10.1071/CH14659_AC

Australian Journal of Chemistry 2015, 68 (5), 844-848

Supplementary Material

An Efficient Microwave Synthesis of Imines

Emily C. Border,[A] Victoria L. Blair,[A] and Philip C. Andrews[A,B]
[A]School of Chemistry, Monash University, Clayton, Vic. 3800, Australia.
[B]Corresponding author. Email: phil.andrews@monash.edu

General procedure for compounds (1-32). To a microwave vial containing 3Å molecular sieves; 3 ml of dry DCM was added and allowed to stir. The selected amine (2 mmol) and the chosen aldehyde (2 mmol) were added consecutively and the microwave vial capped. This was reacted in a microwave reactor at 50°C, 300W for 10 minutes, unless otherwise stated. The reaction mixture is filtered and the solvent removed *in vacuo* to yield the desired product.

(*S*)-N-(4-methoxybenzylidene)-α-methylbenzylamine 1a. The reactants; (*S*)-N--methylbenzylamine (0.26 ml, 2 mmol) and *p*-Anisaldehyde (0.24 ml, 2 mmol) were reacted according to the general procedure. An opaque oil was obtained: 0.47 g, 98 % yield. **^{1}H NMR (400 MHz, CDCl$_3$):** δ 8.21 (1H, S, N=C(*H*)-), 7.64 (2H, d, $^3J_{HH}$: 8.8 Hz, *o*-Ar), 7.34 (2H, d, 7.2 Hz, *o*-Ar), 7.24 (2H, t, $^3J_{HH}$: 7.4 Hz, *m*-Ar), 7.14 (1H, t, $^3J_{HH}$: 8.0 Hz, *p*-Ar), 6.83 (2H, d, $^3J_{HH}$: 8.8 Hz, *m*-Ar), 4.41 (1H, q, $^3J_{HH}$: 6.8 Hz, PhC(*H*)CH$_3$), 3.73 (3H, s, OC*H*$_3$), 1.50 (3H, d, $^3J_{HH}$: 7.2 Hz, PhC(H)C*H*$_3$). **^{13}C NMR (100 MHz, CDCl$_3$):** δ 161.7 (*ipso*-C), 158.9 (N=C), 145.6 (ArC), 129.9 (*ortho*-C), 129.5 (*meta*-C), 128.5 (*ortho*-C), 126.9 (*para*-C), 126.7 (*meta*-C), 114.0 (*meta*-C), 69.7 (Ph*C*H(Me)), 55.4 (O*Me*), 24.9 (PhCH(*Me*)-). **ESI-MS:** *m*/*z* [M+1]$^+$ calcd for $C_{16}H_{17}NO$: 240.3180; found: 240.1385.

(*S*)-N-(2-methoxybenzylidene)-α-methylbenzylamine 1b. The reactants; (*S*)-N--methylbenzylamine (0.26 ml, 2 mmol) and *o*-Anisaldehyde (0.24 ml, 2 mmol) were reacted according to the general procedure. An opaque oil was obtained: 0.47 g, 98 % yield. **^{1}H NMR (300 MHz, CDCl3):** δ 8.90 (1H, s, N=C(*H*)-), 8.14 (1H, dd, $^3J_{HH}$: 7.8 Hz, *o*-Ar), 7.51 (2H, d, $^3J_{HH}$: 7.2 Hz, *o*-Ar), 7.40 (3H, m, *m*-Ar), 7.29 (1H, t, $^3J_{HH}$: 7.4 Hz, *p*-Ar), 7.04 (1H, t, $^3J_{HH}$: 7.5 Hz, *p*-Ar), 6.93 (1H, d, $^3J_{HH}$: 8.4 Hz, *m*-Ar), 4.63 (1H, q, $^3J_{HH}$: 6.3 Hz, PhC(*H*)CH$_3$), 3.90 (3H, s, OC*H*$_3$), 1.67 (3H, d, $^3J_{HH}$: 6.3 Hz, PhC(H)C*H*$_3$). **^{13}C NMR (75 MHz, CDCl$_3$):** δ 158.8 (N=C), 155.5 (ArC-OMe), 145.6 (ArC), 131.8 (*para*-C), 128.4 (*meta*-C), 127.6 (*ortho*-C), 126.8 (*ortho*-C), 126.7 (*para*-C), 124.5 (ArC), 120.8 (*meta*-C), 110.9 (*meta*-C), 70.1 (Ph*C*H(Me)), 55.5 (OMe), 25.1 (PhCH(*Me*)-). **ESI-MS:** *m*/*z* [M+1]$^+$ calcd for $C_{16}H_{17}NO$: 240.3180; found: 240.1382.

(*S*)-N-(2-methoxybenzylidene)-α-methylbenzylamine 1c. The reactants; (*S*)-N--methylbenzylamine (0.26 ml, 2 mmol) and *m*-Anisaldehyde (0.24 ml, 2 mmol) were reacted according to the general procedure. An opaque oil was obtained: 0.46 g, 97 % yield. **^{1}H NMR (300 MHz, CDCl3):** δ 8.30 (1H, s, N=C(*H*)-), 7.39 (3H, t, $^3J_{HH}$: 7.8 Hz, *m*-Ar, *p*-Ar), 7.28 (4H, m, *o*-Ar), 7.20 (1H, t, $^3J_{HH}$: 6.6 Hz, *m*-Ar), 6.92 (1H, m, *o*-*p*-Ar), 4.50 (1H, q, $^3J_{HH}$: 6.6 Hz, PhC(*H*)CH$_3$), 3.79 (3H, s, OC*H*$_3$), 1.56 (3H, d, $^3J_{HH}$: 6.6 Hz, PhC(H)C*H*$_3$). **^{13}C NMR (75 MHz, CDCl$_3$):** δ 159.9 (ArC-OMe), 159.4 (N=*C*), 145.2 (ArC), 137.9 (ArC), 129.6 (*meta*-C), 128.6 (*meta*-C), 128.5 (*ortho*-C), 126.9 (*para*-C), 121.5 (*ortho*-C), 117.2 (*para*-C), 112.1 (*ortho*-C), 69.7 (Ph*C*H(Me)), 55.4 (O*Me*), 24.9 (PhCH(*Me*)-). **ESI-MS:** *m*/*z* [M+1]$^+$ calcd for $C_{16}H_{17}NO$: 240.3180; found: 240.1382.

N-[[4-methoxyphenyl]methylene]-benzenamine 2. The reactants aniline (0.18 ml, 2 mmol) and *p*-Anisaldehyde (0.24 ml, 2 mmol) were reacted according to the general procedure. An off white crystalline solid was obtained: 0.41 g, 98% yield. **^{1}H NMR (300 MHz, $CDCl_3$):** δ 8.39 (1H, s, N=C(*H*)), 7.86 (2H, d, $^3J_{HH}$: 6.9 Hz, *ortho*-H), 7.39 (2H, t, $^3J_{HH}$: 8.4 Hz, *meta*-H), 7.22 (3H, m, *para*-H and *ortho*-H) 7.00 (2H, d, $^3J_{HH}$: 8.7 Hz, *meta*-H), 3.88 (3H, s, OCH_3). **^{13}C NMR (75 MHz, $CDCl_3$):** 162.4 (*ipso*-C), 159.8 (N=*C*H), 152.6 (*ipso*-C), 130.7 (*ipso*-C), 129.3 (*meta*-C), 125.7 (*para*-C), 121.0 (*ortho*-C), 114.3 (*meta*-*C*), 55.6 (O*C*H_3). **ESI-MS:** *m*/*z* $[M+1]^+$ calcd for $C_{14}H_{13}NO$: 212.2640; found: 212.1073.

N-[[4-methoxyphenyl]methylene]-2-propen-1-amine 3. The reactants allylamine (0.15 ml, 2 mmol) and *p*-Anisaldehyde (0.24 ml, 2 mmol) were reacted according to the general procedure. A yellow oil was obtained: 0.34 g, 96 % yield. **^{1}H NMR (300 MHz, $CDCl_3$):** δ 8.21 (1H, s, N=C(*H*)), 7.69 (2H, d, $^3J_{HH}$: 8.4 Hz, *ortho*-H), 6.90 (2H, d, $^3J_{HH}$: 8.4 Hz, *meta*-H), 6.05 (1H, m, -C(*H*)=CH_2), 5.19 (2H, m, -C(H)=CH_2), 4.21 (2H, d, $^3J_{HH}$: 8.8 Hz, N(CH_2)), 3.82 (3H, s, OCH_3). **^{13}C NMR (75 MHz, $CDCl_3$):** δ 161.7 (*para*-*C*-OMe), 1.61.4 (N=*C*), 136.3 (-*C*(H)=CH_2), 129.8 (*ortho*-C-Ar), 129.2 (Ar(*C*)C=N), 115.9 (-C(H)=*C*H_2), 114.0 (*meta*-C-Ar), 63.5 (O*C*H_3), 55.4 (N(*C*H_2)). **ESI-MS:** *m*/*z* $[M+1]^+$ calcd for $C_{11}H_{13}NO$: 176.2310; found: 176.1069.

N-[[4-methoxyphenyl]methylene]-ethanol 4. The reactants ethanolamine (0.12 ml, 2 mmol) and *p*-Anisaldehyde (0.24 ml, 2 mmol) were reacted according to the general procedure. An off white crystalline solid was obtained: 0.34 g, 96 % yield. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.22 (1H, s, N=C(*H*)), 7.60 (2H, d, , $^3J_{HH}$: 14.4 Hz, *ortho*-(*H*)-Ar), 6.85 (2H, d, $^3J_{HH}$: 16.8, *meta*-(*H*)-Ar), 3.90 (2H, t, $^3J_{HH}$: 10.4 Hz, N-CH_2-), 3.84 (3H, s, OCH_3), 3.72 (2H, t, $^3J_{HH}$: 10.4 Hz, CH_2-OH), 2.00 (1H, br s, O*H*). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 162.8 (*ipso*-C), 162.2 (N=*C*), 130.1 (*ortho*-C), 129.2 (*ipso*-C), 114.4 (*meta*-C), 63.5 (N(*C*H_2)), 62.9 ((*C*H_2)OH), 55.7 (O*C*H_3). **ESI-MS:** *m*/*z* $[M+1]^+$ calcd for $C_{11}H_{13}NO_2$: 180.2270; found: 180.1019.

α-methyl-N-(2-hydroxyphenyl)-benzenemethanamine 5. The reactants α-methylbenzylamine (0.26 ml, 2 mmol) and salicaldehyde (0.21 ml, 2 mmol) were reacted according to the general procedure. A bright yellow crystalline solid was obtained: 0.44 g, 98 % yield. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 13.42 (1H, br. S, O*H*), 8.30 (1H, s, N=C(*H*)), 7.20 (7H, m, Ar-*H*), 6.87 (1H, d, $^3J_{HH}$: 8.4 Hz, *meta*(*H*)-Ar(OH)), 6.77 (1H, t, $^3J_{HH}$: 14.8 Hz, *meta*(*H*)-Ar(OH)), 4.45 (1H, q, $^3J_{HH}$: 13.6 Hz, PhC(*H*)CH_3-), 1.54 (3H, d, $^3J_{HH}$: 6.8 Hz, PhC(H)CH_3). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 163.6 ((N=*C*), 161.2 (*ortho*-C-Ar-OH), 143.9 (Ar(*C*)-CH(CH_3)), 132.4 (*para*-C-Ar), 131.5 (*ortho*-C-Ar), 128.8 (*meta*-C-Ar), 127.4 (*ortho*-C-Ar), 126.5 (*para*-C-Ar), 118.9 (*meta*-C-Ar), 118.7 (Ar(*C*)C=N), 117.1 (*meta*-C-Ar), 68.7 (Ar(*C*H)CH_3), 25.1 (CH(*C*H_3). **ESI-MS:** *m*/*z* $[M+1]^+$ calcd for $C_{15}H_{15}NO$: 226.2910; found: 226.1227.

***N*-[(2-hydroxyphenyl)methylene]-benzenamine 6.** The reactants aniline (0.18 ml, 2 mmol) and salicaldehyde (0.21 ml, 2 mmol) were reacted according to the general procedure. A bright yellow crystalline solid was obtained: 0.38 g, 99 % yield. **^{1}H NMR**

(300 MHz, $CDCl_3$): δ 13.24 (1H, br. S, OH), 8.65 (1H, s, N=C(*H*)), 7.43 (4H, m, Ar-*H*), 7.32 (3H, m, Ar-*H*), 7.04 (1H, d, $^3J_{HH}$: 7.5 Hz, *meta*(*H*)-Ar), 6.97 (1H, t, $^3J_{HH}$: 15 Hz, *meta*(*H*)-Ar). **^{13}C NMR (75 MHz, $CDCl_3$):** δ 162.8 (N=*C*), 161.3 (*ortho*-*C*-Ar-OH), 148.6 (Ar(*C*)-N), 133.4 (*para*-C-Ar), 132.5 (*ortho*-C-Ar), 132.5 (*meta*-C-Ar), 129.6 (*para*-C-Ar), 127.1 (*ortho*-C-Ar), 121.3 (*meta*-C-Ar), 119.2 (Ar(*C*)C=N), 117.4 (*meta*-C-Ar). **ESI-MS:** *m*/*z* $[M+1]^+$ calcd for $C_{13}H_{11}NO$: 198.2370; found: 198.0906.

***N*-[(2-hydroxyphenyl)methylene]-2-propen-1-amine 7.** The reactants allylamine (0.15 ml, 2 mmol) and salicaldehyde (0.21 ml, 2 mmol) were reacted according to the general procedure. A bright yellow oil was obtained: 0.31 g, 96 % yield. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 13.37 (1H, br. s, OH), 8.30 (1H, s, N=C(*H*)), 7.26 (1H, t, $^3J_{HH}$: 16 Hz, *para*(*H*)-Ar), 7.20 (1H, d, $^3J_{HH}$: 7.6 Hz, *ortho*(*H*)-Ar), 6.92 (1H, d, $^3J_{HH}$: 8 Hz, *meta*(*H*)-Ar), 6.83 (1H, t, $^3J_{HH}$: 14.8 Hz, *meta*(*H*)-Ar), 65.97 (1H, m, -C(*H*)=CH_2), 5.17 (2H, m, -C(H)=CH_2), 4.18 (2H, d, $^3J_{HH}$: 7.0 Hz, N(CH_2)). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 165.7 (N=*C*), 161.3 (*ortho*-*C*-Ar-OH), 134.9 (*para*-C-Ar), 132.4 (*ortho*-C-Ar), 131.4 (-*C*(H)=CH_2), 118.9 (Ar(*C*)C=N), 118.6 (*meta*-C-Ar), 117.1 (-C(H)=*C*H_2), 116.6 (*meta*-C-Ar), 61.4 (N(*C*H_2)). **ESI-MS:** *m*/*z* $[M+1]^+$ calcd for $C_{10}H_{11}NO$: 162.2040; found: 162.0911.

***N*-[(2-hydroxyphenyl)methylene]-ethanol 8.** The reactants ethanolamine (0.12 ml, 2 mmol) and salicaldehyde (0.21 ml, 2 mmol) were reacted according to the general procedure. An orange was obtained: 0.32 g, 97 % yield. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 13.20 (1H, br. s, OH), 8.37 (1H, s, N=C(*H*)), 7.30 (1H, t, $^3J_{HH}$: 15.6, *ortho*-H), 7.24 (1H, d, $^3J_{HH}$: 7.6 Hz, *para*(*H*)-Ar), 6.94 (1H, d, $^3J_{HH}$: 8.4 Hz, *meta*(*H*)-Ar), 6.87 (1H, t, $^3J_{HH}$: 15.2 Hz, *meta*(*H*)-Ar), 3.90 (2H, t, $^3J_{HH}$: 10.2 Hz, N-CH_2-), 3.75 (2H, t, $^3J_{HH}$: 10.1 Hz, -CH_2OH). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 166.9 (N=*C*), 161.5 (*ortho*-*C*-Ar-OH), 132.6 (*para*-C-Ar), 131.6 (*ortho*-C-Ar), 118.7 (*meta*-C-Ar), 117.2 (*meta*-C-Ar), 62.1 (N=*C*(H)), 62.7 (-*C*H_2OH)). **ESI-MS:** *m*/*z* $[M+1]^+$ calcd for $C_9H_{11}NO_2$: 166.1920; found: 166.0861.

α-methyl-N-(2-bromophenyl)-benzenemethanamine 9. The reactants α-methylbenzylamine (0.26 ml, 2 mmol) and 2-bromobenzaldehyde (0.23 ml, 2 mmol) were reacted according to the general procedure. A light yellow oil was obtained: 0.56 g, 98 % yield. **^{1}H NMR (300 MHz, $CDCl_3$):** δ 8.76 (1H, s, N=C*H*), 8.03 (1H, d, $^3J_{HH}$: 7.8 Hz, *ortho*-Ar), 7.55 (1H, d, $^3J_{HH}$: 7.8 Hz, *ortho*-Ar), 7.46 (2H, d, $^3J_{HH}$: 8.1 Hz, *ortho*-Ar), 7.35 (3H, m, Ar-*H*), 7.26 (2H, m, Ar-*H*), 4.64 (1H, q, $^3J_{HH}$: 19.8 Hz, PhC(*H*)CH_3-), 1.62 (3H, d, $^3J_{HH}$: 6.6 Hz, PhC(H)CH_3). **^{13}C NMR (75 MHz, $CDCl_3$):** δ 158.6 (N=*C*), 145.0 (Ar(*C*)-CH(CH_3)), 134.9 (Ar(*C*)C=N), 133.1 (*meta*-C-Ar), 131.8 (*para*-C-Ar), 129.2 (*meta*-C-Ar), 128.6 (*meta*-C-Ar), 127.7 (*ortho*-C-Ar), 127.0 (*ortho*-C-Ar), 126.7 (*para*-C-Ar), 125.2 (*ortho*-C-Ar(Br)), 69.9 (Ar(*C*H)CH_3), 25.0 (Ar(CH)*C*H_3). **ESI-MS:** *m*/*z* $[M+1]^+$ calcd for $C_{15}H_{14}BrN$: 288.1880; found: found: 288.0379 (^{78}Br) and 290.0358 (^{80}Br).

N-[[2-bromophenyl]methylene]-benzenamine 10. The reactants aniline (0.18 ml, 2 mmol) and 2-bromobenzaldehyde (0.23 ml, 2 mmol) were reacted according to the general procedure. A yellow oil was obtained: 0.51 g, 98 % yield. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.87 (1H, s, N=C(*H*)), 8.25 (1H, d, $^3J_{HH}$: 7.6 Hz, *ortho*-Ar), 7.63 (1H, d, $^3J_{HH}$:

8.0 Hz, *meta*-Ar), 7.43 (3H, m, *meta*-Ar), 7.30 (1H, m, *ortho*-Ar, *para*-Ar). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 159.4 (N=*C*), 151.8 (N-ArC), 134.7 (Ar(*C*)C=N), 133.3 (*meta*-*C*-Ar), 132.5 (*para*-*C*-Ar), 129.3 (*meta*-*C*-Ar), 129.2 (*meta*-*C*-Ar), 127.8 (*para*-*C*-Ar), 126.2 (*ortho*-*C*-Ar), 126.2 (ArC-Br), 121.2 (*ortho*-*C*-Ar). **ESI-MS:** *m*/*z* $[M+1]^+$ calcd for C13H10BrN: 260.1340; found: 260.0068 (^{78}Br) and 262.0050 (^{80}Br).

N-[[2-bromophenyl]methylene]-2-propen-1-amine 11. The reactants allylamine (0.15 ml, 2 mmol) and 2-bromobenzaldehyde (0.23 ml, 2 mmol) were reacted according to the general procedure. A yellow oil was obtained: 0.44 g, 99 % yield. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.57 (1H, s, N=C(*H*)), 7.97 (1H, dd, $^3J_{HH}$: 9.6 Hz, *ortho*-Ar), 7.47 (1H, d, $^3J_{HH}$: 8.0 Hz, *meta*-Ar), 7.20 (2H, m, *meta*-Ar and *para*-Ar), 7.18 (1H, t, -C(*H*)=CH_2), 5.99 (1H, m, -C(*H*)=CH_2) 5.13 (2H, m, -C(H)=CH_2), 4.22 (2H, s, N(CH_2)). **^{13}C NMR (100 MHz, $CDCl_3$):** 161.0 ((N=*C*), 135.7 (*meta*-ArC), 134.6 (Ar(*C*)C=N), 133.1 (*para*-ArC), 131.9 ((-*C*(H)=CH_2), 128.9 (*meta*-ArC), 127.7 (*ortho*-ArC), 125.1 (*ortho*-C-Ar(Br)), 116.4 ((-C(H)=*C*H_2), 63.6 (N(*C*H_2)). **ESI-MS:** *m*/*z* $[M+1]^+$ calcd for $C_{10}H_{10}BrN$: 224.1010; found: 224.0067 (^{78}Br) and 226.0048 (^{80}Br).

N-[[2-bromopheny]methylene]-ethanol 12. The reactants ethanolamine (0.12 ml, 2 mmol) and 2-bromobenzaldehyde (0.23 ml, 2 mmol) were reacted according to the general procedure. A light yellow oil was obtained: 0.44 g, 96 % yield. **^{1}H NMR (300 MHz, $CDCl_3$):** 8.68 (1H, s, N=C(H)), 7.97 (1H, d, $^3J_{HH}$: 9.6 Hz, *ortho*-H), 7.54 (1H, d, $^3J_{HH}$: 9.3 Hz, *meta*-H), 7.27 (2H, m, *meta*-H and *para*-H), 3.90 (2H, m, -CH_2OH), 3.78 (2H, m, NCH_2-), 2.61 (1H, br s, OH). **^{13}C NMR (100 MHz, $CDCl_3$):** 162.2 (N=C), 134.3 (*ipso*-C), 133.1 (*meta*-C), 132.0 (*para*-C), 128.8 (*meta*-C), 127.7 (*ortho*-C), 125.2 (*ipso*-C), 63.4 (-*C*H_2OH), 62.4 (N*C*H_2-). **ESI-MS:** *m*/*z* $[M+1]^+$ calcd for $C_9H_{11}BrNO$: 229.0790; found: 228.0890 (^{78}Br), 230.0874 (^{80}Br).

α-methyl-N-(4-nitrophenyl)-benzenemethanamine 13. The reactants α-methylbenzylamine (0.26 ml, 2 mmol) and 4-nitrobenzaldehyde (0.30 g, 2 mmol) were reacted for 30 mins, according to the general procedure. A bright yellow oil was obtained: 0.49 g, 97 % yield. **^{1}H NMR (400 MHz, $CDCl_3$):** 8.35 (1H, s, N=C(*H*)), 7.16 (2H, d, $^3J_{HH}$: 9.2 Hz, *meta*-ArH), 7.86 (2H, d, $^3J_{HH}$: 8.8 Hz, *ortho*-ArH), 7.34 (2H, d, $^3J_{HH}$: 8.0 Hz, *ortho*-ArH), 7.27 (2H, t, $^3J_{HH}$: 14.8 Hz, *meta*-ArH), 7.18 (1H, t, $^3J_{HH}$: 15.6 Hz, *para*-ArH), 4.52 (1H, q, $^3J_{HH}$: 20.0 Hz, PhC(*H*)CH_3-), 1.53 (3H, d, $^3J_{HH}$: 6.4 Hz, PhC(H)CH_3). **^{13}C NMR (100 MHz, $CDCl_3$):** 157.2 (N=*C*), 144.5 (*para*-C-Ar(NO_2)), 141.9 (Ar(*C*)-CH(CH_3)), 129.1 (*ortho*-ArC), 129.0 (Ar(*C*)C=N),128.7 (*meta*-ArC), 127.3 (*ortho*-ArC), 126.7 (*para*-ArC), 123.9 (*meta*-ArC), 70.2 (Ar(*C*H)CH_3), 24.9 (Ar(CH)*C*H_3). **ESI-MS:** *m*/*z* $[M+1]^+$ calcd for $C_9H_{10}BrNO$: 254.2890; found: 255.1130.

N-[[4-nitrophenyl]methylene]-2-propen-1-amine 15. The reactants allylamine (0.15 ml, 2 mmol) and 4-nitrobenzaldehyde (0.30 g, 2 mmol) were reacted for 30 mins, according to the general procedure. A dark red crystalline solid was obtained: 0.37 g, 97 % yield. **^{1}H NMR (400 MHz, $CDCl_3$):** 8.38 (1H, s, N=C(*H*)), 8.26 (2H, d, $^3J_{HH}$: 8.8 Hz, *meta*-H), 7.92 (2H, d, $^3J_{HH}$: 8.8 Hz, *ortho*-H), 6.07 (1H, m, -C(*H*)=CH_2), 5.22 (2H, m, -C(H)=CH_2), 4.33 (2H, m, N-CH_2-). **^{13}C NMR (100 MHz, $CDCl_3$):** 159.9 (N=*C*), 149.4 (*ipso*-C), 141.9 (*ipso*-C), 135.4 (*ortho*-C), 129.2 (-*C*(H)=CH_2), 124.2 (*meta*-C), 117.1 (-

C(H)=*C*H$_2$), 63.9 (N-*C*H$_2$-). **ESI-MS:** *m*/*z* [M+1]$^+$ calcd for $C_{11}H_{13}NO$: 191.2100; found: 191.0817.

N-[[4-nitrophenyl]methylene]-ethanol 16. The reactants ethanolamine (0.12 ml, 2 mmol) and 4-nitrobenzaldehyde (0.30 g, 2 mmol) were reacted for 30 mins, according to the general procedure. An off white powder was obtained: 0.38 g, 98 % yield. **^{1}H NMR (400 MHz, CDCl$_3$):** 8.43 (1H, s, N=C(*H*)), 8.27 (2H, d, $^3J_{HH}$: 9.0 Hz, *meta*-H), 7.91 (2H, d, $^3J_{HH}$: 9.0 Hz, *ortho*-H), 3.95 (2H, m, N-C*H*$_2$-), 3.83 (2H, m, -C*H*$_2$-OH), 1.88 (1H, s, OH). **^{13}C NMR (100 MHz, CDCl$_3$):** 160.9 (N=*C*), 141.4 (*ipso*-C), 129.0 (*ortho*-C), 127.4 (*ipso*-C), 124.0 (*meta*-C), 63.5 (N-*C*H$_2$-), 62.3 (-*C*H$_2$OH). **ESI-MS:** *m*/*z* [M+1]$^+$ calcd for $C_{11}H_{13}NO$: 195.1980; found: 195.0764.

α-methyl-N-[[2-(trifluoromethyl)phenyl]methylene]-benzenemethanamine 25. The reactants α-methylbenzylamine (0.26 ml, 2 mmol) and 2-trifluoromethylbenzaldehyde (0.27 ml, 2 mmol) were reacted for 30 mins, according to the general procedure. An opaque oil was obtained: 0.55 g, 99 % yield. **^{1}H NMR (400 MHz, CDCl$_3$):** 8.75 (1H, s, N=C(*H*)), 8.30 (1H, d, $^3J_{HH}$: 7.8 Hz, *ortho*-H), 7.68 (1H, d, $^3J_{HH}$: 7.8 Hz, *meta*-H), 7.60 (1H, t, 15.0 Hz, *meta*-H), 7.44 (3H, m, Ar-H), 7.37 (2H, t, $^3J_{HH}$: 15.3 Hz, *meta*-H), 7.26 (2H, m, Ar-H), 4.65 (1H, q, $^3J_{HH}$: 20.0 Hz, N-C*H*(CH$_3$)-), 1.61 (3H, d, $^3J_{HH}$: 6.9 Hz). **^{13}C NMR (100 MHz, CDCl$_3$):** 155.9 (N=*C*), 144.8 (*ipso*-C), 132.1 (*meta*-C), 130.1 (*ortho*-C), 128.9 (*ipso*-C), 128.7 (*meta*-C), 128.6 (*ortho*-C), 127.1 (*meta*-C), 126.7 (*para*-C), 126.5 (*ipso*-C), 125.6 (*C*F$_3$), 70.2 (Ph*C*(CH$_3$)-), 24.9 (*C*H$_3$). **ESI-MS:** *m*/*z* [M+1]$^+$ calcd for $C_{10}H_{10}F_3NO$: 278.2982; found: 278.1140.

N-[[2-(trifluoromethyl)phenyl]methylene]-benzenamine 26. The reactants aniline (0.18 ml, 2 mmol) and 4-trifluoromethylbenzaldehyde (0.27 ml, 2 mmol) were reacted for 30 mins, according to the general procedure. A yellow oil was obtained: 0.49 g, 98 % yield. **^{1}H NMR (400 MHz, CDCl$_3$):** 8.84 (1H, s, (N=C(*H*)), 8.45 (1H, d, $^3J_{HH}$: 7.8 Hz, *ortho*-H), 7.74 (1H, d, $^3J_{HH}$: 7.8 Hz, *meta*-H), 7.66 (1H, t, $^3J_{HH}$: 15.3 Hz, *meta*-H), 7.56 (1H, t, $^3J_{HH}$: 15.0 Hz, *para*-H), 7.43 (2H, t, $^3J_{HH}$: 15.6 Hz, *meta*-H), 7.25 (3H, m, *ortho*-H and *para*-H). **^{13}C NMR (100 MHz, CDCl$_3$):** 156.6 (N=*C*), 151.7 (*ipso*-C), 134.3 (*meta*-C), 132.2 (*ortho*-C), 130.8 (*para*-C), 129.4 (*meta*-C), 128.6 (*para*-C), 126.8 (*meta*-C), 126.0 (*ipso*-C), 125.8 (*C*F$_3$), 122.5 (*ipso*-C), 121.1 (*ortho*-C). **ESI-MS:** *m*/*z* [M+1]$^+$ calcd for $C_{10}H_{10}F_3NO$: 250.2442; found: 250.0837.

N-[[2-(trifluoromethyl)phenyl]methylene]-2-propen-1-amine 27. The reactants allylamine (0.15 ml, 2 mmol) and 4-trifluoromethylbenzaldehyde (0.27 ml, 2 mmol) were reacted for 30 mins, according to the general procedure. A yellow oil was obtained: 0.42 g, 99 % yield. **^{1}H NMR (400 MHz, CDCl$_3$):** 8.66 (1H, s, N=C(*H*)), 8.24 (1H, d, $^3J_{HH}$: 8.0 Hz, *ortho*H), 7.68 (1H, d, $^3J_{HH}$: 7.6 Hz, *meta*-H), 7.59 (1H, t, $^3J_{HH}$: 15.2 Hz, *meta*-H), 7.51 (1H, t, $^3J_{HH}$: 15.2 Hz, *para*-H), 6.07 (1H, m, -CH$_2$C*H*=CH$_2$), 5.22 (1H, m, -CH$_2$CH=C*H*$_2$), 4.32 (2H, d, $^3J_{HH}$: 7.2 Hz, N-CH$_2$-). **^{13}C NMR (100 MHz, CDCl$_3$):** 158.5 (N=*C*), 135.5 (*meta*-C), 134.4 (*ipso*-C), 132.1 (*ortho*-C), 130.2 (*para*-C), 128.4 (-*C*H$_2$=CH$_2$), 126.1 (*ipso*-C), 125.6 (*C*F$_3$), 122.5 (*meta*-C), 116.6 (-CH$_2$=*C*H$_2$), 63.8 (N-*C*H$_2$-). **ESI-MS:** *m*/*z* [M+1]$^+$ calcd for $C_{10}H_{10}F_3NO$: 214.2112; found: 214.0834.

N-[[2-(trifluoromethyl)phenyl]methylene]-ethanol 28. The reactants ethanolamine (0.12 ml, 2 mmol) and 4-trifluoromethylbenzaldehyde (0.27 ml g, 2 mmol) were reacted for 30 mins, according to the general procedure. A light yellow oil was obtained: 0.42 g, 97 % yield. **^{1}H NMR (400 MHz, $CDCl_3$):** 8.70 (1H, s, N=C(*H*)), 8.17 (1H, d, $^3J_{HH}$: 7.2 Hz, *ortho*-H), 7.67 (1H, d, $^3J_{HH}$: 7.5 Hz, *meta*-H), 7.55 (2H, m, *meta*-H and *para*-H), 3.91 (2H, m, N-CH_2-), 3.79 (2H, m, -CH_2OH), 2.61 (1H, br s, OH). **^{13}C NMR (100 MHz, $CDCl_3$):** 159.5 (N=*C*), 134.3 (*ipso*-C), 132.1 (*meta*-C), 130.4 (*ortho*-C), 128.3 (*meta*-C), 126.0 (*ipso*-C), 125.6 (*C*F_3), 122.4 (*para*-C), 63.5 (N-CH_2-), 62.4 (-CH_2OH). **ESI-MS:** *m*/*z* $[M+1]^+$ calcd for $C_{10}H_{10}F_3NO$: 218.1992; found: 218.0787.

α-methyl-N-(2-thienylmethylene)-benzenemethanamine 29. The reactants α-methylbenzylamine (0.26 ml, 2 mmol) and 2-thiophenecarboxaldehyde (0.19 ml, 2 mmol) were reacted for 30 mins, according to the general procedure. A yellow oil was obtained: 0.42 g, 98 % yield. **^{1}H NMR (400 MHz, $CDCl_3$):** 8.44 (1H, s, N=C(*H*)), 7.43 (7H, m, ArH), 7.06 (1H, t, $^3J_{HH}$: 8.7 Hz, *para*-H), 4.54 (1H, q, $^3J_{HH}$: 19.2 Hz, PhC(*H*)CH_3-), 1.60 (3H, d, $^3J_{HH}$: 8.2 Hz, PhC(H)CH_3-). **^{13}C NMR (100 MHz, $CDCl_3$):** 152.9 (N=*C*), 145.1 (*ipso*-C 142.9 (*ipso*-C), 130.5 (*ortho*-C), 128.9 (Ar-C), 128.6 (*meta*-C), 127.4 (*ortho*-C), 126.9 (Ar-C), 126.8 (*para*-C), 69.3 (Ph*C*H(CH_3)-), 24.8 (PhCH(*C*H_3)-). **ESI-MS:** *m*/*z* $[M+1]^+$ calcd for $C_{13}H_{13}NS$: 216.3220; found: 216.0832.

***N*-(2-thienylmethylene)-benzenamine 30.** The reactants aniline (0.18 ml, 2 mmol) and 2-thiophenecarboxaldehyde (0.19 ml, 2 mmol) were reacted for 30 mins, according to the general procedure. An orange oil was obtained: 0.36 g, 96 % yield. **^{1}H NMR (400 MHz, $CDCl_3$):** 8.59 (1H, s, N=C(*H*)), 7.53 (2H, d, $^3J_{HH}$: 5.7 Hz, *ortho*-H), 7.40 (2H, t, $^3J_{HH}$: 15.3 Hz, *meta*-H), 7.26 (3H, m, Ar-H), 7.15 (1H, t, $^3J_{HH}$: 9.6 Hz, *para*-H).**^{13}C NMR (100 MHz, $CDCl_3$):** 153.1 (N=*C*), 151.5 (*ipso*-C), 142.9 (*ipso*-C), 132.4 (Ar-C), 130.5 (Ar-C), 129.3 (*meta*-C), 127.9 (Ar-C), 126.2 (*para*-C), 121.1 (*ortho*-C). **ESI-MS:** *m*/*z* $[M+1]^+$ calcd for $C_{11}H_9NS$: 188.2680; found: 188.0526.

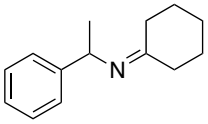
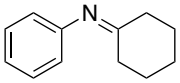
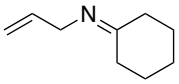
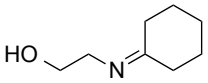
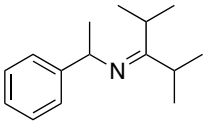
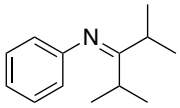
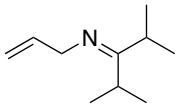
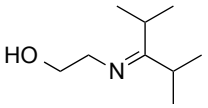
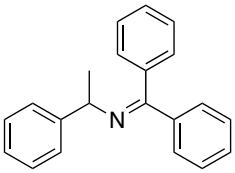
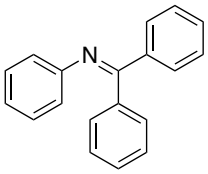
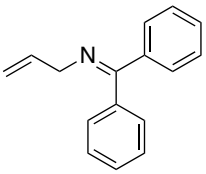
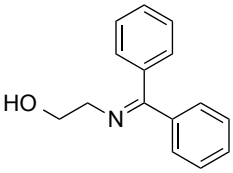
***N*-(2-thienylmethylene)-2-propen-1-amine 31.** The reactants allylamine (0.15 ml, 2 mmol) and 2-thiophenecarboxaldehyde (0.19 ml, 2 mmol) were reacted for 30 mins, according to the general procedure. An orange oil was obtained: 0.29 g, 96 % yield. **^{1}H NMR (400 MHz, $CDCl_3$):** 8.38 (1H, s, N=C(*H*)), 7.40 (1H, d, $^3J_{HH}$: 4.8 Hz, Ar-H), 7.31 (1H, d, $^3J_{HH}$: 3.6 Hz, Ar-H), 7.06 (1H, t, $^3J_{HH}$: 8.8 Hz, Ar-H), 6.03 (1H, m, -CH_2C*H*=CH_2), 5.20 (2H, m, CH_2CH=CH_2), 4.21 (2H, m, CH_2CH=CH_2). **^{13}C NMR (100 MHz, $CDCl_3$):** 155.2 (N=*C*), 142.6 (*ipso*-C), 135.8 (-CH_2*C*H=CH_2), 130.6 (Ar-C), 129.0 (Ar-C), 127.4 (Ar-C), 116.4 (-CH_2CH=*C*H_2), 63.1 (-*C*H_2*C*H=CH_2). **ESI-MS:** *m*/*z* $[M+1]^+$ calcd for C_8H_9NS: 152.2350; found: 152.0525.

2-[(2-thienylmethylene)amino]-ethanol 32. The reactants ethanolamine (0.12 ml, 2 mmol) and 2-thiophenecarboxaldehyde (0.19 ml, 2 mmol) were reacted for 30 mins, according to the general procedure. A a yellow oil was obtained: 0.30 g, 97 % yield. **^{1}H NMR (400 MHz, $CDCl_3$):** 8.38 (1H, s, N=C(*H*)), 7.38 (1H, d, $^3J_{HH}$: 6.9 Hz, Ar-H), 7.28 (1H, d, $^3J_{HH}$: 5.6 Hz, Ar-H), 7.04 (1H, t, $^3J_{HH}$: 12.4 Hz, Ar-H), 3.87 (2H, t, $^3J_{HH}$: 10.2 Hz, -CH_2OH), 3.69 (2H, t, $^3J_{HH}$: 10.2 Hz, N-CH_2-), 2.92 (1H, br s, OH). **^{13}C NMR (100 MHz, $CDCl_3$):** 156.4 (N=*C*), 142 (*ipso*-C), 130.9 (Ar-C), 129.2 (Ar-C), 127.5 (Ar-C),

63.1 (N-CH_2-), 62.2 (-CH_2OH). **ESI-MS:** *m*/*z* $[M+1]^+$ calcd for C_7H_9NOS: 156.2230; found: 156.0474.

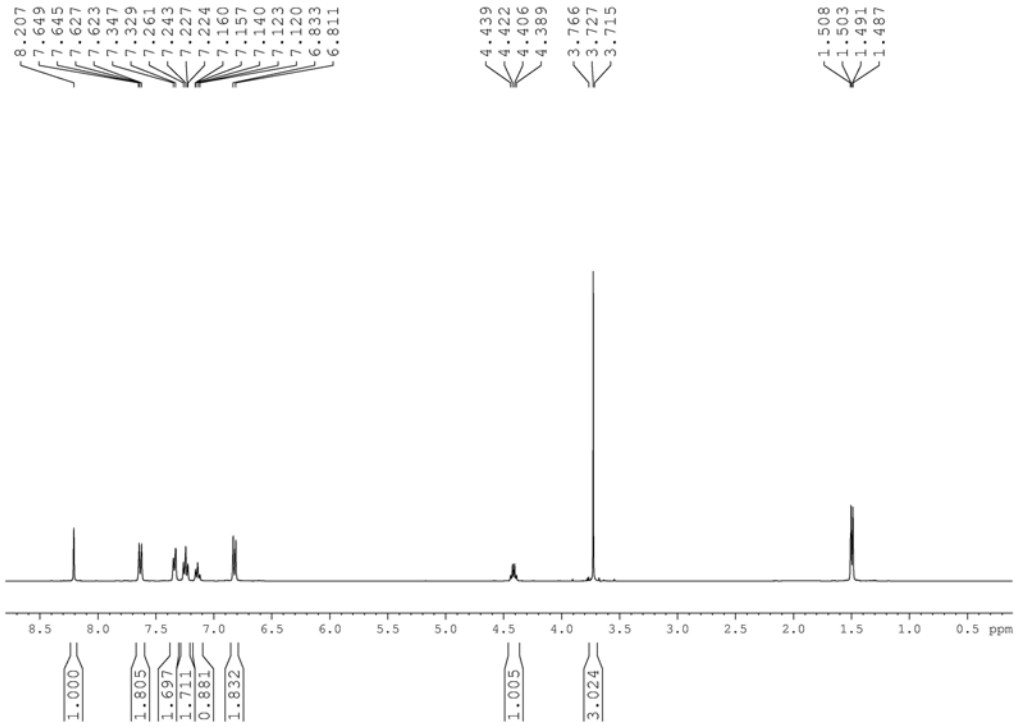
Attempted synthesis of imines from ketones

Table 4. Imine reactions with ketones ([a]Ratios determined via ^{1}H NMR)

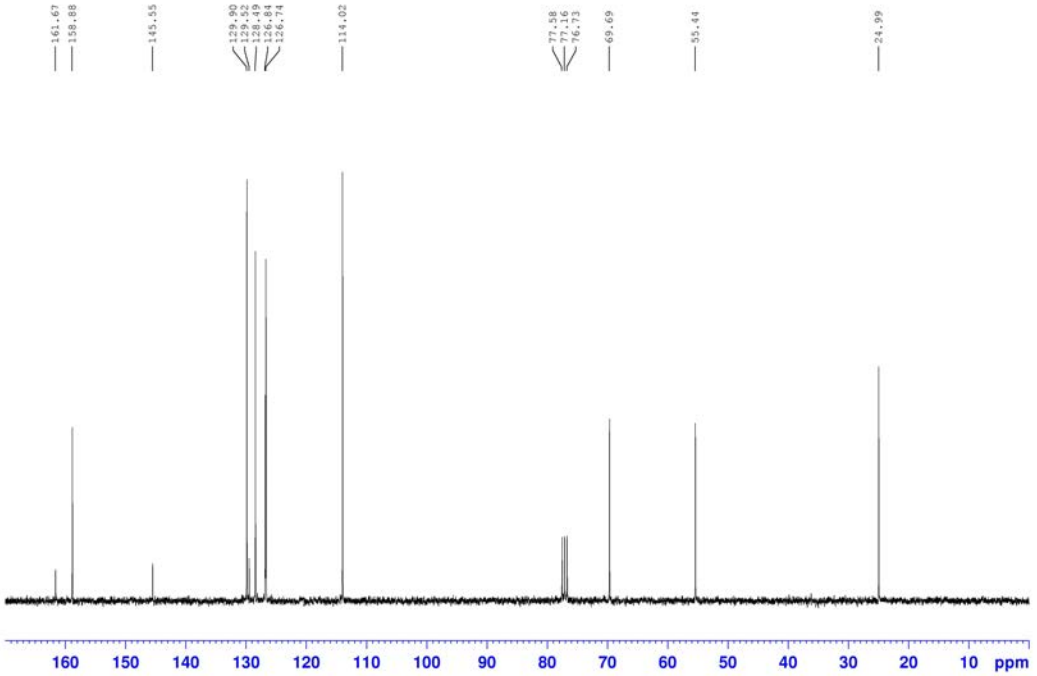
Amine	Ketone	Imine	Conversion (prod: sm)[a]
$PhC(CH_3)NH_2$	$O{=}C_6H_{10}$		78: 22
$PhNH_2$	$O{=}C_6H_{10}$		0: 100
$CH_2{=}CHNH_2$	$O{=}C_6H_{10}$		0: 100
$HO(CH_2)_2NH_2$	$O{=}C_6H_{10}$		0: 100
$PhC(CH_3)NH_2$	$O{=}C(CH(CH_3)_2)_2$		0: 100
$PhNH_2$	$O{=}C(CH(CH_3)_2)_2$		0: 100
$CH_2{=}CHNH_2$	$O{=}C(CH(CH_3)_2)_2$		0: 100
$HO(CH_2)_2NH_2$	$O{=}C(CH(CH_3)_2)_2$		0: 100
$PhC(CH_3)NH_2$	$O{=}C(Ph)_2$		0: 100
$PhNH_2$	$O{=}C(Ph)_2$		0: 100
$CH_2{=}CHNH_2$	$O{=}C(Ph)_2$		0: 100
$HO(CH_2)_2NH_2$	$O{=}C(Ph)_2$		0: 100

(*S*)-N-(4-methoxybenzylidene)--methylbenzylamine 1a

1H NMR:

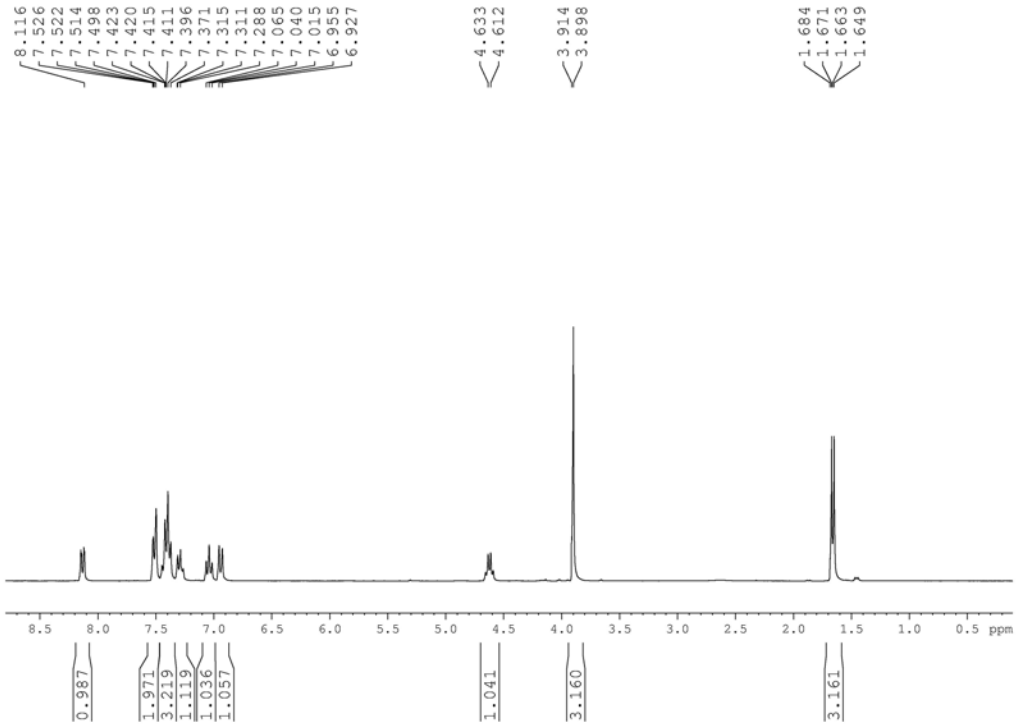


13C NMR:

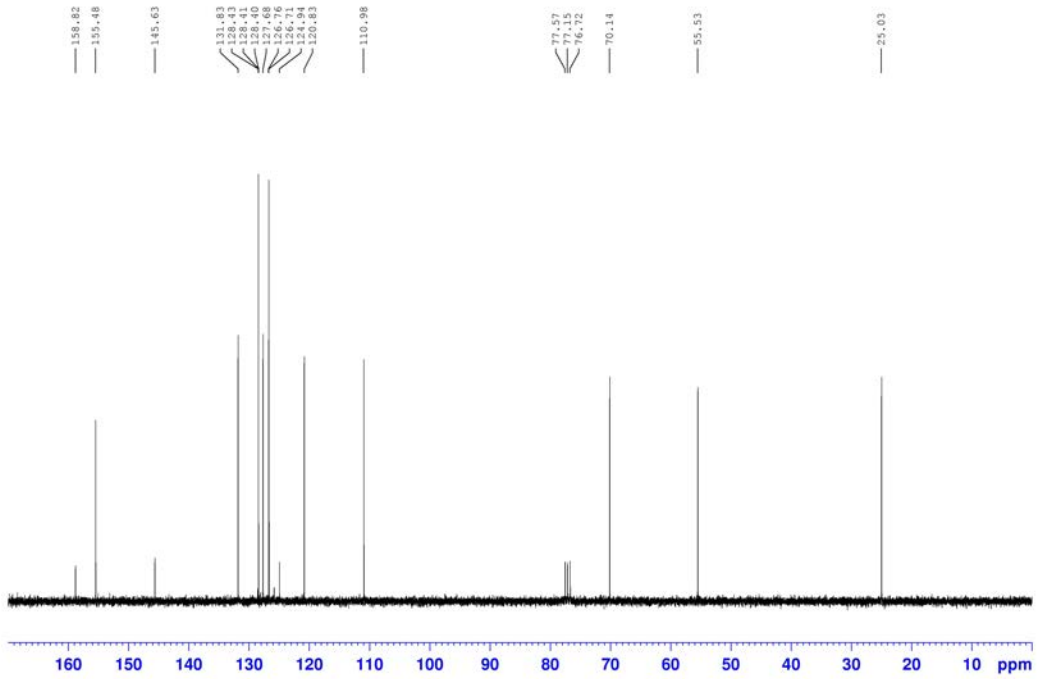


(*S*)-N-(2-methoxybenzylidene)--methylbenzylamine 1b

1H NMR:

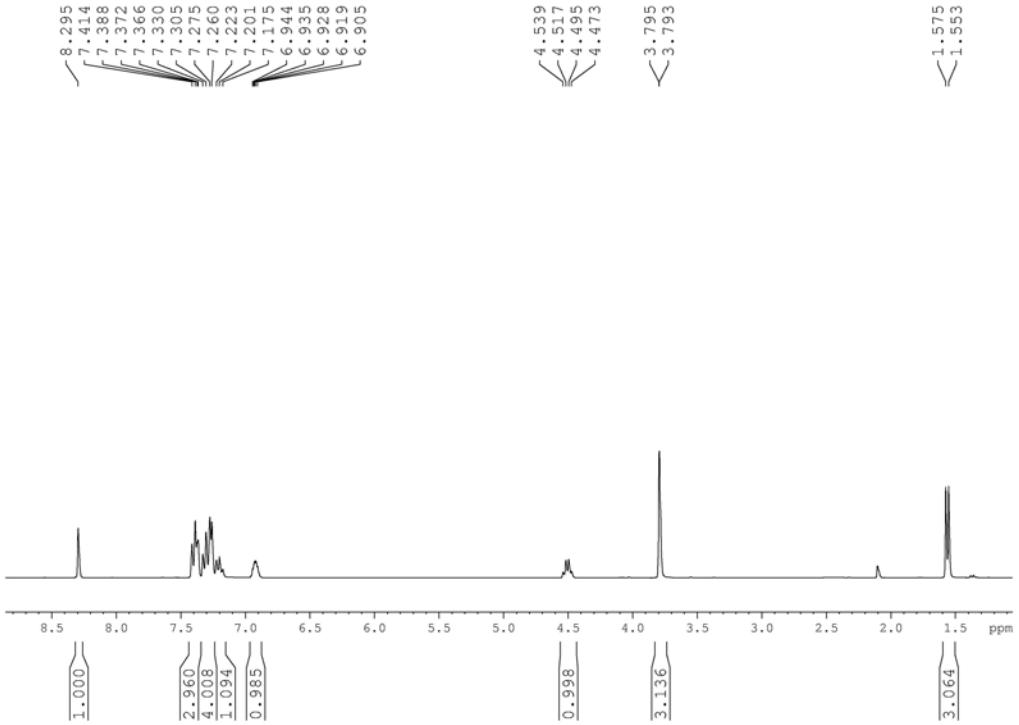


13C NMR:

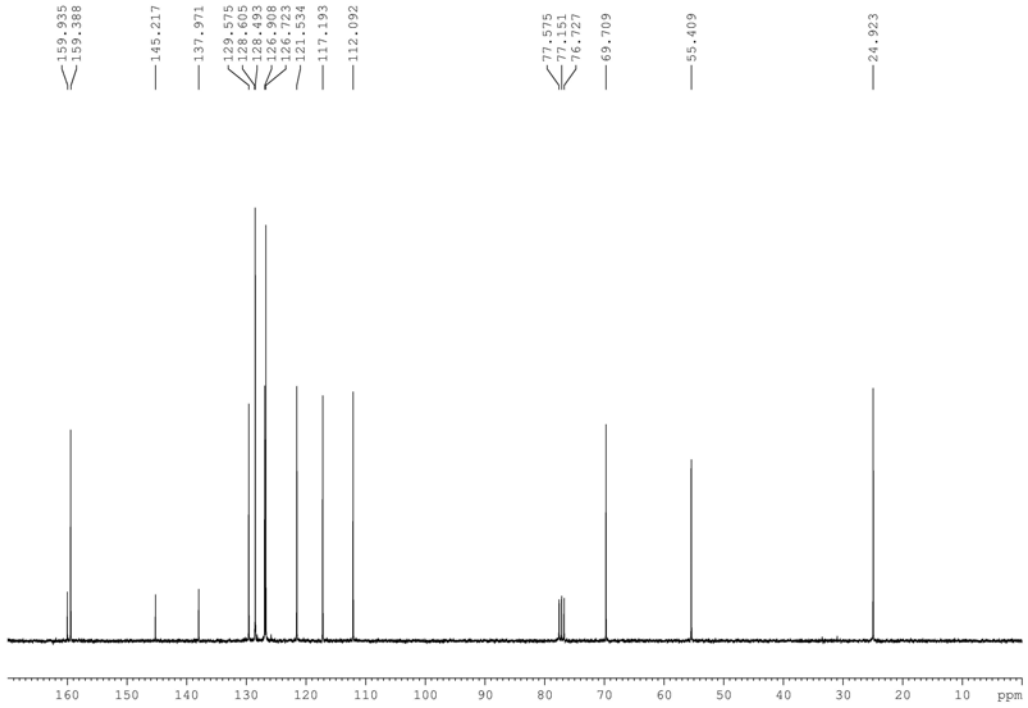


(*S*)-N-(2-methoxybenzylidene)--methylbenzylamine 1c

1H NMR:

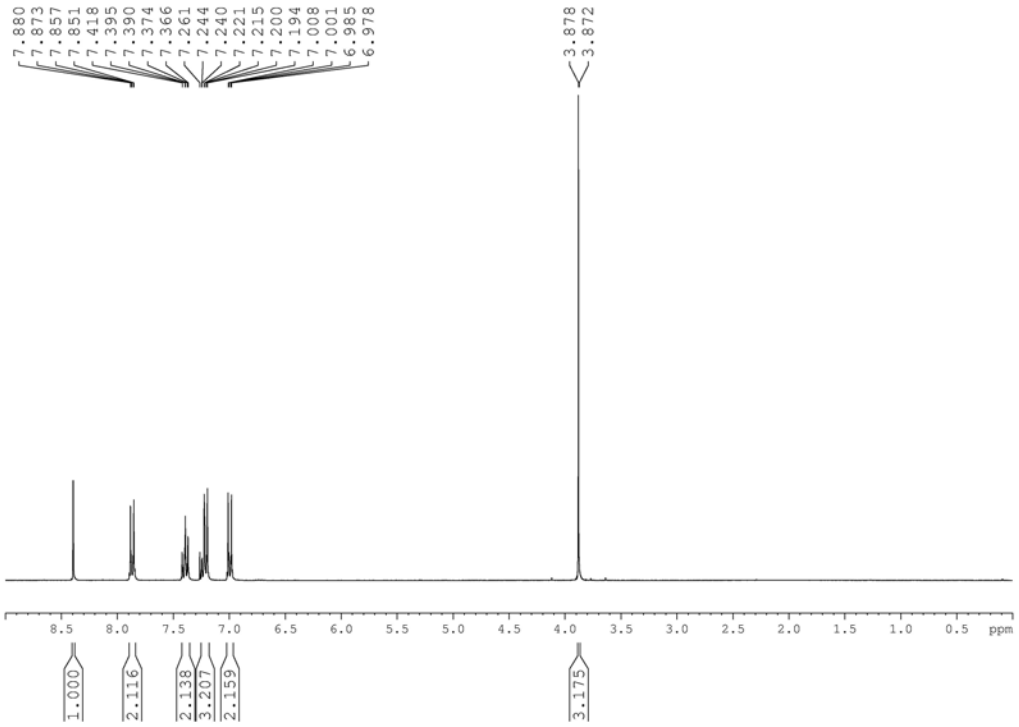


13C NMR:

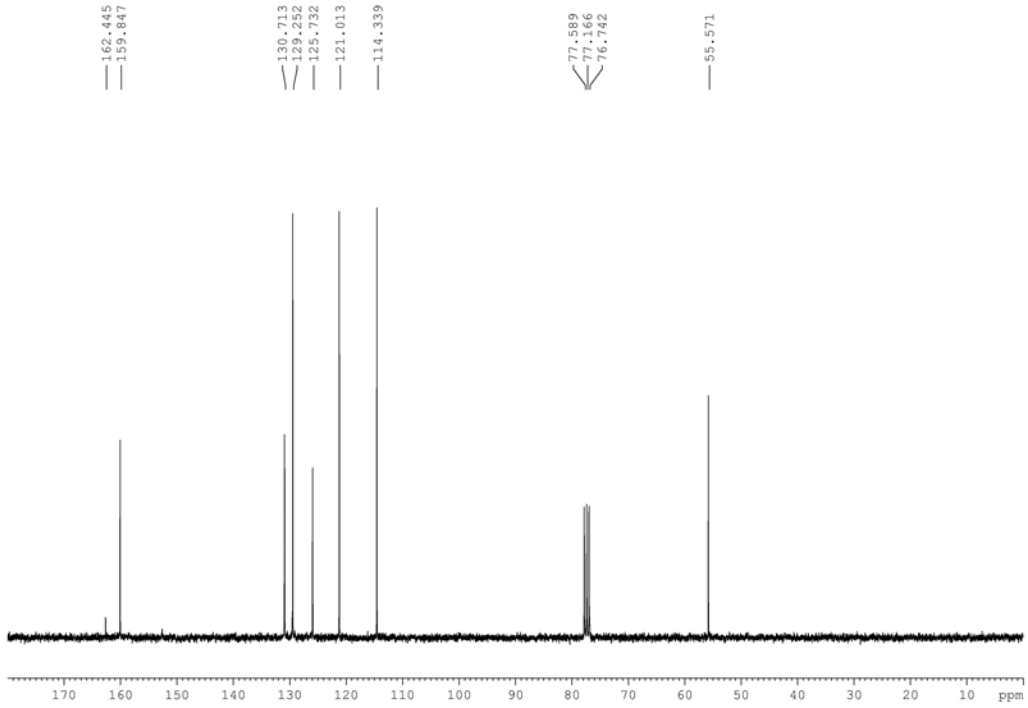


N-[[4-methoxyphenyl]methylene]-benzenamine (2)

1H NMR

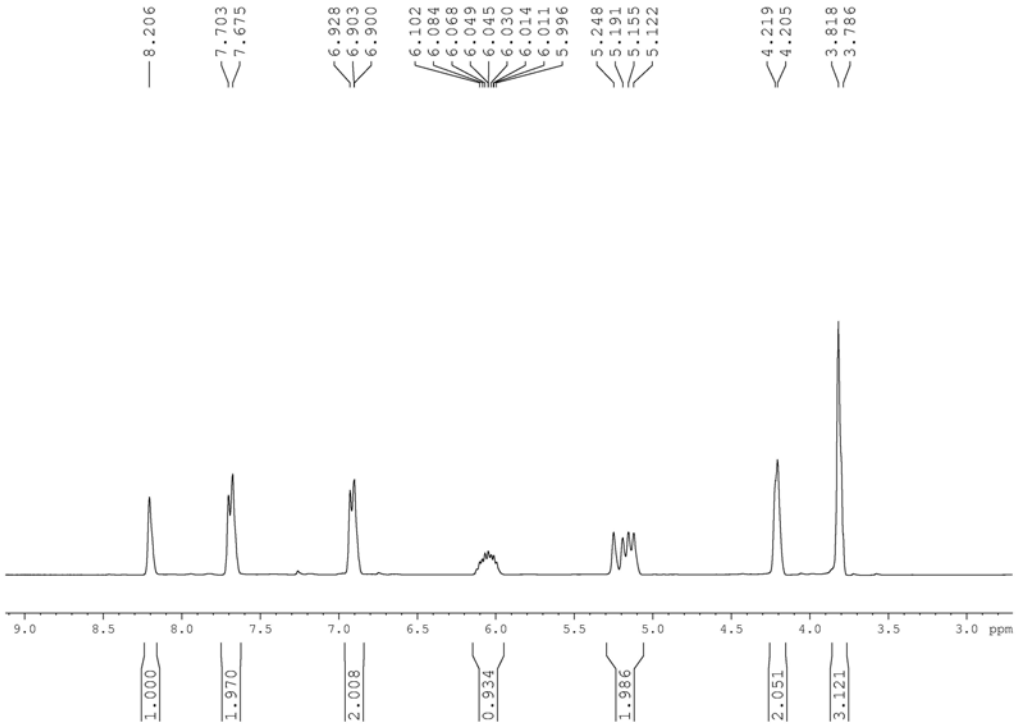


13C NMR:

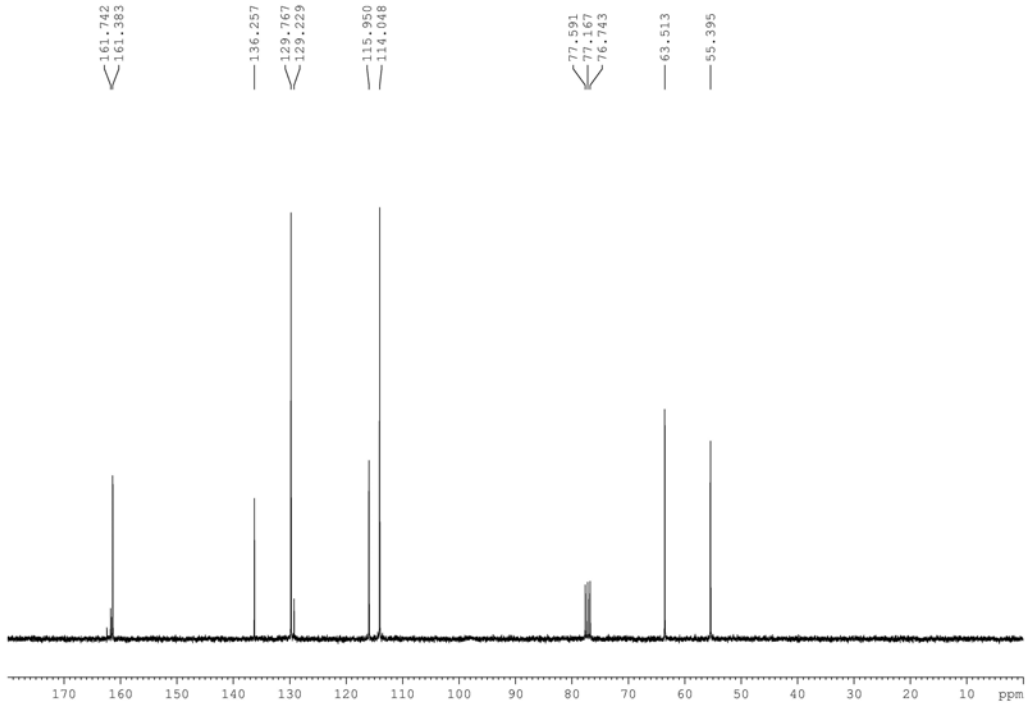


N-[[4-methoxyphenyl]methylene]-2-propen-1-amine (3)

1H NMR:

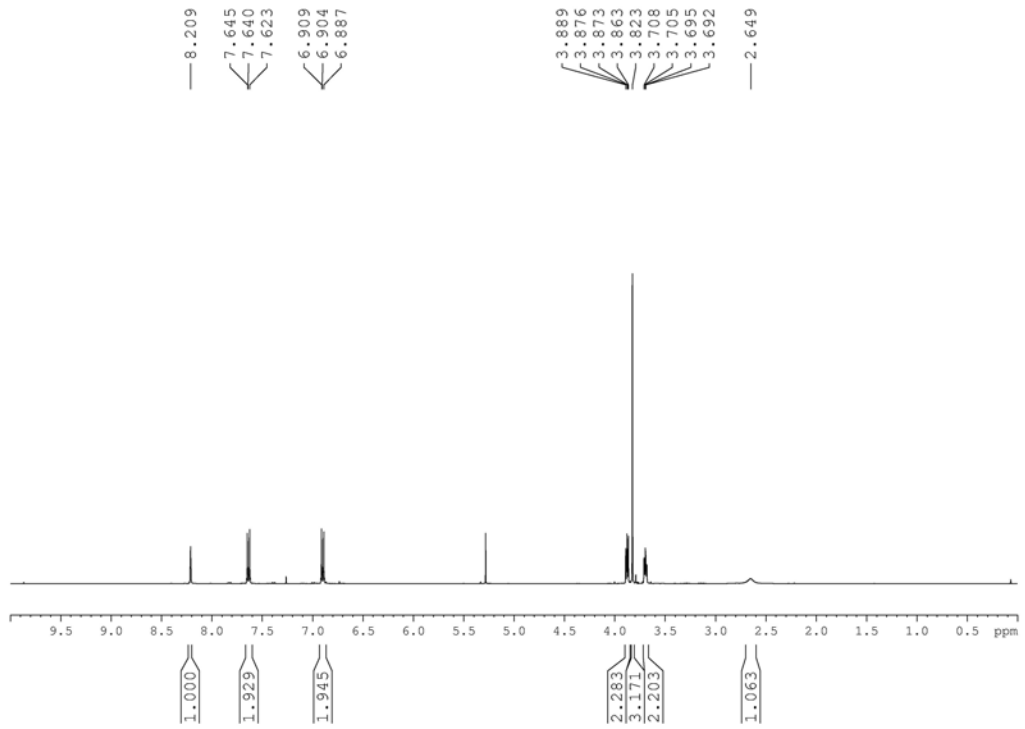


13C NMR

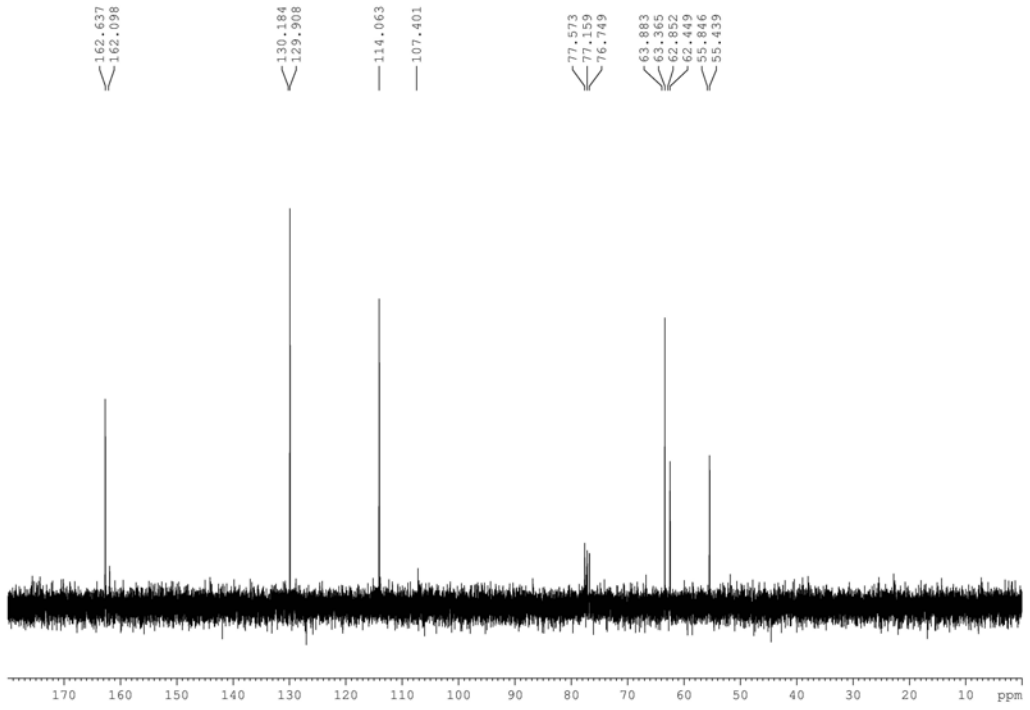


N-[[4-methoxyphenyl]methylene]-ethanol (4)

1H NMR:

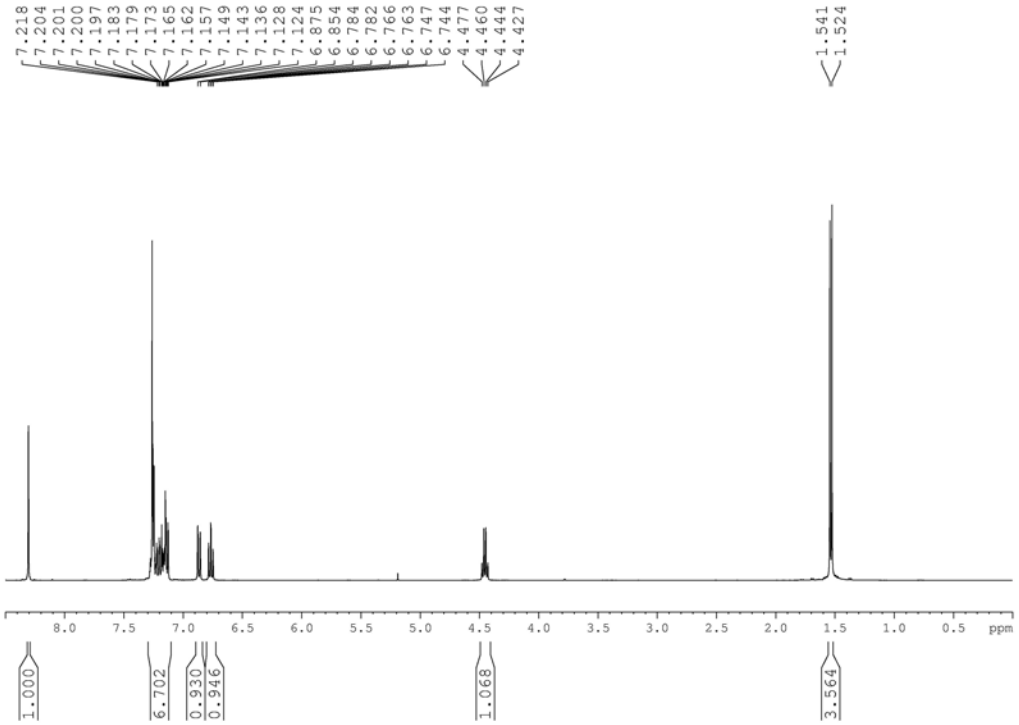


13C NMR:

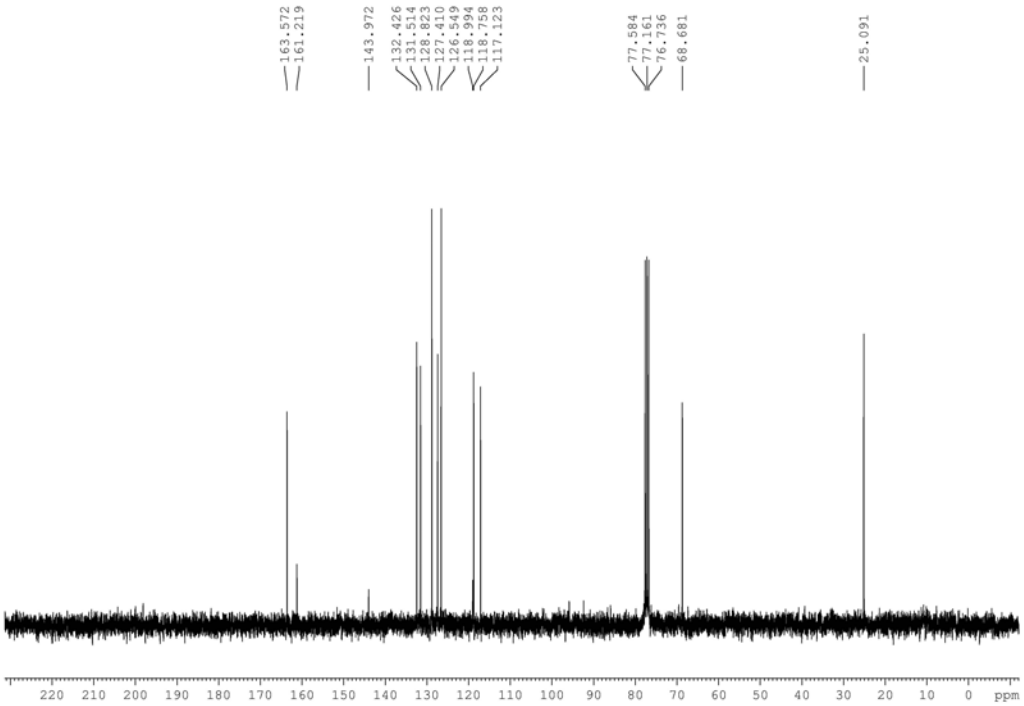


α-methyl-N-(2-hydroxyphenyl)-benzenemethanamine (5)

1H NMR:

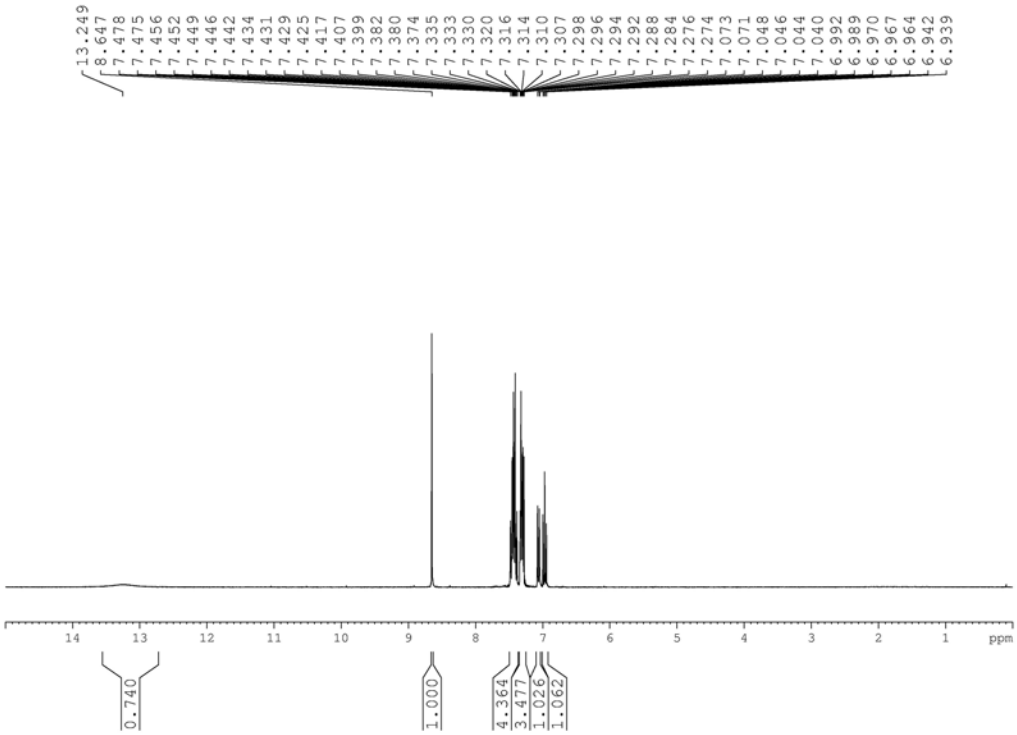


13C NMR:

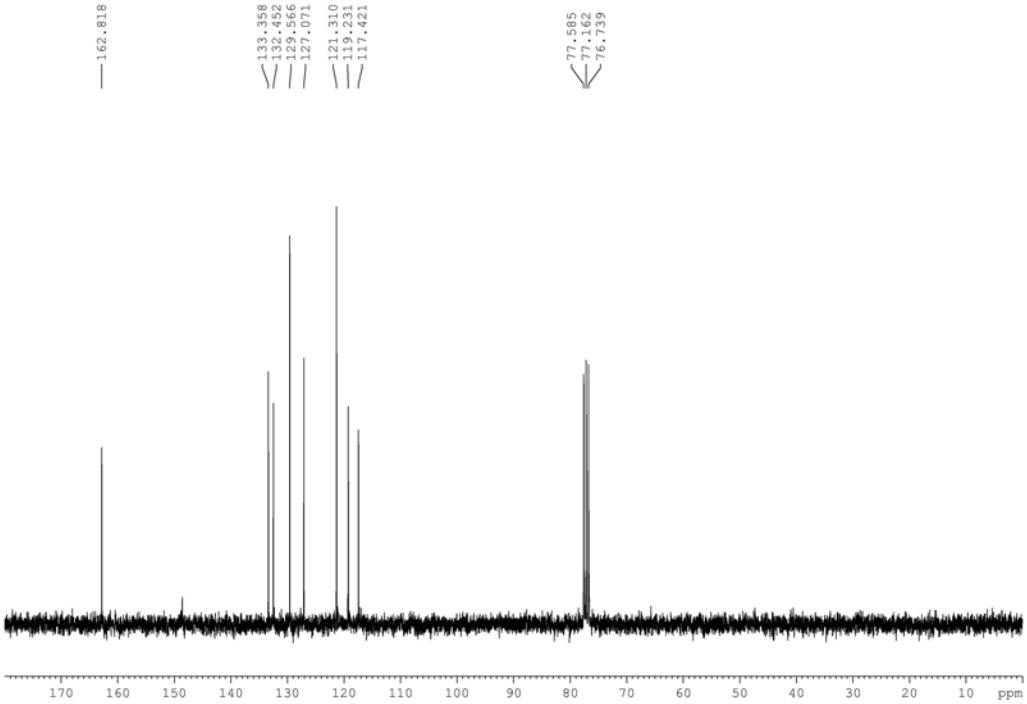


***N*-[(2-hydroxyphenyl)methylene]-benzenamine (6)**

1H NMR:

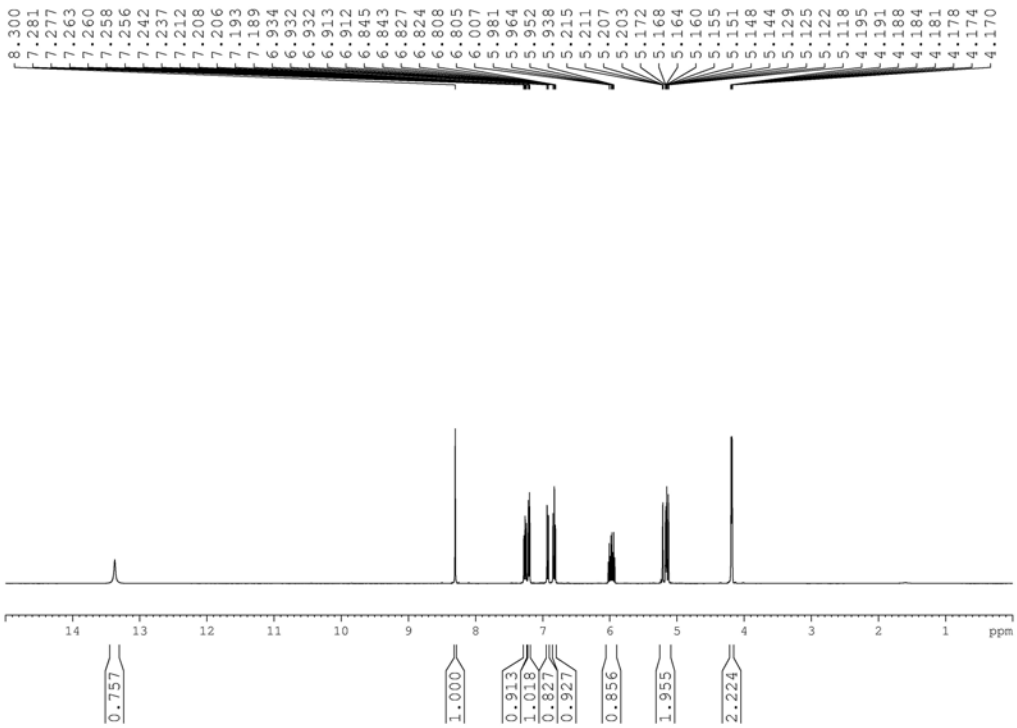


13C NMR:

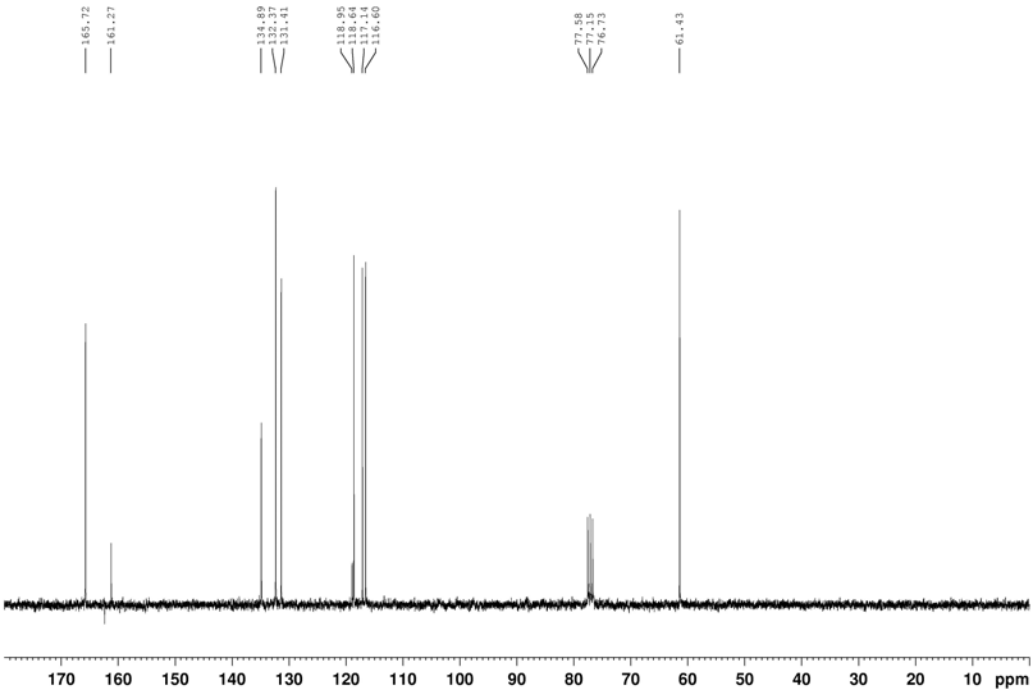


***N*-[(2-hydroxyphenyl)methylene]-2-propen-1-amine (7)**

1H NMR:

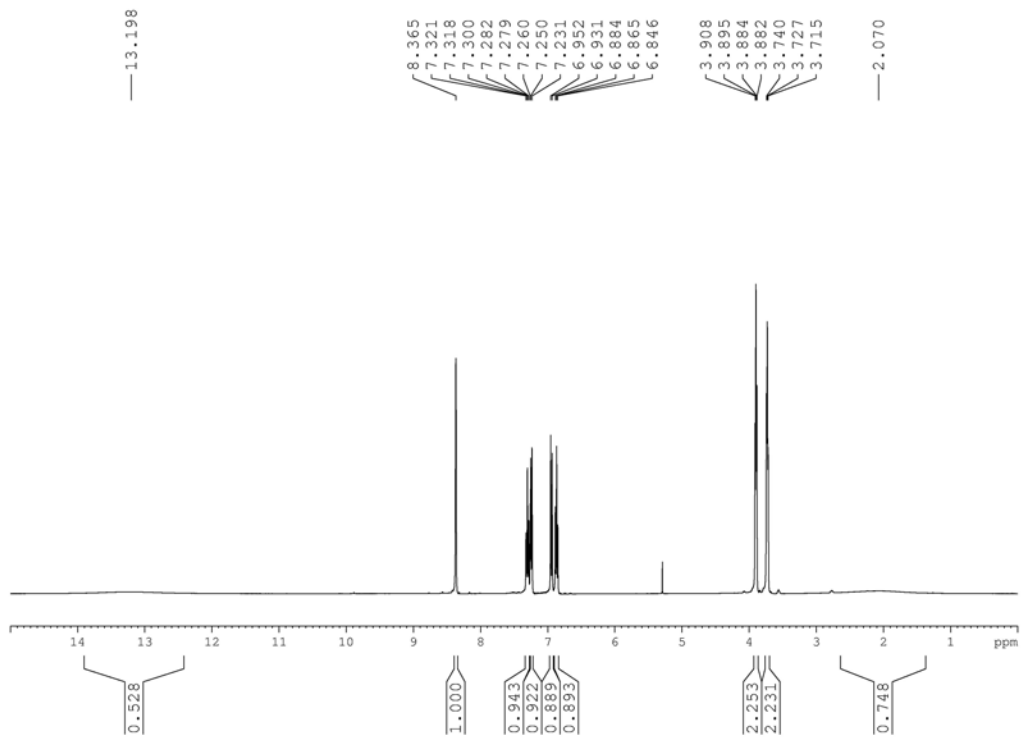


13C NMR:

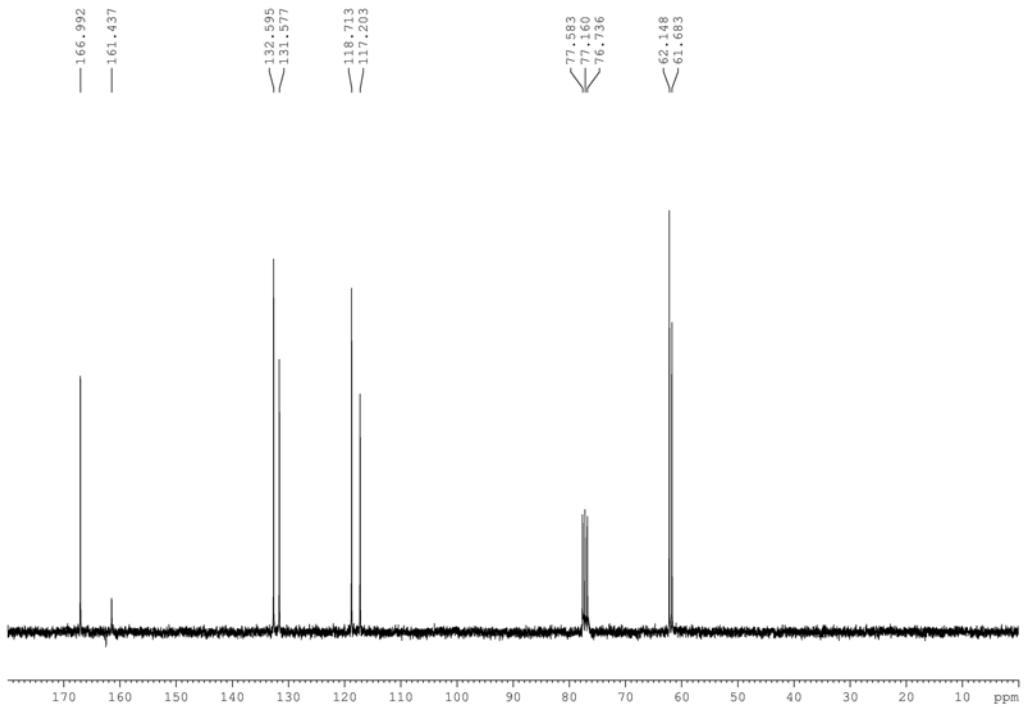


***N*-[(2-hydroxyphenyl)methylene]-ethanol (8)**

1H NMR:

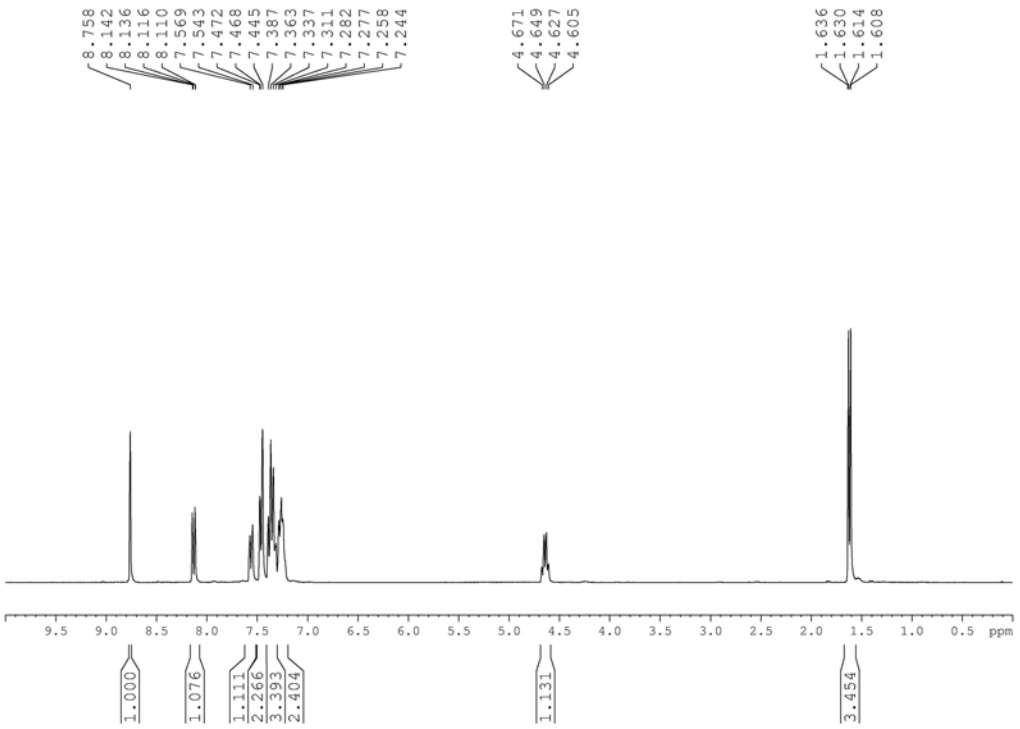


13C NMR:

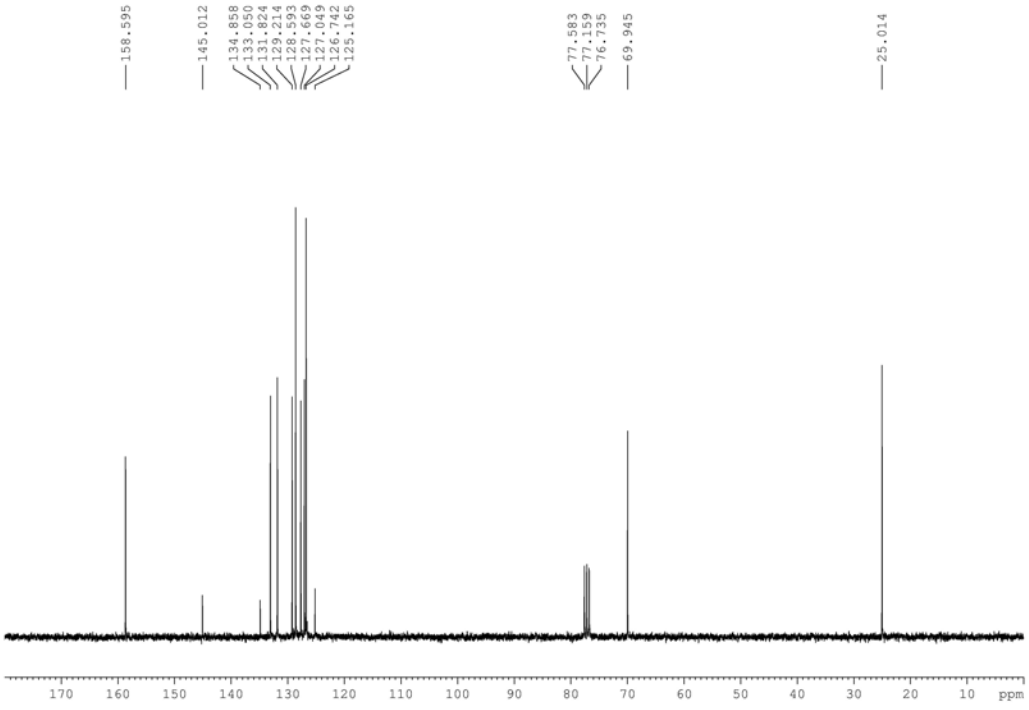


α-methyl-N-(2-bromophenyl)-benzenemethanamine (9)

1H NMR:

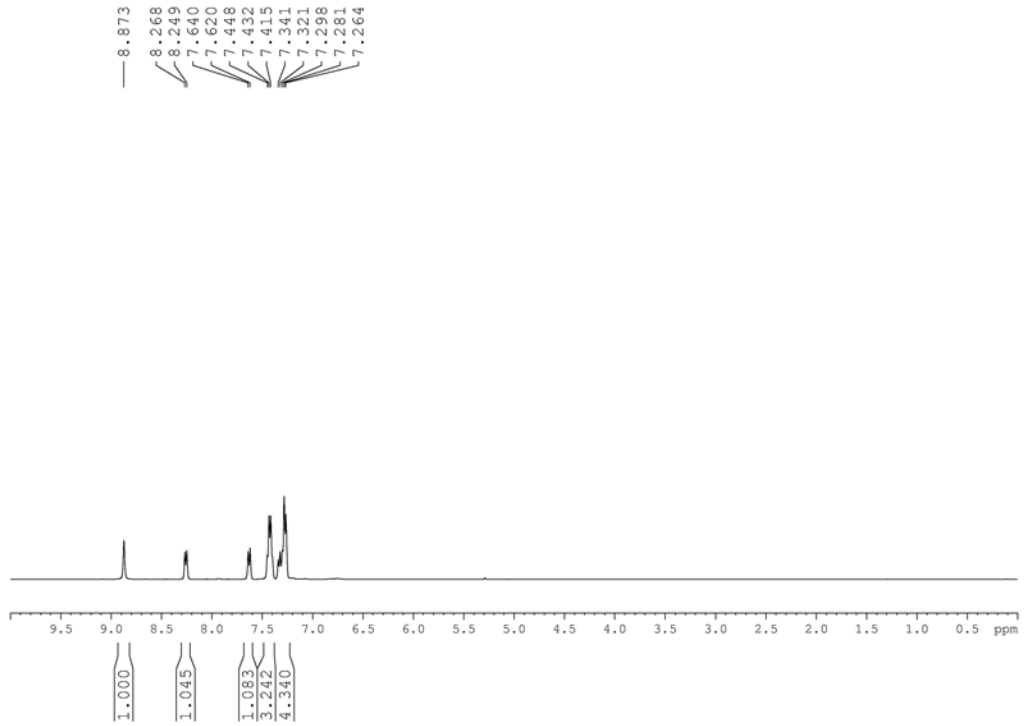


13C NMR:

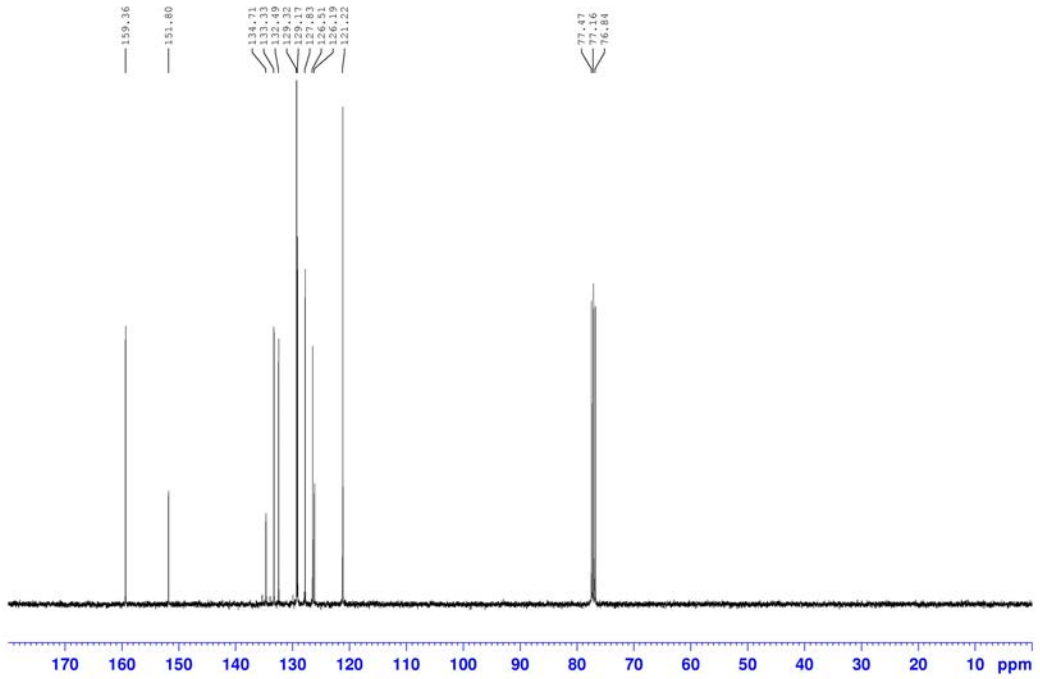


N-[[2-bromophenyl]methylene]-benzenamine (10)

1H NMR:

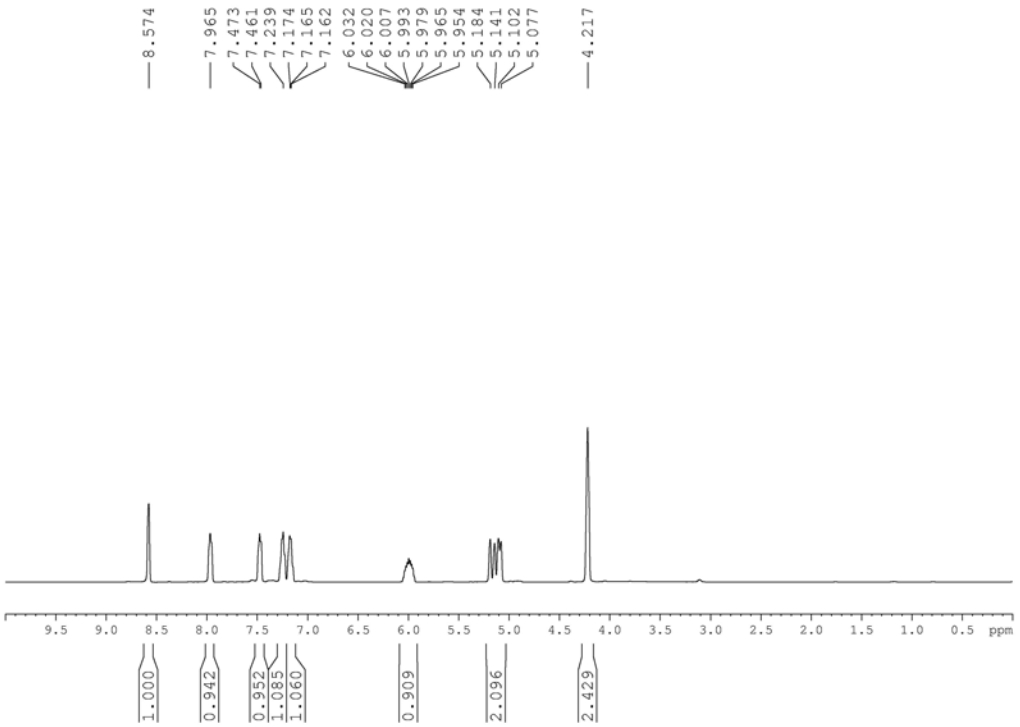


13C NMR:

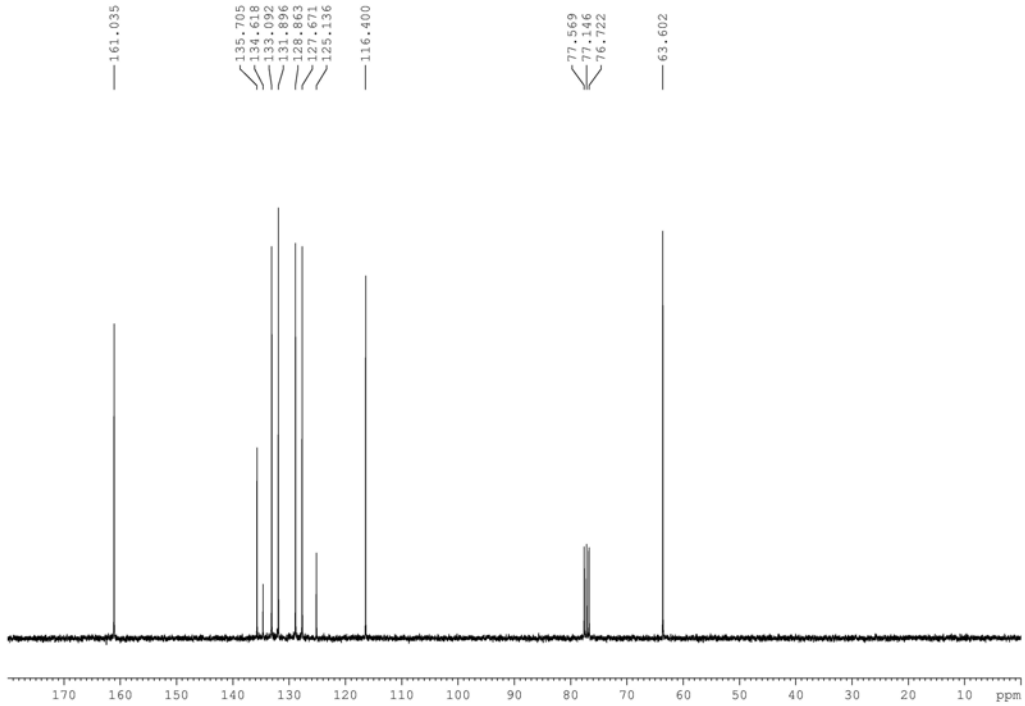


N-[[2-bromophenyl]methylene]-2-propen-1-amine (11)

1H NMR:

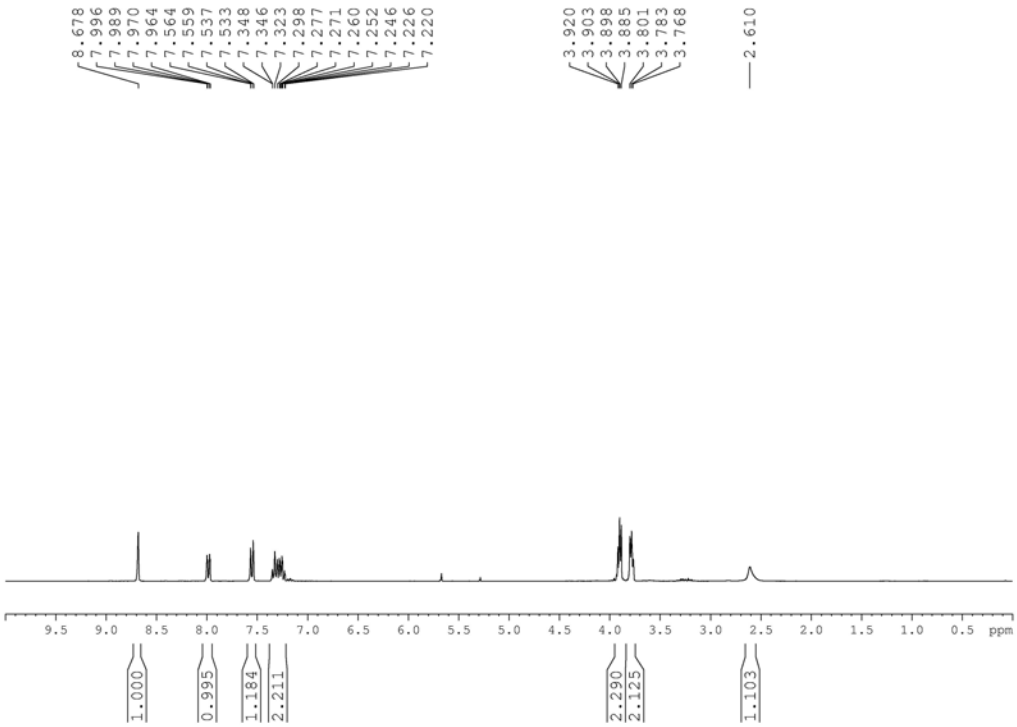


13C NMR:

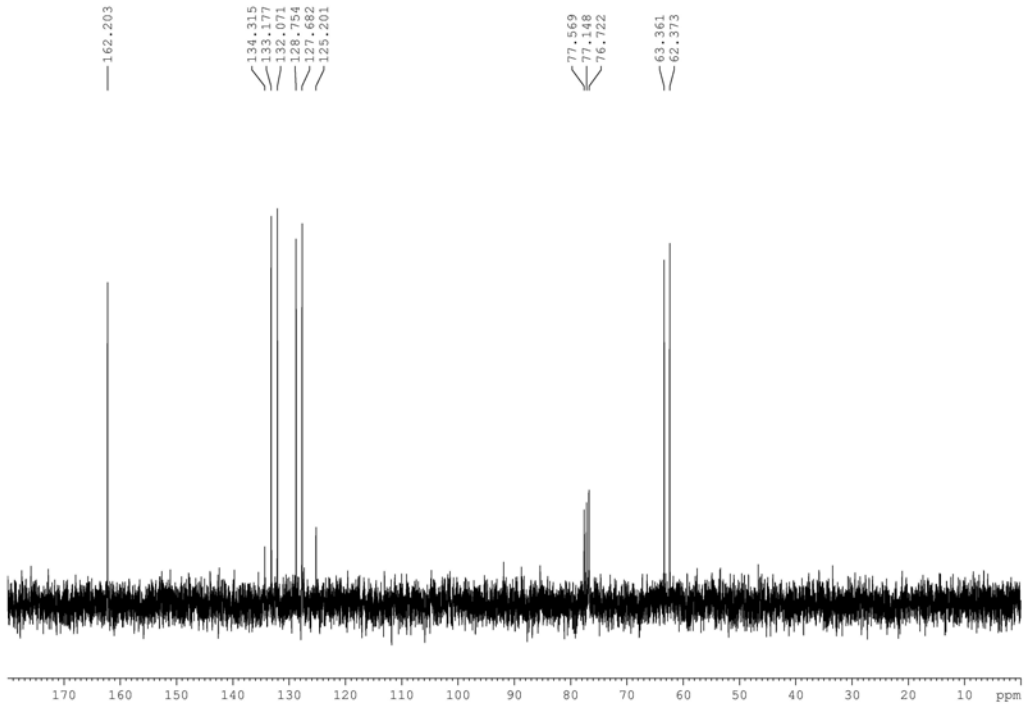


N-[[2-bromopheny]methylene]-ethanol 12.

1H NMR:

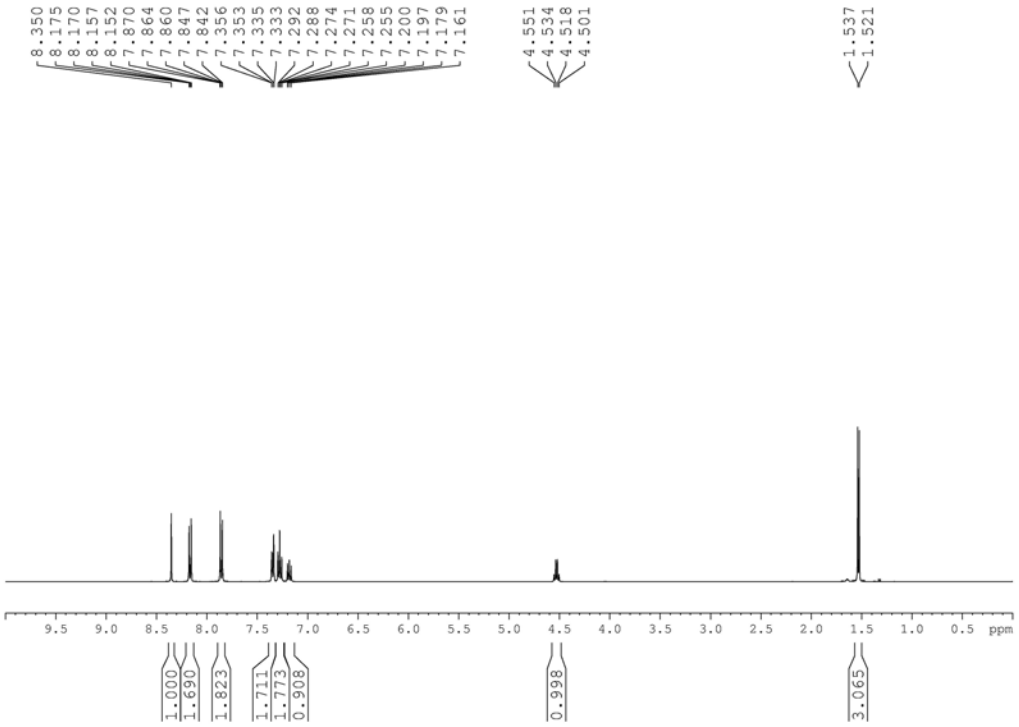


13C NMR:

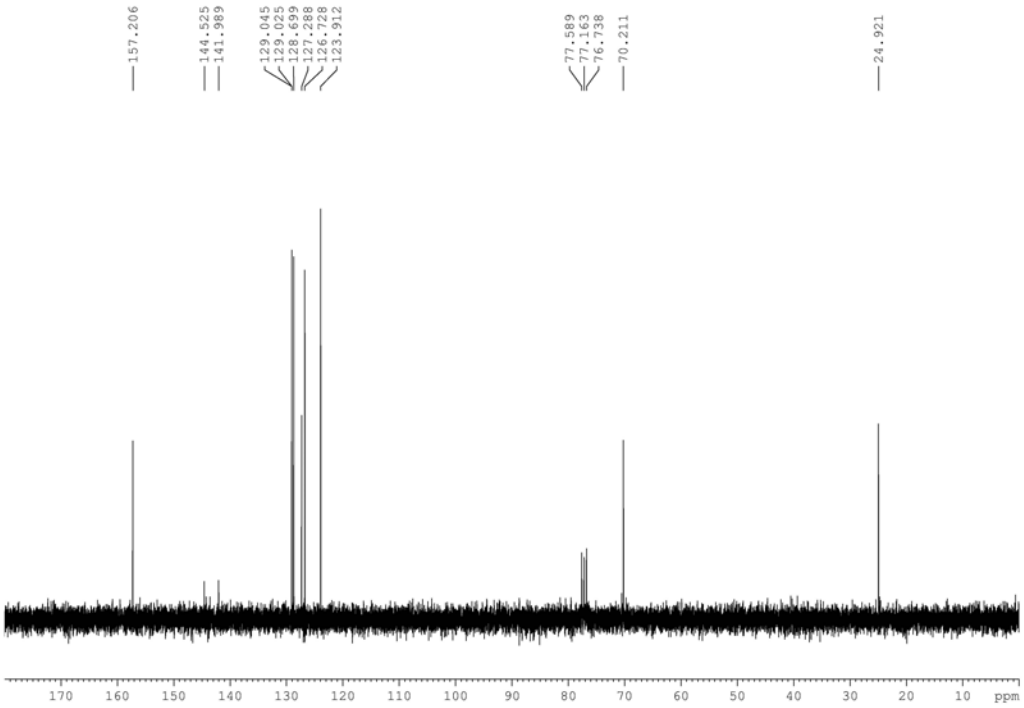


α-methyl-N-(4-nitrophenyl)-benzenemethanamine (13)

1H NMR:

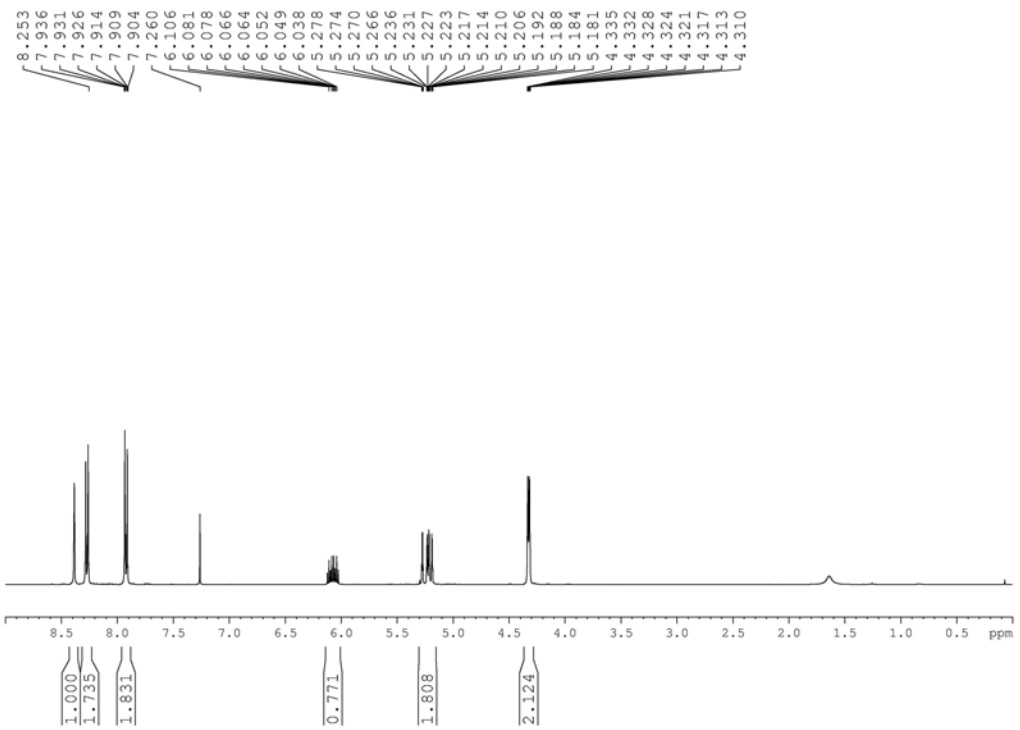


13C NMR:

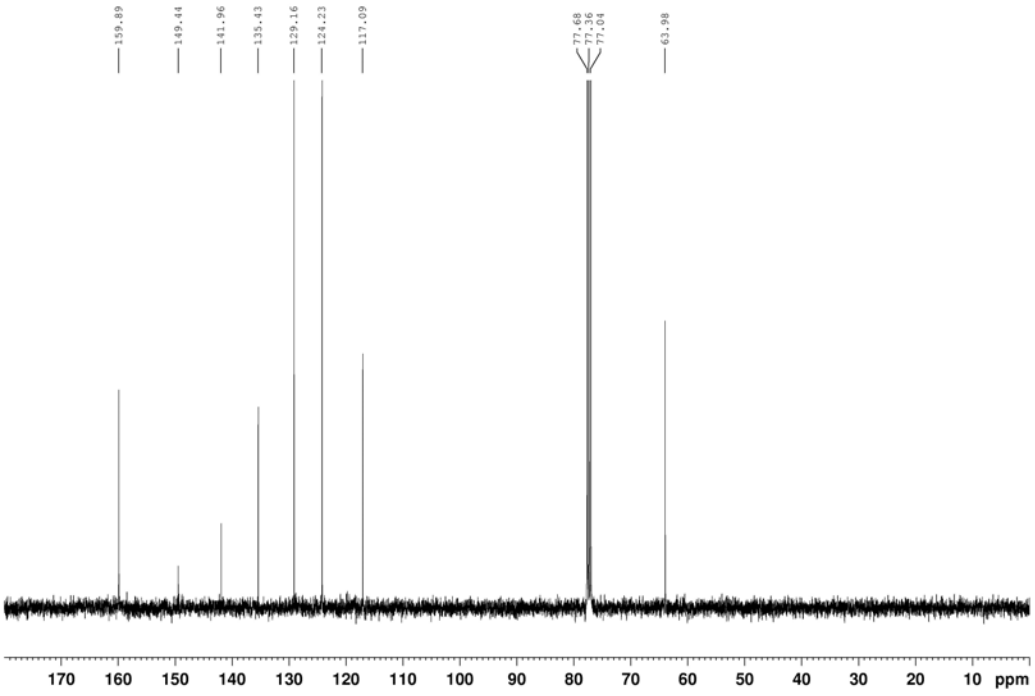


N-[[4-nitrophenyl]methylene]-2-propen-1-amine (15)

1H NMR:

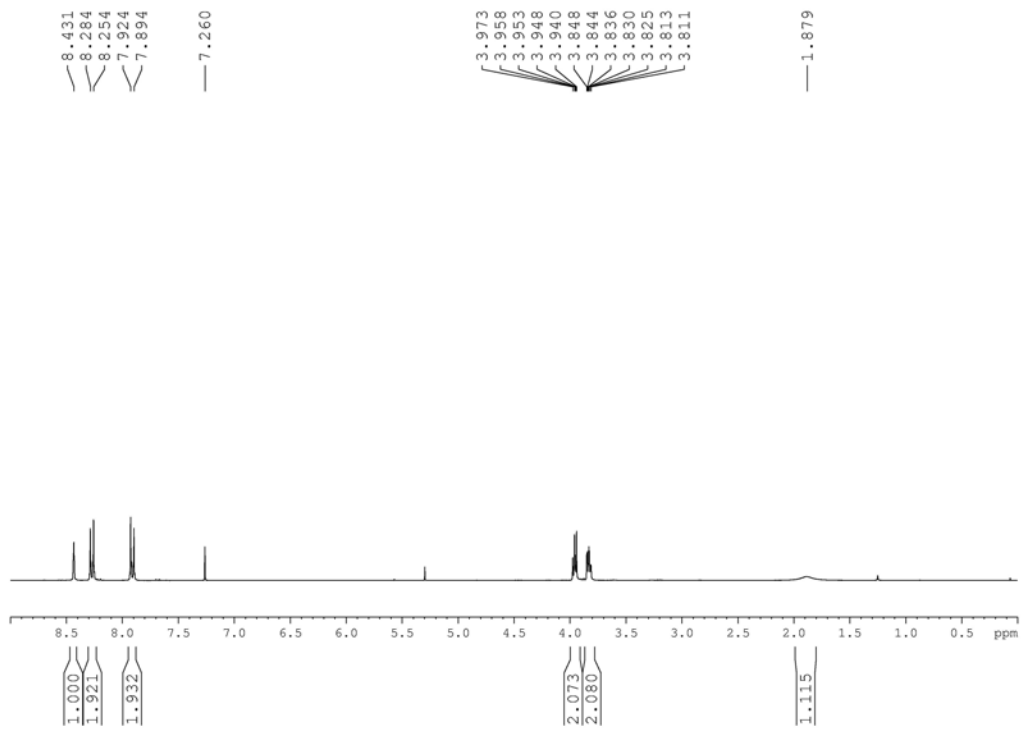


13C NMR:

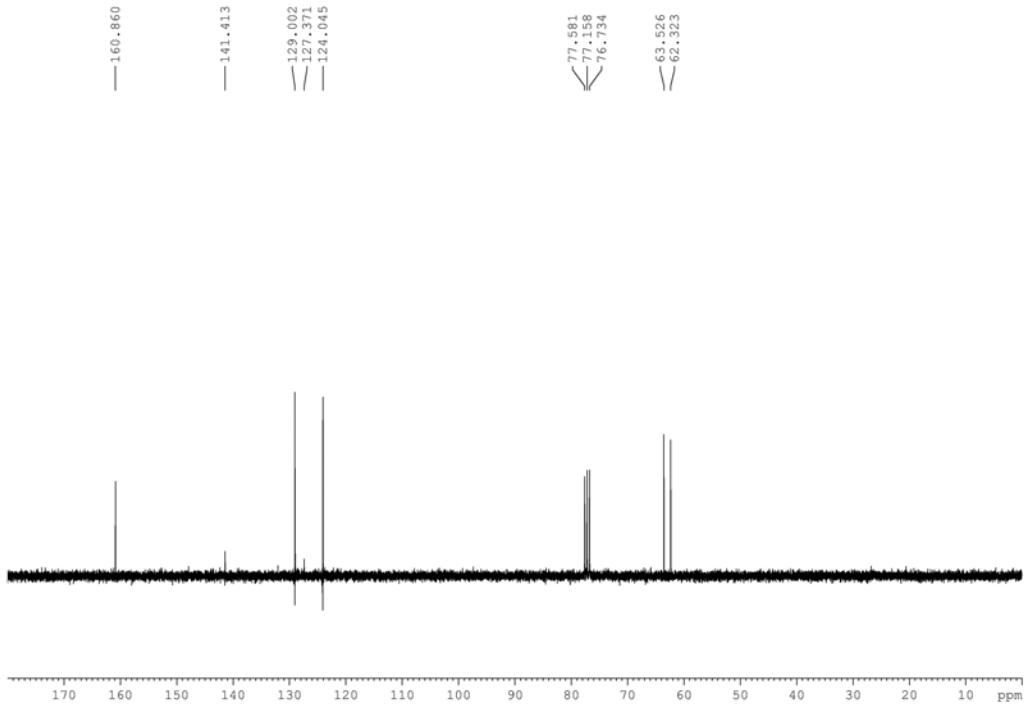


N-[[4-nitrophenyl]methylene]-ethanol (16)

1H NMR:

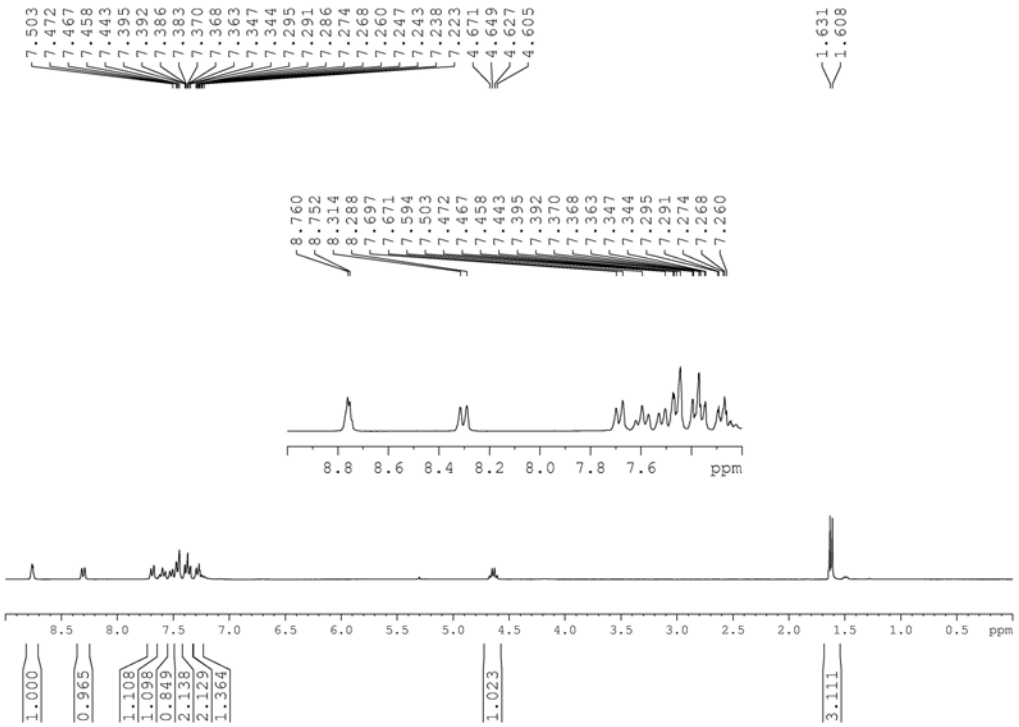


13C NMR:

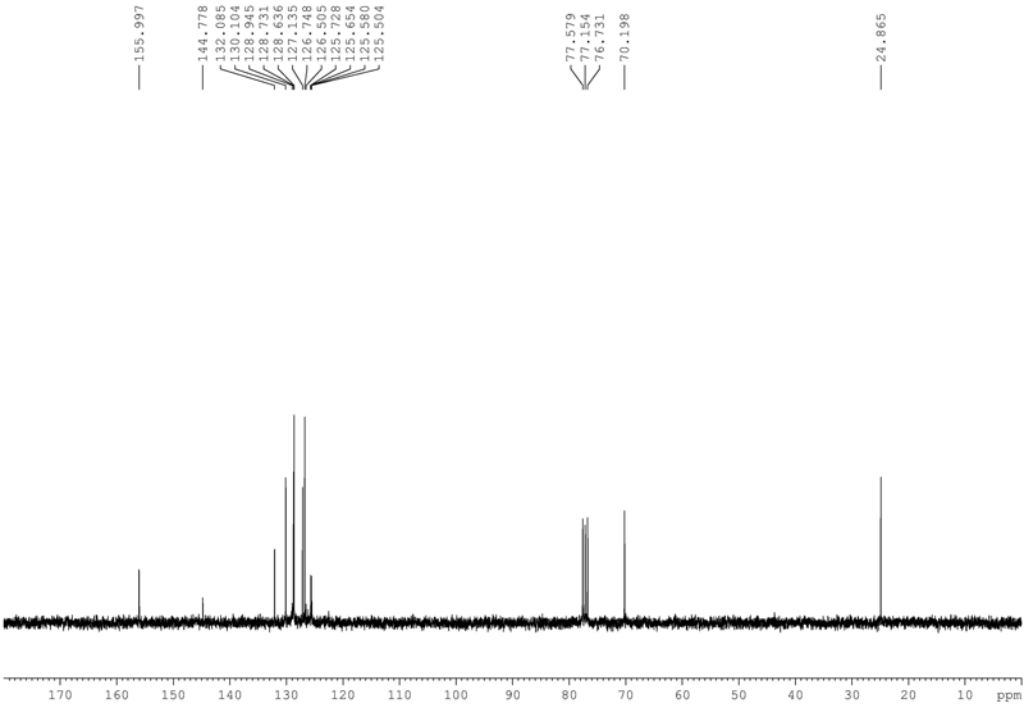


α-methyl-N-[[2-(trifluoromethyl)phenyl]methylene]-benzenemethanamine (25)

1H NMR:

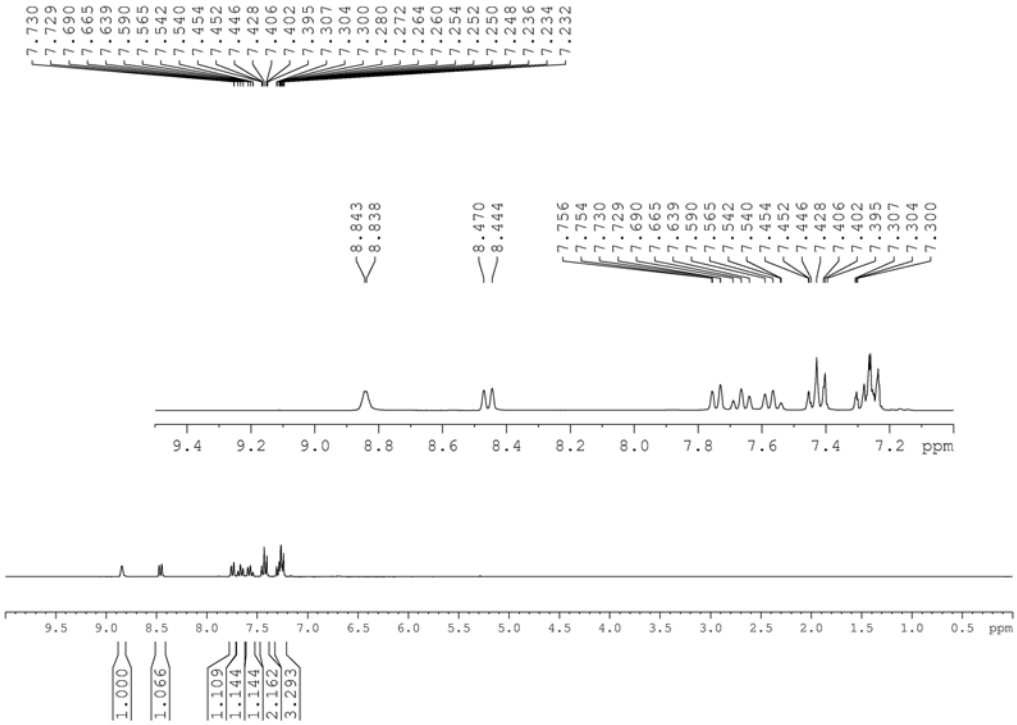


13C NMR:

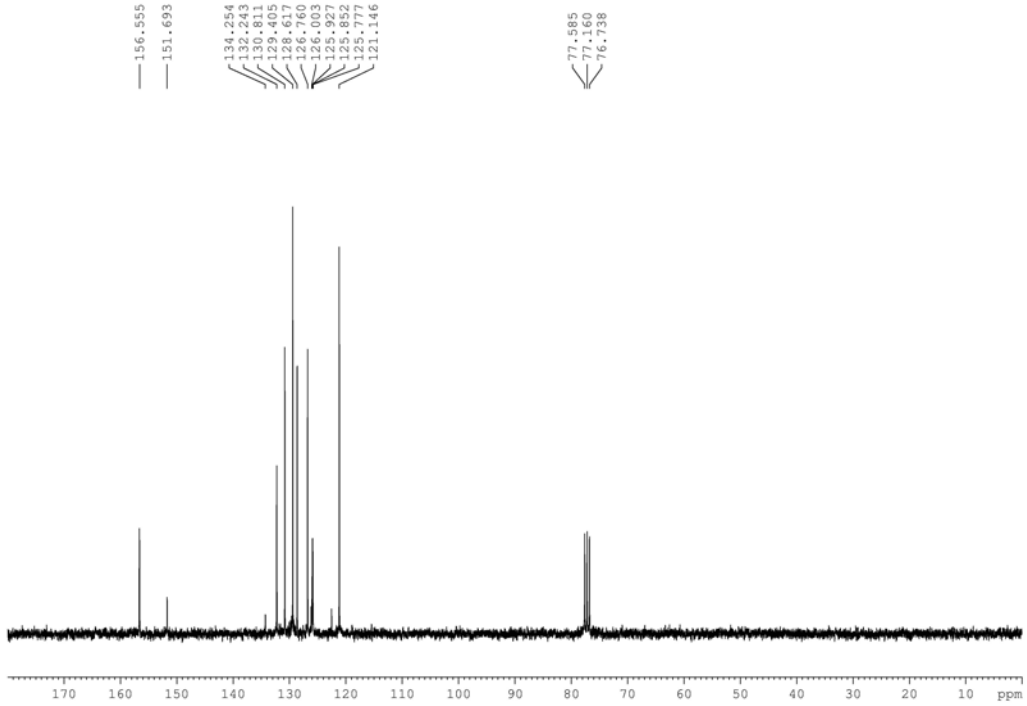


N-[[2-(trifluoromethyl)phenyl]methylene]-benzenamine (26)

1H NMR:

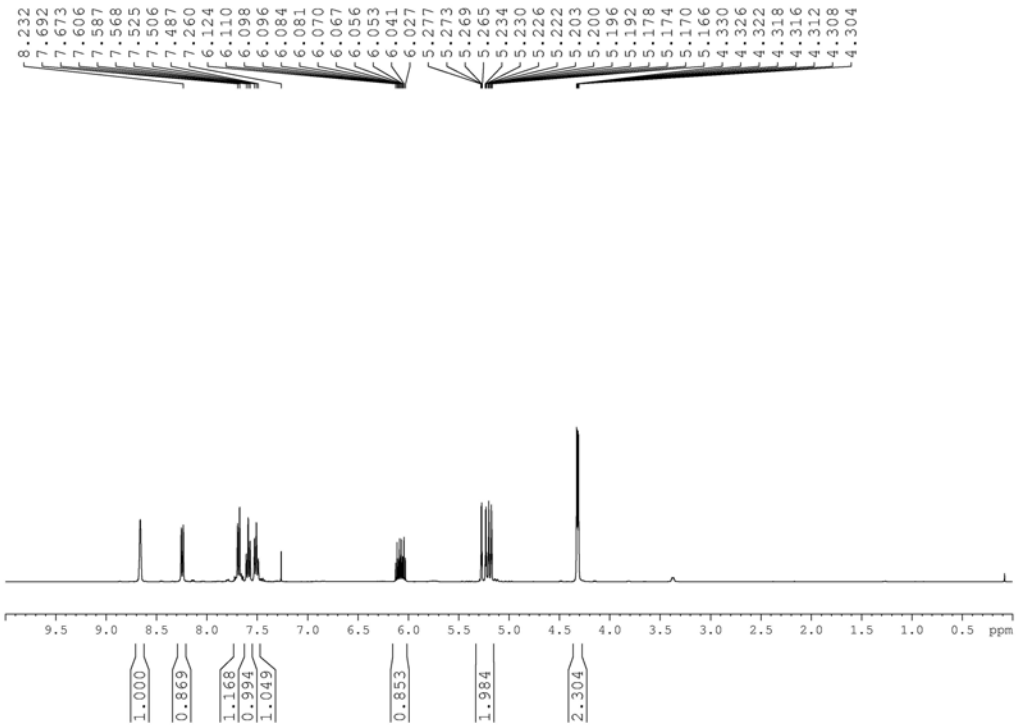


13C NMR:

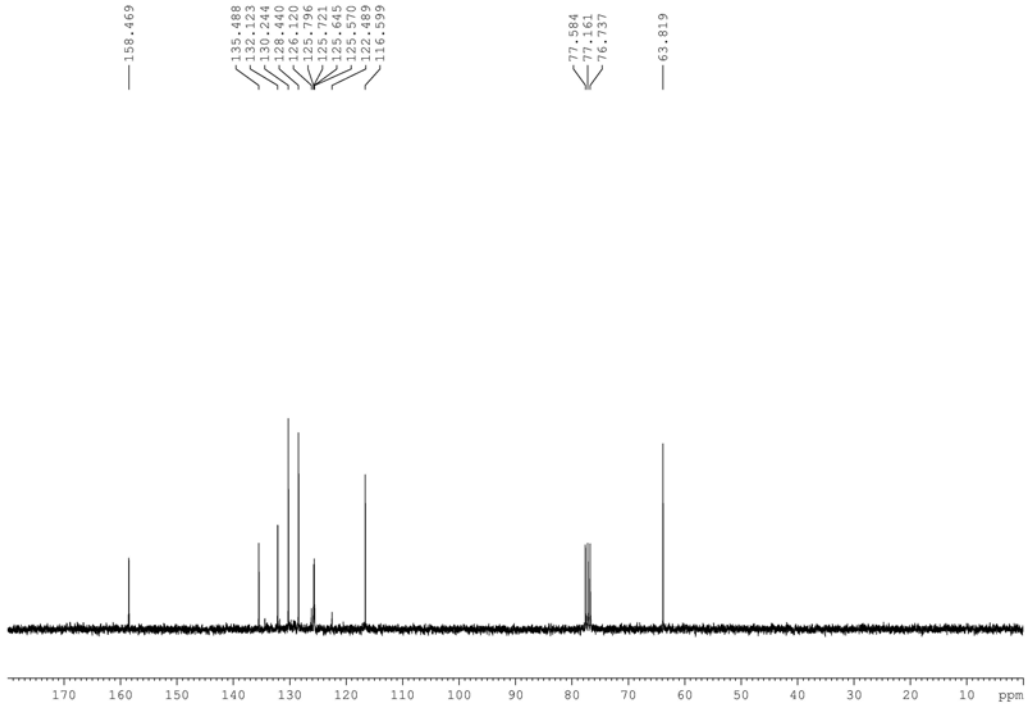


N-[[2-(trifluoromethyl)phenyl]methylene]-2-propen-1-amine (27)

1H NMR:

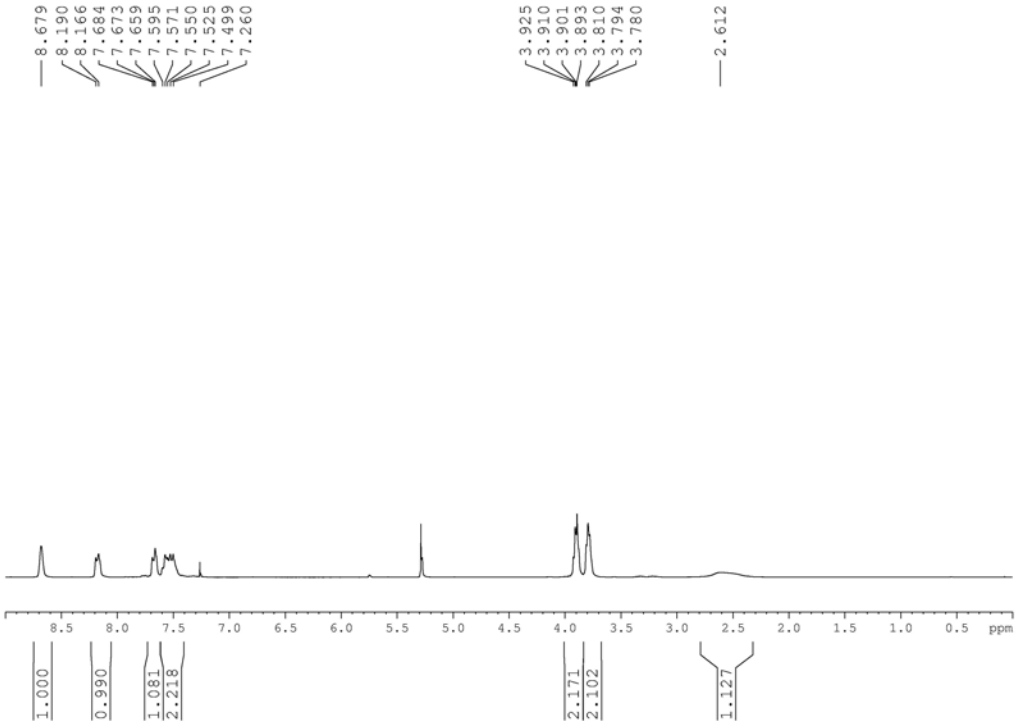


13C NMR:

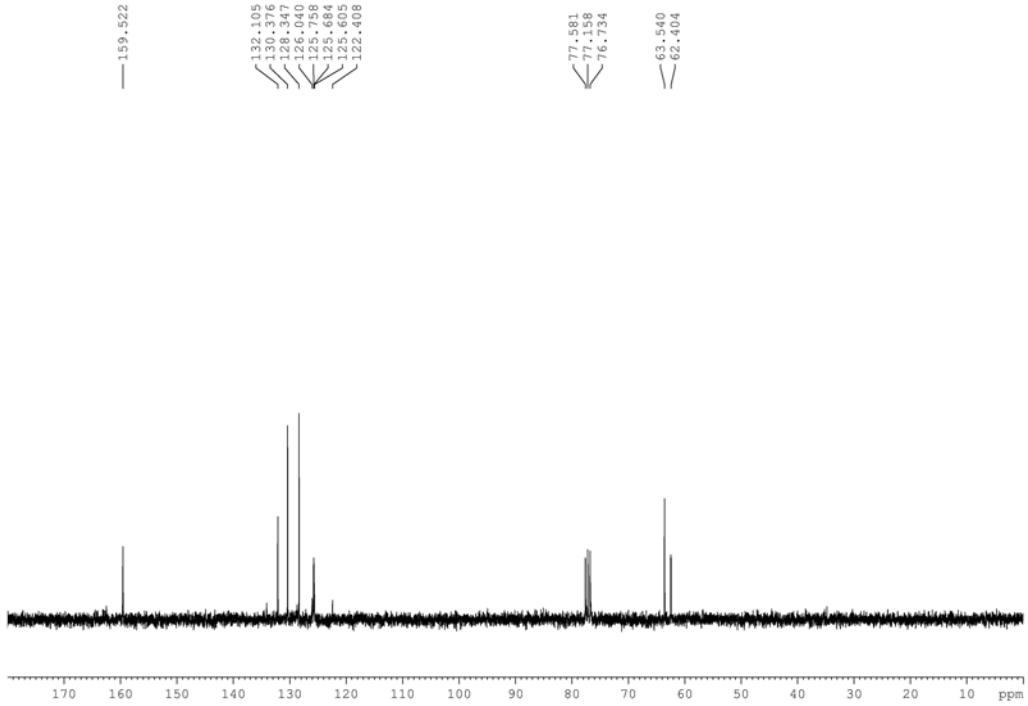


N-[[2-(trifluoromethyl)phenyl]methylene]-ethanol (28)

1H NMR:

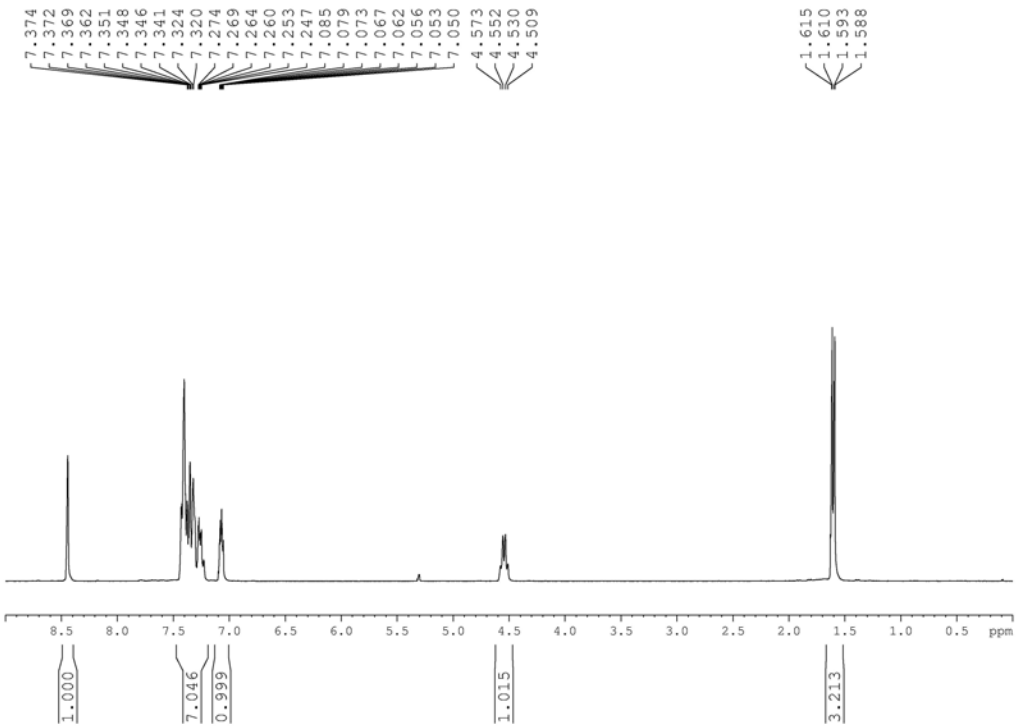


13C NMR:

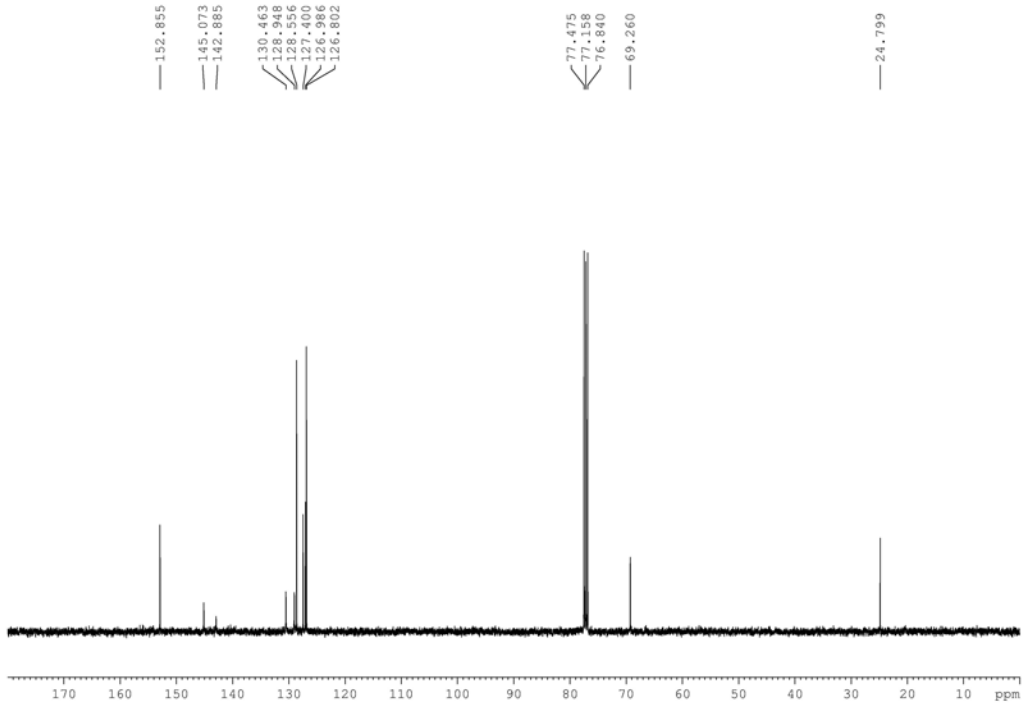


α-methyl-N-(2-thienylmethylene)-benzenemethanamine 29

1H NMR:

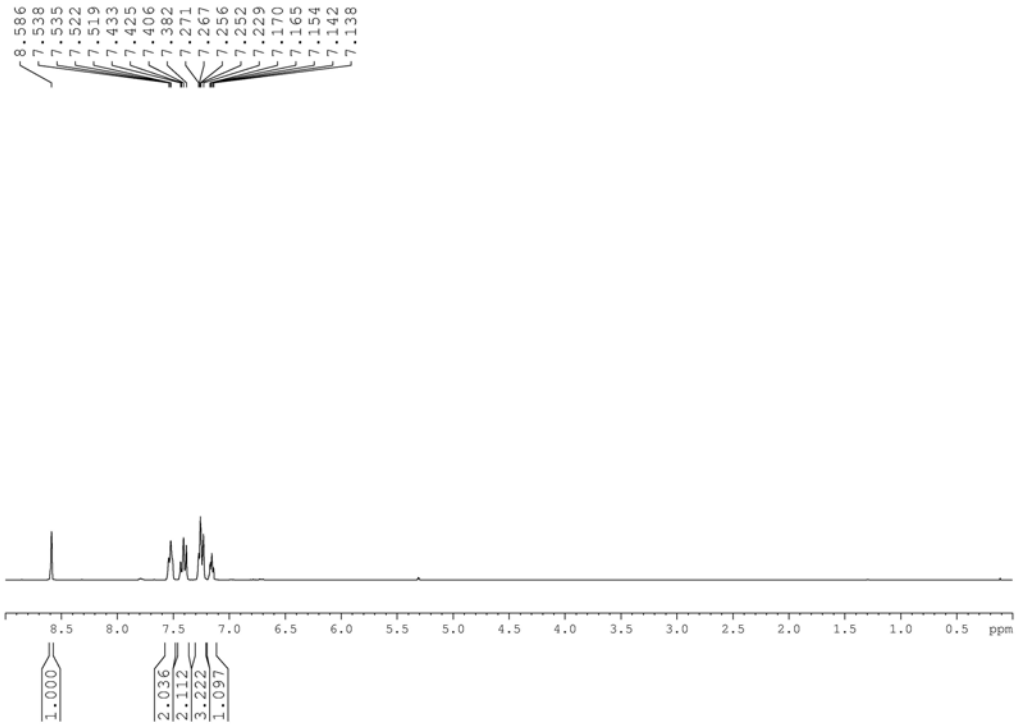


13C NMR

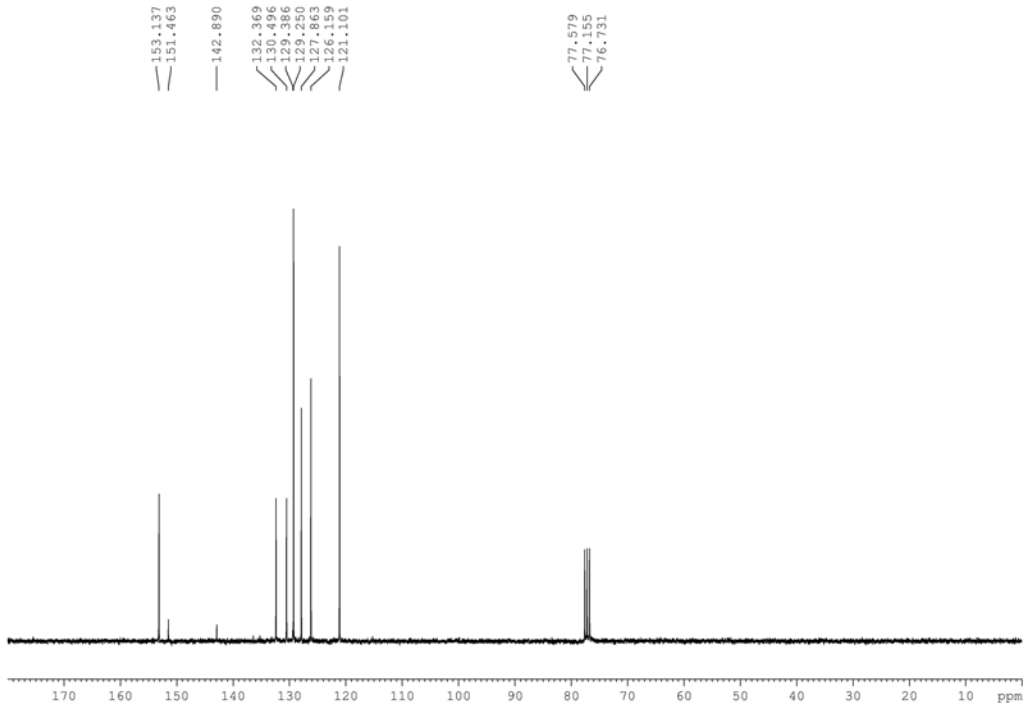


***N*-(2-thienylmethylene)-benzenamine 30**

1H NMR:

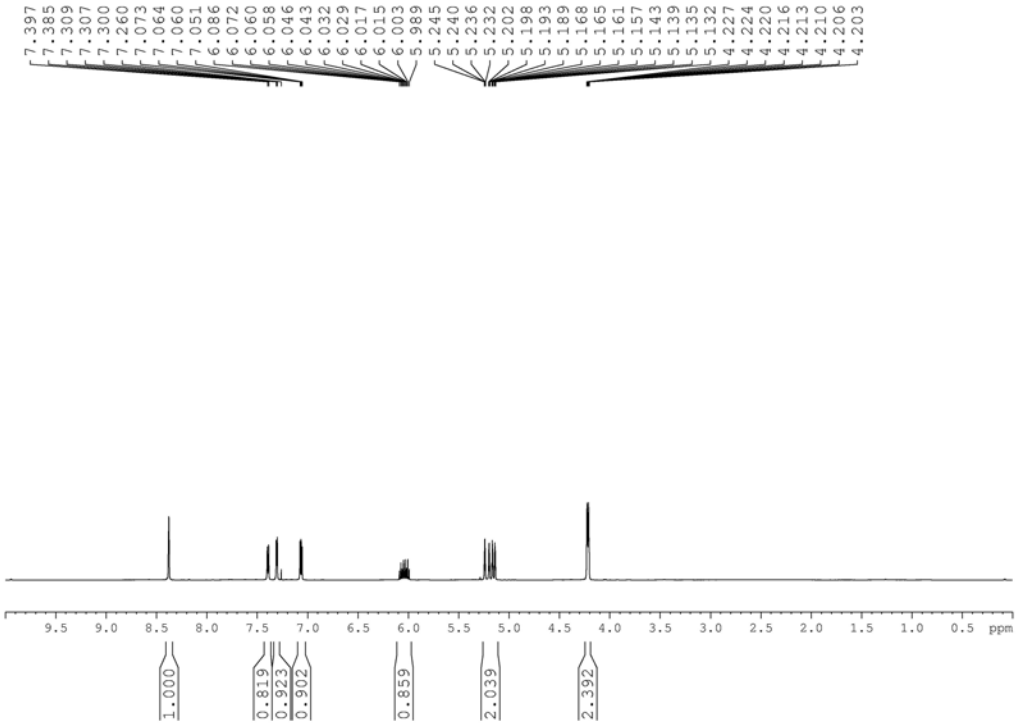


13C NMR:

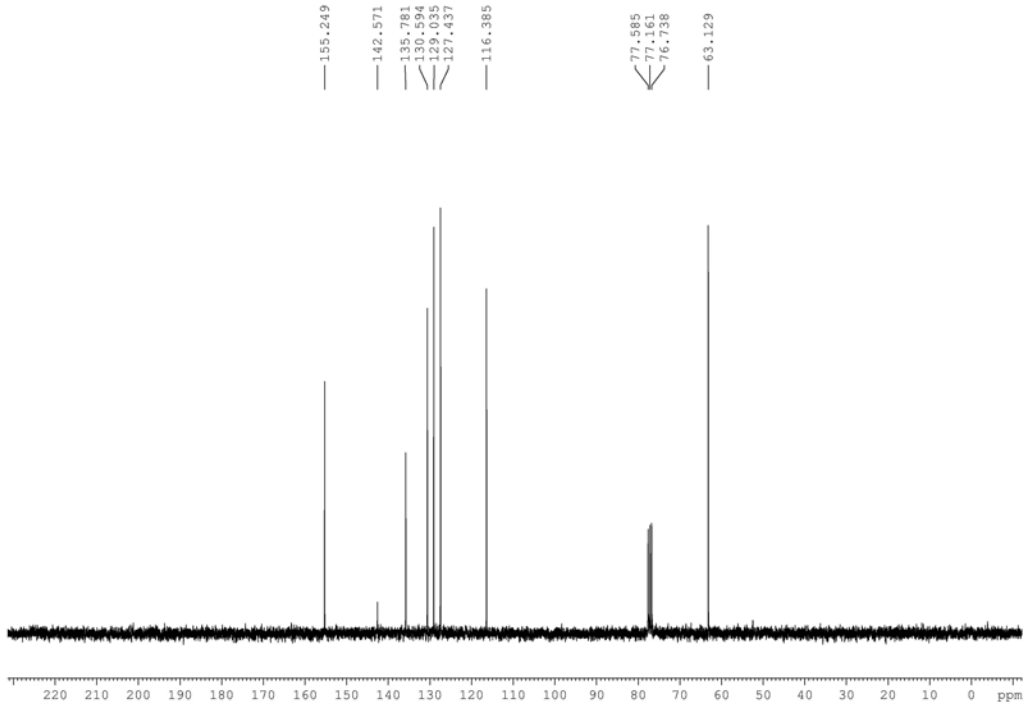


***N*-(2-thienylmethylene)-2-propen-1-amine 31**

1H NMR:

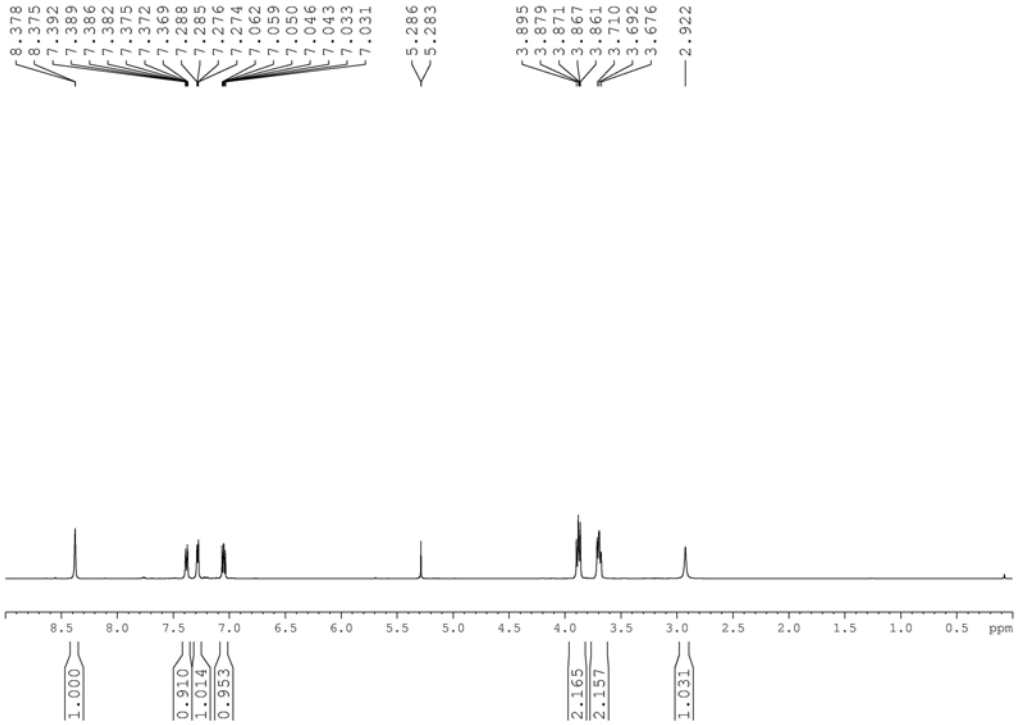


13C NMR:



2-[(2-thienylmethylene)amino]-ethanol 32

1H NMR:



13C NMR: