Electronic Supplementary Material (ESI) for Green Chemistry.

Supporting Information

Cobalt Nanocomposites on N-Doped Hierarchical Porous Carbon for Highly Selective Formation of Anilines and Imines from Nitroarenes

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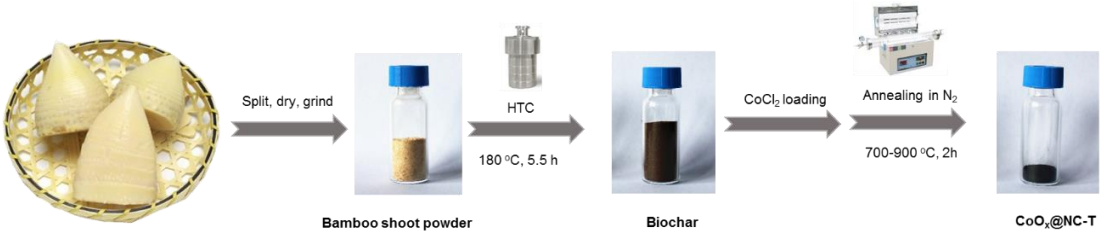
1. General considerations

Unless otherwise noted, all reagents were purchased commercially from Sigma-Aldrich, or Aladdin and used as received without further purification. The fresh bamboo shoots were obtained from Anhui Taiping Test Centre, International Centre for Bamboo and Rattan, Anhui Province, China. All operations were carried out in an argon atmosphere using glovebox and Schlenk techniques unless otherwise specified. Anhydrous tetrahydrofuran (THF), hexanes and toluene were obtained from an argon purged solvent purification system comprised of columns of activated alumina and molecular sieves. Gas chromatography analysis was performed on an Agilent HP-7890 instrument with a flame ionization detector (FID) and an HP-5MS capillary column (30 m, 0.25 mm i.d., 0.25 μm film thicknesses) using helium as the carrier gas. Gas chromatography-mass spectrometry analysis was carried out on an Agilent HP-7890 instrument with an Agilent HP-5975 with triple-axis detector and HP-5 capillary column using helium carrier gas. NMR spectra were received using DRX-400, or DRX-600, Chemical shifts are reported in ppm relative to the residual solvent signal ($CDCl_3$: 7.26 ppm (^1H), 77.16 ppm (^{13}C), Multiplicities were reported using the following abbreviations: s = singlet, d = doublet, dd = doublet of doublets, t = triplet, q = quartet, m = multiplet, brs = broad singlet. High-resolution mass data were recorded on Bruke Maxis UHR TOF mass spectrometers in ESI mode.

2. Preparation of the nanostructured Co nanoparticles catalyst

The functionalized hydrochars were firstly prepared by hydrothermal method using bamboo shoots as raw material. The fresh bamboo shoots were cut into slices, dried and ground into a powder. 2 g of the dried bamboo shoots were added to 20 mL of deionized water in a 100 mL Teflon-inner stainless steel autoclave, which was sealed and heated at 180 ^oC for 5.5 h. The resulting solids were obtained by filtration, washed thoroughly using distilled water to remove any soluble metals, and dried by vacuum freeze-drying. After that, 0.5 g of the obtained hydrochars were mixed with 15 mL of $CoCl_2$ aqueous

solution (0.2 mmol Co) and the suspension was stirred at 60 °C for 2 h and then dried at 100 °C for 10 h to remove water. Afterward, the solids were grinded to fine powders and heated to 700, 800 or 900 °C at a rate of 5 °C/min and maintained at this temperature for 2 h under N_2 atmosphere. After that the oven was cooled down to room temperature. During the whole process, nitrogen was purged through the oven constantly. The as-prepared catalyst was stored in a screw capped vial without any special protection from air at room temperature. The Co based N-doped porous carbon catalysts were named as CoO_x@NC-T, where T represents the calcination temperature, as shown in Scheme S1. For comparison, Co based commercial activated carbon (CoO_x@C-800) was also synthesized under a similar process, which was calcined at 800 °C for 2 h under N_2 atmosphere.



Scheme S1. The schematic illustration of the fabrication of CoO_x@NC-T catalyst.

Yield (in pyrolysis process):
CoO_x@NC-700: 34.5% (wt)
CoO_x@NC-800: 36.3% (wt)
CoO_x@NC-900: 21.1% (wt)
CoO_x@C-800: 93.6% (wt)

Elemental analysis:
CoO_x@NC-700: C (67.34%), H (1.78%), N (4.00%), Co (5.48%)
CoO_x@NC-800: C (66.67%), H (2.18%), N (2.97%), Co (5.39%)
CoO_x@NC-900: C (64.21%), H (1.84%), N (1.74%), Co (8.30%)
CoO_x@C-800: Co (4.96%)

3. Characterization of the as-prepared catalysts

The X-ray diffraction (XRD) powder patterns were recorded on a Bruker D8 Advance X-ray diffraction diffractometer, equipped with CuKa radiation (λ =1.5147 Å). The

magnetic hysteresis loop was measured by using a Quantum Design SQUID-VSM magnetometer. The morphology of the catalysts was examined using a Tecnai G2 F30 high-resolution transmission electron microscope (HRTEM) and a FEI Tecnai G2 F20 scanning transmission electron microscope (STEM). Nitrogen adsorption–desorption data were obtained using a Micromeritics ASAP 2020 static volumetric sorption analyzer. The specific surface area of the samples was calculated using the Brunauer–Emmett–Teller (BET) method. The micropore volume was calculated using a t-plot method. The pore size distribution was determined using non-local density functional theory (DFT). The X-ray photoelectron spectroscopy (XPS) data were obtained using a Thermo ESCALAB250 instrument with a monochromatized Al Ka line source. All the binding energies obtained were calibrated based on the C 1s peak at 284.6 eV. The elemental composition analysis was conducted using a Vario El elemental analyzer. Inductively coupled plasma atomic emission spectroscopy (ICP-AES) measurements were taken on a Perkin Elmer Optima 5300 DV instrument. Fourier transformed infrared (FT-IR) spectra was recorded on a Thermo Nicolet FTIR Spectrometer. Raman spectra were collected on a Horiba Jobin Yvon LabRAM HR800 Raman spectrometer system using a 532 nm wavelength laser at room temperature. Magnetic measurement was carried out using a SQUID MPMS-XL5 from Quantum Design with the field range of -3 to 3 T in hysteresis mode. The sample was prepared in a gelatine capsule held in a plastic straw under protective atmosphere. The raw data were corrected for the diamagnetic part of the sample holder.

4. Test of as-prepared catalysts

4.1. General procedure for anilines synthesis

A 50 mL high-pressure autoclave was charged with a magnetic stirring, 0.5 mmol nitroarene, a given amount of catalyst with fixed Co content of 10 mol%, 2 mL H_2O. The autoclave was flushed three times with 5 MPa of hydrogen. The autoclave was pressured with 5 MPa of hydrogen and the reaction was stirred for 5 h at 110 °C. After completion of the reaction, the reaction mixture was cooled to room temperature and

the hydrogen was gently released. The liquid was analyzed by GC and GC-MS to determine the conversion and selectivity using dodecane as an internal standard. The aniline was structurally confirmed by comparison with the its authentic sample by GC based on the retention time.

4.2. General procedure for imine synthesis

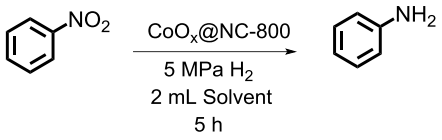
A 50 mL high-pressure autoclave was charged with a magnetic stirring, 0.5 mmol nitroarene, 2.0 mmol aldehyde, 20 mg CoO_x@NC-800, 3.2 mL THF, 0.8 mL H_2O. The autoclave was flushed three times with 5 MPa of hydrogen. The autoclave was pressured with 5 MPa of hydrogen and the reaction was stirred for 24 h at 110 °C. After completion of the reaction, the reaction mixture was cooled to room temperature and the hydrogen was gently released. The catalyst was remove
d by centrifugation and the organic was analyzed by GC and GC-MS to determine the conversion and selectivity using dodecane as an internal standard. The products were purified by column chromatography or recrystallization and structurally confirmed by NMR.

4.3. Catalyst recycling

The model reaction was chosen to investigate the recyclability of the novel cobalt nanocomposite catalyst. A 50 mL high-pressure autoclave was charged with a magnetic stirring, 0.5 mmol nitrobenzene,10 mg CoO_x@NC-800, 2 mL H_2O. The autoclave was flushed three times with 5 MPa of hydrogen. The autoclave was pressured with 5 MPa of hydrogen and the reaction was stirred for 5 h at 110 °C. After completion of the reaction, the reaction mixture was cooled to room temperature and the hydrogen was gently released. The catalyst was recovered by centrifugation (10000 rpm and 15 min) or was separated by external magnet and the liquid was carefully decanted out. 5 mL of ethanol and 5mL water were added and the resulting mixture was stirred for 10 min by followed by centrifugation again to remove any residuals on the catalyst. Such operation was repeated for 3 times. Finally, the obtained black solid was dried under vacuum at 40^{o}C overnight for successive use.

4.4. Influencing factors of reaction

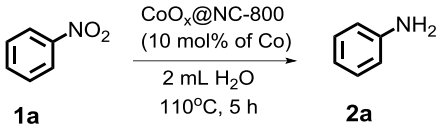
Table S1. Solvent effect on nitrobenzene hydrogenation[a]



Entry	Solvent	Polarity[b]	Conversion (%)[c]	Selectivity (%)[c]
1	Hexane	0.06	trace	-
2	Toluene	2.40	25	>99
3	THF	4.20	45	>99
4	EtOH	4.30	40	>99
5	CH_3CN	6.20	55	>99
6	MeOH	6.60	73	>99
7	H_2O	10.2	100	>99

[a]Reaction conditions: nitroarene (0.5 mmol), CoO_x@NC-800 (10 mg, 10 mol% of Co), solvent (2 mL), H_2 (5 MPa), 110°C. [b]Based on data available from Empirical Parameters of Solvent Polarity in *Solvents and Solvent Effects in Organic Chemistry*, Fourth Edition. Edited by C. Reichardt, T. Welton, 2011, WILEY-VCH GmbH & Co. KGaA, Weinheim. [c]Determined by GC and GC-MS using dodecane as an internal standard sample and confirmed with their corresponding authentic samples.

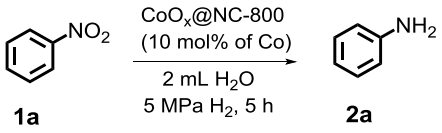
Table S2. H_2 pressure effect on nitrobenzene hydrogenation[a]



Entry	H_2 (MPa)	Conversion (%)[b]	Selectivity (%)[b]
1	1 atm (H_2 balloon)	0	-
2	1	65	>99
3	2	78	>99
4	3	84	>99
5	4	96	>99
6	5	100	>99

[a]Reaction conditions: nitroarene (0.5 mmol), CoO_x@NC-800 (10 mg, 10 mol% of Co), H_2O (2 mL), H_2 (0-5 MPa), 110°C. [b]Determined by GC and GC-MS using dodecane as an internal standard sample and confirmed with their corresponding authentic samples.

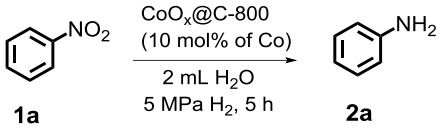
Table S3. Reaction temperature effect on nitrobenzene hydrogenation[a]



Entry	Temperature (°C)	Conversion (%)[b]	Selectivity (%)[b]
1	110	100	>99
2	100	83	>99
3	90	56	>99
4	80	21	>99

Reaction conditions: nitroarene (0.5 mmol), CoO_x@NC-800 (10 mg, 10 mol% of Co), H_2O (2 mL), H_2 (5 MPa), temperature (80-110°C). [b]Determined by GC and GC-MS using dodecane as an internal standard sample and confirmed with their corresponding authentic samples.

Table S4. The N role on the hydrogenation of nitrobenzene[a]

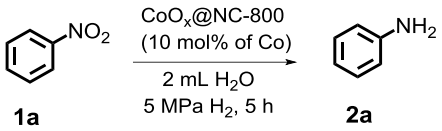


Entry	Catalyst	N Content (wt%)[b]	Conversion (%)[c]	Selectivity (%)[c]
1	CoO_x@C-800	0	50	>99
2	CoO_x@C-800-N	0.57	83	>99
3	CoO_x@C-800-N	1.85	100	>99

Reaction conditions: nitroarene (0.5 mmol), CoO_x@C-800 (10 mol% of Co), H_2O (2 mL), H_2 (5 MPa), 110°C. [b]Determined by elemental analysis. [c]Determined by GC and GC-MS using dodecane as an internal standard sample and confirmed with their corresponding authentic samples.

The catalyst CoO_x@C-800-N was prepared by directly pyrolysis of the homogeneous mixture of activated carbon, $CoCl_2$, and a given amount of melamine as external N source at 800°C with similar procedure to the preparation of CoO_x@NC-800. The N content in the catalysts were determined by elemental analysis. Under otherwise identical conditions, the reaction rate was significantly enhanced upon incorporation of N atoms in the catalyst and had a N content dependent to a certain extent, indicating the N doping indeed played a critical role on activating hydrogen molecules and nitro compounds, thereby confirming the effect of N of the catalysts CoO_x@NC-T.

Table S5. The recyclability of the catalyst CoO_x@NC-800 for nitrobenzene hydrogenation.[a]

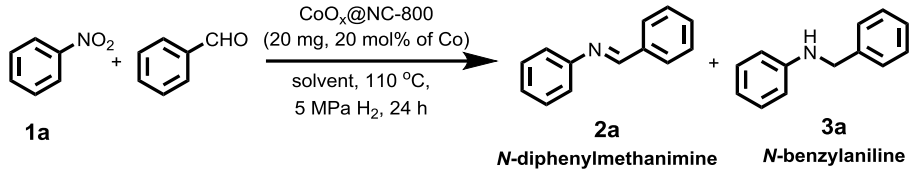


1a 2a

Cycle	Conversion (%)[b]	Selectivity (%)[b]
0	100	>99
1st	97	>99
2nd	93	>99
3rd	90	>99
4th	86	>99

Reaction conditions: nitroarene (0.5 mmol), CoO_x@NC-800 (10 mg, 10 mol% of Co), H_2O (2 mL), H_2 (5 MPa), temperature (80-110°C). [b]Determined by GC and GC-MS using dodecane as an internal standard sample and confirmed with their corresponding authentic samples.

Table S6. Optimization of reaction conditions for the coupling of nitrobenzene with benzyl aldehye[a]



Entry	Solvent	Time	Conversion	Selectivity (%)[b]	
		(h)	(%)[b]	**2a**	**3a**
1	THF/H_2O	24	100	69	31
2	(15/1)	24	100	75	25
3	THF/H_2O	24	100	83	17
4	(10/1)	24	100	98	2
5	THF/H_2O (6/1)	22	100	100	0
6	THF/H_2O (4/1)	12	55	100	0
7	THF/H_2O (4/1)	16	81	100	0
8	THF/H_2O (4/1)	36	100	31	61
9	THF/H_2O (4/1)	48	100	5	78
10[c]	THF/H_2O (4/1)	24	100	63	37
11[d]	THF/H_2O (4/1)	24	100	21	76
12	H_2O	24	100	73	27
13[e]	THF/H_2O (4/1)	24	100	85	15

[a]Reaction conditions: nitrobenzene (0.5 mmol), benzaldehyde (2 mmol), CoO_x@NC 800 (20 mg, 20 mol% of Co), Solvent (4 mL), H_2 (5 MPa), 110 °C, 24 h. [b]Determined by GC using dodecane as internal standard. [c] 150°C. [d]170°C. [e]nitrobenzene (0.5 mmol), benzaldehyde (1.5 mmol).

Table S7. The nitrogen types and their corresponding distributions on surface of the carbon matrix for the catalysts CoO_x@NC-T by XPS analysis

Sample	Graphitic N (401.2 eV)	Pyrrolic N or CoN_x (399.6 eV)	Pyridinic N (398.2 eV)
CoO_x@NC-700	61%	10%	29%
CoO_x@NC-800	66%	12%	22%
CoO_x@NC-900	83%	7%	11%

Table S8. The different cobalt phases and their corresponding distributions, particle size on surface of the catalysts CoO_x@NC-T by XPS and XRD analysis.

Catalyst	Co^0 (778.9 eV) (nm)	CoO (782.9 eV) (nm)	Co_3O_4 (780.8 eV) (nm)
CoO_x@NC-700	21% (31.6)	32% (16.7)	47% (13.8)
CoO_x@NC-800	15% (36.4)	32% (13.7)	53% (10.8)
CoO_x@NC-900	17% (32.7)	26% (20.9)	57% (12.2)

Note: particle size was calculated by Scherrer equation.

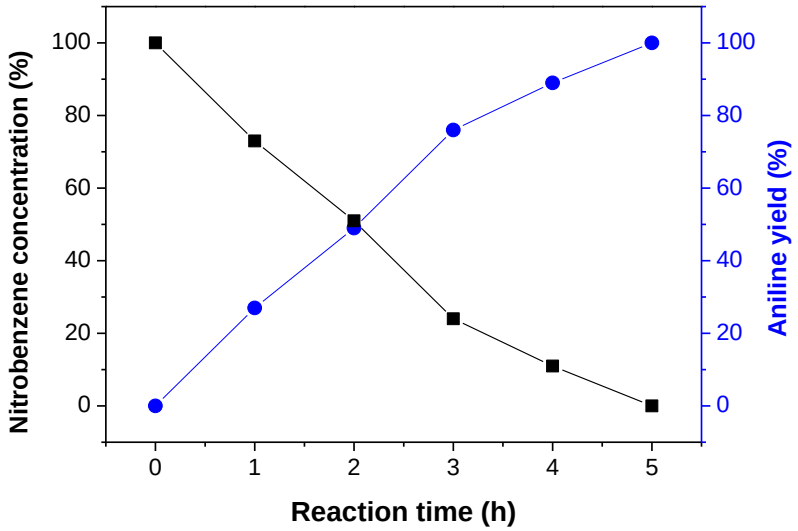


Figure S1. Kinetic data of hydrogenation of nitrobenzene with CoO_x@NC-800 catalyst. The plot is based on the results of different reactions stopped at different times.

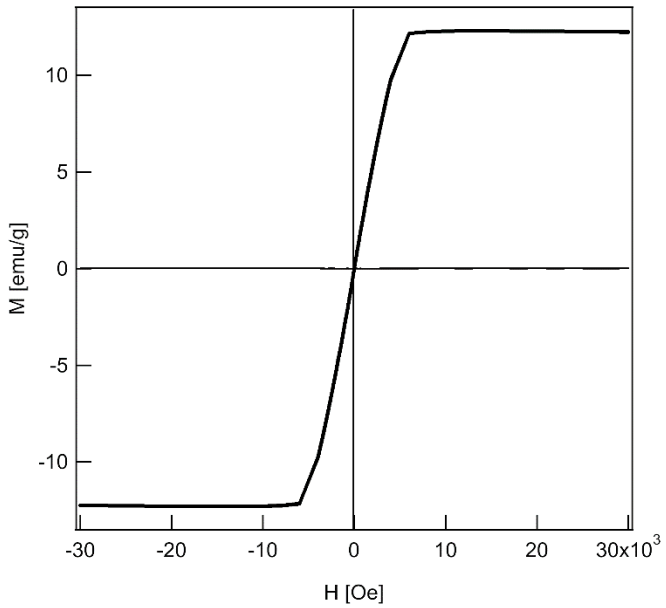


Figure S2.

5. Control experiments

5.1 Benzaldehyde hydrogenation

The Co nanocatalyst was tested in the hydrogenation of benzaldehyde. A 50mL high-pressure autoclave was charged with a magnetic stirring, 0.5 mmol benzaldehyde, 20 mg catalyst, 3.8 mL THF and 0.2 mL H_2O. The autoclave was flushed three times with 5 MPa of hydrogen. The autoclave was pressured with 5 MPa of hydrogen and the reaction was stirred for 22 h at 110 °C. Yields were determined by GC and GC-MS using dodecane as an internal standard.

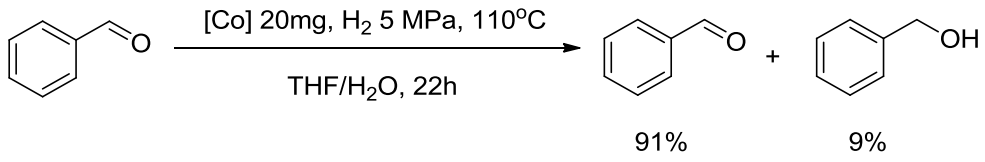


Figure S3. Product distribution for the hydrogenation of sole benzaldehyde.

The hydrogenation of benzaldehyde took place, However, only 14 % of benzylalcohol could be detected, This indicated that the catalysis system has very low activity for the

hydrogenation of benzaldehyde.

5.2 Imine hydrogenation

The Co nanocatalyst was tested in the hydrogenation of imine. A 50 mL high-pressure autoclave was charged with a magnetic stirring, 0.5 mmol imine, 20 mg catalyst, 3.8 mL THF and 0.2 mL H_2O. The autoclave was flushed three times with 5 MPa of hydrogen. The autoclave was pressured with 5 MPa of hydrogen and the reaction was stirred for 22 h at 110 °C. Yields were determined by GC and GC-MS using dodecane as an internal standard. The 63% of amine was detected along with 37% of hydrolytic products.

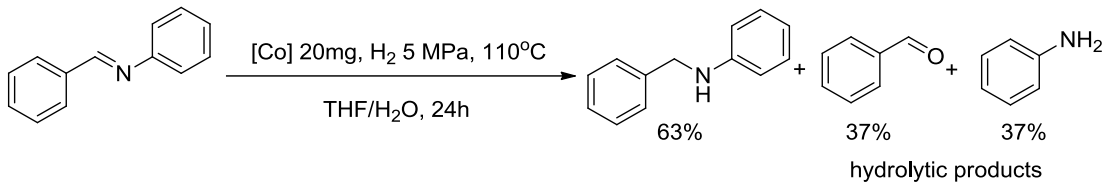


Figure S4. Product distribution for the hydrogenation of imine.

5.3 The influence of the nitro compound

To investigate the influence of the nitro compound, further studies were accomplished. The reactions were repeated as described above, but in this case 0.5 mmol nitrobenzene and imine were added to the reaction mixture.

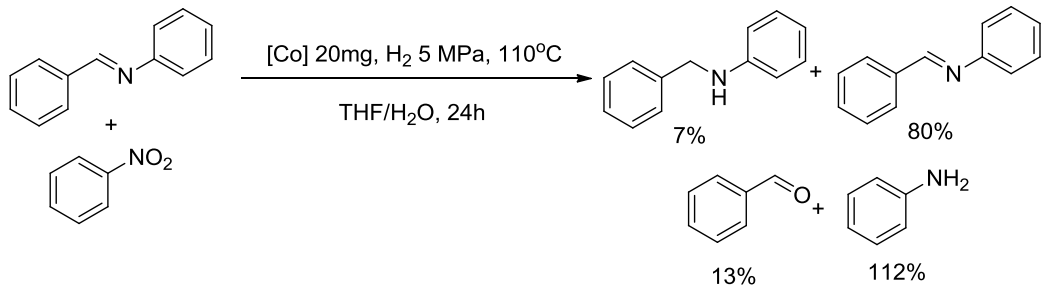
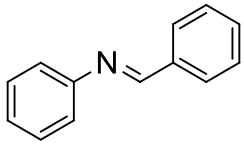


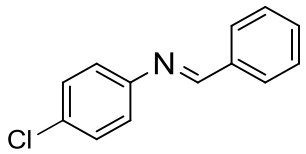
Figure S5. Product distribution for the hydrogenation of a mixture consisting of benzaldehyde and nitrobenzene.

In this case, no benzaldehyde hydrogenation product was observed, 80% of imine along with only 7% of amine was detected. This is especially interesting in comparison to the hydrogenation of sole imine, where nearly 60 % of amine could be detected. This indicates that the hydrogenation of the substrates with nitrogen functionalities is highly favored under the reaction conditions, and the nitroarenes may prevent imines from further reduction. This could be the basis of the imine syntheses from nitroarenes and aldehydes.

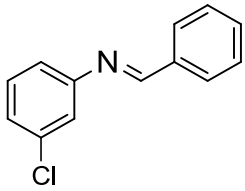
6. Characterization of the obtained products



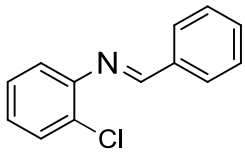
***(E)-N*-benzylideneaniline (2a)** [1], Light yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.37 (s, 1H), 7.79-7.81 (m, 2H), 7.45-7.30 (m, 5H), 7.23-7.11 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 160.4, 152.2, 136.4, 131.5, 129.3, 128.9, 128.9, 126.1, 121.0. The spectroscopic data matched that previously report [*Angew. Chem. Int. Ed.* **2016**, *55*, 15175–15179].



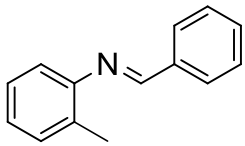
***(E)-N*-benzylidene-4-chloroaniline (2b)**[1], White solid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.40 (s, 1H), 7.88 (d, J = 6.2 Hz, 2H), 7.50-7.42 (d, J = 5.9 Hz, 3H), 7.33 (d, J = 8.3 Hz, 2H), 7.13 (d, J = 8.2 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 160.7, 150.5, 135.9, 131.7, 131.5, 129.3, 128.9, 128.9, 122.3. The spectroscopic data matched that previously report [*Angew. Chem. Int. Ed.* **2016**, *55*, 15175–15179].



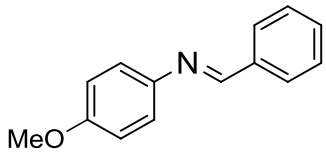
***(E)-N*-benzylidene-3-chloroaniline (2c)**[1], White solid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.38 (s, 1H), 8.06-7.69 (m, 2H), 7.451-7.41 (d, *J* = 6.7 Hz, 3H), 7.28 (t, *J* = 8.1 Hz, 1H), 7.18 (d, *J* = 1.4 Hz, 2H), 7.07 (d, *J* = 7.7 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 161.4, 153.4, 135.9, 134.8, 131.8, 130.2, 129.0, 128.9, 125.9, 120.9, 119.4. The spectroscopic data matched that previously report [*Angew. Chem. Int. Ed.* **2016**, *55*, 15175–15179].



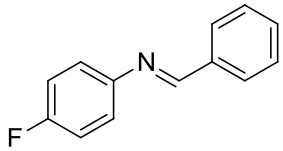
***(E)-N*-benzylidene-2-chloroaniline (2d)**[2],Yellow oil; ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.32 (s, 1H), 7.91 (d, *J* = 7.5 Hz, 2H), 7.55-7.31 (m, 4H), 7.22 (t, *J* = 7.6 Hz, 1H), 7.09 (t, *J* = 7.7 Hz, 1H), 6.97 (d, *J* = 7.8 Hz, 1H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 162.1, 149.6, 135.9, 131.9, 130.0, 129.2, 128.9, 127.9, 127.7, 126.5, 120.1. The spectroscopic data matched that previously report [*Catal. Lett.* **2017**,*147*, 20-28].



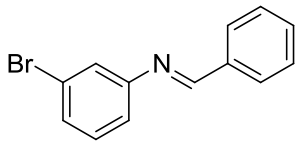
***(E)-N*-benzylidene-2-methylaniline (2e)**[3], Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.35 (s, 1H), 8.04-7.72 (m, 2H), 7.55-7.34 (m, 3H), 7.30-7.16 (m, 2H), 7.16 -7.05 (m, 1H), 6.91 (d, *J* = 7.8 Hz, 1H), 2.36 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 159.5, 151.2, 136.5, 131.9, 131.3, 130.3, 128.8 (2C), 126.8, 125.7 117.7, 17.9. The spectroscopic data matched that previously report [*Green Chem.* **2012**, *14*, 3423–3428].



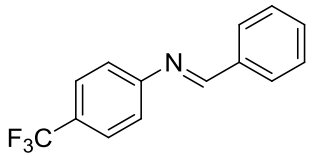
***(E)-N*-benzylidene-4-methoxyaniline (2f)**[3], White solid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.45 (s, 1H), 7.98-7.74 (m, 2H), 7.58-7.35 (m, 3H), 7.22 (d, *J* = 8.8 Hz, 2H), 6.91 (d, *J* = 8.9 Hz, 2H), 3.79 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 158.4, 158.3, 144.9, 136.5, 131.1, 128.8, 128.6, 122.3, 114.4, 55.5. The spectroscopic data matched that previously report [*Green Chem.* **2012**, *14*, 3423–3428].



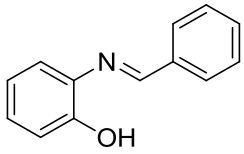
***(E)-N*-benzylidene-4-fluoroaniline (2g)**[3], Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.45 (s, 1H), 7.98-7.74 (m, 2H), 7.58-7.35 (m, 3H), 7.22 (d, *J* = 8.8 Hz, 2H), 6.91 (d, *J* = 8.9 Hz, 2H), 3.79 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 161.3 (d, *J* = 244.6 Hz), 160.2, 148.09, 148.07, 136.1, 131.5, 128.83, 128.81, 122.3 (d, *J* = 8.2 Hz), 115.9 (d, *J* = 22.5 Hz). The spectroscopic data matched that previously report [*Green Chem.* **2012**, *14*, 3423–3428].



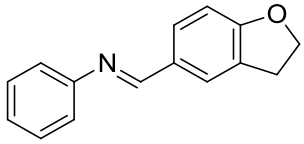
***(E)-N*-benzylidene-3-bromoaniline (2h)**[3], White solid; ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.35 (s, 1H), 7.86 (d, *J* = 7.3 Hz, 2H), 7.52-7.38 (m, 3H), 7.38-7.26 (m, 2H), 7.21 (t, *J* = 7.8 Hz, 1H), 7.10 (d, *J* = 7.8 Hz, 1H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 161.2, 153.4, 135.7, 131.7, 130.4, 128.9, 128.8, 128.6, 123.6, 122.7, 119.9. The spectroscopic data matched that previously report [*Green Chem.* **2012**, *14*, 3423–3428].



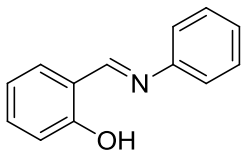
***(E)-N*-benzylidene-4-(trifluoromethyl)aniline (2i)**[3], White solid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.34 (s, 1H), 7.90-7.75 (m, 2H), 7.56 (d, *J* = 8.3 Hz, 2H), 7.49-7.33 (m, 3H), 7.26-7.04 (m, 2H).^{13}C NMR (101 MHz, $CDCl_3$): δ 162.0, 155.2, 135.7, 132.0, 129.1, 128.9, 127.7 (q, *J* = 32.5 Hz), 126.4 (q, *J* = 3.8 Hz), 124.34 (d, *J* = 271.7 Hz), 121.0. The spectroscopic data matched that previously report [*Green Chem.* **2012**, *14*, 3423–3428].



***(E)-2*-(benzylideneamino)phenol (2j)**[4], yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.71 (s, 1H), 7.95 (d, *J* = 5.5 Hz, 2H), 7.53 (d, *J* = 5.4 Hz, 3H), 7.40 (brs, 1H), 7.34 (d, *J* = 7.8 Hz, 1H), 7.26 (t, *J* = 7.5 Hz, 1H), 7.11 (d, *J* = 7.9 Hz, 1H), 6.97 (t, *J* = 7.4 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 157.2, 152.4, 135.9, 135.6, 131.7, 129.0, 128.91, 128.89, 120.2, 116.0, 115.1. The spectroscopic data matched that previously repor*t* [*Journal of Molecular Structure* **2016**, *1106*, 154-169].

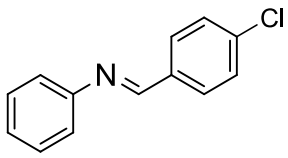


***(E)-N*-((*2,3*-dihydrobenzofuran-*5*-yl)methylene)aniline (2k)**, Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.39 (s, 1H), 7.91 (s, 1H), 7.63 (d, *J* = 8.0 Hz, 1H), 7.41 (t, *J* = 7.6 Hz, 2H), 7.33-7.08 (m, 3H), 6.88 (d, *J* = 8.2 Hz, 1H), 4.68 (t, *J* = 8.7 Hz, 2H), 3.29 (t, *J* = 8.6 Hz, 2H).^{13}C NMR (101 MHz, $CDCl_3$): δ 190.8, 163.3, 159.9, 131.1, 129.2, 128.2, 125.6 124.8, 120.9, 115.1, 109.4, 72.0, 29.2; HRMS (*m/z*): calcd. for $C_{15}H_{14}NO$ [M+H], 224.1070; found, 224.1073.

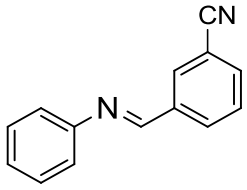


***(E)-2*-((phenylimino)methyl)phenol (2l)**[5], Yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$):

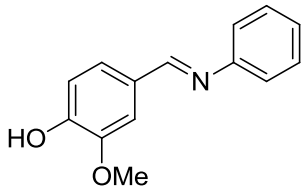
δ 13.25 (brs, 1H), 8.54 (d, *J* = 1.5 Hz, 1H), 7.42-7.29 (m, 4H), 7.27-7.17 (m, 3H), 7.00 (dd, *J* = 8.6, 3.7 Hz, 1H), 6.92-6.81 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 162.7, 161.2, 148.5, 133.2, 132.4, 129.5, 126.9, 121.3, 119.3, 119.1, 117.3. The spectroscopic data matched that previously report [*Dalton Trans.* **2017**, *46*, 5003-5007].



***(E)-N*-(4-chlorobenzylidene)aniline (2m)**[3], White solid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.37 (s, 1H), 7.80 (d, *J* = 8.4 Hz, 2H), 7.51-7.32 (m, 4H), 7.26-7.11 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 158.8, 151.7, 137.4, 134.8, 130.0, 129.3, 129.1, 126.3, 120.9. The spectroscopic data matched that previously report [*Green Chem.* **2012**, *14*, 3423–3428].

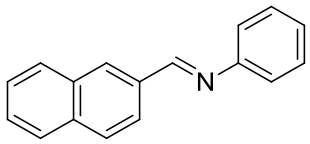


***(E)-3*-((phenylimino)methyl)benzonitrile (2n)**[6], White solid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.38 (s, 1H), 8.11 (s, 1H), 8.05 (d, *J* = 7.9 Hz, 1H), 7.72-7.60 (m, 1H), 7.51 (t, *J* = 7.8 Hz, 1H), 7.38 (t, *J* = 7.8 Hz, 2H), 7.29-7.13 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 157.4, 150.9 137.3, 134.2, 132.8, 132.1, 129.7 129.4 126.9, 121.0, 118.4, 113.1. The spectroscopic data matched that previously report [*Magnetic Resonance in Chemistry* **2015**, *53*, 520-525].

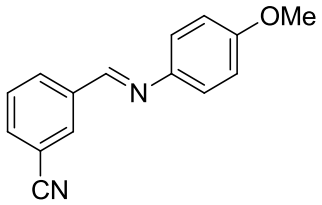


***(E)-2*-methoxy-*4*-((phenylimino)methyl)phenol (2o)**[7], yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.34 (s, 1H), 7.62 (d, *J* = 1.6 Hz, 1H), 7.38 (t, *J* = 7.8 Hz, 2H), 7.26-7.12 (m, 4H), 6.97 (d, *J* = 8.1 Hz, 1H), 3.93 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ

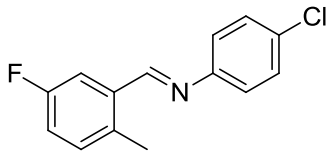
160.3, 152.1, 149.2, 147.3, 129.2, 129.0, 125.7, 125.4, 120.9, 114.3, 108.6, 56.0. The spectroscopic data matched that previously report [*Bioorganic & medicinal chemistry letters* **2010**, *20*, 2417-2420].



***(E)-N*-(naphthalen-*2*-ylmethylene)aniline (2p)**[6], White solid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.57 (s, 1H), 8.19-8.11 (m, 2H), 7.93-7.78 (m, 3H), 7.58-7.45 (m, 2H), 7.40 (t, *J* = 7.8 Hz, 2H), 7.31-7.16 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 160.4, 152.2, 135.1, 134.0, 133.2, 131.3, 129.3, 128.8, 128.7, 128.0, 127.6, 126.7, 126.1, 123.9, 121.0. The spectroscopic data matched that previously report [*Journal of Enzyme Inhibition and Medicinal Chemistry*, **2016**, *31*, 79-88].

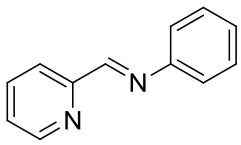


***(E)-3*-(((4-methoxyphenyl)imino)methyl)benzonitrile (2q)**[6], White solid; ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.46 (s, 1H), 8.13 (d, *J* = 49.1 Hz, 2H), 7.63 (d, *J* = 85.2 Hz, 2H), 7.26 (s, 2H), 6.94 (s, 2H), 3.83 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 158.9, 154.9, 143.7, 137.6, 133.8, 132.5, 131.8, 129.6, 122.5, 118.4, 114.5, 113.1, 55.5. The spectroscopic data matched that previously report [*Magnetic Resonance in Chemistry* **2015**, *53*, 520-525].

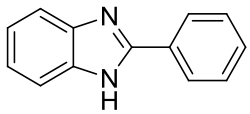


***(E)*-4-chloro-N-(5-fluoro-2-methylbenzylidene)aniline (2r)**, White solid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.69 (s, 1H), 7.82 (d, *J* = 8.4 Hz, 1H), 7.39 (d, *J* = 8.2 Hz, 2H), 7.33 – 6.98 (m, 4H), 2.56 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 161.5 (d, *J* = 224),

157.9, 150.5, 135.5, 134.3, 132.5, 131.8, 129.3, 122.3, 118.2 (d, J = 21.6), 113.8 (d, *J* = 22.6), 18.5. HRMS (*m/z*): calcd. for $C_{14}H_{12}ClFN$ [M+H], 248.0637; found, 248.0637.

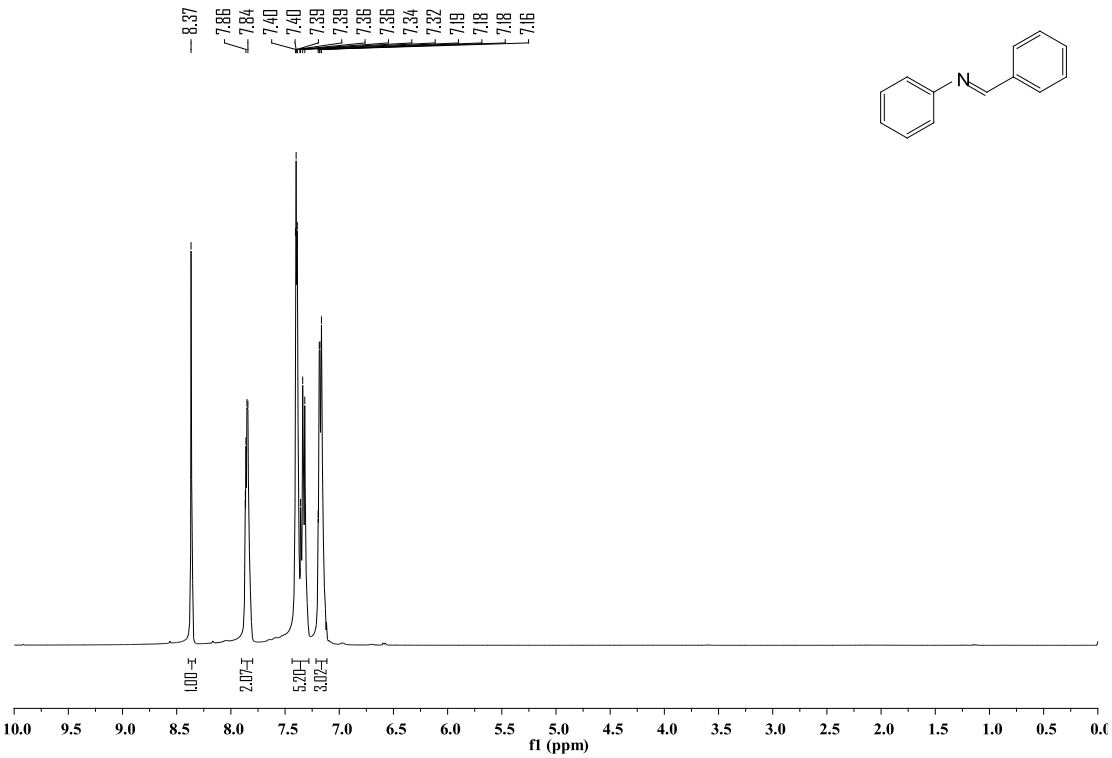


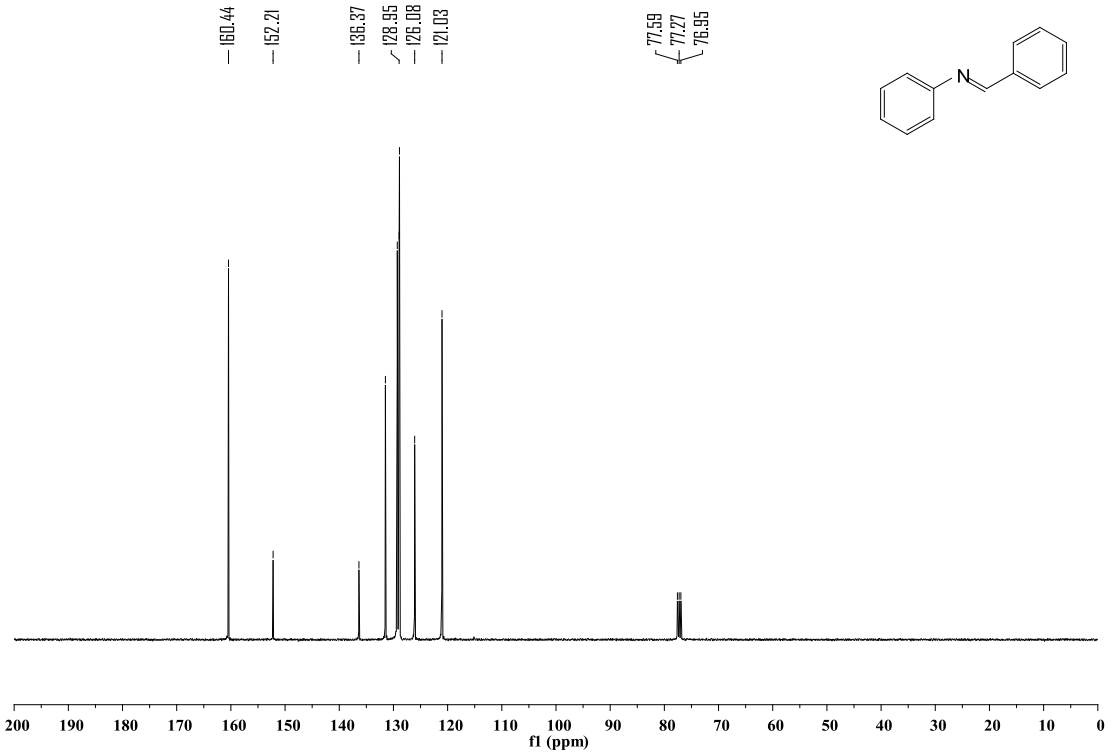
***(E)-N*-(pyridin-2-ylmethylene)aniline (2s)**, yellow oil; ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.71-8.63 (m, 1H), 8.62 (s, 1H), 8.27-8.07 (m, 1H), 7.85-7.59 (m, 1H), 7.47-7.33 (m, 2H), 7.33-7.14 (m, 4H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 160.6, 154.6, 151.0 149.7, 136.6, 129.2, 126.7, 125.1, 121.9, 121.2. HRMS (*m/z*): calcd. for $C_{12}H_{11}N_2$ [M+H], 183.0917; found, 183.0917.



2-phenyl-1H-benzo[d]imidazole (2t)[8]**,** white solid; ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.34 (d, *J* = 7.4 Hz, 2H), 7.73 (dd, *J* = 5.7, 3.2 Hz, 2H), 7.59 (t, *J* = 7.5 Hz, 2H), 7.51 (t, *J* = 7.3 Hz, 1H), 7.33-7.20 (m, 2H); ^{13}C NMR (151 MHz, DMSO-d_6): δ 151.3, 143.8, 135.2, 130.2, 129.7, 128.9, 126.5, 122.1, 118.7, 111.4. The spectroscopic data matched that previously report [*Chem. Eur. J.* **2018***, 24,* 3481-3487].

7. ^{1}H and ^{13}C NMR spectra of products


8.37
7.86
7.84
7.40
7.40
7.39
7.39
7.36
7.36
7.34
7.32
7.19
7.18
7.18
7.16
1.00
2.07
5.20
3.07
N
10.0 9.5 9.0 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
f1 (ppm)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152.21
136.37
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126.08
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77.59
77.27
76.95
N
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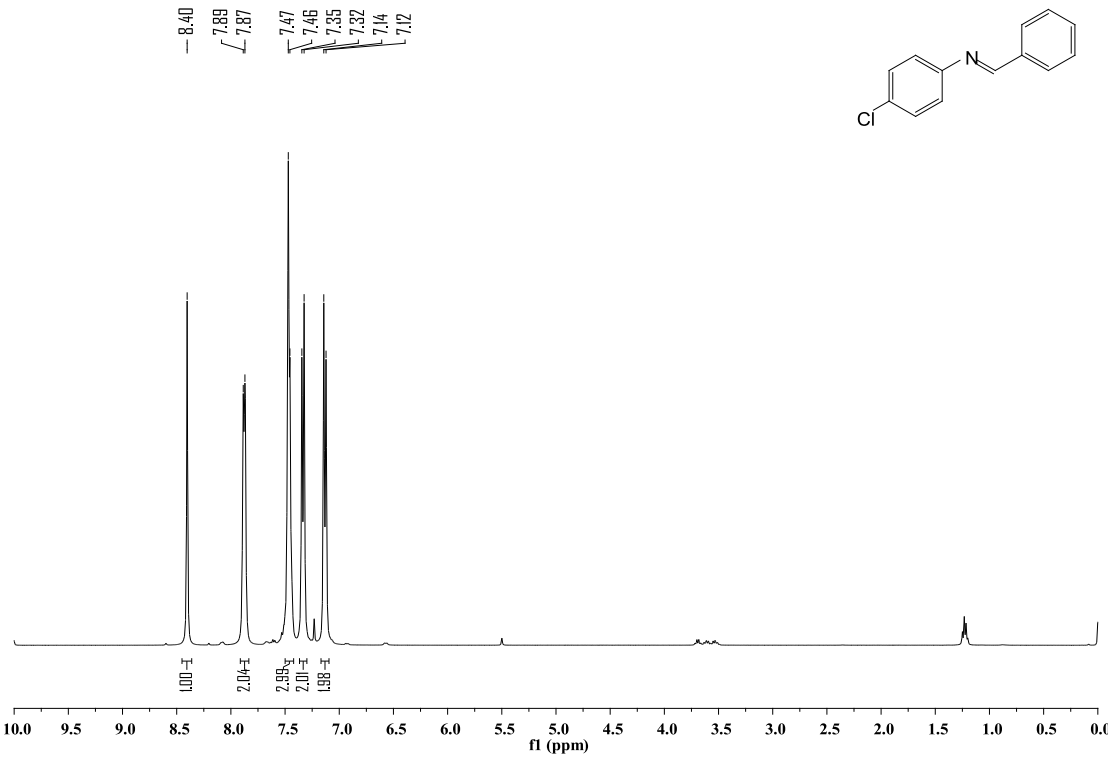
f1 (ppm)


8.40
7.89
7.87
7.47
7.46
7.35
7.32
7.14
7.12
Cl
N
1.00
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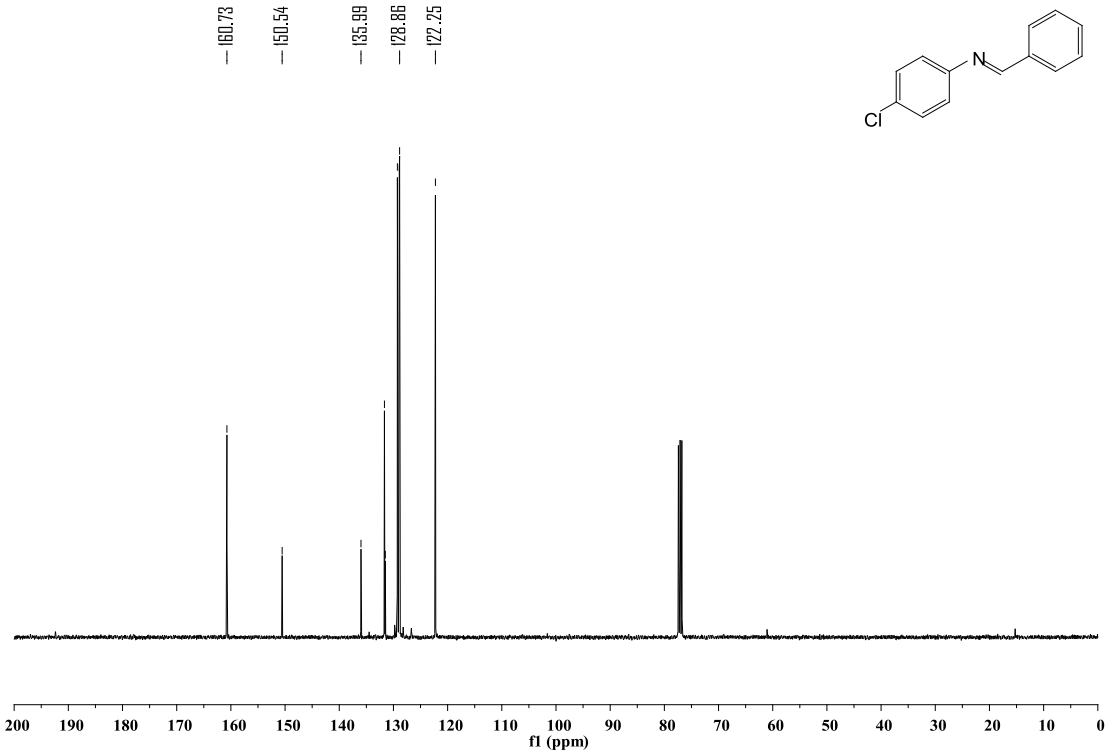
2.95
2.01
1.98
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)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N
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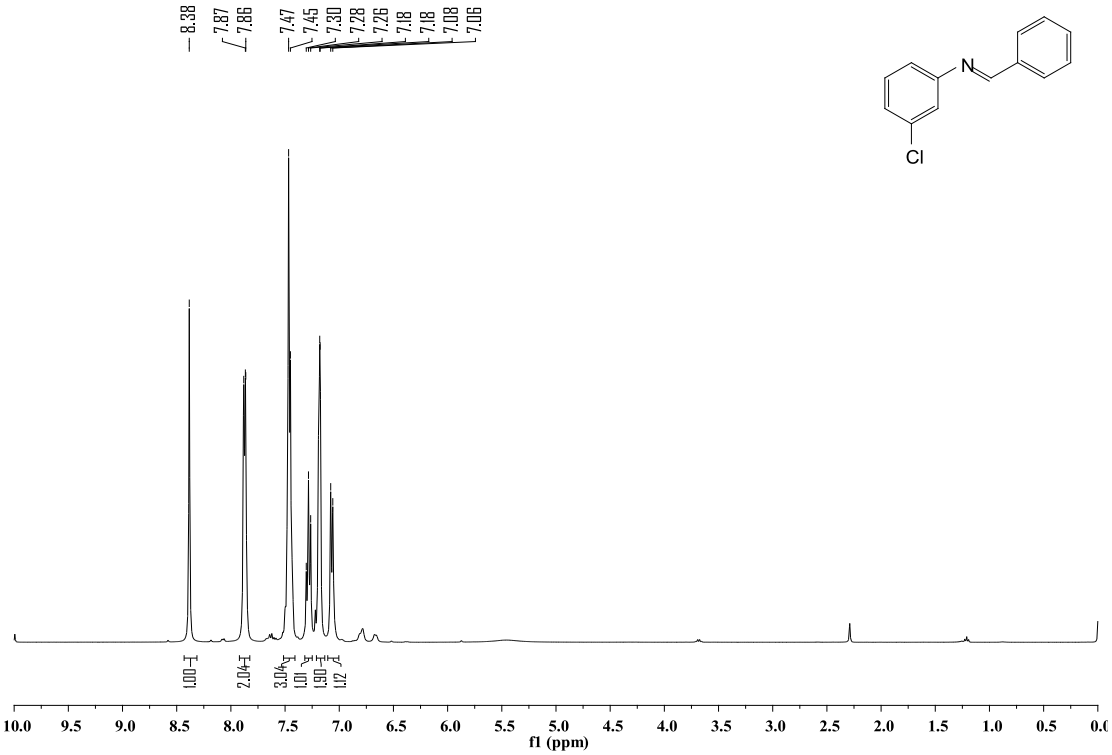
f1 (ppm)


8.38
7.87
7.86
7.47
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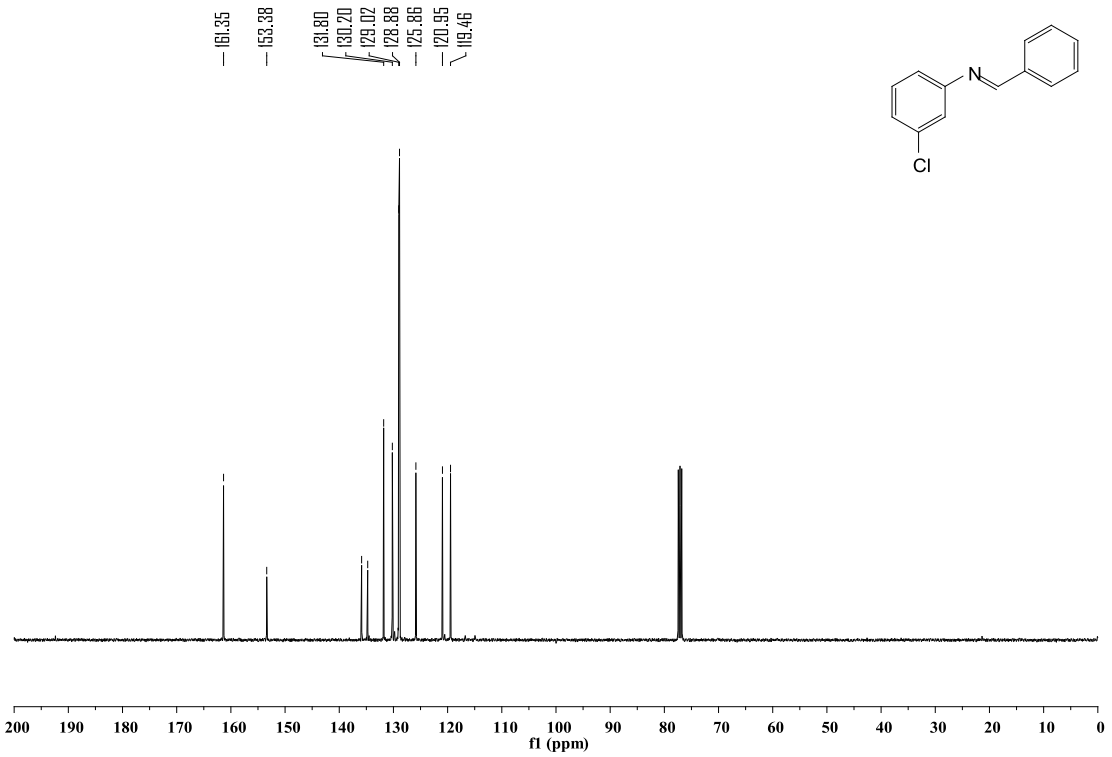
7.28
7.26
7.18
7.18
7.08
7.06
N
Cl
1.00
2.04
3.04
1.01
1.90
1.12
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)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153.38
131.80
130.20
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120.95
119.46
N
Cl
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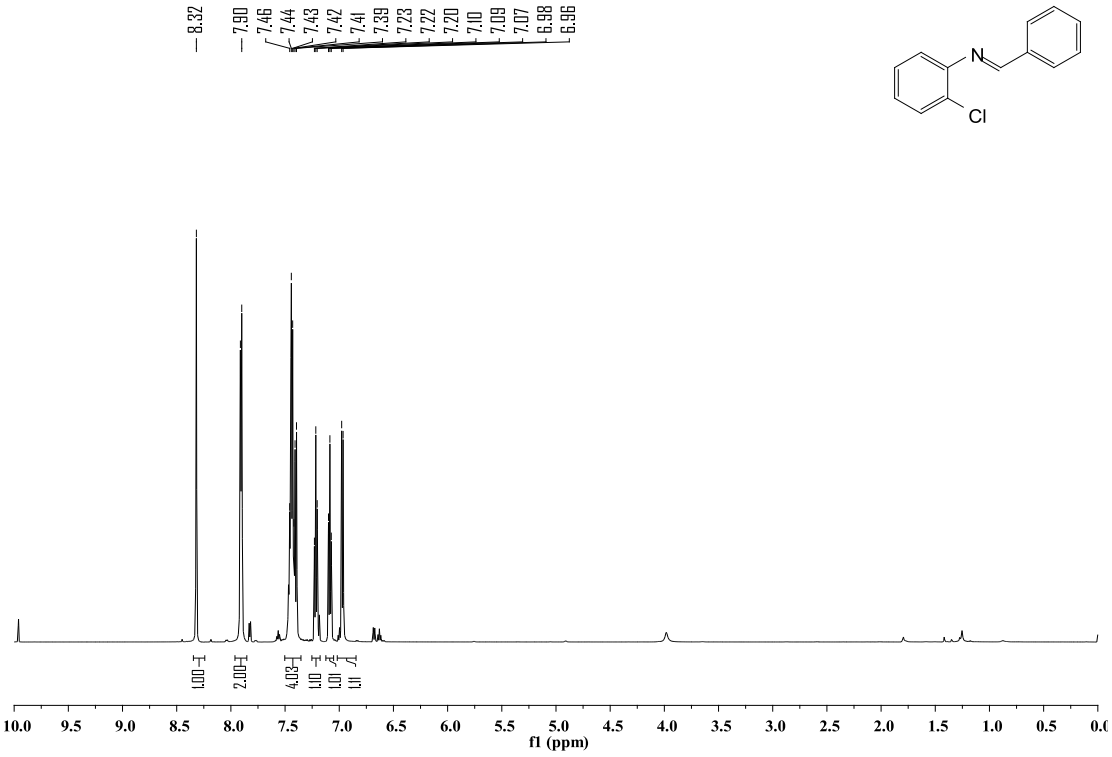
f1 (ppm)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7.10
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6.96
N
Cl
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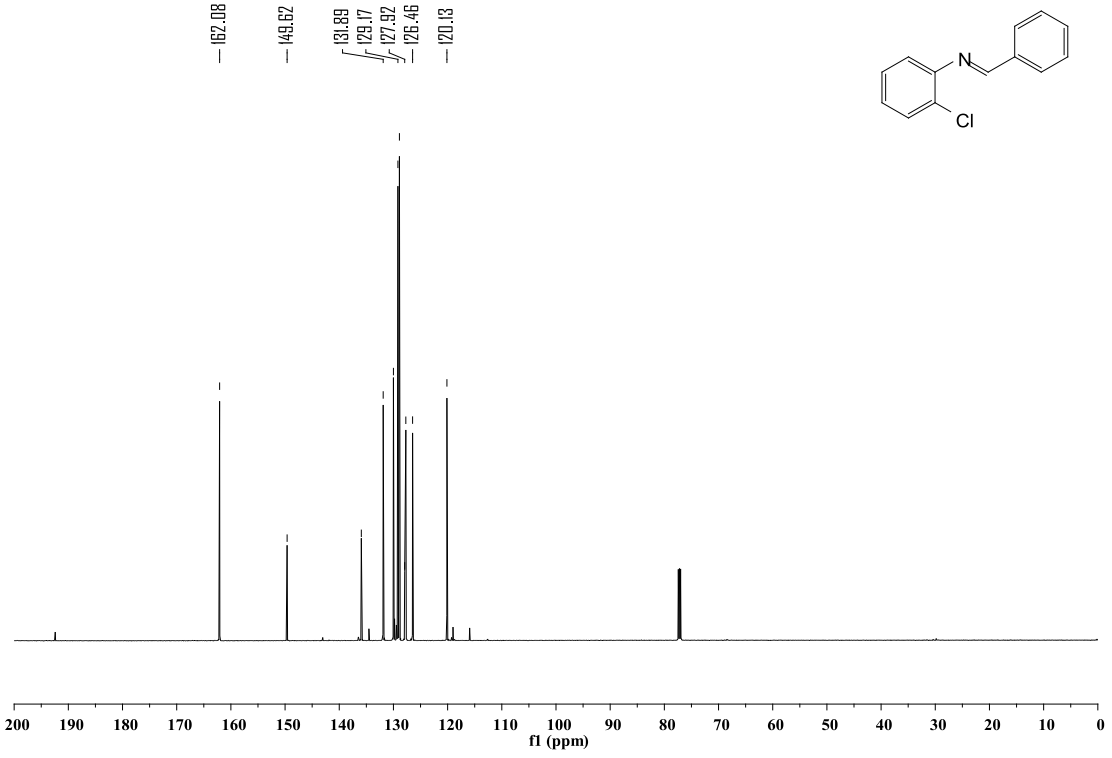
4.03
1.10
1.01
1.01
1.11
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)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120.13
N
Cl
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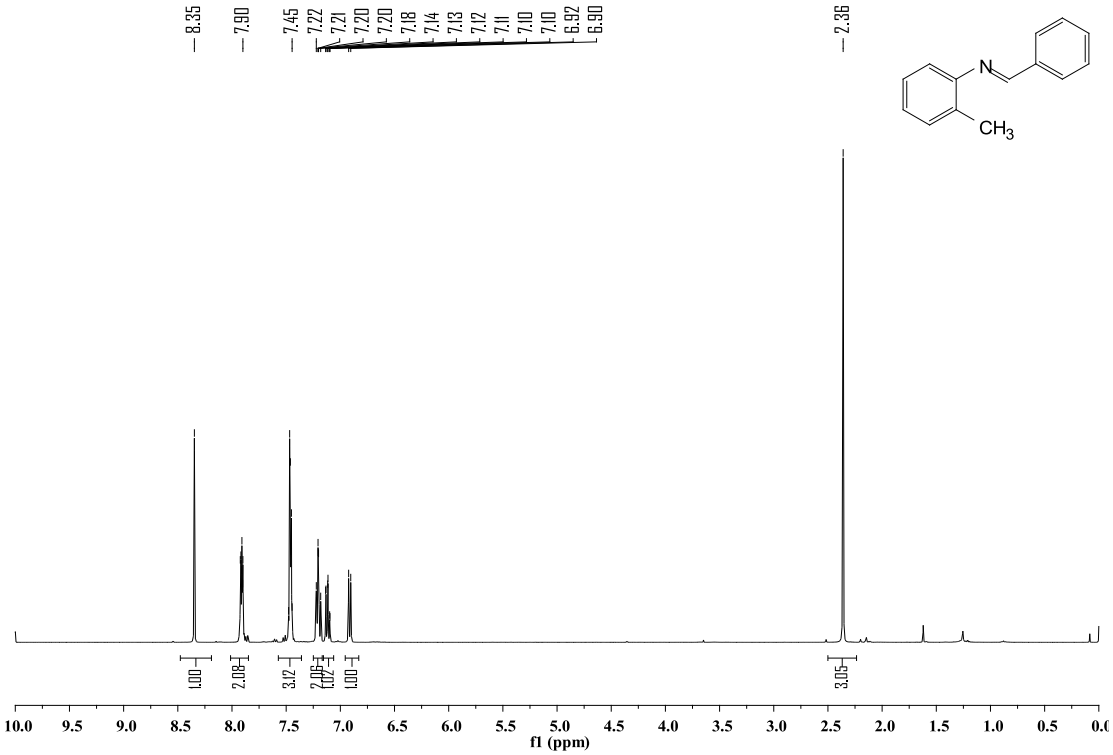
f1 (ppm)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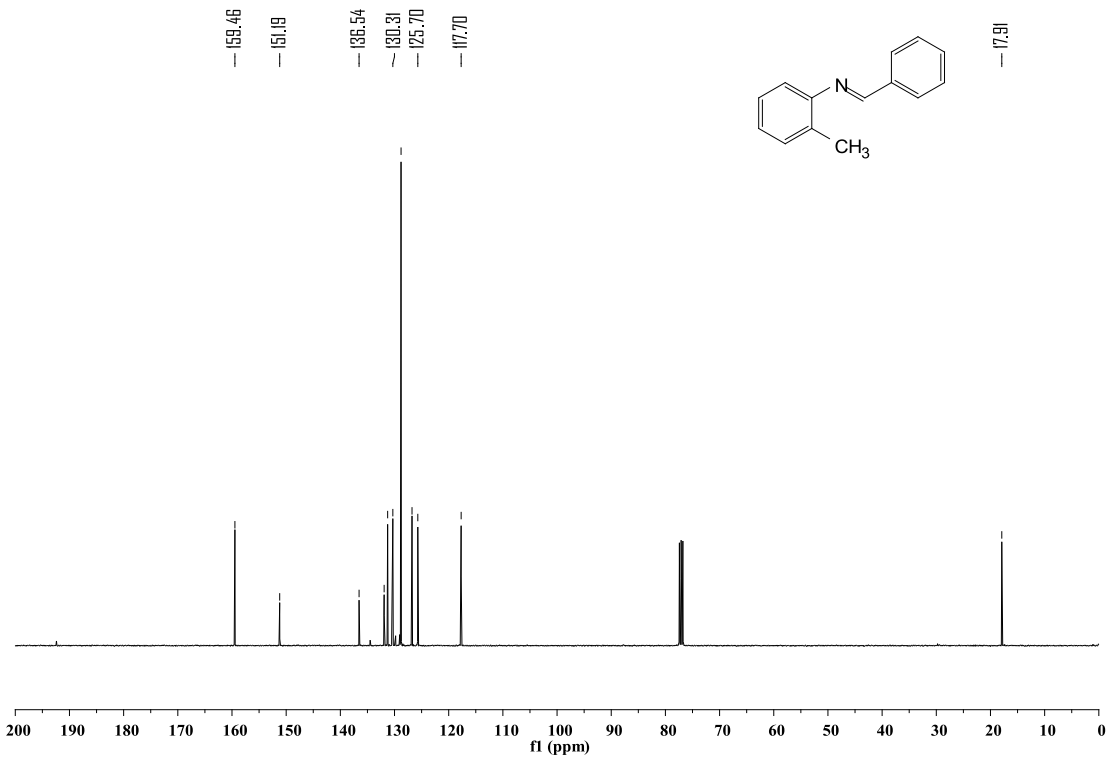
7.21
7.20
7.20
7.18
7.14
7.13
7.12
7.11
7.10
7.10
6.92
6.90
2.36
N
CH3
1.00
2.08
3.12
2.06
1.02
1.00
3.05
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


159.46
151.19
136.54
130.31
125.70
117.70
17.91
N
CH3
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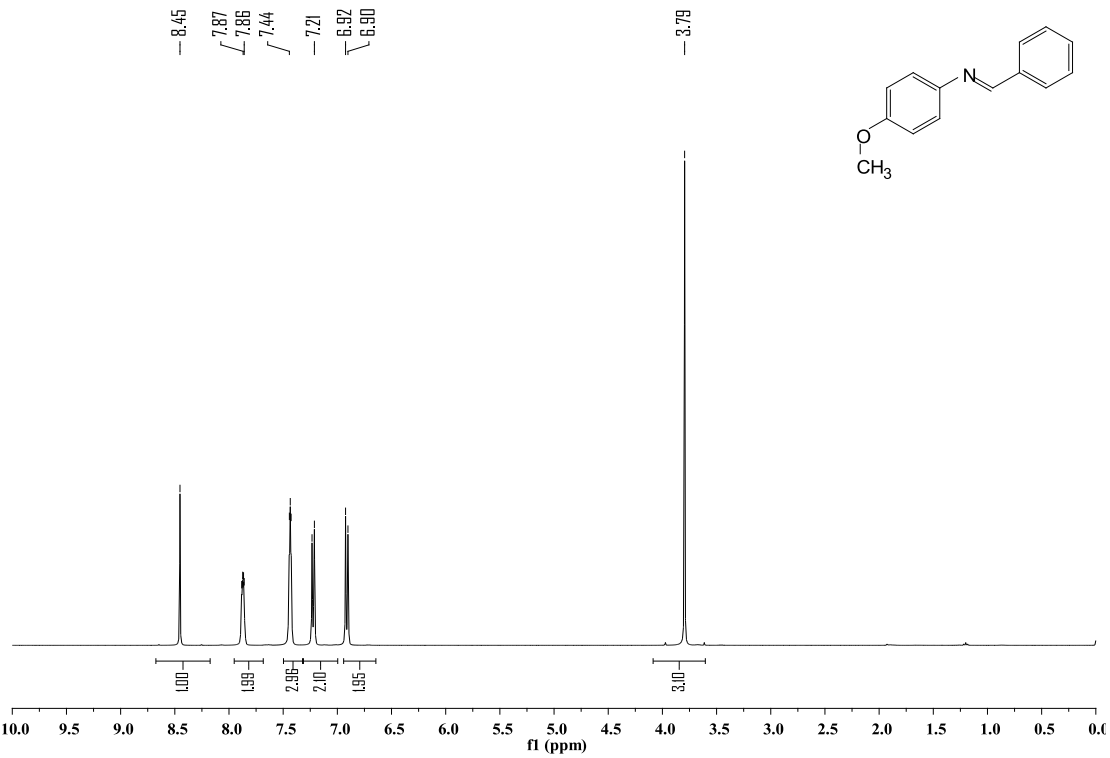
f1 (ppm)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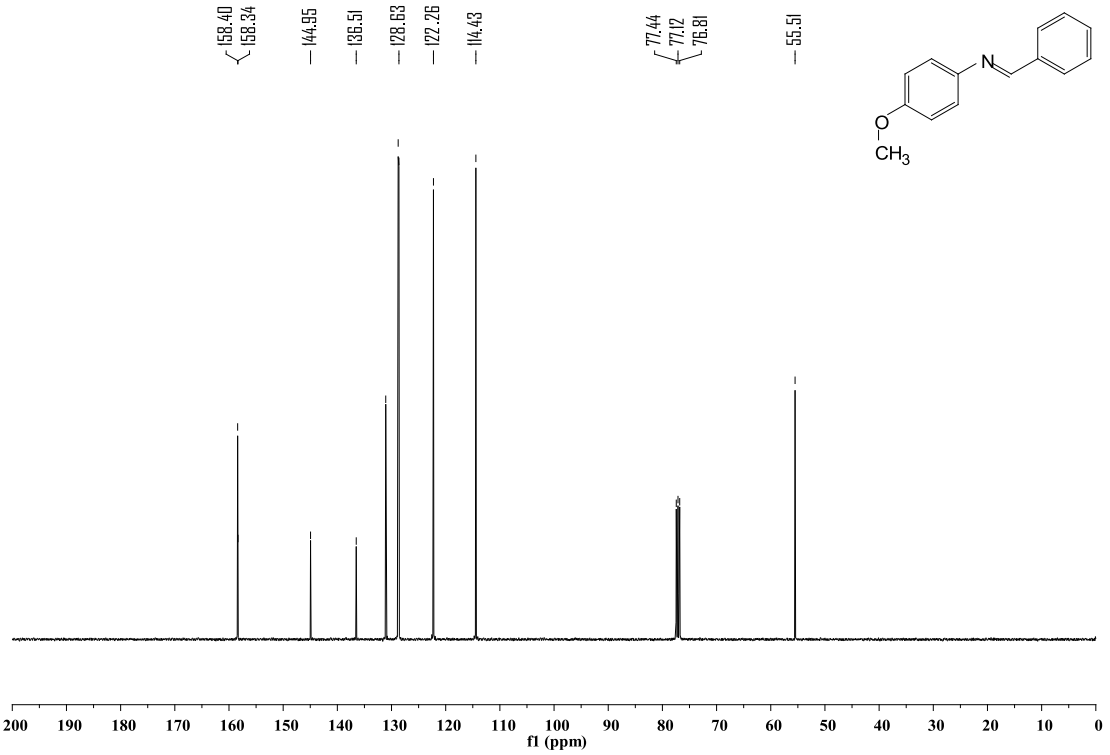
7.86
7.44
7.21
6.92
6.90
3.79
1.00
1.99
2.96
2.10
1.95
3.10
N
O
CH3
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)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144.95
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128.63
122.28
114.43
77.44
77.12
76.81
55.51
N
O
CH3
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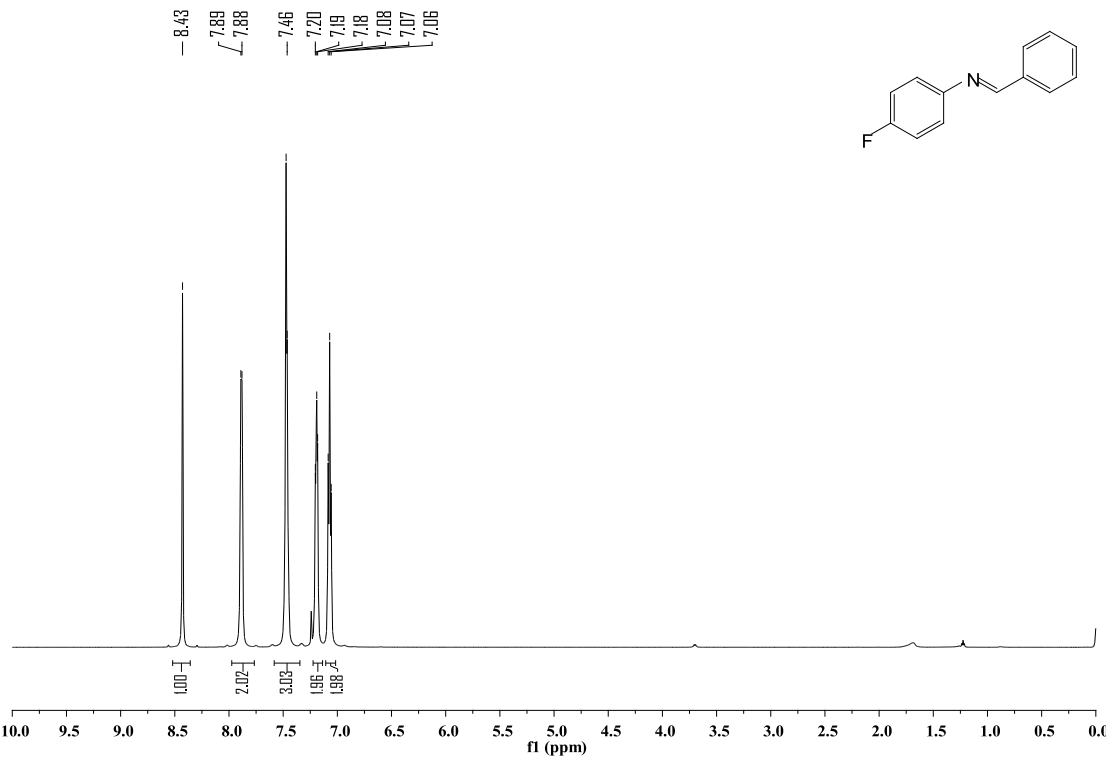
f1 (ppm)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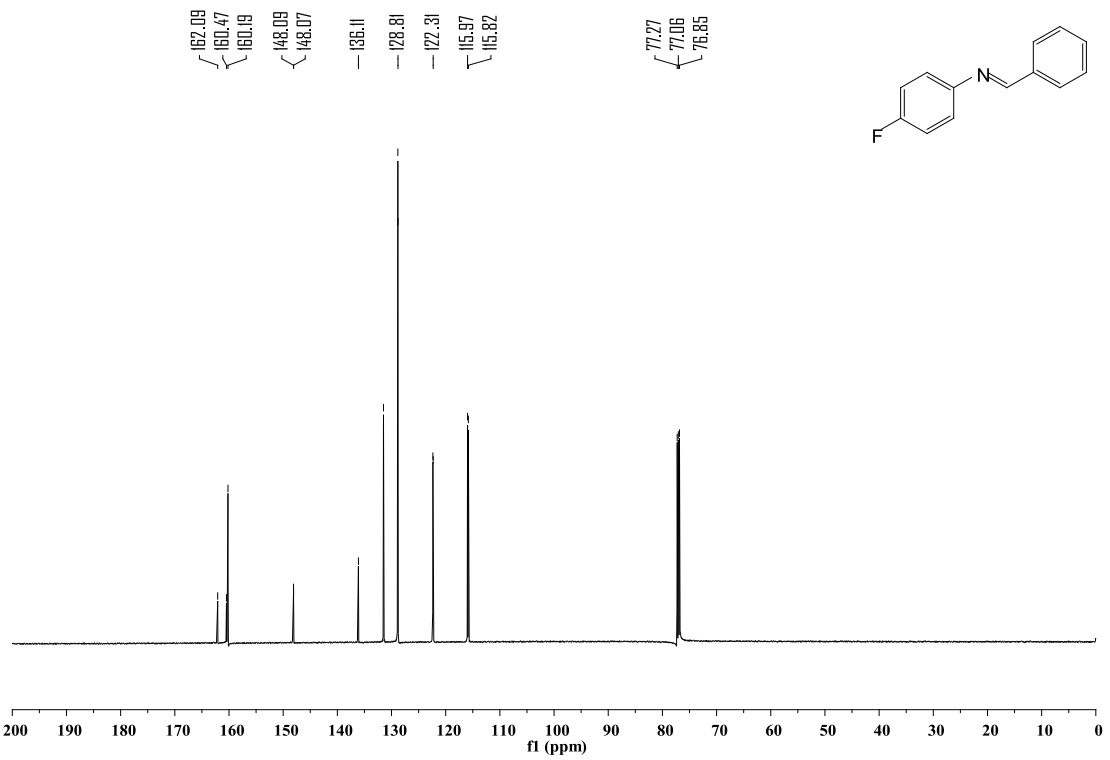
7.18
7.08
7.07
7.06
1.00
2.02
3.03
1.96
1.98
N
F
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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136.11
128.81
122.31
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77.06
76.85
N
F
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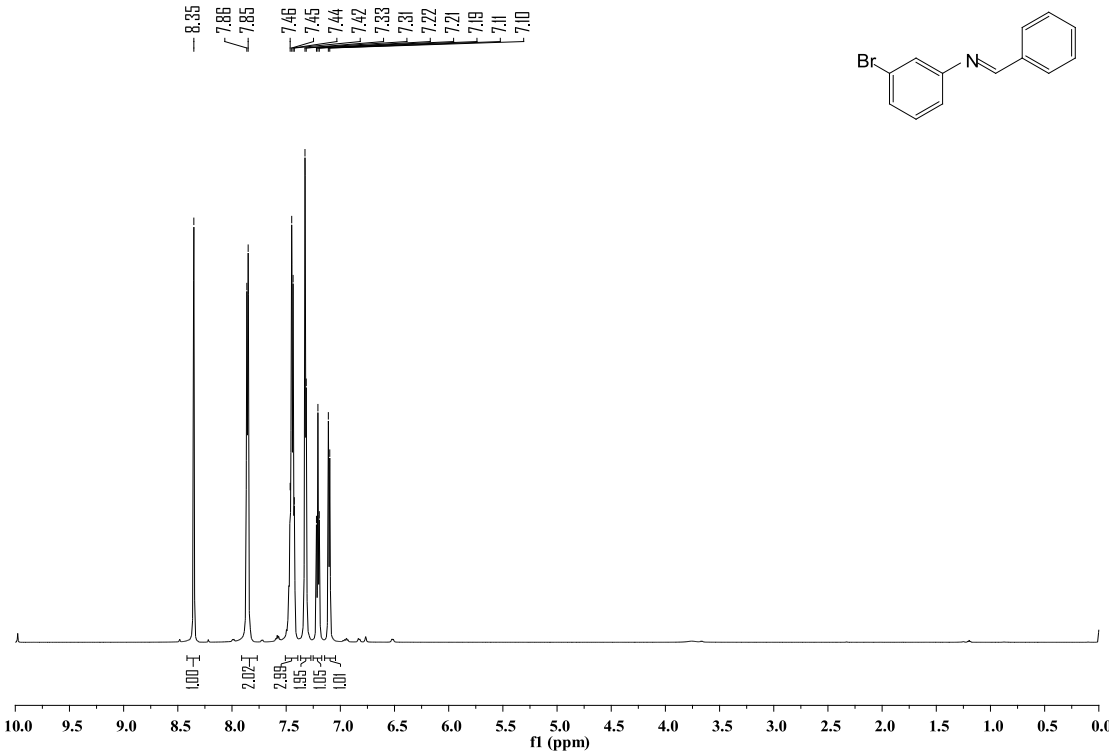
f1 (ppm)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7.85
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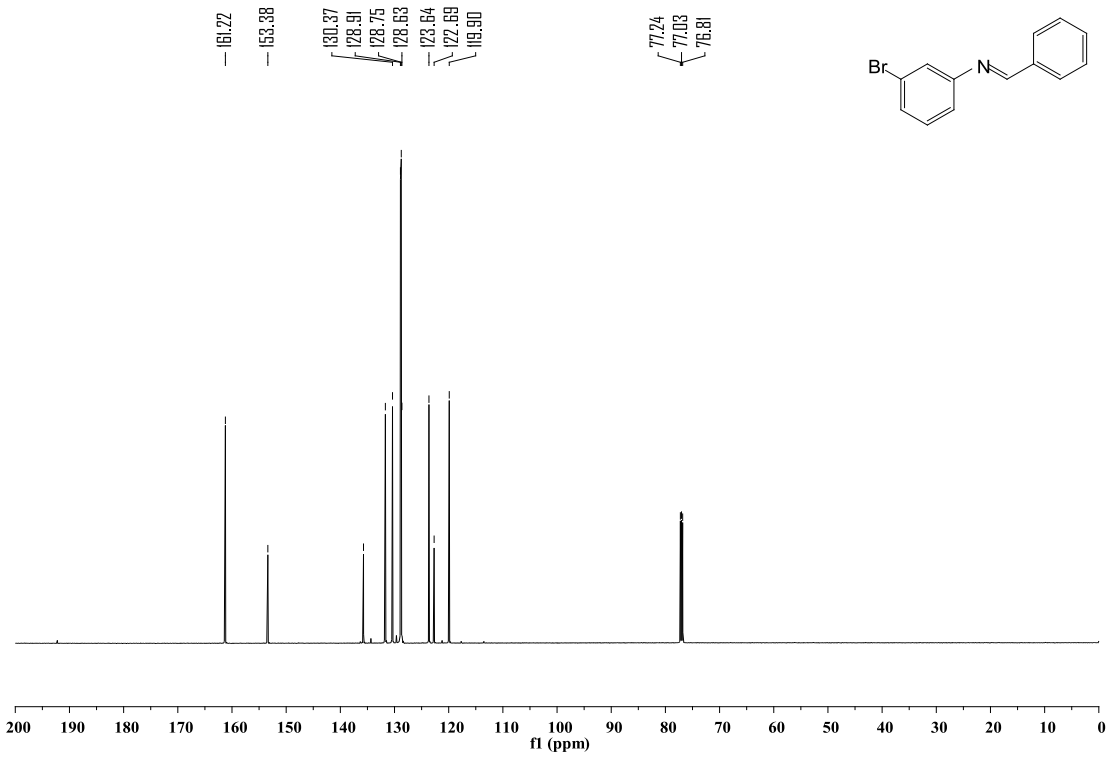
7.44
7.42
7.33
7.31
7.22
7.21
7.19
7.11
7.10
Br
N
1.00
2.02
2.99
1.95
1.05
1.01
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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153.38
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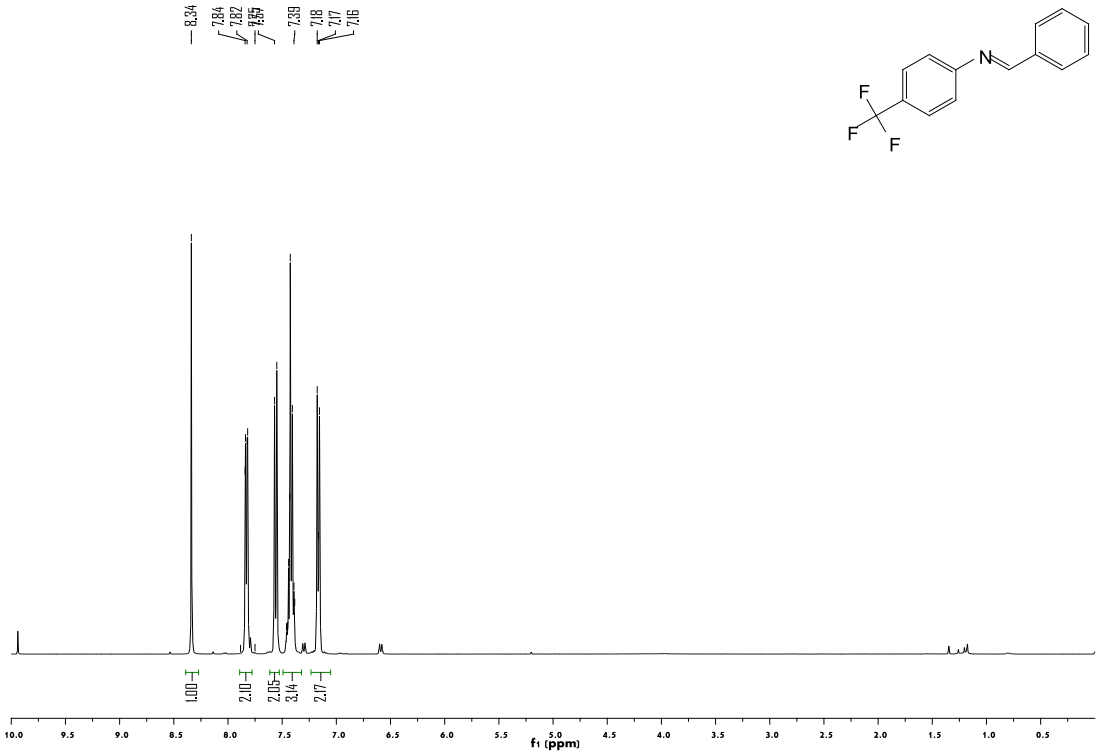
128.63
123.64
122.69
119.90
77.24
77.03
76.81
Br
N
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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N
F
F
F
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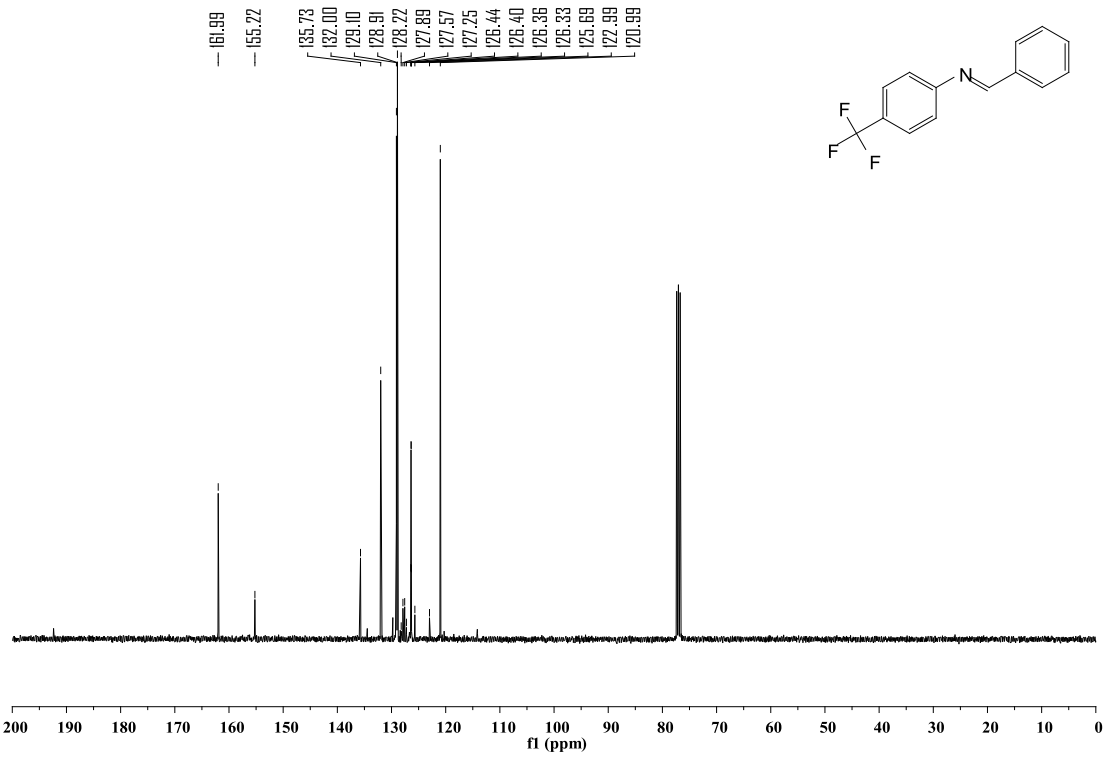
2.05
3.14
2.17
f1 (ppm)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126.40
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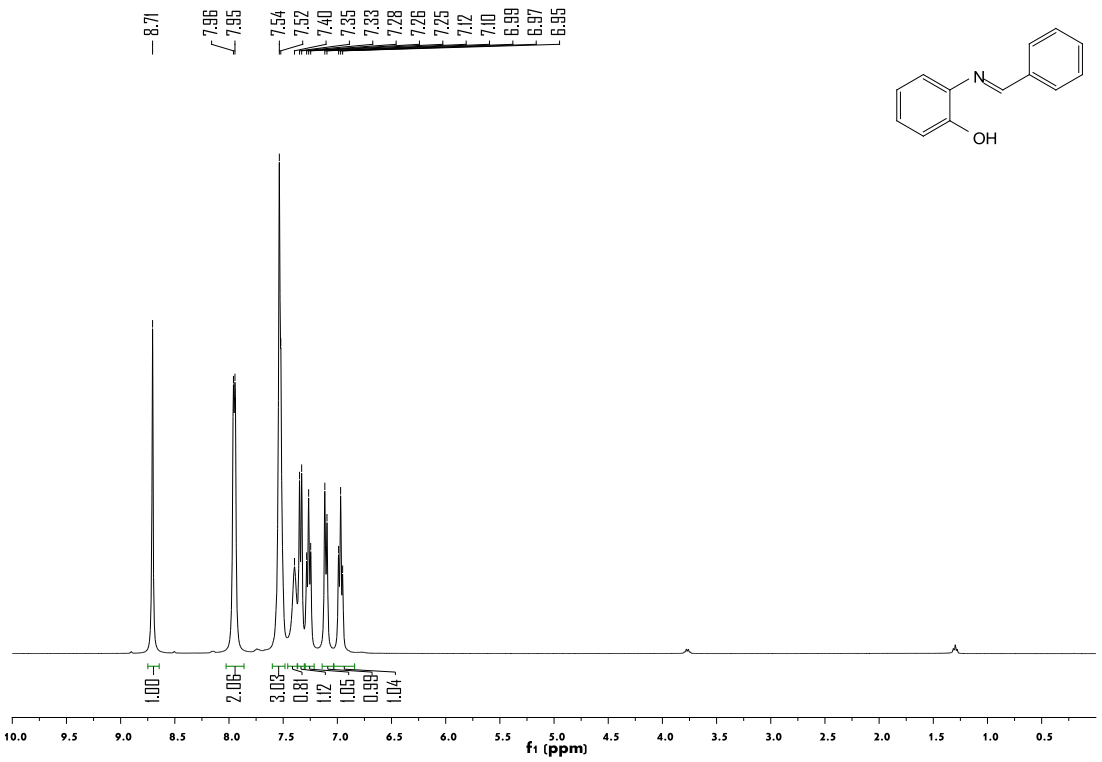
125.69
122.99
120.99
N
F
F
F
f1 (ppm)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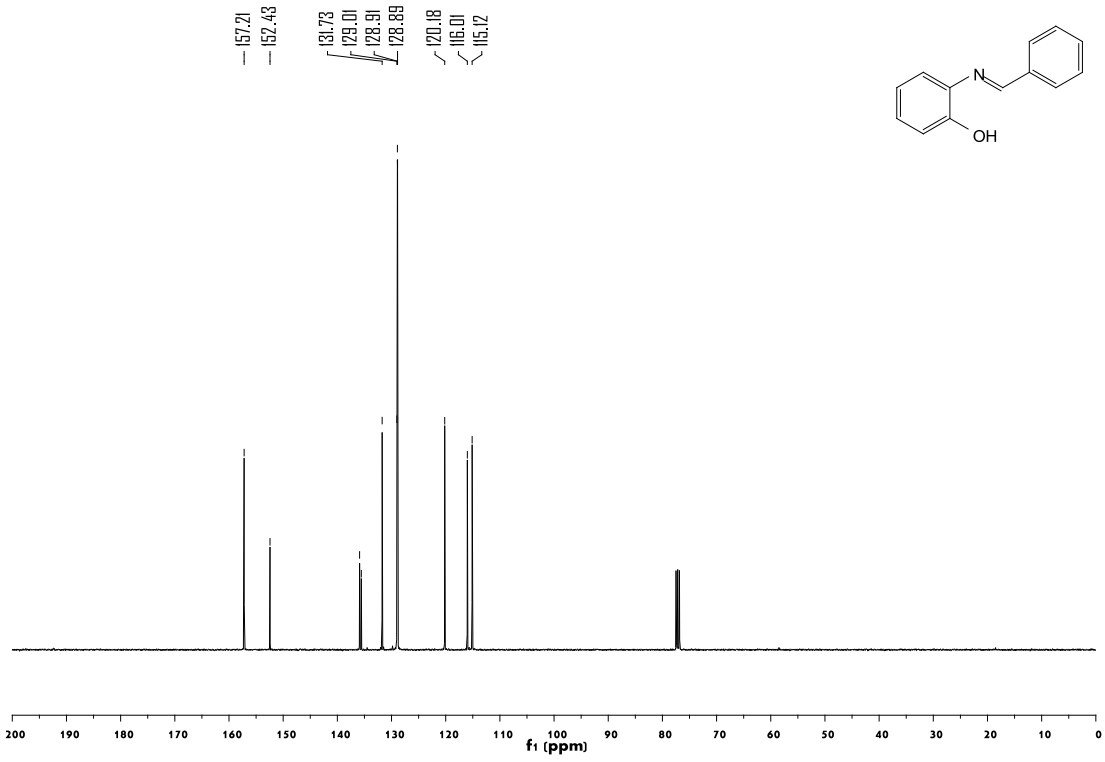
7.35
7.33
7.28
7.26
7.25
7.12
7.10
6.99
6.97
6.95
N
OH
1.00
2.06
3.03
0.81
1.12
1.05
0.99
1.04
f1 (ppm)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152.43
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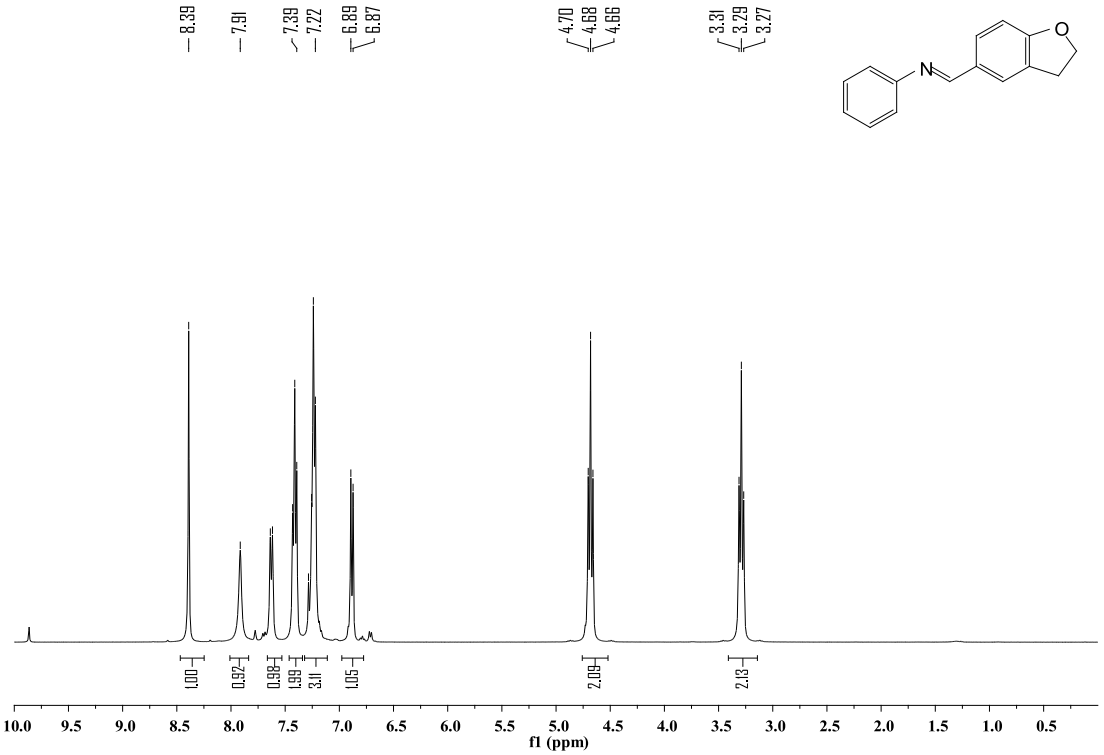
128.91
128.89
120.18
116.01
115.12
N
OH
f1 (ppm)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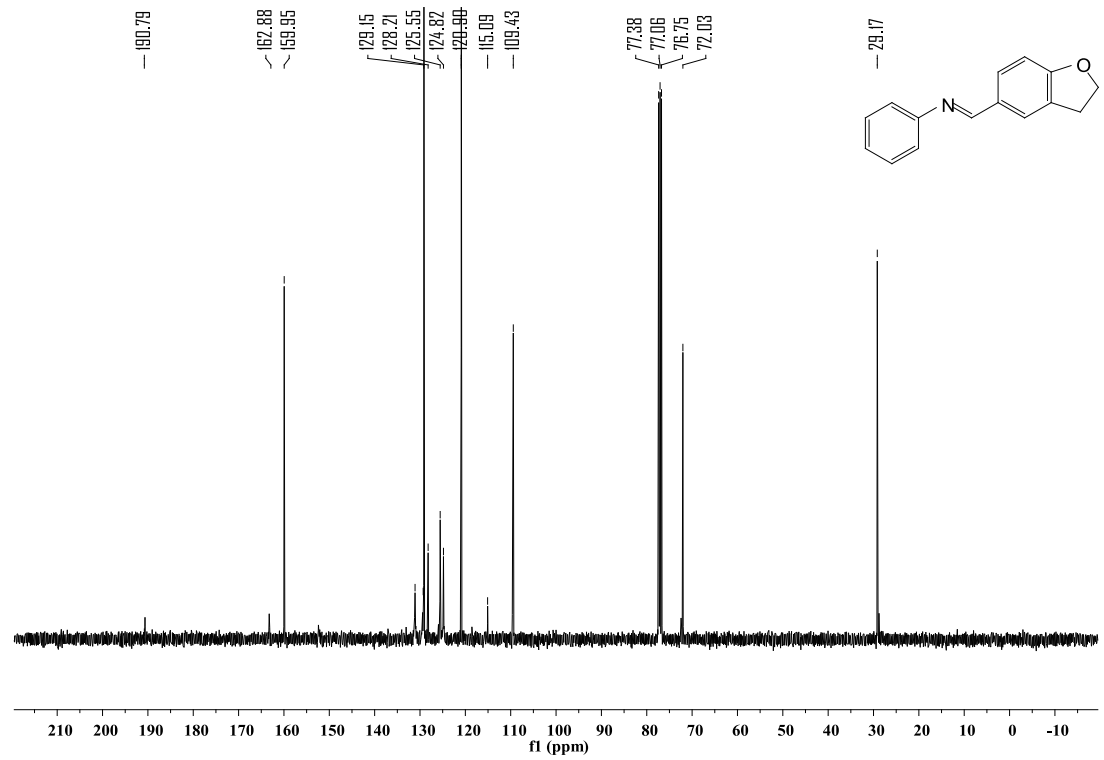
7.39
7.22
6.89
6.87
4.70
4.68
4.66
3.31
3.29
3.27
O
N
1.00
0.92
0.98
1.99
3.11
1.05
2.09
2.13
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)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159.95
129.15
128.21
125.55
124.82
120.98
115.09
109.43
77.38
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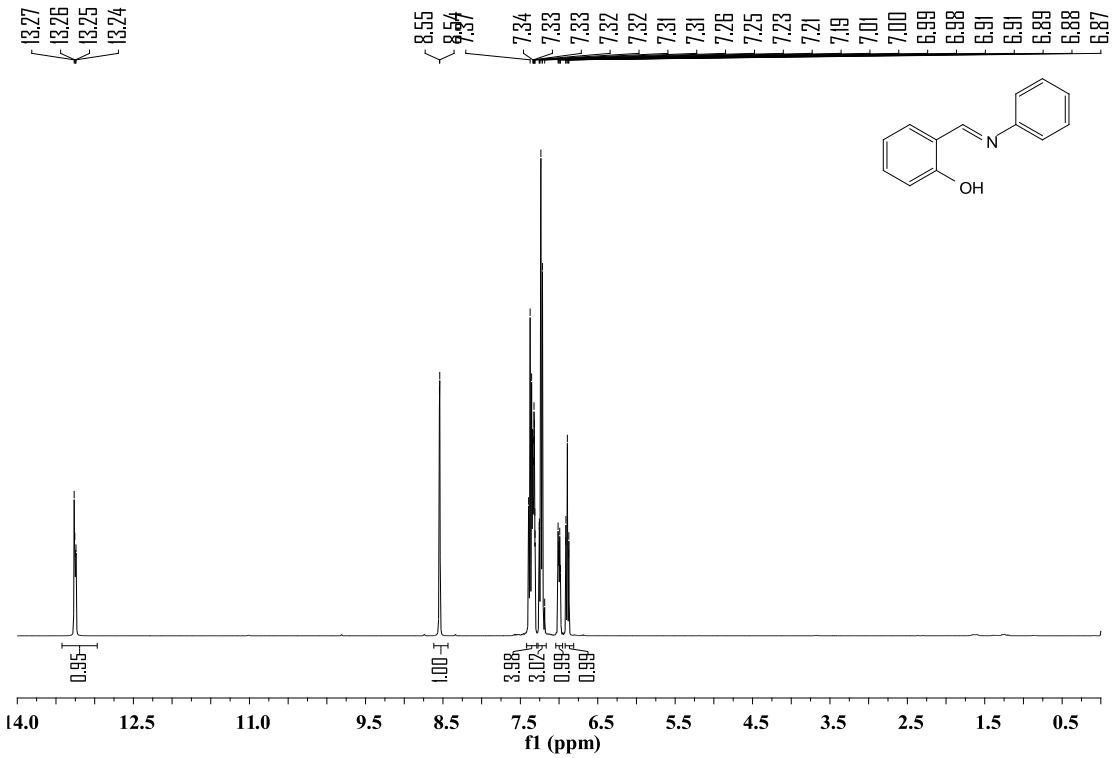
76.75
72.03
29.17
O
N
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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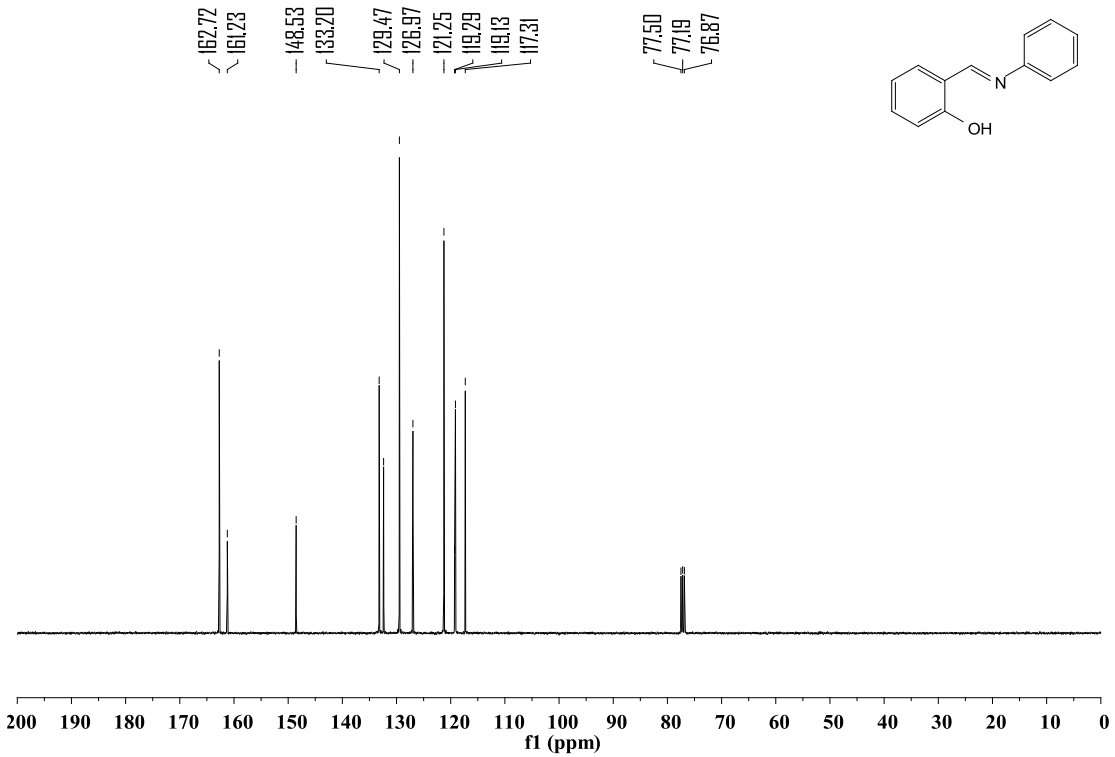
13.26
13.25
13.24
8.55
8.54
8.54
7.37
7.34
7.33
7.33
7.32
7.32
7.31
7.31
7.26
7.25
7.23
7.21
7.19
7.01
7.00
6.99
6.98
6.91
6.91
6.89
6.88
6.87
N
OH
0.95
1.00
3.98
3.02
0.99
0.99
14.0
12.5
11.0
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
f1 (ppm)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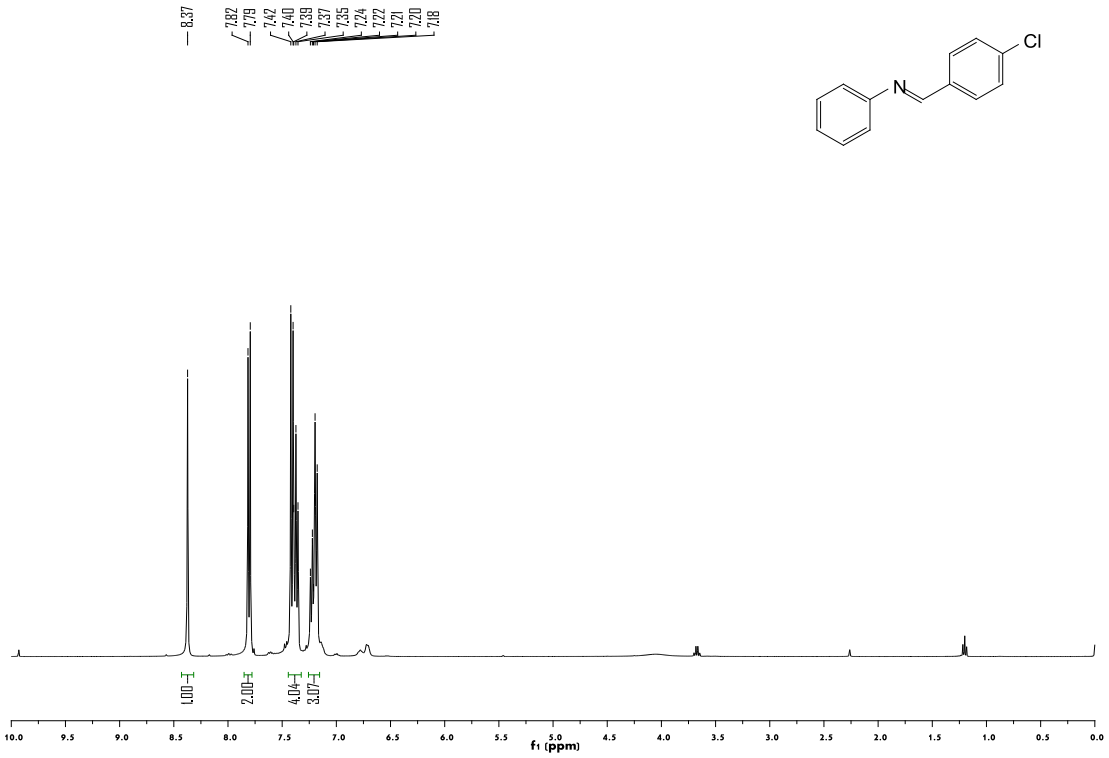
161.23
148.53
133.20
129.47
126.97
121.25
119.29
119.13
117.31
77.50
77.19
76.87
N
OH
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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7.79
7.42
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7.38
7.37
7.35
7.24
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7.21
7.20
7.18
Cl
N
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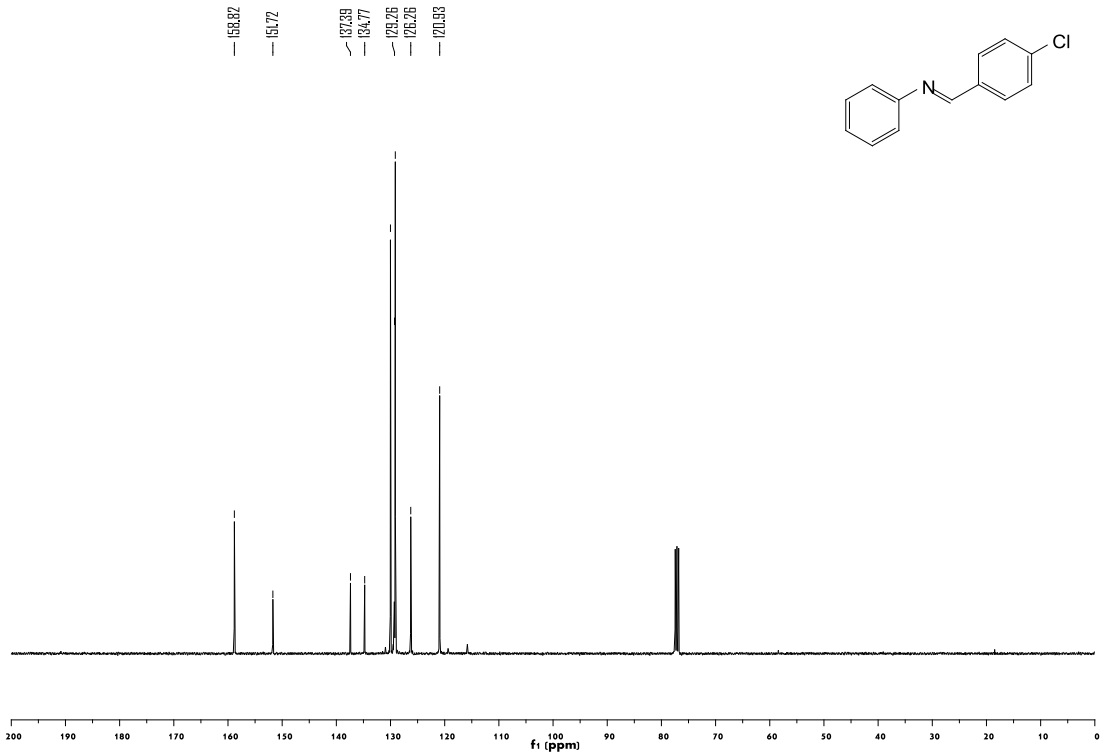
2.00
4.04
3.07
f1 (ppm)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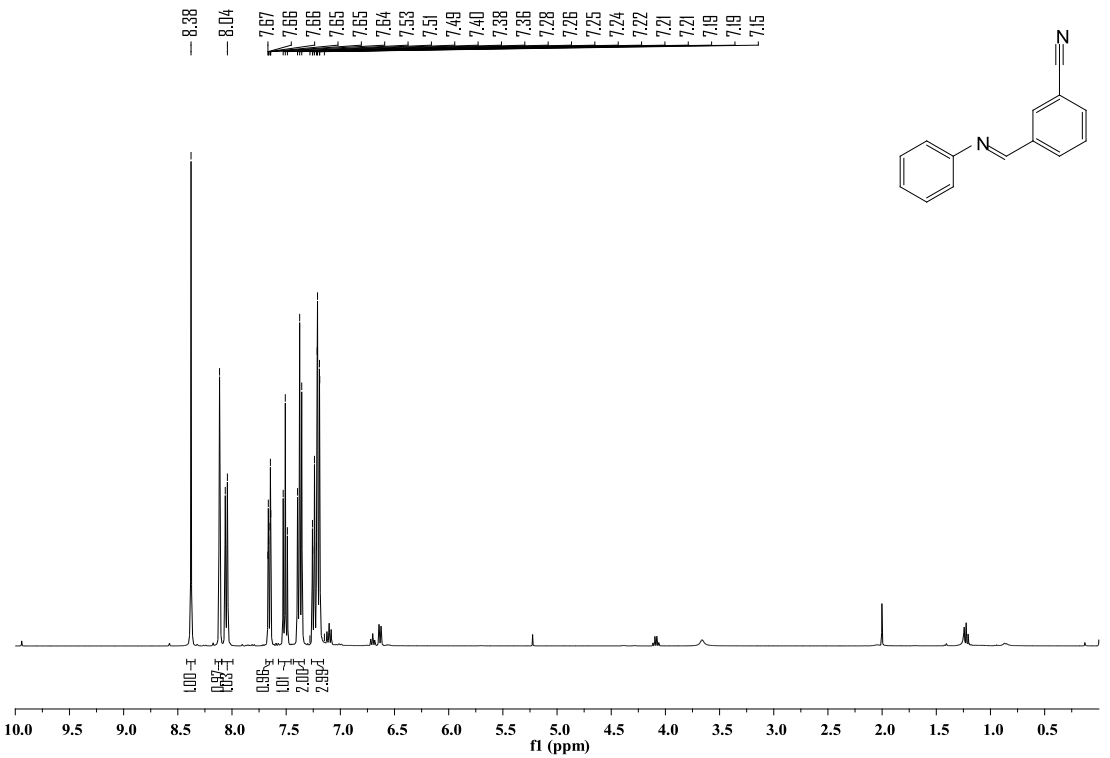
Cl
N
f1 (ppm)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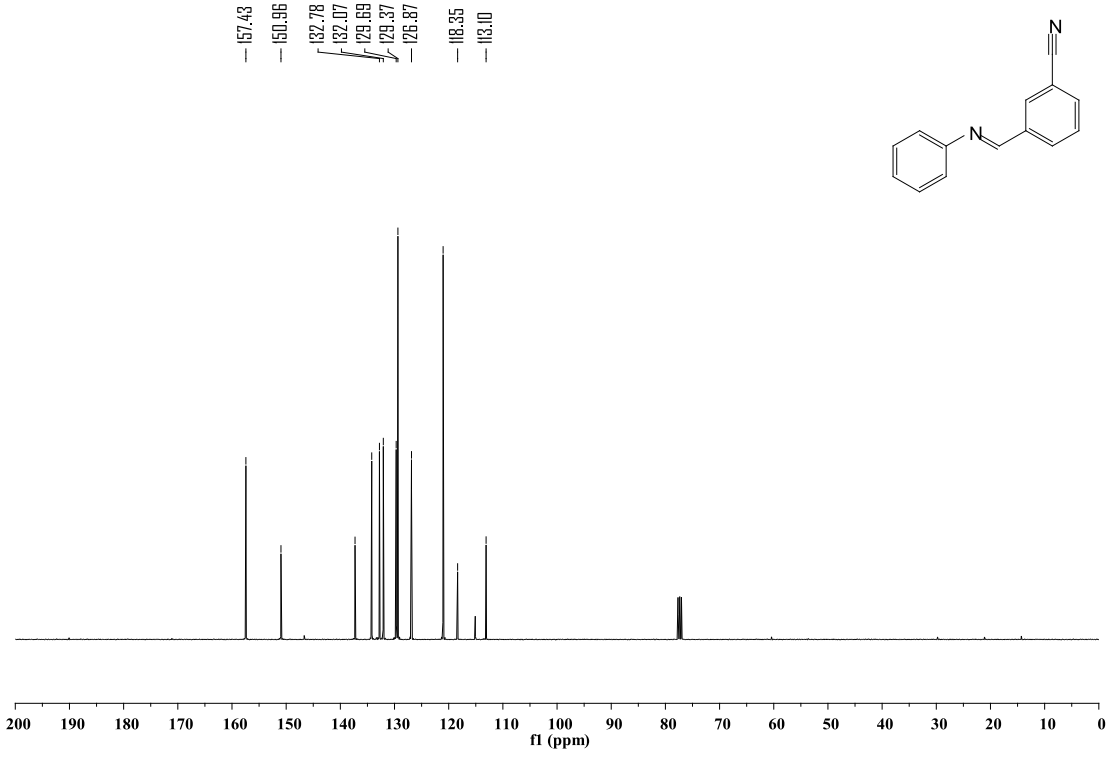
7.65
7.65
7.64
7.53
7.51
7.49
7.40
7.38
7.36
7.28
7.26
7.25
7.24
7.22
7.21
7.21
7.19
7.19
7.15
1.00
0.87
0.83
0.96
1.01
2.00
2.99
N
N
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)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150.96
132.78
132.07
129.69
129.37
126.87
118.35
113.10
N
N
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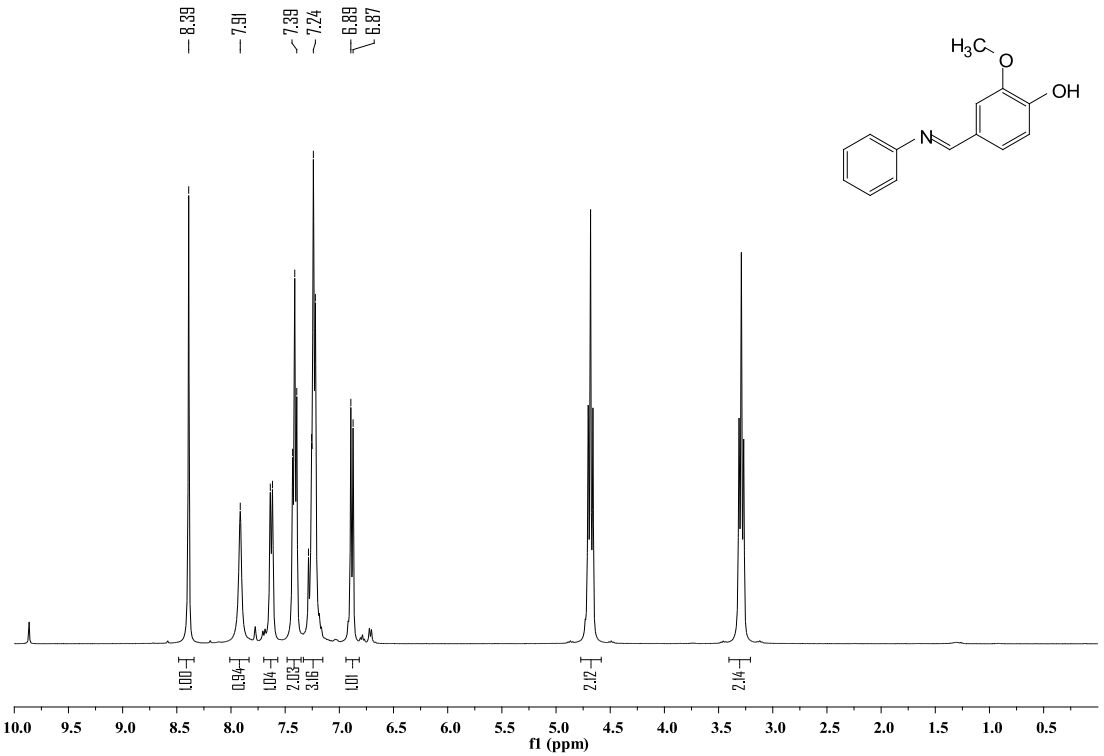
f1 (ppm)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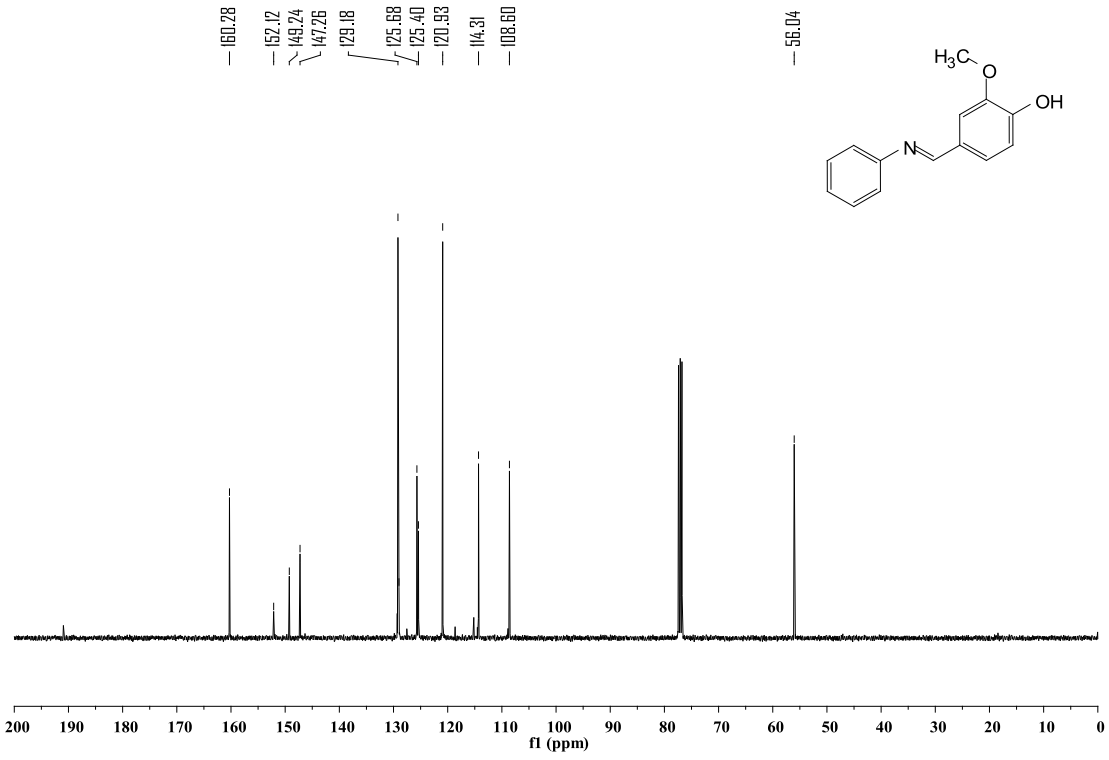
7.91
7.39
7.24
6.89
6.87
1.00
0.94
1.04
2.03
3.16
1.01
2.12
2.14
H3C
O
OH
N
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)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114.31
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56.04
H3C
O
OH
N
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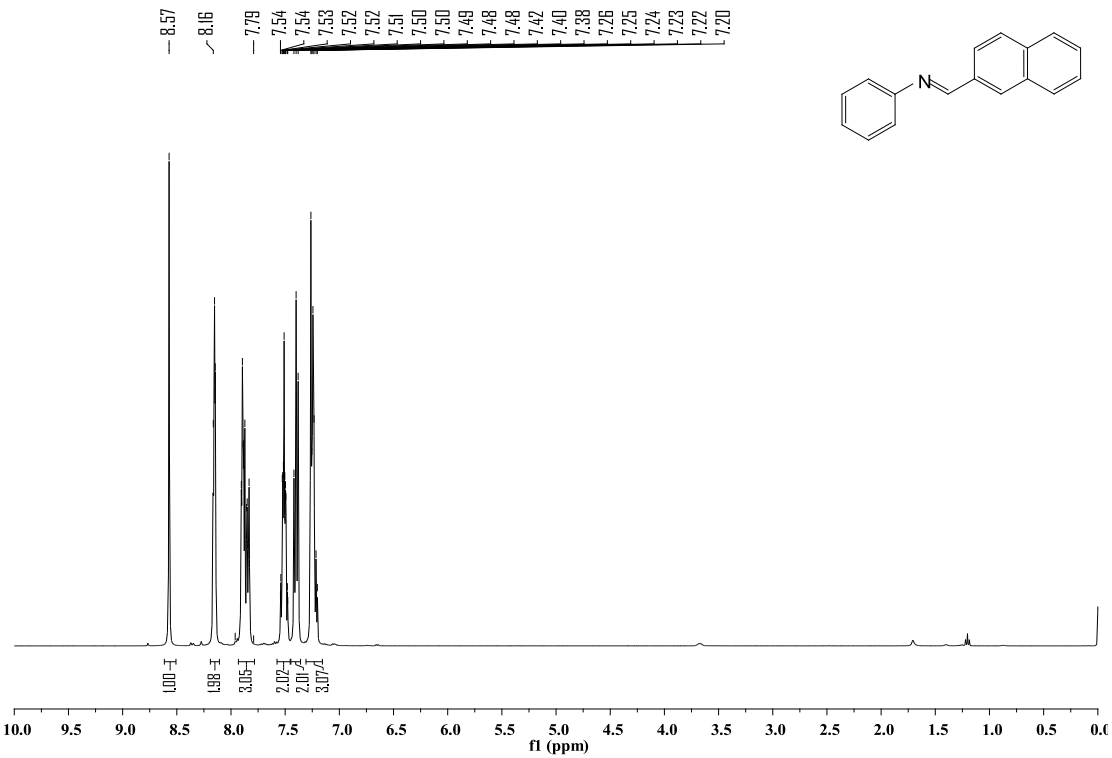
f1 (ppm)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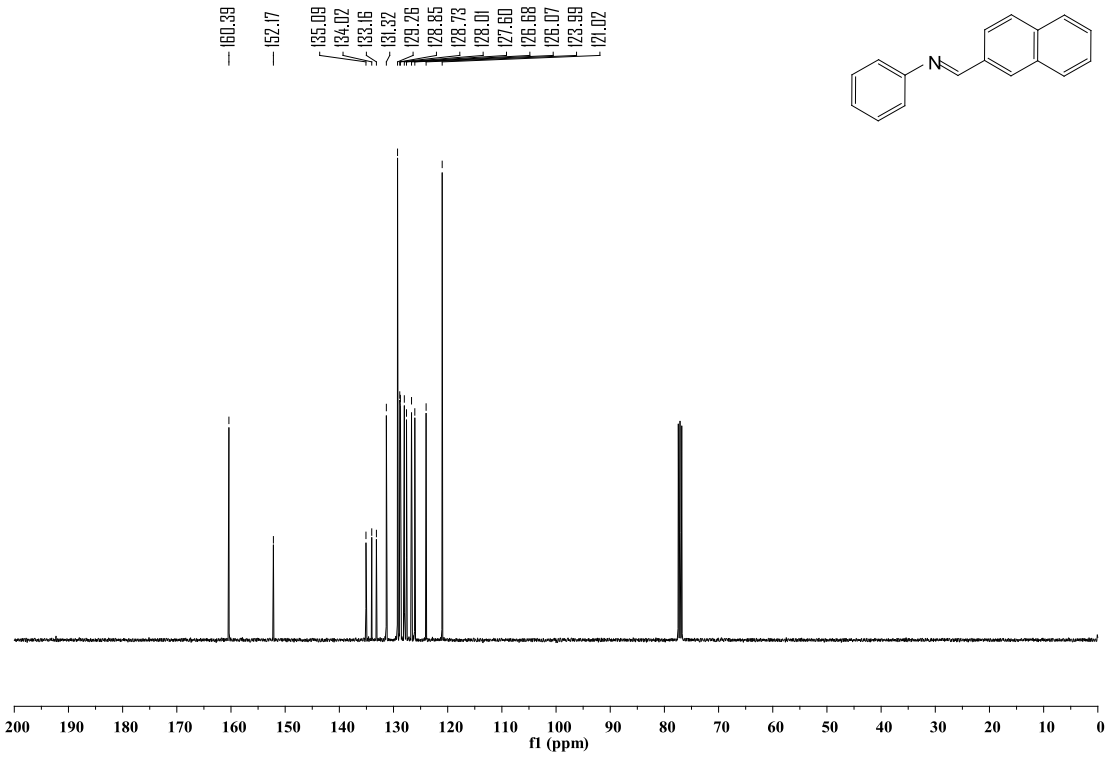
7.48
7.48
7.42
7.40
7.38
7.26
7.25
7.24
7.23
7.22
7.20
N
1.00
1.98
3.05
2.02
2.01
3.07
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)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133.16
131.32
129.26
128.85
128.73
128.01
127.60
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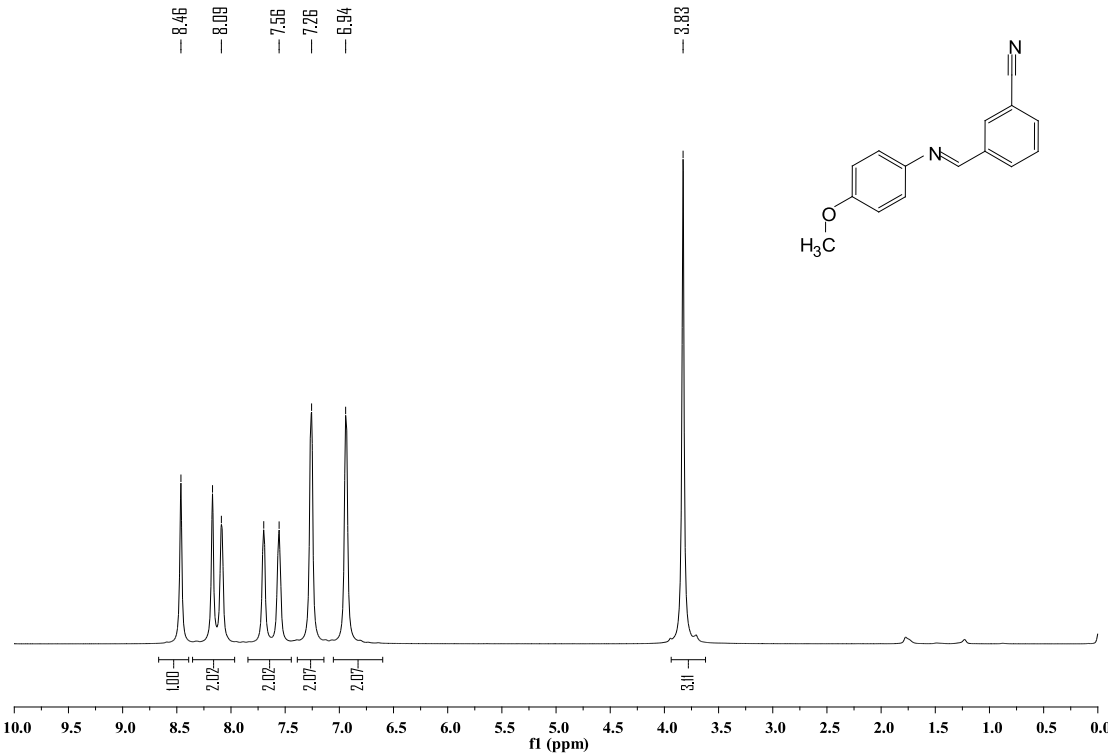
126.07
123.99
121.02
N
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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8.09
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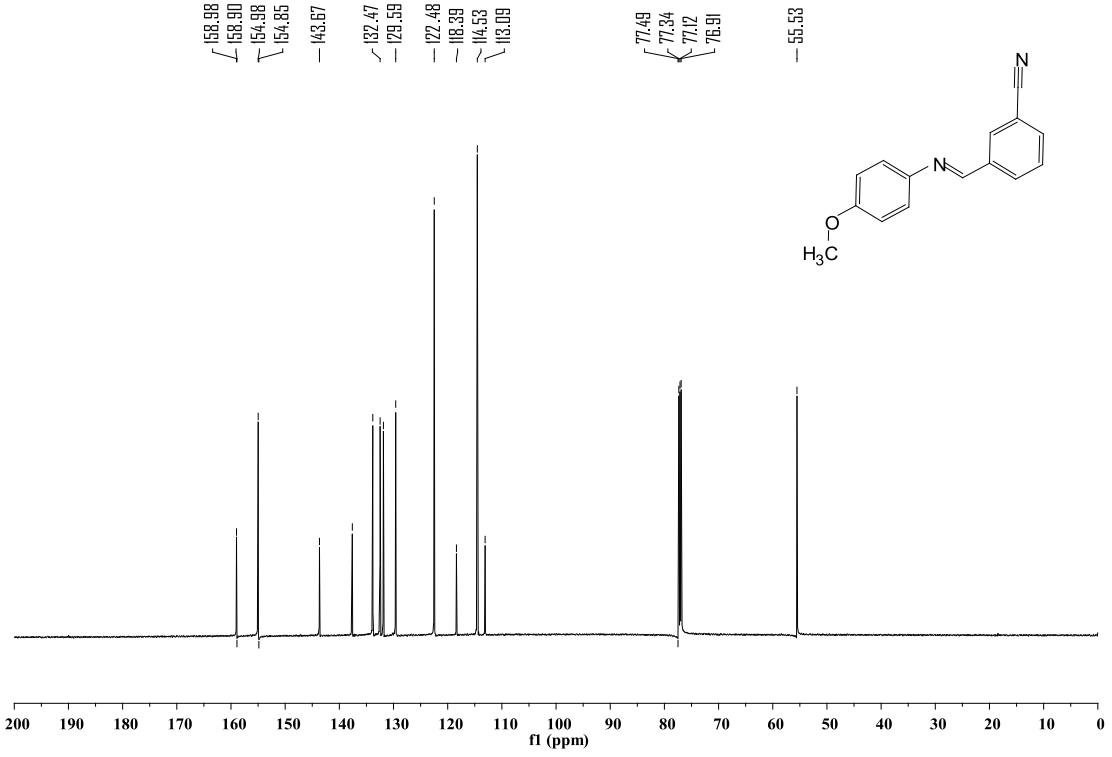
7.26
6.94
3.83
N
N
O
H3C
1.00
2.02
2.02
2.07
2.07
3.11
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)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122.48
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77.49
77.34
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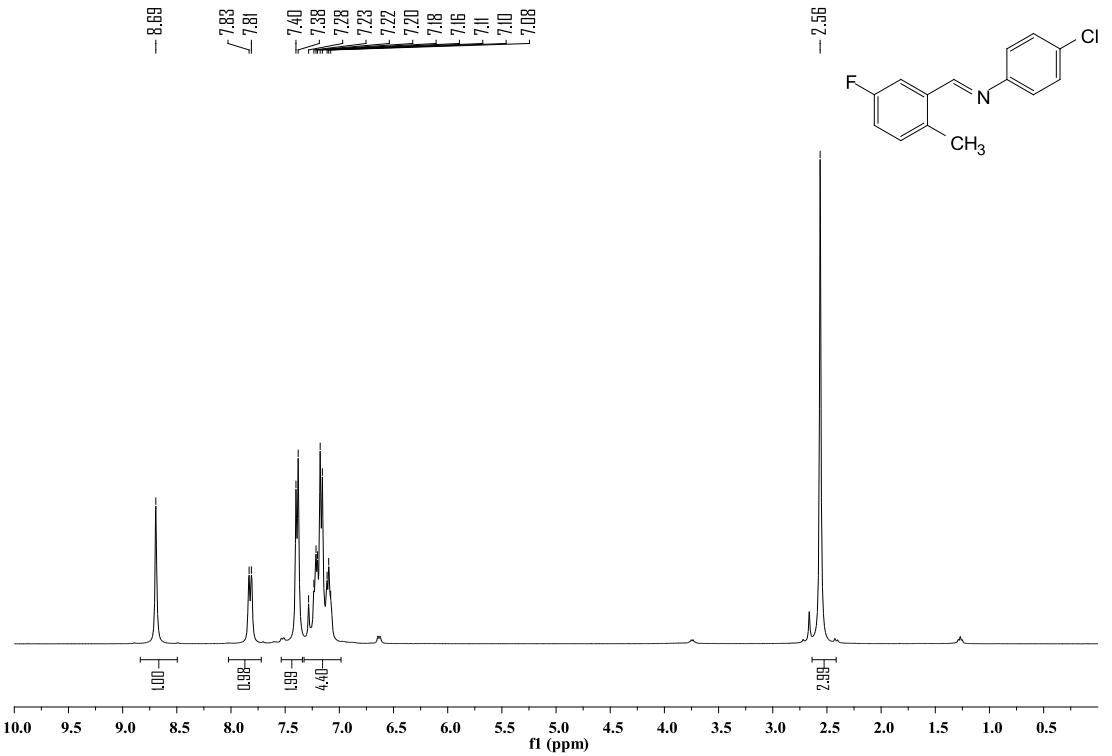
55.53
N
N
O
H3C
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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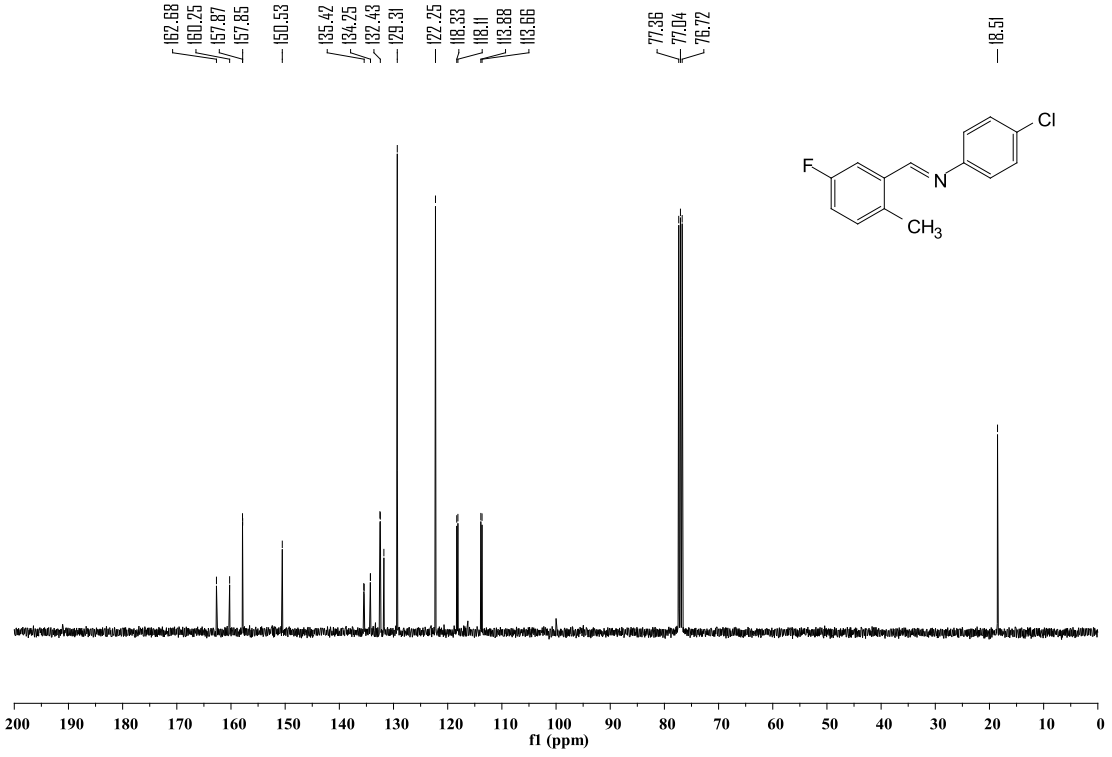
7.28
7.23
7.22
7.20
7.18
7.16
7.11
7.10
7.08
2.56
Cl
F
N
CH3
1.00
0.98
1.93
4.40
2.99
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)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122.25
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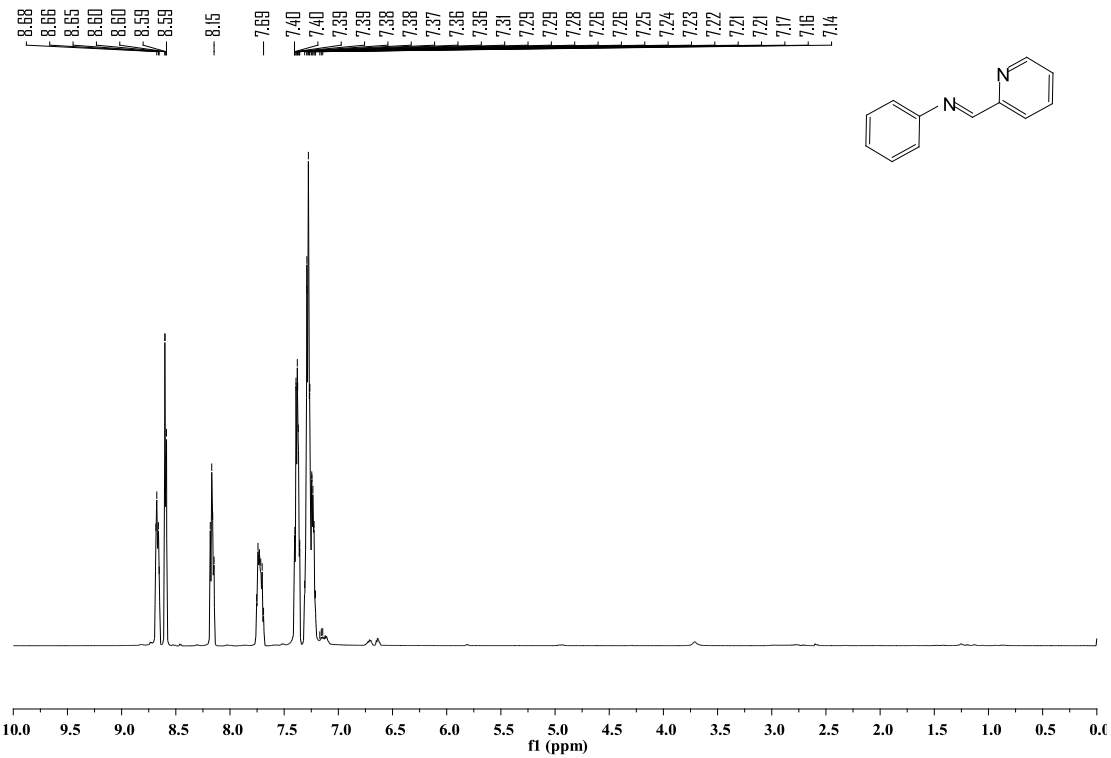
118.11
113.88
113.66
77.36
77.04
76.72
18.51
Cl
F
N
CH3
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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7.38
7.38
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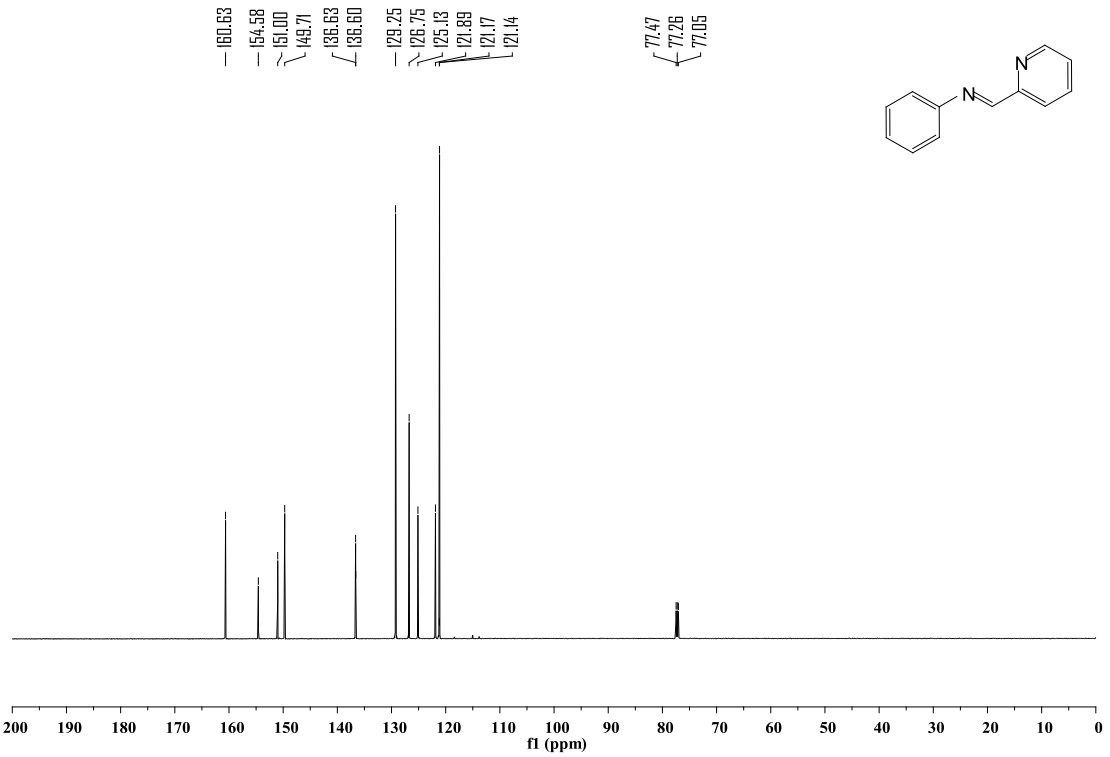
7.31
7.29
7.29
7.28
7.26
7.26
7.25
7.24
7.23
7.22
7.21
7.21
7.17
7.16
7.14
N
N
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)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126.75
125.13
121.89
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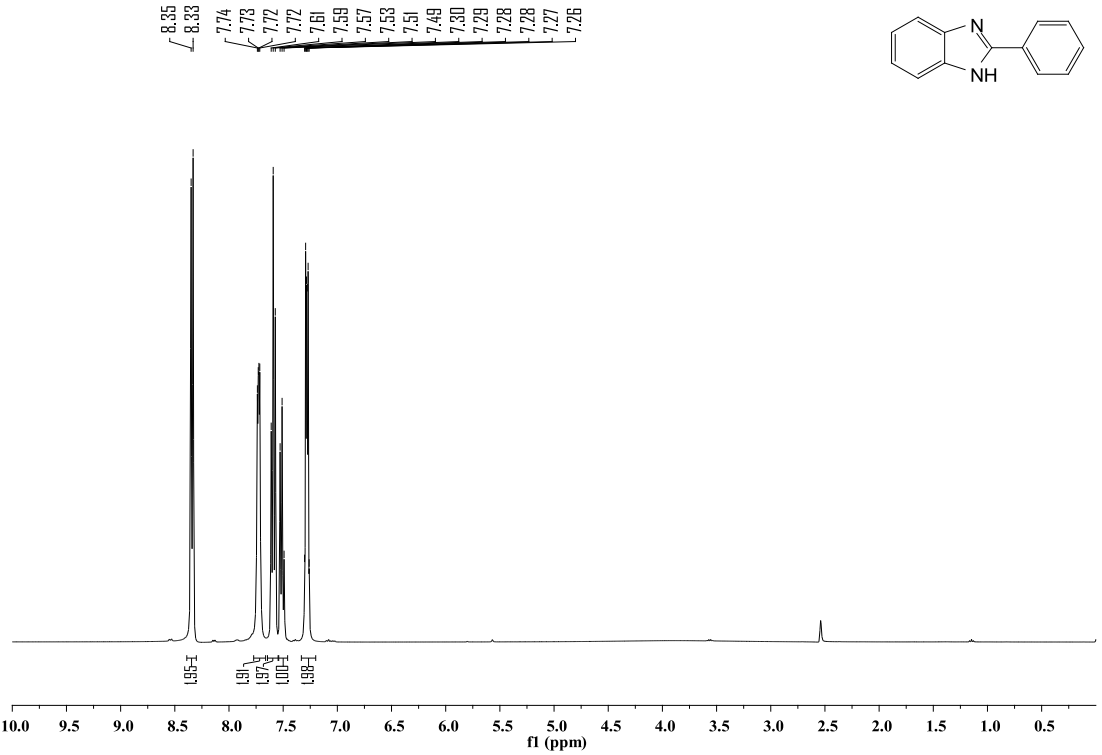
121.14
77.47
77.26
77.05
N
N
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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8.33
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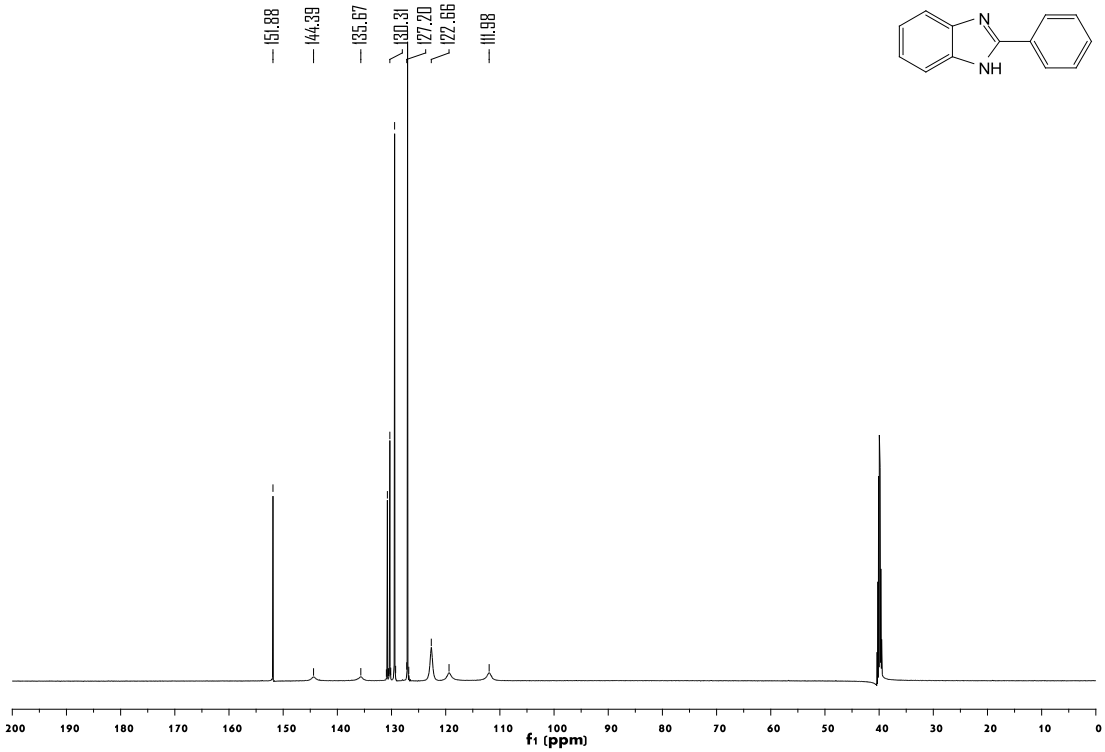
7.72
7.72
7.61
7.59
7.57
7.53
7.51
7.49
7.30
7.29
7.28
7.28
7.27
7.26
N
NH
1.95
1.91
1.97
4.00
1.99
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)


151.88
144.39
135.67
130.31
127.20
122.66
111.98
N
NH
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

8. Reference

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