Supporting Information

Manuscript Title:

Oxidation of C-H bonds to C=O bonds by O_2 only: Synthesis of Δ^1-bipyrrolinones from 2,6-diazasemibullvalenes and O_2

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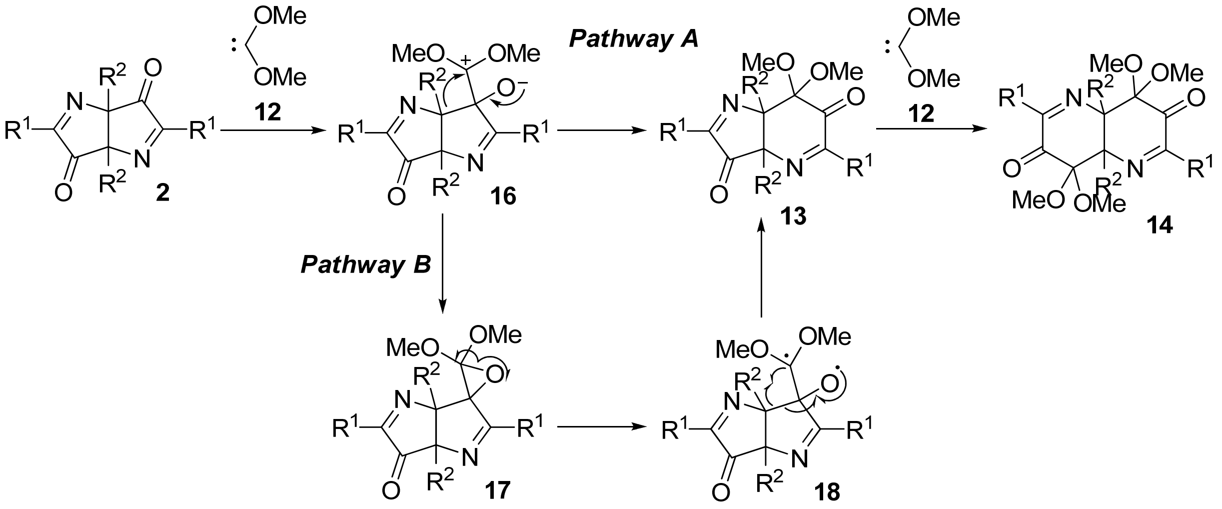
Contents:

1) Details of proposed mechanisms

a) Reactions of Δ^1-bipyrrolinones **2** with oxadiazoline **11**



SScheme 1. Proposed mechanism for the reactions of Δ^1-bipyrrolinones **2** with oxadiazoline **11**.

Given in SScheme 1 are two proposed reaction pathways. Upon heating, **11** would decompose and release dinitrogen, acetone and carbene **12**.[1] In **Pathway A**, nucleophilic addition of *in situ* generated **12** to the C=O bond would generate the zwitterionic intermediate **16**. Migration of the α-carbon leads to the ring-expansion product **13**.[1] In **Pathway B**, [2+1] cycloaddition of **12** with the C=O bond affords the spiro compound **17**. Homolysis of the C-O bond gives the diradical intermediate **18** and promotes C-C bond cleavage of the pyrrolinone ring and radical C-C coupling to construct the dihydropyridone ring in **13**. Further reaction of the pyrroline ring in **13** with carbene **12** gives the double ring-expansion product **14**.

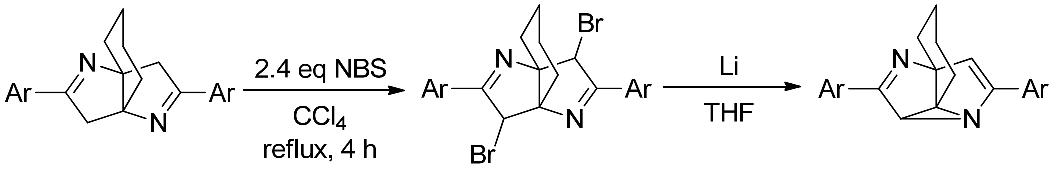
2) Experimental details and characterization data for all new compounds

General Methods: All reactions were conducted under a slightly positive pressure of dry nitrogen using standard Schlenk line techniques or under a nitrogen atmosphere in a Mikrouna Super (1220/750) glovebox. The nitrogen in the glove box was constantly circulated through a copper/molecular sieves catalyst unit. The oxygen and moisture concentrations in the glovebox atmosphere were monitored by an O_2/H_2O Combi-Analyzer to ensure both were always below 1 ppm. Unless otherwise noted, all starting materials were commercially available and were used without further purification. Solvents were purified by an Mbraun SPS-800 Solvent Purification System and dried over fresh Na chips in the glovebox. *n*-BuLi and *t*-BuLi were obtained from Acros. Oxadiazoline[1] was prepared according to the reported procedures. 2,6-Diazasemibullvalenes **1** and Δ^1-bipyrrolines **19** were prepared according to our previous work.[2,3]

Organometallic samples for NMR spectroscopic measurements were prepared in the glovebox by use of J. Young valve NMR tubes (Wilmad 528-JY). ^{1}H and ^{13}C NMR spectra were recorded on a Bruker-500 spectrometer (FT, 500 MHz for ^{1}H; 126 MHz for ^{13}C), Bruker-400 spectrometer (FT, 400 MHz for ^{1}H; 100 MHz for ^{13}C) or a JEOL-AL300 spectrometer (FT, 300 MHz for ^{1}H; 75 MHz for ^{13}C) at room temperature, unless otherwise noted. High-resolution mass spectra (HRMS) were recorded on a Bruker Apex IV FTMS mass spectrometer using ESI (electrospray ionization). Micro elemental analyses were performed on an Elemental Analyzer vario EL apparatus.

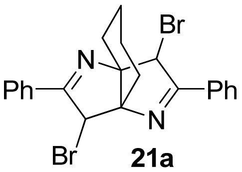
Experimental details and characterization data for all new compounds:

a) Synthesis of 3,7-diaryl-2,6-diazasemibullvalenes 1f-h[4]



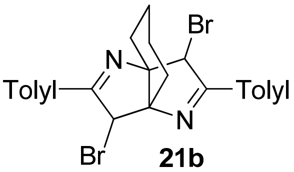
20a: R = Ph	**21a**: 48%	**1f**: NMR yield: > 95%
20b: R = 4'-Me-C_6H_4	**21b**: 49%	**1g**: NMR yield: > 95%
20c: R = 4'-MeO-C_6H_4	**21c**: 46%	**1h**: NMR yield: > 95%

Synthesis of Δ^1-bipyrroline dibromides 21: To a solution of Δ^1-bipyrroline **20** (1.0 mmol) in 5 mL of CCl_4 in a 50 ml round-bottom flask was added *N*-bromosuccinimide (390 mg, 6.0 mmol), and the mixture was refluxed and stirred for 4 h. After cooled down, the mixture was poured into 10 ml water and extracted with diethyl ether. The combined organic layer was washed with water and brine and dried over $MgSO_4$. The solvent was evaporated in vacuum to give crude products, which was purified by column chromatography (silica gel, petroleum ether/diethyl ether/triethyl amine = 100:3:1) to afford **21**.



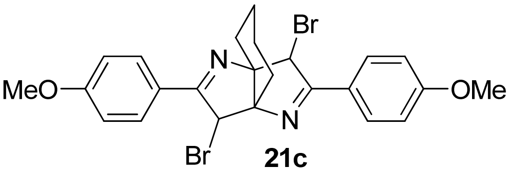
21a

21a: Colorless solid, isolated yield 48% (226 mg). ^{1}H NMR (300MHz, $CDCl_3$, 25 °C): δ = 7.74-7.77 (m, 4H, CH), 7.27-7.35 (m, 6H, CH), 5.56 (s, 2H, CH), 2.73-2.81 (m, 2H, CH_2), 2.01-2.07 (m, 2H, CH_2), 1.46-1.78 (m, 4H, CH_2); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 168.09, 131.47, 131.27, 128.49, 128.45, 81.14, 56.03, 33.44, 22.36; HRMS: *m/z*: calcd for $C_{22}H_{21}Br_2N_2$ $[M+H]^+$: 471.0066, found 471.0058.



21b

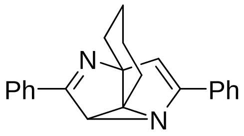
21b: Colorless solid, isolated yield 49% (244 mg). ^{1}H NMR (300MHz, $CDCl_3$, 25 °C): δ = 7.73 (d, *J* = 8.4 Hz, 4H, CH), 7.20 (d, *J* = 8.4 Hz, 4H, CH), 5.62 (s, 2H, CH), 2.82-2.86 (m, 2H, CH_2), 2.36 (s, 6H, CH_3), 2.08-2.15 (m, 2H, CH_2), 1.55-1.79 (m, 4H, CH_2); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 168.15, 141.84, 129.26, 128.85, 128.54, 80.99, 56.21, 33.41, 22.29, 21.38; HRMS: *m/z*: calcd for $C_{24}H_{25}Br_2N_2$ $[M+H]^+$: 499.0379, found 499.0379.



21c

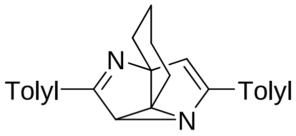
21c: Colorless solid, isolated yield 46% (244 mg); ^{1}H NMR (300MHz, $CDCl_3$, 25 °C): δ = 7.79 (d, *J* = 9.0 Hz, 4H, CH), 6.89 (d, *J* = 9.0 Hz, 4H, CH), 5.58 (s, 2H, CH),3.81 (s, 6H, CH_3), 2.80-2.85 (m, 2H, CH_2), 2.08-2.15 (m, 2H, CH_2), 1.54-1.74 (m, 4H, CH_2); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 167.55, 162.11, 130.33, 124.18, 113.86, 80.89, 56.31, 55.31, 33.48, 22.31; HRMS: *m/z*: calcd for $C_{24}H_{25}Br_2N_2O_2$ $[M+H]^+$: 531.0277, found 531.0274.

Synthesis of 3,7-diaryl-2,6-diazasemibullvalenes 1f-h: In the glovebox, to a solution of Δ^1-bipyrroline dibromide **21** (0.1 mmol) in 1 mL of THF in a 25 ml round-bottom flask was added pieces of metal lithium (1.4 mg, 0.2 mmol), and the mixture was stirred for 2-4 h until all pieces of metal lithium disappeared. The mixture was dried up under vacuum, extracted with diethyl ether and filtered. The filtrate was dryed up to afford **1f-h**.



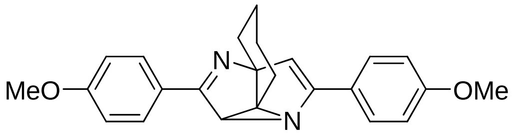
1g

1f: Colorless solid, isolated yield 92% (28 mg); ^{1}H NMR (300MHz, THF-d_8, 25 °C): δ = 7.71-7.74 (m, 4H, CH), 7.19-7.26 (m, 6H, CH), 5.55 (s, 2H, CH), 2.16-2.23 (m, 2H, CH_2), 1.68-1.78 (m, 2H, CH_2), 1.29-1.36 (m, 4H, CH_2); ^{13}C NMR (75 MHz, THF-d_8, Me_4Si, 25 °C): δ = 153.14, 135.81, 129.51, 128.88, 127.56, 100.74, 79.47, 28.94, 22.49.



1g

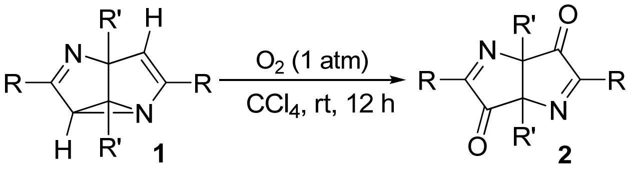
1g: Colorless solid, isolated yield 93% (31 mg); ^{1}H NMR (300MHz, THF-d_8, 25 °C): δ = 7.60 (d, *J* = 8.1 Hz, 4H, CH), 7.03 (d, *J* = 8.1 Hz, 4H, CH), 5.47 (s, 2H, CH), 2.23 (s, 6H, CH_3), 2.11-2.36 (m, 2H, CH_2), 1.61-1.72 (m, 4H, CH_2), 1.28-1.35 (m, 2H, CH_2); ^{13}C NMR (75 MHz, THF-d_8, 25 °C): δ = 153.00, 139.45,133.26, 129.57, 127.59, 100.21, 79.17, 28.89, 22.42, 21.18.



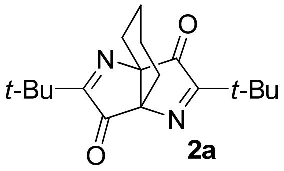
1h

1h: Colorless solid, isolated yield 81% (30 mg); ^{1}H NMR (300MHz, THF-d_8, 25 °C): δ = 1.28-1.36 (m, 4H, CH_2), 1.67-1.77 (m, 2H, CH_2), 2.14-2.19 (m, 2H, CH_2), 3.71 (s, 6H, CH_3), 5.40 (s, 2H, CH), 6.77 (d, *J* = 9.0 Hz, 4H, CH), 7.65 (d, *J* = 9.0 Hz, 4H, CH); ^{13}C NMR (75 MHz, THF-d_8, 25 °C): δ = 161.54, 152.56, 129.05, 128.73, 114.29, 99.50, 79.14, 55.42, 29.03, 22.47.

b) Synthesis of Δ^1-bipyrrolinones 2

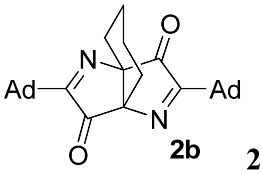


General procedure for preparation of Δ^1-bipyrrolinones 2 from NSBV 1 and oxygen: O_2 gas was bubbled into a solution of NSBV **1** (0.5 mmol) in 5 mL of CCl_4 at room temperature for ca.10 min. The reaction mixture was allowed to stirr for 12 h under O_2 atmosphere. Solvents were removed and the crude product was purified by column chromatography (silica gel, petroleum ether/diethyl ether/triethylamine = 100:1:1) to afford the desired product.



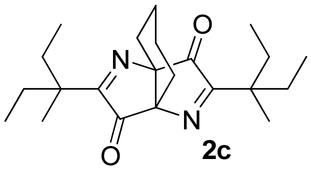
2a

2a: Yellow solid, isolated yield 93% (140 mg); ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.50-2.42 (m, 2H, CH_2), 1.65-1.53 (m, 6H, CH_2), 1.23 (s, 18H, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$) δ 197.98, 177.72, 74.97, 35.02, 28.70, 26.91, 18.93. IR (neat): *v* 1742 (C=O), cm^{-1}; HRMS: *m/z*: calcd for $C_{18}H_{27}N_2O_2$ [M+H]$^+$: 303.2073, found 303.2070. Elemental Analysis Calcd (%) for $C_{18}H_{26}N_2O_2$: C, 71.49; H, 8.67; N, 9.26; Found: C, 71.31; H, 8.70; N, 9.13.



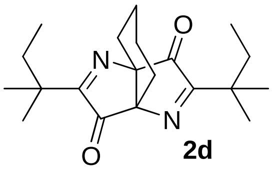
2b

2b: Yellow solid, isolated yield 90% (206 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.47-2.35 (m, 2H, CH_2), 2.03 (s, 4H, CH_2), 1.90 (s, 8H, CH_2), 1.76-1.71 (m, 8H, CH and CH_2), 1.65-1.47 (m, 4H, CH), 1.25 (s, 12H, CH_2). ^{13}C NMR (101 MHz, $CDCl_3$) δ 198.11, 176.98, 75.13, 38.45, 37.54, 36.51, 29.71, 28.65, 27.77, 18.70. IR (neat): *v* 1744 (C=O), cm^{-1}; HRMS: *m/z*: calcd for $C_{30}H_{39}N_2O_2$ [M+H]$^+$: 459.3012, found 459.3006. Elemental Analysis Calcd (%) for $C_{30}H_{38}N_2O_2$: C, 78.56; H, 8.35; N, 6.11; Found: C, 78.42; H, 8.58; N, 5.99. Single crystals of **2b** suitable for X-ray analysis were grown in hexane/CH_2Cl_2 (1:1) at room temperature.



2c

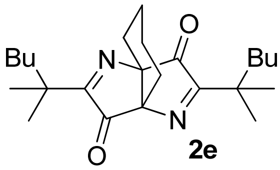
2c: Yellow oil, isolated yield 95% (170 mg); ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.47-2.42 (m, 2H, CH_2), 1.85-1.71 (m, 4H, CH_2), 1.56-1.44 (m, 8H, CH_2), 1.21-1.03 (m, 2H, CH_2), 1.07 (s, 6H, CH_3), 0.62 (t, J = 7.5 Hz, 6H, CH_3), 0.55 (t, J = 7.5 Hz, 6H, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$) δ 197.81, 176.45, 75.26, 42.05, 30.01, 29.97, 29.34, 20.51, 19.20, 8.57, 8.47. IR (neat): *v* 1745 (C=O), cm^{-1}; HRMS: *m/z*: calcd for $C_{22}H_{35}N_2O_2$ [M+H]$^+$: 359.2699, found 359.2697.



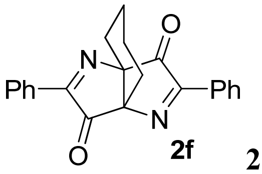
2d

2d: Yellow oil, isolated yield 92% (151 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.54-2.44 (m, 2H, CH_2), 1.72 (q, J = 7.4 Hz, 4H, CH_2), 1.64-1.50 (m, 4H, CH_2), 1.28-1.23 (m, 2H,

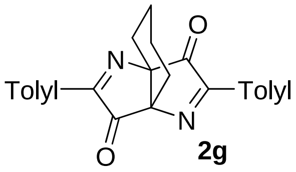
CH_2), 1.21 (s, 6H, CH_3), 1.17 (s, 6H, CH_3), 0.64 (t, J = 7.5 Hz, 6H, CH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ 198.01, 177.12, 75.23, 38.66, 31.79, 29.06, 24.88, 24.67, 19.22, 9.08. IR (neat): *v* 1743 (C=O), cm^{-1}; HRMS: *m/z*: calcd for $C_{20}H_{31}N_2O_2$ $[M+H]^+$: 331.2386, found 331.2381.



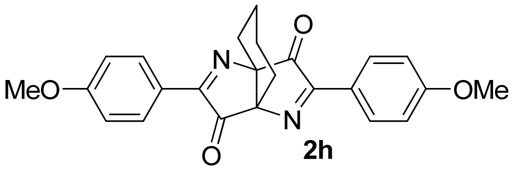
2e **2e:** Yellow oil, isolated yield 96% (183 mg); ^1H NMR (400 MHz, $CDCl_3$) δ 2.57-2.45 (m, 2H, CH_2), 1.78-1.69 (m, 2H, CH_2), 1.67-1.60 (m, 2H, CH_2), 1.29-1.23 (m, 4H, CH_2), 1.22 (s, 6H, CH_3), 1.18 (s, 6H, CH_3), 1.59-1.51 (m, 4H, CH_2), 1.05-0.85 (m, 6H, CH_2), 0.82 (t, J = 7.3 Hz, 6H, CH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ 198.03. 177.22, 75.19, 38.84, 38.36, 29.12, 27.16, 25.57, 25.12, 23.12, 19.40, 13.97. IR (neat): *v* 1747 (C=O), cm^{-1}; HRMS: *m/z*: calcd for $C_{24}H_{39}N_2O_2$ $[M+H]^+$: 387.3012, found 387.3008.



2f **2f:** Yellow solid, isolated yield 94% (160 mg); ^1H NMR (400 MHz, $CDCl_3$) δ 8.30 (d, J = 7.2 Hz, 4H, C_6H_5), 7.54 (t, J = 7.4 Hz, 2H, C_6H_5), 7.46 (t, J = 7.5 Hz, 4H, C_6H_5), 2.66 (dt, J = 14.3, 5.3 Hz, 2H, CH_2), 2.00-1.89 (m, 2H, CH_2), 1.72-1.61 (m, 2H, CH_2), 1.49-1.37 (m, 2H, CH_2). ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.99, 165.45, 132.34, 129.59, 128.76, 128.67, 75.99, 29.17, 18.74. IR (neat): *v* 1741 (C=O), cm^{-1}; HRMS: *m/z*: calcd for $C_{22}H_{19}N_2O_2$ $[M+H]^+$: 343.1447, found 343.1449. Elemental Analysis Calcd (%) for $C_{22}H_{18}N_2O_2$: C, 77.17; H, 5.30; N, 8.18; Found: C, 77.10; H, 5.28; N, 8.17.

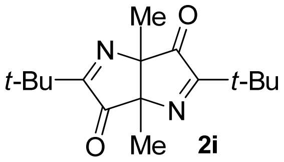


2g **2g:** Yellow solid, isolated yield 83% (155 mg);^1H NMR (400 MHz, $CDCl_3$) δ 8.17 (d, J = 8.2 Hz, 4H, C_6H_4), 7.23 (d, J = 8.1 Hz, 4H, C_6H_4), 2.60 (dt, J = 14.2, 5.2 Hz, 2H, CH_2), 2.38 (s, 6H, CH_3), 1.95-1.84 (m, 2H, CH_2), 1.68-1.57 (m, 2H, CH_2), 1.46-1.33 (m, 2H, CH_2). ^{13}C NMR (101 MHz, $CDCl_3$) δ 198.36, 165.21,142.93, 129.38, 128.71, 126.93, 75.80, 29.12, 21.67, 18.69. IR (neat): *v* 1743 (C=O), cm^{-1}; HRMS: *m/z*: calcd for $C_{24}H_{23}N_2O_2$ $[M+H]^+$: 371.1760, found 371.1762. Elemental Analysis Calcd (%) for $C_{24}H_{22}N_2O_2$: C, 77.81; H, 5.99; N, 7.56; Found: C, 77.67; H, 6.13; N, 7.42.



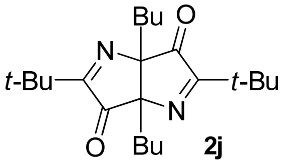
2h

2h: Yellow solid, isolated yield 79% (158 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.27 (dd, J = 8.8, 1.5 Hz, 4H, C_6H_4), 6.92 (dd, J = 8.8, 1.5 Hz, 4H, C_6H_4), 3.82 (s, 6H, CH_3), 2.62-2.53 (m, 2H, CH_2), 1.94-1.83 (m, 2H, CH_2), 1.63-1.56 (m, 2H, CH_2), 1.43-1.34 (m, 2H, CH_2). ^{13}C NMR (101 MHz, $CDCl_3$) δ 198.81, 164.43, 162.92, 130.61, 130.56, 122.32, 114.07, 113.93, 75.60, 55.40, 29.09, 18.63. IR (neat): ν 1740 (C=O), cm^{-1}; HRMS: m/z: calcd for $C_{24}H_{23}N_2O_4$ [M+H]$^+$: 403.1658, found 403.1654.



2i

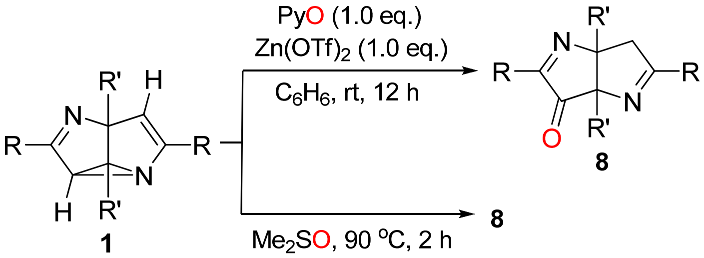
2i: Yellow solid, isolated yield 81% (111 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.43 (s, 6H, CH_3), 1.22 (s, 18H, CH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.39, 176.88, 75.31, 34.99, 26.91, 16.95. IR (neat): ν 1746 (C=O), cm^{-1}; HRMS: m/z: calcd for $C_{16}H_{25}N_2O_2$ [M+H]$^+$: 277.1916, found 277.1916. Elemental Analysis Calcd (%) for $C_{16}H_{24}N_2O_2$: C, 69.53; H, 8.75; N, 10.14; Found: C, 69.43; H, 8.72; N, 10.18.



2j

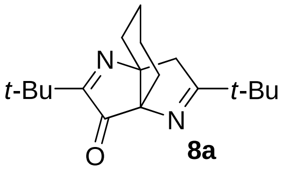
2j: Yellow oil, isolated yield 77% (138 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.32 (ddd, J = 14.1, 12.4, 5.1 Hz, 2H, CH_2), 1.60-1.52 (m, 2H, CH_2), 1.37-1.29 (m, 8H, CH_2), 1.21 (s, 18H, CH_3), 0.89 (t, J = 7.3 Hz, 6H, CH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.68, 176.95, 78.38, 35.16, 29.52, 26.96, 26.08, 23.11, 13.74. IR (neat): ν 1744 (C=O), cm^{-1}; HRMS: m/z: calcd for $C_{22}H_{37}N_2O_2$ [M+H]$^+$: 361.2855, found 361.2859.

c) Synthesis of pyrrolino[3,2-*b*]pyrrolinones 8



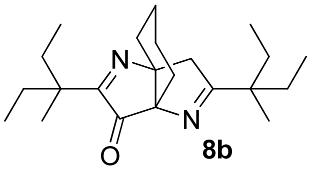
General procedure for preparation of pyrrolino[3,2-*b*]pyrrolinones 8 from NSBV 1 and pyridine oxide or DMSO: To a solution of NSBV **1** (0.5 mmol) in 5 mL of benzene in a 25 ml Schlenk tube was added pyridine oxide (0.5 mmol, 47 mg) and $Zn(OTf)_2$ (0.5 mmol, 181 mg) at room temperature, and the mixture was stirred for 12 h. The solvent was evaporated in vacuum to give crude products, which was purified by column chromatography (silica gel, petroleum ether/diethyl ether/triethylamine = 100:1:1) to afford the desired product.

The solution of NSBV **1** (0.5 mmol) in 5 mL of DMSO in a 25 ml round bottom flask was stirred at 90 °C for 2 h. The reaction mixture was poured into 20 mL of water and extracted with diethyl ether. The organic layer was washed with water and brine and dried over $MgSO_4$. The solvent was evaporated in vacuum to give crude products, which was purified by column chromatography (silica gel, petroleum ether/diethyl ether/triethyl amine = 100:1:1) to afford **8**.



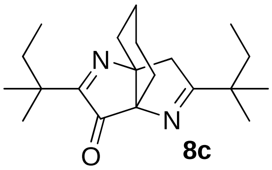
8a

8a: Yellow solid, isolated yield 92% (133 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.95 (dd, *J* = 43.6, 18.1 Hz, 2H, CH_2), 2.54 (dt, *J* = 13.9, 3.7 Hz, 1H, CH_2), 2.32 (dt, *J* = 8.1, 3.7 Hz, 1H, CH_2), 1.65-1.45 (m, 2H, CH_2), 1.41-1.30 (m, 2H, CH_2), 1.24 (s, 9H, CH_3), 1.22-1.18 (m, 1H, CH_2), 1.08 (s, 9H, CH_3), 1.03-0.91 (m, 1H, CH_2). ^{13}C NMR (101 MHz, $CDCl_3$) δ 200.43, 186.23, 175.47, 80.72, 73.71, 44.88, 36.08, 34.36, 32.93, 28.45, 27.86, 27.06, 20.41, 20.37. IR (neat): *v* 1740 (C=O), cm^{-1}; HRMS: *m/z*: calcd for $C_{18}H_{29}N_2O$ $[M+H]^+$: 289.2280, found 289.2284. Elemental Analysis Calcd (%) for $C_{18}H_{28}N_2O$: C, 74.96; H, 9.78; N, 9.71; Found: C, 74.84; H, 9.82; N, 9.69.



8b

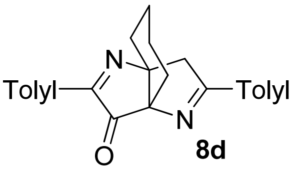
8b: Yellow oil, isolated yield 79% (136 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.99 (d, *J* = 18.1 Hz, 1H, CH_2), 2.83 (d, *J* = 18.1 Hz, 1H, CH_2), 2.58 (d, *J* = 13.9 Hz, 1H, CH_2), 2.38-2.33 (m, 1H, CH_2), 1.92-1.84 (m, 2H, CH_2), 1.61-1.51 (m, 8H, CH_2), 1.46-1.38 (m, 4H, CH_2), 1.15 (s, 3H, CH_3), 0.99 (s, 3H, CH_3), 0.77-0.72 (m, 6H, CH_3), 0.70-0.65 (m, 6H, CH_3).^{13}C NMR (126 MHz, $CDCl_3$) δ 200.73, 184.90, 174.38, 80.92, 74.23, 45.36, 42.96, 41.47, 33.84, 32.07, 31.78, 30.33, 30.10, 20.93, 20.92, 20.73, 20.69, 8.80, 8.67, 8.64, 8.54. IR (neat): *v* 1739 (C=O), cm^{-1}; HRMS: *m/z*: calcd for $C_{22}H_{37}N_2O$ $[M+H]^+$: 345.2906, found 345.2904.



8c

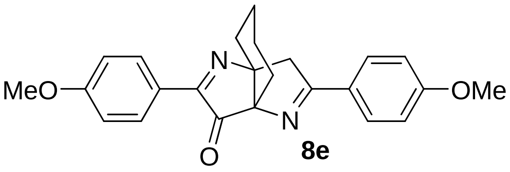
8c: Yellow oil, isolated yield 81% (128 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.99 (d, *J* = 18.1 Hz, 1H, CH_2), 2.86 (d, *J* = 18.1 Hz, 1H, CH_2), 2.56 (dt, *J* = 14.0, 3.4 Hz, 1H,

CH_2), 2.35 (dt, J = 13.5, 3.5 Hz, 1H, CH_2), 1.77-1.72 (m, 2H, CH_2), 1.63-1.50 (m, 3H, CH_2), 1.49-1.43 (m, 2H, CH_2), 1.22 (s, 3H, CH_3), 1.19 (s, 3H, CH_3), 1.06 (s, 3H, CH_3), 1.03 (s, 3H, CH_3), 0.90-0.82 (m, 3H, CH_3), 0.74-0.65 (m, 6H, CH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ 200.56, 185.45, 174.85, 80.82, 74.00, 45.03, 39.53, 37.94, 33.63, 33.37, 31.84, 29.71, 28.91, 25.72, 25.29, 25.04, 24.81, 20.58, 20.53, 9.13, 8.96. IR (neat): ν 1741 (C=O), cm^{-1}; HRMS: *m/z*: calcd for $C_{20}H_{33}N_2O$ [M+H]$^+$: 317.2593, found 317.2591.



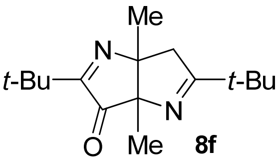
8d

8d: Yellow solid, isolated yield 94% (168 mg); ^{1}H NMR (400 MHz, C_6D_6) δ 8.51 (d, J = 8.1 Hz, 2H, C_6H_4), 7.71 (d, J = 8.1 Hz, 2H, C_6H_4), 6.92 (d, J = 8.1 Hz, 2H, C_6H_4), 6.85 (d, J = 8.0 Hz, 2H, C_6H_4), 3.36 (d, J = 17.9 Hz, 1H, CH_2), 2.92 (d, J = 17.9 Hz, 1H, CH_2), 2.87 (t, J = 3.9 Hz, 1H, CH_2), 2.17 (dt, J = 13.6, 4.1 Hz, 1H, CH_2), 1.99 (s, 3H, CH_3), 1.95 (s, 3H, CH_3), 1.46-1.37 (m, 1H, CH_2), 1.32-1.26 (m, 2H, CH_2), 1.23-1.16 (m, 1H, CH_2), 1.08--0.97 (m, 1H, CH_2), 0.93-0.85 (m, 1H, CH_2). ^{13}C NMR (101 MHz, C_6D_6) δ 200.58, 173.14, 163.57, 141.63, 141.13, 131.83, 129.36, 129.12, 128.83, 128.66, 128.30, 82.31, 74.92, 46.39, 33.17, 29.18, 21.22, 21.18, 20.19. IR (neat): ν 1737 (C=O), cm^{-1}; HRMS: *m/z*: calcd for $C_{24}H_{25}N_2O$ [M+H]$^+$: 356.1889, found 356.1891. Elemental Analysis Calcd (%) for $C_{24}H_{24}N_2O$: C, 80.87; H, 6.79; N, 7.86; Found: C, 80.88; H, 6.81; N, 7.66.



8e

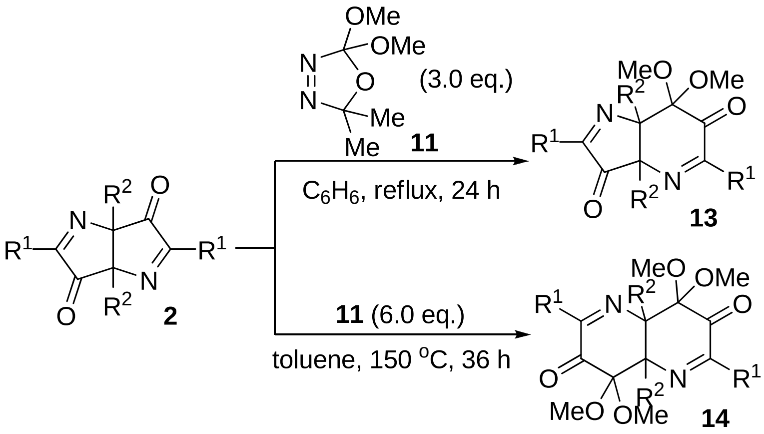
8e: Yellow solid, isolated yield 83% (161 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.22 (d, J = 8.9 Hz, 2H, C_6H_4), 7.75 (d, J = 8.8 Hz, 2H, C_6H_4), 6.93 (d, J = 8.9 Hz, 2H, C_6H_4), 6.86 (d, J = 8.8 Hz, 2H, C_6H_4), 3.82 (s, 3H, OCH_3), 3.80 (s, 3H OCH_3), 3.48 (d, J = 17.9 Hz, 1H, CH_2), 3.36 (d, J = 17.9 Hz, 1H, CH_2), 2.64 (dt, J = 13.9, 4.3 Hz, 1H, CH_2), 2.48-2.39 (m, 1H, CH_2), 1.69-1.61 (m, 1H, CH_2), 1.60-1.45 (m, 4H, CH_2), 1.17-1.08 (m, 1H, CH_2). ^{13}C NMR (126 MHz, $CDCl_3$) δ 200.90, 173.06, 162.82, 162.31, 162.05, 130.18, 129.64, 126.54, 123.20, 113.95, 113.78, 81.79, 77.35, 77.09, 76.84, 74.59, 55.35, 55.34, 46.46, 33.08, 28.92, 19.98, 19.89. IR (neat): ν 1742 (C=O), cm^{-1}; HRMS: *m/z*: calcd for $C_{24}H_{23}N_2O_3$ [M+H]$^+$: 389.1865, found 389.1861.



8f

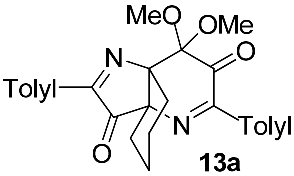
8f: Yellow solid, isolated yield 51% (66 mg); ^{1}H NMR (400 MHz, CDCl$_3$) δ 3.01 (d, *J* = 18.3 Hz, 1H, CH$_2$), 2.81 (d, *J* = 18.3 Hz, 1H, CH$_2$), 1.35 (s, 3H, CH$_3$), 1.24 (s, 9H, CH$_3$), 1.23 (s, 3H, CH$_3$), 1.07 (s, 9H, CH$_3$). ^{13}C NMR (75 MHz, CDCL$_3$) δ 200.68, 186.07, 175.58, 81.78, 74.45, 46.99, 27.86, 27.09, 22.18, 15.59. IR (neat): *v* 1741 (C=O), cm^{-1}; HRMS: *m/z*: calcd for $C_{16}H_{27}N_2O$ [M+H]$^+$: 263.2123, found 263.2119. Elemental Analysis Calcd (%) for $C_{16}H_{26}N_2O$: C, 73.24; H, 9.99; N, 10.68; Found: C, 73.18; H, 10.02; N, 10.64.

d) Reactions of Δ^1-bipyrrolinones 2 with oxadiazoline 11



Reactions of Δ^1-bipyrrolinones 2 with oxadiazoline 11: The solution of Δ^1-bipyrrolinones **2** (0.25 mmol, 65 mg) and oxadiazoline **11** (0.75 mmol, 120 mg) in 5 mL of benzene in a 25 ml Schlenk tube was refluxed for 24 h. The solvent was evaporated and the crude product was purified by column chromatography (silica gel, petroleum ether/diethyl ether/triethylamine = 100:5:1) to afford **13**.

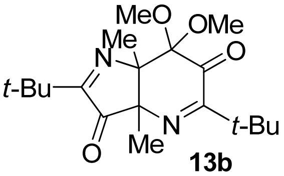
The solution of Δ^1-bipyrrolinones **2** (0.25 mmol, 65 mg) and oxadiazoline **11** (1.5 mmol, 240 mg) in 5 mL of toluene in a 25 ml Schlenk tube was refluxed for 36 h. The solvent was evaporated and the crude product was purified by column chromatography (silica gel, petroleum ether/diethyl ether/triethylamine = 100:5:1) to afford **14**.



13a

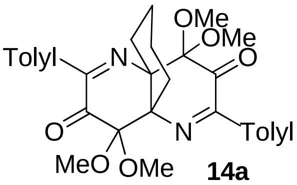
13a: Yellow solid, isolated yield 63% (69 mg); ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.20 (d, *J* = 8.1 Hz, 2H, C$_6$H$_4$), 7.86 (d, *J* = 8.2 Hz, 2H, C$_6$H$_4$), 7.31 (d, *J* = 8.0 Hz, 2H, C$_6$H$_4$), 7.23 (d, *J* = 8.1 Hz, 2H, C$_6$H$_4$), 3.51 (s, 3H, OCH$_3$), 3.12 (s, 3H, OCH$_3$), 2.52 (d, *J* = 14.8

Hz, 1H, CH_2), 2.44 (s, 3H, CH_3), 2.39 (s, 3H, CH_3), 2.35 (d, J = 15.6 Hz, 1H, CH_2), 1.76-1.66 (m, 2H, CH_2), 1.62-1.49 (m, 2H, CH_2), 1.34-1.27 (m, 1H, CH_2), 1.18-1.07 (m, 1H, CH_2). ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.99, 192.78, 166.59, 160.94, 142.59, 141.59, 130.54, 129.45, 129.09, 128.75, 128.49, 128.07, 99.38, 77.92, 73.10, 53.31, 51.87, 33.74, 28.99, 21.71, 21.49, 21.14, 20.79. IR (neat): *v* 1749 (C=O), 1727 (C=O), cm^{-1}; HRMS: *m/z*: calcd for $C_{27}H_{29}N_2O_4$ $[M+H]^+$: 445.2127, found 445.2125. Elemental Analysis Calcd (%) for $C_{27}H_{28}N_2O_4$: C, 72.95; H, 6.35; N, 6.30; Found: C, 72.81; H, 6.50; N, 6.16. Single crystals of **13a** suitable for X-ray analysis were grown in hexane/EtOAc/CH_2Cl_2 (1:1:1) at room temperature.



13b

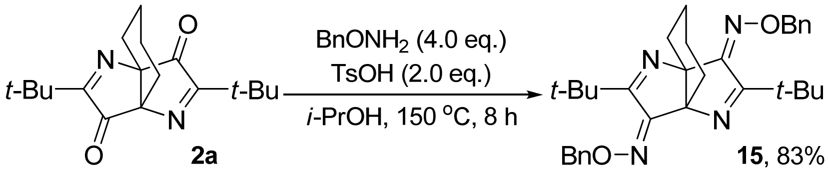
13b: Yellow oil, isolated yield 92% (80 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.41 (s, 3H, OCH_3), 3.08 (s, 3H, OCH_3), 1.31 (s, 9H, CH_3), 1.30 (s, 3H, CH_3), 1.27 (s, 9H, CH_3), 1.20 (s, 3H, CH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.16, 191.61, 177.95, 169.09, 98.32, 77.42, 72.34, 53.02, 51.41, 38.94, 35.18, 28.36, 26.89, 23.11, 16.10. IR (neat): ν 1751 (C=O), 1729 (C=O), cm^{-1}; HRMS: *m/z*: calcd for $C_{19}H_{31}N_2O_4$ $[M+H]^+$: 351.2284, found 351.2280.



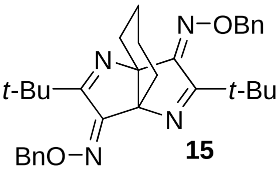
14a

14a: Yellow solid, isolated yield 54% (70 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, J = 8.1 Hz, 4H, C_6H_4), 7.25 (d, J = 7.5 Hz, 4H, C_6H_4), 3.39 (s, 6H, OCH_3), 3.30 (s, 6H, CH_3), 2.41 (s, 6H, CH_3), 2.18 (d, J = 13.3 Hz, 2H, CH_2), 1.84-1.75 (m, 2H, CH_2), 1.63-1.57 (m, 4H, CH_2). ^{13}C NMR (126 MHz, $CDCl_3$) δ 184.66, 164.22, 140.86, 132.28, 128.96, 128.89, 95.71, 68.54, 52.79, 52.37, 30.72, 21.47, 21.44. IR (neat): ν 1734 (C=O), cm^{-1}; HRMS: *m/z*: calcd for $C_{30}H_{35}N_2O_6$ $[M+H]^+$: 519.2495, found 519.2492. Elemental Analysis Calcd (%) for $C_{30}H_{34}N_2O_6$: C, 69.48; H, 6.61; N, 5.40; Found: C, 69.35; H, 6.89; N, 5.28.

e) Reactions of Δ^1-bipyrrolinones 2 and *O*-benzylhydroxylamine



Reactions of Δ^1-bipyrrolinones 2 and *O*-benzylhydroxylamine: The solution of Δ^1-bipyrrolinones **2** (0.25 mmol, 65 mg), *p*-toluenesulfonic acid hydrate (0.5 mmol, 95 mg) and *O*-benzylhydroxylamine (1.0 mmol, 121 mg) in 3 mL of isopropanol in a 25 ml Schlenk tube was stirred at 150 °C for 8 h. The solvent was evaporated and the crude product was purified by column chromatography (silica gel, petroleum ether/diethyl ether/triethylamine = 100:5:1) to afford **15**.



15

15: Yellow oil, isolated yield 63% (80 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (d, *J* = 7.4 Hz, 4H, C_6H_5), 7.31 (t, *J* = 7.2 Hz, 4H, C_6H_5), 7.26 (d, *J* = 5.0 Hz, 2H, C_6H_5), 5.25 (s, 4H, OCH_2), 2.32 (d, *J* = 14.0 Hz, 2H, CH_2), 2.04 (d, *J* = 14.0 Hz, 2H, CH_2), 1.32-1.28 (m, 4H, CH_2), 1.21 (s, 18H, CH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ 177.16, 157.96, 138.40, 128.15, 127.69, 127.48, 79.82, 76.89, 36.21, 28.11, 26.36, 15.76. HRMS: *m/z*: calcd for $C_{32}H_{41}N_4O_2$ $[M+H]^+$: 513.3230, found 513.3226.

3) X-ray crystallographic studies

The single crystals of **2b** and **13a** suitable for X-ray analysis were grown as shown in the experimental section. Data collections for **13a** were performed at 20 °C, and for **2b** were performed at −100 °C on a Rigaku RAXIS RAPID IP diffractometer, using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). The determination of crystal class and unit cell parameters was carried out by the Rapid-AUTO (Rigaku 2000) program package for **2b**, **13a**. The raw frame data were processed using Crystal Structure (Rigaku/MSC 2000) for **2b**, **13a** to yield the reflection data file. The structures of **2b**, **13a** were solved by use of SHELXTL program. Refinement was performed on F^2 anisotropically for all the non-hydrogen atoms by the full-matrix least-squares method. The hydrogen atoms were placed at the calculated positions and were included in the structure calculation without further refinement of the parameters. Crystal data, data collection and processing parameters for compounds **2b**, **13a** are summarized in **Table S1**. Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-924924 (**2b**), CCDC-924925 (**13a**). Copies of these data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. [5]

Table S1. Crystallographic data and structure refinement details for **2b, 13a**.

	2b	**13a**
Formula	$C_{30}H_{38}N_2O_2$	$C_{27}H_{28}N_2O_4$
Mw	458.62	444.51
crystal system	Monoclinic	Triclinic
space group	P2(1)/c	P-1
a [Å]	11.152(2)	9.1255(18)
b [Å]	31.613(6)	11.865(2)
c [Å]	7.0253(14)	12.456(3)
α	90	72.38(3)
β [°]	94.34(3)	87.22(3)
γ	90	67.72(3)
V [Å^3]	2469.7(8)	1186.1(4)
Z	4	2
ρ_{calcd} [gcm^{-3}]	1.233	1.245
μ [mm^{-1}]	0.077	0.084
F(000)	992	472
θ range [°]	1.29-25.00	1.72-26.02
no of reflns collected	16970	6490
no of indep reflns	4343	4429
no of variables	526	302
GOF	1.299	1.168

R [$I > 2\sigma(I)$]	0.0935	0.0588
Rw	0.1492	0.1685

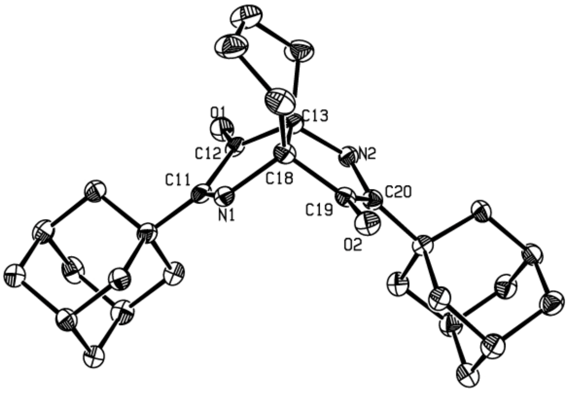


Figure S1. ORTEP drawing of **2b** with 30% probability thermal ellipsoids.

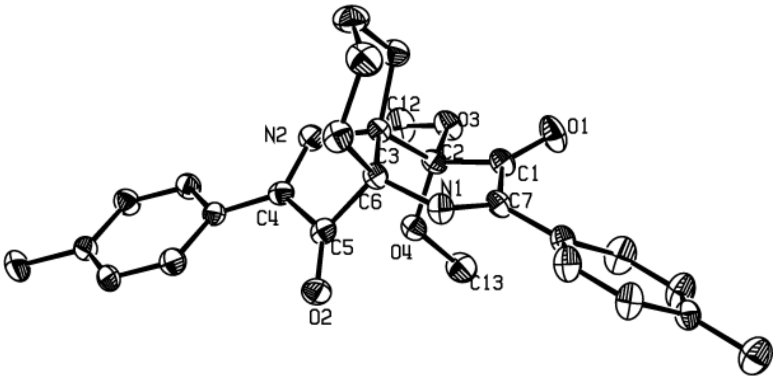
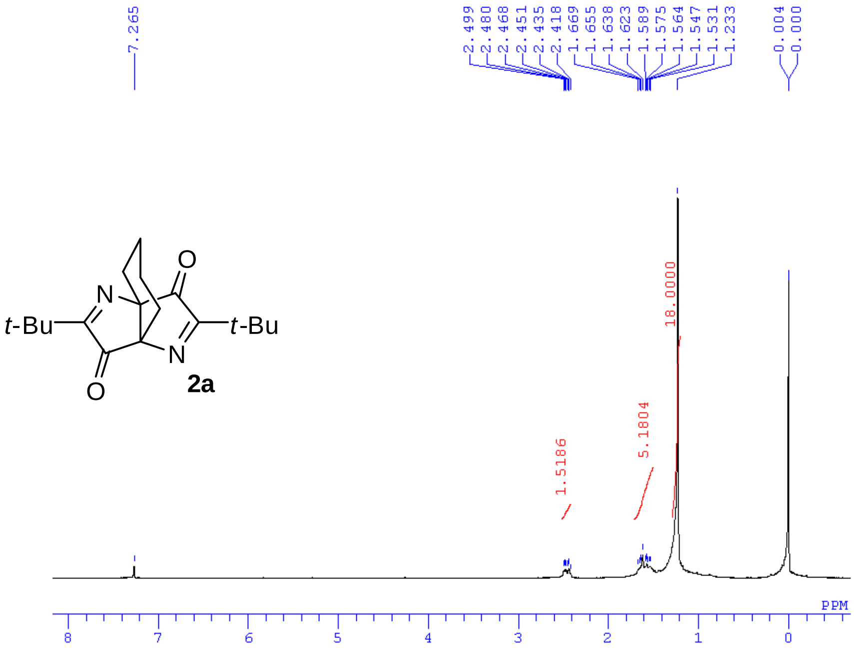


Figure S2. ORTEP drawing of **13a** with 30% probability thermal ellipsoids. Hydrogen atoms have been omitted for clarity.

4) Scanned ^{1}H NMR and ^{13}C NMR spectra of all new compounds

^{1}H NMR-**2a**



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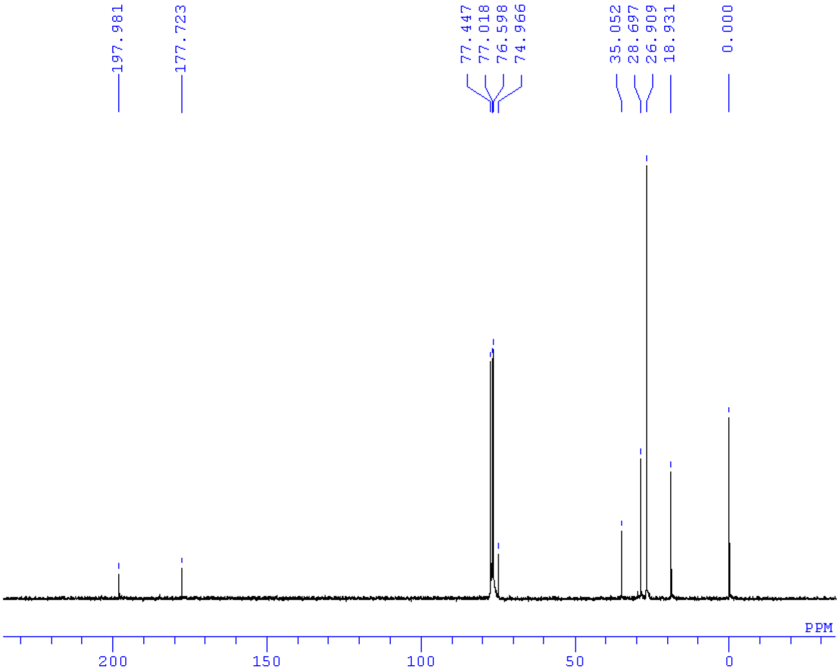
^{13}C NMR-**2a**



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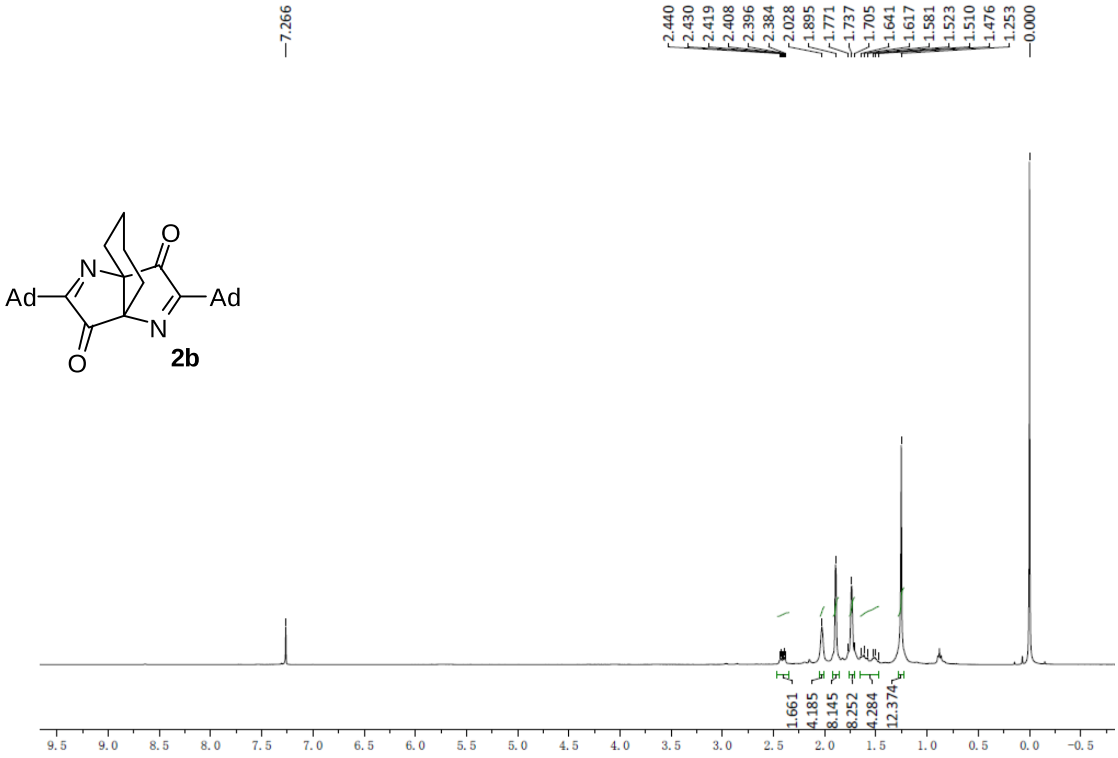
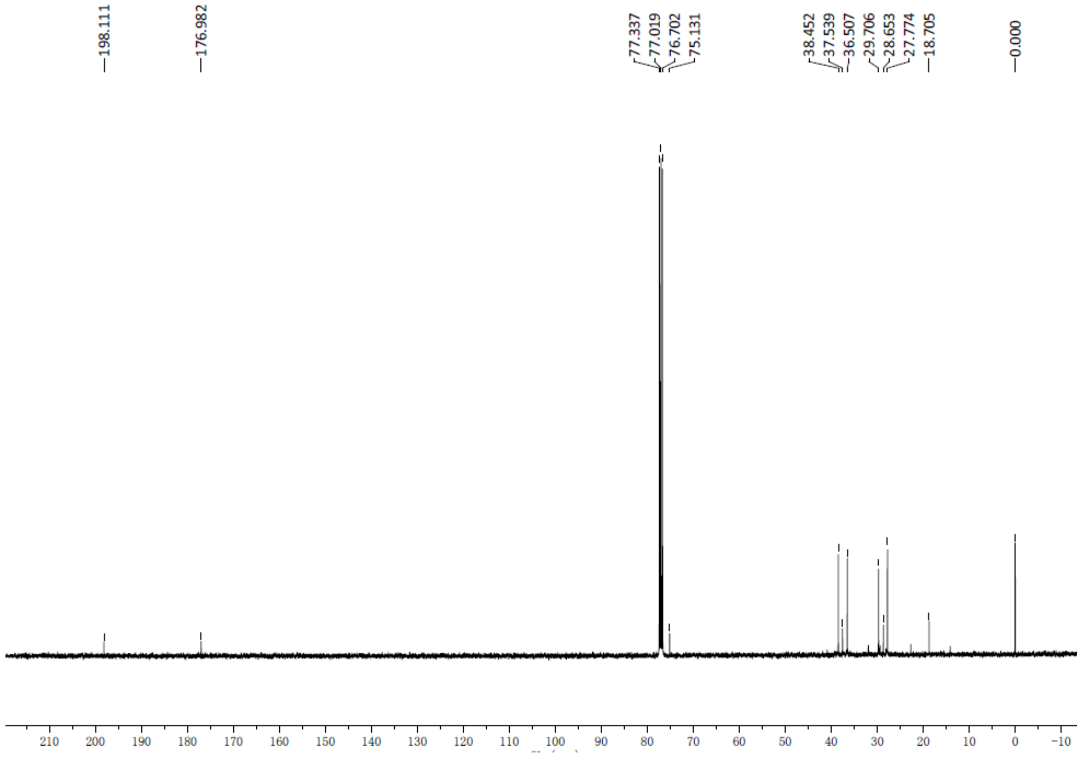
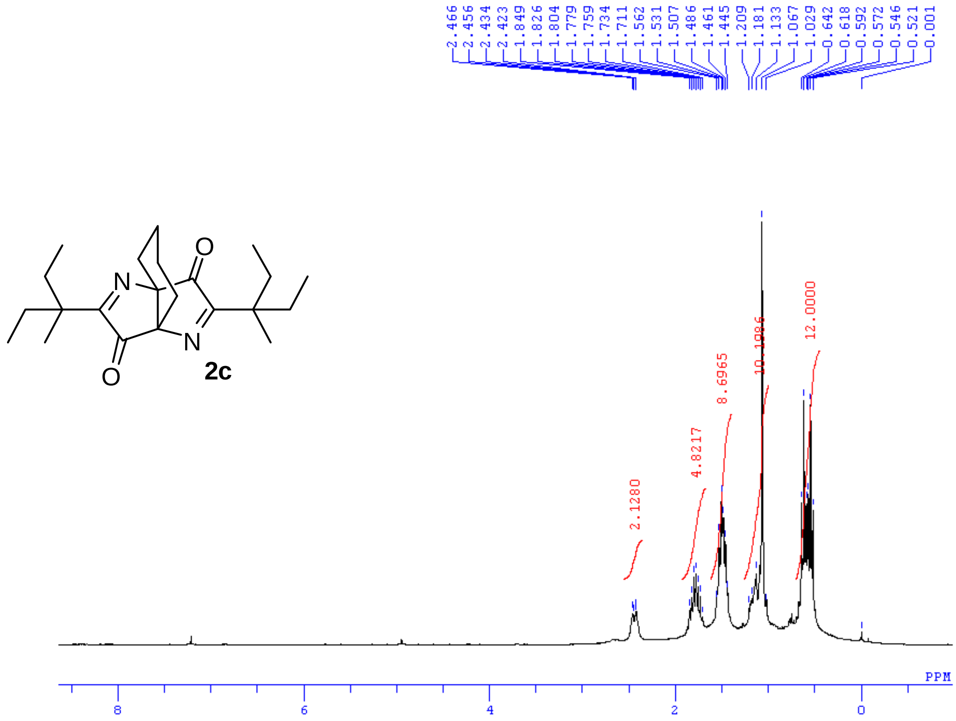
^{1}H NMR-**2b**



^{13}C NMR-**2b**



^{1}H NMR-**2c**



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RGAIN            13
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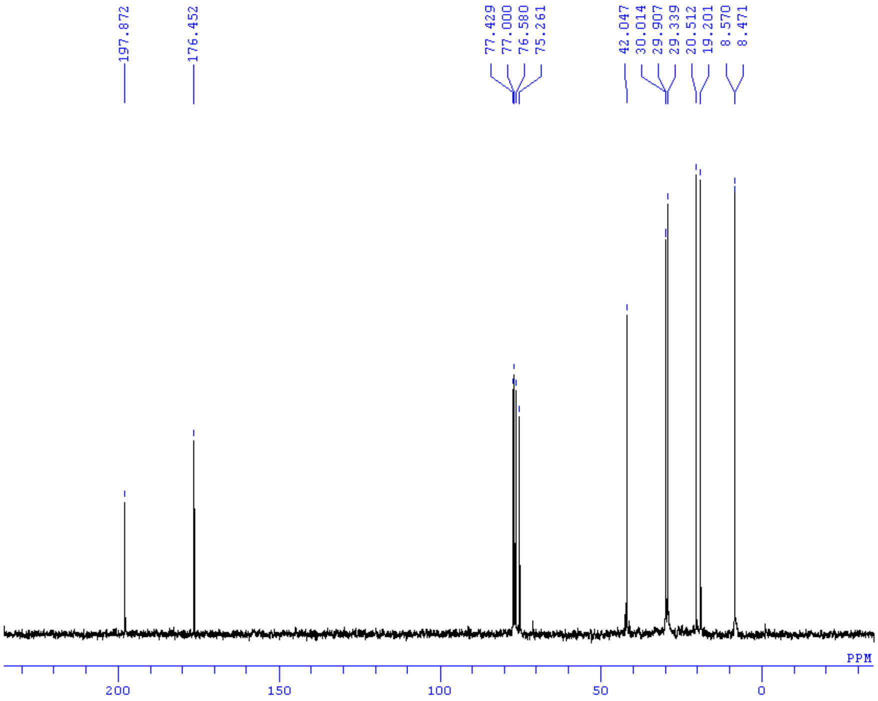
^{13}C NMR-**2c**



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PD            1.394 sec
PW1             4.2 us
IRNUC   1H
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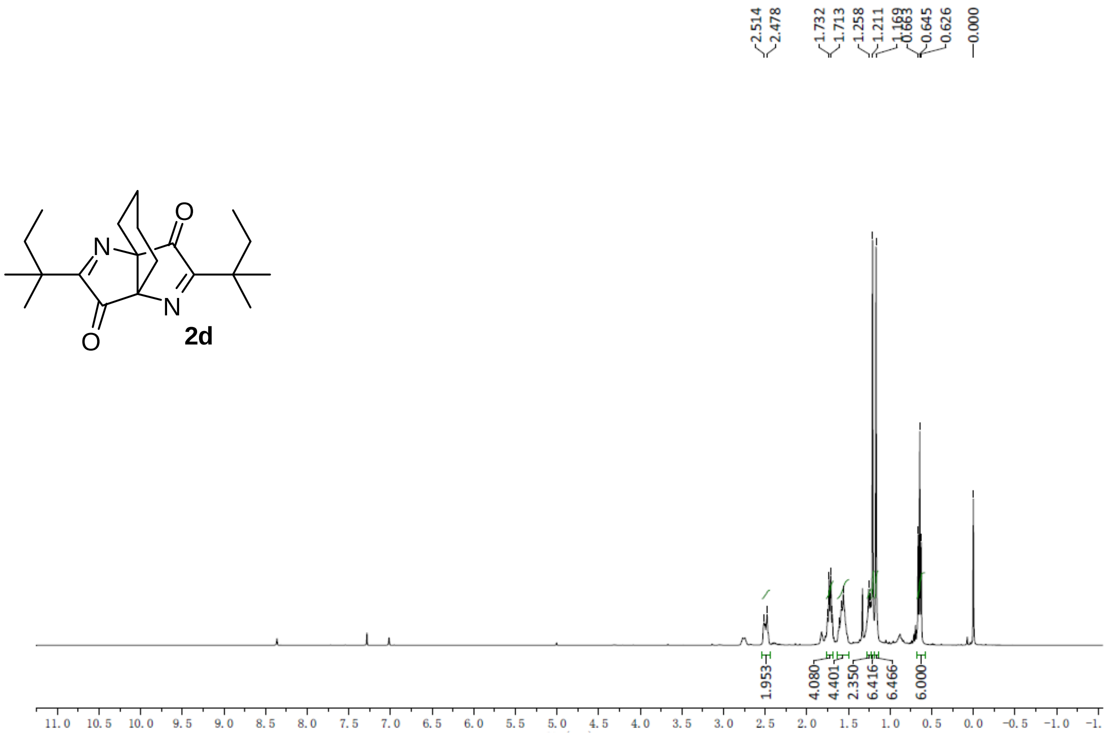

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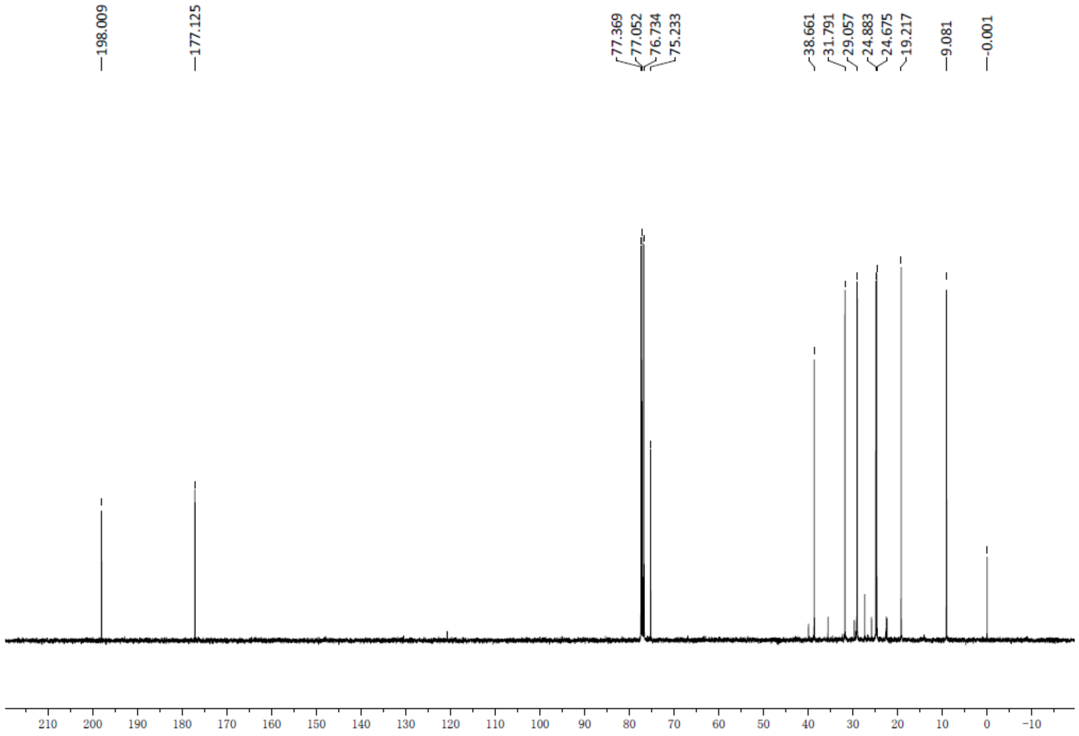
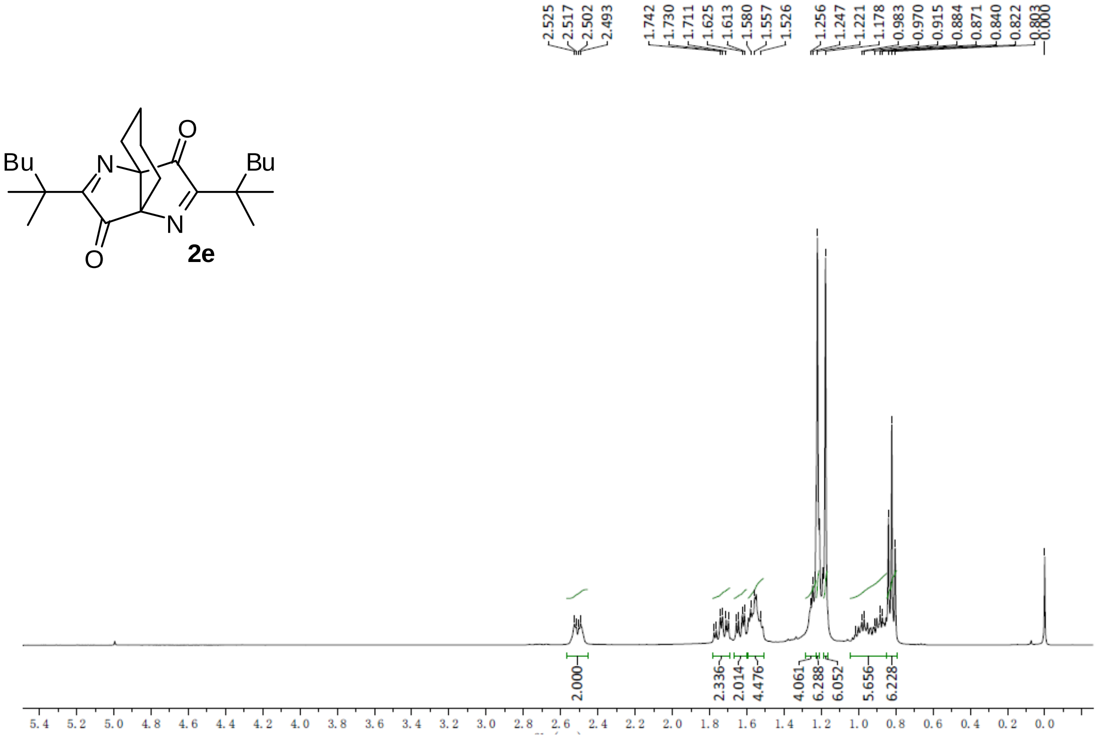


^{1}H NMR-**2e**

2e



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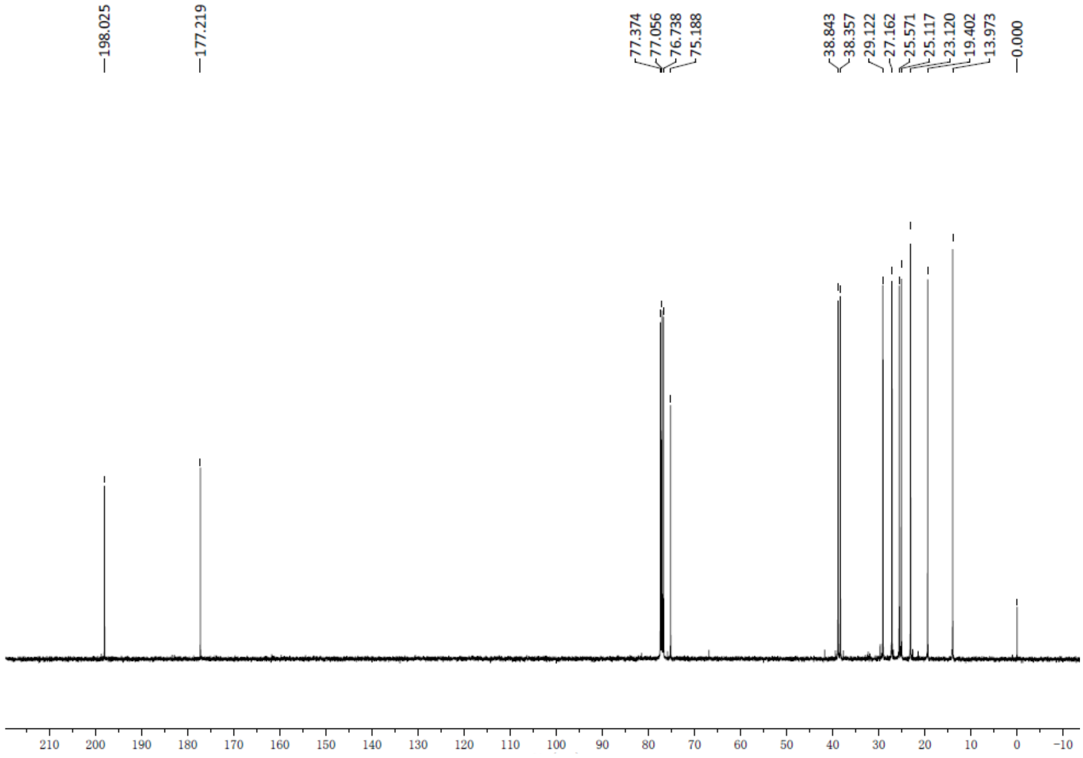

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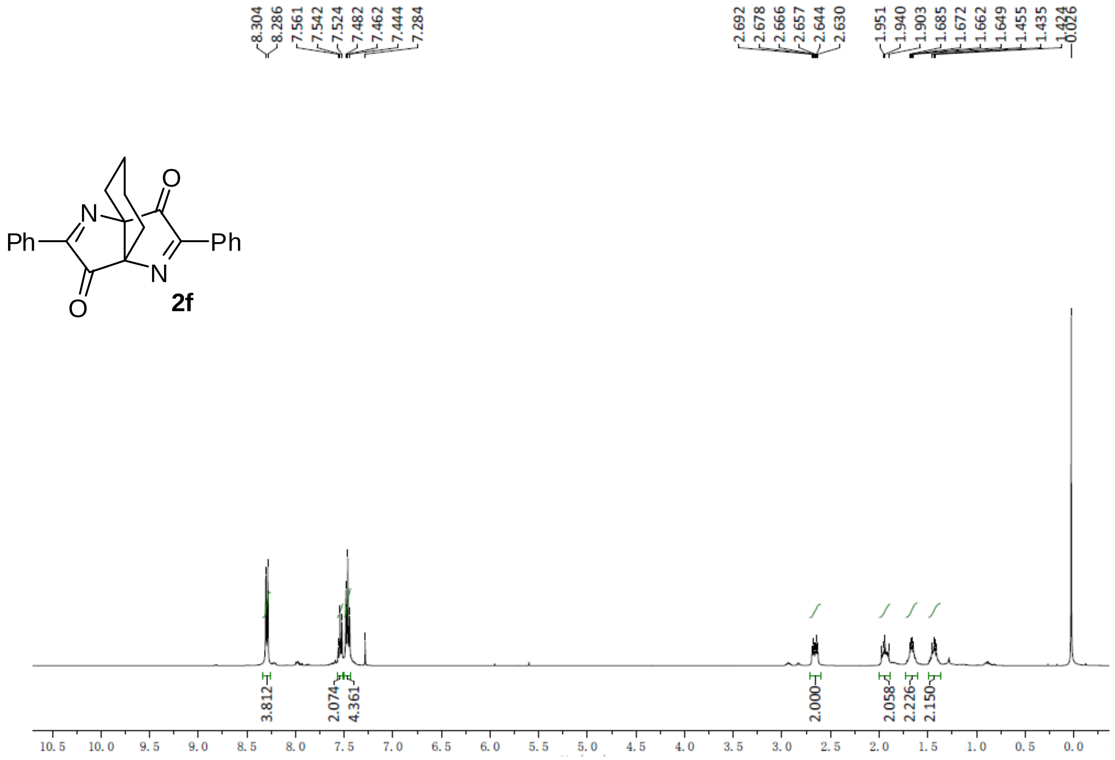

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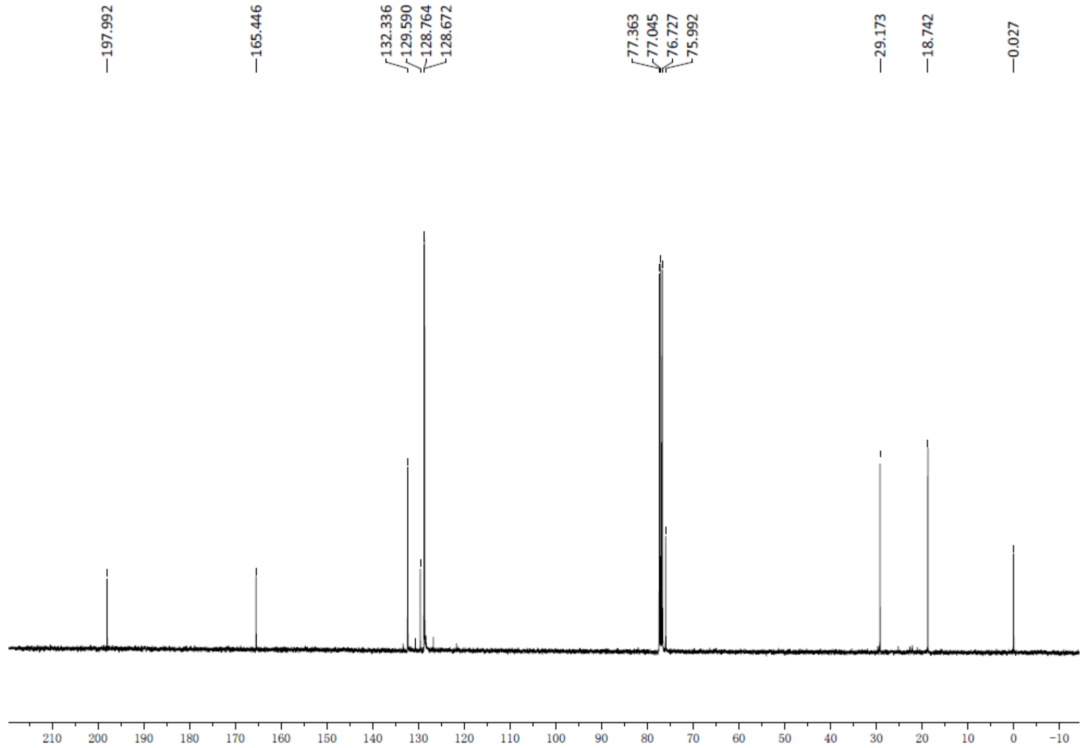

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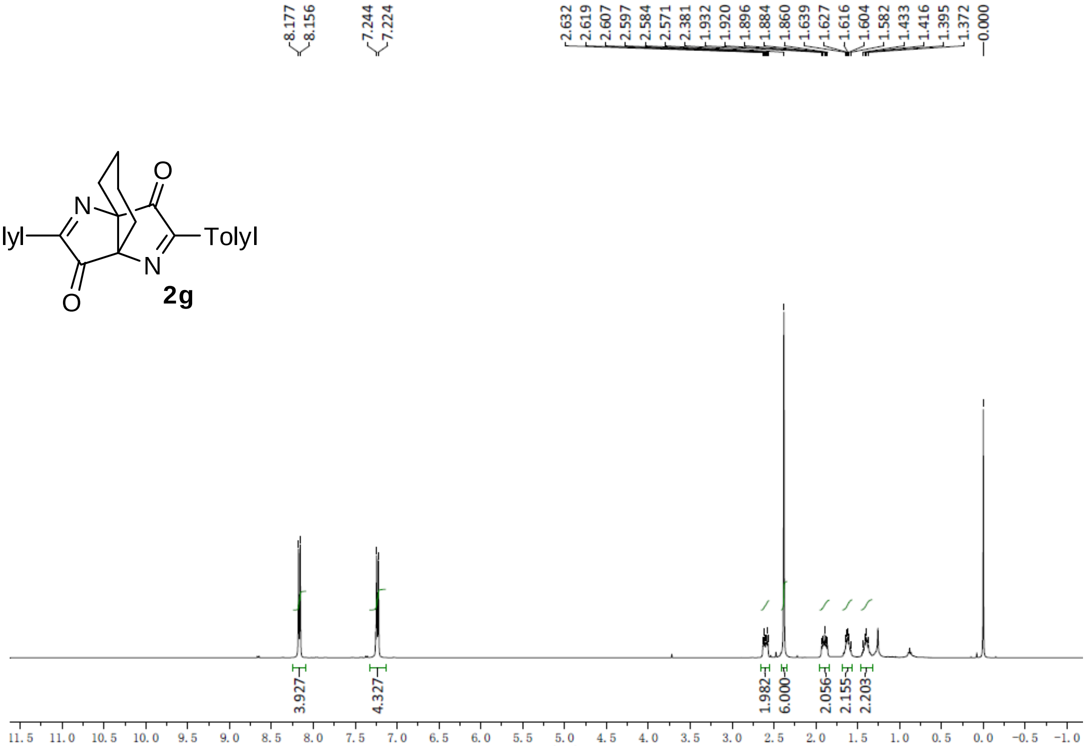

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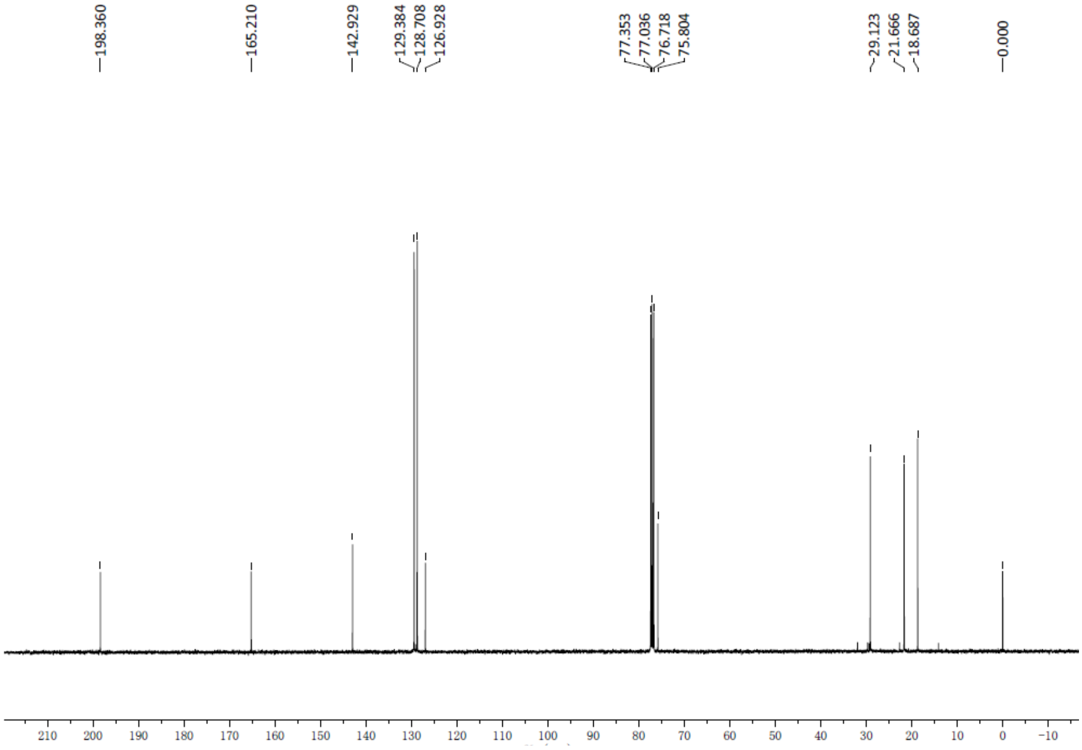

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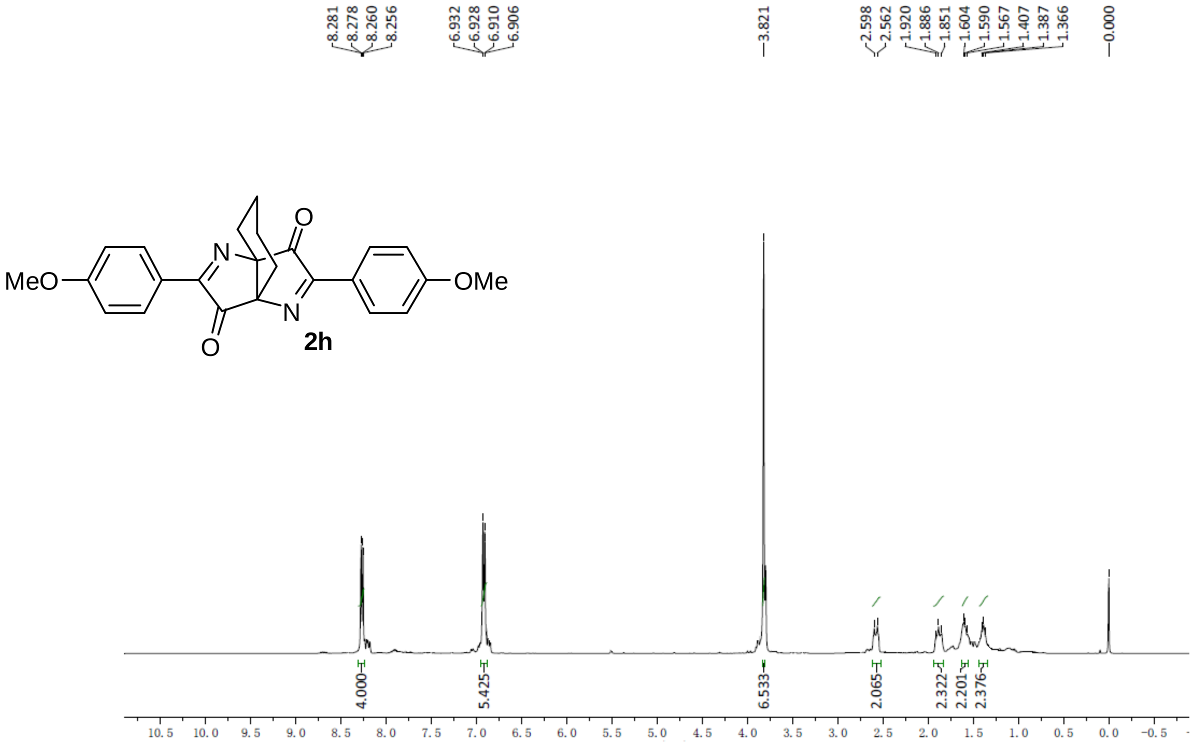

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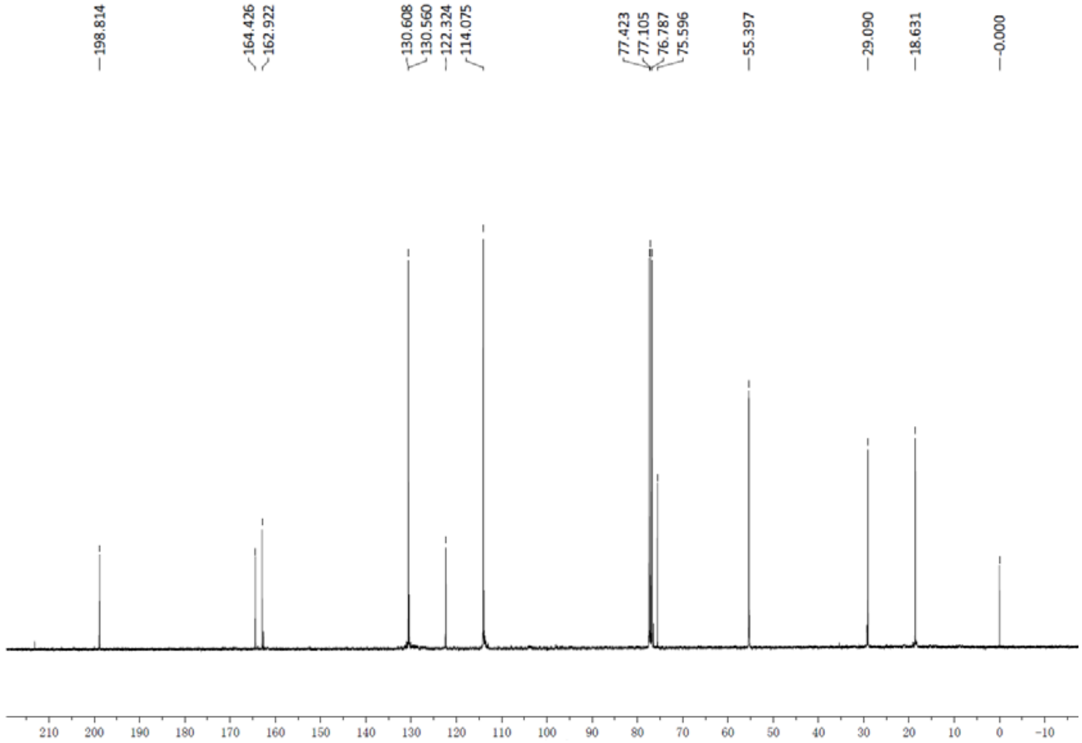

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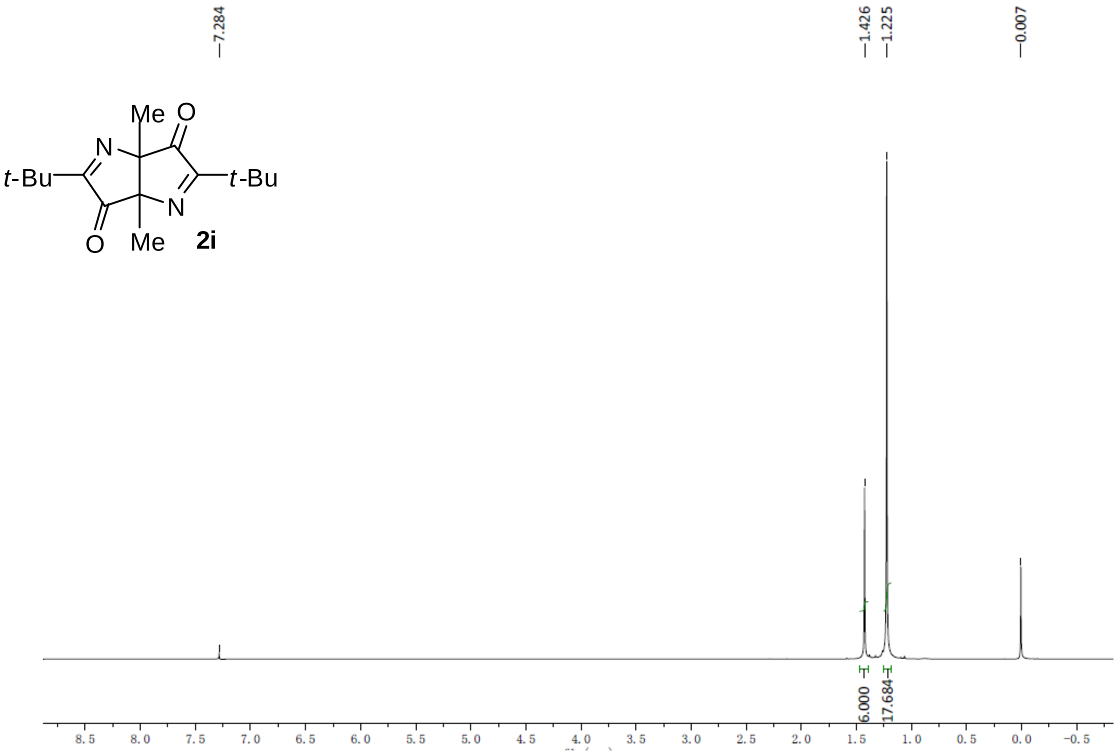

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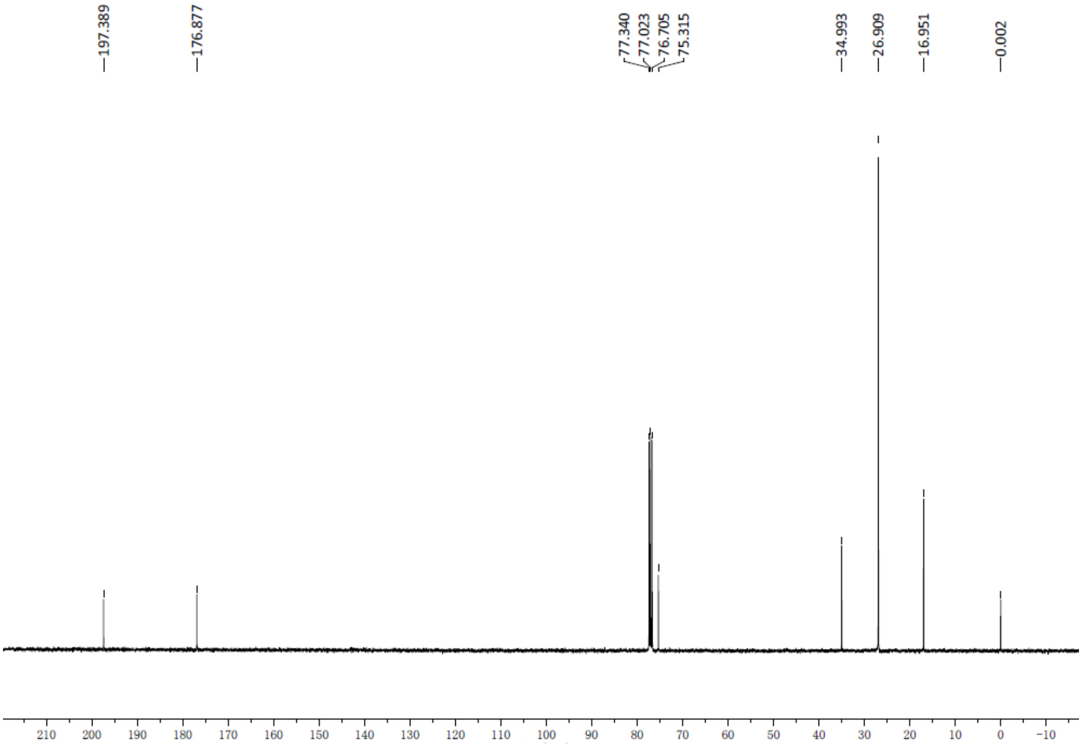

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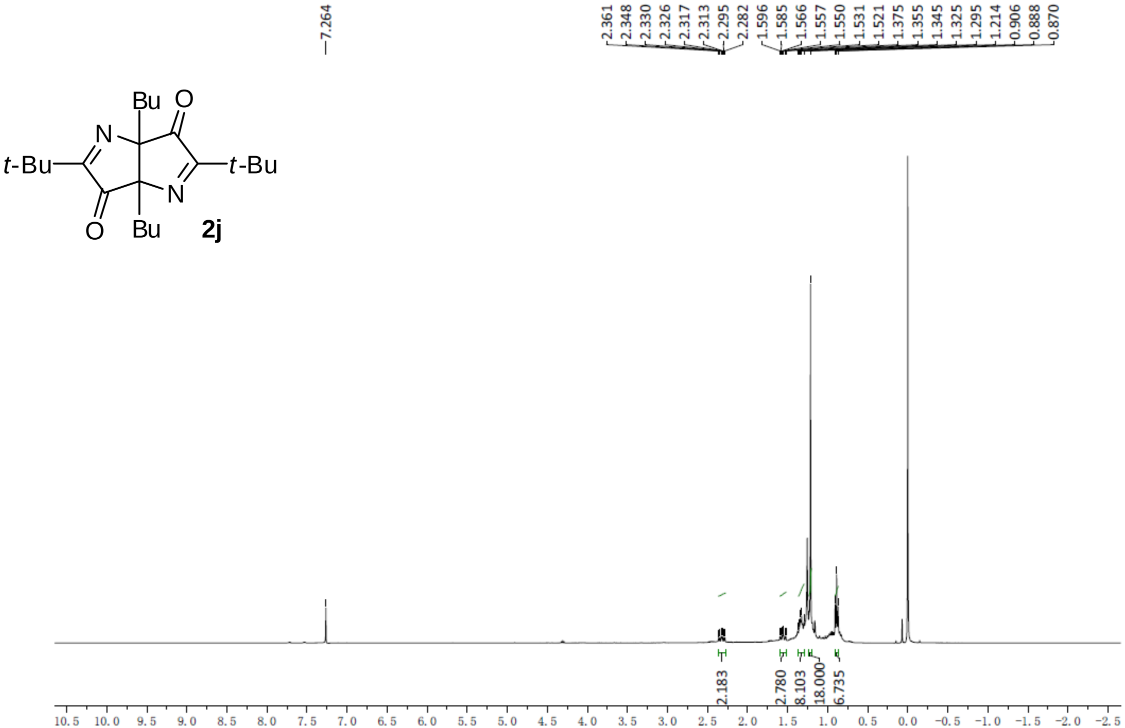

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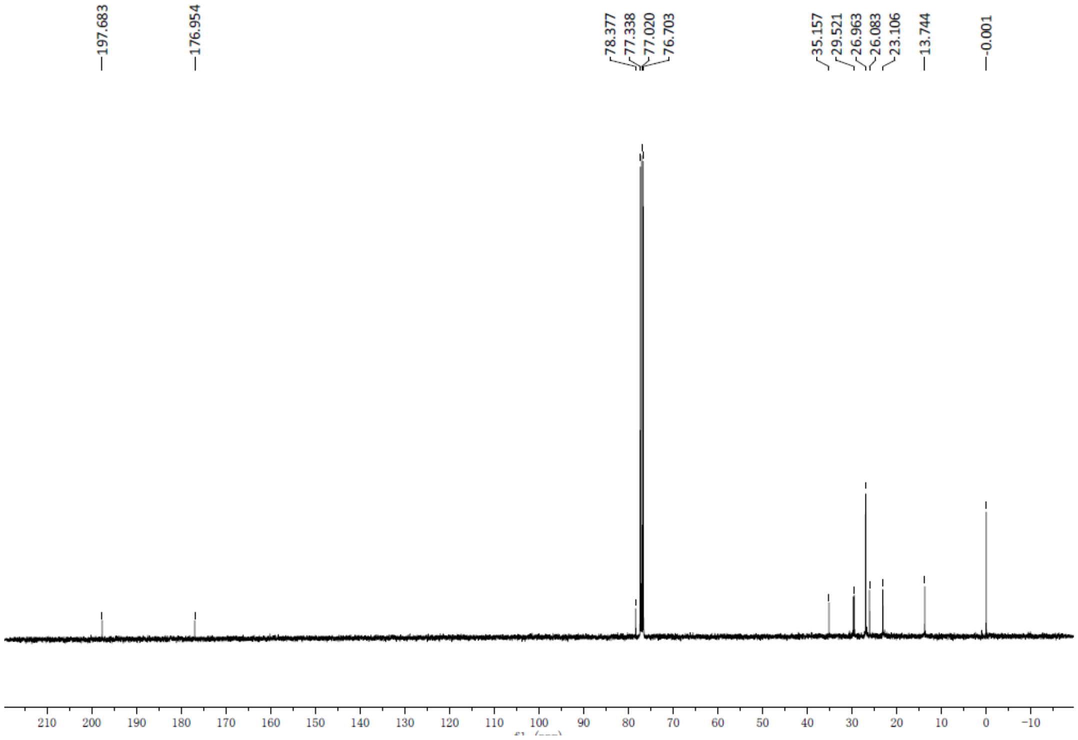

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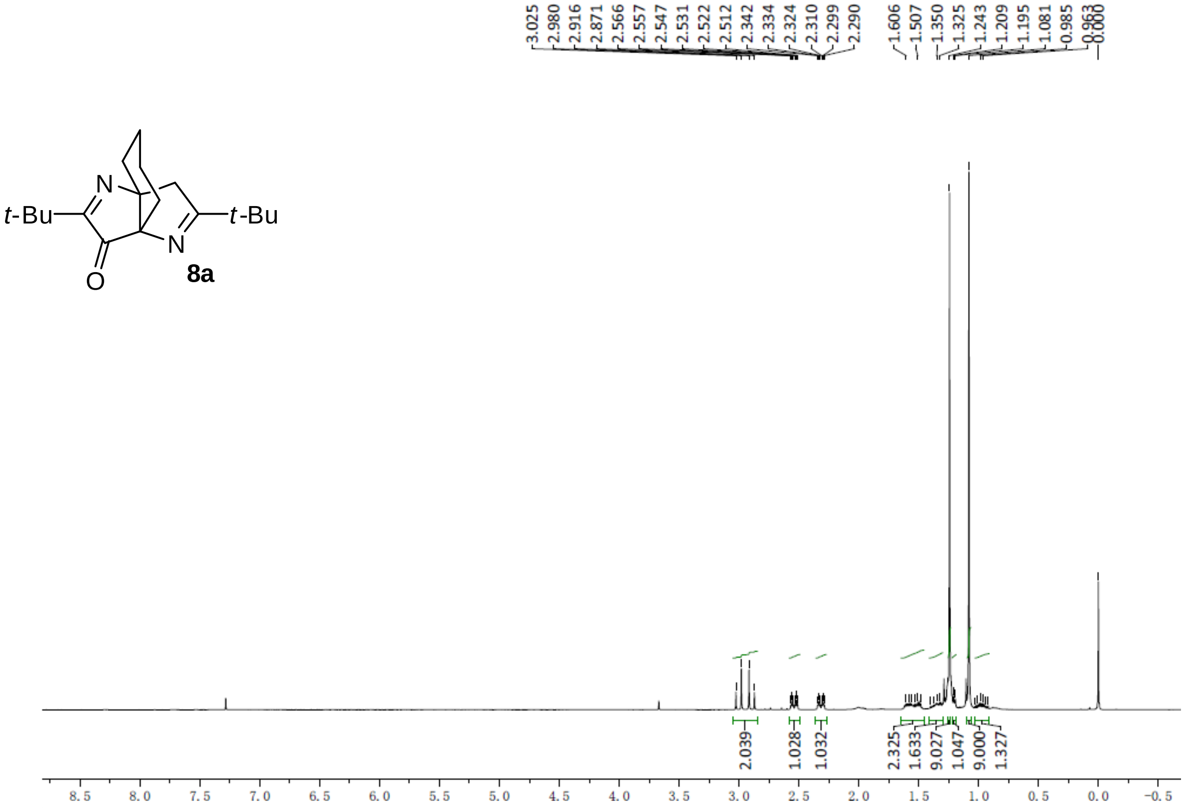
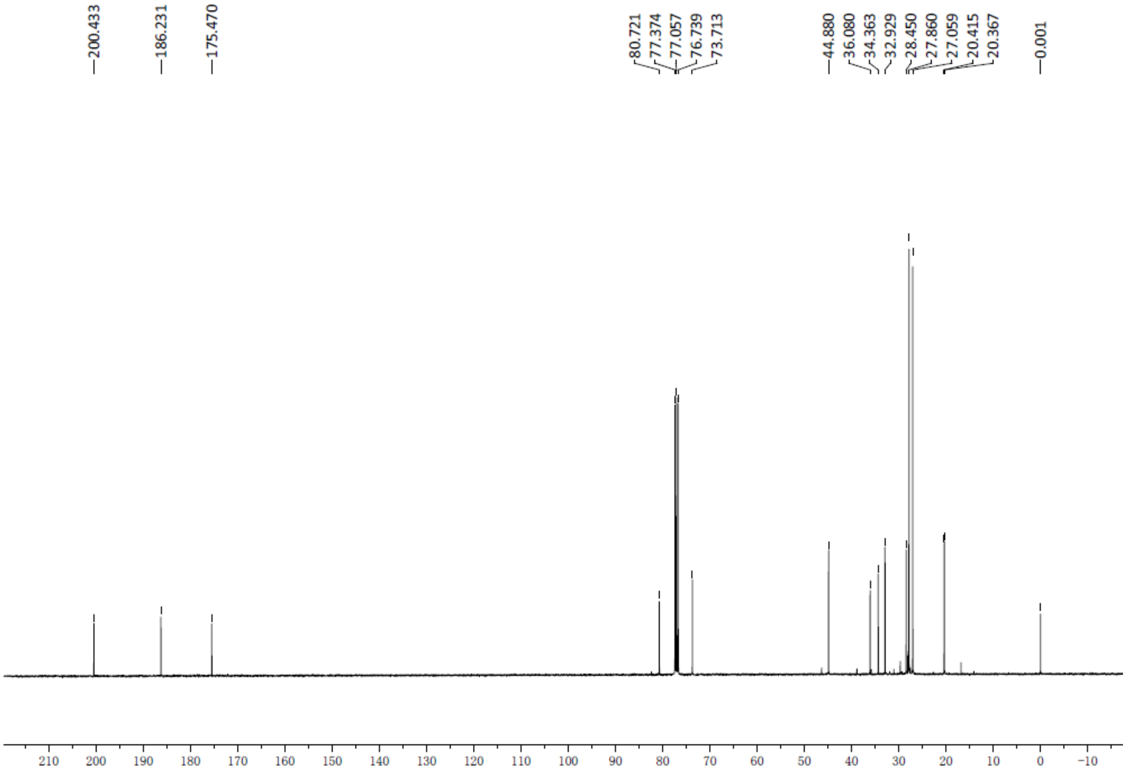


8a

^{13}C NMR-**8a**



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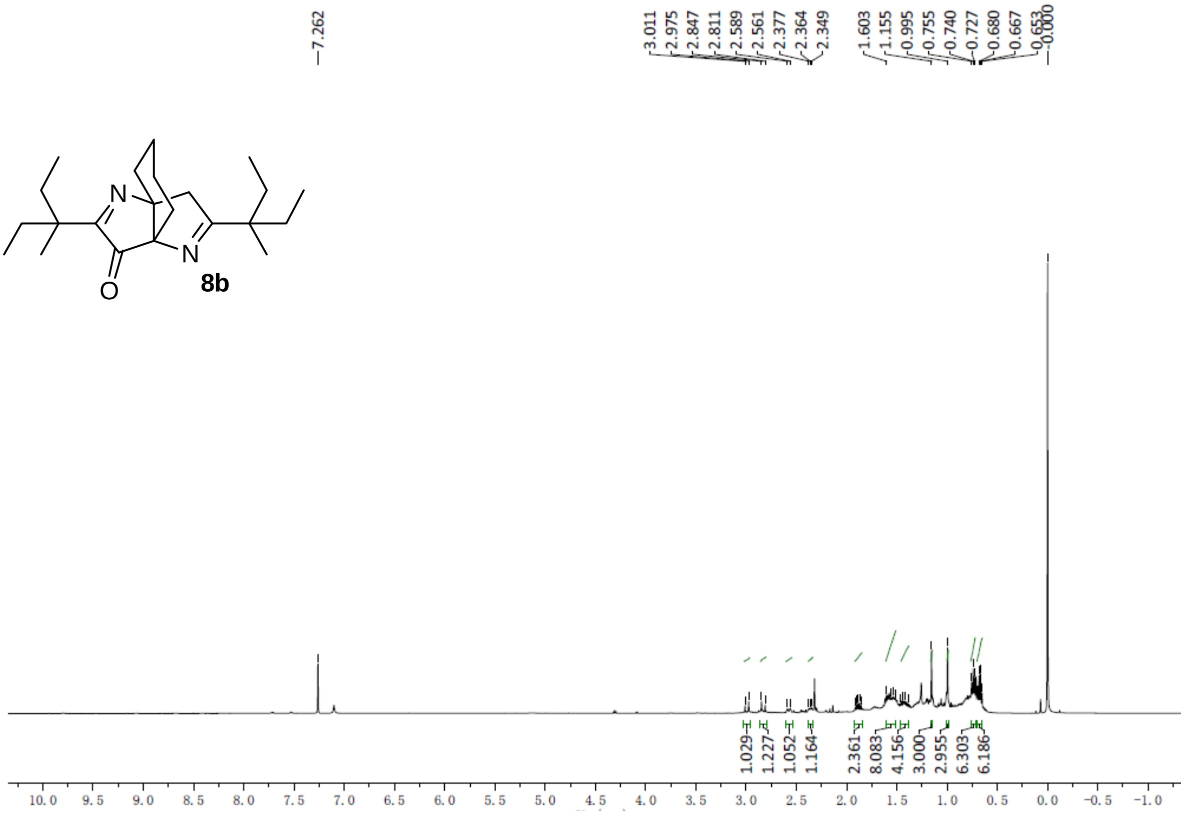

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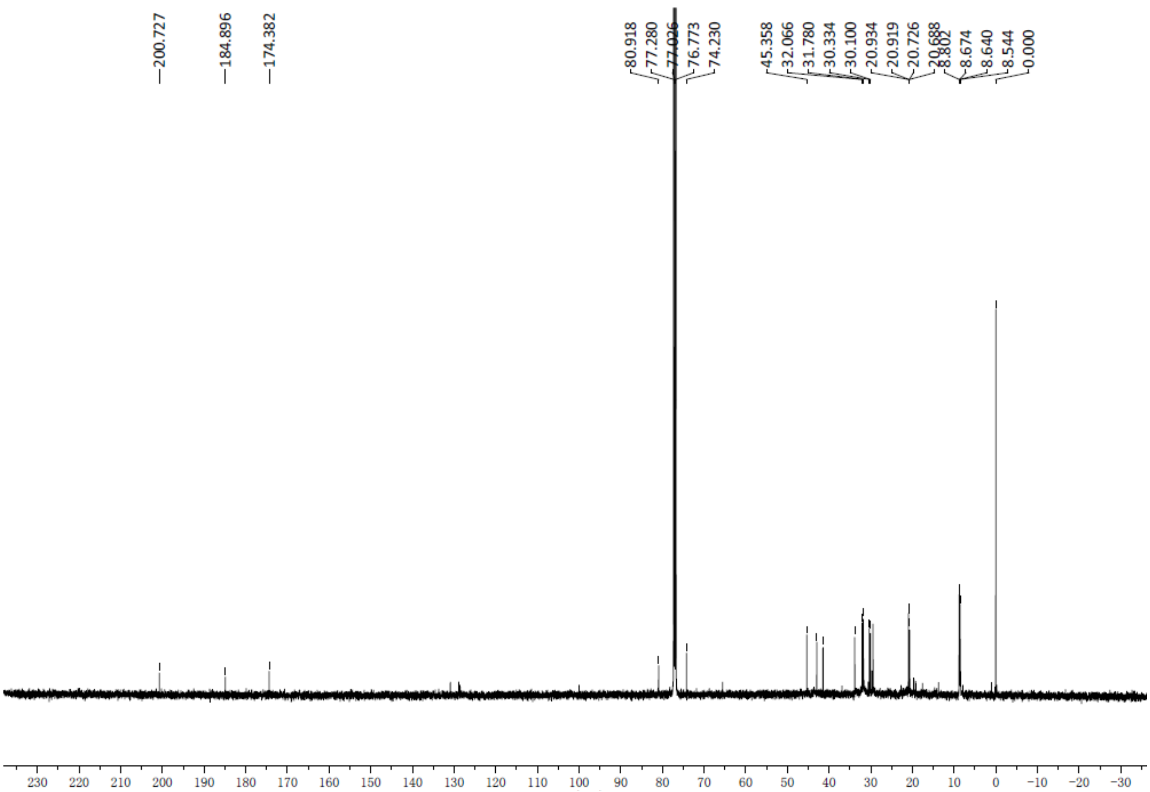

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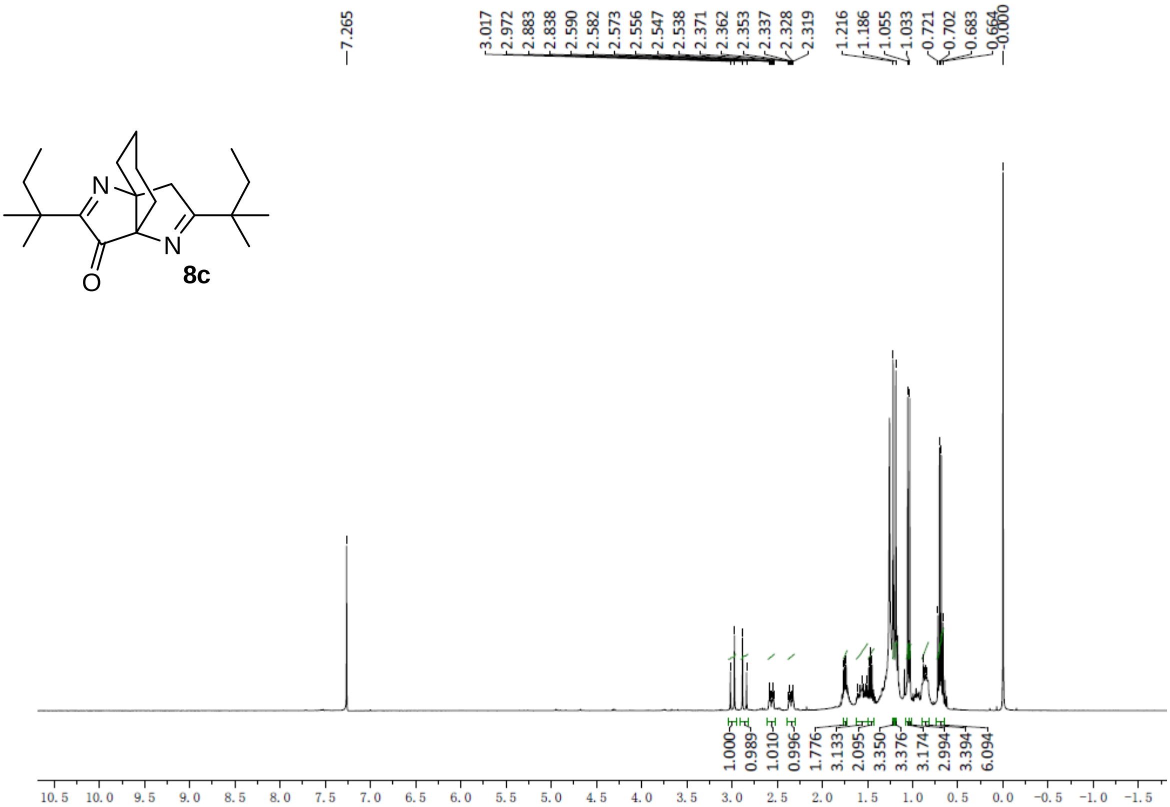

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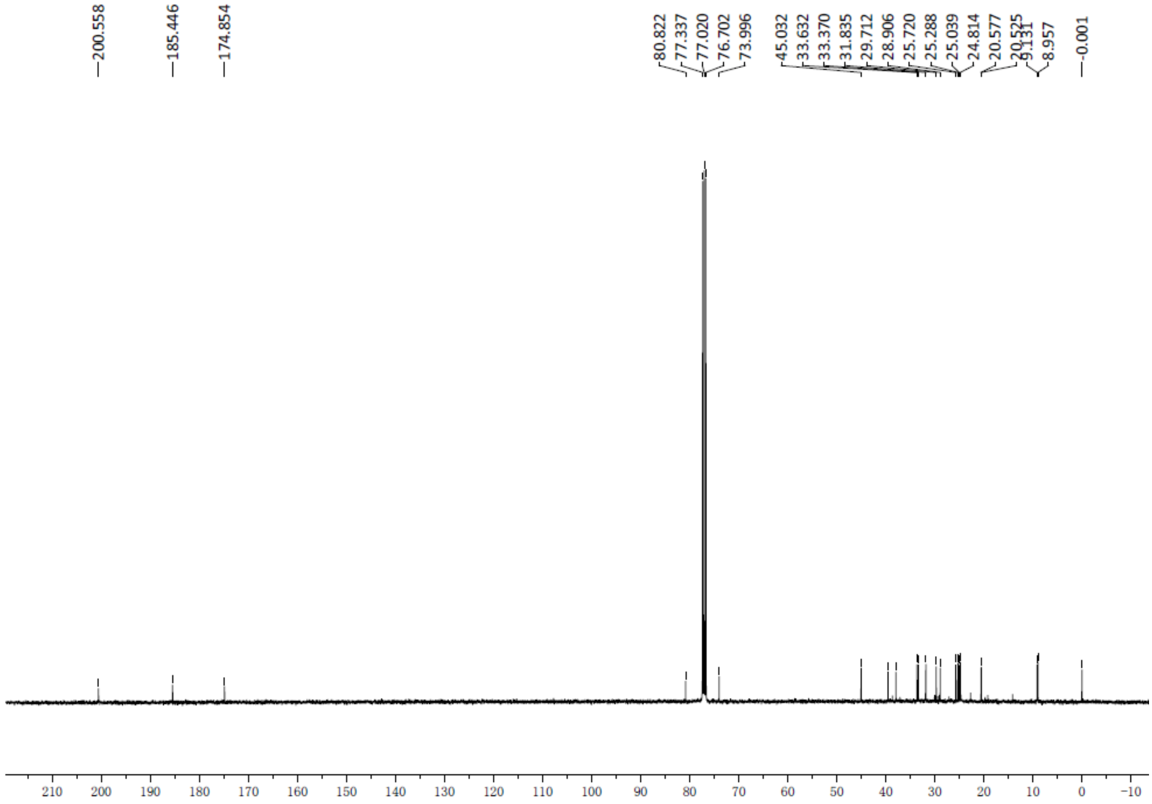

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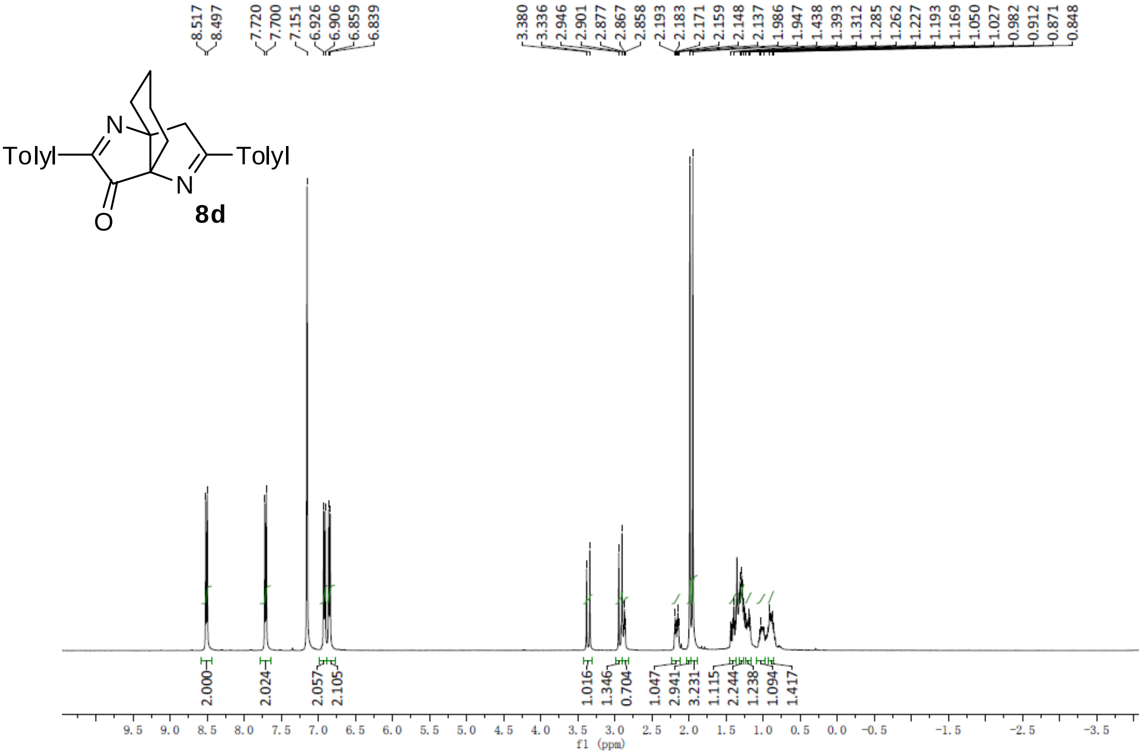

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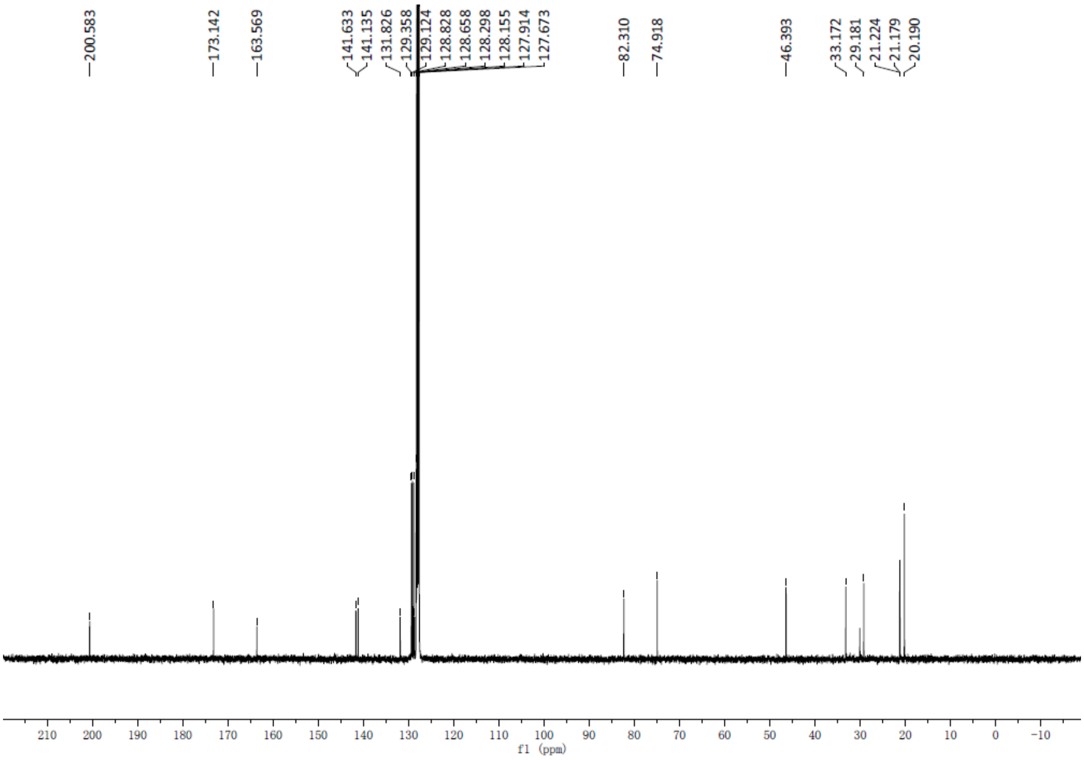

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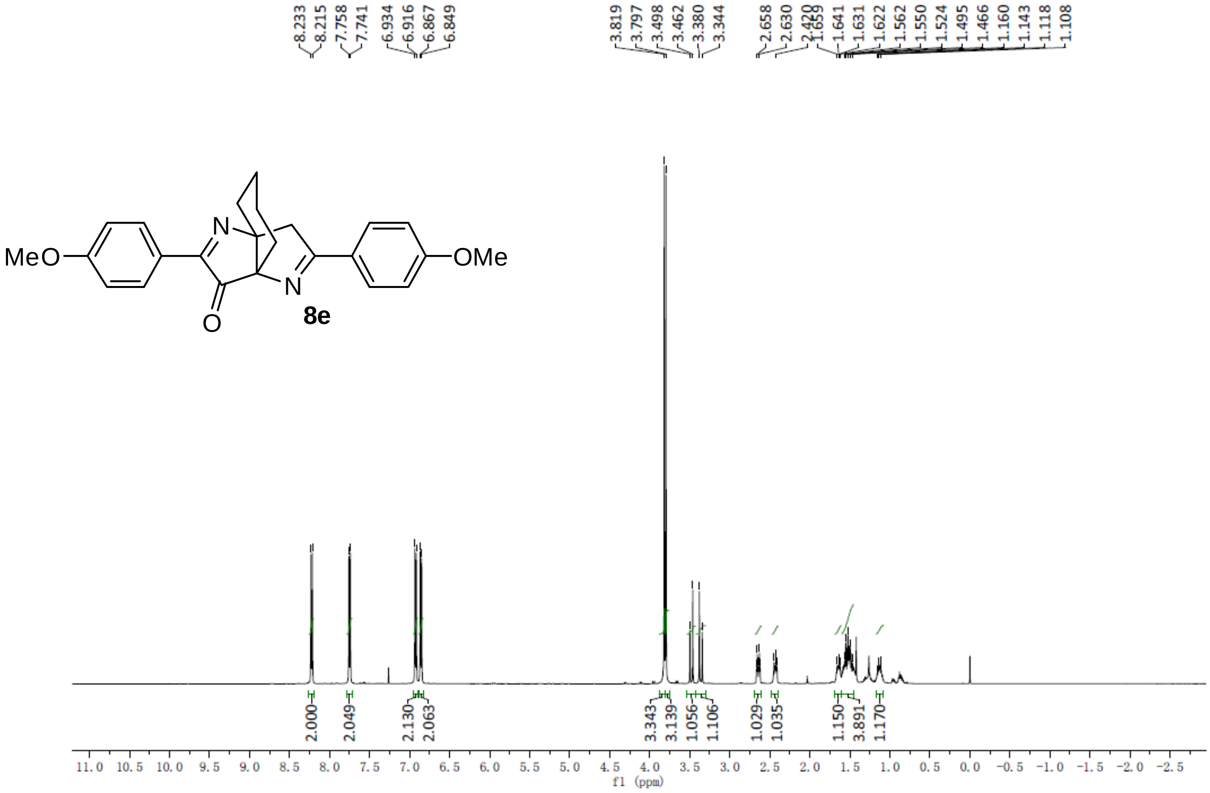

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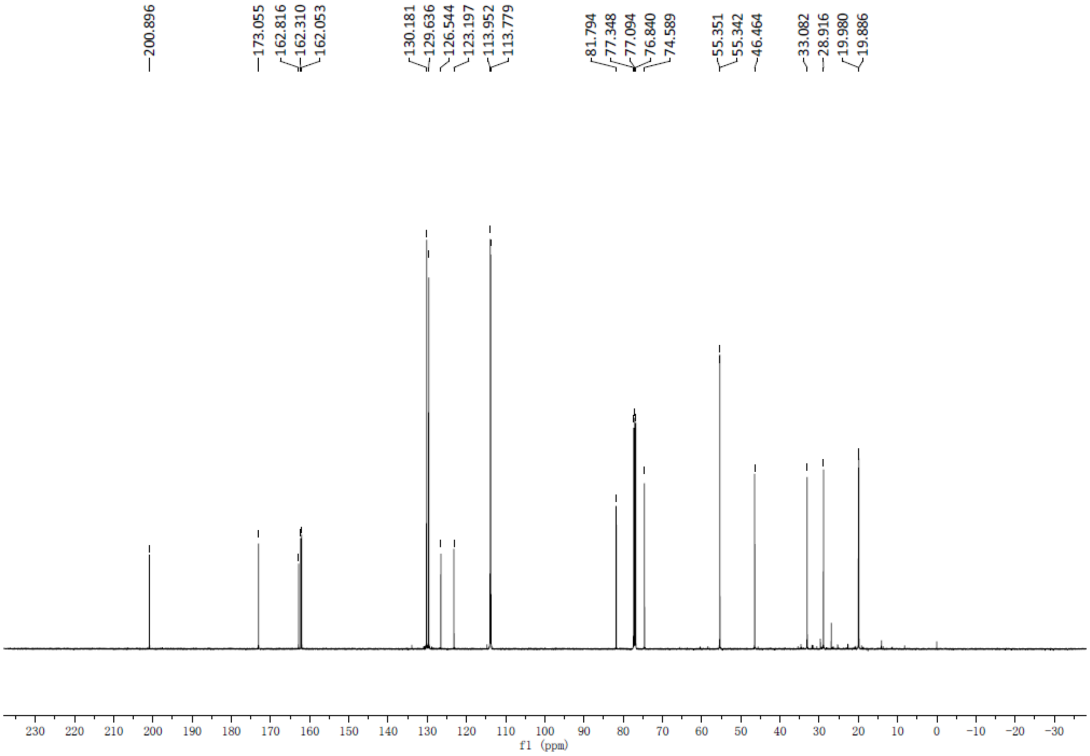

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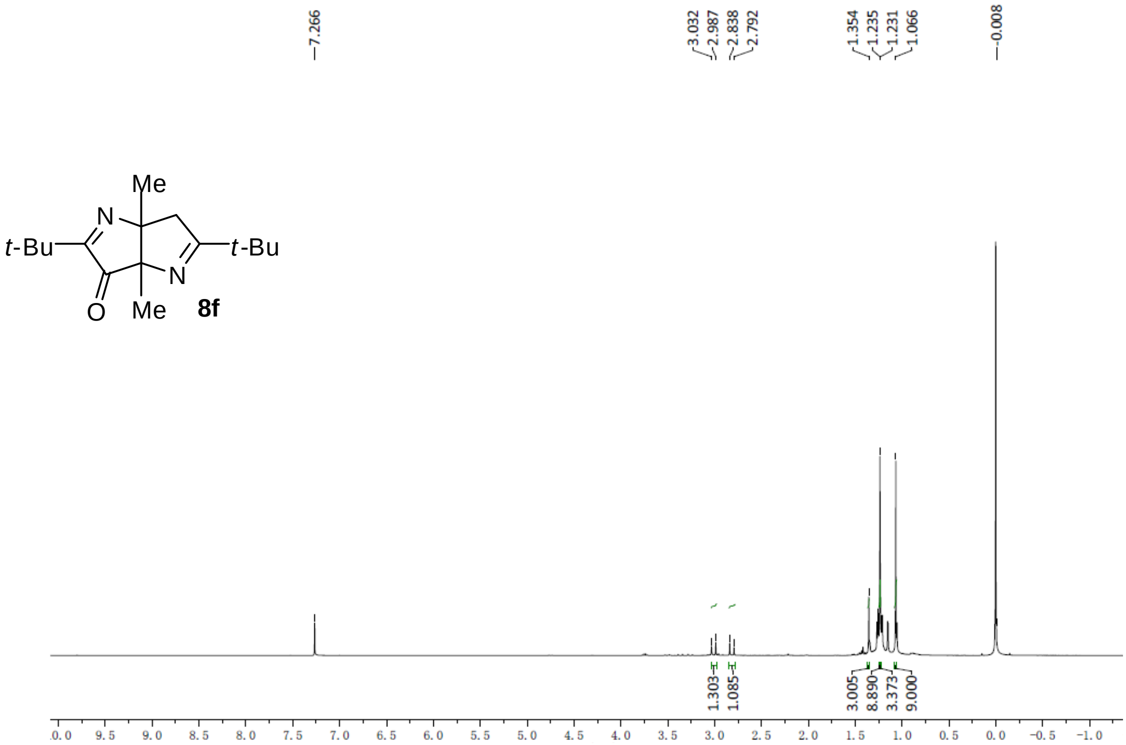
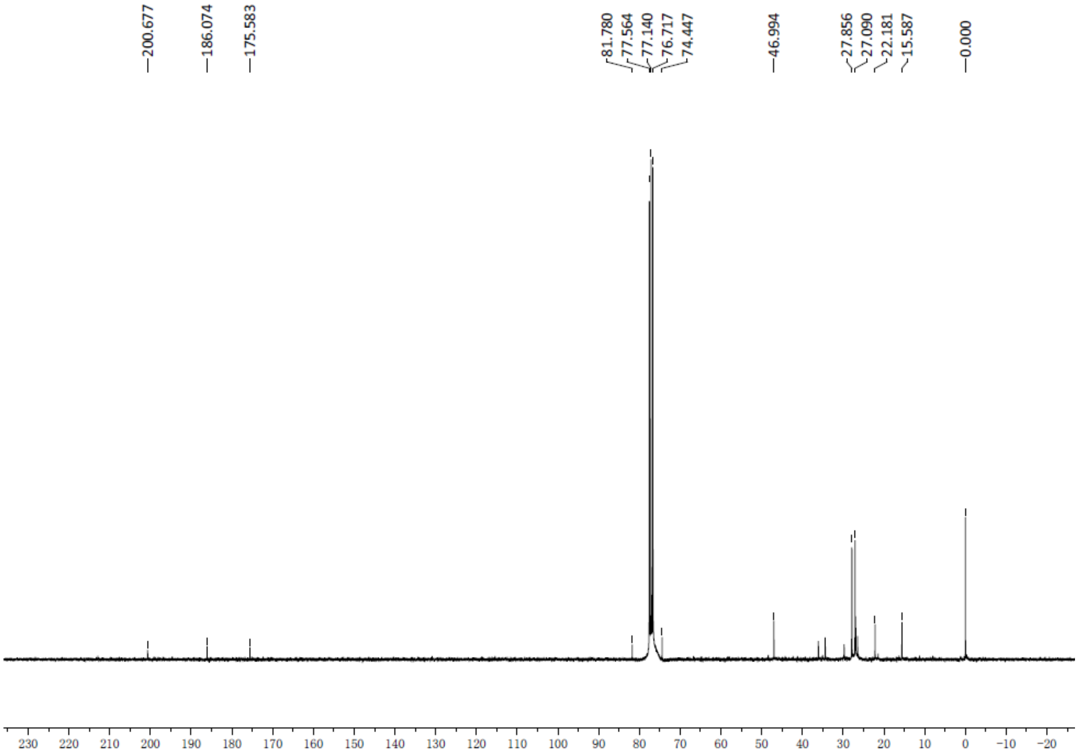


^{13}C NMR- **8f**



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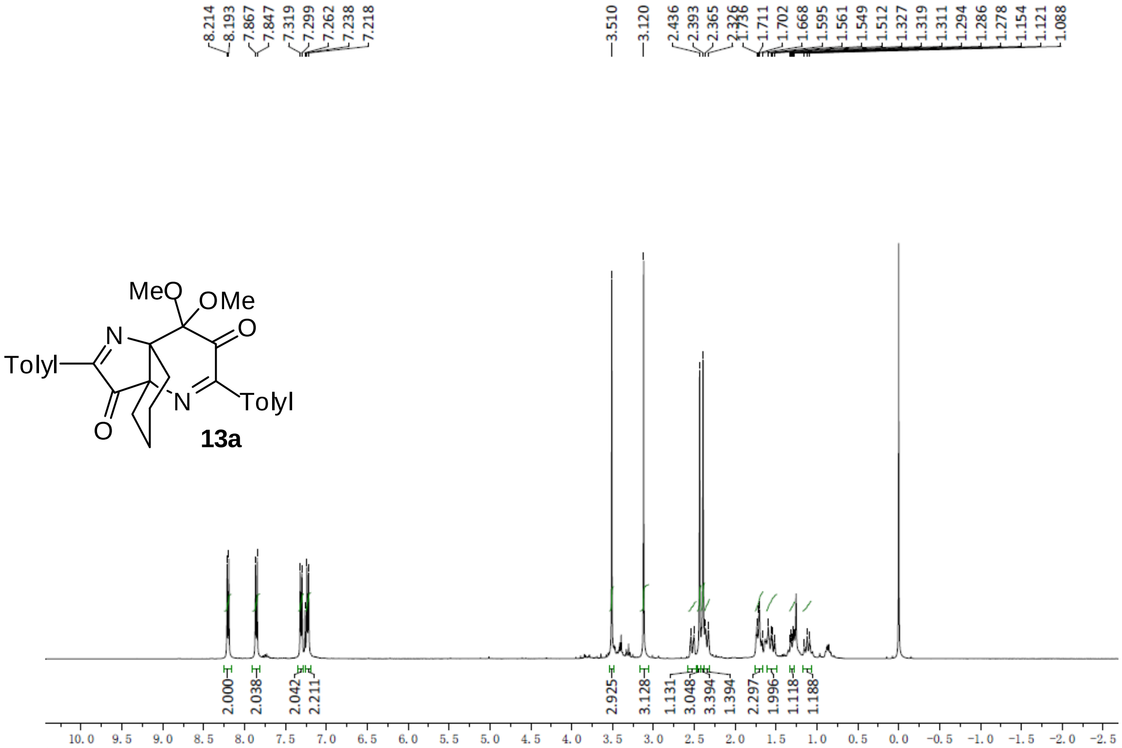

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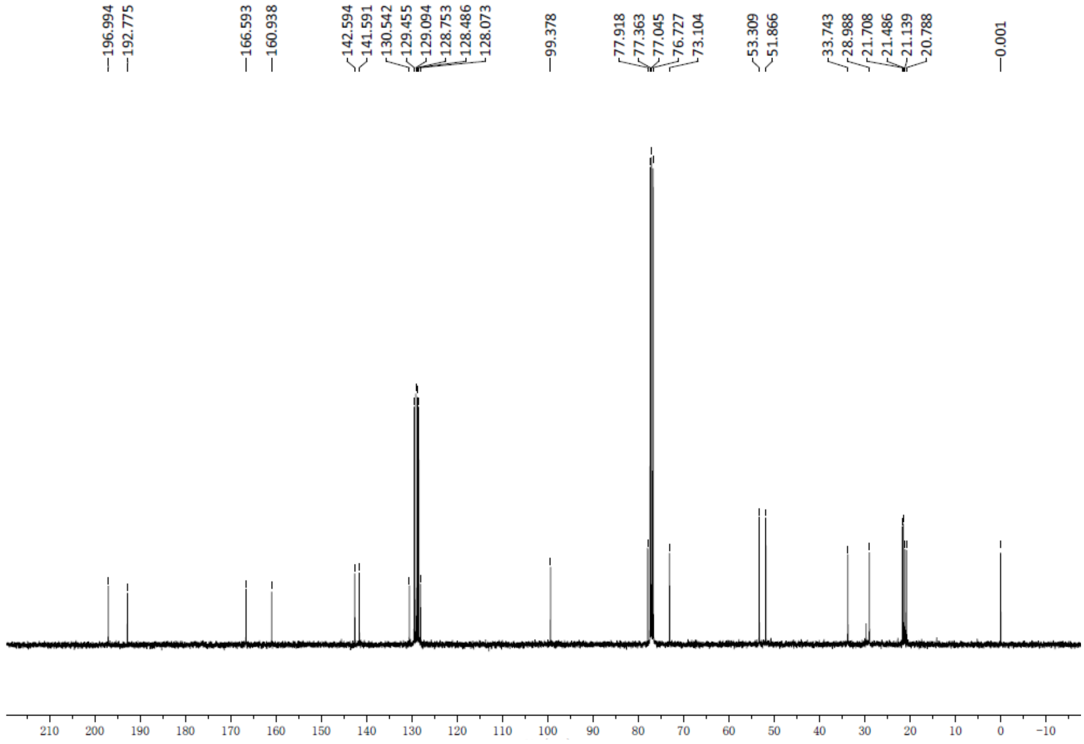

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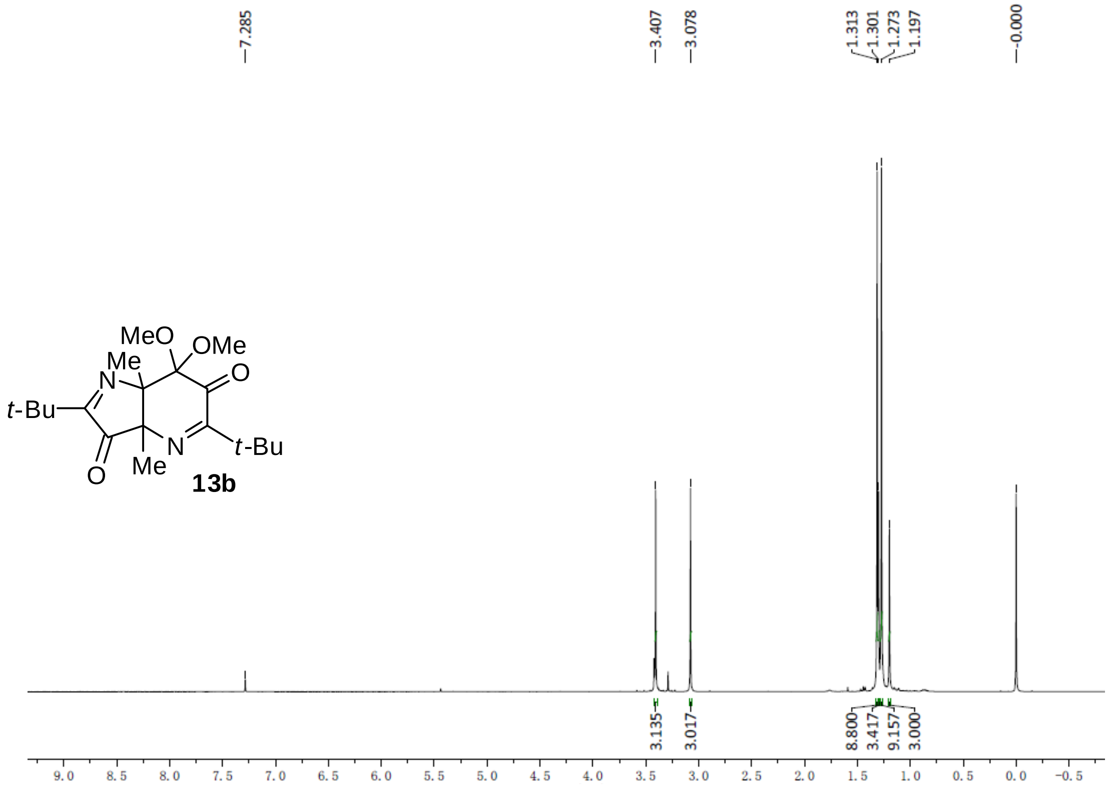

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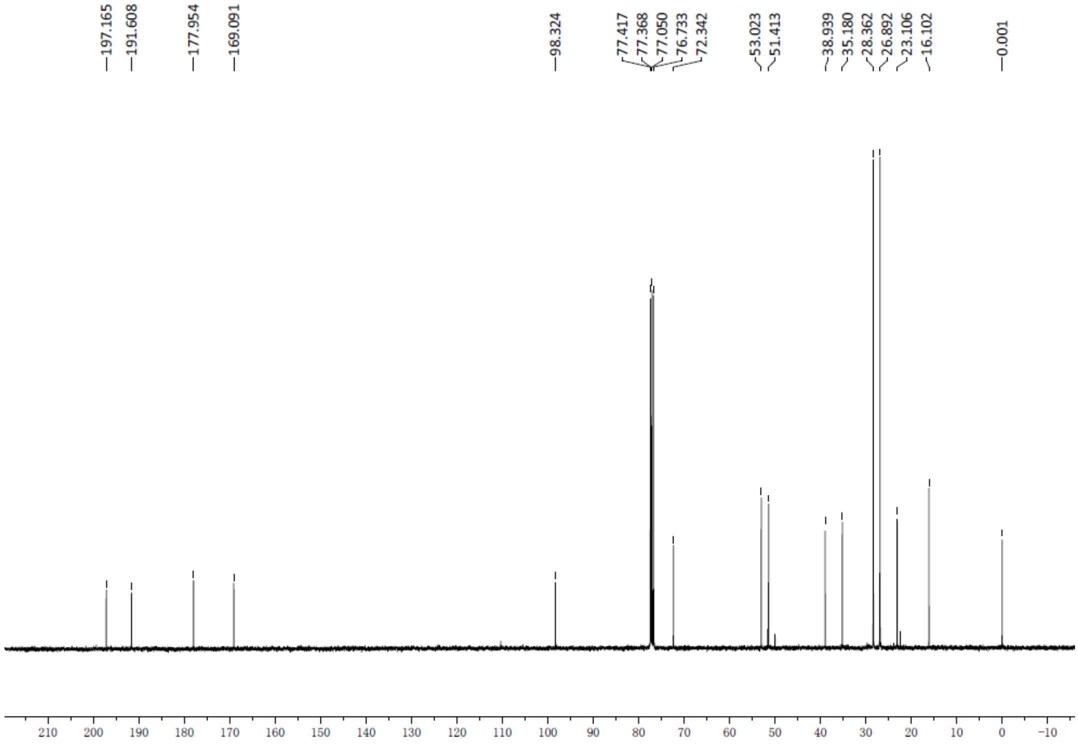

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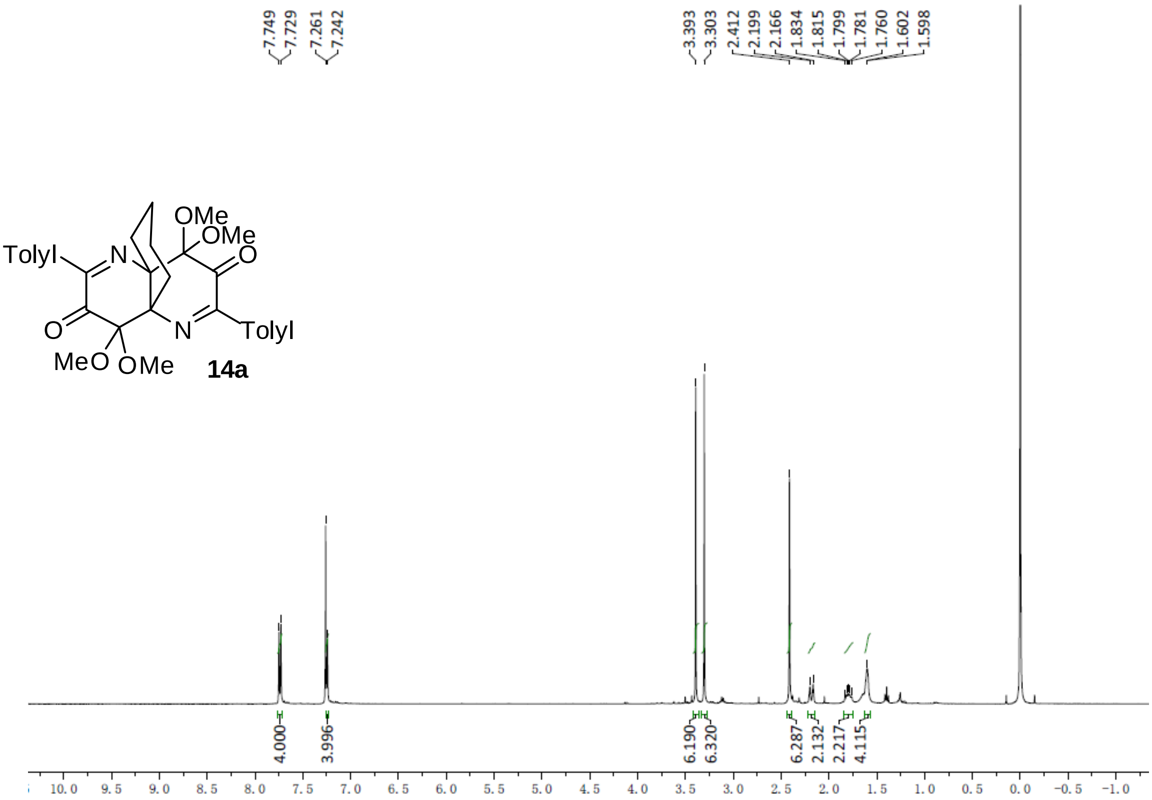

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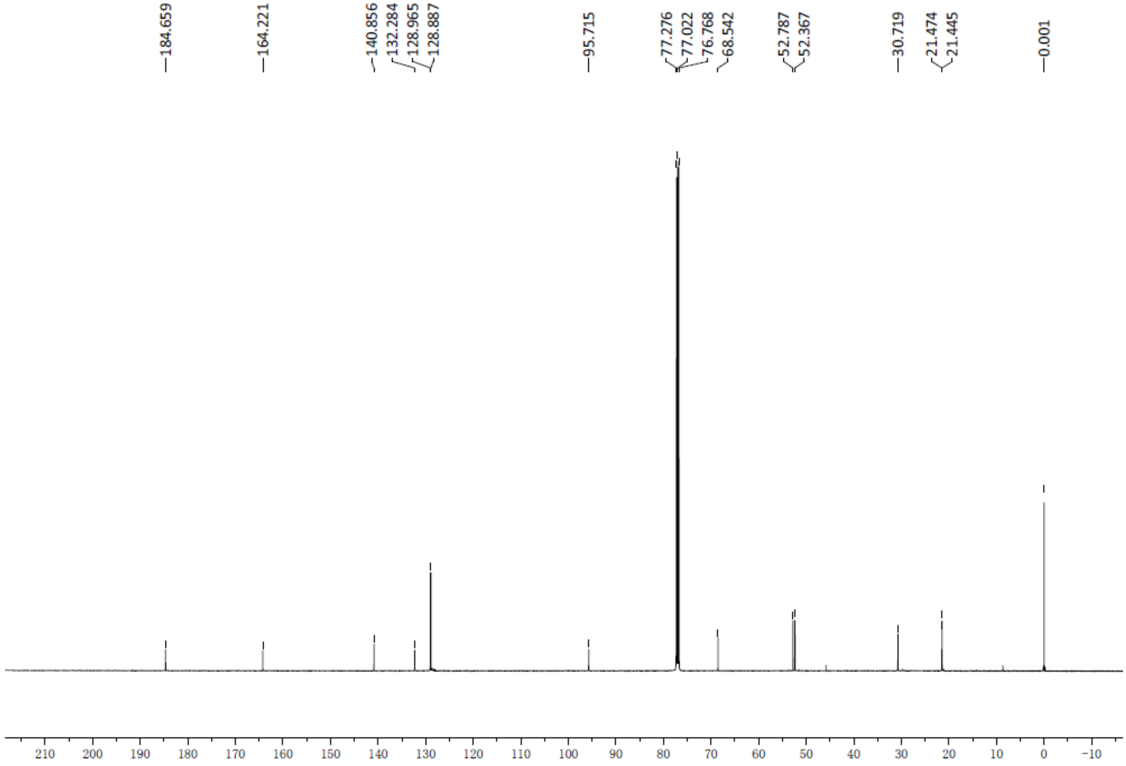

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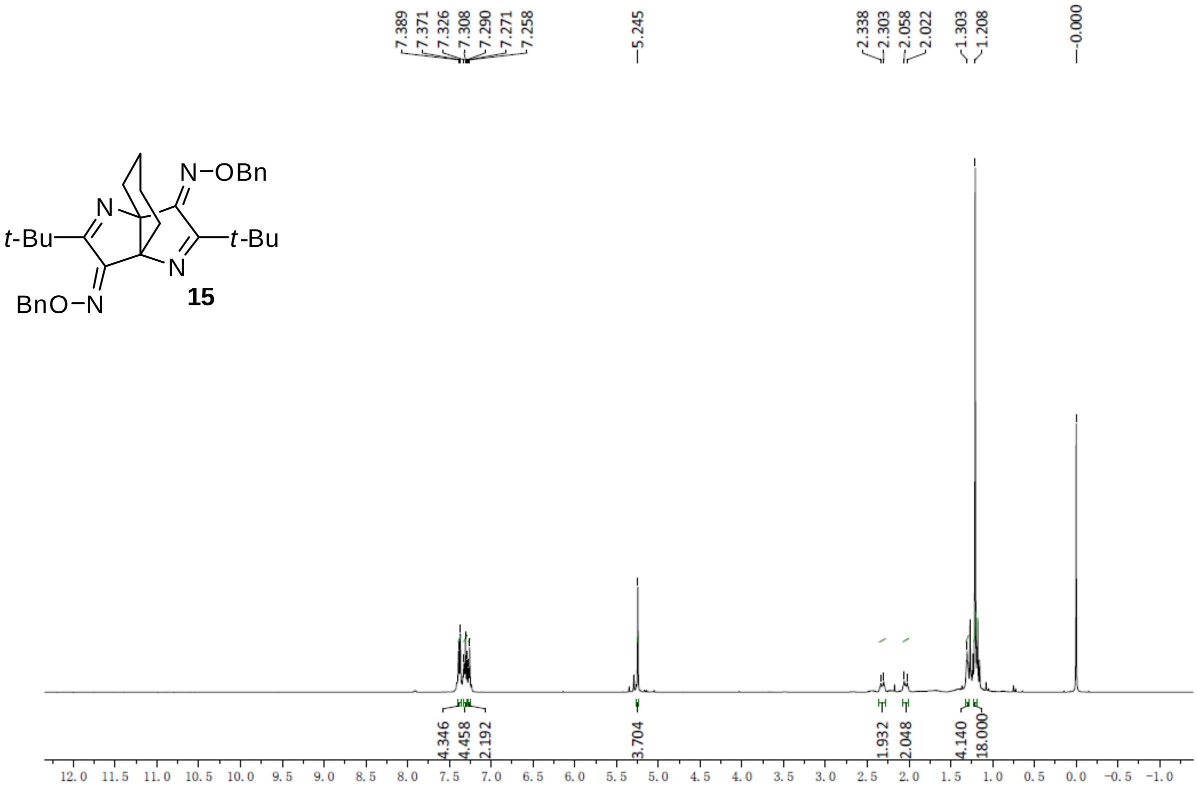

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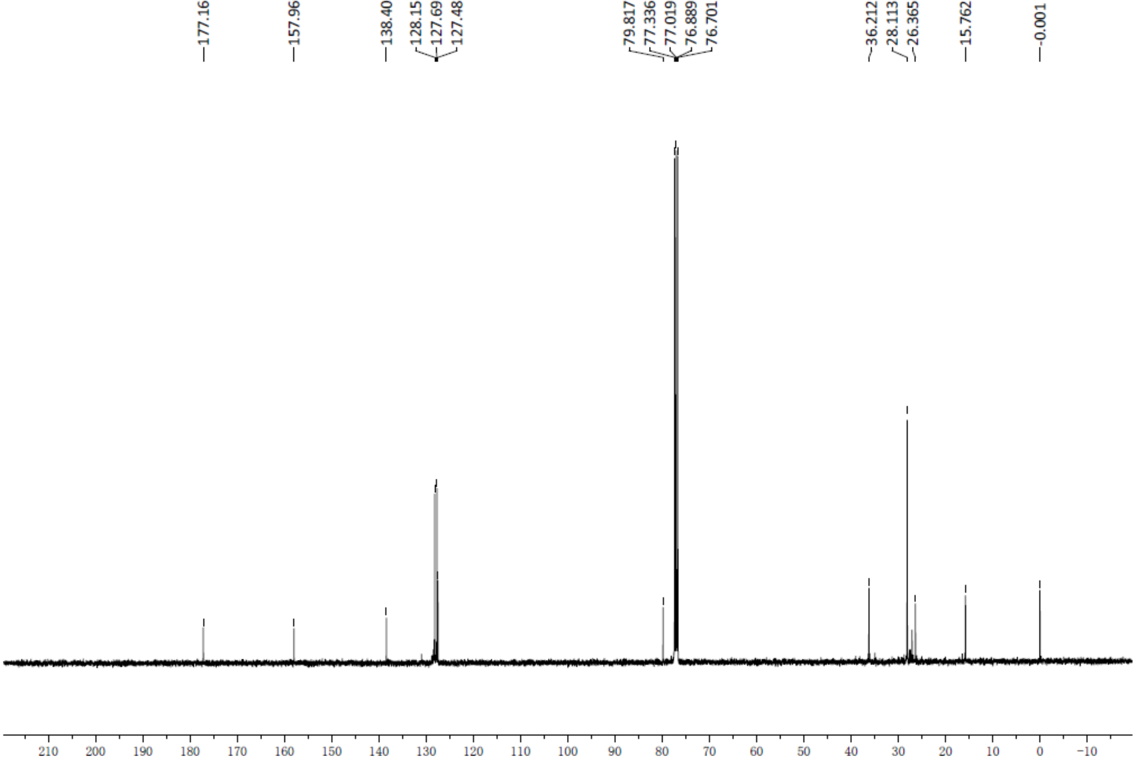

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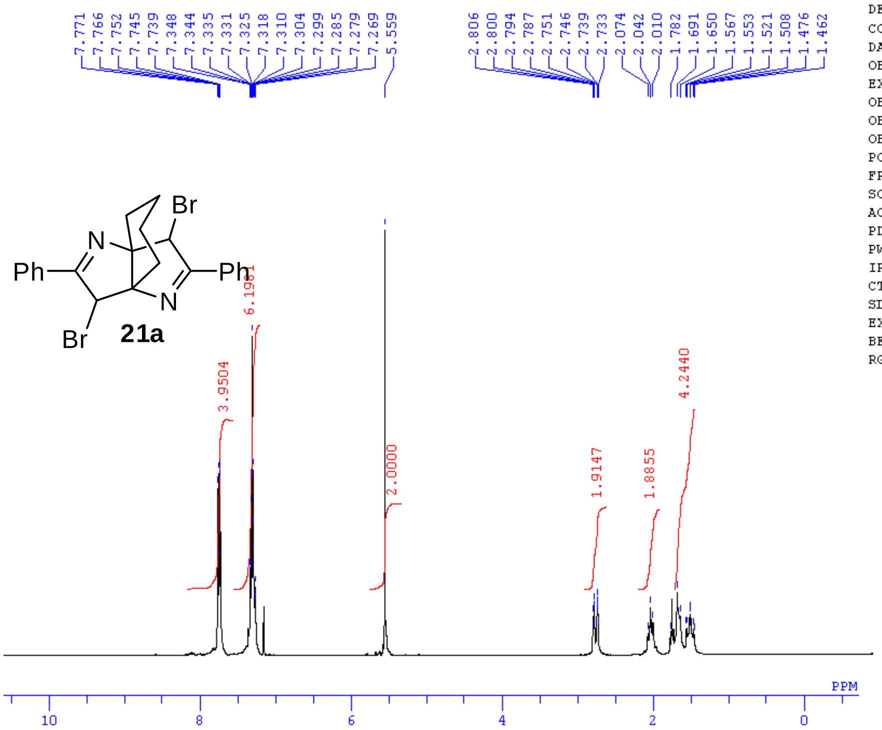

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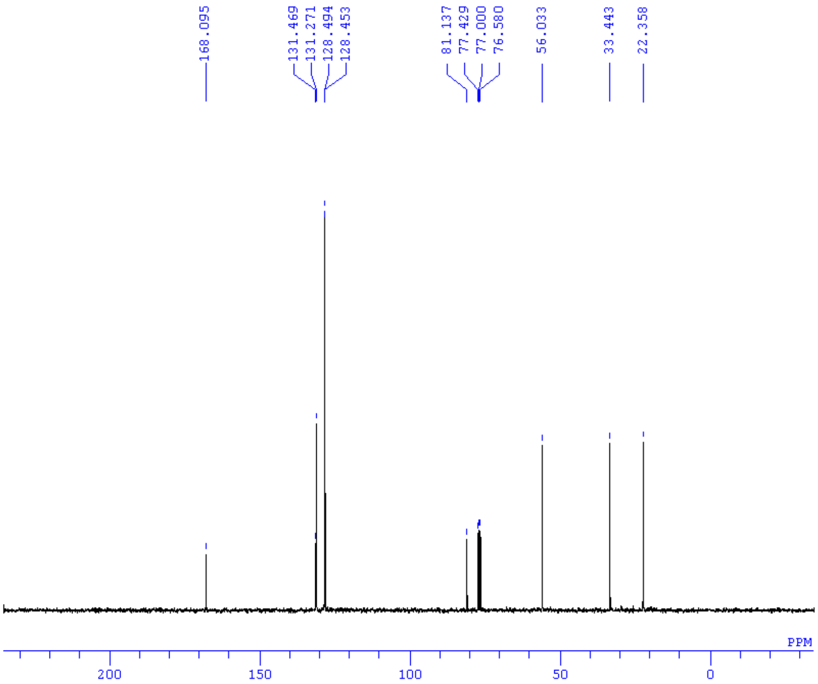

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PW1            5.0 us
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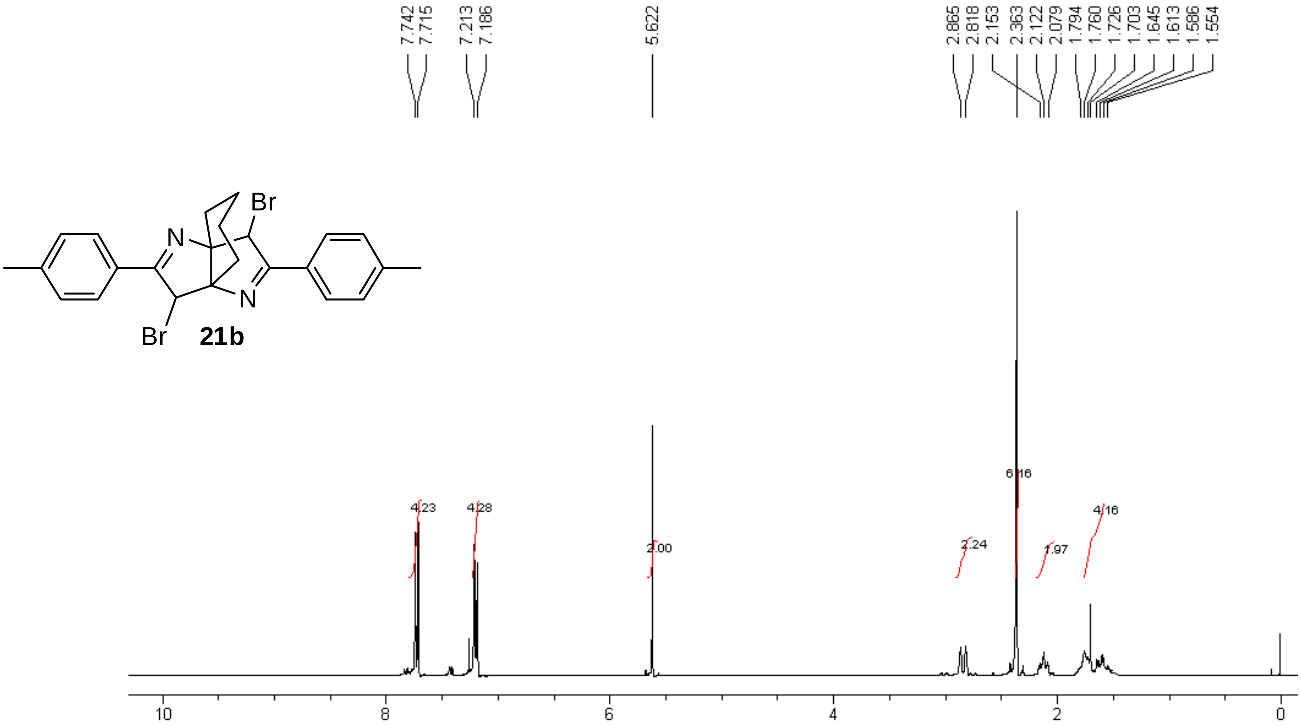

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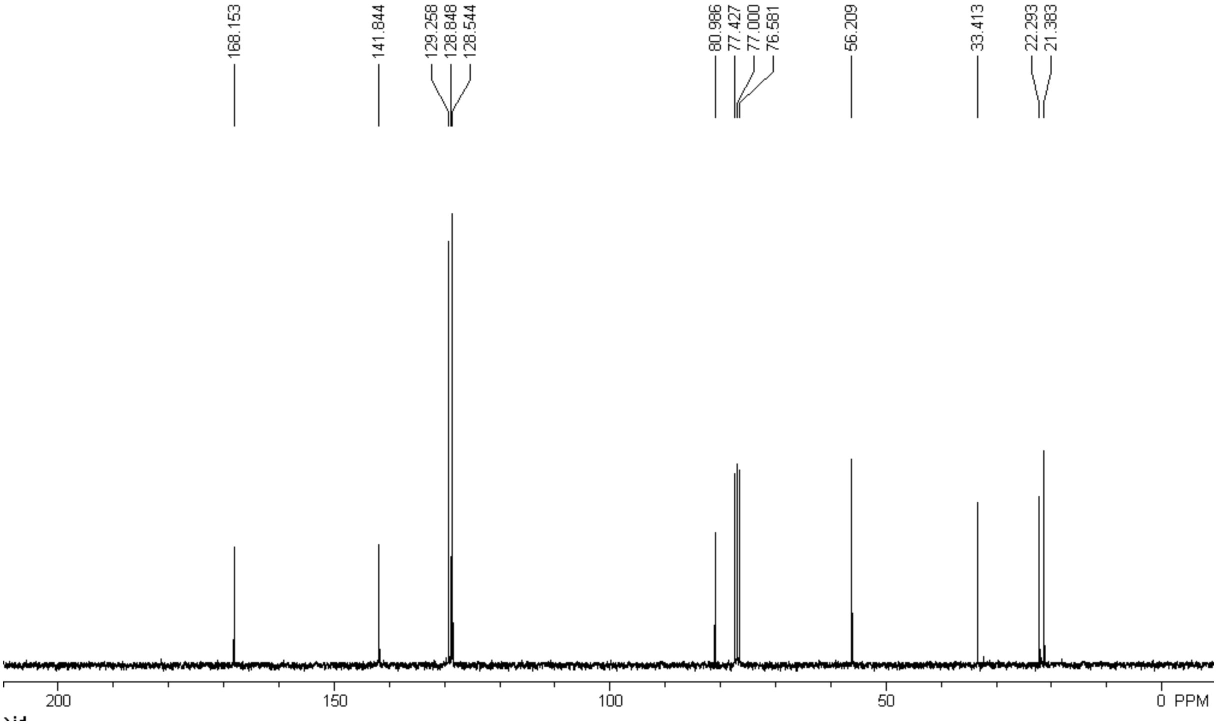

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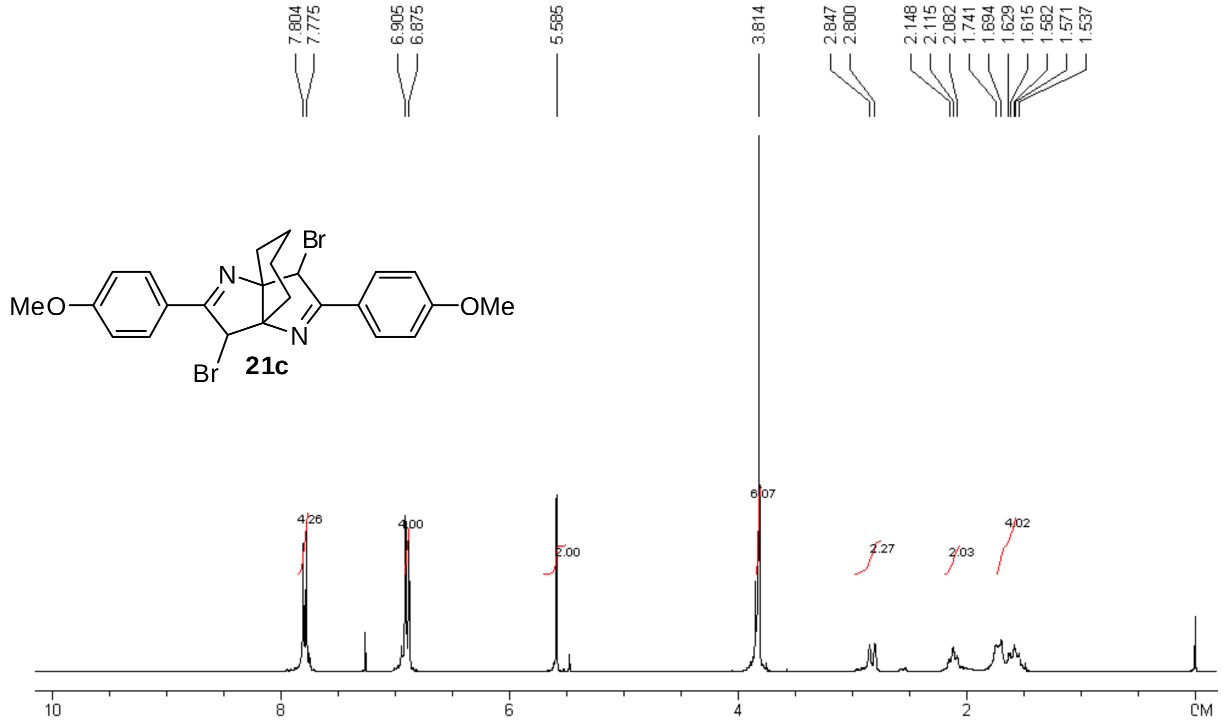

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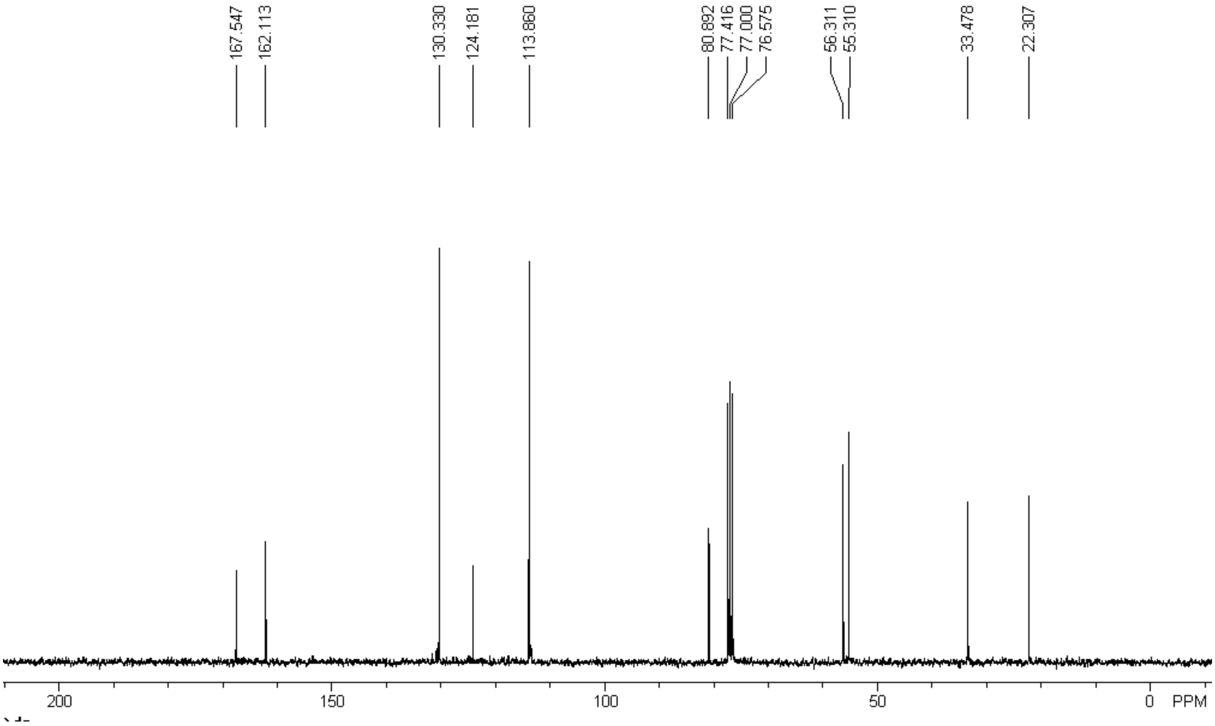

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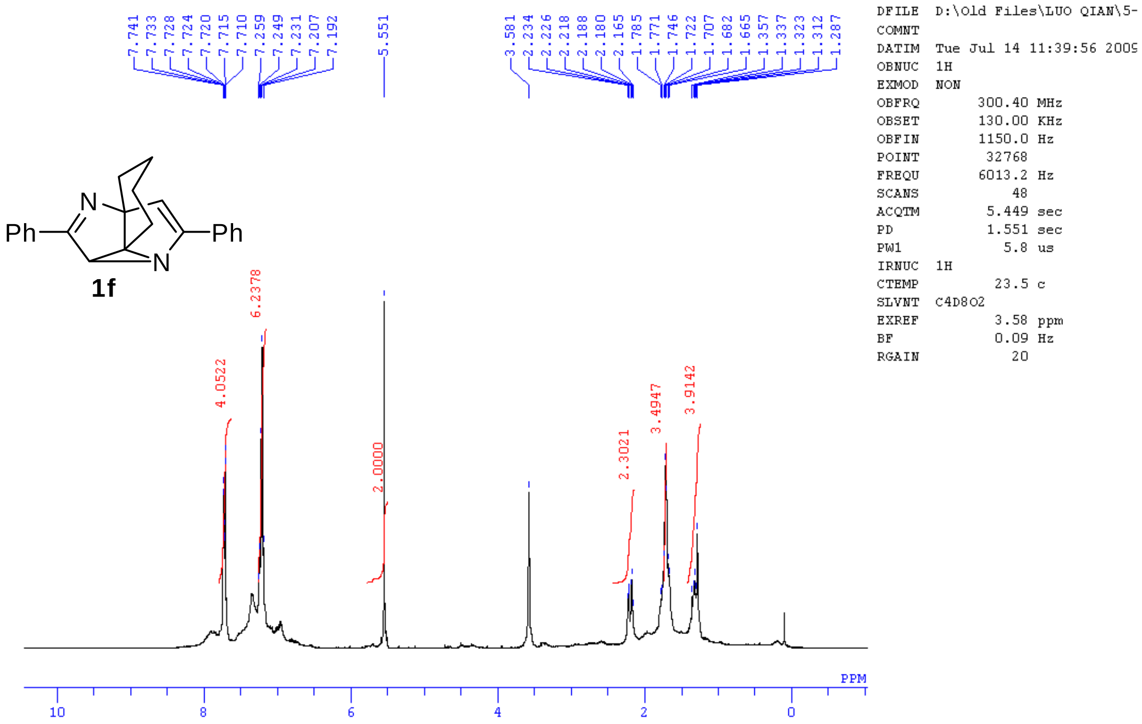

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FREQU       6013.2 Hz
SCANS           48
ACQTM        5.449 sec
PD           1.551 sec
PW1            5.8 us
IRNUC  1H
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RGAIN           20
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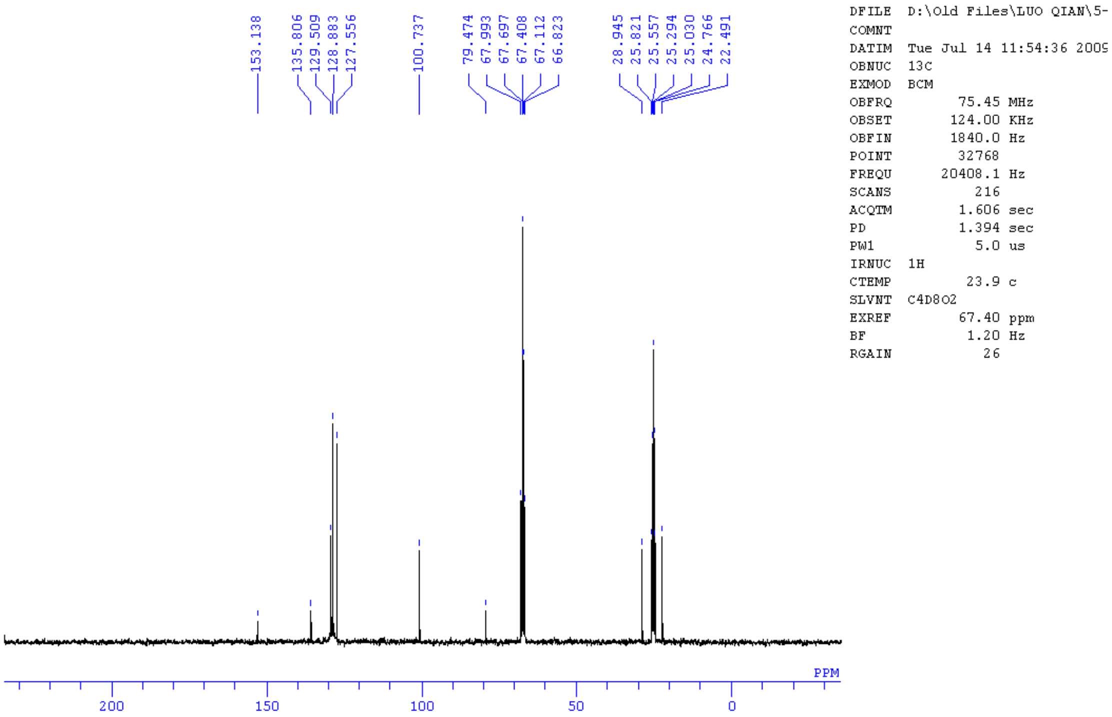
^{13}C NMR-**1f**



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OBFIN       1840.0 Hz
POINT        32768
FREQU      20408.1 Hz
SCANS          216
ACQTM        1.606 sec
PD           1.394 sec
PW1            5.0 us
IRNUC  1H
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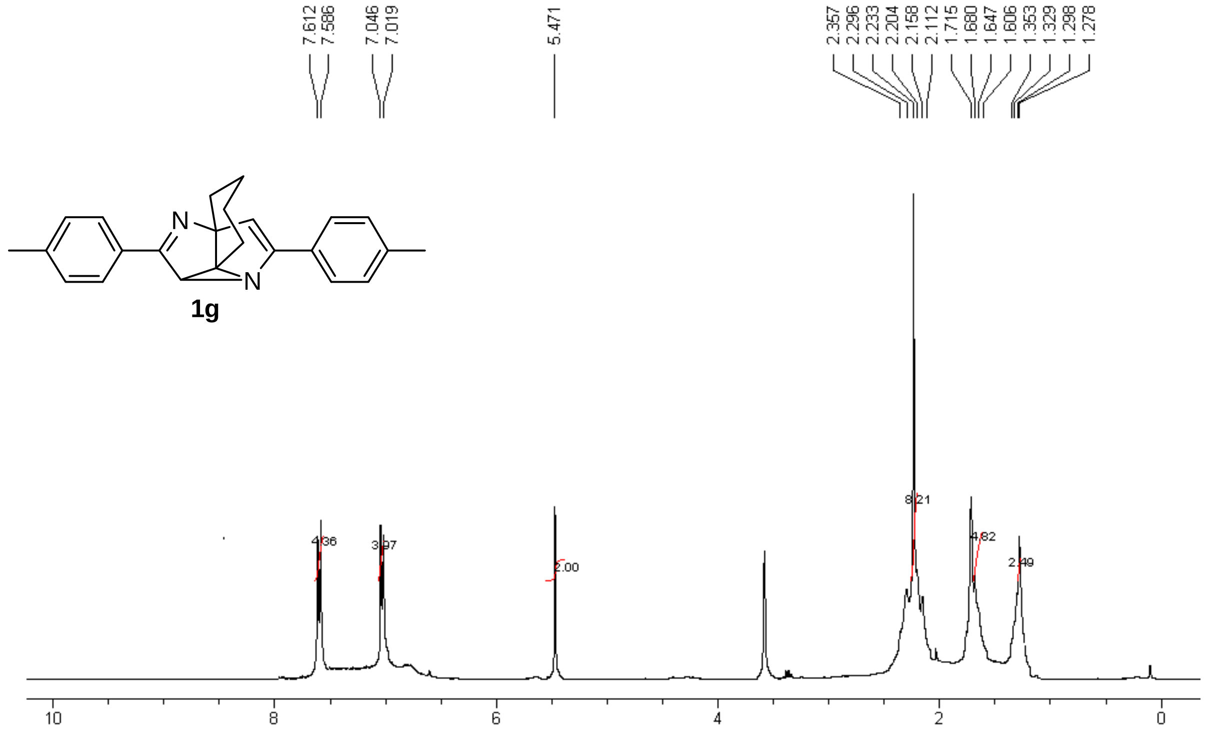
^{1}H NMR- **1g**



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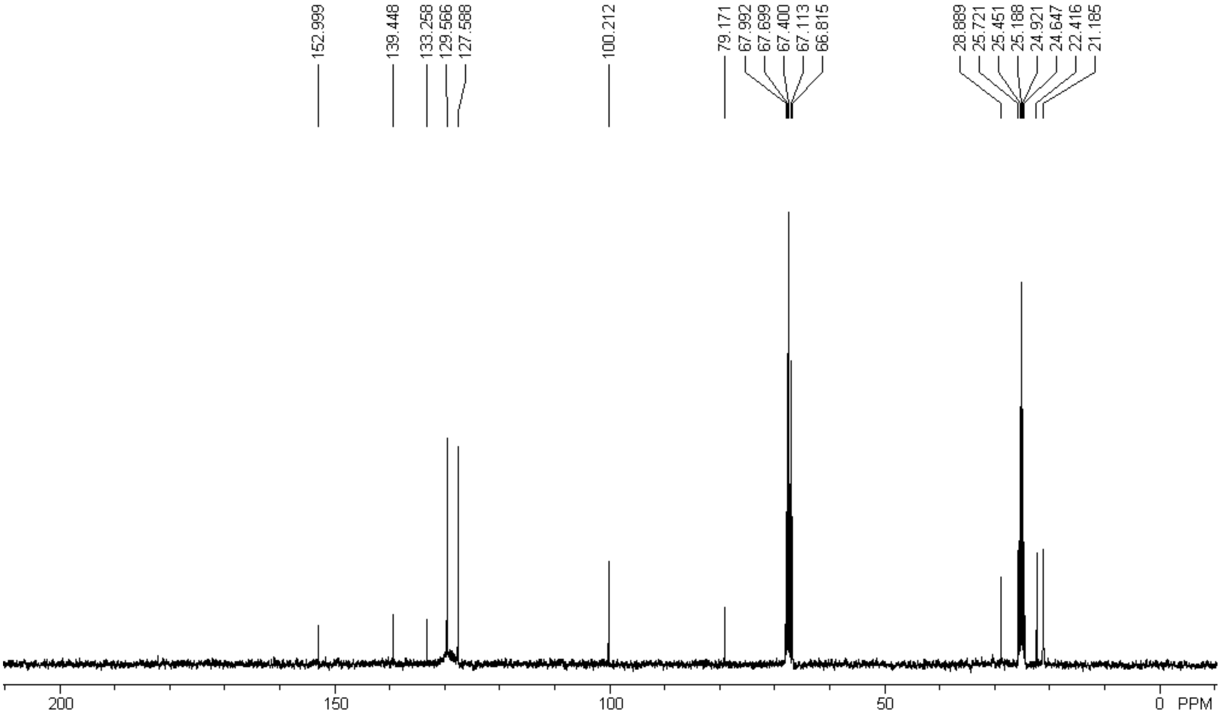

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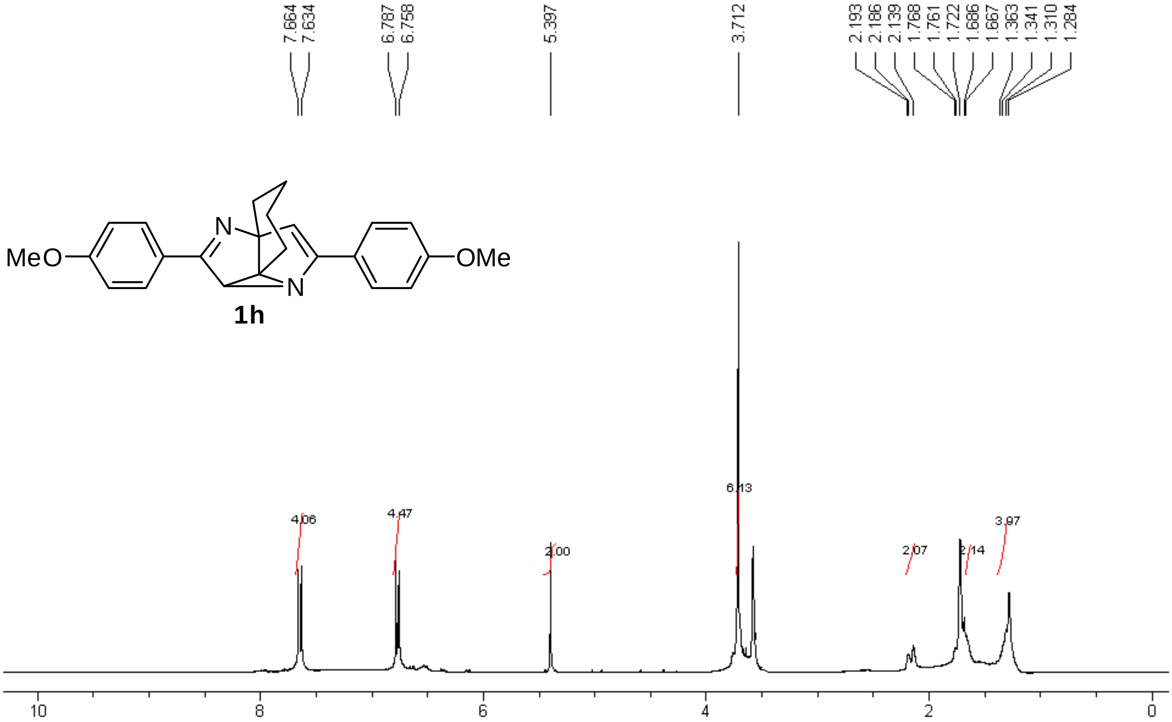

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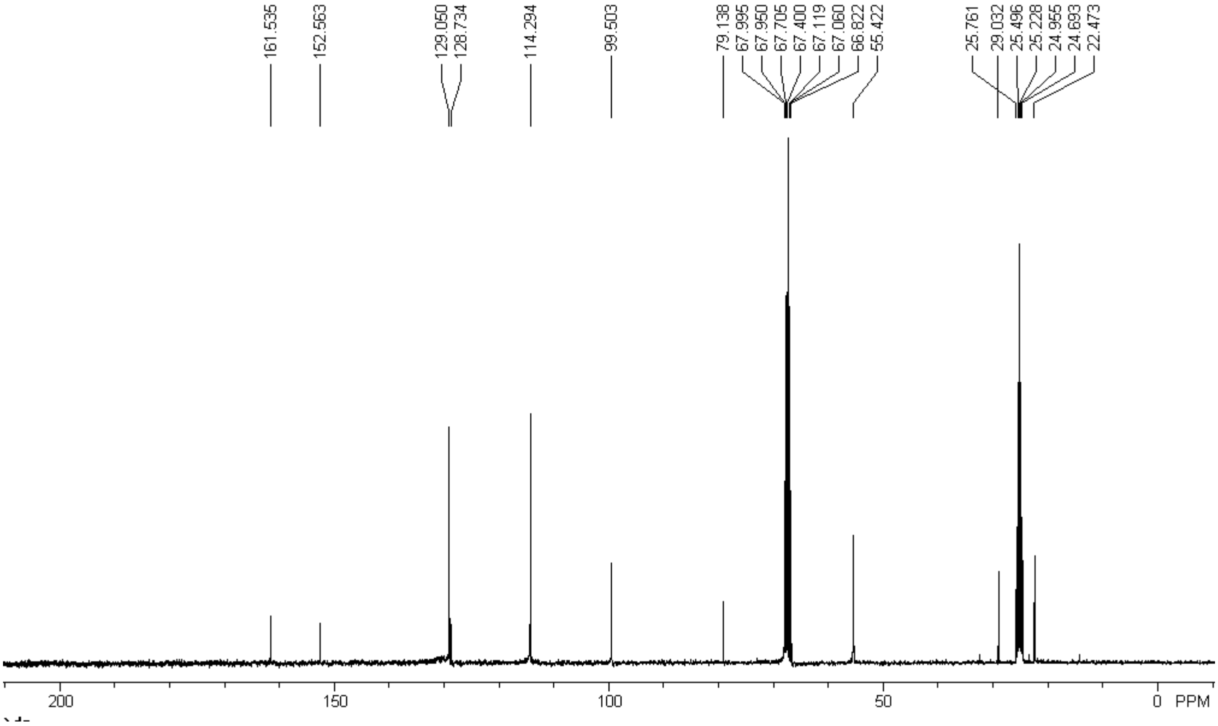

5) References

(1) a) Nair, V.; Deepthi, A.; Poonoth, M.; Santhamma, B.; Vellalath, S.; Babu, B. P.; Mohan, R.; Suresh, E. *J. Org. Chem.* **2006**, *71*, 2313; b) Dawid, M.; Mloston, G.; Warkentin, J. *Chem. Eur. J.* **2002**, *8*, 2184.

(2) Yu, N.; Wang, C.; Zhao, F.; Liu, L.; Zhang, W.-X.; Xi, Z. *Chem. Eur. J.* **2008**, *14*, 5670.

(3) Zhang, S.; Wei, J.; Zhan, M.; Luo, Q.; Wang, C.; Zhang, W.-X.; Xi, Z. *J. Am. Chem. Soc.* **2012**, *134*, 11964.

(4) Schnieders, C.; Altenbach, H. J.; Müllen, K. *Angew. Chem. Int. Ed. Engl.* **1982**, *21*, 637.

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