Lewis Acid Catalyzed Formation of Tetrahydroquinolines via an Intramolecular Redox Process

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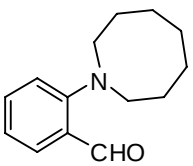
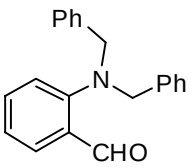
Supporting Information

General Information: Starting materials, reagents and solvents were purchased from commercial sources and were used as received with the exception of acetonitrile which was distilled from calcium hydride prior to use. Reactions were run under an atmosphere of nitrogen unless mentioned otherwise. Purifications of reaction products were carried out by flash chromatography using EM Reagent silica gel 60 (230–400 mesh). Analytical thin layer chromatography was performed on EM Reagent 0.25 mm silica gel 60 F_{254} plates. Visualization was accomplished with UV light and permanganate stain, followed by heating. Melting points were recorded on a Thomas Hoover capillary melting point apparatus. Infrared spectra were recorded on an ATI Mattson Genesis Series FT–Infrared spectrophotometer. Proton nuclear magnetic resonance spectra (^{1}H–NMR) were recorded on a Varian VNMRS-500 MHz instrument and are reported in ppm using solvent as an internal standard ($CDCl_3$ at 7.26 ppm). Data are reported as app = apparent, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, comp = complex; br = broad; integration; coupling constant(s) in Hz. Proton-decoupled carbon nuclear magnetic resonance spectra (^{13}C–NMR) spectra were recorded on a Varian VNMRS-500 MHz instrument and are reported in ppm using solvent as an internal standard ($CDCl_3$ at 77.0 ppm). Mass spectra were recorded on a Finnigan LCQ–DUO mass spectrometer. Optical rotations were recorded on a Perkin-Elmer 343 polarimeter at 589 nm and 293 K. HPLC analyses were carried out on an Agilent 1100 series HPLC with auto sampler and a multiple wavelength detector. The starting material 2-(pyrrolidin-1-yl)benzaldehyde (**3a**),[1] 2-(piperidin-1-yl)benzaldehyde (**3j**),[1] 2-morpholinobenzaldehyde (**3k**),[2] 2-(azepan-1-yl)benzaldehyde (**3l**),[3] 2-(3,4-dihydroisoquinolin-2(1H)-yl)benzaldehyde (**3n**),[4] 2-(2-methylpyrrolidin-1-yl)benzaldehyde (**3o**),[1] dimethyl 2-(2-(pyrrolidin-1-yl)benzylidene)malonate (**1a**),[2] and 2-(2-(pyrrolidin-1-yl)benzylidene)malononitrile (**1i**),[2] were prepared according to literature methods.

General procedure for the preparation of aminobenzaldehyde:
To a solution of 2-fluorobenzaldehyde (2.48 g, 20 mmol) and potassium carbonate (3.18 g, 23 mmol) in DMF (20 mL) was added the amine (23 mmol). The resulting reaction mixture was heated under reflux until complete consumption of 2-fluorobenzaldehyde as judged by TLC analysis. The reaction mixture was subsequently allowed to cool to room temperature, diluted with water (100 mL), and extracted with ethyl acetate (3 x 75 mL). The combined organic layers were washed with a saturated NH_4C1 solution (3 x 75 mL) and subsequently dried (Na_2SO_4). The solvent was removed under reduced pressure, and the residue was purified by column chromatography.

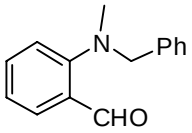


2-(azocan-1-yl)benzaldehyde (3m): The title compound was prepared according to the general procedure (3 h) and isolated as a liquid in 65% yield. (R_f = 0.50 in 80% DCM/Hex); IR (film) 2924, 2849, 1681, 1594, 1483, 1449, 1374, 1274, 1186, 1160, 756 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) 10.23 (d, *J* = 4.6Hz, 1H), 7.68 (d, *J* = 7.7Hz, 1H), 7.49 – 7.26 (m, 1H), 7.07 (d, *J* = 8.4Hz, 1H), 6.86 (t, *J* = 7.4Hz, 1H), 3.48 – 3.19 (comp, 4H), 1.87 – 1.46 (comp, 10H).; ^{13}C NMR (125 MHz, $CDCl_3$) 191.3, 155.8, 134.6, 130.6, 127.7, 119.9, 119.5, 55.5, 27.8, 27.4, 25.2; *m/z* (ESIMS) 218.6 $[M + H]^+$.



2-(dibenzylamino)benzaldehyde (3p): The title compound was prepared according to the general procedure (12 h) and isolated as a liquid in 25% yield (R_f = 0.61 in 80% DCM/Hex);

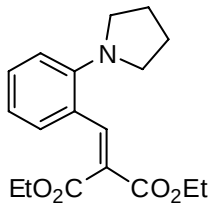
IR (film) 3062, 3028, 2938, 2840, 2733, 1686, 1595, 1494, 1481, 1452, 1384, 1365, 1276, 1254, 1189, 1161, 1028, 833, 749 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) 10.57 (s, 1H), 7.91 – 7.81 (m, 1H), 7.51 – 7.41 (m, 1H), 7.39 – 7.24 (comp, 6H), 7.20 (d, *J* = 7.7Hz, 4H), 7.09 (app dt, *J* = 9.7, 20.3Hz, 2H), 4.30 (s, 4H).; ^{13}C NMR (125 MHz, $CDCl_3$) 191.31, 154.42, 137.12, 134.44, 129.83, 129.57, 128.64, 128.43, 127.44, 122.89, 122.40, 58.70; *m/z* (ESIMS) 324.7 $[M + Na]^+$.



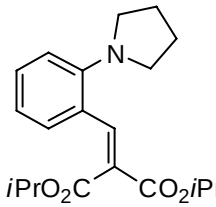
2-(benzyl)methyl)amino)benzaldehyde (3q): The title compound was prepared according to the general procedure (4 h) and isolated as a liquid in 75% yield (R_f = 0.42 in 15% EtOAc/Hex); IR (film) 2843, 1684, 1596, 1483, 1452, 1276, 1190, 945, 832, 763, 734, 698 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) 10.42 (s, 1H), 7.84 (dd, *J* = 1.7, 7.7, 1H), 7.49 (ddd, *J* = 1.8, 7.2, 8.3, 1H), 7.41 – 7.22 (comp, 5H), 7.20 – 7.01 (comp, 2H), 4.35 (s, 2H), 2.83 (s, 3H).; ^{13}C NMR (125 MHz, $CDCl_3$) 191.14, 155.57, 137.30, 134.57, 130.07, 128.45, 128.25, 128.02, 127.34, 121.54, 119.41, 62.26, 42.24.; *m/z* (ESIMS) 258.1 $[M + Na]^+$.

General procedure for the preparation of alkylidenemalonates:

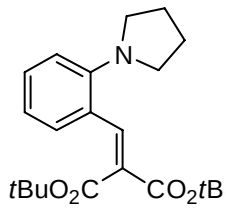
A mixture of aminobenzaldehyde (20 mmol), malonate (21 mmol), piperidine (3.4 mmol) and benzoic acid (2.2 mmol) in benzene (21 ml) was refluxed using a Dean-Stark trap. After completion of the reaction as judged by TLC, benzene was evaporated off and the reaction mixture was dissolved in ethyl acetate (50 mL). This solution was washed sequentially with water (20 ml), 5% aqueous HCl (2 x 20 ml), saturated aqueous sodium bicarbonate (2 x 20 ml), brine (20 ml) followed by drying over magnesium sulfate. The solvent was evaporated off and the crude reaction mixture was purified by either by triturating with methanol or by column chromatography.



diethyl 2-(2-(pyrrolidin-1-yl)benzylidene)malonate (1b): The reaction was carried out according to the general procedure (12 h). The product was obtained as a yellow liquid in 90% yield. (R_f = 0.49 in 20% EtOAc/Hex); IR (film) 2979, 2873, 2834, 1732, 1620, 1597, 1481, 1451, 1373, 1349, 1257, 1207, 1163, 1096, 1066, 1025, 955, 755 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) 7.99 (d, J = 6.1, 1H), 7.28 – 7.17 (comp, 2H), 6.81 (d, J = 8.2, 1H), 6.75 (app t, J = 7.5, 1H), 4.29 (q, J = 7.1, 2H), 4.27 – 4.21 (m, 2H), 3.40 – 3.21 (m, 4H), 2.01 – 1.85 (m, 4H), 1.42 – 1.29 (m, 3H), 1.20 (app q, J = 7.1, 3H).; ^{13}C NMR (125 MHz, $CDCl_3$) 166.68, 164.70, 150.07, 144.73, 130.55, 129.68, 123.58, 122.71, 118.40, 114.41, 61.28, 61.25, 52.26, 25.62, 14.17, 13.87; *m/z* (ESIMS) 656.9 $[2M + Na]^+$.

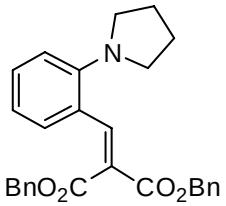


diisopropyl 2-(2-(pyrrolidin-1-yl)benzylidene)malonate (1c): The reaction was carried out according to the general procedure (24 h). The product was obtained as a yellow solid in 94% yield. (R_f = 0.40 in 15% EtOAc/Hex); mp: 90 – 91 °C; IR (KBr) 2980, 2932, 2967, 2935, 1728, 1709, 1612, 1599, 1495, 1484, 1467, 1452, 1375, 1357, 1275, 1210, 1193, 1108, 1096, 1063, 929, 911, 760 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) 7.91 (s, 1H), 7.27 (d, *J* = 7.7, 1H), 7.18 (t, *J* = 7.7, 1H), 6.77 (d, *J* = 8.3, 1H), 6.72 (t, *J* = 7.5, 1H), 5.20 – 5.08 (comp, 2H), 3.27 (t, *J* = 6.3, 4H), 1.90 (app dd, *J* = 5.0, 7.7, 4H), 1.29 (d, *J* = 6.3, 6H), 1.21 (d, *J* = 6.3, 6H).; ^{13}C NMR (125 MHz, $CDCl_3$) 165.98, 163.97, 149.80, 143.57, 130.27, 129.52, 124.35, 122.67, 118.20, 114.29, 68.54, 68.50, 52.03, 25.38, 21.63, 21.30.; *m/z* (ESIMS) 346.2 $[M + H]^+$.

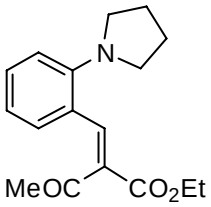


di-*tert*-butyl 2-(2-(pyrrolidin-1-yl)benzylidene)malonate (1d): The reaction was carried out according to the general procedure (12 h). The product was obtained as a yellow liquid in 95% yield. (R_f = 0.47 in 15% EtOAc/Hex); IR (film) 2976, 2873, 1712, 1622, 1597, 1481, 1451, 1392, 1367, 1272, 1158, 1096, 1067, 1031, 849, 753 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) 7.78 (s, 1H), 7.32 (d, *J* = 7.7, 1H), 7.23 – 7.16 (m, 1H), 6.79 (d, *J* = 8.3, 1H), 6.74 (app t, *J* = 7.4, 1H), 3.28 (t, *J* = 6.6, 4H), 1.96 – 1.87 (m, 4H), 1.54 (s, 9H),

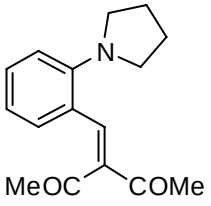
1.50 – 1.43 (s, 9H).; ^{13}C NMR (125 MHz, $CDCl_3$) 165.97, 163.95, 149.76, 142.35, 130.07, 129.82, 126.85, 123.13, 118.16, 114.27, 81.64, 81.41, 52.04, 28.11, 27.88, 27.82, 27.78, 25.54.; *m/z* (ESIMS) 374.2 $[M + H]^+$.



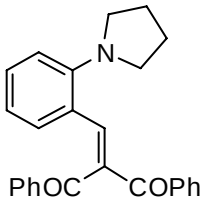
dibenzyl 2-(2-(pyrrolidin-1-yl)benzylidene)malonate (1e): The reaction was carried out according to the general procedure (12h). The product was obtained as a yellow liquid in 95% yield. (R_f = 0.48 in 20% EtOAc/Hex); IR (film) 3064, 3032, 2955, 2872, 1732, 1597, 1496, 1486, 1453, 1378, 1354, 1256, 1191, 1096, 1062, 1028, 955, 911, 749, 697 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) 8.06 (s, 1H), 7.41 – 7.29 (comp, 5H), 7.29 – 7.11 (comp, 7H), 6.79 (d, J = 8.3, 1H), 6.63 (t, J = 7.5, 1H), 5.27 (s, 2H), 5.19 (s, 2H), 3.26 (t, J = 6.5, 4H), 1.94 – 1.80 (m, 4H).; ^{13}C NMR (125 MHz, $CDCl_3$) 166.59, 164.63, 150.36, 146.24, 135.98, 135.46, 130.98, 129.93, 128.74, 128.66, 128.62, 128.38, 128.36, 128.12, 123.12, 122.78, 118.78, 114.74, 67.38, 67.08, 52.53, 25.81; *m/z* (ESIMS) 464.2 $[M + Na]^+$.



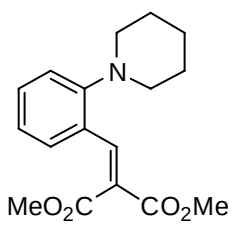
(*E*)-ethyl 3-oxo-2-(2-(pyrrolidin-1-yl)benzylidene)butanoate (1f): The reaction was carried out according to the general procedure (2 h). The product was obtained as a yellow liquid in 91% yield. dr = 47 : 53, determined by integration of one set of ^{1}H-NMR signals (δminor 1.31 ppm, δmajor 1.17 ppm). (R_f = 0.31 in 15% EtOAc/Hex); IR (film) 2974, 1715, 1663, 1596, 1480, 1450, 1250, 1193, 1061, 751 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) (major diastereoisomer) 7.83 (d, *J* = 6.9, 1H), 7.24 – 7.21 (comp, 2H), 6.74 (app dd, *J* = 7.8, 15.6, 2H), 4.22 (dd, *J* = 7.2, 14.3, 2H), 3.28 – 3.25 (m, 4H), 2.39 (s, 3H), 1.93 (app d, *J* = 6.6, 4H), 1.17 (t, *J* = 7.1, 3H). ; ^{13}C NMR of diastereomeric mixture (125 MHz, $CDCl_3$) 202.31, 194.94, 167.80, 165.04, 150.15, 149.94, 143.87, 143.08, 131.87, 130.84, 130.73, 130.70, 130.49, 129.60, 122.92, 122.39, 118.67, 118.56,114.71, 114.52, 61.19, 61.16, 52.33, 52.08, 30.85, 26.86, 25.54, 25.52, 14.14, 13.79; *m/z* (ESIMS) 288.1 $[M + H]^+$.



3-(2-(pyrrolidin-1-yl)benzylidene)penatane-2,4-dione (1g): The reaction was carried out according to the general procedure (1 h). The product was obtained as a yellow liquid in 95% yield. (R_f = 0.23 in 15% EtOAc/Hex); IR (film) 2968, 2871, 1709, 1683, 1657, 1595, 1479, 1450, 1354, 1281, 1239, 1163, 971, 753 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) 7.84 (s, 1H), 7.29 – 7.23 (m, 1H), 7.10 (dd, *J* = 1.5, 7.7, 1H), 6.86 (dd, *J* = 0.7, 8.3, 1H), 6.81 – 6.75 (m, 1H), 3.30 (app dd, *J* = 5.4, 7.8, 4H), 2.39 (s, 3H), 2.26 (s, 3H), 2.02 – 1.91 (m, 4H).; ^{13}C NMR (125 MHz, $CDCl_3$) 204.63, 196.37, 150.06, 142.40, 139.78, 131.29, 130.69, 122.65, 119.08, 114.99, 52.27, 31.15, 27.15, 25.54.; *m/z* (ESIMS) 258.3 $[M + H]^+$.

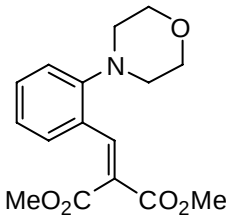


1,3-diphenyl-2-(2-(pyrrolidin-1-yl)benzylidene)propane-1,3-dione (1h): The reaction was carried out according to the general procedure (6 h). The product was obtained as a yellow solid in 92% yield. (R_f = 0.25 in 15% EtOAc/Hex); mp: 134 – 136 °C; IR (KBr) 2974, 2945, 1671, 1627, 1594, 1477, 1446, 1368, 1342, 1284, 1230, 1210, 1175, 875, 761, 725, 691 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) 7.93 – 7.88 (comp, 2H), 7.87 – 7.82 (comp, 2H), 7.78 (s, 1H), 7.54 (ddd, *J* = 1.3, 2.5, 8.7, 1H), 7.50 – 7.42 (comp, 3H), 7.36 (dd, *J* = 4.8, 10.7, 2H), 7.17 (dd, *J* = 1.3, 7.7, 1H), 7.14 – 7.08 (m, 1H), 6.71 – 6.62 (m, 2H), 3.20 (t, *J* = 6.5, 4H), 2.01 – 1.75 (app t, *J*= 6.5, 4H).; ^{13}C NMR (125 MHz, $CDCl_3$) 196.27, 195.28, 150.15, 145.96, 137.74, 136.96, 136.63, 133.18, 132.32, 130.75, 130.68, 129.39, 129.08, 128.50, 128.40, 123.12, 118.81, 114.81, 52.08, 25.44.; *m/z* (ESIMS) 404.1 $[M + Na]^+$.

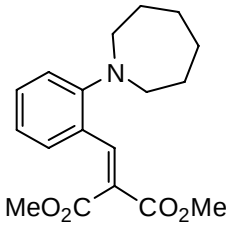


dimethyl 2-(2-(piperidin-1-yl)benzylidene)malonate (1j): The reaction was carried out according to the general procedure (12 h). The product was obtained as a yellow solid in 85% yield. (R_f = 0.48 in 20% EtOAc/Hex); mp: 78 – 80 °C; IR (film) 2936, 2862, 2792, 1735, 1621, 1598, 1485, 1450, 1435, 1379, 1358, 1290, 1258, 1214, 1101, 1069, 763 cm^{-1};

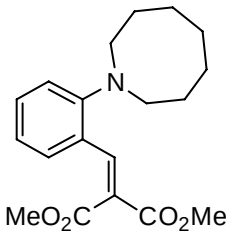
^{1}H NMR (500 MHz, $CDCl_3$) 8.11 (s, 1H), 7.34 (dd, J = 4.6, 12.8, 2H), 7.01 (d, J = 7.9, 1H), 6.96 (t, J = 7.5, 1H), 3.86 (s, 3H), 3.77 (s, 3H), 2.97 – 2.84 (m, 4H), 1.80 – 1.66 (m, 4H), 1.65 – 1.52 (m, 2H).; ^{13}C NMR (125 MHz, $CDCl_3$) 167.27, 164.96, 154.16, 142.45, 131.16, 128.78, 127.33, 124.08, 121.89, 118.43, 54.33, 52.43, 52.40, 26.38, 24.20; *m/z* (ESIMS) 628.9 $[M + H]^+$.



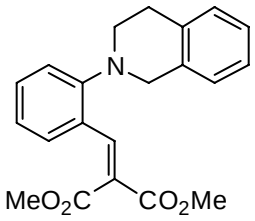
dimethyl 2-(2-morpholinobenzylidene)malonate (1k): The reaction was carried out according to the general procedure (4 h). The product was obtained as a yellow liquid in 98% yield. (R_f = 0.11 in 20% EtOAc/Hex); IR (film) 3037, 2954, 2885, 2852, 1716, 1624, 1597, 1485, 1448, 1362, 1332, 1266, 1165, 1117, 1069, 1042, 936, 920, 765, 735 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) 8.10 (s, 1H), 7.42 – 7.30 (comp, 2H), 7.02 (app t, J = 8.1, 2H), 3.95 – 3.81 (comp, 7H), 3.80 – 3.72 (m, 3H), 3.05 – 2.90 (m, 4H).; ^{13}C NMR (125 MHz, $CDCl_3$) 166.92, 164.64, 152.46, 141.89, 131.29, 129.00, 127.46, 125.01, 122.84, 118.25, 67.09, 53.06, 52.50, 52.42; *m/z* (ESIMS) 306.1 $[M + H]^+$.



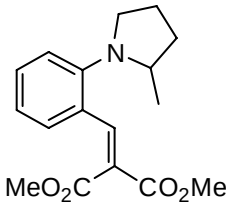
dimethyl 2-(2-(azepan-1-yl)benzylidene)malonate (1l): The reaction was carried out according to the general procedure (1.5 h). The product was obtained as a yellow liquid in 95% yield. (R_f = 0.49 in 20% EtOAc/Hex); IR (film) 2929, 2854, 1735, 1620, 1595, 1486, 1448, 1361, 1259, 1215, 1163, 1104, 1069, 762 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) 8.09 (s, 1H), 7.28 (app t, J = 7.8, 2H), 7.06 (app t, J = 10.0, 1H), 6.89 (app t, J = 7.5, 1H), 3.85 (s, 3H), 3.76 (s, 3H), 3.27 – 3.12 (comp, 4H), 1.86 – 1.66 (comp, 8H).; ^{13}C NMR (125 MHz, $CDCl_3$) 167.20, 164.83, 155.06, 144.04, 130.75, 128.93, 126.64, 123.51, 120.84, 118.96, 56.06, 52.34, 52.31, 29.20, 27.04; *m/z* (ESIMS) 657.0 $[2M + Na]^+$.



dimethyl 2-(2-(azocan-1-yl)benzylidene)malonate (1m): The reaction was carried out according to the general procedure (3 h). The product was obtained as a yellow liquid in 95% yield. (R_f = 0.37 in 15% EtOAc/Hex); IR (film) 2924, 2847, 1735, 1617, 1595, 1462, 1435, 1257, 1211, 1069, 755 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) 8.18 (s, 1H), 7.33 – 7.24 (comp, 2H), 7.14 (d, *J* = 8.2, 1H), 6.89 (app t, *J* = 7.5, 1H), 3.85 (s, 3H), 3.76 (s, 3H), 3.35 – 3.09 (m, 4H), 1.72 (app s, 10H).; ^{13}C NMR (125 MHz, $CDCl_3$) 167.22, 164.84, 154.48, 144.31, 130.96, 129.13, 127.16, 123.64, 121.06, 119.85, 55.21, 52.37, 28.13, 27.58, 25.01.; *m/z* (ESIMS) 332.2 $[M + H]^+$.

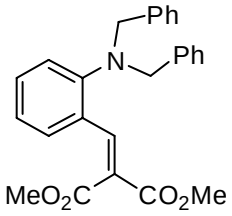


dimethyl 2-(2-(3,4-dihydroisoquinolin-2(1*H*)-yl)benzylidene)malonate (1n): The reaction was carried out according to the general procedure (1 h). The product was obtained as a yellow liquid in 86% yield. (R_f = 0.48 in 20% EtOAc/Hex); IR (film) 3060, 3024, 2951, 2839, 1735, 1622, 1598, 1488, 1455, 1433, 1380, 1358, 1259, 1215, 1165, 1102, 1069, 936, 757 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) 8.13 (s, 1H), 7.38 (dd, *J* = 4.5, 11.3, 2H), 7.23 – 7.18 (comp, 3H), 7.17 – 7.10 (comp, 2H), 7.03 (app t, *J* = 7.5, 1H), 4.30 (s, 2H), 3.86 (s, 3H), 3.81 (s, 3H), 3.29 (t, *J* = 5.8, 2H), 3.03 (t, *J* = 5.7, 2H).; ^{13}C NMR (125 MHz, $CDCl_3$) 167.00, 166.80, 164.68, 152.34, 142.30, 134.40, 134.28, 131.06, 129.00, 128.93, 127.23, 126.30, 125.84, 124.71, 122.19, 118.24, 53.11, 52.74, 52.42, 52.39, 52.36.; *m/z* (ESIMS) 231.1 $[M + H]^+$.

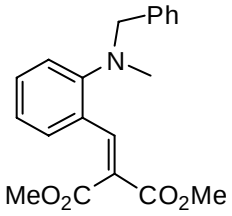


dimethyl 2-(2-(2-methylpyrrolidin-1-yl)benzylidene)malonate (1o): The reaction was carried out according to the general procedure (4 h). The product was obtained as a yellow liquid in 95% yield. (R_f = 0.28 in 15% EtOAc/Hex); IR (film) 2953, 1735, 1620, 1596, 1474, 1352, 1260, 1214, 1057, 743 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) 7.97 (s, 1H), 7.31 – 7.21 (comp, 2H), 6.90 (d, *J* = 8.1, 1H), 6.82 (app t, *J* = 7.5, 1H), 3.85 (d, *J* = 4.4, 3H), 3.81 – 3.73 (comp, 4H), 3.63 – 3.54 (m, 1H), 3.08 (app td, *J* = 2.7, 8.9, 1H), 2.25 –

2.13 (m, 1H), 1.89 (ddd, *J* = 7.2, 9.6, 11.7, 1H), 1.83 – 1.70 (m, 1H), 1.64 (app dq, *J* = 8.0, 11.9, 1H), 1.10 (d, *J* = 6.0, 3H).; ^{13}C NMR (125 MHz, $CDCl_3$) 167.28, 165.17, 149.85, 144.68, 130.56, 129.19, 125.23, 122.92, 119.52, 116.41, 55.50, 55.33, 52.42, 52.37, 34.25, 24.50, 19.09; *m/z* (ESIMS) 304.2 $[M + H]^+$.



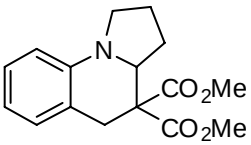
dimethyl 2-(2-(dibenzylamino)benzylidene)malonate (1p): The reaction was carried out according to the general procedure (1.5 h). The product was obtained as a yellow liquid in 95% yield. (R_f = 0.25 in 15% EtOAc/Hex); IR (film) 3035, 2958, 2831, 1734, 1623, 1595, 1489, 1452, 1435, 1363, 1262, 1214, 109, 764, 699 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) 8.47 (s, 1H), 7.44 – 7.39 (m, 1H), 7.32 (dd, *J* = 4.8, 9.8, 4H), 7.29 – 7.22 (comp, 7H), 7.02 (t, *J* = 7.5, 1H), 6.93 (d, *J* = 8.1, 1H), 4.22 (s, 4H), 3.87 (s, 3H), 3.80 (s, 3H).; ^{13}C NMR (125 MHz, $CDCl_3$) 166.82, 164.53, 150.66, 142.95, 137.31, 130.45, 128.86, 128.52, 128.43, 128.23, 127.04, 125.24, 122.63, 121.58, 57.20, 52.34, 52.21.; *m/z* (ESIMS) 438.2 $[M + Na]^+$.



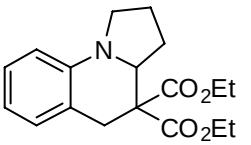
dimethyl 2-(2-(benzyl(methyl)amino)benzylidene)malonate (1q): The reaction was carried out according to the general procedure (1.5 h). The product was obtained as a yellow solid in 96% yield. (R_f = 0.40 in 20% EtOAc/Hex); mp: 93 – 95 °C; IR (film) 3060, 3019, 2949, 2844, 2792, 1727, 1618, 1596, 1487, 1436, 1364, 1298, 1266, 1071, 947, 768, 737, 700 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) 8.25 (s, 1H), 7.39 – 7.21 (comp, 7H), 7.09 – 6.93 (comp, 2H), 4.14 (s, 2H), 3.81 (s, 3H), 3.77 (s, 3H), 2.70 (s, 3H).; ^{13}C NMR (125 MHz, $CDCl_3$) 167.01, 164.68, 152.87, 143.03, 137.69, 130.92, 129.02, 128.35, 128.27, 127.45, 127.17, 124.78, 122.09, 119.23, 61.95, 52.38, 52.36, 40.61; *m/z* (ESIMS) 340.3 $[M + H]^+$.

General procedure for the hydride shift reaction of alkylidenemalonates with gadolinium triflate:

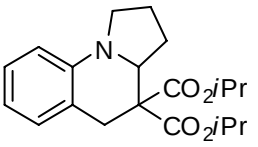
To a stirred solution of the alkylidenemalonate (1 mmol) in 10 mL of CH_3CN was added gadolinium triflate (0.05 mmol) followed by stirring at room temperature. The reaction was monitored by TLC and, after completion, the solvent was evaporated off. The crude product was dissolved in dichloromethane (20 ml) and the resulting solution washed with 25 ml of 1M NaOH. The aqueous layer was extracted with dichloromethane (20 ml x 3). The combined organic layers were washed with brine (25 ml) and dried with sodium sulfate. The solvent was evaporated off and the crude product was purified by column chromatography.



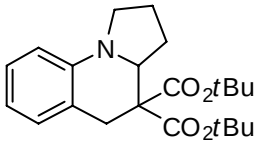
dimethyl 1,2,3,3a-tetrahydropyrrolo[1,2-a]quinoline-4,4(5H)-dicarboxylate (2a): The reaction was carried out according to the general procedure (15 min). The product was obtained as a white solid in 90% yield. (R_f = 0.30 in 15% EtOAc/Hex); mp: 85 – 86 °C; IR (KBr) 2952, 2844, 1753, 1731, 1606, 1506, 1460, 1436, 1292, 1266, 1244, 1209, 1162, 1103, 1062, 750 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) 7.10 (app t, *J* = 7.7, 1H), 7.03 (d, *J* = 7.4, 1H), 6.62 (app t, *J* = 7.4, 1H), 6.48 (d, *J* = 8.1, 1H), 3.85 – 3.76 (comp, 4H), 3.59 (d, *J* = 0.9, 3H), 3.44 – 3.23 (comp, 4H), 2.52 – 2.40 (m, 1H), 2.23 – 2.04 (comp, 2H), 2.03 – 1.90 (m, 1H).; ^{13}C NMR (125 MHz, $CDCl_3$) 171.35, 168.94, 143.70, 128.37, 127.43, 118.56, 115.88, 110.84, 62.02, 53.13, 52.55, 52.01, 47.30, 36.79, 27.77, 23.40.; *m/z* (ESIMS) 290.1 $[M + H]^+$.



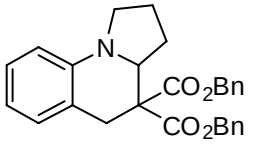
diethyl 1,2,3,3a-tetrahydropyrrolo[1,2-a]quinoline-4,4(5H)-dicarboxylate (2b): The reaction was carried out according to the general procedure (15 mins). The product was obtained as an oil in 82% yield. (R_f = 0.19 in 50% DCM/Hex); IR (film) 3060, 2979, 2897, 2833, 1731, 1605, 1504, 1461, 1366, 1355, 1339, 1296, 1266, 1237, 1161, 1099, 1058, 1042, 745 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) 7.08 (app t, J = 7.7, 1H), 7.02 (d, J = 7.4, 1H), 6.60 (app td, J = 0.9, 7.4, 1H), 6.46 (d, J = 8.0, 1H), 4.33 – 4.20 (comp, 2H), 4.12 – 3.95 (comp, 2H), 3.79 (dd, J = 6.9, 9.0, 1H), 3.33 (app ddt, J = 10.0, 25.1, 32.2, 4H), 2.50 (app dtd, J = 8.7, 10.3, 12.3, 1H), 2.24 – 1.87 (comp, 3H), 1.31 (dd, J = 5.1, 9.2, 3H), 1.06 (dd, J = 5.0, 9.2, 3H).; ^{13}C NMR (125 MHz, $CDCl_3$) 170.96, 168.48, 143.88, 128.44, 127.41, 118.80, 115.82, 110.78, 62.24, 61.38, 60.66, 53.10, 47.43, 37.00, 27.84, 23.54, 14.02, 13.78; *m/z* (ESIMS) 318.2 $[M + H]^+$.



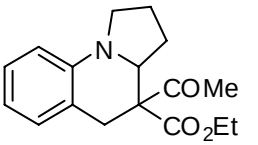
diisopropyl 1,2,3,3a-tetrahydropyrrolo[1,2-a]quinoline-4,4(5H)-dicarboxylate (2c): The reaction was carried out according to the general procedure (10min). The product was obtained as a yellow solid in 87% yield. (R_f = 0.31 in 50% DCM/Hex); mp: 82 – 86 °C; IR (film) 2979, 29332, 2868, 2833, 1727, 1605, 1505, 1461, 1385, 1374, 1357, 1266, 1243, 1201, 1182, 1162, 1109, 744 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) 7.07 (app t, J = 7.7, 1H), 7.00 (d, J = 7.4, 1H), 6.57 (app t, J = 7.1, 1H), 6.45 (d, J = 8.0, 1H), 5.13 (hept, J = 6.3, 1H), 4.88 (hept, J = 6.2, 1H), 3.78 (dd, J = 6.7, 9.2, 1H), 3.40 (app td, J = 2.7, 8.5, 1H), 3.26 (ddd, J = 15.7, 21.9, 22.4, 3H), 2.59 – 2.42 (m, 1H), 2.19 – 2.03 (comp, 2H), 2.02 – 1.86 (m, 1H), 1.28 (dd, J = 1.6, 6.2, 6H), 1.11 (d, J = 6.3, 3H), 0.99 (d, J = 6.2, 3H).; ^{13}C NMR (125 MHz, $CDCl_3$) 170.62, 167.99, 143.90, 128.50, 127.48, 118.71, 115.66, 110.66, 69.00, 68.01, 62.42, 52.64, 47.53, 37.20, 27.79, 23.69, 21.60, 21.56, 21.42, 21.31; *m/z* (ESIMS) 713.1 $[2M + Na]^+$.



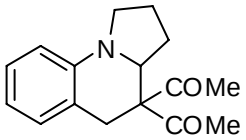
di-*tert*-butyl 1,2,3,3a-tetrahydropyrrolo[1,2-a]quinoline-4,4(5H)-dicarboxylate (2d): The reaction was carried out according to the general procedure (0.5 h). The product was obtained as a white solid in 70% yield. (R_f = 0.60 in 15% EtOAc/Hex); mp: 64 – 65 °C; IR (KBr) 2975, 1724, 1638, 1605, 1504, 1477, 1460, 1392, 1368, 1277, 1250, 1158, 849, 743 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) 7.07 (app t, *J* = 7.7, 1H), 7.01 (d, *J* = 7.3, 1H), 6.57 (app t, *J* = 7.3, 1H), 6.43 (d, *J* = 8.1, 1H), 3.74 (dd, *J* = 6.9, 9.0, 1H), 3.39 (app td, *J* = 2.7, 8.4, 1H), 3.25 (dd, *J* = 8.9, 15.7, 2H), 3.13 (d, *J* = 15.5, 1H), 2.53 (app dt, *J* = 10.3, 20.5, 1H), 2.21 – 2.04 (comp, 2H), 2.02 – 1.89 (m, 1H), 1.51 (s, 9H), 1.24 (s, 9H).; ^{13}C NMR (125 MHz, $CDCl_3$) 170.47, 167.75, 144.04, 128.44, 127.32, 119.25, 115.52, 110.46, 81.75, 80.84, 62.51, 53.77, 47.48, 37.47, 27.91, 27.82, 27.63, 23.76.; *m/z* (ESIMS) 396.1 $[M + Na]^+$.



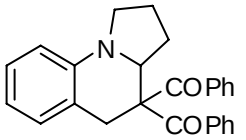
dibenzyl 1,2,3,3a-tetrahydropyrrolo[1,2-a]quinoline-4,4(5H)-dicarboxylate (2e): The reaction was carried out according to the general procedure (2 h). The product was obtained as colorless oil in 57% yield. (R_f = 0.70 in 50% DCM/Hex); IR (film) 3064, 3033, 2958, 2848, 1732, 1605, 1577, 1500, 1459, 1372, 1356, 1339, 1325, 1265, 1227, 1161, 1120, 1099, 1055, 1041, 990, 909, 745, 697 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) 7.41 – 7.28 (comp, 5H), 7.27 – 7.18 (comp, 3H), 7.10 (app t, J = 7.7, 1H), 7.01 (ddd, J = 2.9, 4.9, 7.2, 3H), 6.61 (app td, J = 0.9, 7.4, 1H), 6.45 (d, J = 8.0, 1H), 5.20 (s, 2H), 5.03 (d, J = 12.4, 1H), 4.95 (d, J = 12.5, 1H), 3.81 (dd, J = 6.9, 8.9, 1H), 3.44 (d, J = 15.9, 1H), 3.31 (app dt, J = 9.7, 22.9, 2H), 3.20 (dd, J = 8.3, 15.8, 1H), 2.50 – 2.36 (m, 1H), 2.14 – 2.02 (m, 1H), 2.01 – 1.80 (comp, 2H).; ^{13}C NMR (125 MHz, $CDCl_3$) 170.73, 168.38, 143.88, 135.50, 135.39, 128.59, 128.57, 128.34, 128.32, 128.04, 127.92, 127.83, 127.54, 118.77, 116.06, 111.05, 67.21, 66.64, 62.29, 53.57, 47.35, 36.95, 27.83, 23.44; *m/z* (ESIMS) 464.3 $[M + Na]^+$.



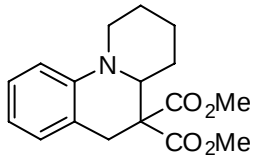
ethyl 4-acetyl-1,2,3,3a,4,5-hexahydropyrrolo[1,2-a]quinoline-4-carboxylate (2f): The reaction was carried out according to the general procedure (5 min). The product was obtained as a pink solid in 55% yield as a mixture of diastereomers (dr = 36 : 64), determined by integration of one set of ^1H-NMR signals (δminor 1.31 ppm, δmajor 1.17 ppm). (R_f = 0.21 in 50% DCM/Hex); IR (film) 2977, 2864, 1738, 1712, 1604, 1577, 1505, 1478, 1460, 1355, 1337, 1297, 1260, 1203, 1161, 1101, 1042, 745, 665 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) (major diastereoisomer) 7.10 (dd, J = 8.5, 16.7, 1H), 7.05 – 7.00 (comp, 1H), 6.65 – 6.57 (comp, 1H), 6.46 (d, J = 8.0, 1H), 4.14 – 4.00 (comp, 2H), 3.70 (dd, J = 6.7, 9.1, 1H), 3.44 – 3.23 (comp, 3H), 3.10 (d, J = 15.5, 1H), 2.43 – 2.24 (comp, 4H), 2.20 – 1.87 (comp, 3H), 1.07 (app t, J = 7.1, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) 204.74, 203.51, 171.56, 169.77, 143.94, 143.74, 128.39, 128.36, 127.86, 127.33, 118.95, 117.59, 115.78, 115.76, 110.98, 110.71, 62.34, 61.86, 61.36, 60.81, 59.07, 57.10, 47.33, 47.01, 36.42, 36.05, 28.04, 27.68, 27.64, 27.56, 23.52, 23.46, 13.98, 13.74; *m/z* (ESIMS) 288.2 $[M + H]^+$.



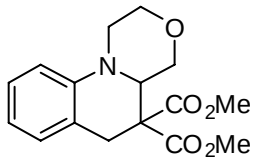
1,1'-(1,2,3,3a,4,5-hexahydropyrrolo[1,2-a]quinoline-4,4-diyl)diethanone (2g): The reaction was carried out according to the general procedure (3 h). The product was obtained as an oil in 76% yield. (R_f = 0.31 in 15% EtOAc/Hex); IR (film) 2083, 1715, 1689, 1643, 1604, 1503, 1442, 1352, 1184 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) 7.12 (app t, *J* = 7.7, 1H), 7.08 (d, *J* = 7.4, 1H), 6.65 (app t, *J* = 7.4, 1H), 6.49 (d, *J* = 8.1, 1H), 3.64 (app dt, *J* = 7.7, 15.2, 1H), 3.36 – 3.23 (comp, 3H), 3.15 (d, *J* = 16.5, 1H), 2.27 – 2.16 (comp, 4H), 2.06 – 1.88 (comp, 6H).; ^{13}C NMR (125 MHz, $CDCl_3$) 207.51, 205.57, 144.06, 128.57, 127.86, 118.09, 116.24, 111.25, 63.81, 61.19, 46.77, 34.52, 29.09, 27.56, 27.43, 23.11.; *m/z* (ESIMS) 258.2 $[M + H]^+$.



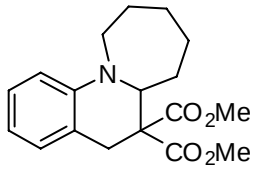
(1,2,3,3a,4,5-hexahydropyrrolo[1,2-a]quinoline-4,4-diyl)bis(phenylmethanone) (2h): The reaction was carried out according to the general procedure (3 h). The product was obtained as yellow oil in 92% yield. (R_f = 0.44 in 15% EtOAc/Hex); IR (film) 3064, 2961, 2848, 1680, 1658, 1604, 1578, 1504, 1460, 1446, 1353, 1337, 1297, 1230, 1203, 1180, 1160, 941, 909, 732, 700 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) 7.94 – 7.89 (comp, 2H), 7.67 – 7.62 (comp, 2H), 7.52 – 7.46 (m, 1H), 7.44 – 7.34 (comp, 3H), 7.27 (t, *J* = 7.5, 2H), 7.11 (t, *J* = 7.7, 1H), 6.81 (d, *J* = 7.3, 1H), 6.61 – 6.50 (comp, 2H), 3.96 (dd, *J* = 6.3, 9.7, 1H), 3.49 (app q, *J* = 16.0, 2H), 3.42 – 3.33 (comp, 2H), 2.19 (app dq, *J* = 9.9, 14.0, 1H), 1.99 (app dt, *J* = 6.1, 10.9, 1H), 1.93 – 1.83 (comp, 2H).; ^{13}C NMR (125 MHz, $CDCl_3$) 198.80, 197.52, 144.68, 138.01, 137.05, 132.85, 132.26, 129.21, 128.84, 128.56, 128.23, 128.16, 127.51, 119.51, 116.35, 111.21, 64.38, 63.26, 47.45, 38.73, 28.78, 23.77.; *m/z* (ESIMS) 404.2 $[M + Na]^+$.



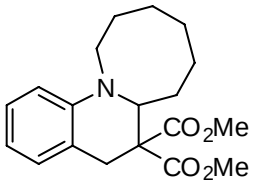
dimethyl 2,3,4,4a-tetrahydro-1*H*-pyrido[1,2-a]quinoline-5,5(6*H*)-dicarboxylate (2j): The reaction was carried out according to the general procedure (3 h). The product was obtained as an oil in 91% yield. (R_f = 0.76 in 50% DCM/Hex); IR (film) 3072, 2996, 2927, 2855, 1735, 1602, 1502, 1456, 1352, 1209, 1144, 1025, 744 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) 7.09 (app t, J = 7.9, 1H), 7.05 (d, J = 7.2, 1H), 6.75 (d, J = 8.3, 1H), 6.66 (app t, J = 7.3, 1H), 4.07 – 3.97 (comp, 2H), 3.76 (s, 3H), 3.62 (s, 3H), 3.38 (d, J = 15.8, 1H), 3.17 (d, J = 16.0, 1H), 3.09 – 2.97 (m, 1H), 1.90 (d, J = 13.1, 1H), 1.81 – 1.56 (comp, 2H), 1.55 – 1.41 (comp, 3H).; ^{13}C NMR (125 MHz, $CDCl_3$) 169.64, 169.34, 143.54, 128.83, 127.39, 120.47, 116.91, 112.09, 59.75, 56.79, 52.62, 52.45, 48.43, 29.79, 25.74, 25.23, 22.47; *m/z* (ESIMS) 628.9 $[2M + Na]^+$.



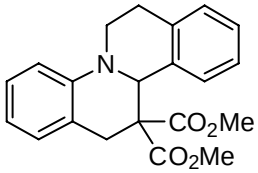
dimethyl 1,2,4,4a-tetrahydro-[1,4]oxazino[4,3-a]quinoline-5,5(6H)-dicarboxylate (2k): The reaction was carried out according to the general procedure (12 h, 40°C). The product was obtained as a solid in 78% yield. (R_f = 0.25 in 20% EtOAc/Hex); mp: 104 – 106 °C; IR (film) 2954, 2854, 1736, 1604, 1496, 1436, 1339, 1256, 1224, 1175, 1123, 1068, 1036, 955, 753, 665 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) 7.16 – 7.09 (m, 1H), 7.03 (d, J = 6.9, 1H), 6.79 – 6.71 (comp, 2H), 3.99 – 3.80 (comp, 3H), 3.77 – 3.62 (comp, 9H), 3.18 (ddd, J = 8.8, 12.3, 20.0, 3H).; ^{13}C NMR (125 MHz, $CDCl_3$) 169.80, 168.81, 144.50, 128.66, 127.69, 121.69, 118.67, 112.66, 67.51, 65.97, 58.54, 55.47, 52.94, 52.63, 48.07, 33.33; m/z (ESIMS) 632.8 $[2M + Na]^+$.



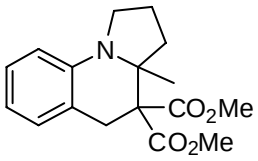
dimethyl 6a,7,8,9,10,11-hexahydroazepino[1,2-a]quinoline-6,6(5*H*)-dicarboxylate (2l): The reaction was carried out according to the general procedure (20 mins). The product was obtained as a white solid in 82% yield. (R_f = 0.23 in 50% DCM/Hex); mp: 111 – 114 °C; IR (film) 2949, 2855, 1739, 1603, 1497, 1457, 1435, 1341, 1236, 1162, 1139, 1070, 1030, 999, 749 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) 7.06 (app t, J = 7.2, 2H), 6.65 – 6.53 (comp, 2H), 4.15 (d, J = 7.8, 1H), 3.97 – 3.85 (m, 1H), 3.78 (d, J = 1.4, 3H), 3.63 (d, J = 1.4, 3H), 3.43 (d, J = 17.0, 1H), 3.31 (d, J = 17.0, 1H), 3.26 – 3.17 (m, 1H), 2.12 – 1.99 (m, 1H), 1.75 – 1.37 (comp, 7H).; ^{13}C NMR (125 MHz, $CDCl_3$) 169.65, 169.47, 142.36, 128.98, 127.28, 116.90, 115.30, 109.72, 60.26, 55.37, 52.53, 49.69, 30.59, 28.47, 27.22, 25.98, 25.61, 25.45; *m/z* (ESIMS) 318.1 $[M + H]^+$.



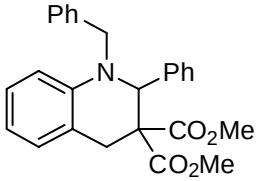
dimethyl 7,8,9,10,11,12-hexahydro-5*H*-azocino[1,2-a]quinoline-6,6(6a*H*)-dicarboxylate (2m): The reaction was carried out according to the general procedure (5 min). The product was obtained as an oil in 81% yield. (R_f = 0.34 in 15% EtOAc/Hex); IR (film) 3023, 2924, 2849, 1733, 1603, 1574, 1500, 1450, 1434, 1350, 1236, 1148, 1061, 1020, 947, 908, 745 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) 7.07 (dd, *J* = 8.1, 17.4, 2H), 6.69 – 6.57 (comp, 2H), 4.19 (dd, *J* = 3.9, 9.8, 1H), 3.88 – 3.73 (comp, 4H), 3.62 (s, 3H), 3.44 – 3.24 (comp, 3H), 1.95 – 1.29 (comp, 10H).; ^{13}C NMR (125 MHz, $CDCl_3$) 170.15, 169.75, 142.81, 129.28, 127.34, 117.87, 115.77, 111.56, 60.38, 55.79, 54.44, 52.84, 52.65, 30.65, 28.57, 27.67, 27.63, 27.38, 25.96.; *m/z* (ESIMS) 332.2 $[M + H]^+$.



dimethyl 11b,13-dihydro-6*H*-isoquinolino[2,1-a]quinoline-12,12(7*H*)-dicarboxylate (2n): The reaction was carried out according to the general procedure (5 mins). The product was obtained as a yellow solid in 87% yield. (R_f = 0.30 in 60% DCM/Hex); mp: 124 – 127 °C; IR (KBr) 3048, 3019, 2951, 2827, 1735, 1602, 1494, 1456, 1433, 1382, 1356, 1250, 1070, 960, 751 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) 7.23 – 7.10 (comp, 6H), 6.82 (d, J = 8.1, 1H), 6.78 (app t, J = 7.4, 1H), 5.09 (s, 1H), 3.98 – 3.91 (m, 1H), 3.76 – 3.69 (comp, 4H), 3.66 (d, J = 11.9, 3H), 3.57 (d, J = 16.5, 1H), 3.34 – 3.18 (comp, 2H), 2.82 – 2.74 (m, 1H).; ^{13}C NMR (125 MHz, $CDCl_3$) 170.74, 169.56, 145.27, 136.81, 134.83, 128.79, 128.52, 126.88, 126.79, 125.83, 125.60, 121.38, 118.08, 112.01, 61.23, 59.39, 52.79, 52.41, 43.75, 34.04, 28.08; *m/z* (ESIMS) 352.2 $[M + H]^+$.

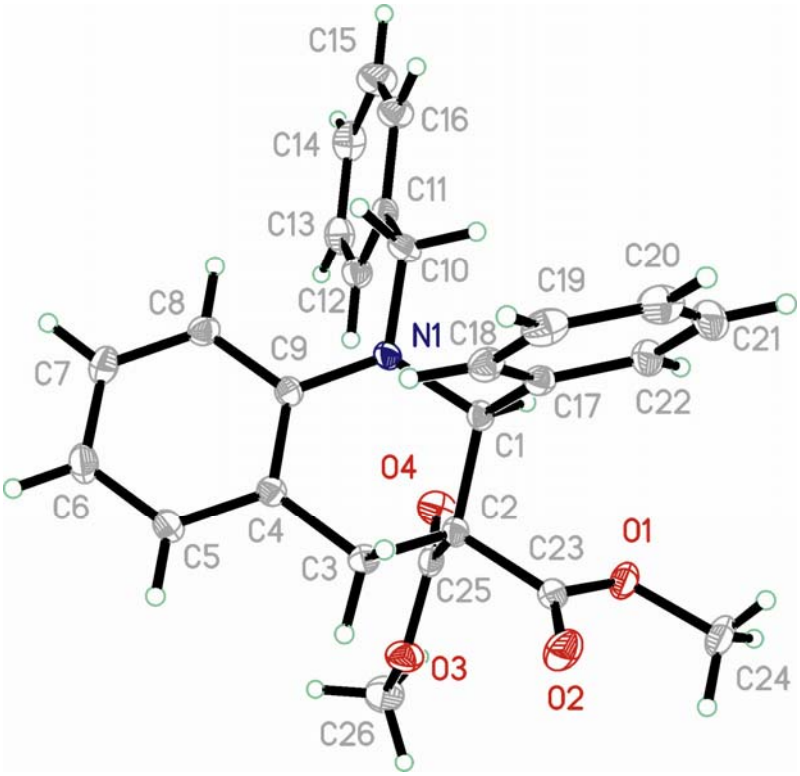


dimethyl 3a-methyl-1,2,3,3a-tetrahydropyrrolo[1,2-a]quinoline-4,4(5*H*)-dicarboxylate (2o): The reaction was carried out according to the general procedure (5 min). The product was obtained as a liquid in 82% yield. (R_f= 0.37 in 15% EtOAc/Hex; IR (film) 2950, 2132, 1732, 1646, 1606, 1499, 1459, 1359, 1272, 1237, 1161, 1060, 745 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) 7.12 (app t, *J* = 7.7, 1H), 7.06 (d, *J* = 7.3, 1H), 6.61 (td, *J* = 1.0, 7.3, 1H), 6.52 (d, *J* = 7.9, 1H), 3.86 – 3.77 (comp, 3H), 3.69 – 3.60 (m, 1H), 3.59 – 3.51 (comp, 4H), 3.39 – 3.30 (m, 1H), 3.21 (d, *J* = 17.2, 1H), 2.65 (app td, *J* = 8.8, 12.0, 1H), 2.21 – 2.04 (comp, 2H), 1.95 (ddd, *J* = 1.5, 7.3, 12.4, 1H), 1.07 (s, 3H).; ^{13}C NMR (125 MHz, $CDCl_3$) 171.01, 169.11, 142.81, 128.58, 127.52, 116.52, 115.14, 111.51, 62.52, 56.15, 52.33, 52.09, 47.74, 35.76, 32.65, 24.19, 22.21.; *m/z* (ESIMS) 304.2 $[M + H]^+$.

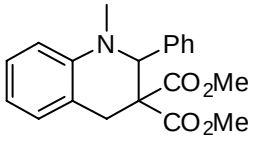


dimethyl 1-benzyl-2-phenyl-1,2-dihydroquinoline-3,3(4*H*)-dicarboxylate (2p): The reaction was carried out according to the general procedure (24 h, 40 °C). The product was obtained as a white solid in 70% yield. (R_f = 0.25 in 15% EtOAc/Hex); mp: 149 – 151 °C; IR (KBr) 2941, 2365, 1760, 1719, 1605, 1498, 1453, 1265, 1229, 1203, 1179, 1170, 1057, 955, 748, 702 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) 7.38 – 7.28 (comp, 7H), 7.25 (ddd, *J* = 3.8, 7.5, 15.0, 1H), 7.20 (app dt, *J* = 3.8, 7.6, 2H), 7.13 (d, *J* = 7.4, 1H), 7.07 (t, *J* = 7.8, 1H), 6.71 (t, *J* = 7.3, 1H), 6.57 (d, *J* = 8.2, 1H), 5.36 (d, *J* = 1.5, 1H), 4.53 (d, *J* = 17.2, 1H), 4.37 (d, *J* = 17.3, 1H), 3.69 (s, 3H), 3.60 (s, 3H), 3.50 – 3.34 (comp, 2H).; ^{13}C NMR (125 MHz, $CDCl_3$) 169.57, 168.65, 144.30, 139.74, 138.42, 129.16, 128.35, 128.31, 128.22, 128.00, 127.95, 126.76, 126.70, 117.75, 116.55, 111.02, 64.71, 57.47, 55.00, 52.91, 52.50, 28.59.; *m/z* (ESIMS) 416.2 $[M + H]^+$.

Product **2p** was further characterized by X–ray crystallography:



The requisite CIF file has been submitted to the journal.



dimethyl 1-methyl-2-phenyl-1,2-dihydroquinoline-3,3(4*H*)-dicarboxylate (2q): The reaction was carried out according to the general procedure (2 h). The product was obtained as a white solid in 94% yield. (R_f = 0.74 in DCM); mp: 126 – 129 °C; IR (film) 3054, 3031, 2952, 2827, 2792, 1740, 1605, 1506, 1453, 1433, 1342, 1292, 1261, 1233, 1176, 1147, 1060, 1001, 748, 704 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) 7.27 (dd, J = 5.9, 9.3, 3H), 7.23 – 7.13 (comp, 3H), 7.08 (d, J = 7.1, 1H), 6.71 – 6.59 (comp, 2H), 5.17 (d, J = 1.1, 1H), 3.62 (s, 6H), 3.37 – 3.21 (comp, 2H), 2.94 (s, 3H).; ^{13}C NMR (125 MHz, $CDCl_3$) 169.63, 168.74, 144.13, 139.50, 128.75, 128.20, 128.08, 128.01, 127.50, 117.12, 115.71, 109.25, 65.58, 57.00, 52.78, 52.36, 37.42, 28.62; *m/z* (ESIMS) 700.8 $[2M + Na]^+$.

Procedure for the catalytic enantioselective 1,5-hydride shift reaction:

To a flask containing $Mg(OTf)_2$ (22 mg, 69 mmol, 0.2 equiv.) and (1*S*,2*R*)-dimethyl-inda-box[5] (27 mg, 76 mmol, 0.22 equiv.) was added 3.5 ml of anhydrous $CHCl_3$ and the mixture was stirred for 2 h. Subsequently, malonate **1a** (100 mg, 0.346 mmol) was added. The reaction mixture was stirred at room temperature until the complete consumption of malonate **1a** as judged by TLC analysis. After completion of the reaction (12 h) the reaction mixture was adsorbed onto silica gel and purified by column chromatography using EtOAc/hexanes (1:9) as eluent to afford analytically pure **2a** as a white solid in 74 % yield. The IR, Mass, ^1H and ^{13}C data were in agreement with that of the racemic compound (**2a**). $[\alpha]_D$ –32.5° (c 1.0, $CHCl_3$, 30% *ee*); Chiral HPLC condition: Daicel Chiralpak OJ-H, hexanes/*i*-PrOH=90/10, Flow rate = 1 mL/min, UV = 254 nm, t_R=15.5 min (major) and t_R=17.1 min (minor).

References:

(1) Nijhuis, W. H. N.; Verboom, W.; Abuelfadl, A.; Harkema, S.; Reinhoudt, D. N. *J. Org. Chem.* **1989**, *54*, 199 – 209.

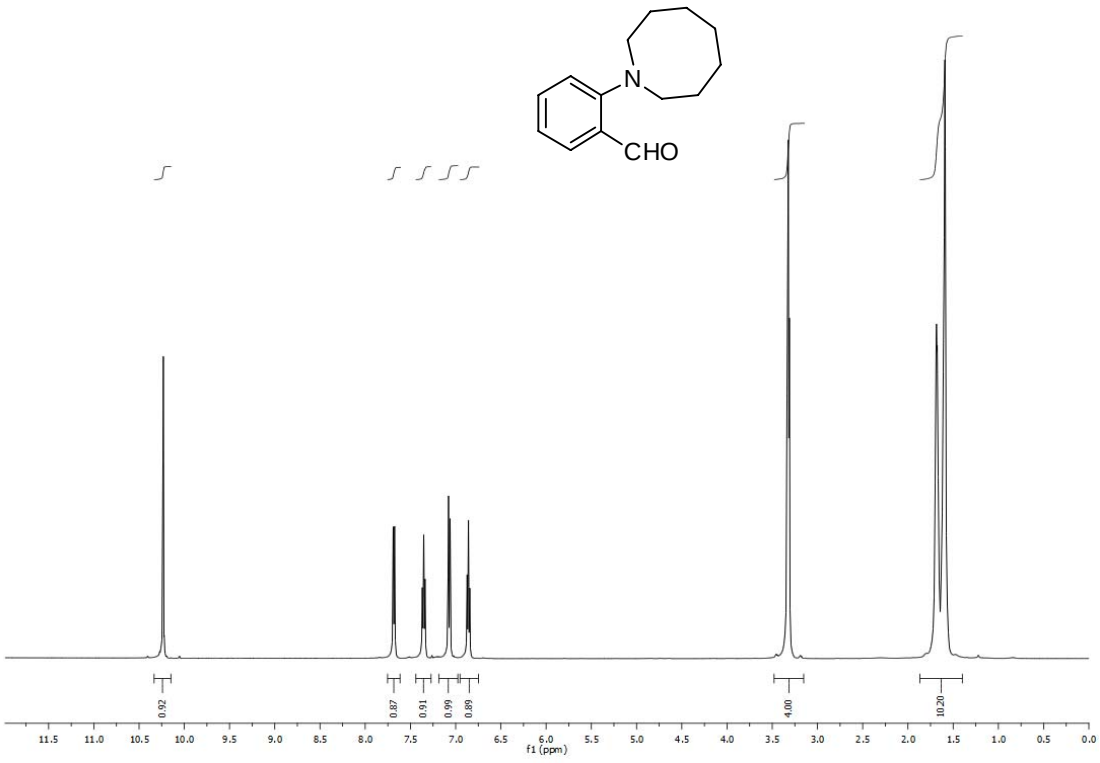
(2) Verboom, W.; Reinhoudt, D. N.; Visser, R.; Harkema, S. *J. Org. Chem.* **1984**, *49*, 269 – 276.

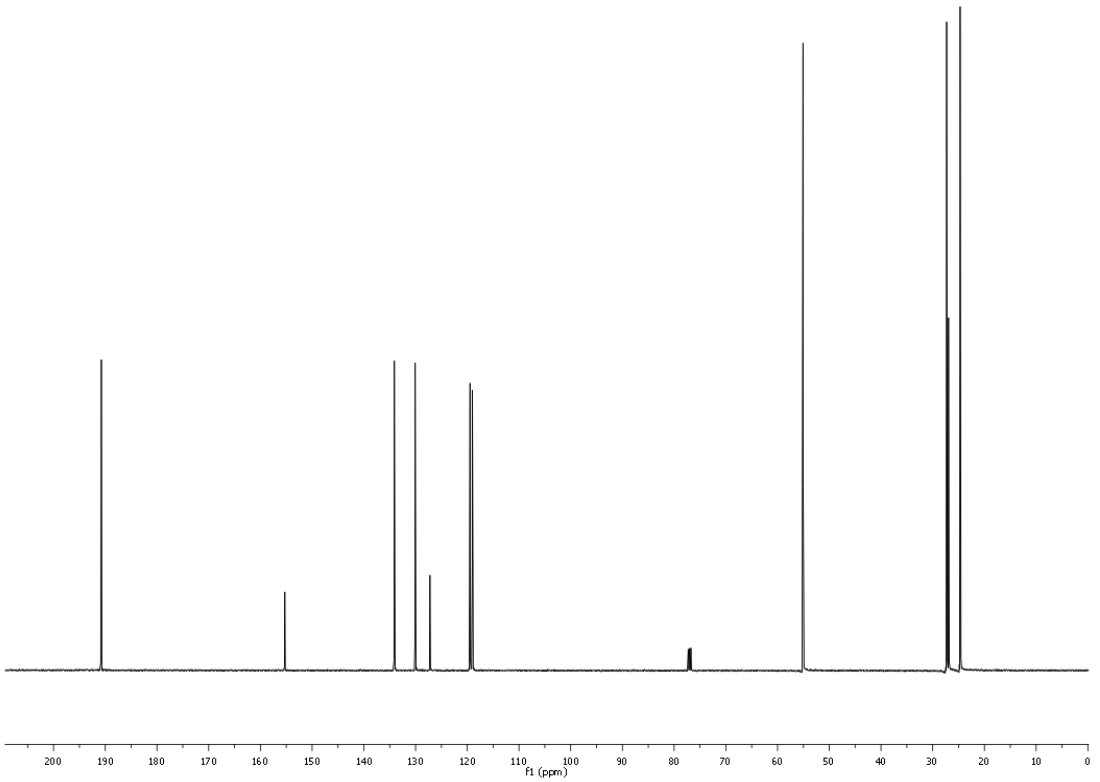
(3) D'yachenko, E. V.; Glukhareva, T. V.; Nikolaenko, E. F.; Tkachev, A. V.; Morzherin, Yu. Yu. *Russ. Chem. Bull.* **2004,** *53*, 1240 – 1247.

(4) Nijhuis, W. H. N.; Leus, G. R. B.; Egberink, R. J. M.; Verboom, W.; Reinhoudt, D. N. *Recl. Trav. Chim. Pays–Bas* **1989**, *108*, 172 – 178.

(5) Kurosu, M.; Porter, J. R.; Foley, M. A. *Tetrahedron Lett*. **2004**, *45*, 145 – 148.

^{1}H–NMR and ^{13}C–NMR of **3m**:





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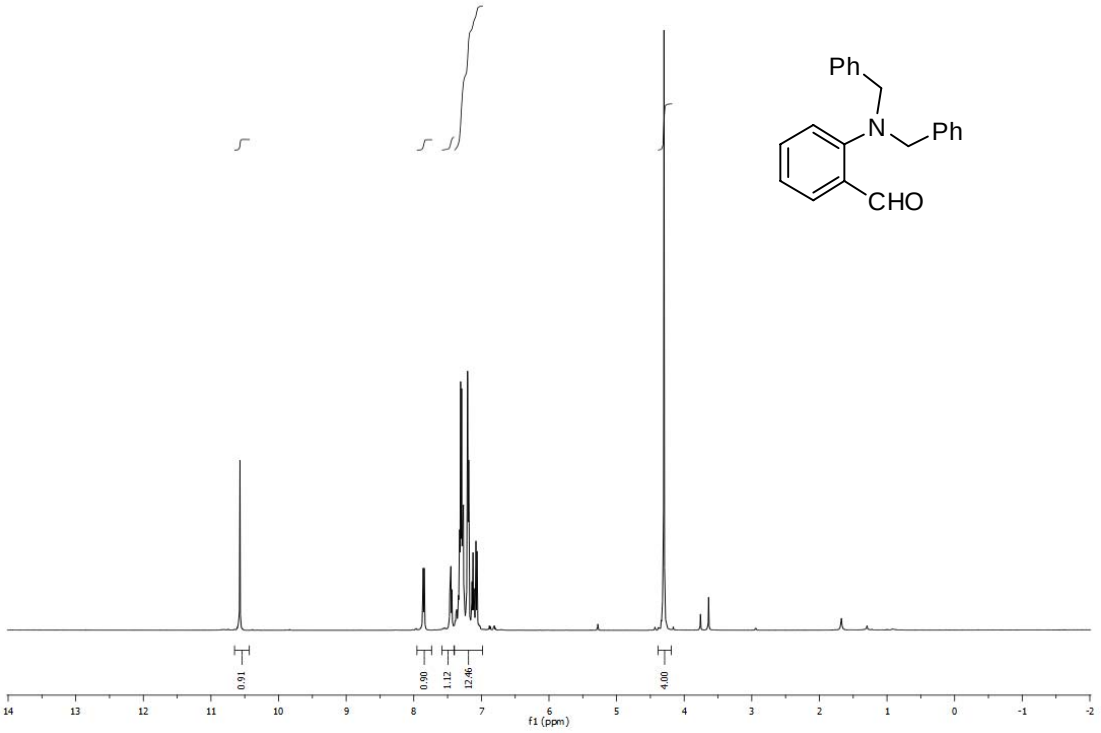
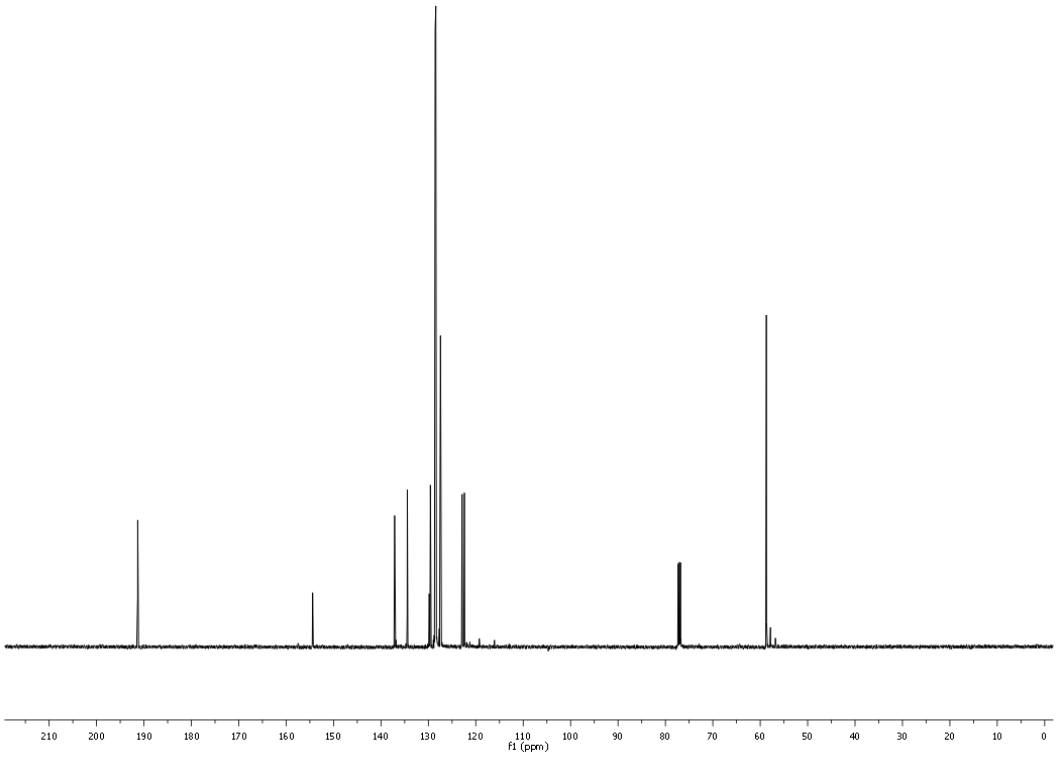
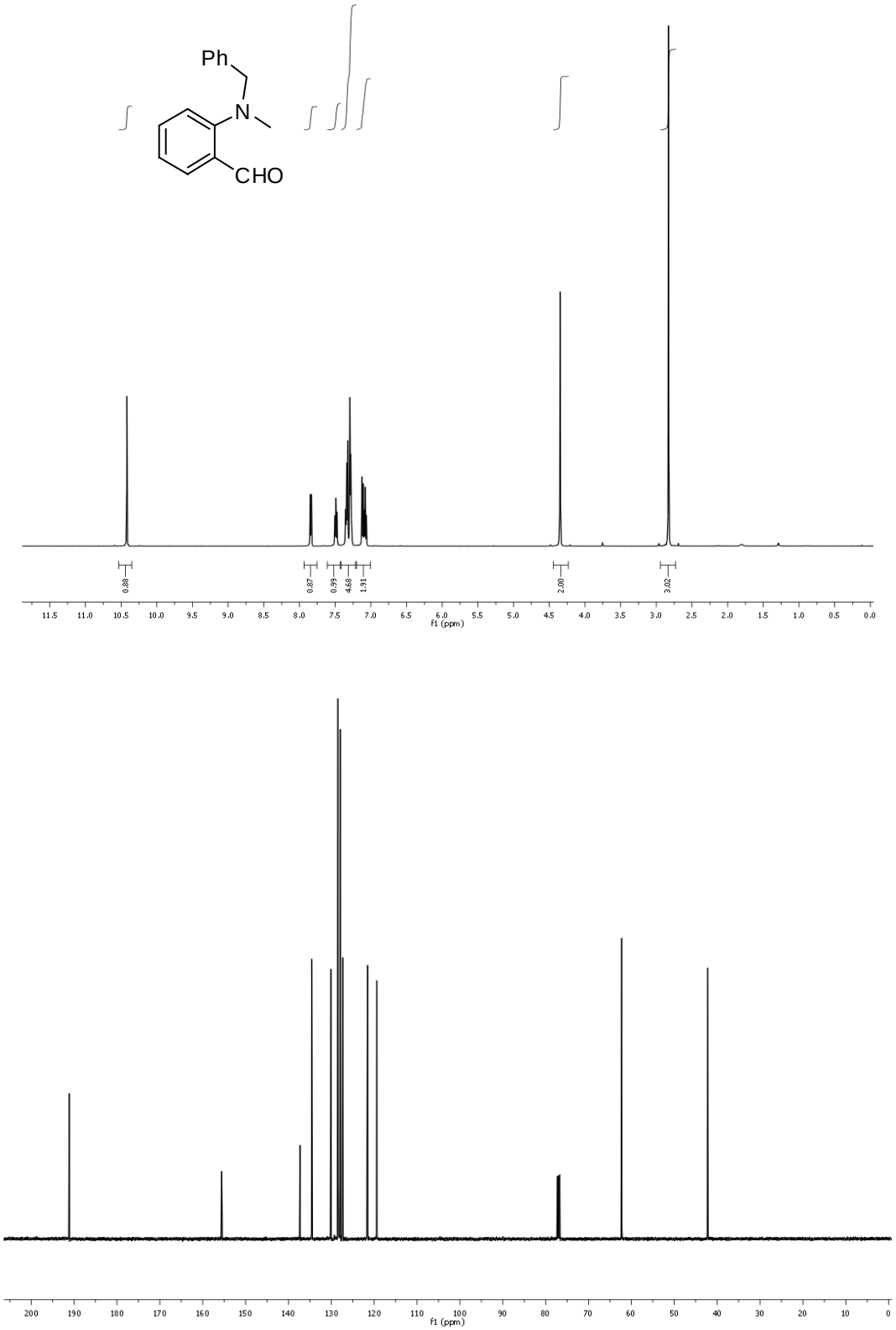
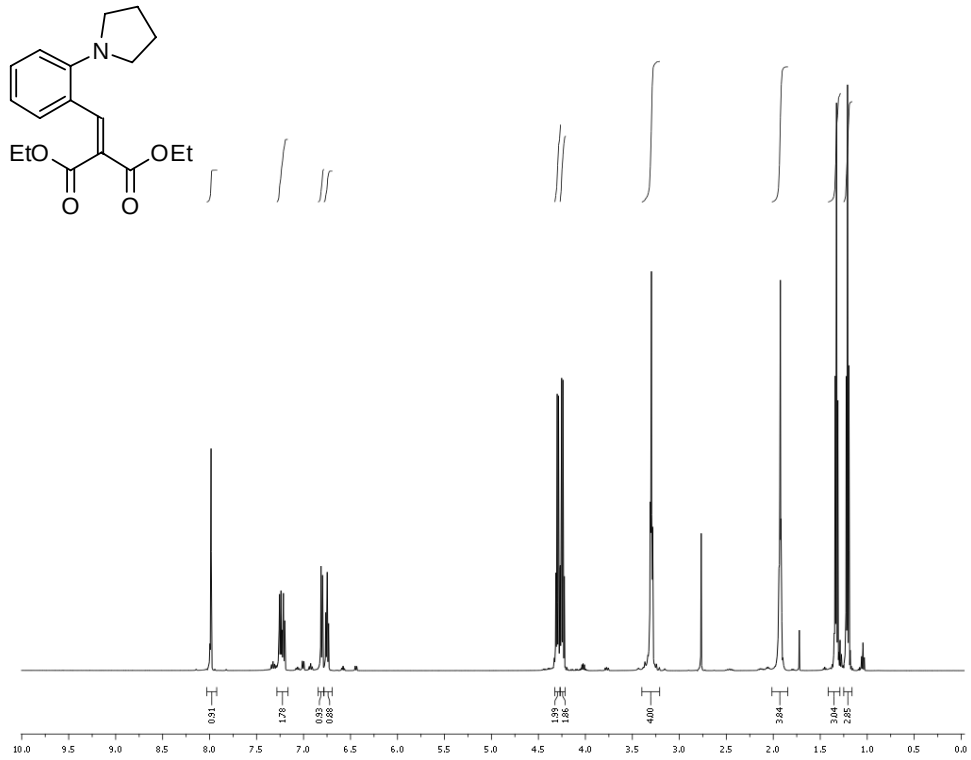


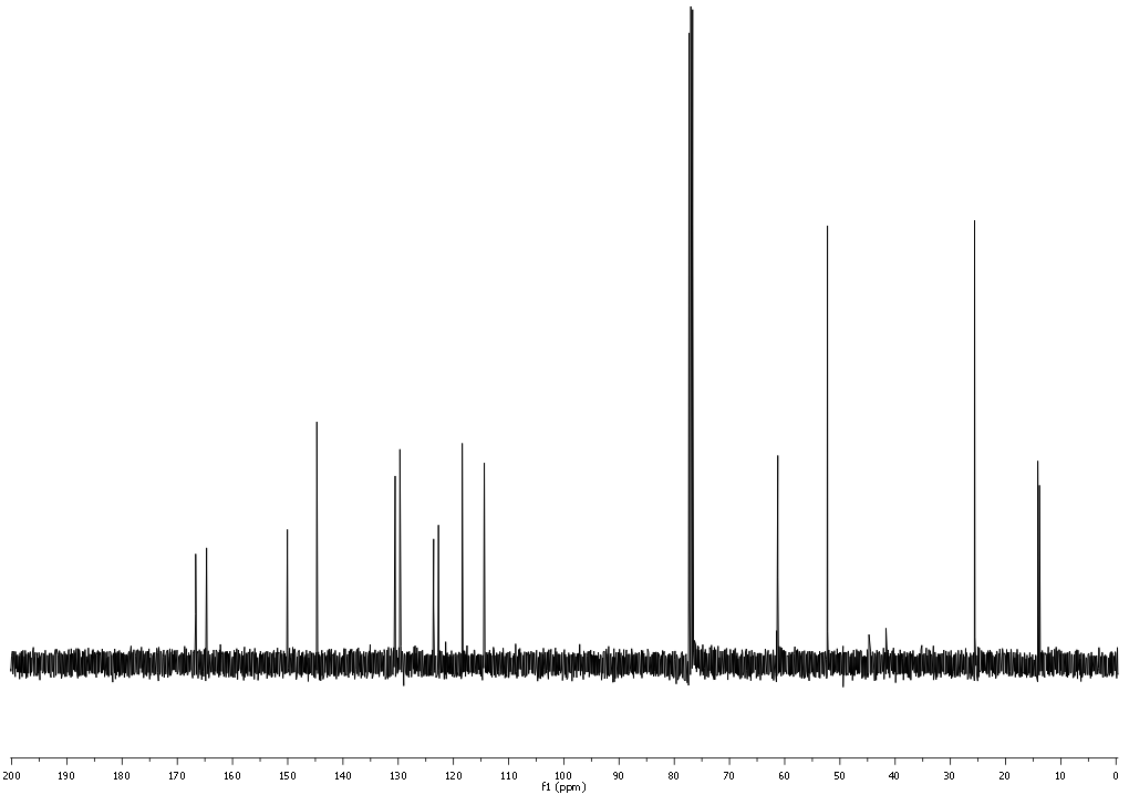


^{1}H–NMR and ^{13}C–NMR of **3q**:

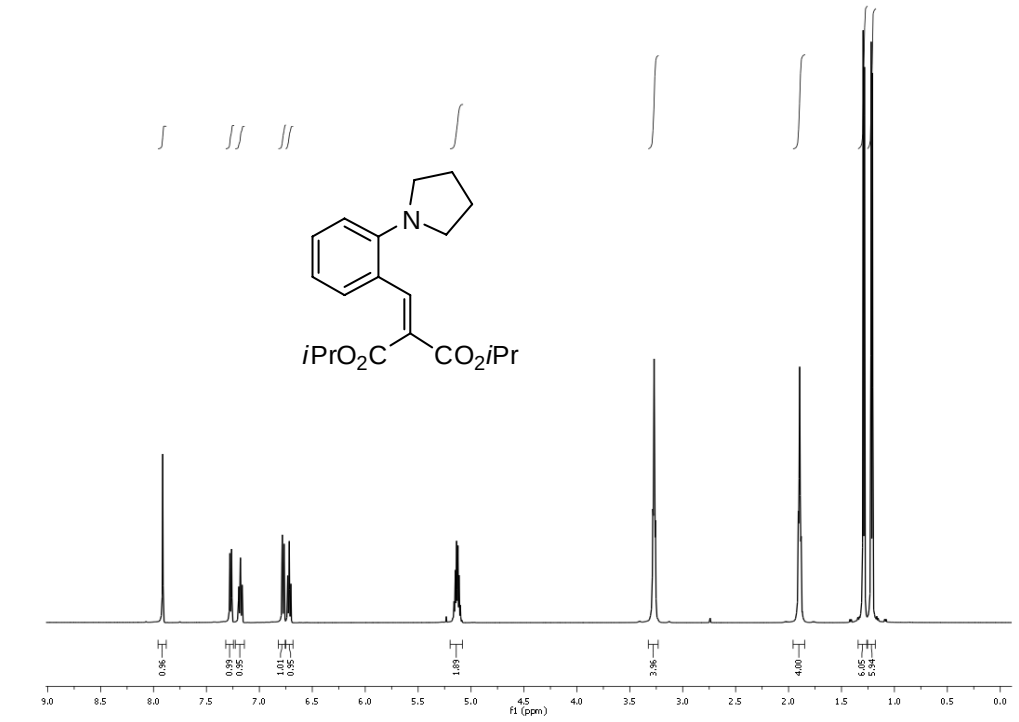


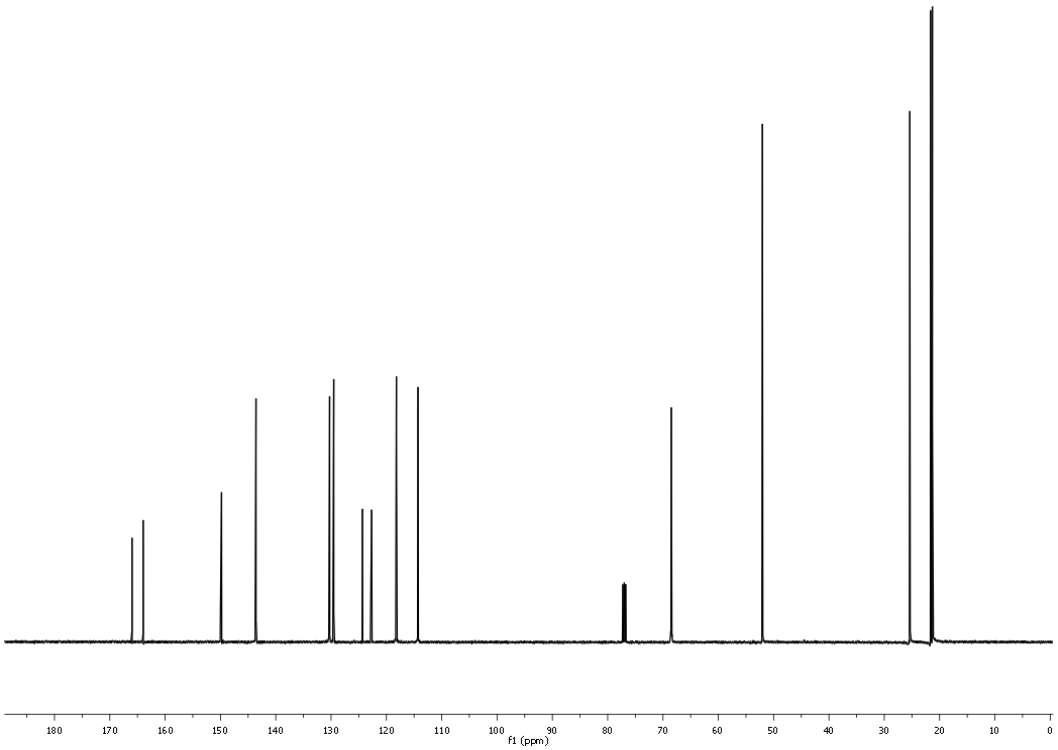
^{1}H–NMR and ^{13}C–NMR of **1b**:



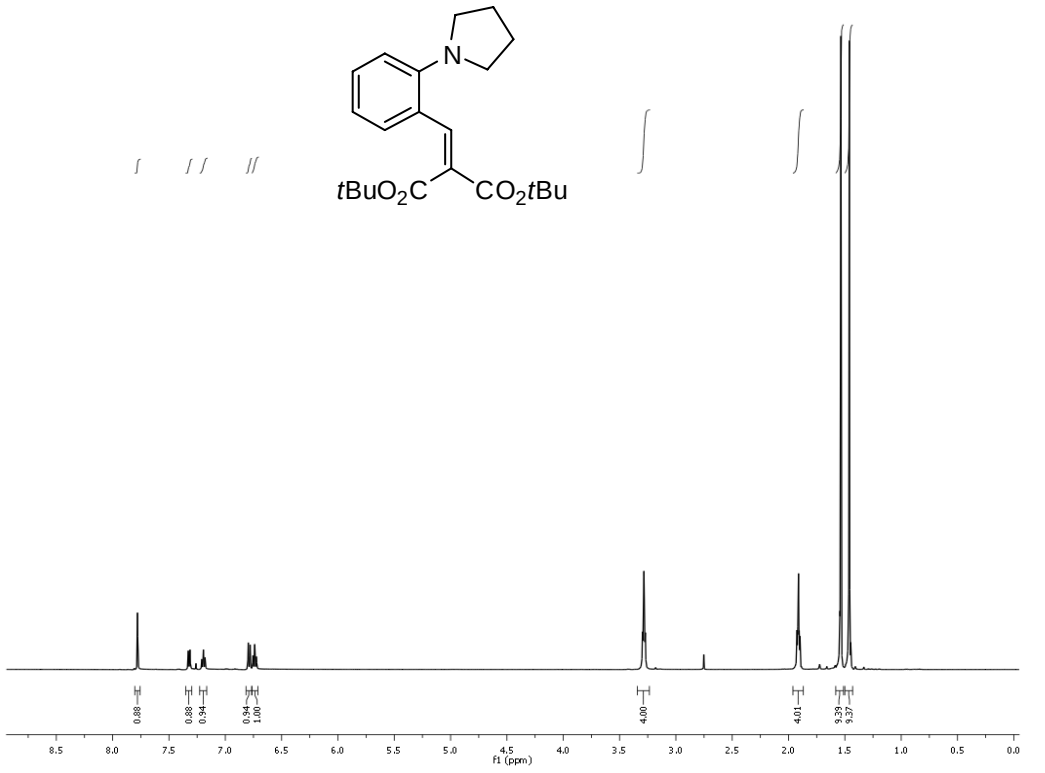


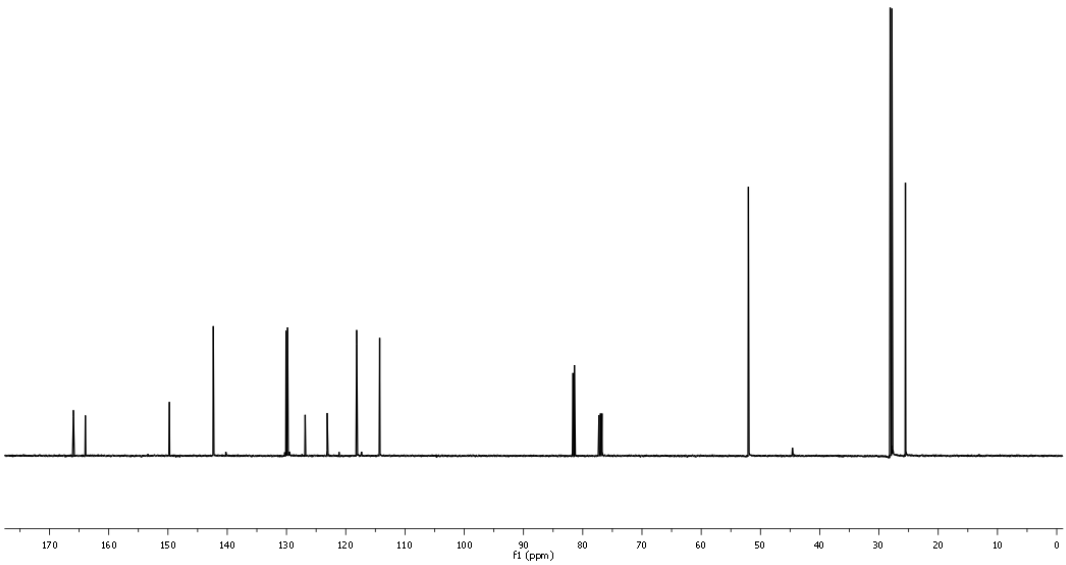
^{1}H–NMR and ^{13}C–NMR of **1c**:



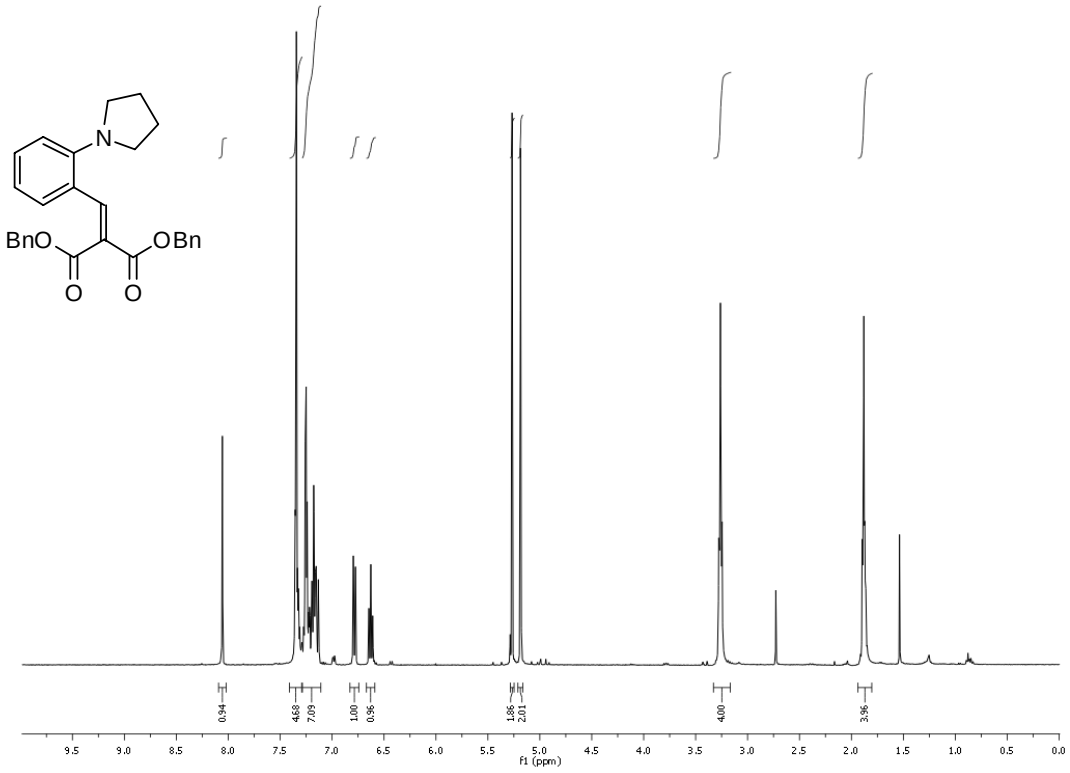


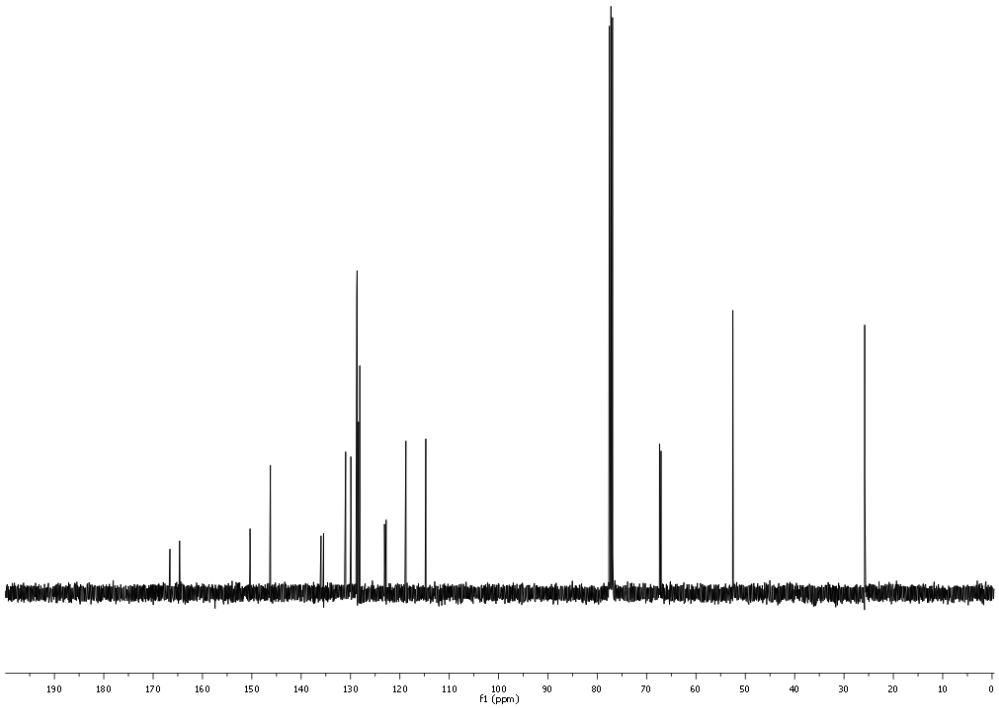
^{1}H–NMR and ^{13}C–NMR of **1d**:



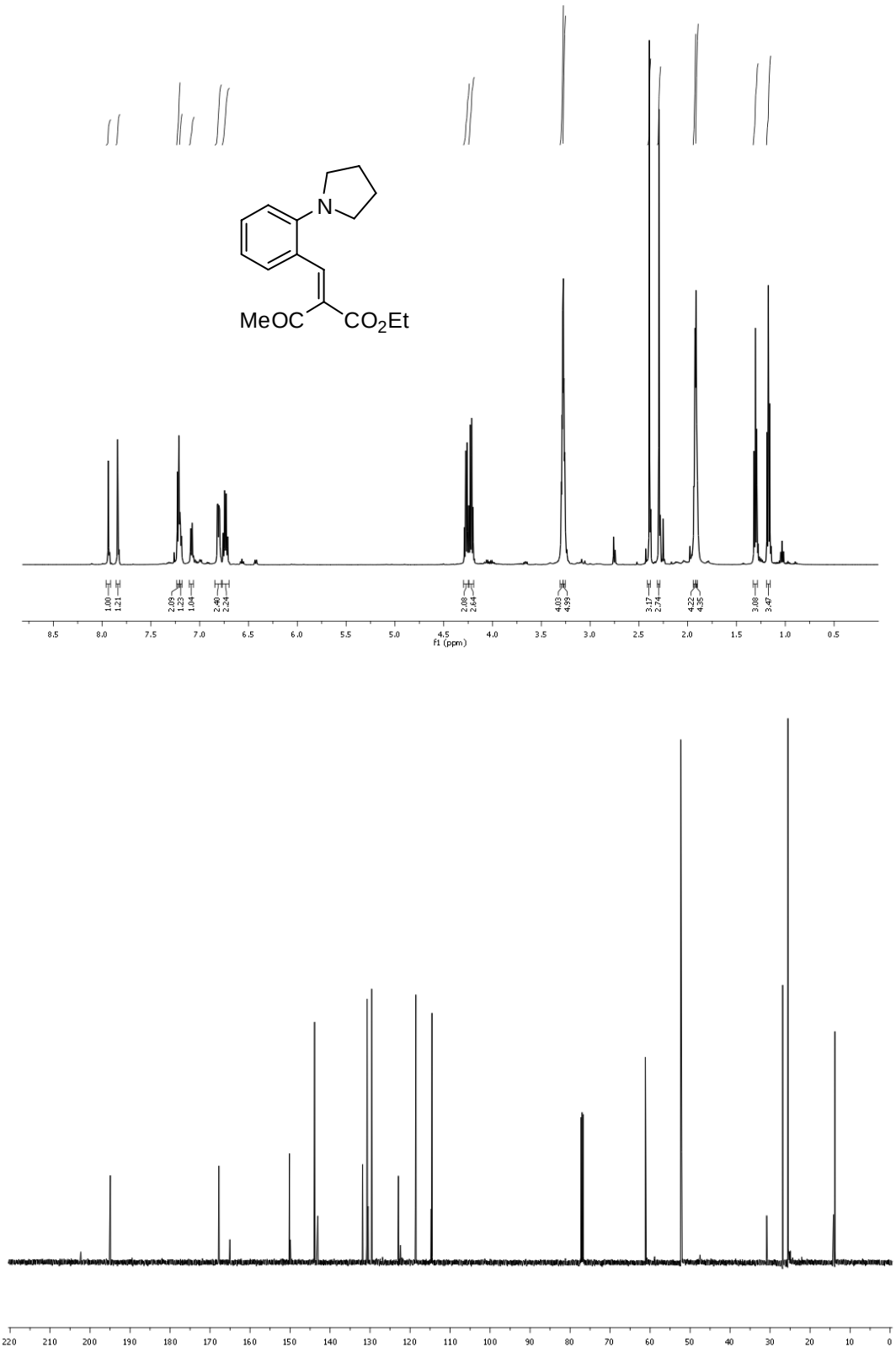


^{1}H–NMR and ^{13}C–NMR of **1e**:

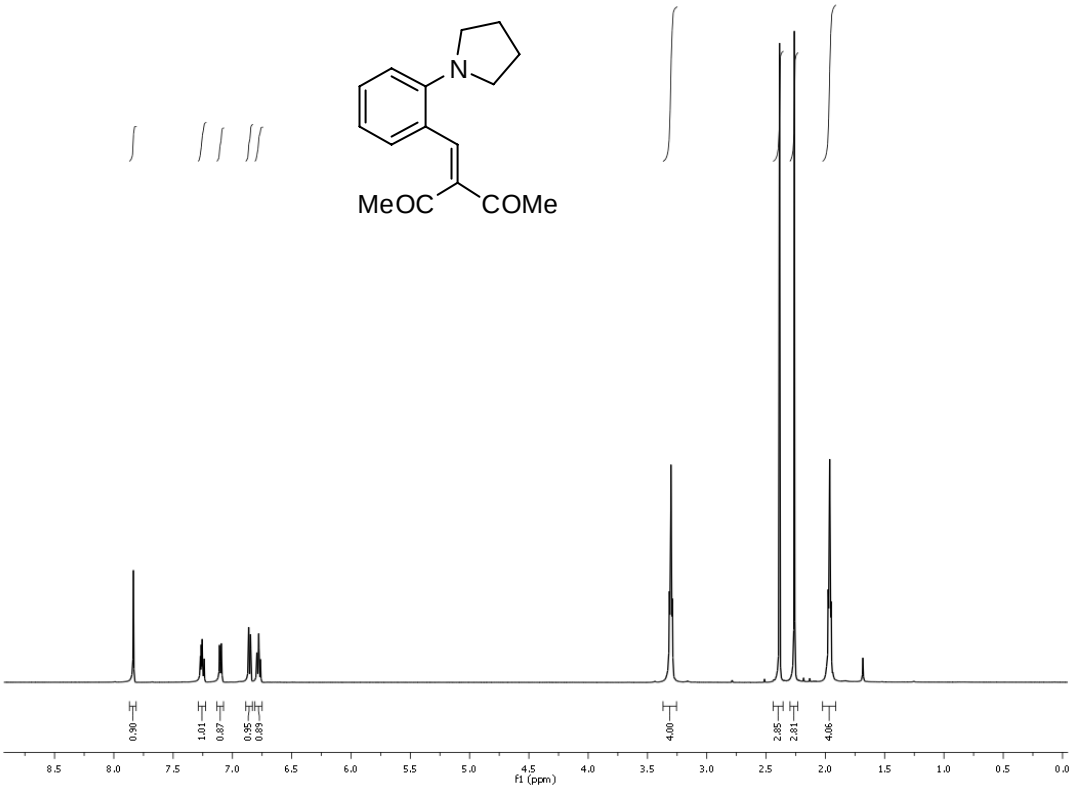


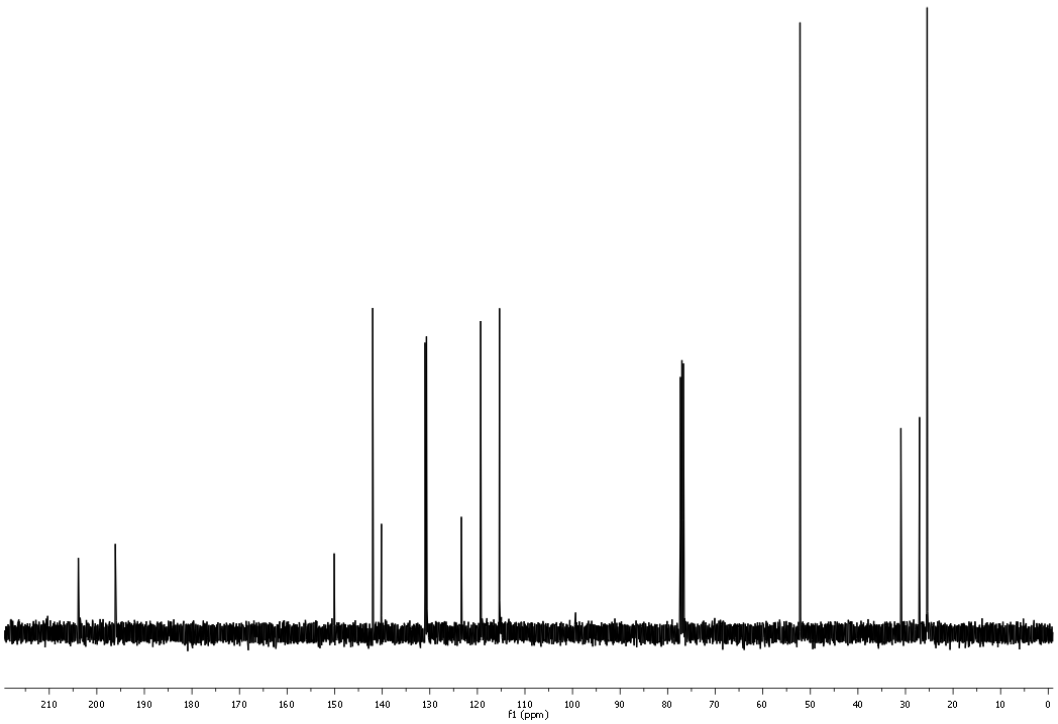


^{1}H–NMR and ^{13}C–NMR of **1f**: (dr = 47 : 53)

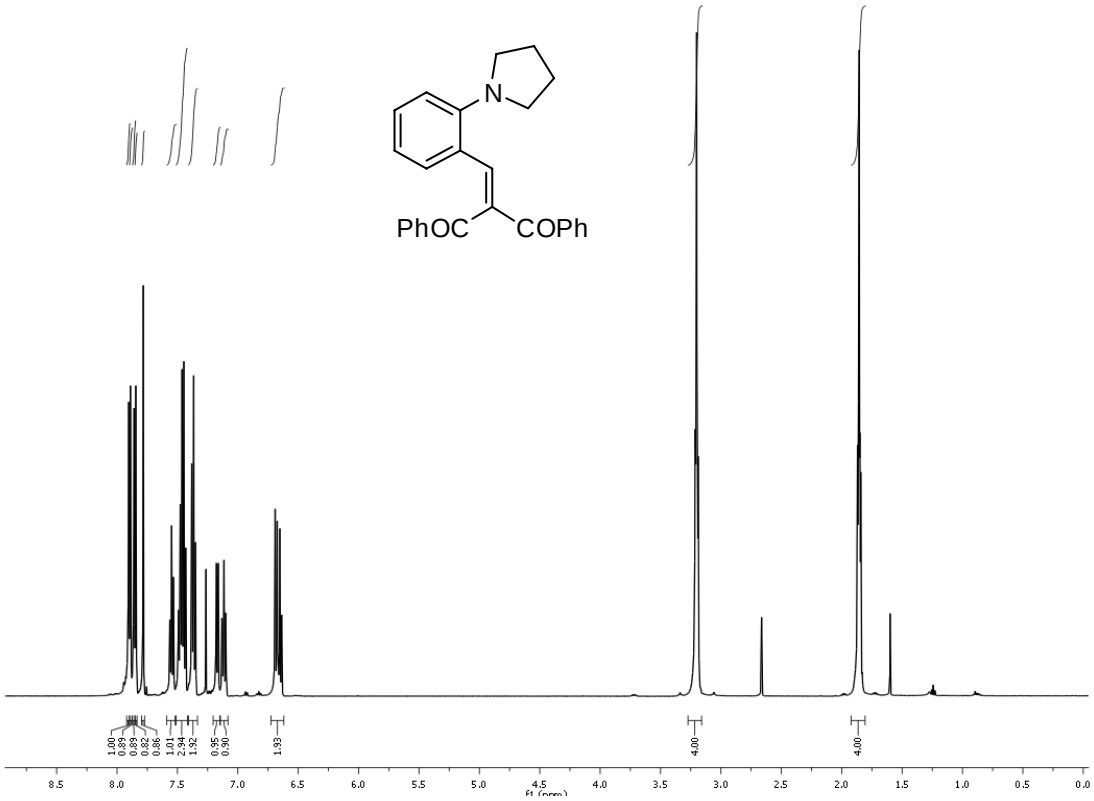


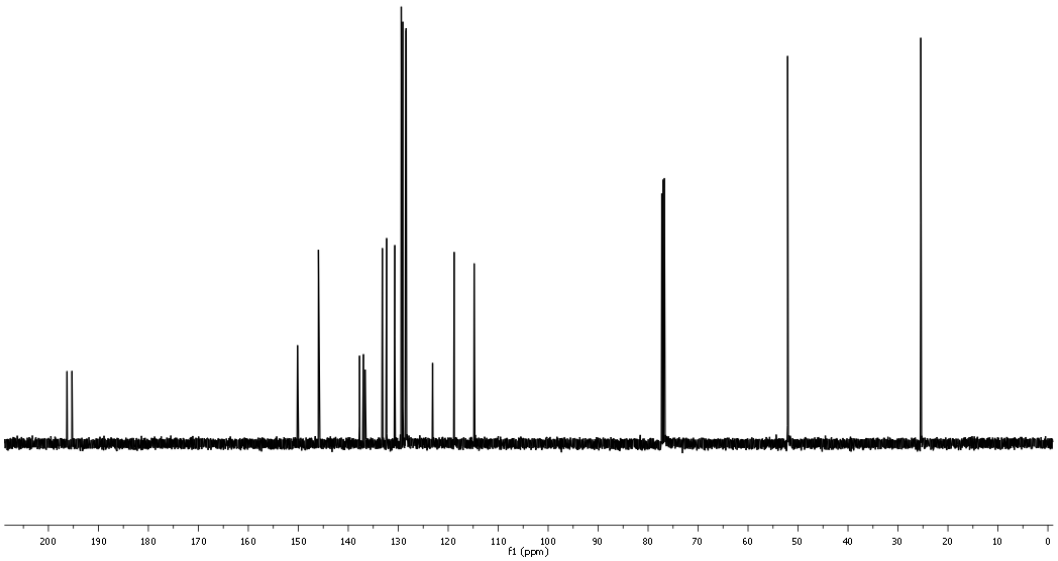
^{1}H–NMR and ^{13}C–NMR of **1g**:



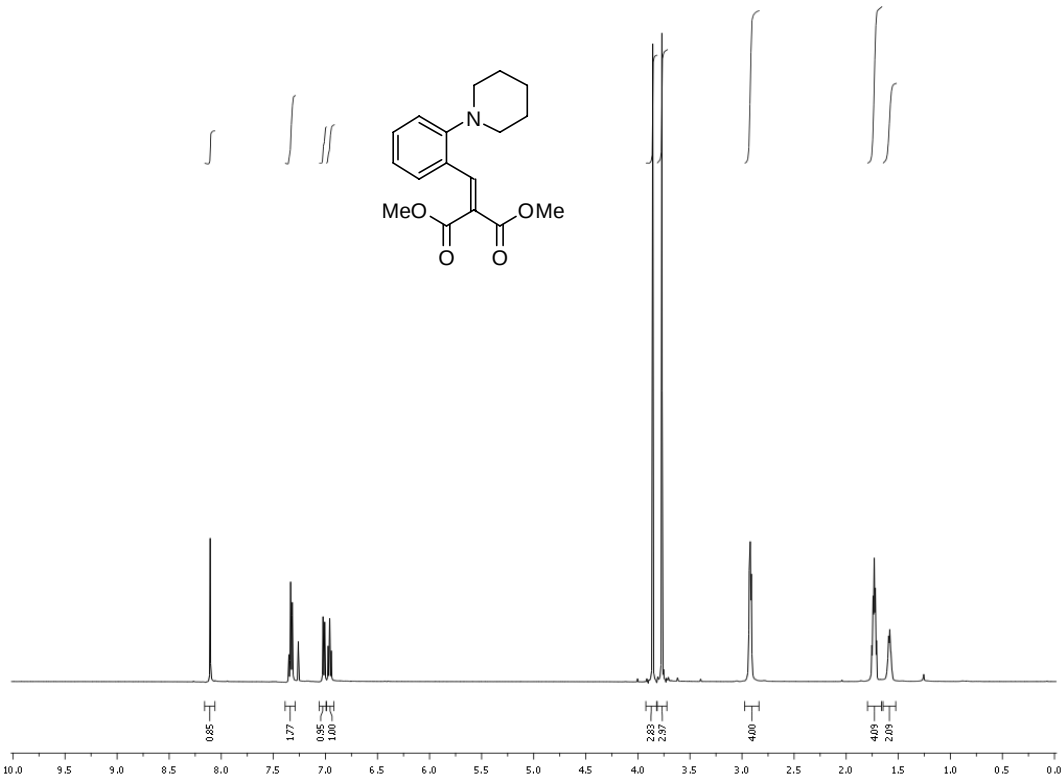


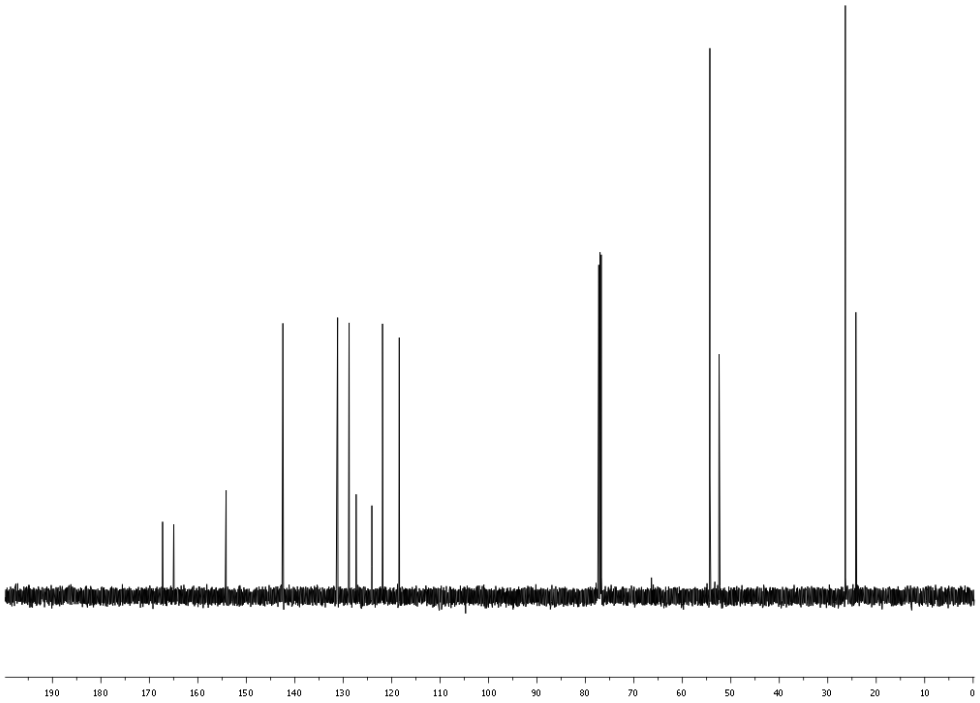
^{1}H–NMR and ^{13}C–NMR of **1h**:



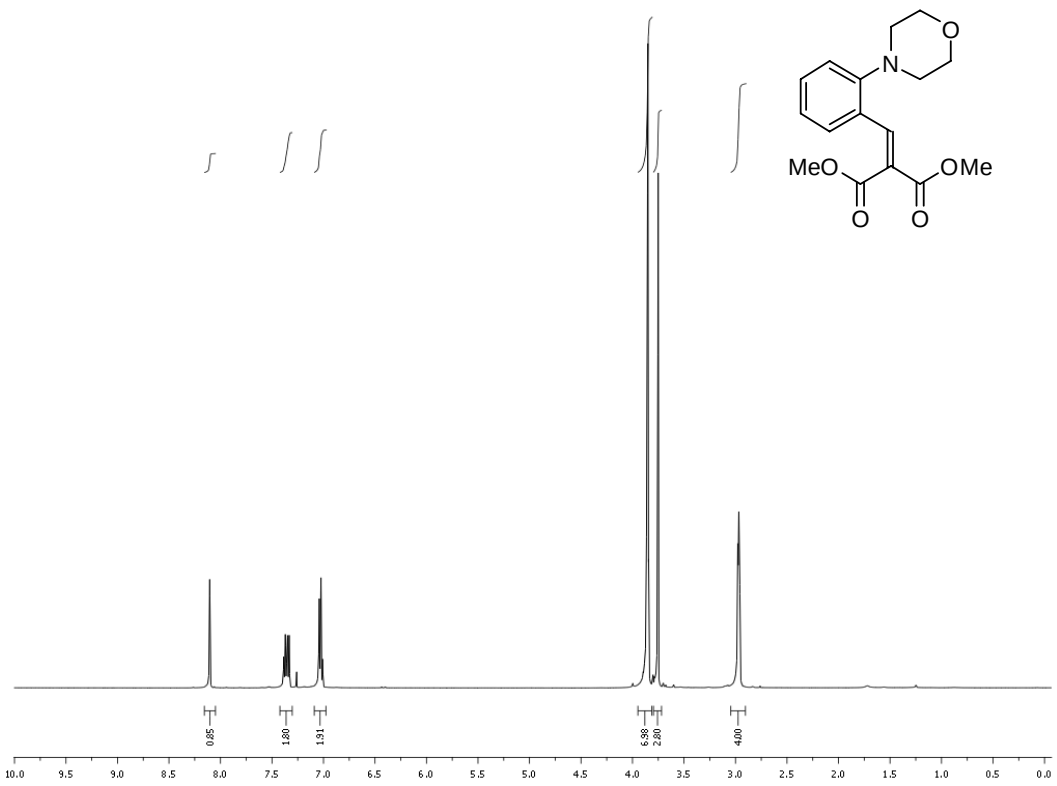


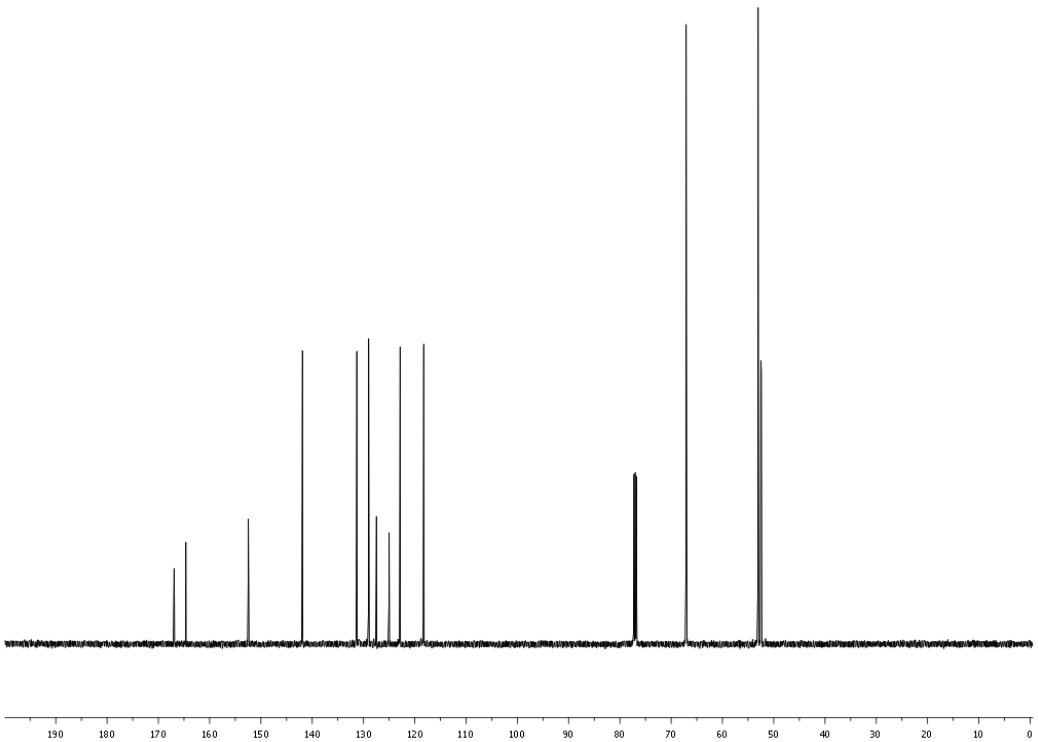
^{1}H–NMR and ^{13}C–NMR of **1j**:



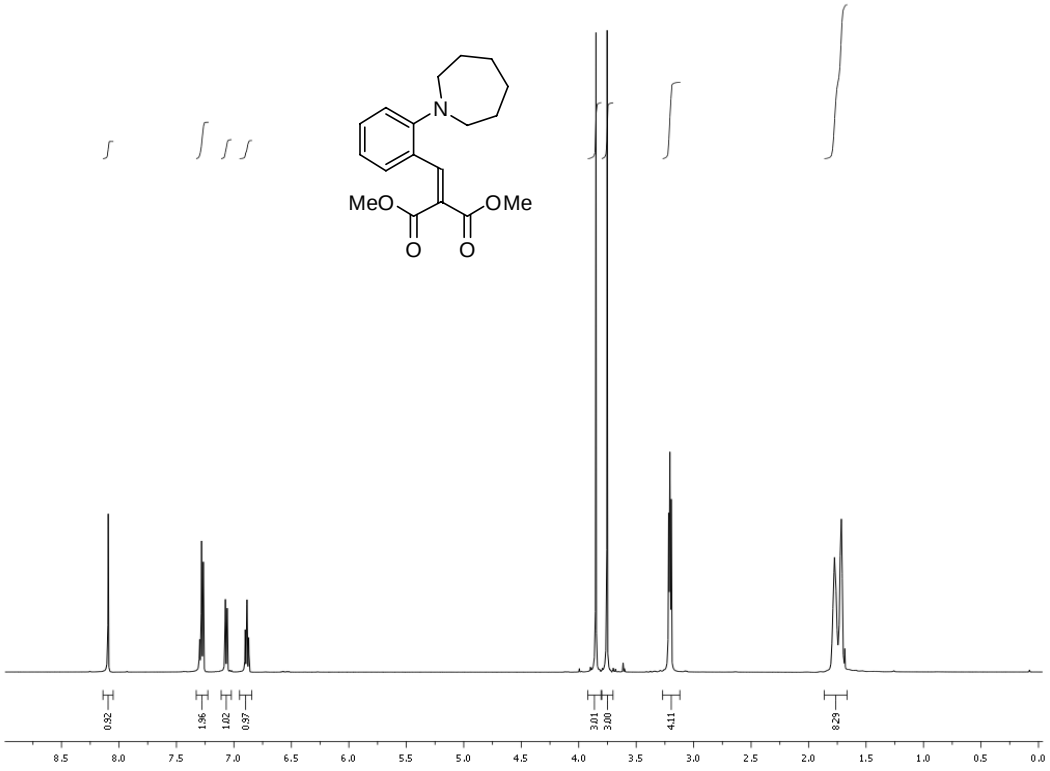


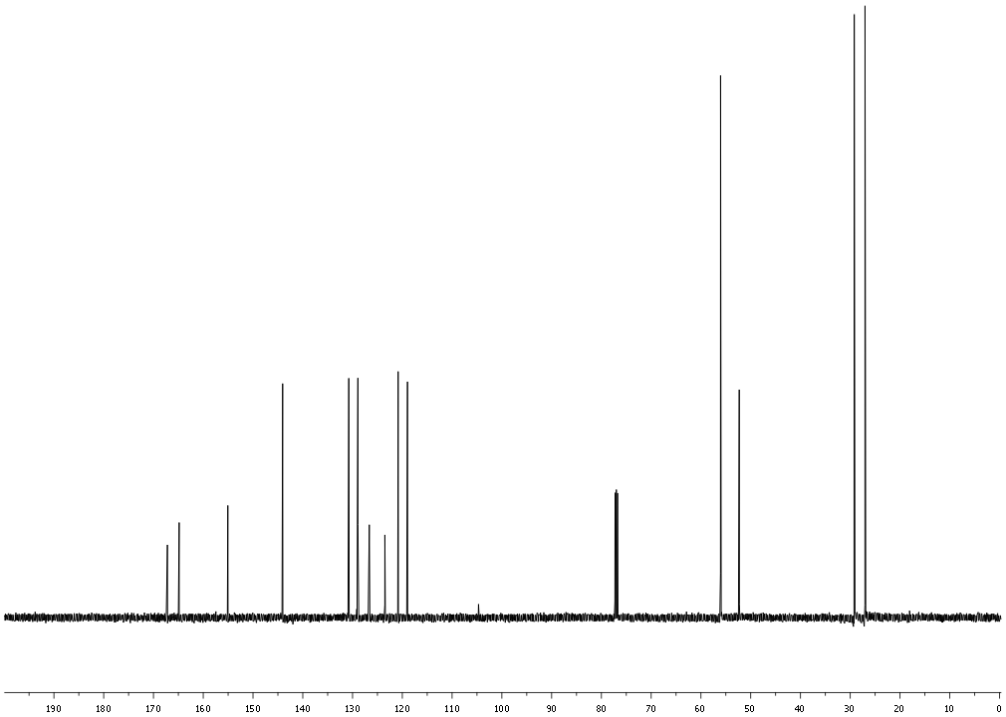
^{1}H–NMR and ^{13}C–NMR of **1k**:



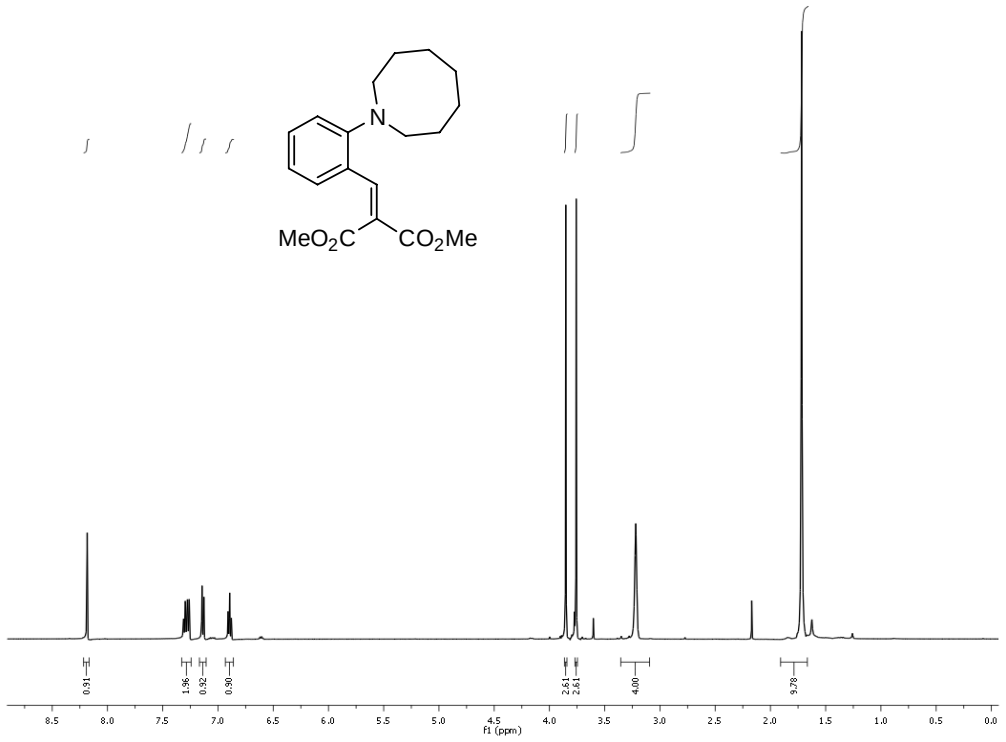


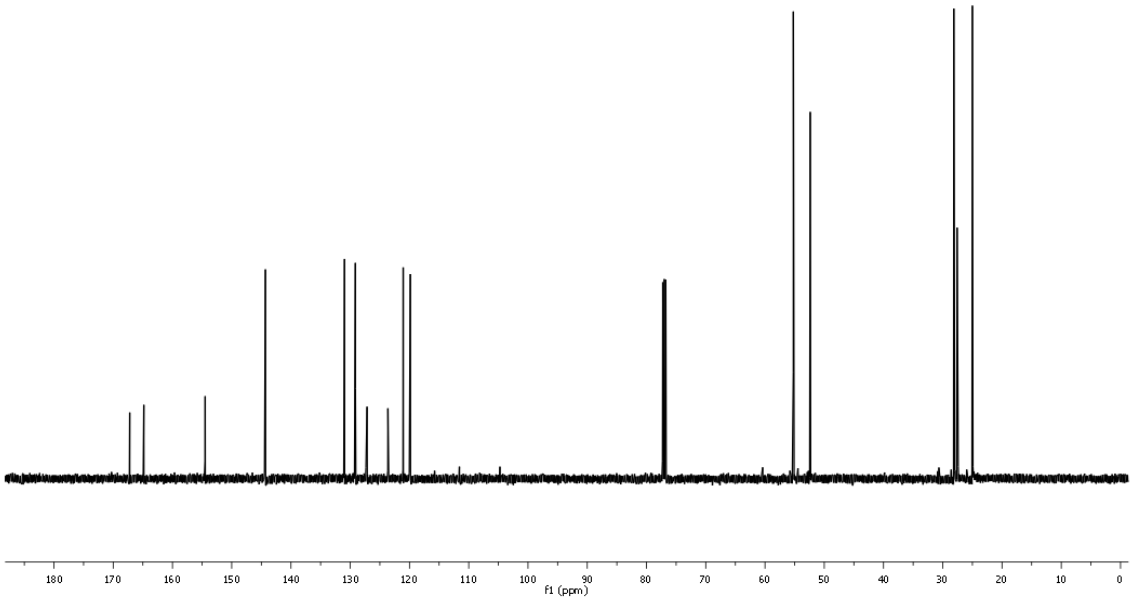
^{1}H–NMR and ^{13}C–NMR of **1l**:



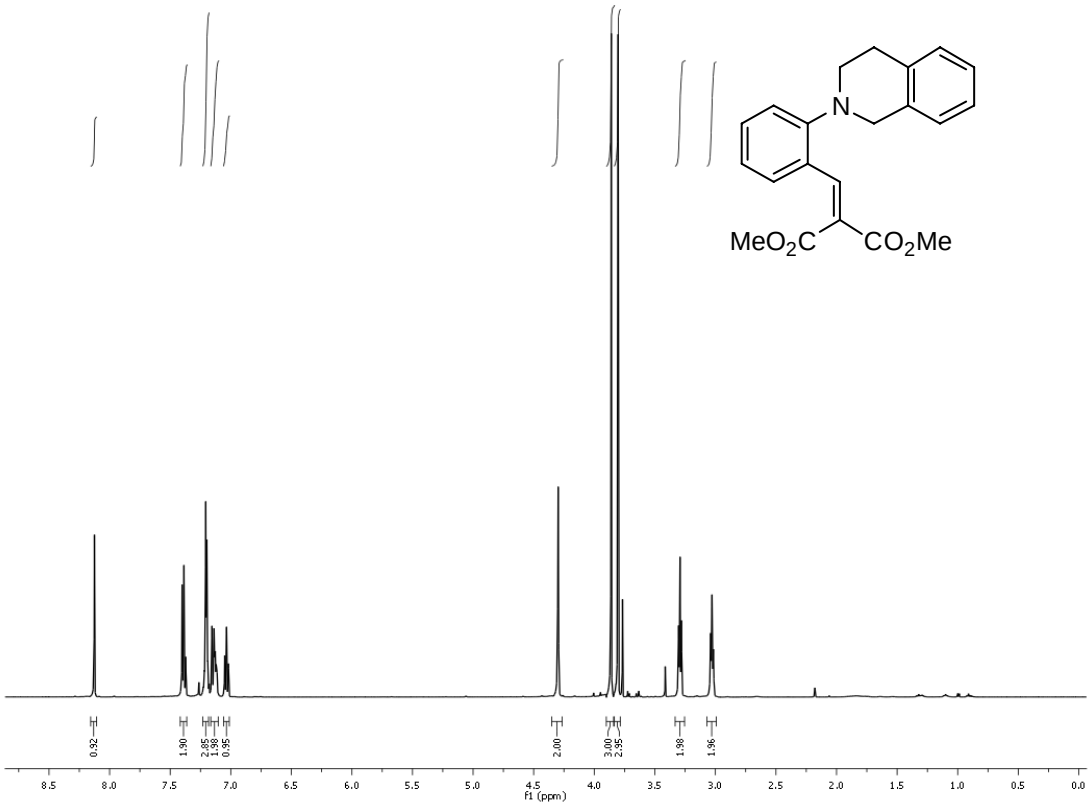


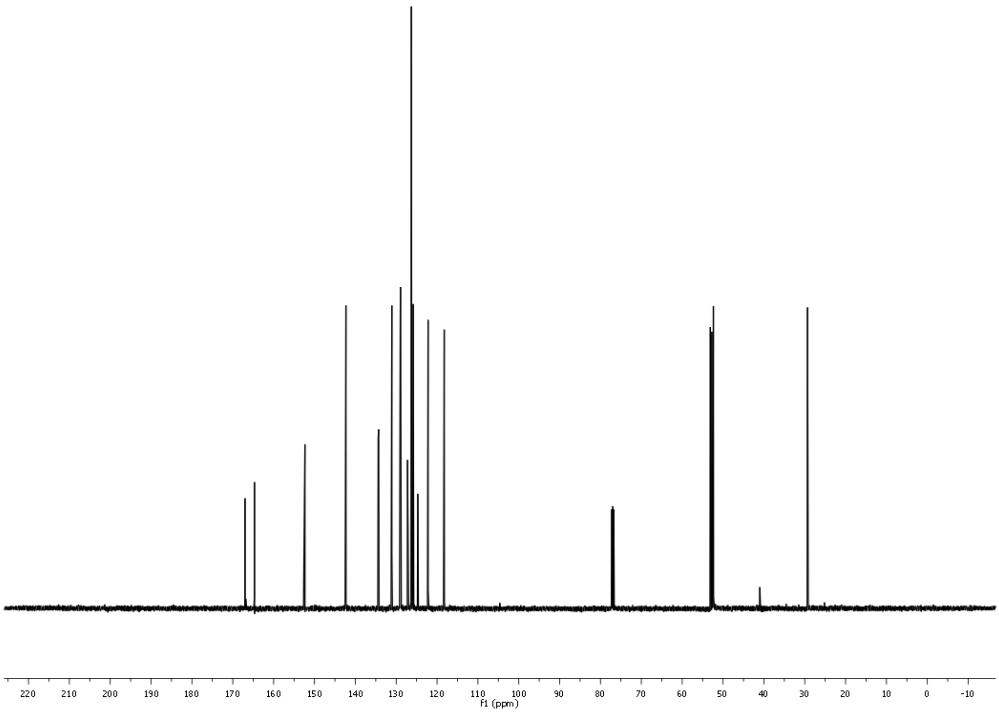
^{1}H–NMR and ^{13}C–NMR of **1m**:



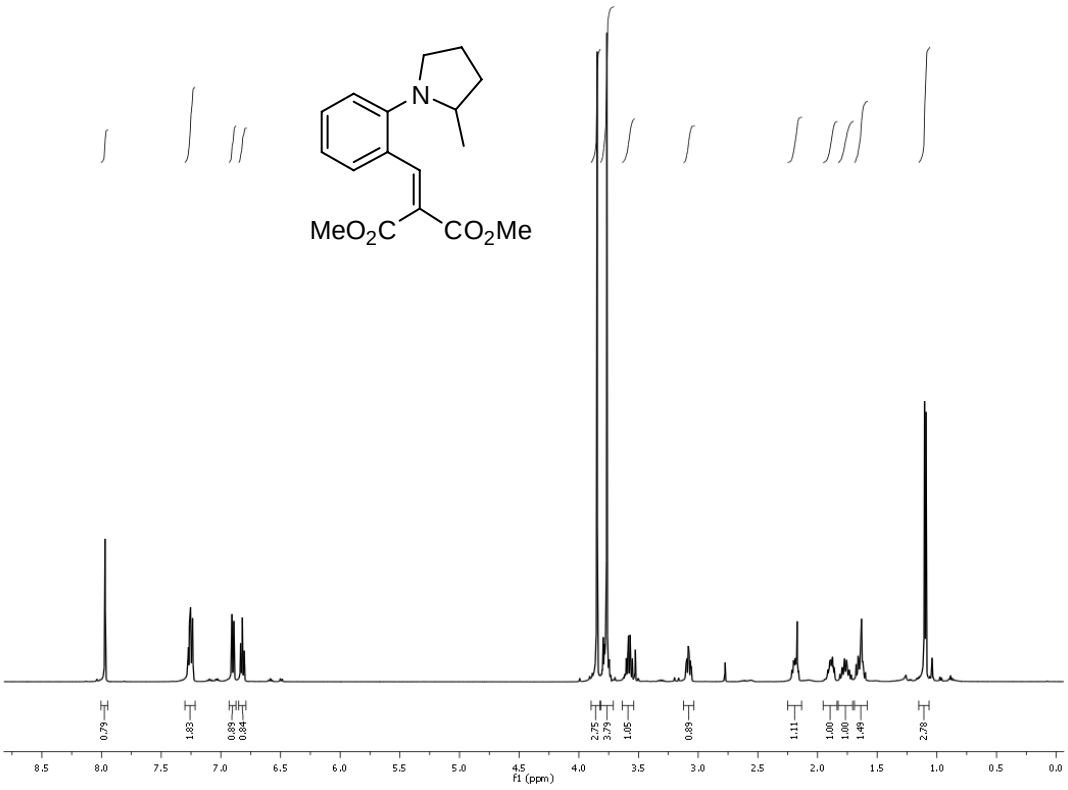


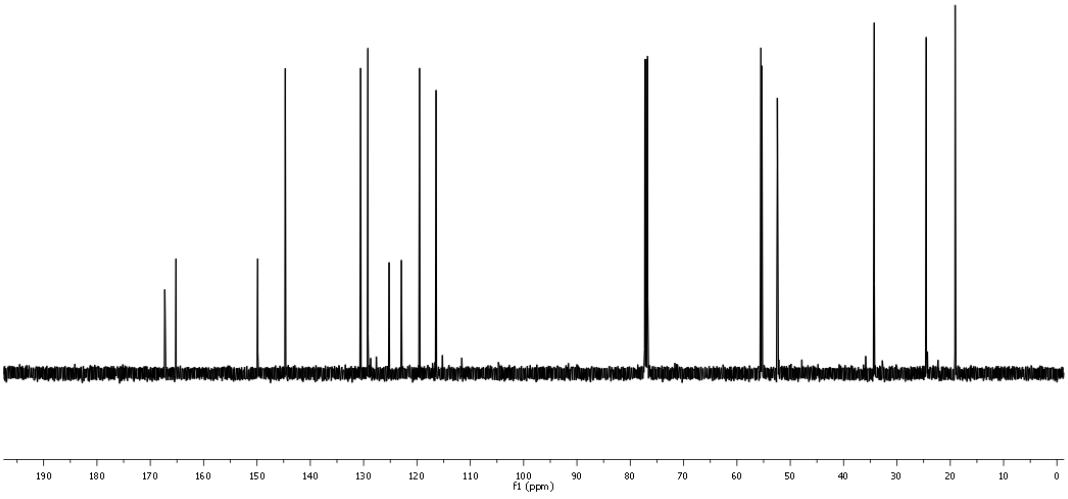
^{1}H–NMR and ^{13}C–NMR of **1n**:



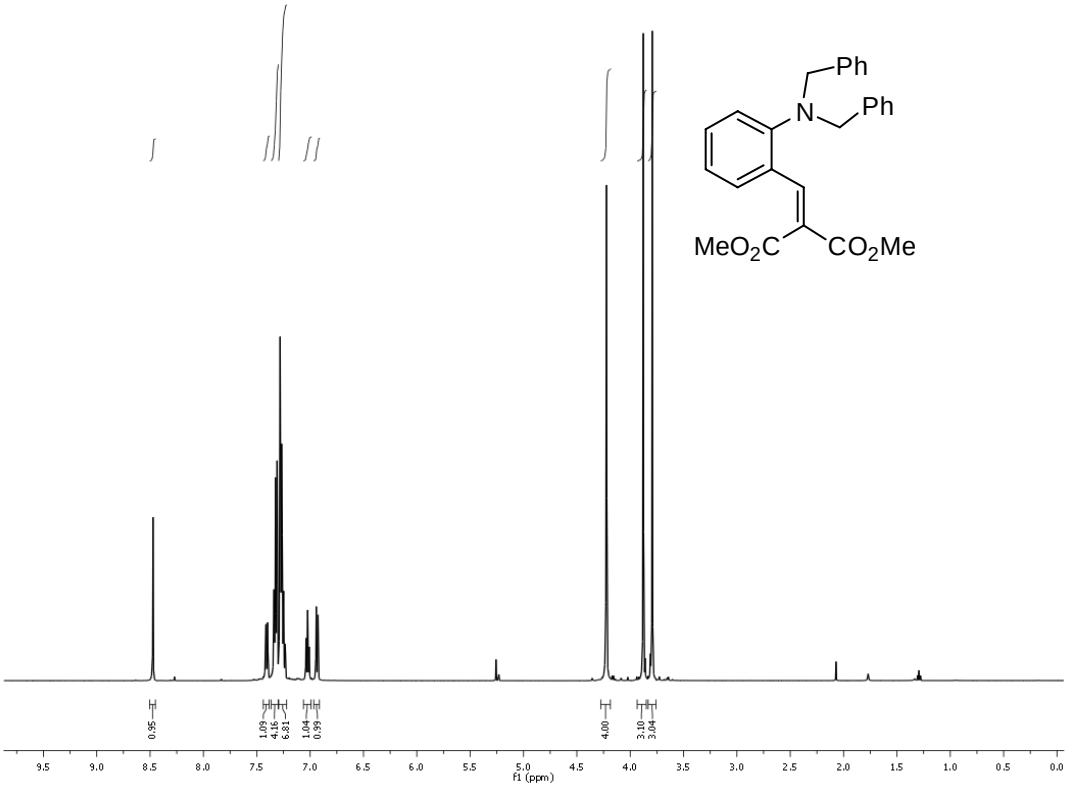


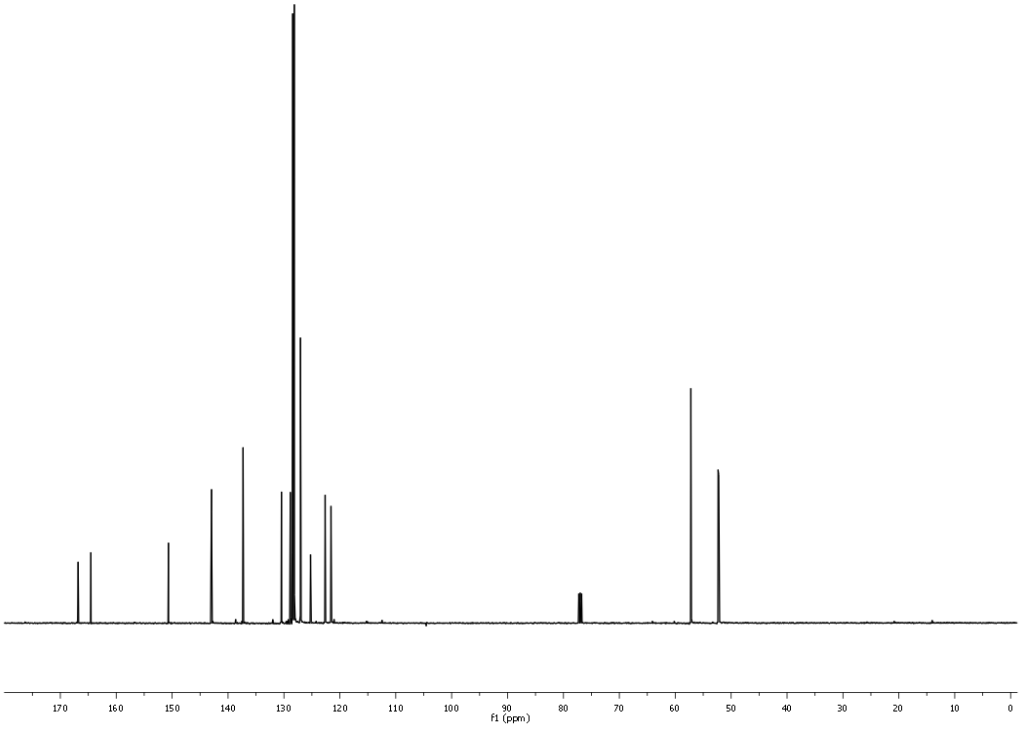
^{1}H–NMR and ^{13}C–NMR of **1o**:


N
MeO2C
CO2Me
0.79
1.83
0.89
0.84
2.75
3.79
1.05
0.89
1.11
1.00
1.00
1.49
2.78
f1 (ppm)

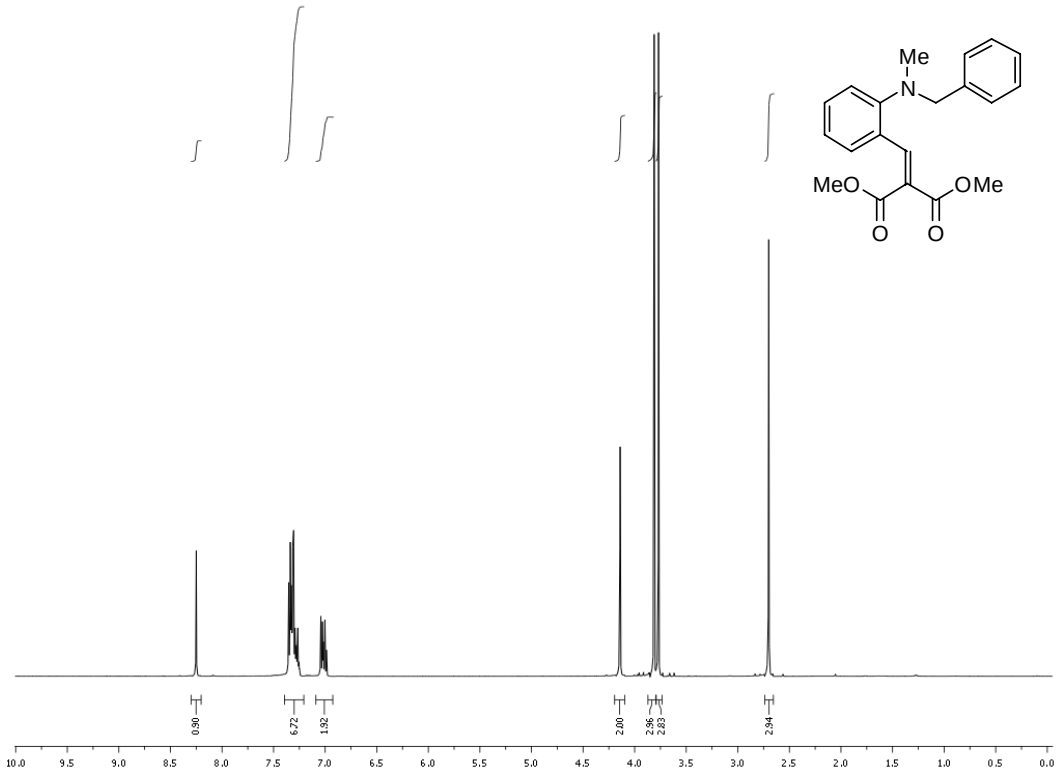

f1 (ppm)

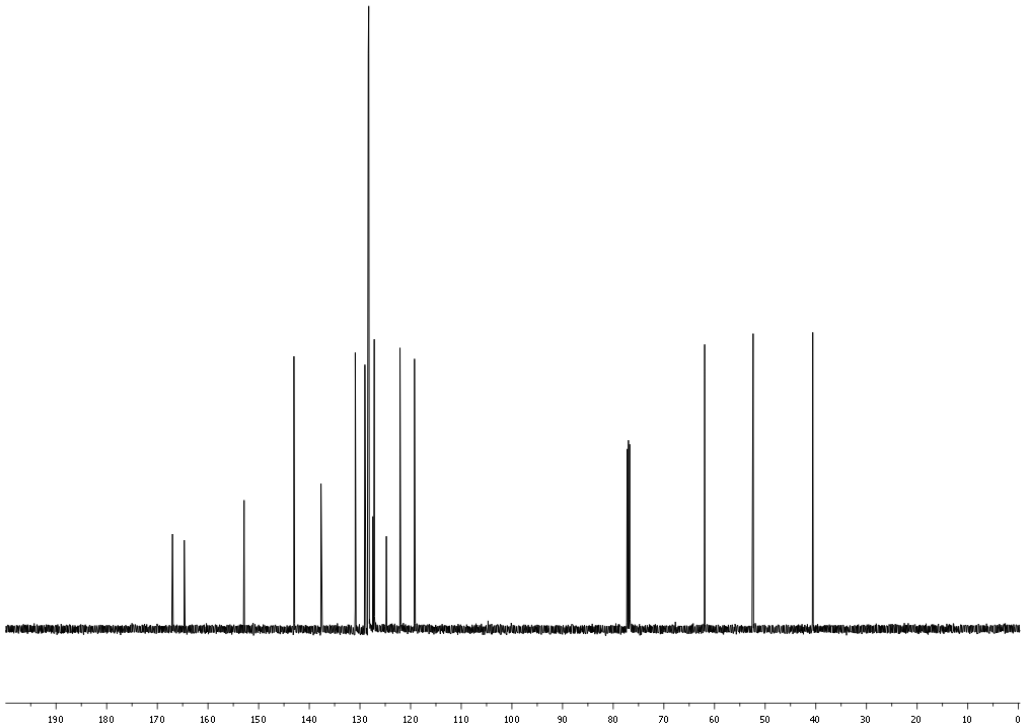
^{1}H–NMR and ^{13}C–NMR of **1p**:



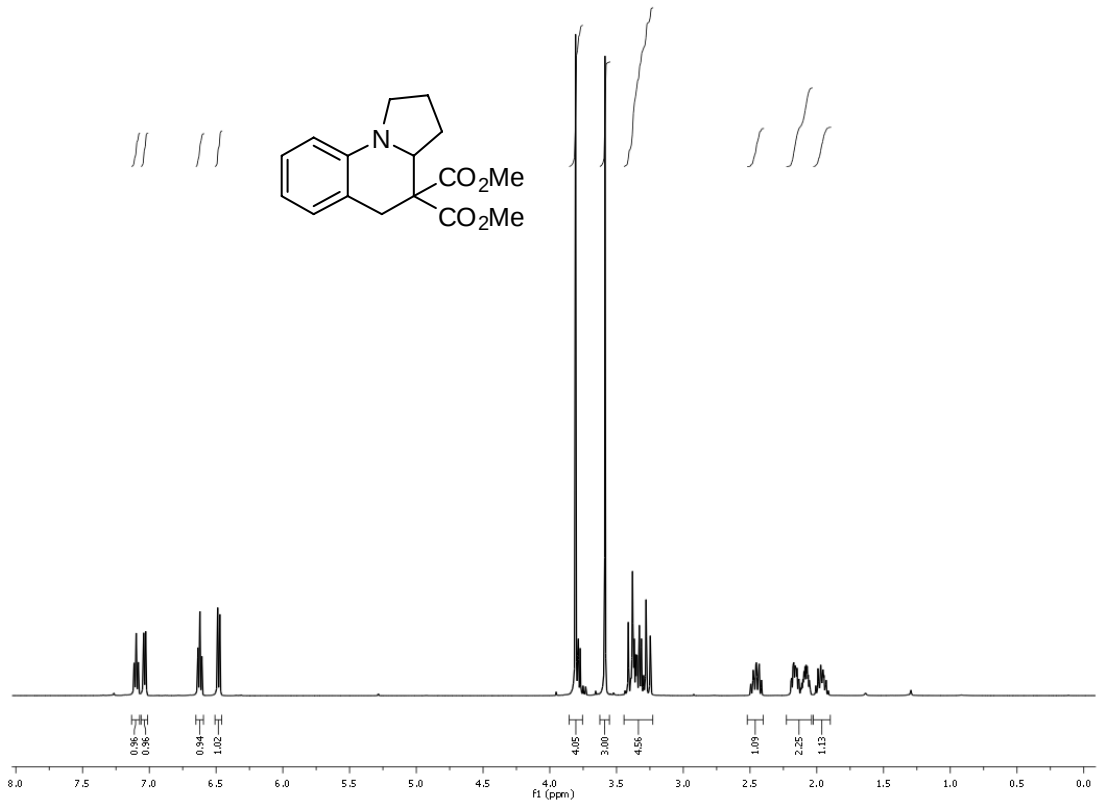


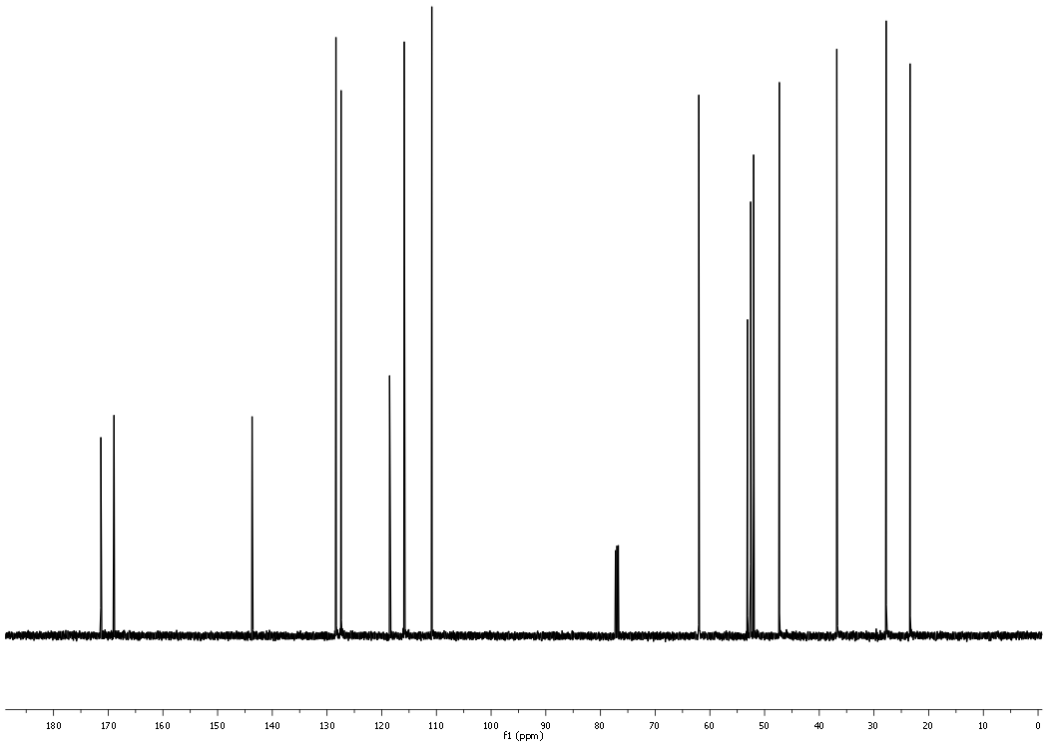
^{1}H–NMR and ^{13}C–NMR of **1q**:



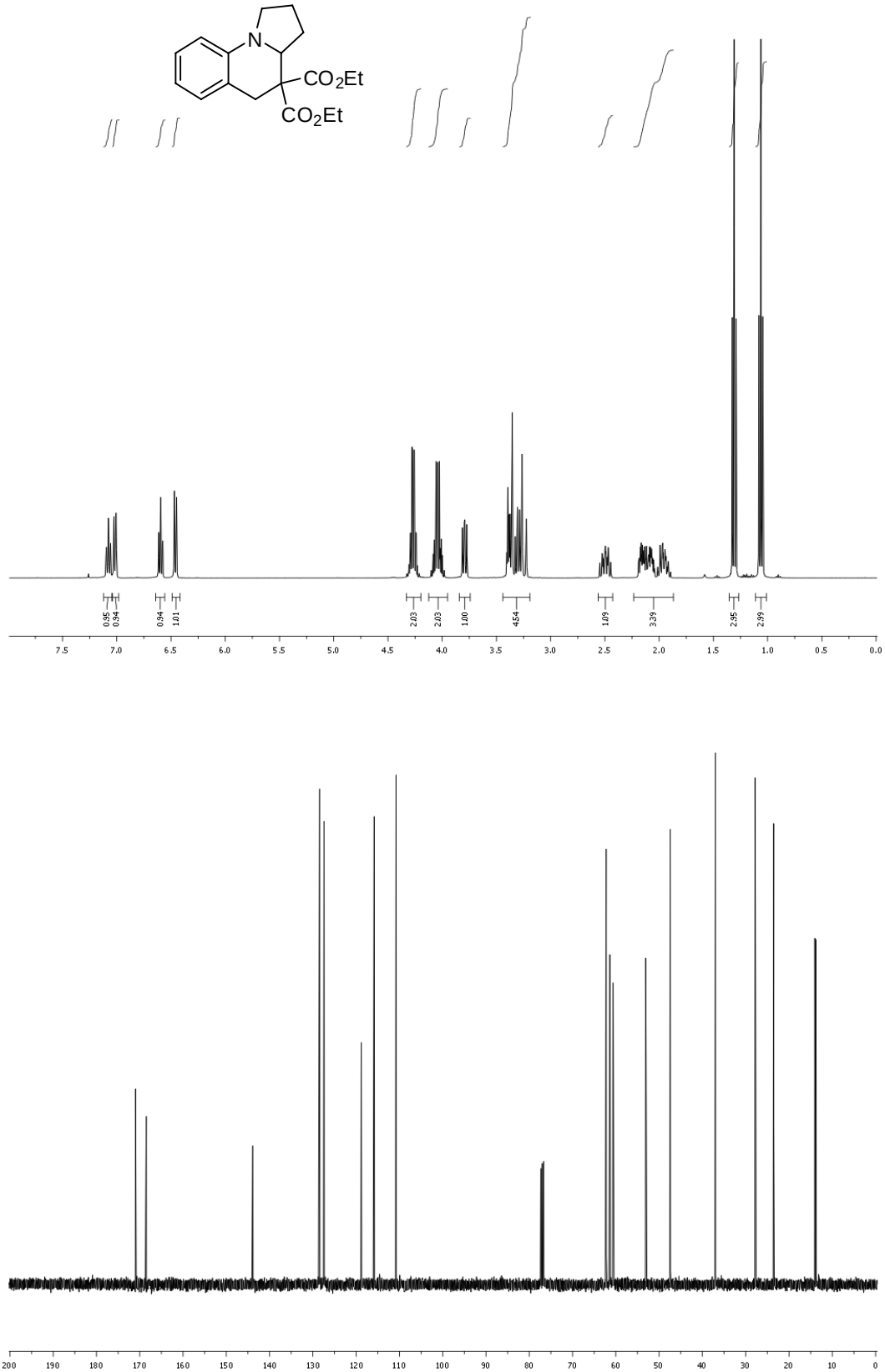


^{1}H–NMR and ^{13}C–NMR of **2a**:

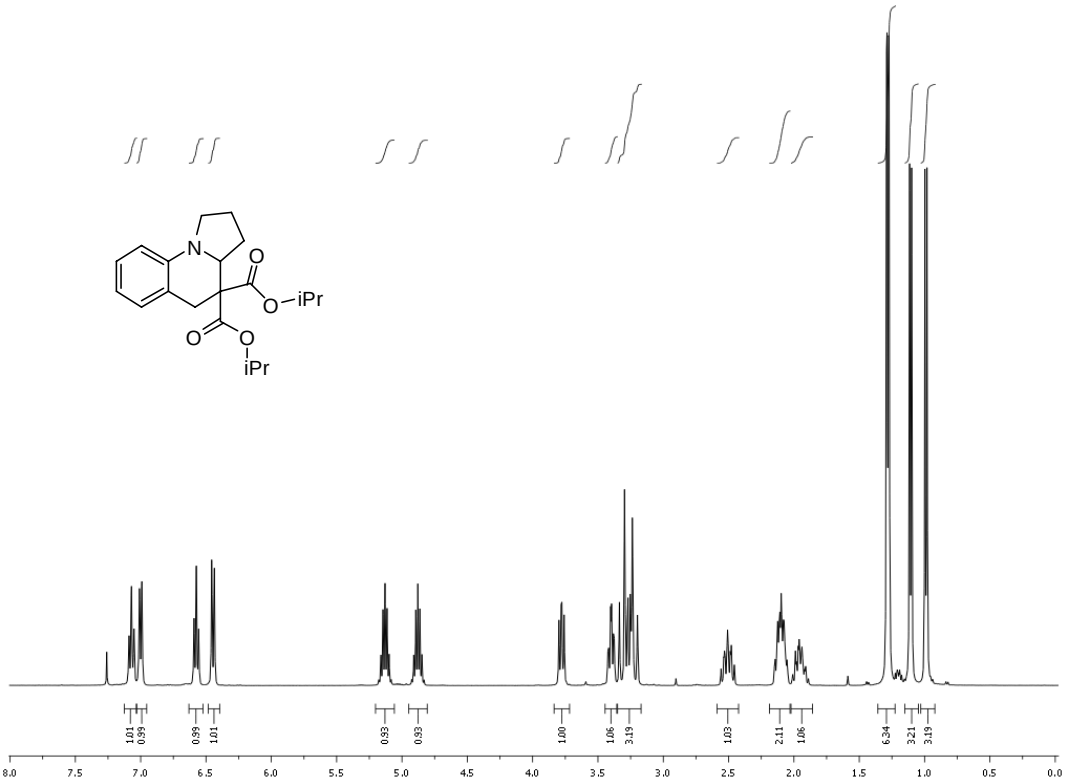


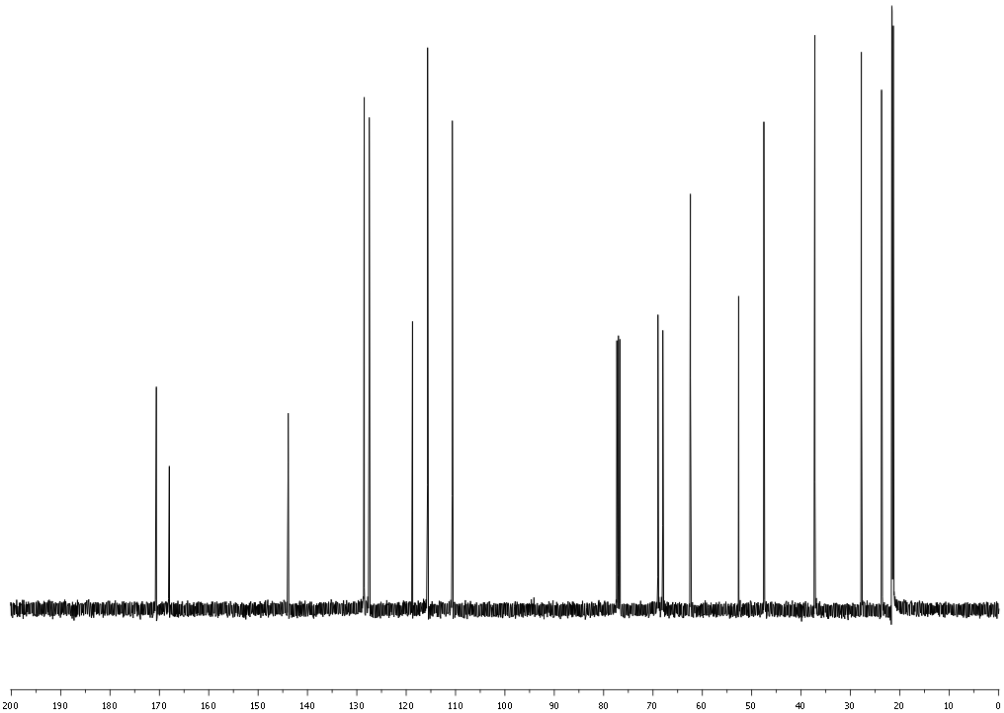


^{1}H–NMR and ^{13}C–NMR of **2b**:

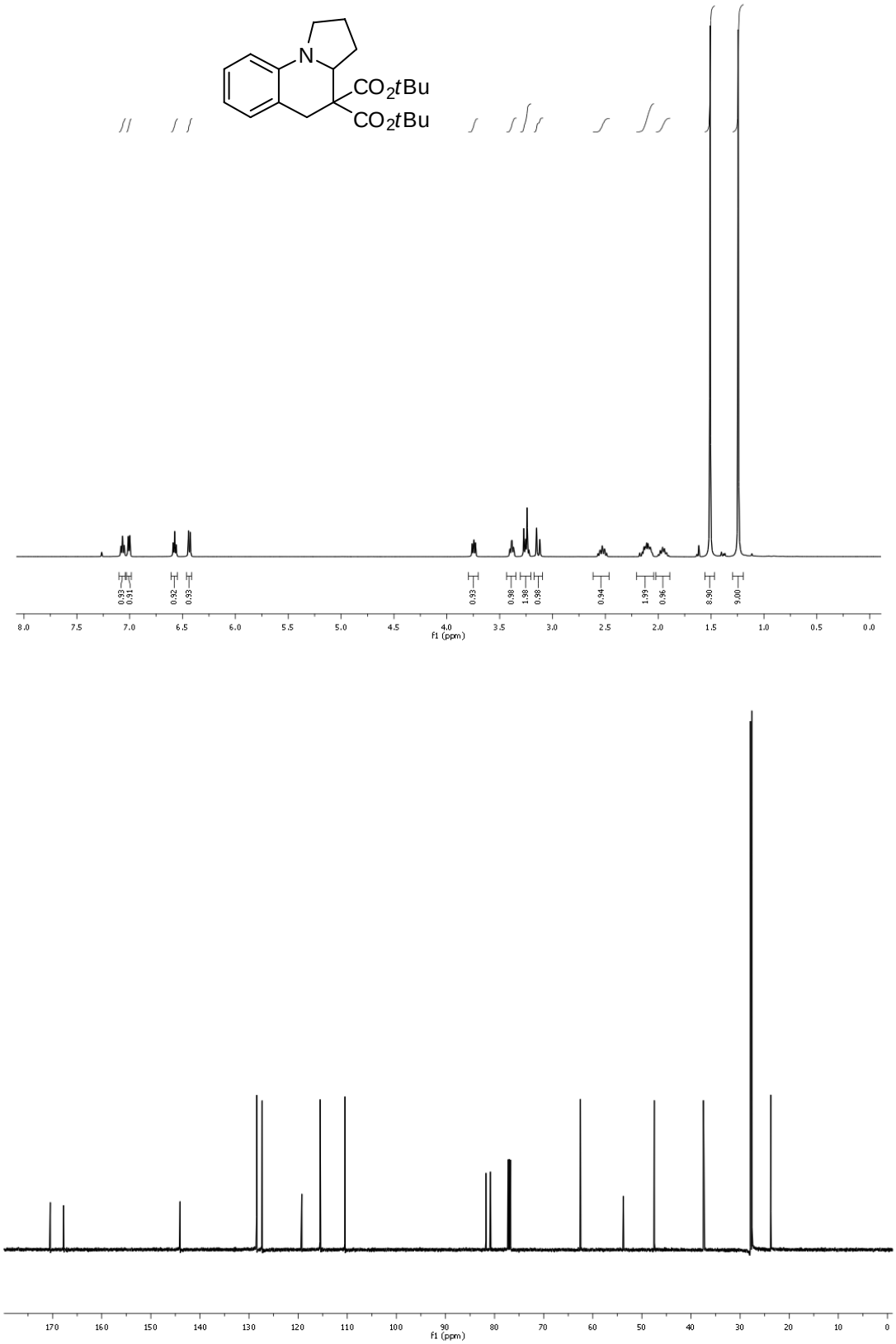


^{1}H–NMR and ^{13}C–NMR of **2c**:

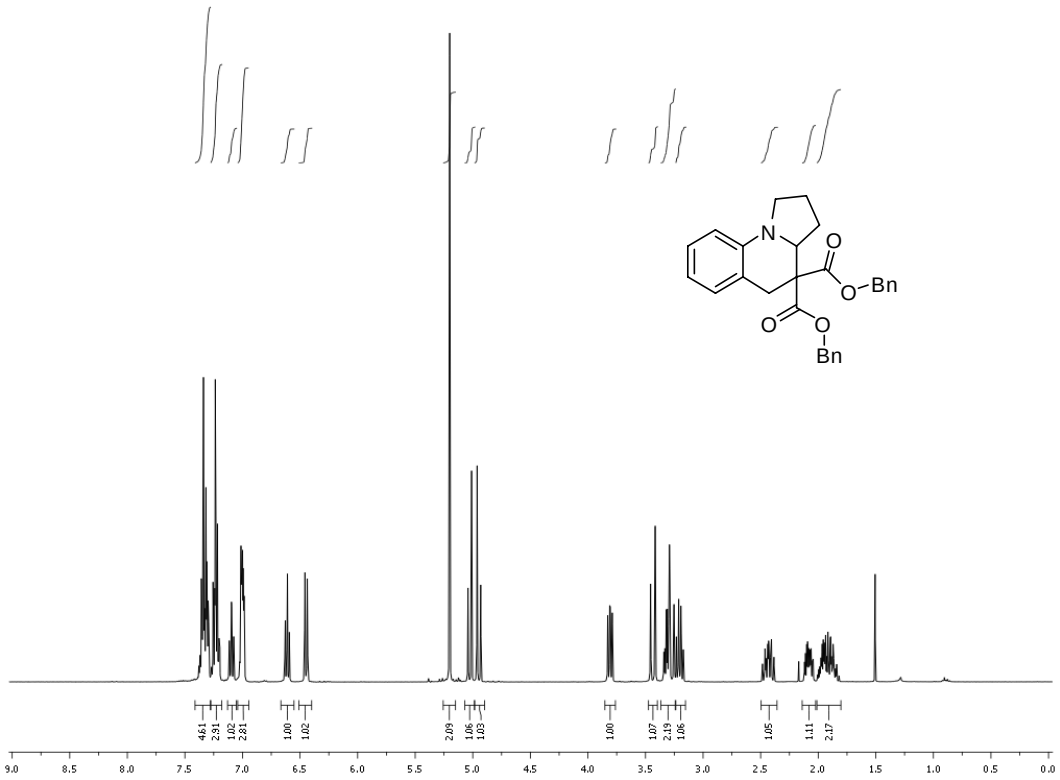


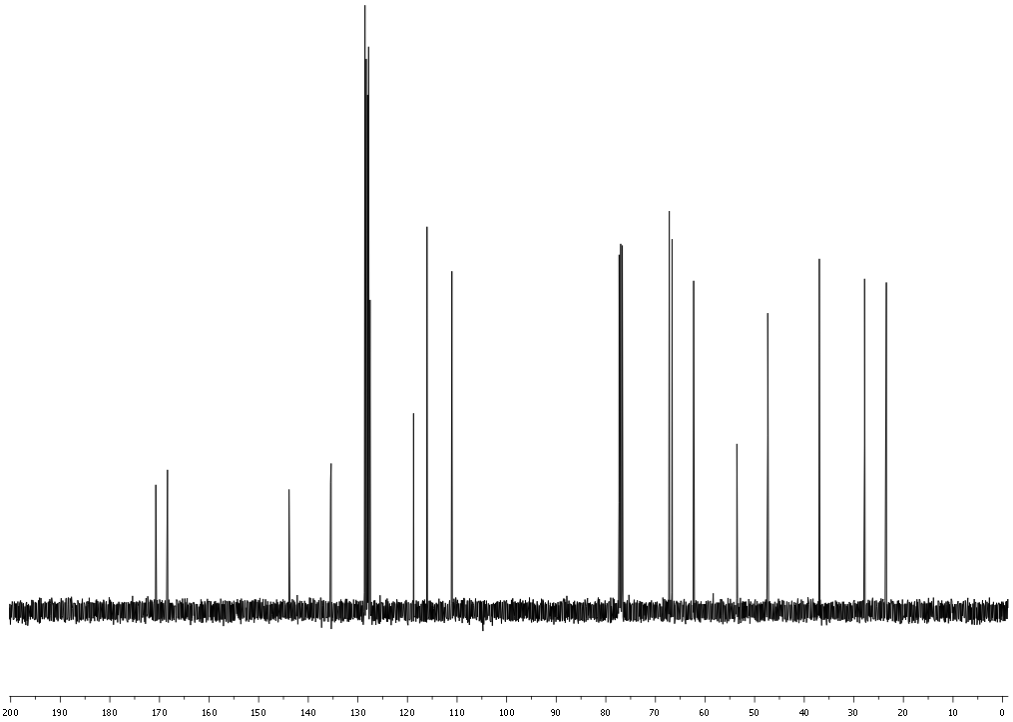


^{1}H–NMR and ^{13}C–NMR of **2d**:

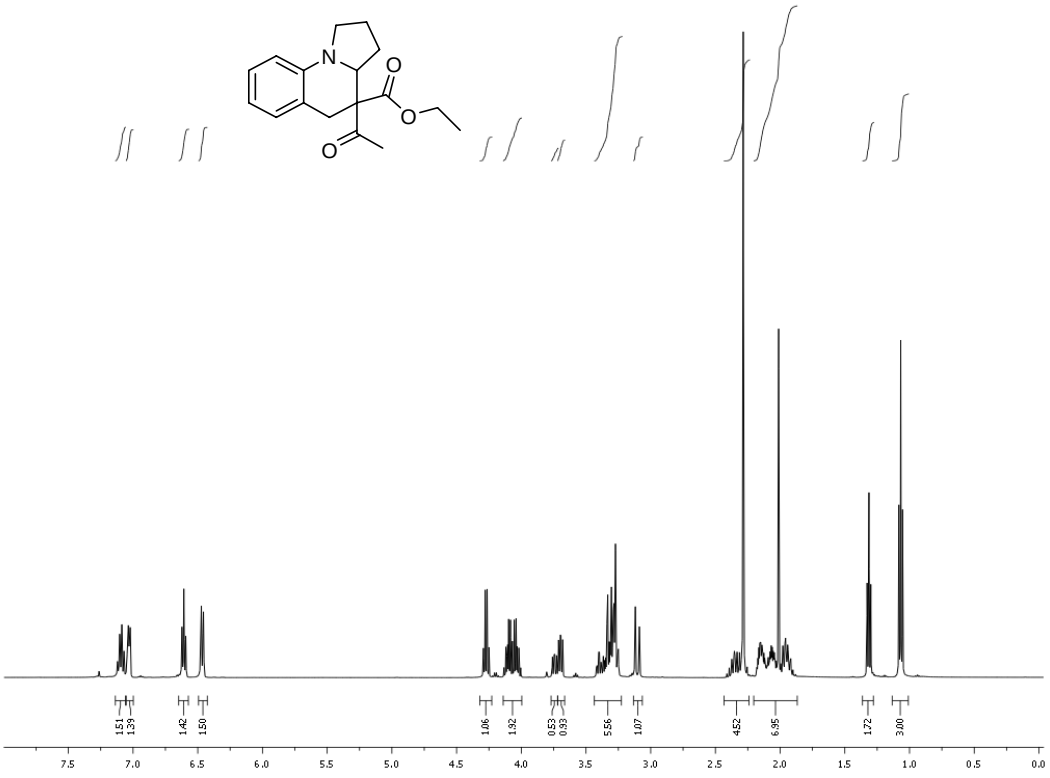


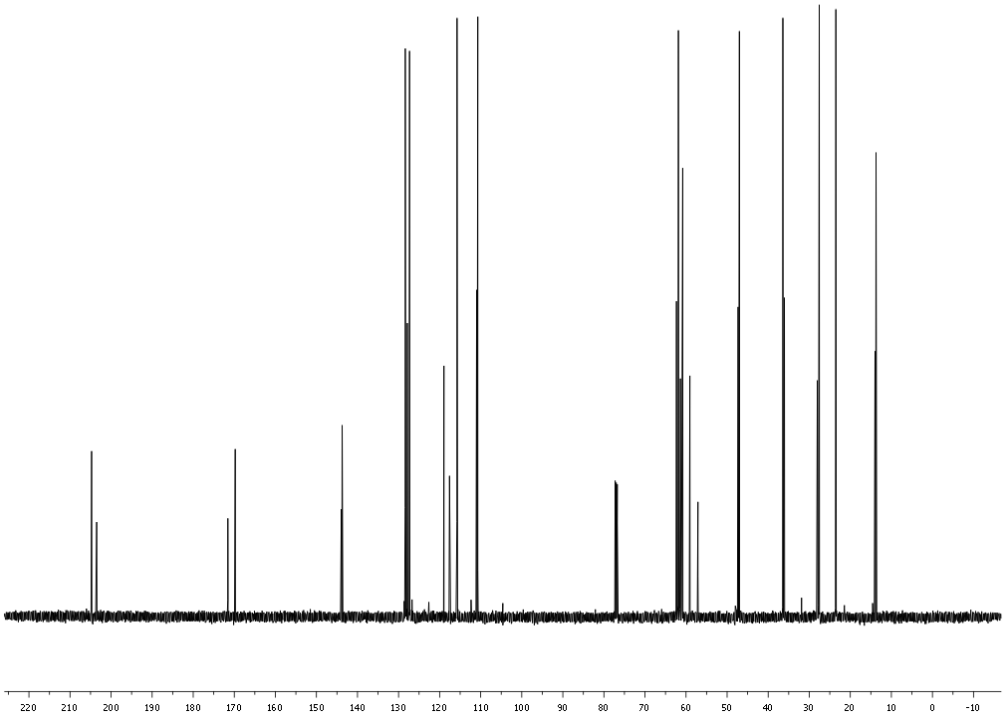
^{1}H–NMR and ^{13}C–NMR of **2e**:



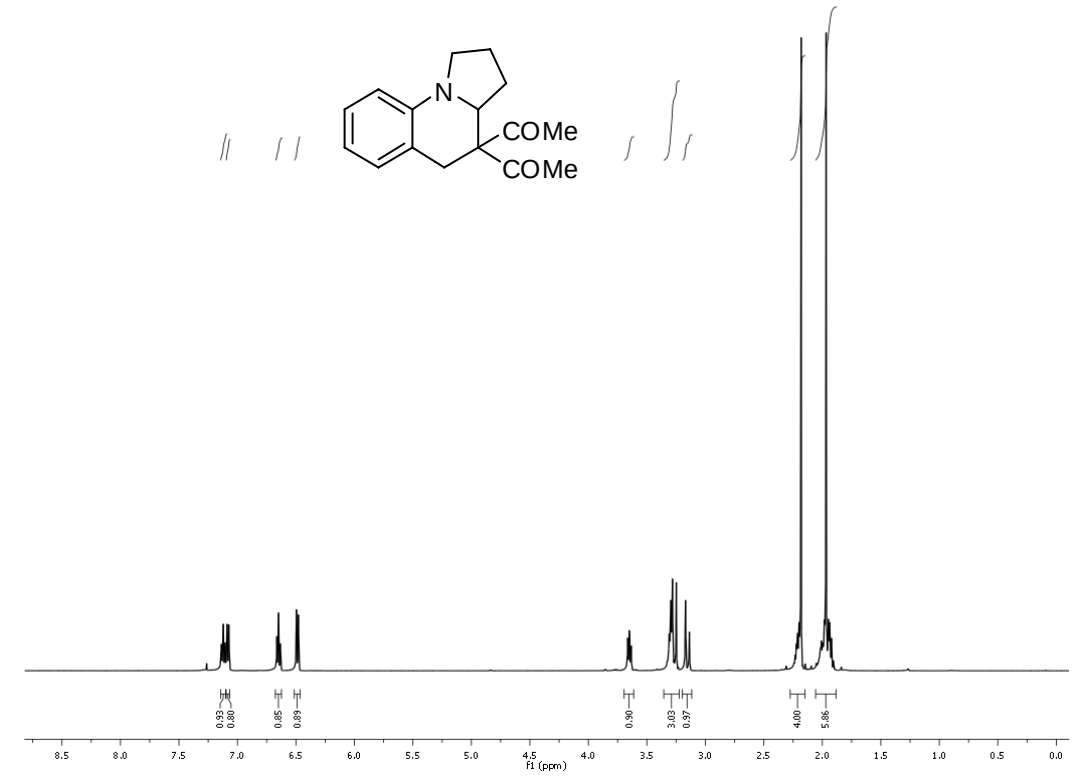


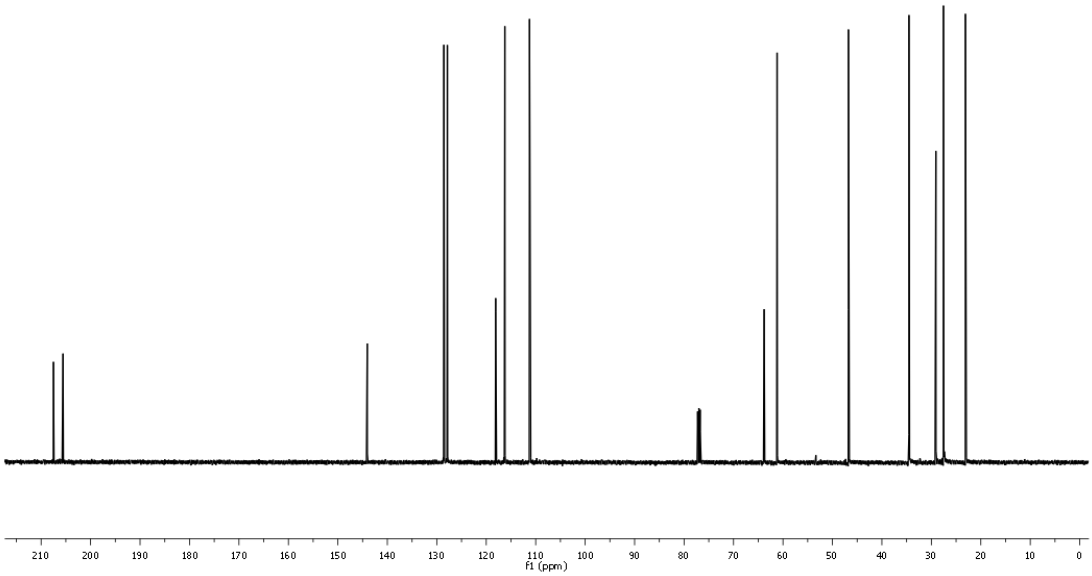
^{1}H–NMR and ^{13}C–NMR of **2f**: (dr = 36 : 64)



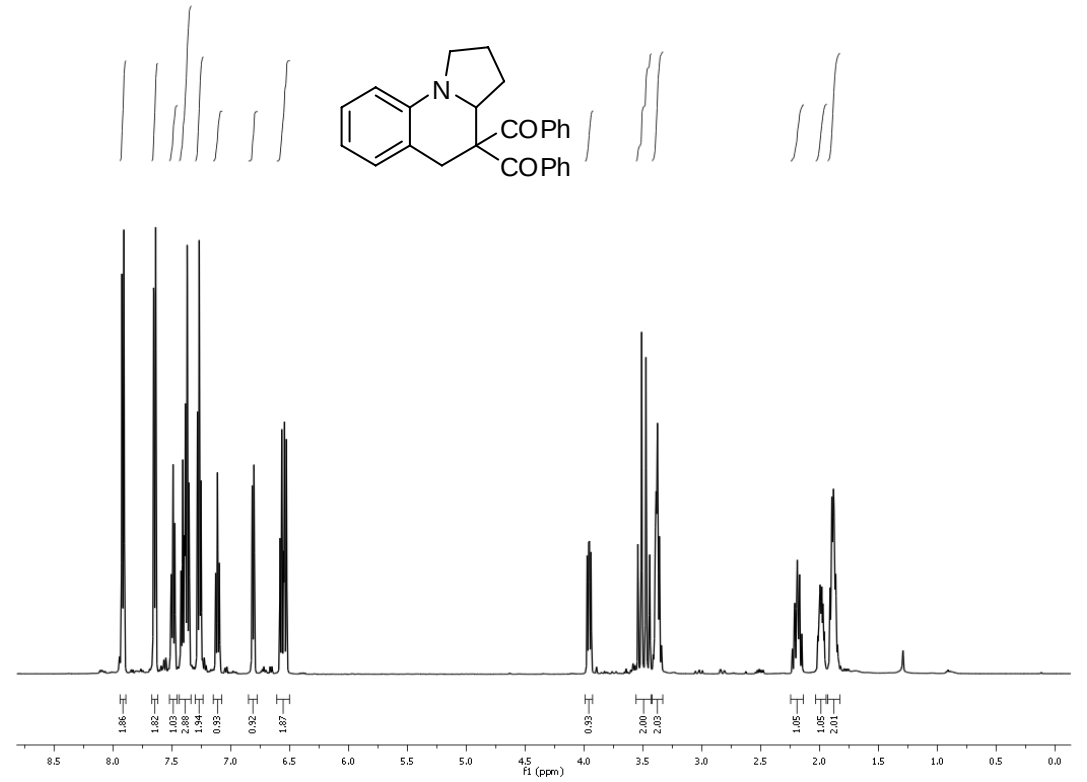


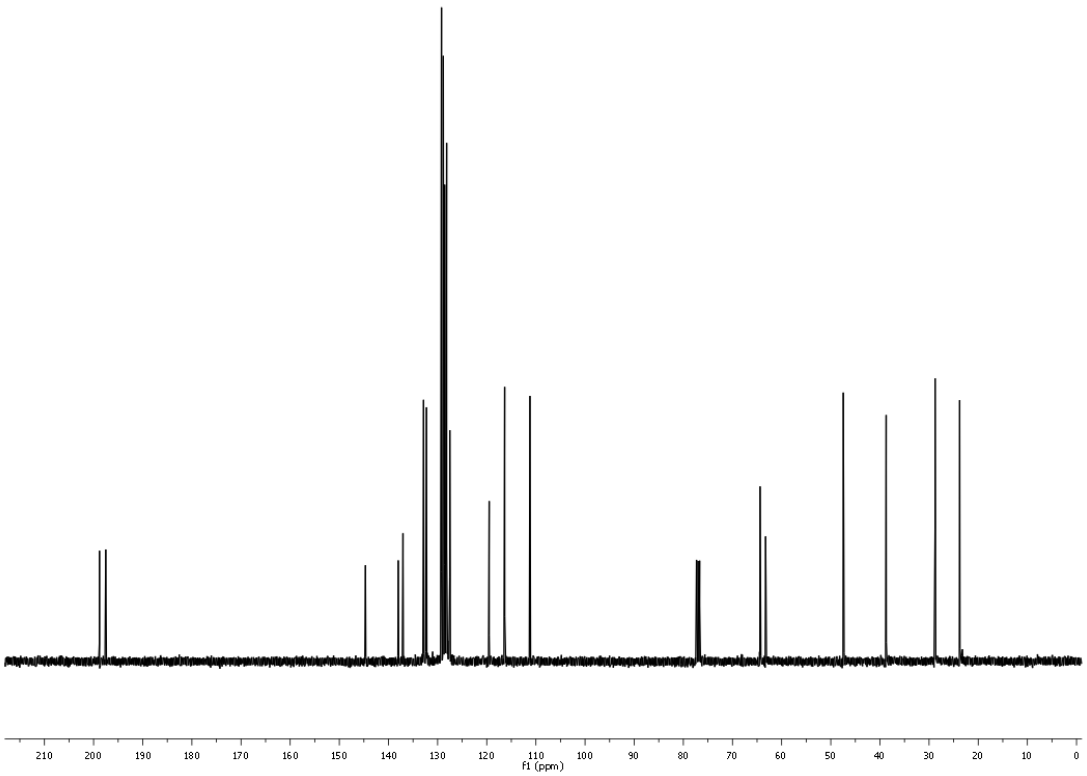
^{1}H–NMR and ^{13}C–NMR of **2g**:



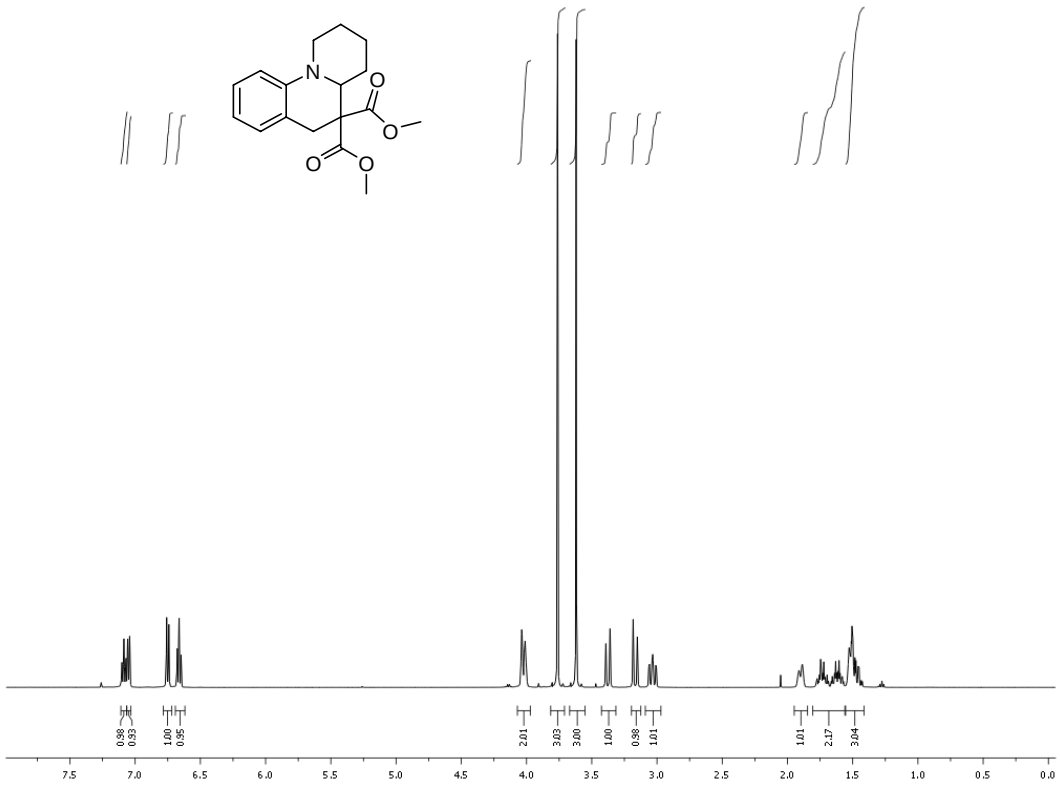


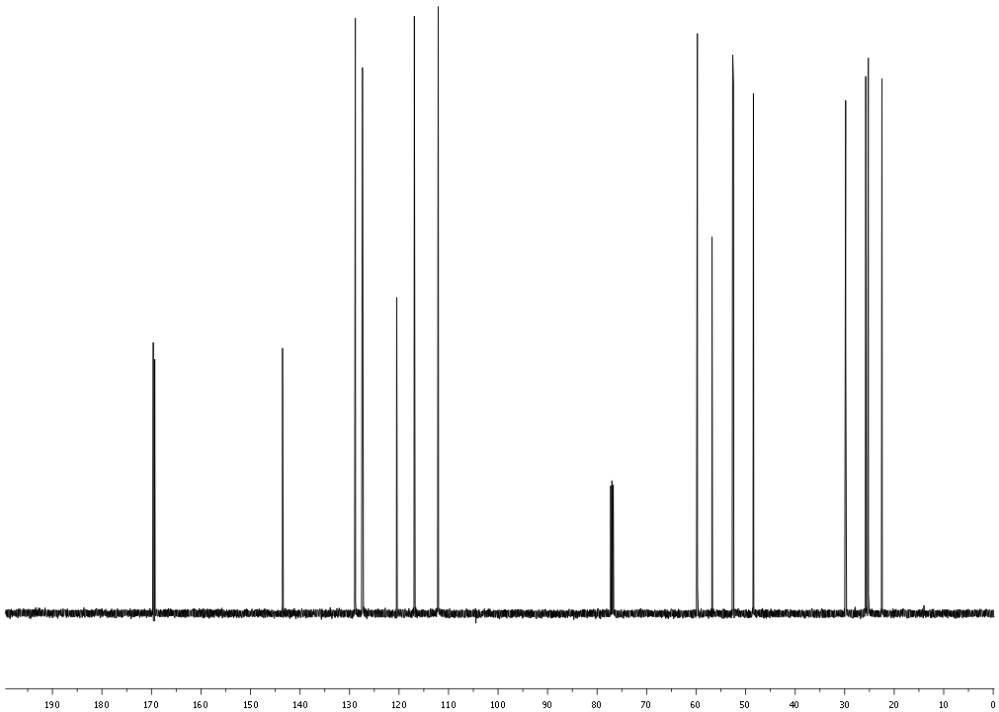
^{1}H–NMR and ^{13}C–NMR of **2h**:



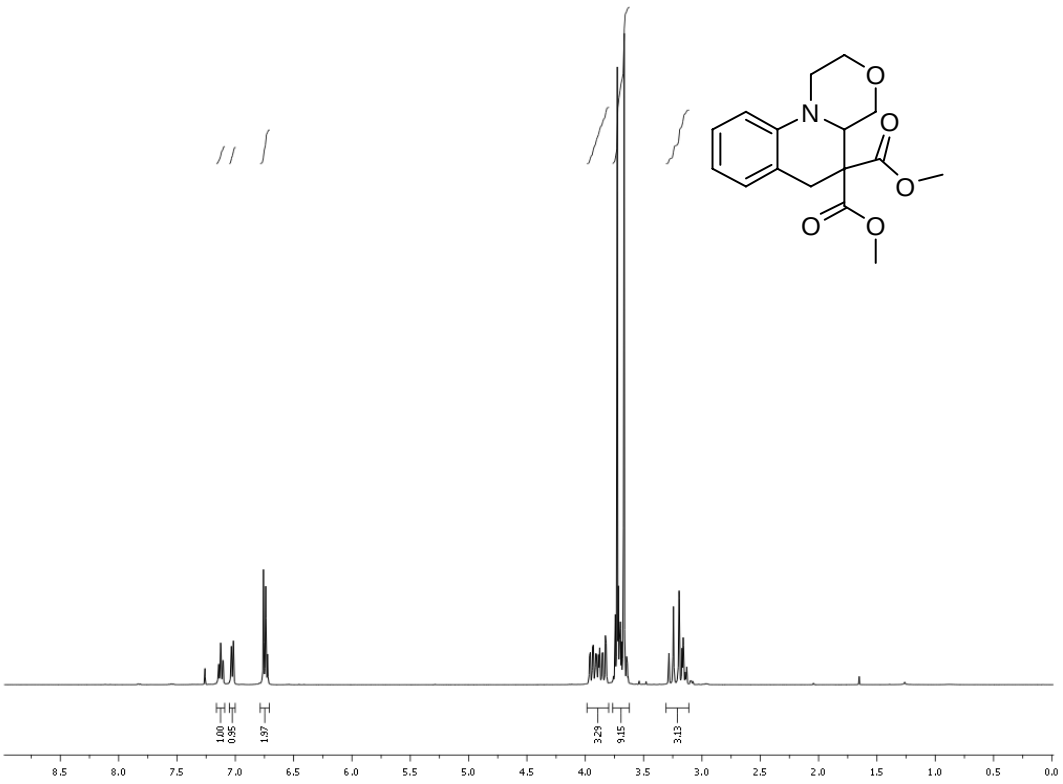


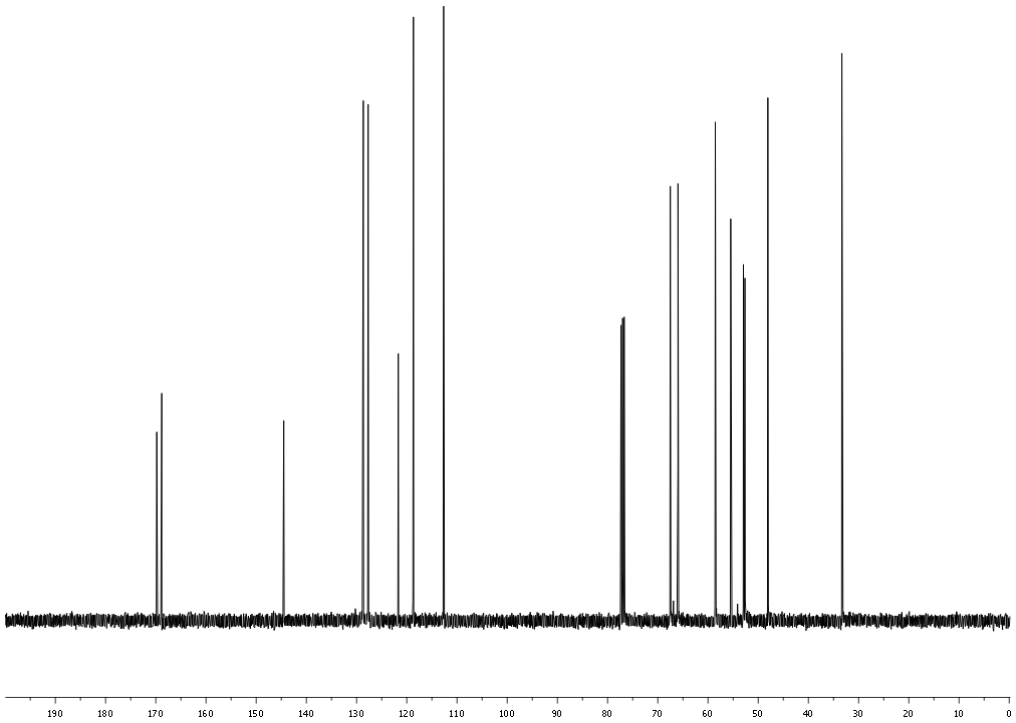
^{1}H–NMR and ^{13}C–NMR of **2j**:



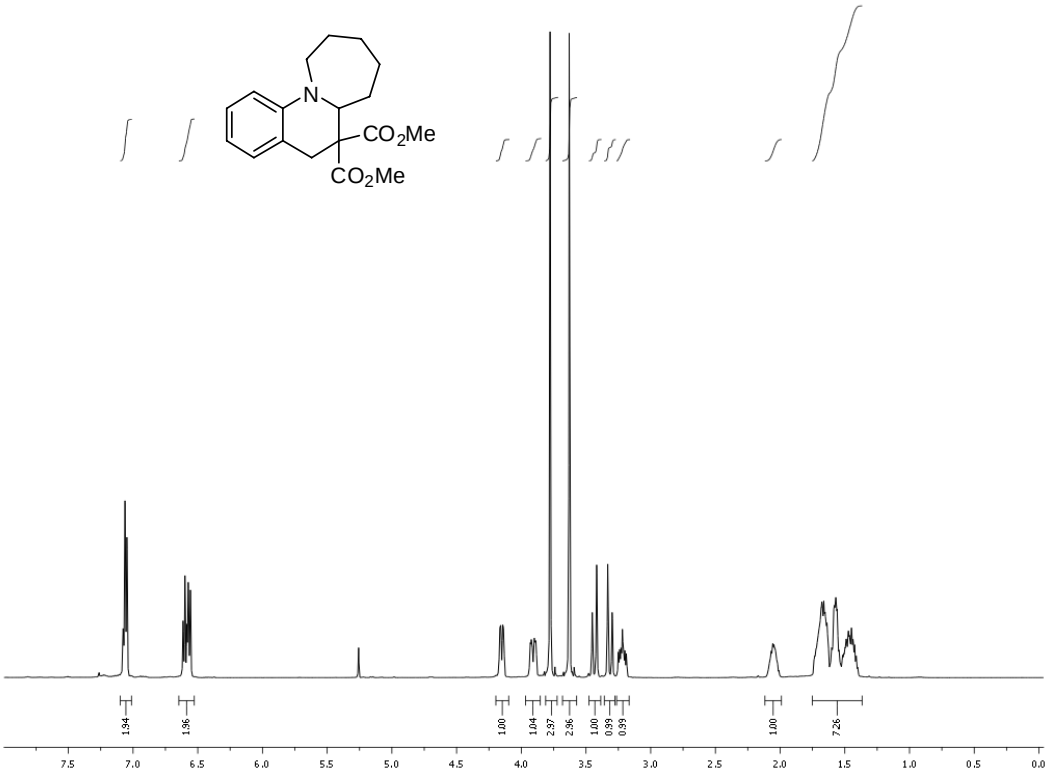


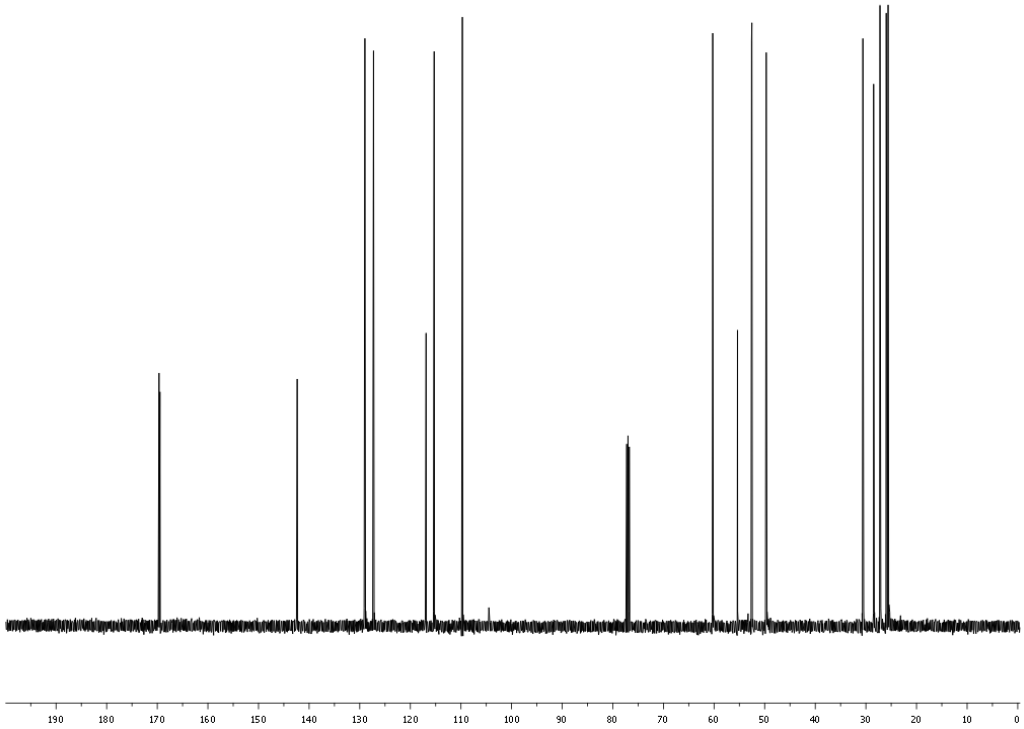
^{1}H–NMR and ^{13}C–NMR of **2k**:



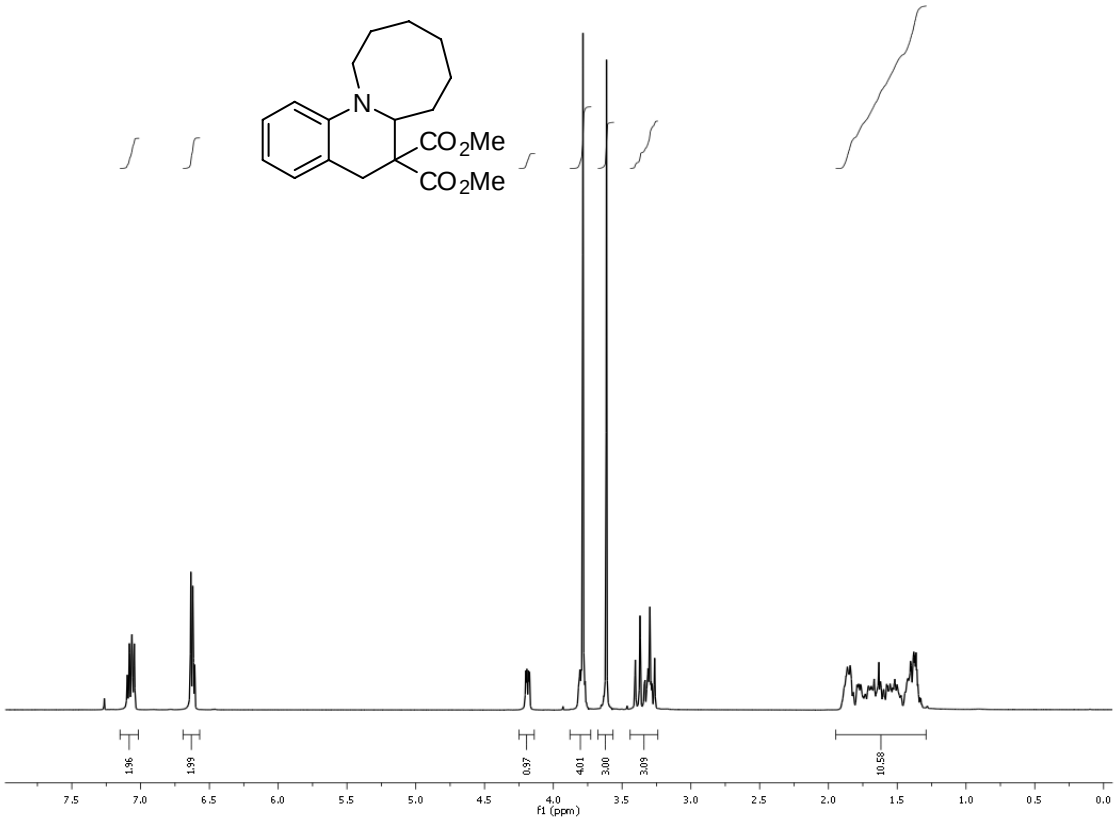


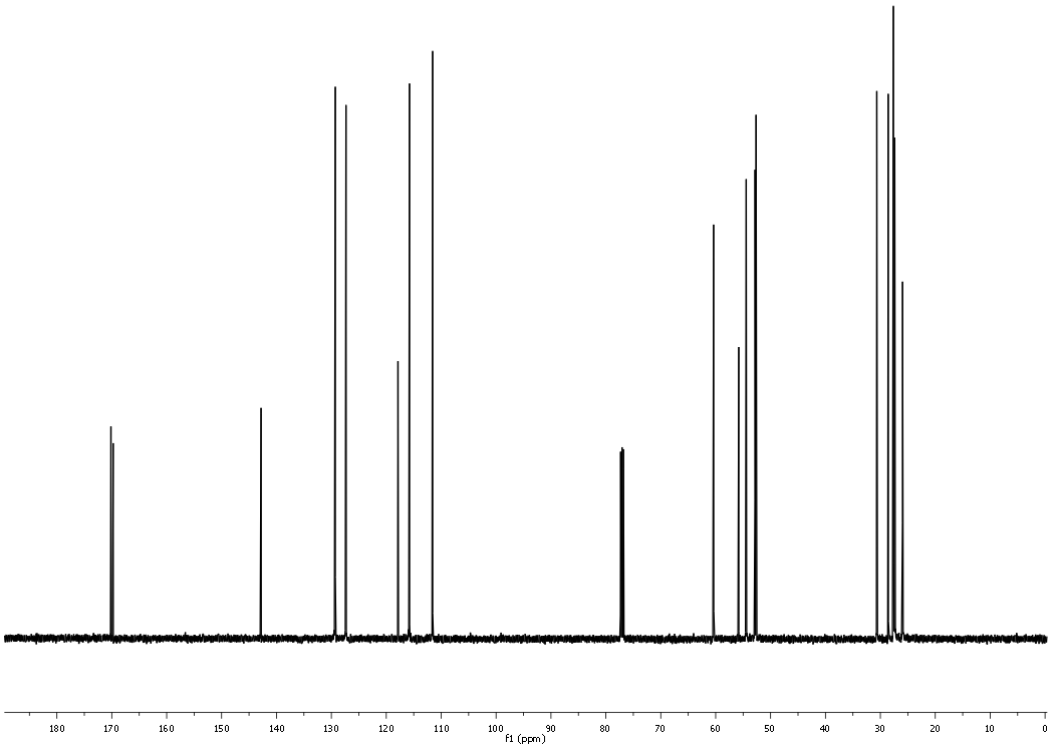
^{1}H–NMR and ^{13}C–NMR of **2l**:



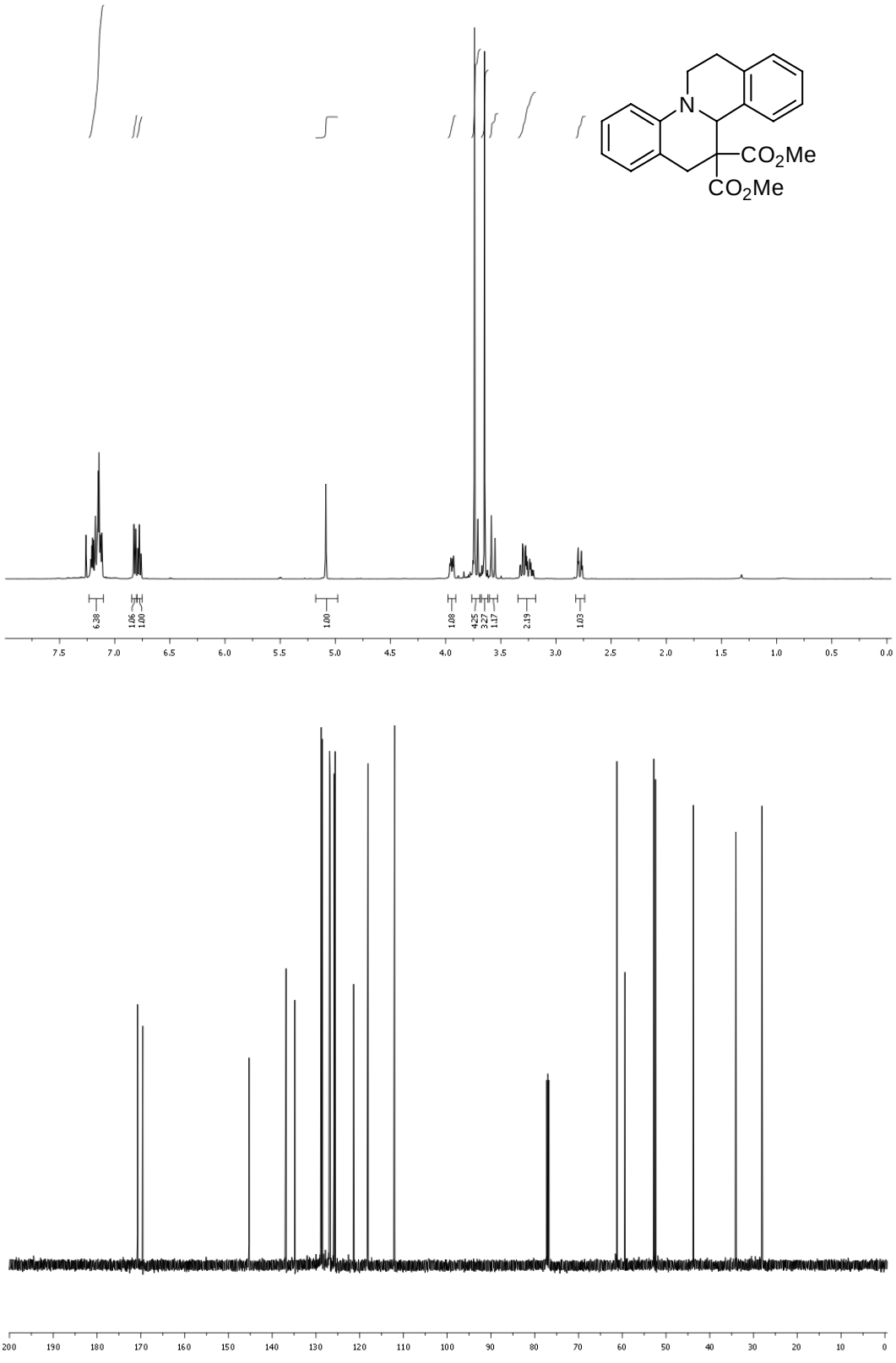


^{1}H–NMR and ^{13}C–NMR of **2m**:

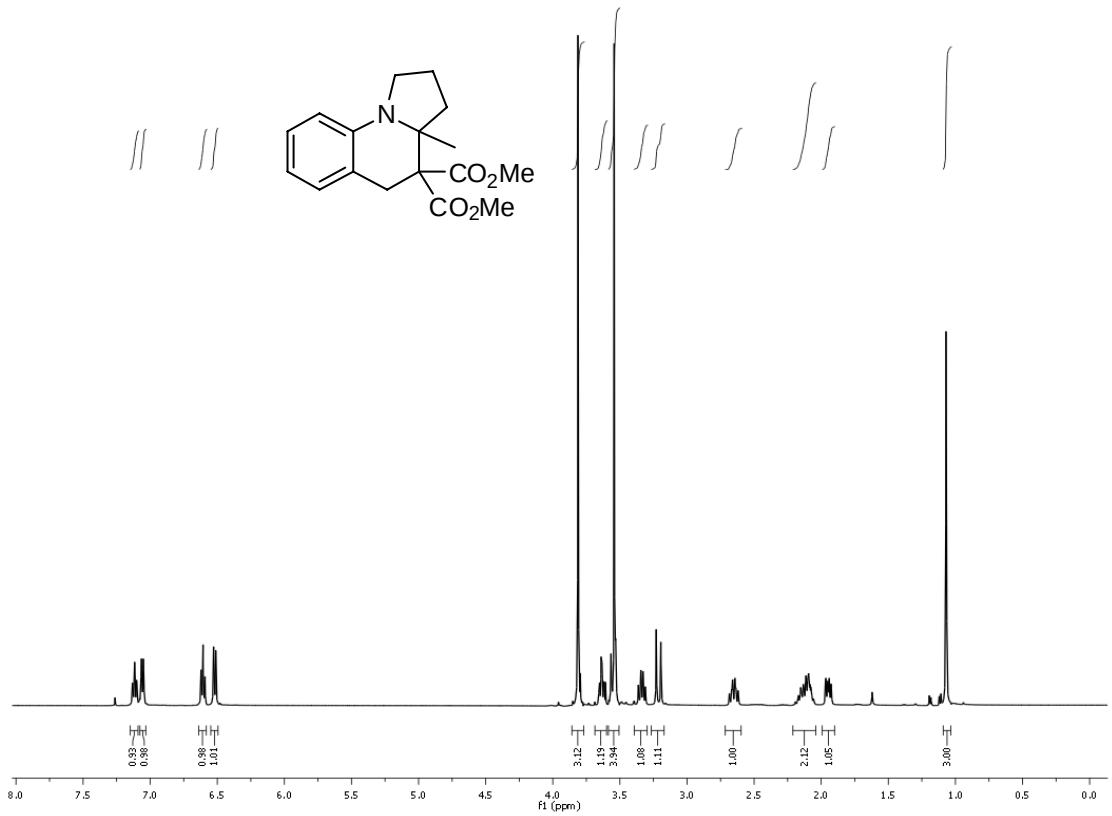


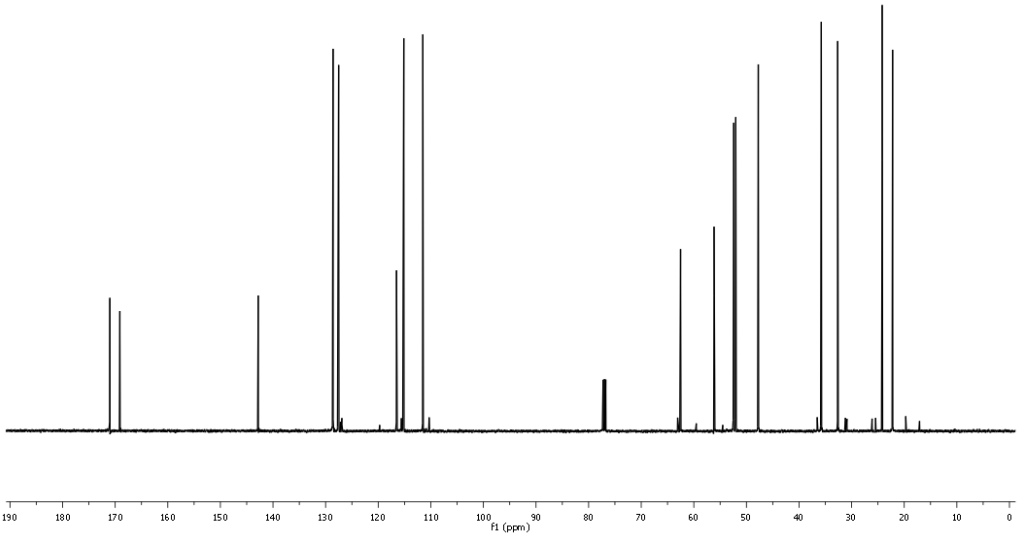


^{1}H–NMR and ^{13}C–NMR of **2n**:

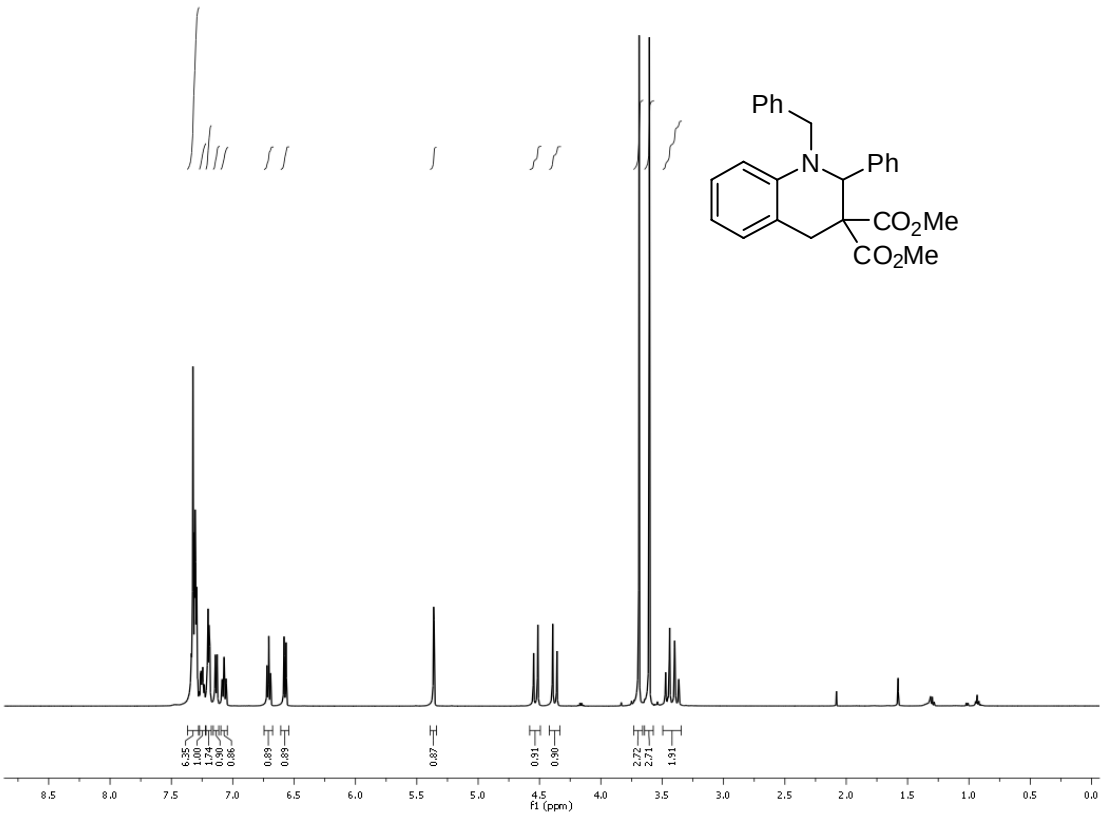


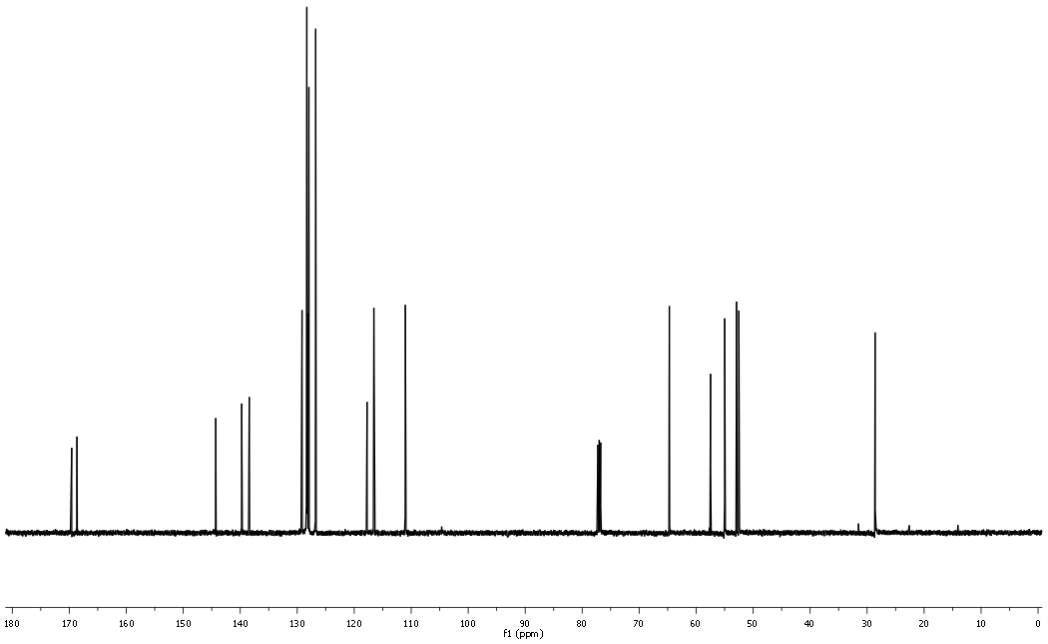
^{1}H–NMR and ^{13}C–NMR of **2o**:



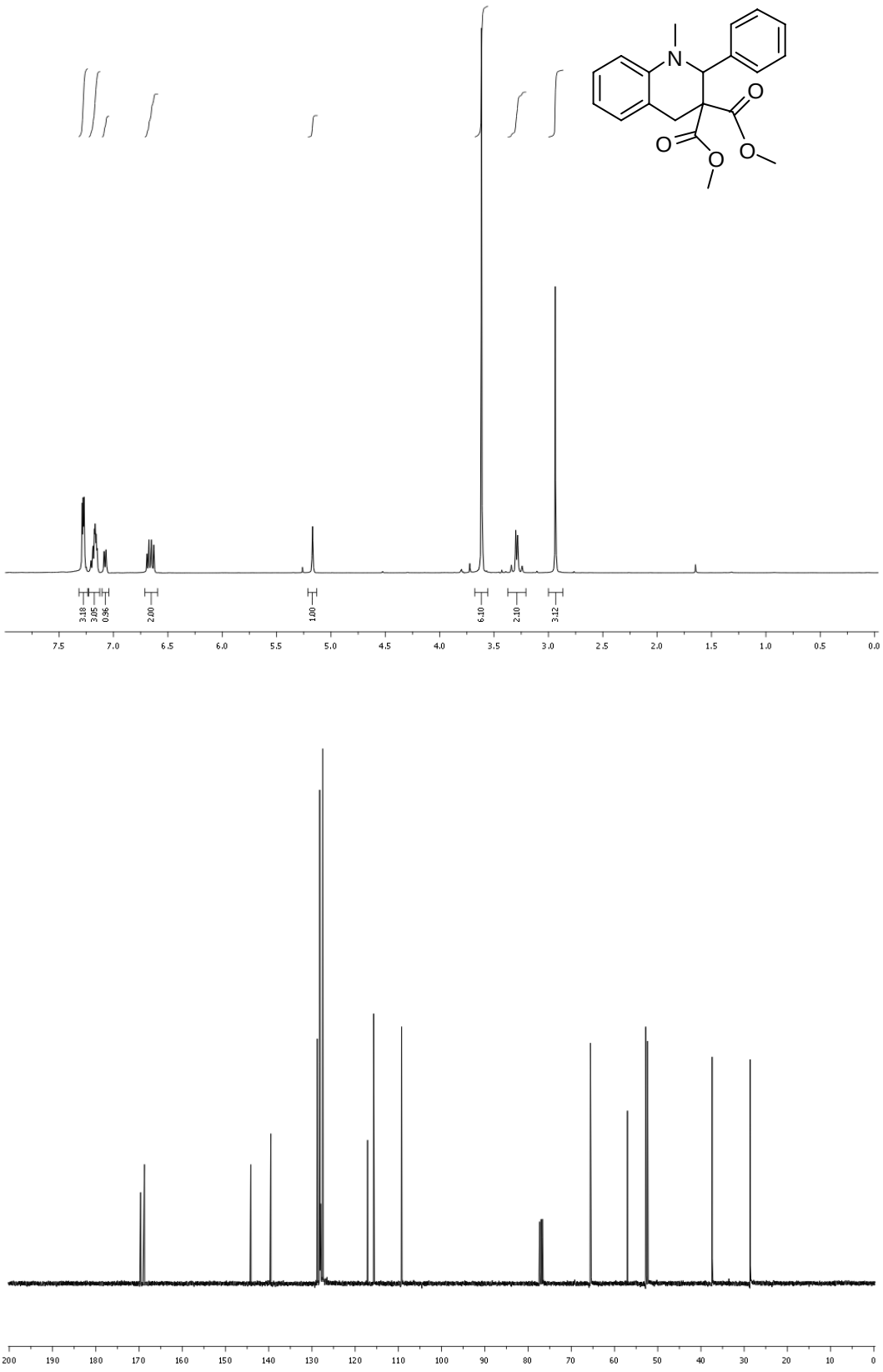


^{1}H–NMR and ^{13}C–NMR of **2p**:

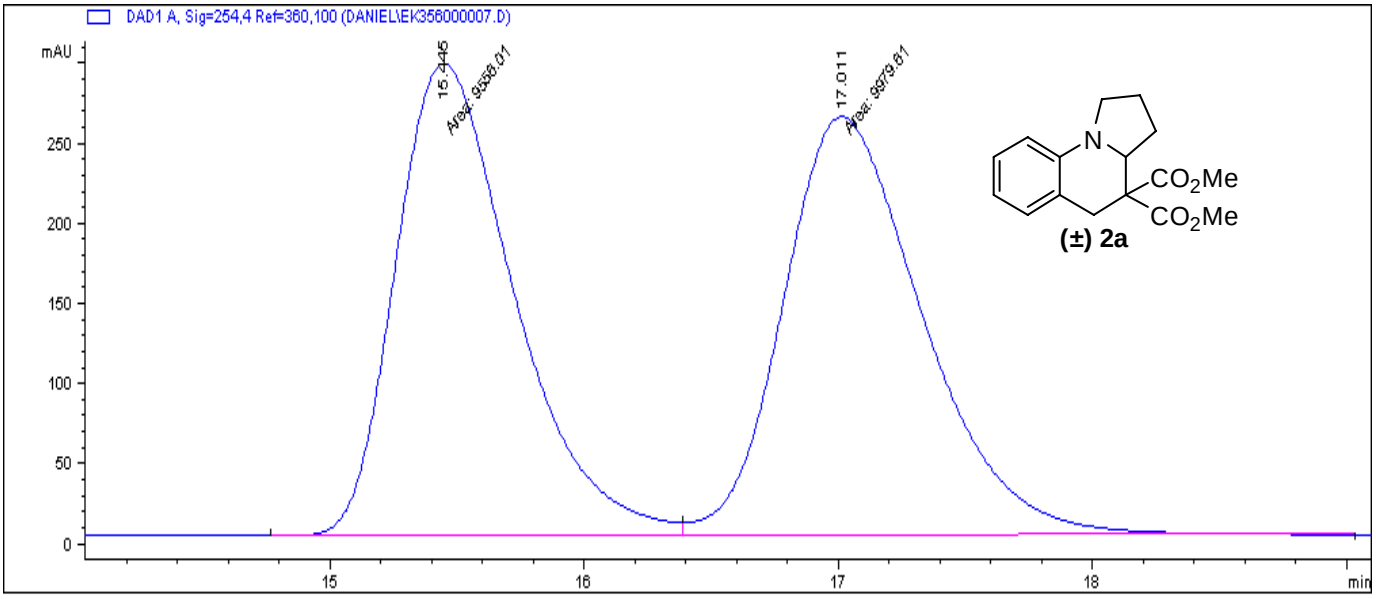


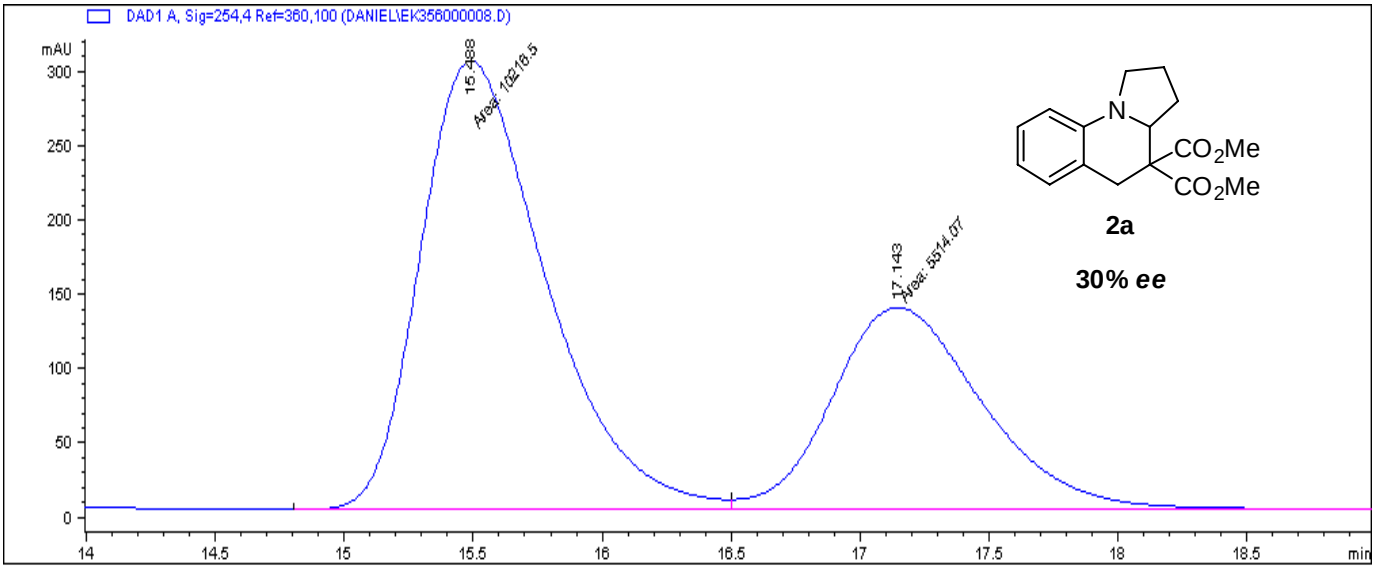


^{1}H–NMR and ^{13}C–NMR of **2q**:



HPLC profile of **2a**


DAD1 A, Sig=254,4 Ref=360,100 (DANIEL\EK356000007.D)
mAU
15.445
Area: 3556.01
17.011
Area: 3979.61
N
CO2Me
CO2Me
(±) 2a
min


DAD1 A, Sig=254,4 Ref=360,100 (DANIEL\EK356000008.D)
mAU
15.488
Area: 10216.5
17.143
Area: 5514.07
N
CO2Me
CO2Me
2a
30% ee
min