

Supporting Information

Cobalt-Catalyzed α -Methoxymethylation and Aminomethylation of Ketones with Methanol as a C1 Source

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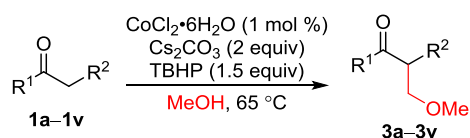
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1. General information

^1H NMR and ^{13}C NMR spectra were recorded on a Varian Mercury-400 Plus or Agilent Technologies DD2 (600 MHz) spectrometers in CDCl_3 , $\text{DMSO}-d_6$ or CD_3OD . Chemical shifts (δ) for NMR were quoted in ppm relative to the solvent peak (7.26 ppm for ^1H and 77.16 ppm for ^{13}C in CDCl_3 , 2.49 ppm for ^1H and 39.5 ppm for ^{13}C in $\text{DMSO}-d_6$, 3.31 ppm for ^1H and 49.00 ppm for ^{13}C in CD_3OD). High-resolution mass spectra (HRMS) were reported from Agilent QTOF 7200 (CI) or Bruker Daltonics APEXII 47e FT-ICR (ESI). Melting points were measured on an XT4A apparatus (uncorrected). Thin-layer chromatography (TLC) analysis of reaction mixtures was performed using commercial silica gel plates (GF254) which were visualized by UV irradiation at 254-360 nm. Unless otherwise indicated, all reagents were purchased from commercial suppliers and used without further purification. Enone **4a** used in the control experiments was prepared according to literature method.^[1]

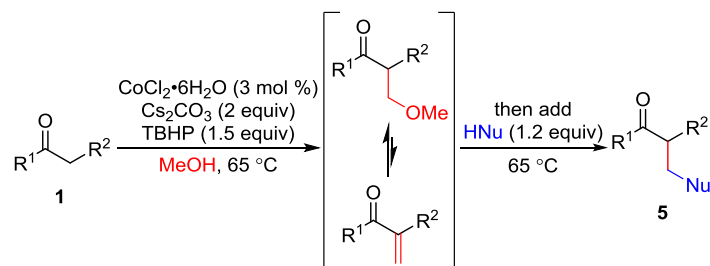
2. Experimental Procedures

2.1 General procedure for α -methoxymethylation of ketones



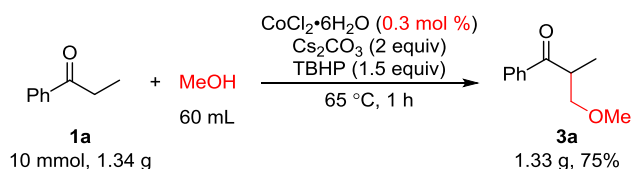
$\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (1.2 mg, 0.005 mmol, 1 mol%), Cs_2CO_3 (325.8 mg, 1.0 mmol, 2 equiv), MeOH (3 mL) and ketone **1** (0.5 mmol) were sequentially added into a 25 mL Schleck tube. Then TBHP (70 wt% in H_2O) (104 μL , 0.75 mmol, 1.5 equiv) was added to the stirred reaction system. The reaction mixture was stirred at 65°C until the reaction was complete (monitored by TLC). The reaction solution was cooled at room temperature and quenched with water (2 mL), extracted with CH_2Cl_2 (3 $\times$ 5 mL). The combined organic phase was dried over anhydrous MgSO_4 , filtrated and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel (PE : EtOAc = 20:1–10:1) to afford the pure products **3**.

2.2 General procedure for one-pot α -aminomethylation of ketones with methanol and N-nucleophiles



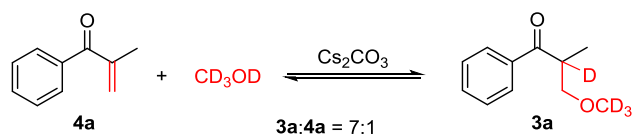
CoCl₂·6H₂O (1.2 mg, 0.005 mmol, 1 mol%), Cs₂CO₃ (325.8 mg, 1.0 mmol, 2 equiv), MeOH (3 mL) and ketone **1** (0.5 mmol) were sequentially added into a 25 mL Schleck tube. Then TBHP (70 wt% in H₂O) (104 μ L, 0.75 mmol, 1.5 equiv) was added to the stirred reaction system. The reaction mixture was stirred at 65 $^{\circ}$ C until first step reaction was complete (monitored by TLC). The reaction solution was cooled at room temperature and N-nucleophile (0.6 mmol, 1.2 equiv) was added. The mixture was stirred at 65 $^{\circ}$ C until second step reaction was complete (monitored by TLC). The reaction solution was cooled at room temperature and quenched with saturated brine (2 mL), extracted with EtOAc (3 $\times$ 5 mL). The combined organic phase was dried over anhydrous Na₂SO₄, filtrated and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel (PE : EtOAc = 20:1–5:1) to afford the pure products **5**.

2.3 Procedure for gram-scale methoxymethylation of ketone **1a**

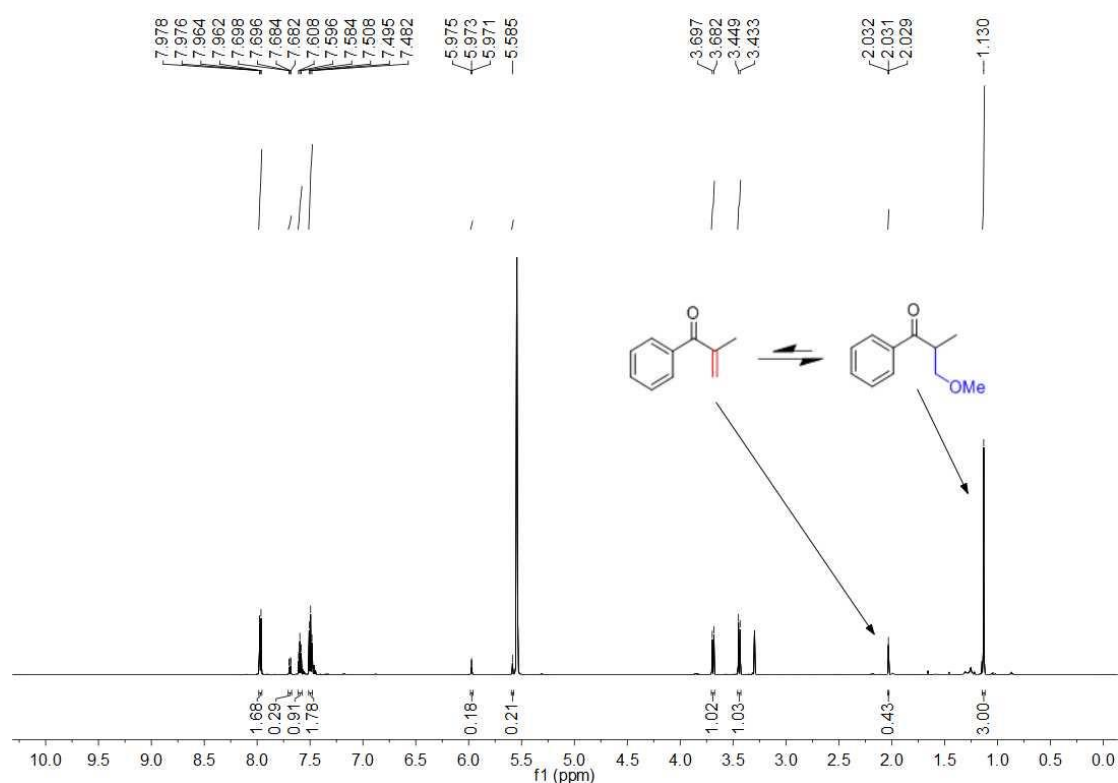


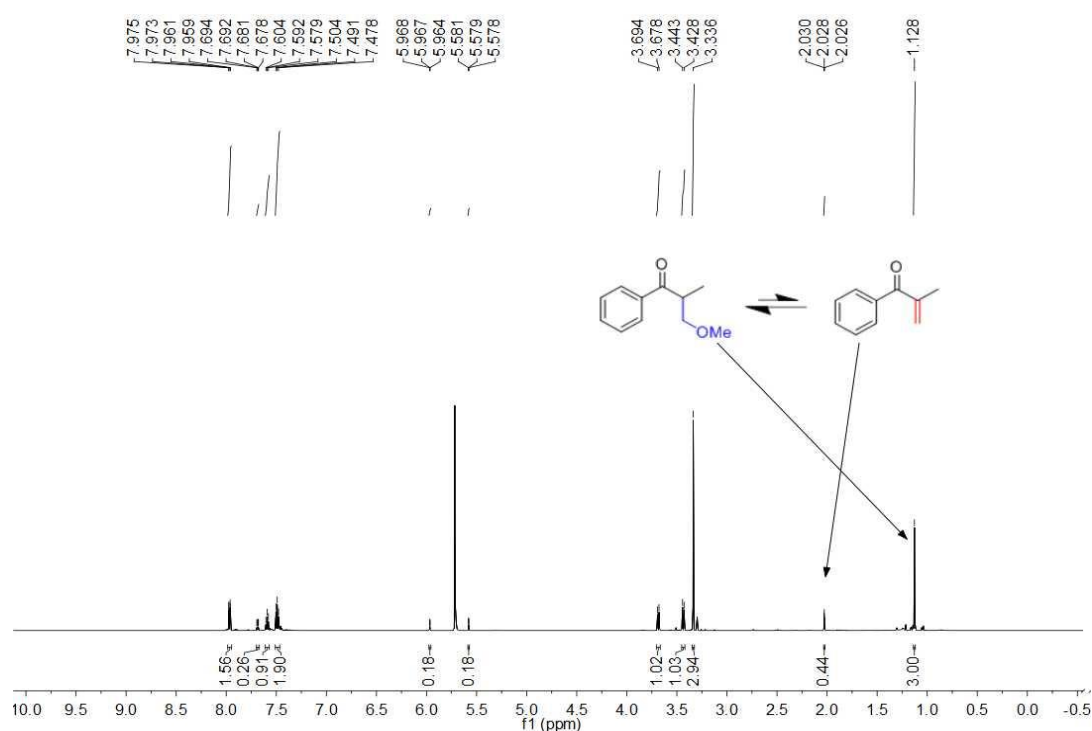
CoCl₂·6H₂O (7.1 mg, 0.03 mmol, 0.3 mol%), Cs₂CO₃ (6.52 g, 20 mmol, 2 equiv), MeOH (60 mL) and ketone **1a** (1.34 g, 10 mmol) were sequentially added into a 200 mL round-bottom flask. Then TBHP (70 wt% in H₂O) (2.1 mL, 15 mmol, 1.5 equiv) was added to the stirred reaction system. The reaction mixture was stirred at 65 $^{\circ}$ C for 1 h. The reaction solution was cooled at room temperature and quenched with saturated brine (20 mL), extracted with CH₂Cl₂ (3 $\times$ 30 mL). The combined organic phase was dried over anhydrous MgSO₄, filtrated and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel (PE : EtOAc = 20:1) to afford the pure product **3a** (1.33 g, 75%).

2.4 Procedure for experiments showing equilibrium between enone **4a** and methoxymethylated product **3a**

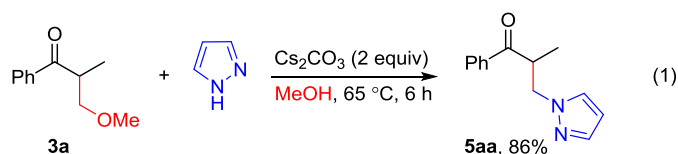


Cs_2CO_3 (97.8 mg, 0.30 mmol, 2 equiv) and **3a** (26.8 mg, 0.15 mmol), Cs_2CO_3 (97.8 mg, 0.30 mmol, 2 equiv) and **4a** (21.9 mg, 0.15 mmol) were dissolved in CD_3OD (1 mL), respectively. After Cs_2CO_3 was completely dissolved, the two solutions were separately transferred to NMR tubes without further treatment, and detected by ^1H NMR. Analysis of the ^1H NMR spectra showed that the ratio of **3a** : **4a** was 7:1 in both cases.

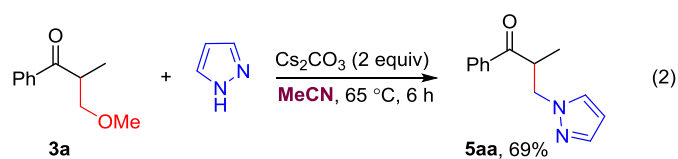




2.5 Procedure for investigation of the effects of the reagents on the α -aminomethylation of ketones



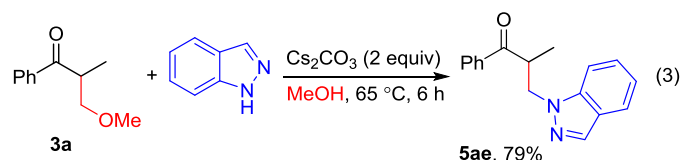
Cs_2CO_3 (228.1 mg, 0.70 mmol, 2 equiv), pyrazole (28.6 mg, 0.42 mmol, 1.2 equiv), **3a** (61.9 mg, 0.35 mmol) and MeOH (2 mL) were sequentially added into a 25 mL Schleck tube. The reaction mixture was stirred at 65 °C for 6 h. The reaction mixture was cooled at room temperature and quenched with saturated brine (2 mL), extracted with EtOAc (3×5 mL). The combined organic phase was dried over anhydrous Na_2SO_4 , filtrated and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel (PE : EtOAc = 10:1) to afford the pure product **5aa** (62.8 mg, 86%).



Cs_2CO_3 (221.5 mg, 0.68 mmol, 2 equiv), pyrazole (27.8 mg, 0.41 mmol, 1.2 equiv), **3a** (60.6 mg, 0.34 mmol) and MeCN (2 mL) were sequentially added into a 25 mL Schleck tube. The

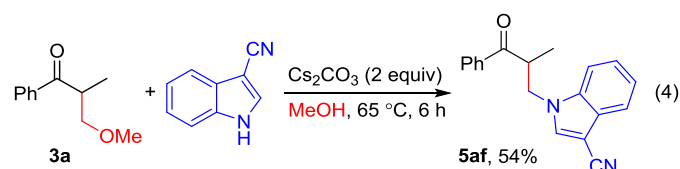
reaction mixture was stirred at 65 °C for 6 h. The reaction mixture was cooled at room temperature and quenched with saturated brine (2 mL), extracted with EtOAc (3×5 mL). The combined organic phase was dried over anhydrous Na₂SO₄, filtrated and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel (PE : EtOAc = 10:1) to afford the pure product **5aa** (50.4 mg, 69%).

2.6 Experimental procedure for synthesis of **5ae**



Cs₂CO₃ (195.8 mg, 0.60 mmol, 2 equiv), indazole (42.5 mg, 0.36 mmol, 1.2 equiv), **3a** (53.5 mg, 0.30 mmol) and MeOH (2 mL) were sequentially added into a 25 mL Schleck tube. The reaction mixture was stirred at 65 °C for 6 h. The reaction mixture was cooled at room temperature and quenched with saturated brine (2 mL), extracted with EtOAc (3×5 mL). The combined organic phase was dried over anhydrous Na₂SO₄, filtrated and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel (PE : EtOAc = 10:1) to afford the pure product **5ae** (62.6 mg, 79%).

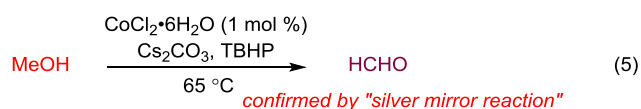
2.7 Experimental procedure for synthesis of **5af**



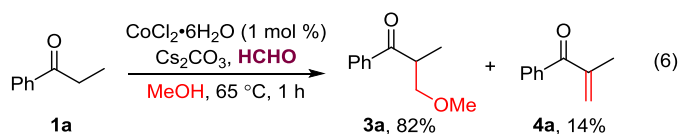
Cs₂CO₃ (195.5 mg, 0.60 mmol, 2 equiv), 3-cyanoindazole (51.2 mg, 0.36 mmol, 1.2 equiv), **3a** (53.5 mg, 0.30 mmol) and MeOH (2 mL) were sequentially added into a 25 mL Schleck tube. The reaction mixture was stirred at 65 °C for 6 h. The reaction mixture was cooled at room temperature and quenched with saturated brine (2 mL), extracted with EtOAc (3×5 mL). The combined organic phase was dried over anhydrous Na₂SO₄, filtrated and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel (PE : EtOAc = 10:1) to afford the pure product **5af** (46.7 mg, 54%).

2.8 Procedure for control experiments

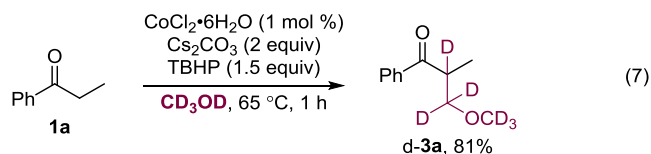
Using silver mirror reaction to detect the *in situ* formed formaldehyde:



To a solution of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (1.2 mg, 0.005 mmol) and Cs_2CO_3 (325.8 mg, 1.0 mmol) in MeOH (3 mL), TBHP (70 wt% in H_2O) (104 μL , 0.75 mmol) was added. After stirring for 30 min, a small amount of the reaction mixture was dropped into the fresh silver ammonia solution in test tube. After shaking, the test tube was warmed in hot water and a layer of metallic silver was found adhering to the inner wall of the test tube. The picture of this phenomenon is shown in follow:

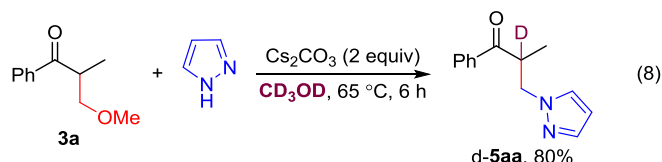


$\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (1.2 mg, 0.005 mmol, 1 mol%), Cs_2CO_3 (325.8 mg, 1.0 mmol, 2 equiv), MeOH (3 mL) and ketone **1a** (66.6 μL , 0.5 mmol) were sequentially added into a 25 mL Schleck tube. Then HCHO (40 % w/v) (52.0 μL , 0.75 mmol, 1.5 equiv) was added to the stirred reaction system. The reaction mixture was stirred at 65 $^\circ\text{C}$ for 1 h. The reaction solution was cooled at room temperature and quenched with water (2 mL), extracted with CH_2Cl_2 (3 $\times$ 5 mL). The combined organic phase was dried over anhydrous MgSO_4 , filtrated and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel (Hexane : EtOAc = 20:1) to afford the pure product **3a** (72.7 mg, 82%) and **4a** (9.9 mg, 14%).



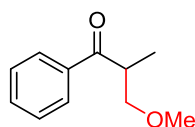
$\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (0.8 mg, 0.0035 mmol, 1 mol%), Cs_2CO_3 (228.2 mg, 0.70 mmol, 2 equiv), CD_3OD (2 mL) and ketone **1a** (46.6 μL , 0.35 mmol) were sequentially added into a 25 mL Schleck tube. Then TBHP (70 wt% in H_2O) (72.7 μL , 0.53 mmol, 1.5 equiv) was added to the

stirred reaction system. The reaction mixture was stirred at 65 °C for 1 h. The reaction solution was cooled at room temperature and quenched with saturated brine (2 mL), extracted with EtOAc (3×5 mL). The combined organic phase was dried over anhydrous Na₂SO₄, filtrated and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel (PE : EtOAc = 20:1) to afford the pure product *d*-**3a** (52.2 mg, 81%).



Cs₂CO₃ (215.1 mg, 0.66 mmol, 2 equiv), pyrazole (27.2 mg, 0.40 mmol, 1.2 equiv), **3a** (58.8 mg, 0.33 mmol) and CD₃OD (2 mL) were sequentially added into a 25 mL Schleck tube. The reaction mixture was stirred at 65 °C for 6 h. The reaction mixture was cooled at room temperature and quenched with saturated brine (2 mL), extracted with EtOAc (3×5 mL). The combined organic phase was dried over anhydrous Na₂SO₄, filtrated and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel (PE : EtOAc = 10:1) to afford the pure product *d*-**5aa** (56.8 mg, 80%).

3. Characterization data for all synthesized compounds



3-Methoxy-2-methyl-1-phenylpropan-1-one (**3a**)

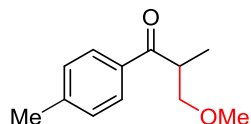
Colorless oil; yield: 73.6 mg (83%).

¹H NMR (400 MHz, CDCl₃): δ 7.98 – 7.96 (m, 2H), 7.56 (t, *J* = 7.6 Hz, 1H), 7.46 (t, *J* = 7.6 Hz, 2H), 3.79 – 3.73 (m, 2H), 3.47 – 3.45 (m, 1H), 3.32 (s, 3H), 1.20 (d, *J* = 6.8 Hz, 3H).

¹³C NMR (100 MHz, CDCl₃): δ 202.7, 136.6, 133.0, 128.6, 128.4, 74.9, 59.1, 41.2, 14.8.

IR (film): 2955, 2856, 2653, 1988, 1685, 1601, 1513, 1395, 1253, 1090, 1024, 973, 699 cm⁻¹.

HRMS (CI): *m/z* [M+H]⁺ calcd for C₁₁H₁₅O₂: 179.1067; found: 179.1072.



3-Methoxy-2-methyl-1-(*p*-tolyl)propan-1-one (3b)

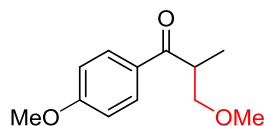
Colorless oil; yield: 87.9 mg (91%).

^1H NMR (400 MHz, CDCl_3): δ 7.88 (d, J = 8.0 Hz, 2H), 7.27 (d, J = 8.0 Hz, 2H), 3.77 – 3.75 (m, 2H), 3.44 (q, J = 4.0 Hz, 1H), 3.32 (s, 3H), 2.41 (s, 3H), 1.20 (d, J = 6.4 Hz, 3H).

^{13}C NMR (100 MHz, CDCl_3): δ 202.2, 143.8, 134.1, 129.2, 128.5, 75.0, 59.0, 41.0, 21.6, 14.9.

IR (film): 3163, 2965, 1689, 1523, 1580, 1448, 1282, 1223, 1172, 1044, 752, 705 cm^{-1} .

HRMS (CI): m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{12}\text{H}_{17}\text{O}_2$: 193.1223; found: 193.1228.



3-Methoxy-1-(4-methoxyphenyl)-2-methylpropan-1-one (3c)

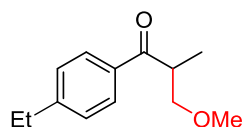
Colorless oil; yield: 89.6 mg (86%).

^1H NMR (400 MHz, CDCl_3): δ 7.97 (d, J = 9.2 Hz, 2H), 6.94 (d, J = 9.2 Hz, 2H), 3.87 (s, 3H), 3.78 – 3.71 (m, 2H), 3.44 (dd, J = 128, 9.6 Hz, 1H), 3.32 (s, 3H), 1.19 (d, J = 6.4 Hz, 3H).

^{13}C NMR (100 MHz, CDCl_3): δ 201.1, 163.5, 130.6, 129.6, 113.7, 75.1, 59.0, 55.4, 40.8, 15.0.

IR (film): 3055, 2985, 2833, 1685, 1523, 1488, 1426, 1322, 1163, 1072, 979, 821, 763 cm^{-1} .

HRMS (CI): m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{12}\text{H}_{17}\text{O}_3$: 209.1172; found: 209.1178.



1-(4-Ethylphenyl)-3-methoxy-2-methylpropan-1-one (3d)

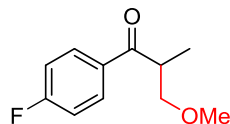
Colorless oil; yield: 67.1 mg (65%).

^1H NMR (600 MHz, CDCl_3): δ 7.90 (d, J = 8.4 Hz, 2H), 7.28 (d, J = 8.4 Hz, 2H), 3.79 – 3.73 (m, 2H), 3.46 – 3.42 (m, 1H), 3.31 (s, 3H), 2.70 (dd, J = 10.4, 5.2 Hz, 2H), 1.25 (t, J = 7.8 Hz, 3H), 1.19 (d, J = 6.6 Hz, 3H).

^{13}C NMR (150 MHz, CDCl_3): δ 202.3, 150.0, 134.3, 128.6, 128.1, 75.0, 59.1, 41.1, 28.9, 15.2, 14.9.

IR (film): 2969, 2931, 2877, 1679, 1606, 1456, 1414, 1222, 1184, 1112, 979, 957, 846, 701, 599 cm^{-1} .

HRMS (ESI): m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{13}\text{H}_{19}\text{O}_2$: 207.1380; found: 207.1380.



1-(4-Fluorophenyl)-3-methoxy-2-methylpropan-1-one (3e)

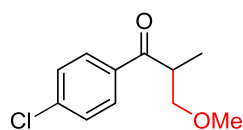
Colorless oil; yield: 75.4 mg (77%).

^1H NMR (600 MHz, CDCl_3): δ 8.00 – 7.97 (m, 2H), 7.11 (t, J = 9.0 Hz, 2H), 3.73 – 3.69 (m, 2H), 3.45 – 3.41 (m, 1H), 3.29 (s, 3H), 1.17 (d, J = 6.6 Hz, 3H).

^{13}C NMR (150 MHz, CDCl_3): δ 201.2, 165.7 (d, J = 253.2 Hz), 133.1 (d, J = 3.0 Hz), 131.0 (d, J = 9.15 Hz), 115.6 (d, J = 21.75 Hz), 75.0, 59.0, 41.2, 14.7.

IR (film): 2969, 2931, 2877, 1679, 1606, 1456, 1414, 1222, 1184, 1112, 979, 846, 701, 599 cm^{-1} .

HRMS (CI): m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{11}\text{H}_{14}\text{FO}_2$: 197.0972; found: 197.0979.



1-(4-Chlorophenyl)-3-methoxy-2-methylpropan-1-one (3f)

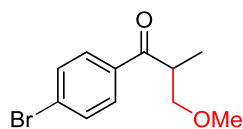
Colorless oil; yield: 78.2 mg (74%).

^1H NMR (600 MHz, CDCl_3): δ 7.90 (d, J = 8.4 Hz, 2H), 7.42 (d, J = 8.4 Hz, 2H), 3.73 – 3.69 (m, 2H), 3.45 – 3.42 (m, 1H), 3.30 (s, 3H), 1.17 (d, J = 6.6 Hz, 3H).

^{13}C NMR (150 MHz, CDCl_3): δ 201.6, 139.4, 135.0, 129.8, 128.9, 74.9, 59.0, 41.2, 14.6.

IR (film): 3349, 3067, 2570, 1919, 1791, 1683, 1589, 1482, 1396, 1219, 1098, 976, 840, 752, 527, 480 cm^{-1} .

HRMS (CI): m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{11}\text{H}_{14}\text{ClO}_2$: 213.0677; found: 213.0675.



1-(4-Bromophenyl)-3-methoxy-2-methylpropan-1-one (3g)

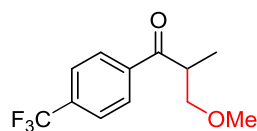
Colorless oil; yield: 90.9 mg (71%).

^1H NMR (400 MHz, CDCl_3): δ 7.84 (d, J = 8.4 Hz, 2H), 7.60 (d, J = 8.8 Hz, 2H), 3.72 (dd, J = 12.4, 7.6 Hz, 2H), 3.45 (dd, J = 13.2, 7.6 Hz, 1H), 3.30 (s, 3H), 1.19 (d, J = 6.4 Hz, 3H).

^{13}C NMR (100 MHz, CDCl_3): δ 201.7, 135.4, 131.8, 129.9, 128.1, 74.9, 59.0, 41.2, 14.6.

IR (film): 3730, 3626, 3349, 1683, 1584, 1456, 1394, 1250, 1215, 977, 838, 749, 469 cm^{-1} .

HRMS (CI): m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{11}\text{H}_{14}\text{BrO}_2$: 257.0172; found: 257.0176.



3-Methoxy-2-methyl-1-(4-(trifluoromethyl)phenyl)propan-1-one (3h)

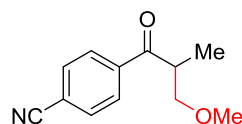
Pale yellow oil; yield: 38.1 mg (31%).

^1H NMR (400 MHz, CDCl_3): δ 8.07 (d, J = 8.0 Hz, 2H), 7.73 (d, J = 8.0 Hz, 2H), 3.78-3.71 (m, 2H), 3.48 (dd, J = 8.4, 4.8 Hz, 1H), 3.31 (s, 3H), 1.21 (d, J = 6.8 Hz, 3H).

^{13}C NMR (100 MHz, CDCl_3): δ 202.0, 139.5, 134.2 (q, J = 32.6, Hz), 128.7, 125.6 (q, J = 3.7 Hz), 123.6 (q, J = 270.9 Hz), 74.9, 59.1, 41.7, 14.5.

IR (film): 3349, 3064, 2976, 2880, 1687, 1584, 1456, 1394, 1190, 1109, 1072, 473 cm^{-1} .

HRMS (CI): m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{12}\text{H}_{14}\text{F}_3\text{O}_2$: 247.0940; found: 247.0939.



4-(3-Methoxy-2-methylpropanoyl)benzonitrile (3i)

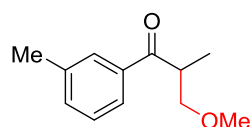
Colorless oil; yield: 39.2 mg (62%).

^1H NMR (600 MHz, CDCl_3): δ 8.04 (d, J = 8.4 Hz, 2H), 7.76 (d, J = 8.4 Hz, 2H), 3.75-3.68 (m, 2H), 3.48-3.46 (m, 1H), 3.29 (s, 3H), 1.19 (d, J = 6.6 Hz, 3H).

^{13}C NMR (150 MHz, CDCl_3): δ 201.8, 140.0, 132.5, 128.8, 118.0, 116.2, 74.9, 59.1, 41.7, 14.4.

IR (film): 3215, 2976, 2714, 2246, 1680, 1662, 1437, 1368, 1099, 875, 501 cm^{-1} .

HRMS (CI): m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{12}\text{H}_{14}\text{NO}_2$: 204.1019; found: 204.1021.



3-Methoxy-2-methyl-1-(*m*-tolyl)propan-1-one (3j)

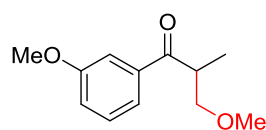
Colorless oil; yield: 73.0 mg (76%).

^1H NMR (600 MHz, CDCl_3): δ 7.77 – 7.45 (m, 2H), 7.36 – 7.32 (m, 2H), 3.78 – 3.72 (m, 2H), 3.44 – 3.42 (m, 1H), 3.30 (s, 3H), 2.39 (s, 3H), 1.18 (d, J = 6.6 Hz, 3H).

^{13}C NMR (150 MHz, CDCl_3): δ 202.9, 138.4, 136.7, 133.8, 128.9, 128.5, 125.6, 75.0, 59.1, 41.3, 21.4, 14.9.

IR (film): 3351, 2970, 2736, 1681, 1586, 1307, 1140, 1108, 1025, 979, 684 cm^{-1} .

HRMS (ESI): m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{12}\text{H}_{17}\text{O}_2$: 193.1223; found: 193.1223.



3-Methoxy-1-(3-methoxyphenyl)-2-methylpropan-1-one (3k)

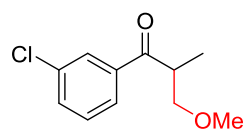
Colorless oil; yield: 71.3 mg (69%).

^1H NMR (600 MHz, CDCl_3): δ 7.54 (d, J = 7.8 Hz, 1H), 7.49 – 7.48 (m, 1H), 7.36 (t, J = 7.8 Hz, 1H), 7.10 – 7.09 (m, 1H), 3.84 (s, 3H), 3.76 – 3.72 (m, 2H), 3.44 (dd, J = 6.0, 2.4 Hz, 1H), 3.31 (s, 3H), 1.19 (d, J = 6.6 Hz, 3H).

^{13}C NMR (150 MHz, CDCl_3): δ 202.5, 159.8, 138.0, 129.5, 120.9, 119.5, 112.6, 74.9, 59.0, 55.4, 41.4, 14.8.

IR (film): 3074, 2839, 1679, 1583, 1458, 1287, 1169, 1043, 987, 681 cm^{-1} .

HRMS (ESI): m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{12}\text{H}_{17}\text{O}_3$: 209.1172; found: 209.1170.



1-(3-Chlorophenyl)-3-methoxy-2-methylpropan-1-one (3l)

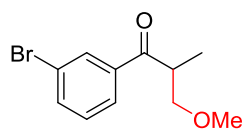
Colorless oil; yield: 66.1 mg (62%).

^1H NMR (600 MHz, CDCl_3): δ 7.92 (t, J = 2.4 Hz, 1H), 7.82 (d, J = 7.8 Hz, 1H), 7.52–7.50 (m, 1H), 7.39 (t, J = 7.8 Hz, 1H), 3.72 – 3.69 (m, 2H), 3.46 – 3.42 (m, 1H), 3.29 (s, 3H), 1.17 (d, J = 6.6 Hz, 3H).

^{13}C NMR (150 MHz, CDCl_3): δ 201.6, 138.3, 134.9, 132.9, 129.9, 128.5, 126.4, 74.9, 59.1, 41.4, 14.6.

IR (film): 3069, 1686, 1570, 1459, 1215, 1109, 987, 799, 674, 420 cm^{-1} .

HRMS (CI): m/z $[M+H]^+$ calcd for $C_{11}H_{14}ClO_2$: 213.0677; found: 213.0685.



1-(3-Bromophenyl)-3-methoxy-2-methylpropan-1-one (3m)

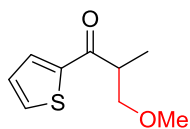
Colorless oil; yield: 75.3 mg (59%).

1H NMR (400 MHz, $CDCl_3$): δ 8.10 (s, 1H), 7.89 (d, J = 8.0 Hz, 1H), 7.68 (dd, J = 8.0, 0.4 Hz, 1H), 7.35 (t, J = 8.0 Hz, 1H), 3.74 – 3.69 (m, 2H), 3.45 (dd, J = 12.4, 9.6 Hz, 1H), 3.31 (s, 3H), 1.19 (d, J = 6.4 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 201.5, 138.5, 135.8, 131.4, 130.2, 126.9, 123.0, 74.9, 59.1, 41.4, 14.6.

IR (film): 3125, 2298, 1689, 1448, 1419, 1109, 997, 968, 625, 623, 405 cm^{-1} .

HRMS (CI): m/z $[M+H]^+$ calcd for $C_{11}H_{14}BrO_2$: 257.0172; found: 257.0180.



3-Methoxy-2-methyl-1-(thiophen-2-yl)propan-1-one (3n)

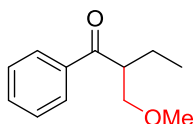
Colorless oil; yield: 80.0 mg (87%).

1H NMR (400 MHz, $CDCl_3$): δ 7.76 (dd, J = 4.0, 1.0 Hz, 1H), 7.65 (dd, J = 4.8, 1.2 Hz, 1H), 7.14 (dd, J = 4.8, 3.6 Hz, 1H), 3.74 (dd, J = 8.8, 7.6 Hz, 1H), 3.66 – 3.56 (m, 1H), 3.44 (dd, J = 9.2, 5.6 Hz, 1H), 3.32 (s, 3H), 1.23 (d, J = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 195.4, 144.1, 133.9, 132.1, 128.1, 74.9, 59.0, 43.0, 14.9.

IR (film): 3074, 2926, 1679, 1583, 1458, 1259, 1169, 987, 824, 796, 747, 624 cm^{-1} .

HRMS (CI): m/z $[M+H]^+$ calcd for $C_9H_{13}O_2S$: 185.0631; found: 185.0634.



2-(Methoxymethyl)-1-phenylbutan-1-one (3o)

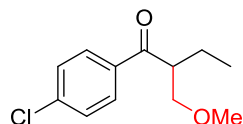
Pale yellow oil; yield: 71.4 mg (74%).

^1H NMR (600 MHz, CDCl_3): δ 7.97 – 7.95 (m, 2H), 7.53 (t, J = 7.2 Hz, 1H), 7.44 (t, J = 7.2 Hz, 2H), 3.72 – 3.66 (m, 2H), 3.50 (dd, J = 8.4, 4.8 Hz, 1H), 3.27 (s, 3H), 1.78 – 1.72 (m, 1H), 1.61 – 1.57 (m, 1H), 0.88 (t, J = 7.8 Hz, 3H).

^{13}C NMR (150 MHz, CDCl_3): δ 202.8, 137.6, 132.9, 128.5, 128.2, 73.7, 59.0, 48.0, 22.8, 11.6.

IR (film): 3058, 2926, 2879, 1681, 1595, 1452, 1384, 1265, 1217, 1109, 963, 897, 738, 705 cm^{-1} .

HRMS (ESI): m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{12}\text{H}_{17}\text{O}_2$: 193.1223; found: 193.1220.



1-(4-Chlorophenyl)-2-(methoxymethyl)butan-1-one (3p)

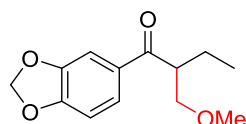
Colorless oil; yield: 79.8 mg (71%).

^1H NMR (600 MHz, CDCl_3): δ 7.91 (d, J = 9.0 Hz, 2H), 7.43 (d, J = 9.0 Hz, 2H), 3.70 – 3.67 (m, 1H), 3.63 – 3.60 (m, 1H), 3.50 (q, J = 4.8 Hz, 1H), 3.28 (s, 3H), 1.77 – 1.71 (m, 1H), 1.60 – 1.56 (m, 1H), 0.88 (t, J = 7.8 Hz, 3H).

^{13}C NMR (150 MHz, CDCl_3): δ 201.9, 139.4, 136.1, 129.8, 128.9, 73.8, 59.1, 48.2, 22.8, 11.7.

IR (film): 2964, 2877, 1682, 1589, 1460, 1400, 1260, 1215, 1094, 1009, 964, 841, 746, 531 cm^{-1} .

HRMS (ESI): m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{12}\text{H}_{16}\text{ClO}_2$: 227.0833; found: 227.0834.



1-(Benzo[d][1,3]dioxol-5-yl)-2-(methoxymethyl)butan-1-one (3q)

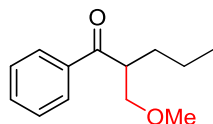
Colorless oil; yield: 67.8 mg (58%).

^1H NMR (600 MHz, CDCl_3): δ 7.58 (dd, J = 7.8, 1.8 Hz, 1H), 7.45 (d, J = 1.8 Hz, 1H), 6.84 (d, J = 8.4 Hz, 1H), 6.01 (s, 2H), 3.67 (t, J = 8.4 Hz, 1H), 3.59-3.55 (m, 1H), 3.47 (dd, J = 9.0, 5.4 Hz, 1H), 3.27 (s, 3H), 1.75 – 1.70 (m, 1H), 1.58 – 1.57 (m, 1H), 0.86 (t, J = 7.8 Hz, 3H).

^{13}C NMR (150 MHz, CDCl_3): δ 200.9, 151.7, 148.2, 132.6, 124.6, 108.1, 107.8, 101.8, 74.0, 59.0, 47.8, 23.0, 11.7.

IR (film): 2965, 2926, 2886, 1607, 1488, 1442, 1362, 1197, 1101, 1038, 933, 807, 750, 578 cm^{-1} .

HRMS (ESI): m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{13}\text{H}_{17}\text{O}_4$: 237.1121; found: 237.1117.



2-(Methoxymethyl)-1-phenylpentan-1-one (3r)

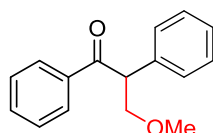
Colorless oil; yield: 77.6 mg (75%).

^1H NMR (400 MHz, CDCl_3): δ 8.01 – 7.96 (m, 2H), 7.56 (t, J = 7.6 Hz, 1H), 7.47 (t, J = 7.6 Hz, 2H), 3.79 – 3.70 (m, 2H), 3.51 (dd, J = 8.4, 4.8 Hz, 1H), 3.29 (s, 3H), 1.77 – 1.66 (m, 1H), 1.56 – 1.47 (m, 1H), 1.30 (dd, J = 15.6, 7.6 Hz, 2H), 0.88 (t, J = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, CDCl_3): δ 203.1, 137.7, 132.9, 128.5, 128.3, 74.2, 59.0, 46.5, 32.0, 20.6, 14.2.

IR (film): 2985, 2711, 1658, 1423, 1326, 1312, 1193, 1023, 1011, 897, 856, 733, 579 cm^{-1} .

HRMS (CI): m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{13}\text{H}_{19}\text{O}_2$: 207.1380; found: 207.1382.



3-Methoxy-1,2-diphenylpropan-1-one (3s)

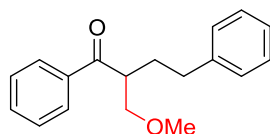
Colorless oil; yield: 37.9 mg (32%).

^1H NMR (400 MHz, CDCl_3): δ 7.92 – 7.88 (m, 2H), 7.41 (t, J = 7.6 Hz, 1H), 7.33 – 7.21 (m, 6H), 7.18 – 7.13 (m, 1H), 4.82 (dd, J = 8.4, 5.2 Hz, 1H), 4.11 (t, J = 8.8 Hz, 1H), 3.57 (dd, J = 9.2, 5.2 Hz, 1H), 3.27 (s, 3H).

^{13}C NMR (100 MHz, CDCl_3): δ 198.2, 136.7, 136.3, 133.0, 129.0, 128.7, 128.5, 128.3, 127.5, 74.7, 59.1, 53.8.

IR (film): 3011, 2785, 1697, 1389, 1321, 1085, 987, 856, 823, 714, 525 cm^{-1} .

HRMS (CI): m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{16}\text{H}_{17}\text{O}_2$: 241.1223; found: 241.1228.



2-(Methoxymethyl)-1,4-diphenylbutan-1-one (3t)

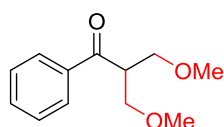
Colorless oil; yield: 108.5 mg (81%).

^1H NMR (600 MHz, CDCl_3): δ 7.92 – 7.86 (m, 2H), 7.55 (t, J = 7.8 Hz, 1H), 7.44 (t, J = 7.8 Hz, 2H), 7.25 (dd, J = 7.8, 3.0 Hz, 2H), 7.17 (t, J = 7.2 Hz, 1H), 7.11 (d, J = 7.2 Hz, 2H), 3.78 – 3.72 (m, 2H), 3.54 (dd, J = 8.4, 5.4 Hz, 1H), 3.28 (s, 3H), 2.65 – 2.56 (m, 2H), 2.11 (dd, J = 16.1, 6.8 Hz, 1H), 1.90 – 1.84 (m, 1H).

^{13}C NMR (150 MHz, CDCl_3): δ 202.6, 141.4, 137.4, 133.0, 128.5, 128.42, 128.35, 128.3, 126.0, 74.1, 59.1, 46.0, 33.4, 31.3.

IR (film): 2926, 2864, 1680, 1596, 1450, 1390, 1222, 1116, 964, 748, 701 cm^{-1} .

HRMS (ESI): m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{18}\text{H}_{21}\text{O}_2$: 269.1536; found: 269.1531.



3-Methoxy-2-(methoxymethyl)-1-phenylpropan-1-one (3u).

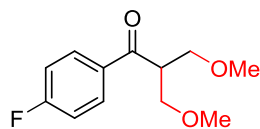
Pale yellow oil; yield: 75.4 mg (73%).

^1H NMR (600 MHz, CDCl_3): δ 7.97 (d, J = 7.8 Hz, 2H), 7.54 (t, J = 7.4 Hz, 1H), 7.45 (t, J = 8.4 Hz, 2H), 4.02 – 3.97 (m, 1H), 3.71 (dd, J = 9.0, 7.2 Hz, 2H), 3.60 (dd, J = 9.6, 6.0 Hz, 2H), 3.28 (s, 6H).

^{13}C NMR (150 MHz, CDCl_3): δ 200.7, 137.2, 133.0, 128.5, 128.4, 71.4, 59.0, 47.7.

IR (film): 3061, 2893, 1972, 1723, 1681, 1596, 1448, 1219, 1108, 959, 795, 713, 655, 544 cm^{-1} .

HRMS (ESI): m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{12}\text{H}_{17}\text{O}_3$: 209.1172; found: 209.1168.



1-(4-Fluorophenyl)-3-methoxy-2-(methoxymethyl)propan-1-one (3v)

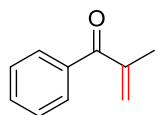
Pale yellow oil; yield: 66.7 mg (59%).

^1H NMR (400 MHz, CDCl_3): δ 8.02 (dd, J = 8.8, 5.4 Hz, 2H), 7.13 (t, J = 8.8 Hz, 2H), 4.01 – 3.93 (m, 1H), 3.69 (dd, J = 9.2, 7.2 Hz, 2H), 3.59 (dd, J = 9.2, 5.6 Hz, 2H), 3.29 (d, J = 1.6 Hz, 6H).

^{13}C NMR (100 MHz, CDCl_3): δ 199.4, 165.8 (d, J = 253 Hz), 133.8 (d, J = 3 Hz), 131.2 (d, J = 9 Hz), 115.6 (d, J = 22 Hz), 71.5, 59.1, 47.7.

IR (film): 3085, 2973, 2836, 1923, 1685, 1621, 1586, 1201, 1052, 936, 796, 628, 589 cm^{-1} .

HRMS (CI): m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{12}\text{H}_{16}\text{FO}_3$: 227.1078; found: 227.1084.



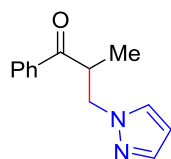
2-Methyl-1-phenylprop-2-en-1-one (4a)¹

Colorless oil; yield: 9.9 mg (14%)

¹H NMR (600 MHz, CDCl₃): δ 7.74 – 7.71 (m, 1H), 7.55 – 7.50 (m, 1H), 7.45 – 7.40 (m, 2H), 5.91 – 5.90 (m, 1H), 5.62 (d, *J* = 0.8 Hz, 1H), 2.07 (d, *J* = 0.9 Hz, 3H).

¹³C NMR (150 MHz, CDCl₃): δ 198.3, 143.8, 137.7, 132.0, 129.4, 128.1, 127.0, 18.6.

IR (film): 3166, 2815, 1936, 1687, 1596, 1563, 1010, 954, 723, 615 cm⁻¹.



2-Methyl-1-phenyl-3-(1H-pyrazol-1-yl)propan-1-one (5aa)

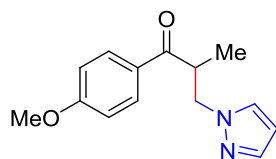
Colorless oil; yield: 78.2 mg (73%).

¹H NMR (600 MHz, CDCl₃): δ 7.89 (dd, *J* = 8.4, 1.2 Hz, 2H), 7.53 (t, *J* = 8.4 Hz, 1H), 7.47 (d, *J* = 1.8 Hz, 1H), 7.42 (t, *J* = 7.8 Hz, 2H), 7.37 (d, *J* = 2.4 Hz, 1H), 6.13 (t, *J* = 2.4 Hz, 1H), 4.58 (dd, *J* = 16.2, 10.2 Hz, 1H), 4.23 – 4.17 (m, 2H), 1.19 (d, *J* = 7.2 Hz, 3H).

¹³C NMR (150 MHz, CDCl₃): δ 202.1, 139.7, 135.9, 133.3, 130.4, 128.7, 128.3, 105.0, 54.0, 41.8, 16.0.

IR (film): 2955, 2856, 1601, 1513, 1395, 1253, 1090, 1025, 751 cm⁻¹.

HRMS (ESI): *m/z* [M+H]⁺ calcd for C₁₃H₁₄N₂O: 215.1179; found: 215.1178.



1-(4-Methoxyphenyl)-2-methyl-3-(1H-pyrazol-1-yl)propan-1-one (5ca)

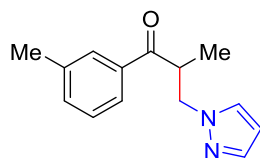
Colorless oil; yield: 96.1 mg (78%).

¹H NMR (600 MHz, CDCl₃): δ 7.89 (d, *J* = 8.4 Hz, 2H), 7.48 (d, *J* = 1.2 Hz, 1H), 7.36 (d, *J* = 2.4 Hz, 1H), 6.89 (d, *J* = 9.0 Hz, 2H), 6.13 (t, *J* = 2.4 Hz, 1H), 4.57 (dd, *J* = 13.2, 7.8 Hz, 1H), 4.21 – 4.14 (m, 2H), 3.84 (s, 3H), 1.18 (d, *J* = 7.2 Hz, 3H).

¹³C NMR (150 MHz, CDCl₃): δ 200.5, 163.7, 139.6, 130.7, 130.5, 128.8, 113.8, 105.0, 55.5, 54.2, 41.4, 16.2.

IR (film): 3107, 2926, 1679, 1585, 1458, 1379, 1258, 1096, 975, 751 cm^{-1} .

HRMS (ESI): m/z $[M+H]^+$ calcd for $\text{C}_{14}\text{H}_{16}\text{N}_2\text{O}_2$: 245.1285; found: 245.1281.



2-Methyl-3-(1H-pyrazol-1-yl)-1-(m-tolyl)propan-1-one (5ja)

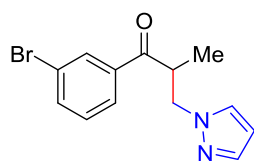
Pale yellow oil; yield: 61.7 mg (54%).

^1H NMR (600 MHz, CDCl_3): δ 7.69 (d, $J = 7.2$ Hz, 2H), 7.49 (d, $J = 1.2$ Hz, 1H), 7.38 (d, $J = 2.4$ Hz, 1H), 7.36 (d, $J = 7.8$ Hz, 1H), 7.31 (t, $J = 7.8$ Hz, 1H), 6.15 (t, $J = 2.4$ Hz, 1H), 4.65 – 4.57 (m, 1H), 4.25 – 4.19 (m, 2H), 2.38 (s, 3H), 1.19 (d, $J = 6.6$ Hz, 3H).

^{13}C NMR (150 MHz, CDCl_3): δ 202.3, 139.4, 138.5, 135.8, 134.2, 130.7, 128.9, 128.6, 125.6, 105.2, 54.0, 41.9, 21.3, 16.1.

IR (film): 3107, 2926, 1679, 1585, 1458, 1379, 1258, 1096, 975, 751 cm^{-1} .

HRMS (ESI): m/z $[M+H]^+$ calcd for $\text{C}_{14}\text{H}_{16}\text{N}_2\text{O}$: 229.1335; found: 229.1335.



1-(3-Bromophenyl)-2-methyl-3-(1H-pyrazol-1-yl)propan-1-one (5ma)

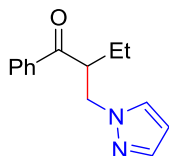
Pale yellow oil; yield: 82.3 mg (56%).

^1H NMR (600 MHz, CDCl_3): δ 8.01 (t, $J = 1.8$ Hz, 1H), 7.84 – 7.79 (m, 1H), 7.67 – 7.65 (m, 1H), 7.49 (d, $J = 1.2$ Hz, 1H), 7.36 (d, $J = 2.4$ Hz, 1H), 7.31 (t, $J = 8.4$ Hz, 1H), 6.14 (t, $J = 2.4$ Hz, 1H), 4.56 (dd, $J = 13.8, 8.4$ Hz, 1H), 4.22 (dd, $J = 13.2, 6.0$ Hz, 1H), 4.20 – 4.13 (m, 1H), 1.20 (d, $J = 7.2$ Hz, 3H).

^{13}C NMR (150 MHz, CDCl_3): δ 200.9, 139.8, 137.6, 136.2, 131.4, 130.5, 130.2, 126.8, 123.1, 105.2, 53.9, 42.0, 16.0.

IR (film): 3111, 2930, 1565, 1457, 1283, 1178, 985, 752, 618 cm^{-1} .

HRMS (ESI): m/z $[M+H]^+$ calcd for $\text{C}_{13}\text{H}_{13}\text{BrN}_2\text{O}$: 293.0284; found: 293.0280.



2-((1H-pyrazol-1-yl)methyl)-1-phenylbutan-1-one (50a)

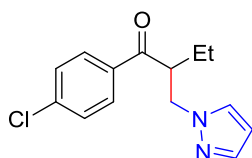
Colorless oil; yield: 97.7 mg (86%).

^1H NMR (600 MHz, CDCl_3): δ 7.84 (dd, $J = 8.4, 1.2$ Hz, 2H), 7.51 (t, $J = 7.8$ Hz, 1H), 7.44 (d, $J = 1.8$ Hz, 1H), 7.39 (dd, $J = 8.0, 7.6$ Hz, 2H), 7.31 (d, $J = 2.4$ Hz, 1H), 6.08 (t, $J = 2.4$ Hz, 1H), 4.54 (dd, $J = 13.8, 8.4$ Hz, 1H), 4.27 (dd, $J = 13.8, 5.4$ Hz, 1H), 4.17 – 4.12 (m, 1H), 1.79 – 1.71 (m, 1H), 1.63 – 1.56 (m, 1H), 0.88 (t, $J = 7.8$ Hz, 3H).

^{13}C NMR (150 MHz, CDCl_3): δ 202.3, 139.6, 136.8, 133.2, 130.3, 128.5, 128.1, 105.0, 52.6, 48.2, 23.9, 11.1.

IR (film): 3061, 2935, 1678, 1596, 1580, 1448, 1282, 1223, 1172, 1044, 752, 699 cm^{-1} .

HRMS (ESI): m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{14}\text{H}_{16}\text{N}_2\text{O}$: 229.1335; found: 229.1332.



2-((1H-pyrazol-1-yl)methyl)-1-(4-chlorophenyl)butan-1-one (5pa)

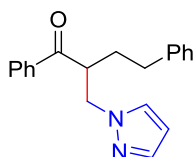
Colorless oil; yield: 59.5 mg (45%).

^1H NMR (600 MHz, CDCl_3): δ 7.77 (d, $J = 9.0$ Hz, 2H), 7.44 (d, $J = 1.2$ Hz, 1H), 7.36 (d, $J = 8.4$ Hz, 2H), 7.29 (d, $J = 2.4$ Hz, 1H), 6.08 (t, $J = 2.4$ Hz, 1H), 4.51 (dd, $J = 13.2, 8.4$ Hz, 1H), 4.27 (dd, $J = 13.2, 5.4$ Hz, 1H), 4.13-4.08 (m, 1H), 1.79 – 1.70 (m, 1H), 1.64 – 1.56 (m, 1H), 0.88 (t, $J = 7.8$ Hz, 3H).

^{13}C NMR (150 MHz, CDCl_3): δ 201.4, 139.8, 139.7, 135.2, 130.3, 129.6, 128.9, 105.2, 52.7, 48.2, 23.9, 11.2.

IR (film): 3106, 2965, 2876, 1588, 1456, 1282, 1173, 1045, 967, 750, 617, 533 cm^{-1} .

HRMS (ESI): m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{14}\text{H}_{15}\text{ClN}_2\text{O}$: 263.0946; found: 263.0942.



2-((1H-pyrazol-1-yl)methyl)-1,4-diphenylbutan-1-one (5ta)

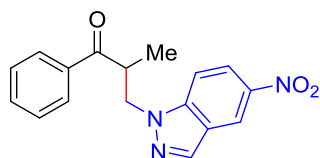
White solid; yield: 97.3 mg (64%); m.p. 94 – 97 °C.

^1H NMR (600 MHz, CDCl_3): δ 7.76 (dd, J = 8.4, 1.2 Hz, 2H), 7.52 (t, J = 7.8 Hz, 1H), 7.47 (d, J = 1.2 Hz, 1H), 7.38 (t, J = 7.8 Hz, 2H), 7.31 (d, J = 1.8 Hz, 1H), 7.23 (t, J = 7.8 Hz, 2H), 7.17 (t, J = 7.8 Hz, 1H), 7.06 (d, J = 7.2 Hz, 2H), 6.10 (t, J = 2.4 Hz, 1H), 4.58 (dd, J = 13.8, 8.4 Hz, 1H), 4.33 (dd, J = 13.6, 5.4 Hz, 1H), 4.24 – 4.21 (m, 1H), 2.63 – 2.51 (m, 2H), 2.10 – 2.06 (m, 1H), 1.87 – 1.83 (m, 1H).

^{13}C NMR (150 MHz, CDCl_3): δ 202.2, 140.9, 139.7, 136.6, 133.3, 130.3, 128.6, 128.42, 128.36, 128.2, 126.1, 105.2, 53.1, 46.4, 33.0, 32.4.

IR (film): 3733, 3028, 2859, 1678, 1595, 1449, 1282, 1178, 1046, 965, 751, 698 cm^{-1} .

HRMS (ESI): m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{20}\text{H}_{20}\text{N}_2\text{O}$: 305.1648; found: 305.1642.



2-Methyl-3-(5-nitro-1H-indazol-1-yl)-1-phenylpropan-1-one (5ab)

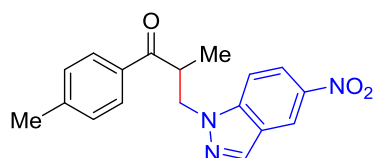
Pale yellow oil; yield: 80.6 mg (52%).

^1H NMR (600 MHz, CDCl_3): δ 8.64 (d, J = 2.0 Hz, 1H), 8.26 (dd, J = 9.6, 2.4 Hz, 1H), 8.16 (s, 1H), 7.86 (dd, J = 8.4, 1.2 Hz, 2H), 7.63 (d, J = 9.2 Hz, 1H), 7.53 (t, J = 7.4 Hz, 1H), 7.41 (dd, J = 8.0, 7.6 Hz, 2H), 4.90 (dd, J = 13.6, 8.4 Hz, 1H), 4.45 (dd, J = 13.6, 5.4 Hz, 1H), 4.41-4.35 (m, 1H), 1.29 (d, J = 7.2 Hz, 3H).

^{13}C NMR (150 MHz, CDCl_3): δ 201.7, 142.4, 141.8, 136.3, 135.5, 133.5, 128.7, 128.3, 122.7, 121.6, 118.7, 109.9, 51.1, 41.4, 16.4.

IR (film): 3103, 2954, 2925, 2295, 1678, 1614, 1517, 1453, 1338, 1170, 1069, 974, 703 cm^{-1} .

HRMS (ESI): m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{17}\text{H}_{15}\text{N}_3\text{O}_3$: 310.1186; found: 310.1179.



2-Methyl-3-(5-nitro-1H-indazol-1-yl)-1-(p-tolyl)propan-1-one (5bb)

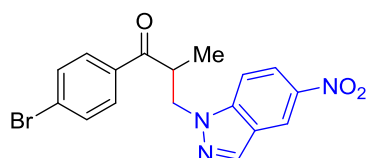
Pale yellow oil; yield: 53.4 mg (33%).

^1H NMR (600 MHz, CDCl_3): δ 8.62 (d, $J = 1.2$ Hz, 1H), 8.25 – 8.20 (m, 1H), 8.15 (s, 1H), 7.76 (d, $J = 7.8$ Hz, 2H), 7.61 (d, $J = 9.0$ Hz, 1H), 7.19 (d, $J = 7.8$ Hz, 2H), 4.88 (dd, $J = 13.8, 7.8$ Hz, 1H), 4.44 (dd, $J = 13.8, 6.0$ Hz, 1H), 4.37 – 4.31 (m, 1H), 2.35 (s, 3H), 1.27 (d, $J = 7.2$ Hz, 3H).

^{13}C NMR (150 MHz, CDCl_3): δ 201.2, 144.5, 142.3, 141.7, 136.3, 133.0, 129.4, 128.4, 122.6, 121.5, 118.7, 109.9, 51.1, 41.2, 21.6, 16.4.

IR (film): 3094, 2974, 2875, 2626, 1676, 1520, 1495, 1339, 1274, 1180, 819, 783, 744 cm^{-1} .

HRMS (ESI): m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{18}\text{H}_{17}\text{N}_3\text{O}_3$: 324.1343; found: 324.1339.



1-(4-Bromophenyl)-2-((5-nitro-1H-indazol-1-yl)methyl) butan-1-one (5gb)

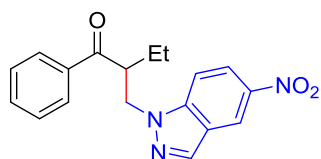
Pale yellow oil; yield: 71.6 mg (37%).

^1H NMR (600 MHz, CDCl_3): δ 8.65 (d, $J = 1.8$ Hz, 1H), 8.27 (dd, $J = 9.6, 2.4$ Hz, 1H), 8.16 (s, 1H), 7.72 (d, $J = 9.0$ Hz, 2H), 7.61 (d, $J = 9.0$ Hz, 1H), 7.55 (d, $J = 9.0$ Hz, 2H), 4.87 (dd, $J = 13.8, 8.4$ Hz, 1H), 4.44 (dd, $J = 13.8, 6.0$ Hz, 1H), 4.36 – 4.30 (m, 1H), 1.28 (d, $J = 7.2$ Hz, 3H).

^{13}C NMR (150 MHz, CDCl_3): δ 200.8, 142.4, 141.7, 136.4, 134.2, 132.1, 129.8, 128.9, 122.7, 121.7, 118.8, 109.8, 51.0, 41.3, 16.3.

IR (film): 2964, 1677, 1519, 1451, 1217, 1070, 941, 813, 754, 702 cm^{-1} .

HRMS (ESI): m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{17}\text{H}_{14}\text{BrN}_3\text{O}_3$: 388.0291; found: 388.0284.



2-((5-Nitro-1H-indazol-1-yl)methyl)-1-phenylbutan-1-one (5ob)

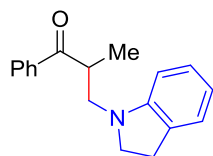
Pale yellow oil; yield: 107.3 mg (66%).

^1H NMR (600 MHz, CDCl_3): δ 8.61 (d, $J = 1.8$ Hz, 1H), 8.24 (dd, $J = 9.6, 2.4$ Hz, 1H), 8.14 (s, 1H), 7.80 (dd, $J = 8.4, 1.2$ Hz, 2H), 7.59 (d, $J = 9.0$ Hz, 1H), 7.50 (t, $J = 7.2$ Hz, 1H), 7.37 (t, $J = 7.8$ Hz, 2H), 4.90 (dd, $J = 13.8, 9.0$ Hz, 1H), 4.49 (dd, $J = 13.8, 5.4$ Hz, 1H), 4.31 – 4.29 (m, 1H), 1.90 – 1.82 (m, 1H), 1.72 – 1.69 (m, 1H), 0.96 (t, $J = 7.8$ Hz, 3H).

^{13}C NMR (150 MHz, CDCl_3): δ 201.9, 142.3, 141.6, 136.5, 136.3, 133.4, 128.6, 128.1, 122.6, 121.5, 118.7, 109.9, 49.7, 47.7, 24.1, 11.3.

IR (film): 3125, 1685, 1597, 1486, 1336, 1217, 1022, 976, 731, 689 cm^{-1} .

HRMS (ESI): m/z $[M+H]^+$ calcd for $\text{C}_{18}\text{H}_{17}\text{N}_3\text{O}_3$: 324.1343; found: 324.1339.



3-(Indolin-1-yl)-2-methyl-1-phenylpropan-1-one (5ac)

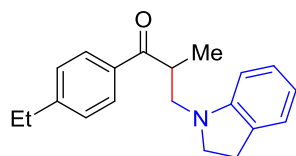
Pale yellow oil; yield: 82.5 mg (62%).

^1H NMR (600 MHz, DMSO-d_6): δ 8.03 – 7.93 (m, 2H), 7.61 (t, $J = 7.2$ Hz, 1H), 7.51 (t, $J = 7.8$ Hz, 2H), 6.95 – 6.92 (m, 2H), 6.50 (dd, $J = 15.0, 7.8$ Hz, 2H), 4.02 – 3.95 (m, 1H), 3.41 (dd, $J = 13.2, 7.8$ Hz, 1H), 3.29 – 3.23 (m, 2H), 3.06 (dd, $J = 13.2, 6.0$ Hz, 1H), 2.81 – 2.71 (m, 2H), 1.14 (d, $J = 7.2$ Hz, 3H).

^{13}C NMR (150 MHz, DMSO-d_6): δ 203.5, 152.8, 136.6, 133.7, 129.5, 129.3, 128.6, 127.5, 124.5, 117.5, 107.0, 54.0, 53.3, 39.7, 28.5, 16.4.

IR (film): 2958, 2928, 1797, 1678, 1599, 1461, 1395, 1330, 1261, 1181, 1020, 973, 744 cm^{-1} .

HRMS (ESI): m/z $[M+H]^+$ calcd for $\text{C}_{18}\text{H}_{19}\text{NO}$: 266.1539; found: 266.1524.



1-(4-Ethylphenyl)-3-(indolin-1-yl)-2-methylpropan-1-one (5dc)

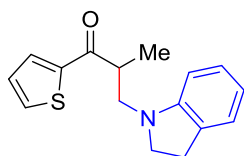
Colorless oil; yield: 74.8 mg (51%).

^1H NMR (600 MHz, DMSO-d_6): δ 7.94 (d, $J = 7.8$ Hz, 2H), 7.36 (d, $J = 8.4$ Hz, 2H), 6.97 (t, $J = 7.2$ Hz, 2H), 6.53 (dd, $J = 15.6, 8.4$ Hz, 2H), 4.01 – 3.94 (m, 1H), 3.43 (dd, $J = 13.8, 7.8$ Hz, 1H), 3.32 – 3.24 (m, 2H), 3.08 (dd, $J = 13.2, 6.0$ Hz, 1H), 2.84 – 2.74 (m, 2H), 2.67 (q, $J = 7.8$ Hz, 2H), 1.19 (t, $J = 7.8$ Hz, 3H), 1.16 (d, $J = 7.2$ Hz, 3H).

^{13}C NMR (150 MHz, DMSO-d_6): δ 207.7, 157.6, 154.9, 139.1, 134.2, 133.6, 133.4, 132.3, 129.2, 122.2, 111.7, 58.8, 58.1, 44.3, 33.3, 33.2, 21.2, 20.3.

IR (film): 3047, 2965, 2929, 1677, 1606, 1489, 1375, 1249, 1223, 1180, 974, 846, 744 cm^{-1} .

HRMS (ESI): m/z $[M+H]^+$ calcd for $\text{C}_{20}\text{H}_{23}\text{NO}$: 294.1852; found: 294.1847.



3-(Indolin-1-yl)-2-methyl-1-(thiophen-2-yl)propan-1-one (5nc)

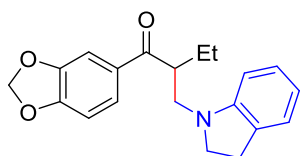
Pale yellow oil; yield: 62.4 mg (46%).

^1H NMR (600 MHz, DMSO- d_6): δ 8.04 – 8.02 (m, 1H), 7.99 (d, J = 4.8 Hz, 1H), 7.25 – 7.19 (m, 1H), 6.94 (t, J = 6.6 Hz, 2H), 6.50 (dd, J = 18.0, 7.8 Hz, 2H), 3.87–3.81 (m, 1H), 3.42 (dd, J = 13.8, 9.0 Hz, 1H), 3.36 – 3.32 (m, 1H), 3.22 (q, J = 17.4 Hz, 1H), 3.02 (dd, J = 13.8, 6.0 Hz, 1H), 2.83 – 2.72 (m, 2H), 1.15 (d, J = 7.2 Hz, 3H).

^{13}C NMR (150 MHz, DMSO- d_6): δ 196.5, 152.7, 144.1, 135.8, 133.8, 129.5, 129.3, 127.5, 124.5, 117.6, 107.1, 54.0, 53.5, 41.3, 28.4, 16.6.

IR (film): 3415, 2253, 2126, 2000, 1792, 1654, 1415, 1226, 1051, 1026, 825, 763, 626 cm^{-1} .

HRMS (ESI): m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{16}\text{H}_{17}\text{NOS}$: 272.1104; found: 272.1101.



1-(Benzo[d][1,3]dioxol-5-yl)-2-(indolin-1-ylmethyl)butan-1-one (5qc)

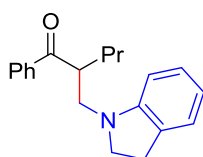
Colorless oil; yield: 91.6 mg (57%).

^1H NMR (600 MHz, DMSO- d_6): δ 7.56 (d, J = 8.4 Hz, 1H), 7.44 (d, J = 1.8 Hz, 1H), 7.07 (t, J = 7.8 Hz, 1H), 7.02 (d, J = 7.2 Hz, 1H), 6.83 (d, J = 7.8 Hz, 1H), 6.64 (s, 1H), 6.54 (s, 1H), 6.03 (s, 2H), 3.70 (s, 1H), 3.51 (dd, J = 13.2, 8.4 Hz, 1H), 3.36 – 3.17 (m, 3H), 2.93 – 2.82 (m, 2H), 1.84 – 1.78 (m, 1H), 1.70 – 1.62 (m, 1H), 0.93 (t, J = 7.8 Hz, 3H).

^{13}C NMR (150 MHz, DMSO- d_6): δ 201.5, 152.8, 152.0, 148.4, 132.4, 129.5, 127.5, 125.0, 124.5, 117.5, 108.5, 107.8, 107.0, 102.5, 54.1, 52.2, 45.7, 28.4, 24.4, 11.8.

IR (film): 3432, 2358, 2334, 2251, 2125, 1658, 1490, 1443, 1361, 1250, 1027, 824, 763, 623 cm^{-1} .

HRMS (ESI): m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{20}\text{H}_{21}\text{NO}_3$: 324.1594; found: 324.1584.



2-(Indolin-1-ylmethyl)-1-phenylpentan-1-one (5rc)

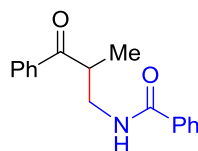
Pale yellow oil; yield: 114.8 mg (78%).

^1H NMR (600 MHz, DMSO- d_6): δ 7.98 (d, J = 7.2 Hz, 2H), 7.58 (t, J = 7.2 Hz, 1H), 7.48 (t, J = 7.8 Hz, 2H), 6.97 – 6.90 (m, 2H), 6.53 – 6.45 (m, 2H), 3.97–3.94 (m, 1H), 3.44 (dd, J = 13.8, 9.0 Hz, 1H), 3.29 (q, J = 16.2, 1H), 3.17 (q, J = 17.4, 1H), 3.08 (dd, J = 13.8, 5.4 Hz, 1H), 2.77 – 2.65 (m, 2H), 1.67 – 1.60 (m, 1H), 1.54 – 1.46 (m, 1H), 1.28 – 1.17 (m, 2H), 0.80 (t, J = 7.8 Hz, 3H).

^{13}C NMR (150 MHz, DMSO- d_6): δ 203.6, 152.7, 137.6, 133.6, 129.5, 129.2, 128.4, 127.5, 124.5, 117.6, 107.0, 54.1, 52.6, 44.7, 33.4, 28.5, 20.5, 14.6.

IR (film): 3053, 2957, 2929, 2866, 1678, 1604, 1462, 1376, 1211, 1180, 976, 790, 744, 555 cm^{-1} .

HRMS (ESI): m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{20}\text{H}_{23}\text{NO}$: 294.1852; found: 294.1847.



***N*-(2-methyl-3-oxo-3-phenylpropyl)benzamide (5ad)**

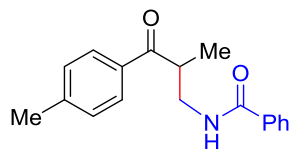
Colorless oil; yield: 82.1 mg (61%).

^1H NMR (600 MHz, CDCl_3): δ 7.97 (dd, J = 8.4, 1.2 Hz, 2H), 7.71 (dd, J = 8.4, 1.2 Hz, 2H), 7.57 (t, J = 7.8 Hz, 1H), 7.51 – 7.41 (m, 3H), 7.38 (t, J = 7.8 Hz, 2H), 6.77 (s, 1H), 3.94 – 3.88 (m, 1H), 3.81 – 3.77 (m, 1H), 3.71–3.67 (m, 1H), 1.27 (d, J = 7.2 Hz, 3H).

^{13}C NMR (150 MHz, CDCl_3): δ 204.0, 167.6, 135.8, 134.4, 133.4, 131.4, 128.8, 128.5, 128.4, 126.9, 42.0, 40.9, 16.0.

IR (film): 3062, 2973, 1676, 1644, 1577, 1536, 1451, 1301, 1215, 1079, 973, 795, 702 cm^{-1} .

HRMS (ESI): m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{17}\text{H}_{17}\text{NO}_2$: 268.1332; found: 268.1328.



***N*-(2-methyl-3-oxo-3-(*p*-tolyl)propyl)benzamide (5bd)**

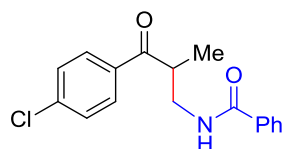
Pale yellow oil; Yield: 60.1 mg (43%).

^1H NMR (600 MHz, CDCl_3): δ 7.87 (d, J = 7.2 Hz, 2H), 7.70 (dd, J = 8.4, 1.2 Hz, 2H), 7.48 – 7.43 (m, 1H), 7.38 (t, J = 7.8 Hz, 2H), 7.27 (s, 2H), 6.76 (s, 1H), 3.91 – 3.85 (m, 1H), 3.80–3.76 (m, 1H), 3.77 – 3.66 (m, 1H), 2.40 (s, 3H), 1.26 (d, J = 7.2 Hz, 3H).

^{13}C NMR (150 MHz, CDCl_3): δ 203.6, 167.6, 144.4, 134.4, 133.3, 131.4, 129.5, 128.6, 128.5, 126.9, 42.0, 40.8, 21.6, 16.1.

IR (film): 3061, 2972, 2873, 2360, 1672, 1645, 1537, 1456, 1300, 1182, 972, 828, 700 cm^{-1} .

HRMS (ESI): m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{18}\text{H}_{19}\text{NO}_2$: 282.1489; found: 282.1484.



***N*-(3-(4-chlorophenyl)-2-methyl-3-oxopropyl)benzamide (5fd)**

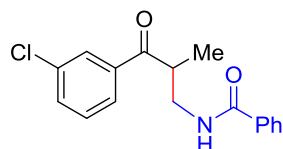
Pale yellow oil; yield: 50.2 mg (33%).

^1H NMR (600 MHz, CDCl_3): δ 7.91 (d, J = 9.0 Hz, 2H), 7.74 (dd, J = 9.0, 2.4 Hz, 1H), 7.70 (dd, J = 8.4, 1.8 Hz, 2H), 7.46 – 7.42 (m, 2H), 7.40 – 7.35 (m, 2H), 6.76 (s, 1H), 3.90 – 3.85 (m, 1H), 3.77 – 3.72 (m, 1H), 3.70 – 3.66 (m, 1H), 1.25 (d, J = 7.2 Hz, 3H).

^{13}C NMR (150 MHz, CDCl_3): δ 202.6, 167.6, 139.9, 134.2, 134.1, 131.5, 129.9, 129.1, 128.5, 126.8, 42.0, 40.9, 15.8.

IR (film): 3066, 2974, 2875, 1682, 1642, 1537, 1487, 1425, 1303, 1209, 1079, 986, 799 cm^{-1} .

HRMS (ESI): m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{17}\text{H}_{16}\text{ClNO}_2$: 302.0942; found: 302.0940.



***N*-(3-(3-chlorophenyl)-2-methyl-3-oxopropyl)benzamide (5ld)**

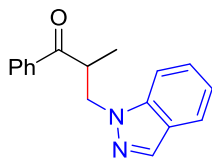
Pale yellow oil; yield: 86.1 mg (57%).

^1H NMR (600 MHz, CDCl_3): δ 7.94 (t, J = 1.8 Hz, 1H), 7.84 (d, J = 7.8 Hz, 1H), 7.75 – 7.67 (m, 2H), 7.53 (d, J = 7.8 Hz, 1H), 7.47 (t, J = 7.8 Hz, 1H), 7.40 (q, J = 16.2 Hz, 3H), 6.73 (s, 1H), 3.90 – 3.84 (m, 1H), 3.80 – 3.75 (m, 1H), 3.70–3.65 (m, 1H), 1.27 (d, J = 7.2 Hz, 3H).

^{13}C NMR (150 MHz, CDCl_3): δ 202.6, 167.6, 137.4, 135.2, 134.2, 133.3, 131.5, 130.1, 128.6, 128.5, 126.9, 126.6, 41.9, 41.2, 15.8.

IR (film): 3064, 2930, 1678, 1645, 1587, 1488, 1300, 1092, 1013, 974, 841, 698 cm^{-1} .

HRMS (ESI): m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{17}\text{H}_{16}\text{ClNO}_2$: 302.0942; found: 302.0937.



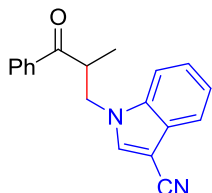
3-(1*H*-indazol-1-yl)-2-methyl-1-phenylpropan-1-one (5ae)

Pale yellow oil; yield: 62.6 mg (79%).

^1H NMR (600 MHz, CDCl_3): δ 7.97 (d, J = 0.6 Hz, 1H), 7.90 (dd, J = 8.4, 1.2 Hz, 2H), 7.66 (d, J = 7.8 Hz, 1H), 7.51 (t, J = 8.4 Hz, 2H), 7.45 – 7.30 (m, 3H), 7.12-7.08 (m, 1H), 4.81 (dd, J = 13.8, 6.6 Hz, 1H), 4.45 (dd, J = 13.8, 6.6 Hz, 1H), 4.39 – 4.33 (m, 1H), 1.23 (d, J = 6.6 Hz, 3H).

^{13}C NMR (150 MHz, CDCl_3): δ 202.3, 140.1, 135.9, 133.6, 133.2, 128.6, 128.3, 126.4, 123.7, 120.9, 120.5, 109.3, 50.7, 41.6, 16.2.

IR (film): 3119, 2932, 2877, 2218, 1815, 1679, 1532, 1460, 1363, 1183, 974, 746, 704 cm^{-1} .



1-(2-Methyl-3-oxo-3-phenylpropyl)-1*H*-indole-3-carbonitrile (5af)

Pale yellow oil; yield: 42.7 mg (54%).

^1H NMR (600 MHz, CDCl_3): δ 7.81 (d, J = 7.8 Hz, 2H), 7.71 (d, J = 7.8 Hz, 1H), 7.64 (s, 1H), 7.54 (t, J = 7.2 Hz, 1H), 7.46 (d, J = 8.4 Hz, 1H), 7.41 (t, J = 7.8 Hz, 2H), 7.35 (t, J = 7.8 Hz, 1H), 7.27 (t, J = 7.8 Hz, 1H), 4.68 (dd, J = 15.0, 8.4 Hz, 1H), 4.27 (dd, J = 14.4, 6.0 Hz, 1H), 4.06 – 4.01 (m, 1H), 1.29 (d, J = 7.2 Hz, 3H).

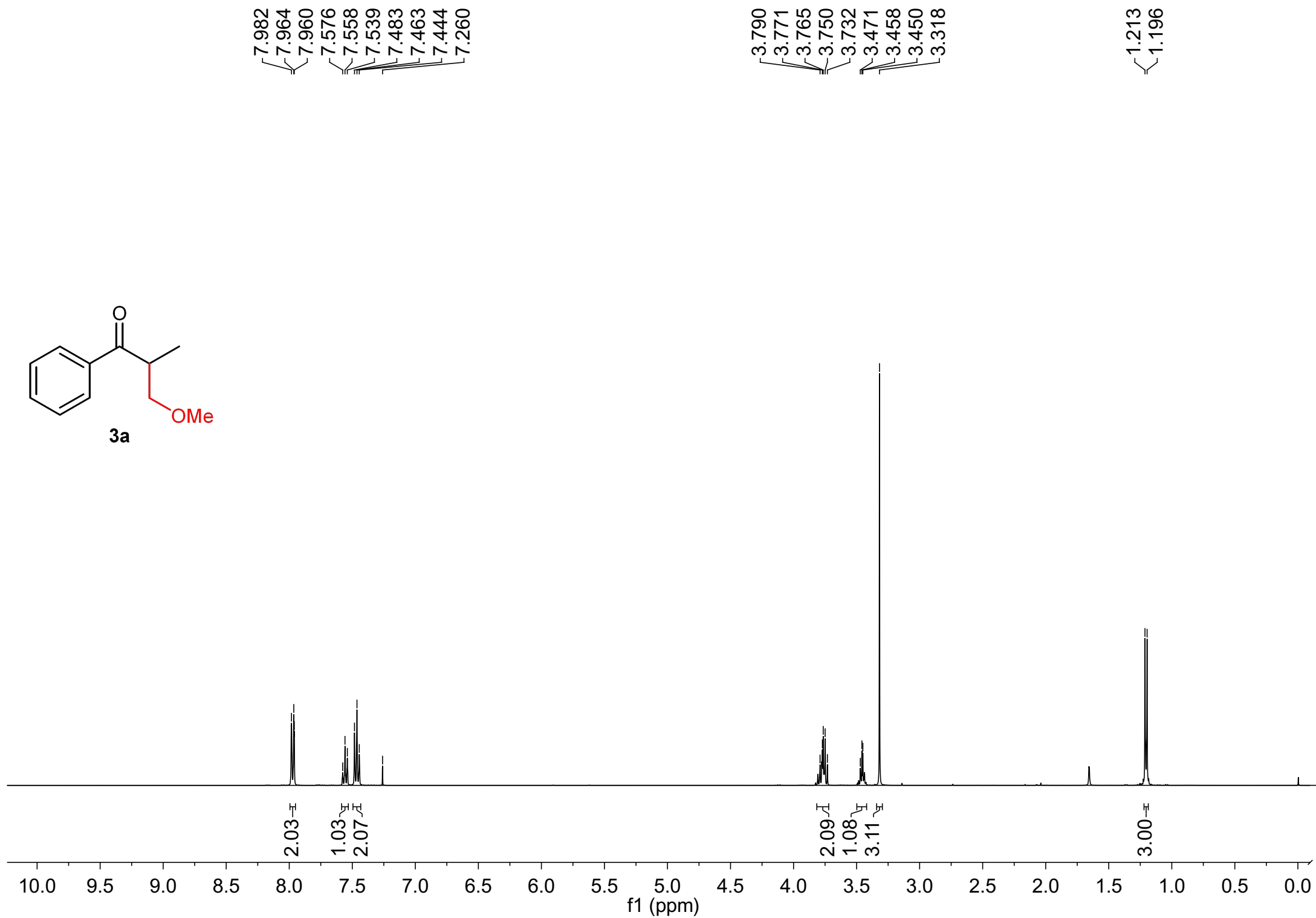
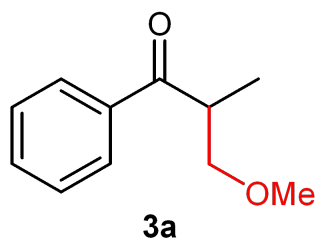
^{13}C NMR (150 MHz, CDCl_3): δ 201.1, 135.7, 135.3, 133.7, 128.8, 128.2, 127.8, 123.9, 122.2, 120.1, 115.7, 110.3, 86.0, 49.0, 41.2, 16.6.

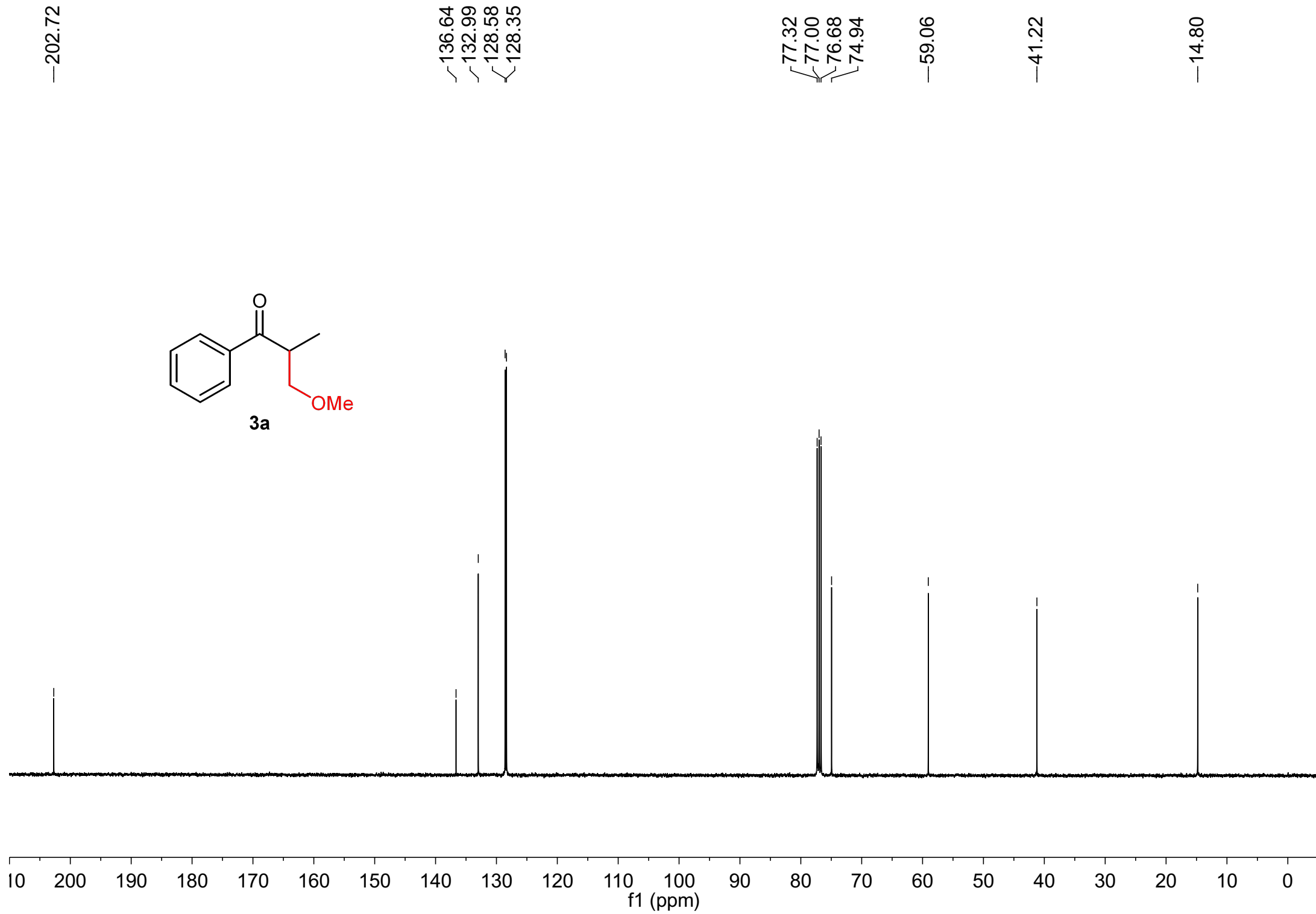
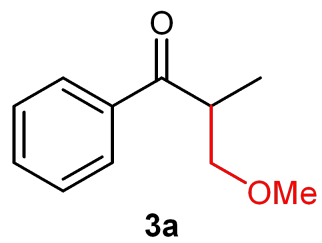
IR (film): 3119, 3057, 2924, 2853, 2218, 1678, 1532, 1392, 1232, 1181, 974, 745, 704 cm^{-1} .

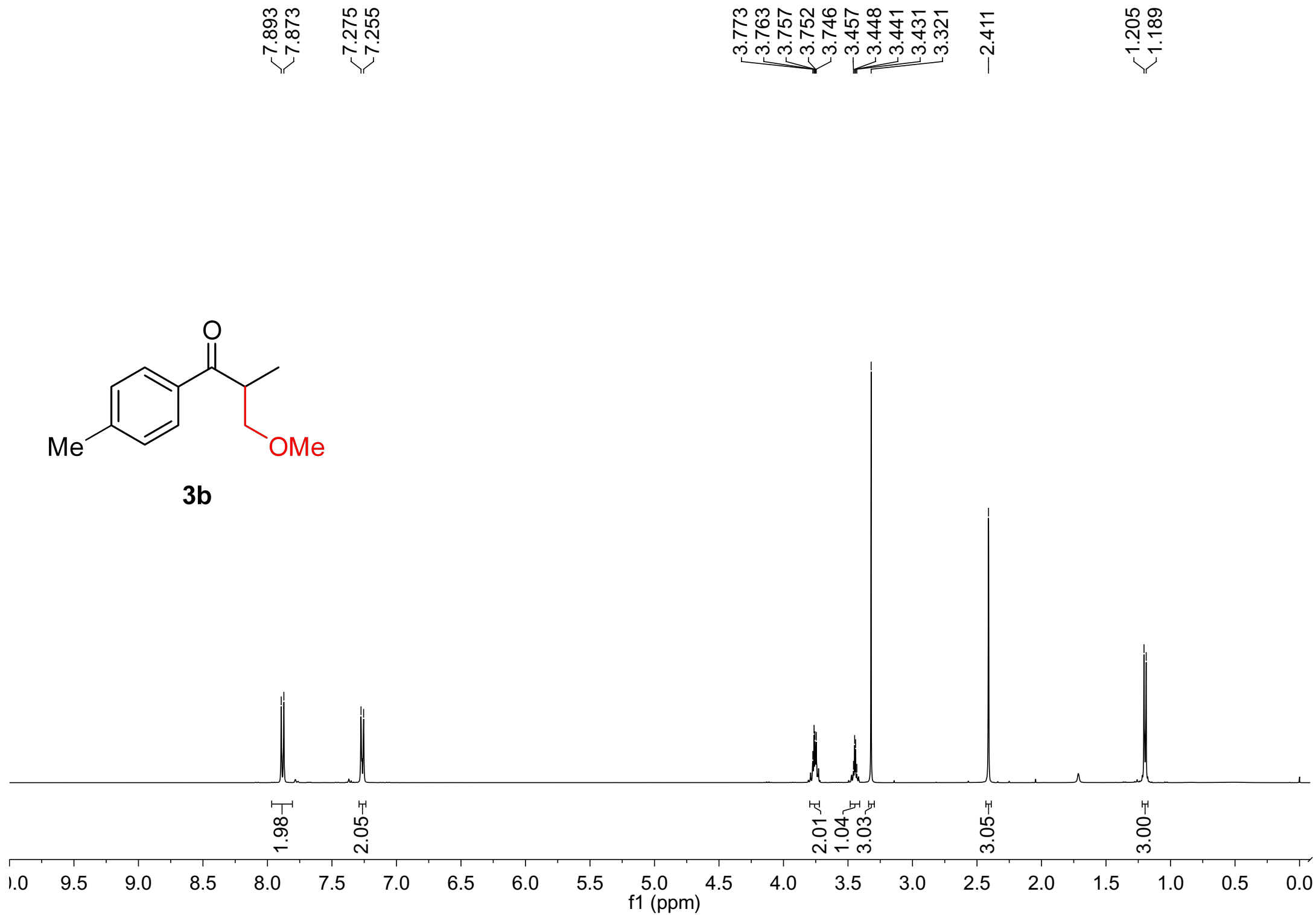
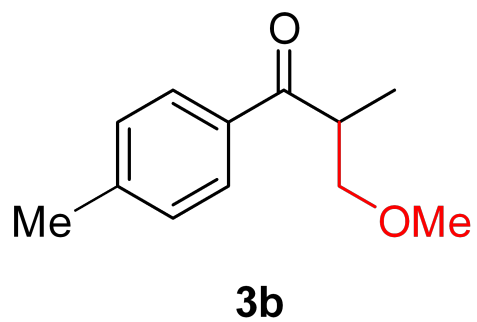
4. References

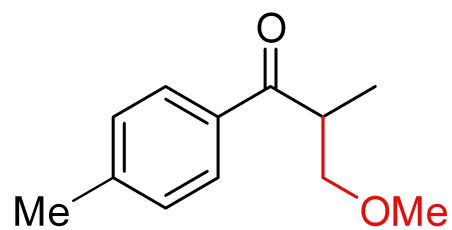
- [1] Gembus, V.; Bonnet, J.-J.; Janin, F.; Bohn, P.; Levacher, V.; Brière, J.-F. *Org. Biomol. Chem.* **2010**, *8*, 3287.

5. Copy of NMR spectra

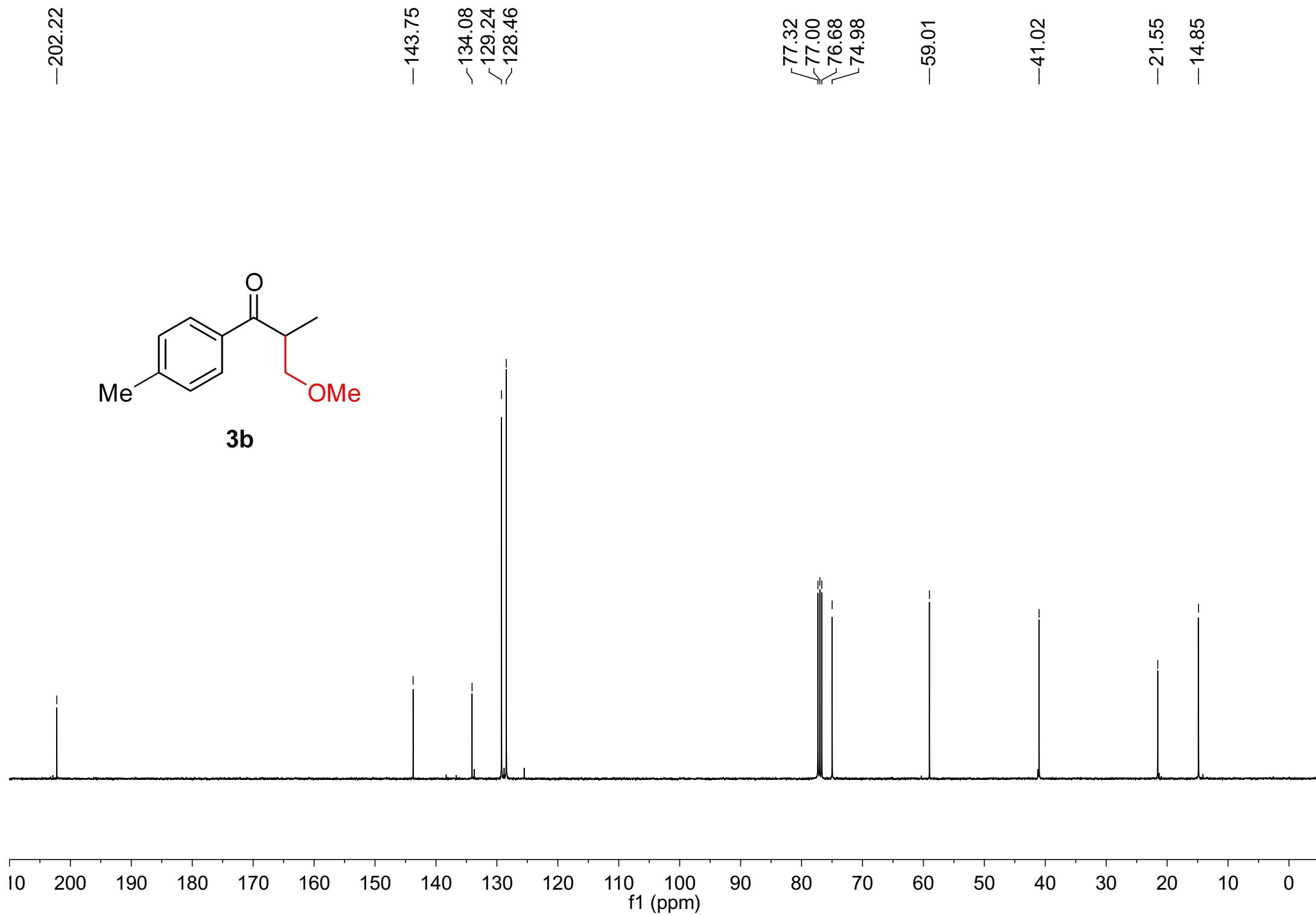


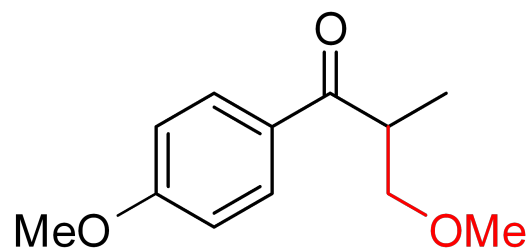




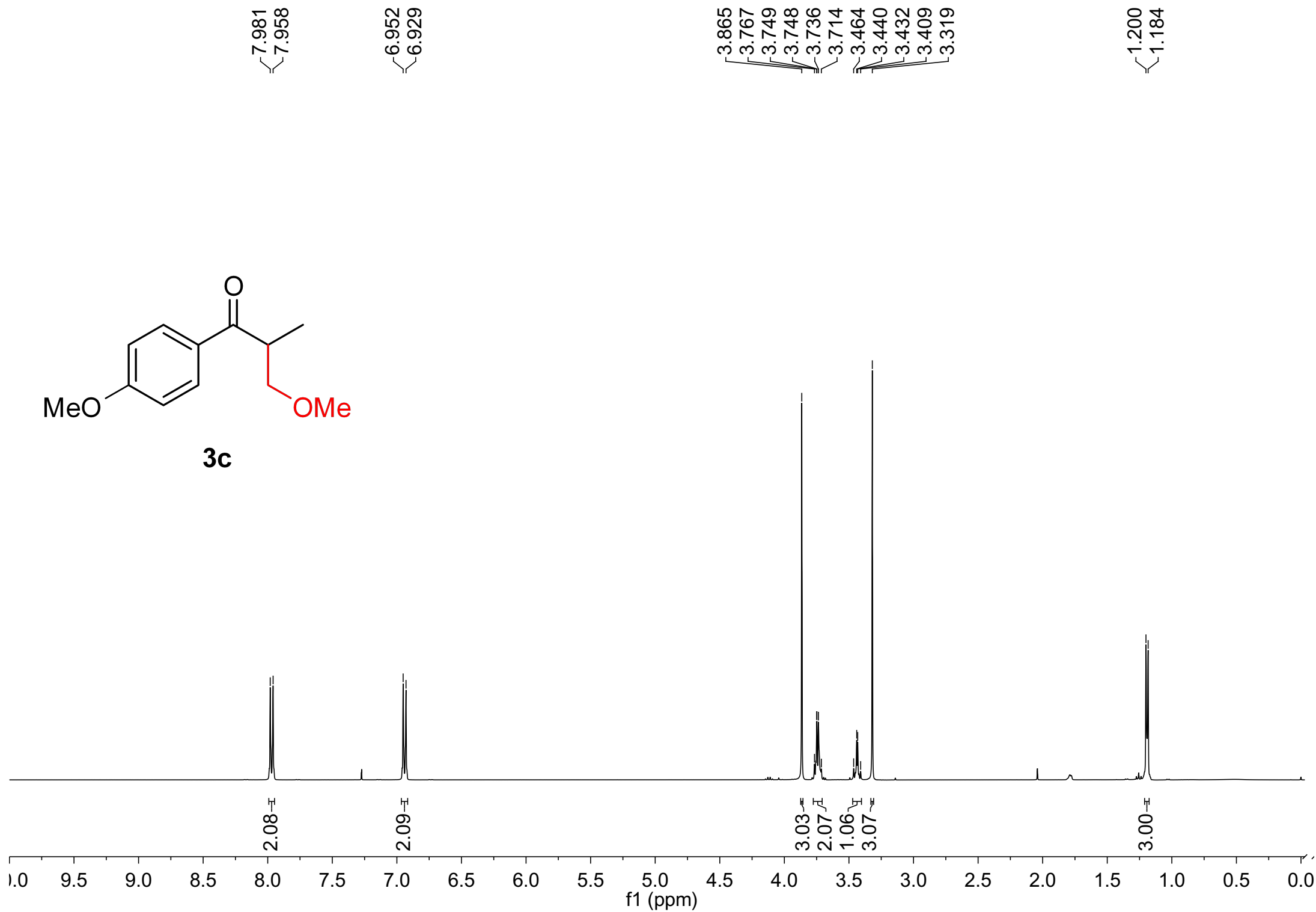


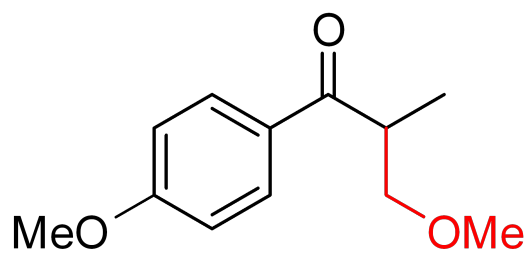
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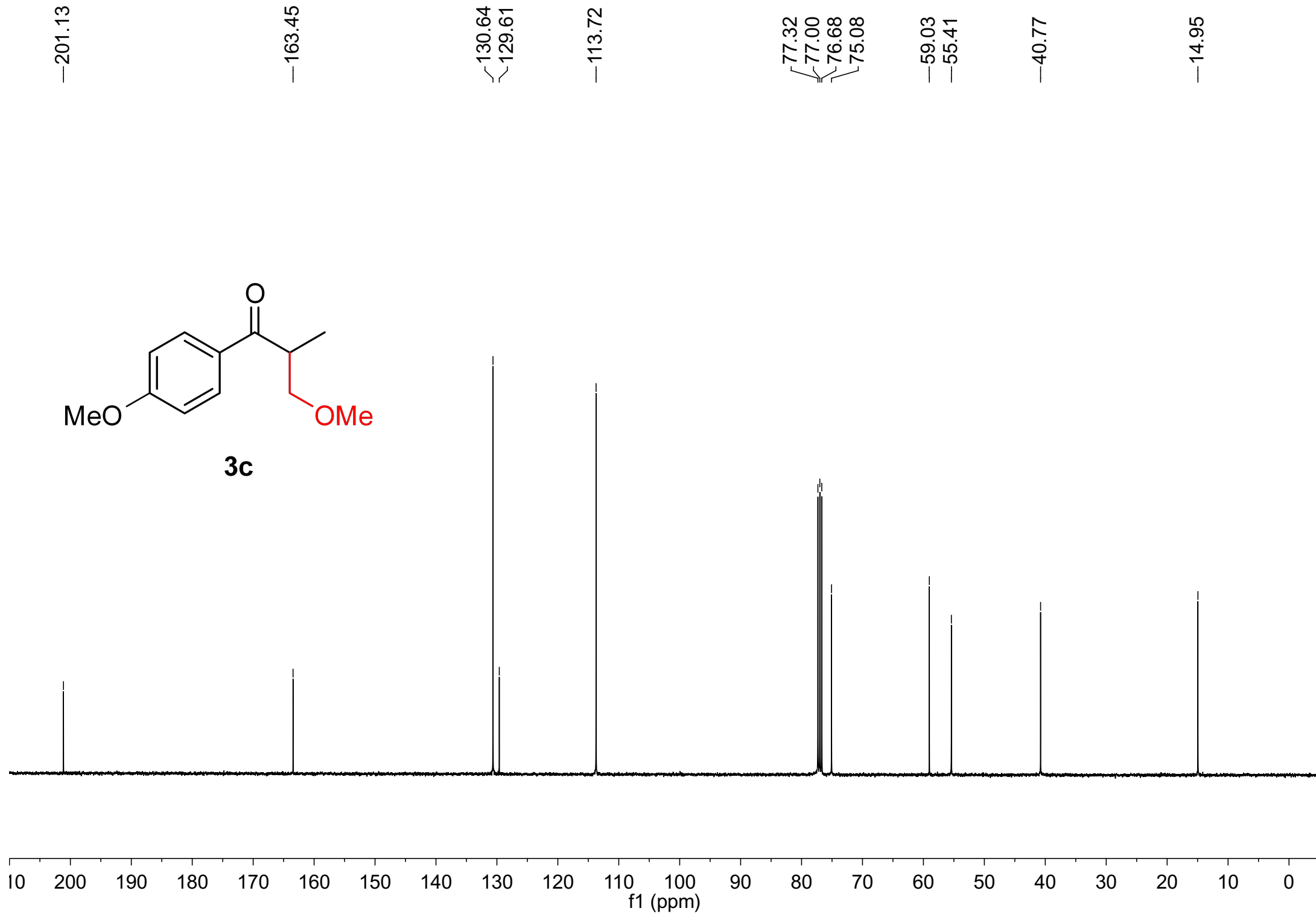


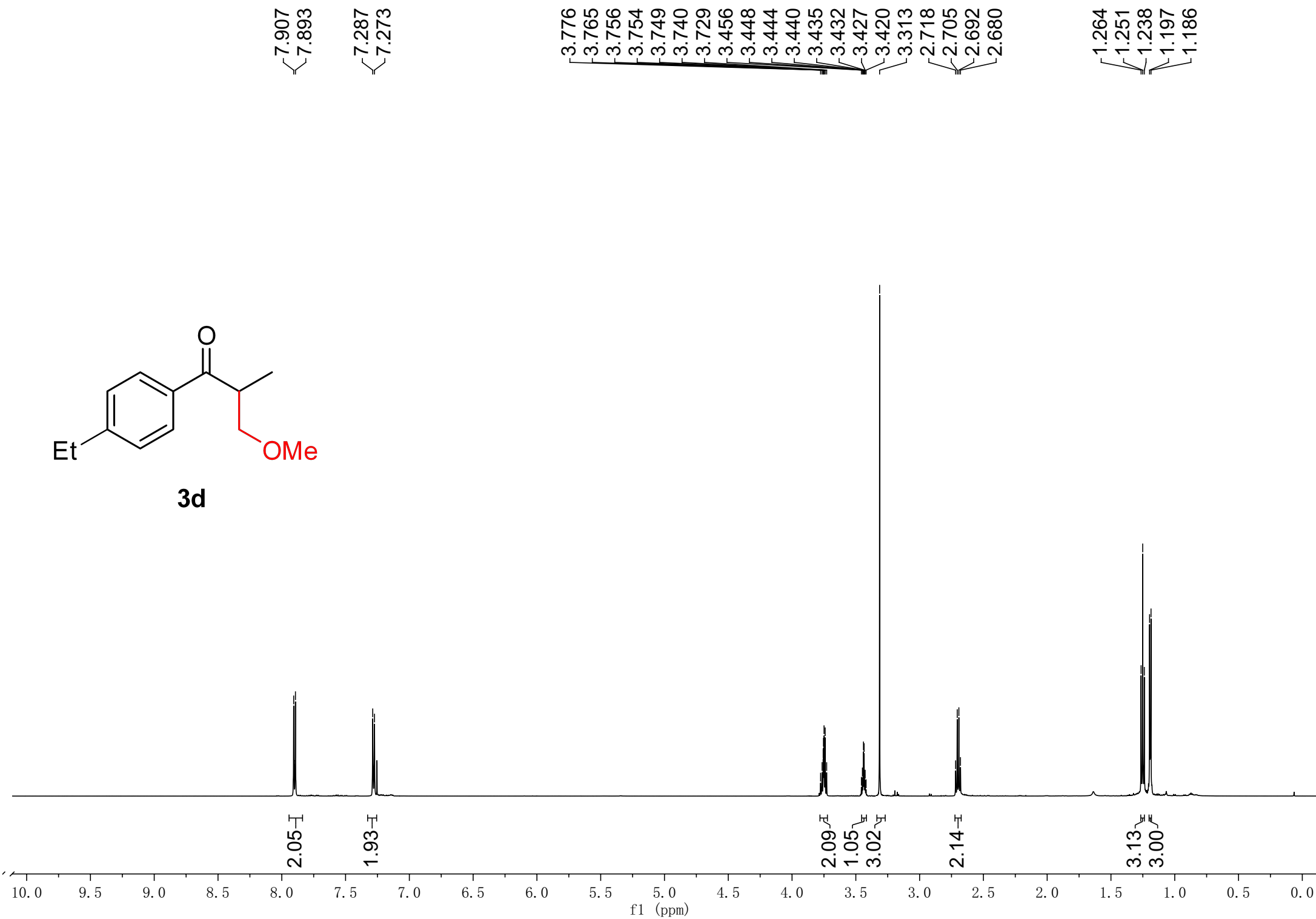
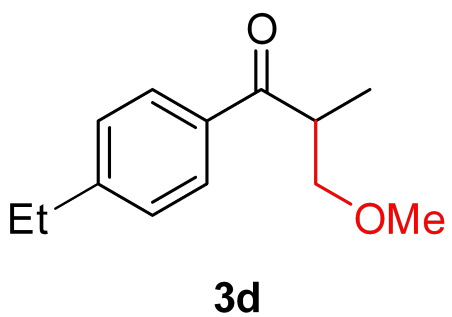
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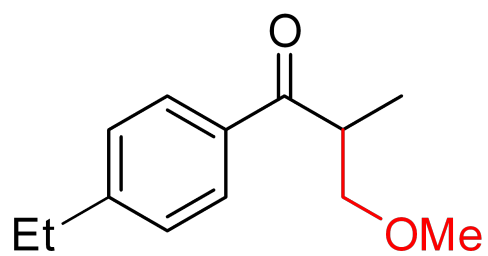




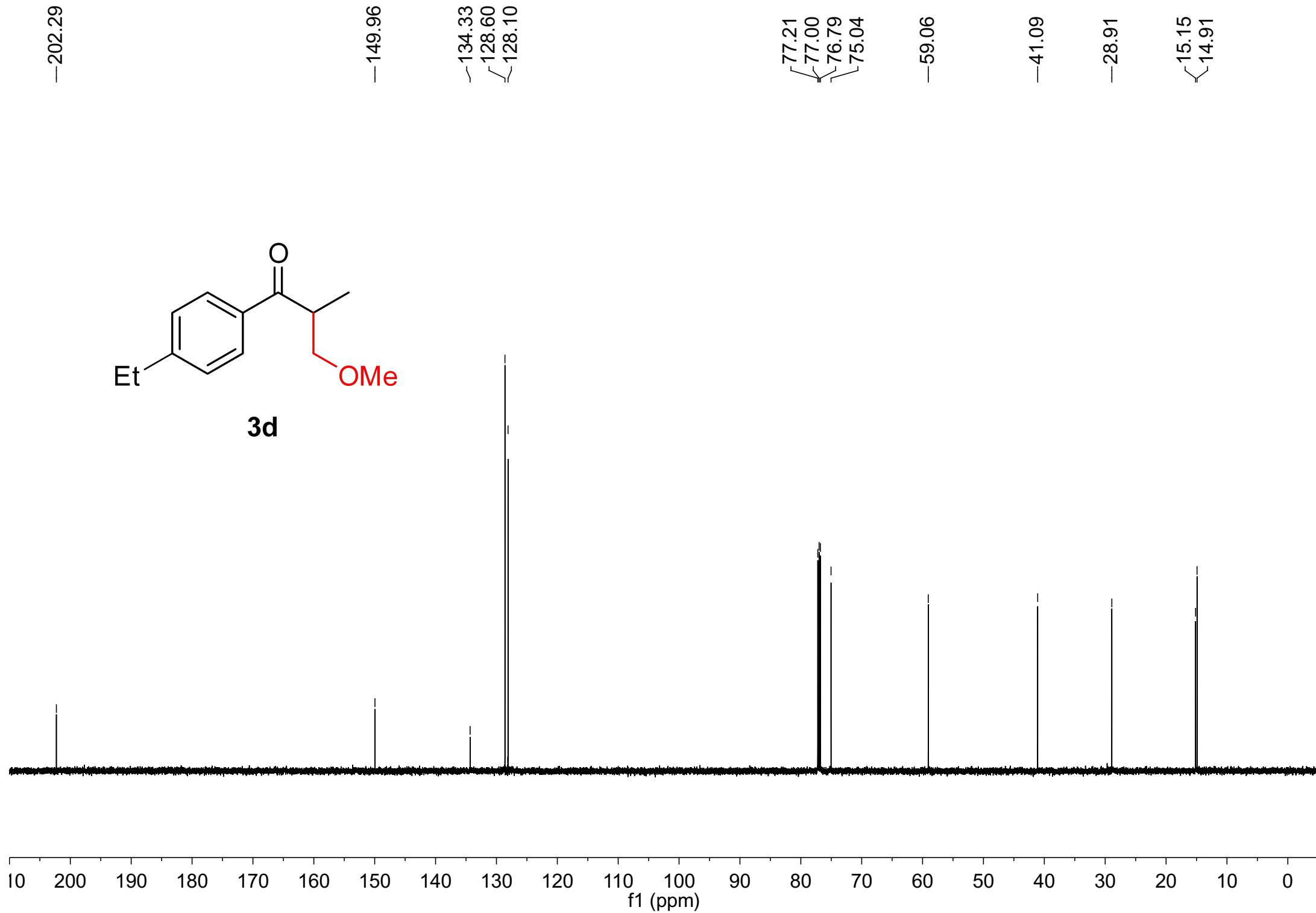
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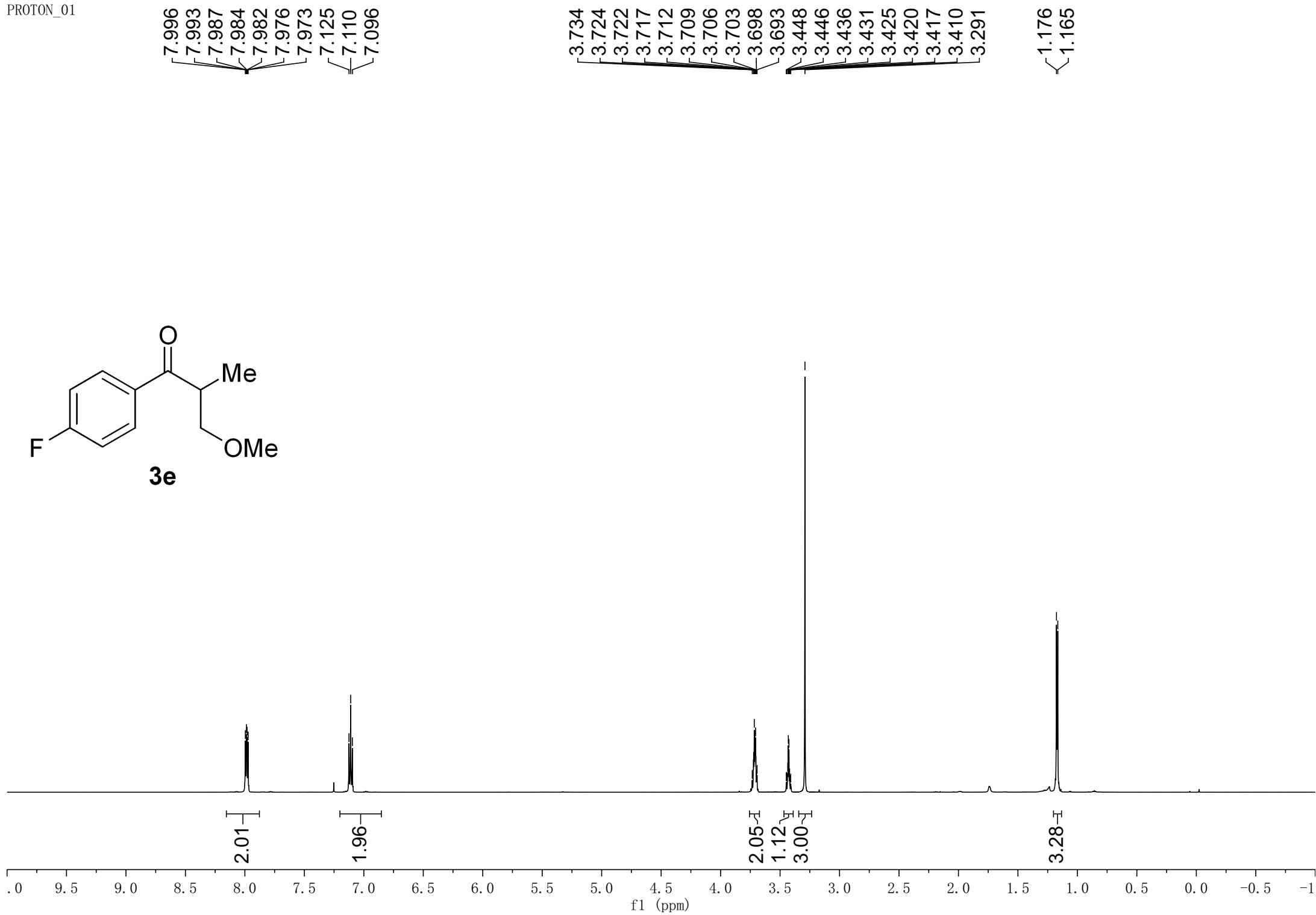




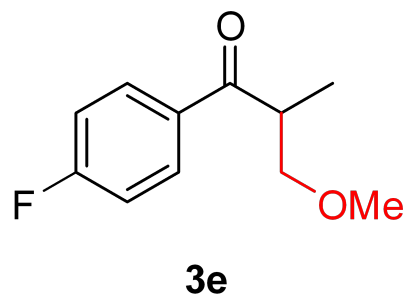


3d





CARBON_01



—201.17

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133.10
133.08
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130.96

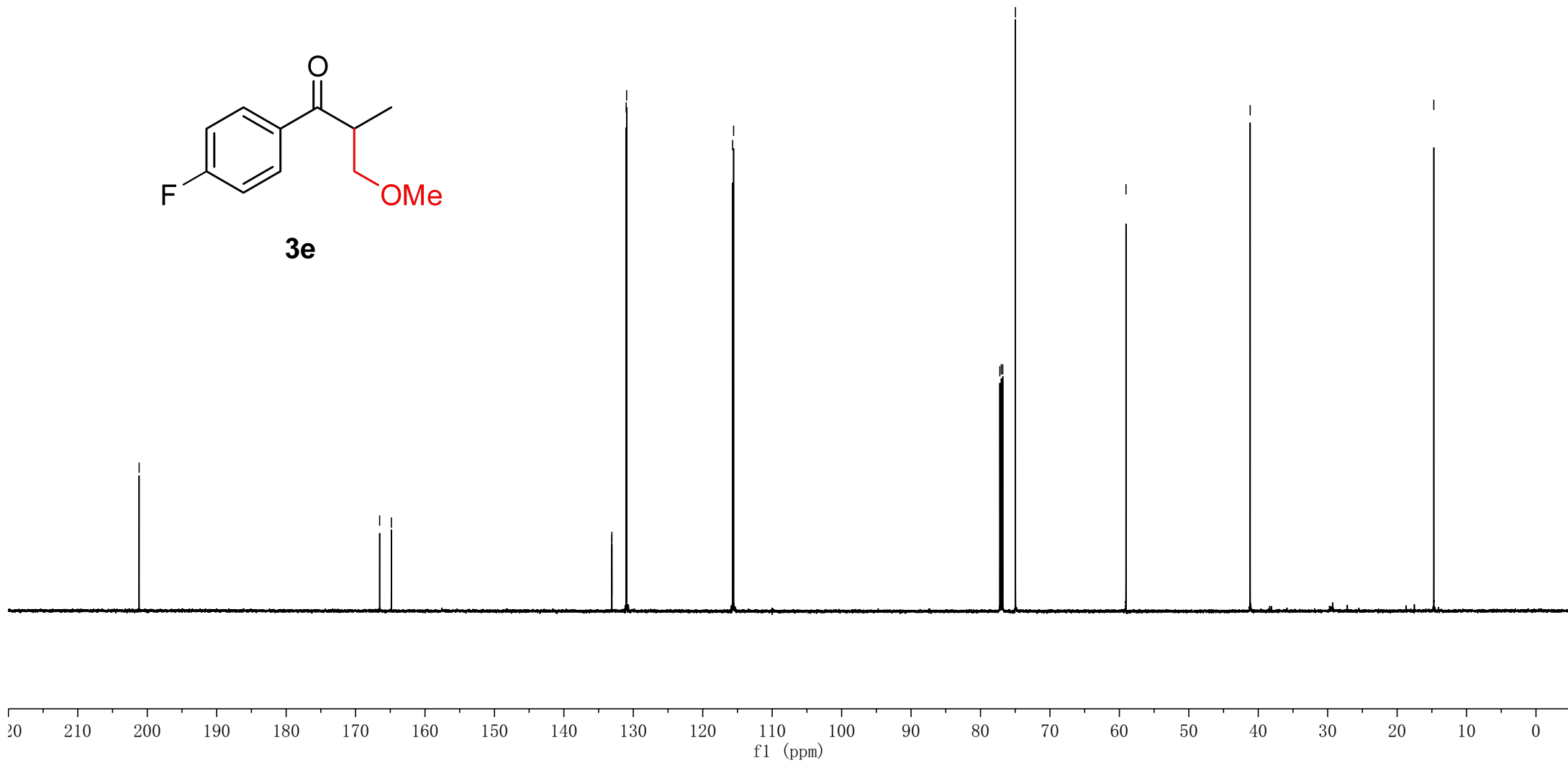
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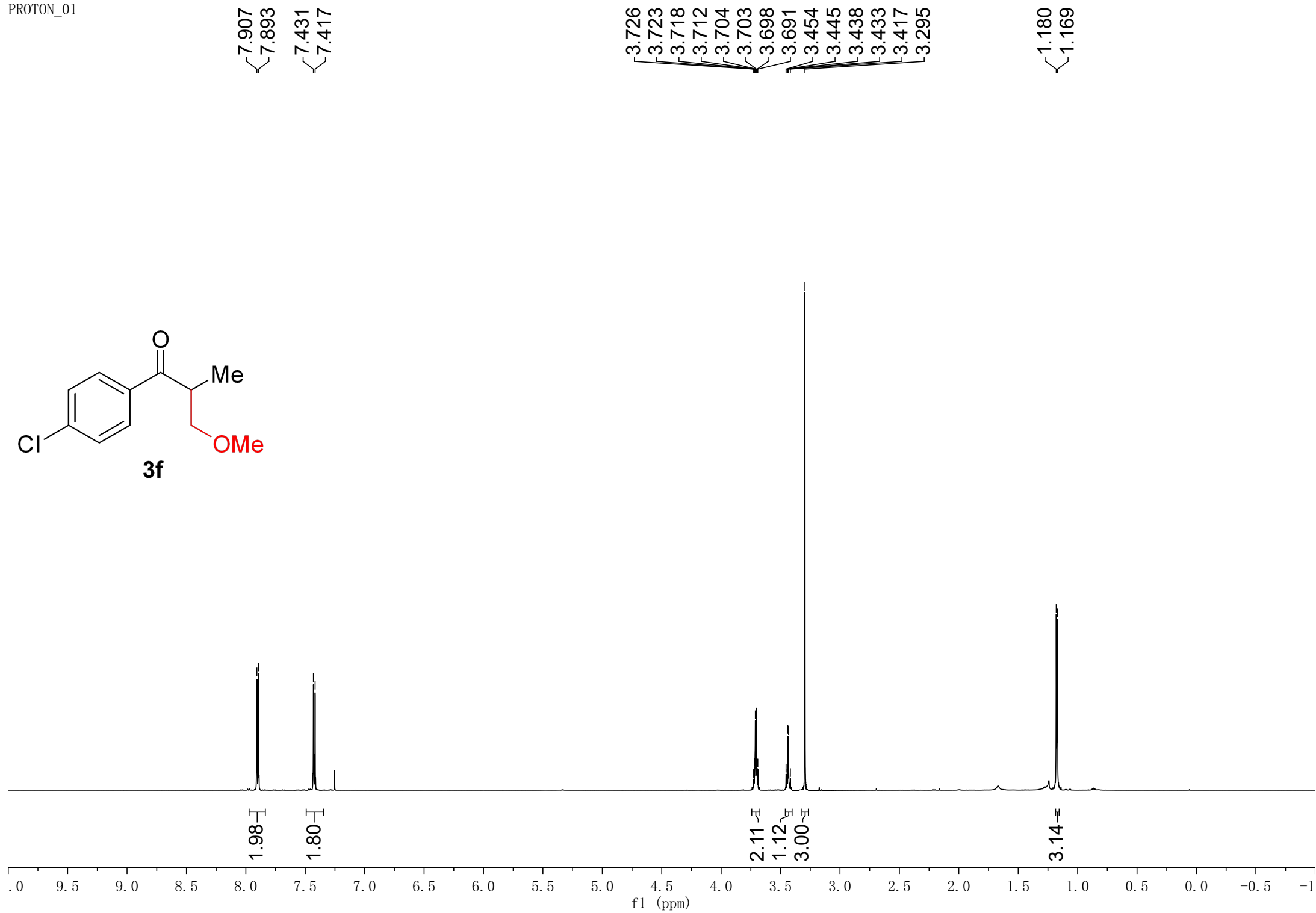
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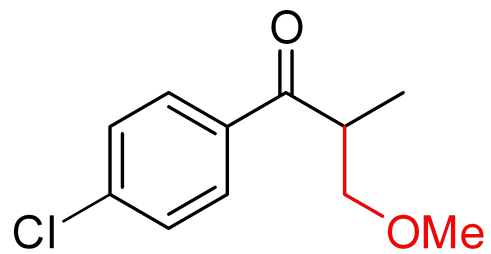
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—41.16

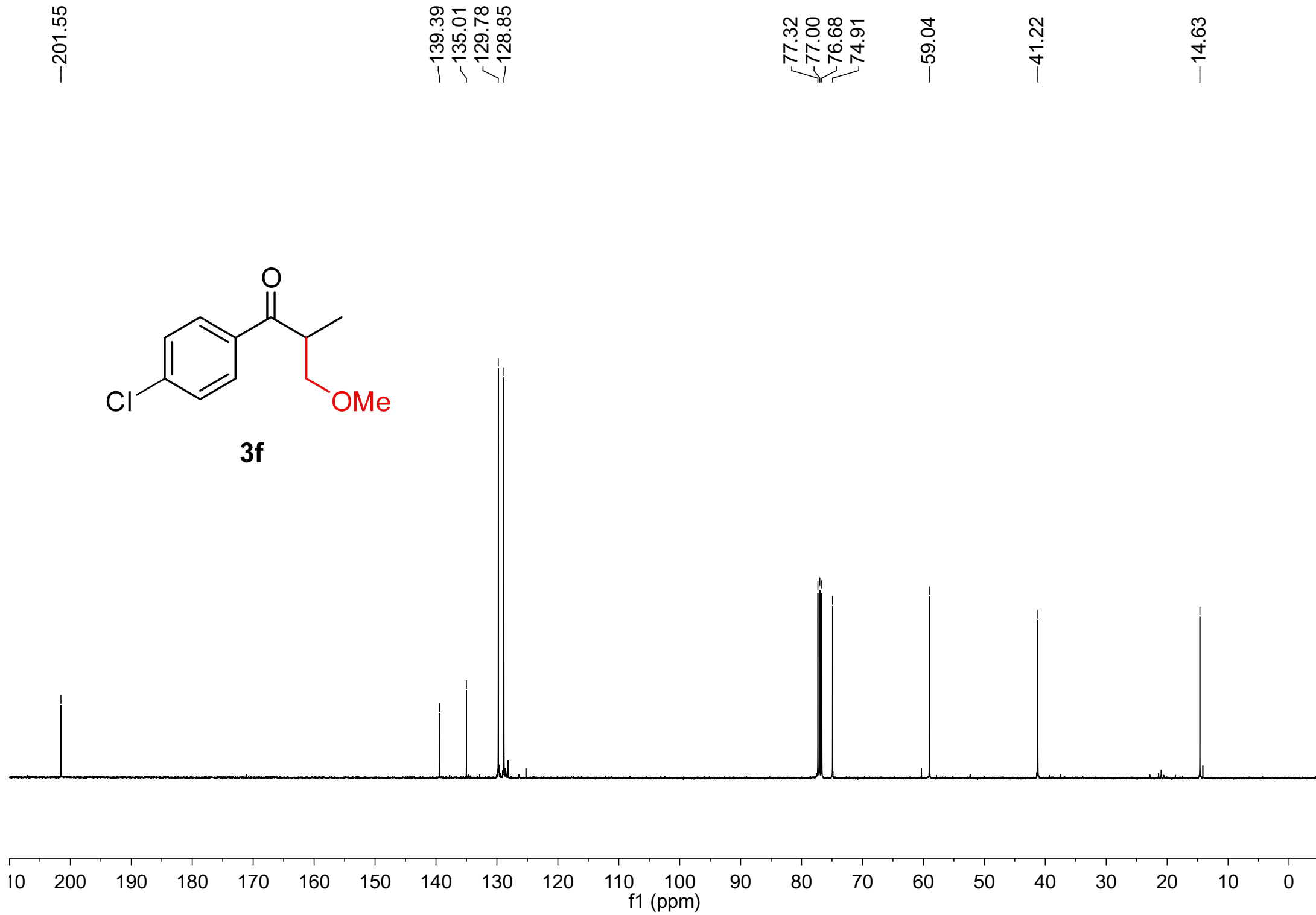
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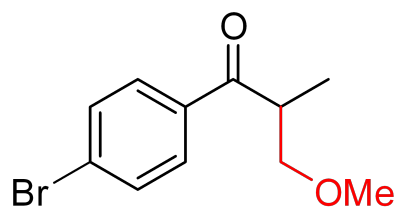




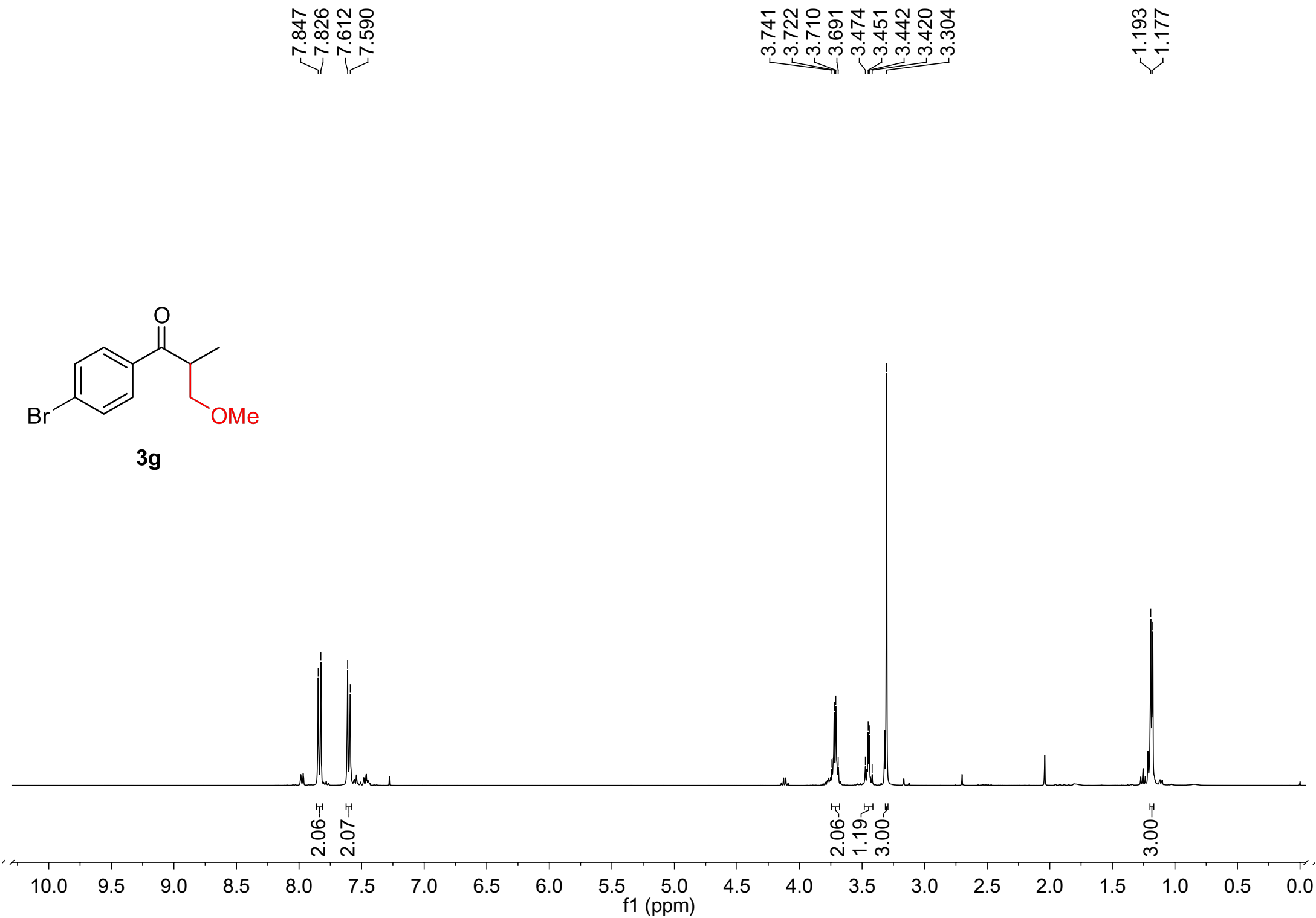


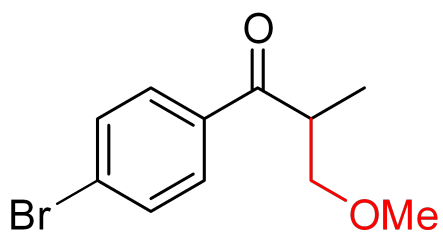
3f





3g





3g

—201.73

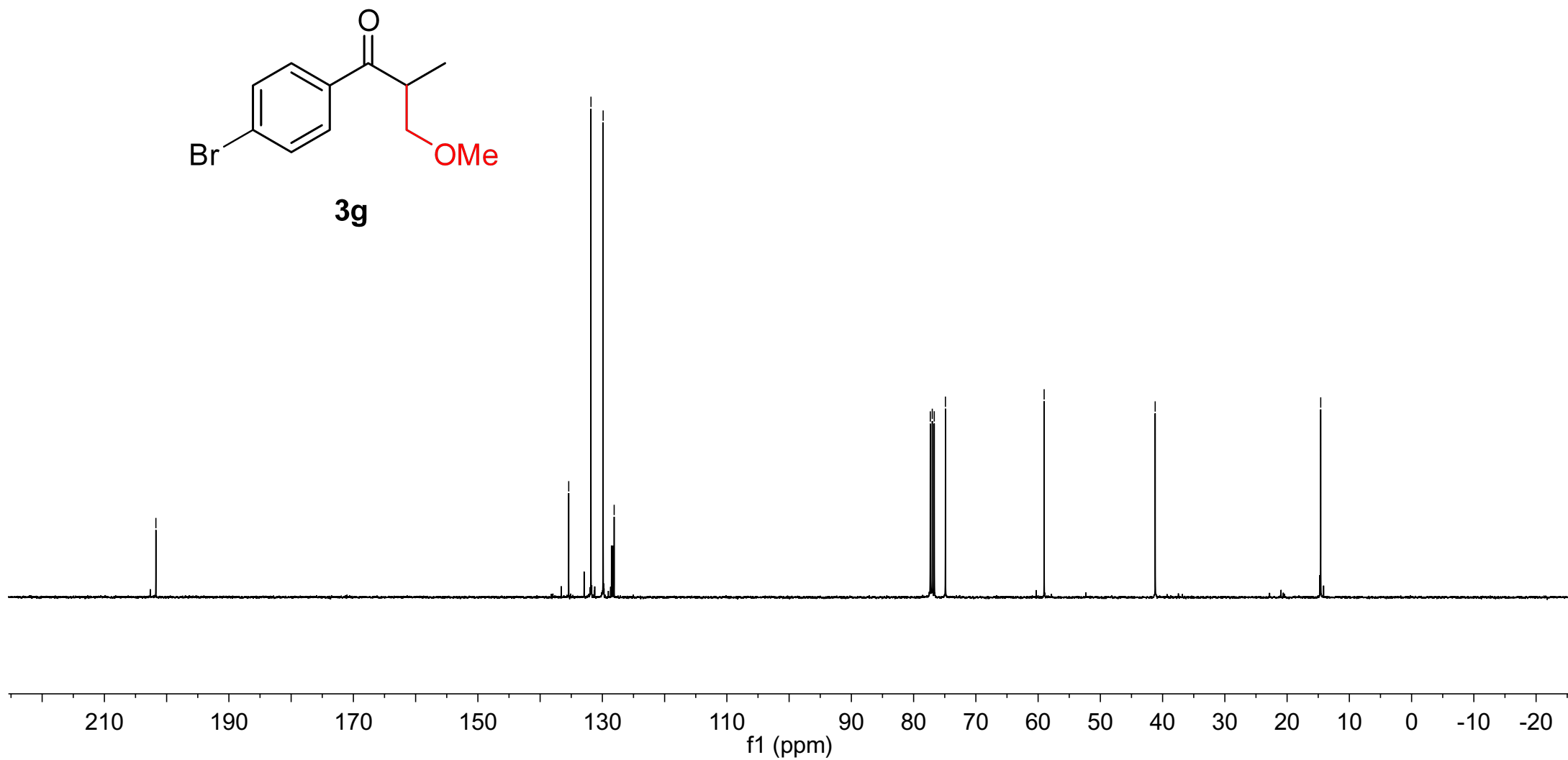
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128.11

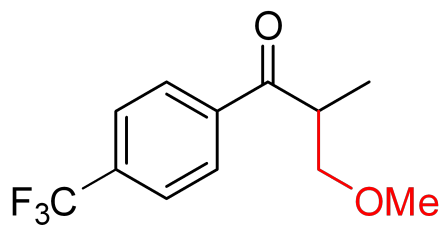
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—59.03

—41.19

—14.60



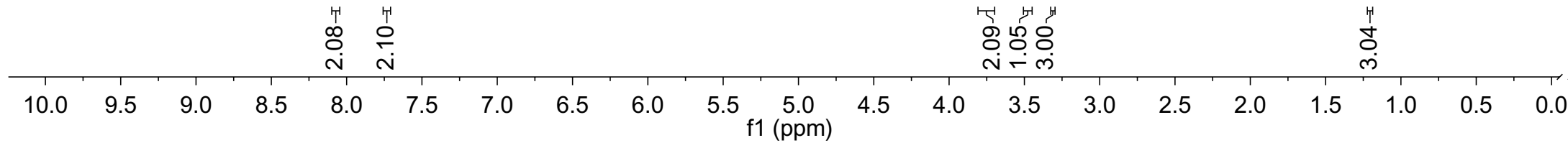


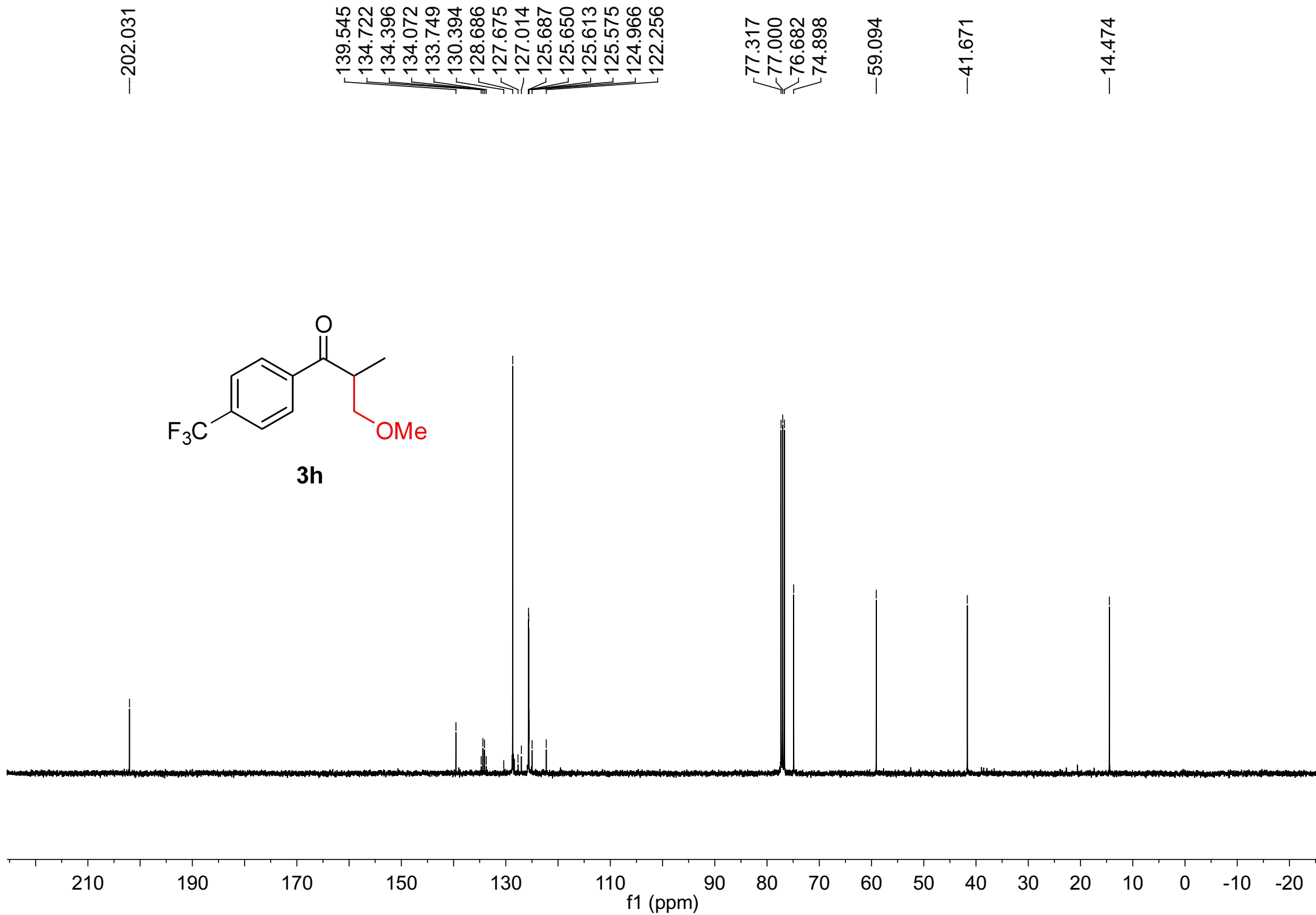
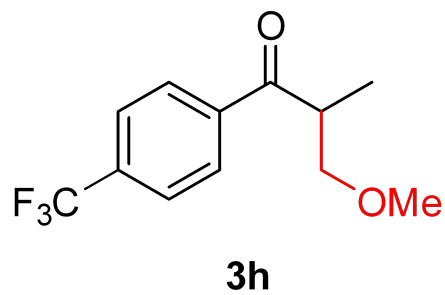
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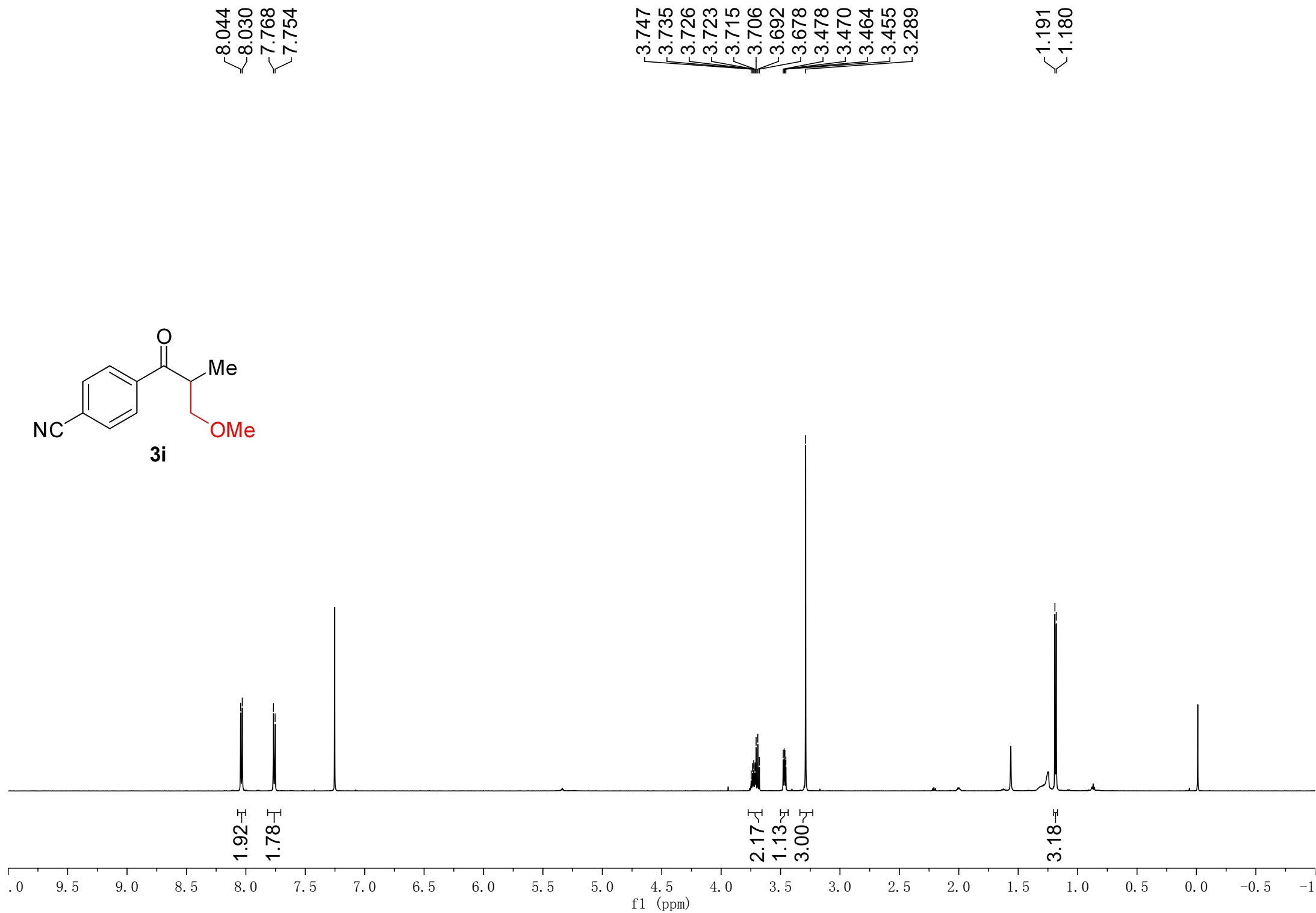
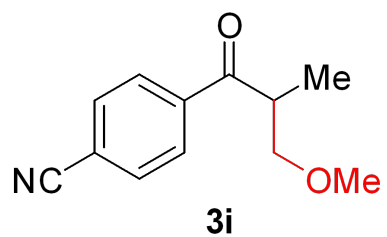
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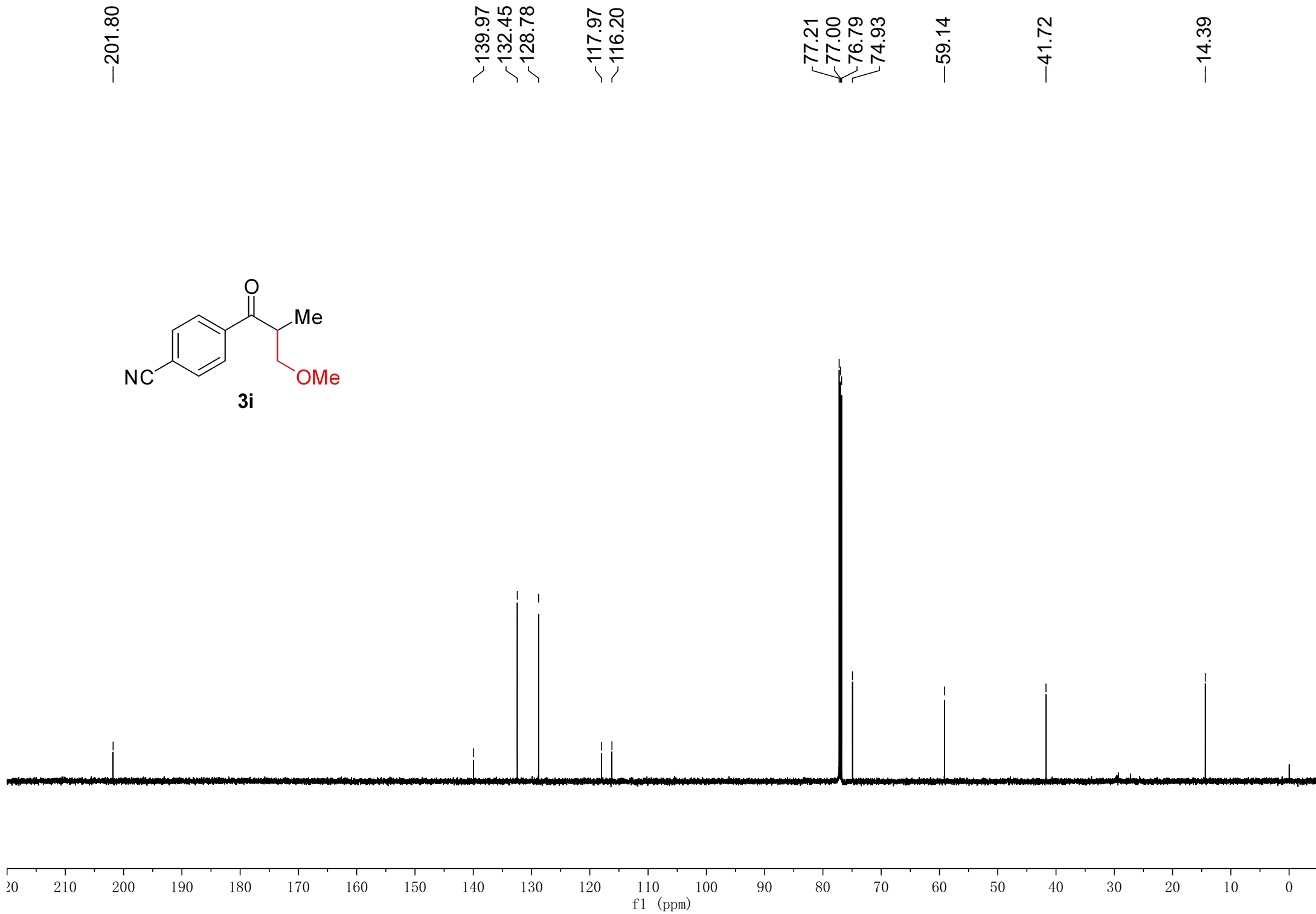
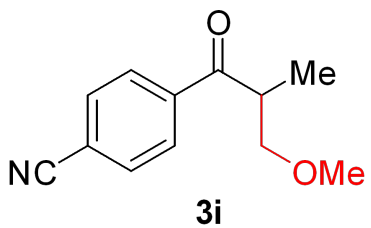
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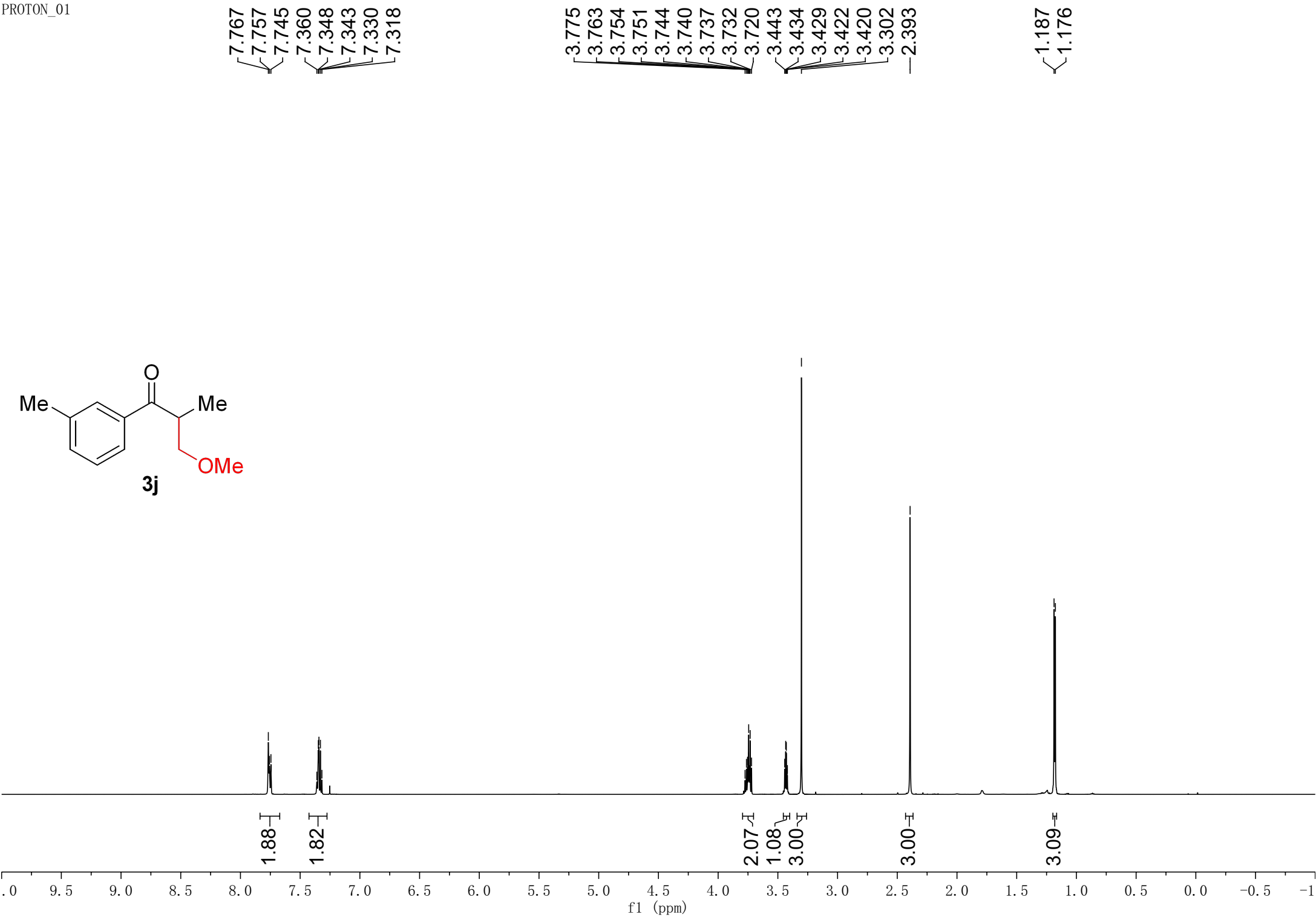
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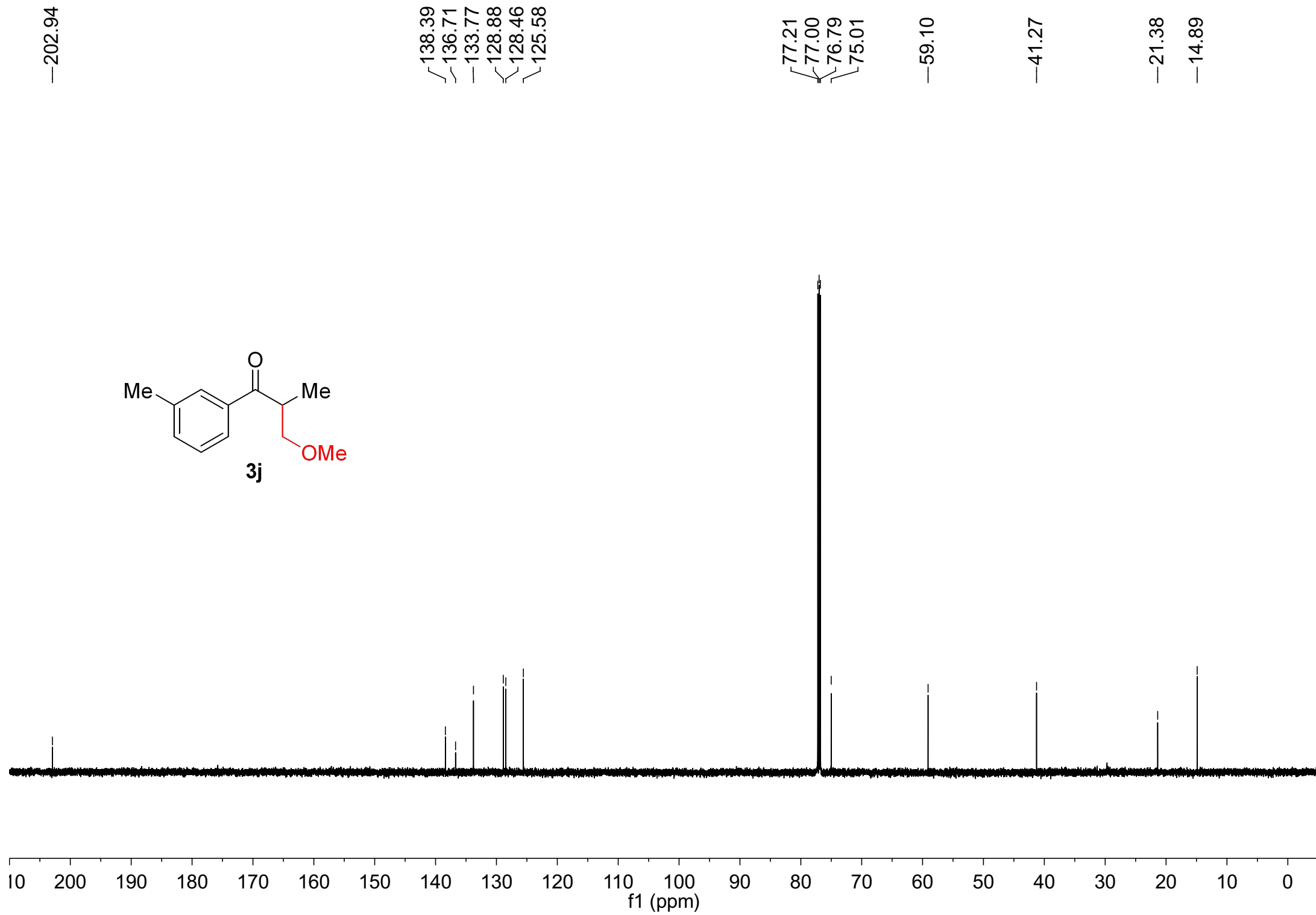
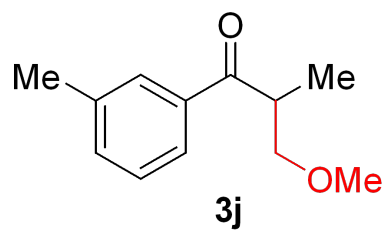


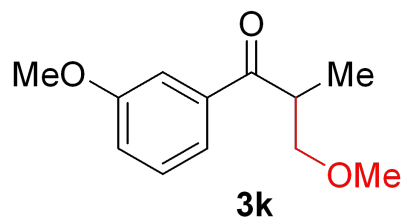








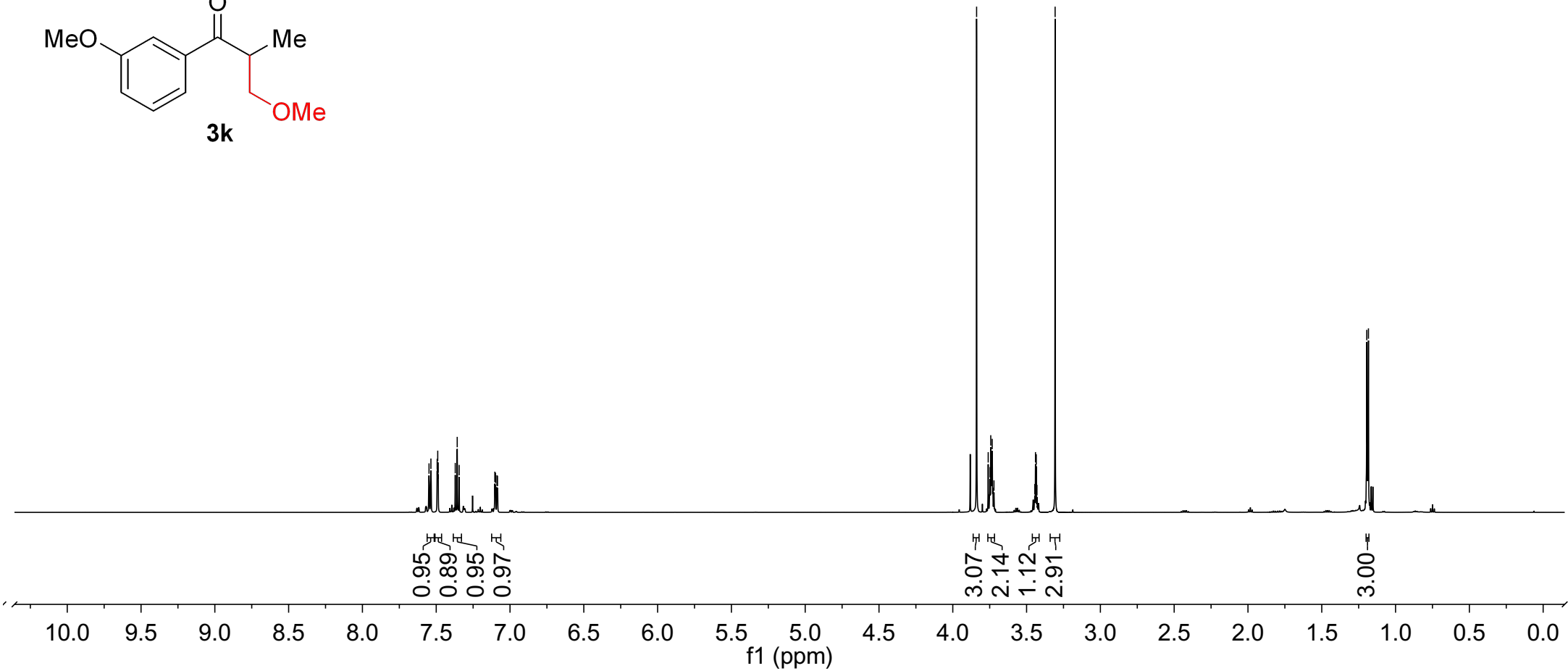


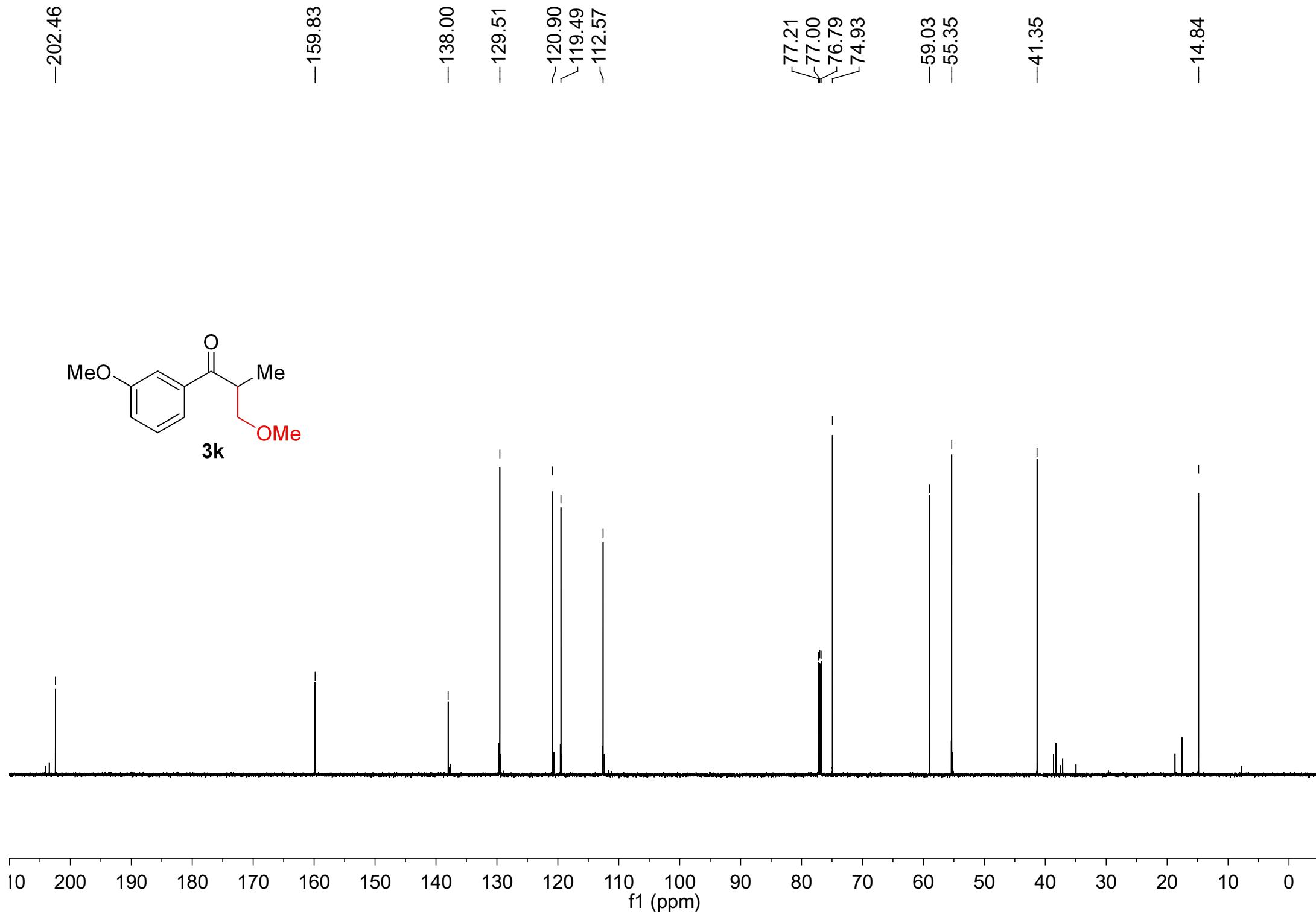
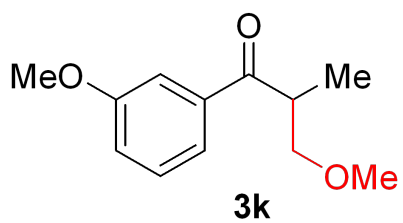


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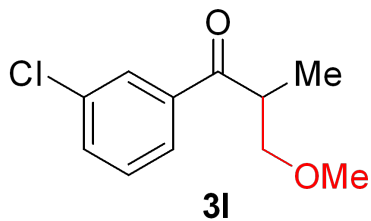
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1.184





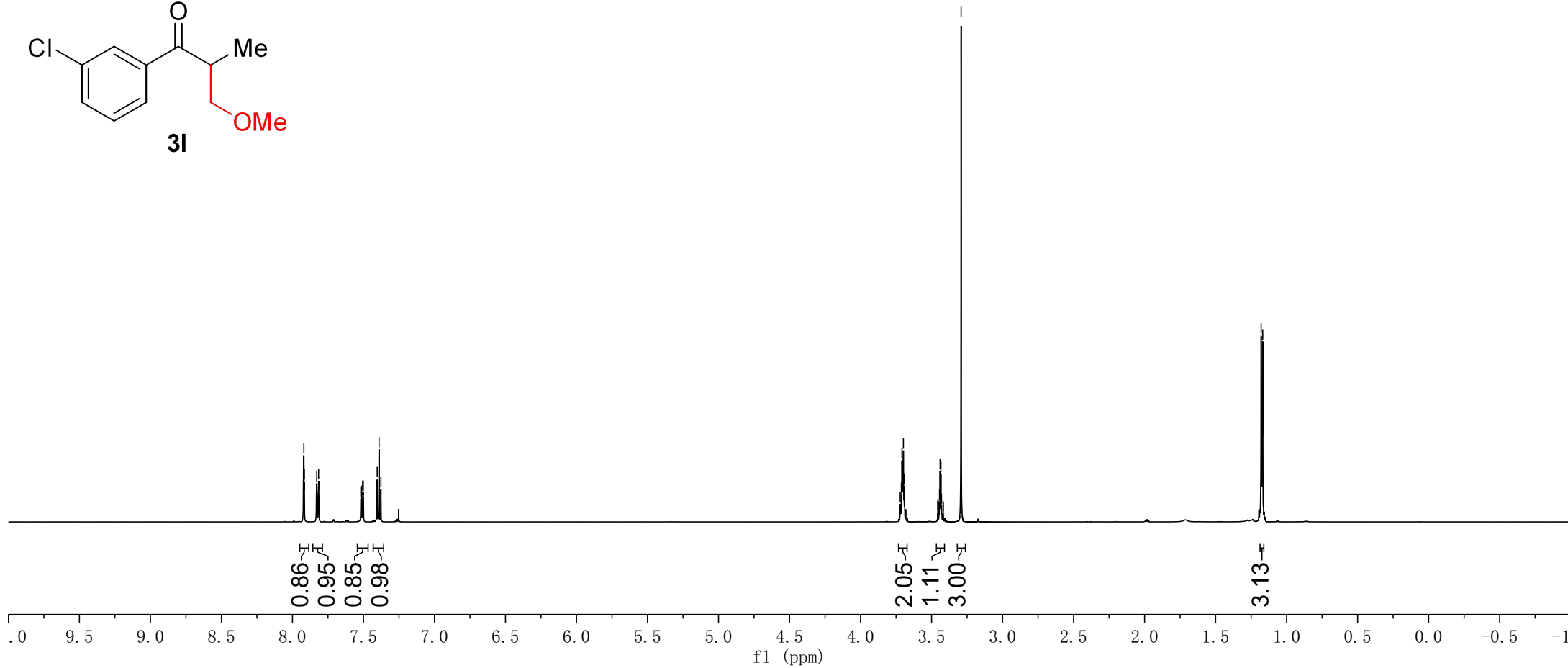
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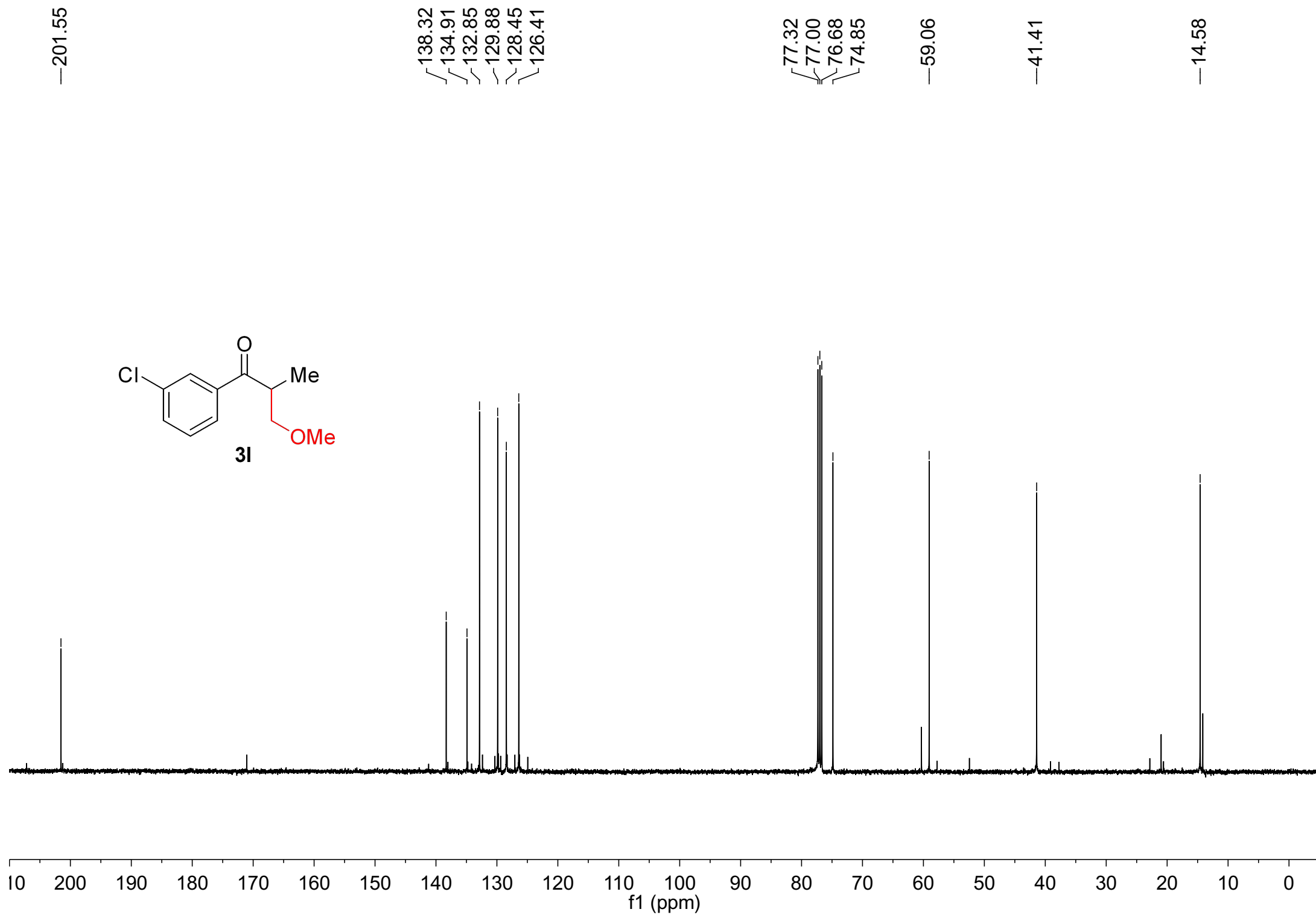
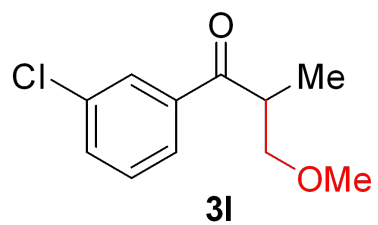


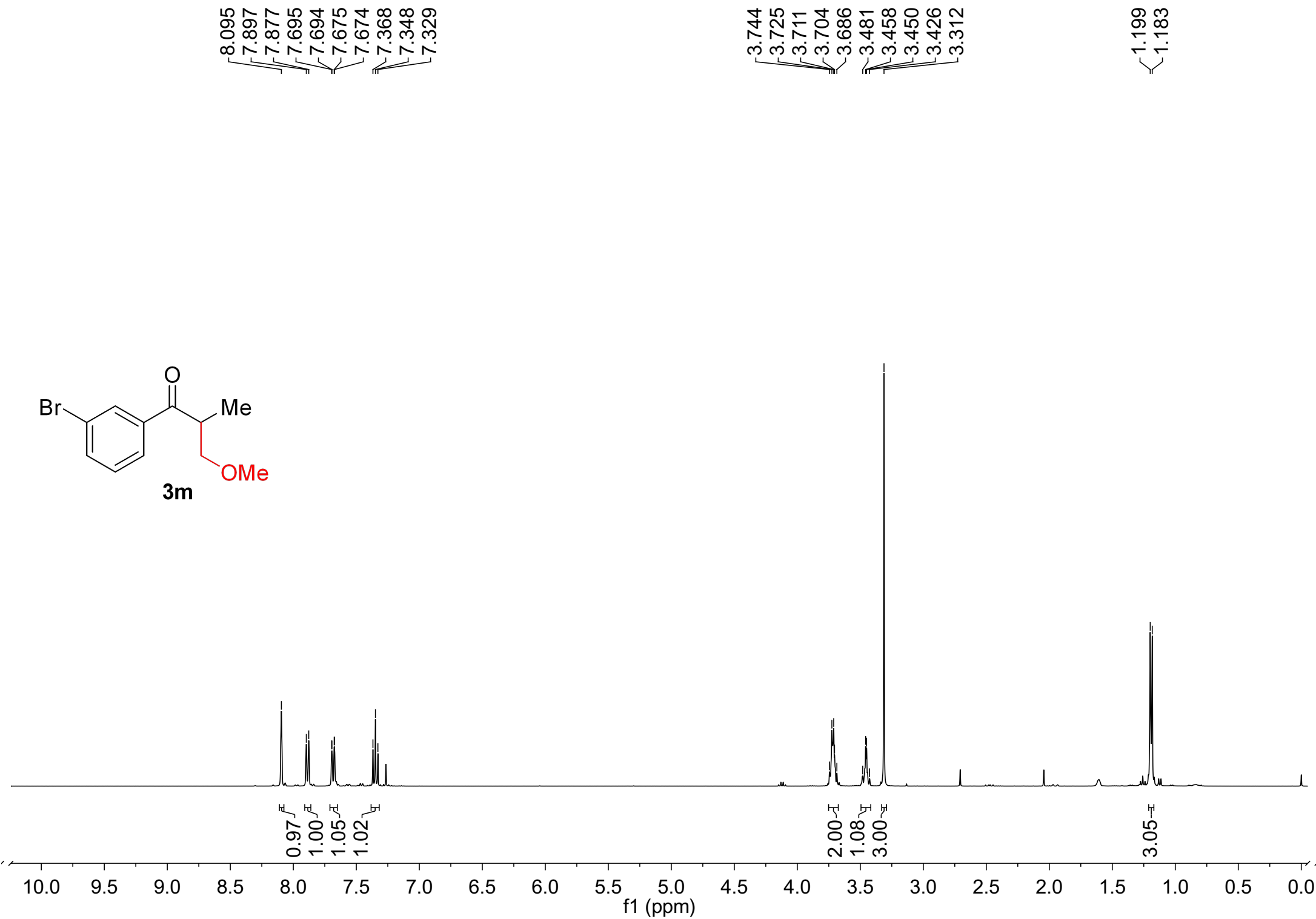
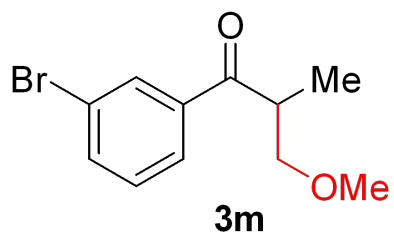
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7.377

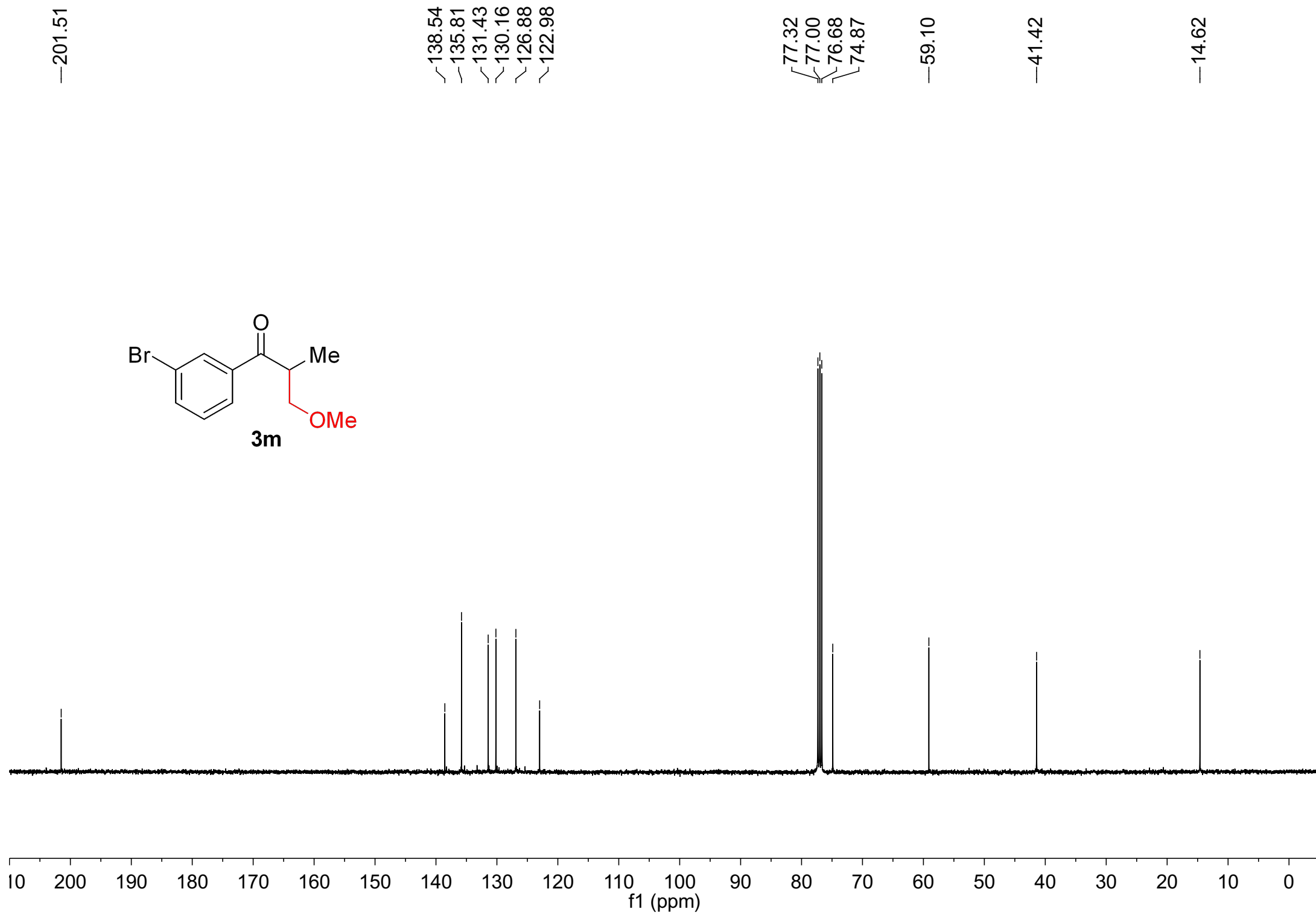
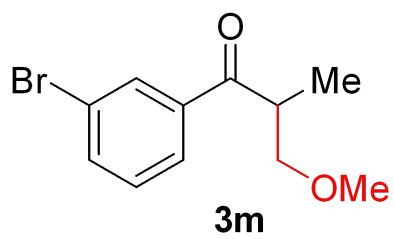
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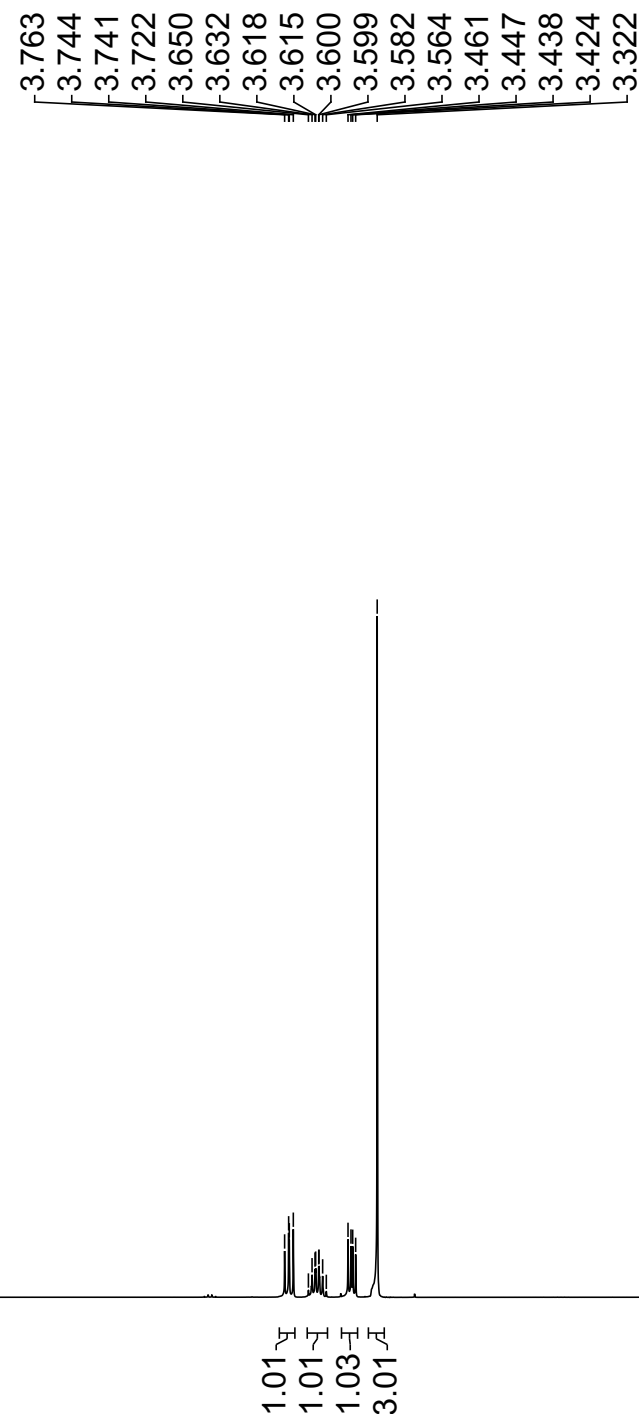
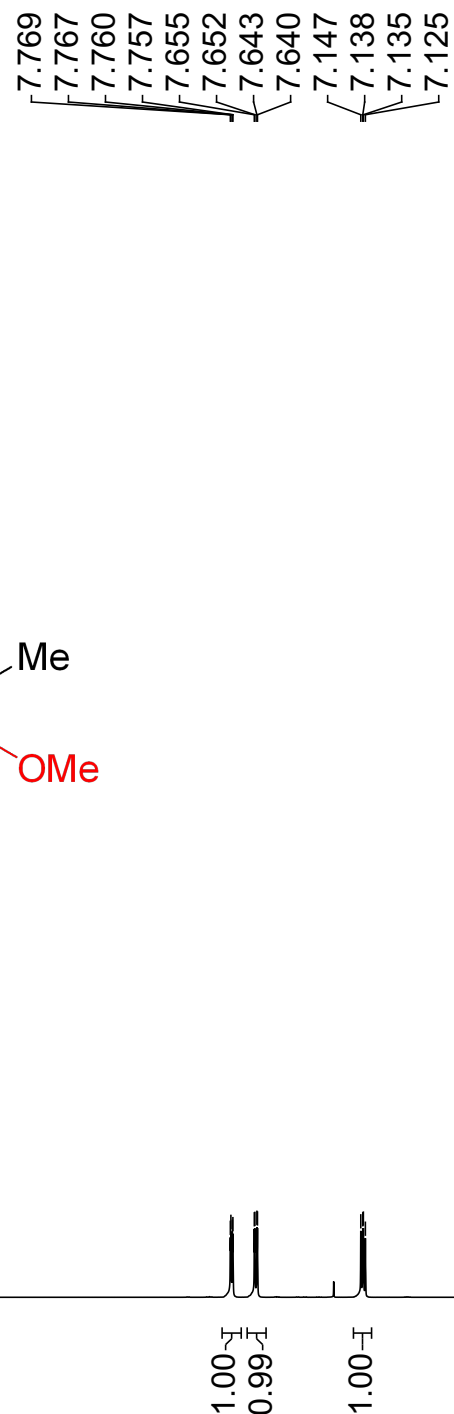
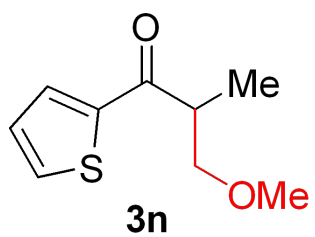
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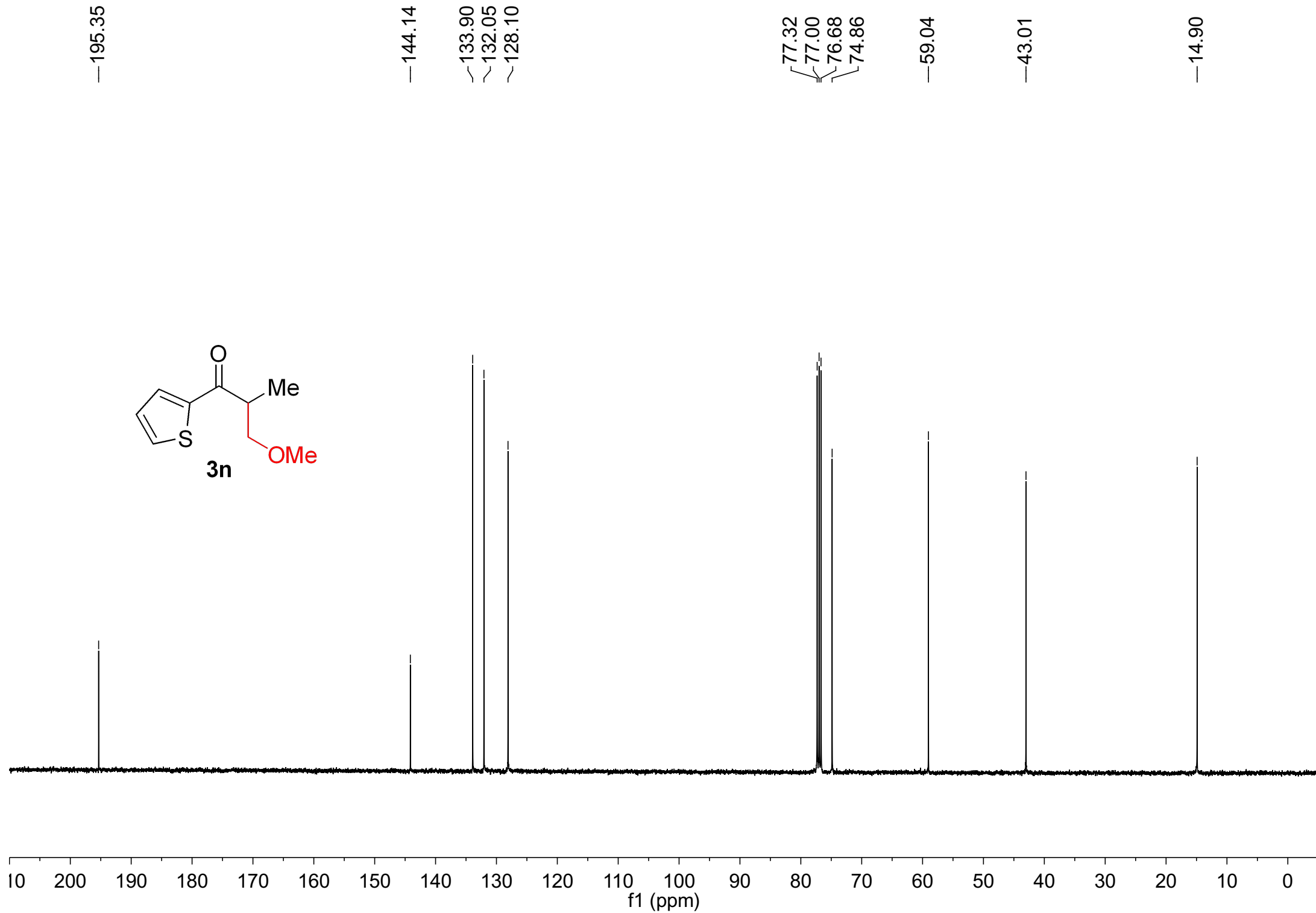
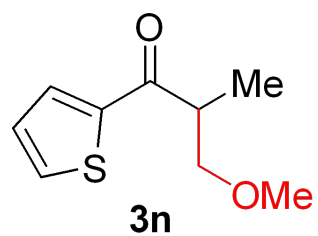


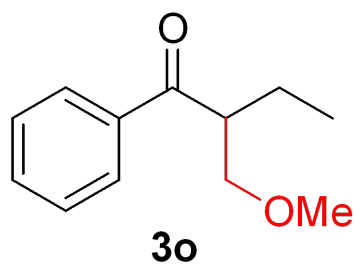




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f1 (ppm)

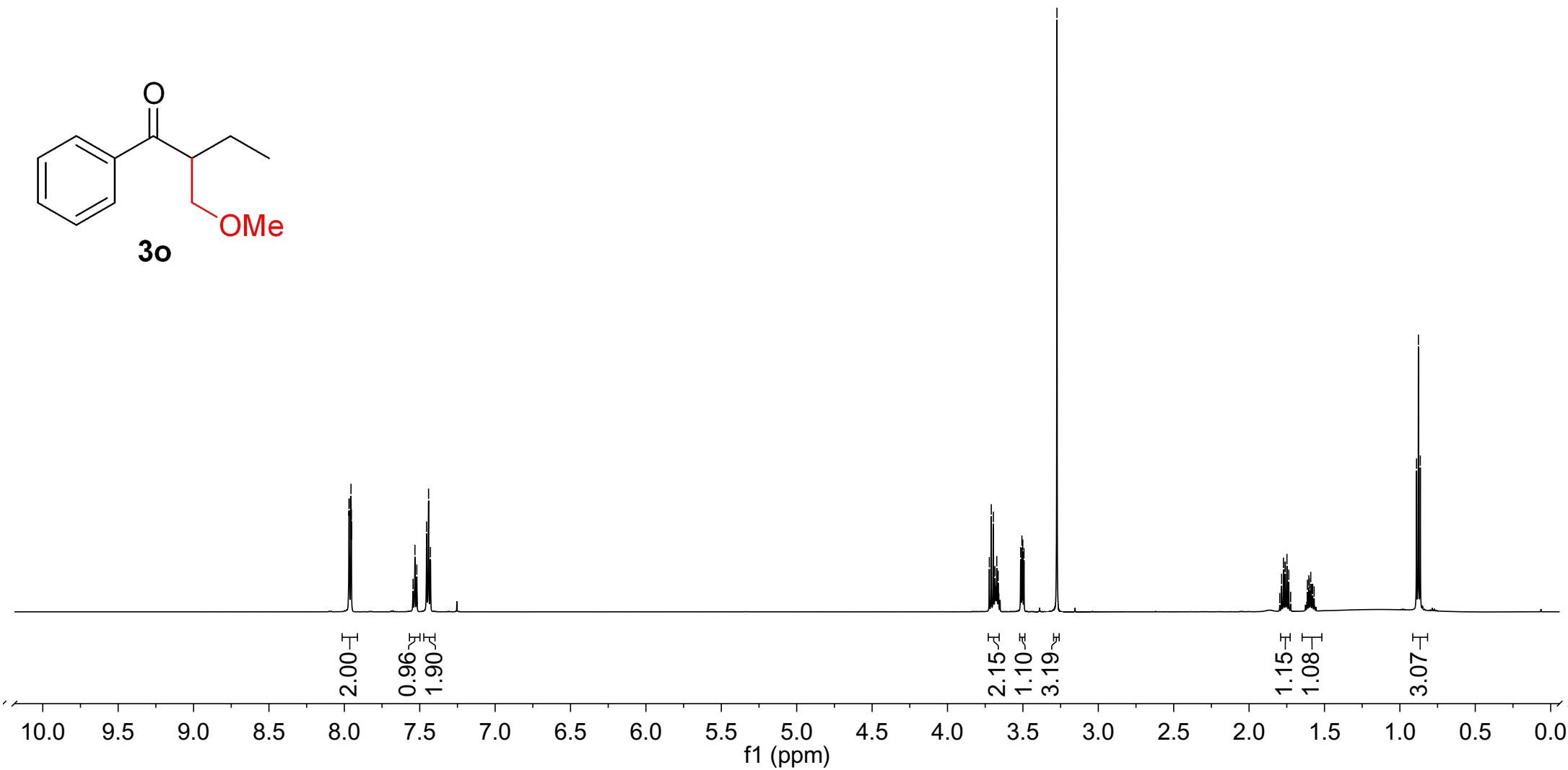


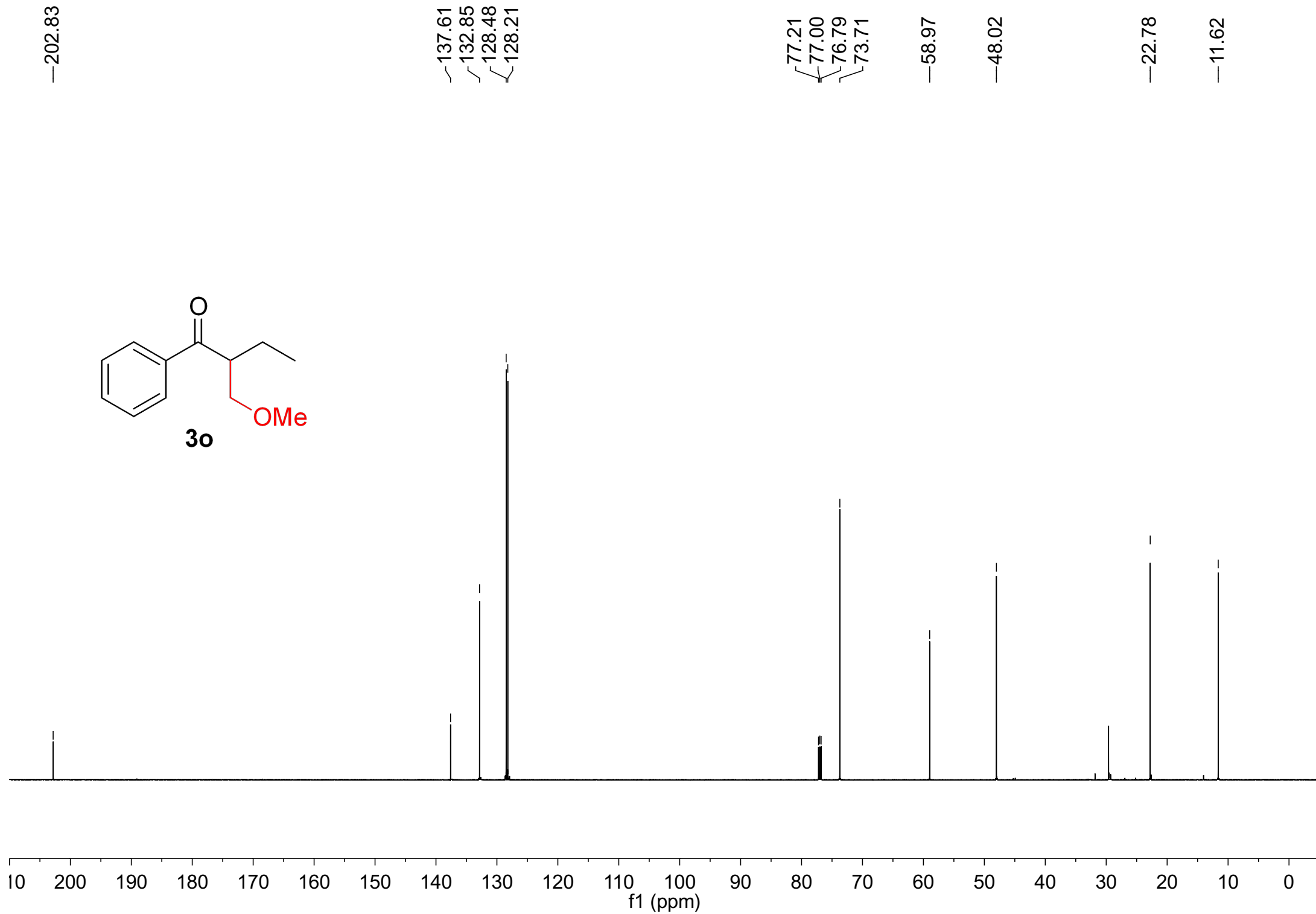
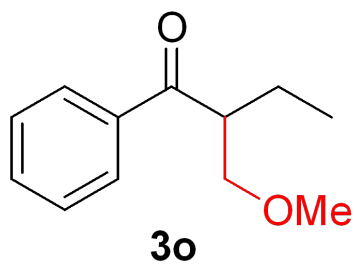


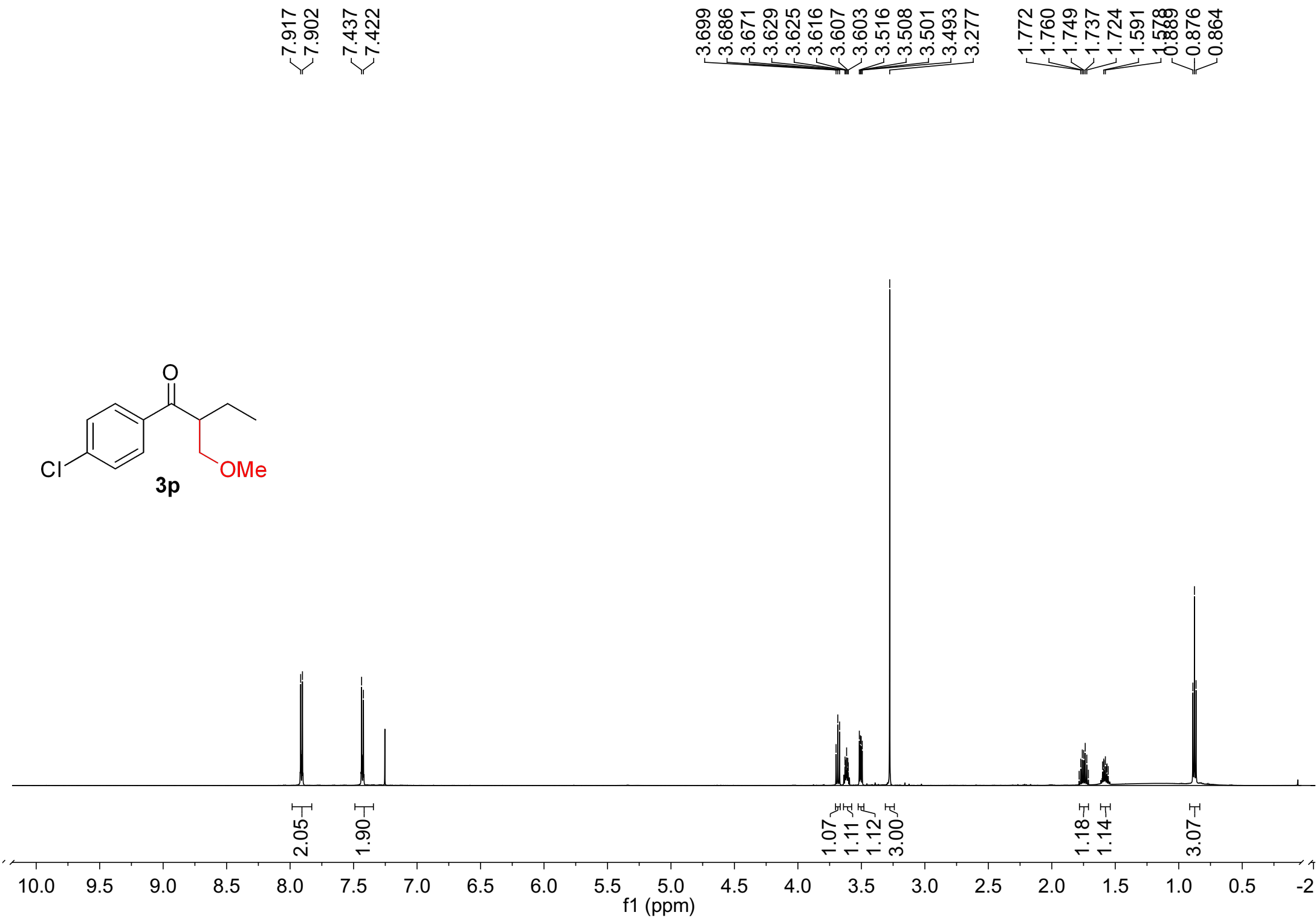
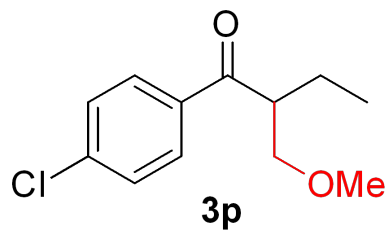
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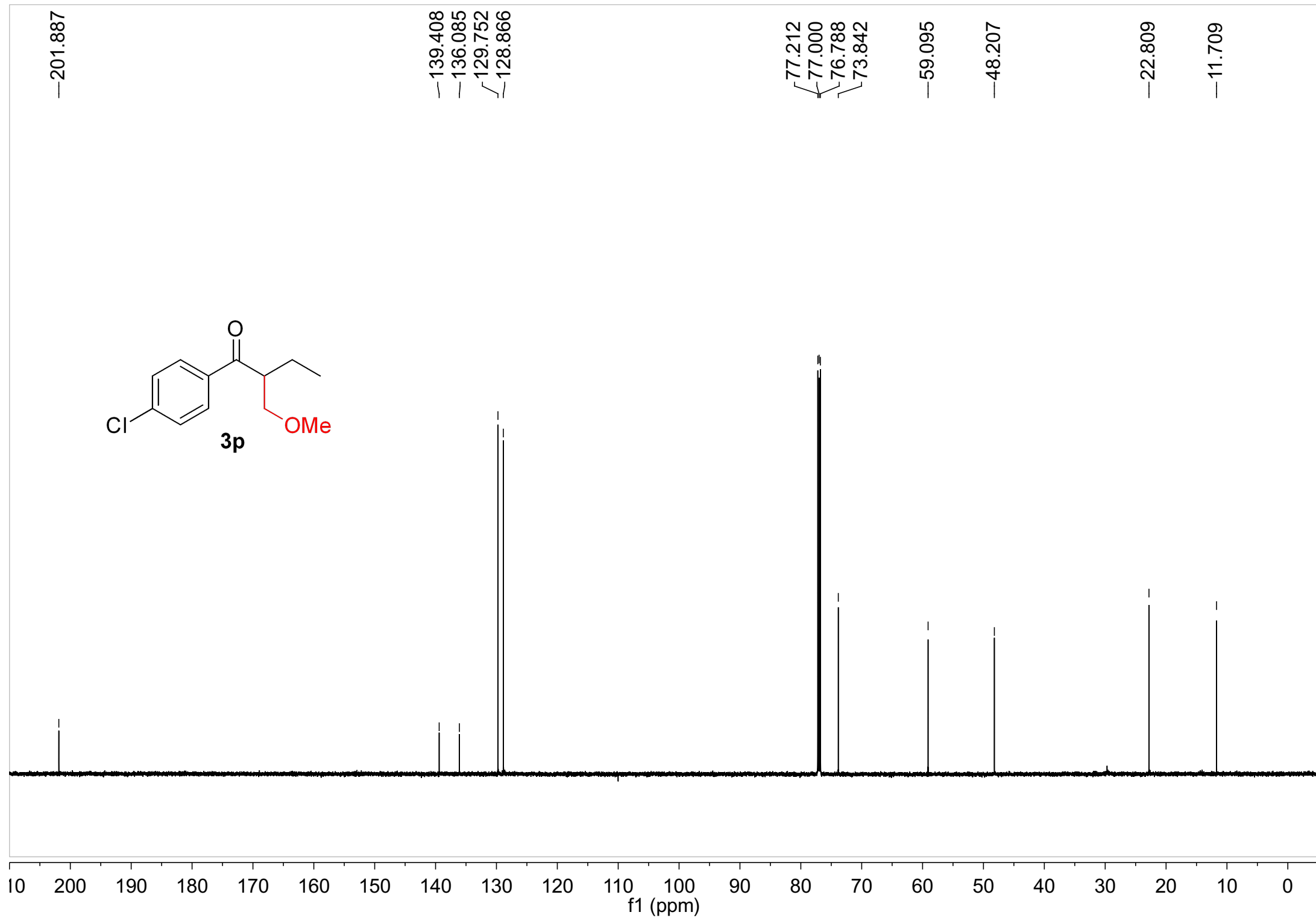
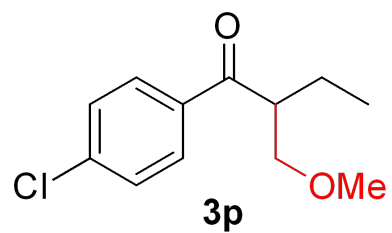
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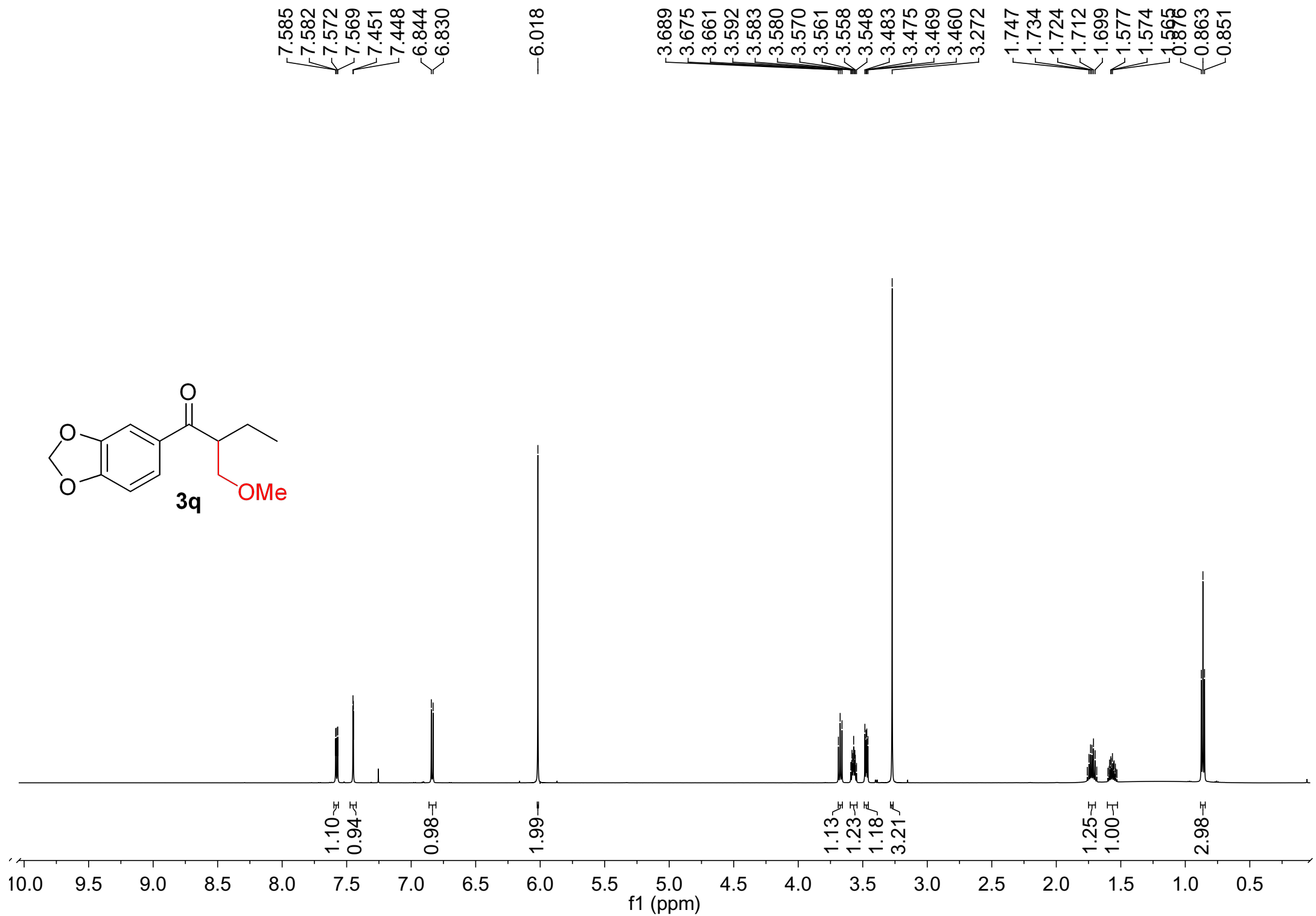
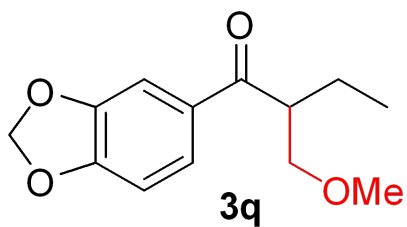
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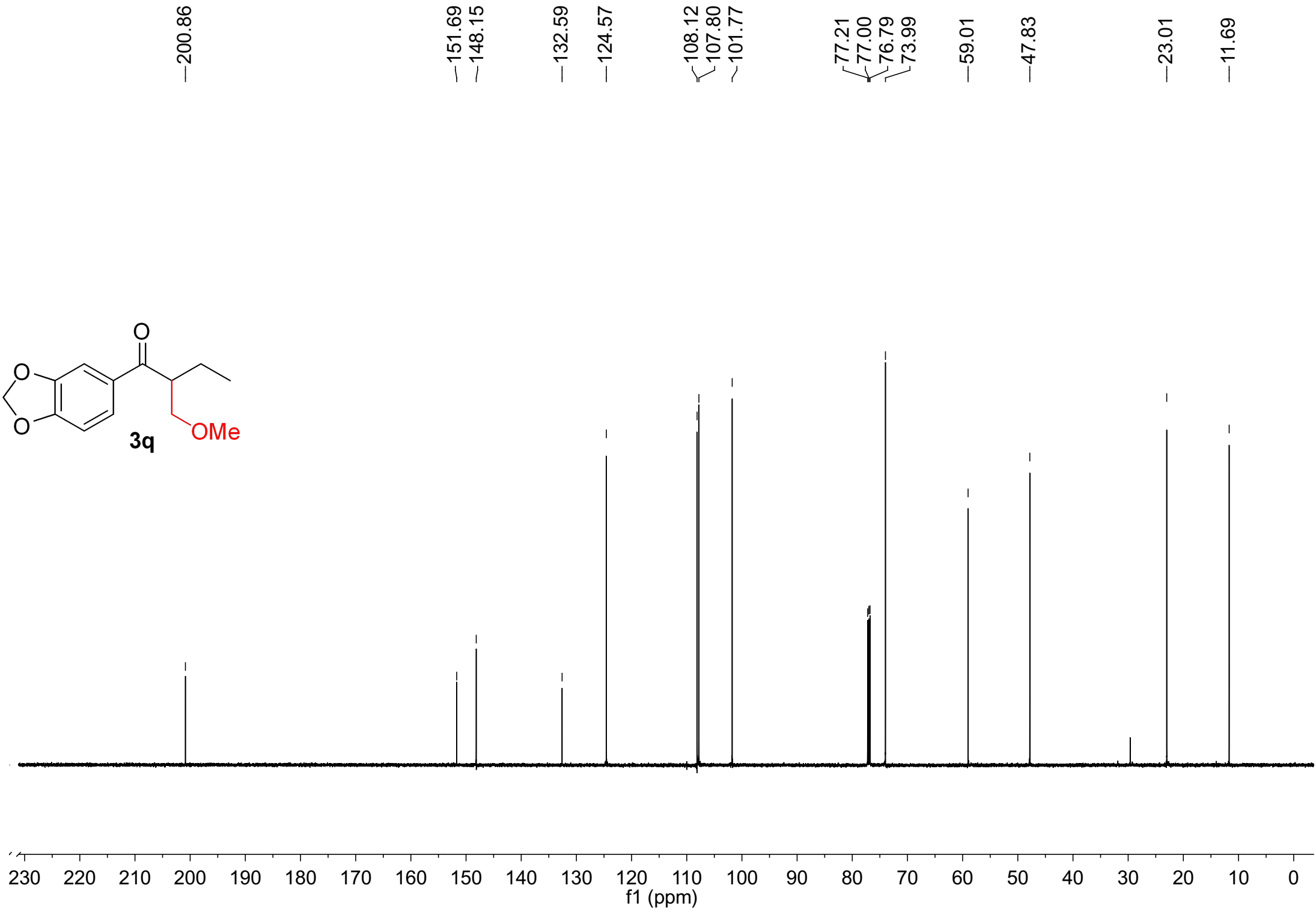
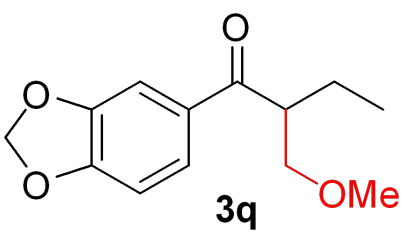


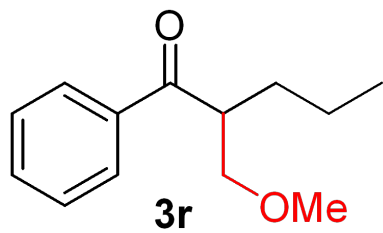








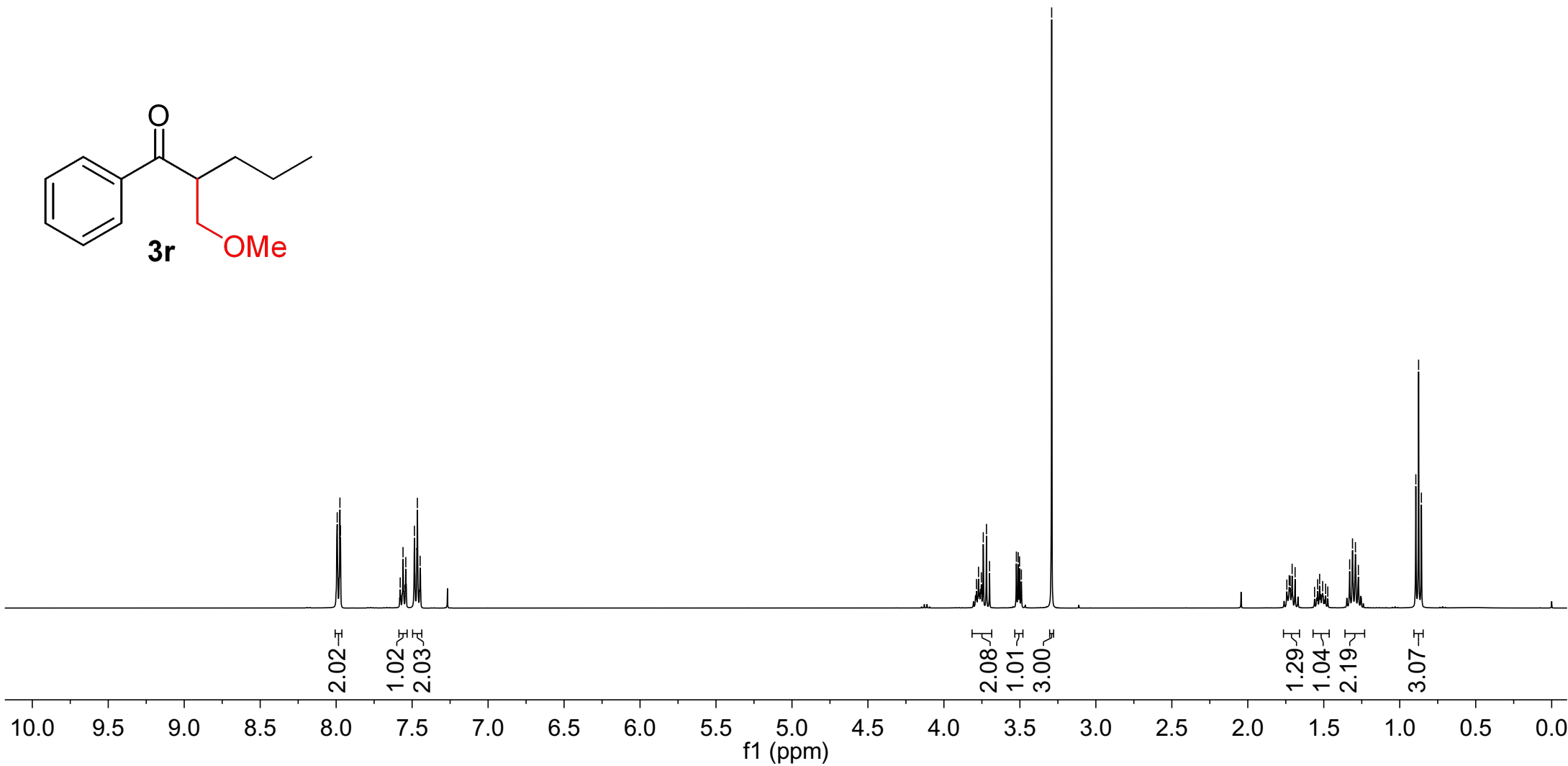


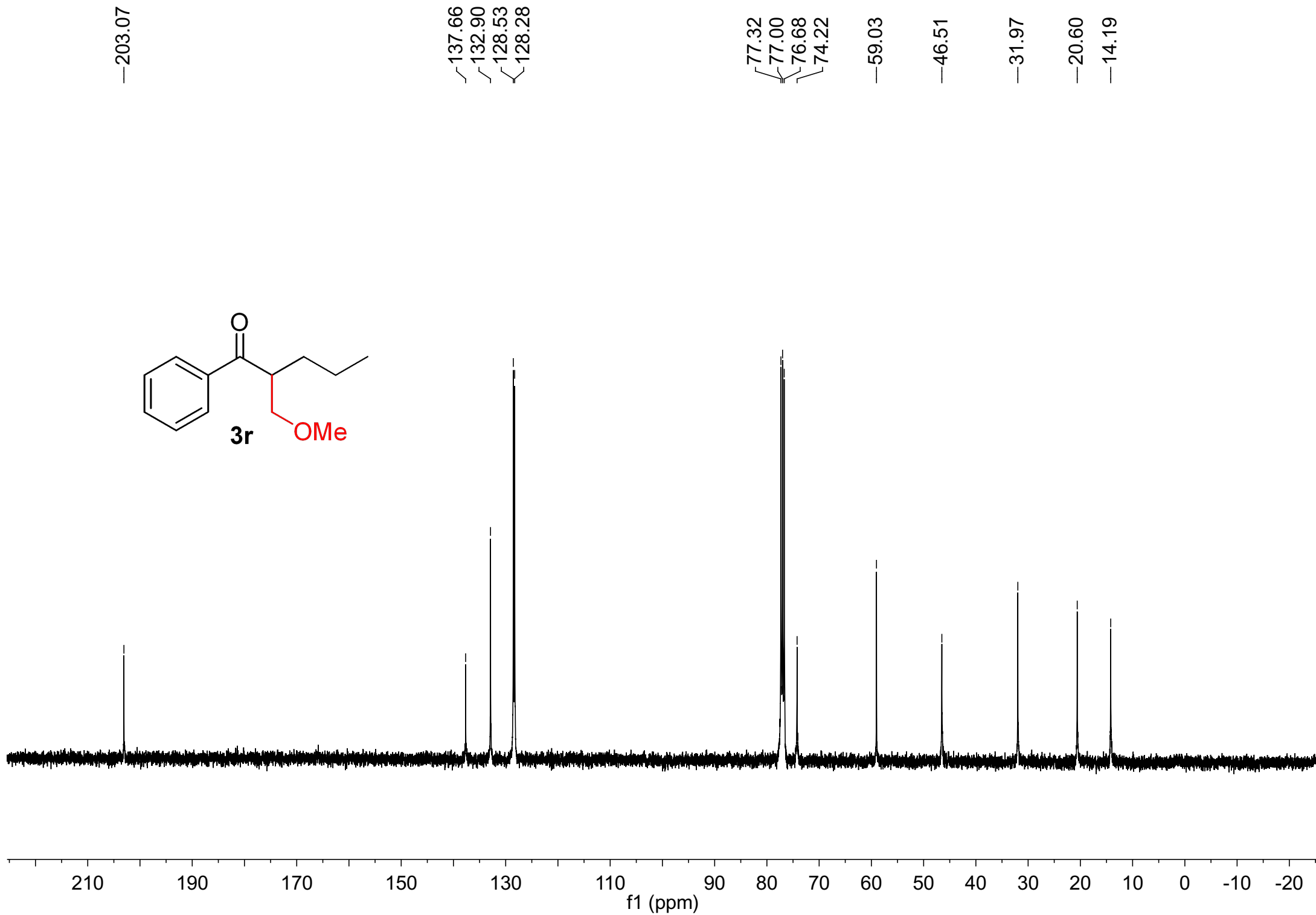
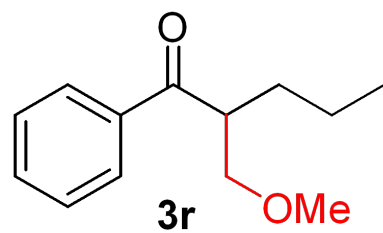


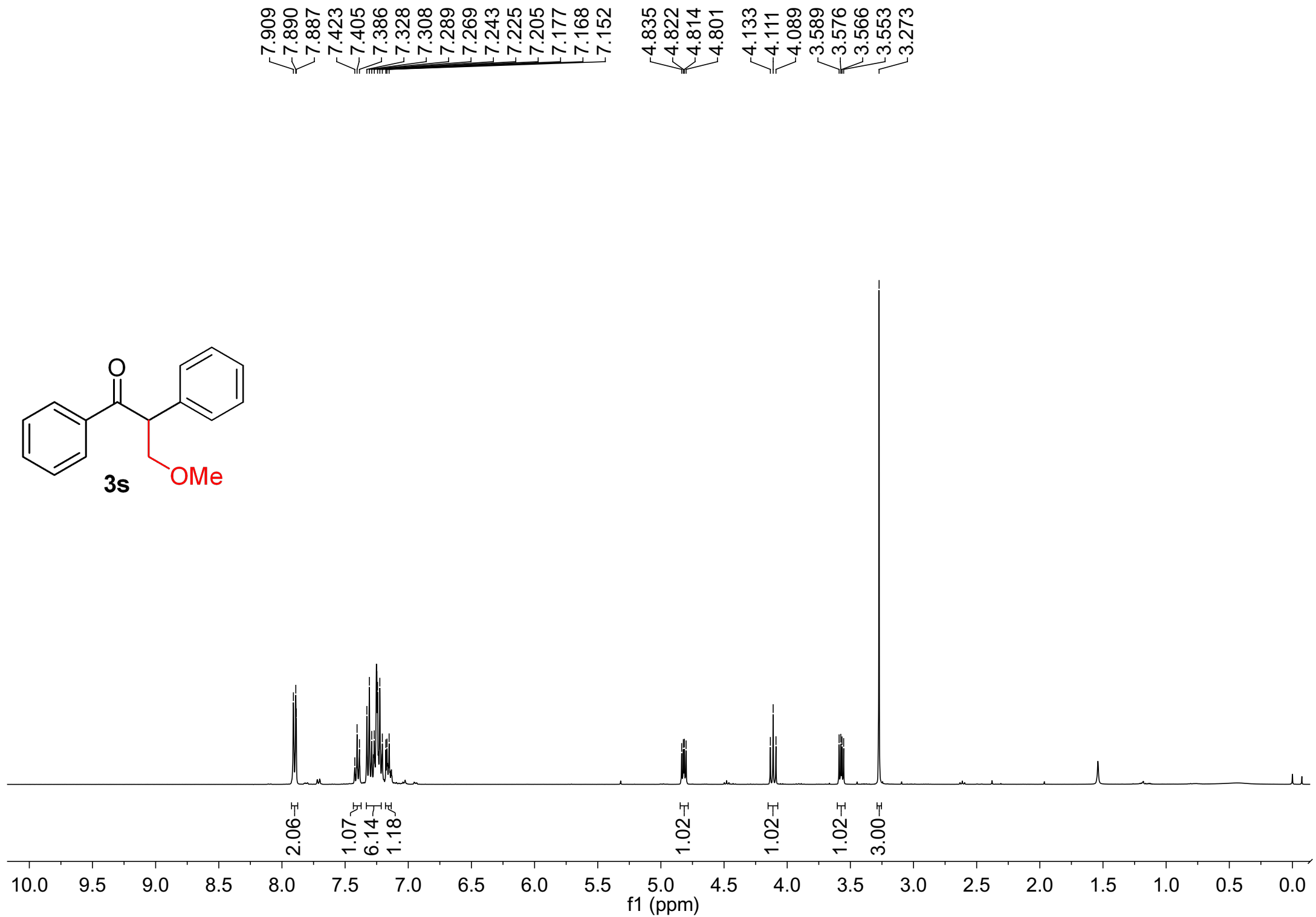
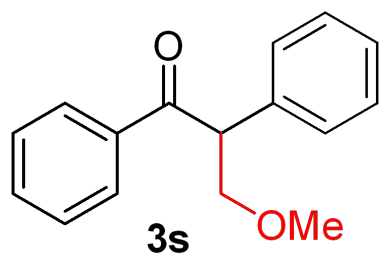
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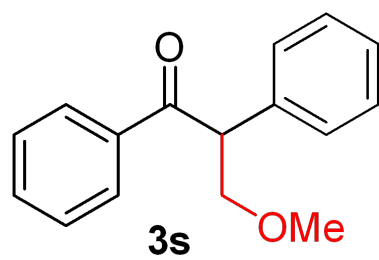
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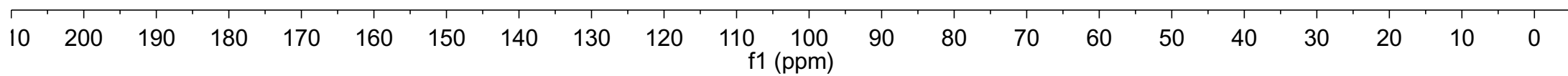


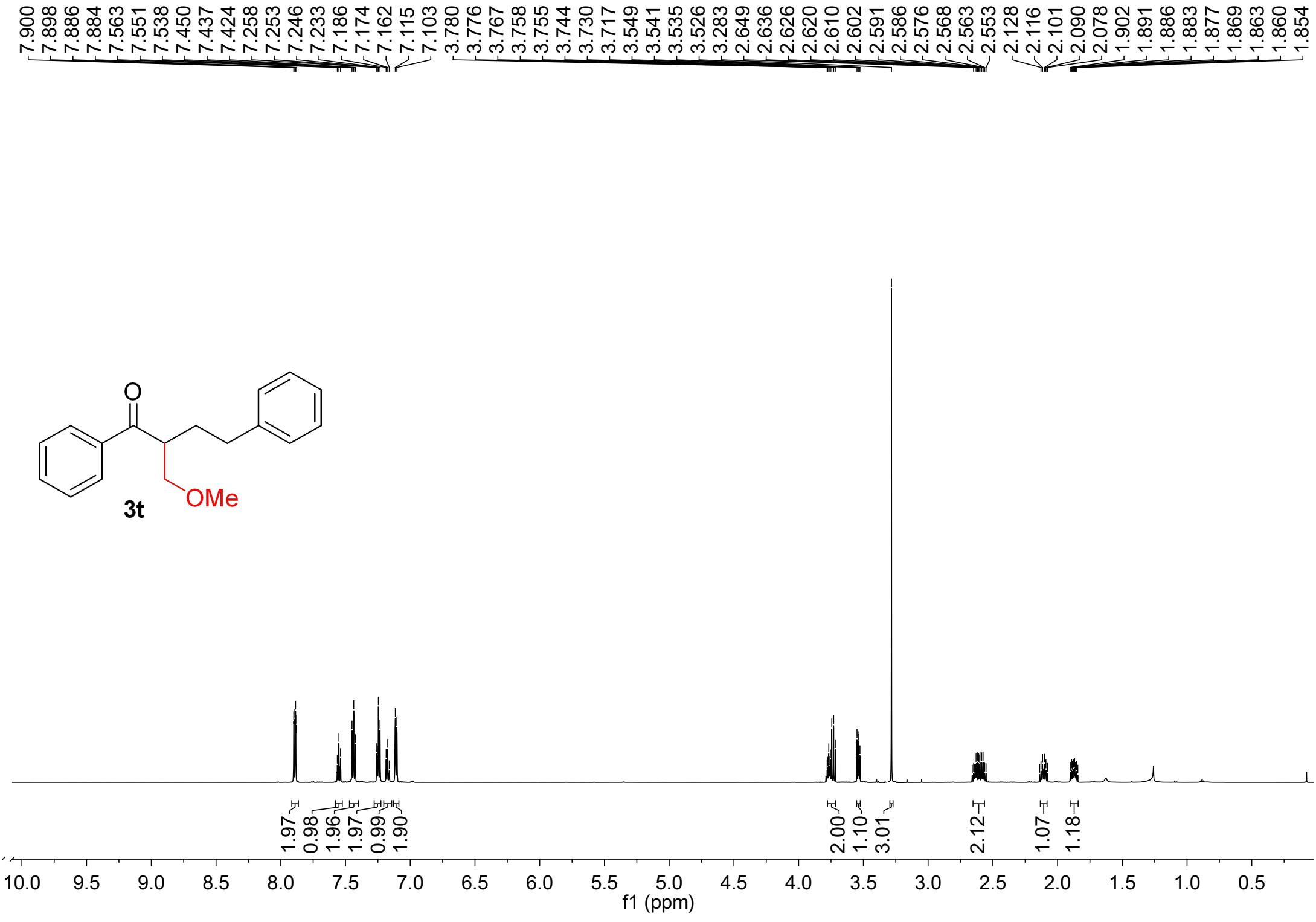
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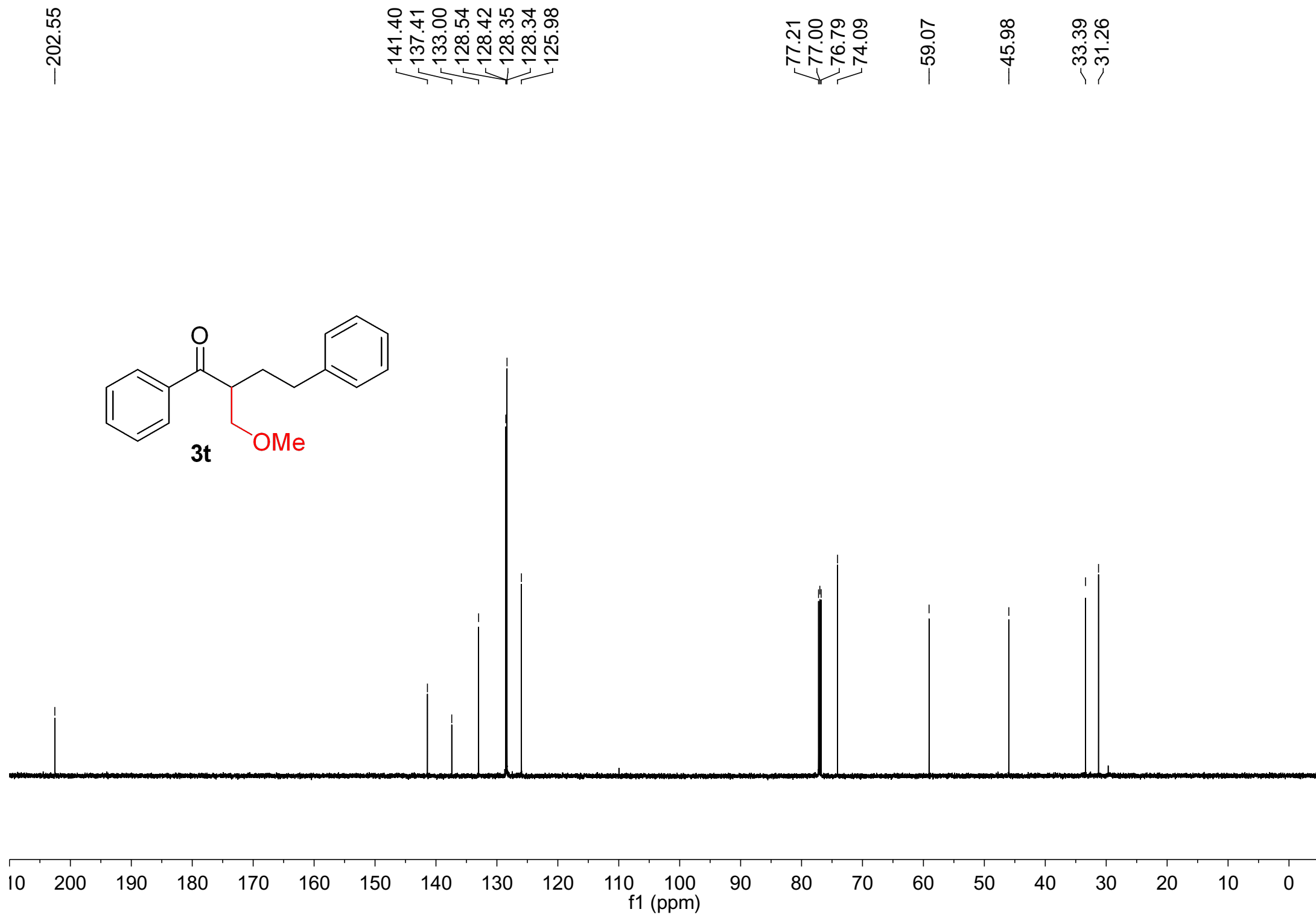
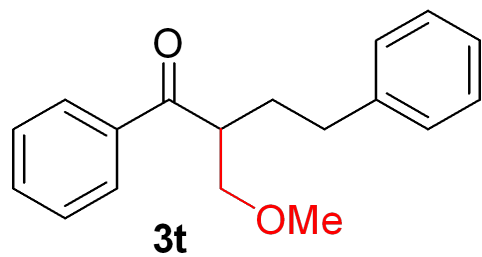
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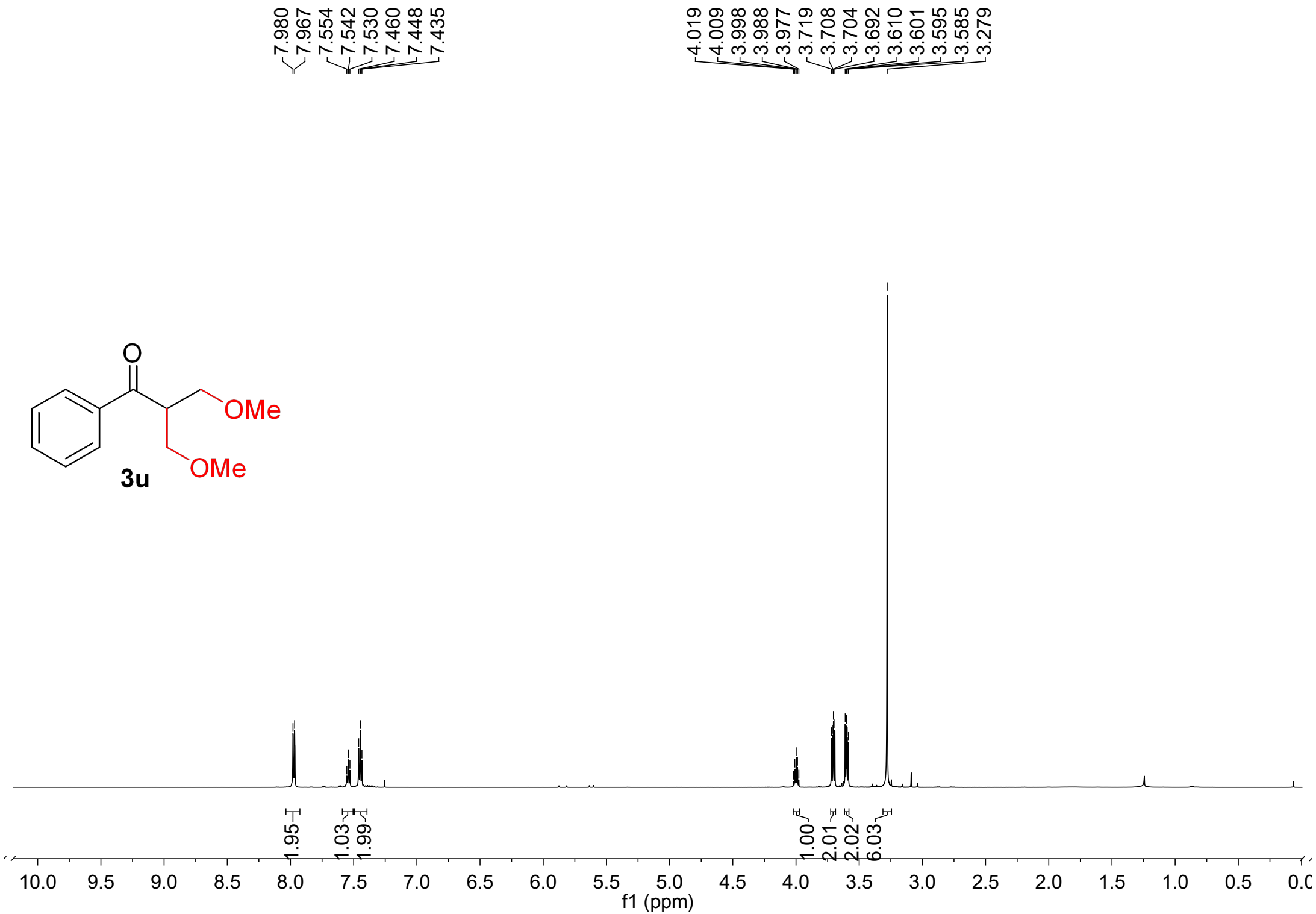
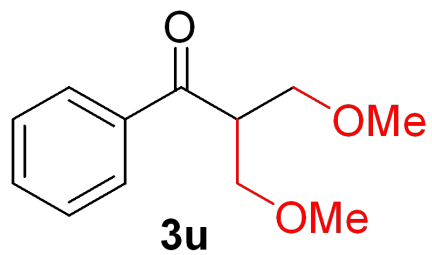
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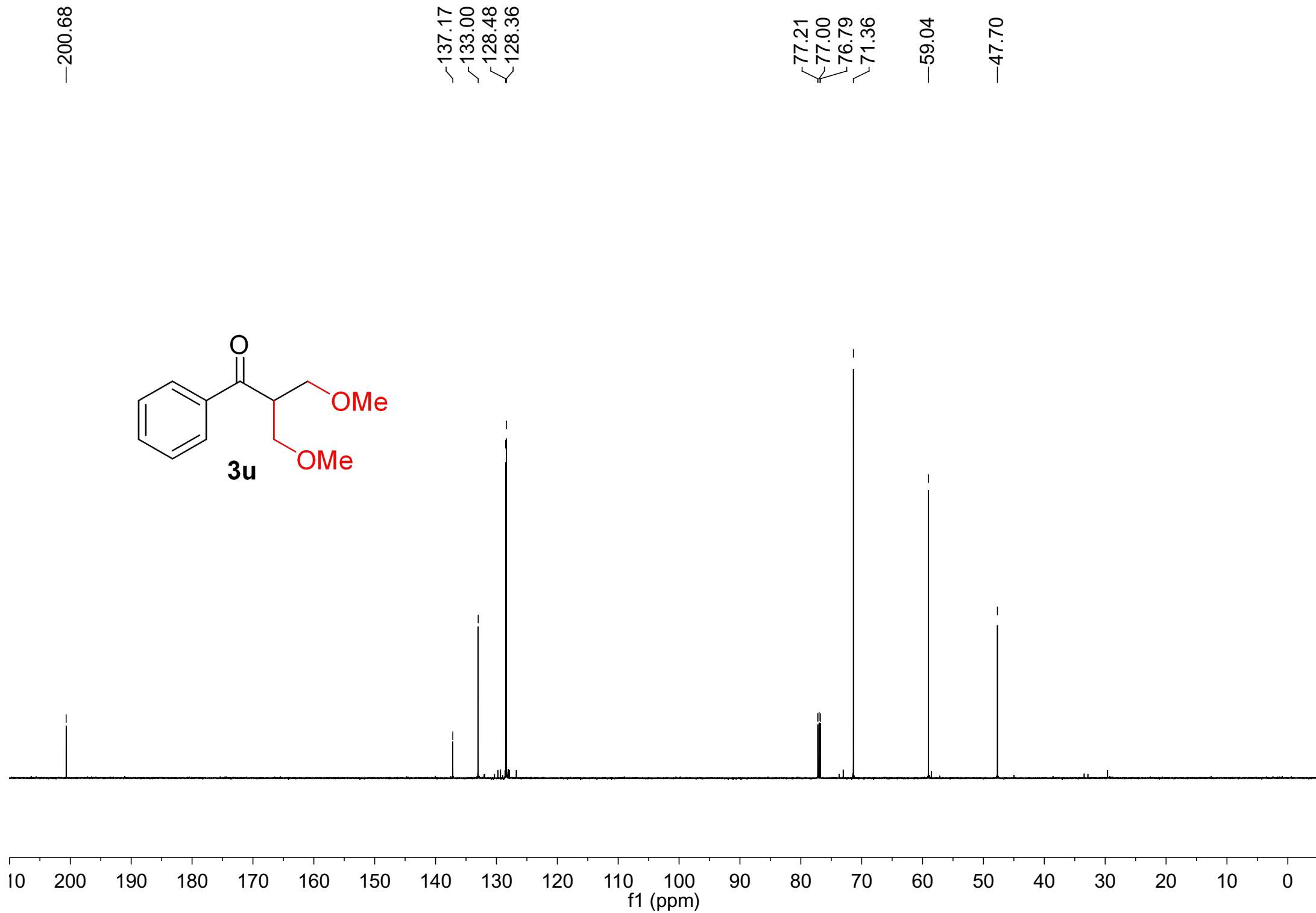
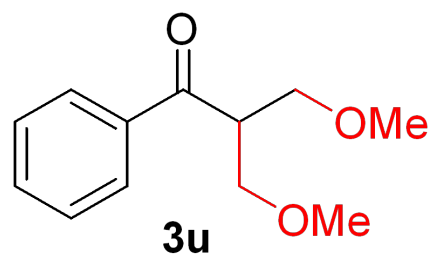
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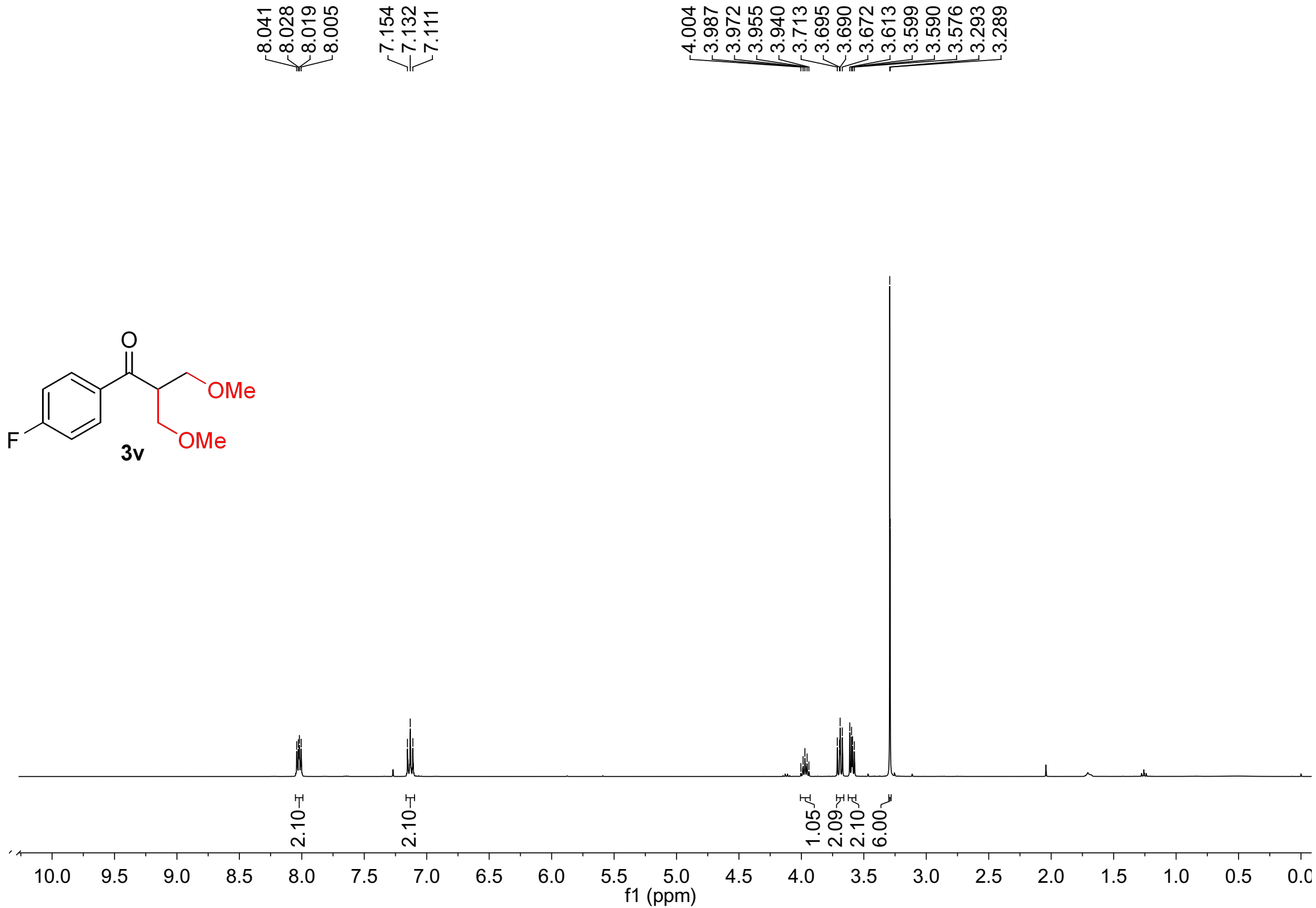


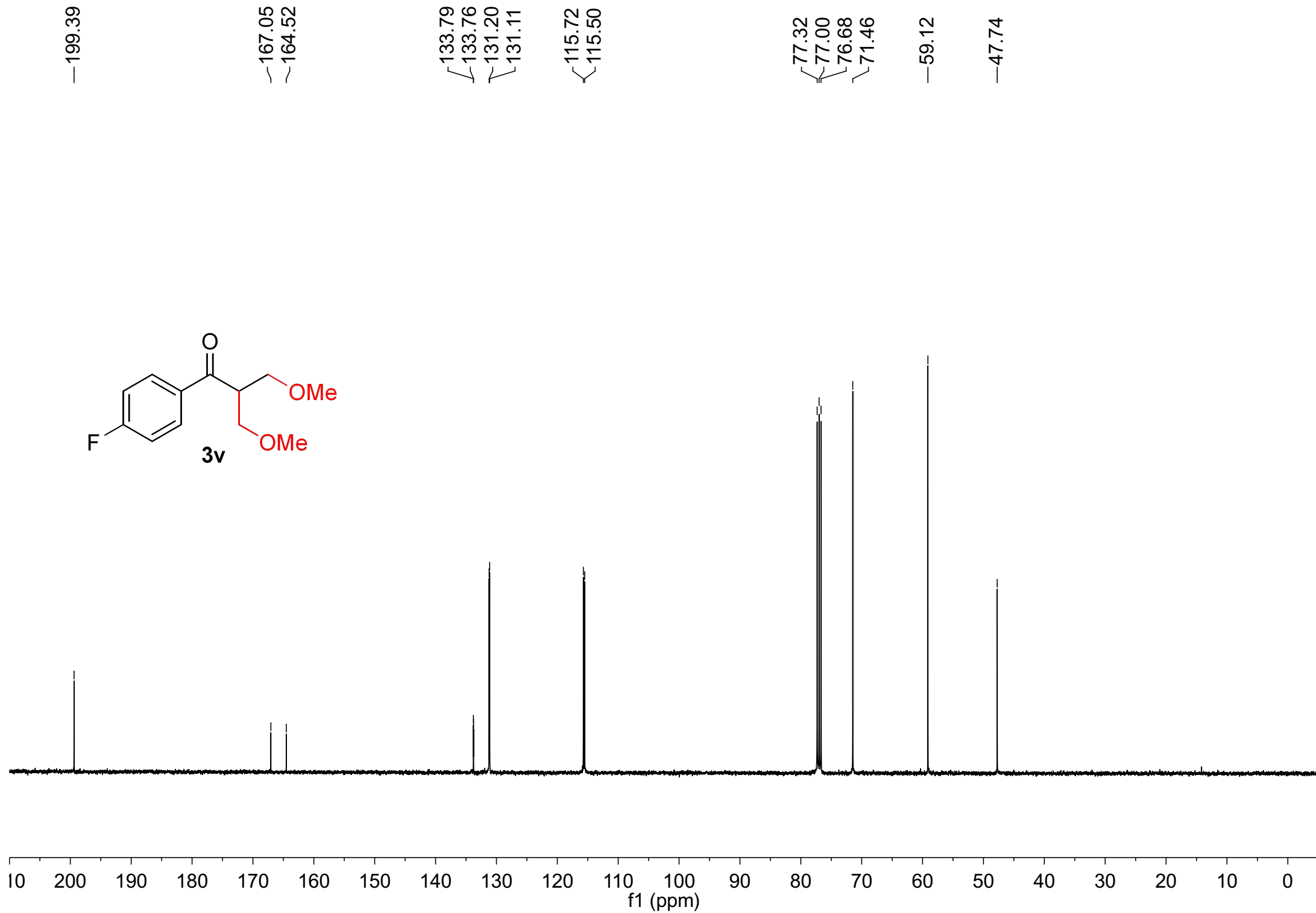


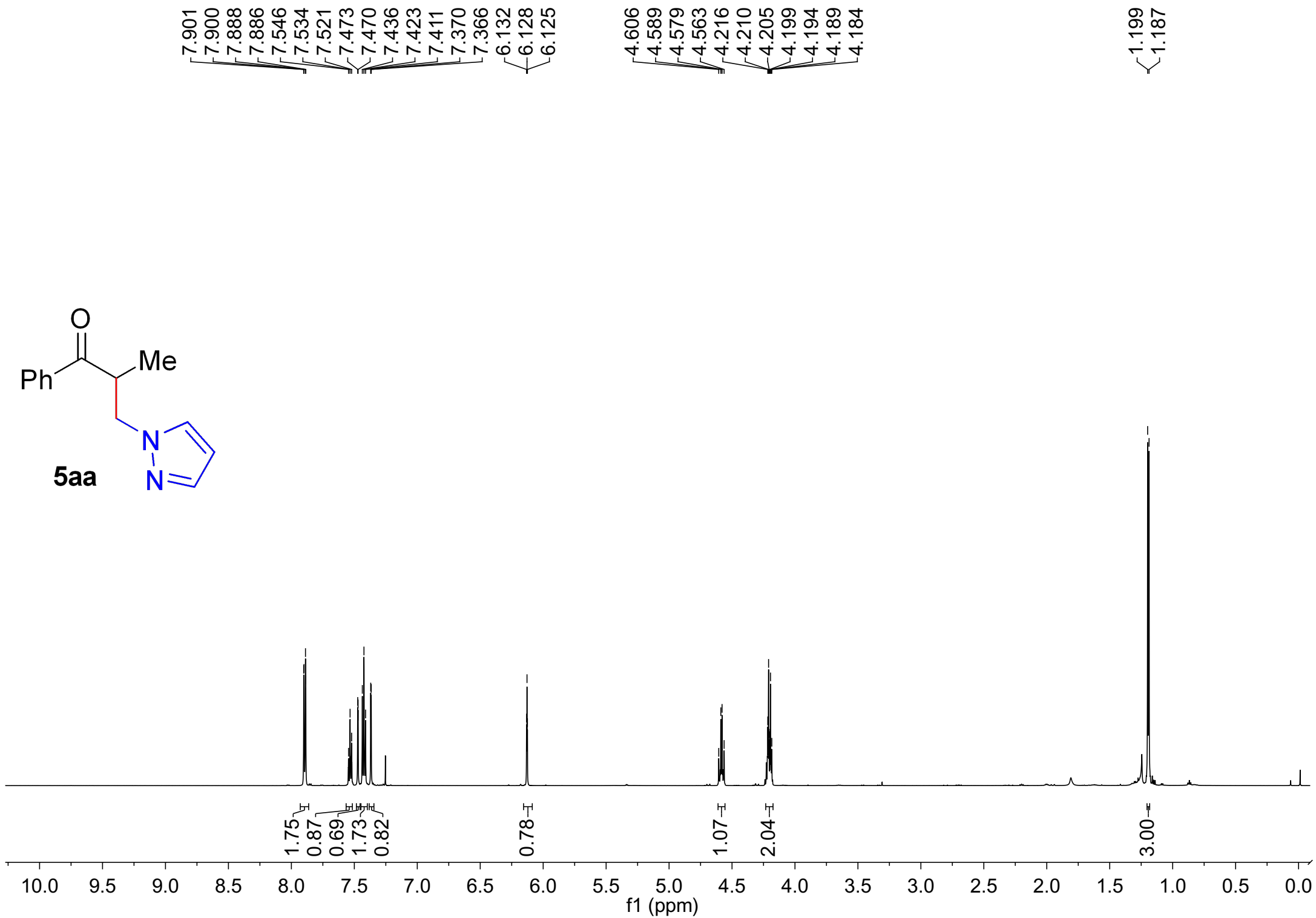
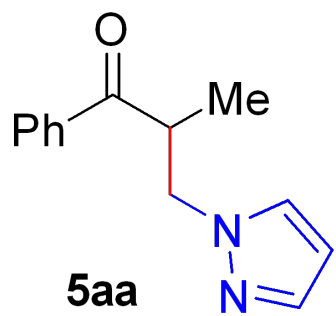


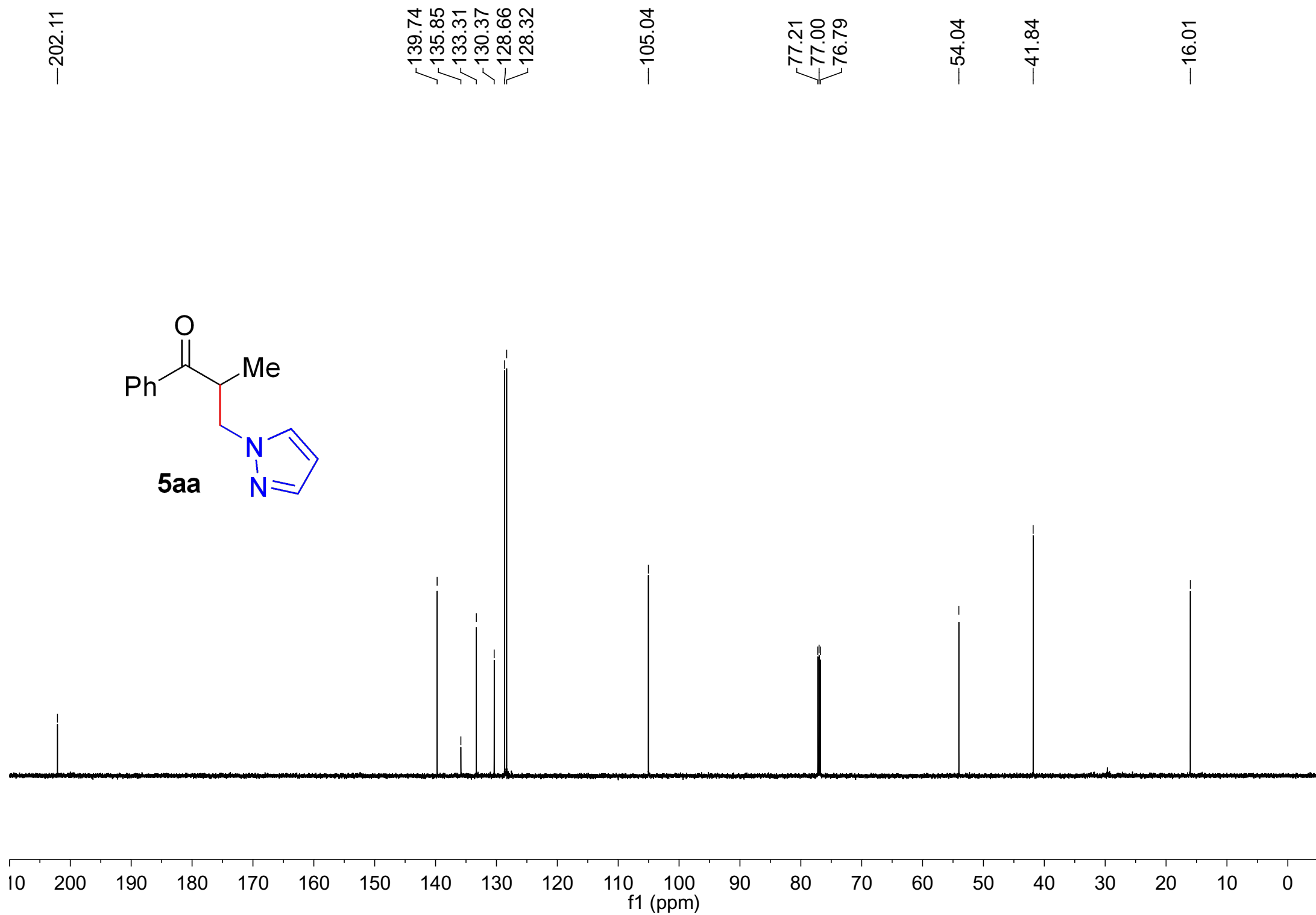
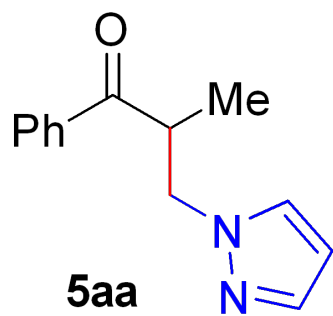


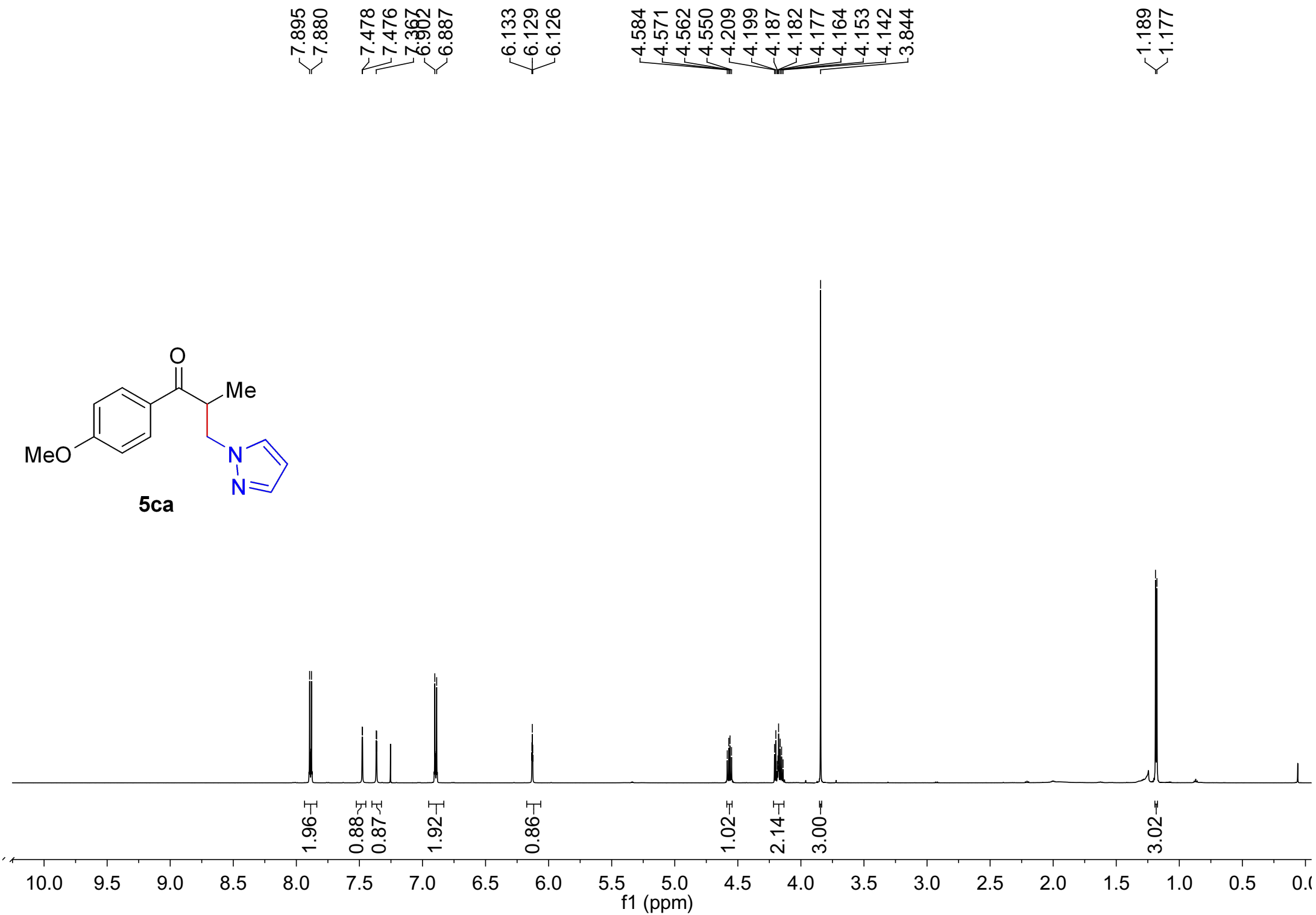
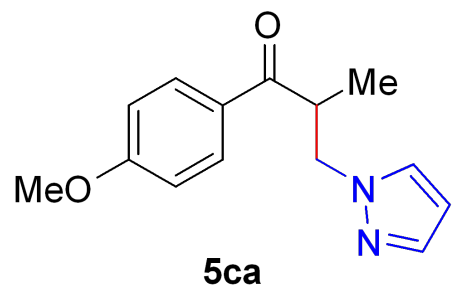


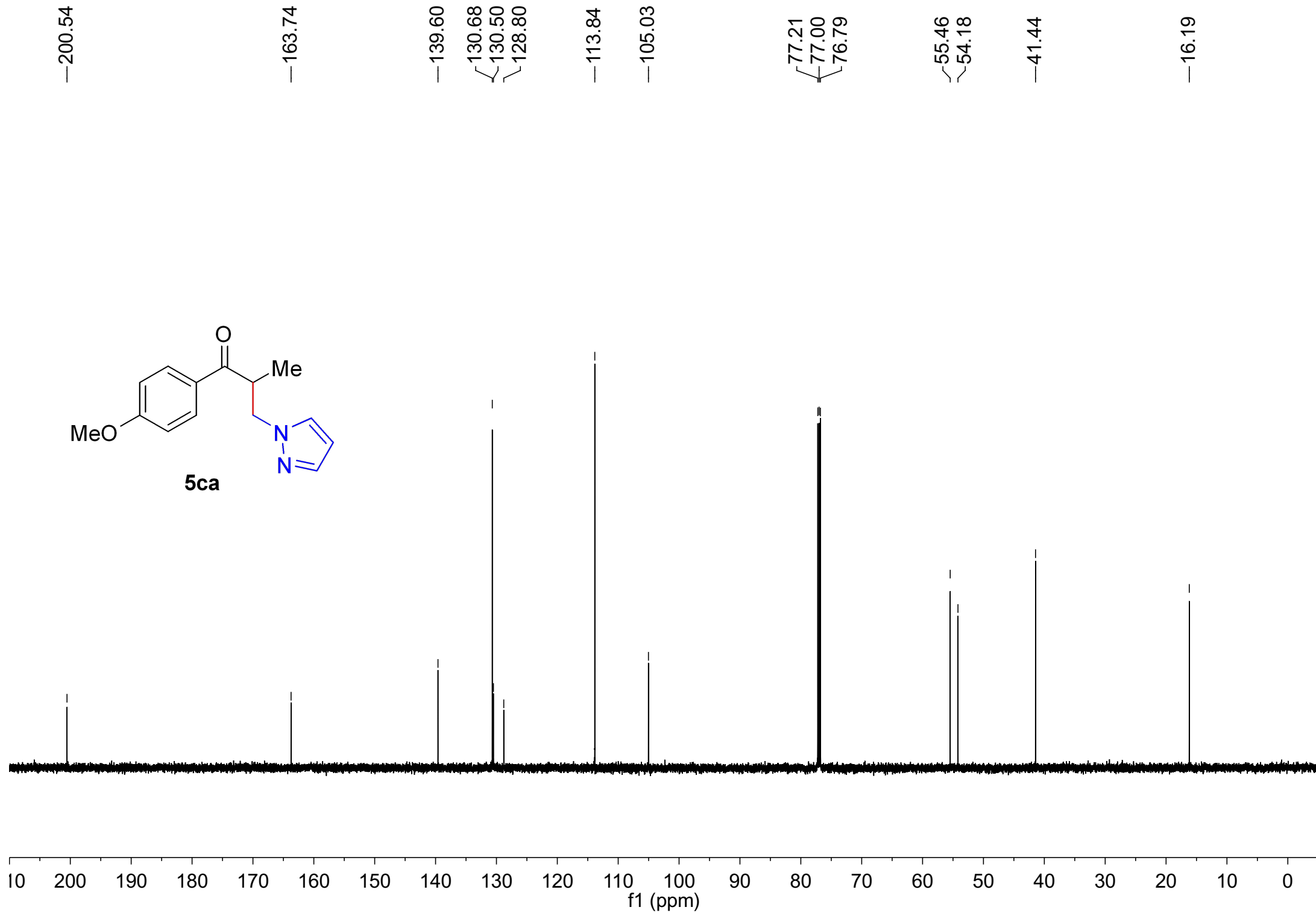
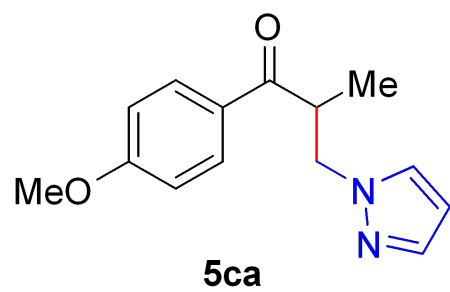


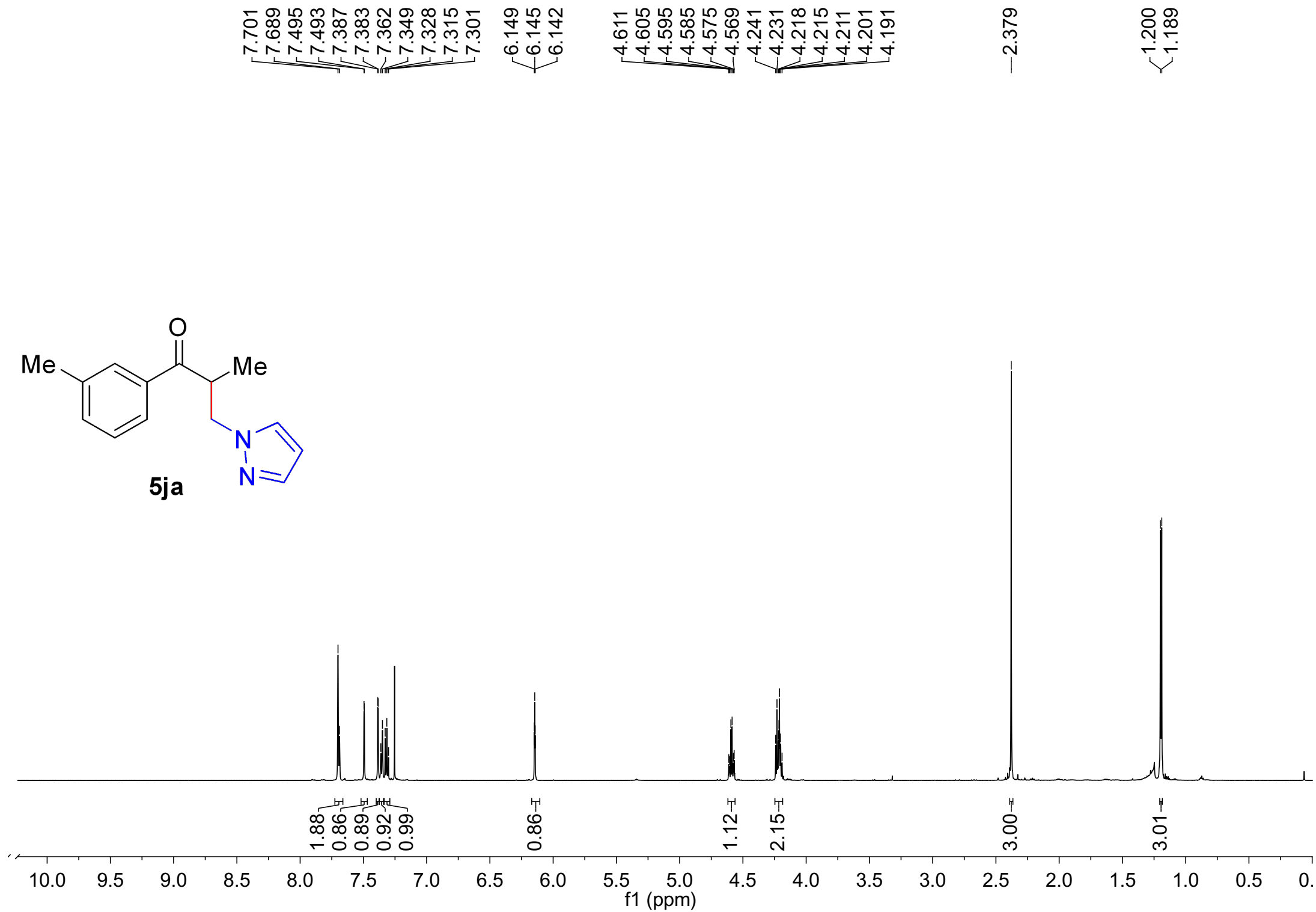
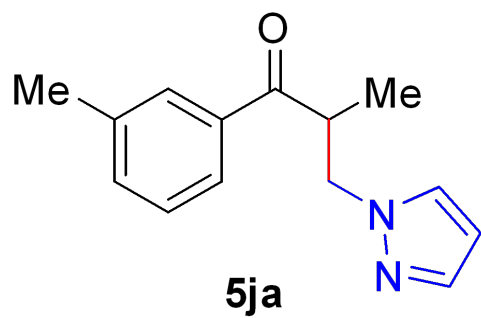


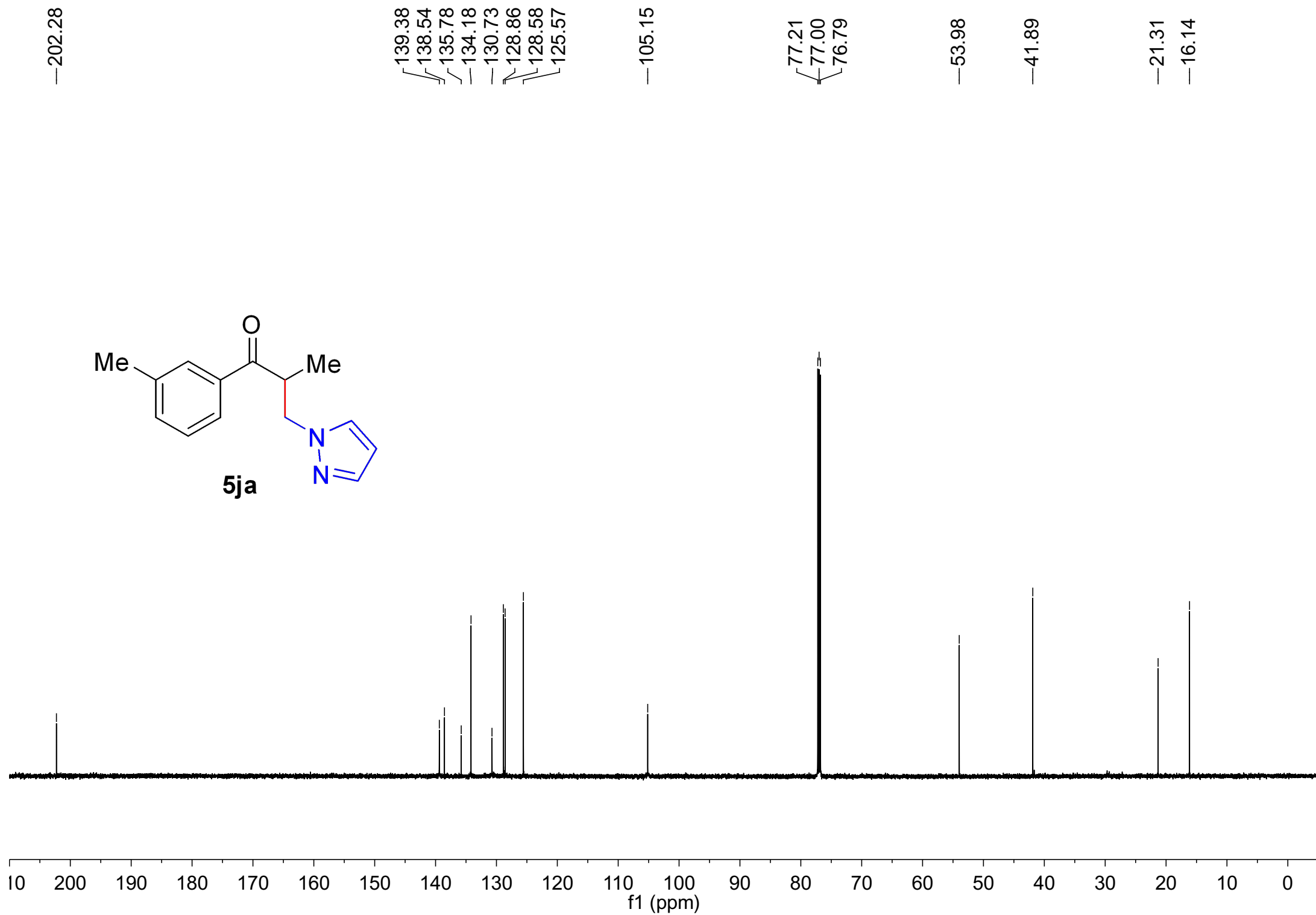
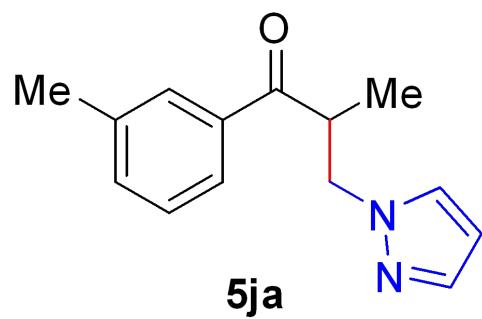


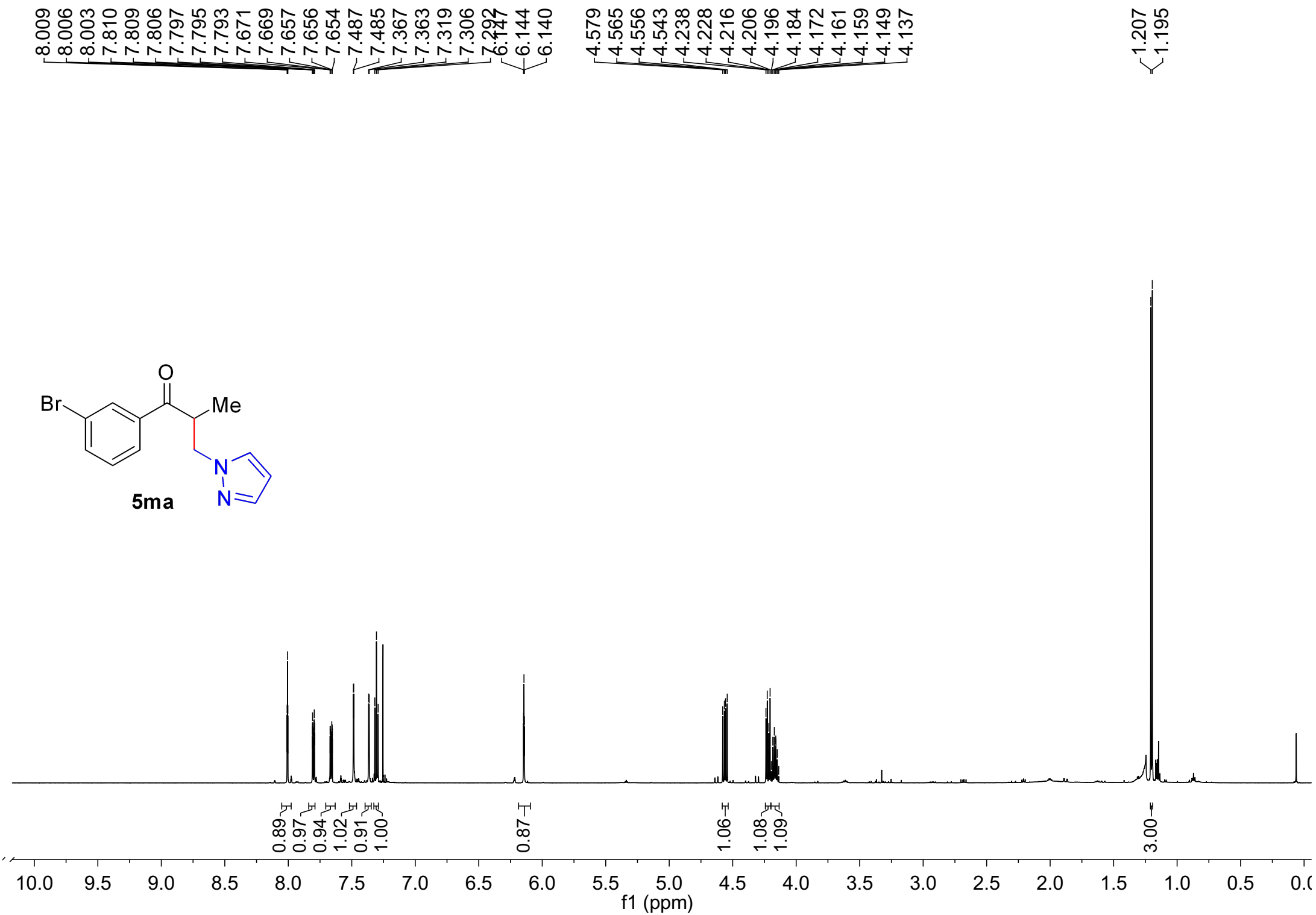


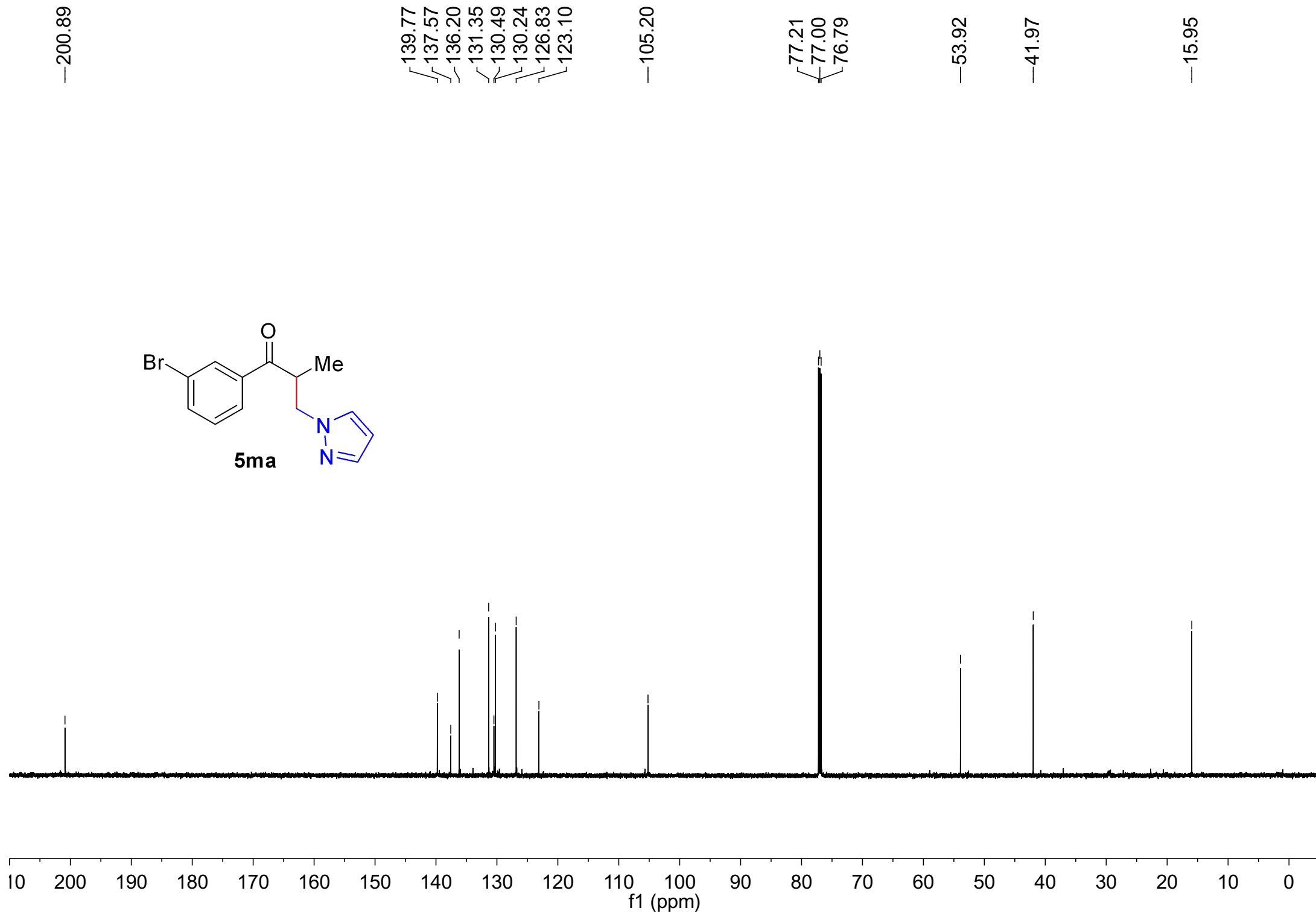
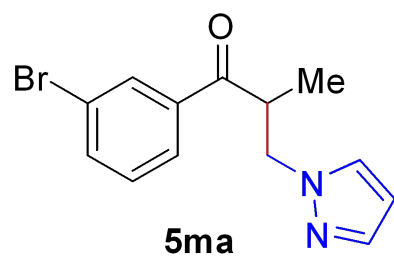


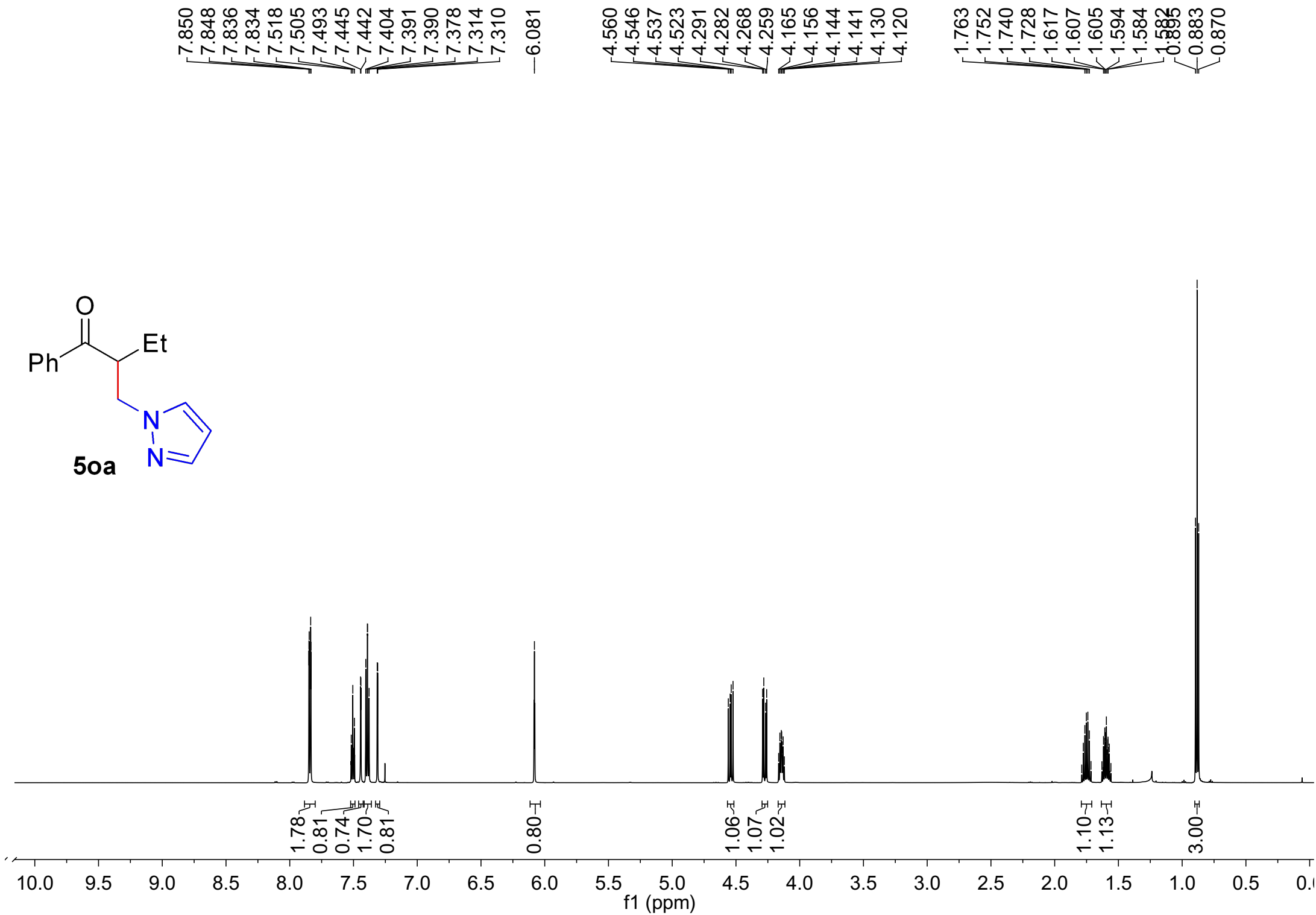
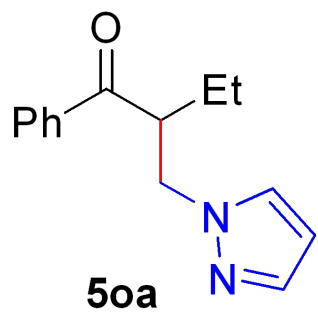


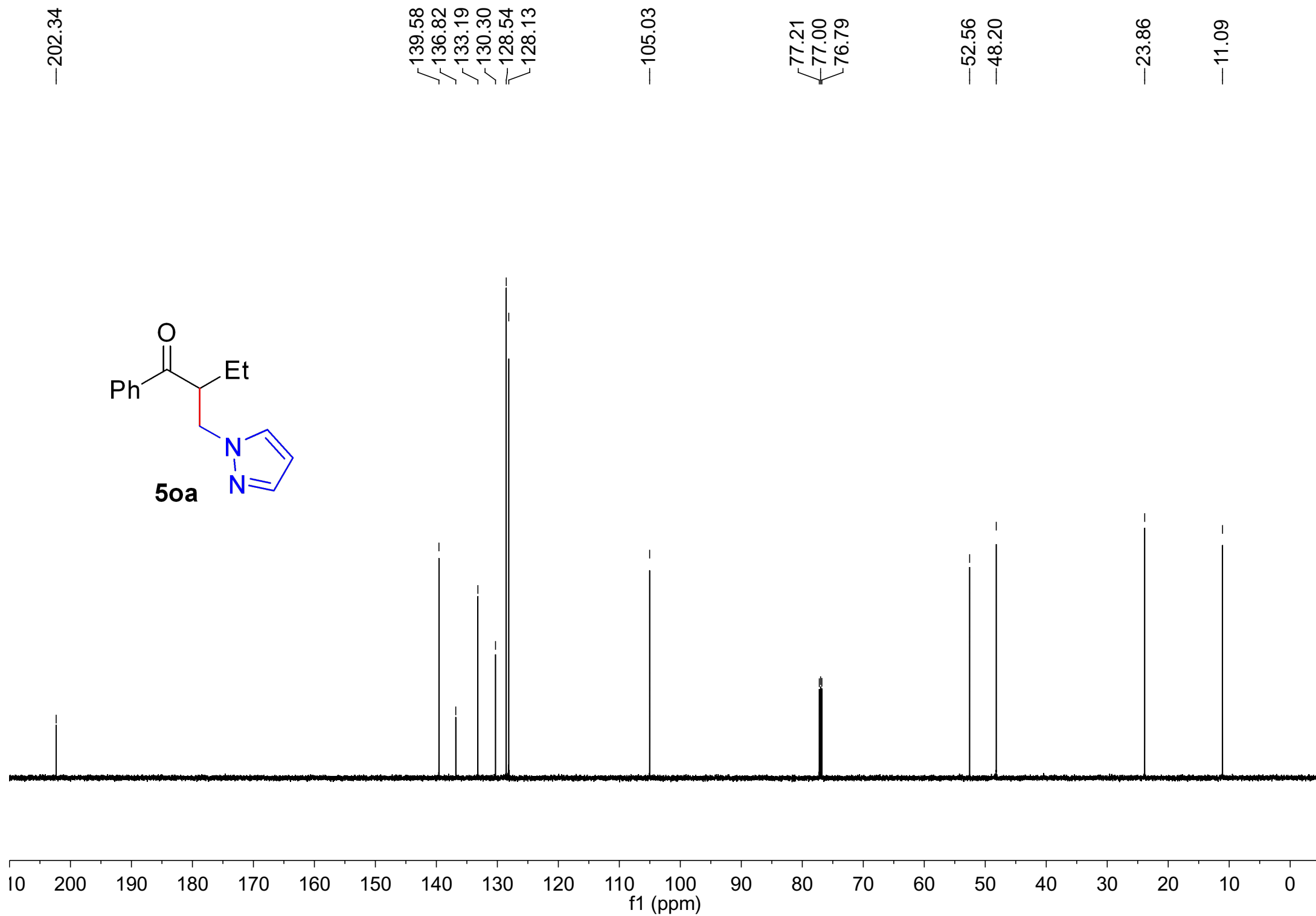
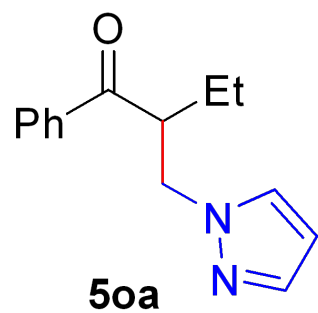


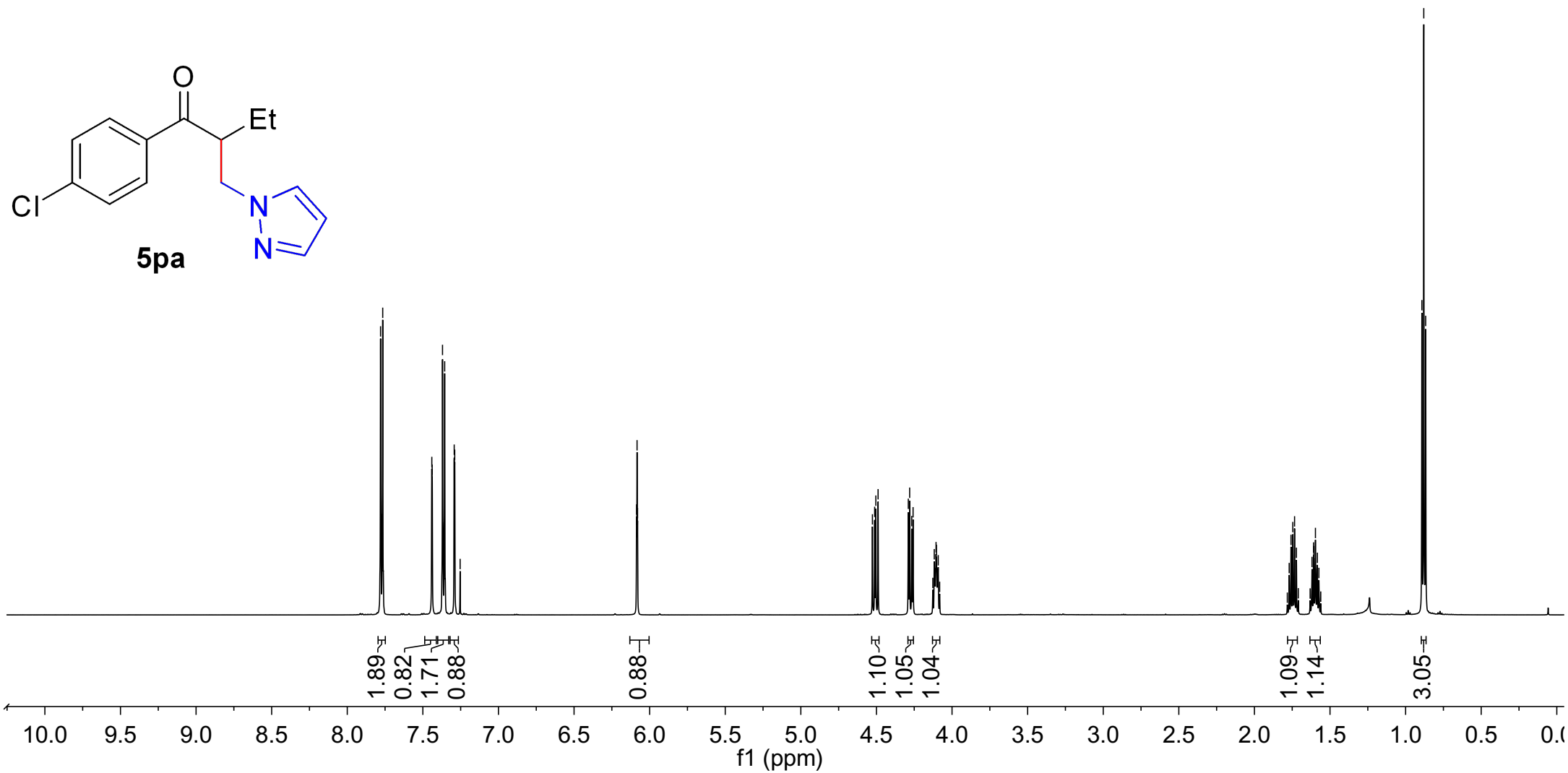


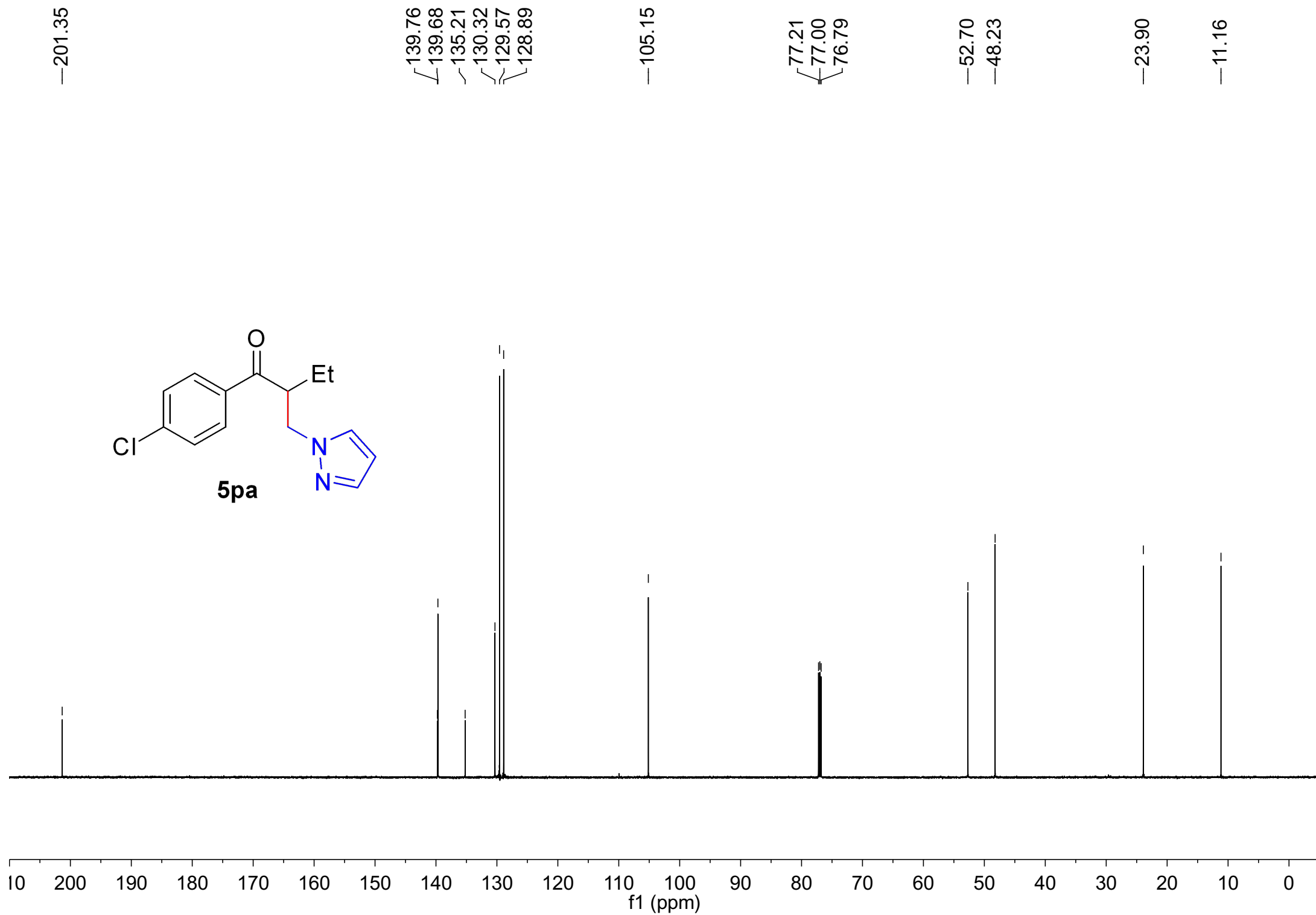
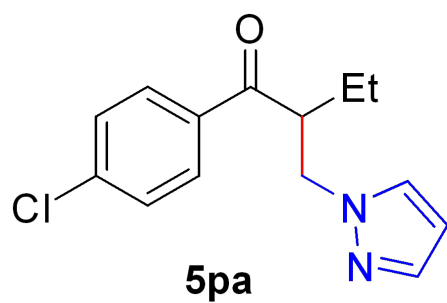


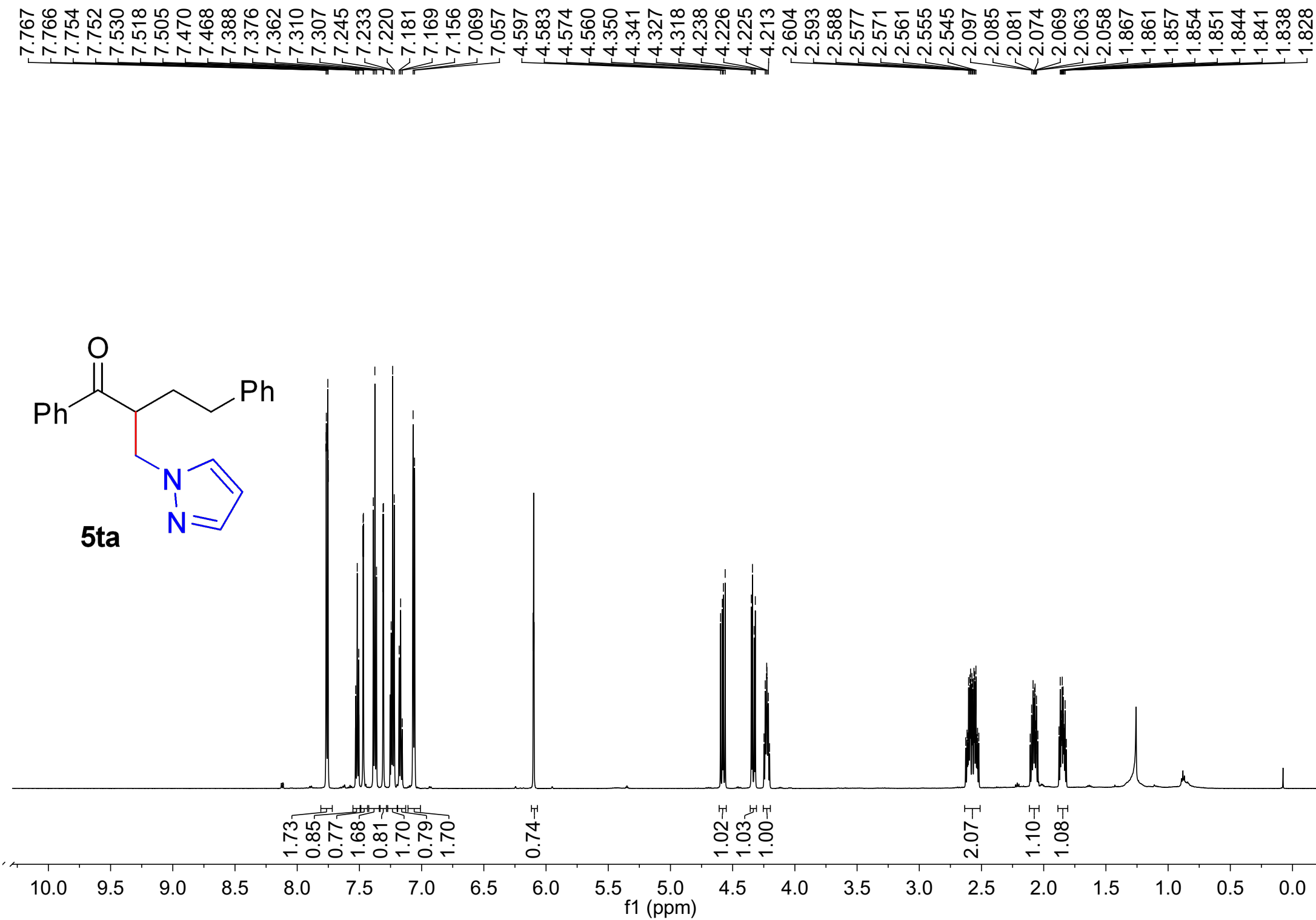
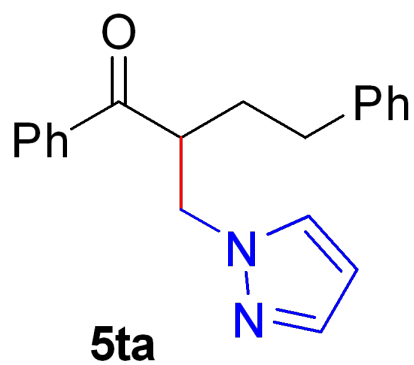


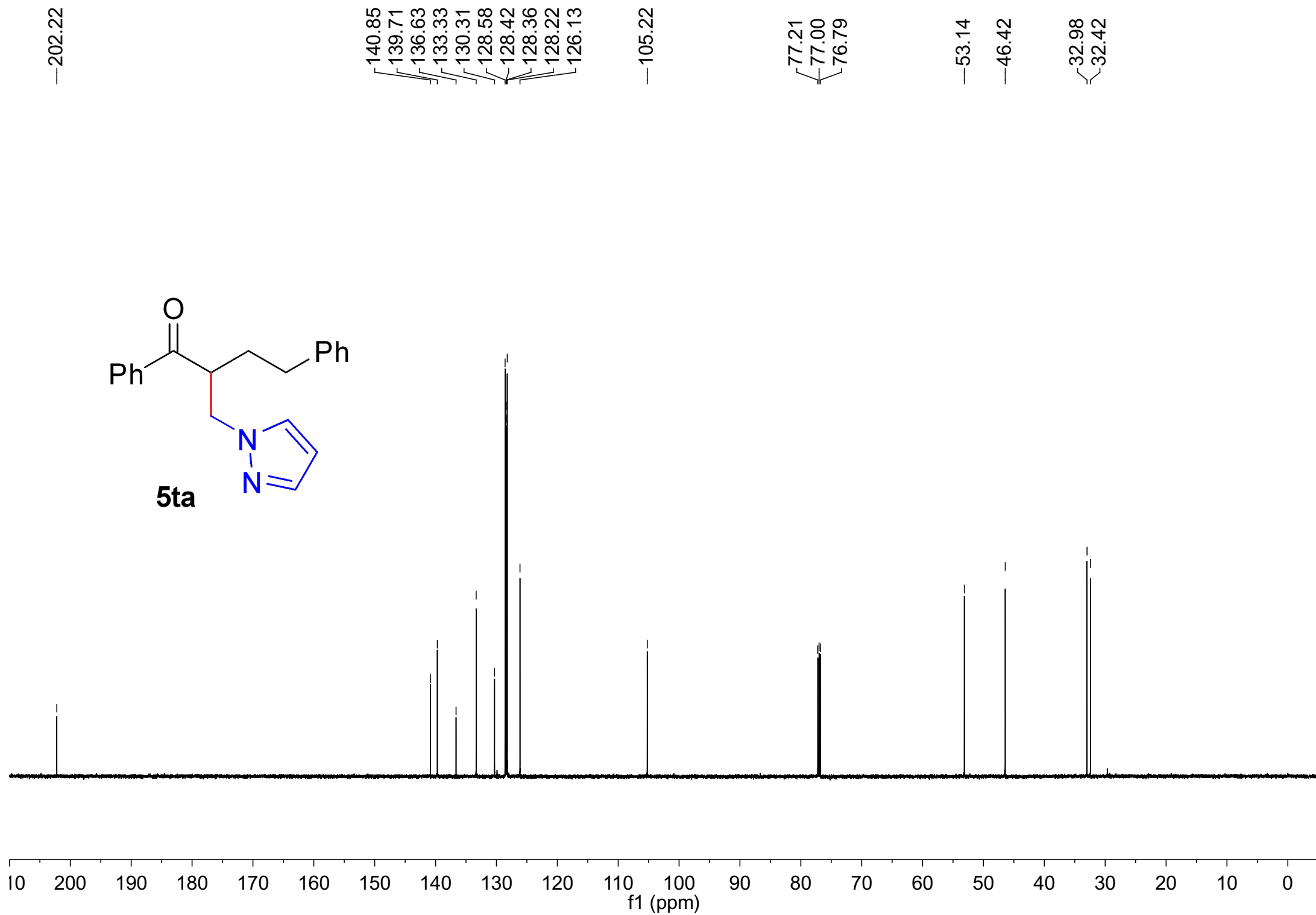
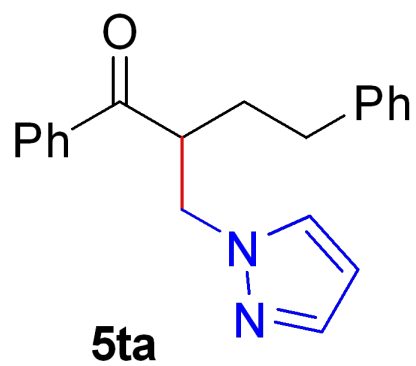


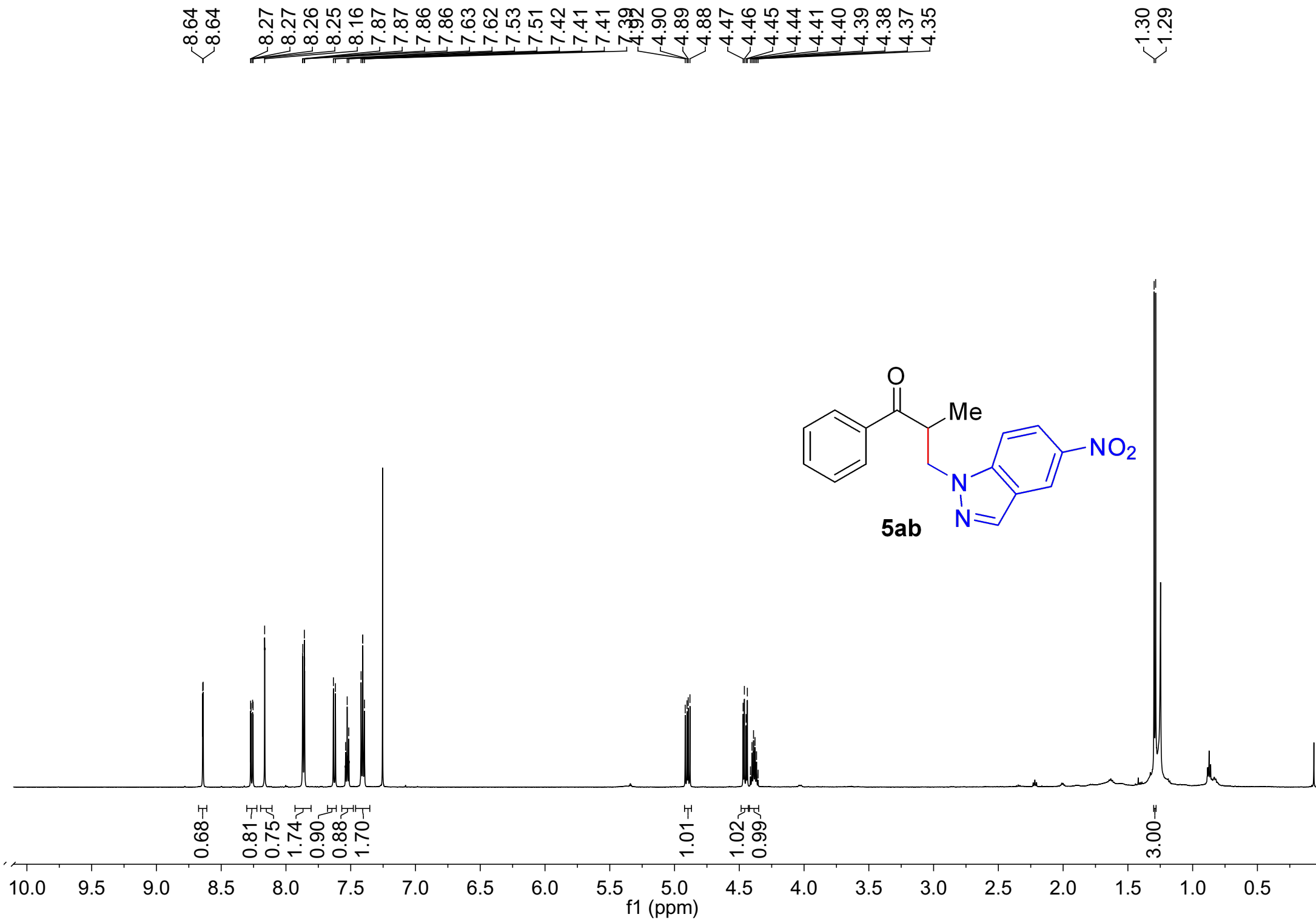




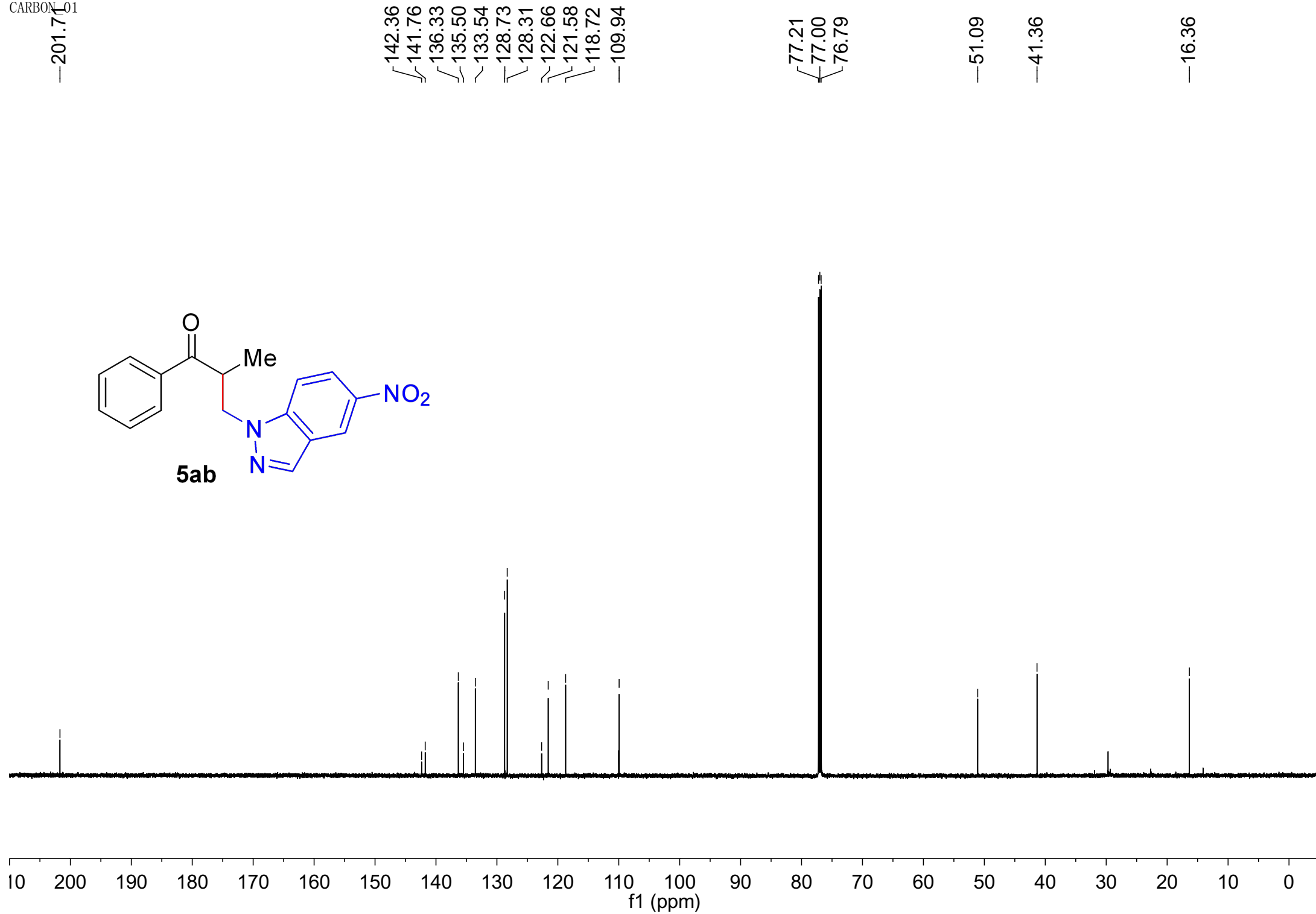
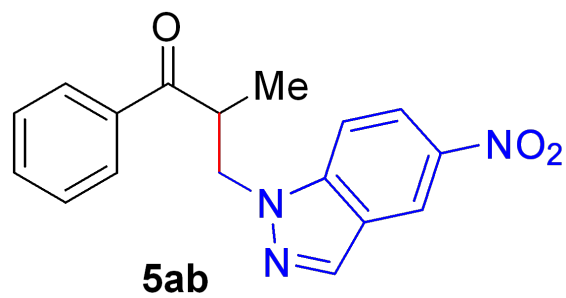


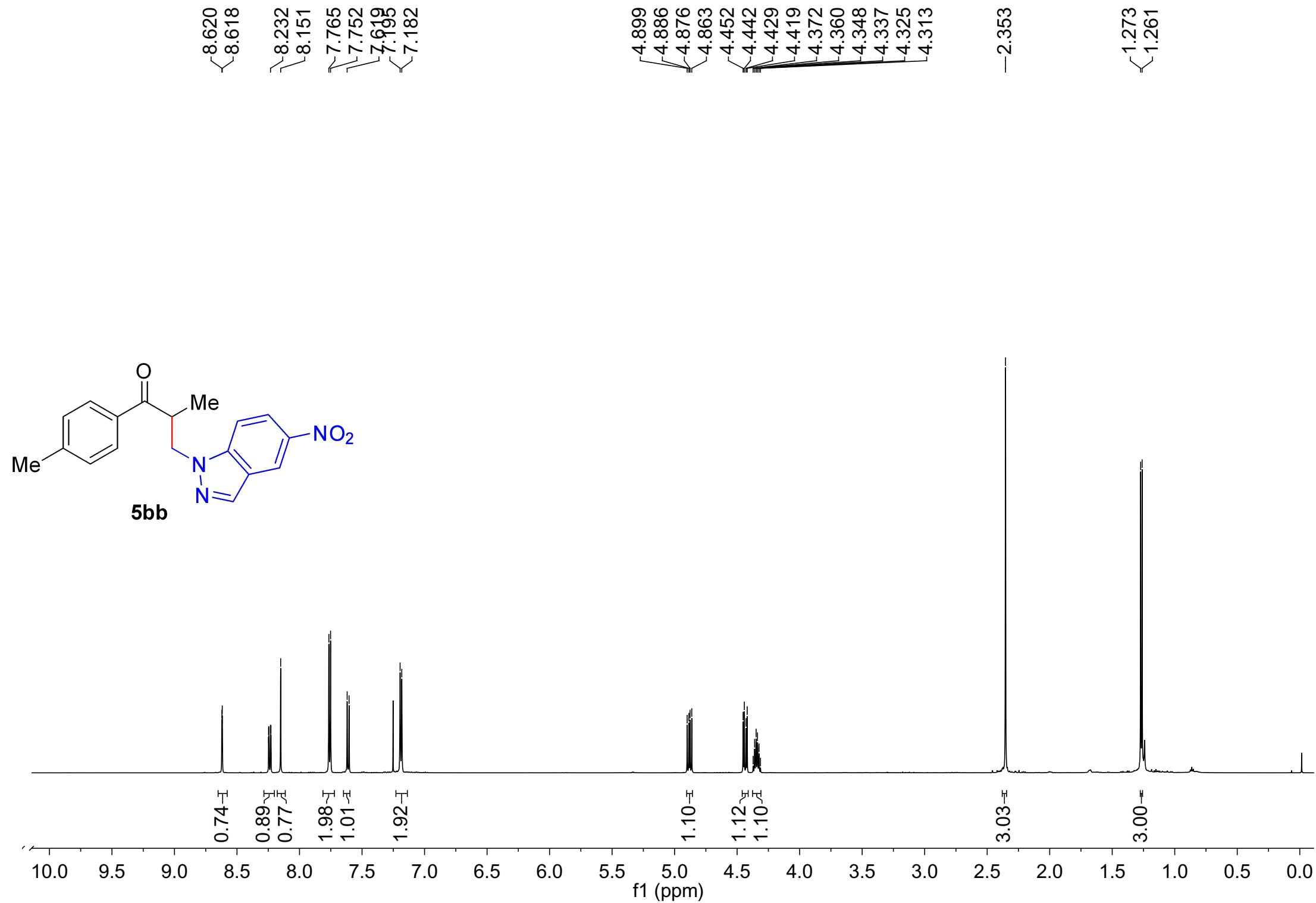


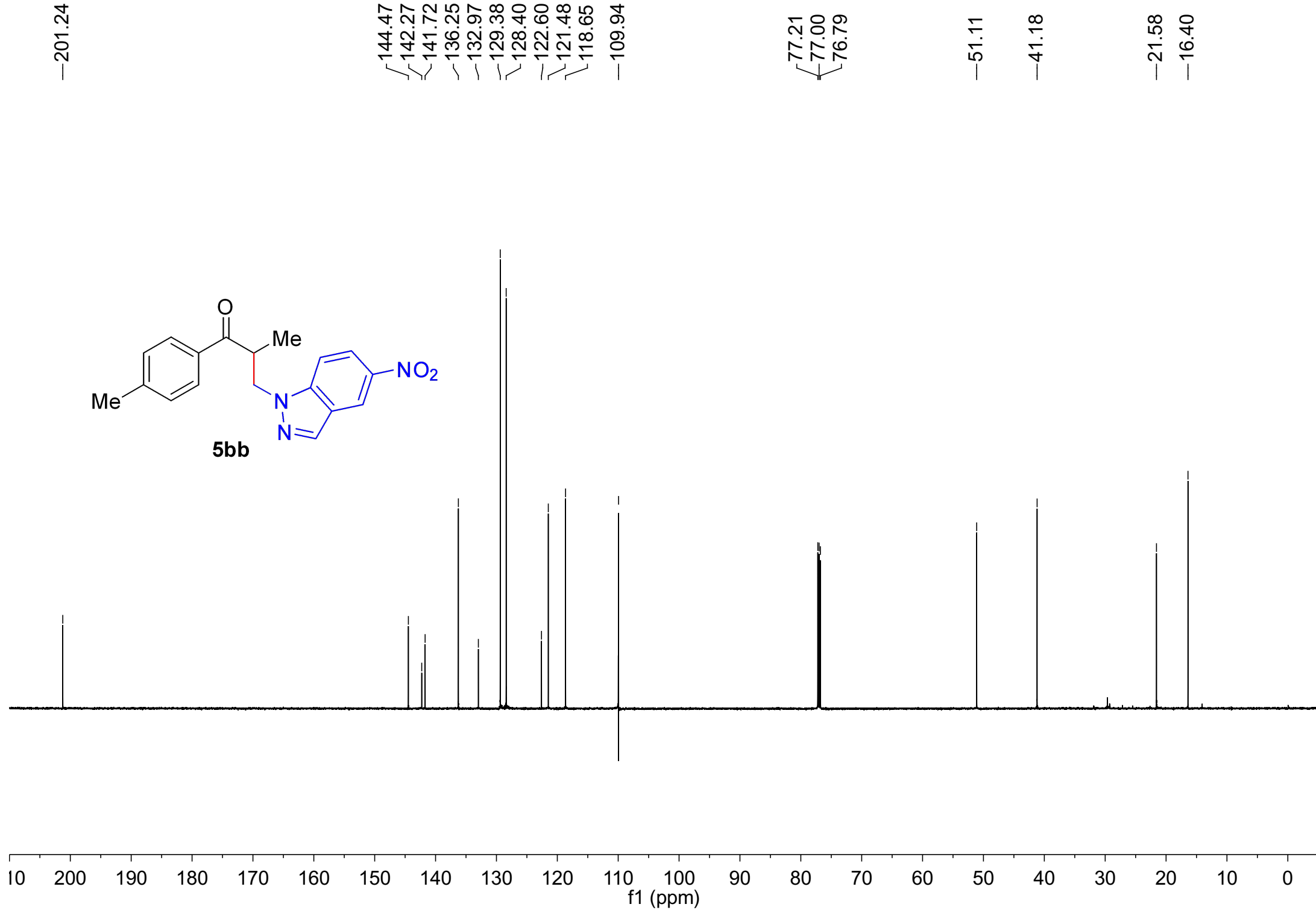
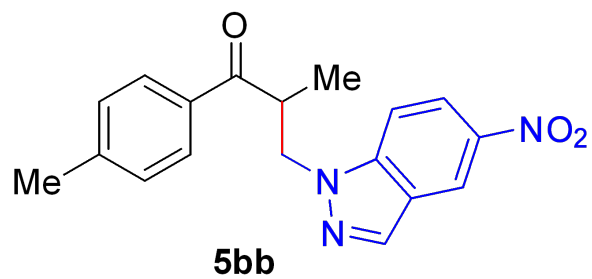


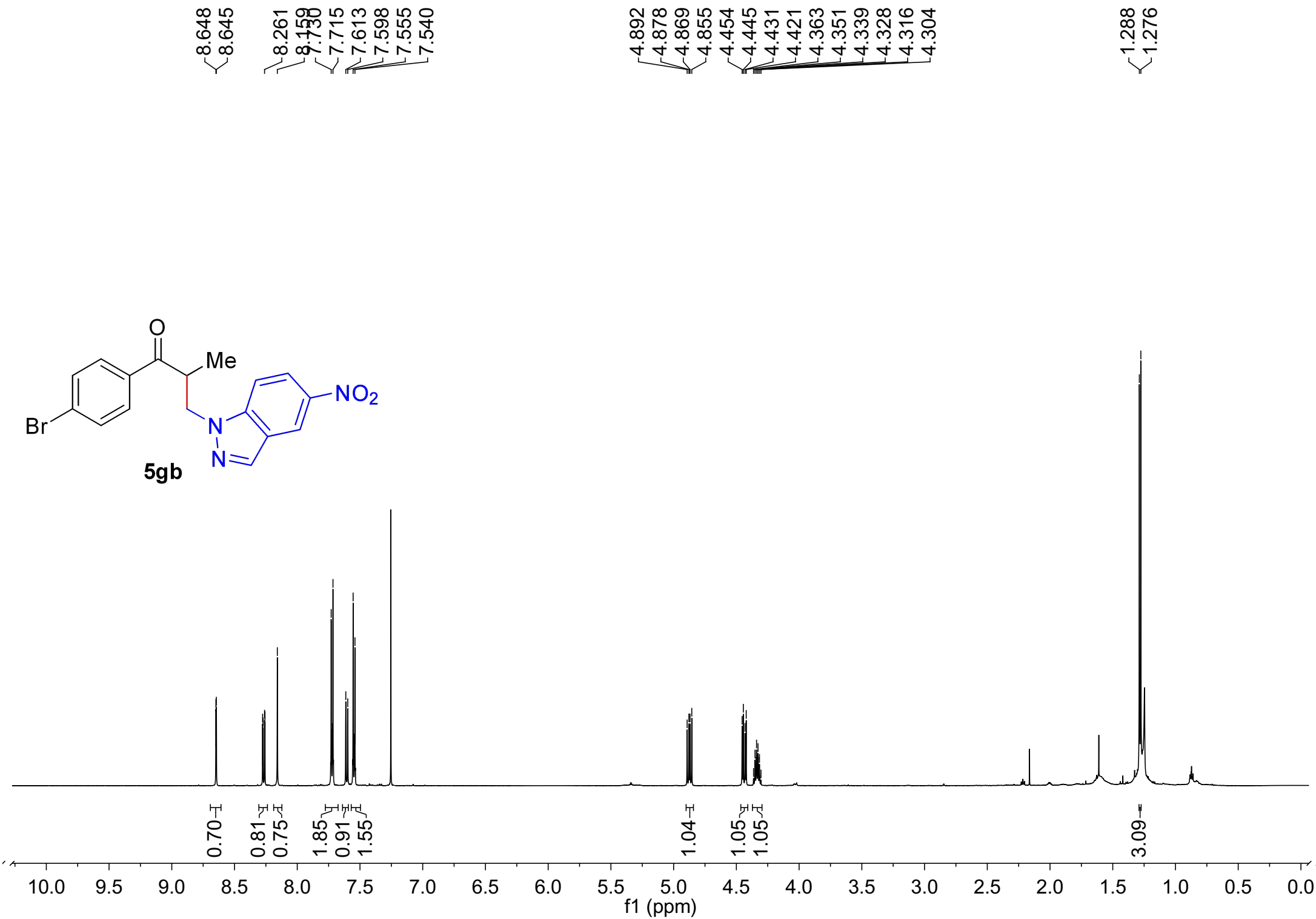
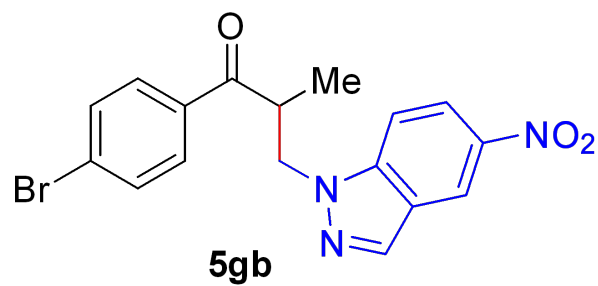


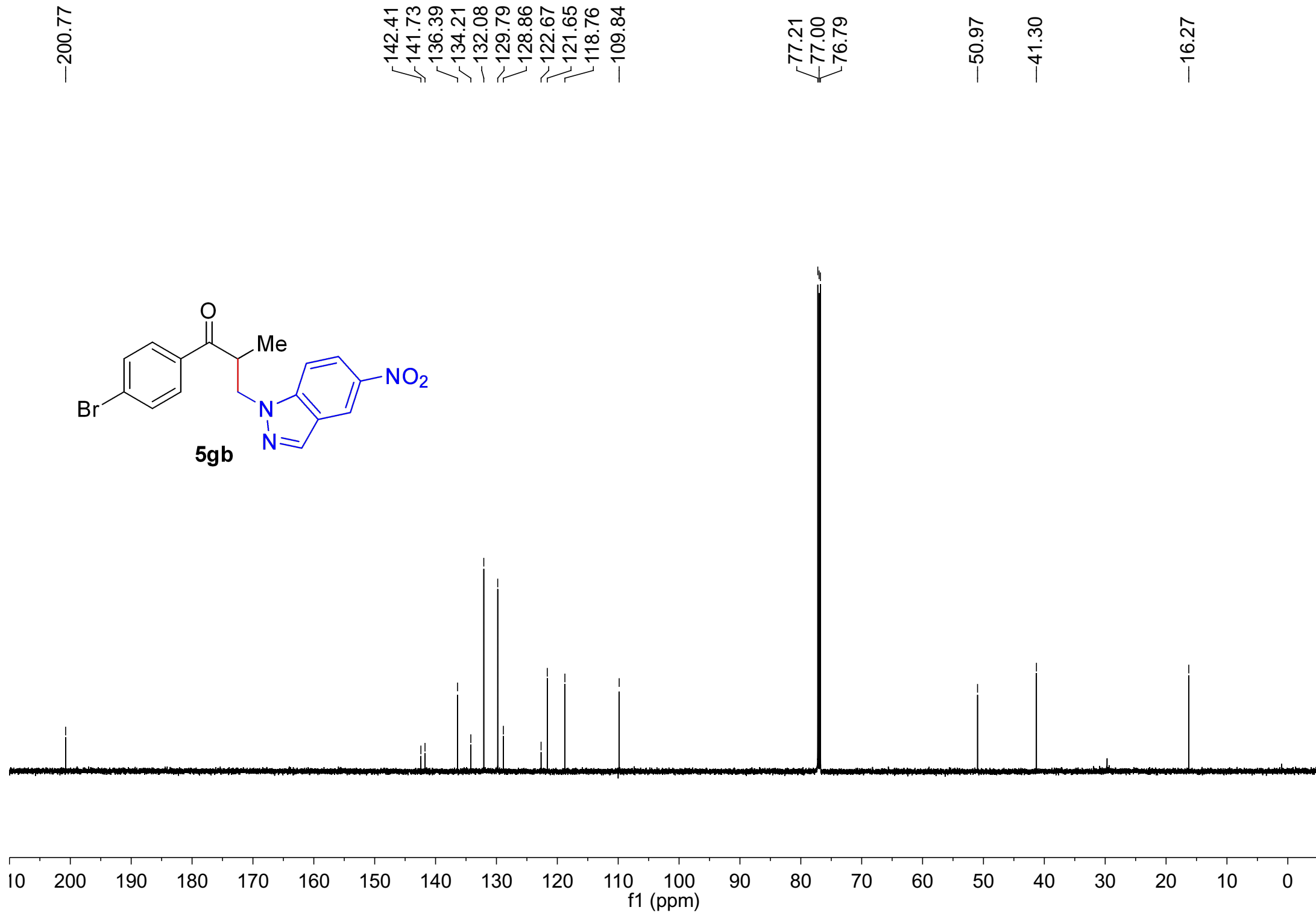
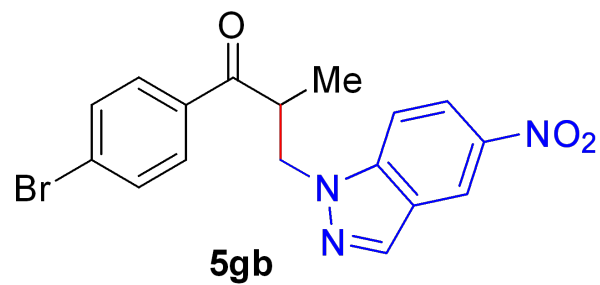
CARBON_01

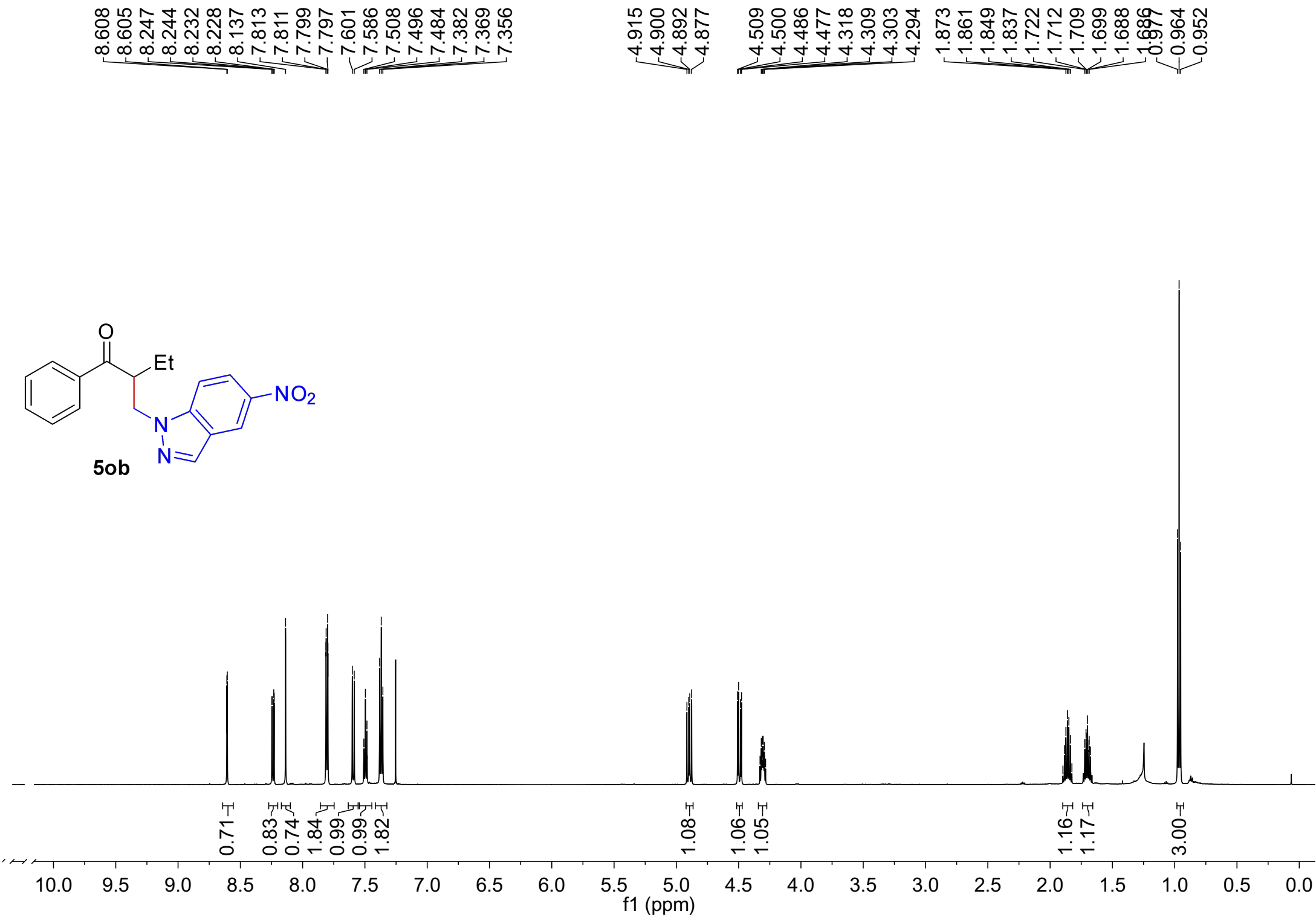
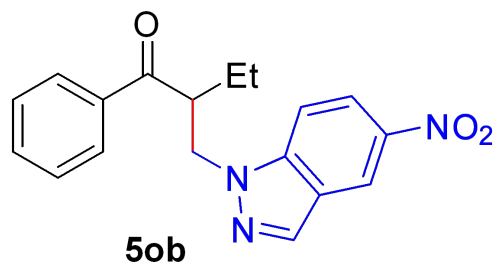


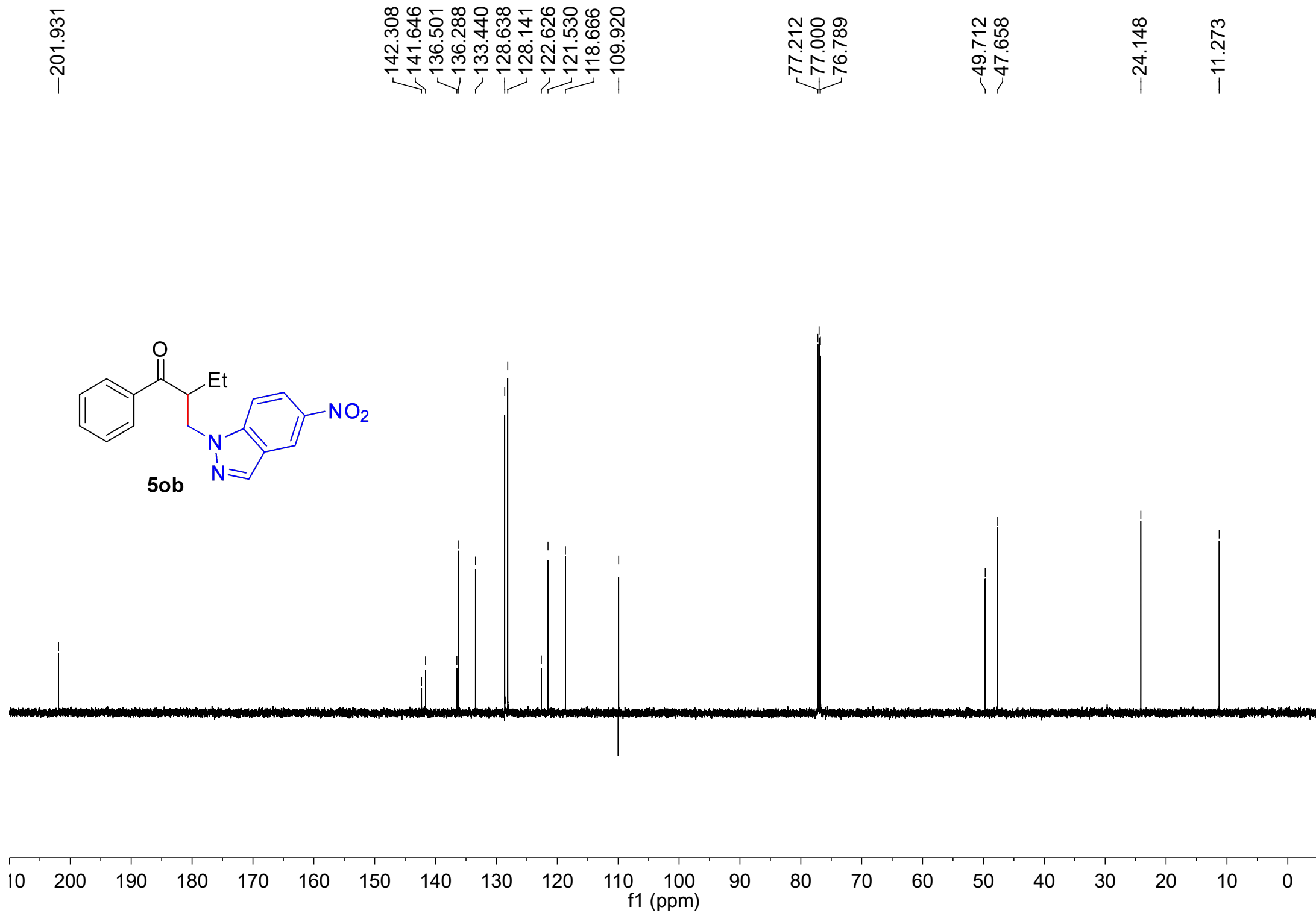
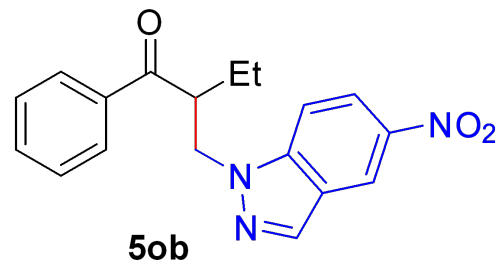


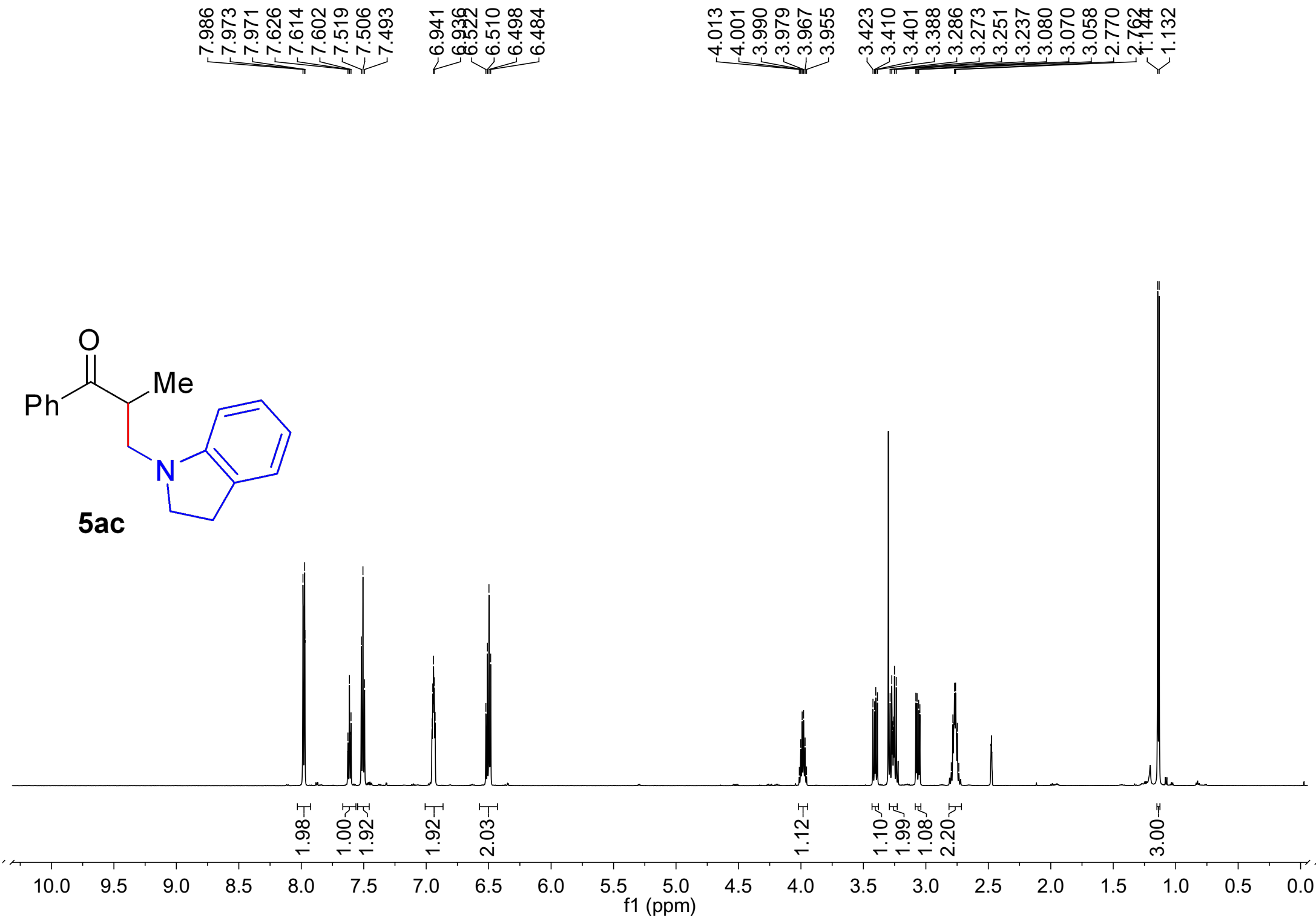
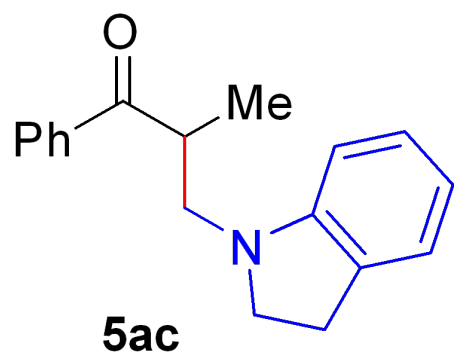


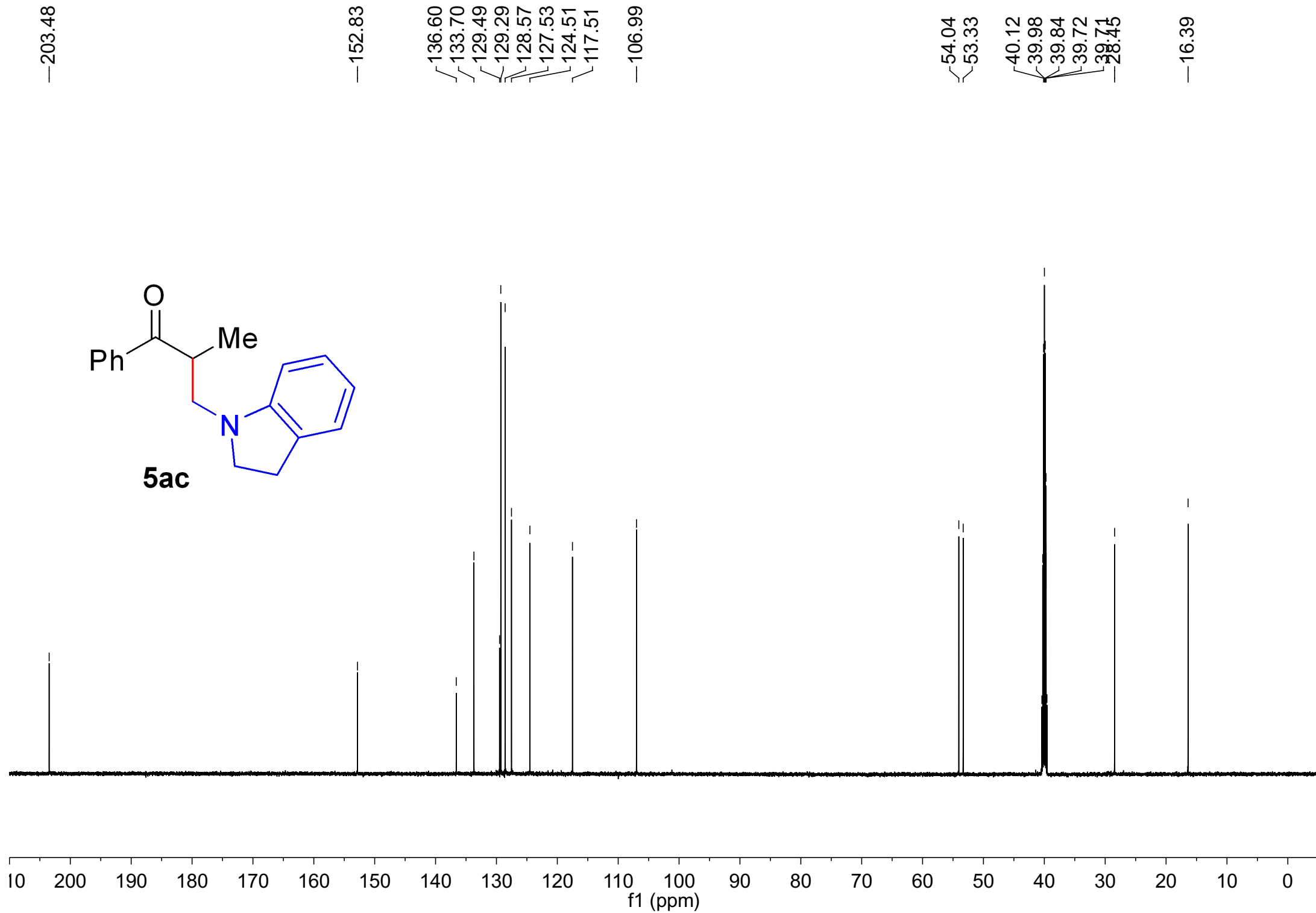


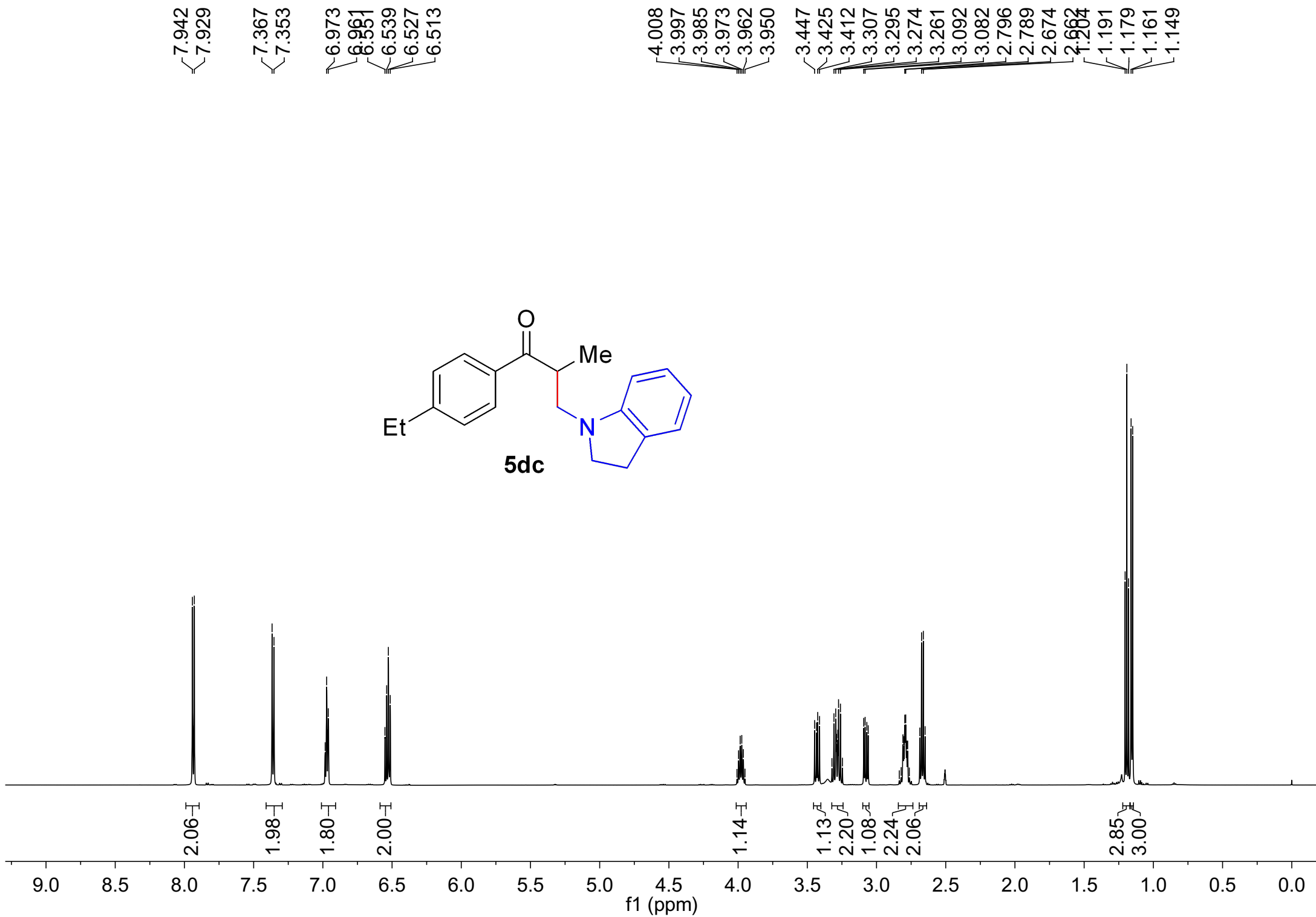












—207.65

~157.59
~154.86

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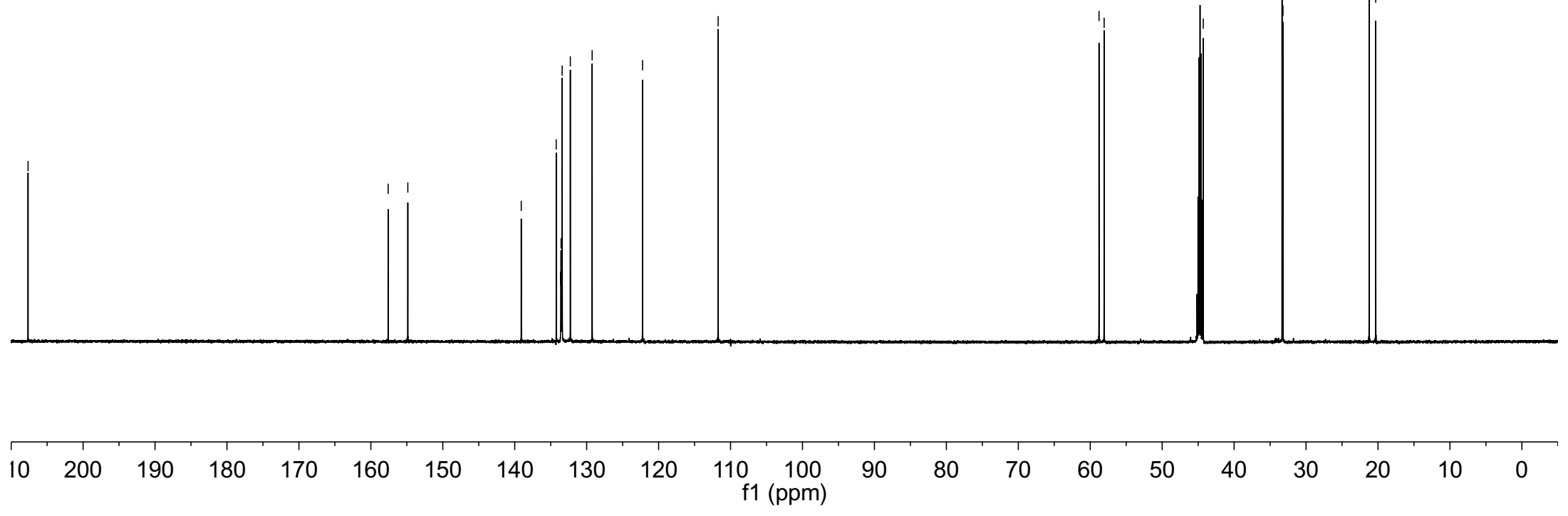
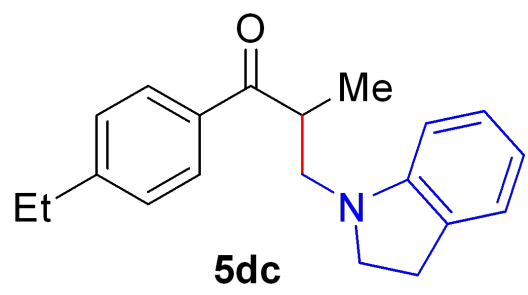
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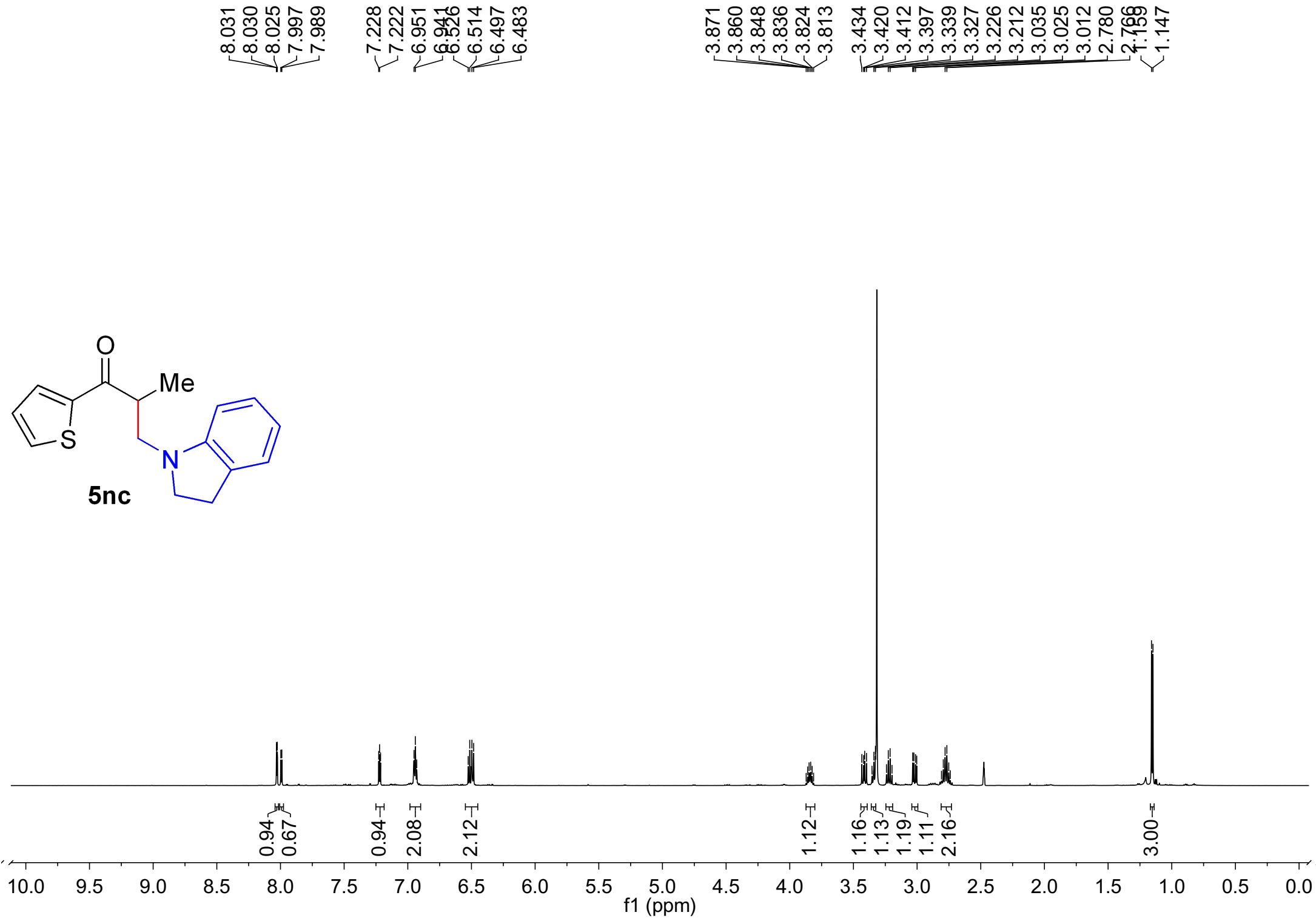
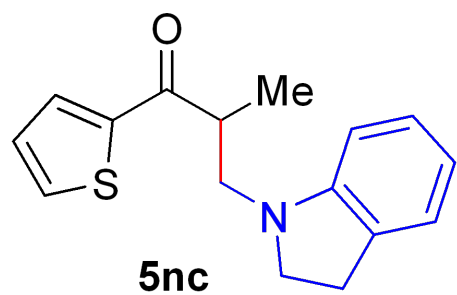
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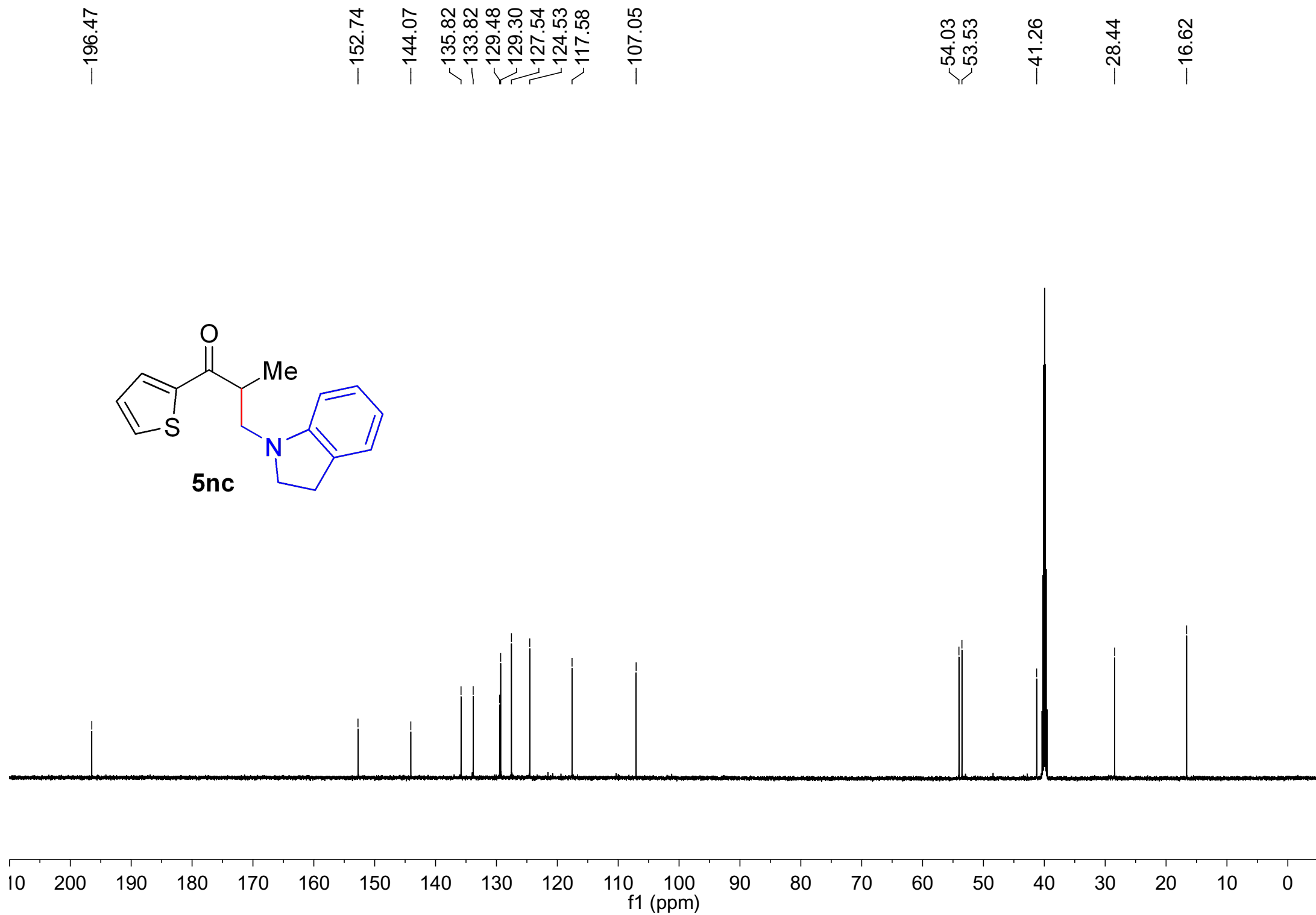
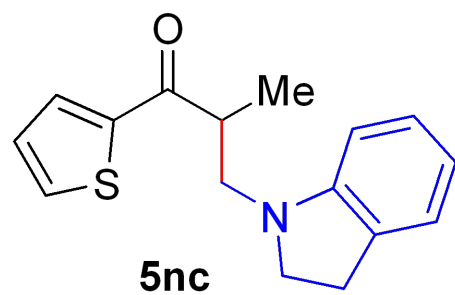
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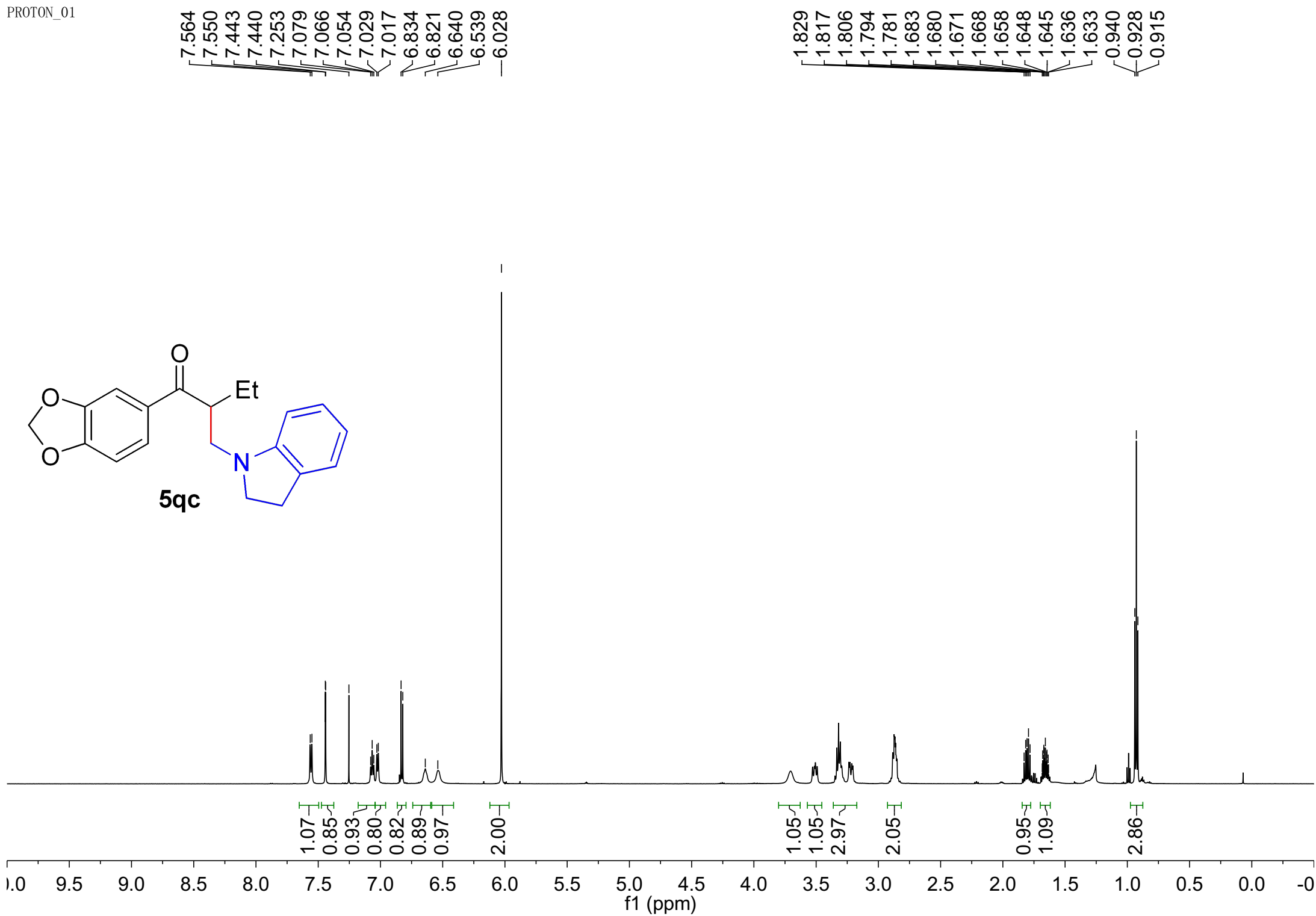
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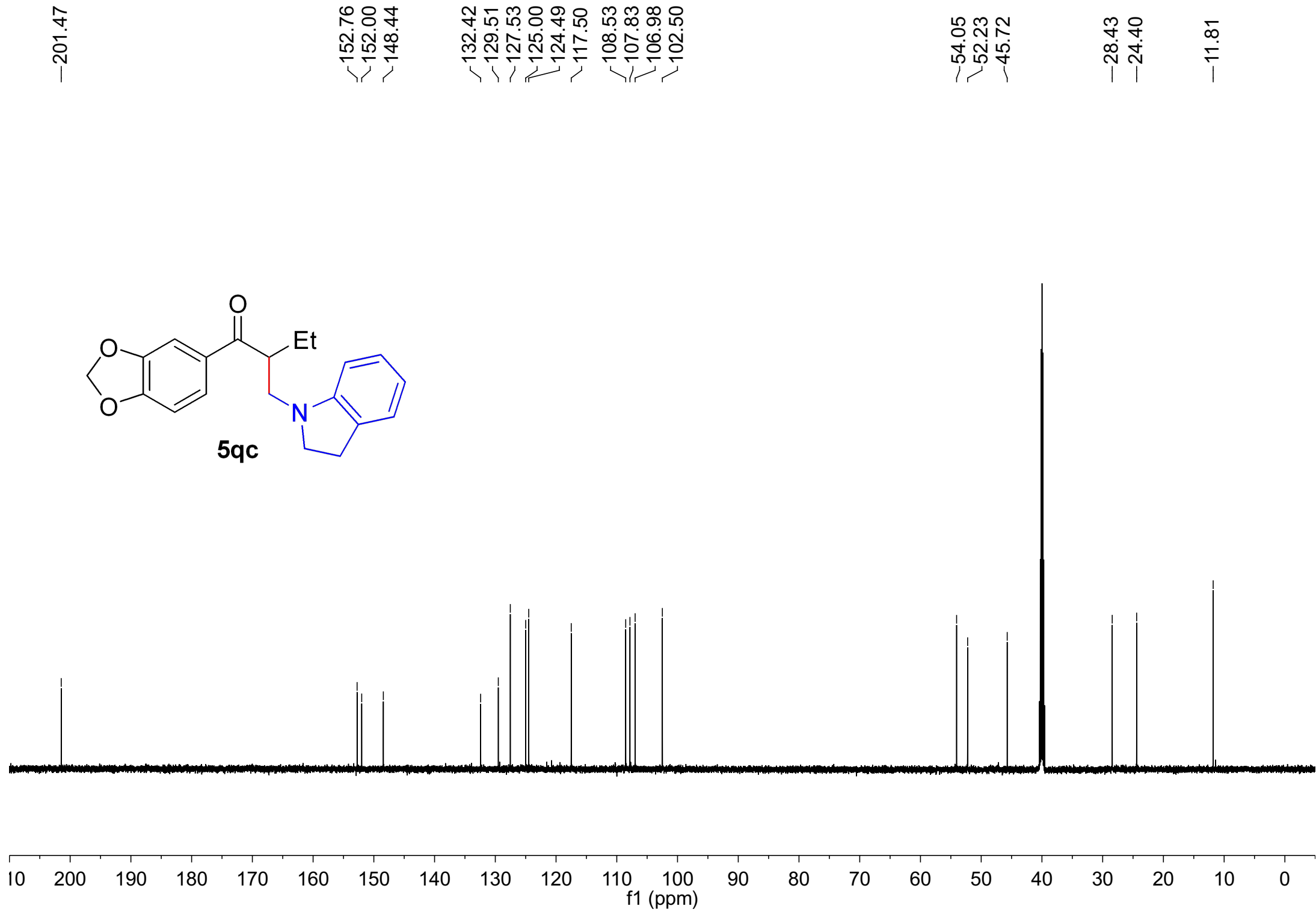
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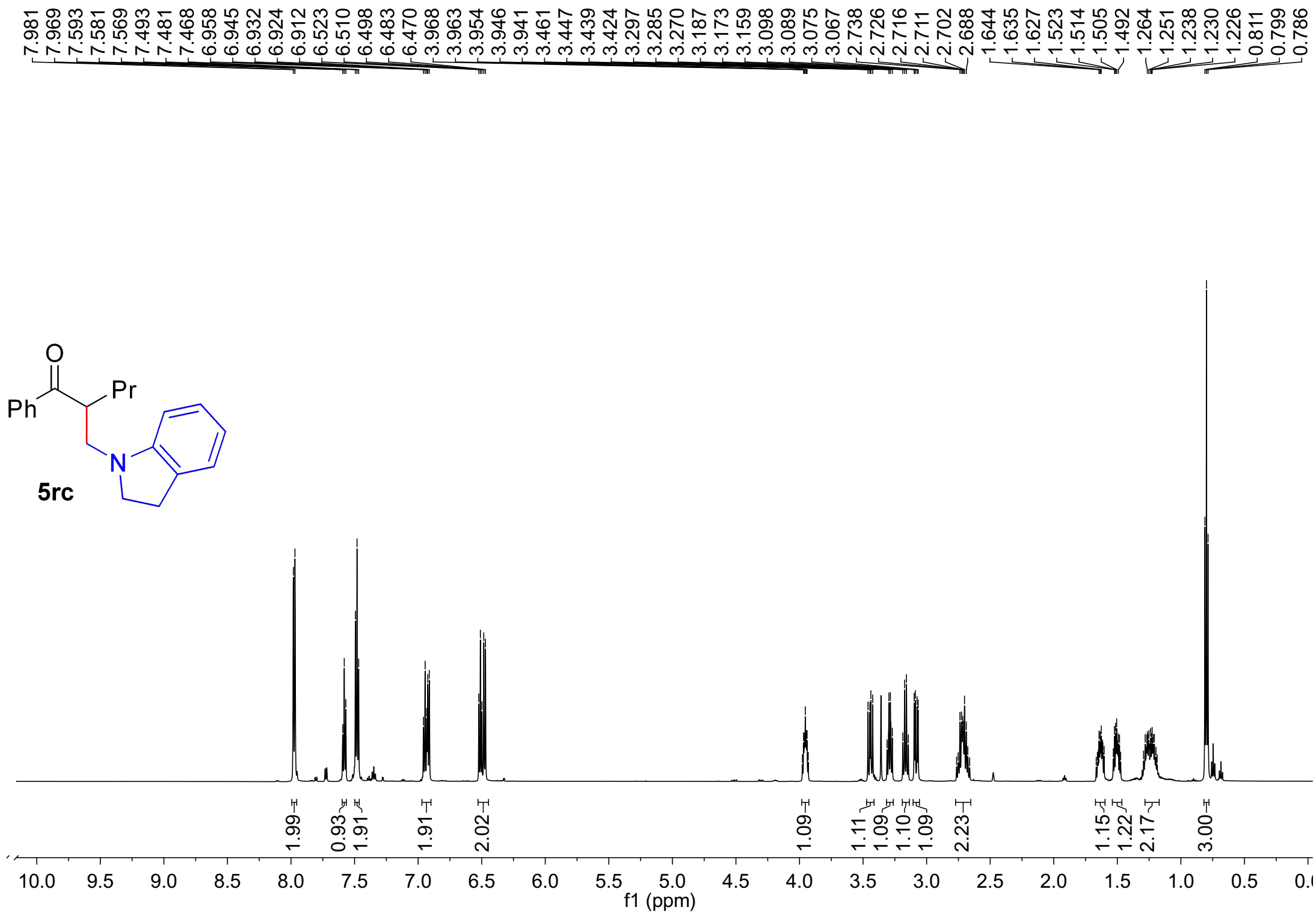
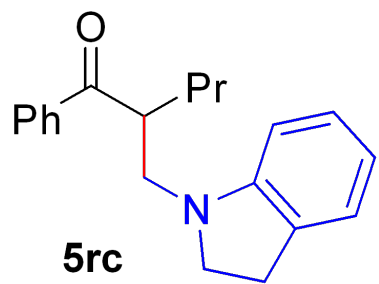


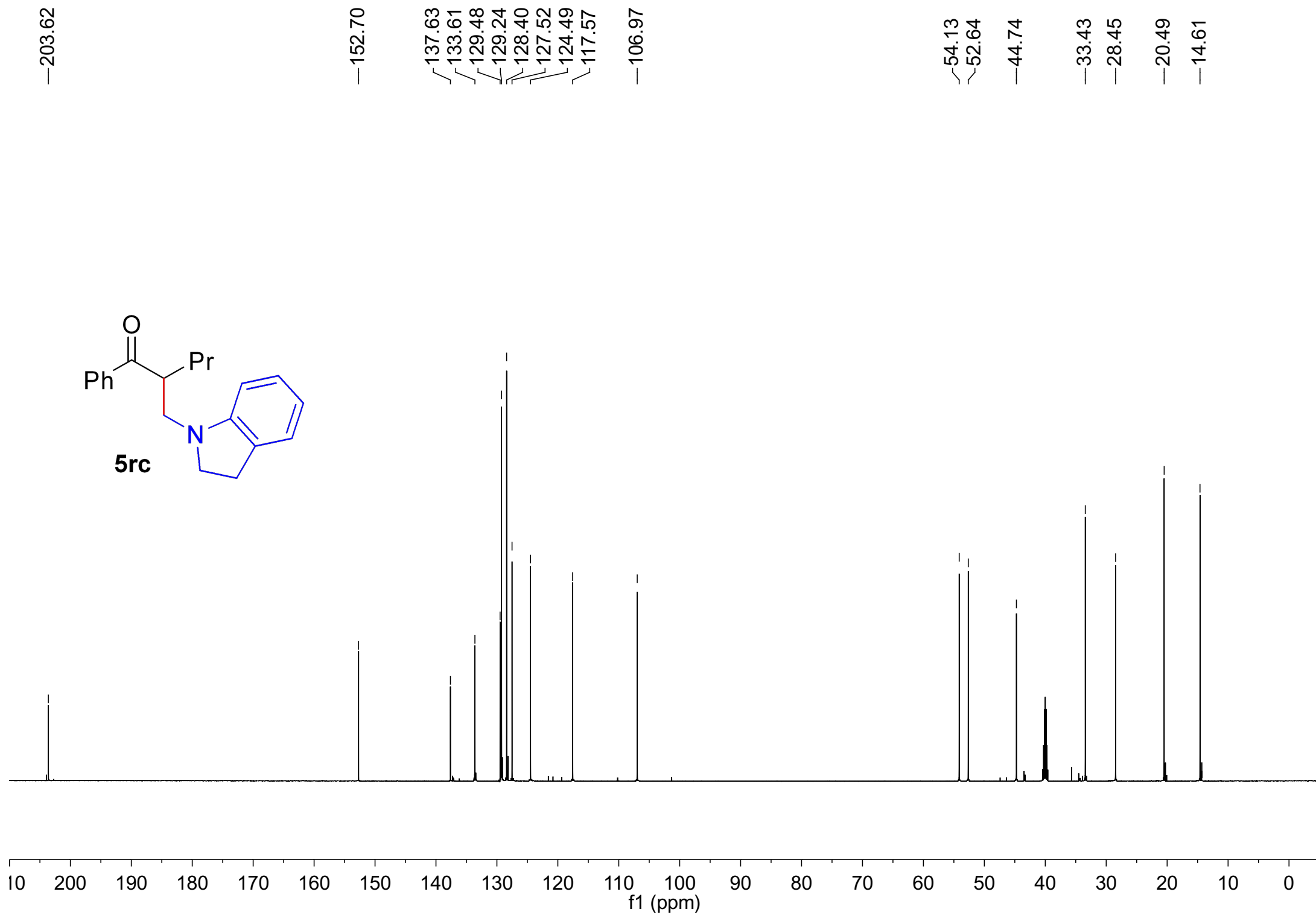
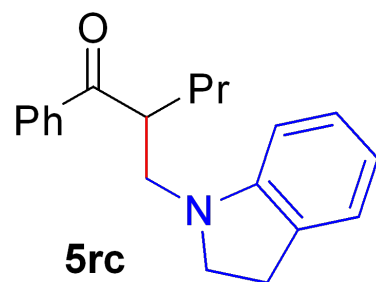


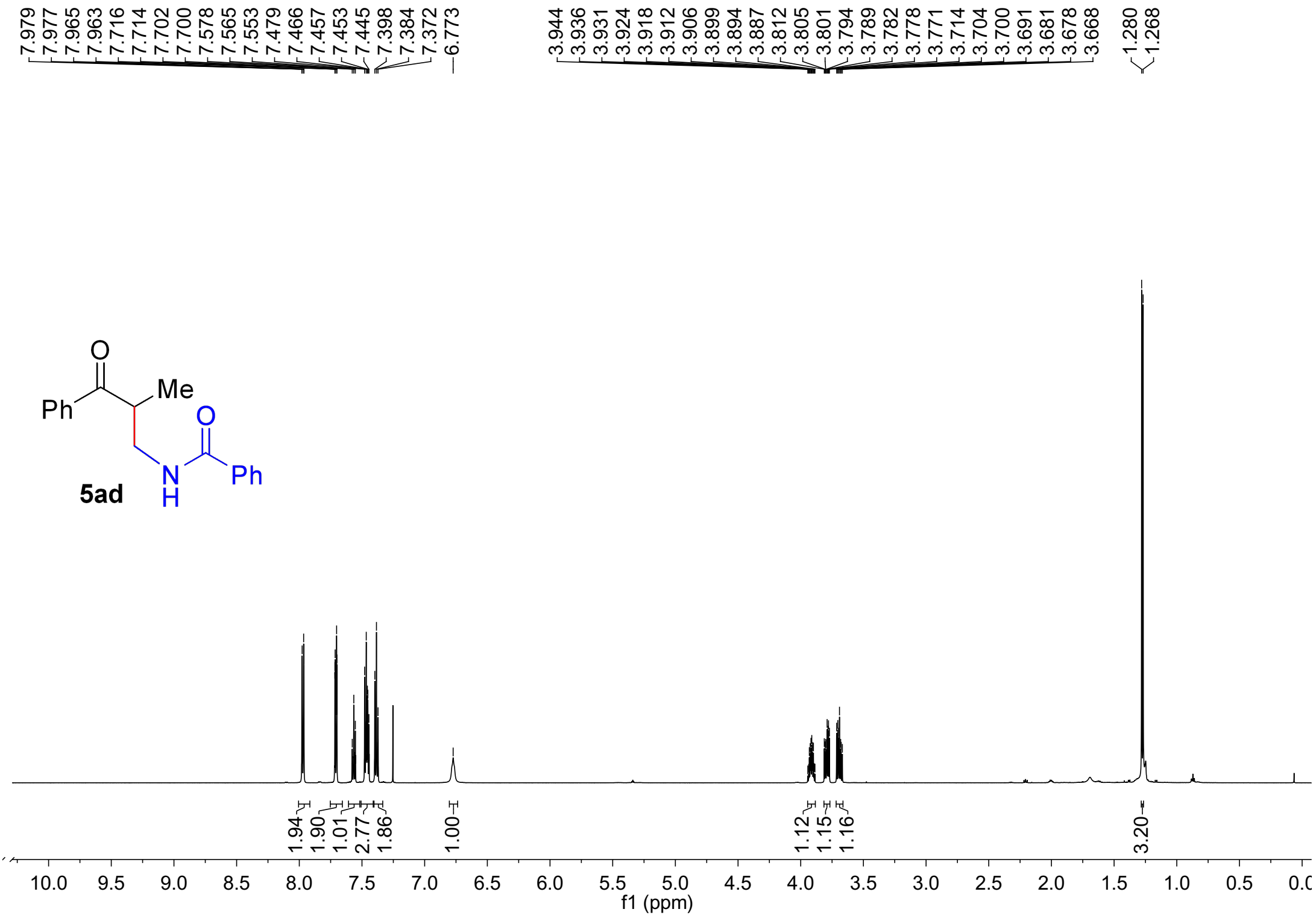
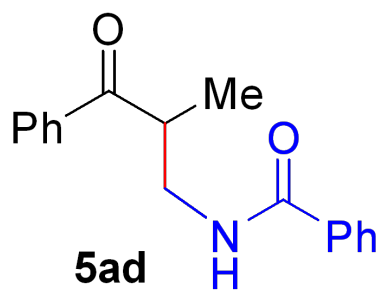


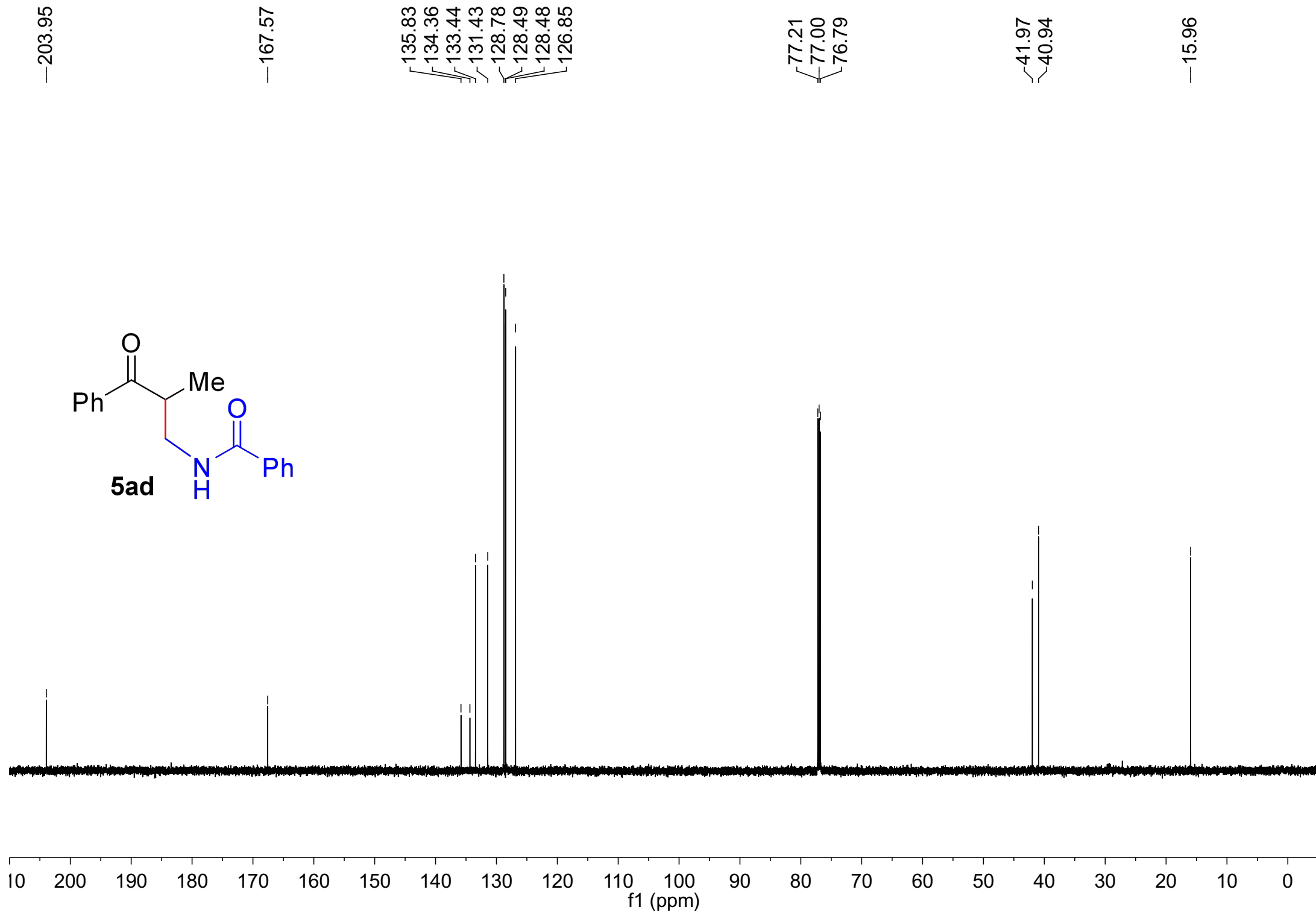
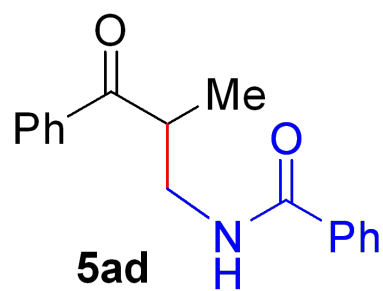








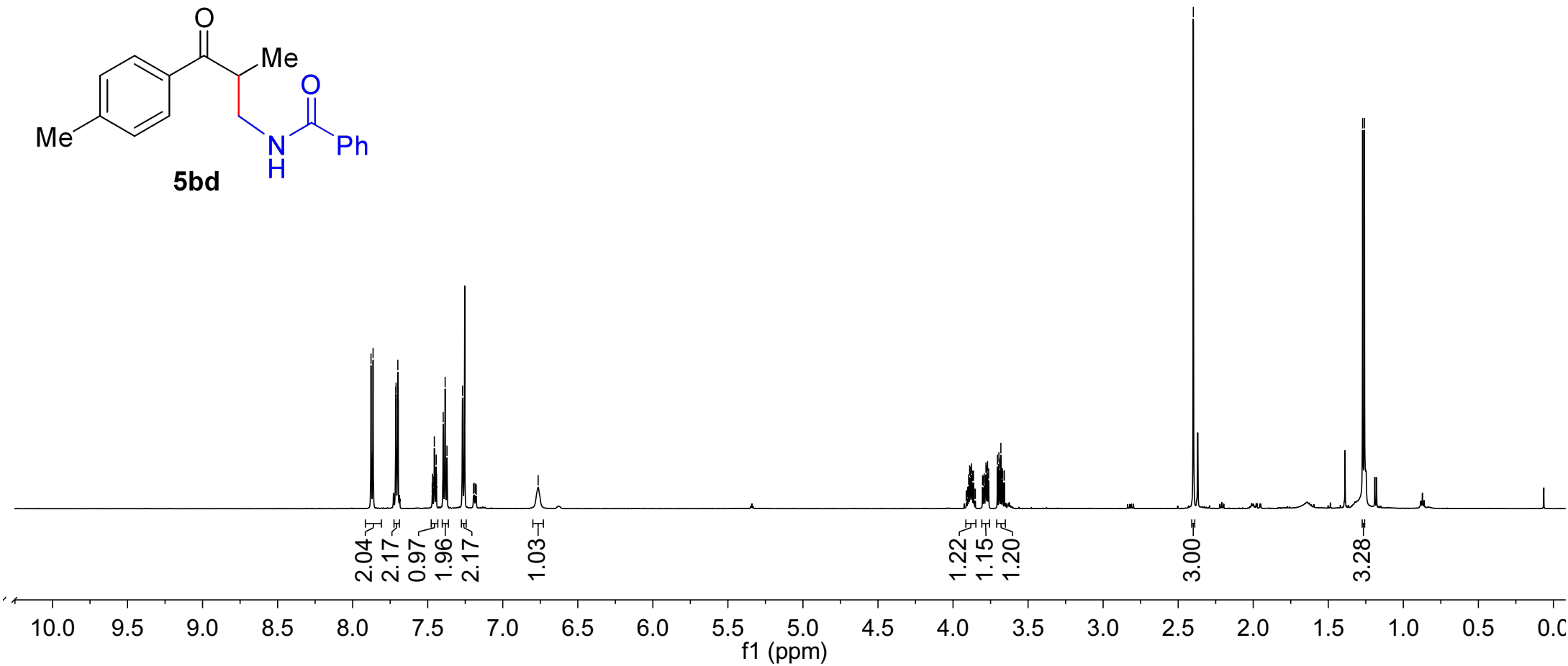
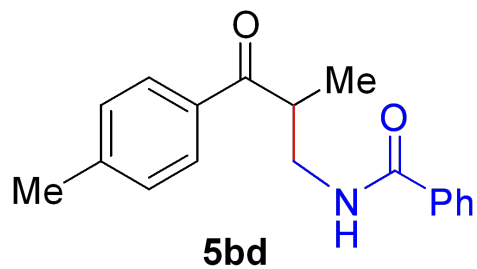


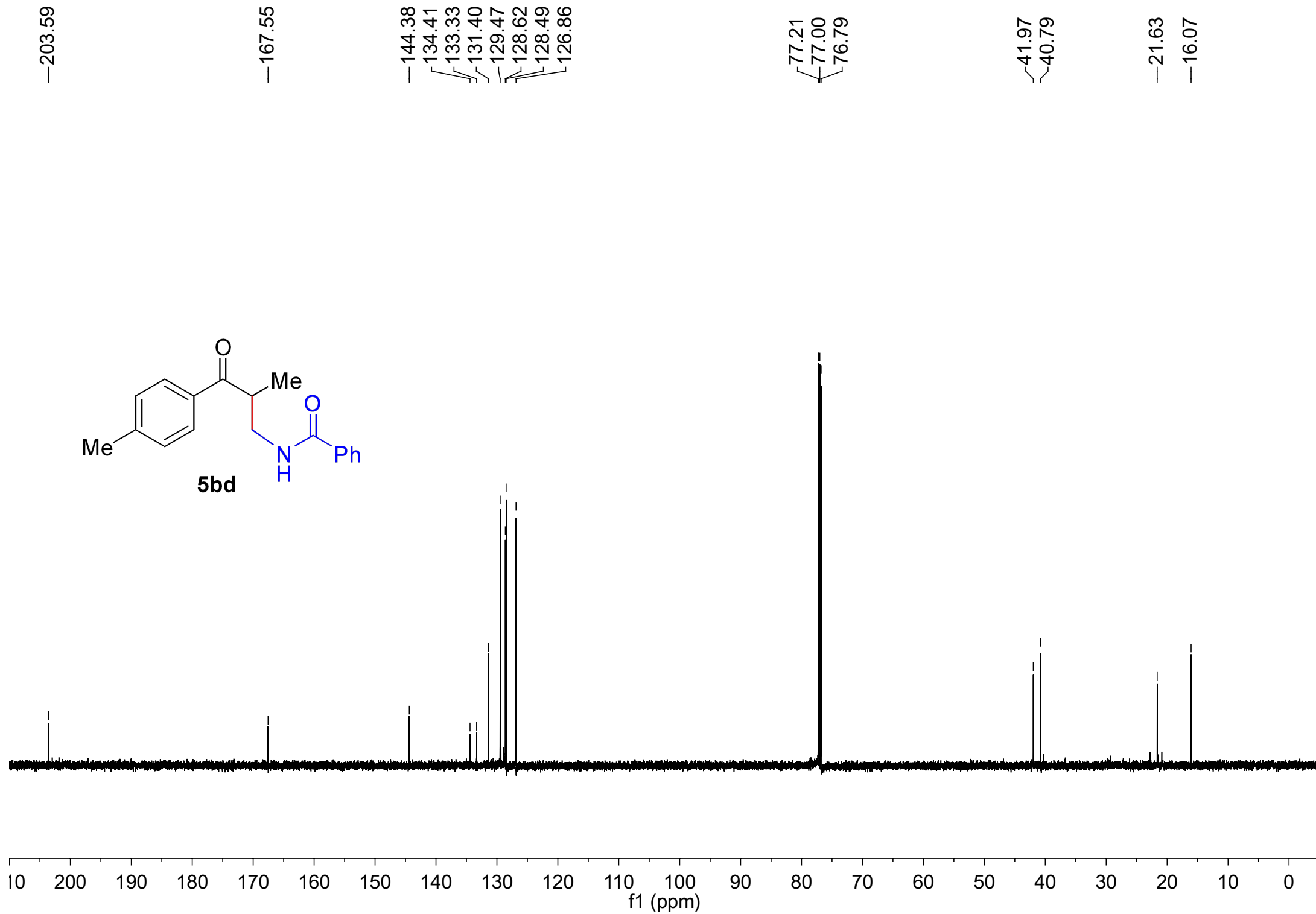
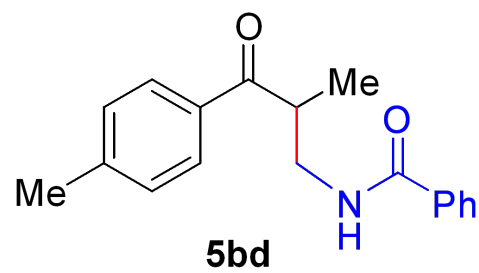


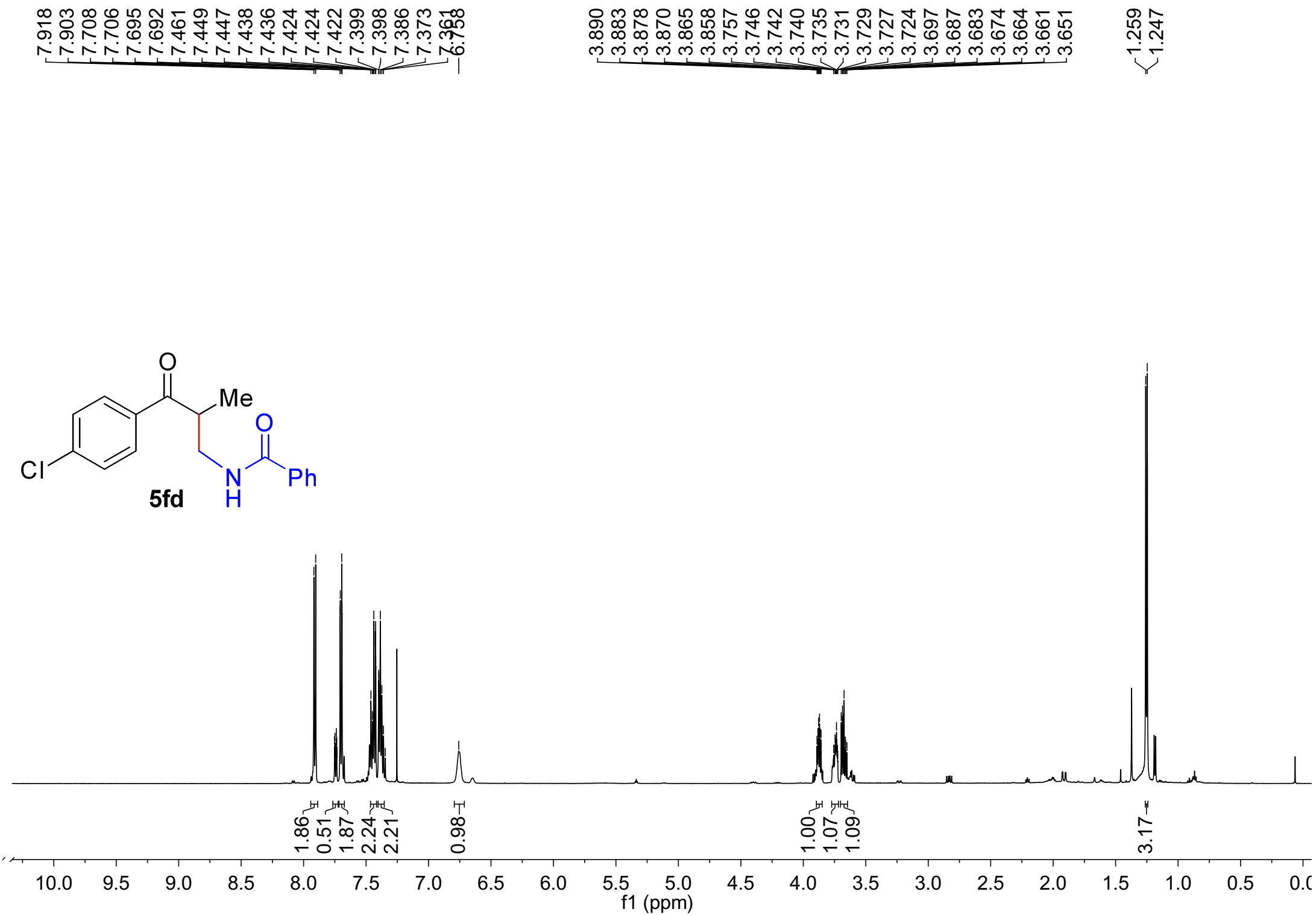
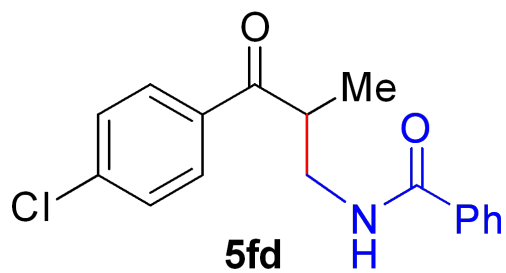
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7.191
6.764

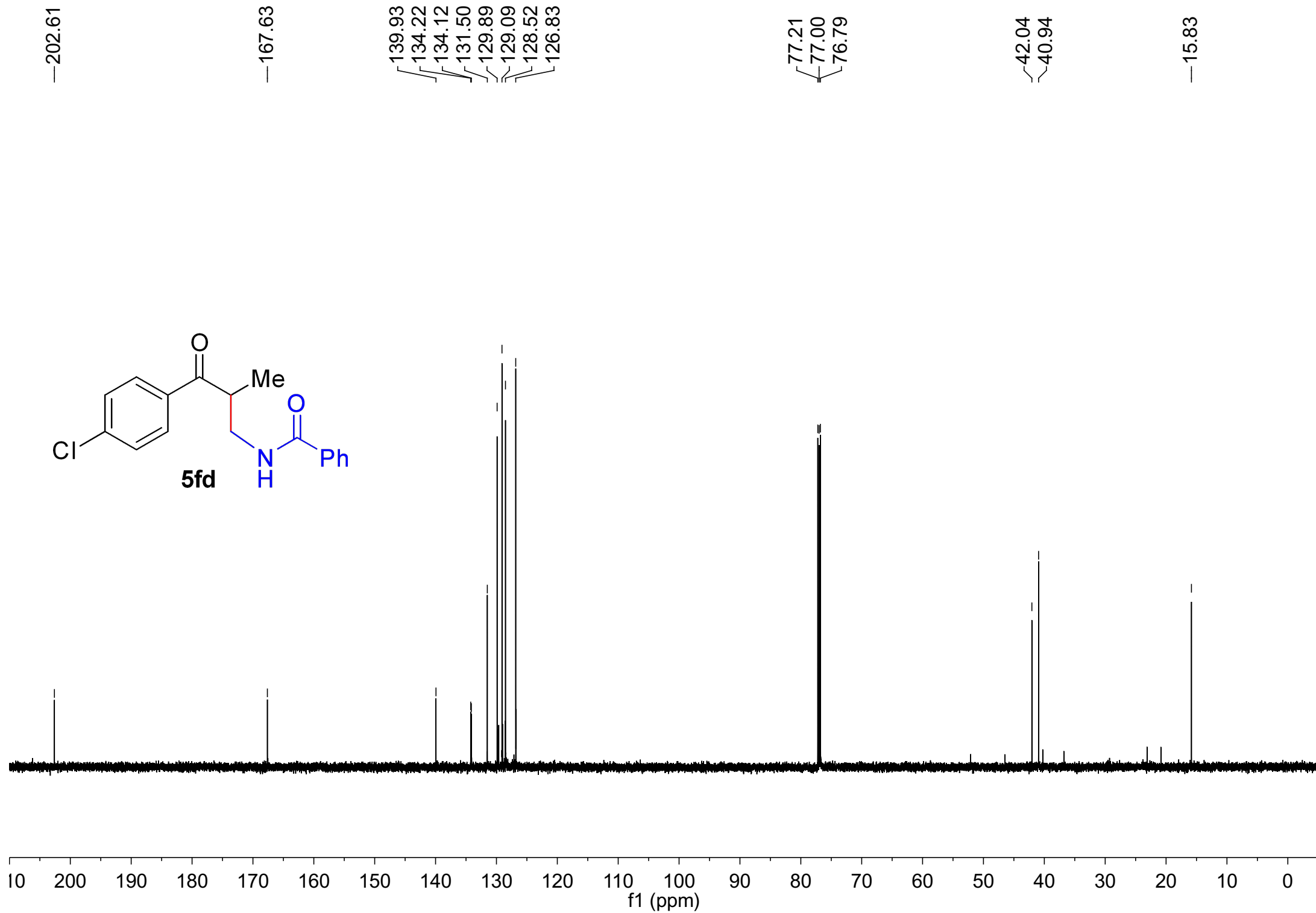
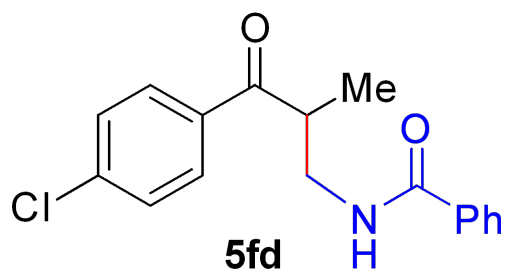
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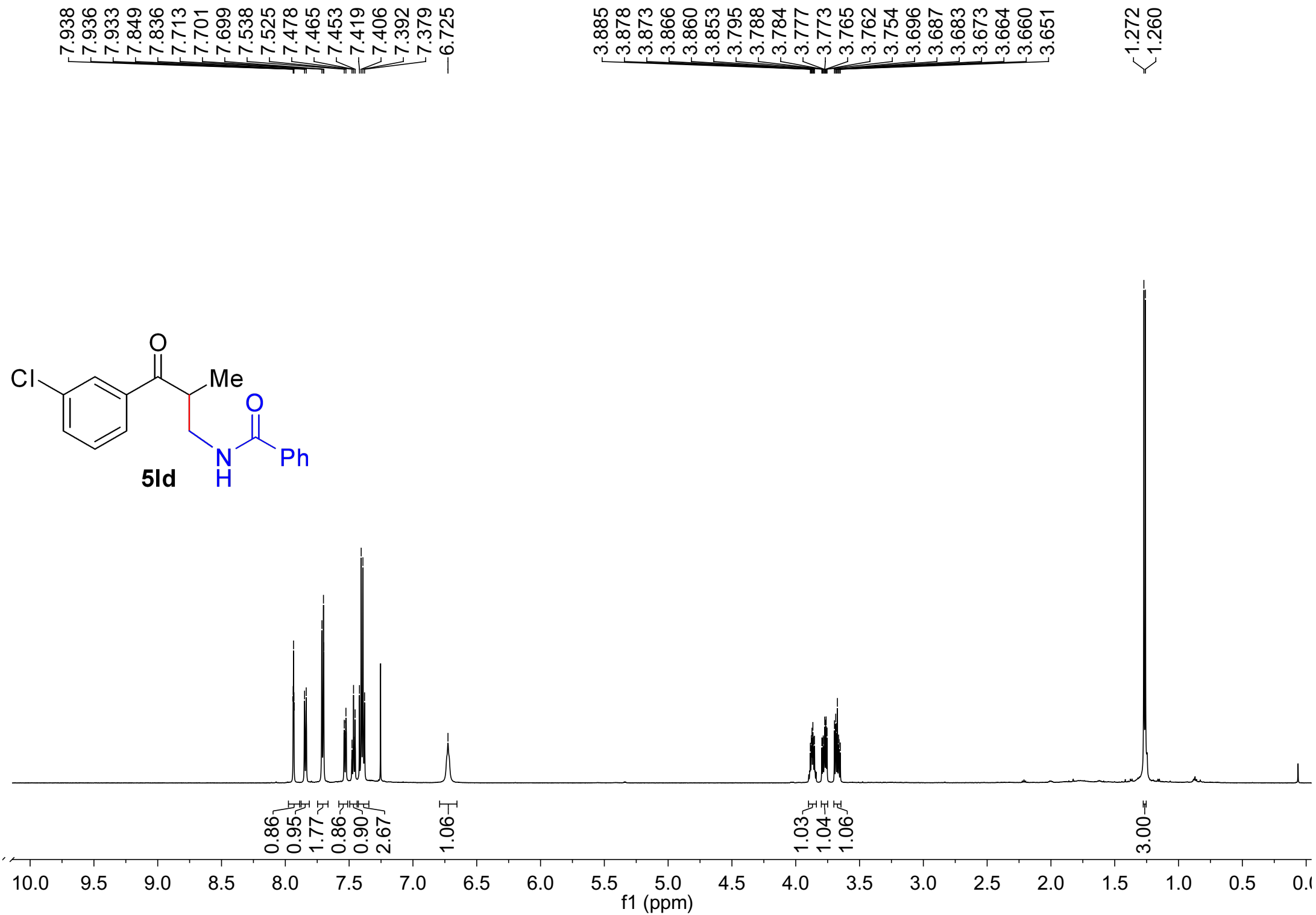
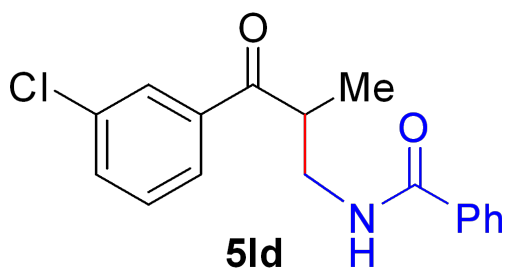
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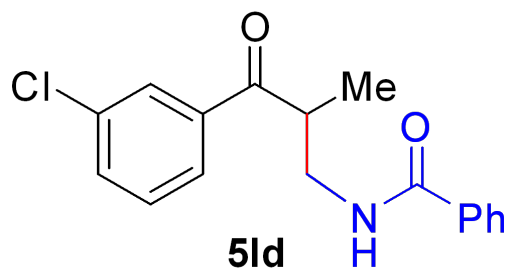




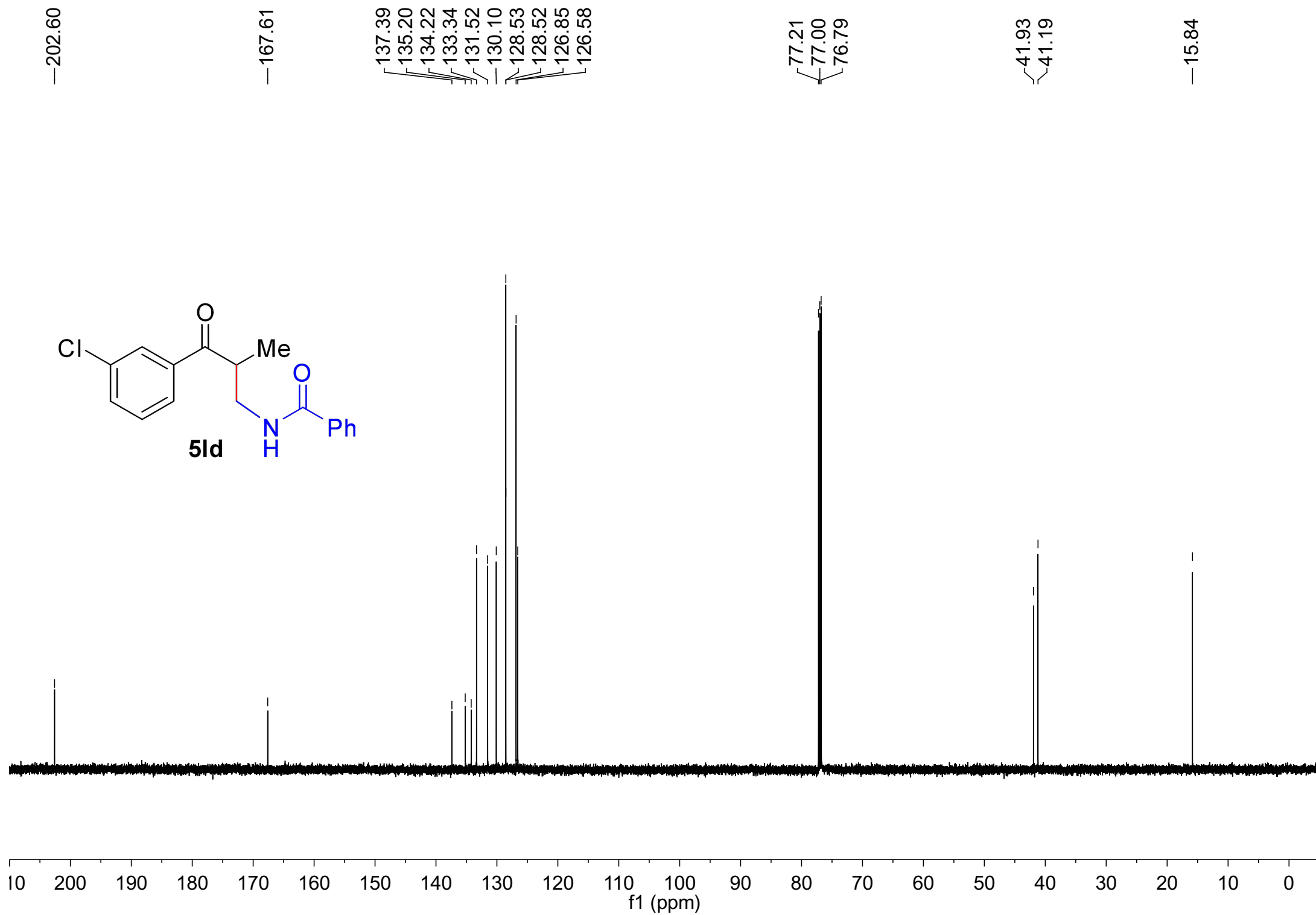


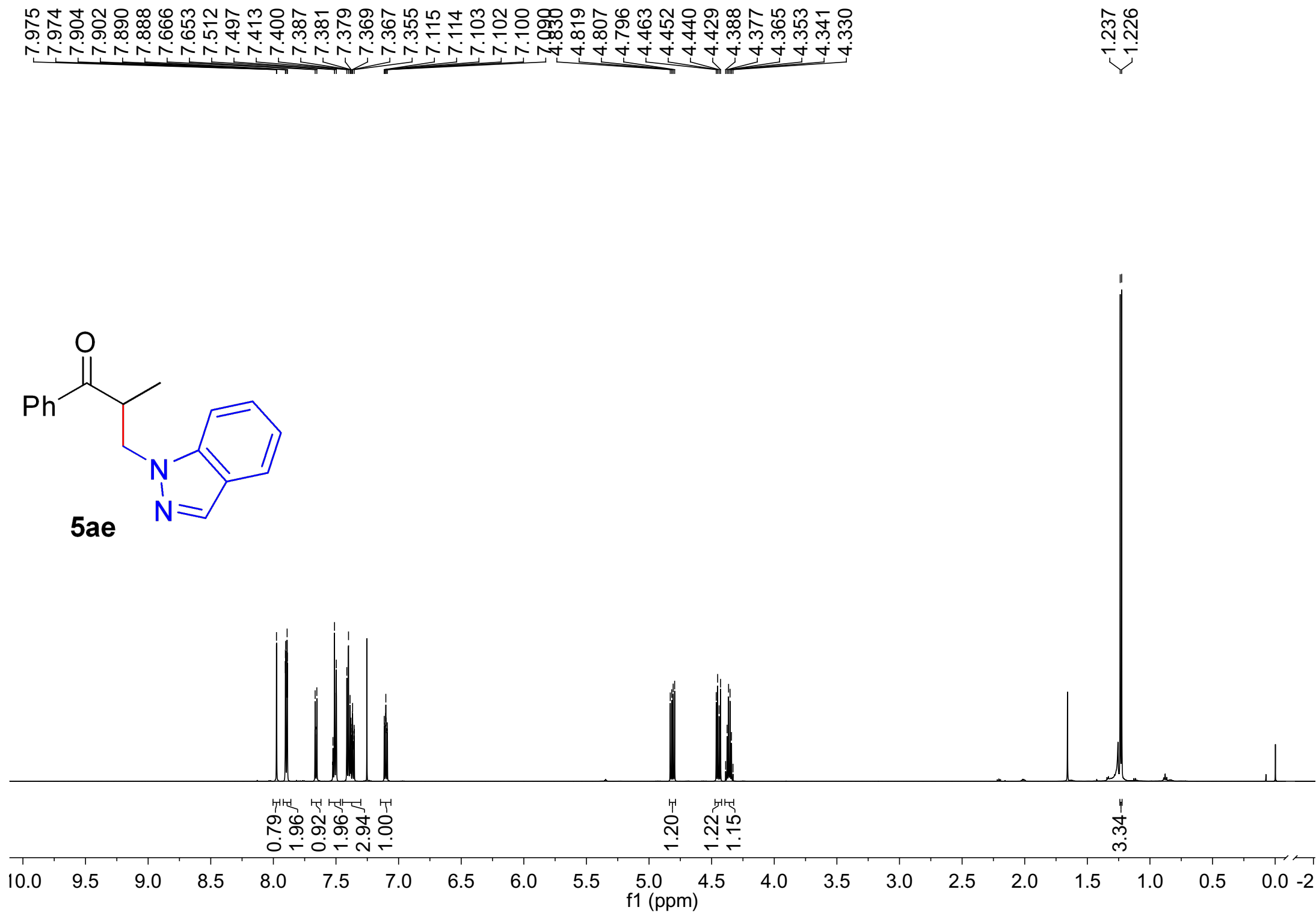
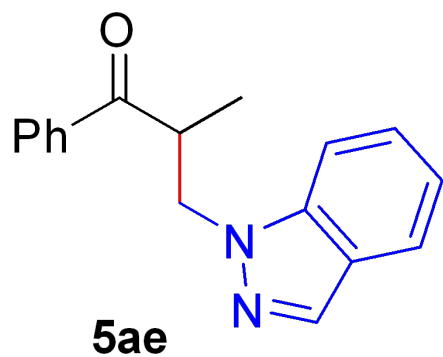


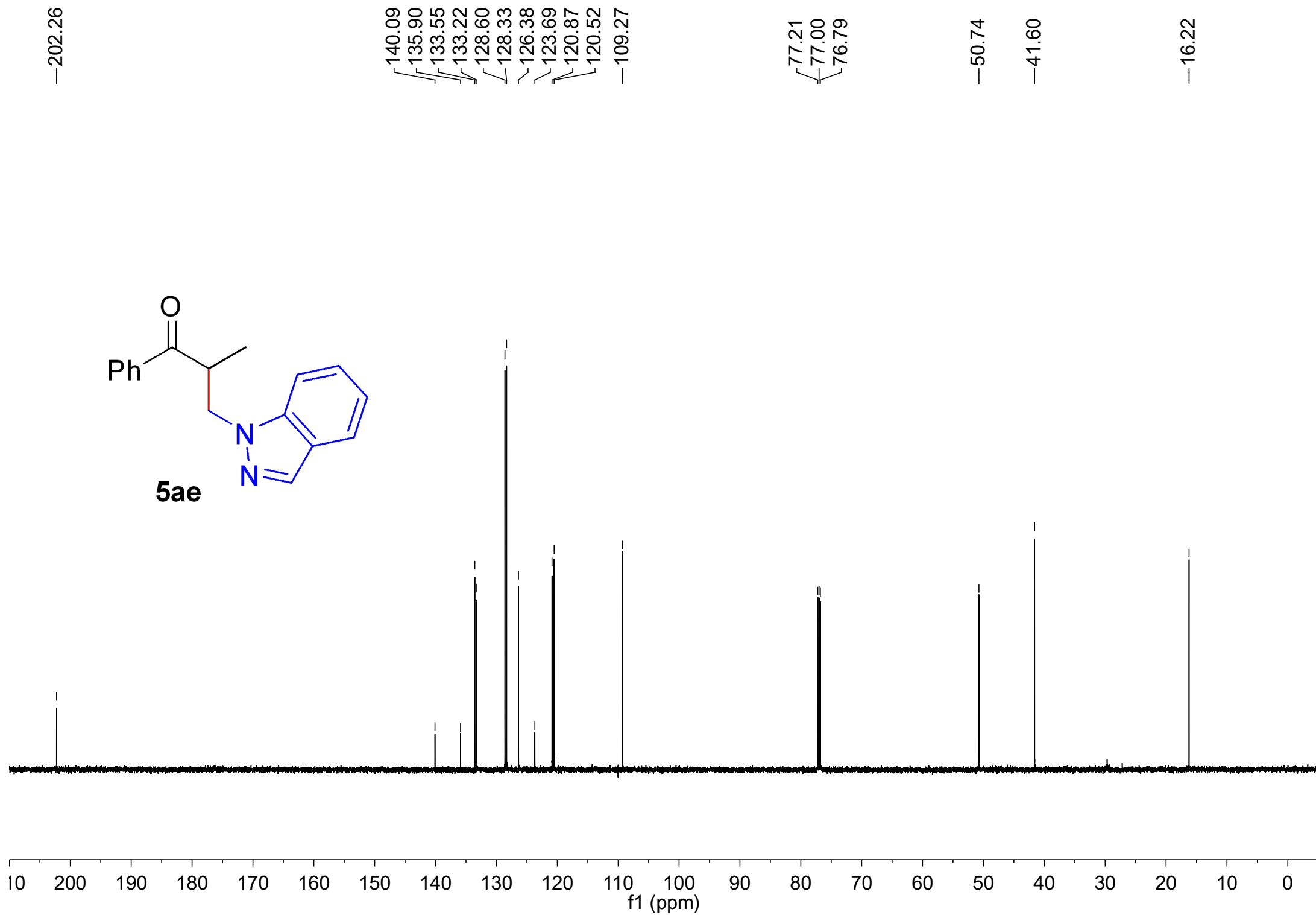
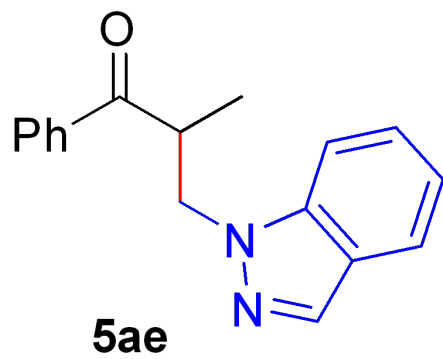




5ld



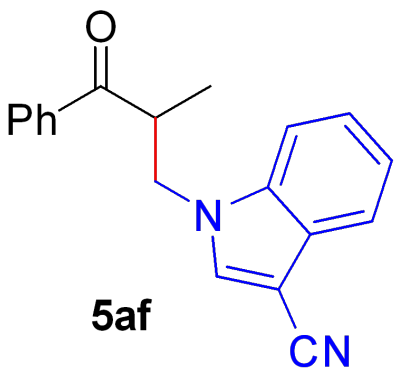




7.818
7.805
7.717
7.704
7.641
7.552
7.540
7.528
7.468
7.454
7.419
7.406
7.393
7.366
7.353
7.341
7.285
7.272
7.260

4.704
4.690
4.679
4.666
4.282
4.272
4.258
4.248
4.067
4.055
4.043
4.032
4.020
4.008

1.297
1.285



1.73
0.75
0.83
0.87
0.89
1.64
0.90
1.02

1.03

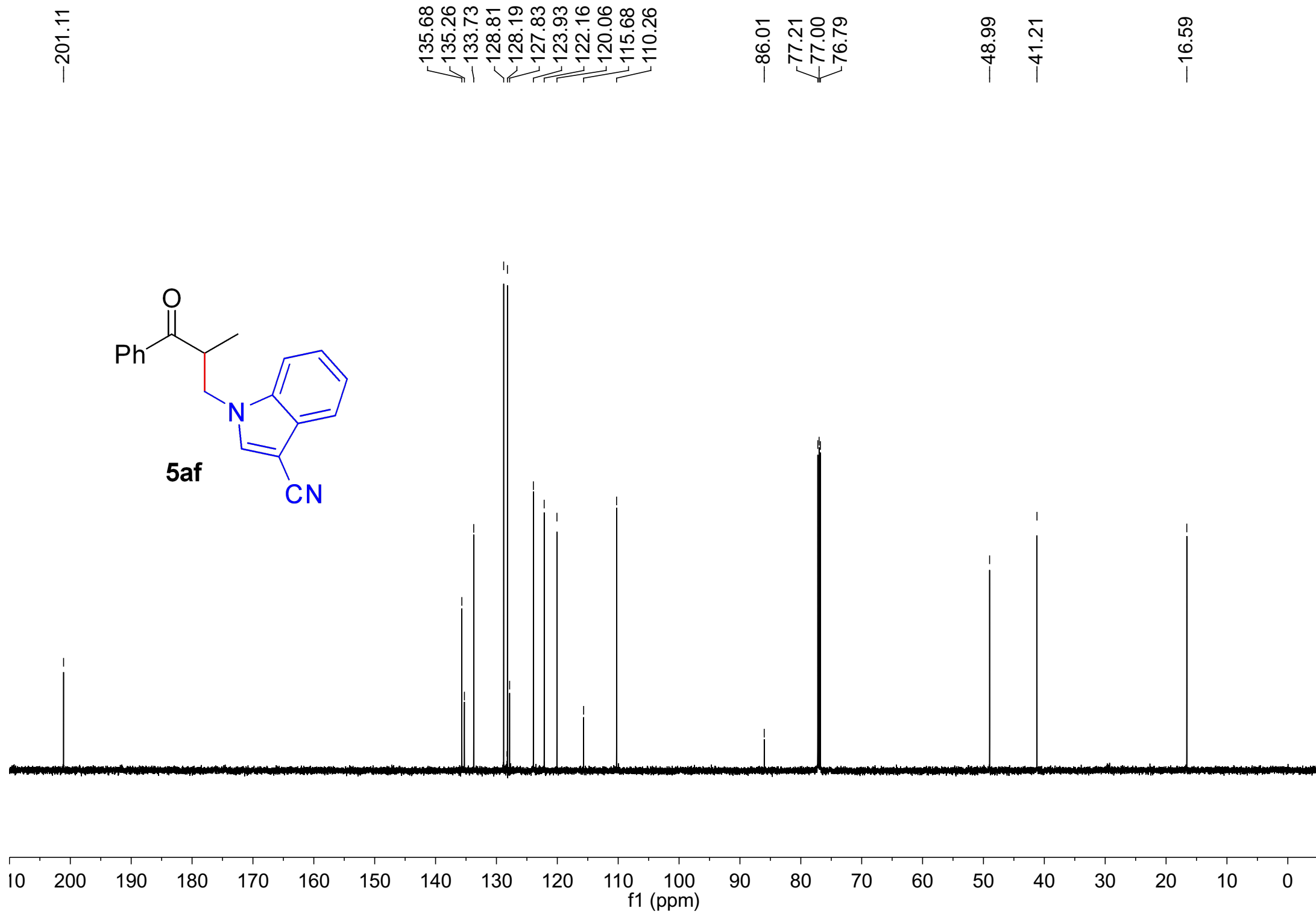
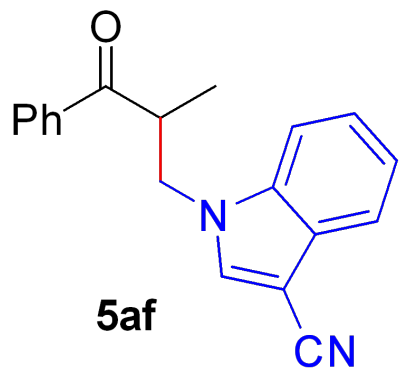
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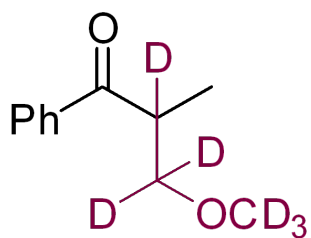
1.01

3.00

10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

f1 (ppm)





d-3a

