Electronic Supplementary Information (ESI)

Photocatalytic [4+2] cyclization of biomass furan into Cantharidin-like skeleton

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I. GENERAL INFORMATION

Materials and reagents. All materials were obtained from commercial suppliers of Shanghai Titan Scientific Co., Ltd. All solvents were used without purification, unless otherwise indicated. Photocatalytic Diels-Alder cycloaddition experiments were performed in a reactor that was irradiated using 6 W 460 nm blue LEDs at room temperature. Reactions were monitored by thin layer chromatography (TLC) on silica gel GF254 plates. UV light, combined with ethanolic phosphomolybdic acid or iodine, was used as the visualizing agent. Products were purified by flash column chromatography performed on silica gel (200–300 mesh) or by recrystallization.

Analytical methods. All compounds were fully characterized by spectroscopic data. The melting points were determined on a X-6 microscopic melting point apparatus and are uncorrected. The ^{1}H and ^{13}C NMR spectra were recorded on Bruker Advance III (300 MHz and 75 MHz, respectively) spectrometers; chemical shifts are reported as δ values in parts per million (ppm) and coupling constants (*J*) are reported in Hz. Tetramethylsilane (TMS, 0.0 ppm) was the internal standard for $CDCl_3$ (7.26 ppm for ^{1}H-NMR, 77.00 ppm for ^{13}C-NMR). The IR spectra were recorded on a Thermo Nicolet IS 50 FT-IR equipped with a crystal diamond ATR module. Mass spectra (HRMS) were recorded using Thermo Fisher UltiMate 3000 HPLC and UHPLC Systems. HRMS data were recorded via electron impact mass spectrometry using a time-of-flight analyzer.

Photocatalysis experiments. The reaction was carried out in a two-necked round-bottomed glass flask placed on a magnetic stirrer, with a magnetic stir bar added to the reaction mixture. The experiment was conducted at room temperature. Two different atmospheres were used for the reaction: when it was performed under air atmosphere, a parafilm covering with holes for air flow was applied to the glass bottle (photo A in Figure); when it was conducted under an O_2 atmosphere, an O_2 balloon was attached to the glass bottle (photo B in Figure). Finally, the experiment proceeded with a blue 6 W LED lamp positioned approximately 5 cm away from the reaction mixture.

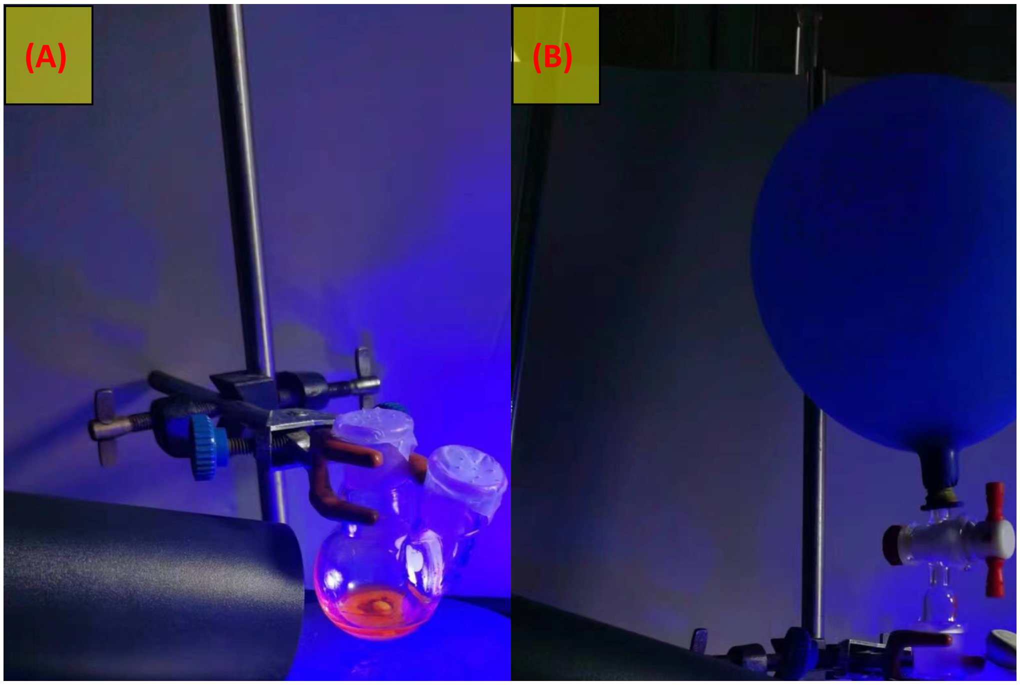


Figure S1. Photocatalysis experiments (A) under air atmosphere; (B) under O_2 atmosphere.

Light ON/OFF experiments

Ten standard reaction mixtures in 10-mL vials were charged with furan **1a** (100.0 mg, 3.0 equiv., 30.55 mmol), maleic anhydride **2a** (48.0 mg, 1.0 equiv., 10.20 mmol), photocatalyst (11.0 mg, 0.003 equiv., 3 mol%), solvent-free, the vials were sealed with poly-tetrafluoro-ethylene-lined caps. The reaction mixture was degassed by oxygen sparging for 10 min. It was conducted under an oxygen atmosphere using an O_2 balloon, then irradiated with 6 W 460 nm blue LEDs and cooled by a fan. After 1 h, the lamps were turned off, and one vial was removed from the irradiation setup for analysis. The remaining nine vials were stirred without light for an additional 1 h. Then, one vial was removed for analysis, and the lamps were turned back on to irradiate the remaining eight reaction mixtures. After an additional 1 h of irradiation, the lamps were turned off, and one vial was removed for analysis. The remaining seven vials were stirred without light for an additional 1 h. Then, a vial was removed for analysis, and the lamps were turned back on to irradiate the remaining six reaction mixtures. After 1 h, the lamps were turned off, and one vial was removed for analysis. The remaining four vials were stirred in the presense of light for an additional 1 h. Then, one vial was removed for analysis, and the lamps were turned back off to irradiate the remaining three reaction mixtures. After 1 h, one vial was removed for analysis, and the lamps were turned back on to irradiate the remaining two reaction mixtures. Finally, the remaining one vial were stirred without light for an additional 1 h, then it was was removed for analysis.

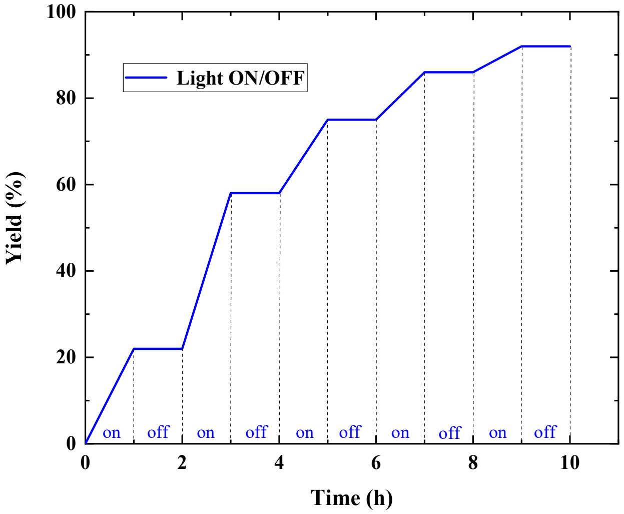


Figure S2. Light ON/OFF experiments for radical propagation test (the yield of [4+2] product was measured by GC analysis).

Measurement of quantum yield experiments

The experiments for measurement of quantum yield were conducted by using the spectrometer of Thorlabs Optical Power/Energy Meter: Model S310C. The light intensity was 3.1 mW·cm^{-2}, the LED light source was 6 W, and the reactions were conducted over a time of 9 h. The reaction quantum yield was calculated as 1.2%, by using ***Equation S4*** as below:[2, 3]

$$\Phi_{so}\ (\%) = \frac{Ne}{Np} \times 100\% \qquad (\boldsymbol{S4})$$

Φso: Quantum Yield, Ne: reactive photons per second, Np: absorbed photons per second.

$$Ne - vtNA \times 100\%$$

v: the average photocatalysis reaction rate (mol·s^{-1}), t: irradiation time (s), N_A is Avogadro's constant, 6.02×10^{23} (mol^{-1}).[4]

$$Np = \frac{IAt\lambda}{hc} \times 100\%$$

I: Optical power density of incident light (W·m^{-2}), A: irradiation area (m^2), λ: wavelength of incident rays (nm), t: time (s), h: Planck constant (6.62×10^{-34} J·s), c: the speed of light (3.0×10^{8} m·s^{-1}).[5]

Table S1. Photocatalysis reaction data

No.	Reactant (mg)	Photocatalyst (mg)	Solvent (mL)	Yield (%)	Reaction time (h)	Light power (W)
1	100	2.3	3	82	9	6
2	85	2.3	3	75	9	6
3	70	2.3	3	64	9	6

Stern−Volmer fluorescence quenching experiments

Stern-Volmer experiments were conducted on a Hitachi F-4600 Fluorescence Luminescence Spectrophotometer. Each component was prepared in MeCN prior to each set of experiments. The solutions were irradiated at λex = 300 nm, and the luminescence was measured at λem = 320 nm. To set up the Stern-Volmer graph, plot the concentration of furfuryl alcohol reactant, [Q], on the x-axis and I_0/I_f on the y-axis according to ***Equation S5***:[6]

$$\frac{I_o}{I_f} = 1 + K_{sv}[Q] \qquad (S5)$$

I_0 and I_f are the luminescence intensities in the absence and presence of furfuryl alcohol. The slope of the Stern-Volmer graph, K_{sv} can be used to compare quenching efficiencies using the assumption that adding quencher (furfuryl alcohol reactant) into the solution does not change the luminophore natural rate of decay ($k_q = k_o$). The value for I_0/I_f from each run was averaged to yield a value of I_0/I_f for the experiment. Linear regression of I_0/I_f against concentration was performed in Origin.

Table S2. Stern−Volmer fluorescence quenching experiments data

reactant and photocatalyst	**Concentration (mM)**
$Ru(bpy)_3Cl_2$	1.7 (1.3 mg in 3 mL MeCN)
maleic anhydride	different concentrations

Table S3. value of I_0/I_f

maleic anhydride (mM)	4.532	4.685	4.839	4.982	5.135	5.289
I^0/I^{-1}	1.215	1.386	1.476	1.577	1.677	1.938
I^0/I^{-1}	1.211	1.380	1.472	1.571	1.675	1.934
I^0/I^{-1} average	1.213	1.383	1.474	1.574	1.676	1.936

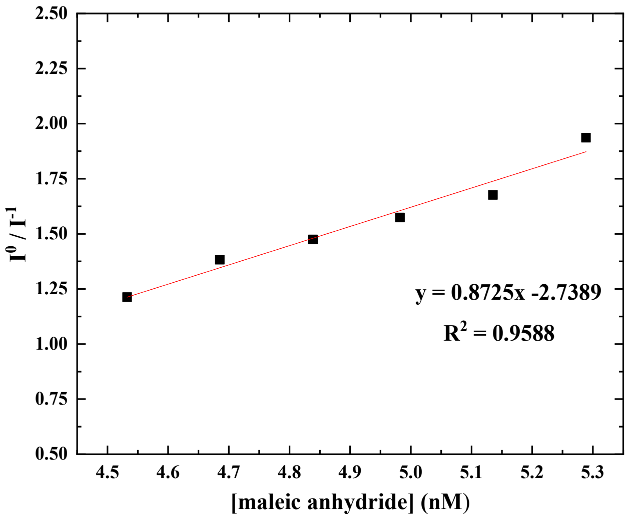


Figure S3. Stern−Volmer plot for furan + maleic anhydride + [Ru] (nM) + O_2 in a furan solution. The solid line is a linear least-square fit of the data. K*sv* from the slope is 8.725×10^9 M^{-1} s^{-1}.

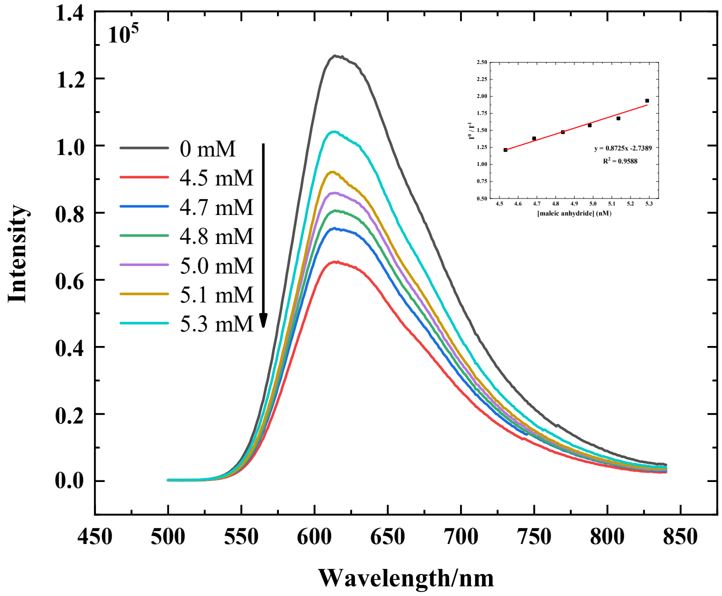
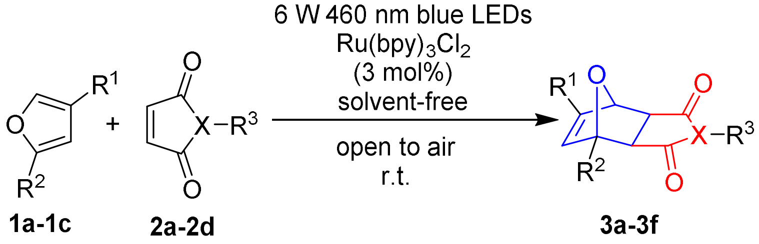


Figure S4. Stern−Volmer analysis based on the steady-state luminescence data.

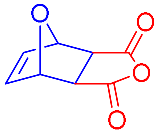
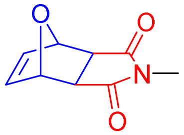
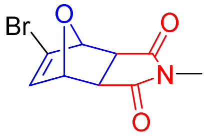
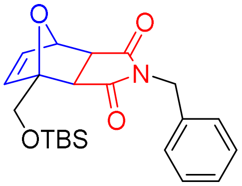
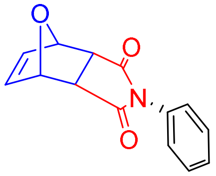
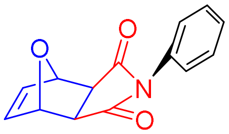
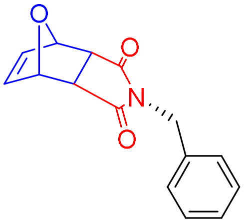
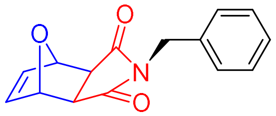
II. PREPARATION OF CANTHARIDIN ANALOGS

Biomass furans photoredox conversion for cantharidin analogs



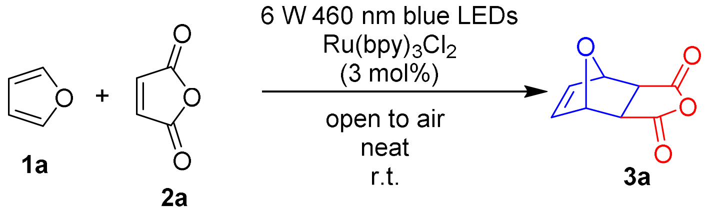
Scheme S1. Biomass furans photoredox conversion for cantharidin analogs

Table S4. Biomass furans photoredox conversion for cantharidin analogs

Entry[a]	Diene	Dienophile	Cycloadduct	Yield[b]
1	1a, R^1, $R^2 = H$,	2a, X = O	 **3a**	92%
2	1a, R^1, $R^2 = H$,	2b X = N, $R^3 = CH_3$	 **3b**	89%
3	1b, $R^1 = Br$, $R^2 = H$,	2b, X = N, $R^3 = CH_3$	 **3c**	94%
4	1c, $R^1 = H$, $R^2 = CH_2OTBS$,	2c, X = N, $R^3 = CH_2C_6H_5$	 **3d**	35%
5	1a, R^1, $R^2 = H$,	2d, X = N, $R^3 = C_6H_5$	 **3e-endo**	60%
			 **3e-exo**	32%
6	1a, R^1, $R^2 = H$,	2c, X = N, $R^3 = CH_2C_6H_5$	 **3f-endo**	50%
			 **3f-exo**	40%

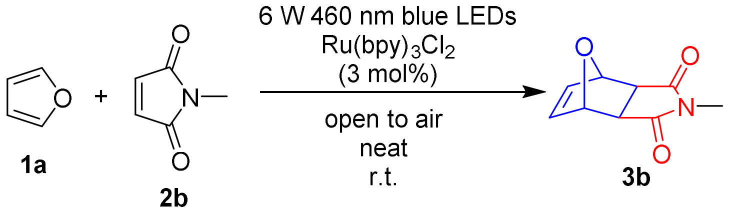
[a] Unless otherwise noted, the reaction conditions are as follows: diene (3.0 equiv.), dienophile (1.0 equiv.), photocatalyst (3 mol%), open to air, solvent-free, 6 W 460 nm blue LEDs at room temperature, and 9 h. [b] Isolated yields.

Synthesis and characterization of 3a-3f



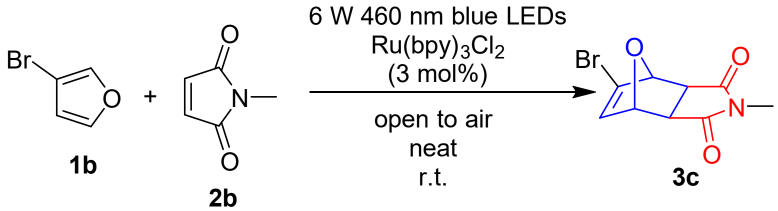
Scheme S2. Synthesis of **3a**

5,6-dehydronorcantharidin **3a** (**Table S1**, entry1) was prepared according to the general procedure with furan **1a** (2.08 g, 30.55 mmol), maleic anhydride **2a** (1.00 g, 10.20 mmol), and Ru(bpy)$_3$Cl$_2$ (20 mg, 0.03 mmol). Compound **3a** was collected as a white solid in 92% yield (1.56 g, 9.40 mmol) after recrystallized from ethyl acetate, Mp: 121-122°C. ^{1}H NMR (300 MHz, CDCl$_3$) δ ppm: 6.58 (s, 2H), 5.46 (s, 2H), 3.18 (s, 2H), 1.57 (s). ^{13}C NMR (75 MHz, CDCl$_3$) δ ppm: 169.9, 137.0, 82.2, 48.7. IR ($\nu_{\max}$, cm^{-1}, neat): 3537.35, 3435.62, 3031.60, 2987.73, 2899.98, 1854.73, 1705.28,1430.95, 1308.49, 1282.93, 1212.54, 1146.49, 1081.89, 1016.80, 945.93, 922.79, 905.43, 875.54, 847.09, 822.02, and 729.94. HRMS (ESI): *m/z* calculated for $C_8H_6O_4$ [M]$^+$ 166.0266; found, 165.0189.



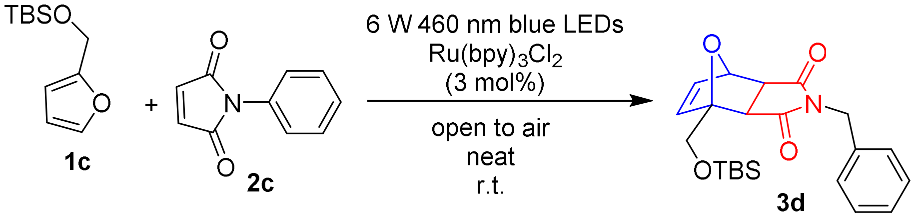
Scheme S3. Synthesis of **3b**

N-methyl-substituted dehydronorcantharimide **3b** (**Table S1**, entry 2) was prepared according to the general procedure with furan **1a** (1.84 g, 27.03 mmol), N-methylmaleimide **2b** (1.00 g, 9.00 mmol), and Ru(bpy)$_3$Cl$_2$ (20 mg, 0.03 mmol). Compound **3a** was collected as a white solid in 89% yield (1.44 g, 8.04 mmol) by flash silica gel column chromatography (3:1 petroleum ether : ethyl acetate). Mp: 86-87°C. ^{1}H NMR (300 MHz, CDCl$_3$) δ ppm: 2.80 (s, 2H), 349-3.54 (m, 3H); 5.30-5.31 (m, 2H), 6.38 (s, 2H). ^{13}C NMR (75 MHz, CDCl$_3$) δ ppm: 174.96, 134.38, 79.26, 46.05, 24.52. IR (ν_{max}, cm^{-1}, neat): 3083.67, 3012.84, 2979.74, 1778.18, 1684.64, 1436.42, 1382.45, 1322.01, 1288.20, 1120.55,1013.35, 932.76, 872.33, 798.22, and 738.50; HRMS (ESI): *m/z* calculated for $C_9H_9NO_3$ $[M+Na]^+$ 202.0480, found 202.0476.



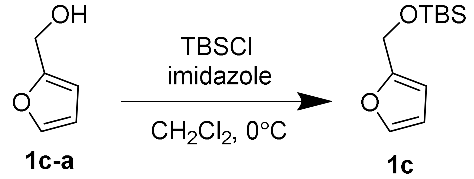
Scheme S4. Synthesis of **3c**

5-bromo-*N*-methyl-substituted dehydronorcantharimide **3c** (**Table S1**, entry 3) was prepared according to the general procedure with 3-bromofuran **1b** (3.97 g, 27.01 mmol), N-methylmaleimide **2b** (1.00 g, 9.00 mmol), and Ru(bpy)$_3$Cl$_2$ (20 mg, 0.03 mmol). Compound **3c** was collected as a white solid in 94% yield (2.18 g, 8.45 mmol) by recrystallized from ethyl acetate. Mp : 177-178°C, ^{1}H NMR (MHz, CDCl$_3$) δ ppm: 2.97-2.99 (m, 3H), 3.02-3.04 (m, 2H), 5.08 (s, 1H), 5.23, 5.24 (d, *J* = 3.0 MHz,1H), 6.51-6.52 (d, *J* = 3.0 MHz, 1H). ^{13}C NMR (75 MHz, CDCl$_3$) δ ppm: 25.09, 46.80, 48.64, 82.80, 85.17, 127.31, 134.92, 175.22; IR (ν_{max}, cm^{-1}, neat): 3015.88, 2926.83, 2853.90, 1773.06, 1682.48, 1582.69, 1436.84, 1382.33, 1282.54, 1255.67, 1210.38, 1146.67, 1019.24, 975.48, 874.15, 864.94, 801.23, 729.07, and 666.12; HRMS (ESI): *m/z* calculated for $C_9H_8BrNO_3$ $[M+Na]^+$ 279.9585, found 279.9582.



Scheme S5. Synthesis of **3d**

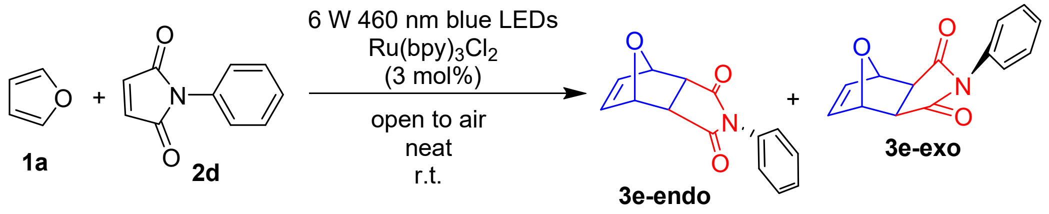
6-^{t}butyldimethylsilyloxymethyl-*N*-phenly substituted dehydronorcantharimide **3d** (**Table S1**, entry 4).



Scheme S6. Synthesis of **1c**

First, *tert*-butyldimethylsilane (TBS) protected furfuryl alcohol, 2-furanmethyl tert-butyldimethylsilyl ether **1c** was synthesized using a modification of the procedure reported by Corey [1]. A solution of furfuryl alcohol **1c-a** (1.50 g, 15.29 mmol) in dichloromethane (CH_2Cl_2) was placed in a 50 mL round-bottomed flask, the vessel was cooled to 0°C, imidazole (1.15 g, 16.82 mmol) and a solution of *tert*-butyldimethylsilyl chloride (TBSCl, 2.54 g, 16.82 mmol) in CH_2Cl_2 was added, the reaction was stirred for 2 h. Then the reaction mixture was extracted with ethyl acetate (10 mL × 3), and washed with water (25 mL × 3) and brine (25 mL × 1). The combined organic extracts were dried over anhydrous Na_2SO_4, filtered, and evaporated *in vacuo*. **1c** was collected as a colorless liquid in 97% yield (3.15 g, 14.83 mmol) by flash silica gel column chromatography (20:1 petroleum ether : ethyl acetate).

Then, **3d** was prepared according to the general procedure with TBS protected furfuryl alcohol **1c** (3.40 g, 16.01 mmol), N-benzylmaleimide **2c** (1.00 g, 5.34 mmol), and $Ru(bpy)_3Cl_2$ (20 mg, 0.03 mmol). A colorless liquid of **3d** in 35% yield was collected by flash silica gel column chromatography (15:1 petroleum ether : ethyl acetate), ^1H NMR(MHz, $CDCl_3$) δ ppm: 0.04 (s, 6H), 0.84 (s, 9H), 3.40-3.43 (d, *J* = 9 Hz, 1H), 3.51-3.55 (m, 1H), 4.39 (s, 2H), 5.16-5.18 (d, *J* = 8 MHz, 1H), 5.88-5.90 (d, *J* = 6.00 Hz, 1H), 6.05-6.07 (d, *J* = 6.00 Hz, 2H), 7.21 (s, 5H). ^{13}C NMR (75 MHz, $CDCl_3$) δ ppm: 174.92, 174.76, 135.53, 135.04, 134.79, 129.06, 128.49, 128.00, 92.69, 79.57, 61.44, 47.88, 44.84, 42.25, 25.93, 18.51. IR (ν_{max}, cm^{-1}, neat): 3456.83, 3033.53, 2964.10, 2951.57, 2930.35, 2888.89, 2853.69, 1767.95, 1699.01, 1470.98, 1434.21, 1392.86, 1343.68, 1312.34, 1288.24, 1255.94, 1169.63, 1106.96, 1089.12, 1069.83, 1009.57, 984.02, 952.68, 885.66, 836.97, 778.63, 753.56, 726.08, and 702.94. HRMS (ESI): *m/z* calculated for $C_{22}H_{29}NO_4Si$ $[M+Na]^+$, 422.1764, found 422.1760.

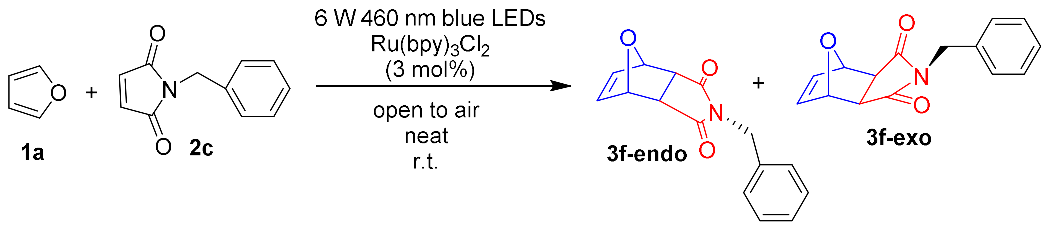


Scheme S7. Synthesis of **3e**

N-phenly- substituted dehydronorcantharimide **3e** (Table S1, entry 5) was prepared according to the general procedure with furan **1a** (1.18 g, 17.33 mmol), N-phenylmaleimide **2d** (1.00 g, 5.77 mmol), and $Ru(bpy)_3Cl_2$ (20 mg, 0.03 mmol). A isomer mixture **3e** in 92% yield was collected by recrystallized from ethyl acetate, the isomers were separated by flash silica gel column chromatography (5:1 petroleum ether : ethyl acetate).

3e-endo was collected as a white solid in 60% yield (0.83 g, 3.44 mmol) by flash silica gel column chromatography (5:1 petroleum ether : ethyl acetate). Mp: 125-126°C. ^{1}H NMR (300 MHz, $CDCl_3$) δ ppm: 3.67-3.69 (m, 2H), 5.42-5.43 (m, 2H), 6.56 (s, 2H), 7.10-7.13 (m, 2H), 7.38-7.47 (m, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ ppm: 45.91, 73.93, 79.77, 126.35, 128.86, 129.19, 131.34, 134.62, 173.96. IR (ν_{max}, cm^{-1}, neat): 3657.88, 3057.15, 2968.92, 2902.39, 1774.22, 1712.03, 1692.74, 1598.73, 1497.96, 1457.46, 1382.73, 1325.36, 1284.38, 1227.00, 1192.29, 1081.89, 1024.52, 917.97, and 857.22. HRMS (ESI): *m/z* calculated for $C_{14}H_{11}NO_3$ $[M+Na]^+$ 264.0637, found 264.0637.

3e-exo was collected as a white solid in 32% yield (0.44 g, 1.82 mmol) by flash silica gel column chromatography (5:1 petroleum ether : ethyl acetate). Mp. 165-166°C. ^{1}H NMR (300 MHz, $CDCl_3$) δ ppm: 2.99 (s, 2H), 5.37 (s, 2H), 6.54 (s, 2H), 7.25-7.27 (m, 2H), 7.40-7.48 (m, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ ppm: 47.52, 73.91, 81.38, 126.55, 128.80, 129.17, 131.62, 136.68, 175.41. IR (ν_{max}, cm^{-1}, neat): 3664.86, 3069.75, 2975.97, 2907.70, 1780.92, 1592.66, 1498.88, 1451.99, 1373.38, 1289.93, 1180.29, 1143.74, 1080.99, 940.31, and 883.08. HRMS (ESI): *m/z* calculated for $C_{14}H_{11}NO_3$ $[M+Na]^+$ 264.0637, found 264.0635.



Scheme S8. Synthesis of **3f**

N-benzyl- substituted dehydronorcantharimide **3f** (**Table S1**, entry 6) was prepared according to the general procedure with furan **1a** (1.09 g, 16.01 mol), N-benzylmaleimide **2c** (1.00 g, 5.34 mmol), and $Ru(bpy)_3Cl_2$ (20 mg, 0.03 mmol). A isomer mixture **3e** was collected in 90% yield by recrystallized from ethyl, the isomers were separated by flash silica gel column chromatography (5:1 petroleum ether : ethyl acetate).

3f-endo was collected as a white solid in 50% yield (0.68 g, 2.66 mmol) by flash silica gel column chromatography (5:1 petroleum ether : ethyl acetate). Mp. 117-118°C. ^{1}H NMR (300 MHz, $CDCl_3$) δ ppm: 3.47-3.49 (m, 2H), 4.46 (s, 2H), 5.26-5.28 (m, 2H), 6.11 (s, 2H), 7.25-7.30 (m, 5H). ^{13}C NMR (75 MHz, $CDCl_3$) δ ppm: 42.26, 45.87, 79.51, 128.04, 128.51, 129.04, 134.26, 135.48, 174.59. IR (ν_{max}, cm^{-1}, neat): 3442.36, 3142.65, 3078.53, 3037.46, 2953.17, 1768.73, 1688.04, 1495.68, 1434.44, 1388.33, 1339.33, 1310.52, 1299.71, 1128.96, 1081.41, 1046.83, 1015.85, 928.67, 907.06, and 868.88. HRMS (ESI): *m/z* calculated for $C_{15}H_{13}NO_3$ $[M+Na]^+$, 278.0793, found 278.0791.

3f-exo was collected as a white solid in 40% yield (0.55 g, 2.15 mmol) by flash silica gel column chromatography (5:1 petroleum ether: ethyl acetate). Mp. 120-121°C. ^{1}H NMR (300 MHz, $CDCl_3$) δ ppm: 2.84 (m, 2H), 4.64 (s, 2H), 5.28 (s, 2H), 6.50 (s, 2H), 7.26-7.31 (m, 5H). ^{13}C NMR (75 MHz, $CDCl_3$) δ ppm: 42.47, 47.55, 80.96, 127.82, 128.15, 128.68, 135.49, 136.60, 175.98. IR (ν_{max}, cm^{-1}): 3442.36, 3082.85, 2995.68, 2951.73, 1833.57, 1772.33, 1692.36, 1577.81, 1490.63, 1430.12, 1403.46, 1337.89, 1314.12, 1217.58, 1174.35, 1152.02, 1093.66, 1049.71, 1015.85, 956.05, 912.10, and 863.11. HRMS (ESI): *m/z* calculated for $C_{15}H_{13}NO_3$ $[M+Na]^+$ 278.0793, found 278.0788.

III. Large-scale synthesis procedure of dehydronorcantharidin 3a under sunlight irradiation

The synthesization process is illustrated in Scheme 1. Furan 10.41 g (3 equiv., 152.93 mmol), maleic anhydride 5.00 g (1 equiv., 50.99 mmol) and 35 mg Ru(bpy)$_3$Cl$_2$ (0.001 equiv., 0.05 mmol) were charged into a round-bottomed glass flask equipped with a magnetic stir bar. The reaction was stirred in the absence of solvent under ambient atmosphere and exposed to sunlight at room temperature for 18 h. Dehydronorcantharidin **3a** was harvested as a white solid at 92% yield (7.76 g, 46.74 mmol) after being recrystallized from ethyl ether.

IV. Control experiments

Table S5. Control experiments for Diels-Alder reaction of furan and maleic anhydride

Entry[a]	Ru(bpy)$_3$Cl$_2$	Light	Solvent	Air	TEMPO	Time	Yield[b]
1[c]	-	+	+	+	-	24 h	92%
2[d]	-	+	-	+	-	24 h	92%
3[e]	-	-	-	+	-	24 h	0
4[f]	-	+	-	+	-	9 h	56%
5[g]	+	-	-	+	-	9 h	0
6[h]	+	+	-	-	-	9 h	62%
7[j]	+	+	-	+	+	9 h	0

[a] Unless otherwise noted, the reaction conditions are as follows: furan (3.0 equiv., 30.55 mmol), maleic anhydride (1.0 equiv., 10.20 mmol), Ru(bpy)$_3$Cl$_2$ (0.003 equiv., 0.03 mmol), Air (1 atm), neat, 6 W blue LEDs (460 nm) at room temperature. [b] Isolated yields. [c] According to reference [2], diethyl ether as solvent, fluorescent lamp, without photocatalyst. [d] Fluorescent lamp, without photocatalyst. [e] Without photocatalyst and visible light. [f] Without photocatalyst. [g] Without visible light irradiation. [h] Degas, without air. [j]Added TEMPO.

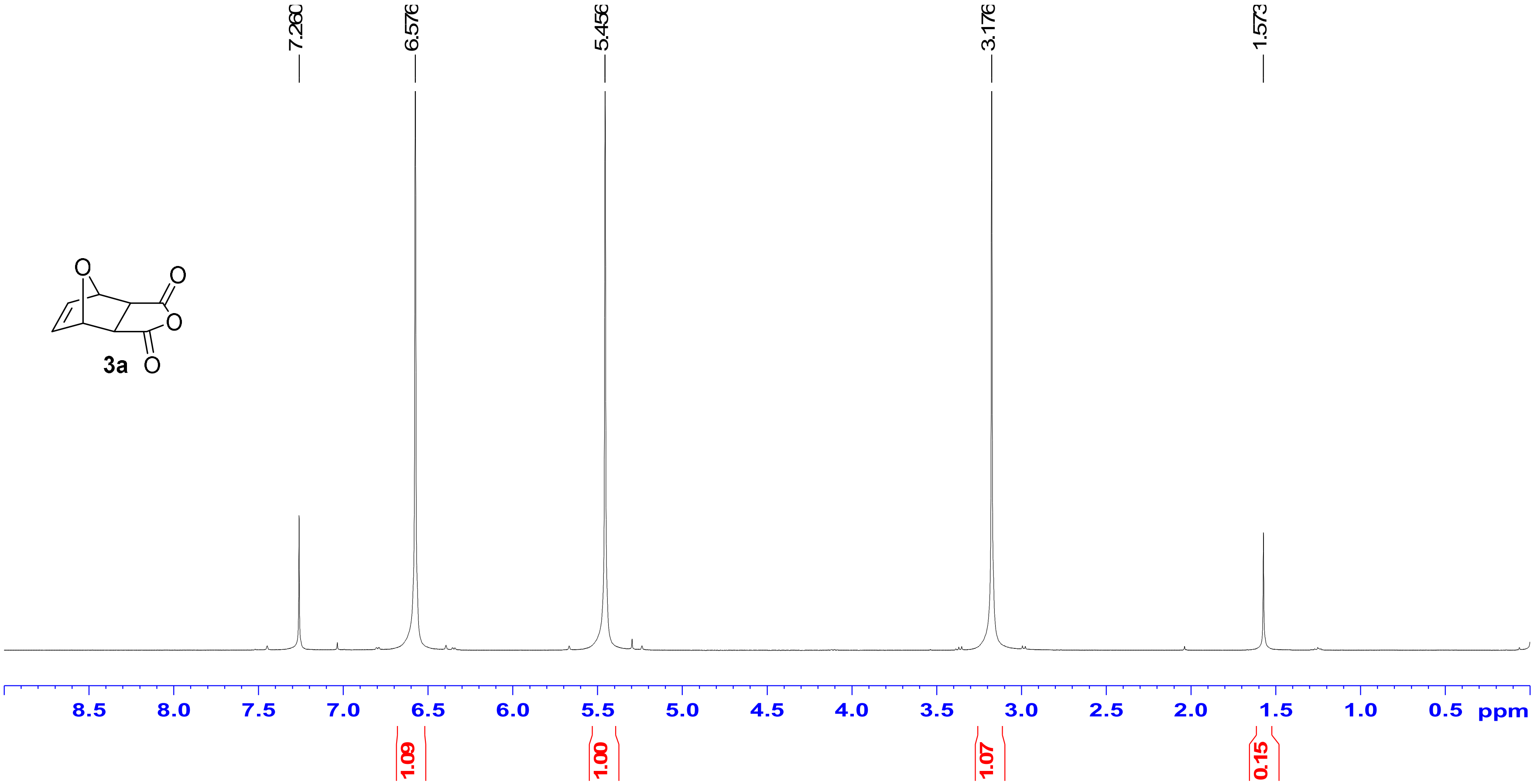
V. Photocatalytic Diels-Alder cycloaddition of furfuryl alcohol and methyl acrylate

Cycloadduct **10** was collected as a yellow liquid in 58% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ ppm: 1.21-1.31 (m, 3H), 1.71-1.83 (m, 2H); 2.22-2.53 (m, 2H), 3.02-3.24 (m, 1H), 3.98-4.29 (m, 2H), 4.97-5.11 (m, 1H), 6.16-6.18 (m, 1H), 6.33-6.48 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ ppm: 14.20, 31.29, 43.30, 60.87, 62.20, 78.78, 91.00, 132.79, 138.09, 172.18. IR (ν_{max}, cm^{-1}): 3421.64, 3091.87, 2987.24, 2953.50, 2870.57, 1789.65, 1720.22, 1448.78, 1369.24, 1323.43, 1188.92, 1036.09, 984.50, 928.57, 849.50, and 708.72. HRMS (ESI): *m/z* calculated. for: $C_{10}H_{14}O_4$ $[M+Na]^+$ 221.0790; found 221.0786.

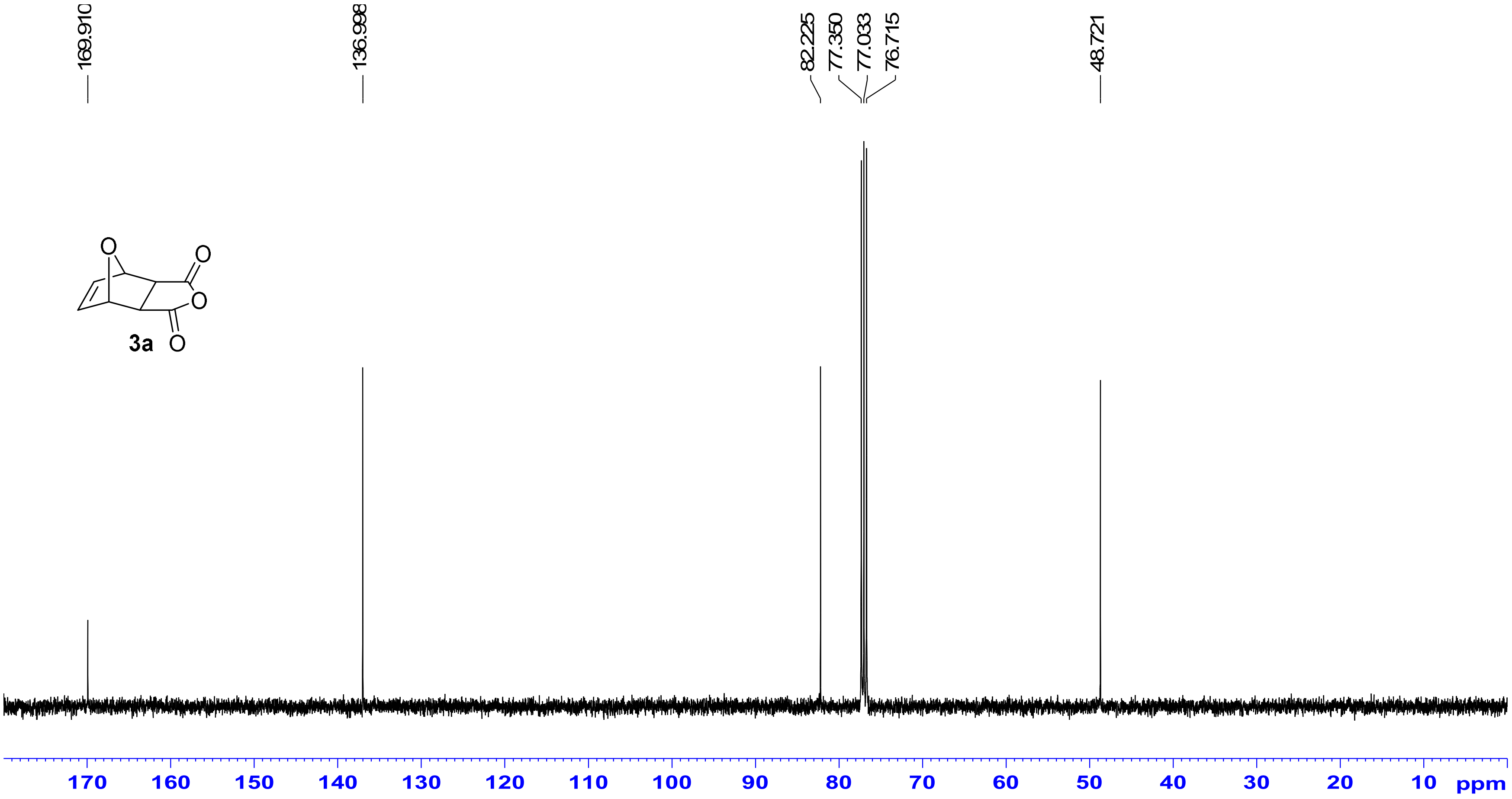
VI. References

1. E. J. Corey and M. C. Noe, *J. Am. Chem. Soc.*, 1996, **118**, 319-329.
2. O. Diels and K. Alder, *Berichte der deutschen chemischen Gesellschaft (A and B Series)*., 1929, **62**, 2081-2087.

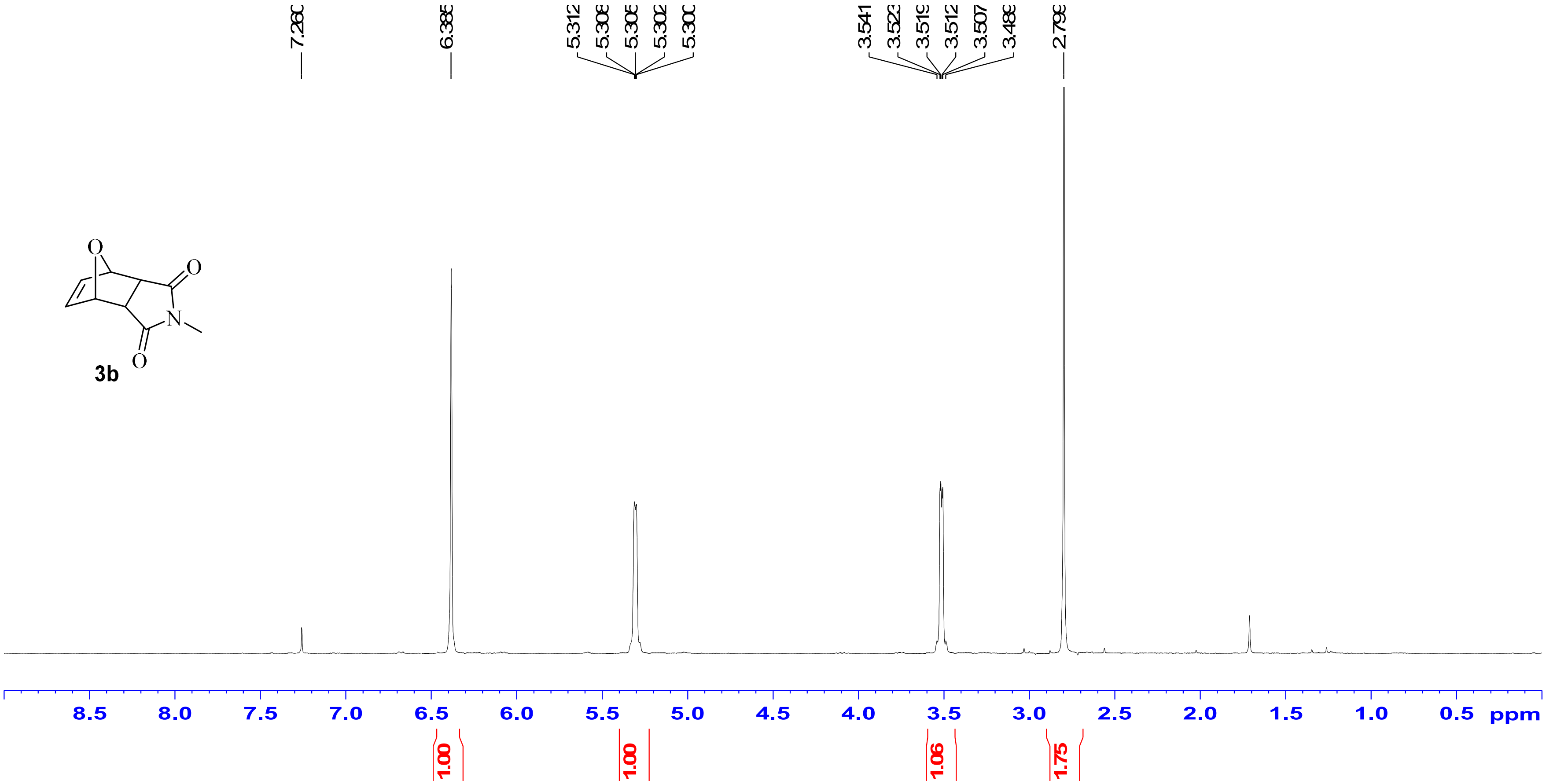
VII. NMR SPECTRA



^{1}H NMR (300 M in CDCl$_3$) of **3a**



^{13}C NMR (75 M in $CDCl_3$) of **3a**



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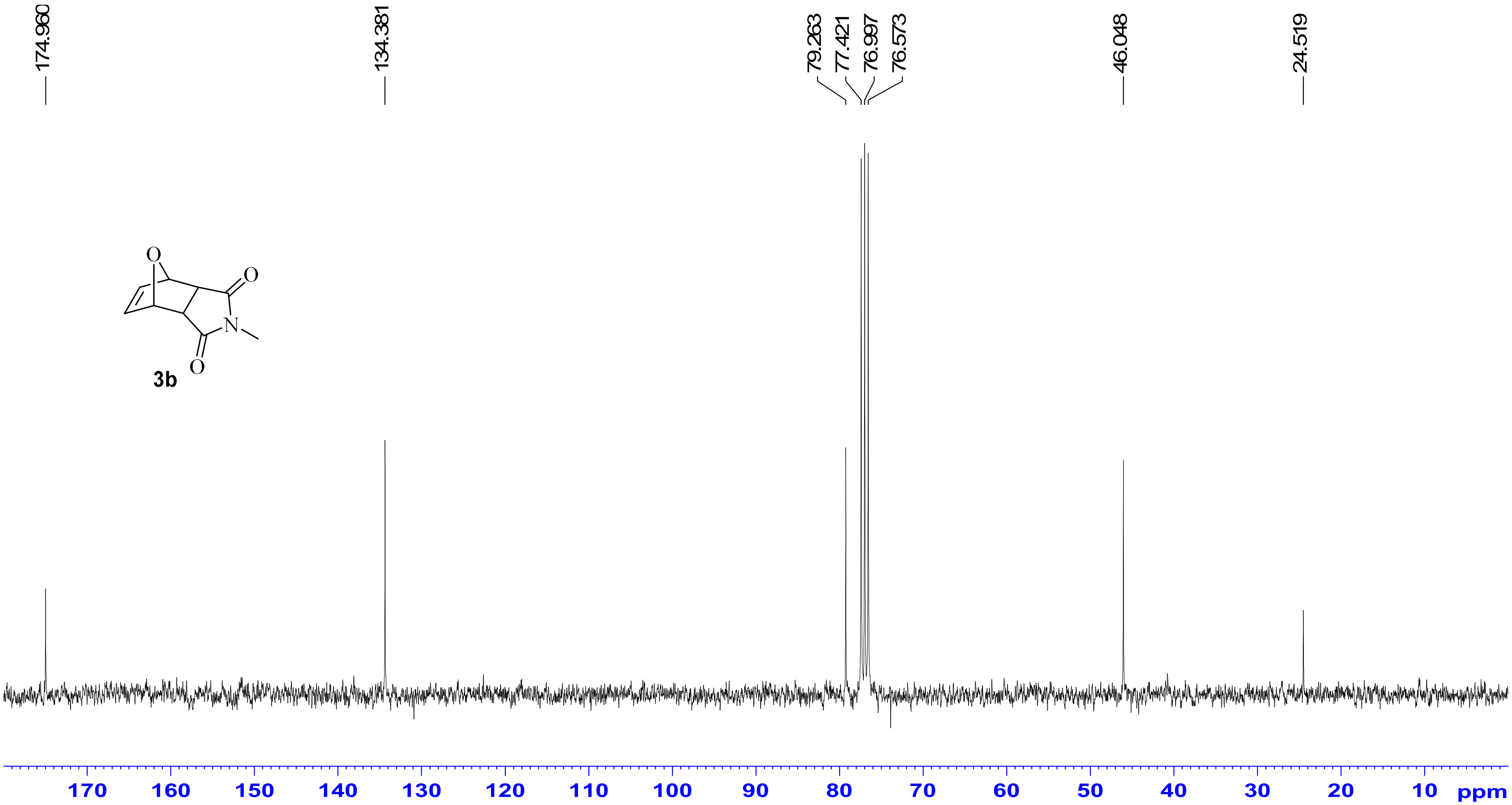

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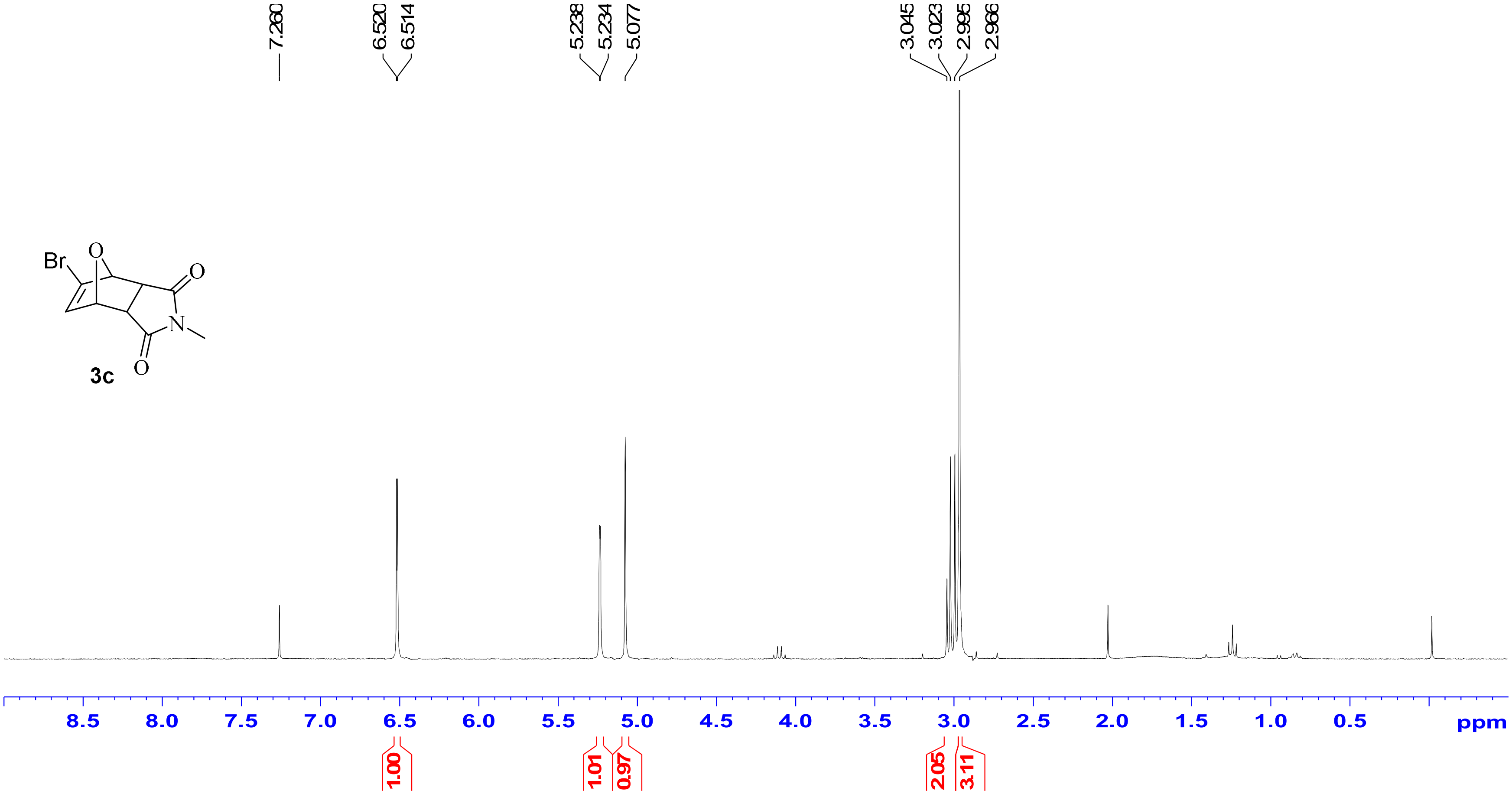

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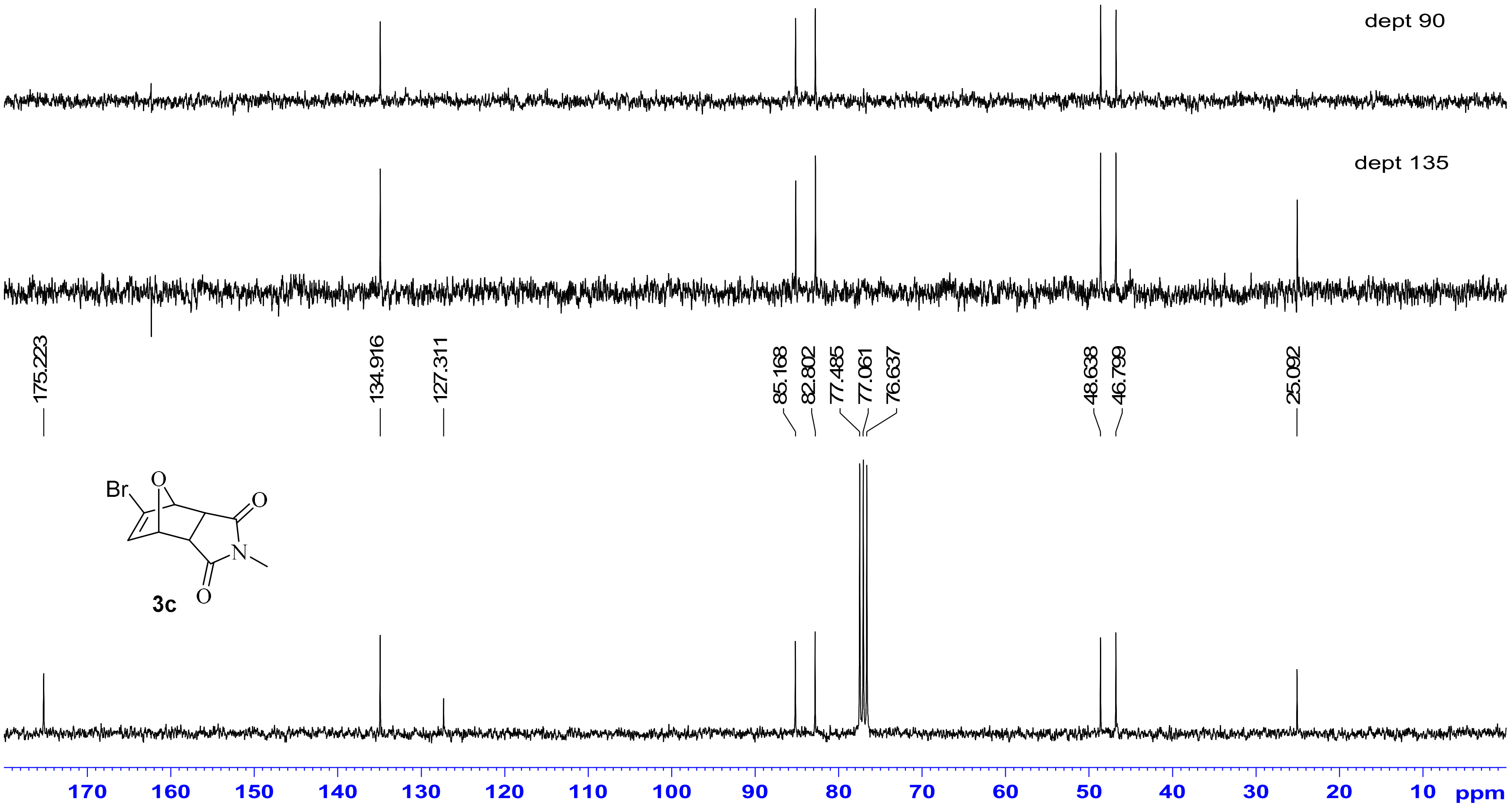

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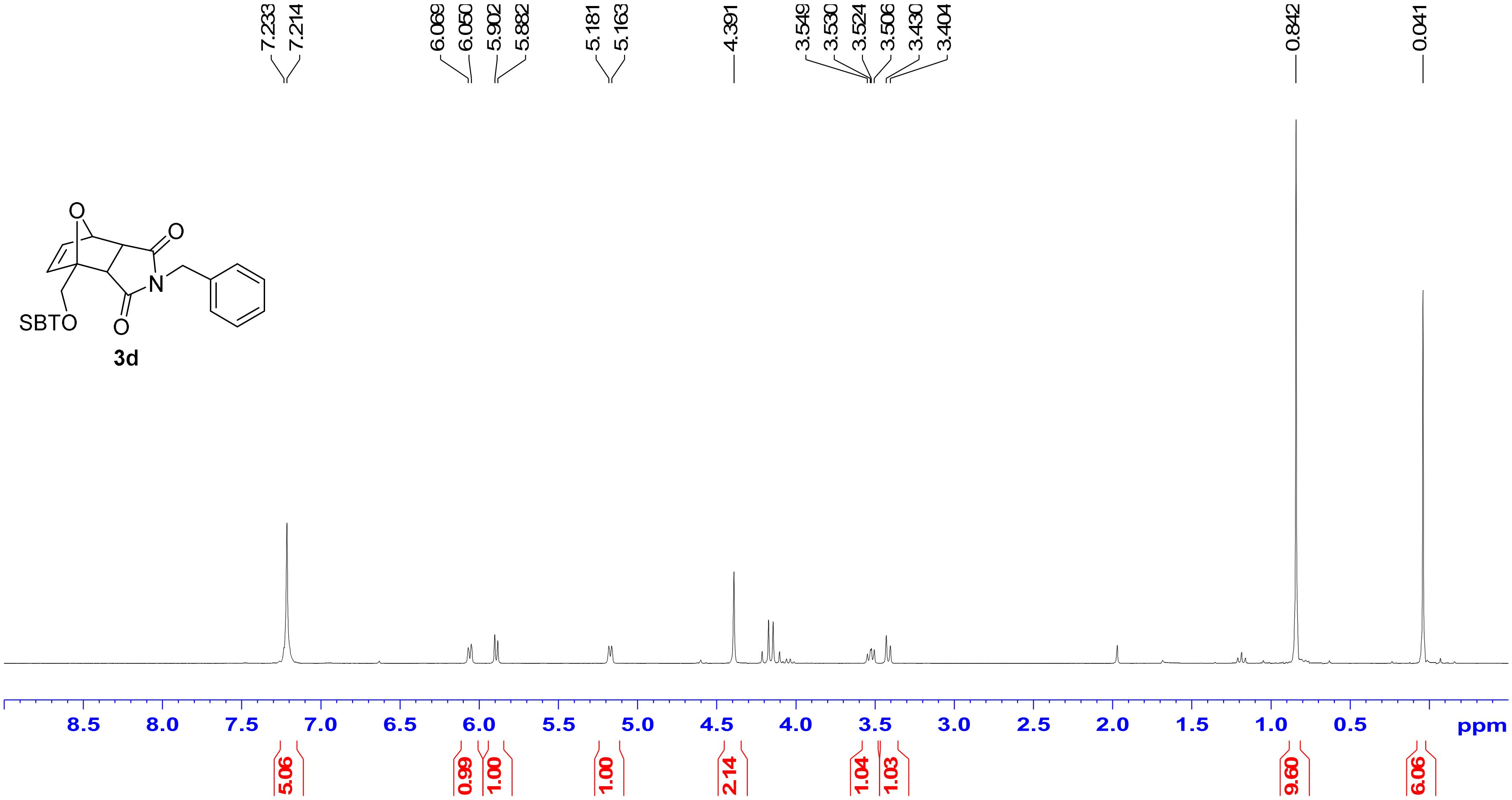

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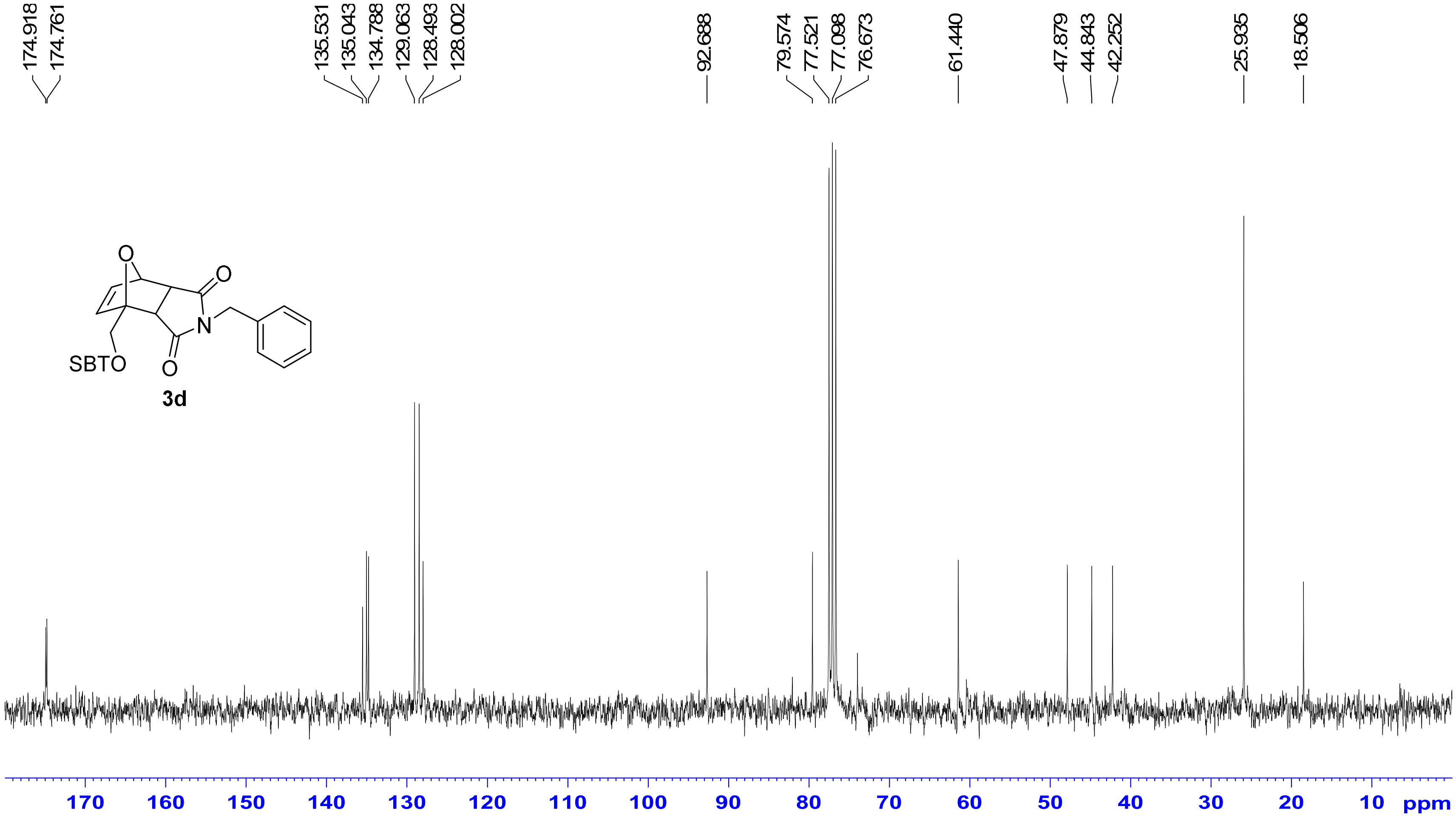

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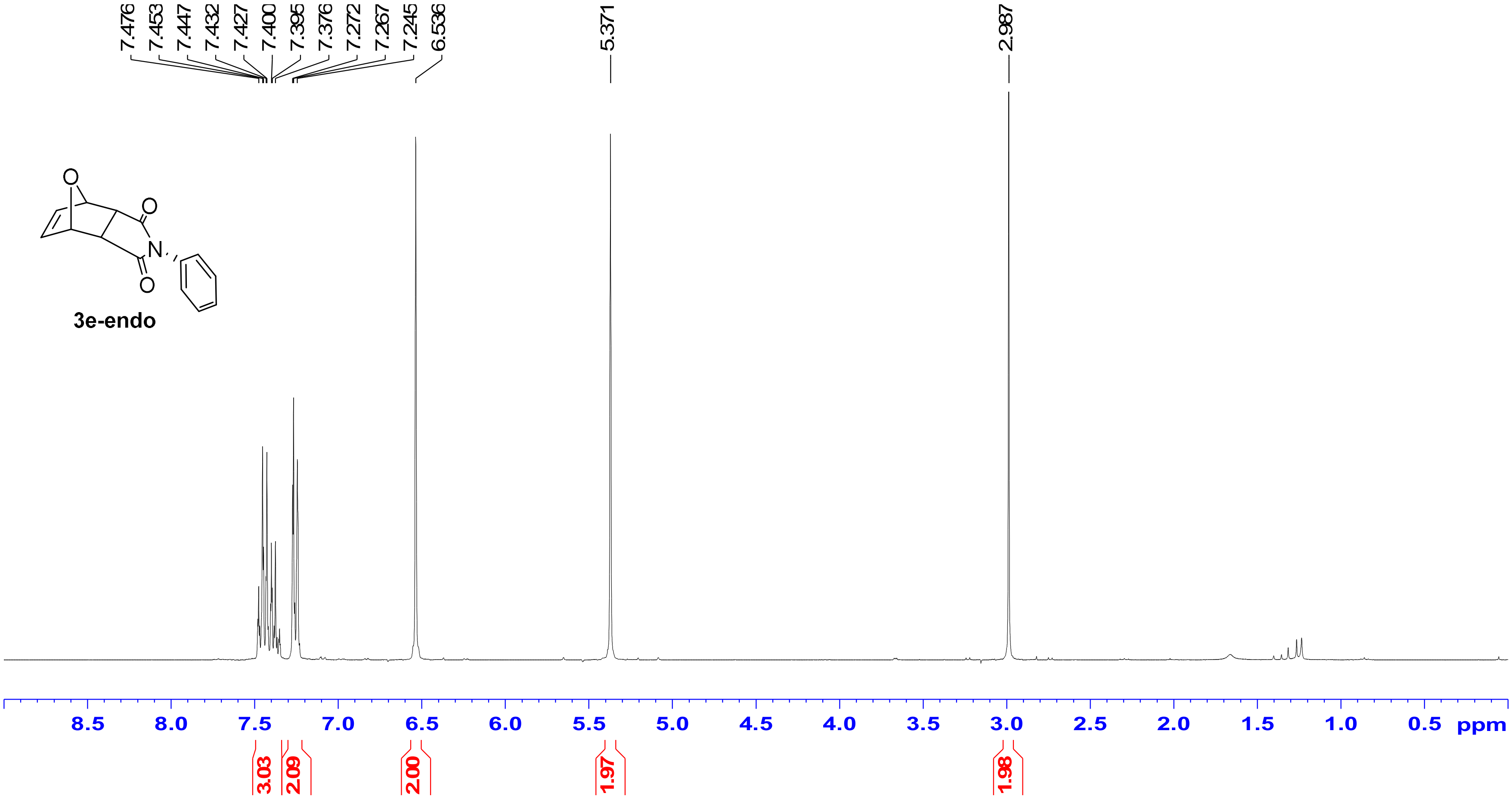

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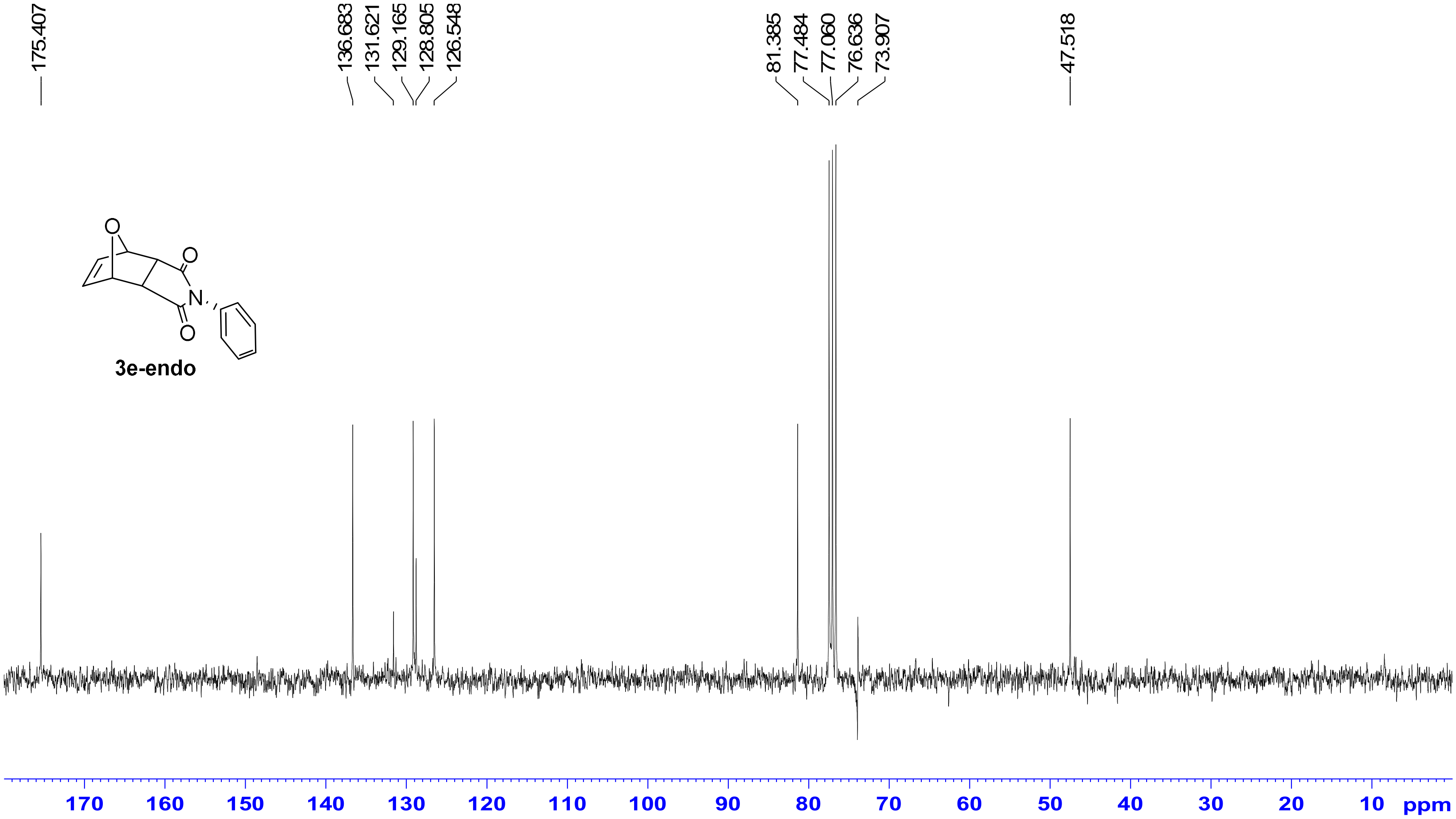

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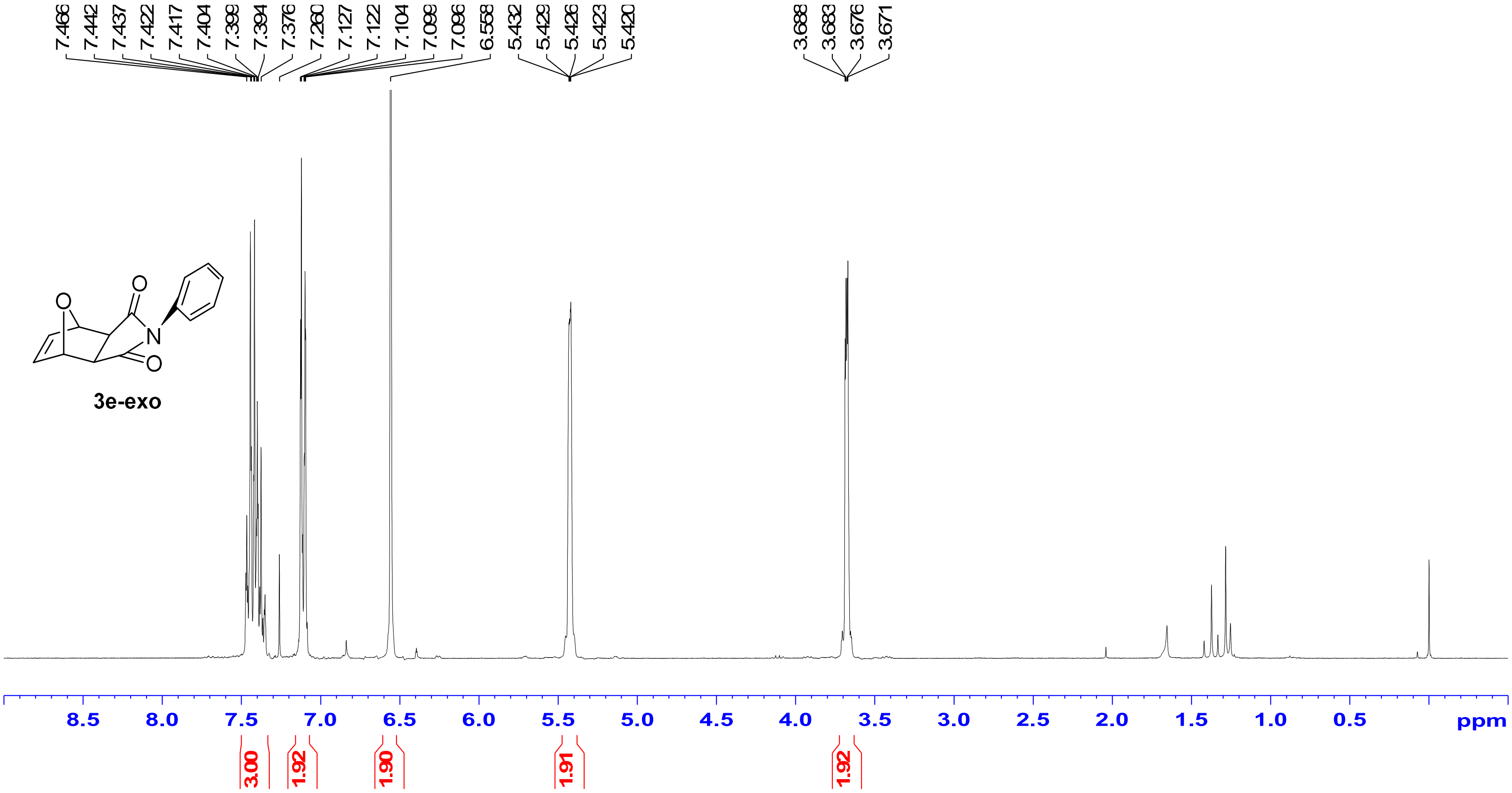

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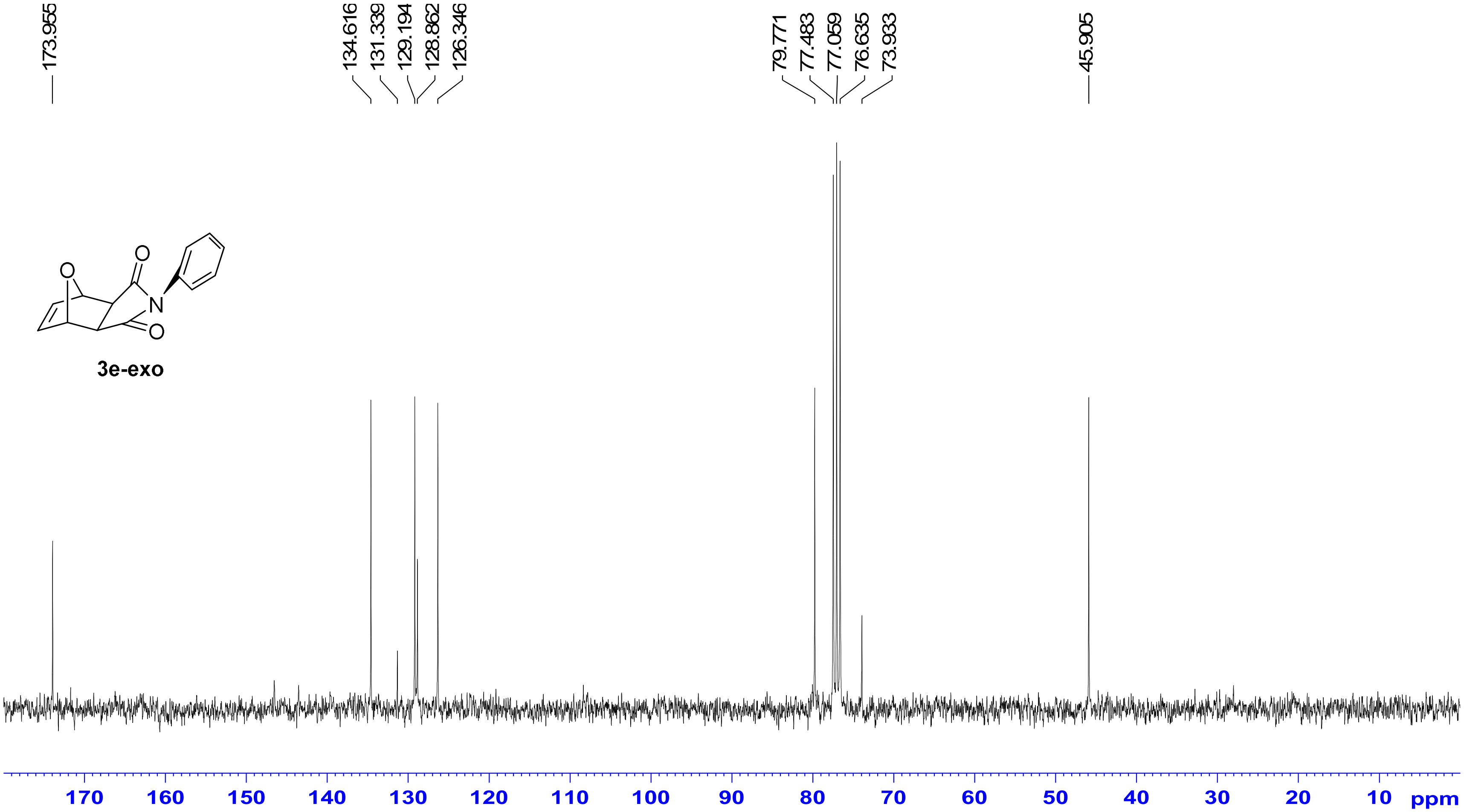

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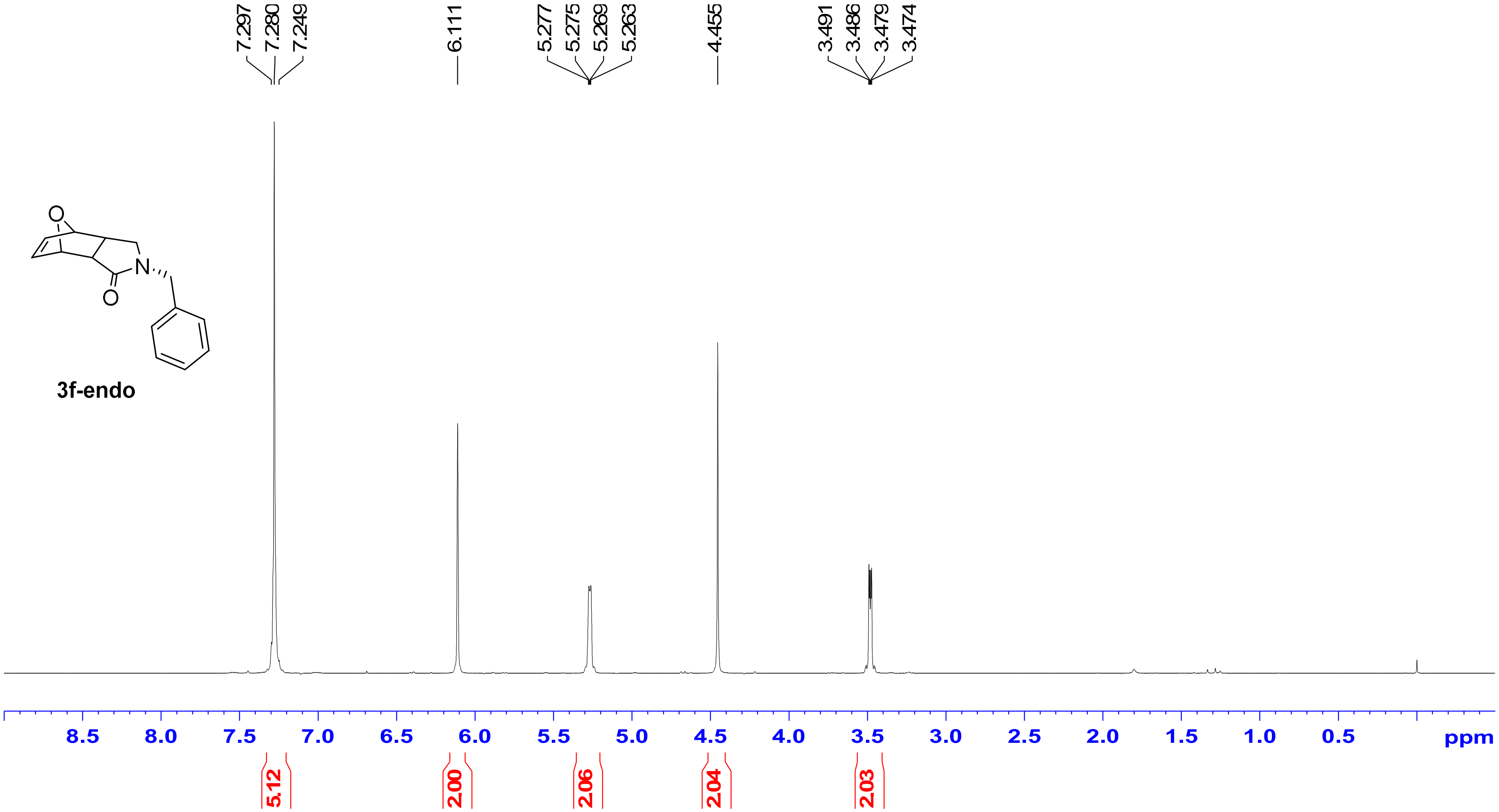

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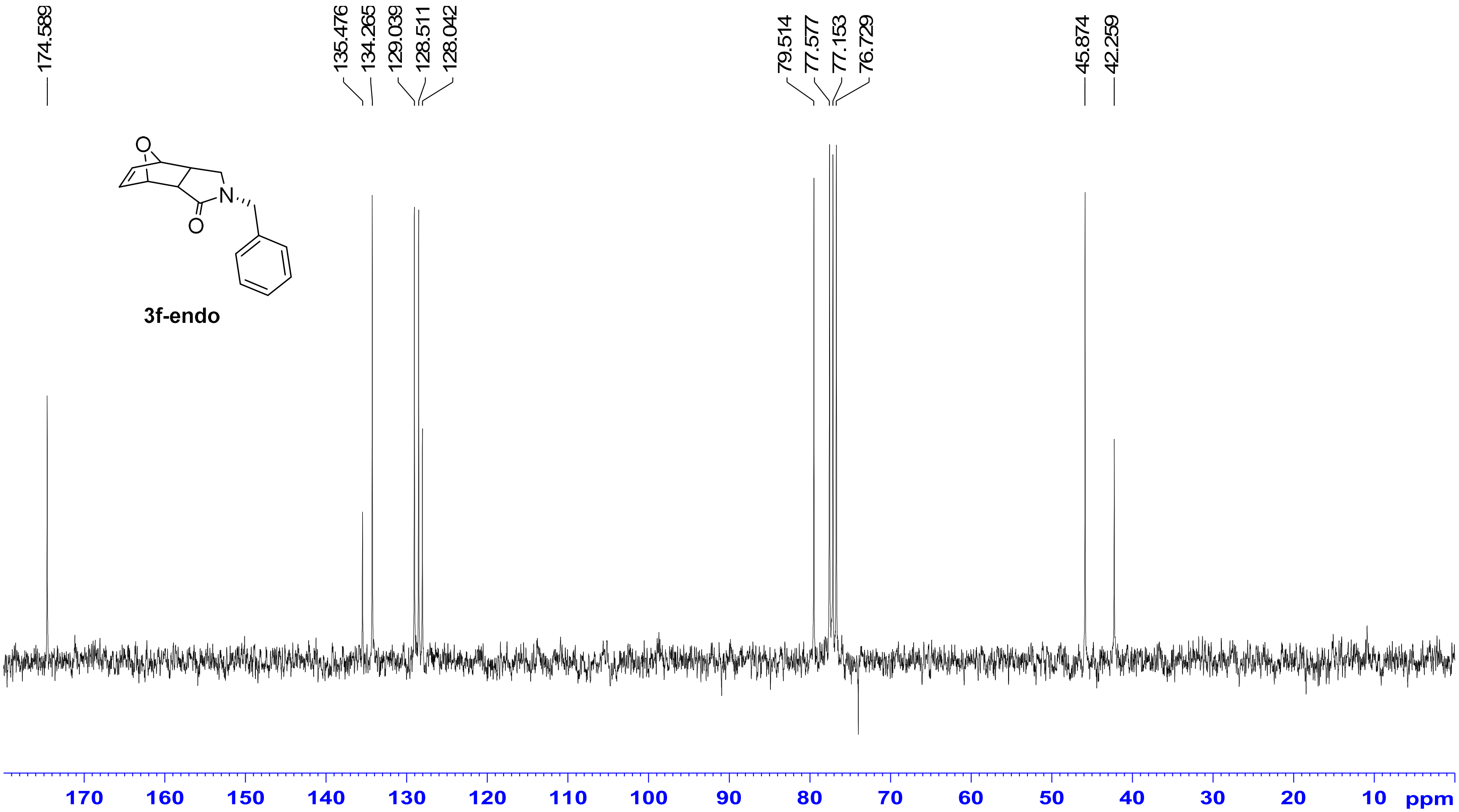

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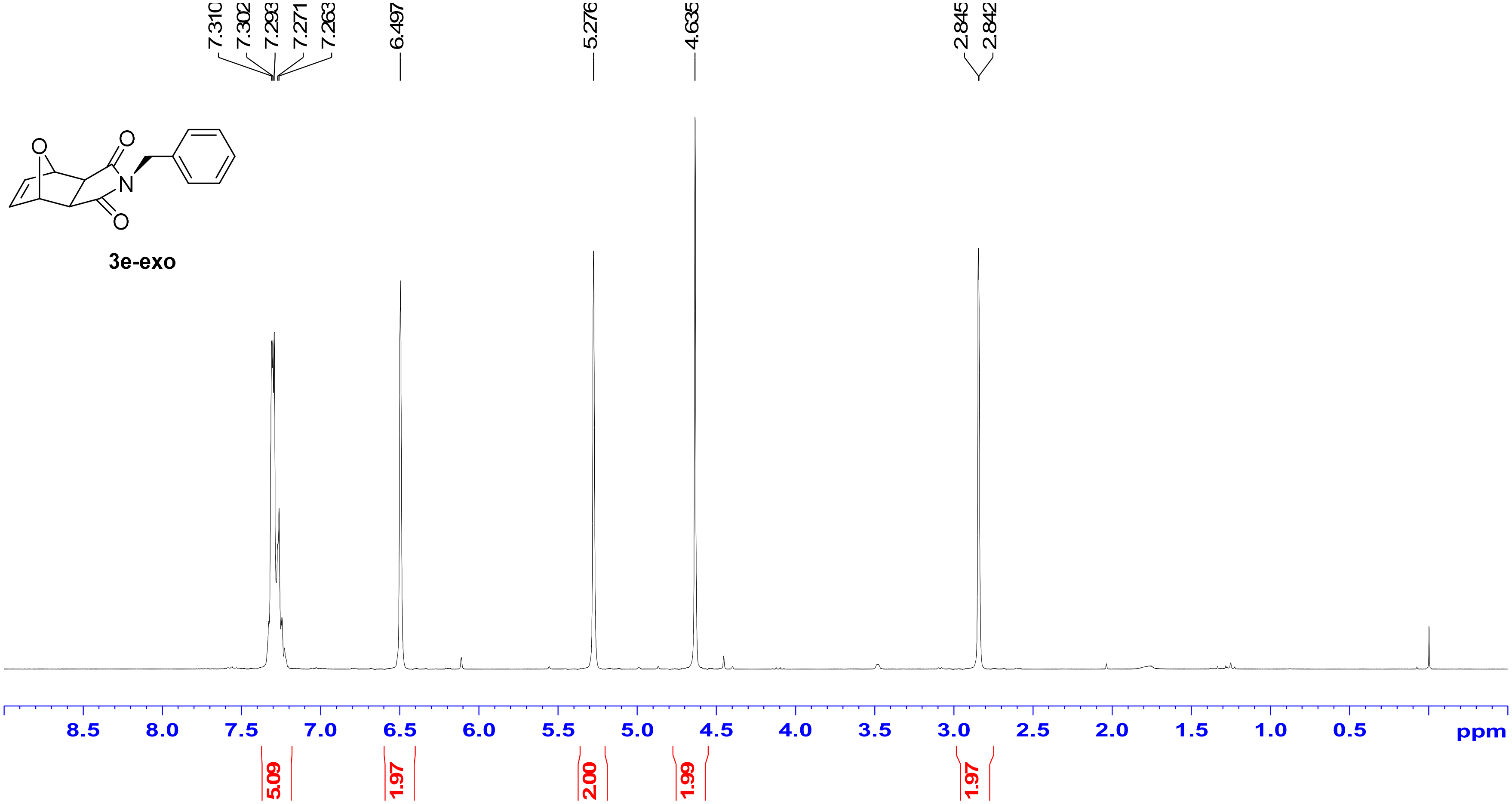

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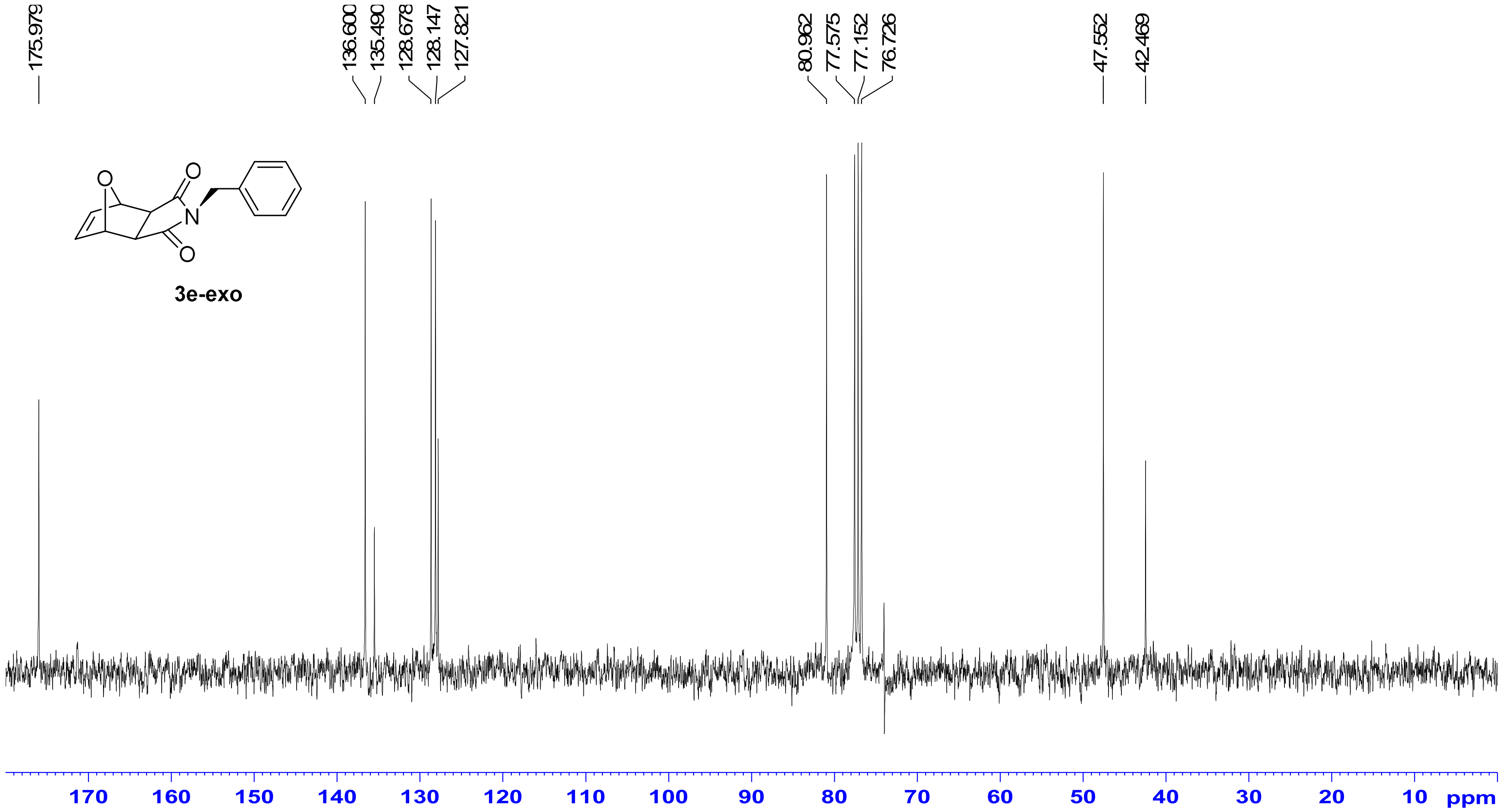

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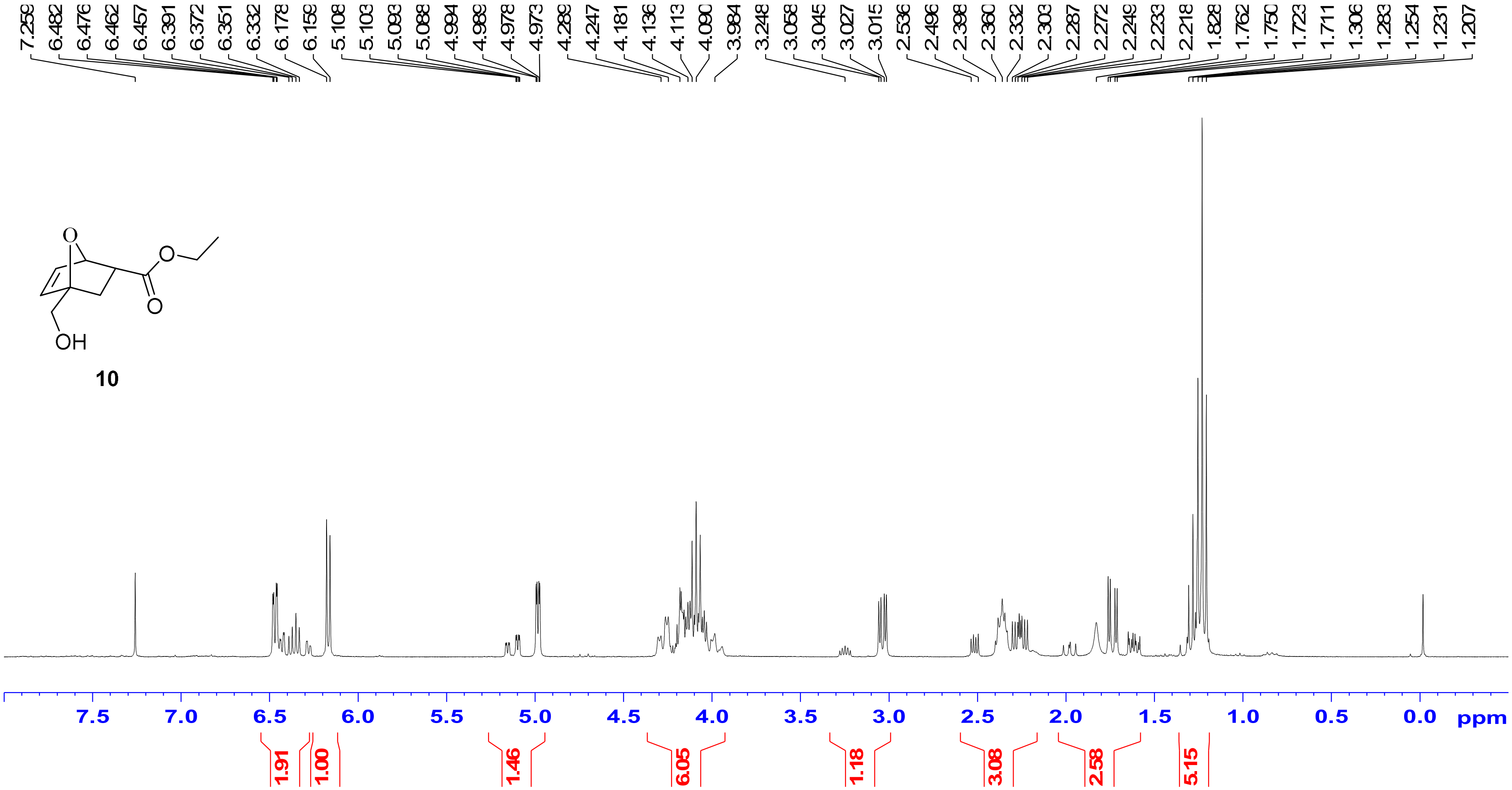

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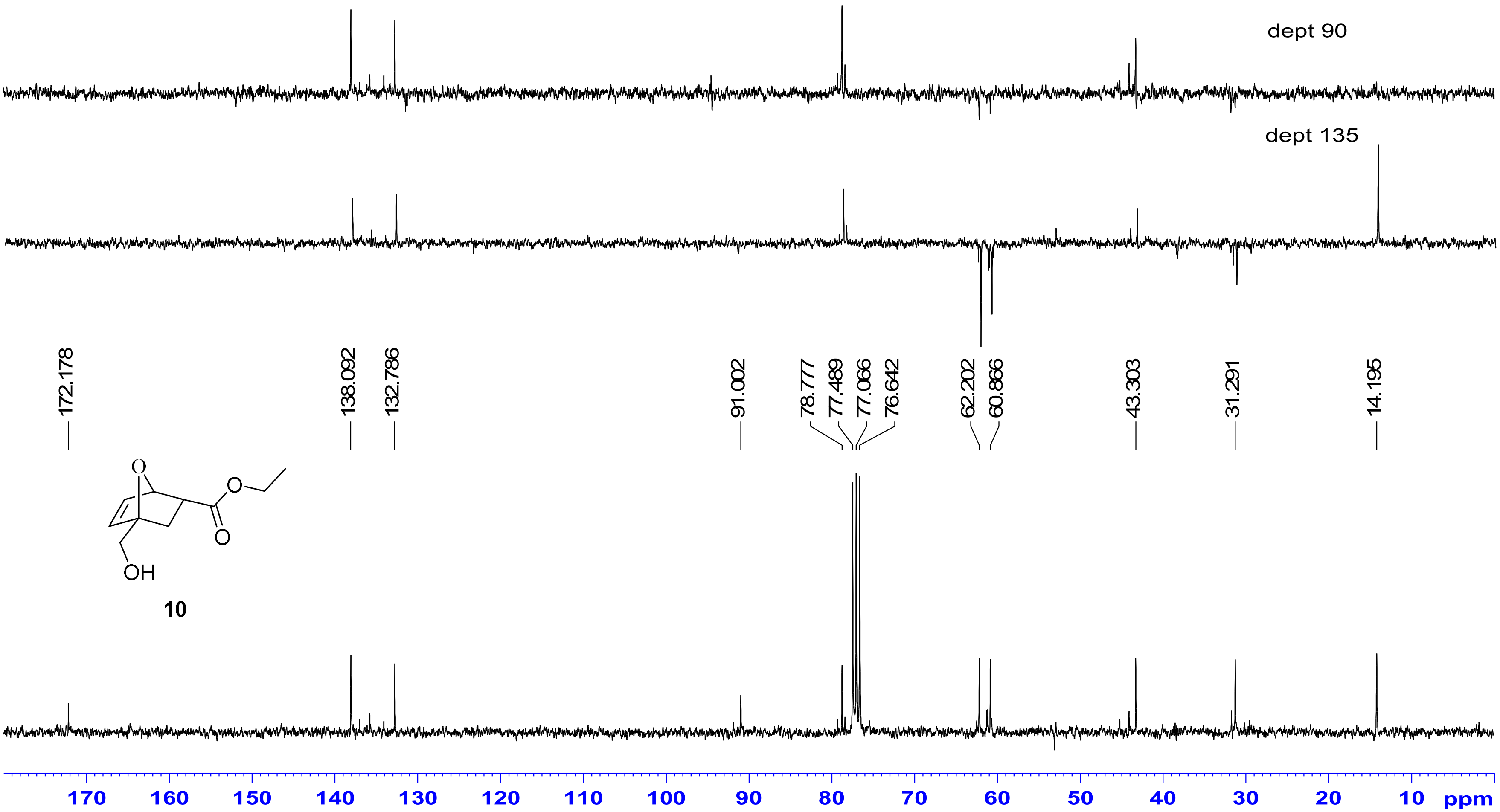

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