Supporting Information

N-Alkylation of amines with alcohols over nanosized zeolite Beta

Marri Mahender Reddy,[a] Macharla Arun Kumar,[a] Peraka Swamy,[a] Mameda Naresh,[a] Kodumuri Srujana,[a] Lanka Satyanarayana,[b] Akula Venugopal[a] and Nama Narender*[a]

[a] *I&PC Division, CSIR-Indian Institute of Chemical Technology, Hyderabad 500 007, India*
Tel.: +91–40-27191703; Fax: +91-40-27160387/27160757; E-mail: narendern33@yahoo.co.in
[b] *Centre for NMR & Structural Chemistry, CSIR-Indian Institute of Chemical Technology, Hyderabad 500 007, India*

Table of Contents……………………………………………………………………Page no.

General information

All chemicals used were reagent grade and used as received without further purification. The FT-IR spectra of the samples recorded on a Nicolet 740 FT-IR spectrometer at ambient conditions using KBr as the diluents. ^{1}H NMR spectra were recorded by using Bruker VX NMR FT-300 or Varian Unity 500 and ^{13}C NMR spectra recorded by using Bruker VX NMR FT-75 MHz spectrometers instrument in $CDCl_3$. The chemical shifts (δ) are reported in ppm units relative to TMS as an internal standard for ^{1}H NMR and $CDCl_3$ for ^{13}C NMR spectra. Coupling constants (J) are reported in hertz (Hz) and multiplicities are indicated as follows: s (singlet), bs (broad singlet), d (doublet), dd (doublet of doublet), t (triplet), q (quartet), m (multiplet). ESI mass spectra were recorded by using Micromass Quattro LC mass spectrometer and High-resolution mass spectra obtained by using ESI-QTOF mass spectrometry. Column chromatography was carried out using silica gel (100-200 mesh).

General procedure

Reactions were performed in a magnetically stirred round bottomed flask fitted with a condenser and placed in a temperature controlled oil bath. Nanosized zeolite Beta (100 mg) was added to the well stirred solution of amine (2 mmol) in alcohol (6 mmol) and the reaction mixture was allowed to stir at 135°C in an open (air) atmosphere. After disappearance of the amine (reaction was monitored by TLC) or after the appropriate time, the reaction mixture was cooled to room temperature. The catalyst was removed by filtration, rinsed with ethyl acetate and removal of solvent in vacuo yielded a crude residue. The crude residue was further purified by column chromatography using silica gel (100-200 mesh) to afford pure products. All the products were identified on the basis of NMR and mass spectral data.

Activity studies and FT-IR spectra of fresh, pyridine and 2,6-dimethylpyridine adsorbed nanosized zeolite Beta

In order to rationalize the role of Bronsted acid sites on the N-alkylation reaction; the surface acid sites were blocked using two different bases such as pyridine (which is a Bronsted and Lewis acid site blocker ~25.8 mmol/h) and the 2,6-dimethylpyridine (selective Bronsted acid site blocker ~ 25.8 mmol/h). These bases were adsorbed on the nanosized zeolite Beta separately. The surface poisoned samples are analyzed by FT-IR spectra and the N-alkylation reaction is performed.

In a typical experiment about 25.8 mmol/h of pyridine vapour was adsorbed on 0.2 g of catalyst at a temperature of 200 °C using N_2 as carrier gas with 30 mL/min. The sample was then flushed in N_2 flow 30 mL/min for 2 h at 200 °C. After flushing the sample temperature was brought down to 35 °C in N_2 flow. The pyridine adsorbed sample was subjected to N-alkylation reaction and also analyzed by FT-IR in order to distinguish the role of Bronsted and Lewis acid sites present on the nanosized zeolite Beta. A similar protocol was maintained for 2,6-dimethylpyridine (25.8 mmol/h) adsorption studies.

Table A N-benzylation of aniline with benzyl alcohol over fresh, pyridine and 2,6-dimethylpyridine adsorbed nanosized zeolite Beta[a]

Entry	Nanosized zeolite Beta	Temperature (°C)	Time (h)	Yield[b] (%)
1	Fresh	100	24	21
2	Pyridine adsorbed	100	24	9
3	2,6-Dimethylpyridine adsorbed	100	24	3

[a] Reaction conditions: Benzyl alcohol (6 mmol), Aniline (2 mmol), Catalyst (100 mg), open atmosphere. [b] Products were characterized by NMR, Mass spectra and isolated yields calculated based on aniline.

The FT-IR spectra of fresh, pyridine and 2,6-dimethylpyridine adsorbed on nanosized zeolite Beta samples are reported in Fig. A. The pyridine adsorbed nanosized zeolite Beta showed a prominent band at 1490.4 cm^{-1}, which is attributed to pyridine adsorbed on both Bronsted and Lewis acid sites. This observation is in good agreement with the earlier results reported by Yashima etal[1] in the pyridine adsorbed IR spectra of Beta zeolite. A vibrational band centred around 1636 cm^{-1} is due to pyridine (PyH^+) and/or 2,6-dimethylpyridine ($2,6\text{-}DMPyH^+$) coordinated to Bronsted acid site appeared in both pyridine and 2,6-dimethylpyridine adsorbed spectra. Two bands at 1447 and 1621 cm^{-1} are related to Lewis bonded pyridine is observed only in pyridine adsorbed sample and these bands are absent in the 2,6-dimethylpyridine adsorbed spectra[2]. These results revealed that pyridine is adsorbed on both Lewis and Bronsted sites, whereas 2,6-dimethylpyridine is selectively adsorbed on Bronsted acid sites present on the nanosized zeolite Beta. The pyridine and 2,6-dimethylpyridine adsorbed nanosized zeolite Beta samples are evaluated for the N-alkylation reaction at a reaction temperature of 100 °C. In order to avoid the desorption of adsorbed

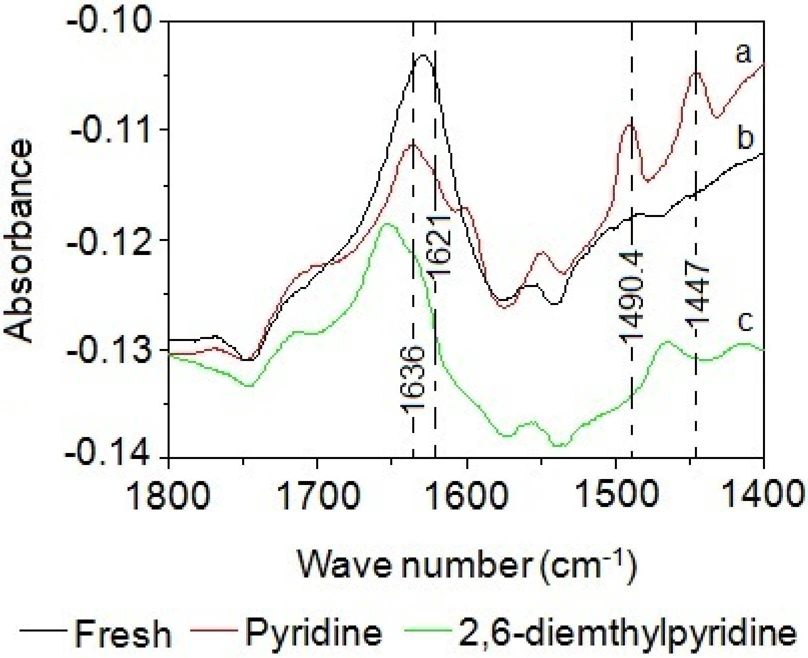


Fig. A FT-IR spectra of a) pyridine adsorbed b) fresh c) 2,6-dimethylpyridine adsorbed nanosized zeolite Beta catalysts

pyridine ($BP_{pyridine}$ = 115.2 °C) the fresh, pyridine and 2,6-dimethylpyridine adsorbed nanosized zeolite Beta samples are evaluated for N-alkylation of aniline with benzyl alcohol at a reaction temperature of 100 °C and the yields are compared (**Table A**). The yield of N-benzylaniline is drastically decreased after poisoning with both pyridine (9%) and 2,6-dimethylpyridine (3%). Reason for very low yield on the sample poisoned with 2,6-dimethylpyridine is because of blockage most of the Bronsted acid sites. On the other hand slightly better yields on pyridine adsorbed sample is due to partial blockage of Bronsted acid sites by pyridine as pyridine is adsorbed both on Bronsted and Lewis acid sites observed in the FT-IR analysis. From these results it can be concluded that Bronsted acid sites are required for the N-alkylation reactions.

Spectral data

_N_-Benzylaniline[3] (Table 2, entry 1)

^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 3.90$ (bs, 1H), 4.29 (s, 2H), 6.53-6.59 (m, 2H), 6.65 (t, 1H, $J = 7.55$ Hz), 7.07-7.36 (m, 7H).

^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 48.1$, 112.7, 117.4, 127.1, 127.4, 128.5, 129.2, 139.3, 148.0.

MS (ESI): $m/z = 184$ ($M^+ + H$); HRMS calcd for $C_{13}H_{14}N$ ($M^+ + H$) 184.1126, found 184.1129.

_N_-Benzyl-2-methylaniline[4] (Table 2, entry 2)

^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 2.15$ (s, 3H), 3.75 (bs, 1H), 4.34 (s, 2H), 6.53 (d, 1H, $J = 7.55$ Hz,), 6.60 (t, 1H, $J = 6.8$ Hz), 6.95-7.11 (m, 2H), 7.29-7.43 (m, 5H).

MS (ESI): $m/z = 198$ ($M^+ + H$).

_N_-Benzyl-4-methylaniline[3] (Table 2, entry 3)

^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 2.22$ (s, 3H), 3.81(bs, 1H), 4.27 (s, 2H), 6.48 (d, 2H, $J = 8.31$ Hz), 6.91 (d, 2H, $J = 8.31$ Hz), 7.17-7.37 (m, 5H).

MS (ESI): $m/z = 198$ ($M^+ + H$); HRMS calcd for $C_{14}H_{16}N$ ($M^+ + H$) 198.1282, found 198.1291.

_N_-Benzyl-2,4-dimethylaniline[5] (Table 2, entry 4)

^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 2.12$ (s, 3H), 2.21 (s, 3H), 3.62 (bs, 1H), 4.31 (s, 2H), 6.45 (d, 1H, $J = 8.01$ Hz), 6.80-6.85 (m, 2H), 7.19-7.36 (m, 5H).

MS (ESI): $m/z = 212$ ($M^+ + H$); HRMS calcd for $C_{15}H_{18}N$ ($M^+ + H$) 212.14338, found 212.14263.

_N_-Benzyl-2-methoxyaniline[6] (Table 2, entry 6)

^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 3.84$ (s, 3H), 4.35 (s, 2H), 4.60 (bs, 1H), 6.56-6.71 (m, 2H), 6.76-6.87 (m, 2H), 7.26-7.39 (m, 5H).

_N_-Benzyl-4-methoxyaniline[7] (Table 2, entry 7)

^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 3.73$ (s, 3H), 3.83 (bs, 1H), 4.28 (s, 2H), 6.60 (d, 2H, $J = 9.06$ Hz), 6.79 (d, 2H, $J = 8.31$ Hz), 7.19-7.41 (m, 5H).

^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 49.1$, 55.7, 114.0, 114.8, 127.1, 127.4, 128.5, 139.6, 142.3, 152.0.

MS (ESI): $m/z = 214$ ($M^+ + H$); HRMS calcd for $C_{14}H_{16}NO$ ($M^+ + H$) 214.1226, found 214.1231.

_N_-Benzyl-4-bromoaniline[3] (Table 2, entry 9)

^{1}H NMR (300 MHz, $CDCl_3$): δ = 4.06 (bs, 1H), 4.29 (s, 2H), 6.49 (d, 2H, J = 8.88 Hz), 7.19-7.41 (m, 7H).

MS (ESI): m/z = 262 (M^+ + H).

N-Benzyl-4-chloroaniline[3] (Table 2, entry 11)

^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.99 (bs, 1H), 4.27 (s, 2H), 6.49 (d, 2H, J = 9.06 Hz), 7.06 (d, 2H, J = 8.31 Hz), 7.19-7.36 (m, 5H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 48.2, 113.8, 122.0, 127.3, 127.5, 128.6, 128.9, 138.8, 146.5.

MS (ESI): m/z = 218 (M^+ + H).

N-Benzyl-3,4-dichloroaniline (Table 2, entry 12)

^{1}H NMR (300 MHz, $CDCl_3$): δ = 4.11 (bs, 1H), 4.28 (s, 2H), 6.33-6.49 (m, 1H), 6.59-6.74 (m, 1H), 7.09-7.39 (m, 6H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 48.0, 112.5, 113.8, 119.8, 127.3, 127.5, 128.4, 128.7, 128.8, 130.5, 132.7, 138.3, 147.4.

MS (ESI): m/z = 252 (M^+ + H).

Methyl 4-(benzylamino)benzoate[3] (Table 2, entry 13)

^{1}H NMR (500 MHz, $CDCl_3$): δ = 3.83 (s, 3H), 4.38 (s, 2H), 4.51 (bs, 1H), 6.58 (d, 2H, J = 8.89 Hz), 7.26-7.38 (m, 5H), 7.85 (d, 2H, J = 8.89 Hz).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 47.5, 51.4, 111.6, 118.5, 127.3, 127.4, 128.7, 131.4, 138.3, 151.7, 167.2.

MS (ESI): m/z = 242 (M^+ + H); HRMS calcd for $C_{15}H_{16}NO_2$ (M^+ + H) 242.11756, found 242.11671.

2-(Benzylamino)benzonitrile[8] (Table 2, entry 14)

^{1}H NMR (500 MHz, $CDCl_3$): δ = 4.43 (d, 2H, J = 5.0 Hz), 5.01 (bs, 1H), 6.58 (d, 1H, J = 8.01 Hz), 6.66 (t, 1H, J = 8.01 Hz), 7.24-7.36 (m, 6H), 7.39 (d, 1H, J = 8.01 Hz).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 47.3, 95.7, 110.9, 116.7, 117.8, 127.0, 127.5, 128.7, 132.6, 134.2, 137.6, 149.9.

4-(Benzylamino)benzonitrile[3] (Table 2, entry 15)

^{1}H NMR (300 MHz, $CDCl_3$): δ = 4.34 (d, 2H, J = 5.29 Hz), 4.63 (bs, 1H), 6.58 (d, 2H, J = 9.06 Hz), 7.24-7.41 (m, 7H).

MS (ESI): m/z = 231 (M^+ + Na).

N-Benzyl-2-nitroaniline[8] (Table 2, entry 16)

^{1}H NMR (300 MHz, CDCl$_3$): δ = 4.55 (d, 2H, J = 5.66 Hz), 6.66 (t, 1H, J = 7.36 Hz), 6.81 (d, 1H, J = 8.69 Hz), 7.15-7.45 (m, 6H), 8.19 (dd, 1H, J = 8.51, 1.13 Hz), 8.43 (bs, 1H).

MS (ESI): m/z = 229 (M$^+$ + H).

_N_-Benzyl-3-nitroaniline[5] (Table 2, entry 17)

^{1}H NMR (300 MHz, CDCl$_3$): δ = 4.38 (s, 2H), 6.87 (dd, 1H, J = 8.99, 2.0 Hz), 7.22-7.39 (m, 6H), 7.41-7.45 (m, 1H), 7.52 (dd, 1H, J = 7.99, 2.0 Hz).

^{13}C NMR (75 MHz, CDCl$_3$): δ = 47.9, 106.5, 112.0, 118.6, 127.4, 127.6, 128.8, 129.7, 138.0, 148.7, 149.3.

_N_-Benzyl-4-nitroaniline[9] (Table 2, entry 18)

^{1}H NMR (300 MHz, CDCl$_3$): δ = 4.43 (d, 2H, J = 5.48 Hz), 4.88 (bs, 1H), 6.57 (d, 2H, J = 9.25 Hz), 7.29-7.60 (m, 5H), 8.09 (d, 2H, J = 9.25 Hz).

MS (ESI): m/z = 229 (M$^+$ + H).

_N_-Benzyl-_N_-methylaniline[9] (Table 2, entry 20)

^{1}H NMR (300 MHz, CDCl$_3$): δ = 3.01 (s, 3H), 4.53 (s, 2H), 6.71-6.78 (m, 2H), 7.15-7.35 (m, 8H).

^{13}C NMR (75 MHz, CDCl$_3$): δ = 38.4, 56.6, 112.3, 116.5, 126.7, 126.8, 128.5, 129.1, 138.9, 149.7.

MS (ESI): m/z = 198 (M$^+$ + H); HRMS calcd for $C_{14}H_{16}N$ (M$^+$ + H) 198.1282, found 198.1278.

_N_-Benzyl-1,2,3,4-tetrahydroquinoline[3] (Table 2, entry 23)

^{1}H NMR (500 MHz, CDCl$_3$): δ = 1.94-2.05 (m, 2H), 2.76-2.85 (m, 2H), 3.31-3.39 (m, 2H), 4.47 (s, 2H), 6.50 (d, 1H, J = 7.99 Hz), 6.56 (t, 1H, J = 6.99 Hz), 6.93-7.02 (m, 2H), 7.19-7.41 (m, 5H).

MS (ESI): m/z = 224 (M$^+$ + H); HRMS calcd for $C_{16}H_{18}N$ (M$^+$ + H) 224.1439, found 224.1450.

_N_-Benzyl-1,2,3,4-tetrahydroisoquinoline[3] (Table 2, entry 24)

^{1}H NMR (500 MHz, CDCl$_3$): δ = 2.72 (t, 2H, J = 5.93 Hz), 2.87 (t, 2H, J = 5.93 Hz), 3.61 (s, 2H), 3.66 (s, 2H), 6.92 (d, 1H, J = 7.91 Hz), 7.01-7.09 (m, 3H), 7.19-7.39 (m, 5H).

^{13}C NMR (75 MHz, CDCl$_3$): δ = 29.0, 50.5, 56.0, 62.7, 125.5, 125.9, 126.5, 127.0, 128.2, 128.6, 129.0, 134.3, 134.8, 138.3.

MS (ESI): m/z = 224 (M$^+$ + H); HRMS calcd for $C_{16}H_{18}N$ (M$^+$ + H) 224.14338, found 224.14254.

***N*-Benzylpyrazole**[10] **(Table 2, entry 25)**

^{1}H NMR (300 MHz, CDCl$_3$): δ = 5.32 (s, 2H), 6.28 (t, 1H, *J* =2.26 Hz), 7.16-7.36 (m, 5H), 7.39 (d, 1H, *J* = 2.26 Hz), 7.55 (d, 1H, *J* = 1.15 Hz).

^{13}C NMR (75 MHz, CDCl$_3$): δ = 55.7, 105.8, 127.4, 127.8, 128.6, 129.1, 136.5, 139.3.

MS (ESI): *m/z* = 159 (M$^+$ + H); HRMS calcd for $C_{10}H_{11}N_2$ (M$^+$ + H) 159.0922, found 159.0920.

***N*-Benzyl-1,2,4-triazole**[10] **(Table 2, entry 27)**

^{1}H NMR (300 MHz, CDCl$_3$): δ = 5.34 (s, 2H), 7.23-7.49 (m, 5H), 7.97 (s, 1H), 8.06 (s, 1H).

MS (ESI): *m/z* = 160 (M$^+$ + H); HRMS calcd for $C_9H_{10}N_3$ (M$^+$ + H) 160.0874, found 160.0882.

***N*-(3-Methylbenzyl)aniline**[6] **(Table 3, entry 1)**

^{1}H NMR (300 MHz, CDCl$_3$): δ = 2.35 (s, 3H), 3.99 (bs, 1H), 4.28 (s, 2H), 6.61-6.67 (m, 2H), 6.71 (t, 1H, *J* = 7.55 Hz), 7.06-7.28 (m, 6H).

^{13}C NMR (75 MHz, CDCl$_3$): δ = 21.3, 48.2, 112.7, 117.4, 124.5, 127.9, 128.2, 128.4, 129.1, 138.2, 139.3, 148.2.

MS (ESI): *m/z* = 198 (M$^+$ + H); HRMS calcd for $C_{14}H_{16}N$ (M$^+$ + H) 198.1282, found 198.1282.

***N*-(4-Methylbenzyl)aniline**[11] **(Table 3, entry 2)**

^{1}H NMR (500 MHz, CDCl$_3$): δ = 2.33 (s, 3H), 3.88 (bs, 1H), 4.24 (s, 2H), 6.53-6.69 (m, 3H), 7.07-7.23 (m, 6H).

MS (ESI): *m/z* = 198 (M$^+$ + H).

***N*-(2-Bromobenzyl)aniline**[11] **(Table 3, entry 3)**

^{1}H NMR (500 MHz, CDCl$_3$): δ = 4.18 (bs, 1H), 4.40 (s, 2H), 6.61 (d, 2H, *J* = 6.99 Hz), 6.71 (t, 1H, *J* = 6.99 Hz), 7.09-7.29 (m, 4H), 7.41 (d, 1H, *J* = 7.99 Hz), 7.57 (d, 1H, *J* = 7.99 Hz).

MS (ESI): *m/z* = 262 (M$^+$ + H); HRMS calcd for $C_{13}H_{13}NBr$ (M$^+$ + H) 262.02259, found 262.02163.

***N*-(4-Bromobenzyl)aniline**[3] **(Table 3, entry 4)**

^{1}H NMR (300 MHz, CDCl$_3$): δ = 4.06 (bs, 1H), 4.29 (s, 2H), 6.59 (d, 2H, *J* = 7.74 Hz), 6.72 (t, 1H, *J* = 7.36 Hz), 7.11-7.27 (m, 4H), 7.45 (d, 2H, *J* = 8.31 Hz).

MS (ESI): *m/z* = 262 (M$^+$ + H).

***N*-(2-Chlorobenzyl)aniline**[11] **(Table 3, entry 5)**

^{1}H NMR (300 MHz, CDCl$_3$): δ = 4.16 (bs, 1H), 4.43 (s, 2H), 6.61 (d, 2H, J = 7.55 Hz), 6.71 (t, 1H, J = 7.55 Hz), 7.13-7.46 (m, 6H).

MS (ESI): m/z = 218 (M^+ + H); HRMS calcd for $C_{13}H_{13}NCl$ (M^+ + H) 218.0736, found 218.0727.

***N*-(1-Phenylethyl)aniline[12] (Table 3, entry 7)**

^{1}H NMR (500 MHz, CDCl$_3$): δ = 1.51 (d, 3H, J = 6.01 Hz), 3.98 (bs, 1H), 4.45 (q, 1H, J = 6.06 Hz), 6.43 (d, 2H, J = 8.01 Hz), 6.58 (t, 1H, J = 8.01 Hz), 7.07-7.14 (m, 2H), 7.24-7.34 (m, 5H).

MS (ESI): m/z = 198 (M^+ + H).

***N*-(1-(4-Bromophenyl)ethyl)aniline[13] (Table 3, entry 8)**

^{1}H NMR (300 MHz, CDCl$_3$): δ = 1.47 (d, 3H, J = 6.81 Hz), 3.98 (bs, 1H), 4.43 (q, 1H, J = 6.81 Hz), 6.47 (d, 2H, J = 8.31 Hz), 6.65 (t, 1H, J = 8.31 Hz), 7.04-7.13 (m, 2H), 7.21-7.29 (m, 2H), 7.41-7.47(m, 2H).

MS (ESI): m/z = 276 (M^+ + H).

***N*-(1-Phenylpropyl)aniline[14] (Table 3, entry 9)**

^{1}H NMR (300 MHz, CDCl$_3$): δ = 0.95 (t, 3H, J = 7.55 Hz), 1.75-1.89 (m, 2H), 4.05 (bs, 1H), 4.22 (t, 1H, J = 6.81 Hz), 6.51 (d, 2H, J = 7.55 Hz), 6.58-6.67 (m, 1H), 7.02-7.11 (m, 2H), 7.17-7.37 (m, 5H).

MS (ESI): m/z = 212 (M^+ + H).

***N*-(1-(2-Naphthyl)ethyl)aniline[12] (Table 3, entry 10)**

^{1}H NMR (300 MHz, CDCl$_3$): δ = 1.58 (d, 3H, J = 6.79 Hz), 4.10 (bs, 1H), 4.63 (q, 1H, J = 6.79 Hz), 6.55 (d, 2H, J = 8.31 Hz), 6.63 (t, 1H, J = 8.31 Hz), 7.07 (t, 2H, J = 8.31 Hz), 7.39-7.54 (m, 3H), 7.75-7.89 (m, 4H).

MS (ESI): m/z = 248 (M^+ + H); HRMS calcd for $C_{18}H_{18}N$ (M^+ + H) 248.1433, found 248.1435.

***N*-(Furan-2-ylmethyl)aniline[15] (Table 3, entry 11)**

^{1}H NMR (300 MHz, CDCl$_3$): δ = 4.31 (s, 2H), 6.23 (d, 1H, J = 3.02 Hz), 6.29-6.32 (m, 1H), 6.67 (d, 2H, J = 8.49 Hz), 6.73 (t, 1H, J = 7.36 Hz), 7.14-7.23 (m, 2H), 7.34-7.39 (m, 1H).

MS (ESI): m/z = 174 (M^+ + H); HRMS calcd for $C_{11}H_{12}NO$ (M^+ + H) 174.0918, found 174.0911.

***N*-(Cyclohex-2-enyl)aniline[6] (Table 3, entry 14)**

^{1}H NMR (300 MHz, CDCl$_3$): δ = 1.53-1.81 (m, 3H), 1.87-2.14 (m, 3H), 3.59 (bs, 1H), 3.94-4.06 (m, 1H), 5.71-5.92 (m, 2H), 6.57-6.79 (m, 3H), 7.11-7.24 (m, 2H).

MS (ESI): *m/z* = 174 (M^+ + H).

(*E*)-*N*-(2-Hexenyl)aniline[16] (Table 3, entry 15)

^{1}H NMR (300 MHz, $CDCl_3$): *δ* = 0.89 (t, 3H, *J* = 7.36 Hz), 1.33-1.47 (m, 2H), 2.02 (q, 2H, *J* = 6.99 Hz), 3.69 (d, 2H, *J* = 5.66 Hz), 3.79 (bs, 1H), 5.51-5.79 (m, 2H), 6.62 (d, 2H, *J* = 8.31 Hz), 6.66-6.74 (m, 1H), 7.12-7.24 (m, 2H).

MS (ESI): *m/z* = 176 (M^+ + H).

***N*-Hexylaniline[17] (Table 3, entry 16)**

^{1}H NMR (300 MHz, $CDCl_3$): *δ* = 0.89 (t, 3H, *J* = 6.81 Hz), 1.29-1.39 (m, 6H), 1.54-1.63 (m, 2H), 3.10 (t, 2H, *J* = 6.81 Hz), 3.64 (bs, 1H), 6.61 (d, 2H, *J* = 7.55 Hz), 6.68 (t, 1H, *J* = 7.55 Hz), 7.13-7.22 (m, 2H).

MS (ESI): *m/z* = 178 (M^+ + H); HRMS calcd for $C_{12}H_{20}N$ (M^+ + H) 178.1595, found 178.1603.

***N*-Octylaniline[3] (Table 3, entry 17)**

^{1}H NMR (300 MHz, $CDCl_3$): *δ* = 0.88 (t, 3H, *J* = 6.79 Hz), 1.23-1.36 (m, 10H), 1.55-1.67 (m, 2H), 3.09 (t, 2H, *J* = 7.55 Hz), 3.62 (bs,1H), 6.59 (d, 2H, *J* = 7.55 Hz), 6.68 (t, 1H, *J* = 7.55 Hz), 7.13-7.22 (m, 2H).

***N*-(2-Nitrobenzylidene)aniline[18] (Table 4, entry 1)**

^{1}H NMR (300 MHz, $CDCl_3$): *δ* = 7.24-7.34 (m, 3H), 7.39-7.47 (m, 2H), 7.59-7.79 (m, 2H), 8.04-8.11 (m, 1H), 8.29-8.34 (m, 1H), 8.95 (s, 1H).

MS (ESI): *m/z* = 227 (M^+ + H).

***N*-(3-Nitrobenzylidene)aniline[19] (Table 4, entry 2)**

^{1}H NMR (300 MHz, $CDCl_3$): *δ* = 7.22-7.36 (m, 3H), 7.39-7.51 (m, 2H), 7.67 (t, 1H, *J* = 7.55 Hz), 8.26 (d, 1H, *J* = 7.55 Hz), 8.31-8.41 (m, 1H), 8.55 (s, 1H), 8.75 (s, 1H).

MS (ESI): *m/z* = 227 (M^+ + H).

***N*-(4-Nitrobenzylidene)aniline[18] (Table 4, entry 3)**

^{1}H NMR (300 MHz, $CDCl_3$): *δ* = 7.22-7.34 (m, 3H), 7.44 (t, 2H, *J* = 7.74 Hz), 8.08 (d, 2H, *J* = 8.69 Hz), 8.34 (d, 2H, *J* = 8.69 Hz), 8.56 (s, 1H).

^{13}C NMR (75 MHz, $CDCl_3$): *δ* = 120.8, 123.8, 126.9, 129.2, 129.2, 141.4, 149.0, 150.7, 157.2.

MS (ESI): *m/z* = 227 (M^+ + H).

***N*-(4-Nitrobenzylidene)-2-methylaniline (Table 4, entry 4)**

^{1}H NMR (300 MHz, $CDCl_3$): *δ* = 2.39 (s, 3H), 6.94-7.01 (m, 1H), 7.15-7.29 (m, 3H), 8.09 (d, 2H, *J* = 9.06 Hz), 8.33 (d, 2H, *J* = 8.31 Hz), 8.47 (s, 1H).

***N*-(4-Nitrobenzylidene)-4-methylaniline[20] (Table 4, entry 5)**

^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.39 (s, 3H), 7.17-7.42 (m, 4H), 8.07 (d, 2H, J = 9.06 Hz), 8.32 (d, 2H, J = 9.06 Hz), 8.57 (s, 1H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 21.0, 120.9, 123.9, 129.2, 129.9, 137.2, 141.7, 148.2, 149.1, 156.2.

MS (ESI): m/z = 241 (M^+ + H).

N-(4-Nitrobenzylidene)-2-methoxyaniline (Table 4, entry 6)

^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.90 (s, 3H), 6.96-7.09 (m, 3H), 7.22-7.29 (m, 1H), 8.09 (d, 2H, J = 9.06 Hz), 8.32 (d, 2H, J = 8.31 Hz), 8.61 (s, 1H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 55.8, 111.6, 120.5, 120.9, 123.8, 127.7, 129.3, 140.3, 141.6, 149.0, 152.3, 158.3.

MS (ESI): m/z = 257 (M^+ + H).

N-(4-Nitrobenzylidene)-4-methoxyaniline[20] (Table 4, entry 7)

^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.85 (s, 3H), 6.96 (d, 2H, J = 8.87 Hz), 7.32 (d, 2H, J = 8.87 Hz), 8.06 (d, 2H, J = 8.69 Hz), 8.32 (d, 2H, J = 8.87 Hz), 8.58 (s, 1H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 55.5, 114.5, 122.6, 123.9, 129.0, 141.9, 143.5, 148.9, 154.7, 159.2.

MS (ESI): m/z = 257 (M^+ + H).

N-(4-Nitrobenzylidene)-4-chloroaniline[20] (Table 4, entry 9)

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.21 (d, 2H, J = 9.06 Hz), 7.40 (d, 2H, J = 8.31 Hz), 8.08 (d, 2H, J = 9.06 Hz), 8.34 (d, 2H, J = 8.31 Hz), 8.54 (s, 1H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 122.3, 123.9, 129.4, 130.4, 132.7, 141.2, 149.2, 149.3, 157.6.

N-(4-Nitrobenzyl)aniline[3]

^{1}H NMR (500 MHz, $CDCl_3$): δ = 4.24 (bs, 1H), 4.47 (s, 2H), 6.56-6.61 (m, 2H), 6.72-6.79 (m, 1H), 7.14-7.21 (m, 2H), 7.53 (d, 2H, J = 8.54 Hz), 8.19 (d, 2H, J = 8.54 Hz).

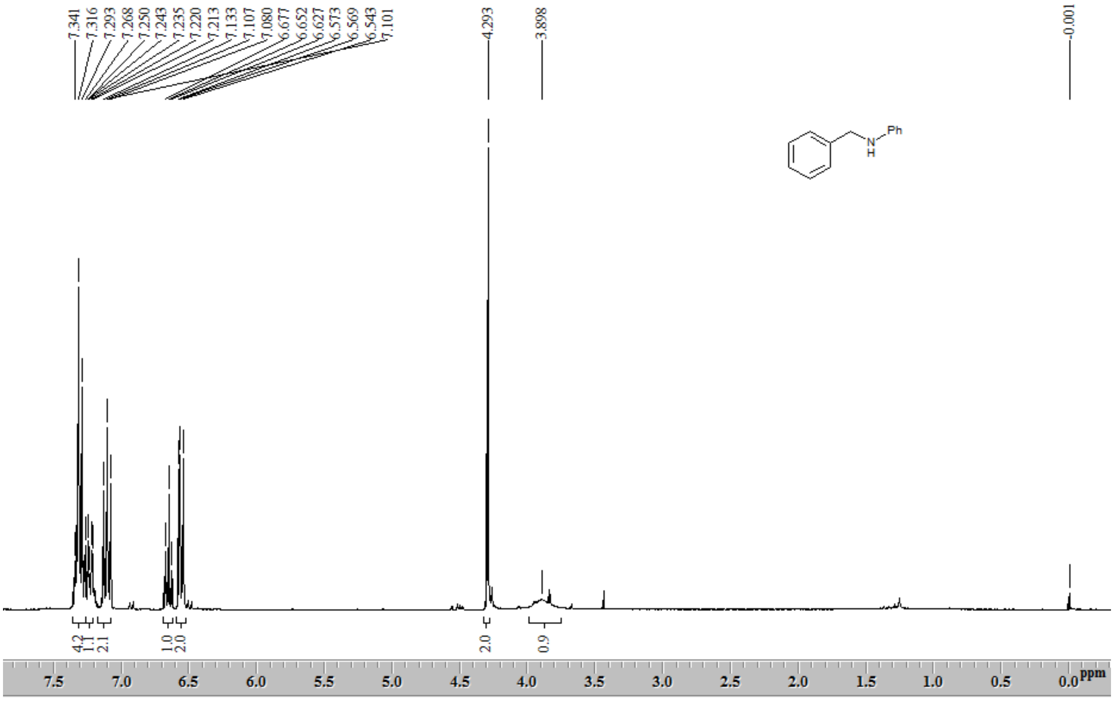
^{13}C NMR (75 MHz, $CDCl_3$): δ = 47.5, 112.8, 118.1, 123.8, 127.6, 129.3, 147.0, 147.2, 147.5.

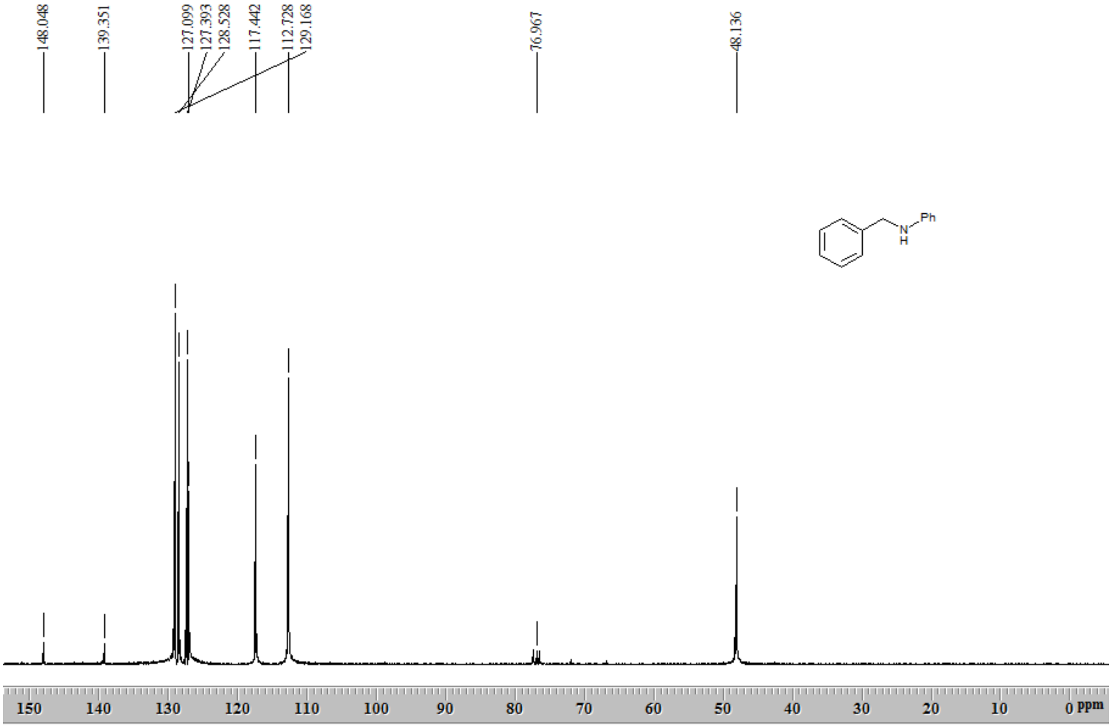
Dibenzyl ether[21]

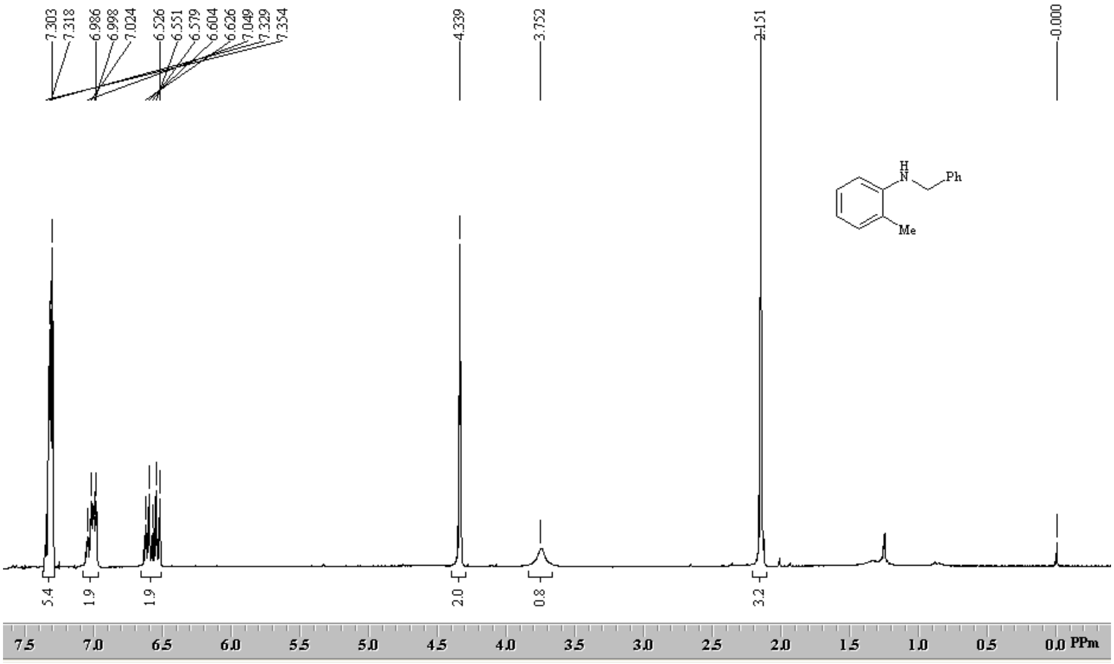
^{1}H NMR (500 MHz, $CDCl_3$): δ = 4.52 (s, 4H), 7.19-7.37 (m, 10H).

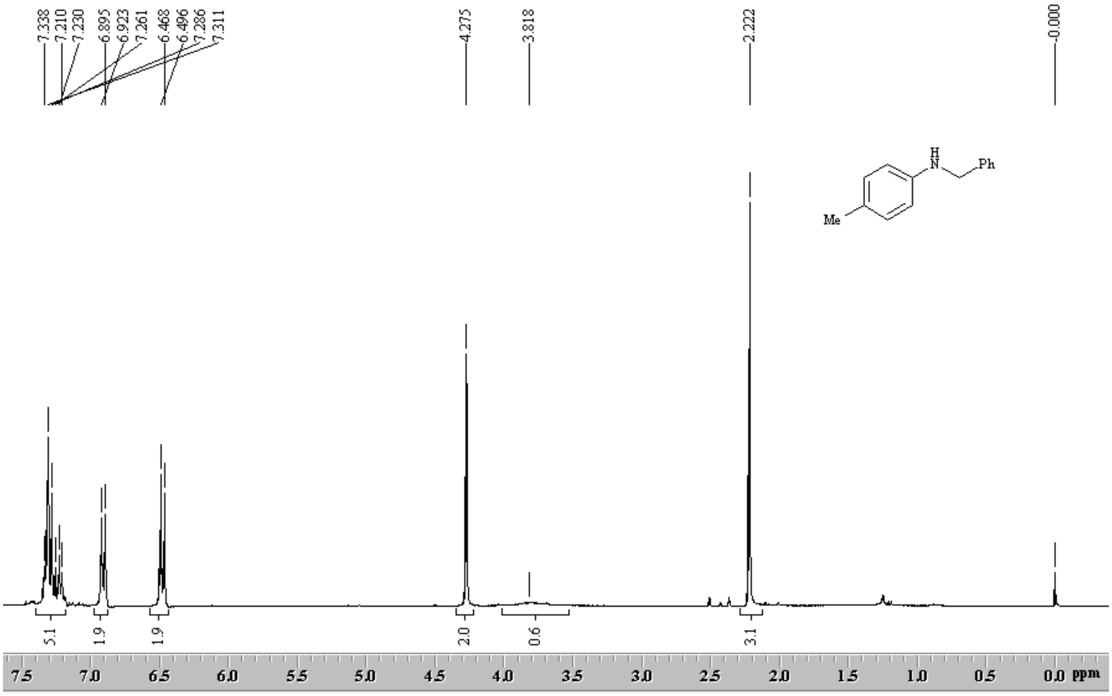
Bis(4-nitrobenzyl) ether[22]

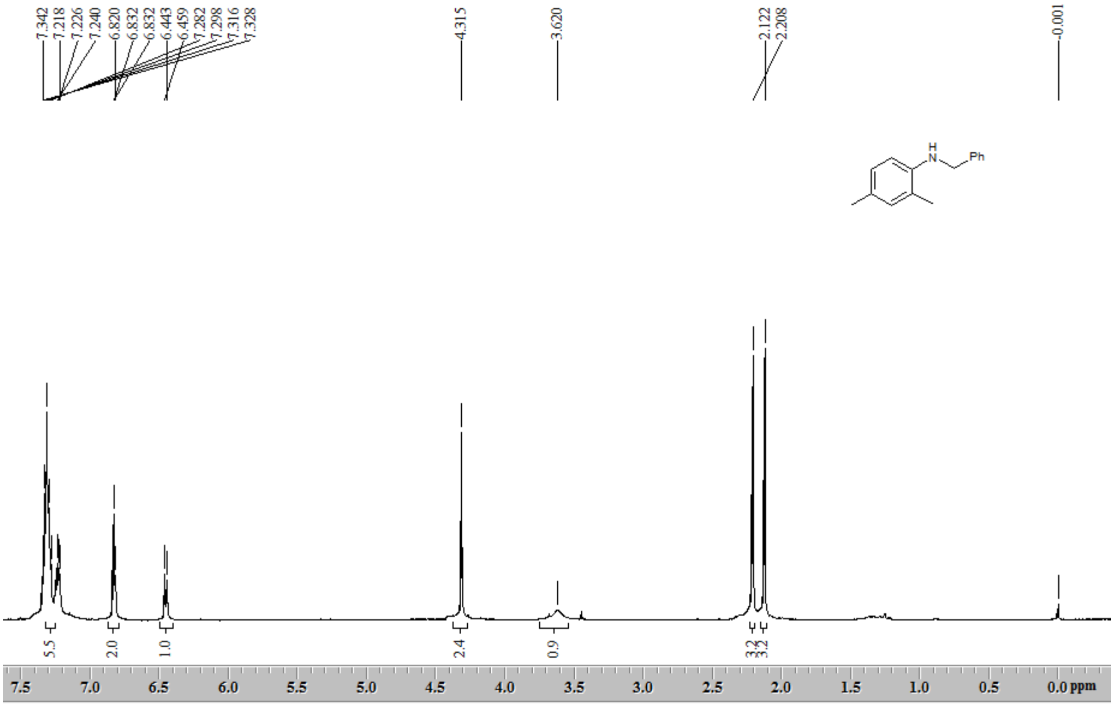
^{1}H NMR (500 MHz, $CDCl_3$): δ = 4.72 (s, 4H), 7.54 (d, 4H, J = 8.85 Hz), 8.23 (d, 4H, J = 8.85 Hz).

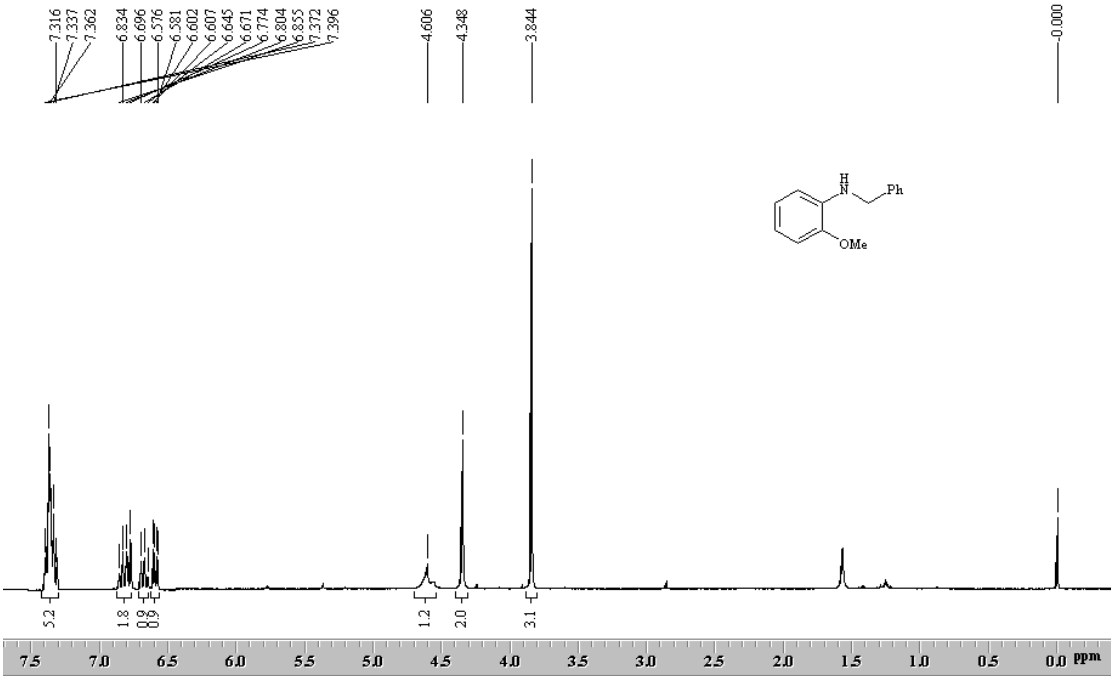

7.341
7.316
7.293
7.268
7.250
7.243
7.235
7.220
7.213
7.133
7.107
7.080
6.677
6.652
6.627
6.573
6.569
6.543
7.101
4.293
3.898
-0.001
N
H
Ph
4.2
1.1
2.1
1.0
2.0
2.0
0.9
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm

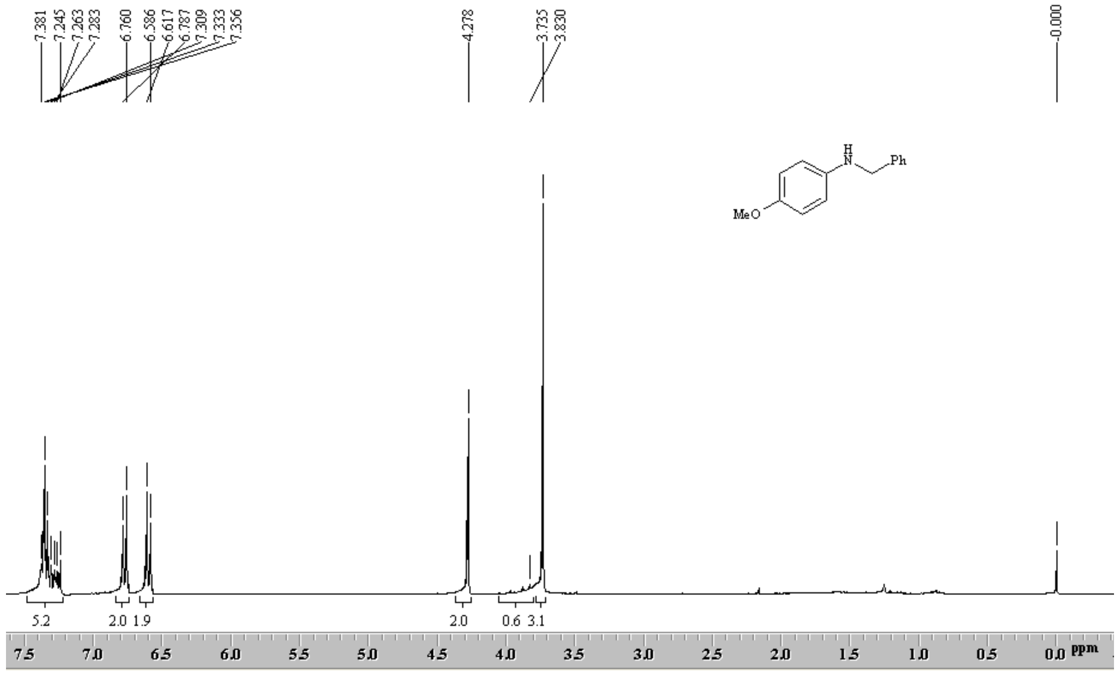

148.048
139.351
127.099
127.393
128.528
117.442
112.728
129.168
76.967
48.136
N
H
Ph
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

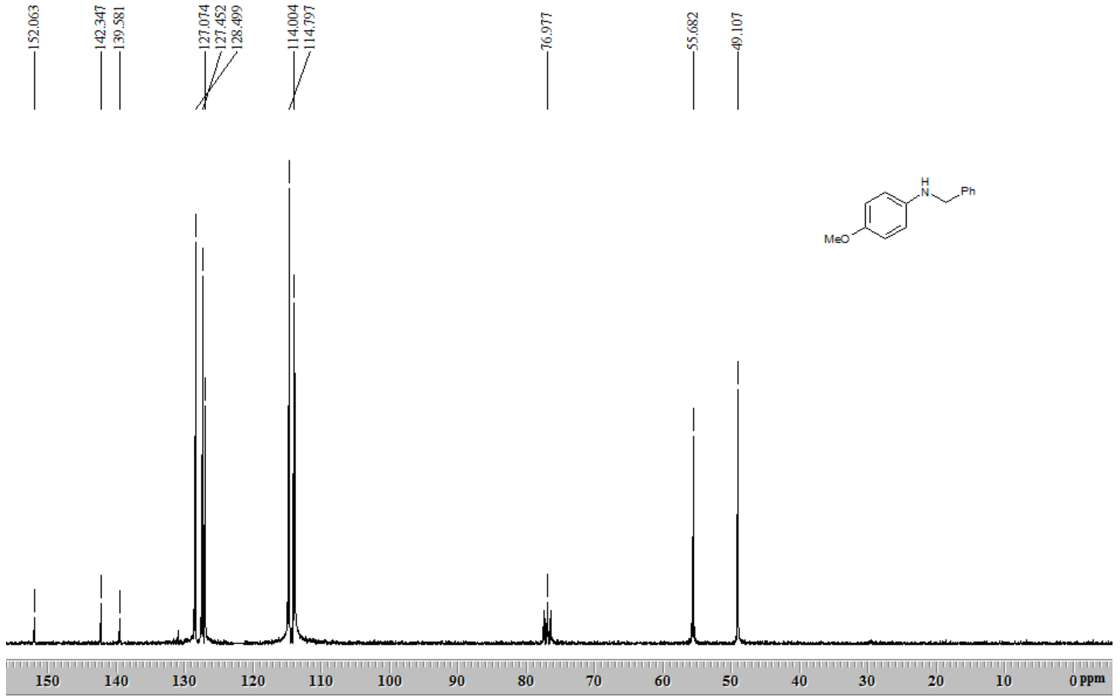

7.303
7.318
6.986
6.998
7.024
6.526
6.551
6.579
6.604
6.626
7.049
7.329
7.354
4.339
3.752
2.151
-0.000
H
N
Ph
Me
5.4
1.9
1.9
2.0
0.8
3.2
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0 PPm

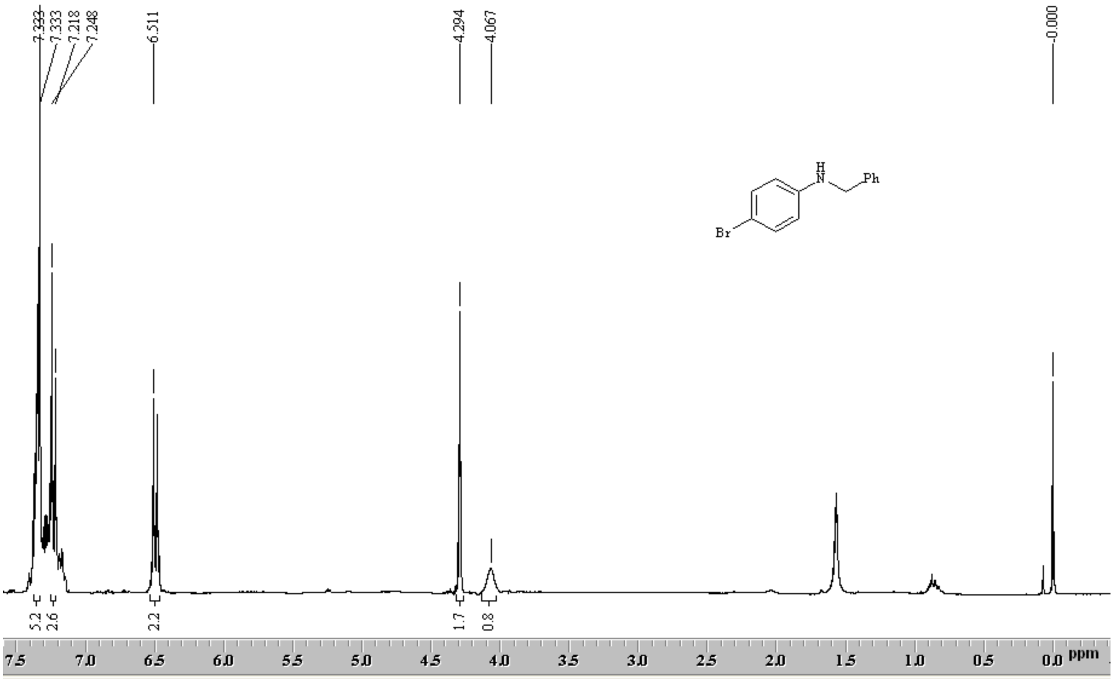

7.338
7.210
7.230
6.895
6.923
7.261
6.468
6.496
7.286
7.311
4.275
3.818
2.222
-0.000
H
N
Ph
Me
5.1
1.9
1.9
2.0
0.6
3.1
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0 ppm

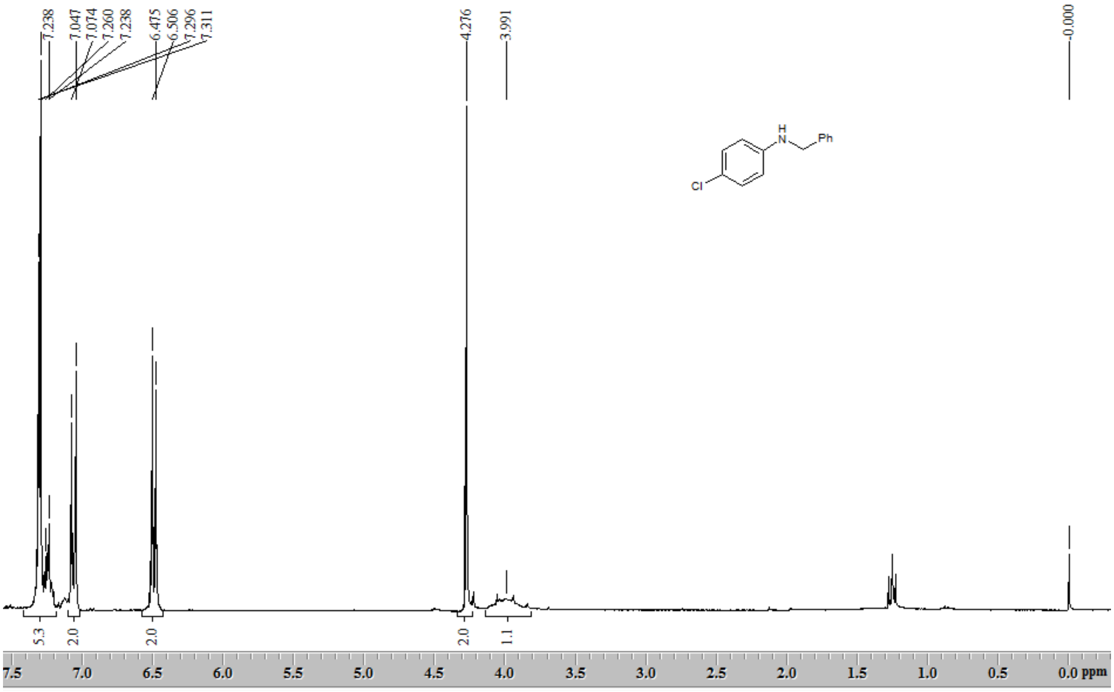

7.342
7.218
7.226
7.240
6.820
6.832
6.832
6.443
6.459
7.282
7.298
7.316
7.328
4.315
3.620
2.122
2.208
-0.001
H
N
Ph
5.5
2.0
1.0
2.4
0.9
3.2
3.2
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0 ppm

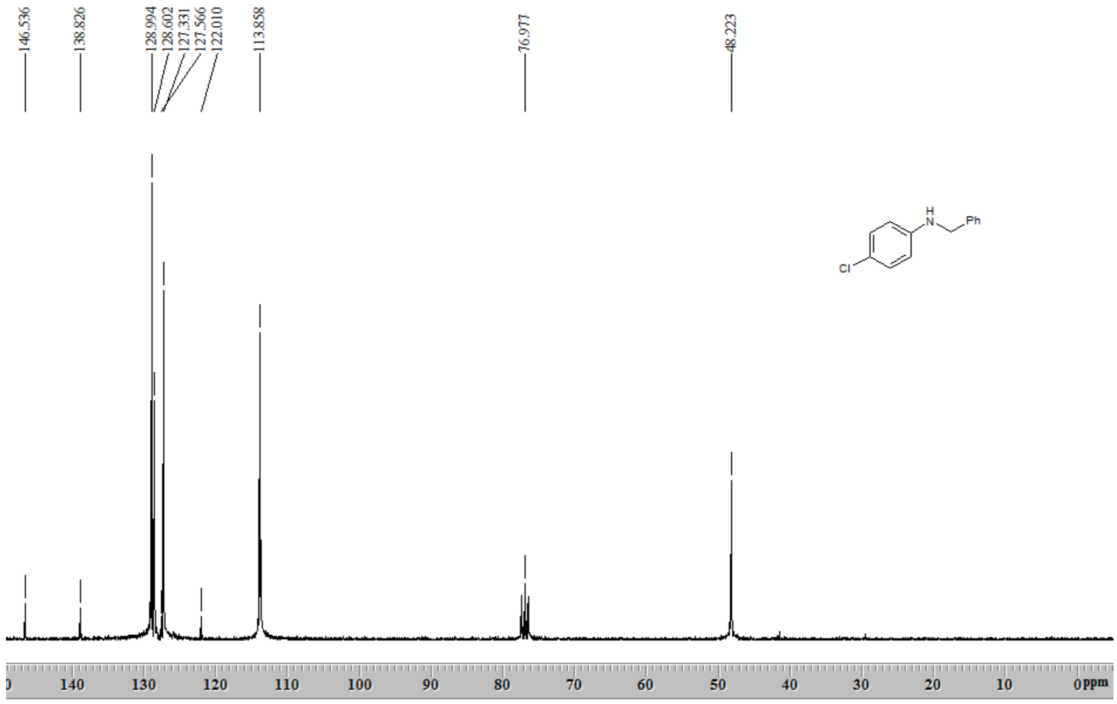

7.316
7.337
7.362
6.834
6.696
6.576
6.581
6.602
6.607
6.645
6.671
6.774
6.804
6.855
7.372
7.396
4.606
4.348
3.844
-0.000
H
N
Ph
OMe
5.2
1.8
0.9
0.9
1.2
2.0
3.1
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0 ppm

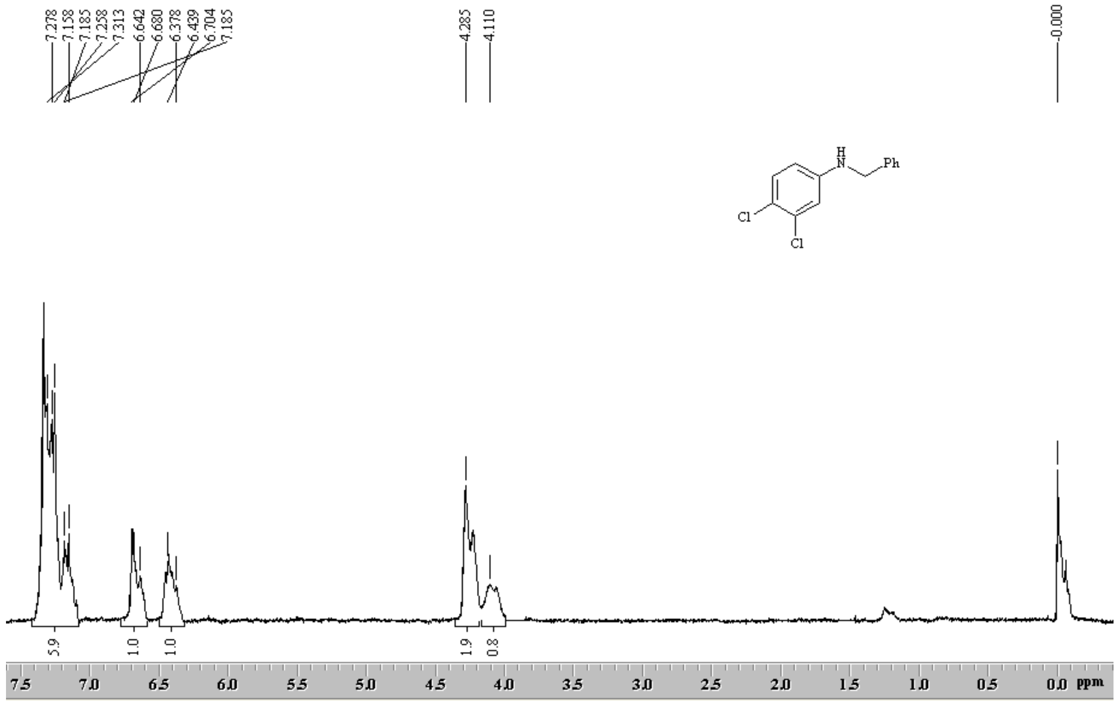

7.381
7.245
7.263
7.283
6.760
6.586
6.617
6.787
7.309
7.333
7.356
4.278
3.735
3.830
0.000
MeO
H
N
Ph
5.2
2.0
1.9
2.0
0.6
3.1
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0 ppm

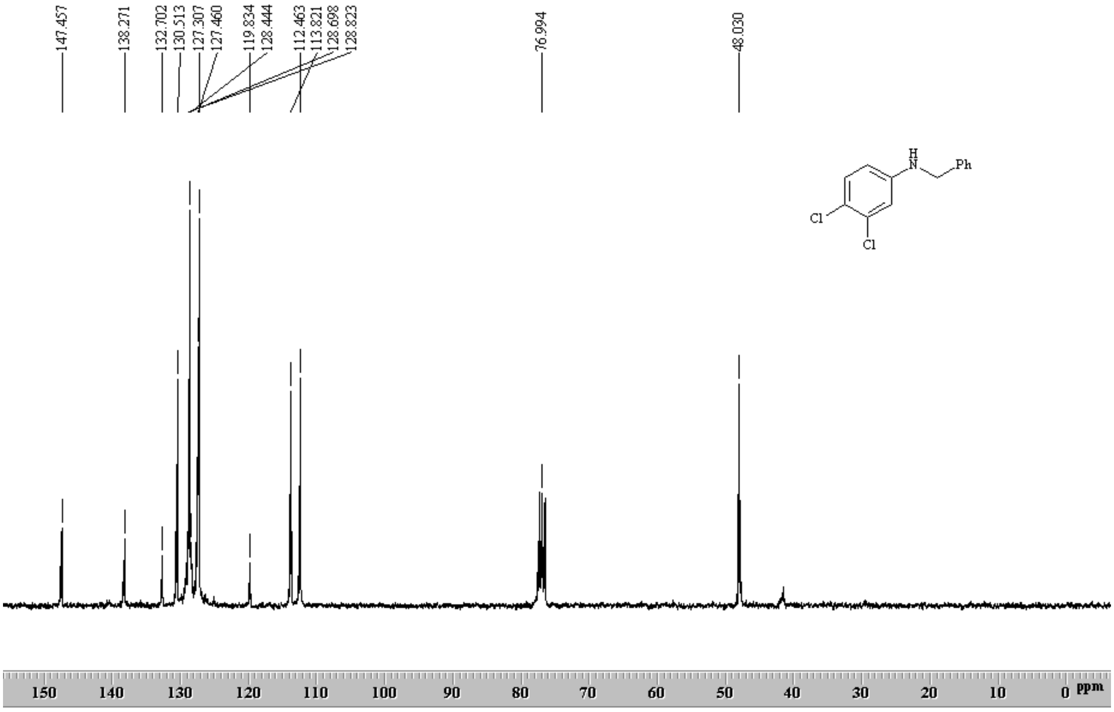

152.063
142.347
139.581
127.074
127.452
128.499
114.004
114.797
76.977
55.682
49.107
MeO
H
N
Ph
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0 ppm

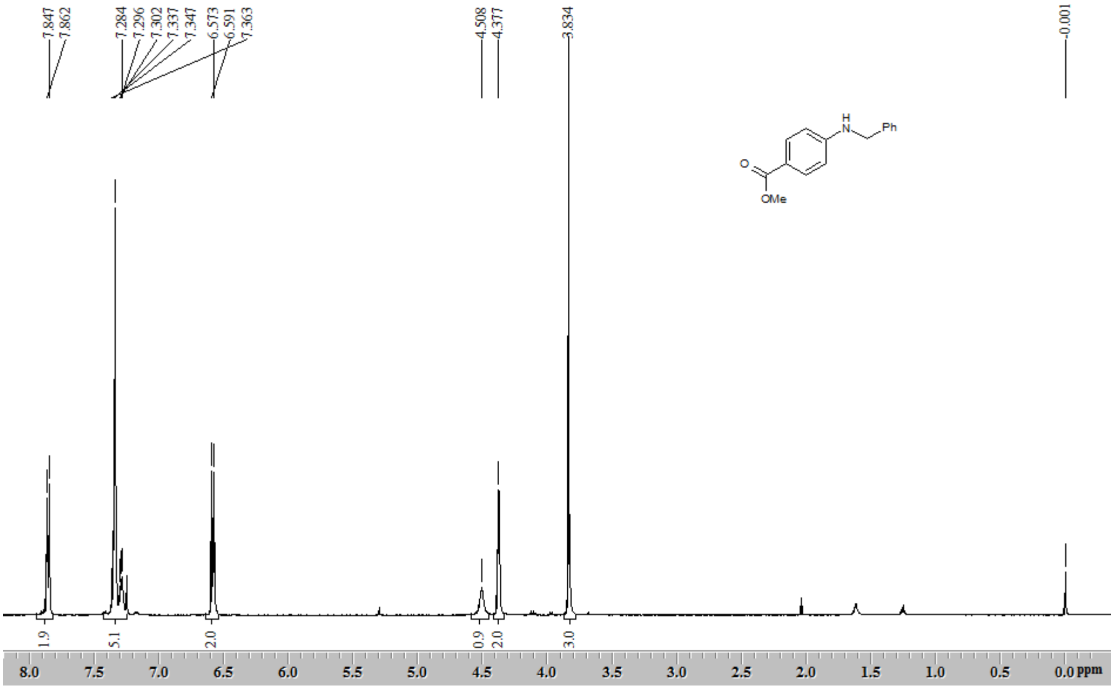

7.333
7.333
7.218
7.248
6.511
4.294
4.067
0.000
H
N
Ph
Br
5.2
2.6
2.2
1.7
0.8
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0 ppm

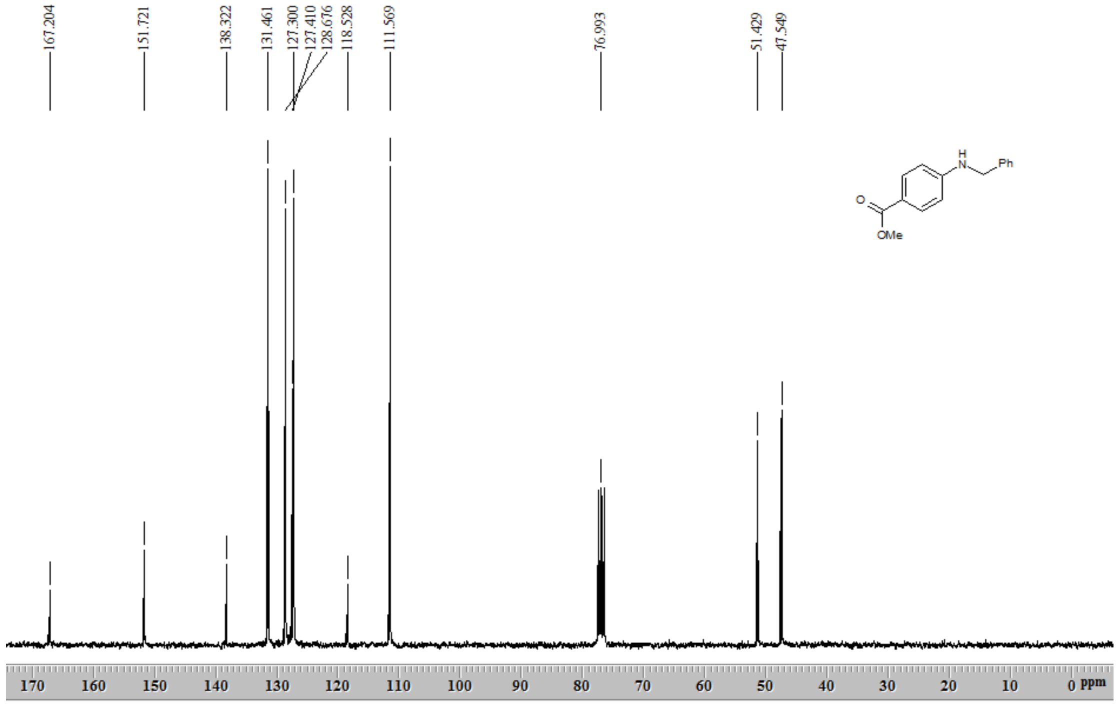

7.238
7.047
7.074
7.260
7.238
6.475
6.506
7.296
7.311
4.276
3.991
0.000
H
N
Ph
Cl
5.3
2.0
2.0
2.0
1.1
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0 ppm

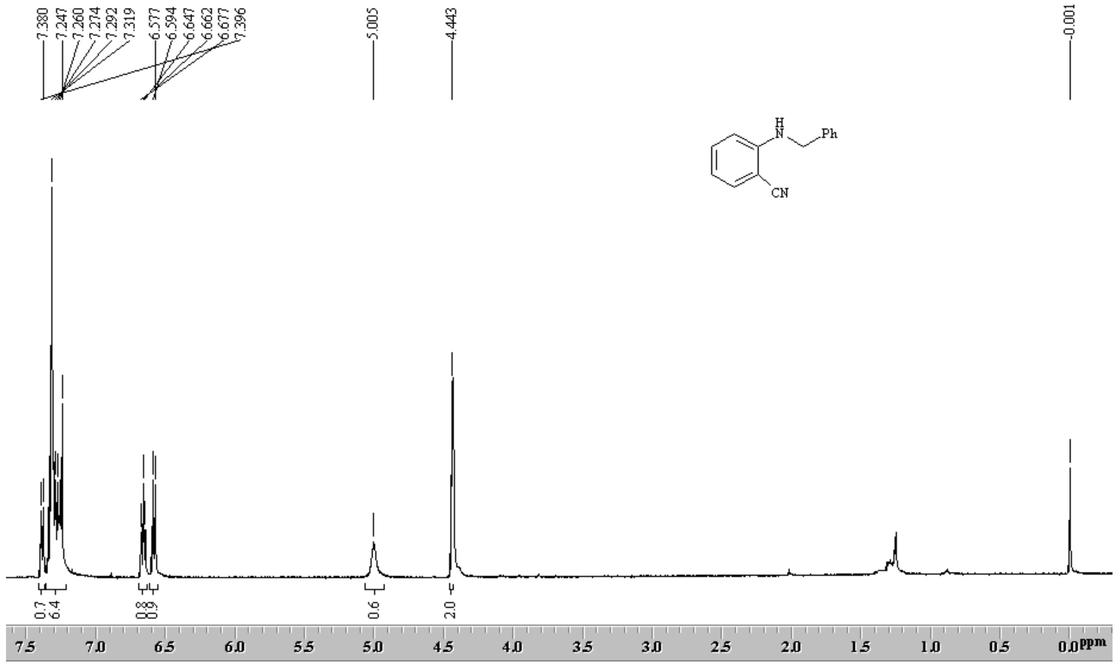

146.536
138.826
128.994
128.602
127.331
127.566
122.010
113.858
76.977
48.223
H
N
Ph
Cl
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0 ppm

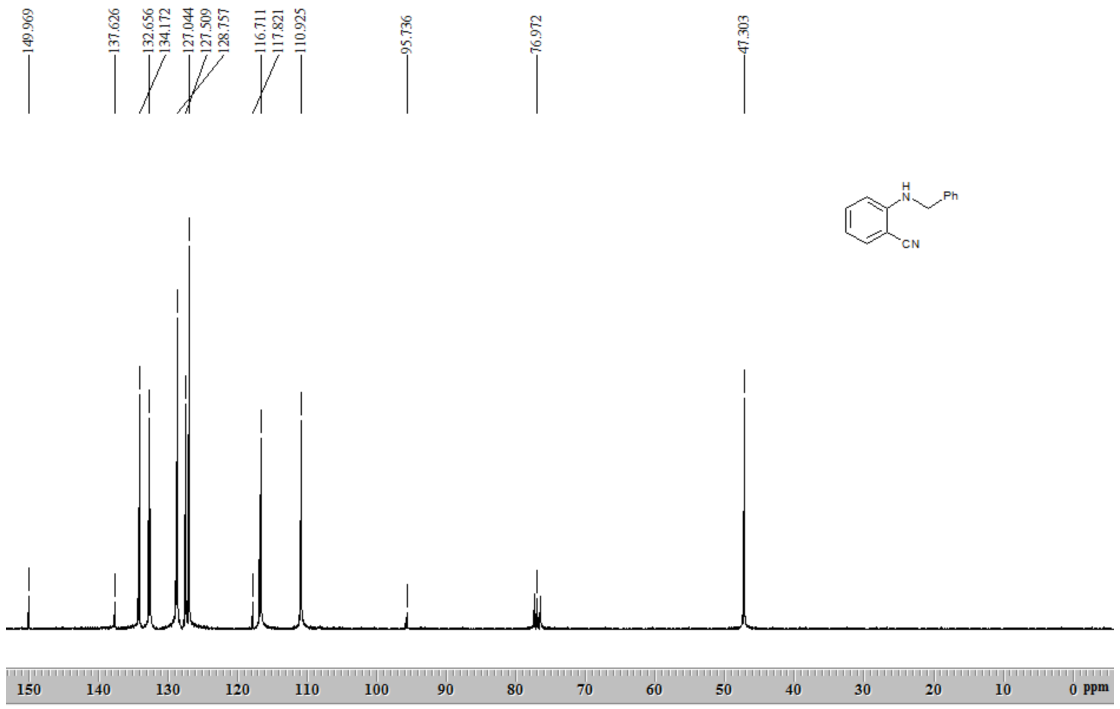

7.278
7.158
7.185
7.258
7.313
6.642
6.680
6.378
6.439
6.704
7.185
4.285
4.110
-0.000
H
N
Ph
Cl
Cl
5.9
1.0
1.0
1.9
0.8
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0 ppm

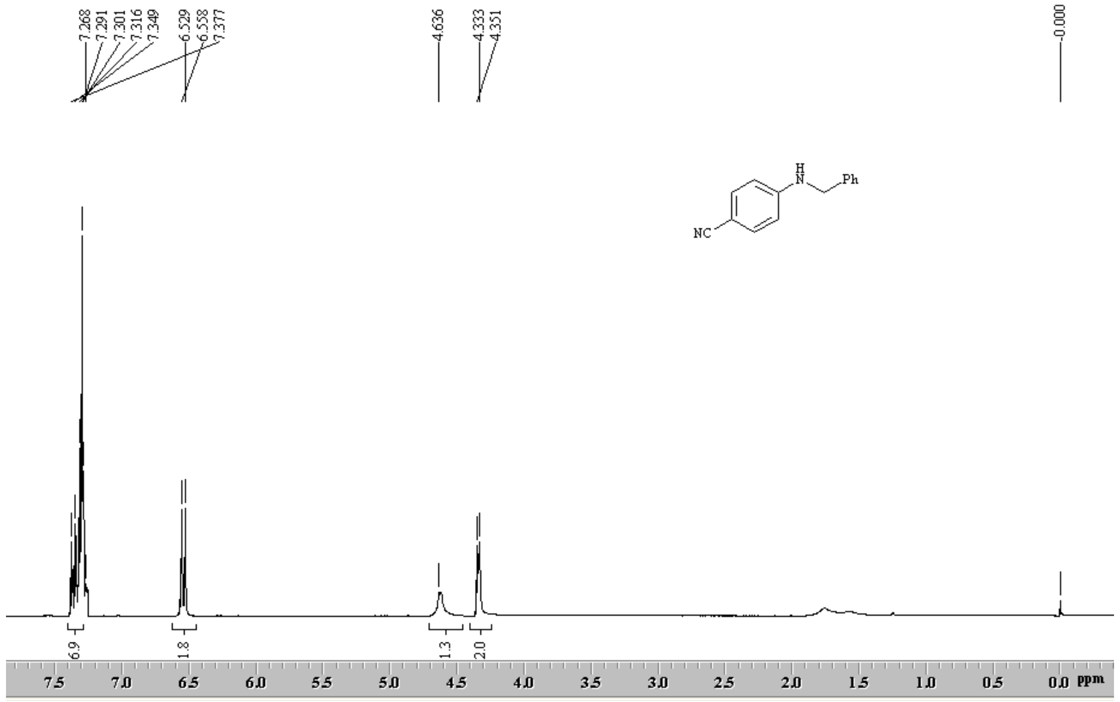

147.457
138.271
132.702
130.513
127.307
127.460
119.834
128.444
112.463
113.821
128.698
128.823
76.994
48.030
H
N
Ph
Cl
Cl
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0 ppm

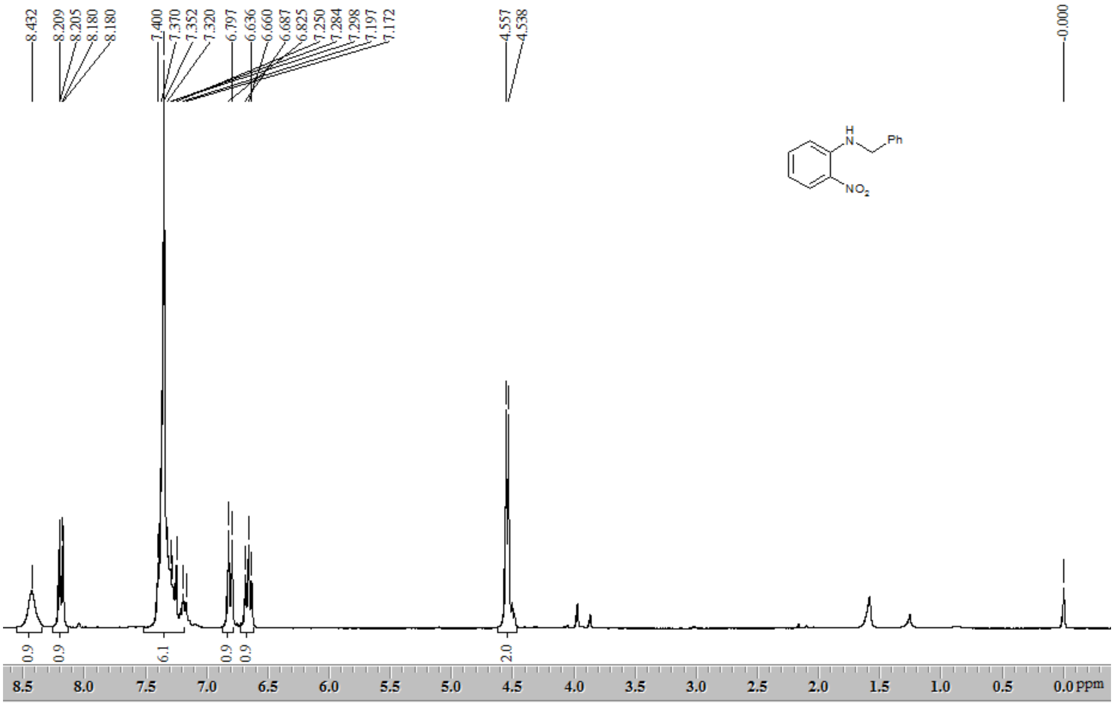

7.847
7.862
7.284
7.296
7.302
7.337
7.347
6.573
6.591
7.363
4.508
4.377
3.834
-0.001
H
N
Ph
O
OMe
1.9
5.1
2.0
0.9
2.0
3.0
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0 ppm

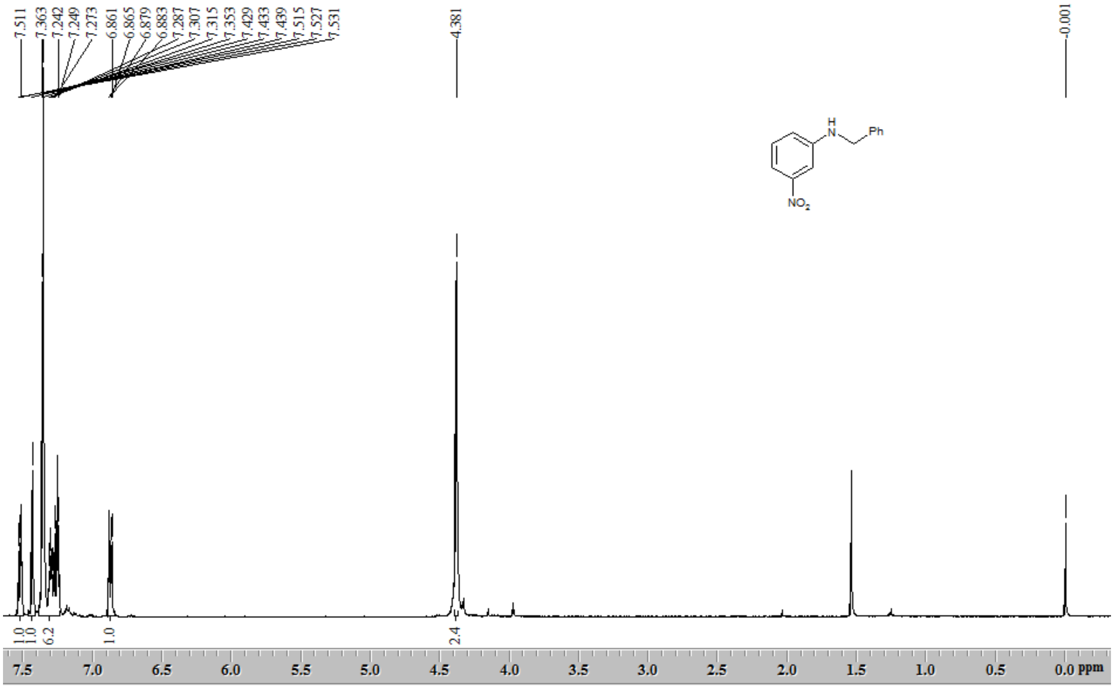

167.204
151.721
138.322
131.461
127.300
127.410
128.676
118.528
111.569
76.993
51.429
47.549
H
N
Ph
O
OMe
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0 ppm

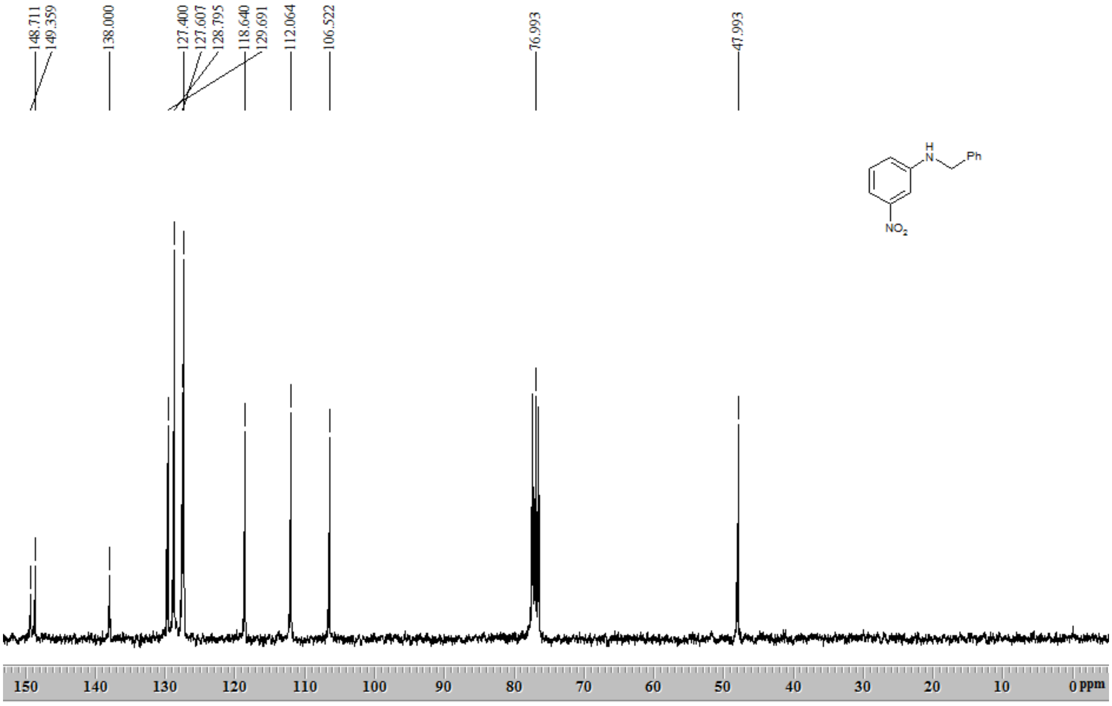

7.380
7.247
7.260
7.274
7.292
7.319
6.577
6.594
6.647
6.662
6.677
7.396
5.005
4.443
-0.001
H
N
Ph
CN
0.7
6.4
0.8
0.9
0.6
2.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0 ppm

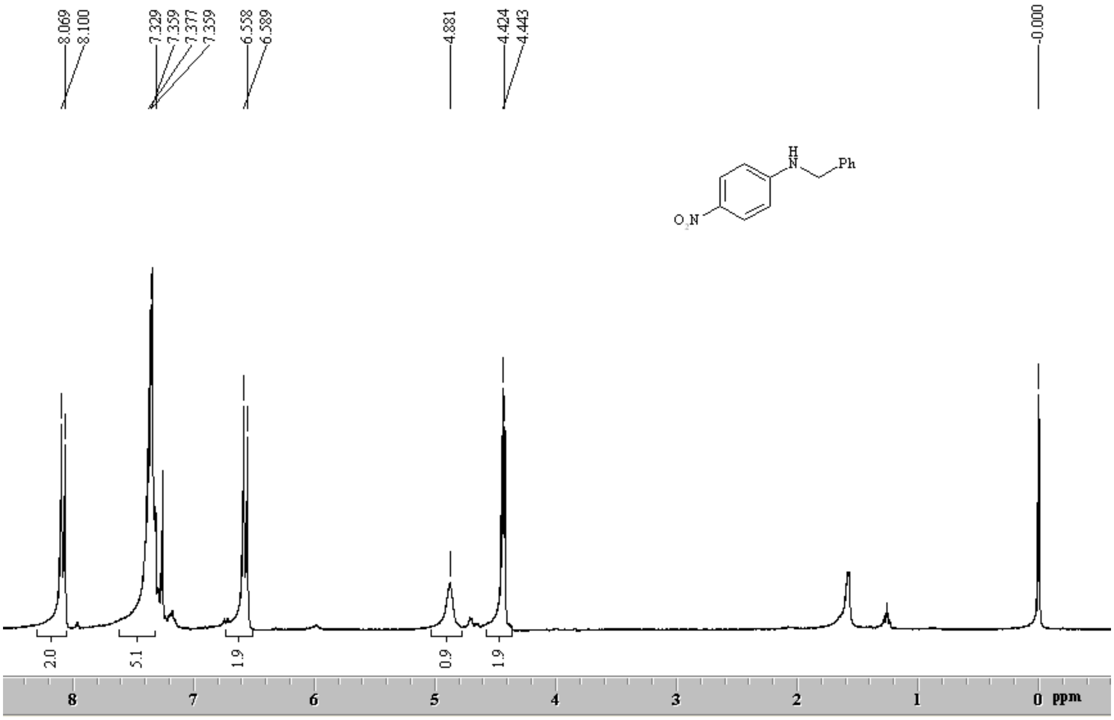

149.969
137.626
132.656
134.172
127.044
127.509
128.757
116.711
117.821
110.925
95.736
76.972
47.303
H
N
Ph
CN
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0 ppm

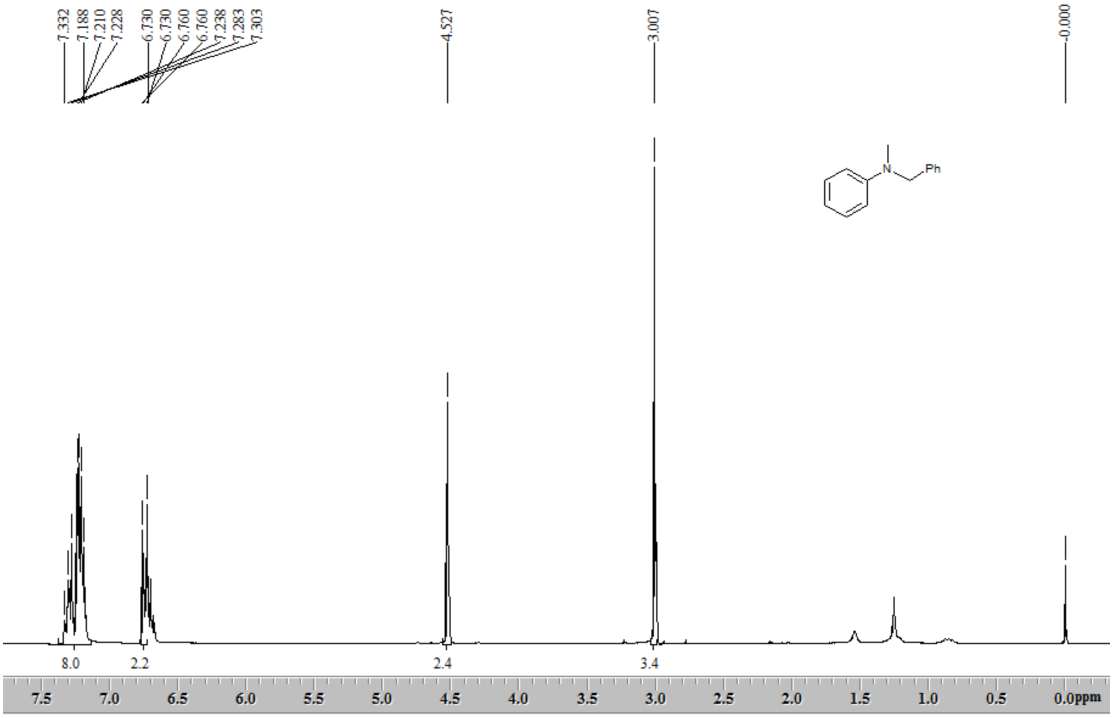

7.268
7.291
7.301
7.316
7.349
6.529
6.558
7.377
4.636
4.333
4.351
-0.000
H
N
Ph
NC
6.9
1.8
1.3
2.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0 ppm

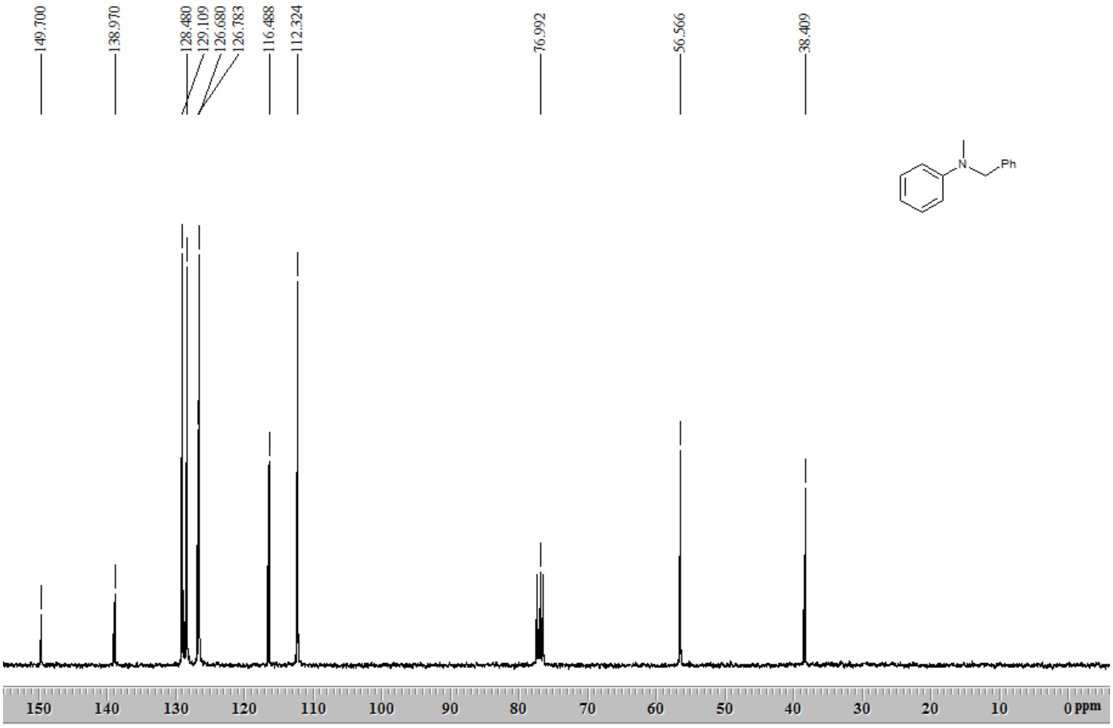

8.432
8.209
8.205
8.180
8.180
7.400
7.370
7.352
7.320
6.797
6.636
6.660
6.687
6.825
7.250
7.284
7.298
7.197
7.172
4.557
4.538
-0.000
H
N
Ph
NO2
0.9
0.9
6.1
0.9
0.9
2.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0 ppm

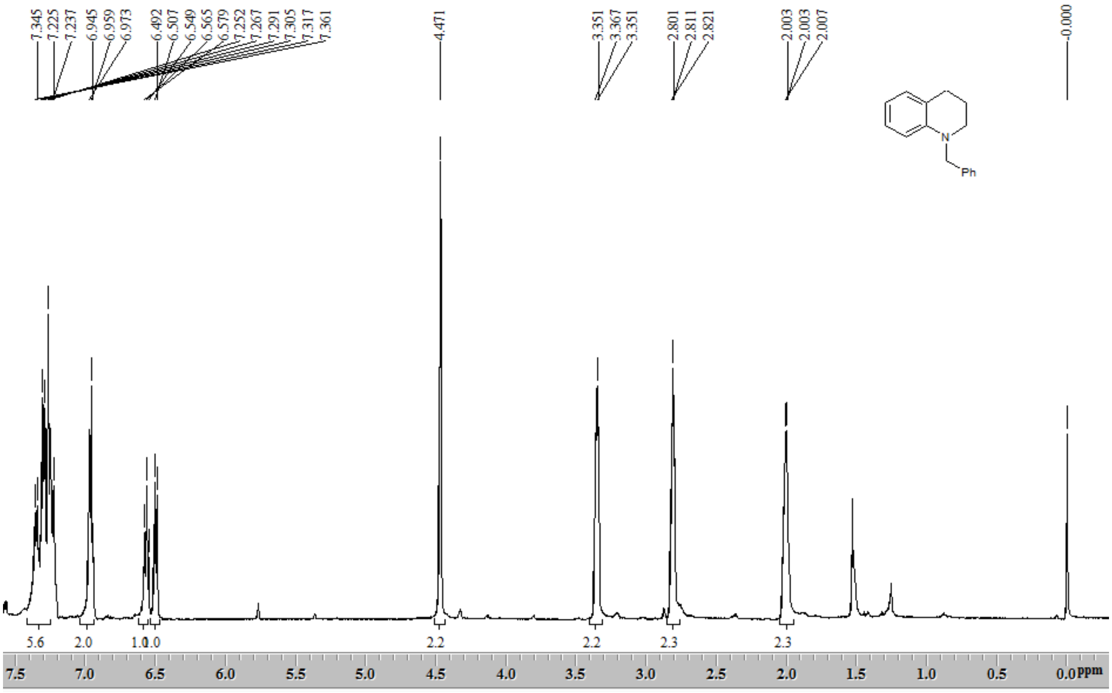

7.511
7.363
7.242
7.249
7.273
6.861
6.865
6.879
6.883
7.287
7.307
7.315
7.353
7.429
7.433
7.439
7.515
7.527
7.531
4.381
-0.001
H
N
Ph
NO2
1.0
1.0
6.2
1.0
2.4
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0 ppm

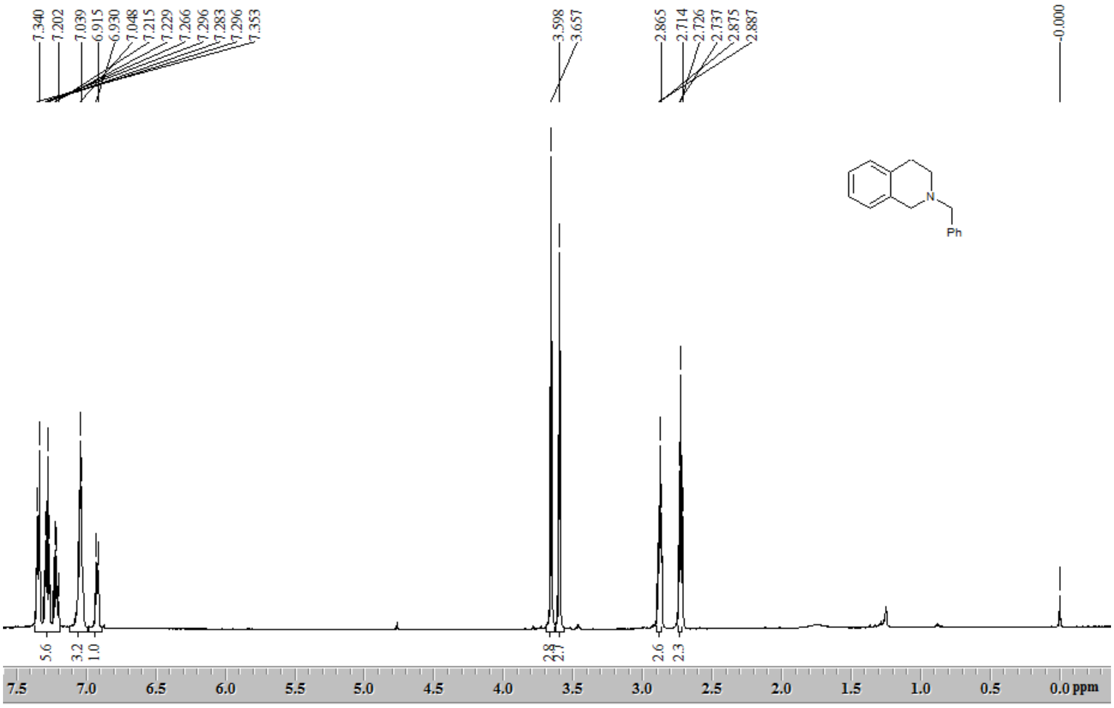

148.711
149.359
138.000
127.400
127.607
128.795
118.640
129.691
112.064
106.522
76.993
47.993
H
N
Ph
NO2
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0 ppm

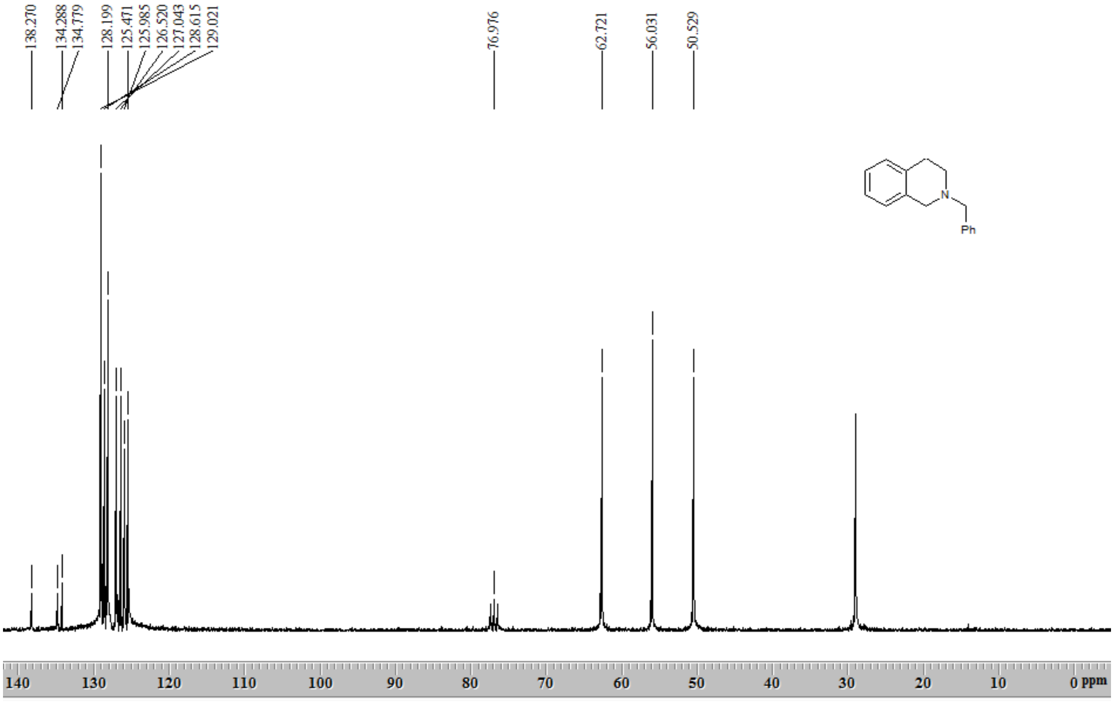

8.069
8.100
7.329
7.359
7.377
7.359
6.558
6.589
4.881
4.424
4.443
-0.000
H
N
Ph
O2N
2.0
5.1
1.9
0.9
1.9
8
7
6
5
4
3
2
1
0 ppm

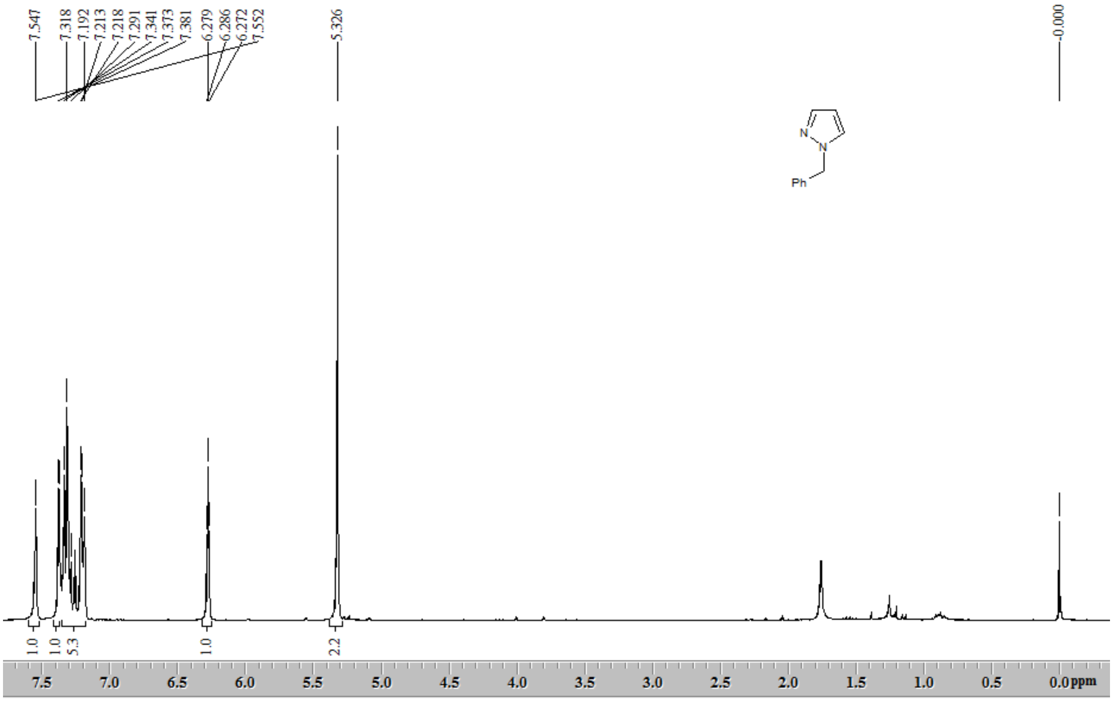

7.332
7.188
7.210
7.228
6.730
6.730
6.760
6.760
7.238
7.283
7.303
4.527
3.007
-0.000
N
Ph
8.0
2.2
2.4
3.4
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0ppm

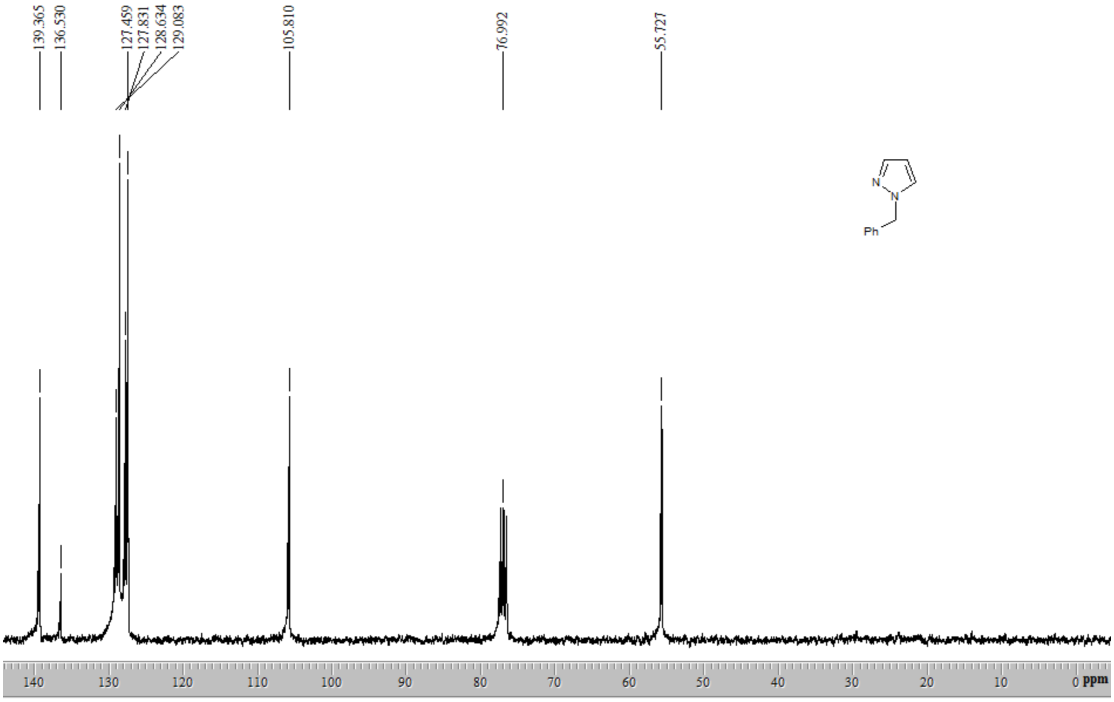

149.700
138.970
128.480
129.109
126.680
126.783
116.488
112.324
76.992
56.566
38.409
N
Ph
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0 ppm

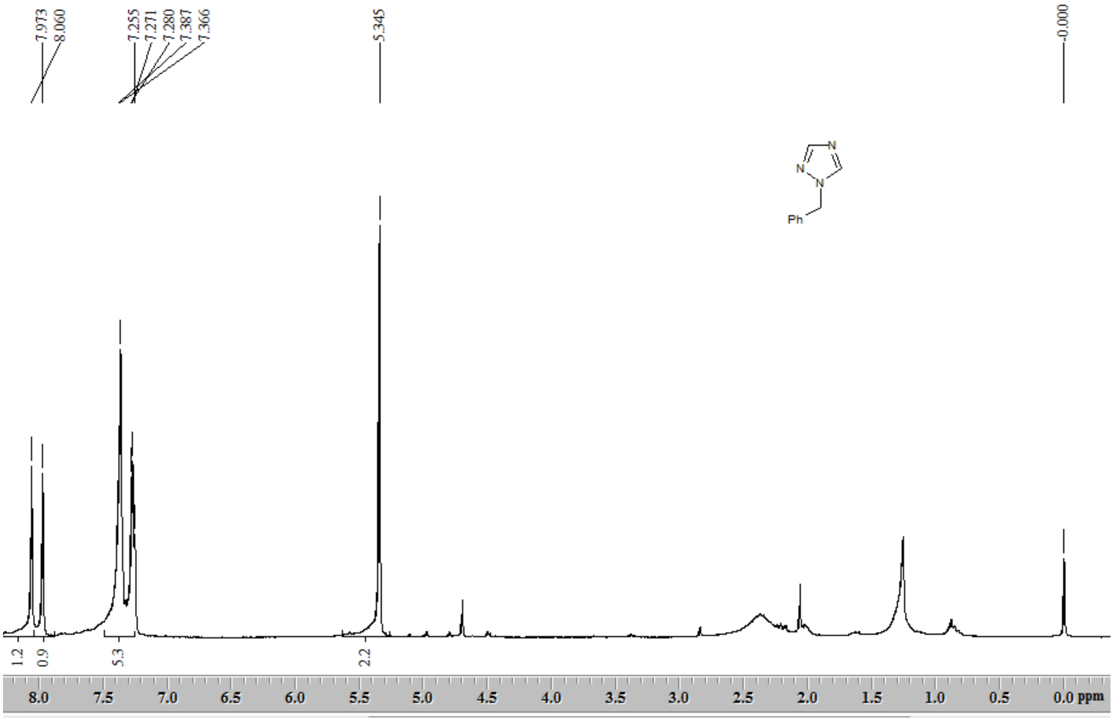

7.345
7.225
7.237
6.945
6.959
6.973
6.492
6.507
6.549
6.565
6.579
7.252
7.267
7.291
7.305
7.317
7.361
4.471
3.351
3.367
3.351
2.801
2.811
2.821
2.003
2.003
2.007
-0.000
N
Ph
5.6
2.0
1.0
1.0
2.2
2.2
2.3
2.3
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0 ppm

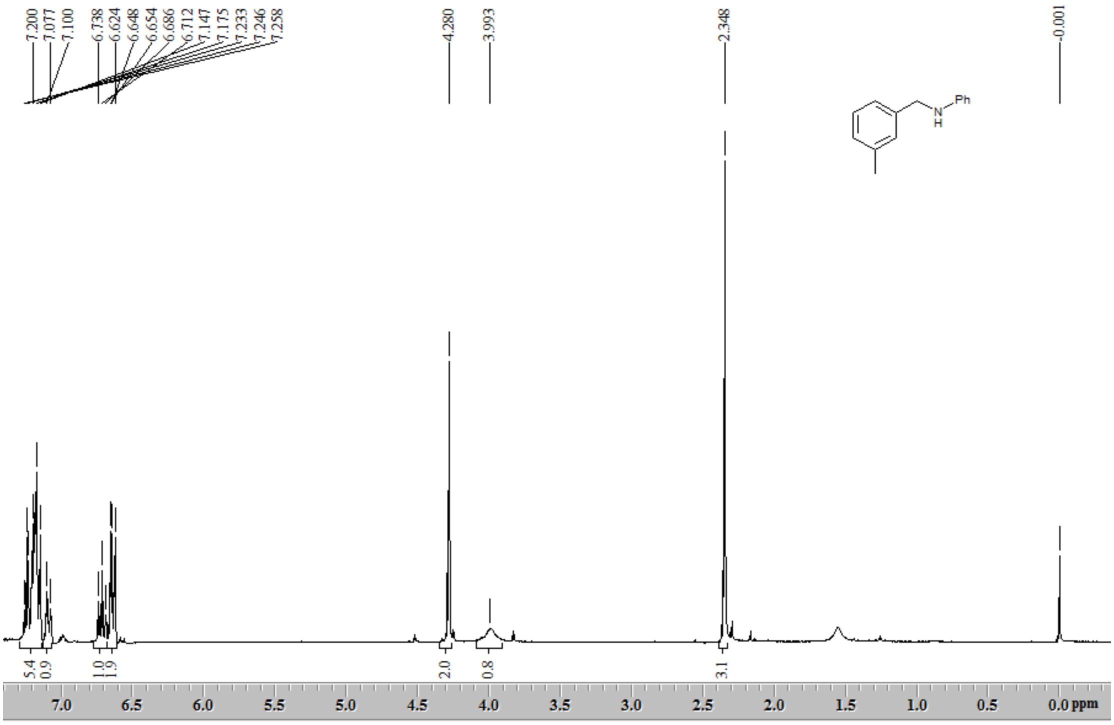

7.340
7.202
7.039
6.915
6.930
7.048
7.215
7.229
7.266
7.283
7.296
7.296
7.353
3.598
3.657
2.865
2.714
2.726
2.737
2.875
2.887
-0.000
N
Ph
5.6
3.2
1.0
2.8
2.7
2.6
2.3
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0 ppm

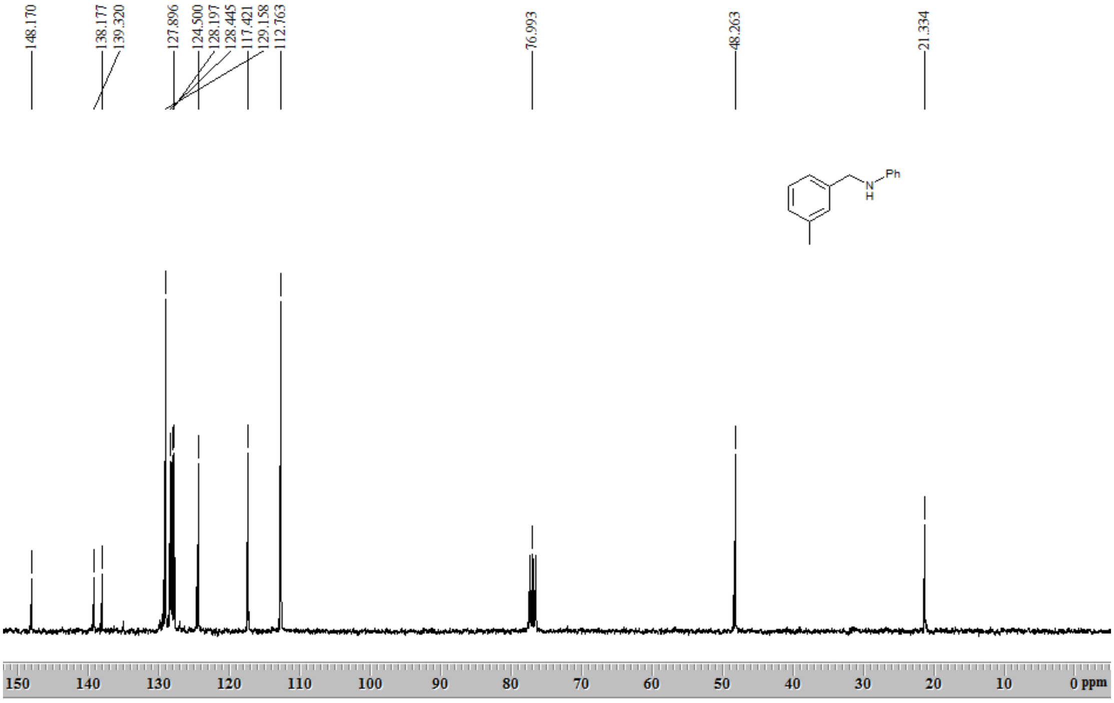

138.270
134.288
134.779
128.199
125.471
125.985
126.520
127.043
128.615
129.021
76.976
62.721
56.031
50.529
N
Ph
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0 ppm

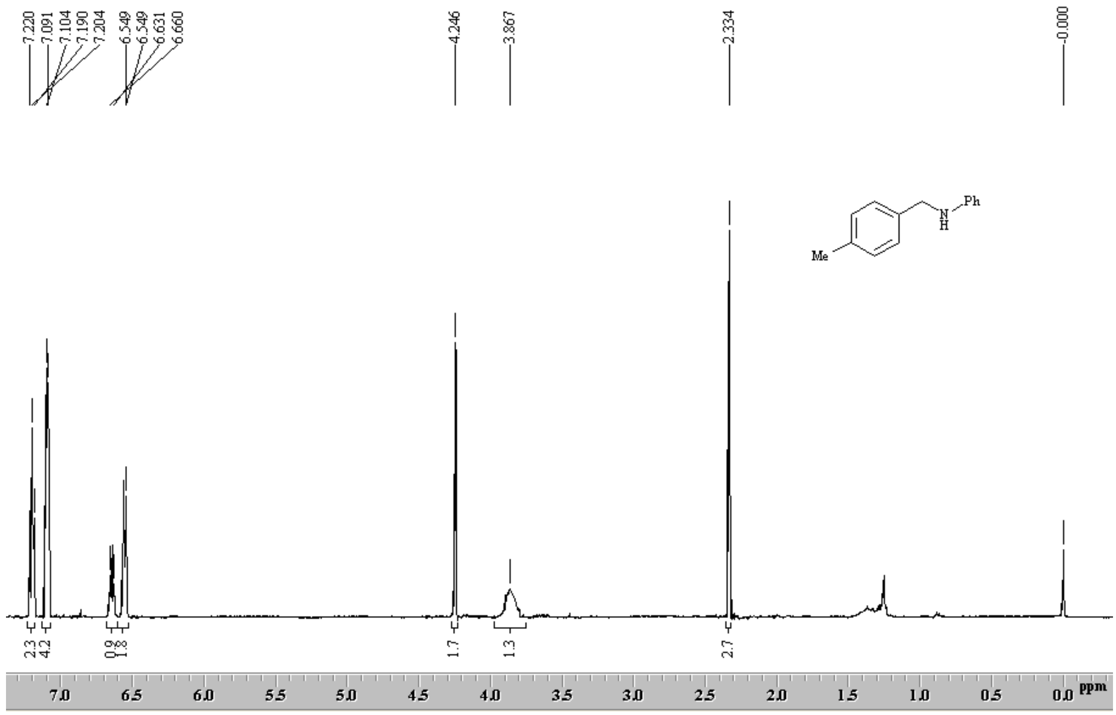

7.547
7.318
7.192
7.213
7.218
7.291
7.341
7.373
7.381
6.279
6.286
6.272
7.552
5.326
-0.000
N
N
Ph
1.0
1.0
5.3
1.0
2.2
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0 ppm

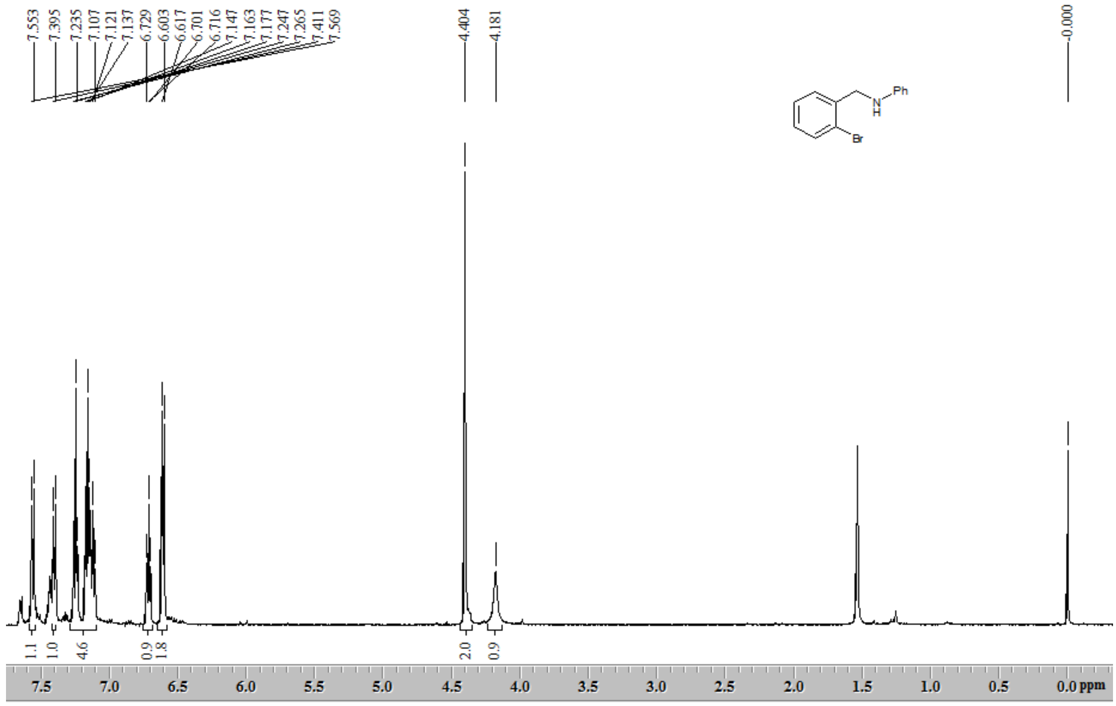

139.365
136.530
127.459
127.831
128.634
129.083
105.810
76.992
55.727
N
N
Ph
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0 ppm

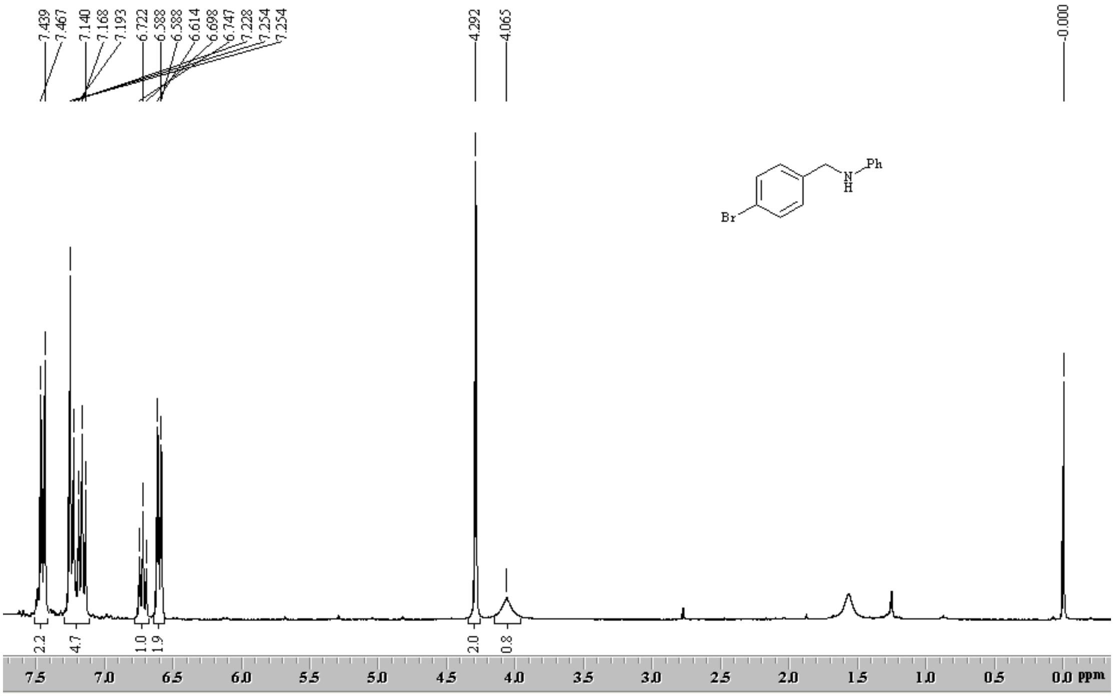

7.973
8.060
7.255
7.271
7.280
7.387
7.366
5.345
-0.000
N
N
N
Ph
1.2
0.9
5.3
2.2
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0 ppm

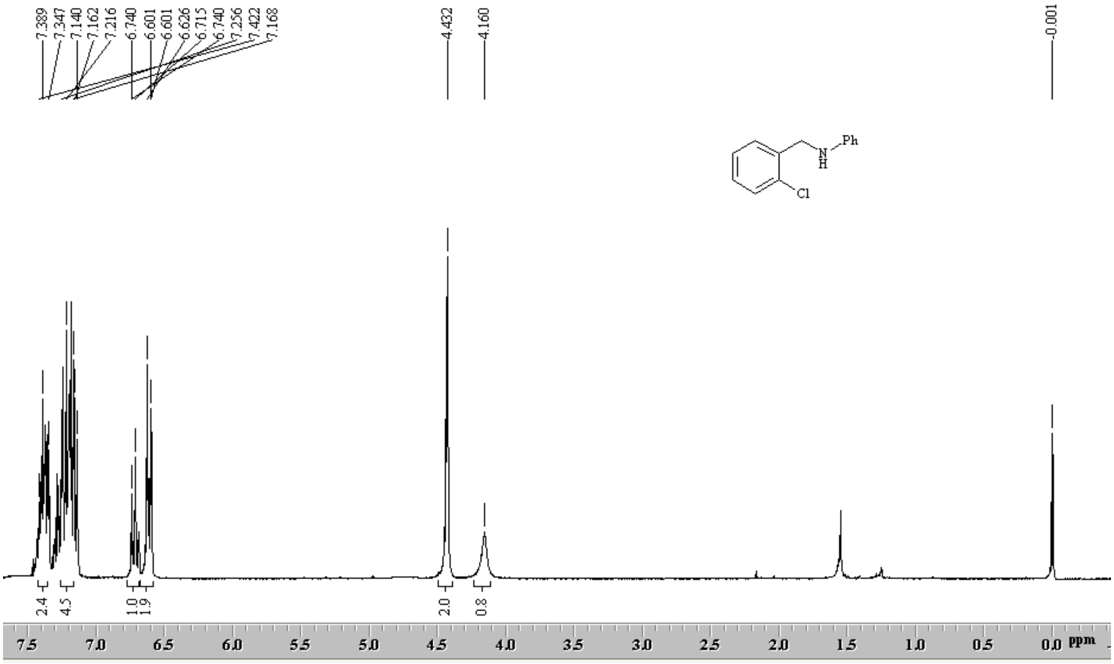

7.200
7.077
7.100
6.738
6.624
6.648
6.654
6.686
6.712
7.147
7.175
7.233
7.246
7.258
4.280
3.993
2.348
-0.001
Ph
N
H
5.4
0.9
1.0
1.9
2.0
0.8
3.1
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0 ppm

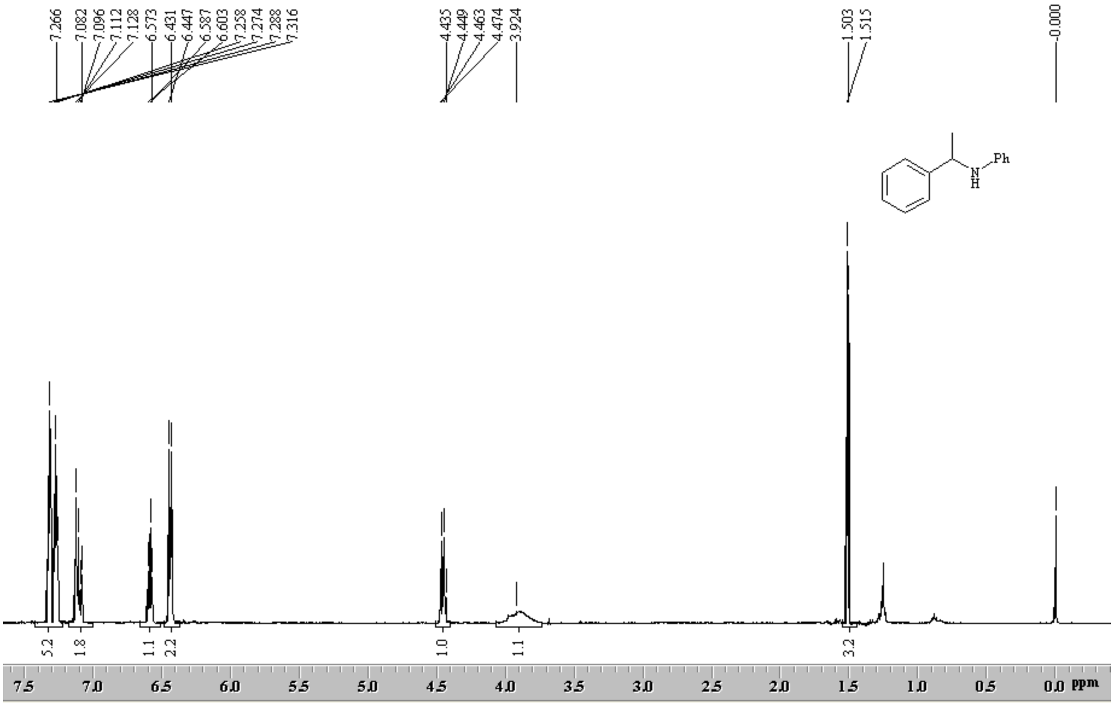

148.170
138.177
139.320
127.896
124.500
128.197
128.445
117.421
129.158
112.763
76.993
48.263
21.334
Ph
N
H
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0 ppm

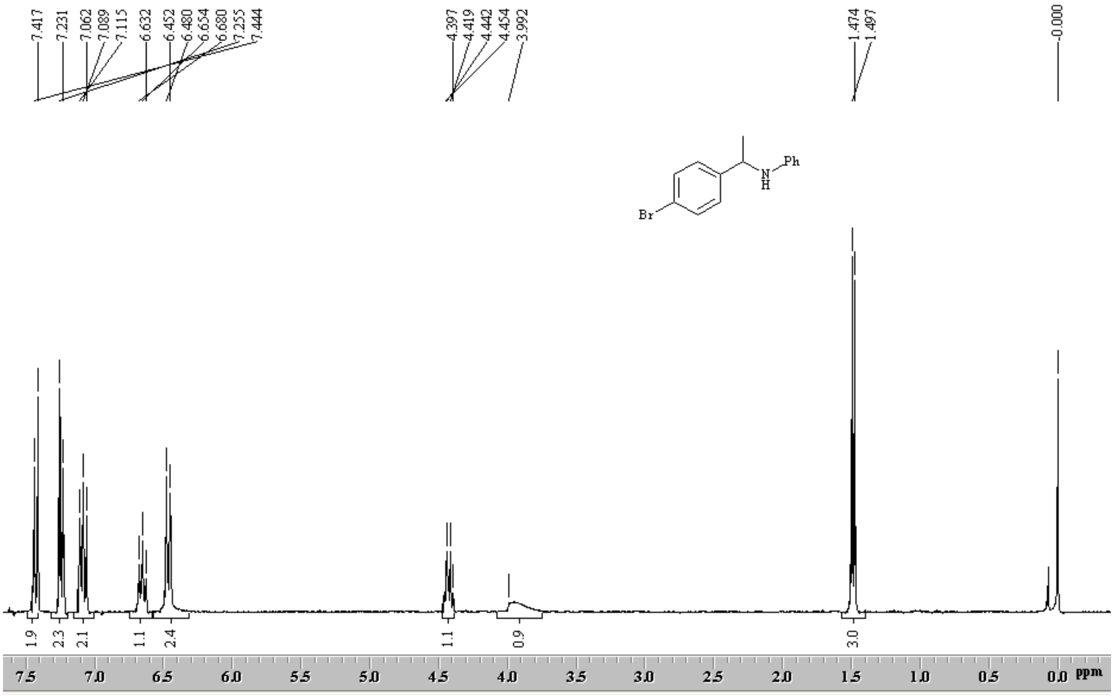

7.220
7.091
7.104
7.190
7.204
6.549
6.549
6.631
6.660
4.246
3.867
2.334
-0.000
Ph
N
H
Me
2.3
4.2
0.9
1.8
1.7
1.3
2.7
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm

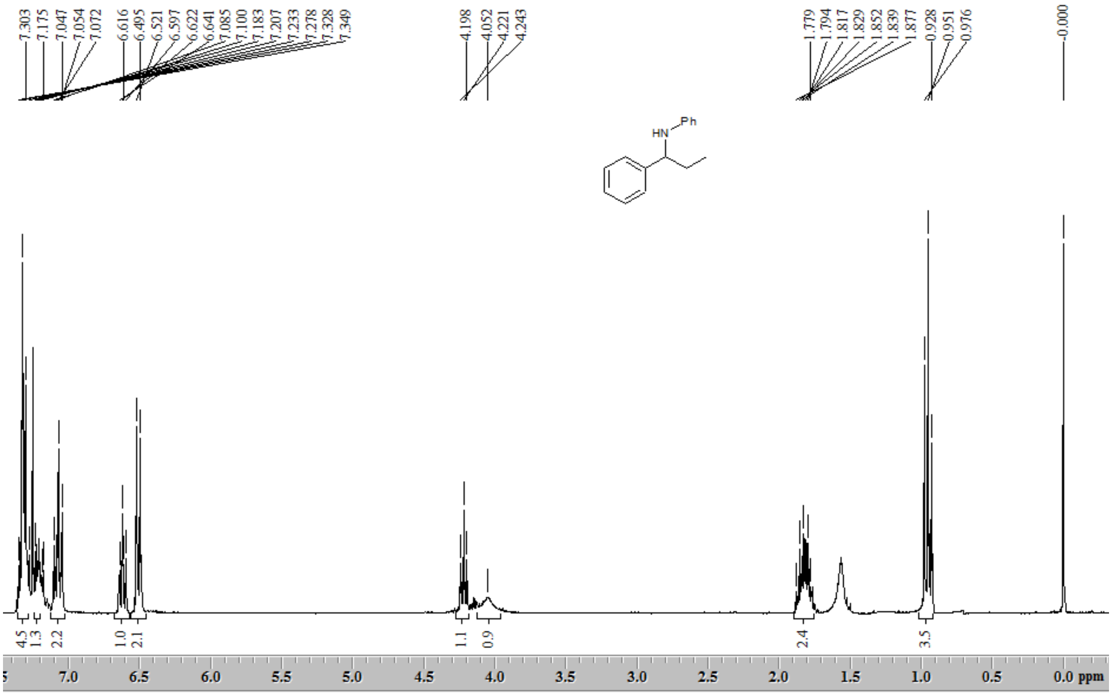

7.553
7.395
7.235
7.107
7.121
7.137
6.729
6.603
6.617
6.701
6.716
7.147
7.163
7.177
7.247
7.265
7.411
7.569
4.404
4.181
-0.000
Ph
N
H
Br
1.1
1.0
4.6
0.9
1.8
2.0
0.9
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0 ppm

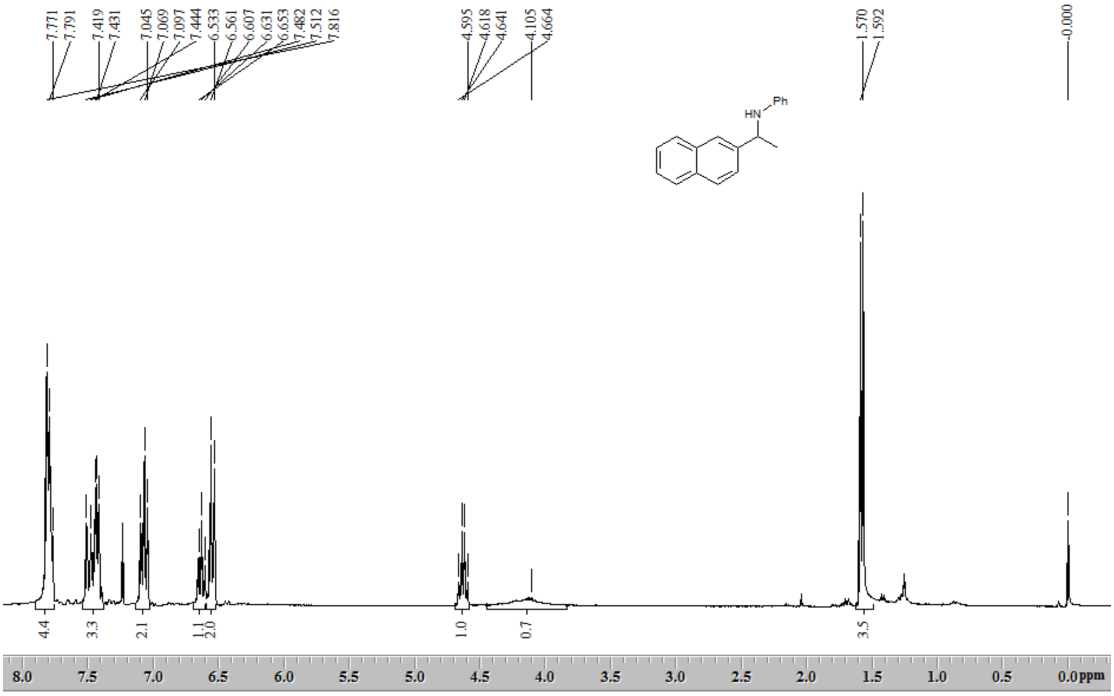

7.439
7.467
7.140
7.168
7.193
6.722
6.588
6.588
6.614
6.698
6.747
7.228
7.254
7.254
4.292
4.065
-0.000
Br
N
H
Ph
2.2
4.7
1.0
1.9
2.0
0.8
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0 ppm

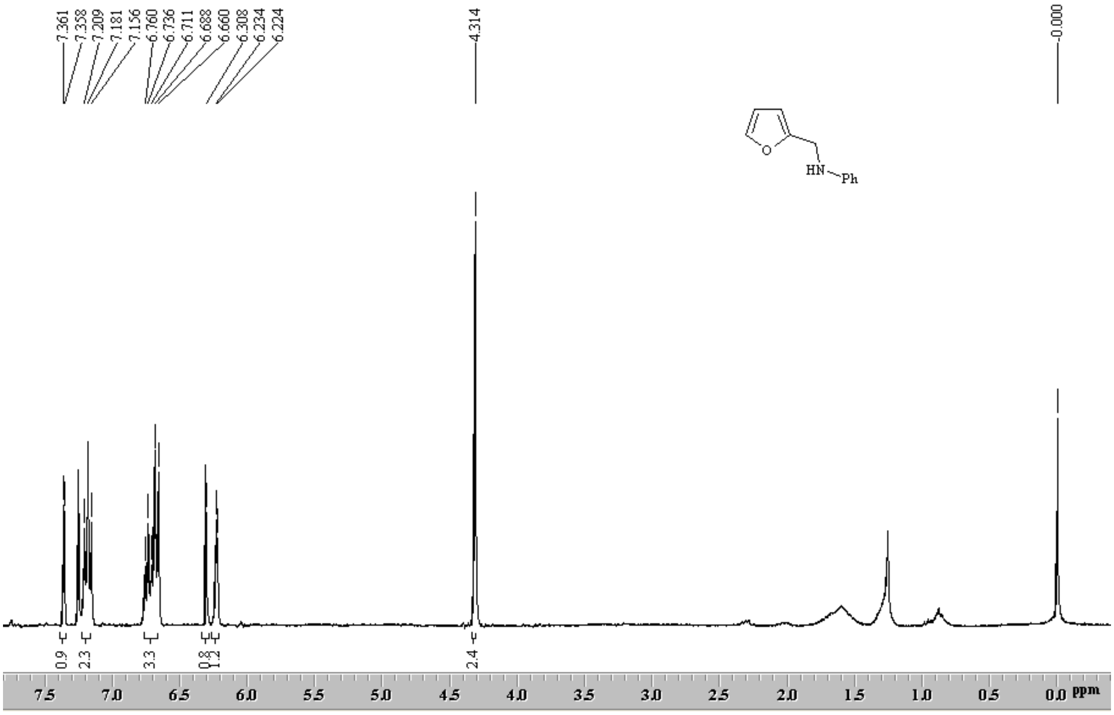

7.389
7.347
7.140
7.162
7.216
6.740
6.601
6.601
6.626
6.715
6.740
7.256
7.422
7.168
4.432
4.160
-0.001
N
H
Ph
Cl
2.4
4.5
1.0
1.9
2.0
0.8
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0 ppm

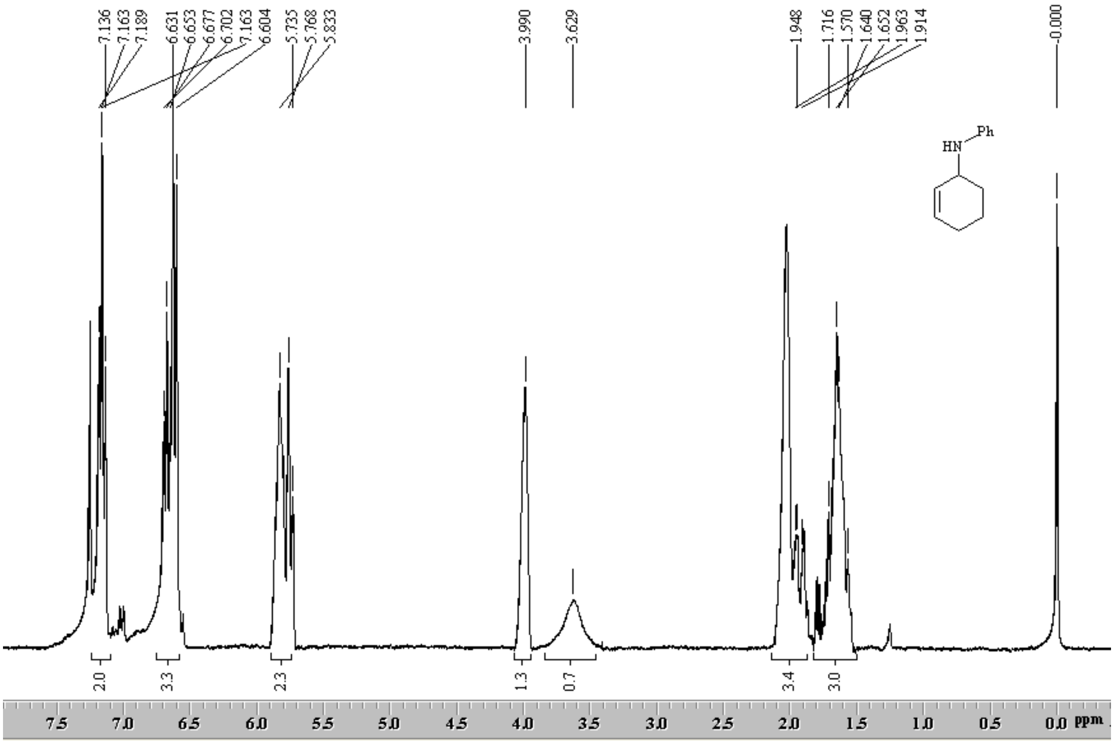

7.266
7.082
7.096
7.112
7.128
6.573
6.431
6.447
6.587
6.603
7.258
7.274
7.288
7.316
4.435
4.449
4.463
4.474
3.924
1.503
1.515
-0.000
Ph
N
H
5.2
1.8
1.1
2.2
1.0
1.1
3.2
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm

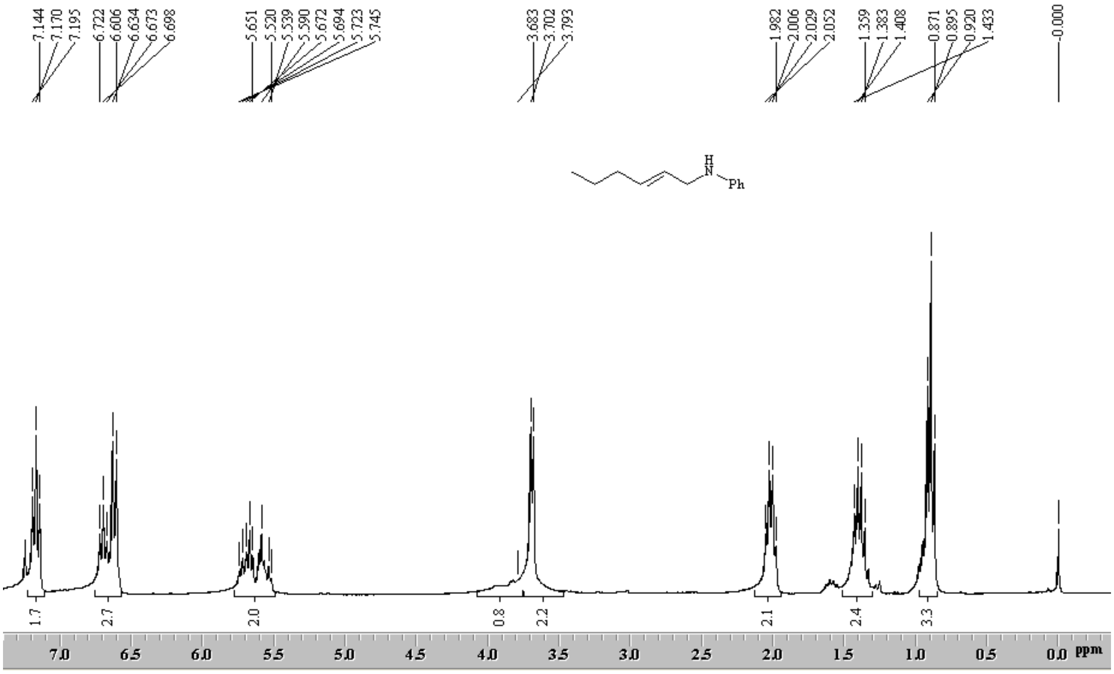

7.417
7.231
7.062
7.089
7.115
6.632
6.452
6.480
6.654
6.680
7.255
7.444
4.397
4.419
4.442
4.454
3.992
1.474
1.497
-0.000
Ph
N
H
Br
1.9
2.3
2.1
1.1
2.4
1.1
0.9
3.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm

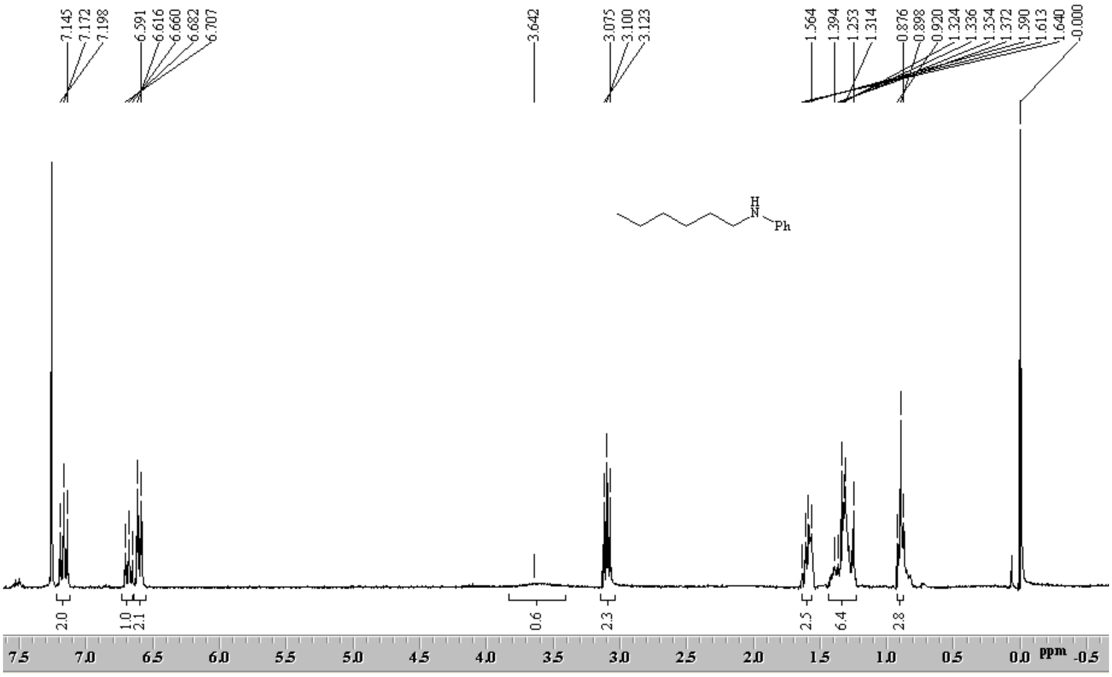

7.303
7.175
7.047
7.054
7.072
6.616
6.495
6.521
6.597
6.622
6.641
7.085
7.100
7.183
7.207
7.233
7.278
7.328
7.349
4.198
4.052
4.221
4.243
1.779
1.794
1.817
1.829
1.852
1.839
1.877
0.928
0.951
0.976
-0.000
HN
Ph
4.5
1.3
2.2
1.0
2.1
1.1
0.9
2.4
3.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0 ppm

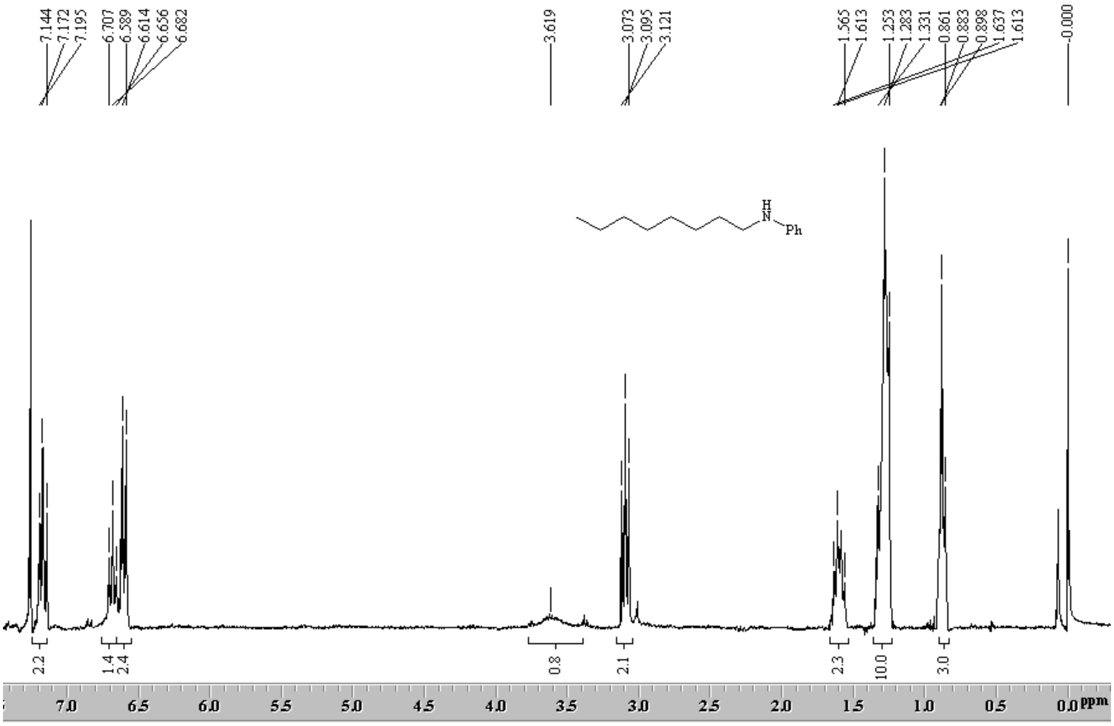

7.771
7.791
7.419
7.431
7.045
7.069
7.097
7.444
6.533
6.561
6.607
6.631
6.653
7.482
7.512
7.816
4.595
4.618
4.641
4.105
4.664
1.570
1.592
-0.000
HN
Ph
4.4
3.3
2.1
1.1
2.0
1.0
0.7
3.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0ppm

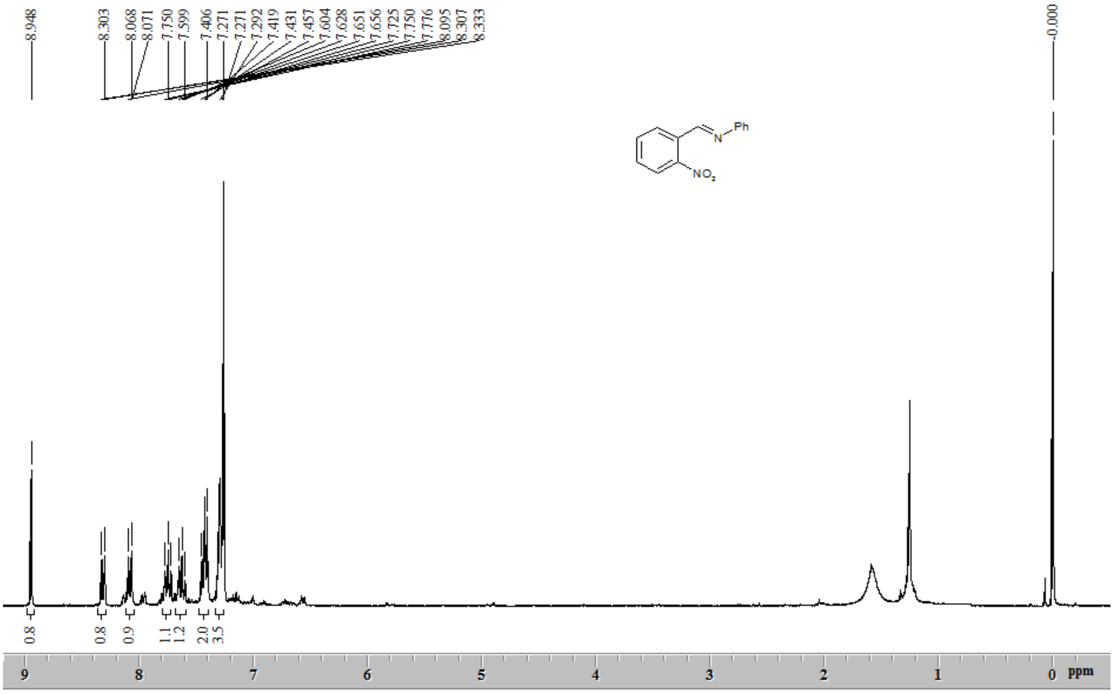

7.361
7.358
7.209
7.181
7.156
6.760
6.736
6.711
6.688
6.660
6.308
6.234
6.224
4.314
-0.000
O
HN
Ph
0.9
2.3
3.3
0.8
1.2
2.4
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm

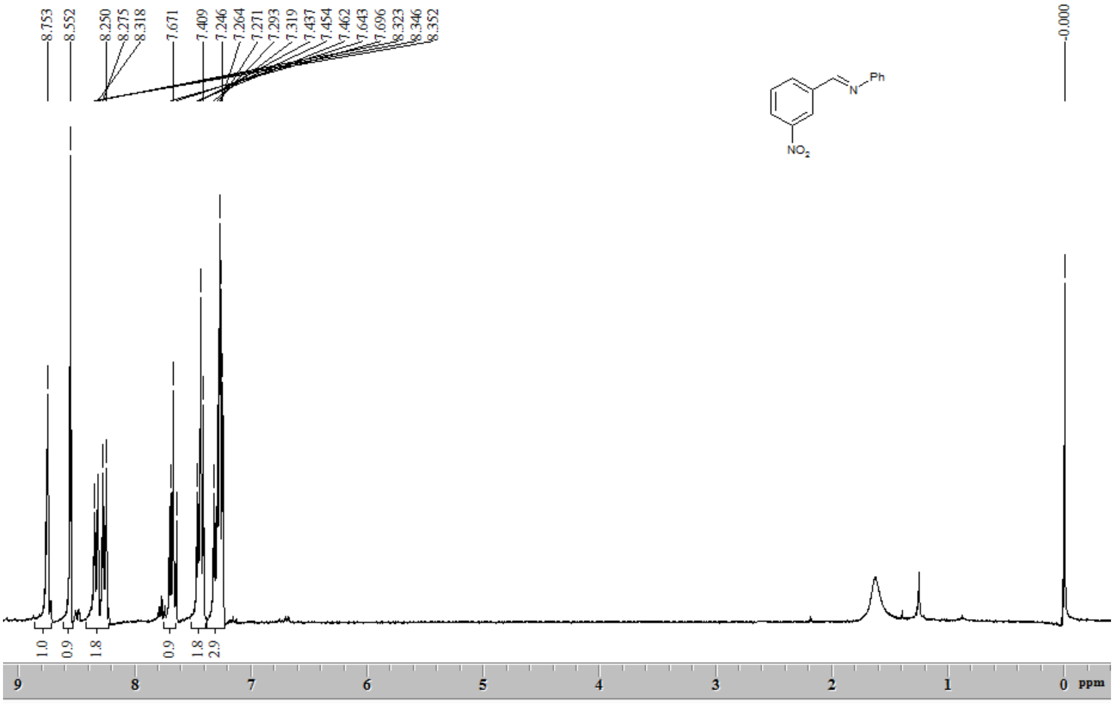

7.136
7.163
7.189
6.631
6.653
6.677
6.702
7.163
6.604
5.735
5.768
5.833
3.990
3.629
1.948
1.716
1.570
1.640
1.652
1.963
1.914
-0.000
HN
Ph
2.0
3.3
2.3
1.3
0.7
3.4
3.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm

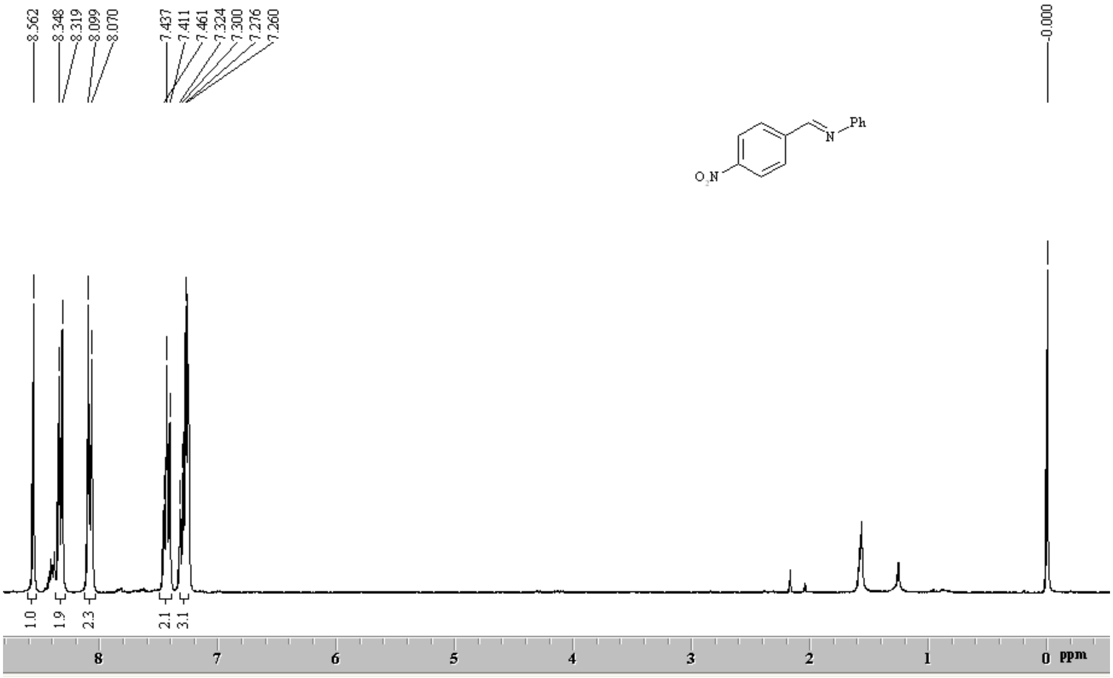

7.144
7.170
7.195
6.722
6.606
6.634
6.673
6.698
5.651
5.520
5.539
5.590
5.672
5.694
5.723
5.745
3.683
3.702
3.793
1.982
2.006
2.029
2.052
1.359
1.383
1.408
0.871
0.895
0.920
1.433
-0.000
H
N
Ph
1.7
2.7
2.0
0.8
2.2
2.1
2.4
3.3
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm

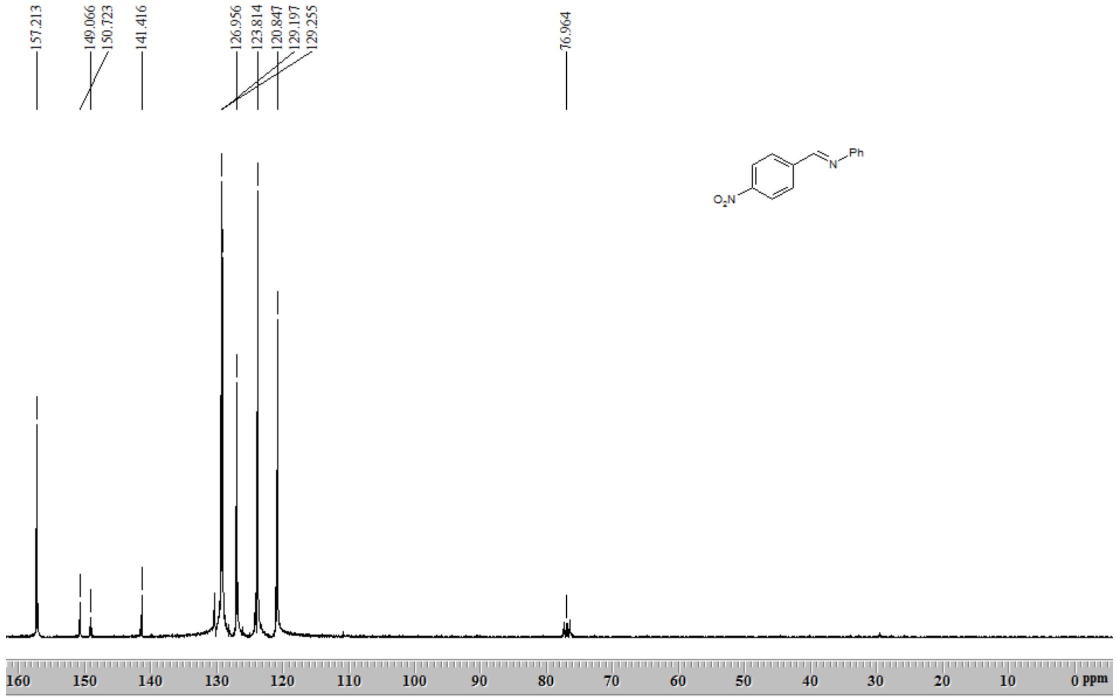

7.145
7.172
7.198
6.591
6.616
6.660
6.682
6.707
3.642
3.075
3.100
3.123
1.564
1.394
1.253
1.314
0.876
0.898
0.920
1.324
1.336
1.354
1.372
1.590
1.613
1.640
-0.000
H
N
Ph
2.0
1.0
2.1
0.6
2.3
2.5
6.4
2.8
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
-0.5

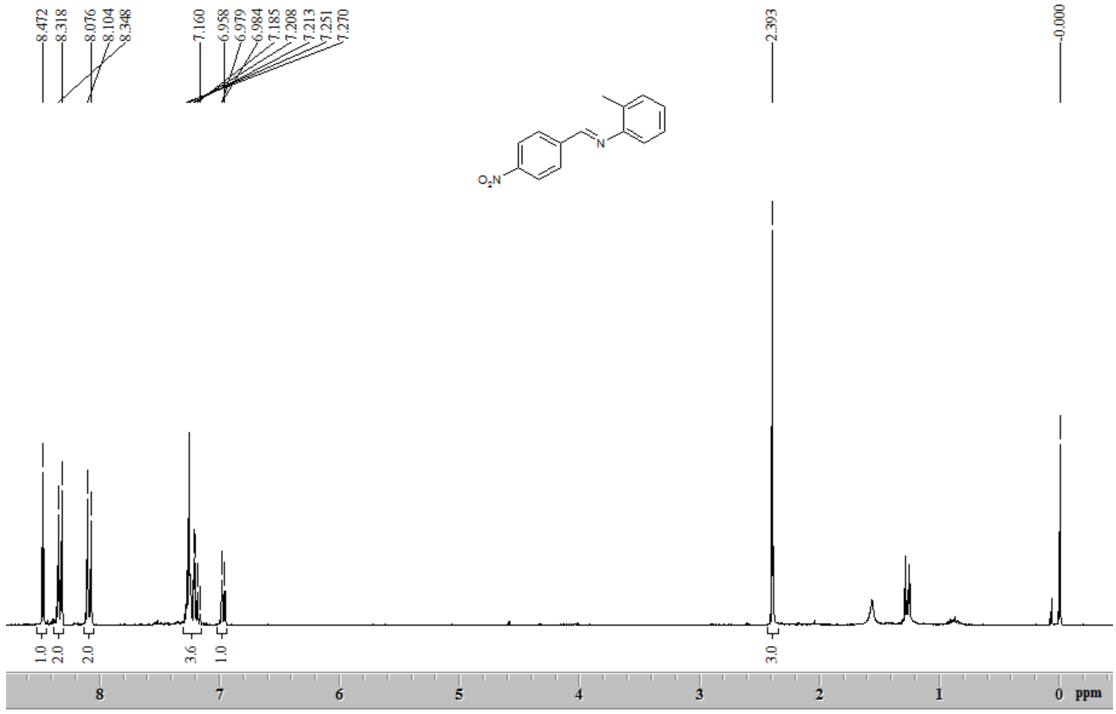

7.144
7.172
7.195
6.707
6.589
6.614
6.656
6.682
3.619
3.073
3.095
3.121
1.565
1.613
1.253
1.283
1.331
0.861
0.883
0.898
1.637
1.613
0.000
H
N
Ph
2.2
1.4
2.4
0.8
2.1
2.3
10.0
3.0
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm

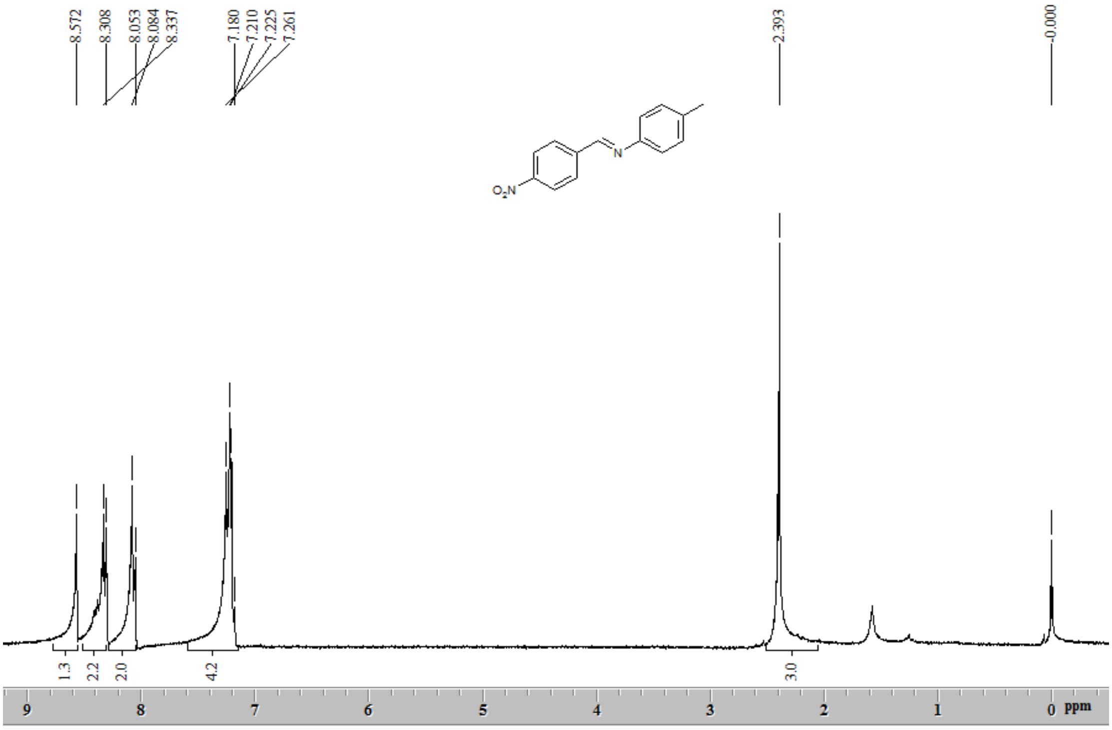

8.948
8.303
8.068
8.071
7.750
7.599
7.406
7.271
7.271
7.292
7.419
7.431
7.457
7.604
7.628
7.651
7.656
7.725
7.750
7.776
8.095
8.307
8.333
0.000
Ph
N
NO2
0.8
0.8
0.9
1.1
1.2
2.0
3.5
9
8
7
6
5
4
3
2
1
0
ppm

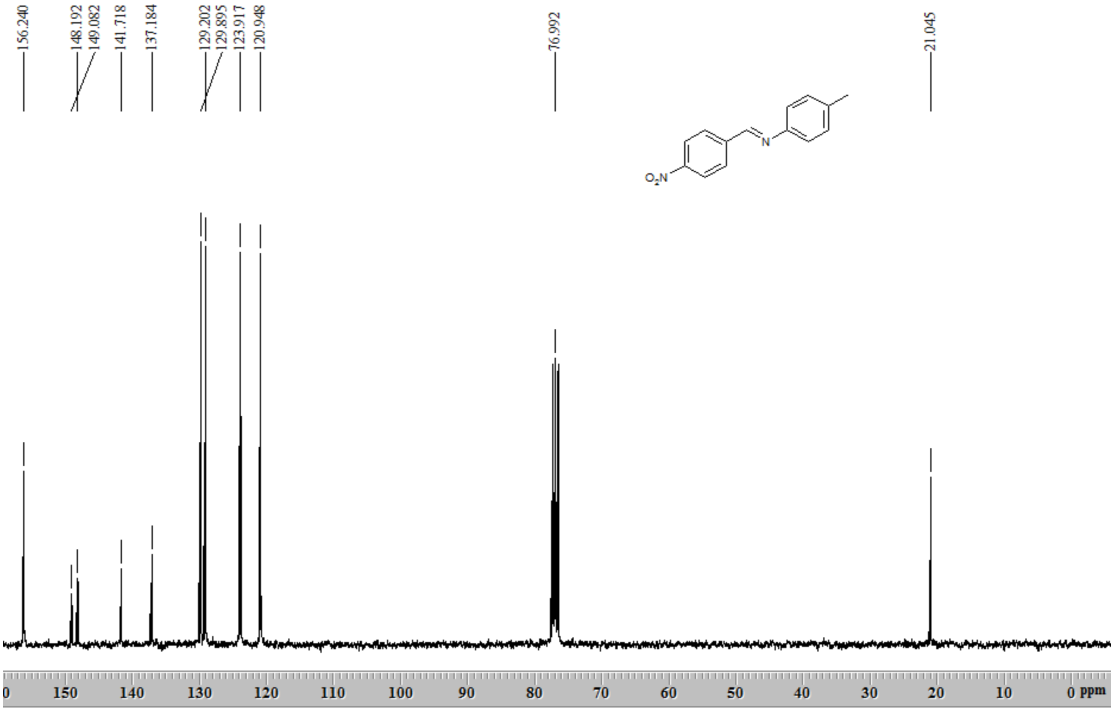

8.753
8.552
8.250
8.275
8.318
7.671
7.409
7.246
7.264
7.271
7.293
7.319
7.437
7.454
7.462
7.643
7.696
8.323
8.346
8.352
-0.000
N
Ph
NO$_2$
1.0
0.9
1.8
0.9
1.8
2.9
9
8
7
6
5
4
3
2
1
0
ppm

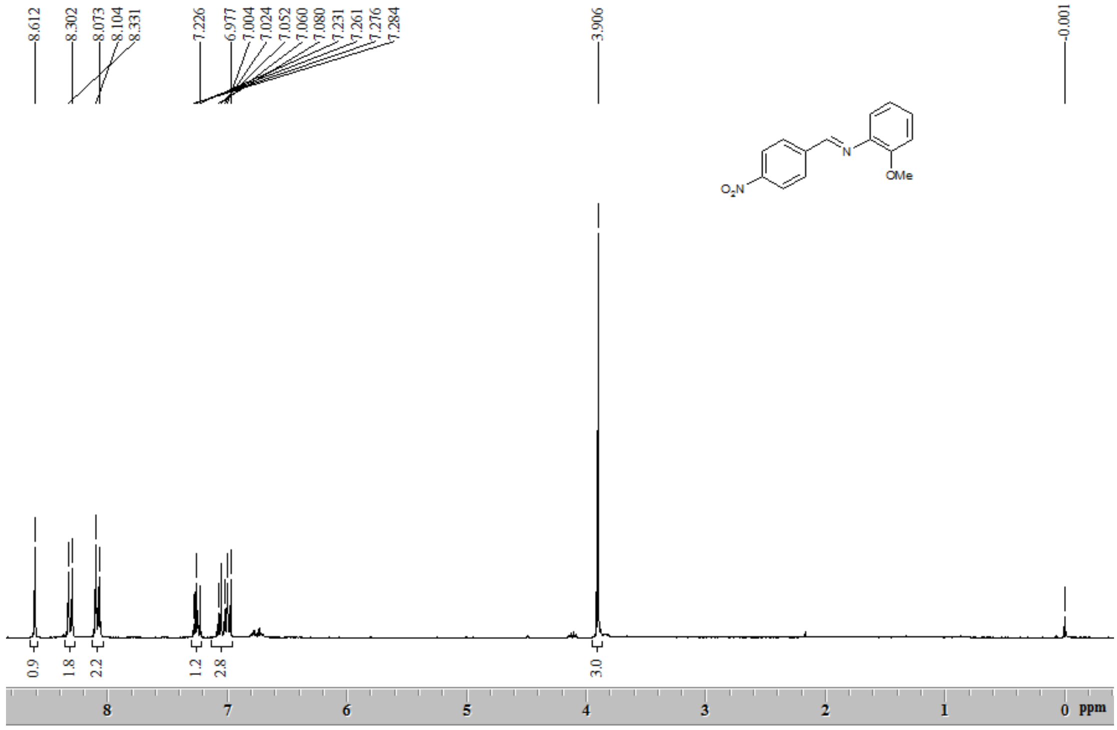

8.562
8.348
8.319
8.099
8.070
7.437
7.411
7.461
7.324
7.300
7.276
7.260
-0.000
N
Ph
O$_2$N
1.0
1.9
2.3
2.1
3.1
8
7
6
5
4
3
2
1
0
ppm

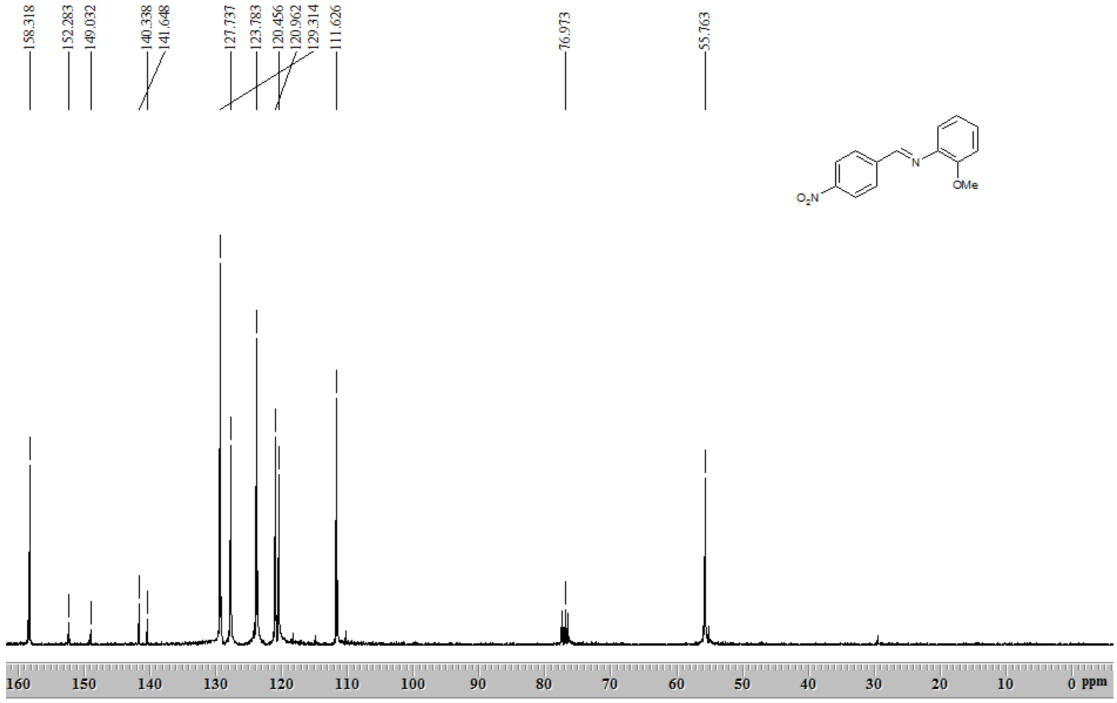

157.213
149.066
150.723
141.416
126.956
123.814
120.847
129.197
129.255
76.964
O2N
N
Ph
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0 ppm

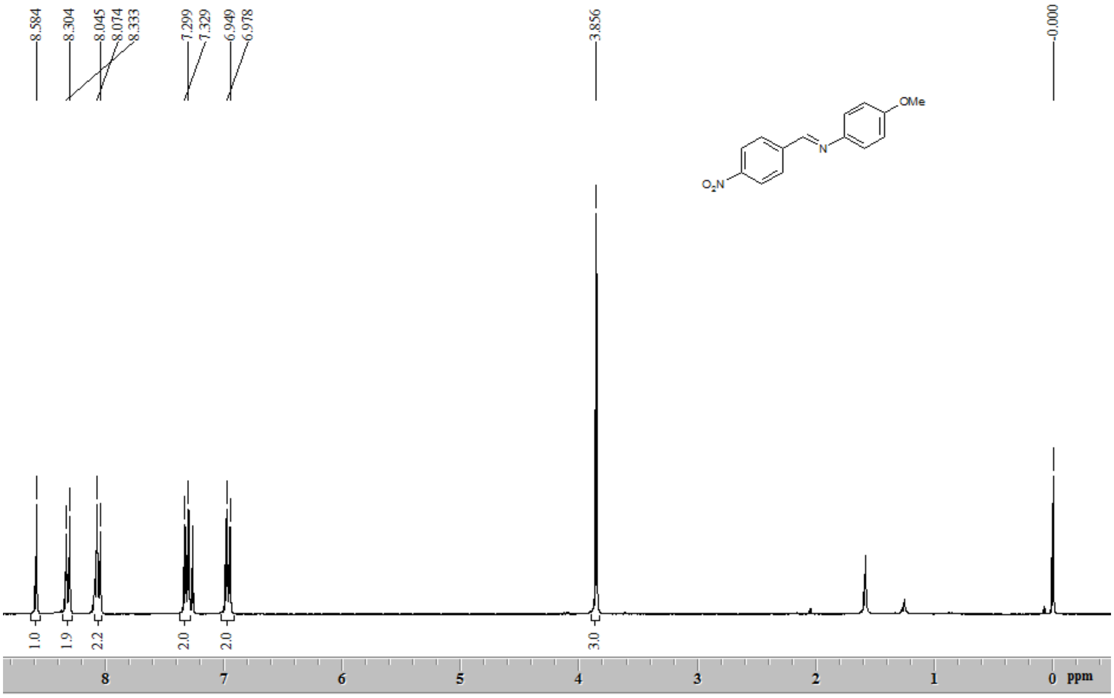

8.472
8.318
8.076
8.104
8.348
7.160
6.958
6.979
6.984
7.185
7.208
7.213
7.251
7.270
2.393
-0.000
O2N
N
1.0
2.0
2.0
3.6
1.0
3.0
8
7
6
5
4
3
2
1
0
ppm

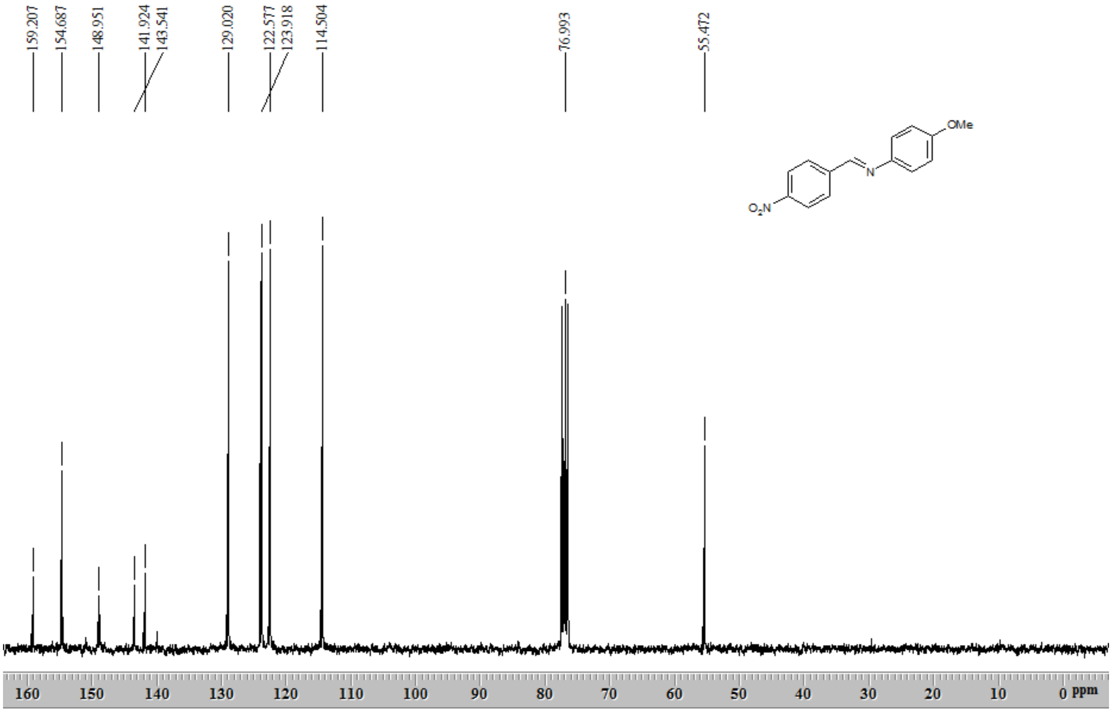

8.572
8.308
8.053
8.084
8.337
7.180
7.210
7.225
7.261
2.393
0.000
O2N
N
1.3
2.2
2.0
4.2
3.0
9
8
7
6
5
4
3
2
1
0 ppm

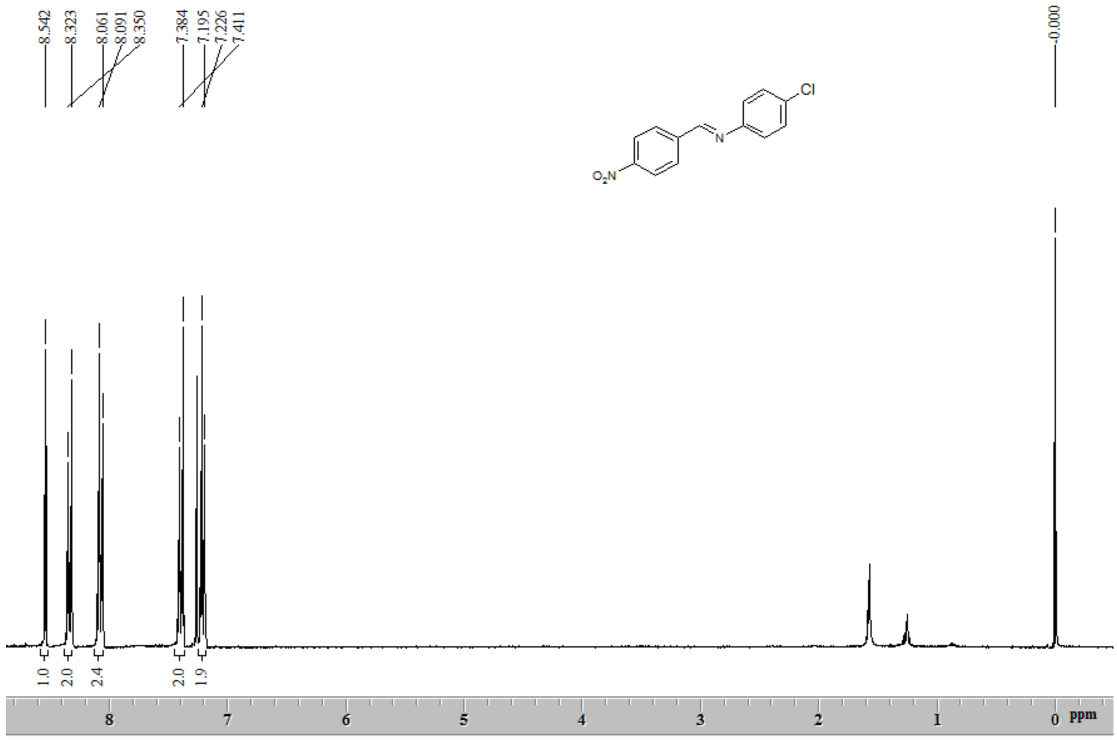

156.240
148.192
149.082
141.718
137.184
129.202
129.895
123.917
120.948
76.992
21.045
O2N
N
0
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0 ppm

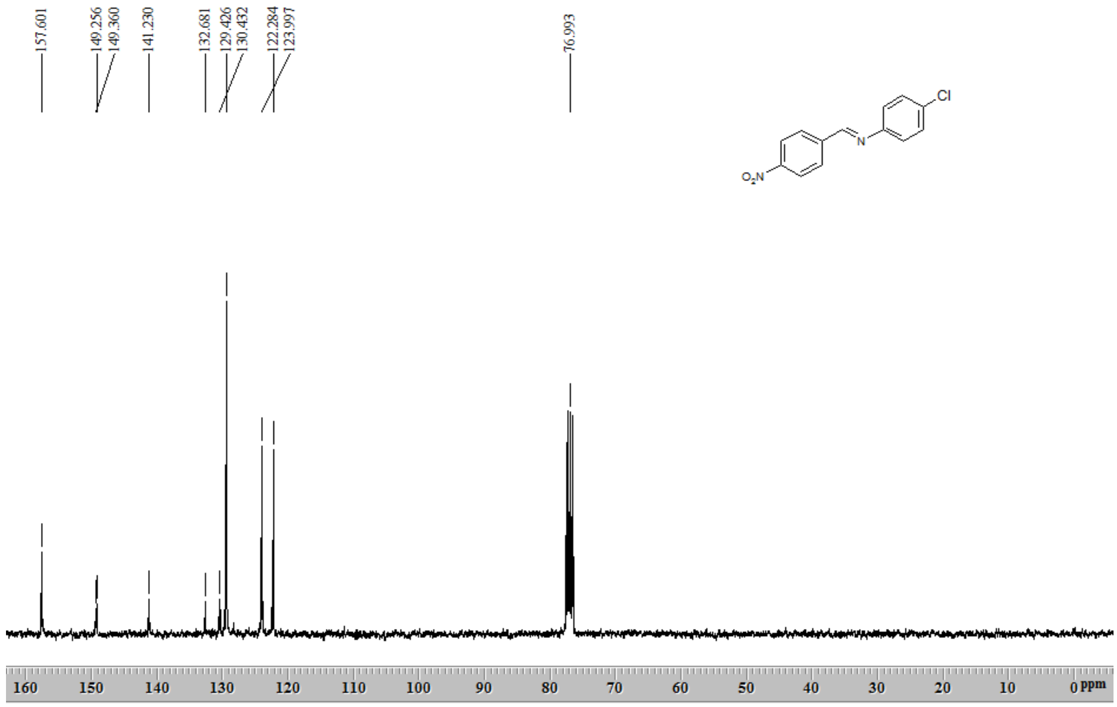

8.612
8.302
8.073
8.104
8.331
7.226
6.977
7.004
7.024
7.052
7.060
7.080
7.231
7.261
7.276
7.284
3.906
-0.001
O2N
N
OMe
0.9
1.8
2.2
1.2
2.8
3.0
8
7
6
5
4
3
2
1
0 ppm

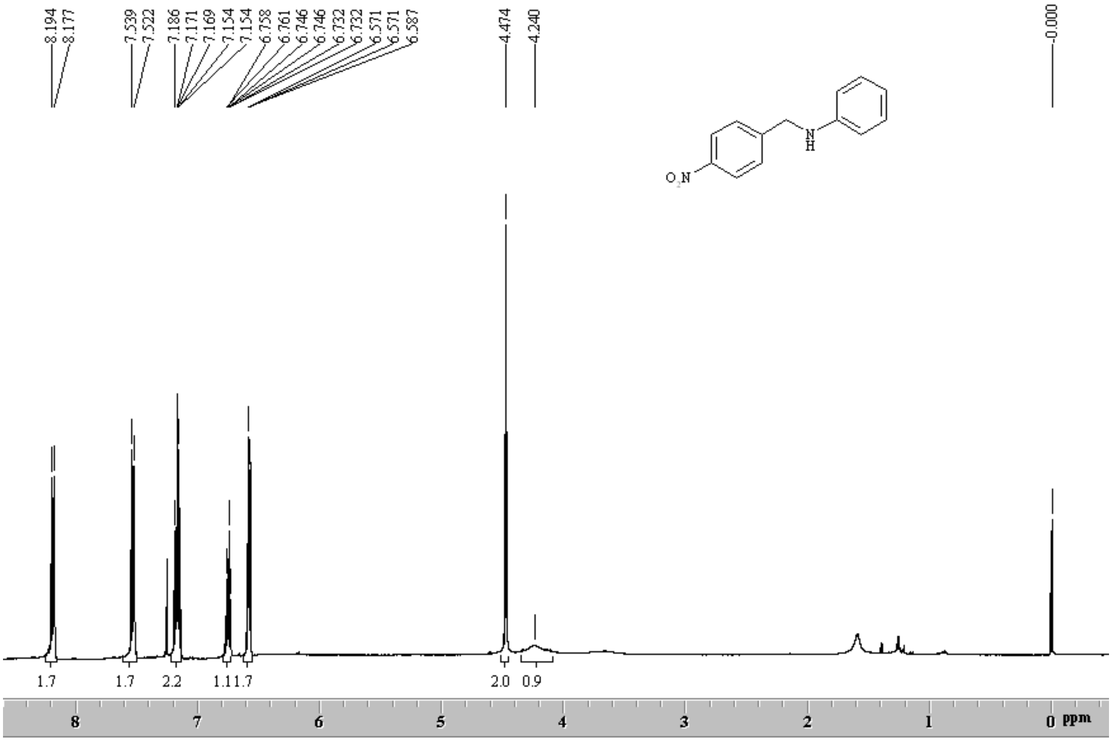

158.318
152.283
149.032
140.338
141.648
127.737
123.783
120.456
120.962
129.314
111.626
76.973
55.763
O2N
N
OMe
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0 ppm

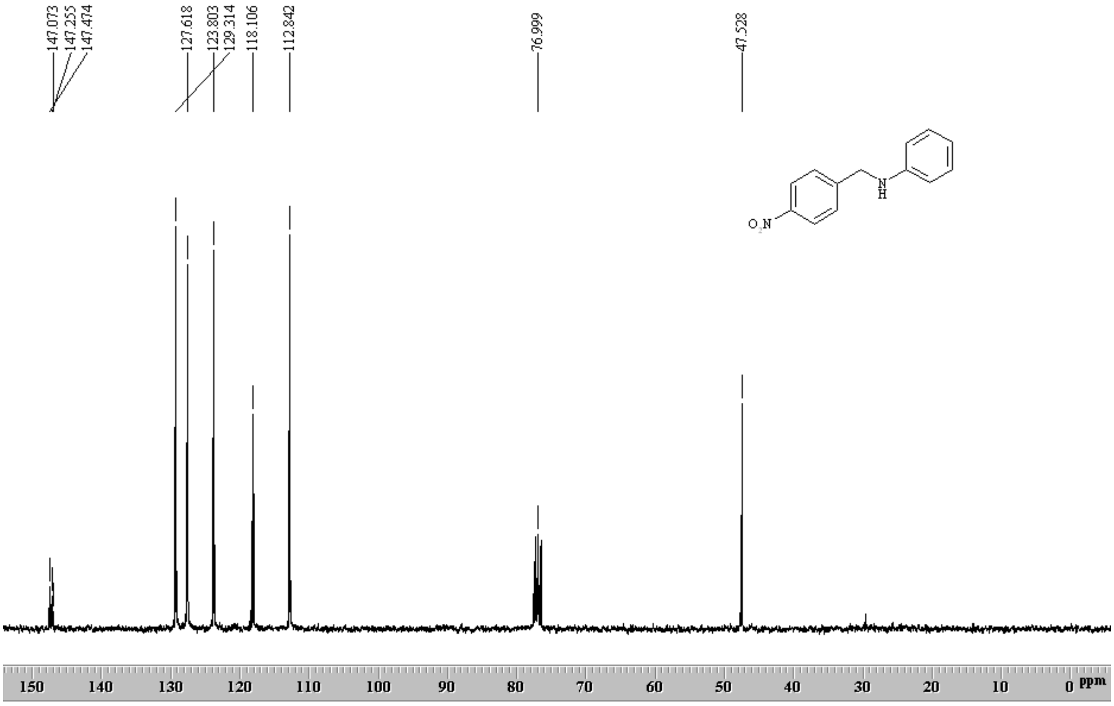

8.584
8.304
8.045
8.074
8.333
7.299
7.329
6.949
6.978
3.856
-0.000
OMe
N
O_2N
1.0
1.9
2.2
2.0
2.0
3.0
8
7
6
5
4
3
2
1
0 ppm

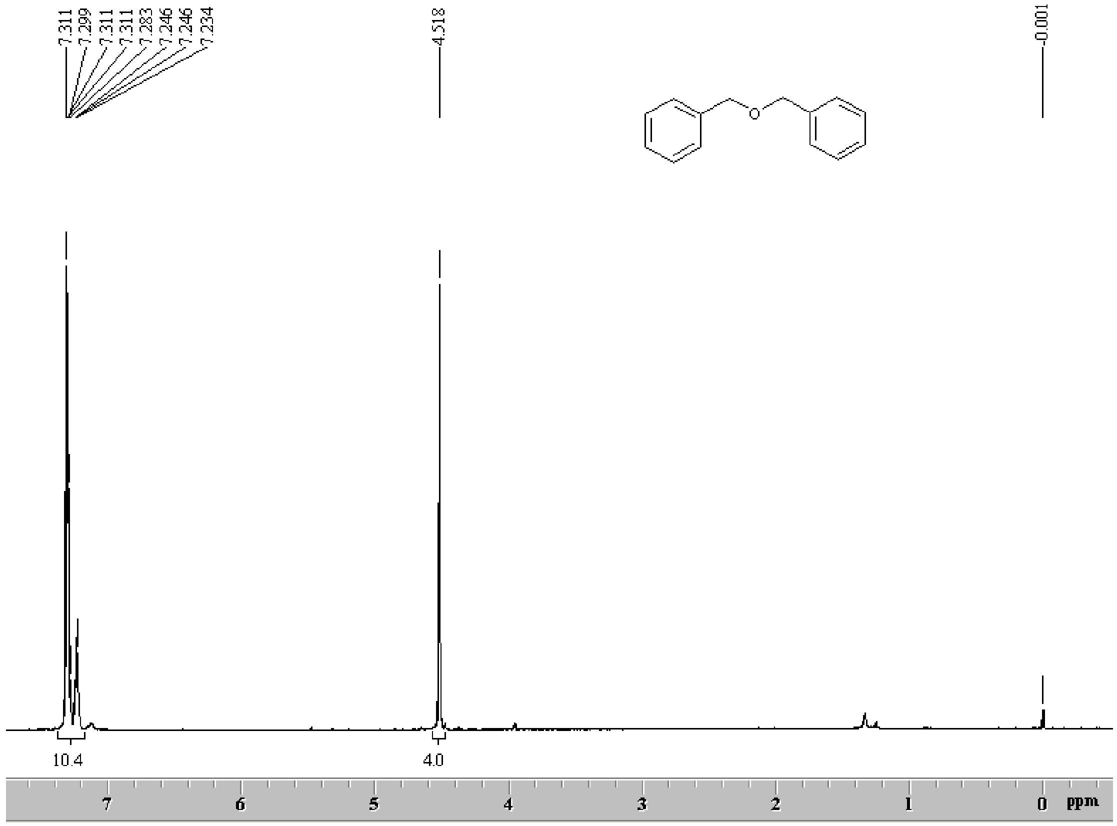

159.207
154.687
148.951
141.924
143.541
129.020
122.577
123.918
114.504
76.993
55.472
OMe
N
O_2N
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0 ppm

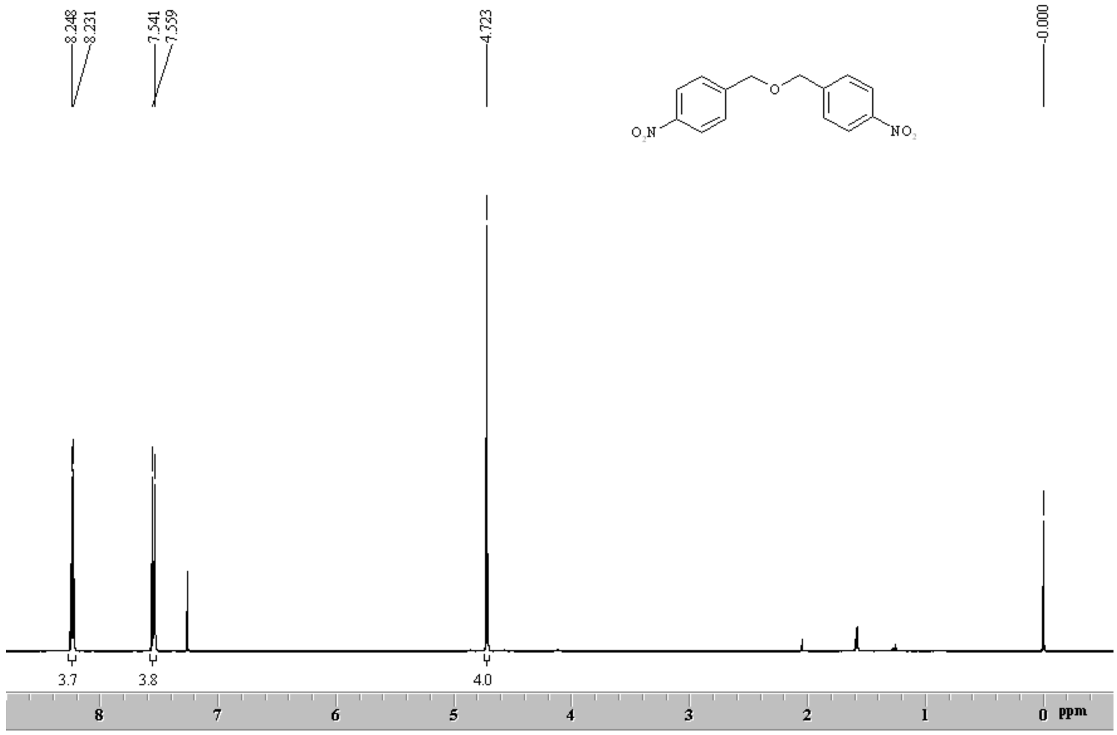

8.542
8.323
8.061
8.091
8.350
7.384
7.195
7.226
7.411
-0.000
Cl
N
O2N
1.0
2.0
2.4
2.0
1.9
8
7
6
5
4
3
2
1
0
ppm


157.601
149.256
149.360
141.230
132.681
129.426
130.432
122.284
123.997
76.993
Cl
N
O2N
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


8.194
8.177
7.539
7.522
7.186
7.171
7.169
7.154
7.154
6.758
6.761
6.746
6.746
6.732
6.732
6.571
6.571
6.587
4.474
4.240
-0.000
O_2N
N
H
1.7
1.7
2.2
1.1
1.7
2.0
0.9
8
7
6
5
4
3
2
1
0 ppm


147.073
147.255
147.474
127.618
123.803
129.314
118.106
112.842
76.999
47.528
O_2N
N
H
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0 ppm


7.311
7.299
7.311
7.311
7.283
7.246
7.246
7.234
4.518
-0.001
O
10.4
4.0
7
6
5
4
3
2
1
0
ppm


8.248
8.231
7.541
7.559
4.723
-0.000
O
O_2N
NO_2
3.7
3.8
4.0
8
7
6
5
4
3
2
1
0
ppm

Notes and references

1 T. Yashima and N. Hara, *J. Catal.,* 1972, **27,** 329-333.
2 T. Barzetti, E. Selli, D. Moscotti and L. Forni, *J. Chem. Soc., Faraday Trans.,* 1996, **92,** 1401-1407
3 R. Kawahara, K. Fujita and R. Yamaguchi, *Adv. Synth. Catal*., 2011, **353,** 1161–1168.
4 C. T. Yang, Y. Fu, Y. B. Huang, J. Yi, Q. X. Guo and L. Liu, *Angew. Chem., Int. Ed.,* 2009, **121,** 7534–7537.
5 J. P. Wolfe and S. L. Buchwald, *J. Org. Chem.,* 1997, **62,** 1264-1267.
6 Y. Zhao, S. W. Foo and S. Saito, *Angew. Chem., Int. Ed.,* 2011, **50,** 3006-3009.
7 X. Cui, Y. Zhang, F. Shi, and Y. Deng, *Chem. Eur. J.,* 2011, **17,** 2587–2591.
8 P. R. Likhar, R. Arundhathi, M. L. Kantam and P. S. Prathima, *Eur. J. Org. Chem.***,** 2009, 5383–5389.
9 V. Kumar, U. Sharma, P. K. Verma, N. Kumar and B. Singh, *Adv. Synth. Catal.,* 2012, **354,** 870–878.
10 S. Hayat, Atta-ur-Rahman, M. I. Choudhary, K. M. Khan, W. Schumann and E. Bayer, *Tetrahedron,* 2001, **57,** 9951-9957.
11 M. Zhang, H. Yang, Y. Zhang, C. Zhu, W. Li, Y. Cheng and H. Hu, *Chem. Commun.,* 2011, **47,** 6605–6607.
12 A. Hu, M. Ogasawara, T. Sakamoto, A. Okada, K. Nakajima, T. Takahashi and W. Lin, *Adv. Synth. Catal.,* 2006, **348,** 2051-2056.
13 Z. Wang, C. Wang, L. Zhou and J. Sun, *Org. Biomol. Chem.,* 2013, **11,** 787–797.
14 H. Duan, S. Sengupta, J. L. Petersen, N. G. Akhmedov and X. Shi, *J. Am. Chem. Soc.,* 2009, **131,** 12100–12102.
15 A. Martinez-Asencio, D. J. Ramon and M. Yus, *Tetrahedron,* 2011, **67,** 3140-3149.
16 F. Ozawa, H. Okamoto, S. Kawagishi, S. Yamamoto, T. Minami and M. Yoshifuji, *J. Am. Chem. Soc.,* 2002, **124,** 10968-10969.
17 B. P. Fors, D. A. Watson, M. R. Biscoe and S. L. Buchwald, *J. Am. Chem. Soc.,* 2008, **130,** 13552–13554.
18 C. W. Chen, M. C. Tseng, S. K. Hsiao, W. H. Chen and Y. H. Chu, *Org. Biomol. Chem.,* 2011, **9,** 4188–4193.
19 R. Torregrosa, I. M. Pastor and M. Yus, *Tetrahedron,* 2005, **61,** 11148–11155.
20 R. Akaba, H. Sakuragi and K. Tokumaru, *Bull. Chem. Soc. Jpn.,* 1985, **58,** 1186-1195.
21 R. Hevey and C. C. Ling, *Org. Biomol. Chem*., 2013, **11,** 1887-1895.
22 J. Chen, L. Dang, Q. Li, Y. Ye, S. Fu and W. Zeng, *Synlett*, 2012, 595-600.