Supporting Information for

Organo-cyanamides: convenient reagents for catalytic amidation of carboxylic acids

Li-Jing Li,[a] Zhong-Qiang Zhou,[*a] Zi-Kui Liu,[a] Yuan-Yuan He,[a] Feng-Cheng Jia[*b] and Xiao-Qiang Hu*

[a] Key Laboratory of Catalysis and Energy Materials Chemistry of Ministry of Education & Hubei Key Laboratory of Catalysis and Materials Science, School of Chemistry and Materials Science, South-Central Minzu University, Wuhan 430074, China. E-mail: hxq071303127@126.com.

[b] School of Chemistry and Environmental Engineering, Wuhan Institute of Technology, Wuhan 430073, China. E-mail: fengcheng-Jia@wit.edu.cn.

hxq071303127@126.com

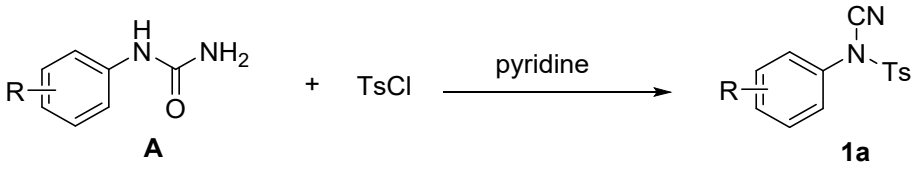
Table of Contents

1. General information

Unless otherwise noted, materials were purchased from commercial suppliers (Alfa, TCI and Sigma-Aldrich etc.), and used without further purification. All the solvents were treated according to general methods. All reactions were monitored by thin-layer chromatography (TLC) on silica gel plates using UV light as visualizing agent (if applicable). Flash column chromatography was performed using 200-300 mesh silica gel. ^{1}H NMR spectra were recorded on 400 and 600 MHz spectrophotometers. Chemical shifts are reported in delta (δ (ppm)) units in parts per million (ppm) relative to the singlet (0 ppm) for tetramethylsilane (TMS). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, m = multiplet), coupling constants (Hz) and integration. 13C NMR spectra were recorded on Varian Mercury 100 MHz with complete proton decoupling spectrophotometers ($CDCl_3$: 77.0 ppm). The high resolution mass spectra (HRMS) were measured on a Shimadzu LCMS-IT-TOF mass spectrometer or DIONEX UltiMate 3000 & Bruker Compact TOF mass spectrometer by ESI. Measured values are reported to 4 decimal places of the calculated value. The calculated values are based on the most abundant isotope. The high resolution mass spectra (HRMS) were measured on a Shimadzu LCMS-IT-TOF mass spectrometer or DIONEX UltiMate 3000 & Bruker Compact TOF mass spectrometer by ESI.

2. Preparation of substrates

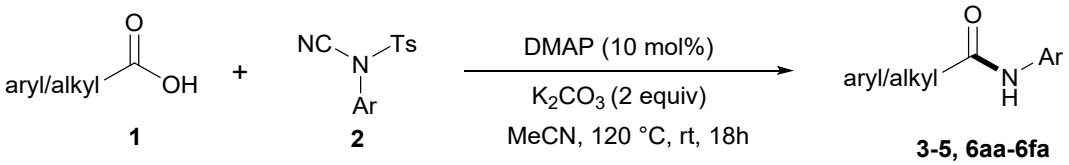
2.1 General procedure for preparation of product 1a[1]



To a round-bottom flask, **1** (300 mg, 1 equiv), TsCl (477 mg, 2.5 equiv) and pyridine (2 mL) was added. The reaction mixture was stirred at room temperature for 15 minutes, and then added to ice-cooled water. The precipitate was collected by vacuum filtration. The mixture was removed under reduced pressure and the residue was purified by column chromatography to afford **1a**.

3. General Procedure and Spectral Data of the Amidation Products

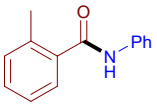
3.1 General procedure for preparation **3-5, 6aa-6fa**



To an oven-dried round-bottom flask equipped with a magnetic stir bar, **1** (0.2 mmol, 1.0 equiv), carboxylic acid **2** (0.4 mmol, 2.0 equiv), K_2CO_3 (0.4 mmol, 2.0 equiv) and DMAP (2.44 mg, 10 mol%) were added. The vessel was evacuated and filled with nitrogen (3 times). After that, the solvent was slowly added into the flask with a syringe in nitrogen atmosphere, maintaining at a temperature of 120 °C. The system was stirred for 18 hours as monitored by TLC analysis. The crude product was purified by flash chromatography on silica gel to afford pure product **3-5**, **6aa-6fa**.

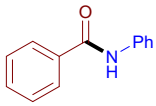
3.2 Spectral data of the products 3-5, 6aa-6fa

Product 3aa (known compound, CAS: 7055-03-0)[2]



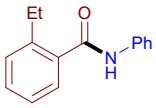
The crude product was purified by column chromatography (SiO_2, petroleum ether/ethyl acetate = 20:1 to 10:1), yielding **3aa** as a white solid (29.3 mg, 74% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ= 7.66 – 7.53 (m, 3H), 7.46 (d, *J* = 7.5 Hz, 1H), 7.36 (t, *J* = 7.8 Hz, 3H), 7.27 – 7.23 (m, 2H), 7.15 (t, *J* = 7.4 Hz, 1H), 2.49 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 168.1, 138.0, 136.5, 136.4, 131.3 130.3, 129.1, 126.6, 125.9, 124. 6, 119.9, 19.8. M.P.: 126 – 128 °C.

Product 3ba (known compound, CAS: 93-98-1)[3]



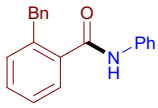
The crude product was purified by column chromatography (SiO_2, petroleum ether/ethyl acetate = 20:1 to 10:1), yielding **3ba** as a white solid (29.3 mg, 74% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ= 7.92 (s, 1H), 7.86 (d, *J* = 7.6 Hz, 2H), 7.64 (d, *J* = 7.9 Hz, 2H), 7.54 (t, *J* = 7.3 Hz, 1H), 7.47 (t, *J* = 7.5 Hz, 2H), 7.36 (t, *J* = 7.9 Hz, 2H), 7.15 (t, *J* = 7.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 165.9, 138.0, 135.0, 131.9, 129.1, 128.8, 127.1, 124.6, 120.3. M.P.: 163 – 164 °C.

Product 3ca (known compound, CAS:56776-51-3)[4]



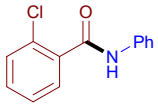
The crude product was purified by column chromatography (SiO_2, petroleum ether/ethyl acetate = 20:1 to 10:1), yielding **3ca** as a white solid (39.5 mg, 88%). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.61 (d, *J* = 7.7 Hz, 2H), 7.50 (s, 1H), 7.45 (d, *J* = 7.4 Hz, 1H), 7.40 – 7.35 (m, 3H), 7.31 (d, *J* = 7.6 Hz, 1H), 7.27 – 7.23 (m, 1H), 7.15 (t, *J* = 7.4 Hz, 1H), 2.88 – 2.83 (m, 2H), 1.27 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 168.3, 142.6, 138.0, 136.2, 130.4, 129.7, 129.2, 126.6, 125.9, 124.6, 119.9, 26.4, 16.0. M.P.: 128 – 130 °C.

Product 3da (known compound, CAS:90292-79-8)[5]



The crude product was purified by column chromatography (SiO_2, petroleum ether/ethyl acetate = 20:1 to 10:1), yielding **3da** as a white solid (40.7 mg, 71% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.54 (d, *J* = 7.4 Hz, 1H), 7.45 – 7.41 (m, 4H), 7.35 – 7.26 (m, 6H), 7.24 – 7.12 (m, 4H), 4.25 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 168.0, 140.6, 138.6, 137.8, 136.9, 131.3, 130.5, 129.0, 128.9, 128.7, 127.5, 126.7, 126.4, 124.5, 119.9, 39.0. M.P.: 123 – 125 °C.

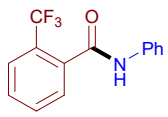
Product 3ea (known compound, CAS:6833-13-2)[6]



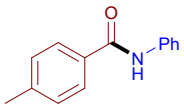
The crude product was purified by column chromatography (SiO_2, petroleum ether/ethyl acetate = 20:1 to 10:1), yielding **3ea** as a white solid (30.9 mg, 67%). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.89 (s, 1H), 7.77 (d, *J* = 7.3 Hz, 1H), 7.65 (d, *J* = 8.0 Hz, 2H), 7.48 – 7.34 (m, 5H), 7.18 (t, *J* = 7.3 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 164.4, 137.6, 135.2, 131.8, 130.6 (overlap), 130.4, 129.2, 127.4, 124.9, 120.1. M.P.: 114 – 115 °C.

Product 3fa (known compound, CAS:22978-42-3)[7]

The crude product was purified by column chromatography (SiO_2, petroleum ether/ethyl acetate = 20:1 to 10:1), yielding **3fa** as a yellow solid(35 mg, 66% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.72 (d, *J* = 7.4 Hz, 1H), 7.64 (s, 1H), 7.61 – 7.56 (m, 4H), 7.36 (t, *J* = 7.8 Hz, 2H), 7.17 (t, *J* = 7.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 165.8, 137.5, 135.8, 132.2, 130.2, 129.1, 128.6, 127.1, 126.5 (q, *J* = 4.9 Hz), 126.0 (q, *J* = 211.9 Hz), 125.0, 120.3. M.P.: 146 – 148 °C. ^{19}F NMR (376 MHz, $CDCl_3$) δ = -58.89.



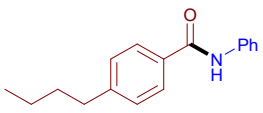
Product 3ga (known compound, CAS: 6833-18-7)[8]



The crude product was purified by column chromatography (SiO_2, petroleum ether/ethyl acetate = 20:1 to 10:1), yielding **3ga** as a white solid (20.7 mg, 54% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.84 (s, 1H), 7.77 (d, *J* = 8.0 Hz, 2H), 7.64 (d, *J* = 8.0 Hz, 2H), 7.36 (t, *J* = 7.9 Hz, 2H), 7.28 (d, *J* = 8.0 Hz, 2H), 7.14 (t, *J* = 7.4 Hz, 1H), 2.42 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 165.7, 142.4, 138.1, 132.2, 129.4, 129.1, 127.0, 124.4, 120.2, 21.5. M.P.: 132 – 133 °C.

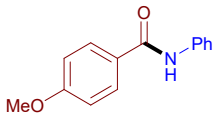
Product 3ha (known compound, CAS:1029437-56-6)[9]

The residue was purified by column chromatography (SiO_2, petroleum ether/ethyl acetate = 20:1 to 10:1),



yielding **3ha** as a white solid (58.4 mg, 87% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ= 7.79 (d, *J* = 8.0 Hz, 3H), 7.66 – 7.61 (m, 2H), 7.37 (t, *J* = 7.8 Hz, 2H), 7.28 (d, *J* = 8.0 Hz, 2H), 7.15 (t, *J* = 7.08 Hz, 1H), 2.68 (t, *J* = 7.7 Hz, 2H), 1.68 – 1.61 (m, 2H), 1.41 – 1.34 (m, 2H), 0.94 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 165.7, 147.4, 138.1, 132.4, 129.1, 128.8, 127.0, 124.4, 120.2, 35.6, 33.3, 22.3, 13.9. M.P.: 116 – 118 °C.

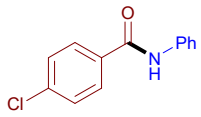
Product 3ia (known compound, CAS:7465-88-5)[8]



The crude product was purified by column chromatography (SiO_2, petroleum ether/ethyl acetate = 20:1 to 10:1), yielding **3ia** as a white solid (24.7 mg, 54% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.84 (d, *J* = 8.6 Hz, 2H), 7.63 (d, *J* = 8.0 Hz, 2H), 7.36 (t, *J* = 7.8 Hz, 2H), 7.14 (t, *J* = 7.3 Hz, 1H), 6.96 (d, *J* = 8.7 Hz, 2H), 3.87 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 165.2, 162.5, 138.1, 129.1, 128.9, 127.2, 124.4, 120.2, 114.0, 55.5. M.P.: 162 – 163 °C.

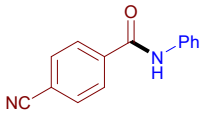
Product 3ja (known compound, CAS:6833-15-4)[3]

The crude product was purified by column chromatography (SiO_2, petroleum ether/ethyl acetate = 20:1 to 10:1), yielding **3ja** as a white solid (30.5 mg, 66 % yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.82 (d, *J* = 8.4 Hz, 2H), 7.77 (s, 1H), 7.63 (d, *J* = 7.9 Hz, 2H), 7.47 (d, *J* = 8.5 Hz, 2H), 7.38 (t, *J* = 7.8 Hz, 2H), 7.17 (t, *J* = 7.4 Hz, 1H). ^{13}C NMR (101 MHz, DMSO-d_6) δ = 164.9, 139.4, 136.8, 134.1, 130.1, 129.1, 128.9, 124.3, 120.9. M.P.: 196-197 °C.



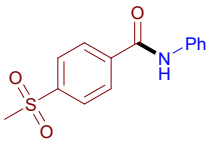
Product 3ka (known compound, CAS:17922-96-2)[8]

The crude product was purified by column chromatography (SiO_2, petroleum ether/ethyl acetate = 20:1 to 10:1), yielding **3ka** as a white solid (29.8 mg, 67% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.97 (d, *J* = 8.0 Hz, 2H), 7.92 (s, 1H), 7.78 (d, *J* = 8.0 Hz, 2H), 7.63 (d, *J* = 8.0 Hz, 2H), 7.39 (t, *J* = 7.8 Hz, 2H), 7.20 (t, *J* = 7.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 163.9, 138.9, 137.3, 132.6, 129.2, 127.8, 125.3, 120.4, 117.9, 115.4. M.P.: 192 – 193 °C.

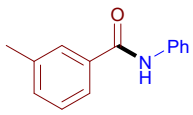


Product 3la (known compound, CAS:878952-07-9)[10]

The crude product was purified by column chromatography (SiO_2, petroleum ether/ethyl acetate = 20:1 to 10:1), yielding **3la** as a white solid (33 mg, 60% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ =8.09 – 8.03 (m, 4H), 7.92 (s, 1H), 7.66 (d, *J* = 7.7 Hz, 2H), 7.41 (t, *J* = 7.7 Hz, 2H), 7.21 (t, *J* = 7.4 Hz, 1H), 3.10 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d6) δ = 164.8, 143.6, 140.0, 139.2, 129.2, 129.1, 127.5, 124.6, 120.9, 43.8. M.P.: 206 – 208 °C.

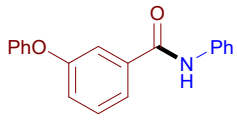


Product 3ma (known compound, CAS: 23099-05-0)[11]



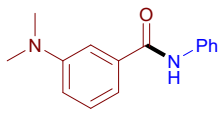
The crude product was purified by column chromatography (SiO_2, petroleum ether/ethyl acetate = 20:1 to 10:1), yielding **3ma** as a white solid (33.7 mg, 80% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ =7.91 (s, 1H), 7.68 – 7.61 (m, 4H), 7.38 – 7.35 (m, 4H), 7.14 (t, *J* = 7.1 Hz, 1H), 2.41 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 166.0, 138.7, 138.0, 135.0, 132.6, 129.1, 127.8, 124.5, 124.0, 120.2, 21.4. M.P.: 124 – 125 °C.

Product 3na (known compound, CAS:228423-11-8)[12]



The crude product was purified by column chromatography (SiO_2, petroleum ether/ethyl acetate = 20:1 to 10:1), yielding **3na** as a white solid (33.5 mg, 58% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.82 (s, 1H), 7.61 (d, *J* = 8.0 Hz, 2H), 7.56 (d, *J* = 7.7 Hz, 1H), 7.50 (s, 1H), 7.43 (t, *J* = 7.9 Hz, 1H), 7.37 – 7.34 (m, 4H), 7.19 – 7.13 (m, 3H), 7.04 (d, *J* = 8.0 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 165.1, 158.0, 156.5, 137.8, 136.9, 130.2, 130.0, 129.1, 124.7, 124.0, 121.9, 121.4, 120.2, 119.3, 117.2. M.P.: 105 – 106 °C.

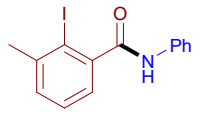
Product 3oa (known compound, CAS:92579-24-3)[13]



The crude product was purified by column chromatography (SiO_2, petroleum ether/ethyl acetate = 20:1 to 10:1), yielding **3oa** as a yellow solid (26.3 mg, 55% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.89 (s, 1H), 7.65 (d, *J* = 7.9 Hz, 2H), 7.36 (t, *J* = 7.8 Hz, 2H), 7.30 (t, *J* = 7.9 Hz, 1H), 7.14 (t, *J* = 7.4 Hz, 1H), 7.07 (d, *J* = 7.9 Hz, 1H), 6.87 (dd, *J* = 8.3, 2.8 Hz, 1H), 3.00 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 166.6, 150.8, 138.2, 135.9, 129.3, 129.1, 124.4, 120.1, 115.5, 113.9, 111.4, 40.5. M.P.: 133 – 134 °C.

Product 3pa (known compound, CAS:1379820-76-4)[14]

The crude product was purified by column chromatography (SiO_2, petroleum ether/ethyl acetate = 20:1 to 10:1), yielding **3pa** as a white solid (44.5 mg, 66% yield). ^{1}H NMR (400 MHz, CDCl3) δ = 7.63 (d, *J* = 7.9 Hz, 2H), 7.43 (s, 1H), 7.38 (t, *J* = 7.9 Hz, 2H), 7.31 (d, *J* = 4.8 Hz, 2H), 7.26 – 7.22 (m, 1H), 7.17 (t, J = 7.4 Hz, 1H), 2.51 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 168.3, 143.8, 143.1, 137.6, 130.8, 129.2, 128.3, 125.2, 124.9, 120.1, 99.3, 29.2. M.P.: 146 – 147 °C.



Product 3qa (known compound, CAS:1916324-03-2)[15]

The crude product was purified by column chromatography (SiO_2, petroleum ether/ethyl acetate = 20:1 to 10:1), yielding **3qa** as a white solid(34.5 mg,70% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.53 (d, *J* = 7.5 Hz, 2H), 7.48 (s, 1H), 7.34 – 7.28 (m, 3H), 7.19 – 7.14 (m, 2H), 7.09 (t, *J* = 7.4 Hz, 1H), 2.40 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 167.1, 138.6, 137.8, 136.1, 134.8, 131.2, 129.2, 128.0, 126.0, 124.8, 120.0, 19.8. M.P.: 165 – 166 °C.

Product 3ra (known compound, CAS:70021-83-9)[8]

The crude product was purified by column chromatography (SiO_2, petroleum ether/ethyl acetate = 20:1 to 10:1), yielding **3ra** as a white solid (28.5 mg, 58% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.39 (s, 1H), 8.08 (s, 1H), 7.96 – 7.91 (m, 4H), 7.73 (d, *J* = 7.9 Hz, 2H), 7.64 – 7.56 (m, 2H), 7.42 (t, *J* = 7.8 Hz, 2H), 7.20 (t, *J* = 7.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 165.8, 138.0, 134.9, 132.6, 132.4, 129.2, 129.0, 128. 8, 127.92, 127.83, 127.5, 127.0, 124.6, 123.6, 120.3. M.P.: 165 – 167 °C.

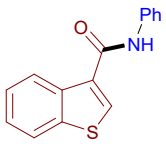
Product 3sa

The crude product was purified by column chromatography (SiO_2, petroleum ether/ethyl acetate = 20:1 to 10:1), yielding **3sa** as a white solid (46 mg, 87% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.54 (d, *J* = 7.8 Hz, 2H), 7.39 (s, 1H), 7.29 (t, *J* = 7.8 Hz, 2H), 7.19 (s, 1H), 7.09 (d, *J* = 7.7 Hz, 3H), 2.87 (s, 2H), 2.75 (s, 2H), 1.74 – 1.71 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 168.6, 138.8, 135.9, 134.6, 132.3, 131.3, 129.1, 125.4, 125.4, 124.2, 123.8, 119.8, 29.8, 27.0, 22.8, 22.5. M.P.: 136.5 – 138.5 °C. HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{17}H_{18}Cl_2NO_2$: 252.1383; found: 252.1381.

Product 3ta (known compound, CAS:1914890-72-4)[16]

The crude product was purified by column chromatography (SiO_2, petroleum ether/ethyl acetate = 20:1 to 10:1), yielding **3ta** as a white solid (36.6 mg, 74 % yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 9.21 (s, 1H), 8.51 (d, *J* = 6.0 Hz, 1H), 8.13 (d, *J* = 6.0 Hz, 1H), 8.02 (d, *J* = 8.2 Hz, 1H), 7.91 (d, *J* = 7.0 Hz, 1H), 7.84 (s, 1H), 7.65 – 7.55 (m, 3H), 7.35 (t, *J* = 7.7 Hz, 2H), 7.17 – 7.11 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 166.1, 152.8, 144.3, 137.9, 133.2, 133.0, 130. 7, 129.2, 128.6, 126.2, 125.0, 120.1, 118.0. M.P.: 166 – 168 °C.

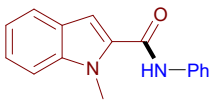
Product 3ua (known compound, CAS:70608-29-6)[17]



The crude product was purified by column chromatography (SiO_2, petroleum ether/ethyl acetate = 20:1 to 10:1), yielding **3ua** as a white solid (43.1 mg, 85% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.41 (d, *J* = 7.9 Hz, 1H), 7.98 (s, 1H), 7.89 (d, *J* = 7.9 Hz, 1H), 7.81 (s, 1H), 7.65 (d, *J* = 8.0 Hz, 2H), 7.49 – 7.35 (m, 4H), 7.17 (t, *J* = 7.3 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 162.1, 140.3, 137.7, 136.7, 132.4, 129.6, 129.2, 125.4, 124.7, 124.3, 122.6, 120.3. M.P.: 172 – 174 °C.

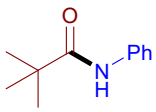
Product 3va (known compound, CAS:39167-76-5)[18]

The crude product was purified by column chromatography (SiO_2, petroleum ether/ethyl acetate = 20:1 to 10:1), yielding **3va** as a white solid (37.4 mg, 50% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.97 (s, 1H), 7.67 – 7.61 (m, 3H), 7.42 – 7.34 (m, 4H), 7.20 – 7.15 (m, 2H), 6.98 (s, 1H), 4.07 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 160.6, 139.4, 137.8, 132.0, 129.2, 126.0, 124.57, 124.52, 122.0, 120.8, 120.1, 110.3, 104.4, 31.6. M.P.: 170 – 172 °C.



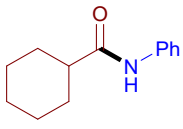
Product 3wa (known compound, CAS:6625-74-7) [10]

The crude product was purified by column chromatography (SiO_2, petroleum ether/ethyl acetate = 20:1 to 10:1), yielding **3wa** as a white solid(24.5 mg, 69 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.55 – 7.50 (m, 2H), 7.32 (t, *J* = 7.8 Hz, 3H), 7.10 (t, *J* = 7.5 Hz, 1H), 1.32 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 176.6, 138.0, 129.0, 124.2, 120.7, 39.6, 27.6. M.P.: 133 – 135 °C.



Product 3xa (known compound, CAS:2719-26-8)[19]

The crude product was purified by column chromatography (SiO_2, petroleum ether/ethyl acetate = 20:1 to 10:1), yielding **3xa** as a white solid (46 mg, 87% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.52 (d, *J* = 7.8 Hz, 2H), 7.31 (t, *J* = 7.8 Hz, 2H), 7.18 – 7.05 (m, 2H), 2.25 – 2.19 (m, 1H), 1.96 (d, *J* = 13.0 Hz, 2H), 1.86 – 1.83 (m, 2H), 1.72 – 1.69 (m, 1H), 1.56 – 1.50 (m, 1H), 1.36 – 1.24 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 174.2, 138.1, 129.0, 124.1, 119.7, 46.6, 29.7, 25.7 (overlap). M.P.: 132 – 134 °C.



Product 3ya (known compound, CAS:79455-25-7)[20]

The crude product was purified by column chromatography (SiO_2, petroleum ether/ethyl acetate = 20:1 to 10:1), yielding **3ya** as a white solid (50.3 mg, 99% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.51 (d, *J* = 8.0 Hz, 3H), 7.33 – 7.27 (m, 4H), 7.21 (t, *J* = 7.2 Hz, 1H), 7.11 (d, *J* = 7.4 Hz, 3H), 2.58 (dd, *J* = 13.1, 6.4 Hz, 1H), 1.73 (d, *J* = 6.3 Hz, 2H), 1.38 – 1.34 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 170.2, 140.5, 138.0, 129.0, 128.5, 126.5 126.1, 124.2, 119.7, 27.8, 25.9, 16.4. M.P.: 180 – 182 °C.

Product 3za (known compound, CAS: 58265-36-4)[21]

The crude product was purified by column chromatography (SiO_2, petroleum ether/ethyl acetate = 20:1 to 10:1), yielding **3za** as a white solid (31 mg, 65% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.46 – 7.39 (m, 4H), 7.37 – 7.30 (m, 3H), 7.27 (d, *J* = 7.6 Hz, 2H), 7.06 (t, *J* = 7.1 Hz, 1H), 6.79 (s, 1H), 1.67 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 175.6, 144.6, 138.0, 129.0, 128.9, 127.4, 126.5, 124.1, 119.6, 48.1, 27.0. M.P.: 171 – 172 °C.

Product 4 (known compound, CAS:3796-79-0)[8]

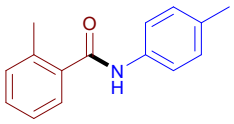
The crude product was purified by column chromatography (SiO_2, petroleum ether/ethyl acetate = 20:1 to 10:1), yielding **4** as a white solid (39.8 mg, 78% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.54 (d, *J* = 7.7 Hz, 2H), 7.32 (t, *J* = 7.1 Hz, 3H), 7.10 (t, *J* = 7.1 Hz, 1H), 2.11 (s, 3H), 1.97 (s, 6H), 1.80 – 1.73 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 176.1, 138.0, 129.0, 124.1, 120.0, 41.5, 39.3, 36.4, 28.1. M.P.: 144 – 146 °C.

Product 5 (known compound, CAS:54200-39-4)[16]

The crude product was purified by column chromatography (SiO_2, petroleum ether/ethyl acetate = 20:1 to 10:1), yielding **5** as a yellow solid (38.7 mg, 71% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.16 (s, 1H), 7.59 (d, *J* = 7.9 Hz, 2H), 7.35 (t, *J* = 7.8 Hz, 2H), 7.16 (t, *J* = 7.3 Hz, 1H), 2.65 – 2.57 (m, 1H), 2.04 – 1.97 (m, 2H), 1.78 – 1.72 (m, 1H), 1.16 (d, *J* = 9.1 Hz, 6H), 0.99 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 178.0, 165.2, 136.8, 129.1, 125.0, 120.0, 92.4, 55.5, 54.4, 30.5, 29.1, 16.8, 16.6, 9.7. M.P.: 98 - 100 °C.

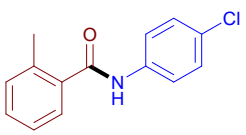
Product 3ab (known compound, CAS: 58249-89-1)[4]

The crude product was purified by column chromatography (SiO_2, petroleum ether/ethyl acetate = 20:1 to 10:1), yielding **3ab** as a white solid (28.1 mg, 62%). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.51 – 7.44 (m, 4H), 7.35 (t, *J* = 7.4 Hz, 1H), 7.28 – 7.24 (m, 2H), 7.17 (d, *J* = 7.9 Hz, 2H), 2.50 (s, 3H), 2.34 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 168.0, 136.6, 136.4, 135.4, 134.2, 131.2, 130.2, 129.6, 126.6, 125.9, 120.0, 20.9, 19.8. M.P.: 140 – 142 °C.



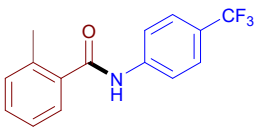
Product 3ac (known compound, CAS: 65492-63-9)[4]

The crude product was purified by column chromatography (SiO_2, petroleum ether/ethyl acetate = 20:1 to 10:1), yielding **3ac** as a white solid (16.7 mg, 34%). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.63 (s, 1H), 7.56 (d, *J* = 8.2 Hz, 2H), 7.44 (d, *J* = 7.4 Hz, 1H), 7.36 (t, *J* = 7.5 Hz, 1H), 7.31 (d, *J* = 8.6 Hz, 2H), 7.27 – 7.21 (m, 2H), 2.47 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 168.1, 136.6, 136.5, 136.0, 131.4, 130.5, 129.5, 129.1, 126.6 126.0, 121.2, 19.8. M.P.: 128 – 130 °C.



Product 3ad (known compound, CAS: 708248-47-9)[10]

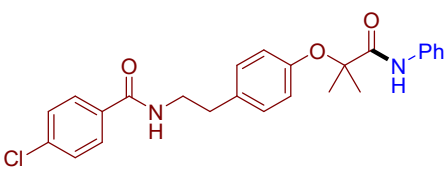
The crude product was purified by column chromatography (SiO_2, petroleum ether/ethyl acetate = 20:1 to 10:1), yielding **3ad** as a white solid (16.7 mg, 34%).



^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.92 (s, 1H), 7.83 (d, *J* = 7.6 Hz, 1H), 7.65 (s, 1H), 7.48 (d, *J* = 7.7 Hz, 2H), 7.39 (dd, *J* = 13.3, 7.3 Hz, 2H), 7.30 – 7.26 (m, 2H), 2.51 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 168.2, 138.5, 136.6, 135.8, 131.5, 130.7, 129.7, 126.6, 126.0, 122.9, 121.11, 121.07, 116.6, 19.9. ^{19}F NMR (376 MHz, $CDCl_3$) δ = -62.67. M.P.: 115 – 117 °C.

Product 6aa (known compound, CAS: 2180449-13-0)[22]

The crude product was purified by column chromatography (SiO_2, petroleum ether/ethyl acetate = 15:1 to 5:1), yielding **6aa** as a white solid (52.5 mg, 60 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.59 (s, 1H), 7.62 (d, *J* = 8.3 Hz, 2H), 7.57 (d, *J* = 8.0 Hz, 2H), 7.33 (t, *J* = 7.6 Hz, 4H), 7.14 (d, *J* = 7.9 Hz, 3H), 6.93 (d, *J* = 8.3 Hz, 2H), 6.37 (t, *J* = 5.9 Hz, 1H), 3.68 – 3.63 (m, 2H), 2.88 (t, *J* = 7.0 Hz, 2H), 1.56 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 173.0, 166.5, 152.7, 137.7, 137.5, 134.3, 133.0, 129.7, 129.1, 128.8, 128.3, 124.5, 122.0, 119.8, 82.0, 41.3, 34.9, 25.0. M.P.: 138 – 139 °C.



Product 6ba (known compound, CAS: 136772-55-9)[22]

The crude product was purified by column chromatography (SiO_2, petroleum ether/ethyl acetate = 15:1 to 5:1), yielding **6ba** as a white solid (23.4 mg, 36 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.51 (d, *J* = 7.9 Hz, 2H), 7.36 – 7.29 (m, 3H), 7.11 (t, *J* = 7.4 Hz, 1H), 7.00 (d, *J* = 7.4 Hz, 1H), 6.66 (d, *J* = 7.5 Hz, 1H), 6.60 (s, 1H), 3.94 (s, 2H), 2.29 (s, 3H), 2.17 (s, 3H), 1.82 (s, 4H), 1.34 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 175.6, 156.9, 137.9, 136.6, 130.3, 129.0, 124.3, 123.6, 120.9, 120.1, 112.2, 67.9, 42.8, 37.8, 25.6, 25.2, 21.4, 15.8. M.P.:108 – 110 °C.

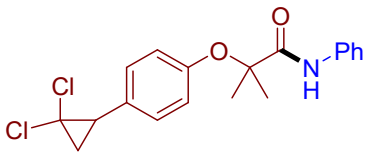
Product 6ca (known compound, CAS: 190125-59-8)[23]

The crude product was purified by column chromatography (SiO_2, petroleum ether/ethyl acetate = 15:1 to 5:1), yielding **6ca** as a white solid (30.8 mg, 48 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.54 (d, *J* = 7.4 Hz, 2H), 7.52 – 7.41 (m, 5H), 7.38 (t, *J* = 7.3 Hz, 1H), 7.30 (t, *J* = 7.8 Hz, 3H), 7.22 – 7.13 (m, 2H), 7.10 (t, *J* = 7.4 Hz, 1H), 3.76 – 3.71 (m, 1H), 1.62 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 171.5, 161.2, 158.7, 142.3 (d, *J* = 7.4 Hz), 137.7, 135.3, 131.3 (d, *J* = 4.0 Hz), 129.00, 128.9 (d, *J* = 2.9 Hz), 128.5, 127.8, 124.5, 123.6 (d, *J* = 3.3 Hz), 119.8, 115.5 (d, *J* = 23.3 Hz), 47.7, 18.6. ^{19}F NMR (376 MHz, $CDCl_3$) δ = -116.71. M.P.: 168 – 170 °C.

Product 6da (known compound, CAS: 2644046-41-1)[16]

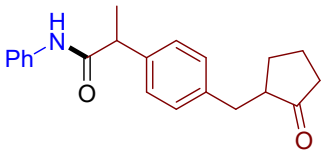
The crude product was purified by column chromatography (SiO_2, petroleum ether/ethyl acetate = 15:1 to 5:1), yielding **6da** as a white solid (32 mg, 33% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.78 (s, 1H), 7.52 (d, *J* = 7.9 Hz, 2H), 7.29 (t, *J* = 7.0 Hz, 2H), 7.08 (t, *J* = 7.4 Hz, 1H), 2.95 – 2.81 (m, 3H), 2.43 (ddd, *J* = 18.2, 9.1, 4.7 Hz, 2H), 2.32 (td, *J* = 14.2, 5.7 Hz, 4H), 2.26 – 2.07 (m, 5H), 1.99 (dd, *J* = 30.6, 14.1 Hz, 6H), 1.83 (dt, *J* = 11.3, 5.6 Hz, 1H), 1.62 (dd, *J* = 14.6, 4.4 Hz, 1H), 1.39 (s, 5H), 1.06 (s, 3H), 0.86 (d, *J* = 6.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 212.3, 209.4, 209.1, 171.9, 138.2, 128.9, 124.0, 119.80, 56.9, 51.8, 49.0, 46.8, 45.4, 45.4, 45.0, 42.8, 38.7, 36.5, 36.0, 35.34, 35.24, 34.2, 30.8, 27.6, 25.2, 21.9, 18.8, 11.9. M.P.: 118 – 120 °C.

Product 6ea



The crude product was purified by column chromatography (SiO_2, petroleum ether/ethyl acetate = 15:1 to 5:1), yielding **6ea** as a white solid (50 mg, 66%). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.56 (s, 1H), 7.58 (d, *J* = 7.9 Hz, 2H), 7.35 (t, *J* = 7.8 Hz, 2H), 7.21 – 7.11 (m, 3H), 6.98 (d, *J* = 8.4 Hz, 2H), 2.91 – 2.83 (m, 1H), 1.97 (dd, *J* = 10.7, 7.4 Hz, 1H), 1.81 (t, *J* = 7.9 Hz, 1H), 1.59 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 172.8, 153.4, 137.5, 130.2, 130.0, 129.1, 124.5, 121.6, 119.9, 82.2, 60.7, 34.8, 25.9, 25.05, 25.01 M.P.: 136.0 – 139.0 °C. HRMS (ESI-TOF) m/z: $[M+Na]^+$ calcd for $C_{19}H_{19}Cl_2NO_2Na$: 386.0685; found: 386.0680.

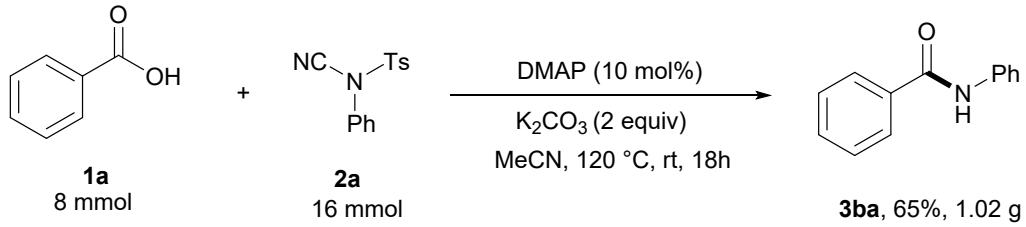
Product 6fa (known compound, CAS: 2644046-40-0)[24]



The crude product was purified by column chromatography (SiO_2, petroleum ether/ethyl acetate = 15:1 to 5:1), yielding **6fa** as a white solid (24.1 mg, 37% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.45 (d, *J* = 8.0 Hz, 2H), 7.33 – 7.24 (m, 5H), 7.18 (d, *J* = 7.8 Hz, 2H), 7.08 (t, *J* = 7.4 Hz, 1H), 3.73 – 3.68 (m, 1H), 3.15 (dd, *J* = 13.9, 4.1 Hz, 1H), 2.57 – 2.54 (m, 1H), 2.42 – 2.29 (m, 2H), 2.17 – 2.06 (m, 2H), 2.02 – 1.94 (m, 1H), 1.79 – 1.68 (m, 1H), 1.61 – 1.50 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 220.3, 172.5, 139.3, 138.8, 137.9, 129.6, 128.9, 127.8, 124.2, 119.7, 51.0, 47.7, 38.2, 35.2, 29.3, 20.6, 18.6. M.P.: 109 – 110 °C.

5. Gram-Scale Reaction

Procedure for Gram-Scale Reaction

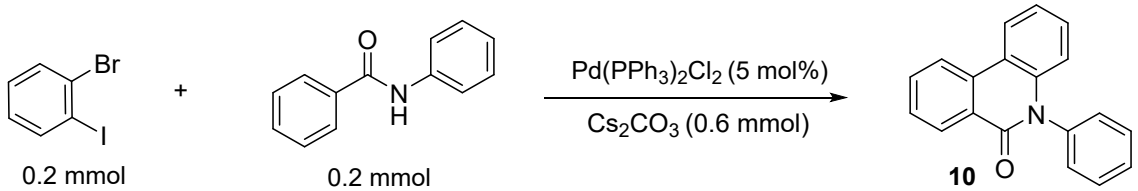


To an over dried round-bottom flask equipped with a magnetic stir bar, **1a** (8 mmol, 1.0 equiv.), carboxylic acid **2a** (16 mmol, 2.0 equiv.), K_2CO_3 (2.21 mg, 2.0 equiv.) and DMAP (97.7 mg, 10 mol%) were added. The flask was evacuated and filled with nitrogen (3 times). After that, add the solvent (80

mL) slowly with a syringe in nitrogen atmosphere, maintaining at a temperature of 120 °C. Then thee system stirred for 18 hours. The crude product was purified by flash chromatography on silica gel to afford pure product **3ba** in 65% yield (1.02 g).

6. Synthetic Application

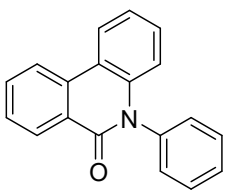
6.1 General procedure and spectral data for preparation **10**



0.2 mmol 0.2 mmol **10**

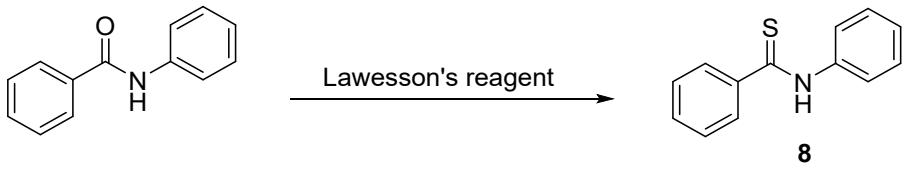
To a solution of compound 1 (1.0 eq.) and 2 (1.0 eq.) in anhydrous and oxygen free DMF (2.5 ml), was added $Pd(PPh_3)_2Cl_2$ (0.1 eq.) as catalyst and Cs_2CO_3 as base and then the reaction mixture was stirred at 150 °C in a sealed tube under N_2. After completion of the reaction, monitored by TLC, the reaction mixture was diluted with ethyl acetate, filtered through celite bed and then washed with cold water (4× 10 mL) and brine (2×10 mL). Thereafter, the organic layer was collected and dried over Na_2SO_4 and was evaporated under reduced pressure to get crude solid. It was then subjected to column chromatography (silica gel 100-200 mesh size, ethyl acetate: pet ether) for further purification to get the desired compound **10** in 95% yield.

Product 10 (known compound, CAS:13355-65-2)[25]



yield as yellow solid (51.8 mg, 95% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ= 8.56 (d, *J* = 8.0 Hz, 1H), 8.33 (dd, *J* = 13.7, 8.8 Hz, 2H), 7.82 (t, *J* = 7.7 Hz, 1H), 7.62 (t, *J* = 7.5 Hz, 3H), 7.54 (t, *J* = 7.4 Hz, 1H), 7.38 – 7.27 (m, 4H), 6.72 – 6.66 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ=161.7, 139.2, 138.3, 134.0, 132.8, 130. 2, 129.1, 129.1, 128.8, 128.2, 125.9, 123.0, 122.7, 121.8, 119.1, 117.0.

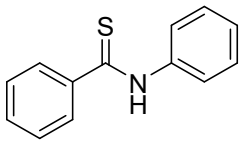
6.2 General procedure and spectral data for preparation **8**



8

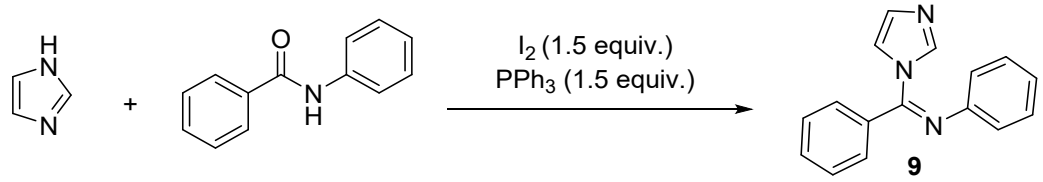
A mixture of benzamide (0.2 mmol) and Lawesson's reagent (0.1 mmol) in anhydrous and oxygen free toluene (2 mL) was heated at reflux under atmosphere of nitrogen for 2 h, after which it was concentrated, purified by column chromatography (EtOAc/hexanes 1:4) and recrystallized from hexane /ethyl acetate, yielding product **8** in 98% yield.

Product 8 (known compound, CAS:636-04-4)[26]



yield as a yellow solid (40.8 mg, 98% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ= 9.05 (s, 1H), 7.79 (dd, *J* = 33.3, 7.3 Hz, 4H), 7.49 – 7.42 (m, 5H), 7.29 (t, *J* = 7.5 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ=198.5, 143.2, 139.1, 131.3, 129.1, 128.6, 127.0, 126.7, 123.8.

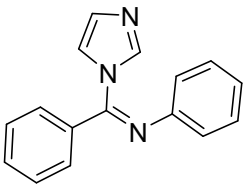
6.3 General procedure and spectral data for preparation **9**



9

Add I_2 (0.42 mmol) to a solution of Ph_3P (0.42 mmol) in dichloromethane (2 mL) at 0 °C under N_2. Add resulting solution with amide (0.277 mmol), followed by triethylamine (1.4 mmol) to the reaction mixture at 0 °C. Stir the reaction mixture continuously at 0 °C for 1 hour. Add Et_3N (0.34 mmol) to the mixture. Allow the solution to warm up to room temperature. Stir the solution until completion of the reaction. Purify the crude material by column chromatography (ethyl acetate/hexane = 1:2), yielding product **9** in 81% yield.

Product 9 (CAS:54598-45-7)[27]



yield as a white solid (85 mg, 81% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ= 7.84 (s, 1H), 7.56 (s, 1H), 7.41 (t, *J* = 7.3 Hz, 1H), 7.35 (t, *J* = 7.4 Hz, 2H), 7.26 (s, 2H), 7.19 – 7.14 (m, 3H), 6.98 (t, *J* = 7.4 Hz, 1H), 6.73 (d, *J* = 7.8 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ=151.2, 147.1, 137.5, 130.6, 130.4, 130.3, 129.4, 128.8, 128.7, 124.0, 121.4, 117.8.

References:

[1] Wang, C. C.; Qu, Y. L.; Liu, X. H.; Ma, Z. W.; Yang, B.; Liu, Z. J.; Chen, X. P.; Chen, Y. J. *J. Org. Chem*. **2021**, 86, 3546-3554.

[2] Verma, A.; Patel, S.; Meenakshi, M.; Kumar, A.; Yadav, A.; Kumar, S.; Jana, S.; Sharma, S.; Prasad, C. D.; Kumar, S. *Chem. Commun*. **2015**, *51*, 1371-1374.

[3] Mahajan, S.; Slathia, N.; Kapoor, K. K. *Tetrahedron Lett.* **2020**, *61*, 151859.

[4] Nozawa-Kumada, K.; Kadokawa, J.; Kameyama, T.; Kondo, Y. *Org. Lett.* **2015**, *17*, 4479-4481.

[5] Nozawa-Kumada, K.; Matsuzawa, Y.; Ono, K.; Shigeno, M.; Kondo, Y. *Chem. Commun.* **2021**, *57*, 8604-8607.

[6]Fang, Y.; Tranmer, G. K. *Med. Chem. Commun.* **2016**, *7*, 720-724.

[7] Weidmann, N.; Nishimura, R. H. V.; Knochel, P.; Harenberg, J. H. *Synthesis* **2020**, *53*, 557-568.

[8] Joseph, D.; Park, M. S.; Lee, S. *Org. Biomol. Chem.* **2021**, *19*, 6227-6232.

[9] Correa, A.; Martin, R. *J. Am. Chem. Soc.* **2014**, *136*, 7253-7256.

[10]]Wang, S. M.; Zhao, C.; Zhang, X.; Qin, H. L. *Org. Biomol. Chem.* **2019**, *17*, 4087-4101.

[11] Zand, Z.; Kazemi, F.; Partovi, A. *Journal of Photochemistry and Photobiology B: Biology* **2015**, *152*, 58-62.

[12] Ueda, S.; Nagasawa, H. *J. Org. Chem.* **2009**, *74*, 4272-4277.

[13] Wu, G.; Li, Y.; Yu, X.; Gao, Y.; Chen, H. *Adv. Synth. Catal.* **2016**, *359*, 687-692.

[14] Bhakuni, B. S.; Kumar, A.; Balkrishna, S. J.; Sheikh, J. A.; Konar, S.; Kumar, S. *Org. Lett.* **2012**, *14*, 2838-2841.

[15] Liu, H.; Deng, X.; Huang, X.; Ji, N.; He, W. *Org. Biomol. Chem*. **2020**, *18*, 3654-3658.

[16] Ning, Y.; Wang, S.; Li, M.; Han, J.; Zhu, C.; Xie, J. *Nat. Commun.* **2021**, *12*, 4637.

[17] Antonow, D.; Marrafa, T.; Dawood, I.; Ahmed, T.; Haque, M. R.; Thurston, D. E.; Zinzalla, G. *Chem. Commun.* **2010**, *46*, 2289.

[18] Tulichala, R. N. P.; Shankar, M.; Swamy, K. C. K. *J. Org. Chem.* **2018**, *83*, 4375-4383.

[19] Zhou, Z.; Kweon, J.; Jung, H.; Kim, D.; Seo, S.; Chang, S. *J. Am. Chem. Soc.* **2022**, *144*, 9161-9171.

[20] Yang, H. Y.; Yao, Y. H.; Chen, M.; Ren, Z. H.; Guan, Z. H. *J. Am. Chem. Soc.* **2021**, *143*, 7298-7305.

[21] Li, G.; Szostak, M. *Nat. Commun.* **2018**, *9*, 4165.

[22] Wang, X.; Chen, Z.; Liu, Q.; Lin, W.; Xiong, X. *Chem. Commun.* **2022**, 58, 13325-13328.

[23] Yao, Y. H.; Yang, H. Y.; Chen, M.; Wu, F.; Xu, X. X.; Guan, Z. H. *J. Am. Chem. Soc.* **2020**, *143*, 85-91.

[24] Zhang, J.; Hou, Y. X.; Tang, Y. L.; Xu, J. H.; Liu, Z. K.; Gao, Y.; Hu, X.-Q. *Org. Chem. Front.* **2021**, *8*, 3434-3439.

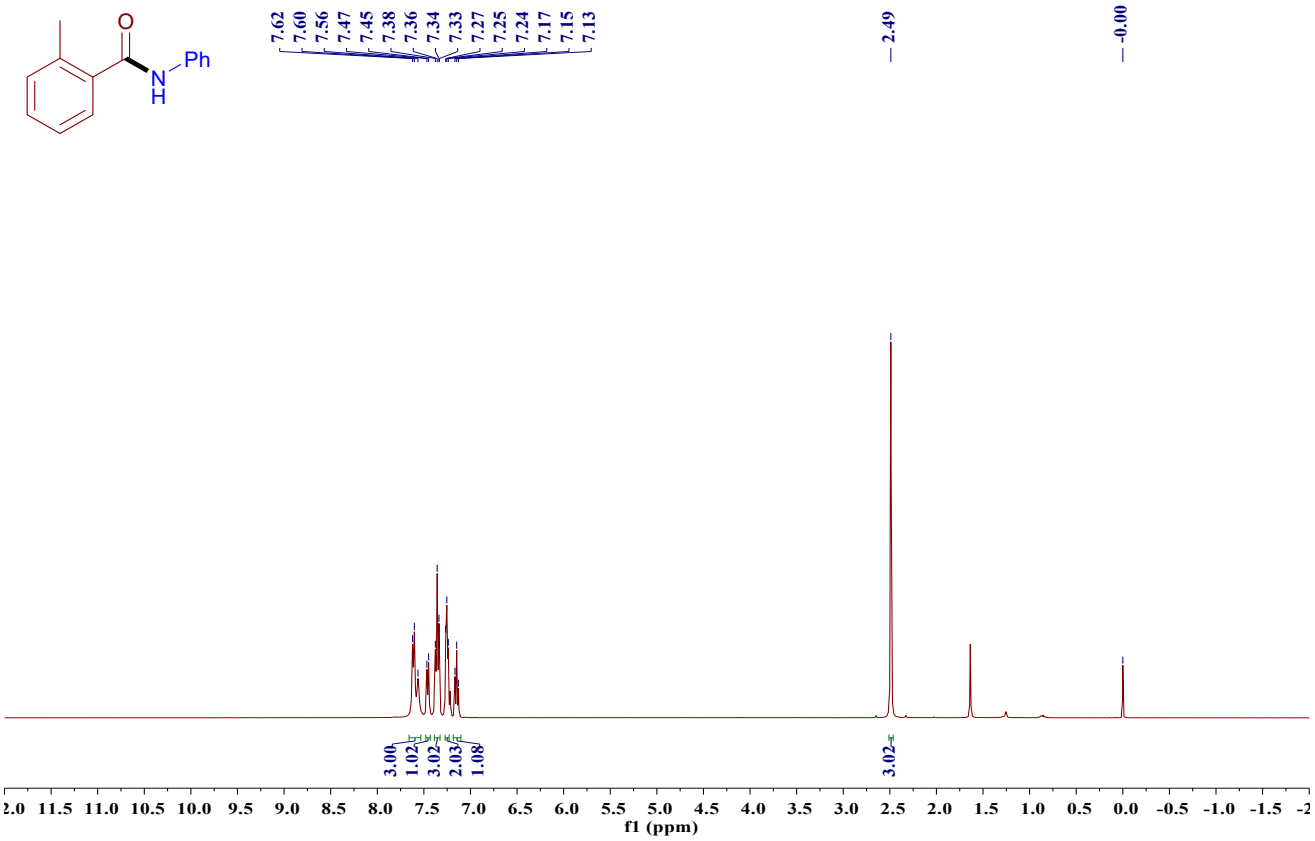
[25] Usami, K.; Yamaguchi, E.; Tada, N.; Itoh, A. *Eur. J. Org. Chem.* **2019**, *2020*, 1496-1504.

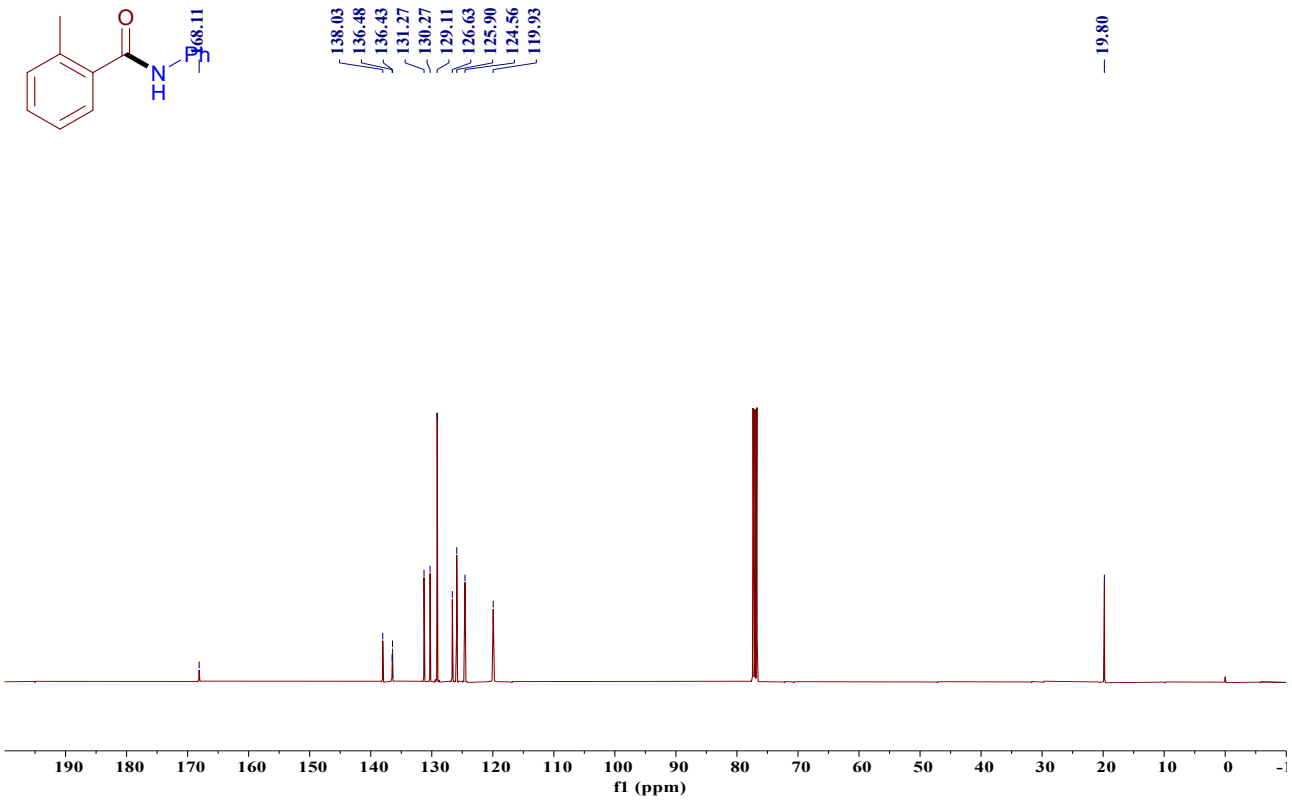
[26] Qiao, M.; Zhang, J.; Chen, L.; Zhou, F.; Zhang, Y.; Zhou, L.; Wu, Y. *Org. Biomol. Chem.* **2019**, 17, 3790-3796.

[27] Phakhodee, W.; Wangngae, S.; Wiriya, N.; Pattarawarapan, M. *Tetrahedron Lett.* **2016**, *57*, 5351-5354.

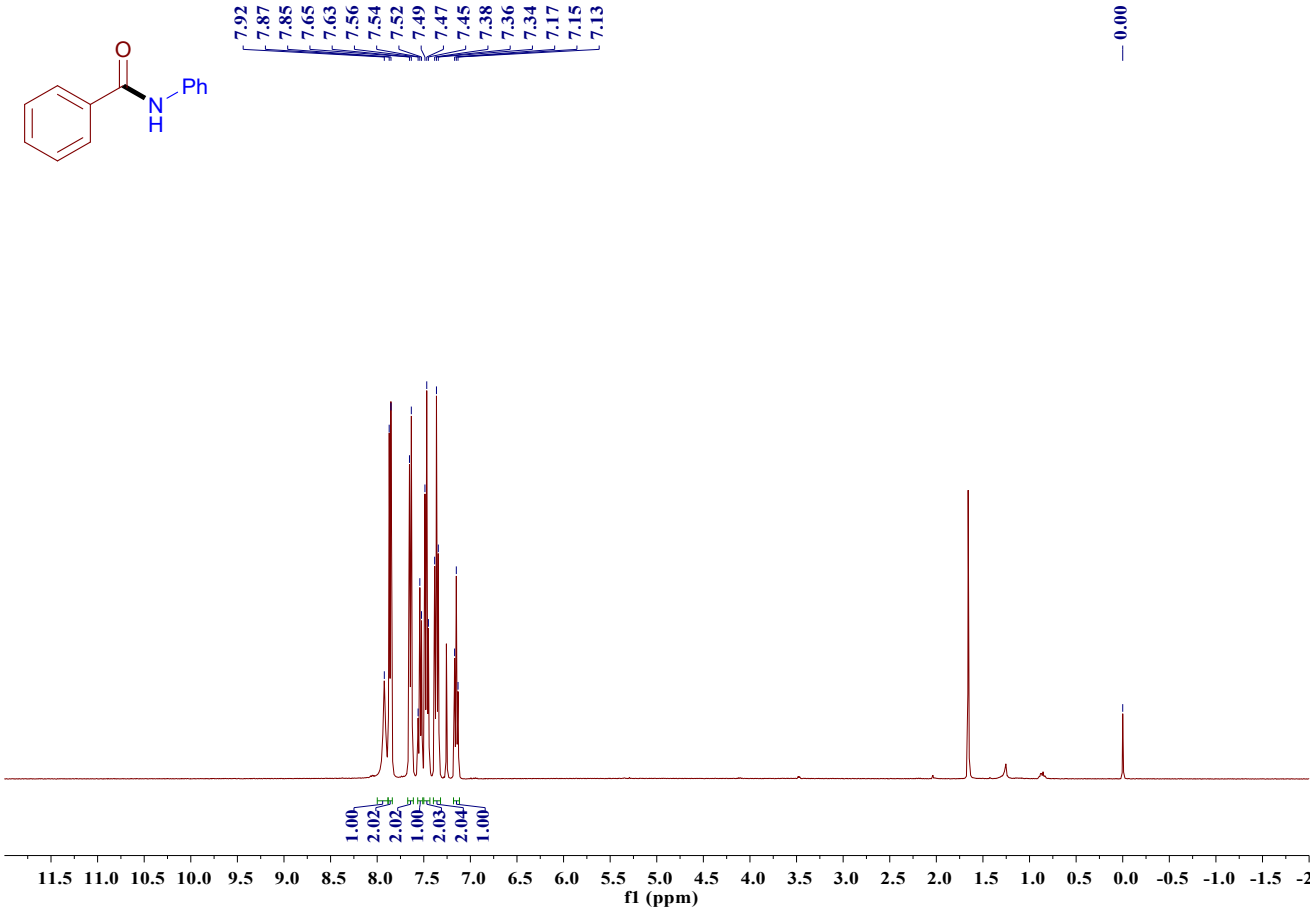
7. NMR Spectra of products 3-5, 6aa-6fa, 8-10

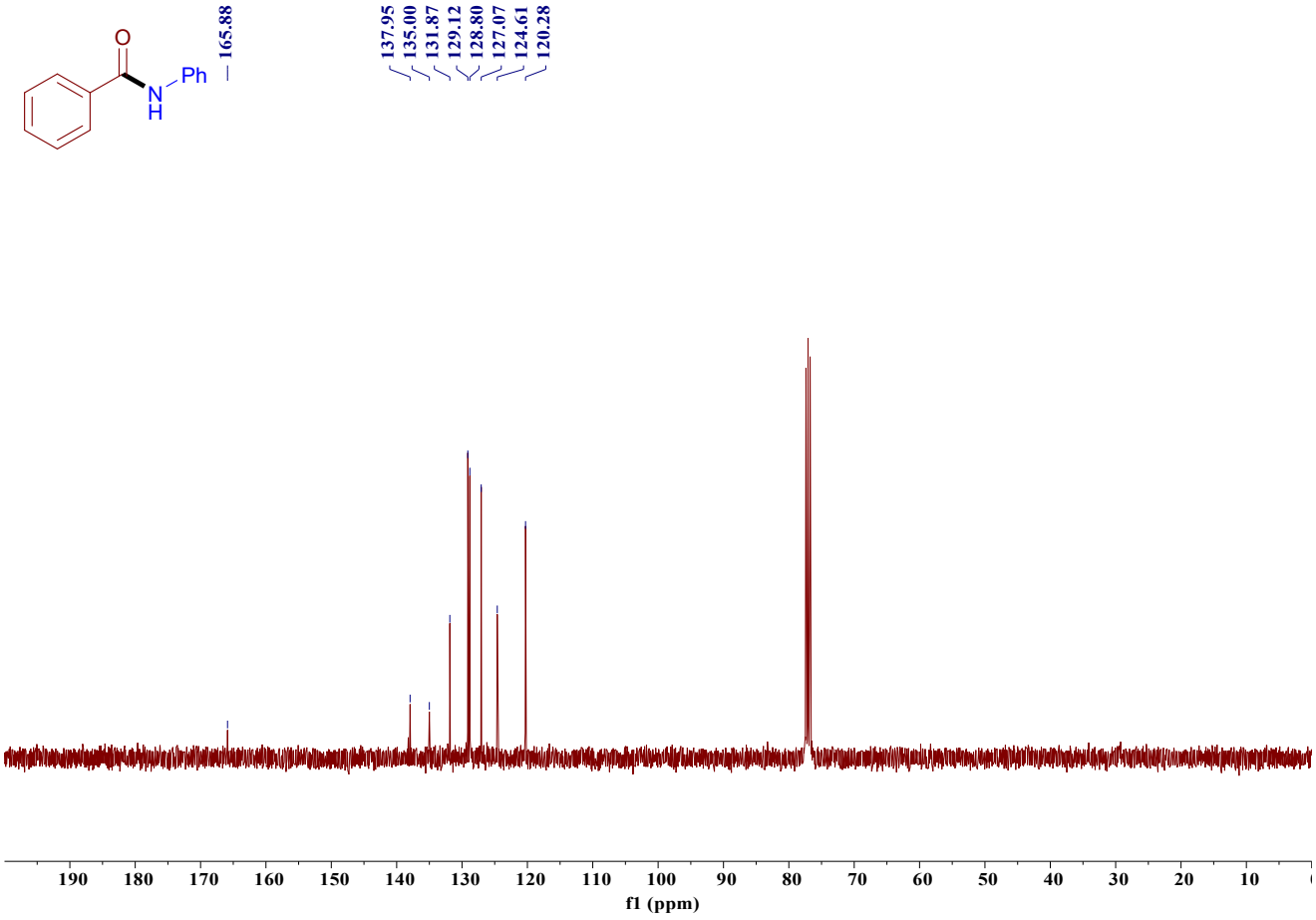
^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) of product 3aa



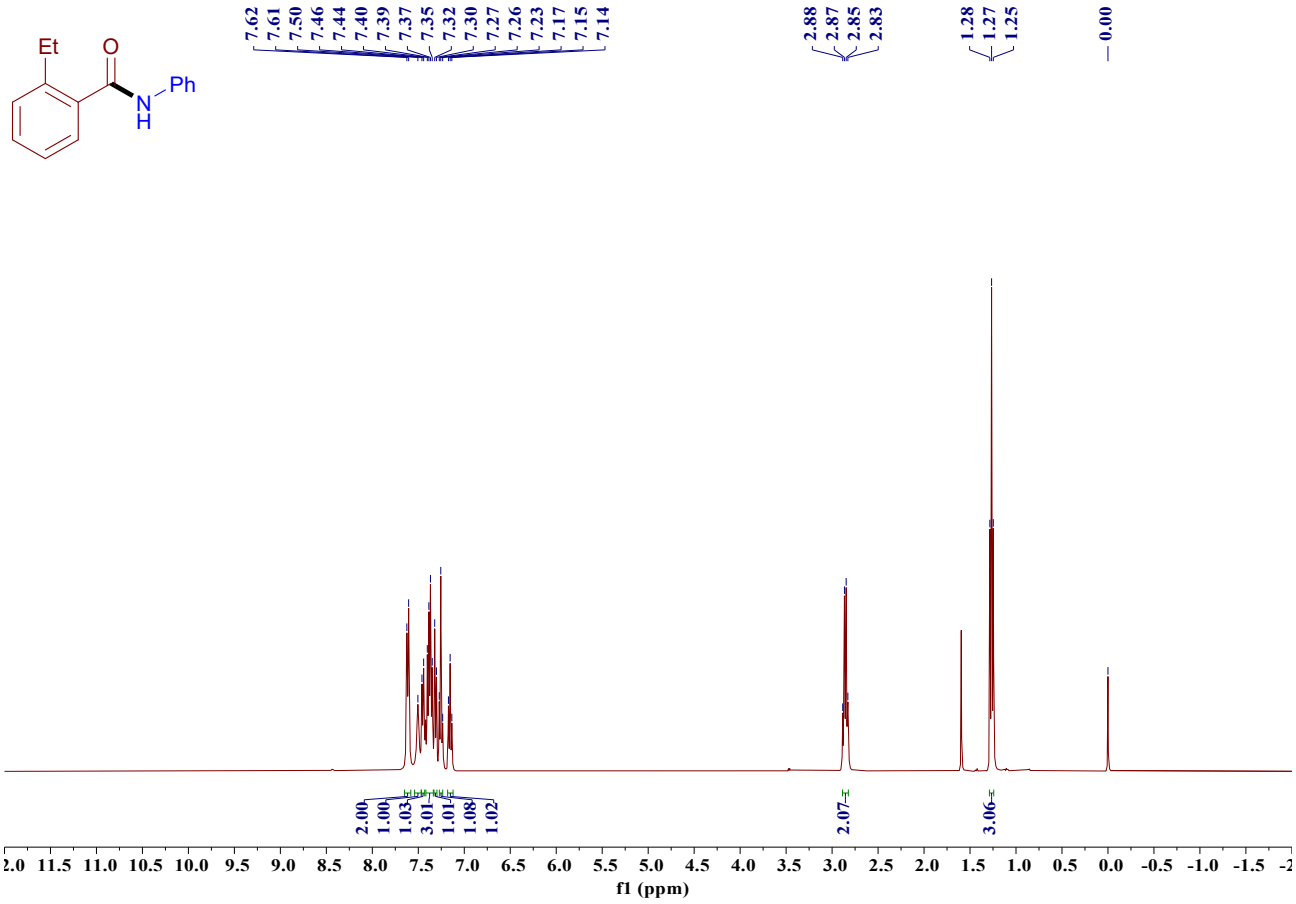


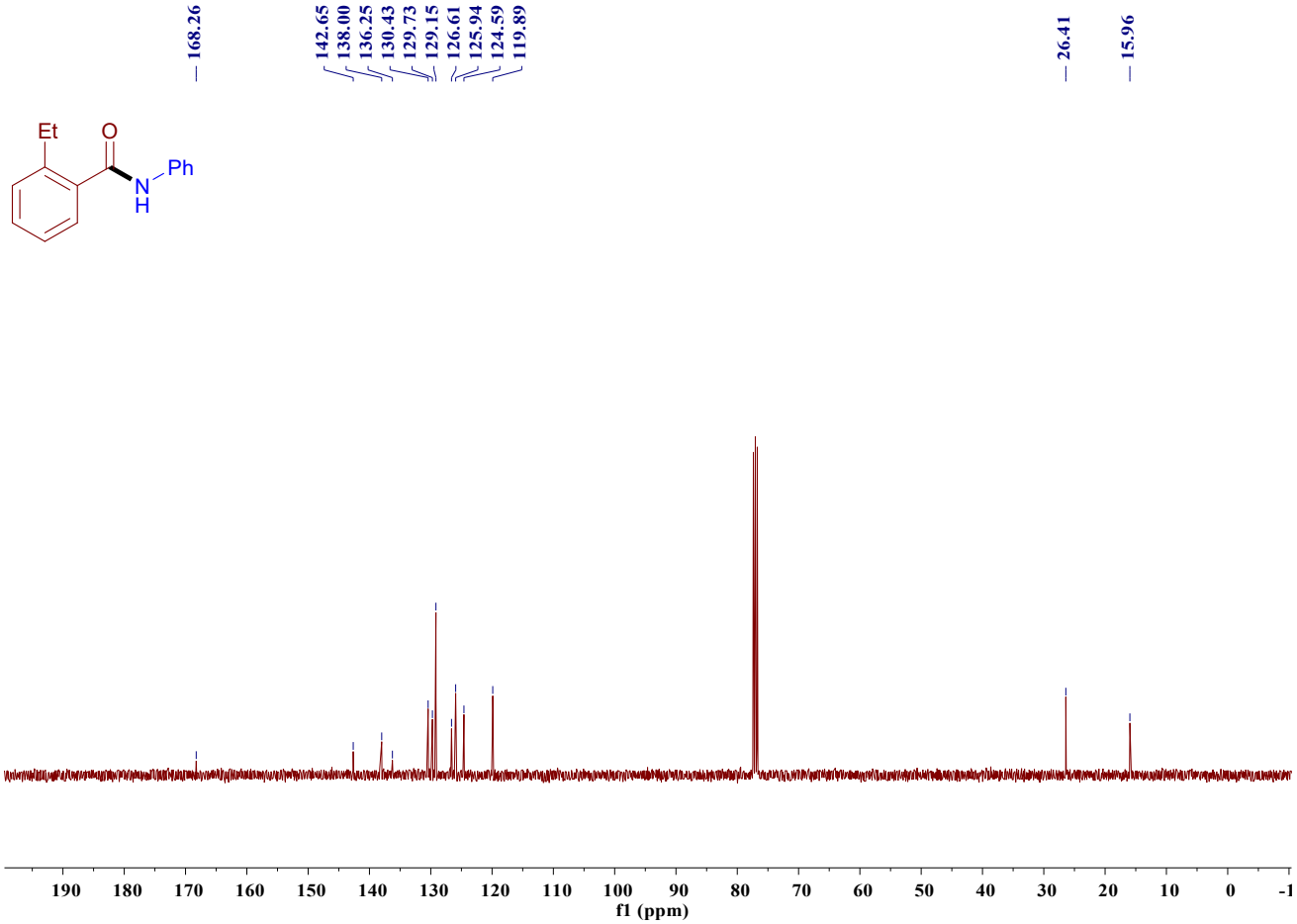
^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) of product 3ba



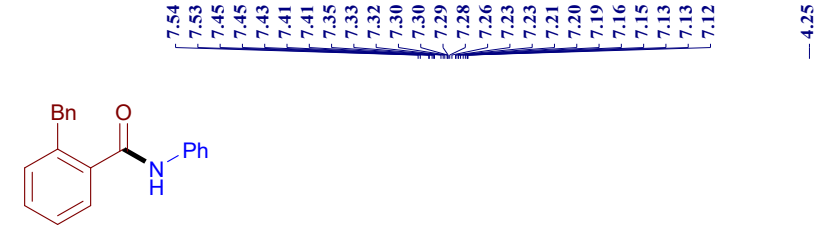


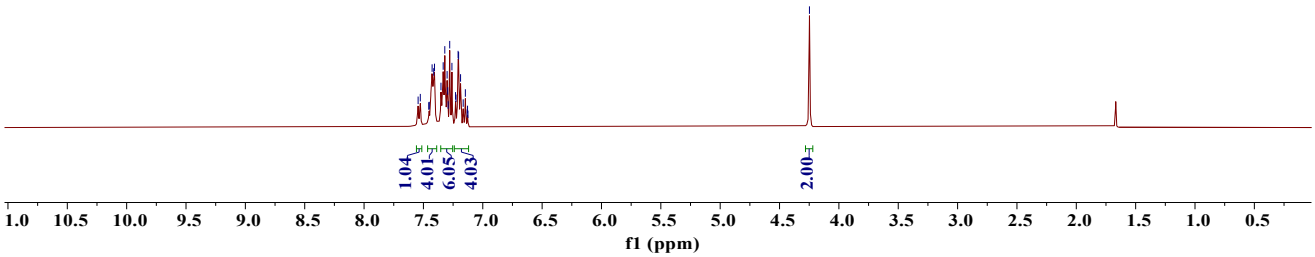
^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) of product 3ca

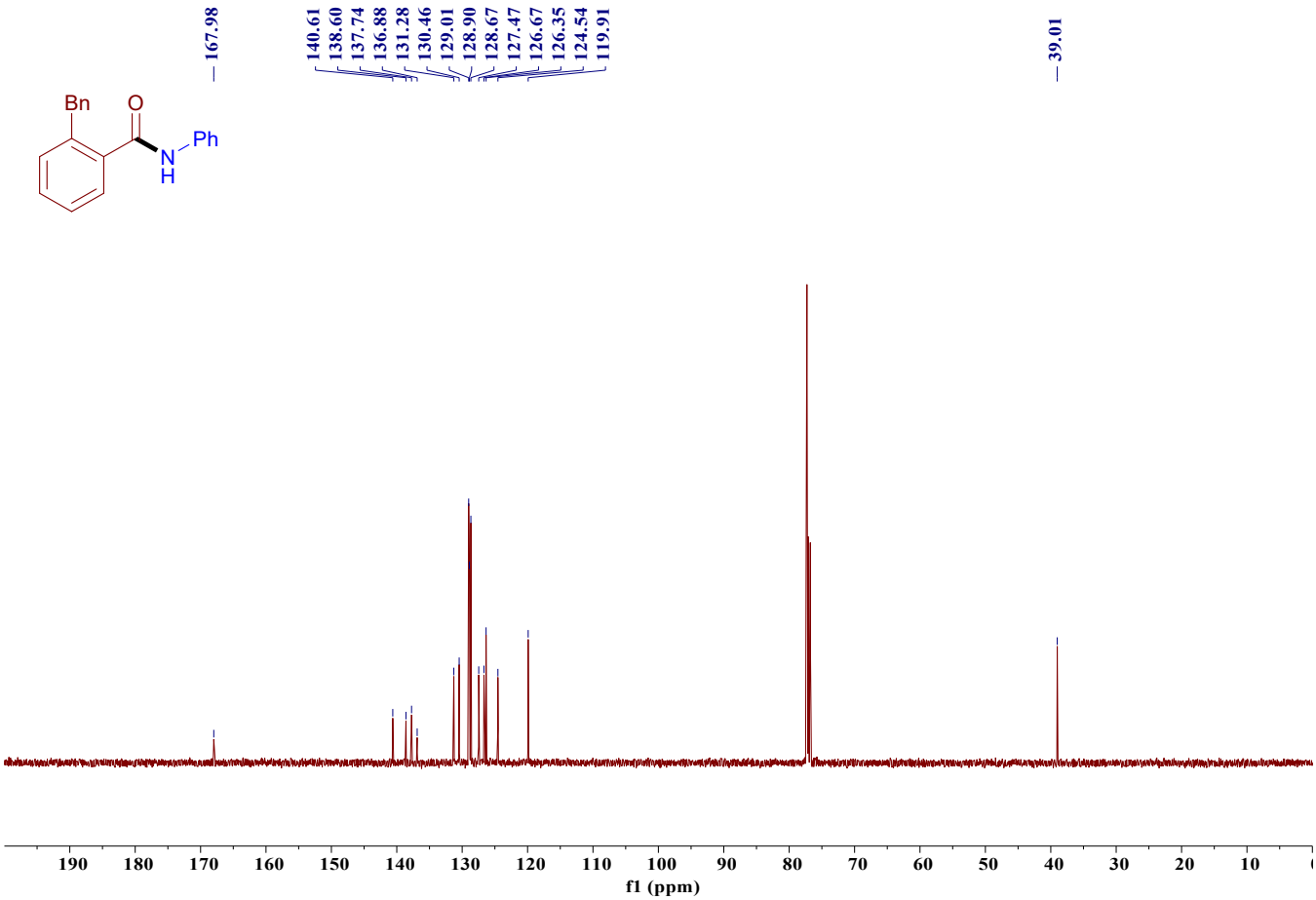




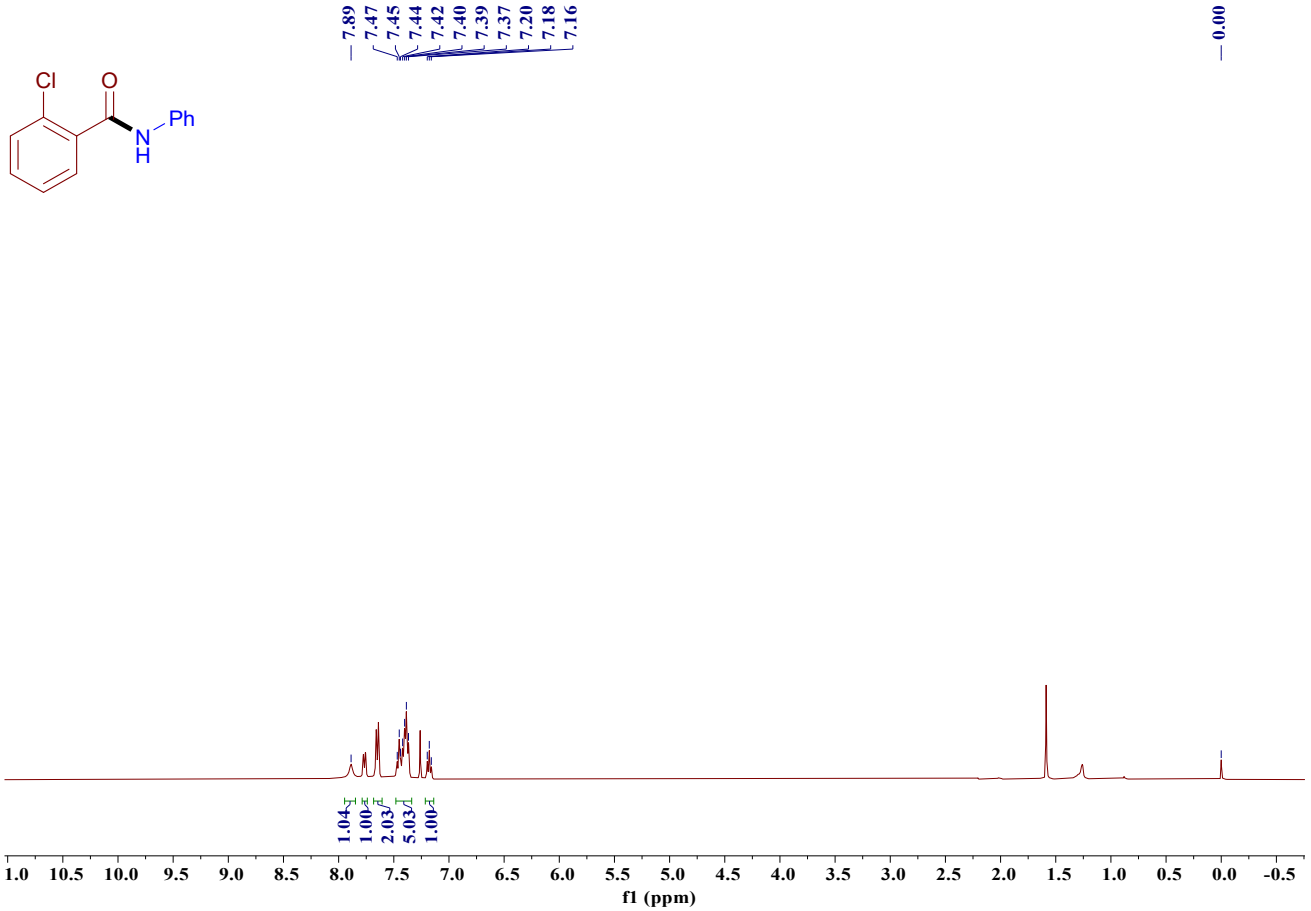
^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) of product 3da

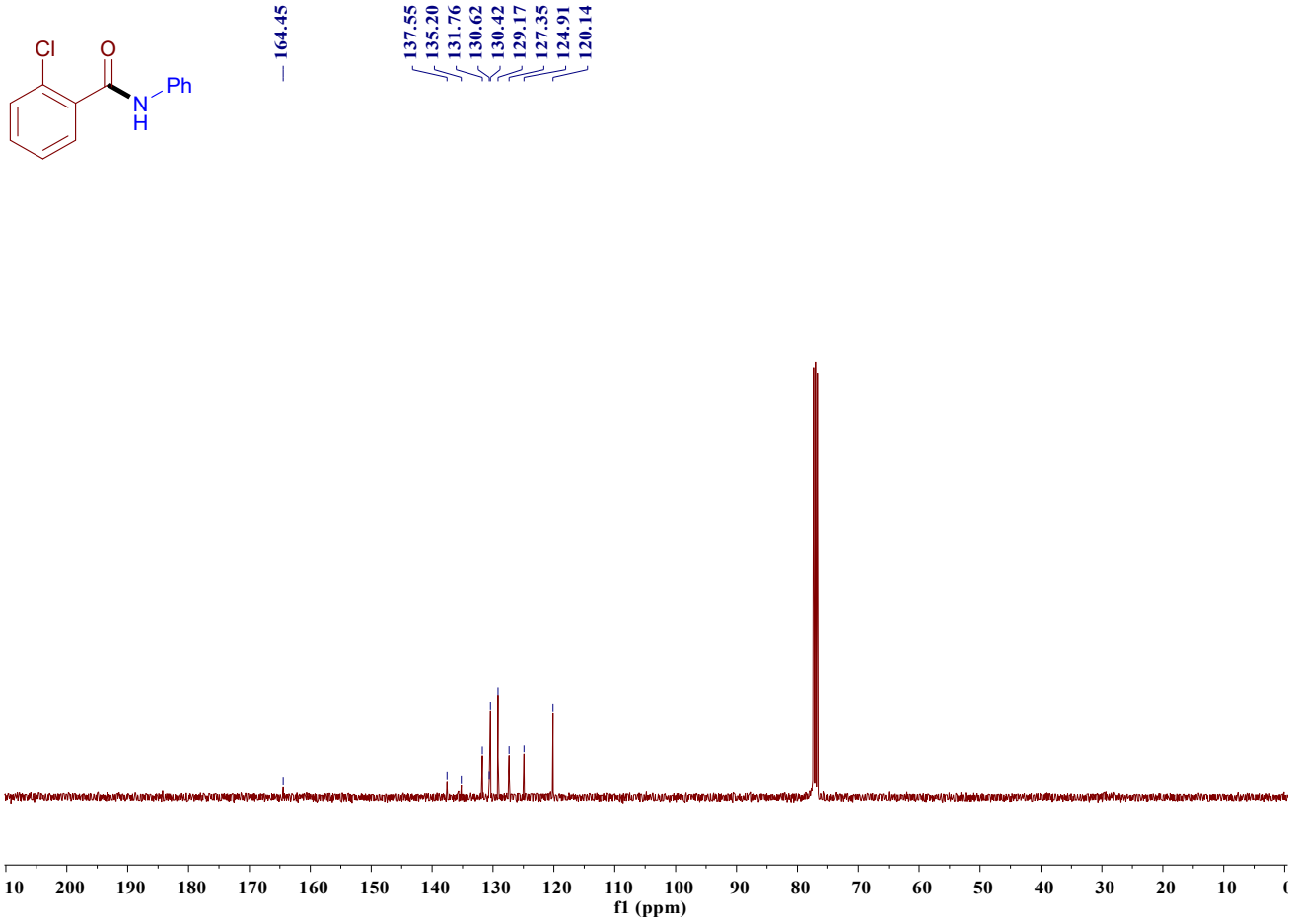




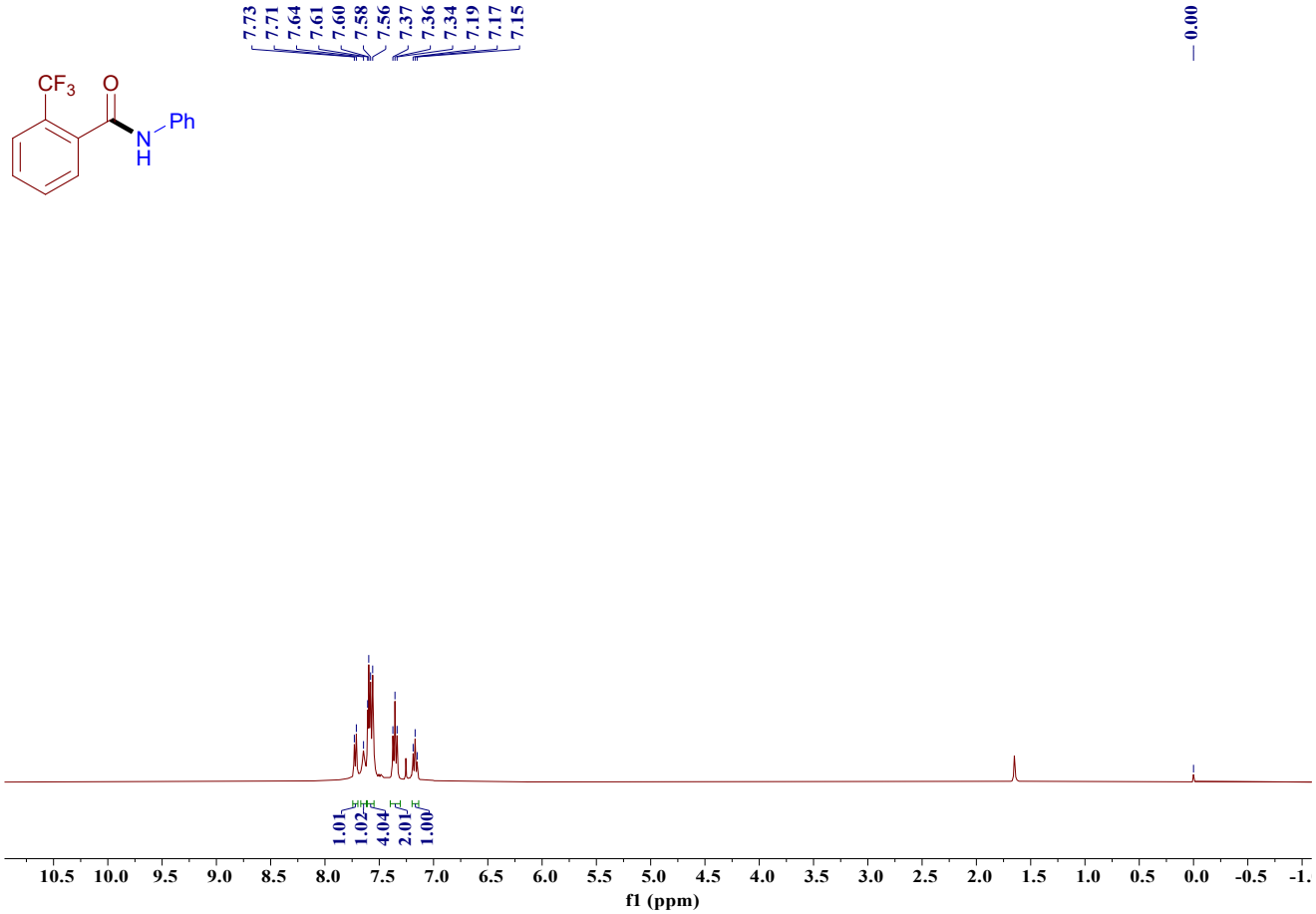


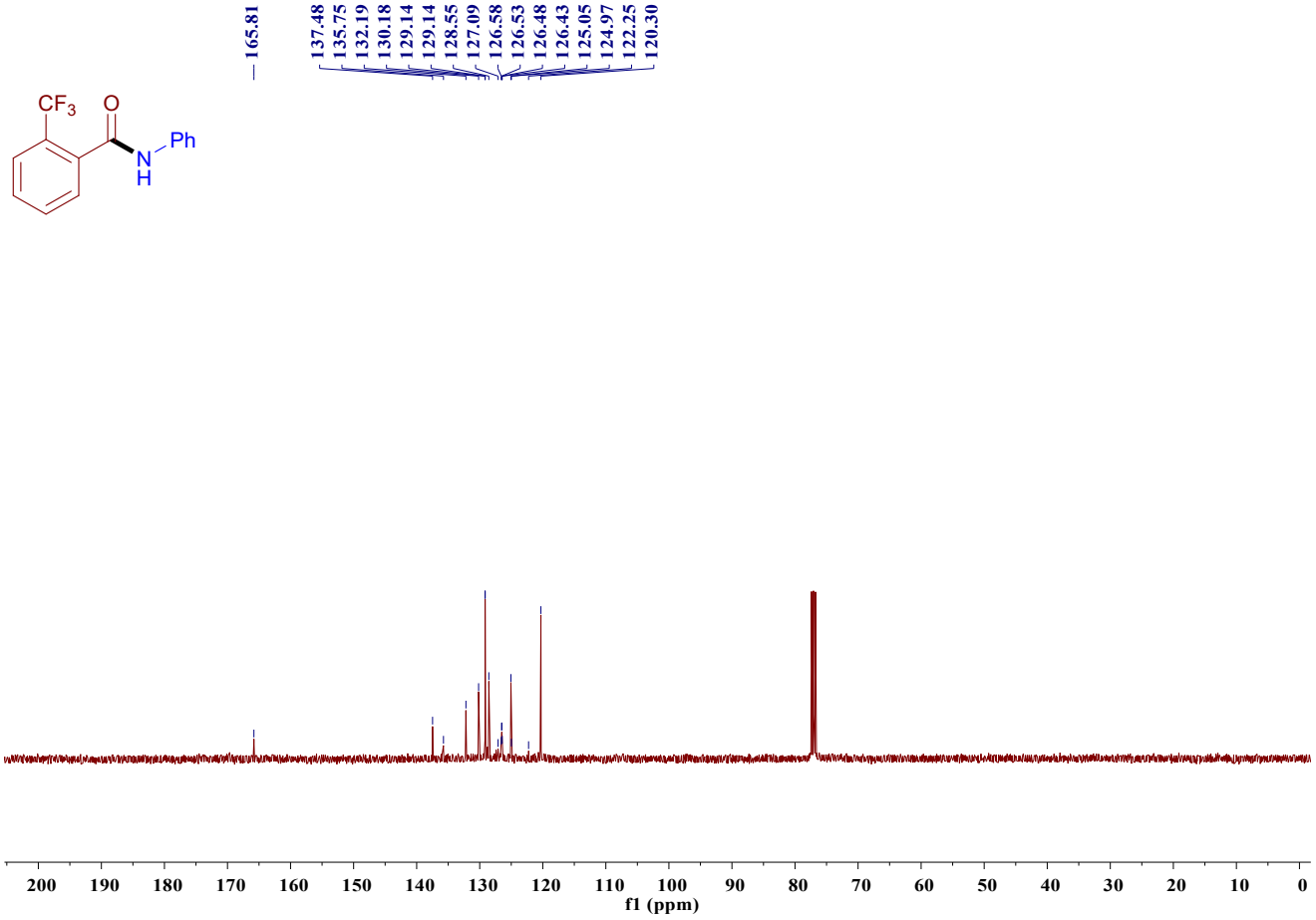
^{11}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) of product 3ea

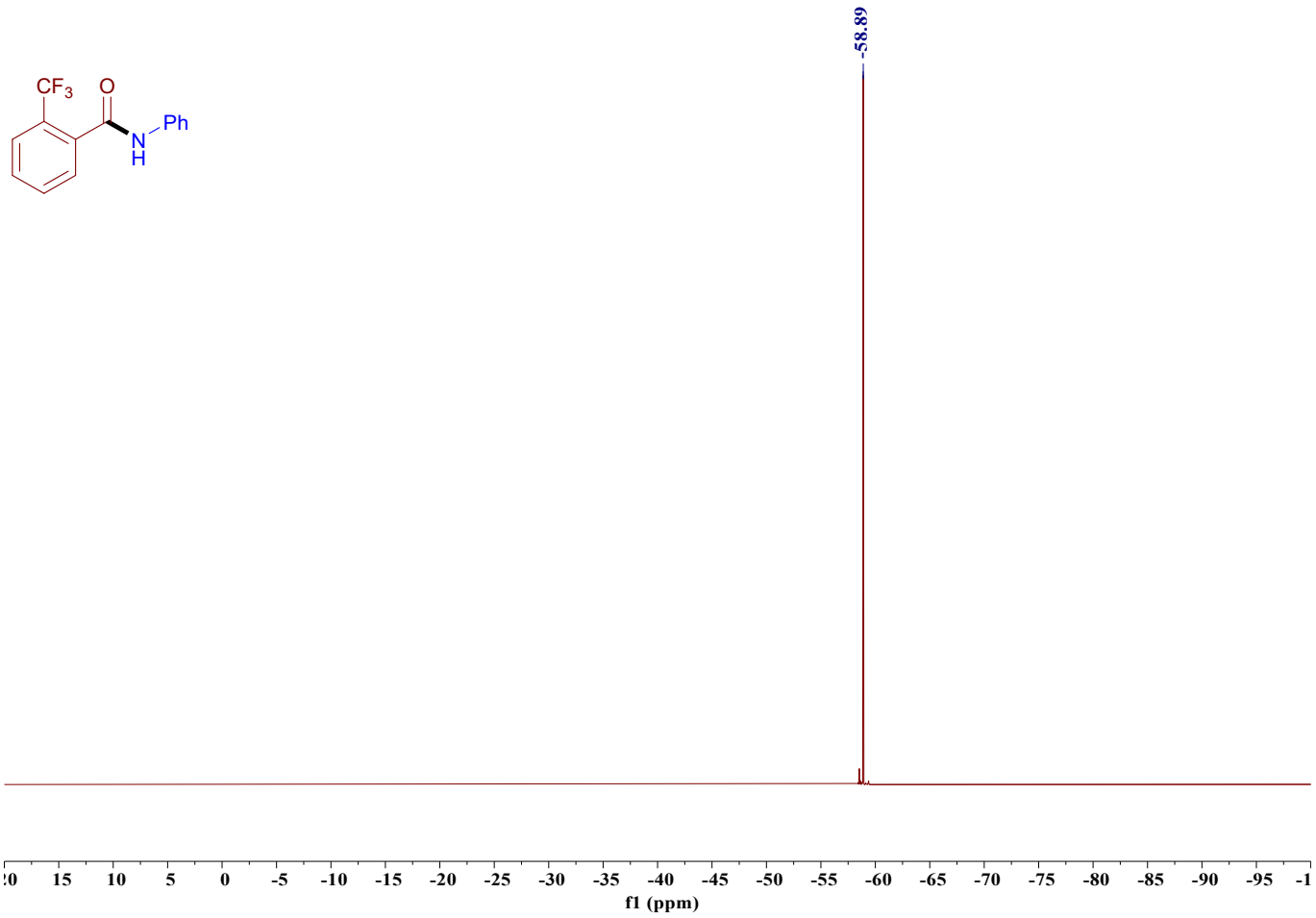




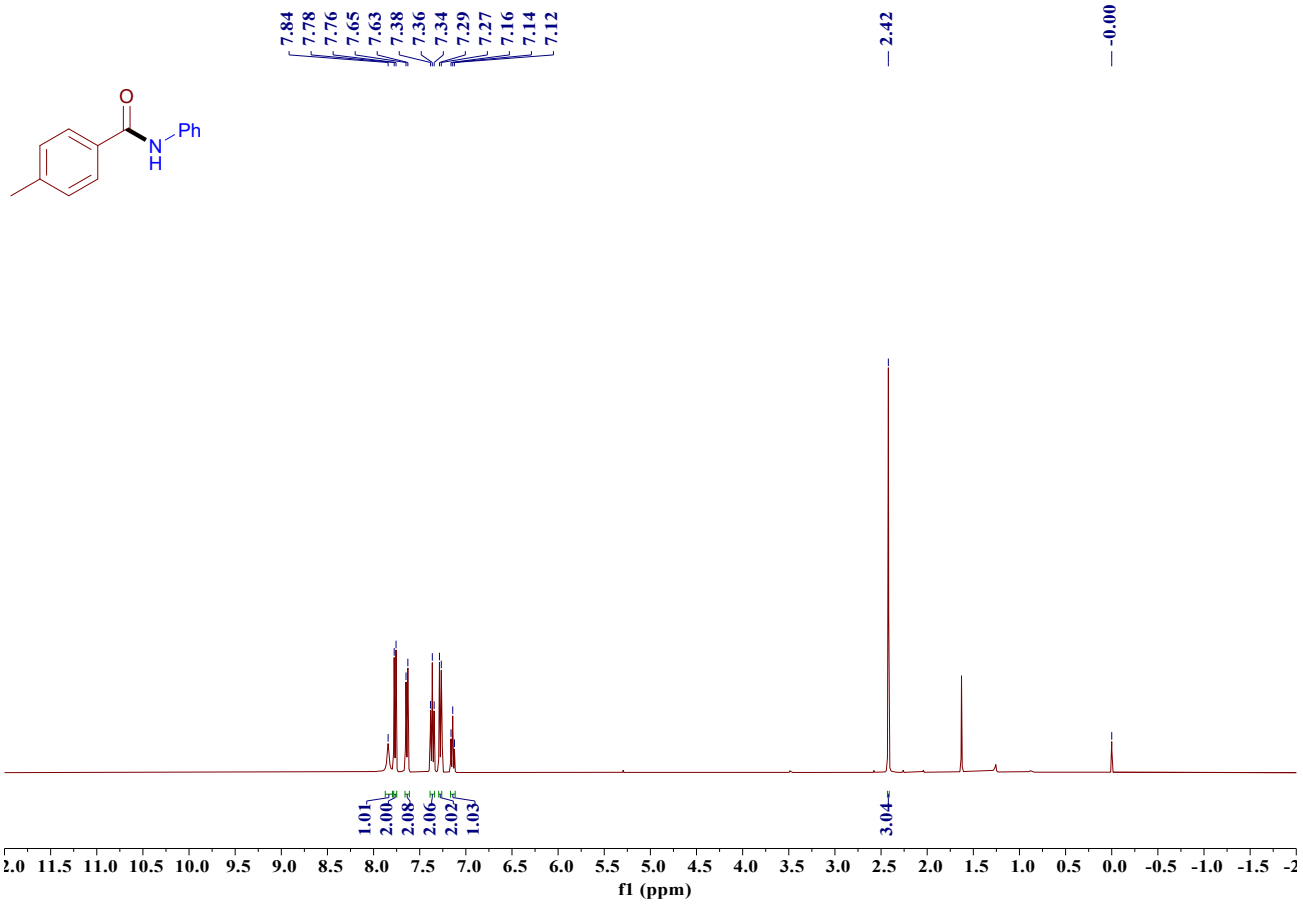
^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$), ^{19}F NMR (376 MHz, $CDCl_3$) of product 3fa

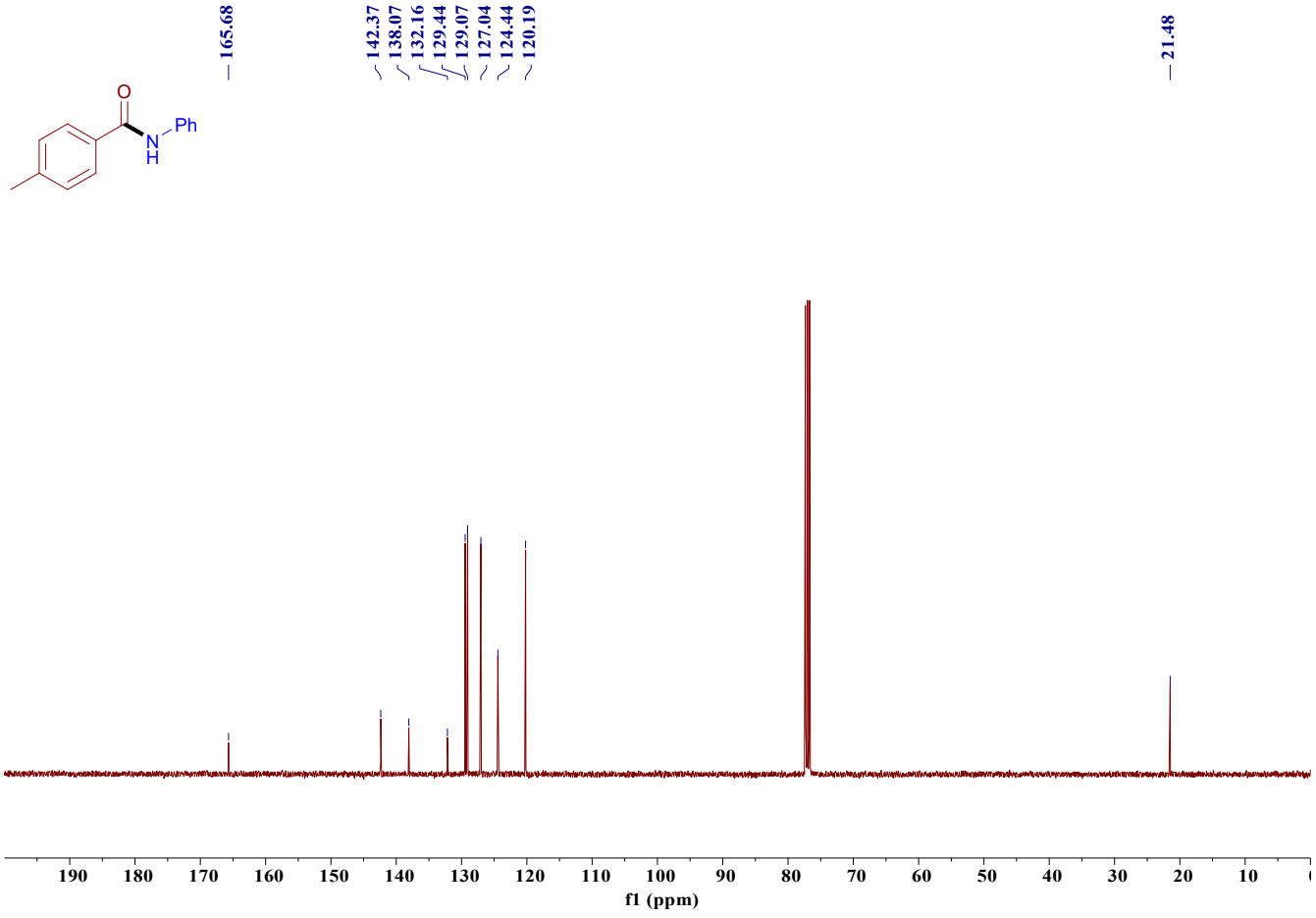




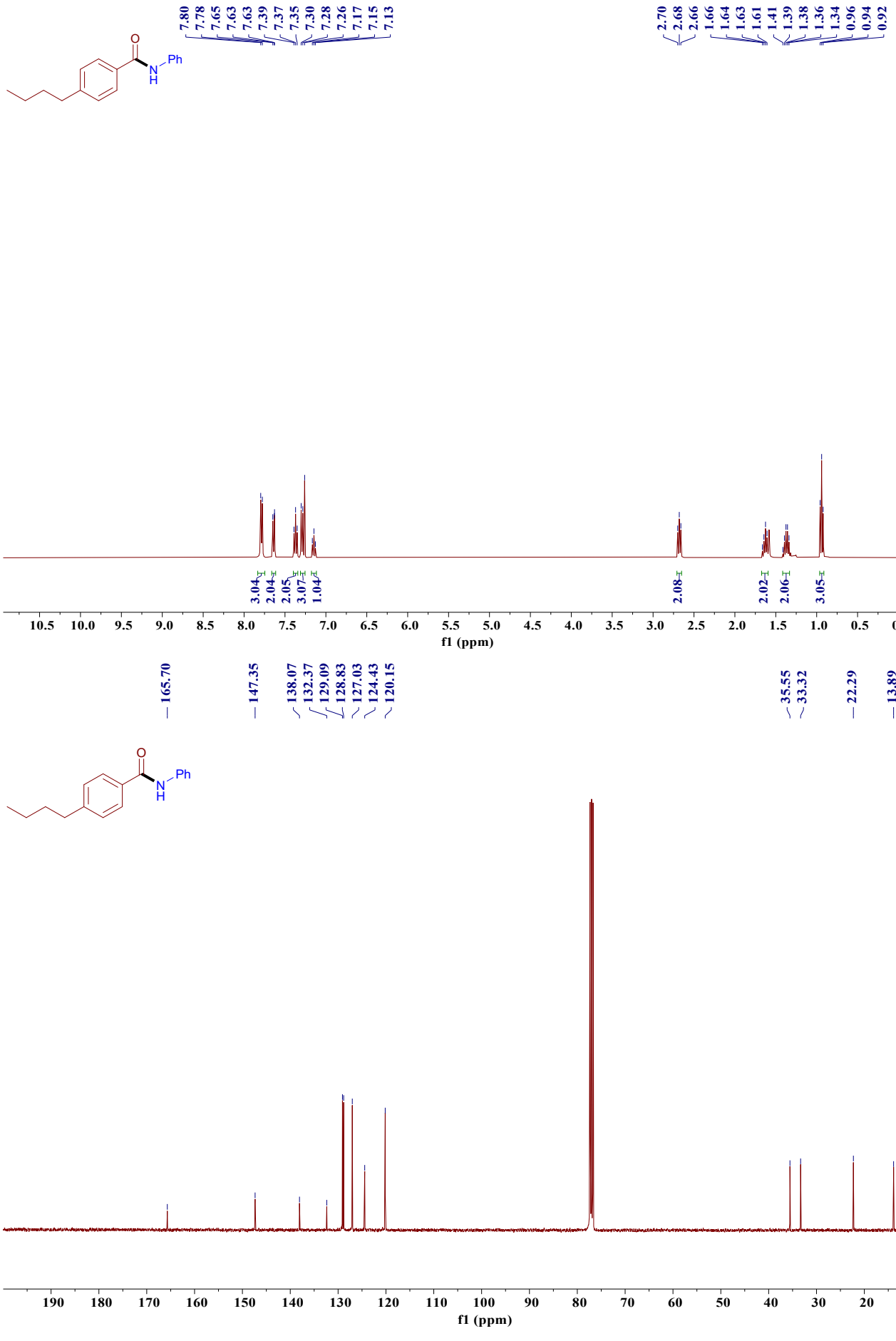

CF3
O
N
H
Ph
-58.89
20 15 10 5 0 -5 -10 -15 -20 -25 -30 -35 -40 -45 -50 -55 -60 -65 -70 -75 -80 -85 -90 -95 -1
f1 (ppm)

^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) of product 3ga

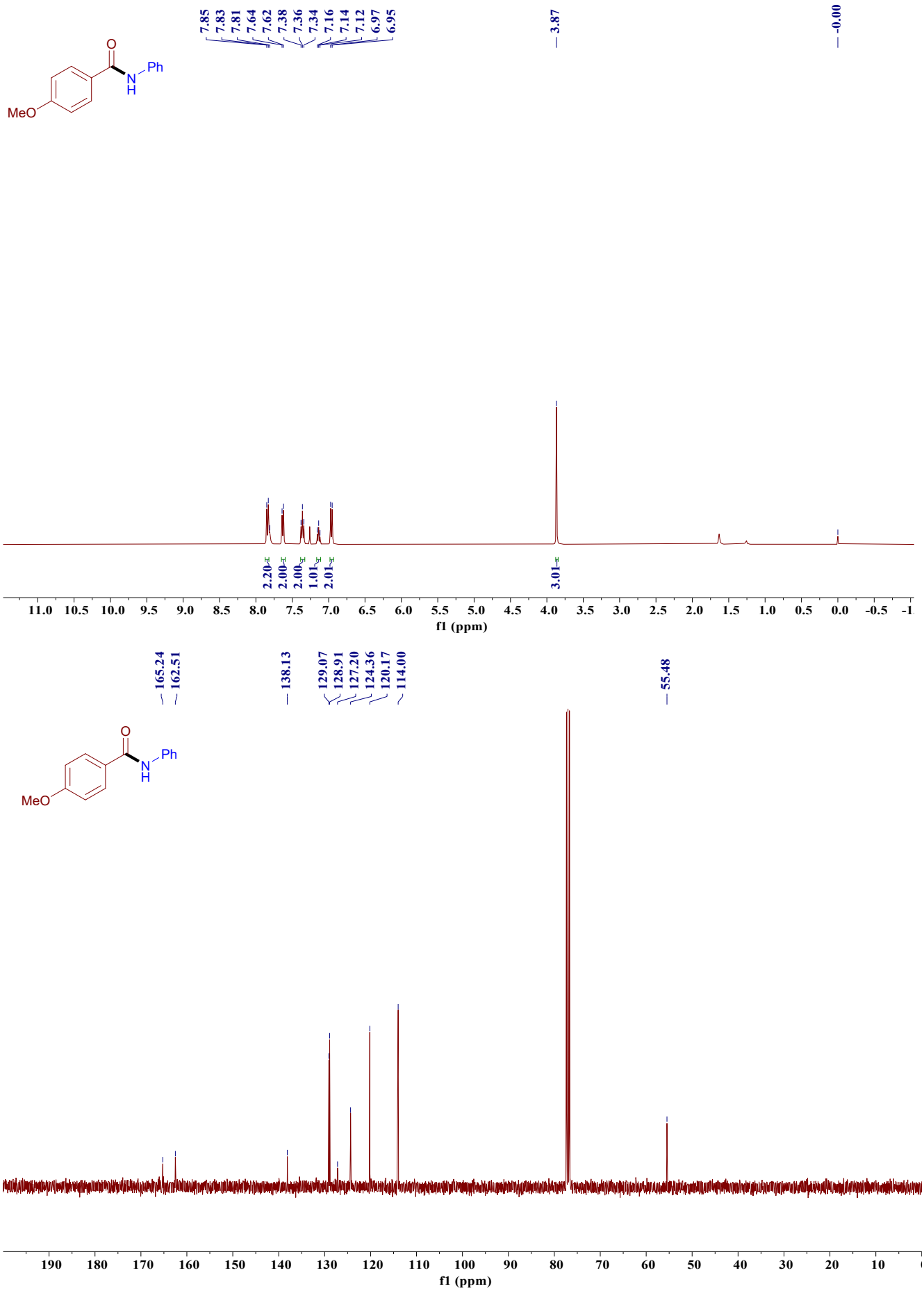




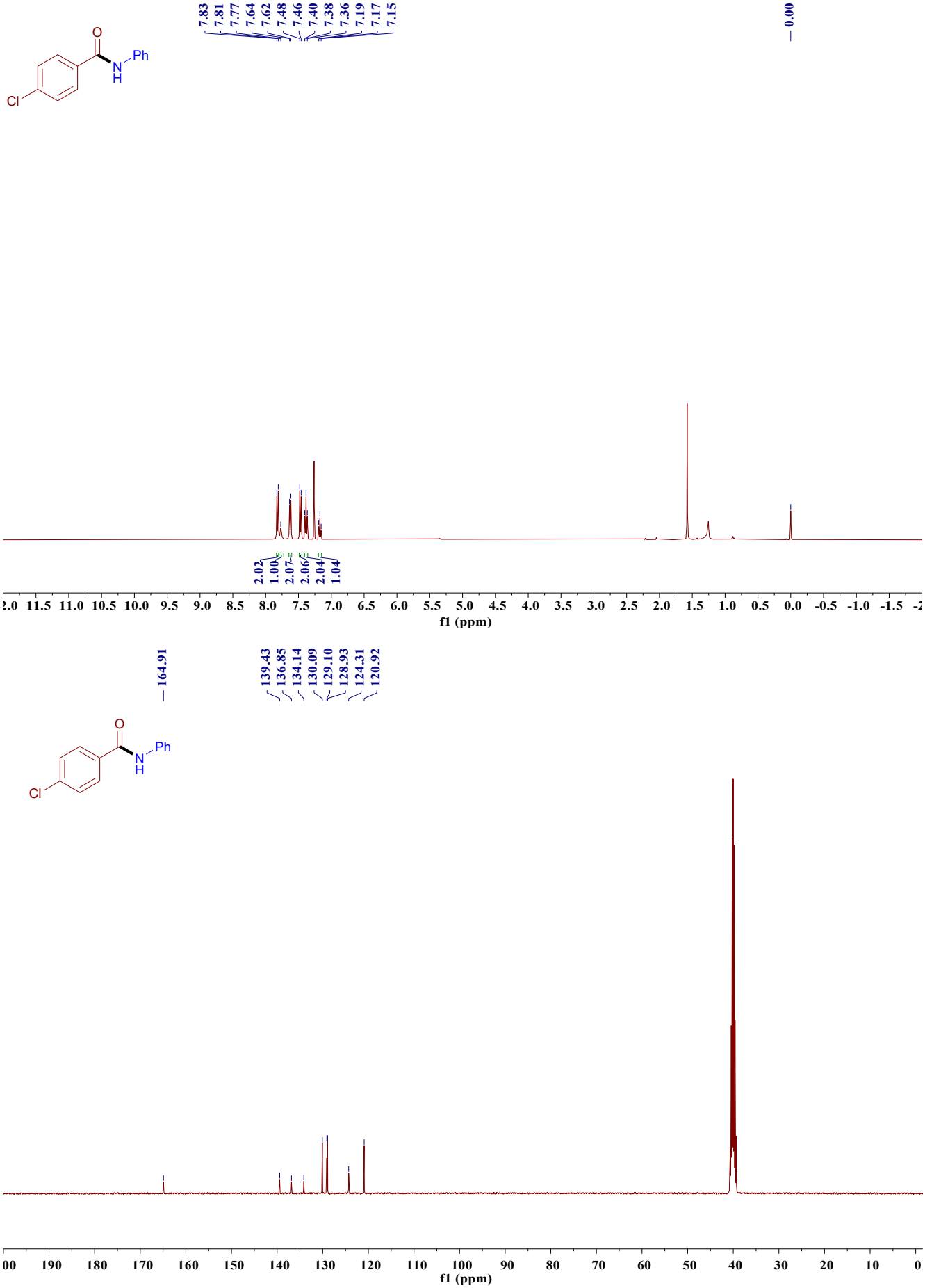
^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) of product 3ha



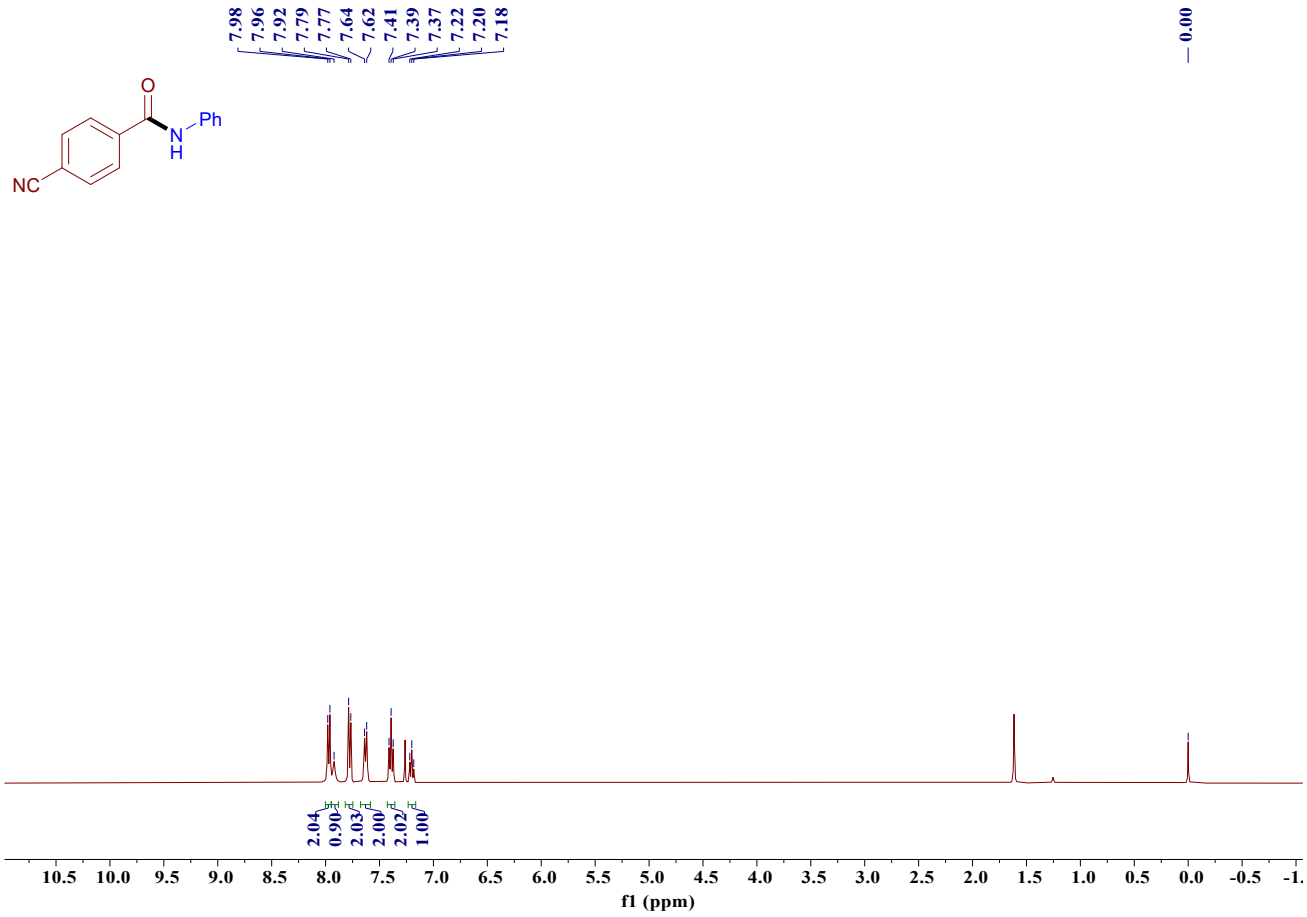
^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) of product 3ia

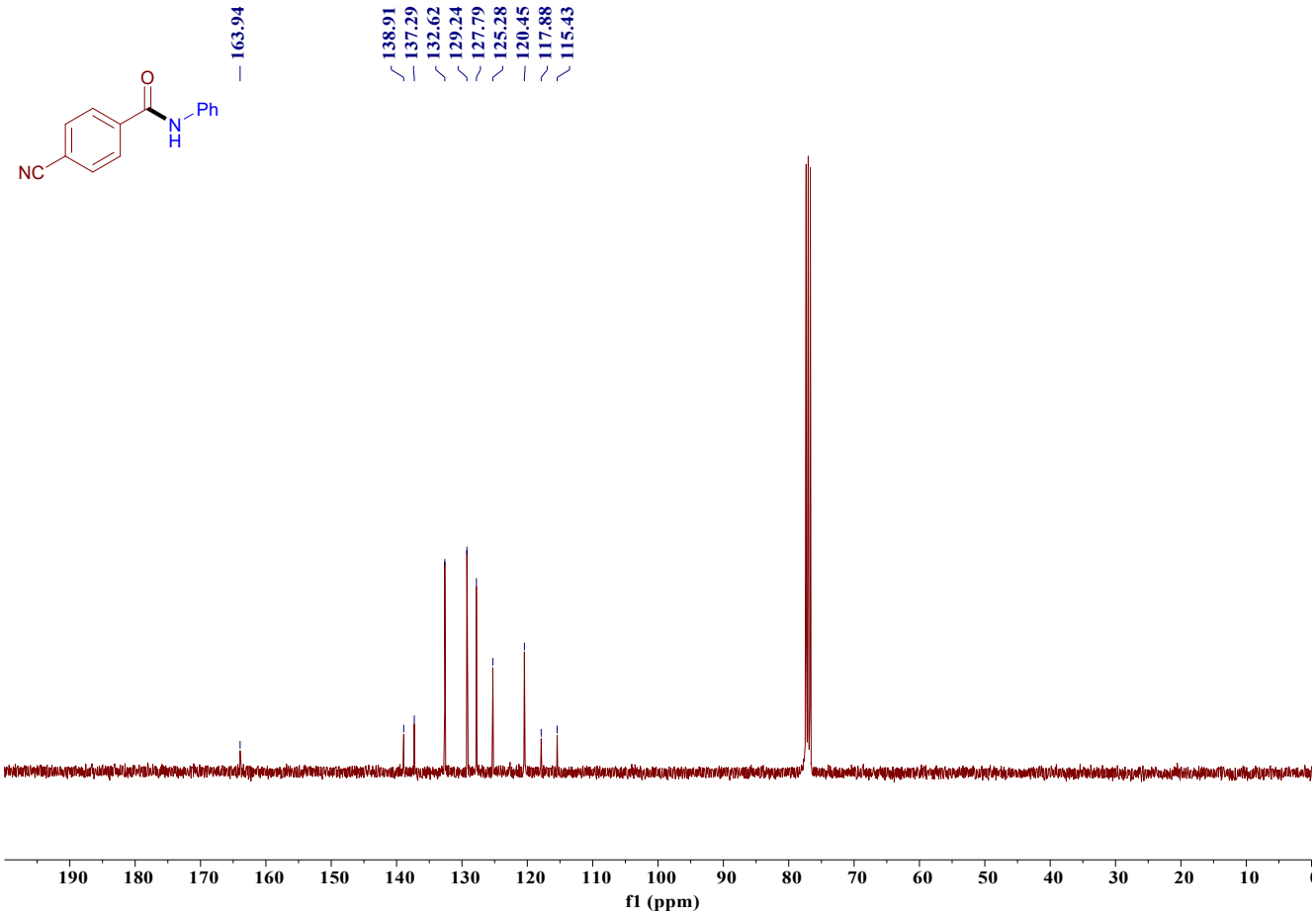


^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, DMSO-d_6) of product 3ja

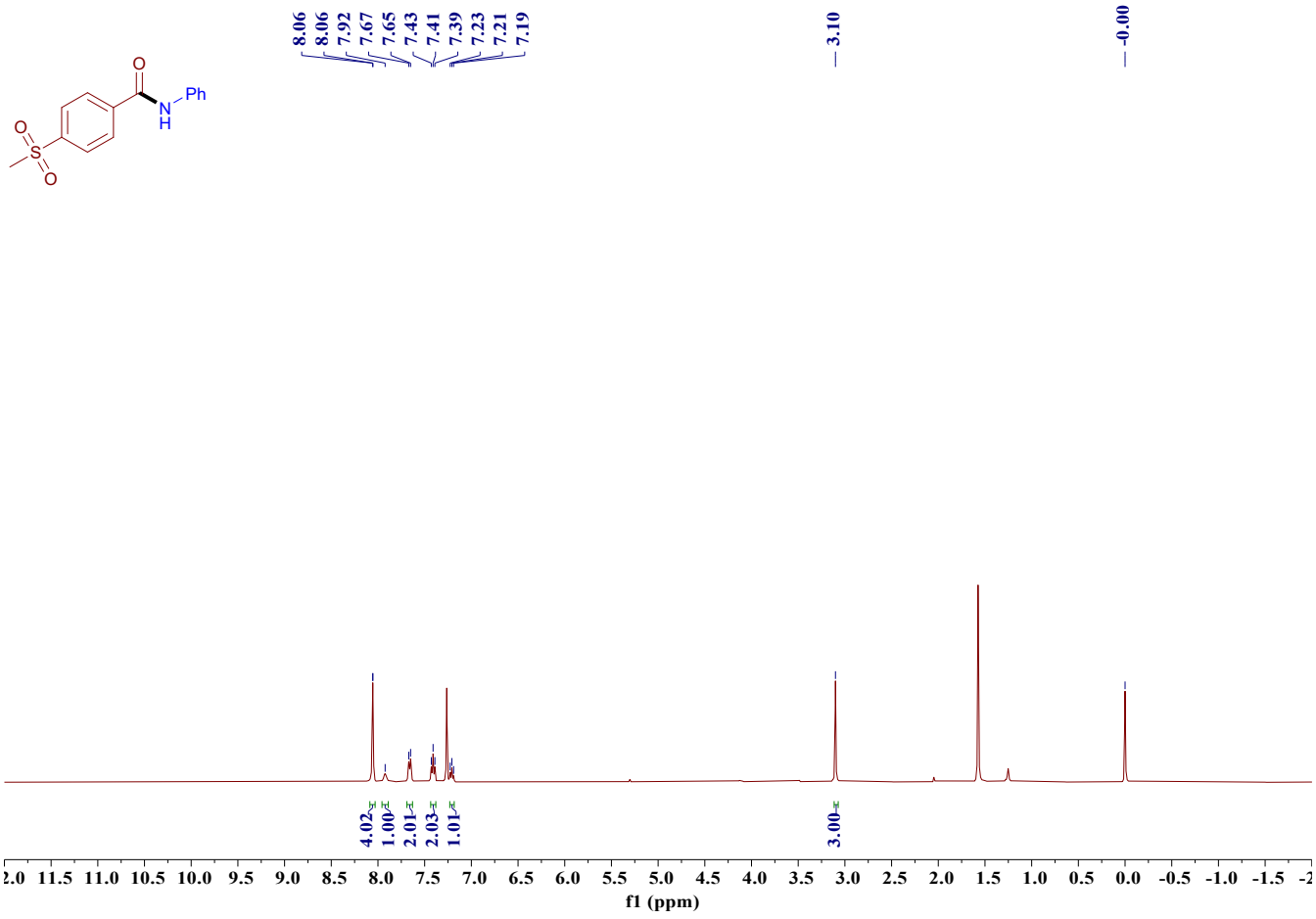


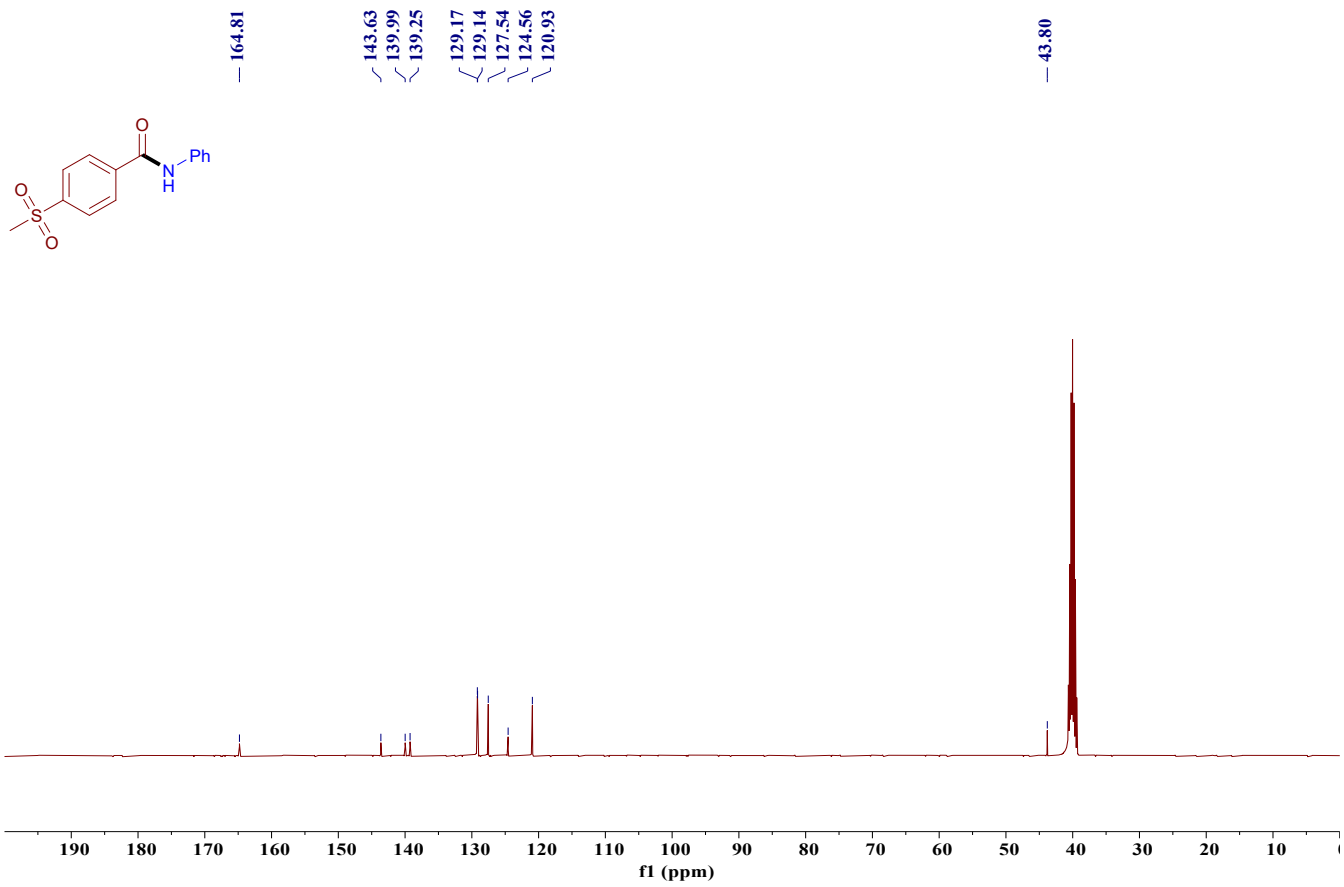
^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) of product 3ka



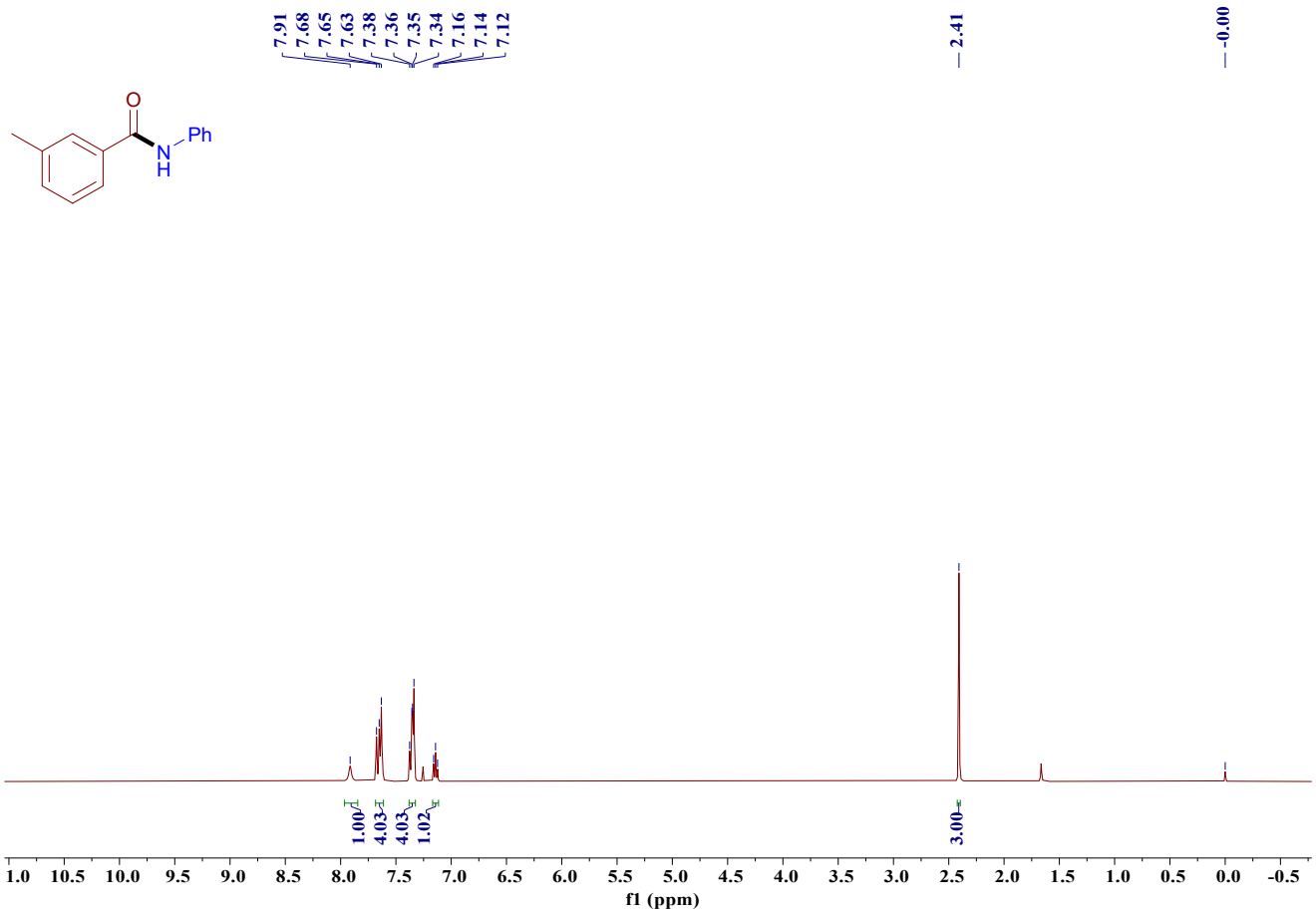


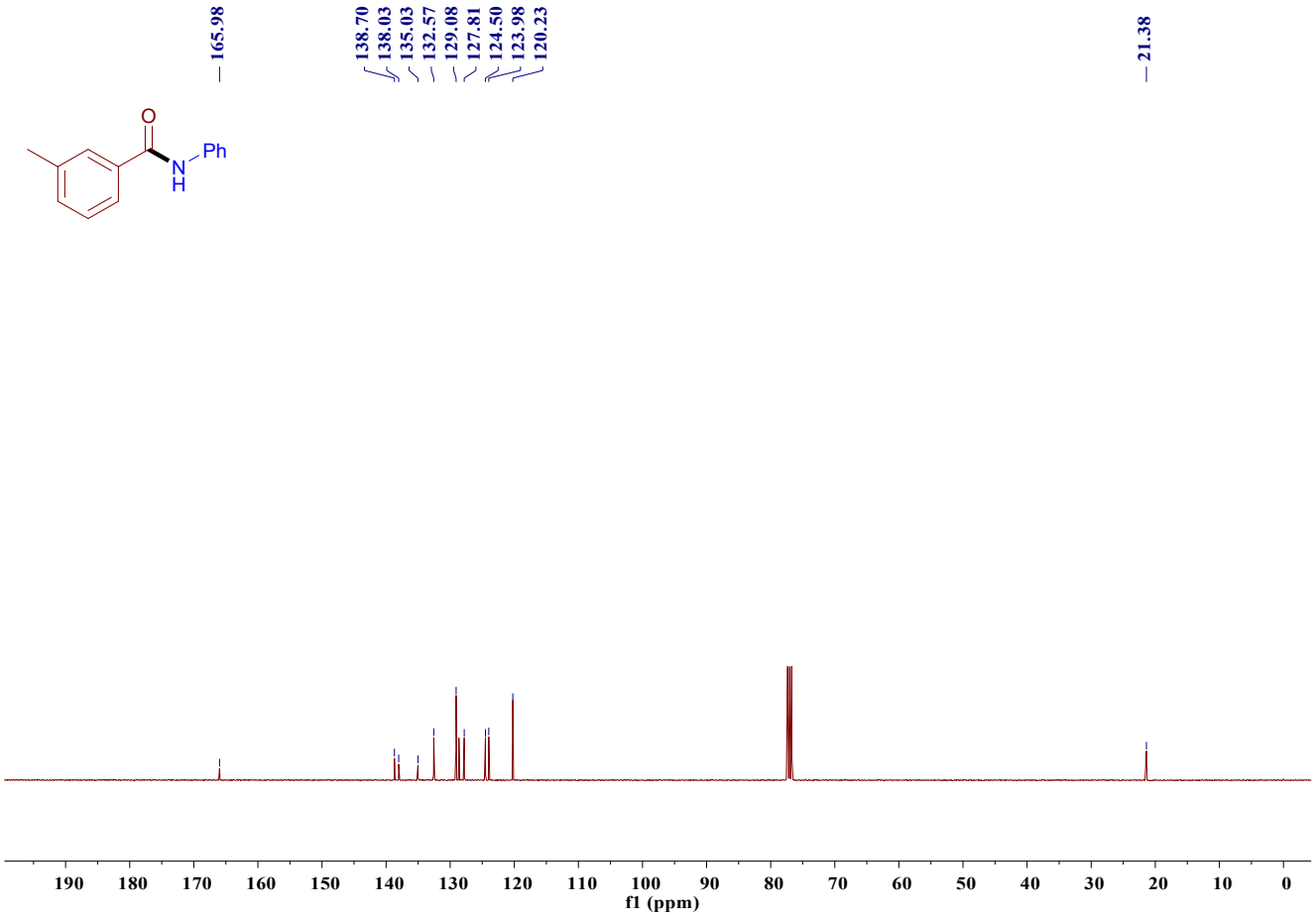
^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, DMSO-d_6) of product 3la



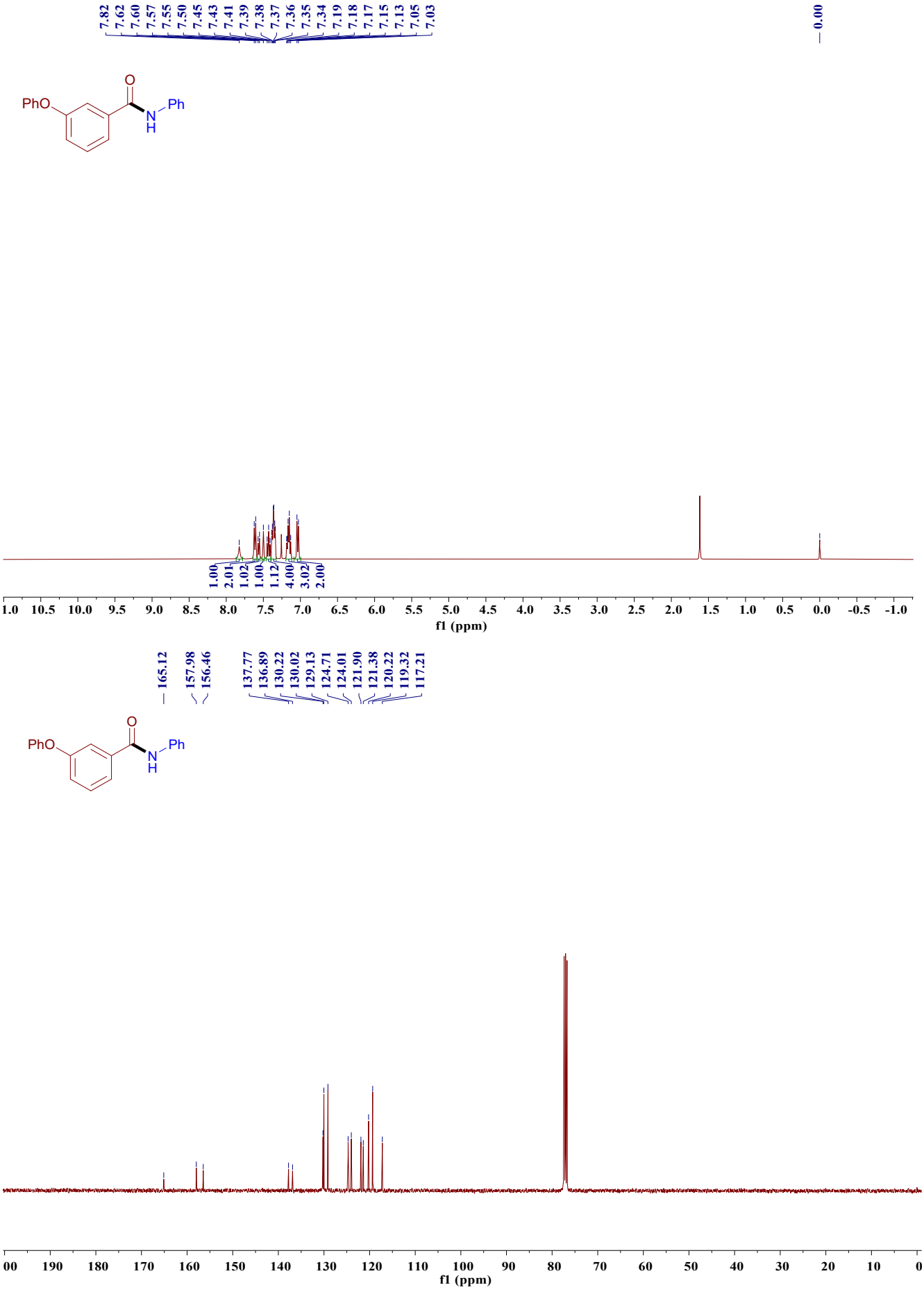


^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) of product 3ma

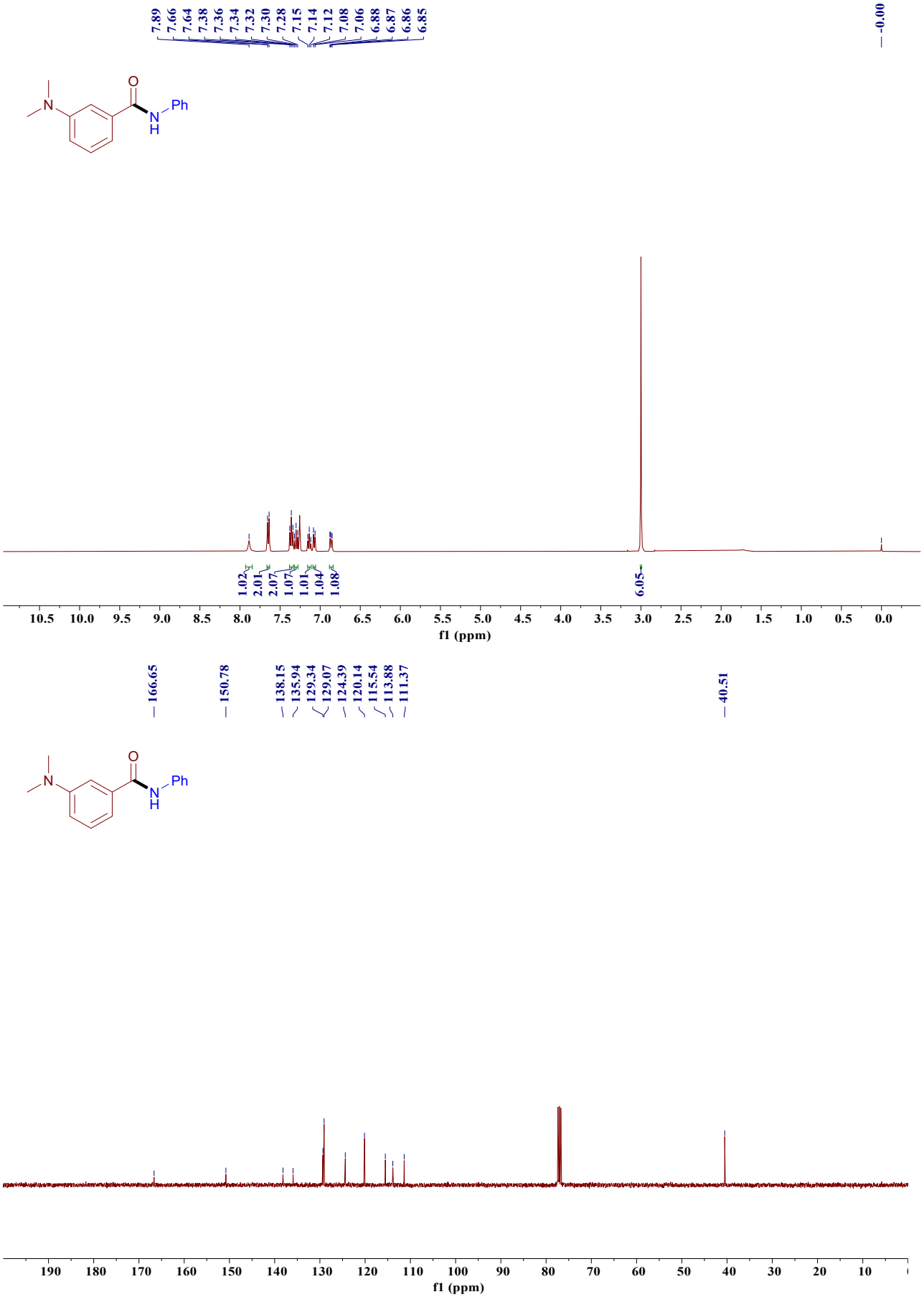




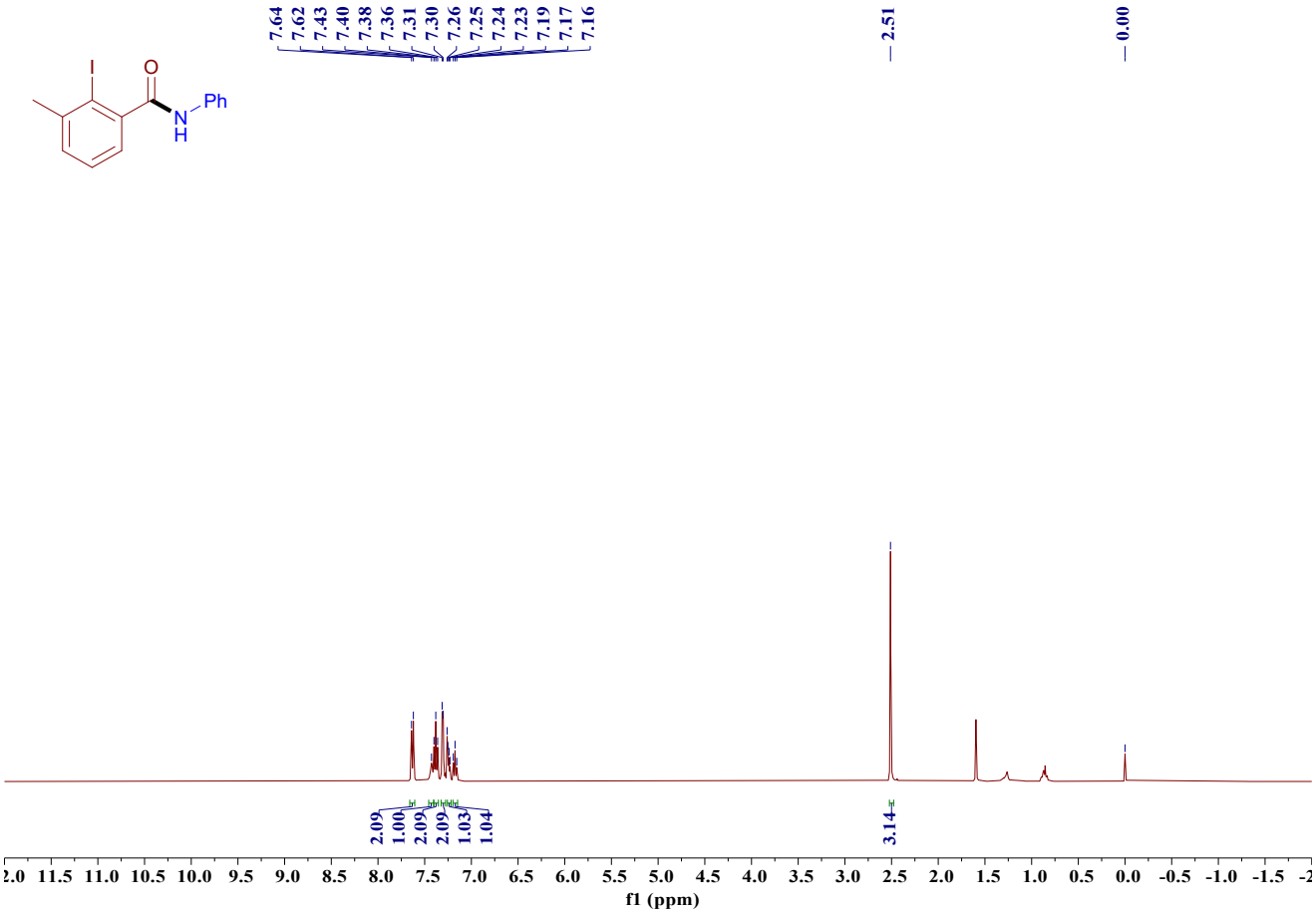
^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) of product 3na

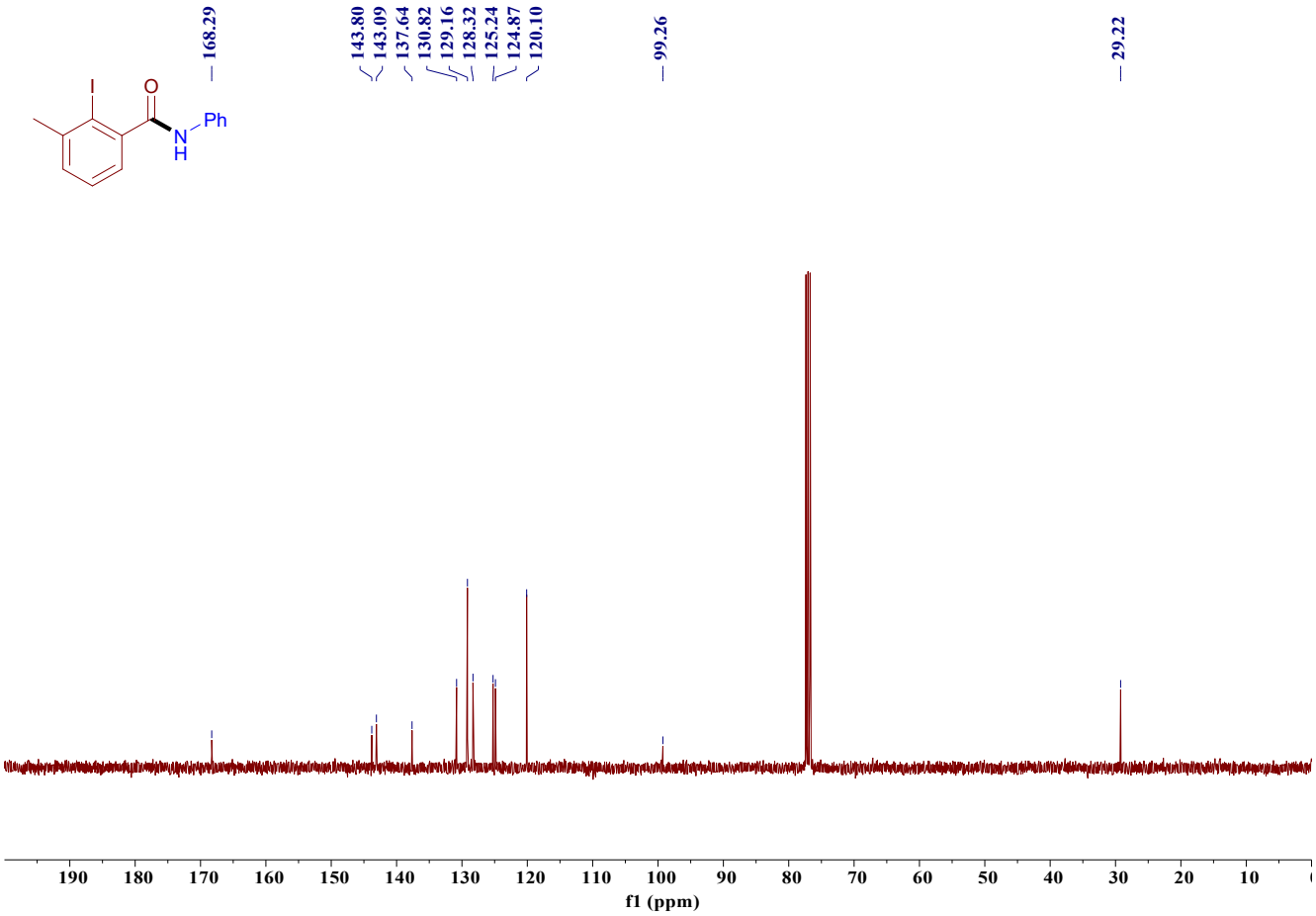


^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) of product 3oa

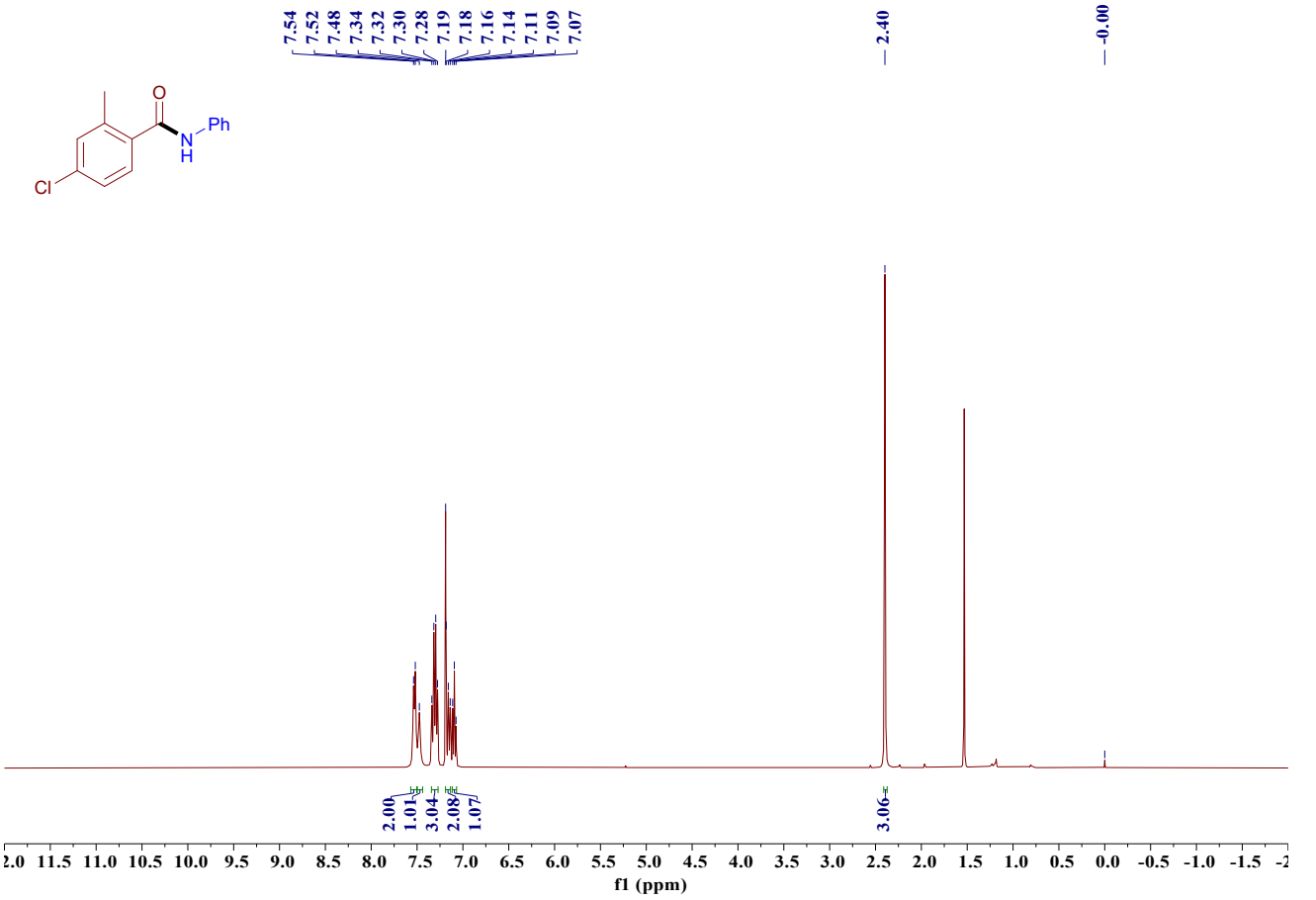


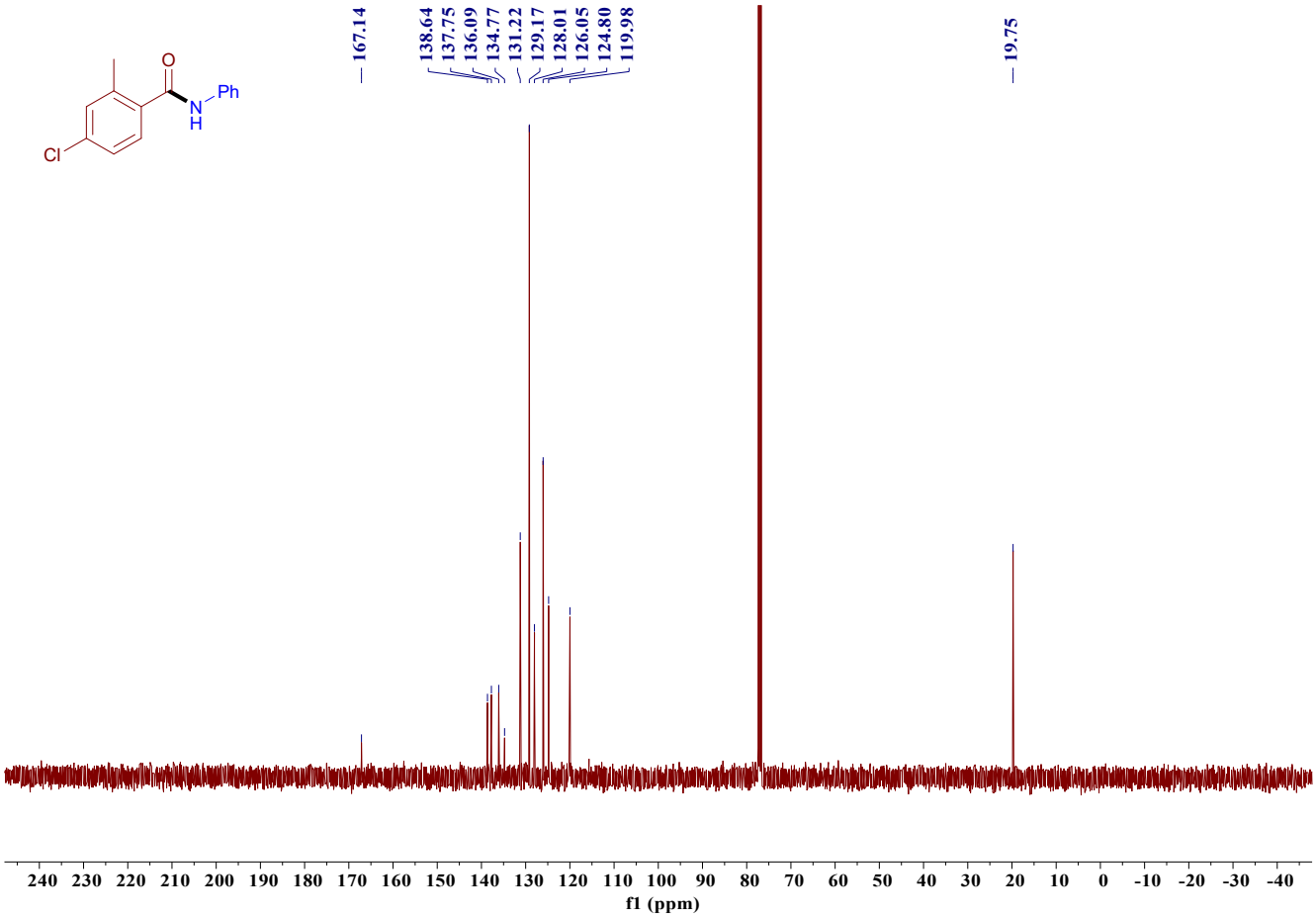
^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) of product 3pa



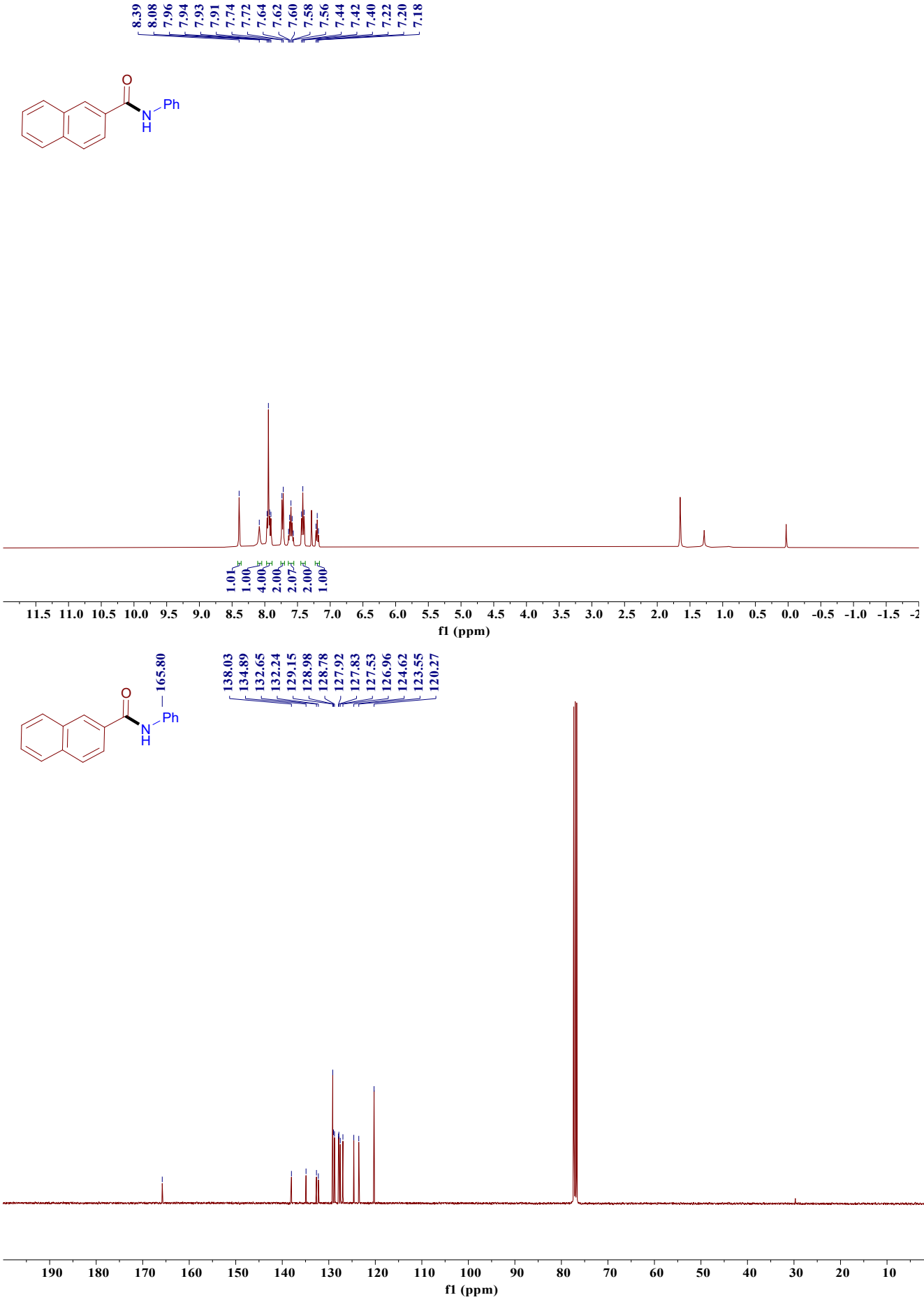


^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) of product 3qa

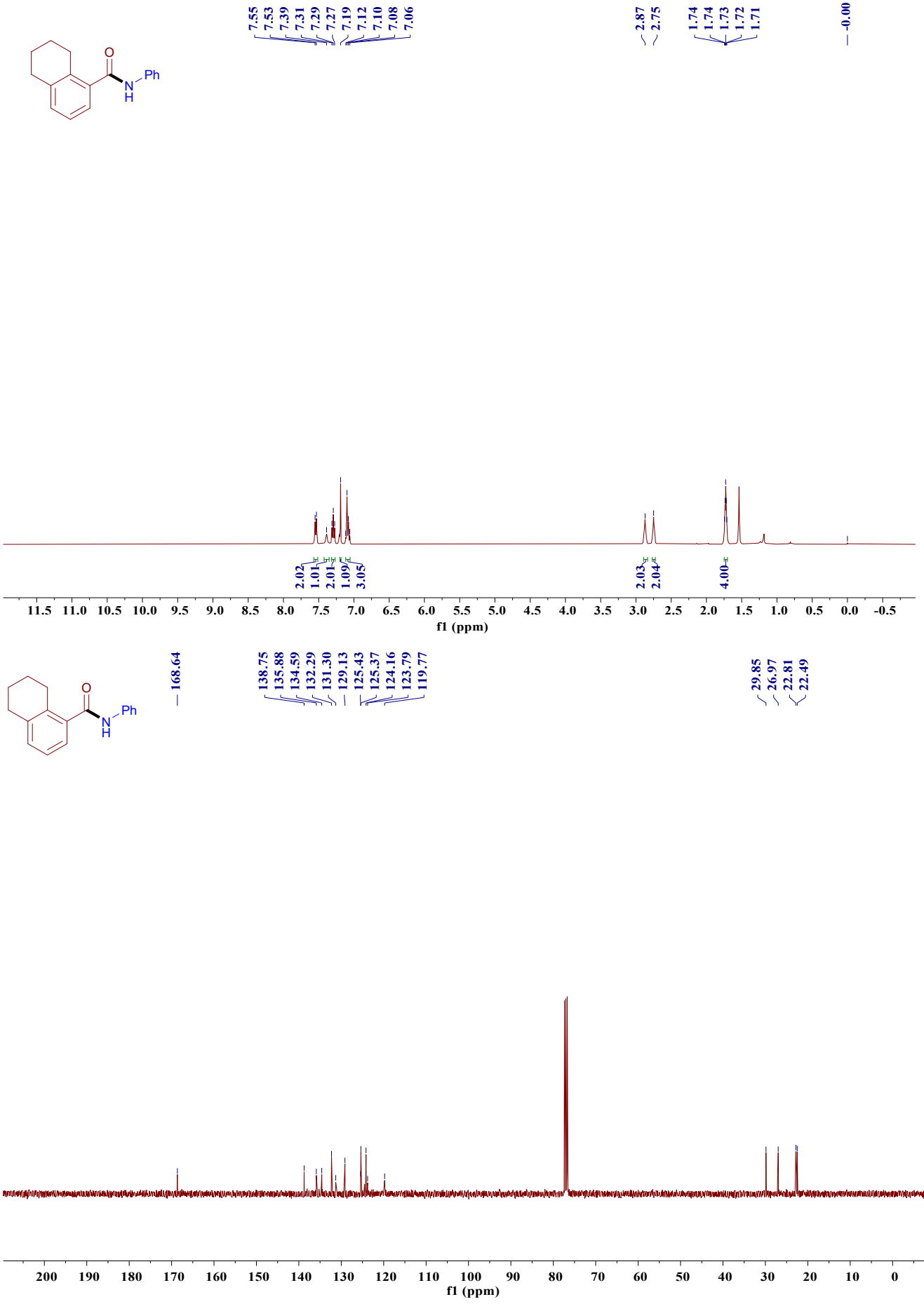




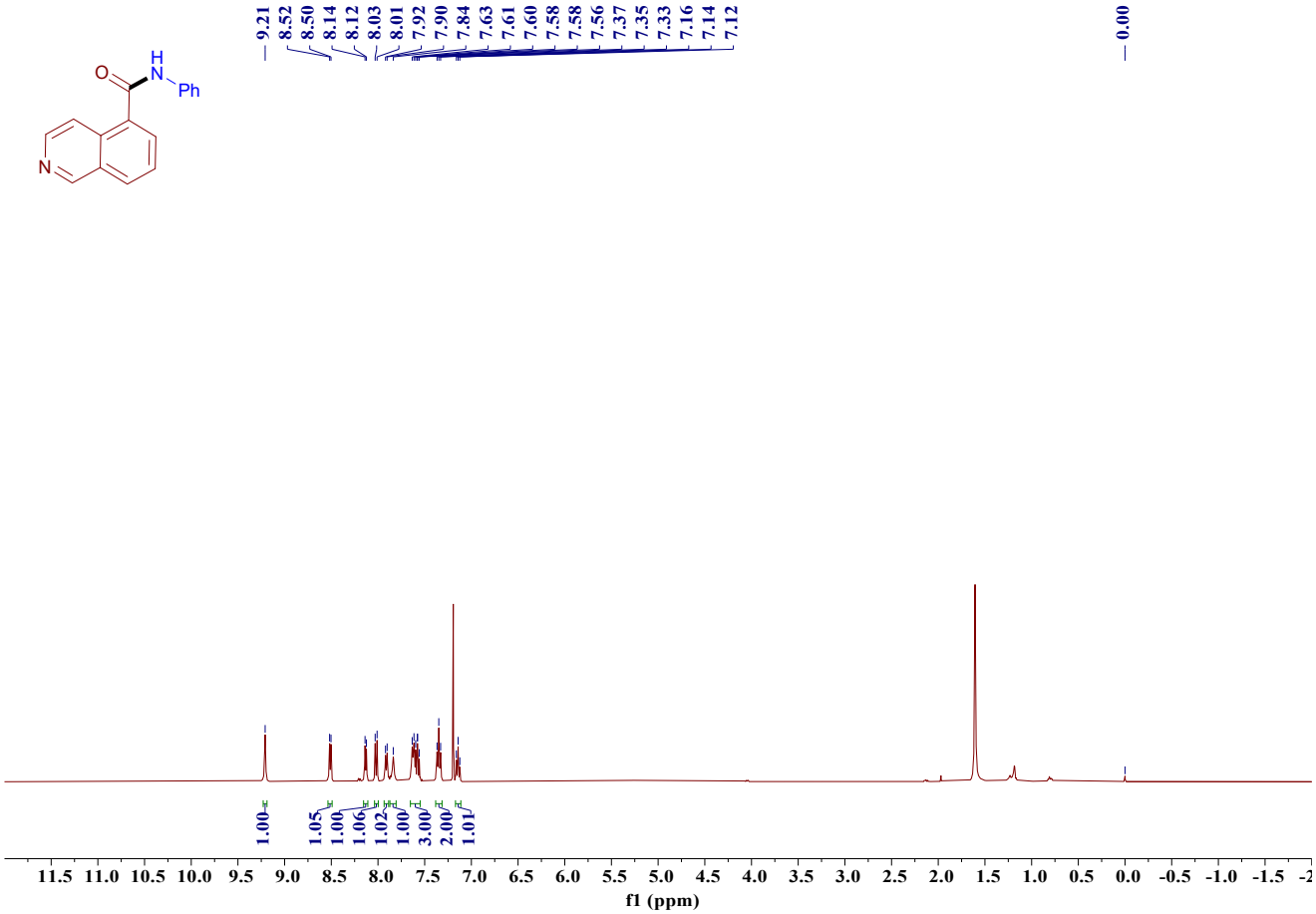
^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) of product 3ra

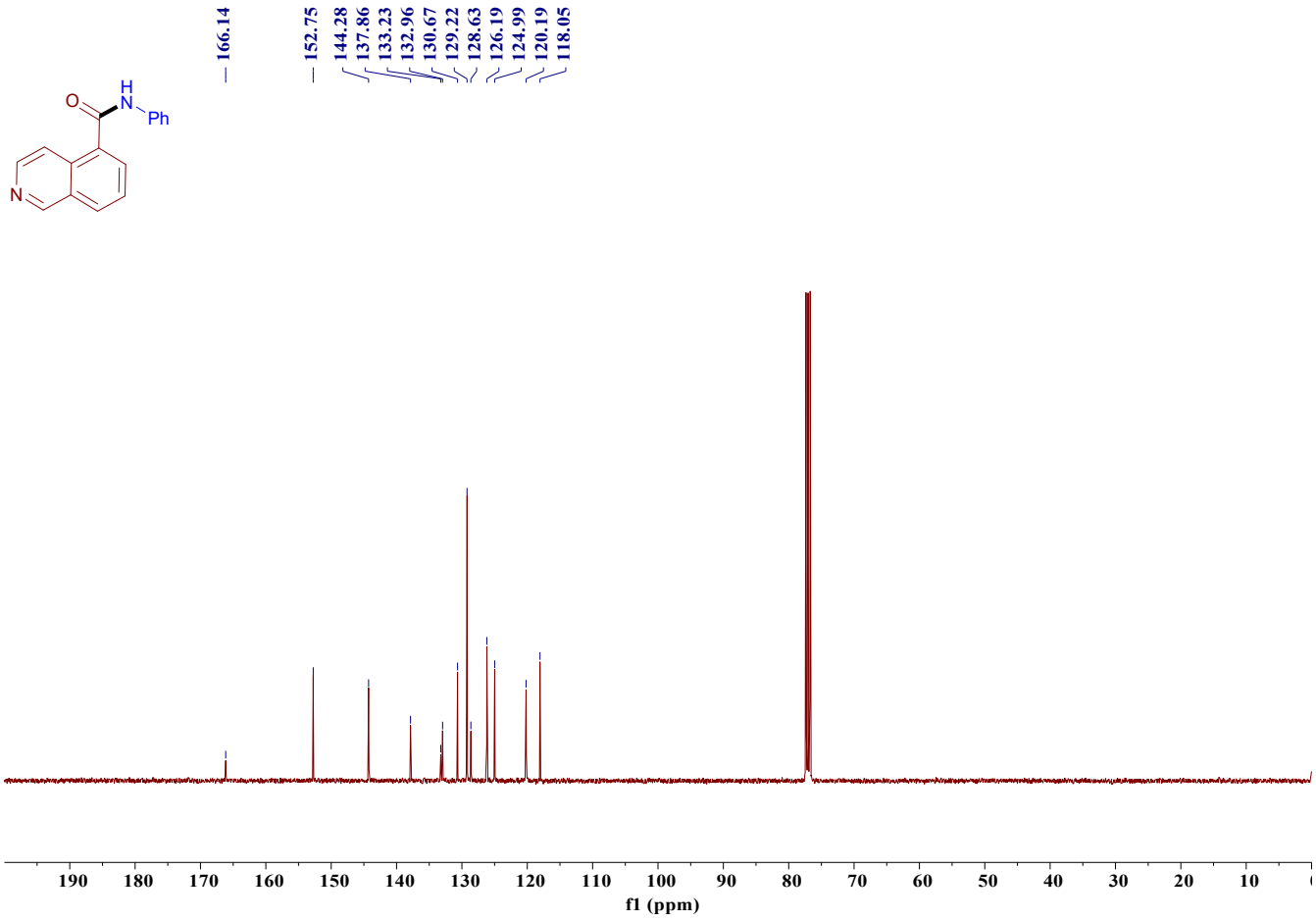


^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) of product 3sa

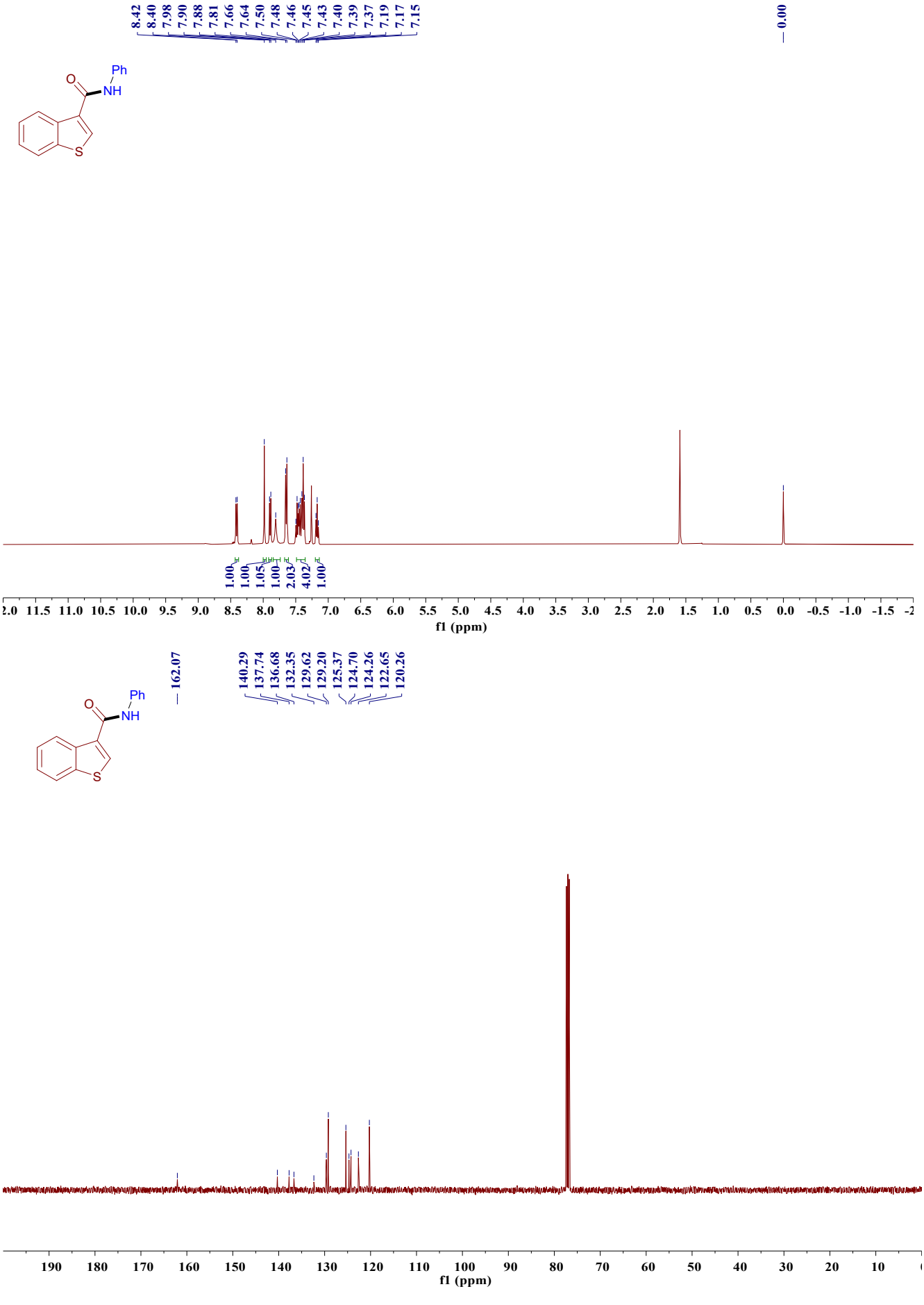


^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) of product 3ta

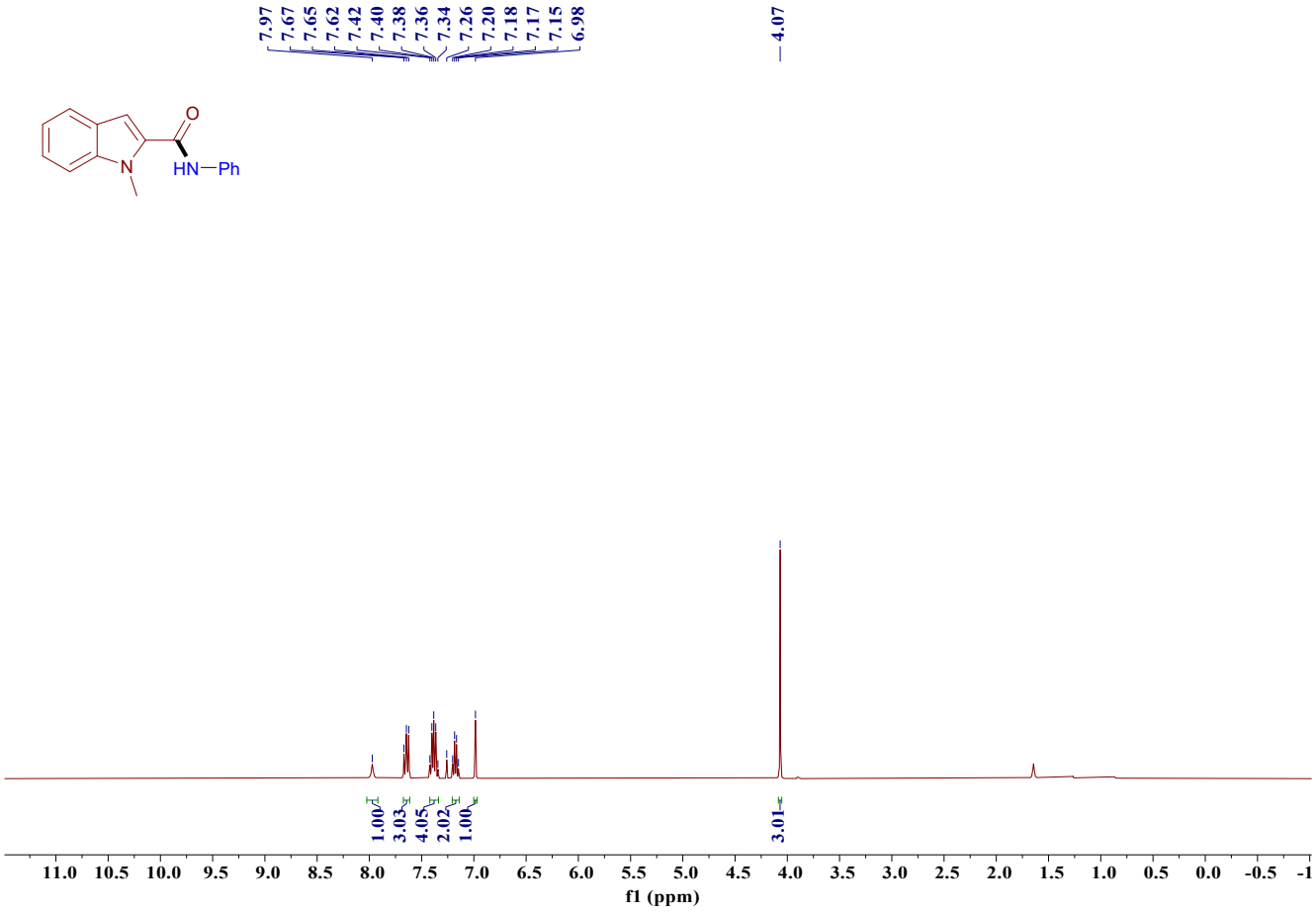


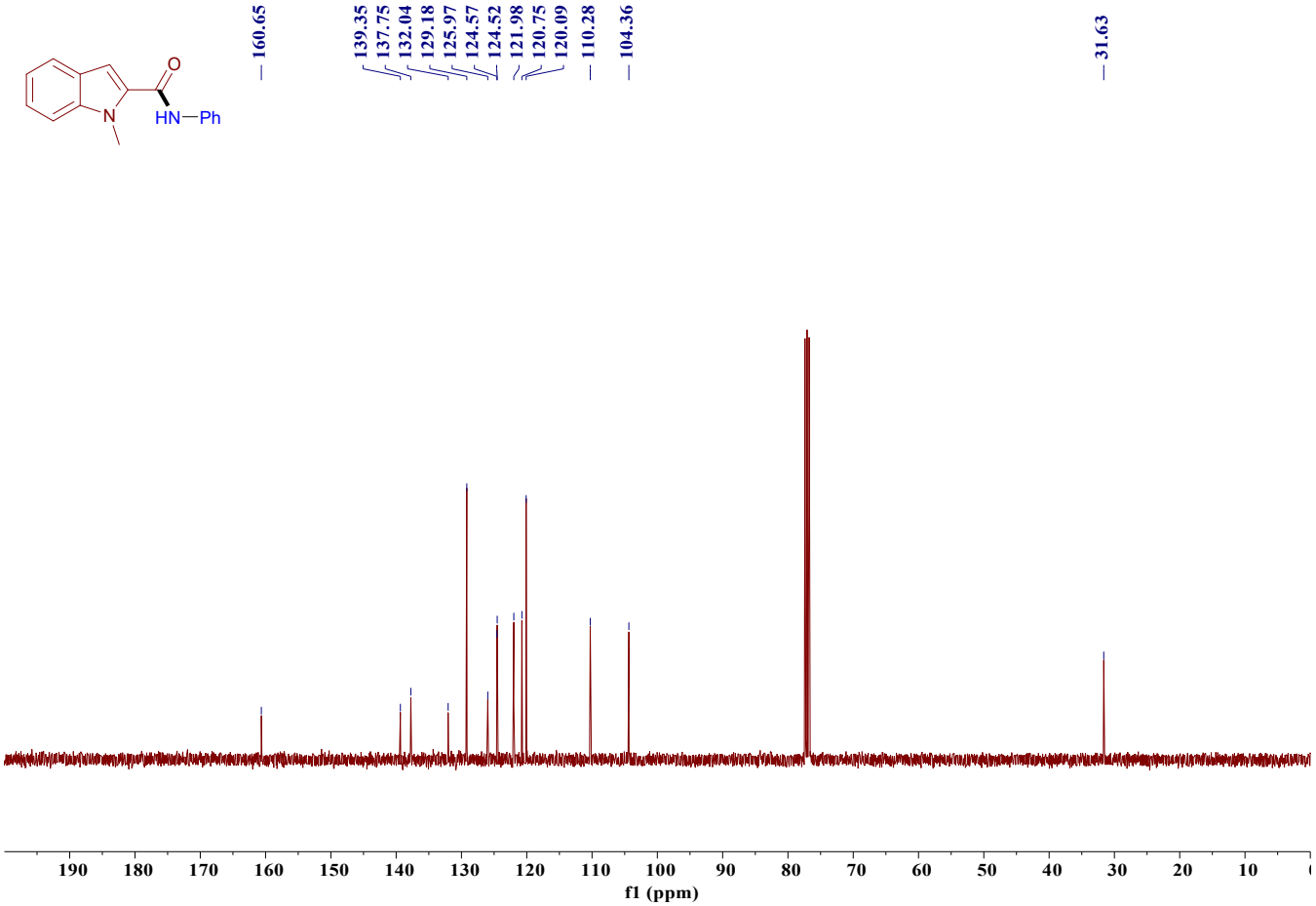


^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) of product 3ua

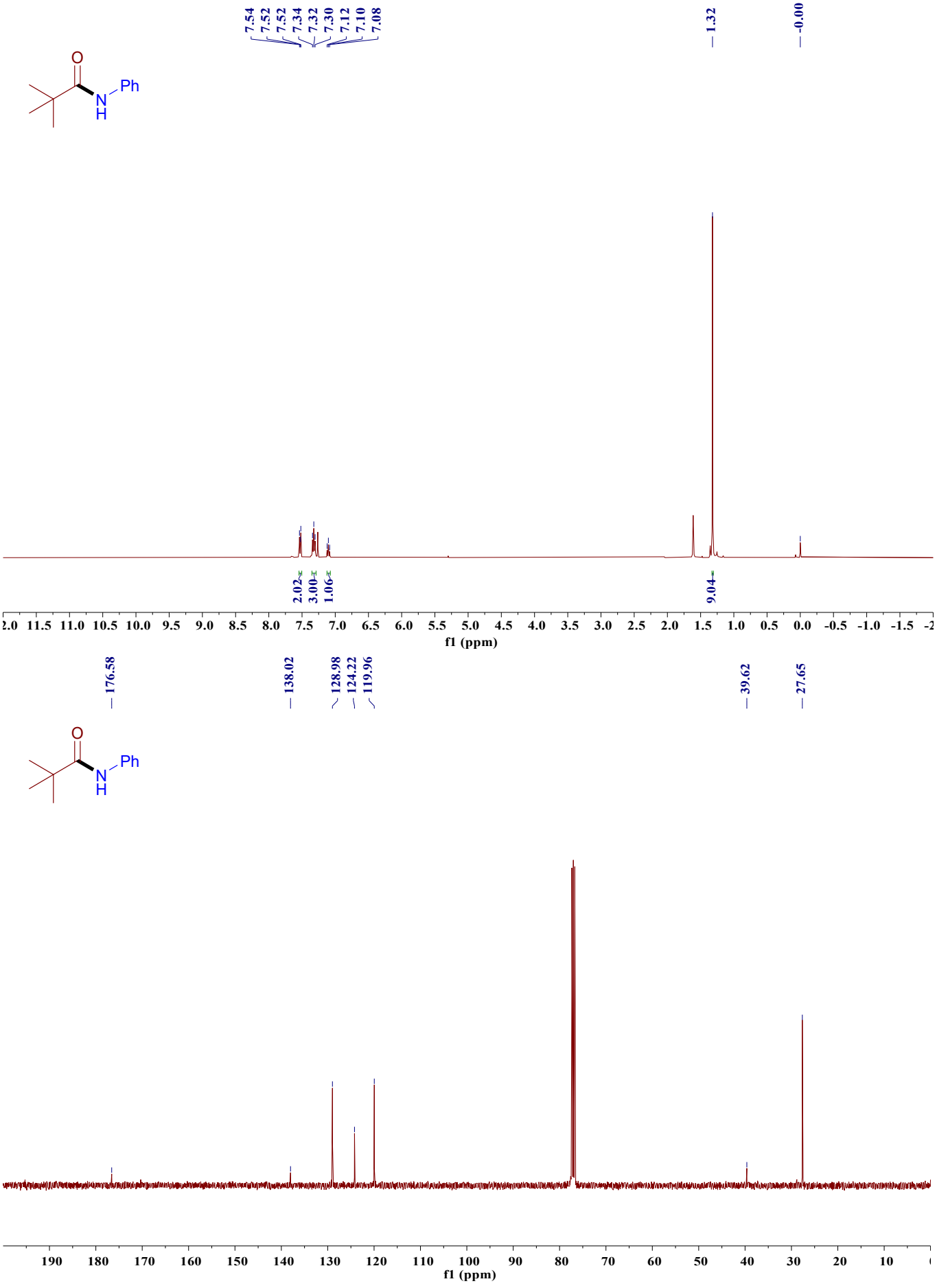


^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) of product 3va

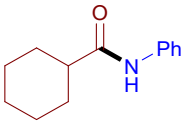


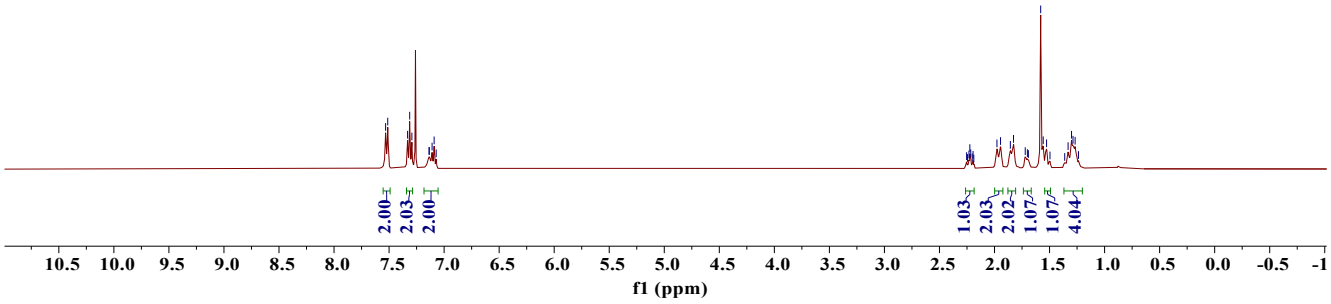


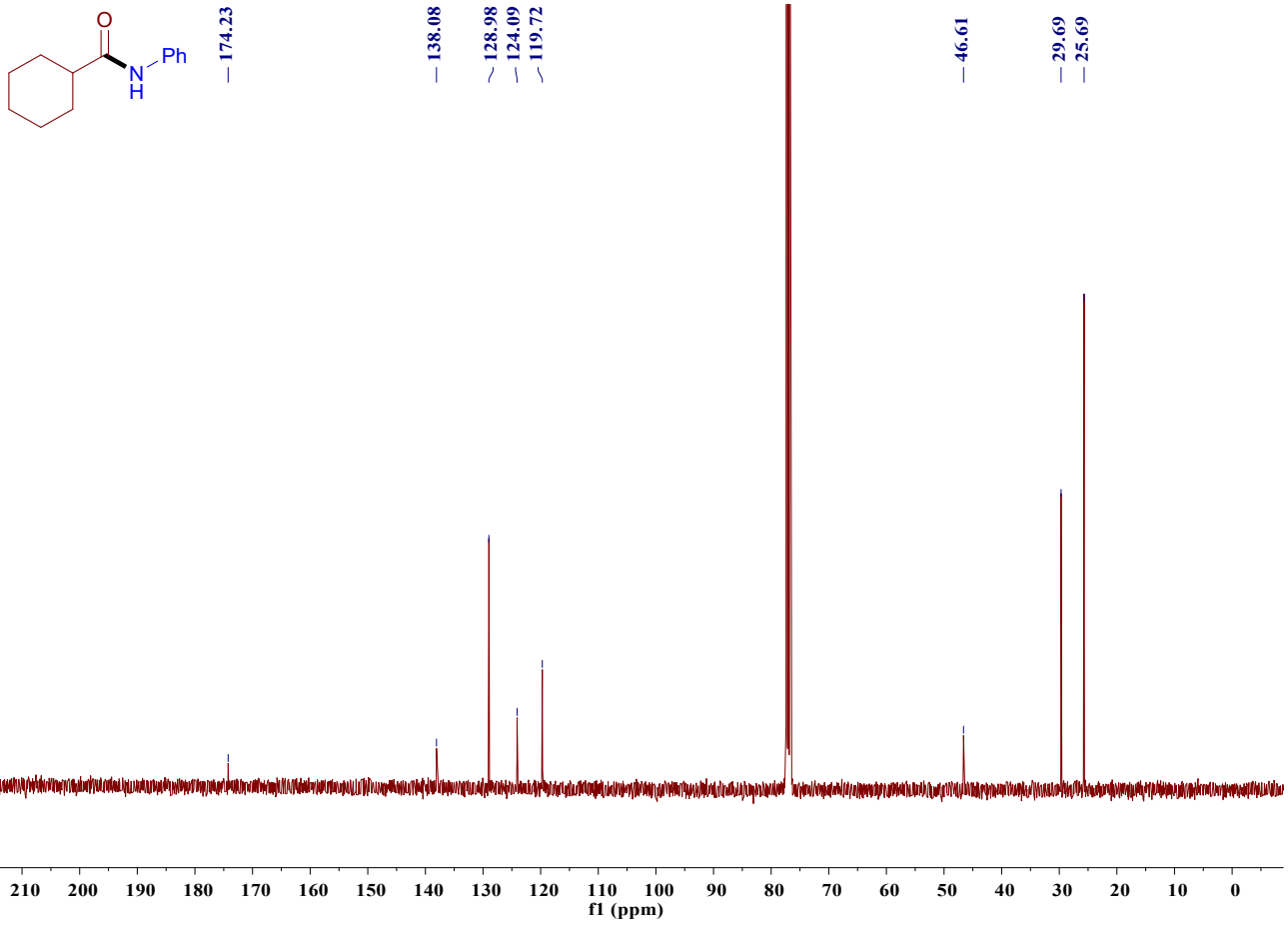
^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) of product 3wa



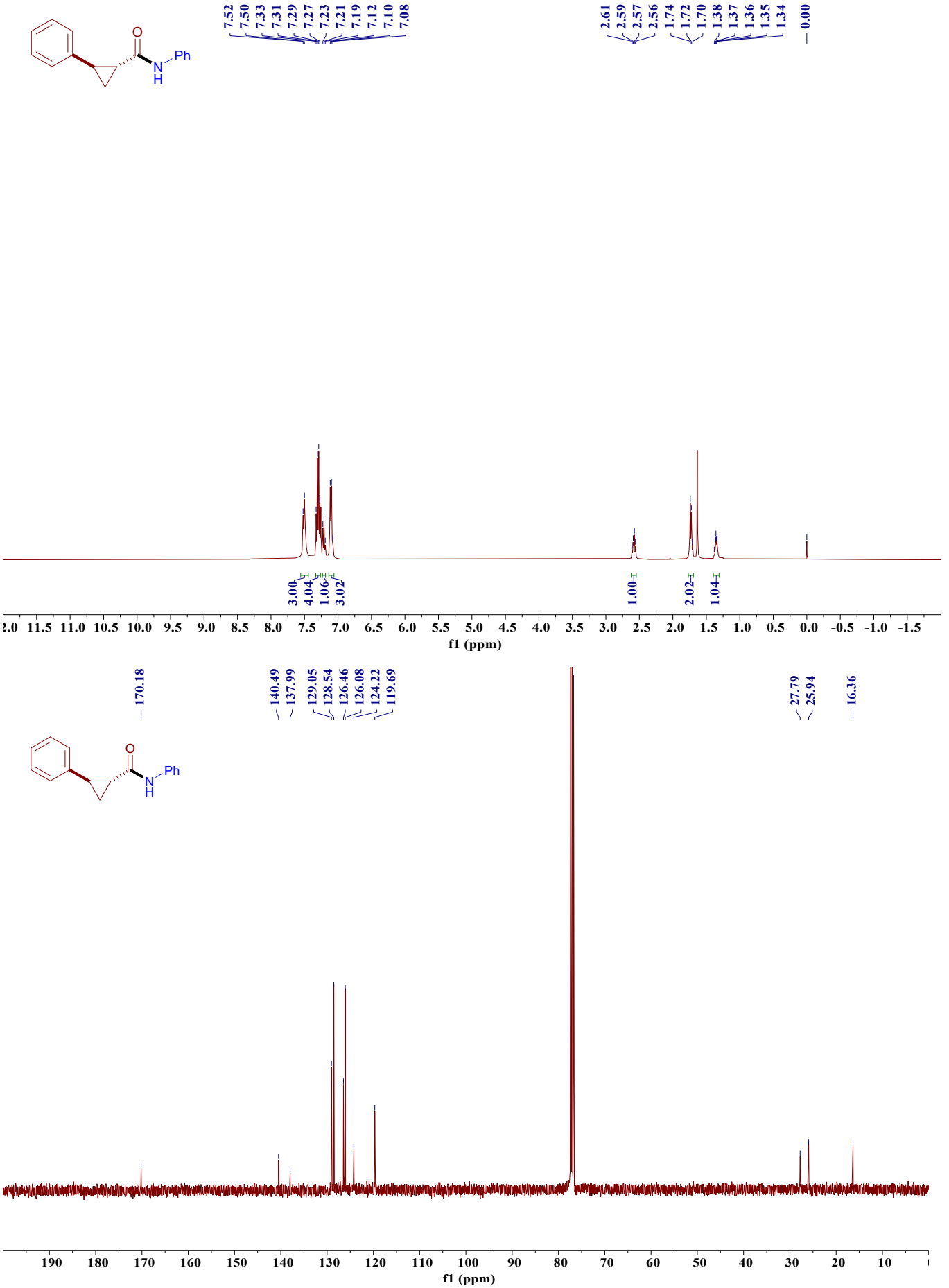
^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) of product 3xa



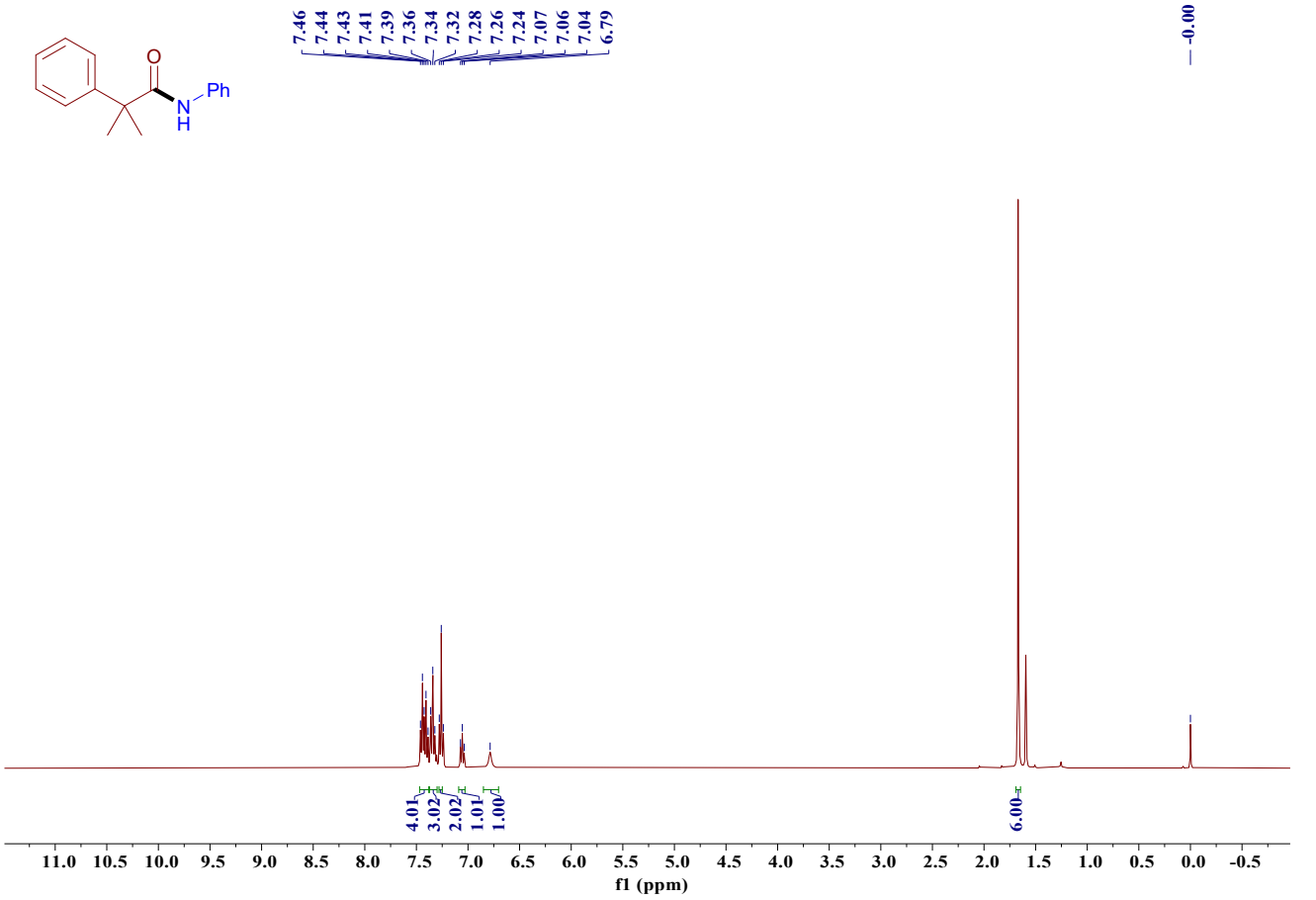


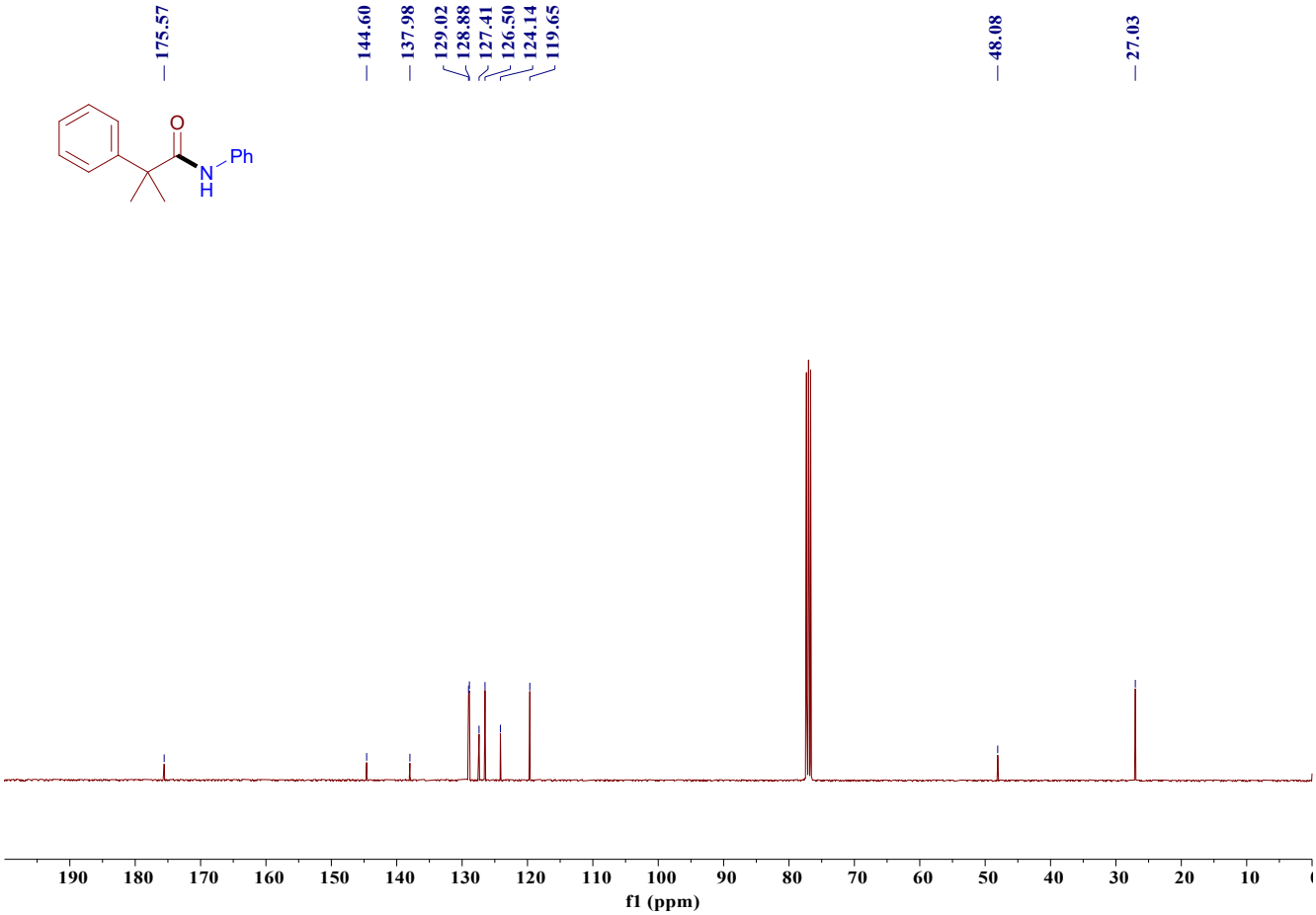


^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) of product 3ya

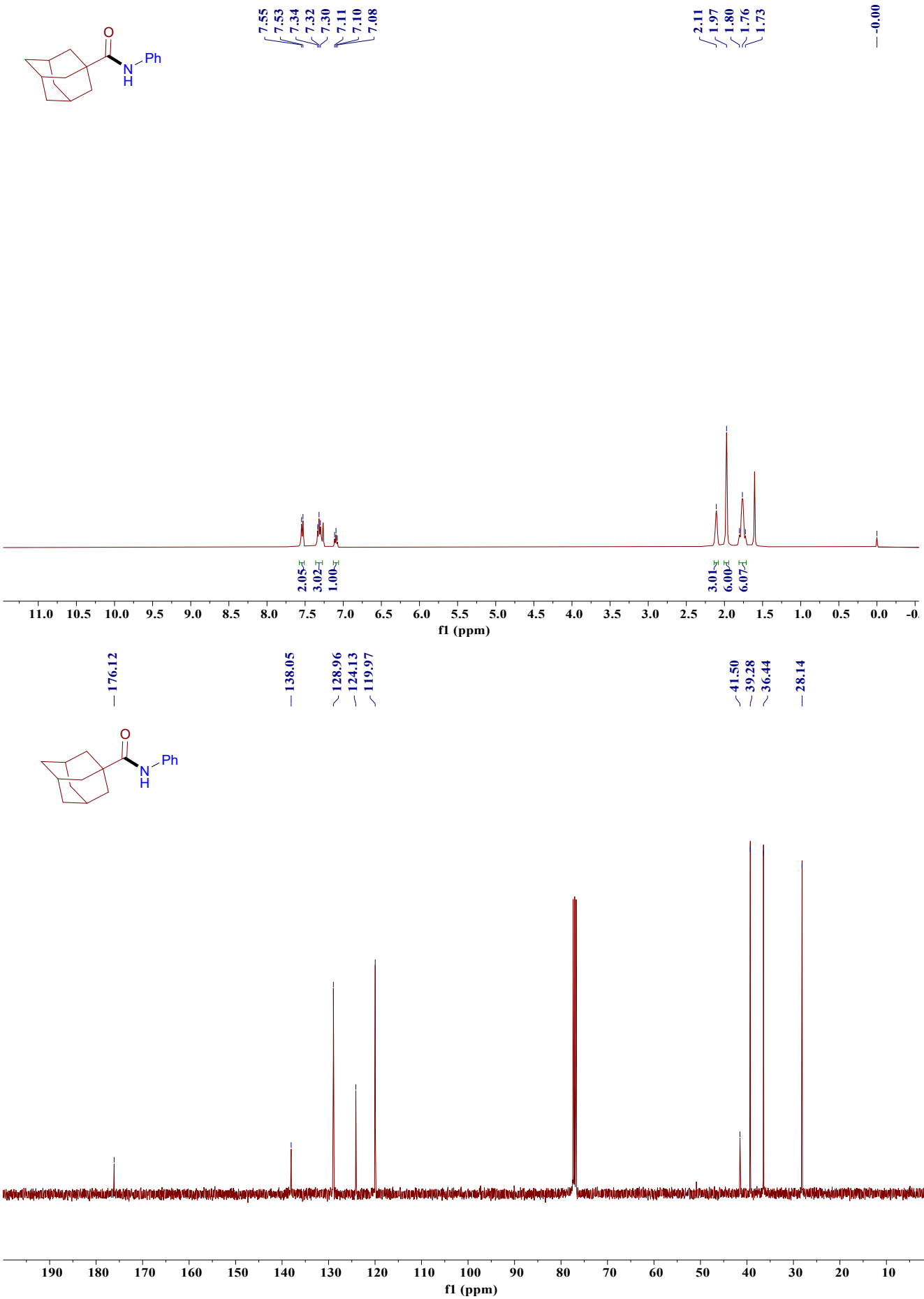


^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) of product 3za

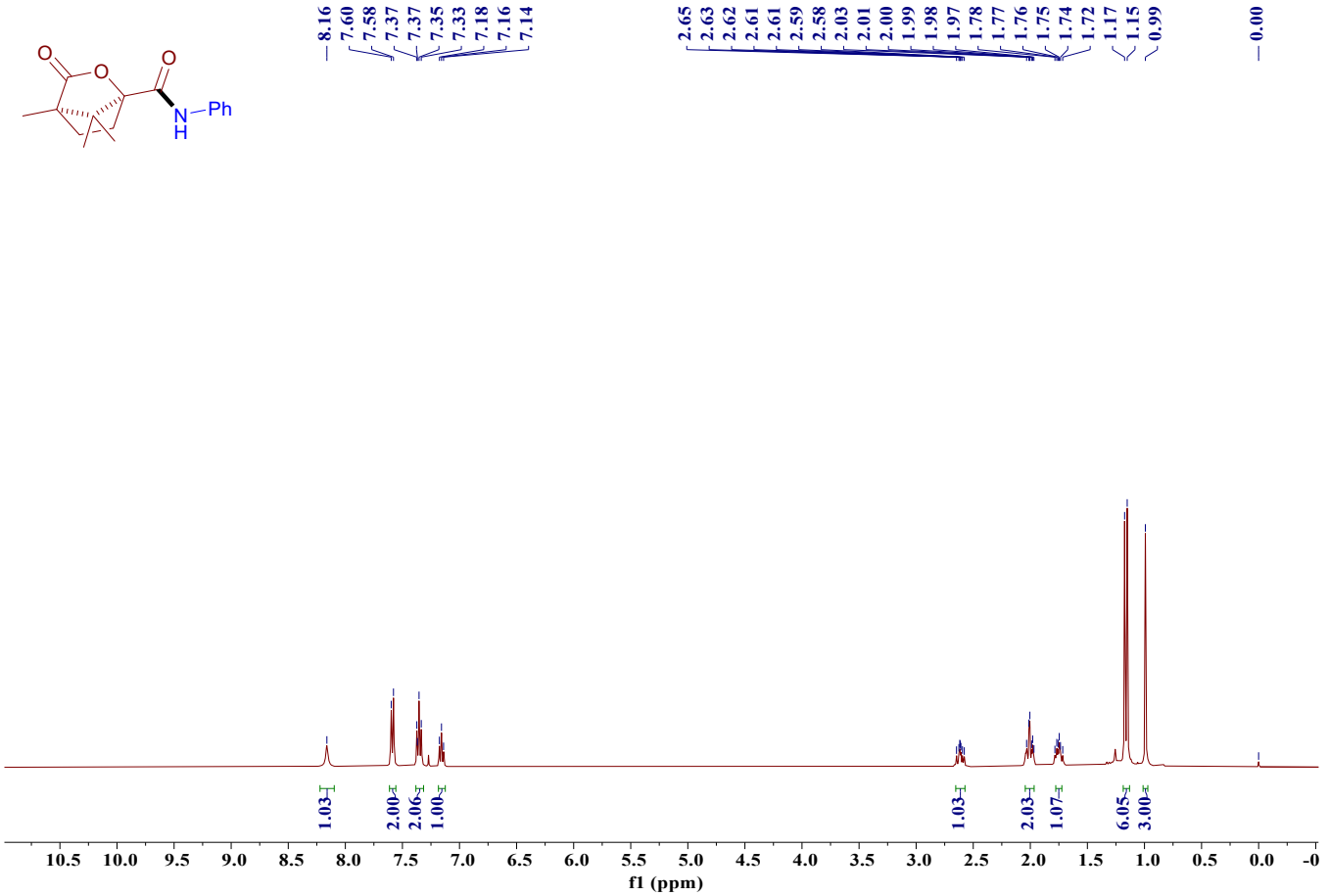


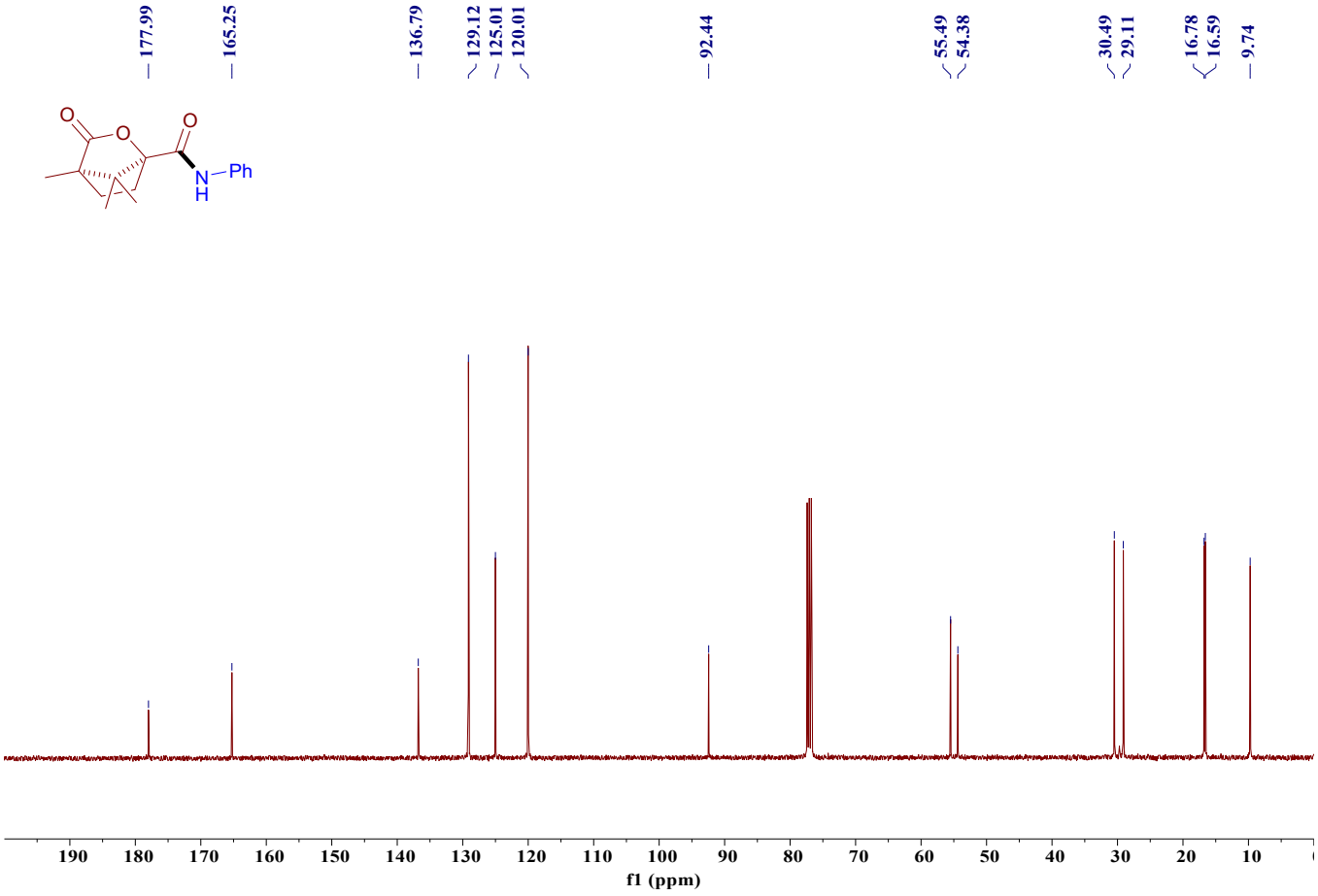


^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) of product 4

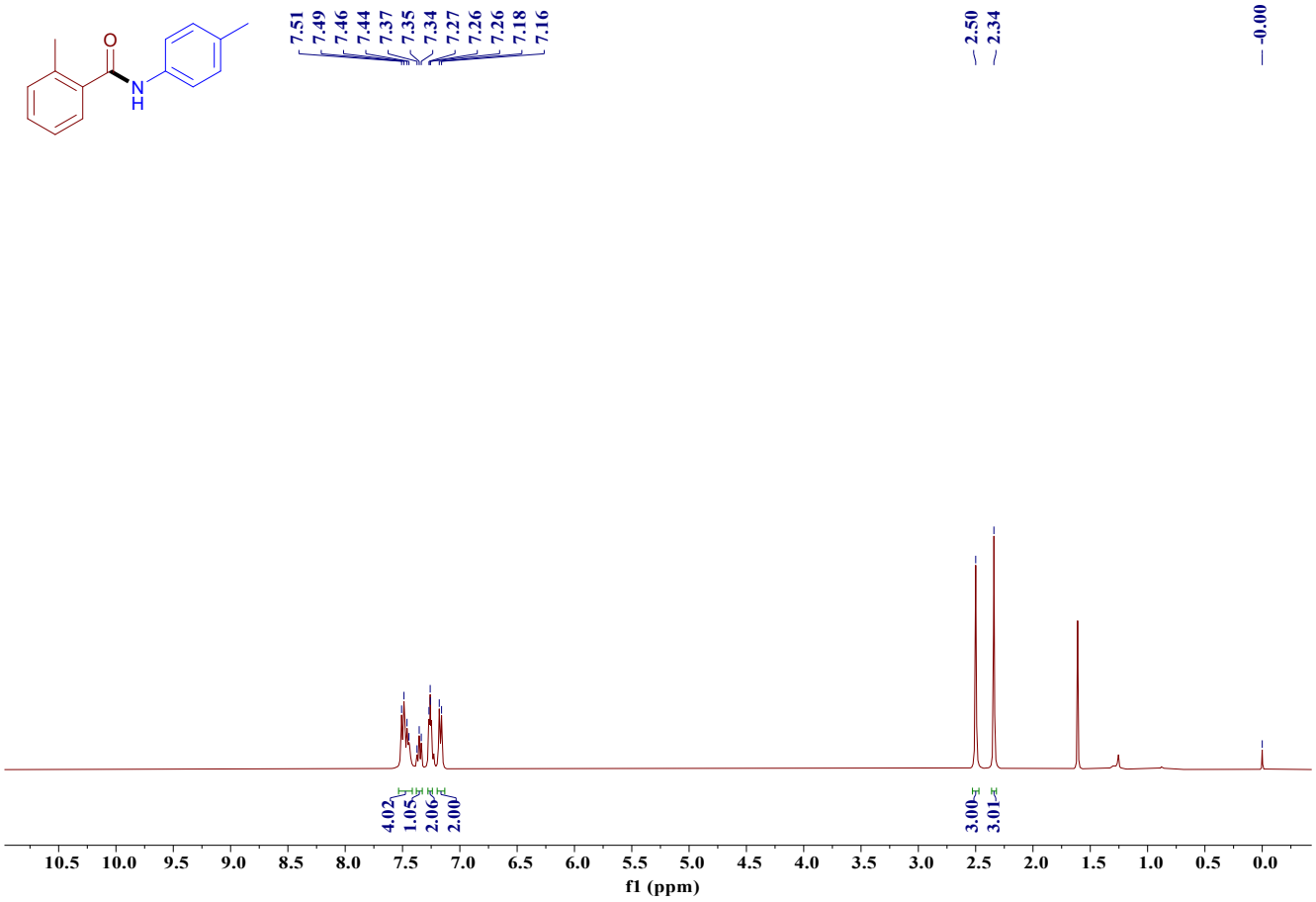


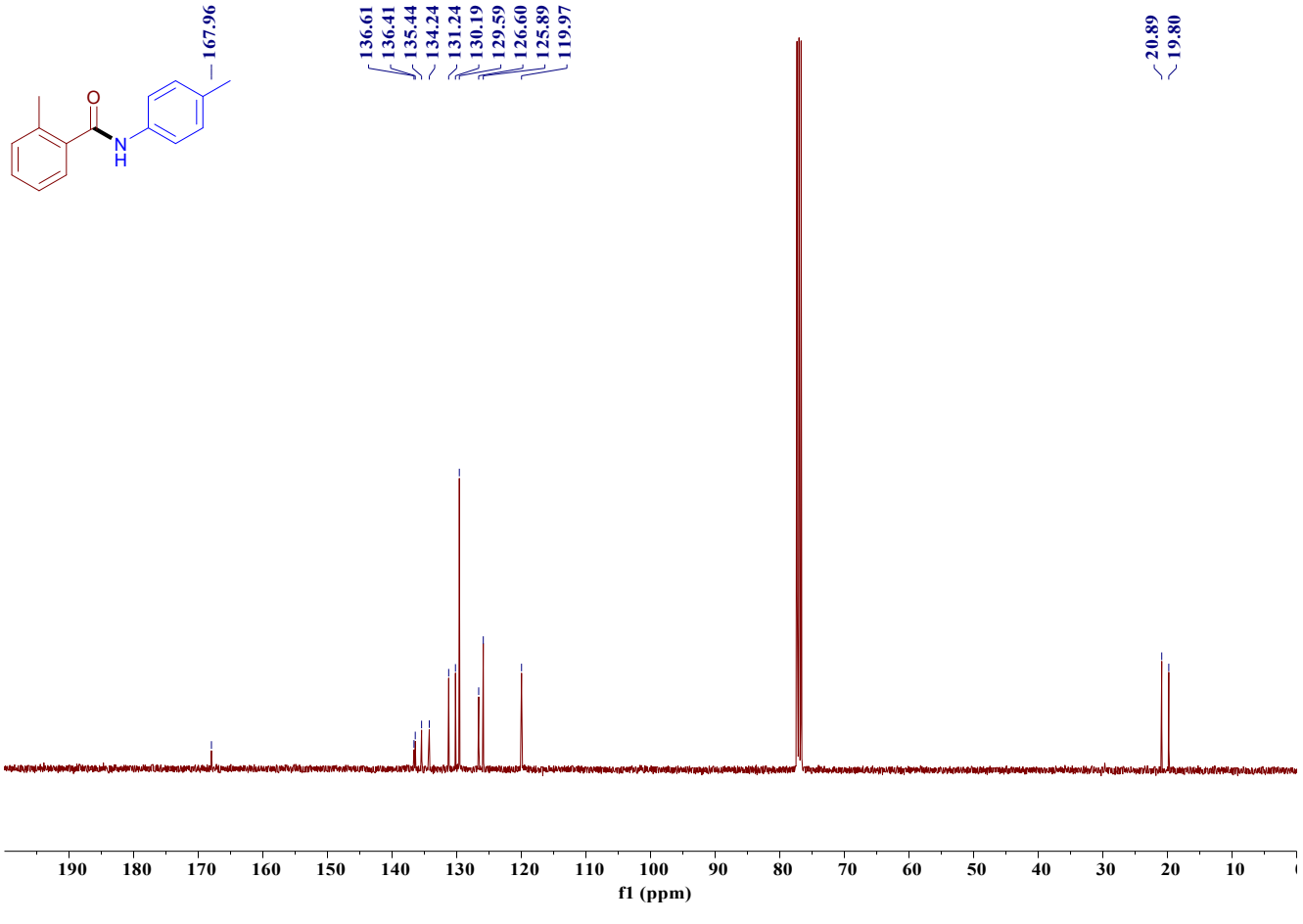
^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) of product 5



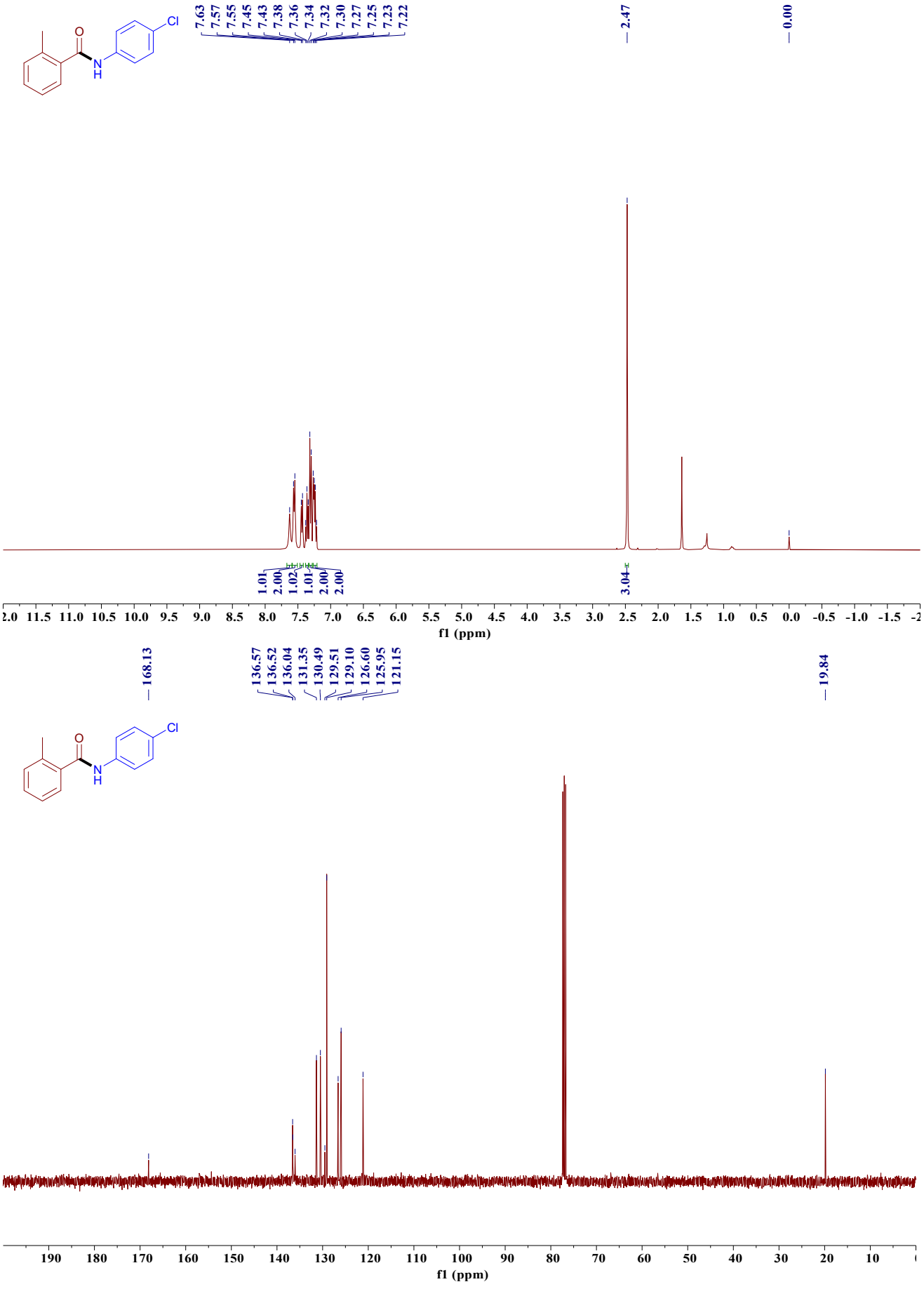


^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) of product 3ab

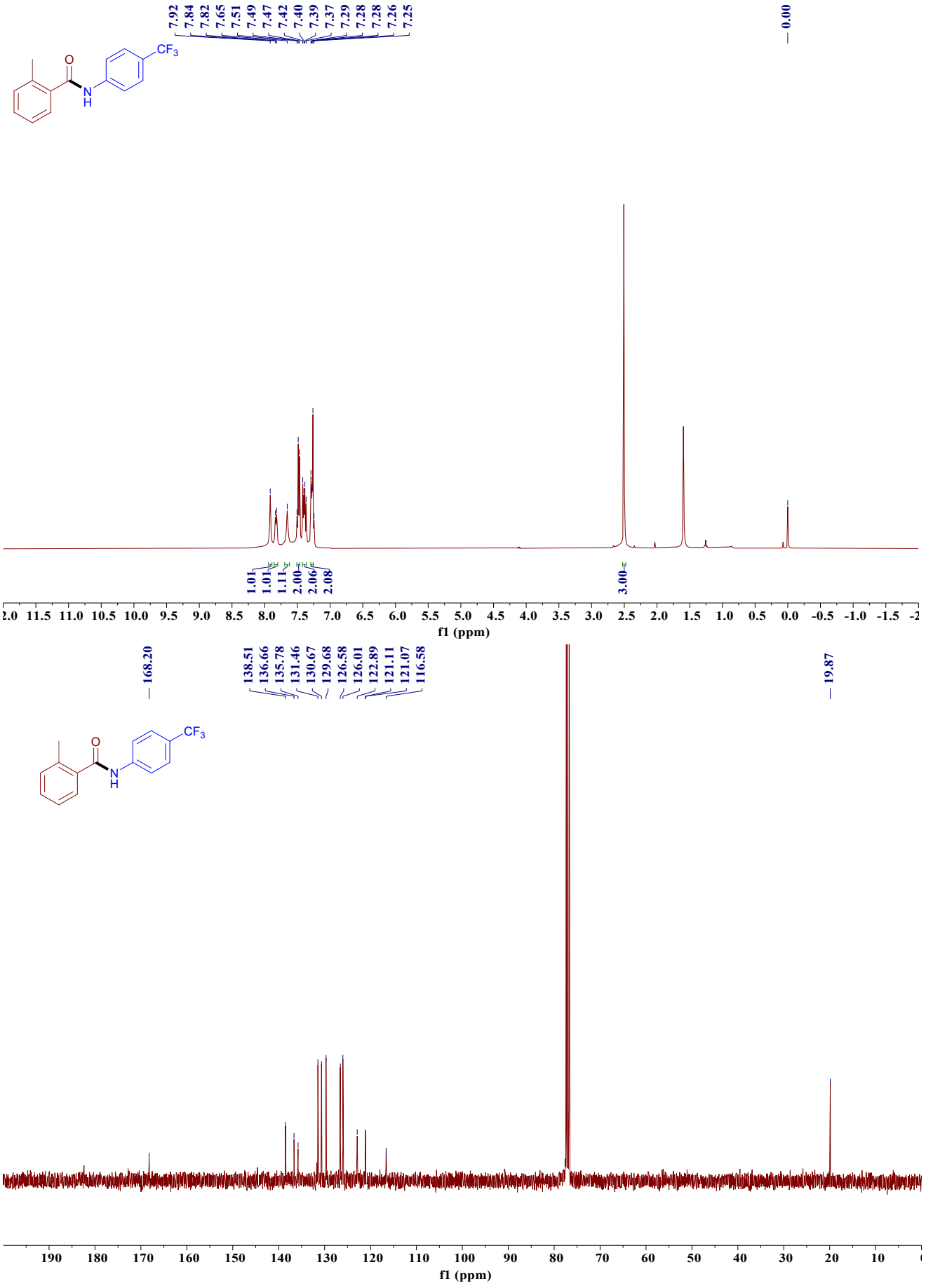


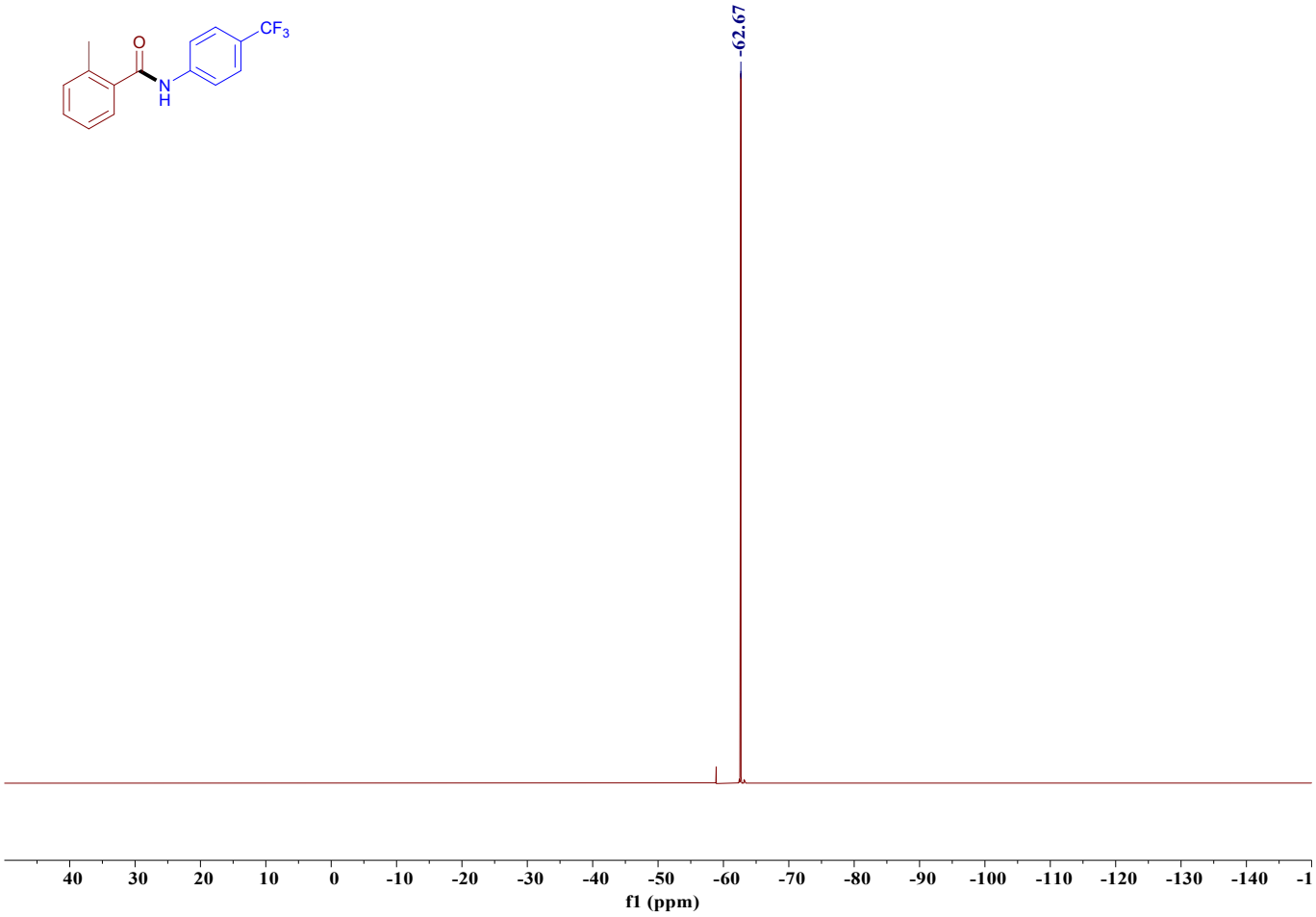


^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) of product 3ac

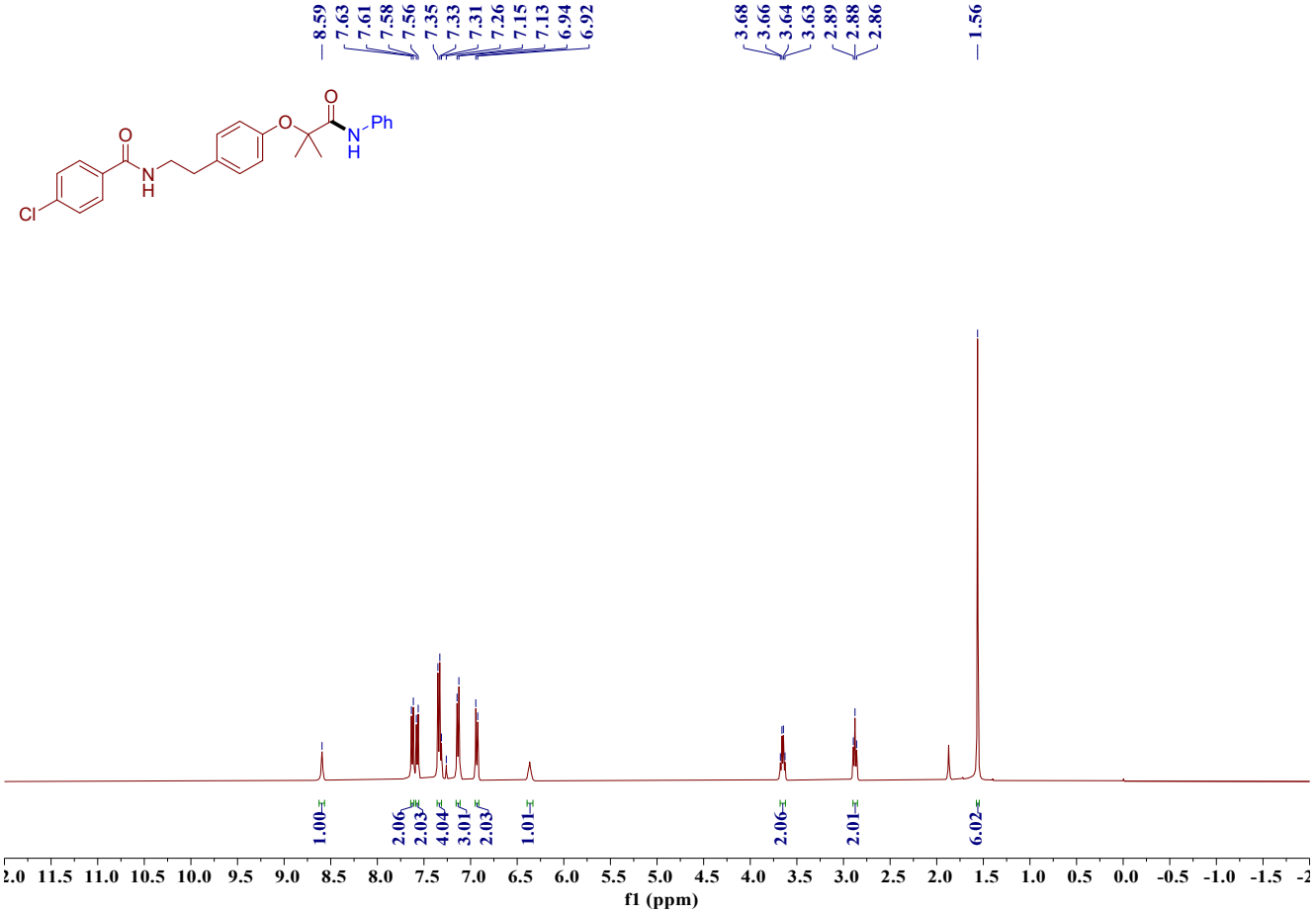


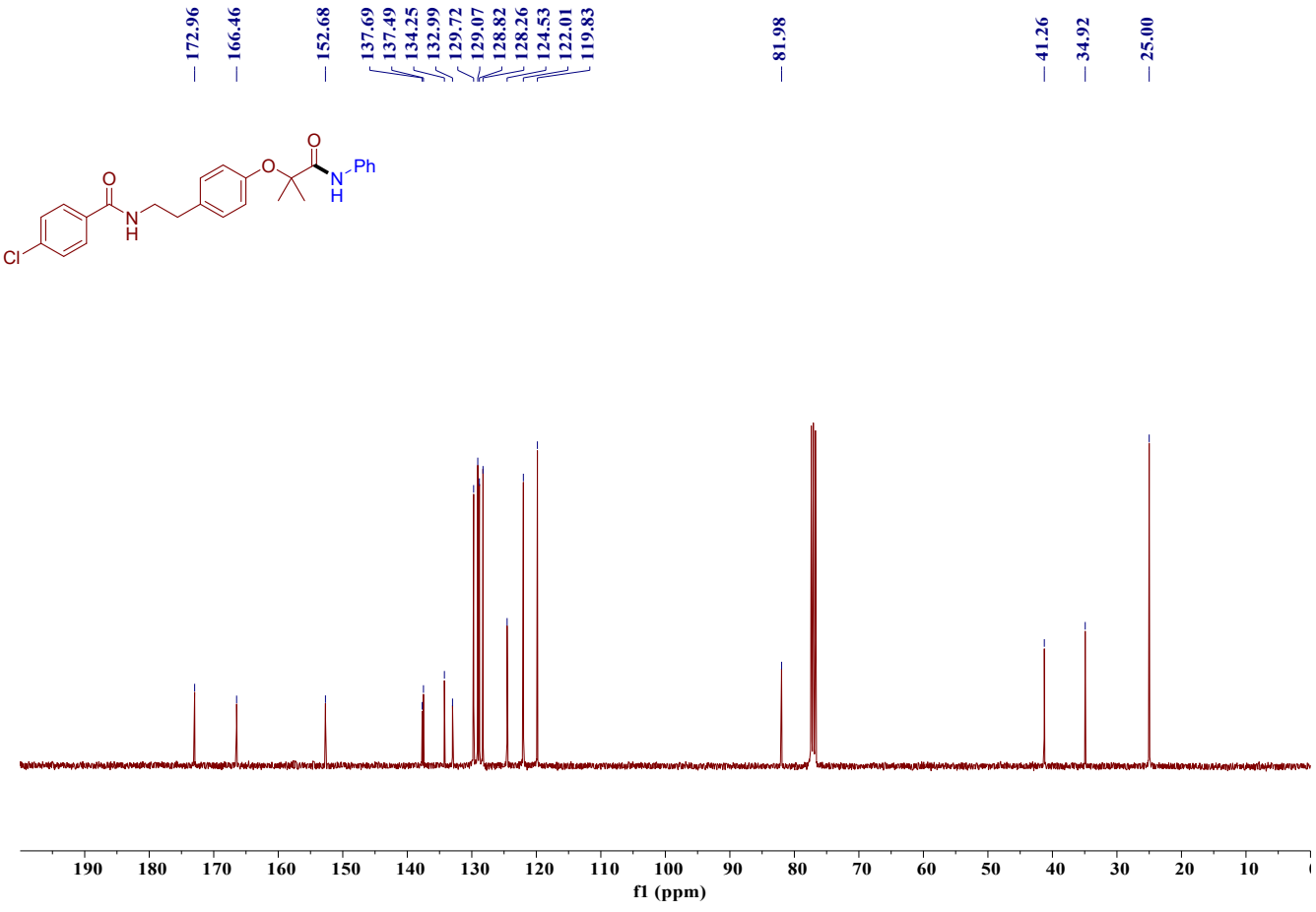
^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$), ^{19}F NMR (376 MHz, $CDCl_3$) of product 3ad



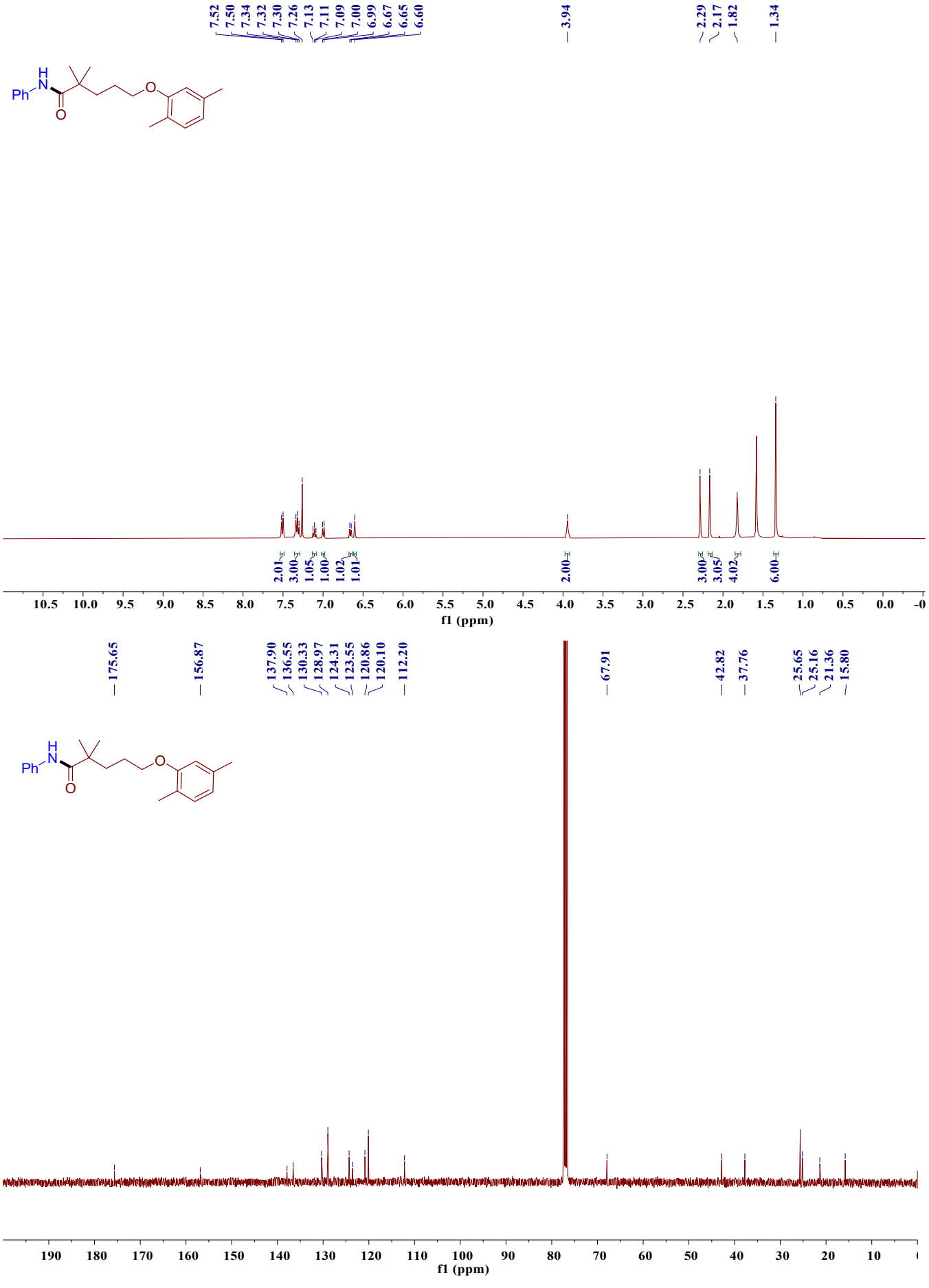

O
N
H
CF3
-62.67
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-1
f1 (ppm)

^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) of product 6aa

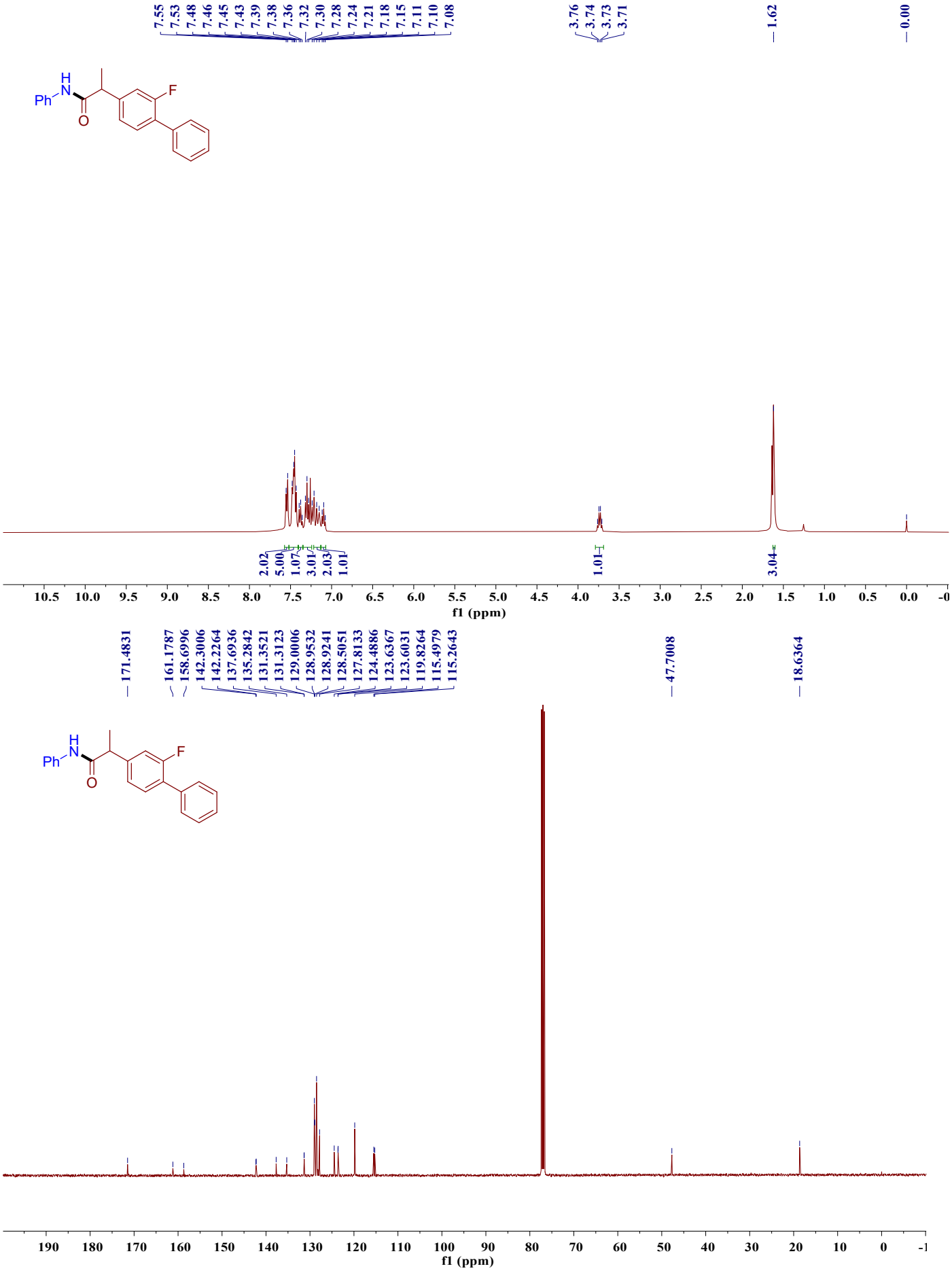


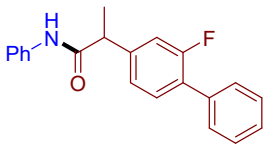


^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) of product 6ba



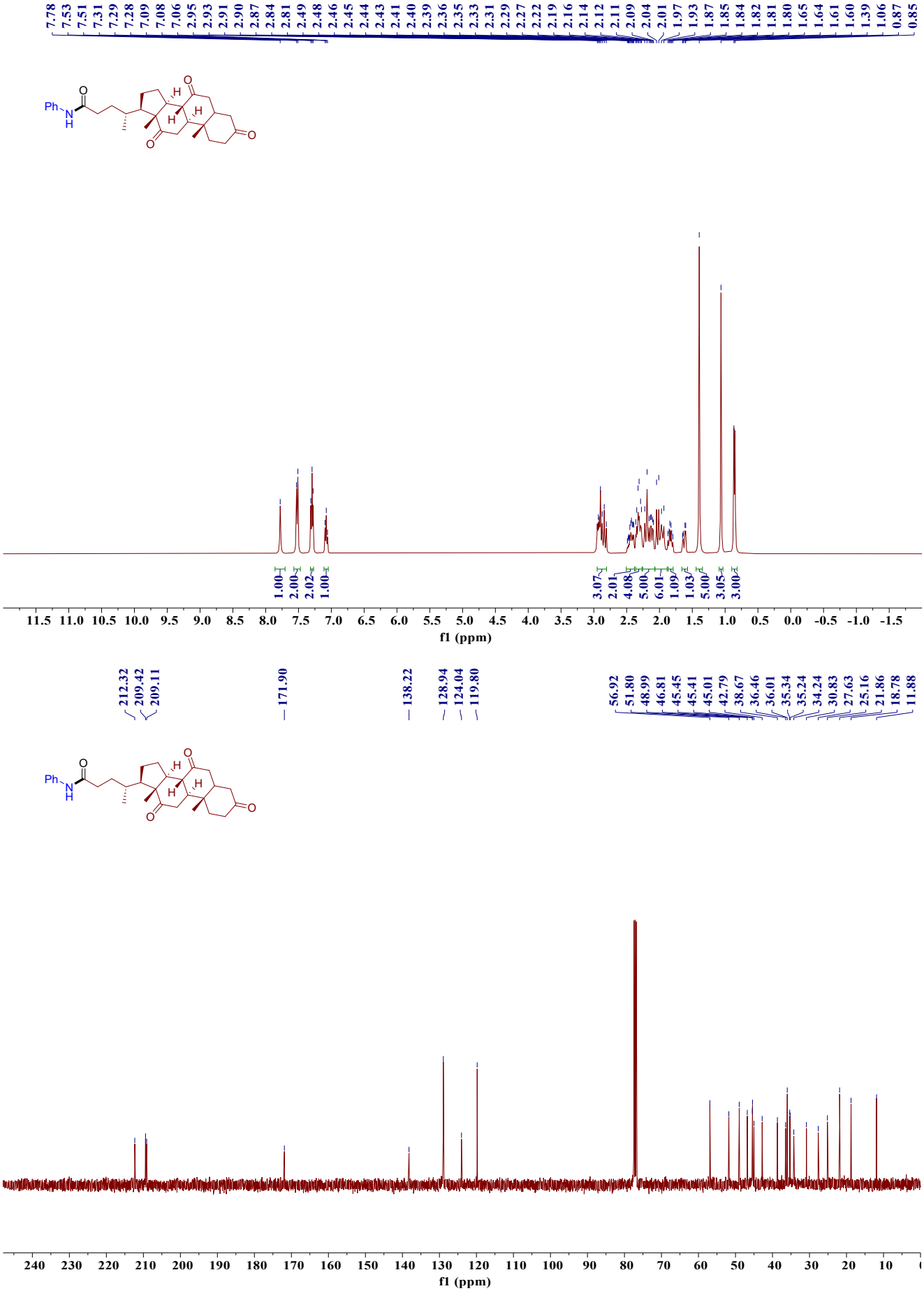
^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$), ^{19}F NMR (376 MHz, $CDCl_3$) of product 6ca



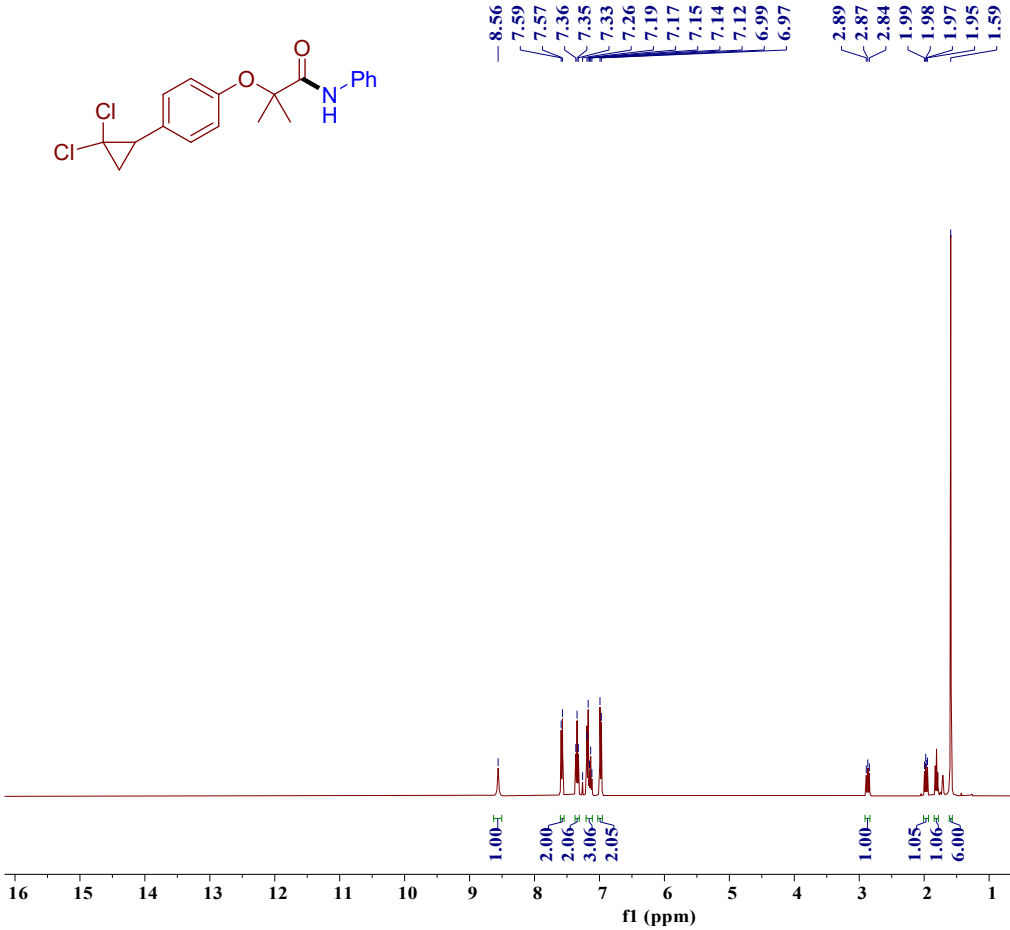

H
N
Ph
O
F

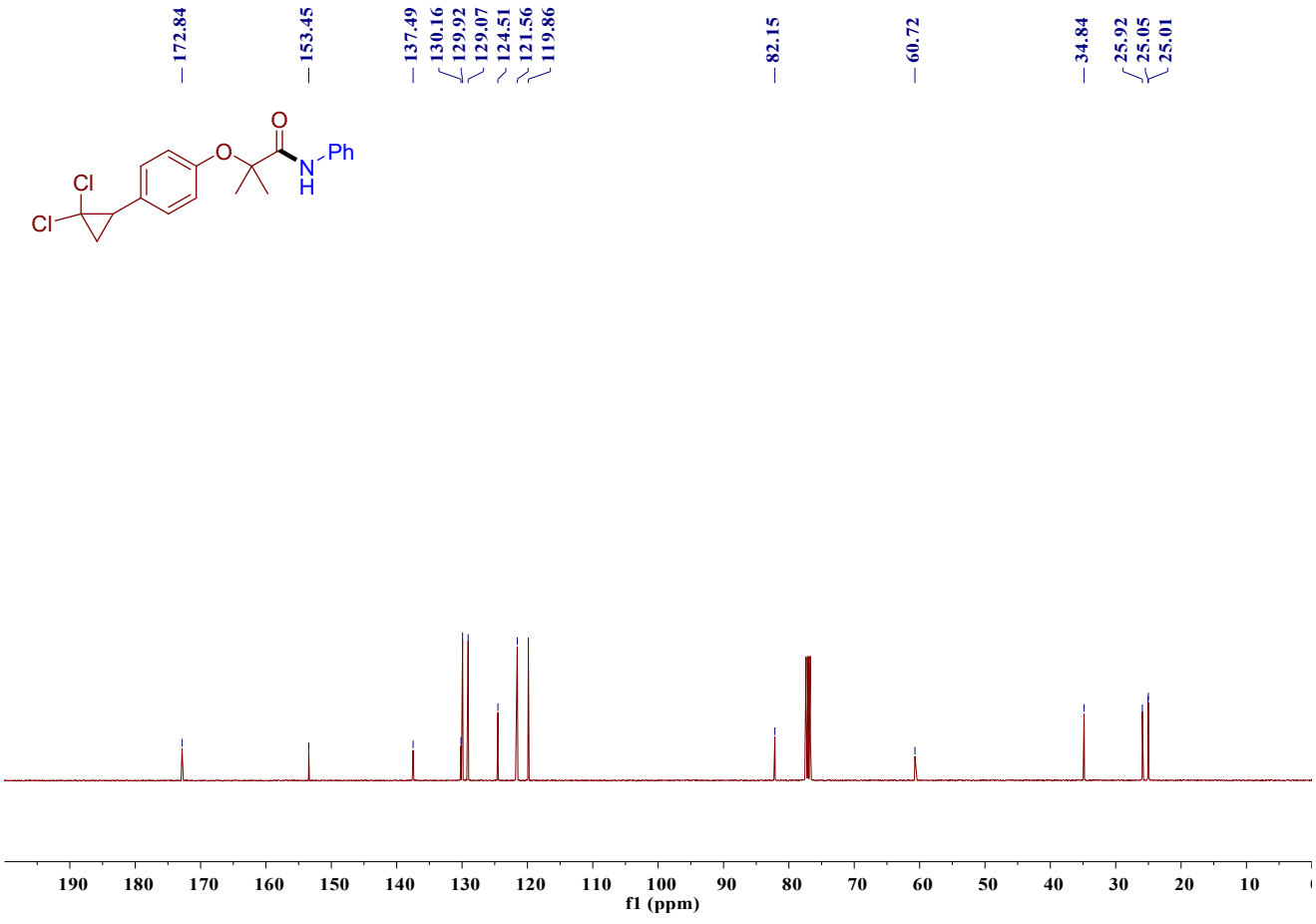
-116.71
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
f1 (ppm)

^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) of product6da

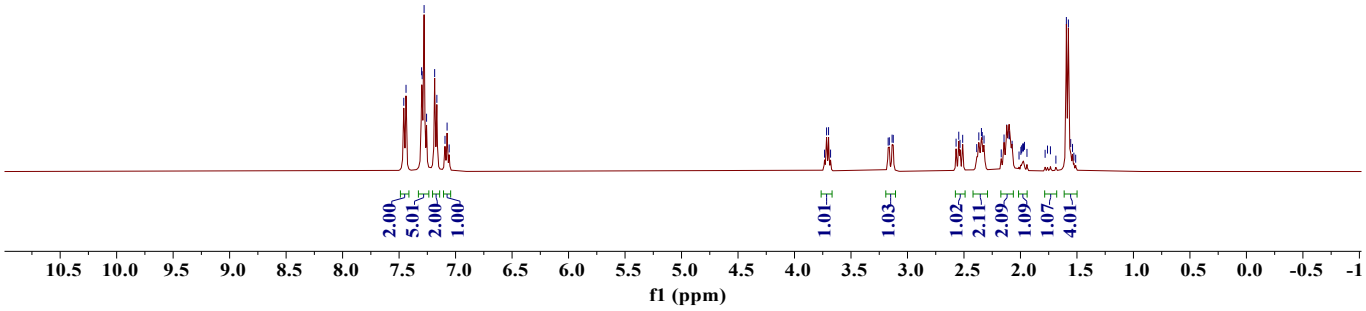


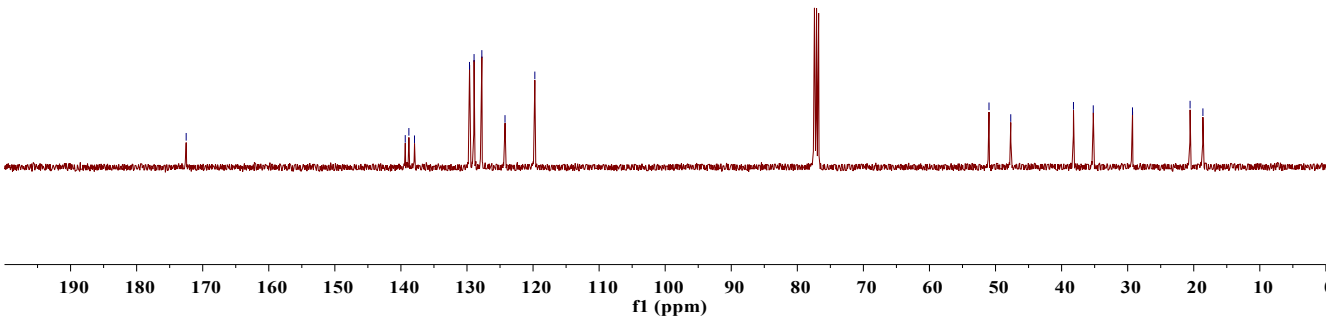
^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) of product 6ea



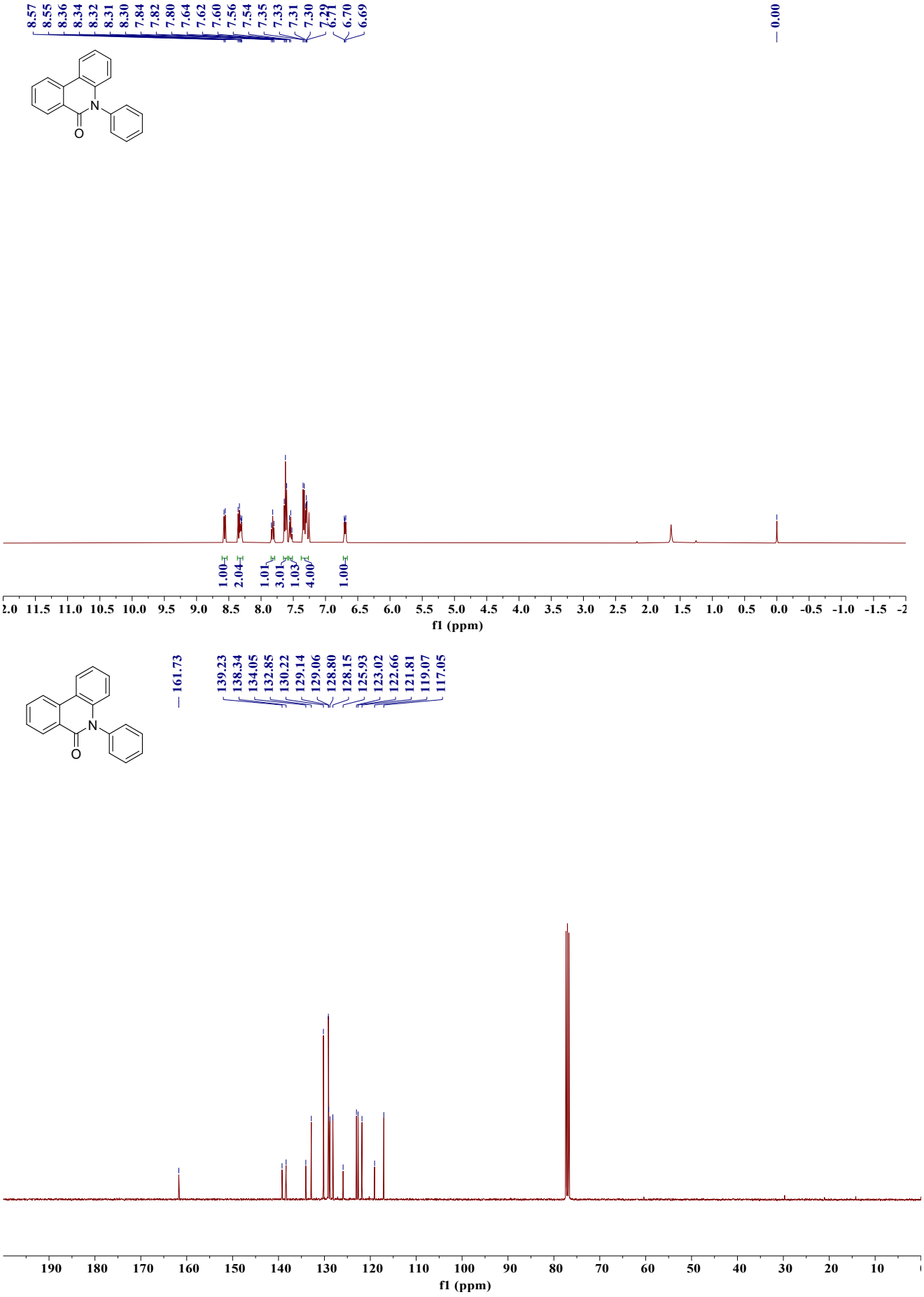


^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) of product 6fa

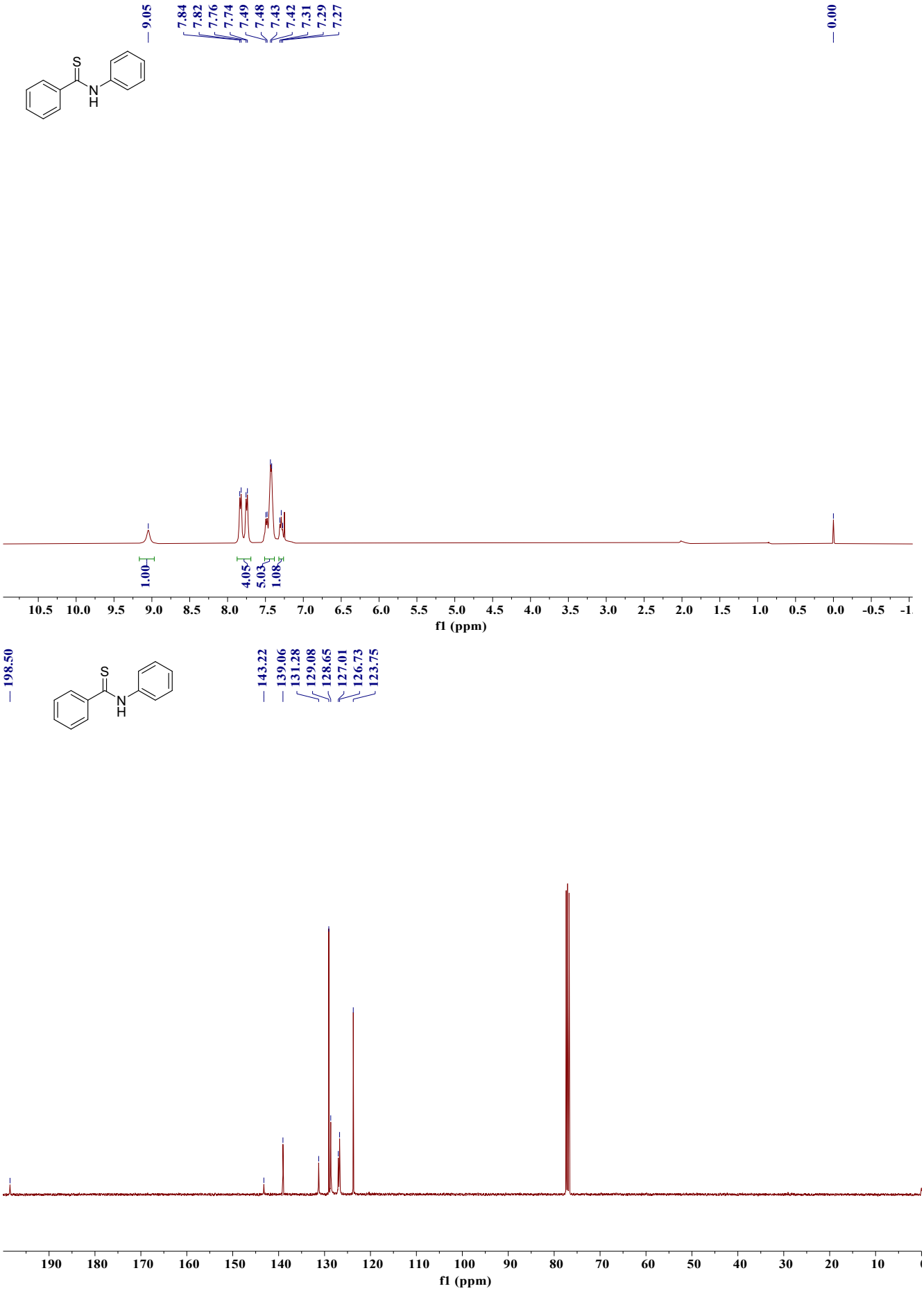




^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) of product 7



^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) of product 8



^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) of product 9