Supporting Information

Visible-Light-Mediated Addition of α-Aminoalkyl Radicals Generated from α-Silylamines to α,β-Unsaturated Carbonyl Compounds

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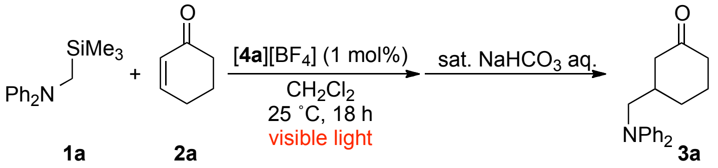
General Method.

^{1}H NMR (270 MHz) and ^{13}C NMR (67.8 MHz) spectra were recorded on a JEOL Excalibur 270 spectrometer in suitable solvent. Mass spectra were measured on a JEOL JMS-700 mass spectrometer. GC-MS analyses were carried out on a Shimazu GC-MS QP-5000 spectrometer. Gel permeation chromatography (GPC) was performed using a JAI model LC-908-G30 recycling preparative HPLC equipped wtih JAIGEL-1H and 2H with chloroform as eluent. Absorption spectra was recorded on Shimazu MultiSpec-1500 spectrometer. All reactions were carried out under dry nitrogen atmosphere. Solvents were dried by the general methods, and degassed before use. Photoirradiation was carried out with 14 W white LED (400 nm to 750 nm). α-Silylmines were prepared according to the literature procedures.[S1] α,β-Unsaturated carbonyl compounds except for 3-(3-methylpent-4-enoyl)oxazolidin-2-one, which was prepared according to the literature procedure,[S2] are commercially available.

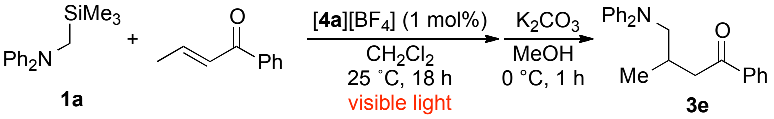
Photocatalytic Reactions of α-Silylamines (1) with α,β-Unsaturated Carbonyl Compounds (2).

Procedure for the synthesis of **3a**, **3b**, **3c**, **3d**, **3g**, **3h**, **3i**, **3j**, and **3n** are as follows.



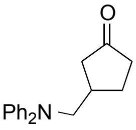
A typical experimental procedure for the reaction of diphenyl(trimethylsilylmethyl)amine (**1a**) with 2-cyclohexenone (**2a**) is described below. In a 20 mL Schlenk flask (diameter: 2.5 cm) were placed [**4a**][BF$_4$] (2.6 mg, 0.0030 mmol) and dichloromethane (2.5 mL) under N$_2$, and then **1a** (63.4 mg, 0.248 mmol) and **2a** (35.8 mg, 0.372 mmol) were added. The reaction flask was placed in a water bath and illuminated with 14W white LED (approximately 2 cm from the light source) at 25 °C for 18 h. The solution was poured into sat. NaHCO$_3$ aq. (20 mL) and the resulting mixture was extracted with dichloromethane (10 mL x 3). The combined organic layer was dried over anhydrous Na$_2$SO$_4$ and concentrated in vacuo. The residue was purified by column chromatography (SiO$_2$) with hexane/ethyl acetate (95/5 to 93/7) to give 3-(diphenylaminomethyl)cyclohexanone (**3a**) as a pale yellow oil (61.9 mg, 0.222 mmol, 90% yield). ^{1}H NMR (C$_6$D$_6$) δ 7.14-7.07 (m, 4H), 6.89-6.82 (m, 6H), 3.23 (d, 2H, J = 7.0 Hz), 2.38-2.30 (m, 1H), 2.15-1.91 (m, 2H), 1.81-1.68 (m, 1H), 1.60-1.55 (m, 2H), 1.46-1.35 (m, 1H), 1.08-0.91 (m, 1H), 0.82-0.67 (m, 1H). ^{13}C NMR (C$_6$D$_6$) δ 207.8, 149.1, 129.6, 121.8, 121.6, 58.2, 45.7, 41.3, 37.9, 29.3, 24.8. HRMS (EI) Calcd. for $C_{19}H_{21}NO$ [M]: 279.1623. Found: 279.1620.

Procedure for the synthesis of **3e**, **3f**, **3k**, **3l**, and **3m** are as follows.



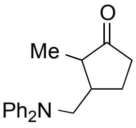
A typical experimental procedure for the reaction of diphenyl(trimethylsilylmethyl)amine (**1a**) with (*E*)-1-phenyl-2-buten-1-one is described below. In a 20 mL Schlenk flask (diameter: 2.5 cm) were placed [**4a**][BF_4] (2.3 mg, 0.0027 mmol) and dichloromethane (2.5 mL) under N_2, and then **1a** (62.7 mg, 0.245 mmol) and (*E*)-1-phenyl-2-buten-1-one (56.0 mg, 0.383 mmol) were added. The reaction flask was placed in a water bath and illuminated with 14W white LED (approximately 2 cm from the light source) at 25 °C for 18 h. The solvent was removed under reduced pressure, then methanol (2.5 mL) and potassium carbonate (69.0 mg, 0.499 mmol) were added. After stirring at 0 °C for 1 h, the solvent was removed under reduced pressure, and then acetic acid (100 μL) and dichloromethane (2.5 mL) was added. The solution was poured into sat. $NaHCO_3$ aq. (20 mL) and the resulting mixture was extracted with dichloromethane (10 mL x 3). The combined organic layer was dried over anhydrous Na_2SO_4 and concentrated in vacuo. The residue was was purified by column chromatography (SiO_2) with hexane/ethyl acetate (95/5) to give 4-(diphenylamino)-3-methyl-1-phenylbutan-1-one (**3e**) as a pale yellow oil (73.3 mg, 0.223 mmol, 91% yield). ^1H NMR (C_6D_6) δ 7.78-7.74 (m, 2H), 7.13-7.09 (m, 6H), 7.08-6.98 (m, 5H), 6.88-6.82 (m, 2H), 3.56 (dd, 1H, *J* = 14.7 and 7.4 Hz), 3.30 (dd, 1H, *J* = 14.7 and 7.6 Hz), 2.84 (dd, 1H, *J* = 15.9 and 5.5 Hz), 2.76-2.63 (m, 1H), 2.37 (dd, 1H, *J* = 15.9 and 7.6 Hz), 0.88 (d, 3H, *J* = 6.8 Hz). ^{13}C NMR (C_6D_6) δ 198.5, 149.3, 137.6, 132.6, 129.5, 128.6, 128.3, 121.9, 121.7, 58.5, 43.5, 29.0, 18.1. HRMS (EI) Calcd. for $C_{23}H_{23}NO$ [M]: 329.1780. Found: 329.1780.

Isolated yields and spectroscopic data of other products are as follows:



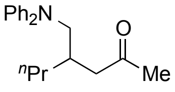
3b

3b: 79% Yield. A pale yellow oil. ^1H NMR (C_6D_6) δ 7.11-7.07 (m, 4H), 6.89-6.82 (m, 6H), 3.25 (d, 2H, *J* = 7.0 Hz), 2.24-2.06 (m, 1H), 1.99-1.77 (m, 2H), 1.64-1.34 (m, 3H), 1.02-0.85 (m, 1H). ^{13}C NMR (C_6D_6) δ 215.4, 148.9, 129.6, 121.9, 121.6, 56.9, 43.0, 37.8, 36.0, 27.3. HRMS (EI) Calcd. for $C_{18}H_{19}NO$ [M]: 265.1467. Found: 265.1476.



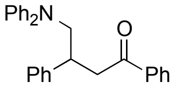
3c

3c: 63% Yield (isomeric ratio 15:1). A pale yellow solid. Major isomer: ^1H NMR (C_6D_6) δ 7.16-7.08 (m, 4H), 6.94-6.83 (m, 6H), 3.57 (dd, 1H, *J* = 14.8, and 5.1 Hz), 3.22 (dd, 1H, *J* = 14.8 and 8.5 Hz), 1.94-1.70 (m, 2H), 1.65-1.44 (m, 2H), 1.38-1.23 (m, 1H), 0.99 (d, 3H, *J* = 7.0 Hz), 0.91-0.74 (m, 1H). ^{13}C NMR (C_6D_6) δ 217.0, 149.0, 129.5, 121.8, 121.6, 56.9, 48.2, 43.5, 36.8, 26.5, 13.2. Minor isomer: ^{1}H NMR (C_6D_6) δ 3.46 (dd, 1H, J = 14.5 and 5.5 Hz), 3.15 (dd, 1H, J = 14.5 and 9.7 Hz), 0.76 (d, 3H, J = 7.6 Hz). ^{13}C NMR (C_6D_6) δ 129.6, 121.9, 121.7, 45.6, 38.5. HRMS (EI) Calcd. for $C_{19}H_{21}NO$ [M]: 279.1623. Found: 279.1612.



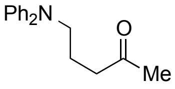
3d

3d: 69% Yield. A pale yellow oil. ^{1}H NMR (C_6D_6) δ 7.14-7.11 (m, 4H), 7.08-7.02 (m, 4H), 6.87-6.81 (m, 2H), 3.54 (dd, 1H, J = 14.4 and 7.7 Hz), 3.38 (dd, 1H, J = 14.4 and 7.2 Hz), 2.50-2.35 (m, 1H), 2.11 (dd, 1H, J = 16.9 and 6.2 Hz), 1.99 (dd, 1H, J = 16.9 and 6.3 Hz), 1.59 (s, 3H), 1.39-1.24 (m, 1H), 1.24-0.98 (m, 3H), 0.76 (t, 3H, J = 7.2 Hz). ^{13}C NMR (C_6D_6) δ 206.2, 149.4, 129.5, 121.9, 121.8, 56.5, 45.9, 34.6, 33.0, 29.8, 20.1, 14.4. HRMS (EI) Calcd. for $C_{20}H_{25}NO$ [M]: 295.1936. Found: 295.1949.



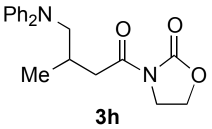
3f

3f: 52% Yield. A pale yellow oil. ^{1}H NMR (C_6D_6) δ 7.75-7.71 (m, 2H), 7.13-6.91 (m, 16H), 6.86-6.80 (m, 2H), 4.13-3.98 (m, 2H), 3.55-3.45 (m, 1H), 3.07 (dd, 1H, J = 17.1 and 7.3 Hz), 2.96 (dd, 1H, J = 17.1 and 6.1 Hz). ^{13}C NMR (C_6D_6) δ 197.7, 149.2, 143.2, 137.5, 132.7, 129.5, 128.6, 128.53, 128.45, 128.3, 126.9, 121.9, 121.8, 58.8, 42.5, 39.6. HRMS (EI) Calcd. for $C_{28}H_{25}NO$ [M]: 391.1936. Found: 391.1947.



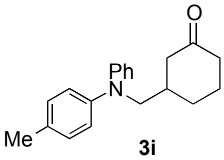
3g

3g: 56% Yield. A pale yellow oil. ^{1}H NMR (C_6D_6) δ 7.16-7.10 (m, 4H), 7.03-6.98 (m, 4H), 6.87-6.81 (m, 2H), 3.50-3.45 (m, 2H), 1.83-1.74 (m, 4H), 1.54 (s, 3H). ^{13}C NMR (C_6D_6) δ 205.8, 148.6, 129.6, 121.6, 121.4, 51.4, 40.0, 29.2, 21.8. HRMS (EI) Calcd. for $C_{17}H_{19}NO$ [M]: 253.1467. Found: 253.1454.



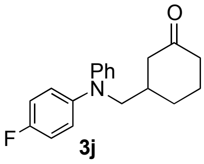
3h

3h: 91% Yield. A pale yellow oil. ^{1}H NMR (C_6D_6) δ 7.18-7.09 (m, 8H), 6.87-6.81 (m, 2H), 3.67 (dd, 1H, J = 14.5 and 6.8 Hz), 3.36 (dd, 1H, J = 14.5 and 7.7 Hz), 3.13-3.00 (m, 3H), 2.97-2.88 (m, 2H), 2.85-2.64 (m, 2H), 0.98 (d, 3H, J = 6.2 Hz). ^{13}C NMR (C_6D_6) δ 171.7, 153.2, 149.4, 129.5, 121.9, 121.7, 61.2, 58.5, 42.0, 40.1, 28.8, 18.2. HRMS (EI) Calcd. for $C_{20}H_{22}N_2O_3$ [M]: 338.1630. Found: 338.1641.



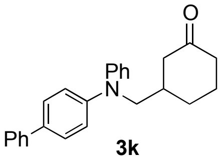
3i

3i: 87% Yield. A pale yellow oil. ^{1}H NMR (C_6D_6) δ 7.16-7.09 (m, 2H), 6.96-6.79 (m, 7H), 3.26 (d, 2H, J = 7.0 Hz), 2.41-2.33 (m, 1H), 2.13 (s, 3H), 2.09-1.89 (m, 2H), 1.82-1.70 (m, 1H), 1.63-1.54 (m, 2H), 1.49-1.37 (m, 1H), 1.12-0.95 (m, 1H), 0.89-0.71 (m, 1H). ^{13}C NMR (C_6D_6) δ 207.9, 149.6, 146.4, 132.4, 130.3, 129.4, 123.9, 120.4, 119.3, 58.3, 45.7, 41.3, 38.0, 29.4, 24.9, 20.7. HRMS (FAB) Calcd. for $C_{20}H_{24}NO$ [M+H]: 294.1858. Found: 294.1863.



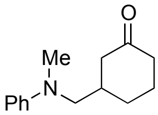
3j

3j: 79% Yield. A pale yellow oil. ^{1}H NMR (C_6D_6) δ 7.14-7.08 (m, 2H), 6.85-6.61 (m, 7H), 3.11 (d, 2H, J = 7.3 Hz), 2.35-2.28 (m, 1H), 2.16-2.08 (m, 1H), 2.00-1.71 (m, 2H), 1.59-1.37 (m, 3H), 1.12-0.95(m, 1H), 0.81-0.60 (m, 1H). ^{13}C NMR (C_6D_6) δ 207.8, 159.1 (d, $^1J_{C\text{-}F}$ = 241.4 Hz), 149.3, 145.0 (d, $^4J_{C\text{-}F}$ = 2.8 Hz), 129.5, 125.1 (d, $^3J_{C\text{-}F}$ = 7.9 Hz), 120.9, 119.5, 116.3 (d, $^2J_{C\text{-}F}$ = 22.3 Hz), 58.4, 45.6, 41.3, 37.8, 29.3, 24.8. HRMS (EI) Calcd. for $C_{19}H_{20}NOF$ [M]: 297.1529. Found: 297.1538.



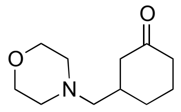
3k

3k: 82% Yield. A pale yellow oil. ^{1}H NMR (C_6D_6) δ 7.56-7.52 (m, 2H), 7.46-7.41 (m, 2H), 7.28-7.22 (m, 2H), 7.14-7.11 (m, 3H), 6.95-6.86 (m, 5H), 3.27 (d, 2H, J = 7.3 Hz), 2.41-2.33 (m, 1H), 2.16-1.95 (m, 2H), 1.83-1.70 (m, 1H), 1.64-1.54 (m, 2H), 1.49-1.36 (m, 1H), 1.14-0.95 (m, 1H), 0.91-0.71 (m, 1H). ^{13}C NMR (C_6D_6) δ 207.7, 148.9, 148.3, 141.3, 134.5, 129.7, 129.1, 128.2, 126.93, 126.91, 122.4, 122.3, 121.2, 58.2, 45.7, 41.3, 37.9, 29.4, 24.8. HRMS (FAB) Calcd. for $C_{25}H_{26}NO$ [M+H]: 356.2014. Found: 356.2002.



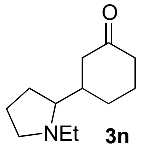
3l

3l: 70% Yield. A pale yellow oil. ^{1}H NMR (C_6D_6) δ 7.28-7.20 (m, 2H), 6.83-6.76 (m, 1H), 6.58-6.53 (m, 2H), 2.70 (d, 2H, J = 7.3 Hz), 2.47 (s, 3H), 2.25-2.09 (m, 2H), 1.89-1.70 (m, 2H), 1.55-1.30 (m, 3H), 1.15-0.97 (m, 1H), 0.77-0.58 (m, 1H). ^{13}C NMR (C_6D_6) δ 208.0, 149.8, 129.5, 116.8, 112.5, 58.5, 45.7, 41.3, 39.1, 38.1, 29.2, 25.0. HRMS (EI) Calcd. for $C_{14}H_{19}NO$ [M]: 217.1467. Found: 217.1475.



3m

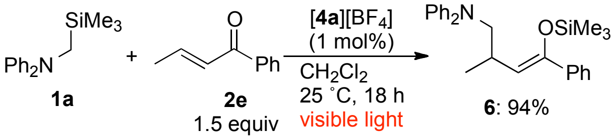
3m: 63% Yield. A pale yellow oil. ^{1}H NMR (C_6D_6) δ 3.54-3.51 (m, 4H), 2.46-2.34 (m, 1H), 2.26-2.16 (m, 1H), 2.03-2.00 (m, 4H), 1.92-1.71 (m, 3H), 1.66-1.49 (m, 4H), 1.39-1.17 (m, 1H), 0.94-0.77 (m, 1H). ^{13}C NMR (C_6D_6) δ 208.6, 67.0, 64.7, 54.3, 46.2, 41.6, 36.0, 29.6, 25.1. HRMS (EI) Calcd. for $C_{11}H_{19}NO_2$ [M]: 197.1416. Found: 197.1407.



3n

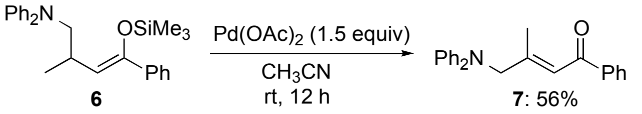
3n: 48% Yield. A pale yellow oil (isomeric ratio 1.8:1 determined by GC-MS). ^{1}H NMR (C_6D_6) δ 3.02-3.00 (m, 1H), 2.58-2.51 (m, 2H), 2.29-2.24 (m, 1H), 2.06-1.57 (m, 7H), 1.46-1.19 (m, 6H), 0.99-0.89 (m, 4H). ^{13}C NMR (C_6D_6) Major isomer: δ 209.5, 67.8, 53.6, 48.8, 45.8, 42.3, 41.7, 29.1, 25.9, 25.8, 23.2, 14.1. Minor isomer: δ 209.0, 67.8, 54.0, 49.3, 42.0, 41.7, 41.2, 26.3, 25.6, 25.5, 23.5, 14.1. HRMS (EI) Calcd. for $C_{12}H_{21}NO$ [M]: 195.1623. Found: 195.1619.

Photocatalytic Reaction of 1a with (*E*)-1-Phenyl-2-Buten-1-One into Silyl Enol Ether (6).



In a 20 mL Schlenk flask (diameter: 2.5 cm) were placed [**4a**][BF_4] (2.1 mg, 0.0025 mmol) and dichloromethane (2.5 mL) under N_2, and then **1a** (64.1 mg, 0.251 mmol) and (*E*)-1-phenyl-2-buten-1-one (54.8 mg, 0.375 mmol) were added. The reaction flask was placed in a water bath and illuminated with 14W white LED (approximately 2 cm from the light source) at 25 °C for 18 h. The solvent was removed under reduced pressure and the residue was extracted with *n*-hexane (10 mL). The extract was filtered through Celite and the filtrate was concentrated under reduced pressure. The residue was was purified by GPC with chloroform to give the silyl enol ether (**6**) as a pale yellow oil (94.4 mg, 0.235 mmol, 94% yield). ^{1}H NMR (C_6D_6) δ 7.47-7.43 (m, 2H), 7.19-7.08 (m, 11H), 6.89-6.83 (m, 2H), 4.96 (d, 1H, J = 9.2 Hz), 3.69 (dd, 1H, J = 14.1 and 6.2 Hz), 3.46 (dd, 1H, J = 14.1 and 8.2 Hz), 3.40-3.29 (m, 1H), 1.11 (d, 3H, J = 6.5 Hz), 0.01 (s, 9H). ^{13}C NMR (C_6D_6) δ 150.2, 149.3, 139.7, 129.5, 128.3, 127.9, 126.2, 121.8, 121.5, 115.3, 58.7, 30.5, 18.8, 0.5. HRMS (EI) Calcd. for $C_{26}H_{31}NOSi$ [M]: 401.2175. Found: 401.2186. The structure on the alkene moiety of **6** was determined to be (*Z*) structure by the NOE measurements.

Reaction of 6 with Pd(OAc)$_2$.



In a 20 mL Schlenk flask were placed **6** (86.6 mg, 0.216 mmol) and acetonitrile (2.2 mL) under air, and then Pd(OAc)$_2$ (72.6 mg, 0.323 mmol) was added. The reaction mixture was stirred at room temperature for 12 h. The solution was poured into sat. $NaHCO_3$ aq. (20 mL) and the resulting mixture was extracted with dichloromethane (10 mL x 3). The combined organic layer was dried over anhydrous $MgSO_4$ and concentrated in vacuo. The residue was purified by column chromatography (SiO_2) with hexane/ethyl acetate (98/2 to 90/10) to give the corresponding α,β-unsaturated ketone **7** as colorless crystals (mp 100.8-102.1 °C) (39.7 mg, 0.121 mmol, 56% yield). ^{1}H NMR (C_6D_6) δ 7.84-7.79 (m, 2H), 7.13-6.93 (m, 12H), 6.87-6.81 (m, 2H), 3.983-3.980 (m, 2H), 2.006-2.002 (m, 3H). ^{13}C NMR (C_6D_6) δ 190.6, 152.9, 148.0, 139.6, 132.2, 129.6, 128.53, 128.50, 121.9, 120.8, 120.7, 59.7, 17.1. HRMS (EI) Calcd. for $C_{23}H_{21}NO$ [M]: 327.1623. Found: 327.1624. The structure on **7** was determined by X-ray analysis.

Determination of Quantum Yield.

When the quantum yield of a photochemical reaction was determined, the reaction mixture was irradiated using an Ushio high pressure mercury lamp USH-250SC (250 W) with an 440 nm band-pass filter (Kenko B-440 filter). The irradiated light intensity was estimated to 1.02 x 10^{-7} einstein s^{-1} by using $K_3[Fe(C_2O_4)_3]$ as an actinometer.[S3] The initial reaction rate of **1a** with 1.5 equiv of (*E*)-1-phenyl-2-buten-1-one in the presence of 1 mol% of [**4a**][BF_4] in 2.5 mL of dicloromethane (6.91 x 10^{-8} mol s^{-1}) was converted to quantum yield (Φ = 0.68).

Photoirradiation Source

We have confirmed that the range of wavelength of the white LED used in this paper is 400 nm to 750 nm according to the irradiation spectrum of the white LED (Figure S1). This fact indicates that the effect of UV light is negligible in our reaction system. In addition, as describe above, when the quantum yield of a photochemical reaction was determined, we used Hg lamp with a 440 nm band-pass filter. In this case, the reaction proceeded smoothly to give the adduct. This result also supports that our reaction reported in this paper is mediated by only visible-light irradiation effectively. Separately, we confirmed that no reaction occurred at all when the reaction flask was placed under a household ceiling light.

X-ray Diffraction Study of 7. Diffraction data for **7** were collected for the 2θ range of 6 to 55° at –90 °C on a Rigaku R-AXIS RAPID imaging plate area detector with graphite monochromated Mo Kα (λ = 0.71075 Å) radiation with VariMax optics. Intensity data were corrected for empirical absorptions and for Lorentz and polarization effects. Friedel pairs were averaged, thus Flack parameter was not refined. The structure solution and refinements were carried out by using CrystalStructure package.[S4] The positions of non-hydrogen atoms were determined by direct methods (SHELXS97)[S5] and subsequent Fourier syntheses (DIRDIFF-99),[S6] and were refined on F_o^2 using all the unique reflections by full-matrix least squares with anisotropic thermal parameters. All the hydrogen atoms were placed at the calculated positions with fixed isotropic parameters. Goodness of fit indicator $[\Sigma w(|F_o| - |F_c|)^2/(N_{obs} - N_{params})]^{1/2}$ was refined to the value of 1.000. Anomalous dispersion effects were included in F_c, and neutral atom scattering factors and the values for $\Delta f'$ and $\Delta f''$ were taken from ref. S7. An ORTEP drawing of **7** is depicted in Figure S2. Details of the crystal and data collection parameters are summarized in Table S1

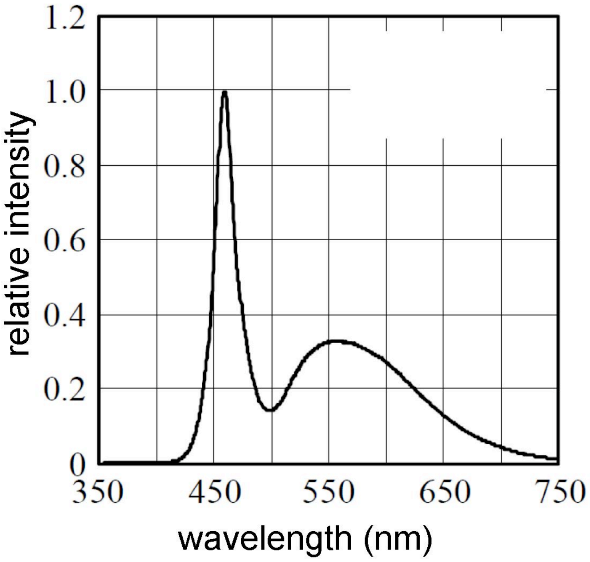


Figure S1. Irradiation Spectrum of the White LED

Table S1. Crystallographic Data for **7**.

	7
chemical forumula	$C_{23}H_{21}NO$
formula weight	327.43
crystal size	0.50 × 0.08 × 0.02
crystal color, habit	colorless, needle
temperature (°C)	–90
crystal system	orthorhombic
space group	$Pca2_1$ (no. 29)
a (Å)	17.419(7)
b (Å)	10.587(5)
c (Å)	9.567(4)
α (deg)	90
β (deg)	90
γ (deg)	90
V (Å^3)	1764.5(13)
Z	4
D_{calcd} (g cm^{-3})	1.232
F(000)	696
μ_{calcd} (cm^{-1})	0.747
transmission factors range	0.235–0.999
no. measured reflections	12689
no. unique reflections	2145
R_{int}	0.01223
no. refined parameters	247
$R1$ ($I > 2\sigma(I)$)[a]	0.1192
$wR2$ (all data)[b]	0.1060
max/min residual peaks (e$^-$/Å^3)	+0.807/–0.715

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$.

[b] $wR2 = [\Sigma(w(F_o^2 - F_c^2)^2)/\Sigma w(F_o^2)^2]^{1/2}$; $w = 4F_o^2/[2.605\sigma(F_o^2)]$.

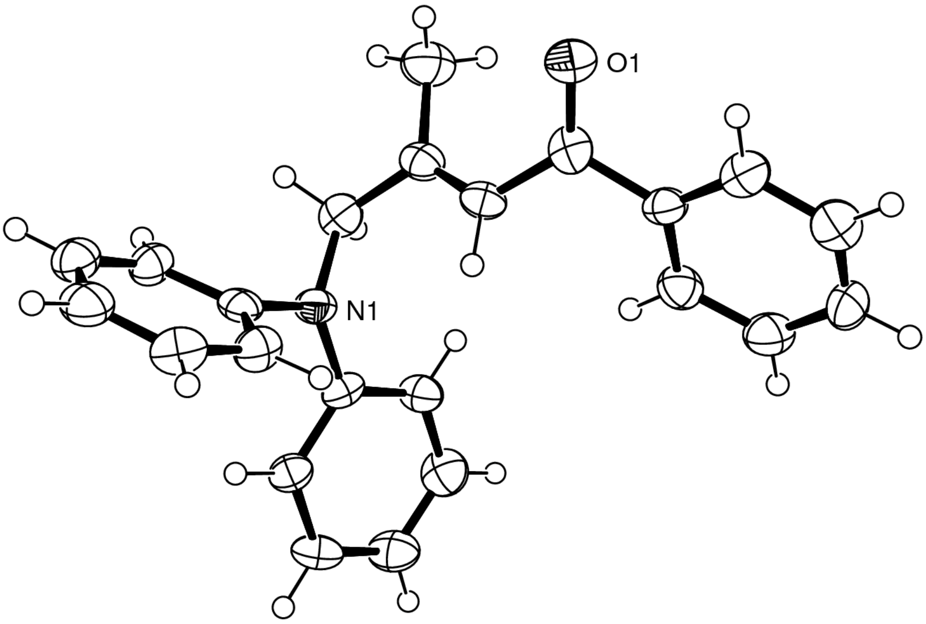


Figure S2. An ORTEP Drawing of **7**. Thermal ellipsoids are given at the 50% probability level

References.

[S1] (a) Ashweek, N. J.; Brandt, P.; Coldham, I.; Dufour, S.; Gawley, R. E.; Hæffner, F.; Klein, R.; Sanchez-Jimenez, G. *J. Am. Chem. Soc.* **2005**, *127*, 449. (b) Zhang, X.-M.; Mariano, P. S. *J. Org. Chem.* **1991**, *56*, 1655. (c) Sato, Y.; Aoyama, T.; Shirai, H. *J. Organomet. Chem.* **1974**, *82*, 21.

[S2] Nakamura, T.; Oshida, M.; Nomura, T.; Nakazaki, A.; Kobayashi, S. *Org. Lett.* **2007**, *9*, 5533.

[S3] Calvert, J. G.; Pitts, J. N. *Photochemistry*; Wiley and Sons: New York, 1996.

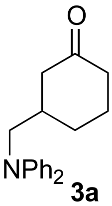
[S4] (a) *CrystalStructure 4.0*: *Single Crystal Structure Analysis Software*; Rigaku Corp: Tokyo, Japan and MSC: The Woodlands, TX, 2010. (b) Carruthers, J. R.; Rollett, J. S.; Betteridge, P. W.; Kinna, D.; Pearce, L.; Larsen, A.; Gabe, E. *CRYSTALS Issue 11*; Chemical Crystallography Laboratory: Oxford, UK, 1999.

[S5] Sheldrick, G. M. *Acta Crystallogr*., *Sect. A* **2008**, *64*, 112.

[S6] Beurskens, P. T.; Beurskens, G.; de Gelder, R.; García-Granda, S.; Gould, R. O.; Israël, R.; Smits, J. M. M. *The DIRDIF-99 program system*; Crystallography Laboratory, University of Nijmegen: Nijmegen, The Netherlands, 1999.

[S7] (a) Cromer, D. T.; Waber, J. T. *International Tables for X-ray Crystallography*; Ibers, J. A., Hamilton, W. C. Eds.; Kynoch Press: Birmingham, England, 1974; Vol. IV., Table 2.2 A. (b) Creagh, D. C.; Hubbell, J. H. *International Tables for X-ray Crystallography*; Wilson, A. J. C. Ed.; Kluwer Academic Publishers: Boston, MA, 1992; Vol. (c) Creagh, D. C.; McAuley, W. J. *International Tables for X-ray Crystallography*; Wilson, A. J. C. Ed.; Kluwer Academic Publishers: Boston, MA, 1992; Vol. C. Table 4.2.6.8.

^{1}H and ^{13}C NMR spectra.



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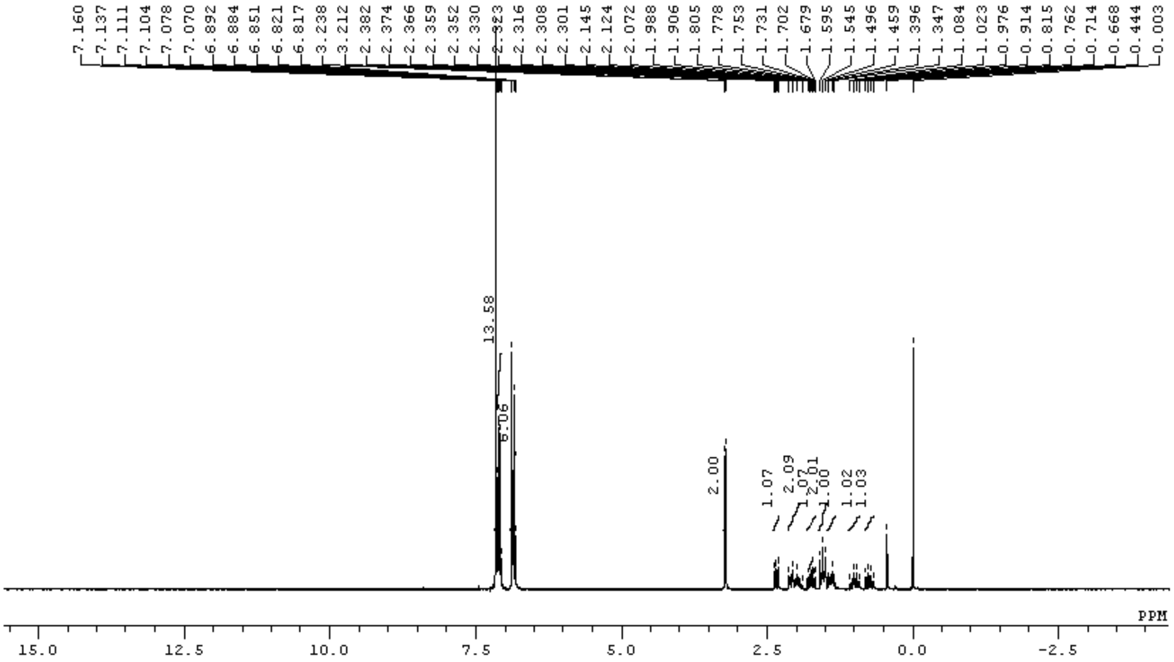

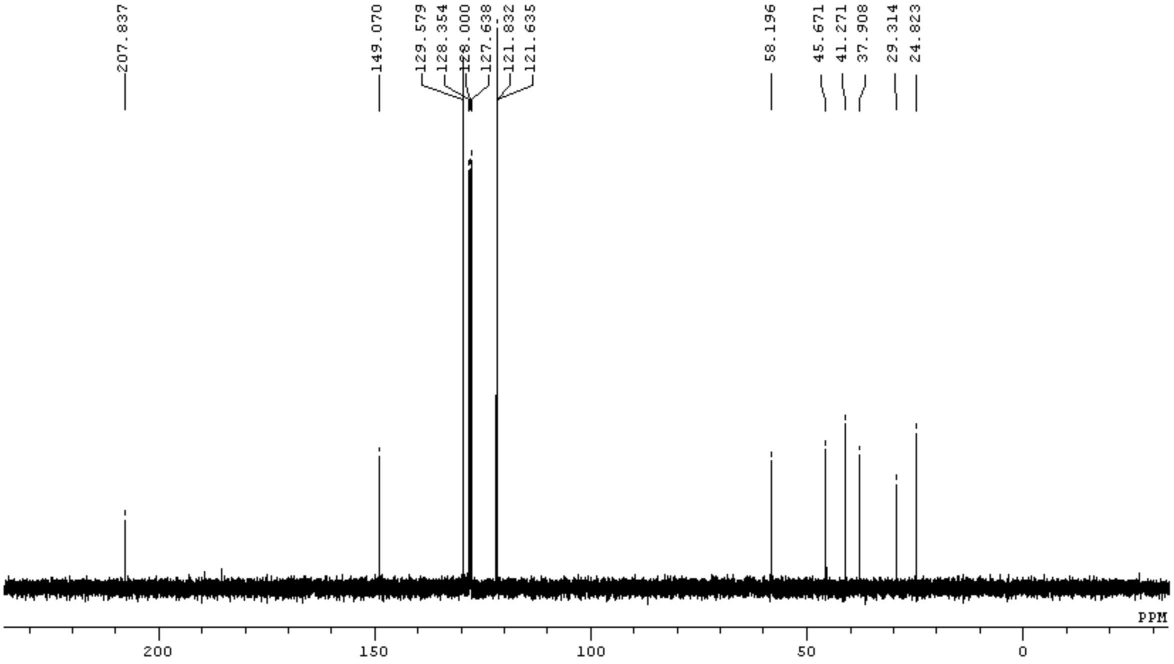

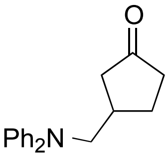
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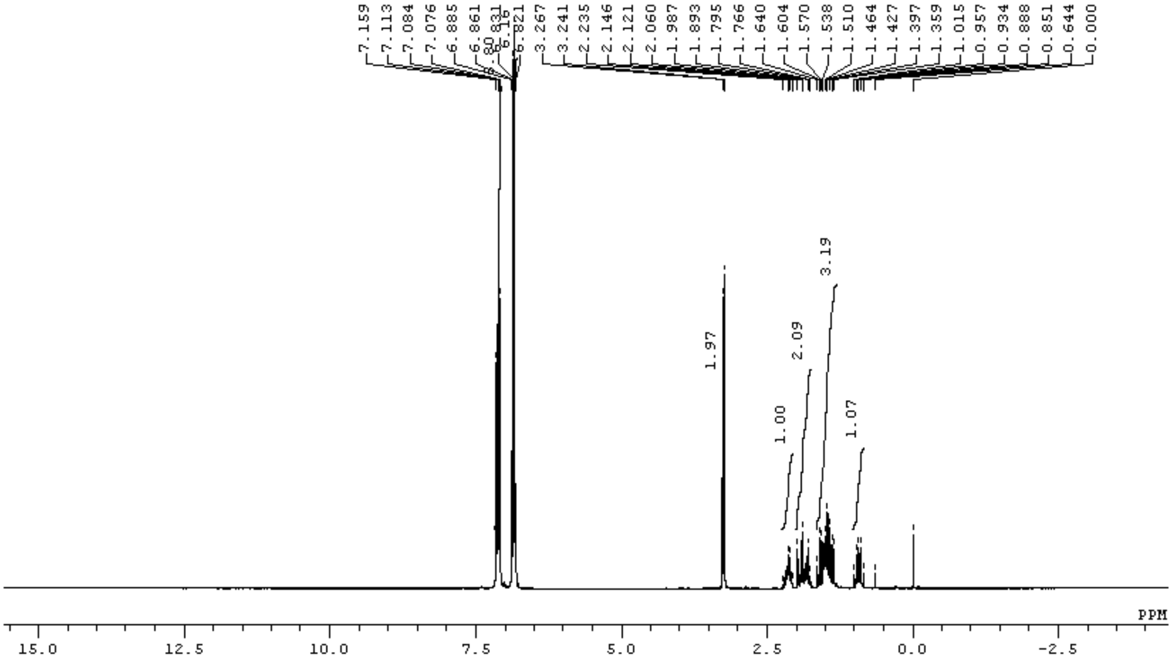
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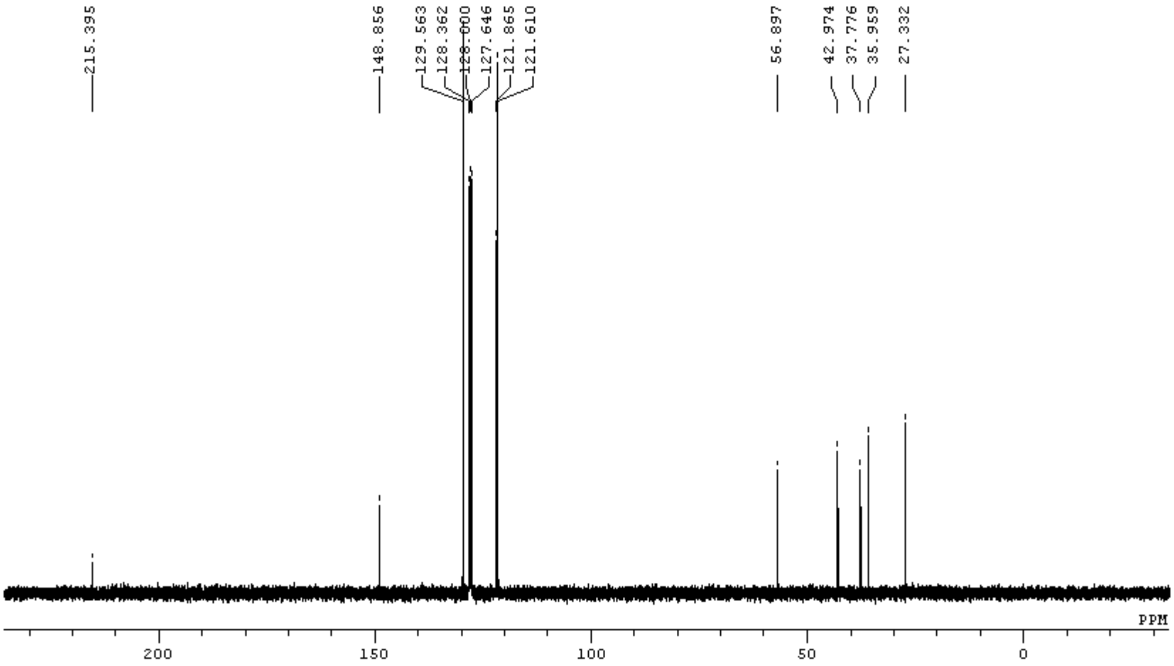
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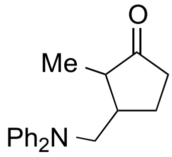
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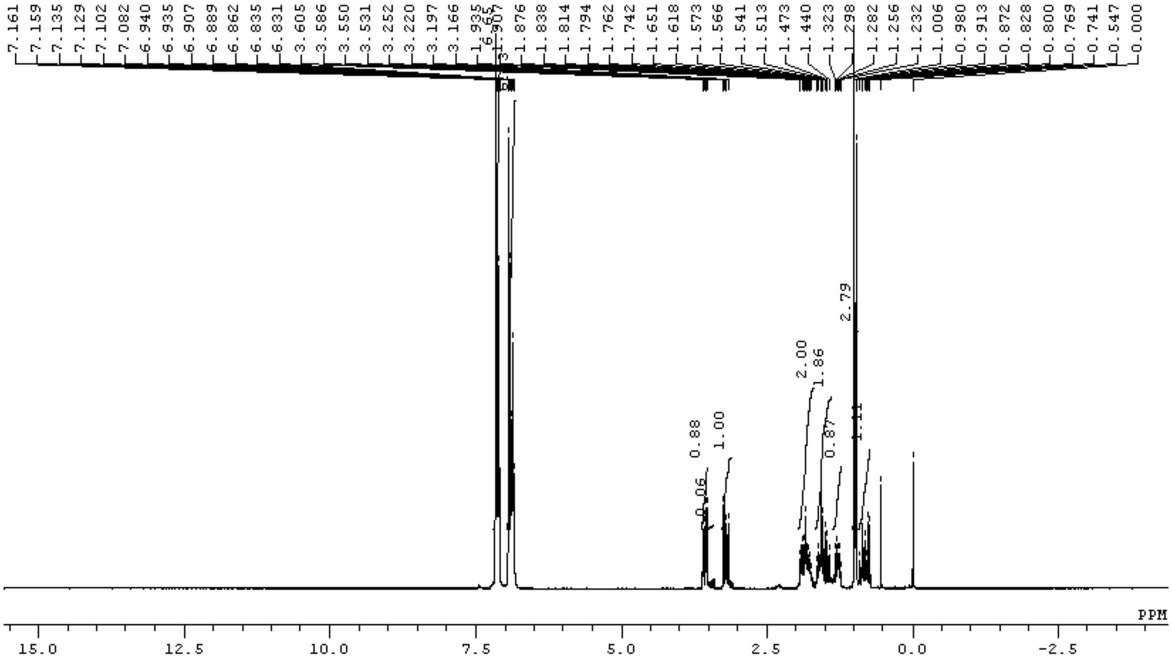
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3.252
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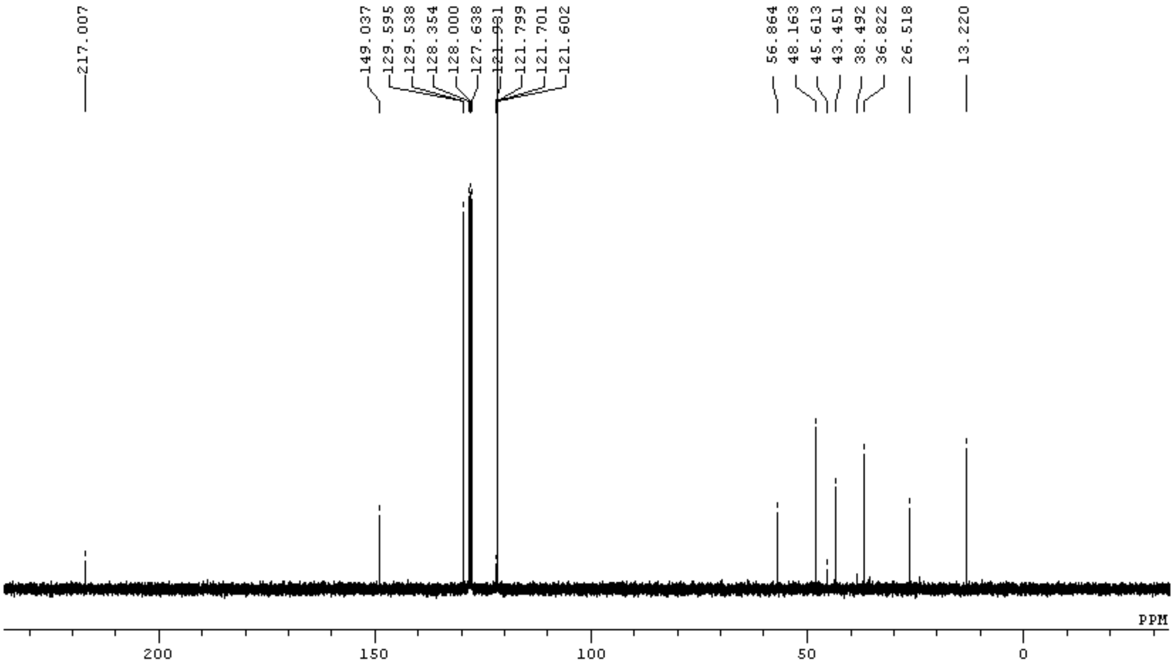
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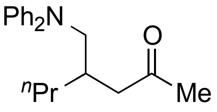
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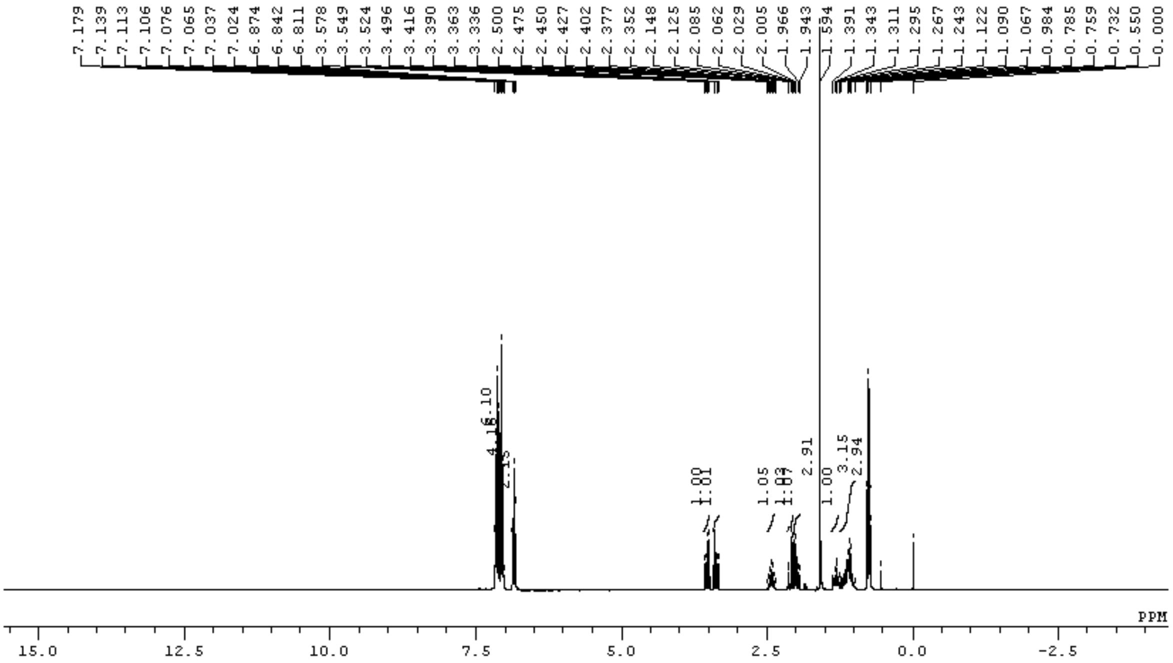
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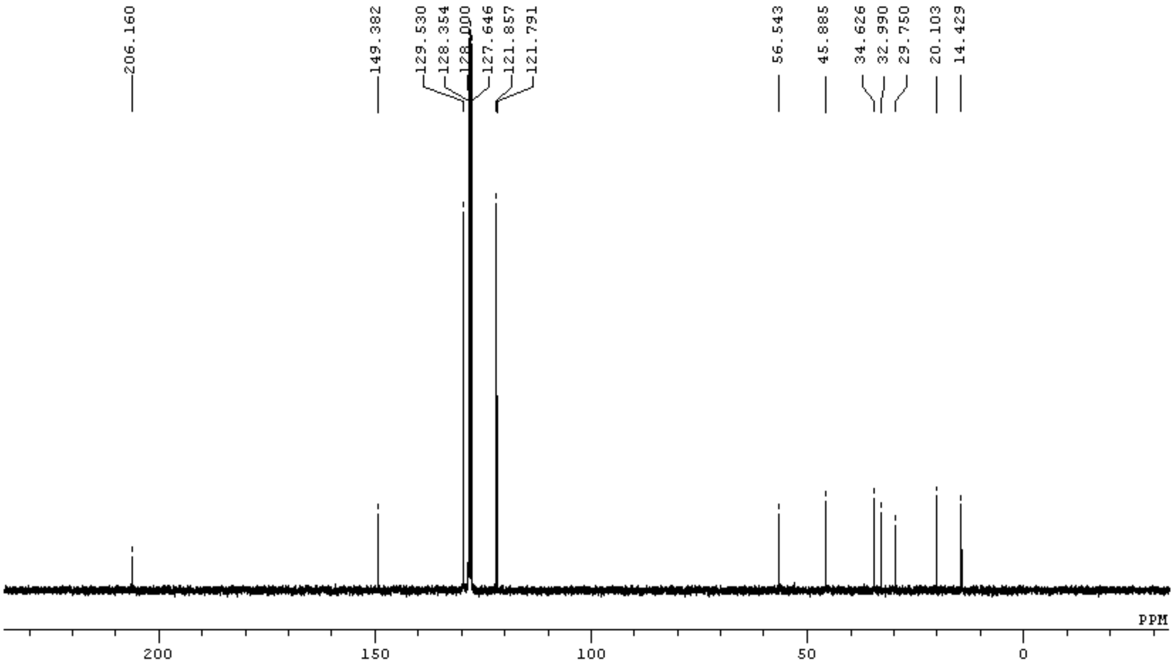
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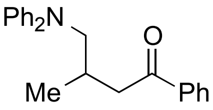
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Ph

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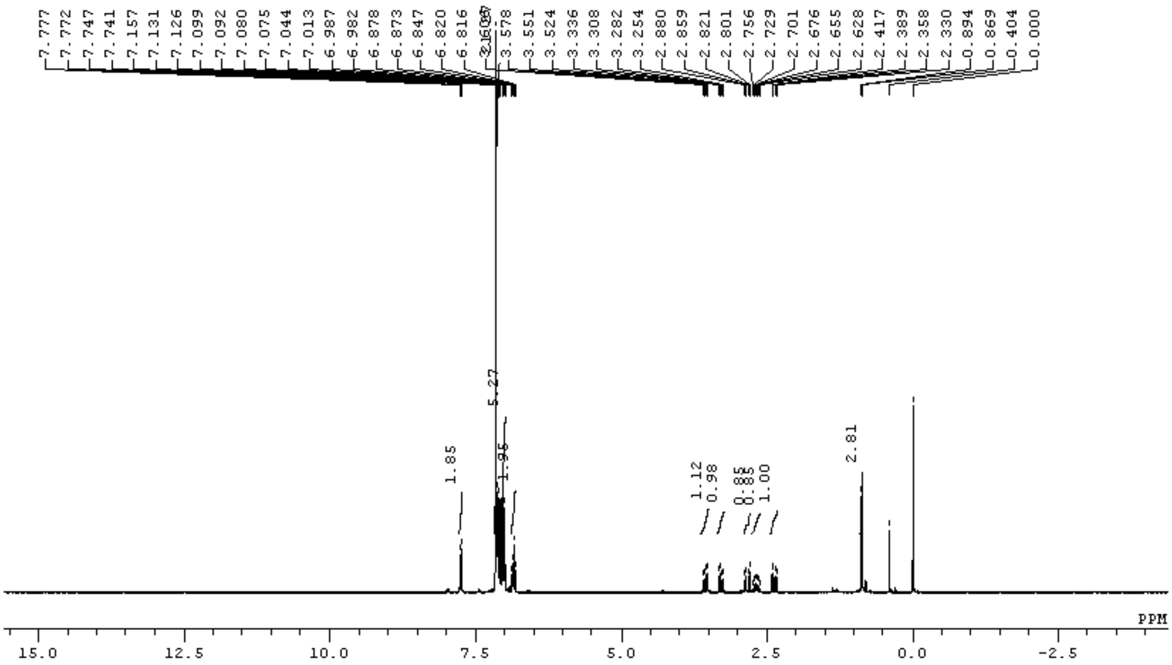
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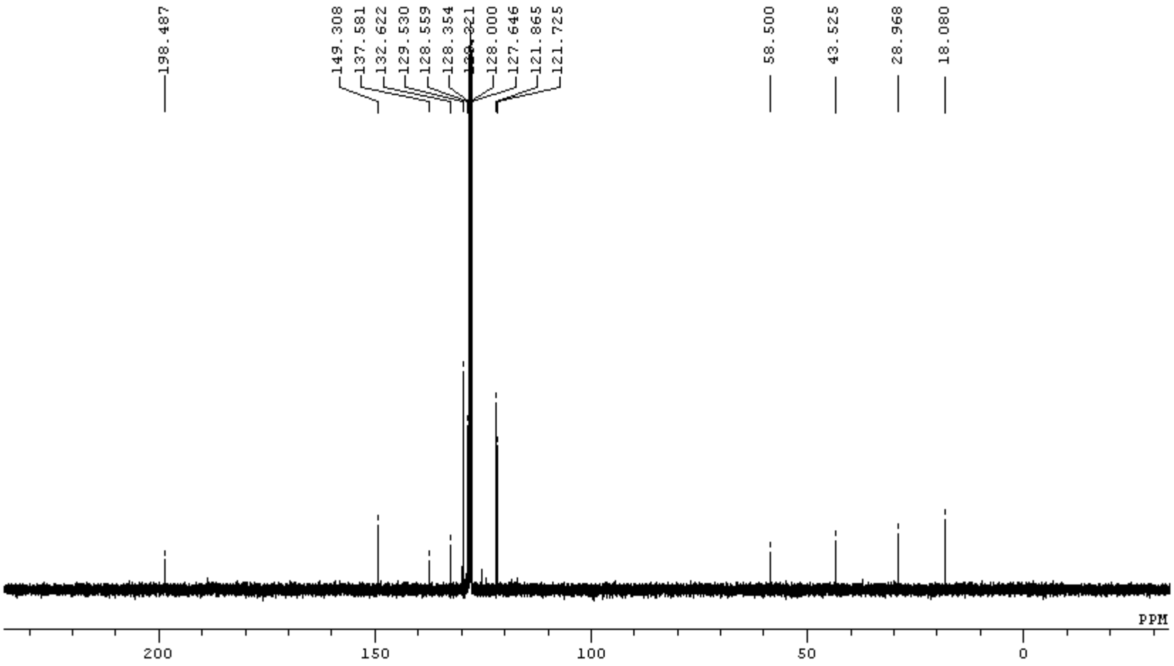
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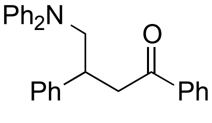
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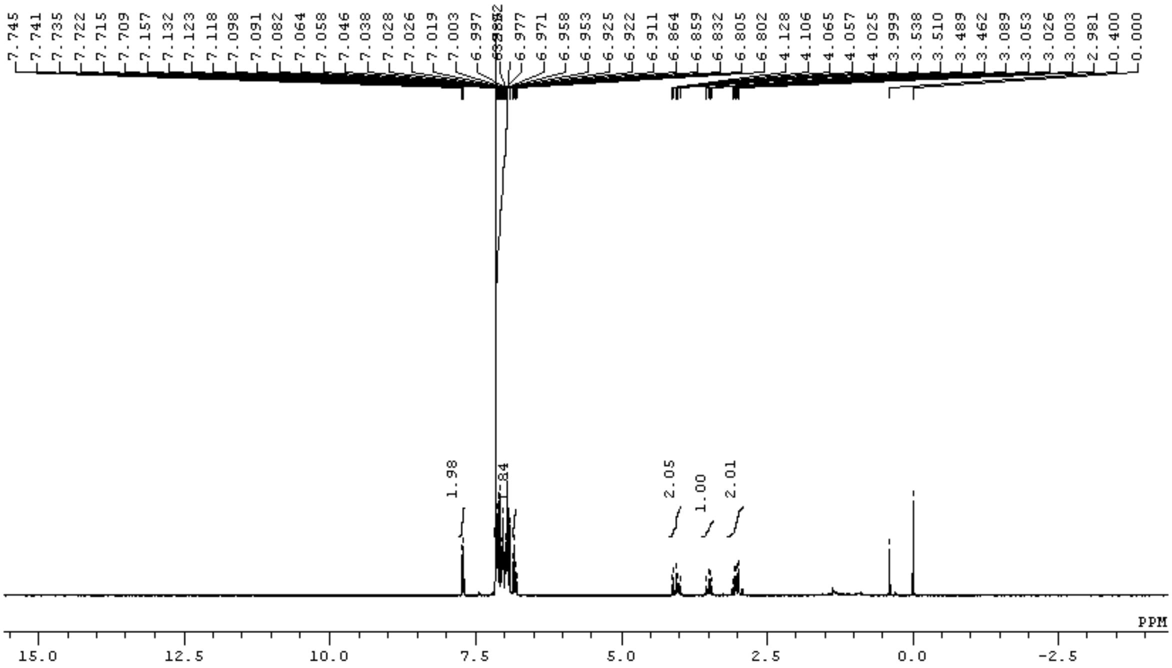
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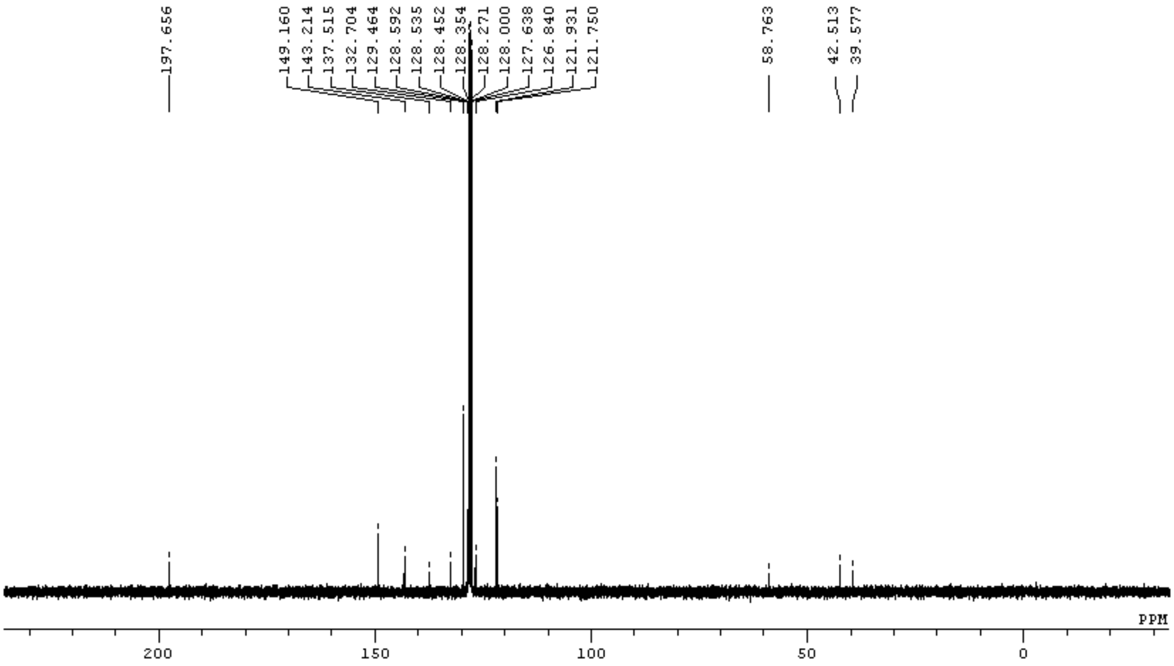
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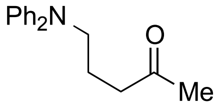
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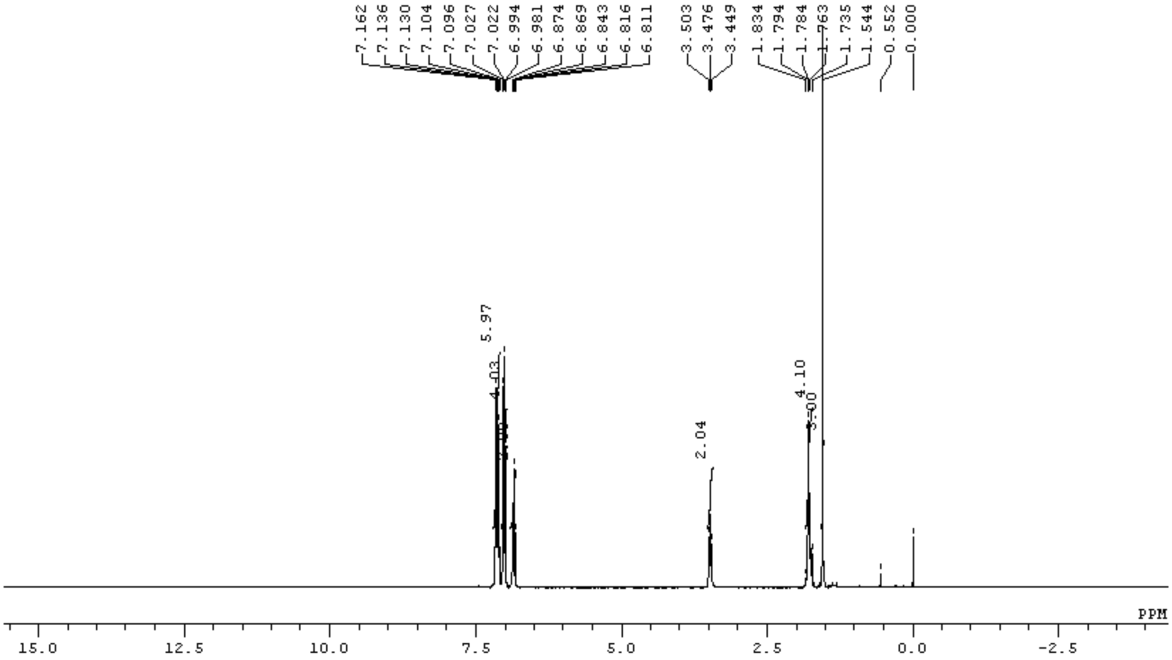
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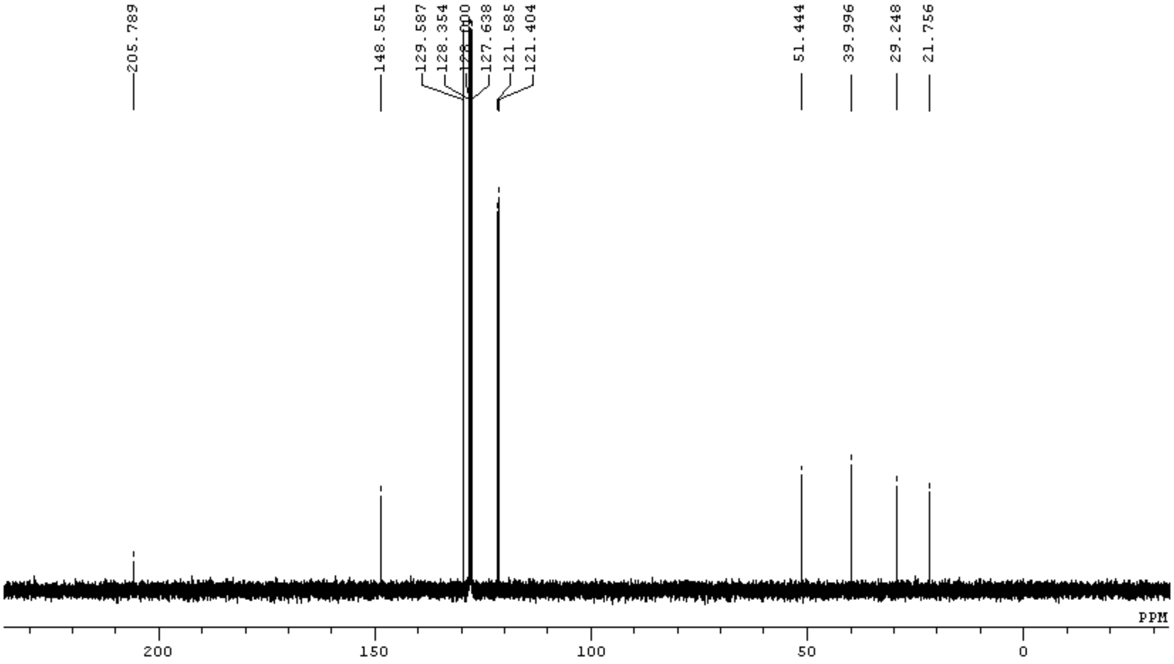
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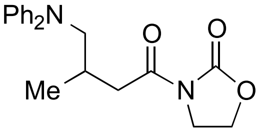
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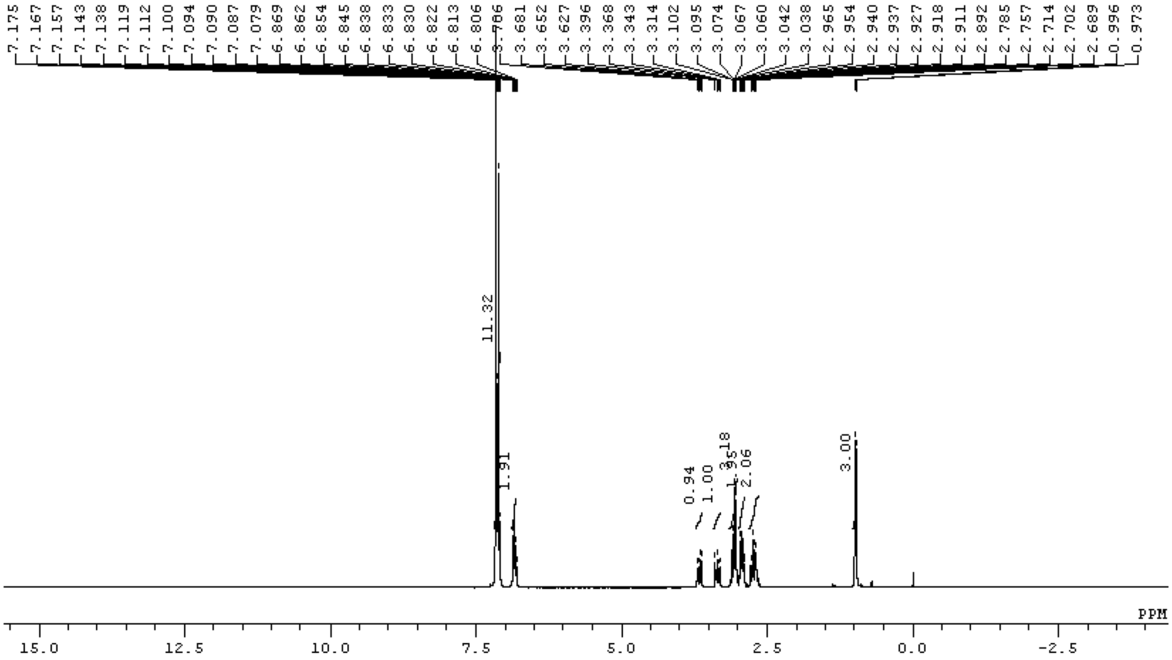
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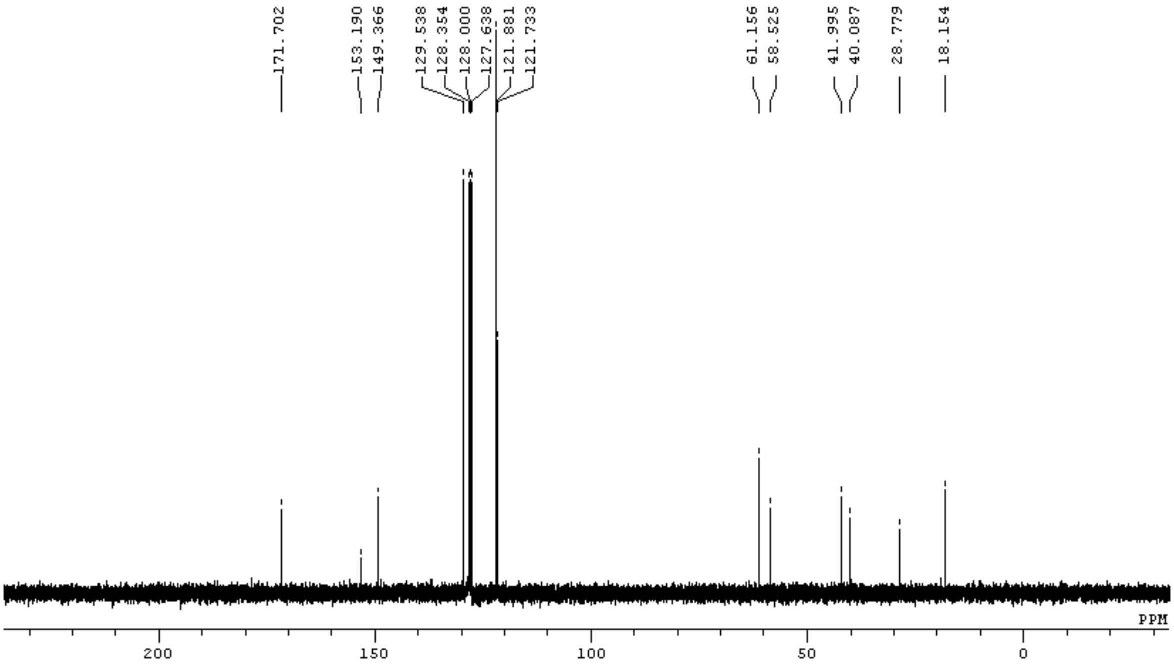
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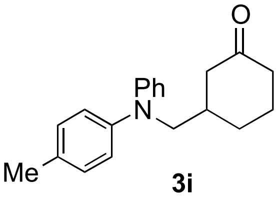
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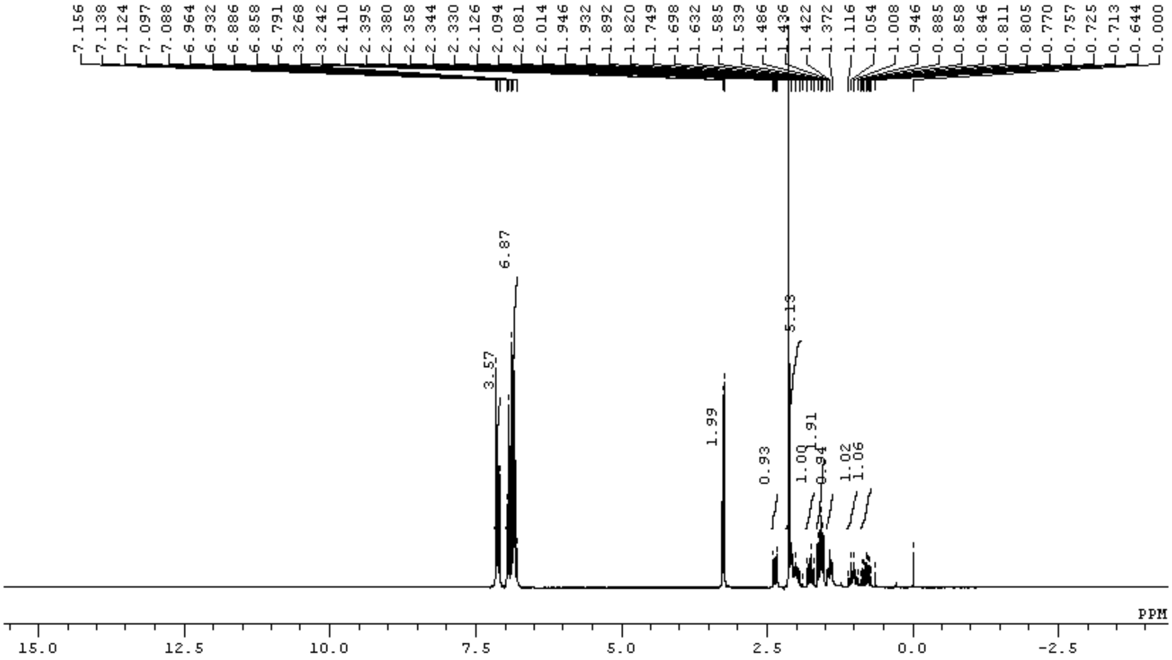
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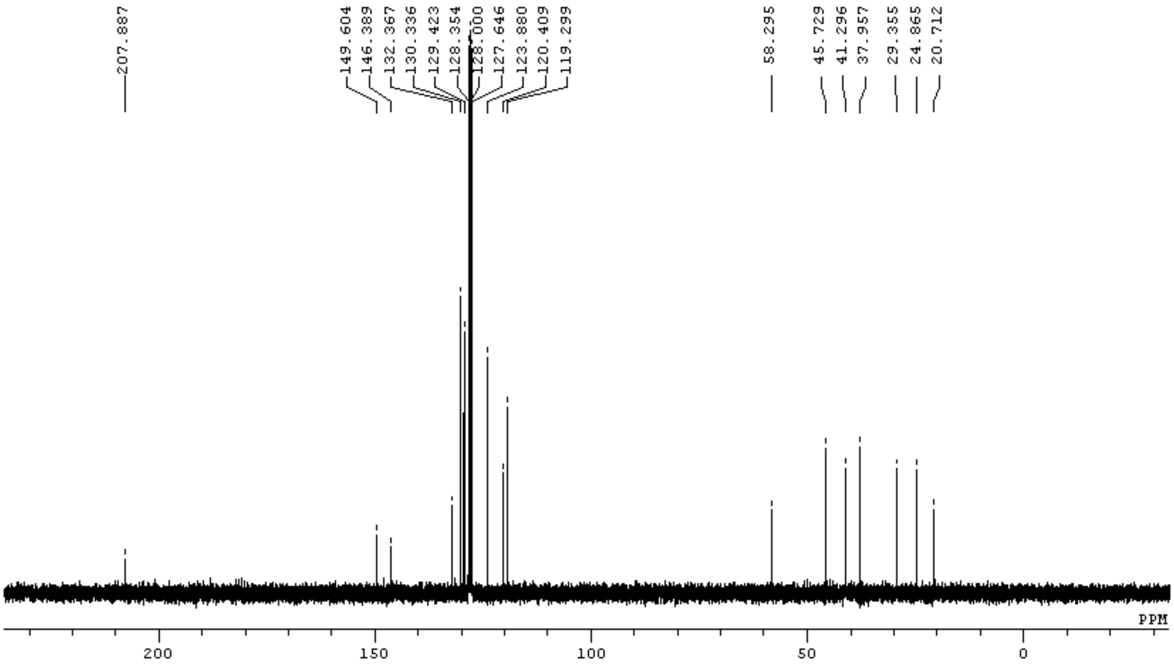
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PPM
200
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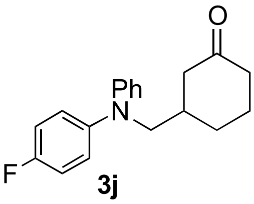
O
Ph
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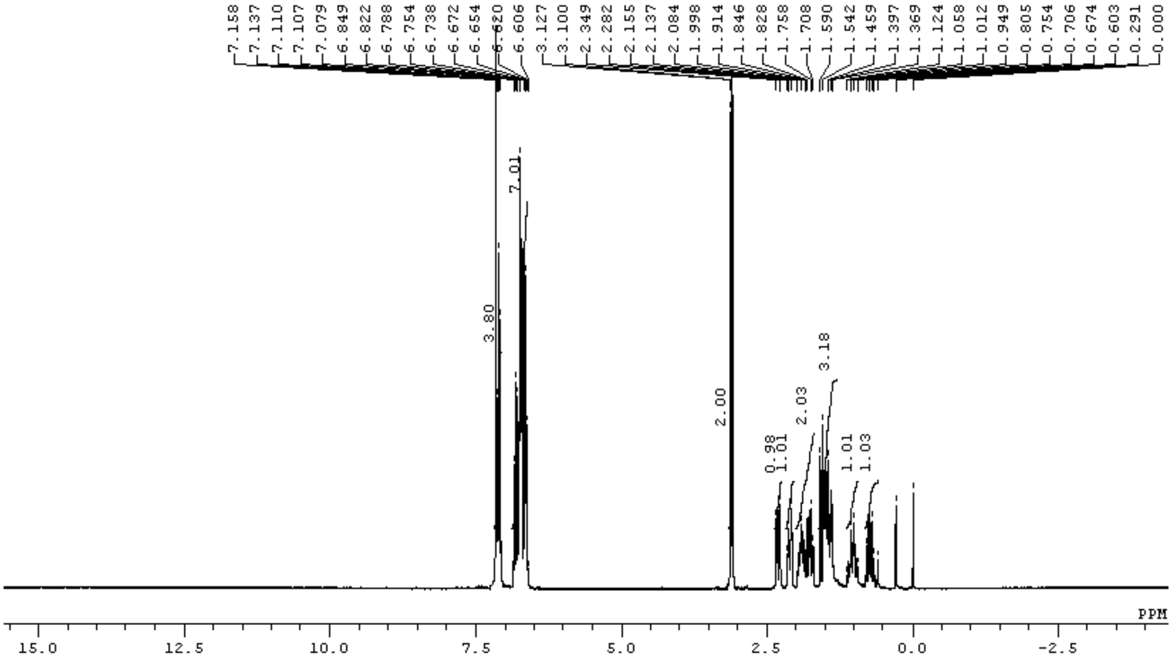
F

3j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6.606
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3.100
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2.155
2.137
2.084
1.998
1.914
1.846
1.828
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1.708
1.590
1.542
1.459
1.397
1.369
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1.058
1.012
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0.754
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2.00
0.98
1.01
2.03
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1.03
PPM
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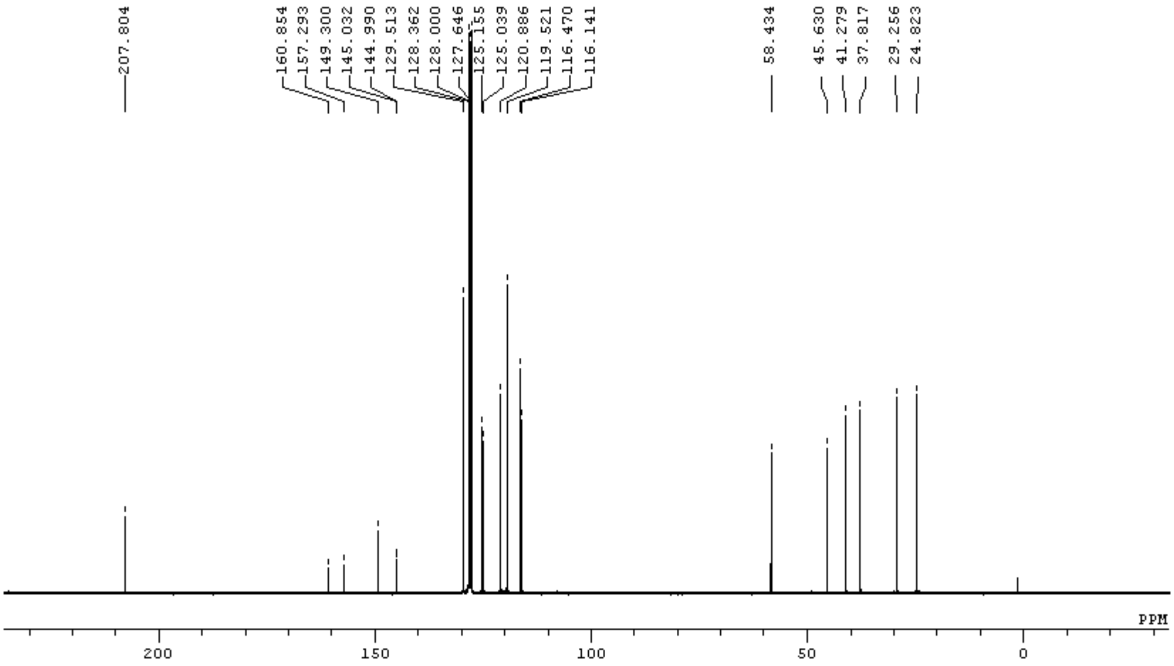
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128.362
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120.886
119.521
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45.630
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37.817
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24.823
PPM
200
150
100
50
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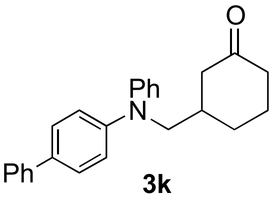
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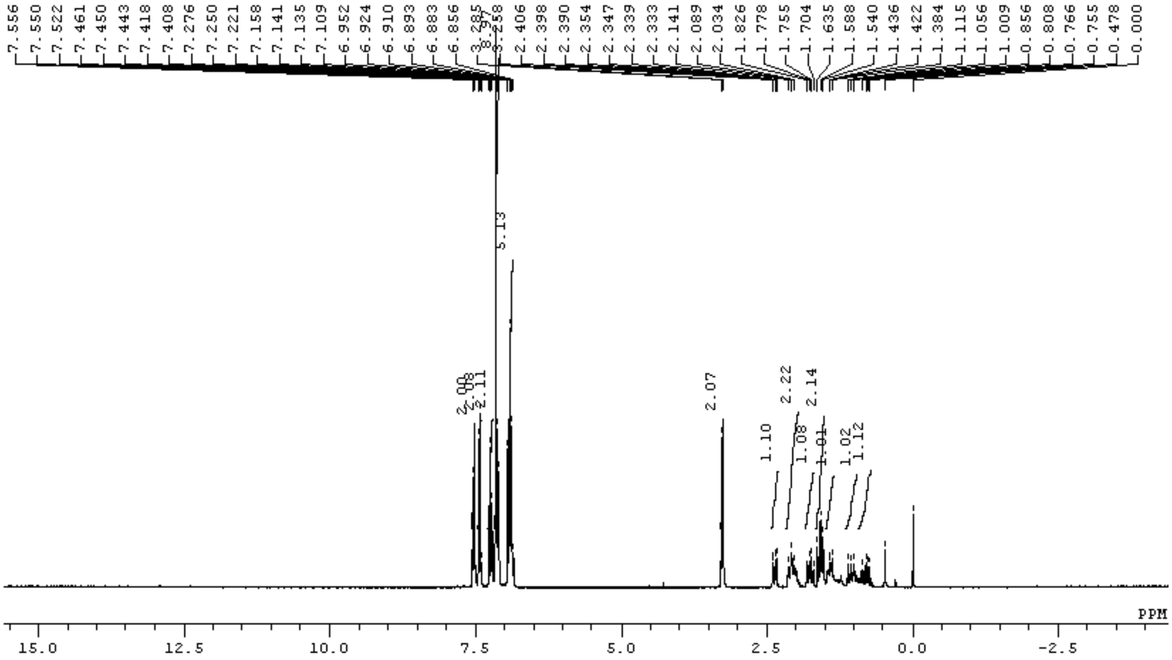
Ph
N
Ph

3k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7.141
7.135
7.109
6.952
6.924
6.910
6.893
6.883
6.856
3.285
3.258
2.406
2.398
2.390
2.354
2.347
2.339
2.333
2.141
2.089
2.034
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1.778
1.755
1.704
1.635
1.588
1.540
1.436
1.422
1.384
1.115
1.056
1.009
0.856
0.808
0.766
0.755
0.478
0.000
2.00
2.08
2.11
8.97
5.13
2.07
1.10
2.22
1.08
2.14
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PPM
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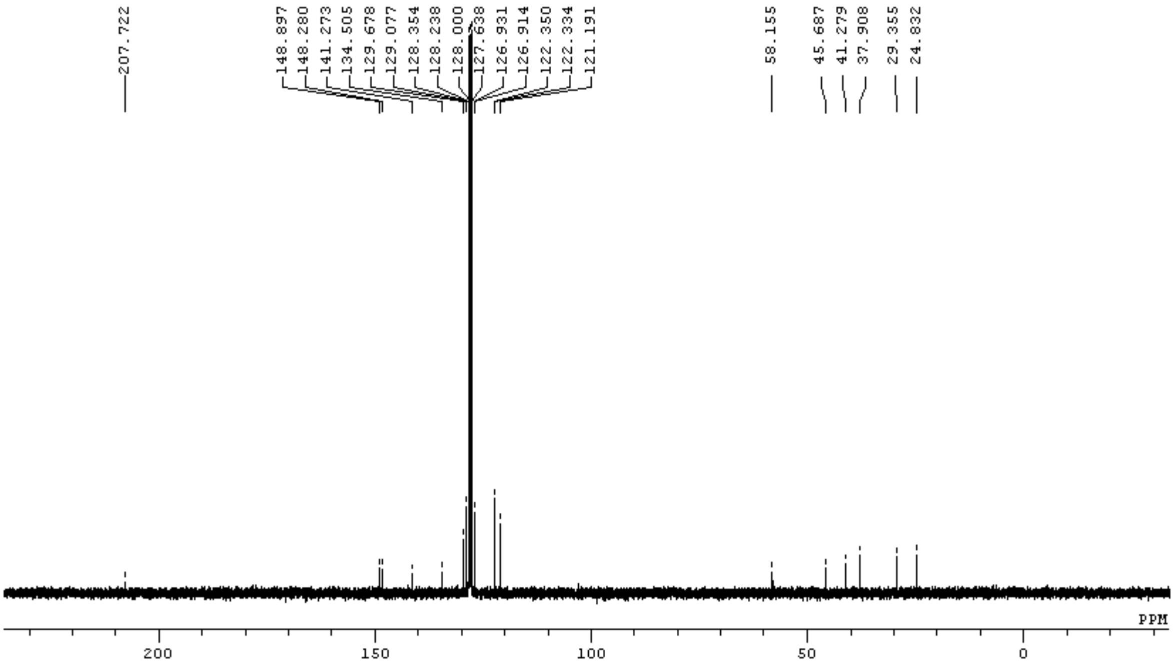
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126.914
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45.687
41.279
37.908
29.355
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150
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50
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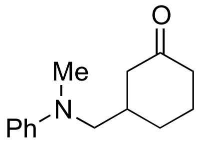
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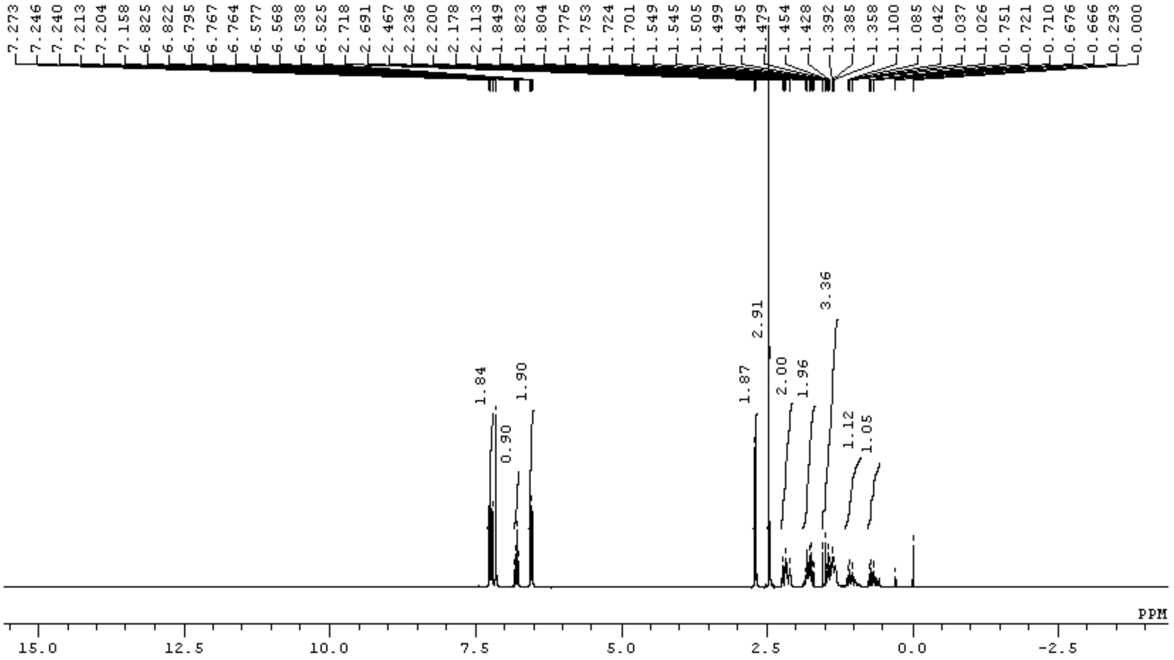
Me
N
Ph

3l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6.568
6.538
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2.691
2.467
2.236
2.200
2.178
2.113
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1.823
1.804
1.776
1.753
1.724
1.701
1.549
1.545
1.505
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1.495
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1.454
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1.392
1.385
1.358
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1.085
1.042
1.037
1.026
0.751
0.721
0.710
0.676
0.666
0.293
0.000
1.84
0.90
1.90
1.87
2.91
2.00
1.96
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1.05
PPM
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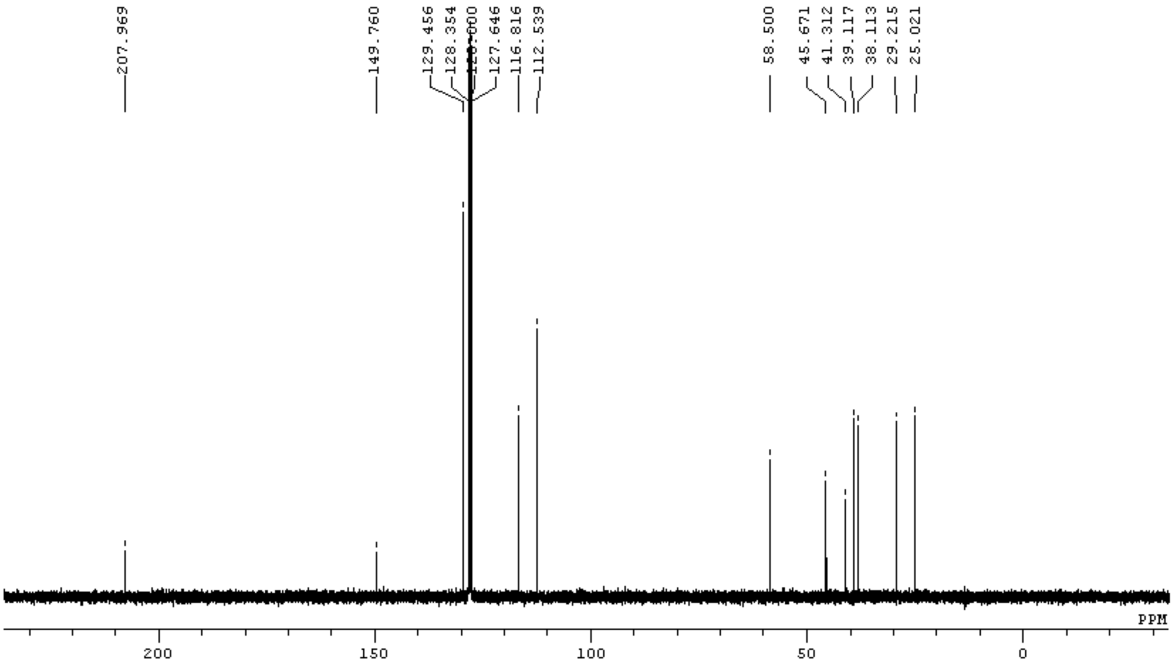
12.5
10.0
7.5
5.0
2.5
0.0
-2.5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PPM
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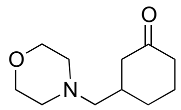
150
100
50
0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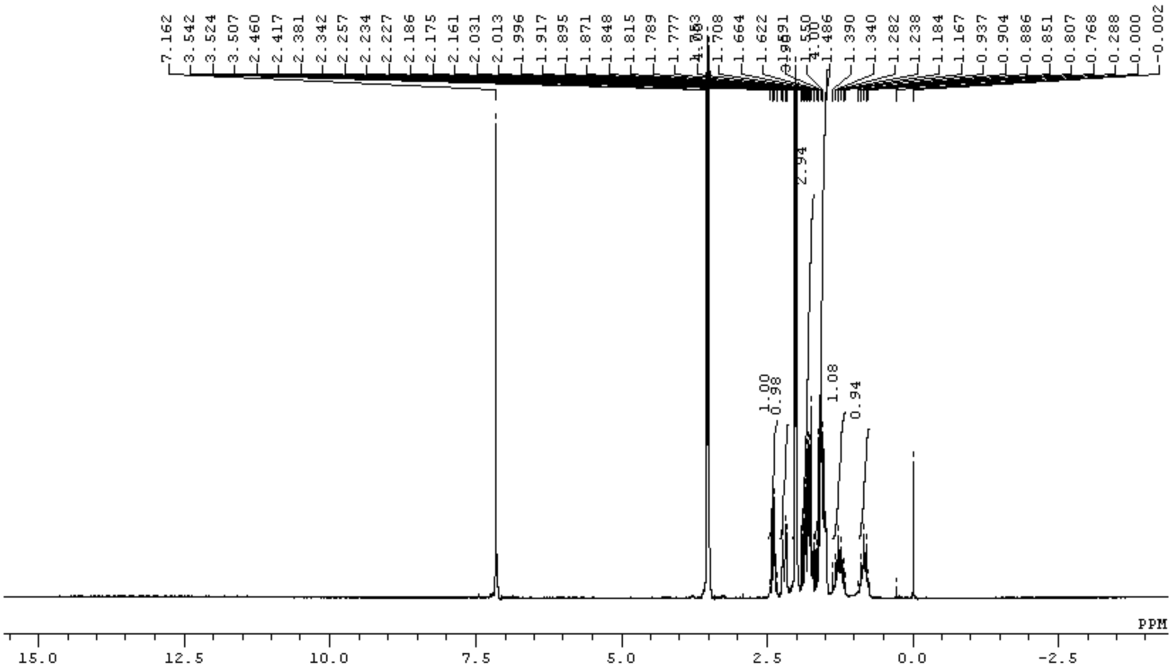
O
N

3m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2.175
2.161
2.031
2.013
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1.917
1.895
1.871
1.848
1.815
1.789
1.777
1.708
1.664
1.622
1.550
1.486
1.390
1.340
1.282
1.238
1.184
1.167
0.937
0.904
0.886
0.851
0.807
0.768
0.288
0.000
-0.002
2.94
1.00
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0.94
PPM
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12.5
10.0
7.5
5.0
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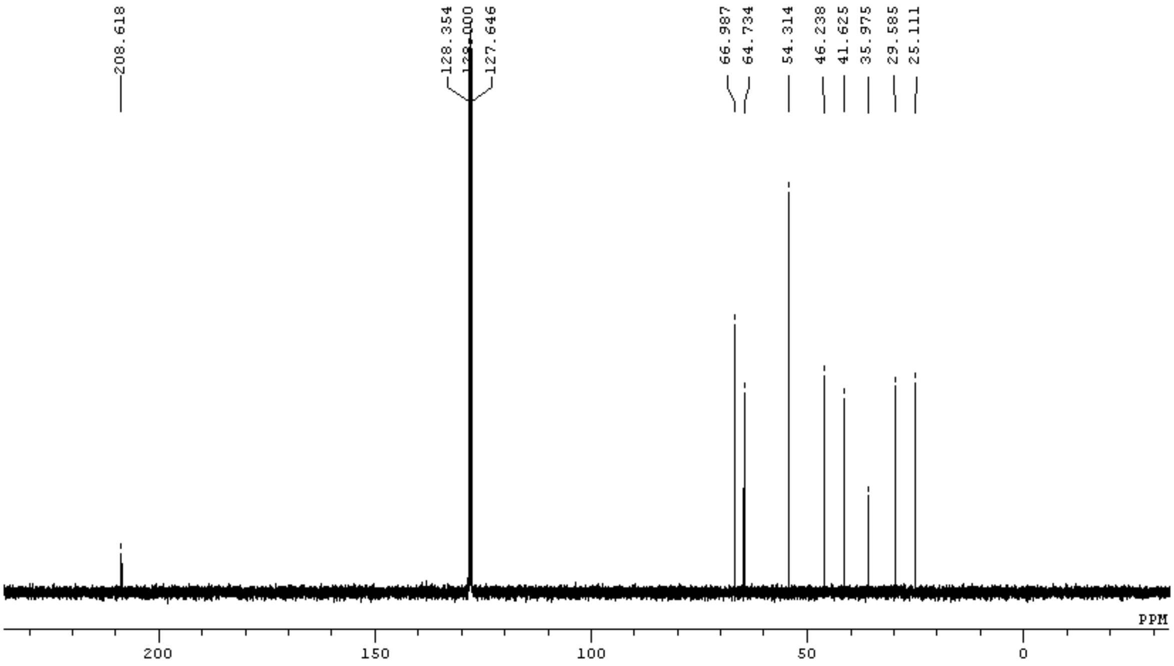
0.0
-2.5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46.238
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35.975
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25.111
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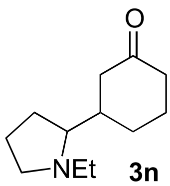
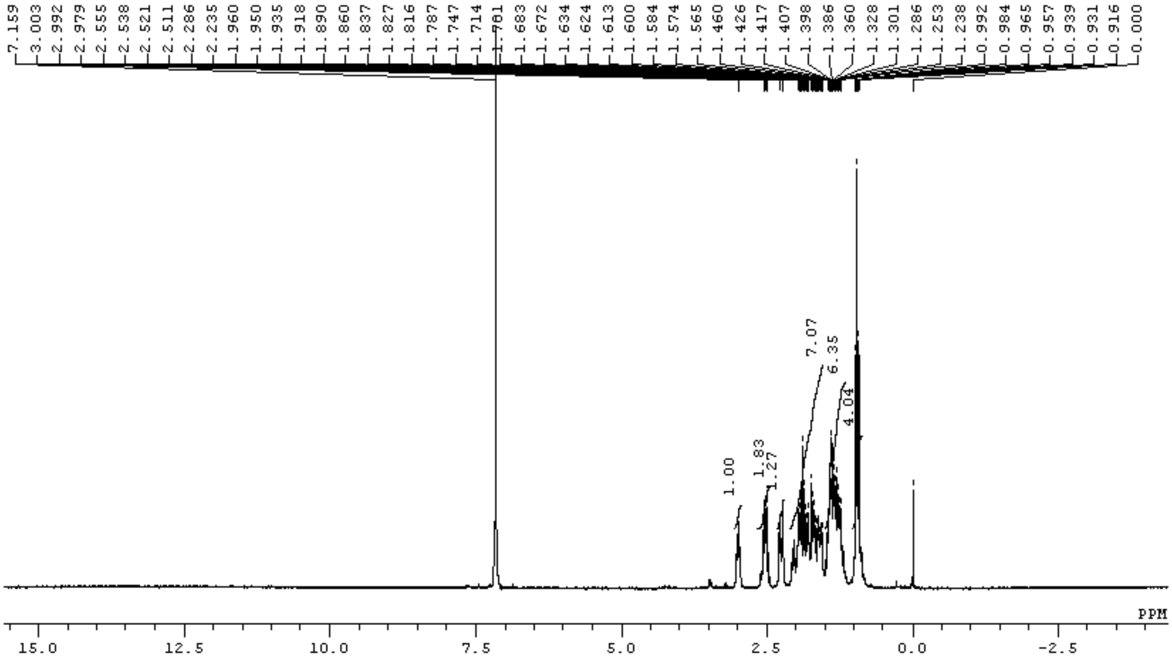
150
100
50
0


O
NEt

3n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1.935
1.918
1.890
1.860
1.837
1.827
1.816
1.787
1.747
1.714
1.701
1.683
1.672
1.634
1.624
1.613
1.600
1.584
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1.360
1.328
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1.286
1.253
1.238
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0.965
0.957
0.939
0.931
0.916
0.000
1.00
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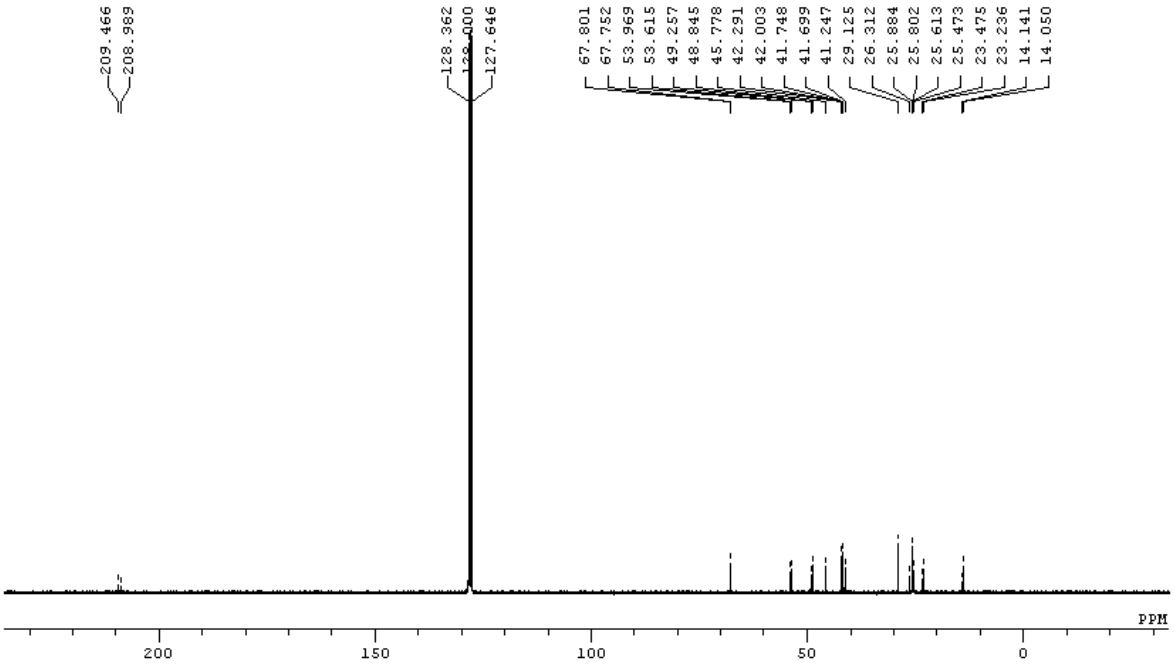
5.0
2.5
0.0
-2.5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29.125
26.312
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50
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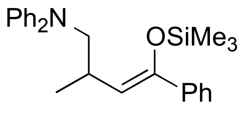
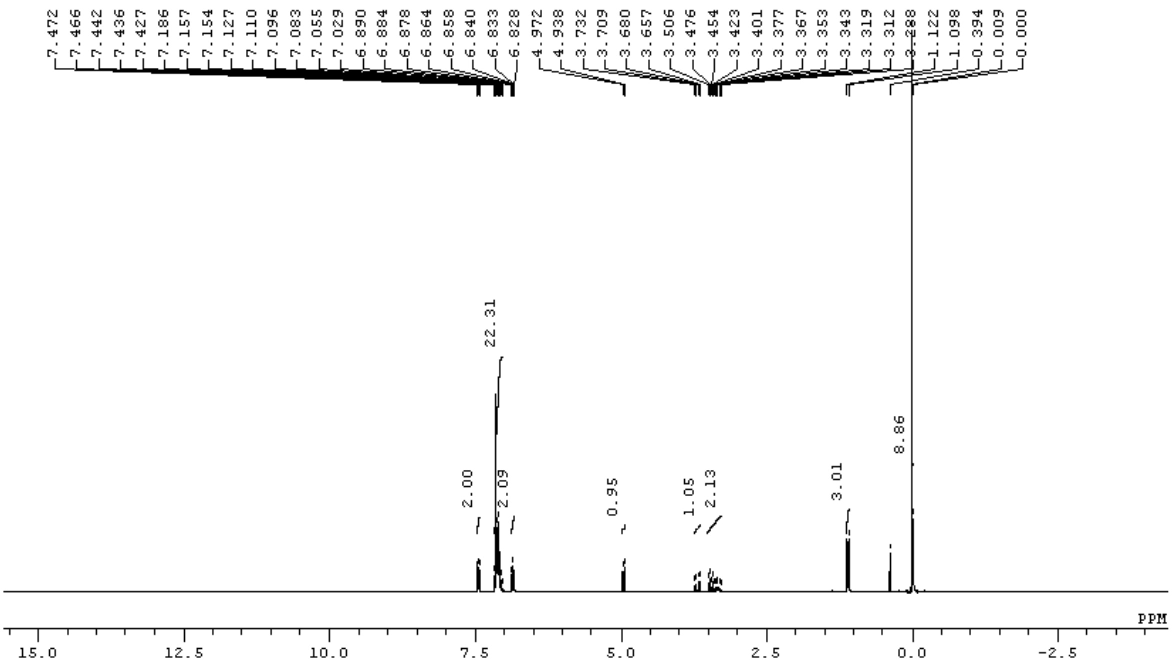

Ph2N
OSiMe3
Ph

6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7.157
7.154
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7.110
7.096
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7.055
7.029
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6.884
6.878
6.864
6.858
6.840
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6.828
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4.938
3.732
3.709
3.680
3.657
3.506
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3.454
3.423
3.401
3.377
3.367
3.353
3.343
3.319
3.312
3.288
1.122
1.098
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0.009
0.000
2.00
2.09
22.31
0.95
1.05
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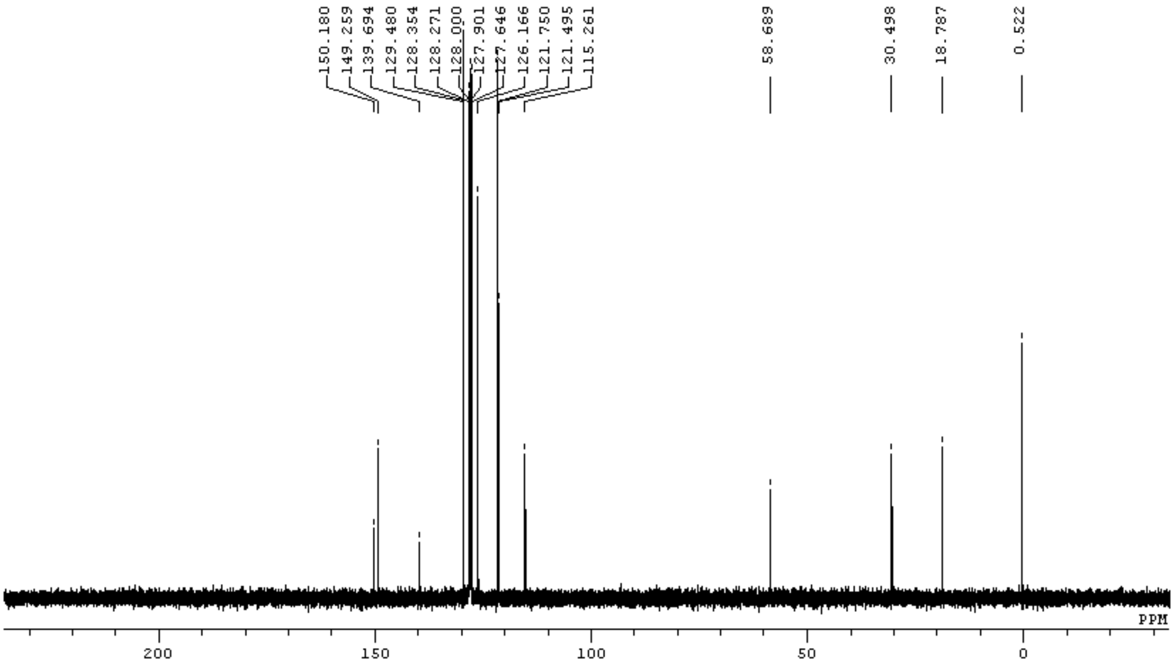
0.0
-2.5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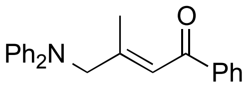
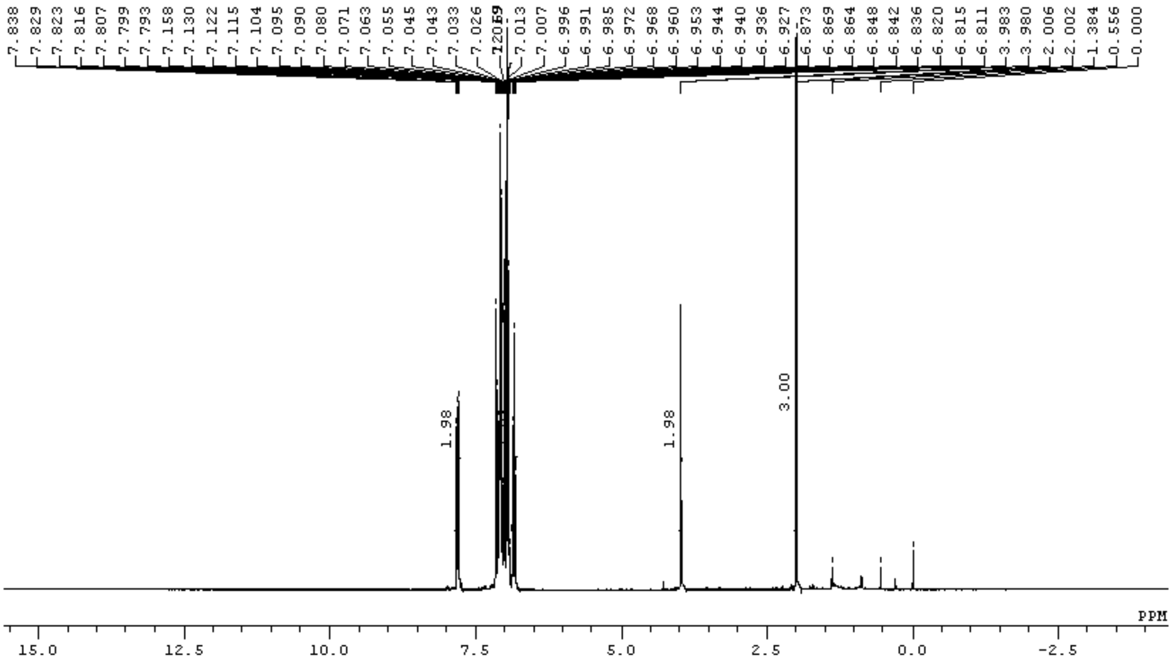

O
Ph$_2$N
Ph

7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7.104
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7.043
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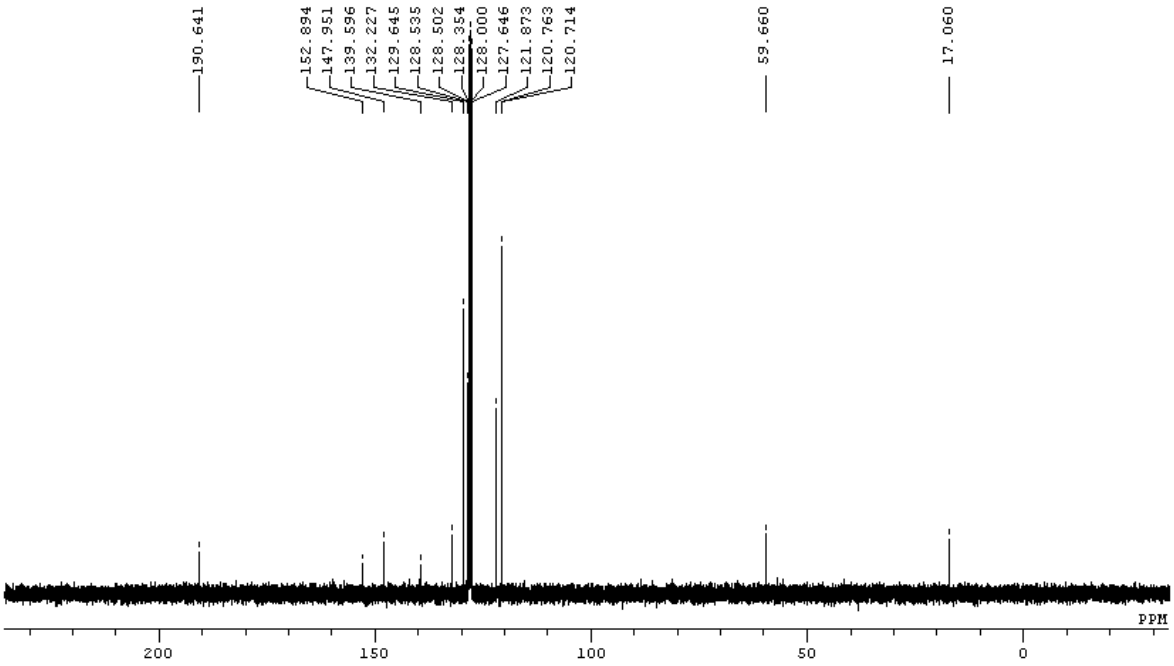
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