Electronic Supplementary Information

Synthetically useful noncatalytic strategy: A stereocontrolled rapid cyclization of a three component assembly to hexahydropyrrolizines

Tista Sengupta, Saikat Khamarui, Srikanta Samanta and Dilip K. Maiti*

Department of Chemistry, University of Calcutta, University College of Science,
92, A. P. C. Road, Kolkata-700009, India

*Corresponding author. Fax: 91-33-2351 9755, Tel: 91-33-2350 1014
maitidk@yahoo.com

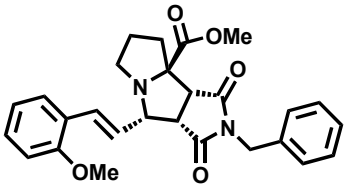
1. Materials and methods

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. THF was dried over sodium and distilled out prior to use. Petroleum ether used in our experiments was in the boiling range of 60°-80° 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. Melting points are reported uncorrected. ^{1}H NMR and ^{13}C NMR spectra (Bruker Advance 300) were recorded at ambient temperature using 300 MHz spectrometers (300 MHz for ^{1}H 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) as KBr pellets (solid sample) and in thin film on NaCl window (liquid sample). Optical rotation of the chiral compounds was measured in a polarimeter (Perkin Elmer 343) using standard 10 cm quartz cell in sodium-D lamp at ambient temperature. EI-MS analysis was performed in GC-MS machine (Perkin Elmer Clarus 600) using column Elite 5 MS (30 m x 0.25 mm x o.25 um) with maximum temperature 300º C. HR-MS data were acquired by electron spray ionization technique on a Q-tof-micro quadruple mass spectrophotometer (Bruker). Single crystal X-ray diffraction studies of the crystalline heterocyclic compound were performed in X-ray diffractometer (Bruker Smart Apex-II).

2. General procedure for synthesis of pyrrolo[3,4-*a*]pyrrolizine (5a-o) and characterization data

A solution of proline ester (**1**, 1 mmol) in DCM (10 mL) was taken in a round-bottom flask (25 mL) and stirred at room temperature. Maleimide (**2**, 1.0 mmol) and α,β-unsaturated aldehyde (**3**, 1.0 mmol) were added. The progress of the reaction was monitored by TLC, and the reaction was complete after 15-40 min depending on the use of the substrates. The post-reaction mixture was filtered, washed with saturated aqueous sodium bicarbonate solution (2 x 10 mL) and brine solution (1 x 10 mL), dried on activated sodium sulphate, and concentrated in a rotary evaporator under reduced pressure at room temperature. Thus, the reaction with L-proline methyl ester (**1a**, 129 mg, 1 mmol), *N*-benzylmaleimide (**2a**, 187 mg, 1.0 mmol) and *o*-methoxycinnamaldehyde (**3a**, 162 mg, 1.0 mmol) afforded **5a** after purification by column chromatography on silica gel (60-120 mesh) with ethyl acetate-petroleum ether (1:13, v/v) as an eluent in a yield of 90 % (414 mg, 0.90 mmol). All of the new hexahydropyrrolizines (**5a-o**) were characterised using NMR, FT-IR and HR-MS spectroscopy and single crystal XRD analyses.

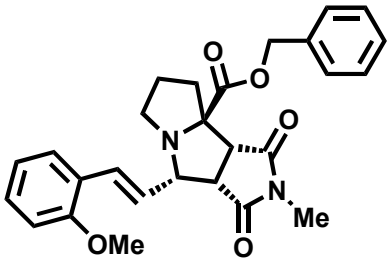
2.1. **2-Benzyl-4-[2-(2-methoxyphenyl)-vinyl]-1,3-dioxooctahydropyrrolo[3,4-*a*]pyrrolizine-8a-carboxylic acid methyl ester (5a)**



5a

Yield: 90 % (414 mg, 0.90 mmol).
Characteristic: Yellow solid.
Melting point: 118-120 °C.
$[\alpha]_D^{25}$ -1.32° (c 1.15, $CHCl_3$).
^{1}H NMR (300 MHz, $CDCl_3$): δ 1.72-1.79 (1H, m), 2.02-2.07 (2H, m), 2.22-2.31 (2H, m), 2.81-2.83 (1H, m), 3.41 (1H, t, *J* = 8.1 Hz), 3.75 (3H, s), 3.79 (3H, s), 3.83-3.86 (1H, m), 4.16 (1H, t, *J* = 8.7 Hz), 4.65 (1H, d, *J* = 13.8 Hz), 4.85 (1H, d, *J* = 13.8 Hz), 6.19 (1H, dd, *J* = 15.9, 9.6 Hz), 6.82 (1H, d, *J* = 8.1 Hz), 6.88-6.93 (1H, m), 7.01 (1H, d, *J* = 15.6 Hz), 7.19-7.28 (4H, m), 7.38-7.41 (3H, m).
^{13}C NMR (75 MHz, $CDCl_3$): δ 24.5, 30.0, 42.6, 48.3, 51.2, 52.2, 53.0, 55.4, 65.3, 110.8, 120.6, 123.4, 125.7, 127.4, 128.1, 128.6, 129.0, 129.2, 130.6, 134.8, 156.9, 174.0, 175.9, 176.5.
FT-IR (KBr, cm^{-1}): 753, 973, 1027, 1246, 1489, 1698, 1729, 2838, 2951.
HR-MS (*m*/*z*) for $C_{27}H_{28}N_2O_5$ (M^+): Calculated 460.1998, found 460.1995.

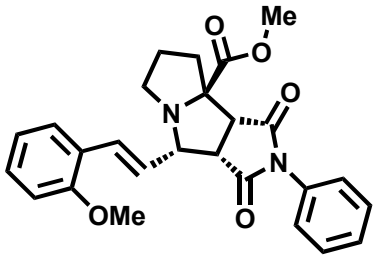
2.2. **4-[2-(2-Methoxyphenyl)-vinyl]-2-methyl-1,3-dioxooctahydropyrrolo[3,4-*a*]pyrrolizine-8a-carboxylic acid benzyl ester (5b)**



5b

Yield: 92 % (423 mg, 0.92 mmol).
Characteristic: Yellow solid.
Melting point: 124-132 °C.
^{1}H NMR (300 MHz, $CDCl_3$): δ 1.79-1.91 (1H, m), 2.04-2.06 (1H, m), 2.38-2.48 (3H, m), 2.59-2.62 (1H, m), 2.98 (3H, s), 3.08-3.09 (1H, m), 3.46 (2H, t, *J* = 8.1 Hz), 3.87 (3H, s), 5.26 (2H, dd, *J* = 19.8, 12.3 Hz), 6.32 (1H, dd, *J* = 15.6, 9.3 Hz), 6.87-6.97 (3H, m), 7.06 (1H, d, *J* = 15.9 Hz), 7.23-7.29 (2H, m), 7.35-7.42 (3H, m), 7.51 (1H, d, *J* = 9.0 Hz).
^{13}C NMR (75 MHz, $CDCl_3$): δ 25.0, 25.1, 29.9, 47.7, 50.8, 52.4, 55.4, 64.6, 67.3, 78.7, 110.8, 120.6, 125.7, 127.3, 128.1, 128.4, 128.6, 129.0, 135.6, 156.9, 176.4. 176.9.
FT-IR (KBr, cm^{-1}): 488, 744, 980, 1140, 1247, 1374, 1436, 1696, 2830, 2948.
HR-MS (*m*/*z*) for $C_{27}H_{28}N_2O_5$ (M^+): Calculated 460.1998, found 460.1992.

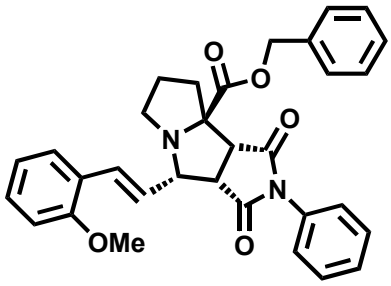
2.3. **4-[2-(2-Methoxyphenyl)-vinyl]-1,3-dioxo-2-phenyloctahydropyrrolo[3,4-*a*]pyrrolizine-8a-carboxylic acid methyl ester(5c)**



5c

Yield: 90 % (401 mg, 0.90 mmol).
Characteristic: Yellow solid.
Melting point: 100-104 °C.
^{1}H NMR (300 MHz, $CDCl_3$): δ 1.79-1.91 (1H, m), 2.36-2.40 (1H, m), 2.50-2.55 (1H, m), 2.68-2.70 (1H, m), 3.13-3.14 (1H, m), 3.56 (1H, t, *J* = 8.1 Hz), 3.75 (3H, s), 3.76 (3H, s), 3.99-4.08 (2H, m), 4.26 (1H, t, *J* = 8.7 Hz), 6.35 (1H, q, *J* = 15.6, 9.3 Hz), 6.76-6.85 (2H, m), 7.04 (1H, d, *J* = 15.9 Hz), 7.12-7.18 (3H, m), 7.32-7.43 (4H, m).
^{13}C NMR (75 MHz, $CDCl_3$): δ 14.1, 24.9, 30.3, 48.6, 51.2, 52.2, 53.1, 55.4, 65.6, 79.4, 110.8, 120.6, 123.8, 125.6, 126.1, 127.4, 128.6, 129.1, 129.2, 130.9, 131.9, 156.9, 173.9, 175.3, 175.9.
FT-IR (KBr, cm^{-1}): 752, 1051, 1176, 1245, 1375, 1489, 1597, 1710, 2952.
HR-MS (*m*/*z*) for $C_{26}H_{26}N_2O_5$ (M^+): Calculated 446.1842, found 446.1838.

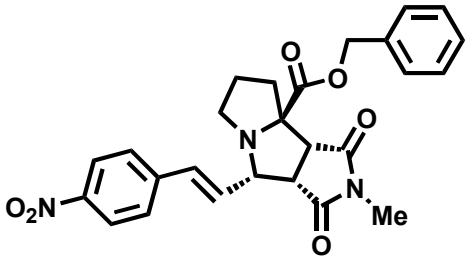
2.4. **4-[2-(2-Methoxyphenyl)-vinyl]-1,3-dioxo-2-phenyloctahydropyrrolo[3,4-*a*]pyrrolizine-8a-carboxylic acid benzyl ester (5d)**



5d

Yield: 92 % (480 mg, 0.92 mmol).
Characteristic: Yellow solid.
Melting point: 108-110 °C.
^{1}H NMR (300 MHz, $CDCl_3$): δ 1.79-1.87 (1H, m), 1.94-2.04 (1H, m), 2.32-2.42 (1H, m), 2.46-2.56 (1H, m), 2.70 (1H, q, *J* = 8.7 Hz), 3.08-3.15 (1H, m), 3.53 (1H, t, *J* = 8.4 Hz), 3.76 (3H, s), 3.96 (1H, d, *J* = 8.1 Hz), 4.24 (1H, t, *J* = 8.7 Hz), 5.20 (2H, q, *J* = 12.3 Hz), 6.34 (1H, dd, *J* = 15.6, 9.3 Hz), 6.77-6.85 (2H, m), 7.02 (1H, d, *J* = 15.9 Hz),7.13-7.18 (4H, m), 7.27-7.34 (4H, m), 7.38-7.43 (4H, m).
^{13}C NMR (75 MHz, $CDCl_3$): δ 25.1, 30.1, 48.4, 51.0, 52.3, 55.4, 65.4, 67.4, 79.3, 110.8, 120.6, 123.5, 125.6, 126.1, 127.5, 128.1, 128.4, 128.7, 129.1, 129.2, 130.8, 131.9, 135.6, 156.9, 173.0, 175.4, 175.9.
FT-IR (KBr, cm^{-1}): 691, 1178, 1244, 1497, 1576, 1712, 2934.
HR-MS (*m*/*z*) for $C_{32}H_{30}N_2O_5$ (M^+): Calculated 522.2155, found 522.2151.

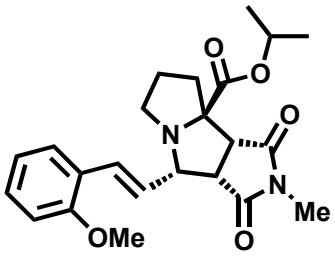
2.5. **2-Methyl-4-[2-(4-nitrophenyl)-vinyl]-1,3-dioxooctahydropyrrolo[3,4-*a*]pyrrolizine-8a-carboxylic acid benzyl ester (5e)**



5e

Yield: 86 % (410 mg, 0.86 mmol).
Characteristic: Brown solid.
Melting point: 148-150 °C.
^{1}H NMR (300 MHz, $CDCl_3$): δ 1.71-1.77 (2H, m), 2.26-2.35 (1H, m), 2.46-2.49 (1H, m), 2.88 (3H, s), 2.95-2.96 (1H, m), 3.38 (1H, t, *J* = 8.1 Hz), 3.75 (1H, d, *J* = 8.1 Hz), 4.01-4.14 (2H, m), 5.09-5.24 (2H, m), 6.45 (1H, dd, *J* = 15.6, 9.0 Hz), 6.66-6.71 (1H, m), 7.18-7.34 (5H, m), 7.46 (2H, d, *J* = 8.7 Hz), 8.09 (2H, d, *J* = 8.7 Hz).
^{13}C NMR (75 MHz, $CDCl_3$): δ 25.0, 25.1, 29.7, 47.7, 50.7,52.4, 63.6, 67.4, 78.7, 124.0, 127.3, 128.2, 128.5, 128.6, 128.9, 133.2, 135.4, 142.9, 147.2, 172.8, 176.4, 176.5.
FT-IR (KBr, cm^{-1}): 696, 979, 1281, 1517, 1596, 1698, 2947.
HR-MS (*m*/*z*) for $C_{26}H_{25}N_3O_6$ (M^+): Calculated 475.1743, found 475.1739.

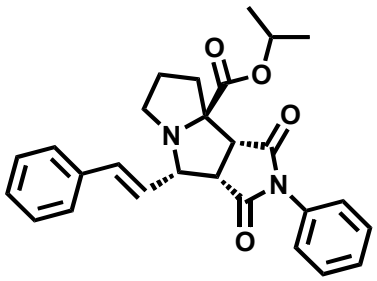
2.6. **4-[2-(2-Methoxyphenyl)-vinyl]-2-methyl-1,3-dioxooctahydropyrrolo[3,4-*a*]pyrrolizine-8a-carboxylic acid isopropyl ester (5f)**



5f

Yield: 88 % (362 mg, 0.88 mmol).
Characteristic: Yellow solid.
Melting point: 124-128 °C.
^{1}H NMR (300 MHz, $CDCl_3$): δ 1.27 (6H, d, *J* = 6.3 Hz), 1.76-1.79 (1H, m), 1.91-1.97 (1H, m), 2.28-2.43 (2H, m), 2.55-2.57 (1H, m), 2.94 (3H, s), 3.45-3.47 (1H, m), 3.74-3.77 (1H, m), 3.80 (3H, s), 4.20-4.36 (2H, m), 5.04 (1H, t, *J* = 6.3 Hz), 6.25 (1H, dd, *J* = 15.9, 9.6 Hz), 6.81-6.91 (2H, m), 7.03 (1H, d, *J* = 15.6 Hz), 7.20 (1H, t, *J* = 7.8 Hz), 7.45 (1H, d, *J* = 7.5 Hz).
^{13}C NMR (75 MHz, $CDCl_3$): δ 21.7, 25.0, 30.0, 47.5, 50.7, 52.6, 55.4, 64.5, 69.4, 78.6, 110.8, 120.6, 124.2, 125.8, 129.0, 130.1, 156.8, 172.6, 176.5, 177.0.
FT-IR (KBr, cm^{-1}): 761, 971, 1100, 1167, 1293, 1372, 1495, 1596, 1710, 1740, 2789, 2979.
HR-MS (*m*/*z*) for $C_{23}H_{28}N_2O_5$ (M^+): Calculated 412.1998, found 412.1995.

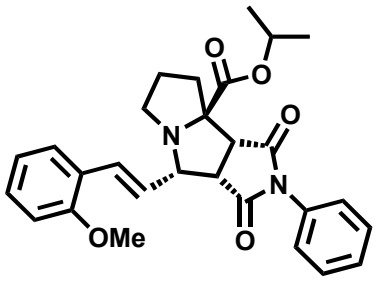
2.7. **1,3-Dioxo-2-phenyl-4-styryloctahydropyrrolo[3,4-*a*]pyrrolizine-8a-carboxylic acid isopropyl ester (5g)**



5g

Yield: 86 % (382 mg, 0.86 mmol).
Characteristic: Grey solid.
Melting point: 148-150 °C.
^{1}H NMR (300 MHz, $CDCl_3$): δ 1.26 (6H, d, *J* = 6.3 Hz), 1.79-1.88 (1H, m), 1.94-2.04 (1H, m), 2.28-2.38 (1H, m), 2.47-2.57 (1H, m), 2.64-2.72 (1H, q, *J* = 8.4 Hz), 3.07-3.14 (1H, m), 3.57 (1H, t, *J* = 8.1 Hz), 3.92 (1H, d, *J* = 8.4 Hz), 4.26 (1H, t, *J* = 8.7 Hz), 5.02-5.06 (1H, m), 6.36 (1H, dd, *J* = 15.6, 9.3 Hz), 6.69-6.78 (1H, m), 7.15-7.23 (5H, m), 7.26-7.44 (5H, m).
^{13}C NMR (75 MHz, $CDCl_3$): δ 21.7, 24.9, 29.9, 48.3, 51.0, 52.3, 64.8, 69.5, 79.3, 123.5, 126.0, 126.1, 126.8, 127.9, 128.5, 128.7, 129.1, 129.2, 131.8, 135.7, 136.6, 172.6, 175.4, 175.9.
FT-IR (KBr, cm^{-1}): 1244, 1514, 1663, 1720, 2869, 2988, 3294, 3754.
HR-MS (*m*/*z*) for $C_{27}H_{28}N_2O_4$ (M^+): Calculated 444.2049, found 444.2044.

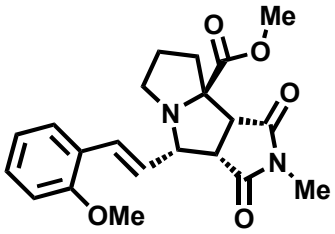
2.8. **4-[2-(2-Methoxyphenyl)-vinyl]-1,3-dioxo-2-phenyloctahydropyrrolo[3,4-*a*]pyrrolizine-8a-carboxylic acid isopropyl ester(5h)**



5h

Yield: 88 % (420 mg, 0.88 mmol).
Characteristic: Yellow solid.
Melting point: 126-130 °C.
$[\alpha]_D^{25}$ +1.87° (c 0.9, $CHCl_3$).
^{1}H NMR (300 MHz, $CDCl_3$): δ 1.33 (6H, d, *J* = 6.3 Hz), 1.88-1.95 (1H, m), 2.07-2.10 (1H, m), 2.35-2.44 (1H, m), 2.52-2.62 (1H, m), 2.76 (1H, q, *J* = 9.0 Hz), 3.13-3.20 (1H, m), 3.64 (1H, t, *J* = 8.1 Hz), 3.82 (3H, s), 4.00 (1H, d, *J* = 8.4 Hz), 4.34 (1H, t, *J* = 8.7 Hz), 5.06-5.14 (1H, m), 6.40 (1H, dd, *J* = 15.6, 9.3 Hz), 6.84-6.92 (2H, m), 7.10 (1H, d, *J* = 15.6 Hz), 7.19-7.42 (3H, m), 7.45-7.51 (4H, m).
^{13}C NMR (75 MHz, $CDCl_3$): δ 21.7, 25.0, 30.0, 48.2, 51.0, 52.5, 55.4, 65.3, 69.5, 79.3, 110.8, 120.6, 124.0, 125.7, 126.1, 127.5, 128.6, 129.0, 129.2, 130.4, 131.9, 156.8, 172.7, 175.4, 176.0.
FT-IR (KBr, cm^{-1}): 761, 971, 1293, 1372, 1495, 1596, 1712, 1740, 2788, 2979.
HR-MS (*m*/*z*) for $C_{28}H_{30}N_2O_5$ (M^+): Calculated 474.2155, found 474.2158.

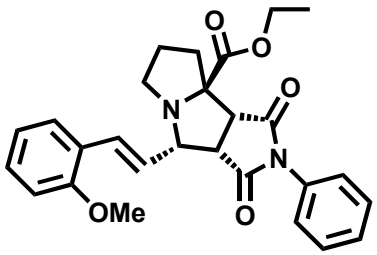
2.9. **4-[2-(2-Methoxyphenyl)-vinyl]-2-methyl-1,3-dioxooctahydropyrrolo[3,4-*a*]pyrrolizine-8a-carboxylic acid methyl ester (5i)**



5i

Yield: 92 % (353 mg, 0.92 mmol).
Characteristic: Yellow solid.
Melting point: 78-82 °C.
^{1}H NMR (300 MHz, $CDCl_3$): δ 1.69-1.72 (1H, m), 1.89-1.93 (1H, m), 2.22-2.31 (1H, m), 2.36-2.49 (2H, m), 2.88 (3H, s), 2.96-3.03 (1H, m), 3.37 (1H, t, *J* = 8.1 Hz), 3.72 (3H, s), 3.75 (3H, s), 3.80 (1H, d, *J* = 8.1 Hz), 4.13 (1H, t, *J* = 8.7 Hz), 6.24 (1H, dd, *J* = 15.9, 9.6 Hz), 6.76-6.86 (2H, m), 6.99 (1H, d, *J* = 15.9 Hz), 7.12-7.18 (1H, m), 7.41 (1H, d, *J* = 9.0 Hz).
^{13}C NMR (75 MHz, $CDCl_3$): δ 25.0, 29.6, 48.1, 51.0, 52.3, 53.0, 55.4, 64.9, 78.7, 110.8, 120.6, 123.6, 125.7, 127.3, 129.0, 130.6, 156.8, 174.0, 176.5, 177.0.
FT-IR (KBr, cm^{-1}): 912, 1059, 1248, 1434, 1698, 1726, 2836, 2951.
HR-MS (*m*/*z*) for $C_{21}H_{24}N_2O_5$ (M^+): Calculated 384.1685, found 384.1681.

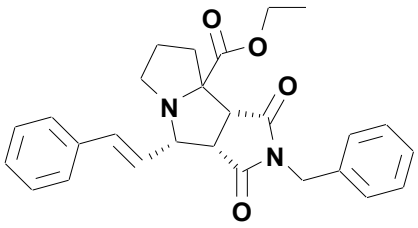
2.10. **4-[2-(2-Methoxyphenyl)-vinyl]-1,3-dioxo-2-phenyloctahydropyrrolo[3,4-a]pyrrolizine-8a-carboxylic acid ethyl ester (5j)**



5j

Yield: 92 % (423 mg, 0.92 mmol).
Characteristic: Yellow oil.
^{1}H NMR (300 MHz, $CDCl_3$): δ 1.27 (3H, t, *J* = 7.2 Hz), 1.81-1.88 (1H, m), 2.01-2.05 (2H, m), 2.32-2.41 (1H, m), 2.48-2.58 (1H, m), 2.70 (1H, q, *J* = 8.7 Hz), 3.10-3.17 (1H, m), 3.58 (1H, t, *J* = 8.1 Hz), 3.75 (3H, s), 4.00 (1H, d, *J* = 8.4 Hz), 4.14-4.31 (2H, m), 6.34 (1H, dd, *J* = 15.9, 9.6 Hz), 6.77-6.85 (2H, m), 7.03 (1H, d, *J* = 15.6 Hz), 7.13-7.18 (3H, m), 7.33-7.44 (4H, m).
^{13}C NMR (75 MHz, $CDCl_3$): δ 14.2, 25.0, 30.2, 48.5, 51.1, 52.3, 55.4, 62.0, 65.5, 79.9, 110.7, 120.6, 123.5, 125.5, 126.1, 127.5, 128.6, 129.2, 130.8, 131.8, 156.8, 173.3, 175.4, 176.0.
FT-IR (KBr, cm^{-1}): 751, 973, 1020, 1160, 1248, 1371, 1494, 1596, 1712, 1739, 2796, 2852, 2923.
HR-MS (*m*/*z*) for $C_{27}H_{28}N_2O_5$ (M^+): Calculated 460.1998, found 460.1996.

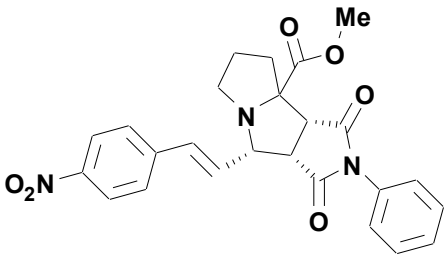
2.11. **2-Benzyl-1,3-dioxo-4-styryloctahydropyrrolo[3,4-*a*]pyrrolizine-8a-carboxylic acid ethyl ester (5k)**



5k

Yield: 86 % (381 mg, 0.86 mmol).
Characteristic: Yellow solid.
Melting point: 108-114 °C.
^{1}H NMR (300 MHz, $CDCl_3$): δ 1.23 (3H, t, *J* = 6.9 Hz), 1.65-1.75 (1H, m), 1.97-2.07 (2H, m), 2.14-2.30 (2H, m), 2.75-2.81 (1H, m), 3.36 (1H, t, *J* = 8.1 Hz), 3.77 (1H, d, *J* = 8.1 Hz), 4.08-4.22 (3H, m), 4.57 (2H, dd, *J* = 18.3, 13.5 Hz), 6.17 (1H, dd, *J* = 15.6, 9.3 Hz), 6.64 (1H, d, *J* = 15.6 Hz), 7.16-7.37 (10H, m).
^{13}C NMR (75 MHz, $CDCl_3$): δ 14.1, 24.6, 29.9, 42.6, 48.2, 51.2, 52.2, 61.9, 64.8, 78.9, 123.4, 126.8, 127.9, 128.1, 128.5, 128.6, 129.2, 134.9, 135.6, 136.6, 173.4, 176.0, 176.4.
FT-IR (KBr, cm^{-1}): 754, 966, 1165, 1391, 1698, 1716, 2850, 2942.
HR-MS (*m*/*z*) for $C_{27}H_{28}N_2O_4$ (M^+): Calculated 444.2049, found 444.2051.

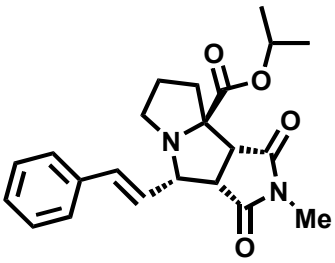
2.12. **4-[2-(4-Nitrophenyl)-vinyl]-1,3-dioxo-2-phenyloctahydropyrrolo[3,4-a]pyrrolizine-8a-carboxylic acid methyl ester (5l)**



5l

Yield: 84 % (387 mg, 0.84 mmol).
Characteristic: Yellow solid.
Melting point: 122-124 °C.
$[\alpha]_D^{25}$ -95.52° (c 0.9, $CHCl_3$).
^{1}H NMR (300 MHz, $CDCl_3$): δ 1.83-1.92 (2H, m), 2.24-2.33 (2H, m), 2.77-2.86 (2H, m), 3.57 (3H, s),3.92- 4.02 (1H, m), 4.16-4.17 (2H, m), 6.39 (1H, d, *J* = 5.1 Hz), 6.82 (1H, dd, *J* = 6.0, 2.4 Hz), 7.35 (2H, d, *J* = 9.0 Hz), 7.42 (2H, d, *J* = 7.8 Hz), 7.56-7.67 (3H, m), 8.13 (2H, dd, *J* = 11.7, 8.7 Hz).
^{13}C NMR (75 MHz,$CDCl_3$): δ 14.1, 24.6, 29.9, 42.6, 48.2, 51.2, 52.2, 61.9, 64.8, 78.9, 123.4, 126.8, 127.9, 128.1, 128.5, 128.6, 129.2, 134.9, 135.6, 136.6, 173.4, 176.0, 176.4.
FT-IR (KBr, cm^{-1}): 692, 1177, 1343, 1519, 1596, 1620, 1713, 2953.
HR-MS (*m*/*z*) for $C_{25}H_{23}N_3O_6$ (M^+): Calculated 461.1587, found 461.1584.

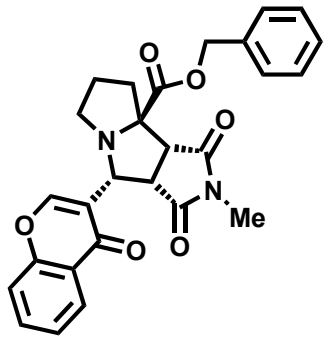
2.13. **2-Methyl-1,3-dioxo-4-styryl-octahydropyrrolo[3,4-a]pyrrolizine-8a-carboxylic acid isopropyl ester (5m)**



5m

Yield: 88 % (336 mg, 0.88 mmol).
Characteristic: Yellow solid.
Melting point: 98-102 °C.
^{1}H NMR (300 MHz, $CDCl_3$): δ 1.30 (6H, d, *J* = 6.3 Hz), 1.78-1.81 (1H, m), 2.33-2.37 (1H, m), 2.41-2.46 (1H, m), 2.58 (1H, q, *J* = 9.0 Hz), 2.96 (3H, s), 3.06-3.12 (1H, m), 3.49 (1H, t, *J* = 8.4 Hz), 3.78 (1H, d, *J* = 8.1 Hz), 4.10 (1H, q, *J* = 7.2 Hz), 4.28 (1H, t, *J* = 8.7 Hz), 5.05-5.10 (1H, m), 6.29 (1H, dd, *J* = 15.9, 9.3 Hz), 6.74 (1H, t, *J* = 15.9 Hz), 7.24-7.30 (3H, m), 7.41 (2H, d, *J* = 8.1Hz).
^{13}C NMR (75 MHz, $CDCl_3$): δ 14.1, 21.6, 24.8, 29.8, 47.7, 50.7, 52.1, 64.2, 69.7, 78.7, 123.0, 126.8, 128.0, 128.5, 134.1, 136.0, 136.4, 172.2, 176.3, 176.6.
FT-IR (KBr, cm^{-1}): 978,1103, 1280, 1381, 1433, 1700, 1771, 2926.
HR-MS (*m*/*z*) for $C_{22}H_{26}N_2O_4(M^+)$: Calculated 382.1893, found 382.1891.

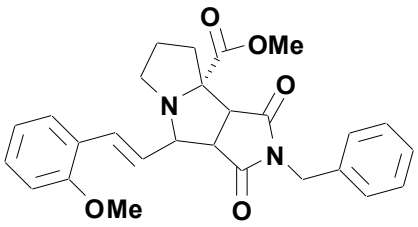
2.14. **2-Methyl-1,3-dioxo-4-[2-(4-oxo-4*H*-chromen-2-yl)-vinyl]-octahydropyrrolo[3,4-*a*]pyrrolizine-8a-carboxylic acid benzyl ester (5n)**



5n

Yield: 92 % (434 mg, 0.92 mmol).
Characteristic: Yellow solid.
Melting point: 182-188 °C.
^{1}H NMR (300 MHz, $CDCl_3$): δ 2.11-2.21 (3H, m), 2.27-2.29 (2H, m), 2.77-2.82 (1H, m), 2.86 (3H, s), 3.57 (1H, d, *J* = 7.5 Hz), 3.98 (1H, t, *J* = 8.1 Hz), 4.68 (1H, d, *J* = 8.4 Hz), 5.15-5.27 (2H, m), 7.33-7.43 (5H, m), 7.60-7.68 (3H, m), 8.23-8.26 (2H, m).
^{13}C NMR (75 MHz, $CDCl_3$): δ 24.8, 26.4, 27.7, 34.0, 47.2, 53.6, 67.2, 78.2, 118.0, 123.6, 125.2, 126.0, 126.1, 128.1, 128.3, 128.5, 128.7, 133.6, 135.3, 152.7, 156.2, 172.4, 175.5, 176.9.
FT-IR (KBr, cm^{-1}): 698, 756, 944, 1159, 1210, 1460, 1641, 1697, 2359, 2964.
HR-MS (*m*/*z*) for $C_{27}H_{24}N_2O_6(M^+)$: Calculated 472.1634, found 472.1630.

2.15. **2-Benzyl-4-[2-(2-methoxyphenyl)-vinyl]-1,3-dioxooctahydropyrrolo[3,4-*a*]pyrrolizine-8a-carboxylic acid methyl ester (5o)**



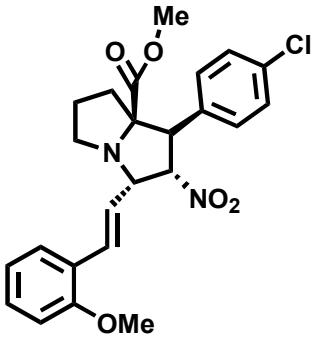
5o

Yield: 90 % (414 mg, 0.90 mmol).
Characteristic: Yellow solid.
Melting point: 04-108 °C.
$[\alpha]_D^{25}$ +4.84° (c 2.5, $CHCl_3$).
^{1}H NMR (300 MHz, $CDCl_3$): δ 1.71-1.81 (1H, m), 2.18-2.37 (2H, m), 2.23-2.32 (2H, m), 2.82-2.88 (1H, m), 3.42 (1H, t, *J* = 8.4 Hz), 3.76 (3H, s), 3.80 (3H, s), 3.86 (1H, d, *J* = 8.1 Hz), 4.09-4.21 (1H, m), 4.62 (2H, dd, *J* = 20.1, 13.8 Hz), 6.21 (1H, dd, *J* = 15.9, 9.6 Hz), 6.84 (1H, d, *J* = 8.1 Hz), 6.92 (1H, t, *J* = 7.5 Hz), 7.02 (1H, d, *J* = 15.9 Hz), 7.20-7.23 (1H, m), 7.25-7.31 (4H, m), 7.39-7.44 (2H, m).
^{13}C NMR (75 MHz, $CDCl_3$): δ 24.5, 30.0, 42.5, 48.3, 51.2, 52.1, 53.0, 55.4, 65.4, 79.0, 110.8, 120.6, 123.4, 125.7, 127.4, 128.1, 128.6, 129.0, 129.1, 130.7, 134.9, 156.9, 173.9, 175.8, 176.4.
FT-IR (KBr, cm^{-1}): 754, 1027, 116, 1246, 1343, 1434, 158, 1700, 1726, 1768, 2838, 2951.
HR-MS (*m*/*z*) for $C_{27}H_{28}N_2O_5$ (M^+): Calculated 460.1998, found 460.1995.

3. General procedure for synthesis of tetrahyropyrrolizines (6a-h) and characterization data

A solution of proline ester (**1**, 1 mmol) in DCM (10 mL) was taken in a round-bottom flask (25 mL) and stirred at room temperature. α,β-Unsaturated aldehyde (**2**, 1.0 mmol) and olefin (**4**, 1.0 mmol) were added and stirred at ambient temperature. The progress of the reaction was monitored by TLC and the reaction was complete after 10-45 min depending on the use of the substrates. The post-reaction mixture was filtered, washed with saturated aqueous sodium bicarbonate solution (2 x 10 mL) and brine solution (1 x 10 mL), dried on activated sodium sulphate, and concentrated in a rotary evaporator under reduced pressure at room temperature. Thus, the reaction with proline methyl ester (**1a**, 129 mg, 1 mmol), *o*-methoxycinnamaldehyde (**1a**, 162 mg, 1.0 mmol) and 4-chloro-β-nitrostyrene (**3a**, 183 mg, 1.0 mmol) afforded **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 82% (374 mg, 0.82 mmol). All of the new tetrahyropyrrolizines (**6a-h)** were characterised using NMR, FT-IR and ESI-MS spectroscopy and single crystal XRD analysis.

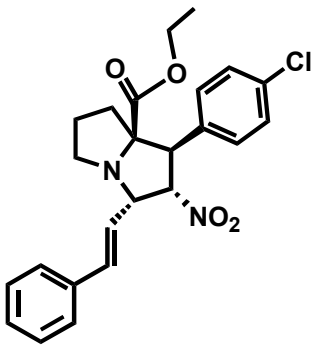
3.1. **1-(4-Chlorophenyl)-3-[2-(2-methoxyphenyl)-vinyl]-2-nitrotetrahydropyrrolizine-7a-carboxylic acid methyl ester (6a)**



6a

Yield: 82 % (374 mg, 0.82 mmol).
Characteristic: Yellow oil.
^{1}H NMR (300 MHz, $CDCl_3$): δ 1.92-2.04 (4H, m), 2.68-2.71 (1H, m), 2.92-2.93 (1H, m), 3.25-3.28 (1H, m), 3.41 (3H, s), 3.83 (3H, s), 4.13 (1H, m), 4.78 (1H, dd, *J* = 10.2, 7.8 Hz), 6.03-6.16 (1H, m), 6.84-6.93 (2H, m), 7.02 (1H, d, *J* = 15.6 Hz), 7.15 (2H, d, *J* = 8.4 Hz), 7.22-7.37 (3H, m), 7.38 (1H, d, *J* = 9.3 Hz).
^{13}C NMR (75 MHz, $CDCl_3$): δ 27.2, 35.4, 48.6, 52.1, 66.4, 66.6, 80.2, 91.7, 91.8, 110.9, 120.6, 122.6, 124.7, 128.0, 129.1, 132.7, 133.4, 134.0, 157.0, 173.3.
FT-IR (KBr, cm^{-1}): 774, 1030, 1180, 1488, 1634, 1505, 1657, 1722, 2920.
HR-MS (*m*/*z*) for $C_{24}H_{25}ClN_2O_5$ (M^+): Calculated 456.1452, found 456.1449 (one of the peaks).

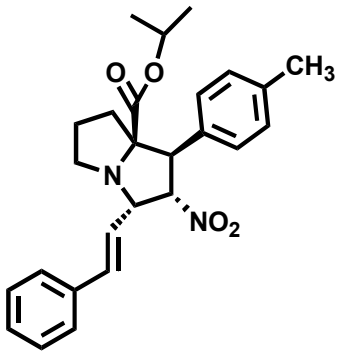
3.2. **1-(4-Chlorophenyl)-2-nitro-3-styryl-tetrahydropyrrolizine-7a-carboxylic acid ethyl ester (6b)**



6b

Yield: 78 % (343 mg, 0.78 mmol).
Characteristic: Yellow solid.
Melting point: 100-108 °C.
^{1}H NMR (300 MHz, $CDCl_3$): δ 0.98 (3H, t, *J* = 6.9 Hz), 1.95-2.04 (3H, m), 2.70-2.75 (1H, m), 2.91-2.96 (1H, s), 3.22-3.25 (1H, m), 3.74-3.80 (1H, m), 3.86-3.92 (1H, m), 4.13-4.15 (2H, m), 4.78 (1H, dd, *J* = 10.2, 7.8 hz), 6.04-6.10 (1H, m), 6.72 (1H, d, *J* = 15.6 Hz), 7.16 (2H, d, *J* = 8.4 Hz), 7.26-7.39 (7H, m).
^{13}C NMR (75 MHz, $CDCl_3$): δ 13.7, 27.3, 35.4, 48.4, 54.7, 61.3, 65.9, 80.0, 92.0, 122.5, 126.9, 128.5, 128.6, 128.9, 132.8, 134.0, 135.7, 138.2, 172.9.
FT-IR (KBr, cm^{-1}): 747, 1093, 1369, 1494, 1549, 1637, 1721, 3434.
HR-MS (*m*/*z*) for $C_{24}H_{25}ClN_2O_4$ (M^+): Calculated 440.1503, found 440.1500 (one of the peaks).

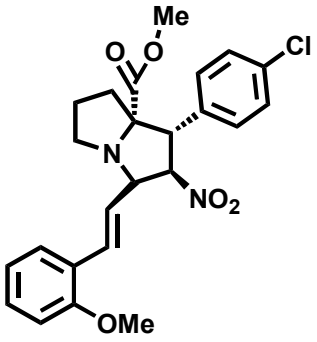
3.3. **2-Nitro-3-styryl-1-(4-methylphenyl)-tetrahydropyrrolizine-7a-carboxylic acid isopropyl ester (6c)**



6c

Yield: 80 % (348 mg, 0.80 mmol).
Characteristic: Yellow oil.
^{1}H NMR (300 MHz, $CDCl_3$): δ 0.76 (3H, d, *J* = 6.3 Hz), 1.04 (3H, d, *J* = 6.3 Hz), 1.25-1.37 (2H, m), 1.92-2.06 (2H, m), 2.30 (3H, s), 2.69-2.74 (1H, m), 2.91-2.96 (1H, m), 3.22-3.25 (1H, m), 4.13 (1H, d, *J* = 11.1 Hz), 4.60-4.64 (1H, m), 4.76-4.82 (1H, m), 6.07-6.13 (1H, m), 6.70 (1H, d, *J* = 15.6 Hz), 7.10 (5H, s), 7.25-7.39 (4H, m).
^{13}C NMR (75 MHz, $CDCl_3$): δ 21.0, 21.4, 27.2, 35.4, 48.3, 55.0, 65.8, 68.8, 80.1, 92.4, 132.0, 126.5, 126.9, 127.2, 128.3, 128.6, 129.3, 131.2, 135.8, 137.6, 137.9, 172.7.
FT-IR (KBr, cm^{-1}): 747, 1105, 1180, 1374, 1550, 1647, 1724, 2925, 2979, 3027.
HR-MS (*m*/*z*) for $C_{26}H_{30}N_2O_4$ (M^+): Calculated 434.2206, found 434.2202.

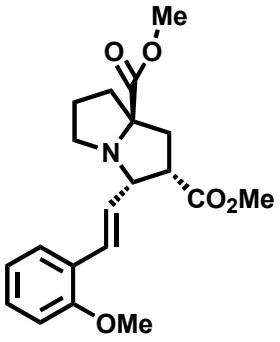
3.4. **1-(4-Chlorophenyl)-3-[2-(2-methoxyphenyl)-vinyl]-2-nitro-tetrahydropyrrolizine-7a-carboxylic acid methyl ester (6d)**



6d

Yield: 75 % (342 mg, 0.75 mmol).
Characteristic: Yellow solid.
Melting point: 56-60 °C.
^{1}H NMR (300 MHz, $CDCl_3$): δ 1.90-2.04 (4H, m), 2.68-2.71 (1H, m), 2.91-2.93 (1H, m), 3.25-3.28 (1H, m), 3.42 (3H, s), 3.84 (3H, s), 4.08-4.15 (1H, m), 4.77 (1H, dd, *J* = 10.2, 7.8 Hz), 6.03-6.16 (1H, m), 6.85-6.93 (1H, m), 7.01 (1H, d, *J* = 15.6 Hz), 7.15 (2H, d, *J* = 8.4 Hz), 7.22-7.37 (4H, m), 7.38 (1H, d, *J* = 9.0 Hz).
^{13}C NMR (75 MHz, $CDCl_3$): δ 27.2, 35.4, 48.5, 52.1, 54.7, 55.5, 66.5, 80.2, 91.8, 111.0, 120.6, 122.8, 124.7, 127.5, 128.6, 129.0, 132.7, 133.3, 134.0, 157.0, 173.3.
FT-IR (KBr, cm^{-1}): 752, 102, 1175, 1246, 1491, 1549, 158, 1642, 1734, 2949.
HR-MS (*m*/*z*) for $C_{24}H_{25}ClN_2O_5$ (M^+): Calculated 456.1452, found 456.1449 (one of the peaks).

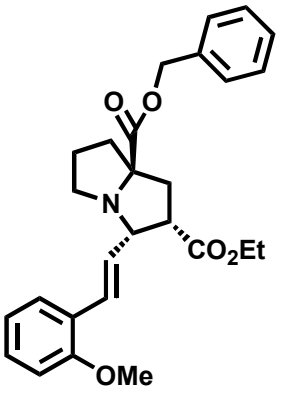
3.5. **3-[2-(2-Methoxyphenyl)-vinyl]-tetrahydropyrrolizine-2,7a-dicarboxylic acid dimethyl ester (6e)**



6e

Yield: 84 % (301 mg, 0.84 mmol).
Characteristic: Yellow oil.
^{1}H NMR (300 MHz, $CDCl_3$): δ 1.79-1.89 (3H, m), 2.14-2.29 (3H, m), 2.60 (1H, q, *J* = 6.6 Hz), 2.84-2.88 (1H, m), 3.09-3.15 (1H, m), 3.54 (3H, s), 3.72 (3H, s), 3.80 (3H, s), 4.17 (1H, dd, *J* = 10.5, 7.5 Hz), 5.94 (1H, dd, *J* = 15.6 Hz, 10.5 Hz), 6.79-6.90 (3H, m), 7.17-7.22 (1H, m), 7.33 (1H, m).
^{13}C NMR (75 MHz, $CDCl_3$): δ 27.7, 36.3, 37.1, 48.7, 49.9, 51.7, 52.4, 55.4, 67.7, 110.8, 120.5, 125.6, 126.2, 127.1, 128.9, 130.2, 156.7, 172.1, 176.9.
FT-IR (KBr, cm^{-1}): 753, 1028, 1196, 1245, 1489, 1597, 1735, 2951.
HR-MS (*m*/*z*) for $C_{20}H_{25}NO_5$ (M^+): Calculated 359.1733, found 359.1737.

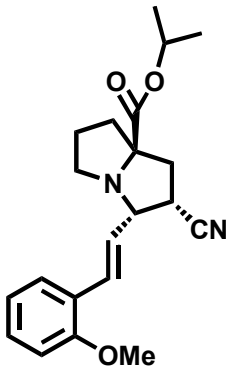
3.6. **3-[2-(2-Methoxyphenyl)-vinyl]-tetrahydropyrrolizine-2,7a-dicarboxylic acid 7a-benzyl ester 2-ethyl ester (6f)**



6f

Yield: 82 % (368 mg, 0.82 mmol).
Characteristic: Yellow oil.
^{1}H NMR (300 MHz, $CDCl_3$): δ 1.11 (3H, t, *J* = 7.2 Hz), 1.75-1.87 (2H, m), 2.16-2.30 (3H, m), 2.62 (1H, q, *J* = 6.6 Hz), 2.88-2.92 (1H, m), 3.12-3.14 (1H, m), 3.49-3.57 (1H, m), 3.82 (3H, s), 3.97-4.04 (2H, m), 4.20 (1H, dd, *J* = 10.5, 7.5 Hz), 5.18-5.19 (2H, m), 5.96 (1H, dd, *J* = 15.9, 10.5 Hz), 6.82-6.92 (2H, m), 7.19-7.26 (3H, m), 7.31-7.38 (5H, m).
^{13}C NMR (75 MHz, $CDCl_3$): δ 14.1, 27.9, 36.2, 37.1, 48.7, 49.9, 55.3, 60.5, 66.6, 67.8, 110.8, 120.5, 125.6, 126.3, 127.1, 127.9, 128.1, 128.5, 128.8, 130.2, 136.2, 156.7, 171.7, 176.2.
FT-IR (KBr, cm^{-1}): 752, 1029, 1179, 1245, 1375, 1489, 1597, 1731, 2957.
HR-MS (*m*/*z*) for $C_{27}H_{31}NO_5$ (M^+): Calculated 449.2202, found 449.2200.

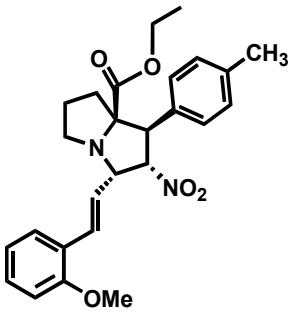
3.7. **2-Cyano-3-[2-(2-methoxyphenyl)-vinyl]-tetrahydropyrrolizine-7a-carboxylic acid isopropyl ester (6g)**



6g

Yield: 80 % (283 mg, 0.80 mmol).
Characteristic: Yellow oil.
^{1}H NMR (300 MHz, $CDCl_3$): δ 1.27-1.31 (6H, m), 1.59-1.65 (1H, m), 1.76-1.83 (1H, m), 2.06 (2H, bs), 2.39 (2H, dd, *J* = 13.2, 8.4 Hz), 2.60-2.68 (1H, s), 2.87-2.94 (1H, m), 3.04-3.07 (1H, m), 3.84 (3H, s), 4.15 (1H, t, *J* = 8.7 Hz), 5.03-5.07 (1H, m), 6.30 (1H, dd, *J* = 16.2, 7.2 Hz), 6.88-6.95 (1H, m), 7.06 (1H, d, *J* = 16.2 Hz), 7.22-7.26 (2H, m), 7.40-7.43 (1H, m).
^{13}C NMR (75 MHz, $CDCl_3$): δ 21.7, 25.6, 29.6, 31.5, 37.4, 40.9, 49.7, 55.5, 68.9, 69.2, 75.1, 111.0, 119.9, 120.6, 124.0, 125.2, 127.2, 129.2, 130.3, 157.0, 174.1.
FT-IR (KBr, cm^{-1}): 1078, 1199, 1352, 1533, 1612, 1701, 2923.
HR-MS (*m*/*z*) for $C_{21}H_{26}N_2O_3$ (M^+): Calculated 354.1943, found 354.1946.

3.3. **3-[2-(2-Methoxyphenyl)-vinyl]-2-nitro-1-(4-methylphenyl)-tetrahydropyrrolizine-7a-carboxylic acid ethyl ester (6h)**



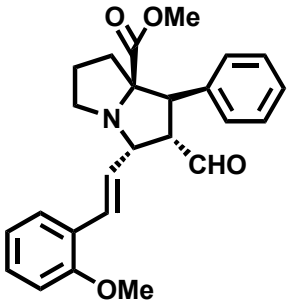
6h

Yield: 88 % (396 mg, 0.88 mmol).
Characteristic: Yellow solid.
Melting point: 112-115 °C.
^{1}H NMR (300 MHz, $CDCl_3$): δ 0.97 (3H, t, *J* = 7.2 Hz), 1.92-2.05 (4H, m), 2.30 (3H, s), 2.70-2.76 (1H, m), 2.89-2.96 (1H, m), 3.24-3.32 (1H, m), 3.73-3.79 (1H, m), 3.83 (3H, s), 3.85-3.91 (1H, m), 4.15 (1H, d, *J* = 11.1 Hz), 4.80 (1H, dd, *J* = 10.2, 8.1 Hz), 6.07-6.20 (1H, m), 6.84-6.94 (2H, m), 7.03 (1H, d, *J* = 15.6 Hz), 7.11 (4H, s), 7.22-7.24 (1H, m), 7.40 (1H, d, *J* = 9.0 Hz).
^{13}C NMR (75 MHz, $CDCl_3$): δ 13.7, 21.0, 27.2, 35.5, 48.6, 55.0, 55.5, 61.1, 66.5, 80.1, 92.1, 111.0, 120.6, 123.3, 124.9, 127.1, 127.5, 129.4, 129.5, 131.2, 132.9, 137.6, 157.0, 173.2.
FT-IR (KBr, cm^{-1}): 774, 1027, 1109, 1187, 1244, 1378, 1488, 1544, 1638, 1724, 107, 2865, 2960.
HR-MS (*m*/*z*) for $C_{26}H_{30}N_2O_5$ (M^+): Calculated 450.2155, found 450.2152.

4. **General procedure for pseudo 3-component reaction to tetrahydropyrrolizines (7a-l) and characterization data**

The solution of proline ester (**1**, 1 mmol) in DCM (10 mL) was taken in a round-bottom flasks (25 mL) and stirred at room temperature. (a) Two different α,β-unsaturated aldehydes (**3X** and **3Y**, 1.0 mmol each) or (b) a single α,β-unsaturated aldehyde (**3**, 2.0 mmol) were added in the reaction mixtures. The progress of the reaction was monitored by TLC and the reaction was complete after 10-17 min depending on the use of the substrates. The post-reaction mixture was filtered, washed with of saturated aqueous sodium bicarbonate solution (2 x 10 mL) and 1 x 10 mL brine solution, dried on activated sodium sulphate, and concentrated in a rotary evaporator under reduced pressure at room temperature. Thus, the reaction with proline methyl ester (**1a**, 129 mg, 1 mmol), *o*-methoxycinnamaldehyde (**3a**, 162 mg, 1.0 mmol) and cinnamaldehyde (**3b**, 132 mg, 1.0 mmol) afforded a mixture of **7a**, **7b**, **7c** and **7d** after purification by column chromatography on silica gel (60-120 mesh) with ethyl acetate-petroleum ether as an eluent in a combined yield of 83 % (0.83 mmol) whereas the reaction with proline methyl ester (**1a**, 129 mg, 1 mmol) and *o*-methoxycinnamaldehyde (**3a**, 325 mg, 2.0 mmol) afforded **7f** (**7b**) after purification by column chromatography on silica gel (60-120 mesh) with ethyl acetate-petroleum ether (1:9, v/v) as an eluent in a yield of 86% (374 mg, 0.86 mmol). The tetrahyropyrrolizines (**7a-l)** were characterized by NMR, FT-IR and ESI-MS spectroscopy.

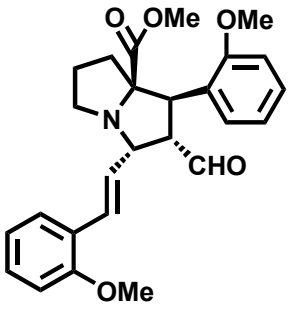
4.1. **2-Formyl-3-[2-(2-methoxyphenyl)-vinyl]-1-phenyl-tetrahydropyrrolizine-7a-carboxylic acid methyl ester (7a)**



7a

Yield: 32 % (130 mg, 0.32 mmol; cross coupling product).
Characteristic: Brown liquid.
^{1}H NMR (300 MHz, $CDCl_3$): δ 1.67-1.78 (2H, m), 2.04-2.11 (2H, m), 2.63-2.71 (1H, m), 3.03-3.05 (1H, m), 3.42-3.51 (1H, m), 3.71 (3H, s), 3.89 (3H, s), 4.55-4.68 (2H, m), 6.38 (1H, dd, J = 15.9, 7.5 Hz), 6.73-6.82 (2H, m), 6.92 (1H, t, J = 7.5 Hz), 7.11-7.40 (7H, m), 9.61 (1H, d, J = 4.8 Hz).
^{13}C NMR (75 MHz, $CDCl_3$): δ 25.7, 31.2, 48.3, 50.9, 52.4, 54.8, 55.9, 65.0, 110.0, 120.5, 124.1, 125.9, 126.6, 127.1, 128.1, 128.4, 135.2, 136.2, 156.9, 175.1, 201.2.
FT-IR (neat, cm^{-1}): 694, 1078, 1170, 1320, 1440, 1530, 1600, 1670, 2978, 3065.
HR-MS (*m*/*z*) for $C_{25}H_{27}NO_4$ (M^+): Calculated 405.1940, found 405.1938.

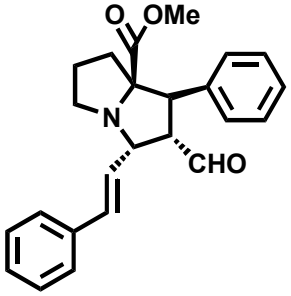
4.2. **2-Formyl-3-(2-methoxyphenyl)-1-[2-(2-methoxyphenyl)-vinyl]-hexahydro-pentalene-3a-carboxylic acid methyl ester (7b)**



7b

Yield: 40 % (173 mg, 0.40 mmol; cross coupling product).
Characteristic: Brown liquid.
^{1}H NMR (300 MHz, $CDCl_3$): δ 1.59-1.65 (2H, m), 1.97-2.01 (2H, m), 2.50-2.59 (1H, m), 2.94-3.02 (1H, m), 3.41-3.49 (1H, m), 3.63 (3H, s), 3.77 (3H, s), 3.82 (3H, s), 4.50-4.60 (2H, m), 6.32 (1H, dd, *J* = 16.2, 7.5 Hz), 6.74 (1H, d, *J* = 8.1 Hz), 6.78-6.87 (3H, m), 6.96-7.03 (1H, m), 7.11-7.34 (3H, m), 7.36 (1H, d, *J* = 1.5 Hz), 9.54 (1H, d, *J* = 4.5 Hz).
^{13}C NMR (75 MHz, $CDCl_3$): δ 14.1, 25.7, 31.2, 48.2, 50.8, 52.4, 54.8, 55.5, 55.8, 65.5, 110.0, 111.0, 120.4, 120.6, 125.4, 126.0, 127.1, 127.2, 128.3, 129.1, 130.2, 137.4, 156.9, 157.0, 201.2.
FT-IR (neat, cm^{-1}): 697, 1075, 1166, 1312, 1348, 1437, 1524, 1596, 1666, 2976, 3065.
HR-MS (*m*/*z*) for $C_{26}H_{29}NO_5$ (M^+): Calculated 435.2046, found 435.2050.

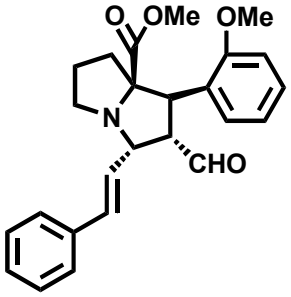
4.3. **2-Formyl-3-phenyl-1-styryl-hexahydropentalene-3a-carboxylic acid methyl ester (7c)**



7c

Yield: 8 % (30 mg, 0.08 mmol; cross coupling product).
Characteristic: Brown liquid.
^{1}H NMR (300 MHz, $CDCl_3$): δ 1.72-1.79 (2H, m), 1.93-2.06 (2H, m), 2.78-2.81 (1H, m), 3.08-3.10 (1H, m), 3.48-3.53 (1H, m), 3.88 (3H, s), 4.44-4.51 (2H, m), 6.39 (1H, dd, *J* = 16.2, 7.5 Hz), 6.74 (1H, d, *J* = 15.9 Hz), 7.18-7.40 (10H, m), 9.62 (1H, d, *J* = 4.2 Hz).
^{13}C NMR (75 MHz, $CDCl_3$): δ 25.6, 32.7, 50.9, 53.0, 56.7, 65.5, 78.6, 126.6, 127.3, 127.5, 128.0, 128.1, 128.6, 129.0, 135.2, 136.1, 136.5, 176.0, 200.9.
FT-IR (neat, cm^{-1}): 734, 1105, 1233, 1385, 147, 1634, 1727, 284, 2919.
HR-MS (*m*/*z*) for $C_{24}H_{25}NO_3$ (M^+): Calculated 375.1834, found 375.1836.

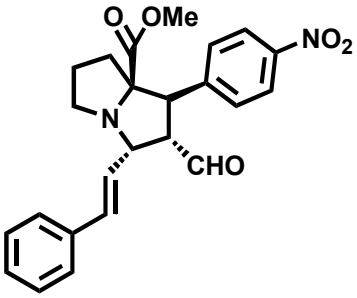
4.4. **2-Formyl-1-(2-methoxyphenyl)-3-styryl-tetrahydropyrrolizine-7a-carboxylic acid methyl ester (7d)**



7d

Yield: 3 % (13 mg, 0.03 mmol; cross coupling product).
Characteristic: Brown liquid.
^{1}H NMR (300 MHz, $CDCl_3$): δ 1.72-1.83 (2H, m), 1.86-1.98 (2H, m), 2.74-2.82 (1H, m), 3.06-3.08 (1H, m), 3.43-3.52 (1H, m), 3.85 (3H, s), 3.88 (3H, s), 4.48 (2H, d, J = 11.7 Hz), 6.41 (1H, dd, J = 15.9, 7.5 Hz), 6.86-6.92 (1H, m), 7.03 (1H, d, J = 15.9 Hz), 7.18-7.43 (8H, m), 9.64 (1H, d, J = 4.5 Hz).
^{13}C NMR (75 MHz, $CDCl_3$): δ 25.6, 29.6, 31.9, 32.7, 50.8, 52.9, 56.7, 65.5, 78.6, 124.2, 126.6, 127.3, 128.0, 128.1, 128.6, 128.8, 129.2, 135.1, 136.2, 136.6, 156.4, 176.1, 200.9.
FT-IR (neat, cm^{-1}): 697, 1075, 1166, 1312, 1348, 1437, 1524, 1596, 1666, 2976, 3065.
HR-MS (*m*/*z*) for $C_{25}H_{27}NO_4$ (M^+): Calculated 405.1940, found 405.1938.

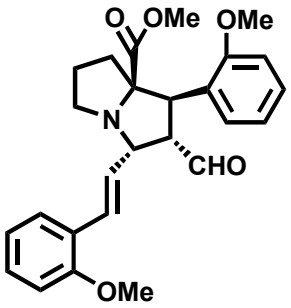
4.5. **2-Formyl-3-[2-(2-methoxyphenyl)-vinyl]-1-(4-nitrophenyl)-tetrahydropyrrolizine-7a-carboxylic acid methyl ester (7e)**



7e

Yield: 21 % (90 mg, 0.21 mmol; cross coupling product).
Characteristic: Brown liquid.
^{1}H NMR (300 MHz, $CDCl_3$): δ 1.74-1.82 (2H, m), 2.72-2.80 (2H, m), 3.07-3.09 (1H, m), 3.14-3.34 (1H, m), 3.44-3.53 (1H, m), 3.88 (3H, s), 4.08-4.13 (1H, m), 4.45-4.52 (1H, m), 6.55-6.60 (1H, m), 6.79 (1H, d, J = 15.9 Hz), 7.17-7.41 (5H, m), 7.52 (2H, d, J = 8.4 Hz), 8.20 (2H, d, J = 8.7 Hz), 9.63 (1H, d, J = 4.5 Hz).
^{13}C NMR (75 MHz, $CDCl_3$): δ 25.6, 29.6, 32.7, 52.9, 53.1, 56.7, 65.1, 78.6, 124.0, 124.0, 127.1, 127.4, 127.9, 128.7, 129.3, 132.9, 136.4, 142.5, 176.0, 200.8.
FT-IR (neat, cm^{-1}): 697, 1075, 1166, 1312, 1348, 1437, 1524, 1596, 1666, 2976, 3065.
HR-MS (*m*/*z*) for $C_{24}H_{24}N_2O_5$ (M^+): Calculated 420.1685, found 420.1682.

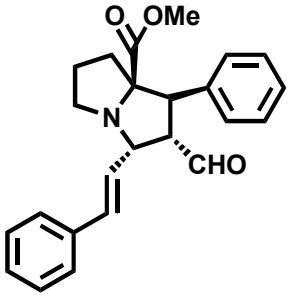
4.2. **2-Formyl-3-(2-methoxyphenyl)-1-[2-(2-methoxyphenyl)-vinyl]-hexahydropentalene-3a-carboxylic acid methyl ester (7f)**



7f (7b)

Yield: 86 % (374 mg, 0.86 mmol).
Characteristic: Brown liquid.
^{1}H NMR (300 MHz, $CDCl_3$): δ 1.59-1.65 (2H, m), 1.97-2.01 (2H, m), 2.50-2.59 (1H, m), 2.94-3.02 (1H, m), 3.41-3.49 (1H, m), 3.63 (3H, s), 3.77 (3H, s), 3.82 (3H, s), 4.50-4.60 (2H, m), 6.32 (1H, dd, *J* = 16.2, 7.5 Hz), 6.74 (1H, d, *J* = 8.1 Hz), 6.78-6.87 (3H, m), 6.96-7.03 (1H, m), 7.11-7.34 (3H, m), 7.36 (1H, d, *J* = 1.5 Hz), 9.54 (1H, d, *J* = 4.5 Hz).
^{13}C NMR (75 MHz, $CDCl_3$): δ 14.1, 25.7, 31.2, 48.2, 50.8, 52.4, 54.8, 55.5, 55.8, 65.5, 110.0, 111.0, 120.4, 120.6, 125.4, 126.0, 127.1, 127.2, 128.3, 129.1, 130.2, 137.4, 156.9, 157.0, 201.2.
FT-IR (neat, cm^{-1}): 697, 1075, 1166, 1312, 1348, 1437, 1524, 1596, 1666, 2976, 3065.
HR-MS (*m*/*z*) for $C_{26}H_{29}NO_5$ (M^+): Calculated 435.2046, found 435.2050.

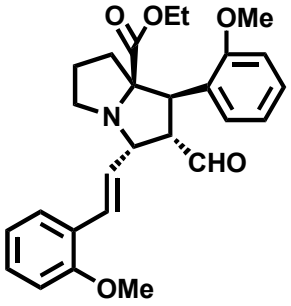
4.3. **2-Formyl-3-phenyl-1-styryl-hexahydropentalene-3a-carboxylic acid methyl ester (7g)**



7g (7c)

Yield: 76 % (285 mg, 0.76 mmol).
Characteristic: Brown liquid.
^{1}H NMR (300 MHz, $CDCl_3$): δ 1.72-1.79 (2H, m), 1.93-2.06 (2H, m), 2.78-2.81 (1H, m), 3.08-3.10 (1H, m), 3.48-3.53 (1H, m), 3.88 (3H, s), 4.44-4.51 (2H, m), 6.39 (1H, dd, *J* = 16.2, 7.5 Hz), 6.74 (1H, d, *J* = 15.9 Hz), 7.18-7.40 (10H, m), 9.62 (1H, d, *J* = 4.2 Hz).
^{13}C NMR (75 MHz, $CDCl_3$): δ 25.6, 32.7, 50.9, 53.0, 56.7, 65.5, 78.6, 126.6, 127.3, 127.5, 128.0, 128.1, 128.6, 129.0, 135.2, 136.1, 136.5, 176.0, 200.9.
FT-IR (neat, cm^{-1}): 734, 1105, 1233, 1385, 147, 1634, 1727, 284, 2919.
HR-MS (*m*/*z*) for $C_{24}H_{25}NO_3$ (M^+): Calculated 375.1834, found 375.1836.

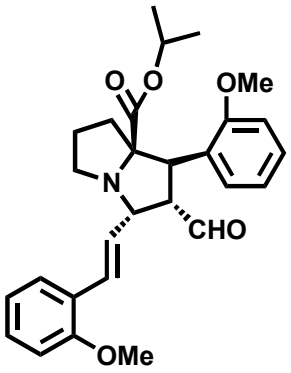
4.6. **2-Formyl-3-(2-methoxyphenyl)-1-[2-(2-methoxyphenyl)-vinyl]-hexahydropentalene-3a-carboxylic acid ethyl ester (7h)**



7h

Yield: 80 % (360 mg, 0.80 mmol).
Characteristic: Brown liquid.
^{1}H NMR (300 MHz, $CDCl_3$): δ 1.40 (3H, t, *J* = 7.2 Hz), 1.66-1.71 (2H, m), 2.04-2.11 (2H, m), 2.63-2.70 (1H, m), 3.00 (1H, t, *J* = 6.6 Hz), 3.44-3.51 (1H, m), 3.70 (3H, s), 3.84 (3H, s), 4.23-4.40 (2H, m), 4.58 (1H, dd, *J* = 10.2, 7.5 Hz), 4.67 (1H, d, *J* = 12.0 Hz), 6.40 (1H, dd, *J* = 16.2, 7.5 Hz), 6.81 (1H, d, *J* = 8.1 Hz), 6.85-6.94 (3H, m), 7.04 (1H, d, *J* = 16.2 Hz), 7.18-7.26 (3H, m), 7.43 (1H, d, *J* = 7.5 Hz), 9.61 (1H, d, *J* = 4.5 Hz).
^{13}C NMR (75 MHz, $CDCl_3$): δ 14.3, 25.8, 31.1, 48.3, 50.8, 54.7, 55.5, 56.1, 61.1, 65.5, 109.9, 110.9, 120.4, 120.5, 125.1, 125.5, 126.5, 127.1, 127.2, 128.2, 129.0, 129.8, 156.9, 157.0, 174.9, 201.6.
FT-IR (neat, cm^{-1}): 752, 1029, 1248, 1463, 1491, 1724, 2850, 2926.
HR-MS (*m*/*z*) for $C_{27}H_{31}NO_5$ (M^+): Calculated 449.2202, found 449.2200.

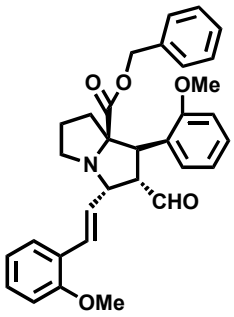
4.7. **2-Formyl-3-(2-methoxyphenyl)-1-[2-(2-methoxyphenyl)-vinyl]-hexahydropentalene-3a-carboxylic acid isopropyl ester (7i)**



7i

Yield: 82 % (380 mg, 0.82 mmol).
Characteristic: Brown liquid.
^{1}H NMR (300 MHz, $CDCl_3$): δ 1.38 (6H, d, *J* = 7.5 Hz), 1.63-1.75 (3H, m), 2.04-2.10 (1H, m), 2.62-2.63 (1H, m), 2.96-2.98 (1H, m), 3.46-3.47 (1H, m), 3.72 (3H, s), 3.85 (3H, s), 4.51-4.57 (1H, m), 4.67 (1H, d, *J* = 11.7 Hz), 5.10-5.15 (1H, m), 6.40 (1H, dd, *J* = 16.2, 7.2 Hz), 6.80-7.03 (4H, m), 7.18-7.42 (4H, m), 7.44 (1H, d, *J* = 1.5 Hz), 9.60 (1H, d, *J* = 4.8 Hz).
^{13}C NMR (75 MHz, $CDCl_3$): δ 22.0, 25.9, 31.0, 48.1, 50.7, 54.6, 55.5, 56.3, 65.3, 68.3, 110.0, 110.0, 120.5, 125.6, 126.8, 127.1, 127.2, 128.1, 128.9, 129.4, 156.9, 157.1, 174.0, 201.7.
FT-IR (neat, cm^{-1}): 825, 1029, 1249, 1290, 1339, 1511, 1633, 1654, 1676, 1724, 2930.
HR-MS (*m*/*z*) for $C_{28}H_{33}NO_5$ (M^+): Calculated 463.2359, found 463.2362.

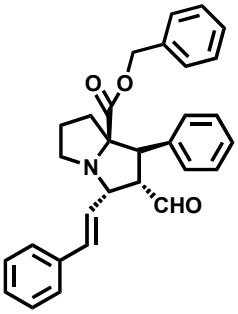
4.8. **2-Formyl-3-(2-methoxyphenyl)-1-[2-(2-methoxyphenyl)-vinyl]-hexahydropentalene-3a-carboxylic acid benzyl ester (7j)**



7j

Yield: 84 % (429 mg, 0.84 mmol).
Characteristic: Brown liquid.
^{1}H NMR (300 MHz, $CDCl_3$): δ 1.65-1.79 (2H, m), 2.04-2.14 (2H, m), 2.64-2.71 (1H, m), 3.04-3.06 (1H, m), 3.42 (3H, s), 3.45-3.56 (1H, m), 3.87 (3H, s), 4.57 (1H, dd, *J* = 10.2, 7.5 Hz), 4.67 (1H, d, *J* = 9.0 Hz), 5.35 (2H, dd, *J* = 42.0, 12.6 Hz), 6.43 (1H, dd, *J* = 16.2, 7.5 Hz), 6.78 (1H, d, *J* = 8.1 Hz), 6.88-6.97 (3H, m), 7.08 (1H, d, *J* = 16.2 Hz), 7.21-7.30 (4H, m), 7.35-7.53 (5H, m), 9.62 (1H, d, *J* = 4.8 Hz).
^{13}C NMR (75 MHz, $CDCl_3$): δ 20.5, 25.8, 31.2, 48.2, 50.8, 54.4, 55.5, 55.9, 65.3, 66.9, 109.9, 111.0, 120.4, 120.6, 124.0, 125.4, 126.2, 126.9, 127.1, 127.2, 127.6, 127.9, 128.0, 128.3, 128.5, 129.1, 130.1, 136.5, 157.0, 174.3, 174.4, 201.2.
FT-IR (neat, cm^{-1}): 1027, 1247, 1462, 1491, 1599, 1731, 2927.
HR-MS (*m*/*z*) for $C_{32}H_{33}NO_5$ (M^+): Calculated 511.2359, found 511.2355.

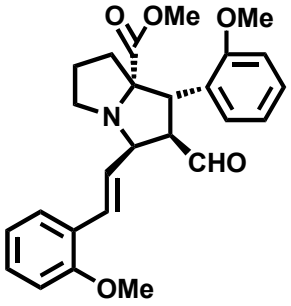
4.9. **2-Formyl-1-phenyl-3-styryl-tetrahydropyrrolizine-7a-carboxylic acid benzyl ester (7k)**



7k

Yield: 80 % (361 mg, .0.80 mmol).
Characteristic**:** Colourless solid.
Melting point: 186-192 °C.
^{1}H NMR (300 MHz, $CDCl_3$): δ 1.72-1.87 (2H, m), 1.93-2.17 (2H, m), 2.75-2.83 (1H, m), 3.09 (1H, t, *J* = 6.9 Hz), 3.41-3.55 (1H, m), 4.47-4.51 (2H, m), 5.33 (2H, q, *J* = 12.3 Hz), 6.40 (1H, dd, *J* = 15.9, 7.2 Hz), 6.72 (1H, d, *J* = 16.2 Hz), 7.05-7.07 (2H, m), 7.21-7.38 (5H, m), 7.41-7.47 (8H, m), 9.58 (1H, d, *J* = 4.5 Hz).
^{13}C NMR (75 MHz, $CDCl_3$): δ 25.7, 32.5, 50.9, 53.0, 56.8, 65.6, 67.2, 78.7, 124.4, 126.6, 127.2, 128.0, 128.1, 128.2, 128.3, 128.5, 128.6, 134.9, 135.9, 136.2, 136.6, 175.4, 201.1.
FT-IR (KBr, cm^{-1}): 697, 751, 1117, 1157, 1451, 1497, 1723, 2925.
HR-MS (*m*/*z*) for $C_{30}H_{29}NO_3$ (M^+): Calculated 451.2147, found 451.2144.

4.10. **2-Formyl-1-(2-methoxyphenyl)-3-[2-(2-methoxyphenyl)-vinyl]-tetrahydropyrrolizine-7a-carboxylic acid methyl ester (7l)**

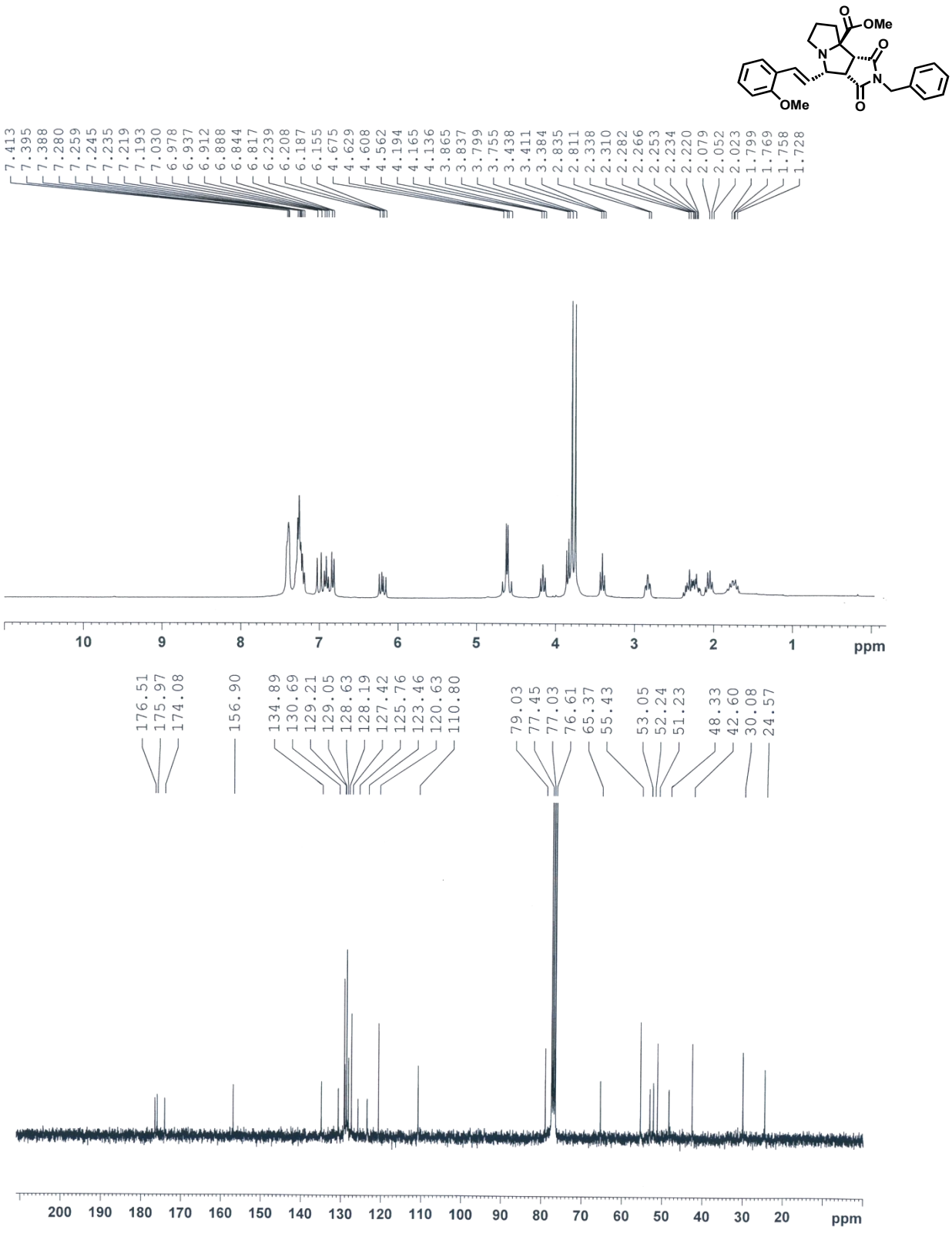


7l

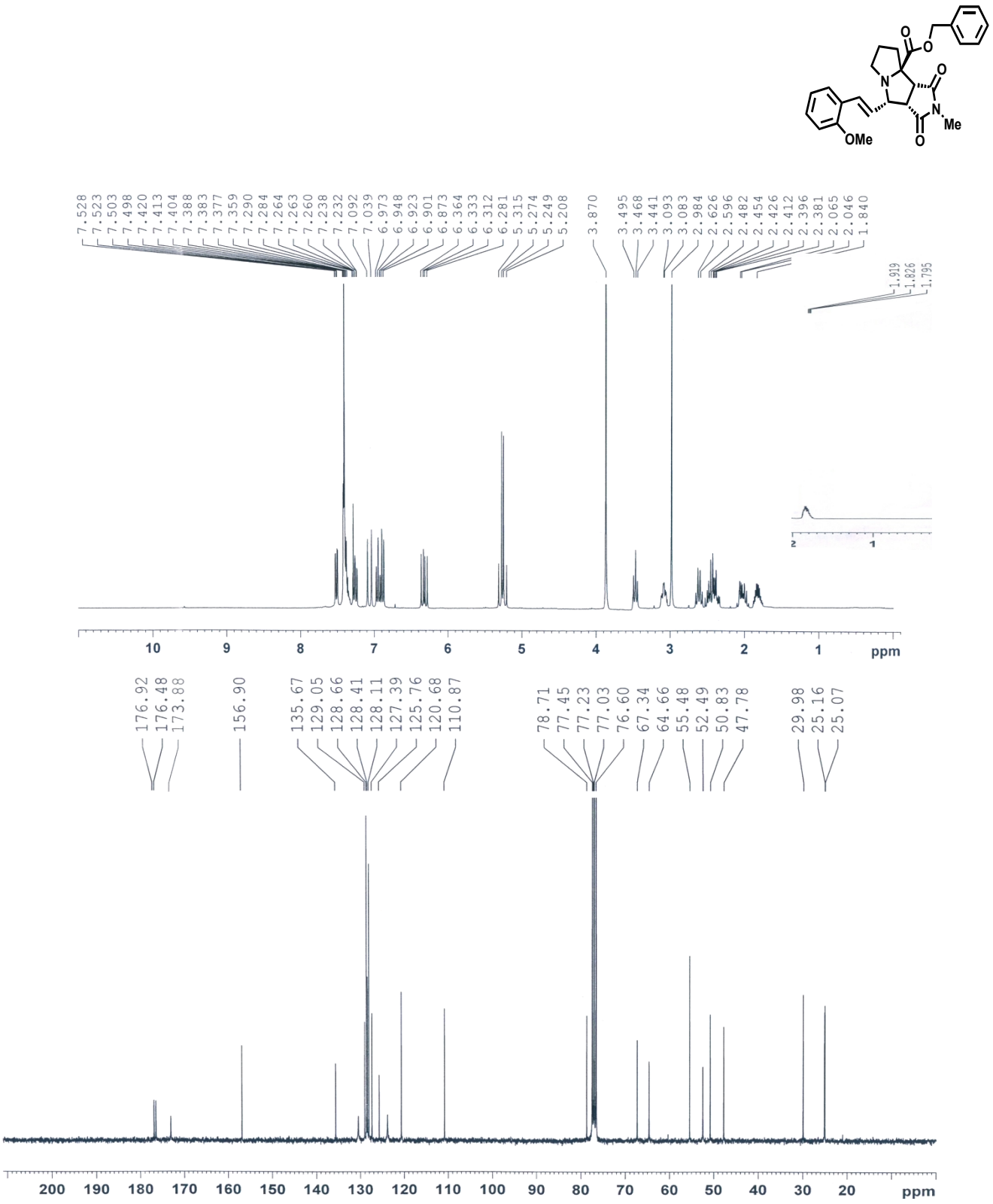
Yield: 85% (318 mg, 0.85 mmol).
Characteristic: Brown liquid.
^{1}H NMR (300 MHz, $CDCl_3$): δ 1.65-1.69 (2H, m), 2.04-2.09 (2H, m), 2.63-2.71 (1H, m), 2.98-3.02 (1H, m), 3.41-3.50 (1H, m), 3.70 (3H, s), 3.84 (3H, s), 3.88 (3H, s), 4.54-4.67 (2H, m), 6.40 (1H, dd, *J* = 15.9, 7.5 Hz), 6.80 (1H, d, *J* = 8.1 Hz), 6.84-6.94 (3H, m), 7.05 (1H, d, *J* = 15.9 Hz), 7.18-7.26 (3H, m), 7.42 (1H, d, *J* = 9.0 Hz), 9.62 (1H, d, *J* = 4.8 Hz).
^{13}C NMR (75 MHz, $CDCl_3$): δ 14.1, 21.0, 25.7, 31.2, 48.3, 50.8, 52.3, 54.8, 55.2, 55.5, 56.0, 60.3, 65.6, 109.9, 110.9, 120.5, 124.9, 125.4, 126.2, 128.8, 127.1, 127.2, 128.2, 129.0, 156.9, 171.1, 175.4, 201.5.
FT-IR (neat, cm^{-1}): 753, 1027, 1121, 1247, 1437, 1462, 1638, 1725, 2925.
HR-MS (*m*/*z*) for $C_{26}H_{29}NO_5$ (M^+): Calculated 435.2046, found 435.2049.

5. ^{1}H and ^{13}C NMR spectra of the all new compounds (5a-o, 6a-h and 7a-l)

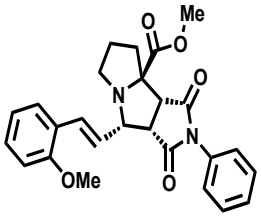
SI Figure 1: ^{1}H and ^{13}C NMR spectra of compound **5a**

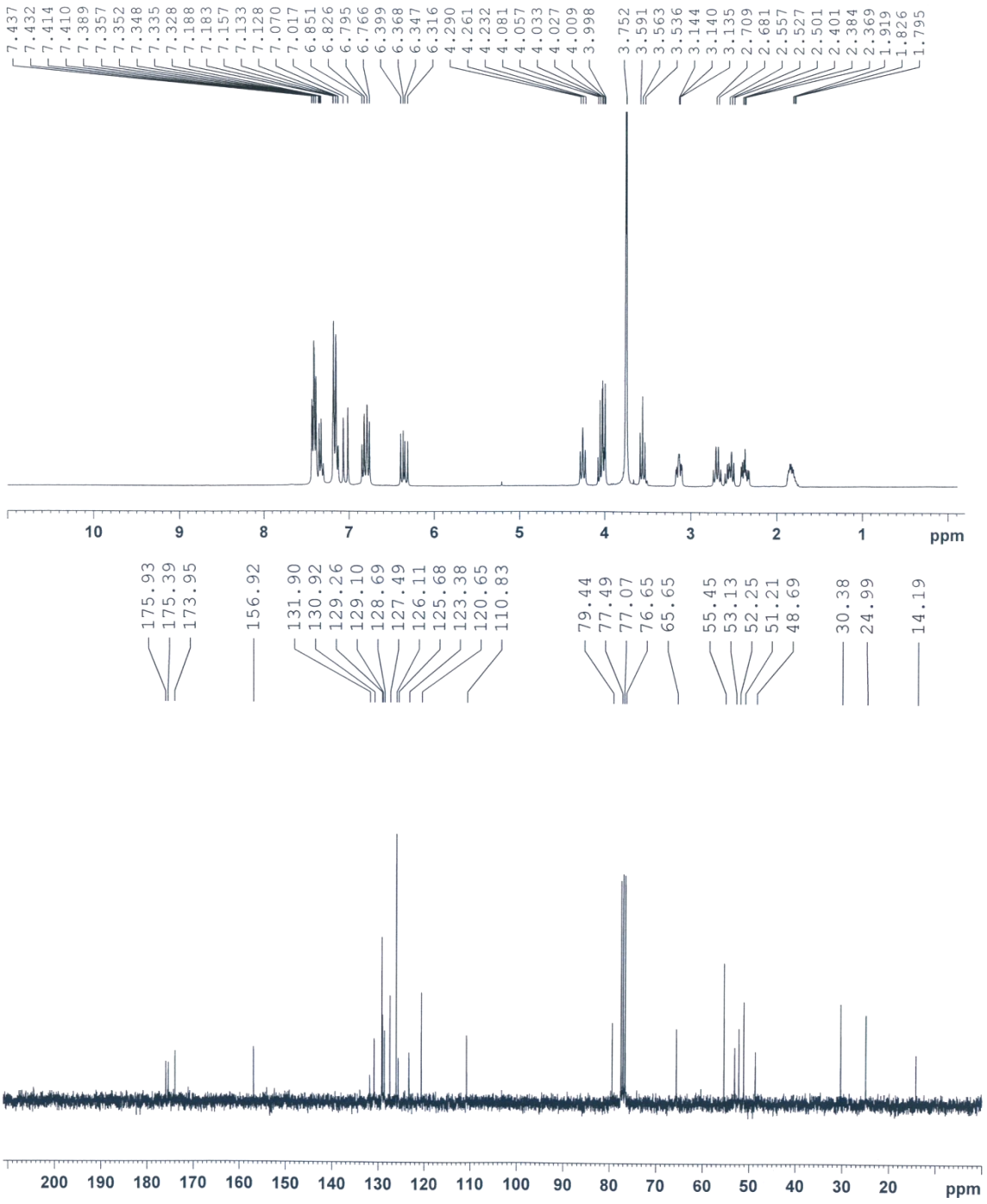


SI Figure 2: ^{1}H and ^{13}C NMR spectra of compound **5b**

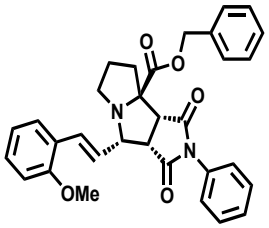


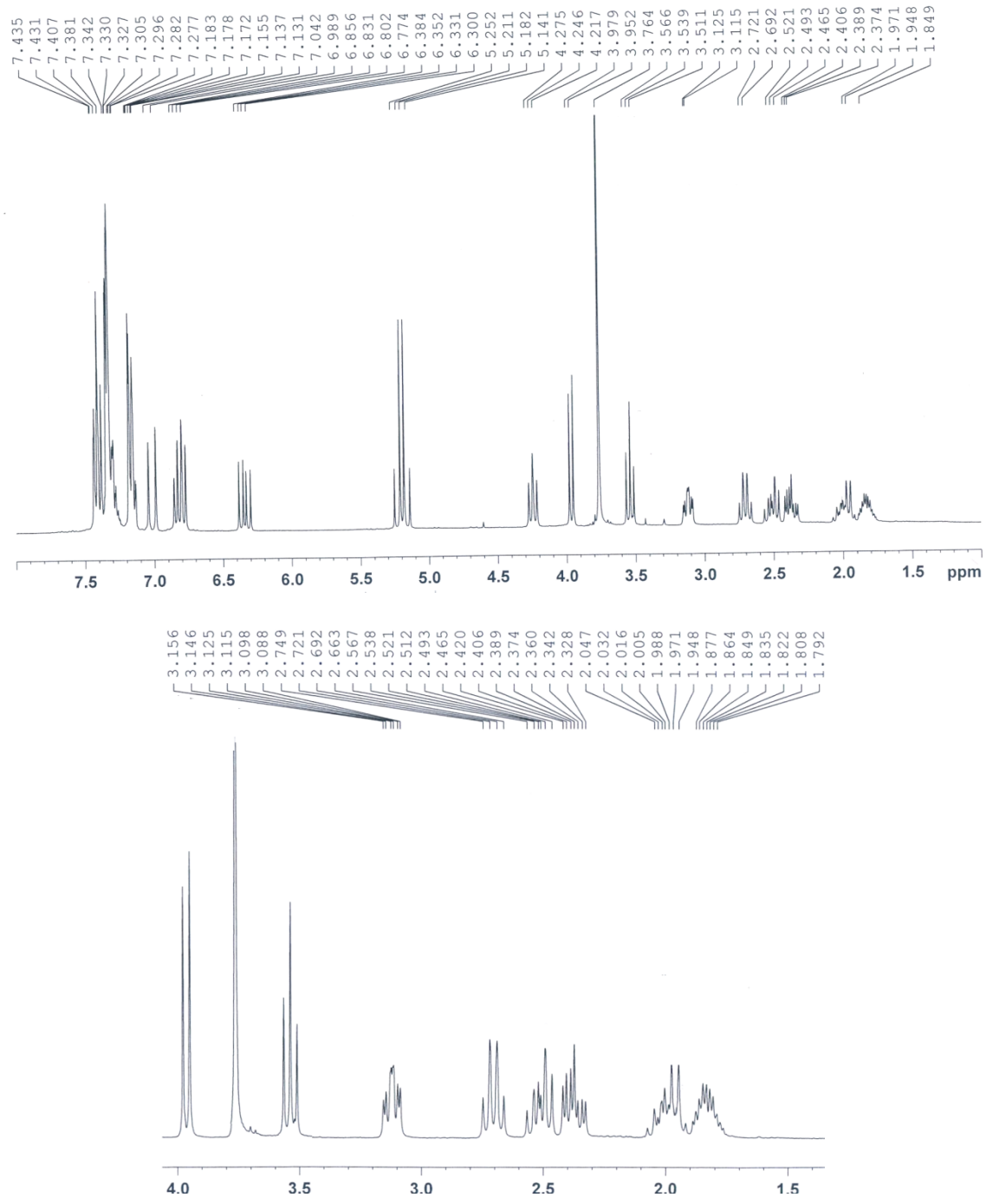
SI Figure 3: ^{1}H and ^{13}C NMR spectra of compound **5c**

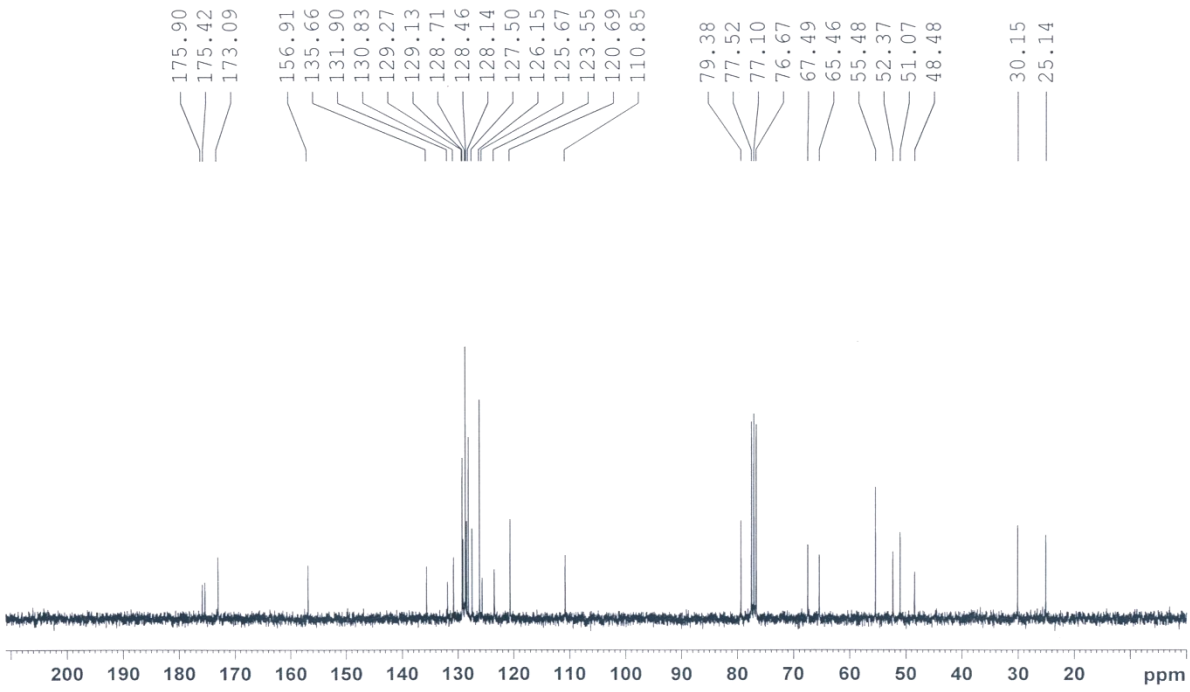




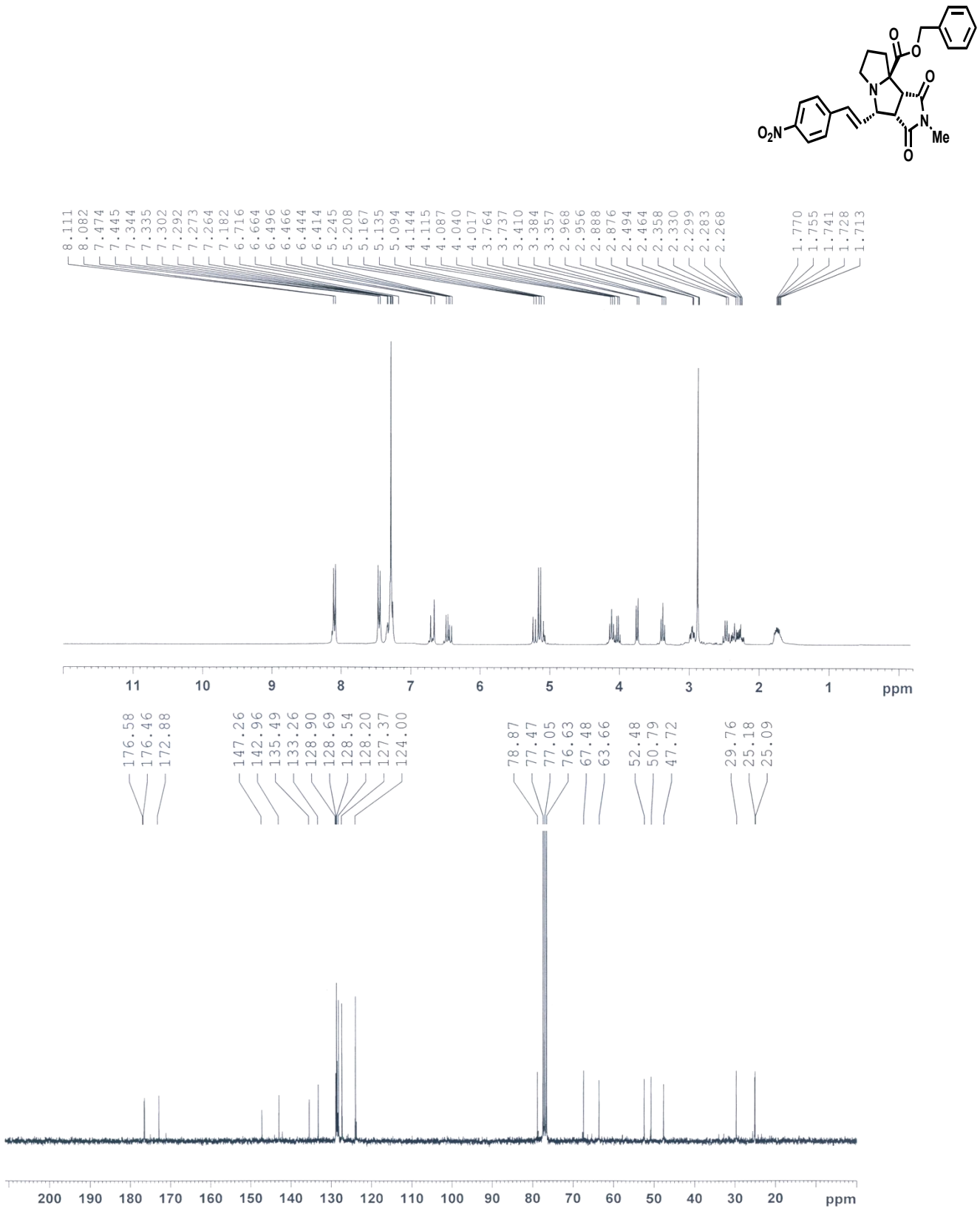
SI Figure 4: ^{1}H and ^{13}C NMR spectra of compound **5d**



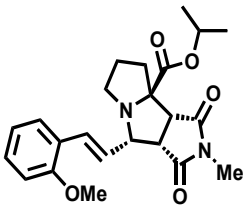


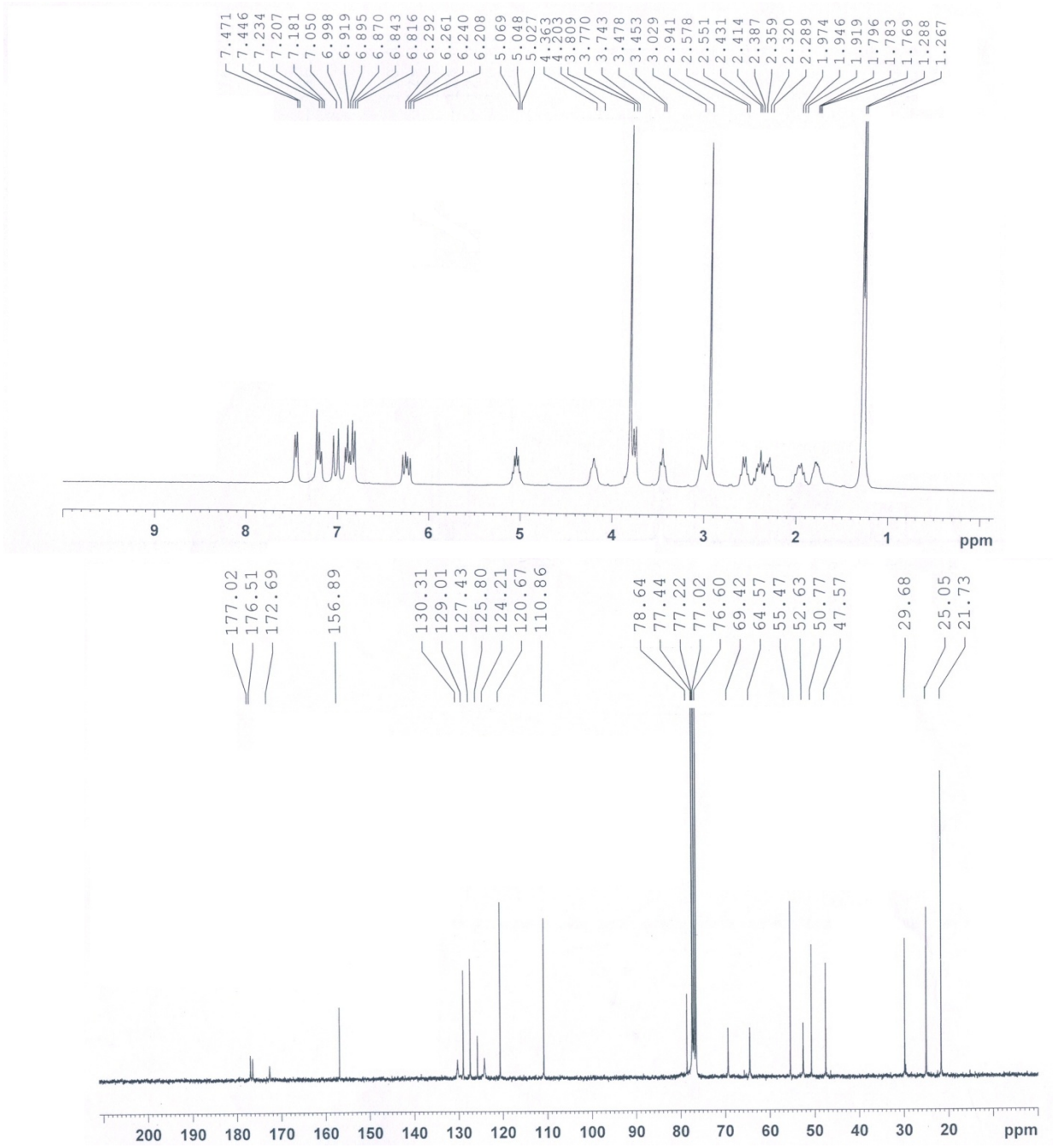

175.90
175.42
173.09
156.91
135.66
131.90
130.83
129.27
129.13
128.71
128.46
128.14
127.50
126.15
125.67
123.55
120.69
110.85
79.38
77.52
77.10
76.67
67.49
65.46
55.48
52.37
51.07
48.48
30.15
25.14
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

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

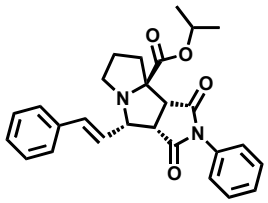


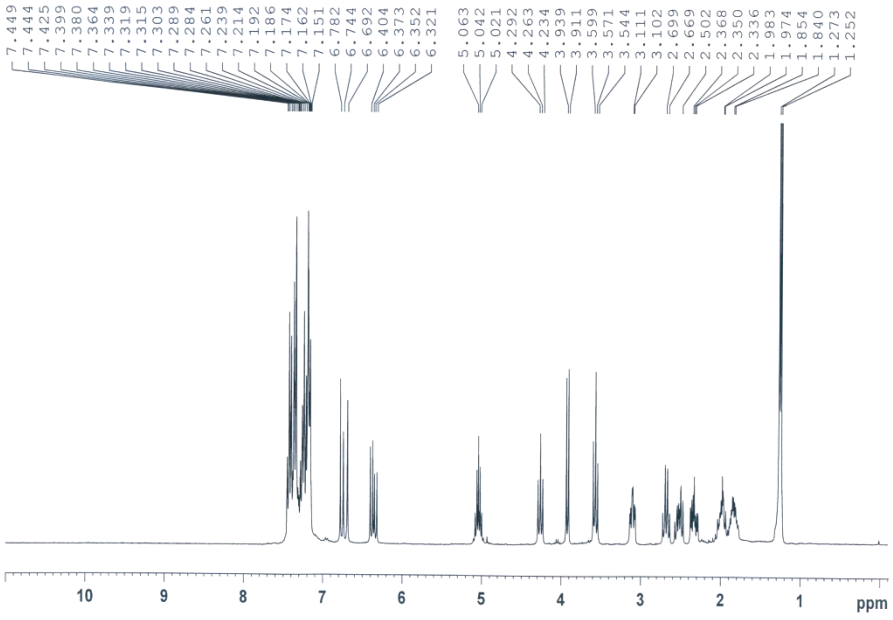
SI Figure 6: ^{1}H and ^{13}C NMR spectra of compound **5f**

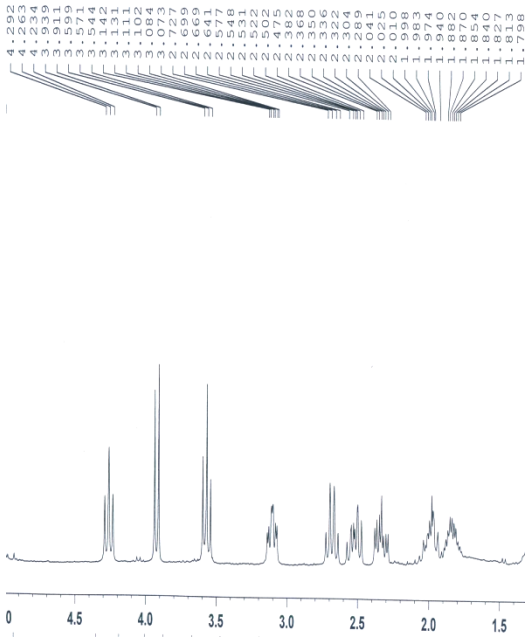


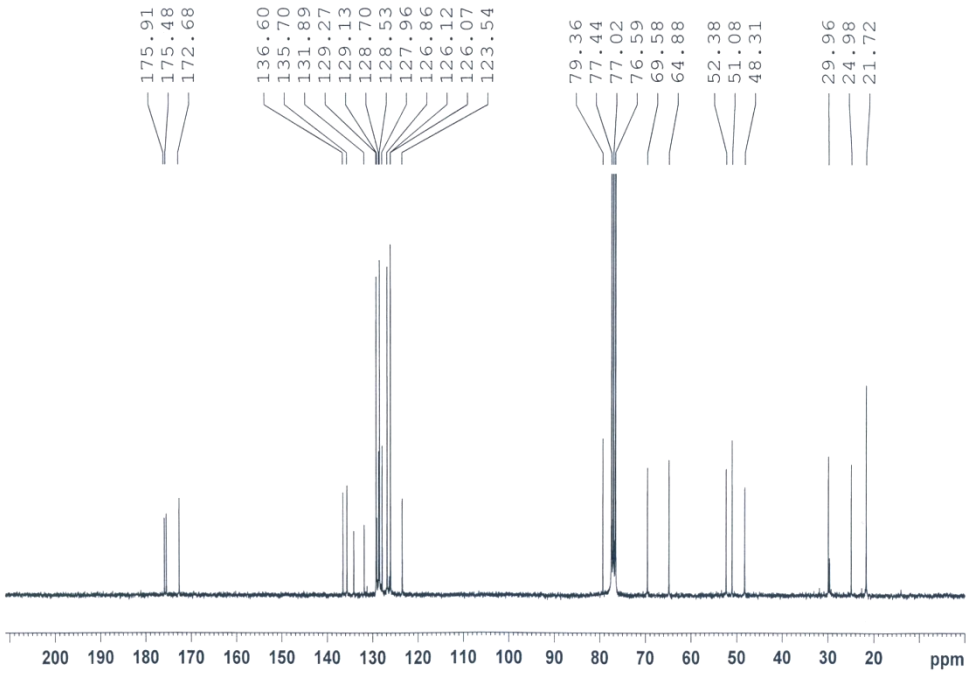


SI Figure 7: ^{1}H and ^{13}C NMR spectra of compound **5g**

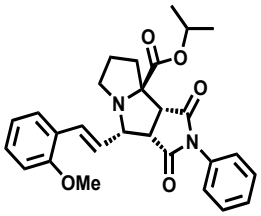


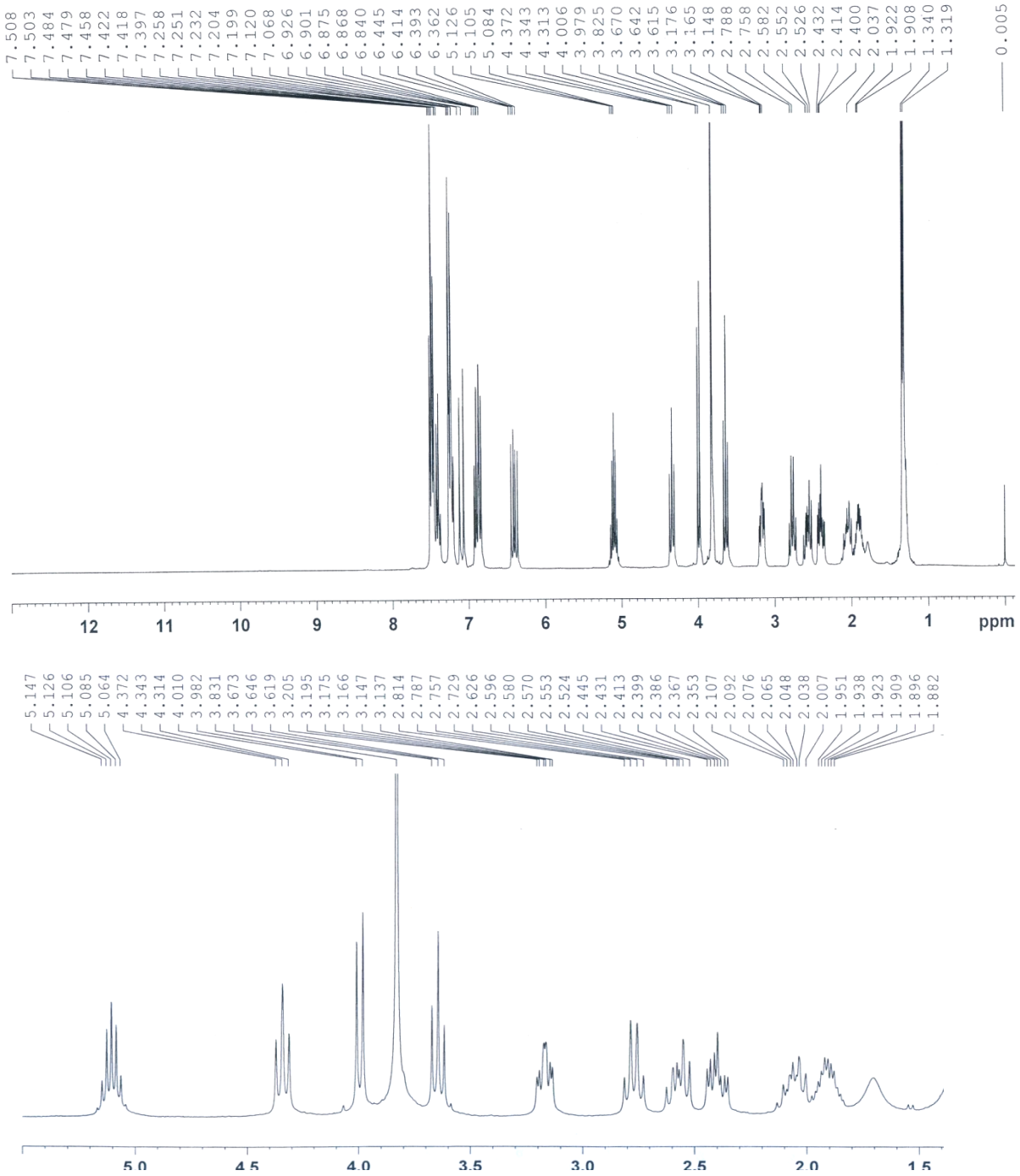


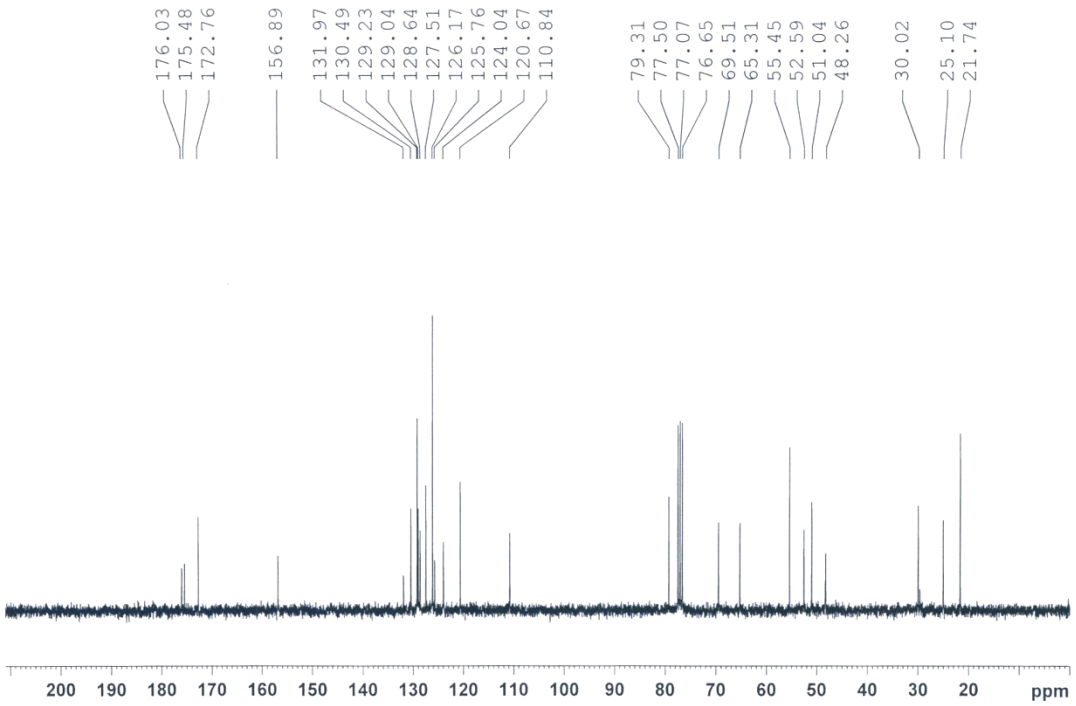



175.91
175.48
172.68
136.60
135.70
131.89
129.27
129.13
128.70
128.53
127.96
126.86
126.12
126.07
123.54
79.36
77.44
77.02
76.59
69.58
64.88
52.38
51.08
48.31
29.96
24.98
21.72
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

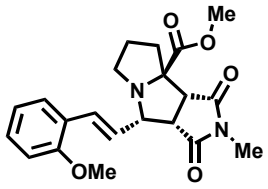
SI Figure 8: ^{1}H and ^{13}C NMR spectra of compound **5h**

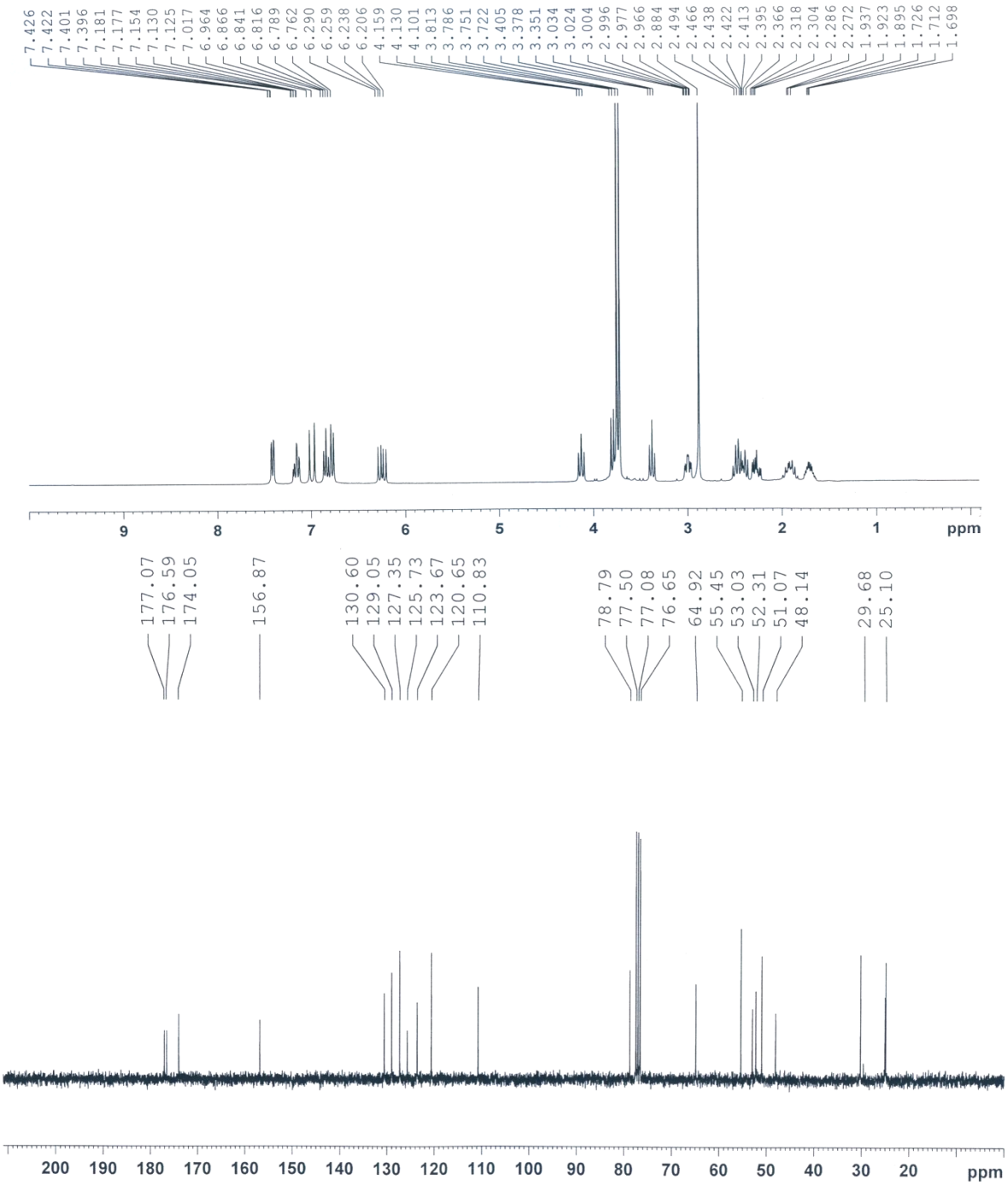




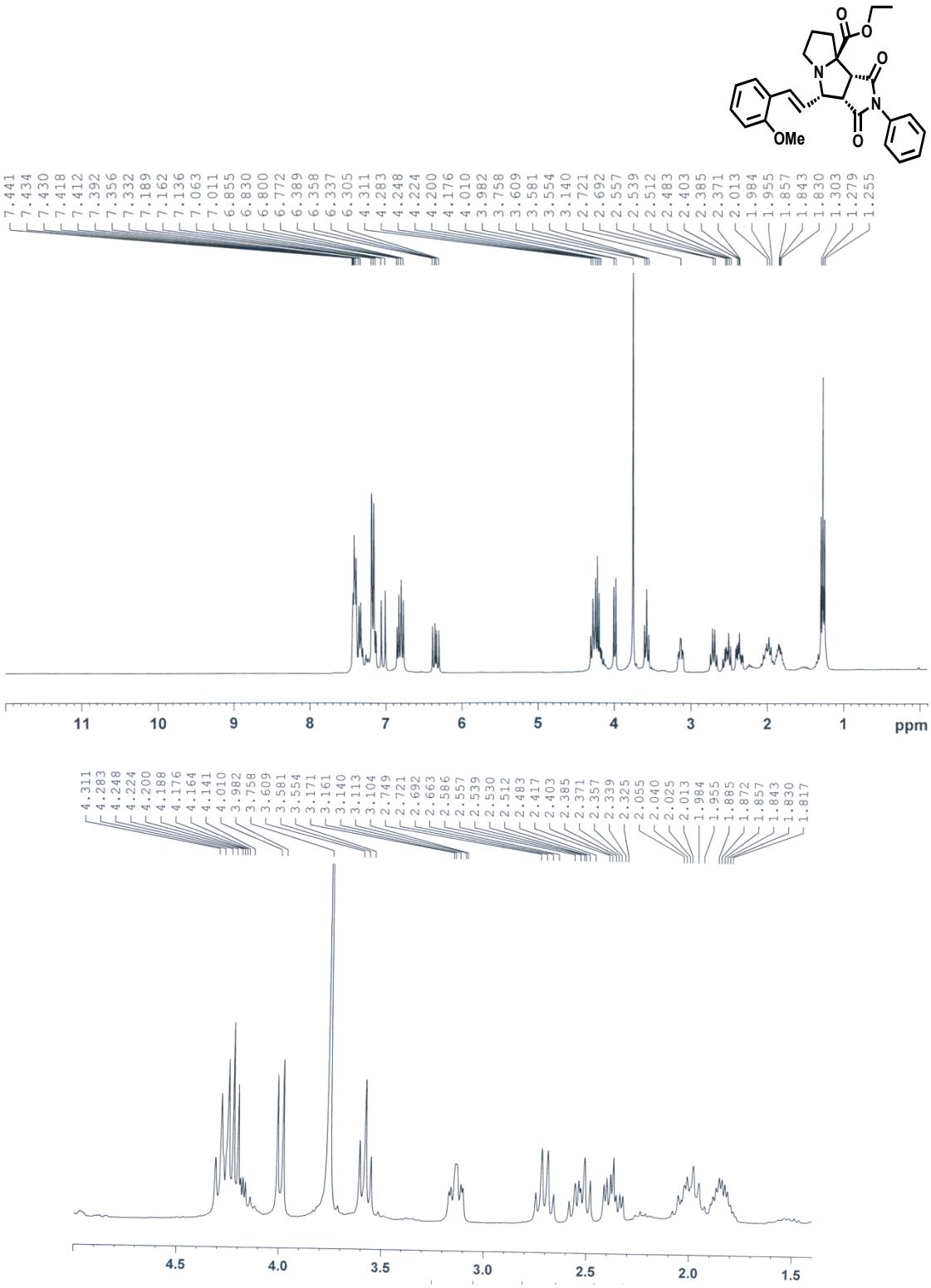


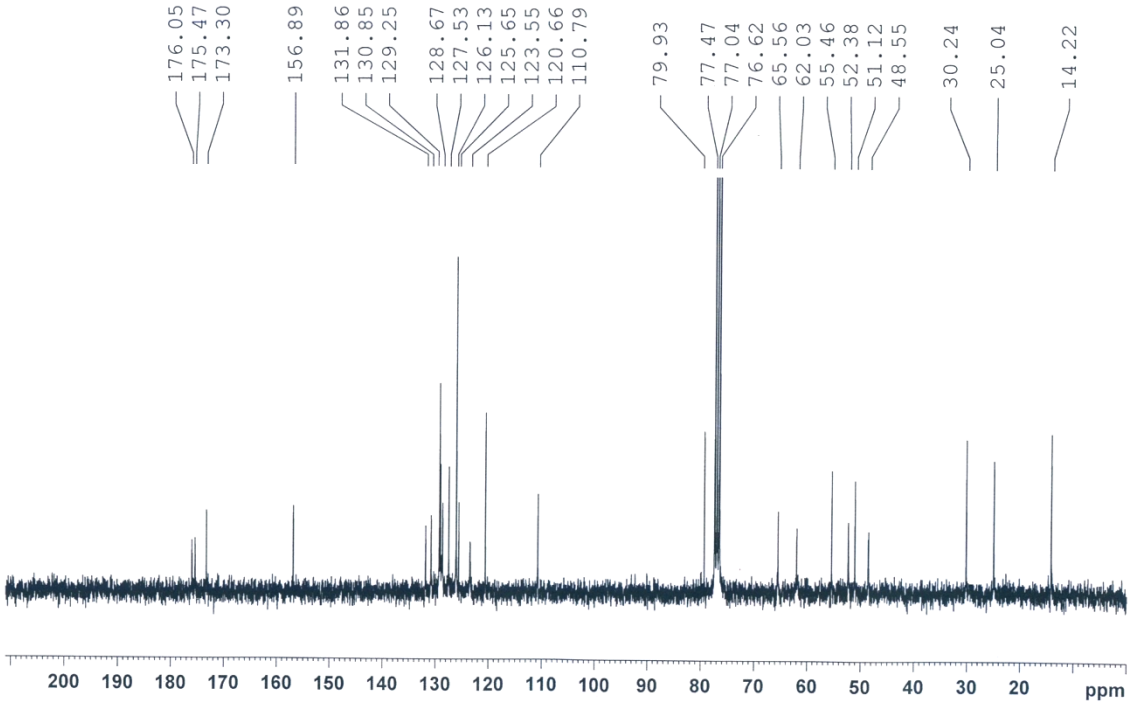
SI Figure 9: ^{1}H and ^{13}C NMR spectra of compound **5i**



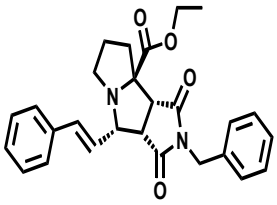


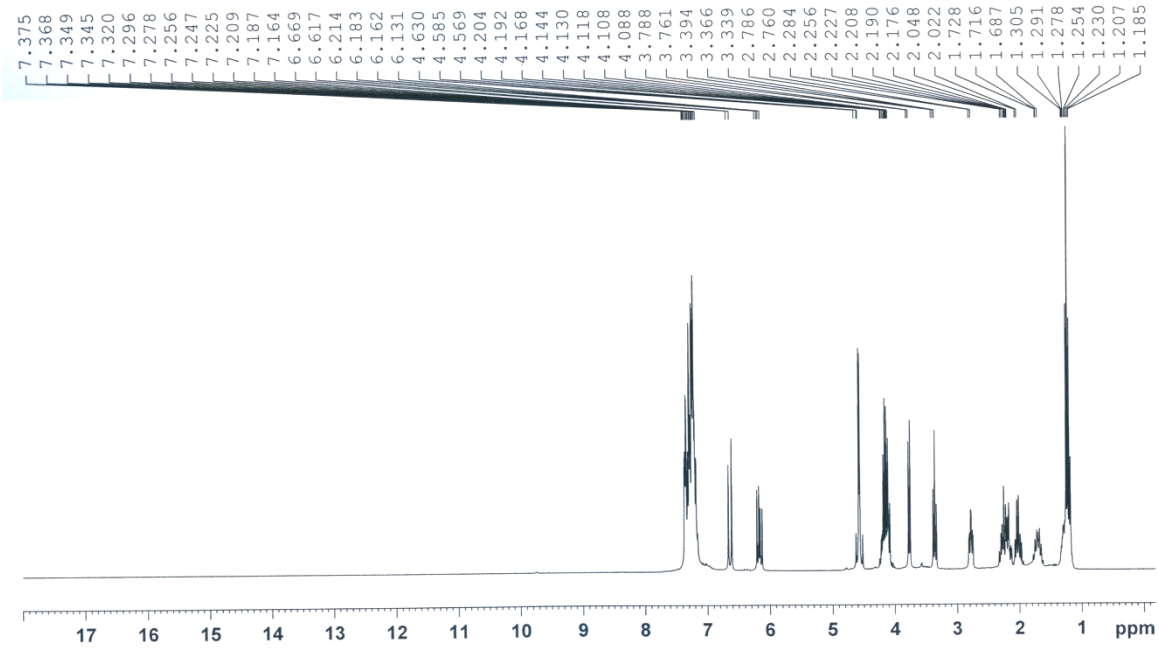
SI Figure 10: ^{1}H and ^{13}C NMR spectra of compound **5j**

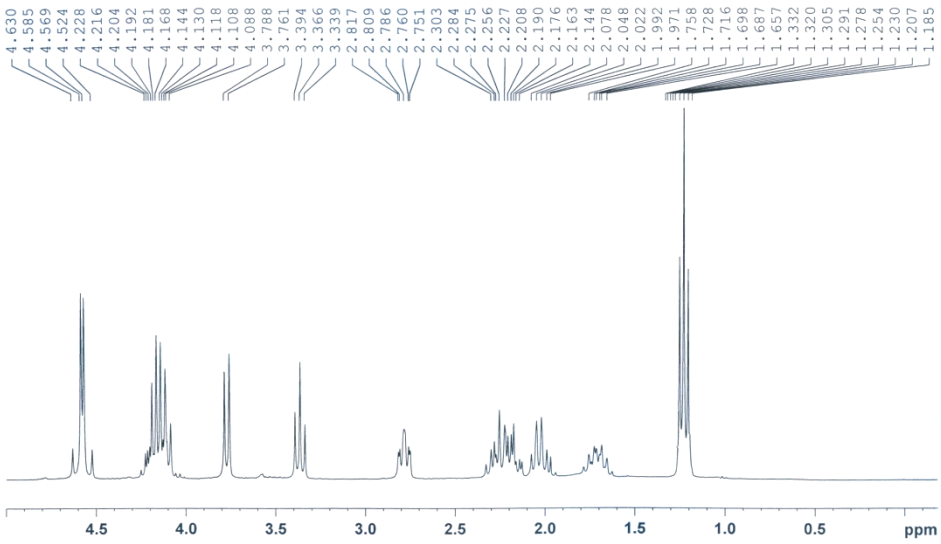


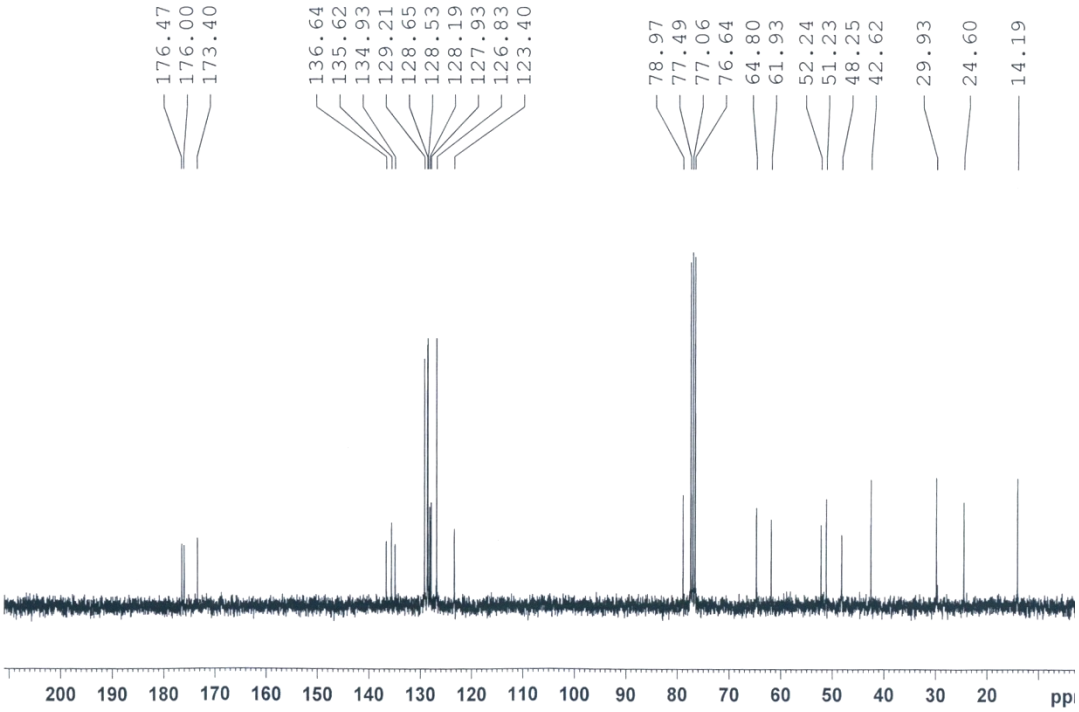

176.05
175.47
173.30
156.89
131.86
130.85
129.25
128.67
127.53
126.13
125.65
123.55
120.66
110.79
79.93
77.47
77.04
76.62
65.56
62.03
55.46
52.38
51.12
48.55
30.24
25.04
14.22
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

SI Figure 11: ^{1}H and ^{13}C NMR spectra of compound **5k**

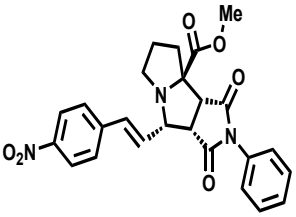


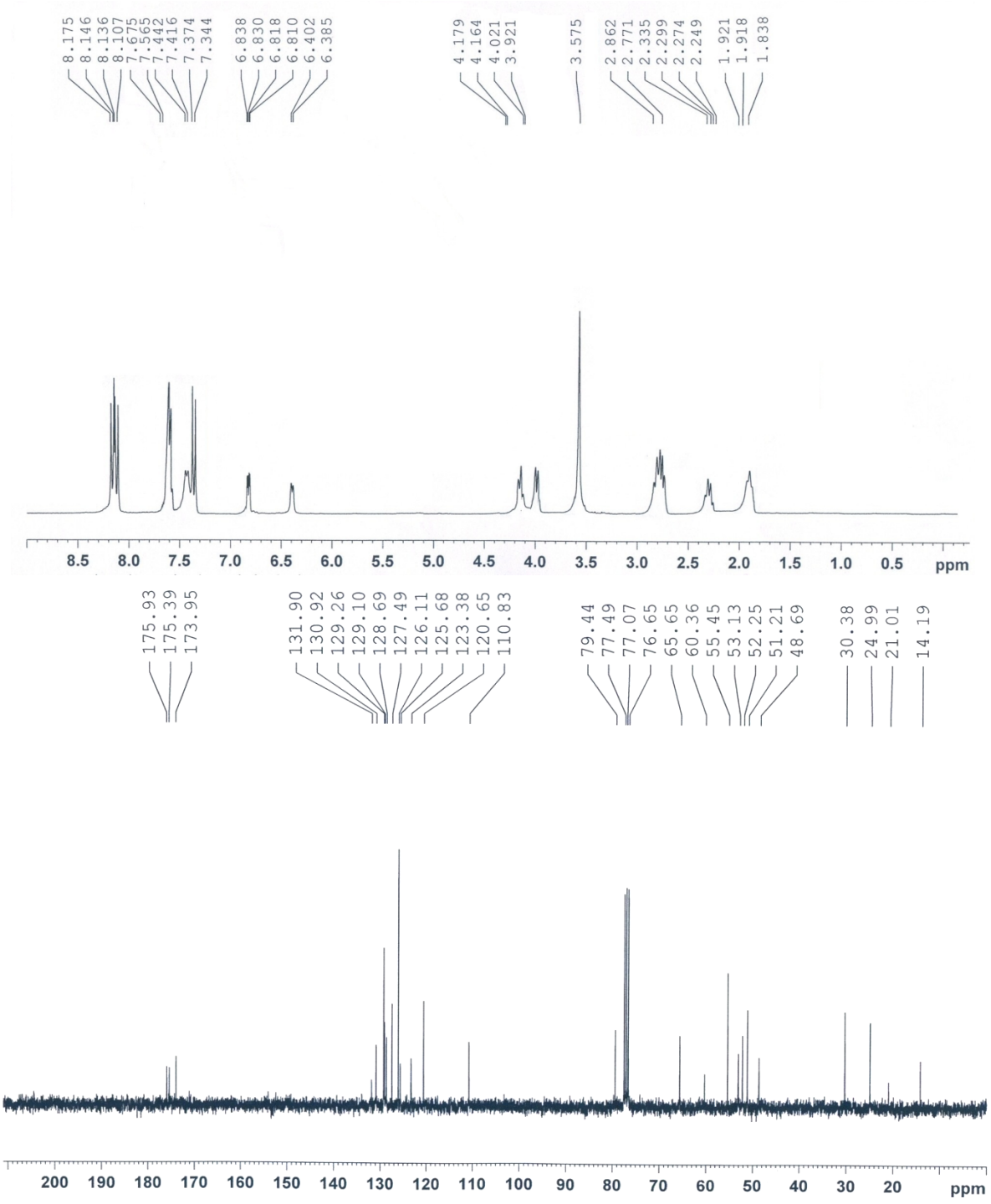




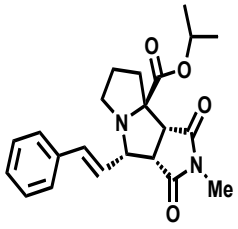


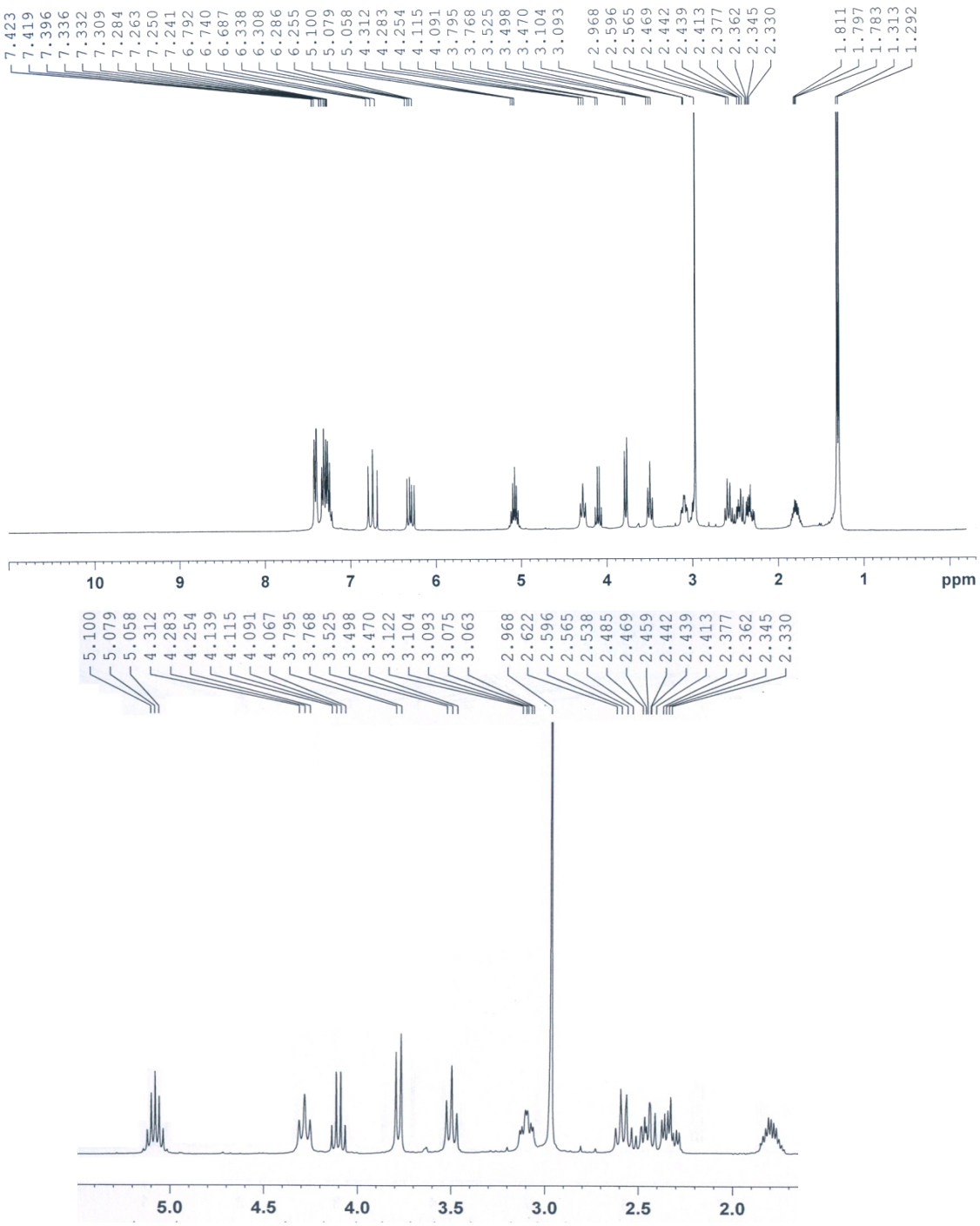
SI Figure 12: ^{1}H and ^{13}C NMR spectra of compound **5l**

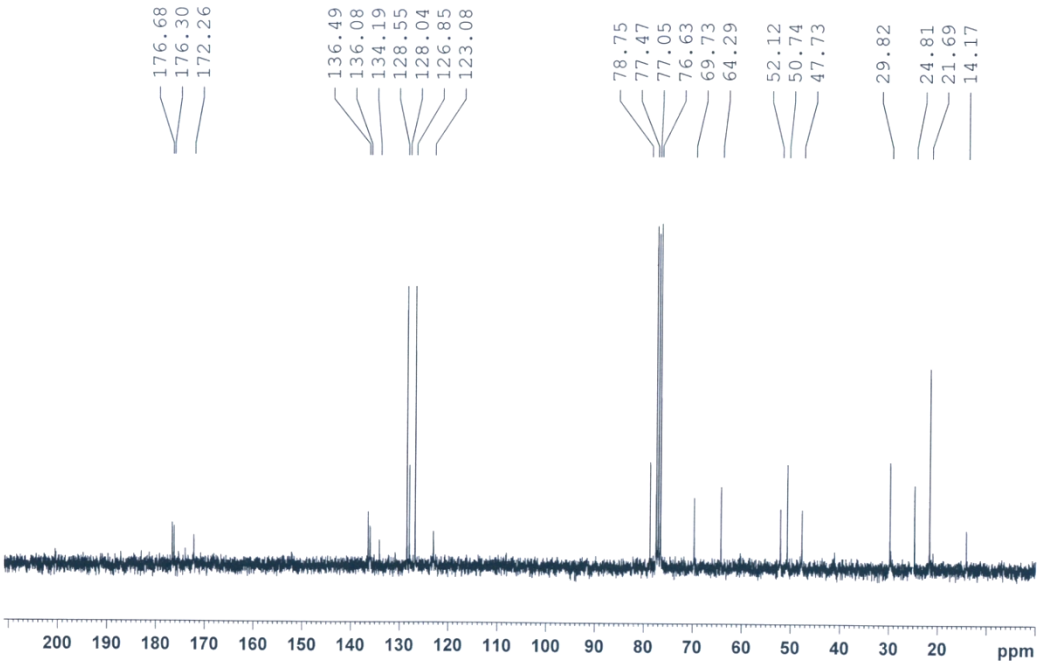




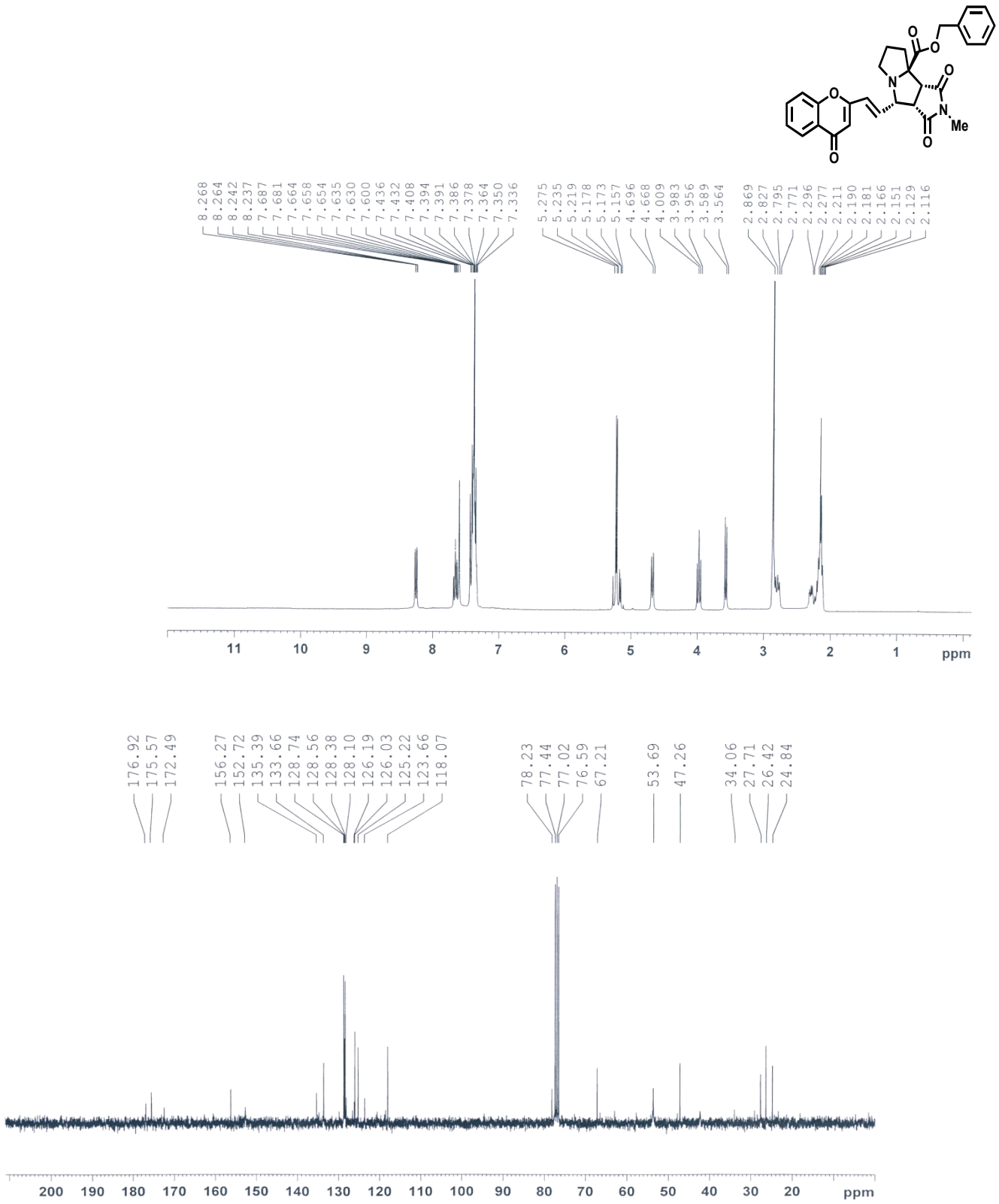
SI Figure 13: ^{1}H and ^{13}C NMR spectra of compound **5m**



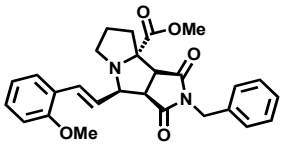


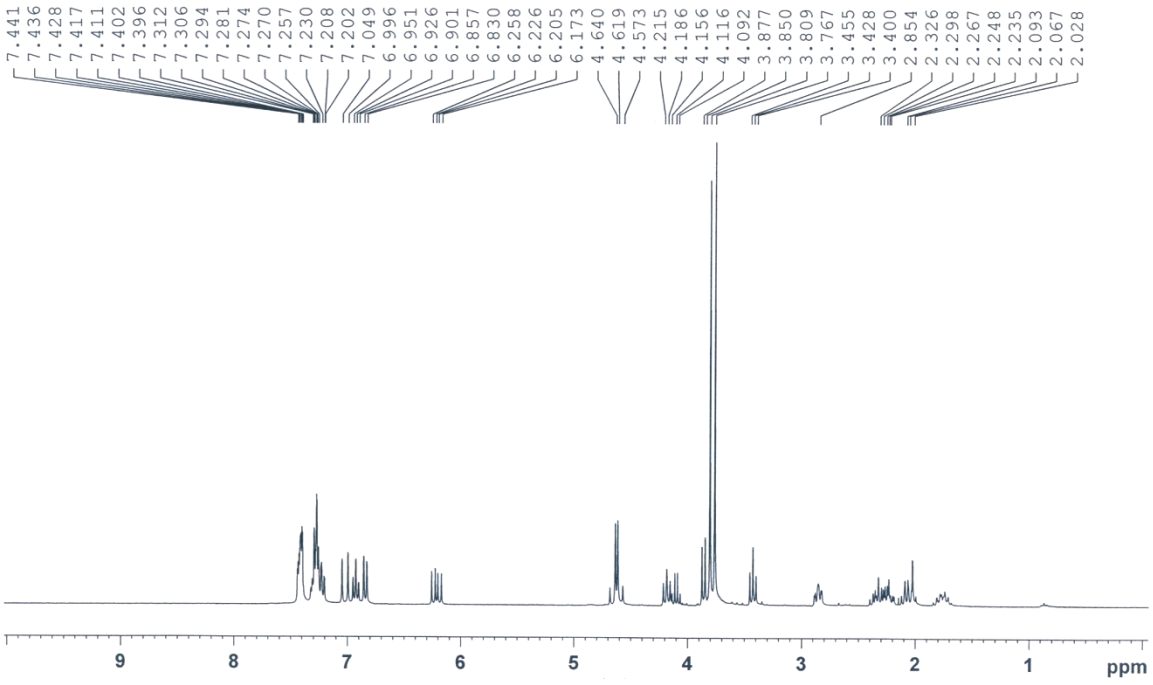

176.68
176.30
172.26
136.49
136.08
134.19
128.55
128.04
126.85
123.08
78.75
77.47
77.05
76.63
69.73
64.29
52.12
50.74
47.73
29.82
24.81
21.69
14.17
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

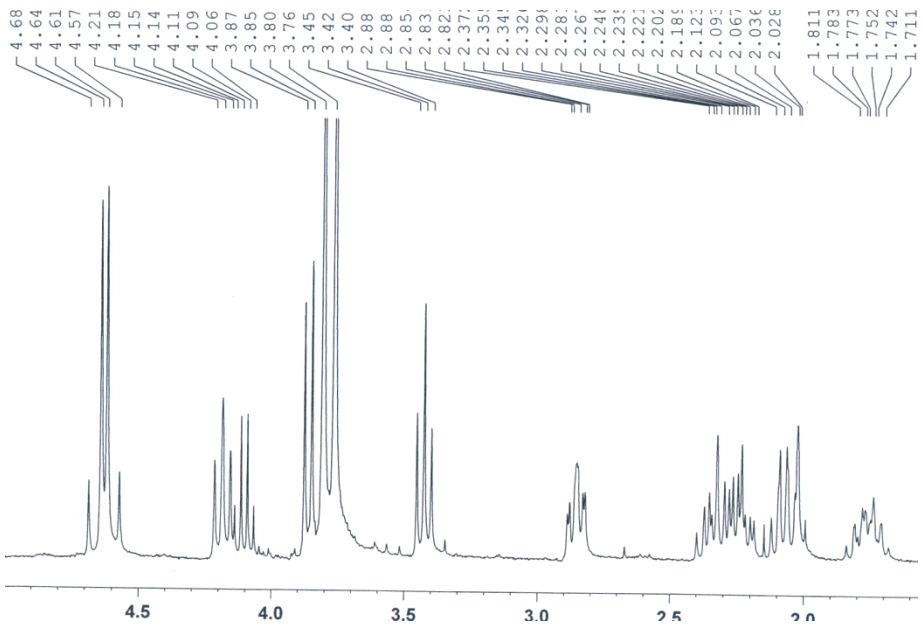
SI Figure 14: ^{1}H and ^{13}C NMR spectra of compound **5n**

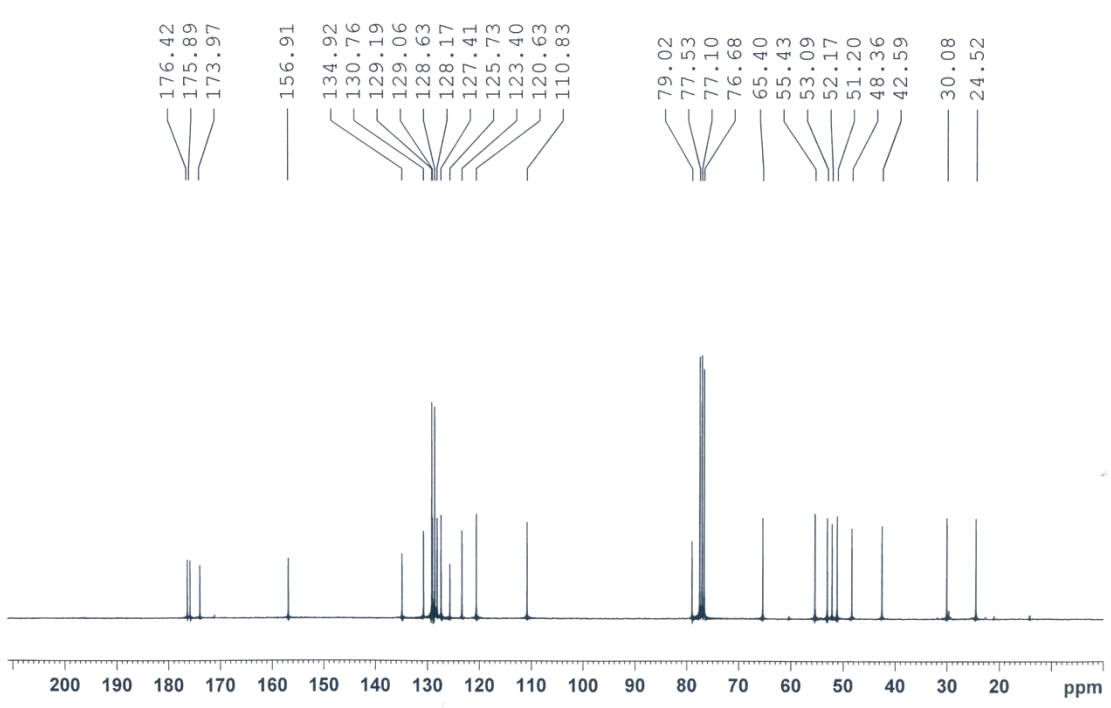


SI Figure 15: ^{1}H and ^{13}C NMR spectra of compound **5o**

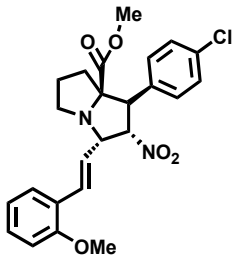


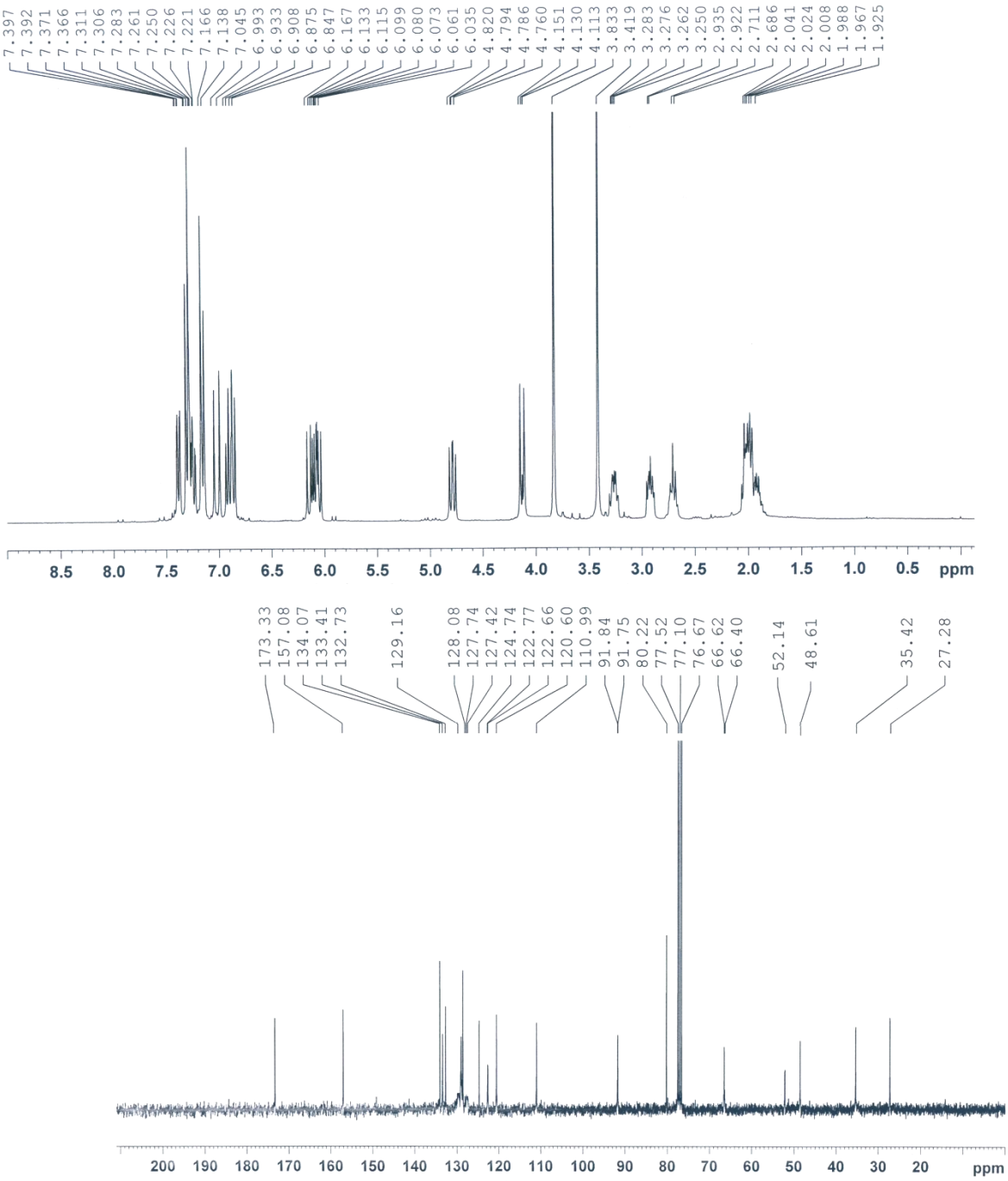




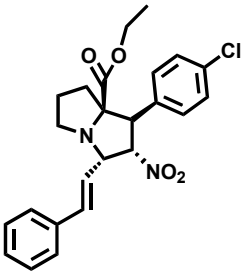

176.42
175.89
173.97
156.91
134.92
130.76
129.19
129.06
128.63
128.17
127.41
125.73
123.40
120.63
110.83
79.02
77.53
77.10
76.68
65.40
55.43
53.09
52.17
51.20
48.36
42.59
30.08
24.52
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

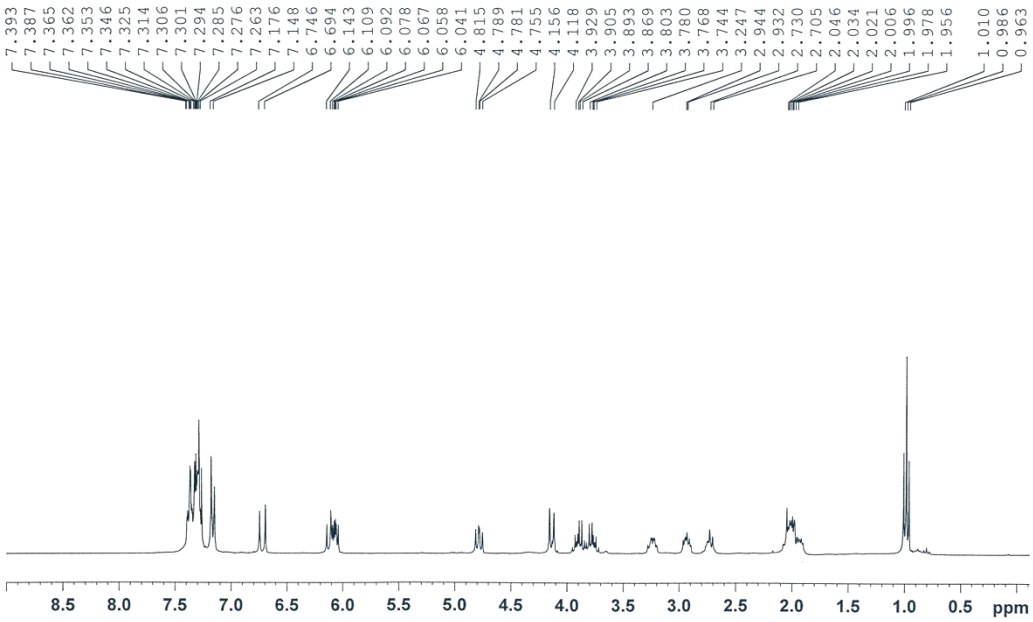
SI Figure 16: ^{1}H and ^{13}C NMR spectra of compound **6a**

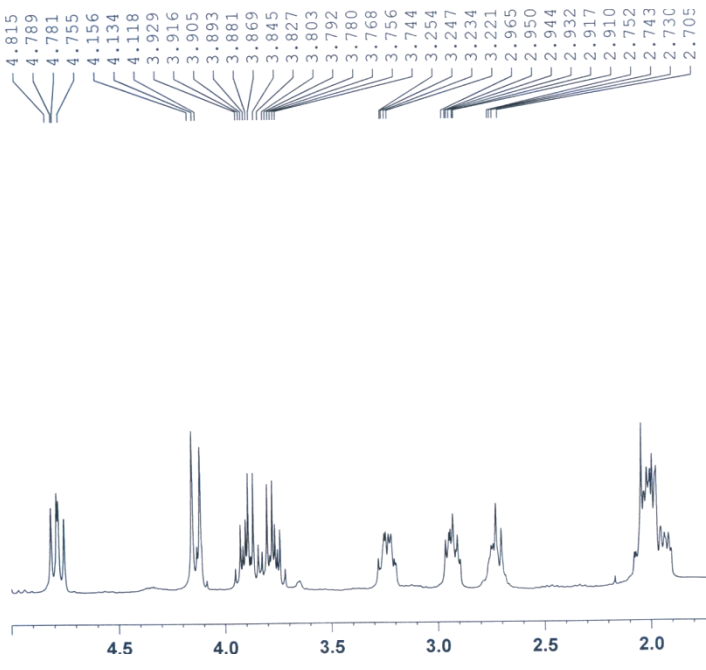


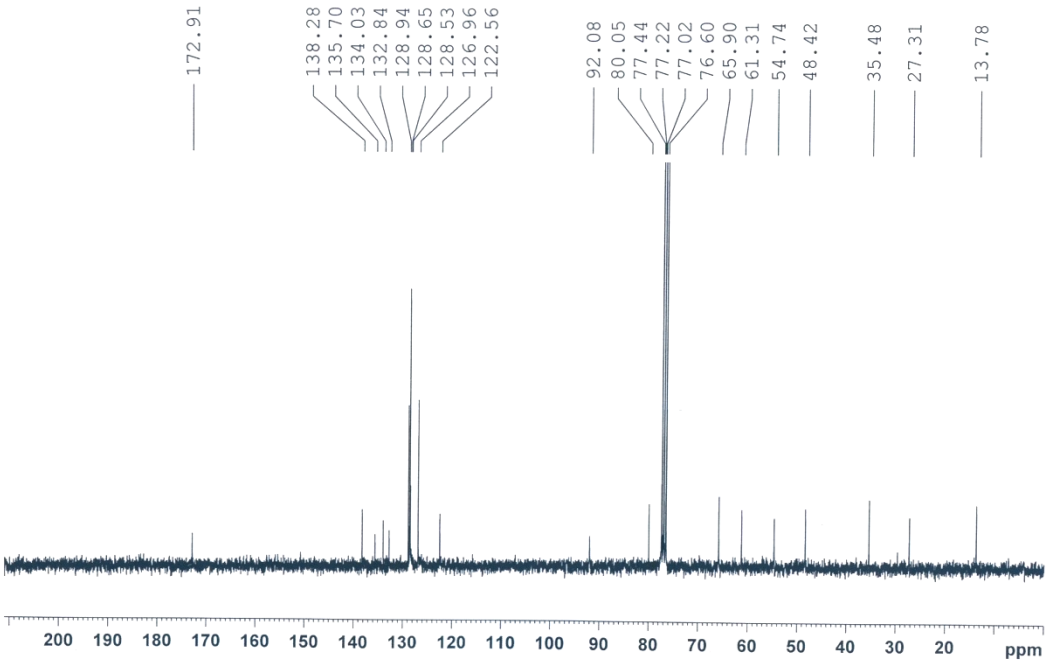


SI Figure 17: ^{1}H and ^{13}C NMR spectra of compound **6b**

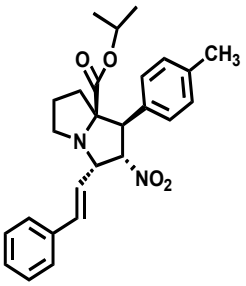


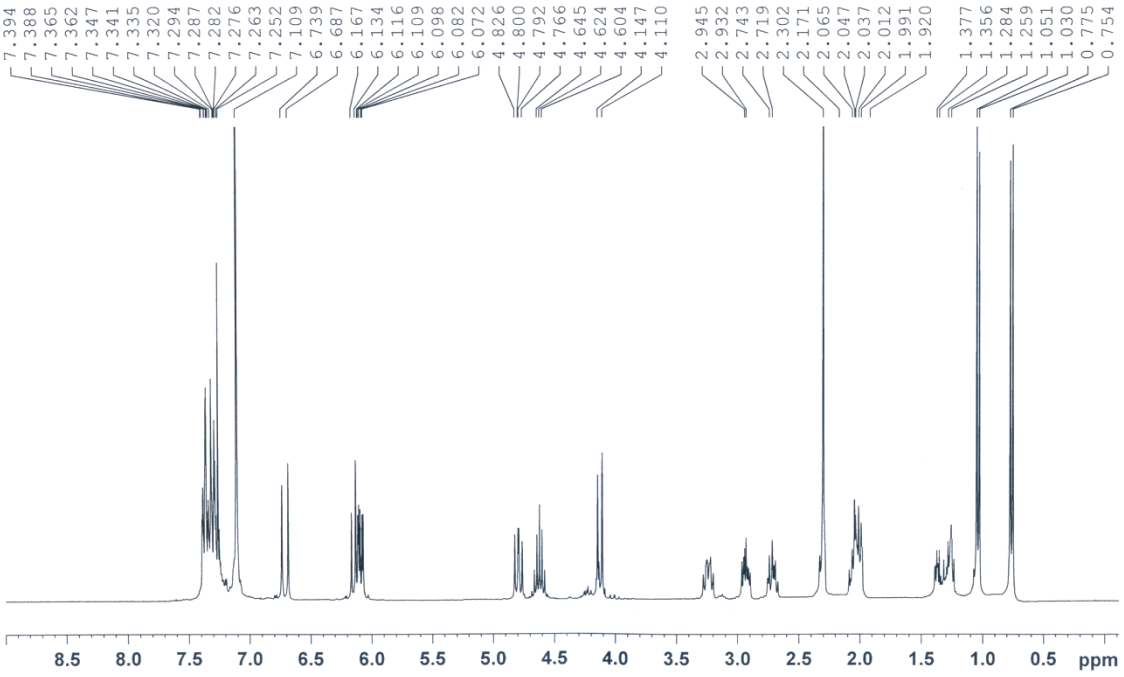


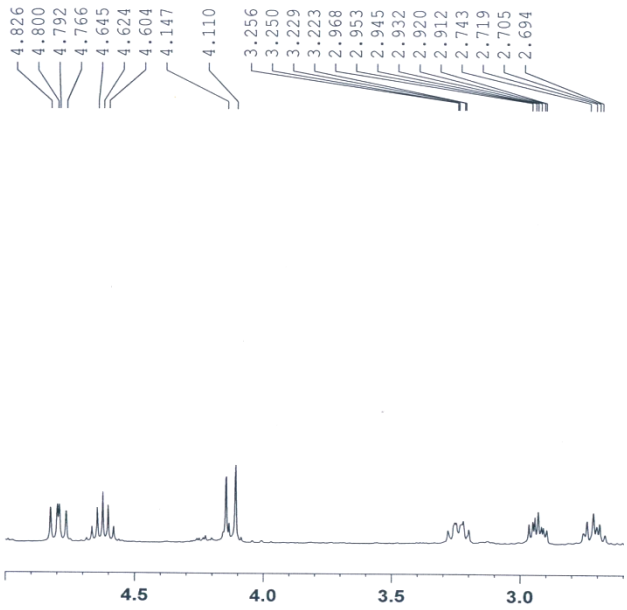


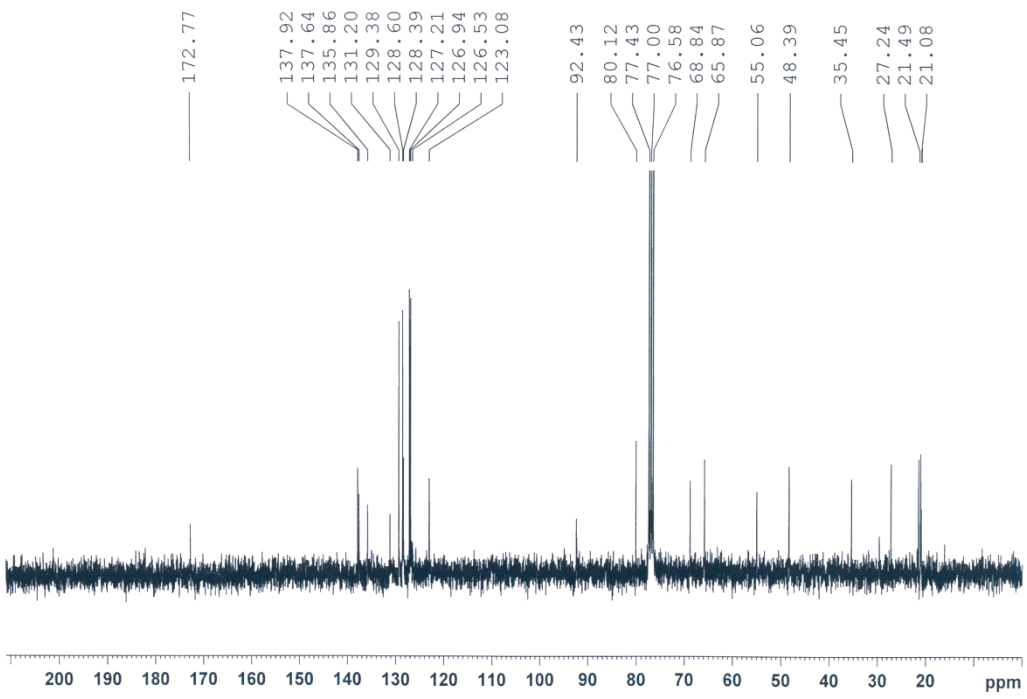

172.91
138.28
135.70
134.03
132.84
128.94
128.65
128.53
126.96
122.56
92.08
80.05
77.44
77.22
77.02
76.60
65.90
61.31
54.74
48.42
35.48
27.31
13.78
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20
ppm

SI Figure 18: ^{1}H and ^{13}C NMR spectra of compound **6c**

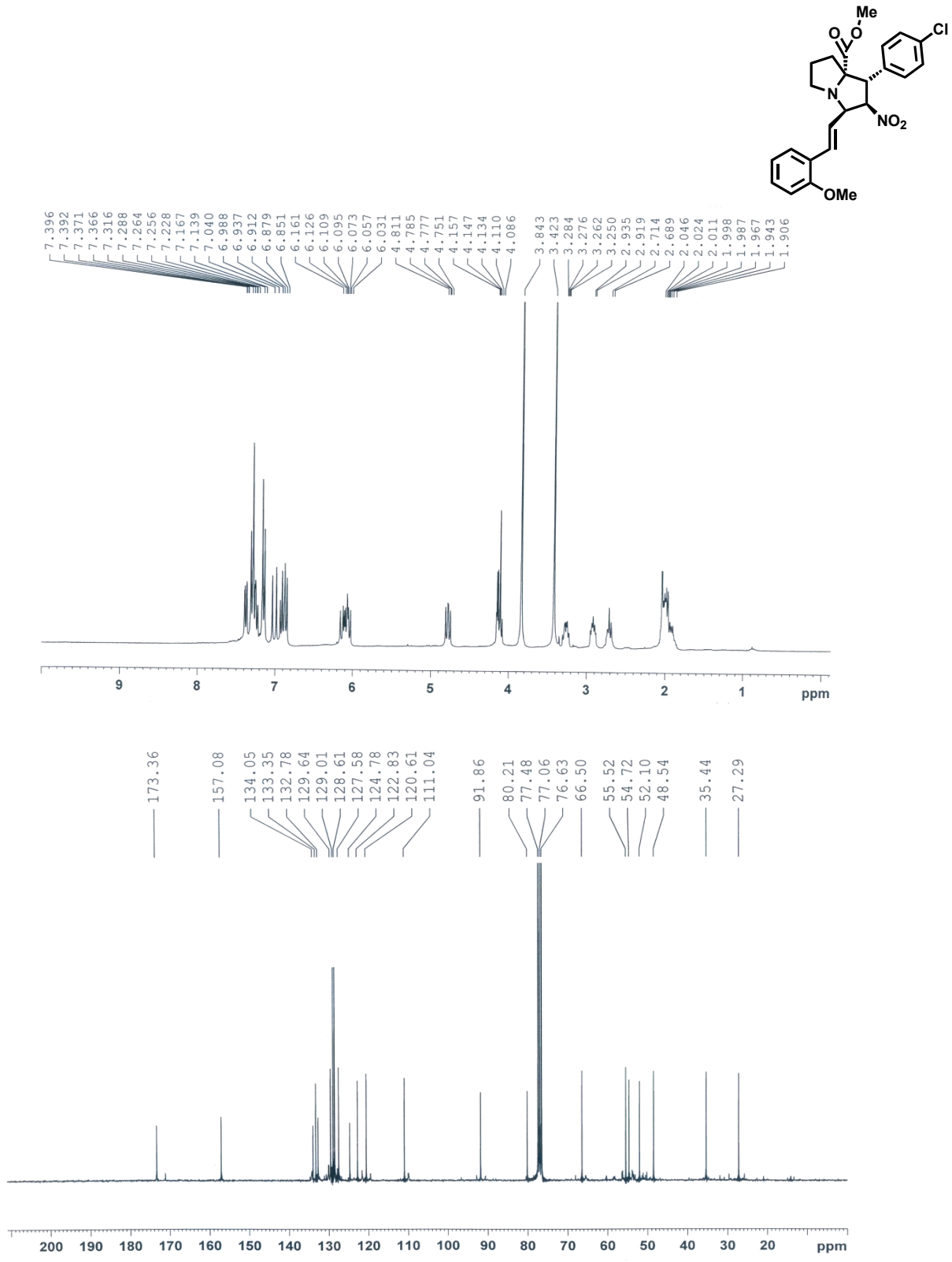




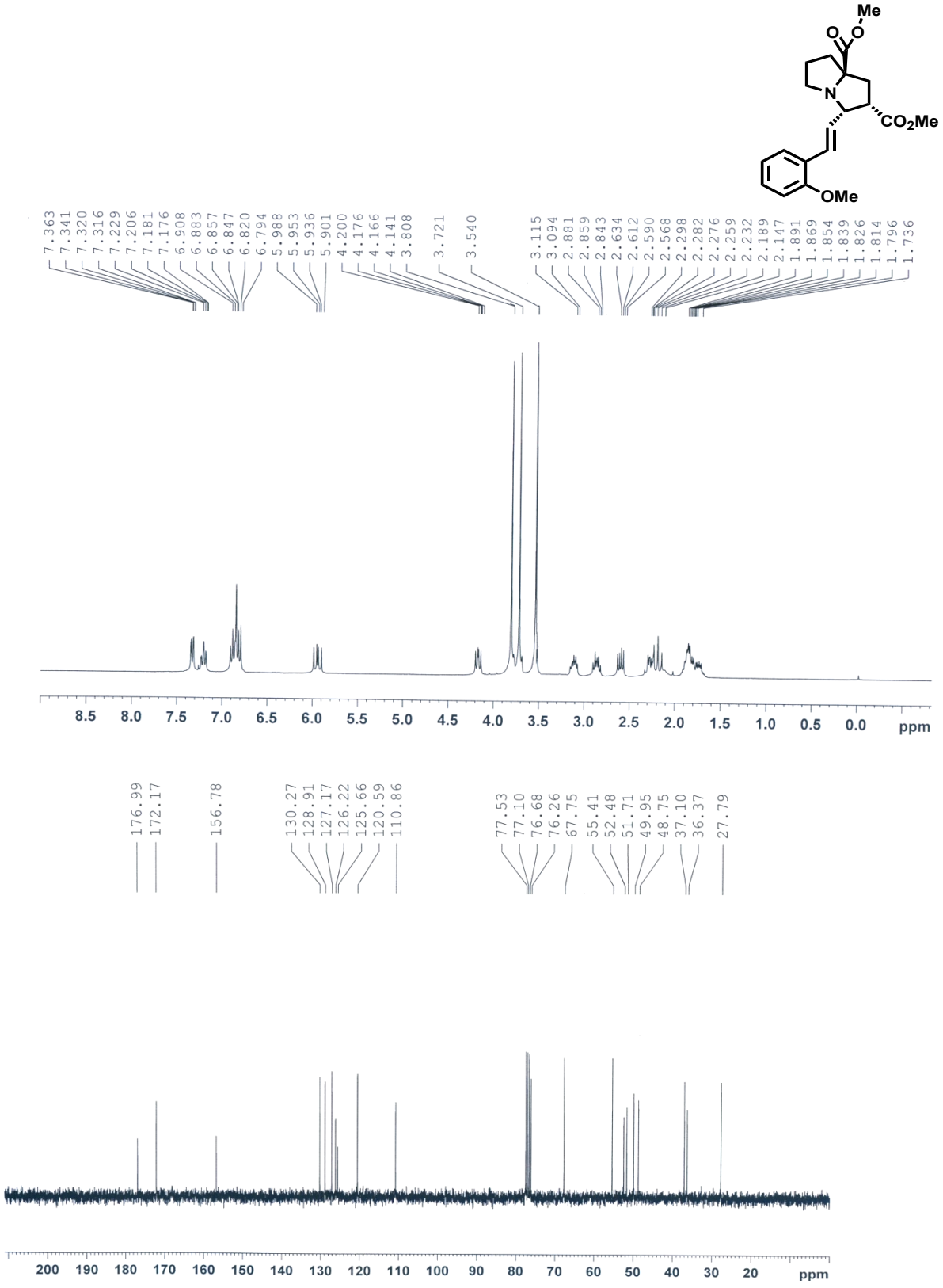



172.77
137.92
137.64
135.86
131.20
129.38
128.60
128.39
127.21
126.94
126.53
123.08
92.43
80.12
77.43
77.00
76.58
68.84
65.87
55.06
48.39
35.45
27.24
21.49
21.08
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

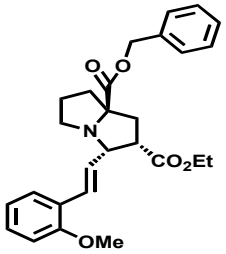
SI Figure 19: ^{1}H and ^{13}C NMR spectra of compound **6d**

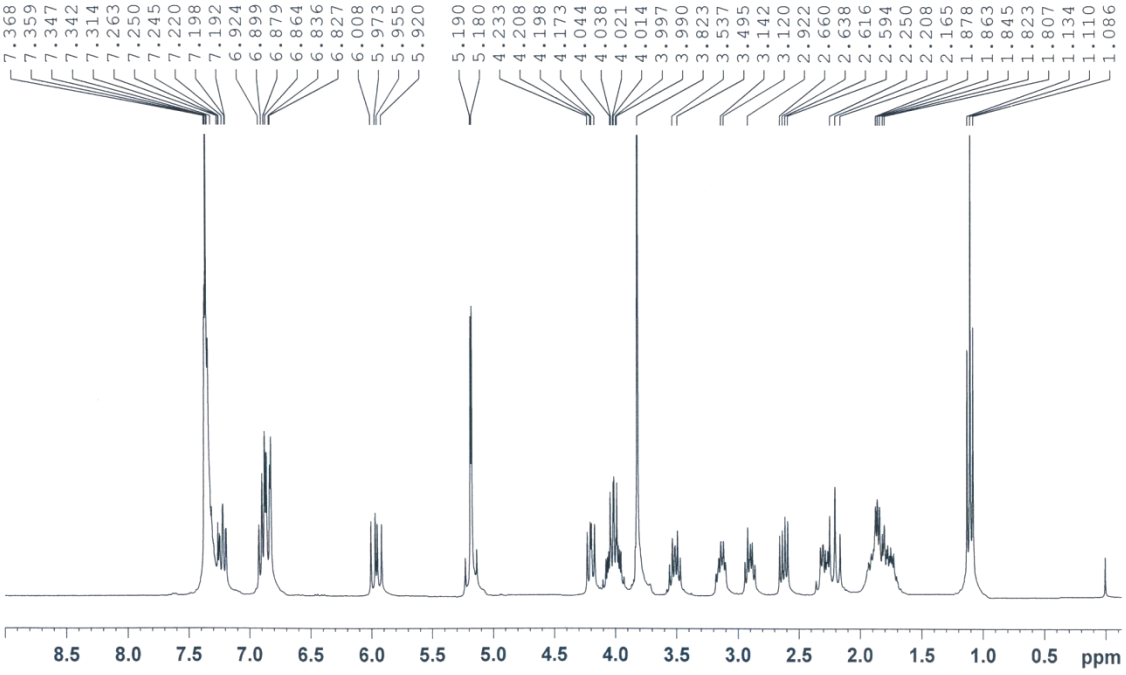


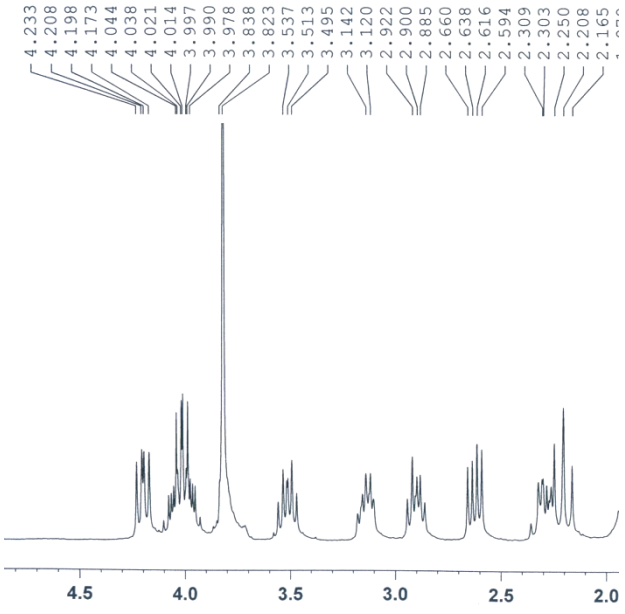
SI Figure 20: ^{1}H and ^{13}C NMR spectra of compound **6e**

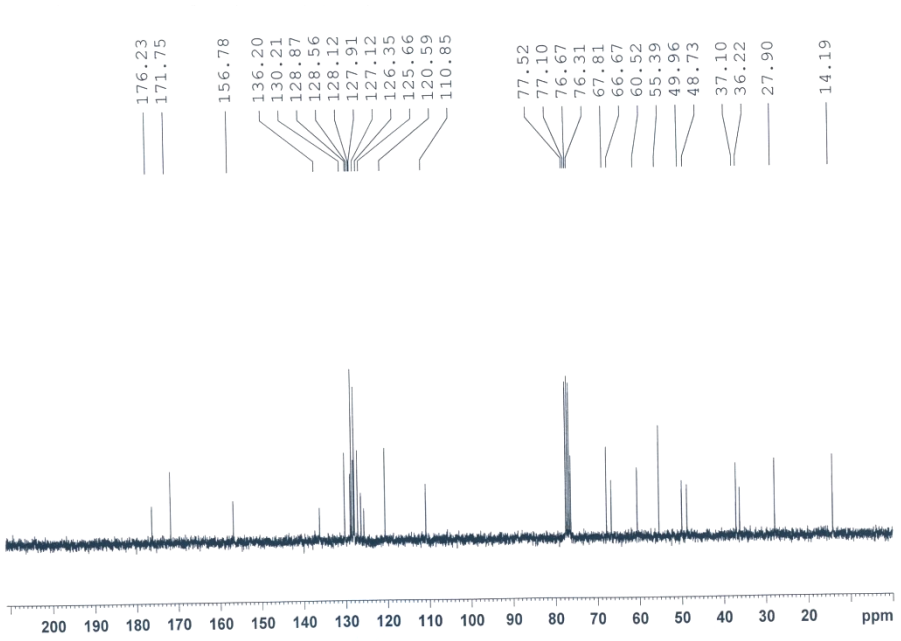


SI Figure 21: ^{1}H and ^{13}C NMR spectra of compound **6f**

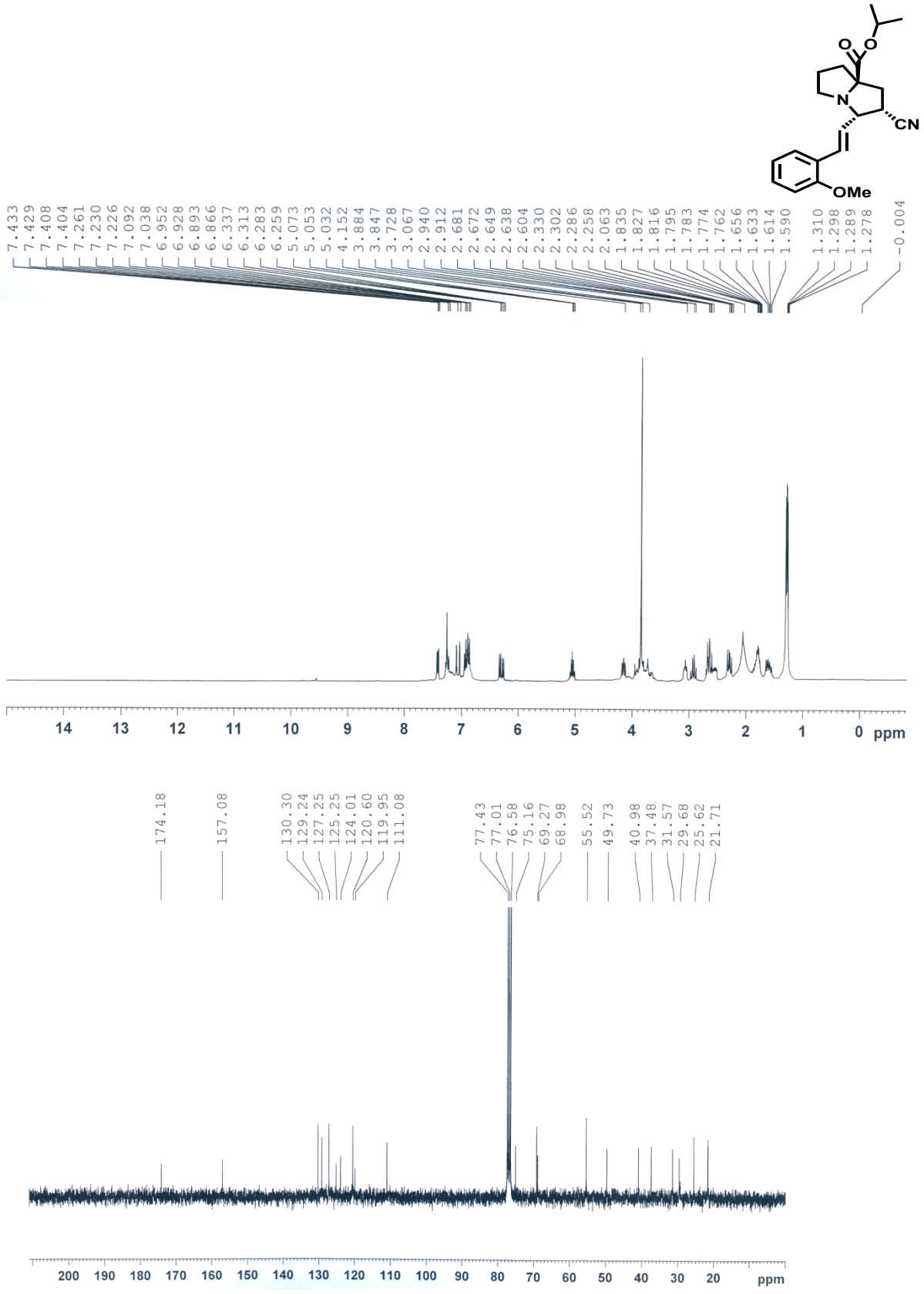




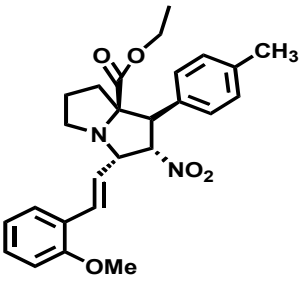


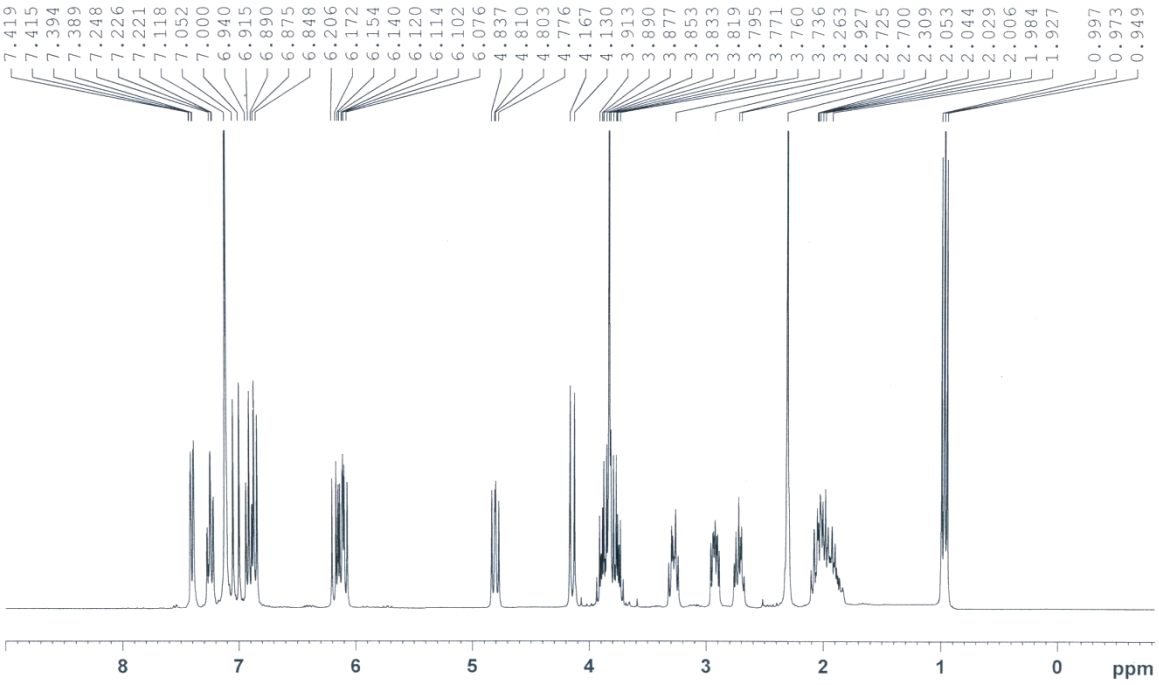

176.23
171.75
156.78
136.20
130.21
128.87
128.56
128.12
127.91
127.12
126.35
125.66
120.59
110.85
77.52
77.10
76.67
76.31
67.81
66.67
60.52
55.39
49.96
48.73
37.10
36.22
27.90
14.19
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

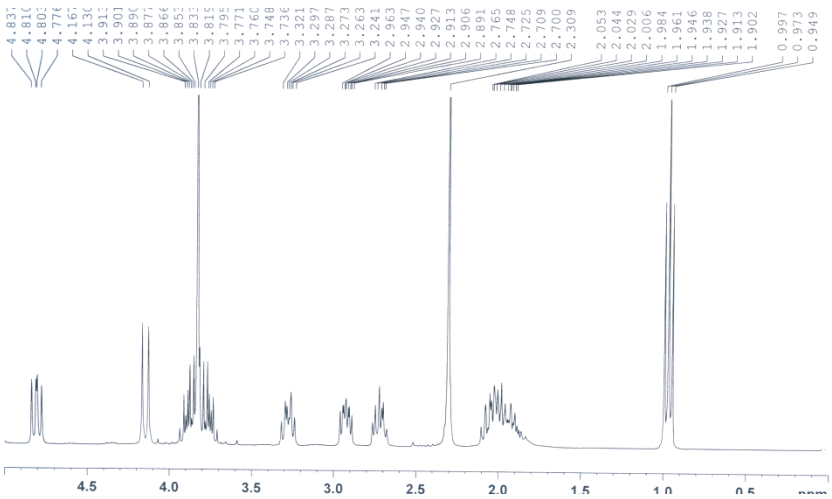
SI Figure 22: ^{1}H and ^{13}C NMR spectra of compound **6g**

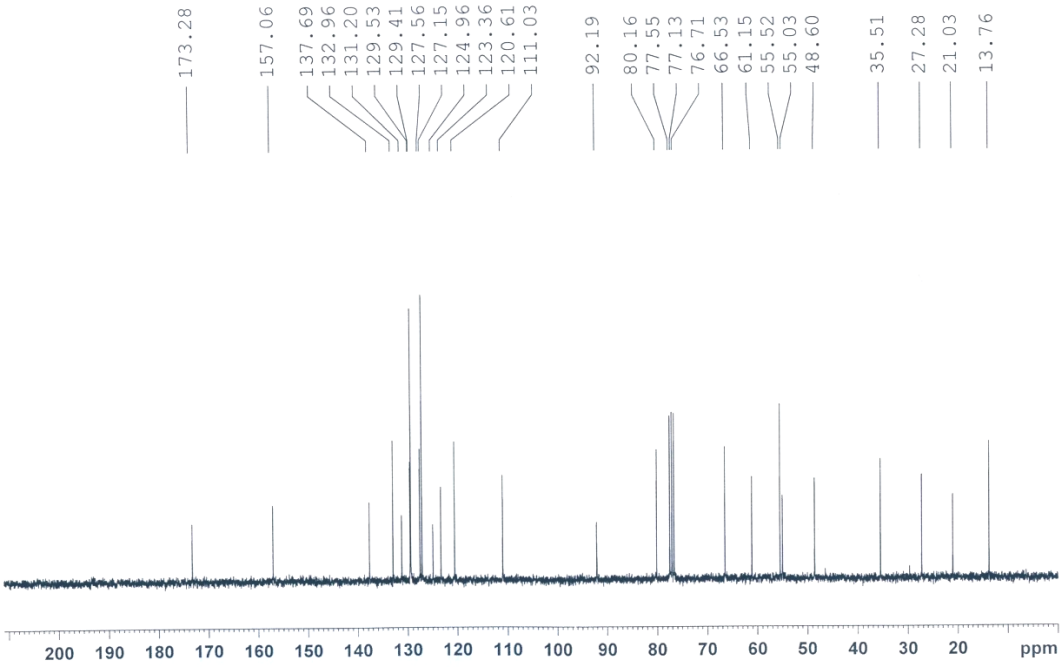


SI Figure 23: ^{1}H and ^{13}C NMR spectra of compound **6h**

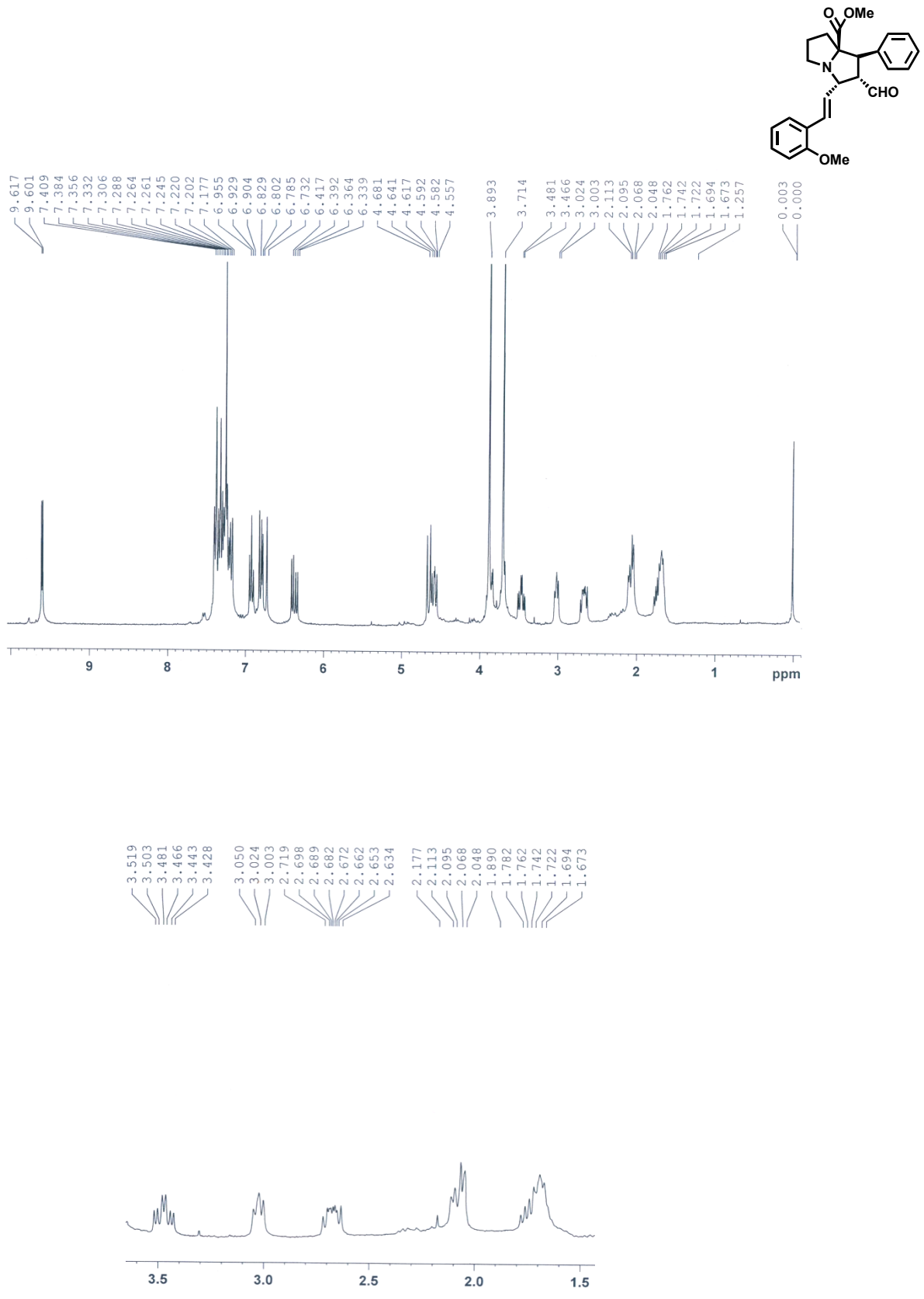


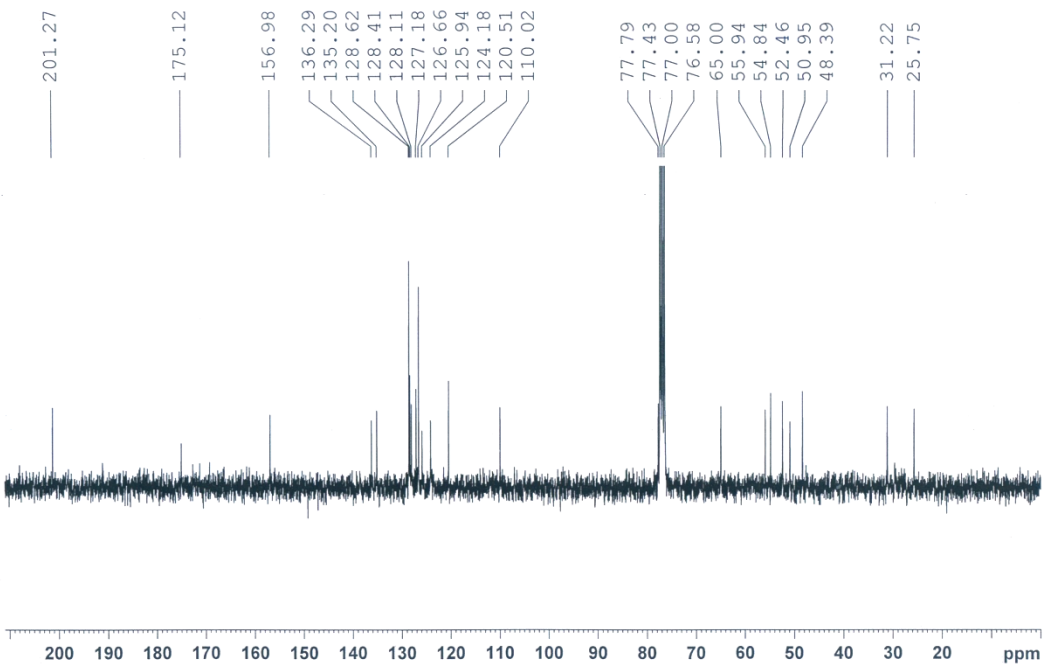




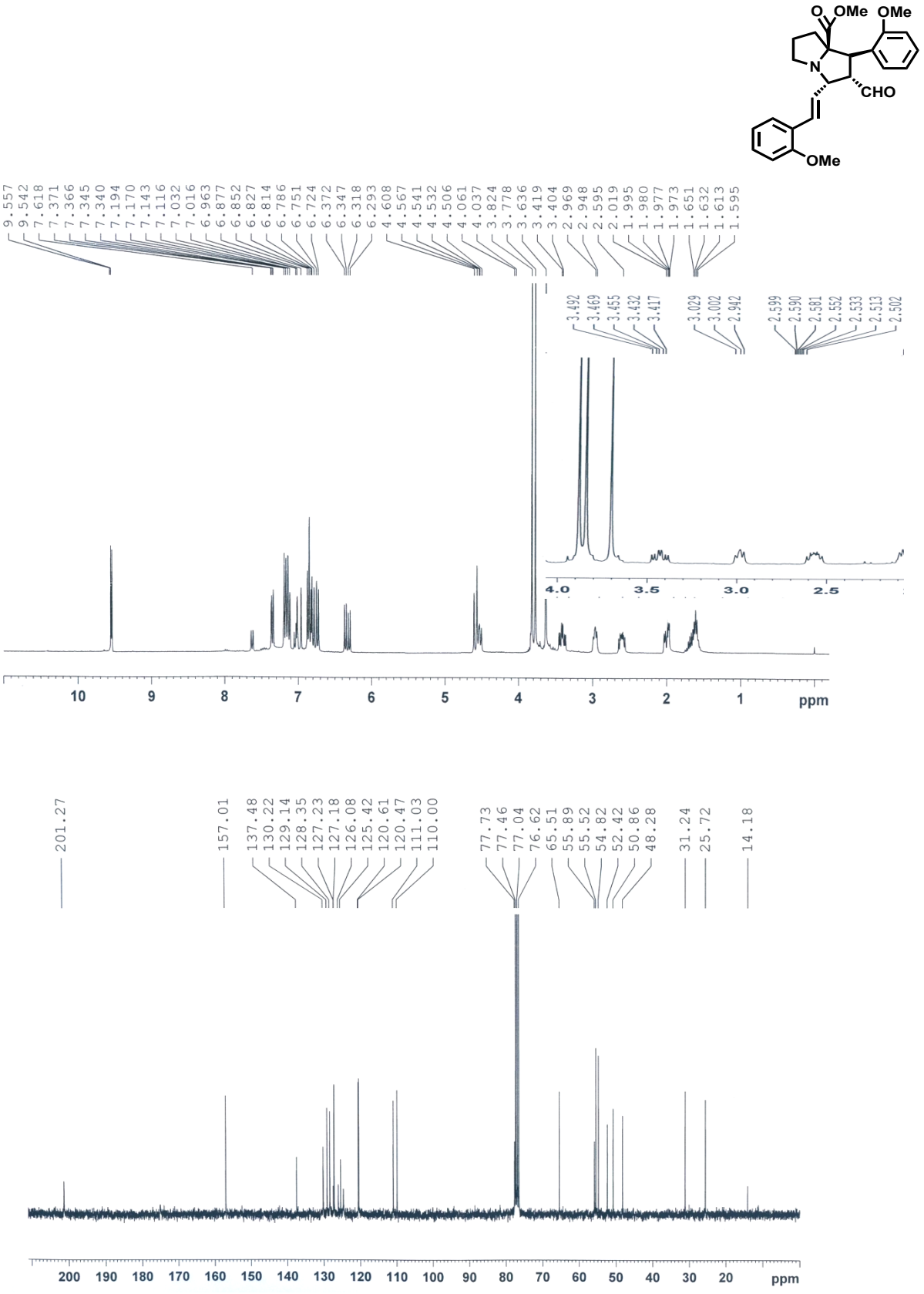

173.28
157.06
137.69
132.96
131.20
129.53
129.41
127.56
127.15
124.96
123.36
120.61
111.03
92.19
80.16
77.55
77.13
76.71
66.53
61.15
55.52
55.03
48.60
35.51
27.28
21.03
13.76
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

SI Figure 24: ^{1}H and ^{13}C NMR spectra of compound **7a**

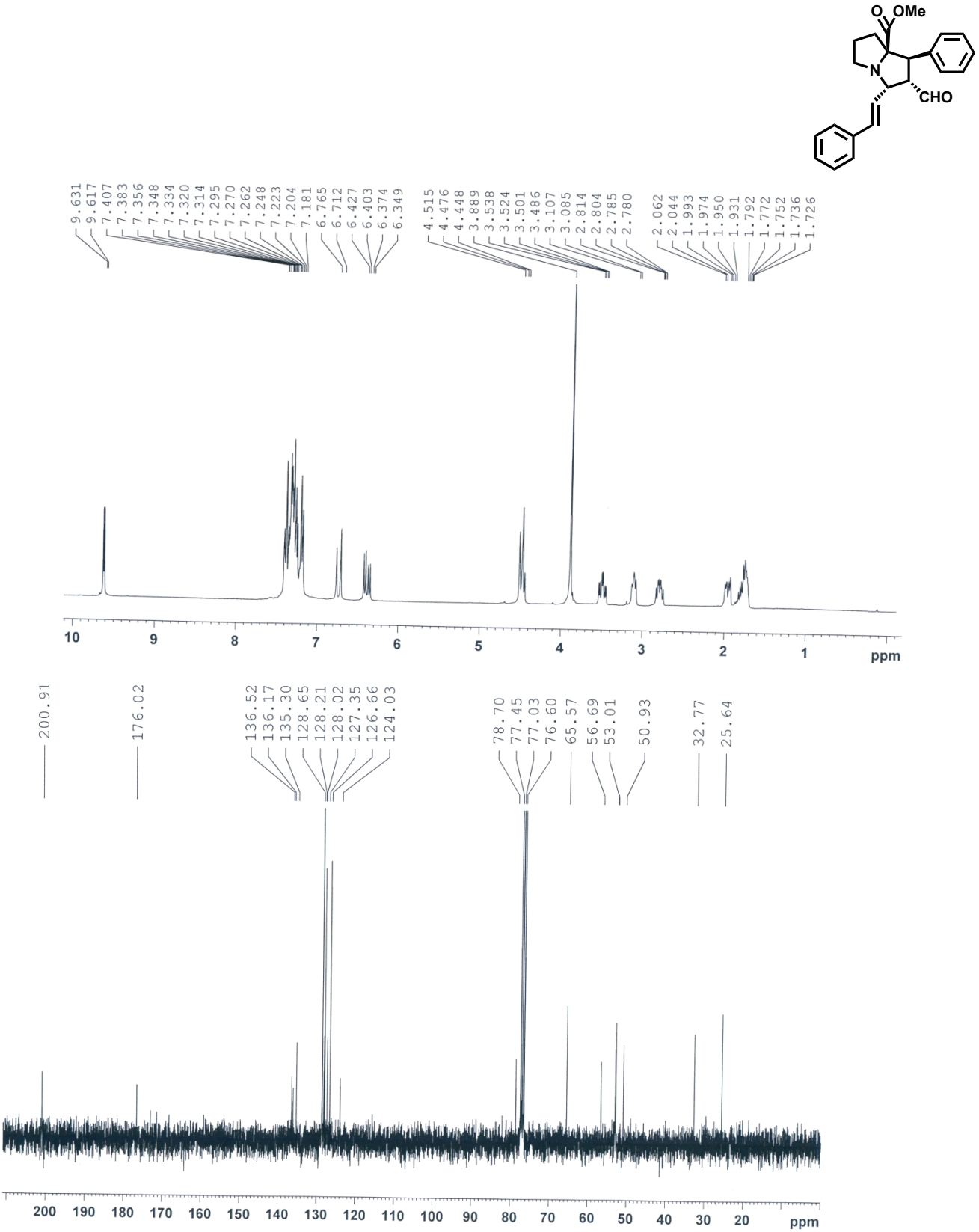



201.27
175.12
156.98
136.29
135.20
128.62
128.41
128.11
127.18
126.66
125.94
124.18
120.51
110.02
77.79
77.43
77.00
76.58
65.00
55.94
54.84
52.46
50.95
48.39
31.22
25.75
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

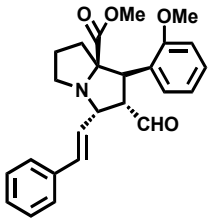
SI Figure 25: ^{1}H and ^{13}C NMR spectra of compound **7b** (**7f**)

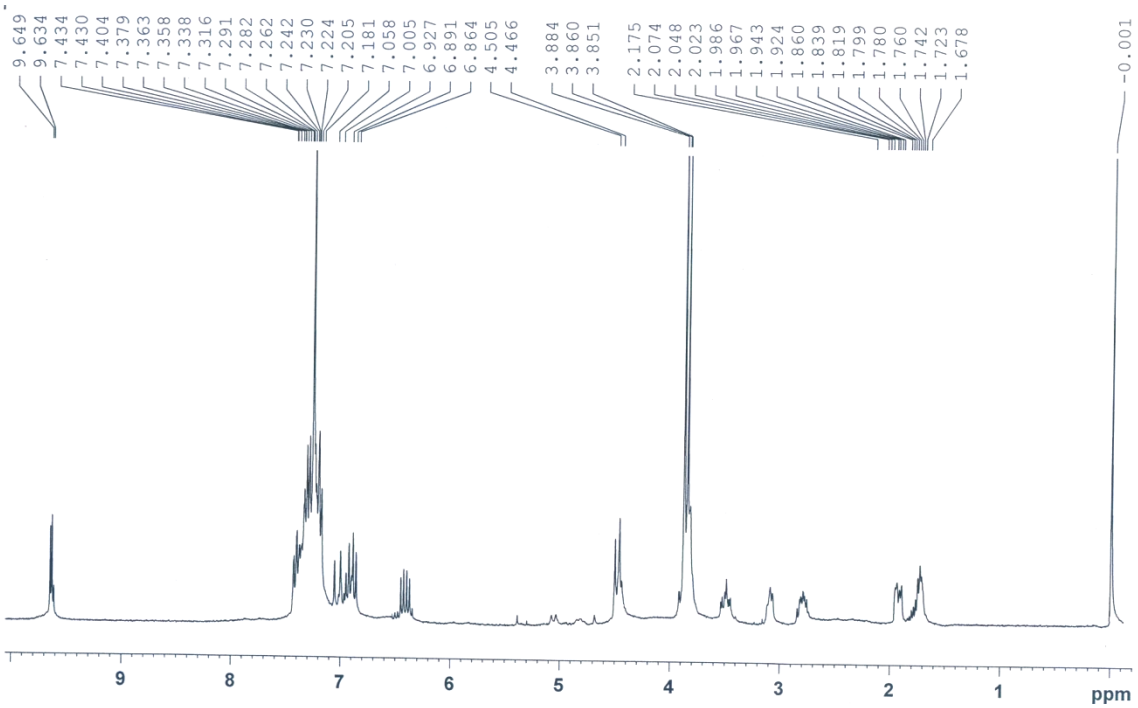


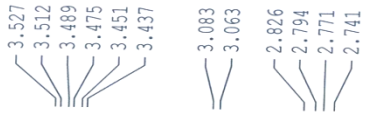
SI Figure 26: ^{1}H and ^{13}C NMR spectra of compound **7c**(**7g**)

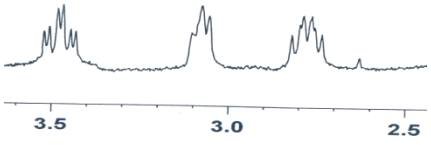


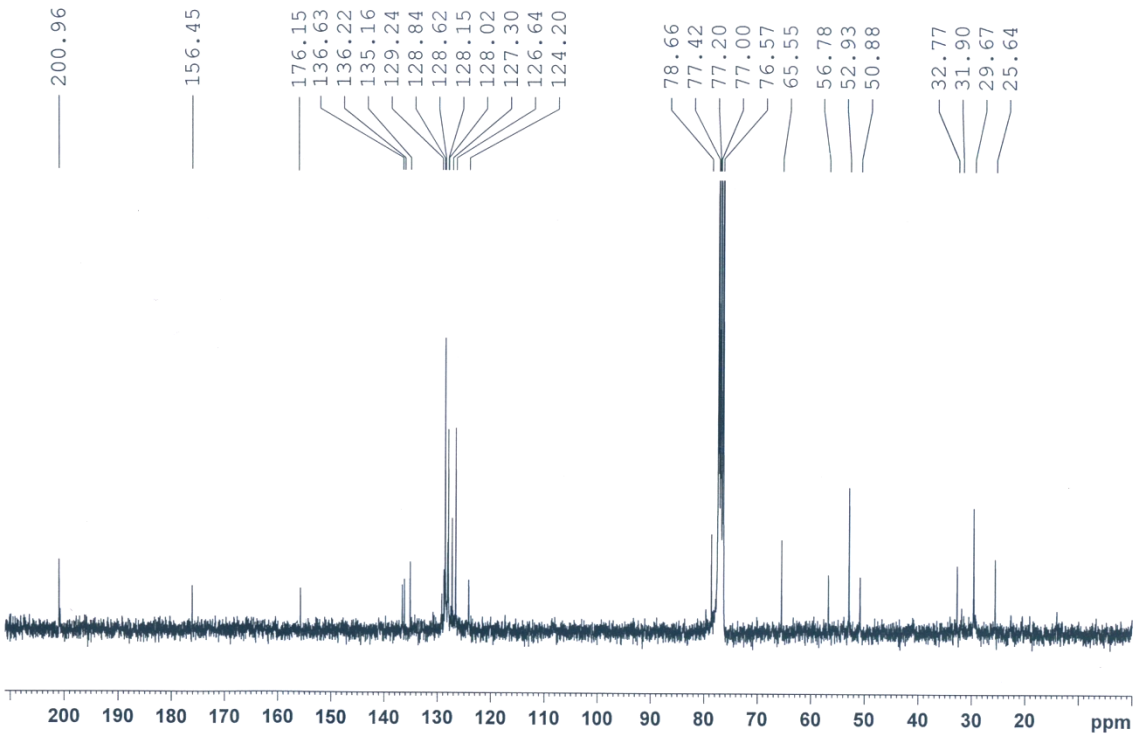
SI Figure 26: ^{1}H and ^{13}C NMR spectra of compound **7d**



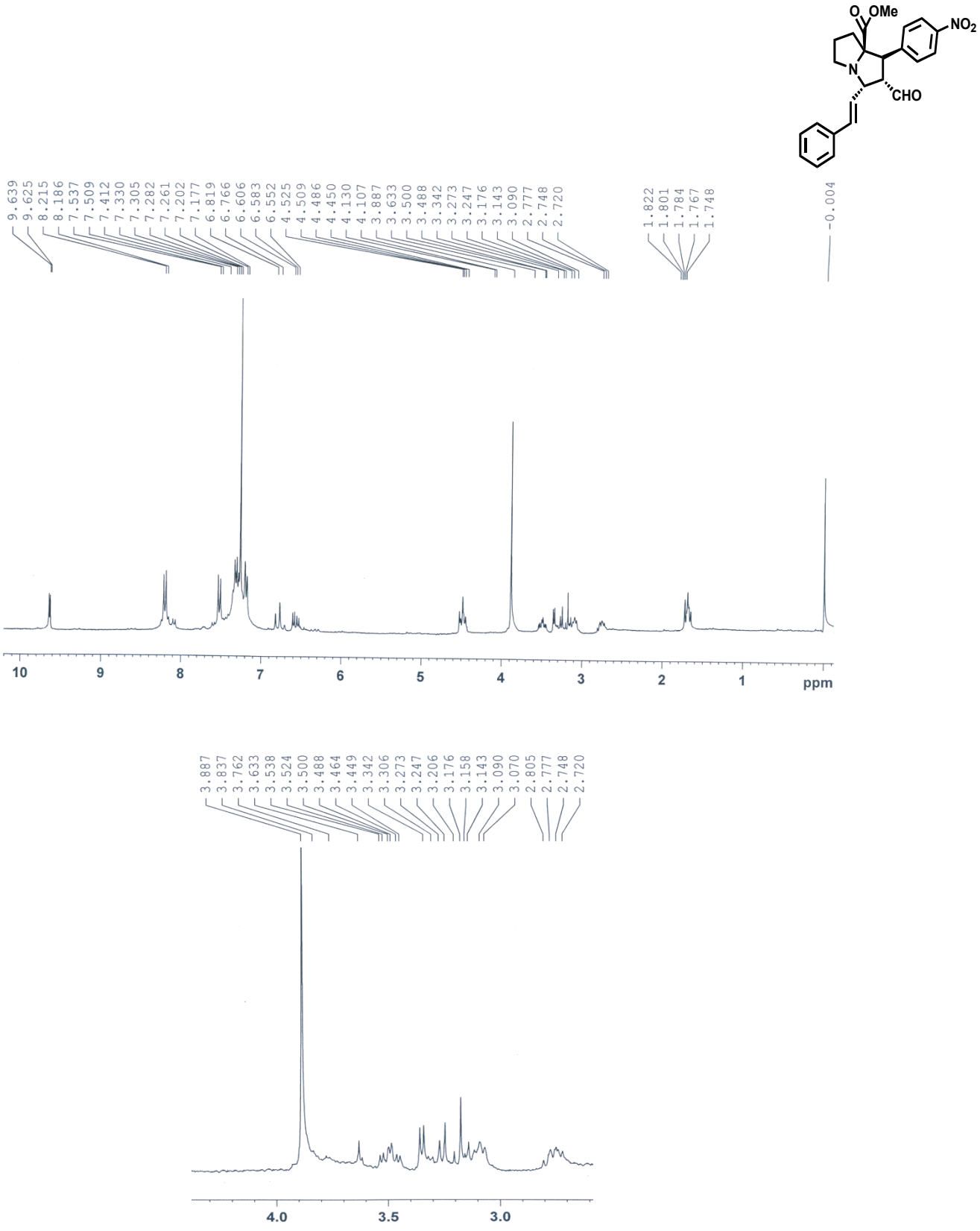


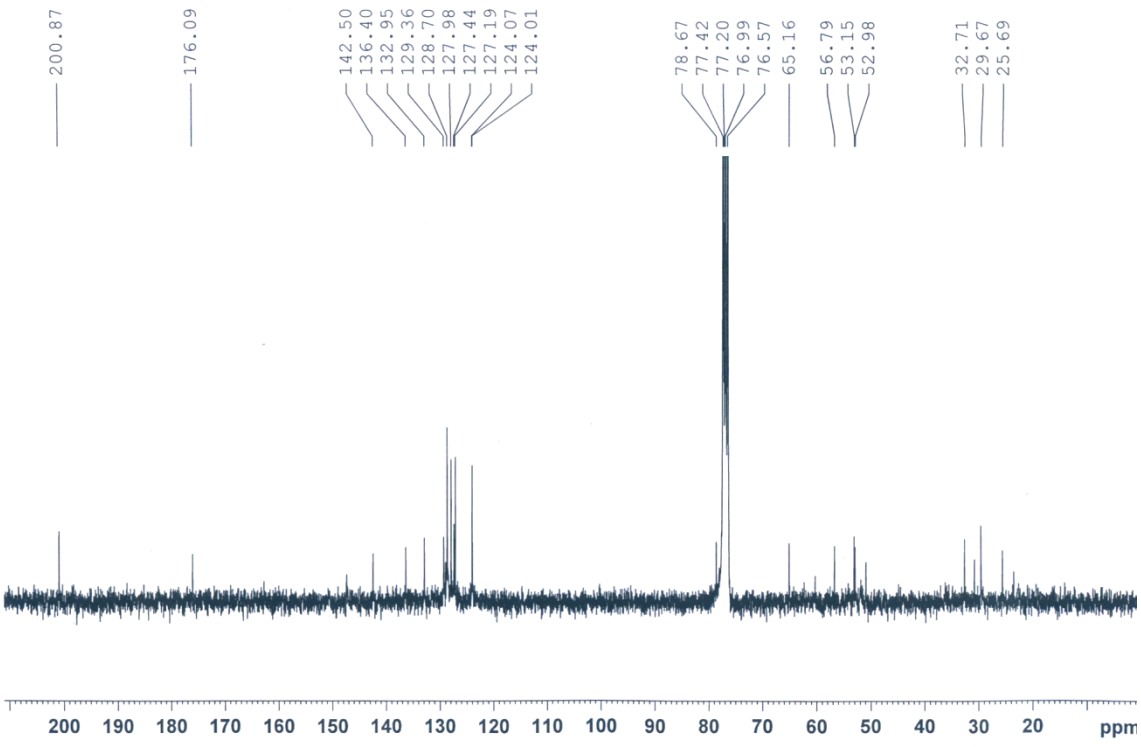




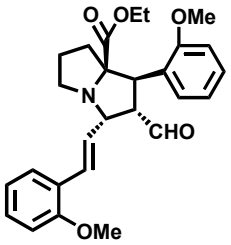

200.96
156.45
176.15
136.63
136.22
135.16
129.24
128.84
128.62
128.15
128.02
127.30
126.64
124.20
78.66
77.42
77.20
77.00
76.57
65.55
56.78
52.93
50.88
32.77
31.90
29.67
25.64
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

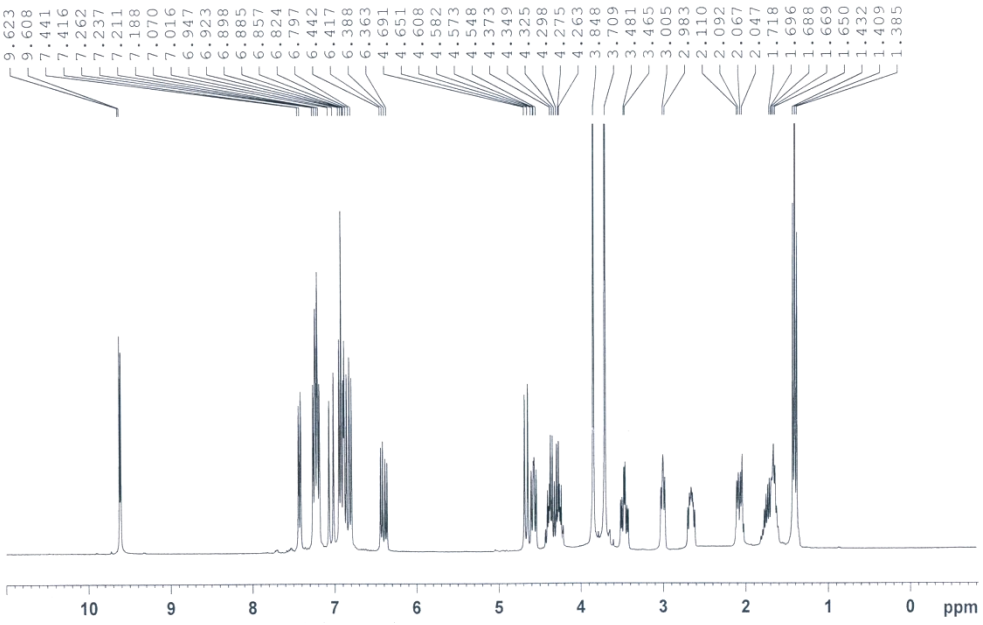
SI Figure 27: ^{1}H and ^{13}C NMR spectra of compound **7e**

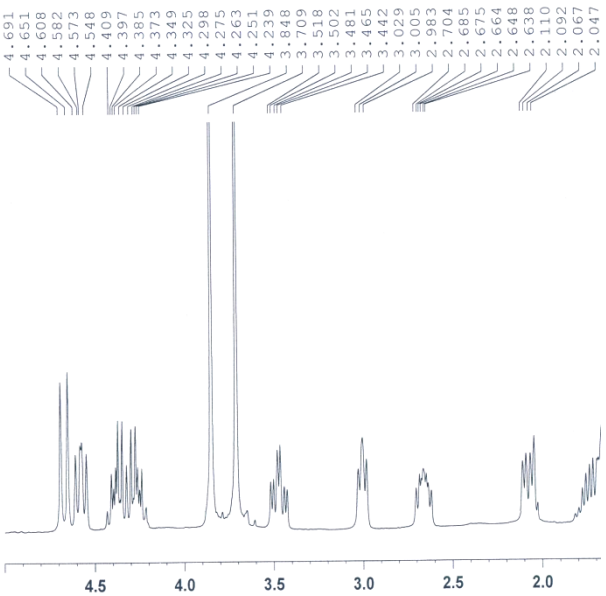


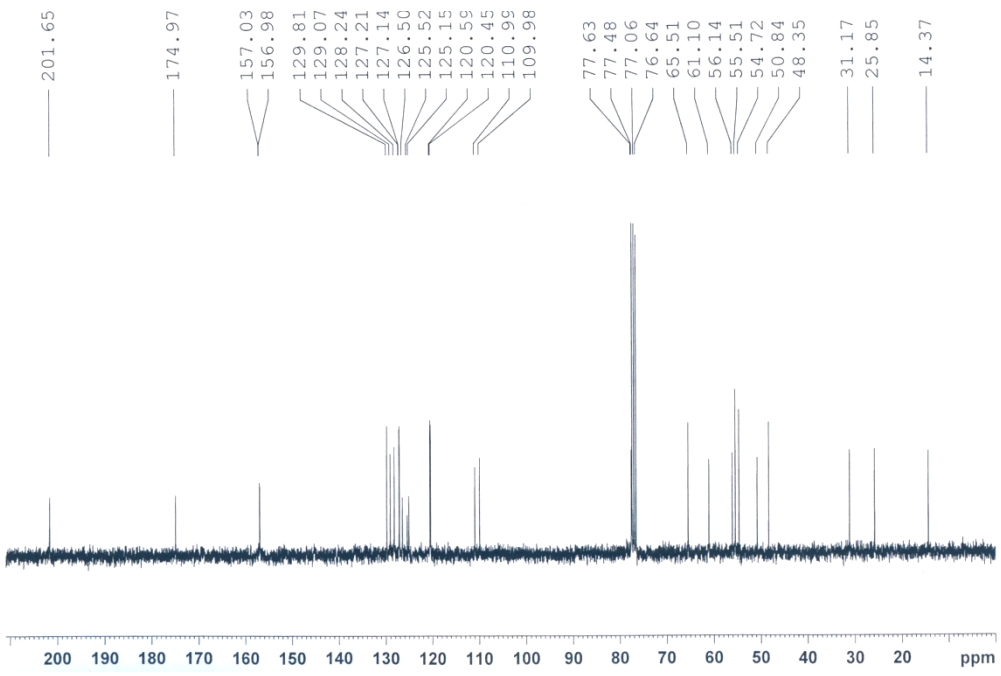


SI Figure 28: ^{1}H and ^{13}C NMR spectra of compound **7h**

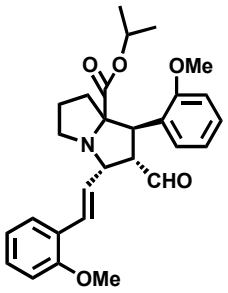


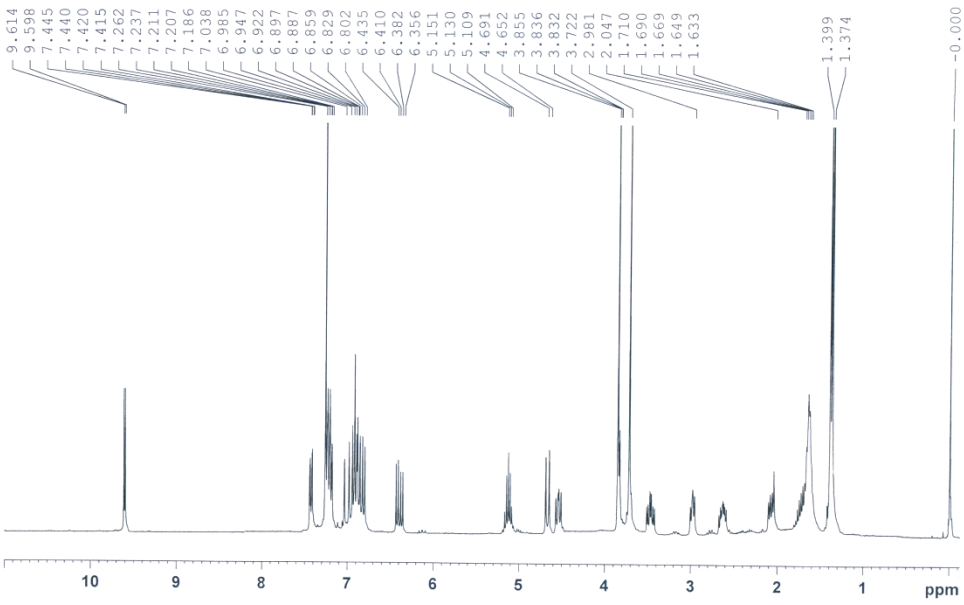


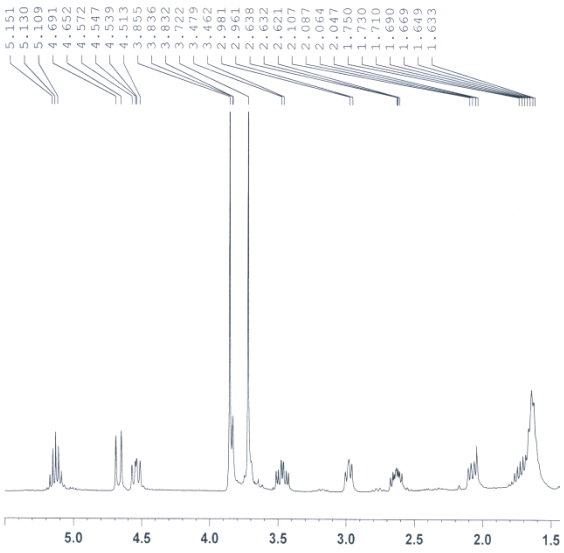


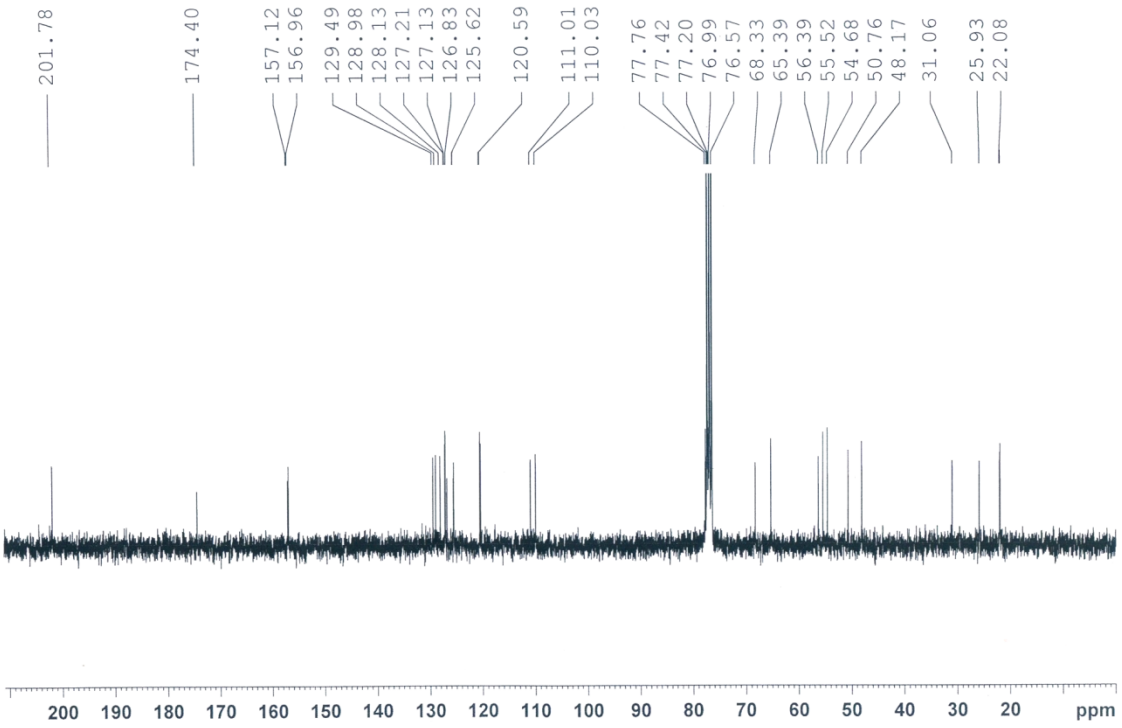

201.65
174.97
157.03
156.98
129.81
129.07
128.24
127.21
127.14
126.50
125.52
125.15
120.59
120.45
110.99
109.98
77.63
77.48
77.06
76.64
65.51
61.10
56.14
55.51
54.72
50.84
48.35
31.17
25.85
14.37
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

SI Figure 29: ^{1}H and ^{13}C NMR spectra of compound **7i**

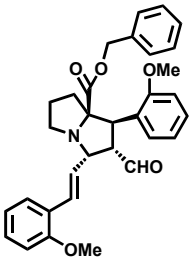


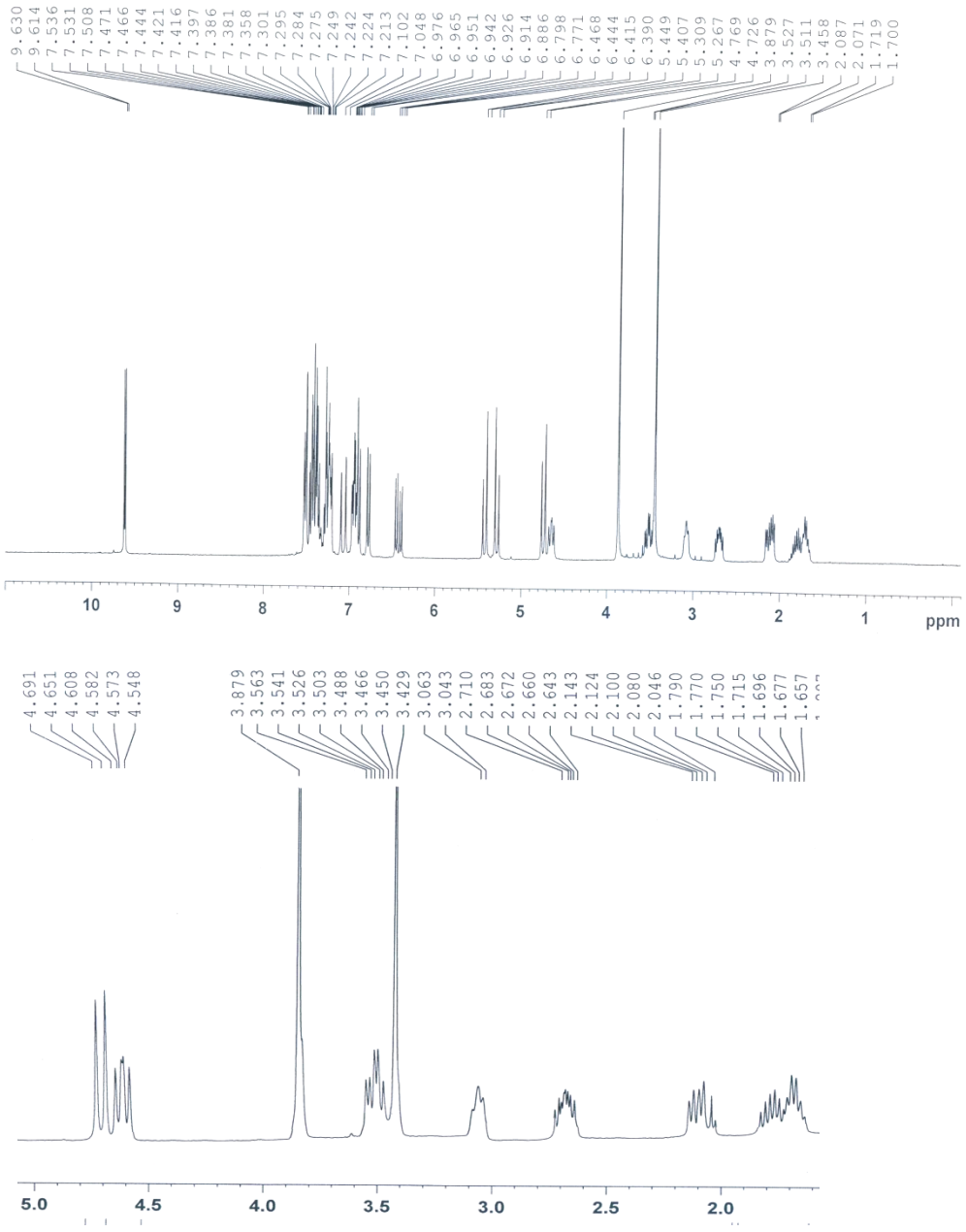


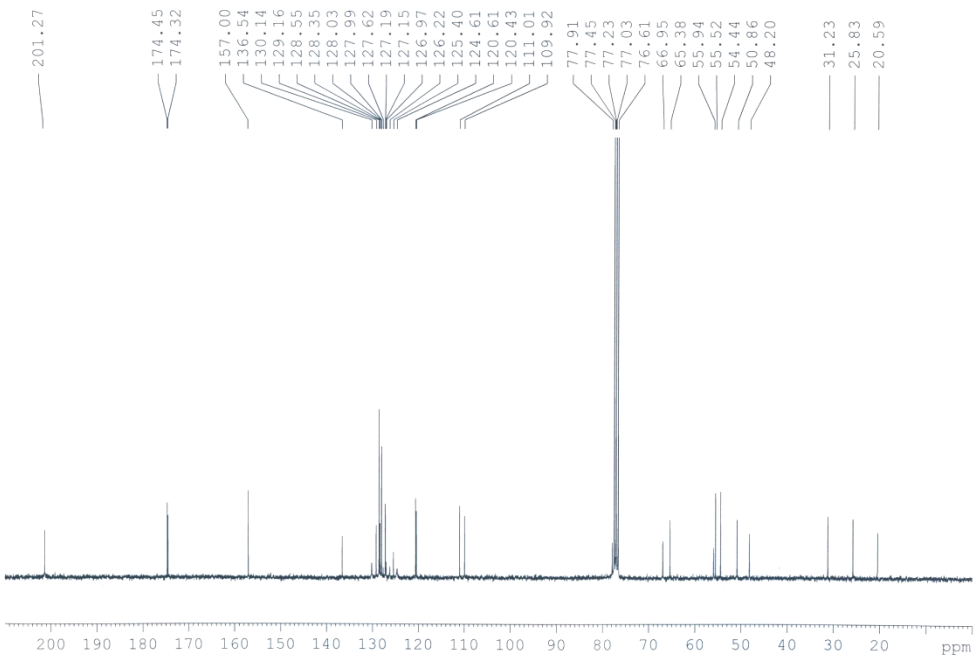



201.78
174.40
157.12
156.96
129.49
128.98
128.13
127.21
127.13
126.83
125.62
120.59
111.01
110.03
77.76
77.42
77.20
76.99
76.57
68.33
65.39
56.39
55.52
54.68
50.76
48.17
31.06
25.93
22.08
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

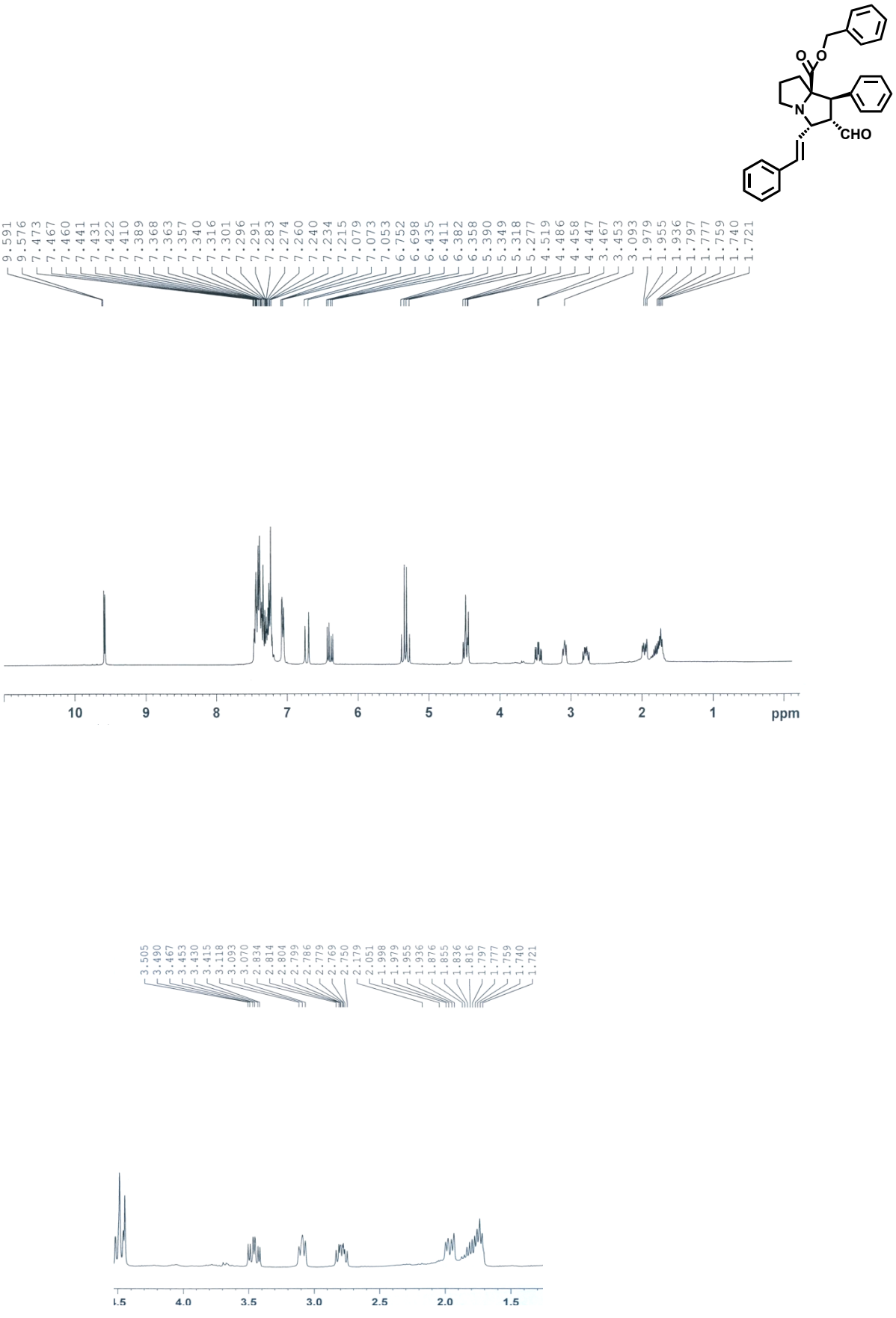
SI Figure 30: ^{1}H and ^{13}C NMR spectra of compound **7j**

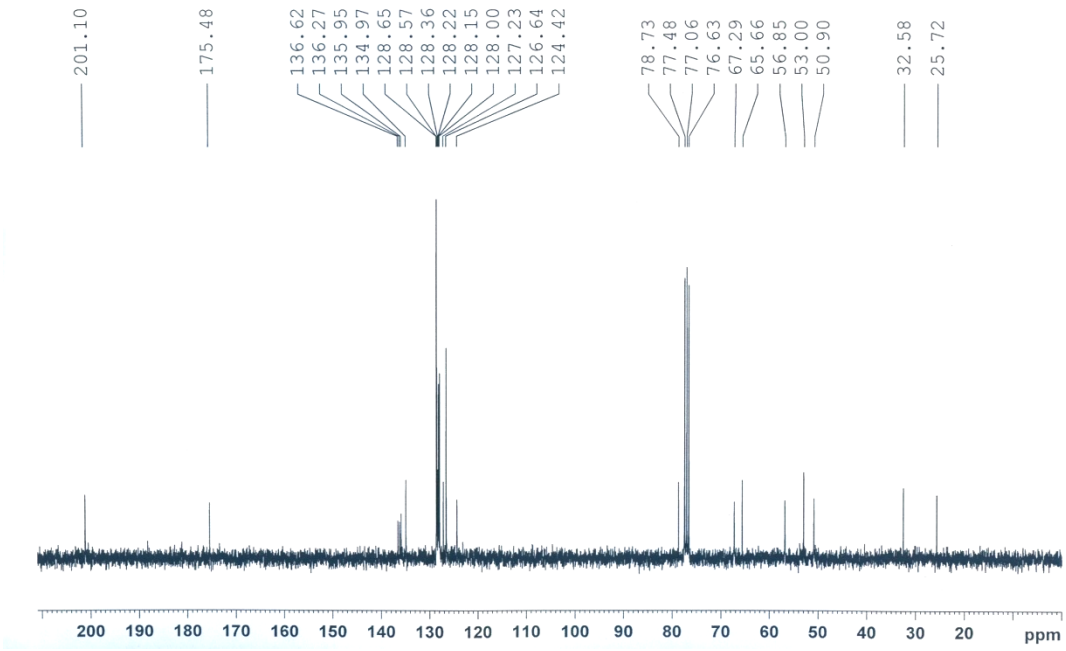




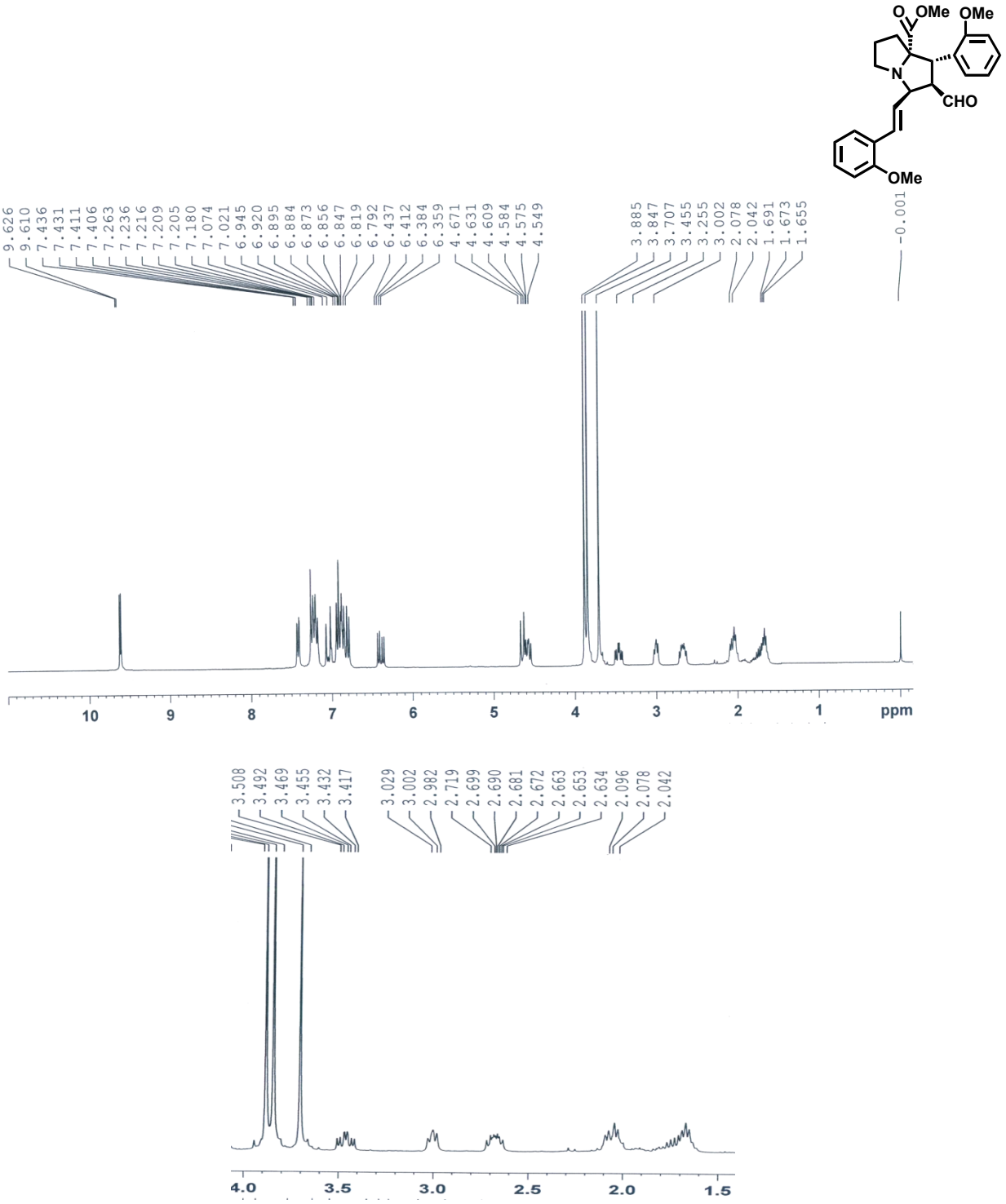

201.27
174.45
174.32
157.00
136.54
130.14
129.16
128.55
128.35
128.03
127.99
127.62
127.19
127.15
126.97
126.22
125.40
124.61
120.61
120.43
111.01
109.92
77.91
77.45
77.23
77.03
76.61
66.95
65.38
55.94
55.52
54.44
50.86
48.20
31.23
25.83
20.59
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20
ppm

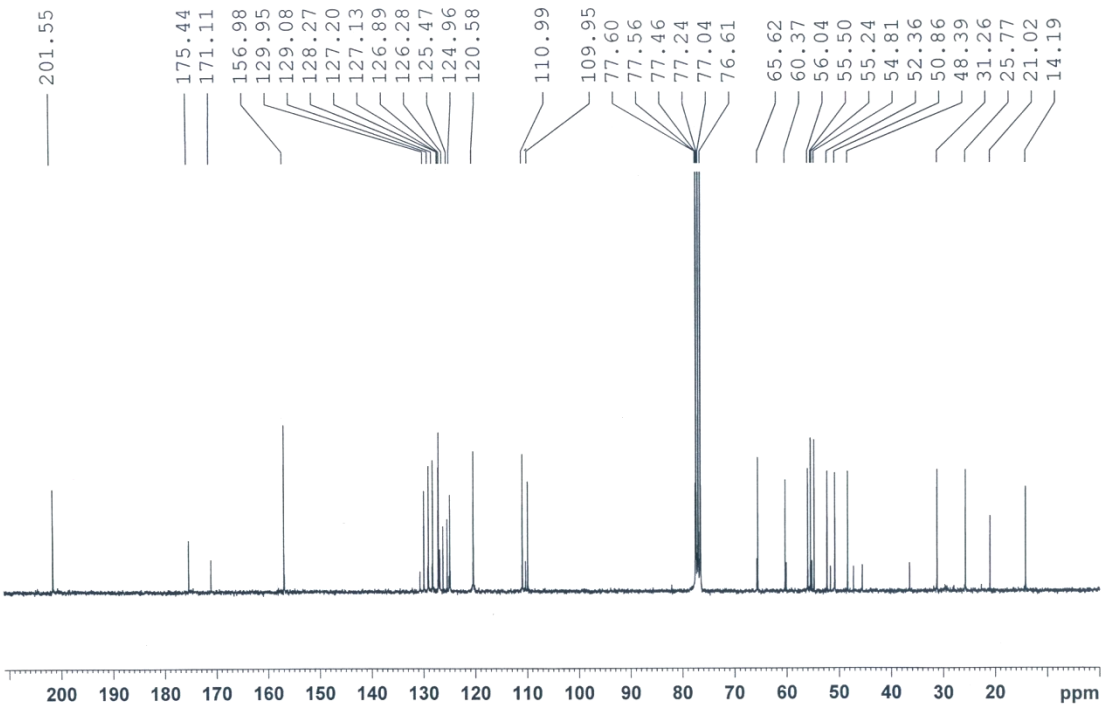
SI Figure 31: ^{1}H and ^{13}C NMR spectra of compound **7k**




201.10
175.48
136.62
136.27
135.95
134.97
128.65
128.57
128.36
128.22
128.15
128.00
127.23
126.64
124.42
78.73
77.48
77.06
76.63
67.29
65.66
56.85
53.00
50.90
32.58
25.72
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

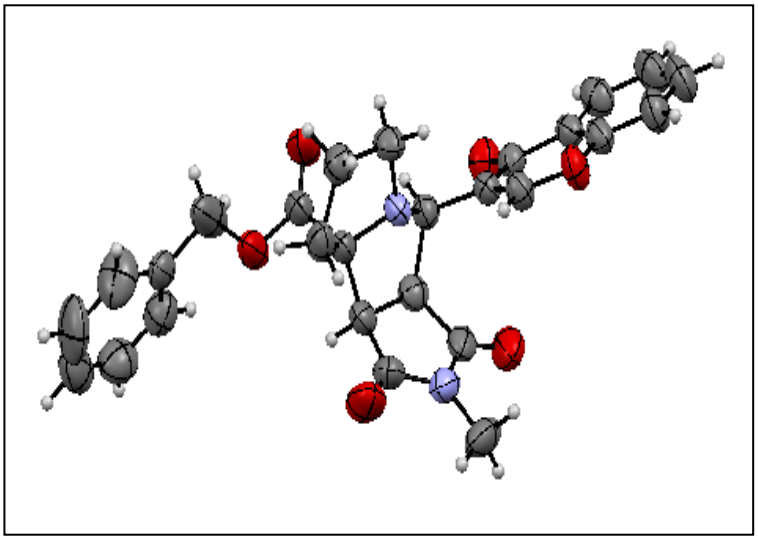
SI Figure 32: ^{1}H and ^{13}C NMR spectra of compound **7l**




201.55
175.44
171.11
156.98
129.95
129.08
128.27
127.20
127.13
126.89
126.28
125.47
124.96
120.58
110.99
109.95
77.60
77.56
77.46
77.24
77.04
76.61
65.62
60.37
56.04
55.50
55.24
54.81
52.36
50.86
48.39
31.26
25.77
21.02
14.19
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

7.1. **Summary of data CCDC 921618 (compound 5n)**

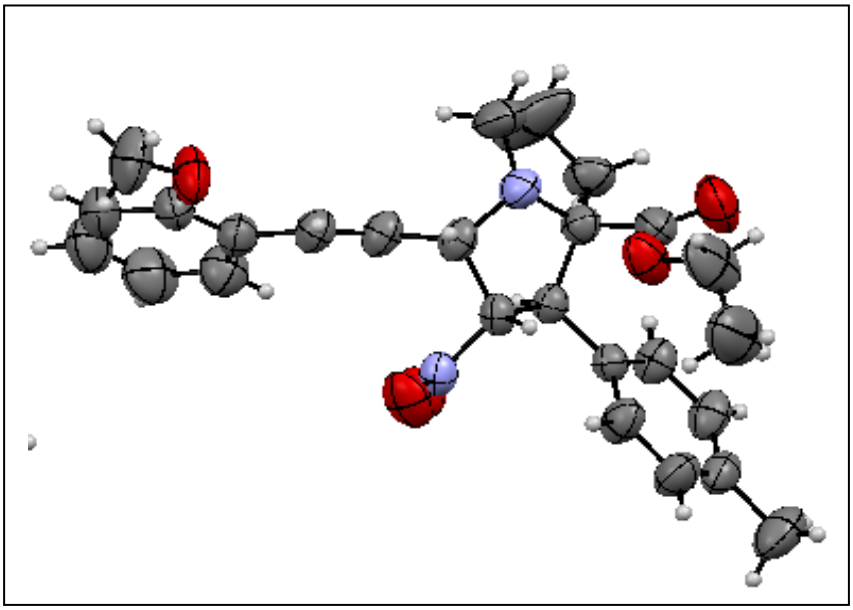
.



- Chemical formula and formula weight (M): C27 H24 N2 O6 and 472.48
- Crystal system: Monoclinic
- Unit-cell dimensions (angstrom or pm, degrees) and volume, with esds: a 13.131(7), b 16.402(9), c 11.331(6), 90.00, 109.361(7), 90.00, 2302(2)
- Temperature: 296 (2)
- Space group symbol: P12(1)/c1
- No. of formula units in unit cell (Z): 4
- Number of reflections measured and/or number of independent reflections, Rint: 3453
- Final R values (and whether quoted for all or observed data): 0.0716

7.2. **Summary of data CCDC 921617 (compound 6h)**

.



- Chemical formula and formula weight (M): C26 H30 N2 O5 and 450.52
- Crystal system: Triclinic
- Unit-cell dimensions (angstrom or pm, degrees) and volume, with esds: a 8.527(8), b 11.707(12), c 24.388(2), 87.45, 88.88(4), 81.91, 2408(4)
- Temperature: 296 (2)
- Space group symbol: P-1
- No. of formula units in unit cell (Z): 4
- Number of reflections measured and/or number of independent reflections, Rint: 7458
- Final R values (and whether quoted for all or observed data): 0.0937