

Electronic Supplementary Information

General base-tuned unorthodox synthesis of amides and ketoesters with water

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<u>Serial No.</u>	<u>Content</u>	<u>Page Numbers</u>
1.	Materials and methods	S-2
2.	General procedure for amidation through cleavage of terminal alkyne	S-2
3.	Characterization data of amides (6a-m)	S-2
4.	General procedure for the synthesis of amides (8) from benzylamines	S-7
5.	Characterization data of amides (8a-g)	S-7
6.	General procedure for the synthesis of ketoesters (9)	S-10
7.	Characterization data of ketoesters (9a-e, D₂-9a)	S-10
8.	General procedure for the synthesis of ketoesters (11) using potassiumcarboxylates	S-12
9.	Characterization data of ketoesters (11a-c)	S-12
10.	References	S-13
11.	¹ H and ¹³ C-NMR spectra of the compounds (6a-m, 8a-g, 9a-e, D₂-9a and 11a-c)	S-14
12.	Crystal summary data of compound 9a (CCDC 973403)	S-44
13.	CIF data of compound 9a (CCDC 973403)	S-44

1. Materials and methods

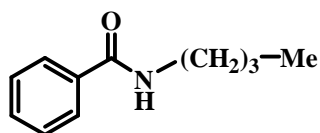
All reagents were purchased from commercial suppliers and used without further purification, unless otherwise specified. Commercially supplied ethyl acetate and petroleum ether were distilled before use. CH_2Cl_2 was dried by distillation over P_2O_5 . Petroleum ether used in our experiments was in the boiling range of $60^\circ\text{-}80^\circ\text{C}$. Column chromatography was performed on silica gel (60-120 mesh, 0.120 mm-0.250 mm). Analytical thin layer chromatography was performed on 0.25 mm extra hard silica gel plates with UV254 fluorescent indicator. Reported melting points are uncorrected. ^1H NMR and ^{13}C NMR spectra (Bruker Advance 300) were recorded at ambient temperature using 300 MHz spectrometers (300 MHz for ^1H and 75 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), d (doublet), dd (double doublet), t (triplet), q (quartet), and m (multiplet). Infrared spectra were recorded on FT-IR spectrometer (Perkin Elmer Spectrum 100) in thin film. HR-MS data were acquired by electron spray ionization technique on a Q-tof-micro quadrupole mass spectrophotometer (Bruker). Optical rotation of the chiral compounds was measured in a polarimeter using standard 10 cm quartz cell in sodium-D lamp at ambient temperature. MIR-ATR spectroscopy of the inline reaction was executed by React IR 15 of Mettler Toledo using iC IR 4.3 software.

2. General procedure for amidation through cleavage of terminal alkyne

Terminal alkyne (**1**, 1.0 mmol, 102 mg) and iodobenzene diacetate (3.0 mmol, 966 mg) were stirred for 30 min. and allowed to react with aqueous sodium bicarbonate solution (2.1 mmol, 176 mg in 2.0 mL of water) under stirring conditions at ambient temperature. After one hour amine (**2**, 1.5 mmol) was added in a drop-wise manner. The reaction was monitored by thin layer chromatography (TLC). The post-reaction mixture was extracted with EtOAc (2x15 mL), and the combined organic layer was washed successively with saturated sodium bicarbonate solution (1x10 mL) and brine (1x10 mL). It was then dried over anhydrous Na_2SO_4 , filtered and evaporated in a rotary evaporator under reduced pressure at room temperature. Thus, the reaction with phenylacetylene (**1a**, 102 mg, 1.0 mmol) and *n*-butylamine (1.5 mmol, 148 mg) afforded *N*-butylbenzamide (**6a**) after purification by column chromatography on silica gel (60-120 mesh) with ethyl acetate-petroleum ether (1:24, v/v) as an eluent in a yield of 85% (150 mg, 0.85 mmol). The structure of the product (**6a**) was confirmed with the help of the literature.¹ The synthesized amides (**6a-l**) were characterized by means of NMR (^1H and ^{13}C), FT-IR, melting point (solid compounds), and mass (HR-MS) spectral analyses.

3. Characterization data of amides (6a-m)

3.1. *n*-Butylbenzamide (**6a**)



Yield: 85% (150 mg, 0.85 mmol).

Characteristic: Yellow oil.

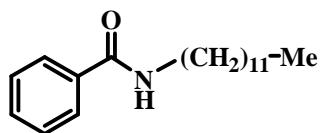
^1H NMR (300 MHz, CDCl_3): δ 0.97 (3H, t, $J = 6.0$ Hz), 1.36-1.48 (2H, m), 1.56-1.66 (2H, m), 3.43-3.50 (2H, m), 6.15 (1H, brs), 7.40-7.52 (3H, m), 7.75-7.78 (2H, m).

^{13}C NMR (75 MHz, CDCl_3): δ 13.7, 20.1, 31.7, 39.8, 126.8, 128.5, 131.3, 134.8, 167.5.

FT-IR (neat, cm^{-1}): 1308, 1490, 1542, 1578, 1603, 1640, 2872, 2931, 2959.

HR-MS (m/z) for $\text{C}_{11}\text{H}_{15}\text{NO}$ (M^+): Calculated 177.1154, found 177.1156.

3.2. n-Dodecylbenzamide (6b)



Yield: 83% (240 mg, 0.83 mmol).

Characteristic: Colourless solid.

Melting range: 66-69 °C

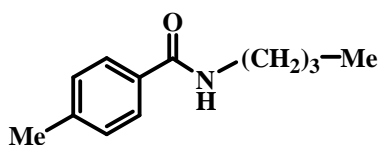
¹H NMR (300 MHz, CDCl₃): δ 0.87 (3H, t, *J* = 6.9 Hz), 1.25-1.31 (18H, m), 1.54-1.61 (2H, m), 3.38-3.44 (2H, m), 6.41 (1H, brs), 7.26-7.46 (3H, m), 7.74-7.77 (2H, m).

¹³C NMR (75 MHz, CDCl₃): δ 14.0, 22.6, 27.0, 29.3, 29.6, 31.9, 40.1, 126.8, 128.4, 131.2, 134.9, 167.5.

FT-IR (KBr, cm⁻¹): 1282, 1303, 1322, 1473, 1531, 1578, 1603, 1631, 2849, 2920, 3340.

HR-MS (*m/z*) for C₁₉H₃₁NO(M⁺): Calculated 289.2406, found 289.2407.

3.3. n-Butyl-4-methylbenzamide (6c)



Yield: 82% (156 mg, 0.82 mmol).

Characteristic: Yellow oil.

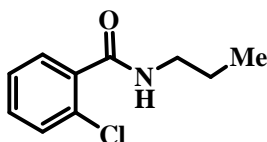
¹H NMR (300 MHz, CDCl₃): δ 0.97 (3H, t, *J* = 6.0 Hz), 1.33-1.47 (2H, m), 1.54-1.64 (2H, m), 2.38 (3H, s), 3.41-3.48 (2H, m), 6.09 (1H, brs), 7.22 (2H, d, *J* = 8.4 Hz), 7.65 (2H, d, *J* = 8.1 Hz).

¹³C NMR (75 MHz, CDCl₃): δ 13.7, 20.1, 21.3, 31.7, 39.7, 126.7, 129.1, 132.0, 141.6, 167.4.

FT-IR (neat, cm⁻¹): 1305, 1464, 1506, 1544, 1614, 1637, 2872, 2929, 2958.

HR-MS (*m/z*) for C₁₂H₁₇NO (M⁺): Calculated 191.1310, found 191.1309.

3.4. n-Propyl-2-chlorobenzamide (6d)



Yield: 62% (122 mg, 0.62 mmol).

Characteristic: Colourless solid.

Melting range: 102-103 °C

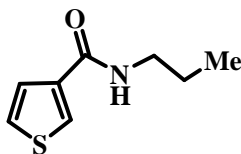
¹H NMR (300 MHz, CDCl₃): δ 0.95 (3H, t, *J* = 7.5 Hz), 1.54-1.66 (2H, m), 3.35 (2H, d, *J* = 7.2 Hz), 6.45 (1H, brs), 7.21-7.35 (3H, m), 7.51-7.54 (1H, m).

¹³C NMR (75 MHz, CDCl₃): δ 11.4, 22.6, 41.7, 126.9, 129.8, 130.0, 130.5, 130.9, 135.5, 166.6.

FT-IR (KBr, cm⁻¹): 1144, 1259, 1314, 1436, 1551, 1595, 1651, 2860, 2935, 2967, 3284.

HR-MS (*m/z*) for C₁₀H₁₂ClNO(M⁺): Calculated 197.0607, found 197.0605 (One of the peaks).

3.5. *n*-Propylthiophene-3-carboxamide (6e)



Yield: 68% (115 mg, 0.68 mmol).

Characteristic: Yellow oil.

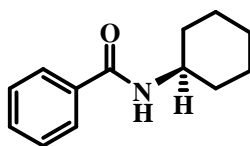
^1H NMR (300 MHz, CDCl_3): δ 0.97 (3H, t, $J = 7.2$ Hz), 1.59-1.68 (2H, m), 3.38 (2H, q, $J = 6.9$ Hz), 5.96 (1H, brs), 7.31-7.38 (2H, m), 7.83 (1H, d, $J = 1.2$ Hz).

^{13}C NMR (75 MHz, CDCl_3): δ 11.3, 22.9, 41.5, 125.9, 126.4, 127.8, 132.3, 168.5.

FT-IR (neat, cm^{-1}): 1094, 1292, 1407, 1551, 1604, 1630, 2927, 2962, 3398.

HR-MS (m/z) for $\text{C}_8\text{H}_{11}\text{NO}$ (M^+): Calculated 169.0561, found 169.0562.

3.6. *N*-Cyclohexylbenzamide (6f)



Yield: 74% (150 mg, 0.74 mmol).

Characteristic: Colourless solid.

Melting range: 90-94 °C

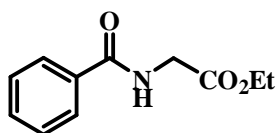
^1H NMR (300 MHz, CDCl_3): δ 1.20-1.42 (5H, m), 1.58-1.62 (1H, m), 1.68-1.72 (2H, m), 1.94-1.98 (2H, m), 3.86-3.98 (1H, m), 6.36 (1H, d, $J = 6.6$ Hz), 7.32-7.45 (3H, m), 7.74 (2H, d, $J = 7.2$ Hz).

^{13}C NMR (75 MHz, CDCl_3): δ 24.9, 25.5, 33.1, 48.7, 126.9, 128.4, 131.1, 135.0, 166.7.

FT-IR (KBr, cm^{-1}): 1291, 1328, 1446, 1488, 1534, 1577, 1603, 1628, 2850, 2929, 3240, 3329.

HR-MS (m/z) for $\text{C}_{13}\text{H}_{17}\text{NO}$ (M^+): Calculated 203.1310, found 203.1312.

3.7. Benzoylamino-acetic acid ethyl ester (6g)



Yield: 60% (124 mg, 0.60 mmol).

Characteristic: Colourless solid.

Melting range: 102-104 °C

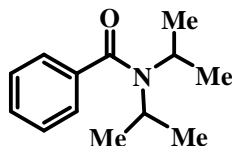
^1H NMR (300 MHz, CDCl_3): δ 1.30 (3H, t, $J = 7.2$ Hz), 4.21-4.28 (4H, m), 6.87 (1H, brs), 7.40-7.53 (3H, m), 7.82 (2H, d, $J = 8.4$ Hz).

^{13}C NMR (75 MHz, CDCl_3): δ 14.1, 41.8, 61.5, 127.0, 128.5, 131.7, 133.8, 167.4, 170.0.

FT-IR (KBr, cm^{-1}): 1175, 1223, 1450, 1603, 1629, 1736, 2945.

HR-MS (m/z) for $\text{C}_{11}\text{H}_{14}\text{NO}_3$ ($\text{M}^+ + \text{H}$): Calculated 208.0975, found 208.0972.

3.8. *N,N*-Diisopropylbenzamide (6h)



Yield: 75% (153 mg, 0.75 mmol).

Characteristic: Yellow solid.

Melting range: 58-60 °C

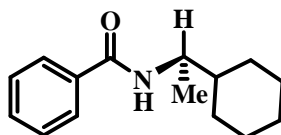
¹H NMR (300 MHz, CDCl₃): δ 0.82-1.83 (12H, broad peak), 3.27-4.02 (2H, broad peak), 7.27-7.41 (5H, m).

¹³C NMR (75 MHz, CDCl₃): δ 20.7, 51.2, 125.5, 128.4, 128.6, 138.8, 171.1.

FT-IR (KBr, cm⁻¹): 1156, 1211, 1340, 1371, 1440, 1605, 1628, 2936, 2968.

HR-MS (*m/z*) for C₁₃H₁₉NO(M⁺): Calculated 205.1467, found 205.1467.

3.9. (*R*)-*N*-(1-Cyclohexylethyl)benzamide (6i)



Yield: 62% (122 mg, 0.62 mmol).

Characteristic: Colorless solid.

Melting range: 105-108 °C

[α]_D²⁰ = -60.9° (c 1.2, CHCl₃).

¹H NMR (300 MHz, CDCl₃): δ 1.03-1.27 (9H, m), 1.43-1.46 (1H, m), 1.66-1.85 (4H, m), 4.07-4.12 (1H, m), 5.97-5.99 (1H, m), 7.41-7.50 (3H, m), 7.76-7.79 (2H, m).

¹³C NMR (75 MHz, CDCl₃): δ 18.0, 26.1, 26.4, 29.1, 43.3, 49.8, 126.8, 128.4, 128.5, 131.2, 135.1, 166.9.

FT-IR (KBr, cm⁻¹): 1230, 1347, 1443, 1539, 1604, 1635, 2857, 2926, 3342.

HR-MS (*m/z*) for C₁₅H₂₁NO(M⁺): Calculated 231.1623, found 231.1626.

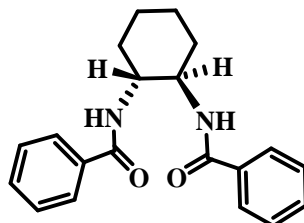
HPLC data:

Column : chiralpak IB (1B00CE-LF003); Detection : Single Peak

Mobile Phase : hex/ea 99:1; Temperature : 25 °C

Flow Rate : 0.8 ml/min; Pressure : 26 kgf.

3.10. (*R,R*)-Bis(*N*-benzoyl)cyclohexyldiamine (6j)



Yield: 68% (219 mg, 0.68 mmol).

Characteristic: Colourless solid.

Melting range: 210-215 °C

[α]_D²⁰ = +111.2° (c 1.6, CHCl₃).

^1H NMR (300 MHz, CDCl_3): δ 1.41-1.52 (4H, m), 1.86 (2H, d, $J = 6.3$ Hz), 2.24 (2H, d, $J = 10.5$ Hz), 4.06 (2H, d, $J = 7.5$ Hz), 7.06 (2H, d, $J = 5.7$ Hz), 7.25 (4H, t, $J = 7.5$ Hz), 7.36-7.41 (2H, m), 7.67-7.72 (4H, m).

^{13}C NMR (75 MHz, CDCl_3): δ 24.8, 32.3, 54.5, 126.9, 128.4, 131.3, 134.2, 168.2.

FT-IR (KBr, cm^{-1}): 1303, 1328, 1489, 1533, 1578, 1602, 1630, 2857, 2933, 3302.

HR-MS (m/z) for $\text{C}_{20}\text{H}_{22}\text{N}_2\text{O}_2(\text{M}^+)$: Calculated 322.1681, found 322.1682.

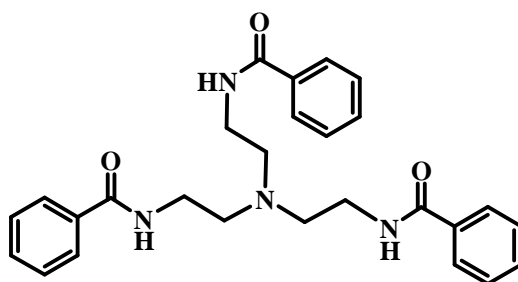
HPLC data:

Column : chiralpak IB (1B00CE-LF003); Detection : Single Peak

Mobile Phase : hex/ea 98:2; Temperature : 25 $^\circ\text{C}$

Flow Rate : 0.9 ml/min; Pressure : 26 kgf.

3.11. *N,N',N''*-(2,2',2''-Nitrilotris(ethane-2,1-diyl))tribenzamide (6k)



Yield: 66% (296 mg, 0.66 mmol).

Characteristic: Yellow solid.

Melting range: 132-135 $^\circ\text{C}$

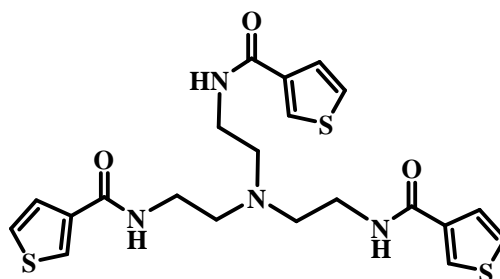
^1H NMR (300 MHz, DMSO-d_6): δ 2.71 (6H, t, $J = 6.3$ Hz), 3.20-3.45 (6H, m), 7.37 (6H, t, $J = 7.2$ Hz), 7.44-7.46 (3H, m), 7.77-7.80 (6H, m), 8.37 (3H, t, $J = 5.1$ Hz).

^{13}C NMR (75 MHz, DMSO-d_6): δ 38.1, 53.7, 127.5, 128.6, 131.4, 134.9, 166.8.

FT-IR (KBr, cm^{-1}): 1311, 1457, 1491, 1542, 1577, 1604, 1632, 2802, 2927, 3289, 3348.

HR-MS (m/z) for $\text{C}_{27}\text{H}_{30}\text{N}_4\text{O}_3(\text{M}^+)$: Calculated 458.2318, found 458.2317.

3.12. *N,N',N''*-(2,2',2''-Nitrilotris(ethane-2,1-diyl))trithiophene-3-carboxamide (6l)



Yield: 61% (267 mg, 0.61 mmol).

Characteristic: Yellow oil.

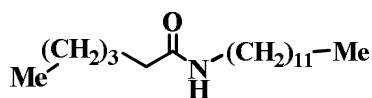
^1H NMR (300 MHz, DMSO-d_6): δ 2.35 (6H, t, $J = 6.3$ Hz), 2.52 (6H, t, $J = 6.3$ Hz), 7.27 (3H, dd, $J = 4.8$, 3.0 Hz), 7.32 (3H, dd, $J = 4.8$, 0.9 Hz), 7.71 (3H, dd, $J = 3.0$, 1.2 Hz).

^{13}C NMR (75 MHz, DMSO-d_6): δ 39.8, 57.8, 124.2, 127.5, 129.8, 132.7, 167.3.

FT-IR (neat, cm^{-1}): 1451, 1542, 1579, 1602, 1631, 2857, 2926, 3230.

HR-MS (m/z) for $\text{C}_{21}\text{H}_{24}\text{N}_4\text{O}_3\text{S}_3(\text{M}^+)$: Calculated 476.1011, found 476.1016.

3.13. Hexanoic acid dodecylamide (6m)



Yield: 65% (183 mg, 0.65 mmol).

Characteristic: Yellow oil.

^1H NMR (300 MHz, DMSO- d_6): δ 0.42-0.45 (14H, m), 0.81-0.95 (12H, m), 1.04-1.13 (4H, m), 1.65-1.87 (4H, m), 2.94 (2H, t, $J = 6.9$ Hz), 5.78 (1H, brs).

^{13}C NMR (75 MHz, DMSO- d_6): δ 13.7, 13.8, 22.3, 22.4, 22.6, 25.5, 25.6, 28.1, 28.8, 29.4, 31.1, 31.2, 31.4, 31.8, 32.7, 33.0, 39.5, 164.5.

FT-IR (neat, cm^{-1}): 1120, 1213, 1456, 1546, 1631, 2857, 2923, 3236.

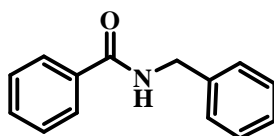
HR-MS (m/z) for $\text{C}_{18}\text{H}_{37}\text{NO}(\text{M}^+)$: Calculated 283.2875, found 283.2872.

4. General procedure for the synthesis of amides (8) from benzylamines

To a suspension of terminal alkynes (1.0 mmol, 102 mg) and iodobenzene diacetate (2.0 mmol, 644 mg) in water (2.0 mL) sodium bicarbonate (3.0 mmol, 252 mg) was added and allowed to stir for 15 min. Then benzylamine (2.0 mmol) was added dropwise under stirring conditions at room temperature. The completeness of the reaction was confirmed by monitoring in thin layer chromatography (TLC). The post reaction mixture was extracted with EtOAc (2x15 mL) and the combined organic layer was washed successively with saturated sodium bicarbonate solution (1x10 mL) and brine (3x10 mL). It was dried over anhydrous Na_2SO_4 , filtered and evaporated in a rotary evaporator under reduced pressure at room temperature. Thus, the reaction with phenylacetylene (**1a**, 102 mg, 1.0 mmol) and 4-methylbenzylamine (1.0 mmol, 121 mg) afforded 4-methyl-*N*-(4-methylbenzyl)benzamide (**8b**) after purification by column chromatography on silica gel (60-120 mesh) with ethyl acetate-petroleum ether (1:19, v/v) as an eluent in a yield of 78% (186 mg, 0.78 mmol). The synthesized amide (**8a-f**) were characterized by means of NMR (^1H and ^{13}C), FT-IR and Mass (HR-MS) spectral analysis and comparing with the literature spectral data and melting points.³

5. Characterization data of amides (8a-g)

5.1. *N*-Benzyl-benzamide (8a)



Yield: 80% (169 mg, 0.80 mmol).

Characteristic: Colourless solid.

Melting range: 101-102 °C

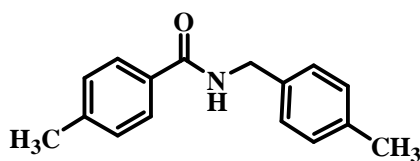
^1H NMR (300 MHz, CDCl_3): δ 4.65 (2H, d, $J = 5.7$ Hz), 6.42 (1H, brs), 7.28-7.53 (8H, m), 7.79 (2H, d, $J = 6.9$ Hz).

^{13}C NMR (75 MHz, CDCl_3): δ 44.1, 126.9, 127.6, 127.9, 128.6, 128.8, 131.5, 134.4, 138.1, 167.3.

FT-IR (KBr, cm^{-1}): 1260, 1314, 1454, 1546, 1578, 1604, 1643, 2854, 2930, 3325.

HR-MS (m/z) for $\text{C}_{14}\text{H}_{13}\text{NO}(\text{M}^+)$: Calculated 211.0997, found 211.0998.

5.2. 4-Methyl-N-(4-methylbenzyl)benzamide (8b)



Yield: 78% (186 mg, 0.78 mmol).

Characteristic: Yellow solid.

Melting range: 140-142 °C

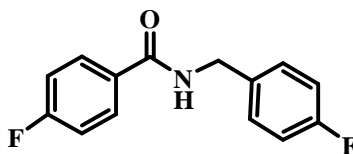
¹H NMR (300 MHz, CDCl₃): δ 2.35 (3H, s), 2.40 (3H, s), 4.60 (2H, d, *J* = 5.4 Hz), 6.33 (1H, brs), 7.12-7.27 (6H, m), 7.68 (2H, d, *J* = 8.1 Hz).

¹³C NMR (75 MHz, CDCl₃): δ 21.0, 21.4, 43.8, 126.9, 127.9, 129.2, 129.4, 131.6, 135.2, 137.3, 141.9, 167.2.

FT-IR (KBr, cm⁻¹): 1256, 1323, 1430, 1513, 1549, 1617, 1640, 2865, 2923, 3316.

HR-MS (*m/z*) for C₁₆H₁₇NO(M⁺): Calculated 239.1310, found 239.1310.

5.3. 4-Fluoro-N-(4-fluorobenzyl)benzamide (8c)



Yield: 65% (160 mg, 0.65 mmol).

Characteristic: Brown solid.

Melting range: 90-93 °C

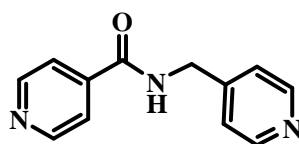
¹H NMR (300 MHz, CDCl₃): δ 4.59 (2H, d, *J* = 5.7 Hz), 6.48 (1H, brs), 6.96-7.14 (4H, m), 7.27-7.34 (2H, m), 7.78-7.80 (2H, m).

¹³C NMR (75 MHz, CDCl₃): δ 43.4, 115.4, 115.7, 129.2, 129.3, 129.5, 129.6, 130.3, 133.8, 166.3.

FT-IR (KBr, cm⁻¹): 1154, 1222, 1511, 1547, 1601, 1634, 3278.

HR-MS (*m/z*) for C₁₄H₁₁F₂NO(M⁺): Calculated 247.0809, found 247.0804 (one of the peaks).

5.4. N-Pyridine-4-ylmethyl-isonicotinamide (8d)



Yield: 60% (128 mg, 0.60 mmol).

Characteristic: Yellow solid.

Melting range: 167-170 °C

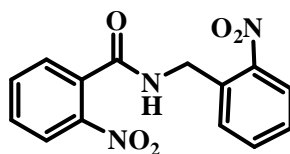
¹H NMR (300 MHz, CDCl₃): δ 5.09 (2H, s), 6.67 (1H, d, *J* = 5.7 Hz), 6.70 (1H, d, *J* = 6.0 Hz), 6.77-6.79 (1H, m), 7.31 (1H, d, *J* = 6.0 Hz), 7.48 (1H, d, *J* = 6.0 Hz), 7.95-8.03 (2H, m), 8.30-8.33 (1H, m), 8.40-8.44 (1H, m).

¹³C NMR (75 MHz, CDCl₃): δ 54.4, 122.7, 122.9, 124.2, 124.3, 144.8, 148.2, 149.6, 149.7, 149.9, 150.0, 167.7.

FT-IR (KBr, cm⁻¹): 1457, 1486, 1574, 1593, 1604, 1632, 2032, 2986.

HR-MS (*m/z*) for C₁₂H₁₁N₃O(M⁺): Calculated 213.0902, found 213.0905.

5.5. 2-Nitro-N-(2-nitrobenzyl)benzamide (8e)



Yield: 73% (220 mg, 0.73 mmol).

Characteristic: Brown solid.

Melting range: 72-74 °C

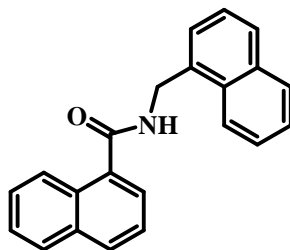
^1H NMR (300 MHz, CDCl_3): δ 5.23 (2H, s), 7.46-7.48 (1H, m), 7.50-7.71 (2H, m), 7.74-7.88 (2H, m), 7.92-7.97 (1H, m), 8.04-8.12 (1H, m), 8.35-8.39 (1H, m), 8.89 (1H, s).

^{13}C NMR (75 MHz, CDCl_3): δ 61.3, 124.3, 124.7, 125.5, 128.0, 129.8, 130.4, 131.0, 133.4, 133.5, 134.1, 135.5, 159.2.

FT-IR (KBr, cm^{-1}): 1207, 1273, 1323, 1339, 1378, 1514, 1570, 1609, 1638, 2850, 2921.

HR-MS (m/z) for $\text{C}_{14}\text{H}_{11}\text{N}_3\text{O}_5(\text{M}^+)$: Calculated 301.0699, found 301.0691.

5.6. Naphthalene-1-carboxylic acid (naphthalen-1-ylmethyl)amide (8f)



Yield: 60% (186 mg, 0.60 mmol).

Characteristic: Colourless solid.

Melting range: 112-113 °C

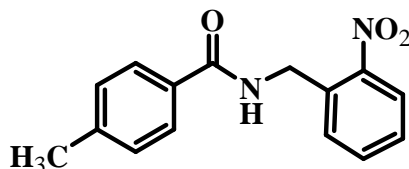
^1H NMR (300 MHz, CDCl_3): δ 5.08 (2H, d, $J = 5.1$ Hz), 6.56 (1H, brs), 7.36-7.58 (8H, m), 7.76-7.91 (4H, m), 8.08-8.11 (2H, m).

^{13}C NMR (75 MHz, CDCl_3): δ 42.3, 123.4, 125.4, 126.0, 126.7, 126.8, 127.0, 128.5, 128.7, 128.8, 131.5, 133.4, 134.3, 167.2.

FT-IR (KBr, cm^{-1}): 1265, 1313, 1549, 1577, 1600, 1634, 2939, 3065, 3280.

HR-MS (m/z) for $\text{C}_{22}\text{H}_{17}\text{NO}(\text{M}^+)$: Calculated 311.1310, found 311.1316.

5.7. 4-Methyl-N-(2-nitrobenzyl)benzamide (8g) [Cross addition product]



Yield: 40% (108 mg, 0.40 mmol).

Characteristic: Yellow solid.

Melting range: 107-110 °C

^1H NMR (300 MHz, CDCl_3): δ 2.37 (3H, s), 5.22 (2H, s), 7.45-7.50 (1H, m), 7.58-7.74 (4H, m), 8.04-8.12 (3H, m), 8.89 (1H, s).

^{13}C NMR (75 MHz, CDCl_3): δ 20.3, 61.3, 124.3, 124.7, 128.0, 129.8, 130.4, 130.8, 131.0, 133.4, 134.3, 141.7, 167.2.

FT-IR (KBr, cm^{-1}): 1257, 1474, 1578, 1605, 1638, 2929, 3060.

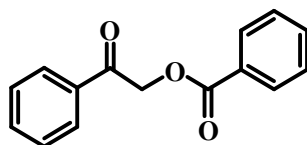
HR-MS (m/z) for $\text{C}_{15}\text{H}_{15}\text{N}_2\text{O}_3$ (M^+H): Calculated 271.1084, found 271.1083.

6. General procedure for the synthesis of ketoesters (9)

To a suspension of aromatic terminal alkynes (1.0 mmol, 102 mg) and iodobenzene diacetate (3.0 mmol, 966 mg) in water (2.0 mL) sodium bicarbonate (2.0 mmol, 168 mg) was added under vigorously stirring condition at room temperature. The appearance of the reaction mixture changed after 10 h. The oil (yellow) was separated out. The formation of product was checked by thin layer chromatography (TLC). The post reaction mixture was extracted with EtOAc (2x15 mL) and the combined organic layer was washed successively with saturated sodium bicarbonate solution (1x10 mL) and brine (1x10 mL). It was dried over anhydrous Na_2SO_4 , filtered and evaporated in a rotary evaporator under reduced pressure at room temperature. Thus, the reaction with phenylacetylene (**1a**, 102 mg, 1.0 mmol) afforded benzoic acid 2-oxo-2-phenyl-ethyl ester (**9a**) after purification by column chromatography on silica gel (60-120 mesh) with ethyl acetate-petroleum ether (1:20, v/v) as an eluent in a yield of 65% (156 mg, 0.65 mmol). The α -ketoesters (**3a-e**) were characterized by means of XRD, NMR (^1H and ^{13}C), FT-IR and Mass (HR-MS) spectral analysis.

7. Characterization data of ketoesters (9a-e, D₂-9a)

7.1. Benzoic acid 2-oxo-2-phenylester (9a)



Yield: 65% (156 mg, 0.65 mmol).

Characteristic: Colourless solid.

Melting range: 117-120 °C

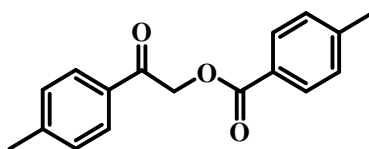
^1H NMR (300 MHz, CDCl_3): δ 5.56(2H, s), 7.42-7.51 (4H, m), 7.55-7.62 (2H, m), 7.93-7.96 (2H, m), 8.06-8.13 (2H, m).

^{13}C NMR (75 MHz, CDCl_3): δ 66.4, 127.8, 128.4, 128.6, 128.8, 129.9, 130.1, 133.3, 133.6, 133.8, 134.4, 166.0, 192.1.

FT-IR (KBr, cm^{-1}): 1073, 1121, 1229, 1282, 1373, 1420, 1449, 1581, 1597, 1694, 1718, 2851, 2921.

HR-MS (m/z) for $\text{C}_{15}\text{H}_{12}\text{O}_3$ (M^+): Calculated 240.0786, found 240.0786.

7.2. 4-Methyl-benzoic acid 2-oxo-2-p-tolyl-ester (9b)



Yield: 70% (187 mg, 0.70 mmol).

Characteristic: Yellow solid.

Melting range: 107-108 °C

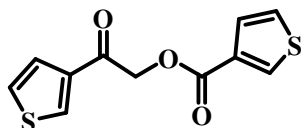
^1H NMR (300 MHz, CDCl_3): δ 2.38 (3H, s), 2.40 (3H, s), 5.51 (2H, s), 7.23-7.28 (4H, m), 7.84 (1H, d, $J = 8.1$ Hz), 7.96-8.02 (3H, m).

^{13}C NMR (75 MHz, CDCl_3): δ 21.7, 66.2, 127.9, 129.1, 129.2, 129.5, 129.7, 130.0, 130.2, 130.6, 131.9, 144.4, 144.7, 166.1, 191.9.

FT-IR (KBr, cm^{-1}): 1129, 1178, 1232, 1281, 1368, 1417, 1605, 1702, 1724, 2934.

HR-MS (m/z) for $\text{C}_{17}\text{H}_{16}\text{O}_3$ (M^+): Calculated 268.1099, found 268.1097.

7.3. Thiophene-3-carboxylic acid 2-(2-thiophen-3-yl-ethylester) (9c)



Yield: 66% (167 mg, 0.66 mmol).

Characteristic: Yellow oil.

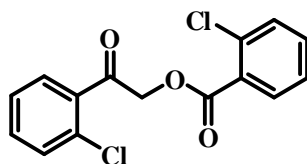
^1H NMR (300 MHz, CDCl_3): δ 5.38 (2H, s), 7.32-7.39 (2H, m), 7.58-7.60 (2H, m), 8.15 (1H, d, $J = 1.8$ Hz), 8.24 (1H, d, $J = 2.4$ Hz).

^{13}C NMR (75 MHz, CDCl_3): δ 66.4, 126.1, 126.5, 126.8, 128.0, 132.2, 132.5, 133.6, 138.8, 161.9, 187.0.

FT-IR (neat, cm^{-1}): 1404, 1465, 1650, 1690, 1718, 2342, 2853.

HR-MS (m/z) for $\text{C}_{11}\text{H}_8\text{O}_3\text{S}_2$ (M^+): Calculated 251.9915, found 251.9911.

7.4. 2-Chloro-benzoic acid 2-(2-chloro-phenyl)-2-oxo-ethyl ester (9d)



Yield: 68% (211 mg, 0.68 mmol).

Characteristic: Yellow oil.

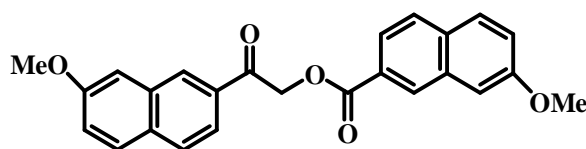
^1H NMR (300 MHz, CDCl_3): δ 5.46 (2H, s), 7.32-7.53 (6H, m), 7.68-7.72 (1H, m), 7.97-8.00 (1H, m).

^{13}C NMR (75 MHz, CDCl_3): δ 68.9, 126.6, 127.2, 130.1, 130.6, 131.1, 132.3, 132.6, 133.0, 133.4, 134.1, 134.6, 135.8, 168.6, 195.0.

FT-IR (neat, cm^{-1}): 1250, 1434, 1474, 1590, 1717, 2928.

HR-MS (m/z) for $\text{C}_{15}\text{H}_{10}\text{Cl}_2\text{O}_3$ (M^+): Calculated 308.0007, found 308.0010 (One of the peaks).

7.5. 7-Methoxy-naphthalene-2-carboxylic acid 2-(7-methoxynaphthalen-2-yl)-2-oxo-ethyl ester (9e)



Yield: 62% (248 mg, 0.62 mmol).

Characteristic: Yellow viscous liquid.

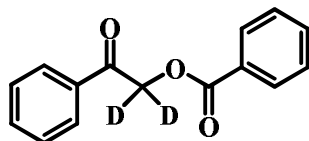
^1H NMR (300 MHz, CDCl_3): δ 3.97 (6H, s), 4.99 (2H, d, $J = 1.2$ Hz), 7.18-7.31 (7H, m), 7.85 (3H, dd, $J = 16.8, 9.0$ Hz), 7.96 (1H, dd, $J = 8.4, 1.5$ Hz), 8.37 (1H, s).

^{13}C NMR (75 MHz, CDCl_3): δ 55.4, 65.3, 105.9, 120.1, 123.8, 127.5, 127.7, 128.7, 129.3, 131.2, 137.9, 167.9, 197.9.

FT-IR (neat, cm^{-1}): 1197, 1269, 1482, 1623, 1688, 1732, 2851, 2925.

HR-MS (m/z) for $C_{25}H_{20}O_5$ (M^+): Calculated 400.1311, found 400.1310.

7.6. Deuteriated benzoic acid 2-oxo-2-phenyl-ethylester (**D₂-9a**)



Yield: 65% (157 mg, 0.65 mmol).

Characteristic: Colourless solid.

Melting range: 119-120 °C

1H NMR (300 MHz, $CDCl_3$): δ 7.47-7.56 (4H, m), 7.60-7.65 (2H, m), 7.98-8.01 (2H, m), 8.15-8.18 (2H, m).

^{13}C NMR (75 MHz, $CDCl_3$): δ 66.4, 127.8, 128.4, 128.6, 128.8, 129.9, 130.1, 133.3, 133.6, 133.8, 134.4, 166.0, 192.1.

FT-IR (KBr, cm^{-1}): 1073, 1121, 1229, 1420, 1449, 1581, 1597, 1694, 1718, 2851, 2921.

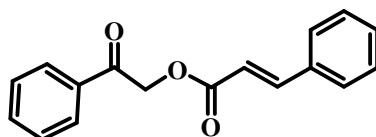
HR-MS (m/z) for $C_{15}H_{10}D_2O_3$ (M^+): Calculated 242.0912, found 242.0915.

8. General procedure for the synthesis of ketoesters (**11**) using potassiumcarboxylates

To a suspension of terminal alkyne (1.0 mmol, 102 mg) and iodobenzene diacetate (1.0 mmol, 322 mg) in water (2.0 mL) potassium salt of carboxylic acid (4.0 mmol) was added. The benzylamine (1.0 mmol) was added dropwise under stirring condition at room temperature. The oil was separated out after 10-15 min. The completeness of the reaction was confirmed by monitoring thin layer chromatography (TLC). The post reaction mixture was extracted with EtOAc (2x15 mL) and the combined organic layer was washed successively with saturated sodium bicarbonate solution (1x10 mL) and brine (1x10 mL). It was dried over anhydrous Na_2SO_4 , filtered and evaporated in a rotary evaporator under reduced pressure at room temperature. Thus, the reaction with phenylacetylene (**1a**, 102 mg, 1.0 mmol) and sodiumcinnamate (4 mmol, 680 mg) afforded 3-phenyl-acrylic acid 2-oxo-2-phenyl-ethyl ester (**11a**) after purification by column chromatography on silica gel (60-120 mesh) with ethyl acetate-petroleum ether (1:18, v/v) as an eluent in an yield of 75% (199 mg, 0.75 mmol). The ketoesters (**11a-c**) were characterized by means of NMR (1H and ^{13}C), FT-IR and Mass (HR-MS) spectral analysis.

9. Characterization data of ketoesters (**11a-c**)

9.1. Cinnamic acid 2-oxo-2-phenyl-ethyl ester (**11a**)



Yield: 75% (199 mg, 0.75 mmol).

Characteristic: Yellow oil.

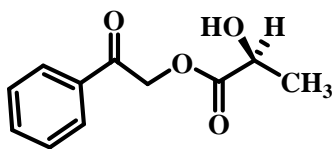
1H NMR (300 MHz, $CDCl_3$): δ 5.84 (2H, s), 6.60 (1H, d, $J = 15.9$ Hz), 7.29-7.41 (4H, m), 7.48-7.65 (4H, m), 7.81 (1H, d, $J = 15.9$ Hz), 7.96 (2H, d, $J = 8.1$ Hz).

^{13}C NMR (75 MHz, $CDCl_3$): δ 66.1, 117.0, 117.8, 128.0, 128.2, 128.5, 128.6, 128.8, 128.9, 129.0, 129.1, 130.5, 133.8, 134.3, 146.1, 166.2, 192.3.

FT-IR (neat, cm^{-1}): 1123, 1201, 1318, 1401, 1449, 1637, 1697, 1707, 2091, 2347.

HR-MS (m/z) for $C_{17}H_{14}O_3$ (M^+): Calculated 266.0943, found 266.0941.

9.2. L-lactic acid 2-oxo-2-phenyl-ethyl ester (11b)



Yield: 69% (144 mg, 0.69 mmol).

Characteristic: Yellow oil.

$[\alpha]_D^{20} = -4.39^\circ$ (c 2.10, CHCl_3).

$^1\text{H NMR}$ (300 MHz, CDCl_3): δ 1.47 (3H, d, $J = 6.9$ Hz), 4.48 (1H, q, $J = 6.9$ Hz), 5.35 (1H, s), 5.39 (1H, s), 7.47-7.49 (2H, m), 7.57-7.62 (1H, m), 7.85-7.89 (2H, m).

$^{13}\text{C NMR}$ (75 MHz, CDCl_3): δ 20.4, 66.5, 66.9, 127.7, 128.9, 133.9, 134.1, 175.0, 191.6.

FT-IR (neat, cm^{-1}): 970, 1129, 1233, 1450, 1598, 1651, 1694, 1727, 3428.

HR-MS (m/z) for $\text{C}_{11}\text{H}_{12}\text{O}_4$ (M^+): Calculated 208.0736, found 208.0735.

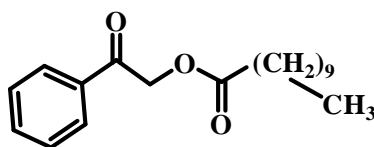
HPLC data:

Column : chiralpak IB (1B00CE-LF003); Detection : Single Peak

Mobile Phase : hex/ea 99:1; Temperature : 25 °C

Flow Rate : 0.8 ml/min; Pressure : 23 kgf.

9.3. Undecanoic acid 2-oxo-2-phenyl-ethyl ester (11c)



Yield: 72% (218 mg, 0.72 mmol).

Characteristic: Yellow oil.

$^1\text{H NMR}$ (300 MHz, CDCl_3): δ 0.87 (3H, t, $J = 6.9$ Hz), 1.08-1.42 (14H, broad peak), 1.64-1.72 (2H, m), 2.48 (2H, t, $J = 7.5$ Hz), 5.33 (2H, s), 7.49 (2H, t, $J = 7.5$ Hz), 7.57-7.60 (1H, m), 7.91 (2H, d, $J = 7.5$ Hz).

$^{13}\text{C NMR}$ (75 MHz, CDCl_3): δ 14.0, 22.6, 24.9, 29.1, 29.2, 29.4, 29.5, 31.8, 33.9, 65.8, 127.7, 128.8, 133.8, 134.3, 173.2, 192.3.

FT-IR (neat, cm^{-1}): 1160, 1223, 1372, 1450, 1598, 1708, 1747, 2855, 2926.

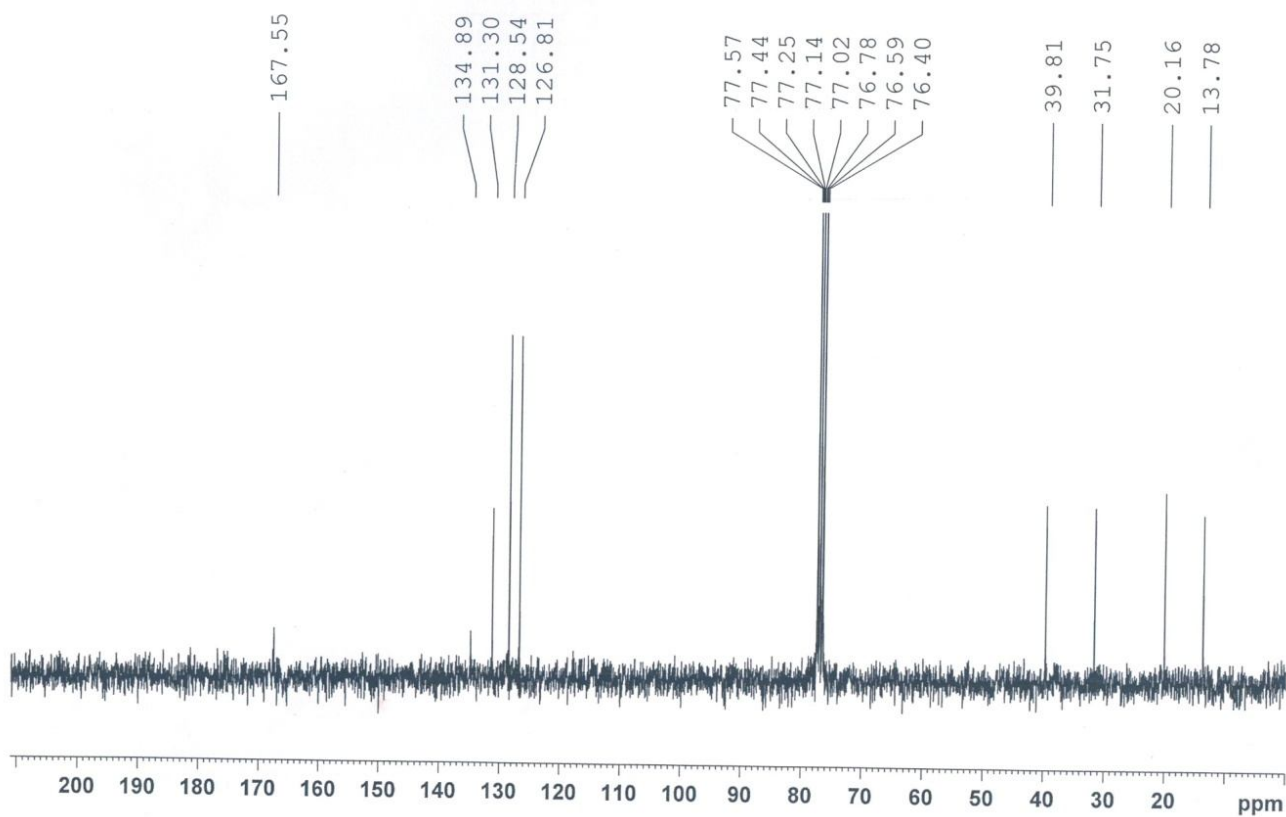
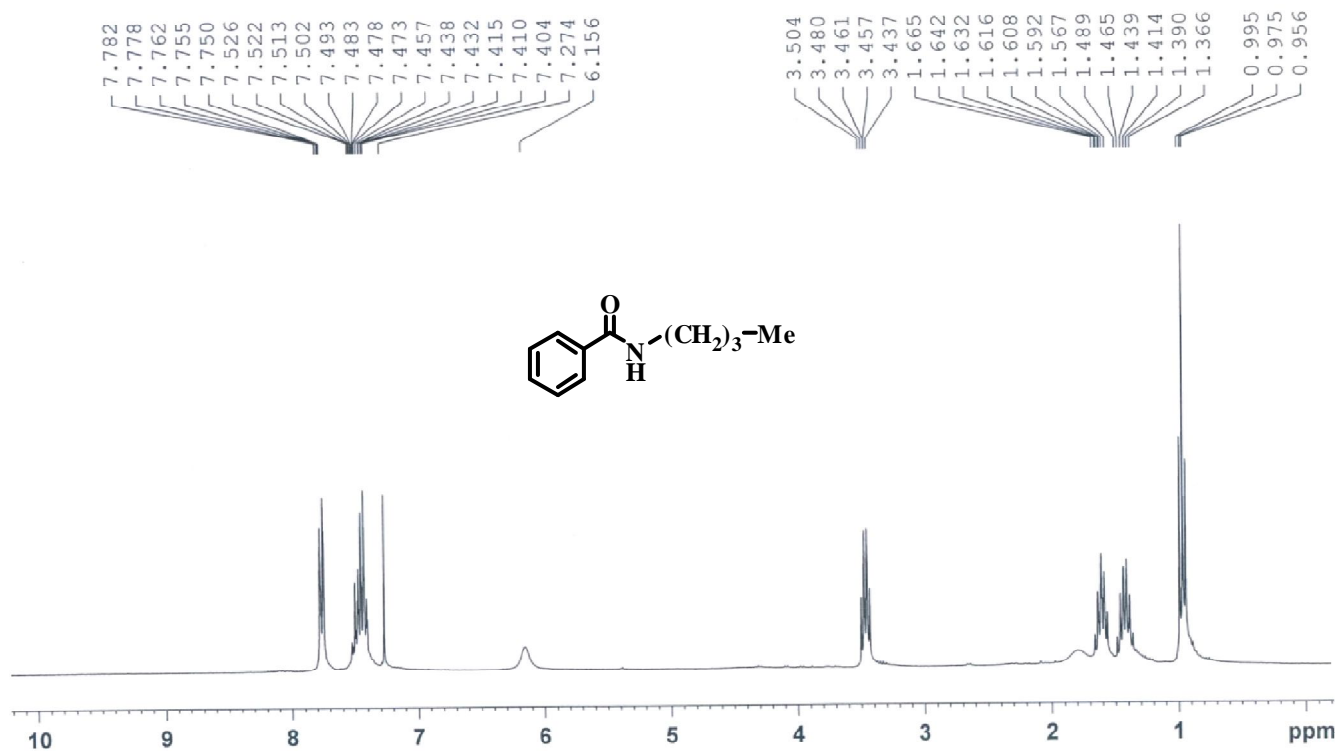
HR-MS (m/z) for $\text{C}_{19}\text{H}_{28}\text{O}_3$ (M^+): Calculated 304.2038, found 304.2037.

10. References

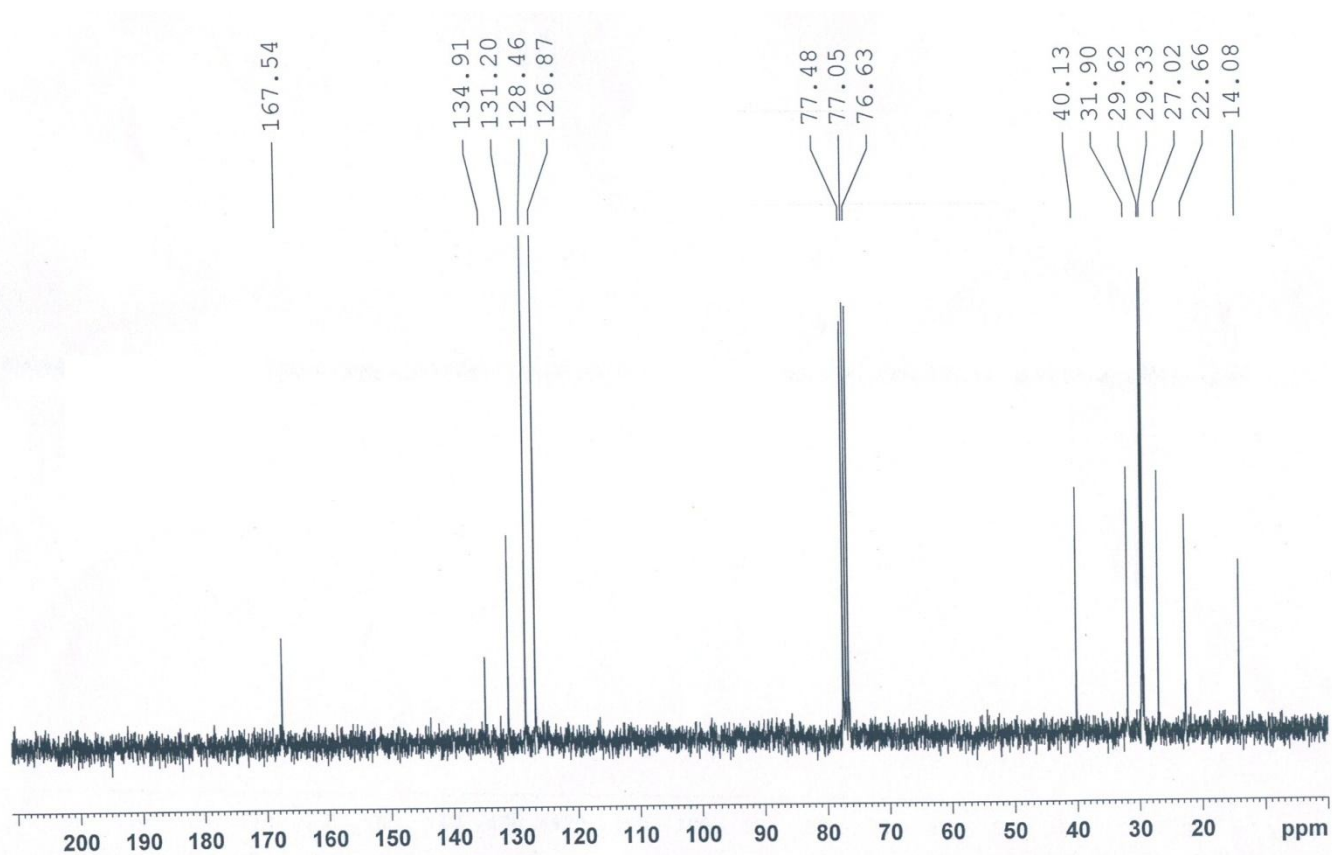
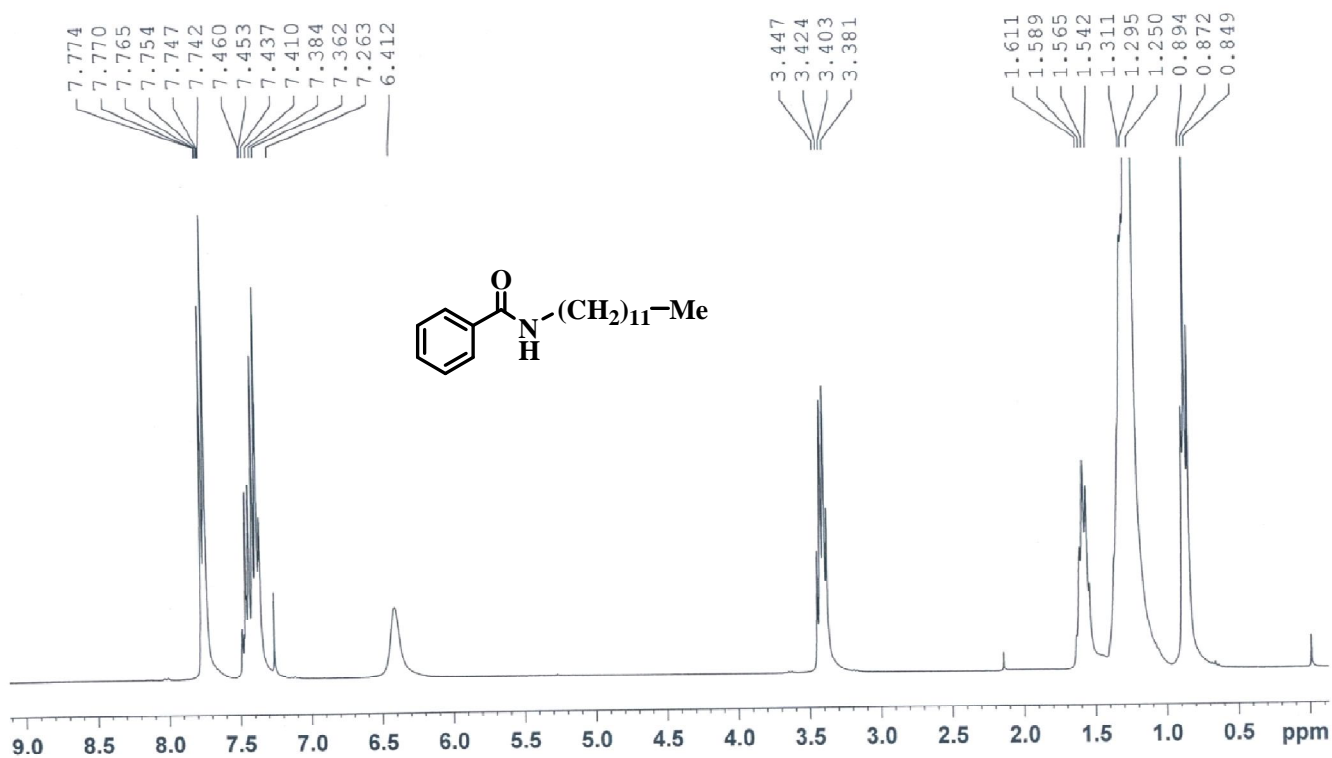
- (1) Muñoz, J. M.; Alcázar, J.; Hoz, A.; Díaz-Ortizb, Á.; Diego, S. A. A. *Green Chem.* **2012**, *14*, 1335-1341.
- (2) Cao, H.; McNamee, L.; Alper, H. *Org. Lett.* **2008**, *10*, 5281-5284.
- (3) T. Ohshima, Y. Hayashi, K. Agura, Y. Fujii, A. Yoshiyamab and K. Mashima; *Chem. Commun.* **2012**, *48*, 5434-5436.
- (4) Mo, D. L.; Doi, L. X.; Hou, X. L. *Tetrahedron Lett.* **2009**, *50*, 5578-5581.

11. ^1H and ^{13}C -NMR spectra of the compounds (6a-m, 8a-g, 9a-e, D₂-9a and 11a-c)

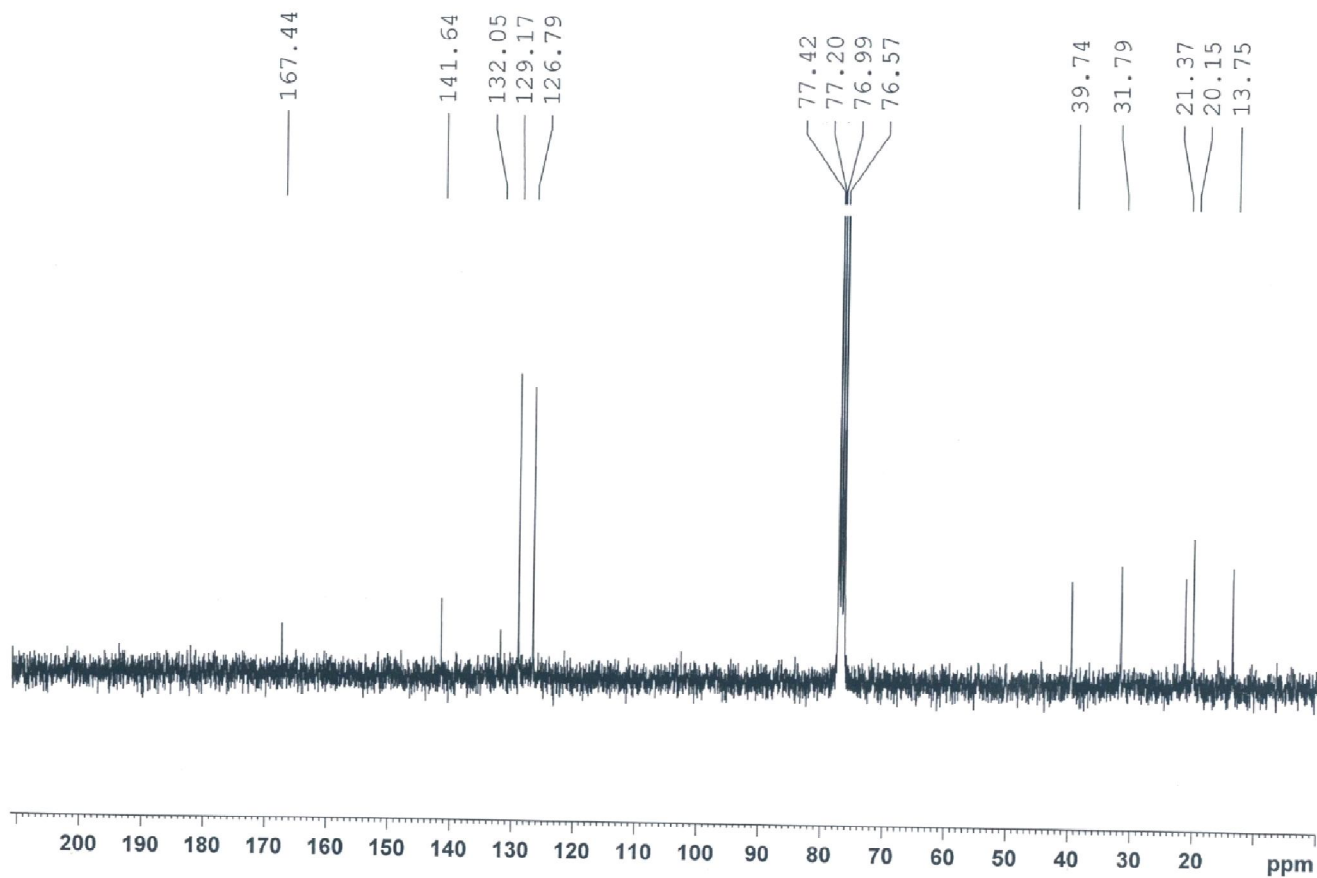
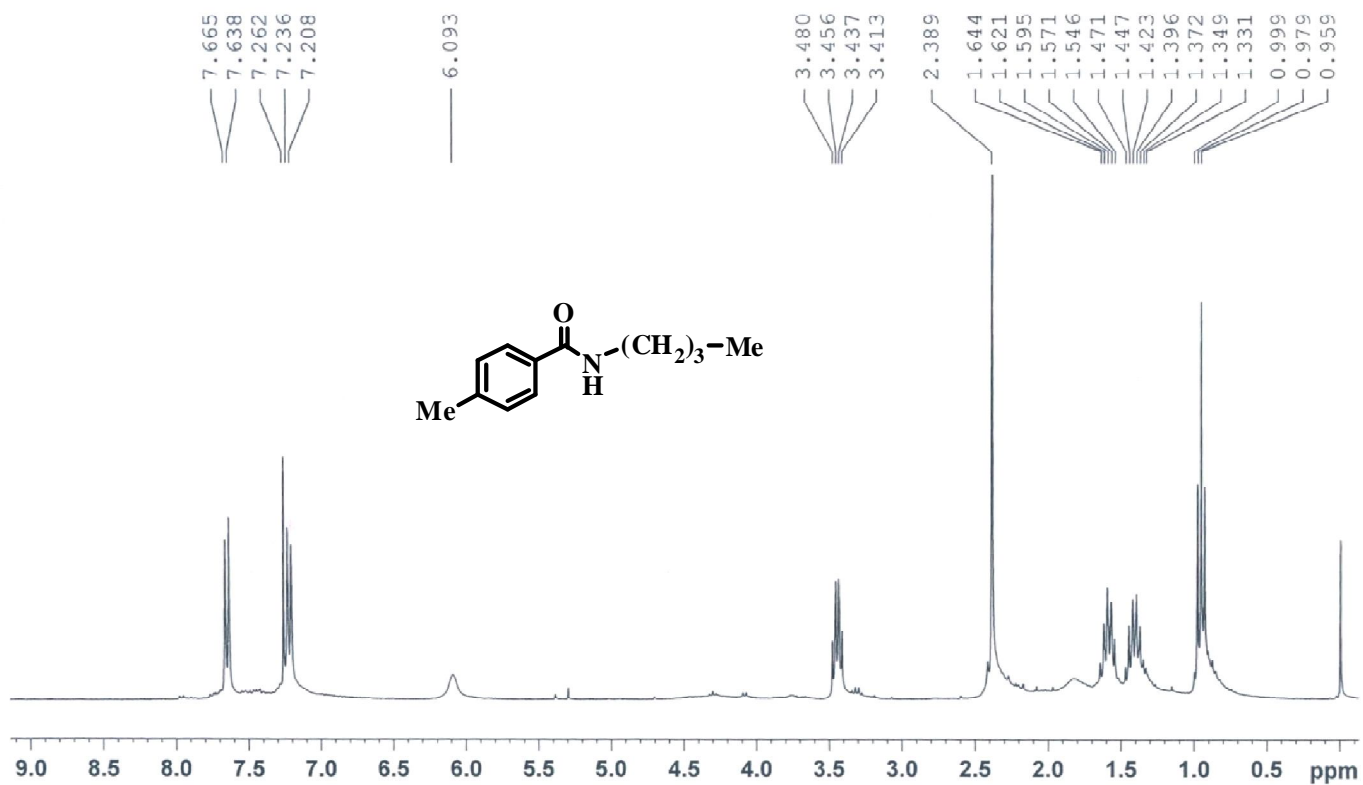
SI Figure 1: ^1H and ^{13}C -NMR spectra of compound 6a



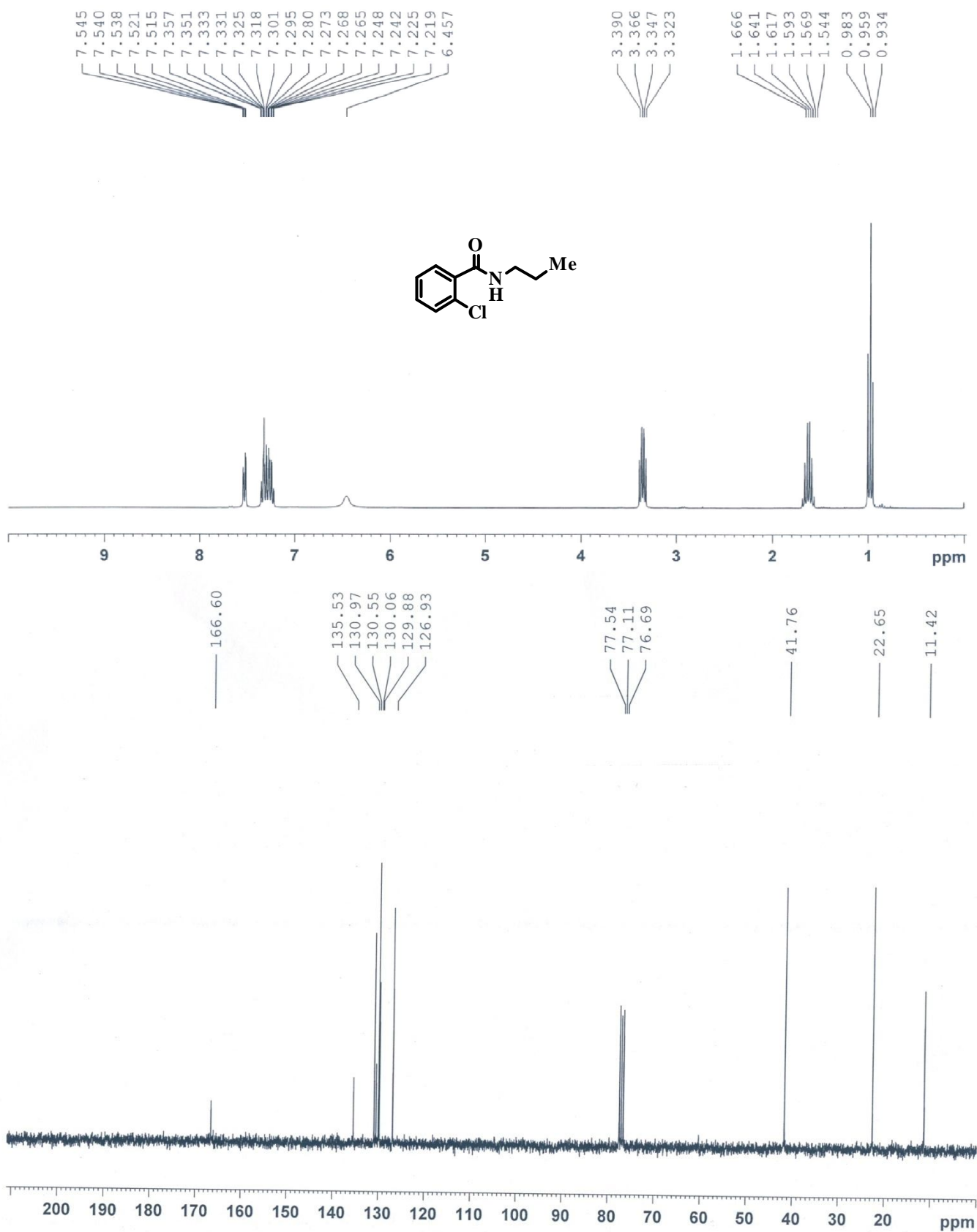
SI Figure 2: ^1H and ^{13}C -NMR spectra of compound **6b**



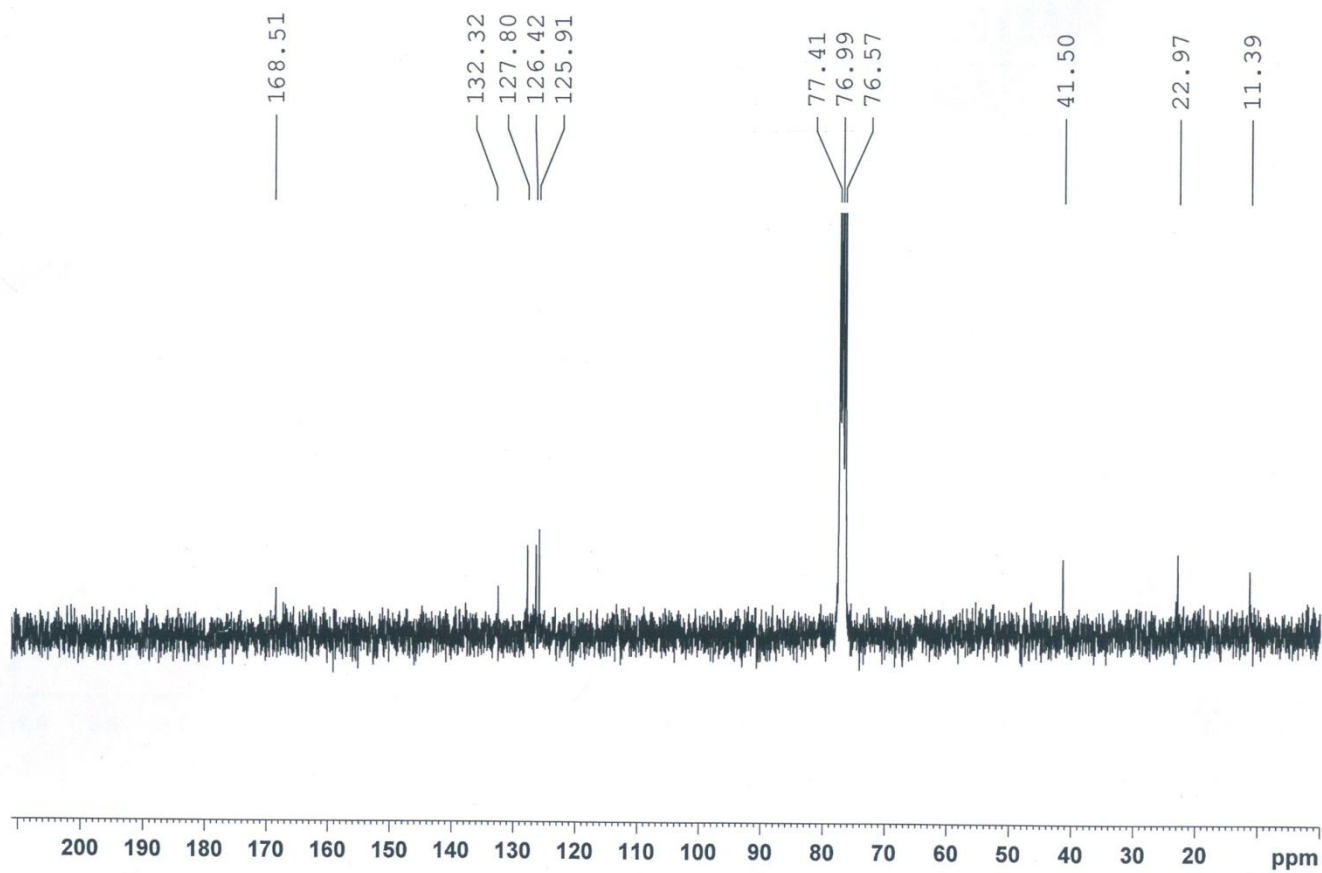
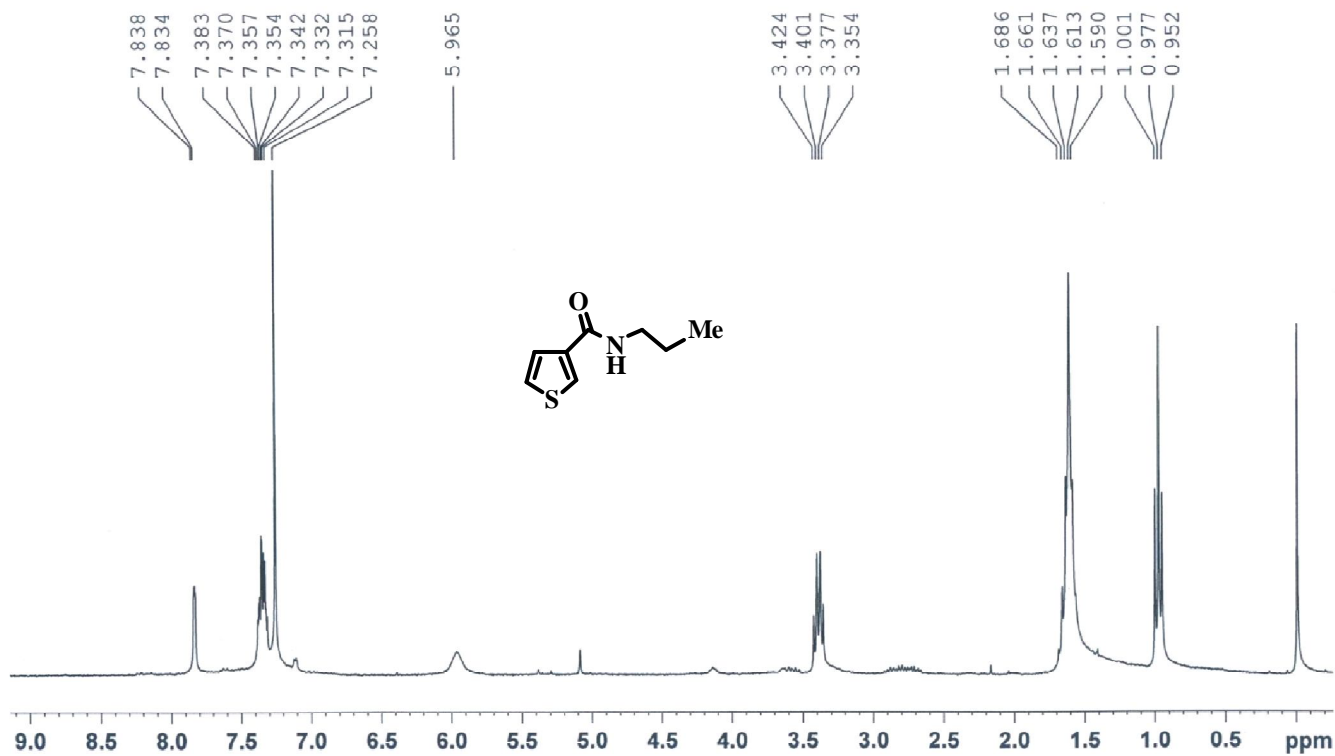
SI Figure 3: ^1H and ^{13}C -NMR spectra of compound **6c**



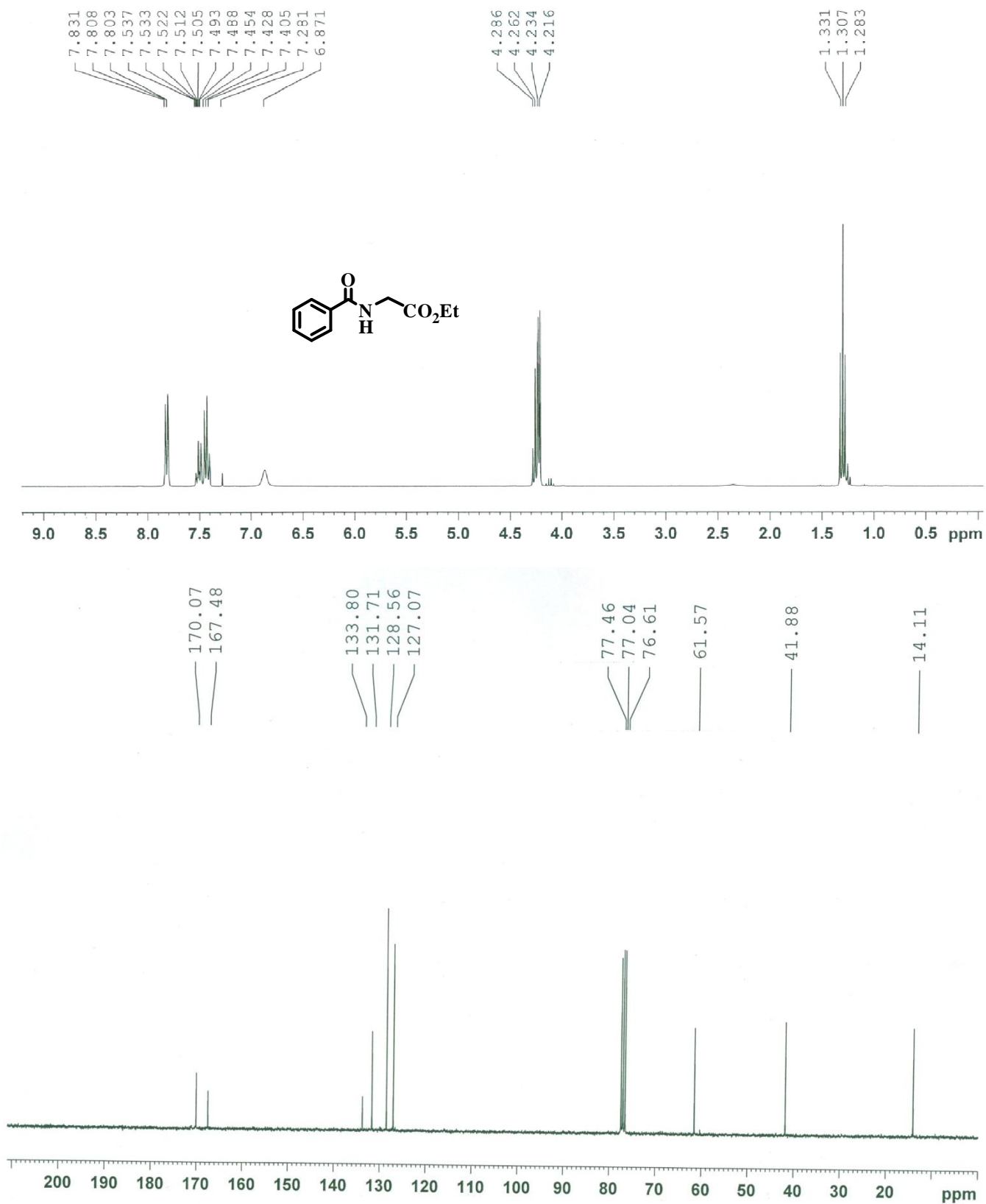
SI Figure 4: ^1H and ^{13}C -NMR spectra of compound **6d**



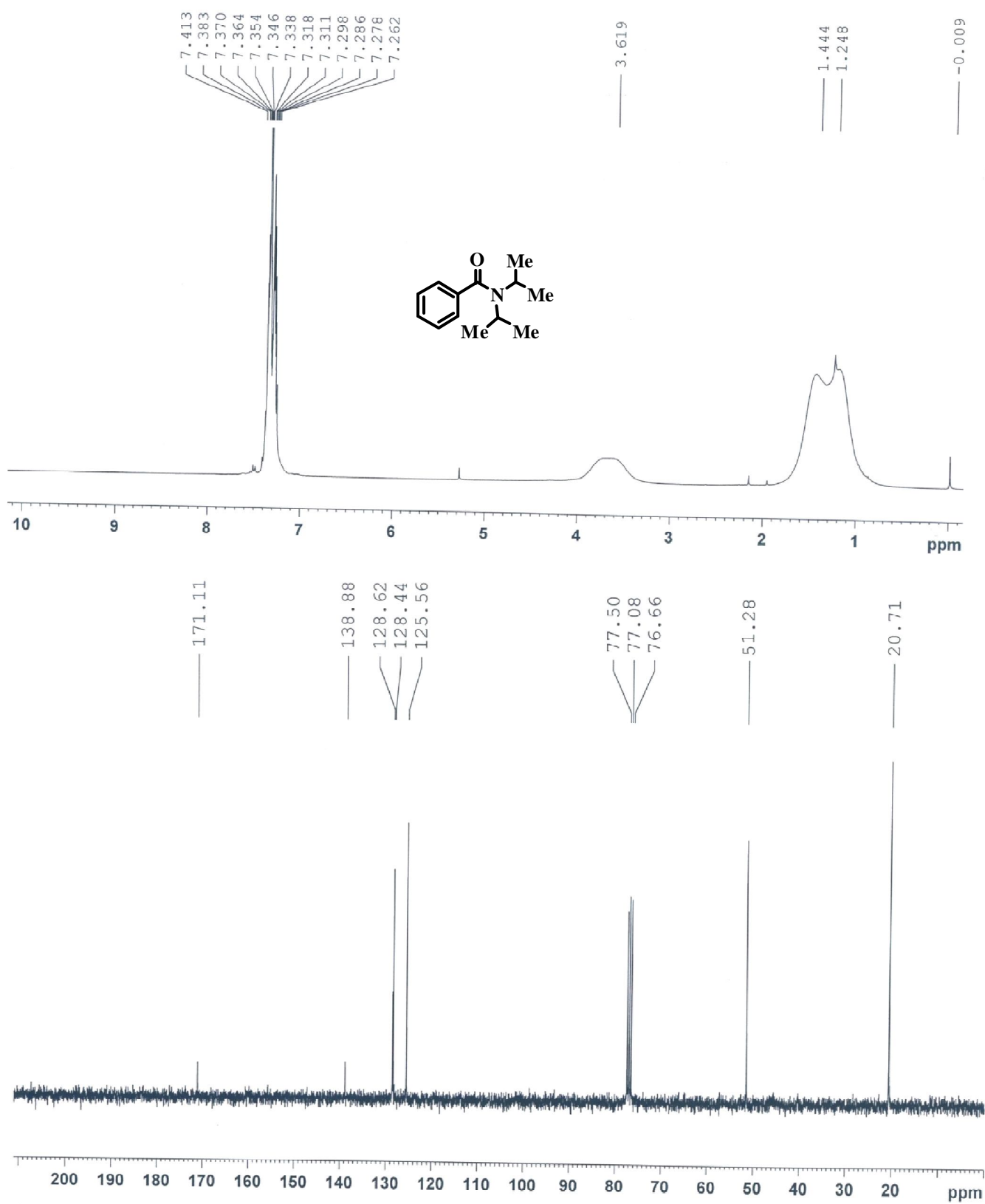
SI Figure 5: ^1H and ^{13}C -NMR spectra of compound **6e**



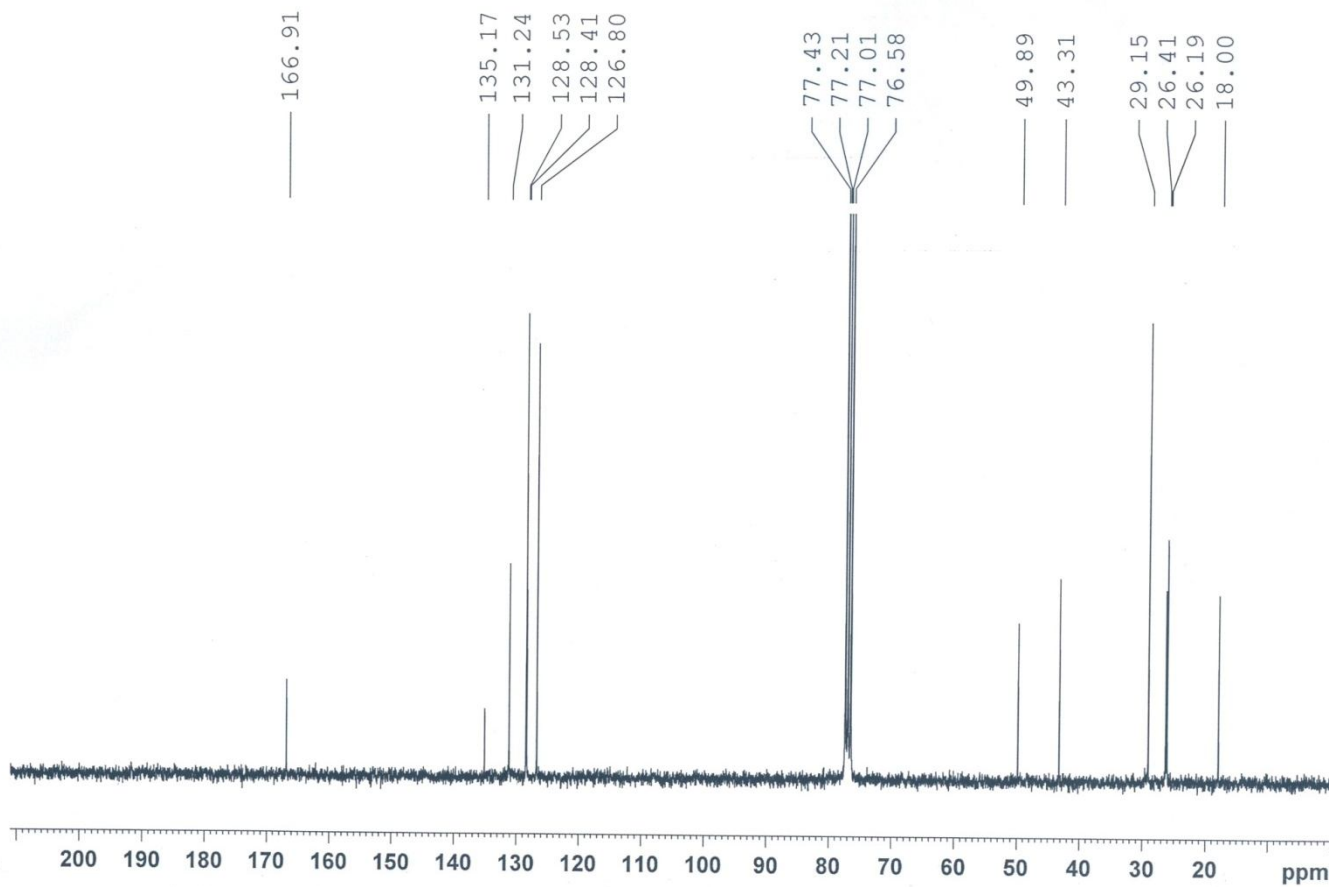
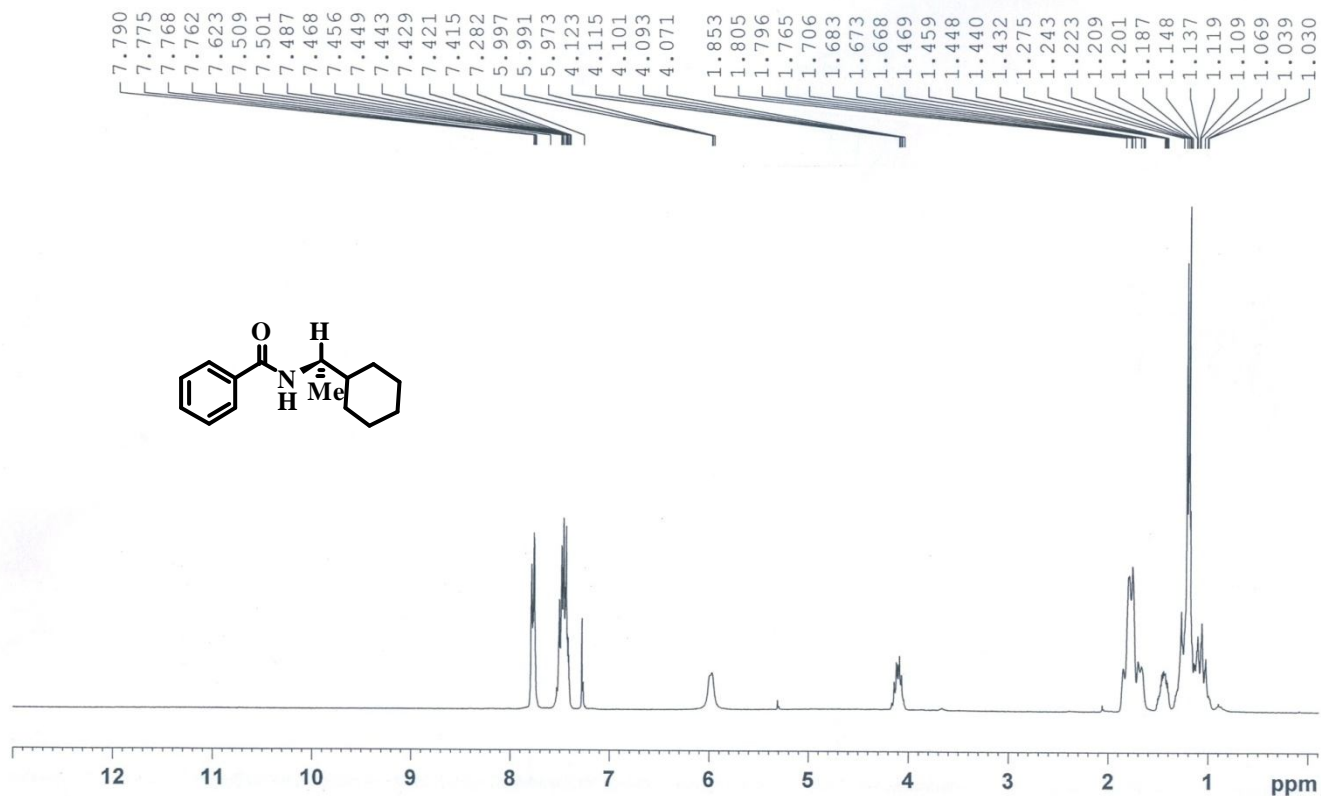
SI Figure 6: ^1H and ^{13}C -NMR spectra of compound **6f**



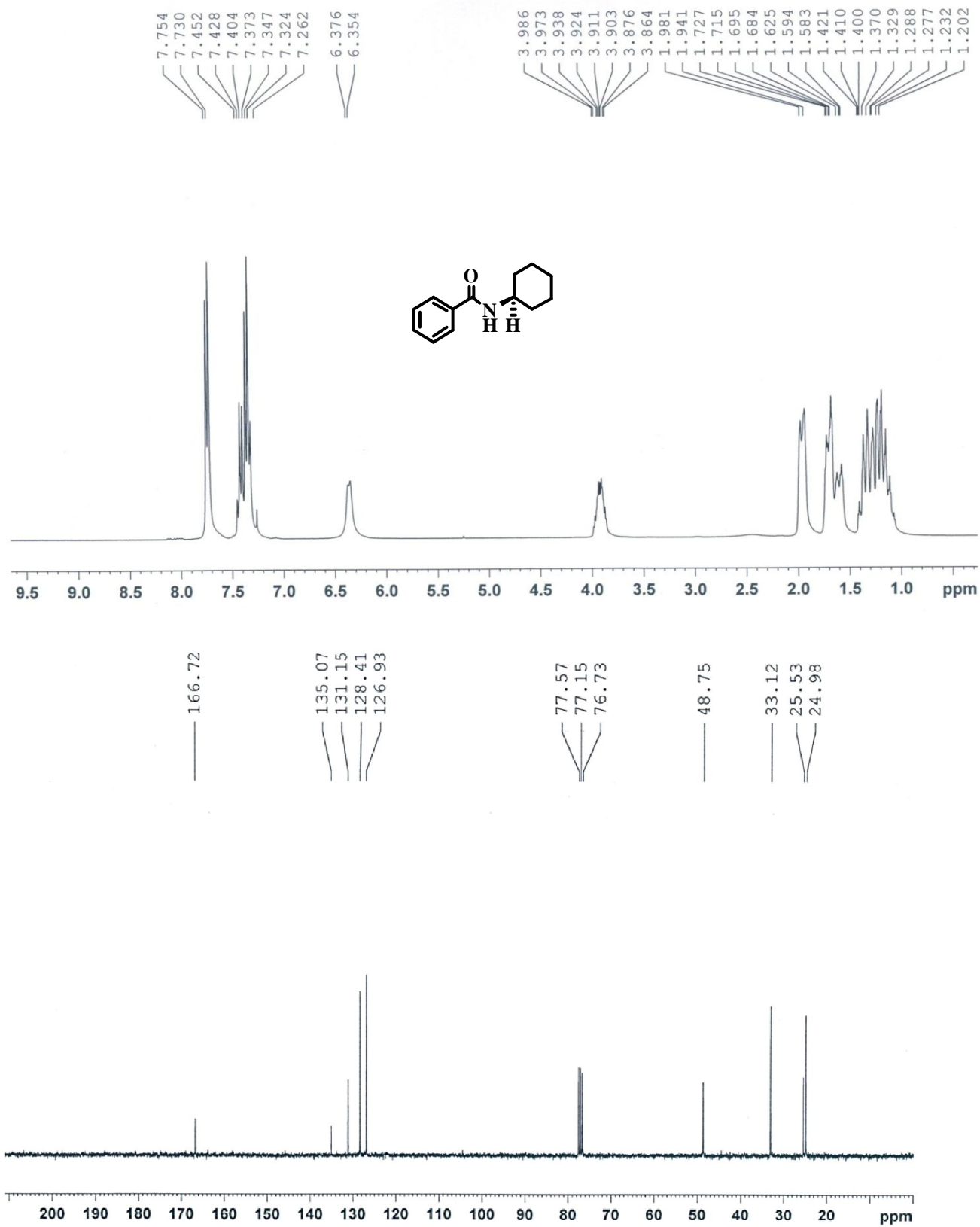
SI Figure 7: ^1H and ^{13}C -NMR spectra of compound **6g**



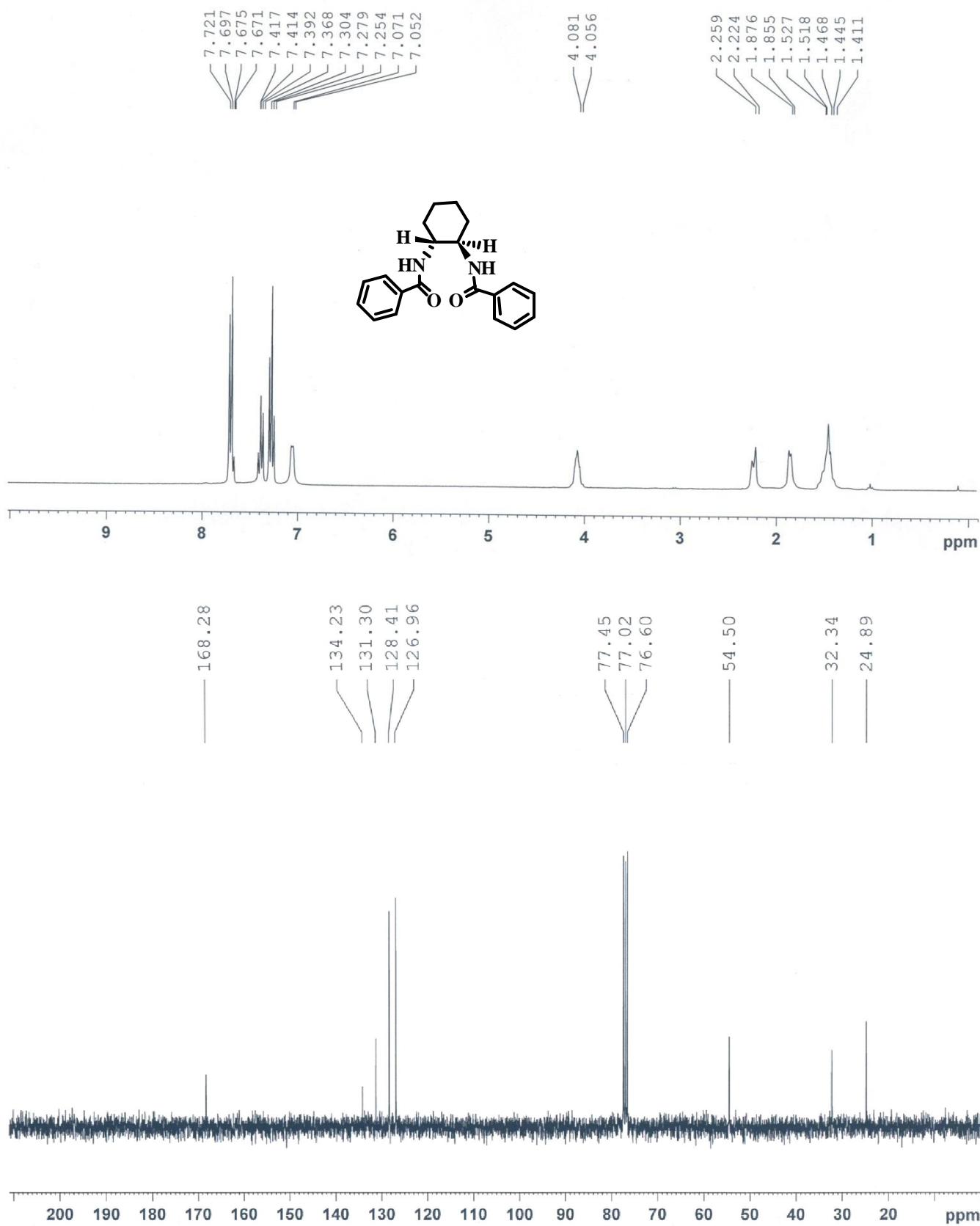
SI Figure 8: ^1H and ^{13}C -NMR spectra of compound **6h**



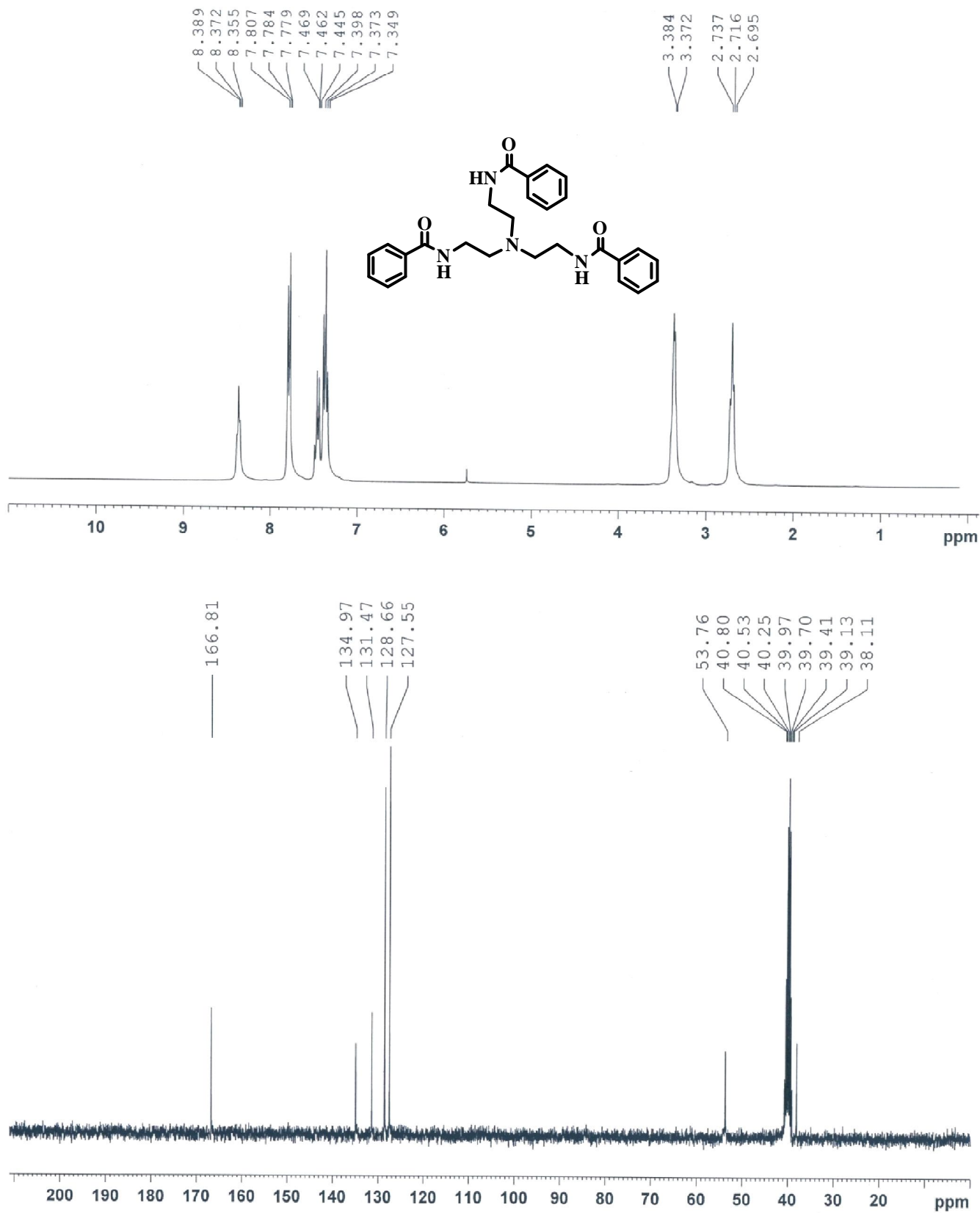
SI Figure 9: ^1H and ^{13}C -NMR spectra of compound **6i**



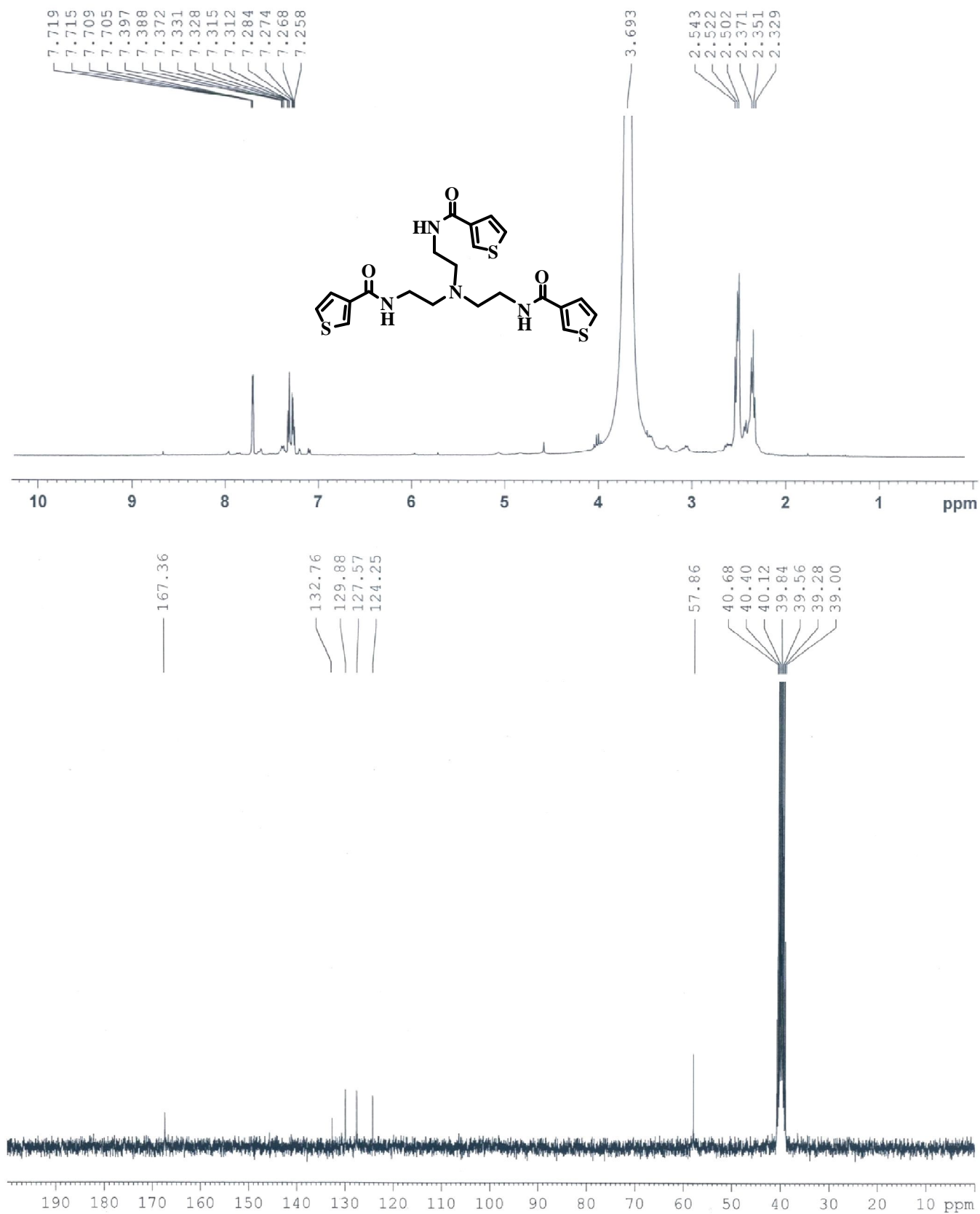
SI Figure 10: ^1H and ^{13}C -NMR spectra of compound **6j**

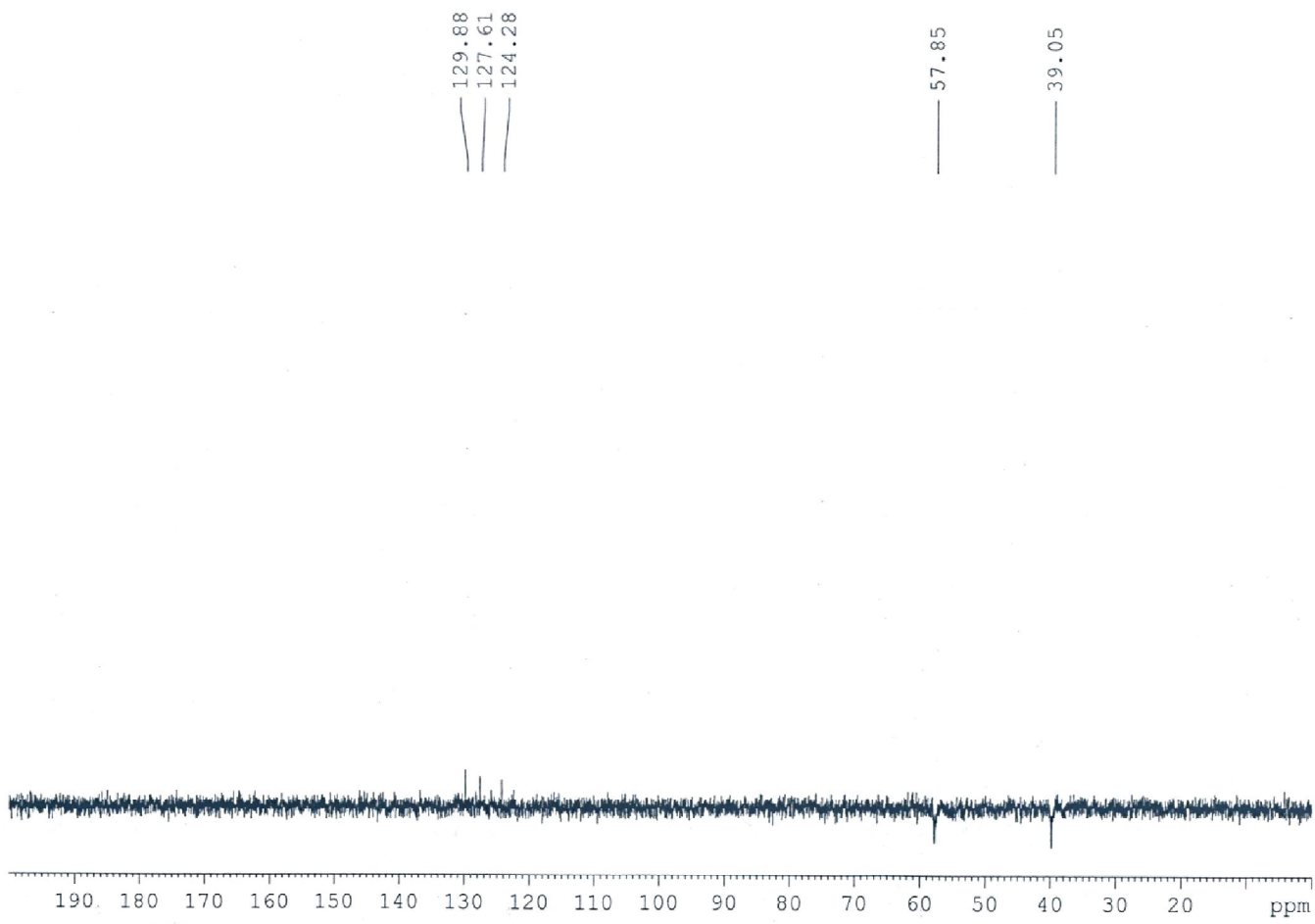


SI Figure 11: ^1H and ^{13}C -NMR spectra of compound 6k

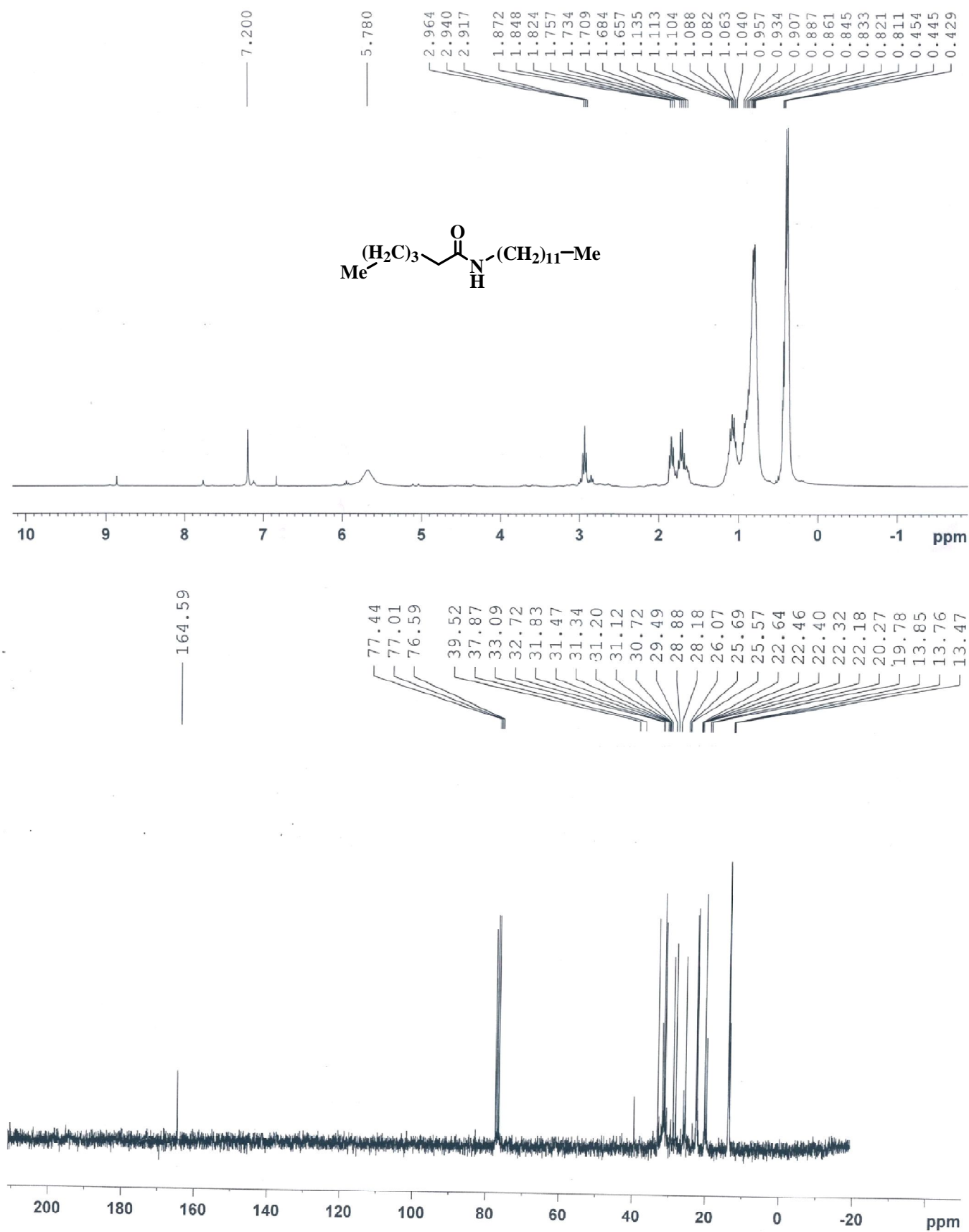


SI Figure 12: ^1H and ^{13}C and DEPT-135 NMR spectra of compound **6l**

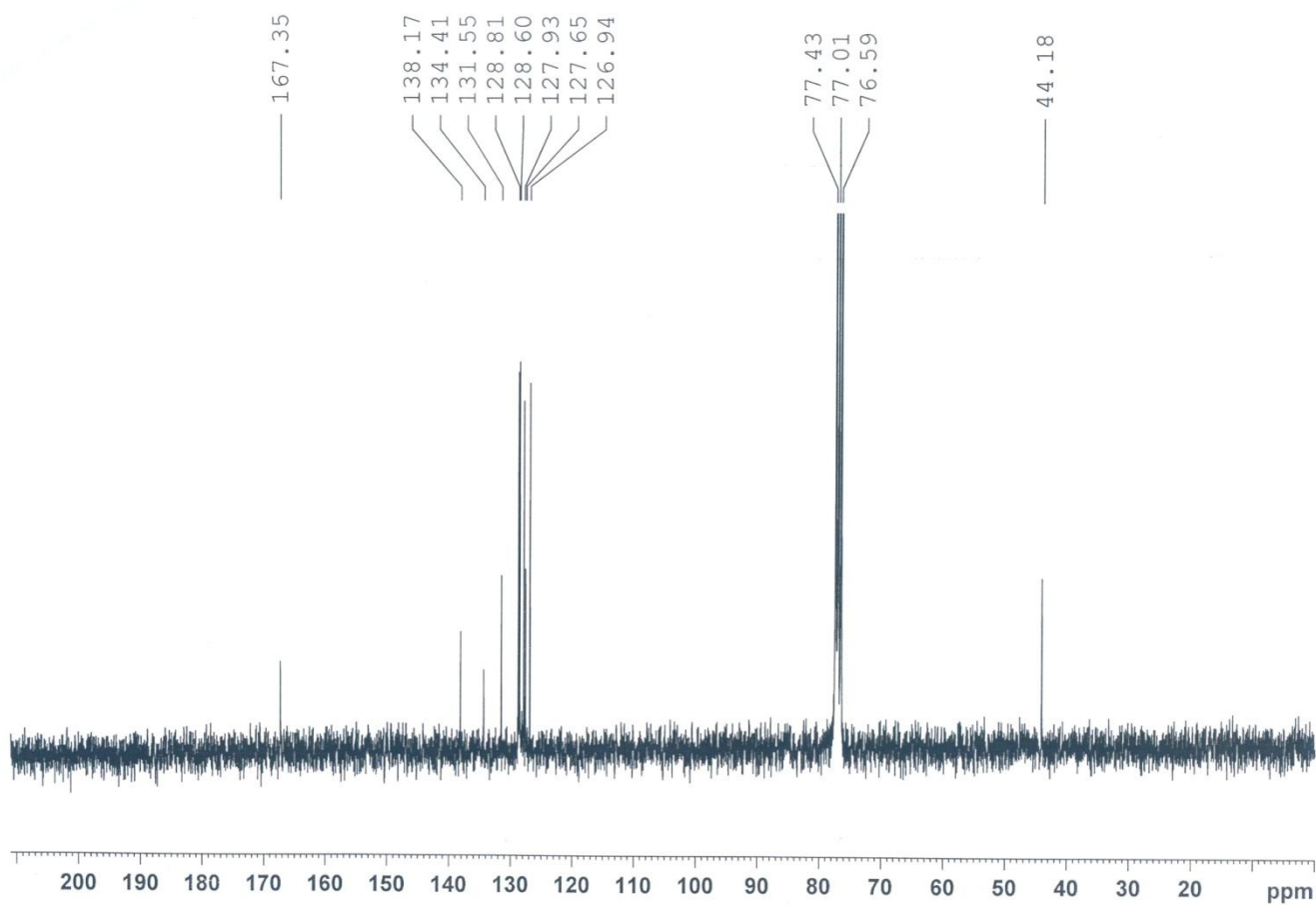
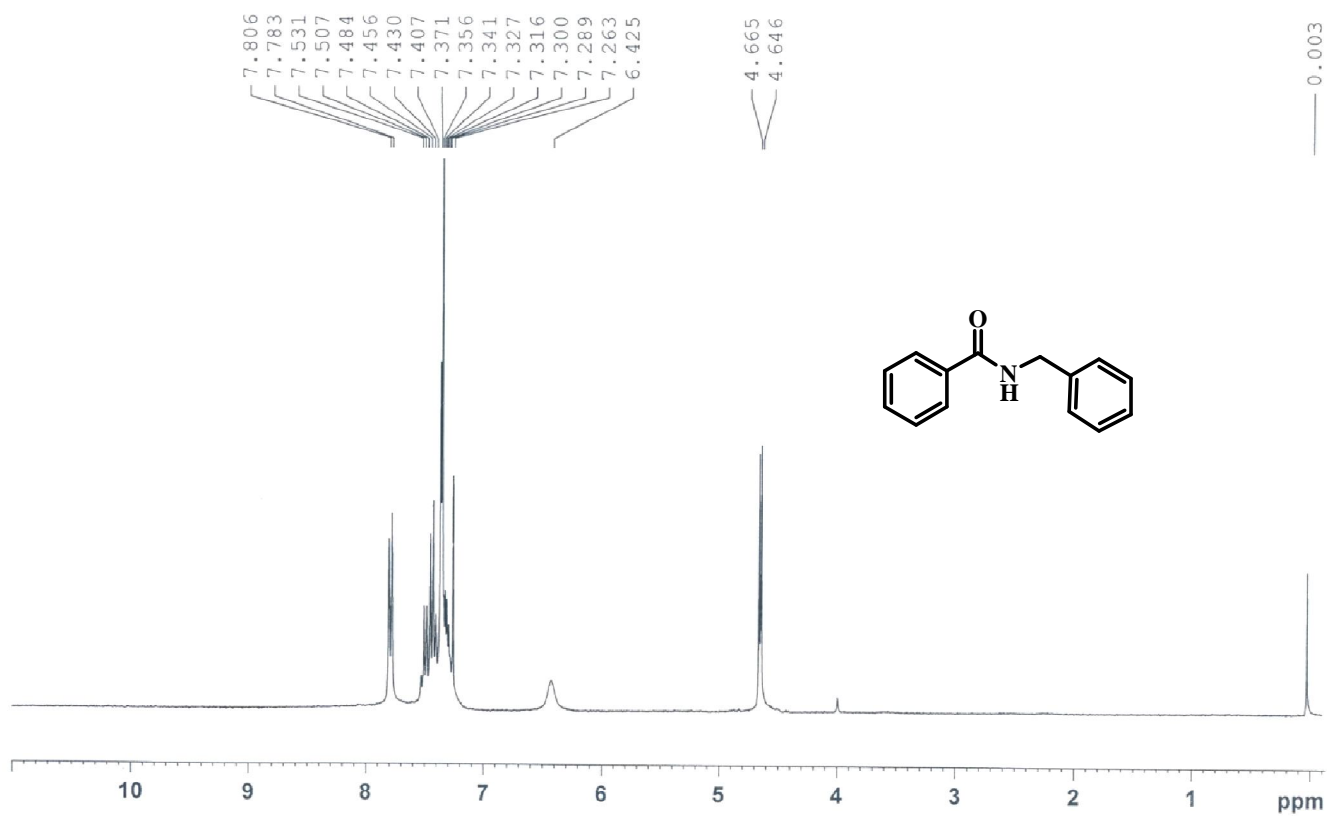




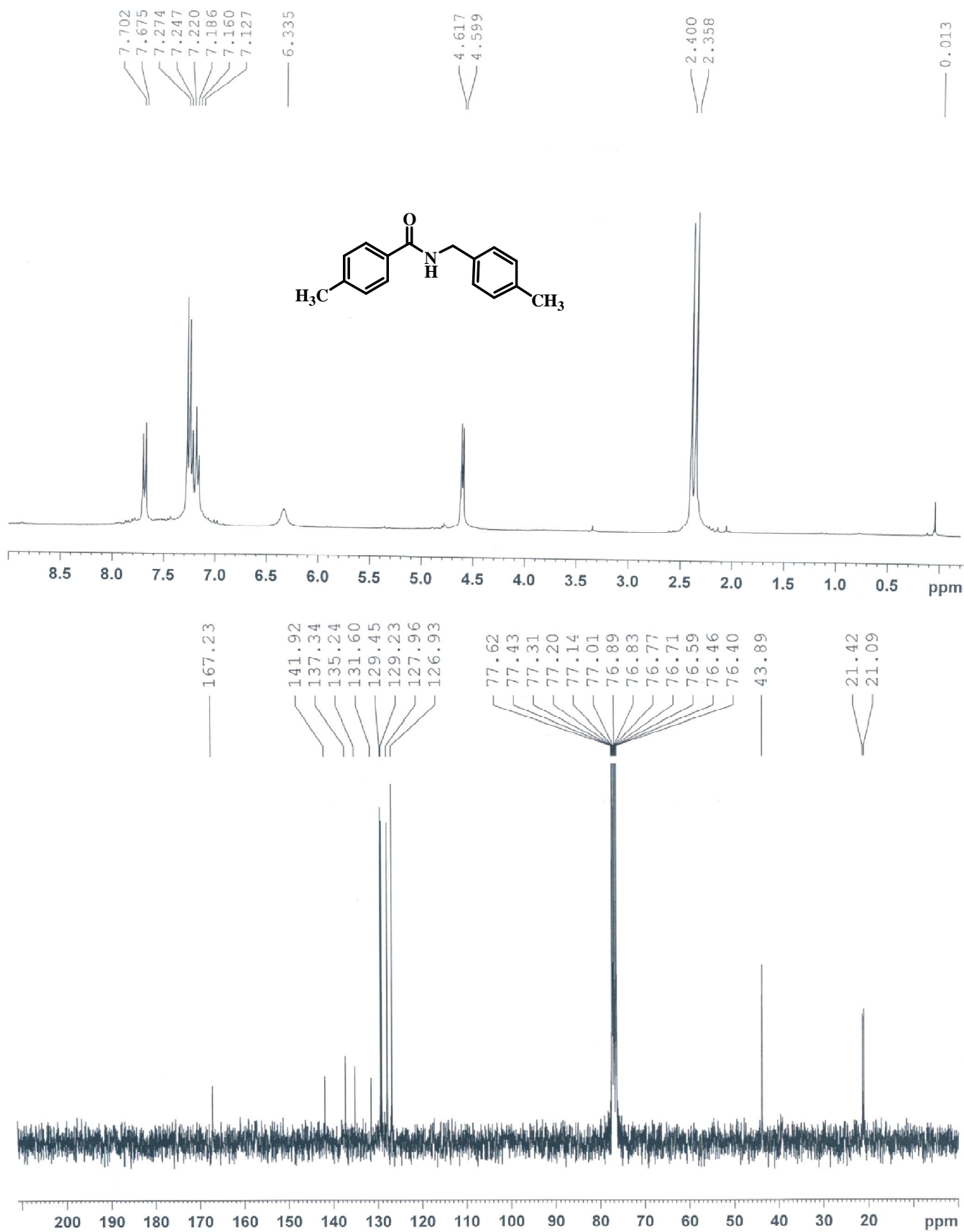
SI Figure 13: ^1H and ^{13}C -NMR spectra of compound **6m**



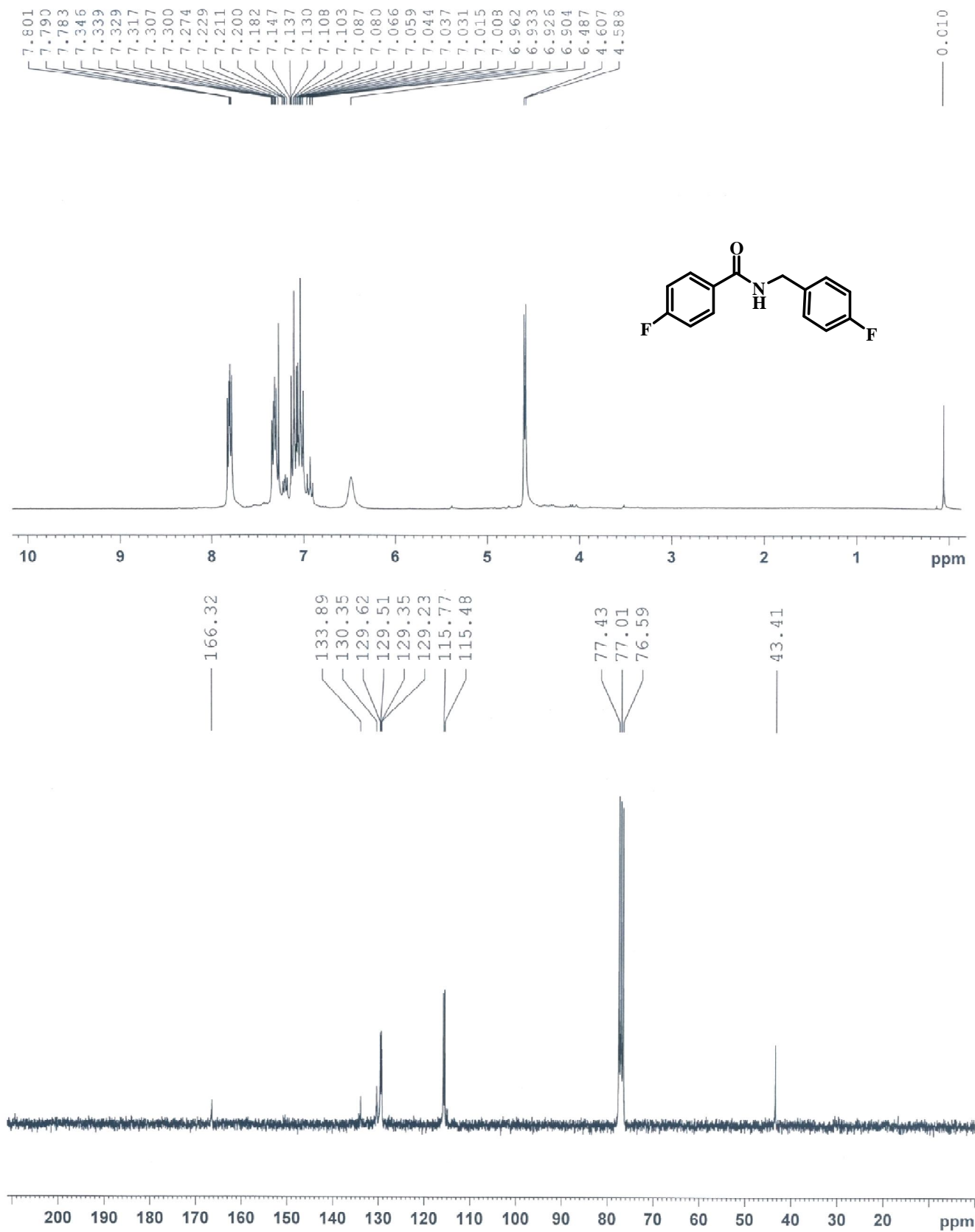
SI Figure 14: ^1H and ^{13}C -NMR spectra of compound **8a**



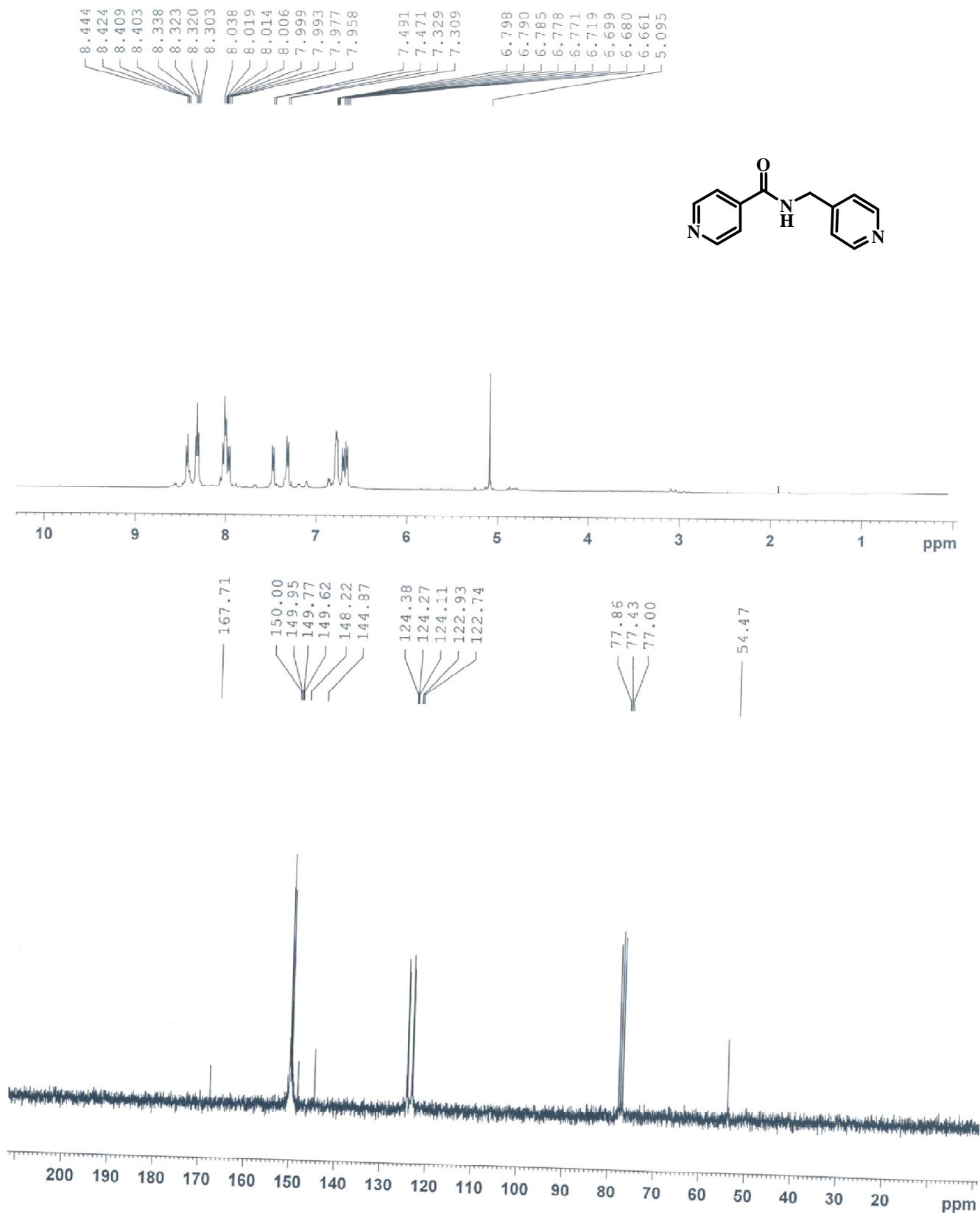
SI Figure 15: ^1H and ^{13}C -NMR spectra of compound **8b**



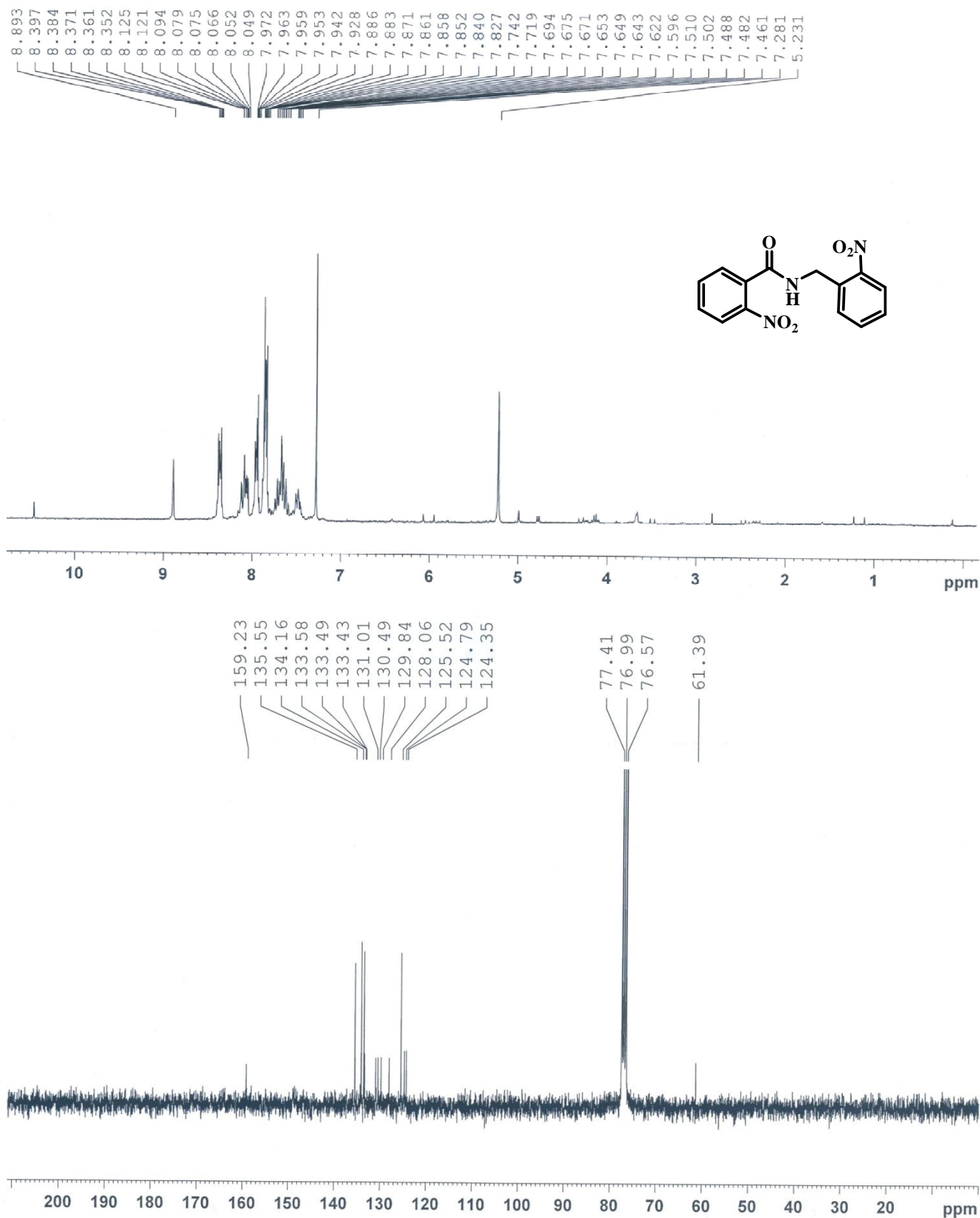
SI Figure 16: ^1H and ^{13}C -NMR spectra of compound **8c**



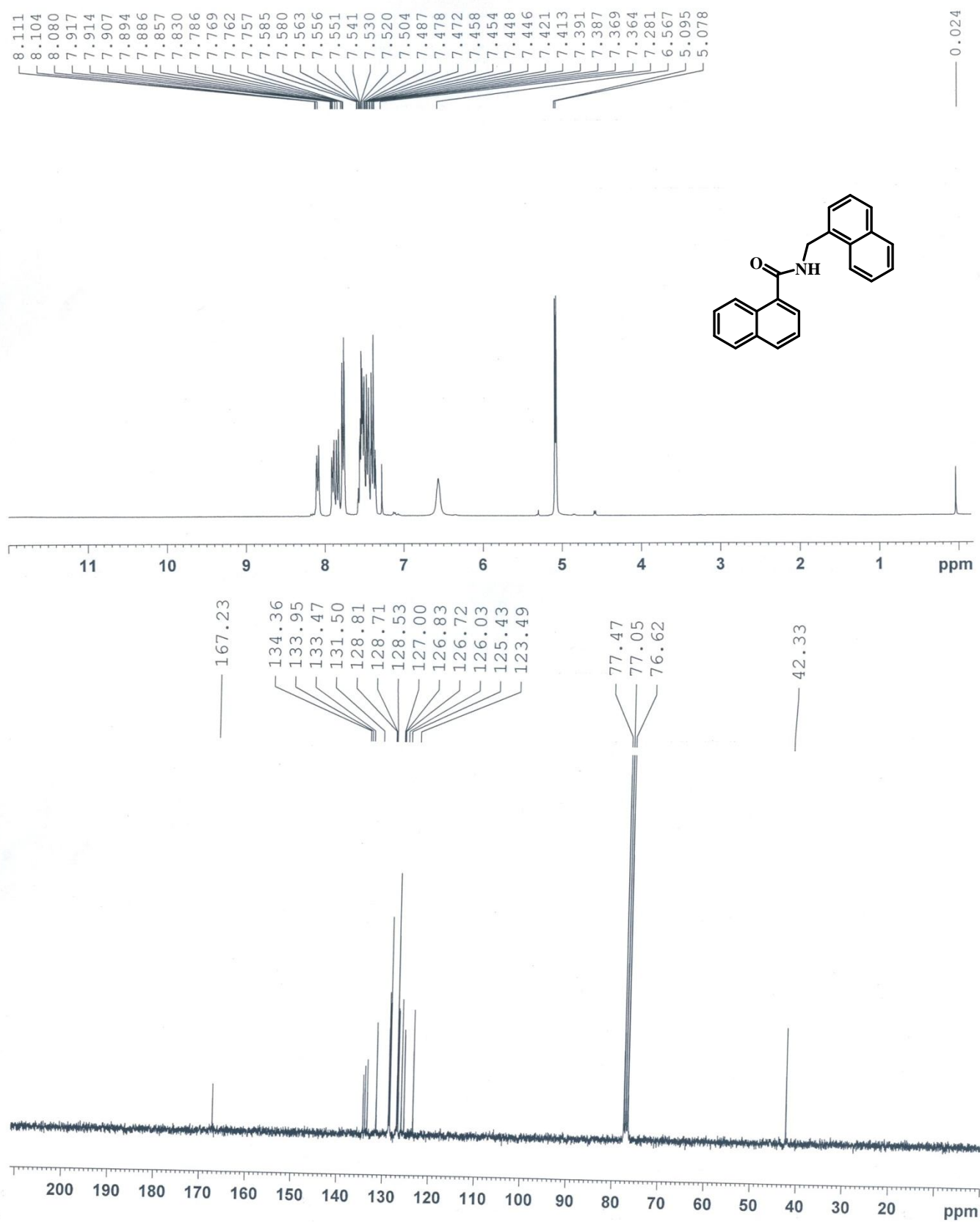
SI Figure 17: ^1H and ^{13}C -NMR spectra of compound **8d**



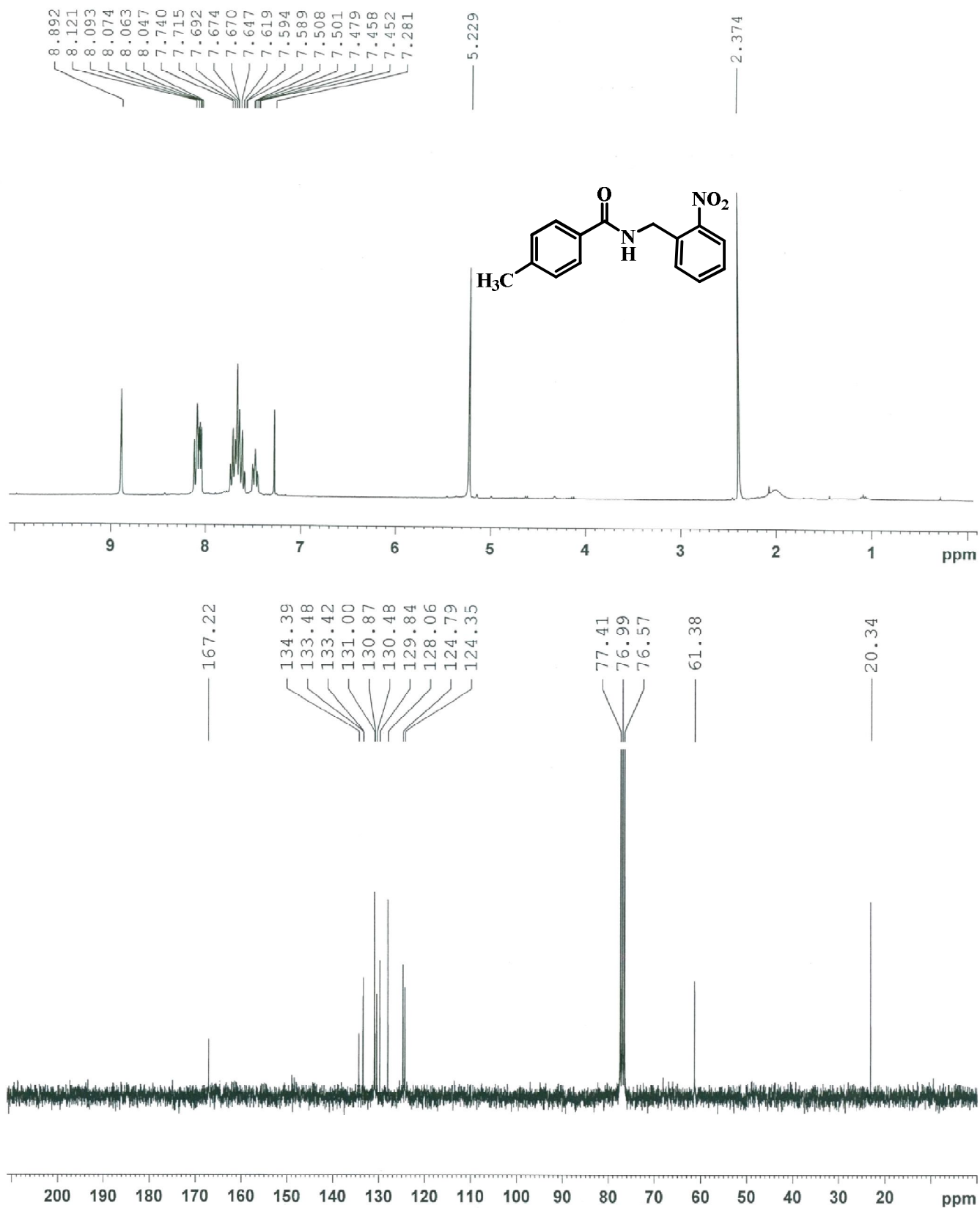
SI Figure 18: ^1H and ^{13}C -NMR spectra of compound **8e**



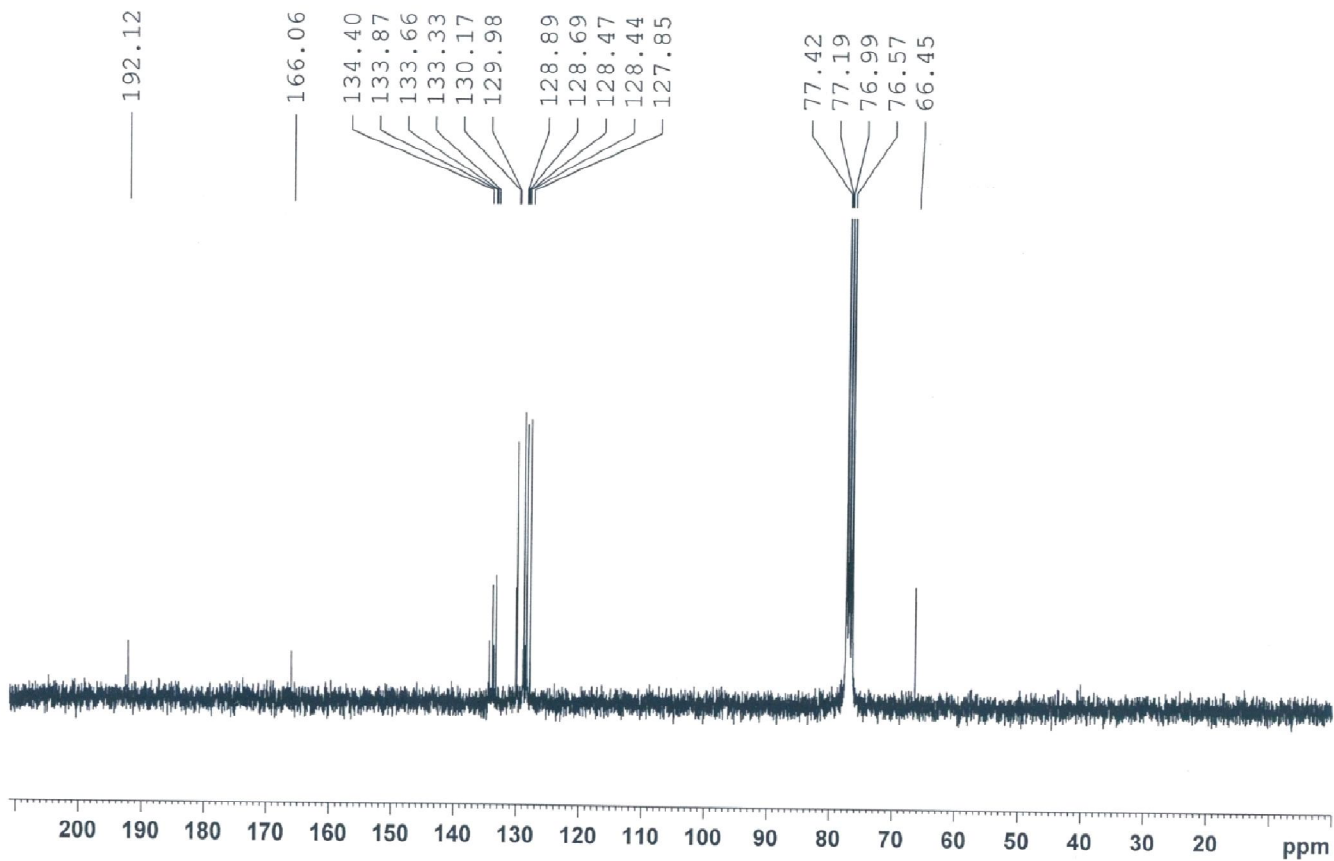
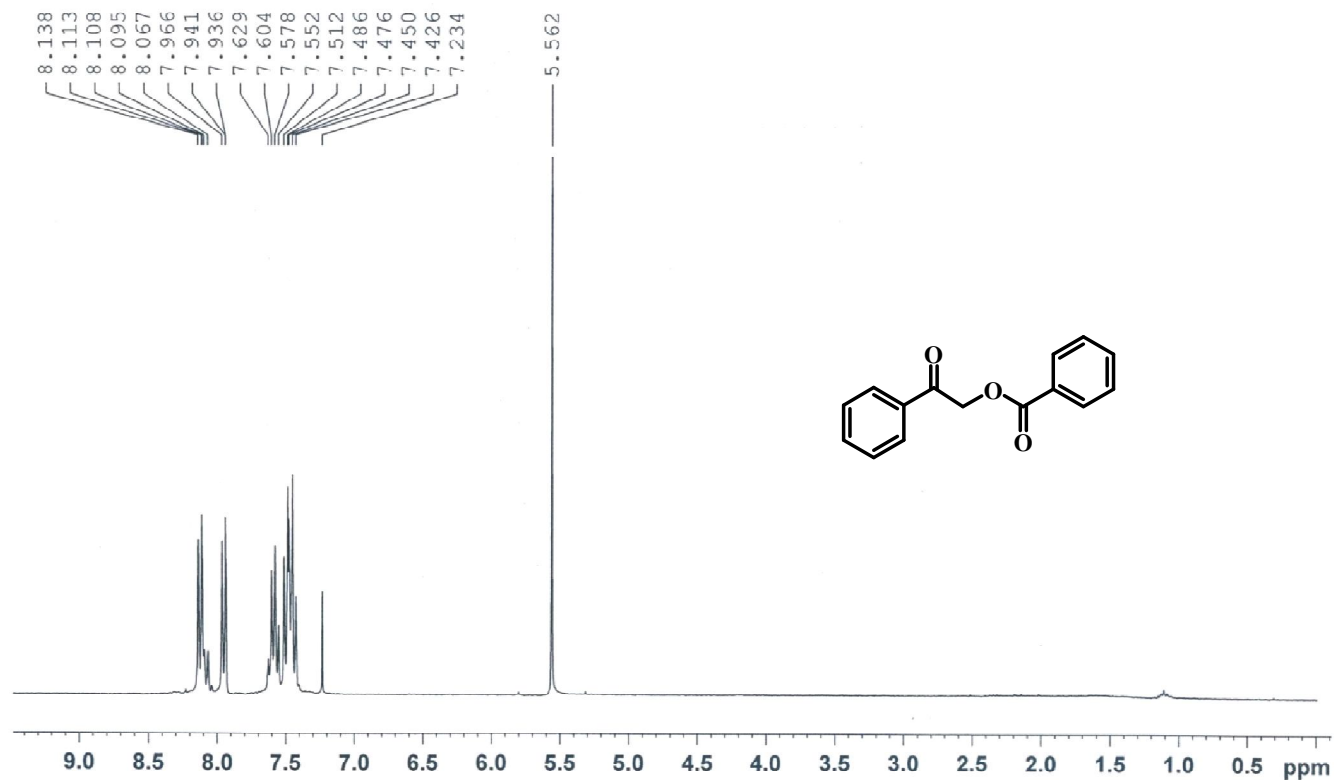
SI Figure 19: ^1H and ^{13}C -NMR spectra of compound **8f**



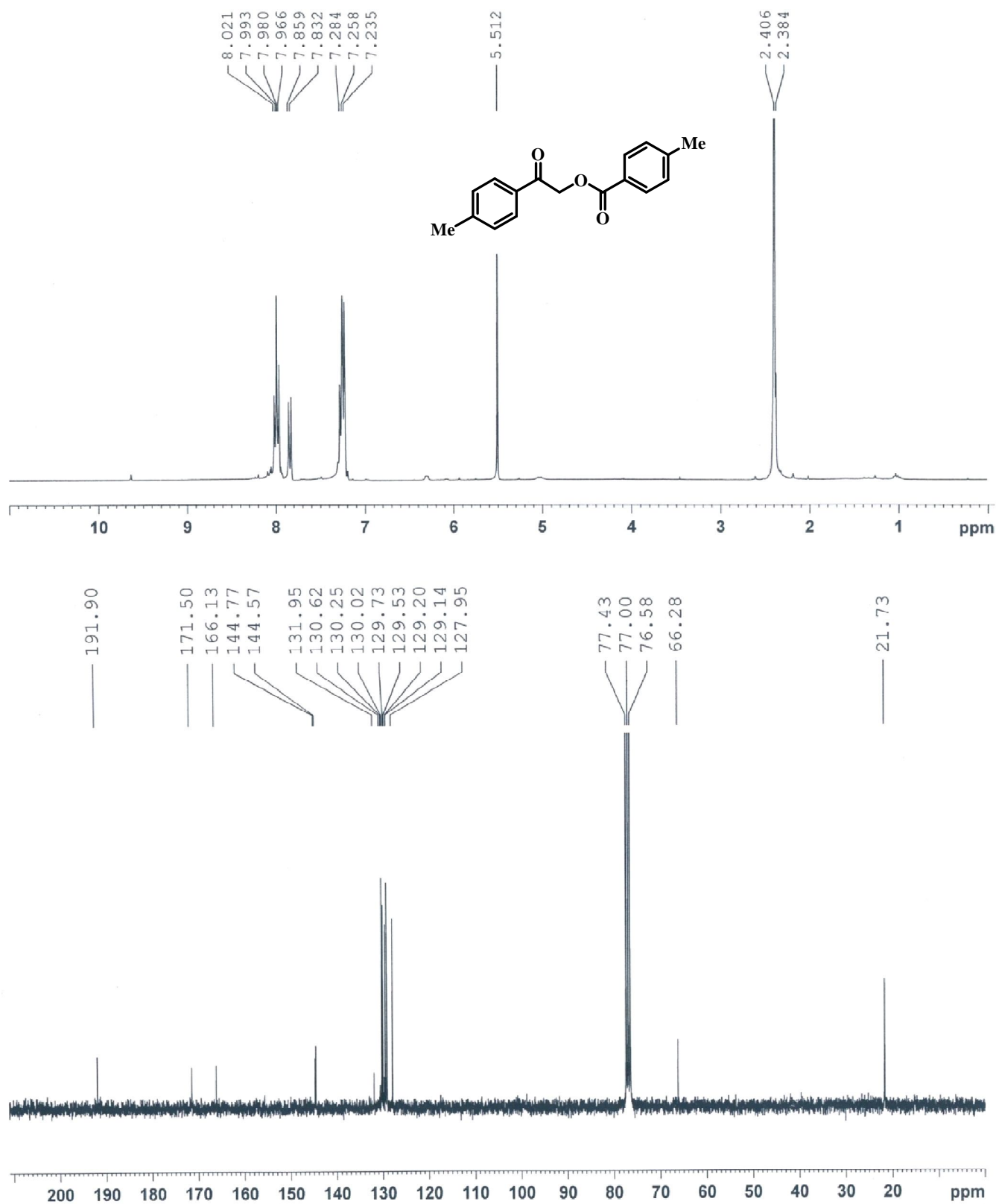
SI Figure 20: ^1H and ^{13}C -NMR spectra of compound **8g**



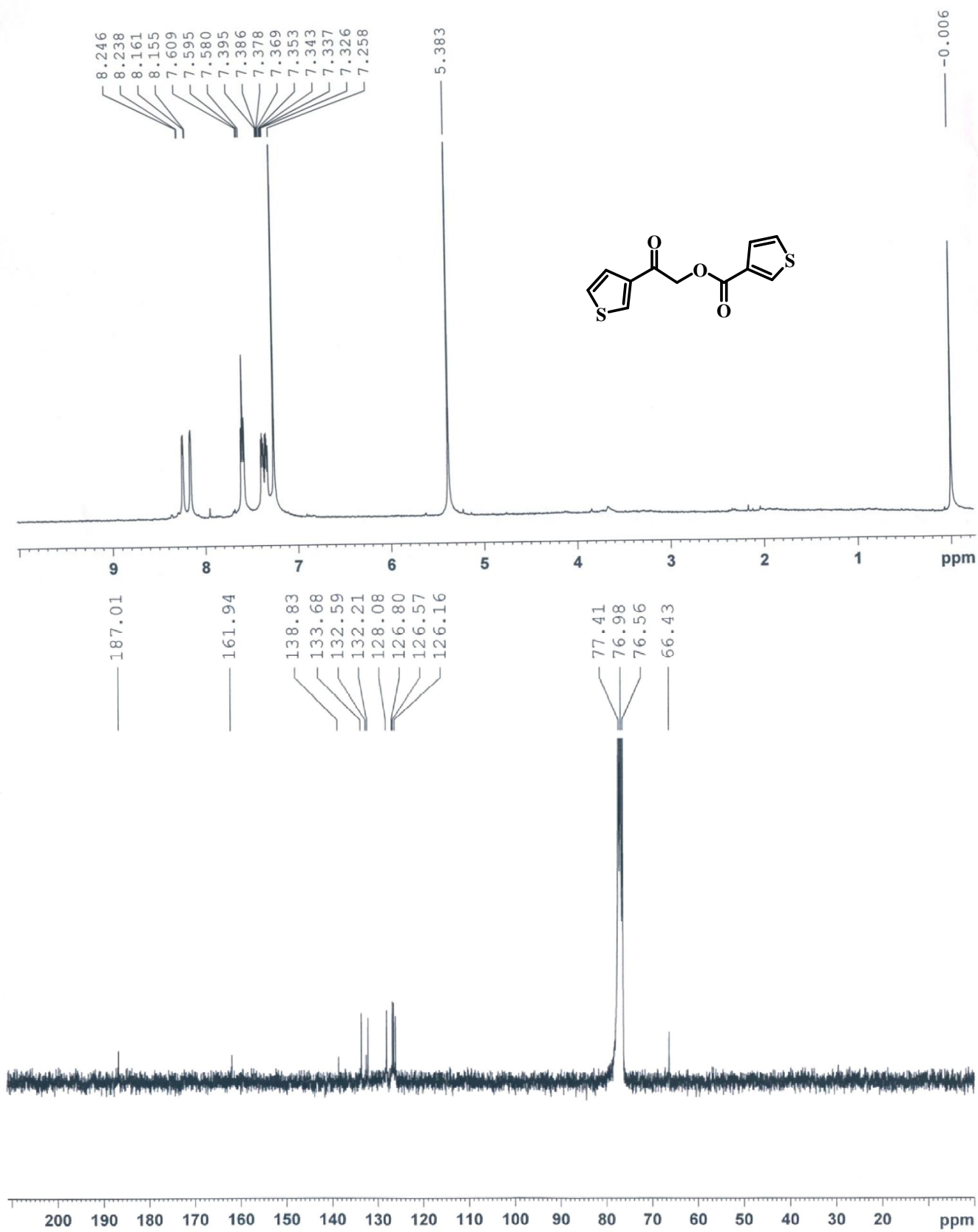
SI Figure 21: ^1H and ^{13}C -NMR spectra of compound **9a**



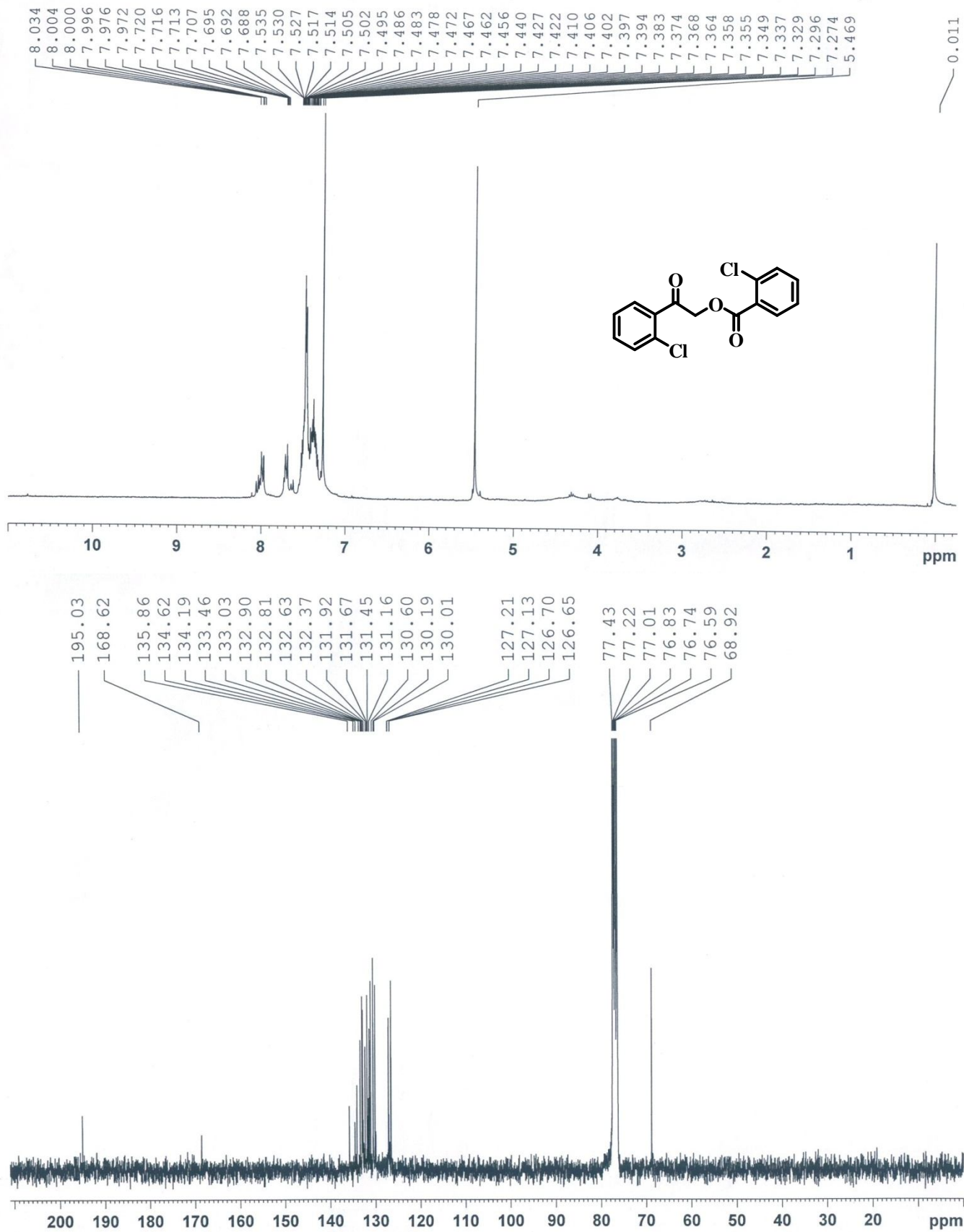
SI Figure 22: ^1H and ^{13}C -NMR spectra of compound **9b**



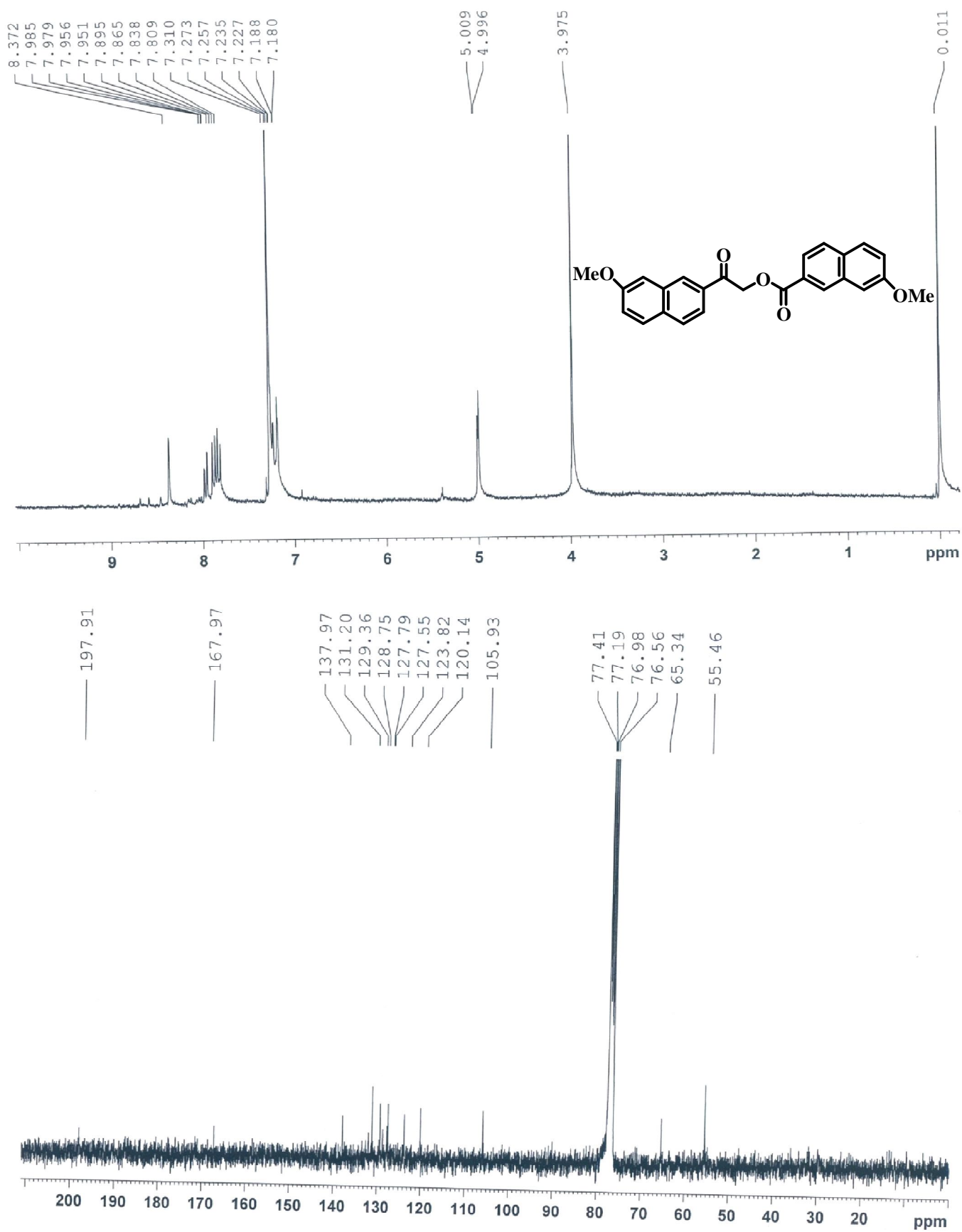
SI Figure 23: ^1H and ^{13}C -NMR spectra of compound **9c**



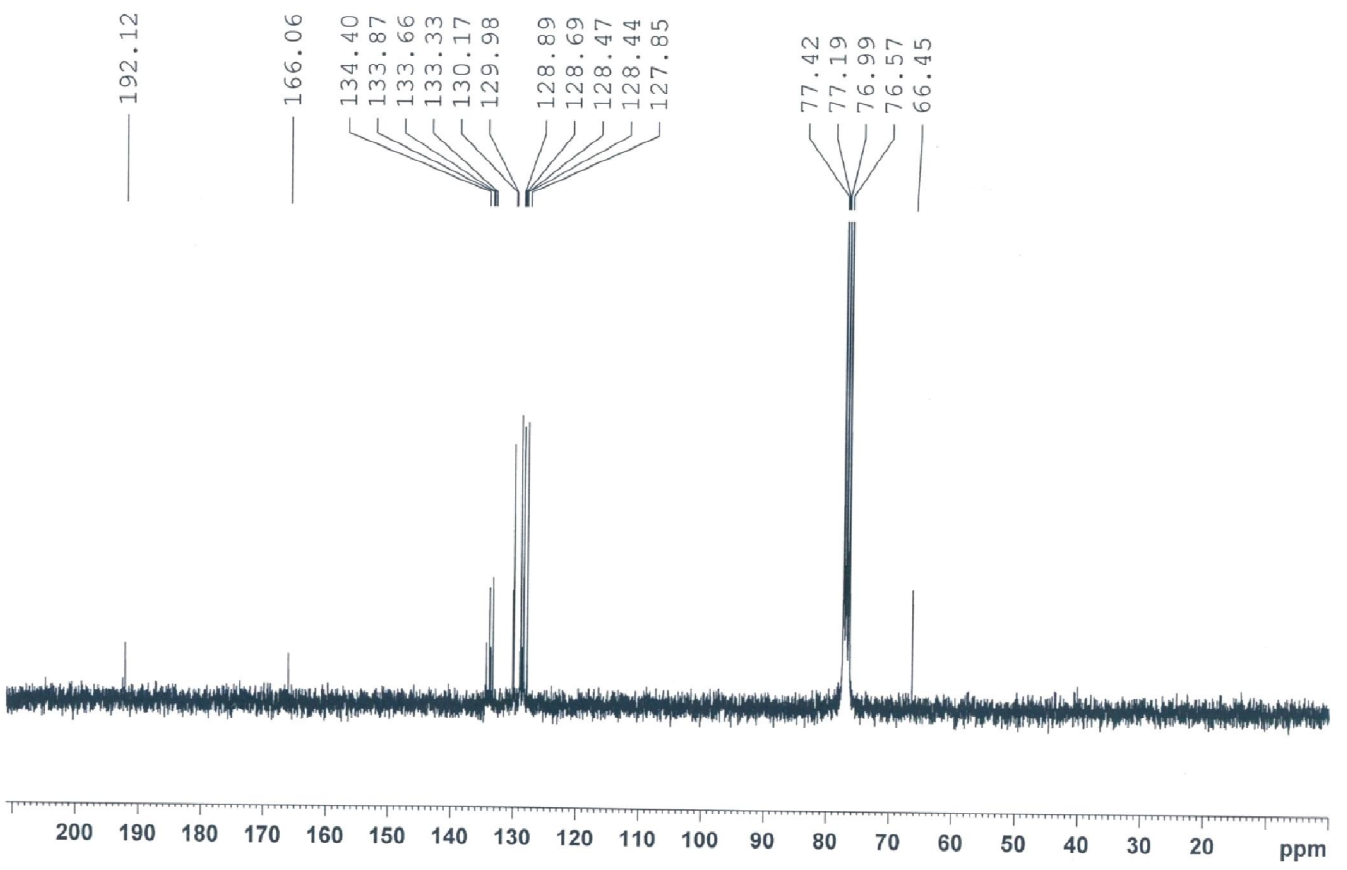
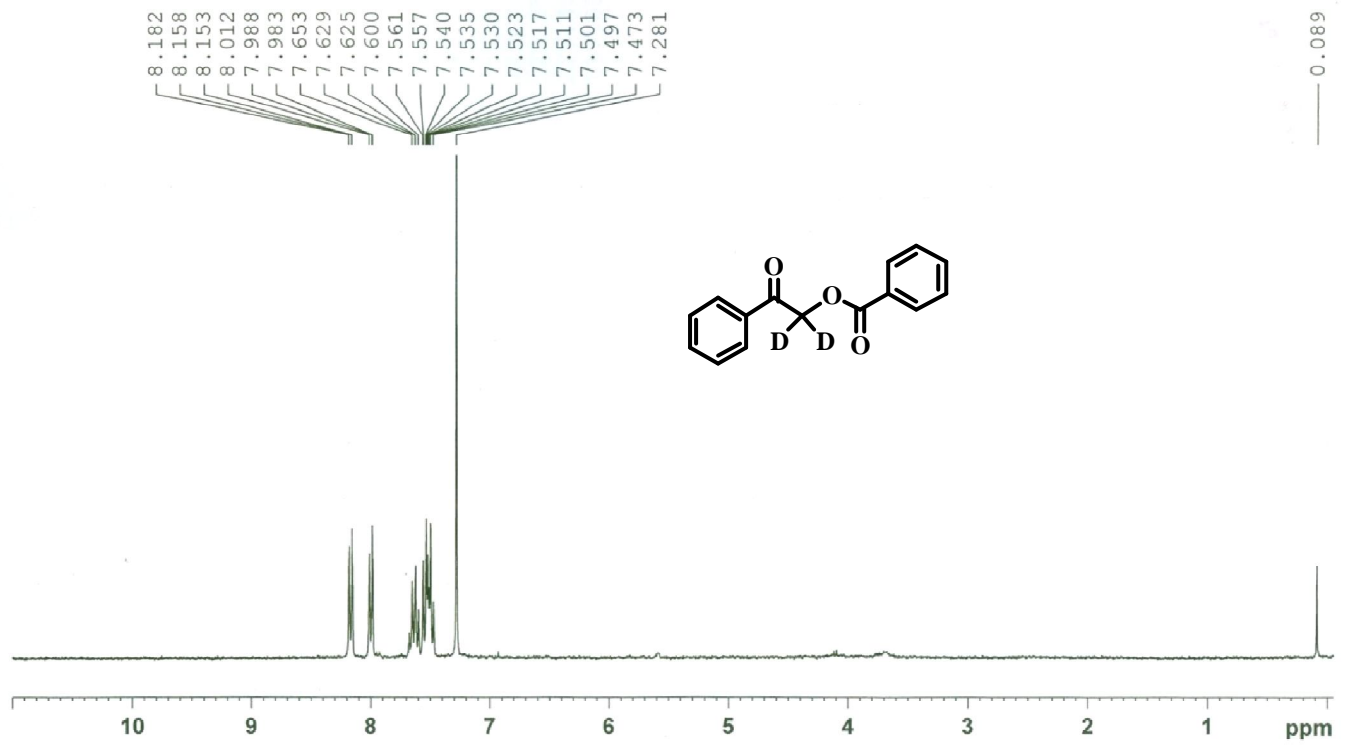
SI Figure 24: ^1H and ^{13}C -NMR spectra of compound **9d**



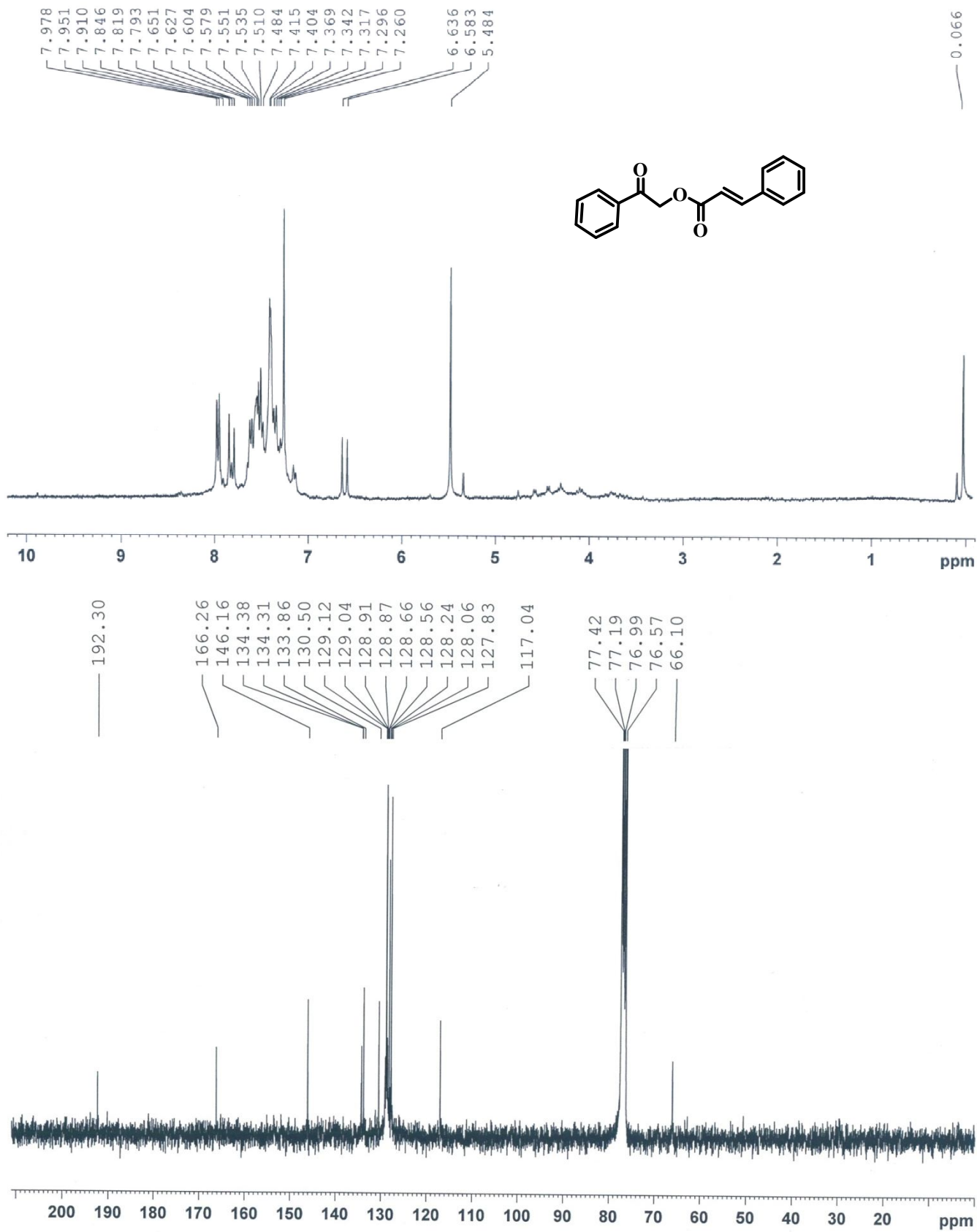
SI Figure 25: ^1H and ^{13}C -NMR spectra of compound **9e**



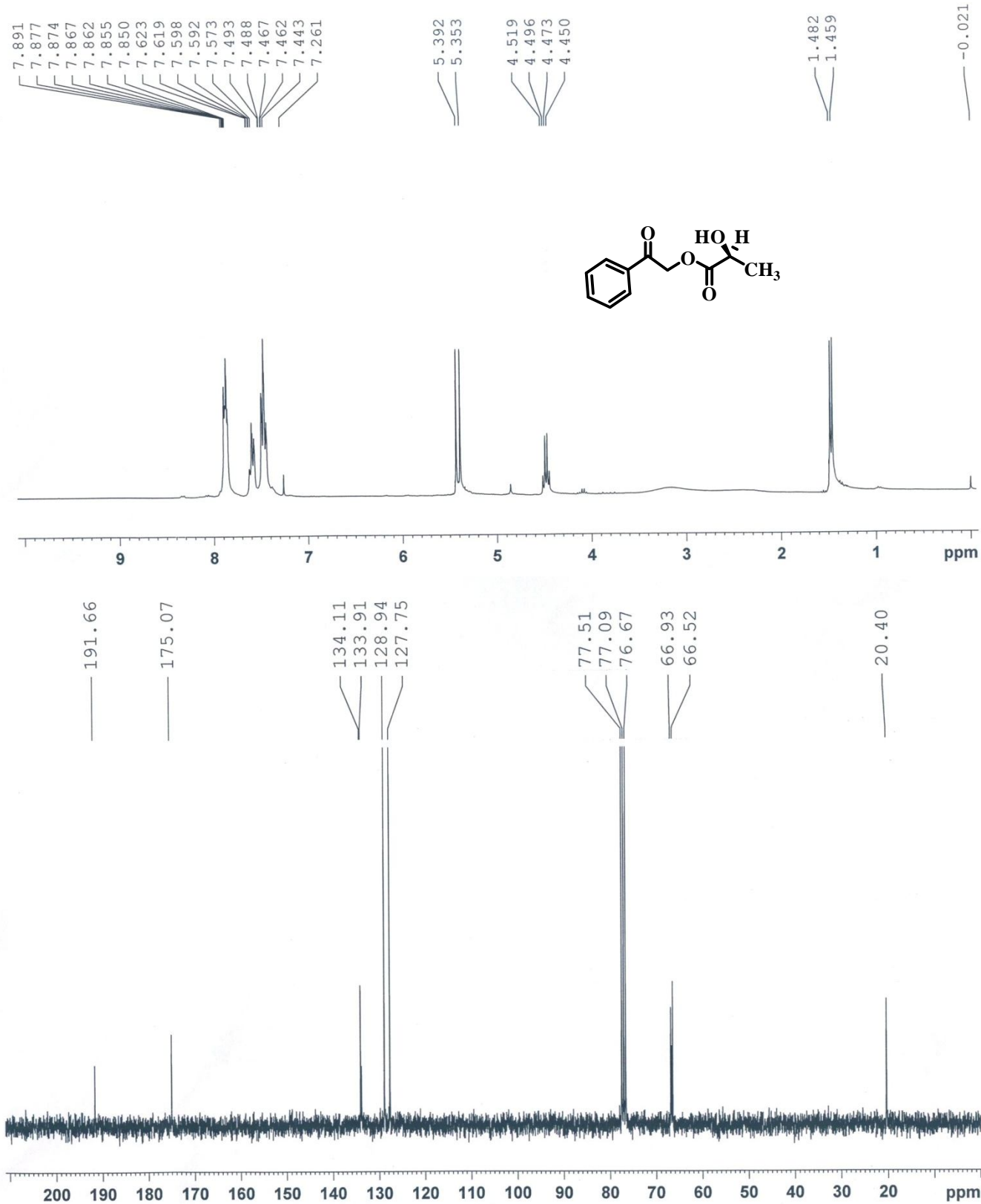
SI Figure 26: ^1H and ^{13}C -NMR spectra of compound **D₂-9a**



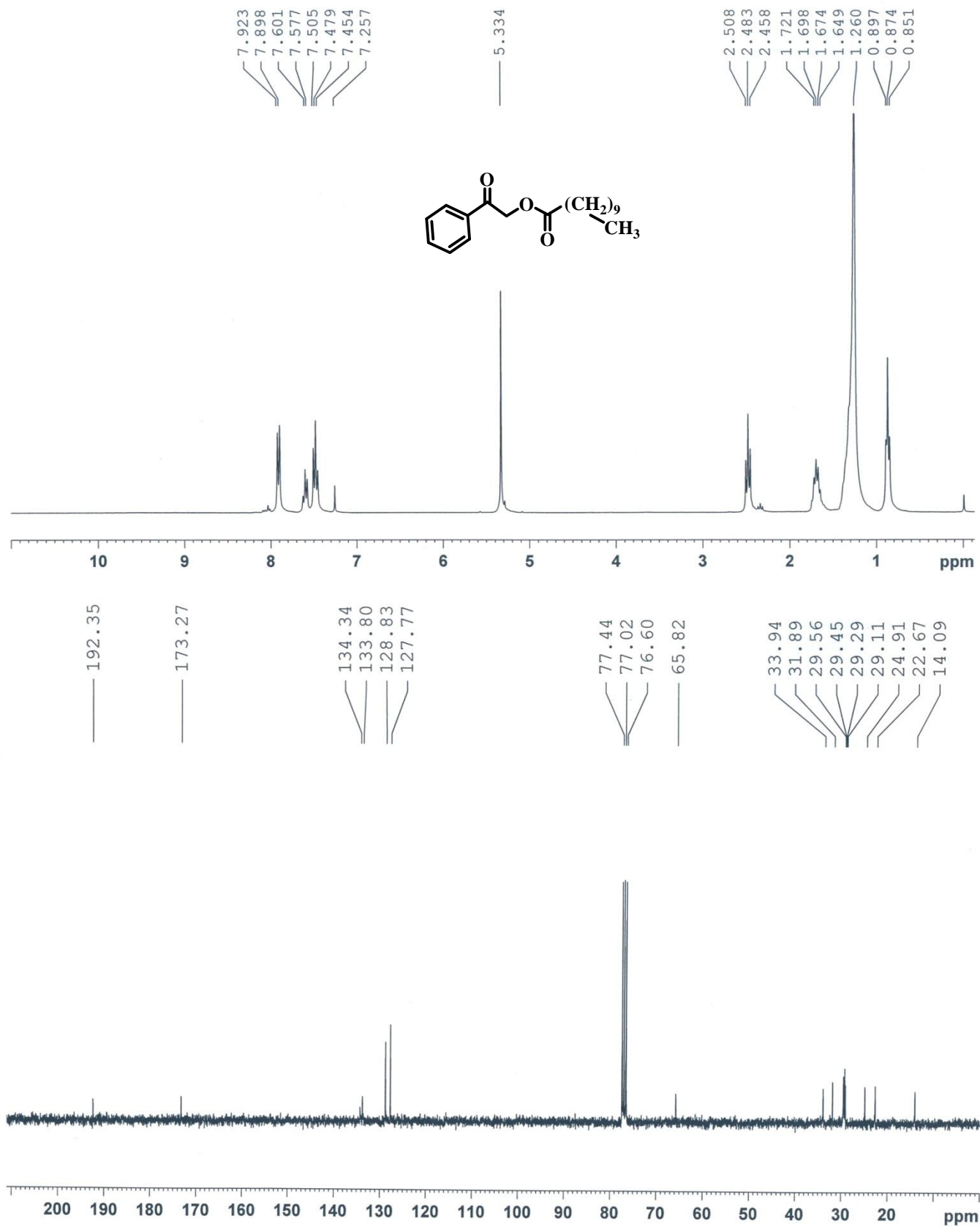
SI Figure 27: ^1H and ^{13}C -NMR spectra of compound **11a**



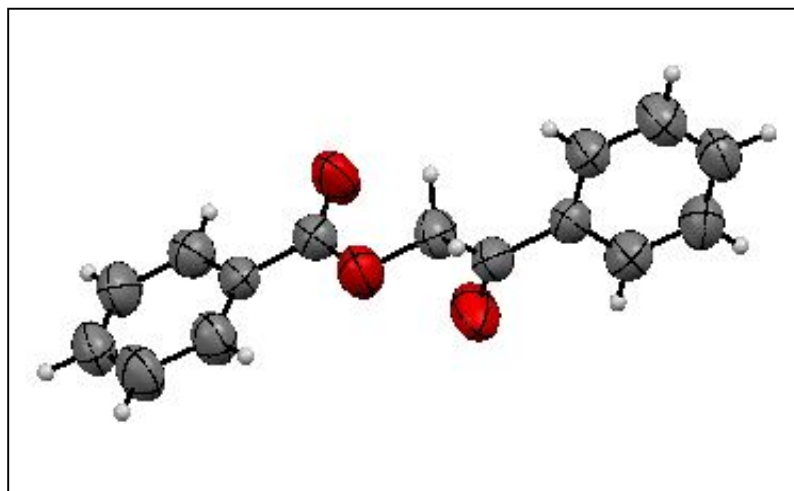
SI Figure 28: ^1H and ^{13}C -NMR spectra of compound **11b**



SI Figure 29: ^1H and ^{13}C -NMR spectra of compound **11c**



12. Crystal Summary Data of Compound 9a (CCDC 973403)



- ❖ Chemical formula and formula weight (M): C₁₅ H₁₂ O₃ and 240.25
- ❖ Crystal system: Monoclinic Unit-cell dimensions (angstrom or pm, degrees) and volume, with edges: a 9.0155(13) b 14.112(2) c 9.6804(14), 90.00, 90.552(5), 90.00, 1231.5(3)
- ❖ Temperature: 296 K
- ❖ Space group symbol: P2(1)/c
- ❖ No. of formula units in unit cell (Z): 4
- ❖ Number of reflections measured and/or number of independent reflections, Rint: 2027
- ❖ Final R values (and whether quoted for all or observed data): 0.0696

13. CIF data of compound 9a (CCDC 973403)

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