Electronic Supplementary Material (ESI) for Green Chemistry.

Supporting Information

Simple Ketone as an Efficient Metal-Free Catalyst for Visible-Light-Mediated Diels-Alder and Aza-Diels-Alder Reactions

Jiri Kollmann†, Yu Zhang†, Waldemar Schilling, Tong Zhang, Daniel Reimer, Shoubhik Das*

Institut für Organische und Biomolekulare Chemie

Georg-August-Universität Göttingen

Tammannstraße 2, Göttingen, Germany

Corresponding Author

*E-mail: shoubhik.das@chemie.uni-goettingen.de

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1. Materials and methods

Commercial reagents were used without purification and reactions were carried out under air. Solvents used for reaction, workup or TLC were distilled. TLC plates with a 0.20 mm silica gel 60 layer on alumina containing a fluorescent indicator F_{254} from MACHEREY NAGEL by MERCK were used for reaction monitoring, retardation factor determination and isolation. ^{1}H NMR spectra (300, 400 MHz) and ^{13}C NMR spectra (75, 100 MHz) were recorded using BRUKER spectrometers AVANCE III 300, AVANCE III 400 and VARIAN spectrometers Mercury VX 300 and VNMRS 300 with $CDCl_3$ as solvent. NMR spectra were calibrated using the solvent residual signals ($CDCl_3$: ^{1}H (s) δ = 7.26 ppm, ^{13}C (t) δ = 77.16 ppm). ESI mass spectra were recorded on BRUKER Daltonic spectrometers maXis (ESI-QTOF-MS) and micrOTOF (ESI-TOF-MS). GC-MS mass spectra were recorded on THERMO FINNIGAN spectrometers TRACE (Varian GC Capillary Column; wcot fused silica coated CP-SIL 8 CB; 30 m x 0.25 mm x 0.25 µm) and DSQ (Varian FactorFour Capillary Column; VF-5ms 30 m x 0.25 mm x 0.25 µm).

2. Setup for photocatalytic reactions

The reaction setup is depicted in **Figure S1**. The reaction setup consists of a self-constructed light source configuration, made up of a crystallizing dish with a diameter of 140 mm. Inside of the crystallizing dish, commercially available 5 m LED-Strip is glued with separable LED elements. In total, 3 m LED strip is used in a crystallizing dish, with a total power of 24 W. Light intensity of the light source can be adjusted by a self-constructed dimmer. Construction of the reaction setup and the dimmer was performed by the electronic services of the faculty for chemistry of the Georg-August-Universität Göttingen. Cooling of the setup is performed by a commercially available 120 mm computer fan. To ensure constant room temperature the dimmer setting was used at 50 % (12 W). During the first experiment the temperature was monitored inside the crystallizing dish and did not exceed the room temperature (25–30 °C). Magnetic stirring was performed with 250 rpm.

Figure S1: LED reaction setup for photocatalytic reactions.

3. General procedure for blue LED-mediated Diels-Alder reactions

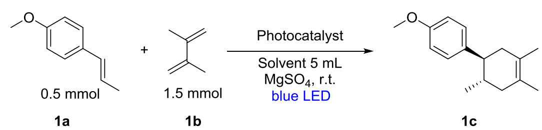
A 10 mL one-necked flask containing a stirring bar was charged with the dienophile (1.00 equiv., 0.50 mmol), fluorenone (3 mol%, 15.0 μmol) and nitromethane (5.0 mL). The diene (3.00 equiv., 1.50 mmol) was added to the stirred solution (for **12c** no diene was added). The resulting mixture was stirred for 2–44 h at room temperature under 12 W blue LED irradiation (the progress can be monitored *via* GC-MS or TLC). The resulting mixture underwent an aqueous workup using brine (3.0 mL) and was extracted three times with ethyl acetate (3 x 3.0 mL). The combined organic layers were dried over anhydrous Na_2SO_4, filtered and concentrated *in vacuo*. The crude product was purified by silica gel preparative TLC using a mixture of *n*-hexane and ethyl acetate as eluent.

4. General procedure for blue LED-mediated hetero-Diels-Alder reactions

A 10 mL one-necked flask containing a stirring bar was charged with the imine (1.00 equiv., 0.10 mmol) or ketone (only for **15ac**), fluorenone (3 mol%, 3.00 μmol) and nitromethane (5.0 mL). Danishefsky's diene (3.00 equiv., 0.30 mmol) was added to the stirred solution (for **14ac** and **15ac** other dienes were used). The resulting mixture was stirred for 2–8 h at room temperature under 12 W blue LED irradiation (the progress can be monitored *via* GC-MS or TLC). The resulting mixture underwent an aqueous workup using brine (3.0 mL) and was extracted three times with ethyl acetate (3 x 3.0 mL). The combined organic layers were dried over anhydrous Na_2SO_4, filtered and concentrated *in vacuo*. The crude product was purified by silica gel preparative TLC using a mixture of *n*-hexane and ethyl acetate as eluent.

5. Optimization for (aza)-Diels-Alder reactions

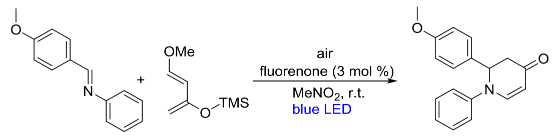
Table S1: Optimization for Diels-Alder reactions



Entry	Catalysts	Catalyst amount	Solvent	Yield [%][b]
1	-	-	$MeNO_2$	0
2	Fluorenone	3 mol%	$MeNO_2$	81
3	Methylene blue	3 mol%	$MeNO_2$	0
4	Rose bengal	3 mol%	$MeNO_2$	0
5	Eosin Y	3 mol%	$MeNO_2$	0
6	Michler's ketone	3 mol%	$MeNO_2$	0
7	Xanthone	3 mol%	$MeNO_2$	6
8	Thioxanthen-9-one	3 mol%	$MeNO_2$	8
9	Acriflavine	3 mol%	$MeNO_2$	0
10	Fluorenone	5 mol%	$MeNO_2$	83
11	Fluorenone	10 mol%	$MeNO_2$	88
12	Fluorenone	3 mol%	$MeNO_2$	81[c]
13	Fluorenone	3 mol%	$MeNO_2$	79[d]
14	Fluorenone	3 mol%	$MeNO_2$	73[e]
15	Fluorenone	3 mol%	$MeNO_2$	74[f]
16	Fluorenone	3 mol%	THF	0
17	Fluorenone	3 mol%	DMF	0
18	Fluorenone	3 mol%	DMSO	0
19	Fluorenone	3 mol%	ACN	50
20	Fluorenone	3 mol%	$MeNO_2$	60[g]

[a] General reaction conditions: air, 12 W blue LED, 0.5 mmol 1a (1 eq.), 1.5 mmol 1b (3 eq.), photocatalyst (3 mol%), 5 mL solvent, 30 mg $MgSO_4$, room temperature, 4 h. [b] Yields were determined by NMR yield using iodoform as an internal standard. [c] No $MgSO_4$. [d] 10 mg $MgSO_4$. [e] 60 mg $MgSO_4$. [f] 100 mg $MgSO_4$. [g] Under nitrogen.

Table S2: Optimization for aza-Diels-Alder reactions



Entry	Catalyst	Solvent	Volume(mL)	Yield [%][b]
1	Fluorenone	$MeNO_2$	5	99
2	Fluorenone	$MeNO_2$	1	23
3	Fluorenone	$MeNO_2$	3	58
4	Fluorenone	$MeNO_2$	5	55[c]
5	Fluorenone	$MeNO_2$	5	96[d]
6	Fluorenone	DCM	5	0
7	Fluorenone	$CHCl_3$	5	0
8	Fluorenone	DMSO	5	25
9	Fluorenone	DMF	5	0

[a] General reaction conditions: air, 12 W blue LED, 0.5 mmol **1aa** (1 eq.), 1.5 mmol **1ab** (3 eq.), photocatalyst (3 mol%), 5 mL solvent, room temperature, 2 h. [b] Yields were determined by NMR yield using iodoform as an internal standard. [c] 0.5 mmol **1aa** (1 eq.), 0.5 mmol **1ab** (1 eq.). [d] 0.5 mmol **1aa** (1 eq.), 1.0 mmol **1ab** (2 eq.).

5. Mechanistic investigations

Stern-Volmer Plot

To determine the reactive species in the beginning of the photocatalytic reaction absorption-emission spectra for a Stern-Volmer plot were acquired. Firstly, a 3D spectrum for excitation and emission of 9-fluorenone was recorded in order to detect the maxima of absorption and emission. The resulting spectrum is depicted in **Figure S2**. The excitation maximum was determined at 402 nm and the emission maximum at 519 nm. These wavelengths were used for further measurements.

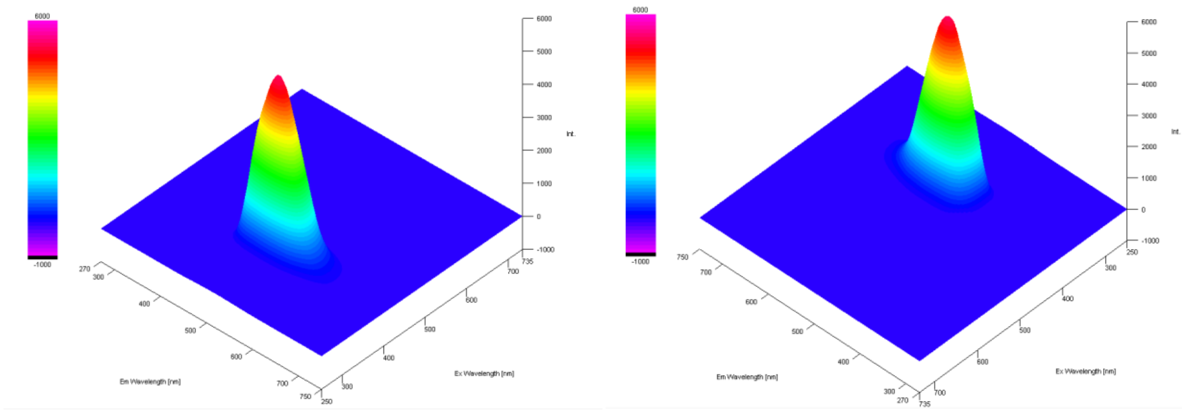


Figure S2: 3D absorbtion-emission spectrum of fluorenone in nitromethane.

A blank sample was recorded without substrates and the received intensity was set as I_0. The effect of varied amounts of *trans*-anethole and 2,3-dimethyl-1,3-butadiene were investigated. **Figure S3** shows a summary of investigations. Depending on the concentration of *trans*-anethole**,** the emission decreases significantly. The concentration of 2,3-dimethyl-1,3-butadiene had no measurable effect on the emission of fluorenone.

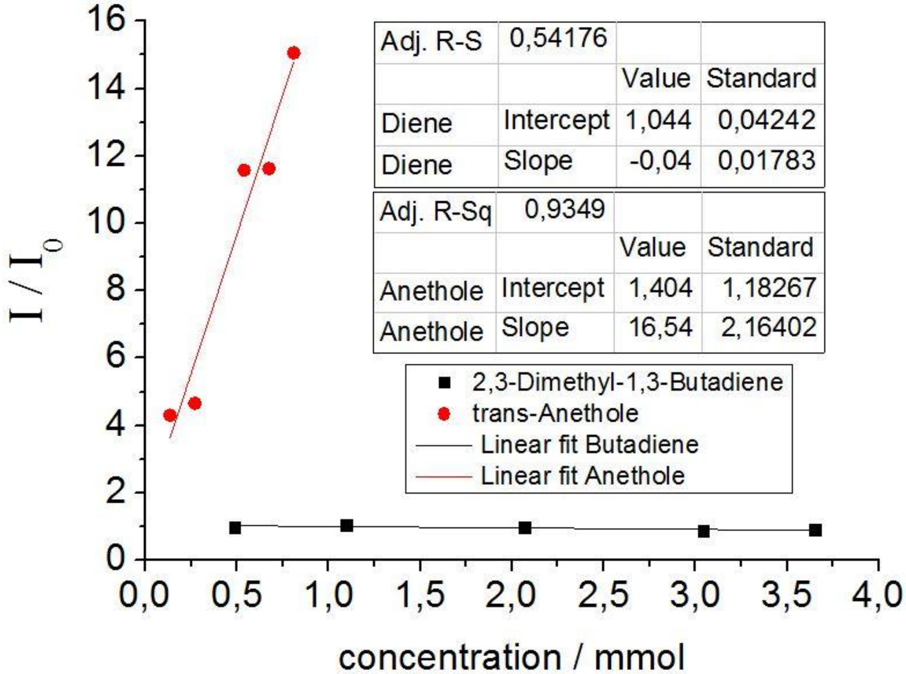
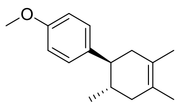
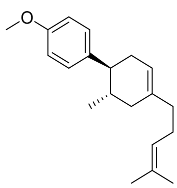


Figure S3: Stern-Volmer plot for different concentrations of *trans*-anethole (red) and 2,3-dimethyl-1,3-butadiene (black).

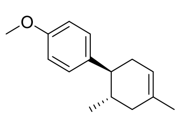
7. Characterization



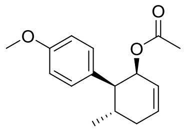
(1*S*,2*S*)-4'-methoxy-2,4,5-trimethyl-1,2,3,6-tetrahydro-1,1'-biphenyl (1c): ^{1}**H NMR** ($CDCl_3$, 300 MHz): δ 7.12 – 7.07 (m, 2H), 6.88 – 6.83 (m. 2H), 3.80 (s, 3H), 2.35 (td, J = 10.2, 6.2 Hz, 1H), 2.22 – 2.05 (m, 3H), 1.94 – 1.78 (m, 2H), 1.66 (s, 3H), 1.63 (s, 3H), 0.71 (d, J = 6.1 Hz, 3H); ^{13}**C NMR** ($CDCl_3$, 75 MHz): δ 157.9, 138.3, 128.6, 125.6, 125.4, 113.8, 55.3, 48.0, 42.0, 41.8, 34.4, 20.2, 18.9, 18.8; **MS (ESI):** *m/z* 231.1 $[M+H]^+$, 253.1 $[M+Na]^+$; $\boldsymbol{R}_{\mathbf{F}}$ = 0.55 (*n*-Hex:EtOAc 19:1); Yield: 74 %.[1]



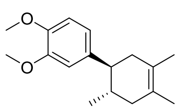
(1*S*,2*S*)-4'-methoxy-2-methyl-4-(4-methylpent-3-en-1-yl)-1,2,3,6-tetrahydro-1,1'-biphenyl (2c): ^{1}**H NMR** ($CDCl_3$, 300 MHz): δ 7.11 – 7.06 (m, 2H), 6.86 – 6.81 (m, 2H), 5.45 (s, 1H), 5.16 – 5.11 (m, 1H), 3.79 (s, 3H), 2.37 – 2.07 (m, 6H), 2.01 – 1.76 (m, 4H), 1.70 (s, 3H), 1.62 (s, 3H), 0.71 (d, J = 6.2 Hz, 3H); ^{13}**C NMR** ($CDCl_3$, 75 MHz): δ 157.9, 138.4, 137.6, 131.6, 128.6, 124.5, 120.6, 113.8, 55.4, 47.2, 38.3, 37.7, 35.3, 34.1, 26.6, 25.9, 20.4, 17.9; **ESI-HRMS**: *m/z* calcd. for $[C_{20}H_{28}O+Na]^+$: 307.2032, found 307.2029; Yield: 82 %.[1]



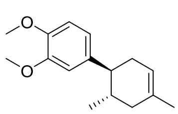
(1*S*,2*S*)-4'-methoxy-2,4-dimethyl-1,2,3,6-tetrahydro-1,1'-biphenyl (3c): ^{1}**H NMR** ($CDCl_3$, 300 MHz): δ 7.11 – 7.06 (m, 2H), 6.87 – 6.82 (m, 2H), 5.45 (s, 1H), 3.80 (s, 3H), 2.31 (td, J = 10.4, 5.3 Hz, 1H), 2.22 – 2.05 (m, 3H), 1.97 – 1.75 (m, 2H), 1.69 (s, 3H), 0.71 (d, J = 6.2 Hz, 3H); ^{13}**C NMR** ($CDCl_3$, 75 MHz): δ 157.9, 138.3, 134.0, 128.6, 121.0, 113.8, 55.4, 47.1, 40.0, 35.4, 34.1, 23.5, 20.4; **MS (ESI):** *m/z* 217.1 $[M+H]^+$; $\boldsymbol{R}_{\mathbf{F}}$ = 0.35 (*n*-Hex:EtOAc 19:1); Yield: 88 %.[1]



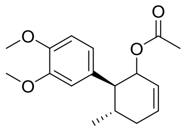
(1*S*,2*S*,6*S*)-4'-methoxy-6-methyl-1,2,5,6-tetrahydro-[1,1'-biphenyl]-2-yl acetate (4c): **^{1}H NMR** ($CDCl_3$, 300 MHz): δ 7.15 – 7.11 (m, 2H), 6.85 – 6.80 (m, 2H), 6.03 (ddd, *J* = 9.9, 4.8, 2.2 Hz, 1H), 5.90 – 5.84 (m, 1H), 5.24 – 5.21 (m, 1H), 3.79 (s, 3H), 2.62 (dd, *J* = 11.8, 3.8 Hz, 1H), 2.43 – 2.27 (m, 2H), 1.91 – 1.78 (m, 1H), 1.88 (s, 3H), 0.79 (d, *J* = 6.3 Hz, 3H); **^{13}C NMR** ($CDCl_3$, 75 MHz): δ 170.3, 158.3, 133.0, 132.4, 130.4, 125.1, 113.5, 70.1, 55.3, 50.8, 35.2, 27.2, 21.3, 20.0; **ESI-HRMS**: *m/z* calcd. for $[C_{16}H_{20}O_3+NH_4]^+$: 278.1751, found 278.1753; calcd. for $[C_{16}H_{20}O_3+Na]^+$: 283.1305, found 283.1306; calcd. for $[C_{16}H_{20}O_3+K]^+$: 299.1044, found 299.1050; Yield: 64 %.[2]



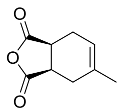
(1*S*,2*S*)-3',4'-dimethoxy-2,4,5-trimethyl-1,2,3,6-tetrahydro-1,1'-biphenyl (5c): **^{1}H NMR** ($CDCl_3$, 300 MHz): δ 6.82 – 6.79 (m, 1H), 6.73 – 6.70 (m, 2H), 3.87 (s, 3H), 3.86 (s, 3H), 2.33 (td, *J* = 10.1, 6.3 Hz, 1H), 2.19 – 2.02 (m, 3H), 1.93 – 1.77 (m, 2H), 1.64 (s, 3H), 1.62 (s, 3H), 0.71 (d, *J* = 6.1 Hz, 3H); **^{13}C NMR** ($CDCl_3$, 75 MHz): δ 149.0, 147.3, 139.0, 125.5, 125.5, 119.7, 111.2, 110.8, 56.0, 56.0, 48.5, 41.9, 41.7, 34.4, 20.1, 18.9, 18.8; **ESI-HRMS**: *m/z* calcd. for $[C_{17}H_{24}O_2+H]^+$: 261.1849, found 261.1848; calcd. for $[C_{17}H_{24}O_2+Na]^+$: 283.1669, found 283.1662; Yield: 80 %.[2]



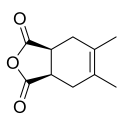
(1*S*,2*S*)-3',4'-dimethoxy-2,4-dimethyl-1,2,3,6-tetrahydro-1,1'-biphenyl (6c): **^{1}H NMR** ($CDCl_3$, 300 MHz): δ 6.82 – 6.79 (m, 1H), 6.73 – 6.70 (m, 2H), 5.44 (s, 1H), 3.87 (s, 3H), 3.86 (s, 3H), 2.29 (td, *J* = 10.3, 4.9 Hz, 1H), 2.23 – 2.04 (m, 3H), 1.96 – 1.74 (m, 2H), 1.69 (s, 3H), 0.72 (d, *J* = 6.2 Hz, 3H); **^{13}C NMR** ($CDCl_3$, 75 MHz): δ 149.0, 147.3, 139.0, 134.0, 120.9, 119.8, 111.2, 110.9, 56.0, 56.0, 47.6, 40.0, 35.3, 34.2, 23.5, 20.4; **ESI-HRMS**: *m/z* calcd. for $[C_{16}H_{22}O_2+H]^+$: 247.1693, found 247.1693; calcd. for $[C_{16}H_{22}O_2+Na]^+$: 269.1512, found 269.1511; Yield: 69 %.[2]



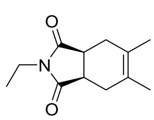
(1*S*,6*S*)-3',4'-dimethoxy-6-methyl-1,2,5,6-tetrahydro-[1,1'-biphenyl]-2-yl acetate (7c): **^{1}H NMR** ($CDCl_3$, 300 MHz): δ 6.81 – 6.77 (m, 3H), 6.03 (ddd, J = 9.9, 4.8, 2.2 Hz, 1H), 5.92 – 5.86 (m, 1H), 5.26 – 5.22 (m, 1H), 3.87 (s, 3H), 3.86 (s, 3H), 2.61 (dd, J = 11.8, 3.7 Hz, 1H), 2.50 – 2.17 (m, 3H), 1.90 (s, 3H), 0.81 (d, J = 6.3 Hz, 3H); **^{13}C NMR** ($CDCl_3$, 75 MHz): δ 170.2, 153.0, 148.5, 137.7, 133.0, 125.1, 121.9, 112.7, 110.9, 70.2, 56.0, 55.9, 51.1, 35.2, 27.3, 21.4, 20.0; **ESI-HRMS**: *m/z* calcd. for $[C_{17}H_{22}O_4+NH_4]^+$: 308.1856, found 308.1860; calcd. for $[C_{17}H_{22}O_4+Na]^+$: 313.1410, found 313.1403; Yield: 77 %.



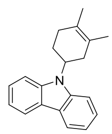
(3a*R*,7a*S*)-5-methyl-3a,4,7,7a-tetrahydroisobenzofuran-1,3-dione (8c): **^{1}H NMR** ($CDCl_3$, 300 MHz): δ 5.63 – 5.58 (m, 1H), 3.43 – 3.29 (m, 2H), 2.55 (ddd, J = 16.3, 6.8, 2.6 Hz, 1H), 2.47 (dd, J = 15.6, 2.8 Hz, 1H), 2.29 – 2.18 (m, 2H), 1.74 (s, 3H); **^{13}C NMR** ($CDCl_3$, 75 MHz): δ 174.6, 174.5, 136.7, 120.2, 40.2, 39.5, 28.5, 24.2, 23.6; **ESI-HRMS**: *m/z* calcd. for $[C_9H_{10}O_3+H]^+$: 167.0703, found 167.0705; calcd. for $[C_9H_{10}O_3+Na]^+$: 189.0522, found 189.0521; Yield: 94 %.[3]



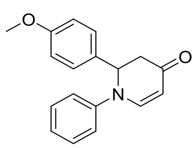
(3a*R*,7a*S*)-5,6-dimethyl-3a,4,7,7a-tetrahydroisobenzofuran-1,3-dione (9c): **^{1}H NMR** ($CDCl_3$, 300 MHz): δ 3.34 – 3.31 (m, 2H), 2.43 (d, J = 15.1 Hz, 2H), 2.25 (d, J = 13.7 Hz, 2H), 1.68 (d, J = 0.9 Hz, 6H); **^{13}C NMR** ($CDCl_3$, 75 MHz): δ 174.7, 127.4, 40.5, 30.5, 19.4; **ESI-HRMS**: *m/z* calcd. for $[C_{10}H_{12}O_3+H]^+$: 181.0859, found 181.0860; calcd. for $[C_{10}H_{12}O_3+Na]^+$: 203.0679, found 203.0678; Yield: 95 %.[4]



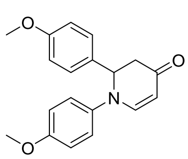
(3a*R*,7a*S*)-2-ethyl-5,6-dimethyl-3a,4,7,7a-tetrahydro-1*H*-isoindole-1,3(2*H*)-dione (10c): **^{1}H NMR** ($CDCl_3$, 300 MHz): δ 3.47 (q, J = 7.2 Hz, 2H), 3.00 – 2.97 (m, 2H), 2.42 (d, *J* = 14.6 Hz, 2H), 2.20 (d, *J* = 14.0 Hz, 2H), 1.64 (d, *J* = 1.0 Hz, 6H), 1.05 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR** ($CDCl_3$, 75 MHz): δ 180.2, 127.0, 40.0, 33.8, 30.9, 19.3, 13.2; **ESI-HRMS**: *m/z* calcd. for $[C_{12}H_{17}O_2+H]^+$: 208.1332, found 208.1328; calcd. for $[C_{12}H_{17}O_2+Na]^+$: 230.1151, found 230.1145; Yield: 86 %.[5]



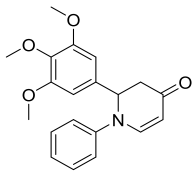
9-(3,4-dimethylcyclohex-3-en-1-yl)-9*H*-fluoren (11c): ^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.11 – 8.07 (m, 2H), 7.52 – 7.49 (m, 2H), 7.43 – 7.37 (m, 2H), 7.22 – 7.16 (m, 2H), 4.82 – 4.71 (m, 1H), 3.06 – 2.94 (m, 1H), 2.72 – 2.58 (m, 1H), 2.43 – 2.31 (m, 1H), 2.25 – 2.16 (m, 2H), 2.04 – 1.99 (m, 1H), 1.72 (s, 3H), 1.66 (s, 3H); **^{13}C NMR** ($CDCl_3$, 125 MHz): δ 139.7, 125.9, 125.3, 124.4, 123.3, 120.3, 118.5, 110.1, 52.4, 34.9, 32.6, 27.8, 19.1, 18.8; **ESI-HRMS**: *m/z* calcd. for $[C_{21}H_{22}+H]^+$: 276.1752, found 276.1759; Yield: 50%.



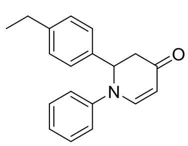
2-(4-methoxyphenyl)-1-phenyl-2,3-dihydropyridin-4(1*H*)-one (1ac): ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.64 (dd, *J* = 7.8, 1.1 Hz, 1H), 7.33 – 7.27 (m, 2H) 7.20 – 7.15 (m, 2H), 7.10 (tt, *J* = 6.9, 1.0 Hz, 1H), 7.04 – 7.00 (m, 2H), 6.86 – 6.81 (m, 2H), 5.27 (dd, *J* = 7.8, 1.1 Hz, 1H), 5.24 (dd, *J* = 6.9, 3.2 Hz, 1H), 3.77 (s, 3H), 3.26 (dd, *J* = 16.3, 7.0 Hz, 1H), 2.76 (ddd, *J* = 16.3, 3.3, 1.1 Hz, 1H); **^{13}C NMR** ($CDCl_3$, 75 MHz): δ 190.6, 159.3, 148.4, 144.9, 129.9, 129.6, 127.5, 124.5, 118.8, 114.5, 102.9, 61.4, 55.4, 43.8; **ESI-HRMS**: *m/z* calcd. for $[C_{18}H_{17}NO_2+H]^+$: 280.1332, found 280.1330; calcd. for $[C_{18}H_{17}NO_2+Na]^+$: 302.1151, found 302.1144; calcd. for $[C_{18}H_{17}NO_2+K]^+$: 318.0891, found 318.0881; Yield: 80 %.[6]



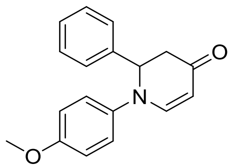
1,2-bis(4-methoxyphenyl)-2,3-dihydropyridin-4(1*H*)-one (2ac): **^{1}H NMR** ($CDCl_3$, 300 MHz): δ 7.19 – 7.14 (m, 2H), 6.98 – 6.93 (m, 2H), 6.85 – 6.77 (m, 4H), 7.50 (d, *J* = 7.8 Hz, 1H), 5.21 (d, *J* = 7.7 Hz, 1H), 5.13 (dd, *J* = 6.9, 4.3 Hz, 1H), 3.77 (s, 3H), 3.76 (s, 3H), 3.21 (dd, *J* = 16.3, 7.0 Hz, 1H), 2.74 (dd, *J* = 16.3, 4.2 Hz, 1H); **^{13}C NMR** ($CDCl_3$, 75 MHz): δ 190.5, 159.3, 157.1, 149.8, 138.5, 130.4, 127.8, 121.5, 114.7, 114.4, 101.6, 62.2, 55.7, 55.4, 43.8; **ESI-HRMS**: *m/z* calcd. for $[C_{19}H_{19}NO_3+H]^+$: 310.1438, found 310.1440; calcd. for $[C_{19}H_{19}NO_3+Na]^+$: 332.1257, found 332.1256; Yield: 89 %. [7]



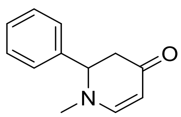
1-phenyl-2-(3,4,5-trimethoxyphenyl)-2,3-dihydropyridin-4(1*H*)-one (3ac): **^{1}H NMR** ($CDCl_3$, 300 MHz): δ 7.66 (dd, *J* = 7.8, 0.8 Hz, 1H), 7.34 – 7.28 (m, 2H), 7.15 – 7.10 (m, 1H), 7.05 – 7.03 (m, 2H), 6.46 (s, 2H), 5.29 (dd, *J* = 7.8, 0.7 Hz, 1H), 5.18 (dd, *J* = 7.1, 2.9 Hz, 1H), 3.81 (s, 3H), 3.77 (s, 6H), 3.28 (dd, *J* = 16.4, 7.2 Hz, 1H), 2.77 (ddd, *J* = 16.3, 3.1, 0.8 Hz, 1H); **^{13}C NMR** ($CDCl_3$, 75 MHz): δ 190.4, 153.7, 148.5, 144.9, 137.7, 133.9, 129.7, 124.8, 119.0, 103.3, 102.7, 62.1, 60.9, 56.3, 43.7; **ESI-HRMS**: *m/z* calcd. for $[C_{20}H_{21}NO_4+H]^+$: 340.1543, found 340.1536; calcd. for $[C_{20}H_{21}NO_4+Na]^+$: 362.1363, found 362.1357; Yield: 91 %.



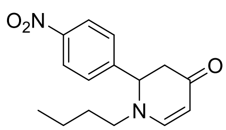
2-(4-ethylphenyl)-1-phenyl-2,3-dihydropyridin-4(1*H*)-one (4ac): **^{1}H NMR** ($CDCl_3$, 300 MHz): δ 7.67 (dd, *J* = 7.8, 1.0 Hz, 1H), 7.32 – 7.27 (m, 2H), 7.19 – 7.08 (m, 5H), 7.08 – 7.02 (m, 2H), 5.29 – 5.24 (m, 2H), 3.29 (dd, *J* = 16.3, 7.1 Hz, 1H), 2.78 (ddd, *J* = 16.3, 3.0, 1.0 Hz, 1H), 2.62 (q, *J* = 7.6 Hz, 2H), 1.21 (t, *J* = 7.6 Hz, 3H); **^{13}C NMR** ($CDCl_3$, 75 MHz): δ 190.5, 148.2, 145.0, 144.0, 135.1, 129.7, 128.6, 126.2, 124.5, 118.7, 103.1, 61.7, 43.7, 28.6, 15.5; **ESI-HRMS**: *m/z* calcd. for $[C_{19}H_{19}NO+H]^+$: 278.1539, found 278.1541; calcd. for $[C_{19}H_{19}NO+Na]^+$: 300.1359, found 300.1358; Yield: 87 %.



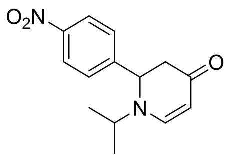
1-(4-methoxyphenyl)-2-phenyl-2,3-dihydropyridin-4(1*H*)-one (5ac): ^{1}**H NMR** ($CDCl_3$, 300 MHz): δ 7.54 (dd, J = 7.8, 0.8 Hz, 1H), 7.34 – 7.22 (m, 5H), 6.98 – 6.93 (m, 2H), 6.83 – 6.77 (m, 2H), 5.23 (dd, J = 7.8, 0.8 Hz, 1H), 5.18 (dd, J = 7.1, 3.9 Hz, 1H), 3.75 (s, 3H), 3.26 (dd, J = 16.4, 7.2 Hz, 1H), 2.77 (ddd, J = 16.4, 3.9, 0.8 Hz, 1H); ^{13}**C NMR** ($CDCl_3$, 75 MHz): δ 190.2, 157.0, 149.7, 138.5, 138.4, 129.1, 128.0, 126.5, 121.3, 114.8, 101.8, 62.6, 55.7, 43.6; **ESI-HRMS**: *m/z* calcd. for $[C_{18}H_{17}NO_2+H]^+$: 280.1332, found 280.1331; calcd. for $[C_{18}H_{17}NO_2+Na]^+$: 302.1151, found 302.1148; Yield: 86 %.[6]



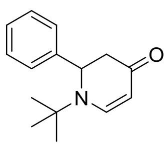
1-methyl-2-phenyl-2,3-dihydropyridin-4(1*H*)-one (6ac): ^{1}**H NMR** ($CDCl_3$, 300 MHz): δ 7.41 – 7.29 (m, 5H), 7.09 (d, J = 7.6 Hz, 1H), 5.03 (d, J = 7.6 Hz, 1H), 4.47 (dd, J = 9.6, 6.7 Hz, 1H), 2.83 (dd, J = 16.5, 6.8 Hz, 1H), 2.83 (s, 3H), 2.69 (dd, J = 16.5, 9.6 Hz, 1H); ^{13}**C NMR** ($CDCl_3$, 75 MHz): δ 190.7, 155.3, 139.0, 129.2, 128.5, 127.1, 98.7, 64.0, 44.1, 41.6; **ESI-HRMS**: *m/z* calcd. for $[C_{12}H_{13}NO+H]^+$: 188.1070, found 188.1072; calcd. for $[C_{12}H_{13}NO+Na]^+$: 210.0889, found 210.0889; Yield: 86 %.[8-9]



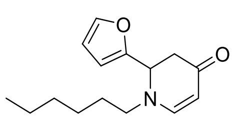
1-butyl-2-(4-nitrophenyl)-2,3-dihydropyridin-4(1*H*)-one (7ac): ^{1}**H NMR** ($CDCl_3$, 300 MHz): δ 8.24 – 8.19 (m, 2H), 7.49 – 7.45 (m, 2H), 7.19 (d, J = 7.6 Hz, 1H), 5.04 (d, J = 7.6 Hz, 1H), 4.73 (dd, J = 7.4, 5.9 Hz, 1H), 3.24 – 3.14 (m, 1H), 3.10 – 2.96 (m, 2H), 2.60 (dd, J = 16.4, 5.9 Hz, 1H), 1.54 (q, J = 7.1 Hz, 2H), 1.39 – 1.25 (m, 2H), 0.91 (t, J = 7.3 Hz, 3H); ^{13}**C NMR** ($CDCl_3$, 75 MHz): δ 188.8, 153.7, 147.9, 146.3, 127.8, 124.5, 98.9, 60.3, 54.1, 43.2, 31.1, 19.9, 13.8; **ESI-HRMS**: *m/z* calcd. for $[C_{15}H_{18}N_2O_3+H]^+$: 275.1390, found 275.1391; calcd. for $[C_{15}H_{18}N_2O_3+Na]^+$: 297.1210, found 297.1206; Yield: 90 %.



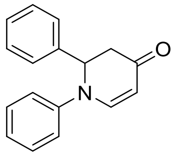
1-isopropyl-2-(4-nitrophenyl)-2,3-dihydropyridin-4(1*H*)-one (8ac): **^{1}H NMR** ($CDCl_3$, 300 MHz): δ 8.23 – 8.18 (m, 2H), 7.51 – 7.46 (m, 2H), 7.33 (d, *J* = 7.7 Hz, 1H), 5.10 (d, *J* = 7.7 Hz, 1H), 4.77 (dd, *J* = 7.3, 5.7 Hz, 1H), 3.41 (sept, *J* = 6.6 Hz, 1H), 3.00 (dd, *J* = 16.3, 7.4 Hz, 1H), 2.57 (dd, *J* = 16.3, 5.5 Hz, 1H), 1.30 (d, *J* = 6.7 Hz, 3H), 1.16 (d, *J* = 6.6 Hz, 3H); **^{13}C NMR** ($CDCl_3$, 75 MHz): δ 188.9, 150.0, 147.3, 127.6, 124.5, 99.4, 59.6, 54.3, 43.4, 21.9; **ESI-HRMS**: *m/z* calcd. for $[C_{14}H_{16}N_2O_3+H]^+$: 261.1234, found 261.1235; calcd. for $[C_{14}H_{16}N_2O_3+Na]^+$: 283.1053, found 283.1050; Yield: 93 %.



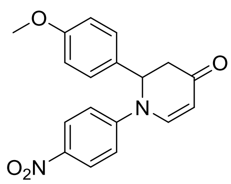
1-(*tert*-butyl)-2-phenyl-2,3-dihydropyridin-4(1*H*)-one (9ac): **^{1}H NMR** ($CDCl_3$, 300 MHz): δ 7.57 (dd, *J* = 7.7, 1.3 Hz, 1H), 7.30 – 7.18 (m, 5H), 5.02 (dd, *J* = 7.7, 1.0 Hz, 1H), 4.95 (d, *J* = 7.7 Hz, 1H), 3.10 (dd, *J* = 16.2, 7.7 Hz, 1H), 2.50 (td, *J* = 16.2, 1.4 Hz, 1H) 1.33 (s, 9H); **^{13}C NMR** ($CDCl_3$, 75 MHz): δ 189.0, 149.3, 140.1, 128.8, 127.6, 126.2, 98.7, 58.7, 56.3, 43.5, 29.4; **ESI-HRMS**: *m/z* calcd. for $[C_{15}H_{19}NO+H]^+$: 230.1539, found 230.1542; calcd. for $[C_{15}H_{19}NO+Na]^+$: 252.1359, found 252.1351; Yield: 94 %.



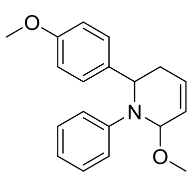
2-(furan-2-yl)-1-hexyl-2,3-dihydropyridin-4(1*H*)-one (10ac): **^{1}H NMR** ($CDCl_3$, 300 MHz): δ 7.38 (dd, *J* = 1.8, 0.8 Hz, 1H), 6.96 (d, *J* = 7.6 Hz, 1H), 6.32 (dd, *J* = 3.3, 1.8 Hz, 1H), 6.28 (d, *J* = 3.3 Hz, 1H), 4.96 (d, *J* = 7.6 Hz, 1H), 4.66 (t, *J* = 6.4 Hz, 1H), 3.31 – 3.09 (m, 2H), 2.83 (dd, *J* = 16.4, 6.6 Hz, 1H), 2.75 (dd, *J* = 16.6, 6.2 Hz, 1H), 1.62 – 1.52 (m, 2H), 1.34 – 1.23 (m, 6H), 0.91 – 0.86 (m, 3H); **^{13}C NMR** ($CDCl_3$, 75 MHz): δ 190.3, 152.9, 151.4, 142.7, 110.5, 108.6, 97.7, 54.4, 54.2, 40.0, 31.5, 29.2, 26.3, 22.6, 14.1; **ESI-HRMS**: *m/z* calcd. for $[C_{15}H_{21}NO_2+H]^+$: 248.1645, found 248.1647; calcd. for $[C_{15}H_{21}NO_2+Na]^+$: 270.1465, found 270.1465; calcd. for $[C_{15}H_{21}NO_2+K]^+$: 286.1204, found 286.1206; Yield: 92 %.



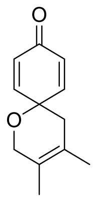
1,2-diphenyl-2,3-dihydropyridin-4(1*H*)-one (11ac): ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.68 (dd, *J* = 7.8, 1.1 Hz, 1H), 7.36 – 7.24 (m, 7H), 7.11 (tt, *J* = 7.4, 1.1 Hz, 1H), 7.04 – 7.00 (m, 2H), 5.29 (dd, *J* = 7.8, 1.0 Hz, 1H), 5.29 – 5.27 (m, 1H), 3.31 (dd, *J* = 16.4, 7.1 Hz, 1H), 2.80 (ddd, *J* = 16.4, 3.2, 1.1 Hz, 1H); **^{13}C NMR** ($CDCl_3$, 75 MHz): δ 190.4, 148.4, 144.9, 138.1, 129.7, 129.1, 128.0, 126.3, 124.6, 118.7, 103.2, 61.9, 43.6; **ESI-HRMS**: *m/z* calcd. for $[C_{17}H_{15}NO+H]^+$: 250.1226, found 250.1227; calcd. for $[C_{17}H_{15}NO+Na]^+$: 272.1046, found 272.1047; Yield: 83 %. [10]



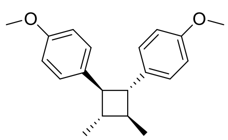
2-(4-methoxyphenyl)-1-(4-nitrophenyl)-2,3-dihydropyridin-4(1*H*)-one (12ac): ^{1}H NMR ($CDCl_3$, 300 MHz): δ 8.20 – 8.15 (m, 2H), 7.72 (dd, *J* = 8.1, 1.2 Hz, 1H), 7.17 – 7.07 (m, 4H), 6.89 – 6.84 (m, 2H), 5.44 (dd, *J* = 8.0, 1.0 Hz, 1H), 5.34 (d, *J* = 5.2 Hz, 1H), 3.78 (s, 3H), 3.31 (dd, *J* = 16.4, 6.9 Hz, 1H), 2.84 (ddd, *J* = 16.4, 2.6, 1.2 Hz, 1H); **^{13}C NMR** ($CDCl_3$, 75 MHz): δ 190.4, 159.6, 149.4, 145.4, 143.2, 128.4, 127.2, 125.8, 117.1, 114.9, 106.6, 61.2, 55.5, 43.9; **ESI-HRMS**: *m/z* calcd. for $[C_{18}H_{16}N_2O_4+H]^+$: 325.1183, found 325.1184; calcd. for $[C_{18}H_{16}N_2O_4+Na]^+$: 347.1002, found 347.1004; Yield: 94 %. [11-12]



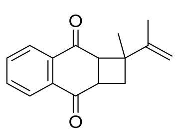
6-methoxy-2-(4-methoxyphenyl)-1-phenyl-1,2,3,6-tetrahydropyridine (13ac): ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.36 – 7.31 (m, 2H), 7.18 (d, *J* = 7.6 Hz, 1H), 7.02 (t, *J* = 7.6 Hz, 1H), 6.92 – 6.87 (m, 2H), 6.68 (td, *J* = 7.5, 1.0 Hz, 1H), 6.53 – 6.49 (m, 2H), 4.71 (dd, *J* = 12.6, 9.6 Hz, 1H), 4.45 (dd, *J* = 11.2, 2.6 Hz, 1H), 3.99 (s, 1H), 3.82 (s, 3H), 3.60 – 3.51 (m, 1H), 3.56 (s, 3H), 2.07 (ddd, *J* = 13.0, 5.5, 2.8 Hz, 1H), 1.97 – 1.85 (m, 1H); **^{13}C NMR** ($CDCl_3$, 75 MHz): δ 159.3, 148.7, 145.1, 136.4, 129.0, 127.8, 124.5, 117.5, 114.1, 106.4, 100.1, 56.1, 55.5, 41.1, 37.5; **ESI-HRMS**: *m/z* calcd. for $[C_{19}H_{21}NO_2+H]^+$: 296.1645, found 296.1642; Yield: 82 %.



3,4-dimethyl-1-oxaspiro[5.5]undeca-3,7,10-trien-9-one (14ac): ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.01 – 6.96 (m, 2H), 6.24 – 6.18 (m, 2H), 4.14 – 4.10 (m, 2H), 2.12 – 2.11 (m, 2H), 1.69 – 1.68 (m, 3H), 1.63 – 1.62 (m, 3H); **^{13}C NMR** ($CDCl_3$, 75 MHz): δ 185.7, 148.4, 128.6, 123.6, 121.6, 69.0, 65.6, 38.6, 18.6, 14.0; **ESI-HRMS**: *m/z* calcd. for $[C_{12}H_{14}O_2+H]^+$: 191.1067, found 191.1065; calcd. for $[C_{12}H_{14}O_2+Na]^+$: 213.0886, found 213.0888; $\boldsymbol{R_F}$ = 0.61 (*n*-Hex:EtOAc 19:1); Yield: 81 %.[13]



4,4'-((1*R*,2*R*,3*S*,4*S*)-3,4-dimethylcyclobutane-1,2-diyl)bis(methoxybenzene) (1d): ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.15 – 7.10 (m, 4H), 6.85 – 6.80 (m, 4H), 3.78 (s, 6H), 2.81 – 2.78 (m, 2H), 1.87 – 1.78 (m, 2H), 1.18 (d, J = 6.0 Hz, 6H); **^{13}C NMR** ($CDCl_3$, 75 MHz): δ 158.1, 136.1, 127.9, 113.8, 55.4, 52.6, 43.4, 19.0; **ESI-HRMS**: *m/z* calcd. for $[C_{20}H_{24}O_2+H]^+$: 297.1849, found 297.1837; calcd. for $[C_{20}H_{24}O_2+NH_4]^+$: 314.2115, found 314.2110; calcd. for $[C_{20}H_{24}O_2+Na]^+$: 319.1669, found 319.1665; Yield: 76 %.[14-15]



1-methyl-1-(prop-1-en-2-yl)-1,2,2a,8a-tetrahydrocyclobuta[*b*]naphthalene-3,8-dione (2d): ^{1}H NMR ($CDCl_3$, 300 MHz): δ 8.16 – 8.09 (m, 2H), 7.80 – 7.74 (m, 2H), 4.99 (s, 1H), 4.86 (quint, J = 1.4 Hz, 1H), 3.75 (dd, J = 9.4, 0.9 Hz, 1H), 3.40 (ddd, J = 0.8, 9.4, 3.9 Hz, 1H), 2.87 – 2.79 (m, 1H), 2.27 (ddd, J = 11.9, 3.9, 1.0 Hz, 1H), 1.81 (dd, J = 1.3, 0.6 Hz, 3H), 1.04 (s, 3H); **^{13}C NMR** ($CDCl_3$, 75 MHz): δ 199.5, 195.8, 151.2, 136.9, 136.0, 134.4, 127.3, 109.6, 51.8, 49.8, 38.6, 37.1, 23.4, 18.3; **ESI-HRMS**: *m/z* calcd. for $[C_{16}H_{16}O_2+H]^+$: 241.1223, found 241.1220; calcd. for $[C_{16}H_{16}O_2+Na]^+$: 263.1043, found 263.1039; Yield: 72 %.[13]

8. References

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9. NMR spectra

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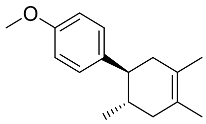
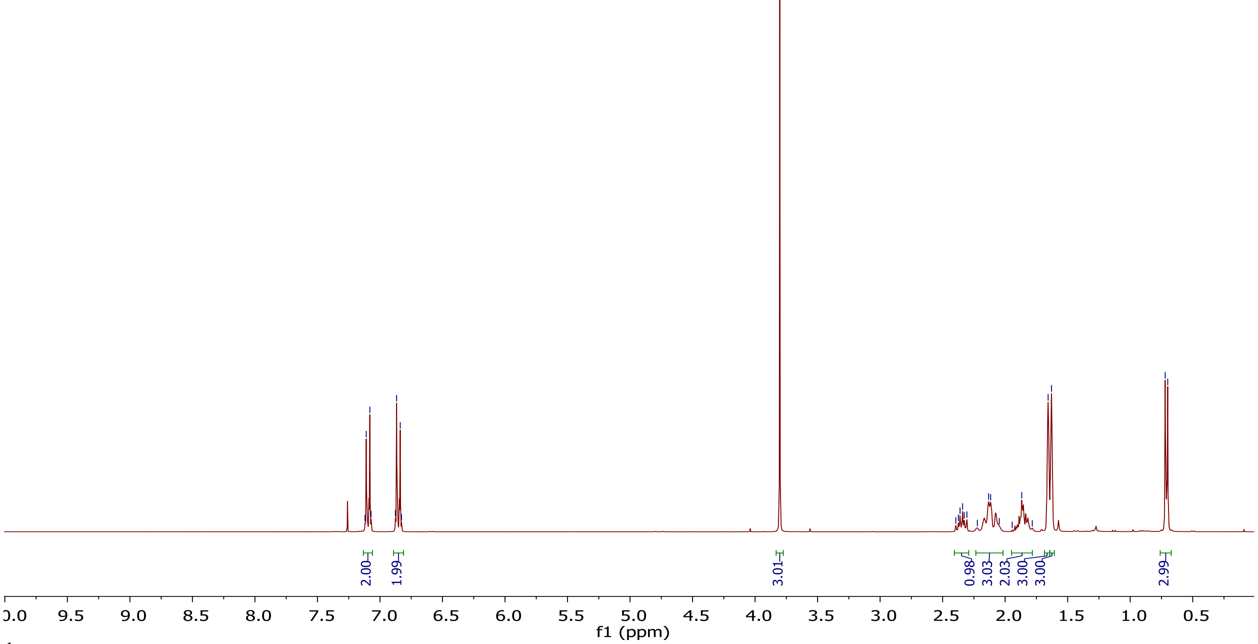
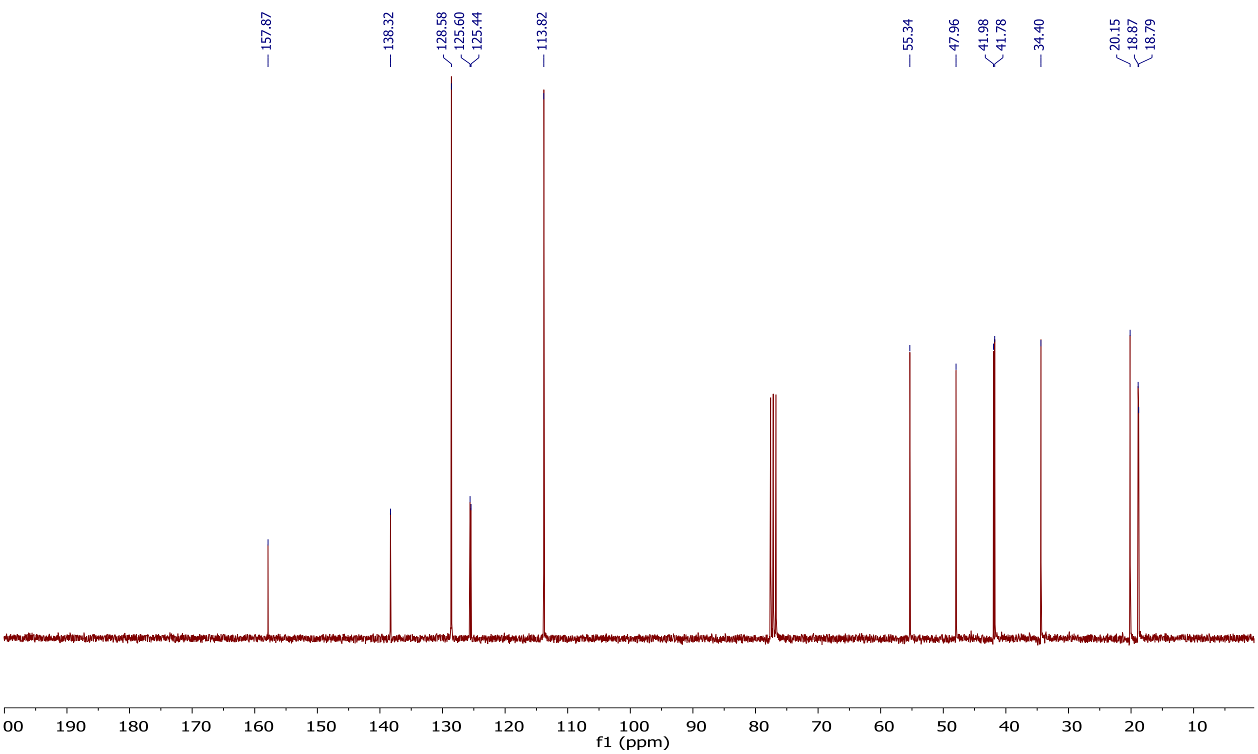


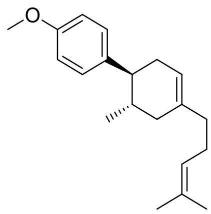


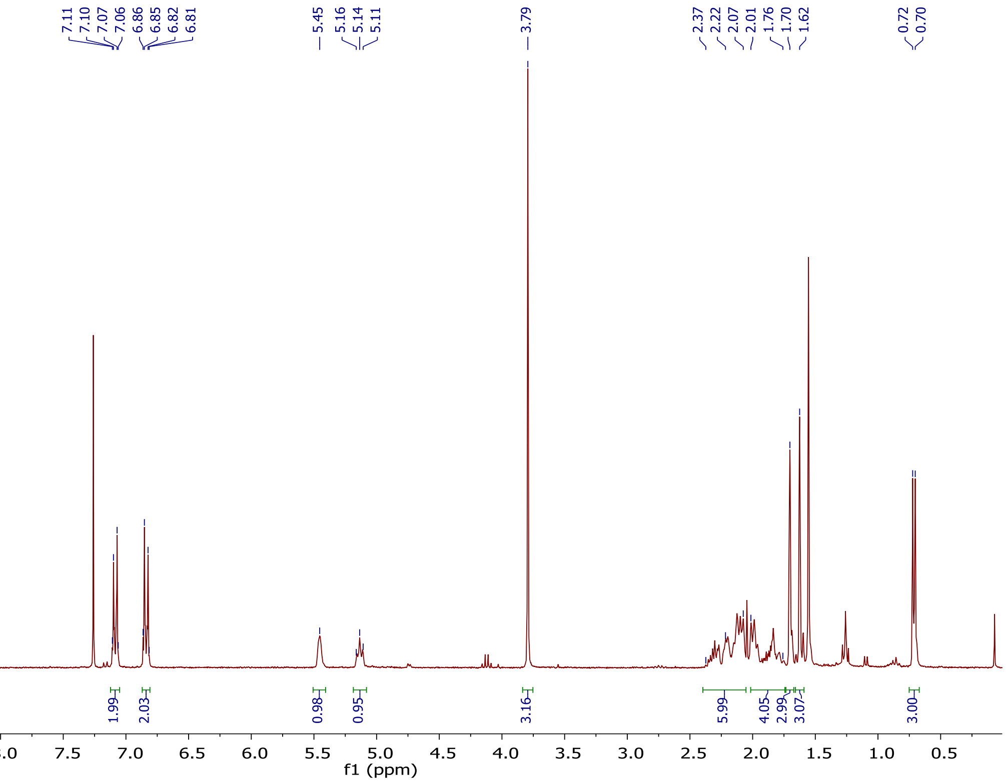
^{1}H NMR spectrum in $CDCl_3$.



^{13}C NMR spectrum in $CDCl_3$.

2c





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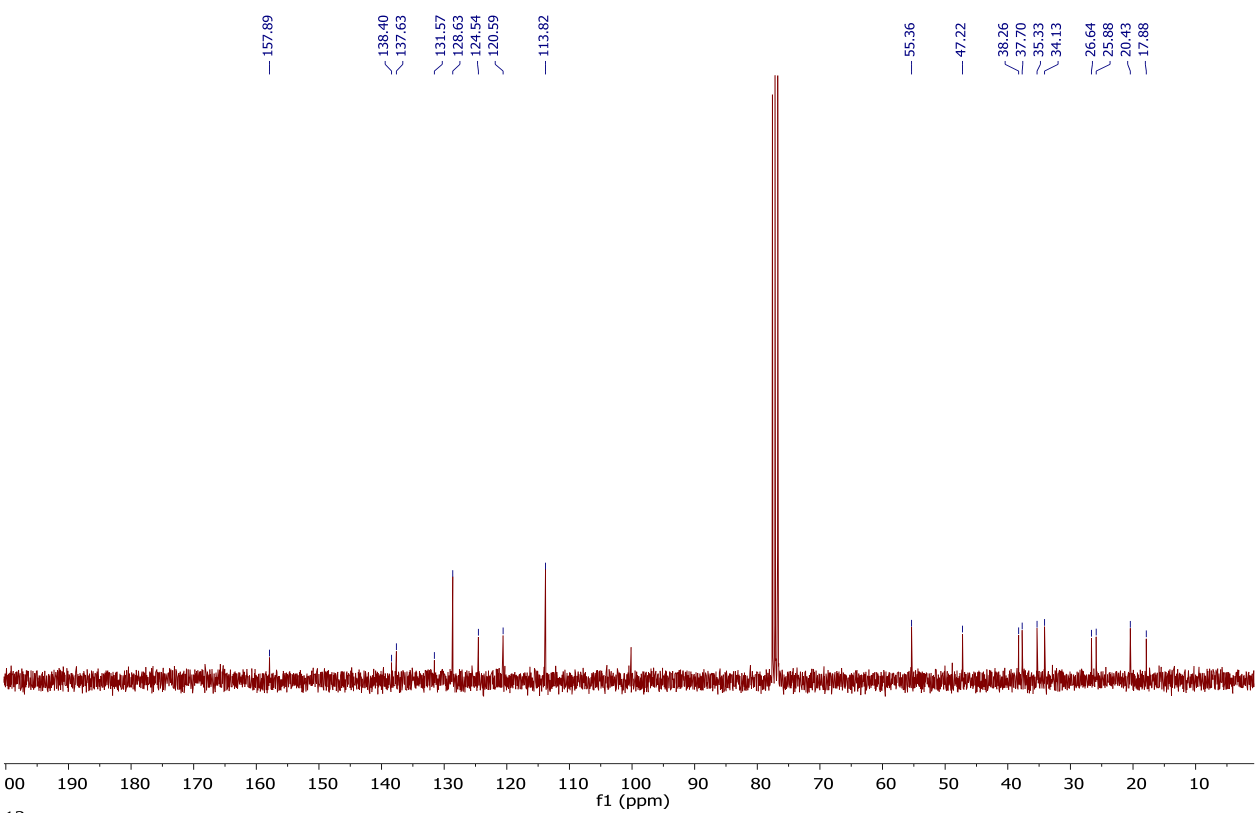

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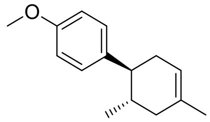

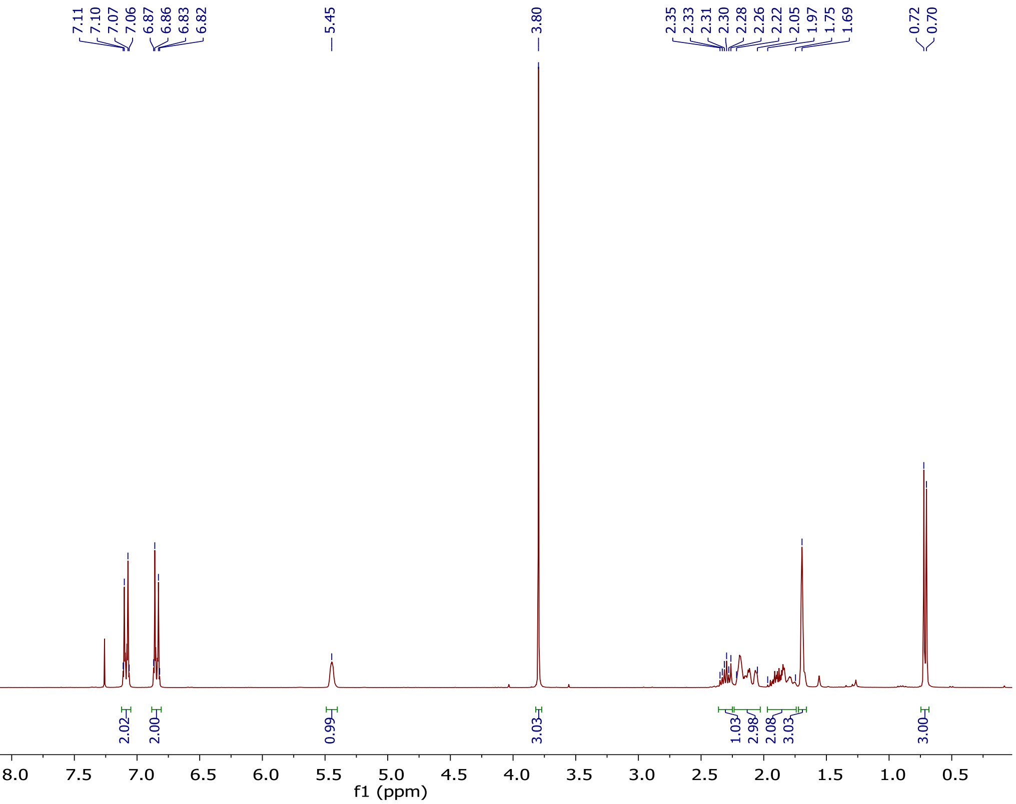

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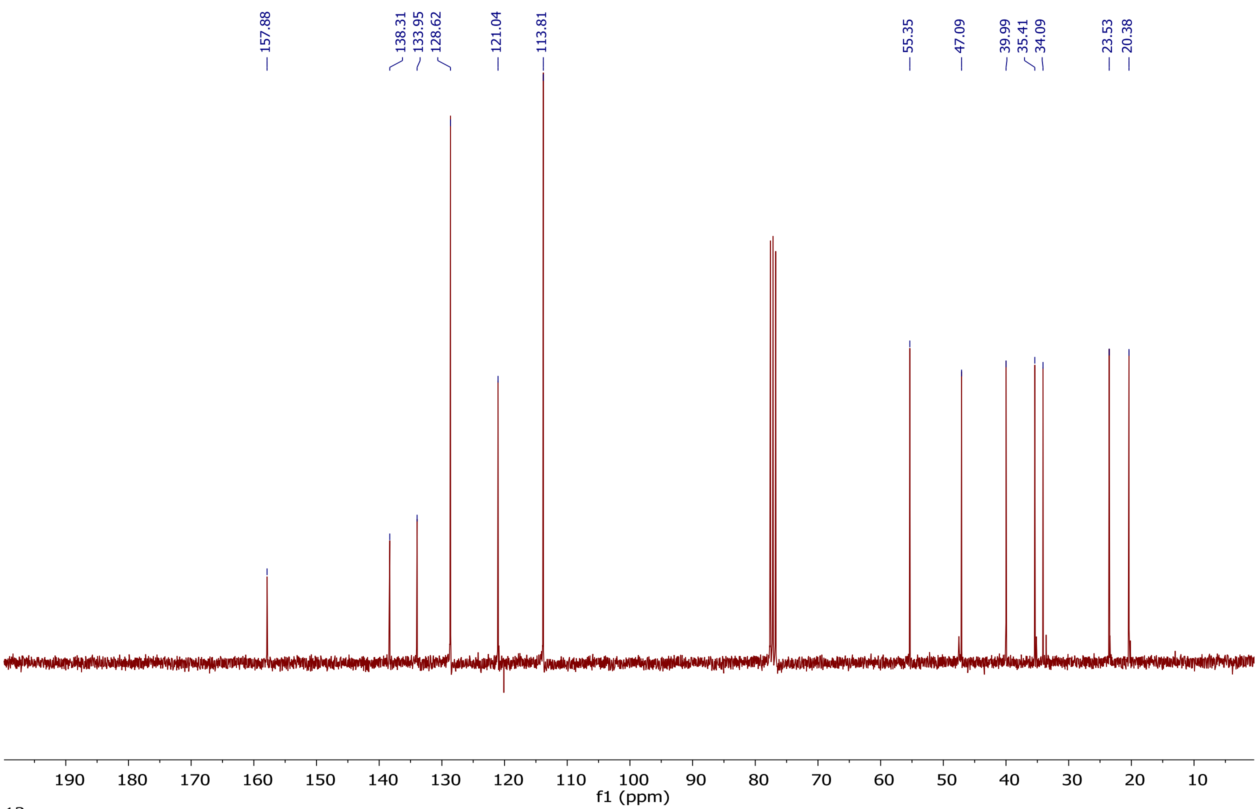

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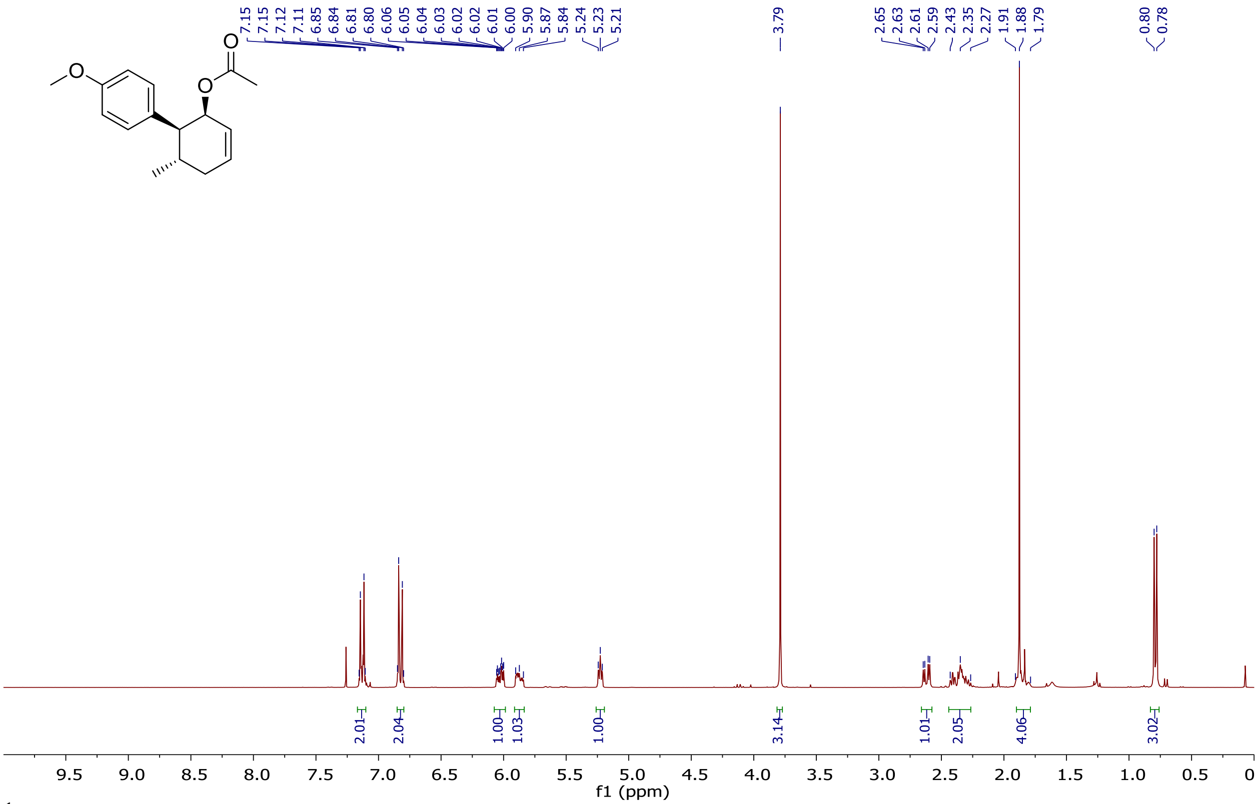

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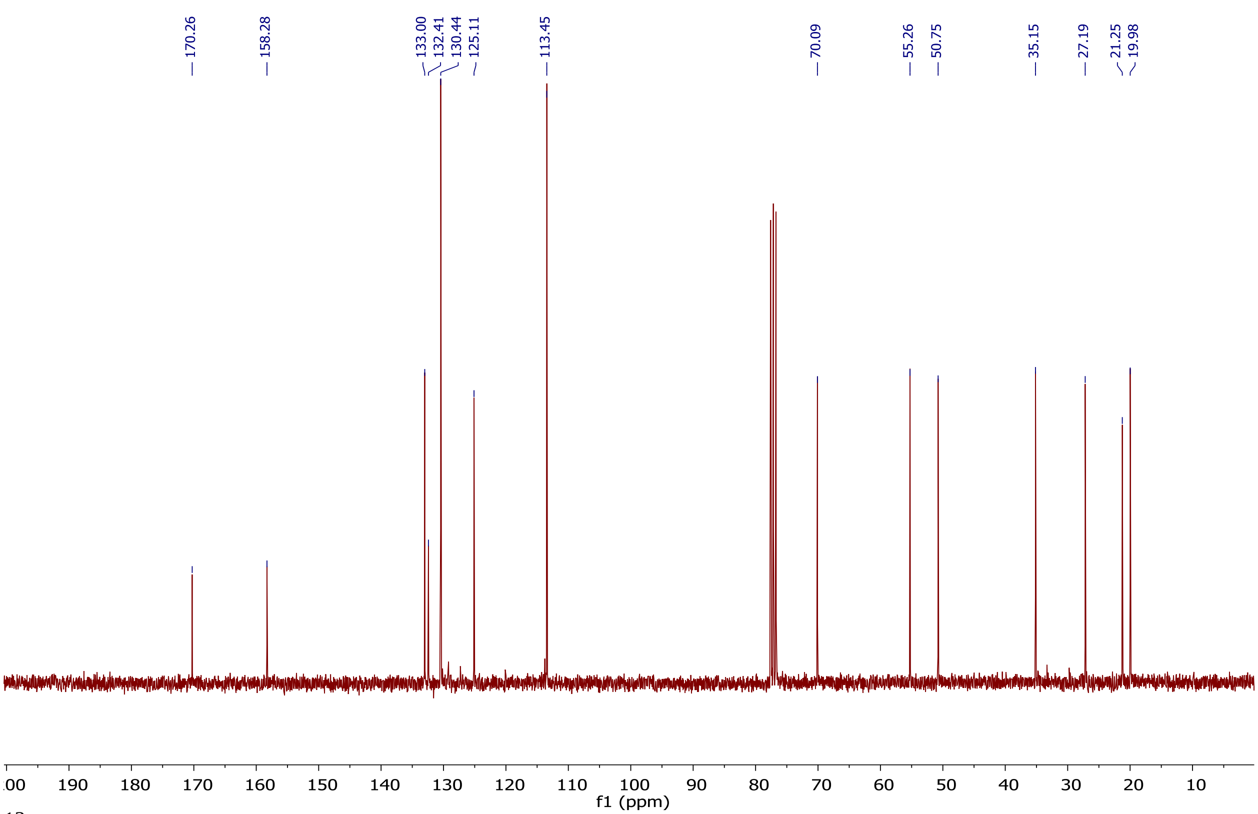

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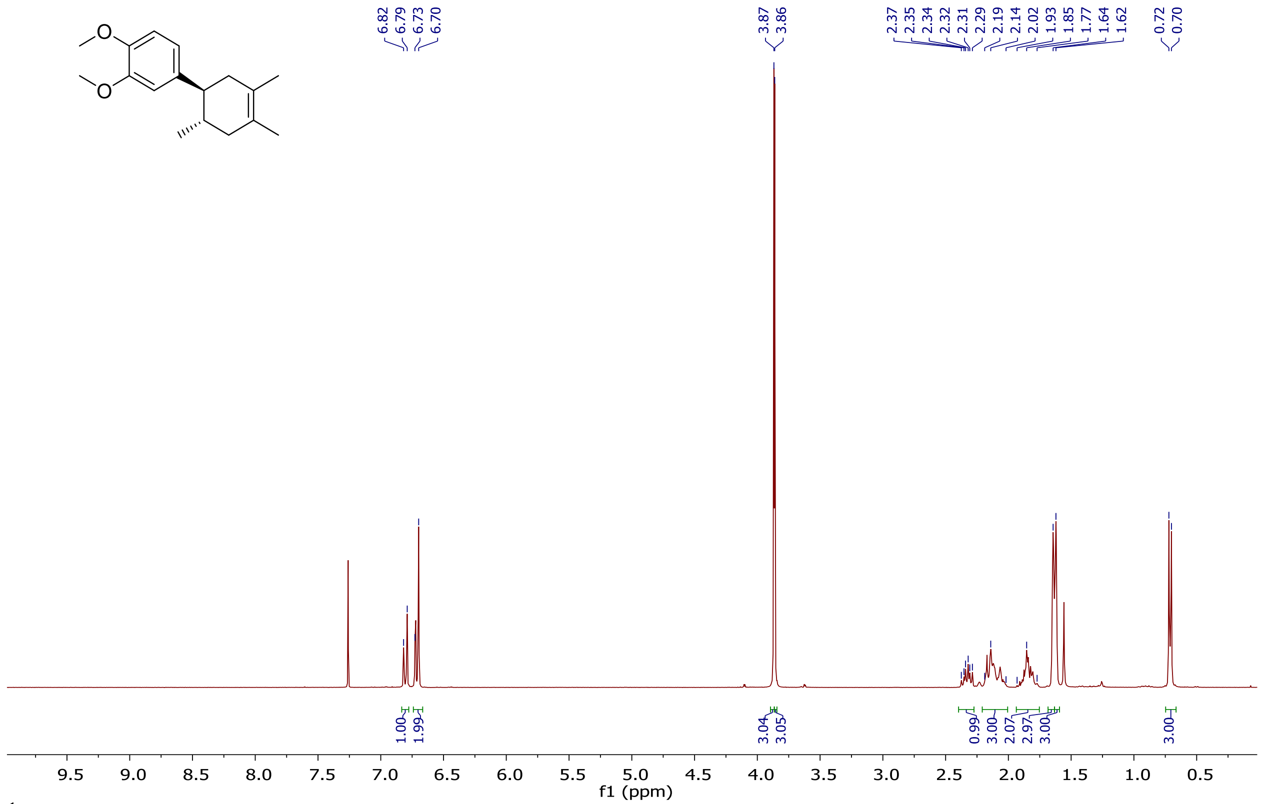

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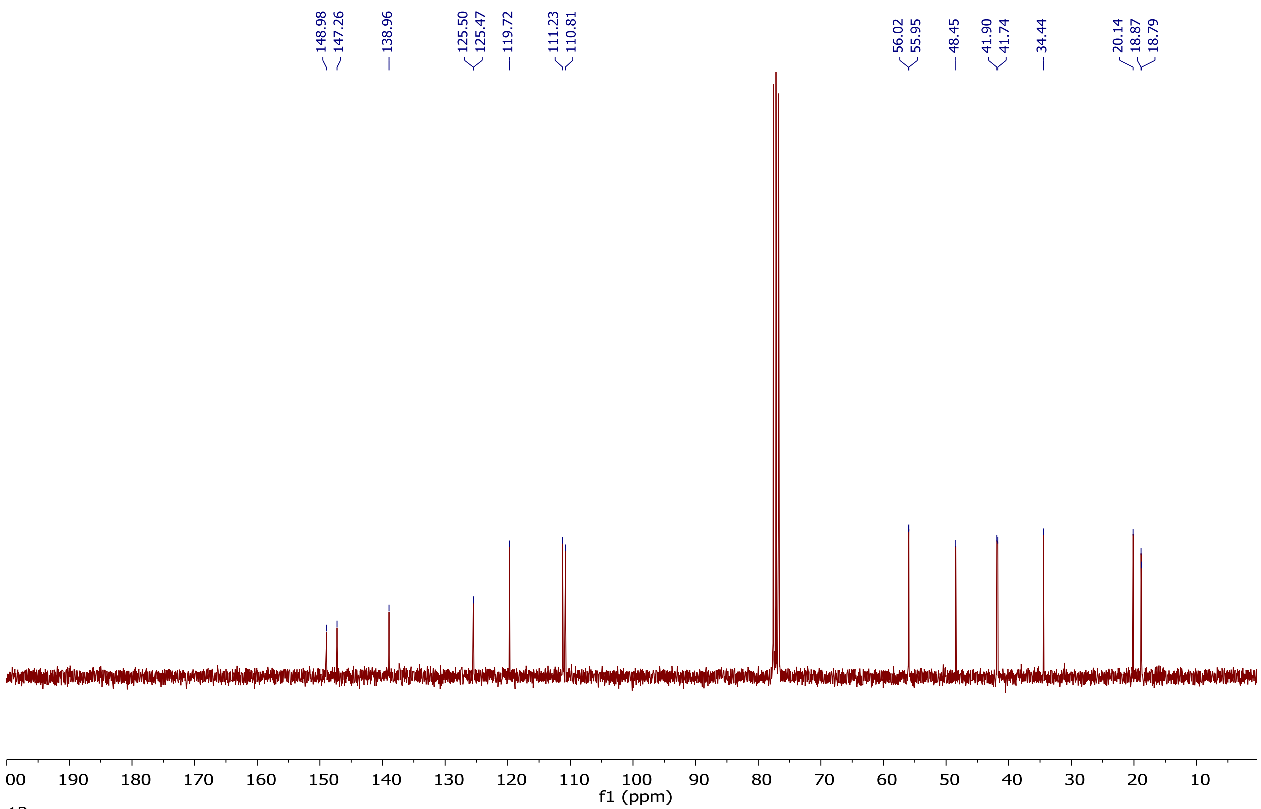

^{13}C NMR spectrum in $CDCl_3$.

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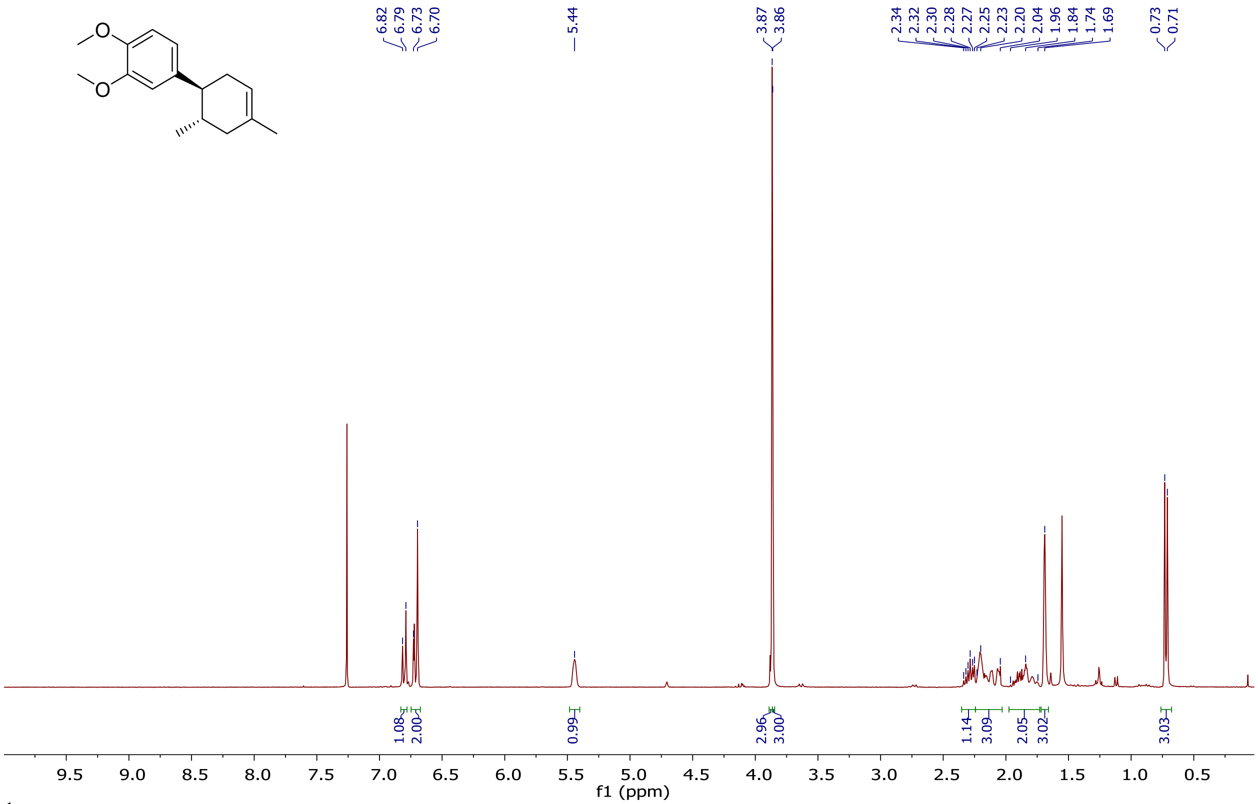

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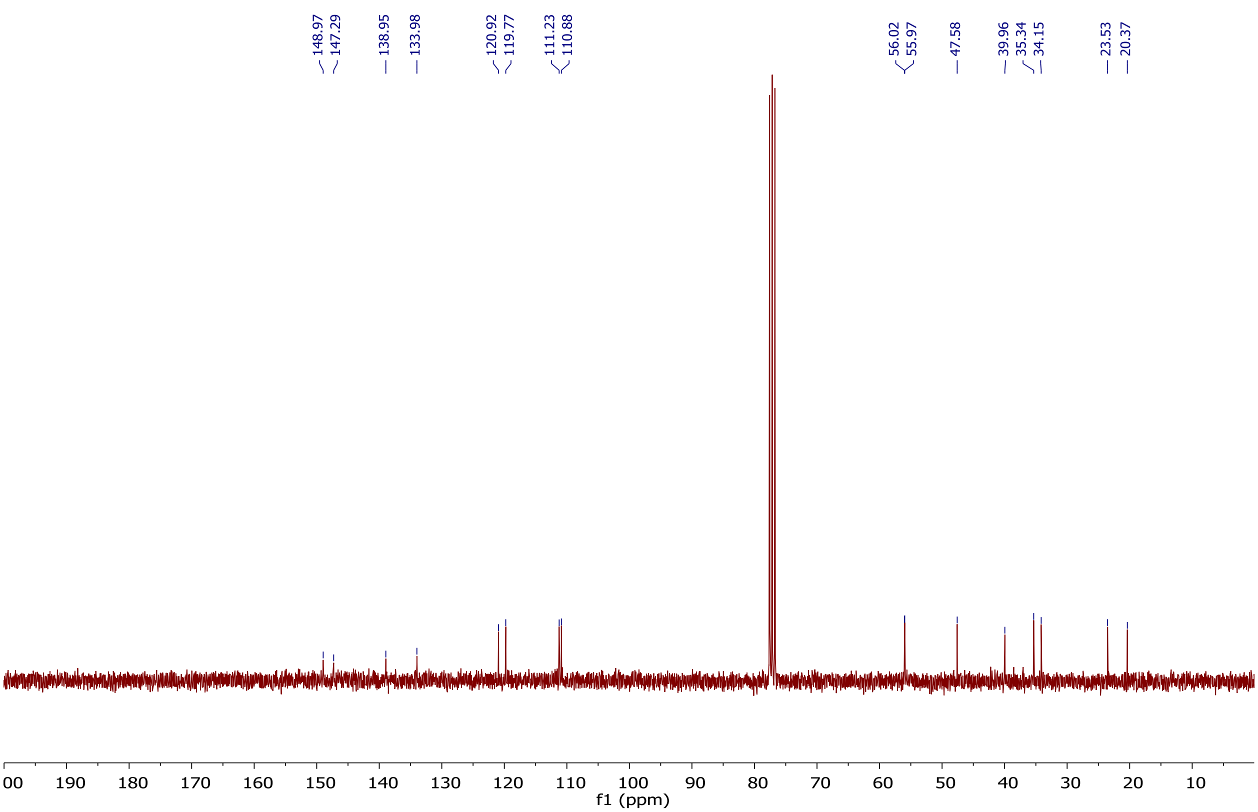
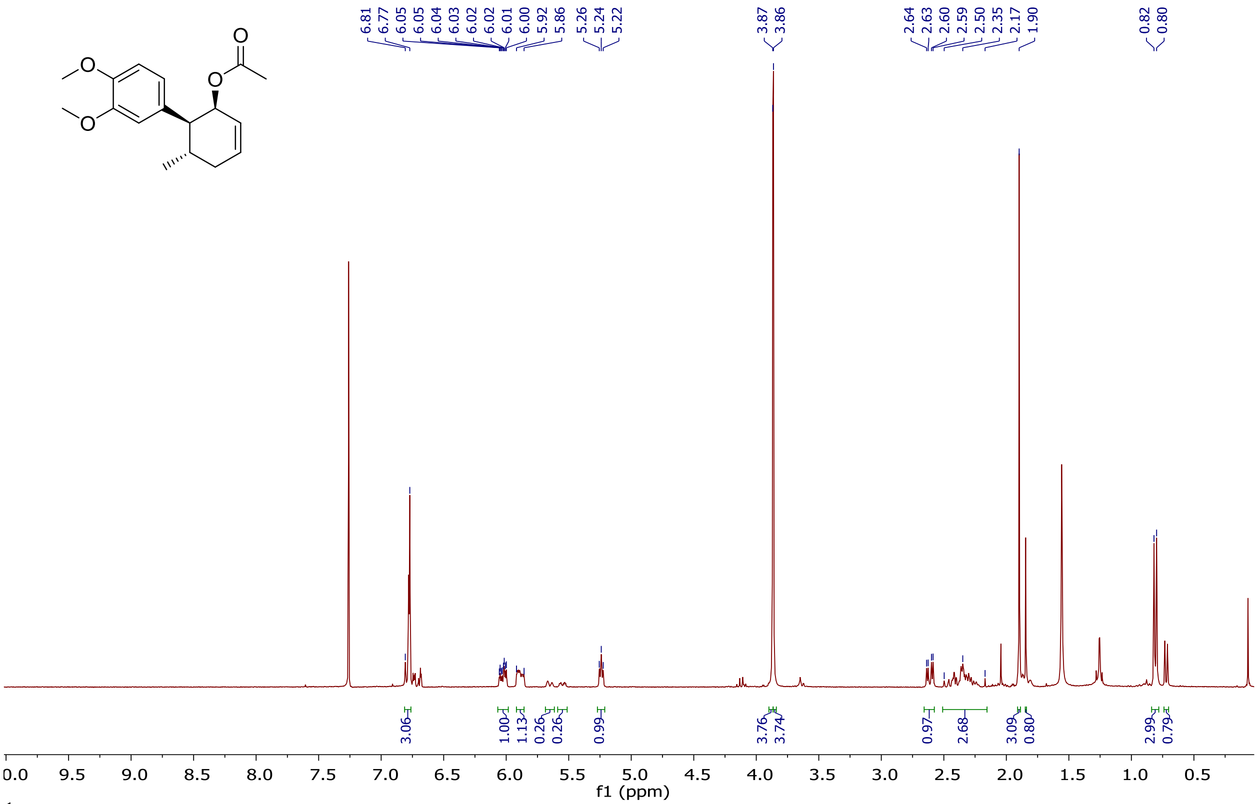


^{13}C NMR spectrum in $CDCl_3$.

7c



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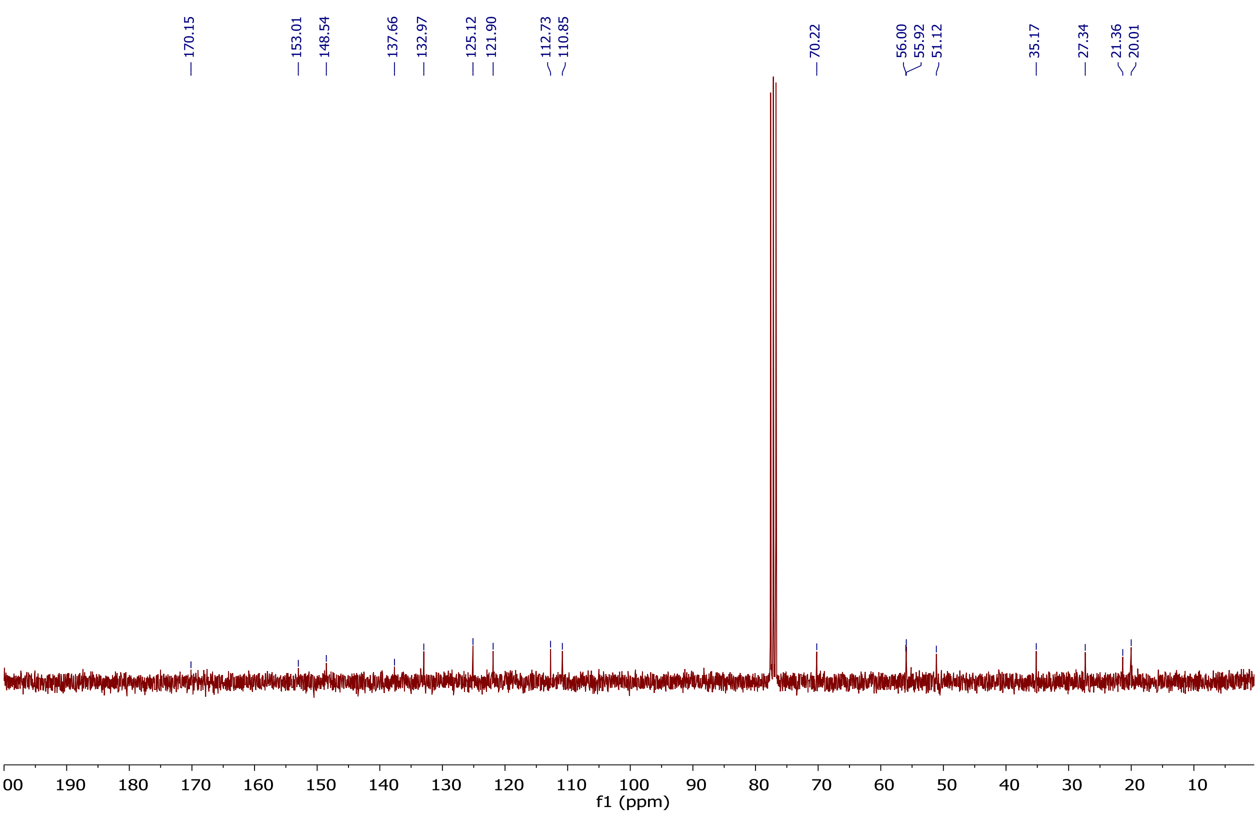

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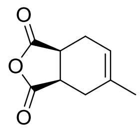
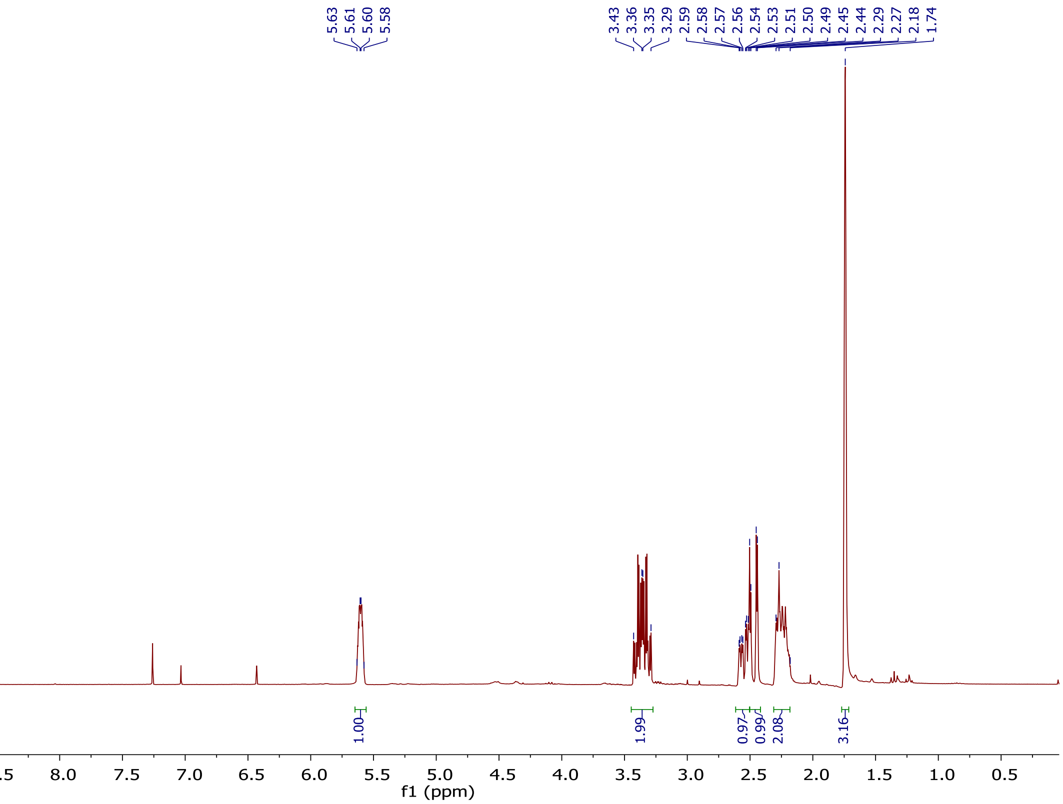
8c





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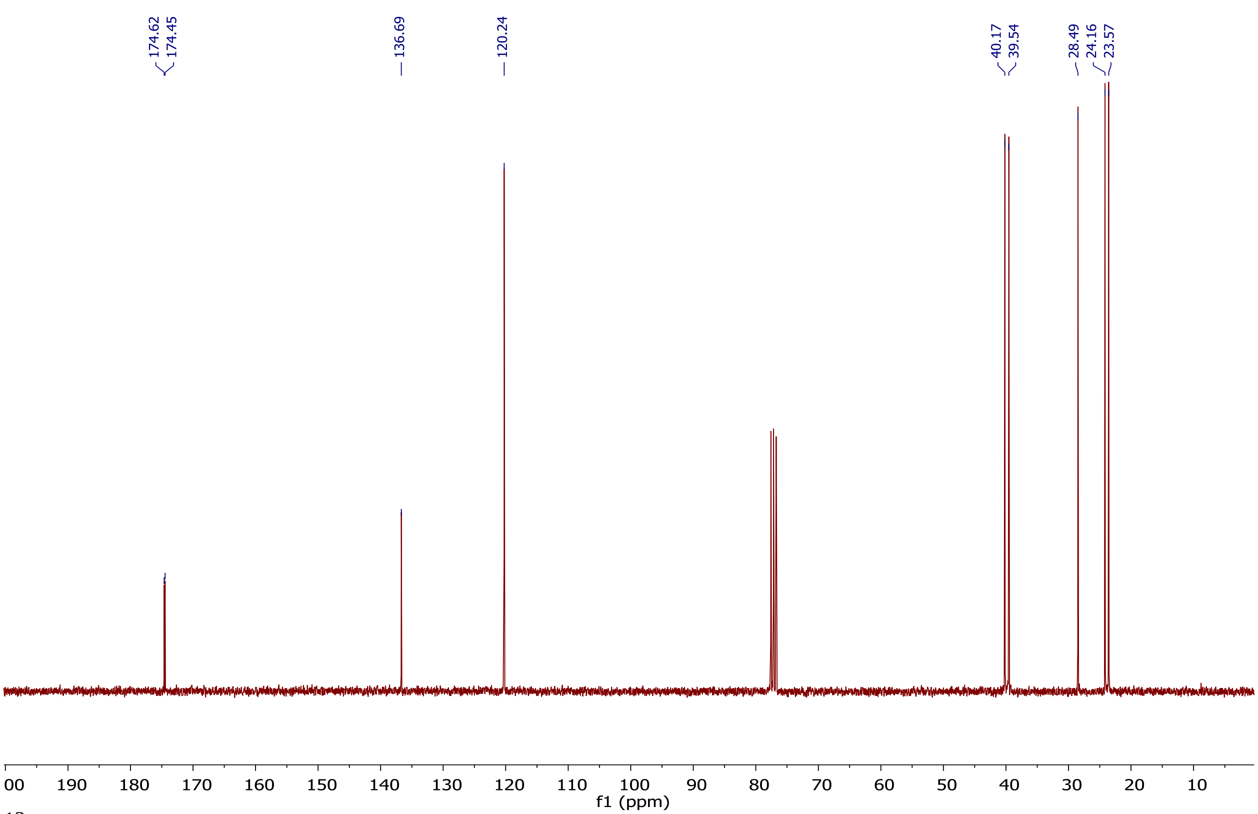
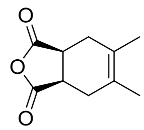
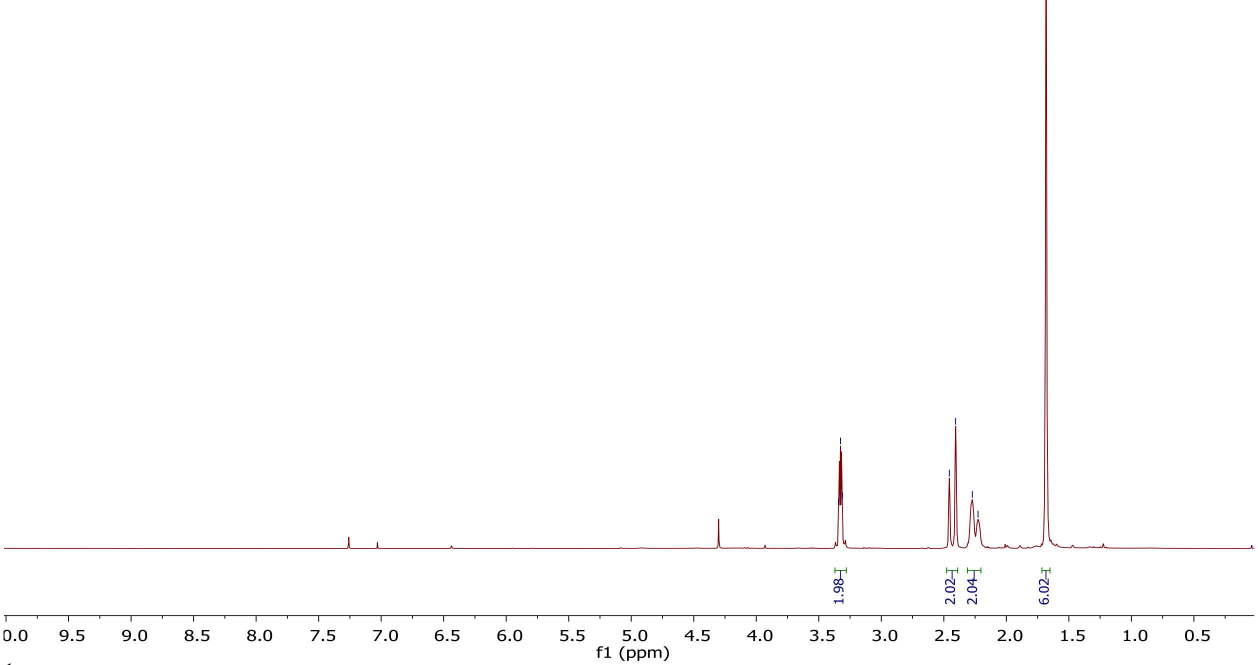


^{13}C NMR spectrum in $CDCl_3$.

9c





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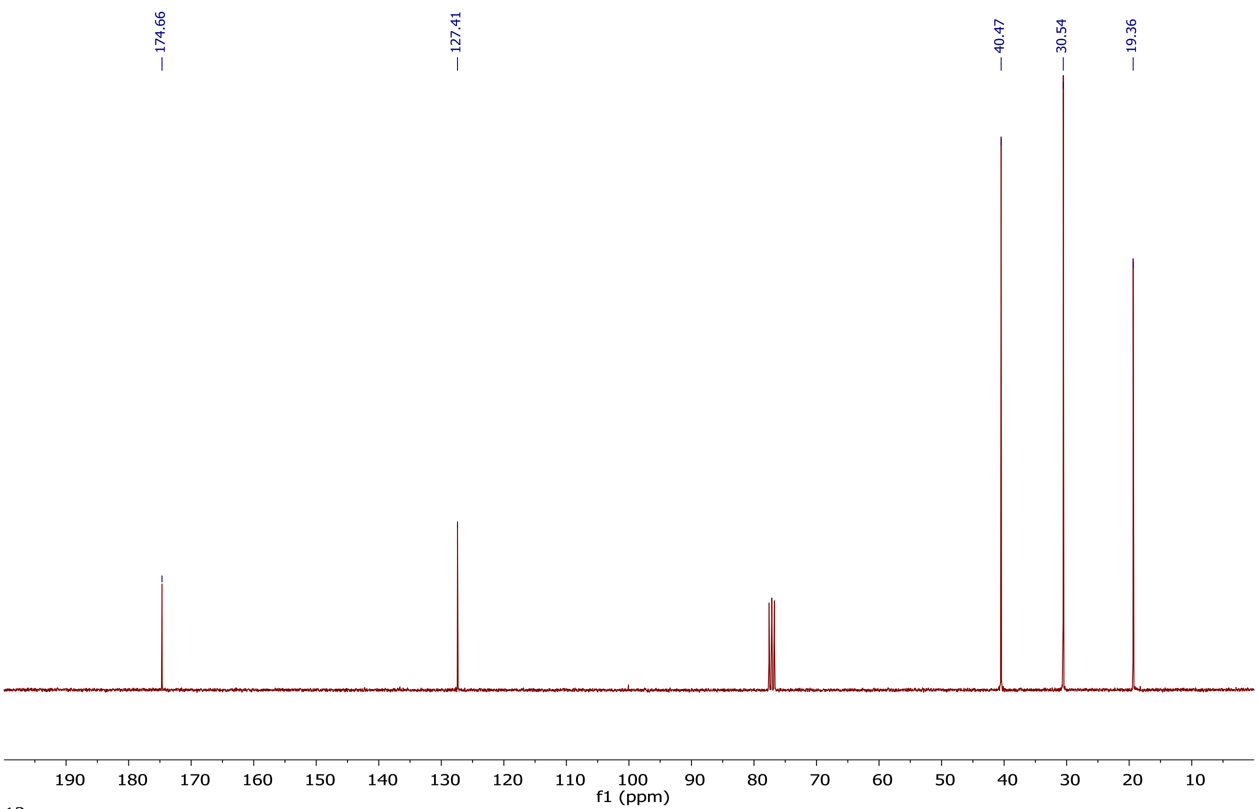

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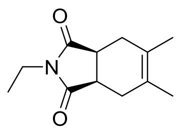

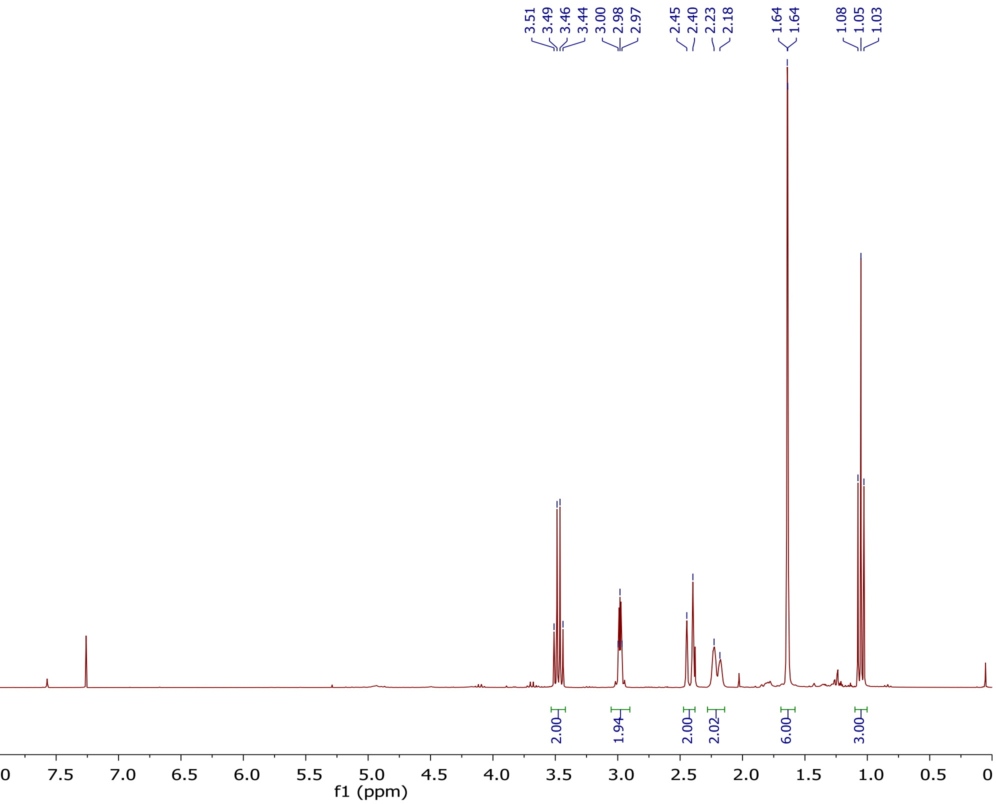

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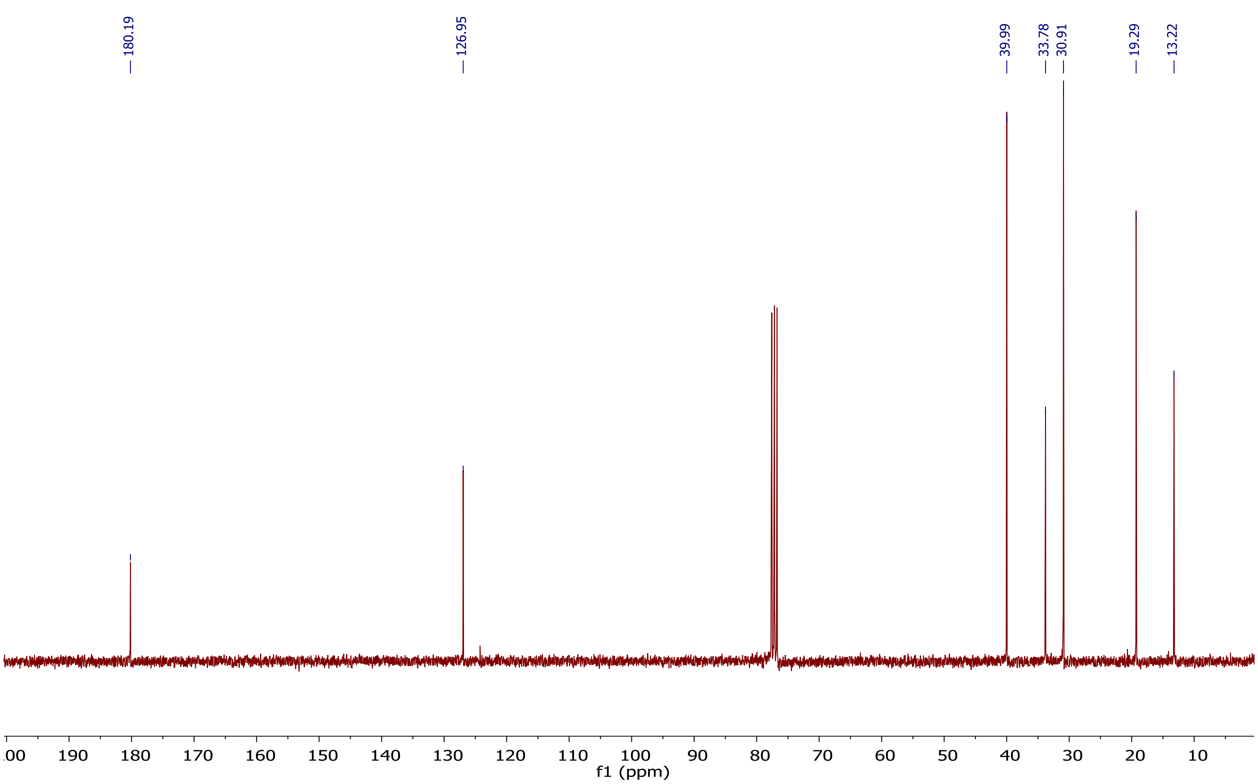

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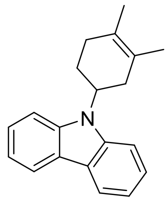

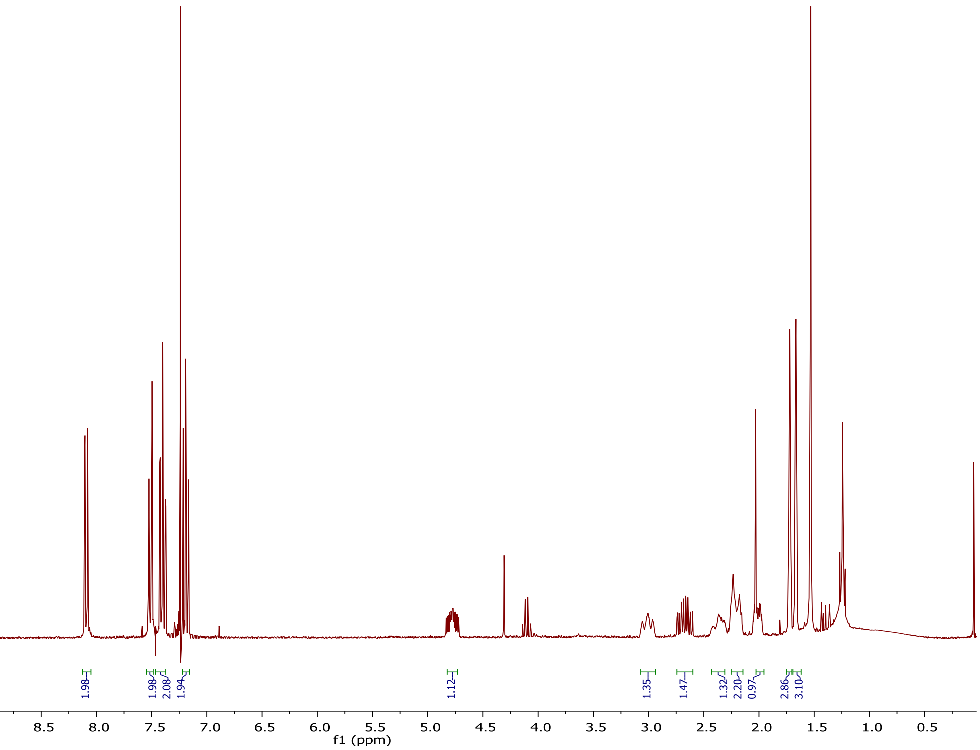

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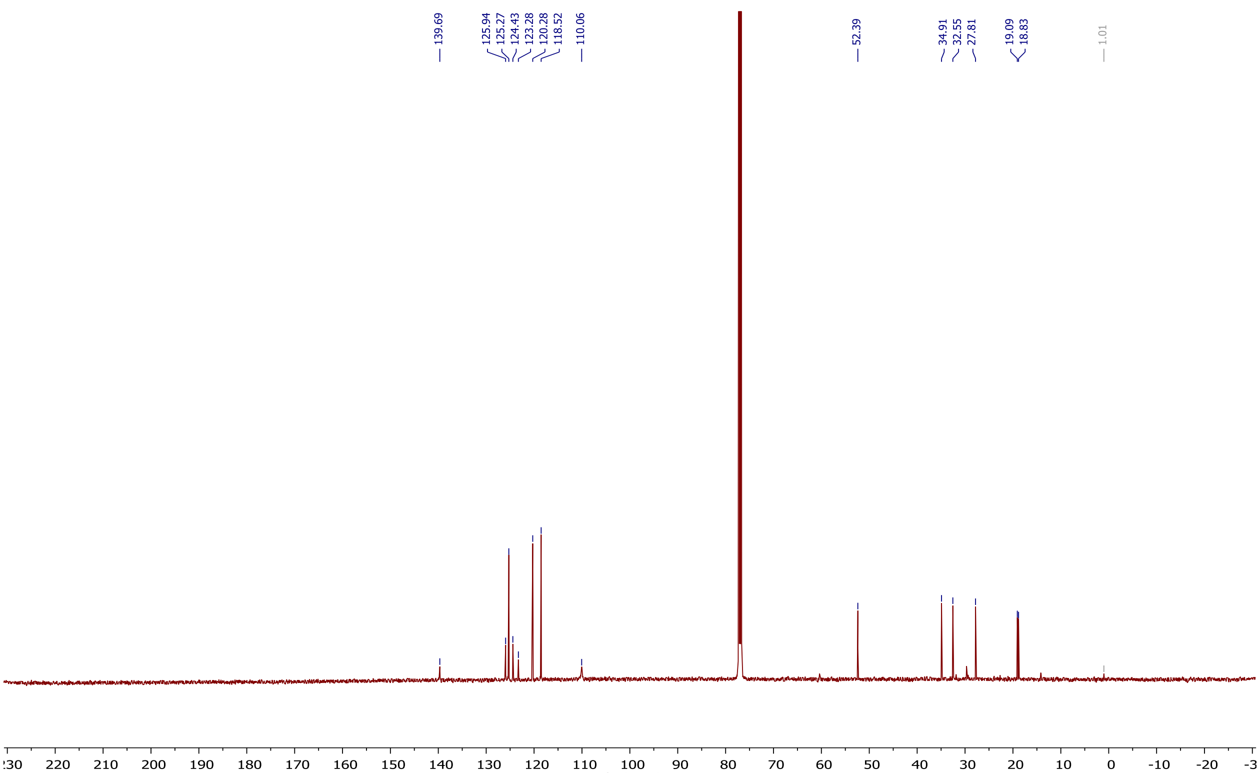

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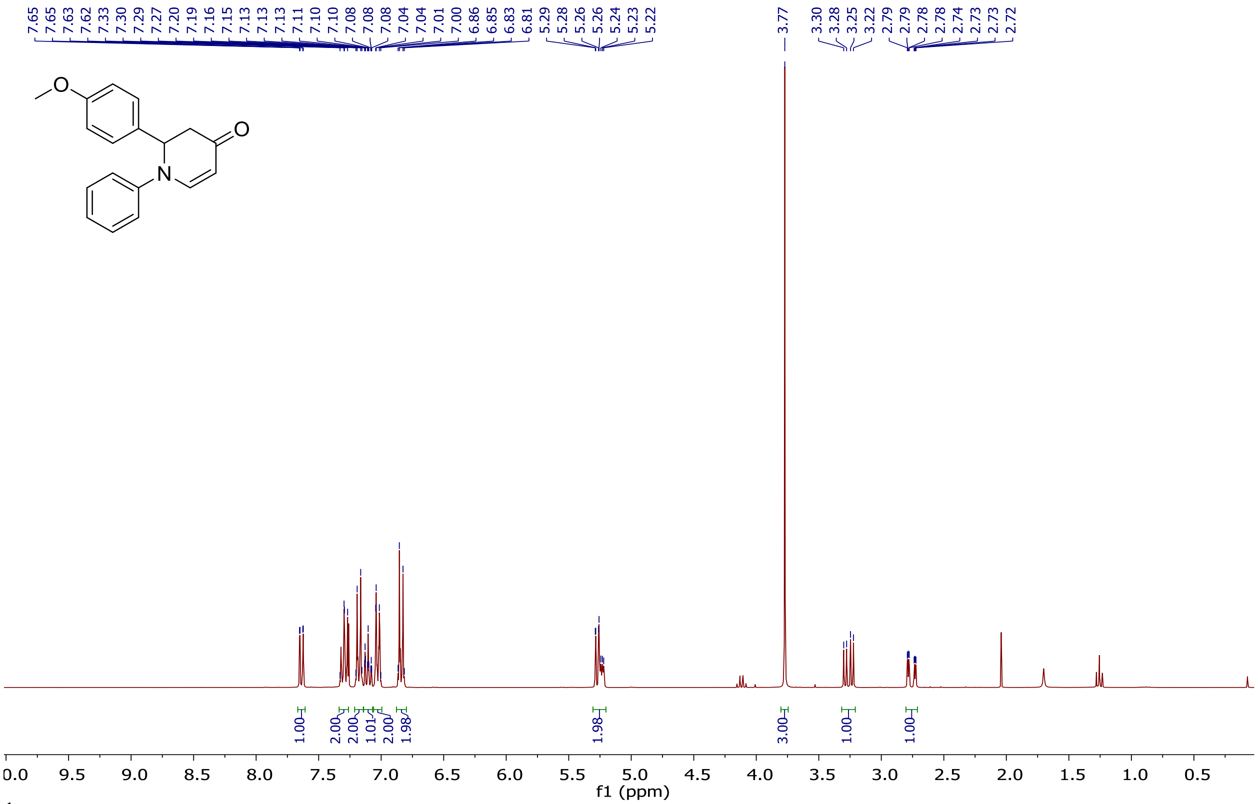
1ac



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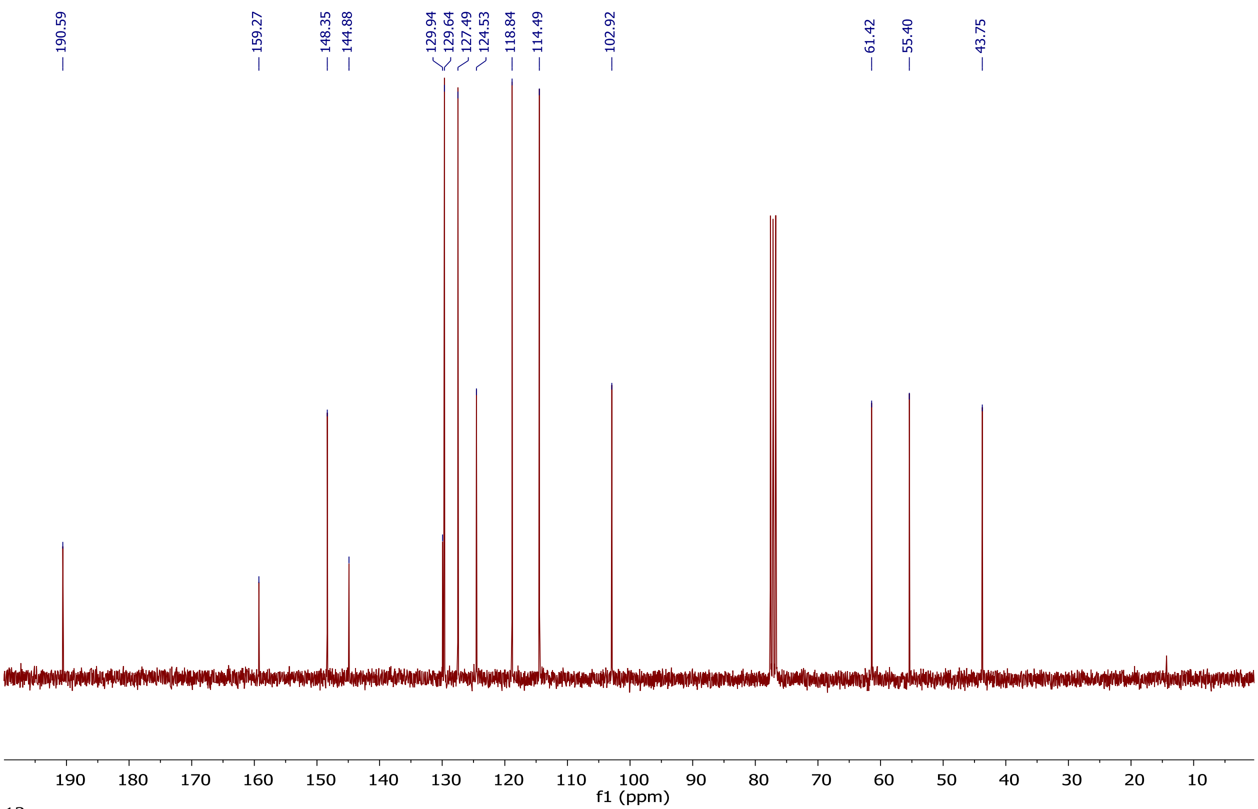

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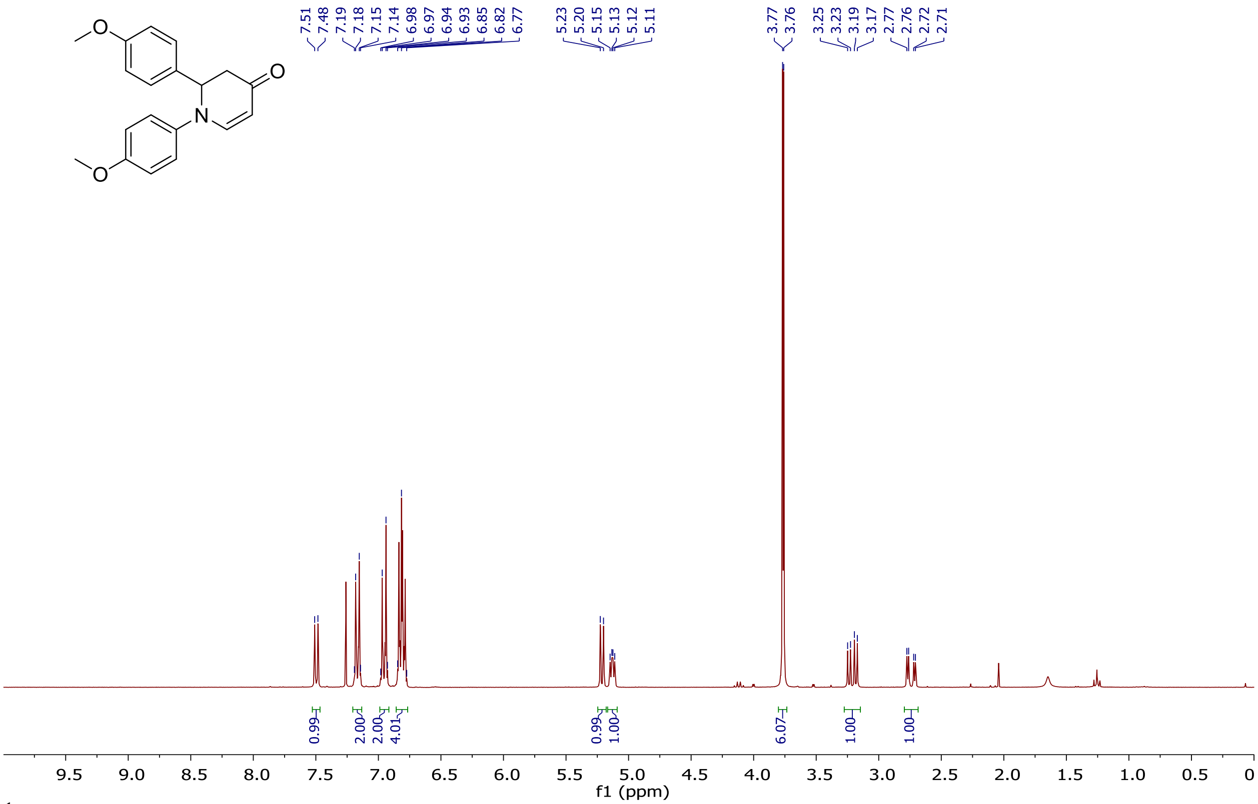

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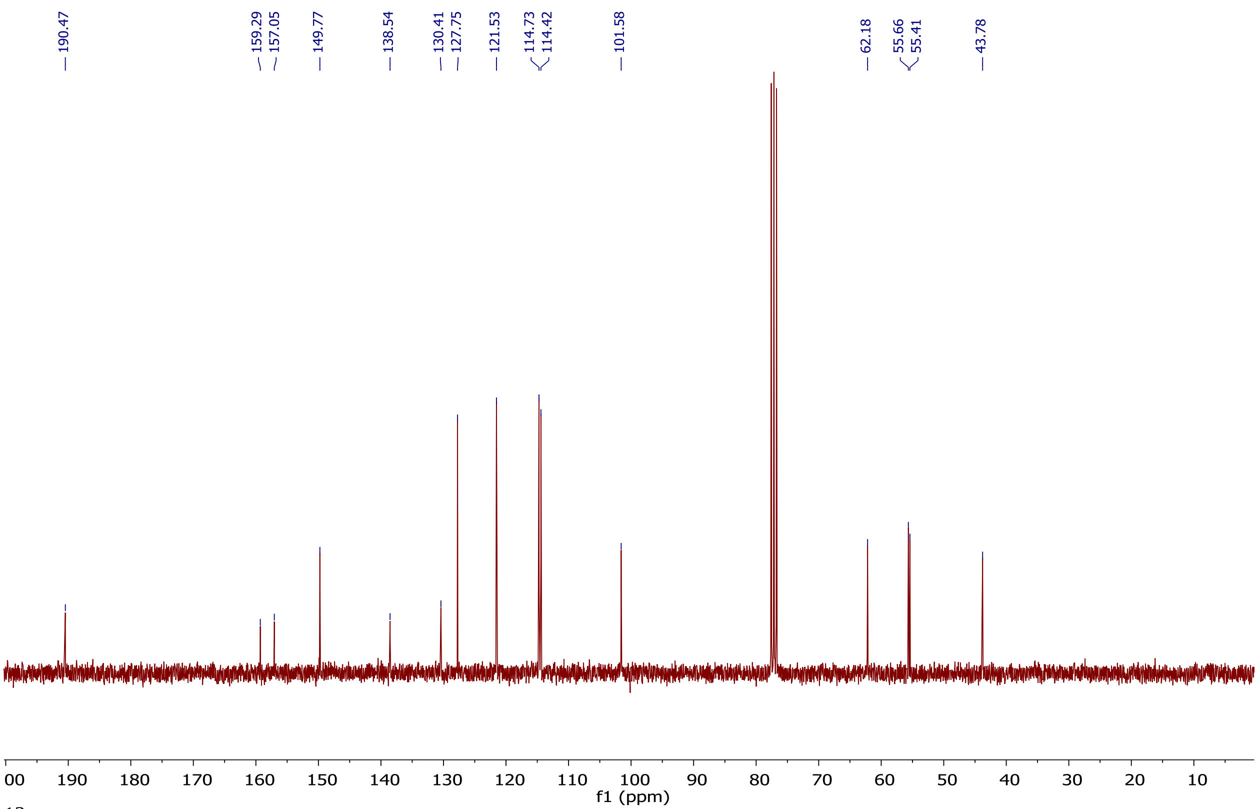

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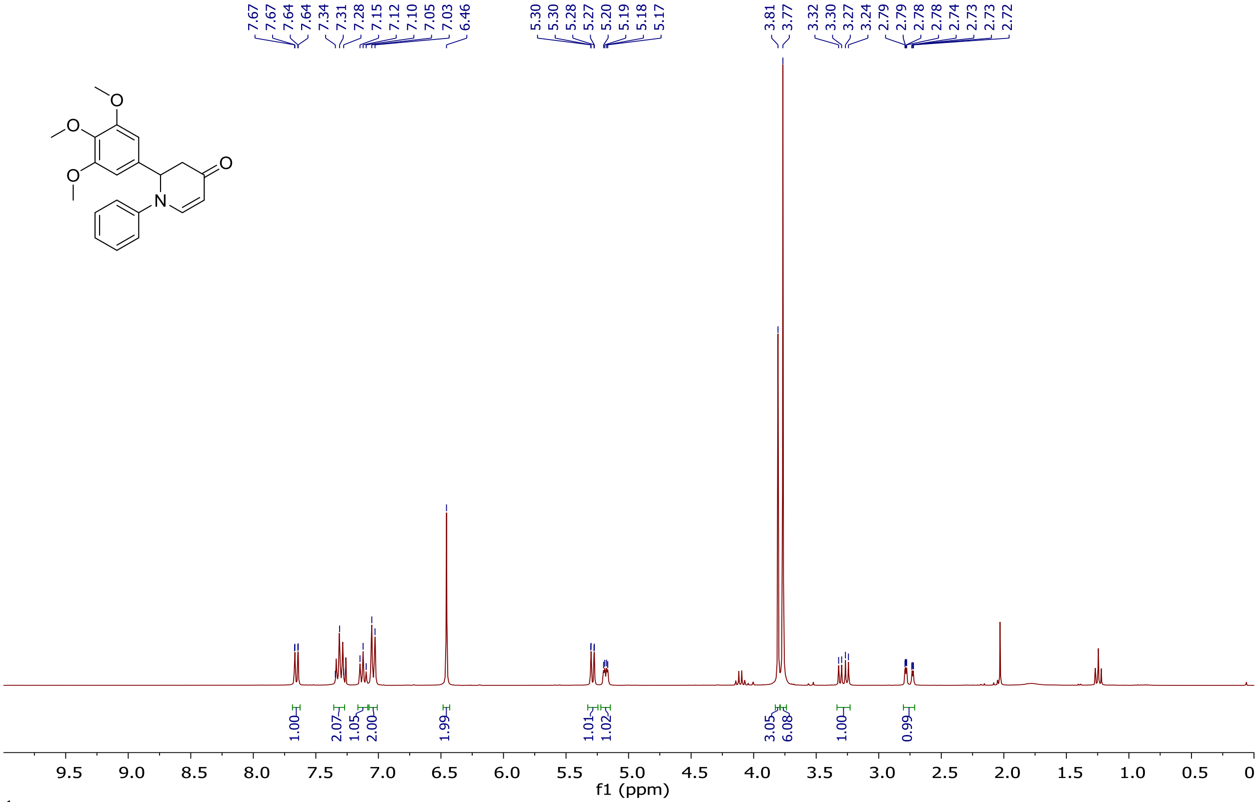

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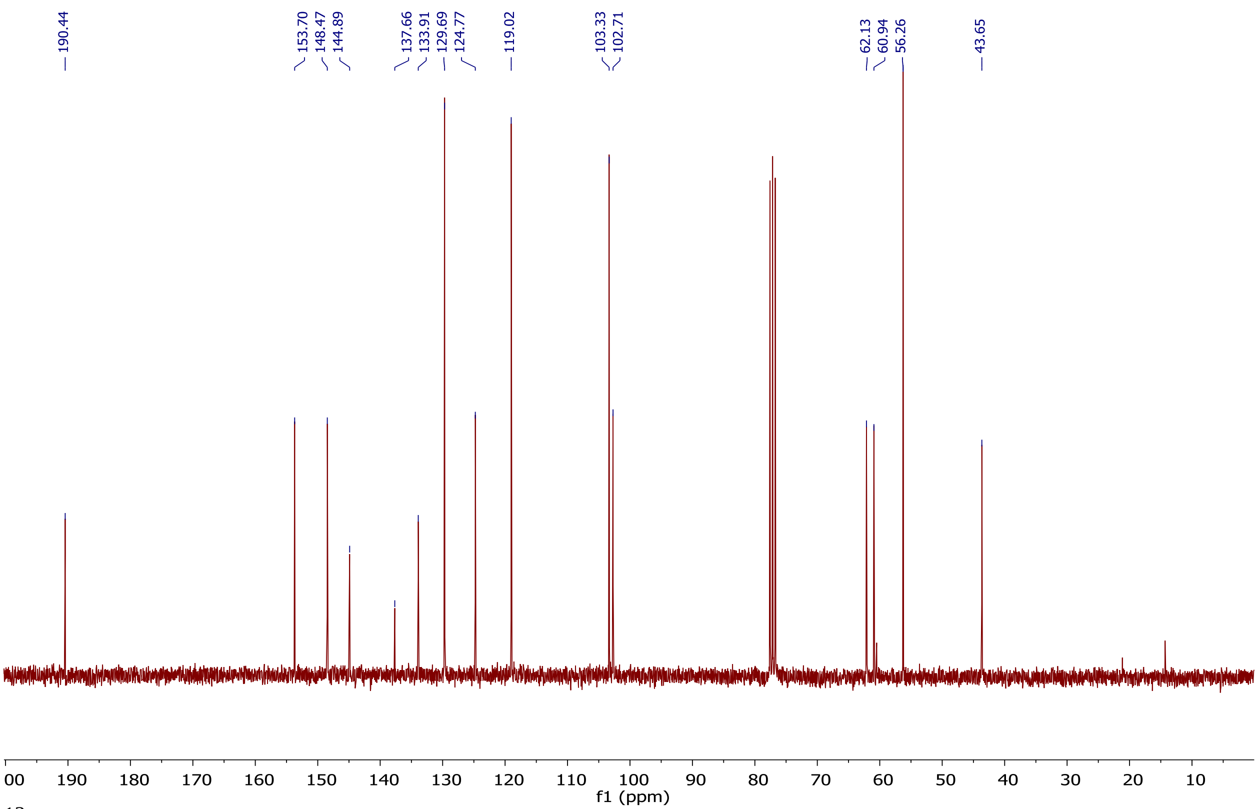

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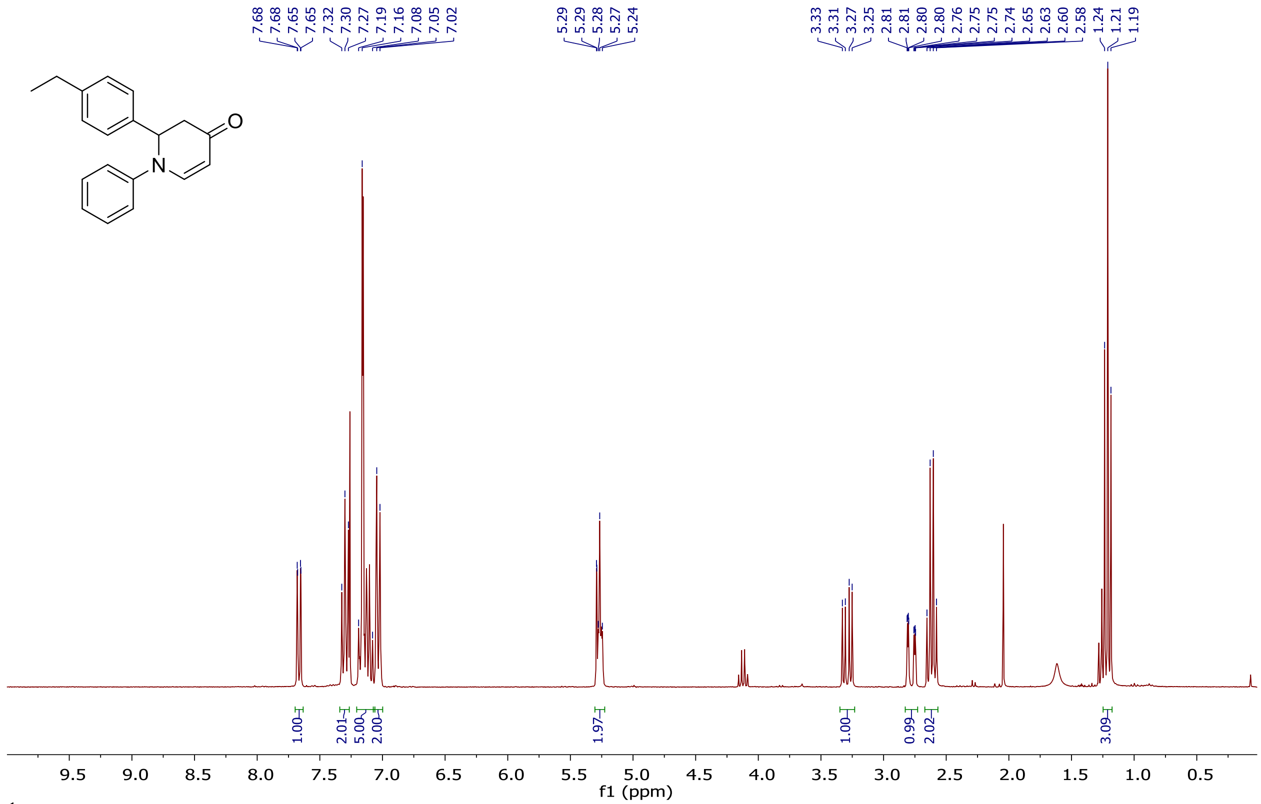

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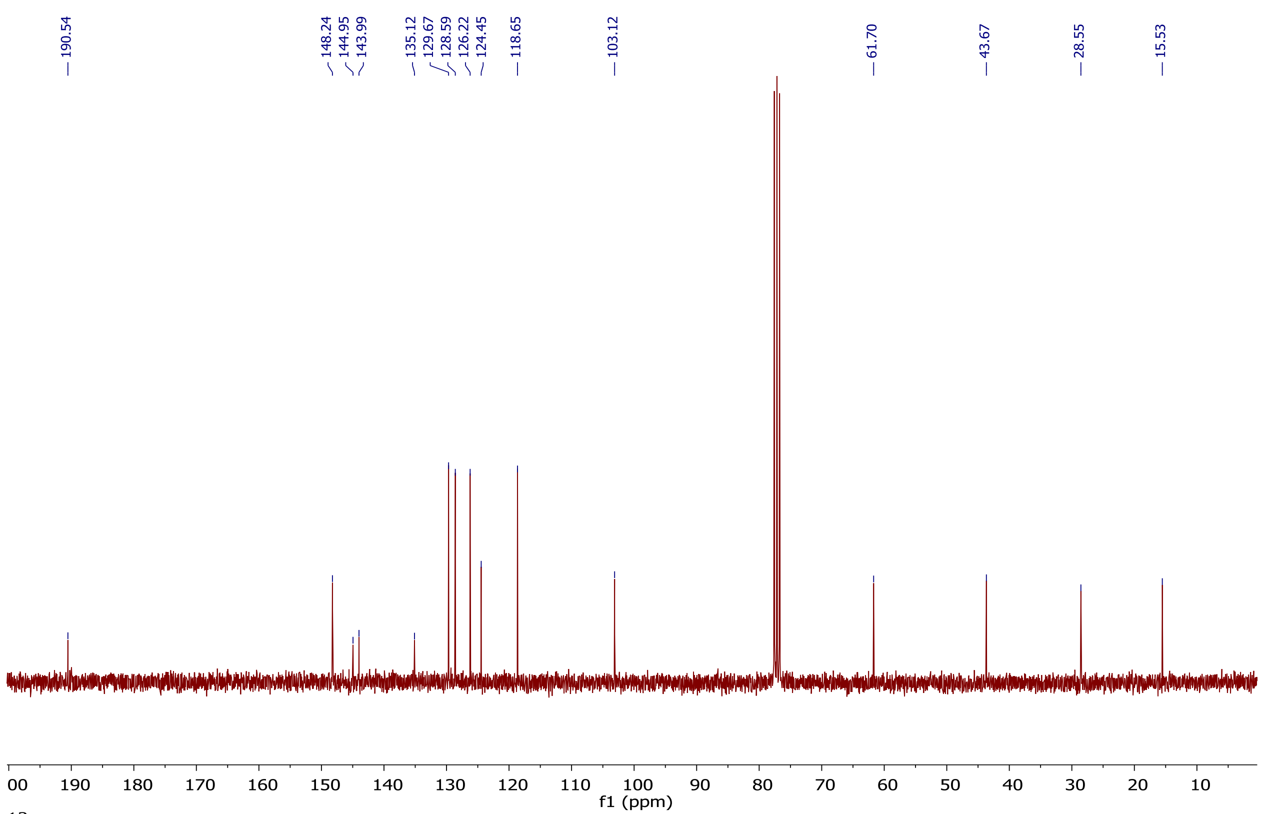

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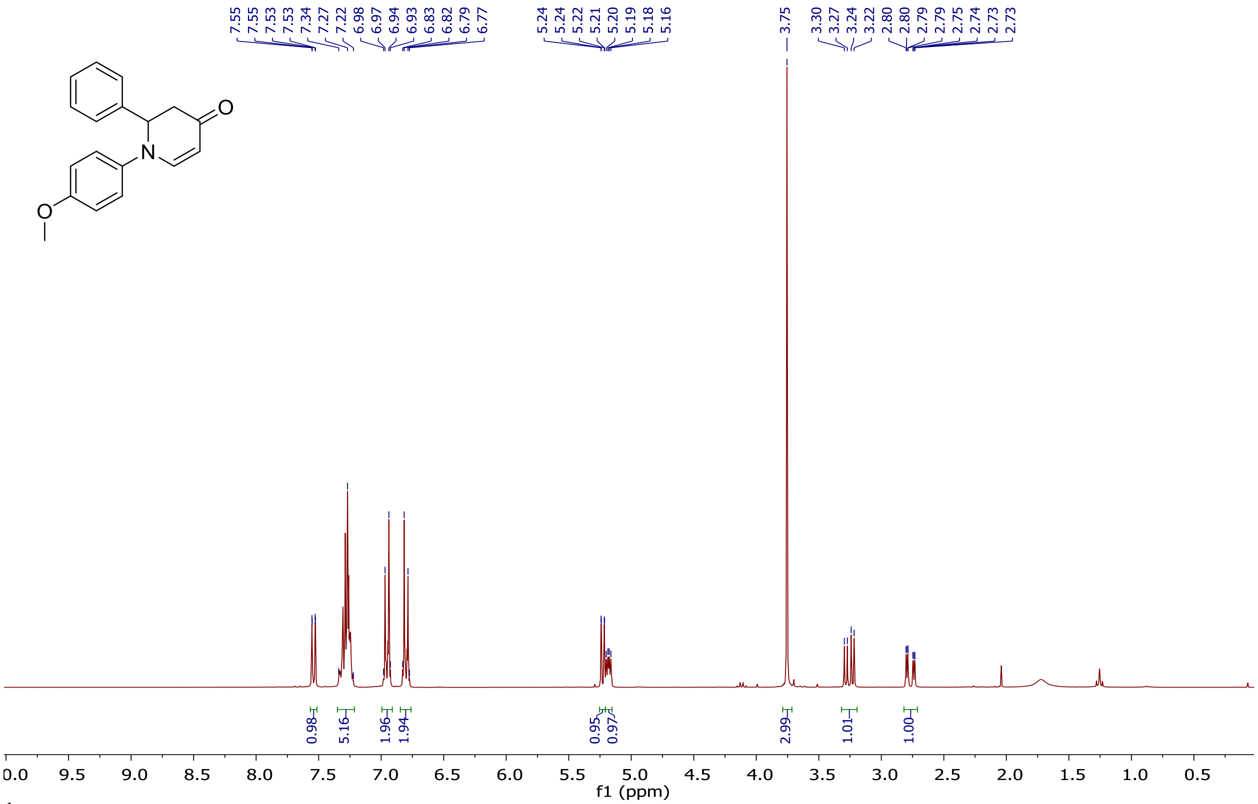

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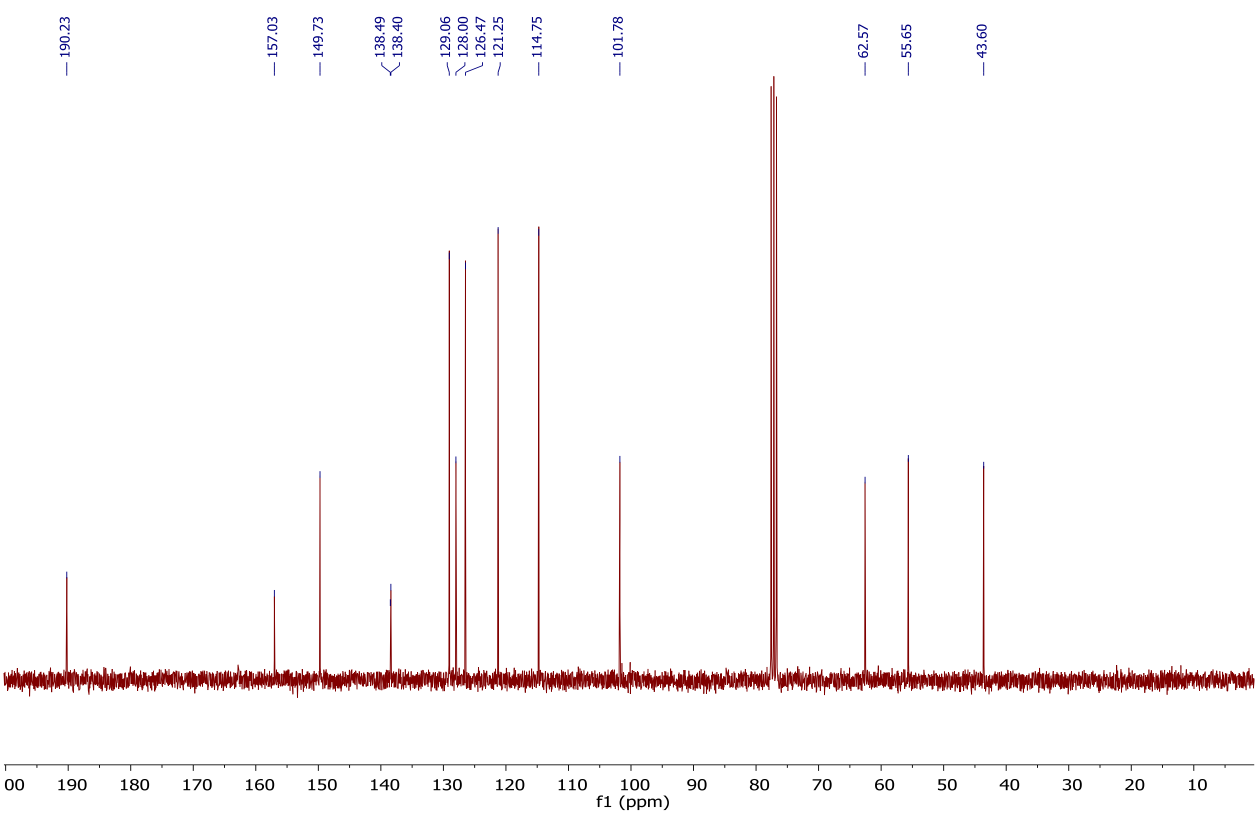

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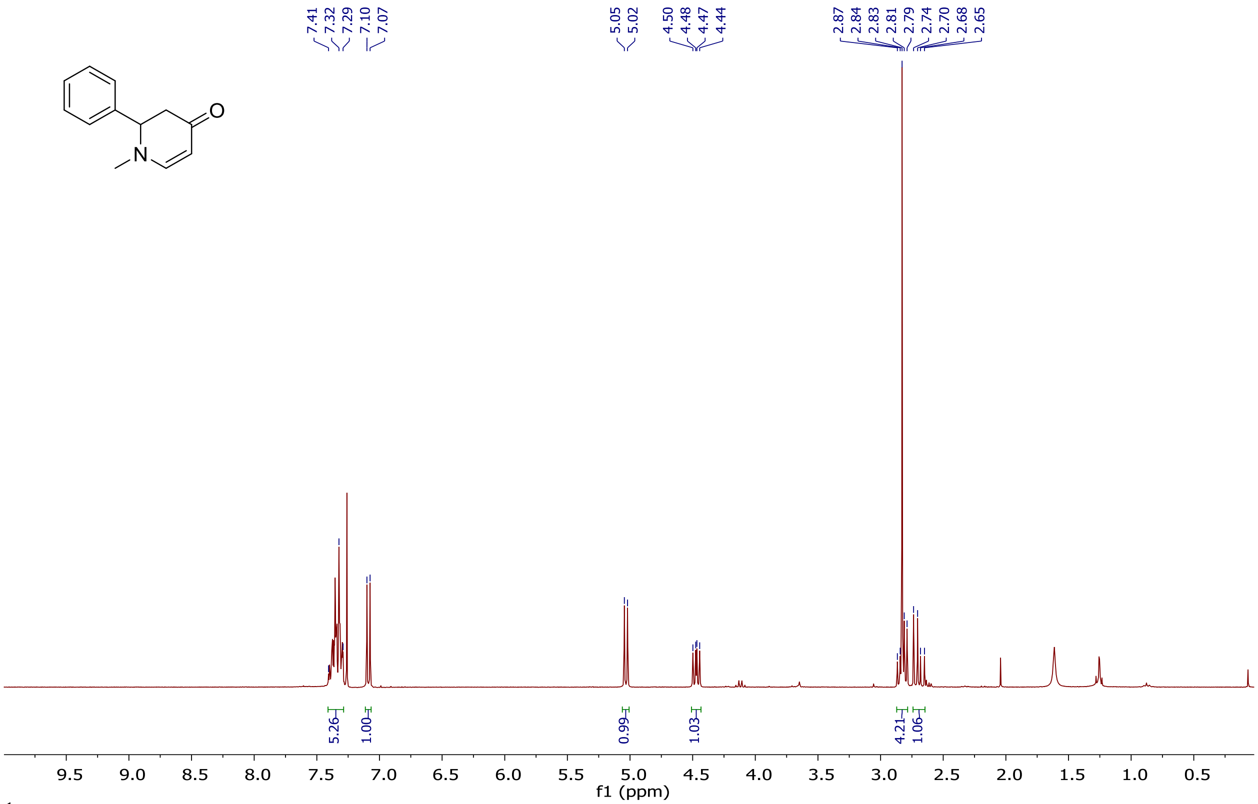

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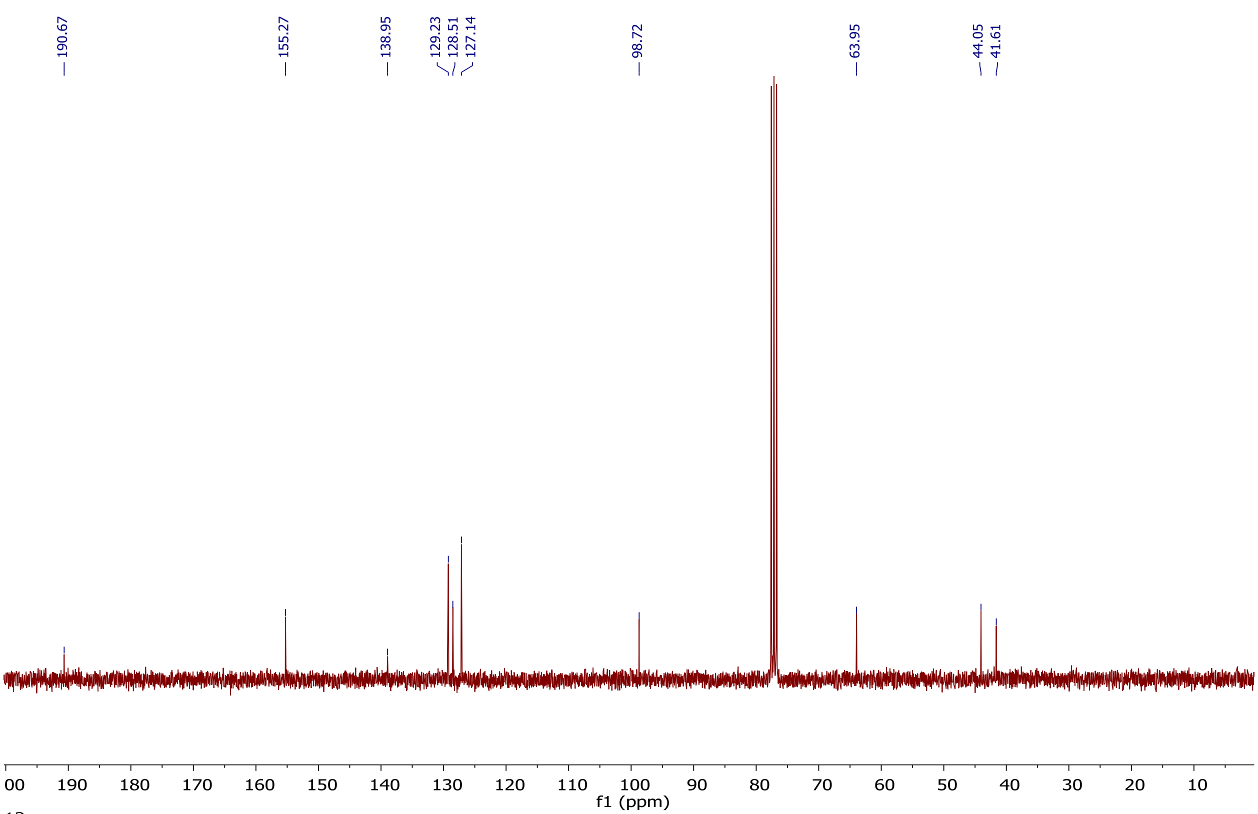

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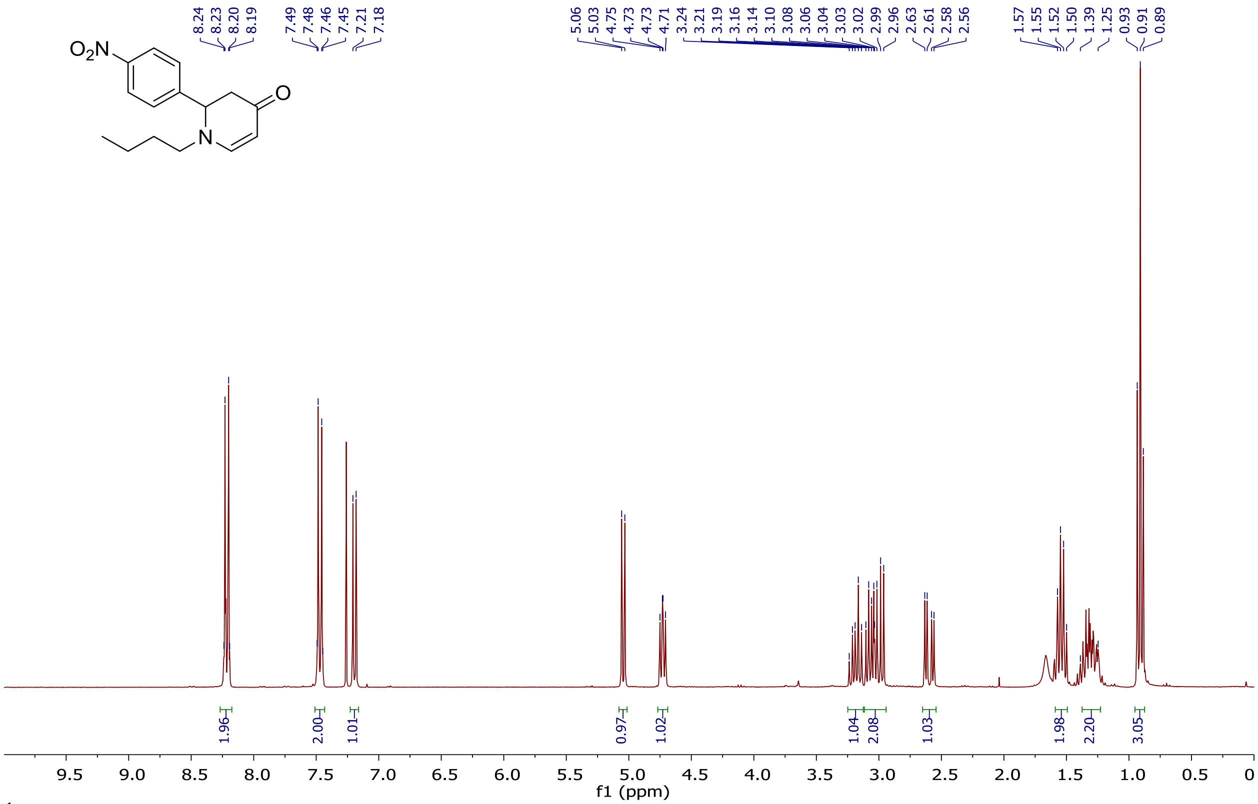

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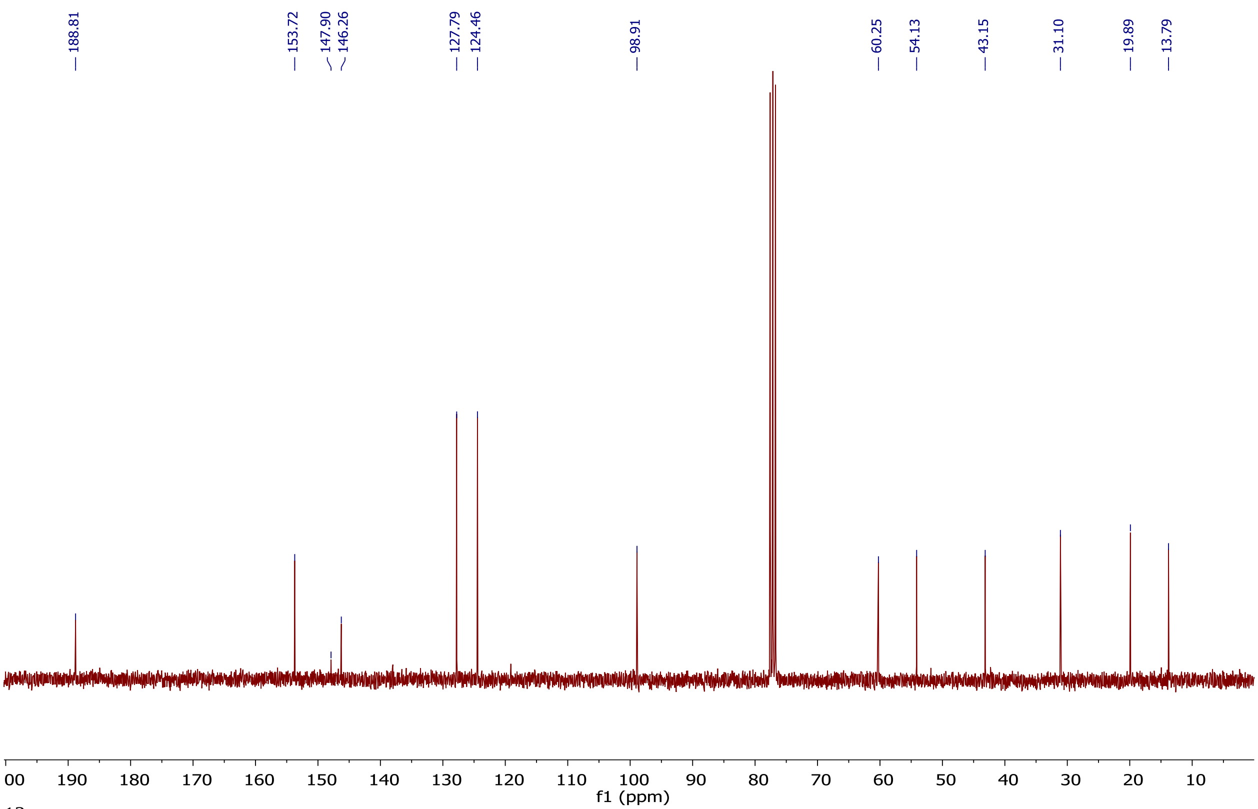

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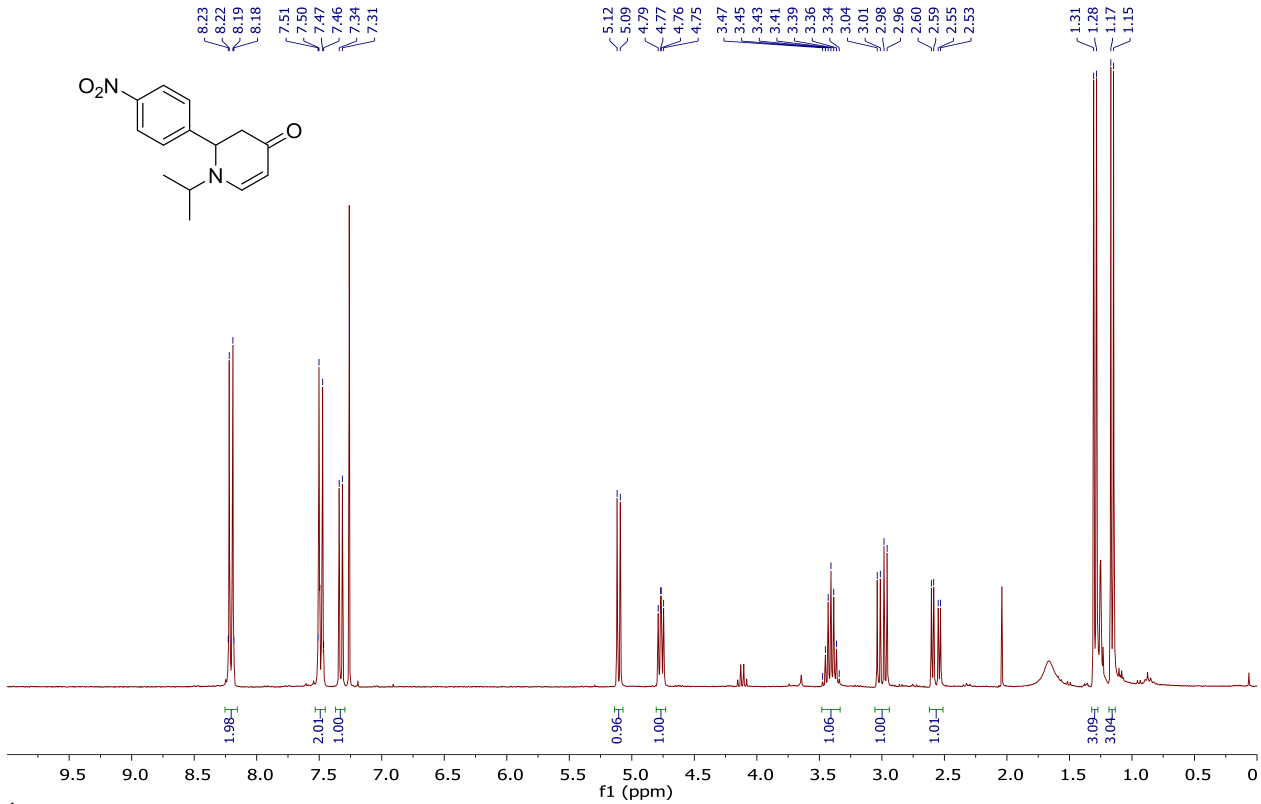

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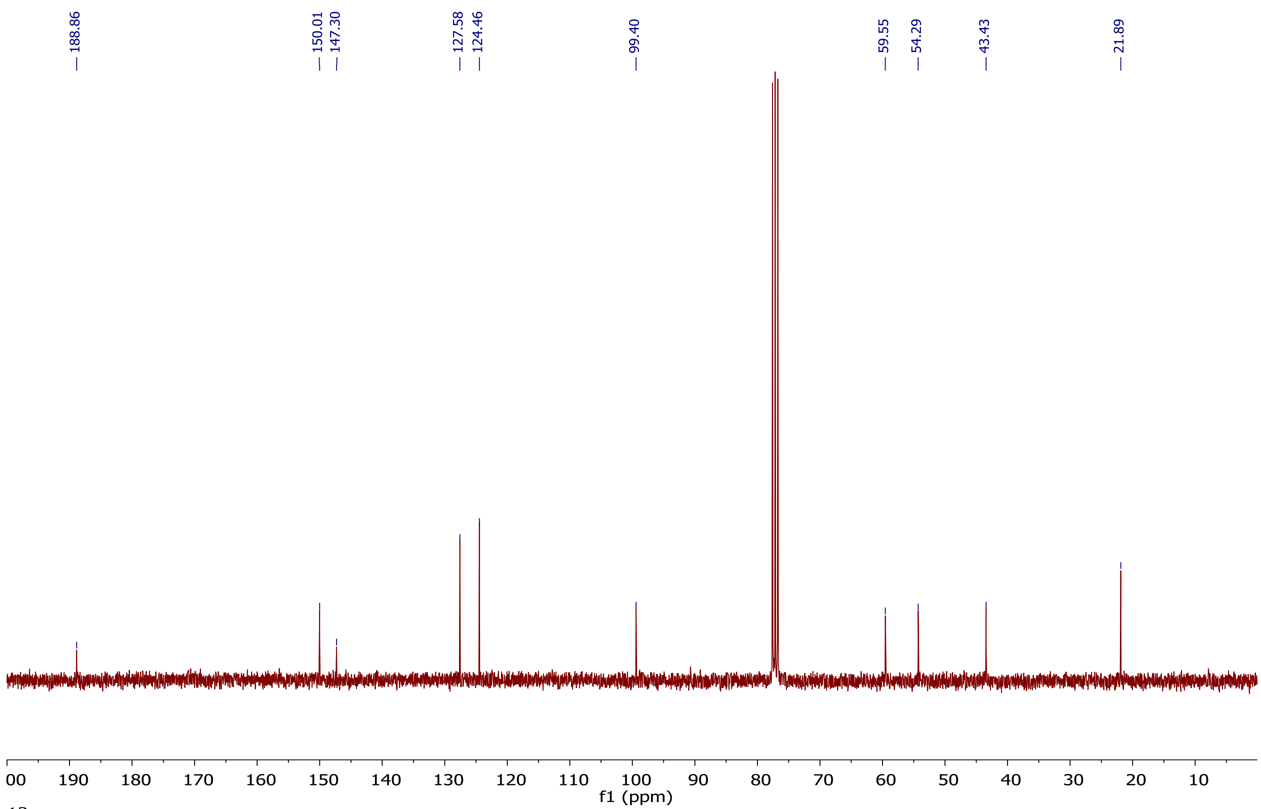

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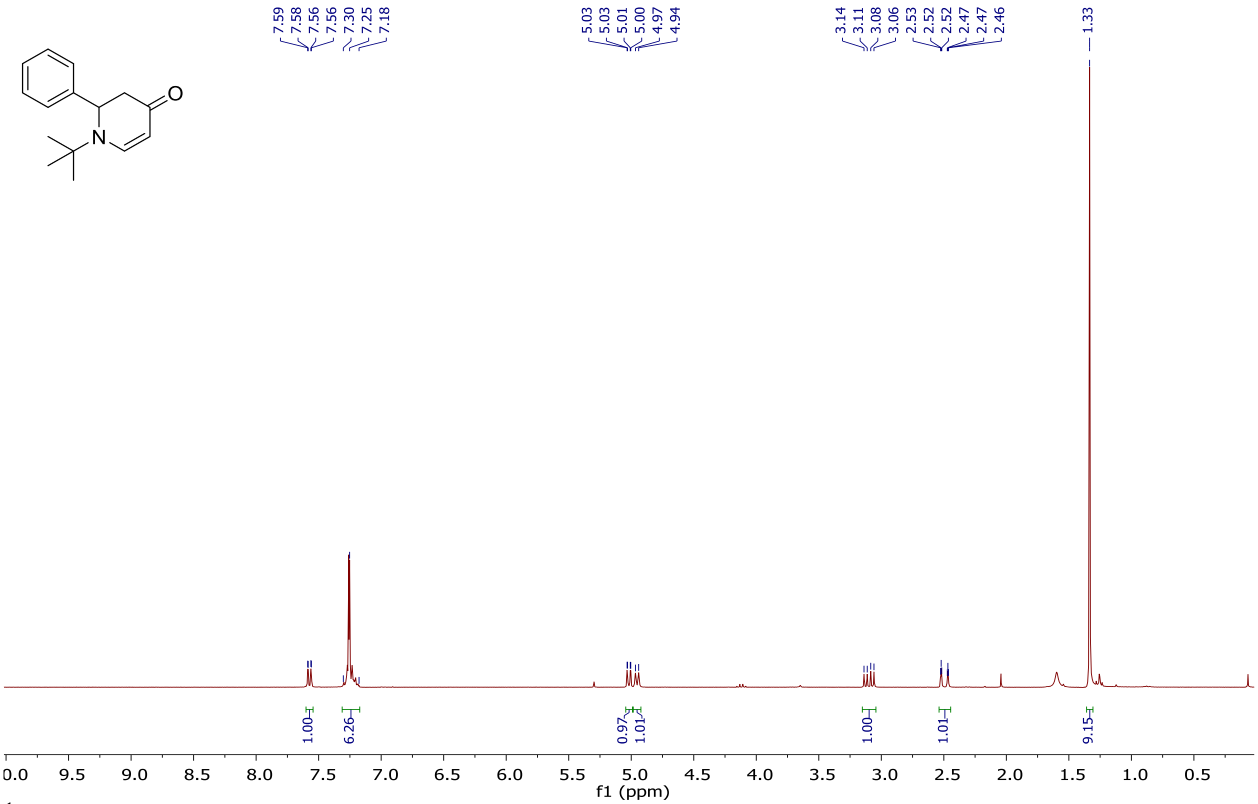

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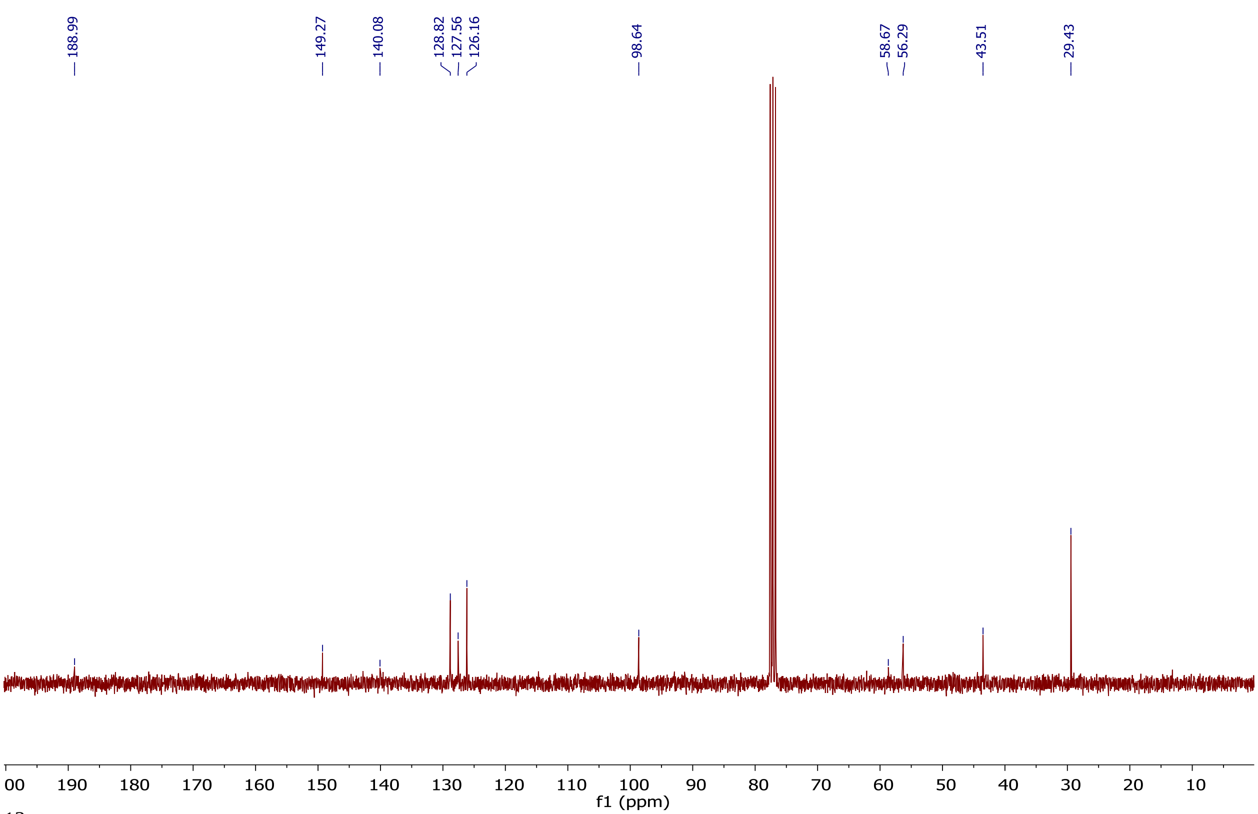

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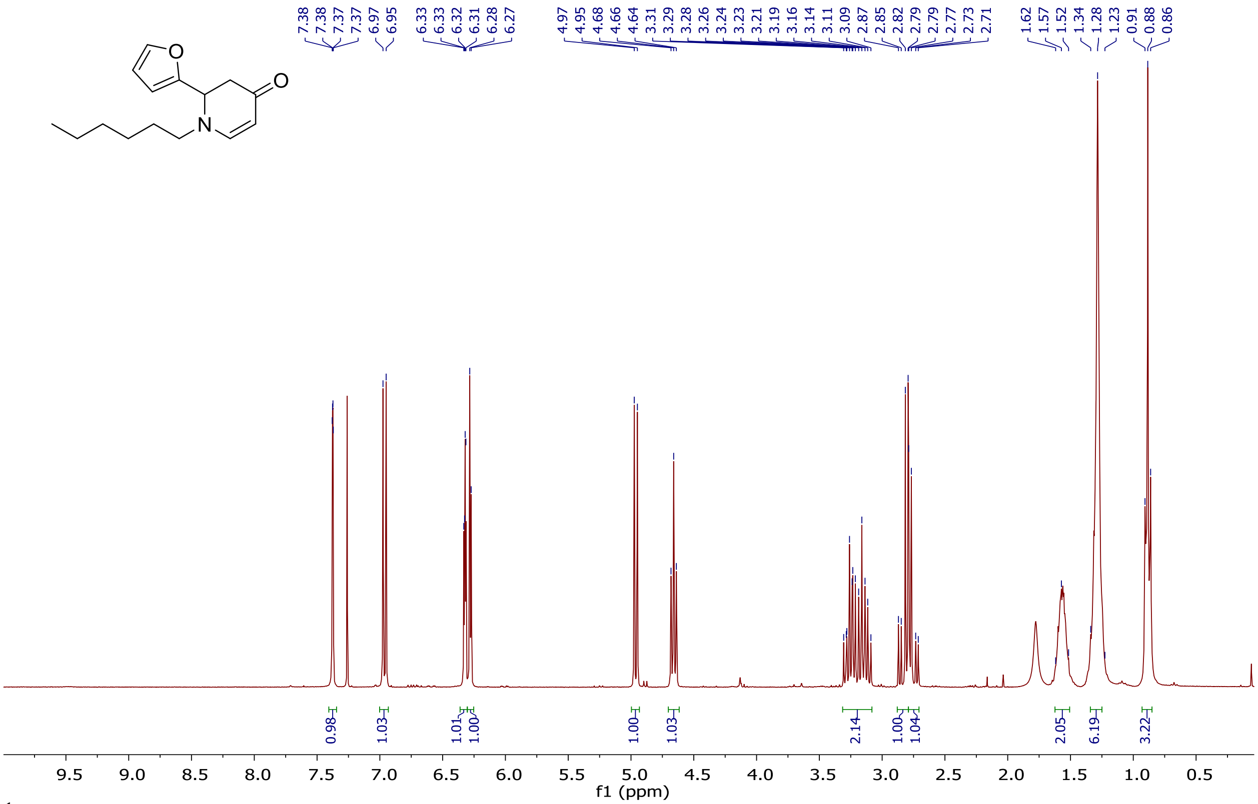

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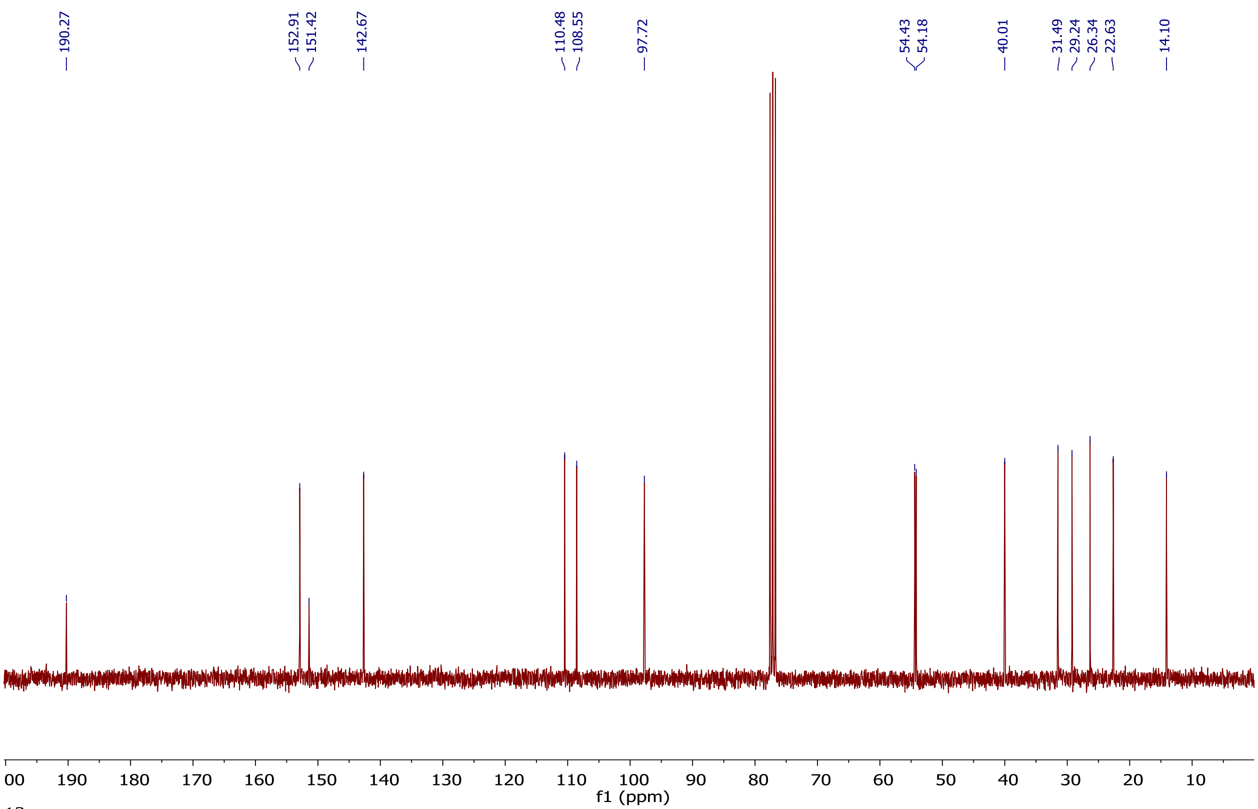

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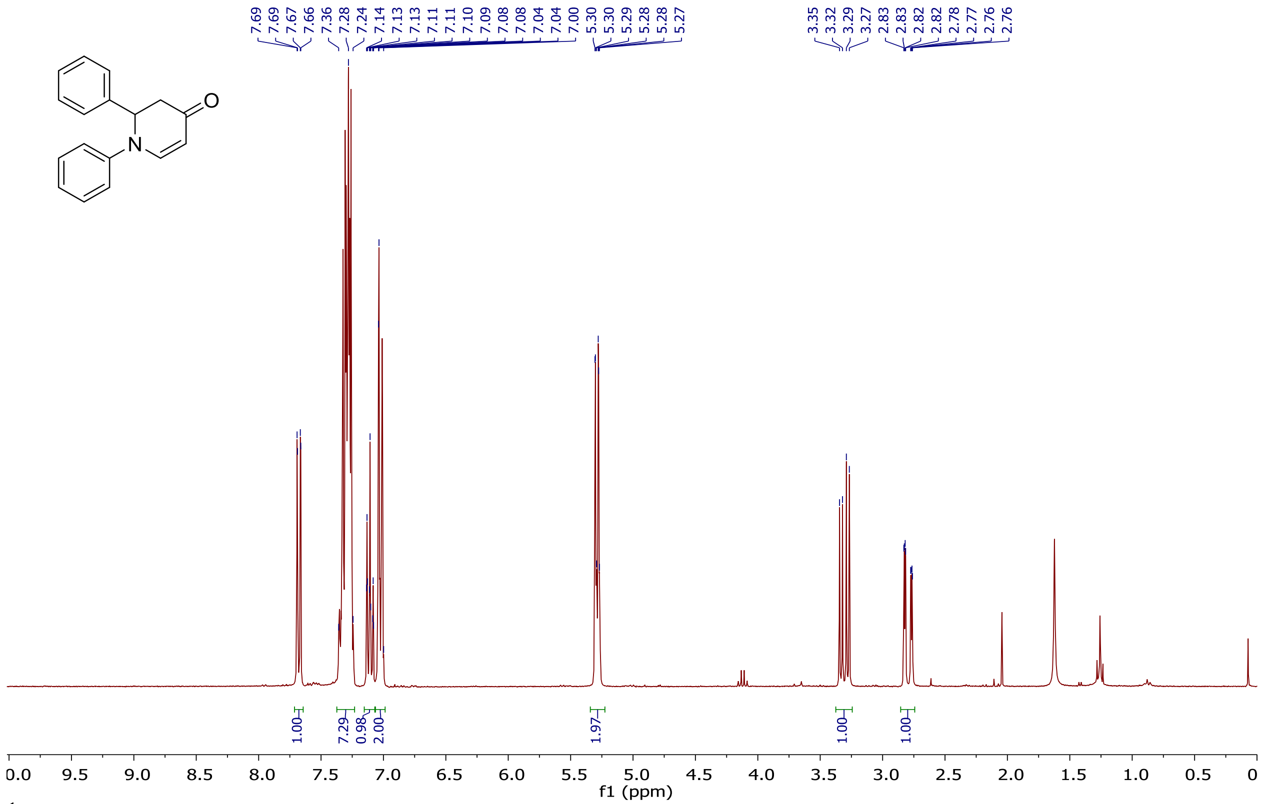

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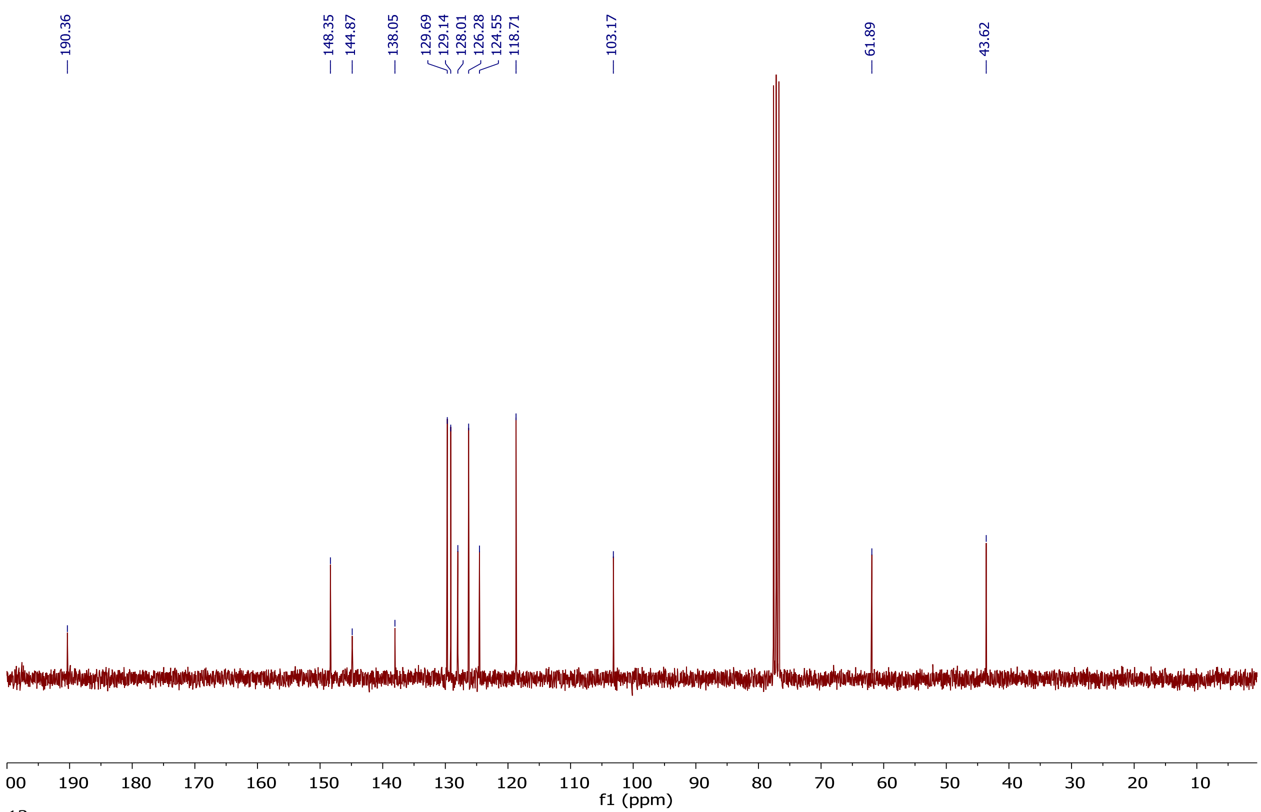

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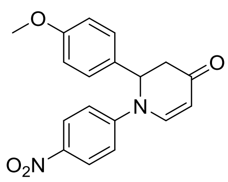

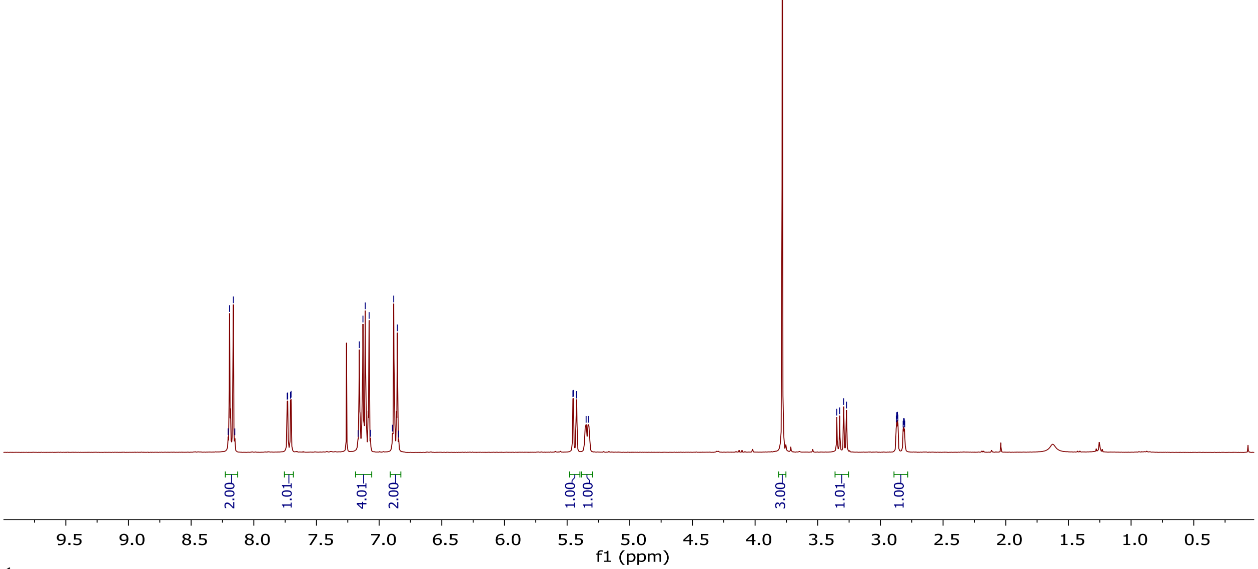

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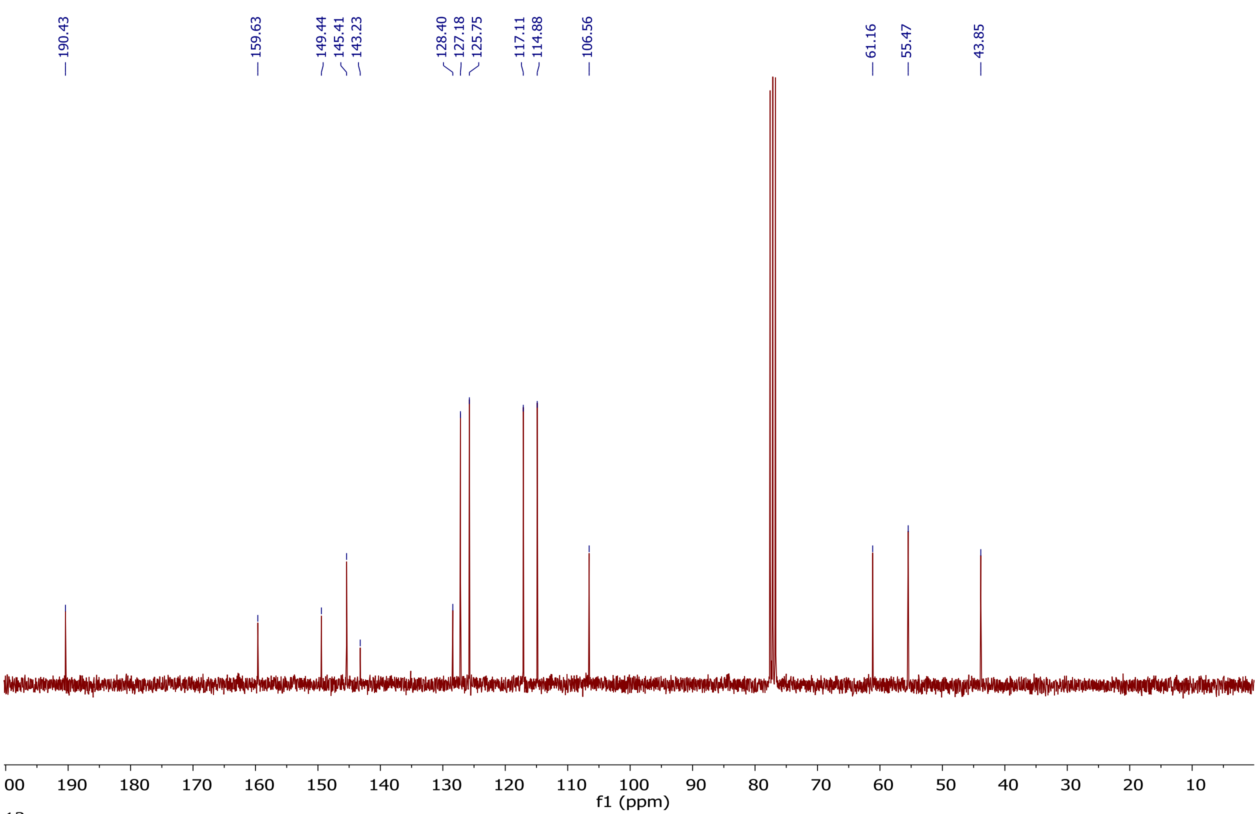

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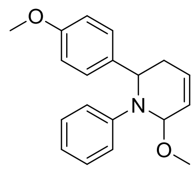
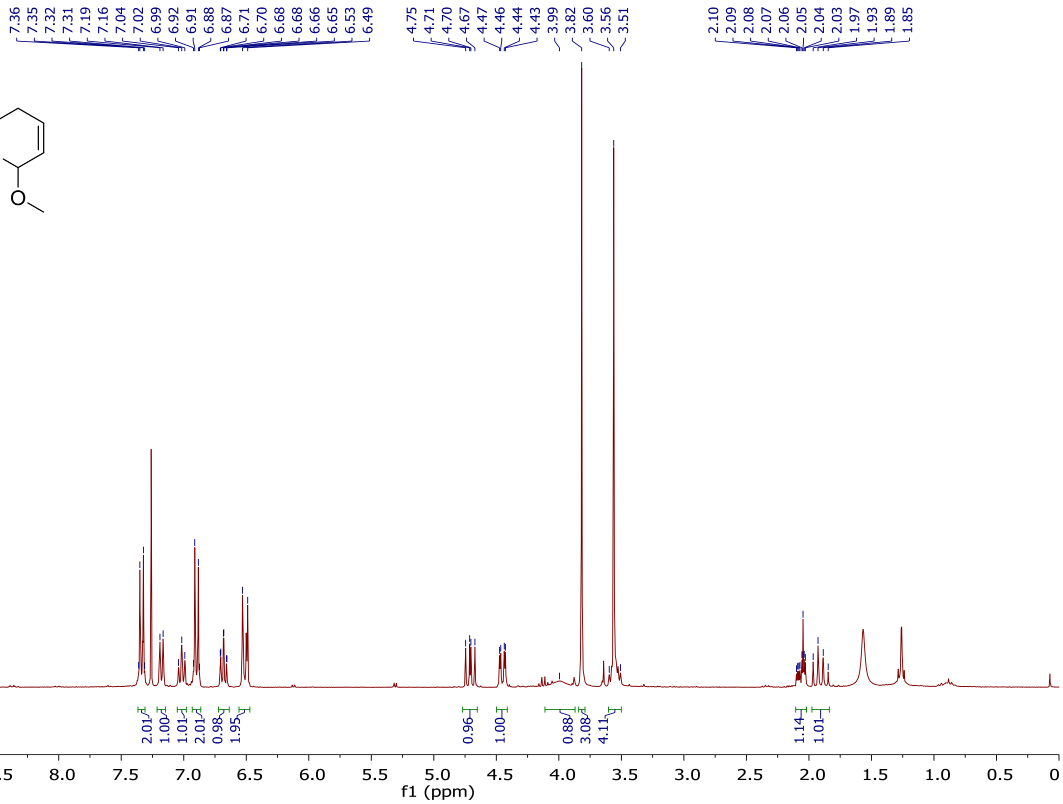
13ac





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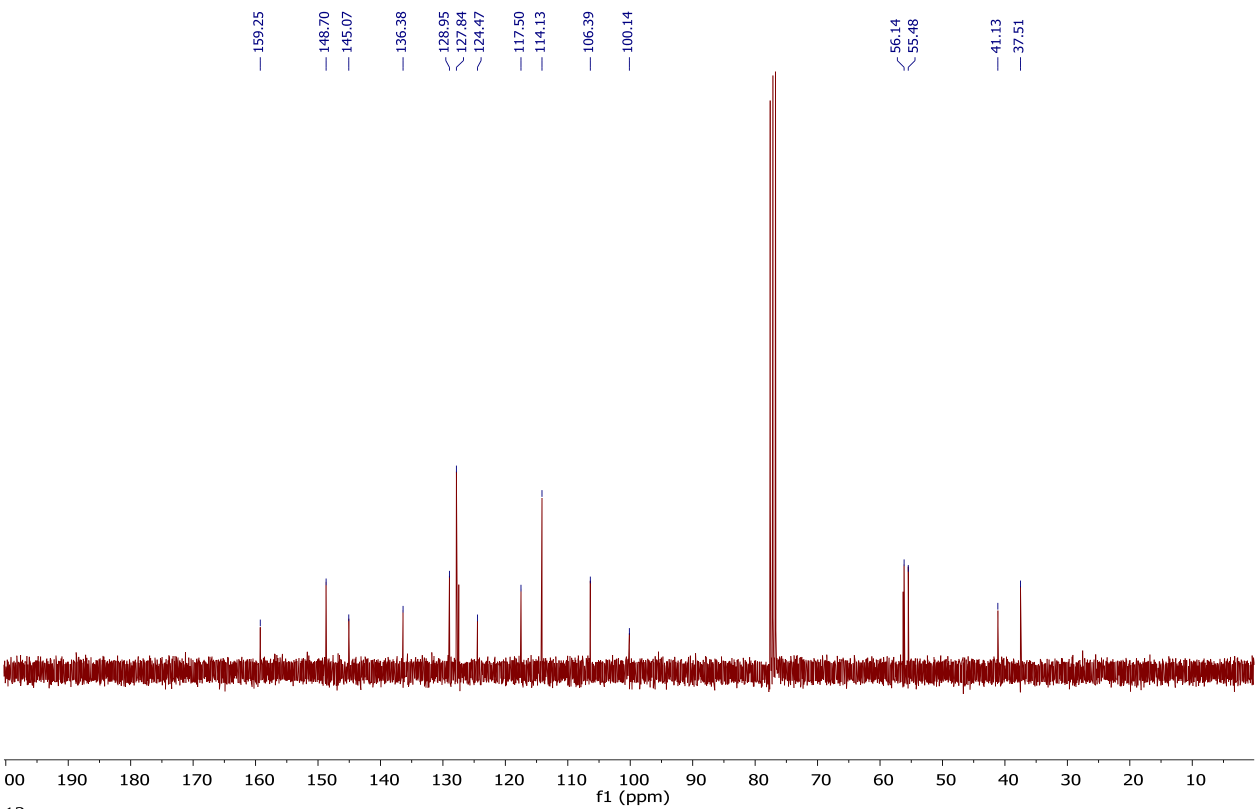

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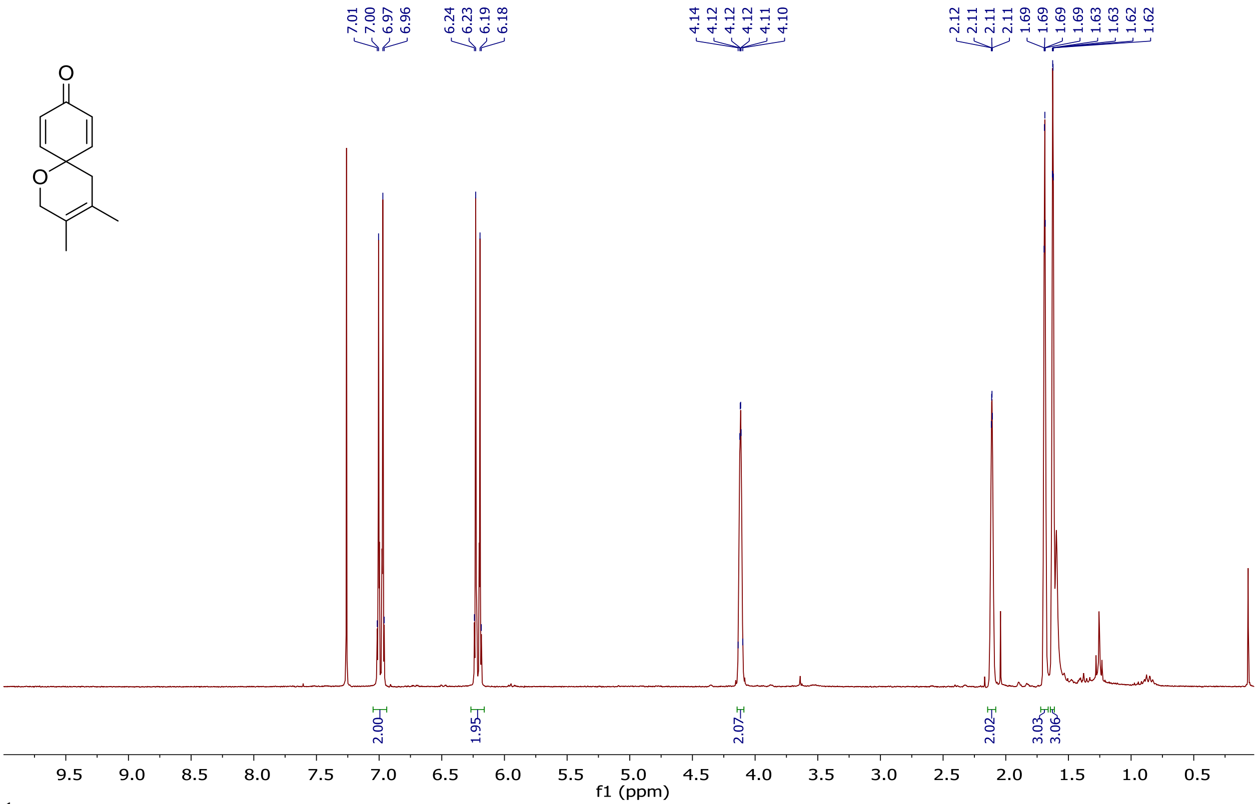
14ac



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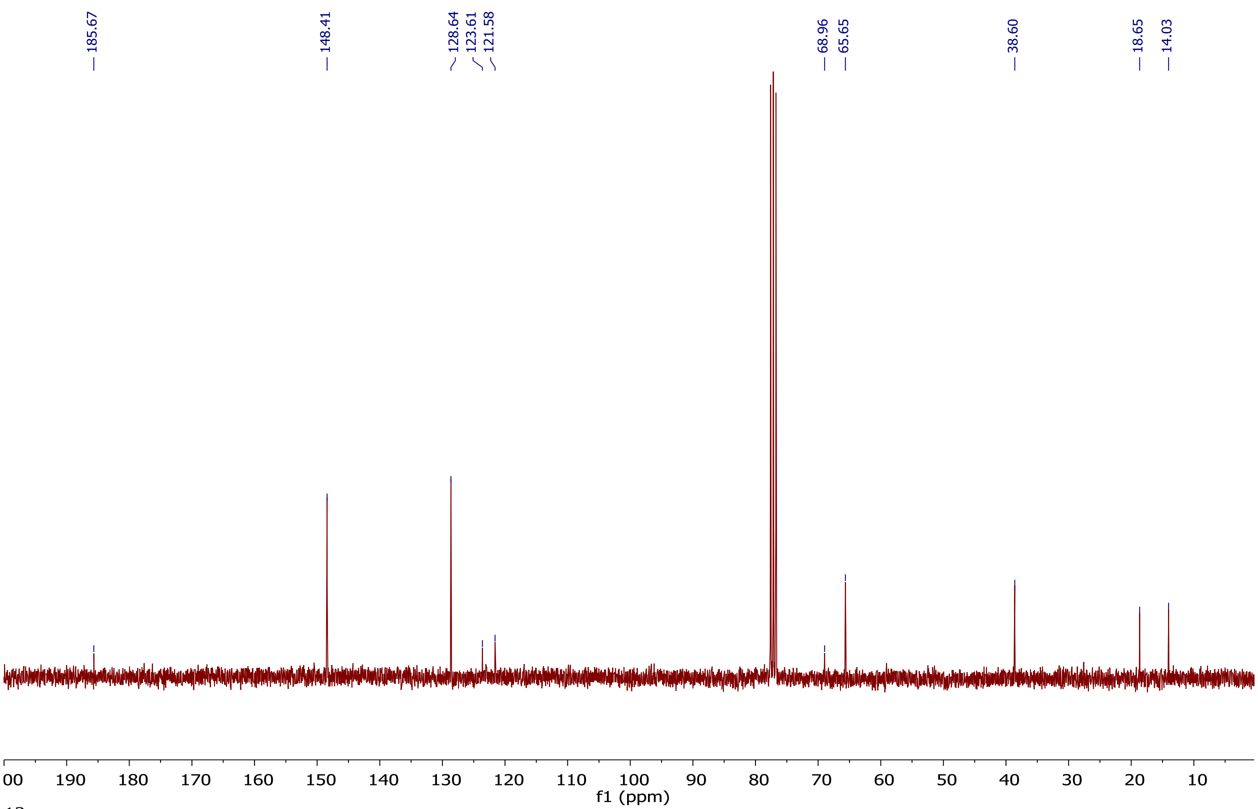

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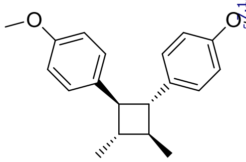

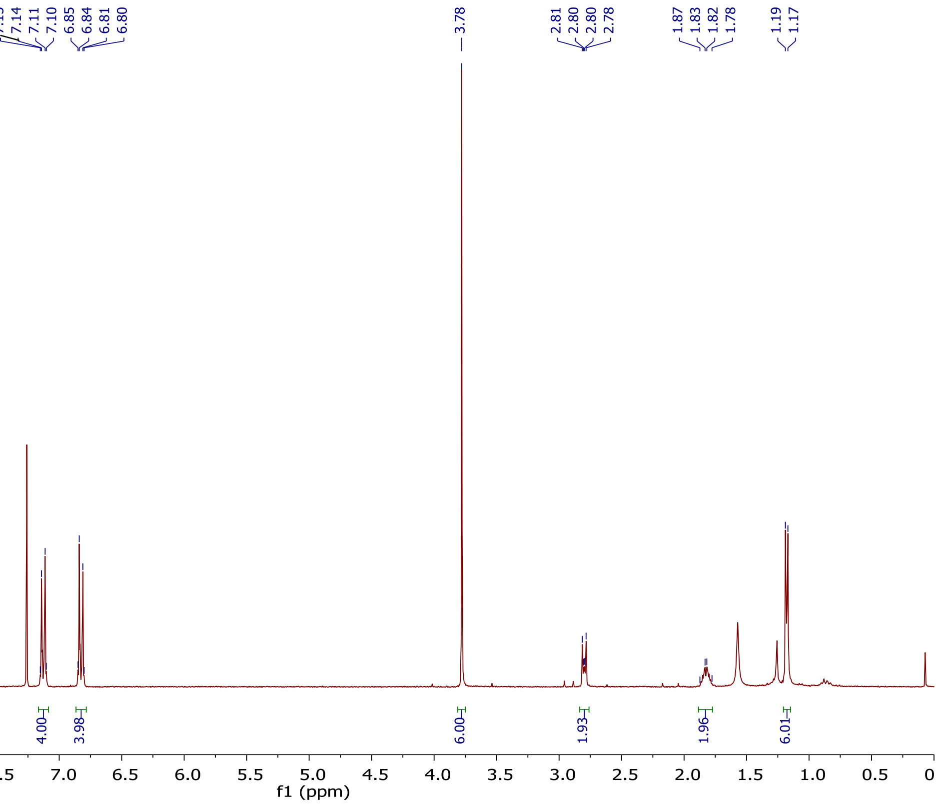

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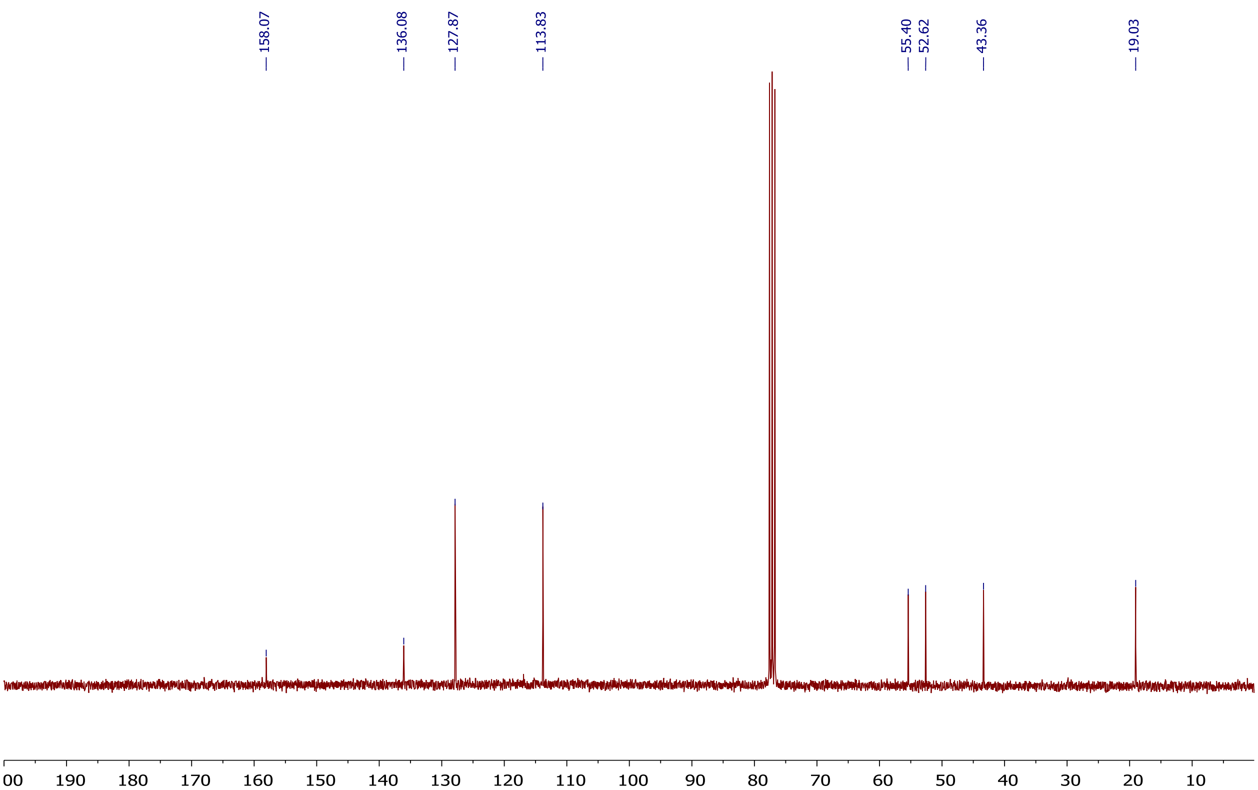

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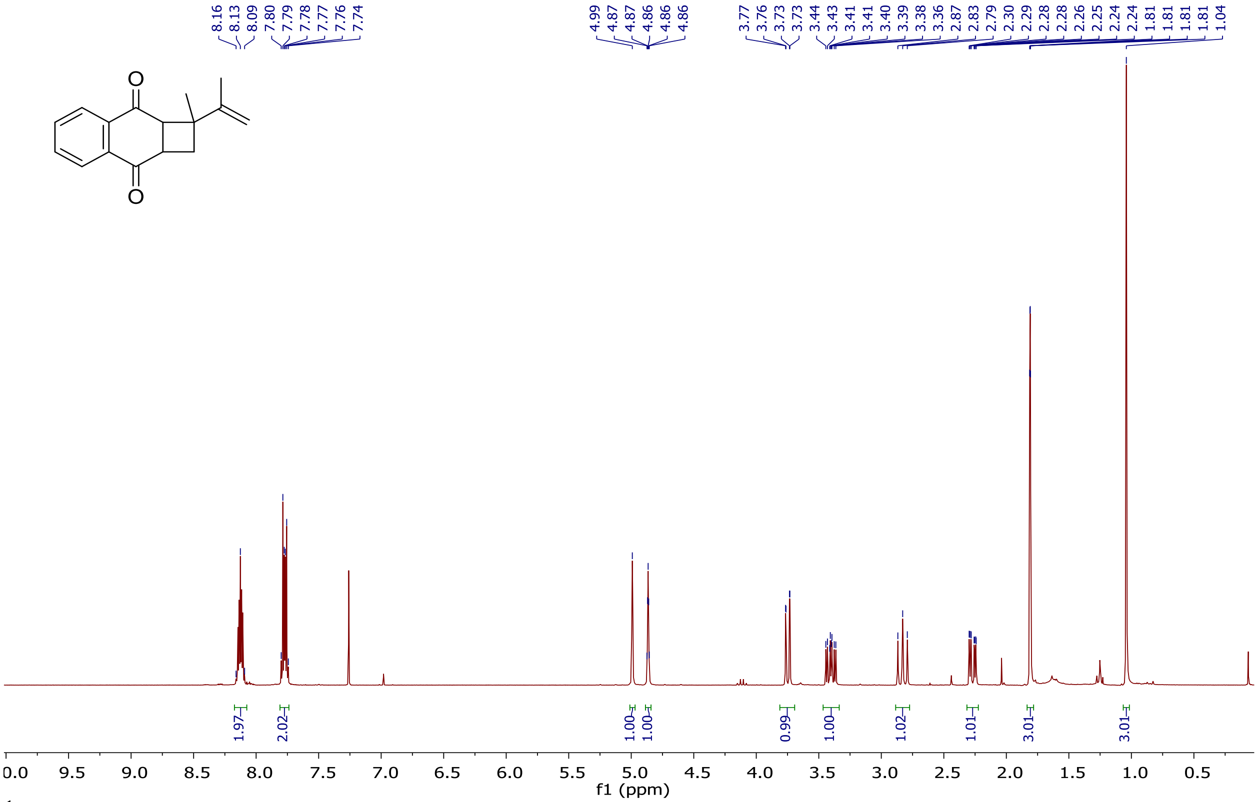

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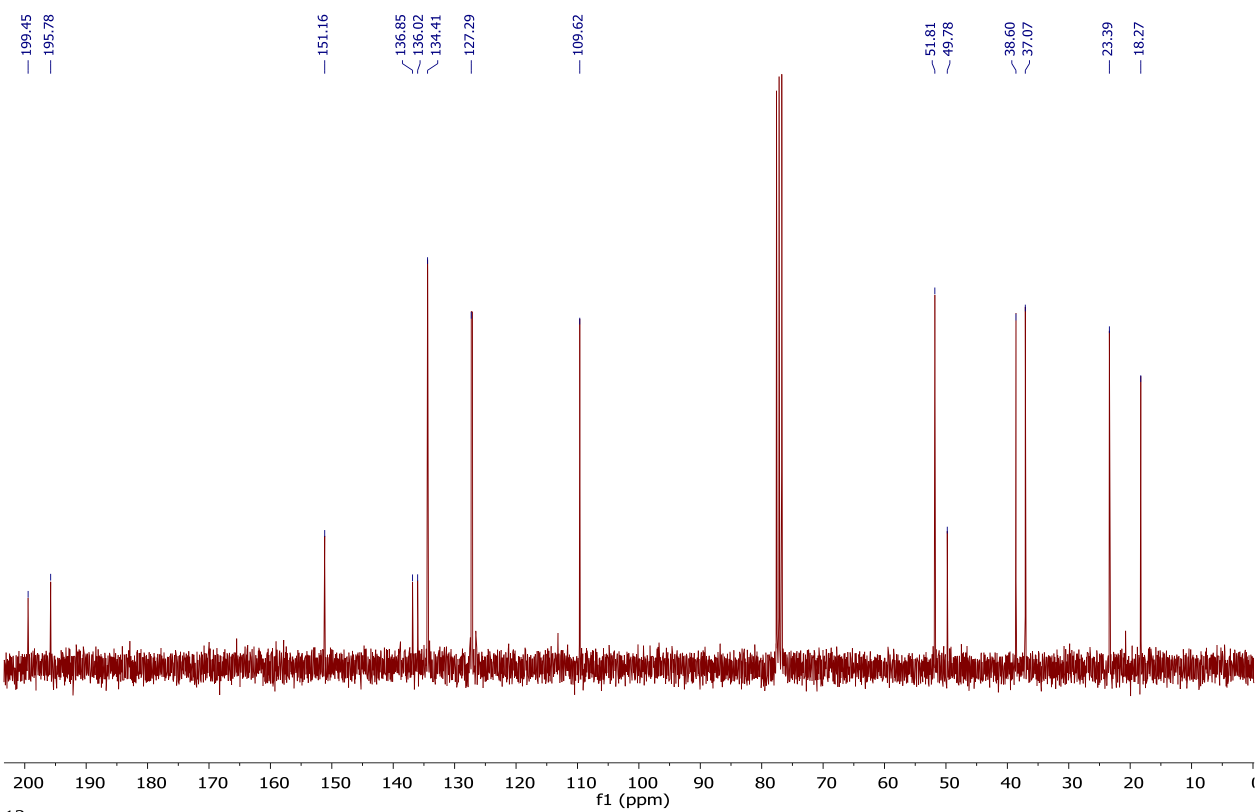

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