Supporting Information

Mechanochemical milling promoted solvent-free imino Diels–Alder reaction: diastereoselective synthesis of *cis*-2, 4-diphenyl-1,2,3,4-tetrahydroquinolines

Ya-Jun Tan, Ze Zhang,* Fang-Jian Wang, Hao-Hao Wu, Qing-Hai Li*

School of Biological and Chemical Engineering, Anhui Polytechnic University, Wuhu, 241000, China

E-mail: zhangze@ustc.edu.cn; liqinghai@ahpu.edu.cn

Contents

1. General Information----------1
2. Typical procedures for synthesis of **3a-3s**----------2
3. Analytical data for **3a-3s**----------2-6
4. ^{1}HNMR and ^{13}CNMR spectra for **3a-3s**----------7-25

1. General Information

NMR spectra were recorded on Bruker AV300, AV400 or AV500 NMR spectrometer in $CDCl_3$ or DMSO-d_6. TMS was used as an internal standard. Chemical shifts (δ) and J values are reported in ppm and Hz, respectively. Single-crystal X-ray diffraction was performed on a Bruker SMART CCD area detector diffractometer. IR spectra were recorded on a Bruker VECTOR-22 instrument in KBr pellet. All melting points were determined on a XT-4 binocular microscope (Beijing Tech Instrument Co., China) and are not corrected. High-resolution mass spectra (HRMS) were recorded on a Micromass GCT-MS spectrometer with ESI mode. Analytical TLC and column chromatography were performed on silica gel GF254, and silica gel H60, respectively. HPLC was conducted on an Agilent 1100 liquid chromatograph with a diode-array detector using a Zorbax Eclipse XDB-C18 (4.6 mm × 250 mm) with *n*-hexane:2-propanol (4:1) as the eluent (2 mL/min), and was monitored at 254 nm. The mixer mill MM 400 (Retsch GmbH, Germany) was used for all ball-milling reactions. Styrene, all liquid benzaldehydes and anilines were further purification in standard manners before use. All solid benzaldehydes and anilines were purchased from Acros or Aldrich Chemical Co, and used without further purification. All solvents were obtained from SCRC (Sinopharm Chemical Reagent Co., Ltd) in AR grade and used without further purification.

2. Typical procedures for synthesis of 3a-3s

Aniline **1** (2.0 mmol) and benzaldehyde **2** (2.0 mmol), together with a stainless ball of 7.0 mm in diameter, were introduced into a stainless jar (25 mL). The same mixture was also introduced into a second parallel jar. The two reaction vessels were sealed with screw caps, fixed on the vibration arms of a ball-milling apparatus (mixer mill MM400, Retsch GmbH, Haan, Germany) and were vibrated vigorously at a rate of 1800 rounds per minute (30 Hz) at room temperature for designated time (Time 1). After the vessels were opened, styrene (2.5 mmol) and $FeCl_3$ (0.5 mmol) were added into the in situ generated imine, and the sealed vessels were continued to vibrate for designated time (Time 2). The reaction mixtures were immersed in 30 mL diluted hydrochloric acid (~0.6 N) with the aid of ultrasonic irradiation. After Büchner filtration and wash with water for several times, the solid was collected and recrystallized from $EtOH/H_2O$ (v/v = 5/1) to afford the desired cis-2, 4-diphenyl-1,2,3,4-tetrahydroquinoline **3**.

3. Analytical data for 3a-3s

***Cis*-2,4-diphenyl-1,2,3,4-tetrahydroquinoline (3a)**

White solid, m. p. 97–100 ^oC; IR (KBr) ν 3386, 3028, 2947, 1603, 1473, 1306, 1250, 752 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ (ppm) 7.48–7.50 (m, 2 H, ArH), 7.26–7.41 (m, 8 H, ArH), 7.02–7.07 (m, 1 H, ArH), 6.66–6.69 (m, 1 H, ArH), 6.58–6.62 (m, 2 H, ArH), 4.64 (dd, J = 10.6, 3.0 Hz, 1 H, CH), 4.34 (dd, J = 11.6, 5.8 Hz, 1 H, CH), 4.11 (brs, 1 H, NH), 2.19–2.35 (m, 2 H, CH_2); ^{13}C NMR ($CDCl_3$, 75 MHz) δ (ppm) 145.4, 144.0, 129.8, 128.8, 128.7, 127.9, 127.4, 126.7, 126.6, 124.8, 117.7, 114.4, 57.3, 45.0, 42.2; HRMS (ESI) *m/z* calcd for $C_{21}H_{20}N$ $(M+H)^+$: 286.1596, found: 286.1587.

***Cis*-2-(4-chlorophenyl)-4-phenyl-1,2,3,4-tetrahydroquinoline (3b)**

Pale-yellow solid, m. p. 147–149 ^oC; IR (KBr) ν 3388, 3086, 2947, 1604, 1475, 1250, 1014, 758 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ (ppm) 7.41 (d, J = 8.4 Hz, 2 H, ArH), 7.31–7.35 (m, 4 H, ArH), 7.24–7.26 (m, 3 H, ArH), 7.03 (t, J = 7.1 Hz, 1 H, ArH), 6.65 (t, J = 7.0 Hz, 1 H, ArH), 6.59–6.61 (m, 2 H, ArH), 4.60 (dd, J = 10.8, 2.6 Hz, 1 H, CH), 4.31 (dd, J = 11.8, 5.5 Hz, 1 H, CH), 4.05 (brs, 1 H, NH), 2.12–2.31 (m, 2 H, CH_2); ^{13}C NMR ($CDCl_3$, 75 MHz) δ (ppm) 145.3, 142.6, 133.4, 129.9, 128.9, 128.8, 128.5, 128.2, 127.8, 127.4, 126.7, 124.8, 118.0, 114.6, 56.8, 45.0, 42.3; HRMS (ESI) *m/z* calcd for $C_{21}H_{19}ClN$ $(M+H)^+$: 320.1206, found: 320.1201.

***Cis*-2-(4-nitrophenyl)-4-phenyl-1,2,3,4-tetrahydroquinoline (3c)**

Yellow solid, m. p. 156–159 ^oC; IR (KBr) ν 3380, 3027, 2954, 1606, 1528, 1349, 1253, 761 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ (ppm) 8.23 (d, J = 8.5 Hz, 2 H, ArH), 7.68 (d, J = 8.5 Hz, 2 H, ArH), 7.24–7.39 (m, 5 H, ArH), 7.10 (t, J = 7.0 Hz, 1 H, ArH), 6.64–6.74 (m, 3 H, ArH), 4.77 (dd, J = 10.8, 2.0 Hz, 1 H, CH), 4.38 (dd, J = 11.9, 5.3 Hz, 1 H, CH), 4.19 (brs, 1 H, NH), 2.21–2.38 (m, 2 H, CH_2); ^{13}C NMR ($CDCl_3$, 75 MHz) δ (ppm) 151.6, 147.4, 144.9, 144.8, 129.8, 128.7 (2 C), 127.5 (2 C), 126.8, 124.8, 124.0, 118.4, 114.8, 56.8, 44.7, 42.1; HRMS (ESI) *m/z* calcd for $C_{21}H_{19}N_2O_2$ $(M+H)^+$: 331.1447, found: 331.1441.

***Cis*-2-(3-nitrophenyl)-4-phenyl-1,2,3,4-tetrahydroquinoline (3d)**

Deep-yellow solid, m. p. 162–164 ^{o}C; IR (KBr) *v* 3370, 3029, 2923, 1604, 1527, 1350, 1253, 757 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ (ppm) 8.37 (s, 1 H, ArH), 8.16 (d, *J* = 7.4 Hz, 1 H, ArH), 7.81 (d, *J* = 7.5 Hz, 1 H, ArH), 7.54 (t, *J* = 7.9 Hz, 1 H, ArH), 7.24–7.32 (m, 5 H, ArH), 7.06 (t, *J* = 6.9 Hz, 1 H, ArH), 6.61–6.69 (m, 3 H, ArH), 4.75 (dd, *J* = 10.8, 2.2 Hz, 1 H, CH), 4.34 (dd, *J* = 11.9, 5.4 Hz, 1 H, CH), 4.14 (brs, 1 H, NH), 2.20–2.35 (m, 2 H, CH_2); ^{13}C NMR ($CDCl_3$, 75 MHz) δ (ppm) 148.5, 146.2, 144.9, 144.8, 132.9, 129.8, 129.7, 128.7 (2 C), 127.5, 126.7, 124.7, 122.8, 121.7, 118.4, 114.8, 56.6, 44.7, 42.3; HRMS (ESI) *m/z* calcd for $C_{21}H_{19}N_2O_2$ (M+H)$^{+}$: 331.1447, found: 331.1443.

***Cis*-6-methyl-2,4-diphenyl-1,2,3,4-tetrahydroquinoline (3e)**

White solid, m. p. 123–125 ^{o}C; IR (KBr) *v* 3401, 3030, 2925, 1589, 1488, 1355, 825, 701 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ (ppm) 7.48 (d, *J* = 7.1 Hz, 2 H, ArH), 7.25–7.40 (m, 8 H, ArH), 6.86 (d, *J* = 7.7 Hz, 1 H, ArH), 6.55 (s, 1 H, ArH), 6.51 (d, *J* = 6.6 Hz, 1 H, ArH), 4.59 (dd, *J* = 10.7, 2.3 Hz, 1 H, CH), 4.32 (dd, *J* = 11.6, 5.7 Hz, 1 H, CH), 3.95 (brs, 1 H, NH), 2.07–2.33 (m, 2 H, CH_2), 2.12 (s, 3 H, CH_3); ^{13}C NMR ($CDCl_3$, 75 MHz) δ (ppm) 145.9, 144.4, 143.4, 130.4, 129.0, 128.9, 128.8, 128.2, 128.0, 127.0, 126.9, 126.8, 125.0, 114.9, 57.7, 45.3, 42.9, 20.9; HRMS (ESI) *m/z* calcd for $C_{22}H_{22}N$ (M+H)$^{+}$: 300.1752, found: 300.1753.

***Cis*-6-methyl-4-phenyl-2-p-tolyl-1,2,3,4-tetrahydroquinoline (3f)**

White solid, m. p. 147–149 ^{o}C; IR (KBr) *v* 3435, 3030, 2920, 1589, 1491, 1357, 1240, 825, 702 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ (ppm) 7.36 (d, *J* = 8.0 Hz, 2 H, ArH), 7.25–7.31 (m, 5 H, ArH), 7.18 (d, *J* = 7.7 Hz, 2 H, ArH), 6.84 (d, *J* = 7.7 Hz, 1 H, ArH), 6.53 (s, 1 H, ArH), 6.50 (d, *J* = 6.7 Hz, 1 H, ArH), 4.54 (dd, *J* = 10.4, 2.7 Hz, 1 H, CH), 4.30 (dd, *J* = 11.4, 6.0 Hz, 1 H, CH), 3.92 (brs, 1 H, NH), 2.36 (s, 3 H, CH_3), 2.18–2.30 (m, 2 H, CH_2), 2.11 (s, 3 H, CH_3); ^{13}C NMR (DMSO-d_6, 100 MHz) δ (ppm) 145.5, 143.6, 141.1, 135.9, 128.7, 128.5, 128.1 (2 C), 127.0, 126.2, 125.9, 124.0, 123.6, 114.3, 55.6, 43.9, 41.9, 20.4, 19.9; HRMS (ESI) *m/z* calcd for $C_{23}H_{24}N$ (M+H)$^{+}$: 314.1909, found: 314.1906.

***Cis*-2-(4-chlorophenyl)-6-methyl-4-phenyl-1,2,3,4-tetrahydroquinoline (3g)**

Pale-yellow solid, m. p. 151–153 ^{o}C; IR (KBr) *v* 3369, 3025, 2946, 1616, 1504, 1248, 1086, 831, 702 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ (ppm) 7.23–7.41 (m, 9 H, ArH), 6.85 (d, *J* = 7.8 Hz, 1 H, ArH), 6.48–6.54 (m, 2 H, ArH), 4.55 (dd, *J* = 10.8, 2.3 Hz, 1 H, CH), 4.28 (dd, *J* = 11.8, 5.6 Hz, 1 H, CH), 3.93 (brs, 1 H, NH), 2.17–2.28 (m, 2 H, CH_2), 2.11 (s, 3 H, CH_3); ^{13}C NMR ($CDCl_3$, 75 MHz) δ (ppm) 145.5, 143.0, 142.7, 133.3, 130.2, 129.1, 128.7, 128.4, 128.0, 127.5, 127.2, 126.6, 124.8, 114.7, 56.9, 45.0, 42.7, 20.6; HRMS (ESI) *m/z* calcd for $C_{22}H_{21}ClN$ (M+H)$^{+}$: 334.1363, found: 334.1355.

***Cis*-6-methyl-2-(4-nitrophenyl)-4-phenyl-1,2,3,4-tetrahydroquinoline (3h)**

Deep-yellow solid, m. p. 139–141 ^{o}C; IR (KBr) *v* 3376, 3041, 2910, 1608, 1522, 1346, 850, 702 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ (ppm) 8.21 (d, *J* = 8.6 Hz, 2 H, ArH), 7.65 (d, *J* = 8.6 Hz, 2 H, ArH), 7.22–7.35 (m, 5 H, ArH), 6.87 (d, *J* = 7.8 Hz, 1 H, ArH), 6.57 (d, *J* = 8.0 Hz, 1 H, ArH), 6.49 (s, 1 H, ArH), 4.70 (dd,

J = 11.0, 2.1 Hz, 1 H, CH), 4.31 (dd, *J* = 11.9, 5.4 Hz, 1 H, CH), 4.03 (brs, 1 H, NH), 2.14–2.32 (m, 2 H, CH_2), 2.12 (s, 3 H, CH_3); ^{13}C NMR ($CDCl_3$, 75 MHz) δ (ppm) 151.7, 147.4, 145.0, 142.5, 130.1, 128.7 (2 C), 128.1, 127.6, 127.5, 126.7, 124.7, 123.9, 114.9, 56.9, 44.8, 42.5, 20.6; HRMS (ESI) *m/z* calcd for $C_{22}H_{21}ClN$ $(M+H)^+$: 345.1603, found: 345.1652.

***Cis*-6-methyl-2-(3-nitrophenyl)-4-phenyl-1,2,3,4-tetrahydroquinoline (3i)**

Orange solid, m. p. 154–156 ^{o}C; IR (KBr) *v* 3367, 3041, 2920, 1616, 1522, 1356, 816, 700 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ (ppm) 8.36 (s, 1 H, ArH), 8.17 (d, *J* = 8.0 Hz, 1 H, ArH), 7.83 (d, *J* = 8.1 Hz, 1 H, ArH), 7.55 (t, *J* = 8.2 Hz, 1 H, ArH), 7.22–7.33 (m, 5 H, ArH), 6.86 (d, *J* = 8.0 Hz, 1 H, ArH), 6.57 (d, *J* = 8.0 Hz, 1 H, ArH), 6.50 (s, 1 H, ArH), 4.70 (dd, *J* = 11.0, 2.7 Hz, 1 H, CH), 4.32 (dd, *J* = 11.9, 5.6 Hz, 1 H, CH), 3.98 (brs, 1 H, NH), 2.17–2.33 (m, 2 H, CH_2), 2.12 (s, 3 H, CH_3); ^{13}C NMR ($CDCl_3$, 75 MHz) δ (ppm) 148.5, 146.4, 145.1, 142.6, 133.0, 130.2, 129.7, 128.7 (2 C), 128.1, 127.6, 126.7, 124.7, 122.7, 121.7, 115.0, 56.8, 44.8, 42.7, 20.6; HRMS (ESI) *m/z* calcd for $C_{22}H_{21}ClN$ $(M+H)^+$: 345.1603, found: 345.1658.

***Cis*-6-methoxy-2,4-diphenyl-1,2,3,4-tetrahydroquinoline (3j)**

Pale solid, m. p. 110–112 ^{o}C; IR (KBr) *v* 3371, 3030, 2927, 1622, 1498, 1227, 1035, 808, 700 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ (ppm) 7.41 (d, *J* = 7.2 Hz, 2 H, ArH), 7.18–7.33 (m, 8 H, ArH), 6.59 (d, *J* = 8.4 Hz, 1 H, ArH), 6.51 (d, *J* = 8.4 Hz, 1 H, ArH), 6.22 (s, 1 H, ArH), 4.49 (dd, *J* = 10.8, 2.1 Hz, 1 H, CH), 4.26 (dd, *J* = 11.8, 5.8 Hz, 1 H, CH), 3.77 (brs, 1 H, NH), 3.55 (s, 3 H, OCH_3), 2.13–2.27 (m, 2 H, CH_2); ^{13}C NMR ($CDCl_3$, 75 MHz) δ (ppm) 152.2, 145.4, 144.1, 139.8, 128.8, 128.7 (2 C), 127.8, 126.8, 126.7, 126.1, 115.6, 115.5, 113.3, 57.6, 55.8, 45.4, 42.5; HRMS (ESI) *m/z* calcd for $C_{22}H_{22}NO$ $(M+H)^+$: 316.1701, found: 316.1704.

***Cis*-6-methoxy-4-phenyl-2-p-tolyl-1,2,3,4-tetrahydroquinoline (3k)**

Pale-yellow solid, m. p. 142–145 ^{o}C; IR (KBr) *v* 3433, 3060, 2929, 1622, 1490, 1360, 1228, 827 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ (ppm) 7.23–7.36 (m, 7 H, ArH), 7.16 (d, *J* = 7.7 Hz, 2 H, ArH), 6.63–6.65 (m, 1 H, ArH), 6.55 (d, *J* = 8.6 Hz, 1 H, ArH), 6.26 (s, 1 H, ArH), 4.51 (dd, *J* = 10.7, 2.3 Hz, 1 H, CH), 4.30 (dd, *J* = 11.6, 5.9 Hz, 1 H, CH), 3.82 (brs, 1 H, NH), 3.60 (s, 3 H, OCH_3), 2.35 (s, 3 H, CH_3), 2.17–2.27 (m, 2 H, CH_2); ^{13}C NMR (DMSO-d_6, 125 MHz) δ (ppm) 151.6, 146.4, 142.4, 141.4, 137.1, 129.7, 129.3 (2 C), 127.5, 127.2, 125.8, 116.2, 115.5, 113.4, 56.9, 56.0, 45.3, 43.1, 21.6; HRMS (ESI) *m/z* calcd for $C_{23}H_{24}NO$ $(M+H)^+$: 330.1858, found: 330.1849.

***Cis*-2-(4-chlorophenyl)-6-methoxy-4-phenyl-1,2,3,4-tetrahydroquinoline (3l)**

White solid, m. p. 134–136 ^{o}C; IR (KBr) *v* 3436, 3028, 2914, 1622, 1498, 1228, 1092, 767 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ (ppm) 7.44 (d, *J* = 8.1 Hz, 2 H, ArH), 7.35 (d, *J* = 8.1 Hz, 2 H, ArH), 7.19–7.28 (m, 5 H, ArH), 6.60 (d, *J* = 8.7 Hz, 1 H, ArH), 6.51 (d, *J* = 8.7 Hz, 1 H, ArH), 6.21 (s, 1 H, ArH), 4.46 (d, *J* = 10.8 Hz, 1 H, CH), 4.25 (dd, *J* = 11.7, 5.5 Hz, 1 H, CH), 3.72 (brs, 1 H, NH), 3.55 (s, 3 H, OCH_3), 2.11–2.22 (m, 2 H, CH_2); ^{13}C NMR ($CDCl_3$, 75 MHz) δ (ppm) 152.2, 145.1, 142.6, 139.4, 133.2, 128.8,

128.7, 128.3, 127.5, 126.7, 126.0, 115.6, 115.4, 113.3, 56.7, 55.7, 45.2, 42.5; HRMS (ESI) *m/z* calcd for $C_{22}H_{21}ClNO$ $(M+H)^+$: 350.1312, found: 350.1317.

***Cis*-2-6-methoxy-2-(4-nitrophenyl)-4-phenyl-1,2,3,4-tetrahydroquinoline (3m)**

Yellow solid, m. p. 131–133 °C; IR (KBr) *v* 3381, 3028, 2918, 1603, 1518, 1348, 1225, 854 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ (ppm) 8.38 (s, 1 H, ArH), 8.21 (d, *J* = 8.6 Hz, 1 H, ArH), 7.66 (d, *J* = 8.4 Hz, 1 H, ArH), 7.59 (s, 1 H, ArH), 7.22–7.31 (m, 5 H, ArH), 6.67 (d, *J* = 8.7 Hz, 1 H, ArH), 6.61 (d, *J* = 8.7 Hz, 1 H, ArH), 6.28 (s, 1 H, ArH), 4.67 (d, *J* = 10.0 Hz, 1 H, CH), 4.32 (m, 1 H, CH), 3.60 (s, 3 H, OCH_3), 2.14–2.28 (m, 2 H, CH_2); ^{13}C NMR ($CDCl_3$, 75 MHz) δ (ppm) 152.4, 151.7, 147.3, 144.8, 138.9, 128.7 (2 C), 127.5, 126.8, 123.9, 115.8, 115.3, 113.4, 57.0, 55.7, 45.0, 42.3; HRMS (ESI) *m/z* calcd for $C_{22}H_{21}N_2O_3$ $(M+H)^+$: 361.1552, found: 361.1544.

***Cis*-2-6-methoxy-2-(3-nitrophenyl)-4-phenyl-1,2,3,4-tetrahydroquinoline (3n)**

Red solid, m. p. 161–163 °C; IR (KBr) *v* 3363, 3029, 2931, 1583, 1503, 1354, 1228, 1037, 798 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ (ppm) 8.37 (s, 1 H, ArH), 8.14 (d, *J* = 8.0 Hz, 1 H, ArH), 7.81 (d, *J* = 7.6 Hz, 1 H, ArH), 7.52 (t, *J* = 7.9 Hz, 1 H, ArH), 7.22–7.34 (m, 5 H, ArH), 6.60–6.70 (m, 2 H, ArH), 6.28 (d, *J* = 1.6 Hz, 1 H, ArH), 4.68 (dd, *J* = 10.9, 2.0 Hz, 1 H, CH), 4.33 (dd, *J* = 11.9, 5.6 Hz, 1 H, CH), 3.90 (brs, 1 H, NH), 3.61 (s, 3 H, OCH_3), 2.17–2.35 (m, 2 H, CH_2); ^{13}C NMR ($CDCl_3$, 75 MHz) δ (ppm) 152.4, 148.5, 146.3, 144.7, 138.9, 132.9, 129.6, 128.7 (2 C), 126.7, 125.9, 122.7, 115.8, 115.3, 113.4, 56.8, 55.7, 45.0, 42.4; HRMS (ESI) *m/z* calcd for $C_{22}H_{21}N_2O_3$ $(M+H)^+$: 361.1552, found: 361.1555.

***Cis*-6-chloro-2-(4-chlorophenyl)-4-phenyl-1,2,3,4-tetrahydroquinoline (3o)**

White solid, m. p. 152–154 °C; IR (KBr) *v* 3438, 3047, 2925, 1589, 1485, 1357, 829, 700 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ (ppm) 7.21–7.40 (m, 9 H, ArH), 6.96 (d, *J* = 8.4 Hz, 1 H, ArH), 6.61 (s, 1 H, ArH), 6.51 (d, *J* = 8.4 Hz, 1 H, ArH), 4.57 (dd, *J* = 11.0, 2.4 Hz, 1 H, CH), 4.25 (dd, *J* = 12.0, 5.4 Hz, 1 H, CH), 4.05 (brs, 1 H, NH), 2.05–2.29 (m, 2 H, CH_2); ^{13}C NMR (DMSO-d_6, 100 MHz) δ (ppm) 144.6, 144.1, 142.6, 131.5, 128.3, 128.2, 128.1, 128.0, 127.5, 126.4, 126.2, 125.5, 119.0, 115.4, 54.8, 43.4, 40.2; HRMS (ESI) *m/z* calcd for $C_{21}H_{18}Cl_2N$ $(M+H)^+$: 354.0816, found: 354.0833.

***Cis*-6-chloro-2-(4-nitrophenyl)-4-phenyl-1,2,3,4-tetrahydroquinoline (3p)**

Yellow solid, m. p. 167–169 °C; IR (KBr) *v* 3377, 3026, 2916, 1599, 1523, 1346, 849, 700 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ (ppm) 8.17 (d, *J* = 8.7 Hz, 2 H, ArH), 7.58 (d, *J* = 8.7 Hz, 2 H, ArH), 7.15–7.31 (m, 5 H, ArH), 6.94 (dd, *J* = 8.4, 1.8 Hz, 1 H, ArH), 6.58 (s, 1 H, ArH), 6.51 (d, *J* = 8.7 Hz, 1 H, ArH), 4.67 (dd, *J* = 10.8, 2.2 Hz, 1 H, CH), 4.23 (dd, *J* = 12.0, 5.4 Hz, 1 H, CH), 4.08 (brs, 1 H, NH), 2.04–2.28 (m, 2 H, CH_2); ^{13}C NMR ($CDCl_3$, 125 MHz) δ (ppm) 151.4, 147.9, 144.2, 143.7, 129.6, 129.3, 129.0, 128.2, 127.9, 127.5, 126.7, 124.2, 123.2, 116.3, 57.1, 45.0, 42.0; HRMS (ESI) *m/z* calcd for $C_{21}H_{18}ClN_2O_2$ $(M+H)^+$: 365.1057, found: 365.1070.

***Cis*-6-chloro-2-(3-nitrophenyl)-4-phenyl-1,2,3,4-tetrahydroquinoline (3q)**

Yellow solid, m. p. 186–188 ^{o}C; IR (KBr) *v* 3359, 3087, 2923, 1599, 1518, 1352, 1095, 704 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ (ppm) 8.34 (s, 1 H, ArH), 8.15 (d, *J* = 7.8 Hz, 1 H, ArH), 7.78 (d, *J* = 7.8 Hz, 1 H, ArH), 7.54 (d, *J* = 7.8 Hz, 1 H, ArH), 7.51 (d, *J* = 7.8 Hz, 1 H, ArH), 7.20–7.35 (m, 4 H, ArH), 6.99 (dd, *J* = 8.4, 1.8 Hz, 1 H, ArH), 6.63 (s, 1 H, ArH), 6.56 (d, *J* = 8.4 Hz, 1 H, ArH), 4.71 (dd, *J* = 11.1, 2.4 Hz, 1 H, CH), 4.27 (dd, *J* = 12.0, 5.4 Hz, 1 H, CH), 4.13 (brs, 1 H, NH), 2.15–2.34 (m, 2 H, CH_2); ^{13}C NMR ($CDCl_3$, 125 MHz) δ (ppm) 149.0, 146.2, 144.3, 143.7, 133.2, 130.1, 129.7, 129.3, 129.0, 127.8, 127.4, 126.7, 123.3, 123.2, 122.0, 116.3, 57.0, 45.0, 42.2; HRMS (ESI) *m/z* calcd for $C_{21}H_{18}ClN_2O_2$ (M+H)$^{+}$: 365.1057, found: 365.1066.

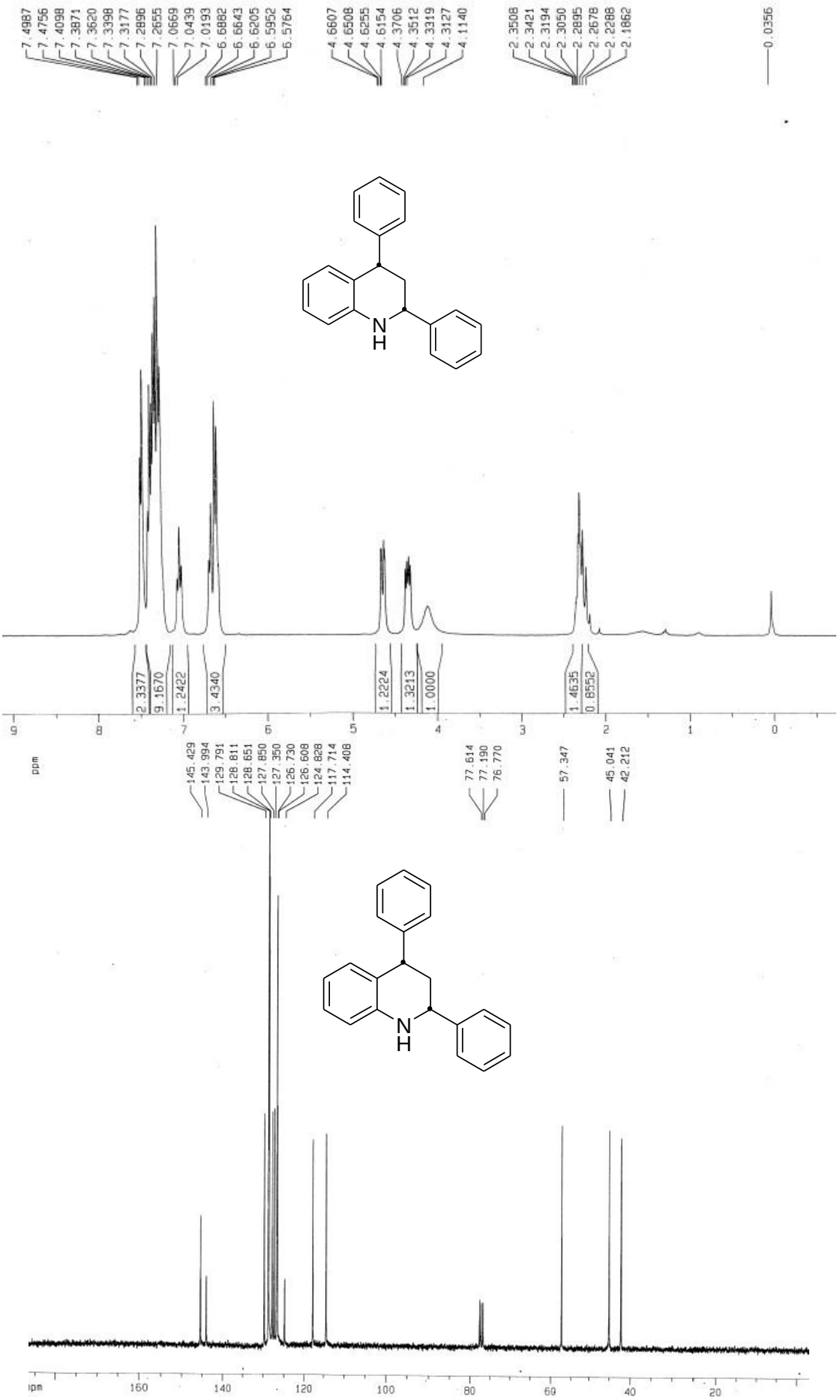
***Cis*-7-chloro-2-(4-nitrophenyl)-4-phenyl-1,2,3,4-tetrahydroquinoline (3r)**

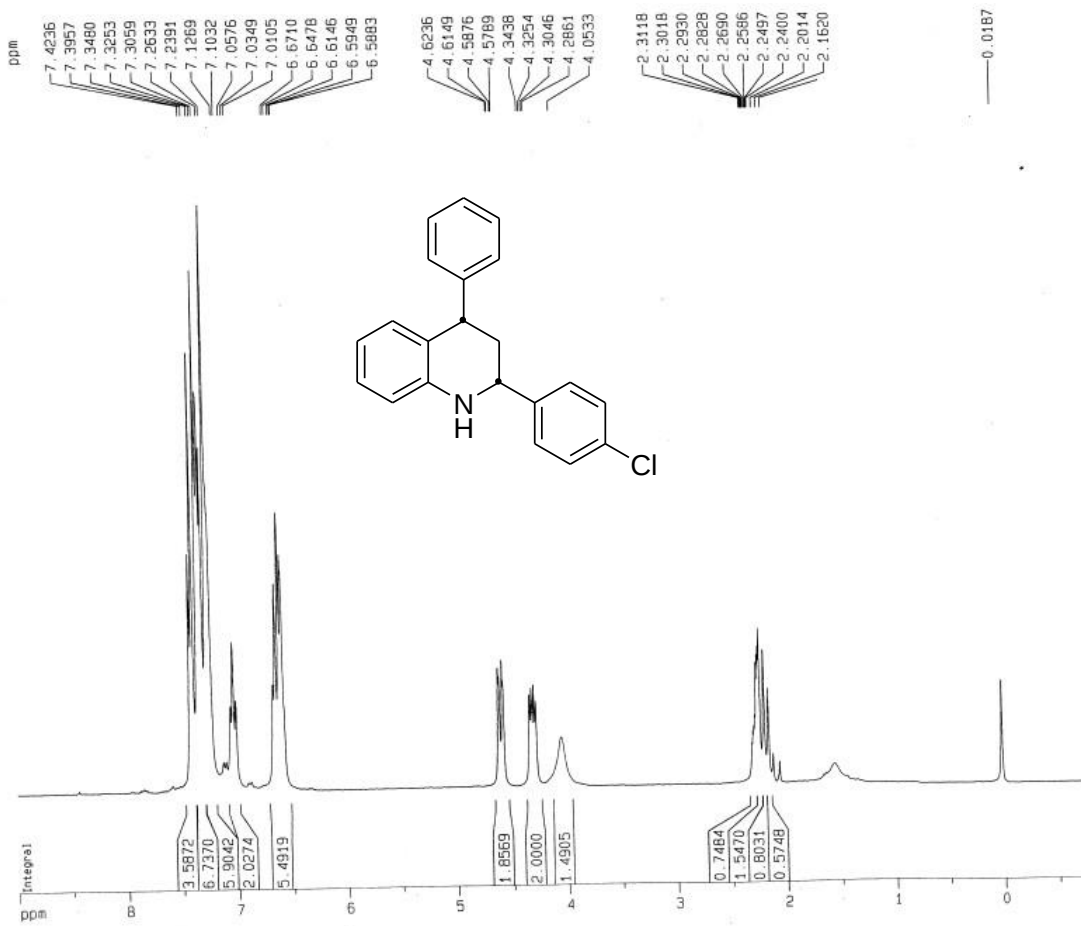
Yellow solid, m. p. 176–178 ^{o}C; IR (KBr) *v* 3369, 3026, 2924, 1603, 1503, 1352, 1092, 746 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ (ppm) 8.22 (d, *J* = 8.6 Hz, 2 H, ArH), 7.63 (d, *J* = 8.6 Hz, 2 H, ArH), 7.20–7.44 (m, 5 H, ArH), 6.61 (d, *J* = 8.2 Hz, 2 H, ArH), 6.57 (s, 1 H, ArH), 4.73 (d, *J* = 11.0 Hz, 1 H, CH), 4.25 (dd, *J* = 12.1, 5.2 Hz, 1 H, CH), 4.16 (brs, 1 H, NH), 2.05–2.33 (m, 2 H, CH_2); ^{13}C NMR (DMSO-d_6, 100 MHz) δ (ppm) 151.3, 146.7, 146.6, 144.0, 131.0, 129.7, 128.3, 128.1, 127.7, 126.3, 123.2, 122.5, 115.4, 112.9, 54.8, 42.9, 40.0; HRMS (ESI) *m/z* calcd for $C_{21}H_{18}ClN_2O_2$ (M+H)$^{+}$: 365.1057, found: 365.1062.

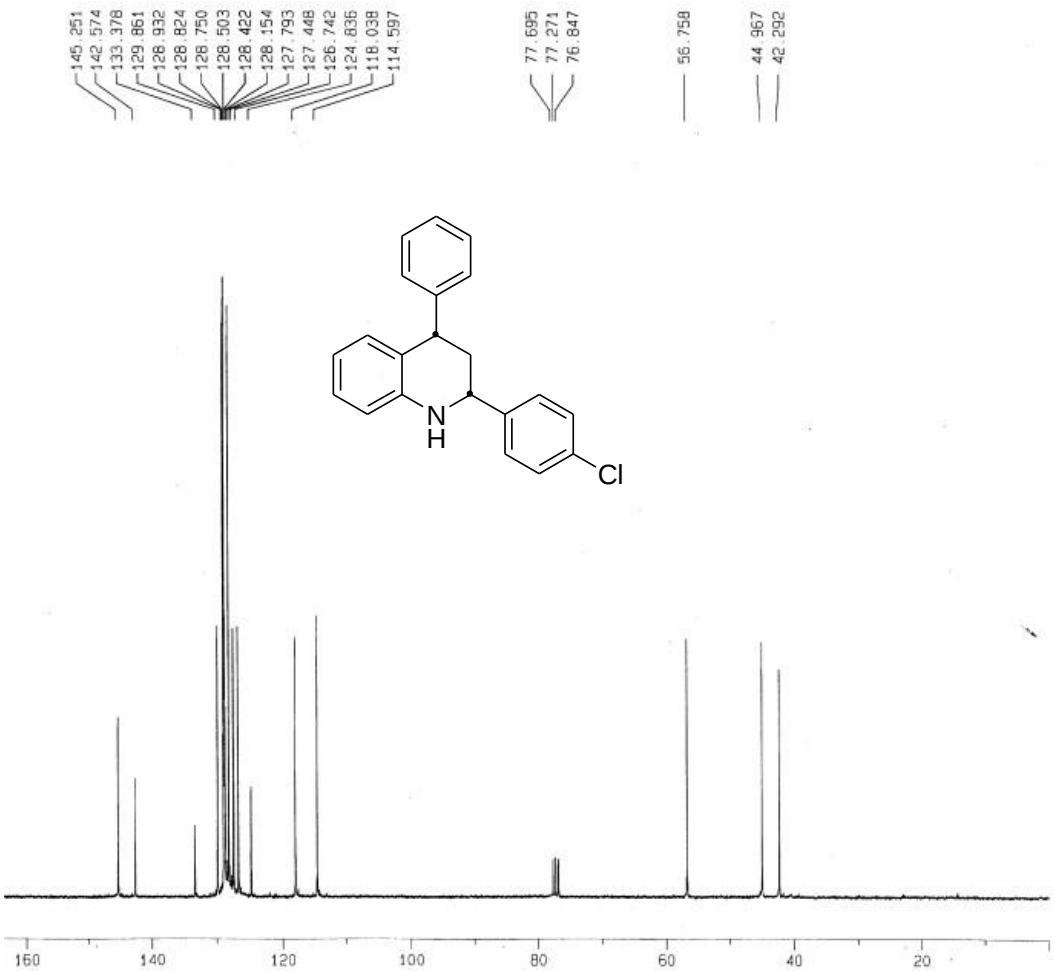
***Cis*-7-chloro-2-(3-nitrophenyl)-4-phenyl-1,2,3,4-tetrahydroquinoline (3s)**

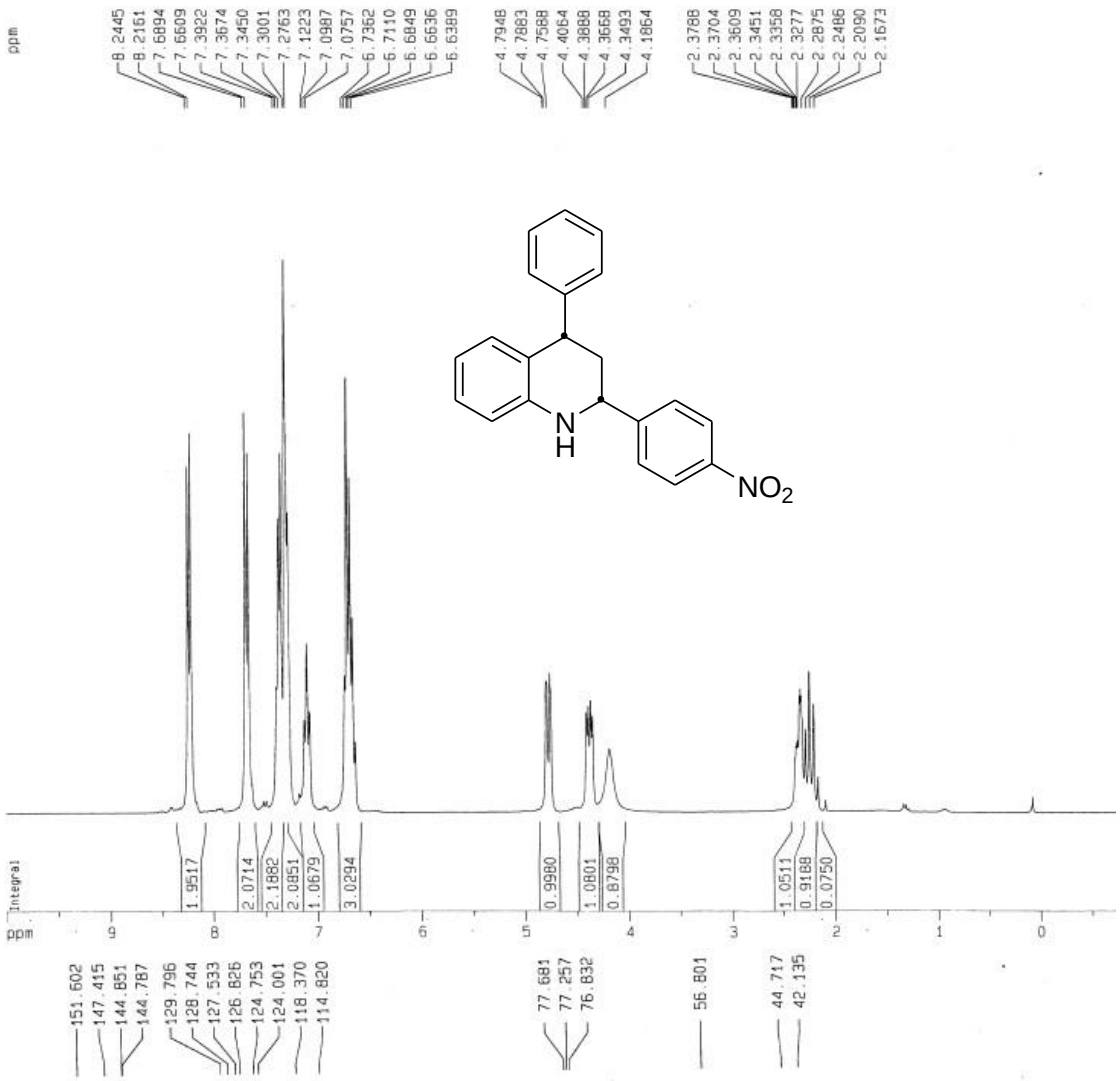
Yellow solid, m. p. 140–142 ^{o}C; IR (KBr) *v* 3405, 3029, 2865, 1603, 1525, 1349, 1088, 706 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ (ppm) 8.34 (s, 1 H, ArH), 8.16 (d, *J* = 8.0 Hz, 1 H, ArH), 7.79 (d, *J* = 7.6 Hz, 1 H, ArH), 7.55 (t, *J* = 7.9 Hz, 1 H, ArH), 7.21–7.35 (m, 5 H, ArH), 6.63 (s, 1 H, ArH), 6.57 (d, *J* = 7.8 Hz, 2 H, ArH), 4.74 (dd, *J* = 10.8, 2.3 Hz, 1 H, CH), 4.26 (dd, *J* = 12.0, 5.3 Hz, 1 H, CH), 4.17 (s, 1 H, NH), 2.12–2.35 (m, 2 H, CH_2); ^{13}C NMR (DMSO-d_6, 75 MHz) δ (ppm) 147.9, 146.9, 146.2, 144.4, 133.7, 131.2, 130.1, 130.0, 128.6, 128.5, 126.6, 122.8, 122.4, 121.4, 115.6, 113.1, 54.8, 43.1, 40.3; HRMS (ESI) *m/z* calcd for $C_{21}H_{18}ClN_2O_2$ (M+H)$^{+}$: 365.1057, found: 365.1073.

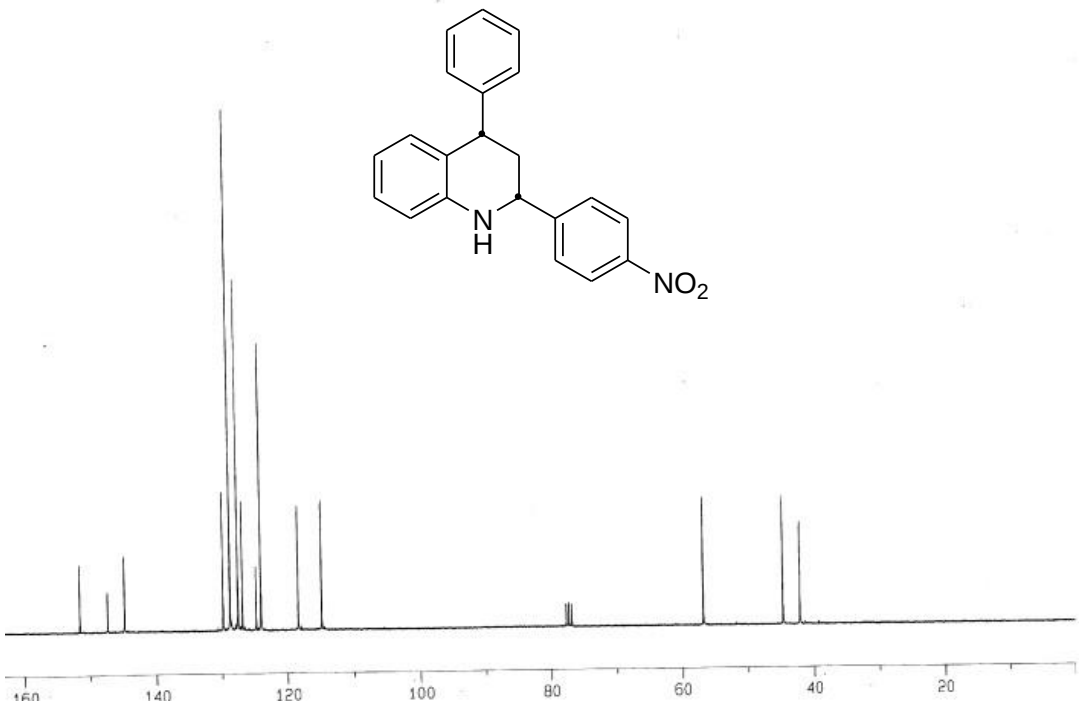
4. ^{1}HNMR and ^{13}CNMR spectra for compounds 3a-3s

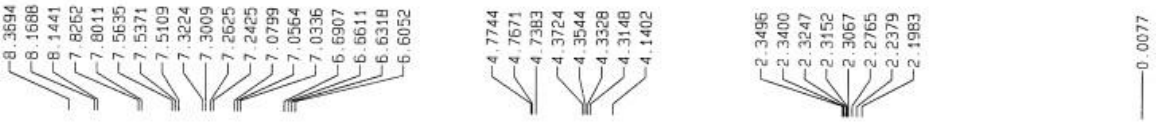


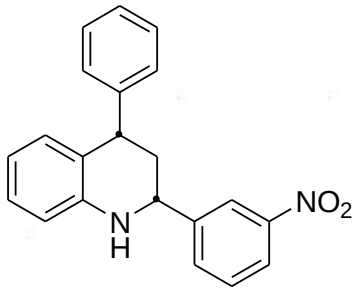

ppm
7.4236
7.3957
7.3480
7.3253
7.3059
7.2633
7.2391
7.1269
7.1032
7.0576
7.0349
7.0105
6.6710
6.6478
6.6146
6.5949
6.5883
4.6236
4.6149
4.5876
4.5769
4.3438
4.3254
4.3046
4.2861
4.0533
2.3118
2.3018
2.2930
2.2828
2.2690
2.2586
2.2497
2.2400
2.2014
2.1620
0.0187
N
H
Cl
Integral
3.5872
6.7370
5.9042
2.0274
5.4919
1.8569
2.0000
1.4905
0.7484
1.5470
0.8031
0.5748
ppm
8
7
6
5
4
3
2
1
0

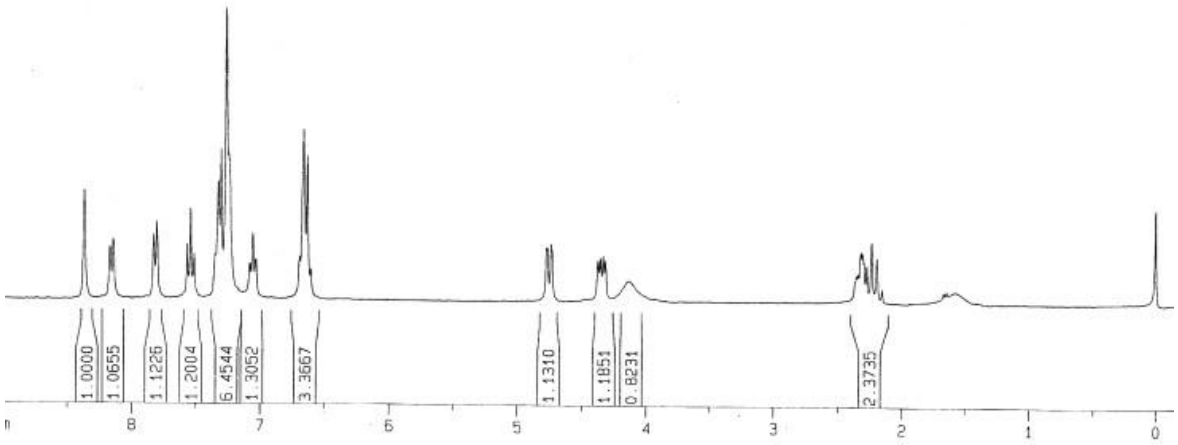

145.251
142.574
133.378
129.861
128.932
128.824
128.750
128.503
128.422
128.154
127.793
127.448
126.742
124.836
118.038
114.597
77.695
77.271
76.847
56.758
44.967
42.292
N
H
Cl
160
140
120
100
80
60
40
20

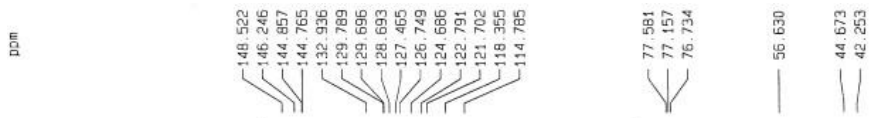

ppm
8.2445
8.2161
7.6894
7.6609
7.3922
7.3674
7.3450
7.3001
7.2763
7.1223
7.0987
7.0757
6.7362
6.7110
6.6849
6.6636
6.6389
4.7948
4.7883
4.7588
4.4064
4.3888
4.3668
4.3493
4.1864
2.3788
2.3704
2.3609
2.3451
2.3358
2.3277
2.2875
2.2486
2.2090
2.1673
N
H
NO2
Integral
1.9517
2.0714
2.1882
2.0851
1.0679
3.0294
0.9980
1.0801
0.8798
1.0511
0.9188
0.0750
ppm
9
8
7
6
5
4
3
2
1
0
151.602
147.415
144.851
144.787
129.796
128.744
127.533
126.826
124.753
124.001
118.370
114.820
77.681
77.257
76.832
56.801
44.717
42.135

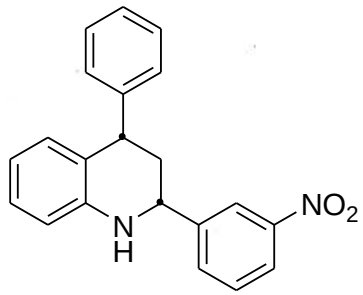

N
H
NO2
160
140
120
100
80
60
40
20


8.3694
8.1688
8.1441
7.8262
7.8011
7.5635
7.5371
7.5109
7.3224
7.3009
7.2625
7.2425
7.0799
7.0564
7.0336
6.6907
6.6611
6.6318
6.6052
4.7744
4.7671
4.7383
4.3724
4.3544
4.3328
4.3148
4.1402
2.3496
2.3400
2.3247
2.3152
2.3067
2.2765
2.2379
2.1983
0.0077

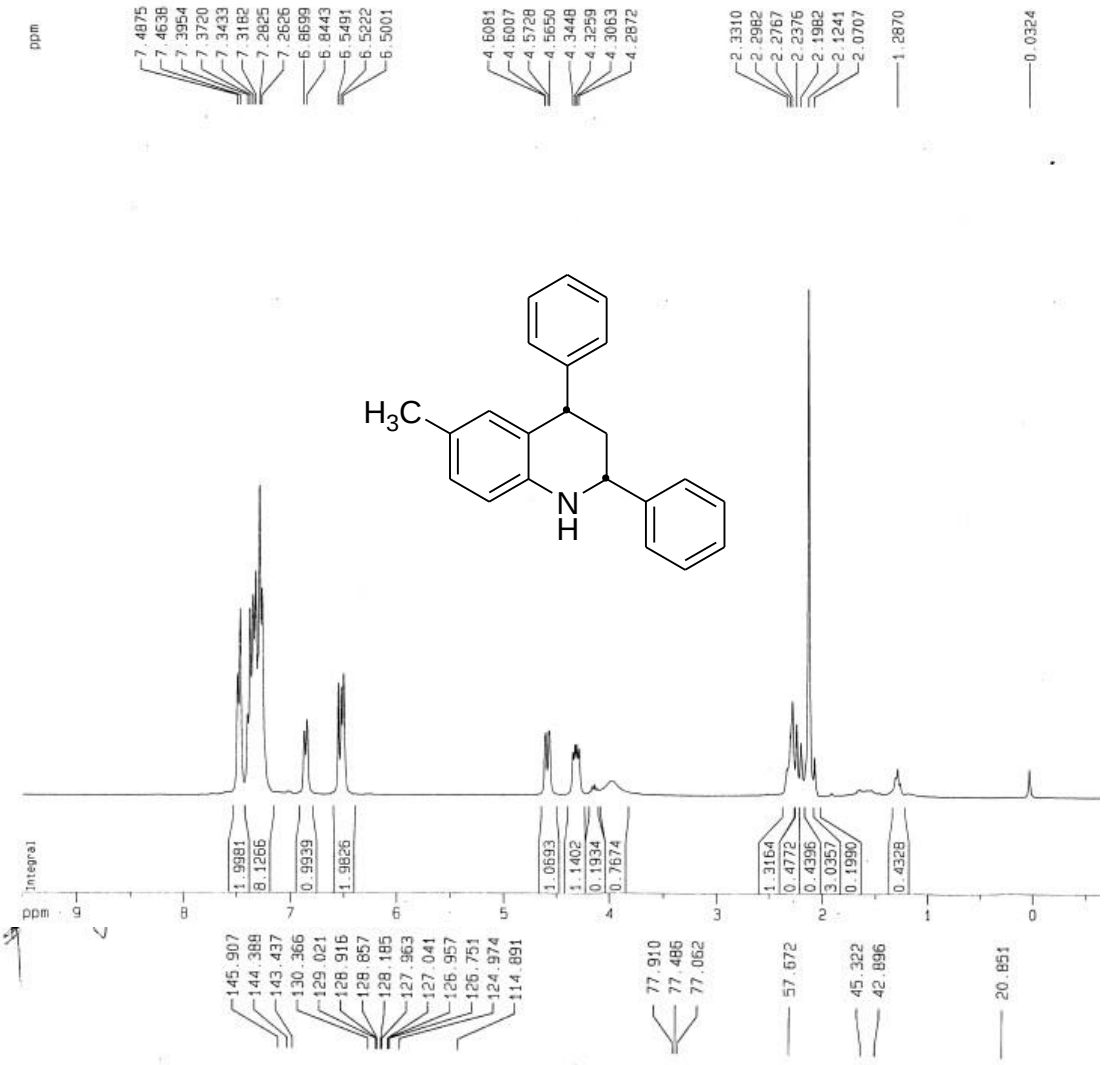

NO2
N
H

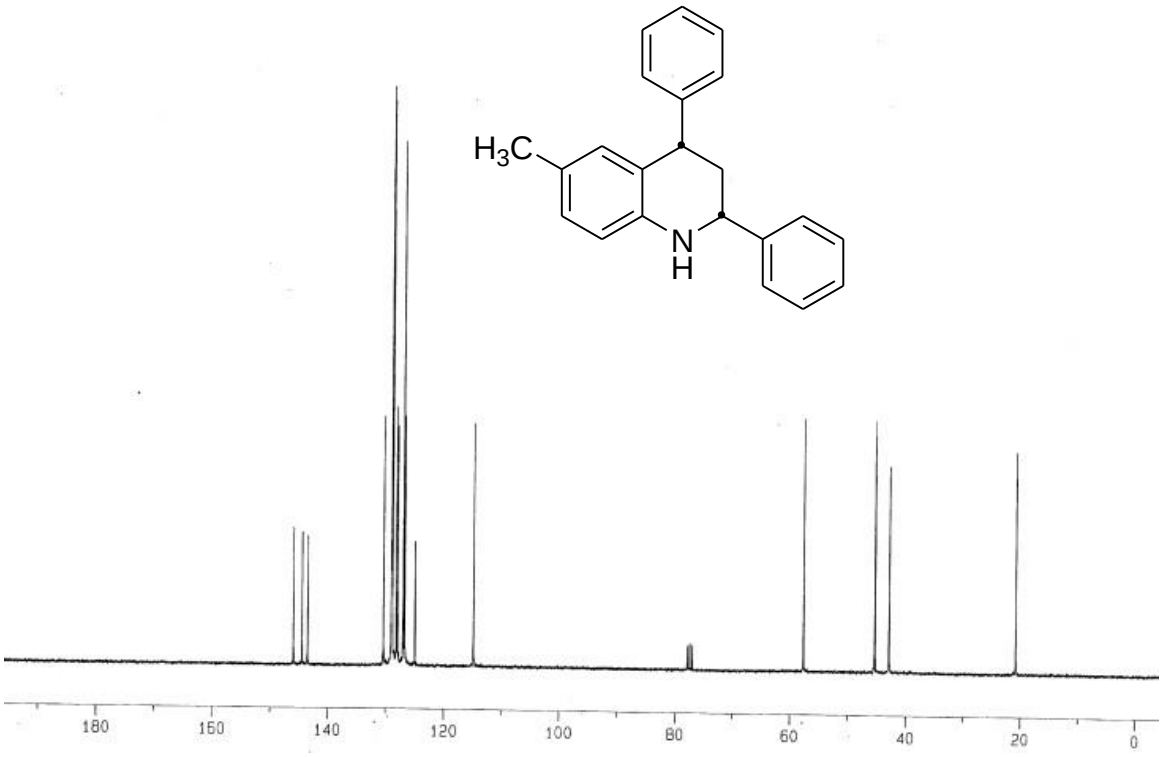

1.0000
1.0655
1.1226
1.2004
6.4544
1.3052
3.3667
1.1310
1.1851
0.8231
2.3735
8
7
6
5
4
3
2
1
0

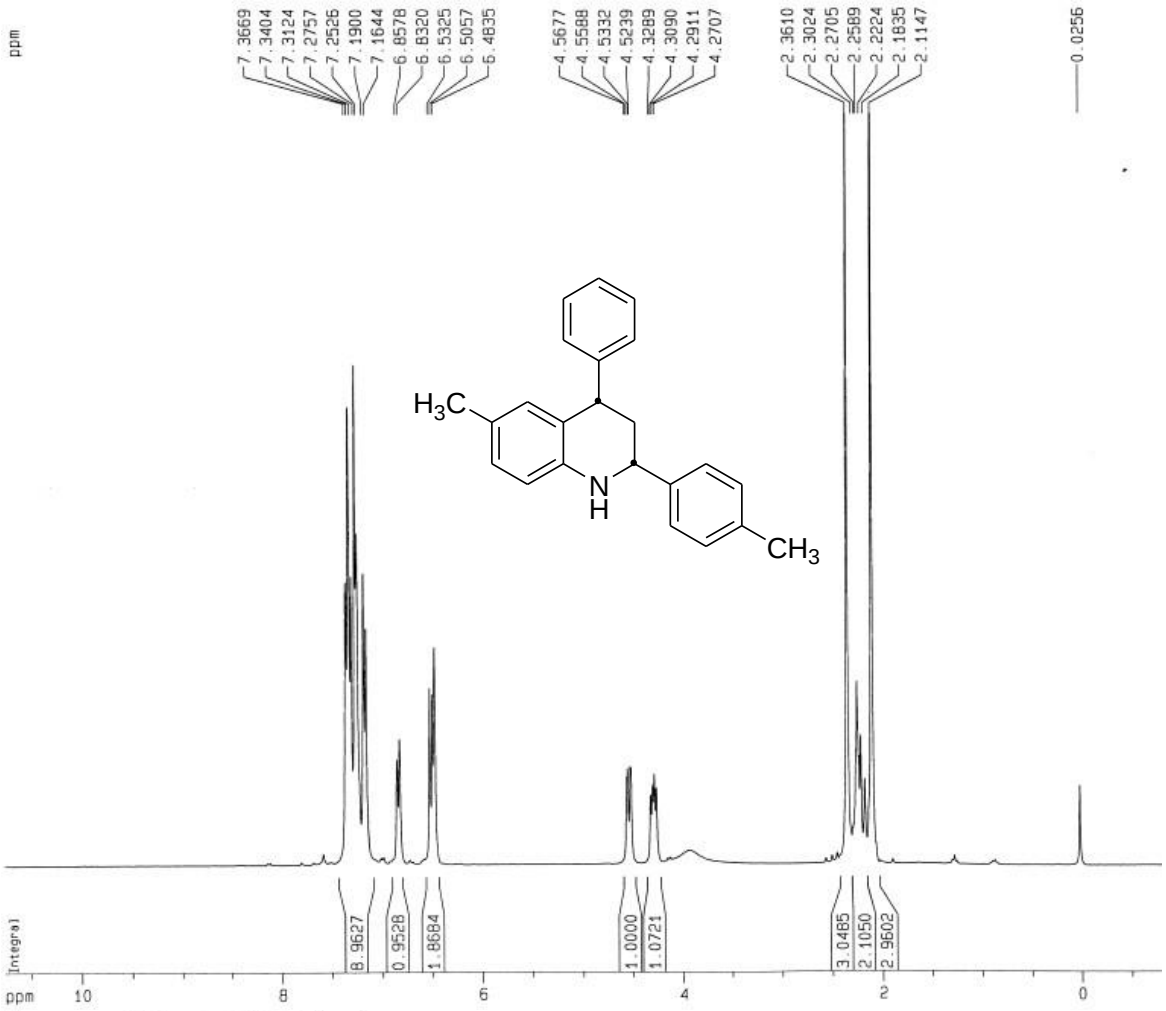

ppm
148.522
146.246
144.857
144.765
132.936
129.789
129.696
128.693
127.465
126.749
124.686
122.791
121.702
118.355
114.785
77.581
77.157
76.734
56.630
44.673
42.253

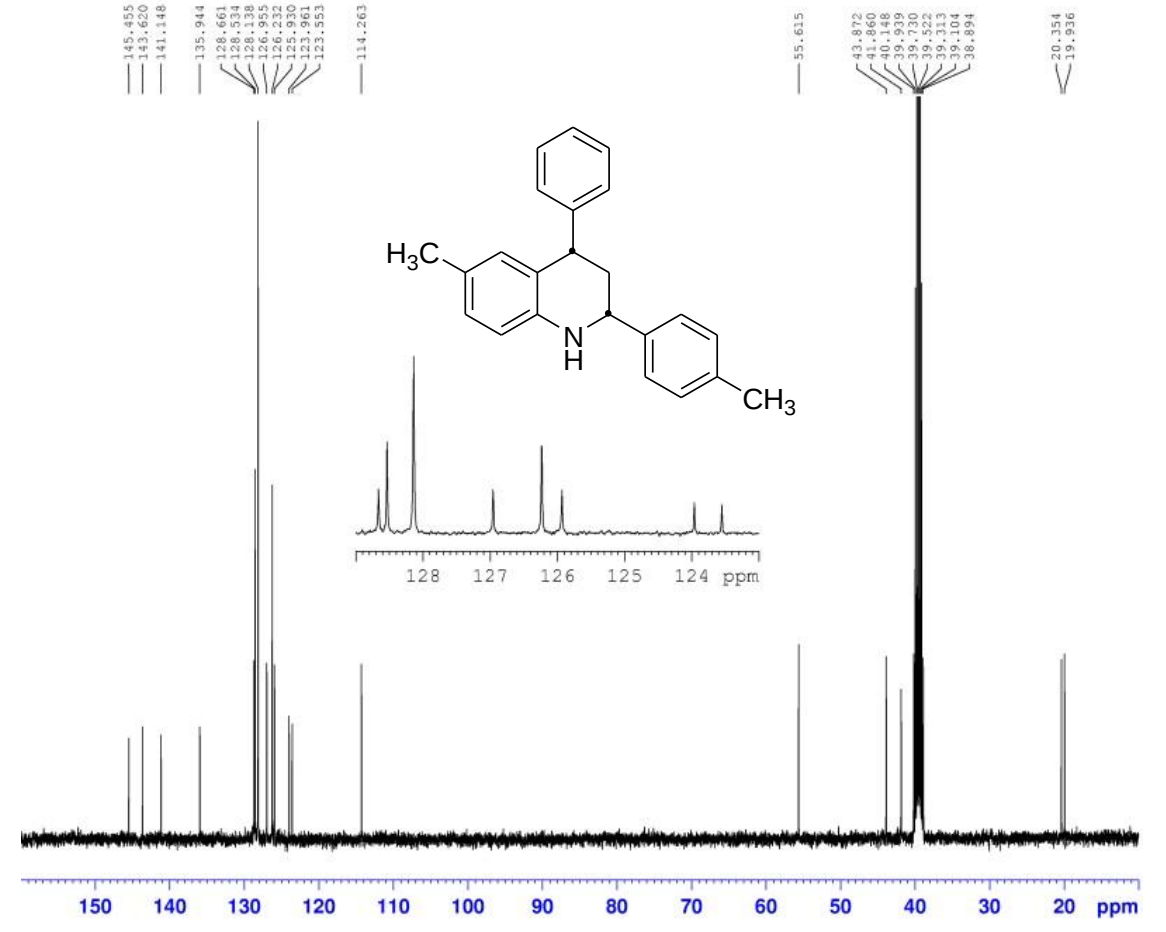

NO2
N
H

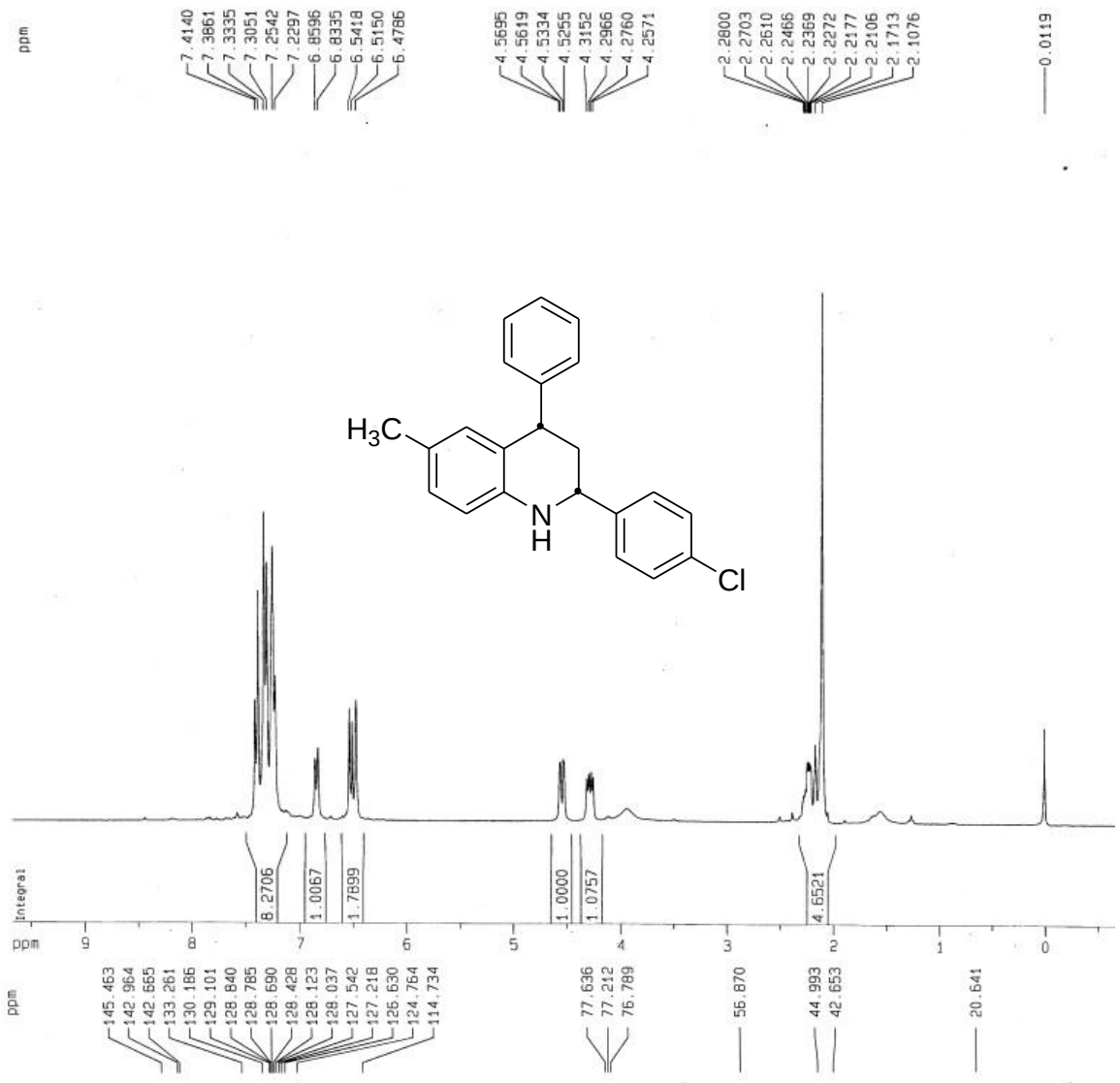
ppm
180
160
140
120
100
80
60
40
20

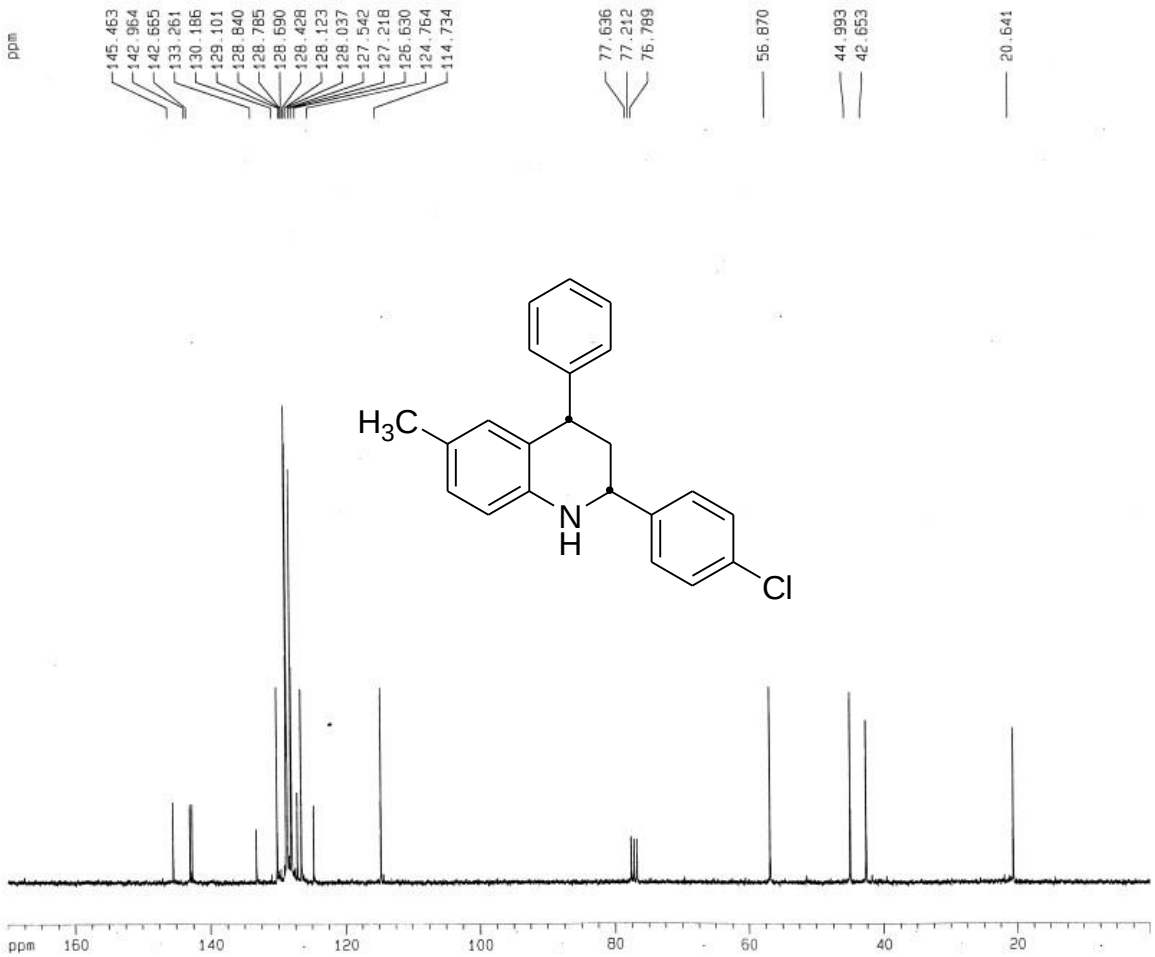

ppm
7.4875
7.4638
7.3954
7.3720
7.3433
7.3182
7.2825
7.2626
6.8699
6.8443
6.5491
6.5222
6.5001
4.6081
4.6007
4.5728
4.5650
4.3448
4.3259
4.3063
4.2872
2.3310
2.2982
2.2767
2.2376
2.1982
2.1241
2.0707
1.2870
0.0324
H3C
N
H
Integral
1.9981
8.1266
0.9939
1.9826
1.0693
1.1402
0.1934
0.7674
1.3164
0.4772
0.4396
3.0357
0.1990
0.4328
ppm
9
8
7
6
5
4
3
2
1
0
145.907
144.389
143.437
130.366
129.021
128.916
128.857
128.185
127.963
127.041
126.957
126.751
124.974
114.891
77.910
77.486
77.062
57.672
45.322
42.896
20.851

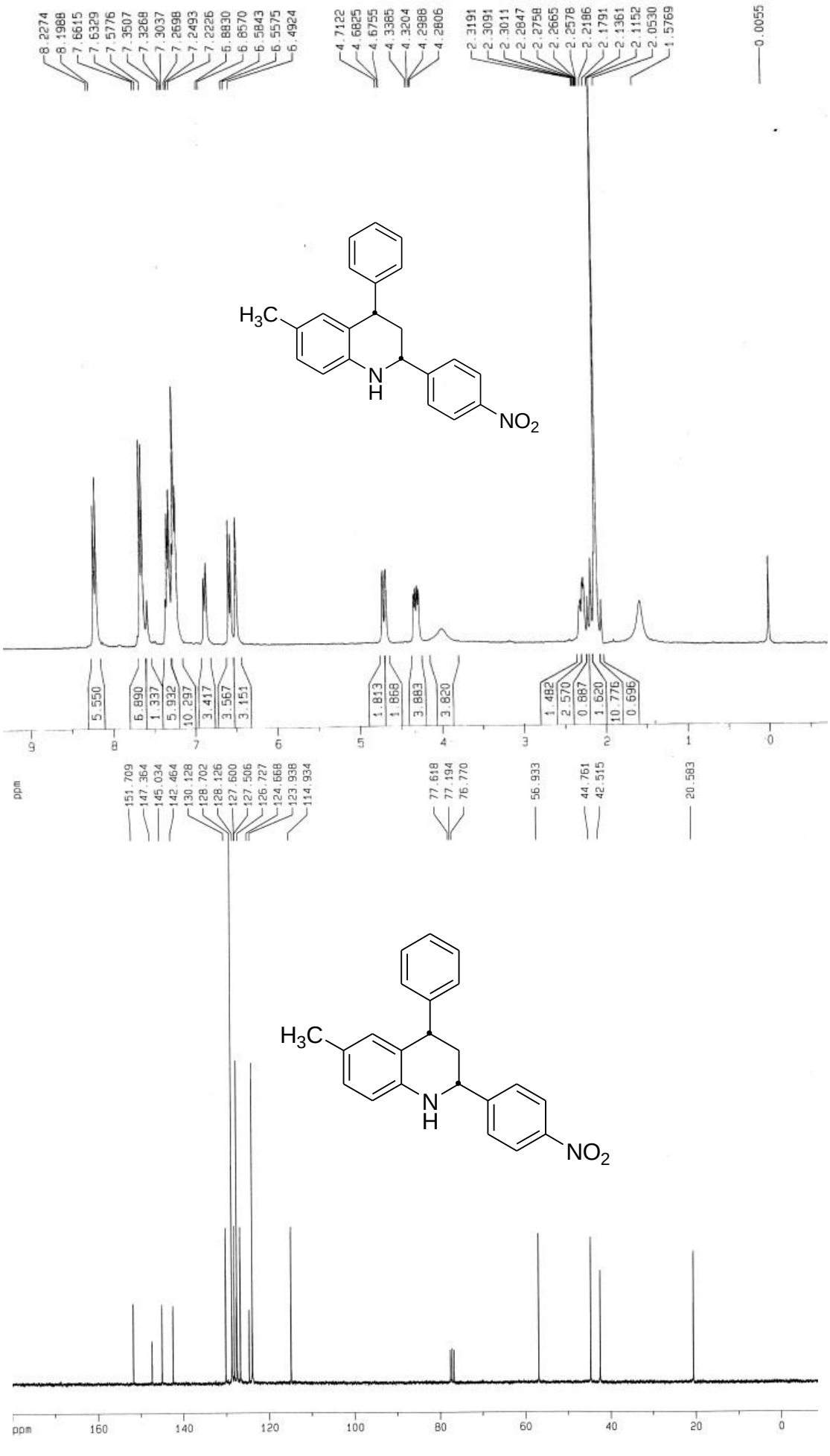

H3C
N
H
180
160
140
120
100
80
60
40
20
0

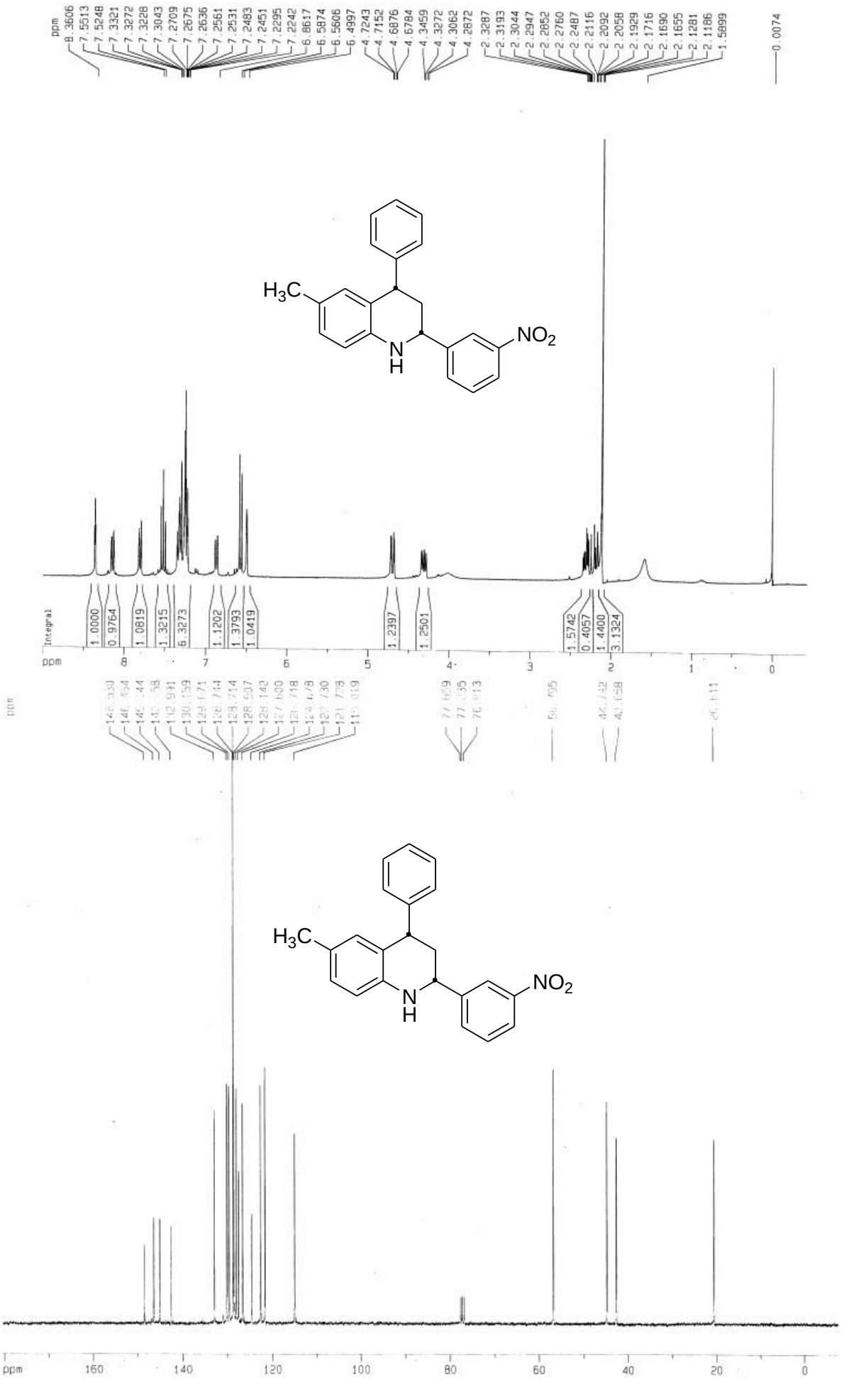

ppm
7.3669
7.3404
7.3124
7.2757
7.2526
7.1900
7.1644
6.8578
6.8320
6.5325
6.5057
6.4835
4.5677
4.5588
4.5332
4.5239
4.3289
4.3090
4.2911
4.2707
2.3610
2.3024
2.2705
2.2589
2.2224
2.1835
2.1147
0.0256
Integral
8.9627
0.9528
1.8684
1.0000
1.0721
3.0485
2.1050
2.9602
ppm
10
8
6
4
2
0
H3C
N
H
CH3

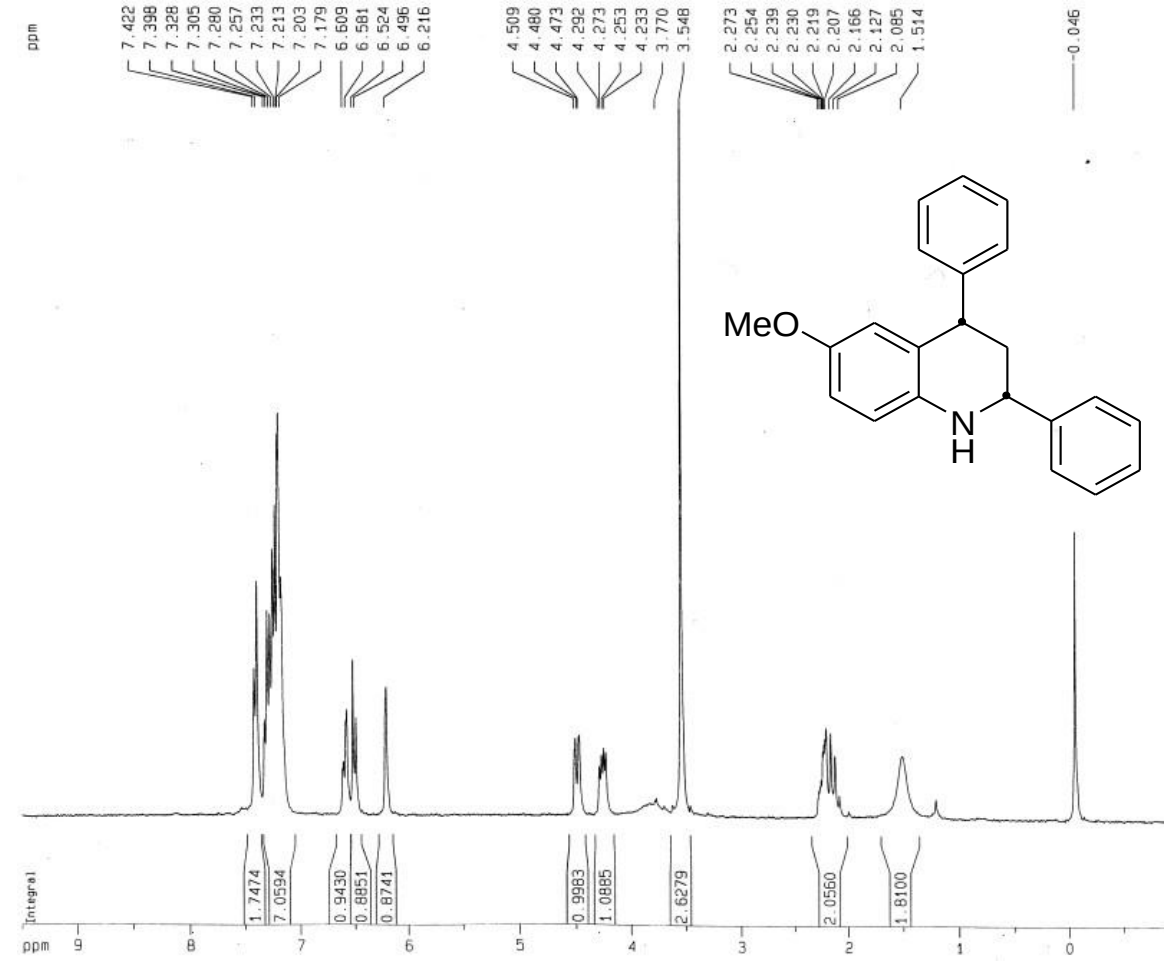

145.455
143.620
141.148
135.944
128.661
128.534
128.338
126.855
126.232
126.030
123.961
123.553
114.263
55.615
43.872
41.860
40.148
39.939
39.730
39.522
39.313
39.104
38.894
20.354
19.936
H3C
N
H
CH3
128
127
126
125
124 ppm
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

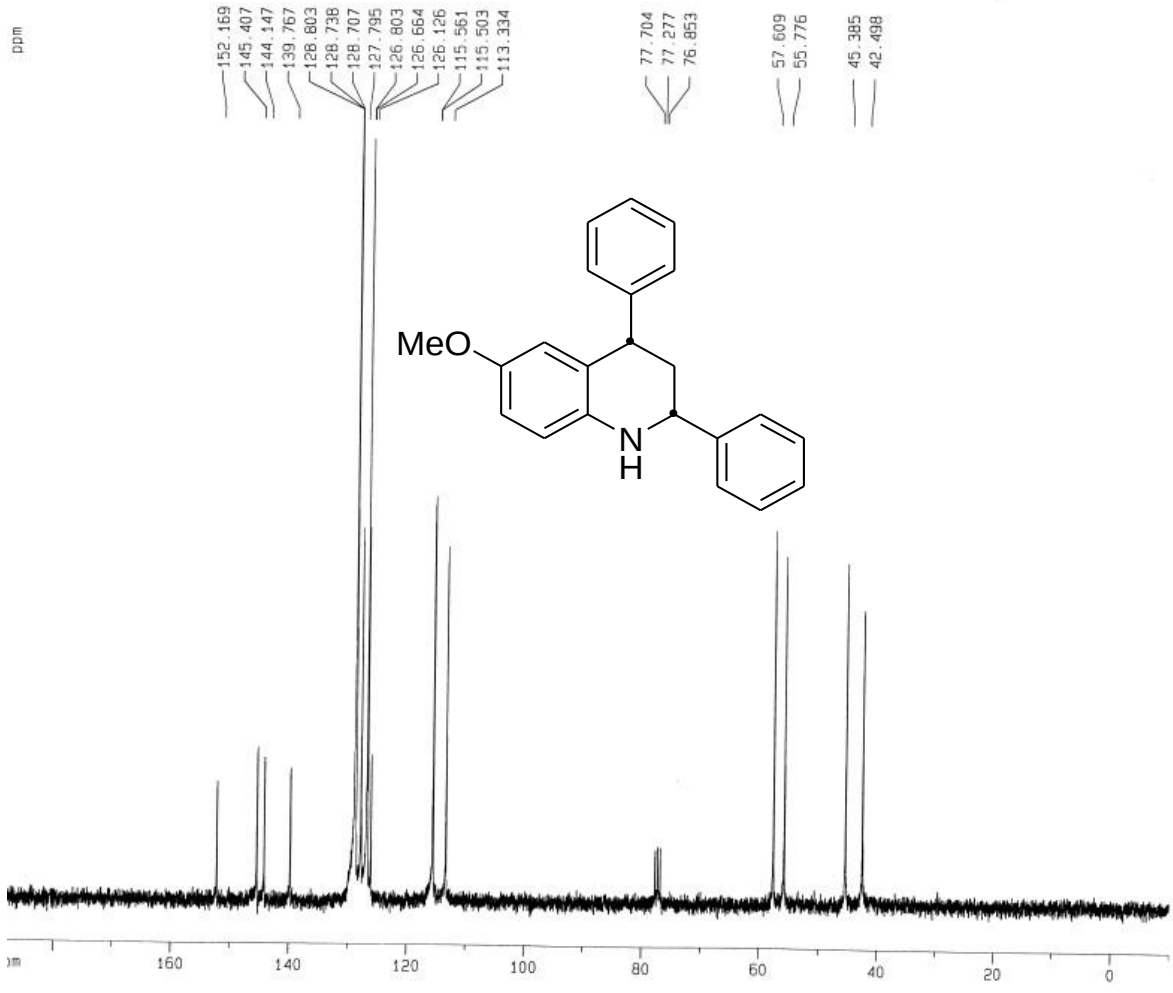

ppm
7.4140
7.3861
7.3335
7.3051
7.2542
7.2297
6.8596
6.8335
6.5418
6.5150
6.4786
4.5695
4.5619
4.5334
4.5255
4.3152
4.2966
4.2760
4.2571
2.2800
2.2703
2.2610
2.2466
2.2369
2.2272
2.2177
2.2106
2.1713
2.1076
0.0119
H3C
N
H
Cl
Integral
8.2706
1.0067
1.7899
1.0000
1.0757
4.6521
ppm
9
8
7
6
5
4
3
2
1
0

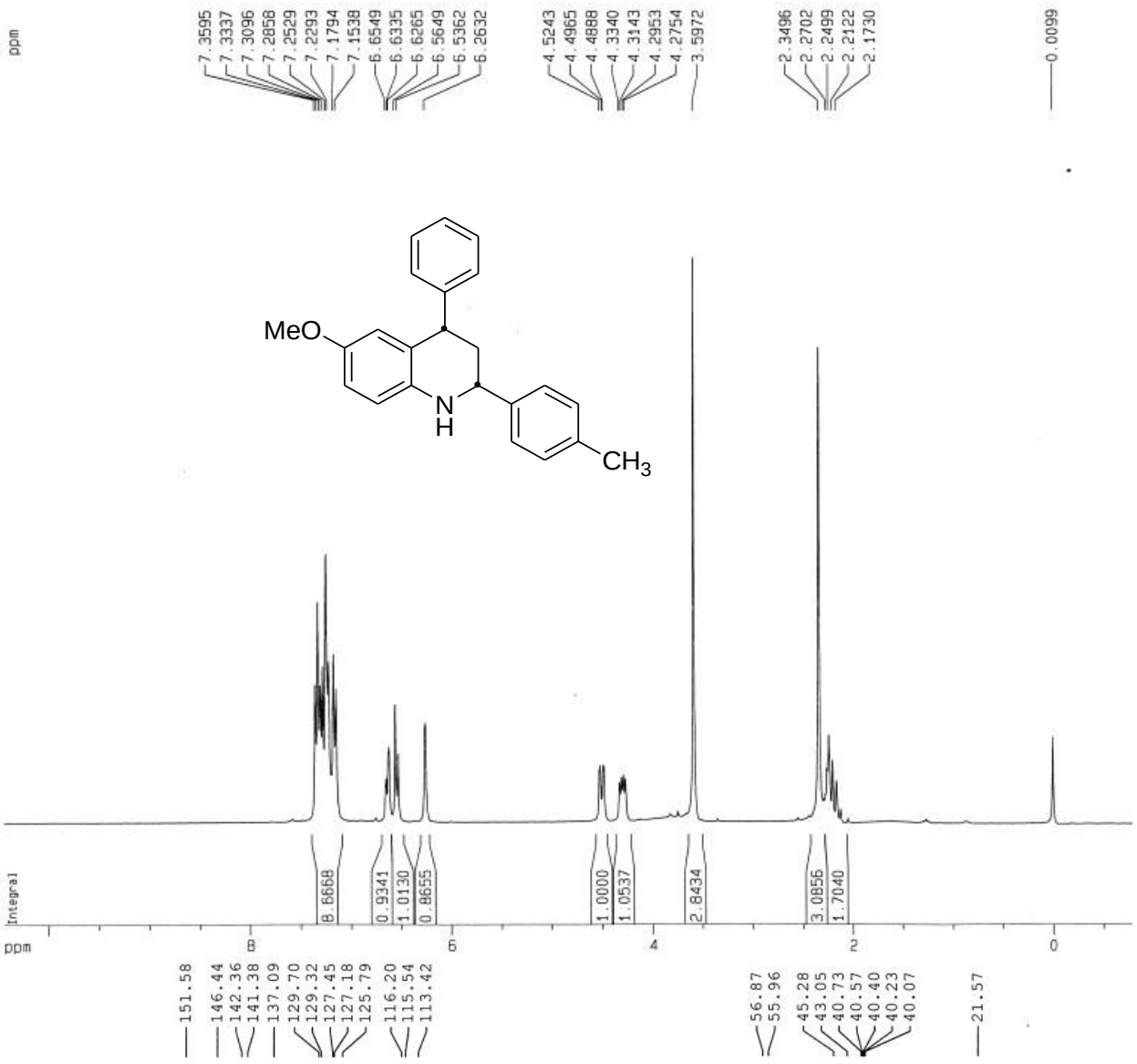

ppm
145.463
142.964
142.665
133.261
130.186
129.101
128.840
128.785
128.690
128.428
128.123
128.037
127.542
127.218
126.630
124.764
114.734
77.636
77.212
76.789
56.870
44.993
42.653
20.641
H3C
N
H
Cl
ppm
160
140
120
100
80
60
40
20

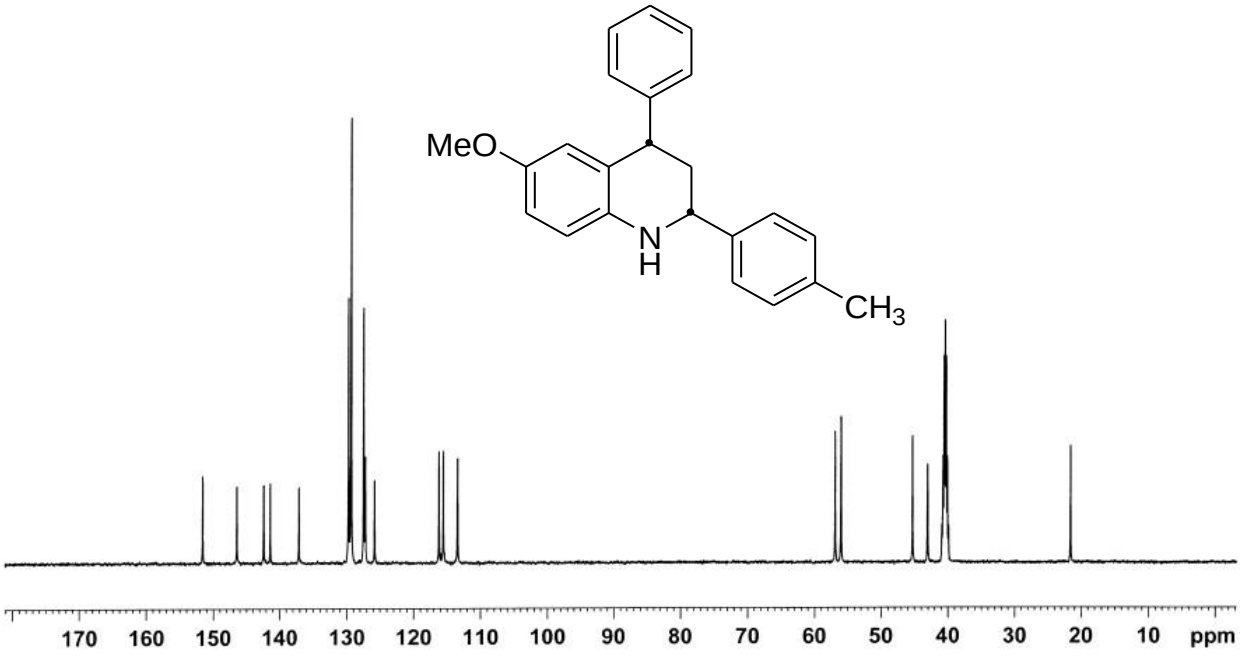

8.2274
8.1988
7.6615
7.6329
7.5776
7.3507
7.3268
7.3037
7.2698
7.2493
7.2226
6.8830
6.8570
6.5843
6.5575
6.4924
4.7122
4.6825
4.6755
4.3385
4.3204
4.2988
4.2806
2.3191
2.3091
2.3011
2.2847
2.2758
2.2665
2.2578
2.2186
2.1791
2.1361
2.1152
2.0530
1.5769
0.0055
H3C
N
H
NO2
5.550
6.890
1.337
5.932
10.297
3.417
3.567
3.151
1.813
1.868
3.883
3.820
1.482
2.570
0.887
1.620
10.776
0.696
ppm
151.709
147.364
145.034
142.464
130.128
128.702
128.126
127.600
127.506
126.727
124.668
123.938
114.934
77.618
77.194
76.770
56.933
44.761
42.515
20.583
H3C
N
H
NO2
ppm

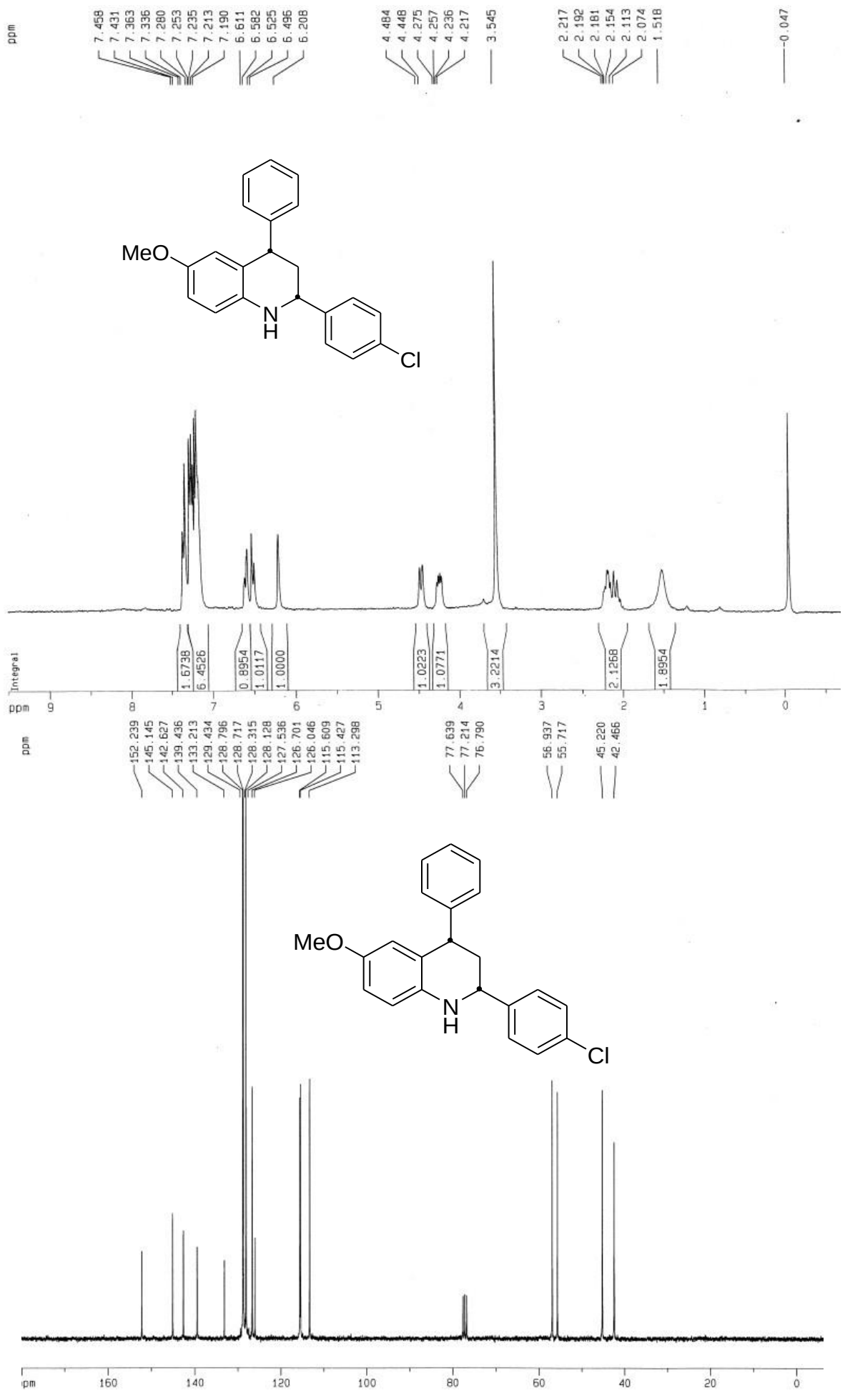

ppm
8.3606
7.5513
7.5248
7.3321
7.3272
7.3228
7.3043
7.2709
7.2675
7.2636
7.2561
7.2531
7.2483
7.2451
7.2295
7.2242
6.8617
6.5874
6.5606
6.4997
4.7243
4.7152
4.6876
4.6784
4.3459
4.3272
4.3062
4.2872
2.3287
2.3193
2.3044
2.2947
2.2852
2.2760
2.2487
2.2116
2.2092
2.2058
2.1929
2.1716
2.1690
2.1655
2.1281
2.1186
1.5899
0.0074
H3C
NO2
N
H
Integral
1.0000
0.9764
1.0819
1.3215
6.3273
1.1202
1.3793
1.0419
1.2397
1.2501
1.5742
0.4057
1.4400
3.1324
ppm
8
7
6
5
4
3
2
1
0
ppm
160
140
120
100
80
60
40
20
0

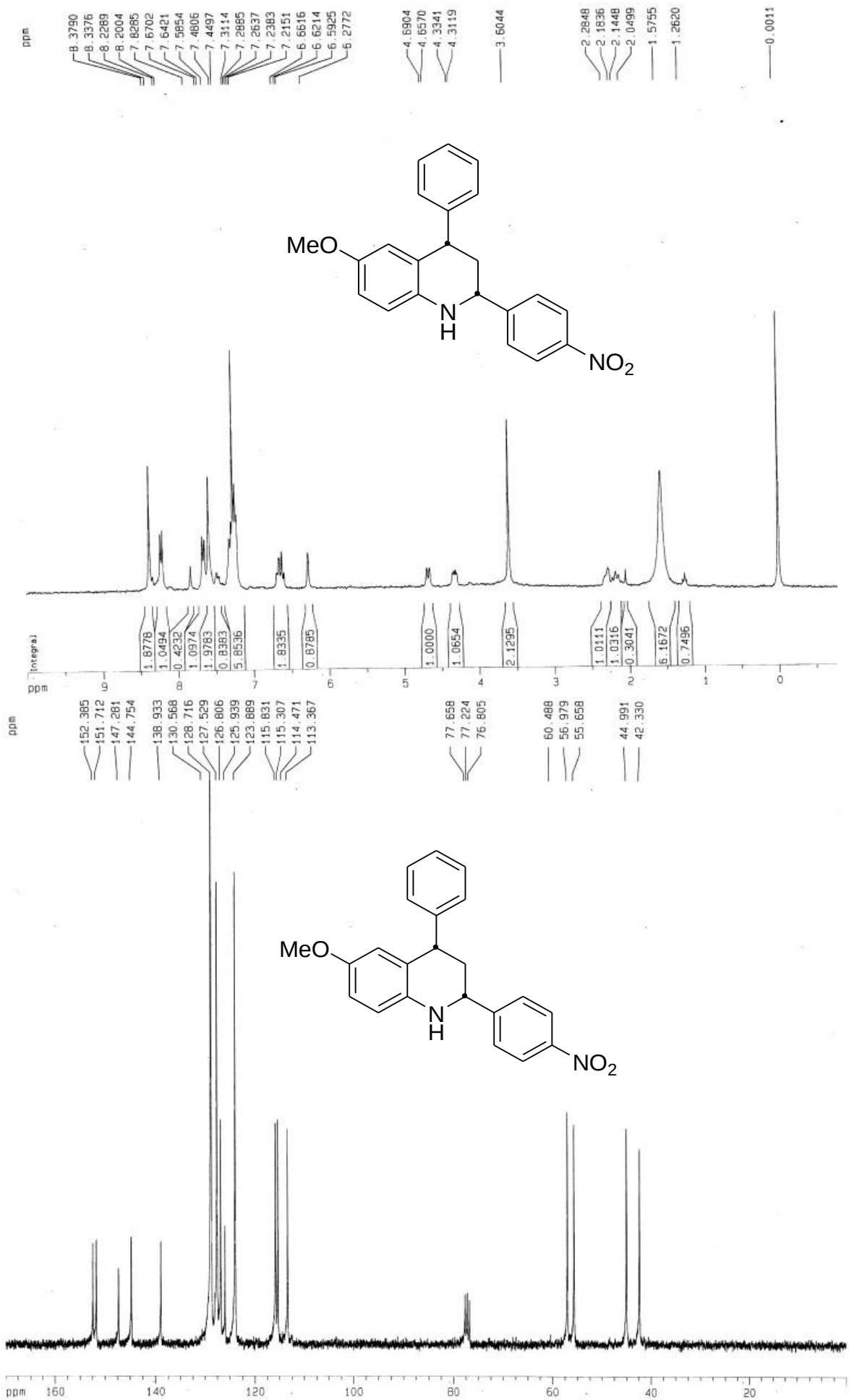

ppm
7.422
7.398
7.328
7.305
7.280
7.257
7.233
7.213
7.203
7.179
6.609
6.581
6.524
6.496
6.216
4.509
4.480
4.473
4.292
4.273
4.253
4.233
3.770
3.548
2.273
2.254
2.239
2.230
2.219
2.207
2.166
2.127
2.085
1.514
0.046
MeO
N
H
Integral
1.7474
7.0594
0.9430
0.8851
0.8741
0.9983
1.0885
2.6279
2.0560
1.8100
ppm

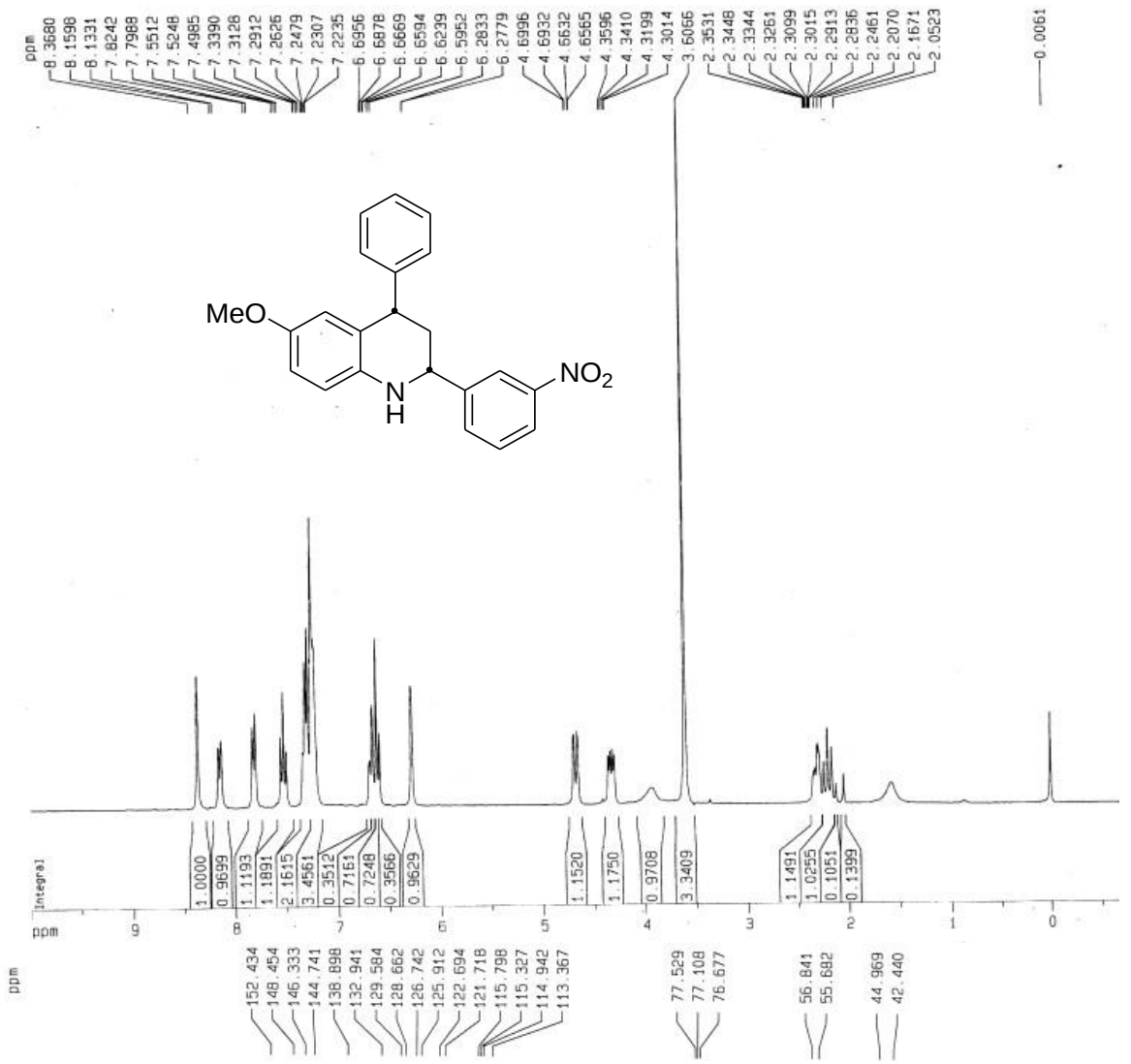

ppm
152.169
145.407
144.147
139.767
128.803
128.738
128.707
127.795
126.803
126.664
126.126
115.561
115.503
113.334
77.704
77.277
76.853
57.609
55.776
45.385
42.498
MeO
N
H

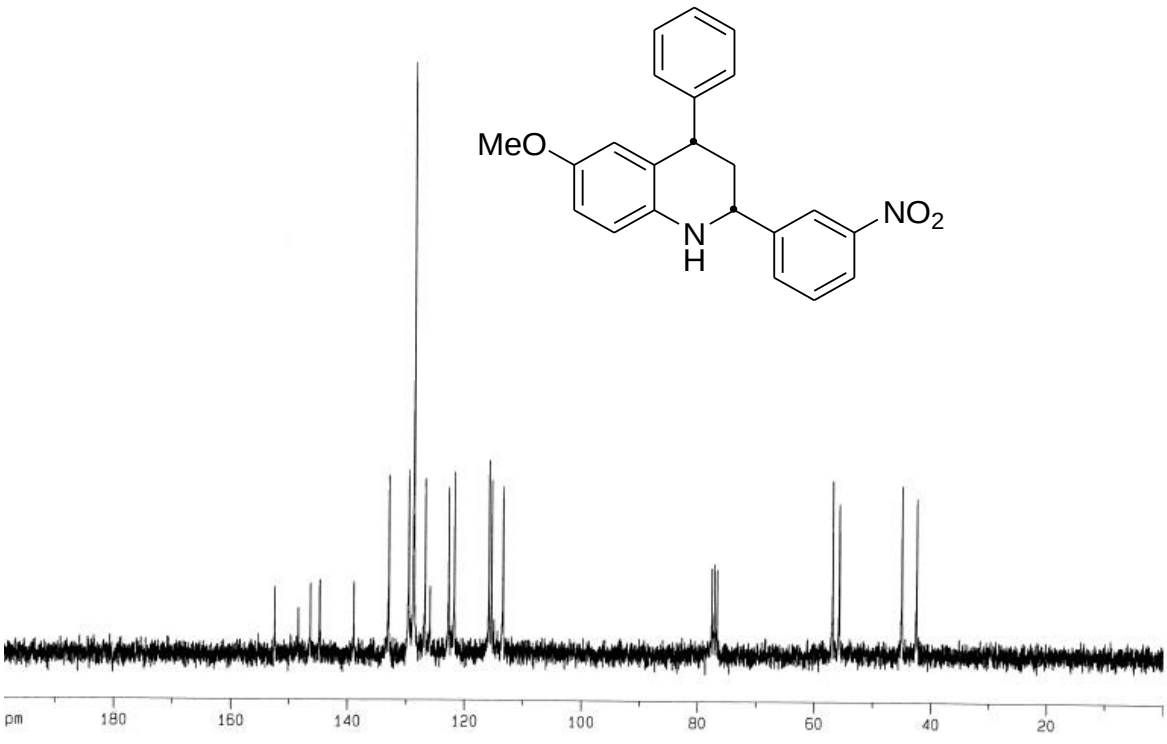

ppm
7.3595
7.3337
7.3096
7.2858
7.2529
7.2293
7.1794
7.1538
6.6549
6.6335
6.6265
6.5649
6.5362
6.2632
4.5243
4.4965
4.4888
4.3340
4.3143
4.2953
4.2754
3.5972
2.3496
2.2702
2.2499
2.2122
2.1730
0.0099
MeO
N
H
CH3
Integral
8.6668
0.9341
1.0130
0.8655
1.0000
1.0537
2.8434
3.0856
1.7040
ppm
8
6
4
2
0
151.58
146.44
142.36
141.38
137.09
129.70
129.32
127.45
127.18
125.79
116.20
115.54
113.42
56.87
55.96
45.28
43.05
40.73
40.57
40.40
40.23
40.07
21.57

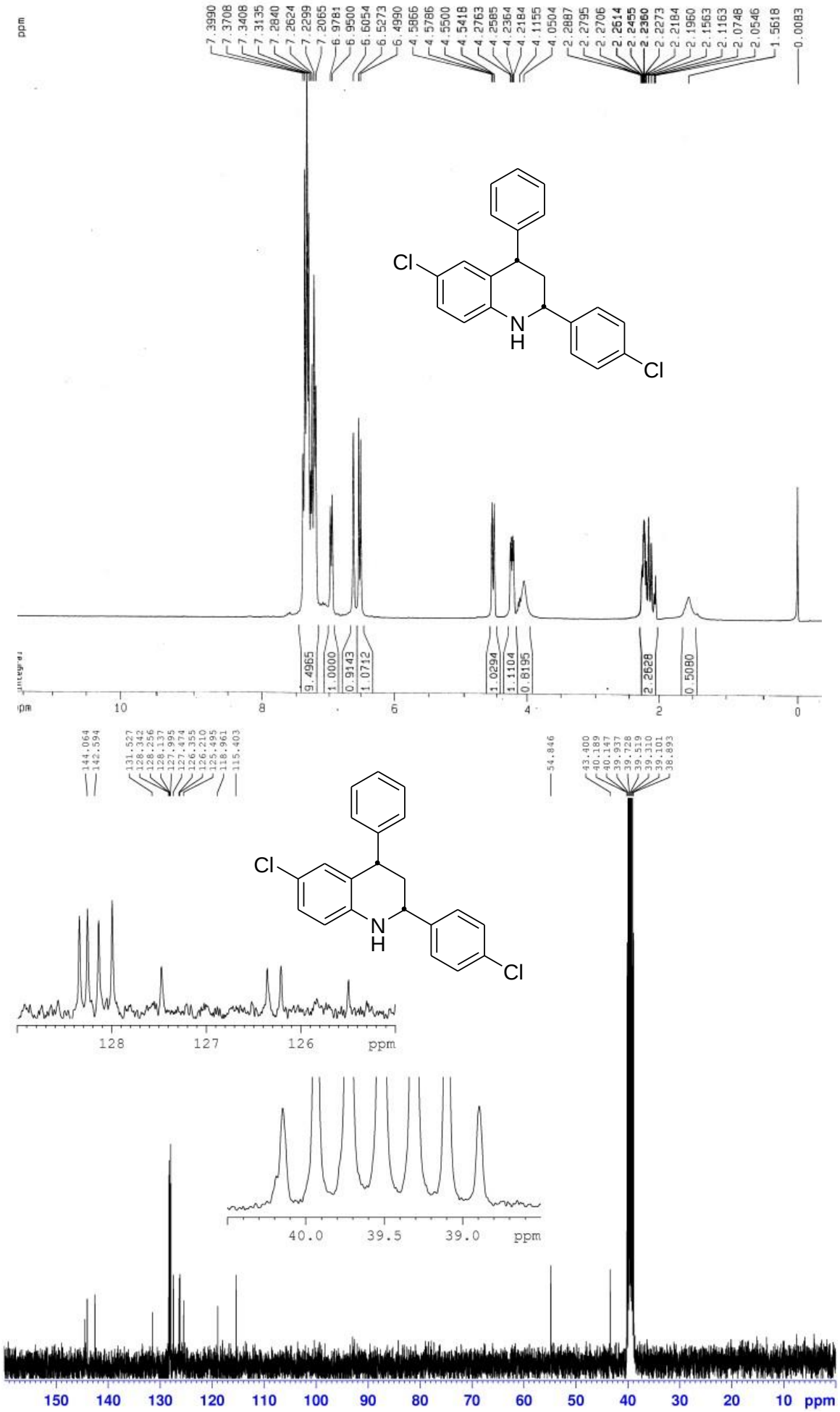

MeO
N
H
CH3
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

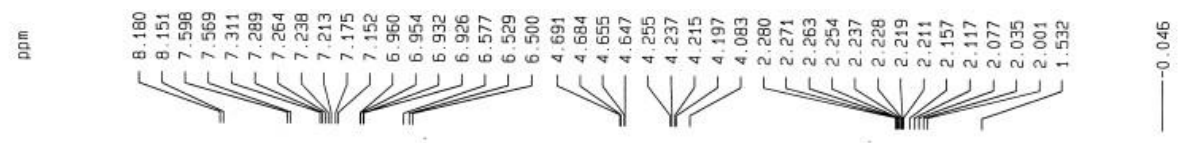

ppm
7.458
7.431
7.363
7.336
7.280
7.253
7.235
7.213
7.190
6.611
6.582
6.525
6.496
6.208
4.484
4.448
4.275
4.257
4.236
4.217
3.545
2.217
2.192
2.181
2.154
2.113
2.074
1.518
0.047
MeO
N
H
Cl
Integral
1.6738
6.4526
0.8954
1.0117
1.0000
1.0223
1.0771
3.2214
2.1268
1.8954
ppm
152.239
145.145
142.627
139.436
133.213
129.434
128.796
128.717
128.315
128.128
127.536
126.701
126.046
115.609
115.427
113.298
77.639
77.214
76.790
56.937
55.717
45.220
42.466
MeO
N
H
Cl
ppm
160
140
120
100
80
60
40
20
0

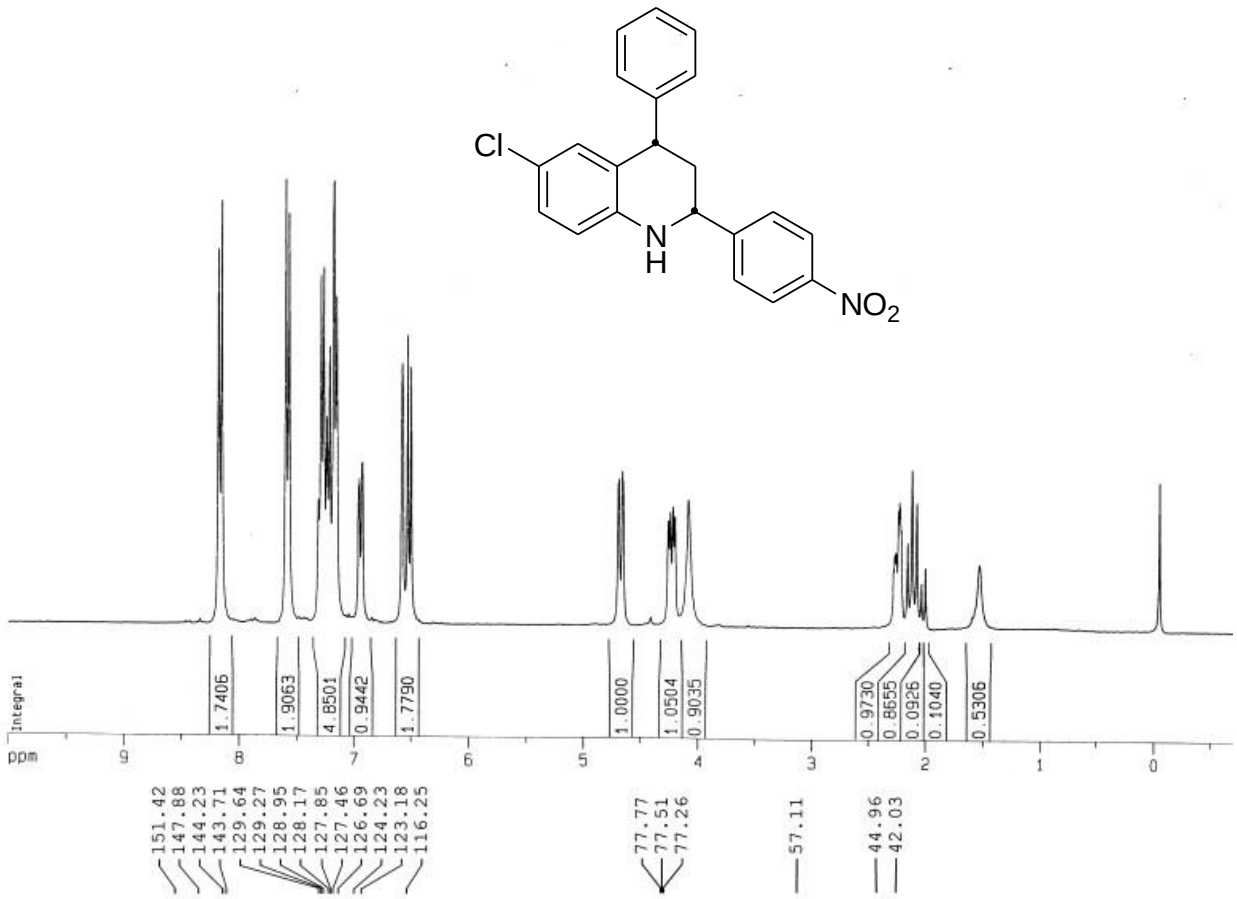

ppm
8.3790
8.3376
8.2289
8.2004
8.0285
7.6702
7.6421
7.5854
7.4806
7.4497
7.3114
7.2885
7.2637
7.2383
7.2151
6.6616
6.6214
6.5925
6.2772
4.6904
4.6570
4.3341
4.3119
3.6044
2.2848
2.1836
2.1448
2.0499
1.5755
1.2620
0.0011
MeO
N
H
NO2
Integral
1.8778
1.0494
0.4232
1.0974
1.9783
0.8383
5.8536
1.8335
0.8785
1.0000
1.0654
2.1295
1.0111
1.0316
0.3041
6.1672
0.7496
ppm
152.385
151.712
147.281
144.754
138.933
130.568
128.716
127.529
126.806
125.939
123.889
115.831
115.307
114.471
113.367
77.658
77.224
76.805
60.488
56.979
55.658
44.991
42.330
MeO
N
H
NO2
ppm

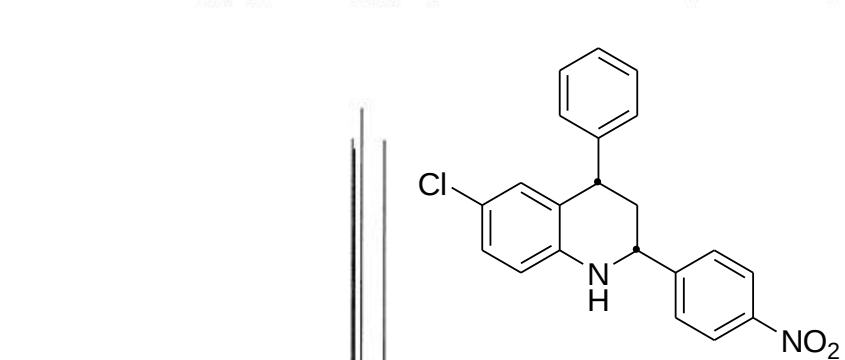

MeO
NO2
N
H


MeO
NO2
N
H

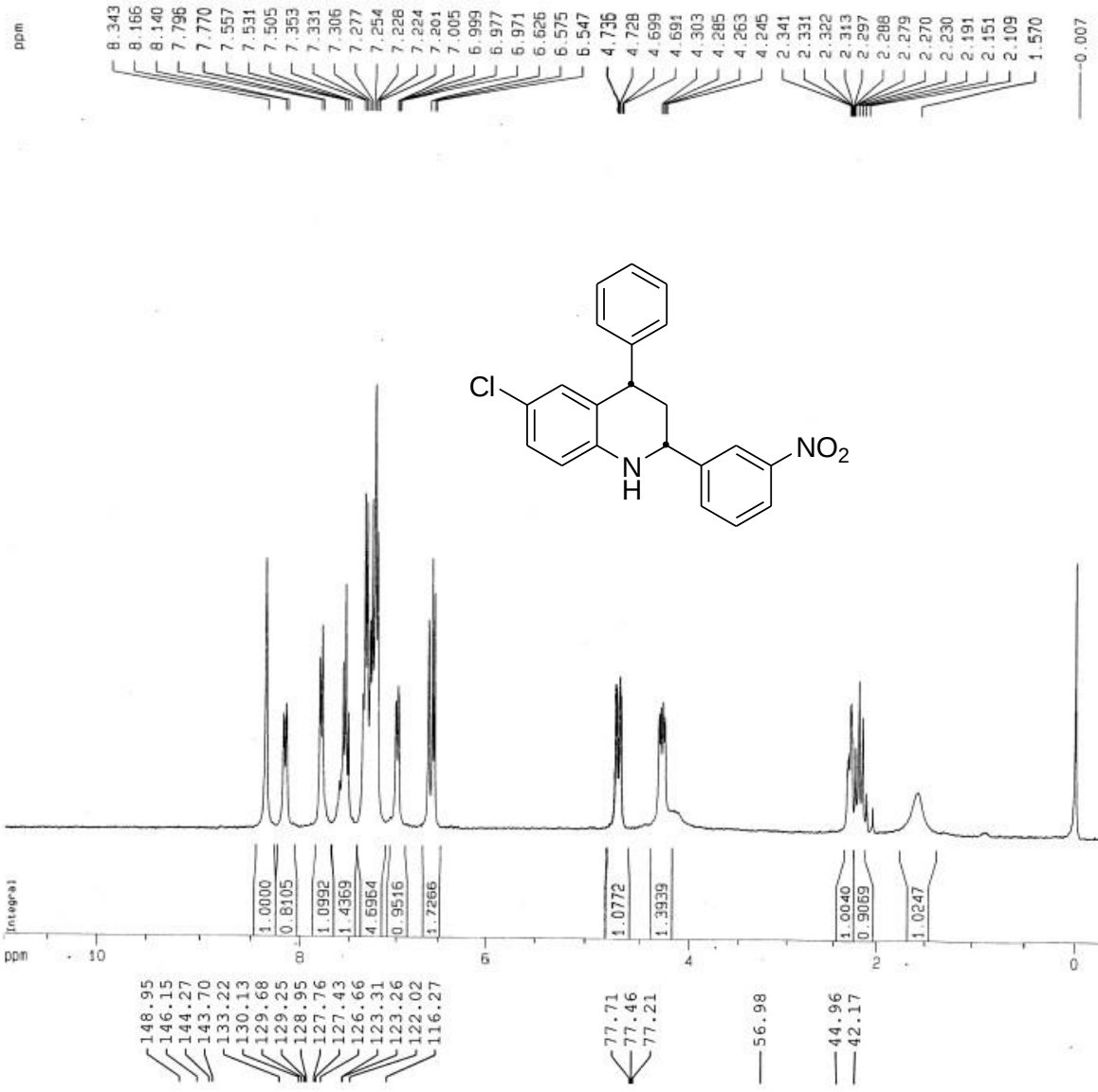

ppm
7.3990
7.3708
7.3408
7.3135
7.2840
7.2624
7.2299
7.2065
6.9781
6.9500
6.6054
6.5273
6.4990
4.5866
4.5786
4.5500
4.5418
4.2763
4.2585
4.2364
4.2184
4.1155
4.0504
2.2887
2.2795
2.2706
2.2614
2.2455
2.2360
2.2273
2.2184
2.1960
2.1563
2.1163
2.0748
2.0546
1.5618
0.0083
Cl
N
H
Cl
9.4965
1.0000
0.9143
1.0712
1.0294
1.1104
0.8195
2.2628
0.5080
10
8
6
4
2
0
144.064
142.594
131.527
128.342
128.256
128.137
127.995
127.474
126.355
126.210
125.495
118.961
115.403
54.846
43.400
40.189
40.147
39.937
39.728
39.519
39.310
39.101
38.893
Cl
N
H
Cl
128
127
126
ppm
40.0
39.5
39.0
ppm
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

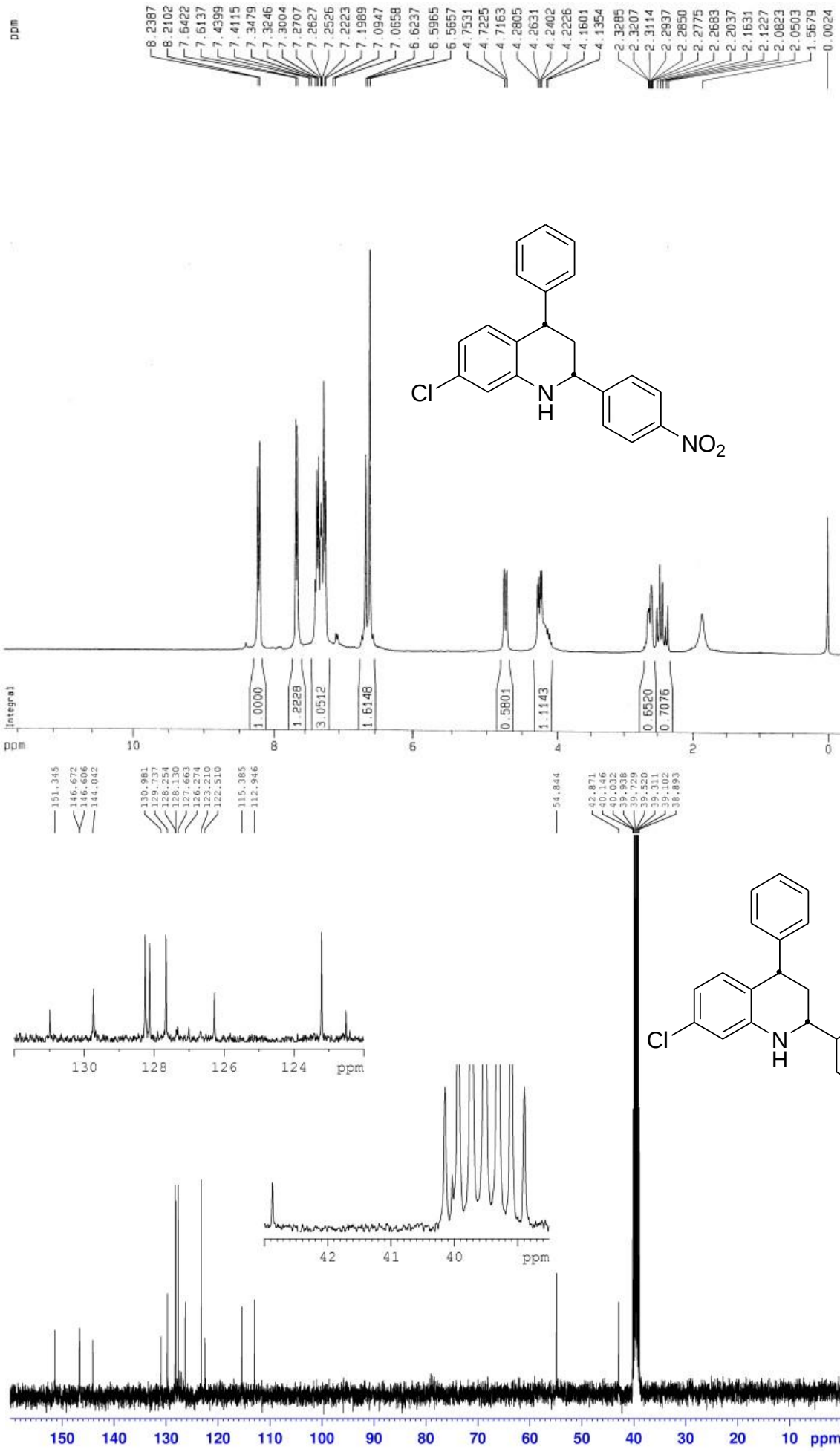

ppm
8.180
8.151
7.598
7.569
7.311
7.289
7.264
7.238
7.213
7.175
7.152
6.960
6.954
6.932
6.926
6.577
6.529
6.500
4.691
4.684
4.655
4.647
4.255
4.237
4.215
4.197
4.083
2.280
2.271
2.263
2.254
2.237
2.228
2.219
2.211
2.157
2.117
2.077
2.035
2.001
1.532
-0.046

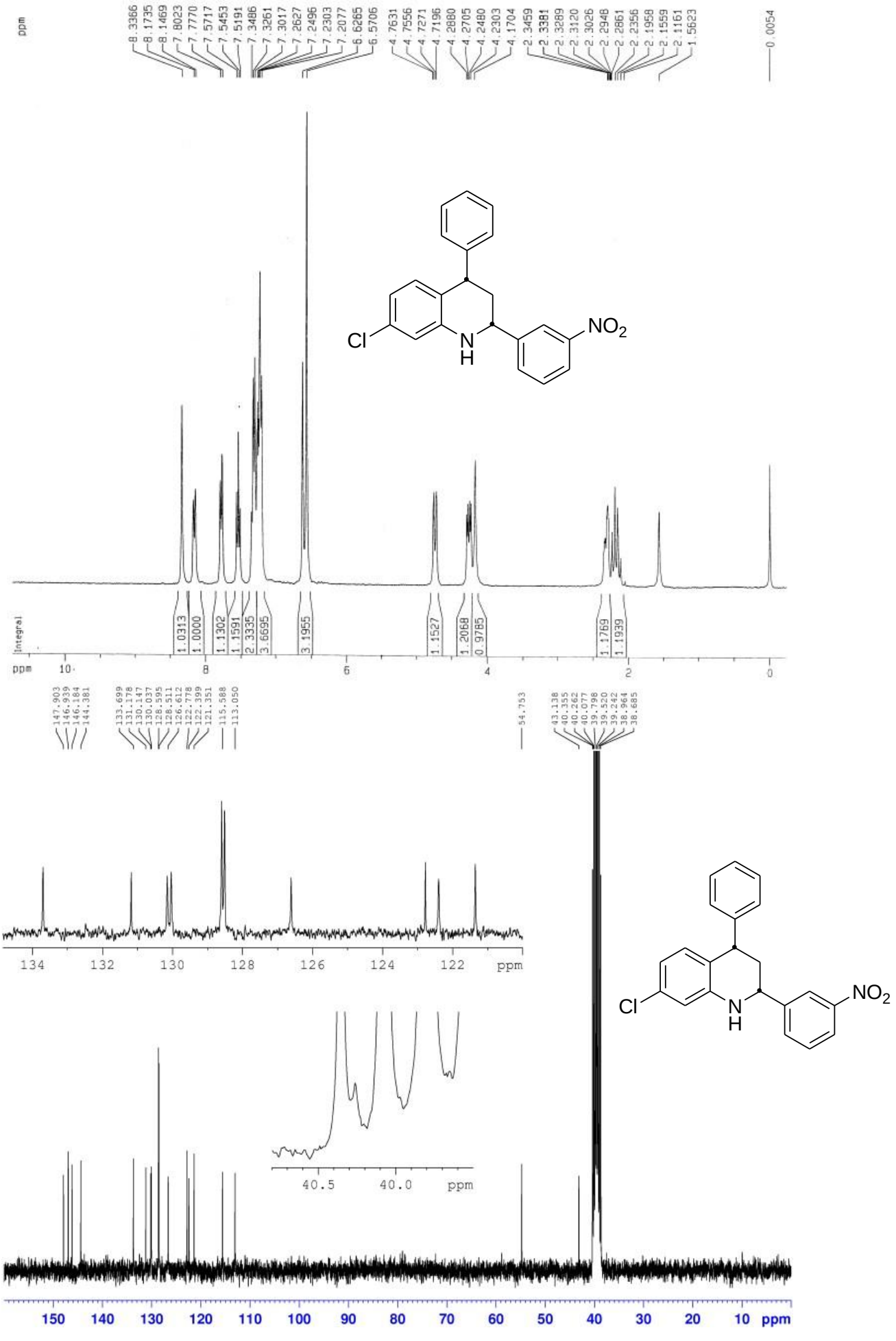

Cl
N
H
NO2
Integral
1.7406
1.9063
4.8501
0.9442
1.7790
1.0000
1.0504
0.9035
0.9730
0.8655
0.0926
0.1040
0.5306
ppm
9
8
7
6
5
4
3
2
1
0


151.42
147.88
144.23
143.71
129.64
129.27
128.95
128.17
127.85
127.46
126.69
124.23
123.18
116.25
77.77
77.51
77.26
57.11
44.96
42.03

Cl
N
H
NO2
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


ppm
8.343
8.166
8.140
7.796
7.770
7.557
7.531
7.505
7.353
7.331
7.306
7.277
7.254
7.228
7.224
7.201
7.005
6.999
6.977
6.971
6.626
6.575
6.547
4.736
4.728
4.699
4.691
4.303
4.285
4.263
4.245
2.341
2.331
2.322
2.313
2.297
2.288
2.279
2.270
2.230
2.191
2.151
2.109
1.570
-0.007
Cl
NO2
N
H
Integral
1.0000
0.8105
1.0992
1.4369
4.6964
0.9516
1.7266
1.0772
1.3939
1.0040
0.9069
1.0247
ppm
10
8
6
4
2
0
148.95
146.15
144.27
143.70
133.22
130.13
129.68
129.25
128.95
127.76
127.43
126.66
123.31
123.26
122.02
116.27
77.71
77.46
77.21
56.98
44.96
42.17
Cl
NO2
N
H
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


ppm
8.2387
8.2102
7.6422
7.6137
7.4399
7.4115
7.3479
7.3246
7.3004
7.2707
7.2627
7.2526
7.2223
7.1989
7.0947
7.0658
6.6237
6.5965
6.5657
4.7531
4.7225
4.7163
4.2805
4.2631
4.2402
4.2226
4.1601
4.1354
2.3285
2.3207
2.3114
2.2937
2.2850
2.2775
2.2683
2.2037
2.1631
2.1227
2.0823
2.0503
1.5679
0.0024
Cl
N
H
NO2
Integral
1.0000
1.2228
3.0512
1.6148
0.5801
1.1143
0.6520
0.7076
ppm
10
8
6
4
2
0
151.345
146.672
146.606
144.042
130.981
129.737
128.254
128.130
127.663
126.274
123.210
122.510
115.385
112.946
54.844
42.871
40.146
40.032
39.938
39.729
39.520
39.311
39.102
38.893
130
128
126
124
ppm
42
41
40
ppm
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


ppm
8.3366
8.1735
8.1469
7.8023
7.7770
7.5717
7.5453
7.5191
7.3486
7.3261
7.3017
7.2627
7.2496
7.2303
7.2077
6.6265
6.5706
4.7631
4.7556
4.7271
4.7196
4.2880
4.2705
4.2480
4.2303
4.1704
2.3459
2.3381
2.3289
2.3120
2.3026
2.2948
2.2861
2.2356
2.1958
2.1559
2.1161
1.5623
0.0054
Cl
N
H
NO2
Integral
1.0313
1.0000
1.1302
1.1591
2.3335
3.6695
3.1955
1.1527
1.2068
0.9785
1.1769
1.1939
ppm
10
8
6
4
2
0
147.903
146.939
146.184
144.381
133.699
131.178
130.147
130.037
128.595
128.511
126.612
122.778
122.399
121.351
115.588
113.050
54.753
43.138
40.355
40.262
40.077
39.798
39.520
39.242
38.964
38.685
134
132
130
128
126
124
122
ppm
40.5
40.0
ppm
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm