Supporting Information

ortho-Alkenylation of anilines with aromatic terminal alkynes over nanosized zeolite beta

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1. Experimental section

I. General information

All chemicals used were reagent grade and used as received without further purification. All the samples were systematically characterized by different spectroscopic techniques. The XRD patterns of the samples were obtained on a Regaku miniflux X-ray Diffractometer using Ni filtered CuKα radiation at 2θ = 2-80^{o} with a scanning rate of 2^{o} min^{-1} and the beam voltage and currents of 30 kV and 15 mA, respectively. ^{1}H NMR spectra were recorded by using Bruker VX NMR FT-300 or Varian Unity 500 and ^{13}C NMR spectra were 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), d (doublet), dd (doublet of doublet), dt (doublet of triplet), t (triplet), m (multiplet). Column chromatography was carried out using silica gel (100-200 mesh).

II. General procedure for the *ortho*-alkenylation of anilines with aromatic terminal alkynes over nanosized zeolite beta

Aniline (2 mmol), aromatic alkyne (2 mmol) and nanosized zeolite beta (100 mg) were added to 1 mL of toluene in sealed vial and the reaction mixture was allowed to stir at 120 ^{o}C for 3 h. Than the reaction mixture was cooled to room temperature, diluted with ethylacetate. The catalyst was separated by filtration and the removal of solvent in vacuo yielded 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 H^{1} and C^{13} NMR spectral data.

2. Spectroscopic data

l-Phenyl-l-(2-aminophenyl)ethylene (3a)[1]

^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 3.54 (bs, 2 H), 5.35 (d, J = 1.34 Hz, 1 H), 5.79 (d, J = 1.34 Hz, 1 H), 6.69 (dd, J = 1.34, 7.94 Hz, 1 H), 6.78 (dt, J = 1.22, 7.45 Hz, 1 H), 7.10–7.18 (m, 2 H), 7.28–7.33 (m, 3 H), 7.35–7.39 (m, 2 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) = 115.51, 116.04, 118.24, 126.56, 127.22, 128.01, 128.49, 128.69, 130.74, 139.57, 143.84, 147.08.

1-Phenyl-l-(2-amino-5-methoxyphenyl)ethylene (3b)[1]

^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 3.29 (bs, 2 H), 3.75 (s, 3 H), 5.35 (d, J = 1.37 Hz, 1 H), 5.80 (d, J = 1.22 Hz, 1 H), 6.65 (d, J = 8.54 Hz, 1 H), 6.72 (d, J = 2.89 Hz, 1 H), 6.77 (dd, J = 2.89, 8.54 Hz, 1 H), 7.29–7.33 (m, 3 H), 7.36–7.38 (m, 2 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) = 55.73, 114.56, 116.08, 116.12, 116.86, 126.58, 128.08, 128.55, 137.56, 139.36, 147.09, 152.46.

1-Phenyl-l-(2-amino-5-methylphenyl)ethylene (3c)[1]

^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 2.26 (s, 3 H), 3.48 (bs, 2 H), 5.34 (d, J = 1.13 Hz, 1 H), 5.78 (d, J = 1.13 Hz, 1 H), 6.62 (d, J = 7.93 Hz, 1 H), 6.93 (s, 1 H), 6.97 (dd, J = 1.51, 7.93 Hz, 1 H), 7.28–7.39 (m, 5 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) = 20.35, 115.85, 115.69, 126.58, 127.41, 127.95, 128.47, 129.23, 131.13, 139.70, 141.34, 147.22.

1-Phenyl-l-(2-amino-3-methoxyphenyl)ethylene (3d)[1]

^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 3.74 (bs, 2 H), 3.86 (s, 3 H), 5.36 (d, J = 1.37 Hz, 1 H), 5.80 (d, J = 1.37 Hz, 1 H), 6.69-6.76 (m, 2 H), 6.80 (dd, J = 1.98, 7.32 Hz, 1 H), 7.27-7.32 (m, 3 H), 7.36-7.38 (m, 2 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) = 55.53, 109.37, 115.93, 117.24, 122.84, 126.63, 127.12, 127.95, 128.46, 133.87, 139.60, 146.88, 147.04.

1-Phenyl-l-(2-amino-3-methylphenyl)ethylene (3e)[1]

^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 2.17 (s, 3 H), 3.54 (bs, 2 H), 5.35 (d, J = 1.13 Hz, 1 H), 5.81 (d, J = 1.51 Hz, 1 H), 6.73 (t, J = 7.36 Hz, 1 H), 7.00 (d, J = 6.60 Hz, 1 H), 7.07 (d, J = 7.93 Hz, 1 H), 7.29–7.39 (m, 5 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) = 17.71, 116.06, 117.78, 122.34, 126.58, 128.01, 128.50, 128.60, 129.84, 139.71, 142.00, 147.35.

1-Phenyl-l-(2-amino-3, 5-dimethylphenyl)ethylene (3f)

^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 2.15 (s, 3 H), 2.24 (s, 3 H), 3.41 (bs, 2 H), 5.33 (d, J = 1.37 Hz, 1 H), 5.79 (d, J = 1.37 Hz, 1 H), 6.81 (s, 1 H), 6.89 (s, 1 H), 7.27-7.32 (m, 3 H), 7.36-7.38 (m, 2 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) = 17.68, 20.33, 115.93, 126.57, 127.97, 128.47, 128.90, 130.56, 139.43, 147.37. MS (ESI): *m/z* = 224 (M^+ + H). Anal.Calcd for $C_{16}H_{17}N$ C, 86.05; H, 7.67; N, 6.27; Found: C, 86.09; H, 7.61; N, 6.19.

1-Phenyl-l-(2-amino-5-chlorophenyl)ethylene (3g)[1]

^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 3.54 (bs, 2 H), 5.36 (d, *J* = 1.66 Hz, 1 H), 5.81 (d, *J* = 1.22 Hz, 1 H), 6.60-6.62 (m, 1 H), 7.09-7.11 (m, 2 H), 7.29–7.36 (m, 5 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) = 116.63, 116.74, 122.79, 126.53, 128.31, 128.49, 128.65, 130.23, 138.88, 142.58, 146.09.

1-Phenyl-l-(2-amino-3-bromophenyl)ethylene (3h)

^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 4.03 (bs, 2 H), 5.36 (d, *J* = 1.32 Hz, 1 H), 5.83 (d, *J* = 1.13 Hz, 1 H), 6.65 (t, *J* =7.74 Hz, 1 H), 7.06 (dd, *J* =7.74 Hz, 1 H), 7.30-7.44 (m, 6 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) = 109.66, 116.61, 118.58, 126.50, 128.21, 128.29, 128.63, 129.81, 131.97, 138.86, 141.66, 146.66. MS (ESI): *m/z* = 274 (M^+ + H). Anal.Calcd for $C_{14}H_{12}BrN$ C, 61.33; H, 4.41; N, 5.11; Found: C, 61.30; H, 4.40; N, 5.19.

1-Phenyl-l-(2-amino-5-bromophenyl)ethylene (3i)[1]

^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 3.55 (bs, 2 H), 5.35 (d, *J* = 1.05 Hz, 1 H), 5.89 (d, *J* = 1.22 Hz, 1 H), 6.57 (d, *J* = 9.15 Hz, 1 H), 7.22-7.25 (m, 2 H), 7.30-7.37 (m, 5 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) = 109.84, 116.77, 117.02, 126.51, 128.31, 128.64, 129.02, 131.36, 132.99, 138.83, 143.05, 145.98.

1-Phenyl-l-(2-amino-5-nitrophenyl)ethylene (3j)[1]

^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 4.28 (bs, 2 H), 5.44 (d, *J* = 0.91 Hz, 1 H), 5.90 (d, *J* = 0.91 Hz, 1 H), 6.64 (d, *J* = 9.46 Hz, 1 H), 7.34-7.38 (m, 5 H), 8.06-8.09 (m, 2 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) = 109.38, 116.07, 117.29, 122.88, 126.69, 128.03, 128.52, 133.90, 139.64, 146.91

1-Phenyl-l-(2-*N*-methylaminophenyl)ethylene (3m)[1]

^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 2.71 (s, 3 H), 3.71 (bs, 1 H), 5.33 (d, *J* = 1.37 Hz, 1 H), 5.82 (d, *J* = 1.37 Hz, 1 H), 6.65 (d, *J* = 8.24 Hz, 1 H), 6.74 (td, *J* = 1.06, 7.47 Hz, 1 H), 7.08 (dd, *J* = 1.67, 7.47 Hz, 1 H) 7.24-7.36 (m, 6 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) = 30.76, 109.93, 116.08, 116.60, 126.50, 128.01, 128.47, 128.9, 130.34, 139.66, 146.60, 147.07.

l-Phenyl-l-(2-amino-l-anthryl)ethylene (3o)[1]

^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 3.94 (bs, 2 H), 5.29 (s, 1 H), 5.49 (d, *J* = 1.46 Hz, 1 H), 6.33 (d, *J* = 1.46 Hz, 1 H), 7.07 (d, *J* = 8.92 Hz, 1 H), 7.25-7.34 (m, 5 H), 7.42-7.45 (m, 2 H), 7.74-7.77 (m, 1 H) 7.87-7.91 (m, 2 H), 8.08 (s, 1 H), 8.29 (s, 1 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) = 116.71, 118.01, 119.86, 121.67, 123.94, 125.18, 126.18, 126.39, 127.65, 127.93, 128.08, 128.64, 129.22, 129.34, 132.11, 132.34, 139.06, 139.86, 144.05.

2-(1-p-tolylvinyl)Aniline (3p)

^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 2.33 (s, 3 H), 3.55 (bs, 2 H), 5.30 (d, J = 1.52 Hz, 1 H), 5.75 (d, J = 1.52 Hz, 1 H), 6.69 (dd, J = 1.06, 8.08 Hz, 1 H), 6.78 (dt, J = 1.06, 7.32 Hz, 1 H), 7.10-7.17 (m, 4 H), 7.25-7.27 (m, 2 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) = 21.13, 115.17, 115.49, 118.24, 126.48, 128.48, 128.63, 129.22, 130.74, 136.72, 137.93, 143.88, 146.94. MS (ESI): *m/z* = 210 (M^+ + H). Anal.Calcd for $C_{15}H_{15}N$ C, 86.08; H, 7.22; N, 6.69; Found: C, 86.07; H, 7.21; N, 6.68.

2-(1-(4-fluorophenyl)vinyl)Aniline (3q)

^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 3.55 (bs, 2 H), 5.33 (d, J = 1.06 Hz, 1 H), 5.74 (d, J = 1.06 Hz, 1 H), 6.70 (dd, J = 1.06, 8.08 Hz, 1 H), 6.78 (dt, J = 1.06, 7.32 Hz, 1 H), 6.97-7.01 (m, 2 H). 7.09 (dd, J = 1.67, 7.62 Hz, 1 H), 7.16 (dt, J = 1.67, 8.08 Hz, 1 H), 7.31-7.35 (m, 2 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) = 115.38 (J_{CF} = 22.07 Hz), 115.70 (J_{CF} = 19.08 Hz), 118.35, 127.01, 128.30 (J_{CF} = 8.06 Hz), 128.86, 130.68, 135.72, 143.78, 146.07, 162.72 (J_{CF} = 247.94 Hz). MS (ESI): *m/z* = 214 (M^+ + H). Anal.Calcd for $C_{14}H_{12}FN$ C, 78.85; H, 5.66; N, 6.57; Found: C, 78.86; H, 5.66; N, 6.56.

2-(1-(3-chlorophenyl)vinyl)Aniline (3r)

^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 3.55 (bs, 2 H), 5.40 (d, J = 1.22 Hz, 1 H), 5.81 (d, J = 1.21 Hz, 1 H), 6.70 (dd, J = 1.58, 7.58 Hz, 1 H), 6.79 (dt, J = 1.10, 7.45 Hz, 1 H), 7.08 (dd, J = 1.58, 7.58 Hz, 1 H), 7.14-7.20 (m, 1 H), 7.22-7.28 (m, 3 H), 7.35-7.36 (m, 1 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) = 115.66, 117.27, 118.39, 124.86, 126.62, 128.06, 129.00, 129.75, 130.73, 134.53, 141.64, 143.79, 145.99, MS (ESI): *m/z* = 230 (M^+ + H). Anal.Calcd for $C_{14}H_{12}ClN$ C, 73.20; H, 5.27; N, 6.10; Found: C, 73.20; H, 5.28; N, 6.09.

2-(1-(4-bromophenyl)vinyl)aniline (3s)

^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 3.56 (bs, 2 H), 5.37 (d, J = 1.22 Hz, 1 H), 5.80 (d, J = 1.21 Hz, 1 H), 6.70 (dd, J = 1.06, 8.08 Hz, 1 H), 6.79 (dt, J = 1.22, 7.47 Hz, 1 H), 7.07 (dd, J = 1.37, 7.47 Hz, 1 H), 7.16-7.18 (m, 1 H), 7.22-7.25 (m, 2 H), 7.41-7.45 (m, 2 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) = 115.06, 116.56, 118.38, 122.19, 126.61, 128.23, 128.95, 130.72, 131.62, 138.54, 143.76, 146.07. MS (ESI): *m/z* = 274 (M^+ + H). Anal.Calcd for $C_{14}H_{12}BrN$ C, 61.33; H, 4.41; N, 5.11; Found: C, 61.32; H, 4.42; N, 5.12.

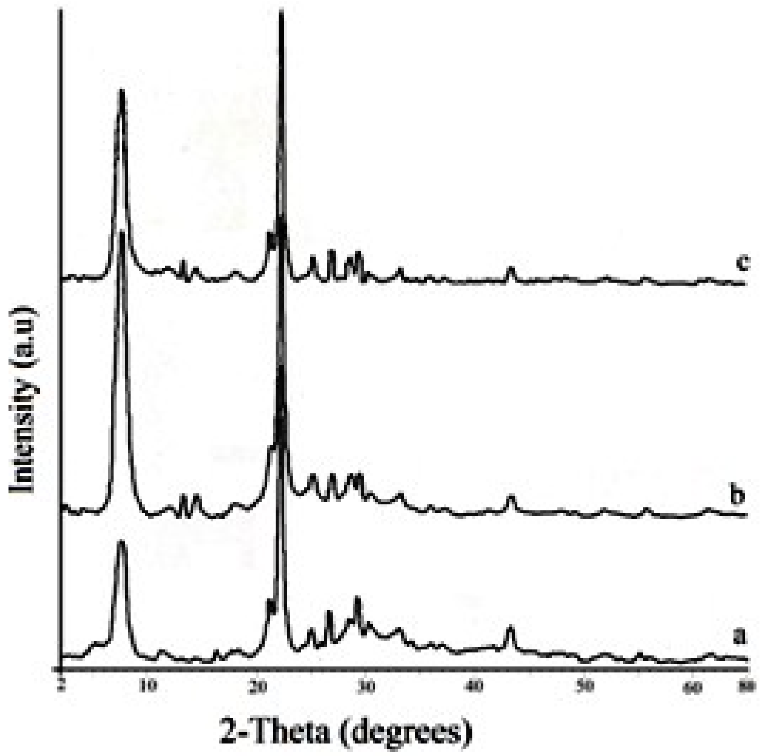
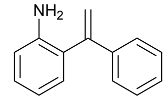


Figure S1. XRD patterns of nanosized zeolite beta samples: (a) uncalcined; (b) calcined; (c) reused catalyst.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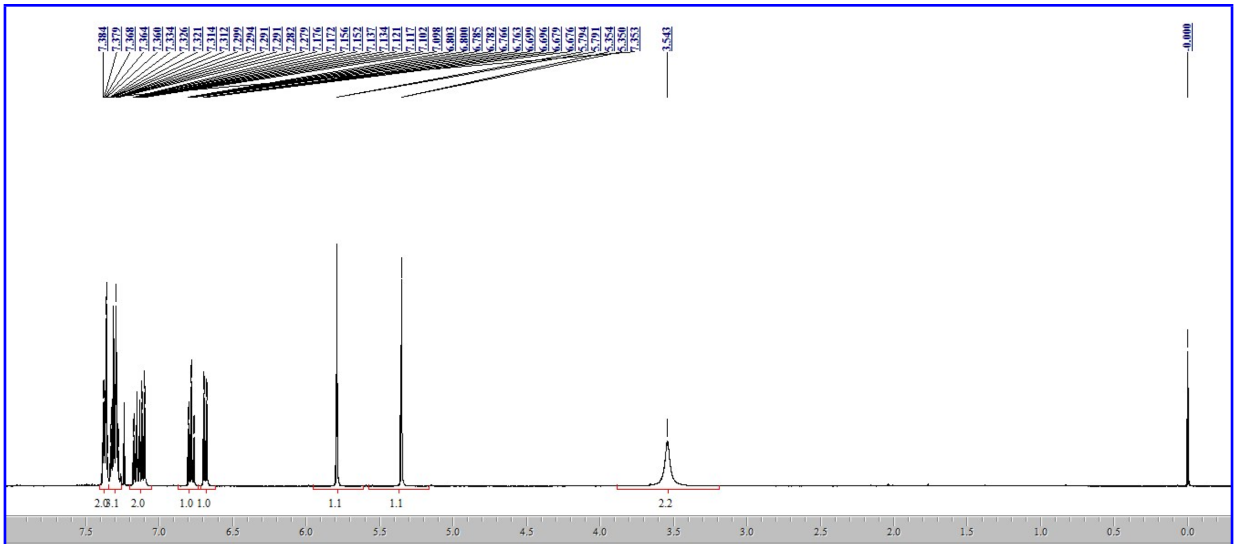
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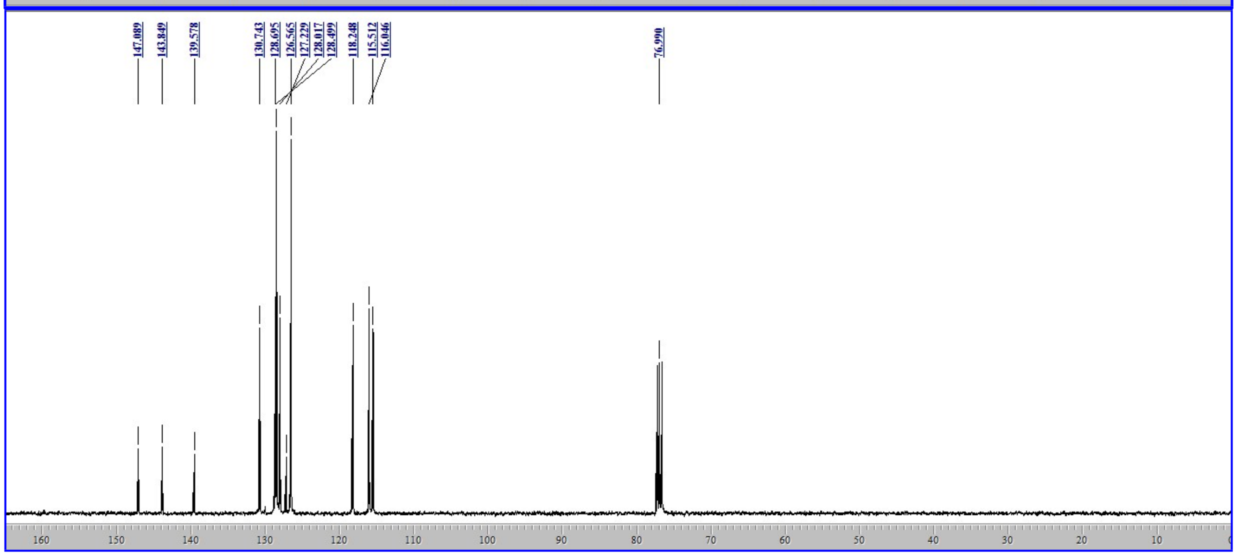
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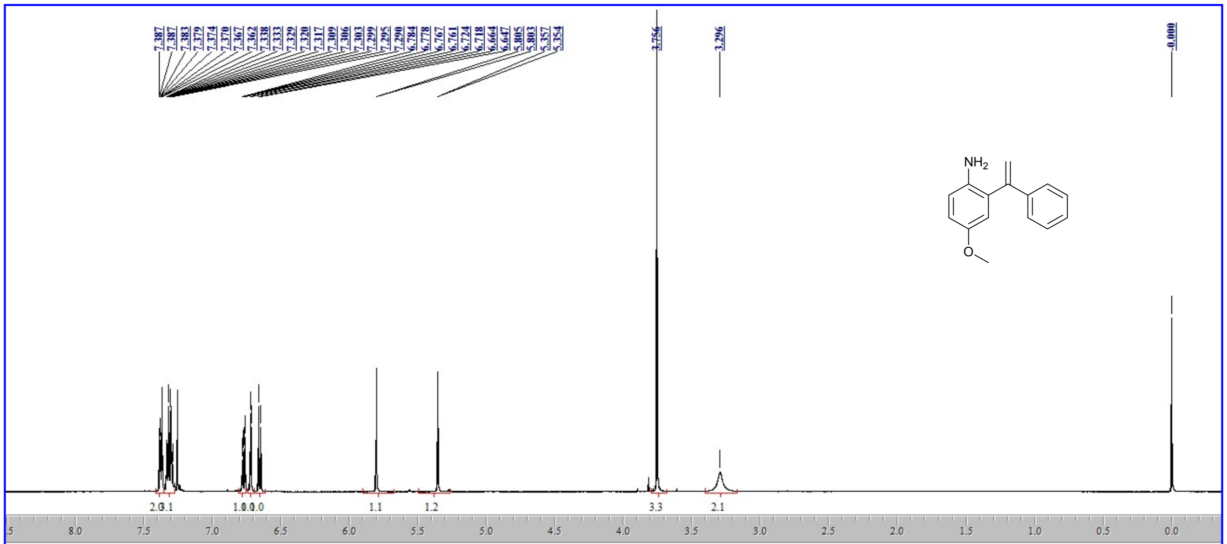

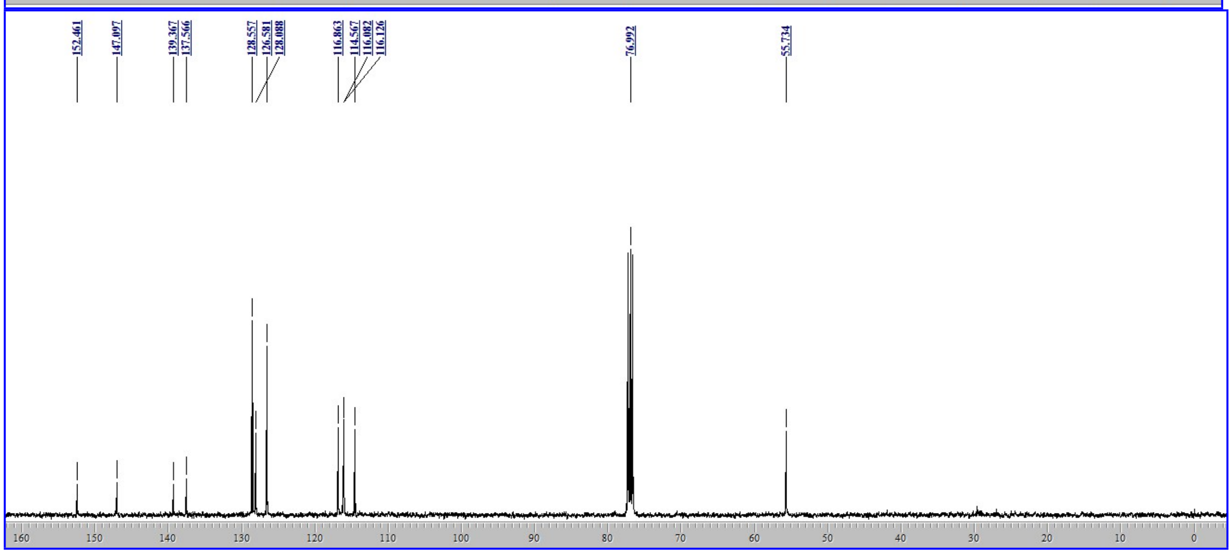

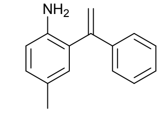
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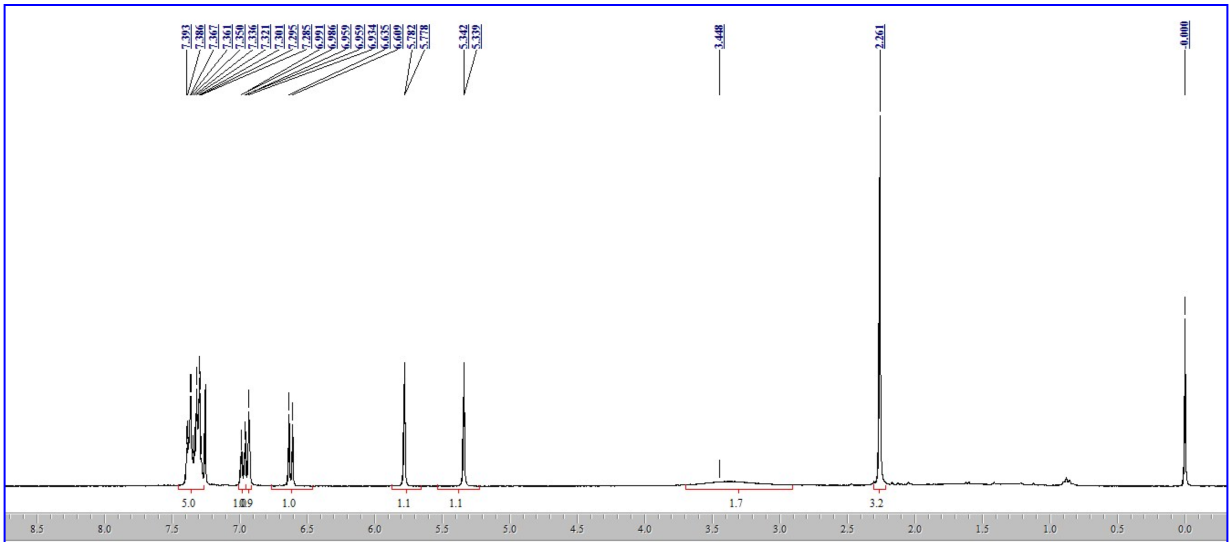
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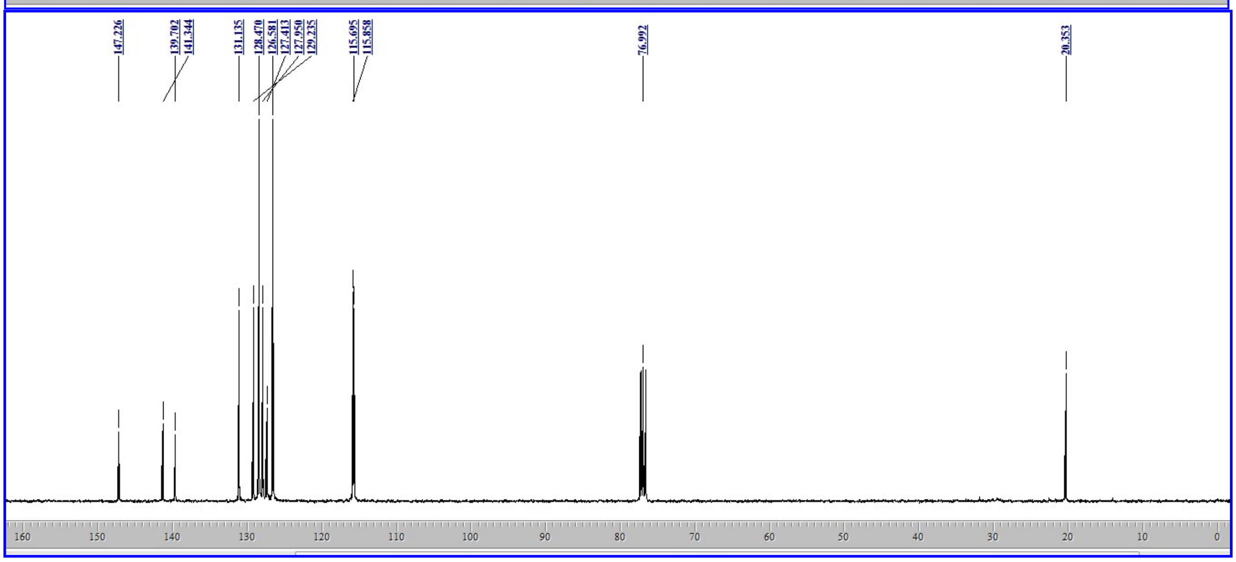
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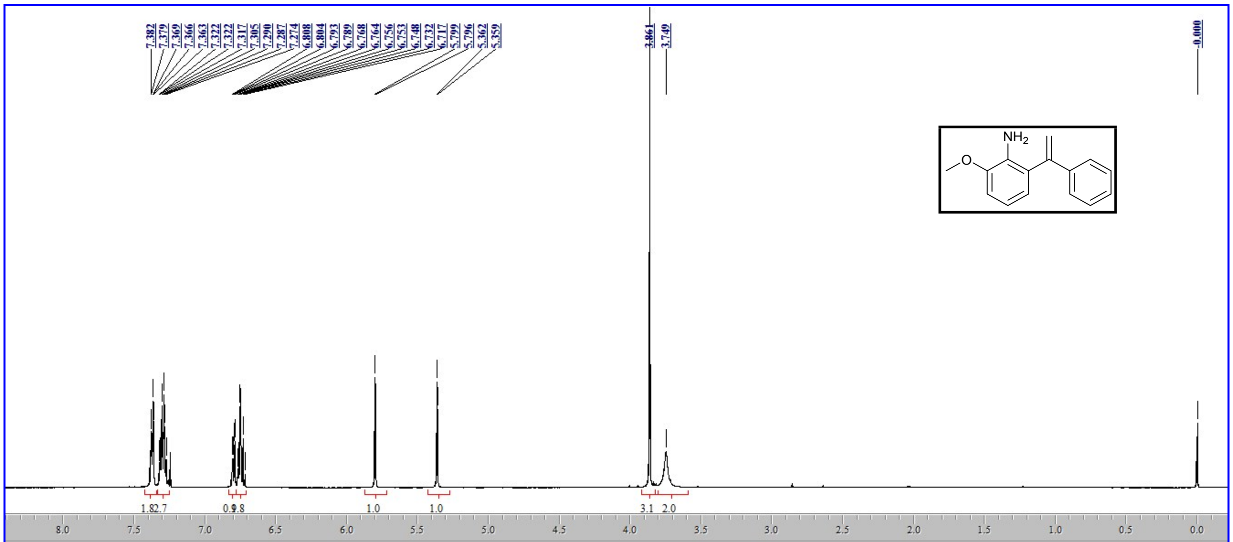
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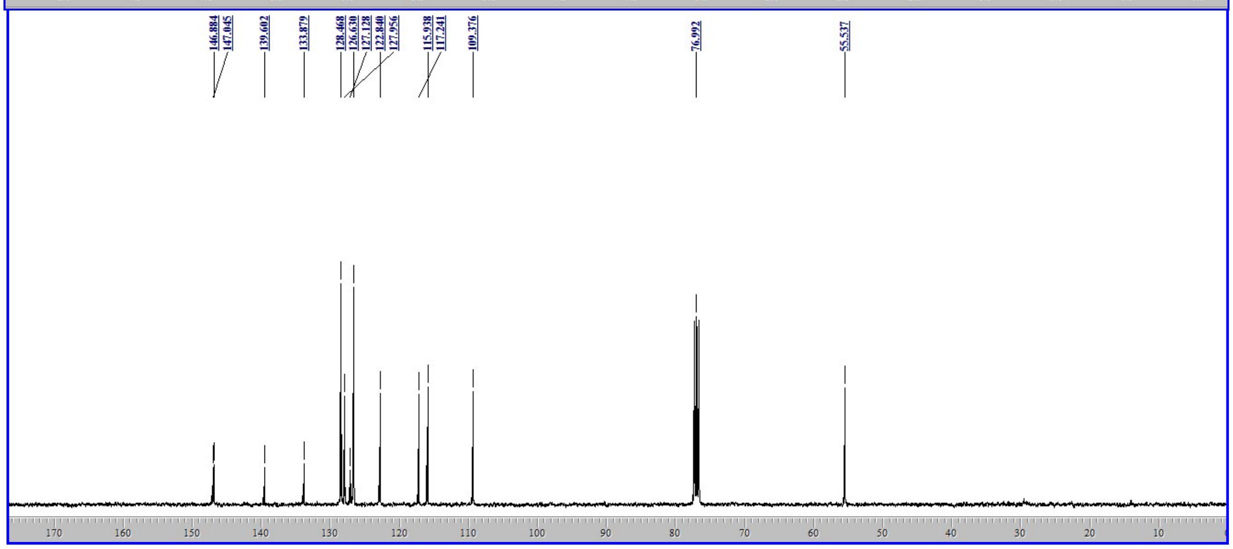

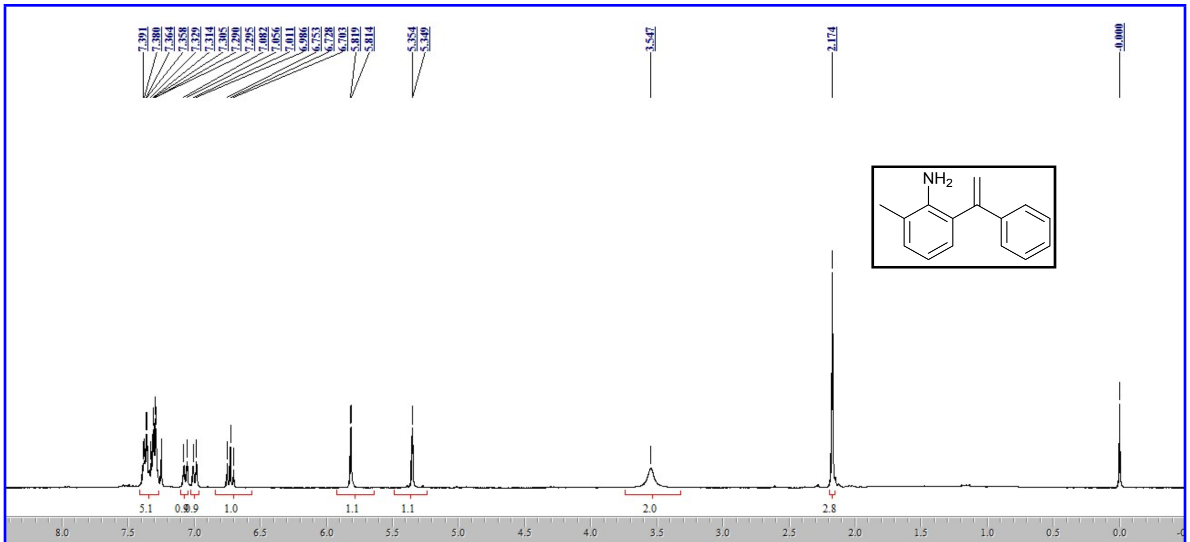
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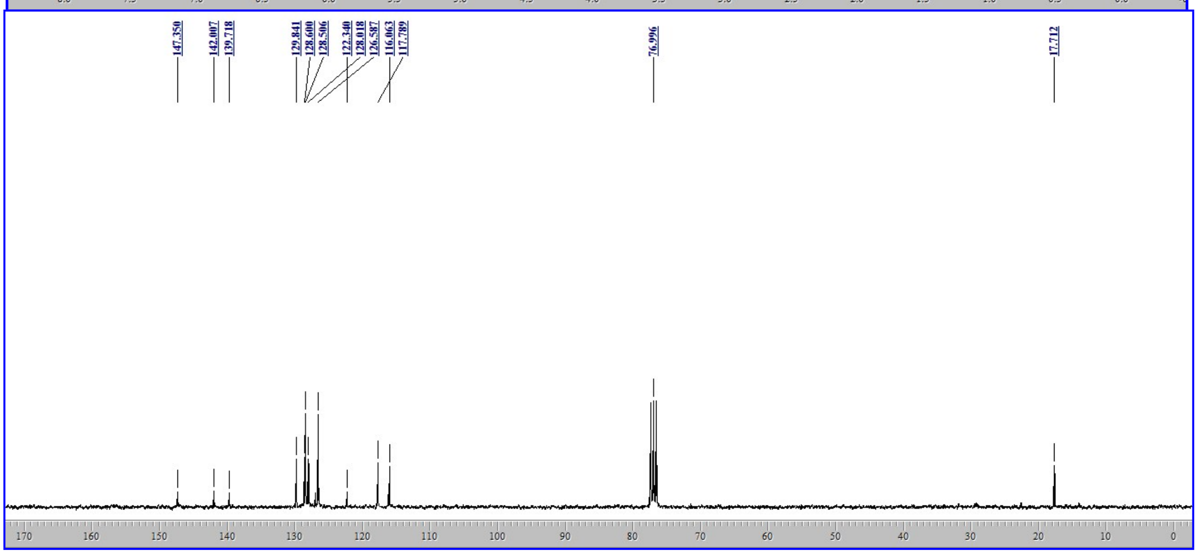
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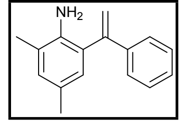

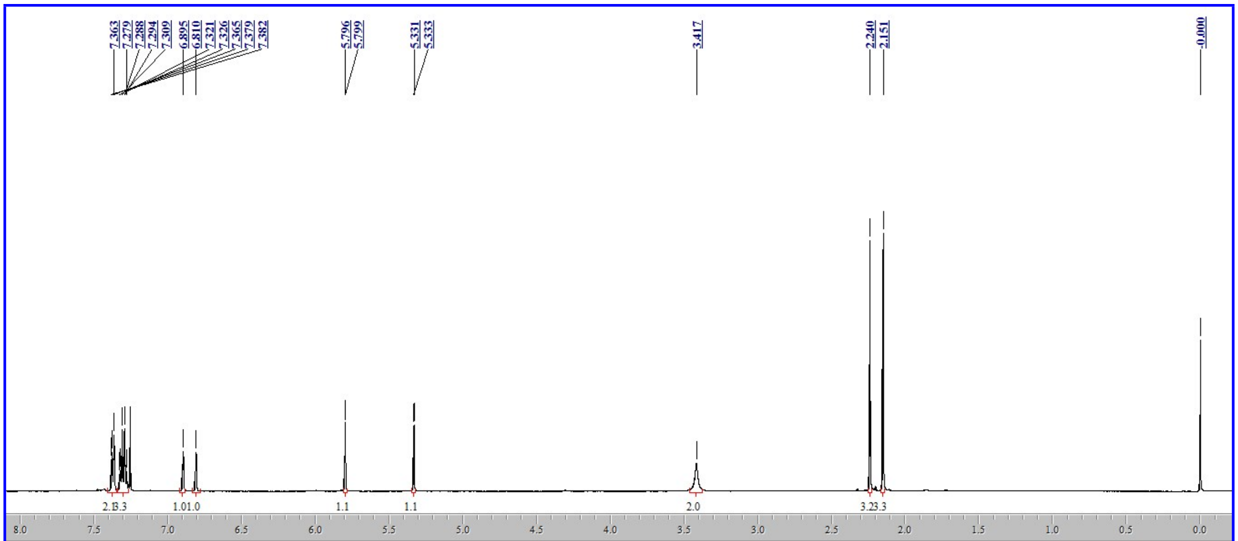
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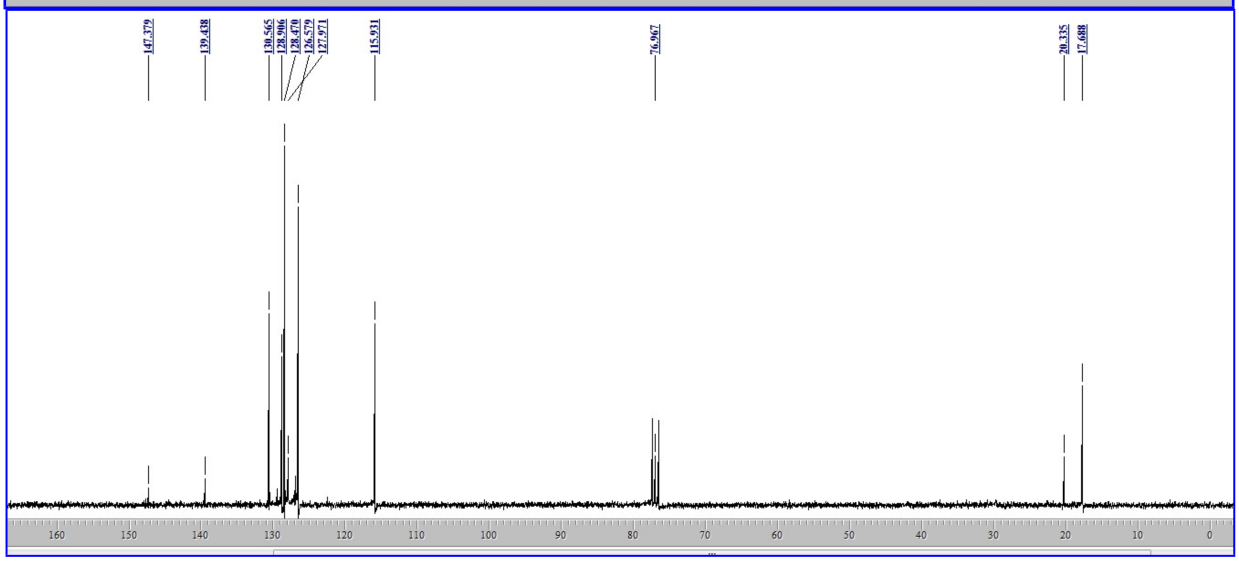
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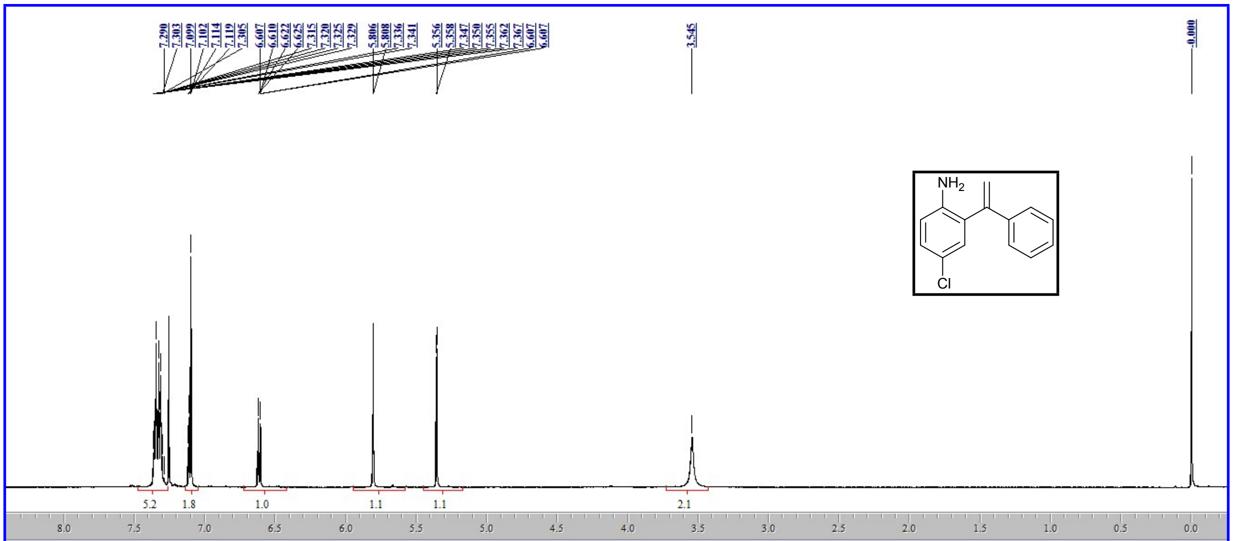

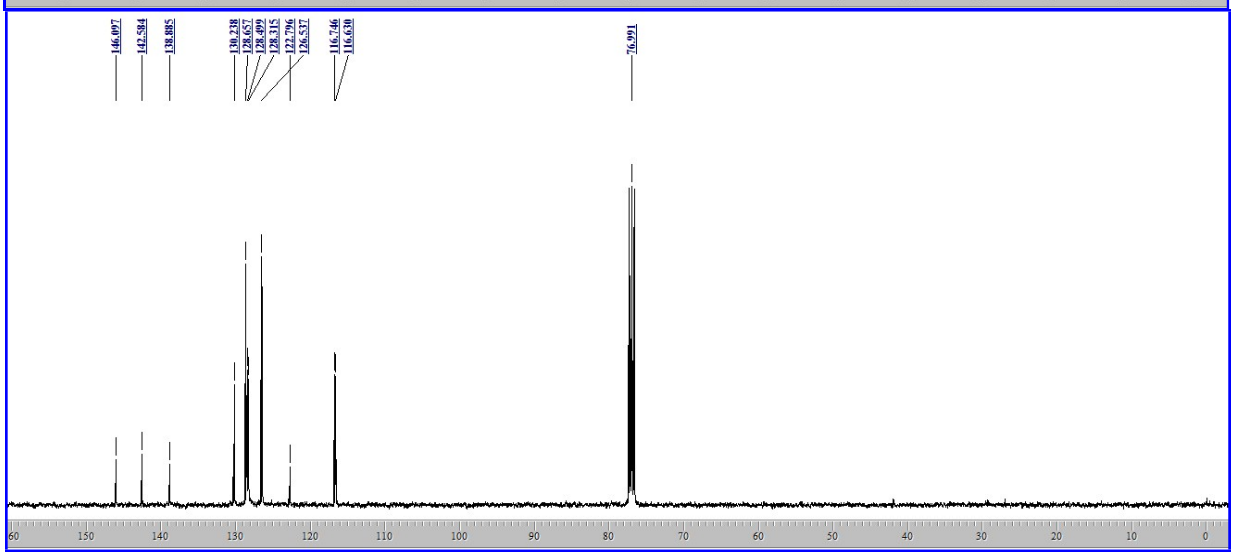

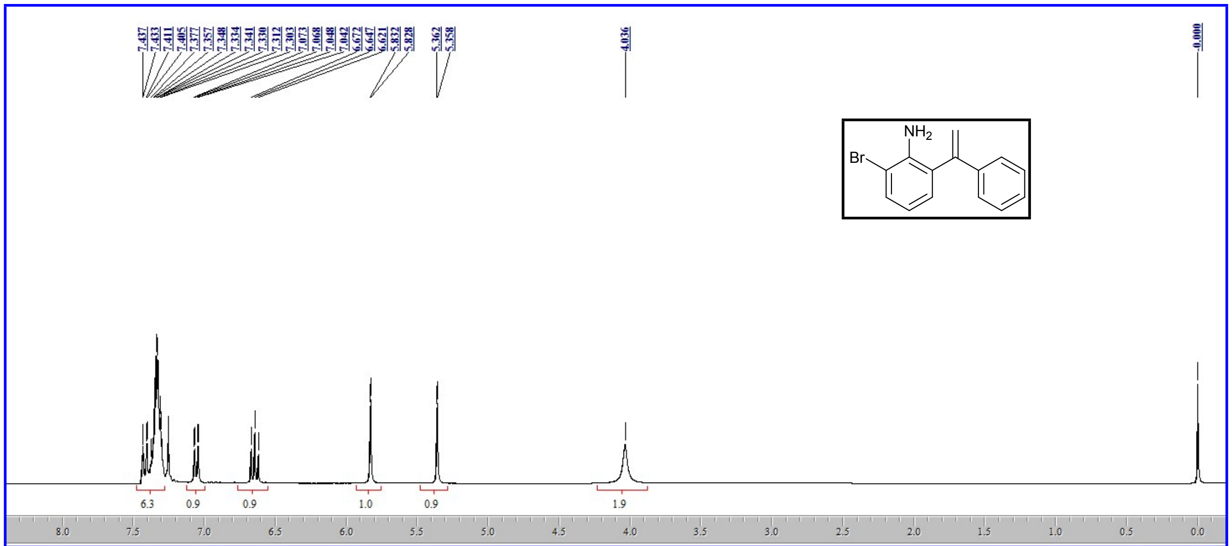

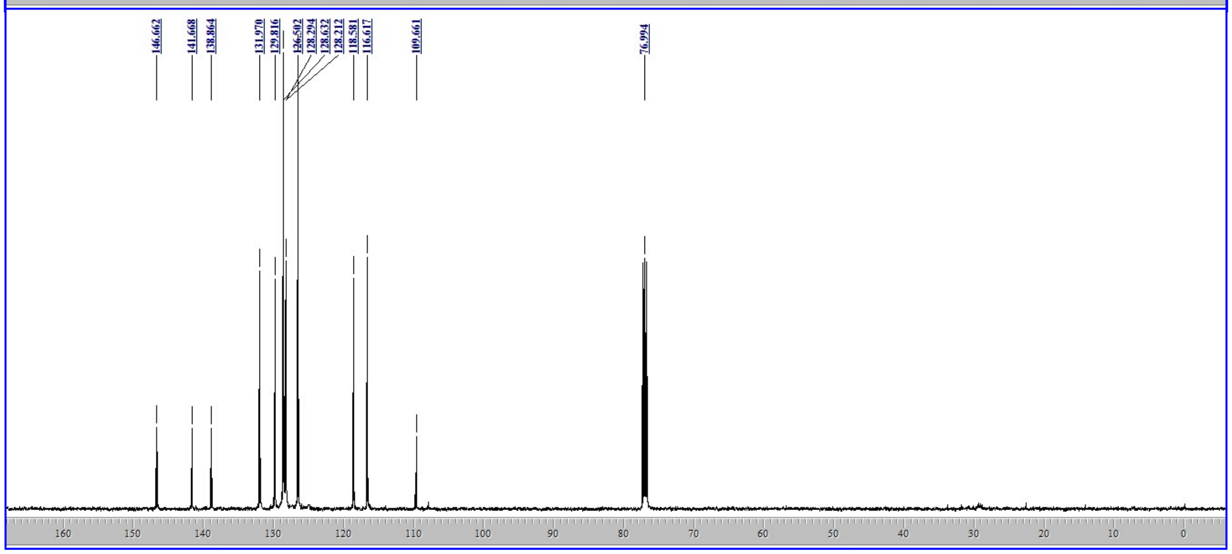

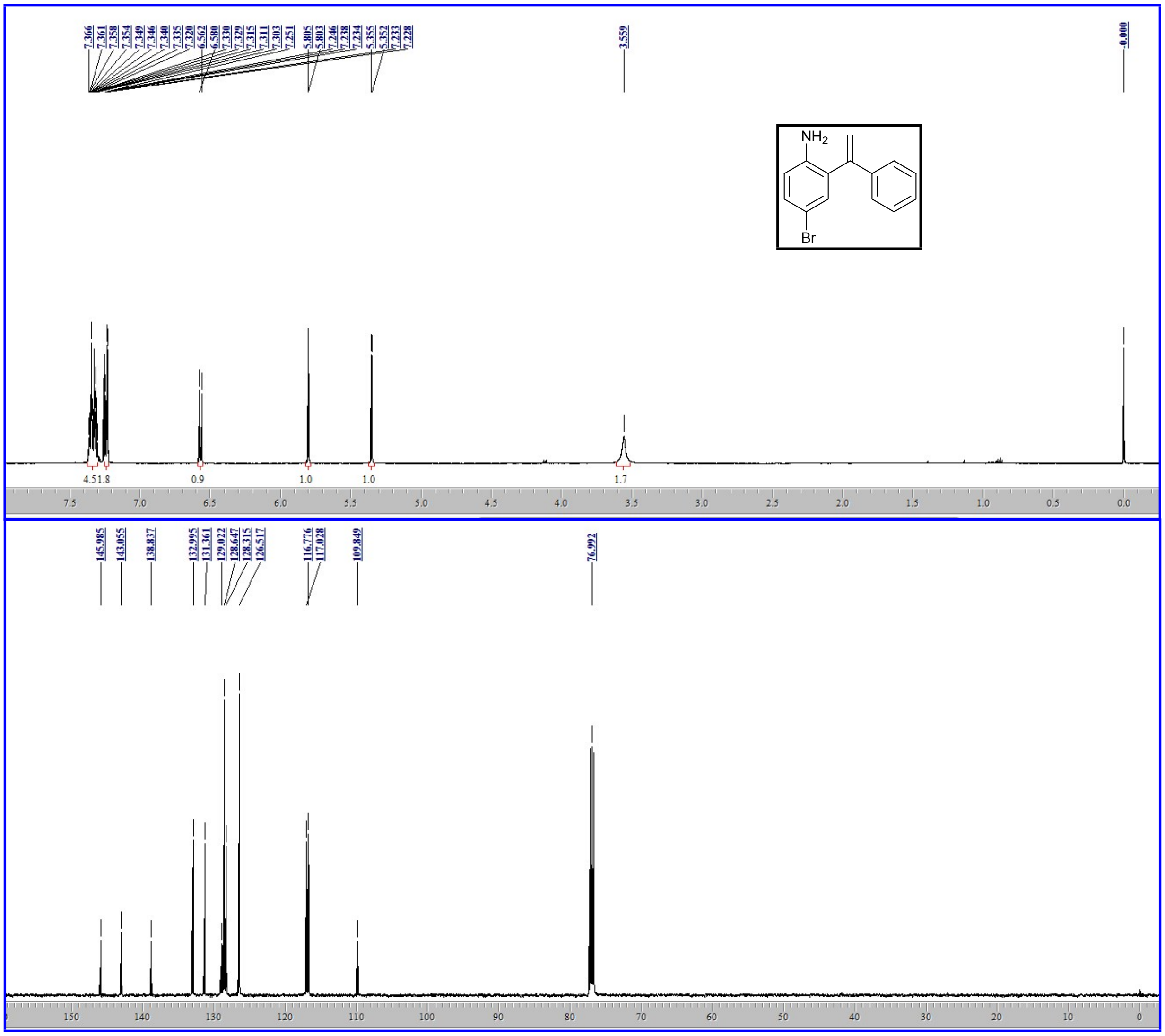
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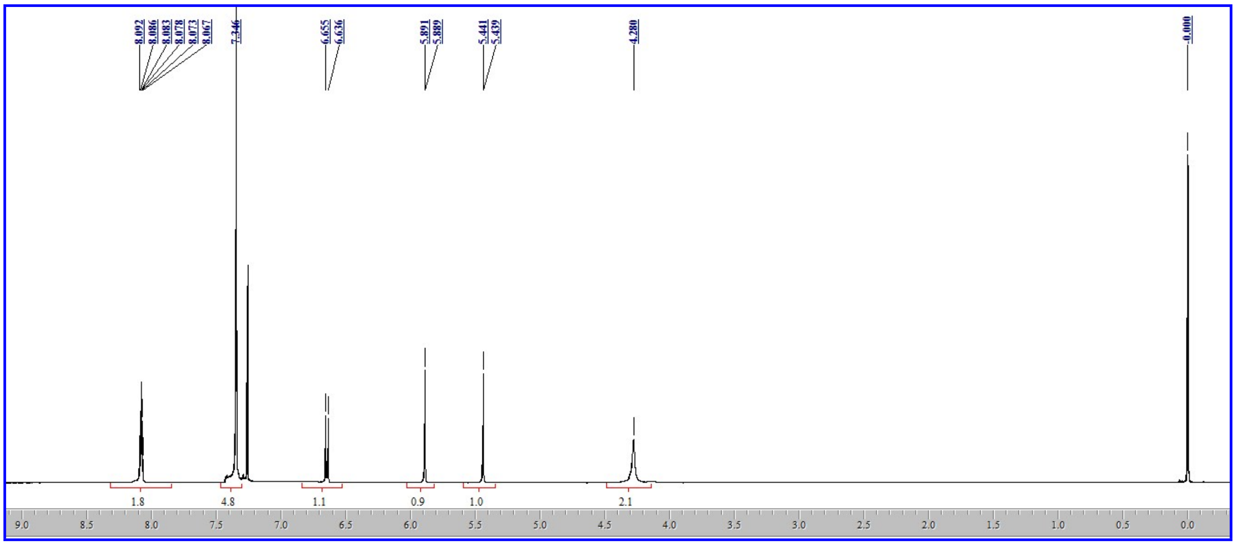
5.803
7.246
7.238
7.234
5.355
5.352
7.233
7.228
3.559
0.000
NH2
Br
4.5
1.8
0.9
1.0
1.0
1.7
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
145.985
143.055
138.837
132.995
131.361
129.022
128.647
128.315
126.517
116.776
117.028
109.849
76.992
150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0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5.439
4.280
0.000
1.8
4.8
1.1
0.9
1.0
2.1
9.0
8.5
8.0
7.5
7.0
6.5
6.0
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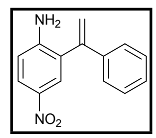
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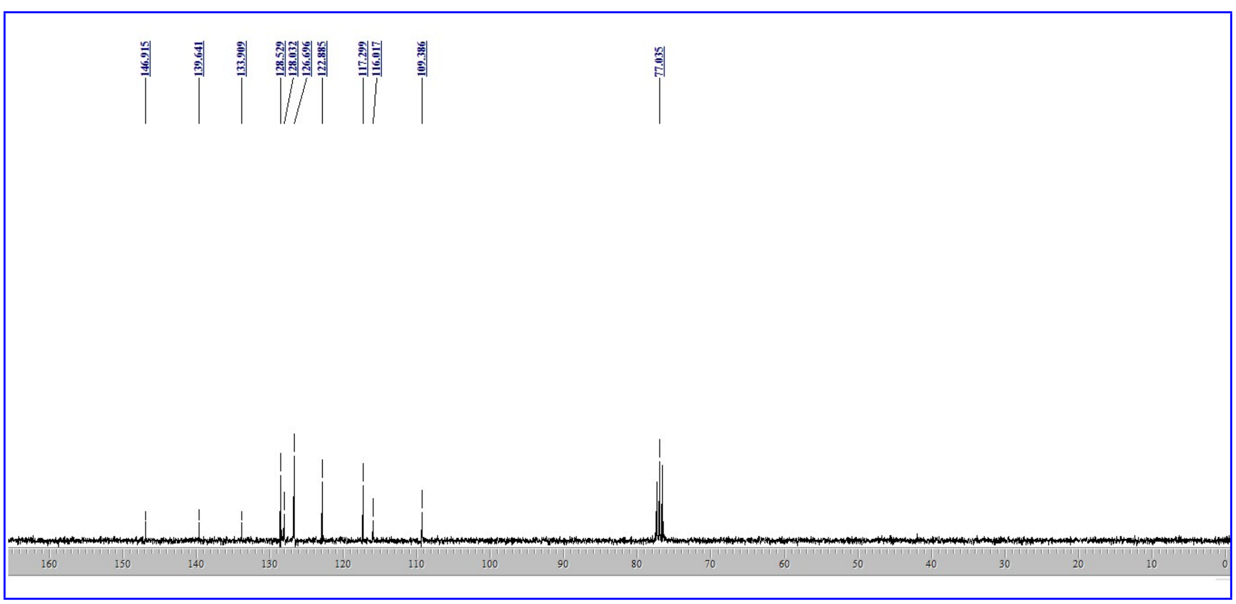
NO2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150
140
130
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80
70
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30
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10
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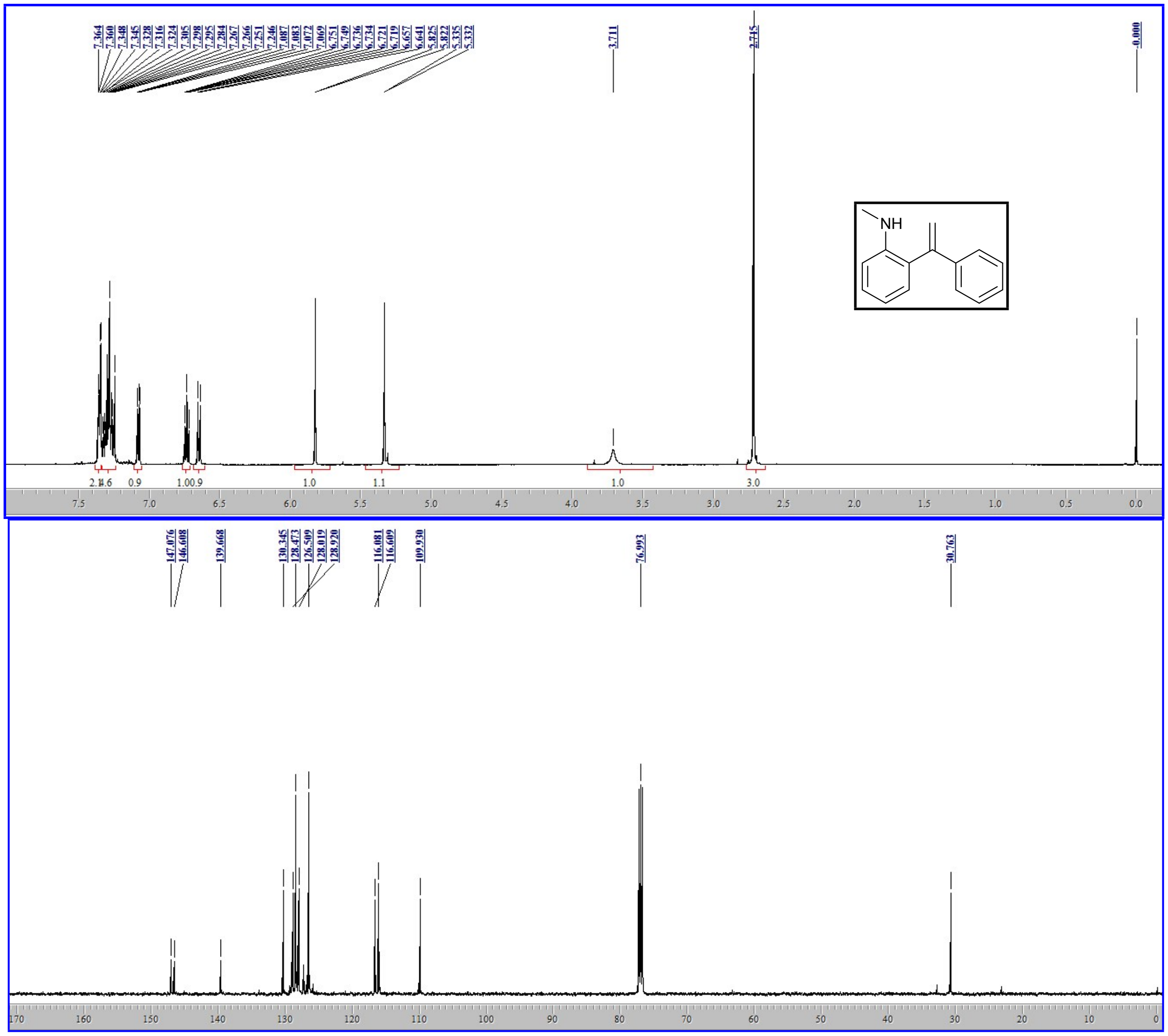

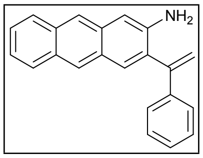
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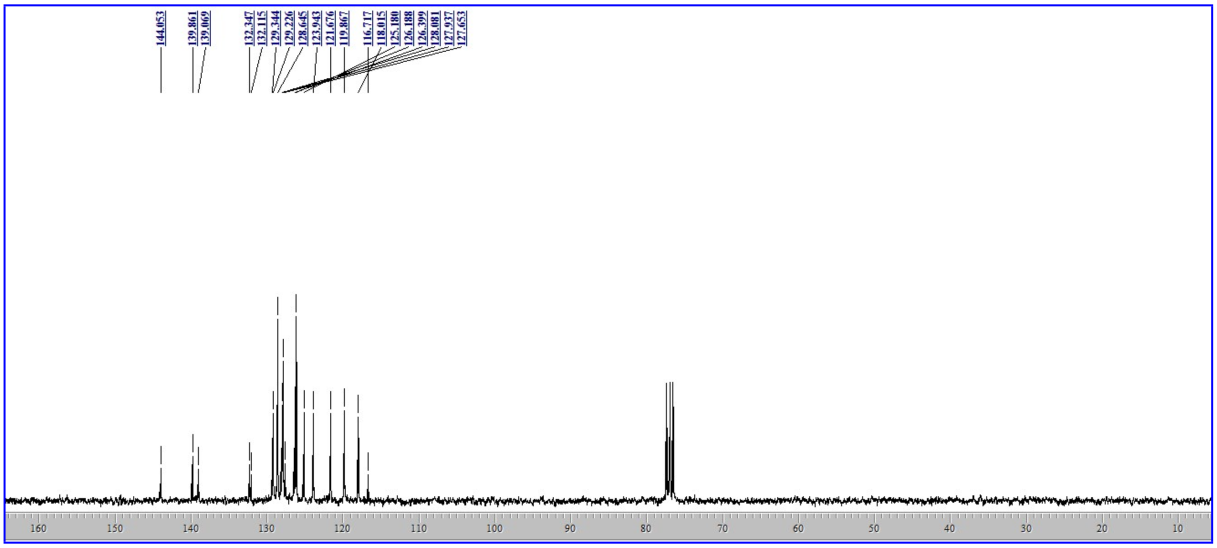

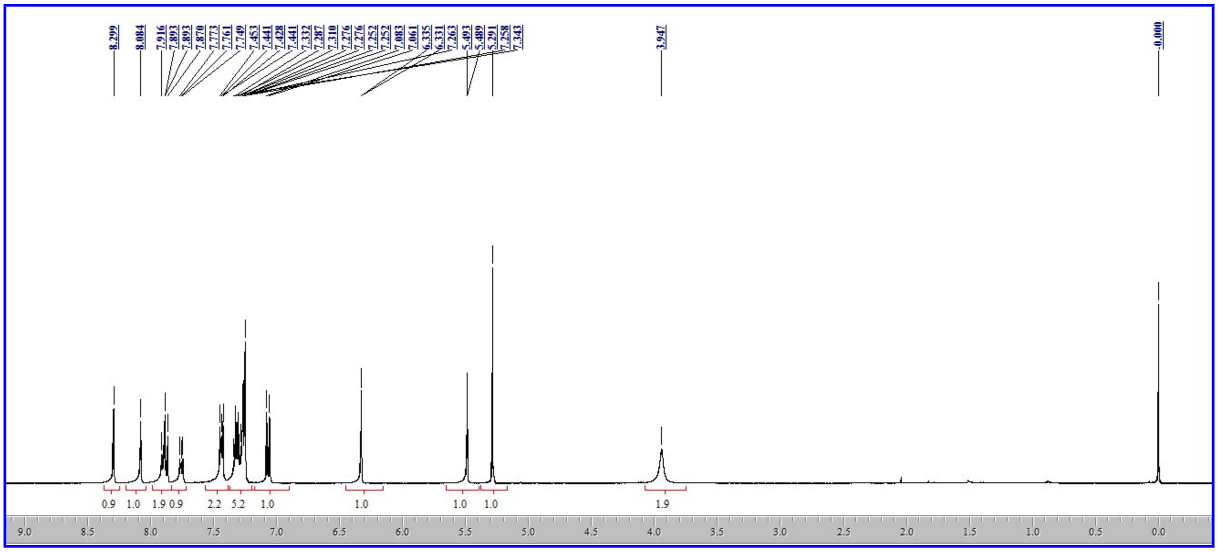
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7.441
7.332
7.287
7.310
7.276
7.276
7.252
7.252
7.083
7.061
6.335
6.331
7.263
5.493
5.489
5.291
7.258
7.343
3.947
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1.9
0.9
2.2
5.2
1.0
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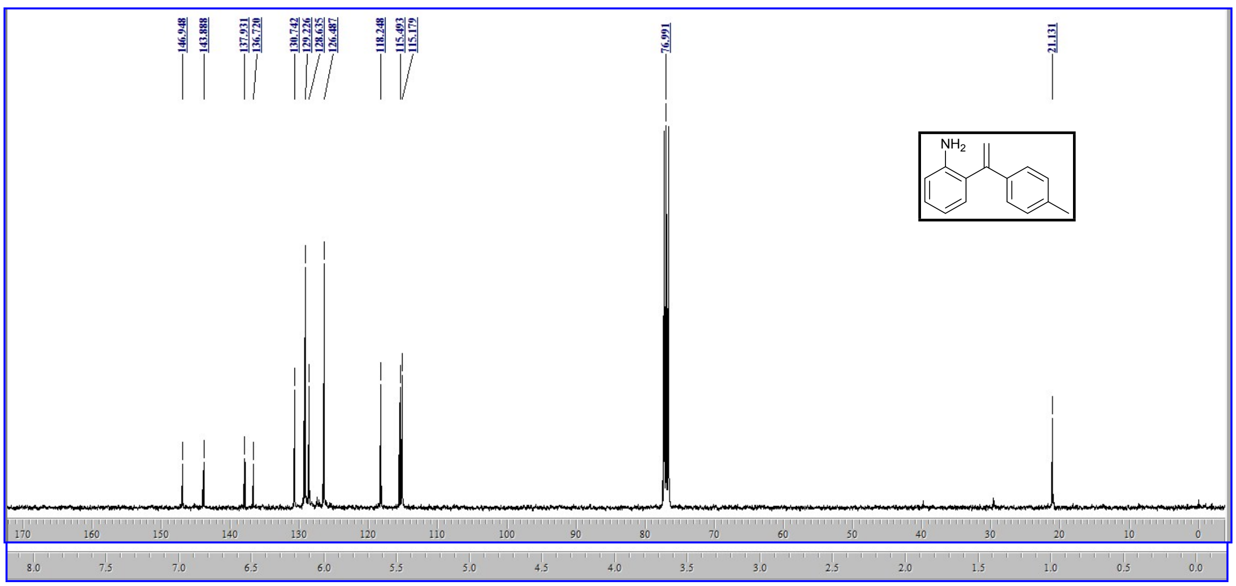
1.0
1.0
1.9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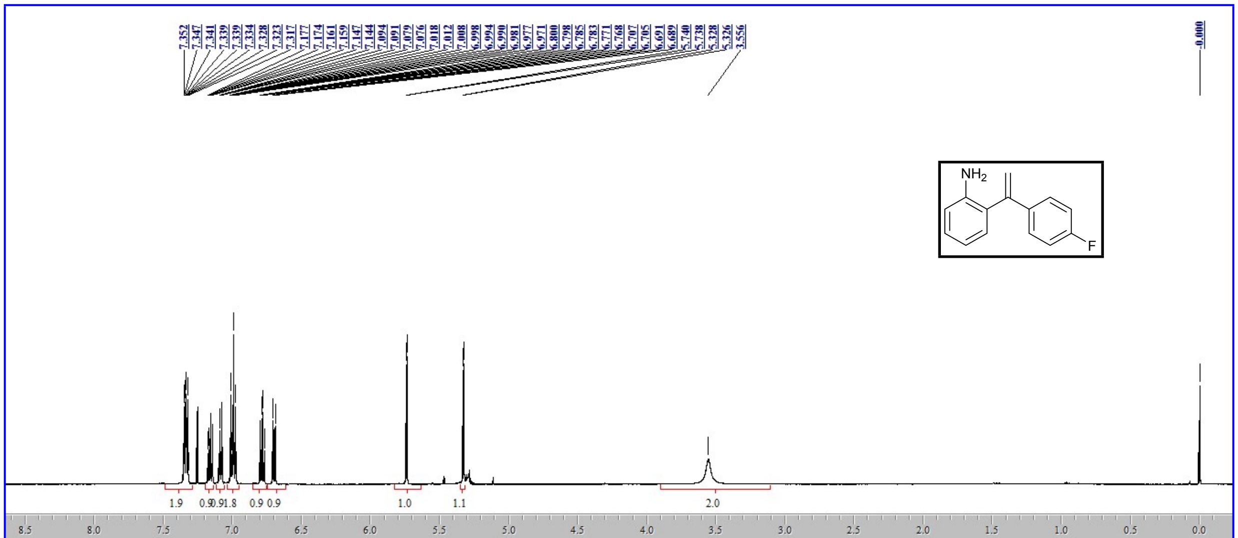
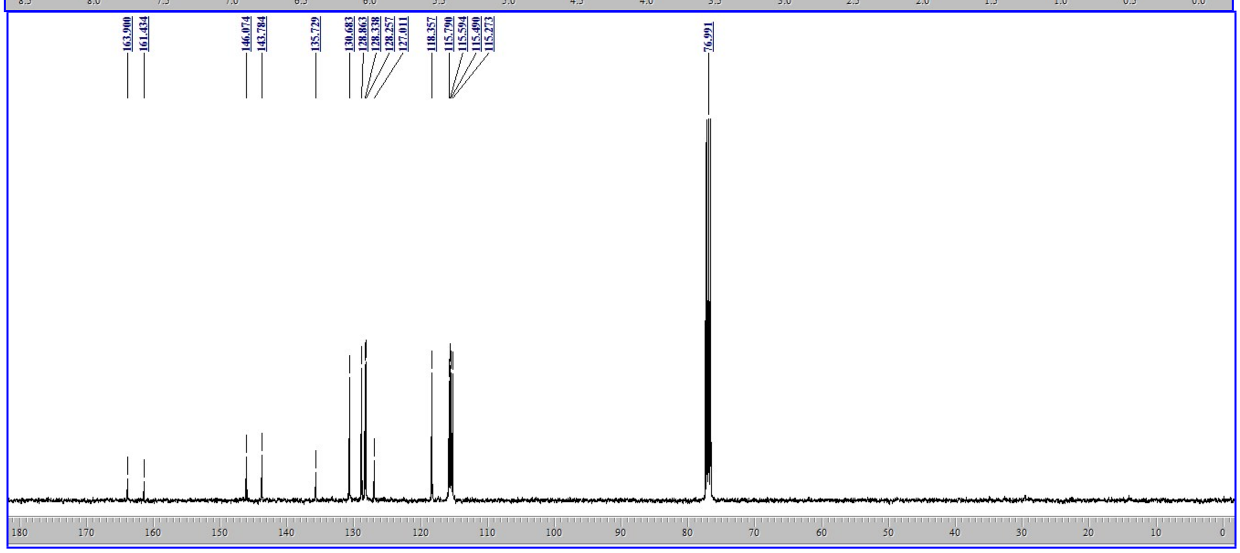
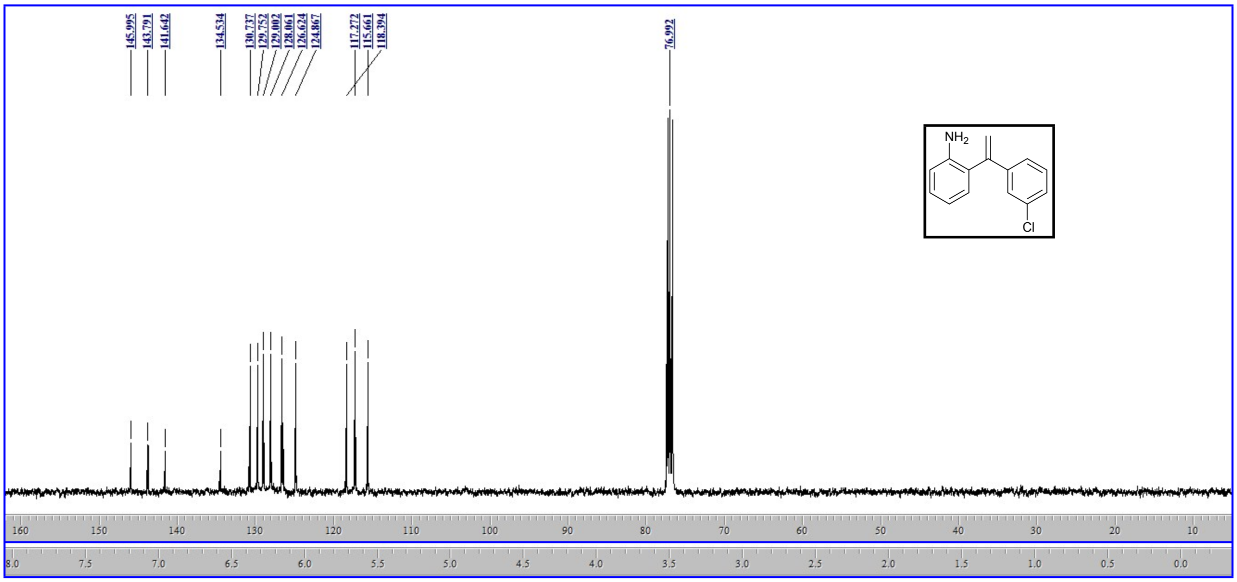
21.131
NH2



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141.642
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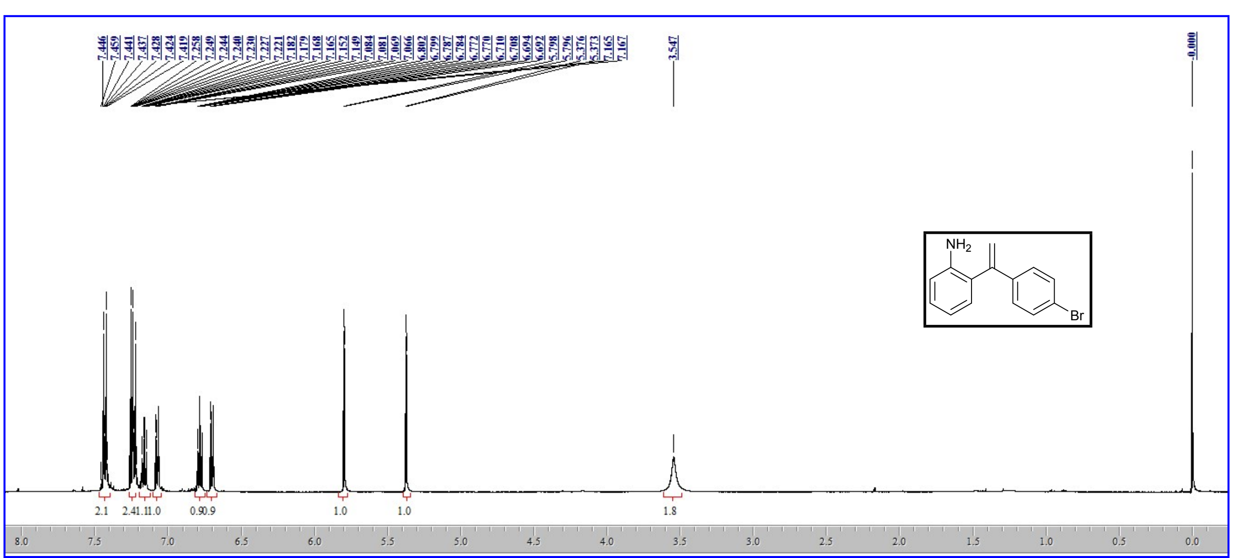
118.394
76.992
NH2
Cl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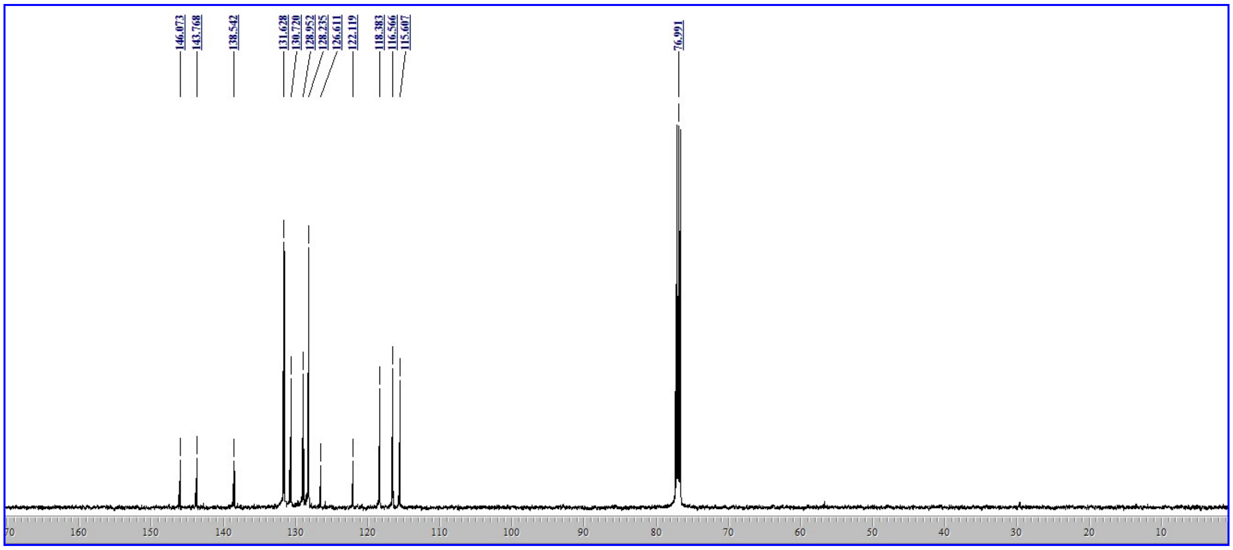
0.9
0.9
1.0
1.0
1.8



Notes and references

1. A. Arienti, F. Bigi, R. Maggi, E. Marzi, P. Moggi, M. Rastelli, G. Sartori and F. Tarantola, *Tetrahedron,* 1997, **53**, 3795-3804.