SUPPORTING INFORMATION

Dehydrogenative Synthesis of Imines from Alcohols and Amines Catalyzed by a Ruthenium N-Heterocyclic Carbene Complex

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General experimental methods

All experiments were carried out under an argon flow using Schlenk flask techniques unless specified differently. Dry solvents were obtained by distillation from sodium and benzophenone under an argon atmosphere. The imidazolium salts 1,3-dimethylimidazolium iodide[1] and 1,3-di-*tert*-butylimidazolium chloride[2], as well as complexes $[RuCl_2(I\textit{i}Pr)(\textit{p}\text{-cymene})]$ (**1**)[3] and $[RuCl_2(IMe)(\textit{p}\text{-cymene})]$[4-5] were synthesized following established procedures. Alcohol and amine conversions were obtained on a GCMS instrument equipped with an Equity-5 capillary column (30 m × 0.25 mm, 0.25 μm film) using nonane as internal standard. During the GC analysis the injector temperature was 280 °C, and the temperature program was: 60 °C, hold 5 min, 20 °C/min to 280 °C, hold 5 min total run time 18 min. The GC was coupled to a mass spectrometer operating in positive EI mode.

General procedure for imination with Ru complexes 1 and $[RuCl_2(IMe)(\textit{p}\text{-cymene})]$

Ruthenium complex (22.9 mg, 0.05 mmol), DABCO (11.2 mg, 0.1 mmol) and 4 Å molecular sieves (150 mg) were placed in an oven-dried Schlenk flask equipped with a cold finger. Vacuum was applied and the flask was then filled with argon (repeated twice). Freshly distilled toluene or mesitylene (1 mL), alcohol (1 mmol), amine (1 mmol) and nonane (0.2 mmol, internal standard) were added via syringe and the mixture was refluxed with stirring for 24 hours. After cooling to room temperature a sample of 50 μL was taken, transferred to a GC vial, diluted to 1 mL with CH_2Cl_2 and then subjected to GCMS analysis. After removal of the solvent, the crude product was purified by silica gel column chromatography (hexane:Et_2O 10:0 to 9:1 with 2% of Et_3N) to afford the pure imine.

General procedure for imination with catalysts generated in situ

$[RuCl_2(\textit{p}\text{-cymene})]_2$ (15.3 mg, 0.025 mmol), DABCO (11.2 mg, 0.1 mmol), imidazolium salt (0.05 mmol), KO*t*Bu (11.2 mg, 0.05 mmol) and 4 Å molecular sieves (150 mg) were placed in an oven-dried Schlenk flask equipped with a cold finger. Vacuum was applied and the flask was then filled with argon (repeated twice). Freshly distilled toluene (1 mL) was added and the mixture was refluxed with stirring for 20 minutes. Benzyl alcohol (108 mg, 1 mmol), *tert*-

octylamine (129 mg, 1 mmol) and nonane (0.2 mmol, internal standard) were added via syringe and the mixture was refluxed with stirring for 24 hours. After cooling to room temperature a sample of 50 μL was taken, transferred to a GC vial, diluted to 1 mL with CH_2Cl_2 and then subjected to GCMS analysis.

Determination of hydrogen development

Benzyl alcohol (213 mg, 2 mmol), *tert*-octylamine (262 mg, 2 mmol) and 4 Å molecular sieves (300 mg) were placed in an oven-dried Schlenk flask and subjected to the imination reaction following the general procedure for imination with ruthenium complex **1**.

A separate flask containing diphenylacetylene (213 mg, 0.2 mmol), $Pd(OAc)_2$ (3 mg, 0.01 mmol), charcoal (2.6 mg) and methanol (1 mL) was equipped with a septum and connected to the above Schlenk flask with a needle. The reaction mixtures were stirred over night at room temperature. In this way, the hydrogen gas developed during the imination was transferred to the separate flask causing the reduction of the alkyne bond.[6] GCMS analysis of the hydrogenation reaction showed the complete conversion of the alkyne into 1,2-diphenylethane (EI, Pos; RT = 12.16; $[M]^+ = 182$).

Addition of allylmetal reagents to (*R*)-*N*-benzylidene-1-phenylethylamine

Addition of allylzinc bromide

Crude (*R*)-*N*-benzylidene-1-phenylethylamine, synthesized following the imination procedure with ruthenium complex **1**, was dissolved in anhydrous THF (6 mL) and added drop wise to a THF (5 mL) solution of allylzinc bromide (4 mmol, prepared according to a reported procedure[7]) at -78 °C under an argon atmosphere. The reaction mixture was then stirred over night, while being allowed to reach room temperature. A sample was taken out and analyzed by GC-MS showing the complete conversion of the imine and formation of the corresponding homoallylic amine[8-10] as a mixture of the two diastereomers (S,R/R,R 54:46). The reaction was then quenched by addition of 10% aqueous NaOH (20 mL), the organic phase was separated and the aqueous phase was extracted three times with Et_2O (10 mL). The combined organic phases

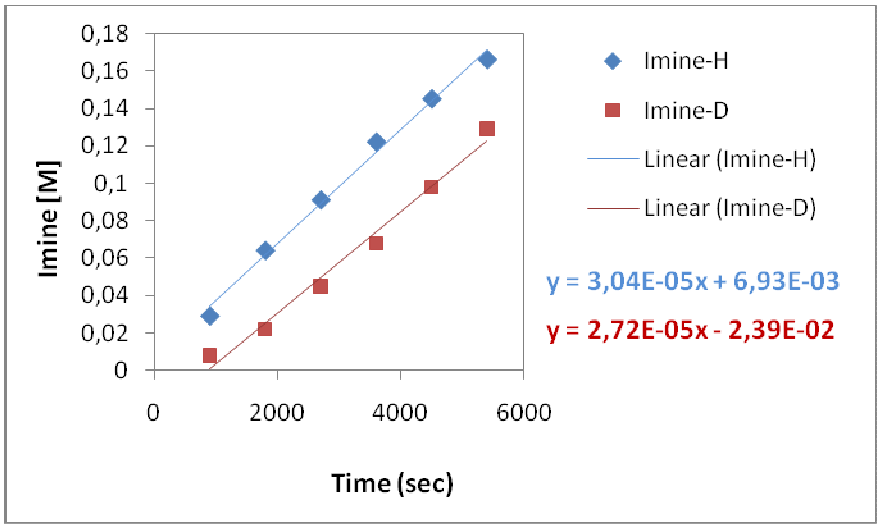
were dried over Na_2SO_4 and concentrated at reduced pressure to leave the crude amine. This was then purified by column chromatography (hexane:Et_2O, 9.5:0.5) to afford 154 mg of the pure diastereomeric mixture (61% yield over two steps).

Addition of B-allyl-9-BBN

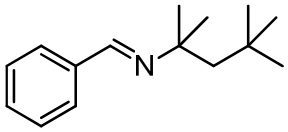
B-allyl-9-BBN was generated *in situ* following the procedure reported by Fang *et al*.[11] An oven-dried Schlenk flask was charged with *B*-methoxy-9-BBN (1.0 M solution in hexane, 3 mL, 3 mmol). The hexane was removed under reduced pressure and the borinic ester was dissolved in anhydrous Et_2O (6 mL). The solution was cooled to -78 °C and allylmagnesium chloride (2 M solution in THF, 1.5 mL, 3 mmol) was added drop wise. The reaction mixture was warmed to room temperature and then stirred for 30 min followed by evaporation of the solvent. The resulting white solid was suspended in anhydrous hexane (9 mL) and stirred for 3 h at room temperature during which time the borane formed and the magnesium salt precipitated. After evaporation of the solvent dry Et_2O (3 mL) was added and the suspension, containing the borane reagent, was cooled to -78 °C. The crude imine, synthesized following the imination procedure with ruthenium complex **1**, was dissolved in anhydrous Et_2O (6 mL) and added drop wise to the borane solution. The reaction mixture was stirred at -78 °C for 1 h and then allowed to reach room temperature over night. A sample was taken out and analyzed by GCMS showing the complete conversion of the imine. The reaction was then quenched at 0 °C by addition of 37% hydrochloric acid (0.8 mL) and stirred for further 12 h at room temperature. Then 10% NaOH was added to the mixture until reaching pH 11, the organic phase was separated and the aqueous phase was extracted three times with Et_2O (10 mL). The combined organic phases were dried over Na_2SO_4 and concentrated at reduced pressure. A sample of the organic phase was taken out and analyzed by GCMS indicating the formation of the corresponding homoallylic amine[8-10] with a diastereomeric ratio of 90:10 (S,R/R,R). The crude amine was then subjected to column chromatography (hexane:Et_2O, 9.5:0.5) to afford 134 mg of the pure diastereomeric mixture (53.4% yield over two steps).

Determination of deuterium isotope effect

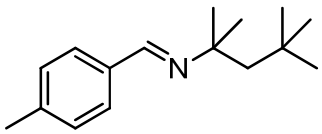
Benzyl alcohol (108 mg, 1 mmol) and *tert*-octylamine (129 mg, 1 mmol) were placed in an oven-dried Schlenk flask and subjected to the imination reaction following the general procedure with ruthenium complex **1**. The reaction mixture was refluxed with stirring for 1.5 h. Every 15 minutes the reaction mixture was cooled to room temperature and a sample of 50 µL was taken out, transferred to a GC vial diluted to 1 mL with CH_2Cl_2, and then subjected to GCMS analysis to follow the formation of *N*-benzylidene-*tert*-octylamine. The same procedure was repeated using benzyl alcohol-α,α-d_2[12] (110 mg, 1 mmol), *tert*-octylamine (129 mg, 1 mmol) and toluene-d_8 (1 mL) as solvent. In this case, before starting the reaction, the alcohol and the amine were dissolved in methanol-d_4 which was then evaporated (repeated twice). Each experiment was repeated four times and the initial rate (r) determined. The mean initial rate for the reaction of benzyl alcohol was $r_H = 3.04\ 10^{-5} \pm 0.56\ 10^{-5}$. The mean initial rate for the reaction of benzyl alcohol-α,α-d_2 was $r_D = 2.72\ 10^{-5} \pm 0.67\ 10^{-5}$. The isotope effect was k_H/k_D = 1.1 ± 0.3.



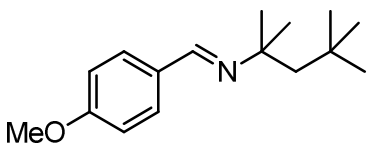
Characterization data



***N*-benzylidene-*tert*-octylamine:** Following the imination procedure with ruthenium complex **1**, the imine was isolated as a light yellow oil (174 mg, 80% yield). **^{1}H NMR** (300 MHz, $CDCl_3$): δ 8.26 (s, 1H, N=CH), 7.78-7.75 (m, 2H, Ar), 7.43-7.40 (m, 3H, Ar), 1.72 (s, 2H, CH_2), 1.35 (s, 6H, 2 × CH_3), 0.98 (s, 9H, 3 × CH_3); **^{13}C NMR** (75 MHz, $CDCl_3$): δ 154.3 (N=CH), 137.3 (Ar-quat-C), 129.9, 128.5, 127.8 (Ar), 60.9 (quat-C), 56.5 (CH_2), 32.0 (quat-C), 31.8, 29.6 (CH_3); NMR data are in accordance with literature values;[13] **GCMS** (EI, Pos): RT = 12.6 min; *m/z* 202 $[M\text{-}CH_3]^+$.

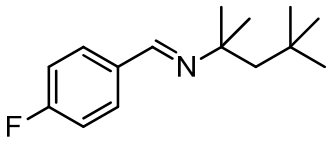


***N*-(4-methylbenzylidene)-*tert*-octylamine:** Following the imination procedure with ruthenium complex **1**, the imine was isolated as a colorless oil (177 mg, 77% yield). **^{1}H NMR** (300 MHz, $CDCl_3$): δ 8.21 (s, 1H, N=CH), 7.64 (d, 2H, *J* = 8.1 Hz, Ar), 7.21 (d, 2H, *J* = 8.1 Hz, Ar), 2.38 (s, 3H, CH_3), 1.69 (s, 2H, CH_2), 1.32 (s, 6H, 2 × CH_3), 0.96 (s, 9H, 3 × CH_3); **^{13}C NMR** (75 MHz, $CDCl_3$): δ 154.2 (N=CH), 140.0 (Ar-quat-C), 134.8 (Ar-quat-C), 129.1, 127.8 (Ar), 60.8 (quart-C), 56.6 (CH_2), 32.0 (quat-C), 31.7, 29.6, 21.4 (CH_3); **GCMS** (EI, Pos): RT = 13.3 min, *m/z* 216 $[M\text{-}CH_3]^+$; **HRMS** (ESI, Pos): *m/z*: calcd for $C_{16}H_{26}N$: 232.2021 $[M+H]^+$, found: 232.2059.

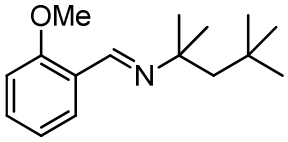


***N*-(4-methoxybenzylidene)-*tert*-octylamine:** Following the imination procedure with ruthenium complex **1**, the imine was isolated as a colorless oil (155 mg, 63% yield). **^{1}H NMR** (300 MHz, $CDCl_3$): δ 8.18 (s, 1H, N=CH), 7.70 (d, 2H, *J* = 8.7 Hz, Ar), 6.93 (d, 2H, *J* = 8.7 Hz,

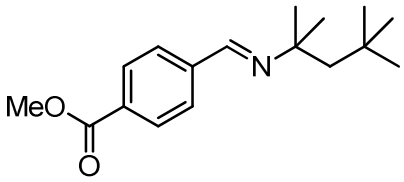
Ar), 3.84 (s, 3H, OCH_3), 1.68 (s, 2H, CH_2), 1.32 (s, 6H, 2 × CH_3), 0.96 (s, 9H, 3 × CH_3); **^{13}C NMR** (75 MHz, $CDCl_3$): δ 161.0 (Ar-quat-C), 153.6 (N=CH), 130.4 (Ar-quat-C), 129.3, 113.8 (Ar), 60.6 (quat-C), 56.6 (CH_2), 55.3 (OCH_3), 32.0 (quat-C), 31.8, 29.7 (CH_3); **GCMS** (EI, Pos): RT = 14.2 min, *m/z* 232 $[M\text{-}CH_3]^+$; **HRMS** (ESI, Pos): *m/z*: calcd for $C_{16}H_{26}NO$: 248.1970 $[M+H]^+$, found: 248.2010.



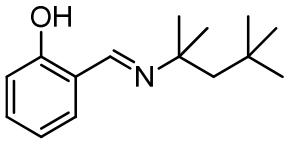
***N*-(4-fluorobenzylidene)-*tert*-octylamine:** Following the imination procedure with ruthenium complex **1**, the imine was isolated as a colorless oil (168 mg, 72% yield). **^{1}H NMR** (300 MHz, $CDCl_3$): δ 8.21 (s, 1H, N=CH), 7.76-7.70 (m, 2H, Ar), 7.10 (bt, 2H, Ar), 1.69 (s, 2H, CH_2), 1.32 (s, 6H, 2 × CH_3), 0.96 (s, 9H, 3 × CH_3); **^{13}C NMR** (75 MHz, $CDCl_3$): δ 163.8 (d, $J_{C\text{-}F}$ = 248.0 Hz, Ar-quat-C), 152.9 (N=CH), 133.6 (d, $J_{C\text{-}F}$ = 2.85 Hz, Ar-quat-C), 129.6 (d, $J_{C\text{-}F}$ = 8.4 Hz, Ar), 115.5 (d, $J_{C\text{-}F}$ = 21.6 Hz, Ar), 60.9 (quat-C), 56.5 (CH_2), 32.0 (quat-C), 31.7, 29.6 (CH_3); **GCMS** (EI, Pos): RT = 12.5 min, *m/z* 220 $[M\text{-}CH_3]^+$; **HRMS** (ESI, Pos): *m/z*: calcd for $C_{15}H_{23}FN$: 236.1770 $[M+H]^+$, found: 236.1809.



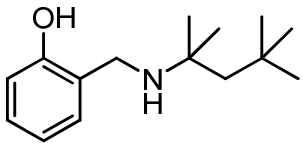
***N*-(2-methoxybenzylidene)-*tert*-octylamine:** Following the imination procedure with ruthenium complex **1**, the imine was isolated as a colorless oil (170 mg, 69% yield). **^{1}H NMR** (300 MHz, $CDCl_3$): δ 8.67 (s, 1H, N=CH), 7.96 (bd, 1H, Ar), 7.35 (bt, 1H, Ar), 6.98 (bt, 1H, Ar), 6.91 (bd, 1H, Ar), 3.87 (s, 3H, OCH_3), 1.70 (s, 2H, CH_2), 1.33 (s, 6H, 2 × CH_3), 0.96 (s, 9H, 3 × CH_3); **^{13}C NMR** (75 MHz, $CDCl_3$): δ 158.6 (Ar-quat-C), 150.4 (N=CH), 131.0, 127.0 (Ar), 125.8 (Ar-quat-C), 120.8, 110.8 (Ar), 61.3 (quat-C), 56.6 (CH_2), 55.4 (OCH_3), 32.0 (quat-C), 31.8, 29.8 (CH_3); **GCMS** (EI, Pos): RT = 13.8 min, *m/z* 232 $[M\text{-}CH_3]^+$; **HRMS** (ESI, Pos): *m/z*: calcd for $C_{16}H_{26}NO$: 248.1970 $[M+H]^+$, found: 248.2008.



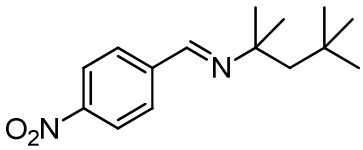
***N*-(4-carbomethoxybenzylidene)-*tert*-octylamine:** Following the imination procedure with ruthenium complex **1**, the imine was isolated as a light yellow solid (162 mg, 59% yield). **^{1}H NMR** (300 MHz, $CDCl_3$): δ 8.27 (s, 1H, N=CH), 8.07 (d, 2H, *J* = 8.1 Hz, Ar), 7.80 (d, 2H, *J* = 8.1 Hz, Ar), 3.93 (s, 3H, OCH_3), 1.70 (s, 2H, CH_2), 1.33 (s, 6H, 2 × CH_3), 0.95 (s, 9H, 3 × CH_3); **^{13}C NMR** (75 MHz, $CDCl_3$): δ 166.8 (C=O), 153.5 (N=CH), 141.2, 131.1 (Ar-quat-C), 129.7, 127.7 (Ar), 61.5 (quat-C), 56.5 (CH_2), 52.2 (OCH_3), 32.0 (quat-C), 31.7, 29.5 (CH_3); **GCMS** (EI, Pos): RT = 15.1 min, *m/z* 260 $[M\text{-}CH_3]^+$; **HRMS** (ESI, Pos): *m/z*: calcd for $C_{17}H_{26}NO_2$: 276.1919 $[M+H]^+$, found: 276.1960.



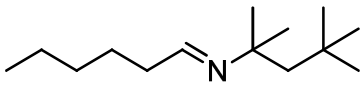
***N*-(2-hydroxybenzylidene)-*tert*-octylamine:** Following the imination procedure with ruthenium complex **1**, the imine was isolated as an intense yellow oil (77 mg, 33% yield). **^{1}H NMR** (300 MHz, $CDCl_3$): δ 8.23 (s, 1H, N=CH), 7.24-7.16 (m, 2H, Ar), 6.86 (d, 1H, *J* = 7.8 Hz, Ar), 6.77 (td, 1H, J_1 = 7.5, J_2 = 0.9, Ar), 1.64 (s, 2H, CH_2), 1.30 (s, 6H, 2 × CH_3), 0.88 (s, 9H, 3 × CH_3); **^{13}C NMR** (75 MHz, $CDCl_3$): δ 162.2 (Ar-quat-C), 159.5 (N=CH), 131.9, 131.2 (Ar), 118.8 (Ar-quat-C), 117.9, 117.3 (Ar), 60.5 (quat-C), 56.2 (CH_2), 31.9 (quat-C), 31.6, 29.4 (CH_3); **GCMS** (EI, Pos): RT = 13.8 min, *m/z* 218 $[M\text{-}CH_3]^+$; **HRMS** (ESI, Pos): *m/z*: calcd for $C_{15}H_{24}NO$: 234.1813 $[M+H]^+$, found: 234.1854.



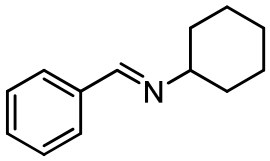
2-hydroxybenzyl-*tert*-octylamine: Following the imination procedure with ruthenium complex **1**, the amine was isolated as a light brown oil (88 mg, 37% yield). **^{1}H NMR** (300 MHz, $CDCl_3$): δ 7.15 (bt, 1H, Ar), 7.00 (bd, 1H, Ar), 6-84-6.74 (m, 2H, 2 × Ar), 3.94 (s, 2H, CH_2), 1.54 (s, 2H, CH_2), 1.26 (s, 6H, 2 × CH_3), 1.04 (s, 9H, 3 × CH_3); **^{13}C NMR** (75 MHz, $CDCl_3$): δ 158.3 (Ar-quat-C), 128.5, 127.9 (Ar), 123.5 (Ar-quat-C), 118.8, 116.4 (Ar), 54.3 (quat-C), 53.4, 45.6 (CH_2), 31.7 (CH_3), 31.6 (quat-C), 28.2 (CH_3); **HRMS** (ESI, Pos): *m/z*: calcd for $C_{15}H_{26}NO$: 236.1936 $[M+H]^+$, found: 236.2009.



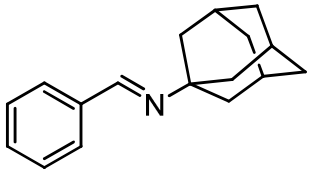
***N*-(4-nitrobenzylidene)-*tert*-octylamine:** Following the imination procedure with ruthenium complex **1**, the imine was isolated as a light brown oil (126 mg, 48% yield). **^{1}H NMR** (300 MHz, $CDCl_3$): δ 8.30 (s, 1H, N=CH), 8.26 (d, 2H, *J* = 8.7 Hz, Ar), 7.91 (d, 2H, *J* = 8.7 Hz, Ar), 1.71 (s, 2H, CH_2), 1.34 (s, 6H, 2 × CH_3), 0.94 (s, 9H, 3 × CH_3); **^{13}C NMR** (75 MHz, $CDCl_3$): δ 152.3 (N=CH), 142.7 (Ar-quat-C), 128.5, 123.8 (Ar), 61.9 (quat-C), 56.5 (CH_2), 32.0 (quat-C), 31.7, 29.5 (CH_3); **GCMS** (EI, Pos): RT = 15.2 min, *m/z* 247 $[M-CH_3]^+$; **HRMS** (ESI, Pos): *m/z*: calcd for $C_{15}H_{23}N_2O_2$: 263.1715 $[M+H]^+$, found: 263.1753.



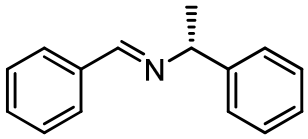
***N*-hexylidene-*tert*-octylamine:** Following the imination procedure with ruthenium complex **1**, the imine was isolated as a yellow oil (84 mg, 40% yield). **^{1}H NMR** (300 MHz, $CDCl_3$): δ 7.55 (t, 1H, *J* = 4.8, N=CH), 2.25-2.19 (m, 2H, CH_2), 1.59 (s, 2H, CH_2), 1.52-1.45 (m, 2H, CH_2), 1.32-1.28 (m, 4H, 2 × CH_2), 1.18 (s, 6H, 2 × CH_3), 0.91 (bs, 12H, 4 × CH_3); **^{13}C NMR** (75 MHz, $CDCl_3$): δ 158.6 (N=CH), 60.3 (quat-C), 55.8 (CH_2), 36.4 (CH_2), 32.0 (quat-C), 31.7 (CH_3), 30.0 (CH_3), 29.2, 25.9, 22.5 (CH_2), 14.0 (CH_3); **GCMS** (EI, Pos): RT = 11.1 min, *m/z* 196 $[M-CH_3]^+$.



***N*-benzylidenecyclohexylamine:** Following the imination procedure with ruthenium complex **1**, the imine was isolated as a yellow oil (113 mg, 60% yield). **^{1}H NMR** (300 MHz, $CDCl_3$): δ 8.32 (s, 1H, N=CH), 7.75-7.71 (m, 2H, Ar), 7.41-7.39 (m, 3H, Ar), 3.24-3.15 (m, 1H, CH), 1.87-1.54 (m, 8H, 4 × CH_2), 1.44-1.26 (m, 2H, CH_2); **^{13}C NMR** (75 MHz, $CDCl_3$): δ 158.6 (N=CH), 136.5 (Ar-quat-C), 130.3, 128.5, 127.9 (Ar), 70.0 (CH), 34.3, 25.6, 24.8 (CH_2); NMR data are in accordance with literature values;[14] **GCMS** (EI, Pos): RT = 12.8 min, *m/z* 187 $[M]^+$.

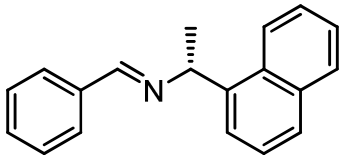


***N*-benzylidene-1-adamantanylamine:** Following the imination procedure with ruthenium complex **1**, the imine was isolated as a white solid (169 mg, 70% yield). **^{1}H NMR** (300 MHz, $CDCl_3$): δ 8.28 (s, 1H, N=CH), 7.77-7.74 (m, 2H, 2 × Ar), 7.41-7.38 (m, 3H, 3 × Ar), 2.18 (bs, 3H, 3 × CH), 1.82 (bd, 6H, 3 × CH_2), 1.73 (bs, 6H, 3 × CH_2); **^{13}C NMR** (75 MHz, $CDCl_3$): δ 154.8 (N=CH), 137.2 (Ar-quat-C), 130.1, 128.4, 127.8 (Ar), 57.4 (quat-C), 43.1, 36.5, 29.5 (aliphatic -C); NMR data are in accordance with literature values;[15] **GCMS** (EI, Pos): RT = 15.6 min, *m/z* 239 $[M]^+$.

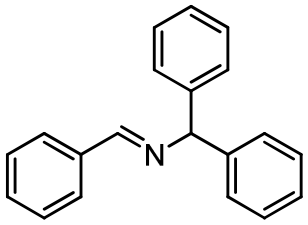


(*R*)-*N*-benzylidene-1-phenylethylamine: Following the imination procedure with ruthenium complex **1**, the imine was isolated as a light yellow oil (132 mg, 63% yield). $[\alpha]_D^{20}$ = -64.6 (c = 1.6 g, $CHCl_3$) (ref.[16] $[\alpha]_D^{27}$ = -64.7 (c = 1.0, $CHCl_3$)); **^{1}H NMR** (300 MHz, $CDCl_3$): δ 8.30 (s,

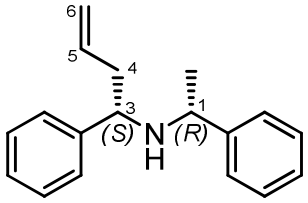
1H, N=CH), 7.72-7.69 (m, 2H, 2 × Ar), 7.34-7.24 (m, 8H, 8 × Ar), 4.47 (q, 1H, *J* = 6.6 Hz, CH), 1.52 (d, 3H, *J* = 6.6 Hz, CH_3); **^{13}C NMR** (75 MHz, $CDCl_3$): δ 159.4 (N=C), 145.1, 136.4 (Ar-quat-C), 130.5, 128.5, 128.4, 126.8, 126.6 (Ar), 69.7 (CH), 24.8 (CH_3); NMR data are in accordance with literature values;[16] **GCMS** (EI, Pos): RT = 13.9 min, *m/z* 209 $[M]^+$.



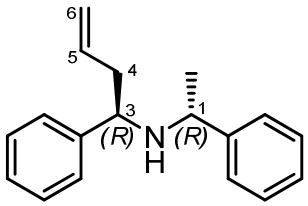
(*R*)-*N*-benzylidene-1-(1-naphthyl)ethylamine: Following the imination procedure with ruthenium complex **1**, the imine was isolated as an orange solid (133.4 mg, 51.5% yield). $[\alpha]_D^{20}$ = -242.0 (c = 1.1, $CHCl_3$) (ref.[16] $[\alpha]_D^{15}$ = -250.3 (c = 1.04, $CHCl_3$)); **^{1}H NMR** (300 MHz, $CDCl_3$): δ 8.45 (s, 1H, N=CH), 8.28 (d, 1H, *J* = 8.4 Hz, Ar), 7.91-7.67 (m, 5H, 5 × Ar), 7.58-7.48 (m, 3H, 3 × Ar), 7.44-7.42 (m, 3H, 3 × Ar), 5.38 (q, 1H, *J* = 6.6 Hz, CH), 1.76 (d, 3H, *J* = 6.6 Hz, CH_3); **^{13}C NMR** (75 MHz, $CDCl_3$): δ 159.6 (N=CH), 141.1, 136.4, 133.9, 130.6 (Ar-quat-C), 130.5, 128.9, 128.5, 128.2, 127.3, 125.7, 125.6, 125.3, 123.9, 123.6 (Ar), 65.5 (CH), 24.5 (CH_3); NMR data are in accordance with literature values;[16] **GCMS** (EI, Pos): RT = 16.8 min, *m/z* 259 $[M]^+$.



***N*-benzylidene-1,1-diphenylmethylamine:** Following the imination procedure with ruthenium complex **1**, the imine was isolated as a white solid (108 mg, 40% yield). **^{1}H NMR** (300 MHz, $CDCl_3$): δ 8.34 (s, 1H, N=CH), 7.78-7.74 (m, 2H, 2 × Ar), 7.34-7.31 (m, 7H, 7 × Ar), 7.26-7.21 (bt, 4H, 4 × Ar) 7.17-7.12 (m, 2H, 2 × Ar), 5.51 (s, 1H, CH); **^{13}C NMR** (75 MHz, $CDCl_3$): δ 160.7 (N=CH), 143.8, 136.2, 130.7, 128.5, 128.4, 128.4, 127.6, 126.9 (Ar), 77.8 (CH); NMR data are in accordance with literature values;[17] **GCMS** (EI, Pos): RT = 16.8 min, *m/z* 271 $[M]^+$.



(*S*)-1-phenyl-*N*-((*R*)-1-phenylethyl)but-3-en-1-yl-amine: Following the procedure for addition of *B*-allyl-9-BBN to (*R*)-*N*-benzylidene-1-phenylethylamine, the pure S,R diastereomer was isolated as a light yellow oil (99 mg, 39 % yield). $[\alpha]_D^{20}$ = +3.6 (c = 1.1, $CHCl_3$); **^{1}H NMR** (300 MHz, $CDCl_3$): δ 7.25-7.12 (m, 10H, Ar), 5.66-5.33 (m, 1H, CH-5), 4.98-4.91 (m, 2H, CH_2-6), 3.69 (t, 1H, *J* = 6.6 Hz, CH-3), 3.64 (q, 1H, *J* = 6.6 Hz, CH-1), 2.37 (bq, 2H, CH_2-4), 1.53 (s, 1H, NH), 1.25 (d, 3H, *J* = 6.6, CH_3); **^{13}C NMR** (75 MHz, $CDCl_3$): δ 146.0, 143.9 (Ar-quat), 135.4 (CH-5), 128.3, 128.2, 127.1, 126.8, 126.7, 126.5 (Ar), 117.2 (CH_2-6), 59.6, 54.5 (CH-1, CH-3), 42.1 (CH_2-4), 22.5 (CH_3); NMR data are in accordance with literature values;[8,9] **GCMS** (EI, Pos): RT = 14.4 min, *m/z* 236 $[M\text{-}CH_3]^+$.



(*R*)-1-phenyl-*N*-((*R*)-1-phenylethyl)but-3-en-1-yl-amine:[9] Following the procedure for addition of allylmetal reagents to (*R*)-*N*-benzylidene-1-phenylethylamine, the R,R diastereomer was isolated in mixture with the S,R diastereomer. The reported ^{1}H NMR signals were deduced from one of the most enriched chromatographic fractions. While ^{13}C NMR signals were deduced from the spectra of the diastereomeric mixture. **^{1}H NMR** (300 MHz, $CDCl_3$): δ 7.27-7.07 (m, 10H, Ar), 5.67-5.48 (m, 1H, CH-5), 5.00-4.91 (m, 2H, CH_2-6), 3.41 (q, 1H, *J* = 6.6 Hz, CH-1), 3.30 (t, 1H, *J* = 6.9 Hz, CH-3), 2.25 (bt, 2H, CH_2-4), 1.62 (bs, 1H, NH), 1.19 (d, 3H, *J* = 6.6 Hz, CH_3); **^{13}C NMR** (75 MHz, $CDCl_3$): δ 145.7, 144.2 (Ar-quat), 135.6 (CH-5), 128.3, 128.3, 127.2, 126.8, 126.7, 126.5 (Ar), 117.3 (CH_2-6), 58.9, 54.8 (CH-1, CH-3), 43.3 (CH_2-4), 24.8 (CH_3);

^{13}C NMR data in accordance with literature values;[10] **GCMS** (EI, Pos): RT = 14.2 min, *m/z* 236 $[M\text{-}CH_3]^+$.

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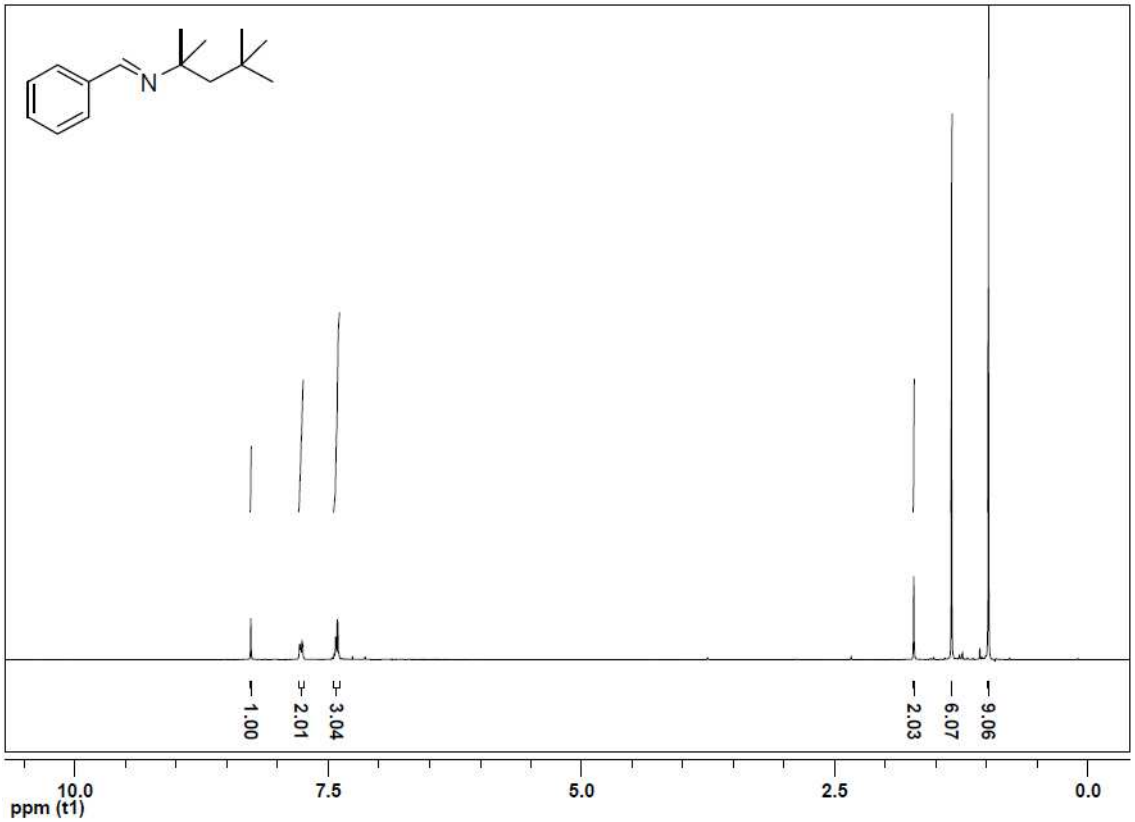
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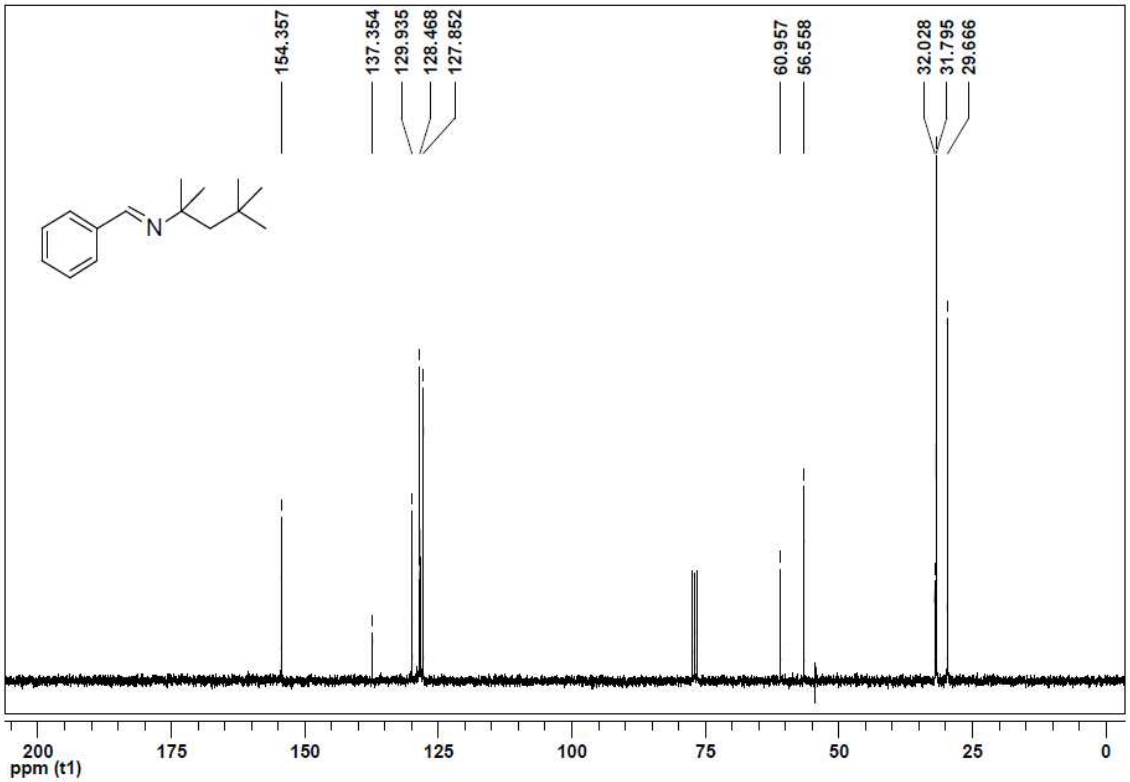
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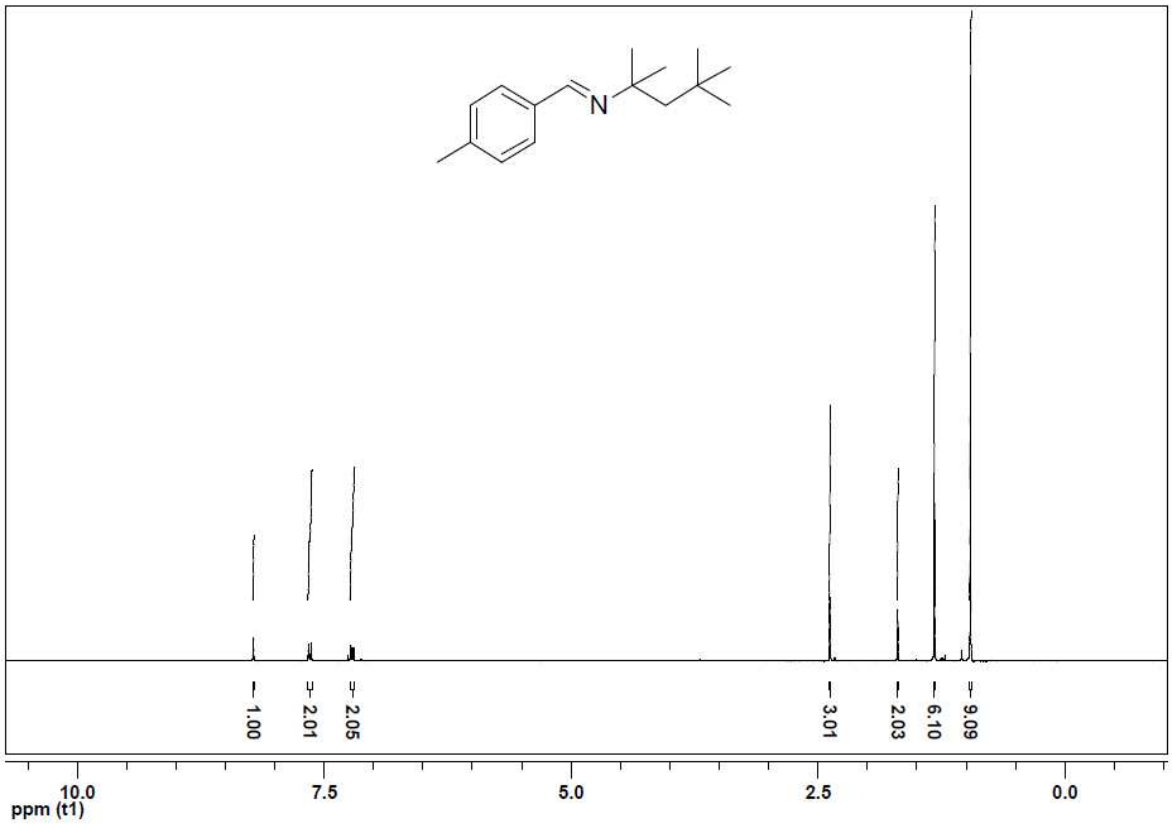
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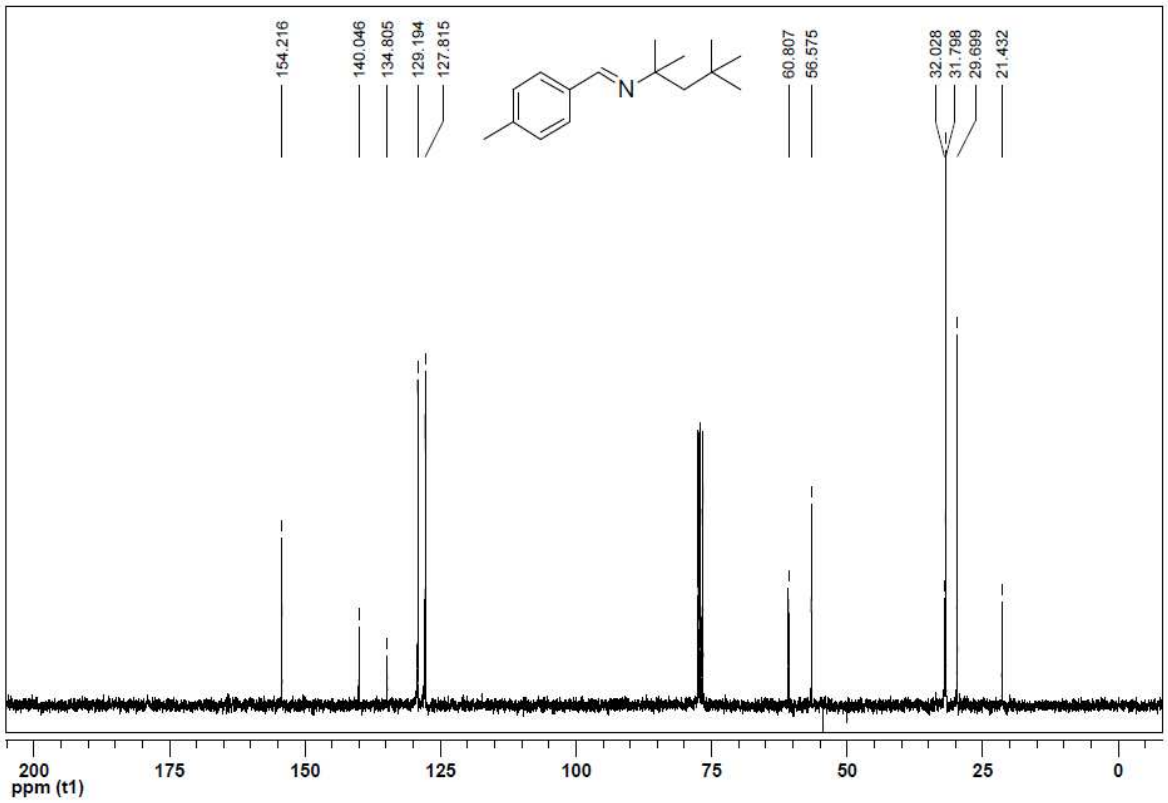
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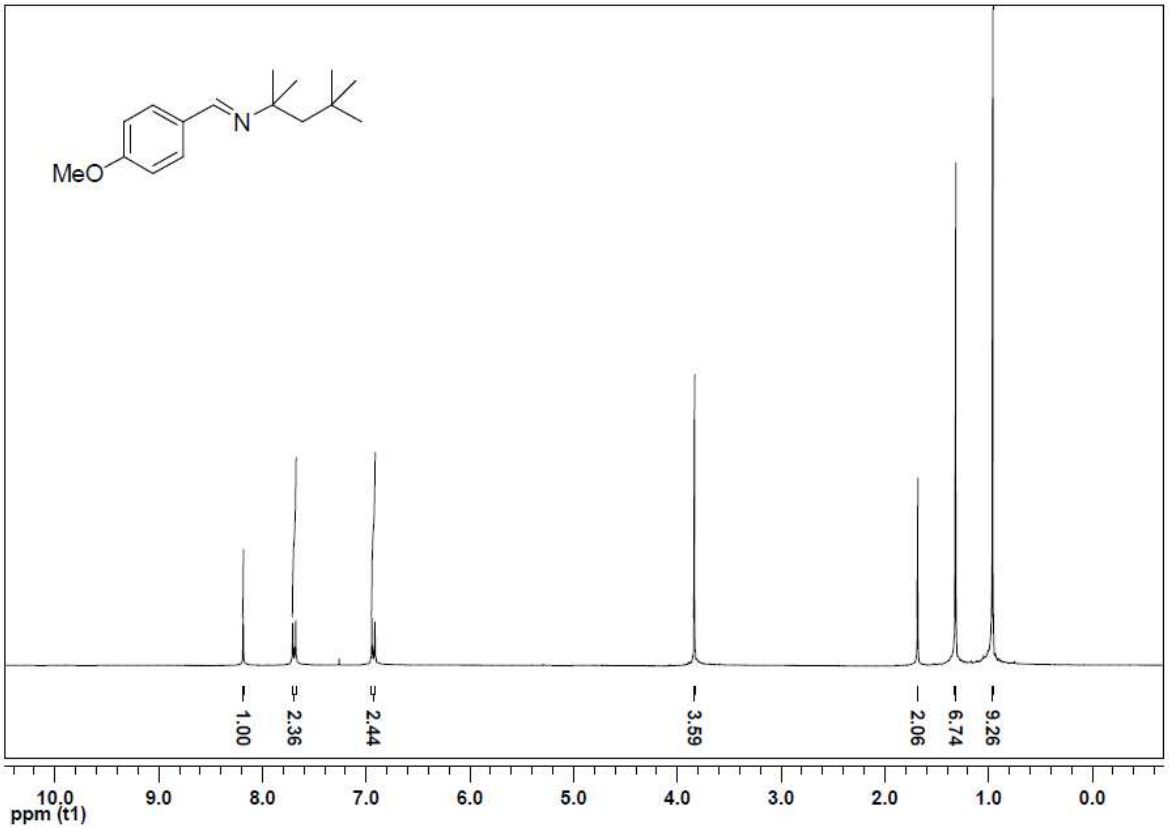
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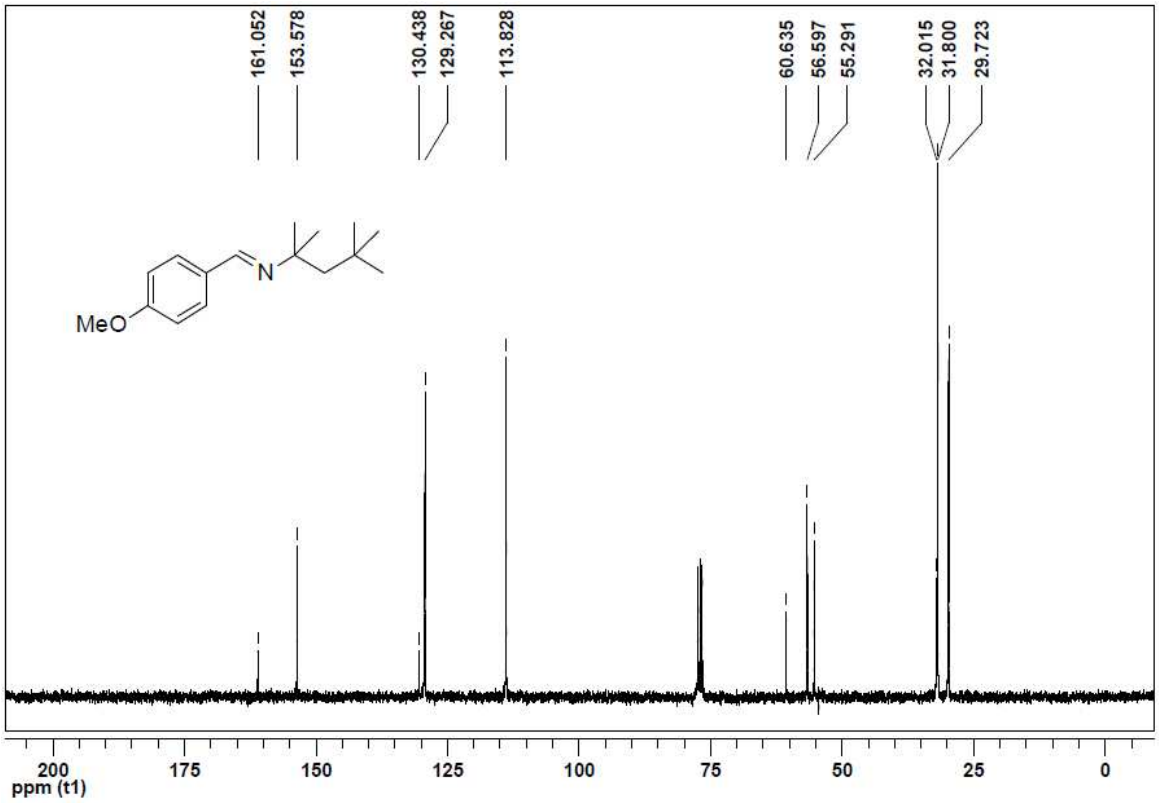
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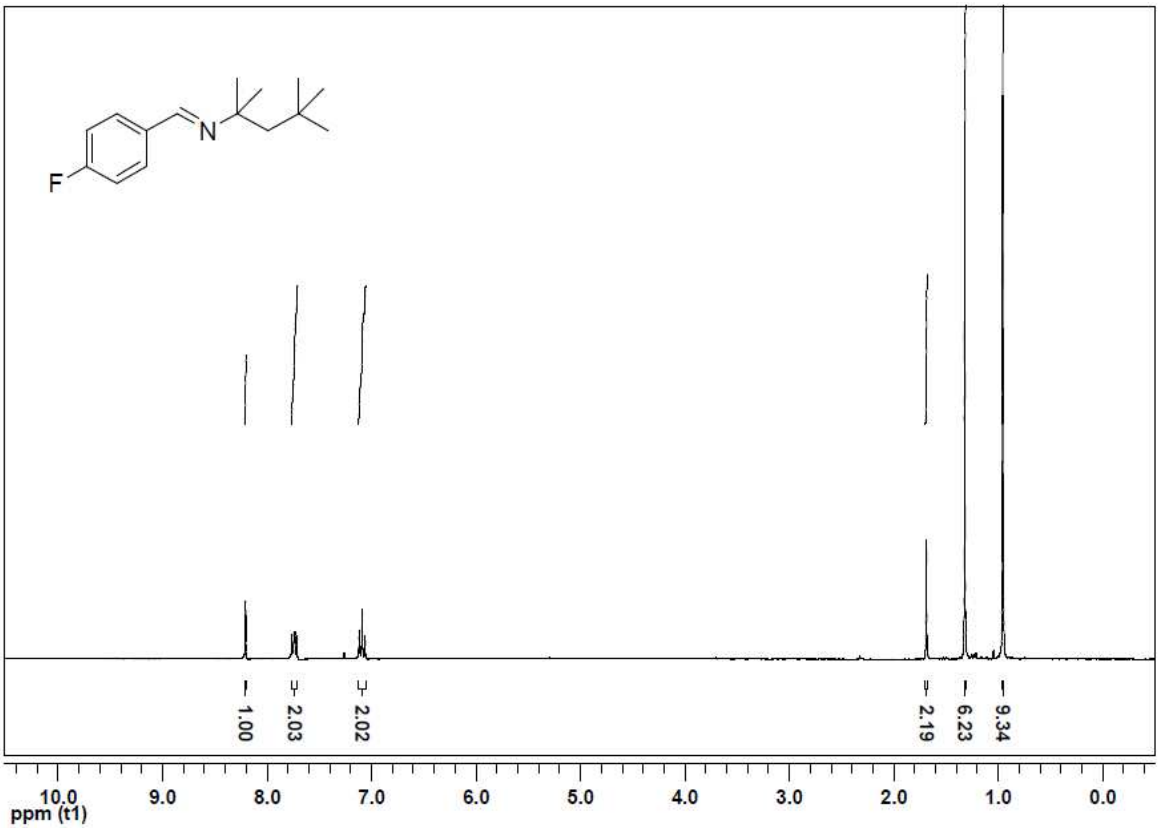
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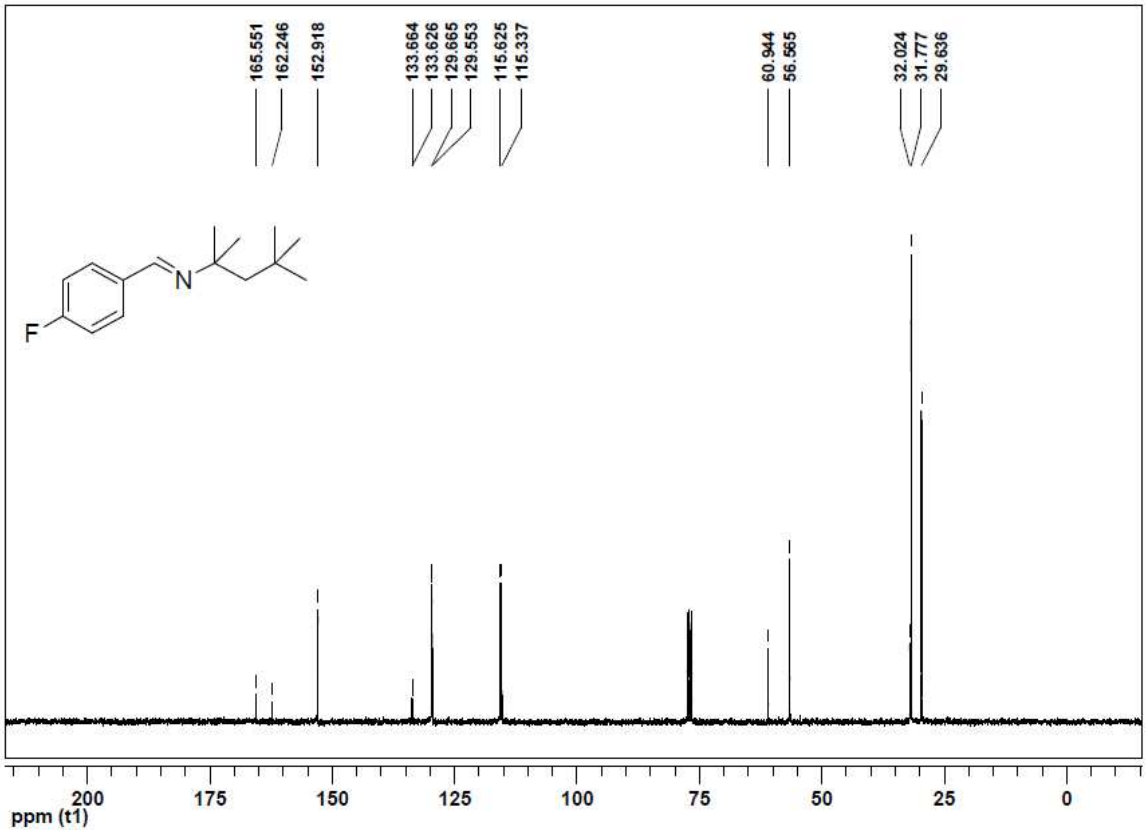
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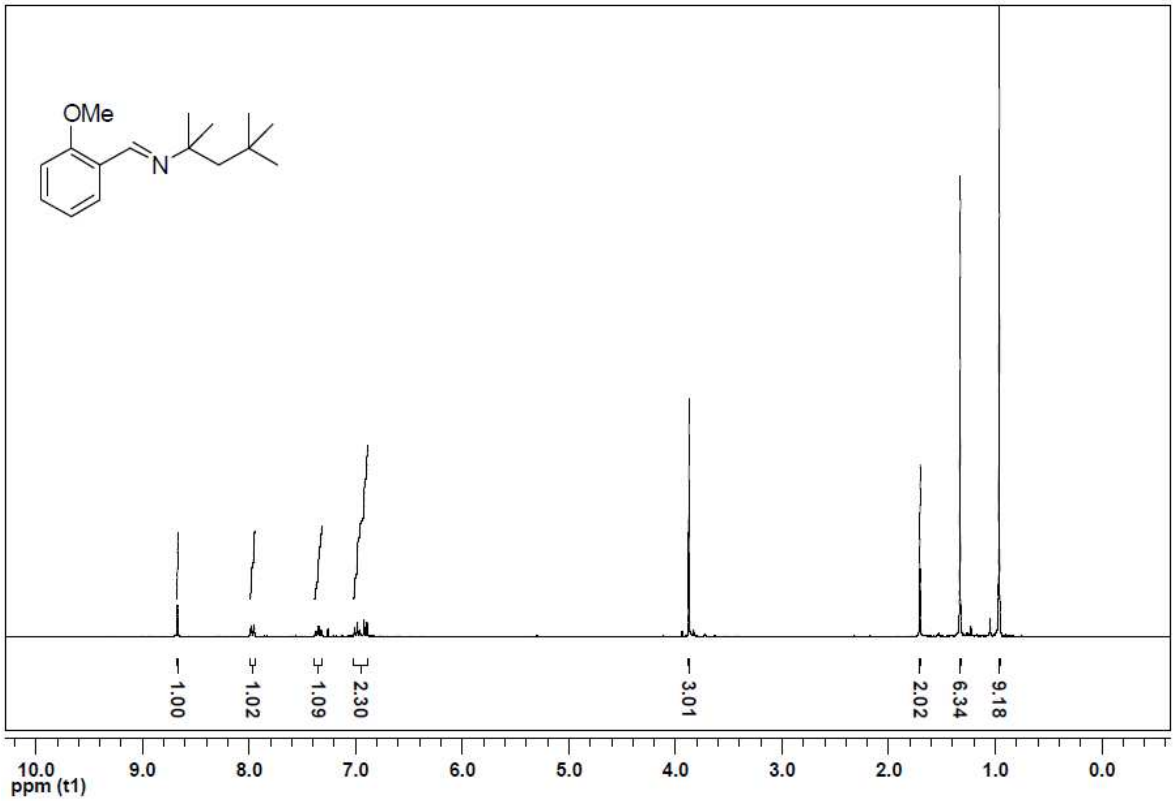
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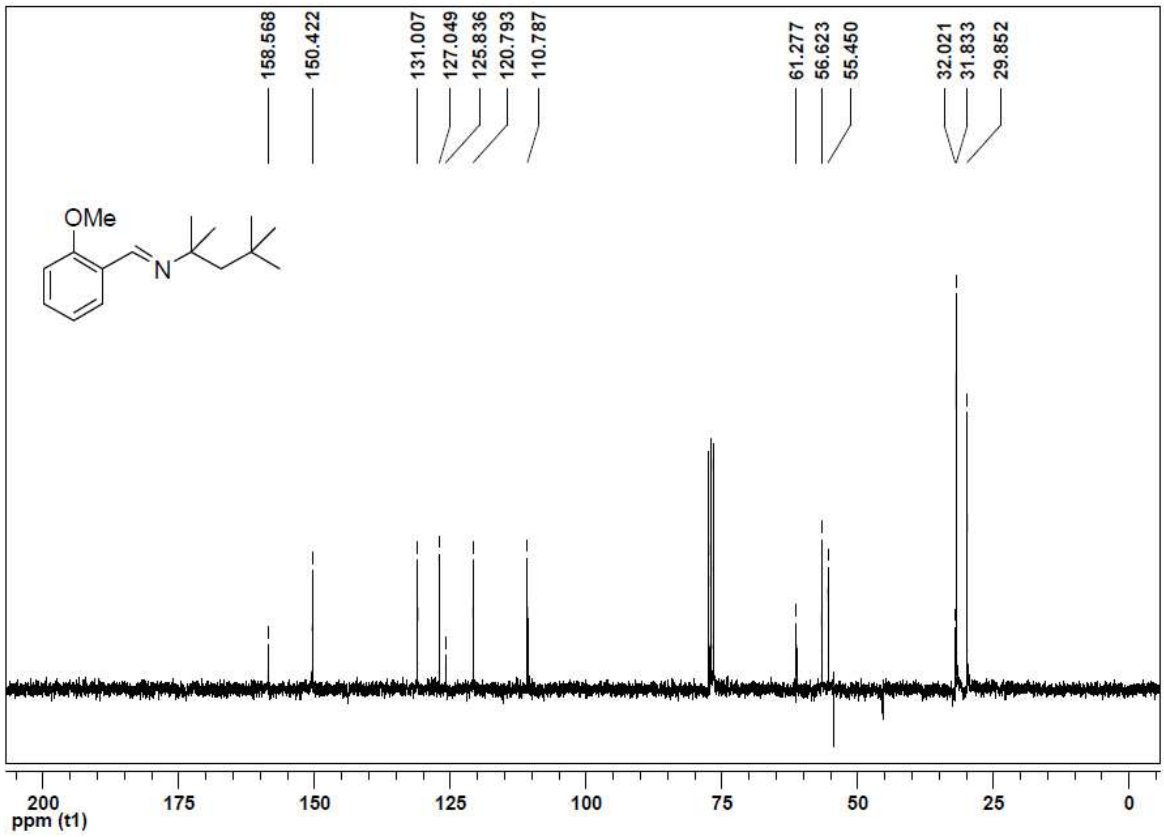
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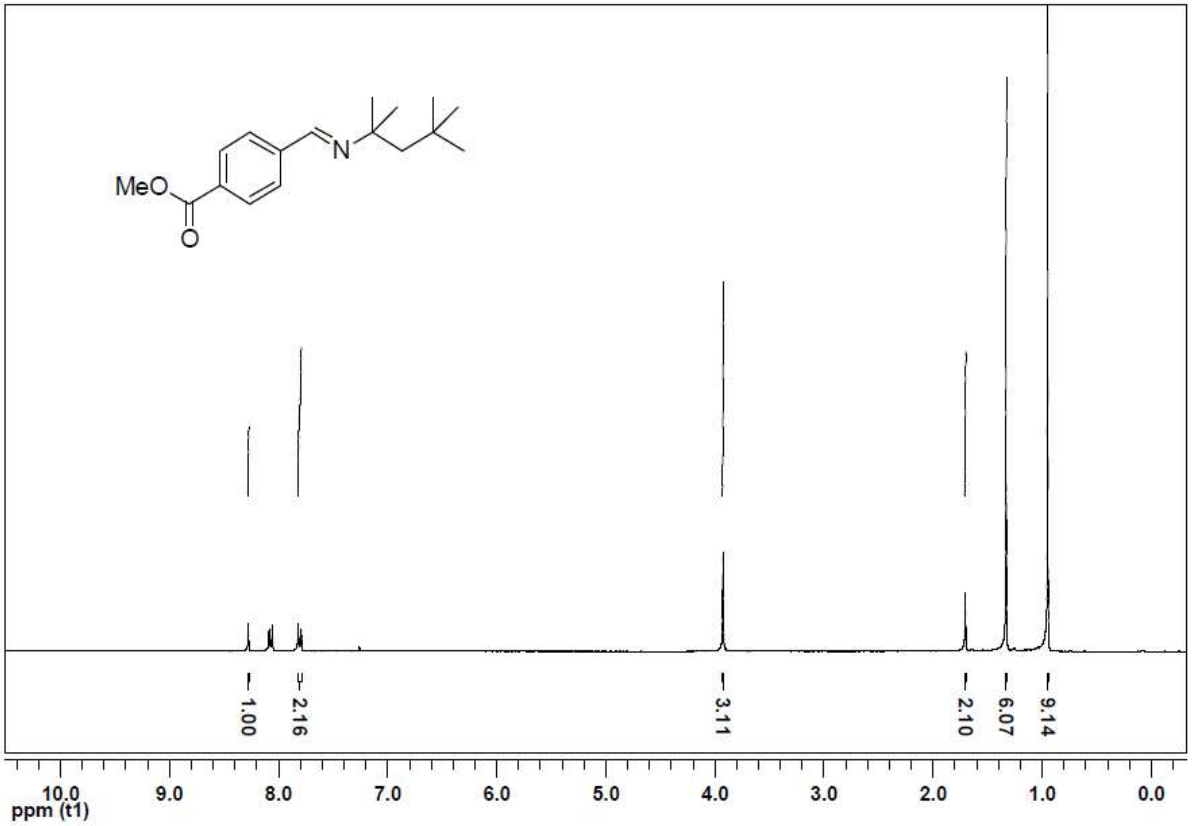
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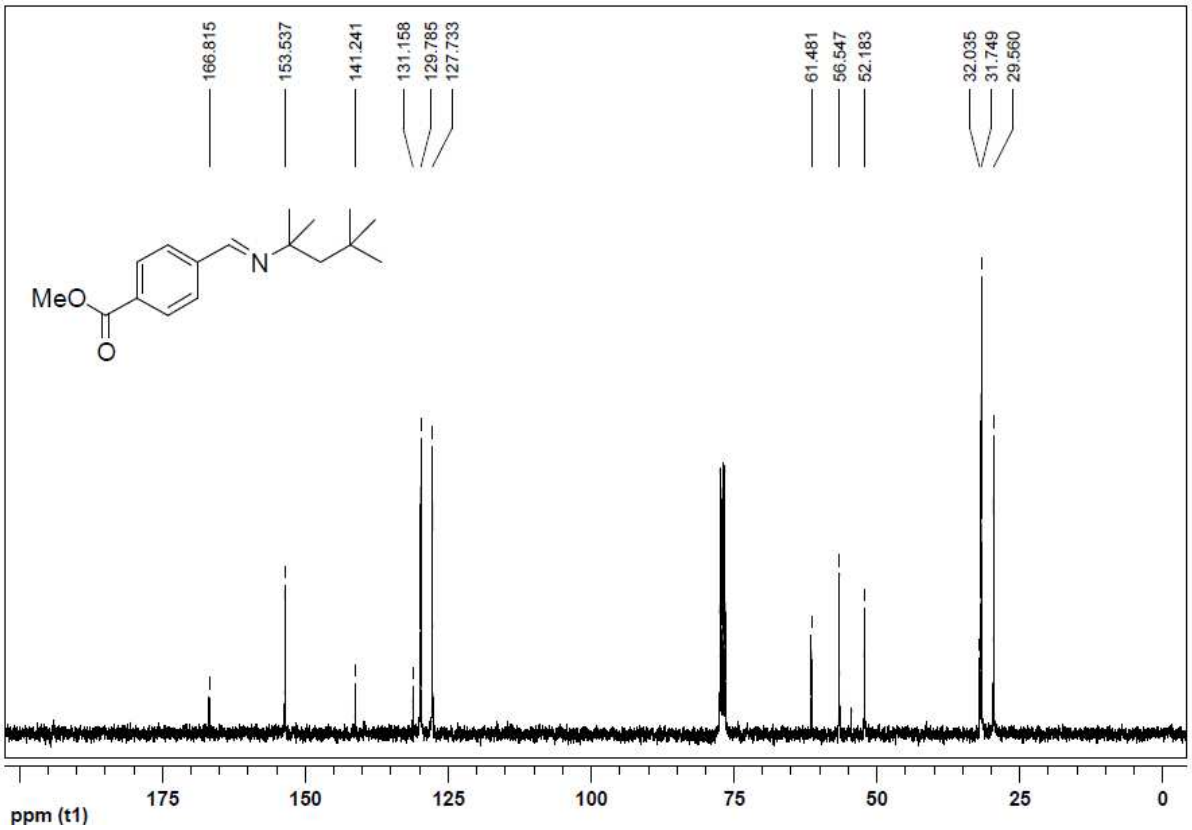
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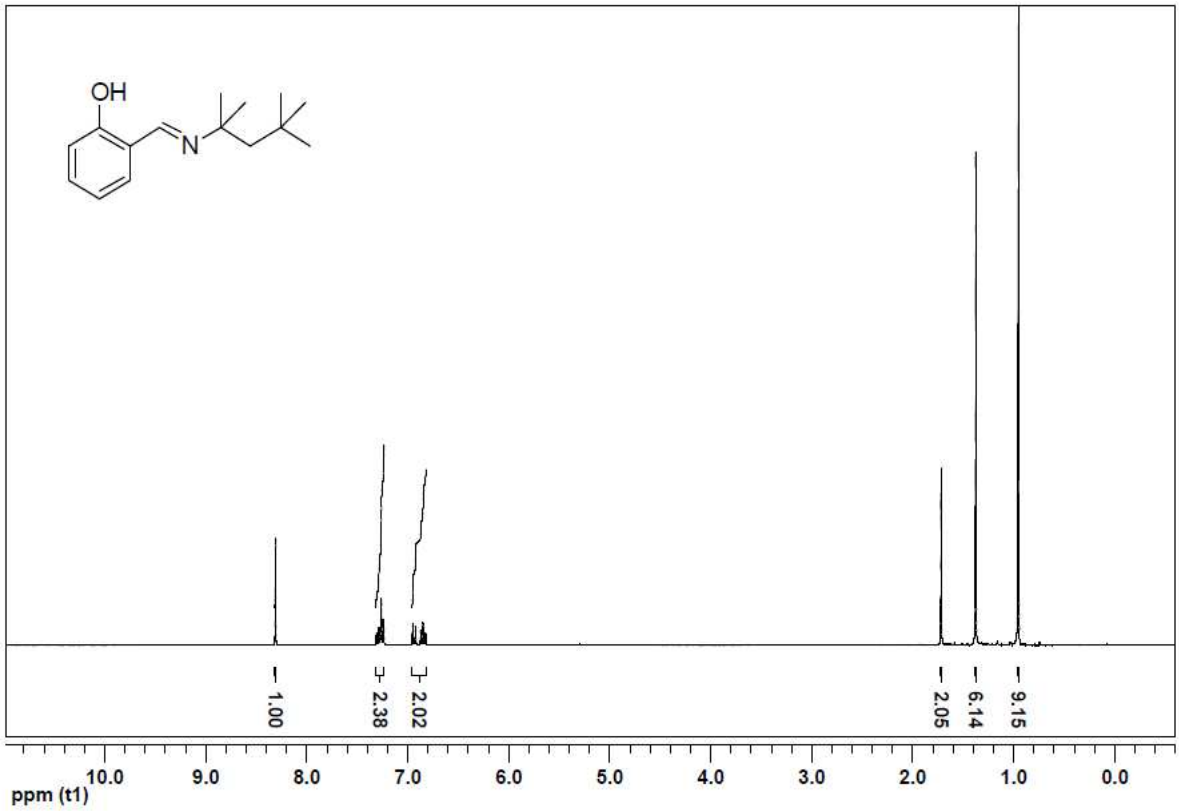
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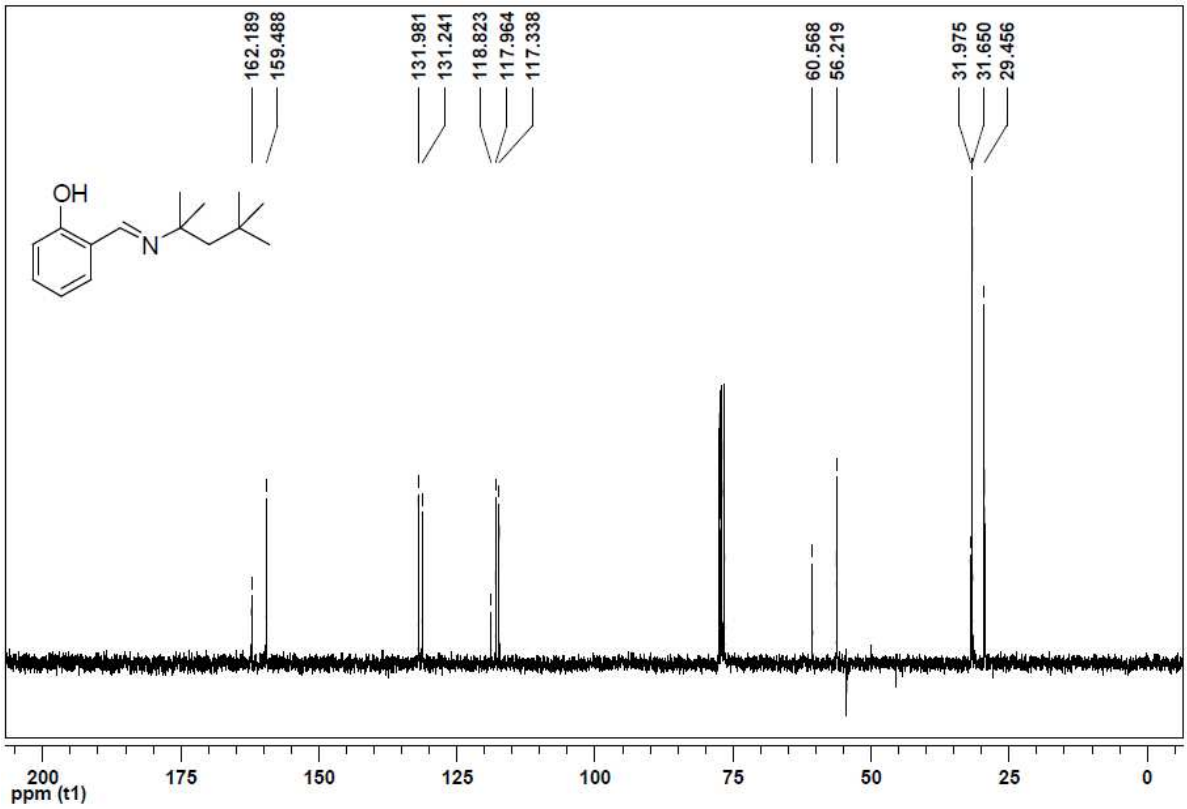
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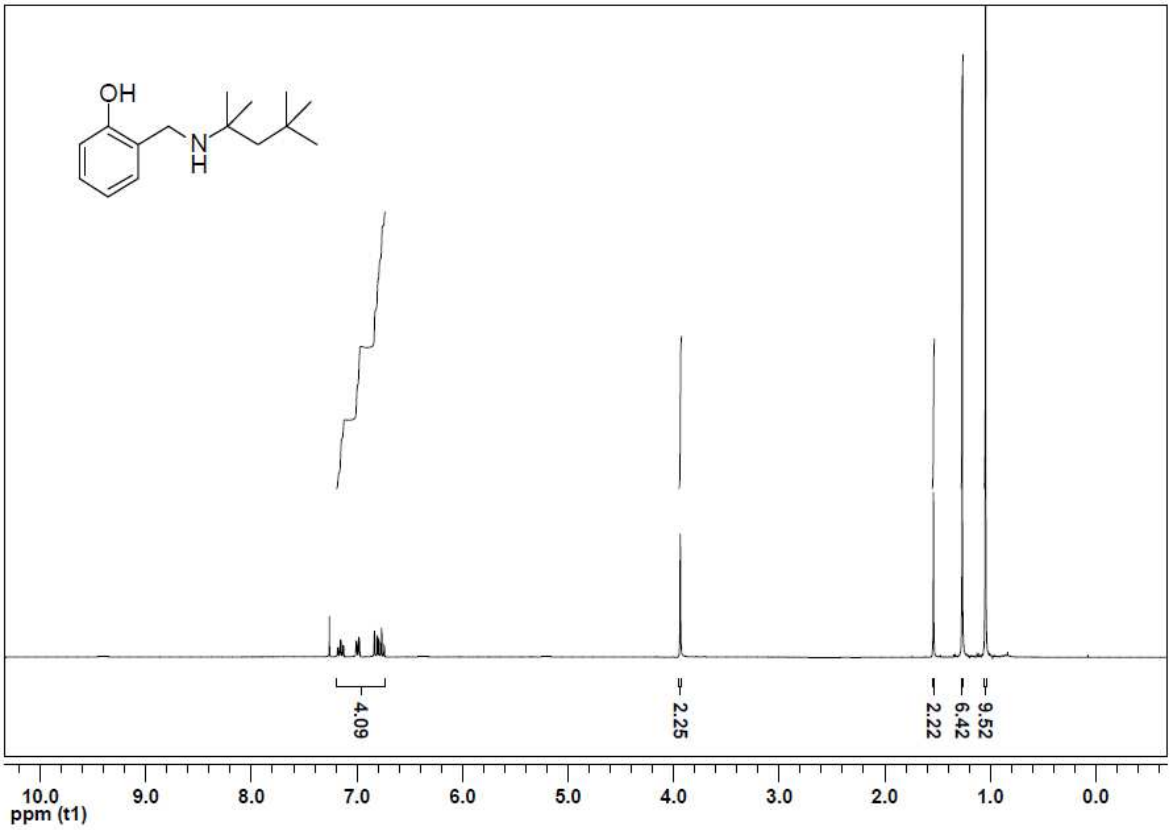
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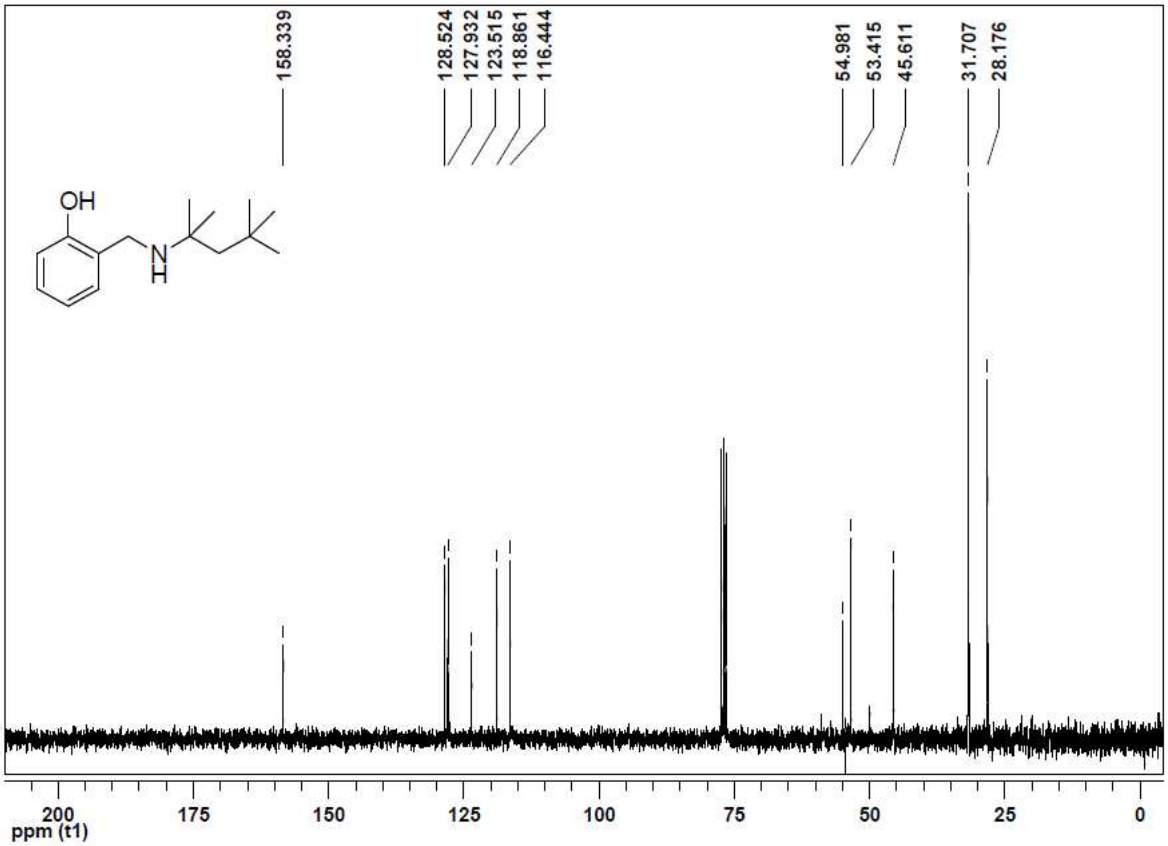
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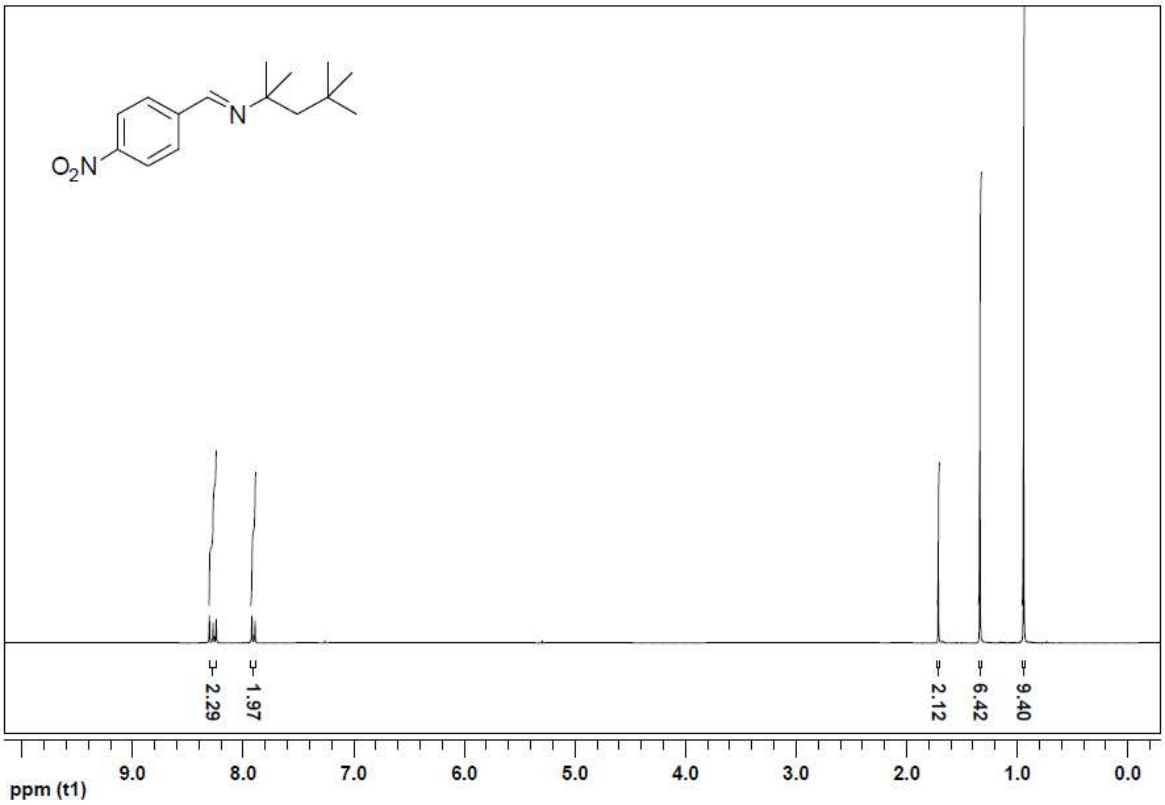
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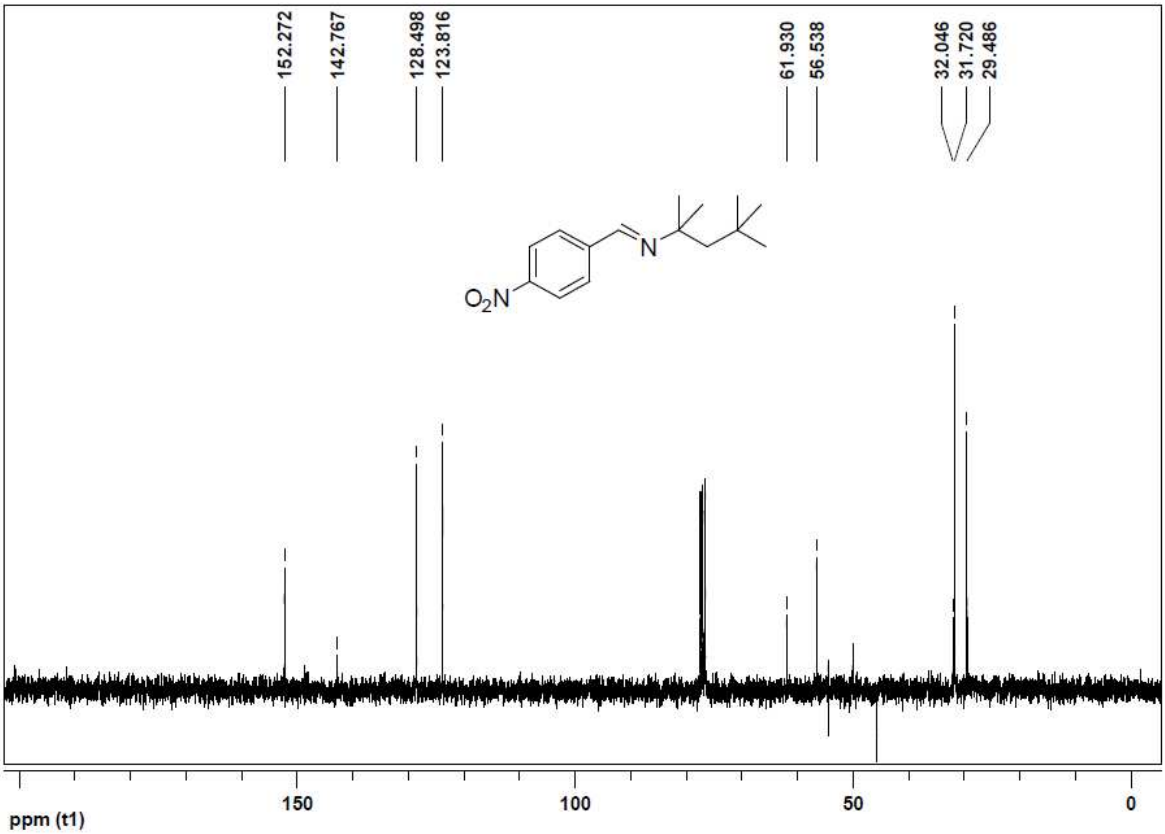
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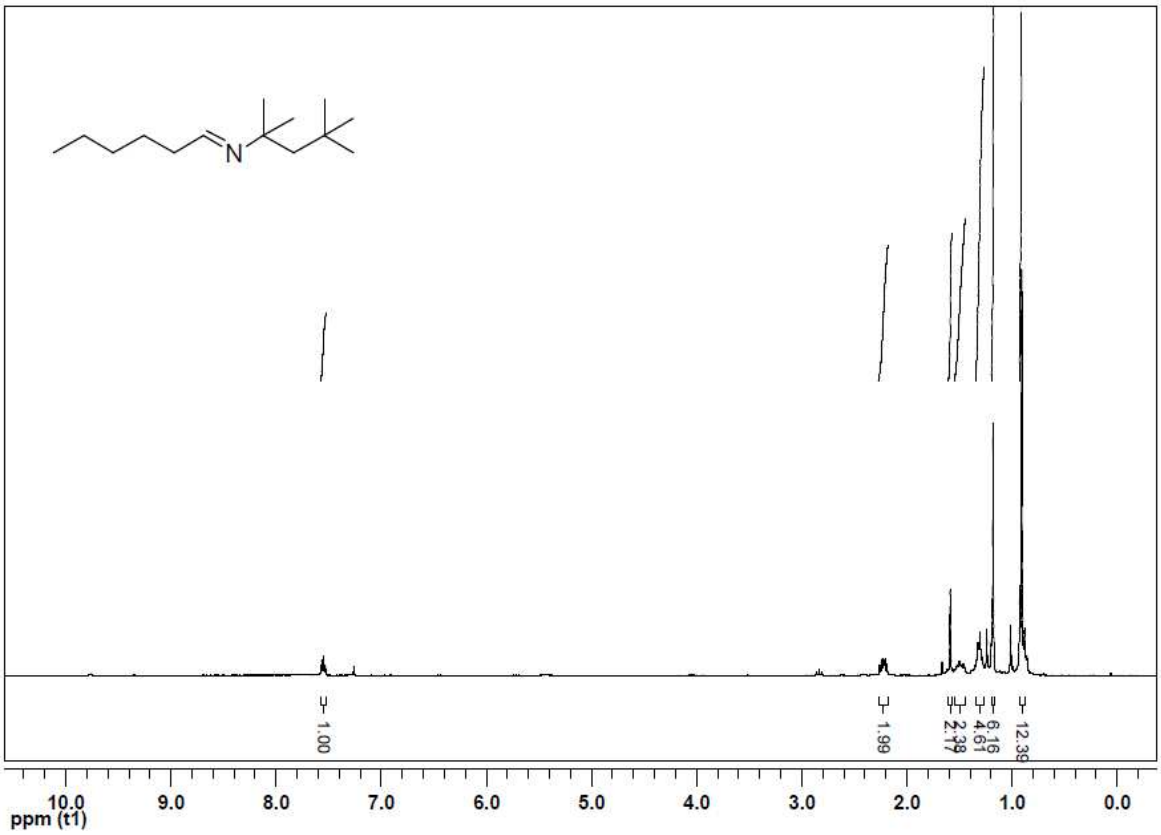
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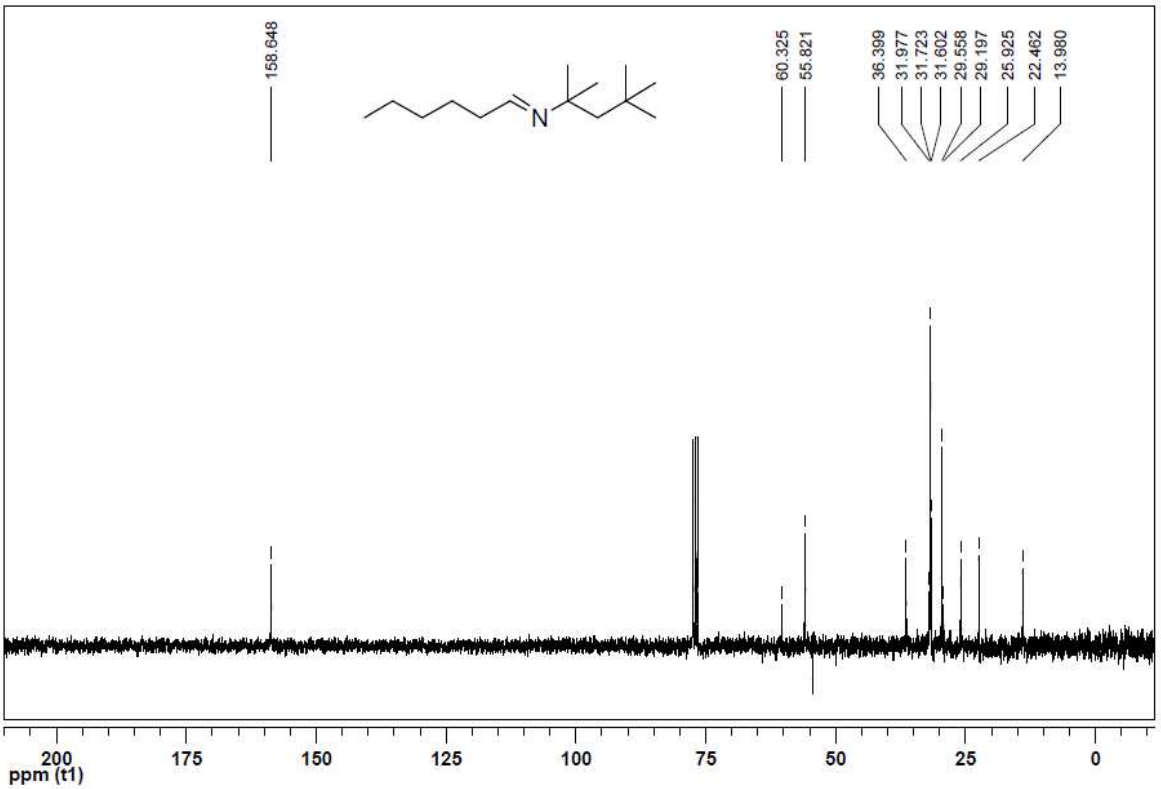
ppm (t1)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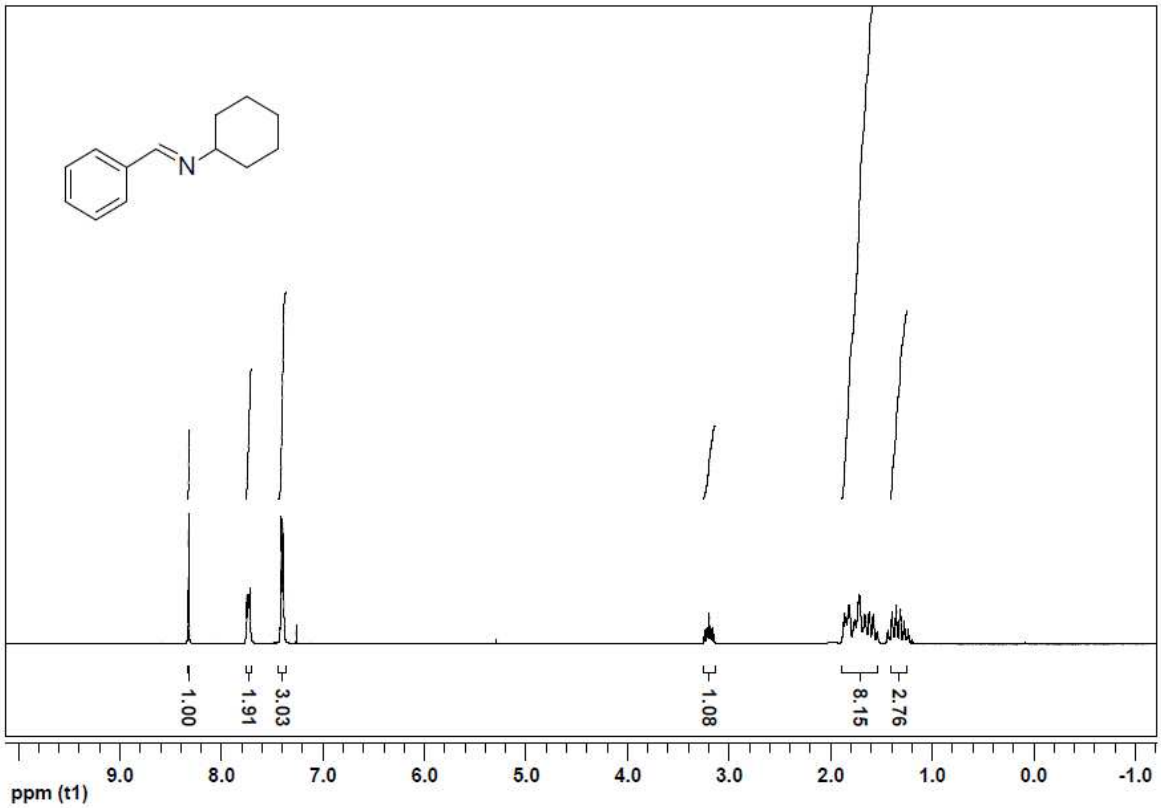
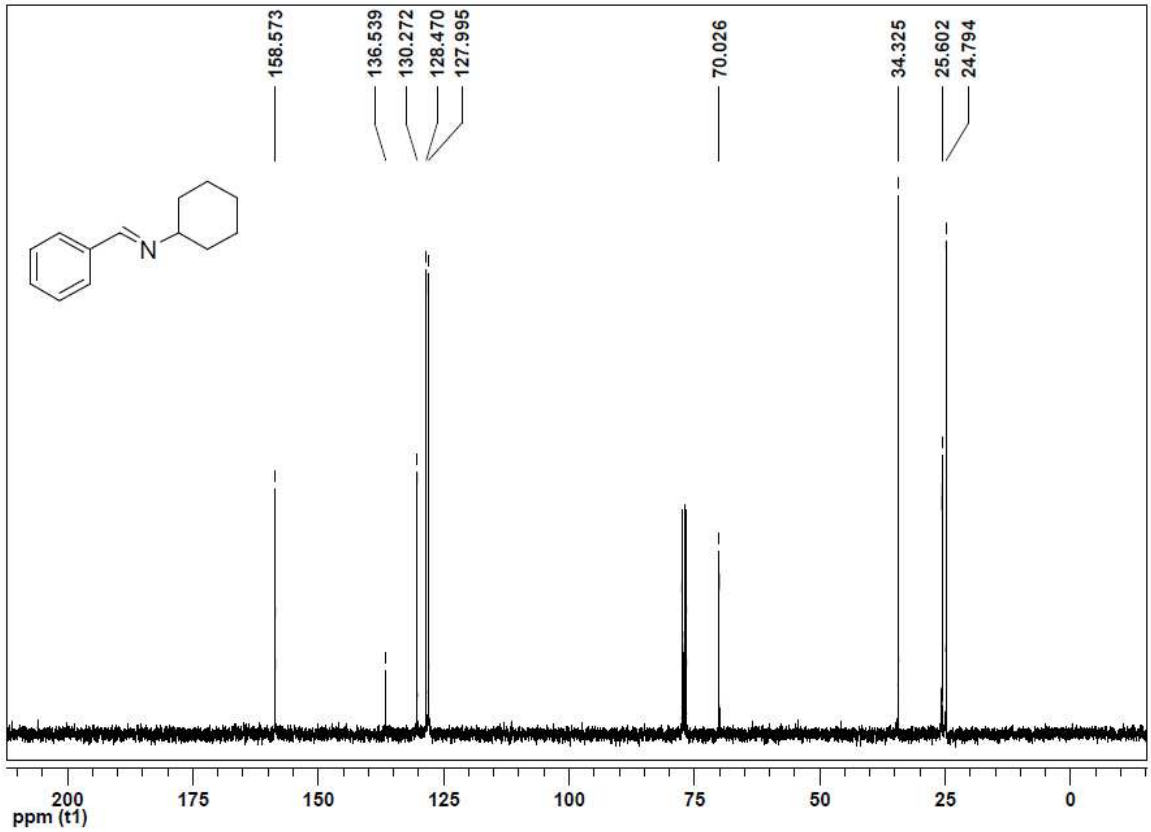
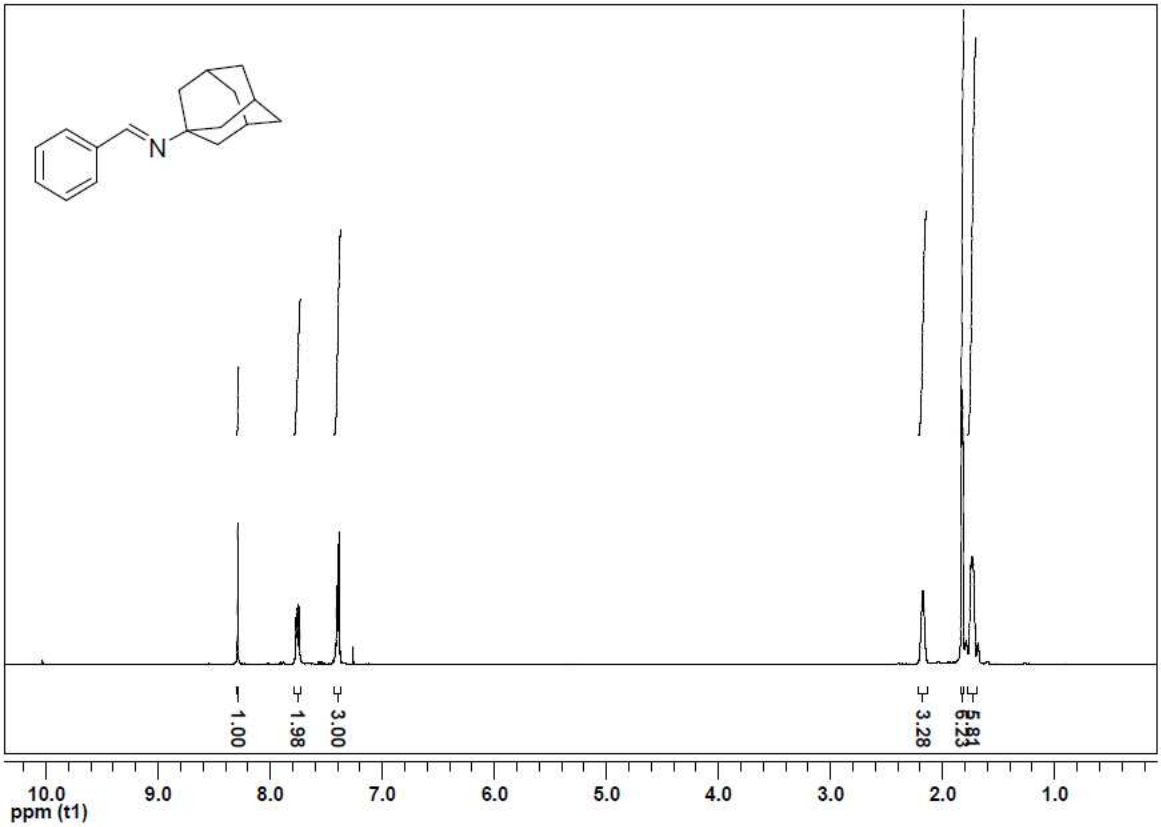
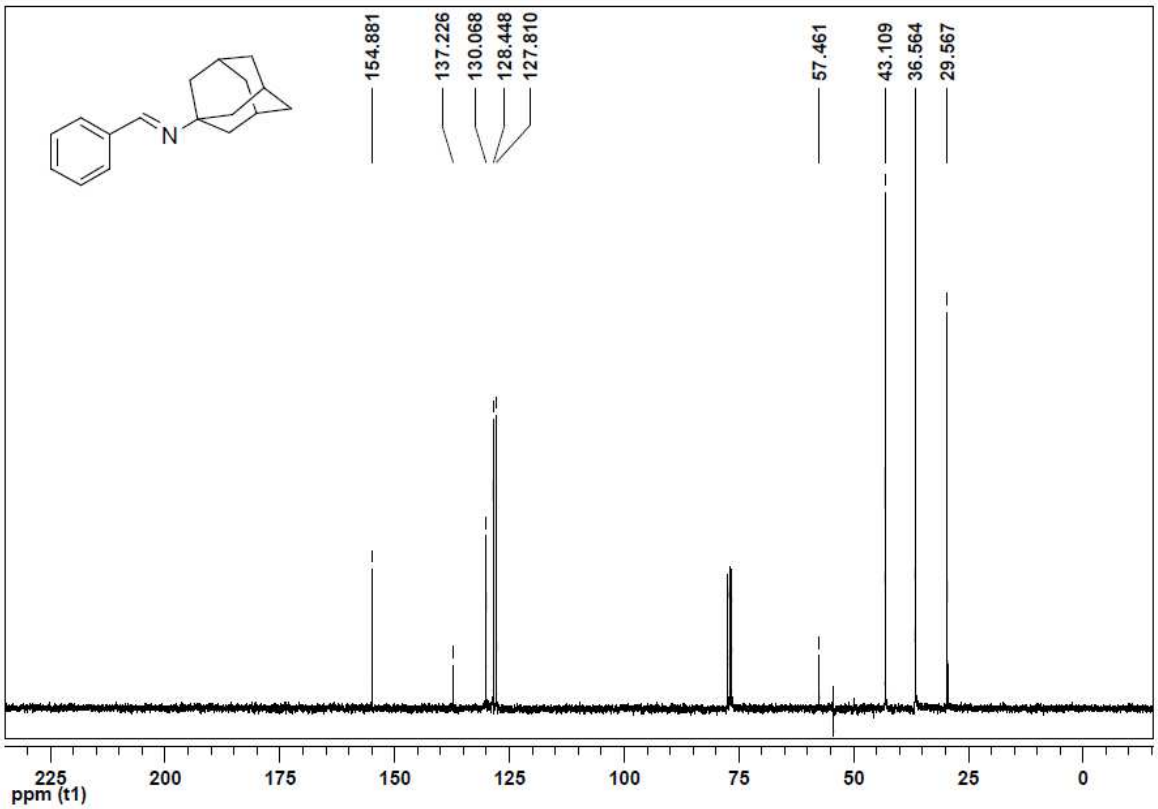
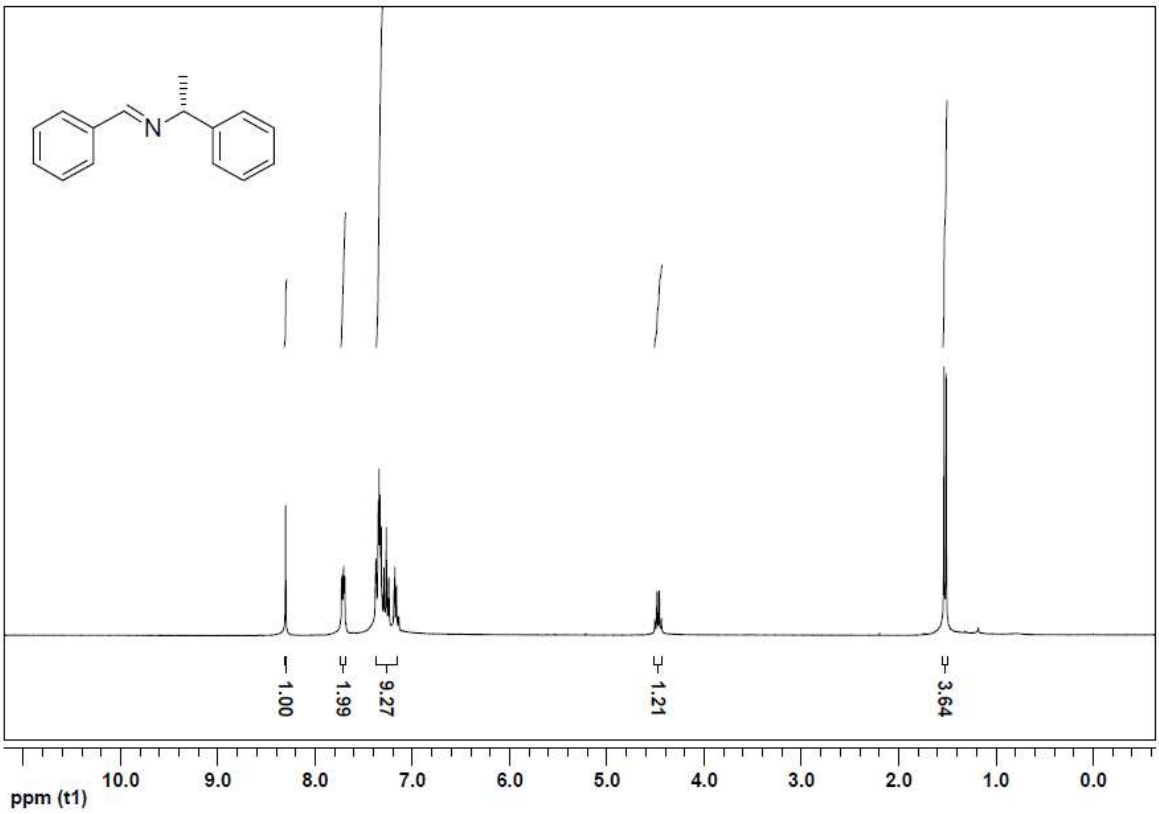
0
ppm (t1)

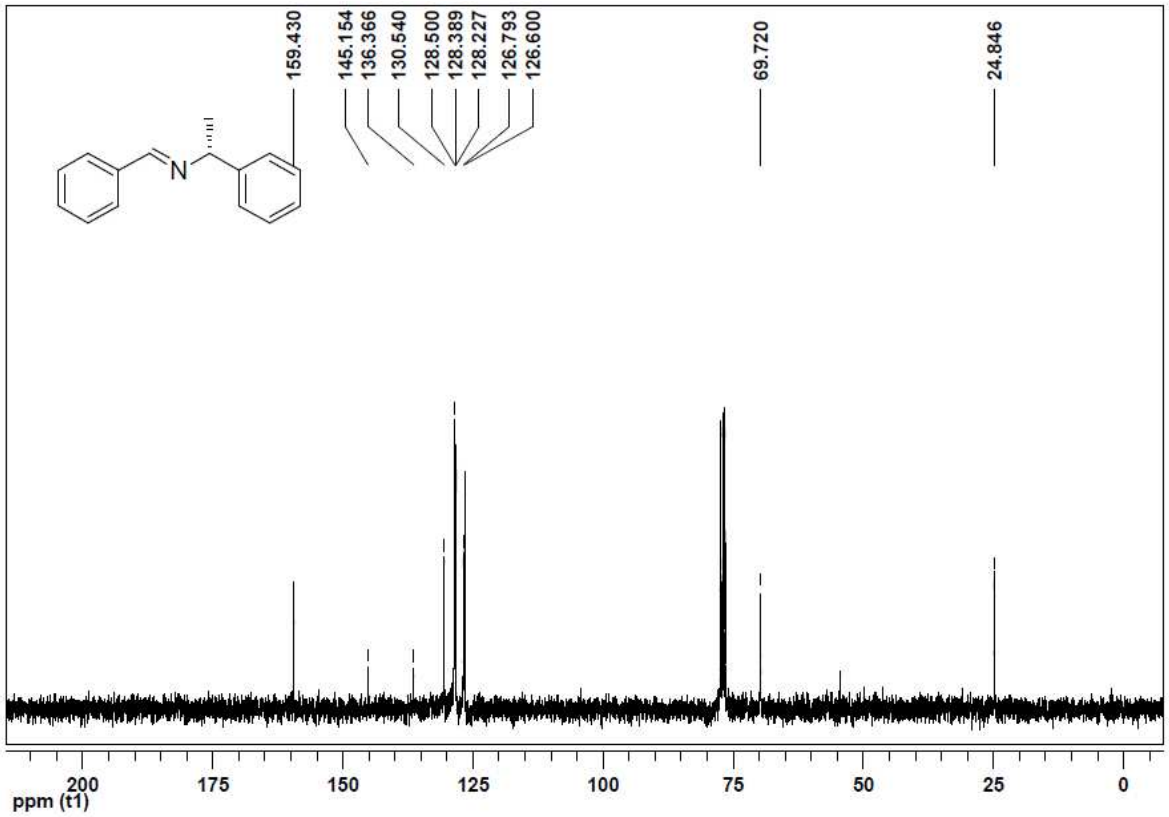

N
1.00
1.91
3.03
1.08
8.15
2.76
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
ppm (t1)

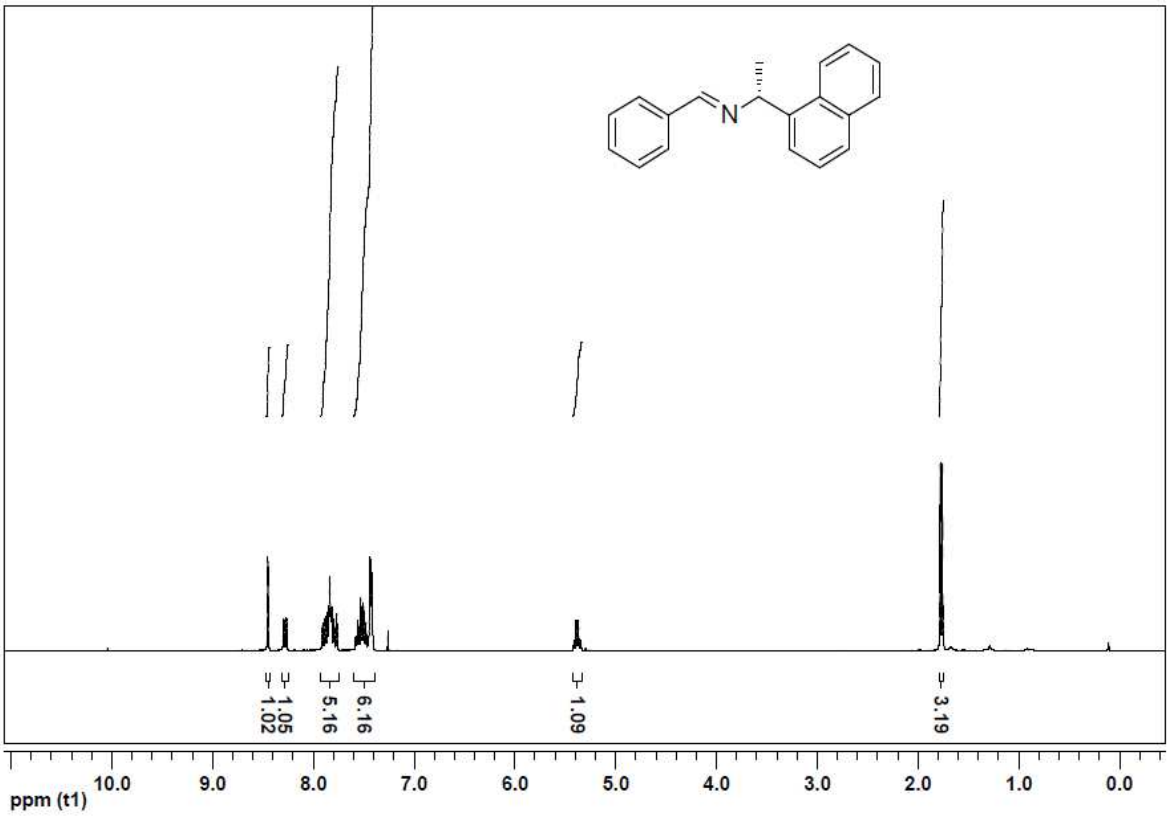

158.573
136.539
130.272
128.470
127.995
70.026
34.325
25.602
24.794
N
200
175
150
125
100
75
50
25
0
ppm (t1)

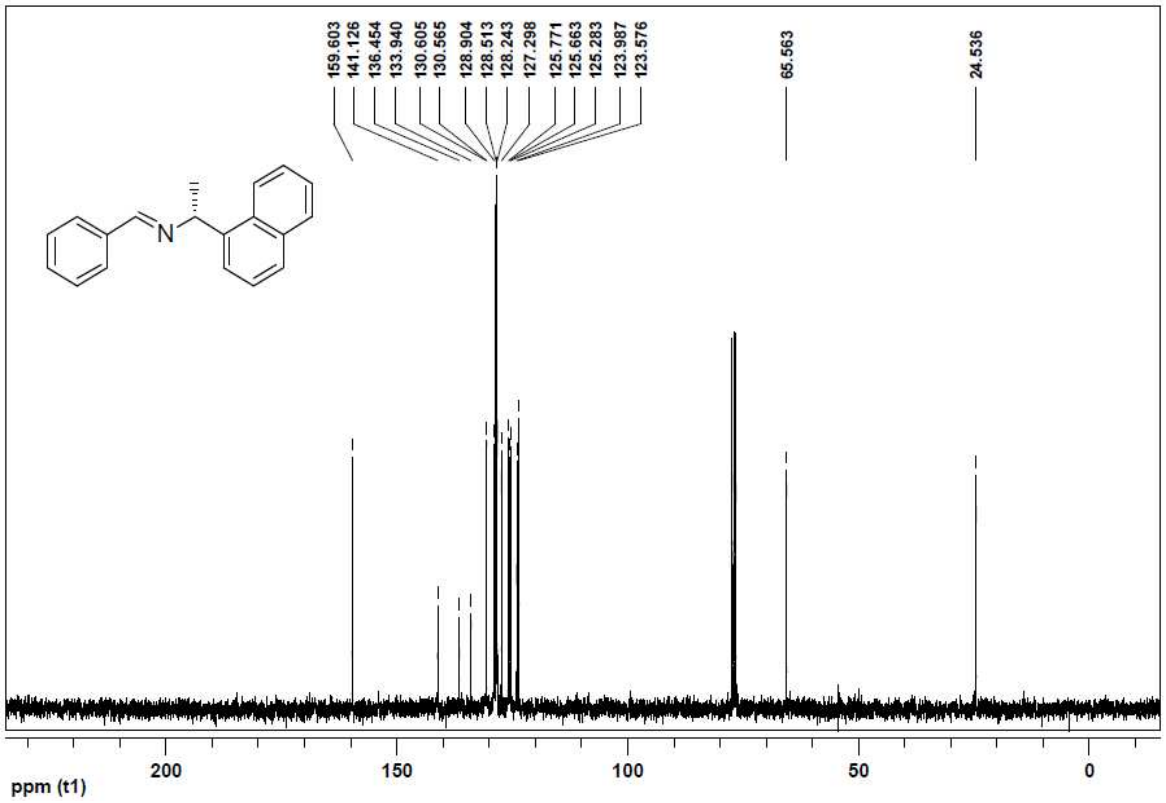

N
1.00
1.98
3.00
3.28
5.81
6.23
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)

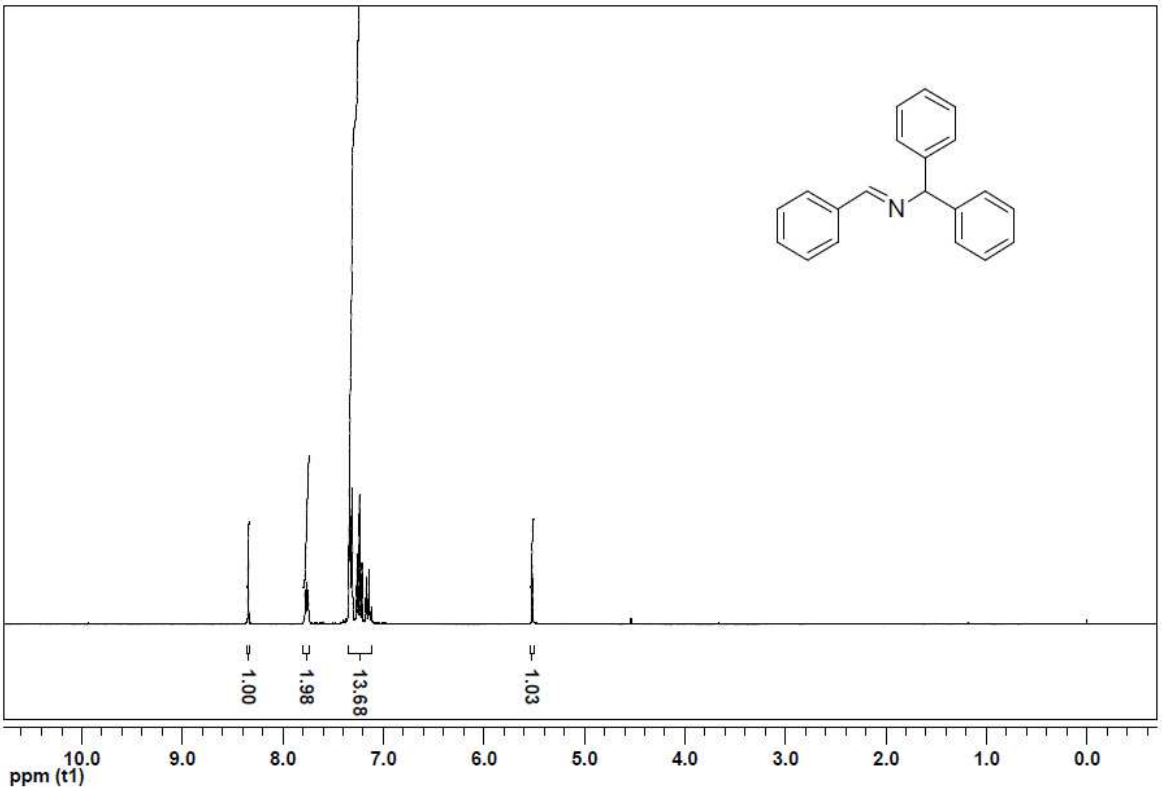

N
154.881
137.226
130.068
128.448
127.810
57.461
43.109
36.564
29.567
225
200
175
150
125
100
75
50
25
0
ppm (t1)

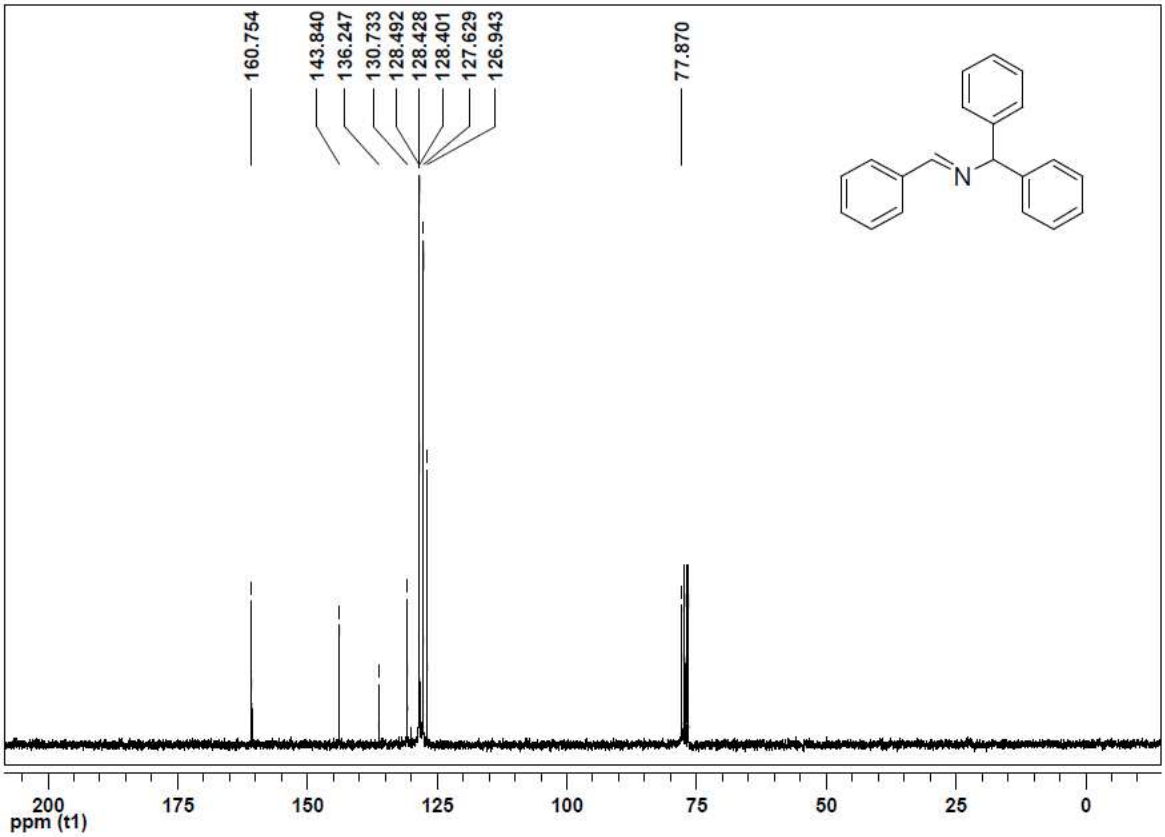

1.00
1.99
9.27
1.21
3.64
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

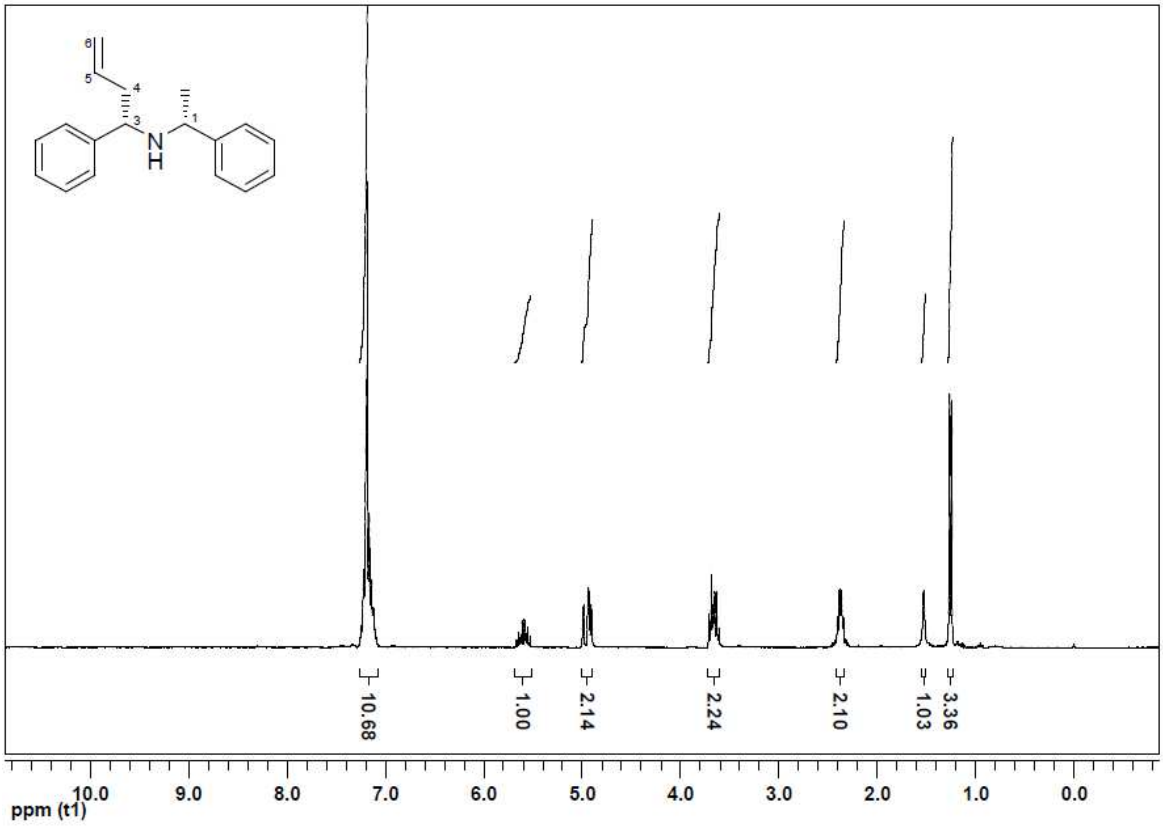

159.430
145.154
136.366
130.540
128.500
128.389
128.227
126.793
126.600
69.720
24.846
200
175
150
125
100
75
50
25
0
ppm (t1)

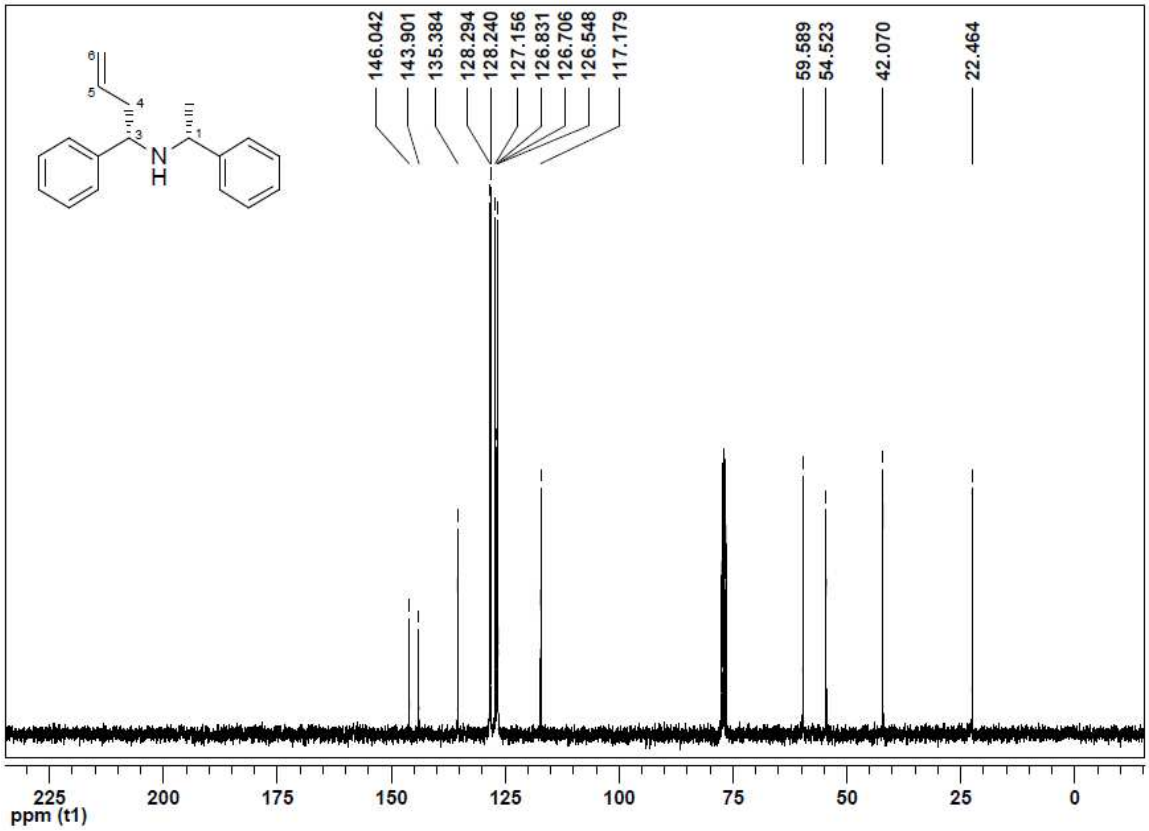

N
1.02
1.05
5.16
9.16
1.09
3.19
ppm (t1)
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0

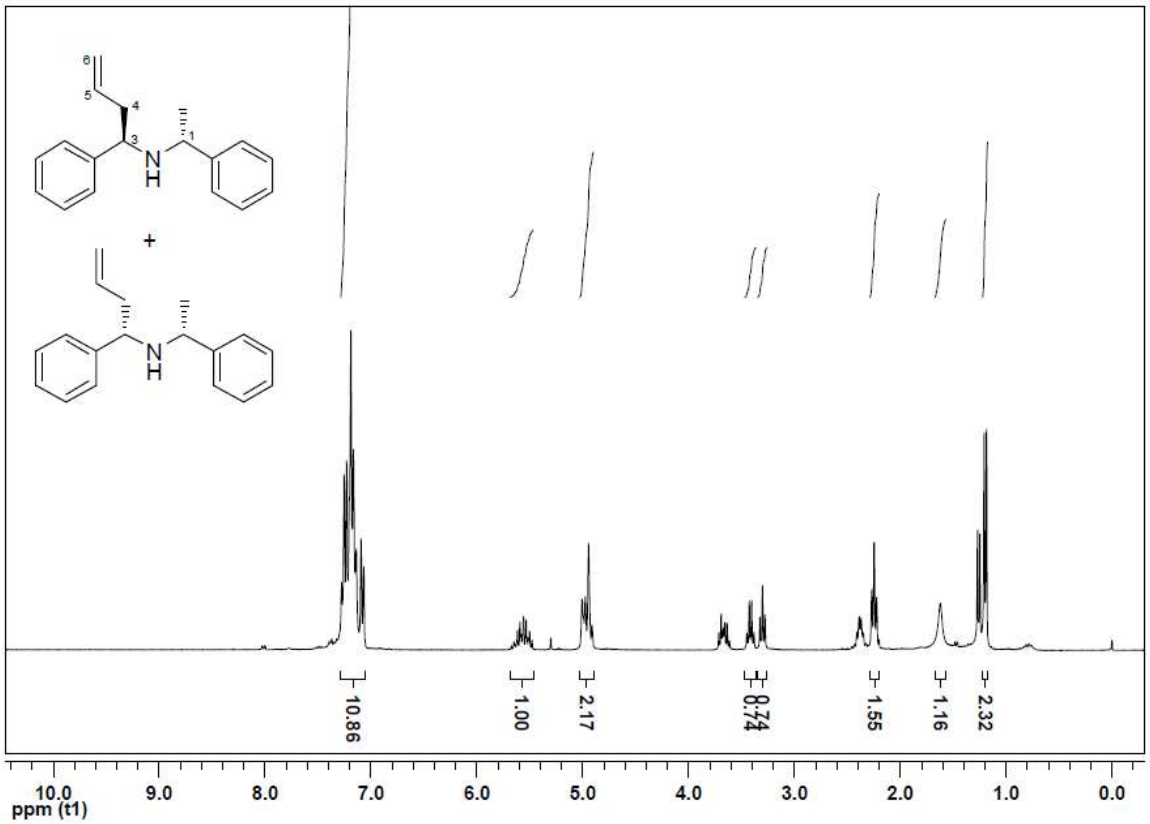

159.603
141.126
136.454
133.940
130.605
130.565
128.904
128.513
128.243
127.298
125.771
125.663
125.283
123.987
123.576
65.563
24.536
N
ppm (t1)
200
150
100
50
0

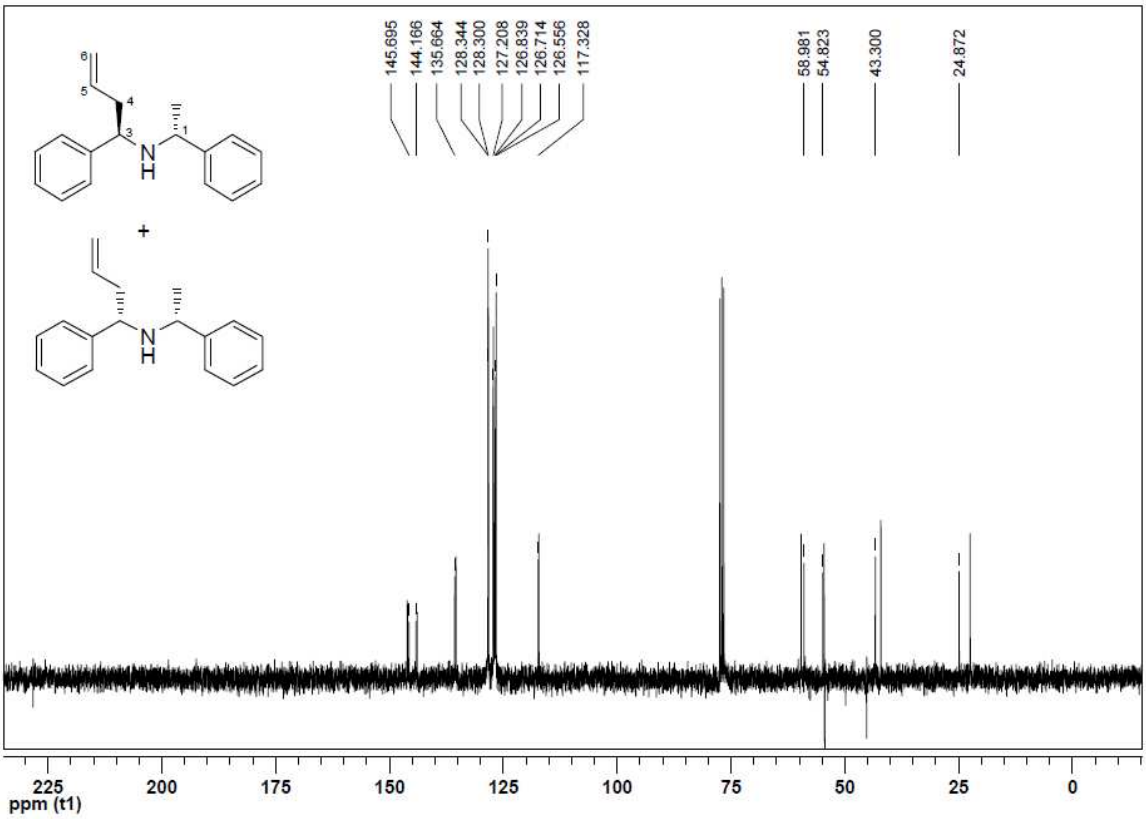

1.00
1.98
13.68
1.03
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)


160.754
143.840
136.247
130.733
128.492
128.428
128.401
127.629
126.943
77.870
200
175
150
125
100
75
50
25
0
ppm (t1)


10.68
1.00
2.14
2.24
2.10
1.03
3.36
ppm (t1)


146.042
143.901
135.384
128.294
128.240
127.156
126.831
126.706
126.548
117.179
59.589
54.523
42.070
22.464
ppm (t1)


10.86
1.00
2.17
0.74
0.74
1.55
1.16
2.32
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)


145.695
144.166
135.664
128.344
128.300
127.208
126.839
126.714
126.556
117.328
58.981
54.823
43.300
24.872
225
200
175
150
125
100
75
50
25
0
ppm (t1)