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Supplementary Material

A Facile and Efficient Method for the Formation of Unsymmetrical Ureas Using DABAL-Me_3

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1. General Information

All chemicals were purchased from Sigma-Aldrich and used without further purification. DABAL-Me_3 is a free-flowing solid and has a hydrolytic stability. The reagent can be treated without the need for an inert atmosphere, and can be weighed out freely in the laboratory as well as stored in standard container. Proton and ^{13}C NMR spectra were recorded on a 600 MHz & 150 MHz respectively JNM-ECA600 spectrometer. The chemical shifts are reported in δ units (ppm) relative to tetramethylsilane (TMS) and the coupling constants (*J*) quoted in Hz. Reaction progress was monitored by thin-layer chromatography (TLC) analysis. TLC analysis was performed using an aluminum plate with silica gel 60 F_{254} and TLC spots were visualized by UV light (254nm) exposure. Flash chromatography was performed using 230-400 mesh silica gel and analytical grade solvent. HRMS spectrometry was performed on a water Q-TOF mass spectrometer to obtain high-resolution mass spectra.

2. General Experimental Procedure

2.1. General procedure for the preparation of urea compounds (**3a-3u**):

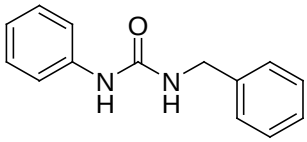
To a solution of benzylamine (0.16 g, 1.52 mmol) in toluene (10 mL) DABAL-Me_3 (0.38 g. 1.52 mmol) was added. The mixture was stirred for 30 min at 40 °C. **1a** (0.27 g, 1.01 mmol) were added and allowed to stir for 3 h at 100 °C. The reaction mixture was quenched by the addition of 1M HCl (2 mL) and extracted with CH_2Cl_2 (2 x 30 mL). The organic layer was dried over magnesium sulfate and concentrated under reduced pressure. The resulting residue was then purified by flash column chromatography on silica gel with hexane-EtOAc as eluent to afford the desired product **3a** (0.215 g, 94%).

2.2. General procedure for the preparation of bis-urea compounds (**3v-3w**):

To a solution of *N*-methylaniline (0.32 g, 3.02 mmol) in toluene (10 mL) DABAL-Me_3 (0.78 g. 3.02 mmol) was added. The mixture was stirred for 30 min at 40 °C. **1g** (0.55 g, 1.01 mmol) were added and allowed to stir for 3 h at 100 °C. The reaction mixture was quenched by the addition of 1M HCl (4 mL) and extracted with CH_2Cl_2 (2 x 50 mL). The organic layer was dried over magnesium sulfate and concentrated under reduced pressure. The resulting residue was then purified by flash column chromatography on silica gel with hexane-EtOAc as eluent to afford the desired product **3v** (0.35 g, 76%).

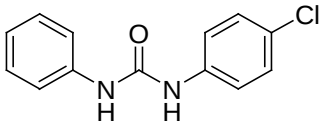
3. Characterization Data of Compounds 3a-3w

1-Benzyl-3-phenylurea (3a)[1]:



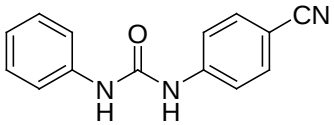
Yellow solid; mp 173–174 ºC; ^{1}H NMR (600 MHz, DMSO-d_6) δ 7.18–7.25 (m, 9H), 6.89 (m,1H), 6.47 (s, 1H), 5.15 (s, 1H), 4.34 (d, *J* = 5.4 Hz, 2H); ^{13}C NMR (150 MHz, DMSO-d_6) δ 155.8, 138.9, 138.4, 129.4, 128.7, 127.6, 127.5, 124.2, 121.5, 44.4; HRMS (ESI) *m*/*z* 227.1179; calcd for $C_{14}H_{15}N_2O$ 227.1184.

1-(4-Chlorophenyl)-3-phenylurea (3b)[2]:



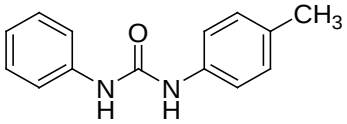
White solid; mp 248–250 °C; ^{1}H NMR (600 MHz, DMSO-d_6) δ 8.79 (s, 1H), 8.68 (s, 1H), 7.43–7.48 (m, 4H), 7.25–7.32 (m, 4H), 6.95 (t, *J* = 7.2 Hz, 1H); ^{13}C NMR (150 MHz, DMSO-d_6) δ 152.9, 140.0, 139.2, 129.3, 129.1, 128.9, 125.8, 122.5, 120.4, 120.2, 118.8, 118.7; HRMS (ESI) *m*/*z* 247.0634; calcd for $C_{13}H_{12}ClN_2O$ 247.0638.

1-(4-Cyanophenyl)-3-phenylurea (3c)[3]:



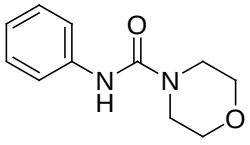
White solid; mp 205–207 °C; ^{1}H NMR (600 MHz, DMSO-d_6) δ 8.91 (s, 1H), 8.84 (s, 1H), 7.73 (d, *J* = 6.6 Hz, 2H), 7.62 (d, *J* = 8.4 Hz, 2H), 7.56 (d, *J* = 7.2 Hz, 2H), 7.37 (t, *J* = 8.4 Hz, 2H), 7.25 (t, *J* = 7.2 Hz, 1H); ^{13}C NMR (150 MHz, DMSO-d_6) δ 153.0, 145.2, 140.1, 134.2, 129.8, 123.3, 120.3, 119.5, 118.9, 104.1; HRMS (ESI) *m*/*z* 238.0982; calcd for $C_{14}H_{12}N_3O_2$ 238.0980.

1-Phenyl-3-*p*-tolylurea (3d)[3]:



White solid; mp 212–213 °C; ^{1}H NMR (600 MHz, DMSO-d_6) δ 8.62 (s, 1H), 8.56 (s, 1H), 7.44 (d, *J* = 4.8 Hz, 2H), 7.33 (d, *J* = 8.4 Hz, 2H), 7.25 (t, *J* = 7.8 Hz, 2H), 7.08 (d, *J* = 8.4 Hz, 2H), 6.94 (t, *J* = 7.2 Hz, 1H), 2.24 (s, 3H); ^{13}C NMR (150 MHz, DMSO-d_6) δ 153.5, 140.8, 138.2, 131.6, 130.1, 129.7, 122.7, 119.2, 119.1, 21.3; HRMS (ESI) *m*/*z* 227.1187; calcd for $C_{14}H_{15}N_2O$ 227.1184.

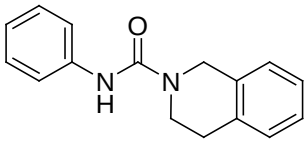
***N*-Phenylmorpholine-4-carboxamide (3e)[4]:**



White solid; mp 150−152 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.27−7.35 (m, 4H), 7.05 (m, 1H), 6.56 (s, 1H), 3.71 (t, *J* = 4.8 Hz, 4H), 3.47 (t, *J* = 5.4 Hz, 4H); ^{13}C NMR (150 MHz, $CDCl_3$) δ

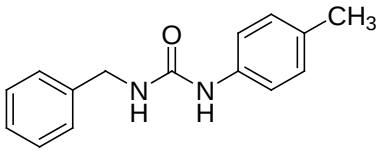
155.3, 138.8, 128.9, 123.5, 120.3, 66.6, 44.3; HRMS (ESI) *m*/*z* 207.1136; calcd for $C_{11}H_{15}N_2O_2$ 207.1134.

_N_-Phenyl-3,4-dihydroisoquinoline-2(1_H_)-carboxamide (3f)[5]:



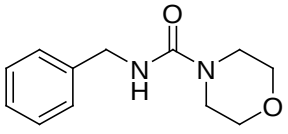
White solid; mp 145−147°C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.41 (m, 2H), 7.28 (m, 2H), 7.11 (m, 4H), 7.03 (t, *J* = 6.6 Hz, 2H), 6.61 (s, 1H), 4.65 (s, 2H), 3.71 (t, *J* = 5.4 Hz, 2H), 2.90 (t, *J* = 6.0 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 139.2, 135.1, 132.3, 128.9, 128.5, 126.9, 126.5, 126.4, 123.2, 120.3, 45.8, 41.7, 29.1; HRMS (ESI) *m*/*z* 253.1346; calcd for $C_{16}H_{17}N_2O$ 253.1341.

1-Benzyl-3-*p*-tolylurea (3g)[6]:



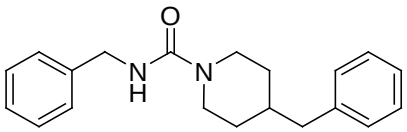
White solid; mp 183−185°C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.21–7.31 (m, 6H), 7.09–7.14 (m, 3H), 6.24(s, 1H), 4.41 (d, *J* = 6.6 Hz, 2H), 2.29 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 156.2, 139.0, 135.5, 134.9, 130.0, 128.7, 127.5, 127.4, 122.5, 44.4, 20.9; HRMS (ESI) *m*/*z* 241.1347; calcd for $C_{15}H_{17}N_2O$ 241.1341.

N-Benzylmorpholine-4-carboxamide (3h)[7]:



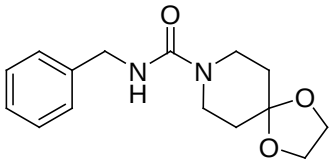
White solid; mp 138−140°C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.25–7.34 (m, 5H), 4.71 (s, 1H), 4.42 (d, *J* = 5.4 Hz, 2H), 3.67 (t, *J* = 4.8 Hz, 4H), 3.35 (t, *J* = 4.8 Hz, 4H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 157.7, 139.2, 128.8, 127.9, 127.5, 66.6, 45.1, 44.1; HRMS (ESI) *m*/*z* 221.1287; calcd for $C_{12}H_{17}N_2O_2$ 221.1290.

***N*,4-Dibenzylpiperidine-1-carboxamide (3i):**



White solid; mp 148–150 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.18–7.33 (m, 8H), 7.12–7.13 (m, 2 H), 4.67 (s, 1H), 4.41 (d, *J* = 5.4 Hz, 2 H), 4.41 (d, *J* = 10.2 Hz, 2 H), 2.72 (m, 2 H), 2.53 (d, *J* = 6.6 Hz, 2 H), 1.68 (m, 3 H), 1.17 (m, 2 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 157.5, 140.2, 139.7, 129.2, 128.7, 128.4, 127.9, 127.3, 126.1, 45.1, 44.4, 43.1, 38.2, 31.9; *m*/*z* (HRMS, ESI) 309.1964; $C_{20}H_{25}N_2O$ $[M + H]^+$ requires 309.1967.

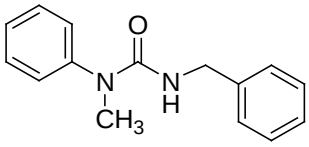
***N*-Benyl-1,4-dioxa-8-azaspiro[4.5] decane-8-carboxamide (3j):**



White solid; mp 170–172 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.24–7.33 (m, 5 H), 4.74 (s, 1H), 4.41 (d, *J* = 5.4 Hz, 2 H), 3.95 (s, 4 H), 3.47 (m, 4 H), 1.68 (m, 4 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 157.2, 139.5, 128.7, 127.9, 127.4, 107.1, 64.5, 45.1, 42.3, 34.9; *m*/*z* (HRMS, ESI)

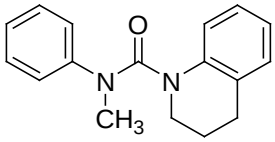
277.1556; $C_{15}H_{21}N_2O_3$ $[M + H]^+$ requires 277.1552.

3-Benzy-1-methyl-1-phenylurea (3k)[8]:



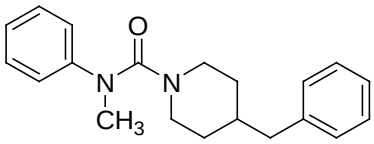
White solid; mp 92–94 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.37–7.43 (m, 2 H), 7.19–7.30 (m, 8 H), 4.67 (s, 1H), 4.37 (d, *J* = 6.6 Hz, 2 H), 3.29 (s, 3 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 157.3, 134.4, 139.6, 130.2, 128.9, 127.5, 127.4, 127.2, 44.8, 37.4; HRMS (ESI) *m*/*z* 241.1345; calcd for $C_{15}H_{17}N_2O$ 241.1341.

***N*-Methyl-*N*-phenyl-3,4-dihydroquinoline-1(2*H*) carboxamide (3l)[9]:**



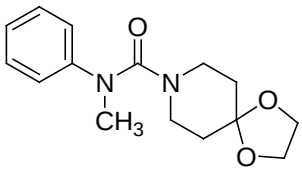
Yellow oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.16–7.26 (m, 3H), 6.98–7.07 (m, 4H), 6.89 (m, 1H), 6.81 (m, 1H), 3.39 (t, *J* = 6.6 Hz, 2H), 3.33 (s, 3H), 2.59 (t, *J* = 6.6 Hz, 2H), 1.84 (m, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 160.2, 145.4, 139.5, 129.0, 128.7, 128.6, 126.1, 125.0, 124.4, 122.5, 121.9, 46.0, 38.9, 26.9, 23.4; HRMS (ESI) *m*/*z* 267.1499; calcd for $C_{17}H_{19}N_2O$ 267.1497.

4-Benzyl-*N*-methyl-*N*-phenylpiperidine-1-carboxamide (3m):



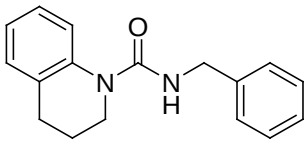
Yellow oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.28 (t, *J* = 7.8 Hz, 2 H), 7.21 (t, *J* = 7.2 Hz, 2 H), 7.13 (t, *J* = 7.2 Hz, 1 H), 7.04–7.07 (m, 5 H), 3.79 (d, *J* = 14.4 Hz, 2 H), 3.19 (s, 3 H), 2.42-2.49 (m, 4H), 1.55 (m, 1H), 1.43 (d, *J* = 12.0 Hz, 2 H), 0.95–1.02 (m, 2H) ; ^{13}C NMR (150 MHz, $CDCl_3$) δ 161.2, 147.2, 140.2, 129.6, 129.4, 129.1, 129.0, 128.3, 125.9, 124.3, 123.9, 123.6, 46.1, 43.1, 39.6, 38.2, 37.4, 31.7; *m*/*z* (HRMS, ESI) 309.1971; $C_{20}H_{25}N_2O$ $[M + H]^+$ requires 309.1967.

_N_-Methyl-_N_-phenyl-1,4-dioxa-8-azaspiro[4.5] decane-8-carboxamide (3n)[10]:



Yellow oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.24–7.27 (m, 2H), 7.02–7.05 (m, 3H), 3.83 (s, 4H), 3.24 (t, *J* = 6.6 Hz, 4H), 3.15 (s, 3H), 1.6 (s, 1H), 1.43 (t, *J* = 6.0 Hz, 4H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 160.9, 147.1, 129.5, 124.6, 123.8, 107.2, 64.4, 43.8, 39.7, 34.6; HRMS (ESI) *m*/*z* 277.1556; calcd for $C_{15}H_{21}N_2O_3$ 277.1552.

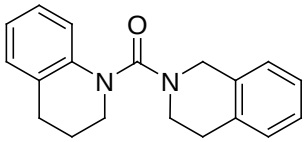
_N_-Benzyl-3,4-dihydroquinoline-1(2_H_)-carboxamide (3o):



Yellow oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.24–7.34 (m, 6H), 7.12–7.16 (m, 2H), 7.01–7.04 (m, 1H), 5.49 (s, 1H), 4.48 (d, *J* = 5.4 Hz, 2H), 3.79 (t, *J* = 6.0 Hz, 2H), 2.76 (t, *J* = 6.0 Hz, 2H), 1.94

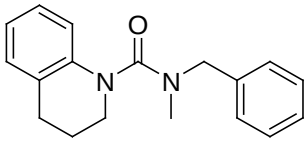
(m, 2H), 1.69 (s, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 156.7, 139.3, 132.4, 129.7, 128.7, 127.6, 127.3, 126.6, 124.3, 123.3, 44.9, 43.6, 27.1, 23.9; *m*/*z* (HRMS, ESI) 267.1494; $C_{17}H_{19}N_2O$ $[M + H]^+$ requires 267.1497.

(3,4-Dihydroisoquinolin-2(1*H*)-yl)(3,4-dihydroquinolin-1(2*H*)-yl)methanone (3p):



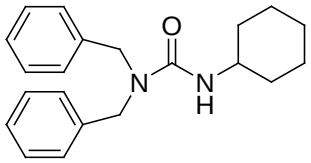
Yellow oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.11–7.16 (m, 4H), 7.00–7.06 (m, 3H), 6.92 (m, 1H), 4.45 (s, 1H), 3.62 (t, *J* = 6.6 Hz, 2H), 3.55 (t, *J* = 5.4 Hz, 2H), 2.83 (t, *J* = 6.6 Hz, 2H), 2.79 (t, *J* = 6.6 Hz, 2H), 1.97 (m, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 160.4, 143.0, 140.8, 134.7, 133.7, 129.2, 128.8, 126.6, 126.5, 126.2, 122.2, 120.6, 119.9, 48.1, 45.6, 43.7, 27.1, 23.7; *m*/*z* (HRMS, ESI) 293.1657; $C_{19}H_{21}N_2O$ $[M + H]^+$ requires 293.1654.

***N*-Benzyl-*N*-methyl-3,4-dihydroquinoline-1(2*H*)-carboxamide (3q):**



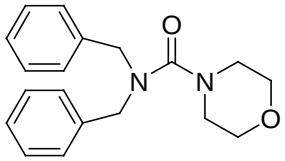
Yellow oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.17–7.44 (m, 5H), 4.52 (s, 2H), 3.71 (t, *J* = 6.6 Hz, 2H), 3.39 (t, *J* = 6.6 Hz, 2H), 2.76–2.87 (m, 5H), 2.02(m, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 161.1, 140.9, 137.7, 129.2, 128.7, 128.6, 127.7, 127.5, 126.5, 121.9, 119.5, 53.6, 45.8, 35.9, 27.1, 23.5; *m*/*z* (HRMS, ESI) 281.1657; $C_{18}H_{21}N_2O$ $[M + H]^+$ requires 281.1654.

1,1-Dibenzyl-3-cyclohexylurea (3r)[11]:



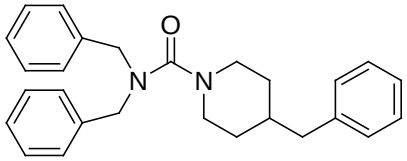
White solid; mp 140–142 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.31–7.35 (m, 4H), 7.22–7.27 (m, 6H), 4.47 (s, 4H), 3.64–3.68 (m, 1H), 1.81–1.83 (m, 2H), 1.52–1.53 (m, 3H), 1.27–1.31 (m, 2H), 1.04–1.07 (m, 1H), 0.91–0.96 (m, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 157.9, 137.9, 128.8, 127.5, 127.3, 50.4, 40.1, 33.7, 25.7, 24.8; HRMS (ESI) *m*/*z* 323.2126; calcd for $C_{21}H_{27}N_2O$ 323.2123.

***N*,*N*-Dibenzylmorpholine-4-carboxamide (3s)[9]:**



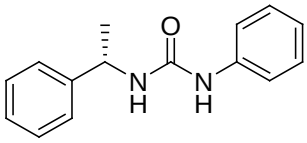
White solid; mp 106–108 °C; ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.17–7.26 (m, 6H), 7.07–7.09 (m, 4H), 4.23 (s, 4H), 3.61–3.62 (m, 4H), 3.24–3.27 (m, 4H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 164.9, 137.3, 128.7, 127.9, 127.5, 66.7, 50.7, 47.8; HRMS (ESI) *m*/*z* 311.1765; calcd for $C_{19}H_{23}N_2O_2$ 311.1760.

***N*,*N*,4-Tribenzylpiperidine-1-carboxamide (3t):**



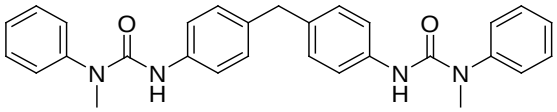
Yellow oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.23–7.36 (m, 8H), 7.12–7.22 (m, 7H), 4.32 (s, 4H), 3.80 (d, *J* = 13.8 Hz, 2H) 2.81 (m, 2H), 2.57 (d, *J* = 7.4 Hz, 2H), 1.67–1.74 (m, 3H), 1.30 (m, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 165.2, 140.3, 137.8, 129.2, 129.1, 128.7, 128.4, 127.9, 127.4, 126.1, 50.8, 47.7, 43.3, 38.5, 32.1; *m*/*z* (HRMS, ESI) 399.2439; $C_{27}H_{31}N_2O$ $[M + H]^+$ requires 399.2436.

(*S*)-1-Phenyl-3-(1-phenylethyl)urea (3u):



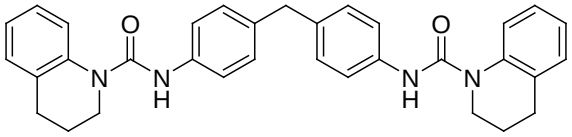
Yellow solid; mp: 148−150 °C; $[\alpha]_D^{20}$ −8.03 (*c* 1.00, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.17−7.34 (m, 10H), 6.97−6.99 (m, 1H), 5.82 (d, *J* = 6.6 Hz, 1H), 4.88 (m, 1H), 1.32 (d, *J* = 6.6 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 155.7, 144.2, 138.9, 129.1, 128.7, 127.2, 125.9, 123.2, 120.2, 49.9, 23.0; *m*/*z* (HRMS, ESI) 241.1345; $C_{15}H_{17}N_2O$ $[M + H]^+$ requires 241.1341.

1,1'-(4,4'-Methylenebis(4,1-phenylene))bis(3-methyl-3-phenylurea) (3v):



White solid; mp 177–179 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.42 (t, *J* = 7.4 Hz, 4H), 7.27–7.33 (m, 6H), 7.16 (m, 4H), 6.98 (d, *J* = 9.0 Hz, 4H), 6.25 (s, 2H), 3.79 (s, 2H), 3.39 (s, 6H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 154.6, 143.1, 137.0, 135.9, 130.3, 130.1, 129.2, 129.0, 127.8, 127.6, 127.4, 119.6, 40.6, 37.3; *m*/*z* (HRMS, ESI) 464.2293; $C_{29}H_{29}N_4O_2$ $[M + H]^+$ requires 465.2291.

***N,N'*-(4,4'-Methylenebis(4,1-phenylene))bis(3,4-dihydroquinoline-1(2*H*)-carboxamide) (3w):**



White solid; mp 164-166 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.17–7.29 (m, 10H), 7.05–7.09 (m, 6H), 6.93 (s, 2H), 3.84 (s, 2H), 3.80 (t, *J* = 6.6 Hz, 4H), 2.78 (t, *J* = 7.4 Hz, 4H), 1.96 (m, 4H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 153.9, 138.9, 136.7, 136.1, 132.7, 129.8, 129.4, 126.9, 124.7, 123.1, 119.5, 43.5, 40.6, 27.1, 24.1; *m*/*z* (HRMS, ESI) 517.2608; $C_{33}H_{33}N_4O_2$ $[M + H]^+$ requires 517.2604.

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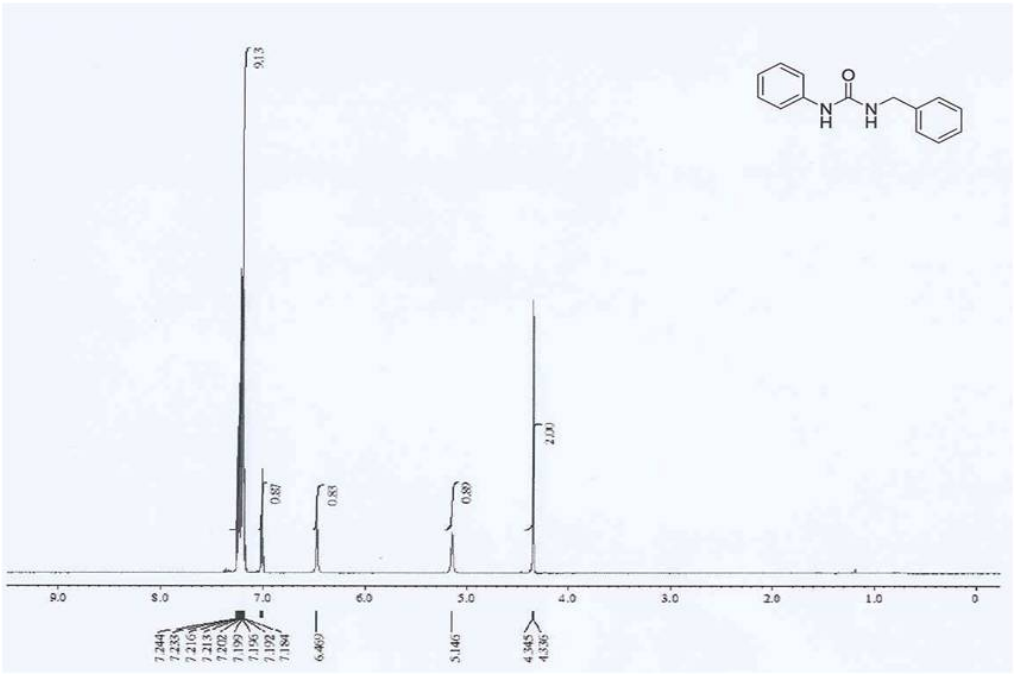
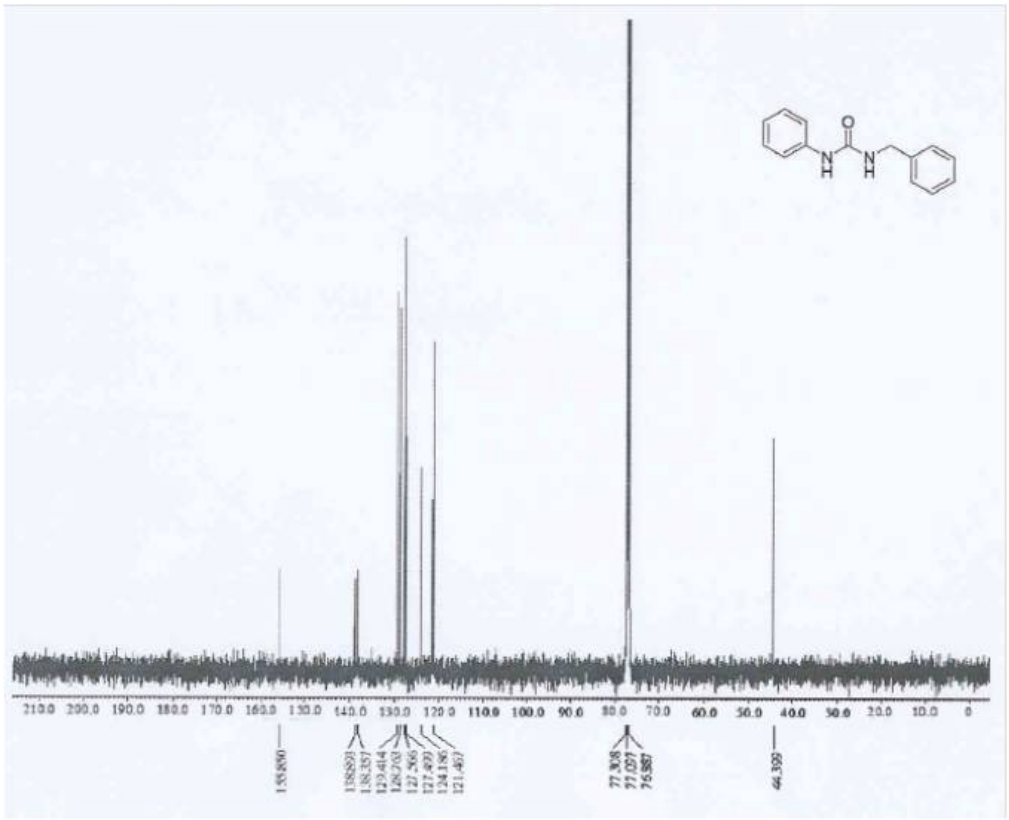
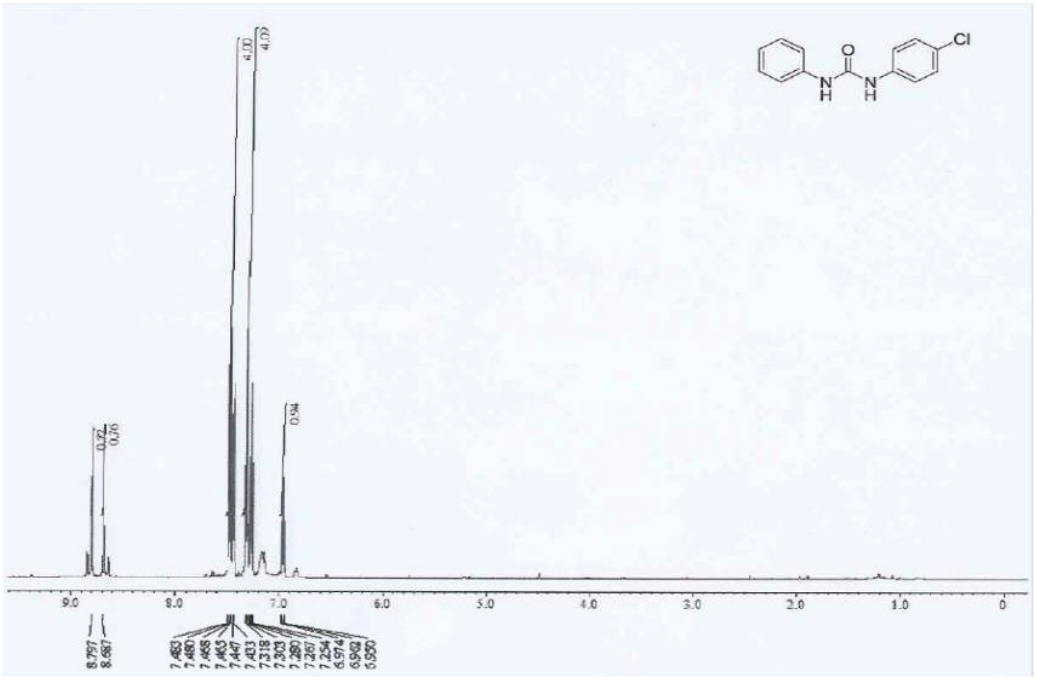
4. ^{1}H and ^{13}C NMR Spectra



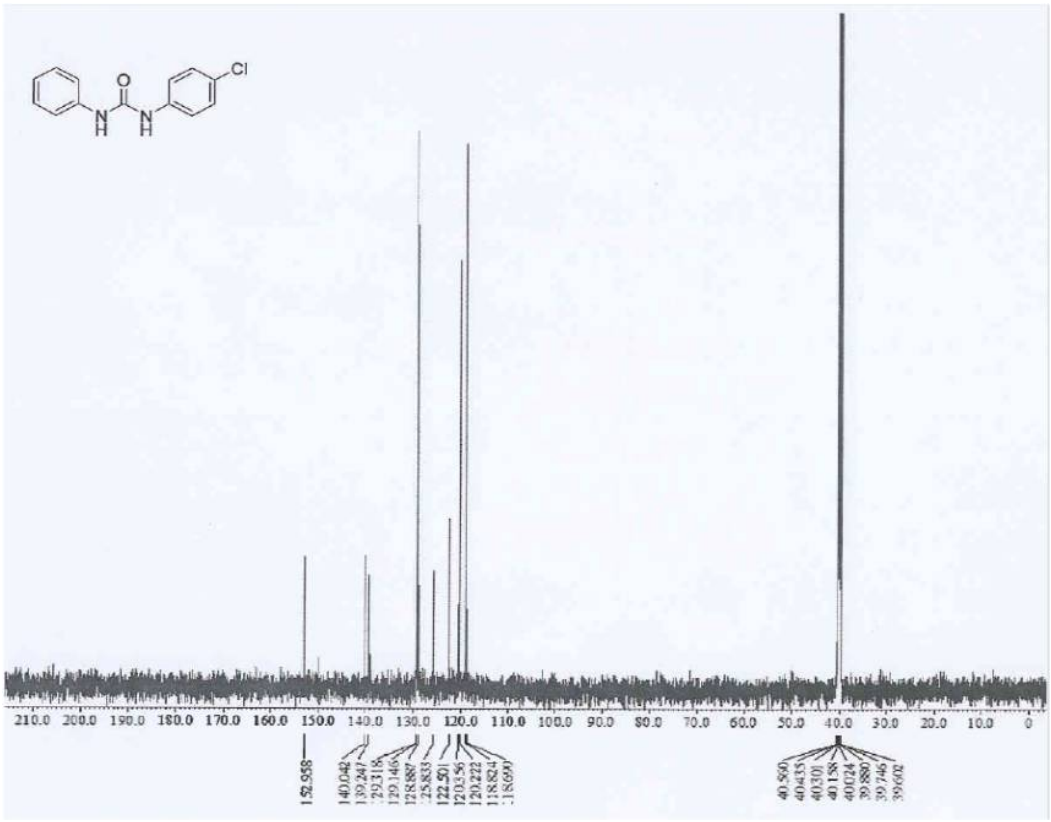
^{1}H NMR spectrum of 1-benzyl-3-phenylurea (3a)



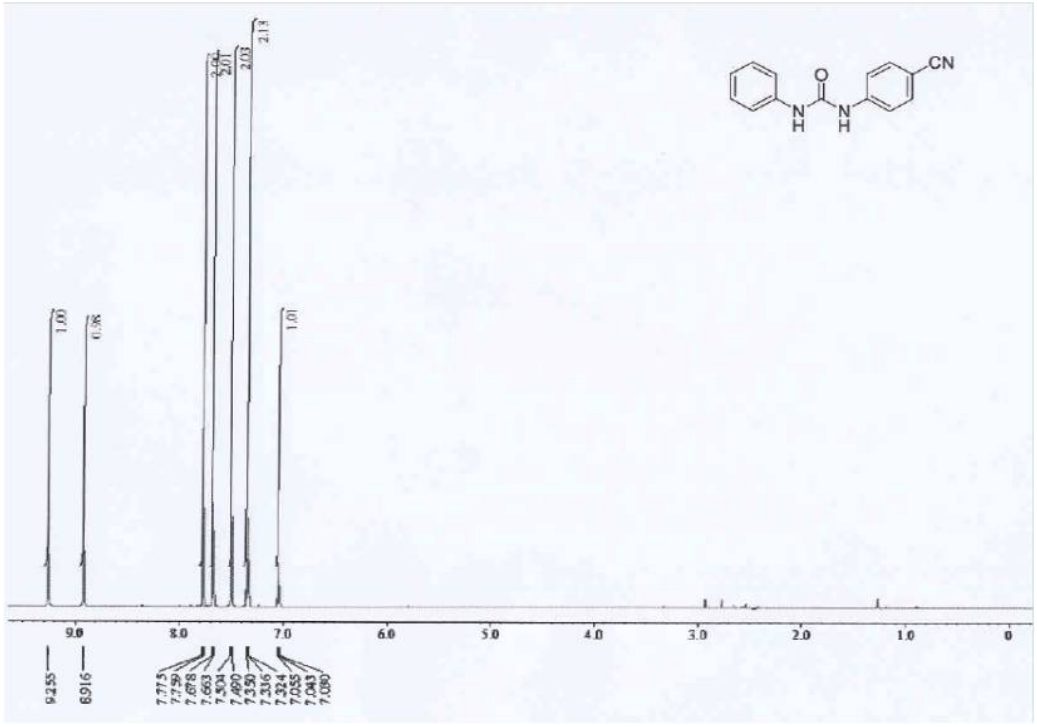
^{13}C NMR spectrum of 1-benzyl-3-phenylurea (3a)



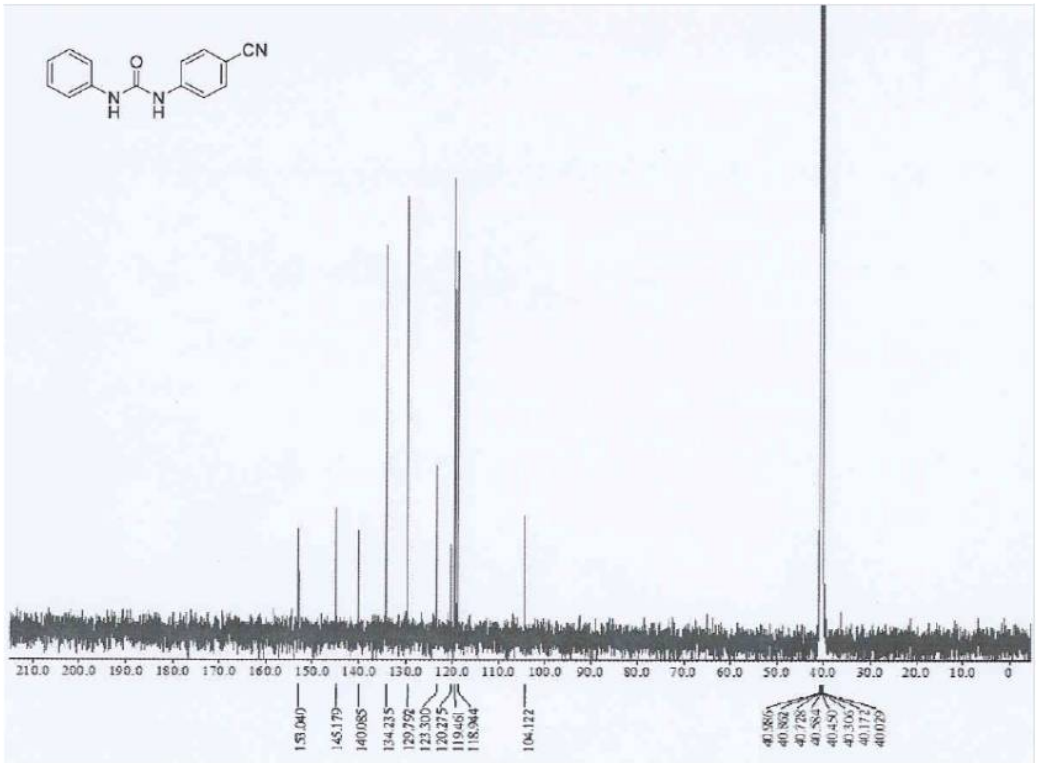
^{1}H NMR spectrum of 1-(4-chlorophenyl)-3-phenylurea (3b)



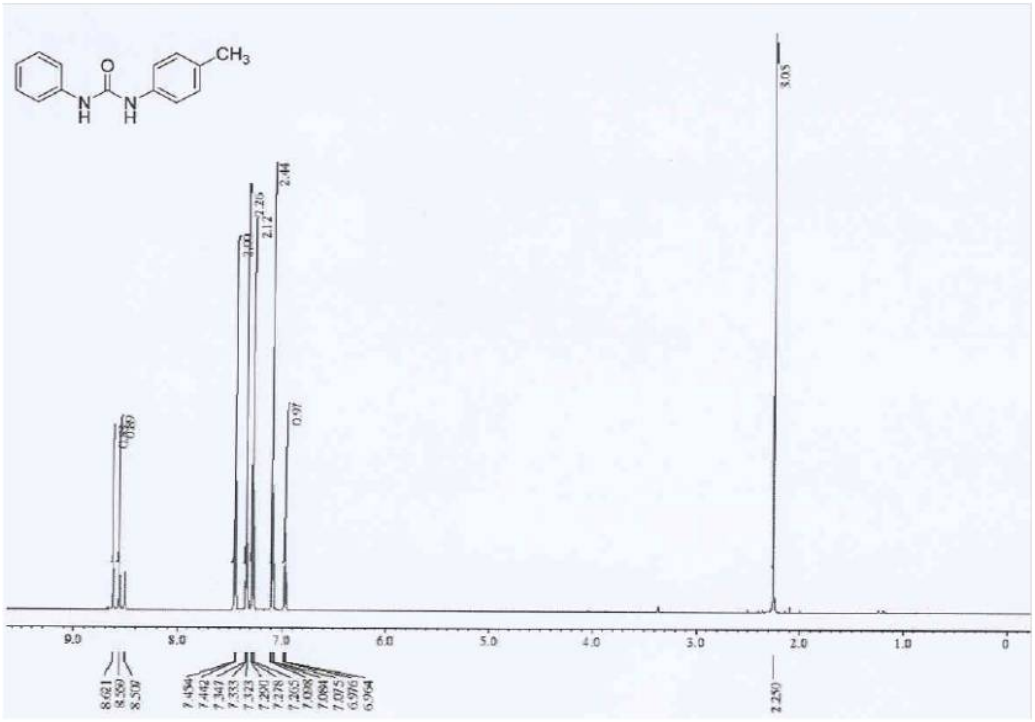
^{13}C NMR spectrum of 1-(4-chlorophenyl)-3-phenylurea (3b)



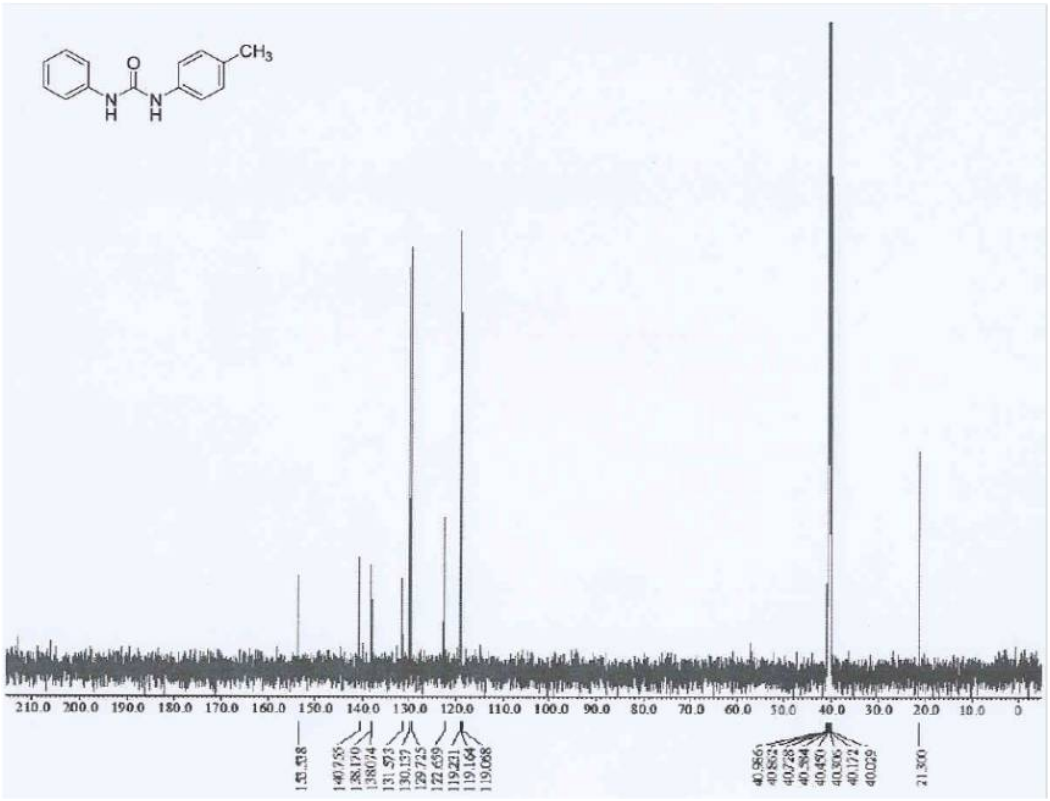
^{1}H NMR spectrum of 1-(4-cyanophenyl)-3-phenylurea (3c)



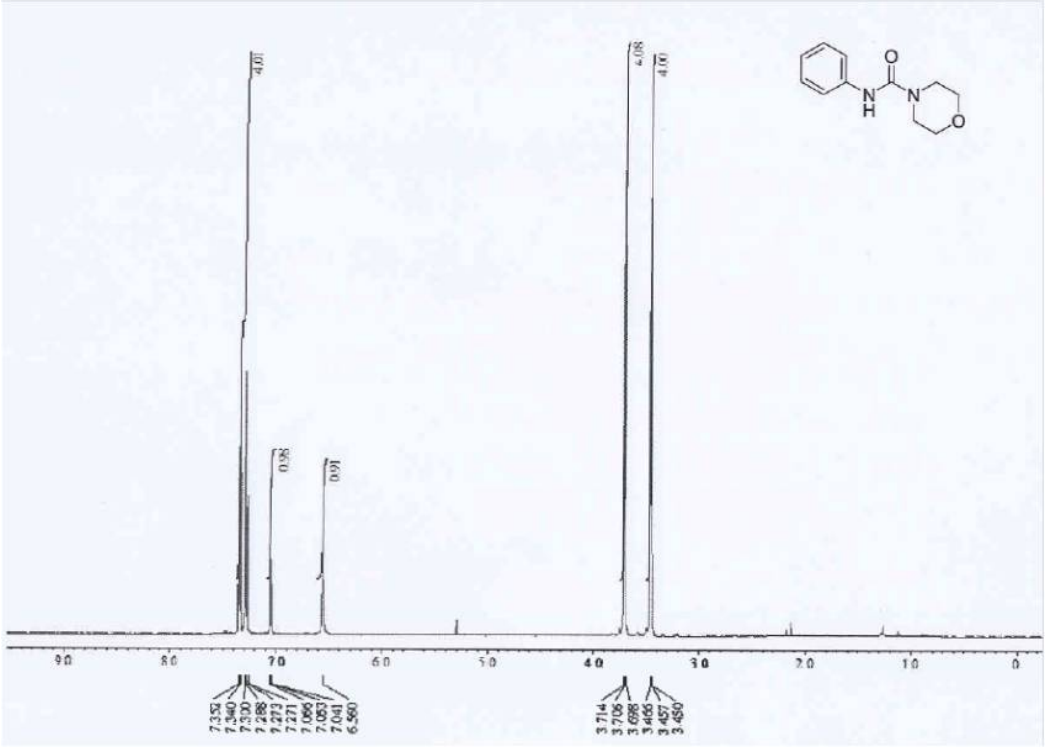
^{13}C NMR spectrum of 1-(4-cyanophenyl)-3-phenylurea (3c)



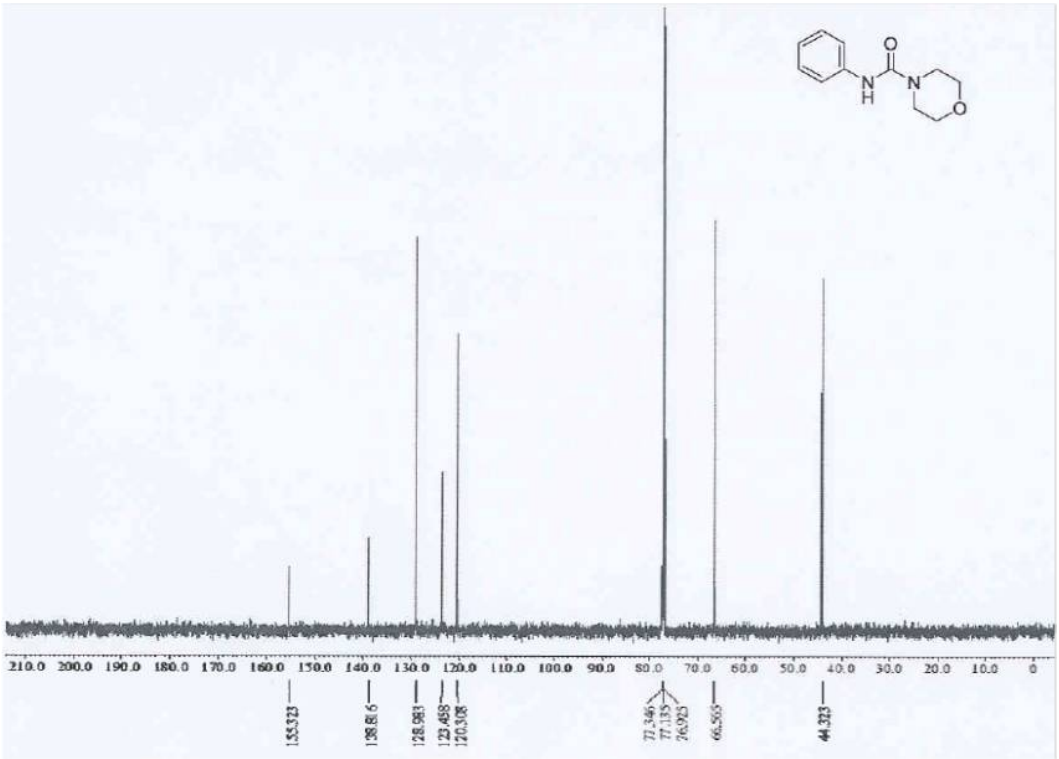
^{1}H NMR spectrum of 1-phenyl-3-*p*-tolylurea (3d)



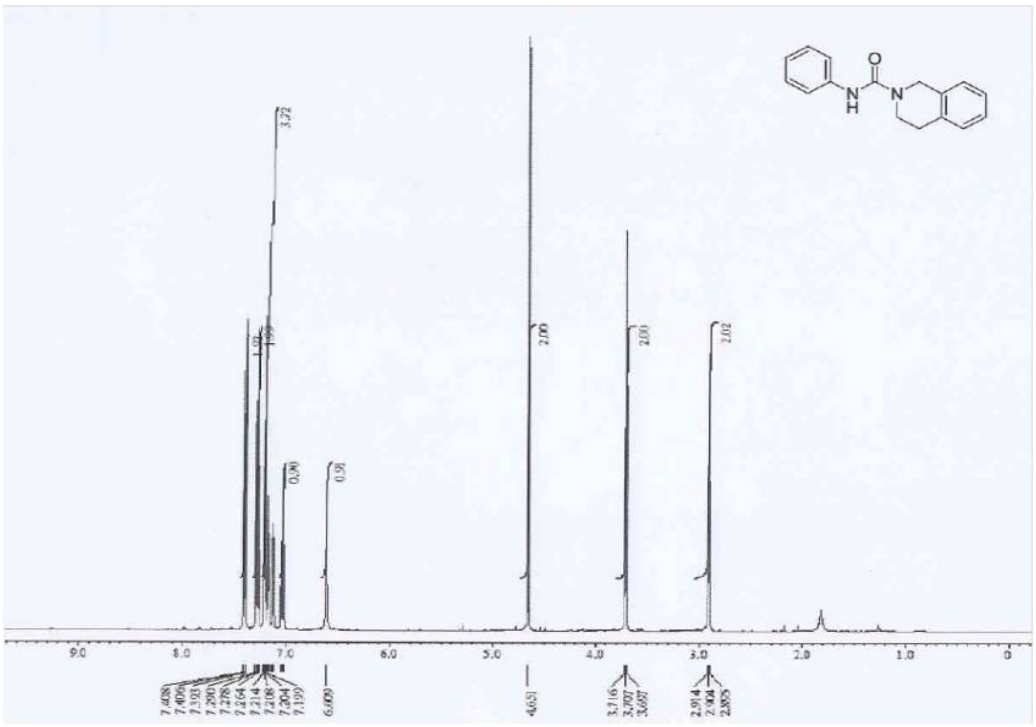
^{13}C NMR spectrum of 1-phenyl-3-*p*-tolylurea (3d)



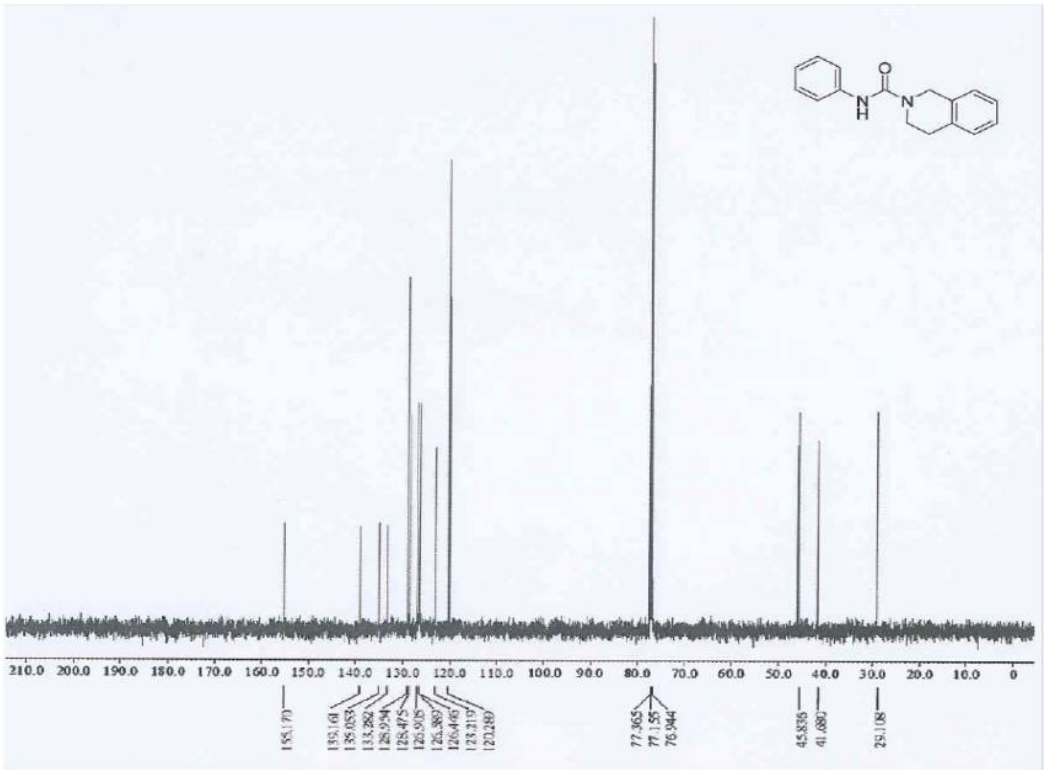
^{1}H NMR spectrum of *N*-phenylmorpholine-4-carboxamide (3e)



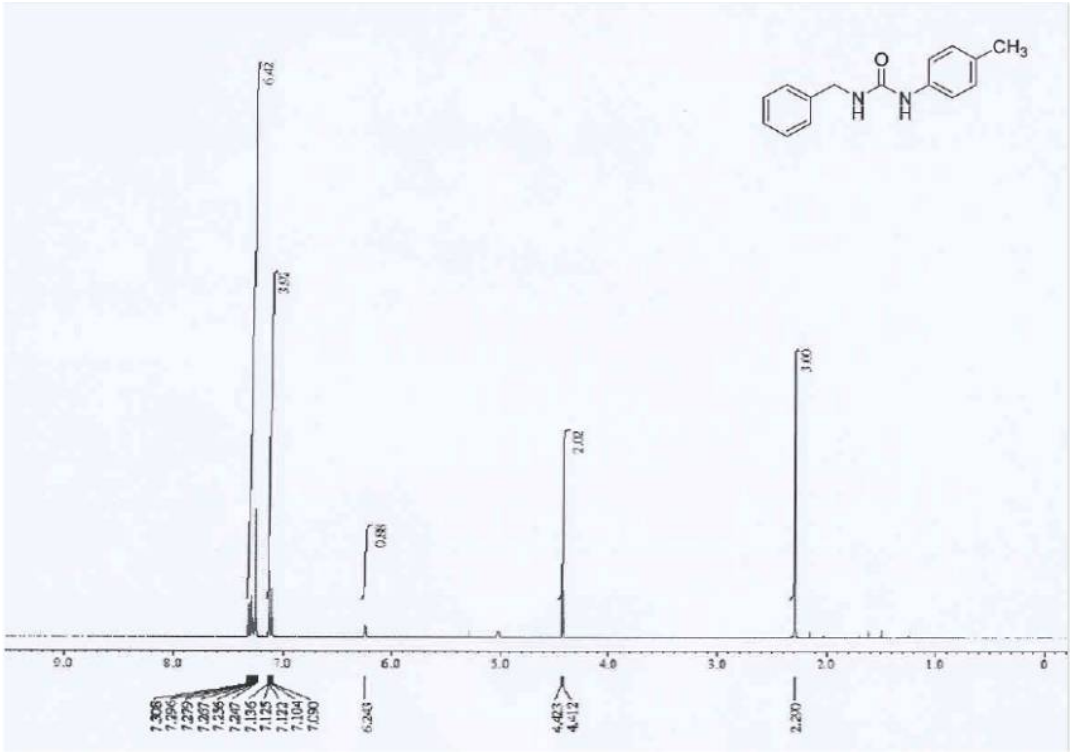
^{13}C NMR spectrum of *N*-phenylmorpholine-4-carboxamide (3e)



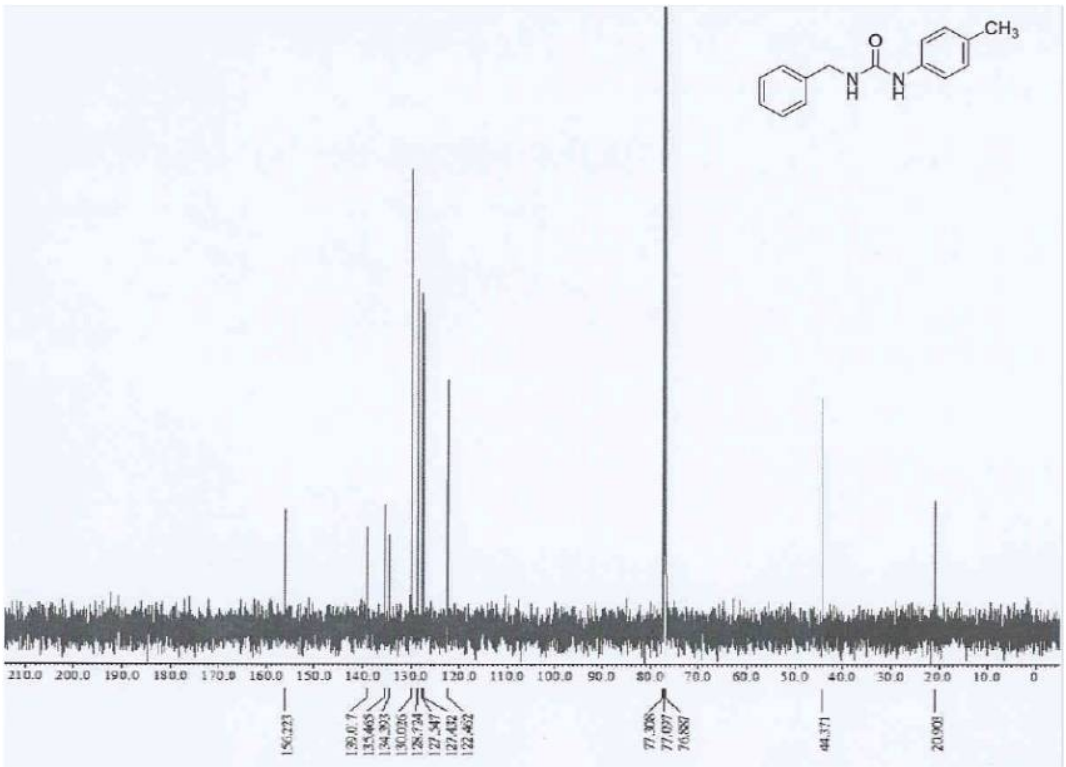
^{1}H NMR spectrum of *N*-phenyl-3,4-dihydroisoquinoline-2(1*H*)-carboxamide (3f)



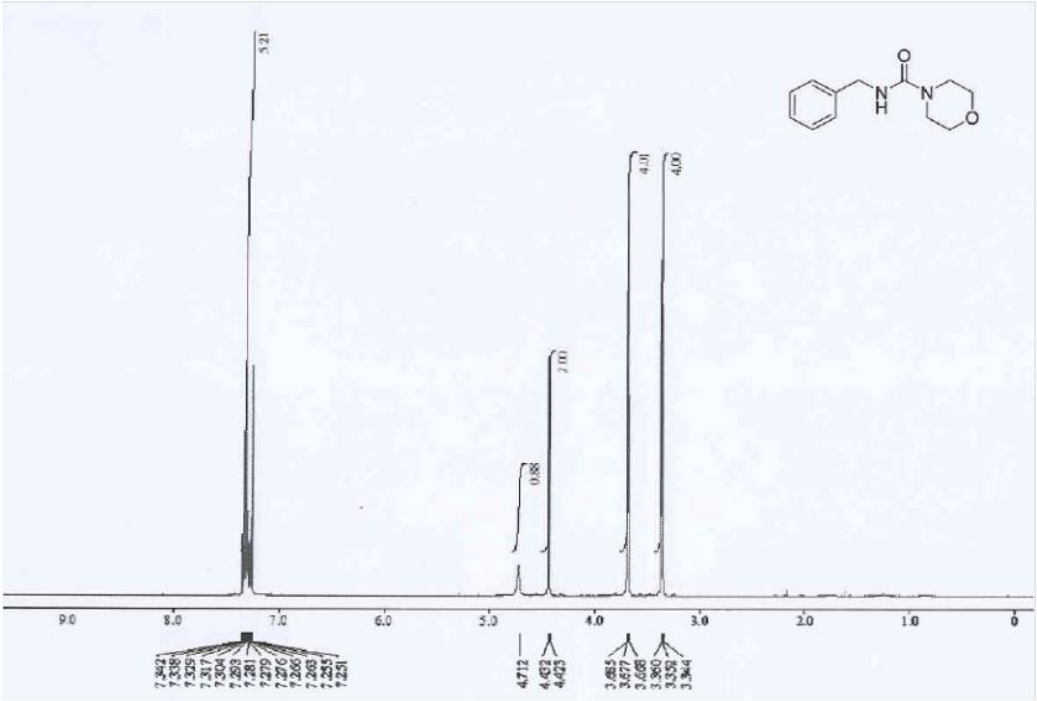
^{13}C NMR spectrum of *N*-phenyl-3,4-dihydroisoquinoline-2(1*H*)-carboxamide (3f)



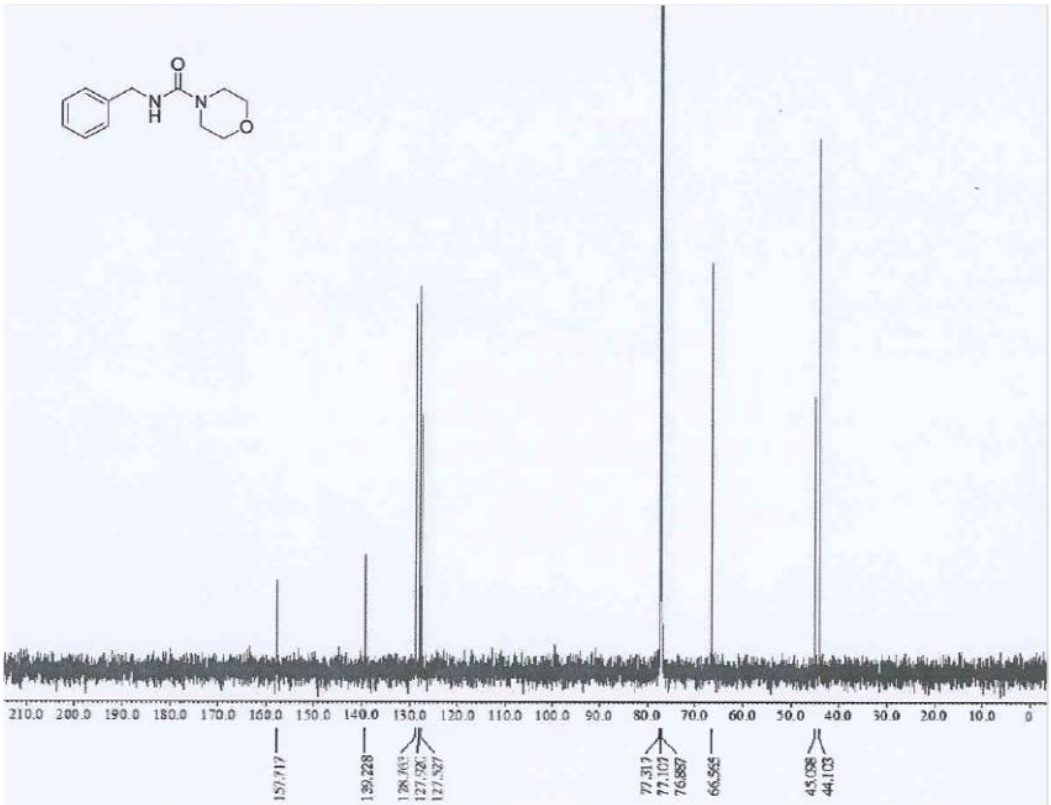
^{1}H NMR spectrum of 1-benzyl-3-*p*-tolylurea (3g)



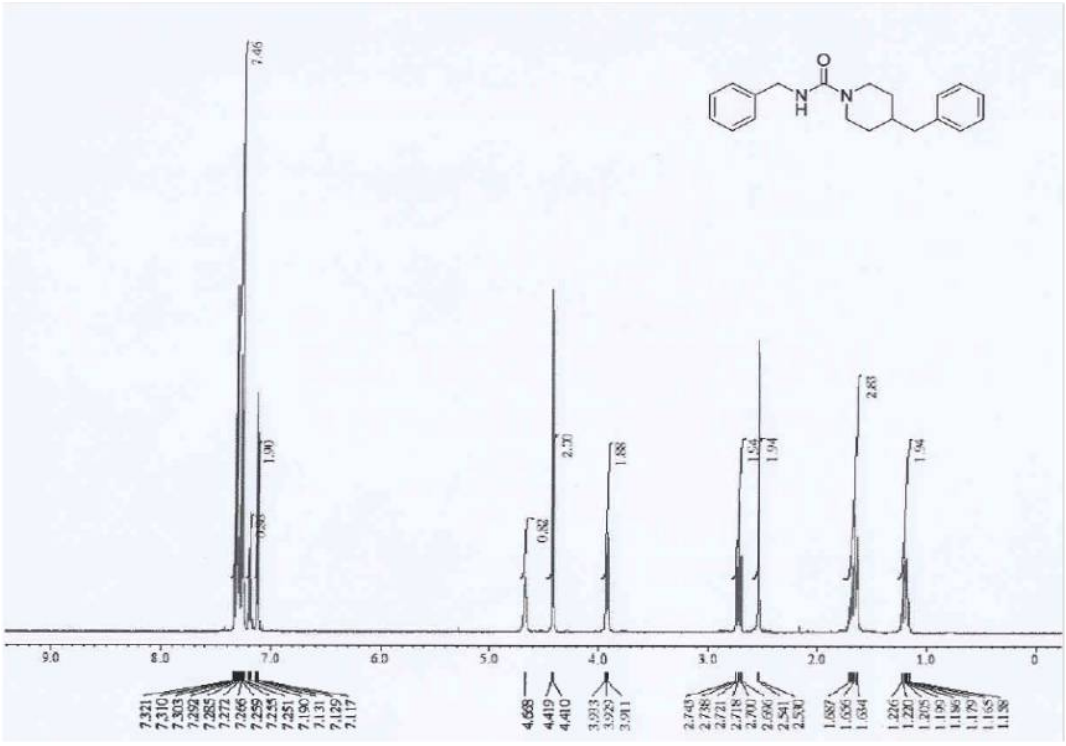
^{13}C NMR spectrum of 1-benzyl-3-*p*-tolylurea (3g)



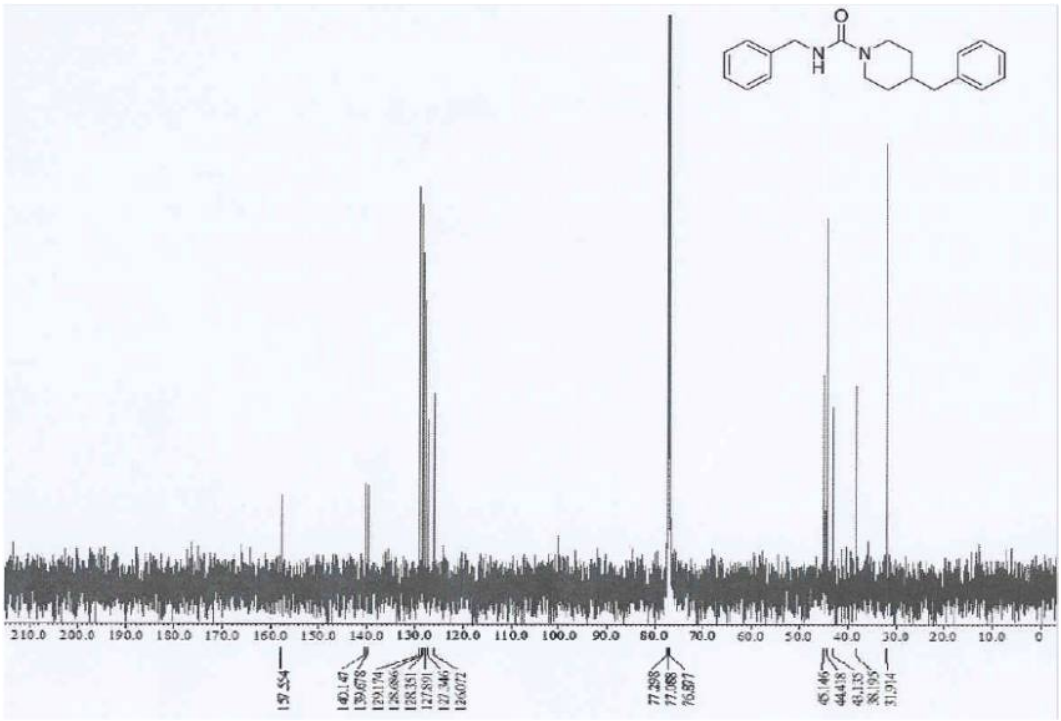
^{1}H NMR spectrum of *N*-benzylmorpholine-4-carboxamide (3h)



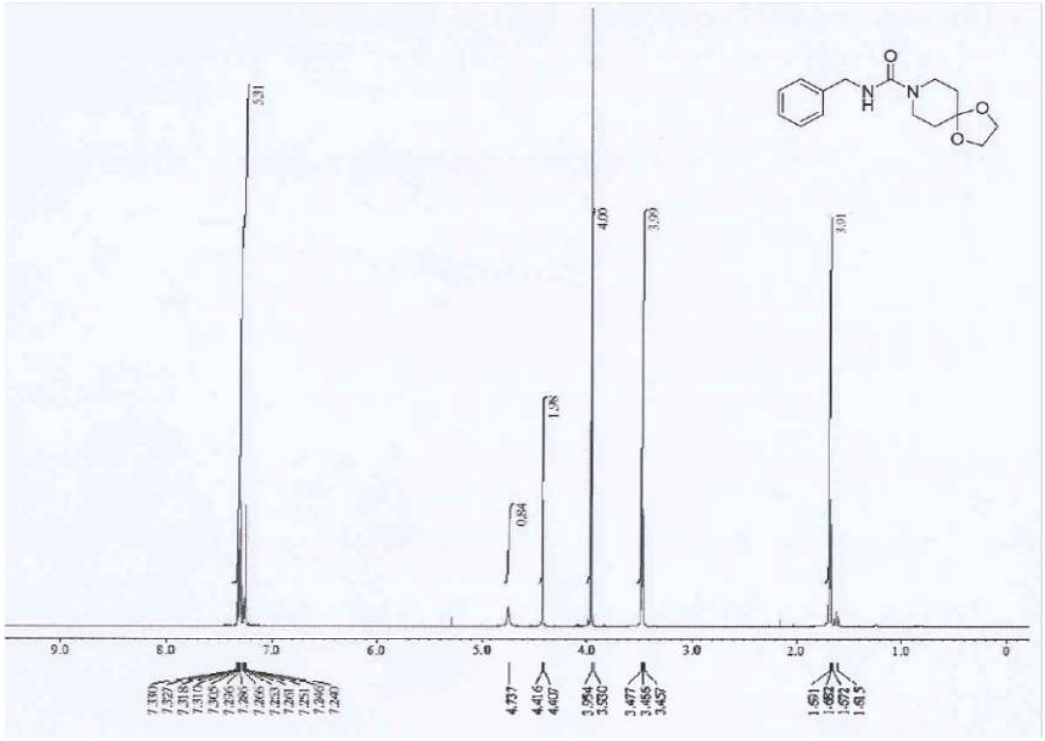
^{13}C NMR spectrum of *N*-benzylmorpholine-4-carboxamide (3h)



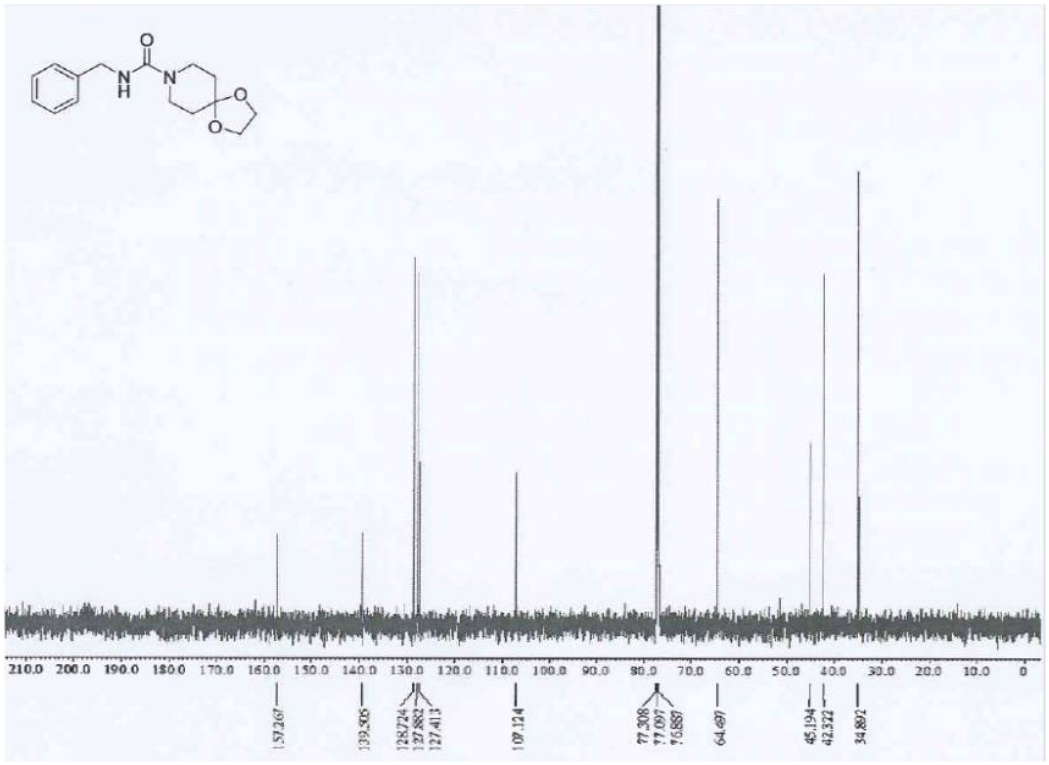
^{1}H NMR spectrum of *N*,4-dibenzylpiperidine-1-carboxamide (3i)



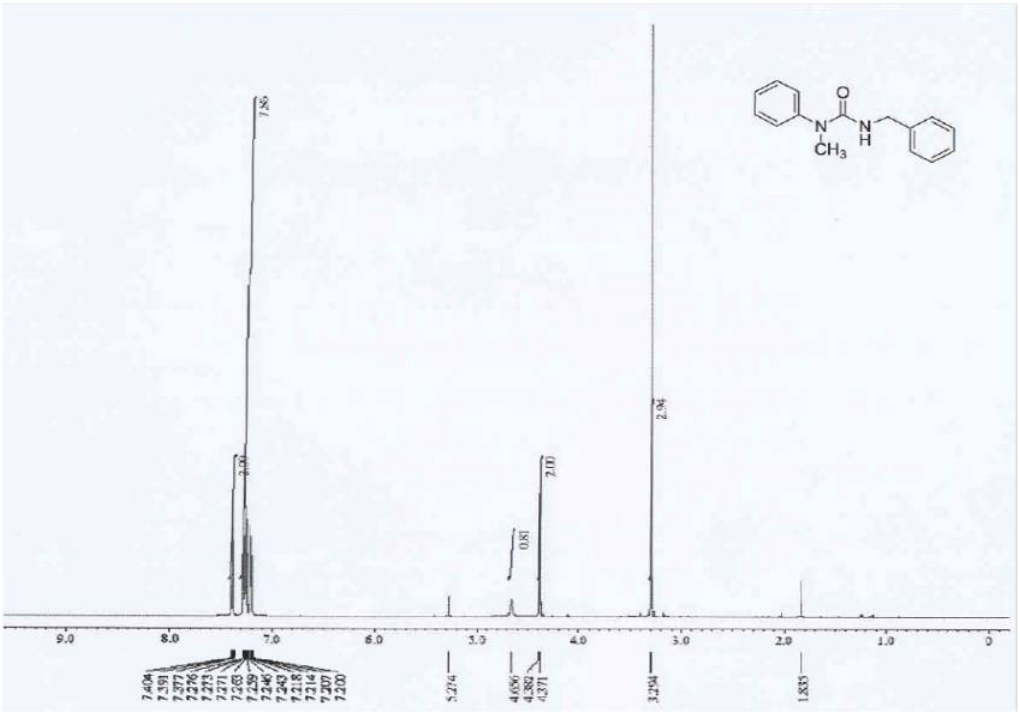
^{13}C NMR spectrum of *N*,4-dibenzylpiperidine-1-carboxamide (3i)



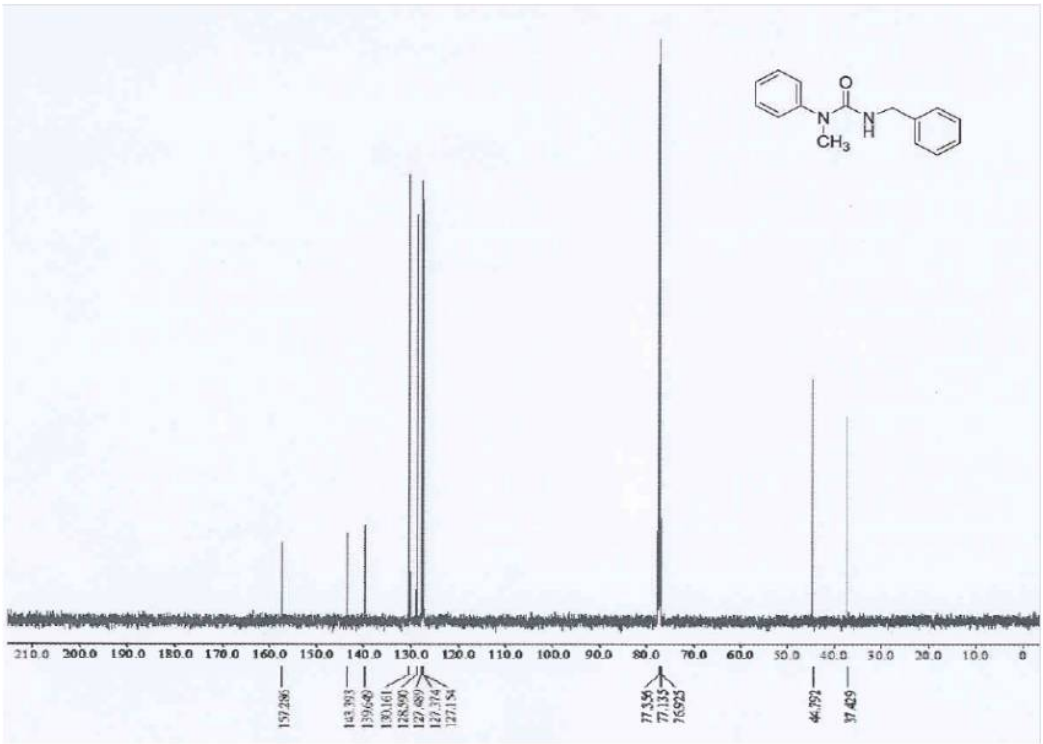
^{1}H NMR spectrum of *N*-benyl-1,4-dioxa-8-azaspiro[4.5] decane-8-carboxamide (3j)



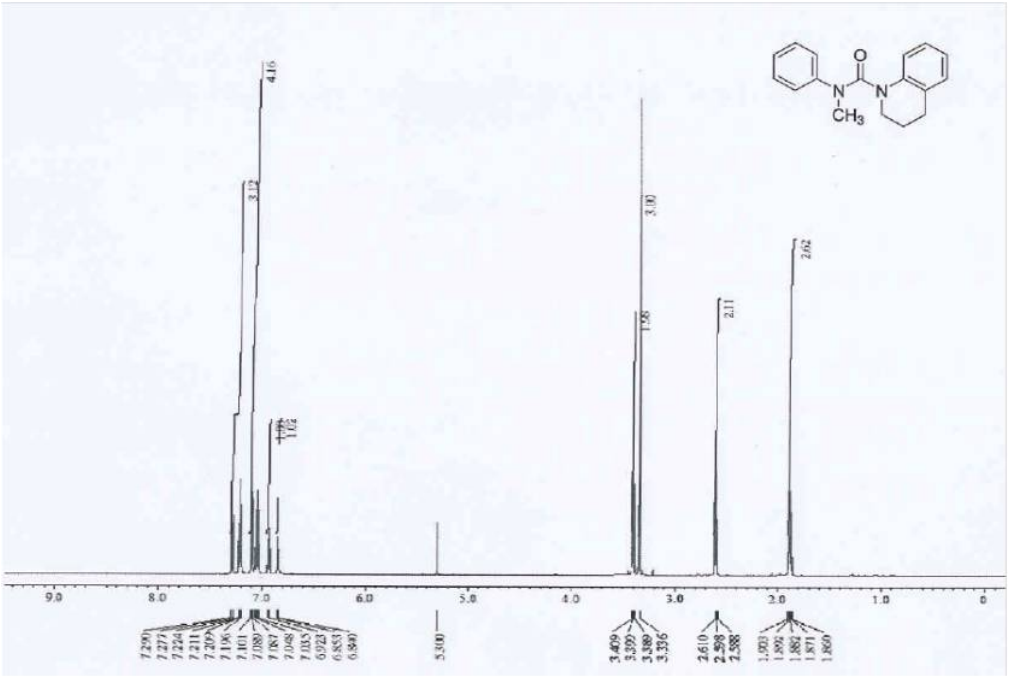
^{13}C NMR spectrum of *N*-benyl-1,4-dioxa-8-azaspiro[4.5] decane-8-carboxamide (3j)



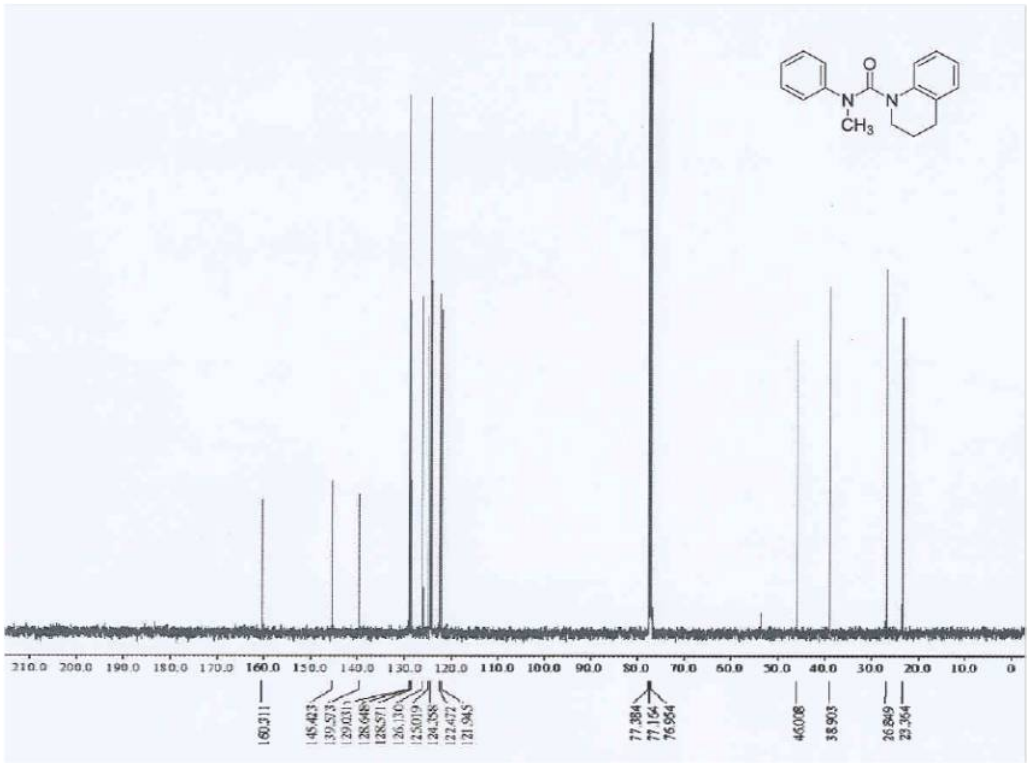
^{1}H NMR spectrum of 3-benzy-1-methyl-1-phenylurea (3k)



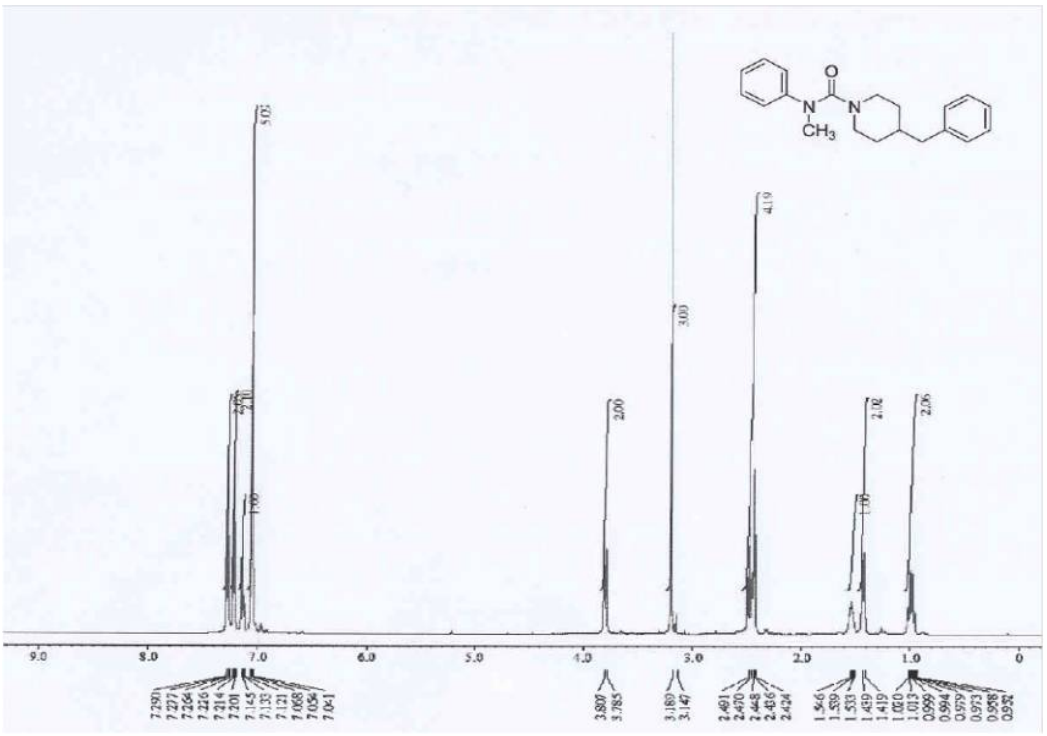
^{13}C NMR spectrum of 3-benzy-1-methyl-1-phenylurea (3k)



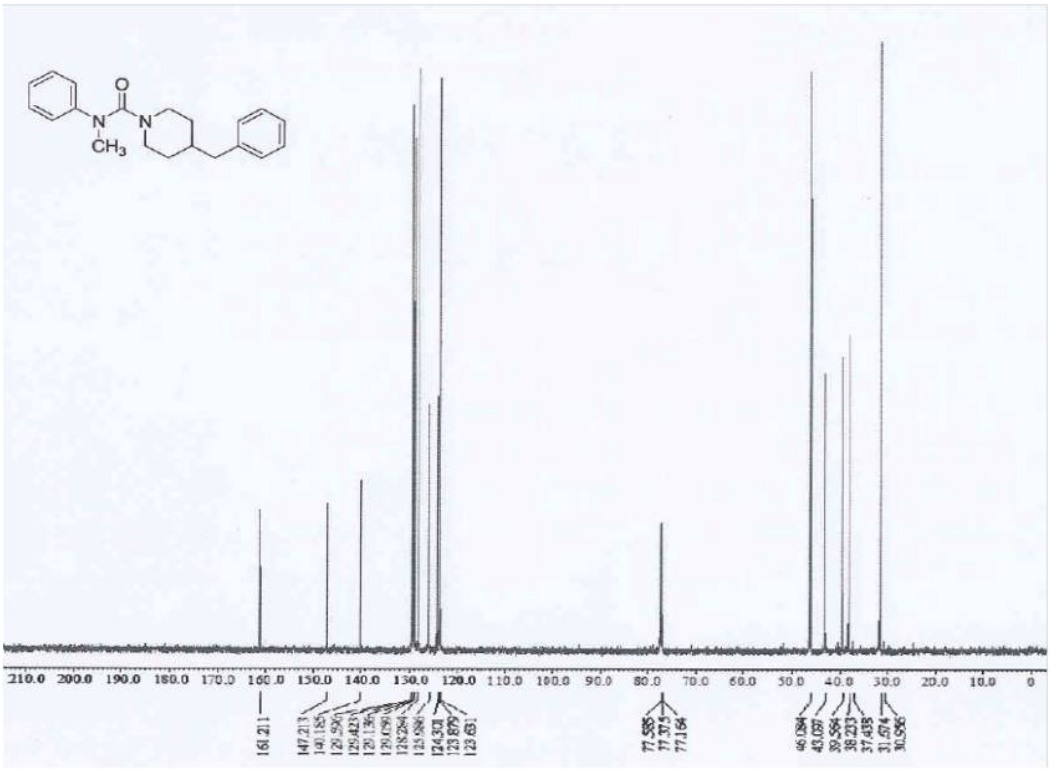
^{1}H NMR spectrum of *N*-methyl-*N*-phenyl-3,4-dihydroquinoline-1(2*H*) carboxamide (3l)



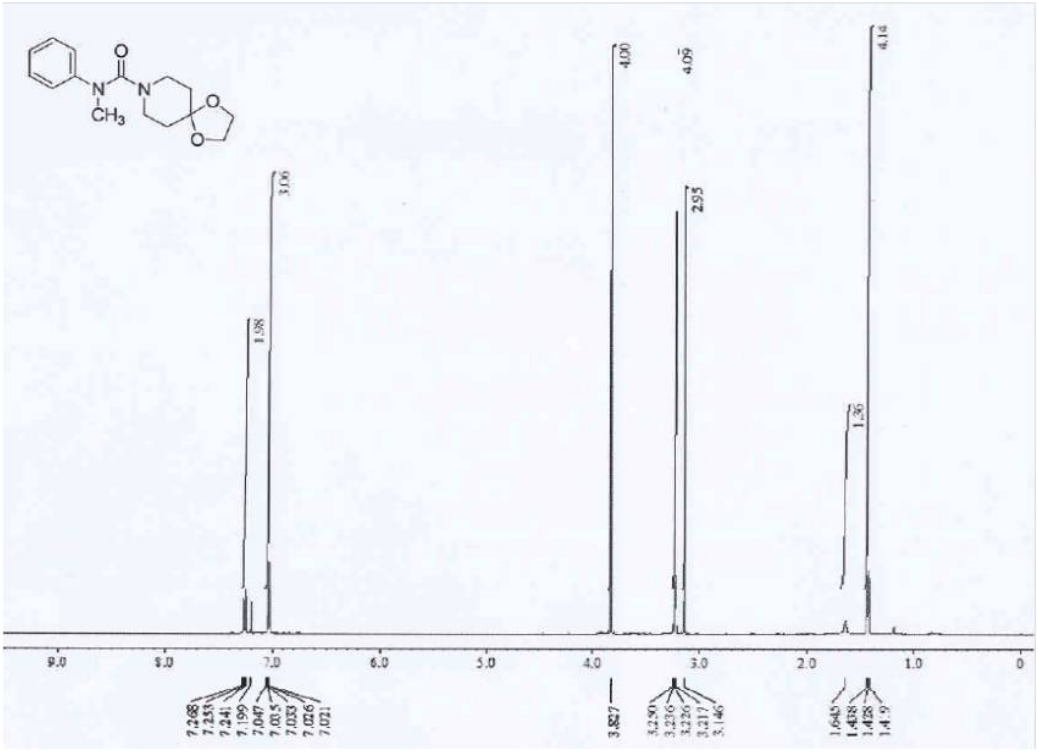
^{13}C NMR spectrum of *N*-methyl-*N*-phenyl-3,4-dihydroquinoline-1(2*H*) carboxamide (3l)



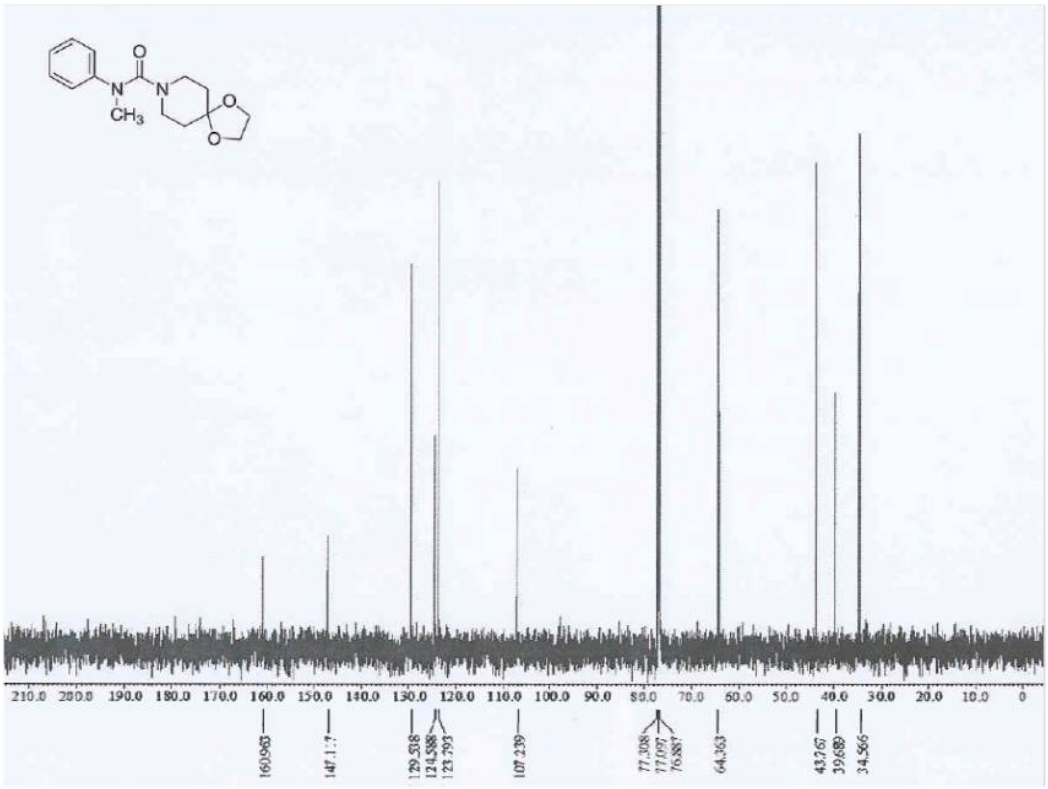
^{1}H NMR spectrum of 4-benzyl-*N*-methyl-*N*-phenylpiperidine-1-carboxamide (3m)



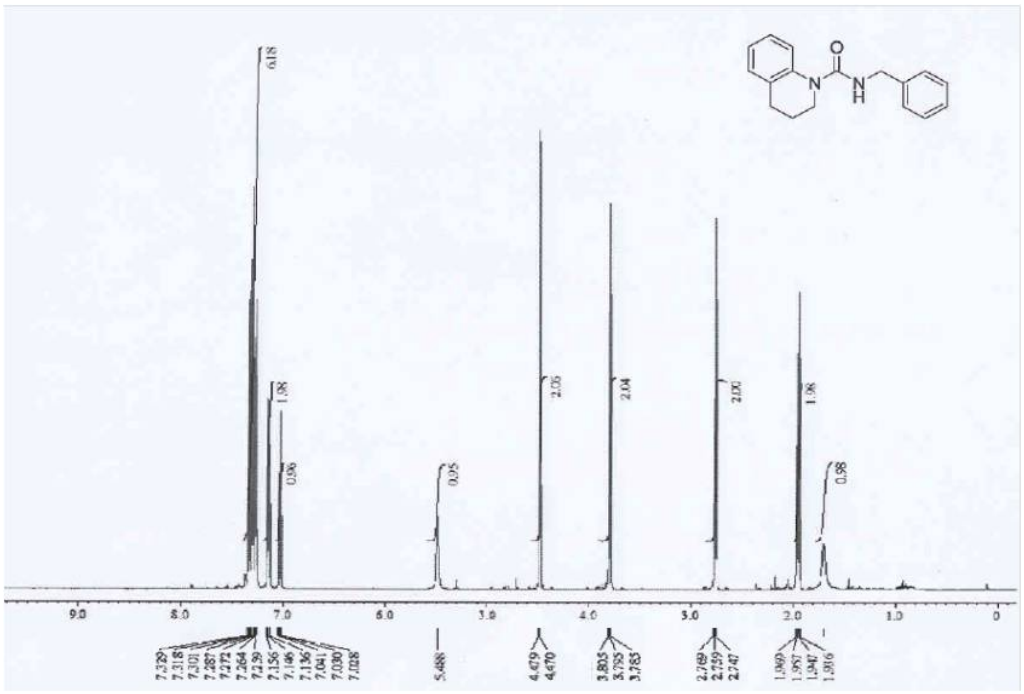
^{13}C NMR spectrum of 4-benzyl-*N*-methyl-*N*-phenylpiperidine-1-carboxamide (3m)



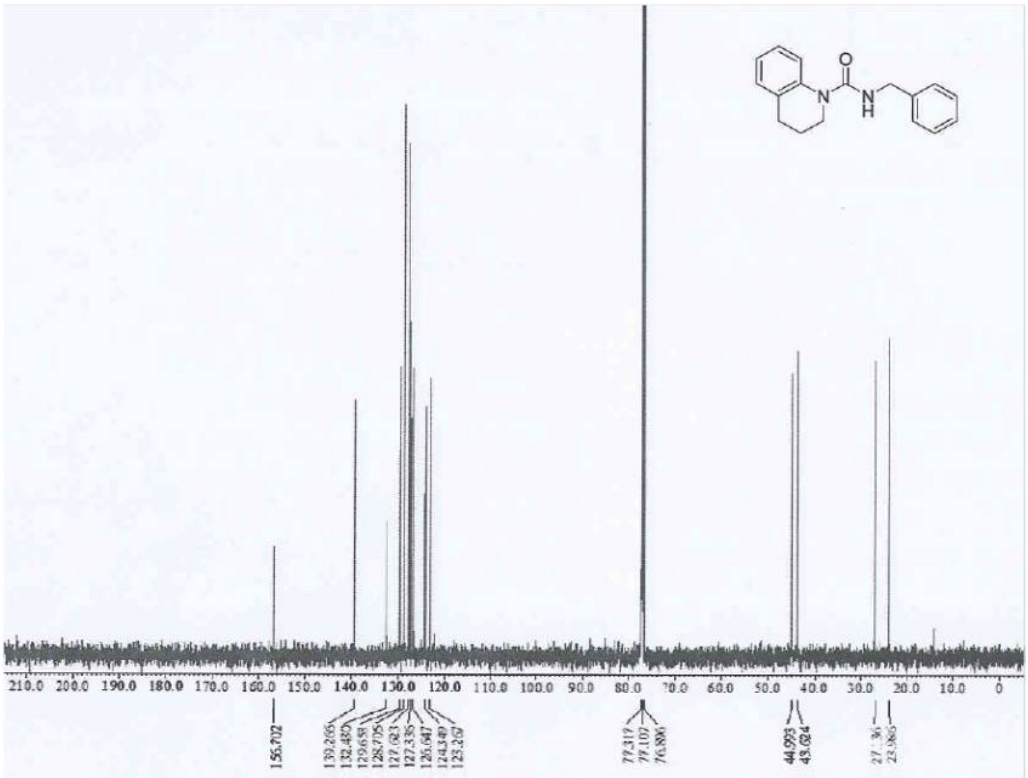
^{1}H NMR spectrum of *N*-methyl-*N*-phenyl-1,4-dioxa-8-azaspiro[4.5] decane-8-carboxamide (3n)



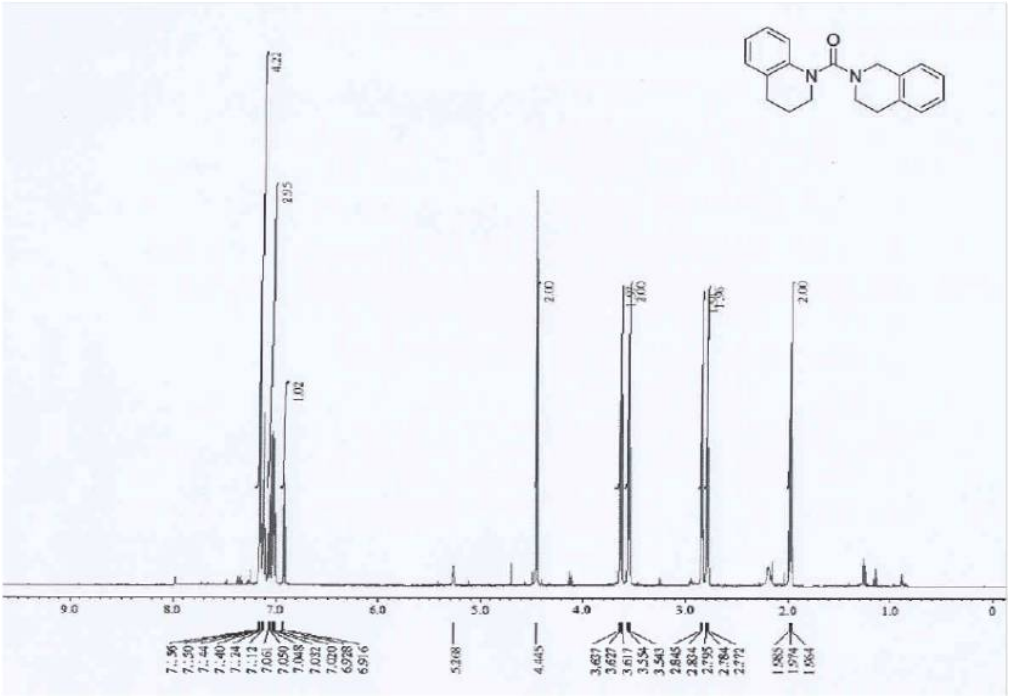
^{13}C NMR spectrum of *N*-methyl-*N*-phenyl-1,4-dioxa-8-azaspiro[4.5] decane-8-carboxamide (3n)



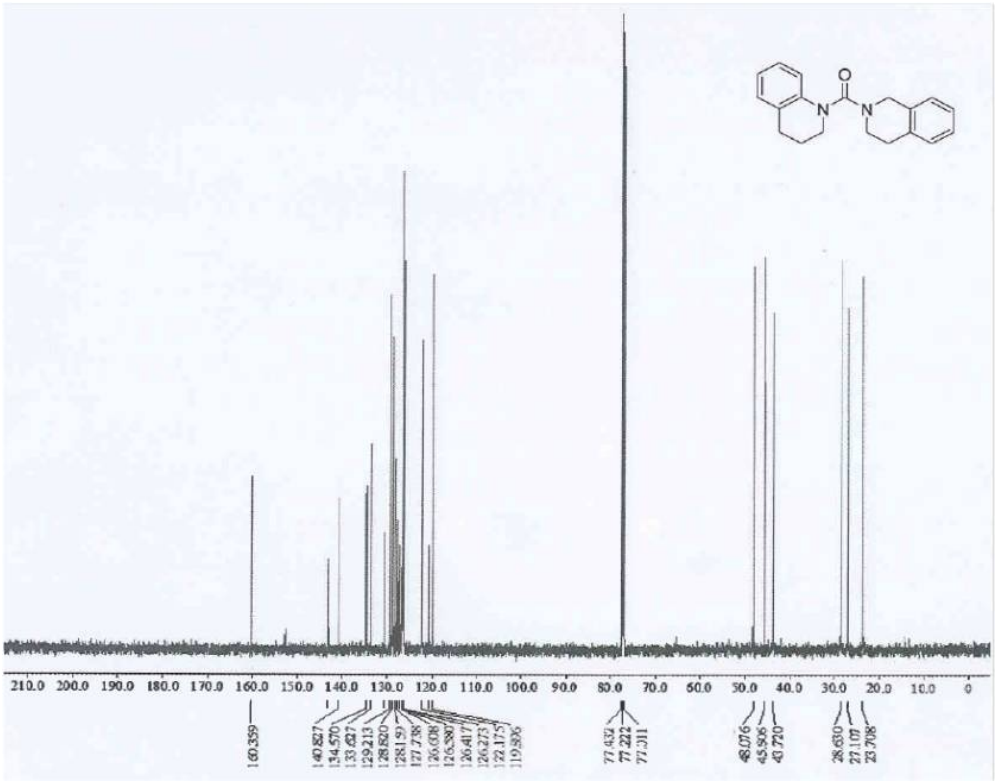
^{1}H NMR spectrum of *N*-benzyl-3,4-dihydroquinoline-1(2*H*)-carboxamide (3o)



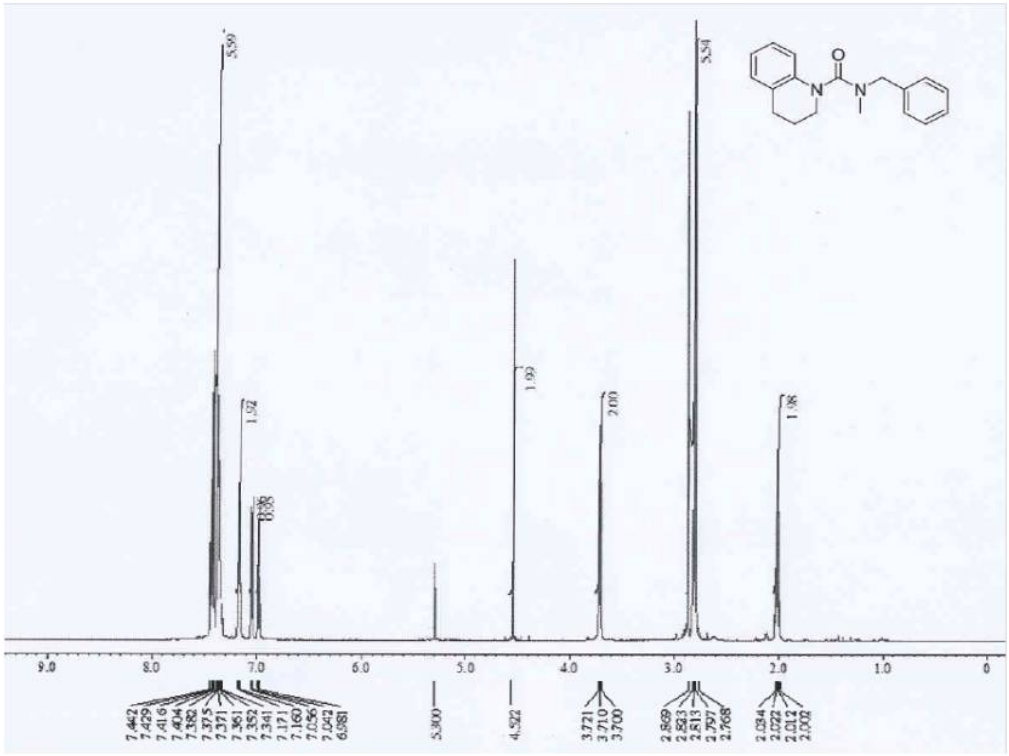
^{13}C NMR spectrum of *N*-benzyl-3,4-dihydroquinoline-1(2*H*)-carboxamide (3o)



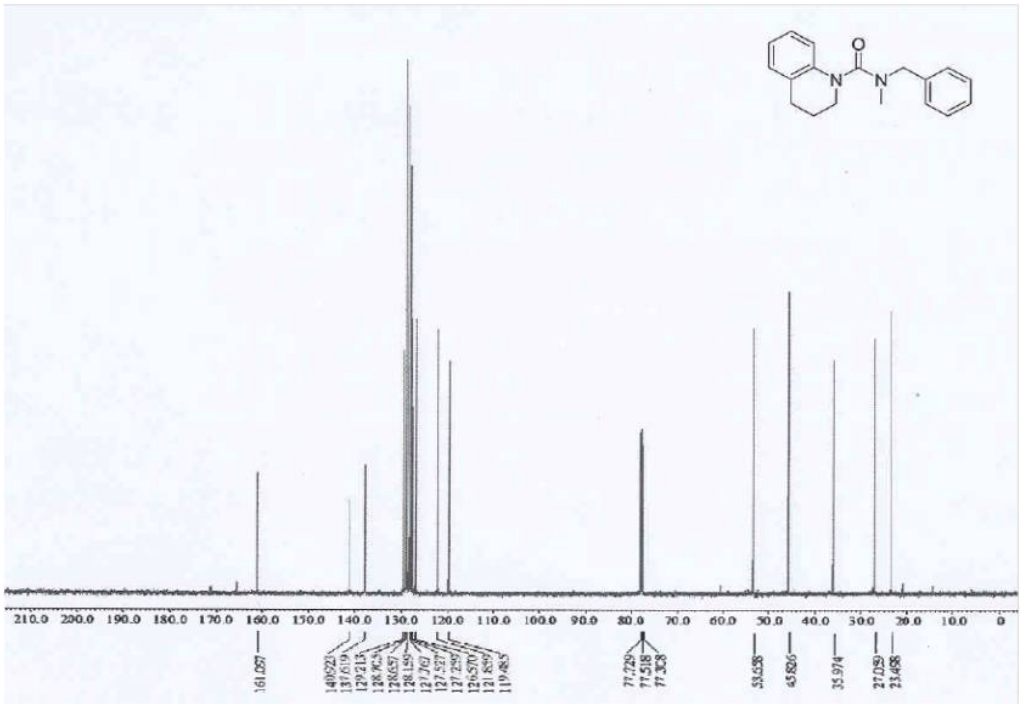
^{1}H NMR spectrum of (3,4-dihydroisoquinolin-2(1*H*)-yl)(3,4-dihydroquinolin-1(2*H*)-yl)methanone (3p)



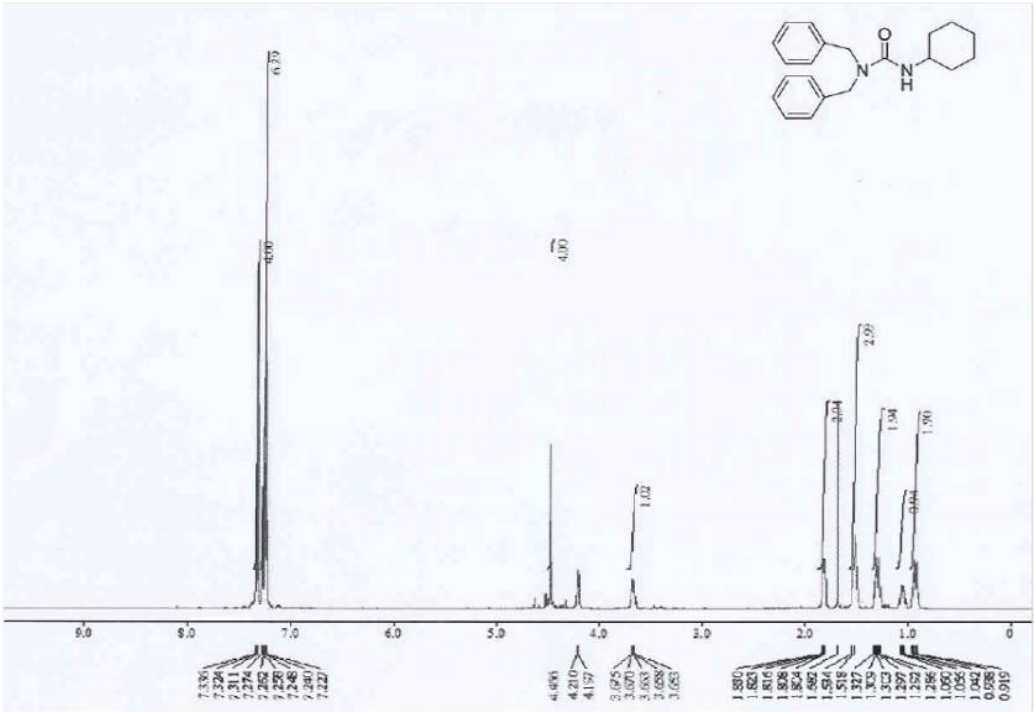
^{13}C NMR spectrum of (3,4-dihydroisoquinolin-2(1*H*)-yl)(3,4-dihydroquinolin-1(2*H*)-yl)methanone (3p)



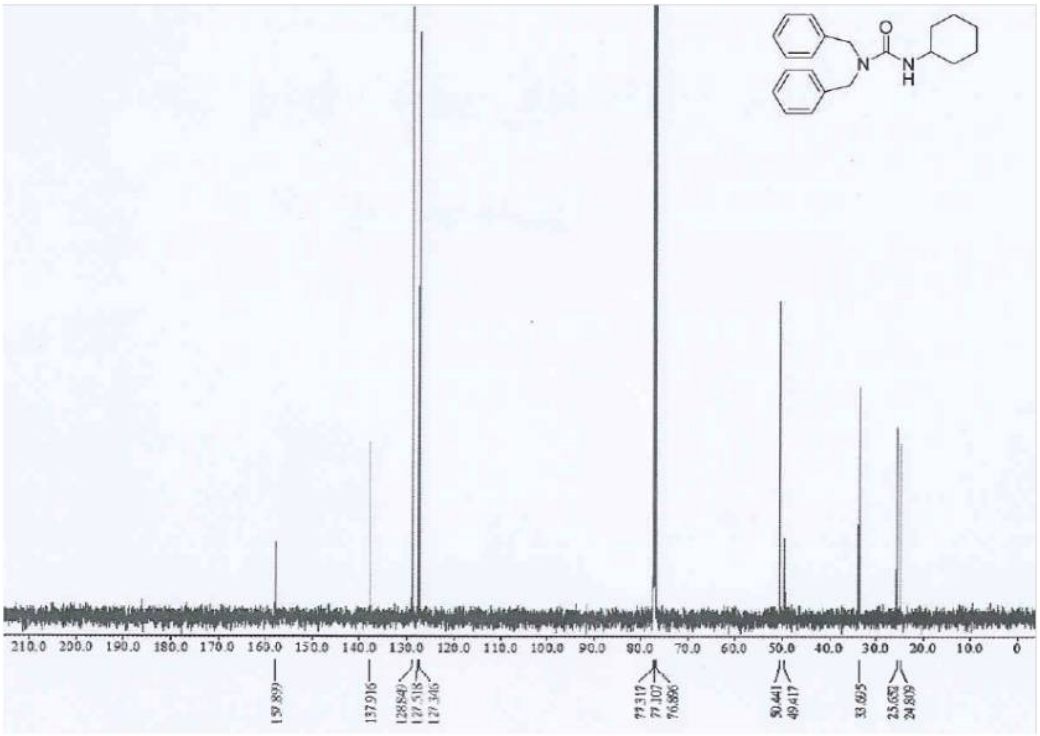
^{1}H NMR spectrum of *N*-benzyl-*N*-methyl-3,4-dihydroquinoline-1(2*H*)-carboxamide (3q)



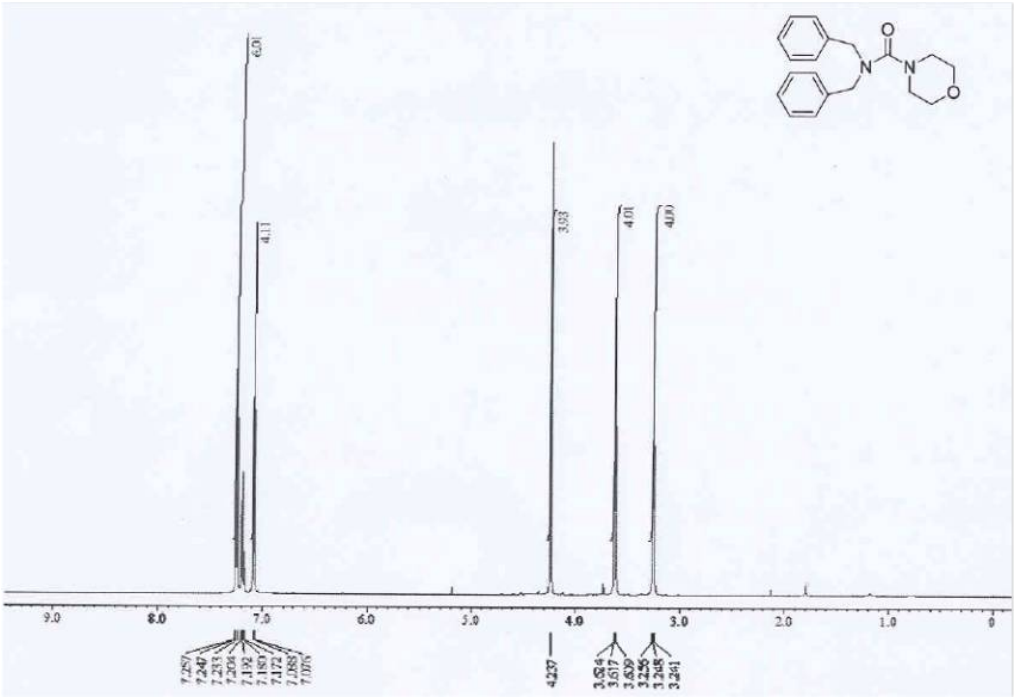
^{13}C NMR spectrum of *N*-benzyl-*N*-methyl-3,4-dihydroquinoline-1(2*H*)-carboxamide (3q)



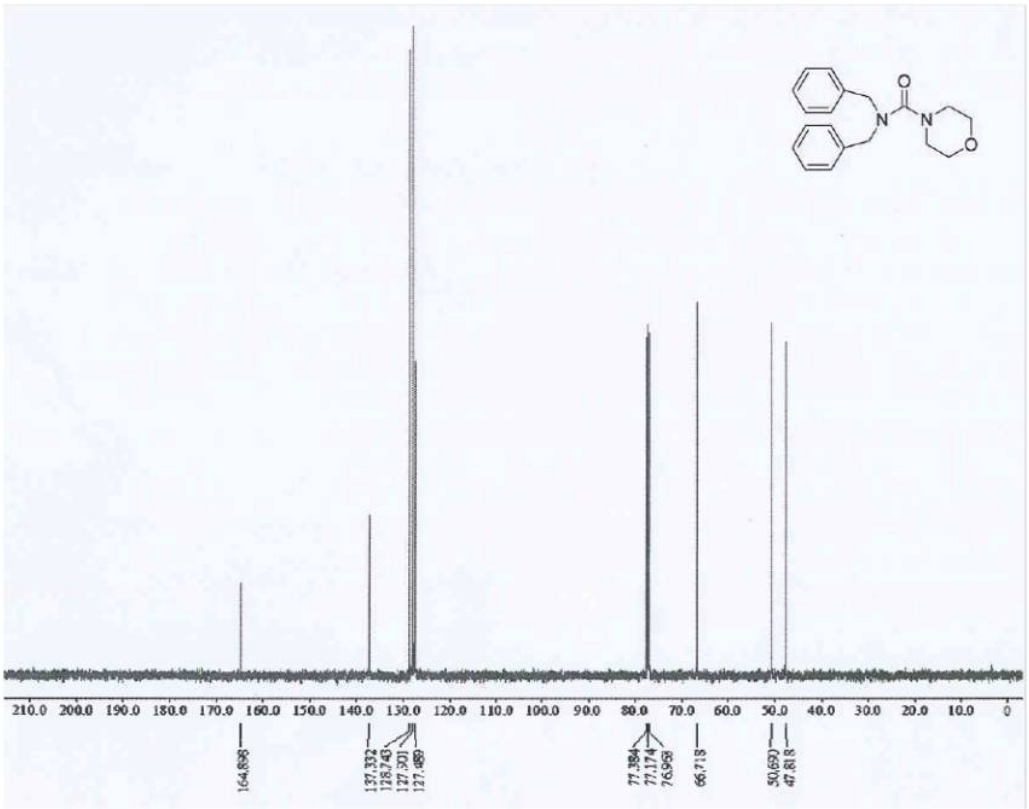
^{1}H NMR spectrum of 1,1-dibenzyl-3-cyclohexylurea (3r)



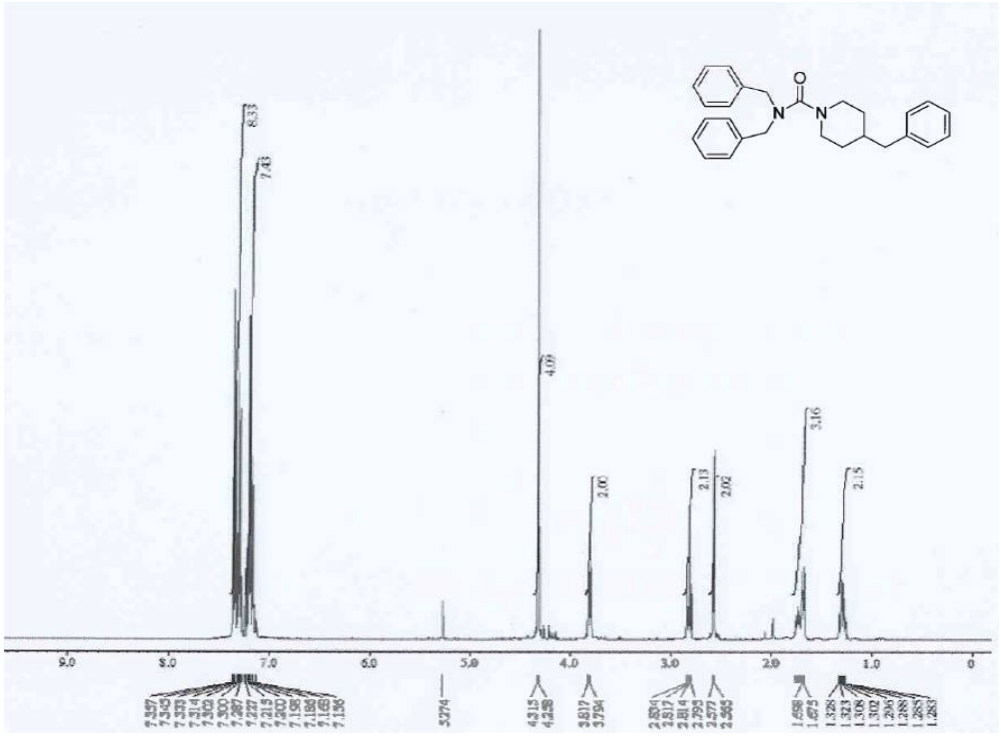
^{13}C NMR spectrum of 1,1-dibenzyl-3-cyclohexylurea (3r)



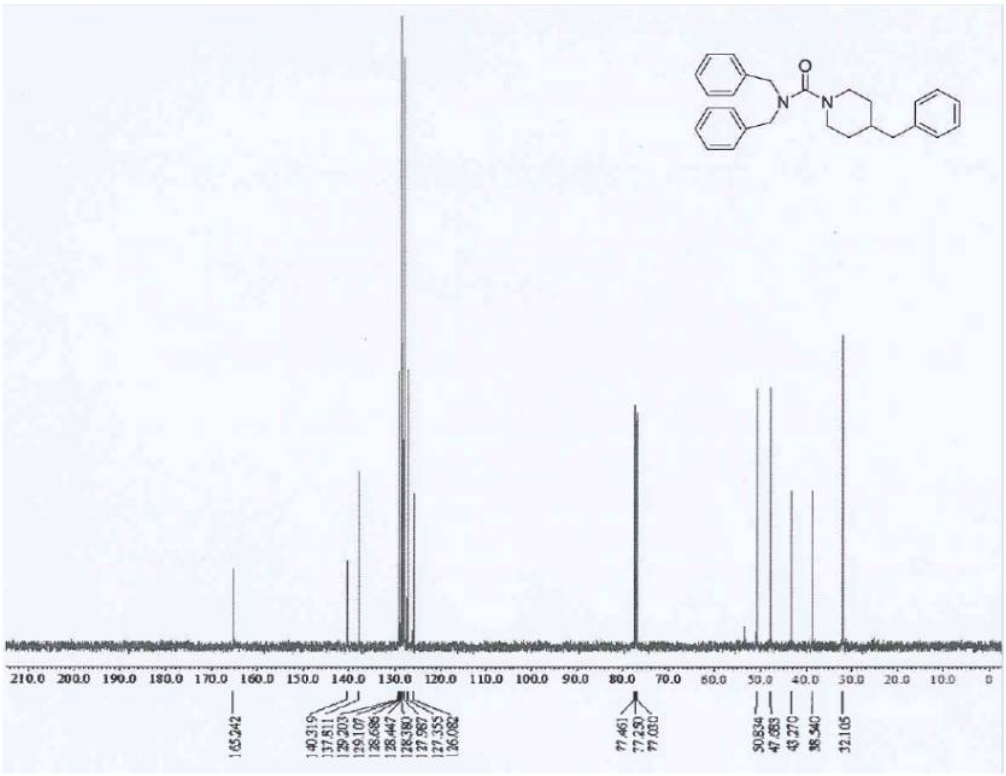
^{1}H NMR spectrum of *N*,*N*-dibenzylmorpholine-4-carboxamide (3s)



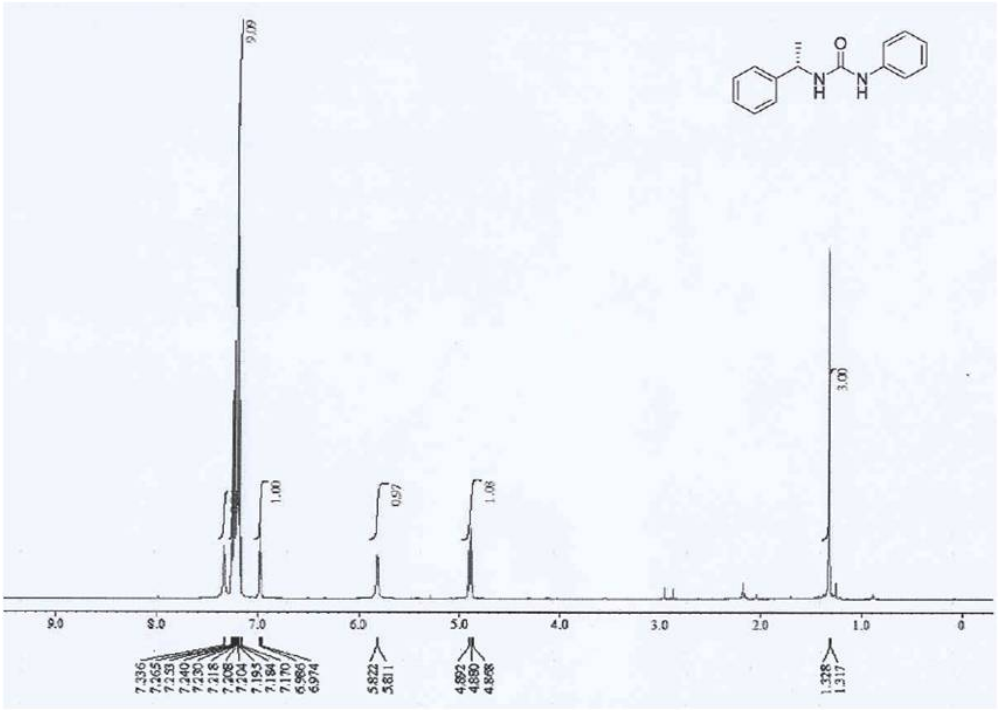
^{13}C NMR spectrum of *N*,*N*-dibenzylmorpholine-4-carboxamide (3s)



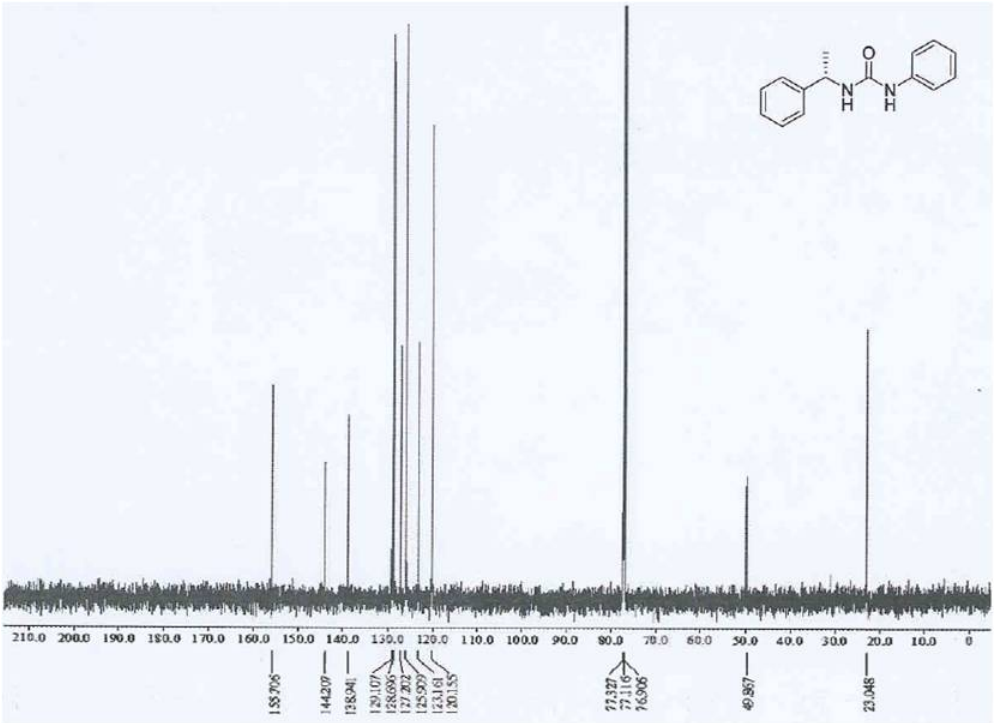
^{1}H NMR spectrum of *N*,*N*,4-tribenzylpiperidine-1-carboxamide (3t)



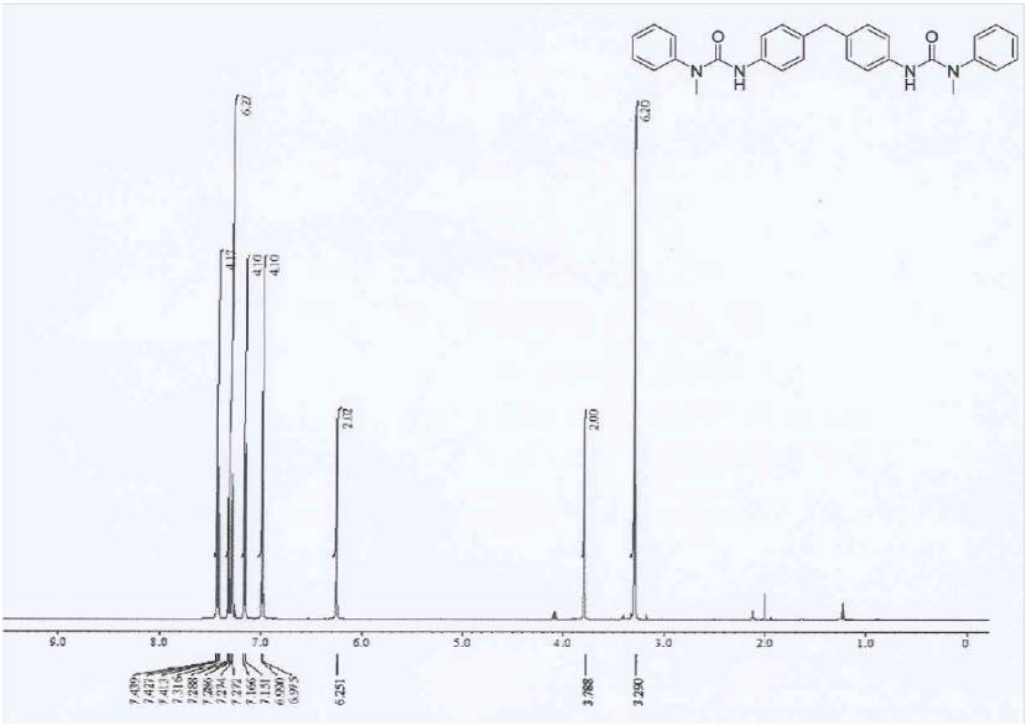
^{13}C NMR spectrum of *N*,*N*,4-tribenzylpiperidine-1-carboxamide (3t)



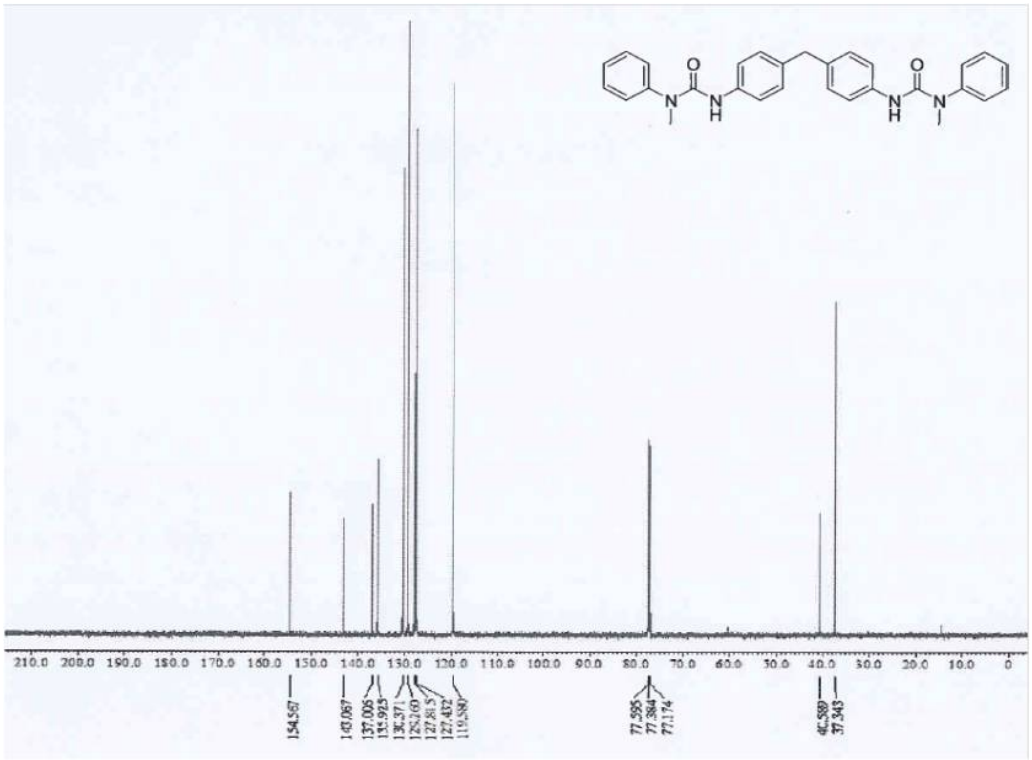
^{1}H NMR spectrum of (*S*)-1-phenyl-3-(1-phenylethyl)urea (3u)



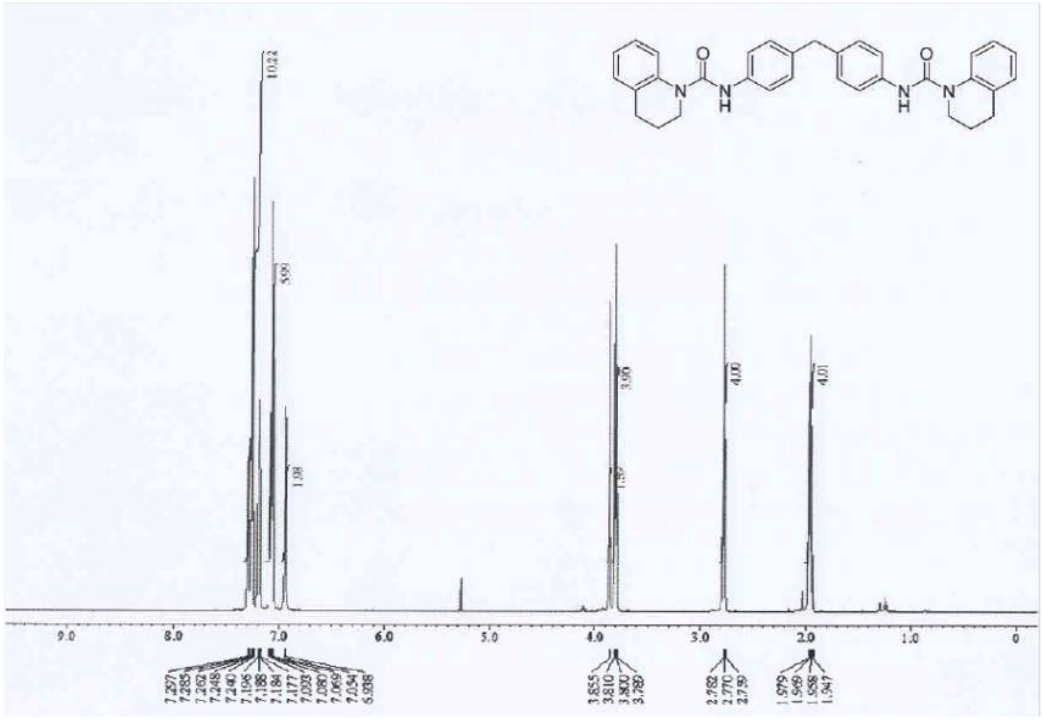
^{13}C NMR spectrum of (*S*)-1-phenyl-3-(1-phenylethyl)urea (3u)



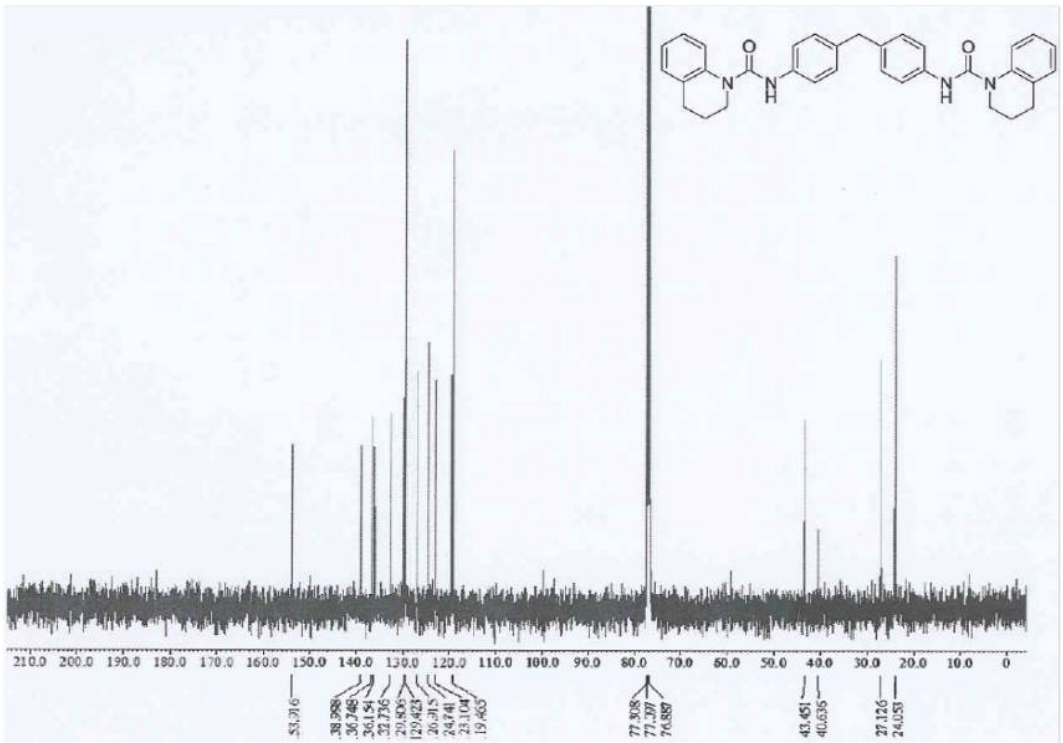
^{1}H NMR spectrum of 1,1'-(4,4'-methylenebis(4,1-phenylene))bis(3-methyl-3-phenylurea) (3v)



^{13}C NMR spectrum of 1,1'-(4,4'-methylenebis(4,1-phenylene))bis(3-methyl-3-phenylurea) (3v)



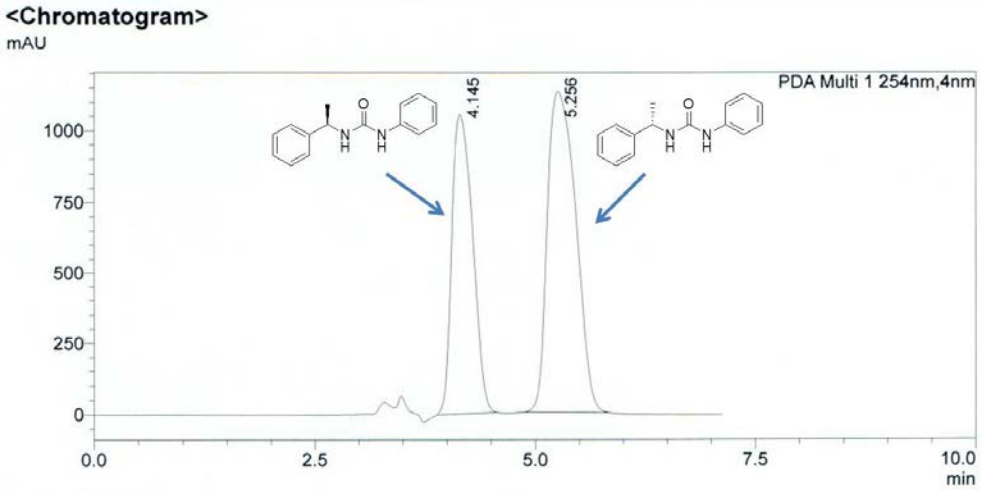
^{1}H NMR spectrum of *N*,*N*′-(4,4'-methylenebis(4,1-phenylene))bis(3,4-dihydroquinoline-1(2*H*)-carboxamide) (3w)



^{13}C NMR spectrum of *N*,*N*′-(4,4'-methylenebis(4,1-phenylene))bis(3,4-dihydroquinoline-1(2*H*)-carboxamide) (3w)

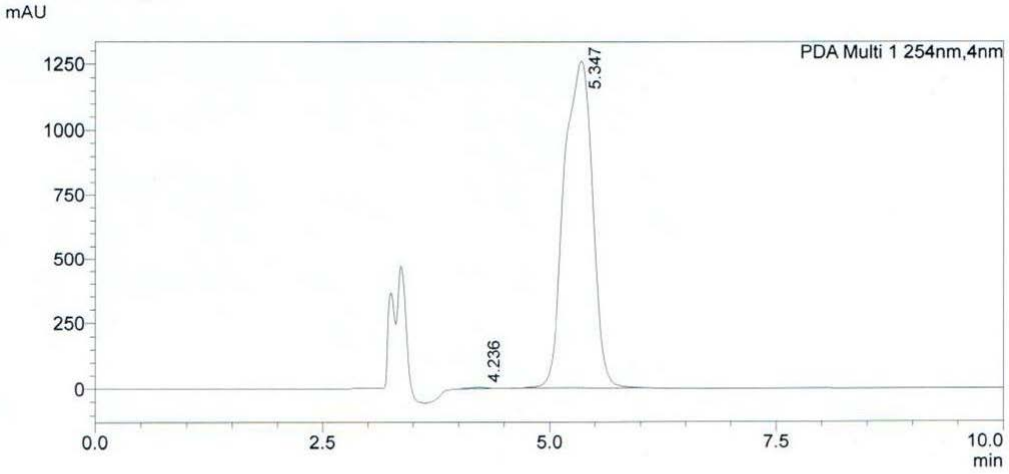
5. Chiral HPLC trace for Compound 3u

The enantiomeric excess of **3u** was determined to be 99% ee by HPLC analysis using chiral column [CHIRALPAK® AD-H (particle size: 5 μm, dimensions: 4.6 mm X 250 mL); eluent: n-hexane/2-propanol = 7:3; flow rate = 1 mL/min; retention time: 5.3 min (major), 4.2min (minor)].



<Peak Table>
PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	4.145	17332601	1052652	0.000		M	
2	5.256	25272181	1129411	0.000		M	
Total		42604782	2182063				



<Peak Table>
PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	4.236	71194	4683	0.000		M	
2	5.347	27402015	1258428	0.000		M	
Total		27473209	1263111				