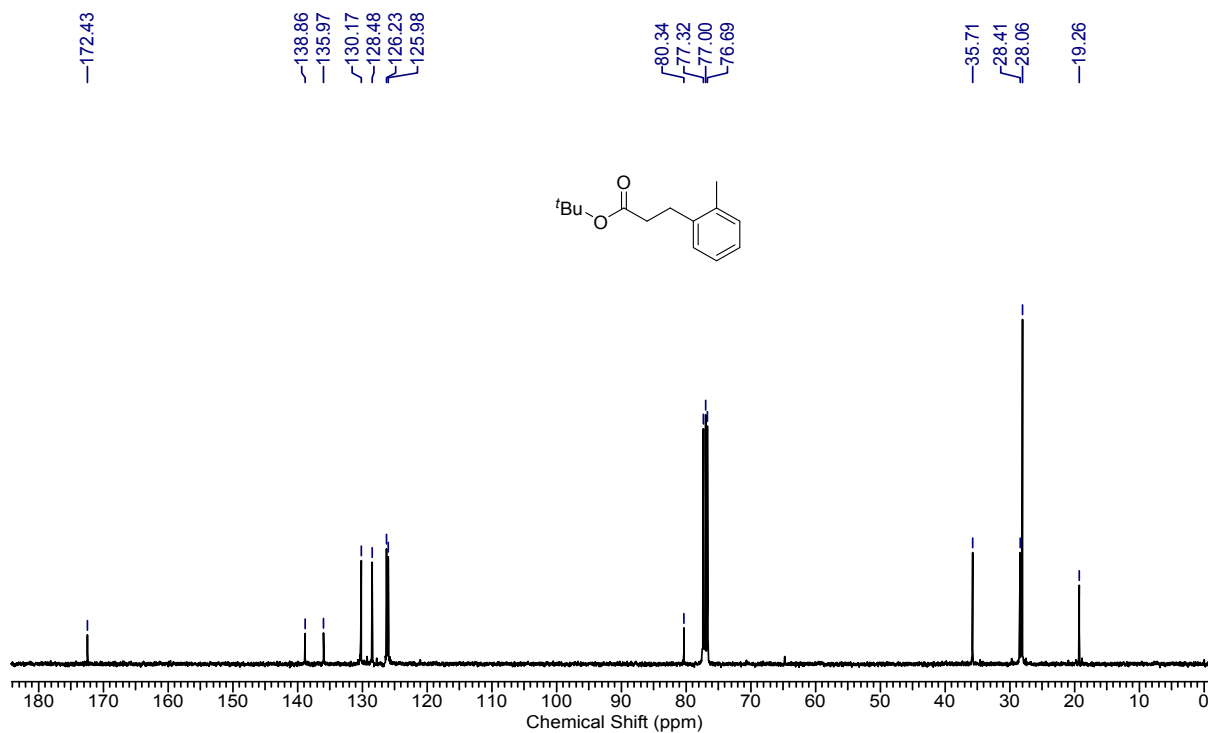
¹H-NMR of **5b**



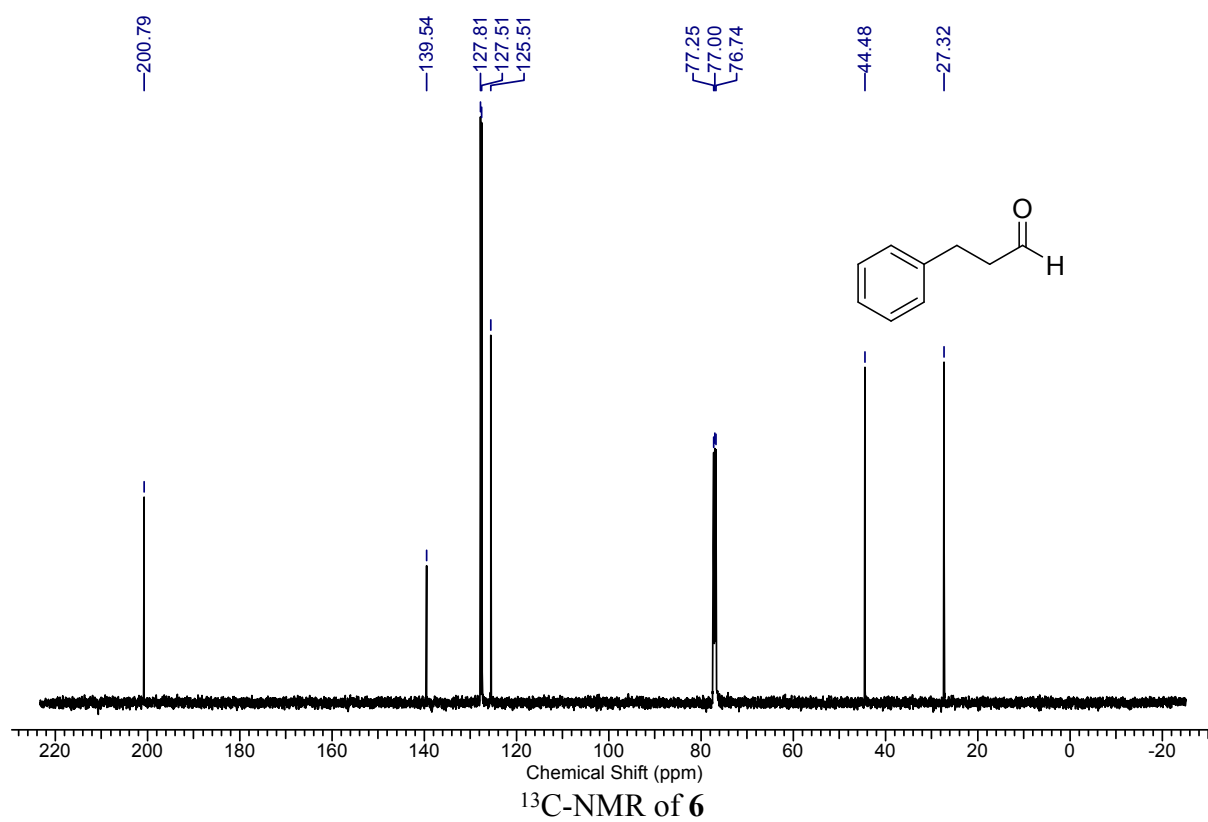
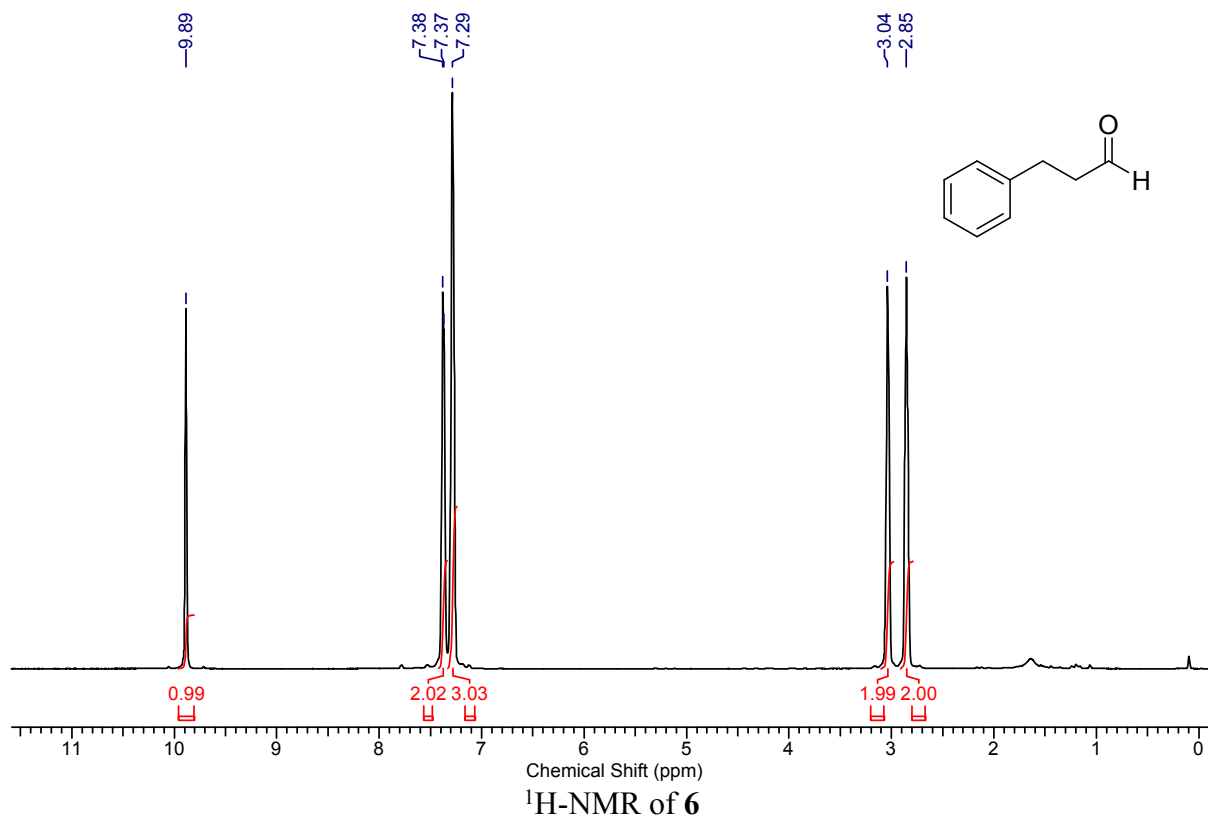
¹³C-NMR of **5b**

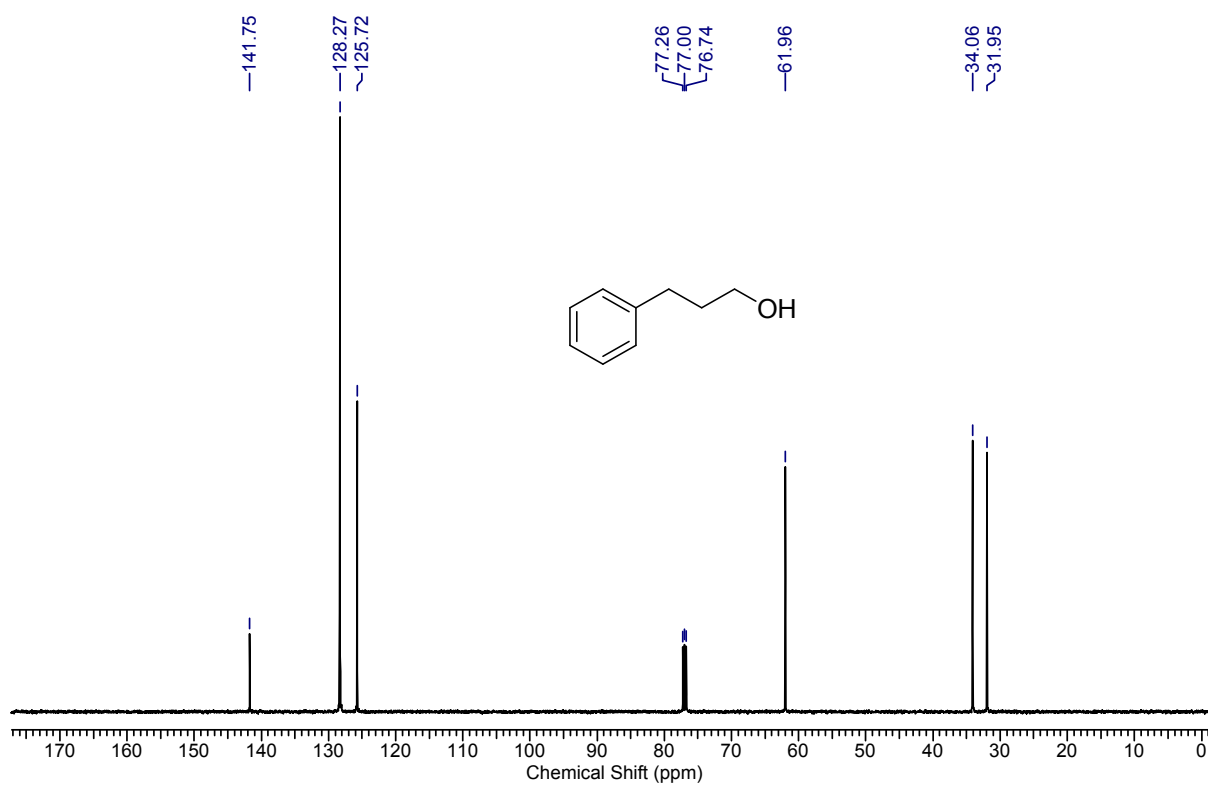
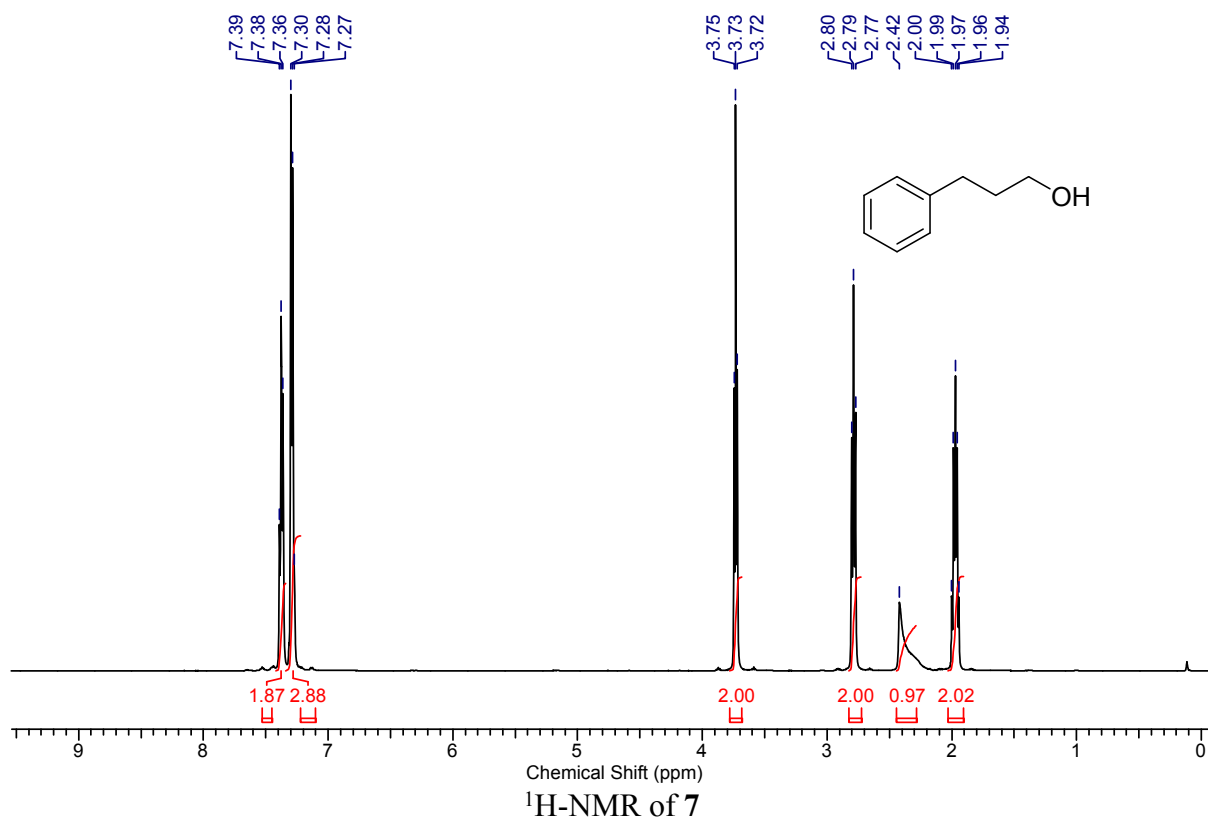


¹H-NMR of 5c



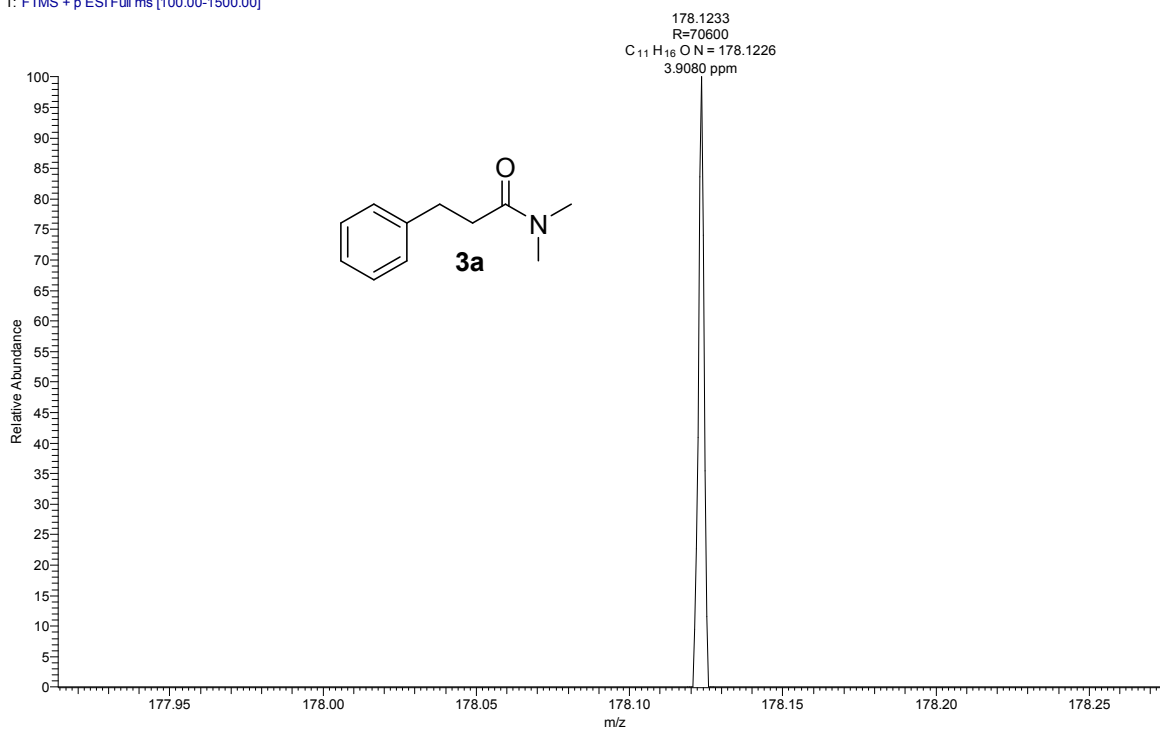
¹³C-NMR of 5c





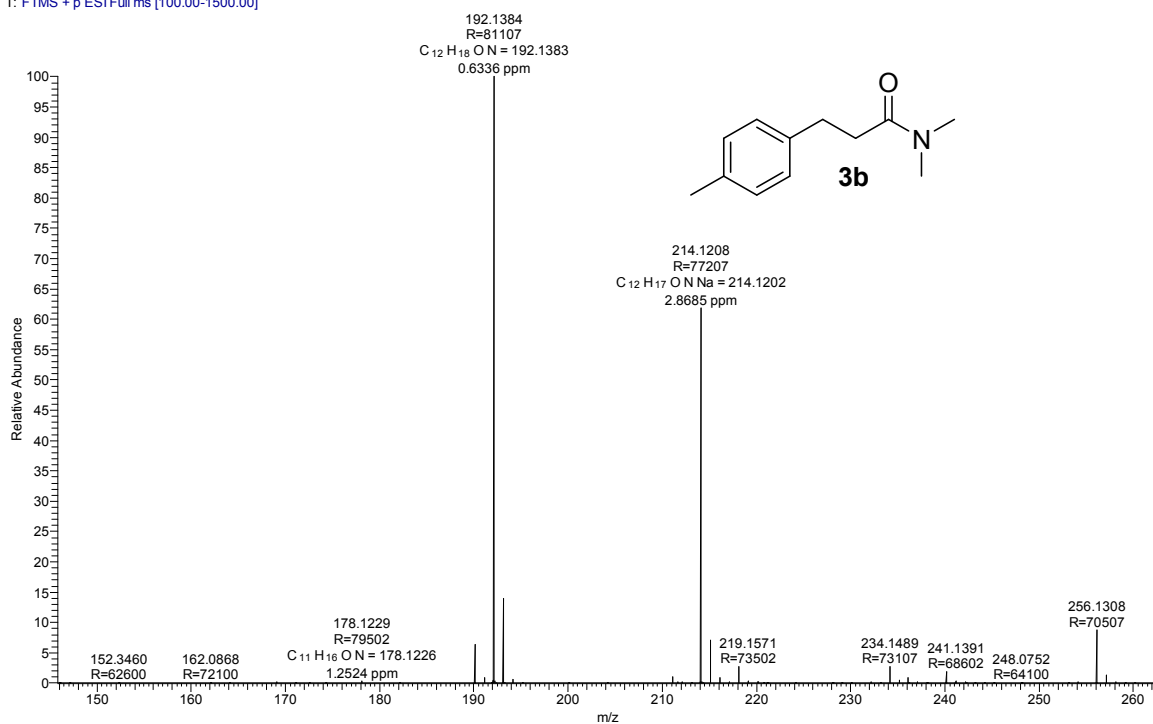
6. HRMS Data

AM-1 #116 RT: 0.51 AV: 1 NL: 5.36E6
T: FTMS + p ESI Full ms [100.00-1500.00]



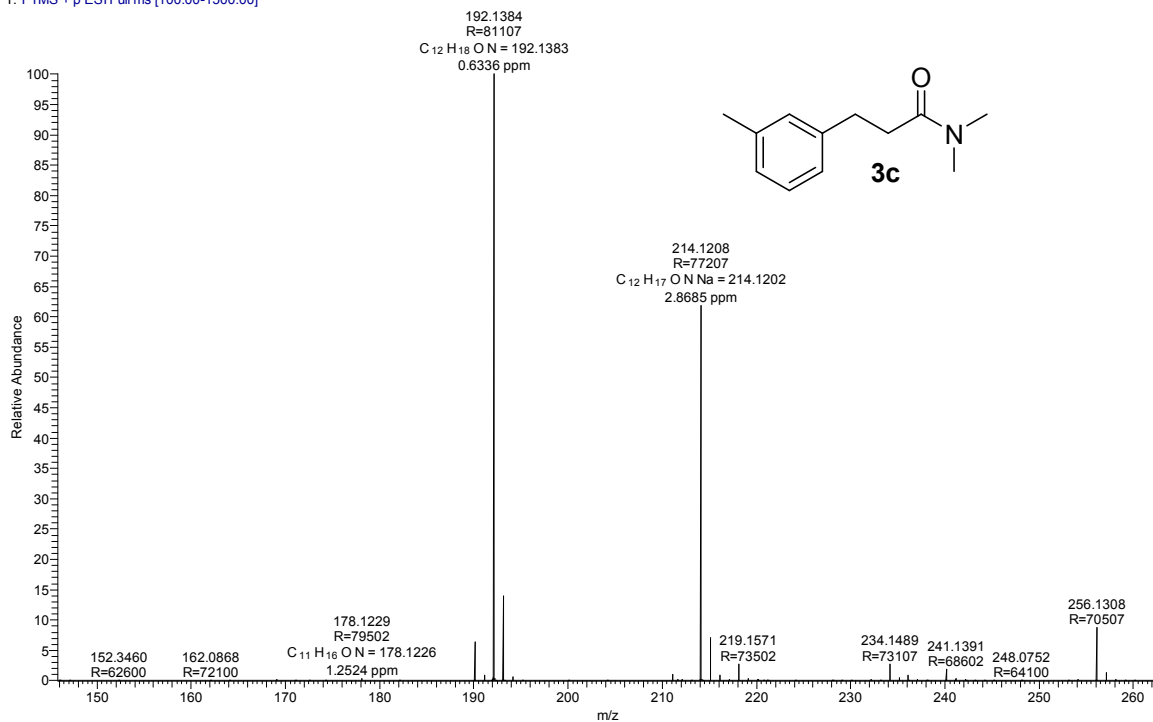
HRMS Data of 3a

AM-3 #117 RT: 0.52 AV: 1 NL: 6.88E9
T: FTMS + p ESI Full ms [100.00-1500.00]



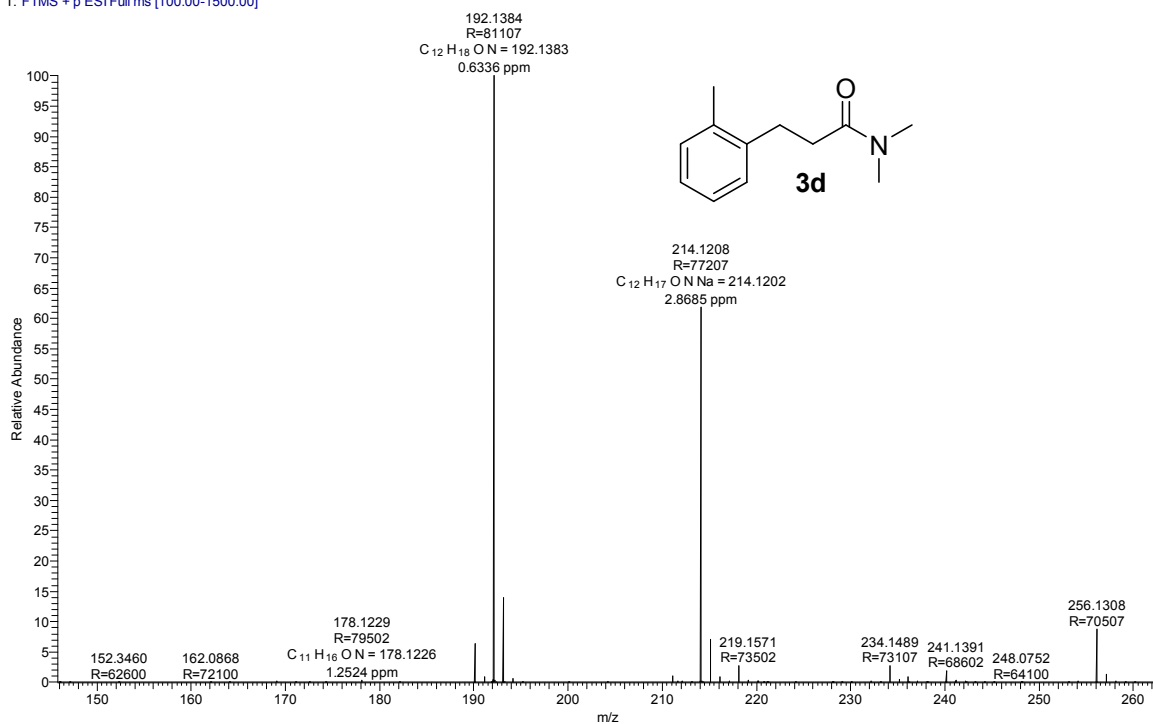
HRMS Data of 3b

AM-3 #117 RT: 0.52 AV: 1 NL: 6.88E9
T: FTMS + p ESI Full ms [100.00-1500.00]



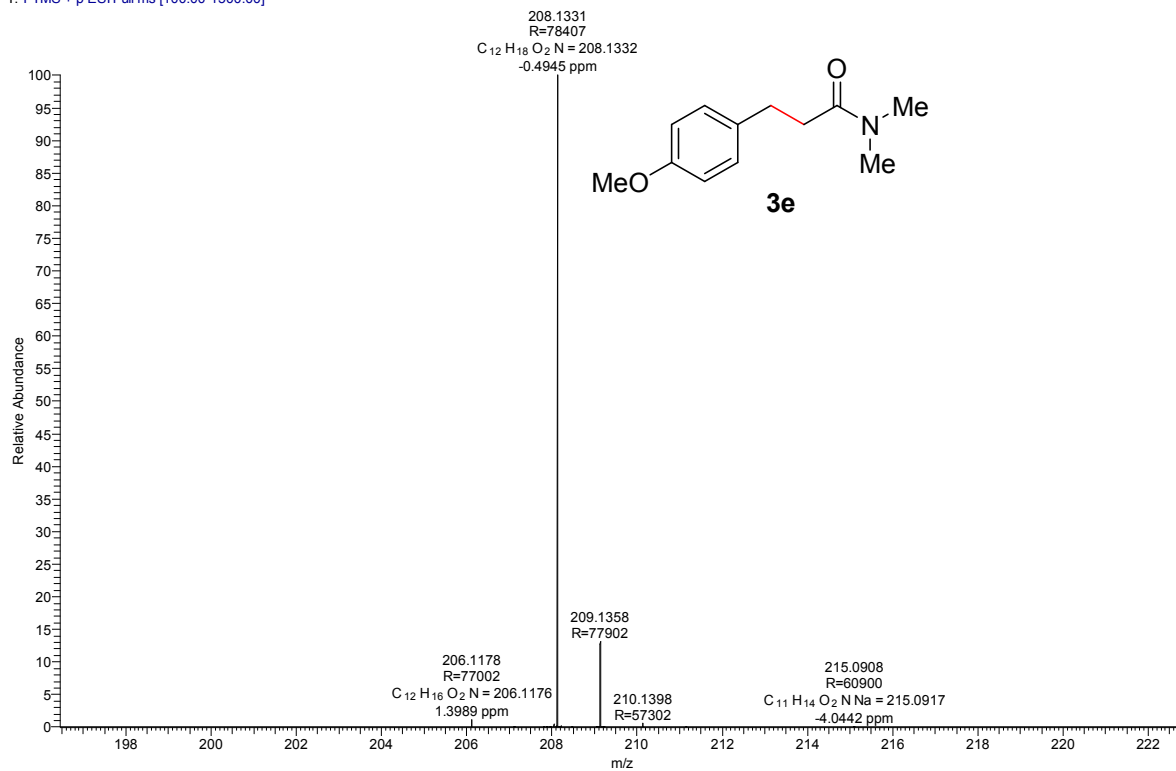
HRMS Data of **3c**

AM-3 #117 RT: 0.52 AV: 1 NL: 6.88E9
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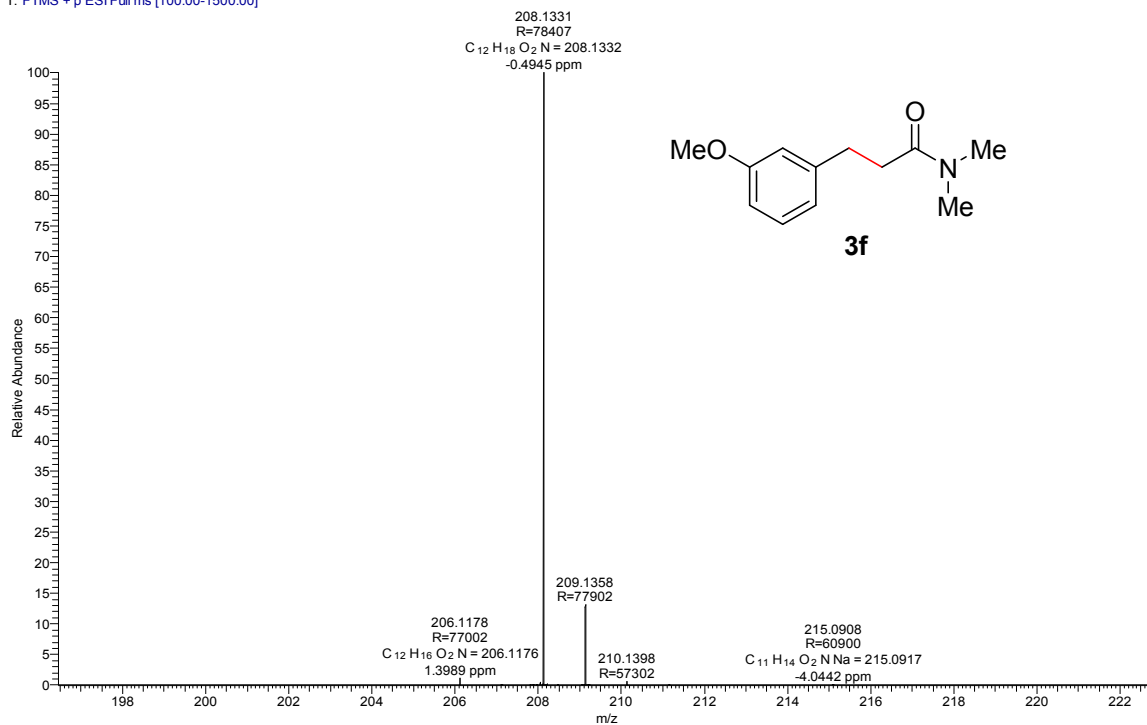
HRMS Data of **3d**

AM-5 #114 RT: 0.51 AV: 1 NL: 4.58E9
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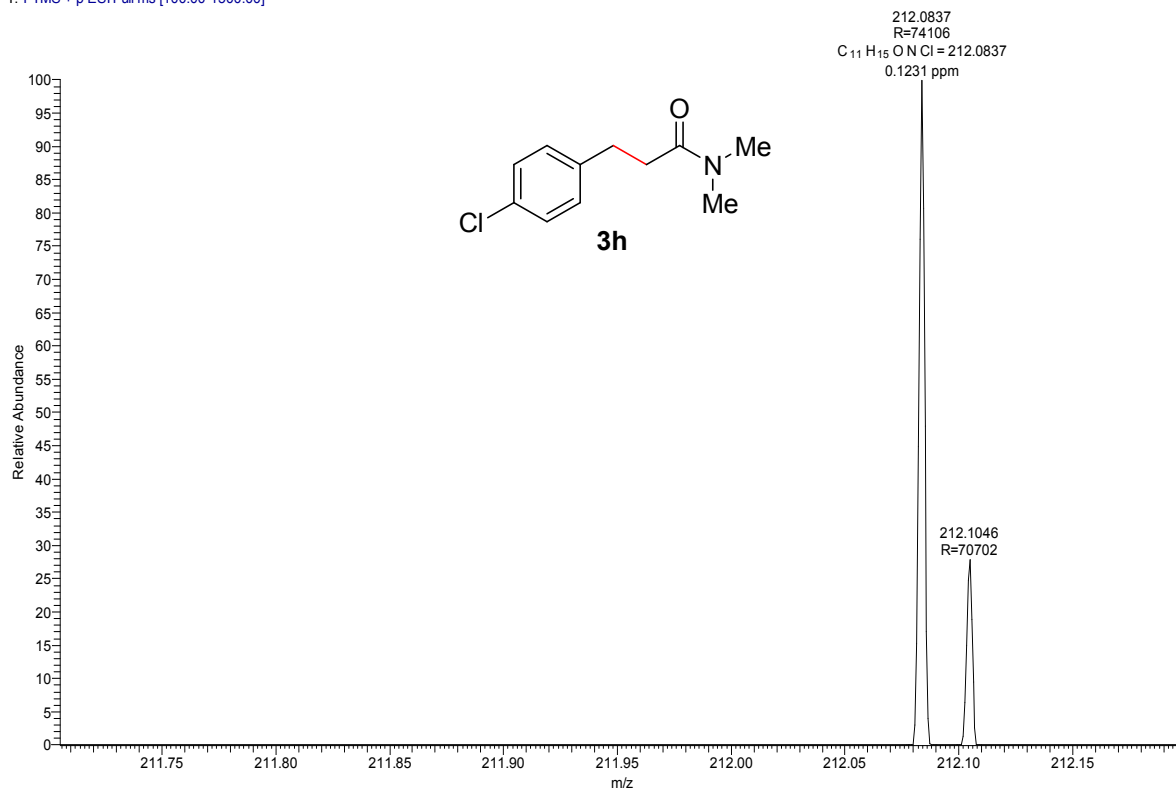
HRMS Data of 3e

AM-5 #114 RT: 0.51 AV: 1 NL: 4.58E9
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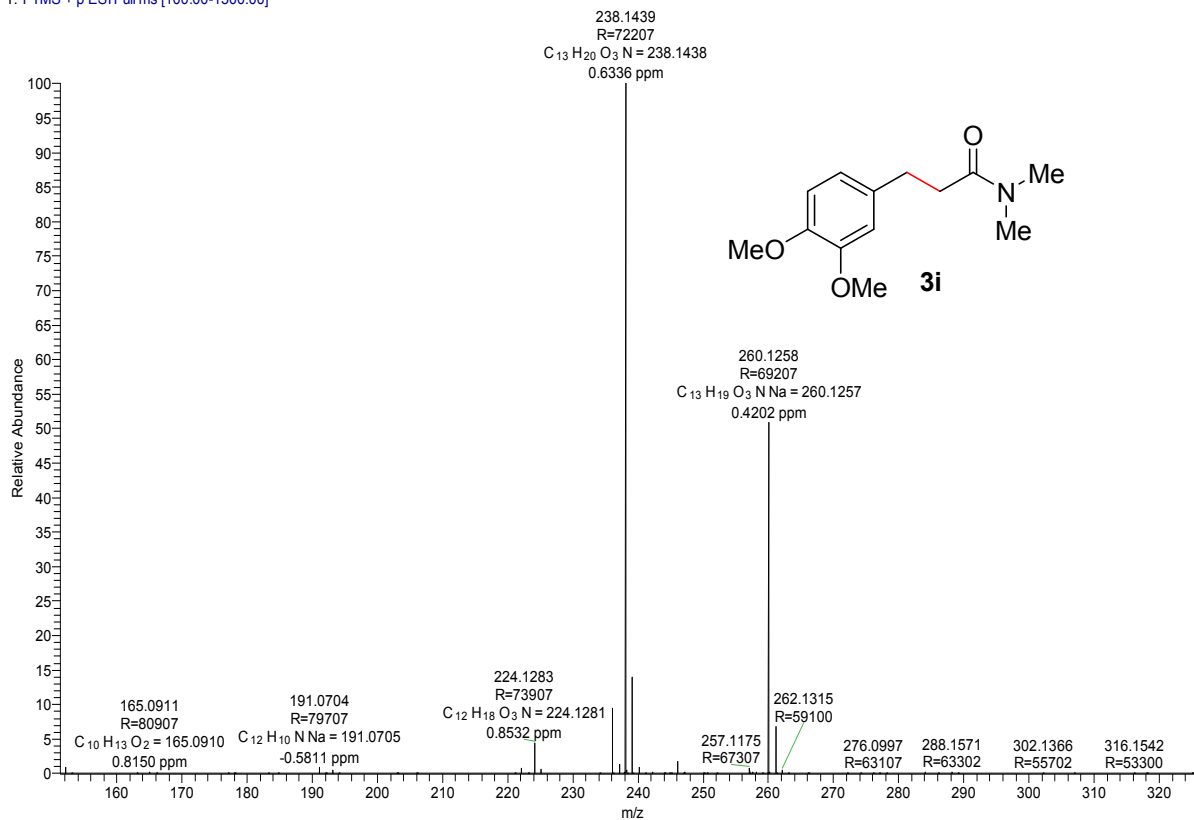
HRMS Data of 3f

AM-8 #108 RT: 0.48 AV: 1 NL: 2.84E7
T: FTMS + p ESIFull ms [100.00-1500.00]



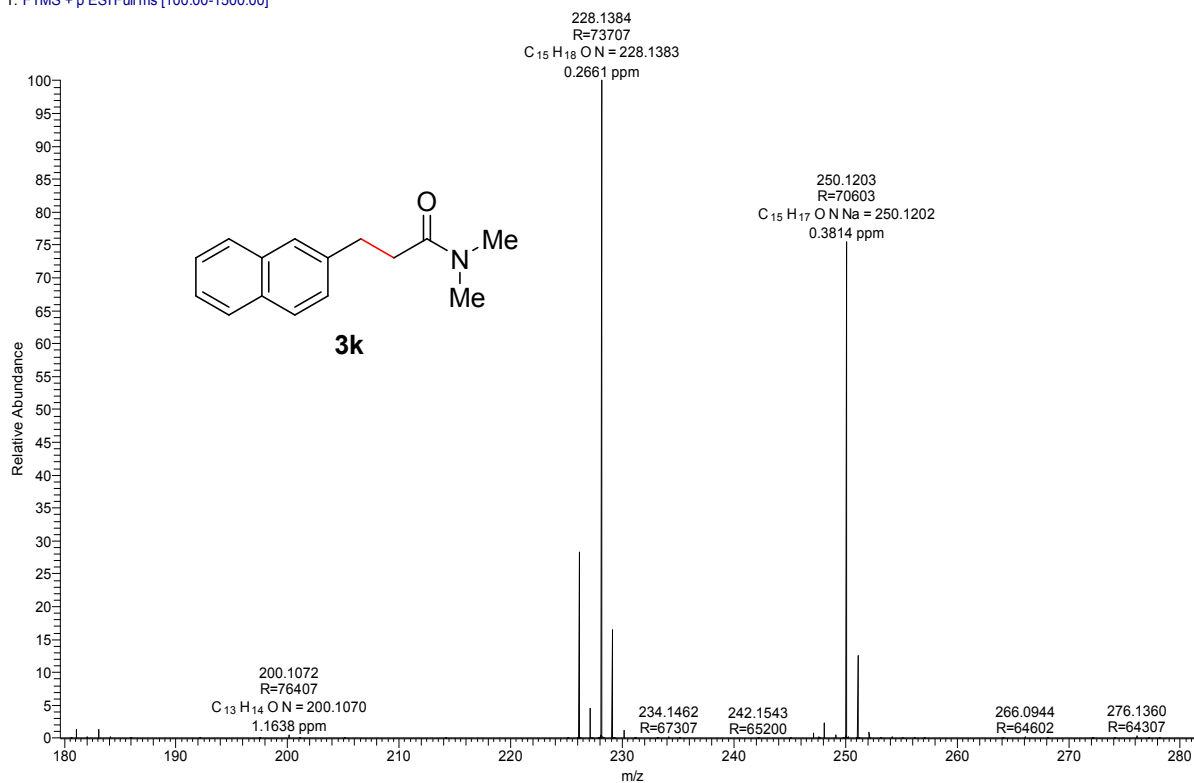
HRMS Data of 3h

AM-9 #101 RT: 0.45 AV: 1 NL: 7.13E9
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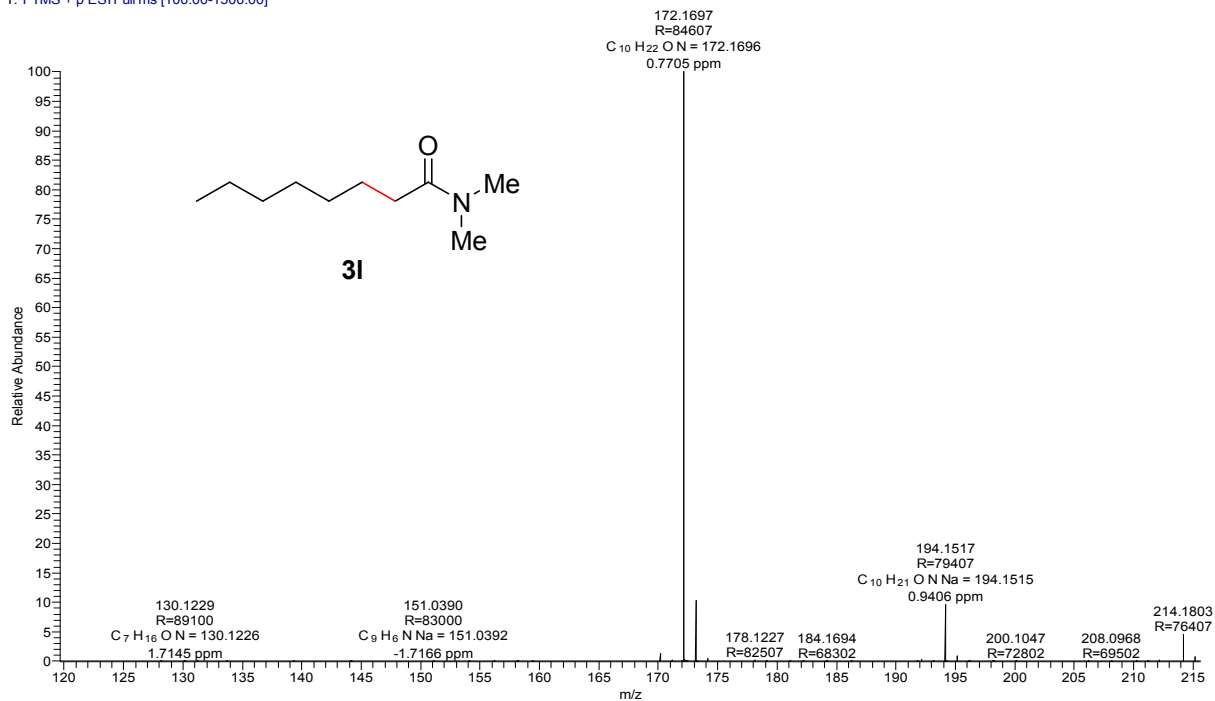
HRMS Data of 3j

AM-13 #119 RT: 0.53 AV: 1 NL: 6.43E9
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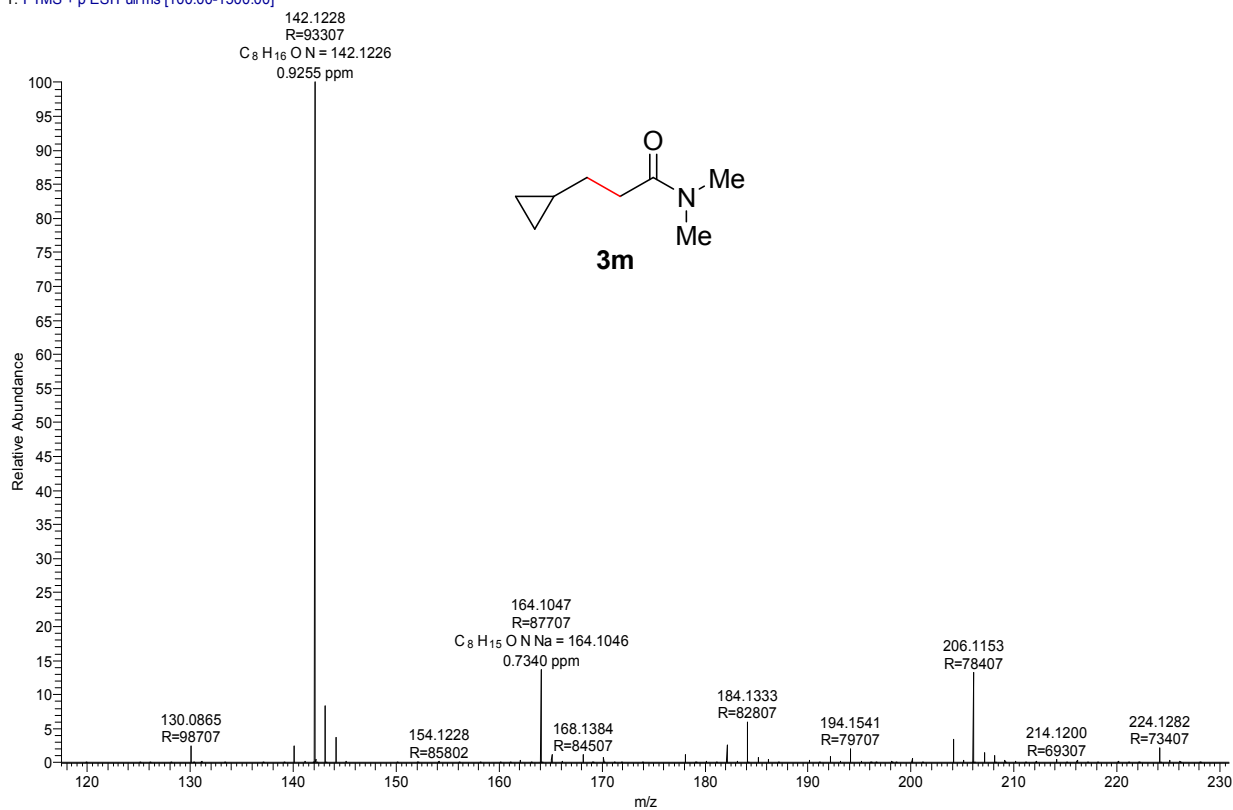
HRMS Data of 3k

AM-6 #122 RT: 0.54 AV: 1 NL: 1.15E10
T: FTMS + p ESI Full ms [100.00-1500.00]



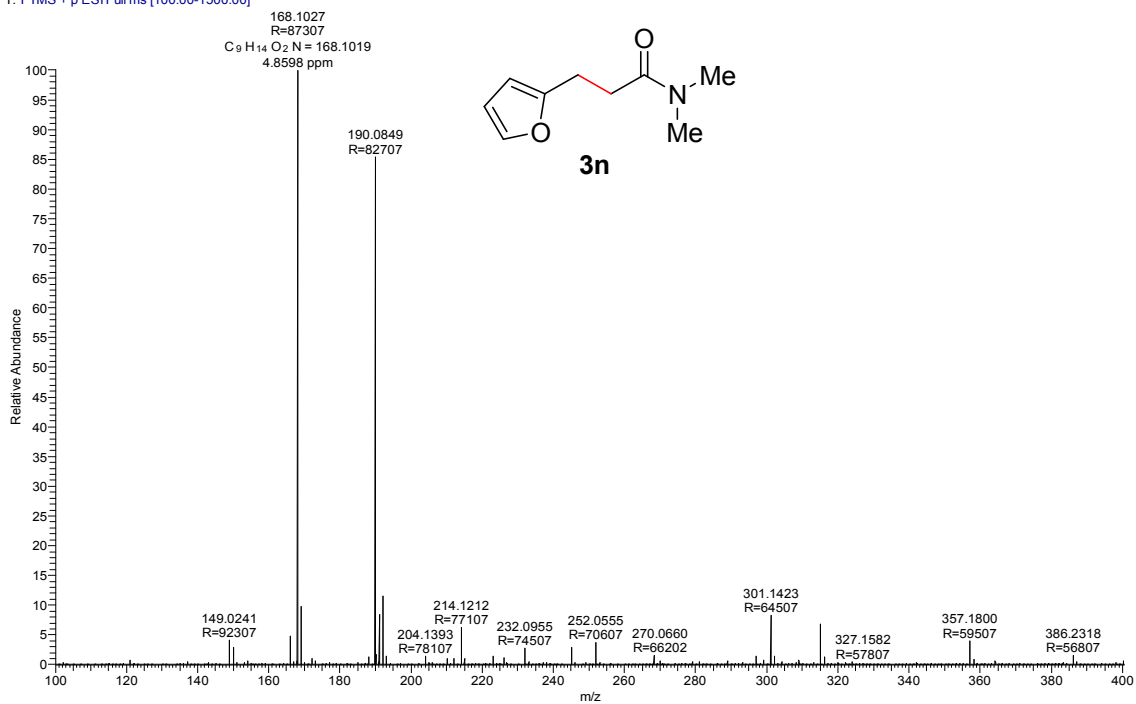
HRMS Data of 3l

AM-7 #105 RT: 0.47 AV: 1 NL: 3.68E9
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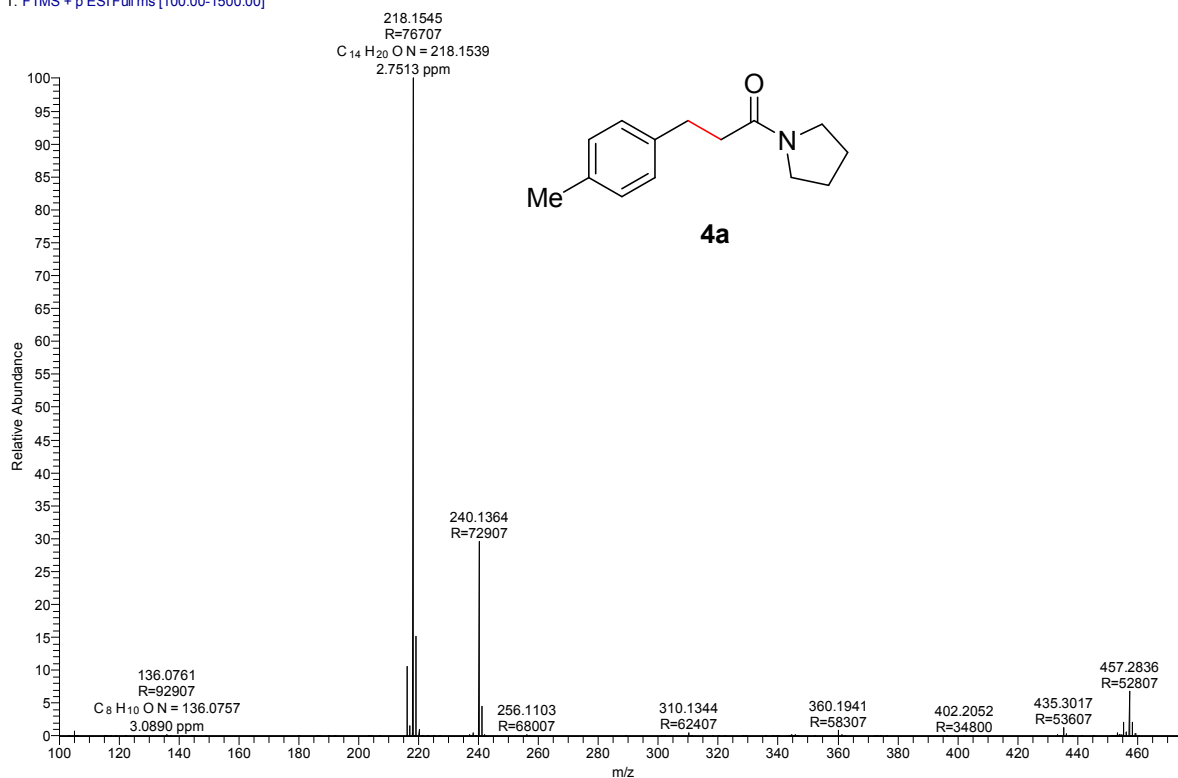
HRMS Data of 3m

AM-14 #148 RT: 0.66 AV: 1 NL: 4.93E8
T: FTMS + p ESI Full ms [100.00-1500.00]



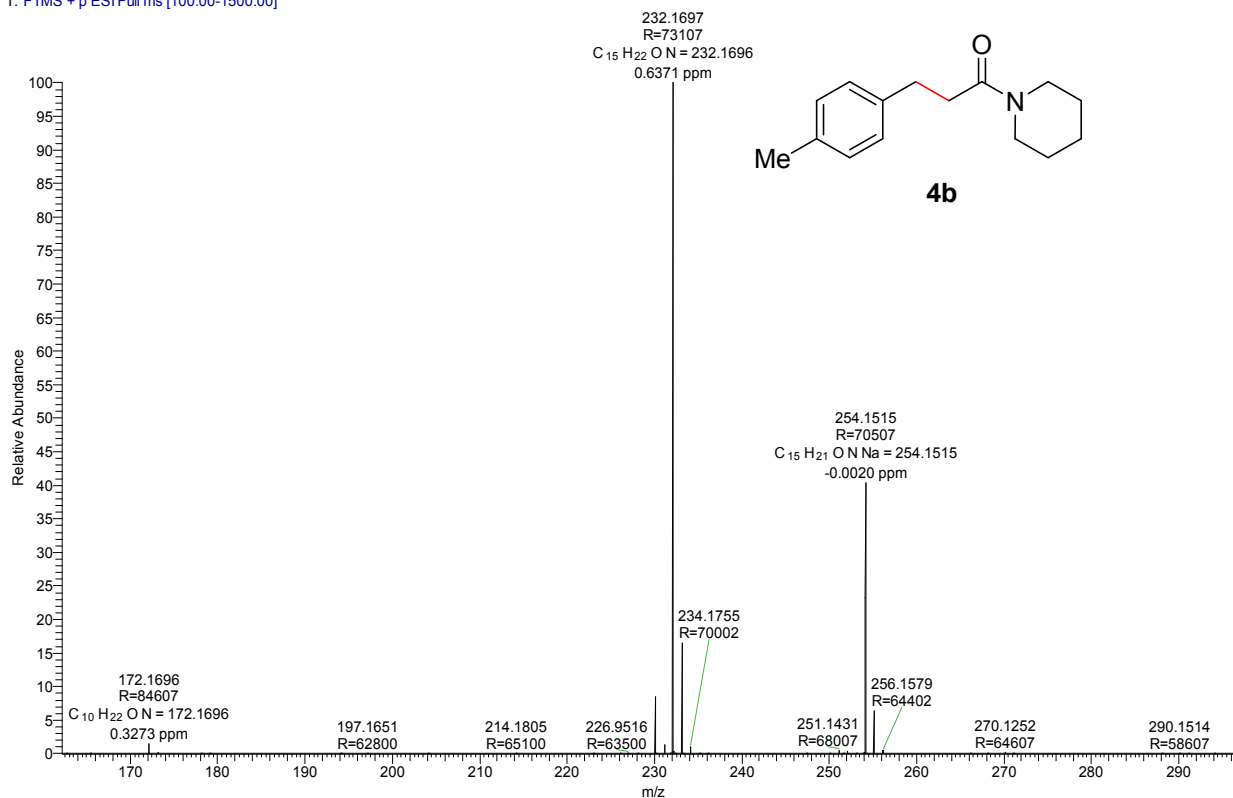
HRMS Data of 3n

AM-15 #135 RT: 0.60 AV: 1 NL: 9.84E9
T: FTMS + p ESI Full ms [100.00-1500.00]



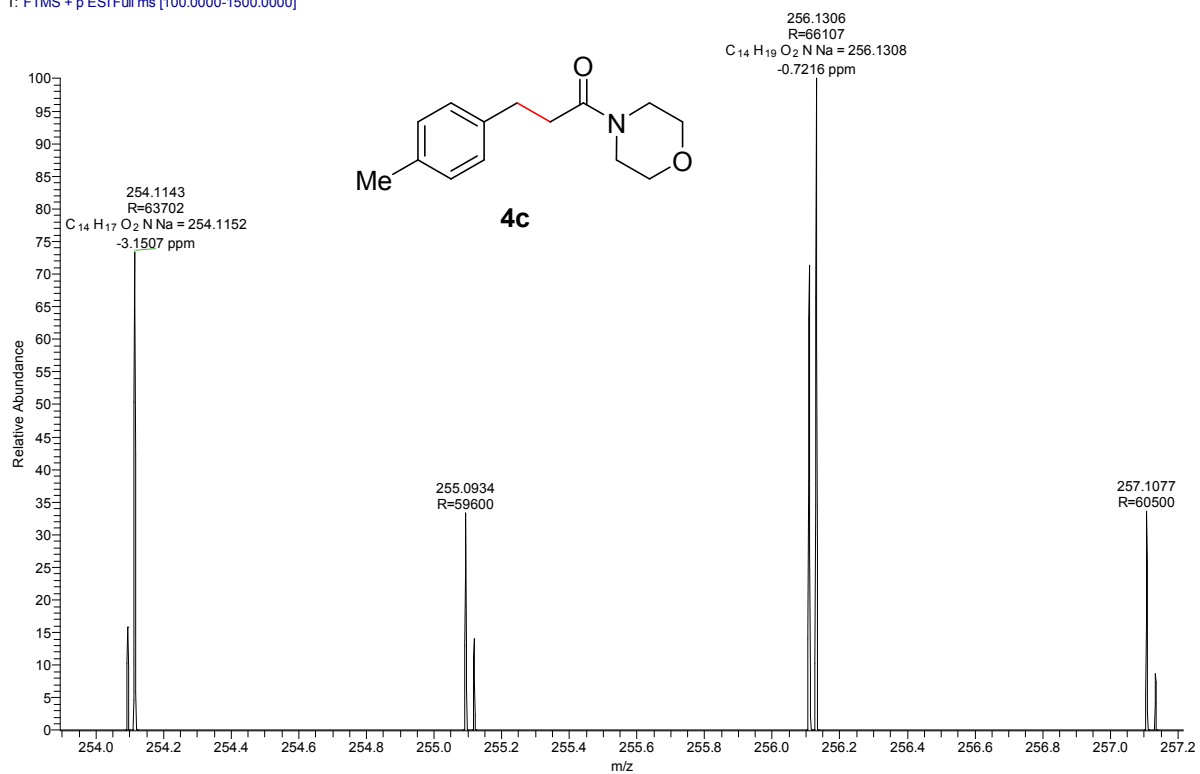
HRMS Data of **4a**

AM-12 #124 RT: 0.55 AV: 1 NL: 1.02E10
T: FTMS + p ESI Full ms [100.00-1500.00]



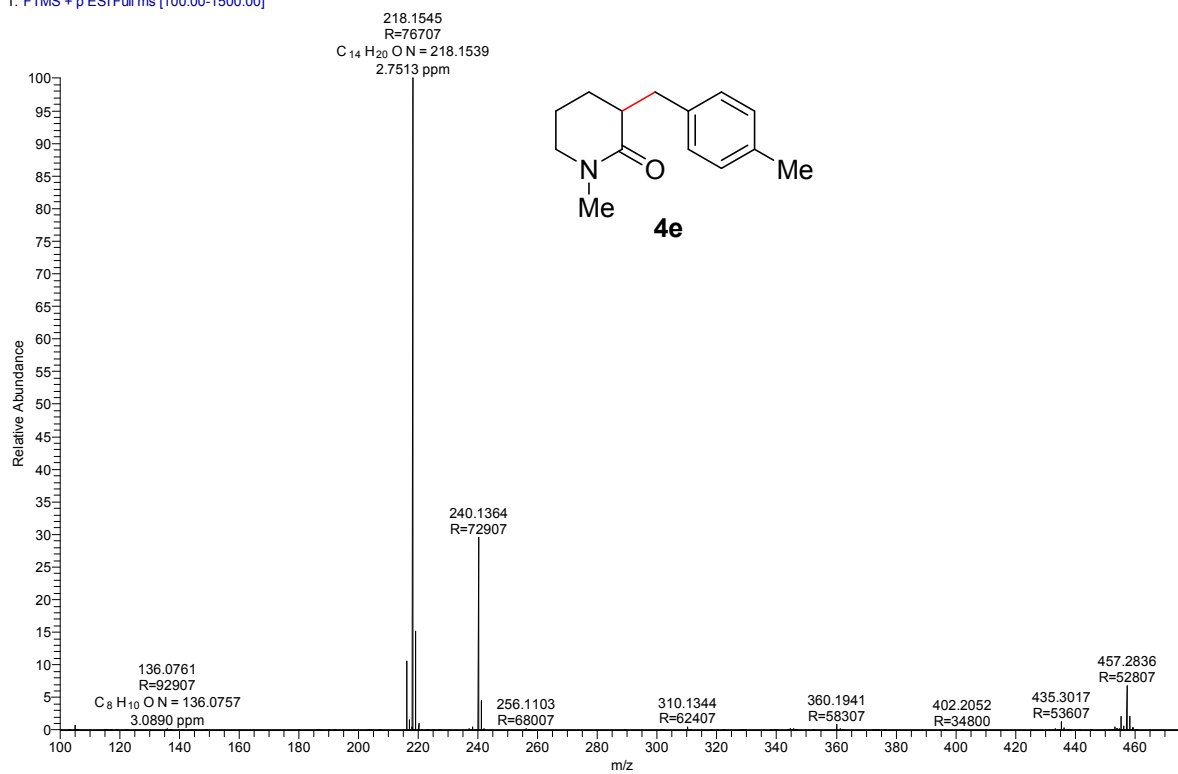
HRMS Data of **4b**

AS-31 #263 RT: 1.17 AV: 1 NL: 2.16E6
T: FTMS + p ESI Full ms [100.0000-1500.0000]



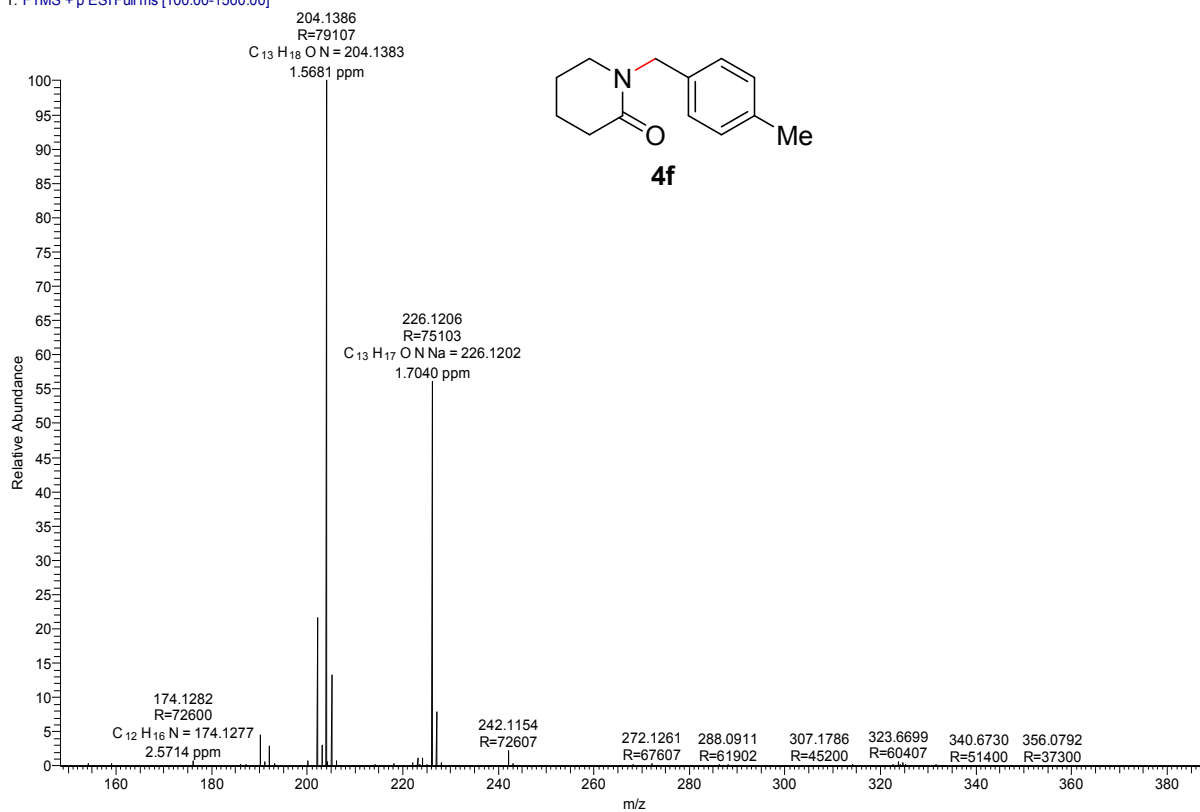
HRMS Data of **4c**

AM-15 #135 RT: 0.60 AV: 1 NL: 9.84E9
T: FTMS + p ESI Full ms [100.00-1500.00]



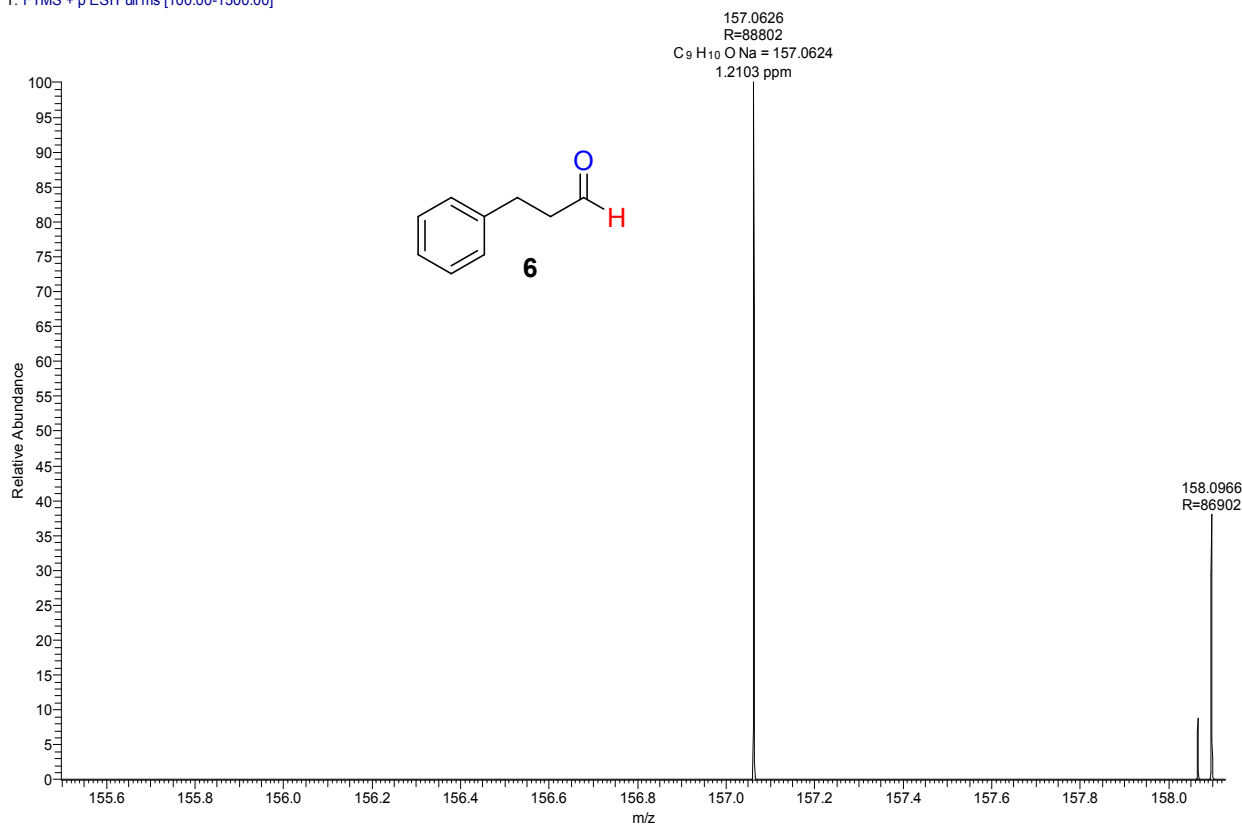
HRMS Data of **4e**

AM-23 #107 RT: 0.48 AV: 1 NL: 6.60E9
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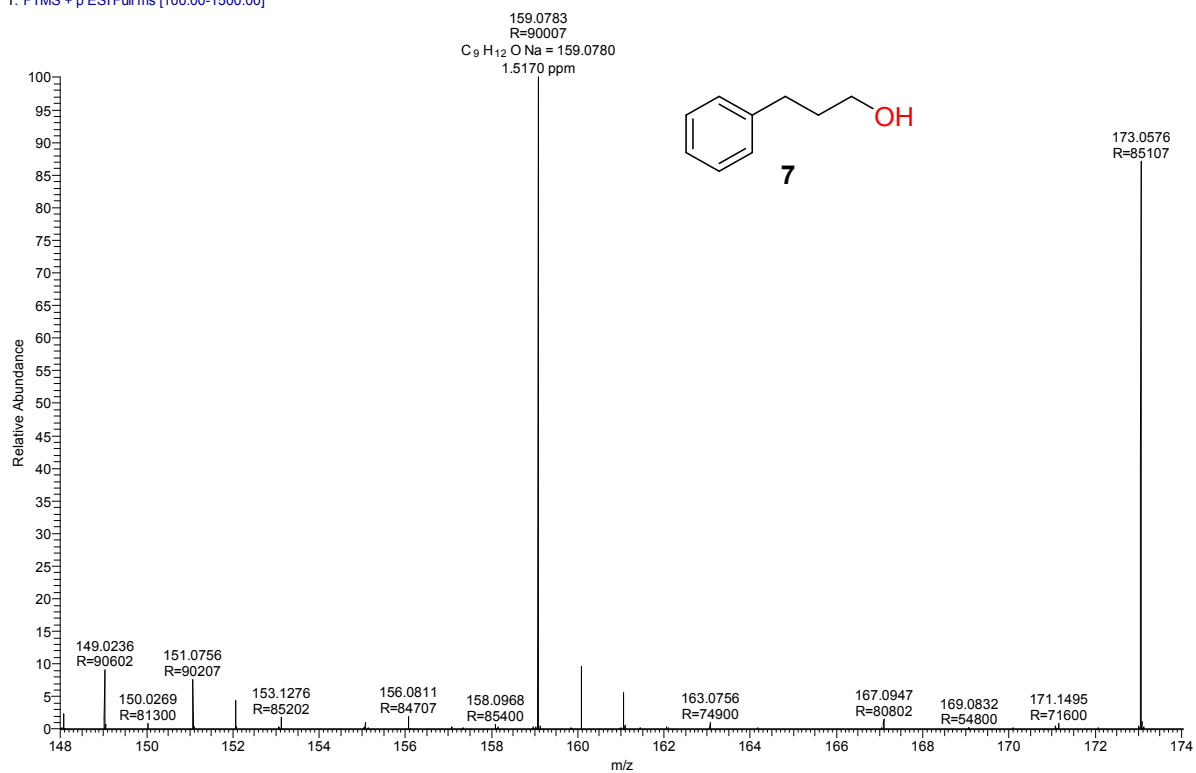
HRMS Data of **4f**

AM-21 #100 RT: 0.45 AV: 1 NL: 5.85E6
T: FTMS + p ESI Full ms [100.00-1500.00]



HRMS Data of **6**

AM-20 #107 RT: 0.48 AV: 1 NL: 8.85E7
T: FTMS + p ESI Full ms [100.00-1500.00]



HRMS Data of 7