Electronic Supplementary Information

Selective amidation by a photocatalyzed umpolung reaction

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Experimental Procedures

1.Materials and methods

All reagents were purchased from commercial suppliers and used without further purification, unless otherwise specified. Commercially supplied ethyl acetate and petroleum ether were distilled before use.Petroleum ether used in our experiments was in the boiling range of 60-80 ºC. Column chromatography was performed on silica gel (100-200 mesh, 0.075-0.150 mm). Analytical thin layer chromatography was performed on 0.25 mm extra hard silica gel plates with UV-254 fluorescent indicator. ^{1}H-NMR and ^{13}C-NMR spectra (300 MHz and 400 MHz) were recorded at ambient temperature using 300 MHz and 400 MHzspectrometers (300 MHzand 400 MHz for ^{1}H and 75 MHzand 100 MHz for ^{13}C). Chemical shift is reported in ppm from internal reference tetramethylsilane and coupling constant in Hz. Proton multiplicities are represented as s (singlet), brs (broadsinglet), d (doublet), dd (double doublet), t (triplet), q (quartet), and m (multiplet). Infrared spectra were recorded on FT-IR spectrometer (IR Spectrophotometer) in thin film (KBr) or neat. HR-MS data were acquired by electron spray ionization technique on a Q-tof-micro quadriple mass spectrophotometer (Qtof ESI-MS). Optical rotation of the chiral compounds was measured in a polarimeter using standard 10 cm quartz cell in sodium-D lamp at ambient temperature.X-RAY crystallographic data was taken in a CCD difractometer.

2. General procedure for the synthesis of α-ketoamides (4a-l, 5a-n)

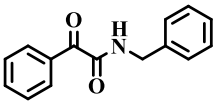
In a 15 mL dry vial,1 mmol of 1,3-diketone (**1**) and 3.5 mmol of iodosobenzene were dissolved in DCM (5 mL), and the reaction mixture was stirred at 0-5 ºC for about 15 min. After a while, 1.2 mmol of amine (**2** or **3**), 5 mol% of CuBr and 1 mol% of eosin Y were added. The vial was immediately sealed and placed under the irradiation of blue LED (30W). The progress of reaction was monitored by thin layer chromatography (TLC). The post-reaction mixture was extracted with DCM (2x10 mL). The combined organic layer was washed with water (3x10 mL) and brine (1x10 mL). It was dried over activated Na_2SO_4, filtered and evaporated in a rotary evaporator under reduced pressure at room temperature. Purification by column chromatography on silica gel (100-200 mesh) with ethyl acetate-petroleum ether (1:5 v/v) as an eluent afforded the corresponding α-ketoamides (**4a-l**, **5a**-**n**).All the synthesised compounds were characterized by relevent spectroscopic analysis and finally structure was confirmed through the single crystal XRD analysis of compound **4e**.

3. General procedure for the synthesis of oxalamides (8a-f)

In a 15 mL dry vial, 1 mmol of acetoacetanilide (**6**) and 3.5 mmol of iodosobenzene were dissolved in DCM (5 mL) and the reaction mixture was stirred at 0-5 ºC for about 15 min. After while, 1.2 mmol of amine (**2** or **3**), 5 mol% of CuBr and 1 mol% of eosin Y were added to it. The vial was immediately sealed and placed under the irradiation of 30W blue LED. The progress of reaction was monitored by thin layer chromatography (TLC). The post-reaction mixture was extracted with DCM (2x10 mL). The combined organic layer was washed with water (3x10 mL) and brine (1x10 mL). It was dried over activated Na_2SO_4, filtered and evaporated in a rotary evaporator under reduced pressure at room temperature. Purification by column chromatography on silica gel (100-200 mesh) with ethyl acetate-petroleum ether (1:5 v/v) as an eluent afforded the corresponding oxalamides (**8a-f**). All the compouds were fully characterized by relevent spectroscopic analysis.

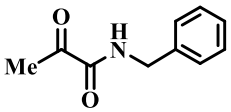
4. Characterization data of the synthesizedα–ketoamides (4a-l)

4.1. *N*-Benzyl-2-oxophenylacetamide (4a)[1]



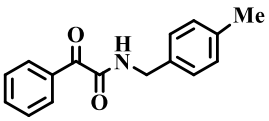
Compound **4a** was prepared using benzoylacetone and benzylamine as starting materials to obtain the product as a yellow solid; yield: 80% (191 mg, 0.80 mmol); m.p. 100-102 ^{o}C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.37 (d, *J* = 7.8 Hz, 2H), 7.64 (t, *J* = 7.2 Hz, 1H), 7.49 (t, *J* = 7.5 Hz, 3H), 7.40-7.34 (m, 5H), 4.58 (d, *J* = 6.0 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 187.5, 161.5, 137.1, 134.4, 133.4, 131.2, 128.9, 128.5, 127.9, 43.5; FT-IR (KBr, cm^{-1}): 3252, 2978, 2912, 1694, 1642, 1551, 1478, 1457; HR-MS (*m*/*z*) for $C_{15}H_{14}NO_2$ (M+H): Calculated 240.1025, found 240.1028.

4.2. *N*-Benzyl-2-oxopropanamide (4b)[2]



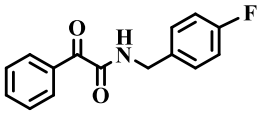
Compound **4b** was prepared using acetylacetone and benzylamine as starting materials to furnish the product as a yellow oil; yield: 62% (110 mg, 0.62 mmol); ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.35-7.25 (m, 6H), 4.47 (d, J = 5.4 Hz, 2H), 2.50 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 196.9, 159.9, 136.9, 128.9, 127.9, 43.9, 24.9; FT-IR (neat, cm^{-1}): 3240, 2923, 1721, 1675, 1530, 1496, 1454, 1358; HR-MS (*m*/*z*) for $C_{10}H_{12}NO_2$ (M+H): Calculated 178.0868, found 178.0864.

4.3. *N*-(4-Methylbenzyl)-2-oxo-2-phenylacetamide (4c)



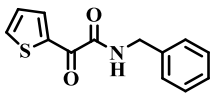
Compound **4c** was prepared using 1,3-diphenyl-1,3-propanedione and 4-methylbenzylamineas starting materials to furnish the product as a yellow thick liquid; yield: 67% (170 mg, 0.67 mmol); ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.35 (d, *J* = 7.8 Hz, 2H), 7.63 (t, *J* = 6.9 Hz, 1H), 7.48 (t, *J* = 7.8 Hz, 2H), 7.39 (brs, 1H), 7.27-7.15 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 187.6, 161.5, 137.6, 134.4, 134.0, 133.4, 131.2, 129.5, 128.5, 127.9, 43.2, 21.1; FT-IR (neat, cm^{-1}): 3229, 2948, 2876, 1706, 1658, 1559, 1478, 1451; HR-MS (*m*/*z*) for $C_{16}H_{15}NO_2$ (M): Calculated 253.1103, found 253.1104.

4.4. *N*-(4-Fluorobenzyl)-2-oxo-2-phenylacetamide (4d)



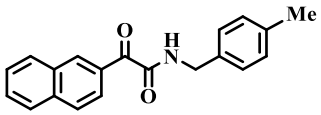
Compound **4d** was prepared using benzoylacetone and 4-fluorobenzylamine as starting materials to give the product as a white solid; yield: 63% (162 mg, 0.63 mmol); m.p. 84-86 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.34 (d, *J* = 7.4 Hz, 2H), 7.62 (t, *J* = 7.4 Hz, 1H), 7.49-7.44 (m, 2H), 7.39 (brs, 1H), 7.32-7.27 (m, 2H), 7.05-6.99 (m, 2H), 4.52 (d, *J* = 6.0 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 187.4, 164.0, 161.5, 160.7, 134.5, 133.3, 132.9, 131.2, 129.7, 129.6, 128.5, 115.9, 115.6, 42.8; FT-IR (KBr, cm^{-1}): 3242, 2966, 2899, 1710, 1672, 1569, 1506, 1487; HR-MS (*m*/*z*) for $C_{15}H_{13}FNO_2$ (M+H): Calculated 258.0930, found 258.0925.

4.5. *N*-Benzyl-2-oxo-2-(thiophen-2-yl)acetamide (4e)[2]



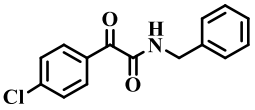
Compound **4e** was prepared using 2-thenoyltrifluoroacetone and benzylamine as starting materials to give the product as a colourless crystalline solid; yield: 70% (172 mg, 0.70 mmol); m.p. 93-95 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.43 (d, *J* = 3.6 Hz, 1H), 7.86-7.83 (m, 1H), 7.64 (brs, 1H), 7.36-7.27 (m, 5H), 7.22-7.18 (m, 1H), 4.56 (d, J = 6.0 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 178.2, 160.6, 138.6, 138.1, 136.9, 129.0, 128.8, 128.2, 127.9, 43.5; FT-IR (KBr, cm^{-1}): 3292, 2960, 2930, 1736, 1693, 1519, 1500; HR-MS (*m*/*z*) for $C_{13}H_{12}NO_2S$ (M+H): Calculated 246.0589, found 246.0593.

4.6. *N*-(4-Methylbenzyl)-2-(naphthalen-2-yl)-2-oxoacetamide (4f)



Compound **4f** was prepared using 4,4,4-trifluoro-1-(2-naphthyl)-1,3-butanedione and 4-methylbenzyl amine as starting materials to give the product as a brown solid; yield: 67% (303 mg, 0.67 mmol); m.p. 151-152 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.24 (s, 1H), 8.23-8.19 (m, 1H), 8.04-8.00 (m, 1H), 7.93-7.86 (m, 2H), 7.68-7.49 (m, 3H), 7.28-7.17 (m, 4H), 4.57 (d, *J* = 6.0 Hz, 2H), 2.36 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 187.0, 161.6, 136.0, 134.9, 134.0, 132.7, 132.3, 130.4, 130.2, 129.6, 129.4, 129.2, 128.2, 127.9, 127.8, 127.6, 126.7, 125.1, 43.2, 20.9; FT-IR (KBr, cm^{-1}): 3230, 2946, 2876, 1708, 1658, 1562, 1478, 1448; HR-MS (*m*/*z*) for $C_{20}H_{17}NO_2$ (M): Calculated 303.1259, found 303.1264.

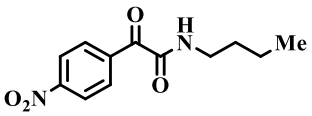
4.7. *N*-Benzyl-2-(4-chlorophenyl)-2-oxoacetamide (4g)[2]



Compound **4g** was prepared using 1-(4-chlorophenyl)-4,4,4-trifluoro-1,3-butanedione and benzylamine as starting materials to give the product as a yellow solid; yield: 62% (170 mg, 0.62 mmol); m.p. 105-106 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.33 (d, *J* = 8.7 Hz, 2H), 7.44

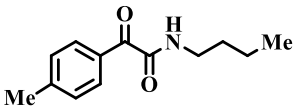
(d, *J* = 8.4 Hz, 2H), 7.36-7.22 (m, 6H), 4.50 (d, *J* = 5.7 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 186.1, 161.2, 141.2, 135.8, 132.7, 129.0, 128.9, 128.3, 127.9, 43.9; FT-IR (KBr, cm^{-1}): 3291, 3031, 2928, 1703, 1667, 1587, 1525; HR-MS (*m*/*z*) for $C_{15}H_{12}ClNO_2$ (M): Calculated 273.0557, found 273.0555 (one of the major peaks).

4.8. *N*-butyl-2-oxo-2-p-tolylacetamide (4h)



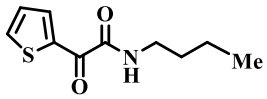
Compound **4h** was prepared using 1-(4-methylphenyl)-1,3-butanedione and butyl amine as starting materials to give the product as a yellow solid; yield: 64% (160 mg, 0.64 mmol); m.p. 109-110 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.28 (d, *J* = 8.6 Hz, 2H), 7.90 (d, *J* = 8.4 Hz, 2H), 6.15 (brs, 1H), 3.48 (q, *J* = 6.5 Hz, 2H), 1.62 (t, *J* = 7.2 Hz, 2H), 1.42 (q, *J* = 7.6 Hz, 2H), 0.97 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 188.8, 165.6, 149.4, 140.3, 128.0, 123.7, 40.7, 31.5, 20.1, 13.7; FT-IR (KBr, cm^{-1}): 3296, 3040, 2932, 1720, 1698, 1568, 1540; HR-MS (*m*/*z*) for $C_{12}H_{14}N_2O_4$ (M): Calculated 250.0954, found 250.0958.

4.9. *N*-butyl-2-oxo-2-p-tolylacetamide (4i)[1]



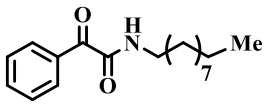
Compound **4i** was prepared using 1-(4-methylphenyl)-4,4,4-trifluoro-1,3-butanedione and butyl amine as starting materials to give the product as a yellow solid; yield: 76% (166 mg, 0.76 mmol); m.p. 69-70 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.26 (d, *J* = 8.2 Hz, 2H), 7.26 (d, *J* = 9.7 Hz, 2H), 7.06 (brs, 1H), 3.38 (q, *J* = 6.6 Hz, 2H), 2.41 (s, 3H), 1.62-1.54 (m, 2H), 1.44-1.35 (m, 2H), 0.95 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 187.4, 162.0, 145.4, 131.2, 130.8, 129.1, 39.0, 31.2, 21.7, 19.9, 13.6; FT-IR (KBr, cm^{-1}): 3280, 3025, 2928, 1695, 1652, 1568, 1525; HR-MS (*m*/*z*) for $C_{13}H_{18}NO_2$ (M+H): Calculated 220.1338, found 220.1332.

4.10. *N*-Butyl-2-oxo-2-(thiophen-2-yl)acetamide (4j)



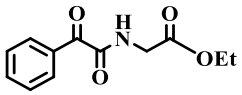
Compound **4j** was prepared using 2-thenoyltrifluoroacetone and n-butylamine as starting materials to give the product as a yellow oil; yield: 78% (165 mg, 0.78 mmol); ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.40 (d, *J* = 2.7 Hz, 2H), 7.83-7.81 (m, 1H), 7.33 (brs, 1H), 7.21-7.17 (m, 1H), 3.41-3.35 (m, 2H), 1.64-1.54 (m, 2H), 1.45-1.33 (m, 2H), 0.97 (t, *J* = 3.9 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 178.5, 160.7, 138.5, 137.9, 136.8, 128.1, 39.2, 31.2, 19.9, 13.6; FT-IR (neat, cm^{-1}): 3295, 2961, 2927, 1718, 1680, 1526, 1505, 1415; HR-MS (*m*/*z*) for $C_{10}H_{14}NO_2S$ (M+H): Calculated 212.0745, found 212.0747.

4.11. *N*-Decyl-2-oxo-2-phenylacetamide (4k)



Compound **4k**, was prepared using benzoylacetone and decylamine as starting materials to give the product as a brown oil; yield: 80% (230mg, 0.80 mmol); ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.33 (dd, *J* = 8.7, 1.2 Hz, 2H), 7.64-7.59 (m, 1H), 7.50-7.45 (m, 2H), 7.10 (brs, 1H), 3.41-3.35 (m, 2H), 1.60 (t, *J* = 6.6 Hz, 2H), 1.33-1.26 (m, 14H), 0.87 (t, *J* = 6.0 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 187.9, 161.7, 134.3, 133.4, 131.2, 128.4, 39.5, 31.9, 29.5, 29.3, 29.2, 26.9, 22.7, 14.1; FT-IR (neat, cm^{-1}): 3232, 2920, 1728, 1682, 1528, 1496, 1453, 1358; HR-MS (*m*/*z*) for $C_{18}H_{28}NO_2$ (M+H): Calculated 290.2120, found 290.2126.

4.12. Ethyl- 2-(2-oxo-2-phenylacetamido)acetate (4l)

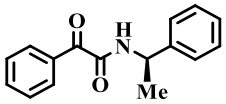


Compound **4j** was prepared using benzoylacetone and ethylglycinateas starting materials to give the product as a pale yellow thick liquid; yield: 70% (165 mg, 0.70 mmol); ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.30 (d, *J* = 8.1 Hz, 2H), 7.63-7.58 (m, 1H), 7.48-7.43 (m, 3H), 4.24 (q, *J* = 7.2 Hz, 2H), 4.14 (d, *J* = 5.7 Hz, 2H), 1.29 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 186.8, 168.9, 161.8, 134.5,

133.0, 131.1, 128.5, 61.7, 41.2, 14.1; FT-IR (neat, cm^{-1}): 3218, 2960, 2930, 1740, 1677, 1604, 1532, 1444; HR-MS (*m*/*z*) for $C_{12}H_{14}NO_4$ (M+H): Calculated 236.0923, found 236.0919.

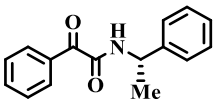
5. Characterization data of the synthesized chiral α-ketoamides (5a-n)

5.1. (*R*)-(+)-2-Oxo-2-phenyl-*N*-(1-phenylethyl)acetamide (5a)



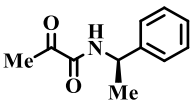
Compound **5a** was prepared using benzoylacetone and (*R*)-(+)-α-methylbenzylamine as starting materials to give the product as a white solid; yield: 64% (162 mg, 0.64 mmol); m.p. 110-112 °C; $[\alpha]_D^{25}$ = +35° (c 0.4, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.34 (d, *J* = 8.1 Hz, 2H), 7.64-7.59 (m, 1H), 7.47 (t, *J* = 7.8 Hz, 2H), 7.38-7.26 (m, 6H), 5.26-5.15 (m, 1H), 1.61 (d, *J* =6.9 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 187.6, 160.7, 142.3, 134.4, 133.4, 131.3, 128.8, 128.5, 127.7, 126.2, 49.1, 21.7; FT-IR (KBr, cm^{-1}): 3260, 2982, 2926, 1684, 1634, 1556, 1493, 1449; HR-MS (*m*/*z*) for $C_{16}H_{16}NO_2$ (M+H): Calculated 254.1181, found 254.1186.

5.2. (*S*)-(-)-2-Oxo-2-phenyl-*N*-(1-phenylethyl)acetamide (5b)[3]



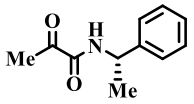
Compound **5b** was prepared using benzoylacetone and (*S*)-(-)-α-methylbenzylamine as starting materials to give the product as a white solid; yield: 68% (172 mg, 0.68 mmol); m.p. 110-112°C; $[\alpha]_D^{25}$ = -106° (c 1.0, ethanol); ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.35 (d, *J* = 7.5 Hz, 2H), 7.64-7.59 (m, 1H), 7.50-7.43 (m, 2H), 7.38-7.27 (m, 6H), 5.26-5.15 (m, 1H), 1.62 (d, *J* =6.9 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 187.6, 160.7, 142.2, 134.3, 133.3, 131.2, 128.8, 128.4, 127.6, 126.1, 49.1, 21.6; FT-IR (KBr, cm^{-1}): 3264, 2978, 2926, 1690, 1634, 1555, 1485, 1447; HR-MS (*m*/*z*) for $C_{16}H_{16}NO_2$ (M+H): Calculated 254.1181, found 254.1184.

5.3. (*R*)-(+)-2-Oxo-*N*-(1-phenylethyl)propanamide (5c)[4]



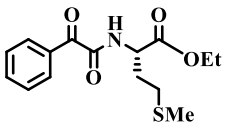
Compound **5c** was prepared using acetylacetone and (*R*)-(+)-α-methylbenzylamine as starting materials to give the product as pale yellow solid; yield: 62% (118 mg, 0.62 mmol); m.p. 70-71 °C; $[\alpha]_D^{25}$ = +106.8° (c 0.34, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.38-7.26 (m, 5H), 7.17 (brs, 1H), 5.11-5.01(m, 1H), 1.54 (d, J = 6.9 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 197.2, 159.1, 142.0, 128.8, 127.7, 126.1, 49.0, 24.3, 21.5; FT-IR (KBr, cm^{-1}): 3226, 2929, 1740, 1682, 1521, 1499, 1454, 1325; HR-MS (*m*/*z*) for $C_{11}H_{14}NO_2$(M+H): Calculated 192.1025, found 192.1021.

5.4. (*S*)-(-)-2-Oxo-*N*-(1-phenylethyl)propanamide (5d)[4]



Compound **5d** was prepared using acetylacetone and (*S*)-(-)-α-methylbenzylamine as starting materials to give the product as a yellow solid; yield: 65% (124 mg, 0.65 mmol); m.p. 68-70 °C; $[\alpha]_D^{25}$ = -98.4° (c 0.37, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.38-7.26 (m, 5H), 7.17 (brs, 1H), 5.12-5.01 (m, 1H), 1.55 (d, *J* = 6.9 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 197.2, 159.1, 142.0, 128.8, 127.7, 126.1, 49.0, 24.3, 21.5; FT-IR (KBr, cm^{-1}): 3226, 2912, 1737, 1689, 1533, 1506, 1457, 1317; HR-MS (*m*/*z*) for $C_{11}H_{14}NO_2$ (M+H): Calculated 192.1025, found 192. 1028.

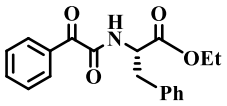
5.5. (*S*)-(+)-Ethyl-4-(methylthio)-2-(2-oxo-2-phenylacetamido)butanoate (5e)



Compound **5e** was prepared using benzoylacetone and L-methionine ethyl ester as starting materials to give the product as a pale yellow thick liquid; yield: 72% (222 mg, 0.72 mmol); $[\alpha]_D^{25}$ = +4.9° (c 0.2, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.32 (d, *J* = 8.1 Hz, 2H),

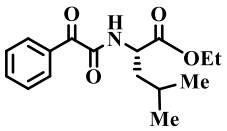
7.69-7.61 (m, 2H), 7.49 (t, *J* = 7.2 Hz, 2H), 4.82-4.76 (m, 1H), 4.26 (q, *J* = 7.2 Hz, 2H), 2.60-2.56 (m, 2H), 2.29-2.21 (m, 2H), 2.12 (s, 3H), 1.32 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 186.9, 170.9, 161.5, 134.5, 133.2, 131.2, 128.5, 61.9, 51.7, 31.7, 29.9, 15.9, 14.2; FT-IR (neat, cm^{-1}): 3226, 2958, 2930, 1744, 1669, 1597, 1524, 1443; HR-MS (*m*/*z*) for $C_{15}H_{20}NO_4S$ (M+H): Calculated 310.1113, found 310.1110.

5.6. (*S*)-(+)-Ethyl-2-(2-oxo-2-phenylacetamido)-3-phenylpropanoate (5f)



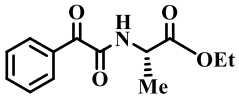
Compound **5f**, was prepared using benzoylacetone and L-phenylalanine ethyl ester as starting materials to give the product as a deep yellow thick liquid; yield: 69% (224 mg, 0.69 mmol); $[\alpha]_D^{25}$ = +3.66° (c 0.41, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.25 (d, *J* = 7.2 Hz, 2H), 7.62 (t, *J* = 7.2 Hz, 1H), 7.47 (t, *J* = 7.5 Hz, 3H), 7.34-7.23 (m, 3H), 7.18 (d, *J* = 7.8 Hz, 2H), 4.97-4.90 (m, 1H), 4.21 (q, *J* = 7.2 Hz, 2H), 3.24-3.14 (m, 2H), 1.26 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 186.8, 170.5, 161.2, 135.3, 134.3, 133.0, 131.0, 129.2, 128.5, 128.4, 127.1, 61.6, 53.2, 37.9, 13.9; FT-IR (neat, cm^{-1}): 3228, 2956, 2935, 1736, 1668, 1592, 1515, 1454; HR-MS (*m*/*z*) for $C_{19}H_{19}NO_4$ (M): Calculated 325.1314, found 325.1310.

5.7. (*S*)-(+)-Ethyl-4-methyl-2-(2-oxo-2-phenylacetamido)pentanoate (5g)



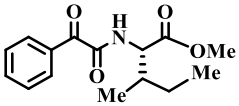
Compound **5g**, was prepared using benzoylacetone and L-leucine ethyl ester as starting materials to give the product as a deep yellow thick liquid; Yield: 68% (198 mg, 0.68 mmol); $[\alpha]_D^{25}$ = +10.88° (c 0.57, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.32 (d, *J* = 8.1 Hz, 2H), 8.09 (brs, 1H), 7.64-7.59 (m, 1H), 7.53-7.42 (m, 2H), 4.68 (t, *J* = 4.2 Hz, 1H), 4.22 (q, *J* = 7.2 Hz, 2H), 1.78-1.67 (m, 3H), 1.30 (t, *J* = 7.2 Hz, 3H), 0.987 (d, *J* = 3.6 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 187.0, 171.9, 161.3, 134.4, 133.2, 131.1, 128.5, 61.6, 50.9, 41.4, 24.9, 22.8, 21.8, 14.1; FT-IR (neat, cm^{-1}): 3225, 2962, 2931, 1736, 1671, 1598, 1515, 1449; HR-MS (*m*/*z*) for $C_{16}H_{22}NO_4$ (M+H): Calculated 292.1549, found 292.1555.

5.8. (*S*)-(+)-Ethyl-2-(2-oxo-2-phenylacetamido)propanoate (5h)



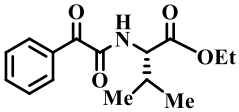
Compound **5h** was prepared using benzoylacetone and L-alanine ethyl ester as starting materials to give the product as a yellow thick liquid; Yield: 74% (184 mg, 0.74 mmol); $[\alpha]_D^{25}$ = +8.09° (c 0.66, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.32 (d, *J* = 7.2 Hz, 2H), 7.63 (t, *J* = 7.5 Hz, 1H), 7.55 (brs, 1H), 7.48 (t, *J* = 7.5 Hz, 2H), 4.69-4.59 (m, 1H), 4.25 (q, *J* = 7.2 Hz, 2H), 1.52 (d, *J* = 7.2 Hz, 3H), 1.31 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 187.0, 171.9, 161.2, 134.4, 133.2, 131.1, 128.5, 61.7, 48.2, 18.1, 14.1; FT-IR (neat, cm^{-1}): 3227, 2960, 2934, 1748, 1675, 1597, 1520, 1443; HR-MS (*m*/*z*) for $C_{13}H_{16}NO_4$ (M+H): Calculated 250.1079, found 250.1082.

5.9. (2*S*,3*R*)-(+)-Methyl-3-methyl-2-(2-oxo-2-phenylacetamido)pentanoate (5i)



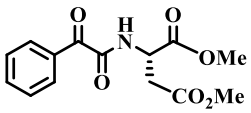
Compound **5i** was prepared using benzoylacetone and L-isoleucine methyl ester as starting materials to give the product as a yellow thick liquid; Yield: 76% (210 mg, 0.76 mmol); $[\alpha]_D^{25}$ = +6.39° (c 0.25, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.32 (d, *J* = 7.8 Hz, 2H), 7.62 (d, *J* = 7.5 Hz, 1H), 7.56-7.45 (m, 3H), 4.68-4.63 (m, 1H), 3.76 (d, *J* = 7.8 Hz, 3H), 2.04-1.99 (m, 1H), 1.53-1.46 (m, 2H), 0.99-0.94 (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 187.0, 171.3, 161.3, 134.4, 133.1, 131.1, 128.4, 56.5, 52.2, 37.9, 25.1, 15.5, 11.4; FT-IR (neat, cm^{-1}): 3221, 2965, 2932, 1742, 1671, 1597, 1515, 1449; HR-MS (*m*/*z*) for $C_{15}H_{20}NO_4$ (M+H): Calculated 278.1392, found 278.1389.

5.10. (*S*)-(+)-Ethyl-3-methyl-2-(2-oxo-2-phenylacetamido)butanoate (5j)



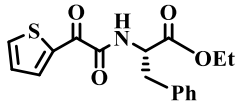
Compound **5j**, was prepared using benzoylacetone and L-valine ethyl ester as starting materials to give the product as a brown thick liquid; Yield: 74% (205 mg, 0.74 mmol); $[\alpha]_D^{25}$ = +11.20˚ (c 0.58, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.32 (d, *J* = 7.2 Hz, 2H), 7.63 (t, *J* = 7.4 Hz, 1H), 7.50-7.45 (m, 3H), 4.62-4.57 (m, 1H), 4.25 (q, *J* = 7.2 Hz, 2H), 2.33-2.28 (m, 1H), 1.31 (t, *J* = 7.2 Hz, 3H), 0.99 (dd, J_1 = 7.2 Hz, J_2 = 2.7 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 187.1, 170.9, 161.6, 134.4, 132.2, 131.1, 128.5, 61.5, 57.3, 31.4, 18.9, 17.7, 14.2; FT-IR (neat, cm^{-1}): 3223, 2968, 2936, 1742, 1670, 1594, 1520, 1452; HR-MS (*m*/*z*) for $C_{15}H_{20}NO_4$ (M+H): Calculated 278.1392, found 278.1394.

5.11. (*S*)-(+)-Dimethyl-2-(2-oxo-2-phenylacetamido)succinate (5k)



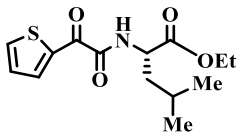
Compound **5k** was prepared using benzoylacetone and L-aspartic acid dimethyl ester as starting materials to give the product as a yellow thick liquid; Yield: 70% (205 mg, 0.70 mmol); $[\alpha]_D^{25}$ = +7.90˚ (c 0.33, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.13 (dd, J_1 = 8.4 Hz, J_2 = 1.2 Hz, 2H), 7.61-7.57 (m, 1H), 7.51-7.46 (m, 3H), 4.98-4.92 (m, 1H), 3.81 (s, 3H), 3.72 (s, 3H), 3.14 (dd, J_1 = 17.2 Hz, J_2 = 4.8 Hz, 1H), 2.94 (dd, J_1 = 17.1 Hz, J_2 = 4.8 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 186.7, 170.9, 170.3, 161.5, 134.5, 133.1, 131.1, 128.5, 52.8, 52.2, 48.7, 35.8; FT-IR (neat, cm^{-1}): 3220, 2966, 2938, 1773, 1740, 1664, 1588, 1515, 1450; HR-MS (*m*/*z*) for $C_{14}H_{16}NO_6$ (M+H): Calculated 294.0978, found 294.0981.

5.12. (*S*)-(+)-Ethyl-2-(2-oxo-2-(thiophen-2-yl)acetamido)-3-phenylpropanoate (5l)



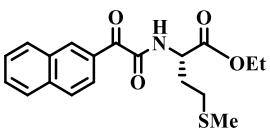
Compound **5l** was prepared using 2-thenoyltrifluoroacetone and L-phenylalanine ethyl ester as starting materials to give the product as a pale yellow thick liquid; Yield: 70% (232 mg, 0.70 mmol); $[\alpha]_D^{25}$ = +48.87˚ (c 0.89, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.38-8.37 (m, 1H), 7.83-7.81 (m, 1H), 7.71 (d, *J* = 7.8 Hz, 1H), 7.32- 7.23 (m, 3H), 7.20-7.15 (m, 3H), 4.92-4.85 (m, 1H), 4.19 (q, *J* = 7.2 Hz, 2H), 3.20 (d, *J* = 6.0 Hz, 2H), 1.24 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 170.4, 165.2, 160.2, 138.6, 138.1, 136.7, 135.3, 129.2, 128.7, 128.3, 127.3, 61.7, 53.4, 38.0, 14.0; FT-IR (neat, cm^{-1}): 3290, 2964, 2928, 1736, 1692, 1520, 1500, 1410; HR-MS (*m*/*z*) for $C_{17}H_{18}NO_4S$ (M+H): Calculated 332.0957, found 332.0962.

5.13. (*S*)-(-)-Ethyl-4-methyl-2-(2-oxo-2-(thiophen-2-yl)acetamido)pentanoate (5m)



Compound **5m**, was prepared using 2-thenoyltrifluoroacetone and L-leucine ethyl ester as starting materials to give the product as a yellow thick liquid; Yield: 77% (230 mg, 0.77 mmol); $[\alpha]_D^{25}$ = -2.61˚ (c 0.54, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.41 (d, *J* = 3.3 Hz, 1H), 7.83 (d, *J* = 4.8 Hz, 1H), 7.63 (d, *J* = 8.4 Hz, 1H), 7.19 (t, *J* = 4.2 Hz, 1H), 4.70-4.64 (m, 1H), 4.22 (q, *J* = 6.9 Hz, 2H), 1.73-1.64 (m, 3H), 1.29 (t, *J* = 7.2 Hz, 3H), 0.97 (d, J = 4.2 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 177.8, 171.8, 160.4, 138.6, 138.2, 136.8, 128.3, 61.6, 51.0, 41.5, 24.9, 22.8, 21.9, 14.1; FT-IR (neat, cm^{-1}): 3292, 2961, 2928, 1737, 1689, 1524, 1500, 1409; HR-MS (*m*/*z*) for $C_{14}H_{20}NO_4S$ (M+H): Calculated 298.1113, found 298.1115.

5.14. (*S*)-(+)-Ethyl-4-(methylthio)-2-(2-(naphthalen-2-yl)-2-oxoacetamido)butanoate (5n)

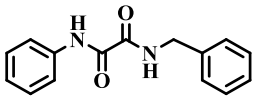


Compound **5n**, was prepared using 4,4,4-trifluoro-1-(2-naphthyl)-1,3-butanedione and L-methionine ethyl ester as starting materials to give the product as a yellow thick liquid; Yield: 78% (280 mg, 0.78 mmol); $[\alpha]_D^{25}$ = +16.4˚ (c 0.25, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.16 (s, 1H), 8.18 (d, *J* = 8.7 Hz, 1H), 7.99 (d, *J* = 8.1 Hz, 1H), 7.93-7.84 (m, 2H), 7.77 (d, *J* = 7.8 Hz, 1H), 7.65-7.52 (m, 2H), 4.85-4.81 (m, 1H), 4.26 (q, *J* = 7.2 Hz, 2H), 2.62-2.57 (m, 2H), 2.30-2.26 (m, 1H), 2.16-2.09 (m, 4H), 1.32 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 186.4, 170.9, 161.7, 136.2, 134.9, 132.4, 130.4, 130.3, 129.4, 128.4, 127.7, 126.8, 125.2, 61.9, 51.7, 31.7, 30.0, 15.5,

14.2; FT-IR (neat, cm^{-1}): 3224, 2956, 2930, 1744, 1671, 1596, 1522, 1444; HR-MS (*m*/*z*) for $C_{19}H_{22}NO_4S$ (M+H): Calculated 360.1270, found 360.1268.

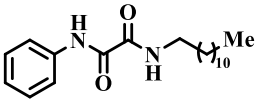
6. Characterization data of the synthesized oxalamide (8a-f)

6.1. *N*^{1}-Benzyl-*N*^{2}-phenyloxalamide (8a)



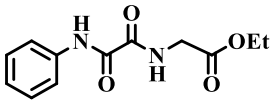
Compound **8a** was prepared using acetoacetanilide and benzylamine as starting materials to give the product as a yellow solid; yield: 78% (198 mg, 0.78 mmol); m.p. 112-114 ^oC; ^1H NMR (300 MHz, $CDCl_3$): δ 9.32 (brs, 1H), 7.93 (brs, 1H), 7.64-7.60 (m, 2H), 7.39-7.28 (m, 7H), 7.20-7.15 (m, 1H), 4.54 (d, *J* = 6.0 Hz, 2H); ^{13}C NMR(75 MHz, $CDCl_3$): δ 159.9, 157.3, 136.3, 129.2, 128.9, 128.0, 127.8, 125.4, 119.8, 44.0; FT-IR (KBr, cm^{-1}): 3343, 3312, 2934, 2850, 1707, 1661, 1595, 1519, 1414, 1354; HR-MS (*m*/*z*) for: $C_{15}H_{14}N_2NaO_2$ (M+Na): Calculated, 277.0953, found 277.0956.

6.2. *N*^{1}-Dodecyl-*N*^{2}-phenyloxalamide (8b)



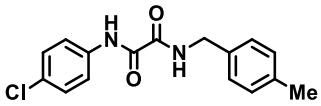
Compound **8b** was prepared using acetoacetanilide and dodecylamine as starting materials to give the product as a yellow solid; yield: 70% (232 mg, 0.70 mmol); m.p. 104-106 ^oC; ^1H NMR (300 MHz, $CDCl_3$): δ 9.25 (brs, 1H), 7.66-7.48 (m,3H), 7.36-7.27 (m, 2H), 7.14 (t, *J* = 7.5 Hz, 1H), 3.33 (q, *J* = 6.9 Hz, 2H), 1.62-1.51 (m, 2H), 1.28-1.22 (m, 18H), 0.84 (t,*J* = 6.6 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ ; 159.7, 157.4, 136.3, 129.0, 125.2, 119.6, 39.9, 31.8, 30.8, 29.5, 29.4, 29.3, 29.2, 29.1, 26.7, 22.5, 14.0; FT-IR (KBr, cm^{-1}): 3324, 3289, 2947, 2938, 1710, 1665, 1622, 1525, 1445, 1368; HR-MS (*m*/*z*) for: $C_{20}H_{33}N_2O_2$ (M+H): Calculated, 333.2542, found 333.2538.

6.3. Ethyl 2-(2-oxo-2-(phenylamino)acetamido)acetate (8c)



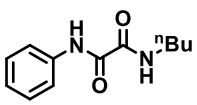
Compound **8c** was prepared using acetoacetanilide and ethylglycinate as starting materials to give the product as a brown solid; yield: 75% (187 mg, 0.75 mmol); m.p. 102-104 ^oC; ^1H NMR (300 MHz, $CDCl_3$): δ 9.19 (brs, 1H), 8.01 (brs, 1H), 7.65 (d, *J* = 7.8 Hz, 2H), 7.41 (t, *J* = 7.5 Hz, 2H), 7.20 (t, *J* = 7.3 Hz, 1H), 4.28 (q, *J* = 7.2 Hz, 2H), 4.16 (d, *J* = 5.7 Hz, 2H), 1.32 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 168.4, 160.2, 156.7, 136.2, 129.2, 125.4, 119.8, 61.9, 41.7, 14.1; FT-IR (KBr, cm^{-1}): 3368, 2978, 1730, 1669, 1604, 1519, 1445, 1413, 1373, 1354; HR-MS (*m*/*z*) for: $C_{12}H_{14}N_2NaO_4$ (M+Na): Calculated, 273.0851, found 273.0854.

6.4. *N*^{1}-(4-Chlorophenyl)-*N*^{2}-(4-methylbenzyl)oxalamide (8d)



Compound **8d** was prepared using 4-chloroacetoacetanilide and 4-methylbenzylamine as starting materials to give the product as a white solid; yield: 76% (230 mg, 0.76 mmol); m.p. 166-168 ^oC; ^1H NMR (300 MHz, $CDCl_3$): δ 9.32 (brs, 1H), 7.82 (brs, 1H), 7.60 (d, *J* = 8.7 Hz, 2H), 7.35 (d, *J* = 8.7 Hz, 2H), 7.23-7.16 (m, 4H), 4.52 (d, *J* = 6.0 Hz, 2H), 2.36 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 159.5, 157.3, 137.8, 134.9, 133.4, 130.4, 129.5, 129.2, 127.8, 120.9, 43.8, 21.0; FT-IR (KBr, cm^{-1}): 3345, 3330, 2950, 2850, 1722, 1672, 1595, 1505, 1414, 1344; HR-MS (*m*/*z*) for: $C_{16}H_{16}ClN_2O_2$ (M+H): Calculated, 303.0900, found 303.0907 (One of the major peaks).

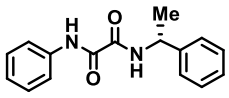
6.5. *N*^{1}-Butyl-*N*^{2}-phenyloxalamide (8e)[5]



Compound **8e** was prepared using acetoacetanilide and butylamine as starting materials to give the product as a White solid; yield: 65% (143 mg, 0.65 mmol); m.p. 148-150 ^oC; ^1H NMR (300 MHz, $CDCl_3$): δ 9.30 (brs, 1H), 7.64-7.61 (m, 3H), 7.39-7.34 (m, 2H), 7.17 (t,

J = 7.2 Hz, 1H), 3.37 (q, J = 6.9 Hz, 2H), 1.61-1.53 (m, 2H), 1.45-1.35 (m, 2H), 0.94 (t, J = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 159.9, 157.6, 136.4, 129.2, 125.3, 119.8, 39.7, 31.2, 20.0, 13.6; FT-IR (KBr, cm^{-1}): 3312, 3283, 2961, 2926, 1710, 1659, 1604, 1525, 1445, 1378; HR-MS (*m*/*z*) for: $C_{12}H_{17}N_2O_2$ (M+H): Calculated, 221.1290, found 221.1292.

6.6. (*S*)-*N*^{1}-Phenyl-*N*^{2}-(1-phenylethyl)oxalamide (8f)

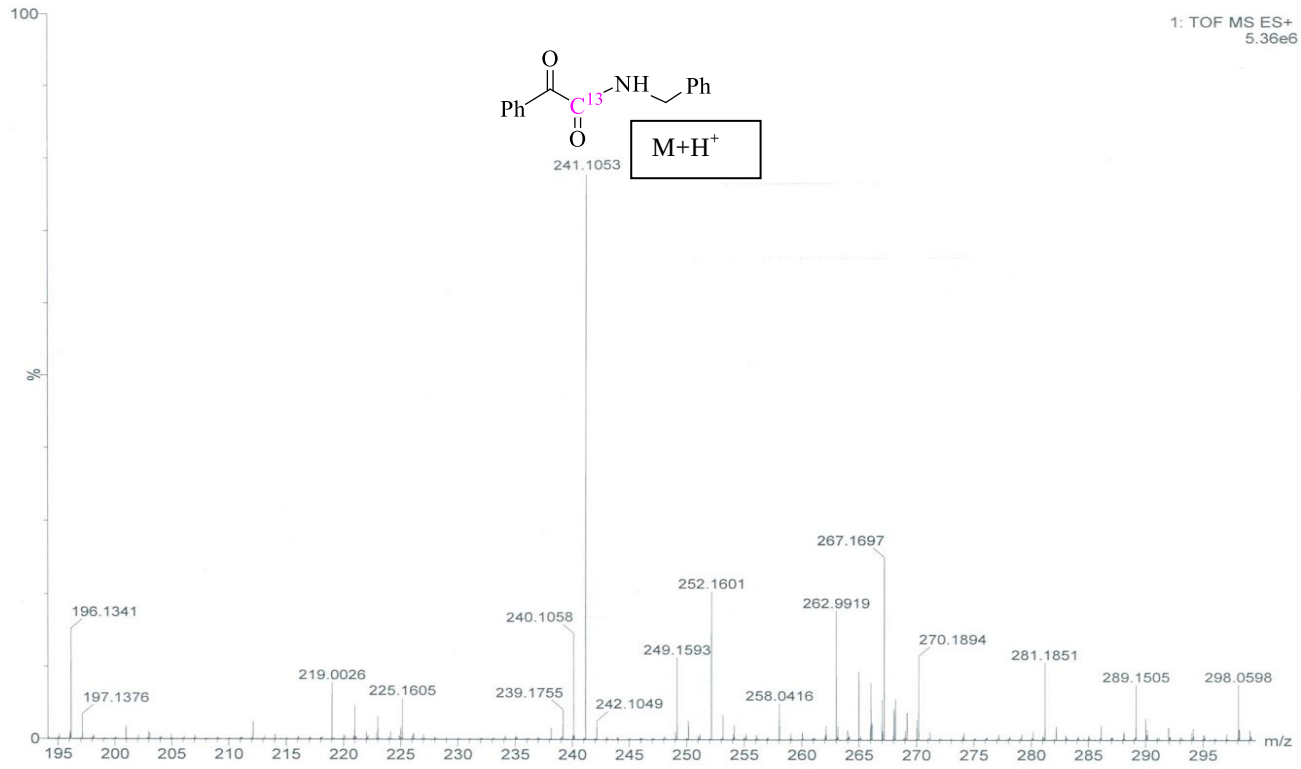


Compound **8e** was prepared using acetoacetanilide and (*S*)-(-)-α-methylbenzylamine as starting materials to give the product as a white solid; yield: 70% (177 mg, 0.70 mmol); m.p. 110-112 °C; $[\alpha]_D^{25}$ = -23.4° (c 0.5, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.30 (brs, 1H), 7.87 (d, J = 7.2 Hz, 1H), 7.63 (d, J = 7.8 Hz, 2H), 7.41-7.29 (m, 7H), 7.19 (t, J = 7.5 Hz, 1H), 5.18-5.09 (m, 1H), 1.57 (d, J = 8.4 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 159.0, 157.3, 141.8, 136.3, 129.1, 128.8, 127.7, 126.0, 125.2, 119.7, 49.7, 21.6; FT-IR (KBr, cm^{-1}): 3343, 3322, 2943, 2850, 1715, 1661, 1595, 1530, 1408, 1354; HR-MS (*m*/*z*) for: $C_{16}H_{17}N_2O_2$ (M+H): Calculated, 269.1290, found 269.1287.

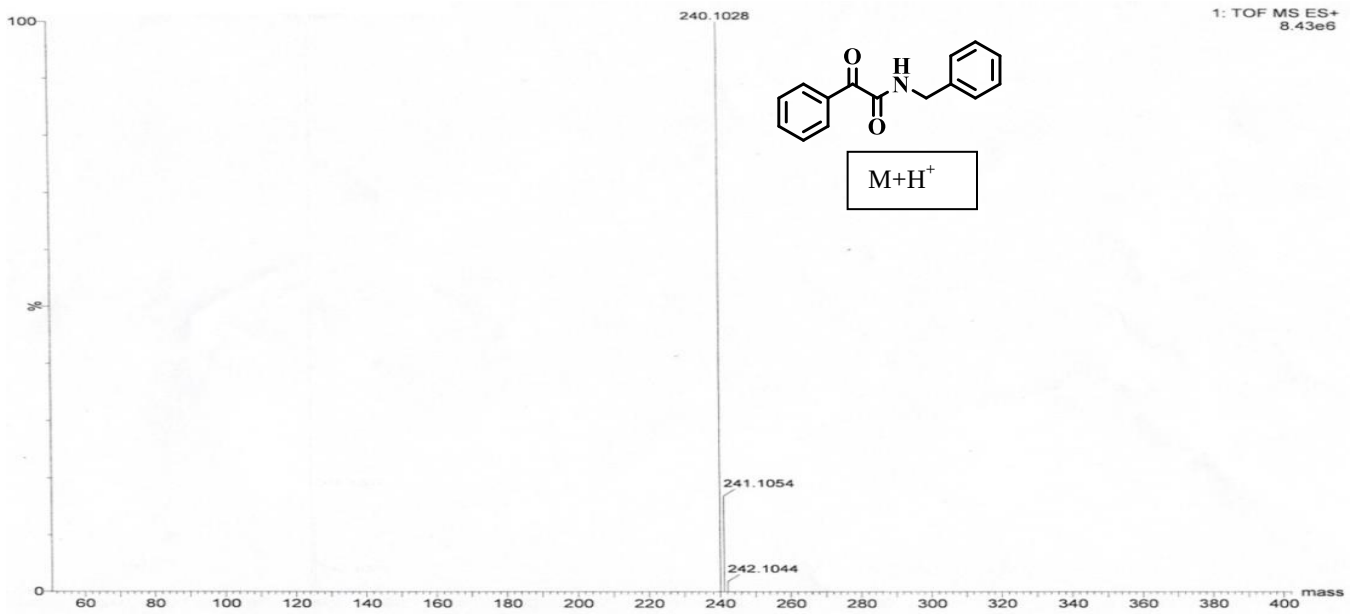
7. Characterization data of controlled experiment products

7.1. C^{13}-isotope lebelling experiment (C^{13}-4a)

Compound C^{13}-**4a**, was prepared using C^{13} labelled 1,3-diphenylpropane-1,3-dione at C-2 position and benzylamine as starting materials following the general method as described above. The desired α-ketoamide (C^{13}-**4a**) was confirmed by performing HRMS analysis with the post reaction mixture. Appearance of a peak at 241.1053 (M^++H) proves that 'acetivemethelene' carbon is converted into 'amide' carbon atom in the developed reaction.



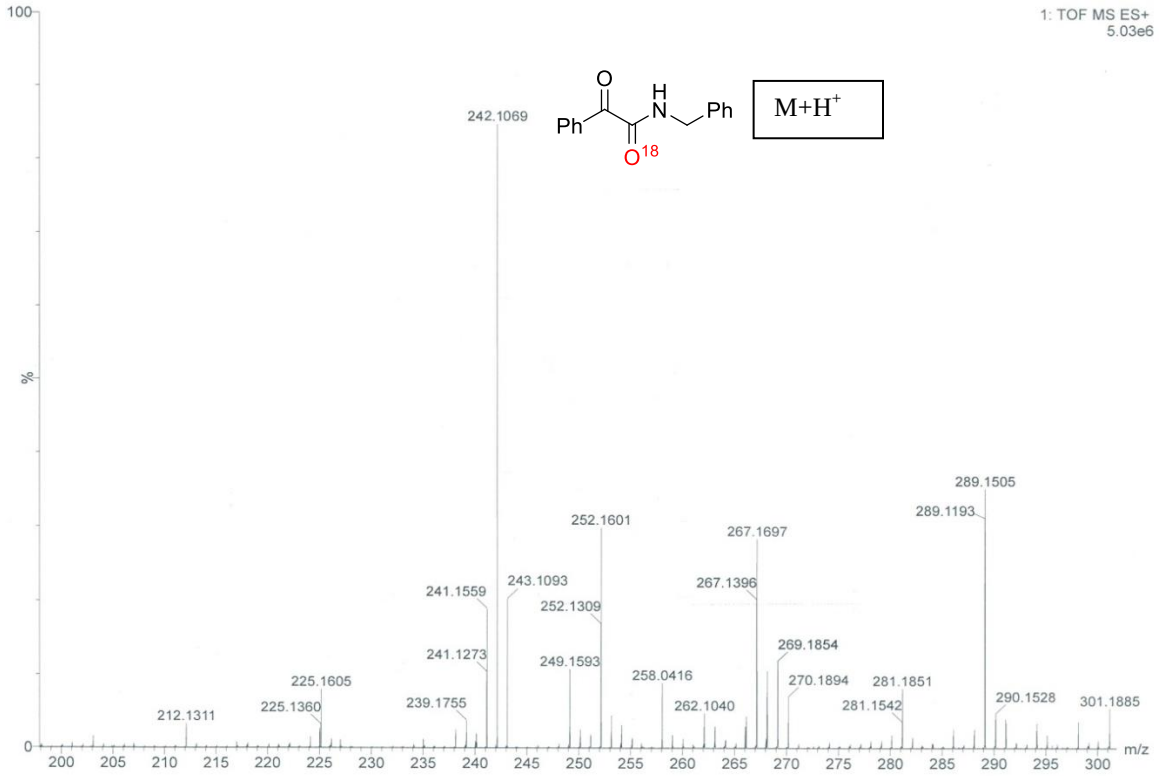
SI Figure 1a: HRMS spectra of C^{13}-**4a**



SI Figure 1b: HRMS spectra of **4a**

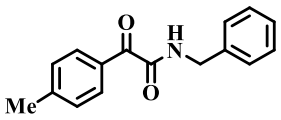
7.2. O^{18}-isotope lebelling experiment (O^{18}-4a)

On treatment of benzoylacetone and benzylamine in presence of $PhIO^{18}$ (as described in the general procedure) the desired α-ketoamide (**O^{18}-4a**) was formed with incorporporation of O^{18}-isotope. It was confirmed through HRMS analysis with the post reaction mixture. The peak at 242.1069 (M^++H) confirms the formation of **O^{18}-4a** and source of oxygen on newly generated amide functionality is PhIO in the desired α-ketoamide.



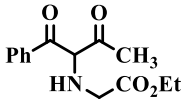
SI Figure 2: HRMS spectra of **O^{18}-4a**

7.3. *N*-benzyl-2-oxo-2-p-tolylacetamide (4m)



Compound **4m** was prepared using 1-Phenyl-3-p-tolylpropane-1,3-dione and benzyl amine as starting materials to give the product as a white solid; yield: 40% (100 mg, 0.40 mmol); m.p. 78-80 ^{0}C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.28 (d, J = 8.0 Hz, 2H), 7.37-7.25 (m, 8H), 4.56 (d, J = 6.0 Hz, 2H), 2.42 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 187.0, 161.8, 145.6, 137.1, 131.3, 130.7, 129.1, 128.7, 127.6, 43.3, 21.2; FT-IR (KBr, cm^{-1}): 3280, 3030, 2928, 1698, 1652, 1560, 1529; HR-MS (*m*/*z*) for $C_{16}H_{16}NO_2$ (M+H): Calculated 254.1181, found 254.1179.

7.4. Characterization data of ethyl 2-(1,3-dioxo-1-phenylbutan-2-ylamino)acetate (12)

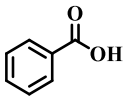


Compound **9** was prepared using benzoylacetone and ethylglycinate as starting materials to give the product as a liquid; Yield: 40% (105 mg, 0.40 mmol); ^{1}H NMR (300 MHz, $CDCl_3$): δ 11.48 (brs, 1H), 7.86 (d,J = 7.2 Hz, 2H), 7.42-7.34(m, 3H), 5.76 (s, 1H), 4.23 (q, J = 7.2 Hz, 2H), 4.08 (d, J = 6.3 Hz, 2H), 2.04 (s, 3H),1.29 (t, J = 6.9 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 196.0, 188.7, 169.0, 140.1, 130.6, 128.1, 127.0, 93.3, 61.6, 44.9, 19.3, 14.1; FT-IR (neat, cm^{-1}): 3260, 2937, 1755, 1710, 1626, 1580, 1488, 1463; HR-MS (*m*/*z*) for $C_{14}H_{17}NO_4Na$ (M^++Na): Calculated 286.1055, found 286.1060.

8. Isolation and detection of byproduct

The aquous layer was collected after bicarbonate wash of the post reaction mixture. Then it was acidified with diluted HCl. Volume was reduced through vacuum distillation. After cooling a white crystalline solid was appeared. It was filtered and washed with cold water. It was dried in a water bath and characterized using spectroscpic analysis.

8.1. Characterization data of benzoic acid (14a)



Compound **14a**; m.p. 122 ^{0}C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 10.82 (brs, 1H), 8.15 (dd, J_1 = 8.2 Hz,J_2 = 1.2 Hz,2H), 7.67-7.61 (m, 1H), 7.53-7.48 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 172.4, 133.8, 130.2, 129.2, 128.5; FT-IR (KBr, cm^{-1}): 3071, 2552, 1679, 1452, 1418, 1287; HR-MS (*m*/*z*) for $C_7H_7O_2$ (M+H): Calculated 123.0446, found 123.0449.

9. References

[1] W. Wei, Y. Shao, H. Hu, F. Zhang, C. Zhang, Y. Xu and X. Wan, *J. Org. Chem.,* 2012, **77**, 7157.

[2] S-S. Weng, M-W. Shen, J-Q. Kao, Y. S. Munot and C-T. Chen, *PNAS.,* 2013, **16**, 3522.

[3] K. Harada and T. Munegumi, *Bull. Chem. Soc. Jap.,* 1984**, 57**, 3203.

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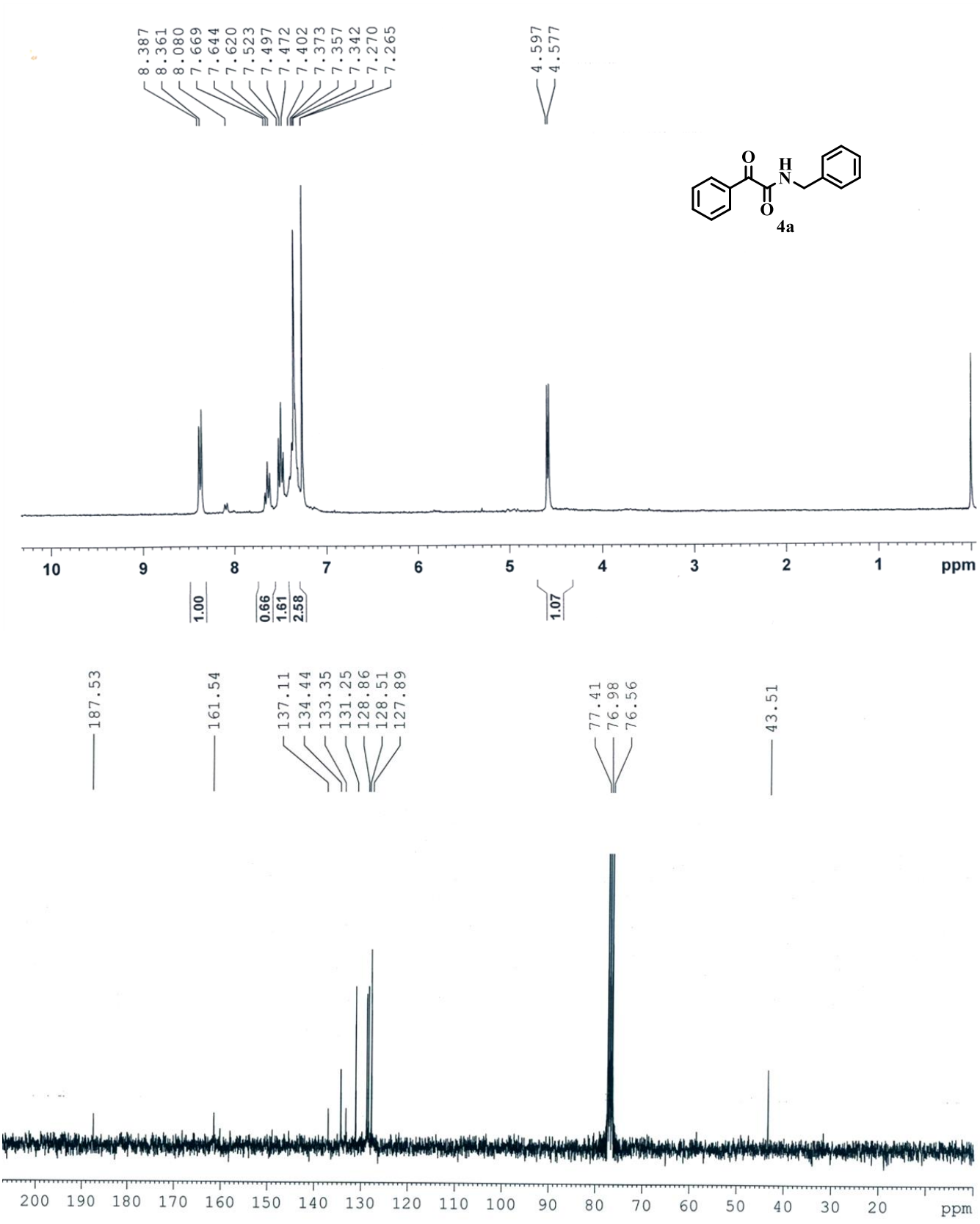
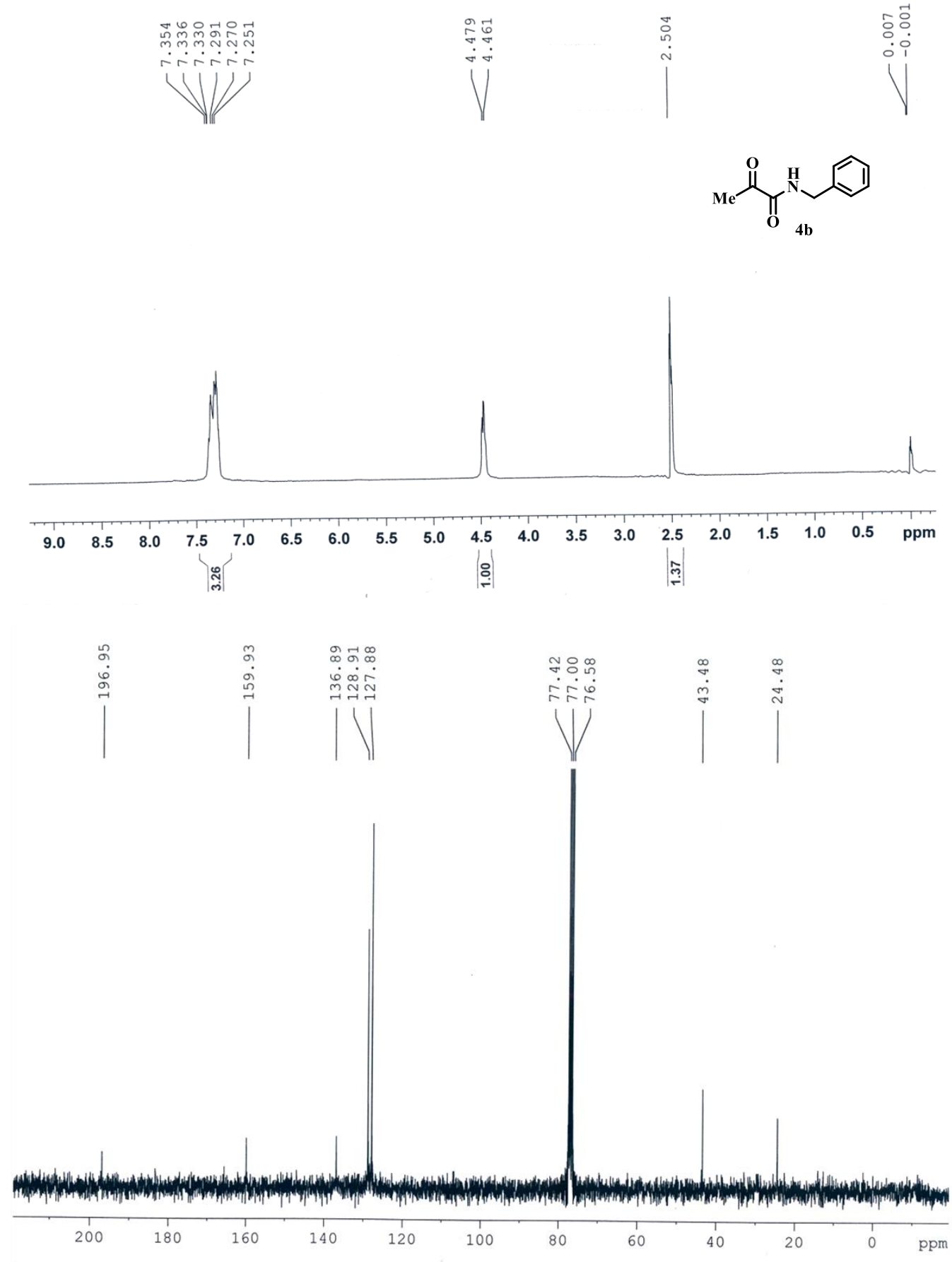
[5] N. Kambe, T. Inoue, T. Takeda, S-I. Fujiwara and N. Sonoda, *J. Am. Chem. Soc.,* 2006, **128**, 12650.

9. ^{1}H and ^{13}C-NMR spectra of synthesized α-ketoamides (4a-l, 5a-n),oxalamides (8a-f), oxalamates (9a-j) and some relevant compounds (4m, 12, 14a)

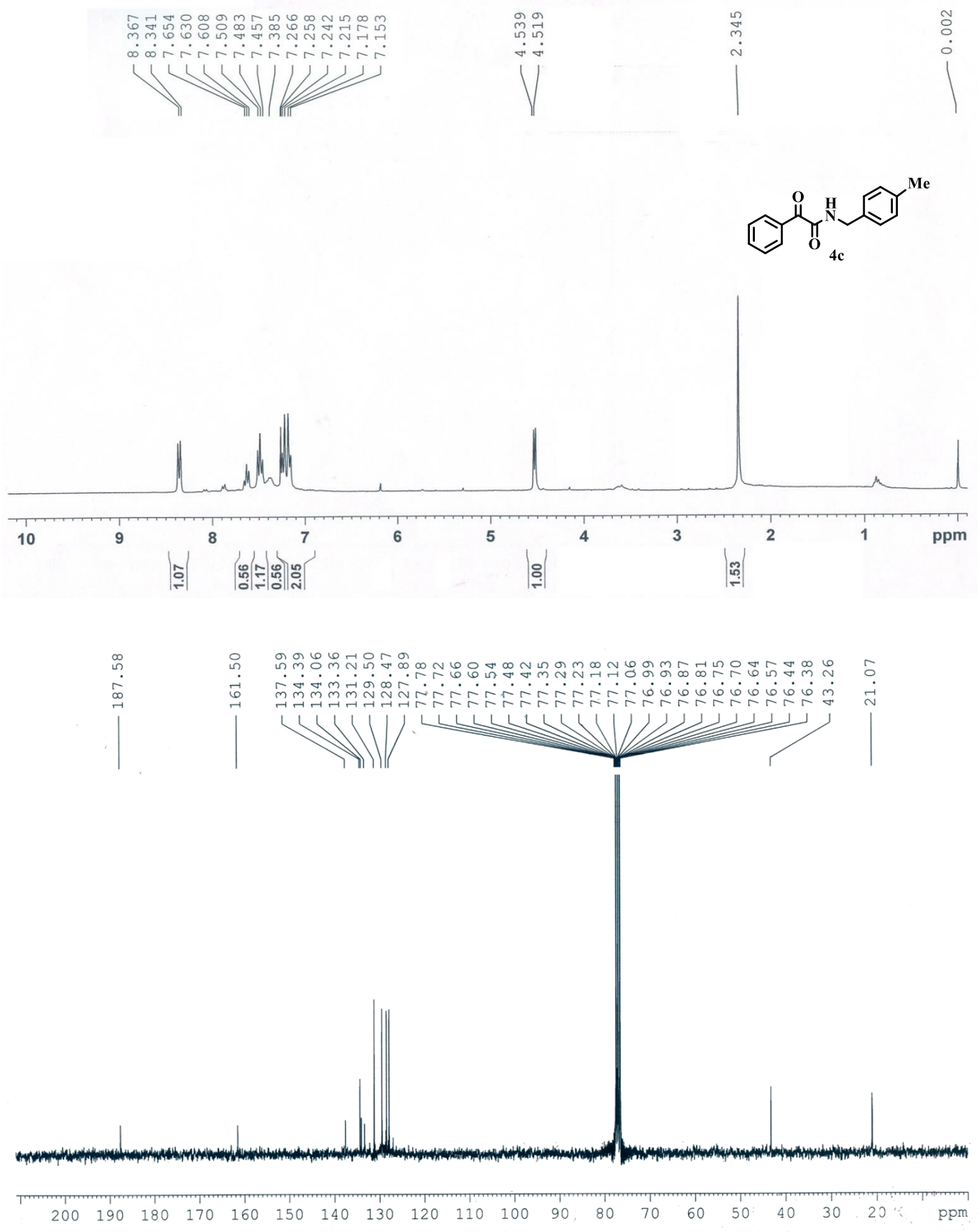
SI Figure 3: ^{1}H and ^{13}C-NMR spectra of compound **4a**



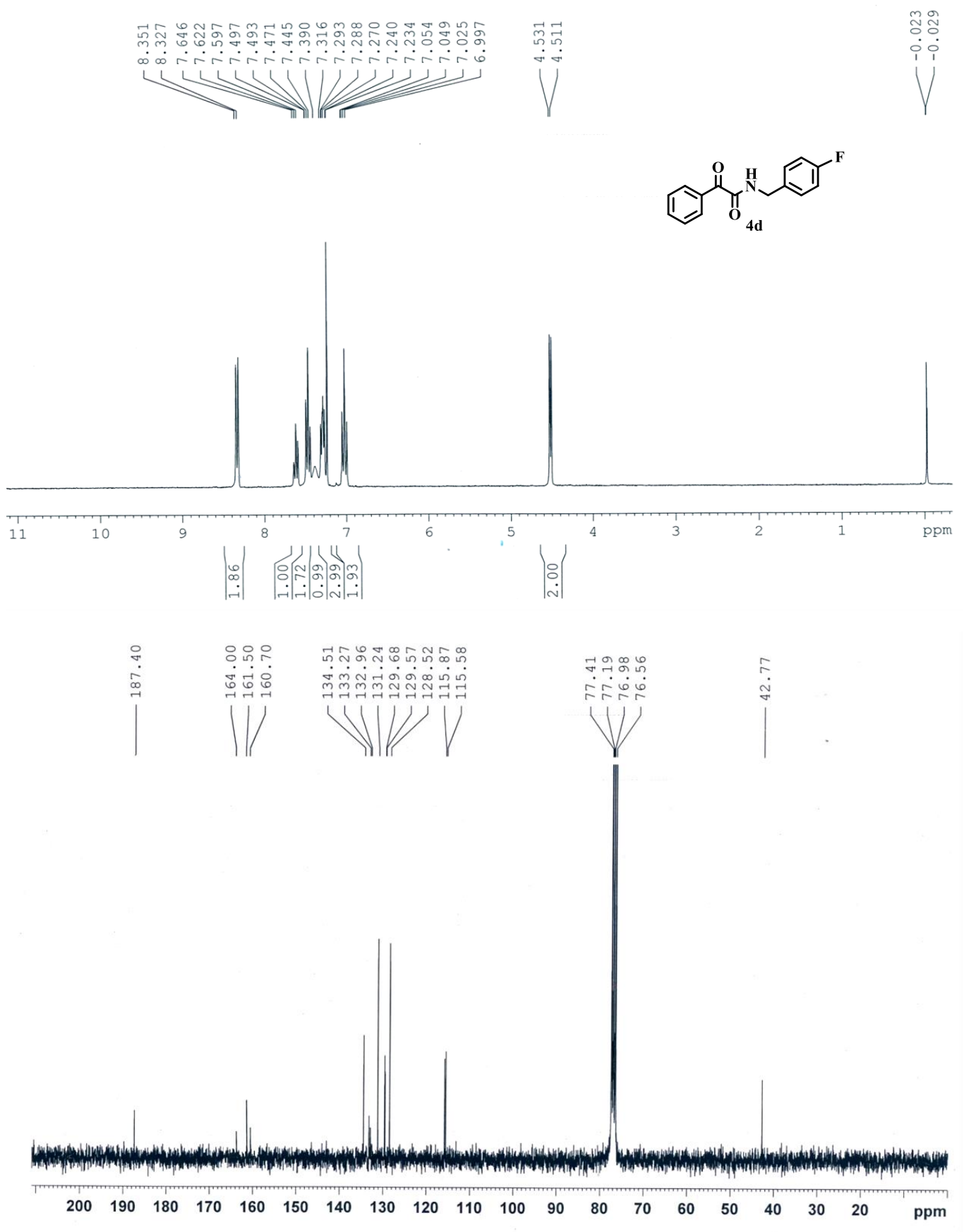
SI Figure4: ^{1}H and ^{13}C-NMR spectra of compound **4b**



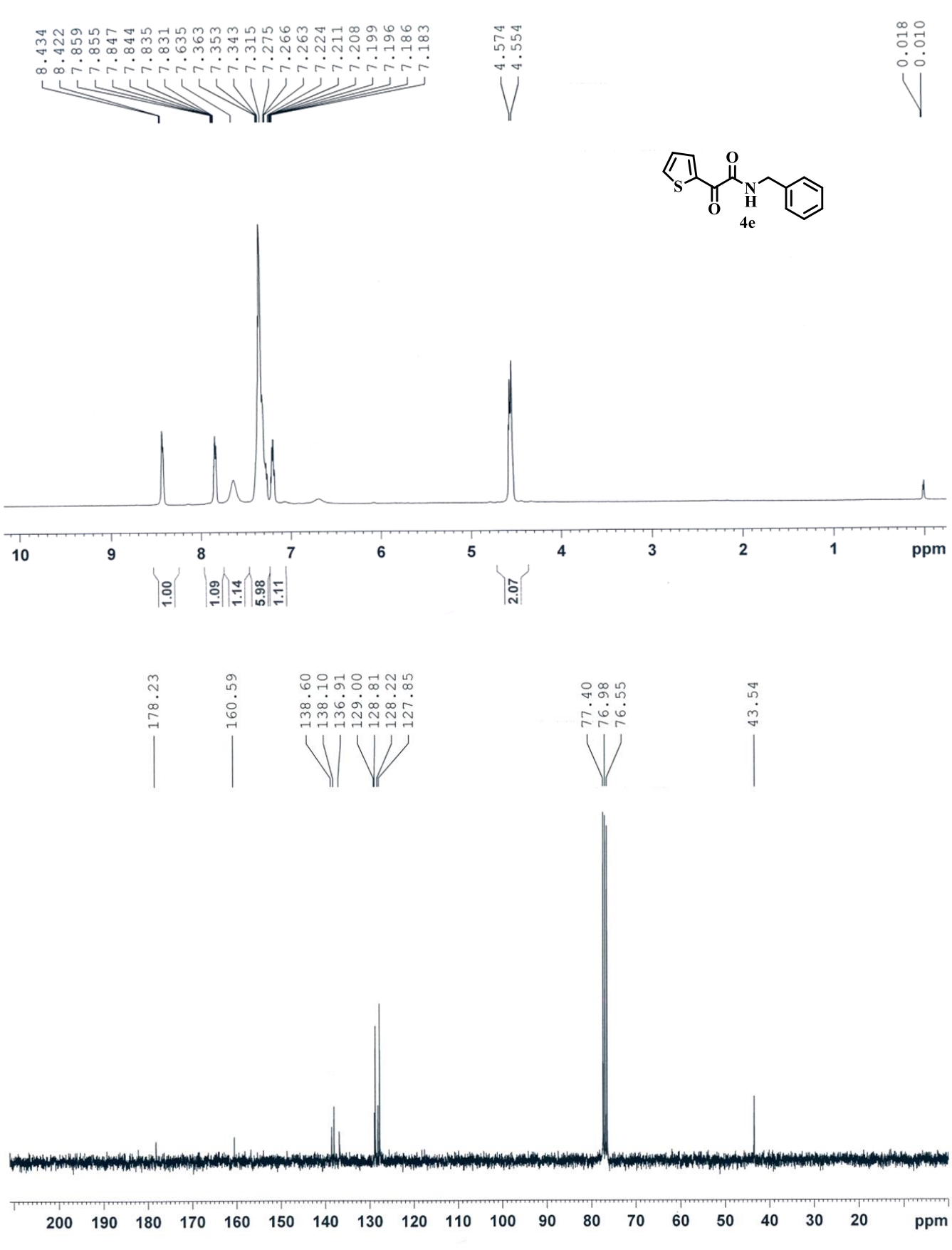
SI Figure 5: ^{1}H and ^{13}C-NMR spectra of compound **4c**



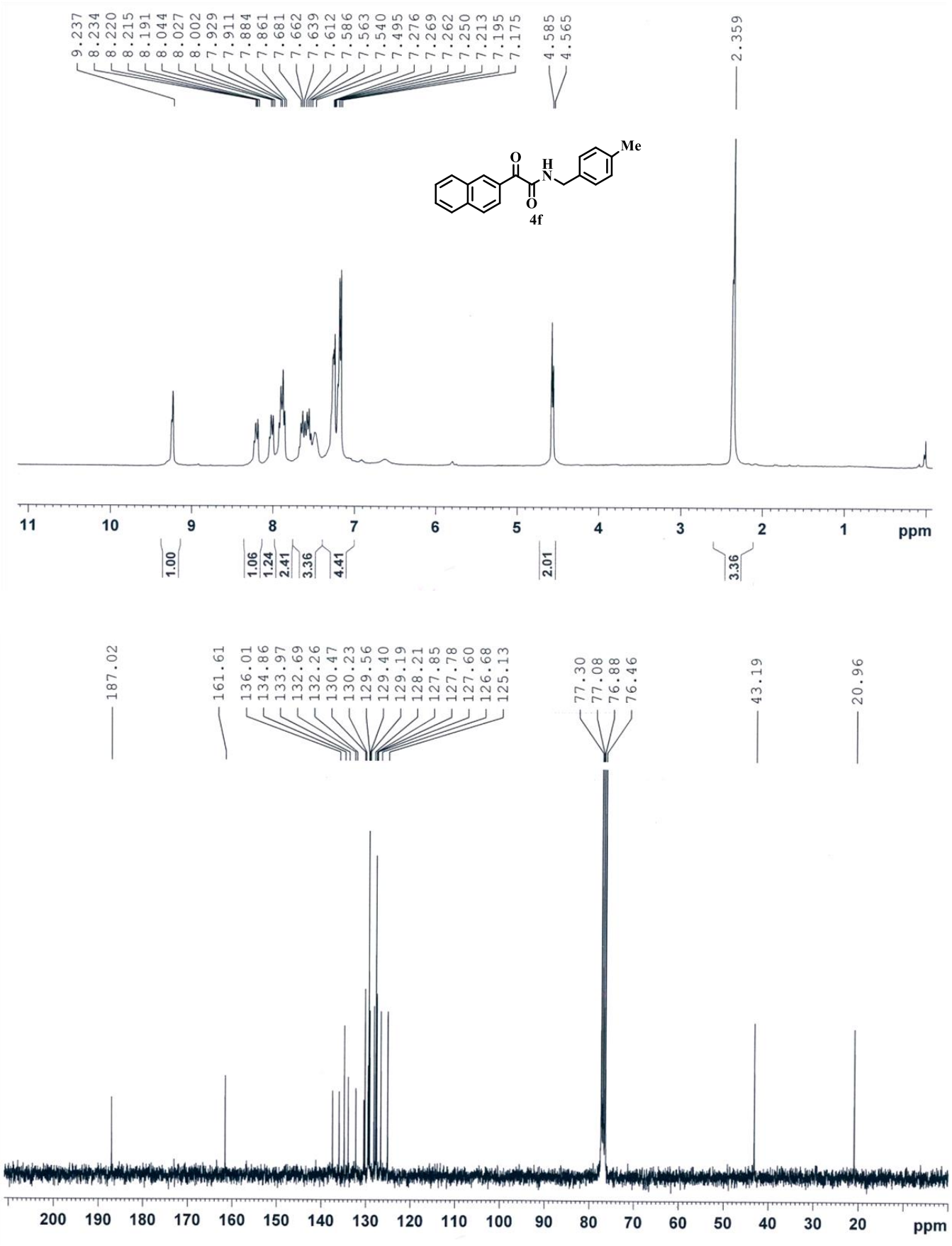
SI Figure 6: ^{1}H and ^{13}C-NMR spectra of compound **4d**



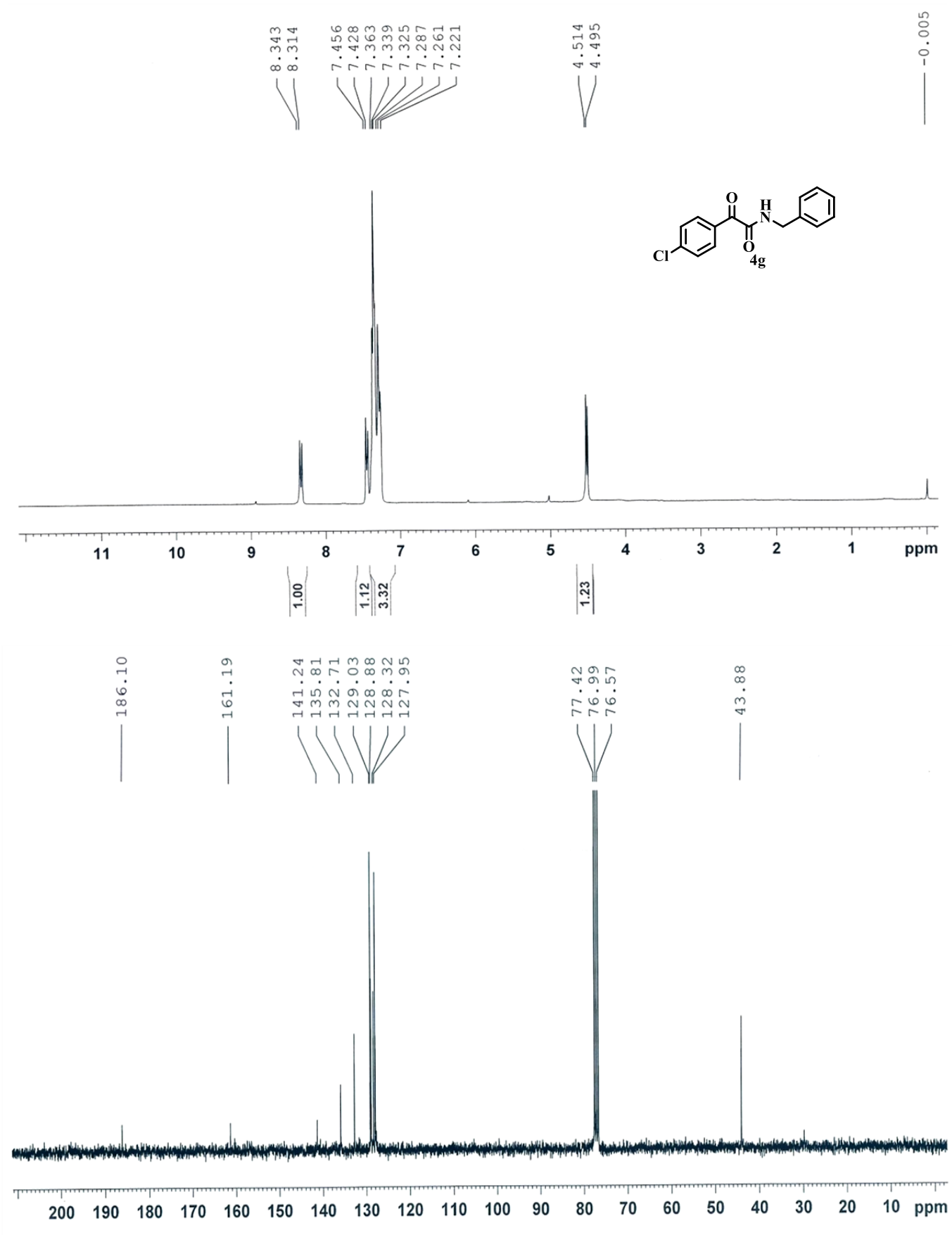
SI Figure 7: ^{1}H and ^{13}C-NMR spectra of compound **4e**



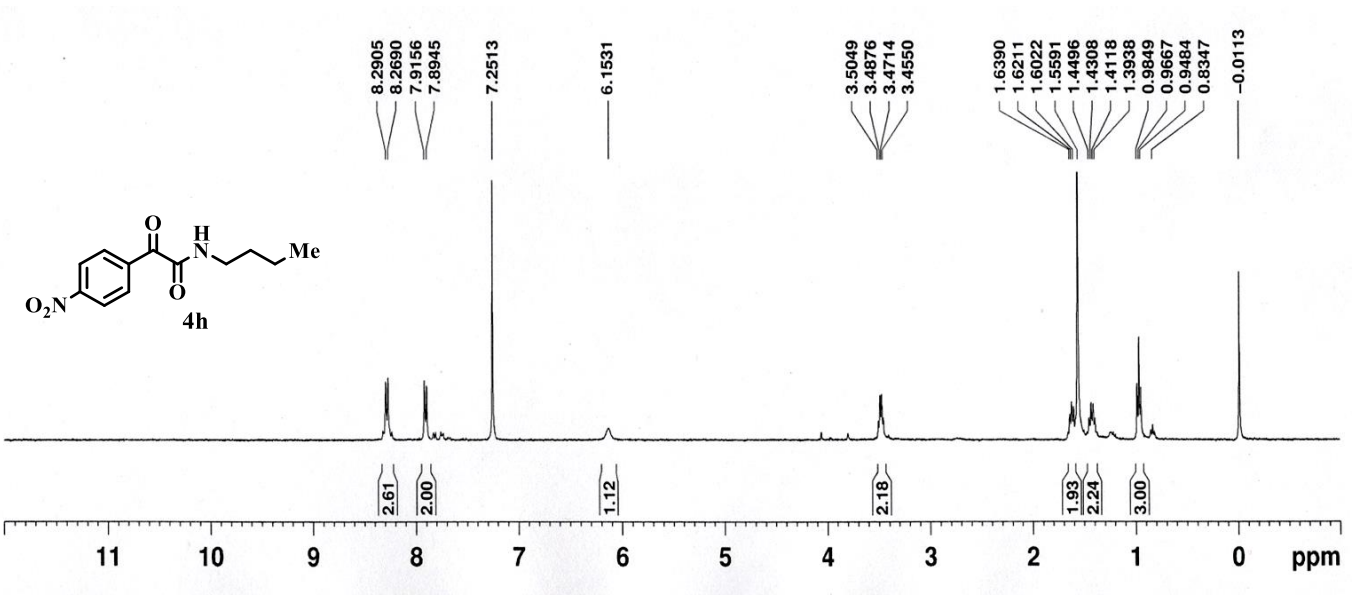
SI Figure 8: ^{1}H and ^{13}C-NMR spectra of compound **4f**

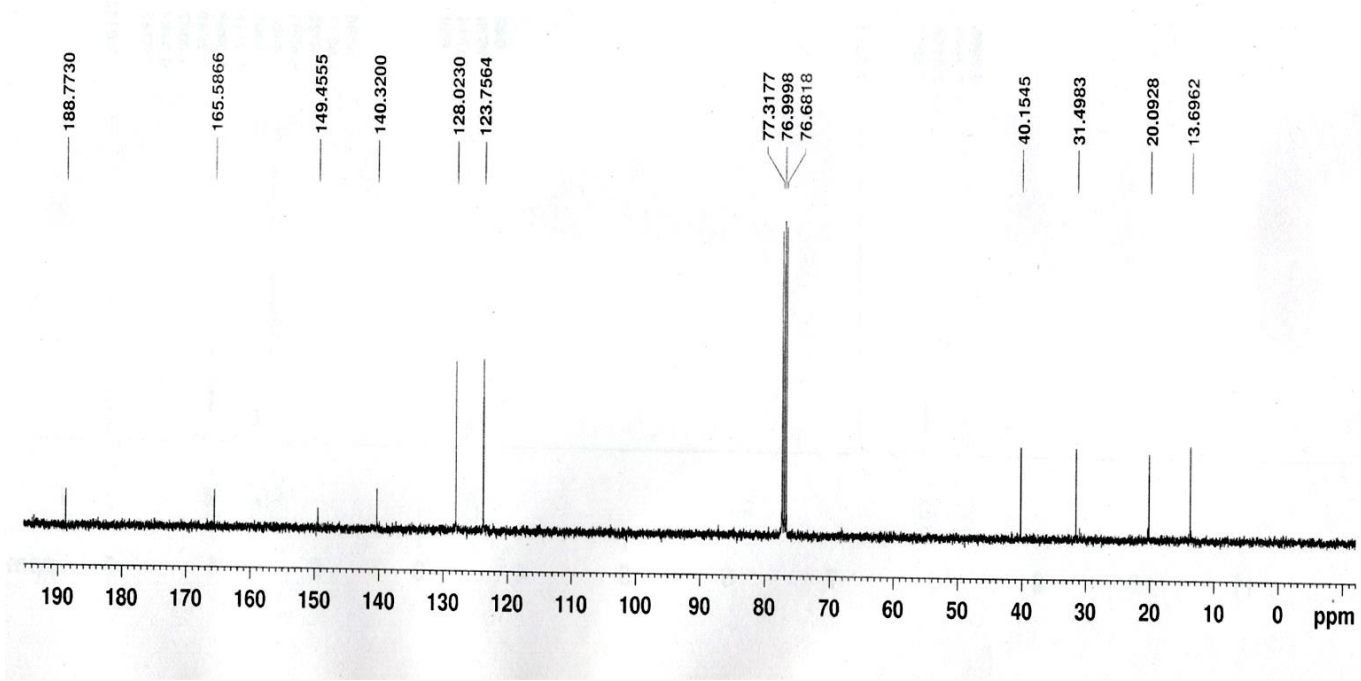


SI Figure 9: ^{1}H and ^{13}C-NMR spectra of compound **4g**

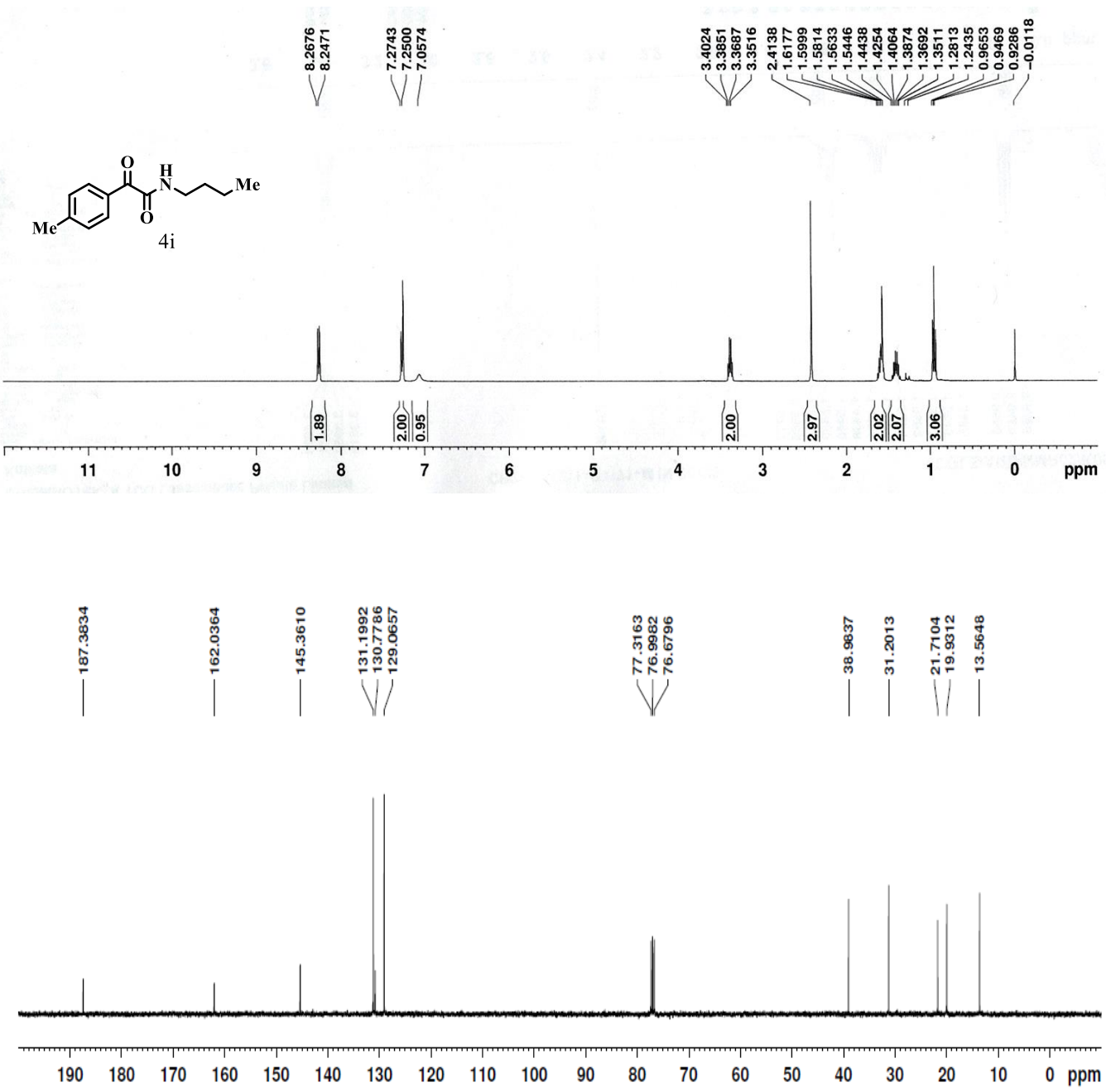


SI Figure 10: ^{1}H and ^{13}C-NMR spectra of compound **4h**

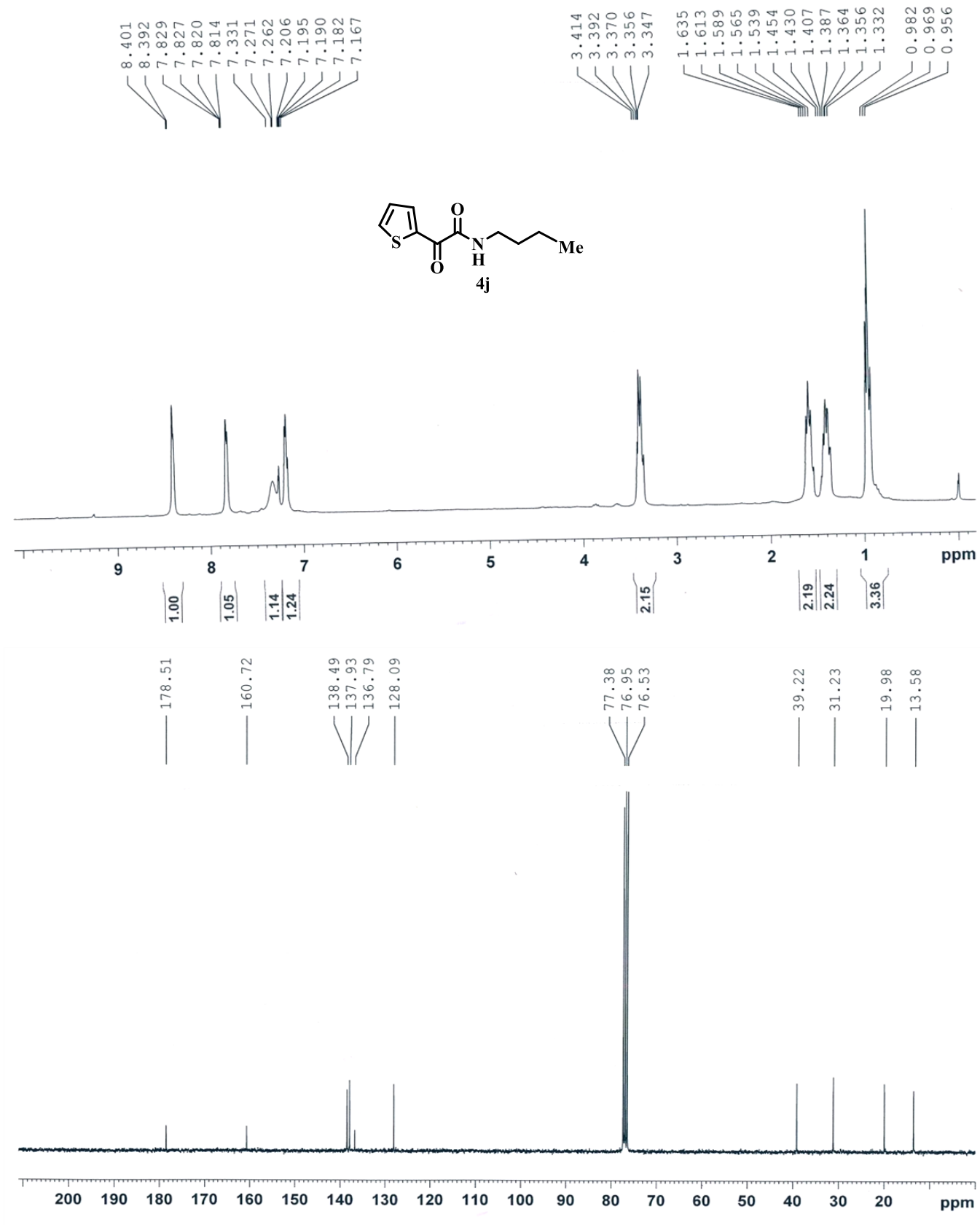




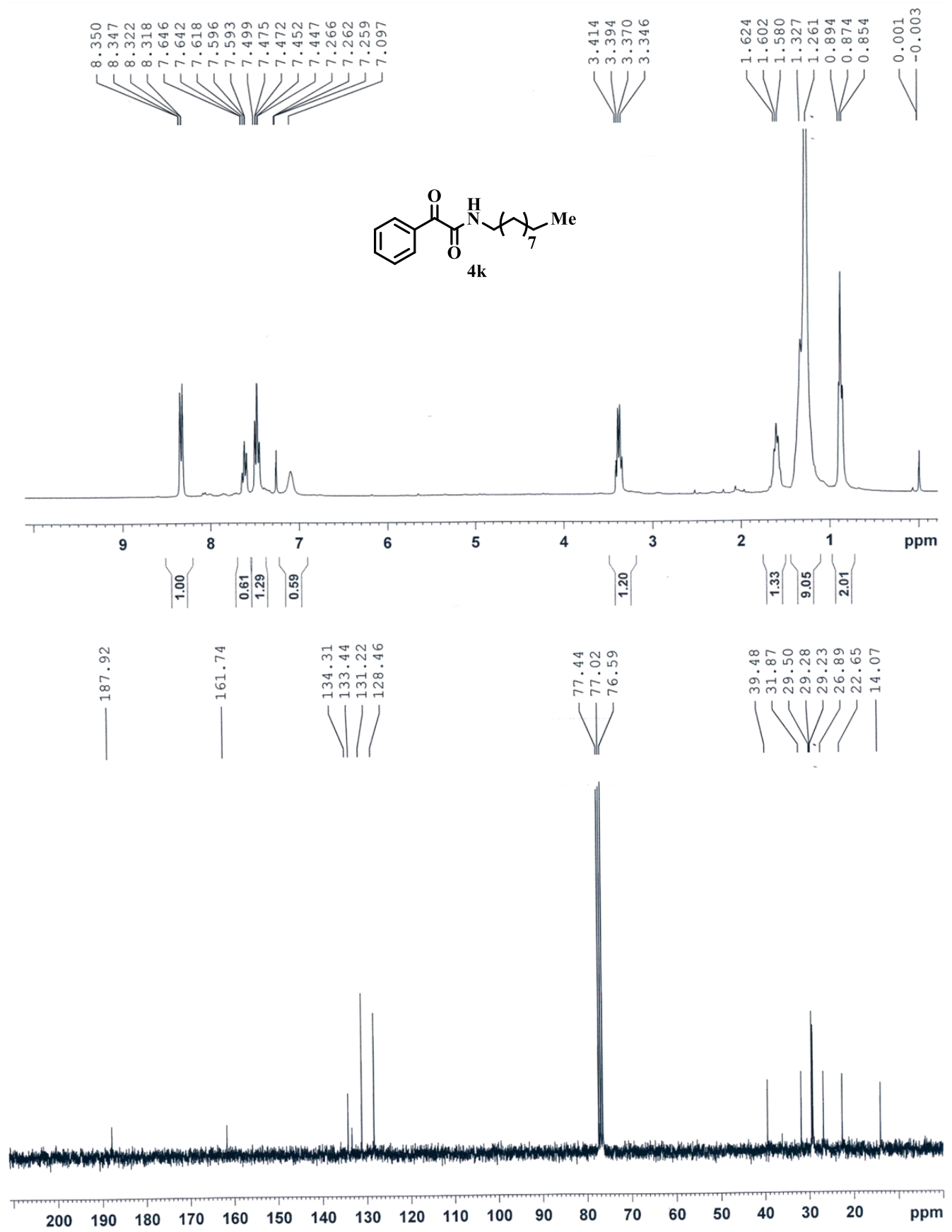
SI Figure 11: ^{1}H and ^{13}C-NMR spectra of compound **4i**



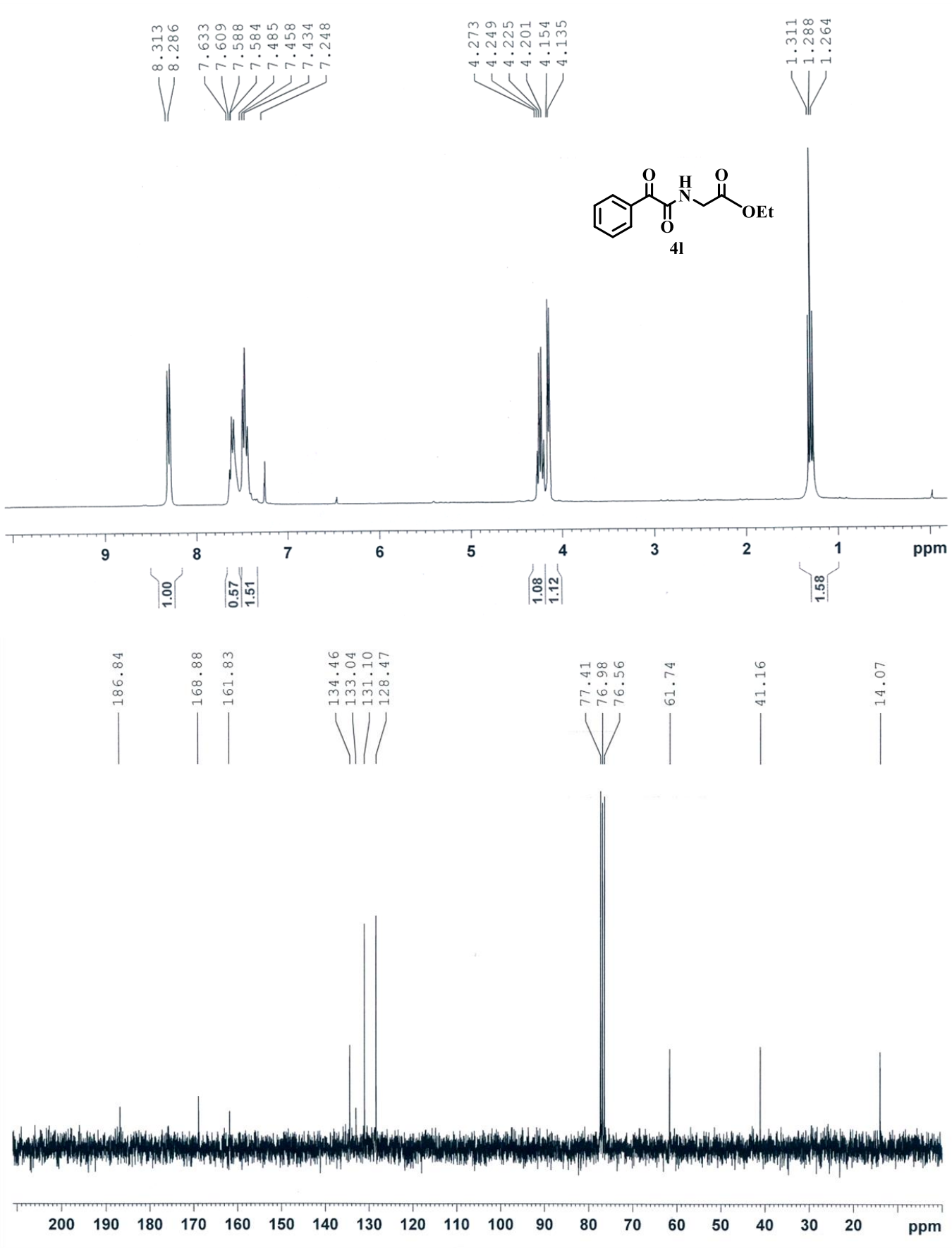
SI Figure 12: ^{1}H and ^{13}C-NMR spectra of compound **4j**



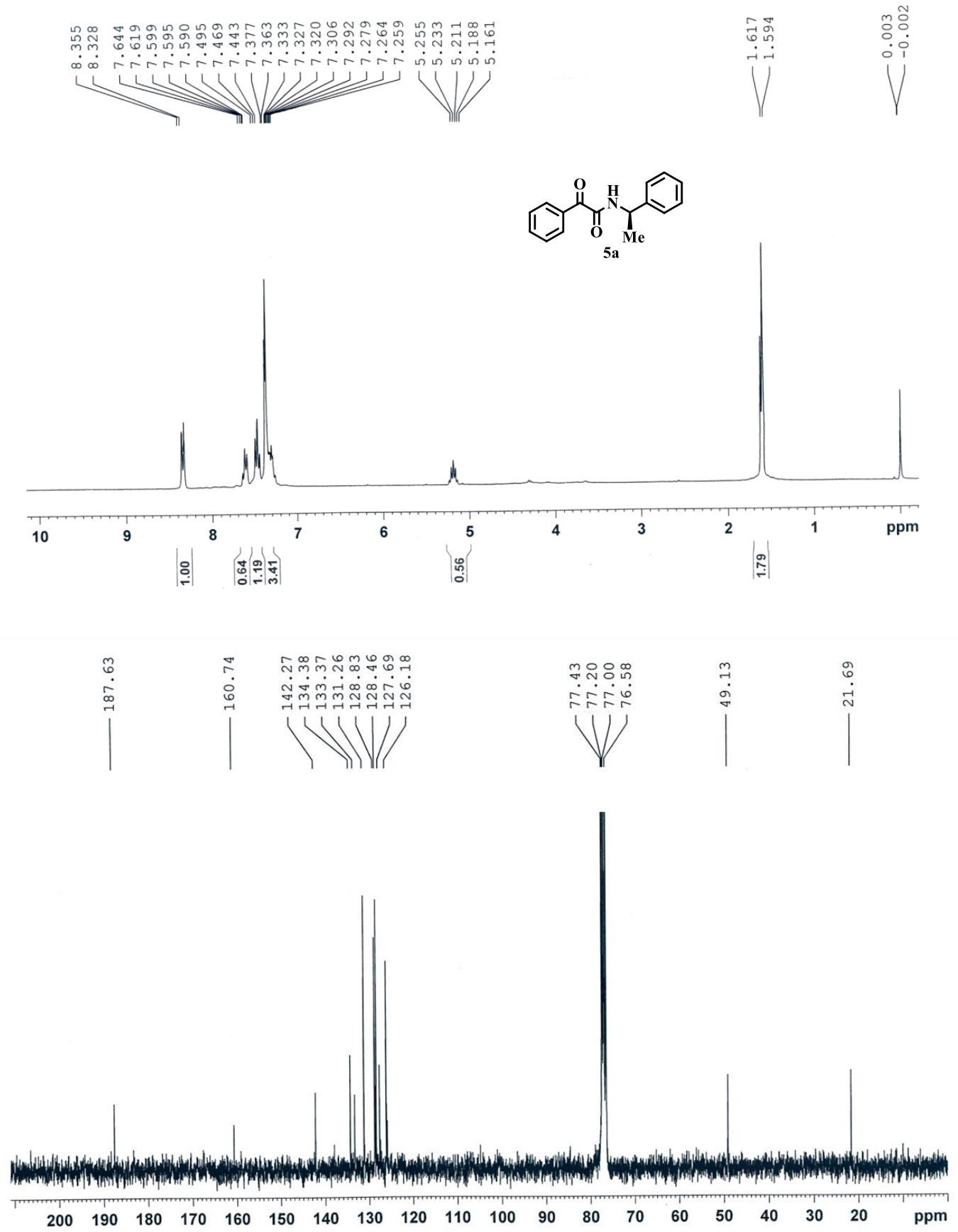
SI Figure 13: ^{1}H and ^{13}C-NMR spectra of compound **4k**



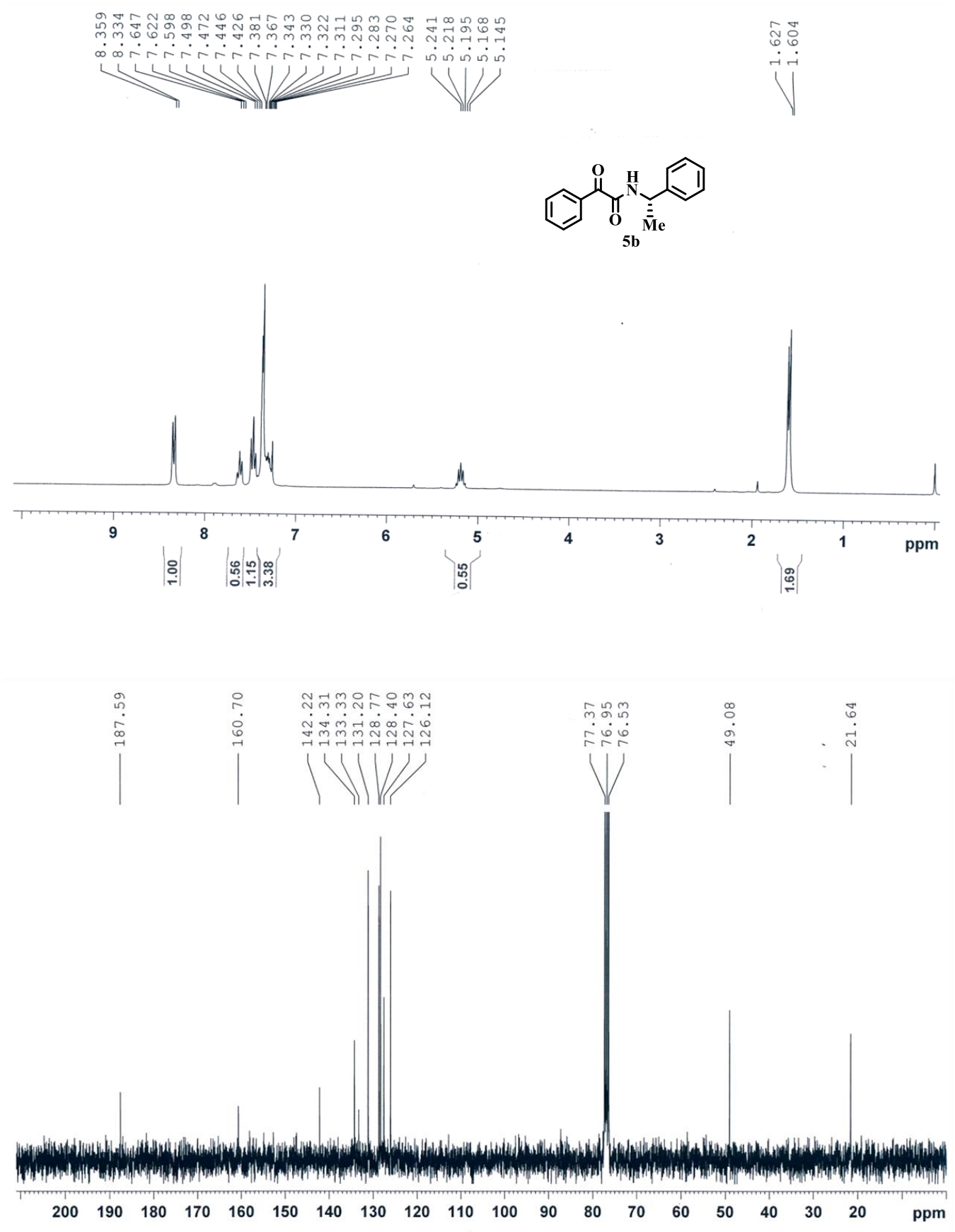
SI Figure 14: ^{1}H and ^{13}C-NMR spectra of compound **4l**



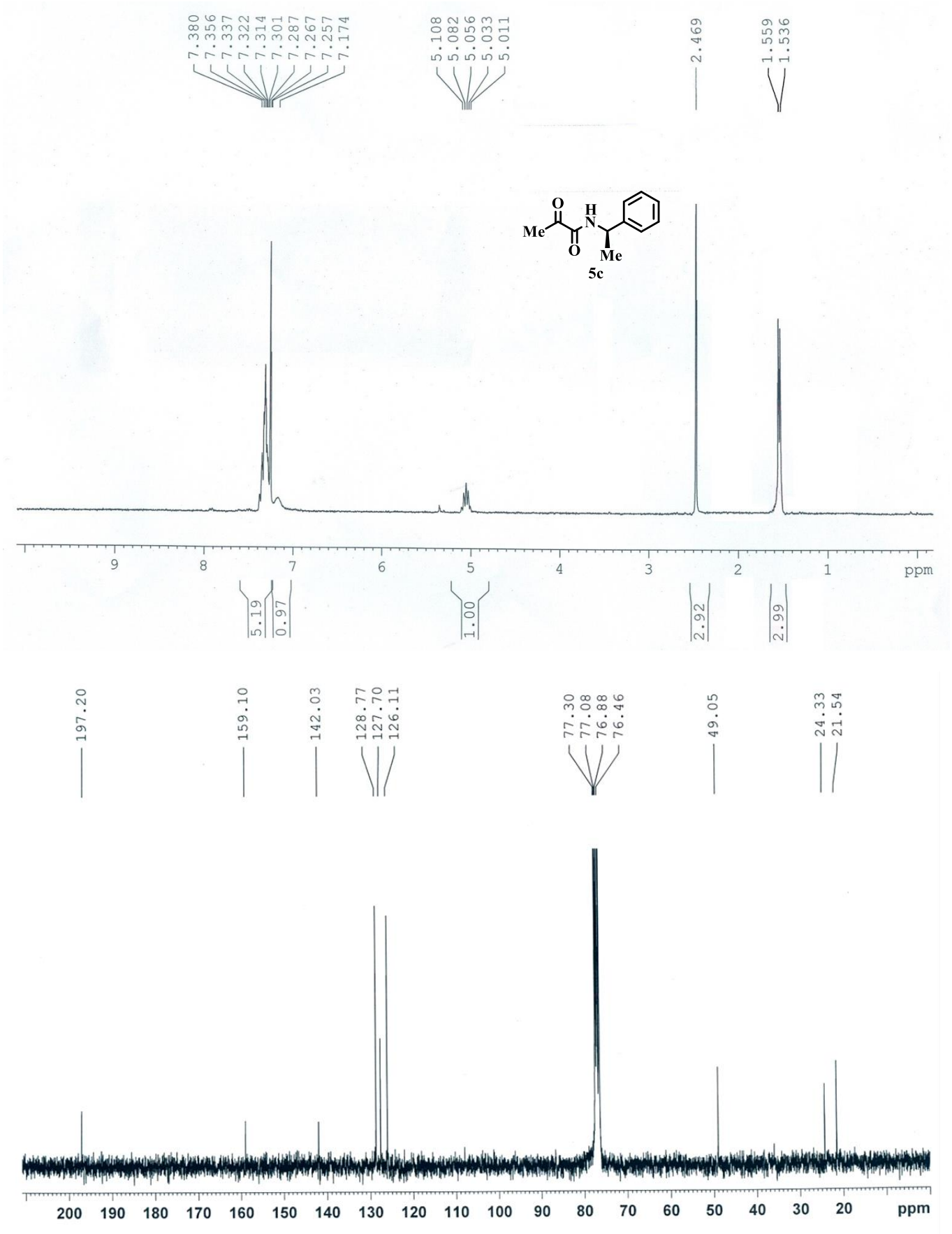
SI Figure 15: ^{1}H and ^{13}C-NMR spectra of compound **5a**



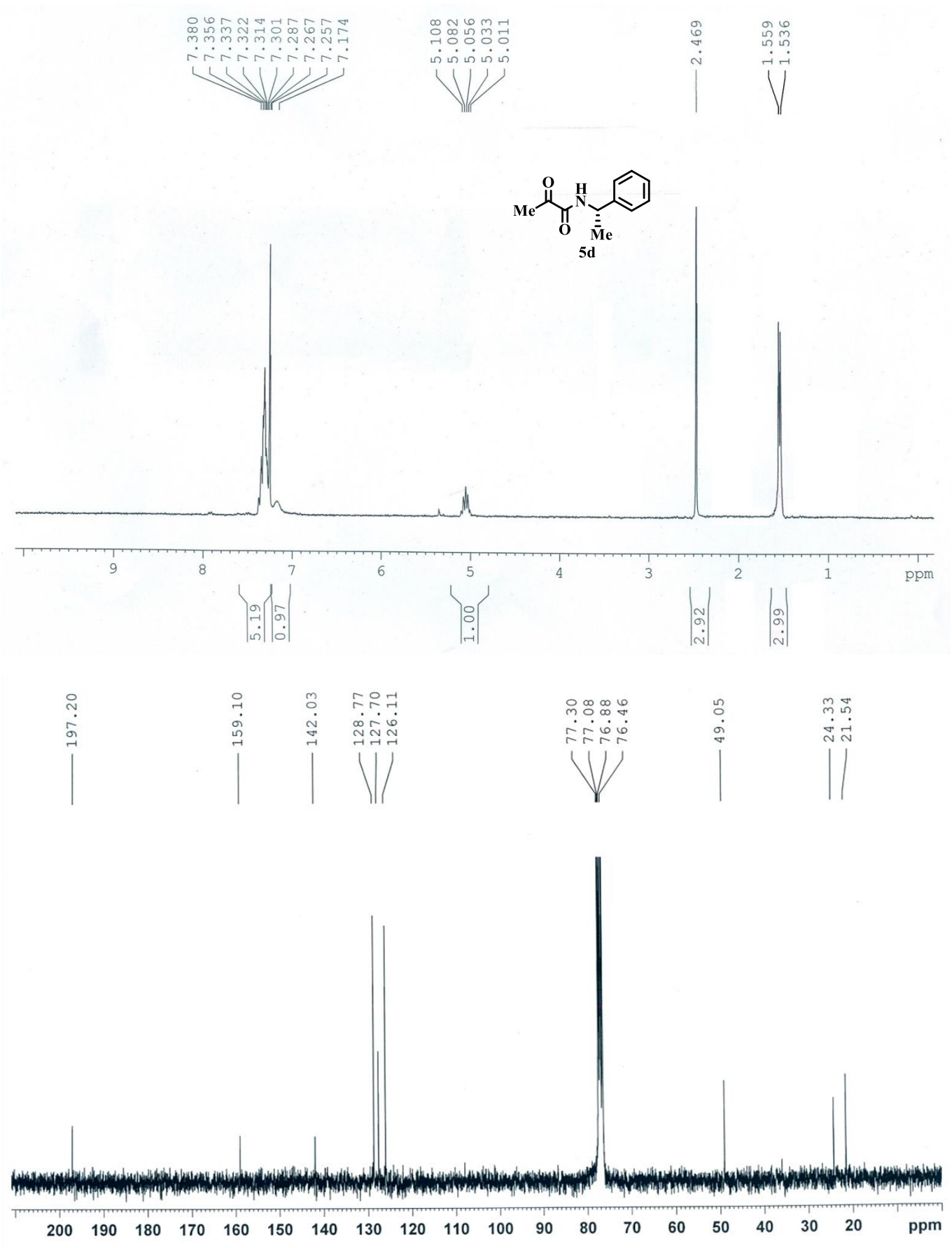
SI Figure 16: ^{1}H and ^{13}C-NMR spectra of compound **5b**



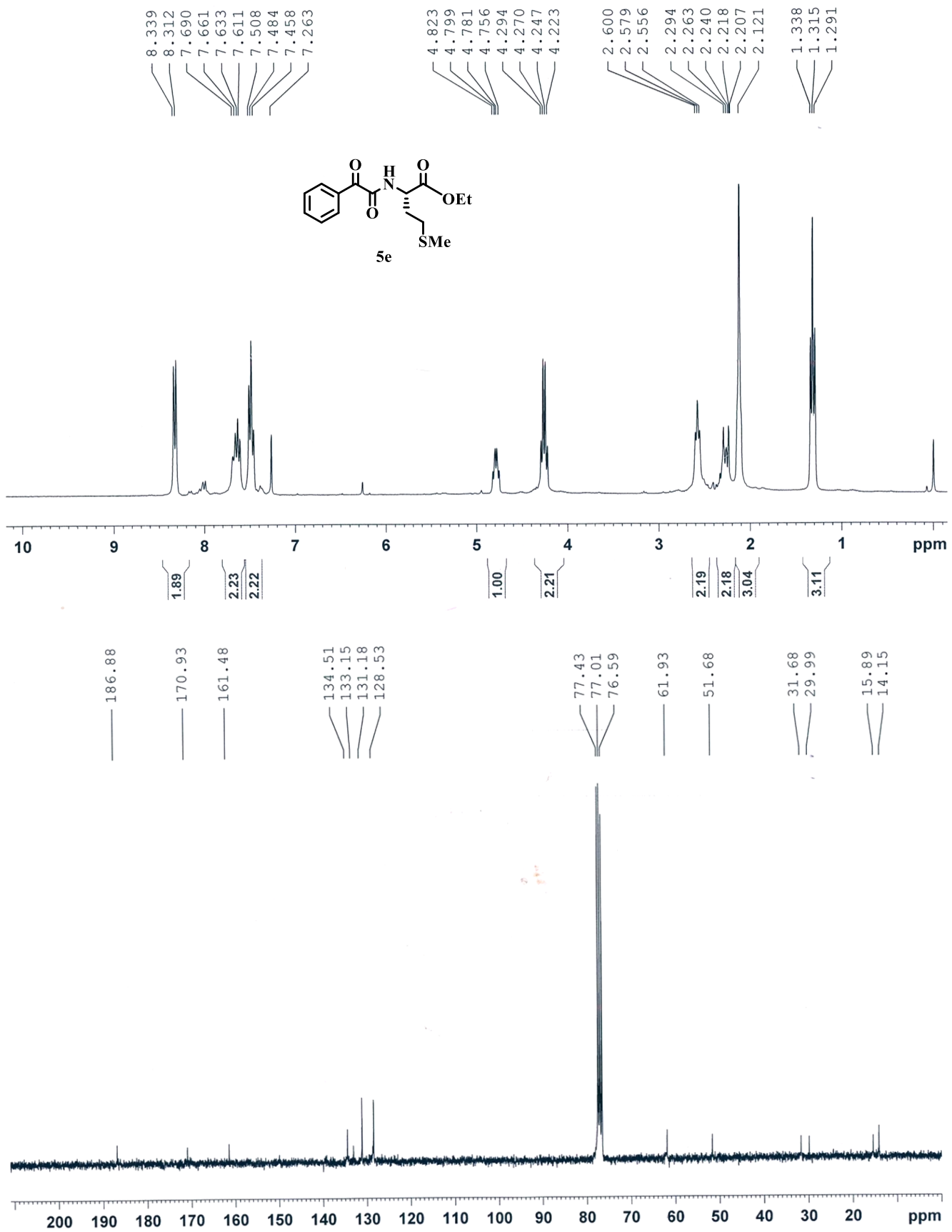
SI Figure 17: ^{1}H and ^{13}C-NMR spectra of compound **5c**



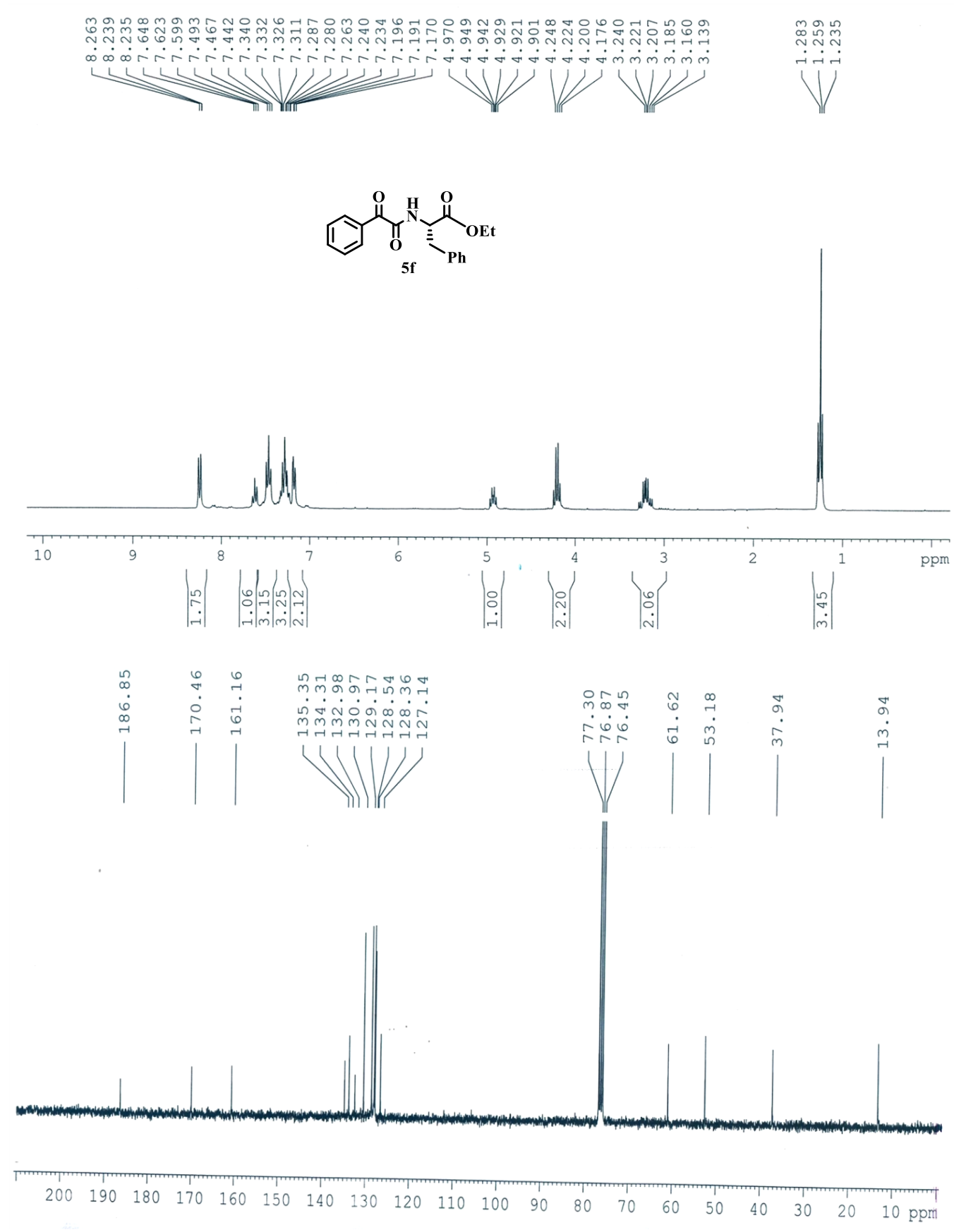
SI Figure 18: ^{1}H and ^{13}C-NMR spectra of compound **5d**



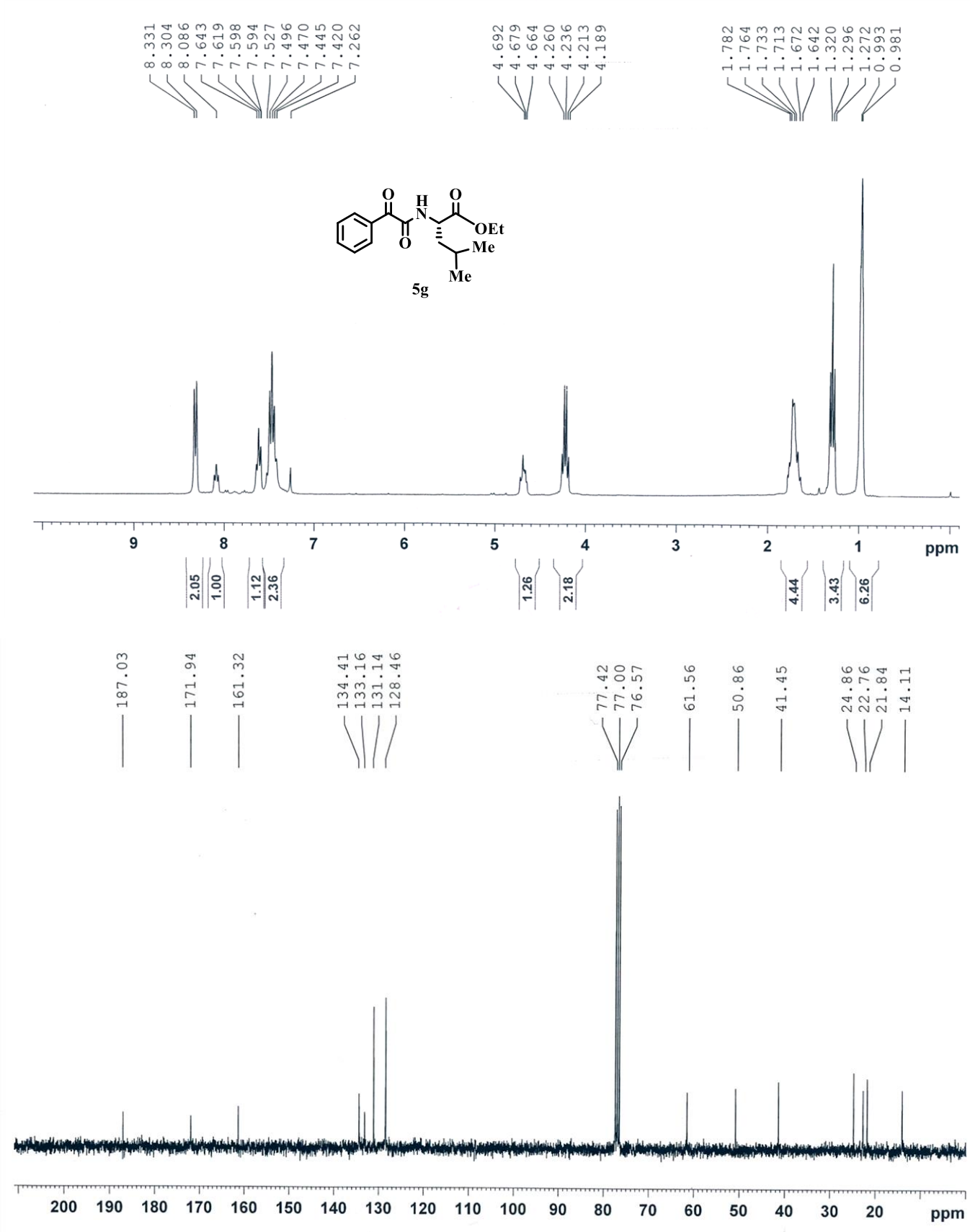
SI Figure 19: ^{1}H and ^{13}C-NMR spectra of compound **5e**



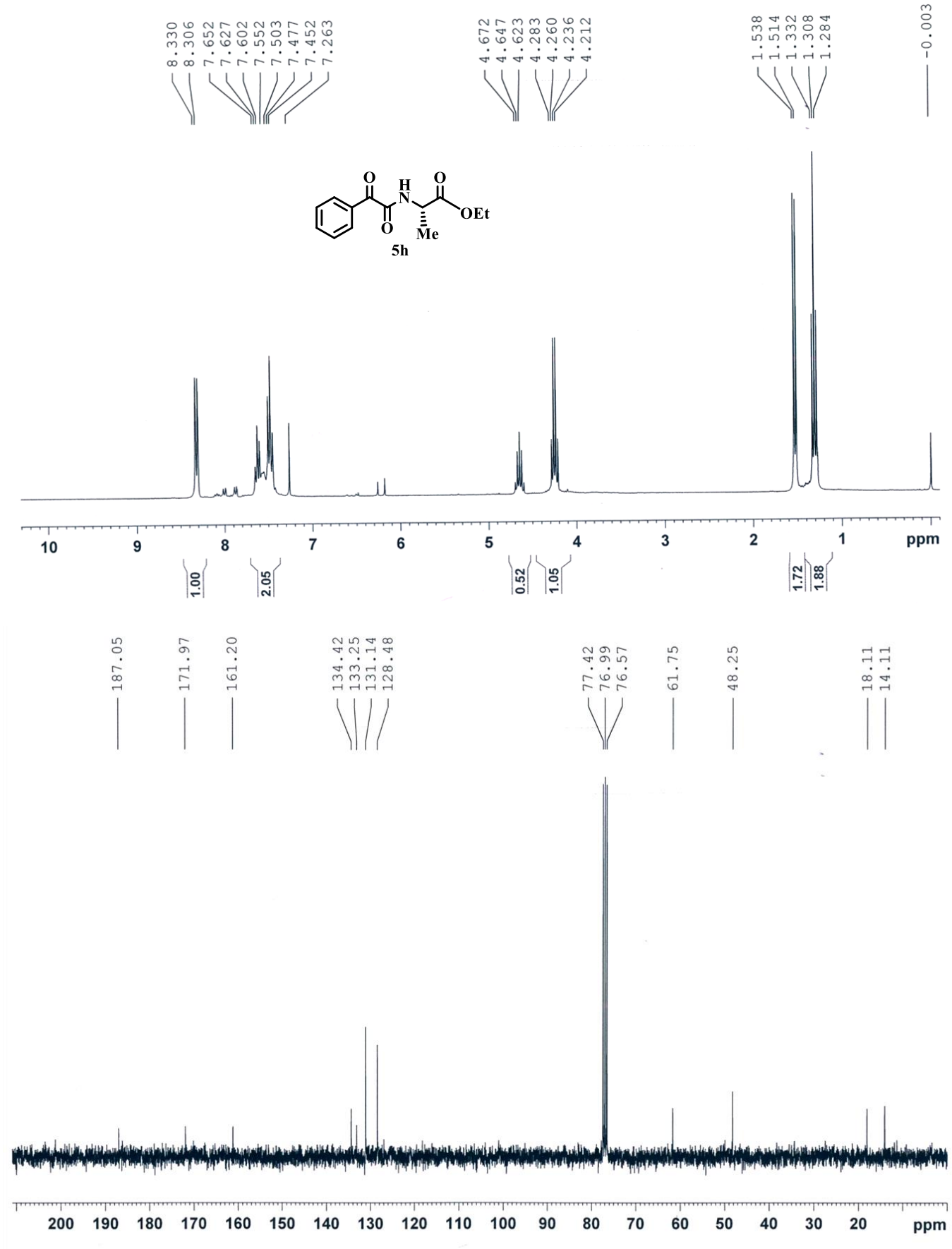
SI Figure 20: ^{1}H and ^{13}C-NMR spectra of compound **5f**



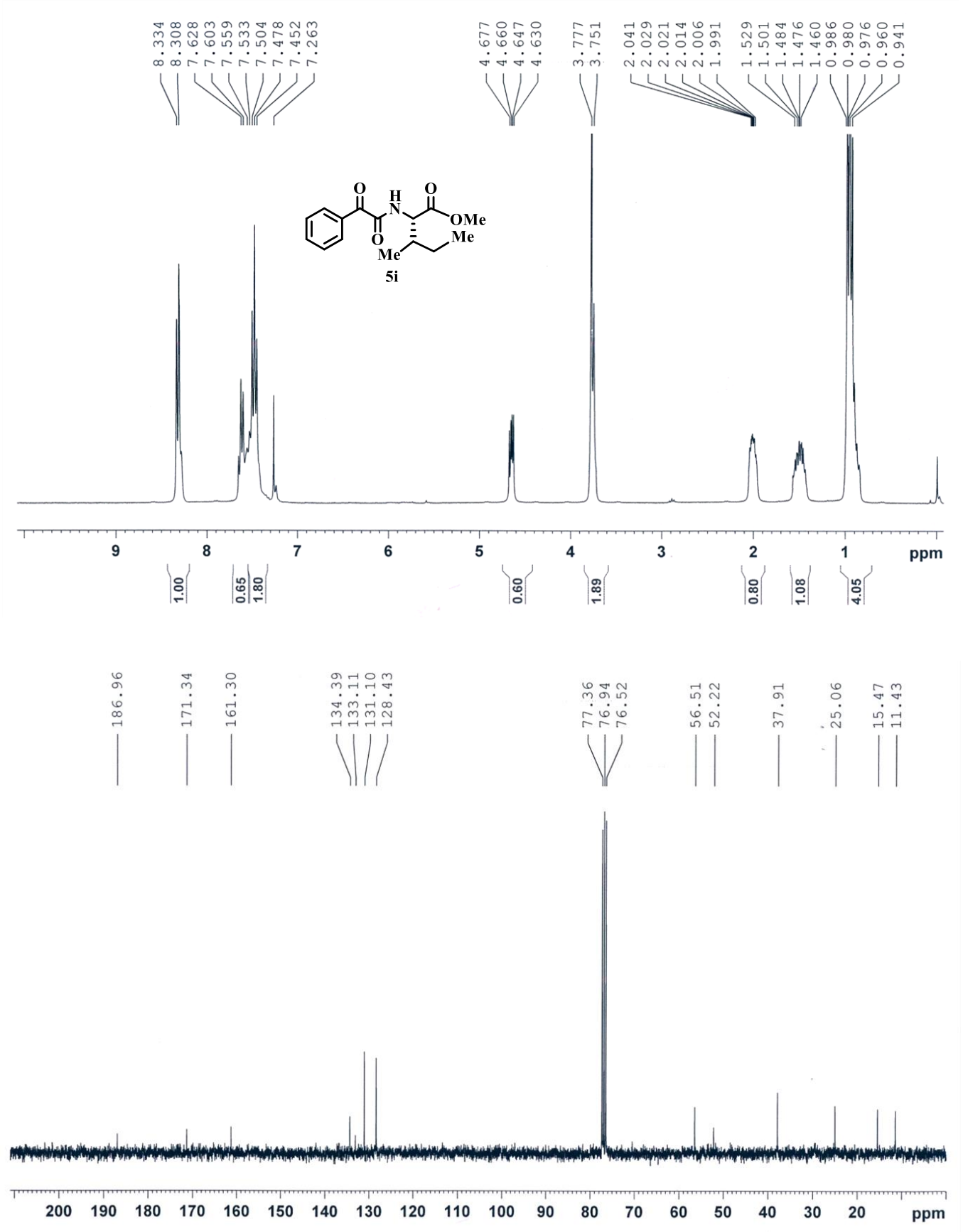
SI Figure 21: ^{1}H and ^{13}C-NMR spectra of compound **5g**



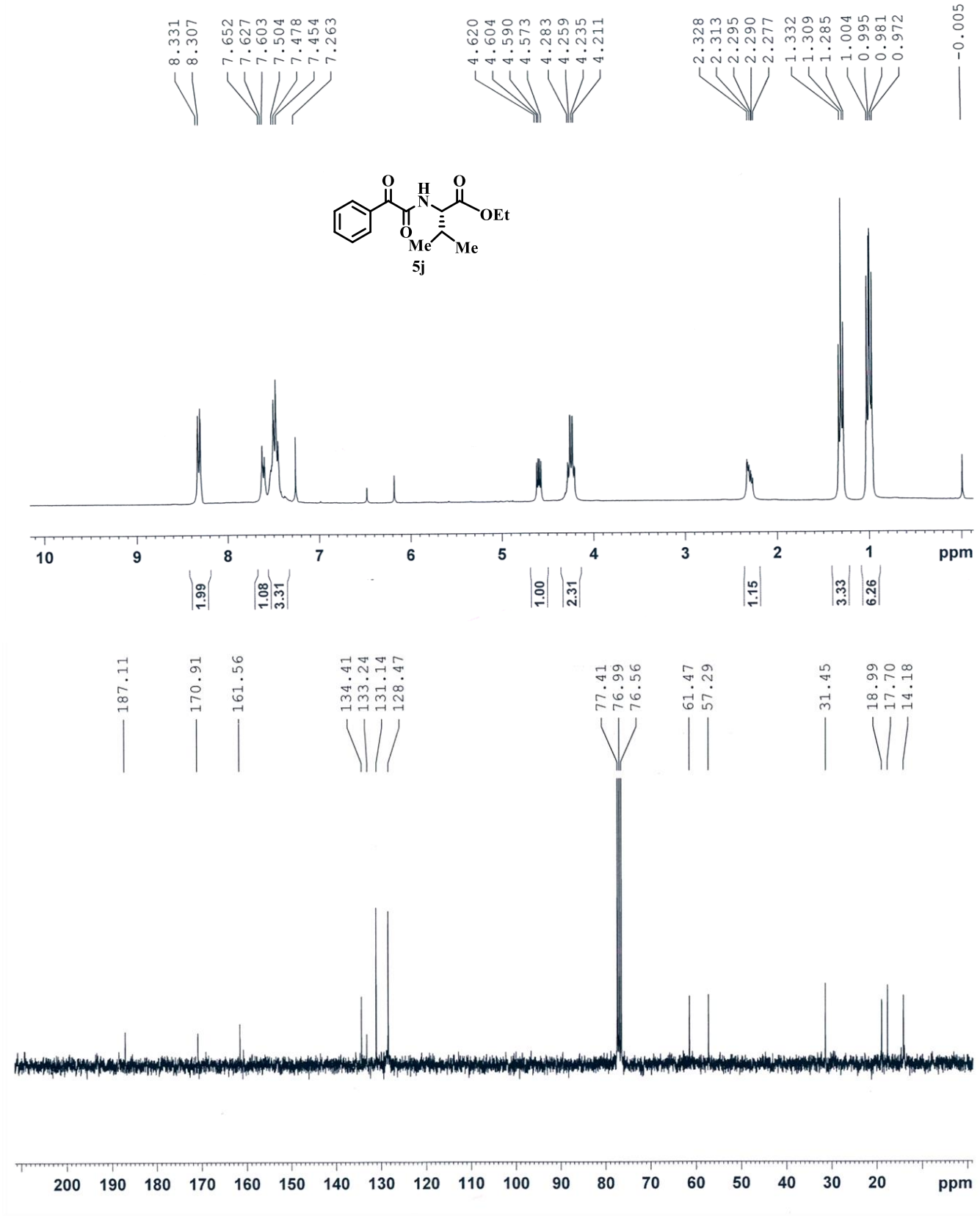
SI Figure 22: ^{1}H and ^{13}C-NMR spectra of compound **5h**



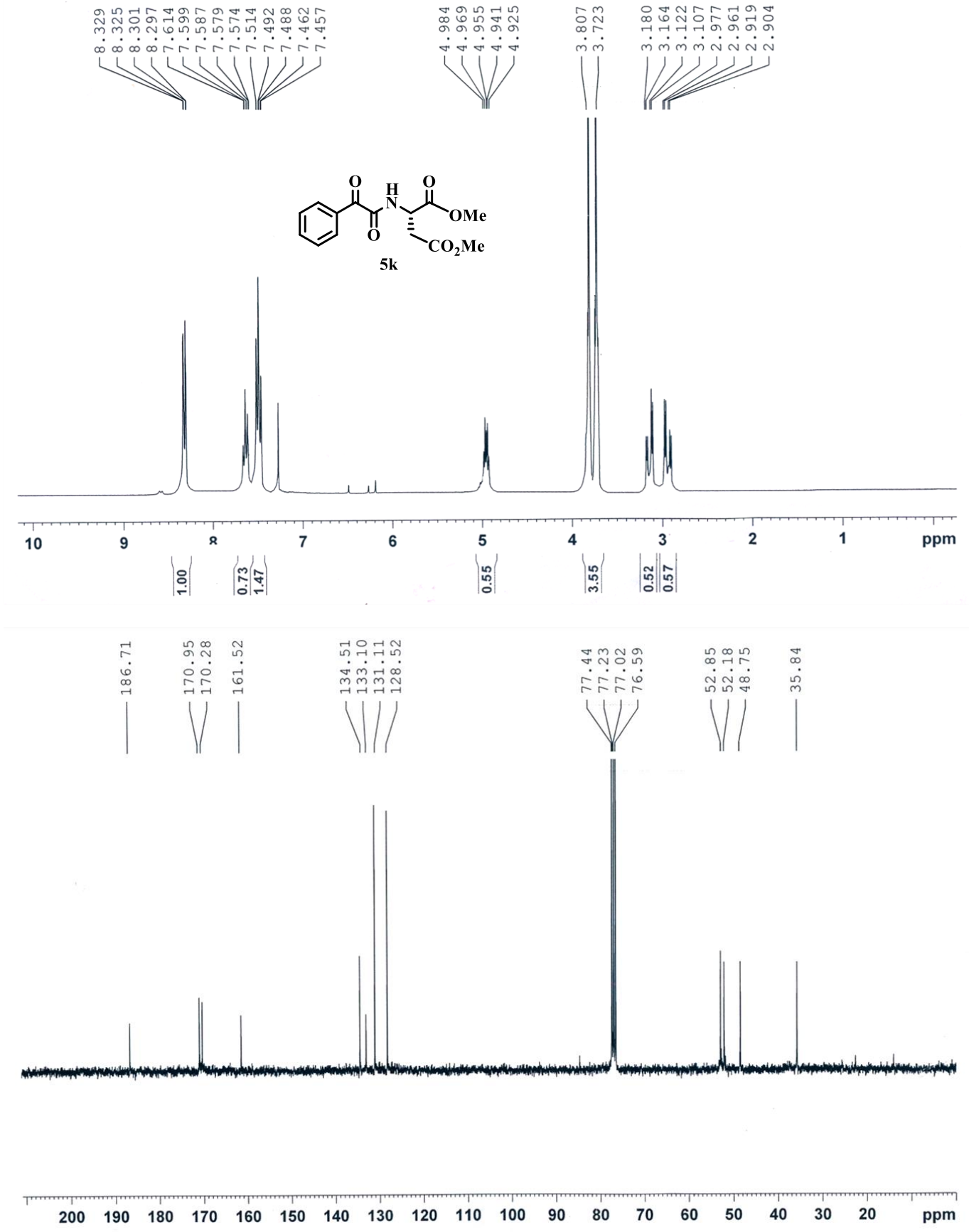
SI Figure 23: ^{1}H and ^{13}C-NMR spectra of compound **5i**



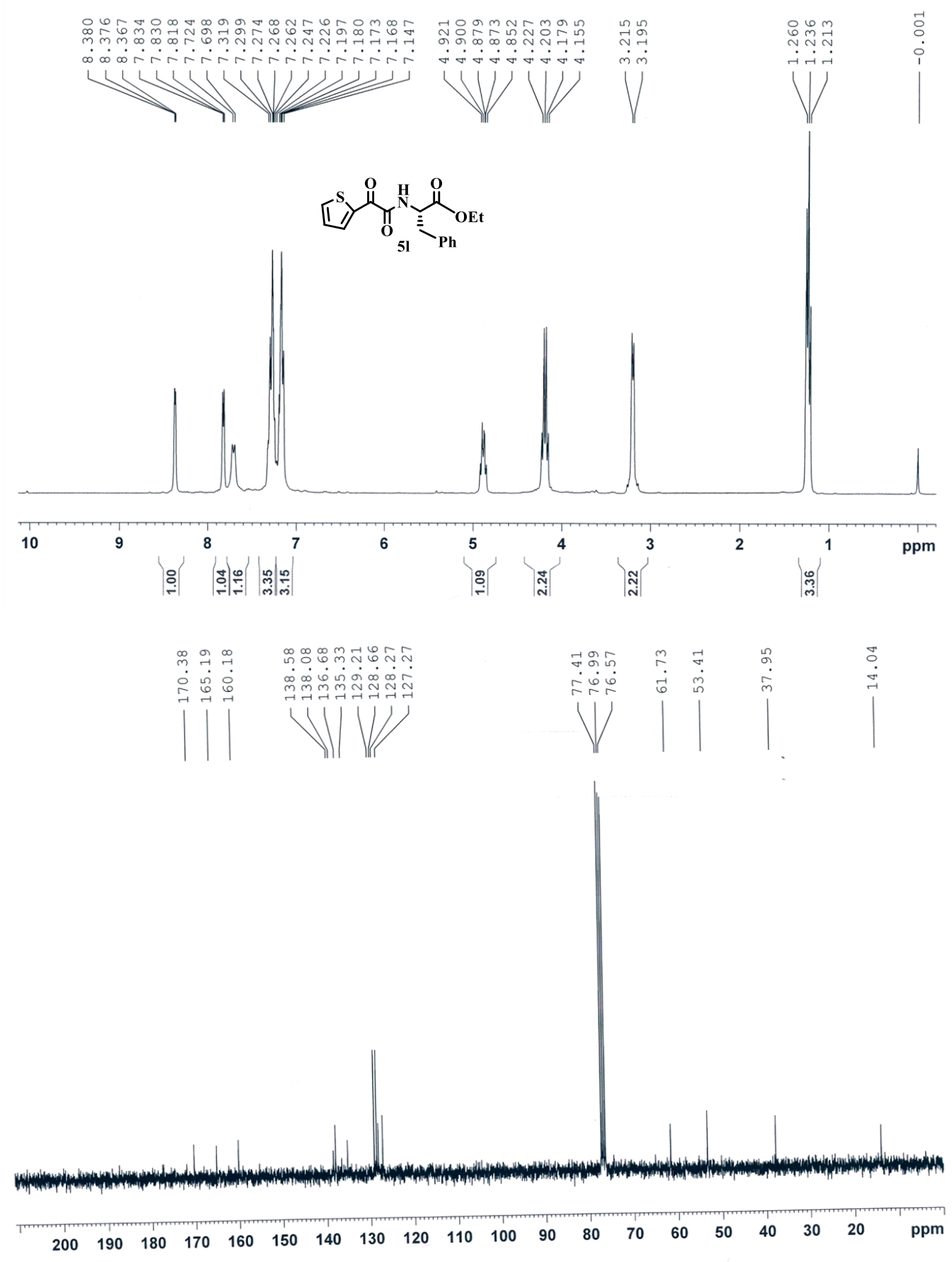
SI Figure 24: ^{1}H and ^{13}C-NMR spectra of compound **5j**



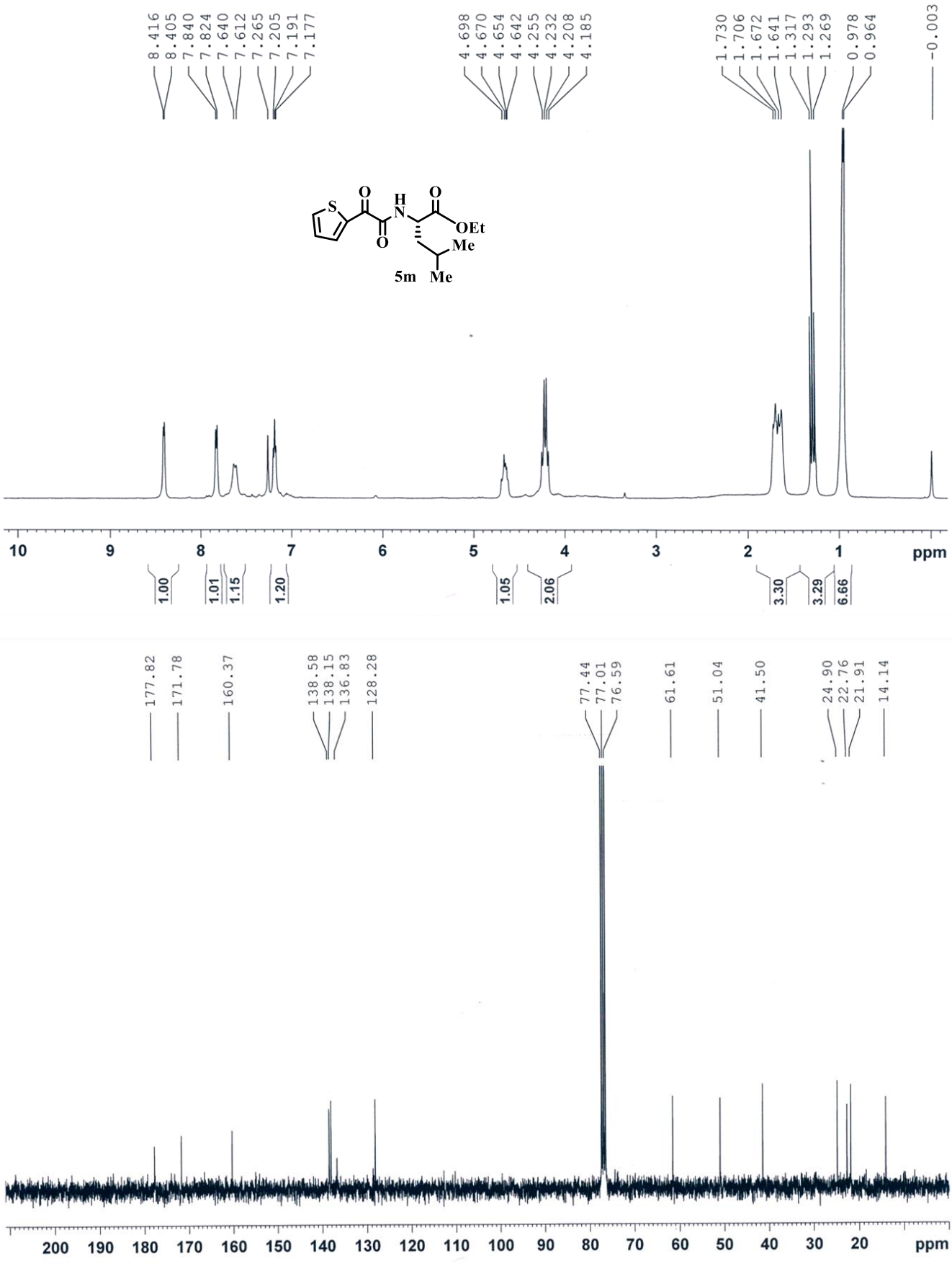
SI Figure 25: ^{1}H and ^{13}C-NMR spectra of compound **5k**



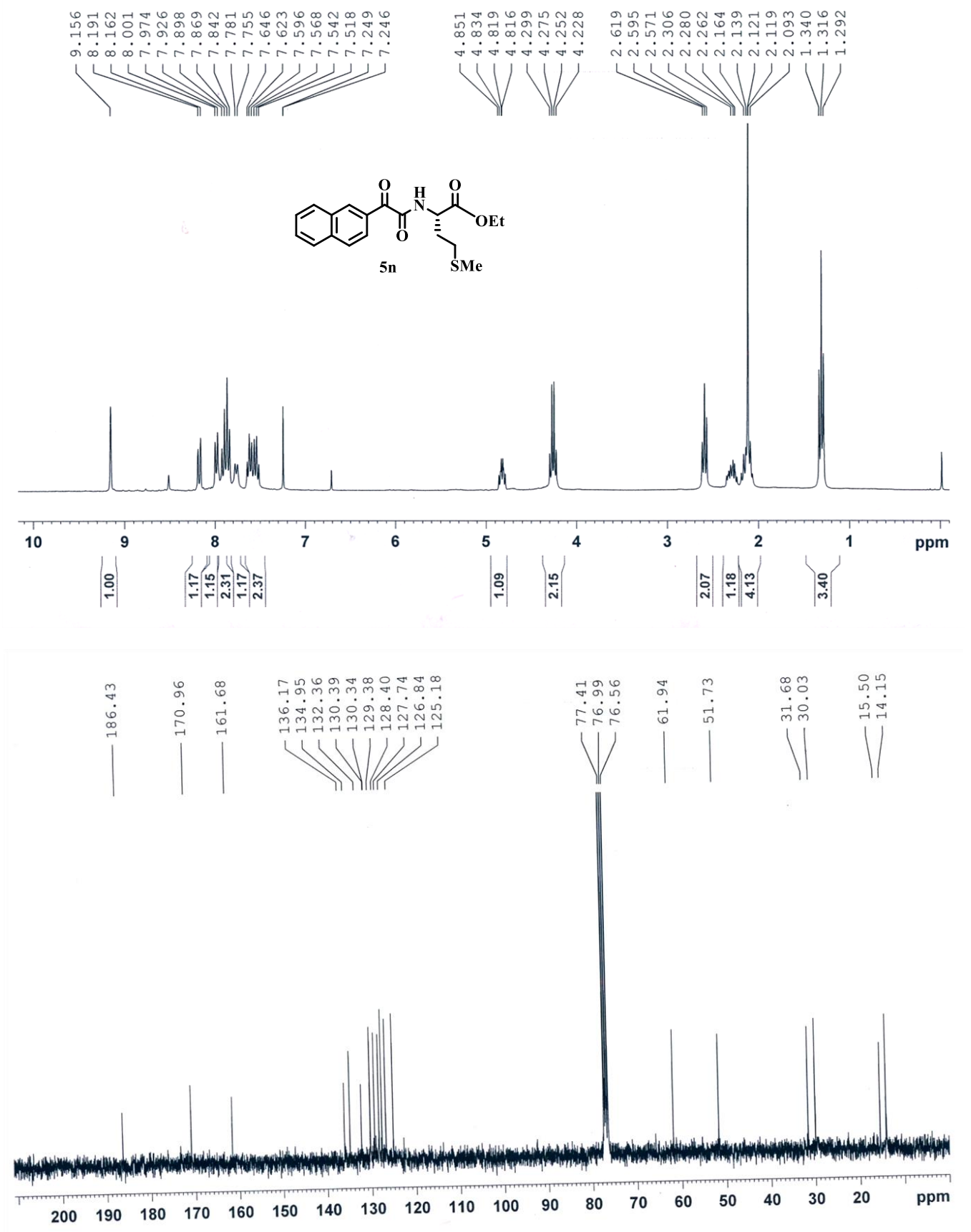
SI Figure 26: ^{1}H and ^{13}C-NMR spectra of compound **5l**



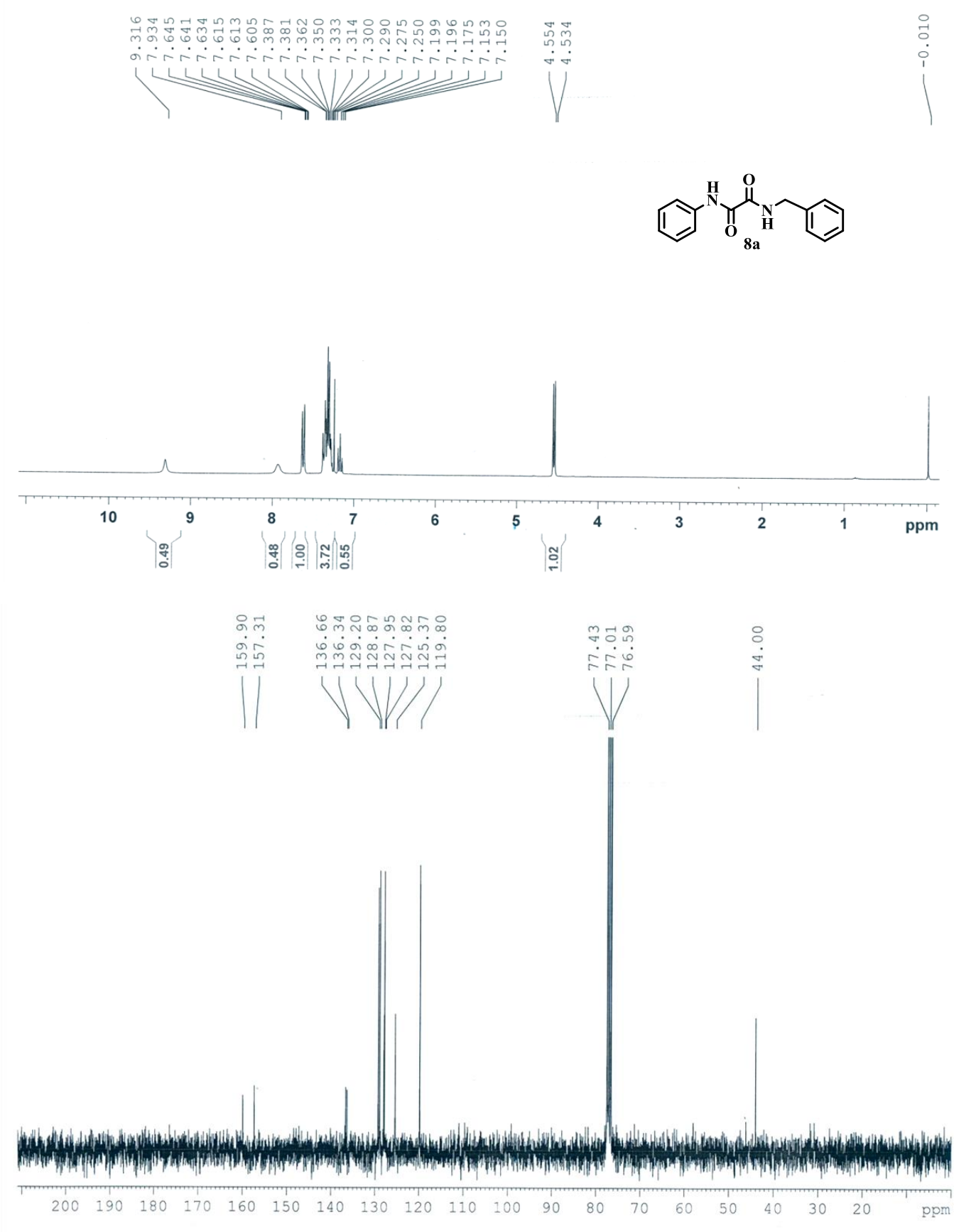
SI Figure 27: ^{1}H and ^{13}C-NMR spectra of compound **5m**



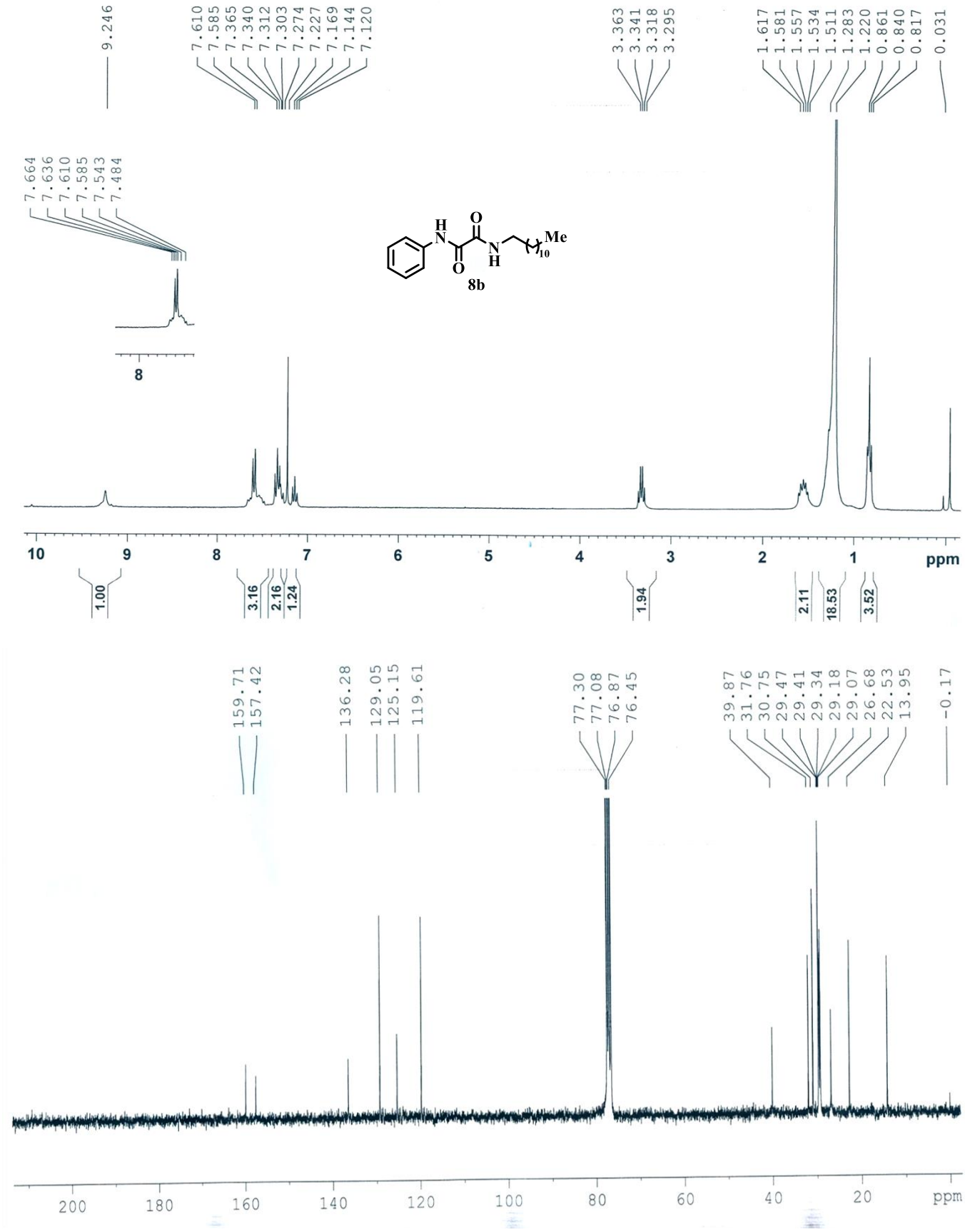
SI Figure 28: ^{1}H and ^{13}C-NMR spectra of compound **5n**



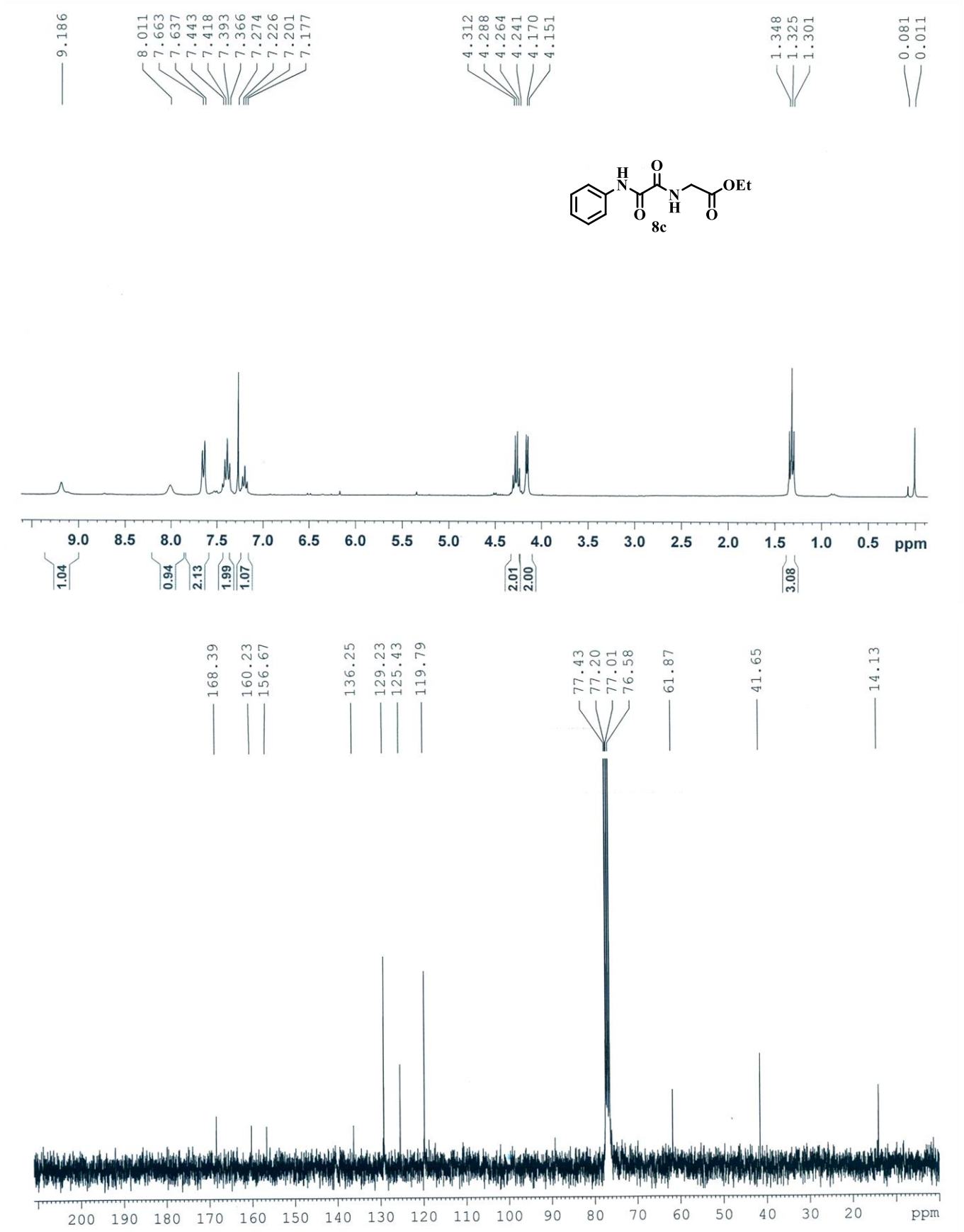
SI Figure 29: ^{1}H and ^{13}C-NMR spectra of compound **8a**



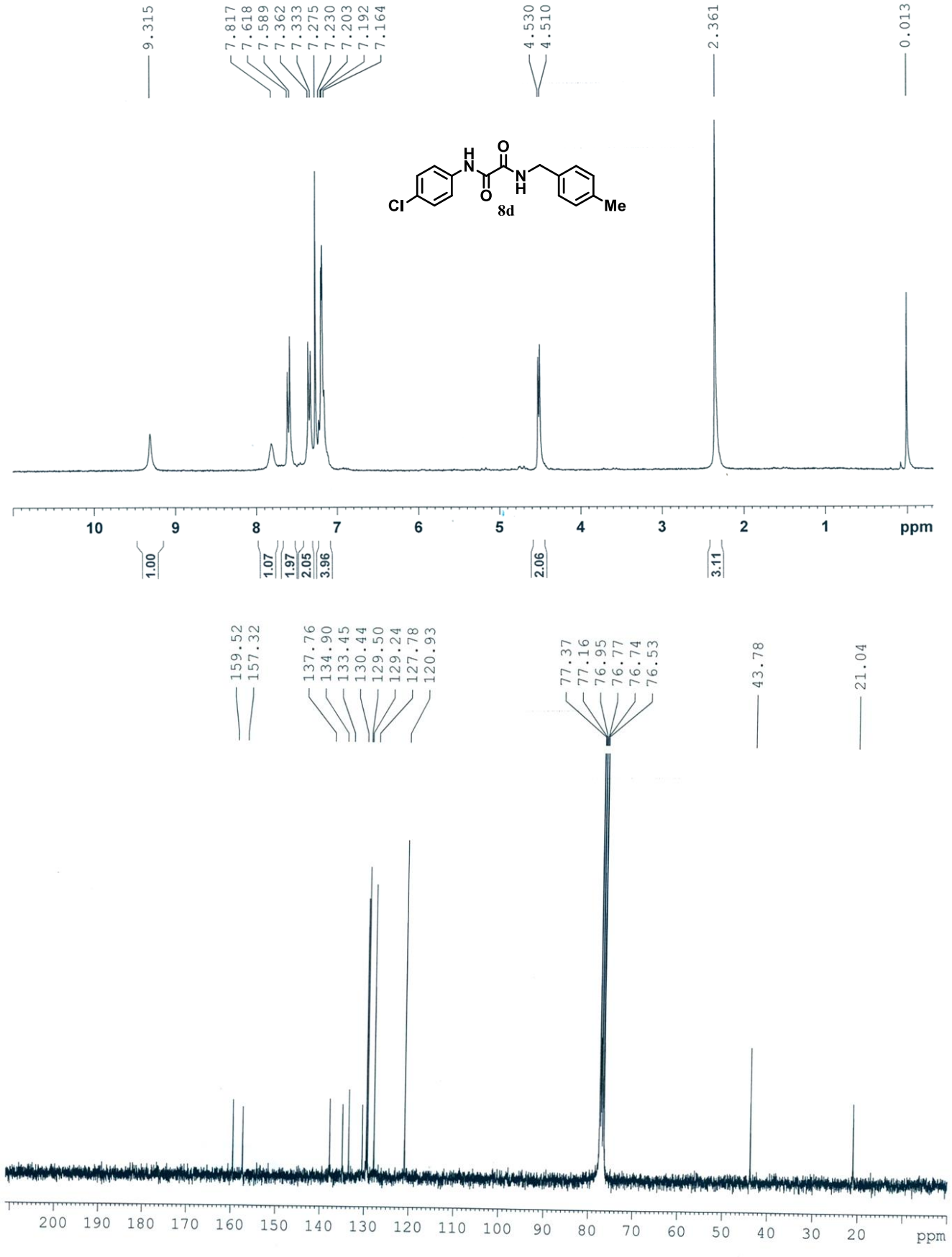
SI Figure 30: ^{1}H and ^{13}C-NMR spectra of compound **8b**



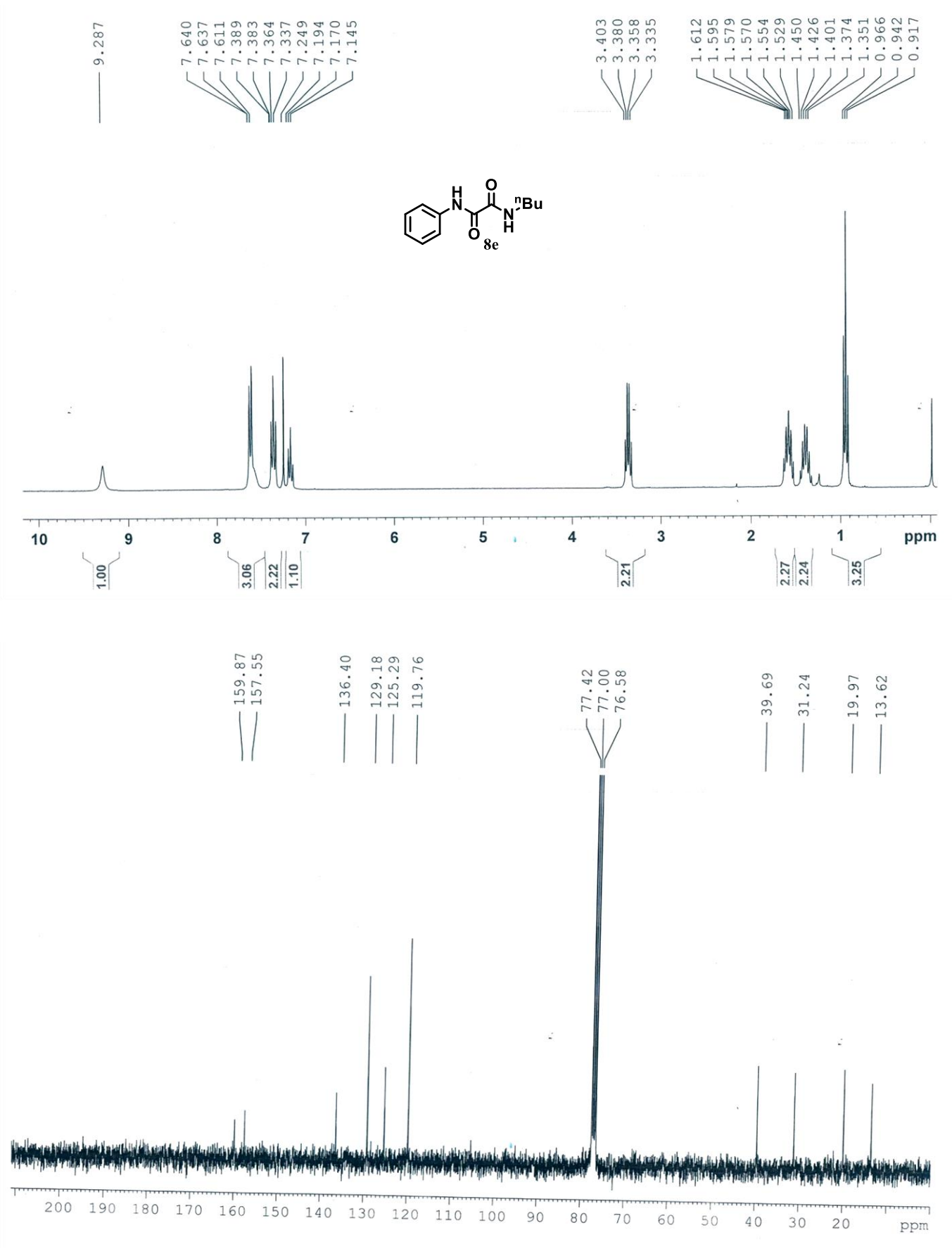
SI Figure 31: ^{1}H and ^{13}C-NMR spectra of compound **8c**



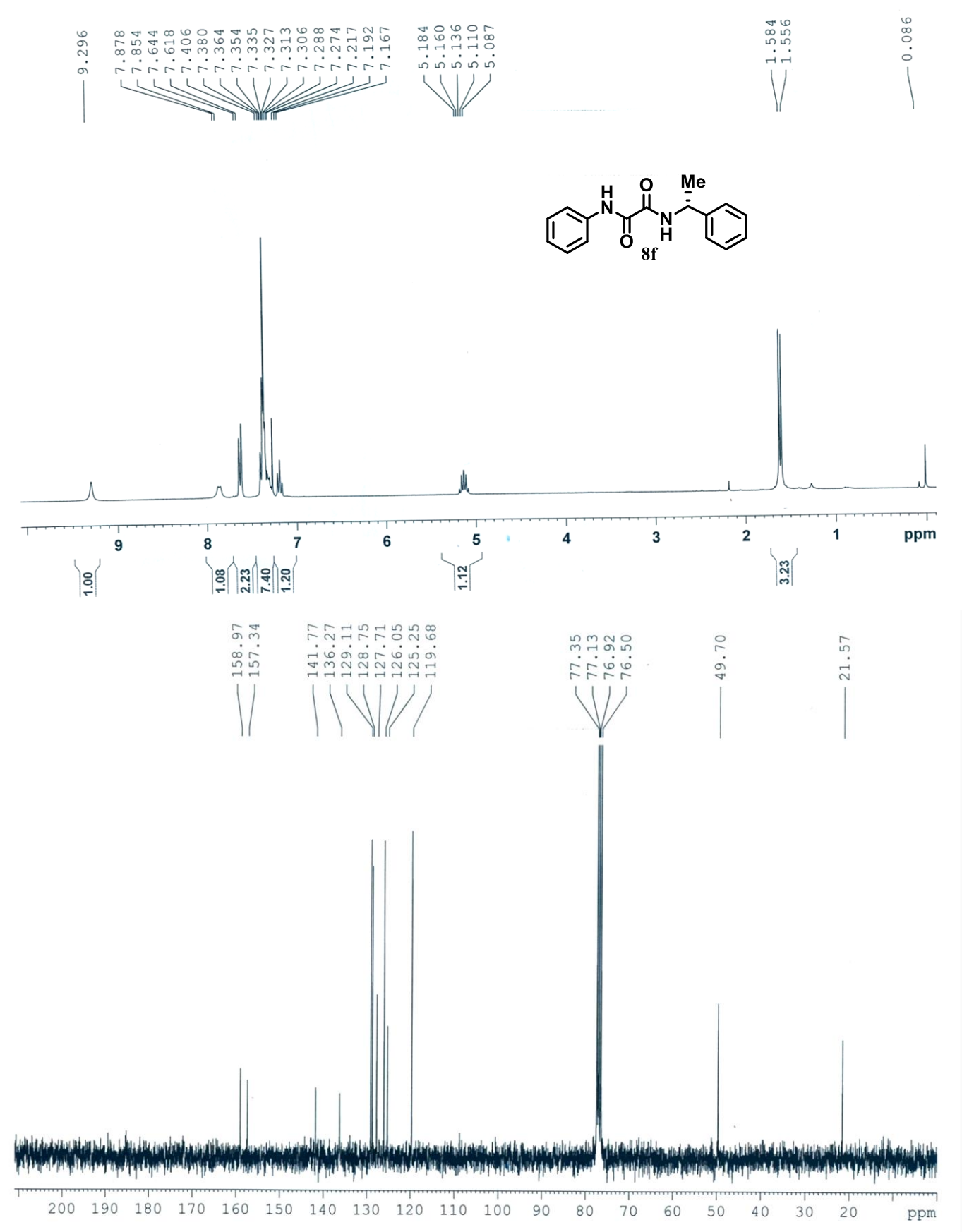
SI Figure 32: ^{1}H and ^{13}C-NMR spectra of compound **8d**



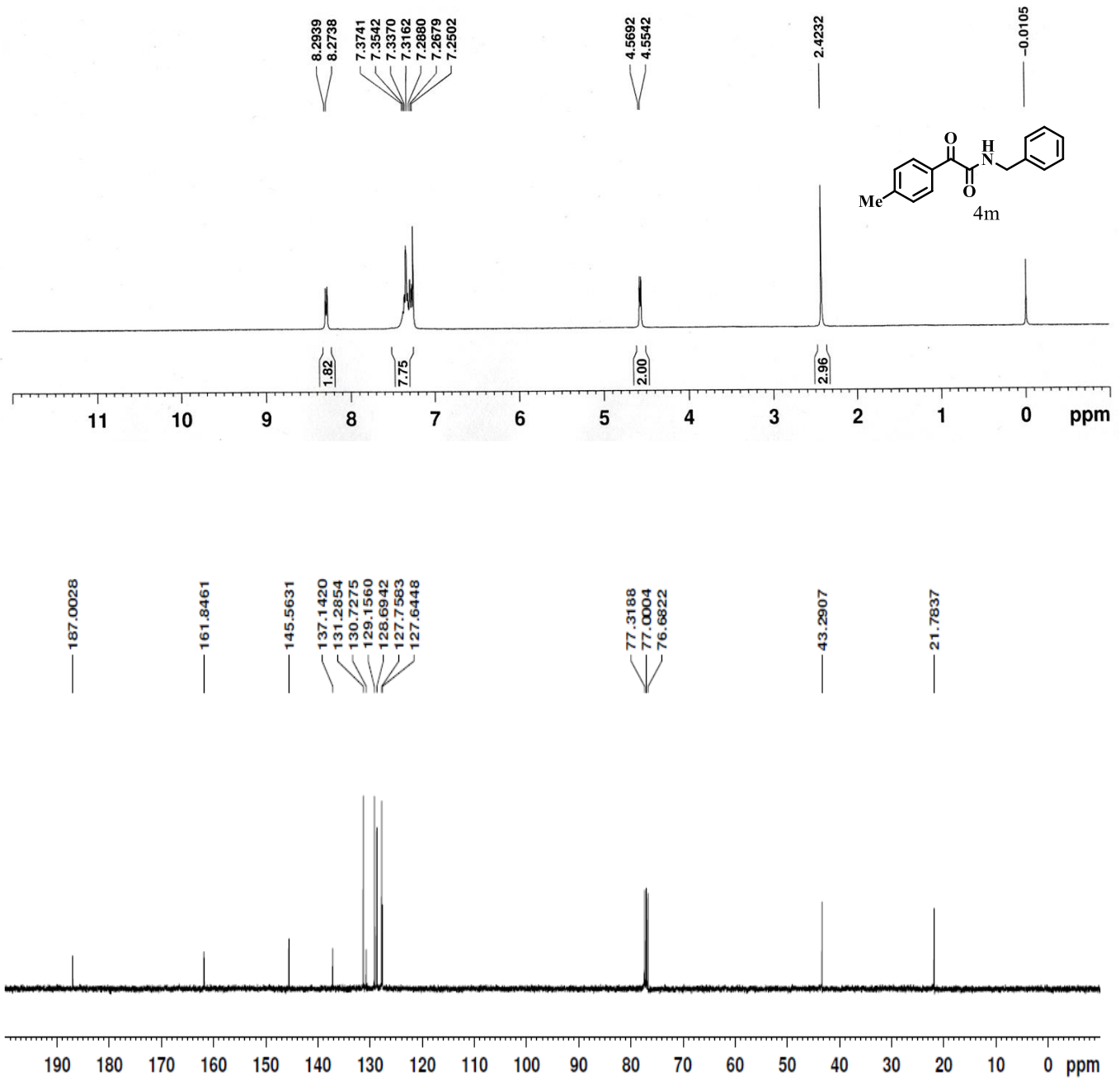
SI Figure 33: ^{1}H and ^{13}C-NMR spectra of compound **8e**



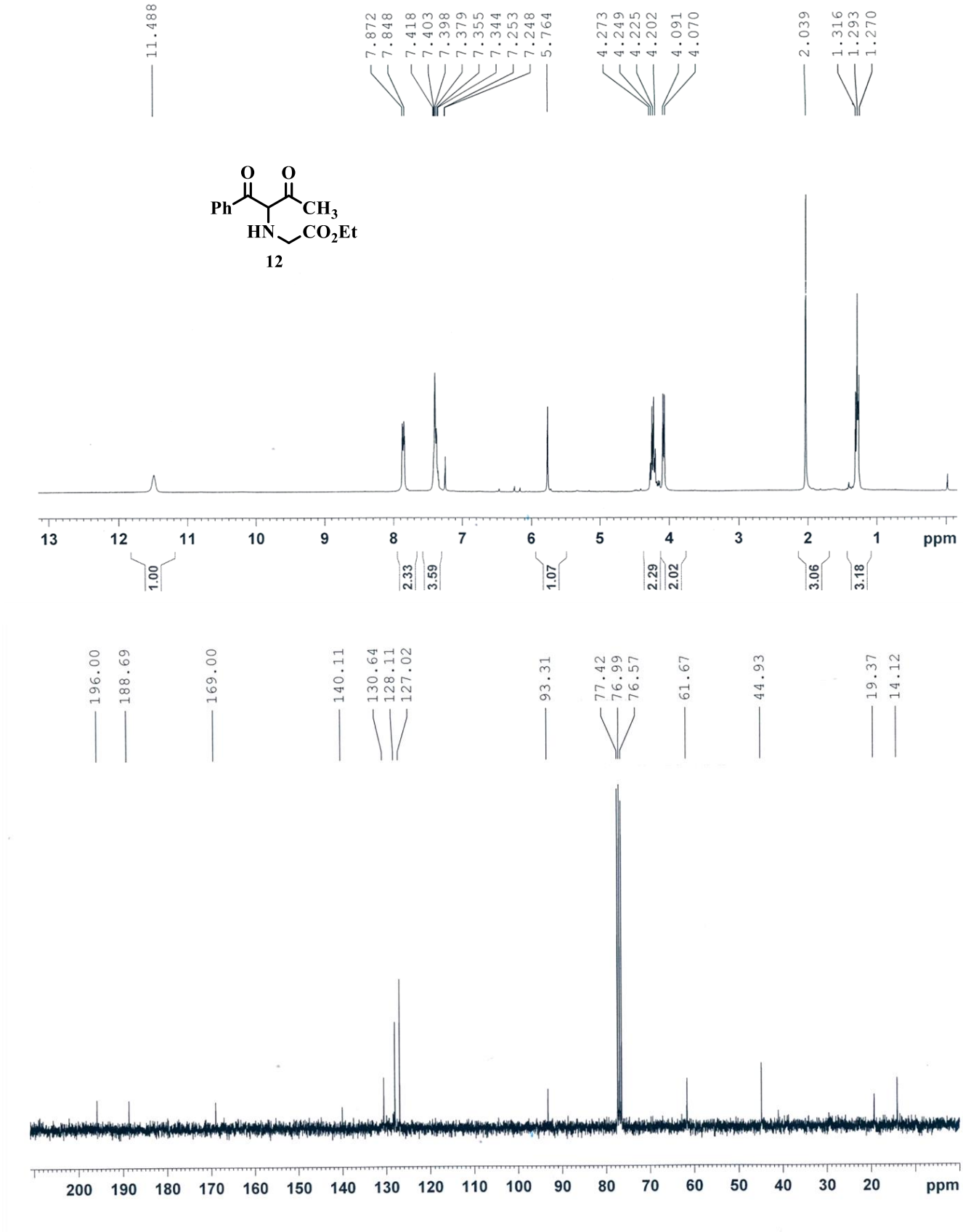
SI Figure 34: ^{1}H and ^{13}C-NMR spectra of compound **8f**



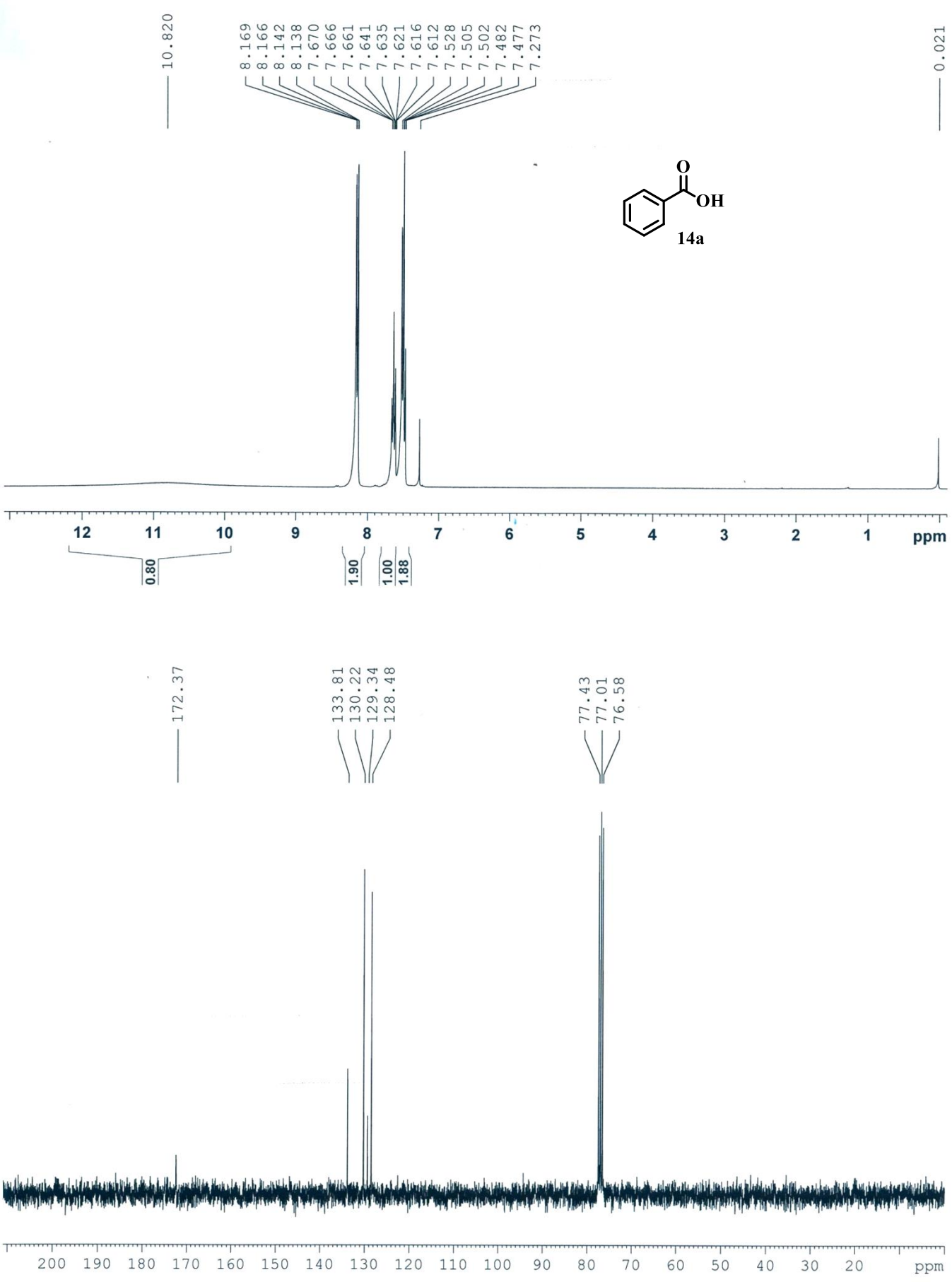
SI Figure 35: ^{1}H and ^{13}C-NMR spectra of compound **4m**



SI Figure 36: ^{1}H and ^{13}C-NMR spectra of compound **12**



SI Figure 37: ^{1}H and ^{13}C-NMR spectra of compound **14a**



11. Screening of visible light wave lengths towards α-ketoamides

In a 15 mL dry vial, 1 mmol 1-phenyl-butane-1,3-dione (**1a**) and 3.5 mmol of iodosobenzene were dissolved in 5 mL DCM, then the reaction mixture was stirred under cold condition for about 15 minutes. After while 1.2 mmol of benzyl amine (**2a**), 5 mol% of CuBr and 0.1 mol% of eosin Y were added to it.. Then the vial was immediately sealed with parafilm and placed under the irradiation of 30W LED (Glitz IP 66). Similar experiment was repeated five times under the irrdiation of differnt visible light wavelengths. Purification of *N*-benzyl-2-oxo-2-phenyl-acetamide (**4a**) made by column chromatography on silica gel (100-200 mesh). The results are summerised below.

LED colour	Wave length (nm)	Yield of 4a (%)
Blue	475	80
Green	535	60
Yellow	580	44
Orange	605	30
Red	685	26

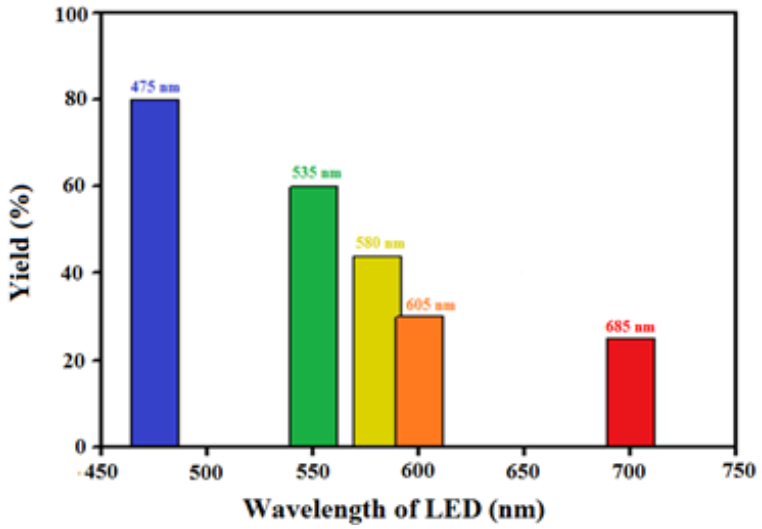
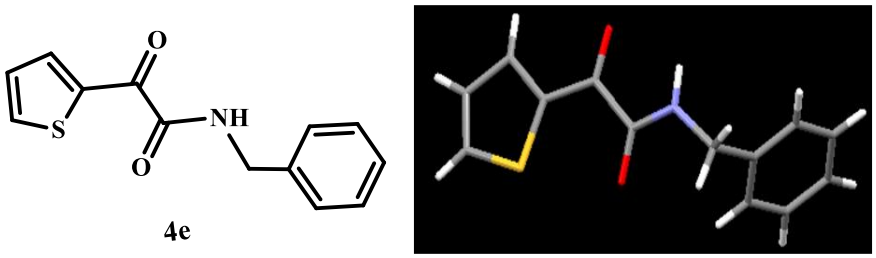


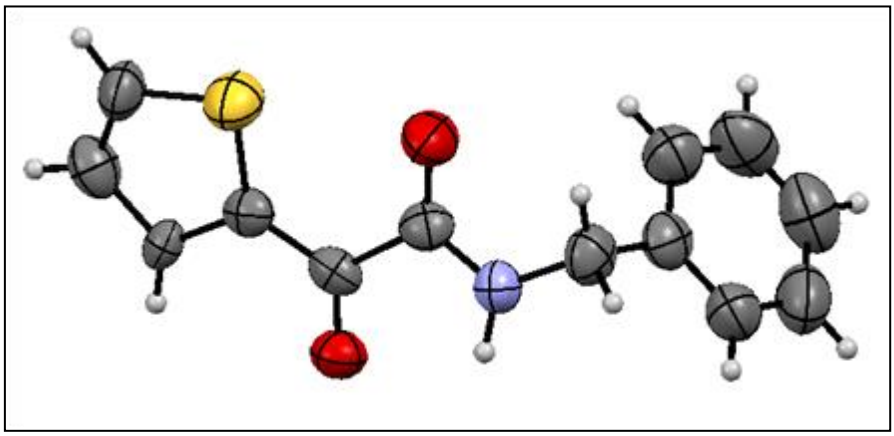
Figure S38. Plot of **4a**-yield(%) vs wavelength of visible light(LED)

12. Crystal structure of compound 4e (CCDC1862562)



SI Figure 39. Single crystal XRD structure of **4e**

13. Crystal summary data of compound 4e (CCDC1862562)



- Chemical formula and formula weight (M): C_{13} H_{11} N O_2 S and 245.29
- Crystal system: Monoclinic Unit-cell dimensions (angstrom, degrees) and volume, with edges: a 12.091(8) b 5.651(4) c 17.732(12), 90.00, 99.197(15), 90.00, 1196.1(14)
- Temperature: 296 K
- Space group symbol: P21/n
- No. of formula units in unit cell (Z): 4
- Number of reflections measured and/or number of independent reflections, Rint: 1942
- Final R values (and whether quoted for all or obrserved data): 0.0772

14. Mass spectra data

Mass spectra were taken in infusion method.

Parameters

Source **-** capillary (kv): 3.06, Sampling cone: 85, source offset: 80

Temp (°C) **-** Source: 120, Desolvation: 300

Gas flows – Cone gas (L/h) 50, Desolvation gas (L/h) 600, Lock spray capillary (kv) 2.50

ESI-MS spectra of 13