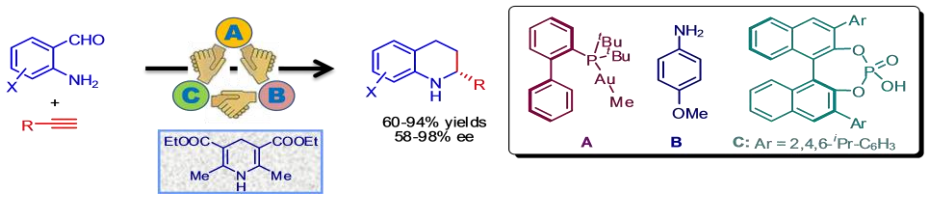
Electronic Supplementary Material (ESI) for Chemical Communications

Enantioselective Cooperative Triple Catalysis: Unique Roles of Au(I)/Amine/Chiral Brønsted Acid Catalysts in the Addition/Cycloisomerization/Transfer Hydrogenation Cascade

Nitin T. Patil, Vivek S. Raut and Ramesh Babu Tella*

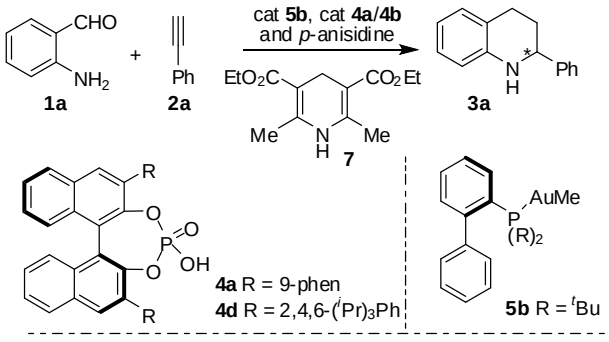


1. General Information:

All reactions were carried out in oven or flame dried vials with magnetic stirring under nitrogen atmosphere. Dried solvents and liquid reagents were transferred by oven-dried syringes or hypodermic syringe cooled to ambient temperature in a desiccators. All experiments were monitored by analytical thin layer chromatography (TLC). TLC was performed on pre-coated silica gel plates. After elution, plate was visualized under UV illumination at 254 nm for UV active materials. Further visualization was achieved by staining $KMnO_4$ and charring on a hot plate. Solvents were removed in vacuo and heated with a water bath at 35 °C. Silica gel finer than 200 mesh was used for flash column chromatography. Columns were packed as slurry of silica gel in hexane and equilibrated with the appropriate solvent mixture prior to use. The compounds were loaded neat or as a concentrated solution using the appropriate solvent system. The elution was assisted by applying pressure with an air pump.

Unless otherwise noted, all commercially available compounds were used as provided without further purification. 2-Aminobenzaldehydes and alkynes were either commercially available or prepared according to the literature known procedures.[1] Solvents for chromatography were HPLC grade and used as provided. NMR spectra were recorded on 300 and 500 MHz spectrometers in appropriate solvents using TMS as internal standard or the solvent signals as secondary standards and the chemical shifts are shown in δ scales. Multiplicities of NMR signals were designated as s (singlet), bs (broad singlet), d (doublet), dd (doublet of doublet), dt (doublet of triplet), t (triplet), td (triplet of doublet), q (quartet), m (multiplet) etc. ^{13}C NMR spectra were recorded on 75, 125 MHz spectrometers. The enantiomeric excess (ee) was determined by HPLC analysis employing a Chiralcel OD-H column. Optical rotations were measured on a digital high sensitive polarimeter at the indicated temperature.

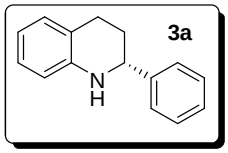
2. Representative Procedure:



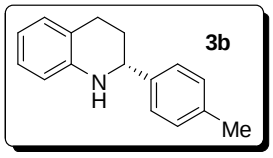
Gold(I) catalyst **5b** (0.004 mmol) was dissolved in dry $CHCl_3$ (0.2 mL) under nitrogen atmosphere in a screw-cap vial (0.5 mL) containing a stirrer bar. Then, phosphoric acid **4a** or **4b** (wherever specified in Table 2, 0.008 mmol) was added and the mixture was stirred at rt for ~5 minutes (until gas bubble ceases). After that 2-aminobenzadehyde **1a** (0.20 mmol), *p*-anisidine (0.04 mmol), phenyl acetylene **2a** (0.25 mmol) and 4 Å molecular sieves (100 mg)

were introduced successively in the reaction mixture. The reaction mixture was stirred at 60 °C for 12-24 h and the progress of the reaction was monitored by TLC. After cooling the reaction mixture to rt, Hantzsch ester **7** (0.51 mmol) in $CHCl_3$ (0.2 mL) was added and reaction mixture stirred at 35°C for 16 h. The reaction mixture was filtered through a plug of silica gel (eluting with CH_2Cl_2) to remove the molecular sieves. The filtrate was concentrated under reduced pressure and resulting residue was purified by column chromatography using silica gel with ethyl acetate/hexane (9.5:0.5) as eluent to afford **3a**.

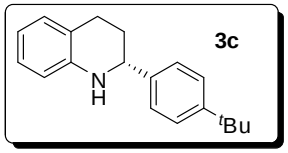
3. Characterization Data of Compounds:



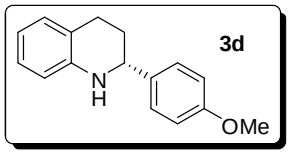
(*R*)-2-phenyl-1,2,3,4-tetrahydroquinoline (3a):[2-7] 92% yield; R_f 0.7 (hexane/EtOAc = 90/10); ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.41-7.24 (m, 5H), 7.03-6.98 (m, 2H), 6.65 (td, *J* = 7.4, 0.9 Hz, 1H), 6.53 (d, *J* = 8.1 Hz, 1H), 4.44 (dd, *J* = 9.3, 3.4 Hz, 1H), 4.08 (bs, 1H), 2.97-2.86 (m, 1H), 2.73 (dt, *J* = 16.2, 4.7 Hz, 1H), 2.16-1.92 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 144.7, 144.6, 129.2, 128.5, 127.3, 126.8, 126.5, 120.7, 117.0, 113.9, 56.1, 30.9, 26.3; $[\alpha]_D^{27}$ = +41.9 (*c* = 1.0, $CHCl_3$). Enantiomeric excess: 98%, determined by HPLC, conditions: Chiracel OD-H, n-hexane/2-propanol = 80/20, flow rate 1.0 mL/min; λ = 250 nm; t_R = 8.23 min (minor), t_R = 10.00 min (major). The absolute configuration was determined with comparison of optical rotation reported in the literature. lit.[2a] $[\alpha]_D^{RT}$ = –37.7 (*c* = 1.0, $CHCl_3$, 97% ee), lit.[2b] $[\alpha]_D^{RT}$ = –30.4 (*c* = 1.0, $CHCl_3$, 92% ee), lit.[3a] $[\alpha]_D^{20}$ = –66.8 (*c* = 1.6, EtOAc, 97% ee), lit.[4] $[\alpha]_D^{19}$ = –35.7 (*c* = 0.8, $CHCl_3$, 91% ee), lit.[5] $[\alpha]_D^{20}$ = –34.8 (*c* = 1.1, $CHCl_3$, 96% ee).



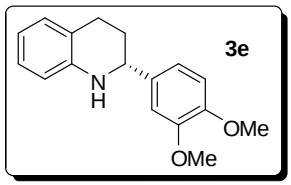
(*R*)-2-*p*-tolyl-1,2,3,4-tetrahydroquinoline (3b):[3a,4] 89% yield; R_f 0.7 (hexane/EtOAc = 90/10); ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.28 (d, *J* = 7.6 Hz, 2H), 7.16 (d, *J* = 7.6 Hz, 2H), 7.03-6.98 (m, 2H), 6.65 (dd, *J* = 9.1, 7.6 Hz, 1H), 6.52 (d, *J* = 9.1 Hz, 1H), 4.39 (dd, *J* = 9.8, 3.0 Hz, 1H), 3.99 (bs, 1H), 2.98-2.87 (m, 1H), 2.78-2.70 (m, 1H), 2.36 (s, 3H), 2.14-1.91 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 144.7, 141.8, 137.0, 129.2, 126.8, 126.4, 120.8, 117.0, 113.9, 55.9, 31.0, 26.4, 21.0; $[\alpha]_D^{27}$ = +35.1 (*c* = 1.0, $CHCl_3$). Enantiomeric excess: 98%, determined by HPLC, conditions: Chiracel OD-H, n-hexane/2-propanol = 90/10, flow rate 0.8 mL/min; λ = 250 nm; t_R = 8.47 min (minor), t_R = 14.63 min (major). The absolute configuration was determined with comparison of optical rotation reported in the literature. lit.[3a] $[\alpha]_D^{20}$ = –39.4 (*c* = 0.70, EtOAc, 98% ee), lit.[4] $[\alpha]_D^{20}$ = –24.3 (*c* = 0.9, $CHCl_3$, 90% ee), lit.[5] $[\alpha]_D^{20}$ = –22.8 (*c* = 1.0, $CHCl_3$, 94% ee).



(*R*)-2-(4-*tert*-butylphenyl)-1,2,3,4-tetrahydroquinoline (3c): 86% yield; R_f 0.8 (hexane/EtOAc = 90/10); ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.37 (d, *J* = 8.4 Hz, 2H), 7.32 (d, *J* = 8.4 Hz, 2H), 7.01-6.97 (m, 2H), 6.63 (td, *J* = 7.4, 0.9 Hz, 1H), 6.51 (dd, *J* = 8.1, 0.9 Hz, 1H), 4.40 (dd, *J* = 9.4, 3.4 Hz, 1H), 4.00 (bs, 1H), 2.98-2.87 (m, 1H), 2.74 (dt, *J* = 16.2, 4.5 Hz, 1H), 2.15-1.92 (m, 2H), 1.32 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 150.3, 144.8, 141.7, 129.2, 126.8, 126.2, 125.4, 120.8, 117.0, 113.9, 55.9, 34.5, 31.4, 30.9, 26.5; $[\alpha]_D^{27}$ = +32.8 (*c* = 1.7, $CHCl_3$). Enantiomeric excess: 94%, determined by HPLC, conditions: Chiracel OD-H, n-hexane/2-propanol = 90/10, flow rate 0.8 mL/min; λ = 250 nm; t_R = 7.31 min (minor), t_R = 8.69 min (major). The absolute configuration was tentatively assigned by analogy.

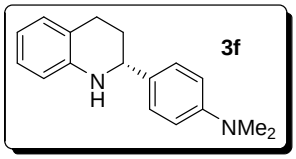


(*R*)-2-(4-methoxyphenyl)-1,2,3,4-tetrahydroquinoline (3d):[2-7] 94% yield; R_f 0.5 (hexane/EtOAc = 90/10); ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.30 (d, *J* = 8.5 Hz, 2H), 7.02-6.97 (m, 2H), 6.88 (d, *J* = 8.5 Hz, 2H), 6.64 (dd, *J* = 8.1, 7.4 Hz, 1H), 6.52 (d, *J* = 8.1 Hz, 1H), 4.37 (dd, *J* = 9.4, 3.2 Hz, 1H), 3.98 (bs, 1H), 3.81 (s, 3H), 2.98-2.87 (m, 1H), 2.73 (dt, *J* = 16.4, 4.5 Hz, 1H), 2.12-1.89 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 158.9, 144.8, 136.8, 129.2, 127.6, 126.8, 120.8, 117.0, 113.9, 55.7, 55.2, 31.0, 26.5; $[\alpha]_D^{27}$ = +29.1 (*c* = 1.4, $CHCl_3$). Enantiomeric excess: 97%, determined by HPLC, conditions: Chiracel OD-H, n-hexane/2-propanol = 90/10, flow rate 1.0 mL/min; λ = 250 nm; t_R = 9.38 min (minor), t_R = 15.41 min (major). The absolute configuration was determined with comparison of optical rotation reported in the literature. lit.[2a] $[\alpha]_D^{RT}$ = –18.6 (*c* = 1.0, $CHCl_3$, 98% ee), lit.[2b] $[\alpha]_D^{RT}$ = –22.1 (*c* = 1.0, $CHCl_3$, 91% ee), lit.[3a] $[\alpha]_D^{20}$ = –43.1 (*c* = 0.55, EtOAc, 98% ee), lit.[3b] $[\alpha]_D^{20}$ = –48.1 (*c* = 0.47, EtOAc, 96% ee), lit.[4] $[\alpha]_D^{20}$ = –26.1 (*c* = 0.94, $CHCl_3$, 86% ee), lit.[5] $[\alpha]_D^{20}$ = –24.3 (*c* = 1.2, $CHCl_3$, 95% ee), lit.[7] $[\alpha]_D^{RT}$ = +31.9 (*c* = 2.35, $CHCl_3$, 92% ee).

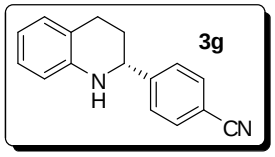


(*R*)-2-(3,4-dimethoxyphenyl)-1,2,3,4-tetrahydroquinoline (3e): 72% yield; R_f 0.2 (hexane/EtOAc = 90/10); ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.03-6.98 (m, 2H), 6.94-6.90 (m, 2H), 6.83 (d, *J* = 7.9 Hz, 1H), 6.64 (dd, *J* = 8.1, 7.6 Hz, 1H), 6.54 (d, *J* = 8.1 Hz, 1H), 4.37 (dd, *J* = 9.8, 3.4 Hz, 1H), 4.00 (bs, 1H), 3.87 (s, 6H), 3.00-2.89 (m, 1H), 2.75 (dt, *J* = 16.2, 4.3 Hz, 1H), 2.14-1.90 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 149.0, 148.2, 144.7, 137.3, 129.2, 126.8, 120.7, 118.5, 117.1, 113.9, 110.9, 109.3, 56.0, 55.8, 55.7, 31.2, 26.6; $[\alpha]_D^{27}$ =

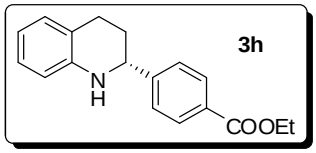
+33.7 (*c* = 1.3, $CHCl_3$). Enantiomeric excess: 95%, determined by HPLC, conditions: Chiracel OD-H, n-hexane/2-propanol = 85/15, flow rate 0.8 mL/min; λ = 235 nm; t_R = 16.96 min (minor), t_R = 28.47 min (major). The absolute configuration was tentatively assigned by analogy.



(*R*)-N,N-dimethyl-4-(1,2,3,4-tetrahydroquinolin-2-yl)aniline (3f): 74% yield; R_f 0.4 (hexane/EtOAc = 90/10); ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.25 (d, *J* = 8.7 Hz, 2H), 7.00-6.96 (m, 2H), 6.72 (d, *J* = 8.7 Hz, 2H), 6.62 (td, *J* = 7.4, 0.9 Hz, 1H), 6.49 (dd, *J* = 8.1, 1.0 Hz, 1H), 4.32 (dd, *J* = 9.4, 3.2 Hz, 1H), 3.96 (bs, 1H), 2.99-2.87 (m, 7H), 2.75 (dt, *J* = 16.6, 4.5 Hz, 1H), 2.11-1.89 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 150.1, 145.0, 132.5, 129.2, 127.3, 126.7, 120.8, 116.8, 113.8, 112.6, 55.7, 40.6, 31.0, 26.7; $[\alpha]_D^{27}$ = +23.7 (*c* = 0.9, $CHCl_3$). Enantiomeric excess: 94%, determined by HPLC, conditions: Chiracel OD-H, n-hexane/2-propanol = 90/10, flow rate 0.8 mL/min; λ = 250 nm; t_R = 11.84 min (minor), t_R = 15.19 min (major). The absolute configuration was tentatively assigned by analogy.

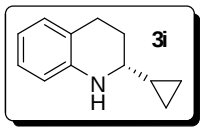


(*R*)-4-(1,2,3,4-tetrahydroquinolin-2-yl)benzonitrile (3g): 67% yield; R_f 0.3 (hexane/EtOAc = 90/10); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.63 (d, *J* = 8.0 Hz, 2H), 7.50 (d, *J* = 8.0 Hz, 2H), 7.06-6.99 (m, 2H), 6.69 (t, *J* = 8.0 Hz, 1H), 6.58 (d, *J* = 8.0 Hz, 1H), 4.53 (dd, *J* = 9.0, 3.0 Hz, 1H), 4.08 (bs, 1H), 2.93-2.86 (m, 1H), 2.66 (dt, *J* = 17.0, 5.0 Hz, 1H), 2.17-2.12 (m, 1H), 2.00-1.93 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 150.3, 143.9, 132.3, 129.3, 127.2, 127.0, 120.6, 118.7, 117.6, 114.1, 111.0, 55.6, 30.6, 25.6; $[\alpha]_D^{27}$ = +27.4 (*c* = 0.9, $CHCl_3$). Enantiomeric excess: 98%, determined by HPLC, conditions: Chiracel OD-H, n-hexane/2-propanol = 85/15, flow rate 0.8 mL/min; λ = 235 nm; t_R = 24.36 min (minor), t_R = 44.88 min (major). The absolute configuration was tentatively assigned by analogy.

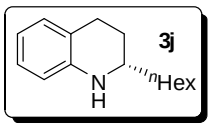


(*R*)-ethyl 4-(1,2,3,4-tetrahydroquinolin-2-yl)benzoate (3h): 69% yield; R_f 0.4 (hexane/EtOAc = 90/10); ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.01 (d, *J* = 8.3 Hz, 2H), 7.45 (d, *J* = 8.3 Hz, 2H), 7.05-6.98 (m, 2H), 6.67 (t, *J* = 7.9 Hz, 1H), 6.57 (d, *J* = 7.9 Hz, 1H), 4.51 (dd, *J* = 8.9, 3.4 Hz, 1H), 4.37 (q, *J* = 7.1 Hz, 2H) 4.09 (bs, 1H), 2.96-2.85 (m, 1H), 2.70 (dt, *J* = 16.4, 4.9 Hz, 1H), 2.17-2.08 (m, 1H), 2.04-1.91 (m, 1H), 1.39 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 166.4, 150.0, 144.3, 129.8, 129.6, 129.3, 127.0, 126.4, 120.7, 117.4, 114.0, 60.9, 55.9, 30.8, 26.0, 14.3; $[\alpha]_D^{27}$ = +36.2 (*c* = 0.7, $CHCl_3$). Enantiomeric excess:

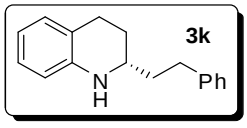
98%, determined by HPLC, conditions: Chiracel OD-H, n-hexane/2-propanol = 85/15, flow rate 0.8 mL/min; λ = 235 nm; t_R = 15.54 min (minor), t_R = 26.11 min (major). The absolute configuration was tentatively assigned by analogy.



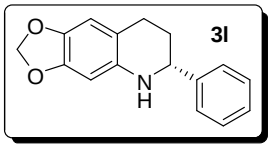
(*R*)-2-cyclopropyl-1,2,3,4-tetrahydroquinoline (3i):[6] 87% yield; R_f 0.6 (hexane/EtOAc = 90/10); ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.98-6.93 (m, 2H), 6.59 (t, *J* = 7.6 Hz, 1H), 6.48 (d, *J* = 7.6 Hz, 1H), 2.80-2.75 (m, 2H), 2.39 (td, *J* = 9.4, 3.0 Hz, 1H), 2.12-2.03 (m, 1H), 1.85-1.72 (m, 1H) 0.95-0.83 (m, 1H) 0.56-0.48 (m, 2H) 0.29-0.18 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 144.5, 129.1, 126.6, 121.1, 116.7, 113.7, 57.4, 28.2, 26.6, 16.9, 1.8; $[\alpha]_D^{27}$ = –81.7 (*c* = 1.0, $CHCl_3$). Enantiomeric excess: 87%, determined by HPLC, conditions: Chiracel OD-H, n-hexane/2-propanol = 90/10, flow rate 1.0 mL/min; λ = 250 nm; t_R = 7.07 min (minor), t_R = 7.97 min (major). The absolute configuration was tentatively assigned by analogy.



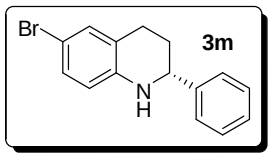
(*S*)-2-hexyl-1,2,3,4-tetrahydroquinoline (3j): 82% yield; R_f 0.8 (hexane/EtOAc = 90/10); ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.96-6.92 (m, 2H), 6.58 (t, *J* = 8.1 Hz, 1H), 6.46 (d, *J* = 8.1 Hz, 1H), 3.74 (bs, 1H), 3.25-3.19 (m, 1H), 2.85-2.69 (m, 2H), 1.97-1.92 (m, 1H), 1.63-1.25 (m, 11H), 0.91-0.88 (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 144.7, 129.2, 126.6, 121.3, 116.8, 114.0, 51.6, 36.7, 31.8, 29.4, 28.1, 26.4, 25.7, 22.6, 14.0; $[\alpha]_D^{27}$ = –31.4 (*c* = 1.4, $CHCl_3$). Enantiomeric excess: 58%, determined by HPLC, conditions: Chiracel OD-H, n-hexane/2-propanol = 90/10, flow rate 1.0 mL/min; λ = 250 nm; t_R = 10.82 min (minor), t_R = 11.46 min (major). The absolute configuration was tentatively assigned by analogy.



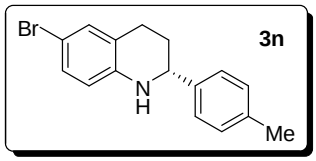
(*S*)-2-phenethyl-1,2,3,4-tetrahydroquinoline (3k):[2a,5] 86% yield; R_f 0.7 (hexane/EtOAc = 90/10); ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.32-7.16 (m, 5H), 6.98-6.93 (m, 2H), 6.60 (t, *J* = 7.6 Hz, 1H), 6.45 (d, *J* = 8.3 Hz, 1H), 3.76 (bs, 1H), 3.34-3.25 (m, 1H), 2.85-2.67 (m, 4H), 2.04-1.95 (m, 1H), 1.87-1.79 (m, 2H) 1.74-1.60 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 144.4, 141.8, 129.2, 128.4, 128.3, 126.7, 125.9, 121.2, 117.0, 114.1, 51.0, 38.2, 32.1, 27.9, 26.2; $[\alpha]_D^{27}$ = –24.6 (*c* = 1.0, $CHCl_3$). Enantiomeric excess: 58%, determined by HPLC, conditions: Chiracel OD-H, n-hexane/2-propanol = 90/10, flow rate 1.0 mL/min; λ = 250 nm; t_R = 11.61 min (minor), t_R = 12.23 min (major). The absolute configuration was determined with comparison of optical rotation reported in the literature. lit.[2a] $[\alpha]_D^{RT}$ = +50.7 (*c* = 1.0, $CHCl_3$, 91% ee), lit.[5] $[\alpha]_D^{20}$ = +64.9 (*c* = 1.1, $CHCl_3$, 93% ee).



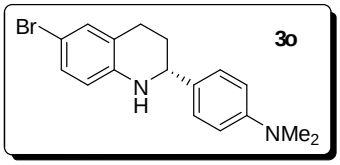
(*R*)-6-phenyl-5,6,7,8-tetrahydro-[1,3]dioxolo[4,5-g]quinoline (3l):[3a] 87% yield; R_f 0.6 (hexane/EtOAc = 90/10); ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.40-7.25 (m, 5H), 6.51 (s, 1H), 6.15 (s, 1H), 5.81 (s, 2H), 4.34 (dd, *J* = 9.3, 3.2 Hz, 1H), 3.78 (bs, 1H), 2.91-2.79 (m, 1H), 2.68-2.59 (m, 1H), 2.13-1.89 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 146.3, 144.7, 139.5, 139.2, 128.5, 127.3, 126.5, 112.5, 108.9, 100.2, 96.3, 56.3, 31.1, 26.4; $[\alpha]_D^{27}$ = +53.9 (*c* = 1.0, $CHCl_3$). Enantiomeric excess: 98%, determined by HPLC, conditions: Chiracel OD-H, n-hexane/2-propanol = 85/15, flow rate 0.8 mL/min; λ = 325 nm; t_R = 19.67 min (minor), t_R = 20.66 min (major). The absolute configuration was determined with comparison of optical rotation reported in the literature. lit.[3a] $[\alpha]_D^{20}$ = –49.4 (*c* = 0.53, EtOAc, 91% ee).



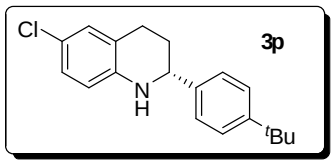
(*R*)-6-bromo-2-phenyl-1,2,3,4-tetrahydroquinoline (3m): 92% yield; R_f 0.7 (hexane/EtOAc = 90/10); ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.36-7.24 (m, 5H), 7.10-7.05 (m, 2H), 6.40 (d, *J* = 8.3 Hz, 1H), 4.41 (dd, *J* = 9.1, 3.0 Hz, 1H), 4.06 (bs, 1H), 2.92-2.81 (m, 1H), 2.68 (dt, *J* = 16.6, 5.3 Hz, 1H), 2.14-2.05 (m, 1H), 2.01-1.88 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 144.2, 143.6, 131.6, 129.5, 128.6, 127.5, 126.4, 122.8, 115.3, 108.4, 56.0, 30.3, 26.0; $[\alpha]_D^{27}$ = +41.6 (*c* = 0.8, $CHCl_3$). Enantiomeric excess: 99%, determined by HPLC, conditions: Chiracel OD-H, n-hexane/2-propanol = 85/15, flow rate 0.8 mL/min; λ = 250 nm; t_R = 13.18 min (minor), t_R = 17.26 min (major). The absolute configuration was tentatively assigned by analogy.



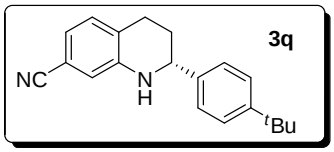
(*R*)-6-bromo-2-*p*-tolyl-1,2,3,4-tetrahydroquinoline (3n): 89% yield; R_f 0.8 (hexane/EtOAc = 90/10); ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.23 (d, *J* = 7.6 Hz, 2H), 7.15 (d, *J* = 7.6 Hz, 2H), 7.09-7.05 (m, 2H), 6.39 (d, *J* = 8.3 Hz, 1H), 4.37 (dd, *J* = 9.1, 3.0 Hz, 1H), 4.03 (bs, 1H), 2.92-2.80 (m, 1H), 2.69 (dt, *J* = 16.6, 4.5 Hz, 1H), 2.34 (s, 3H), 2.13-2.03 (m, 1H), 1.99-1.86 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 143.7, 141.2, 137.2, 131.6, 129.4, 129.2, 126.3, 122.8, 115.3, 108.3, 55.7, 30.4, 26.1, 21.1; $[\alpha]_D^{27}$ = +43.7 (*c* = 1.1, $CHCl_3$). Enantiomeric excess: 98%, determined by HPLC, conditions: Chiracel OD-H, n-hexane/2-propanol = 85/15, flow rate 0.8 mL/min; λ = 250 nm; t_R = 8.00 min (minor), t_R = 22.17 min (major). The absolute configuration was tentatively assigned by analogy.



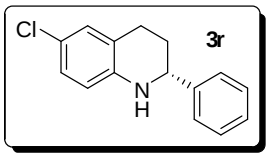
(*R*)-4-(6-bromo-1,2,3,4-tetrahydroquinolin-2-yl)-N,N-dimethylaniline (3o): 78% yield; R_f 0.4 (hexane/EtOAc = 90/10); ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.25-7.21 (m, 2H), 7.09-7.03 (m, 2H), 6.72 (d, *J* = 8.7 Hz, 2H), 6.37 (d, *J* = 8.3 Hz, 1H), 4.30 (dd, *J* = 9.4, 3.2 Hz, 1H), 3.99 (bs, 1H), 2.94 (s, 6H), 2.91-2.82 (m, 1H), 2.70 (dt, *J* = 16.4, 4.5 Hz, 1H), 2.09-1.85 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 150.1, 143.9, 131.9, 131.6, 129.3, 127.2, 122.9, 115.2, 112.6, 108.1, 55.5, 40.6, 30.4, 26.4; $[\alpha]_D^{27}$ = +9.7 (*c* = 0.7, $CHCl_3$). Enantiomeric excess: 92%, determined by HPLC, conditions: Chiracel OD-H, n-hexane/2-propanol = 90/10, flow rate 1.0 mL/min; λ = 260 nm; t_R = 11.47 min (minor), t_R = 19.40 min (major). The absolute configuration was tentatively assigned by analogy.



(*R*)-2-(4-*tert*-butylphenyl)-6-chloro-1,2,3,4-tetrahydroquinoline (3p): 79% yield; R_f 0.7 (hexane/EtOAc = 90/10); ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.37 (d, *J* = 8.3 Hz, 2H), 7.29 (d, *J* = 8.3 Hz, 2H), 6.96-6.92 (m, 2H), 6.43 (d, *J* = 8.3 Hz, 1H), 4.38 (dd, *J* = 9.1, 3.0 Hz, 1H), 4.03 (bs, 1H), 2.93-2.82 (m, 1H), 2.70 (dt, *J* = 16.6, 4.5 Hz, 1H), 2.14-2.04 (m, 1H), 2.01-1.88 (m, 1H), 1.32 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 150.5, 143.3, 141.2, 128.8, 126.6, 126.1, 125.5, 122.3, 121.3, 114.8, 55.8, 34.5, 31.3, 30.3, 26.3; $[\alpha]_D^{27}$ = +21.9 (*c* = 0.9, $CHCl_3$). Enantiomeric excess: 95%, determined by HPLC, conditions: Chiracel OD-H, n-hexane/2-propanol = 85/15, flow rate 0.8 mL/min; λ = 250 nm; t_R = 6.86 min (minor), t_R = 8.77 min (major). The absolute configuration was tentatively assigned by analogy.



(*R*)-2-(4-*tert*-butylphenyl)-1,2,3,4-tetrahydroquinoline-7-carbonitrile (3q): 75% yield; R_f 0.5 (hexane/EtOAc = 90/10); ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.38 (d, *J* = 8.3 Hz, 2H), 7.27 (d, *J* = 8.3 Hz, 2H), 7.03 (d, *J* = 7.6 Hz, 1H), 6.87 (dd, *J* = 7.6, 1.5 Hz, 1H), 6.72 (d, *J* = 1.5 Hz, 1H), 4.44 (dd, *J* = 9.1, 3.7 Hz, 1H), 4.23 (bs, 1H), 2.96-2.85 (m, 1H), 2.76 (dt, *J* = 16.6, 4.5 Hz, 1H), 2.17-2.08 (m, 1H), 2.02-1.89 (m, 1H), 1.32 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 150.7, 145.0, 140.6, 129.7, 126.0, 125.5, 120.1, 119.6, 116.2, 110.2, 55.5, 34.5, 31.3, 29.7, 26.5; $[\alpha]_D^{27}$ = +55.8 (*c* = 1.0, $CHCl_3$). Enantiomeric excess: 95%, determined by HPLC, conditions: Chiracel OD-H, n-hexane/2-propanol = 85/15, flow rate 0.8 mL/min; λ = 270 nm; t_R = 9.30 min (major), t_R = 14.76 min (minor). The absolute configuration was tentatively assigned by analogy.



(*R*)-6-chloro-2-phenyl-1,2,3,4-tetrahydroquinoline (3r):[3a] 89% yield; R_f 0.8 (hexane/EtOAc = 90/10); ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.38-7.26 (m, 5H), 6.96-6.92 (m, 2H), 6.44 (d, *J* = 9.1 Hz, 1H), 4.41 (dd, *J* = 9.1, 3.0 Hz, 1H), 2.92-2.81 (m, 1H), 2.68 (dt, *J* = 16.6, 5.3 Hz, 1H), 2.16-1.89 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 144.3, 143.2, 128.8, 128.6, 127.5, 126.6, 126.4, 122.3, 121.4, 114.9, 56.0, 30.4, 26.1; $[\alpha]_D^{27}$ = +37.5 (*c* = 1.1, $CHCl_3$). Enantiomeric excess: 97%, determined by HPLC, conditions: Chiracel OD-H, n-hexane/2-propanol = 85/15, flow rate 0.8 mL/min; λ = 250 nm; t_R = 12.63 min (minor), t_R = 16.96 min (major). The absolute configuration was determined with comparison of optical rotation reported in the literature. lit.[3a] $[\alpha]_D^{20}$ = –29.4 (*c* = 0.52, EtOAc, 97% ee).

4. References:

[1] (a) N. T. Patil and V. S. Raut, *J. Org. Chem*., 2010, **75**, 6961-6964; (b) N. T. Patil, V. S. Raut, V. S. Shinde, G. Gayatri, and G. N. Sastry, *Chem.–Eur. J*., 2012, **18**, 5530-5535.

[2] (a) M. Rueping, A. P. Antonchick, and T. Theissmann, *Angew. Chem., Int. Ed.*, 2006, **45**, 3683-3686; (b) M. Rueping and T. Theissmann, *Chem. Sci.*, 2010, **1**, 473-476.

[3] (a) Z.-Y. Han, H. Xiao, X.-H. Chen and L.-Z. Gong, *J. Am. Chem. Soc.* 2009, **131**, 9182-9183; (b) X.-F. Tu and L.-Z. Gong, *Angew. Chem. Int. Ed.*, 2012, DOI: 10.1002/anie.201204179.

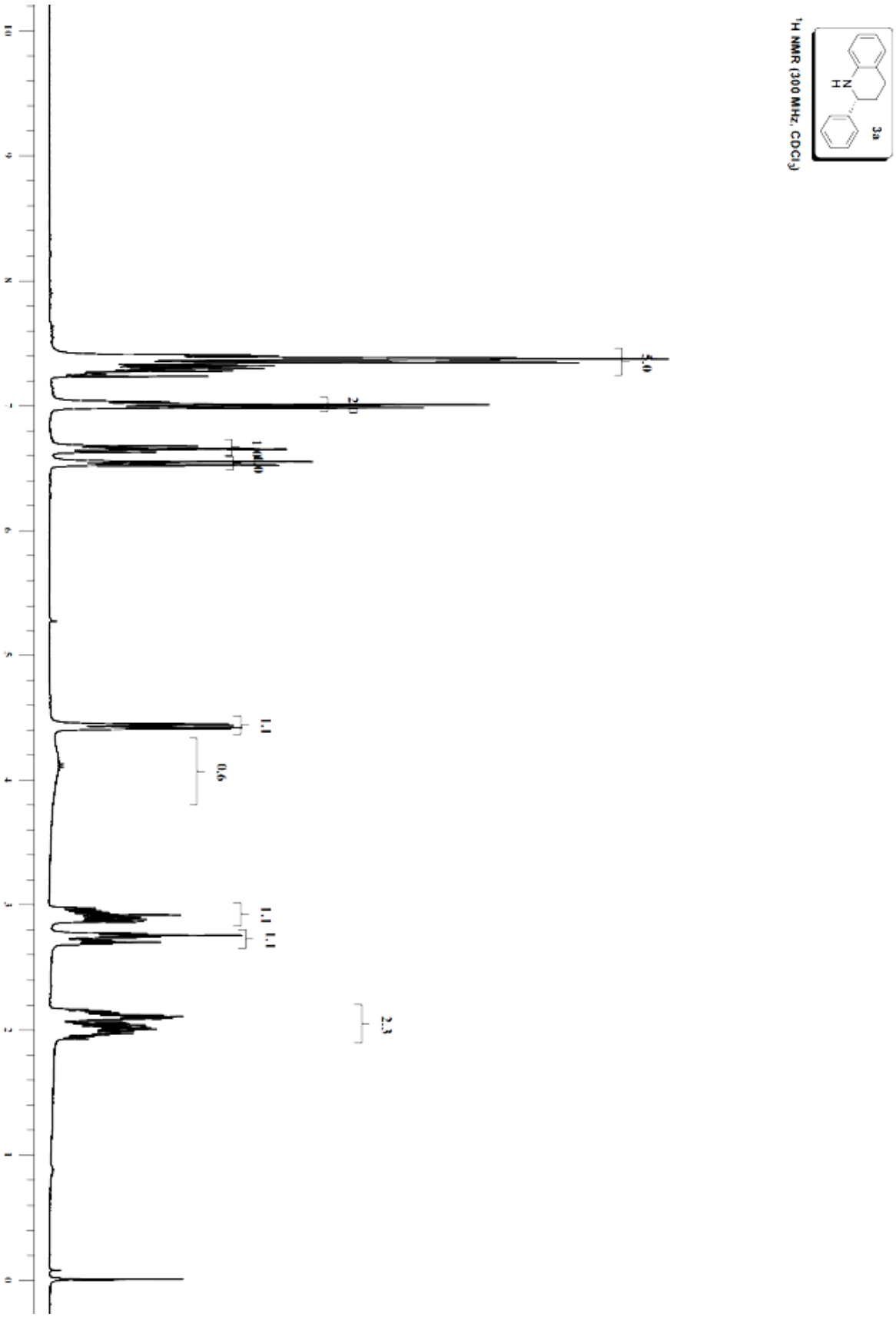
[4] Q.-A. Chen, K. Gao, Y. Duan, Z.-S. Ye, L. Shi, Y. Yang, and Y.-G. Zhou, *J. Am. Chem.Soc.*, 2012, **134**, 2442-2448.

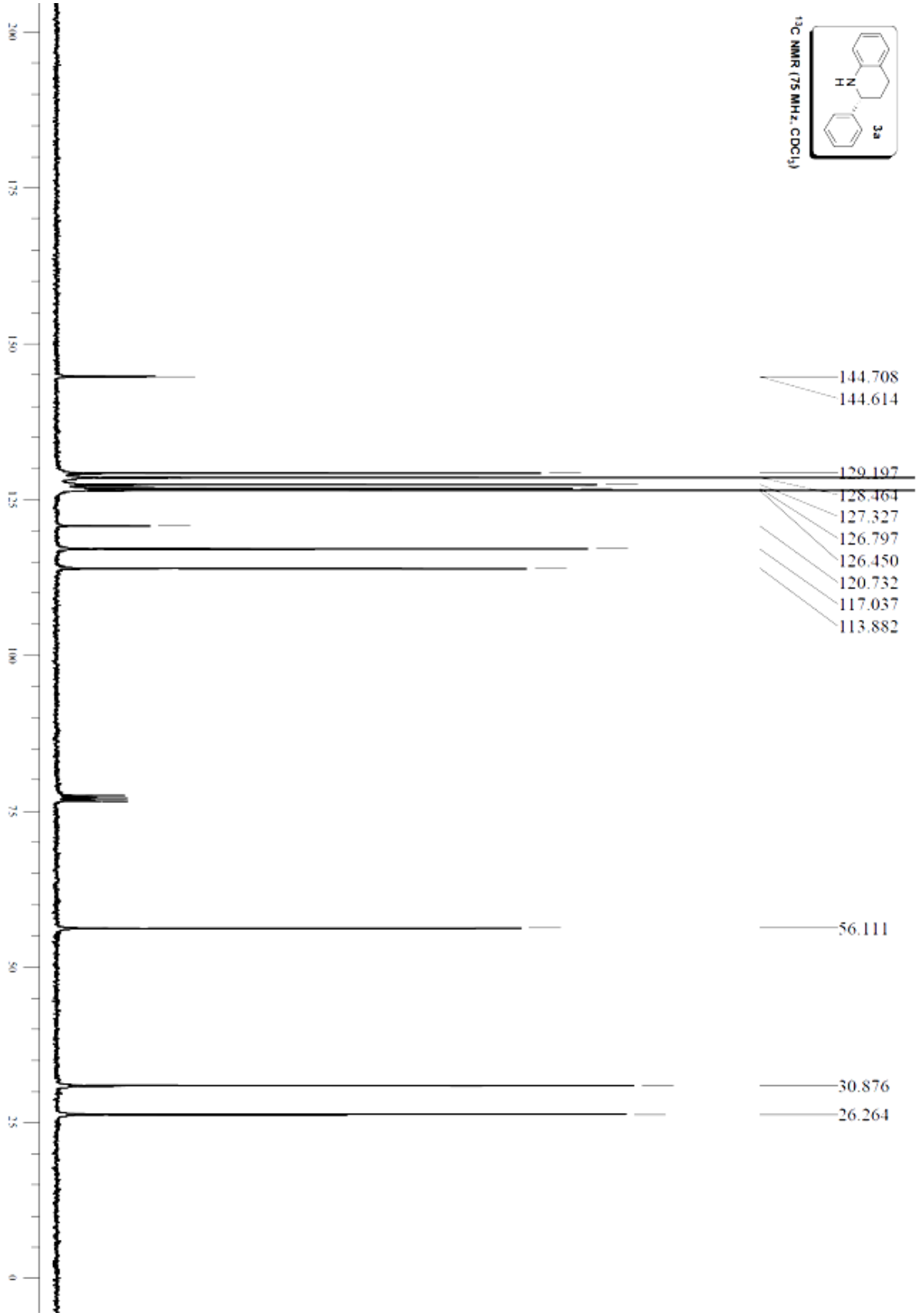
[5] Q.-S. Guo, D.-M. Du, and J. Xu, *Angew. Chem. Int. Ed.*, 2008, **47**, 759 -762.

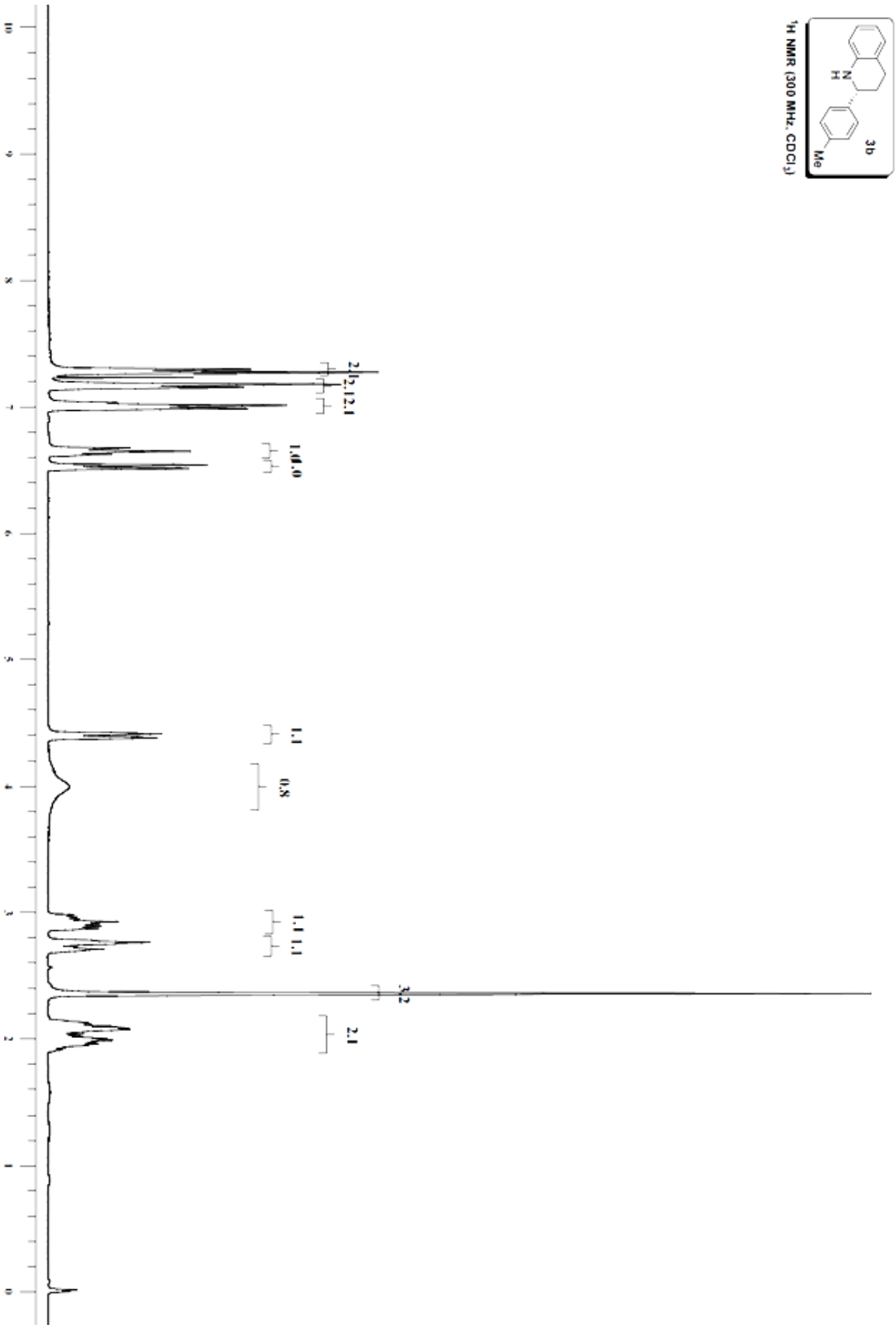
[6] C. Wang, C. Li, X. Wu, A. Pettman and J. Xiao, *Angew. Chem. Int. Ed.*, 2009, **48**, 6524 -6528.

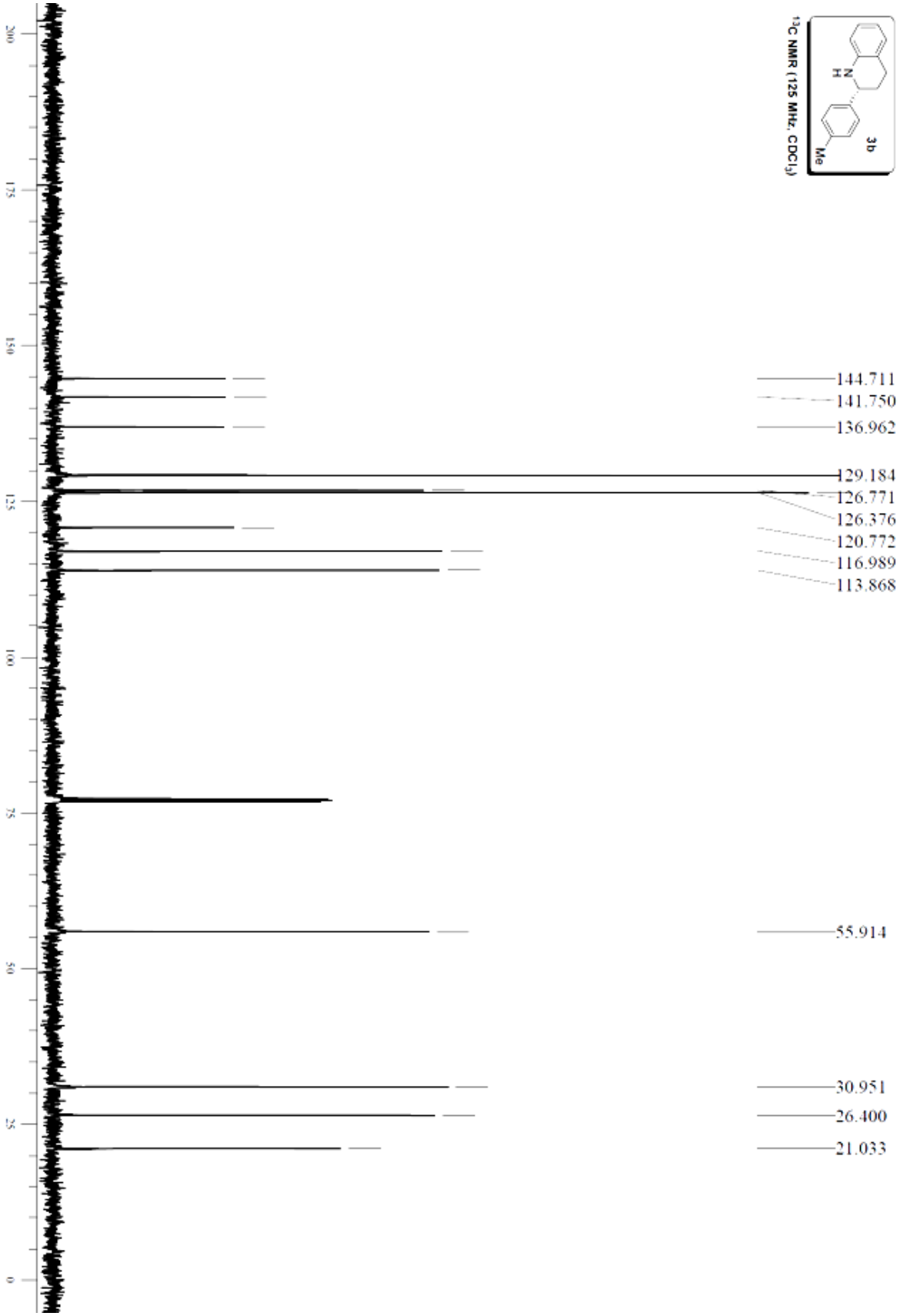
[7] T. Wang, L.-G. Zhuo, Z. Li, F. Chen, Z. Ding, Y. He, Q.-H. Fan, J. Xiang, Z.-X. Yu, and A. S. C. Chan, *J. Am. Chem. Soc.*, 2011, **133**, 9878-9891.

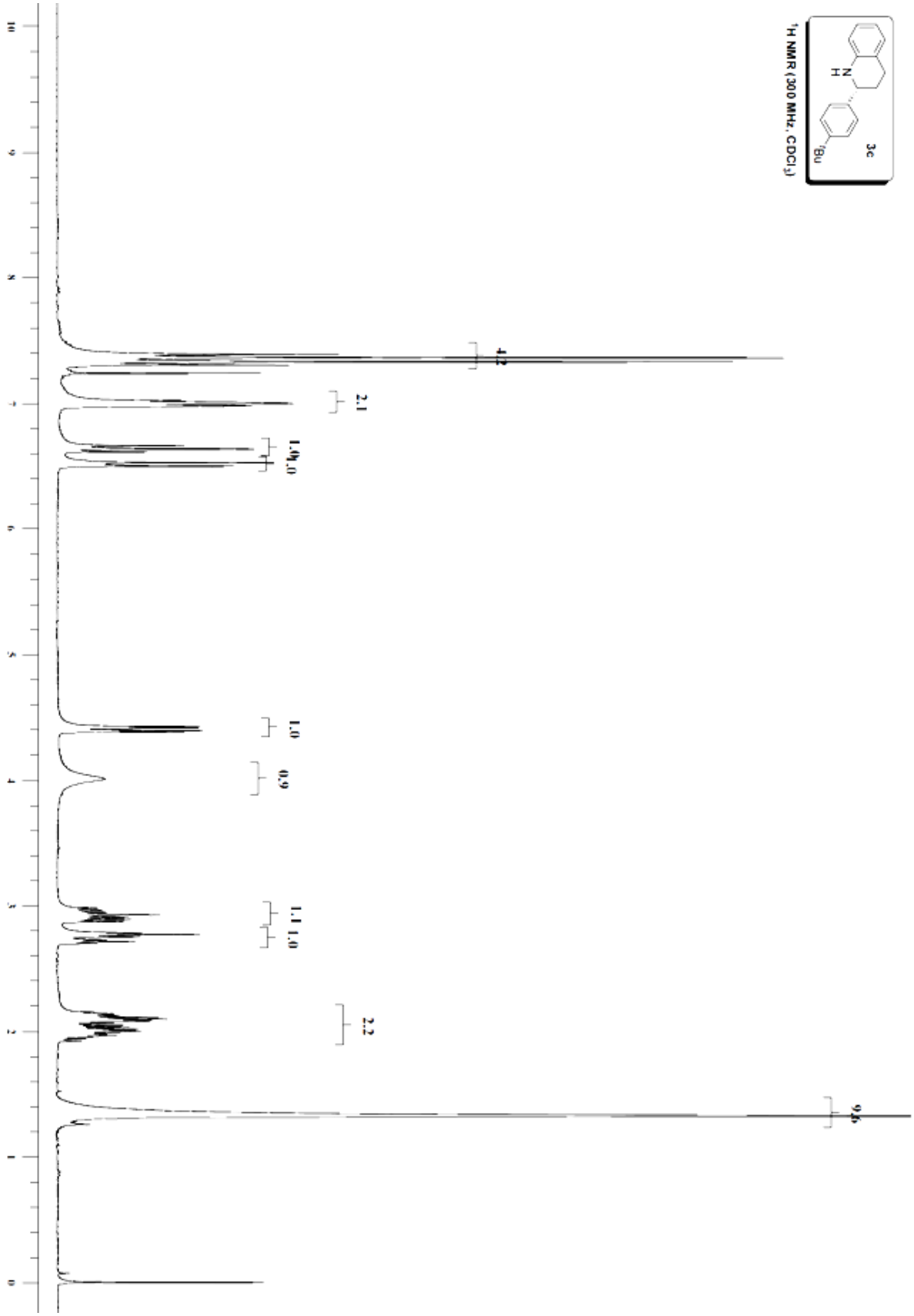
5. ^{1}H NMR and ^{13}C NMR Spectra of Compounds:

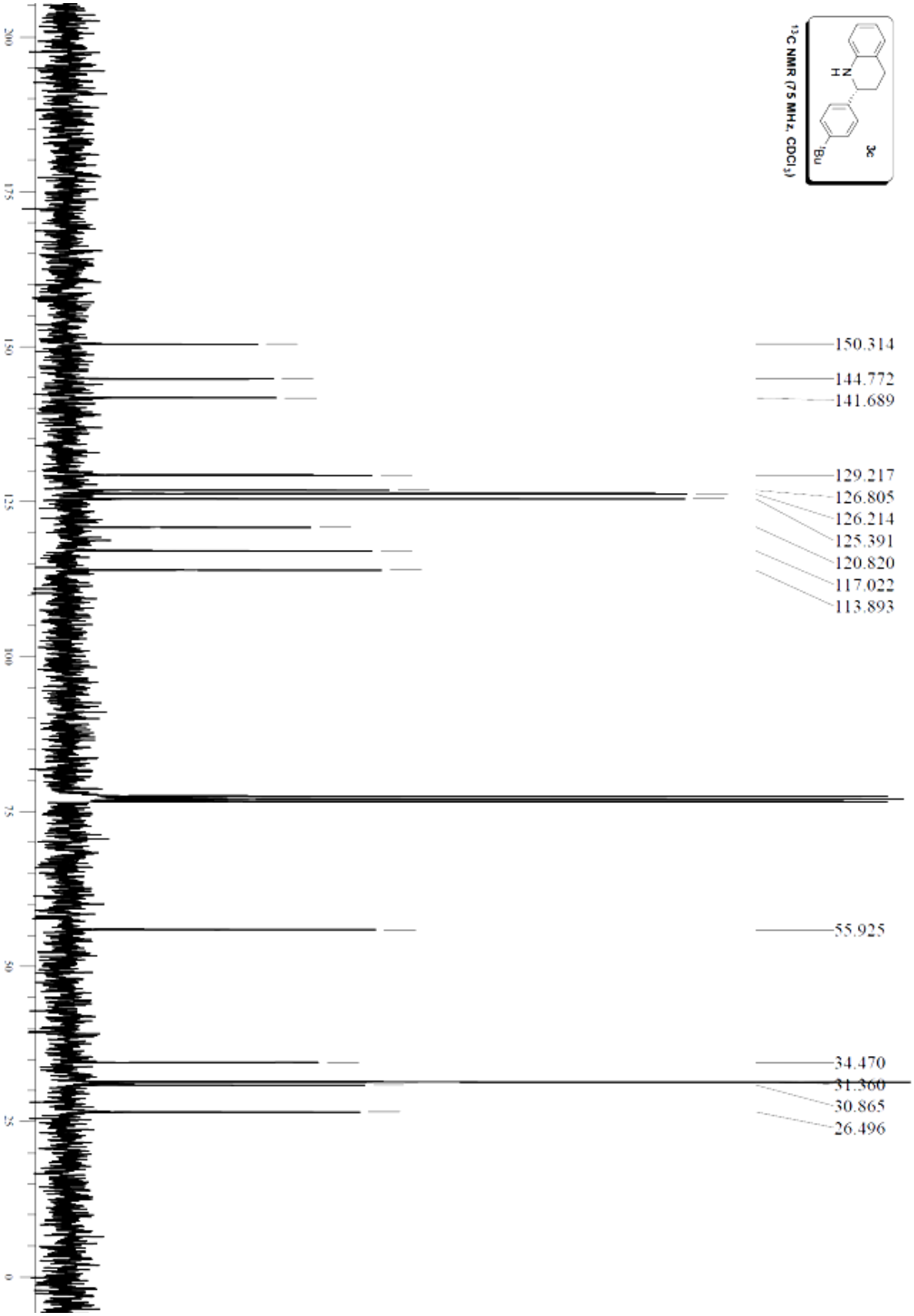


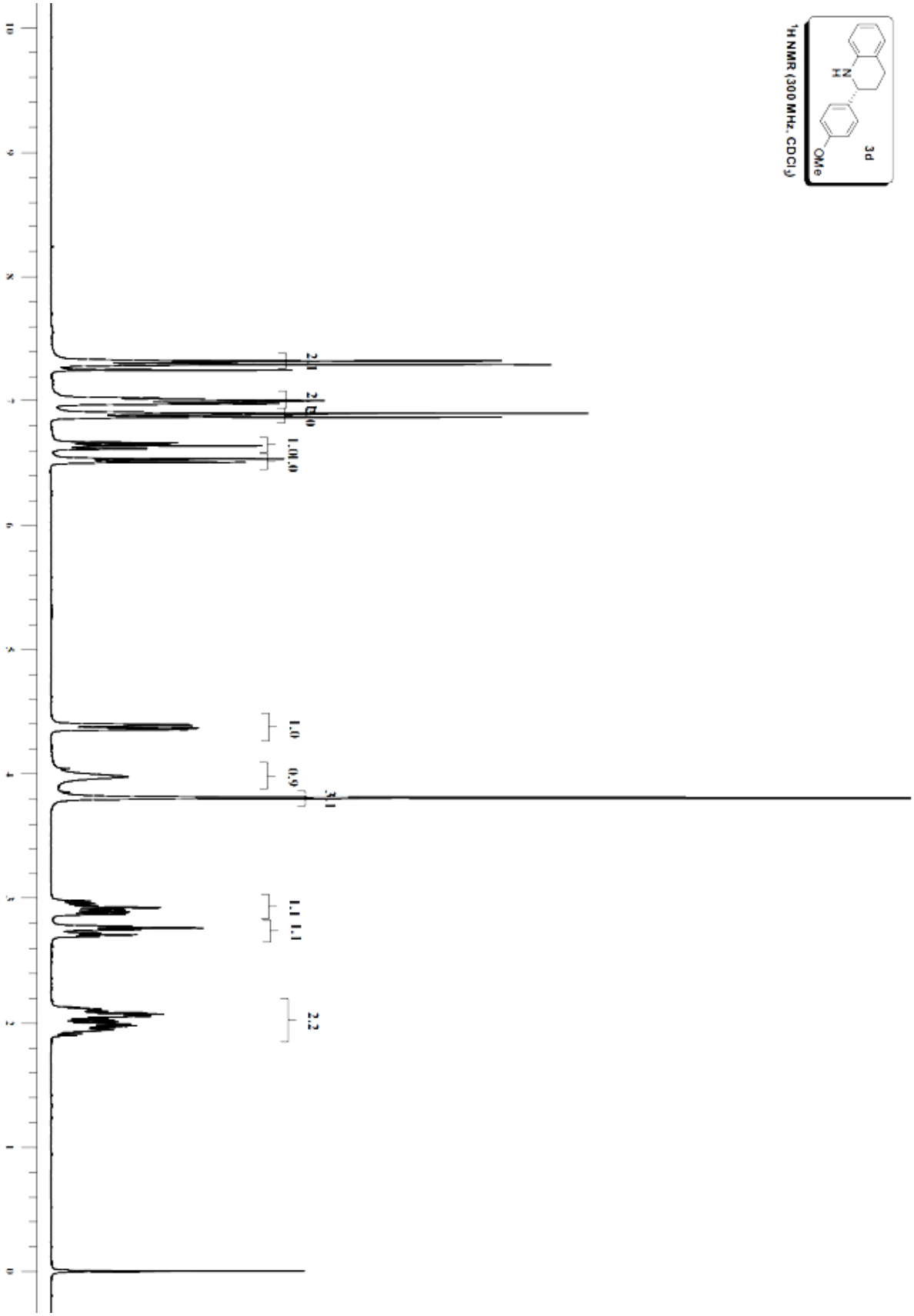

^{13}C NMR (75 MHz, CDCl$_3$)
3a
144.708
144.614
129.197
128.464
127.327
126.797
126.450
120.732
117.037
113.882
56.111
30.876
26.264

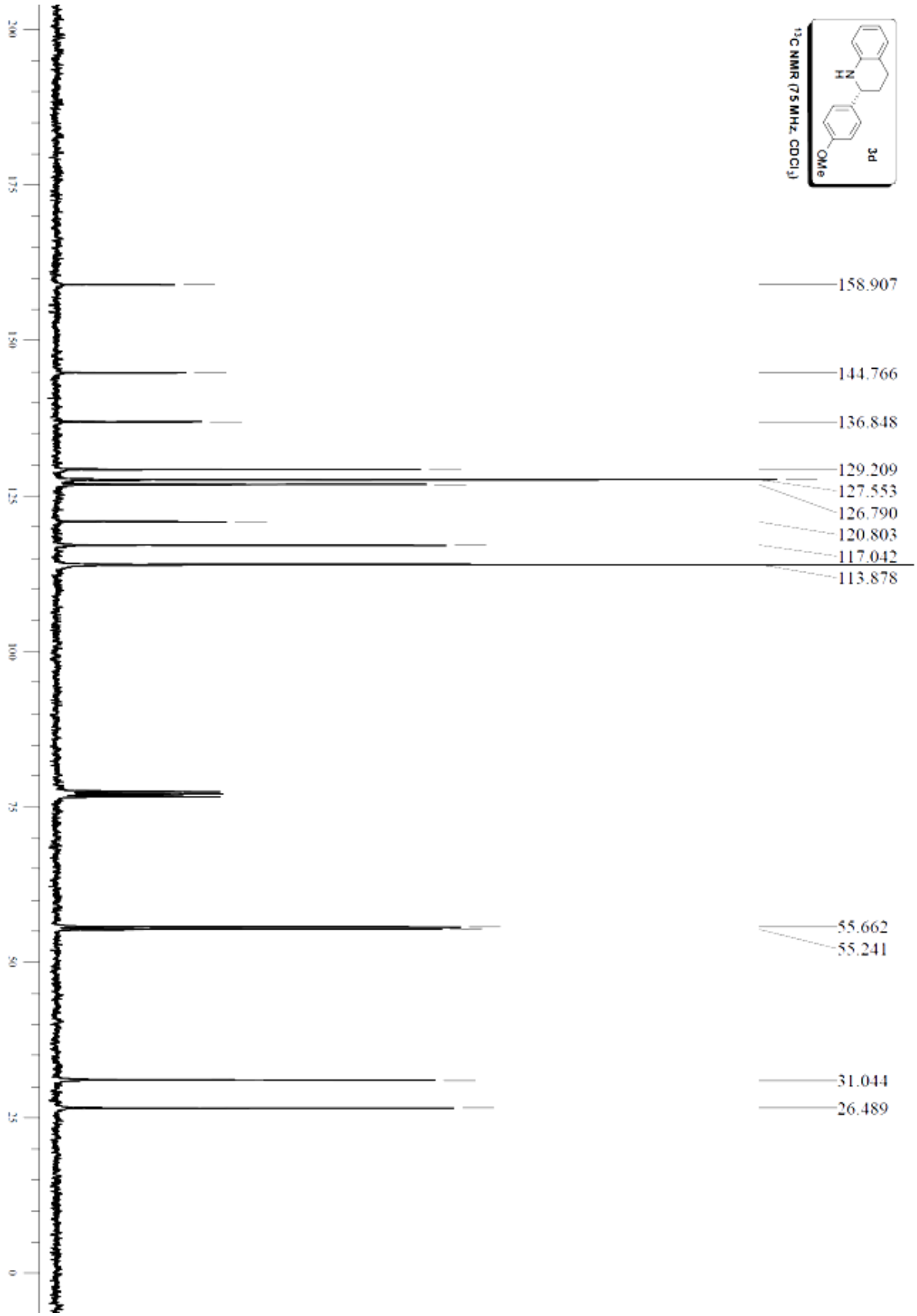

3b
Me
^{1}H NMR (300 MHz, CDCl$_3$)
2.12.1
1.0
1.1
0.8
1.1 1.1
3.2
2.1

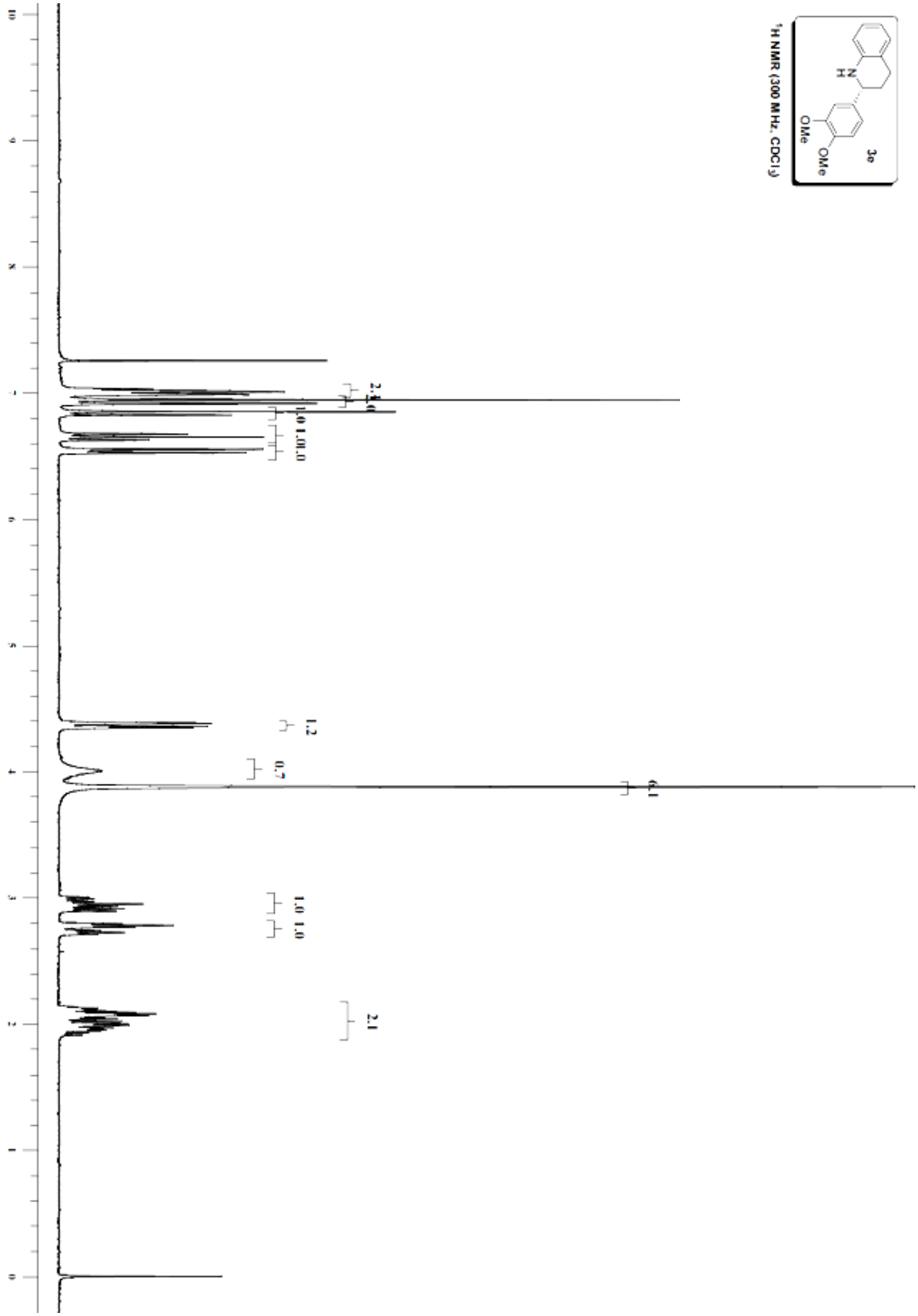

^{13}C NMR (125 MHz, CDCl$_3$)
3b
144.711
141.750
136.962
129.184
126.771
126.376
120.772
116.989
113.868
55.914
30.951
26.400
21.033

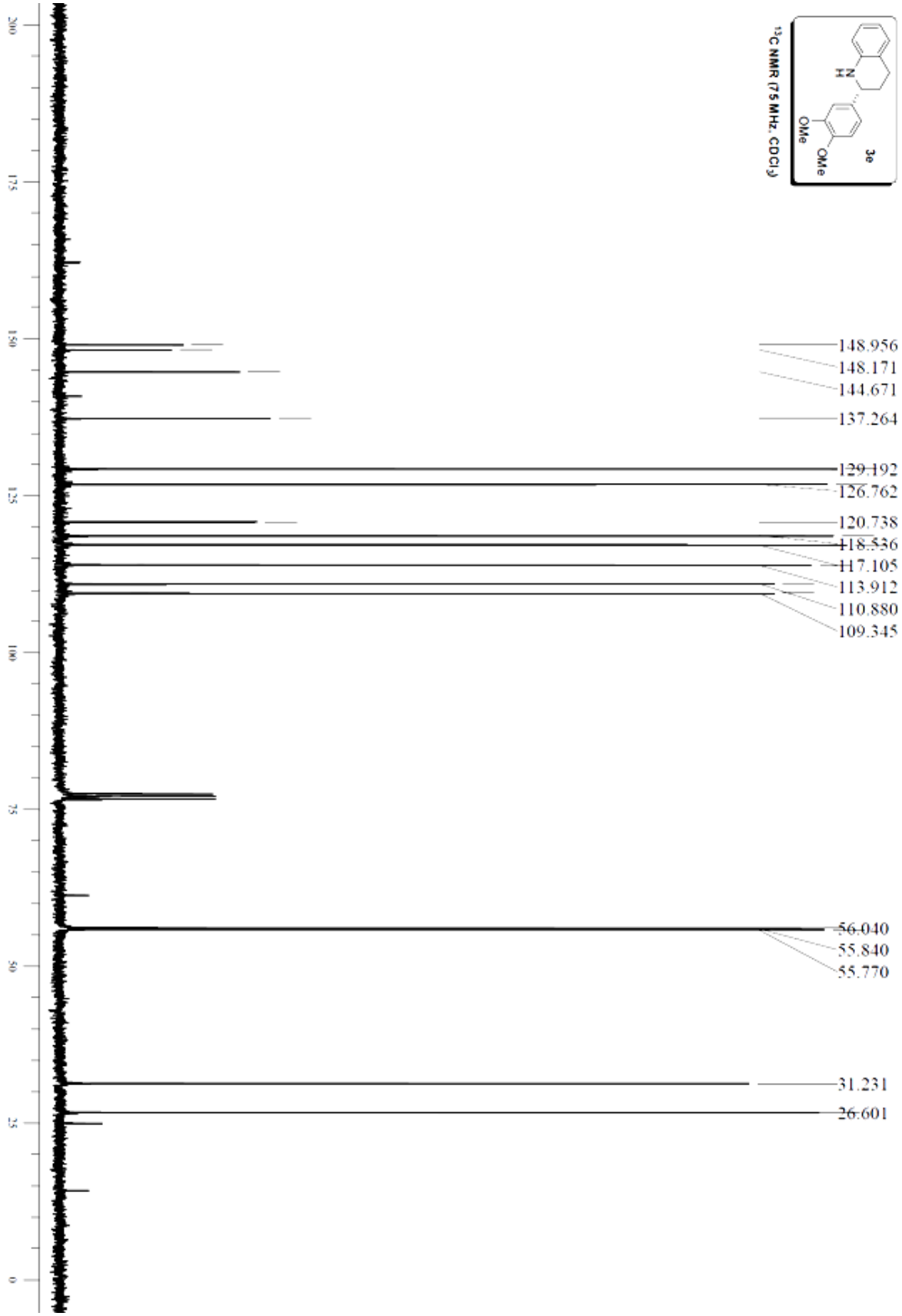

^{1}H NMR (300 MHz, CDCl$_3$)
3c
4.2
2.1
1.0
1.0
0.9
1.1
1.0
2.2
9.0

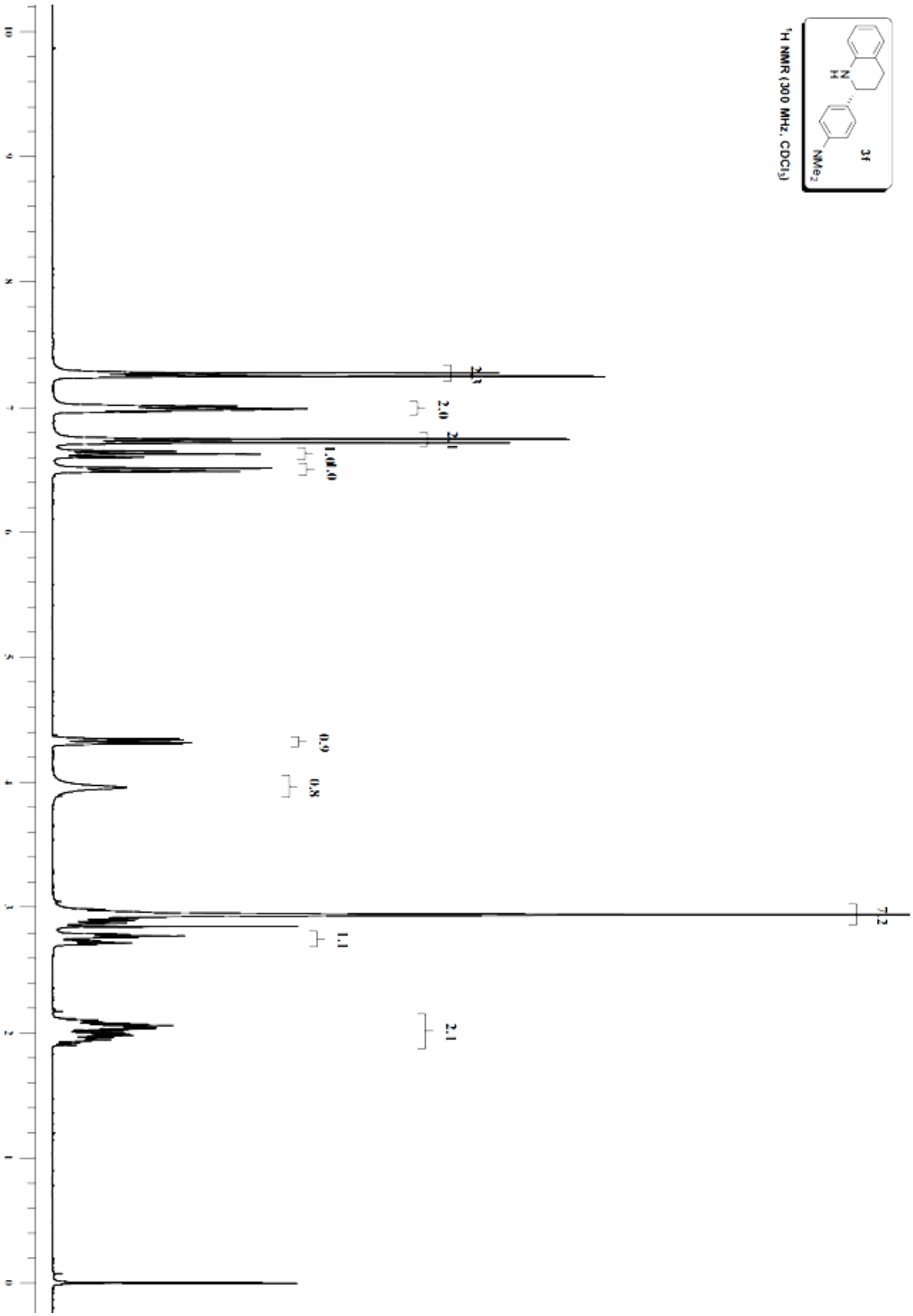

^{13}C NMR (75 MHz, CDCl$_3$)
3c
150.314
144.772
141.689
129.217
126.805
126.214
125.391
120.820
117.022
113.893
55.925
34.470
31.360
30.865
26.496

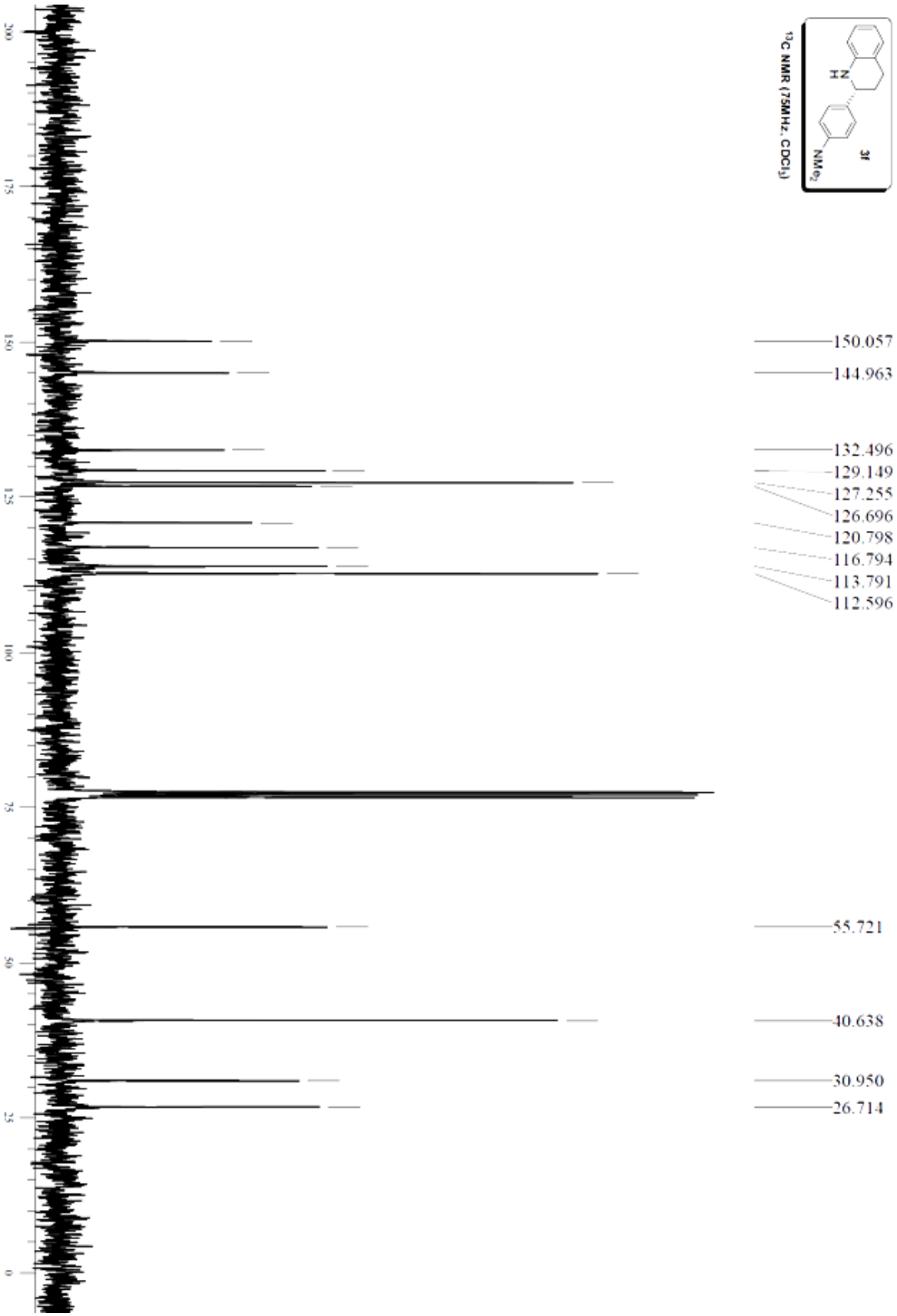

^{1}H NMR (300 MHz, CDCl$_3$)
3d
OMe
2.0
2.0
1.0
1.0
0.9
3.1
1.1
1.1
2.2

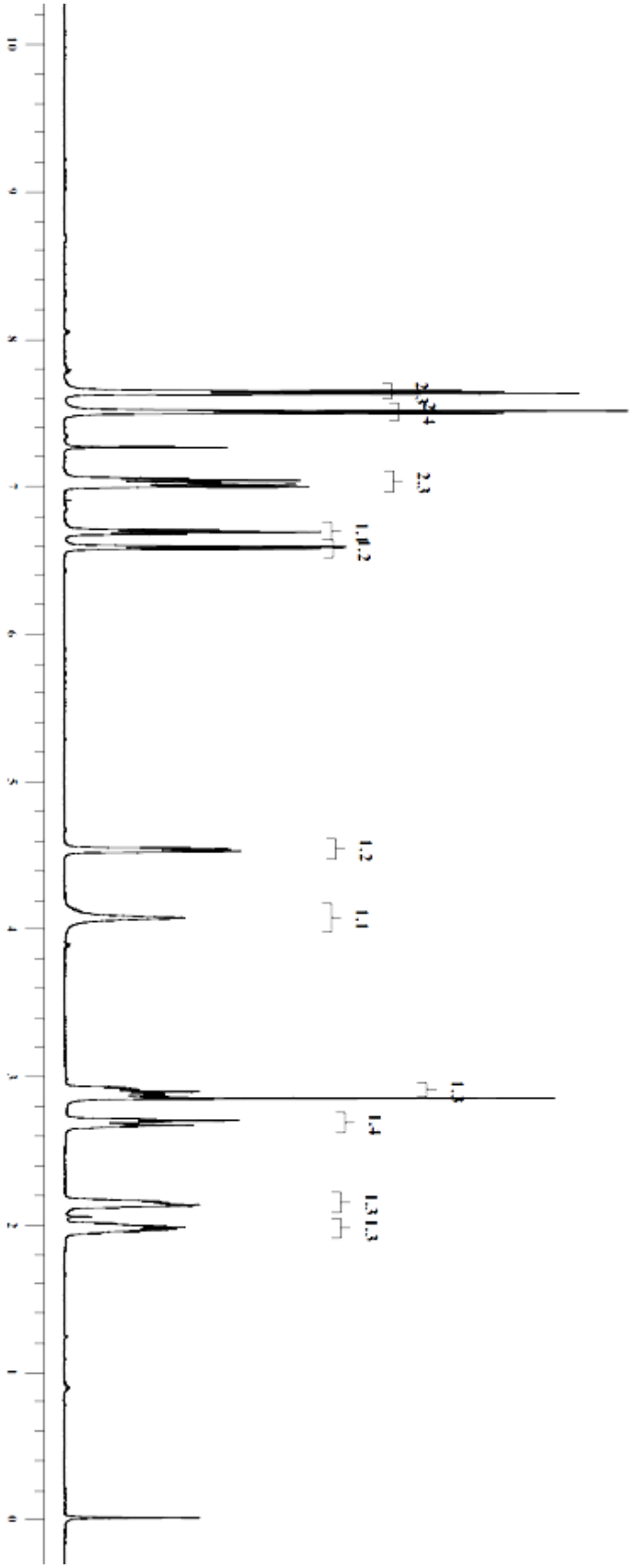

^{13}C NMR (75 MHz, CDCl$_3$)
3d
OMe
158.907
144.766
136.848
129.209
127.553
126.790
120.803
117.042
113.878
55.662
55.241
31.044
26.489


^{1}H NMR (300 MHz, CDCl$_3$)
OMe
OMe
3e
2.1
1.2
0.7
4.1
1.0
1.0
2.1

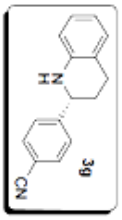

^{13}C NMR (75 MHz, CDCl$_3$)
3e
OMe
OMe
148.956
148.171
144.671
137.264
129.192
126.762
120.738
118.536
117.105
113.912
110.880
109.345
56.040
55.840
55.770
31.231
26.601

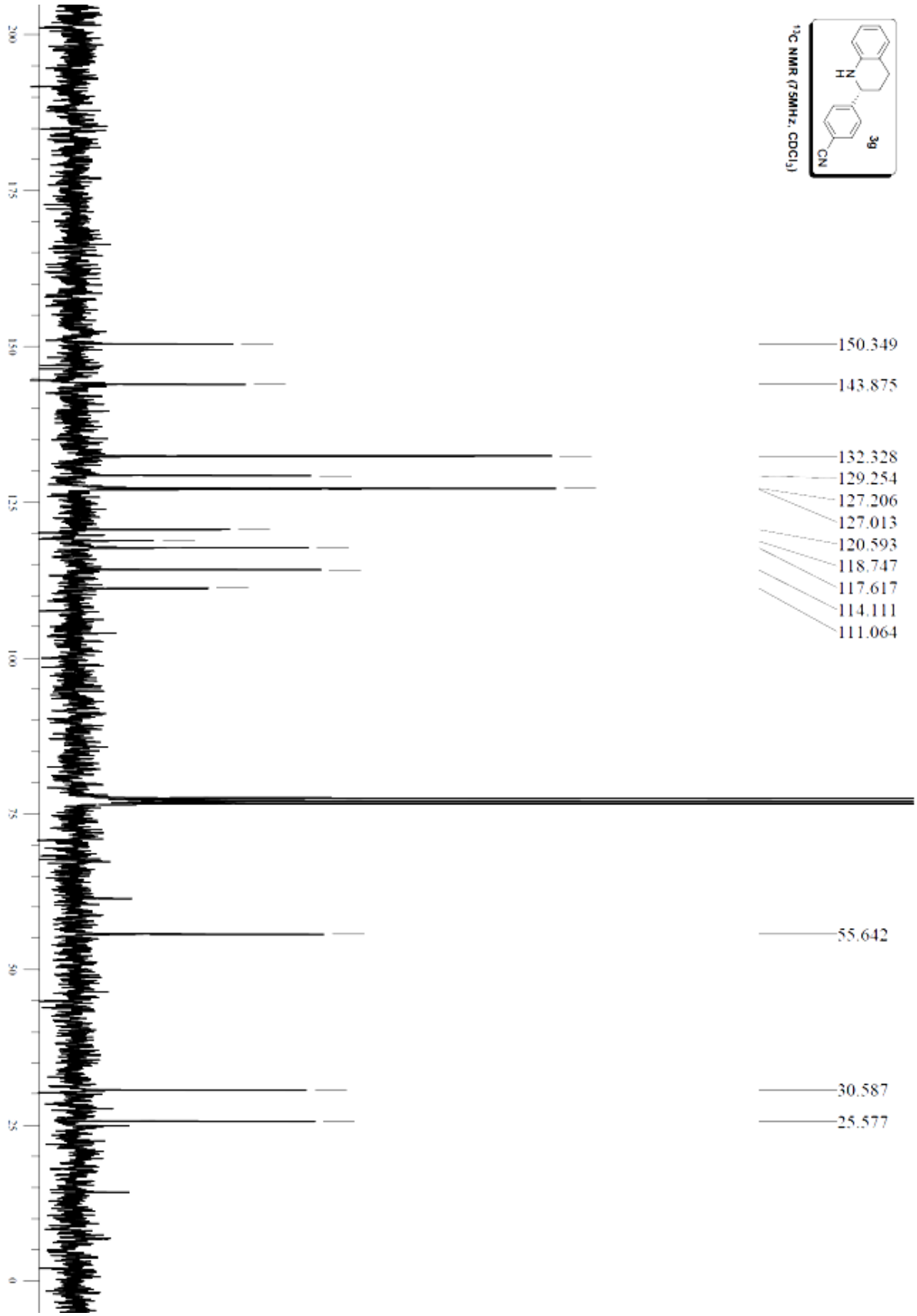

3f
NMe2
1H NMR (300 MHz, CDCl3)
2.3
2.0
3.0
1.0
0.9
0.8
7.2
1.1
2.1

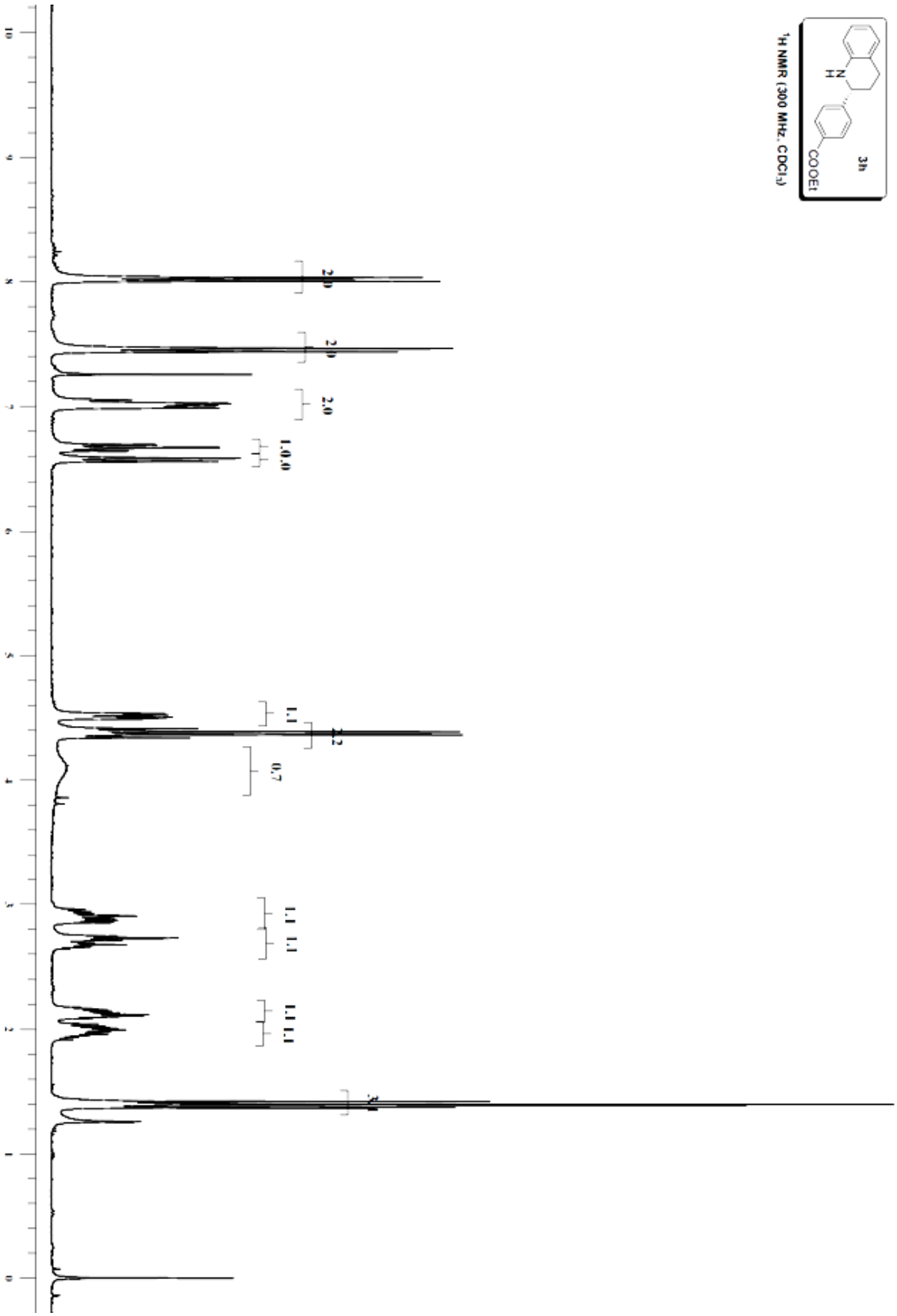

^{13}C NMR (75MHz, CDCl$_3$)
3f
NMe$_2$
150.057
144.963
132.496
129.149
127.255
126.696
120.798
116.794
113.791
112.596
55.721
40.638
30.950
26.714

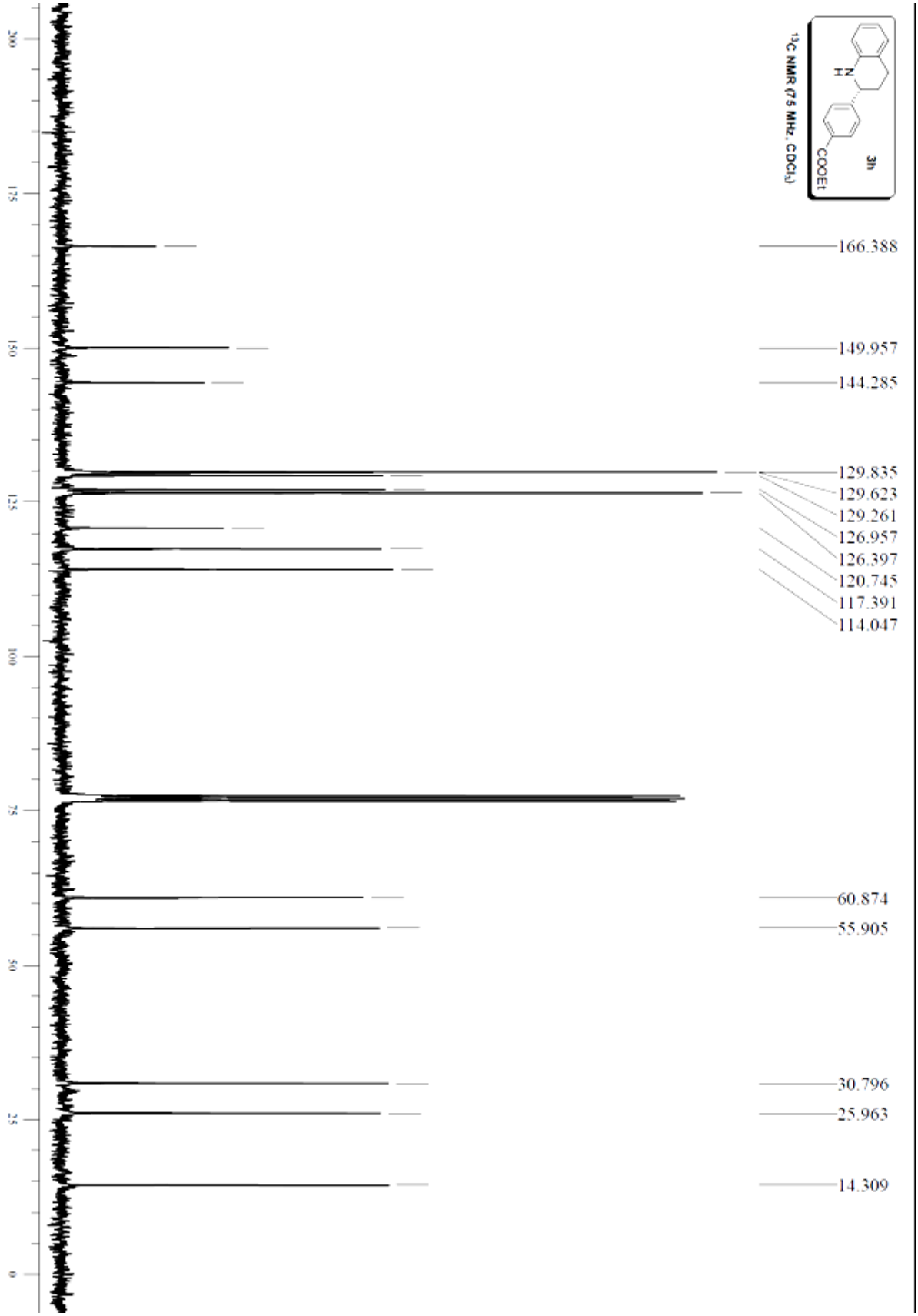


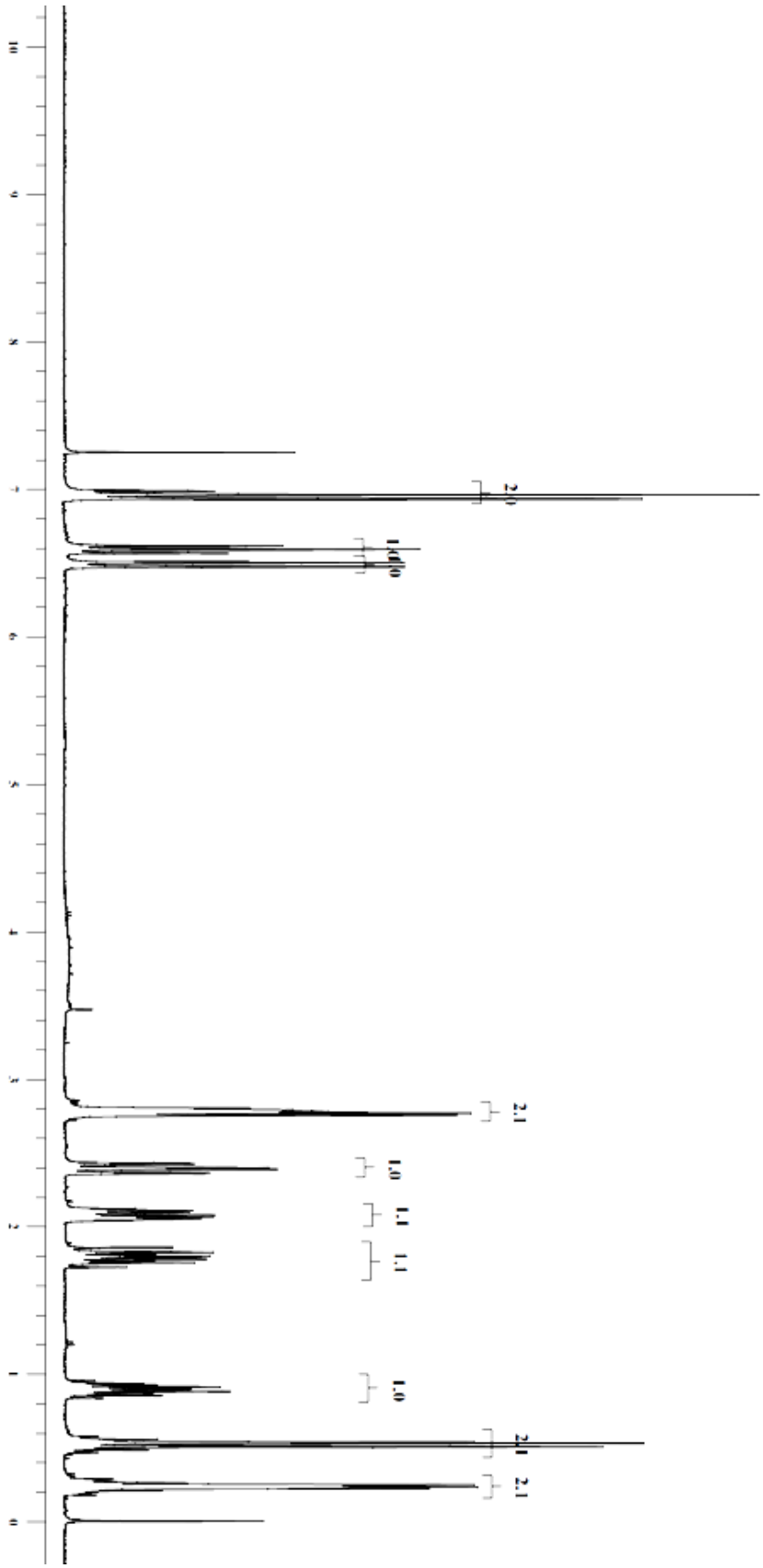
^{1}H NMR (500 MHz, $CDCl_3$)



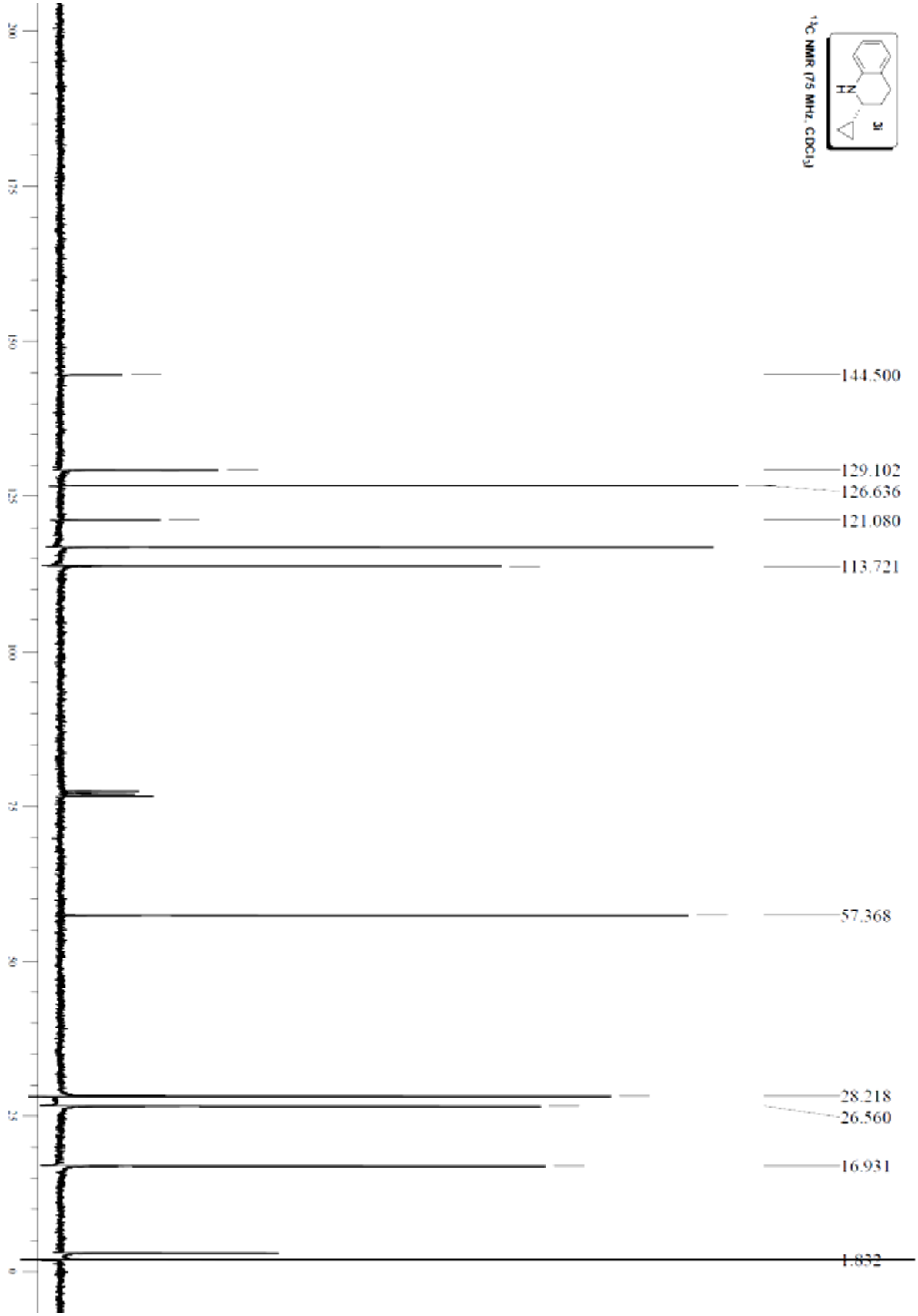

^{13}C NMR (75MHz, CDCl$_3$)
3g
NH
CN
150.349
143.875
132.328
129.254
127.206
127.013
120.593
118.747
117.617
114.111
111.064
55.642
30.587
25.577
200
175
150
125
100
75
50
25
0

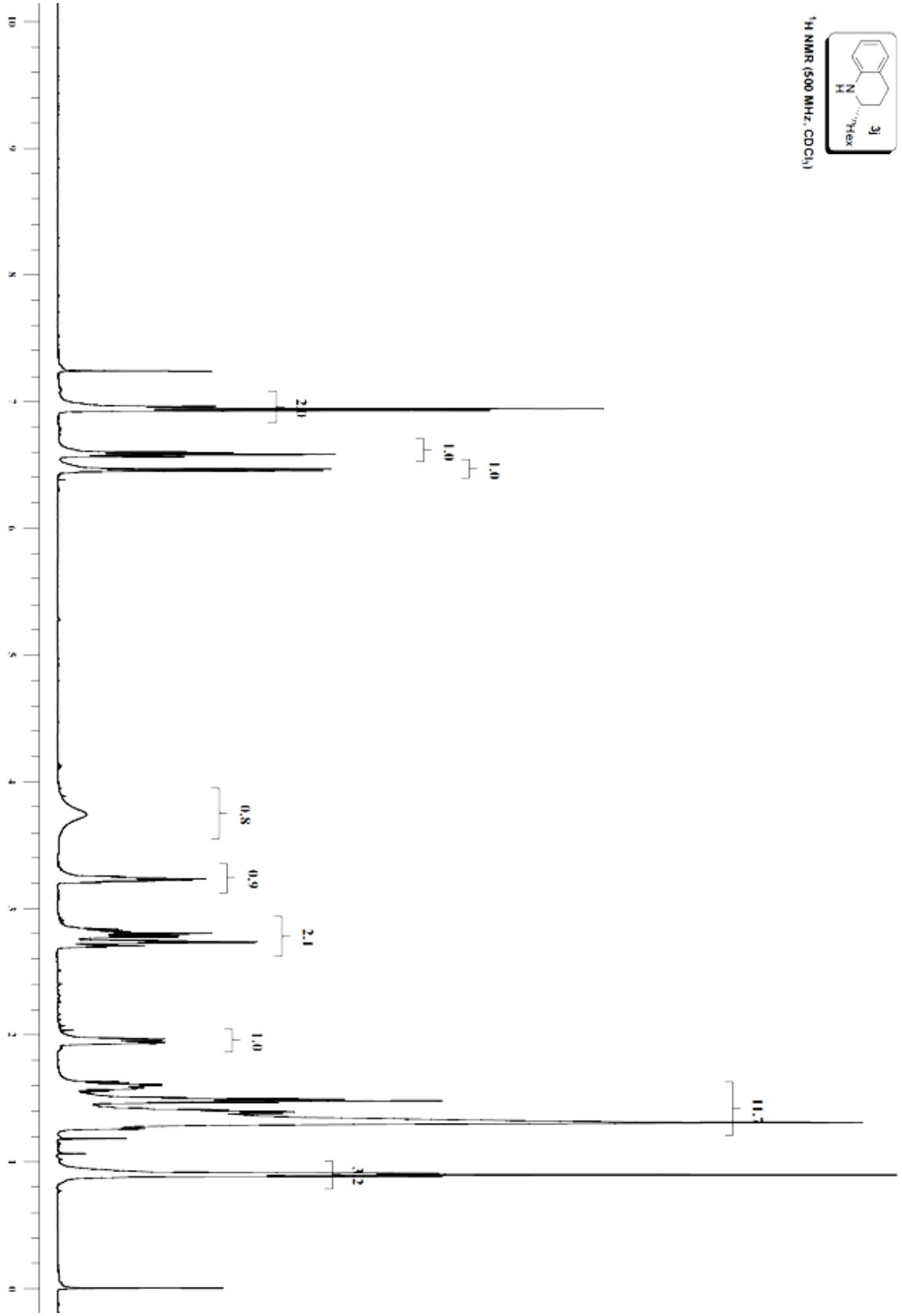


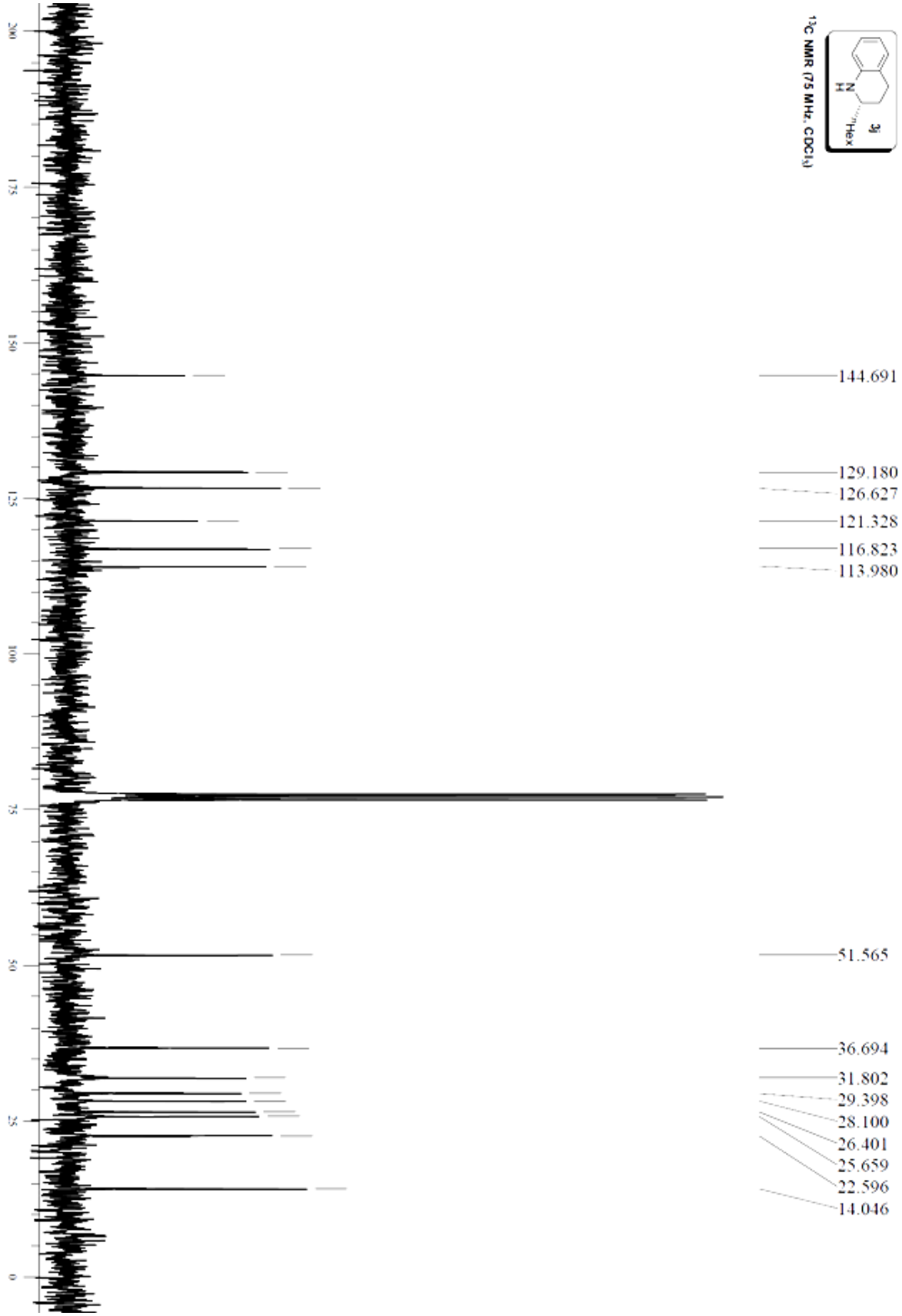

^{13}C NMR (75 MHz, CDCl$_3$)
3h
COOEt
166.388
149.957
144.285
129.835
129.623
129.261
126.957
126.397
120.745
117.391
114.047
60.874
55.905
30.796
25.963
14.309

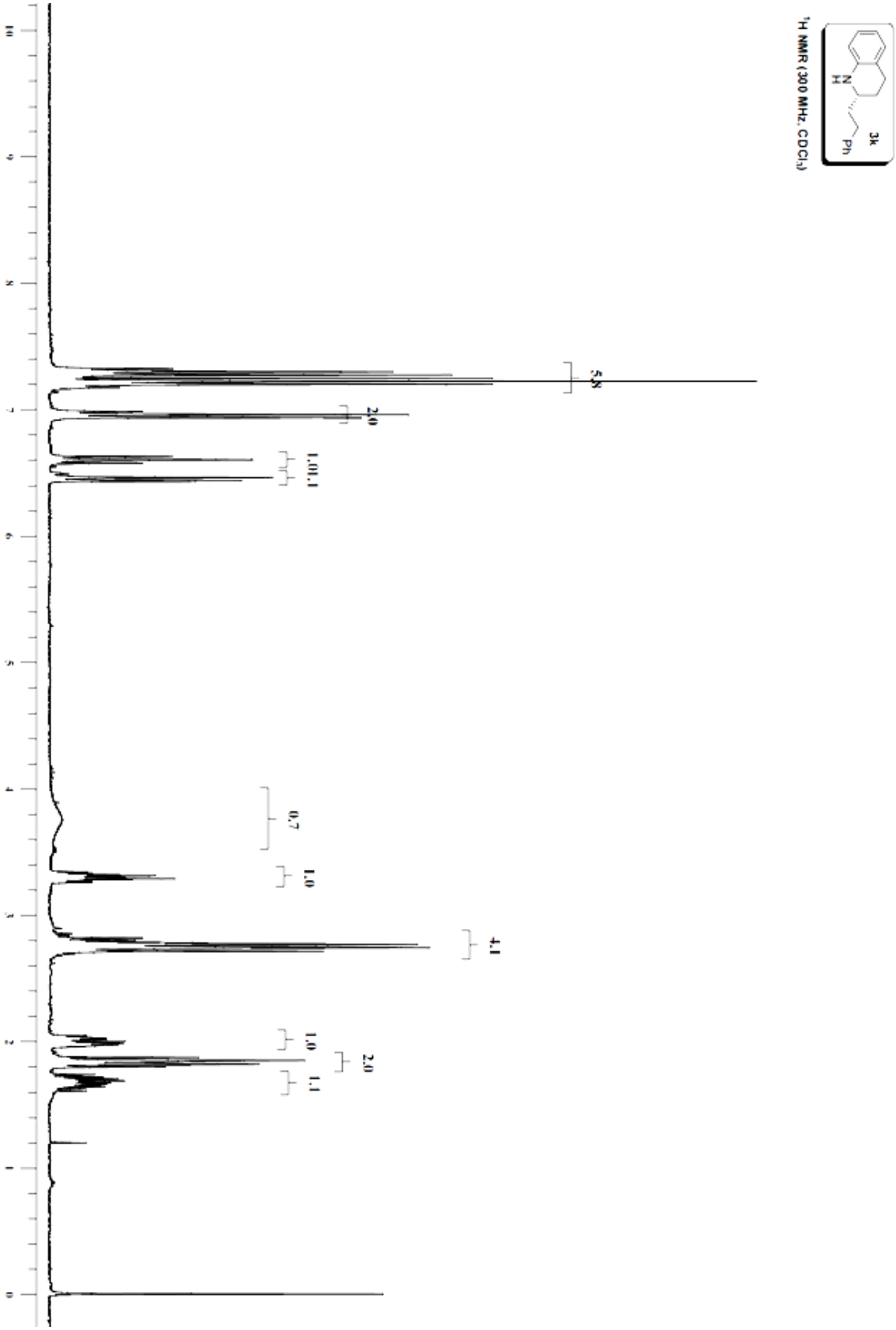


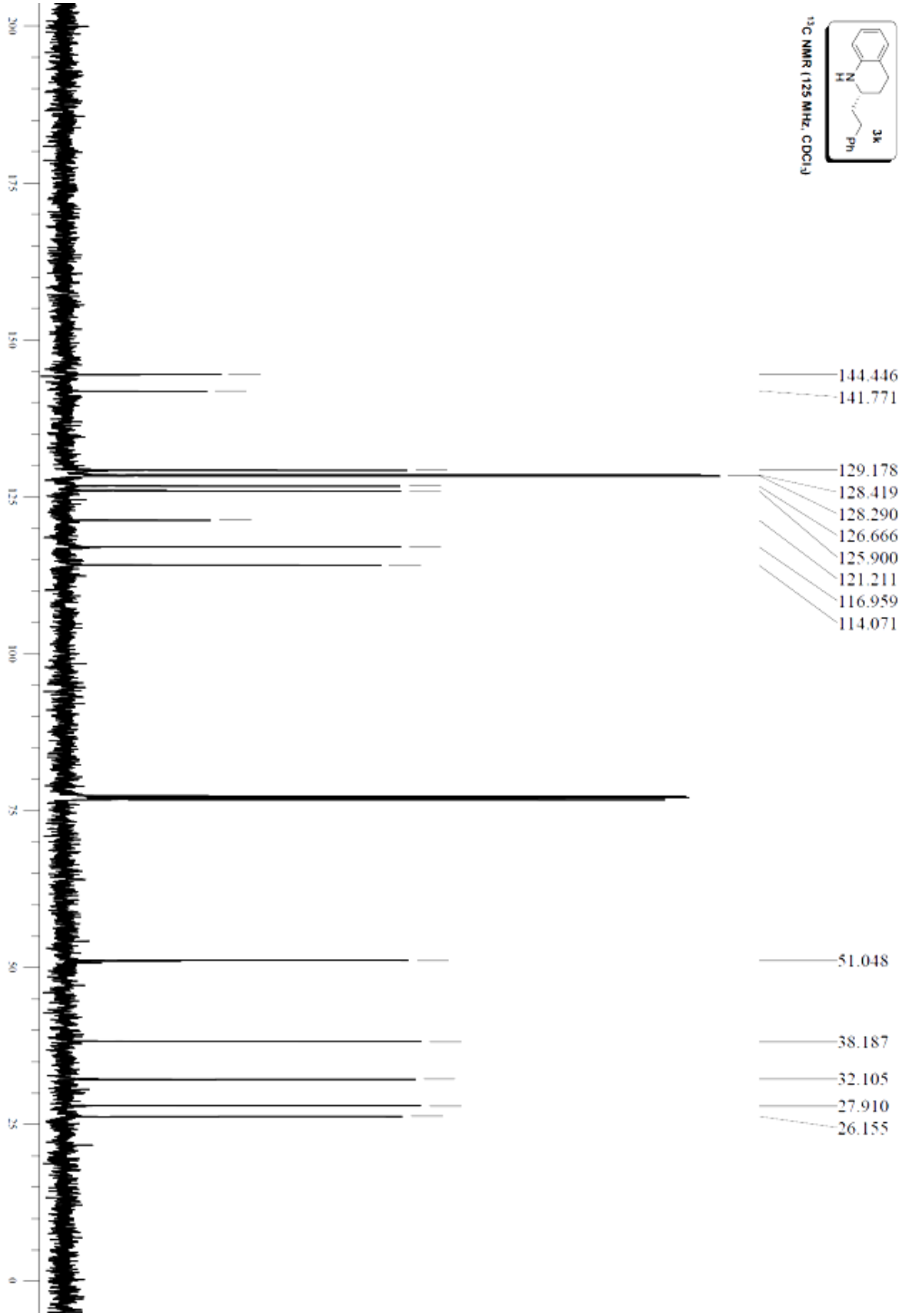
^{1}H NMR (300 MHz, $CDCl_3$)

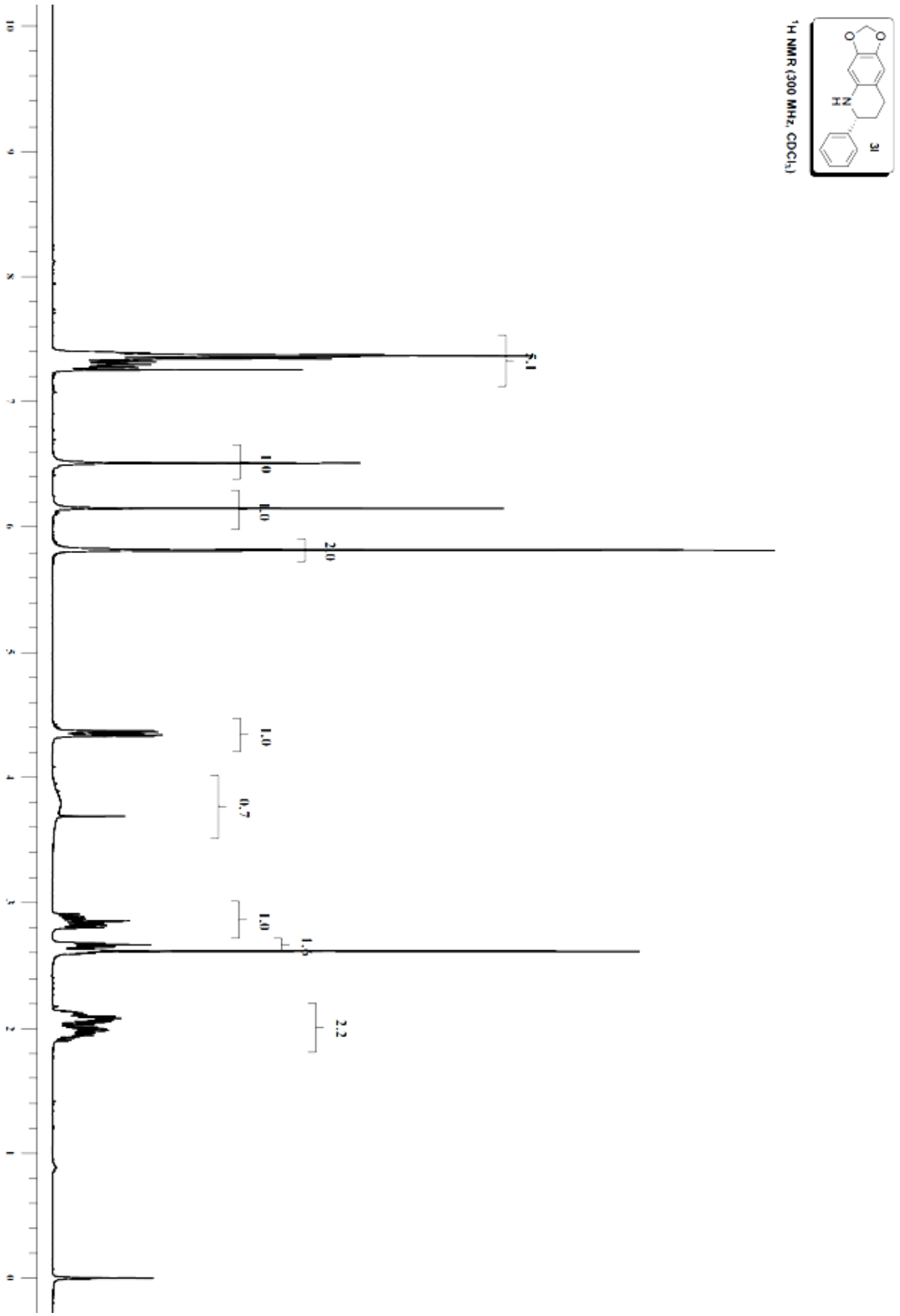


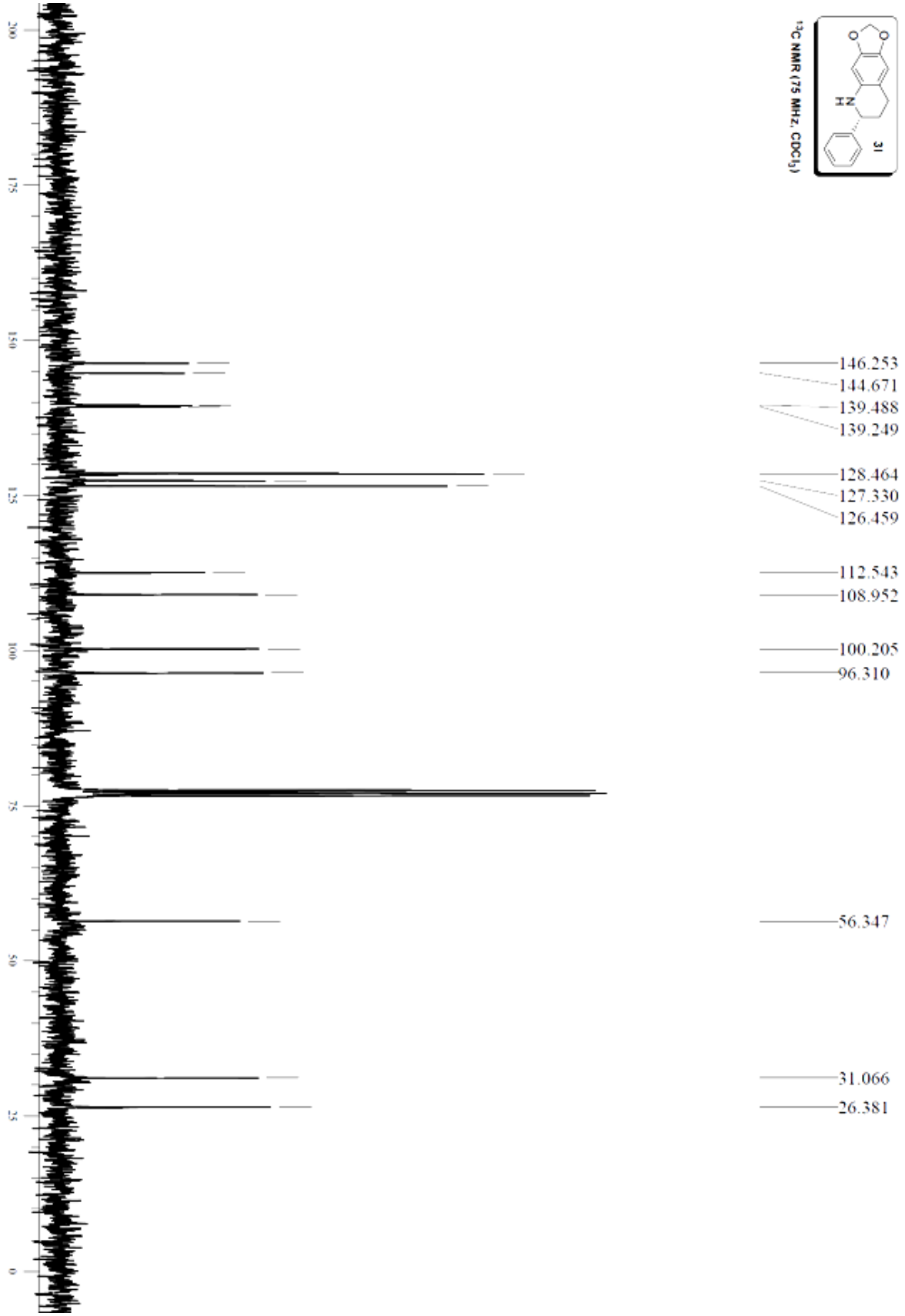

^{1}H NMR (500 MHz, $CDCl_3$)
3i
^{n}Hex
2.0
1.9
1.9
0.8
0.9
2.1
1.0
11.7
3.2

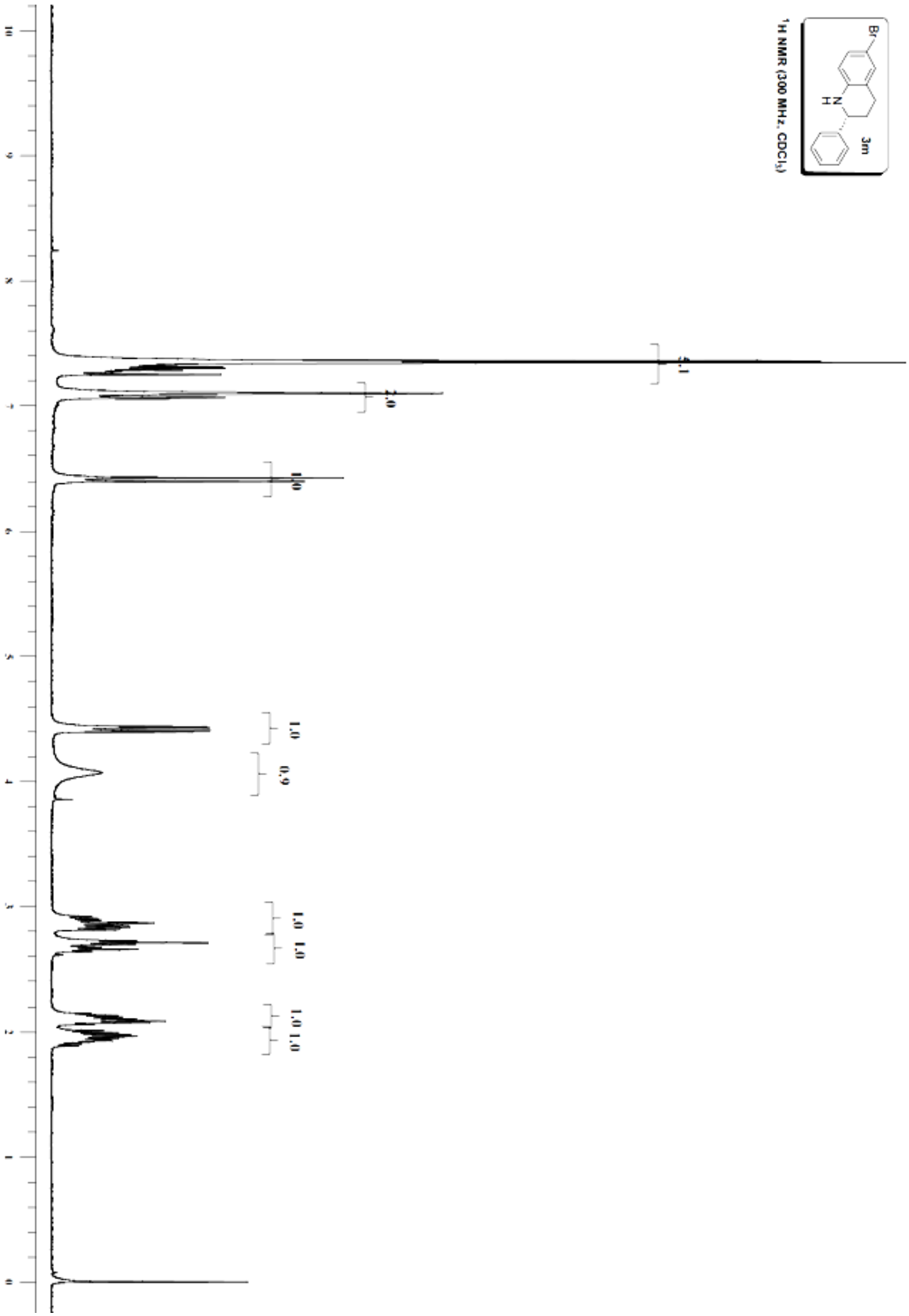

^{13}C NMR (75 MHz, CDCl$_3$)
3g
144.691
129.180
126.627
121.328
116.823
113.980
51.565
36.694
31.802
29.398
28.100
26.401
25.659
22.596
14.046

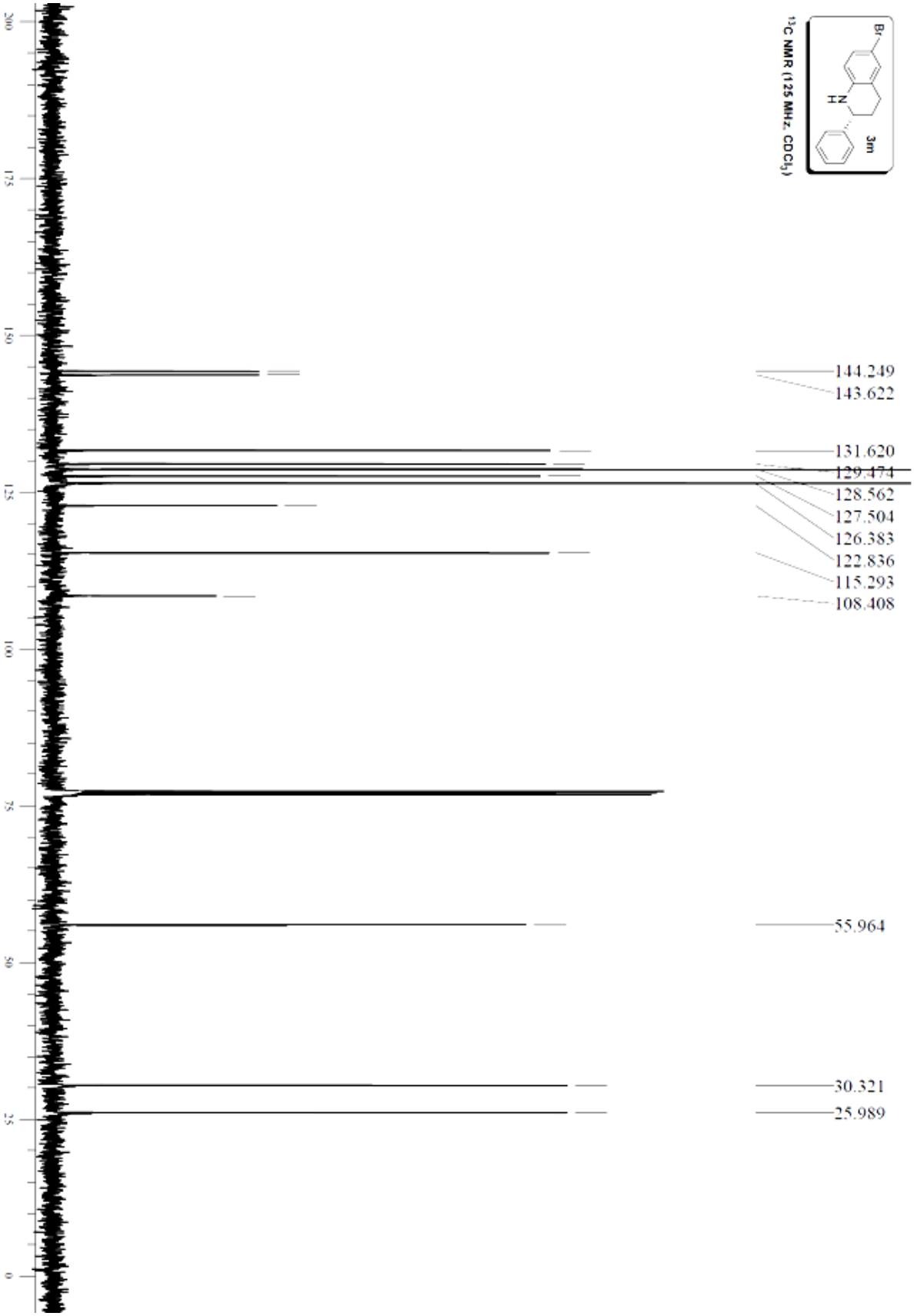

^{1}H NMR (300 MHz, $CDCl_3$)
3k
Ph
N
H
5.8
2.0
1.0
1.0
0.7
1.0
4.1
1.0
2.0
1.1

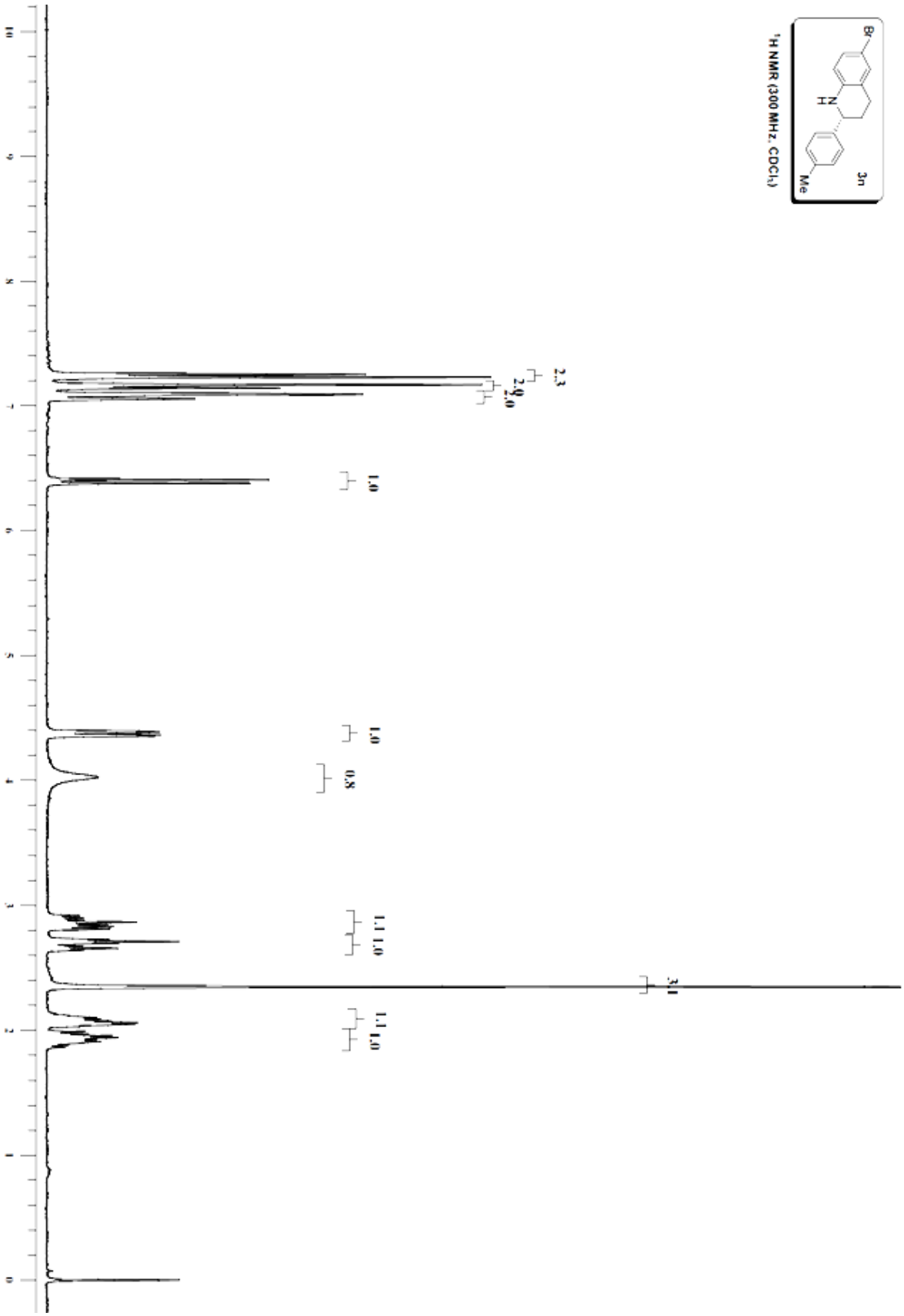

^{13}C NMR (125 MHz, CDCl$_3$)
3k
Ph
144.446
141.771
129.178
128.419
128.290
126.666
125.900
121.211
116.959
114.071
51.048
38.187
32.105
27.910
26.155

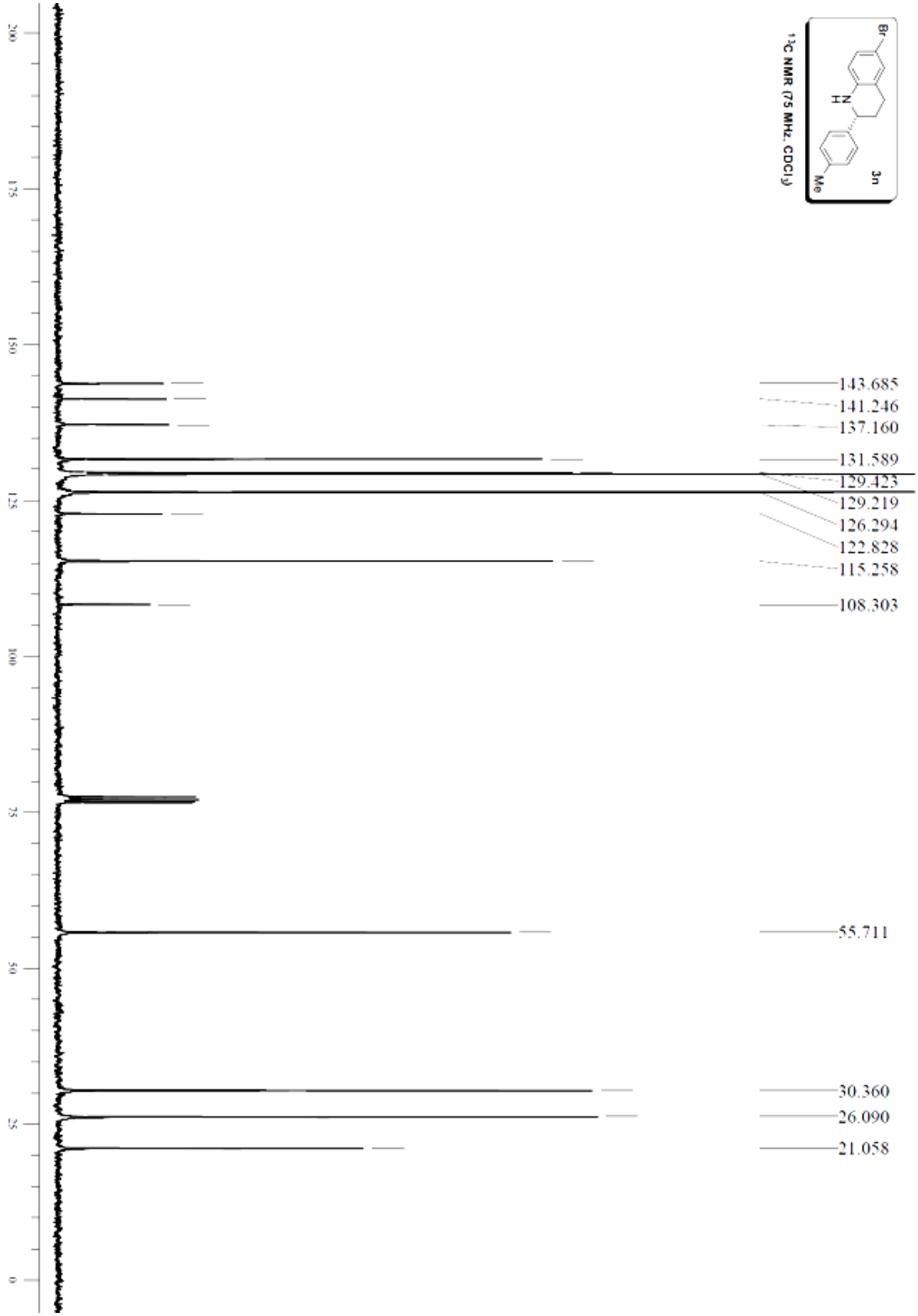

^{1}H NMR (300 MHz, CDCl$_3$)
3l
5.1
1.0
1.0
2.0
1.0
0.7
1.0
1.5
2.2

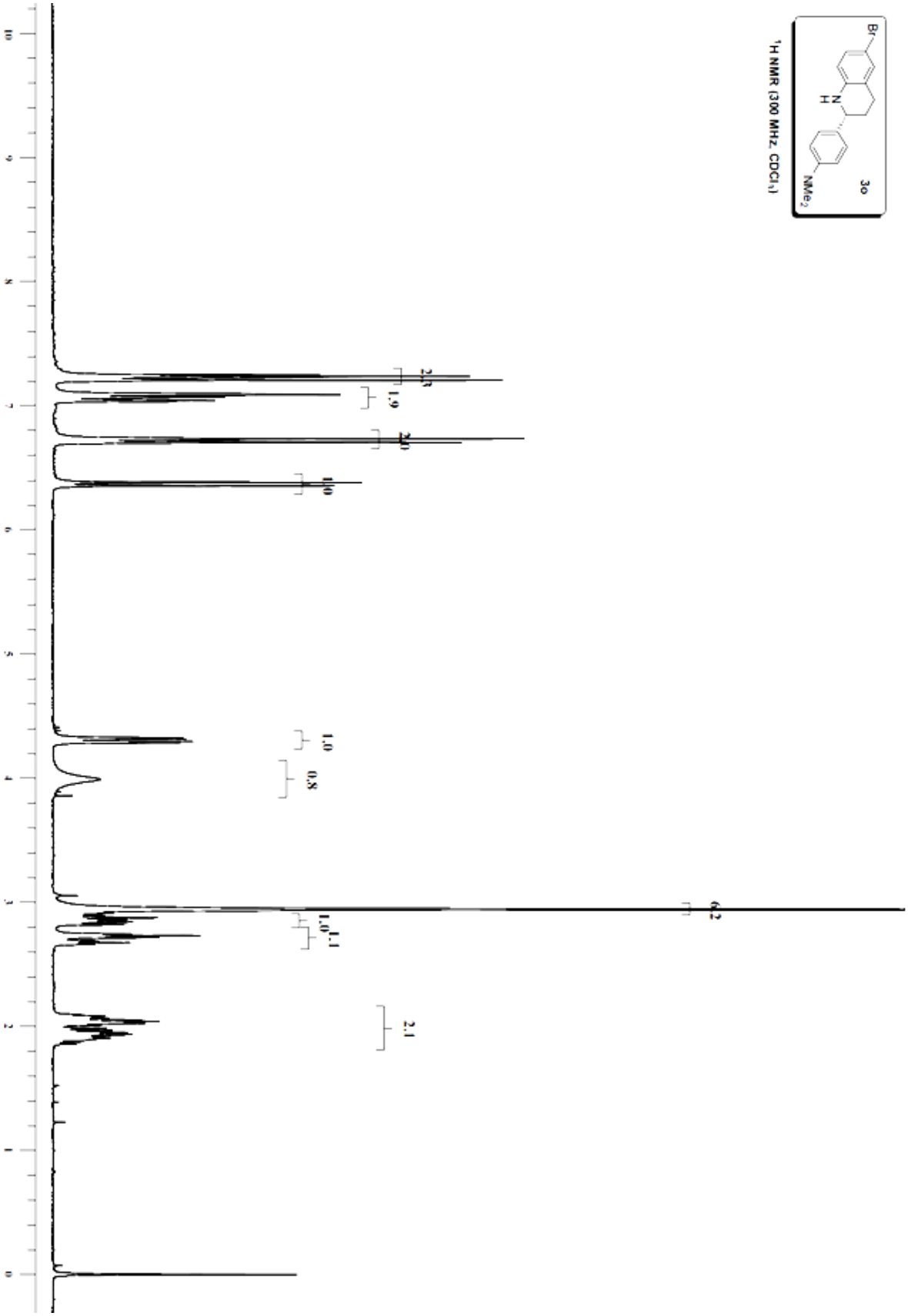

^{13}C NMR (75 MHz, CDCl$_3$)
31
146.253
144.671
139.488
139.249
128.464
127.330
126.459
112.543
108.952
100.205
96.310
56.347
31.066
26.381

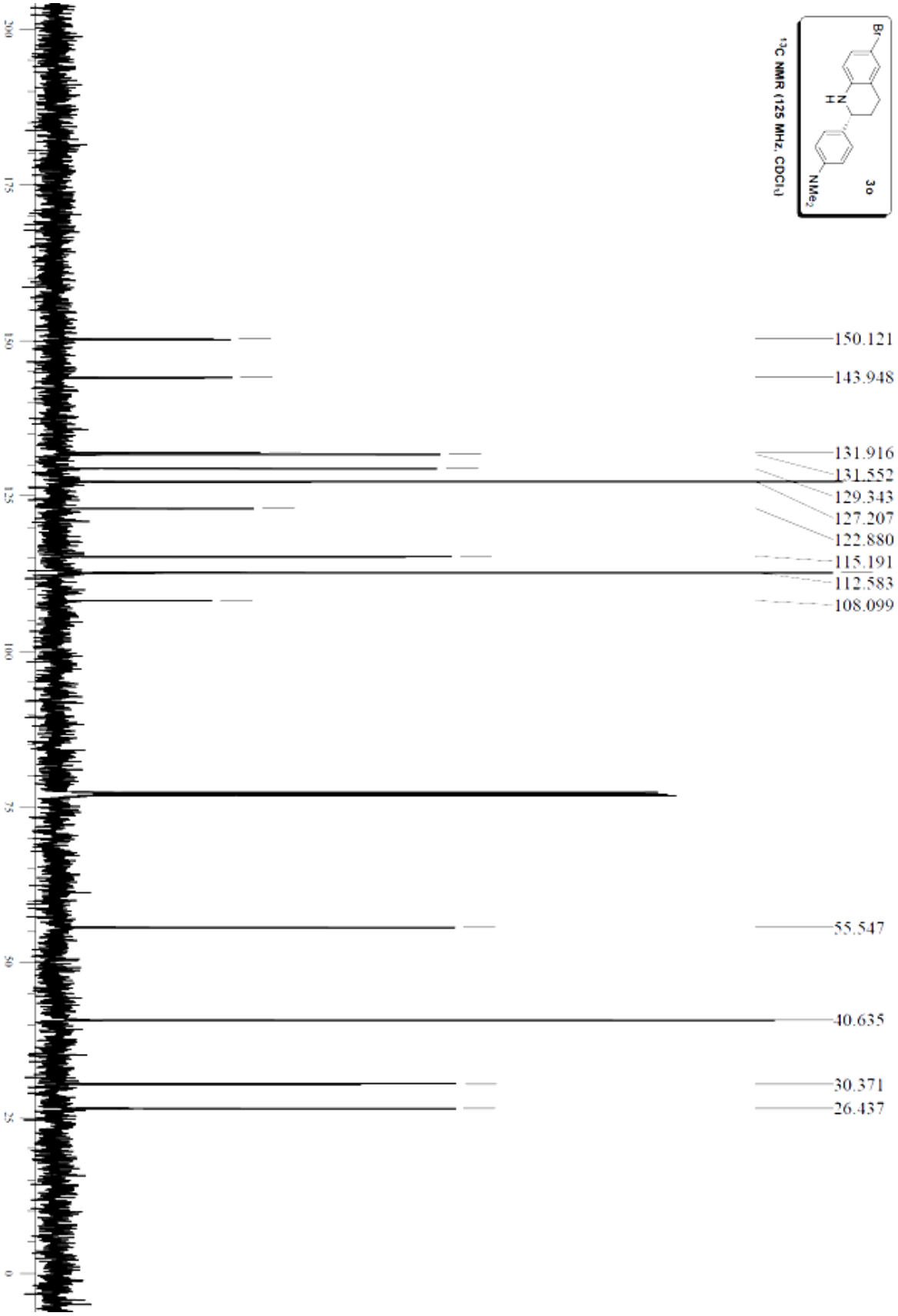

3m
^{1}H NMR (300 MHz, CDCl$_3$)
4.1
2.0
1.0
1.0
0.9
1.0
1.0
1.0
1.0

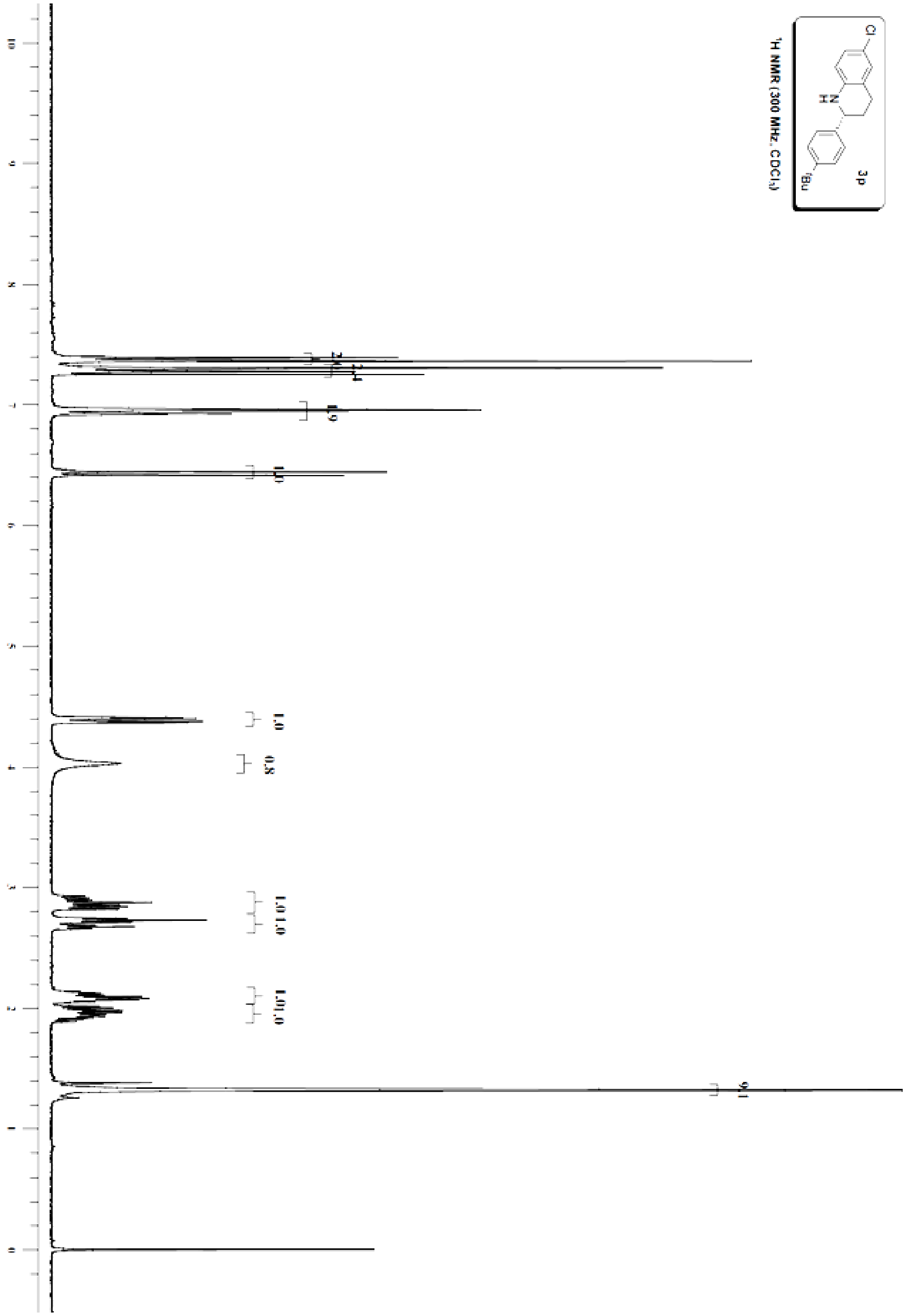

^{13}C NMR (125 MHz, CDCl$_3$)
Br
H
N
3m
144.249
143.622
131.620
129.474
128.562
127.504
126.383
122.836
115.293
108.408
55.964
30.321
25.989
200
175
150
125
100
75
50
25
0

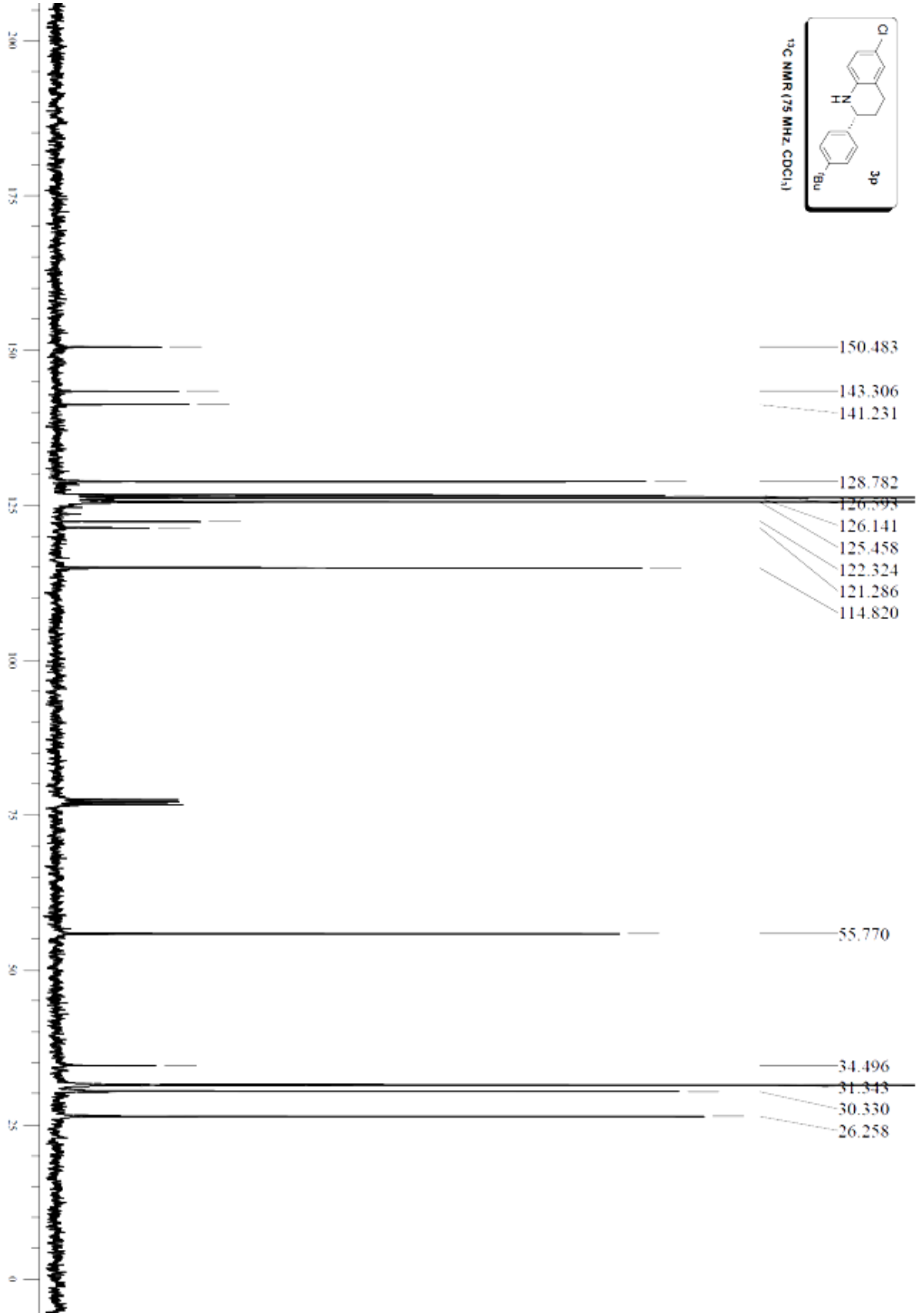

Br
N
H
Me
3n
^{1}H NMR (300 MHz, CDCl$_3$)
2.3
2.9
2.0
1.0
1.0
0.8
1.1
1.0
3.1
1.1
1.0

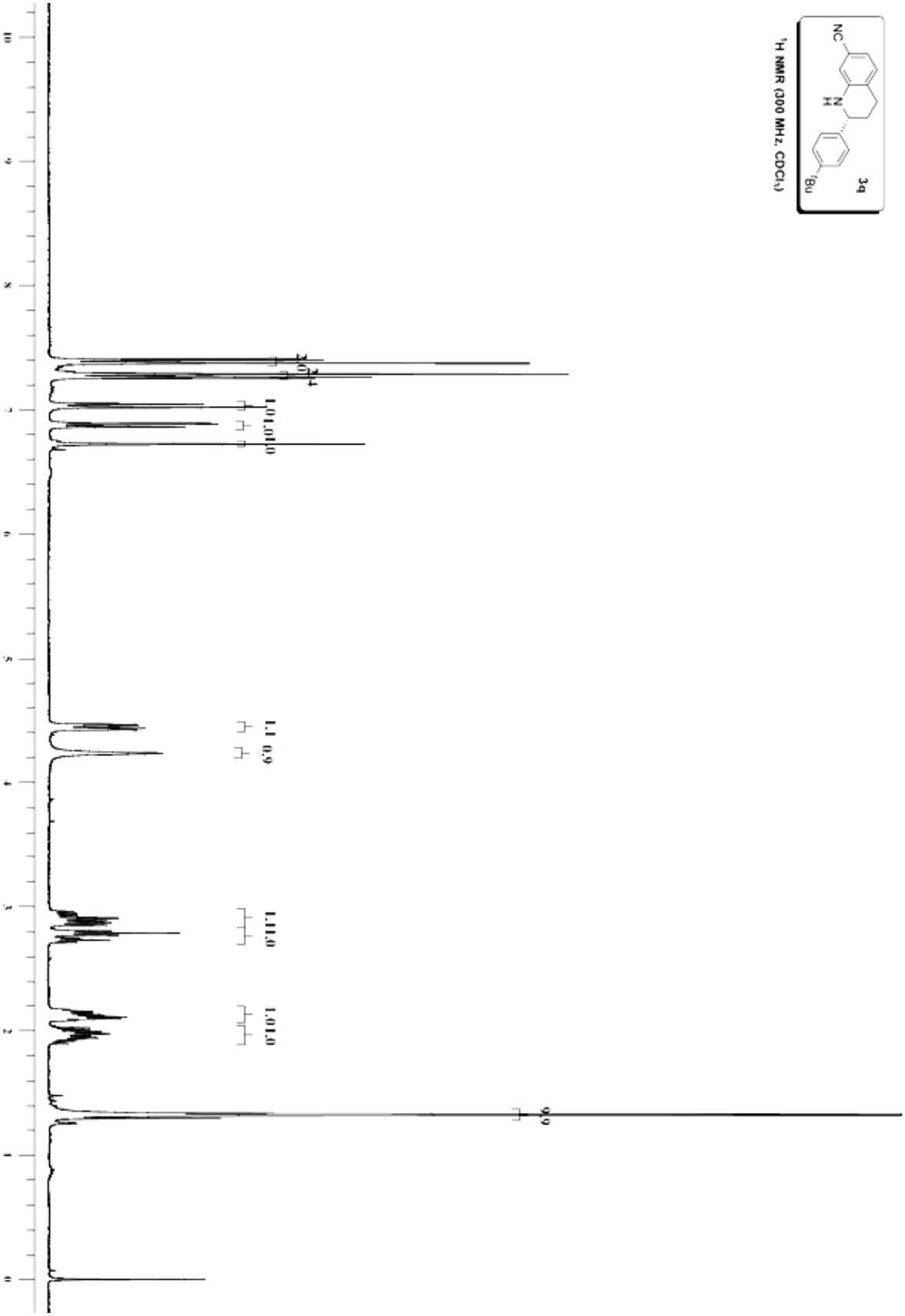

^{13}C NMR (75 MHz, CDCl$_3$)
Br
H
N
Me
3n
143.685
141.246
137.160
131.589
129.423
129.219
126.294
122.828
115.258
108.303
55.711
30.360
26.090
21.058
200
175
150
125
100
75
50
25
0

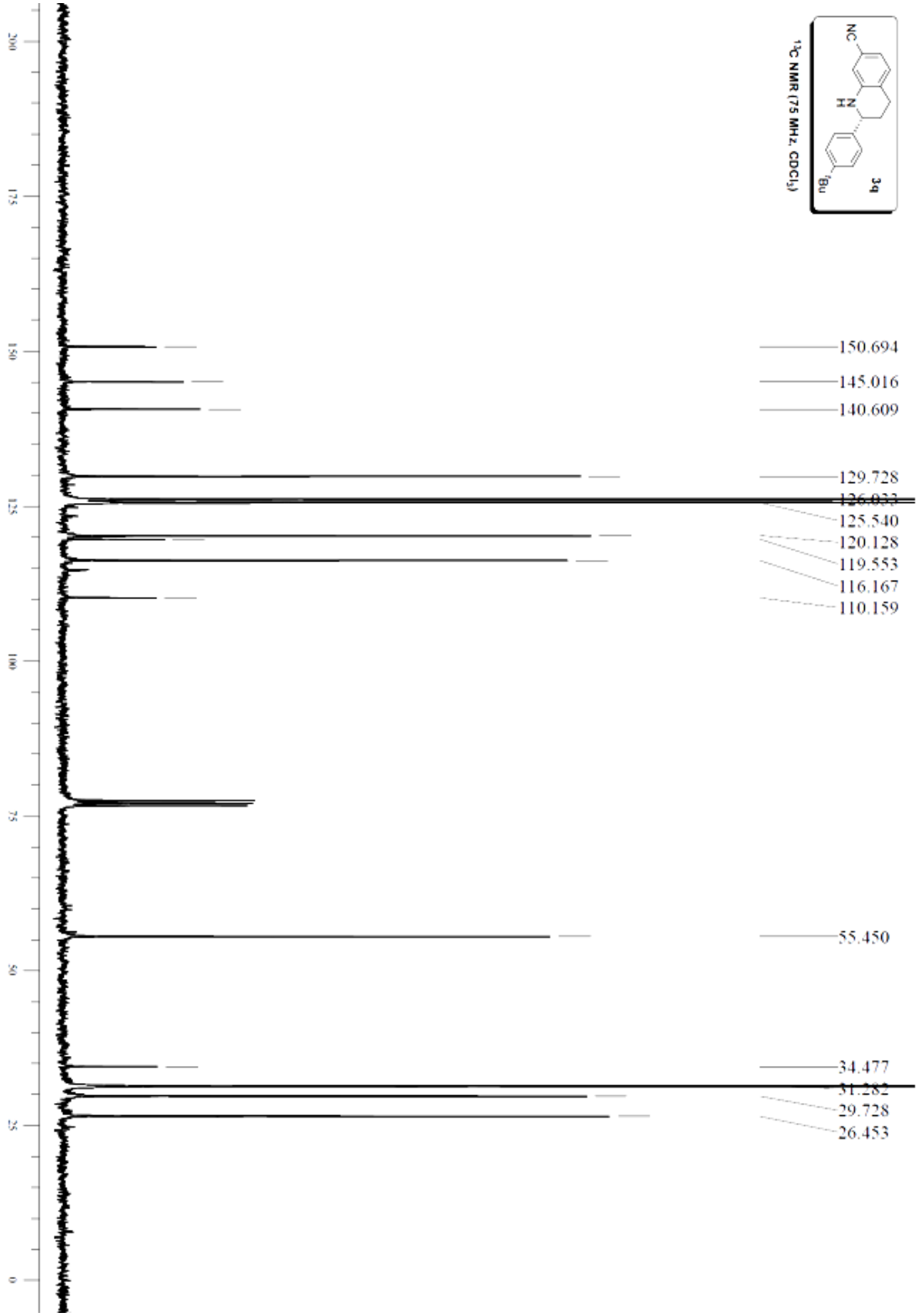

^{1}H NMR (300 MHz, CDCl$_3$)
3o
Br
NMe$_2$
2.3
1.9
2.0
1.0
1.0
0.8
6.2
1.0
1.1
2.1

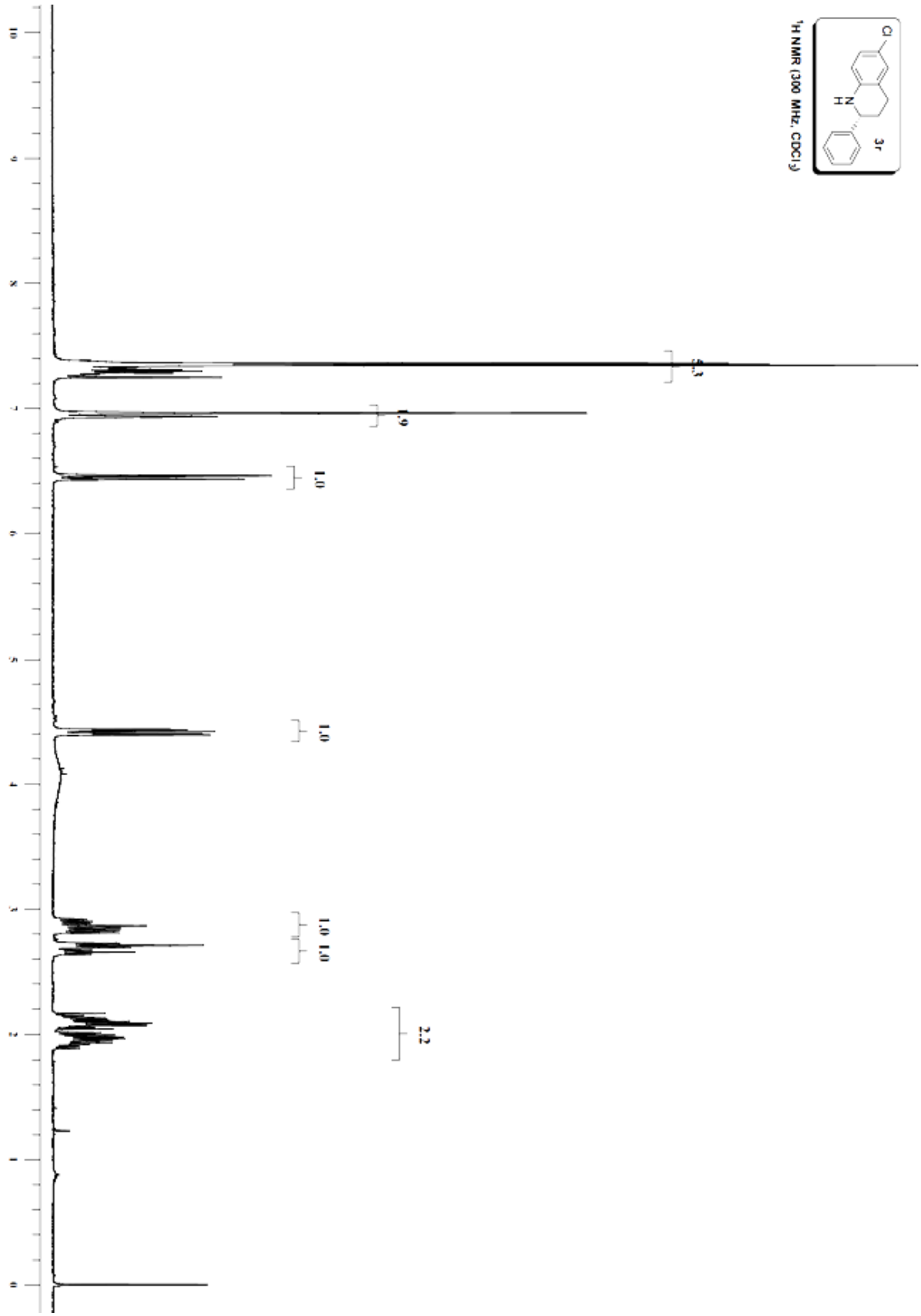

^{13}C NMR (125 MHz, CDCl$_3$)
Br
N
H
NMe$_2$
3o
200
175
150
125
100
75
50
25
0
150.121
143.948
131.916
131.552
129.343
127.207
122.880
115.191
112.583
108.099
55.547
40.635
30.371
26.437

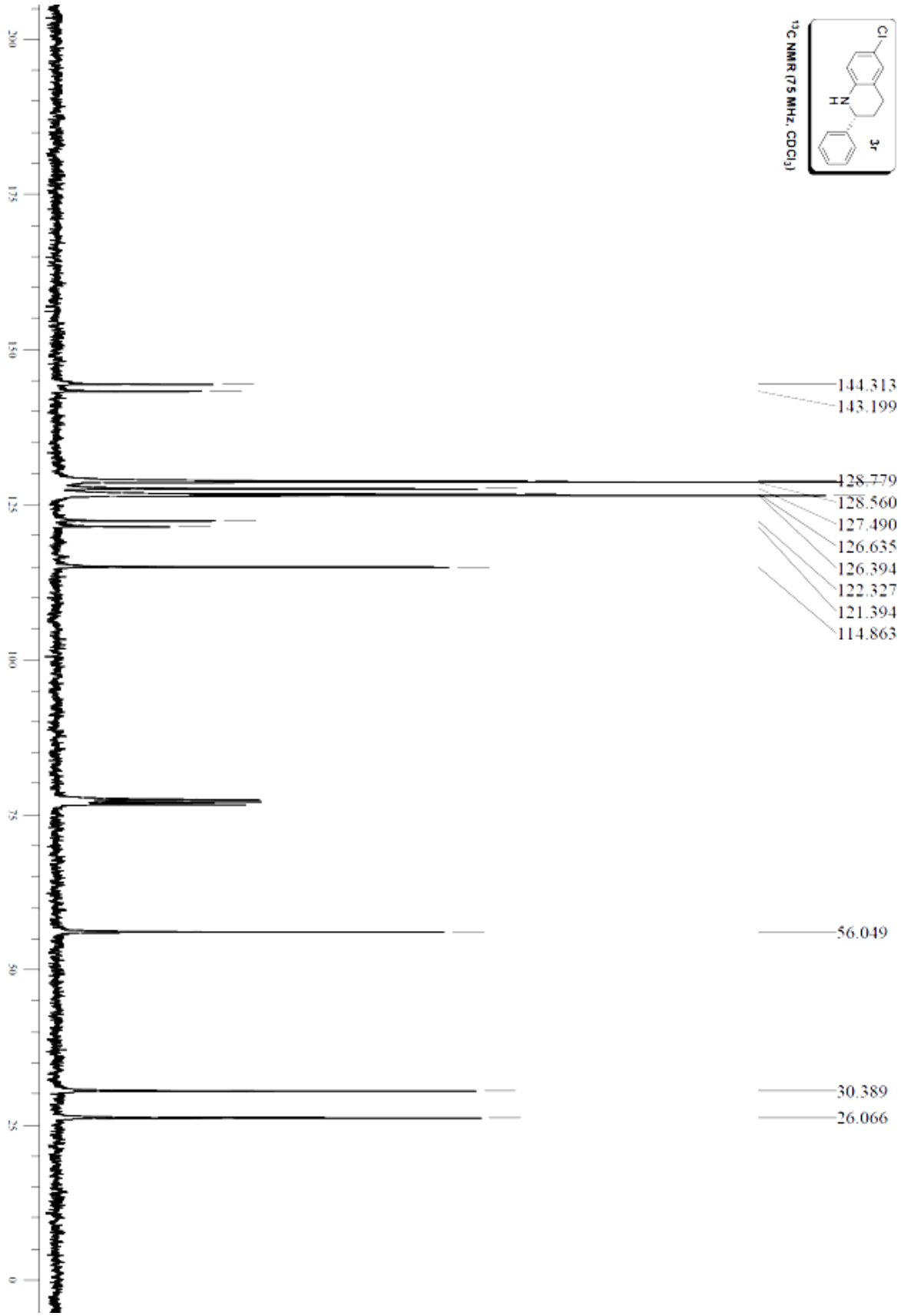



^{13}C NMR (75 MHz, CDCl$_3$)
3p
150.483
143.306
141.231
128.782
126.393
126.141
125.458
122.324
121.286
114.820
55.770
34.496
31.343
30.330
26.258

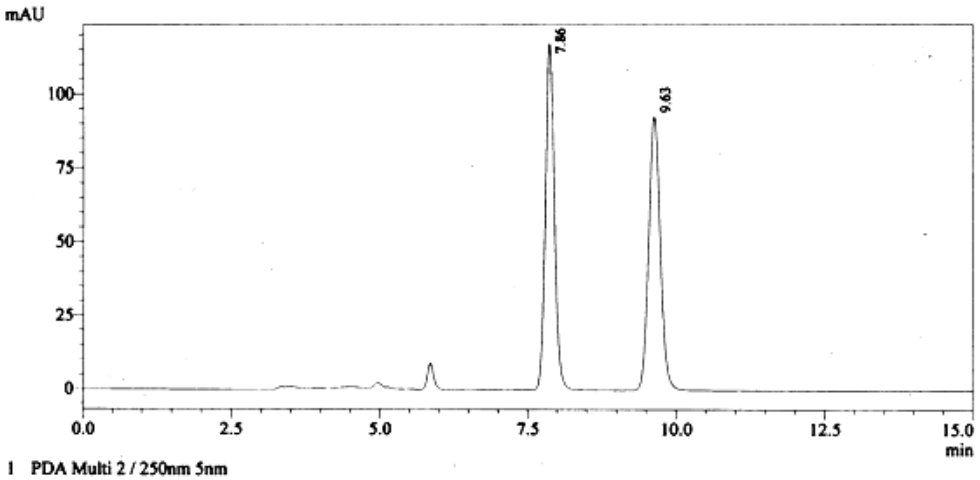

3q
^{1}H NMR (300 MHz, CDCl$_3$)
NC
N
H
^{t}Bu
2.01
1.01
1.01
1.1
0.9
1.11
1.0
1.0
9.0


^{13}C NMR (75 MHz, CDCl$_3$)
NC
HN
^{t}Bu
3q
150.694
145.016
140.609
129.728
126.033
125.540
120.128
119.553
116.167
110.159
55.450
34.477
31.282
29.728
26.453


^{1}H NMR (300 MHz, CDCl$_3$)
3r
Cl
N
H
4.3
1.9
1.0
1.0
1.0
1.0
2.2


^{13}C NMR (75 MHz, CDCl$_3$)
Cl
H
N
3r
144.313
143.199
128.779
128.560
127.490
126.635
126.394
122.327
121.394
114.863
56.049
30.389
26.066
200
175
150
125
100
75
50
25
0

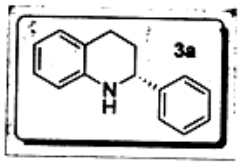
6. HPLC Chromatograms for Compounds:

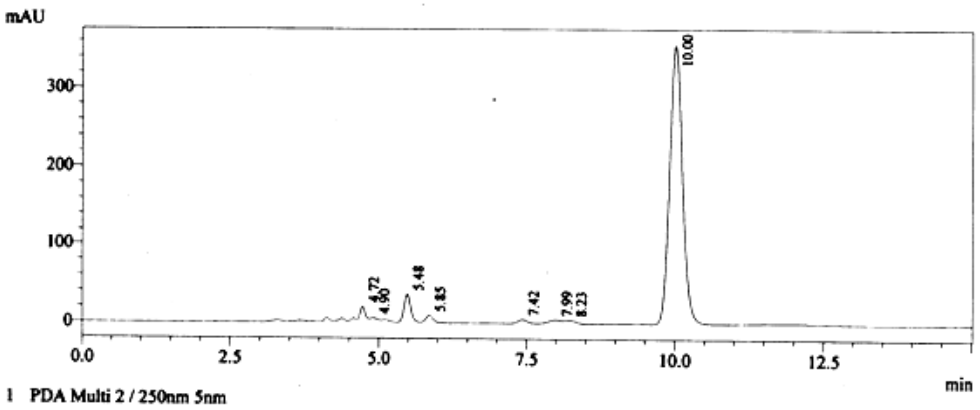


1 PDA Multi 2 / 250nm 5nm

PDA Ch2 250nm 5nm

Peak#	Ret. Time	Area	Area %
1	7.86	1264684	50.01
2	9.63	1264247	49.99
Total		2528931	100.00

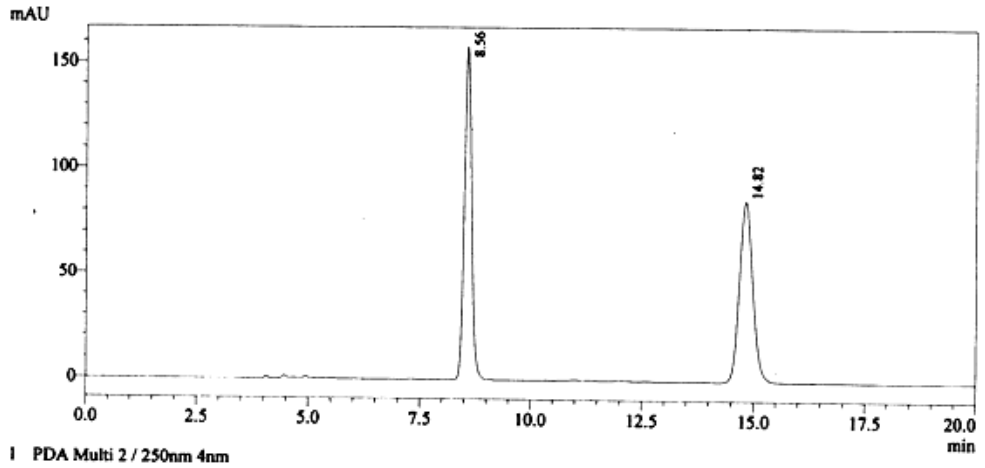




1 PDA Multi 2 / 250nm 5nm

PDA Ch2 250nm 5nm

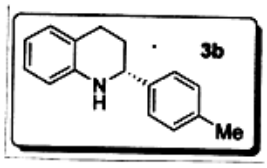
Peak#	Ret. Time	Area	Area %
1	4.72	133283	2.21
2	4.90	59178	0.98
3	5.48	288790	4.78
4	5.85	84853	1.40
5	7.42	54697	0.91
6	7.99	77172	1.28
7	8.23	50487	0.84
8	10.00	5292812	87.61
Total		6041272	100.00

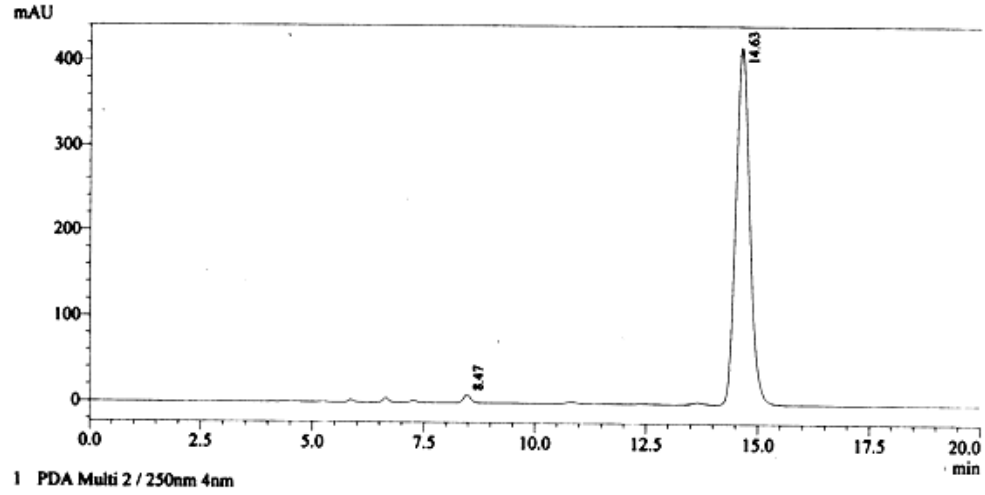


1 PDA Multi 2 / 250nm 4nm

PDA Ch2 250nm 4nm

Peak#	Ret. Time	Area	Area %
1	8.56	1783201	50.02
2	14.82	1781885	49.98
Total		3565086	100.00

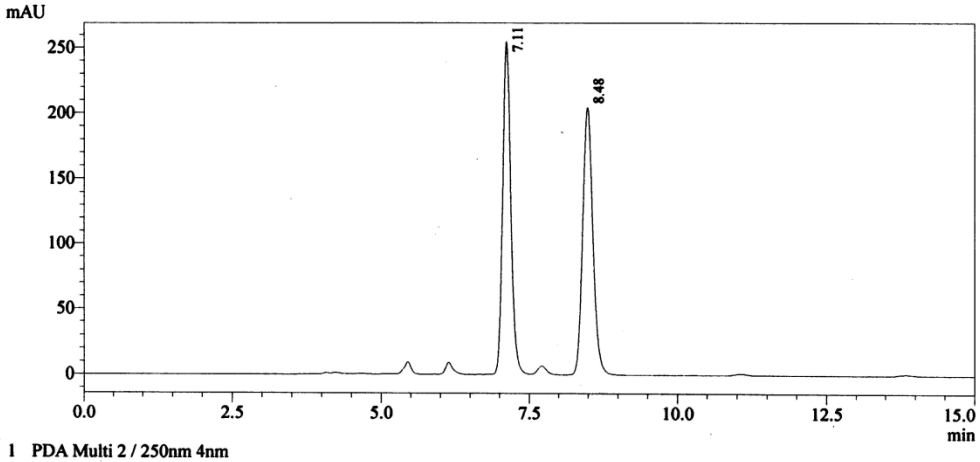




1 PDA Multi 2 / 250nm 4nm

PDA Ch2 250nm 4nm

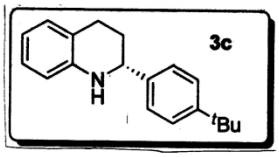
Peak#	Ret. Time	Area	Area %
1	8.47	111786	1.22
2	14.63	9049094	98.78
Total		9160881	100.00

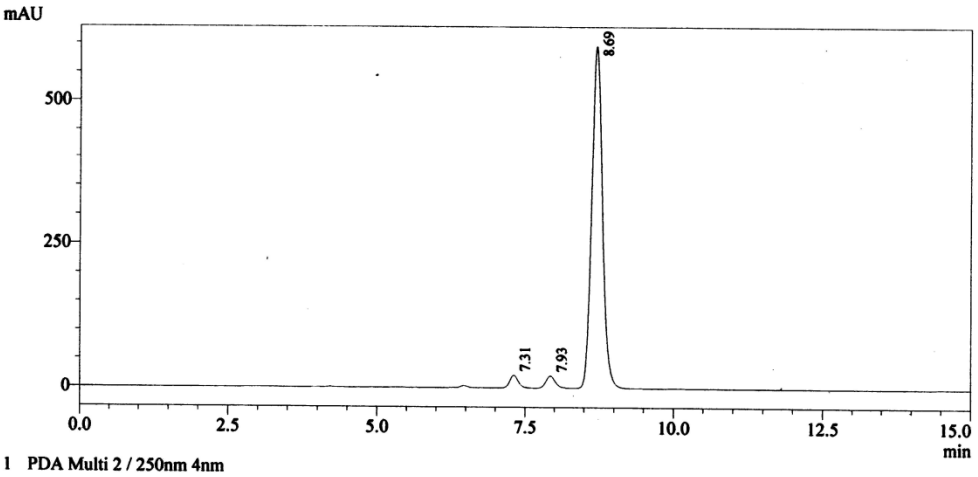


1 PDA Multi 2 / 250nm 4nm

PDA Ch2 250nm 4nm

Peak#	Ret. Time	Area	Area %
1	7.11	2459614	50.02
2	8.48	2457954	49.98
Total		4917568	100.00

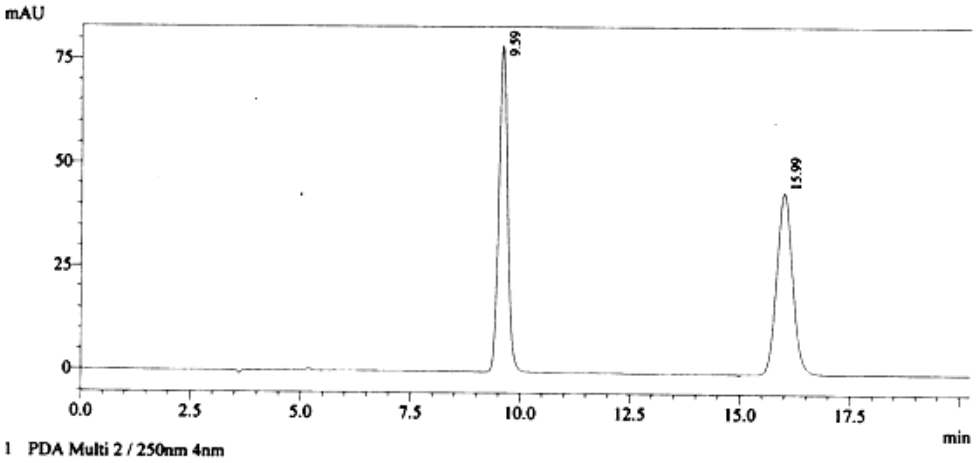




1 PDA Multi 2 / 250nm 4nm

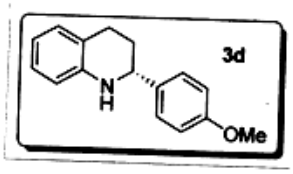
PDA Ch2 250nm 4nm

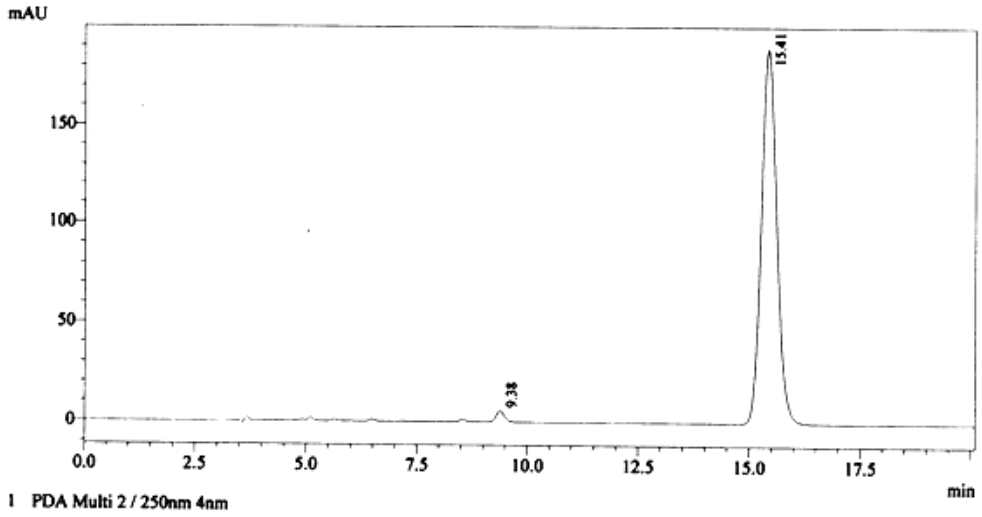
Peak#	Ret. Time	Area	Area %
1	7.31	228035	2.86
2	7.93	244444	3.07
3	8.69	7489271	94.07
Total		7961750	100.00



PDA Ch2 250nm 4nm

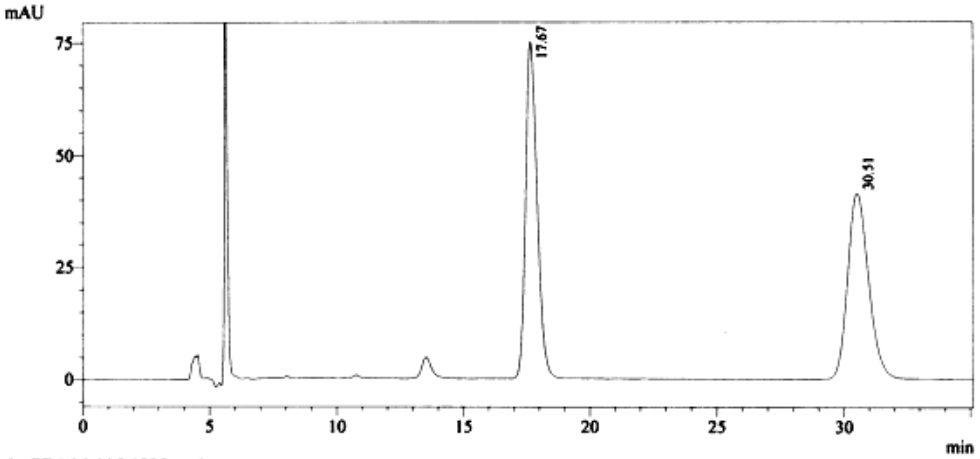
Peak#	Ret. Time	Area	Area %
1	9.59	1101941	50.15
2	15.99	1095378	49.85
Total		2197319	100.00





PDA Ch2 250nm 4nm

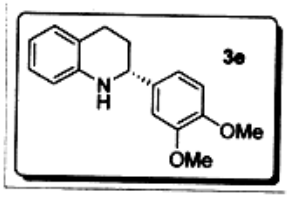
Peak#	Ret. Time	Area	Area %
1	9.38	75119	1.63
2	15.41	4541431	98.37
Total		4616550	100.00

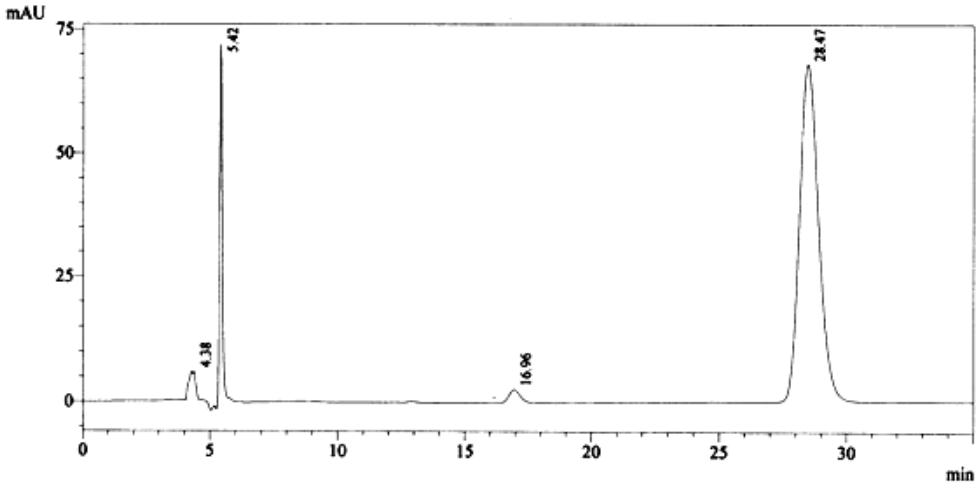


1 PDA Multi 2 / 235nm 4nm

PDA Ch2 235nm 4nm

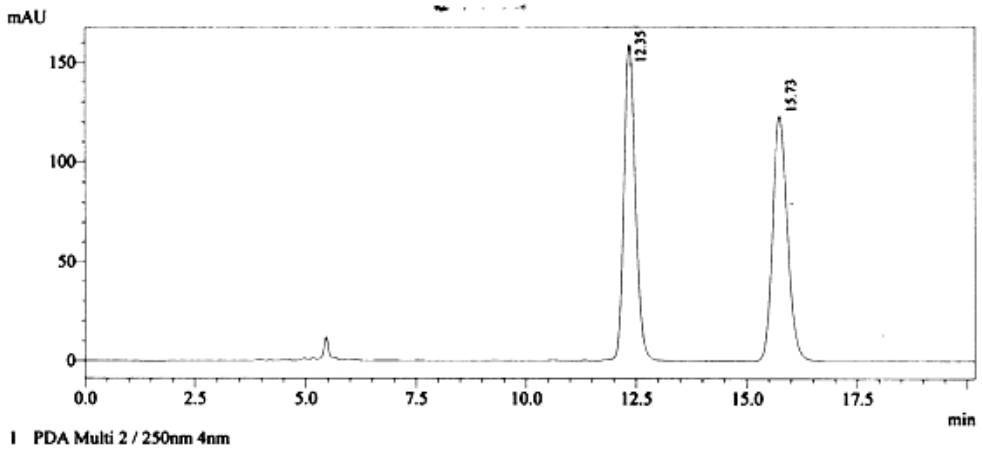
Peak#	Ret. Time	Area	Area %
1	17.67	2379964	49.94
2	30.51	2385722	50.06
Total		4765686	100.00





PDA Ch2 235nm 4nm

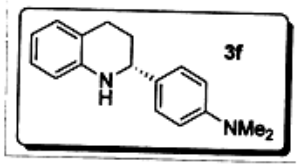
Peak#	Ret. Time	Area	Area %
1	4.38	88305	2.05
2	5.42	612338	14.23
3	16.96	82556	1.92
4	28.47	3518552	81.79
Total		4301752	100.00

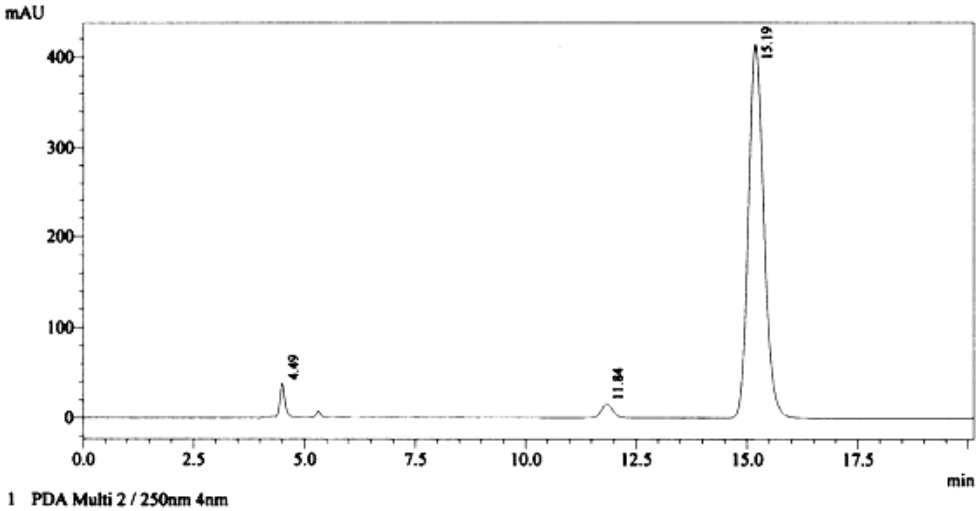


1 PDA Multi 2 / 250nm 4nm

PDA Ch2 250nm 4nm

Peak#	Ret. Time	Area	Area %
1	12.35	2880607	50.08
2	15.73	2870877	49.92
Total		5751484	100.00

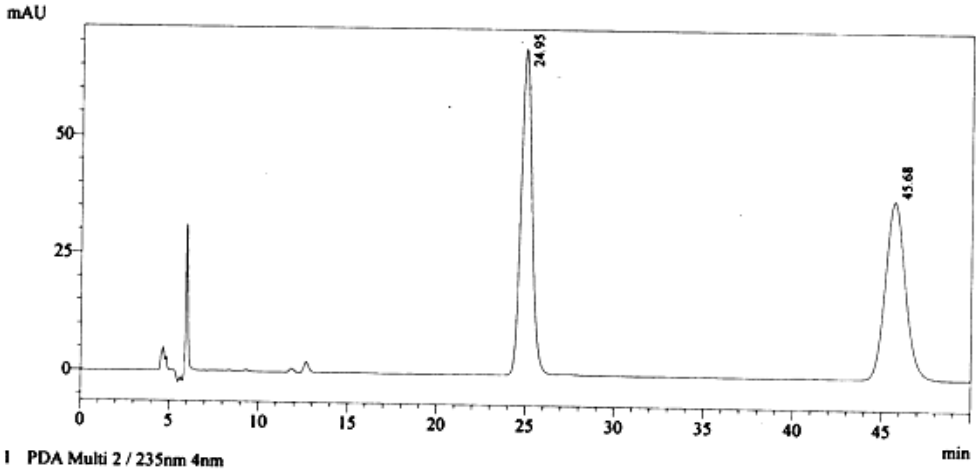




1 PDA Multi 2 / 250nm 4nm

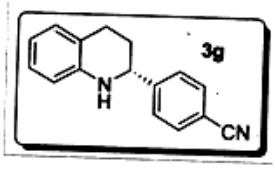
PDA Ch2 250nm 4nm

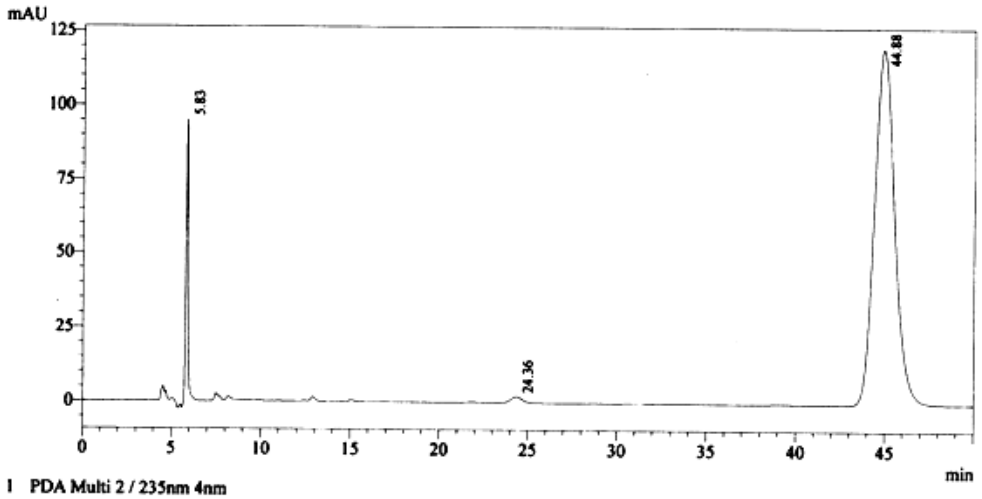
Peak#	Ret. Time	Area	Area %
1	4.49	338731	3.21
2	11.84	281533	2.67
3	15.19	9932991	94.12
Total		10553256	100.00



PDA Ch2 235nm 4nm

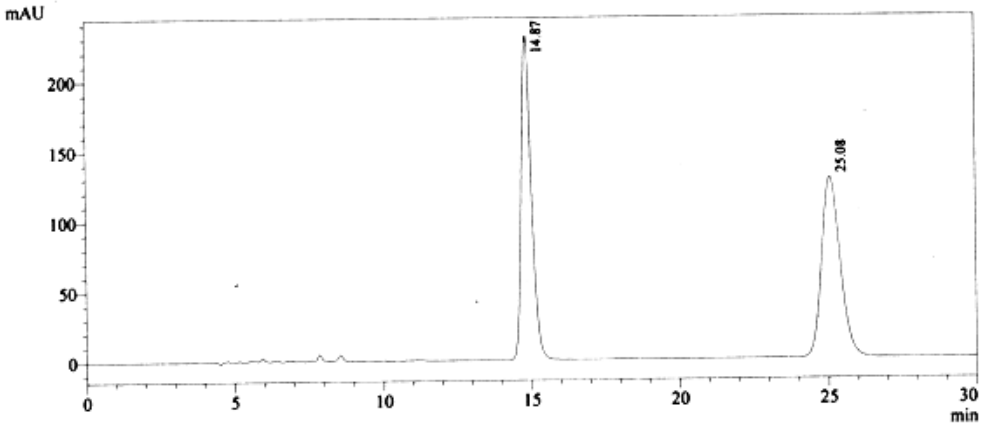
Peak#	Ret. Time	Area	Area %
1	24.95	2973427	50.10
2	45.68	2961273	49.90
Total		5934699	100.00





PDA Ch2 235nm 4nm

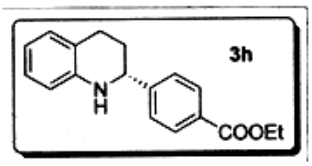
Peak#	Ret. Time	Area	Area %
1	5.83	1089263	10.21
2	24.36	89640	0.84
3	44.88	9490199	88.95
Total		10669101	100.00

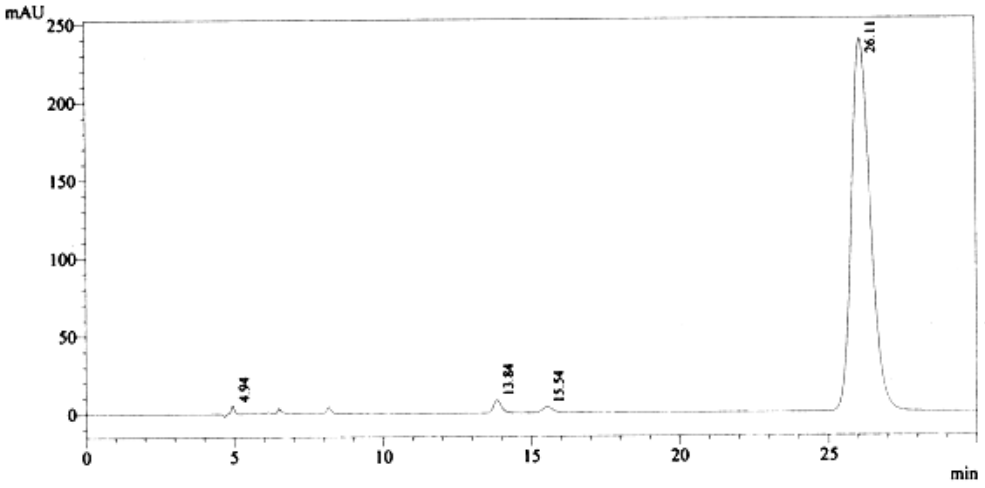


1 PDA Multi 2 / 235nm 4nm

PDA Ch2 235nm 4nm

Peak#	Ret. Time	Area	Area %
1	14.87	5585161	50.02
2	25.08	5580245	49.98
Total		11165406	100.00

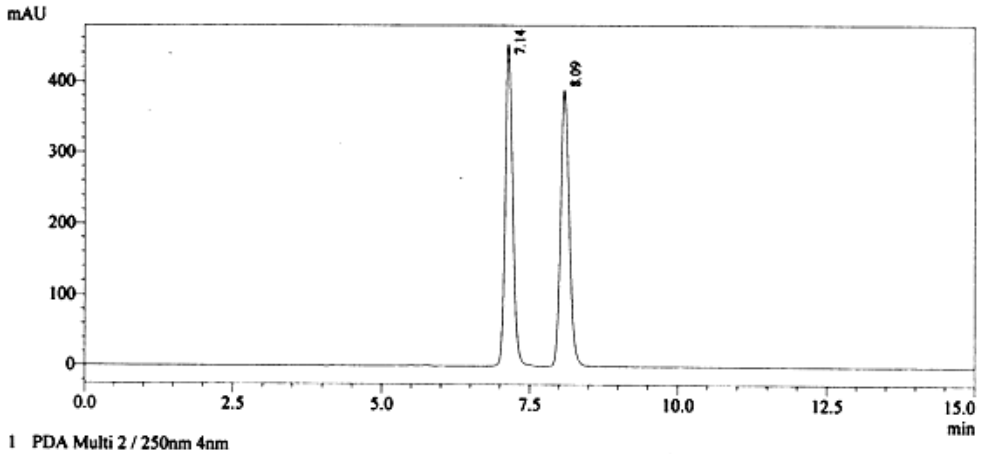




1 PDA Multi 2 / 235nm 4nm

PDA Ch2 235nm 4nm

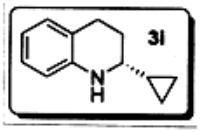
Peak#	Ret. Time	Area	Area %
1	4.94	89016	0.81
2	13.84	152860	1.39
3	15.54	86812	0.79
4	26.11	10653311	97.01
Total		10981999	100.00

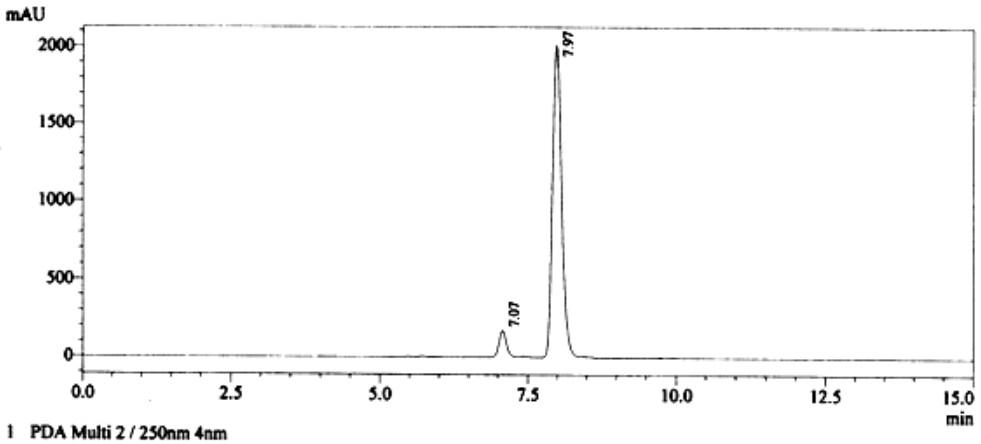


1 PDA Multi 2 / 250nm 4nm

PDA Ch2 250nm 4nm

Peak#	Ret. Time	Area	Area %
1	7.14	4007490	50.09
2	8.09	3992963	49.91
Total		8000453	100.00

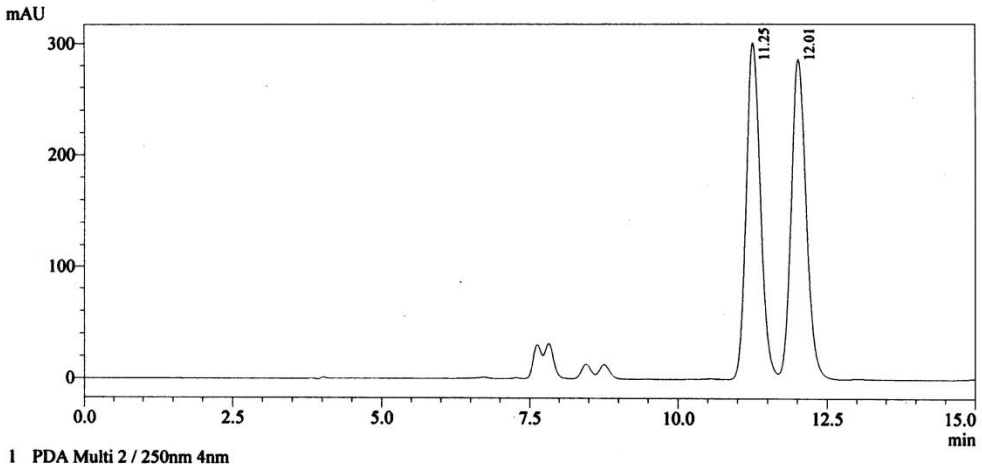




1 PDA Multi 2 / 250nm 4nm

PDA Ch2 250nm 4nm

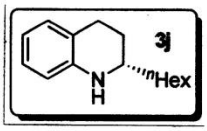
Peak#	Ret. Time	Area	Area %
1	7.07	1511540	6.55
2	7.97	21582128	93.45
Total		23093668	100.00

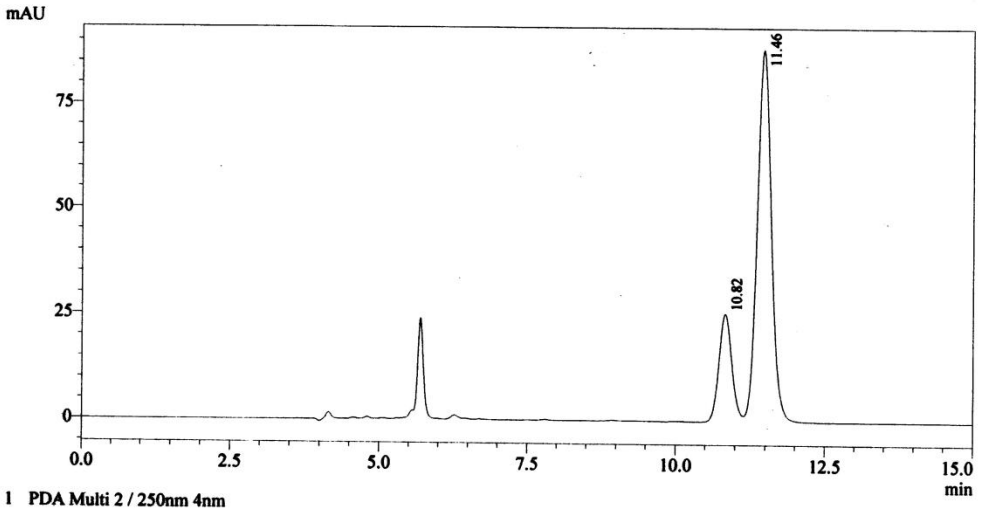


1 PDA Multi 2 / 250nm 4nm

PDA Ch2 250nm 4nm

Peak#	Ret. Time	Area	Area %
1	11.25	4978594	49.84
2	12.01	5010316	50.16
Total		9988911	100.00

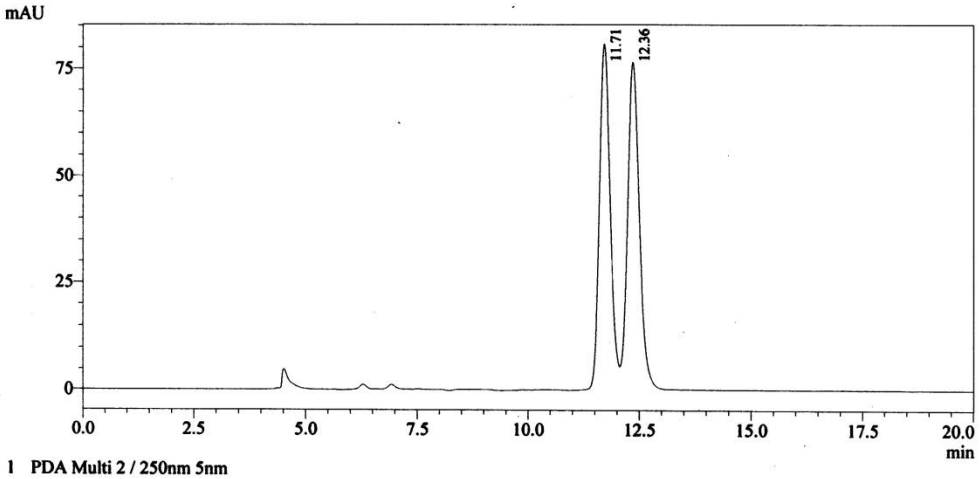




1 PDA Multi 2 / 250nm 4nm

PDA Ch2 250nm 4nm

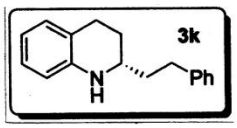
Peak#	Ret. Time	Area	Area %
1	10.82	385348	21.07
2	11.46	1443558	78.93
Total		1828906	100.00

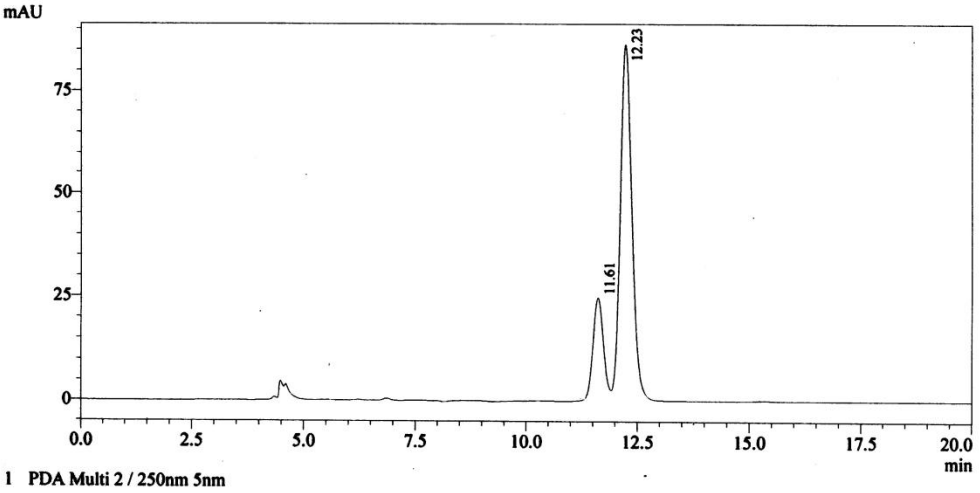


1 PDA Multi 2 / 250nm 5nm

PDA Ch2 250nm 5nm

Peak#	Ret. Time	Area	Area %
1	11.71	1371283	49.25
2	12.36	1412851	50.75
Total		2784134	100.00

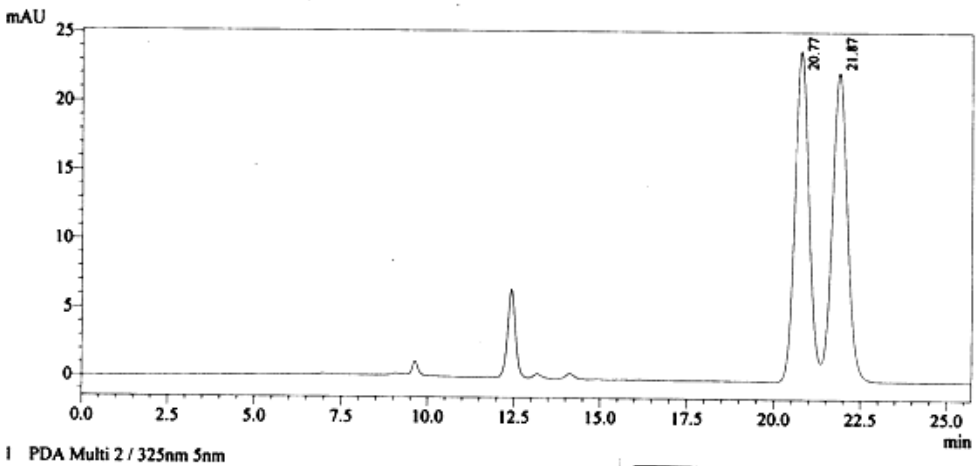




1 PDA Multi 2 / 250nm 5nm

PDA Ch2 250nm 5nm

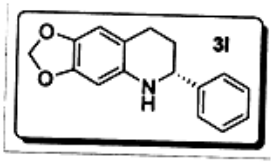
Peak#	Ret. Time	Area	Area %
1	11.61	415692	20.94
2	12.23	1569052	79.06
Total		1984744	100.00

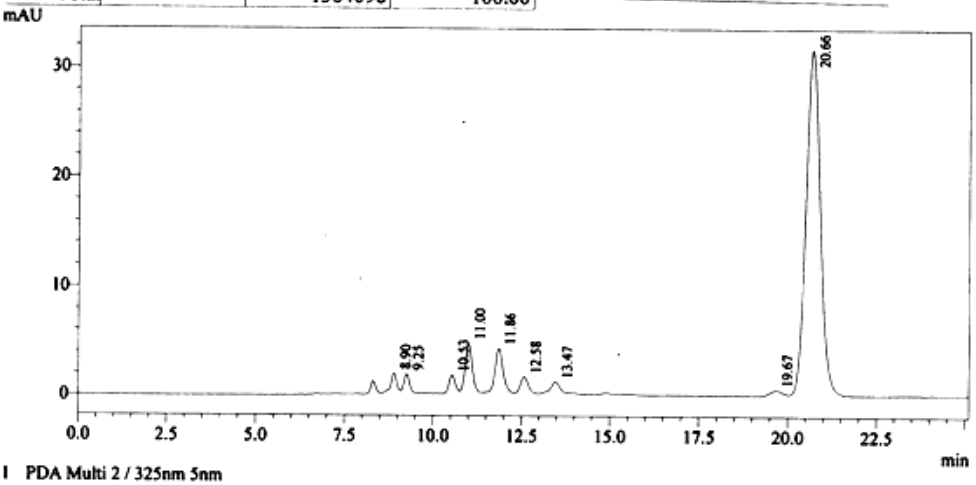


1 PDA Multi 2 / 325nm 5nm

PDA Ch2 325nm 5nm

Peak#	Ret. Time	Area	Area %
1	20.77	679198	49.79
2	21.87	684900	50.21
Total		1364098	100.00

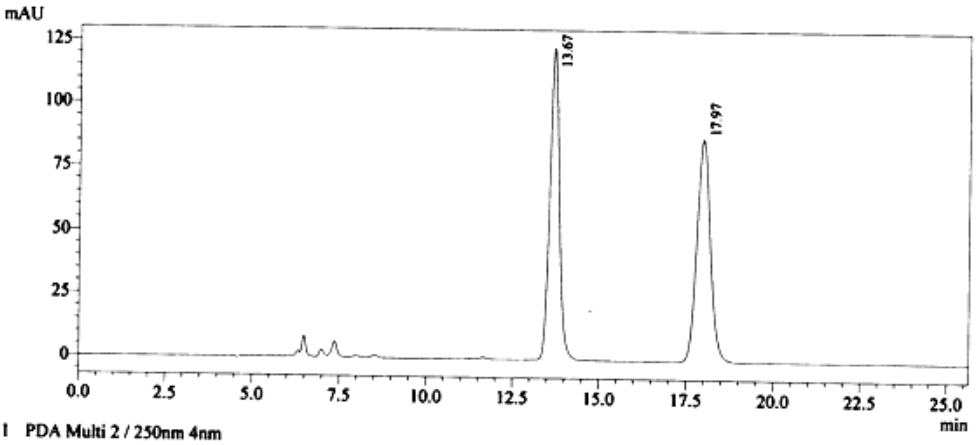




1 PDA Multi 2 / 325nm 5nm

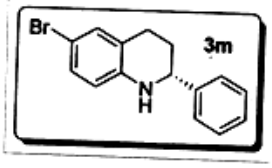
PDA Ch2 325nm 5nm

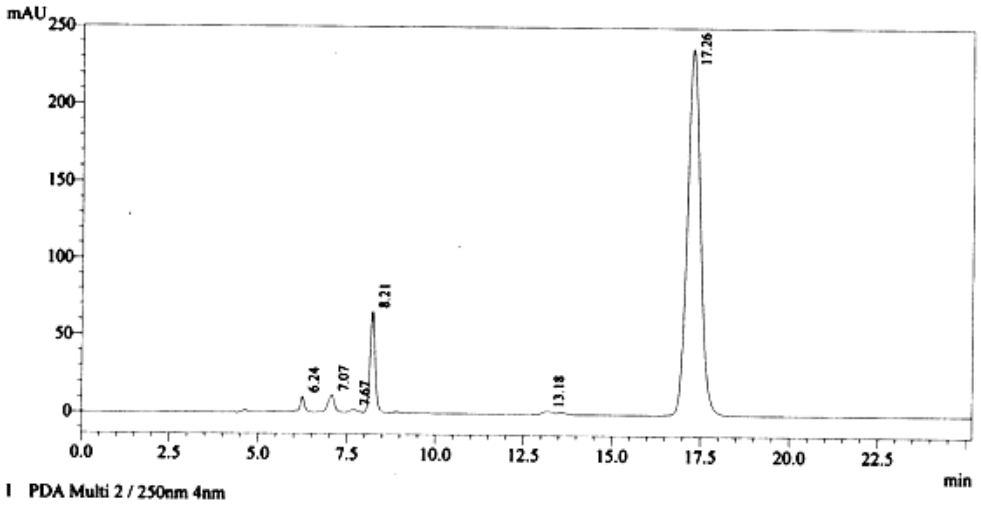
Peak#	Ret. Time	Area	Area %
1	8.90	21852	1.91
2	9.25	19080	1.67
3	10.53	20947	1.83
4	11.00	67403	5.90
5	11.86	68437	5.99
6	12.58	24537	2.15
7	13.47	22137	1.94
8	19.67	12518	1.10
9	20.66	885601	77.51
Total		1142511	100.00



PDA Ch2 250nm 4nm

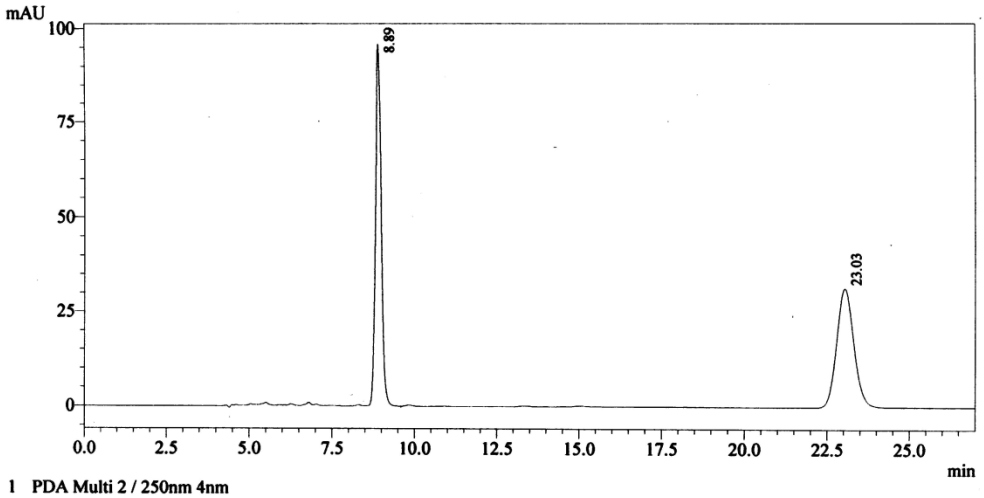
Peak#	Ret. Time	Area	Area %
1	13.67	2362669	49.92
2	17.97	2370447	50.08
Total		4733116	100.00





PDA Ch2 250nm 4nm

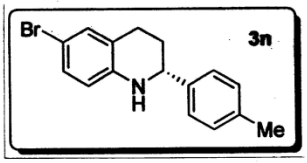
Peak#	Ret. Time	Area	Area %
1	6.24	101359	1.42
2	7.07	162696	2.28
3	7.67	48354	0.68
4	8.21	678435	9.52
5	13.18	42697	0.60
6	17.26	6096438	85.50
Total		7129978	100.00

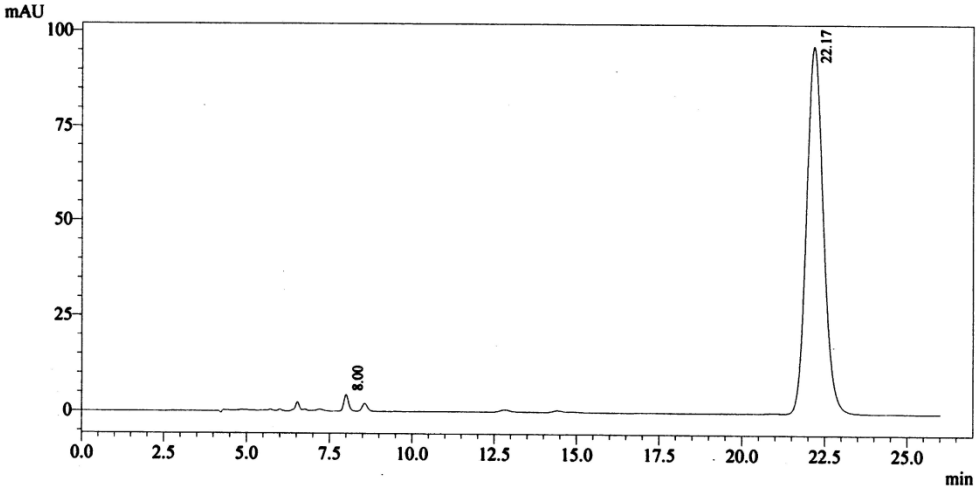


1 PDA Multi 2 / 250nm 4nm

PDA Ch2 250nm 4nm

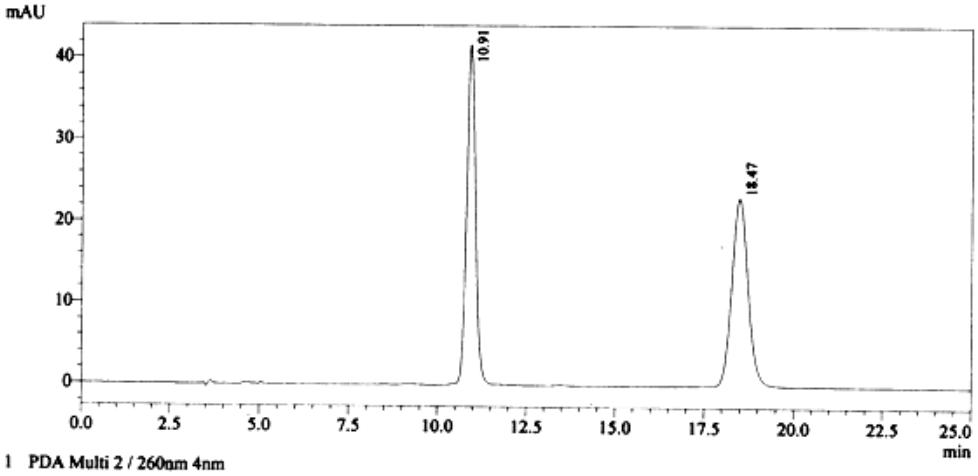
Peak#	Ret. Time	Area	Area %
1	8.89	1151493	50.19
2	23.03	1142952	49.81
Total		2294445	100.00





PDA Ch2 250nm 4nm

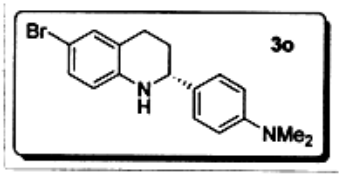
Peak#	Ret. Time	Area	Area %
1	8.00	43215	1.25
2	22.17	3406093	98.75
Total		3449307	100.00

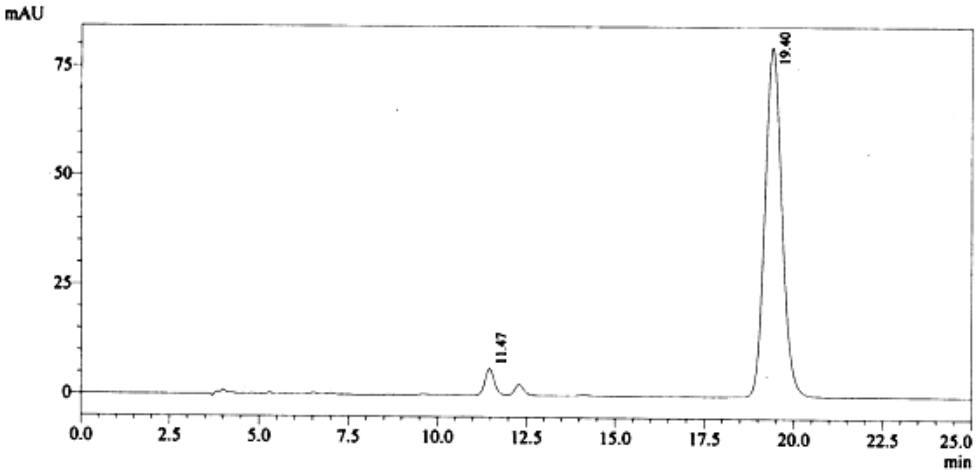


1 PDA Multi 2 / 260nm 4nm

PDA Ch2 260nm 4nm

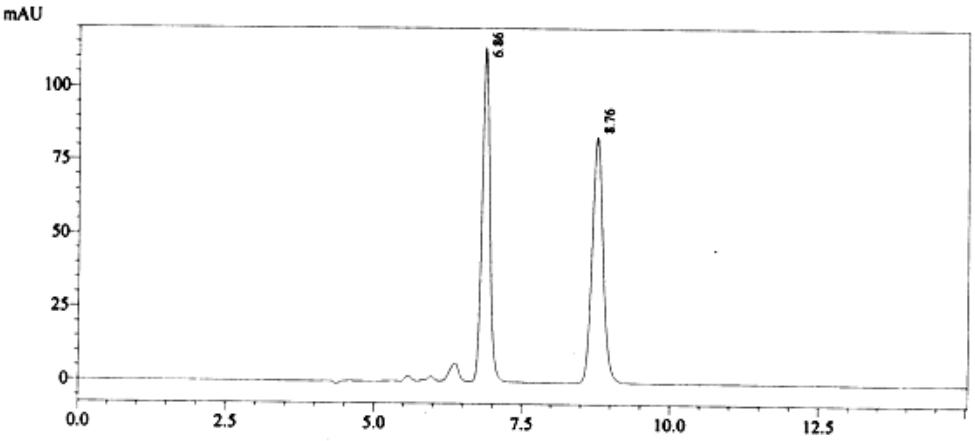
Peak#	Ret. Time	Area	Area %
1	10.91	725400	50.09
2	18.47	722816	49.91
Total		1448217	100.00





PDA Ch2 260nm 4nm

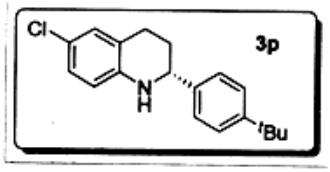
Peak#	Ret. Time	Area	Area %
1	11.47	108831	4.00
2	19.40	2611071	96.00
Total		2719903	100.00

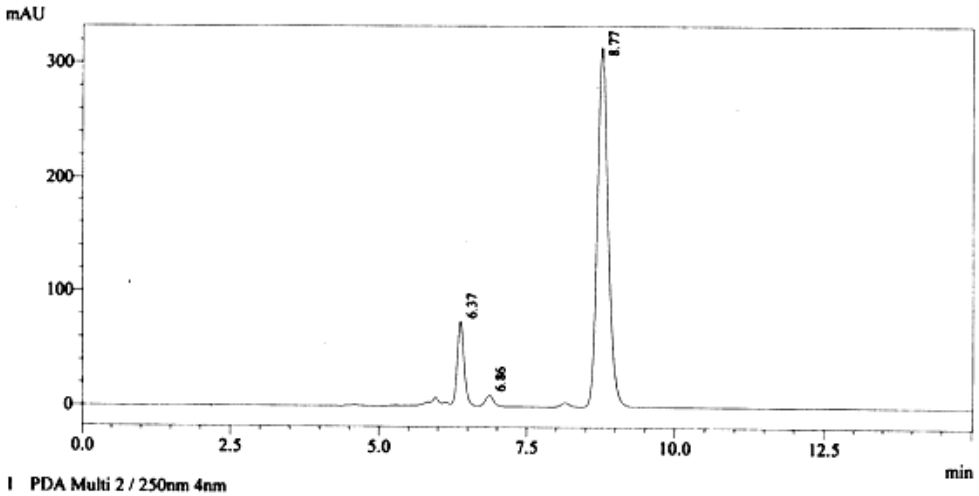


1 PDA Multi 2 / 250nm 4nm

PDA Ch2 250nm 4nm

Peak#	Ret. Time	Area	Area %
1	6.86	1046847	49.39
2	8.76	1072607	50.61
Total		2119454	100.00

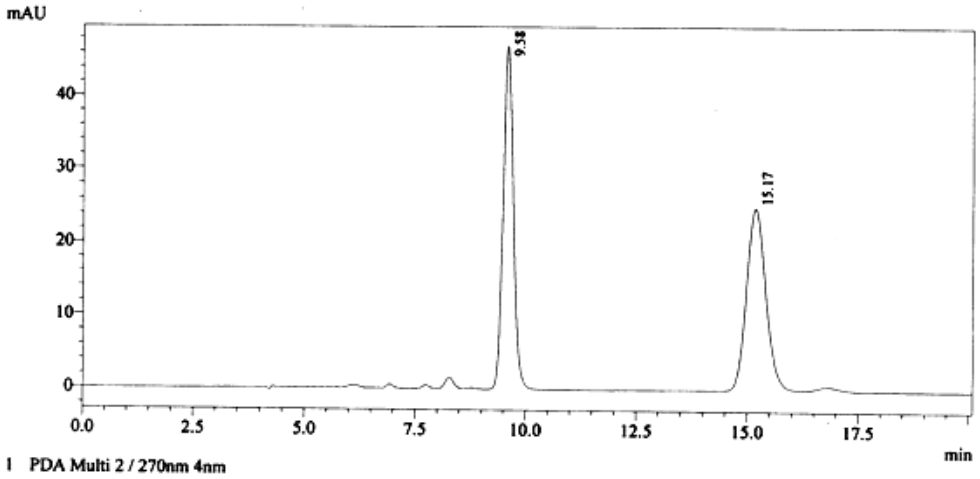




1 PDA Multi 2 / 250nm 4nm

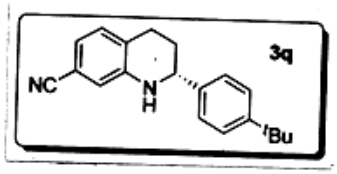
PDA Ch2 250nm 4nm

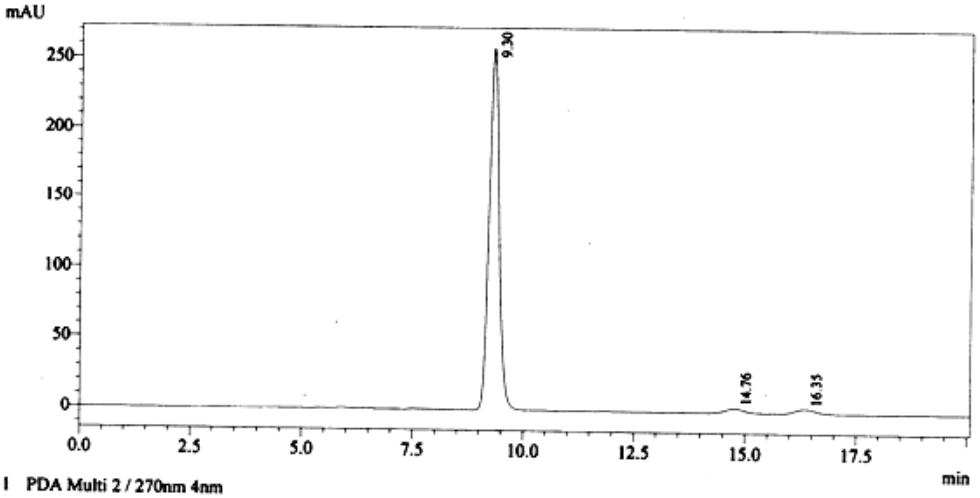
Peak#	Ret. Time	Area	Area %
1	6.37	604789	12.70
2	6.86	97914	2.06
3	8.77	4057640	85.24
Total		4760342	100.00



PDA Ch2 270nm 4nm

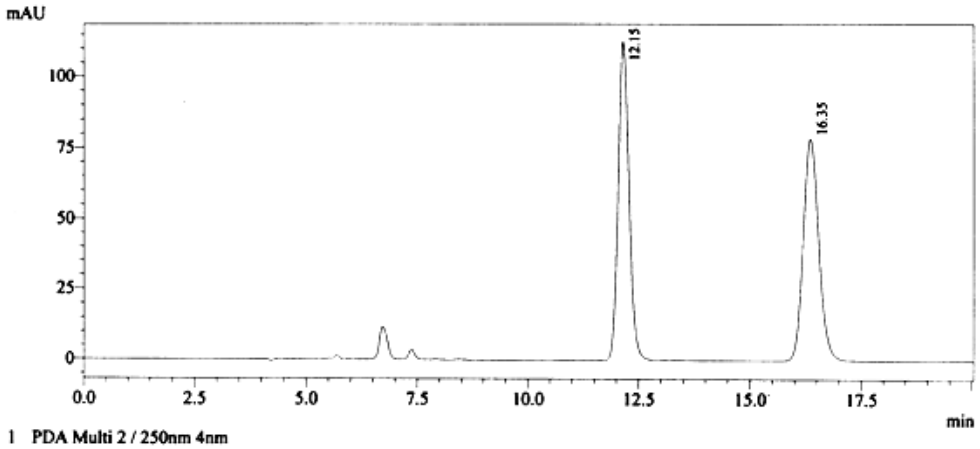
Peak#	Ret. Time	Area	Area %
1	9.58	757506	50.01
2	15.17	757289	49.99
Total		1514795	100.00





PDA Ch2 270nm 4nm

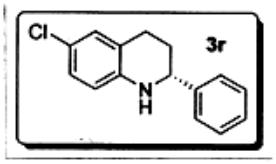
Peak#	Ret. Time	Area	Area %
1	9.30	4099444	95.09
2	14.76	98780	2.29
3	16.35	112925	2.62
Total		4311148	100.00

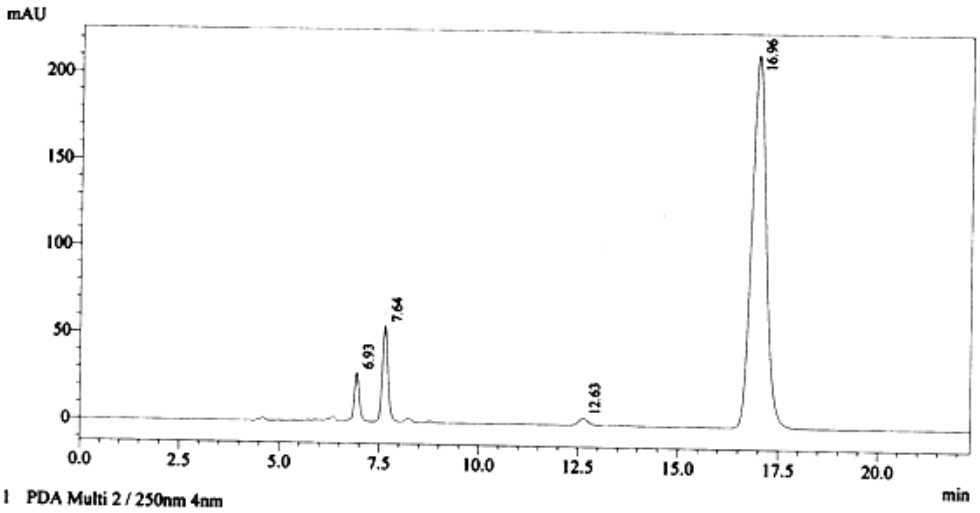


1 PDA Multi 2 / 250nm 4nm

PDA Ch2 250nm 4nm

Peak#	Ret. Time	Area	Area %
1	12.15	1916798	49.94
2	16.35	1921756	50.06
Total		3838555	100.00





1 PDA Multi 2 / 250nm 4nm

PDA Ch2 250nm 4nm

Peak#	Ret. Time	Area	Area %
1	6.93	262104	4.22
2	7.64	546368	8.80
3	12.63	69917	1.13
4	16.96	5327231	85.85
Total		6205620	100.00