Electronic Supplementary Material (ESI) for Chemical Communications.

Pd(II)-Catalyzed alkyne annulation through allylic isomerization: Synthesis of spiro-cyclopentadiene pyrazolones

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Supporting Information

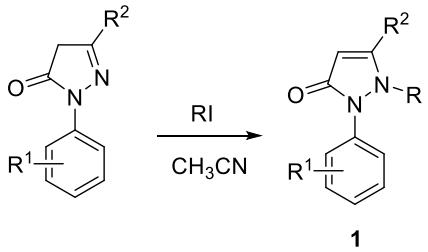
Contents

1. General Information

Melting points were measured with a Buchi B-540 melting point apparatus and are uncorrected. NMR spectra were recorded on Bruker Avance III 500 MHz FT NMR & Jeol Resonance ECZ 400 MHz FT NMR spectrometer using tetramethylsilane (TMS) as an internal standard. All the commercially available regents were used as received. All experiments were monitored by thin layer chromatography. TLC was performed on Merck TLC Silica gel 60 F254 precoated plates. Column chromatography was performed on silica gel of 100-200 mesh obtained from Merck. HRMS data were recorded by electron spray ionization with a Q-TOF mass analyzer. Photophysical properties were evaluated on HITACHI (U-3900) UV-Vis spectrophotometer and Horiba (Fluorlolog-3) fluorescence spectrophotometer

2. Reaction Procedures

2.1 General procedure for the synthesis of antipyrine derivatives (1)[1]



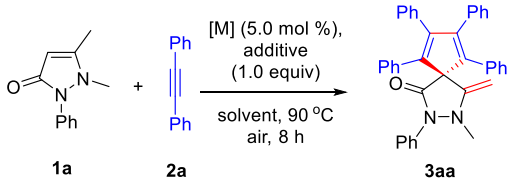
1

Scheme SI-1: Synthesis of antipyrine derivatives

Preparation of antipyrine (1): 2-Phenyl pyrazolones were synthesized by following a known procedure.[1] To a stirred solution of 2-phenyl pyrazolone (1.0 equiv), in acetonitrile (4.0 mL), methyl iodide/alkyl iodide (5.0 equiv) was added. The reaction mixture was heated in a sealed tube for 12 h. The solvent was removed under vacuo and the crude reaction mixture was purified by alumina column chromatography using EtOAc as the eluent to afford antipyrenes **1**.

2.2. Optimization of the reaction conditions for the synthesis of compound 3aa

Table SI-1 Optimization of the reaction conditions for **3aa**[a]



Entry	Catalyst	Additive	Solvent	**3aa** (%)[b]
1	[{$RuCl_2$(*p*-cymene)}$_2$]	$Cu(OAc)_2·H_2O$	1,4-Dioxane	0
2	[$RhCp^*Cl_2]_2$	$Cu(OAc)_2·H_2O$	1,4-Dioxane	0
3	$Pd(OAc)_2$	$Cu(OAc)_2·H_2O$	1,4-Dioxane	48
4	$PdCl_2$	$Cu(OAc)_2·H_2O$	1,4-Dioxane	0
5	$Pd(OAc)_2$	AgOAc	1,4-Dioxane	20
6	$Pd(OAc)_2$	CsOAc	1,4-Dioxane	36
7	$Pd(OAc)_2$	NaOAc	1,4-Dioxane	38
8	$Pd(OAc)_2$	KOAc	1,4-Dioxane	45
9	$Pd(OAc)_2$	$Cu(OAc)_2·H_2O$	Toluene	74
10	$Pd(OAc)_2$	$Cu(OAc)_2·H_2O$	MeCN	15
11	$Pd(OAc)_2$	$Cu(OAc)_2·H_2O$	^{t}AmOH	79
12[c]	$Pd(OAc)_2$	$Cu(OAc)_2·H_2O$	MeOH	47
13	$Pd(OAc)_2$	$Cu(OAc)_2·H_2O$	DMF	0
14	$Pd(OAc)_2$	$Cu(OAc)_2·H_2O$	DMSO	0

[a]Reaction conditions: **1a** (0.5 mmol), **2a** (1.0 mmol), catalyst (5.0 mol %), additive (0.5 mmol) and solvent (5.0 mL) at 90 °C under air for 8 h; unless otherwise mentioned. [b]Isolated yields. [c]Reaction was performed at 64 °C.

2.3 General procedure for the synthesis of spiro-pyrazolone dervatives 3

A mixture of antipyrine (**1**, 0.5 mmol), alkyne (**2**, 1.0 mmol), $Pd(OAc)_2$ (5.0 mol %) and $Cu(OAc)_2.H_2O$ (0.5 mmol) in ^tAmOH (5.0 mL) was stirred at 90 ^oC under open air for 8 hours. The solvent ^tAmOH was removed under vacuo and the crude reaction mixture was poured into water and extracted with ethylacetate (25 mL x 2). The organic layer was then washed with brine and dried over anhydrous Na_2SO_4. The solvent was removed under vacuo and the crude product obtained was purified by silica gel (100-200 mesh) column chromatography using 5% EtOAc in hexane as the eluent to afford spiro-pyrazolones **3**.

2.4 General procedure for one pot synthesis of spiropyrazolone dervatives 4

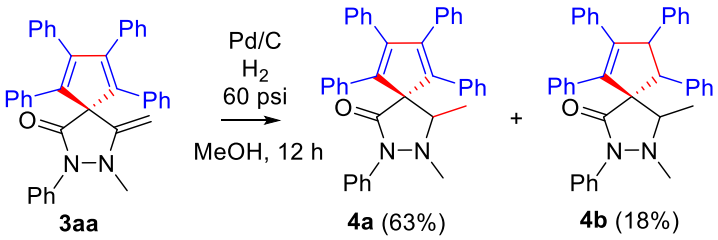
A mixture of antipyrine (**1**, 0.5 mmol), alkyne (**2**, 1.0 mmol), $Pd(OAc)_2$ (5.0 mol %) and $Cu(OAc)_2.H_2O$ (0.5 mmol) in toluene (5.0 mL) was stirred at 90 ^oC for 8 hours. Then Lawessons reagent (1.5 equiv) was added and the mixture was again stirred at 90 ^oC for 6 hours. The solvent toluene was removed under vacuo and the crude reaction mixture was poured into water and extracted with ethylacetate (25 mL x 2). The organic layer was then washed with brine and dried over anhydrous Na_2SO_4. The solvent was removed under vacuo and the crude product obtained was purified by silica gel (100-200 mesh) column chromatography using 5% EtOAc in hexane as the eluant to afford spiropyrazolones **4**.

2.5 General procedure for the two-steps synthesis of spiropyrazolone dervatives 4

A mixture of olefinic product (**3**, 0.5 mmol) and Lawesson's reagent (1.0 equiv) was refluxed for 6 hours using toluene (5.0 mL) as the solvent. The solvent was removed under vacuo and the crude reaction mixture was poured into water and extracted with ethylacetate (25 mL x 2). The organic layer was then washed with brine and dried over anhydrous Na_2SO_4. The solvent was removed under vacuo and the crude product obtained was purified by silica gel (100-200 mesh) column chromatography using 5% EtOAc in hexane as the eluent to afford spiropyrazolones **4**.

3. Transformation of spiro-pyrazolone 3aa

(i) Synthesis of 3,4-dimethyl-2,6,7,8,9-pentaphenyl-2,3-diazaspiro[4.4]nona-6,8-dien-1-one (4a) and 3,4-dimethyl-2,6,7,8,9-pentaphenyl-2,3-diazaspiro[4.4]non-6-en-1-one (4b):



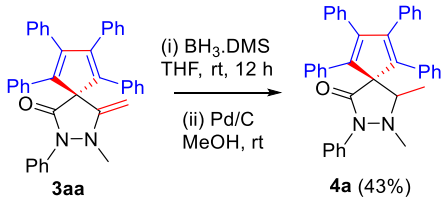
Scheme SI-2

To a stirred solution of **3aa** (54 mg, 0.1 mmol) in MeOH (8 mL), Pd/C 10 wt % (5 mg) was added. The reaction mixture was then stirred at room temperature for 12 hours under H_2 (60 psi). After completion of the reaction, the reaction mixture was filtered through a celite pad and the celite pad was washed with methanol (20 mL). The solvent was removed under vacuo and the crude product obtained was purified by silica gel (100-200 mesh) column chromatography using 5% hexane in ethyl acetate as the eluent to afford **4a** (34 mg, 63%) and **4b** (10 mg, 18%).

Compound **4a**: White solid. M.p.: 156–159 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.24–6.90 (m, 25H), 3.24 (q, J = 5.5 Hz, 1H), 2.20 (s, 3H), 1.27 (d, J =6.6 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 167.6, 147.6, 146.9, 143.1, 142.1, 136.1, 135.9, 135.4, 135.0, 130.7, 130.2, 130.1, 128.4, 128.2, 127.5, 127.4, 127.3, 127.1, 126.7, 126.6, 126.2, 124.0, 74.2, 66.1, 29.6, 11.8. HRMS (+ESI) Calcd for $C_{39}H_{33}N_2O$ $[M+H]^+$: 545.2593; found: 545.2634.

Compound **4b**: White solid. M.p.: 154-156 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38–7.35 (m, 2H), 7.23–6.98 (m, 23H), 4.91 (d, J = 10.0 Hz, 1H), 3.90 (d, J = 10.0 Hz, 1H), 2.98 (q, J = 7.9 Hz, 1H), 2.10 (s, 3H), 1.26 (d, J = 6.6 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 169.2, 145.6, 139.8, 139.2, 137.5, 136.4, 136.2, 136.1, 132.1, 131.3, 129.8, 129.4, 128.5, 127.9, 127.6, 127.3, 126.9, 126.8, 126.7, 126.0, 123.8, 70.7, 66.8, 58.2, 57.9, 43.1, 12.4. HRMS (+ESI) Calcd for $C_{39}H_{35}N_2O$ $[M+H]^+$: 547.2749; found: 547.2817.

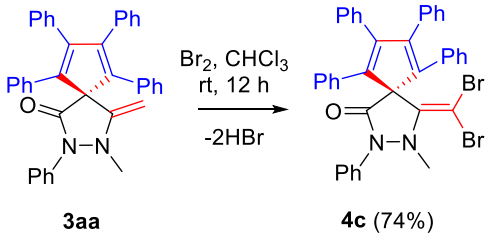
(ii) **Synthesis of 3,4-dimethyl-2,6,7,8,9-pentaphenyl-2,3-diazaspiro[4.4]nona-6,8-dien-1-one (4a):**



Scheme SI-3

To a solution of **3aa** (108 mg, 0.2 mmol) in anhydrous THF, a solution of $BH_3.S(CH_3)_2$ (0.2 mL, 2 M solution in THF, 0.4 mmol) was added at 0 °C and the reaction was stirred at room temperature for 12 h. The solvent was removed under vacuo and to the crude product MeOH was added. Then 10 wt % of Pd/C (10 mg) was added into the reaction mixture under nitrogen atmosphere. The reaction mixture was stirred again at room temperature for 24 h. The solvent was removed under vacuo and the crude product obtained was purified by silica gel (100-200 mesh) column chromatography using 5% hexane in ethylacetate as the eluent to afford **4a** (47 mg, 43%).

(iii) **Synthesis of 4-(dibromomethylene)-3-methyl-2,6,7,8,9-pentaphenyl-2,3-diazaspiro[4.4]nona-6,8-dien-1-one (4c):**



3aa **4c** (74%)

Scheme SI-4

To a solution of **3aa** (108 mg, 0.2 mmol) in anhydrous CH_2Cl_2, Br_2 (64 mg, 0.40 mmol) was added and then the reaction was continued to stir at room temperature for 12 h. The solvent was removed under vacuo and the crude product obtained was purified by silica gel (100-200 mesh) column chromatography using 2% hexane in EtOAc as the eluent to afford **4c** (103 mg, 74%). Pale yellow solid. M.p.: 159-162 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.54 (d, J = 8.5 Hz, 2H), 7.36 (t, J = 7.9 Hz, 2H), 7.20–7.05 (m, 17H), 6.96–6.95 (m, 4H), 2.32 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 164.5, 147.9, 145.6, 139.4, 135.4, 134.6, 134.5, 129.7, 129.3, 129.0, 128.1, 127.5, 127.4, 127.0, 126.1, 121.4, 73.9, 41.4, 29.6. HRMS (+ESI) Calcd for $C_{39}H_{29}Br_2N_2O$ $[M+H]^+$: 699.0647; found: 699.0689.

4. Measurement of fluorescence quantum yield (Φ_F)

Fluorescence quantum yields (Φ_F) of the compounds were calculated using quinine sulfate (0.5 M H_2SO_4 solution) as a standard (Φ = 0.54). Emission spectra of all the compounds were recorded from 360 to 660 nm with excitation at 340 nm. Absorbance (optical density, OD) of all the samples were recorded at 340 nm and quantum yields were calculated according to equation (1), in which Φ_{ref} is the quantum yield of the reference, A_{sample} and A_{ref} are the areas

under the emission spectra of the dimers and the reference, OD_{ref} and OD_{sample} are the absorbances of the reference and the dimers which were measured at the excitation wavelength; n_{sample} and n_{ref} are the refractive indices of the dimers and the reference in solution.

$$\Phi F = \Phi ref \left(\frac{Asample}{Aref}\right) x \left(\frac{ODref}{ODsample}\right) x \left(\frac{nref}{nsample}\right) \quad (1)$$

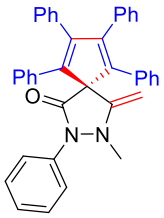
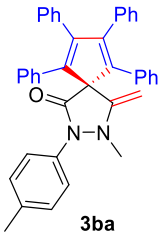
Sl. No	Compound	λ_{max} (nm)	λ_{em} (nm)	$(\Phi_F)^{a,b}$
1	**4aa**	347	449	0.48
2	**4ab**	341	457	0.75
3	**4ad**	340	450	0.64
4	**4ca**	340	450	0.52
5	**4da**	318	450	0.61
6	**4fa**	340	449	0.30
7	**4ga**	345	438	0.47

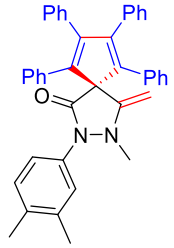
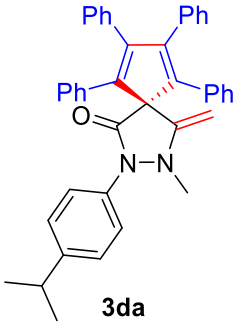
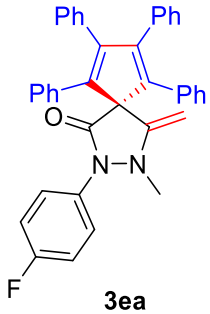
[a]Concentration 2.0 x 10^{-5} M in toluene; [b]All the compounds were excited at 340 nm.

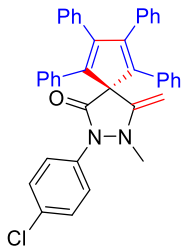
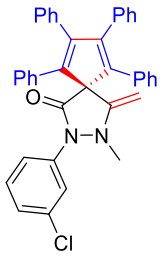
Reference:

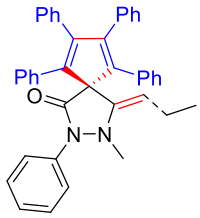
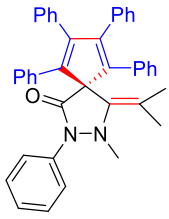
1. S. Baruah, P. Saikia, G. Duarah and S. Gogoi, *Org. Lett.*, 2018, **20**, 3753−3757.

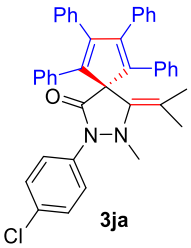
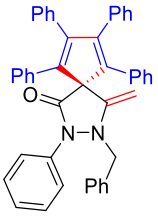
Spectral and Analytical Data of 3ba-ka and 3aa-ak:

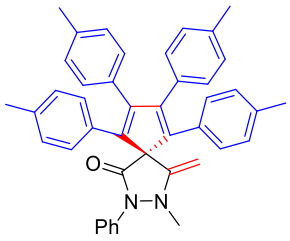
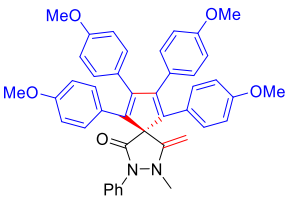
 **3aa**	**3-Methyl-4-methylene-2,6,7,8,9-pentaphenyl-2,3-diazaspiro[4.4]nona-6,8-dien-1-one (3aa):** The title compound was prepared by following the general procedure **2.3** from antipyrine, **1a** (94 mg, 0.5 mmol) and alkyne **2a** (178 mg, 1.0 mmol), which was then purified by column chromatography using 5% EtOAc in hexane to afford white solid of **3aa** (214 mg, 79%). M.p.: 143–145 ^{o}C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.32–6.96 (m, 25H), 4.50 (s, 2H), 2.46 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 167.0, 150.1, 146.1, 145.0, 136.1, 135.0, 130.4, 130.0, 129.1, 128.2, 127.9, 127.4, 127.2, 126.7, 123.3, 89.4, 74.4, 42.4. HRMS (+ESI) Calcd for $C_{39}H_{31}N_2O$ $[M+H]^+$: 543.2436; found: 543.2338.
 **3ba**	**3-Methyl-4-methylene-6,7,8,9-tetraphenyl-2-(*p*-tolyl)-2,3-diazaspiro[4.4]nona-6,8-dien-1-one (3ba):** The title compound was prepared by following the general procedure **2.3** from antipyrine **1b** (101 mg, 0.5 mmol) and alkyne **2a** (178 mg, 1.0 mmol) which was then purified by column chromatography using 5% EtOAc in hexane to afford brown solid of **3ba** (181 mg, 65%). M.p.: 91–94 ^{o}C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.22–7.06 (m, 20H), 6.96 (dd, J =7.8, 1.5 Hz, 4H), 4.48 (s, 2H), 2.45 (s, 3H), 2.31 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.5, 149.9, 145.7, 144.6, 136.5, 134.8, 134.7, 133.2, 130.0, 129.7, 129.4, 127.8, 127.5, 127.1, 126.8, 123.3, 122.3, 88.8, 74.0, 42.0, 21.0. HRMS (+ESI) Calcd for $C_{40}H_{33}N_2O$ $[M+H]^+$: 557.2592; found: 557.2567.

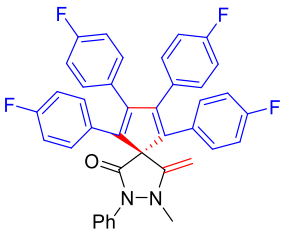
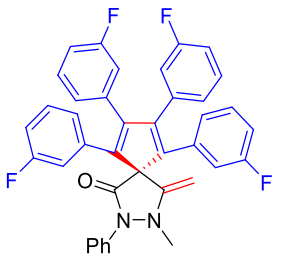
 **3ca**	**2-(3,4-Dimethylphenyl)-3-methyl-4-methylene-6,7,8,9-tetraphenyl-2,3-diazaspiro[4.4]nona-6,8-dien-1-one (3ca):** The titled compound was prepared by following the general procedure **2.3** from antipyrine **1c** (108 mg, 0.5 mmol) and alkyne **2a** (178 mg, 1.0 mmol) which was then purified by column chromatography using using 5% EtOAc in hexane afford off white solid of **3ca** (202 mg, 71 %). M.p.: 80–83 ^{o}C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.23–7.21 (m, 4H), 7.19–7.15 (m, 6H), 7.13–7.06 (m, 7H), 6.97–6.92 (m, 6H), 4.46 (d, J = 3.9 Hz, 2H), 2.45 (s, 3H), 2.21 (s, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.9, 150.3, 146.0, 145.0, 137.5, 135.6, 135.1, 135.0, 133.8, 130.4, 130.1, 128.1, 127.8, 127.4, 127.1, 125.1, 121.4, 88.9, 74.4, 42.2, 20.0, 19.6. HRMS (+ESI) Calcd for $C_{41}H_{35}N_2O$ $[M+H]^+$: 571.2749; found: 571.2693.
 **3da**	**2-(4-Isopropylphenyl)-3-methyl-4-methylene-6,7,8,9-tetraphenyl-2,3-diazaspiro[4.4]nona-6,8-dien-1-one (3da):** The title compound was prepared by following the general procedure **2.3** from antipyrine **1d** (112 mg, 0.5 mmol) and alkyne **2a** (178 mg, 1.0 mmol) which was then purified by column chromatography using 5% EtOAc in hexane to afford brown solid of **3da** (199 mg, 70% yield). M.p.: 83–87 ^{o}C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.23–7.20 (m, 4H), 7.17–7.13 (m, 10H), 7.11–7.06 (m, 6H), 6.97–6.95 (m, 4H), 4.49 (s, 2H), 2.87 (heptet, J = 7.0 Hz, 1H), 2.43 (s, 3H), 1.22 (d, J =7.0 Hz, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.7, 150.3, 147.6, 146.0, 145.0, 135.1, 135.0, 133.6, 130.4, 130.0, 128.1, 127.8, 127.4, 127.1, 123.6, 89.3, 74.3, 42.4, 34.0, 24.2. HRMS (+ESI) Calcd for $C_{42}H_{37}N_2O$ $[M+H]^+$: 585.2905; found: 585.2861.
 **3ea**	**2-(4-Fluorophenyl)-3-methyl-4-methylene-6,7,8,9-tetraphenyl-2,3-diazaspiro[4.4]nona-6,8-dien-1-one (3ea):** The title compound was prepared by following the general procedure **2.3** from antipyrine **1e** (103 mg, 0.5 mmol) and alkyne **2a** (178 mg, 1.0 mmol) which was then purified by column chromatography using 5% EtOAc in hexane to afford yellow solid of **3ea** (179 mg, 64%). M.p.: 95–98 ^{o}C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.20–7.18 (m, 6H), 7.17–7.06 (m, 12H),

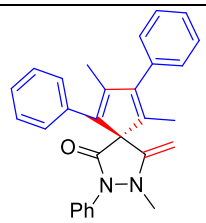
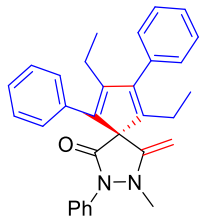
	7.02–6.95 (m, 6H), 4.50 (s, 2H), 2.45 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 167.2, 161.8 (d, J = 245.0 Hz), 149.8, 145.9, 144.6, 134.8 (d, J = 18.8 Hz), 132.0, 130.0 (d, J = 37.5 Hz), 129.8, 128.0 (d, J = 37.5 Hz), 127.3, 127.0, 125.1, 125.0, 115.9, 115.7 (d, J = 22.5 Hz), 89.4, 74.1, 42.2. HRMS (+ESI) Calcd for $C_{39}H_{30}FN_2O$ $[M+H]^+$: 561.2342; found: 561.2330.
 **3fa**	**2-(4-Chlorophenyl)-3-methyl-4-methylene-6,7,8,9-tetraphenyl-2,3-diazaspiro[4.4]nona-6,8-dien-1-one (3fa):** The title compound was prepared by following the general procedure **2.3** from antipyrine, **1f** (111 mg, 0.5 mmol) and alkyne **2a** (178 mg, 1.0 mmol) which was then purified by column chromatography using 5% EtOAc in hexane to afford yellow solid of **3fa** (181 mg, 63%). M.p.: 113-116 ^{o}C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.29–7.26 (m, 2H), 7.23–7.21 (m, 2H), 7.19–7.13 (m, 10H), 7.13–7.06 (m, 6H), 6.96–6.94 (m, 4H), 4.51 (dd, J = 5.0, 2.2 Hz, 2H), 2.47 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 167.1, 149.6, 145.9, 144.4, 134.6, 134.5, 134.4, 131.5, 130.0, 129.7, 128.8, 127.8, 127.5, 127.2, 126.9, 123.8, 89.5, 74.0, 42.3. HRMS (+ESI) Calcd for $C_{39}H_{30}ClN_2O$ $[M+H]^+$: 577.2046; found: 577.2012.
 **3ga**	**2-(3-Chlorophenyl)-3-methyl-4-methylene-6,7,8,9-tetraphenyl-2,3-diazaspiro[4.4]nona-6,8-dien-1-one (3ga):** The title compound was prepared by following the general procedure **2.3** from antipyrine, **1g** (111 mg, 0.5 mmol) and alkyne **2a** (178 mg, 1.0 mmol) which was then purified by column chromatography using 5% EtOAc in hexane to afford yellow solid of **3ga** (161 mg, 56%). M.p.: 105–110 ^{o}C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.26–7.19 (m, 4H), 7.19–7.07 (m, 16H), 6.96–6.94 (m, 4H), 4.52 (dd, J =10.0, 2.0 Hz, 2H), 2.49 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 167.7, 149.8, 146.2, 144.7, 137.4, 134.8, 134.7, 130.3, 130.0, 128.2, 127.9, 127.5, 127.2, 126.5, 122.6, 120.9, 89.9, 74.4, 42.7. HRMS (+ESI) Calcd for $C_{39}H_{30}ClN_2O$ $[M+H]^+$: 577.2046; found: 577.2013.

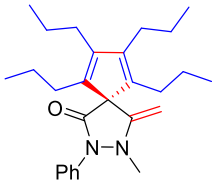
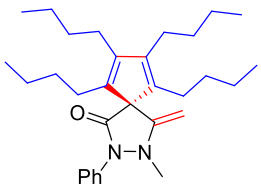
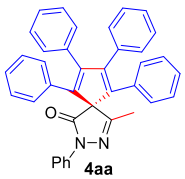
 **3ha**	**(*E*)-3-Methyl-2,6,7,8,9-pentaphenyl-4-propylidene-2,3-diazaspiro[4.4]nona-6,8-dien-1-one and (*Z*)-3-methyl-2,6,7,8,9-pentaphenyl-4-propylidene-2,3-diazaspiro[4.4]nona-6,8-dien-1-one (3ha**, ***E:Z* = 3:1):** The title compound was prepared by following the general procedure **2.3** from antipyrine **1h** (108 mg, 0.5 mmol) and alkyne **2a** (178 mg, 1.0 mmol) which was then purified by column chromatography using 5% EtOAc in hexane to afford white solid of **3ha** (188 mg, 66%). M.p.: 156–160 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.60-7.30 (m, 4H), 7.22–7.05 (m, 17H), 6.98–6.94 (m, 4H), 4.98 (t, *J* = 7.4 Hz, 0.75H), 4.85 (t, *J* = 7.5 Hz, 0.25H), 2.37 (s, 2.25H), 2.18 (t, *J* = 7.5 Hz, 1.5H), 2.12 (t, *J* = 7.5 Hz, 0.5H), 2.08 (s, 0.75H), 1.00 (t, *J* = 6.5 Hz, 2.25H), 0.96 (t, *J* = 6.5 Hz, 0.75H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.5, 166.1, 146.1, 145.4, 145.0, 143.0, 141.0, 139.9, 136.1, 135.2, 135.0, 134.9, 134.8, 130.0, 129.8, 129.7, 129.5, 128.7, 127.8, 127.6, 127.5, 127.1, 127.0, 126.8, 126.7, 126.0, 125.6, 122.4, 121.7, 112.6, 111.5, 73.6, 44.0, 42.9, 20.3, 18.9, 14.4, 13.9. HRMS (+ESI) Calcd for $C_{41}H_{35}N_2O$ $[M+H]^+$: 571.2749; found: 571.2753.
 **3ia**	**3-Methyl-2,6,7,8,9-pentaphenyl-4-(propan-2-ylidene)-2,3-diazaspiro[4.4]nona-6,8-dien-1-one (3ia):** The title compound was prepared by following the general procedure **2.3** from antipyrine, **1i** (108 mg, 0.5 mmol) and alkyne **2a** (178 mg, 1.0 mmol) which was then purified by column chromatography using 5% EtOAc in hexane to afford yellow solid of **3ia** (177 mg, 62%). M.p.: 156–159 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.65 (d, *J* =7.6 Hz, 2H), 7.34 (t, *J* =7.9 Hz, 2H), 7.25–7.05 (m, 17H), 6.95 (d, *J* =6.8 Hz, 4H), 2.0 (s, 3H), 1.73 (s, 3H), 1.71 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.2, 145.7, 143.6, 136.3, 135.0, 129.8, 129.4, 128.7, 127.8, 127.5, 127.0, 126.7, 125.4, 121.2, 116.7, 74.9, 43.0, 20.1, 17.9. HRMS (+ESI) Calcd for $C_{41}H_{35}N_2O$ $[M+H]^+$: 571.2749; found: 571.2784.

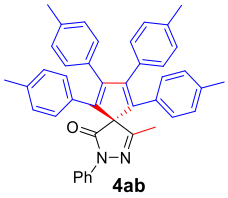
 **3ja**	**2-(4-Chlorophenyl)-3-methyl-6,7,8,9-tetraphenyl-4-(propan-2-ylidene)-2,3-diazaspiro[4.4]nona-6,8-dien-1-one (3ja):** The title compound was prepared by following the general procedure **2.3** from antipyrine **1j** (125 mg, 0.5 mmol) and alkyne **2a** (178 mg, 1.0 mmol) which was then purified by column chromatography using 5% EtOAc in hexane to afford yellow solid of **3ja** (202 mg, 67%). M.p.: 166–170 ^{o}C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.62–7.60 (m, 2H), 7.31–7.29 (m, 2H), 7.12–7.06 (m, 16H), 6.94 (d, J = 6.9 Hz, 4H), 2.00 (s, 3H), 1.73 (s, 3H), 1.71 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.6, 145.8, 143.5, 134.9, 134.7, 130.3, 129.8, 128.8, 127.9, 127.5, 127.1, 126.7, 122.1, 117.2, 74.8, 43.0, 20.1, 17.8. HRMS (+ESI) Calcd for $C_{41}H_{34}ClN_2O$ $[M+H]^+$: 605.2359; found: 605.2364.
 **3ka**	**3-Benzyl-4-methylene-2,6,7,8,9-pentaphenyl-2,3-diazaspiro[4.4]nona-6,8-dien-1-one (3ka):** The title compound was prepared by following the general procedure **2.3** from antipyrine, **1k** (128 mg, 0.5 mmol) and alkyne **2a** (178 mg, 1.0 mmol) which was then purified by column chromatography using 5% EtOAc in hexane to afford yellow solid of **3ka** (238 mg, 77%). M.p.: 191–193 ^{o}C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.29–7.04 (m, 26H), 7.00–6.94 (m, 4H), 4.34 (d, J = 2.0 Hz, 1H), 4.15 (d, J = 2.0 Hz, 1H), 3.81 (s, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.9, 148.6, 145.7, 144.4, 136.7, 135.8, 134.7, 134.6, 130.0, 129.8, 128.8, 128.3, 127.9, 127.8, 127.5, 127.2, 126.8, 126.6, 123.5, 89.7, 74.5, 59.0. HRMS (+ESI) Calcd for $C_{45}H_{35}N_2O$ $[M+H]^+$: 619.2749; found: 619.2725.

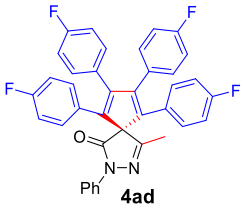
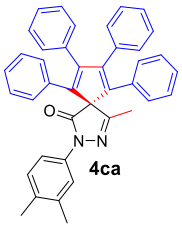
 **3ab**	**3-Methyl-4-methylene-2-phenyl-6,7,8,9-tetra-*p*-tolyl-2,3-diazaspiro[4.4]nona-6,8-dien-1-one (3ab):** The title compound was prepared by following the general procedure **2.3** from antipyrine **1a** (94 mg, 0.5 mmol) and alkyne **2b** (206 mg, 1.0 mmol) which was then purified by column chromatography using 5% EtOAc in hexane to afford yellow solid of **3ab** (227 mg, 76%). M.p.: 112–115 ^{o}C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33–7.32 (m, 3H), 7.19–7.16 (m, 2H), 7.08 (d, J = 8.1 Hz, 4H), 6.94 (d, J = 8.0 Hz, 4H), 6.89 (d, J = 8.0 Hz, 4H), 6.84 (d, J = 8.2 Hz, 4H), 4.47 (d, J = 2.0 Hz, 1H), 4.46 (d, J = 2.0 Hz, 1H), 2.45 (s, 3H), 2.26 (s, 6H), 2.24 (s, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 167.2, 150.4, 145.4, 144.1, 136.5, 136.2, 135.9, 132.0, 131.9, 129.9, 129.5, 128.7, 128.5, 128.2, 126.1, 122.8, 88.8, 73.8, 42.3, 22.6. HRMS (+ESI) Calcd for $C_{43}H_{39}N_2O$ $[M+H]^+$: 599.3062; found: 599.3070.
 **3ac**	**6,7,8,9-Tetrakis(4-methoxyphenyl)-3-methyl-4-methylene-2-phenyl-2,3-diazaspiro[4.4]nona-6,8-dien-1-one (3ac):** The title compound was prepared by following the general procedure **2.3** from antipyrine, **1a** (94 mg, 0.5 mmol) and alkyne **2c** (238 mg, 1.0 mmol) which was then purified by column chromatography using 10% EtOAc in hexane to afford white solid of **3ac** (232 mg, 70%). M.p.: 198–200 ^{o}C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33–7.16 (m, 5H), 7.12 (d, J = 8.8 Hz, 4H), 6.87 (d, J = 8.8 Hz, 4H), 6.69 (d, J = 8.8 Hz, 4H), 6.64 (d, J = 8.7 Hz, 4H), 4.46 (d, J = 11.3 Hz, 2H), 3.73 (s, 12H), 2.50 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 167.7, 158.7, 158.5, 150.9, 144.9, 143.6, 136.2, 131.7, 131.2, 129.0, 127.8, 127.7, 126.5, 123.1, 113.6, 113.3, 89.0, 74.0, 55.2, 42.7. HRMS (+ESI) Calcd for $C_{43}H_{39}N_2O_5$ $[M+H]^+$: 663.2858; found: 663.2833.

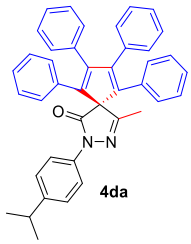
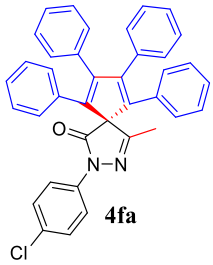
 **3ad**	**6,7,8,9-Tetrakis(4-fluorophenyl)-3-methyl-4-methylene-2-phenyl-2,3-diazaspiro[4.4]nona-6,8-dien-1-one (3ad):** The title compound was prepared by following the general procedure **2.3** from antipyrine, **1a** (94 mg, 0.5 mmol) and alkyne **2d** (214 mg, 1.0 mmol) which was then purified by column chromatography using 7% EtOAc in hexane to afford white solid of **3ad** (203 mg, 66%). M.p.: 190–194 ^{o}C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33 (t, J = 7.8 Hz, 2H), 7.24–7.14 (m, 7H), 6.91–6.85 (m, 8H), 6.80 (t, J = 8.7 Hz, 4H), 4.52 (s, 1H), 4.44 (s, 1H), 2.51 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.5, 163.3 (d, J = 246.3 Hz), 162.1 (d, J = 246.3 Hz), 149.6, 144.9, 144.1, 135.8, 132.0, 131.9, 131.7, 130.6 (d, J = 2.5 Hz), 129.2, 127.0, 123.1, 115.5, 115.2 (d, J = 22.5 Hz), 115.2, 89.6, 74.5, 42.4. HRMS (+ESI) Calcd for $C_{39}H_{27}F_4N_2O$ $[M+H]^+$: 615.2059; found: 615.2382.
 **3ae**	**6,7,8,9-Tetrakis(3-fluorophenyl)-3-methyl-4-methylene-2-phenyl-2,3-diazaspiro[4.4]nona-6,8-dien-1-one (3ae):** The title compound was prepared by following the general procedure **2.3** from antipyrine, **1a** (94 mg, 0.5 mmol) and alkyne **2e** (214 mg, 1.0 mmol) which was then purified by column chromatography using 7% EtOAc in hexane to afford white solid of **3ae** (224 mg, 73%). M.p.: 85-88 ^{o}C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37–7.33 (m, 2H), 7.29–7.29 (m, 2H), 7.21 (t, J = 8.8 Hz, 1H), 7.16–7.08 (m, 4H), 6.99–6.85 (m, 8H), 6.75–6.73 (m, 2H), 6.68–6.65 (m, 2H) 4.56 (d, J = 2.4 Hz, 1H), 4.46 (d, J = 2.3 Hz, 1H), 2.53 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 171.1, 162.3 (d, J = 244.3 Hz), 162.2 (d, J = 244.8 Hz), 148.7, 144.8, 144.4, 136.0, 135.9 (d, J = 5.5 Hz), 135.8 (d, J = 5.5 Hz), 135.3, 129.6 (d, J = 8.3 Hz), 129.5 (d, J = 8.2 Hz), 128.9, 126.8, 125.5 (d, J = 18.6 Hz), 125.4 (d, J = 18.6 Hz), 122.9, 116.6 (d, J = 22.1 Hz), 116.2 (d, J = 22.2 Hz), 114.6 (d, J = 7.5 Hz), 114.5 (d, J = 7.5 Hz), 89.6, 74.1, 42.1. HRMS (+ESI) Calcd for $C_{39}H_{27}F_4N_2O$ $[M+H]^+$: 615.2059; found: 615.2056.

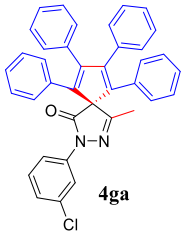
 **3af**	**3,6,8-Trimethyl-4-methylene-2,7,9-triphenyl-2,3-diazaspiro[4.4]nona-6,8-dien-1-one (3ag):** The title compound was prepared by following the general procedure **2.3** from antipyrine, **1a** (94 mg, 0.5 mmol) and alkyne **2g** (116 mg, 1.0 mmol) which was then purified by column chromatography using 7% EtOAc in hexane to afford brown gum of **3ag** (121 mg, 58%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.46 (dd, J =8.7, 1.1 Hz, 2H), 7.41–7.38 (m, 4H), 7.31–7.30 (m, 7H), 7.25–7.21 (m, 2H), 4.42 (d, J =1.9 Hz, 1H), 4.20 (d, J =1.9 Hz, 1H), 2.66 (s, 3H), 1.89 (s, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 168.2, 151.0, 145.2, 141.9, 141.7, 141.6, 136.1, 135.6, 135.3, 129.5, 129.2, 128.9, 128.1, 127.2, 126.9, 126.3, 122.8, 88.1, 73.1, 42.4, 13.9, 11.5. HRMS (+ESI) Calcd for $C_{29}H_{27}N_2O$ $[M+H]^+$: 419.2123; found:. 419.2127.
 **3ag**	**6,8-Diethyl-3-methyl-4-methylene-2,7,9-triphenyl-2,3-diazaspiro[4.4]nona-6,8-dien-1-one (3ag):** The title compound was prepared by following the general procedure **2.3** from antipyrine, **1a** (94 mg, 0.5 mmol) and alkyne **2h** (130 mg, 1.0 mmol) which was then purified by column chromatography using 5% EtOAc in hexane to afford a gum of **3ah** (123 mg, 55%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40-7.19 (m, 15H), 4.45 (s 0.75H), 4.35 (s, 0.25H), 4.25 (s, 0.75H), 4.22 (s, 0.25H), 2.58 (s, 2.25H), 2.45-2.35 (m, 1.5H), 2.35-2.30 (m, 1H), 2.29 (s, 0.75H), 2.24-2.27 (m, 1.5H), 1.14 (t, J = 10.0 Hz, 1.5H), 0.98 (t, J = 10.0 Hz, 2.25H), 0.74 (t, J = 10.0 Hz, 2.25H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 167.8, 167.6, 150.5, 149.9, 147.7, 146.9, 143.4, 142.9, 137.5, 136.1, 135.6, 132.9, 129.5, 129.3, 128.9, 128.6, 128.2, 128.0, 127.9, 127.9, 127.0, 126.1, 126.0, 122.9, 122.5, 88.8, 88.2, 74.1, 72.5, 42.3, 42.2, 19.9, 19.6, 14.8, 13.9. HRMS (+ESI) Calcd for $C_{31}H_{31}N_2O$ $[M+H]^+$: 447.2436; found: 447.2435

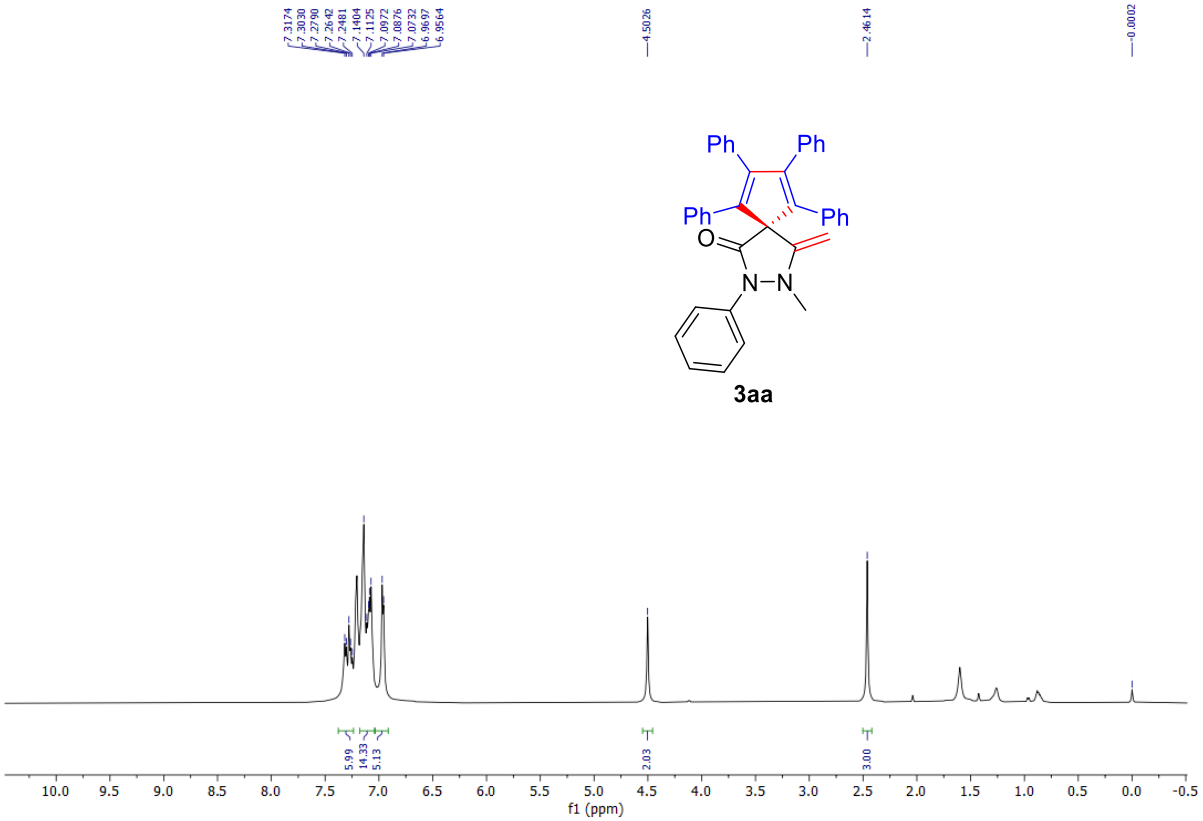
 **3ah**	**3-Methyl-4-methylene-2-phenyl-6,7,8,9-tetrapropyl-2,3-diazaspiro[4.4]nona-6,8-dien-1-one (3ah):** The title compound was prepared by following the general procedure **2.3** from antipyrine, **1a** (94 mg, 0.5 mmol) and alkyne **2h** (110 mg, 1.0 mmol) which was then purified by column chromatography using 5% EtOAc in hexane to afford brown gum of **3ah** (112 mg, 55%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.52 (d, J = 8.5 Hz, 2H), 7.41 (t, J = 7.5 Hz, 2H), 7.21 (t, J = 7.0 Hz, 1H), 4.38 (d, J = 1.6 Hz, 1H), 3.93 (d, J = 1.7 Hz, 1H), 2.89 (s, 3H), 2.22–2.18 (m, 8H), 1.47–1.43 (m, 8H), 0.92 (t, J = 7.5 Hz, 6H), 0.83 (t, J = 7.0 Hz, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 169.1, 152.0, 143.9, 142.0, 136.4, 128.8, 125.7, 122.1, 86.8, 70.8, 42.2, 28.0, 23.0, 22.2, 14.6, 14.2. HRMS (+ESI) Calcd for $C_{27}H_{39}N_2O$ $[M+H]^+$: 407.3062; found: 407.3084.
 **3ai**	**6,7,8,9-Tetrabutyl-3-methyl-4-methylene-2-phenyl-2,3-diazaspiro[4.4]nona-6,8-dien-1-one (3ai):** The title compounds were prepared by following the general procedure **2.3** from antipyrine, **1a** (94 mg, 0.5 mmol) and alkyne **2i** (138 mg, 1.0 mmol) which was then purified by column chromatography using 5% EtOAc in hexane to afford brown gummy of **3ai** (120 mg, 52%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.52 (d, J = 8.5 Hz, 2H), 7.40 (t, J = 7.0 Hz, 2H), 7.20 (t, J = 8.5 Hz, 1H), 4.38 (d, J = 1.6 Hz, 1H), 3.93 (d, J = 1.7 Hz, 1H), 2.9 (s, 3H), 2.27–2.16 (m, 8H), 1.44–1.22 (m, 16H), 0.92 (t, J = 7.5 Hz, 6H), 0.83 (t, J = 7.4 Hz, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 169.3, 152.1, 144.2, 142.0, 136.6, 128.8, 125.8, 122.2, 86.9, 71.0, 42.4, 36.6, 32.3, 31.1, 26.6, 25.8, 23.2, 22.9, 14.0, 13.9. HRMS (+ESI) Calcd for $C_{31}H_{47}N_2O$ $[M+H]^+$: 463.3688; found: 463.3619.
 **4aa**	**4-Methyl-2,6,7,8,9-pentaphenyl-2,3-diazaspiro[4.4]nona-3,6,8-trien-1-one (4aa):** To a solution of **3aa** (100 mg, 0.18 mmol) in anhydrous toluene (20 mL), Lawessons reagent (1.5 equiv) was added. The reaction mixture was then refluxed for 6 hours. The solvent was removed under vacuo and the crude product obtained was purified by silica gel (100-200 mesh) column chromatography using 3% EtOAc

	in hexane as the eluent to afford compound **4aa** (89 mg, 47%). One pot synthesis of **4aa** has been carried out by following the general procedure **2.4** from antipyrine, **1a** (94 mg, 0.5 mmol) and alkyne **2a** (178 mg, 1.0 mmol), which was then purified by column chromatography using 5% EtOAc in hexane to afford **4aa** (153 mg, 29%). white solid, m.p.: 211-213 ^{o}C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.68 (d, J = 8.6 Hz, 2H), 7.35 (t, J = 8.5 Hz, 2H), 7.19–7.09 (m, 13H), 7.03–7.01 (m, 4H), 6.96 (d, J = 8.0 Hz, 4H), 2.06 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 169.6, 158.8, 149.2, 138.0, 137.7, 134.3, 133.5, 129.9, 128.8, 128.5, 128.4, 127.8, 127.6, 127.3, 125.4, 78.5, 14.0. HRMS (+ESI) Calcd for $C_{38}H_{29}N_2O$ $[M+H]^+$: 529.2274; found: 529.2198.
 **4ab**	**4-Methyl-2-phenyl-6,7,8,9-tetra-p-tolyl-2,3-diazaspiro[4.4]nona-3,6,8-trien-1-one (4ab):** To a solution of **3ab** (100 mg, 0.17 mmol) in anhydrous toluene (20 mL), Lawessons reagent (1.5 equiv) was added. The reaction mixture was then refluxed for 6 hours. The solvent was removed under vacuo and the crude product obtained was purified by silica gel (100-200 mesh) column chromatography using 3% EtOAc in hexane as the eluent to afford compound **4ab** (89 mg, 45%). One pot synthesis of **4ab** has been carried out by following the general procedure **2.4** from antipyrine, **1a** (94 mg, 0.5 mmol) and alkyne **2b** (206 mg, 1.0 mmol), which was then purified by column chromatography using 5% EtOAc in hexane to afford **4ab** (198 mg, 34%). White solid, m.p.: 196-200 ^{o}C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.72 (dd, J = 8.6, 1.0 Hz, 2H), 7.38–7.35 (m, 2H), 7.18 (t, J = 7.4 Hz, 1H), 7.0–6.88 (m, 12H), 6.88–6.80 (m, 4H), 2.27 (s, 6H), 2.21 (s, 6H), 2.04 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.0, 159.5, 148.7, 137.8, 137.2, 137.1, 136.8, 131.5, 130.8, 129.8, 129.0, 128.7, 128.5, 128.3, 125.2, 119.5, 78.3, 21.2, 21.1, 13.9. HRMS (+ESI) Calcd for $C_{42}H_{37}N_2O$ $[M+H]^+$: 585.2900; found: 585.2627.

 **4ad**	**6,7,8,9-Tetrakis(4-fluorophenyl)-4-methyl-2-phenyl-2,3-diazaspiro[4.4]nona-3,6,8-trien-1-one (4ad):** To a solution of **3ab** (100 mg, 0.17 mmol) in anhydrous toluene (20 mL), Lawessons reagent (1.5 equiv) was added. The reaction mixture was then refluxed for 6 hours. The solvent was removed under vacuo and the crude product obtained was purified by silica gel (100-200 mesh) column chromatography using 3% EtOAc in hexane as the eluant to afford compound **4ad** (85.6 mg, 42%). One pot synthesis of **4ad** has been carried out by following the general procedure **2.4** from antipyrine, **1a** (94 mg, 0.5 mmol) and alkyne **2d** (214 mg, 1.0 mmol), which was then purified by column chromatography using 5% EtOAc in hexane to afford **4ad** (186 mg, 31%). White solid, m.p.: 185-189 ^{o}C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.67 (d, J = 8.5Hz, 2H), 7.37 (t, J = 8.5 Hz, 2H), 7.20 (t, J = 7.5 Hz, 1H), 6.99–6.97 (m, 4H), 6.92–6.80 (m, 12H), 2.05 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 169.1, 162.1 (d, J = 247.3 Hz), 162.0 (d, J = 247.3 Hz), 158.1, 147.8, 137.4, 137.2, 131.6 (d, J = 8.0 Hz), 130.1 (d, J = 8.1 Hz), 129.6 (d, J = 3.3 Hz), 129.6 (d, J = 3.5 Hz), 128.9, 125.7, 119.4, 115.7 (d, J = 21.4 Hz), 78.5, 14.1. HRMS (+ESI) Calcd for $C_{38}H_{25}F_4N_2O$ $[M+H]^+$: 601.1898; found: 601.1717.
 **4ca**	**2-(3,4-Dimethylphenyl)-4-methyl-6,7,8,9-tetraphenyl-2,3-diazaspiro[4.4]nona-3,6,8-trien-1-one (4ca):** To a solution of **3ca** (100 mg, 0.18 mmol) in anhydrous toluene (20 mL), Lawessons reagent (1.5 equiv) was added. The reaction mixture was then refluxed for 6 hours. The solvent was removed under vacuo and the crude product obtained was purified by silica gel (100-200 mesh) column chromatography using 3% EtOAc in hexane as the eluent to afford compound **4ca** (74 mg, 37%). One pot synthesis of **4ca** has been carried out by following the general procedure **2.4** from antipyrine, **1c** (94 mg, 0.5 mmol) and alkyne **2a** (138 mg, 1.0 mmol) which was then purified by column chromatography using 5% EtOAc in hexane to afford **4ca** (155 mg, 28%). Sticky solid. ^{1}H NMR (400 MHz, $CDCl_3$) ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (d, J = 2.3 Hz,

	1H), 7.39 (dd, *J* = 8.1, 2.4 Hz, 1H), 7.19–6.94 (m, 21H), 2.24 (d, *J* = 6.6 Hz, 6H), 2.07 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 169.6, 158.7, 149.3, 138.2, 137.3, 135.7, 134.5, 134.2, 133.7, 130.2, 130.0, 128.7, 128.6, 128.4, 128.0, 127.8, 127.5, 121.1, 117.5, 78.7, 20.0, 19.4, 14.2. HRMS (+ESI) Calcd for $C_{40}H_{33}N_2O$ $[M+H]^+$: 557.2587; found: 557.2446.
 4da	**2-(4-Isopropylphenyl)-4-methyl-6,7,8,9-tetraphenyl-2,3-diazaspiro[4.4]nona-3,6,8-trien-1-one (4da):** To a solution of **3da** (100 mg, 0.17 mmol) in anhydrous toluene (20 mL), Lawessons reagent (1.5 equiv) was added. The reaction mixture was then refluxed for 6 hours. The solvent was removed under vacuo and the crude product obtained was purified by silica gel (100-200 mesh) column chromatography using 3% EtOAc in hexane as the eluant to afford compound **4da** (79 mg, 41%). One pot synthesis of **4da** has been carried out by following the general procedure **2.4** from antipyrine, **1d** (94 mg, 0.5 mmol) and alkyne **2a** (138 mg, 1.0 mmol) which was then purified by column chromatography using 5% EtOAc in hexane to afford brown gummy of **4da** (159 mg, 28%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (d, *J* = 8.6 Hz, 2H), 7.21 (d, *J* = 2.1 Hz, 1H), 7.20 (d, *J* = 1.9 Hz, 1H), 7.17 – 7.01 (m, 17H), 6.96 (t, *J* = 1.5 Hz, 2H), 6.94 (d, *J* = 1.7 Hz, 2H), 3.00–2.80 (m, 1H), 2.06 (s, 3H), 1.22 (d, *J* = 6.9 Hz, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 169.7, 158.8, 149.3, 146.4, 138.2, 135.6, 134.5, 133.7, 130.1, 128.7, 128.6, 128.4, 128.0, 127.8, 127.5, 126.9, 120.2, 78.6, 33.8, 24.1, 14.2. HRMS (+ESI) Calcd for $C_{41}H_{35}N_2O$ $[M+H]^+$: 571.2744; found: 571.2837.
 4fa	**2-(4-Chlorophenyl)-4-methyl-6,7,8,9-tetraphenyl-2,3-diazaspiro[4.4]nona-3,6,8-trien-1-one (4fa):** To a solution of **3fa** (100 mg, 0.17 mmol) in anhydrous toluene (20 mL), Lawessons reagent (1.5 equiv) was added. The reaction mixture was then refluxed for 6 hours. The solvent was removed under vacuo and the crude product obtained was purified by silica gel (100-200 mesh) column chromatography using 3% EtOAc in hexane as the eluant to afford compound **4fa** (74 mg, 39%). One pot synthesis of **4fa** has

	been carried out by following the general procedure **2.4** from antipyrine, **1f** (94 mg, 0.5 mmol) and alkyne **2a** (138 mg, 1.0 mmol) which was then purified by column chromatography using 5% EtOAc in hexane to afford **4fa** (146 mg, 26%). Sticky solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (d, J = 2.2 Hz, 1H), 7.66 (d, J = 2.2 Hz, 1H), 7.27-7.24 (m, 2H), 7.23–6.92 (m, 20H), 2.06 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 169.8, 159.4, 149.5, 138.8, 137.9, 134.5, 134.2, 133.4, 130.1, 129.9, 128.6, 128.5, 127.9, 127.8, 127.5, 125.2, 119.1, 117.0, 78.6, 14.1. HRMS (+ESI) Calcd for $C_{38}H_{28}N_2OCl$ $[M+H]^+$: 563.1885; found 563.1721.
 **4ga**	**2-(3-Chlorophenyl)-4-methyl-6,7,8,9-tetraphenyl-2,3-diazaspiro[4.4]nona-3,6,8-trien-1-one (4ga):** To a solution of **3aa** (100 mg, 0.17 mmol) in anhydrous toluene (20 mL), Lawessons reagent (1.5 equiv) was added. The reaction mixture was then refluxed for 6 hours. The solvent was removed under vacuo and the crude product obtained was purified by silica gel (100-200 mesh) column chromatography using 3% EtOAc in hexane as the eluant to afford compound **4ga** (68 mg, 36%). One pot synthesis of **4ga** has been carried out by following the general procedure **2.4** from antipyrine, **1g** (94 mg, 0.5 mmol) and alkyne **2a** (138 mg, 1.0 mmol) which was then purified by column chromatography using 5% EtOAc in hexane to afford brown gummy of **4ga** (140 mg, 25%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (s, 1H), 7.66 (s, 1H), 7.30 (d, J = 8.9 Hz, 2H), 7.16 –7.07 (m, 12H), 6.900–6.92(m, 8H), 2.06 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 169.9, 159.4, 149.4, 138.8, 136.4, 134.3, 133.5, 130.6, 130.0, 128.9, 128.6, 128.0, 127.8, 127.6, 120.6, 78.6, 14.1. HRMS (+ESI) Calcd for $C_{38}H_{28}N_2OCl$ $[M+H]^+$: 563.1885; found 563.1707.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3.00
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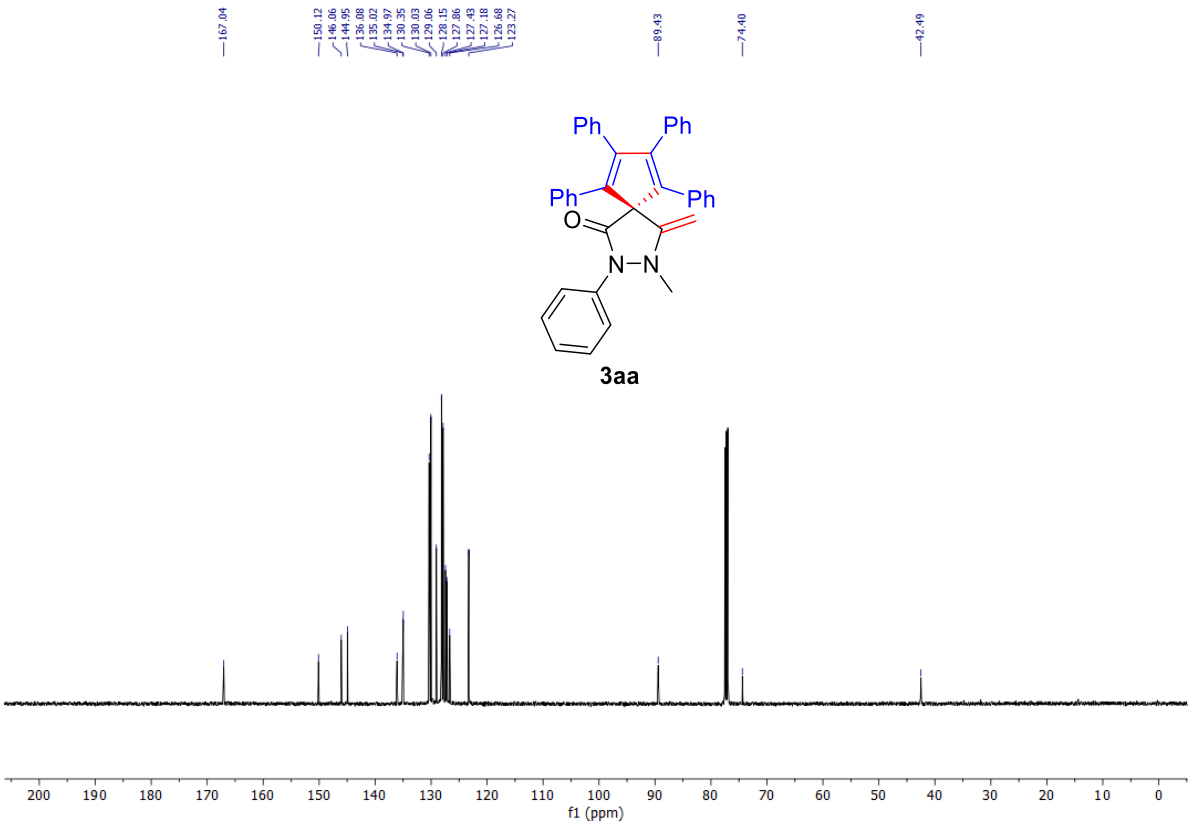
3aa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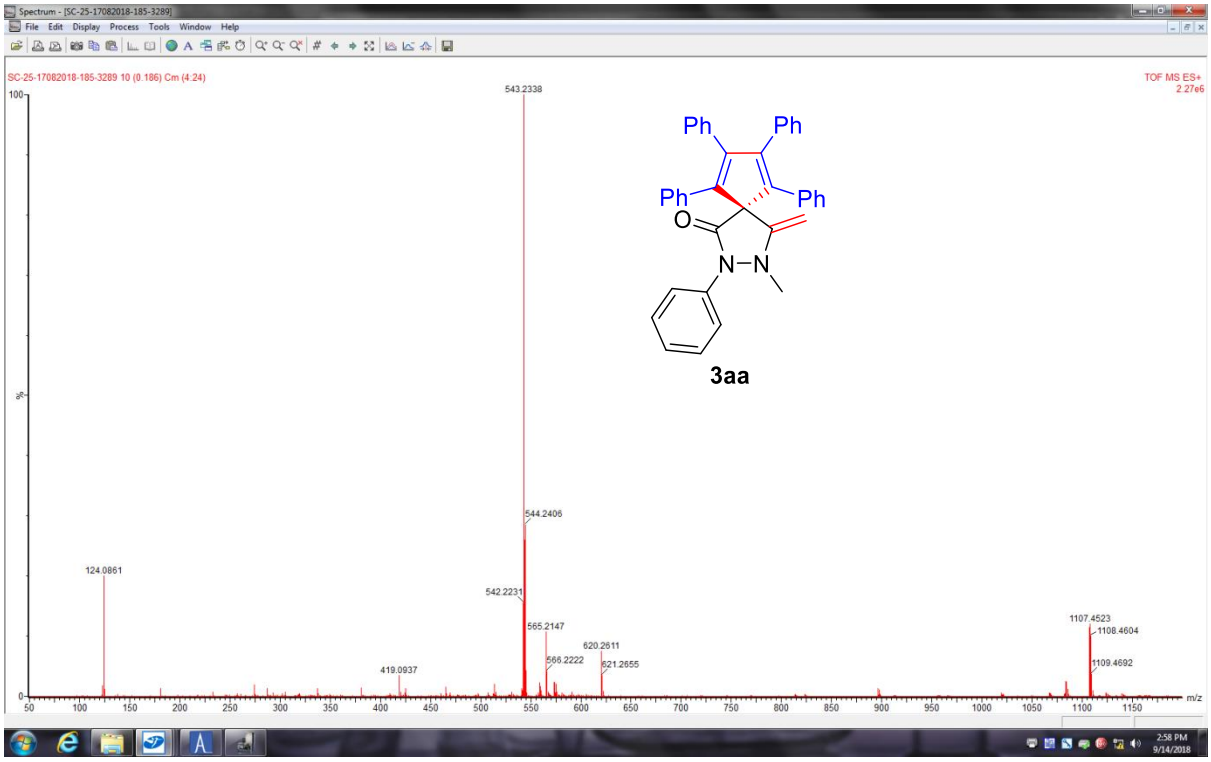
3aa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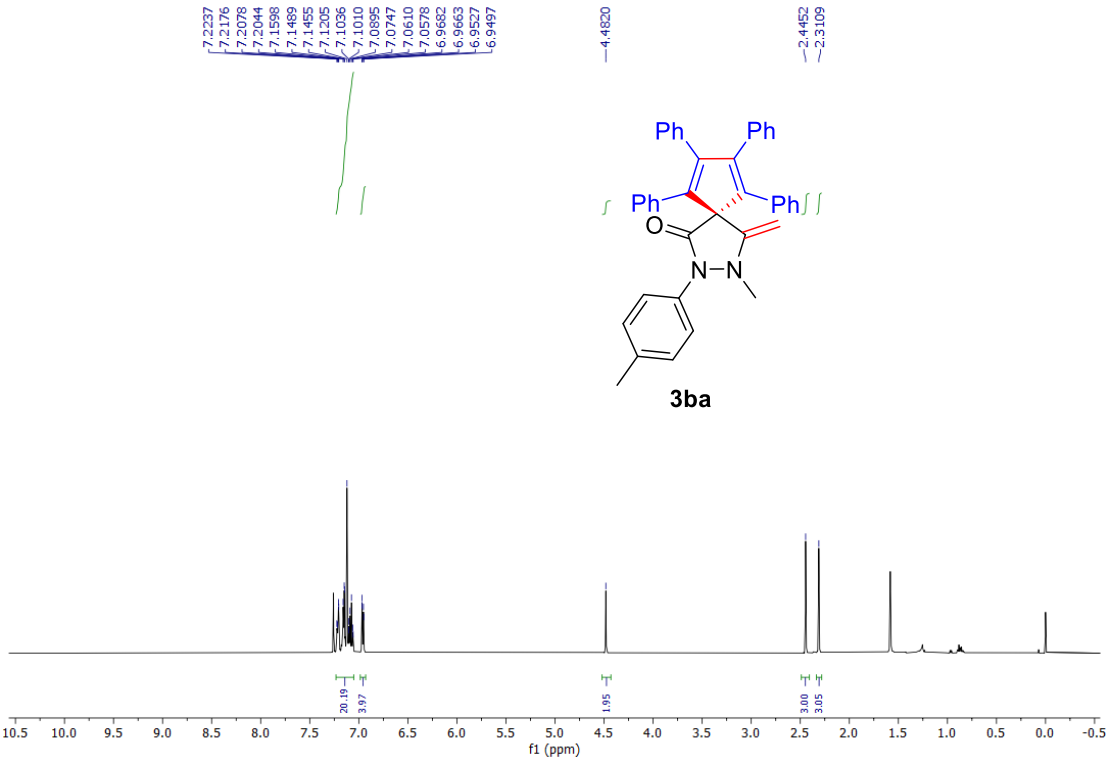
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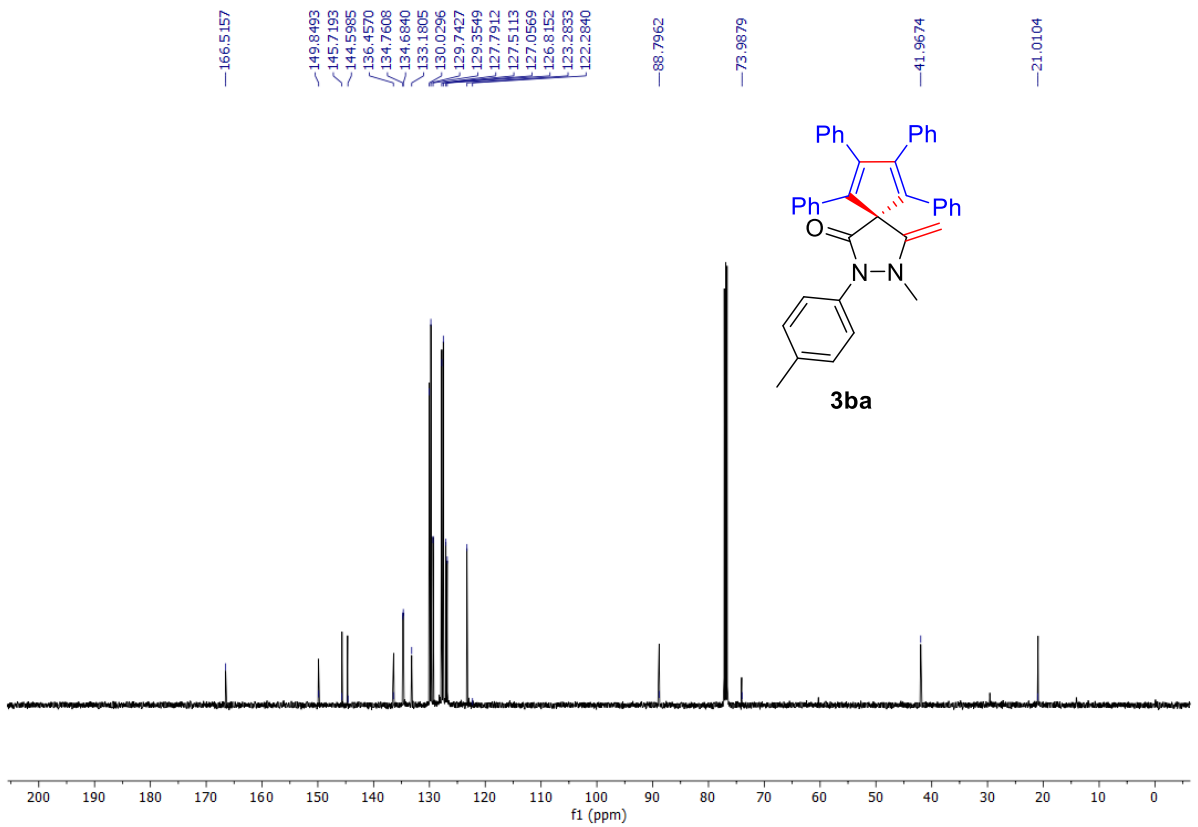
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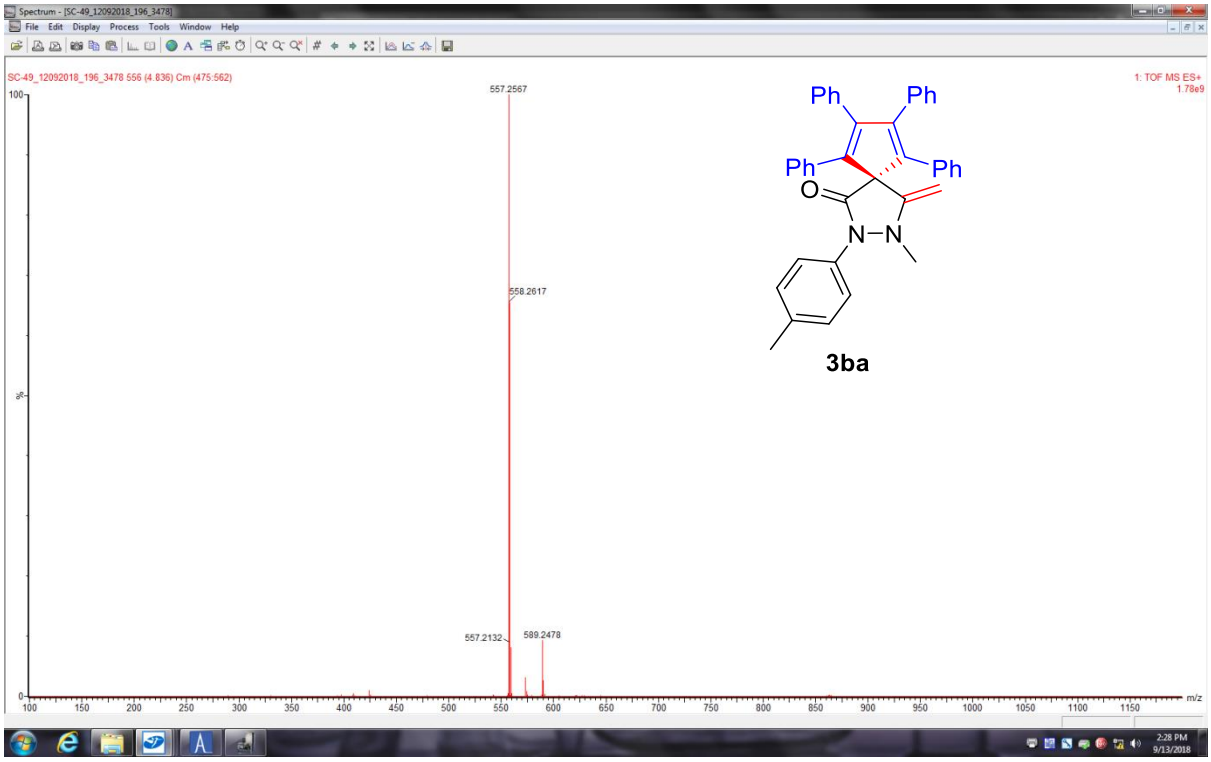
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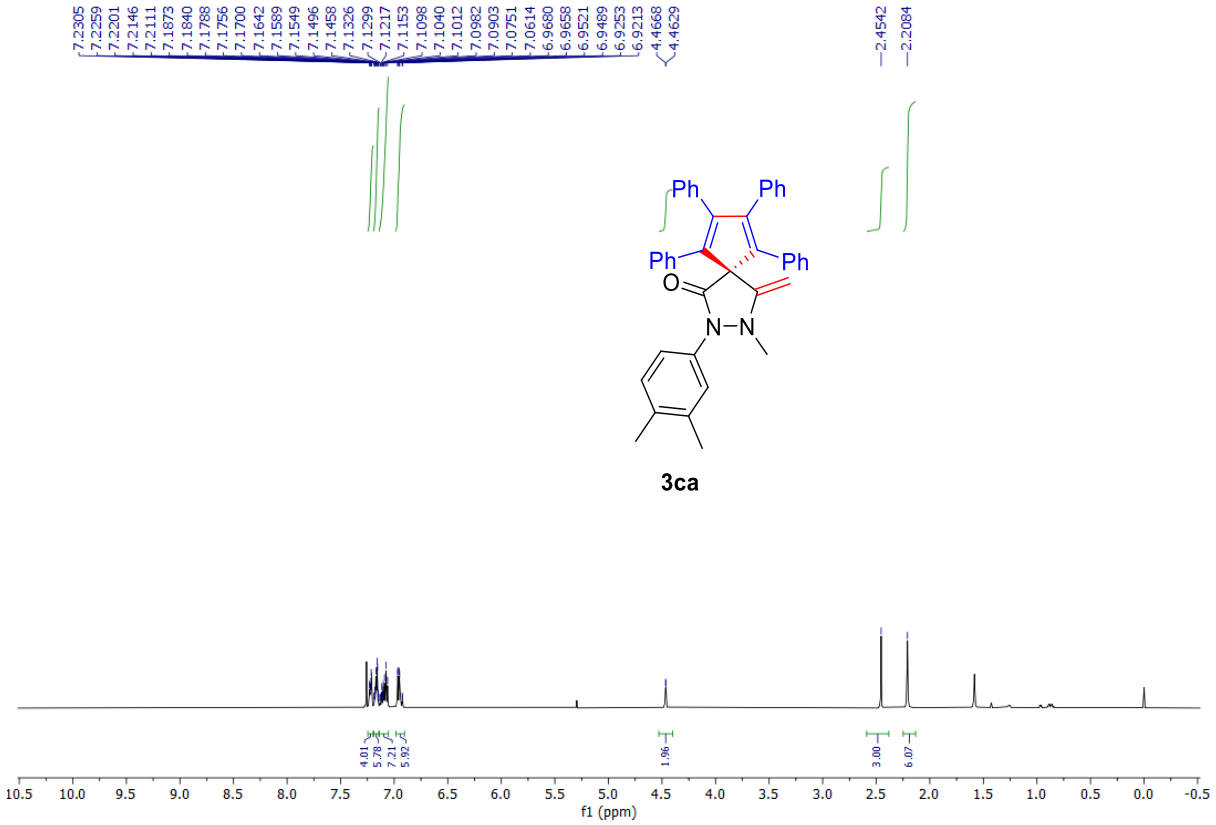
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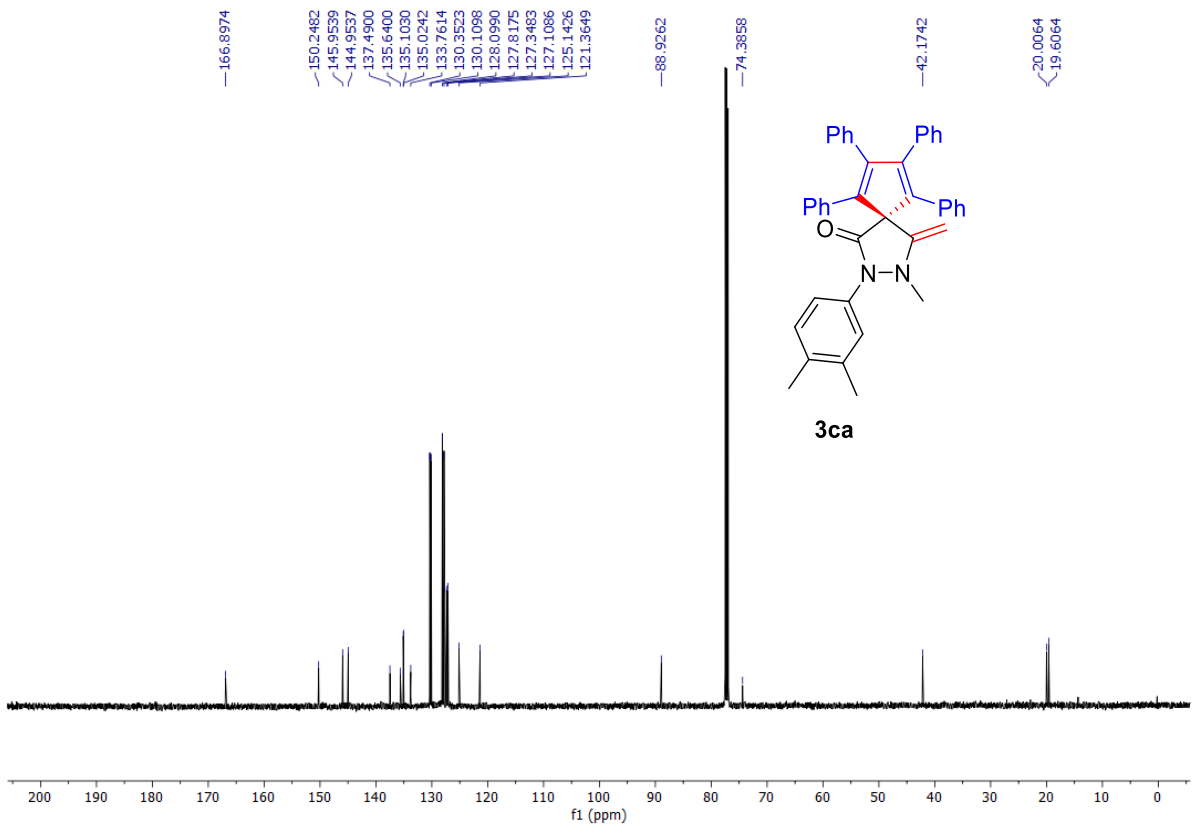
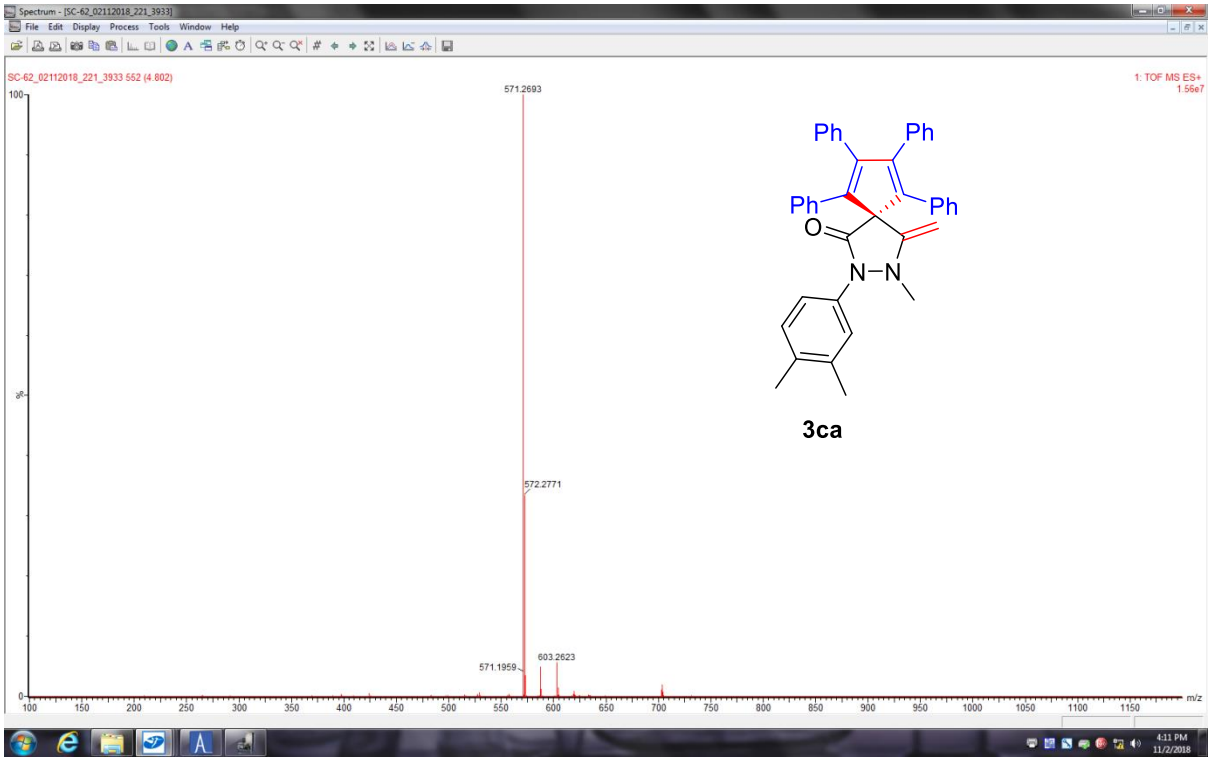
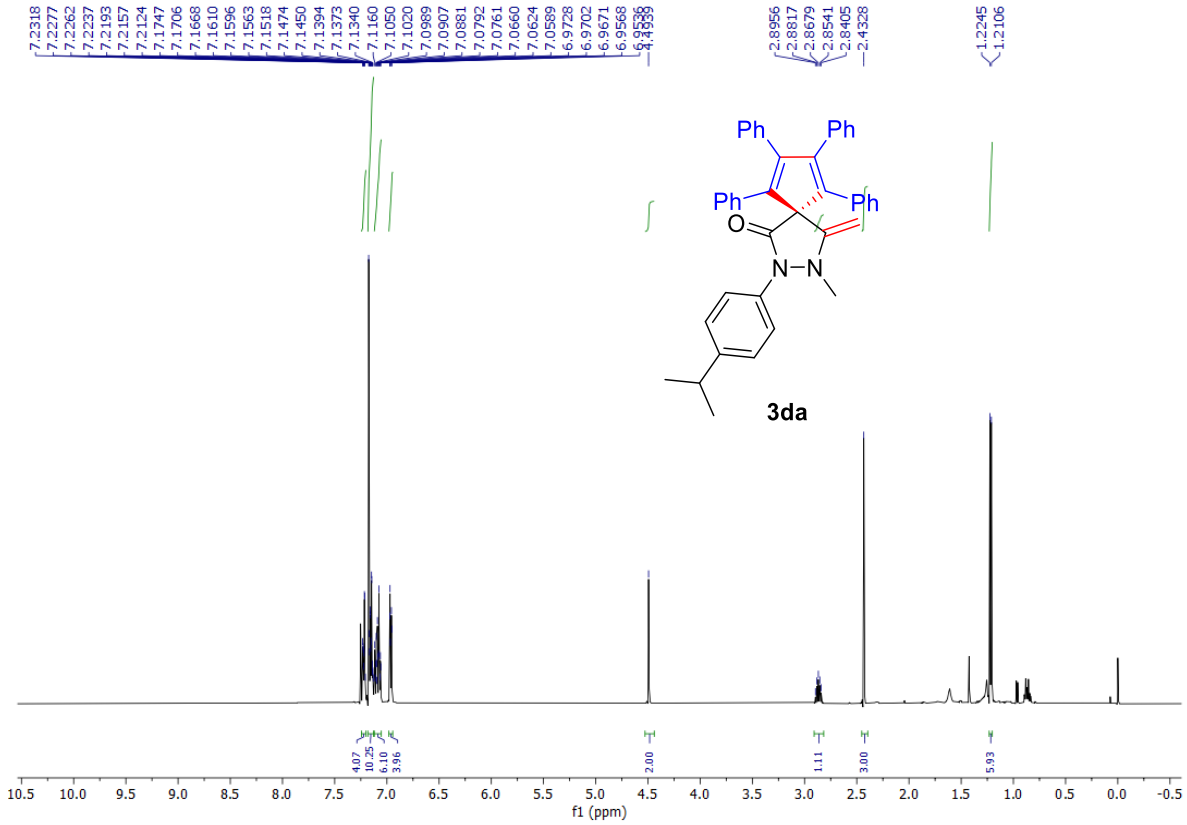
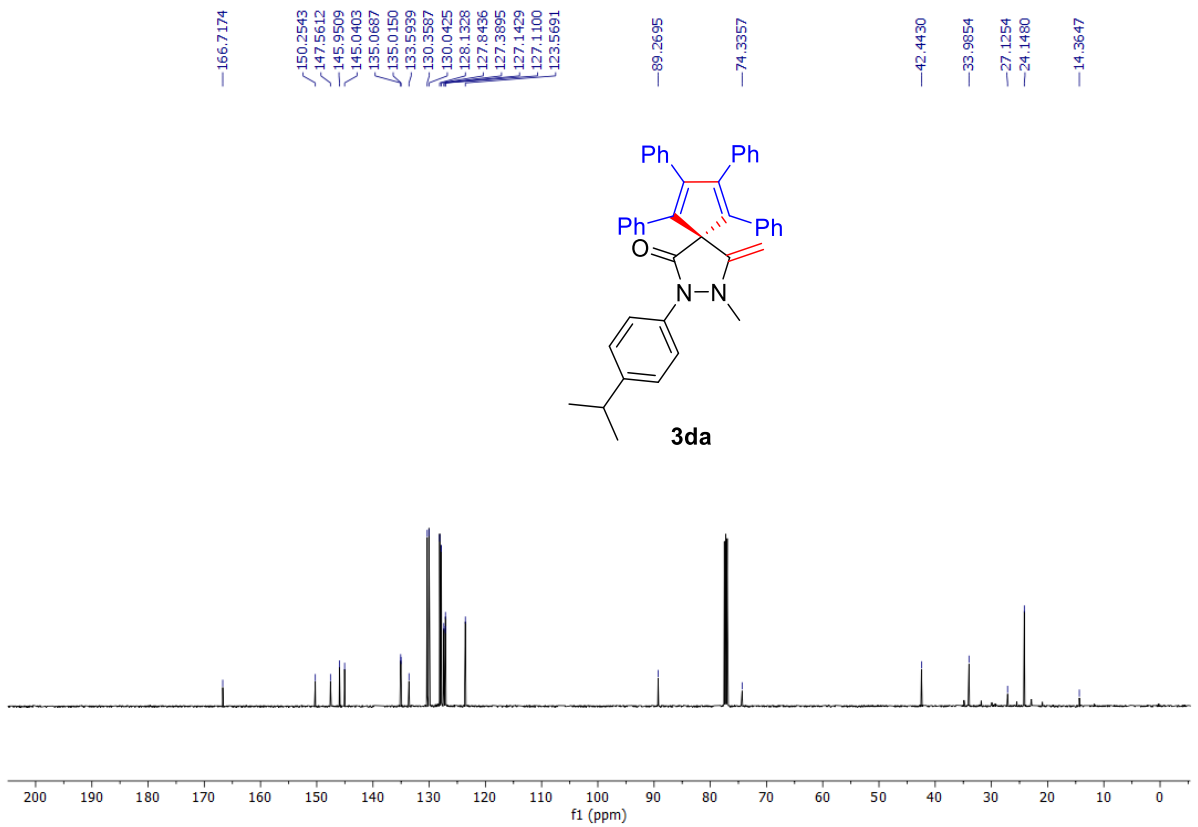
f1 (ppm)

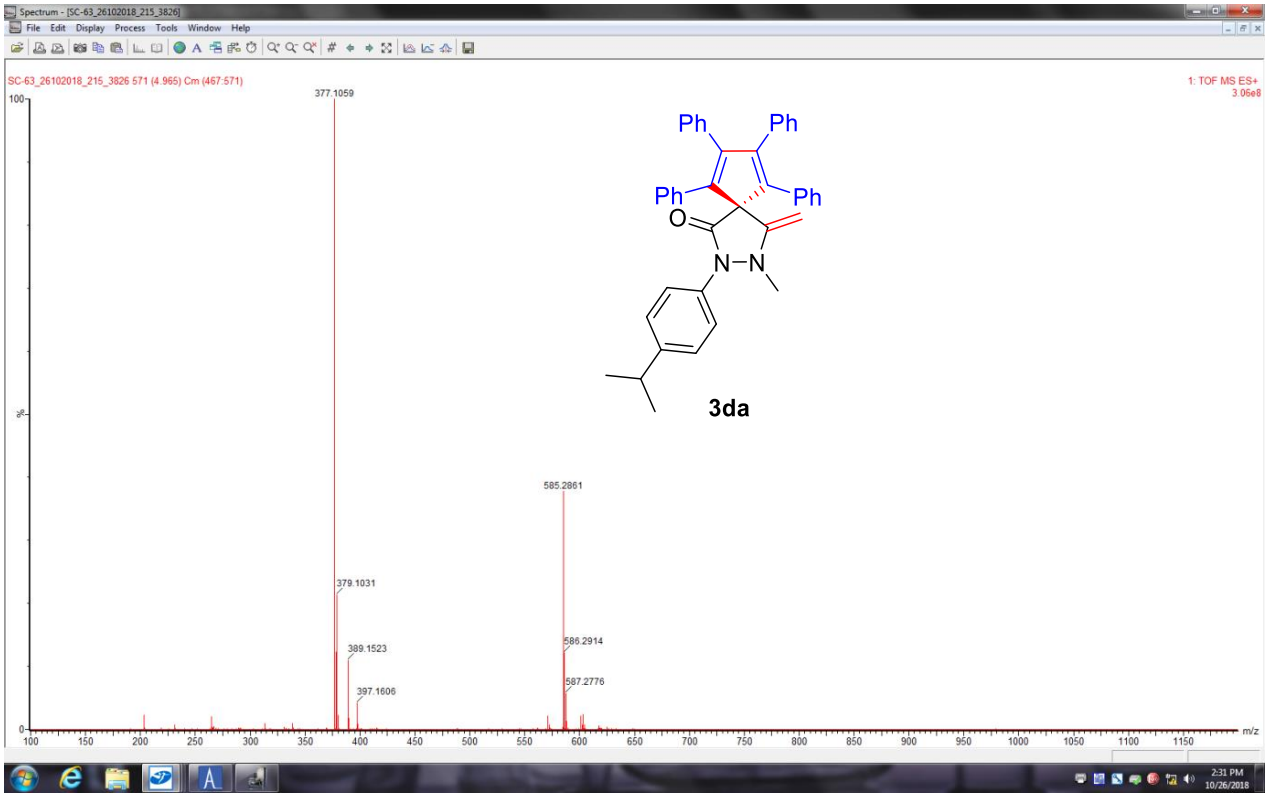
3ca

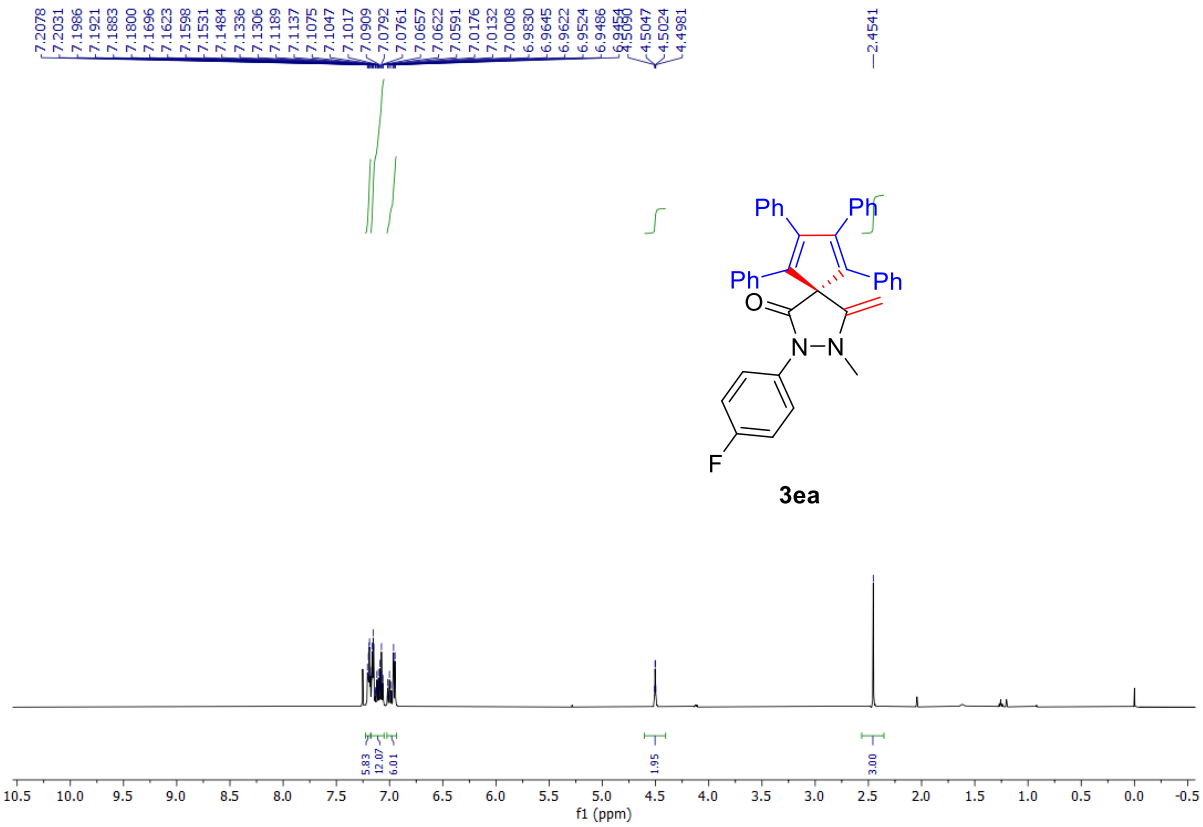

166.8974
150.2482
145.9539
144.9537
137.4900
135.6400
135.1030
135.0242
133.7614
130.3523
130.1098
128.0990
127.8175
127.3483
127.1086
125.1426
121.3649
88.9262
74.3858
42.1742
20.0064
19.6064
Ph
Ph
Ph
Ph
O
N–N
3ca
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


Spectrum - [SC-62_02112018_221_3933]
File Edit Display Process Tools Window Help
SC-62_02112018_221_3933 552 (4.802)
1: TOF MS ES+
1.56e7
571.2693
572.2771
571.1959
603.2623
Ph
Ph
Ph
Ph
O
N–N
3ca
m/z

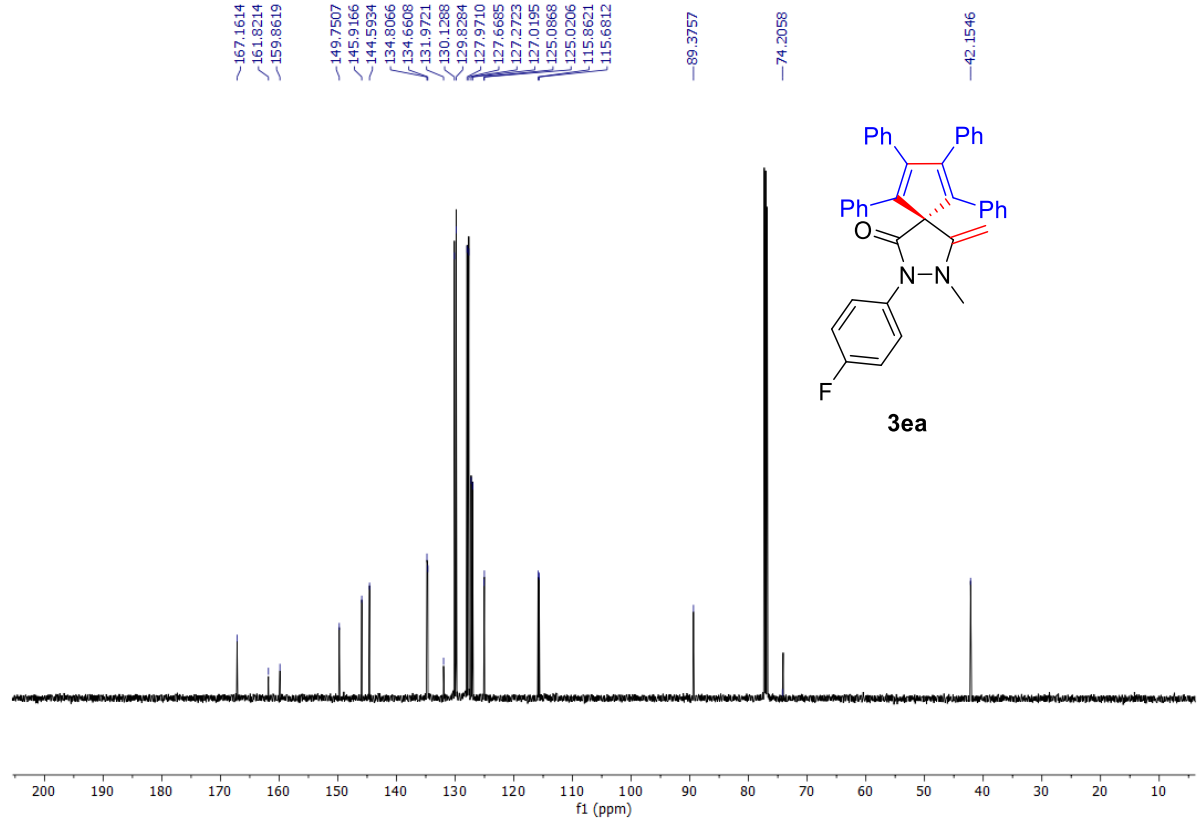

Ph
Ph
Ph
Ph
O
N–N
3da
f1 (ppm)


166.7174
150.2543
147.5612
145.9509
145.0403
135.0687
135.0150
133.5939
130.3587
130.0425
128.1328
127.8436
127.3895
127.1429
127.1100
123.5691
89.2695
74.3357
42.4430
33.9854
27.1254
24.1480
14.3647
Ph
Ph
Ph
Ph
O
N–N
3da
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

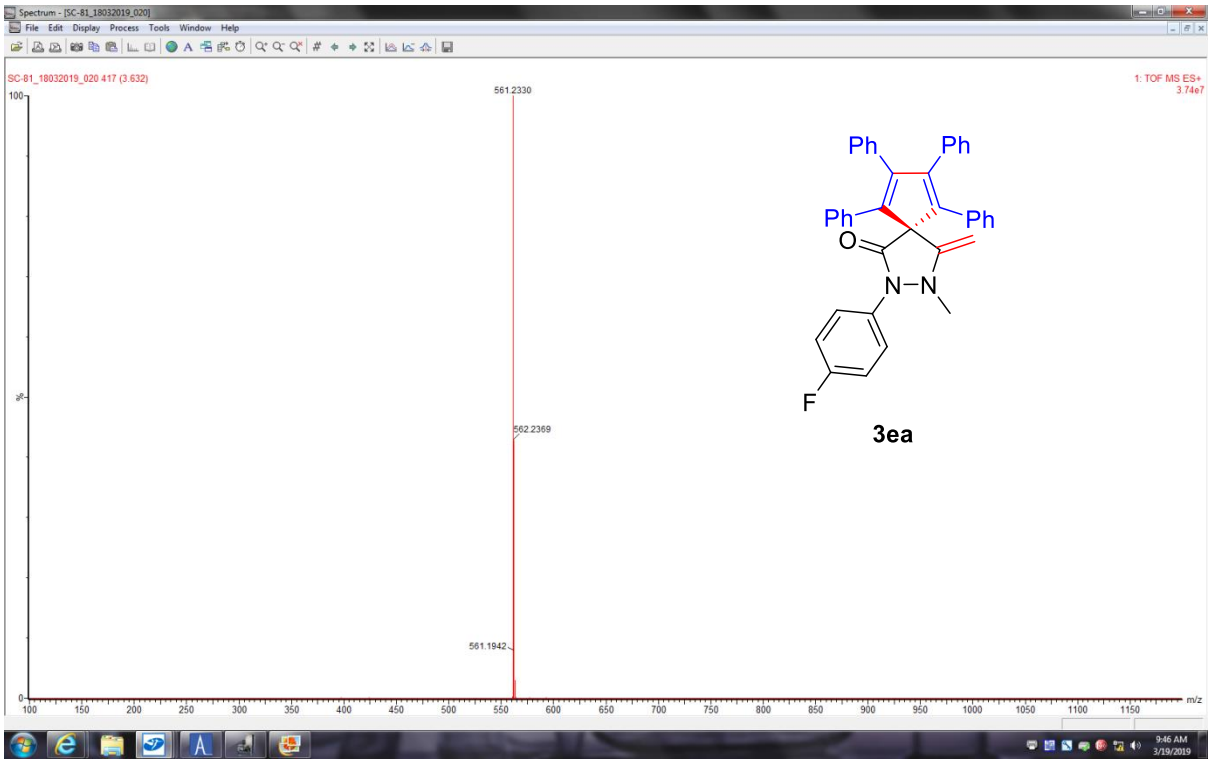

Spectrum - [SC-63_26102018_215_3826]
File Edit Display Process Tools Window Help
SC-63_26102018_215_3826 571 (4.965) Cm (467:571)
1: TOF MS ES+
3.06e8
377.1059
585.2861
379.1031
389.1523
397.1606
586.2914
587.2776
Ph
Ph
Ph
Ph
O
N–N
3da
m/z
2:31 PM
10/26/2018

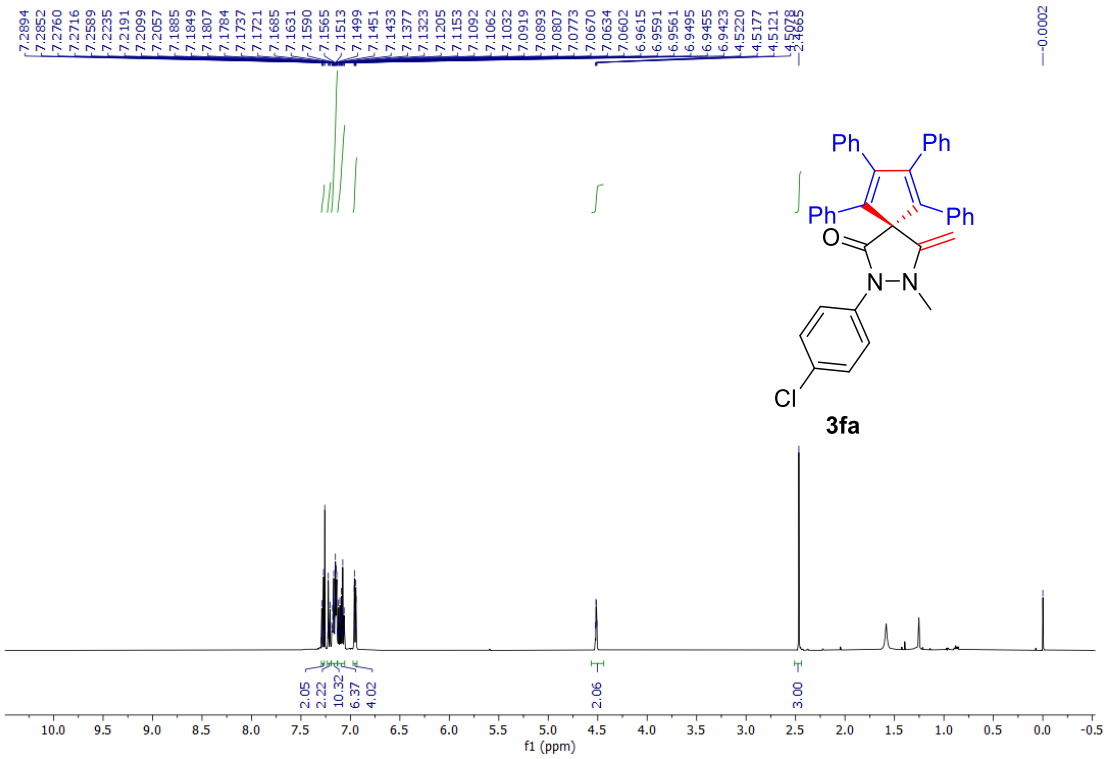

7.2078
7.2031
7.1986
7.1921
7.1883
7.1800
7.1696
7.1623
7.1598
7.1531
7.1484
7.1336
7.1306
7.1189
7.1137
7.1075
7.1047
7.1017
7.0909
7.0792
7.0761
7.0657
7.0622
7.0591
7.0176
7.0132
7.0008
6.9830
6.9645
6.9622
6.9524
6.9486
6.9454
4.5090
4.5047
4.5024
4.4981
2.4541
Ph
Ph
Ph
Ph
O
N–N
F
5.83
12.07
6.01
1.95
3.00
f1 (ppm)

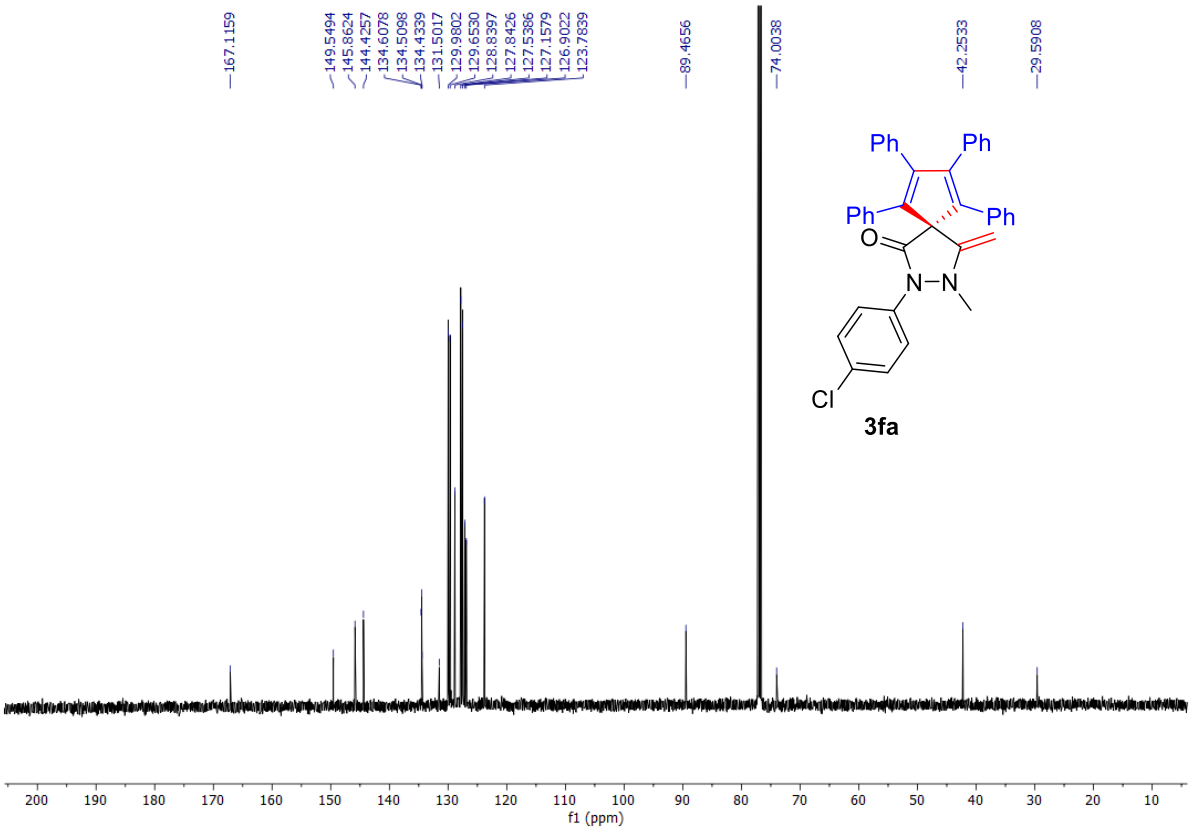
3ea

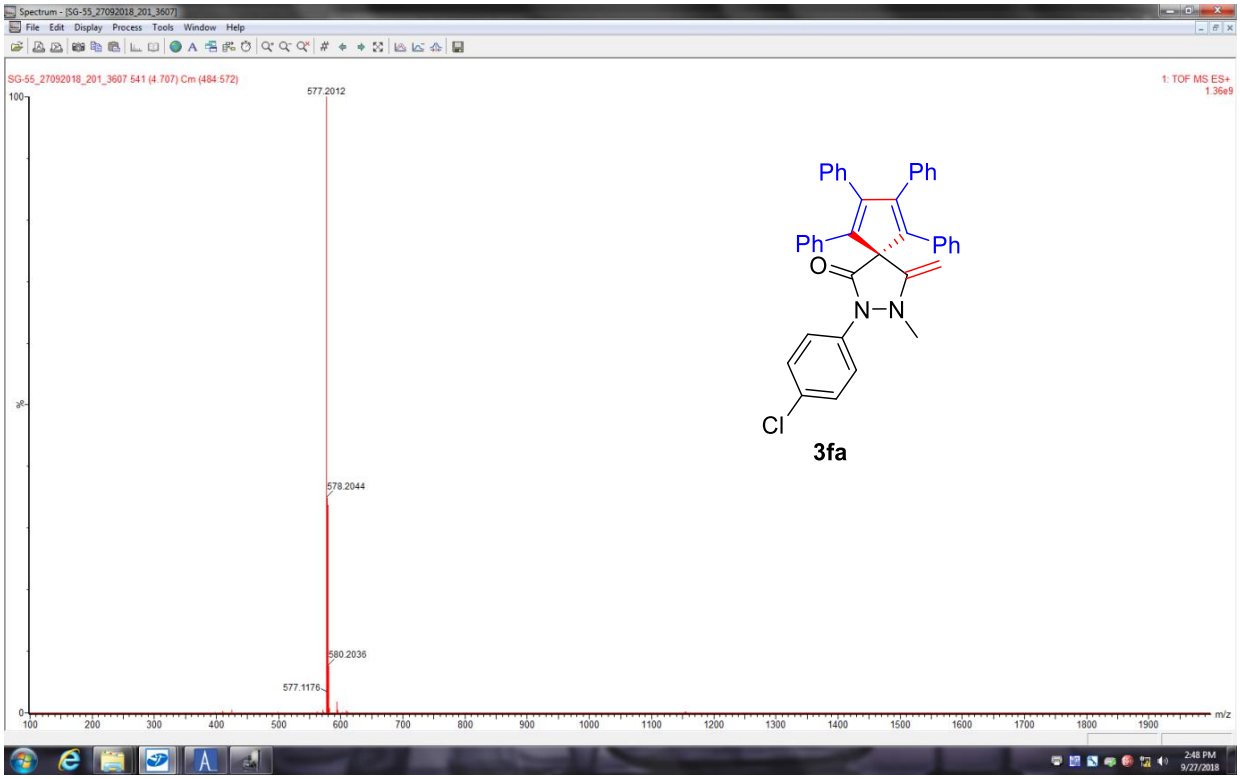

167.1614
161.8214
159.8619
149.7507
145.9166
144.5934
134.8066
134.6608
131.9721
130.1288
129.8284
127.9710
127.6685
127.2723
127.0195
125.0868
125.0206
115.8621
115.6812
89.3757
74.2058
42.1546
Ph
Ph
Ph
Ph
O
N–N
F
f1 (ppm)

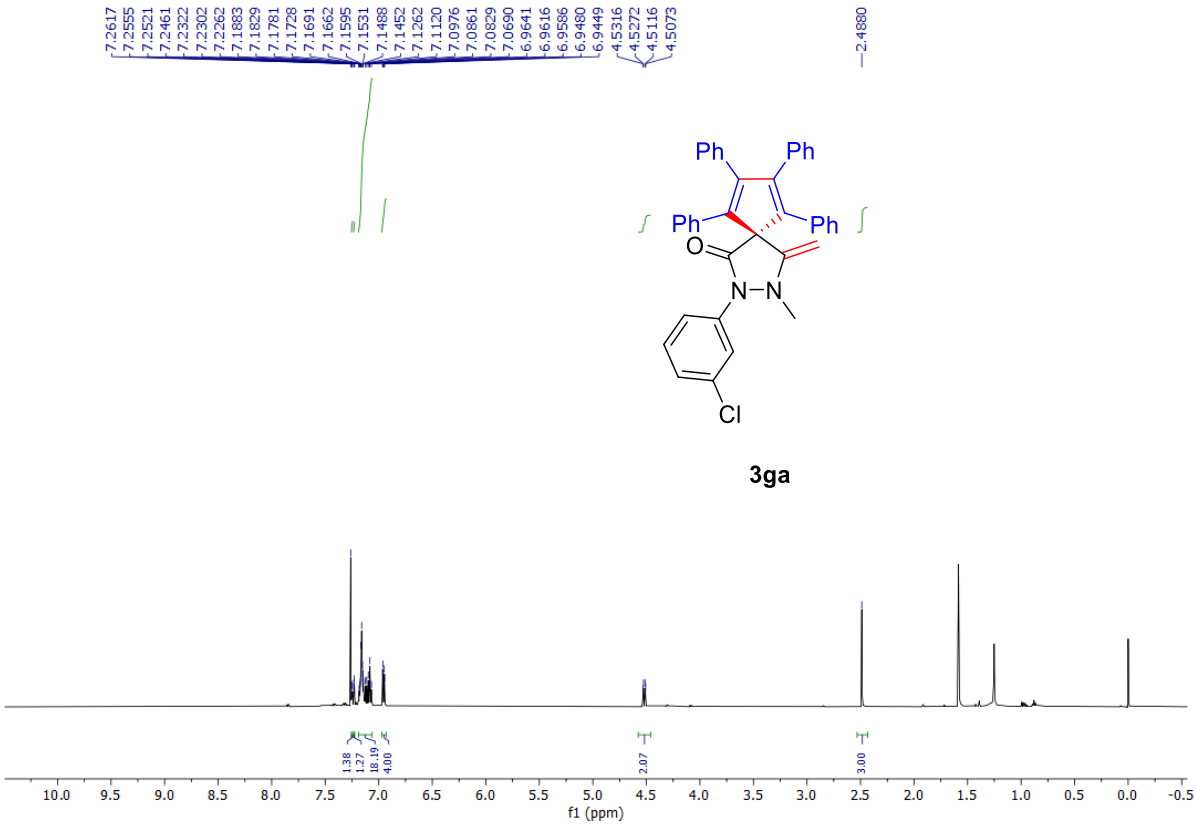
3ea


Spectrum - [SC-81_18032019_020]
File Edit Display Process Tools Window Help
SC-81_18032019_020 417 (3.632)
1: TOF MS ES+
3.74e7
561.2330
562.2369
561.1942
100
%
0
100 150 200 250 300 350 400 450 500 550 600 650 700 750 800 850 900 950 1000 1050 1100 1150
m/z
Ph
Ph
Ph
Ph
O
N–N
F
3ea
9:46 AM
3/19/2019

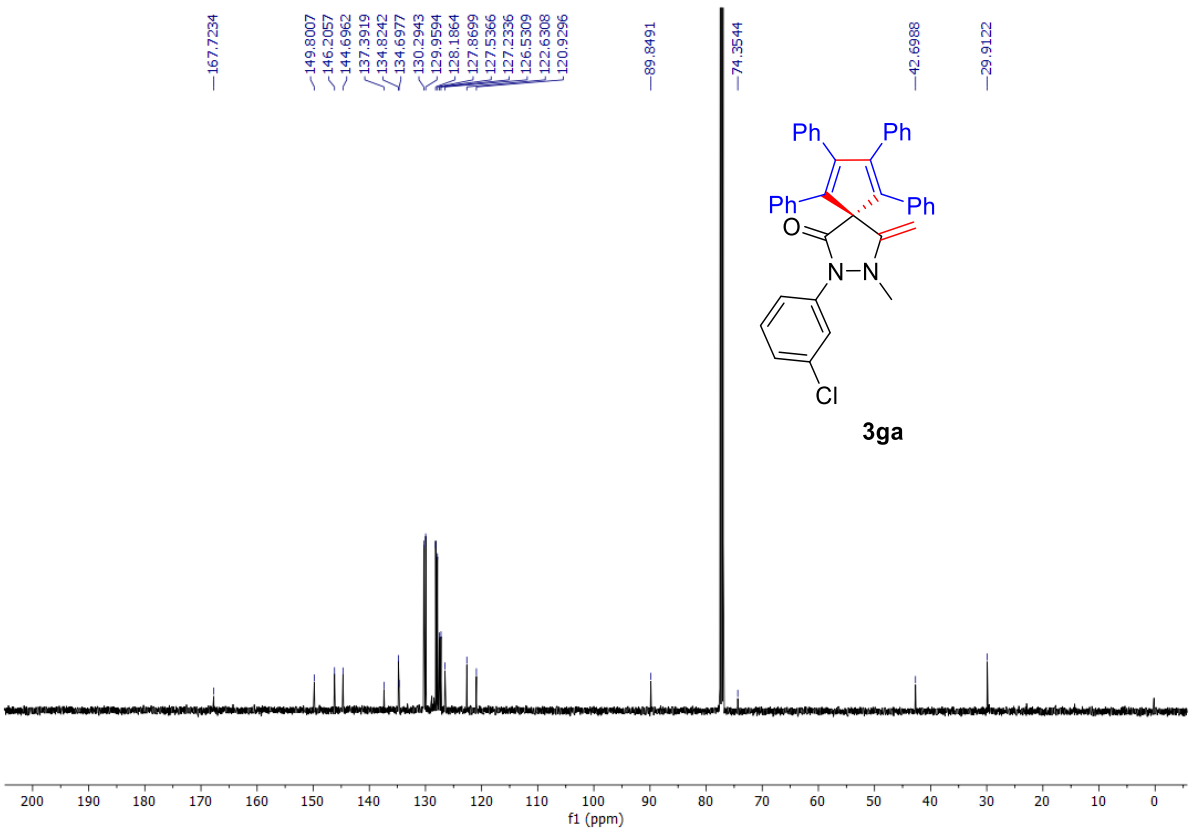

Ph
Ph
Ph
Ph
O
N–N
Cl
3fa
f1 (ppm)


Ph
Ph
Ph
Ph
O
N–N
Cl
3fa
f1 (ppm)

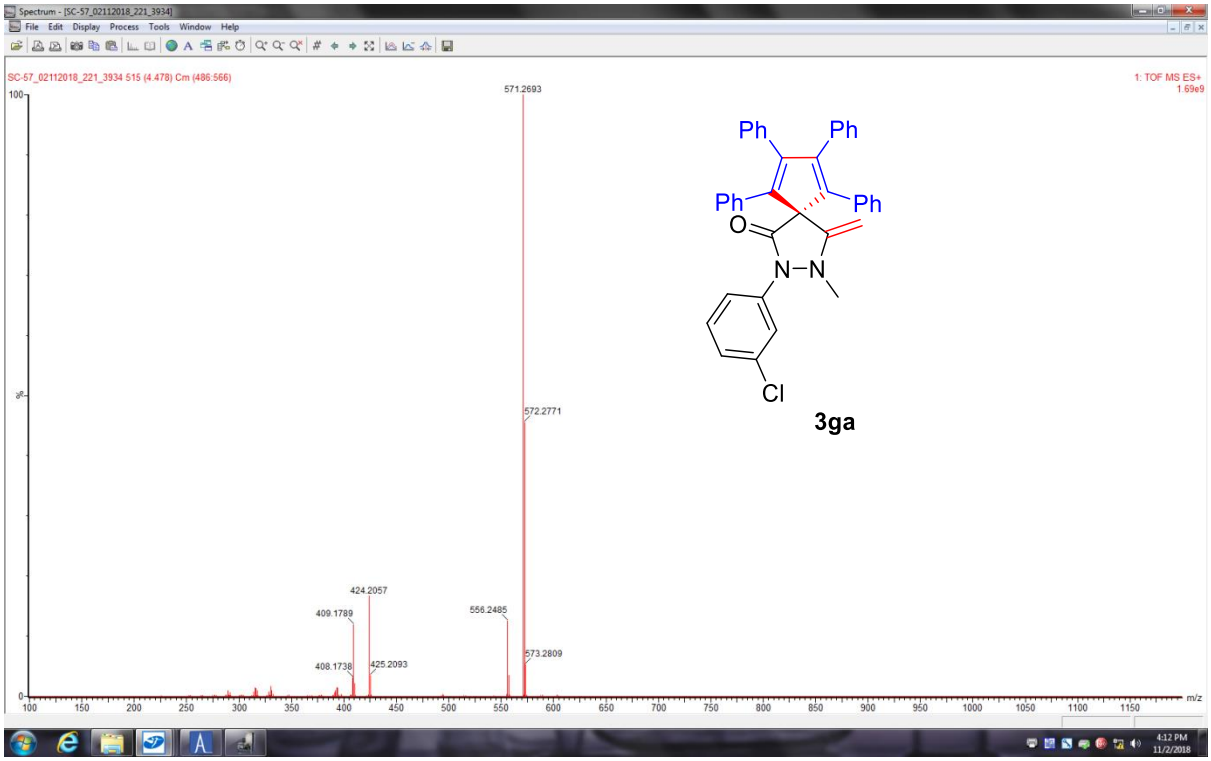

Spectrum - [SG-55_27092018_201_3607]
File Edit Display Process Tools Window Help
SG-55_27092018_201_3607 541 (4.707) Cm (484:572)
1: TOF MS ES+
1.36e9
577.2012
578.2044
580.2036
577.1176
100
%
0
100 200 300 400 500 600 700 800 900 1000 1100 1200 1300 1400 1500 1600 1700 1800 1900
m/z
Ph
Ph
Ph
Ph
O
N–N
Cl
3fa
2:48 PM
9/27/2018

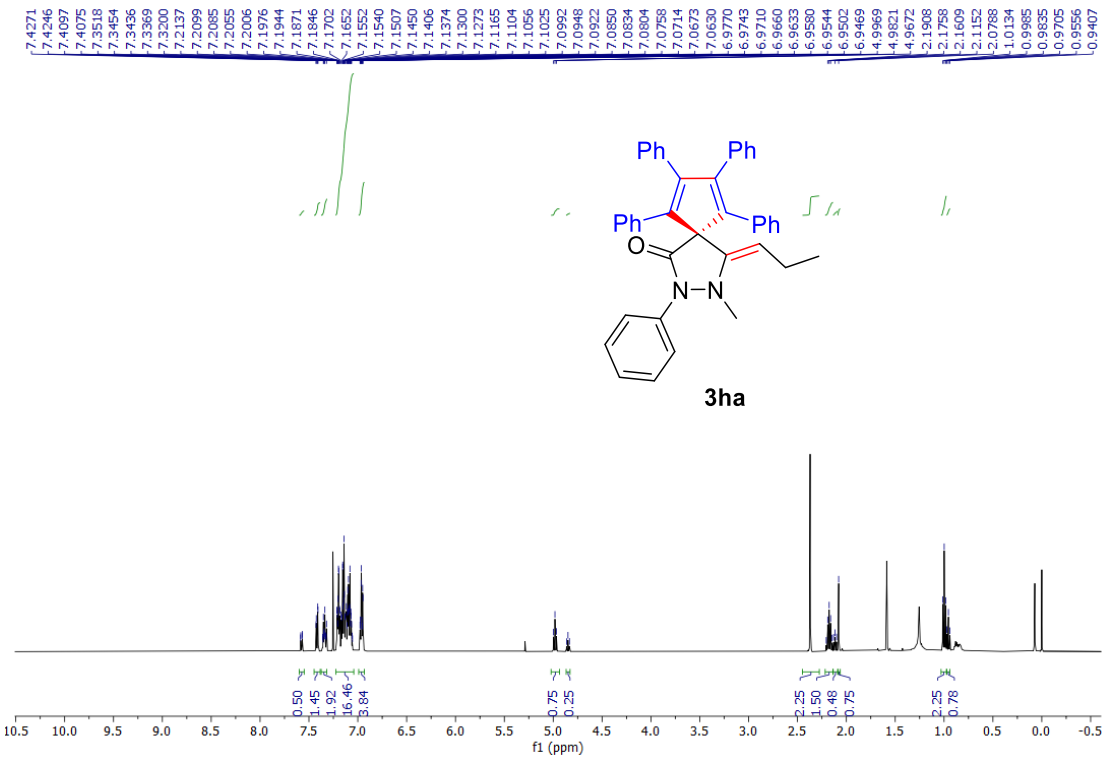

7.2617
7.2555
7.2521
7.2461
7.2322
7.2302
7.2262
7.1883
7.1829
7.1781
7.1728
7.1691
7.1662
7.1595
7.1531
7.1488
7.1452
7.1262
7.1120
7.0976
7.0861
7.0829
7.0690
6.9641
6.9616
6.9586
6.9480
6.9449
4.5316
4.5272
4.5116
4.5073
2.4880
Ph
Ph
Ph
Ph
O
N–N
Cl
1.38
1.27
18.19
4.00
2.07
3.00
f1 (ppm)

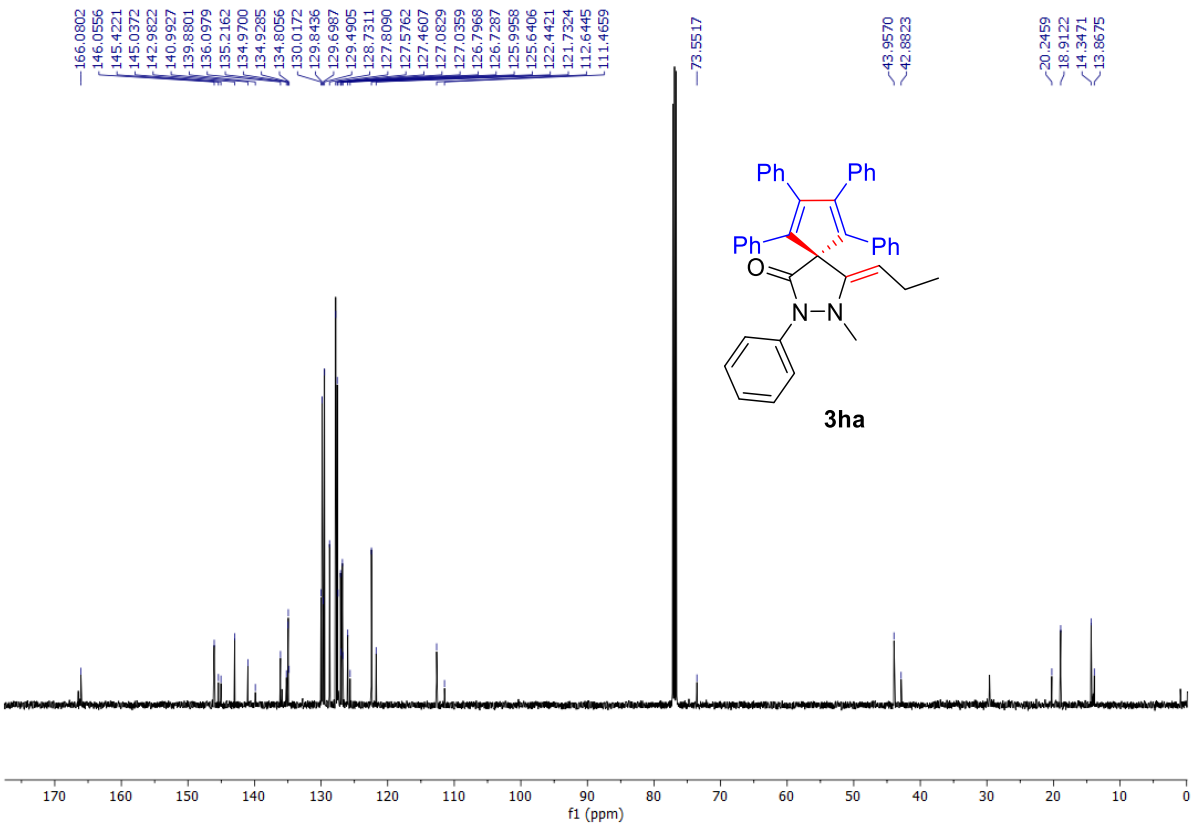
3ga

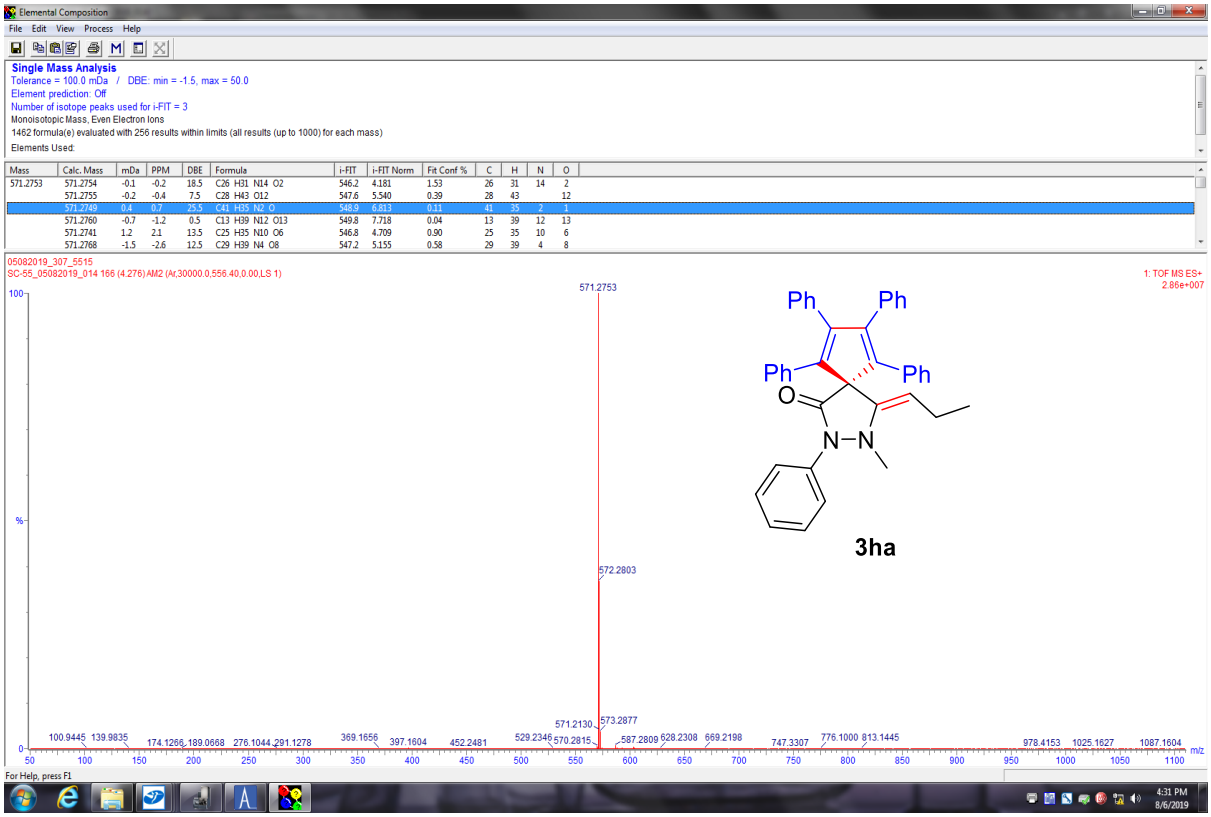

167.7234
149.8007
146.2057
144.6962
137.3919
134.8242
134.6977
130.2943
129.9594
128.1864
127.8699
127.5366
127.2336
126.5309
122.6308
120.9296
89.8491
74.3544
42.6988
29.9122
Ph
Ph
Ph
Ph
O
N–N
Cl
f1 (ppm)

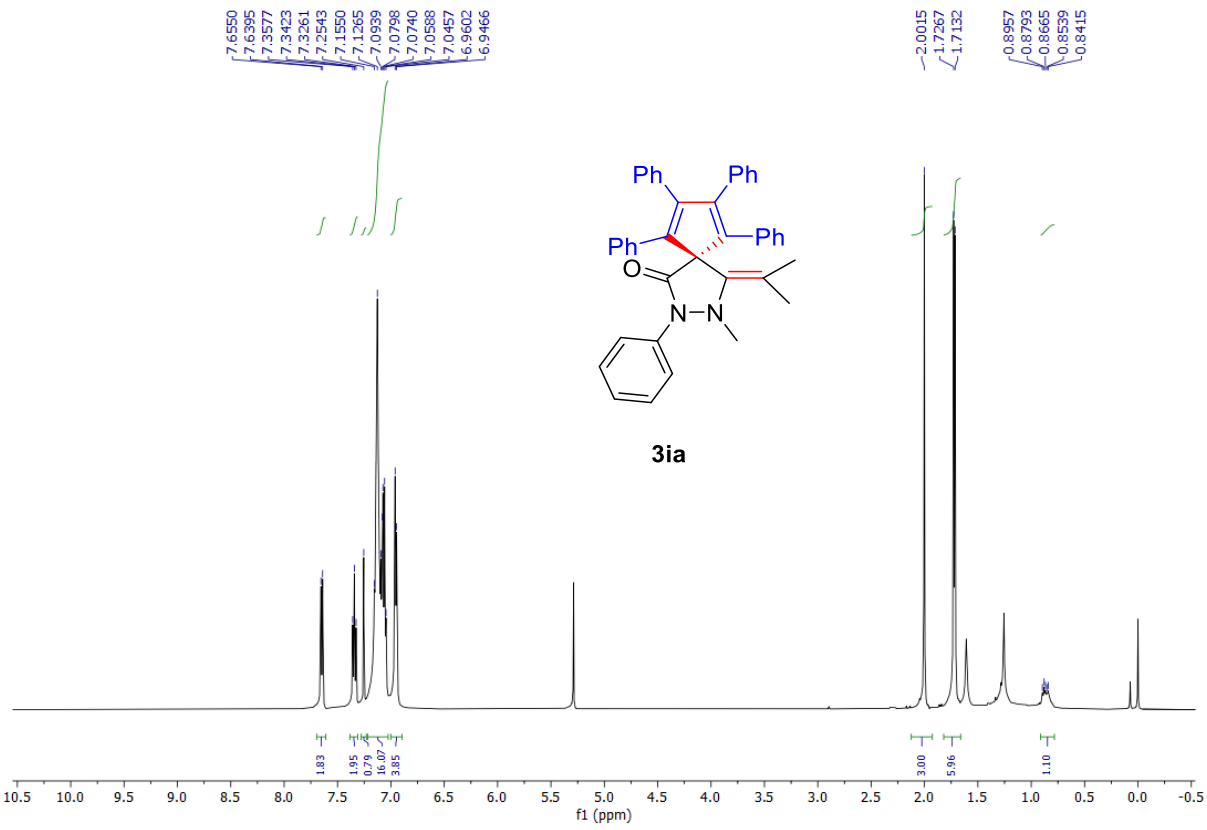
3ga


Spectrum - [SC-57_02112018_221_3934]
File Edit Display Process Tools Window Help
SC-57_02112018_221_3934 515 (4.478) Cm (486:566)
1: TOF MS ES+
1.69e9
571.2693
572.2771
424.2057
409.1789
556.2485
573.2809
408.1738
425.2093
Ph
Ph
Ph
Ph
O
N–N
Cl
3ga
m/z
4:12 PM
11/2/2018

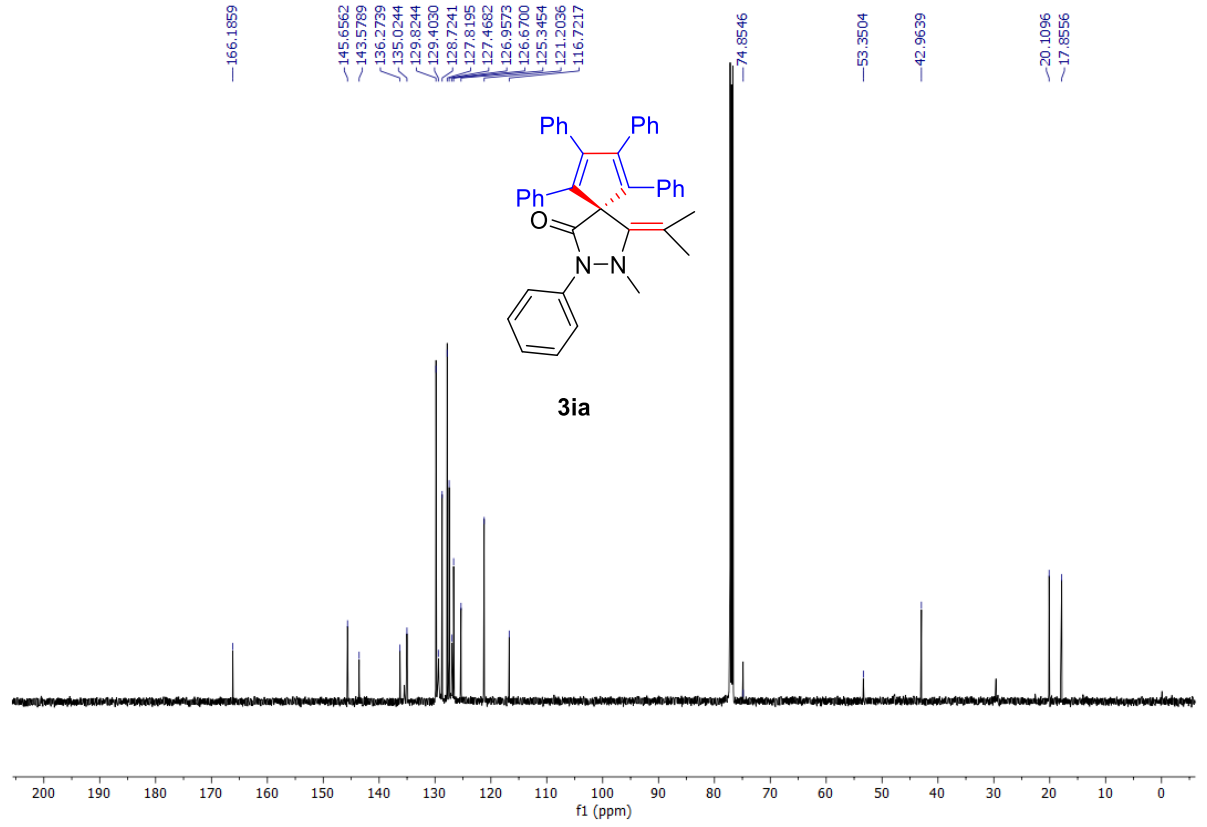

Ph
Ph
Ph
Ph
O
N–N
3ha
0.50
1.45
1.92
16.46
3.84
0.75
0.25
2.25
1.50
0.48
0.75
2.25
0.78
f1 (ppm)


Ph
Ph
Ph
Ph
O
N–N
3ha
f1 (ppm)

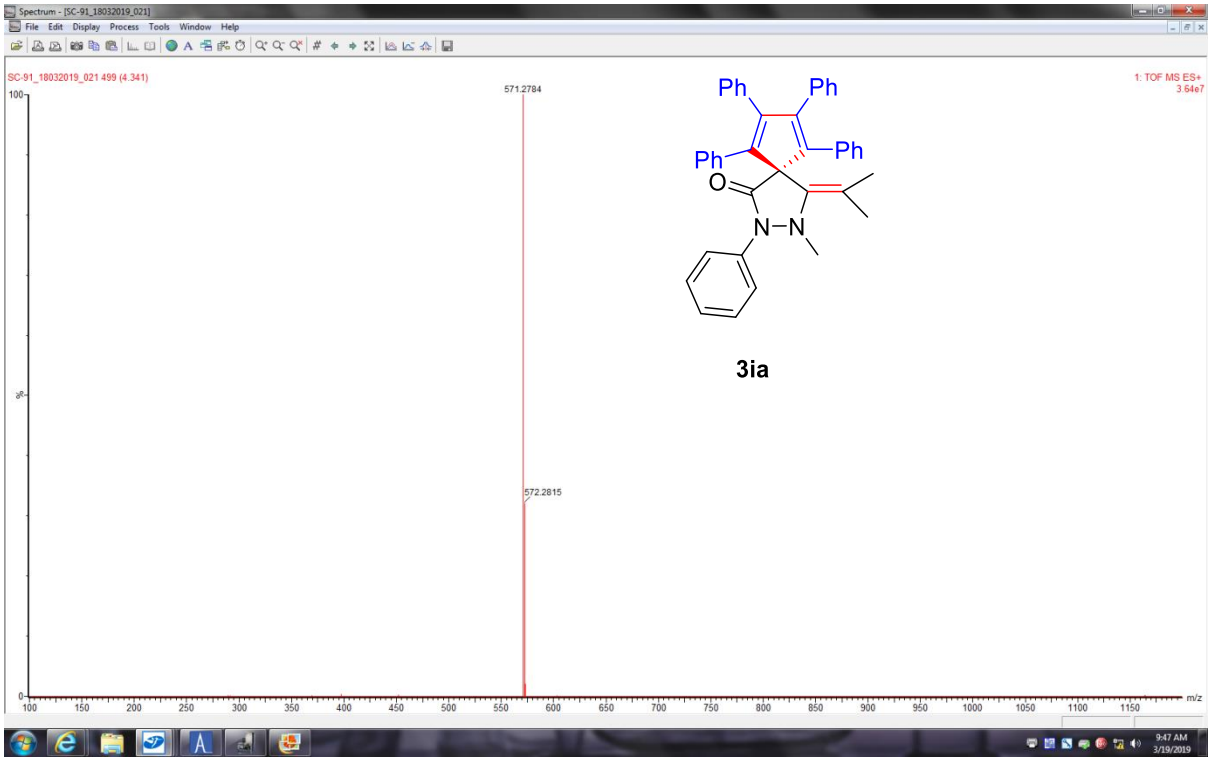

Elemental Composition
File Edit View Process Help
Single Mass Analysis
Tolerance = 100.0 mDa / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3
Monoisotopic Mass, Even Electron Ions
1462 formula(e) evaluated with 256 results within limits (all results (up to 1000) for each mass)
Elements Used:
Mass Calc. Mass mDa PPM DBE Formula i-FIT i-FIT Norm Fit Conf % C H N O
571.2753 571.2754 -0.1 -0.2 18.5 C26 H31 N14 O2 546.2 4.181 1.53 26 31 14 2
571.2755 -0.2 -0.4 7.5 C28 H43 O12 547.6 5.540 0.39 28 43 12
571.2749 0.4 0.7 25.5 C41 H35 N2 O 548.9 6.813 0.11 41 35 2 1
571.2760 -0.7 -1.2 0.5 C13 H39 N12 O13 549.8 7.718 0.04 13 39 12 13
571.2741 1.2 2.1 13.5 C25 H35 N10 O6 546.8 4.709 0.90 25 35 10 6
571.2768 -1.5 -2.6 12.5 C29 H39 N4 O8 547.2 5.155 0.58 29 39 4 8
05082019_307_5515
SC-55_05082019_014 166 (4.276) AM2 (Ar,30000.0,556.40,0.00,LS 1)
1: TOF MS ES+
2.86e+007
100
%
0
571.2753
572.2803
573.2877
571.2130
100.9445 139.9835 174.1266 189.0668 276.1044 291.1278 369.1656 397.1604 452.2481 529.2346 570.2815 587.2809 628.2308 669.2198 747.3307 776.1000 813.1445 978.4153 1025.1627 1087.1604
m/z
50 100 150 200 250 300 350 400 450 500 550 600 650 700 750 800 850 900 950 1000 1050 1100
Ph
Ph
Ph
Ph
O
N–N
3ha
For Help, press F1
4:31 PM
8/6/2019


7.6550
7.6395
7.3577
7.3423
7.3261
7.2543
7.1550
7.1265
7.0939
7.0798
7.0740
7.0588
7.0457
6.9602
6.9466
2.0015
1.7267
1.7132
0.8957
0.8793
0.8665
0.8539
0.8415
Ph
Ph
Ph
Ph
O
N–N
1.83
1.95
0.79
16.07
3.85
3.00
5.96
1.10
f1 (ppm)

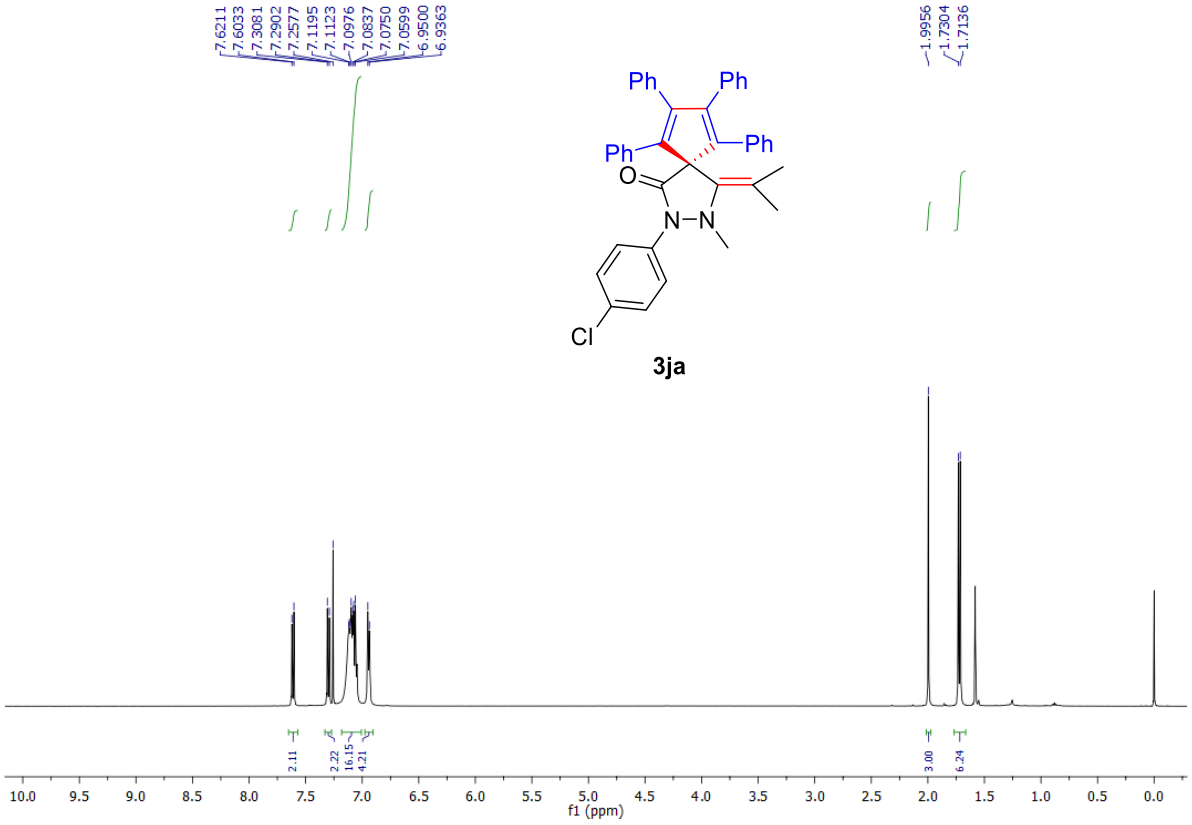
3ia

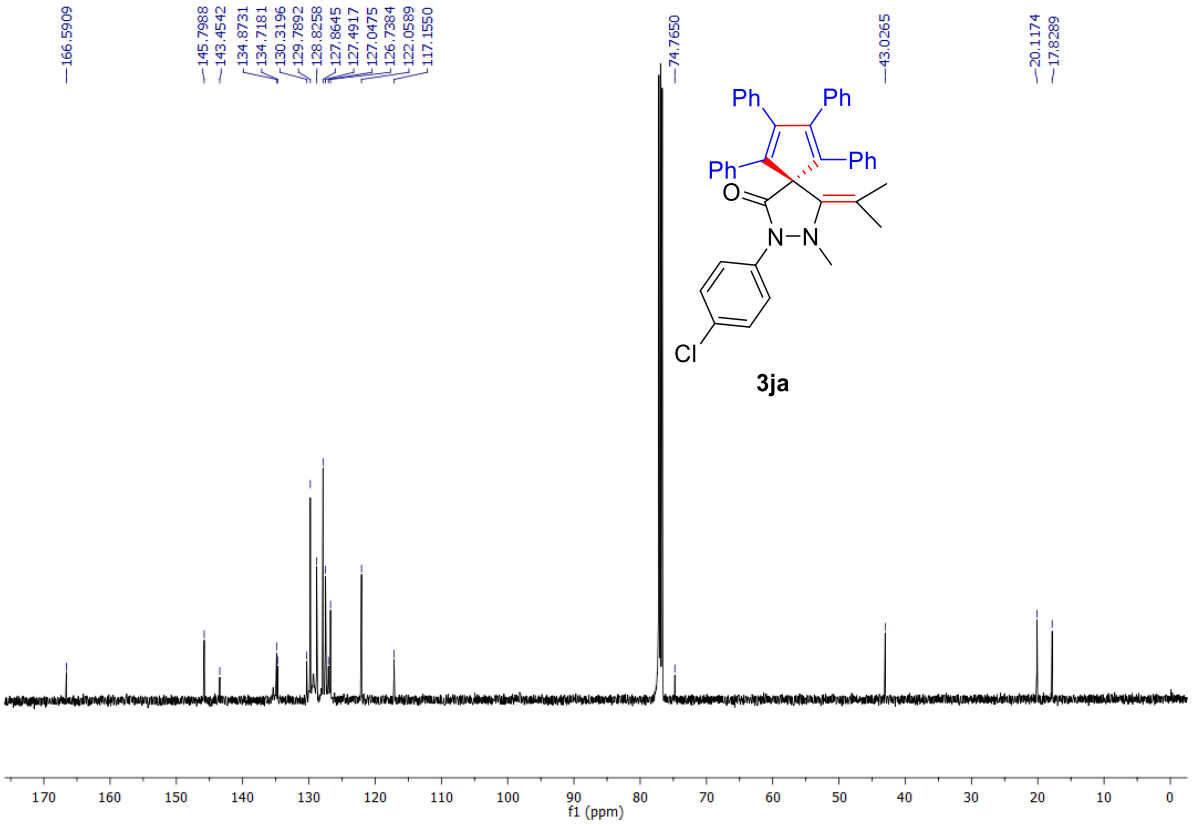

166.1859
145.6562
143.5789
136.2739
135.0244
129.8244
129.4030
128.7241
127.8195
127.4682
126.9573
126.6700
125.3454
121.2036
116.7217
74.8546
53.3504
42.9639
20.1096
17.8556
Ph
Ph
Ph
Ph
O
N–N
f1 (ppm)

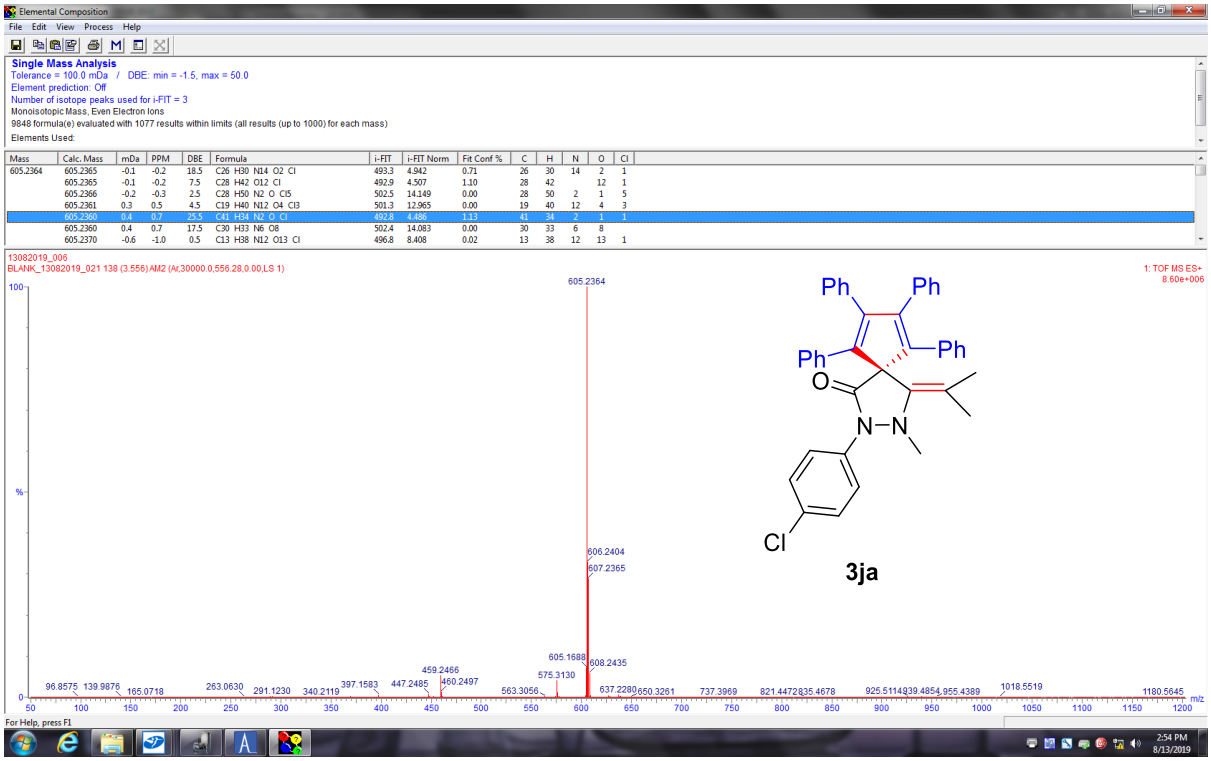
3ia

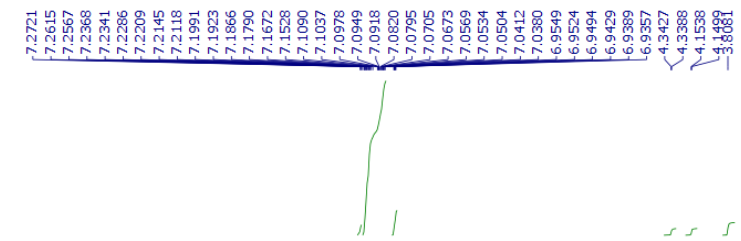

Spectrum - [SC-91_18032019_021]
File Edit Display Process Tools Window Help
SC-91_18032019_021 499 (4.341)
1: TOF MS ES+
3.64e7
571.2784
572.2815
Ph
Ph
Ph
Ph
O
N–N
100
%
0
100 150 200 250 300 350 400 450 500 550 600 650 700 750 800 850 900 950 1000 1050 1100 1150
m/z
9:47 AM
3/19/2019

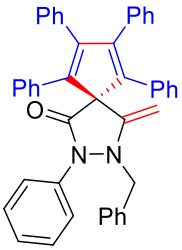
3ia


7.6211
7.6033
7.3081
7.2902
7.2577
7.1195
7.1123
7.0976
7.0837
7.0750
7.0599
6.9500
6.9363
1.9956
1.7304
1.7136
Ph
Ph
Ph
Ph
O
N–N
Cl
3ja
2.11
2.22
16.15
4.21
3.00
6.24
f1 (ppm)

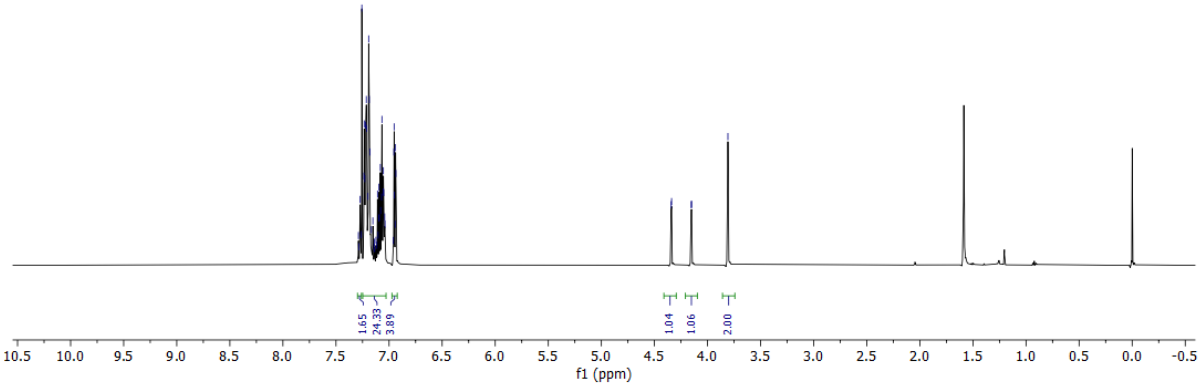

166.5909
145.7988
143.4542
134.8731
134.7181
130.3196
129.7892
128.8258
127.8645
127.4917
127.0475
126.7384
122.0589
117.1550
74.7650
43.0265
20.1174
17.8289
Ph
Ph
Ph
Ph
O
N–N
Cl
3ja
f1 (ppm)

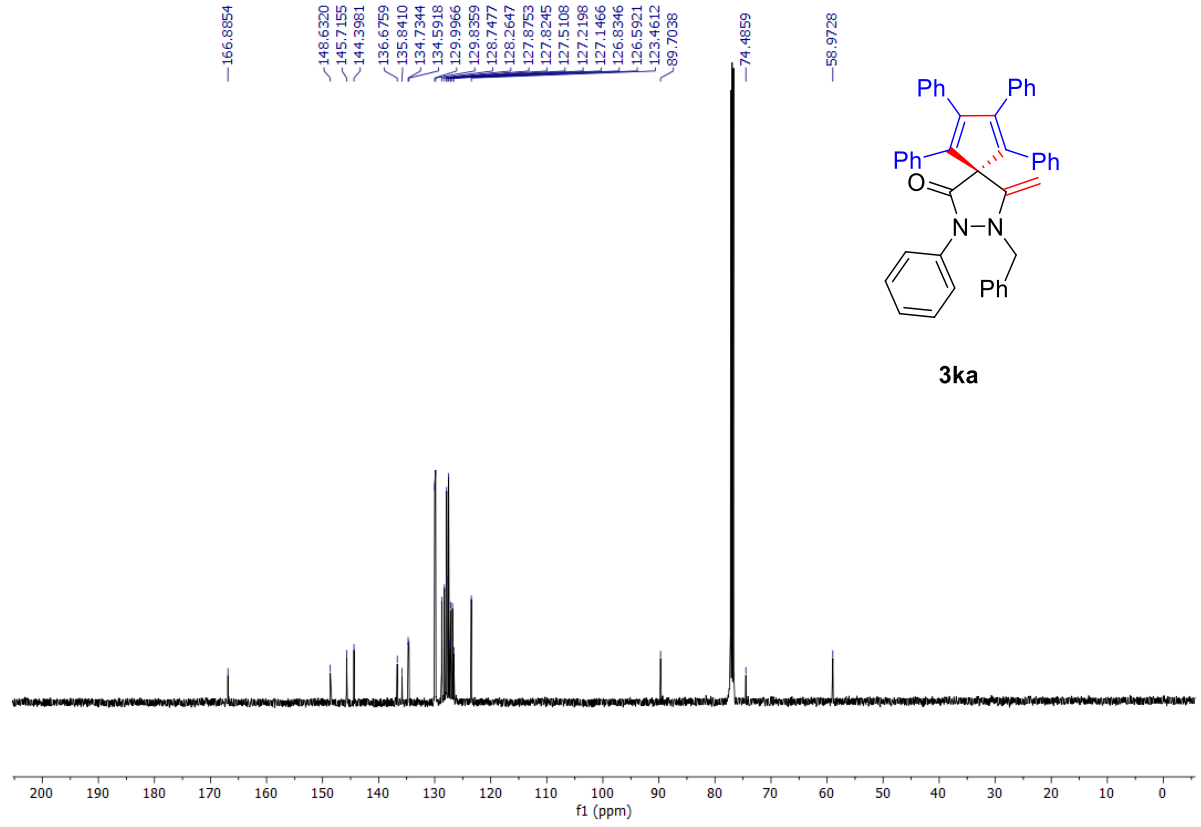

Elemental Composition
File Edit View Process Help
Single Mass Analysis
Tolerance = 100.0 mDa / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3
Monoisotopic Mass, Even Electron Ions
9848 formula(e) evaluated with 1077 results within limits (all results (up to 1000) for each mass)
Elements Used:
Mass Calc. Mass mDa PPM DBE Formula i-FIT i-FIT Norm Fit Conf % C H N O Cl
605.2364 605.2365 -0.1 -0.2 18.5 C26 H30 N14 O2 Cl 493.3 4.942 0.71 26 30 14 2 1
605.2365 -0.1 -0.2 7.5 C28 H42 O12 Cl 492.9 4.507 1.10 28 42 12 1
605.2366 -0.2 -0.3 2.5 C28 H50 N2 O Cl5 502.5 14.149 0.00 28 50 2 1 5
605.2361 0.3 0.5 4.5 C19 H40 N12 O4 Cl3 501.3 12.965 0.00 19 40 12 4 3
605.2360 0.4 0.7 17.5 C30 H33 N6 O8 502.4 14.083 0.00 30 33 6 8
605.2370 -0.6 -1.0 0.5 C13 H38 N12 O13 Cl 496.8 8.408 0.02 13 38 12 13 1
13082019_006
BLANK_13082019_021 138 (3.556) AM2 (Ar,30000.0,556.28,0.00,LS 1)
1: TOF MS ES+
8.60e+006
605.2364
606.2404
607.2365
608.2435
605.1688
575.3130
459.2466
460.2497
447.2485
397.1583
340.2119
291.1230
263.0630
165.0718
139.9876
96.8575
563.3056
637.2280
650.3261
737.3969
821.4472
835.4678
925.5114
939.4854
955.4389
1018.5519
1180.5645
m/z
Ph
Ph
Ph
Ph
O
N–N
Cl
3ja
For Help, press F1
2:54 PM
8/13/2019


7.2721
7.2615
7.2567
7.2368
7.2341
7.2286
7.2209
7.2145
7.2118
7.1991
7.1923
7.1866
7.1790
7.1672
7.1528
7.1090
7.1037
7.0978
7.0949
7.0918
7.0820
7.0795
7.0705
7.0673
7.0569
7.0534
7.0504
7.0412
7.0380
6.9549
6.9524
6.9494
6.9429
6.9389
6.9357
4.3427
4.3388
4.1538
4.1499
3.8081


Ph
Ph
Ph
Ph
O
N–N
Ph

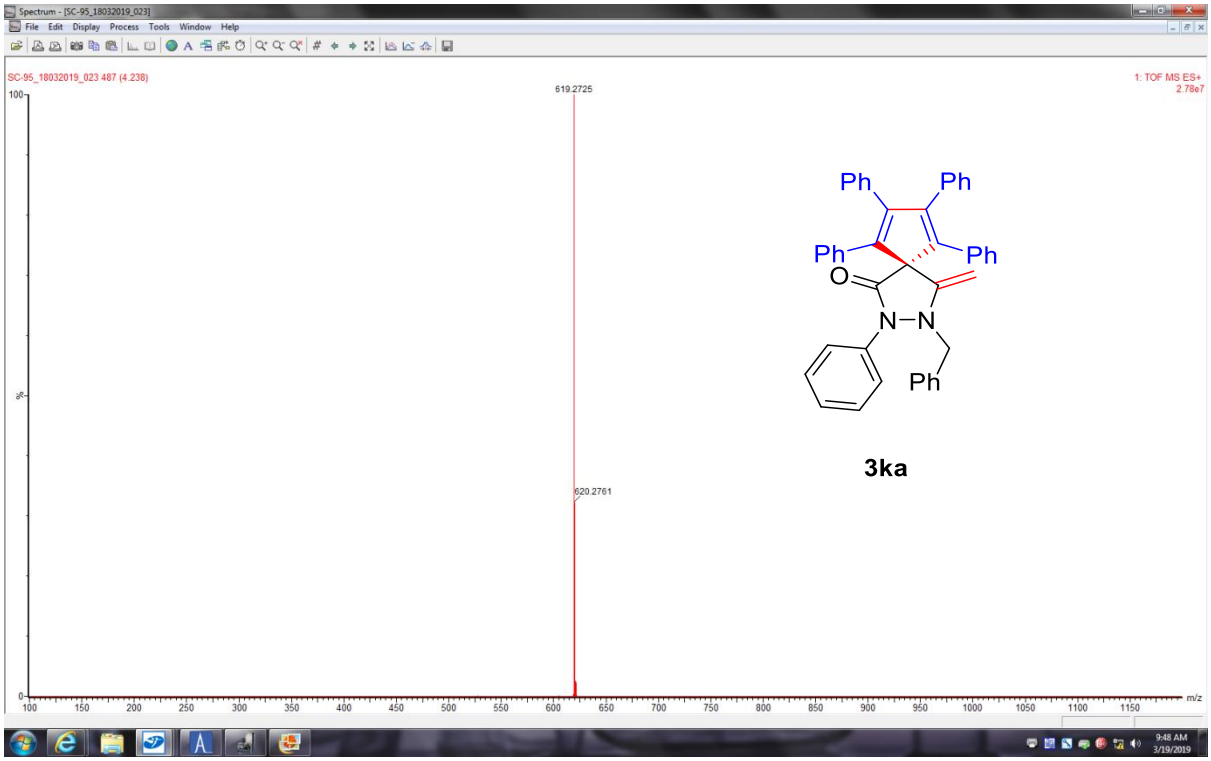
3ka

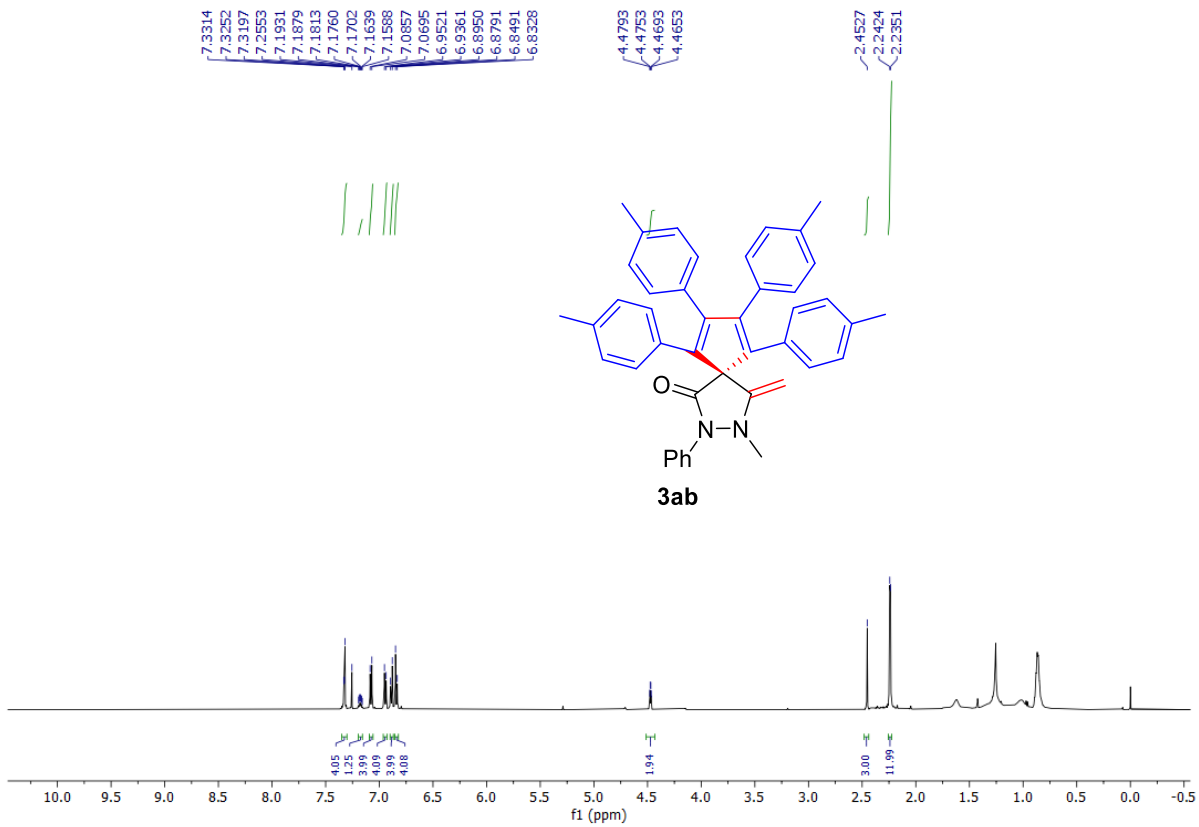

1.65
24.33
3.89
1.04
1.06
2.00
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


166.8854
148.6320
145.7155
144.3981
136.6759
135.8410
134.7344
134.5918
129.9966
129.8359
128.7477
128.2647
127.8753
127.8245
127.5108
127.2198
127.1466
126.8346
126.5921
123.4612
89.7038
74.4859
58.9728
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

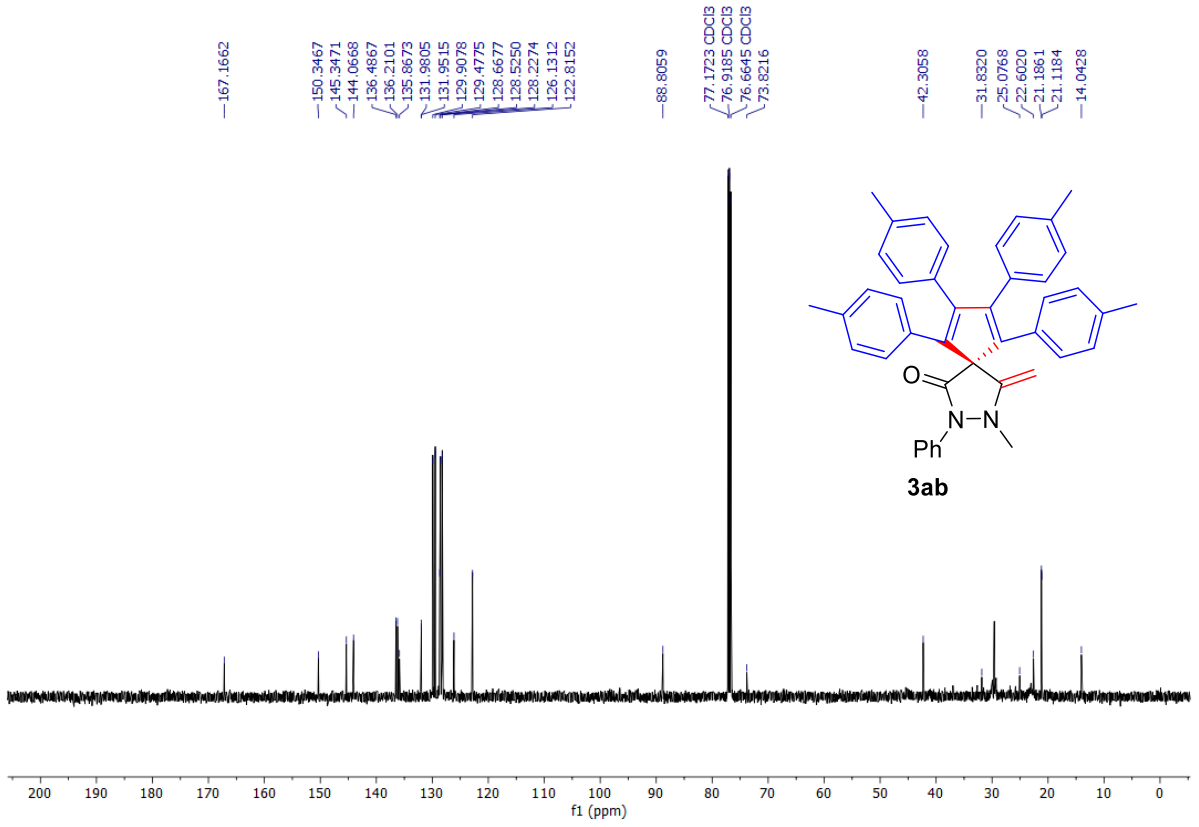
Ph
Ph
Ph
Ph
O
N–N
Ph

3ka

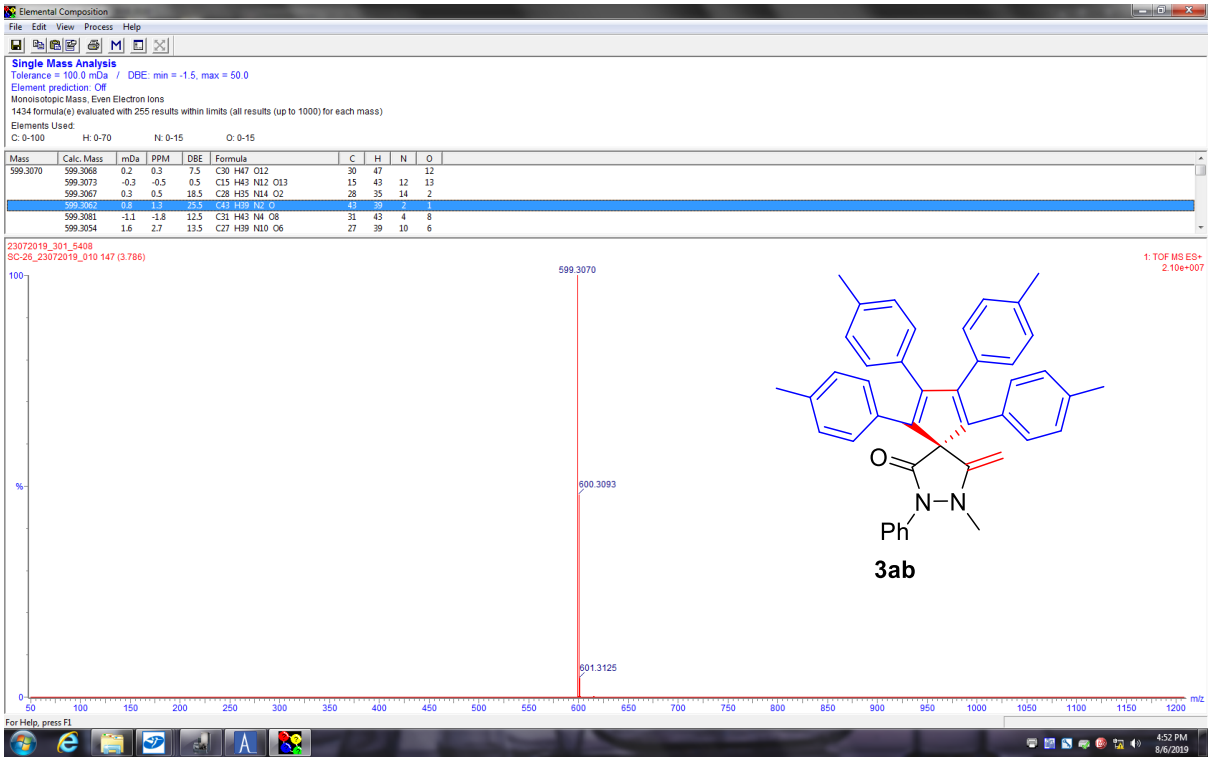

Spectrum - [SC-95_18032019_023]
File Edit Display Process Tools Window Help
SC-95_18032019_023 487 (4.238)
1: TOF MS ES+
2.78e7
619.2725
620.2761
100
%
0
100 150 200 250 300 350 400 450 500 550 600 650 700 750 800 850 900 950 1000 1050 1100 1150
m/z
Ph
Ph
Ph
Ph
O
N–N
Ph
3ka
9:48 AM
3/19/2019

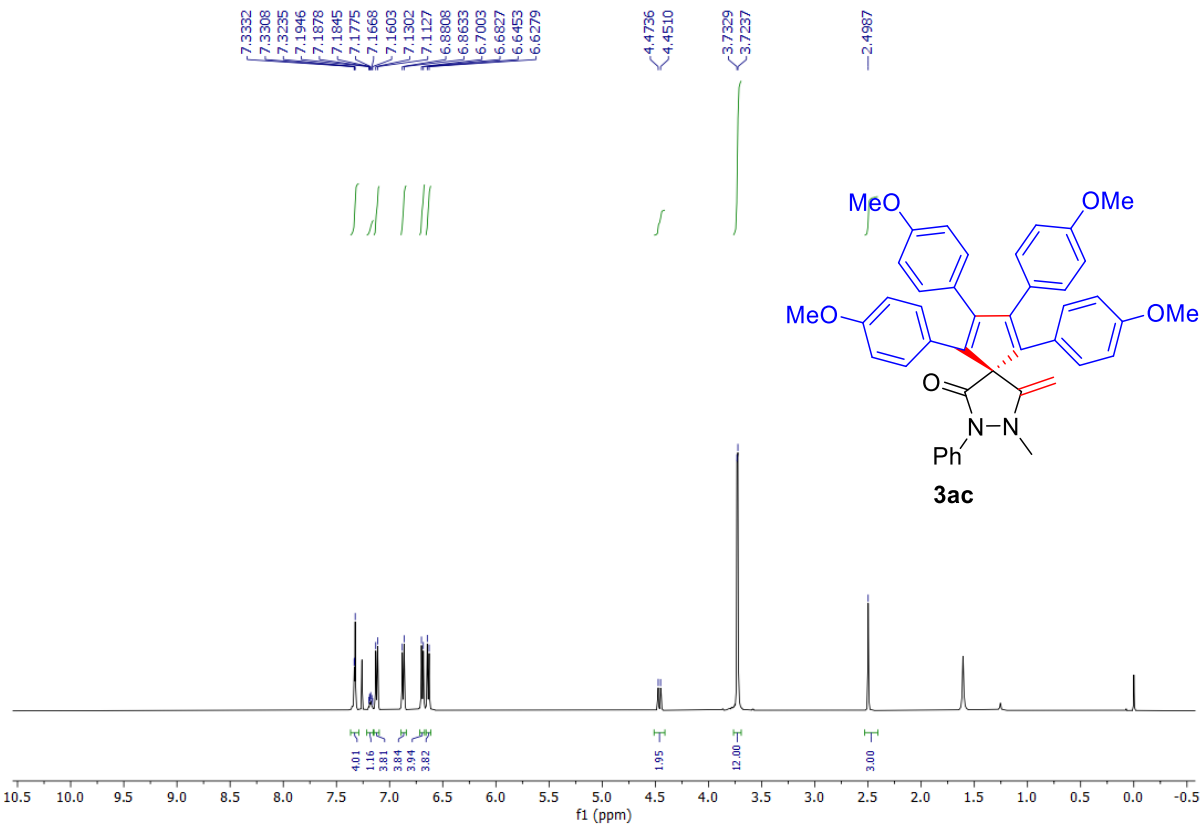

7.3314
7.3252
7.3197
7.2553
7.1931
7.1879
7.1813
7.1760
7.1702
7.1639
7.1588
7.0857
7.0695
6.9521
6.9361
6.8950
6.8791
6.8491
6.8328
4.4793
4.4753
4.4693
4.4653
2.4527
2.2424
2.2351
O
N–N
Ph
4.05
1.25
3.99
4.09
3.99
4.08
1.94
3.00
11.99
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

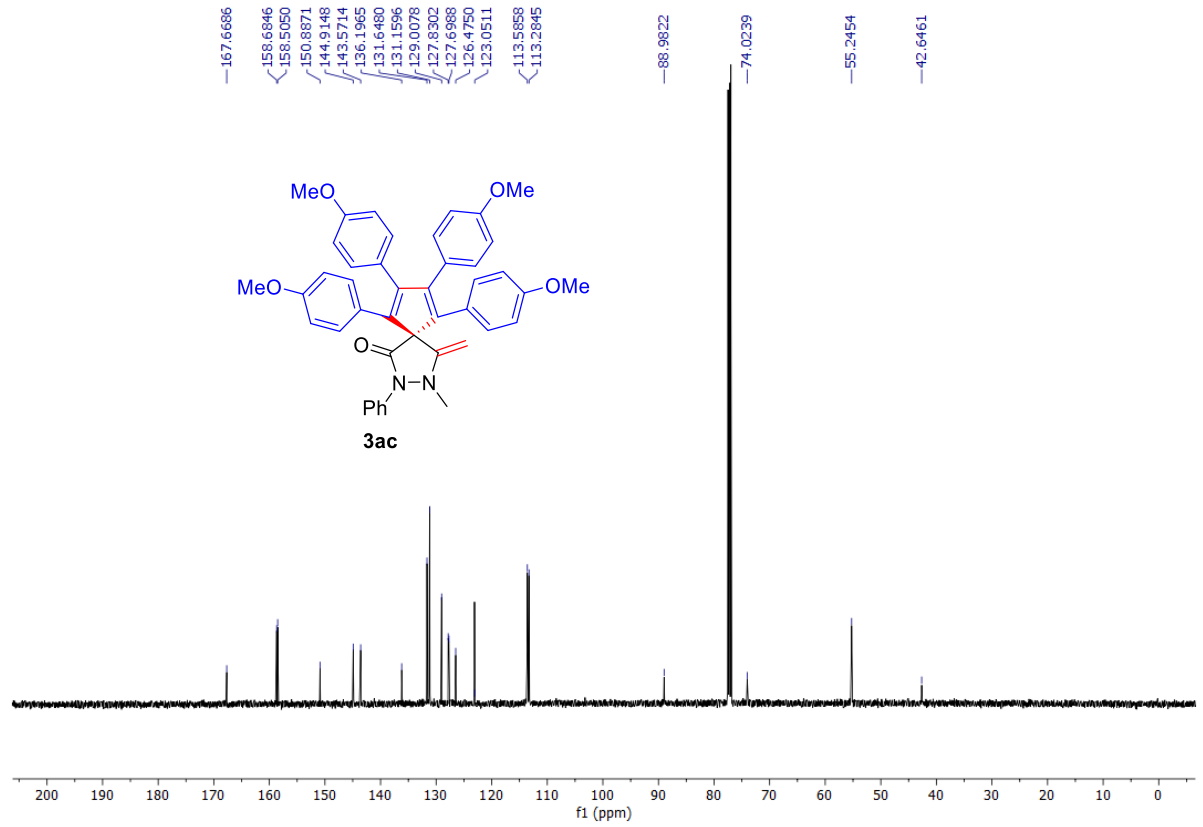
3ab

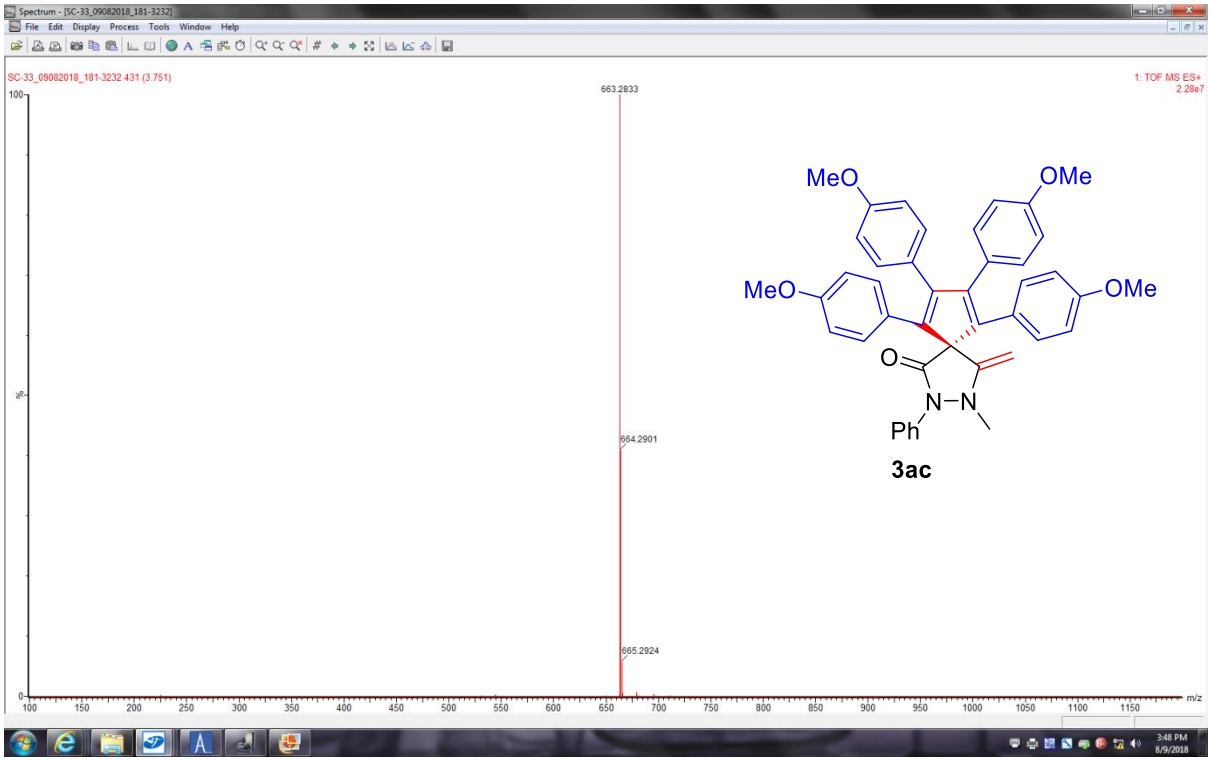

167.1662
150.3467
145.3471
144.0668
136.4867
136.2101
135.8673
131.9805
131.9515
129.9078
129.4775
128.6677
128.5250
128.2274
126.1312
122.8152
88.8059
77.1723 CDCl3
76.9185 CDCl3
76.6645 CDCl3
73.8216
42.3058
31.8320
25.0768
22.6020
21.1861
21.1184
14.0428
O
N–N
Ph
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

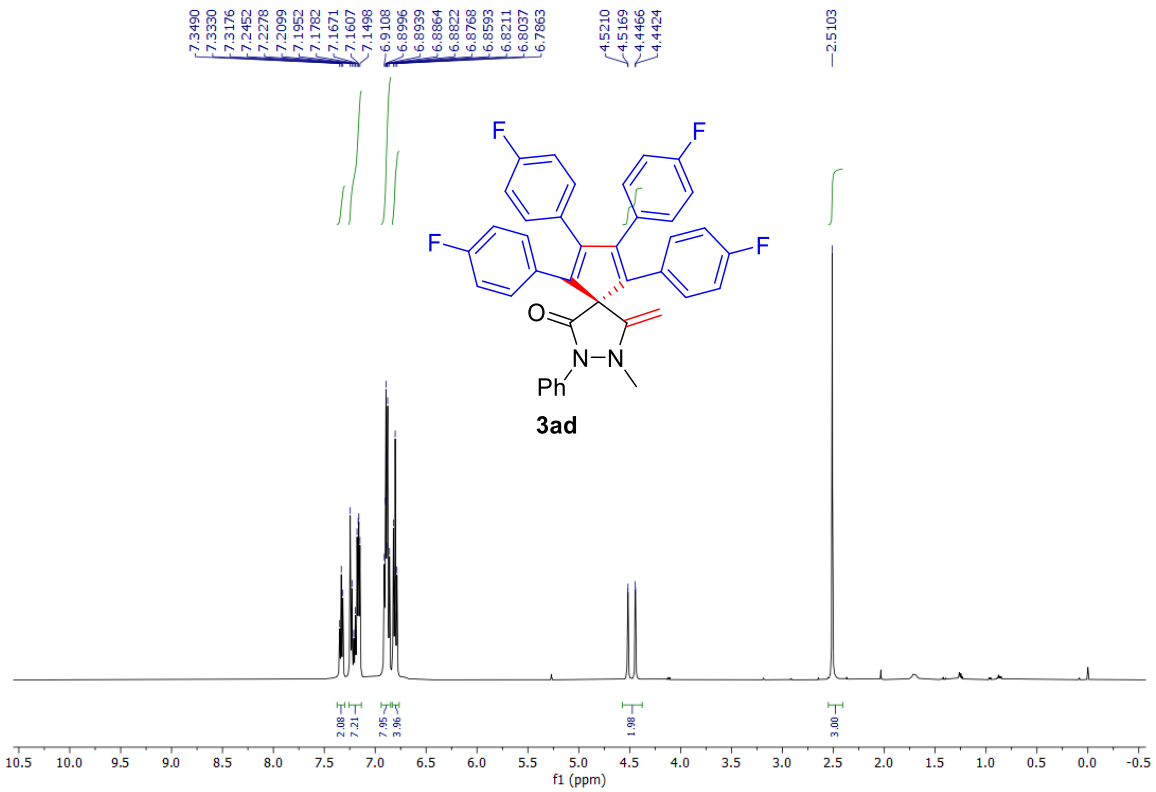
3ab

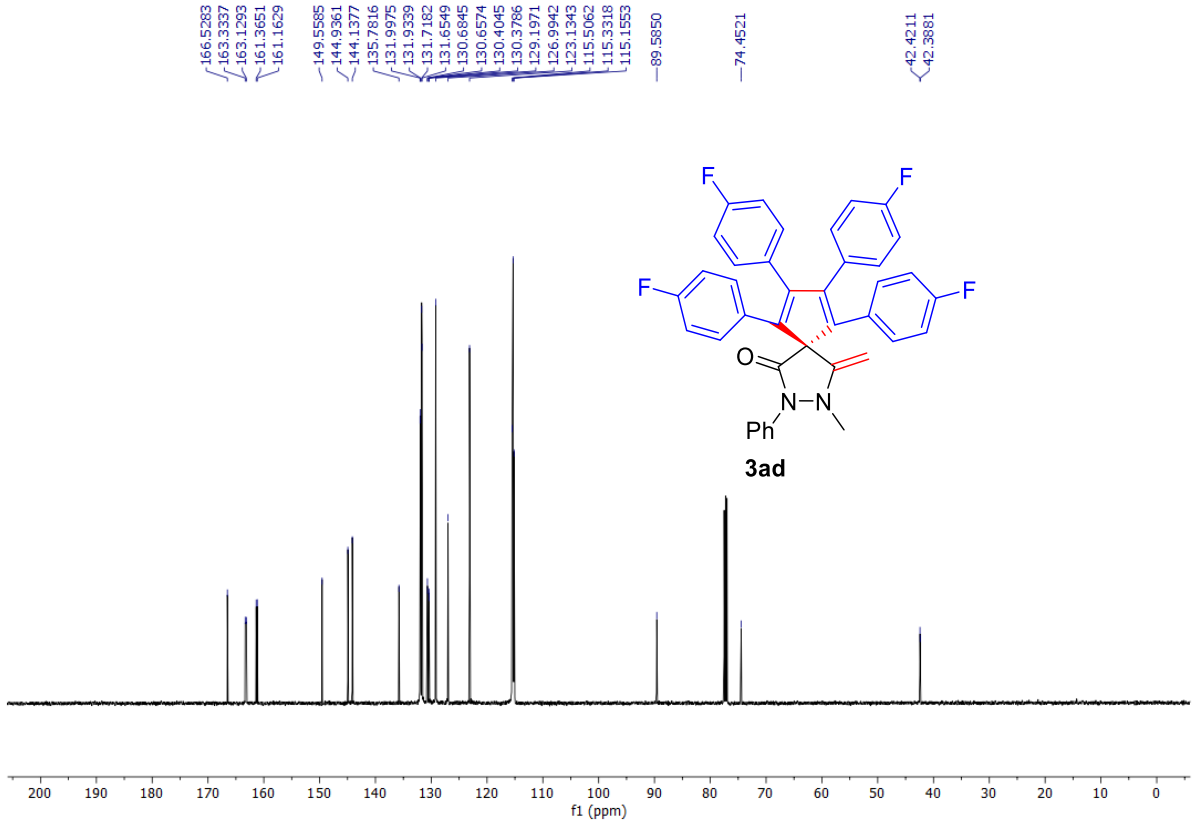

Elemental Composition
File Edit View Process Help
Single Mass Analysis
Tolerance = 100.0 mDa / DBE: min = -1.5, max = 50.0
Element prediction: Off
Monoisotopic Mass, Even Electron Ions
1434 formula(e) evaluated with 255 results within limits (all results (up to 1000) for each mass)
Elements Used:
C: 0-100 H: 0-70 N: 0-15 O: 0-15
Mass Calc. Mass mDa PPM DBE Formula C H N O
599.3070 599.3068 0.2 0.3 7.5 C30 H47 O12 30 47 12
599.3073 -0.3 -0.5 0.5 C15 H43 N12 O13 15 43 12 13
599.3067 0.3 0.5 18.5 C28 H35 N14 O2 28 35 14 2
599.3067 0.8 1.3 25.5 C41 H39 N2 O 43 39 2 1
599.3081 -1.1 -1.8 12.5 C31 H43 N4 O8 31 43 4 8
599.3054 1.6 2.7 13.5 C27 H39 N10 O6 27 39 10 6
23072019_301_5408
SC-26_23072019_010 147 (3.786)
1: TOF MS ES+
2.10e+007
599.3070
600.3093
601.3125
100
%
0
50 100 150 200 250 300 350 400 450 500 550 600 650 700 750 800 850 900 950 1000 1050 1100 1150 1200
m/z
O
N–N
Ph
3ab
For Help, press F1
4:52 PM
8/6/2019

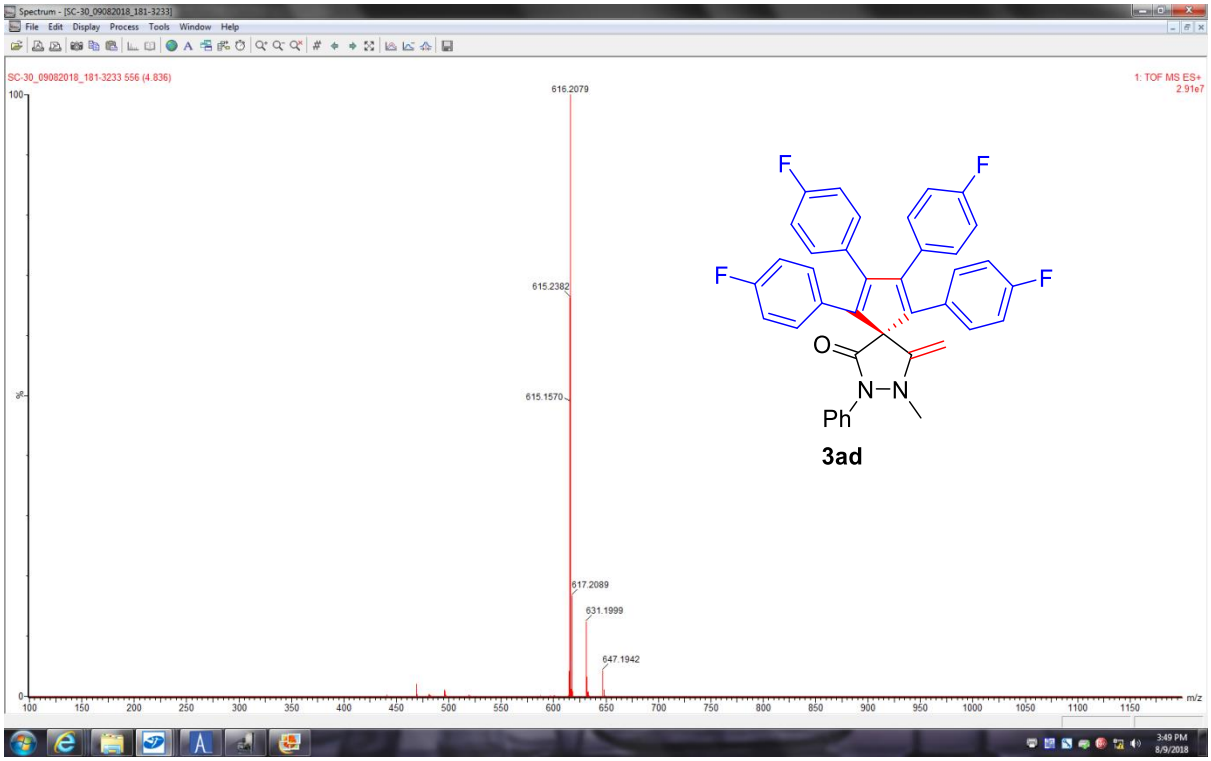

7.3332
7.3308
7.3235
7.1946
7.1878
7.1845
7.1775
7.1668
7.1603
7.1302
7.1127
6.8808
6.8633
6.7003
6.6827
6.6453
6.6279
4.4736
4.4510
3.7329
3.7237
2.4987
MeO
OMe
MeO
OMe
O
N–N
Ph
3ac
4.01
1.16
3.81
3.94
3.82
1.95
12.00
3.00
f1 (ppm)


167.6686
158.6846
158.5050
150.8871
144.9148
143.5714
136.1965
131.6480
131.1596
129.0078
127.8302
127.6988
126.4750
123.0511
113.5858
113.2845
88.9822
74.0239
55.2454
42.6461
MeO
OMe
MeO
OMe
O
N–N
Ph
3ac
f1 (ppm)

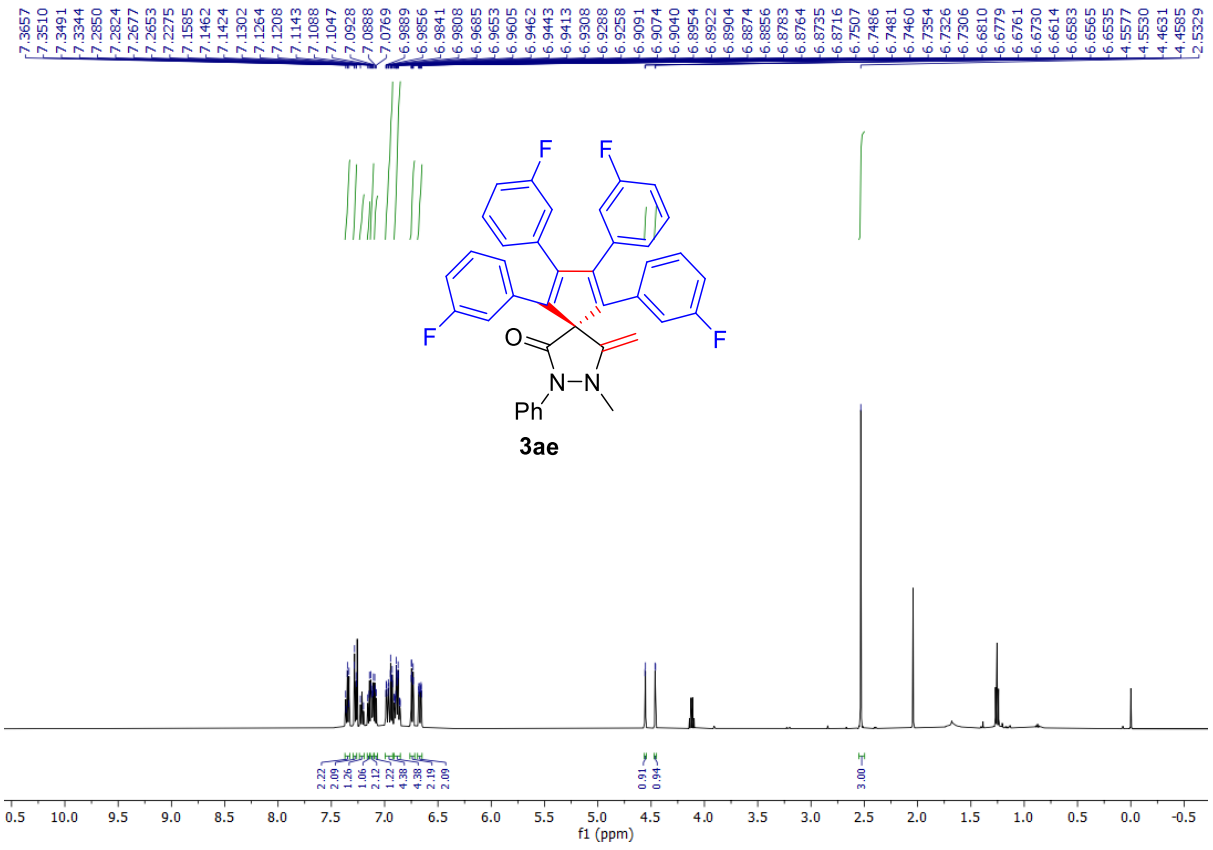

Spectrum - [SC-33_09082018_181-3232]
File Edit Display Process Tools Window Help
SC-33_09082018_181-3232 431 (3.751)
1: TOF MS ES+
2.28e7
663.2833
664.2901
665.2924
MeO
OMe
MeO
OMe
O
N–N
Ph
3ac
m/z

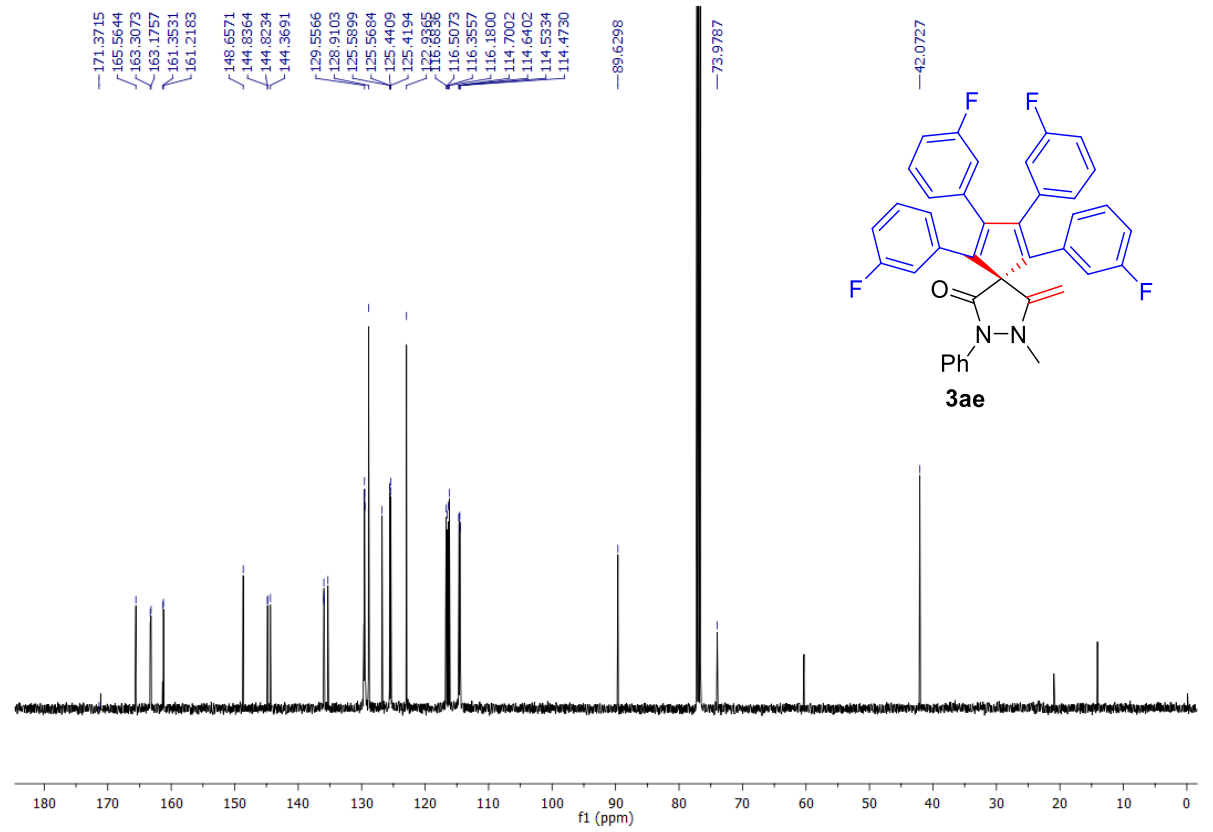

7.3490
7.3330
7.3176
7.2452
7.2278
7.2099
7.1952
7.1782
7.1671
7.1607
7.1498
6.9108
6.8996
6.8939
6.8864
6.8822
6.8768
6.8593
6.8211
6.8037
6.7863
4.5210
4.5169
4.4466
4.4424
2.5103
F
F
F
F
O
N–N
Ph
3ad
2.08
7.21
7.95
3.96
1.98
3.00
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

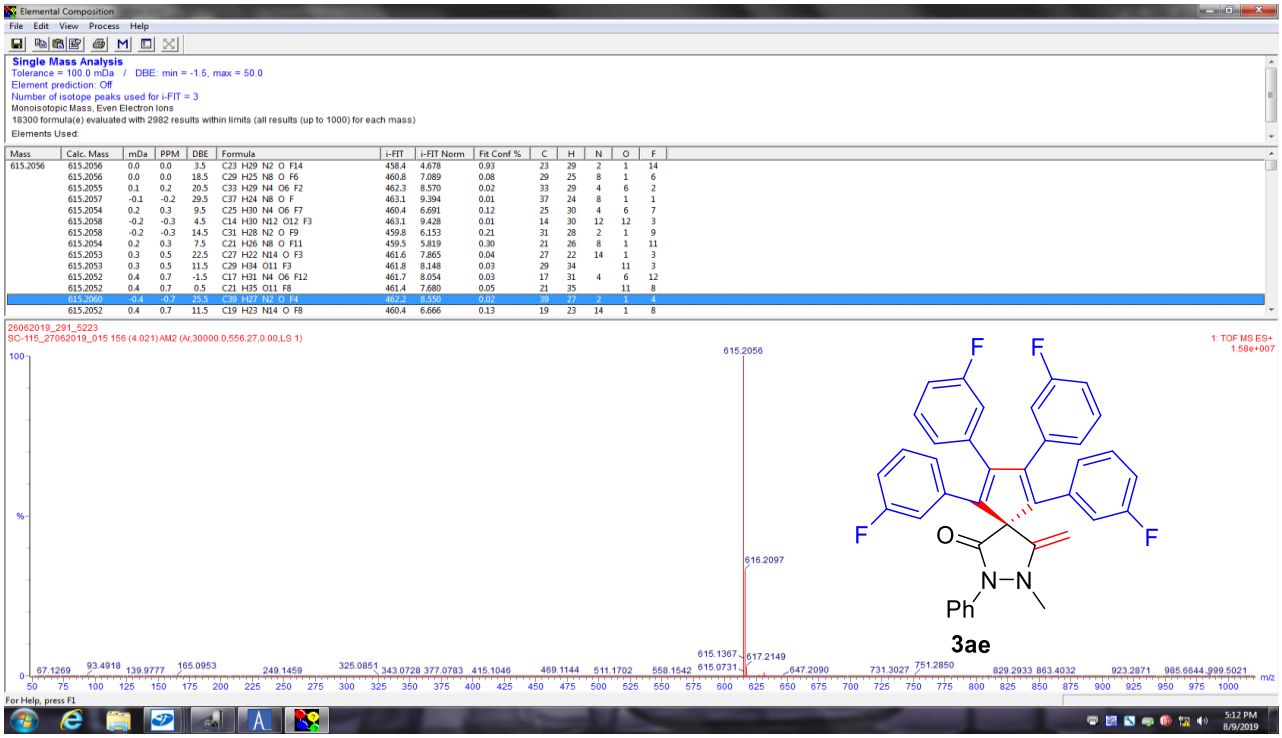

166.5283
163.3337
163.1293
161.3651
161.1629
149.5585
144.9361
144.1377
135.7816
131.9975
131.9339
131.7182
131.6549
130.6845
130.6574
130.4045
130.3786
129.1971
126.9942
123.1343
115.5062
115.3318
115.1553
89.5850
74.4521
42.4211
42.3881
F
F
F
F
O
N–N
Ph
3ad
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

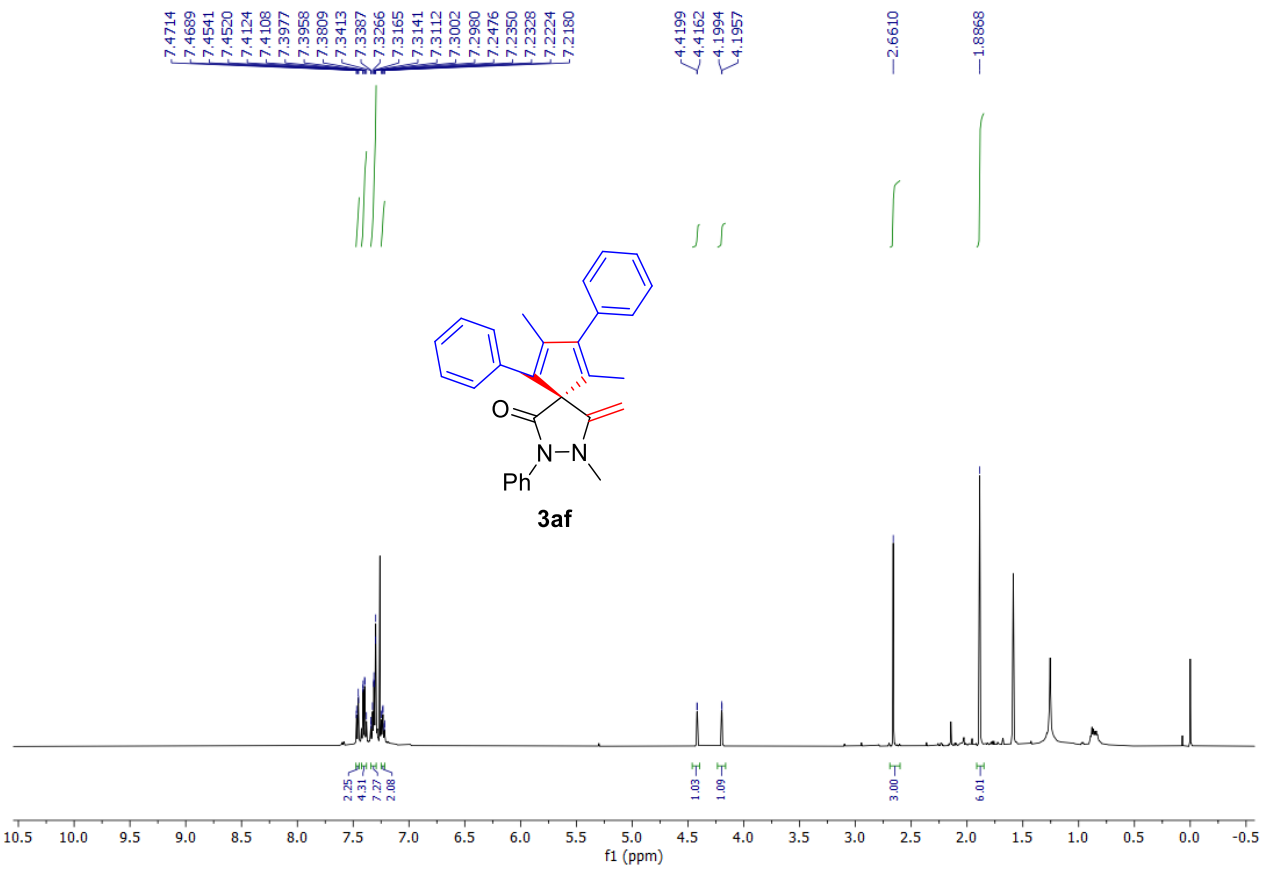

Spectrum - [SC-30_09082018_181-3233]
File Edit Display Process Tools Window Help
SC-30_09082018_181-3233.556 (4.836)
1: TOF MS ES+
2.91e7
100
%
0
616.2079
615.2382
615.1570
617.2089
631.1999
647.1942
100 150 200 250 300 350 400 450 500 550 600 650 700 750 800 850 900 950 1000 1050 1100 1150
m/z
F
F
F
F
O
N
N
Ph
3:49 PM
8/9/2018

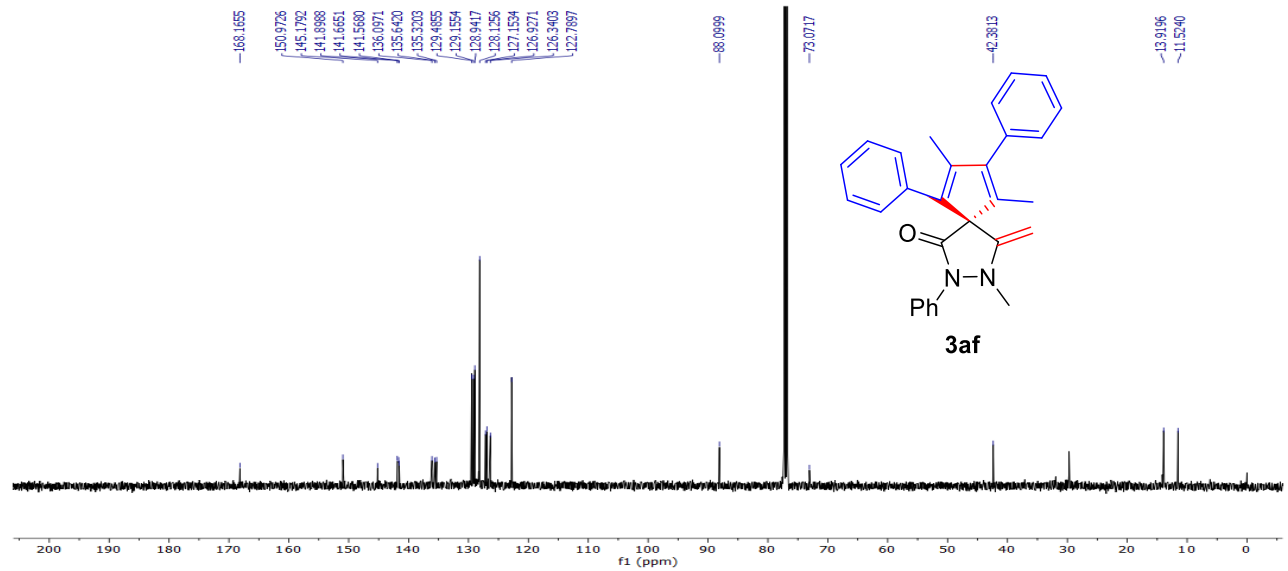
3ad

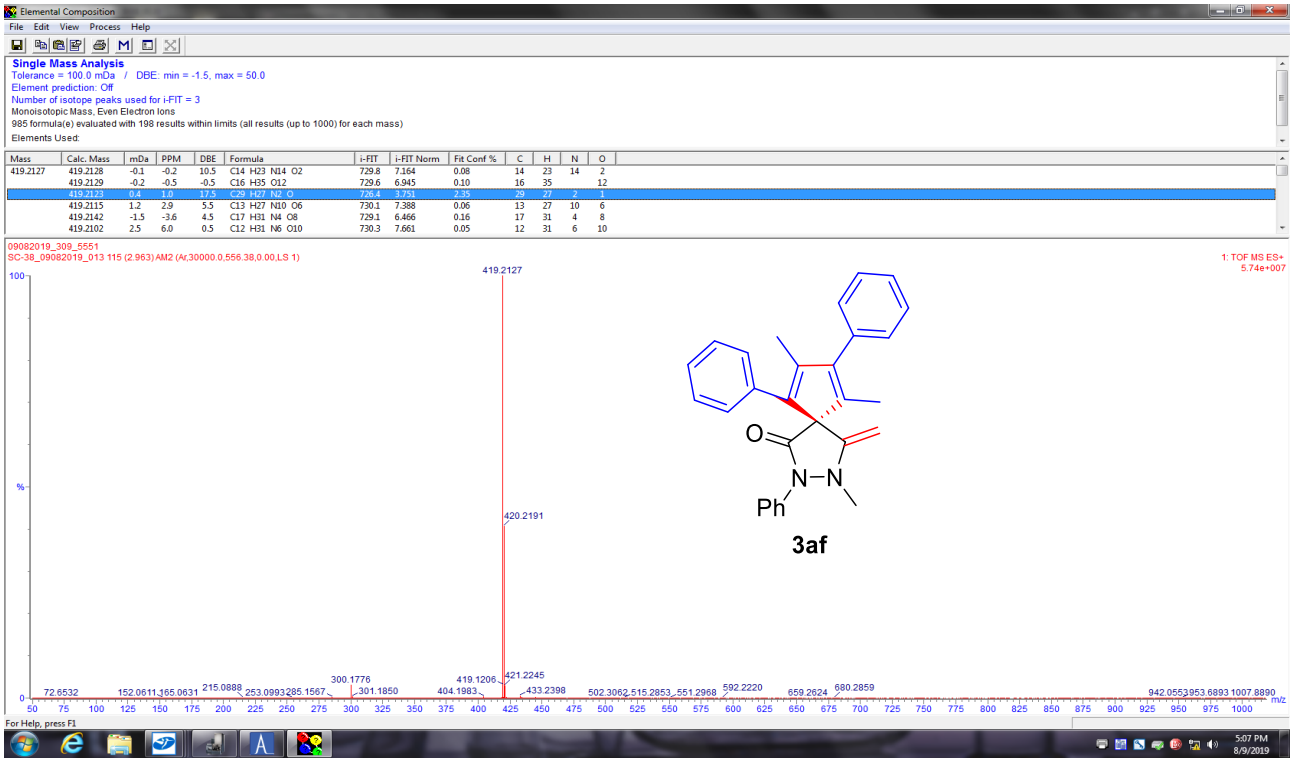

F
F
F
F
O
N–N
Ph
3ae
f1 (ppm)

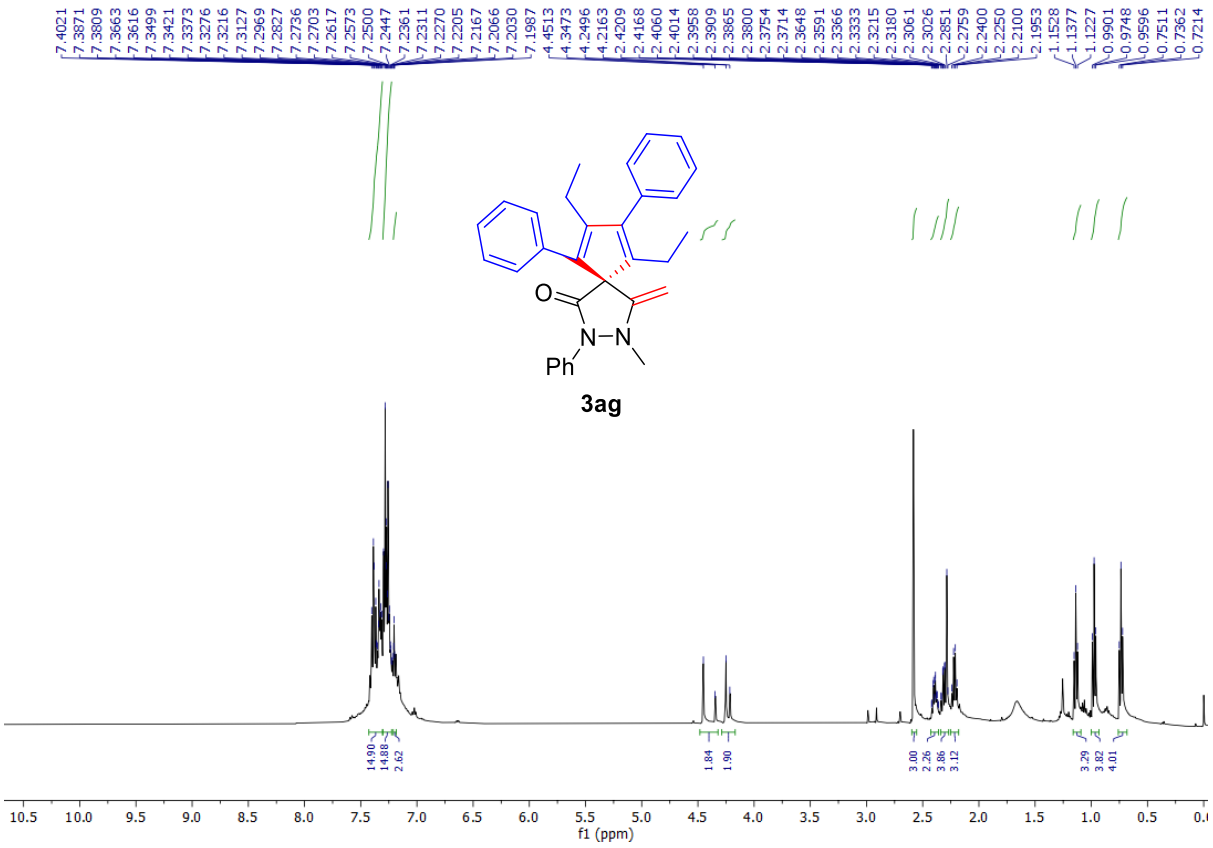

F
F
F
F
O
N–N
Ph
3ae
f1 (ppm)

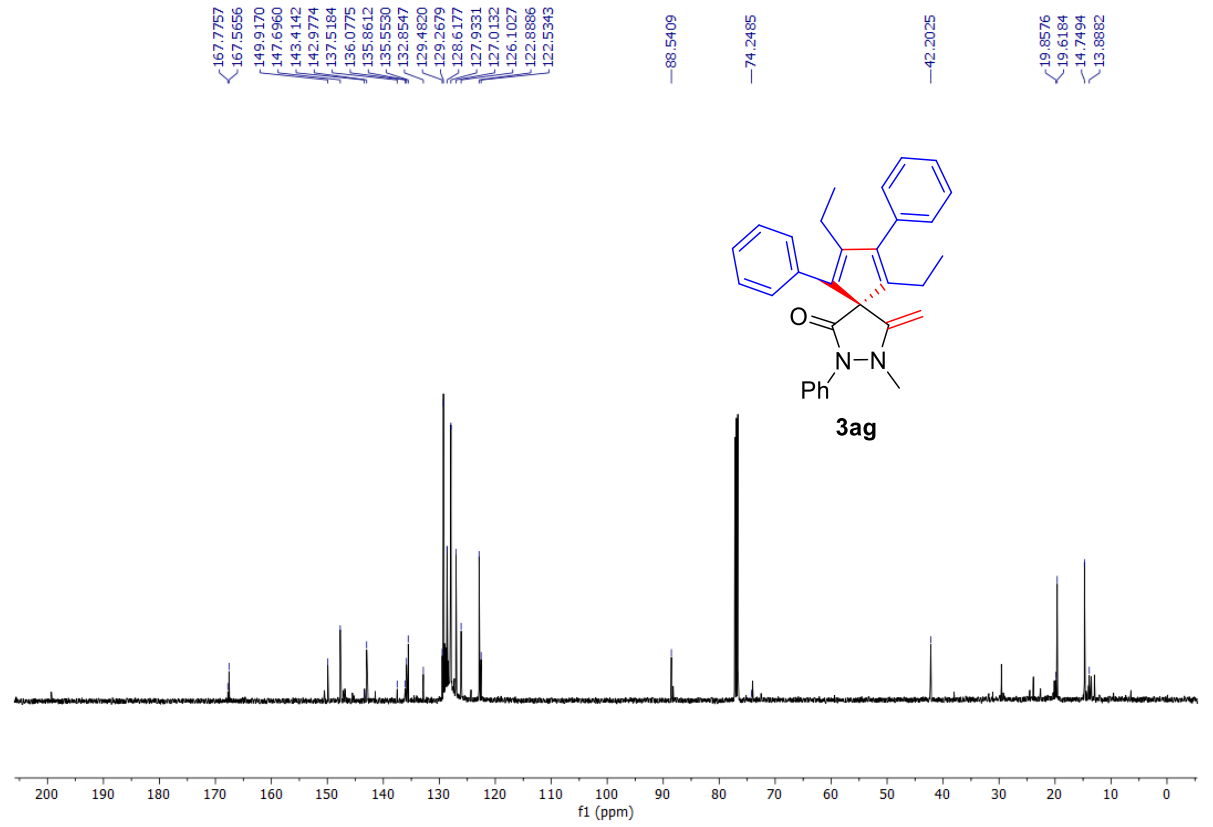

Elemental Composition
File Edit View Process Help
Single Mass Analysis
Tolerance = 100.0 mDa / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3
Monoisotopic Mass, Even Electron Ions
18300 formula(e) evaluated with 2982 results within limits (all results (up to 1000) for each mass)
Elements Used:
Mass | Calc. Mass | mDa | PPM | DBE | Formula | i-FIT | i-FIT Norm | Fit Conf % | C | H | N | O | F
615.2056 | 615.2056 | 0.0 | 0.0 | 3.5 | C23 H29 N2 O F14 | 458.4 | 4.678 | 0.93 | 23 | 29 | 2 | 1 | 14
615.2056 | 615.2056 | 0.0 | 0.0 | 18.5 | C29 H25 N8 O F6 | 460.8 | 7.089 | 0.08 | 29 | 25 | 8 | 1 | 6
615.2055 | 615.2055 | 0.1 | 0.2 | 20.5 | C33 H29 N4 O6 F2 | 462.3 | 8.570 | 0.02 | 33 | 29 | 4 | 6 | 2
615.2057 | 615.2057 | -0.1 | -0.2 | 29.5 | C37 H24 N8 O F | 463.1 | 9.394 | 0.01 | 37 | 24 | 8 | 1 | 1
615.2054 | 615.2054 | 0.2 | 0.3 | 9.5 | C25 H30 N4 O6 F7 | 460.4 | 6.691 | 0.12 | 25 | 30 | 4 | 6 | 7
615.2058 | 615.2058 | -0.2 | -0.3 | 4.5 | C14 H30 N12 O12 F3 | 463.1 | 9.428 | 0.01 | 14 | 30 | 12 | 12 | 3
615.2058 | 615.2058 | -0.2 | -0.3 | 14.5 | C31 H28 N2 O F9 | 459.8 | 6.153 | 0.21 | 31 | 28 | 2 | 1 | 9
615.2054 | 615.2054 | 0.2 | 0.3 | 7.5 | C21 H26 N8 O F11 | 459.5 | 5.819 | 0.30 | 21 | 26 | 8 | 1 | 11
615.2053 | 615.2053 | 0.3 | 0.5 | 22.5 | C27 H22 N14 O F3 | 461.6 | 7.865 | 0.04 | 27 | 22 | 14 | 1 | 3
615.2053 | 615.2053 | 0.3 | 0.5 | 11.5 | C29 H34 O11 F3 | 461.8 | 8.148 | 0.03 | 29 | 34 | | 11 | 3
615.2052 | 615.2052 | 0.4 | 0.7 | -1.5 | C17 H31 N4 O6 F12 | 461.7 | 8.054 | 0.03 | 17 | 31 | 4 | 6 | 12
615.2052 | 615.2052 | 0.4 | 0.7 | 0.5 | C21 H35 O11 F8 | 461.4 | 7.680 | 0.05 | 21 | 35 | | 11 | 8
615.2060 | 615.2060 | -0.4 | -0.7 | 25.5 | C39 H27 N2 O F4 | 462.2 | 8.520 | 0.02 | 39 | 27 | 2 | 1 | 4
615.2052 | 615.2052 | 0.4 | 0.7 | 11.5 | C19 H23 N14 O F8 | 460.4 | 6.666 | 0.13 | 19 | 23 | 14 | 1 | 8
26062019_291_5223
SC-115_27062019_015 156 (4.021) AM2 (Ar,30000.0,556.27,0.00,LS 1)
1: TOF MS ES+
1.58e+007
615.2056
616.2097
615.1367
615.0731
617.2149
647.2090
3ae
For Help, press F1

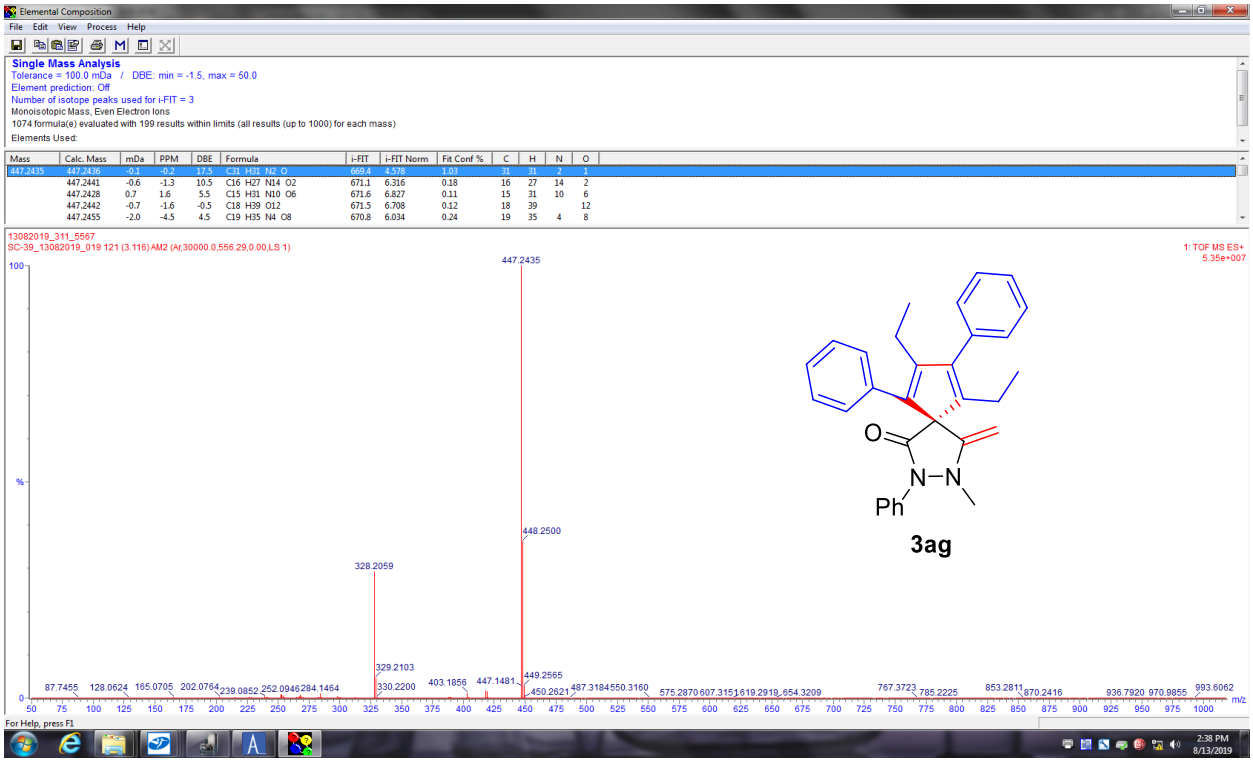

7.4714
7.4689
7.4541
7.4520
7.4124
7.4108
7.3977
7.3958
7.3809
7.3413
7.3387
7.3266
7.3165
7.3141
7.3112
7.3002
7.2980
7.2476
7.2350
7.2328
7.2224
7.2180
4.4199
4.4162
4.1994
4.1957
2.6610
1.8868
O
N–N
Ph
3af
2.25
4.31
7.27
2.08
1.03
1.09
3.00
6.01
f1 (ppm)

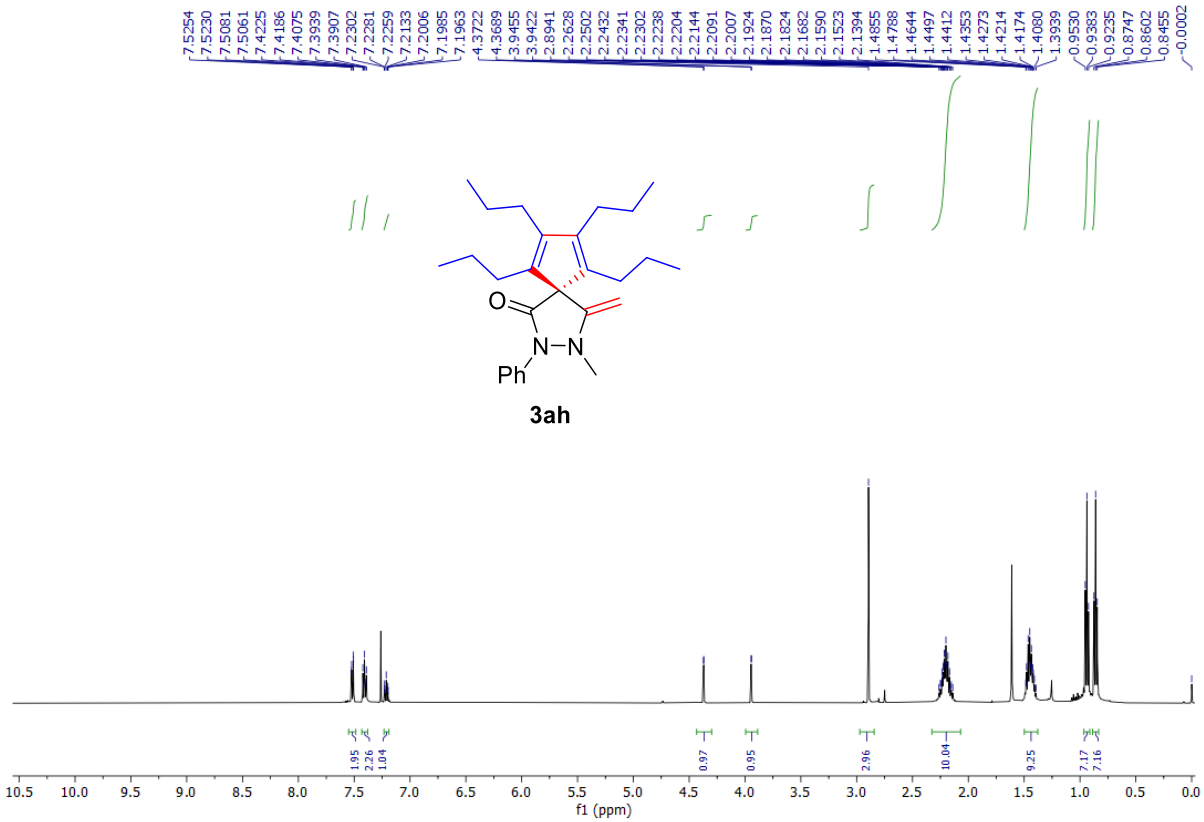

168.1655
150.9726
145.1792
141.8988
141.6651
141.5680
136.0971
135.6420
135.3203
129.4855
129.1554
128.9417
128.1256
127.1534
126.9271
126.3403
122.7897
88.0999
73.0717
42.3813
13.9196
11.5240
O
N–N
Ph
3af
f1 (ppm)

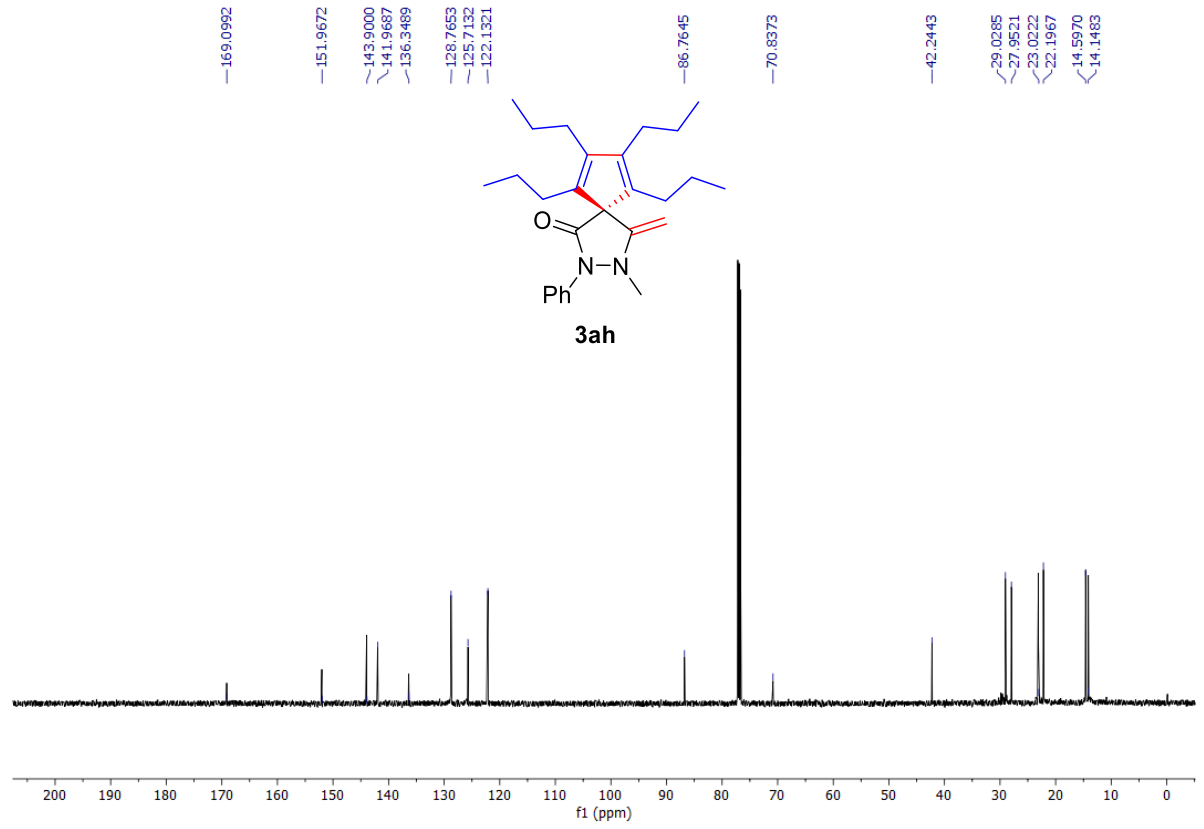

Elemental Composition
File Edit View Process Help
Single Mass Analysis
Tolerance = 100.0 mDa / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3
Monoisotopic Mass, Even Electron Ions
985 formula(e) evaluated with 198 results within limits (all results (up to 1000) for each mass)
Elements Used:
Mass Calc. Mass mDa PPM DBE Formula i-FIT i-FIT Norm Fit Conf % C H N O
419.2127 419.2128 -0.1 -0.2 10.5 C14 H23 N14 O2 729.8 7.164 0.08 14 23 14 2
419.2129 -0.2 -0.5 -0.5 C16 H35 O12 729.6 6.945 0.10 16 35 12
419.2123 0.4 1.0 17.5 C29 H27 N2 O 726.4 3.751 2.35 29 27 2 1
419.2115 1.2 2.9 5.5 C13 H27 N10 O6 730.1 7.388 0.06 13 27 10 6
419.2142 -1.5 -3.6 4.5 C17 H31 N4 O8 729.1 6.466 0.16 17 31 4 8
419.2102 2.5 6.0 0.5 C12 H31 N6 O10 730.3 7.661 0.05 12 31 6 10
09082019_309_5551
SC-38_09082019_013 115 (2.963) AM2 (Ar,30000.0,556.38,0.00,LS 1)
1: TOF MS ES+
5.74e+007
419.2127
420.2191
100
%
0
72.6532
152.0611 165.0631
215.0888
253.0993 285.1567
300.1776
301.1850
404.1983
419.1206
421.2245
433.2398
502.3062 515.2853 551.2968
592.2220
659.2624
680.2859
942.0553 953.6893 1007.8890
m/z
50 75 100 125 150 175 200 225 250 275 300 325 350 375 400 425 450 475 500 525 550 575 600 625 650 675 700 725 750 775 800 825 850 875 900 925 950 975 1000
For Help, press F1
5:07 PM
8/9/2019
O
N–N
Ph
3af

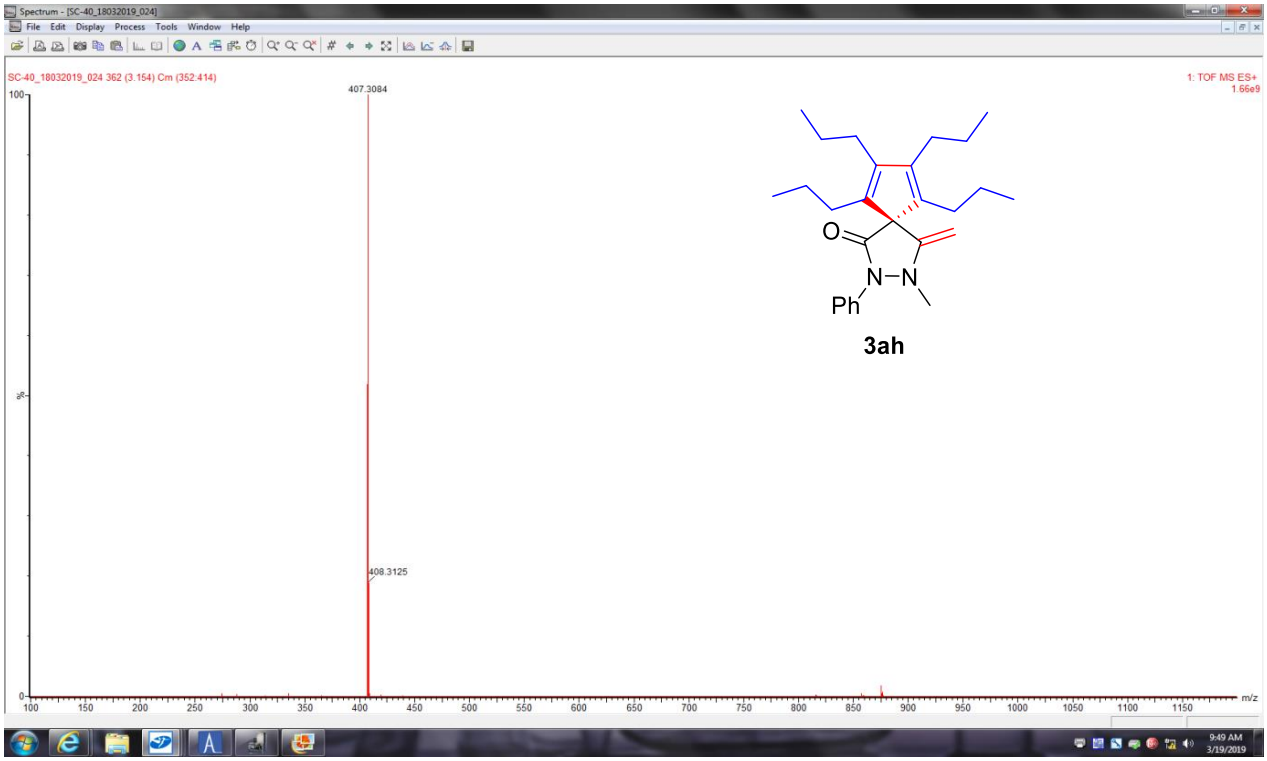

7.4021
7.3871
7.3809
7.3663
7.3616
7.3499
7.3421
7.3373
7.3276
7.3216
7.3127
7.2969
7.2827
7.2736
7.2703
7.2617
7.2573
7.2500
7.2447
7.2361
7.2311
7.2270
7.2205
7.2167
7.2066
7.2030
7.1987
4.4513
4.3473
4.2496
4.2163
4.2209
2.4168
2.4060
2.4014
2.3958
2.3909
2.3865
2.3800
2.3754
2.3714
2.3648
2.3591
2.3366
2.3333
2.3215
2.3180
2.3061
2.3026
2.2851
2.2759
2.2400
2.2250
2.2100
2.1953
1.1528
1.1377
1.1227
0.9901
0.9748
0.9596
0.7511
0.7362
0.7214
O
N–N
Ph
3ag
14.90
14.88
2.62
1.84
1.90
3.00
2.26
3.86
3.12
3.29
3.82
4.01
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)


167.7757
167.5656
149.9170
147.6960
143.4142
142.9774
137.5184
136.0775
135.8612
135.5530
132.8547
129.4820
129.2679
128.6177
127.9331
127.0132
126.1027
122.8886
122.5343
88.5409
74.2485
42.2025
19.8576
19.6184
14.7494
13.8882
O
N–N
Ph
3ag
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

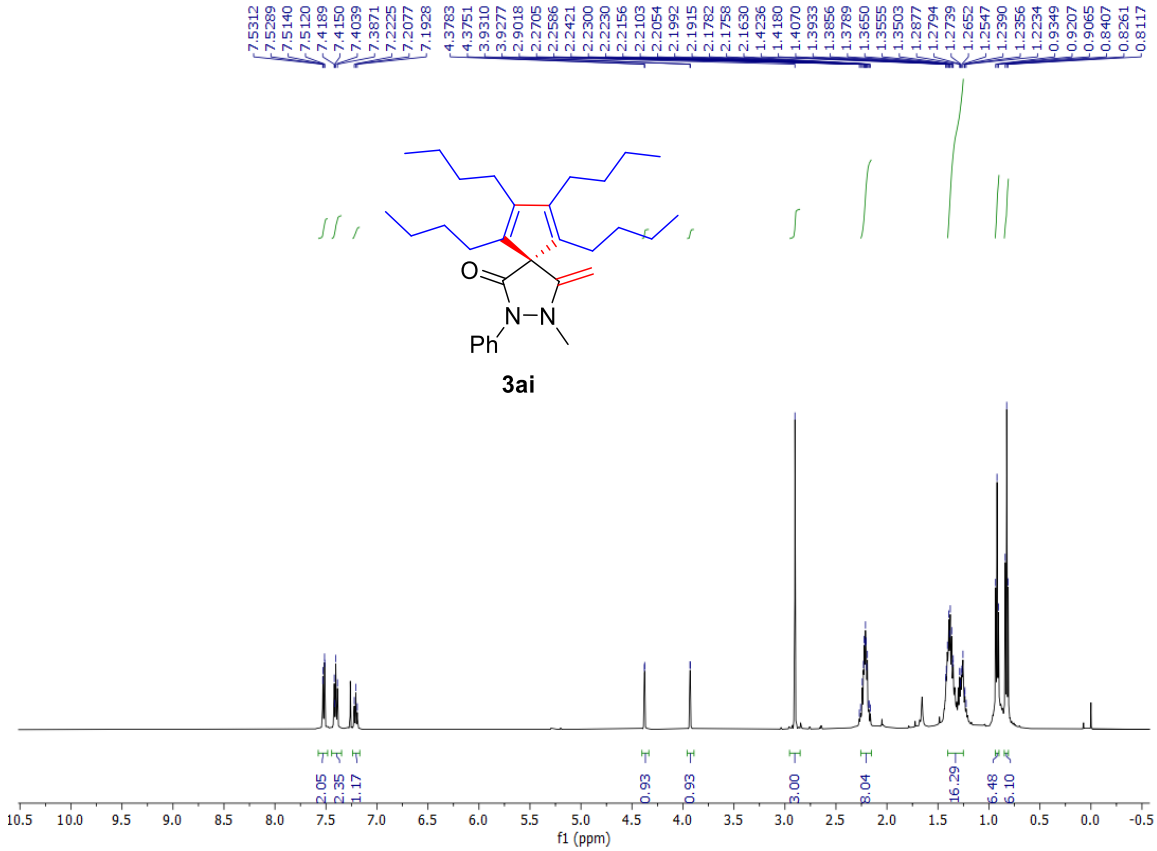

Elemental Composition
File Edit View Process Help
Single Mass Analysis
Tolerance = 100.0 mDa / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3
Monoisotopic Mass, Even Electron Ions
1074 formula(e) evaluated with 199 results within limits (all results (up to 1000) for each mass)
Elements Used:
Mass Calc. Mass mDa PPM DBE Formula i-FIT i-FIT Norm Fit Conf % C H N O
447.2435 447.2436 -0.1 -0.2 17.5 C31 H31 N2 O 669.4 4.578 1.03 31 31 2 1
447.2441 -0.6 -1.3 10.5 C16 H27 N14 O2 671.1 6.316 0.18 16 27 14 2
447.2428 0.7 1.6 5.5 C15 H31 N10 O6 671.6 6.827 0.11 15 31 10 6
447.2442 -0.7 -1.6 -0.5 C18 H39 O12 671.5 6.708 0.12 18 39 12
447.2455 -2.0 -4.5 4.5 C19 H35 N4 O8 670.8 6.034 0.24 19 35 4 8
13082019_311_5567
SC-39_13082019_019 121 (3.116) AM2 (Ar,30000.0,556.29,0.00,LS 1)
1: TOF MS ES+
5.35e+007
447.2435
448.2500
328.2059
329.2103
O
N–N
Ph
3ag
For Help, press F1
2:38 PM
8/13/2019


7.5254
7.5230
7.5081
7.5061
7.4225
7.4186
7.4075
7.3939
7.3907
7.2302
7.2281
7.2259
7.2133
7.2006
7.1985
7.1963
4.3722
4.3689
3.9455
3.9422
2.8941
2.8628
2.2502
2.2432
2.2341
2.2302
2.2238
2.2204
2.2144
2.2091
2.2007
2.1924
2.1870
2.1824
2.1682
2.1590
2.1523
2.1394
1.4855
1.4788
1.4644
1.4497
1.4412
1.4353
1.4273
1.4214
1.4174
1.4080
1.3939
0.9530
0.9383
0.9235
0.8747
0.8602
0.8455
-0.0002
O
N–N
Ph
3ah
1.95
2.26
1.04
0.97
0.95
2.96
10.04
9.25
7.17
7.16
f1 (ppm)

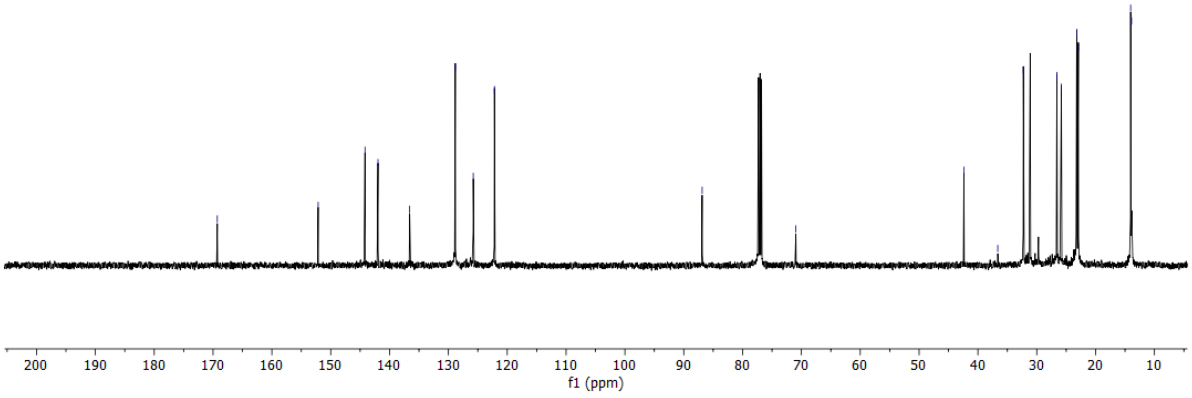

169.0992
151.9672
143.9000
141.9687
136.3489
128.7653
125.7132
122.1321
86.7645
70.8373
42.2443
29.0285
27.9521
23.0222
22.1967
14.5970
14.1483
O
N–N
Ph
3ah
f1 (ppm)


Spectrum - [SC-40_18032019_024]
File Edit Display Process Tools Window Help
SC-40_18032019_024 362 (3.154) Cm (352:414)
1: TOF MS ES+
1.66e9
407.3084
408.3125
100
%
0
100 150 200 250 300 350 400 450 500 550 600 650 700 750 800 850 900 950 1000 1050 1100 1150
m/z
O
N–N
Ph
9:49 AM
3/19/2019

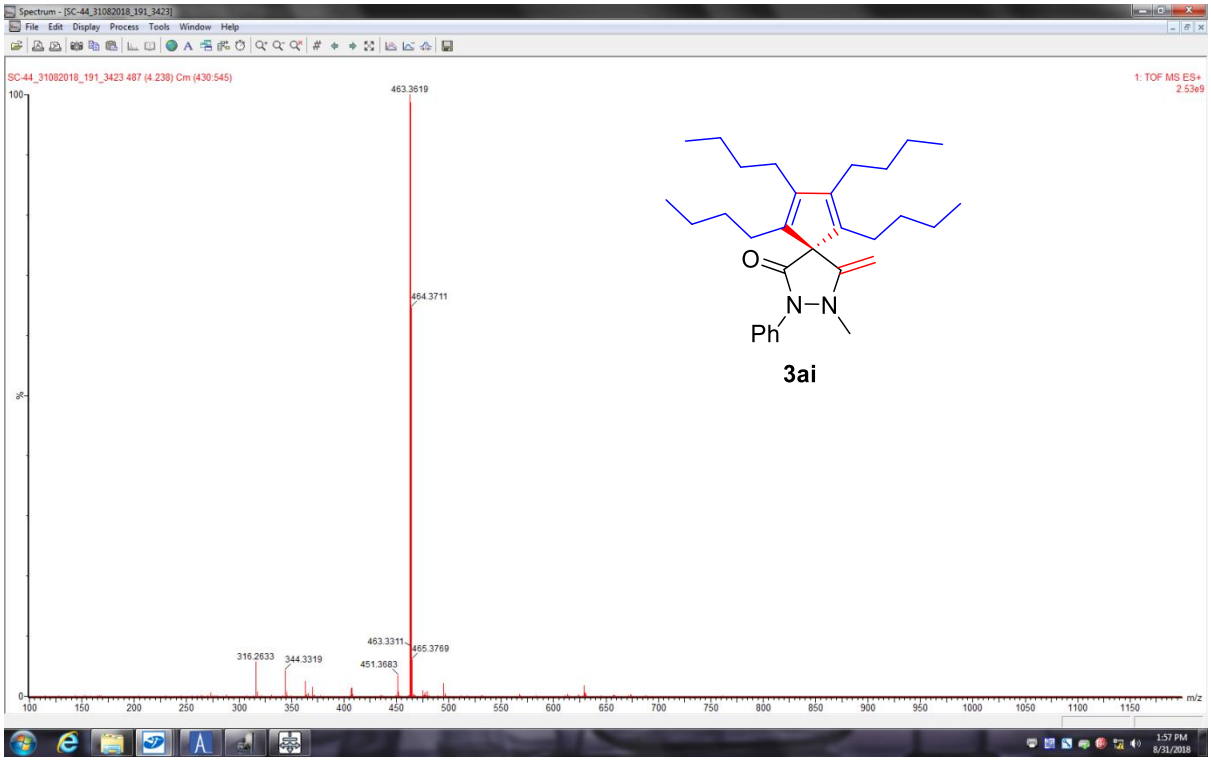
3ah

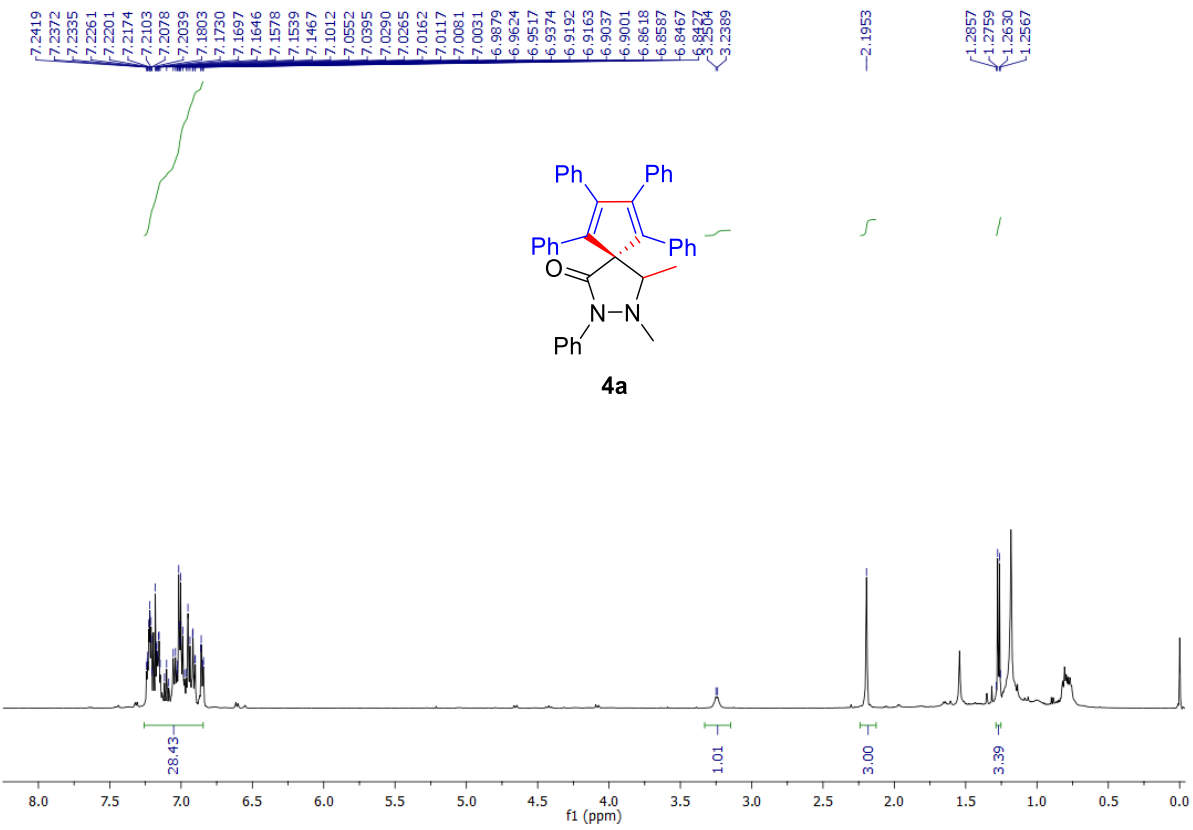

7.5312
7.5289
7.5140
7.5120
7.4189
7.4150
7.4039
7.3871
7.2225
7.2077
7.1928
4.3783
4.3751
3.9310
3.9277
3.9018
2.2705
2.2586
2.2421
2.2300
2.2230
2.2156
2.2103
2.2054
2.1992
2.1915
2.1782
2.1758
2.1630
1.4236
1.4180
1.4070
1.3933
1.3856
1.3789
1.3650
1.3555
1.3503
1.2877
1.2794
1.2739
1.2652
1.2547
1.2390
1.2356
1.2234
0.9349
0.9207
0.9065
0.8407
0.8261
0.8117
O
N–N
Ph
2.05
2.35
1.17
0.93
0.93
3.00
8.04
16.29
6.48
6.10
f1 (ppm)

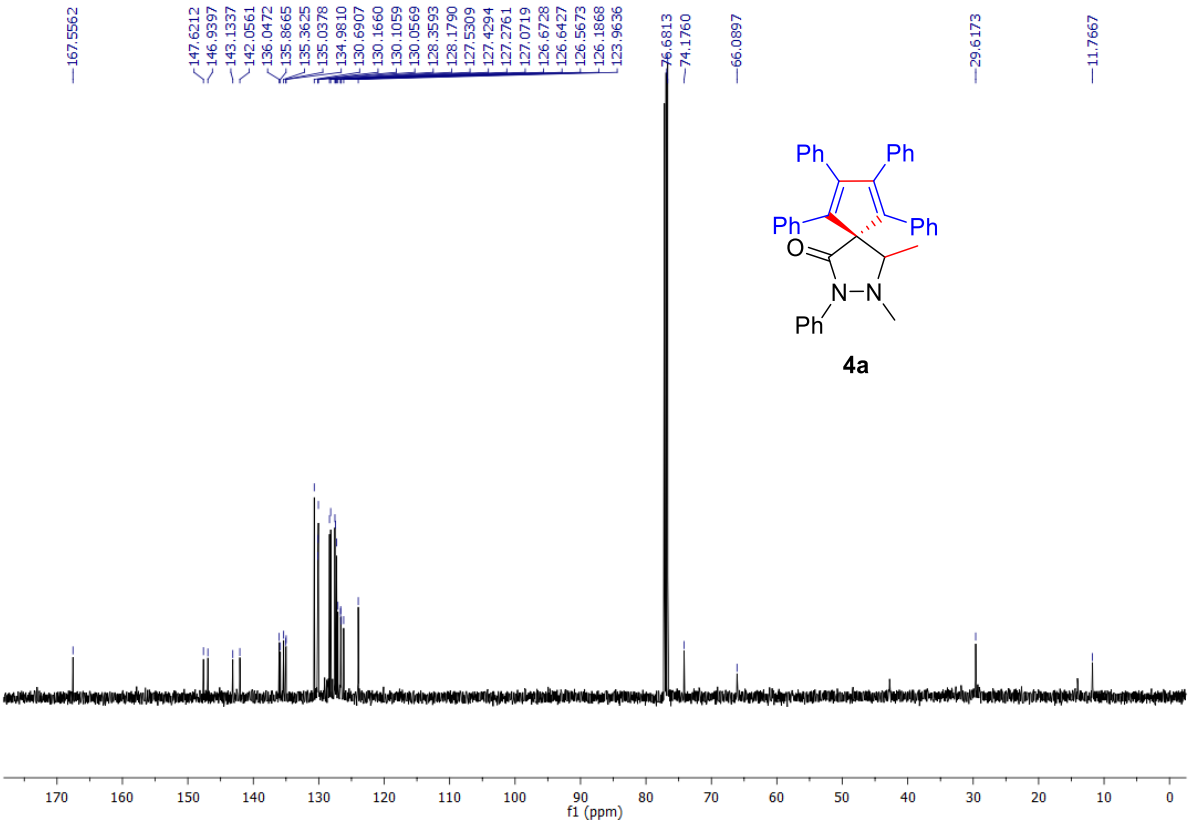
3ai

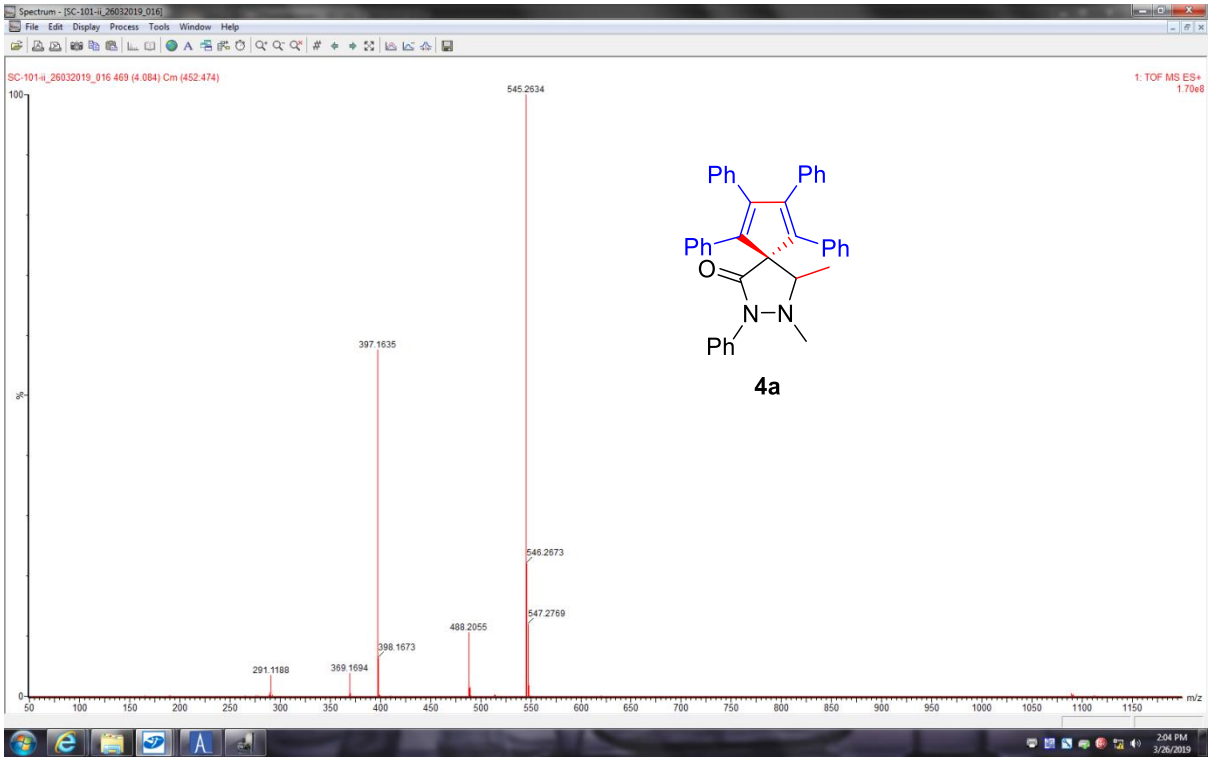

169.2784
152.1343
144.1731
141.9646
136.5834
128.8279
125.7724
122.1732
86.8726
70.9506
42.3840
36.6261
32.2815
26.5800
25.8170
23.2091
22.9249
14.0432
13.8936
f1 (ppm)

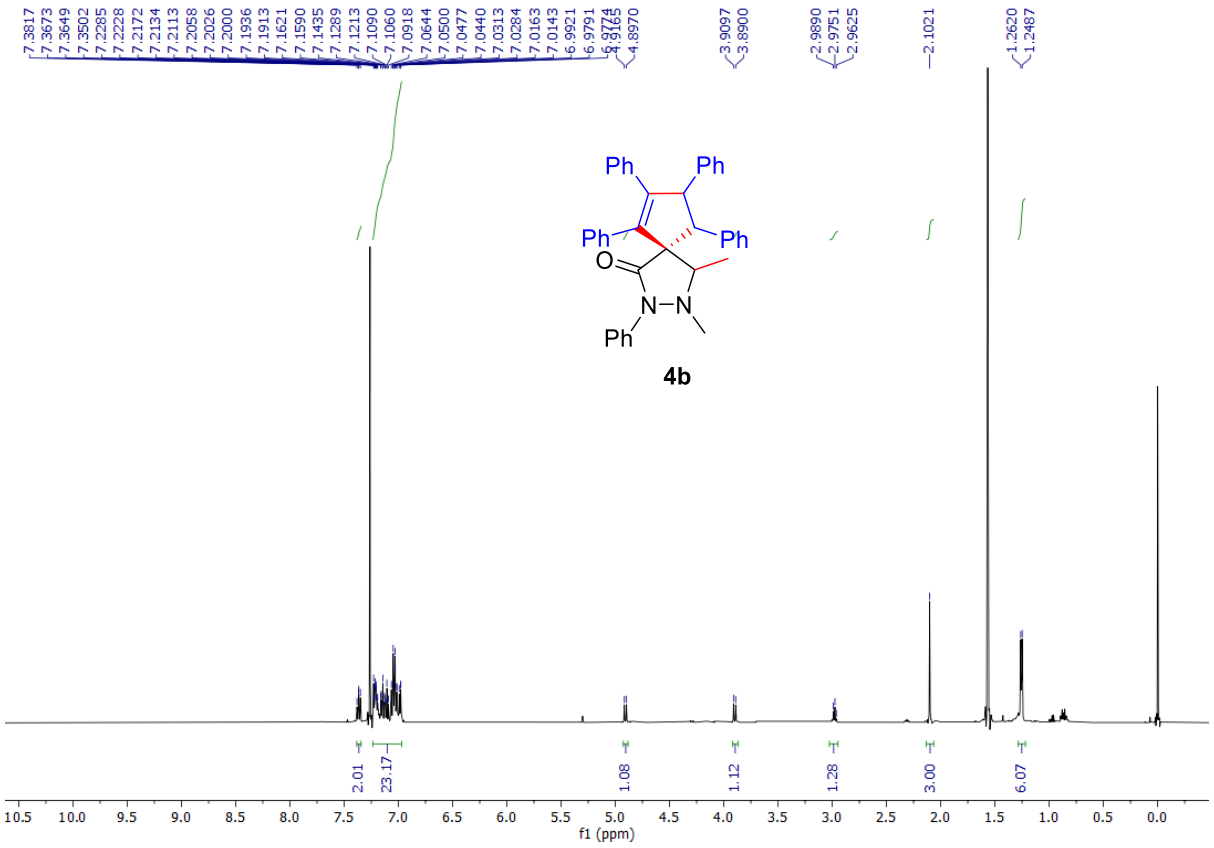
3ai


Spectrum - [SC-44_31082018_191_3423]
File Edit Display Process Tools Window Help
SC-44_31082018_191_3423 487 (4.238) Cm (430:545)
1: TOF MS ES+
2.53e9
100
%
0
463.3619
464.3711
463.3311
465.3769
451.3683
316.2633
344.3319
100 150 200 250 300 350 400 450 500 550 600 650 700 750 800 850 900 950 1000 1050 1100 1150
m/z
O
N–N
Ph
3ai
1:57 PM
8/31/2018

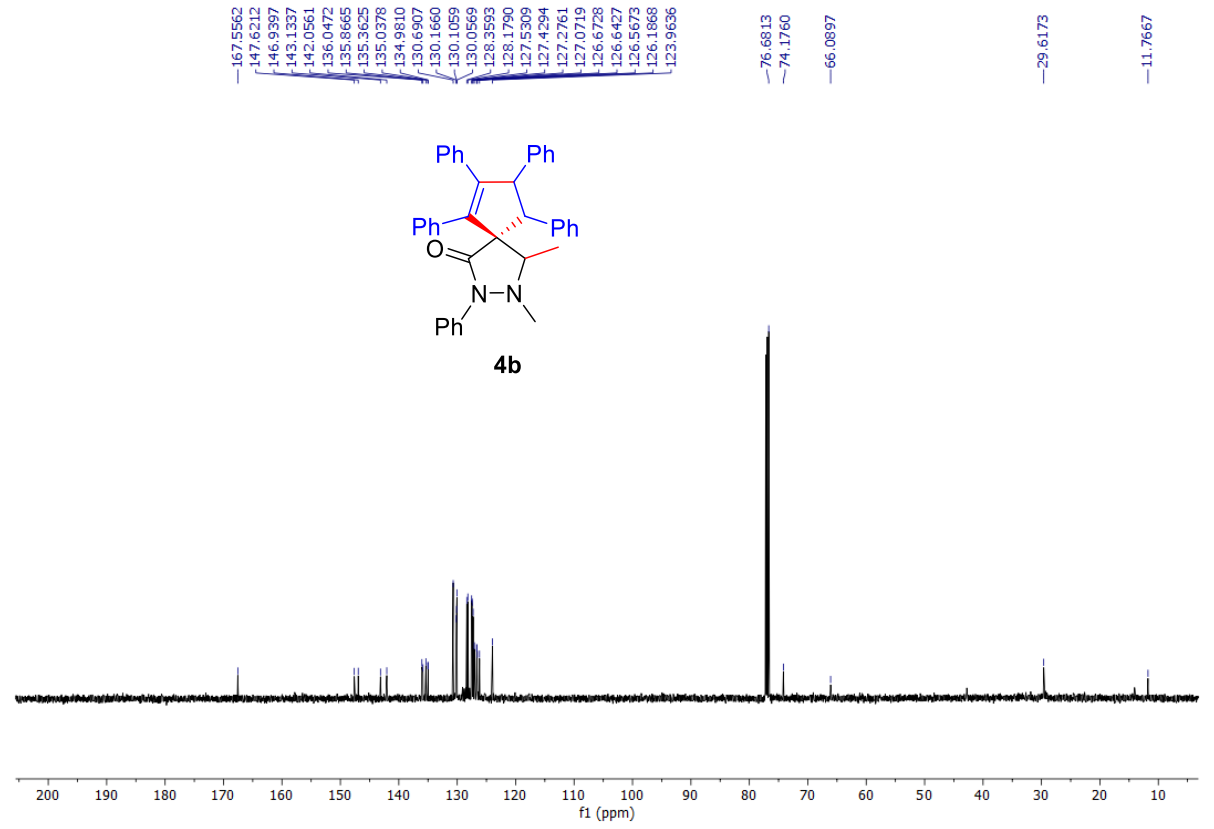

7.2419
7.2372
7.2335
7.2261
7.2201
7.2174
7.2103
7.2078
7.2039
7.1803
7.1730
7.1697
7.1646
7.1578
7.1539
7.1467
7.1012
7.0552
7.0395
7.0290
7.0265
7.0162
7.0117
7.0081
7.0031
6.9879
6.9624
6.9517
6.9374
6.9192
6.9163
6.9037
6.9001
6.8618
6.8587
6.8467
3.2504
3.2389
2.1953
1.2857
1.2759
1.2630
1.2567
Ph
Ph
Ph
Ph
O
N–N
Ph
4a
28.43
1.01
3.00
3.39
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


167.5562
147.6212
146.9397
143.1337
142.0561
136.0472
135.8665
135.3625
135.0378
134.9810
130.6907
130.1660
130.1059
130.0569
128.3593
128.1790
127.5309
127.4294
127.2761
127.0719
126.6728
126.6427
126.5673
126.1868
123.9636
76.6813
74.1760
66.0897
29.6173
11.7667
Ph
Ph
Ph
Ph
O
N–N
Ph
4a
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

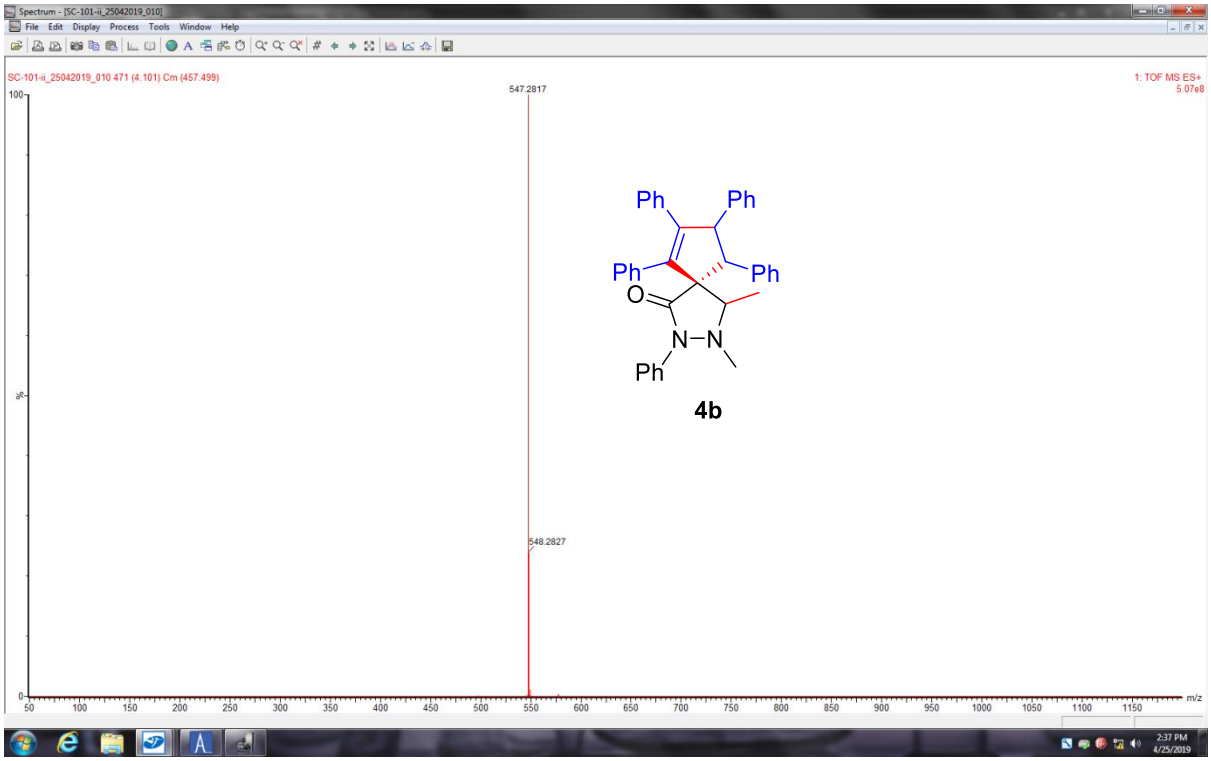

Spectrum - [SC-101-ii_26032019_016]
File Edit Display Process Tools Window Help
SC-101-ii_26032019_016 469 (4.084) Cm (452:474)
1: TOF MS ES+
1.70e8
100
%
0
545.2634
397.1635
546.2673
547.2769
488.2055
398.1673
291.1188
369.1694
50 100 150 200 250 300 350 400 450 500 550 600 650 700 750 800 850 900 950 1000 1050 1100 1150
m/z
Ph
Ph
Ph
Ph
O
N–N
Ph
4a
2:04 PM
3/26/2019


7.3817
7.3673
7.3649
7.3502
7.2285
7.2228
7.2172
7.2134
7.2113
7.2058
7.2026
7.2000
7.1936
7.1913
7.1621
7.1590
7.1435
7.1289
7.1213
7.1090
7.1060
7.0918
7.0644
7.0500
7.0477
7.0440
7.0313
7.0284
7.0163
7.0143
6.9921
6.9791
6.9774
6.9165
4.8970
3.9097
3.8900
2.9890
2.9751
2.9625
2.1021
1.2620
1.2487
Ph
Ph
Ph
Ph
O
N–N
Ph
2.01
23.17
1.08
1.12
1.28
3.00
6.07
f1 (ppm)

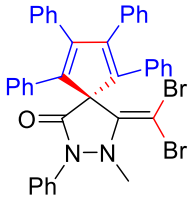
4b


167.5562
147.6212
146.9397
143.1337
142.0561
136.0472
135.8665
135.3625
135.0378
134.9810
130.6907
130.1660
130.1059
130.0569
128.3593
128.1790
127.5309
127.4294
127.2761
127.0719
126.6728
126.6427
126.5673
126.1868
123.9636
76.6813
74.1760
66.0897
29.6173
11.7667
Ph
Ph
Ph
Ph
O
N–N
Ph
f1 (ppm)

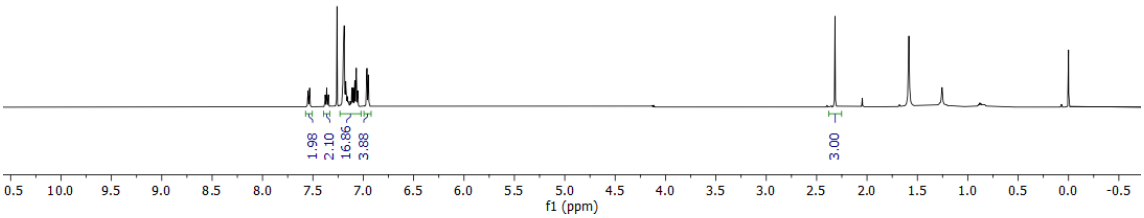
4b

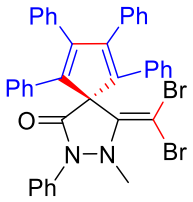

Spectrum - [SC-101-ii_25042019_010]
File Edit Display Process Tools Window Help
SC-101-ii_25042019_010 471 (4.101) Cm (457.499)
1: TOF MS ES+
5.07e8
100
%
0
547.2817
548.2827
50 100 150 200 250 300 350 400 450 500 550 600 650 700 750 800 850 900 950 1000 1050 1100 1150
m/z
Ph
Ph
Ph
Ph
O
N–N
Ph
4b
2:37 PM
4/25/2019

35695.1.fid
Name of Sample:SC-116
Spectrum No :35695

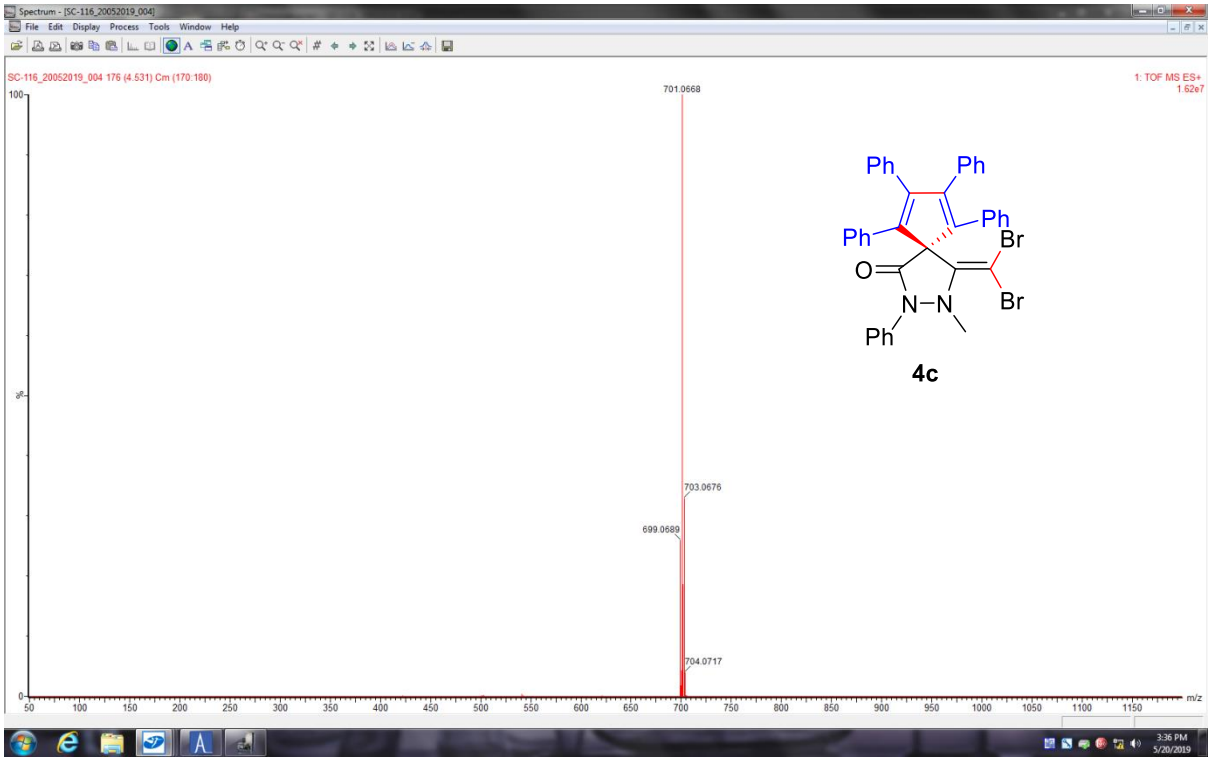


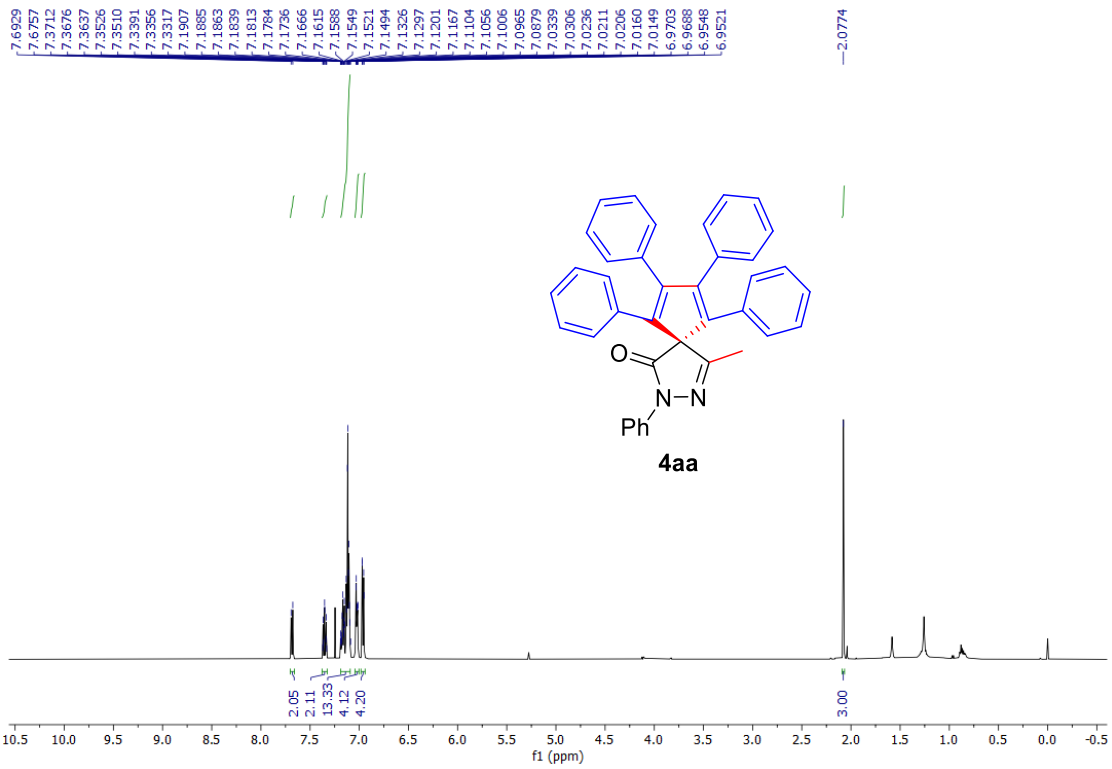
4c

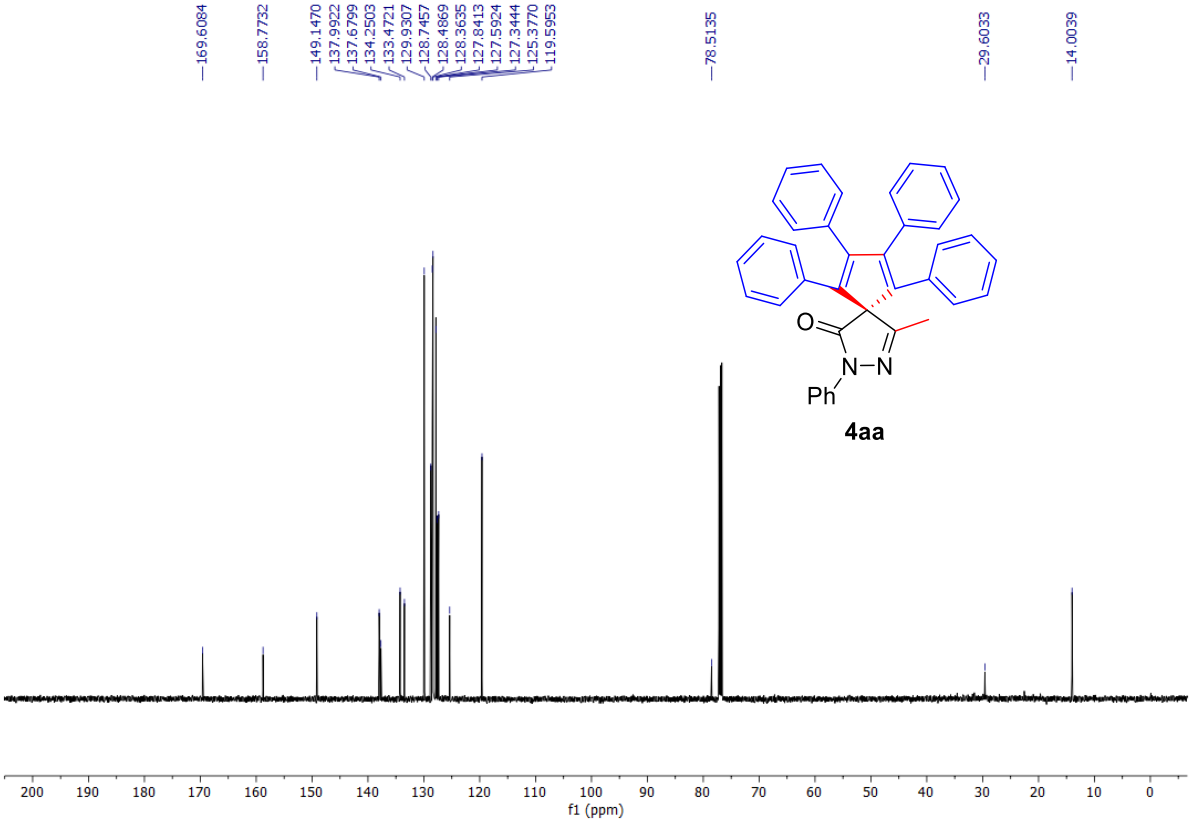


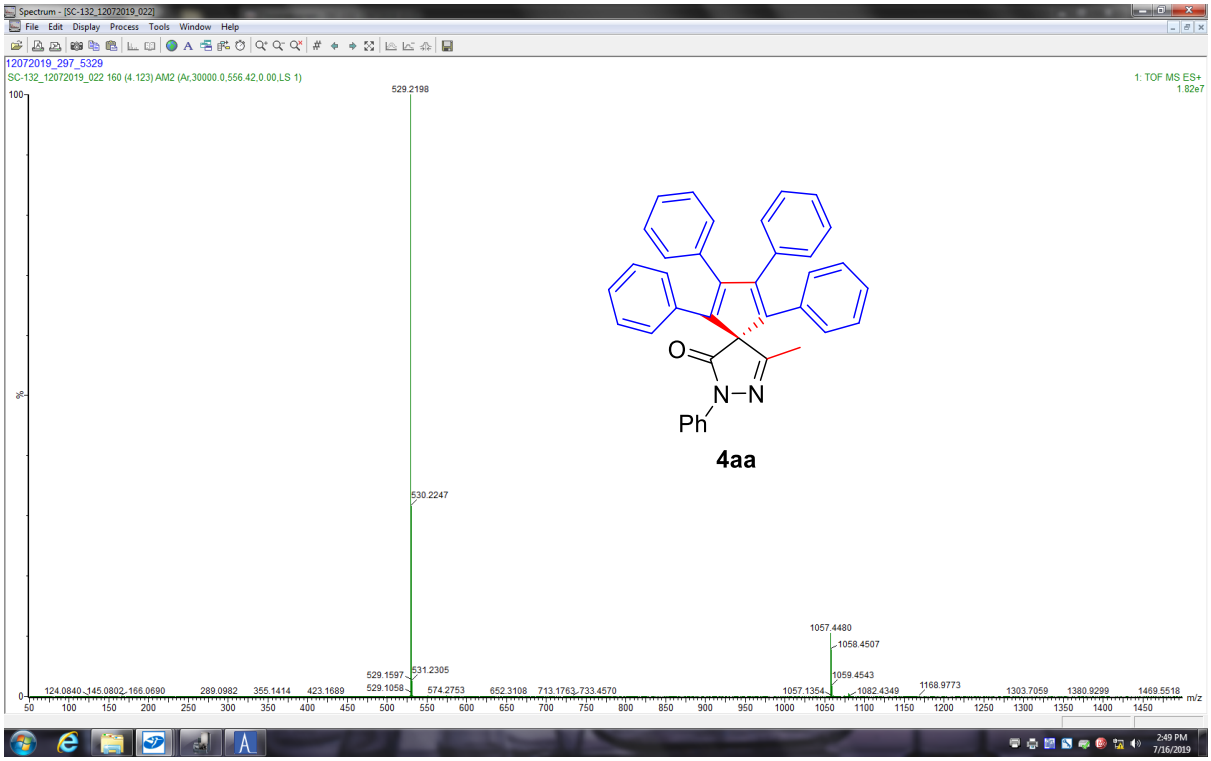


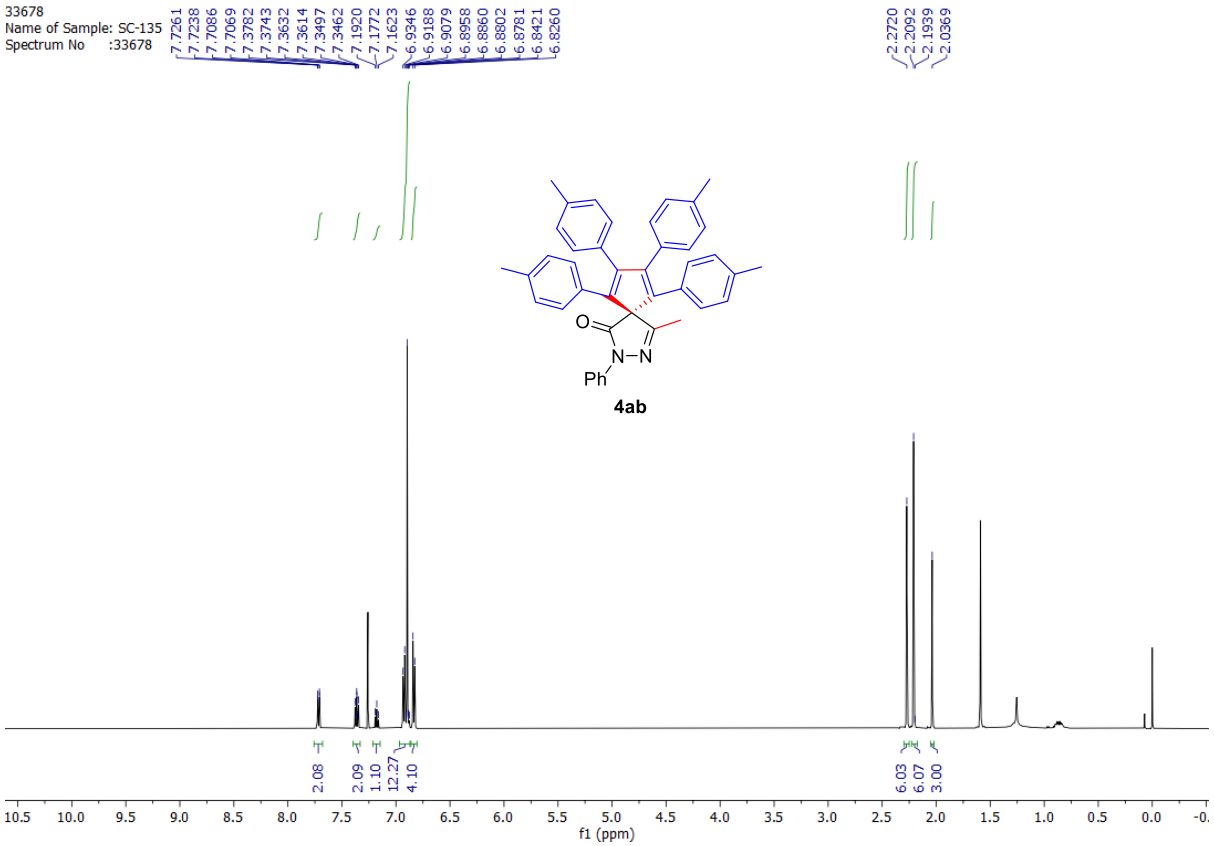
4c


Spectrum - [SC-116_20052019_004]
File Edit Display Process Tools Window Help
SC-116_20052019_004 176 (4.531) Cm (170:180)
1: TOF MS ES+
1.62e7
100
%
0
701.0668
703.0676
699.0689
704.0717
50 100 150 200 250 300 350 400 450 500 550 600 650 700 750 800 850 900 950 1000 1050 1100 1150
m/z
Ph
Ph
Ph
Ph
Br
O
N–N
Br
Ph
4c
3:36 PM
5/20/2019

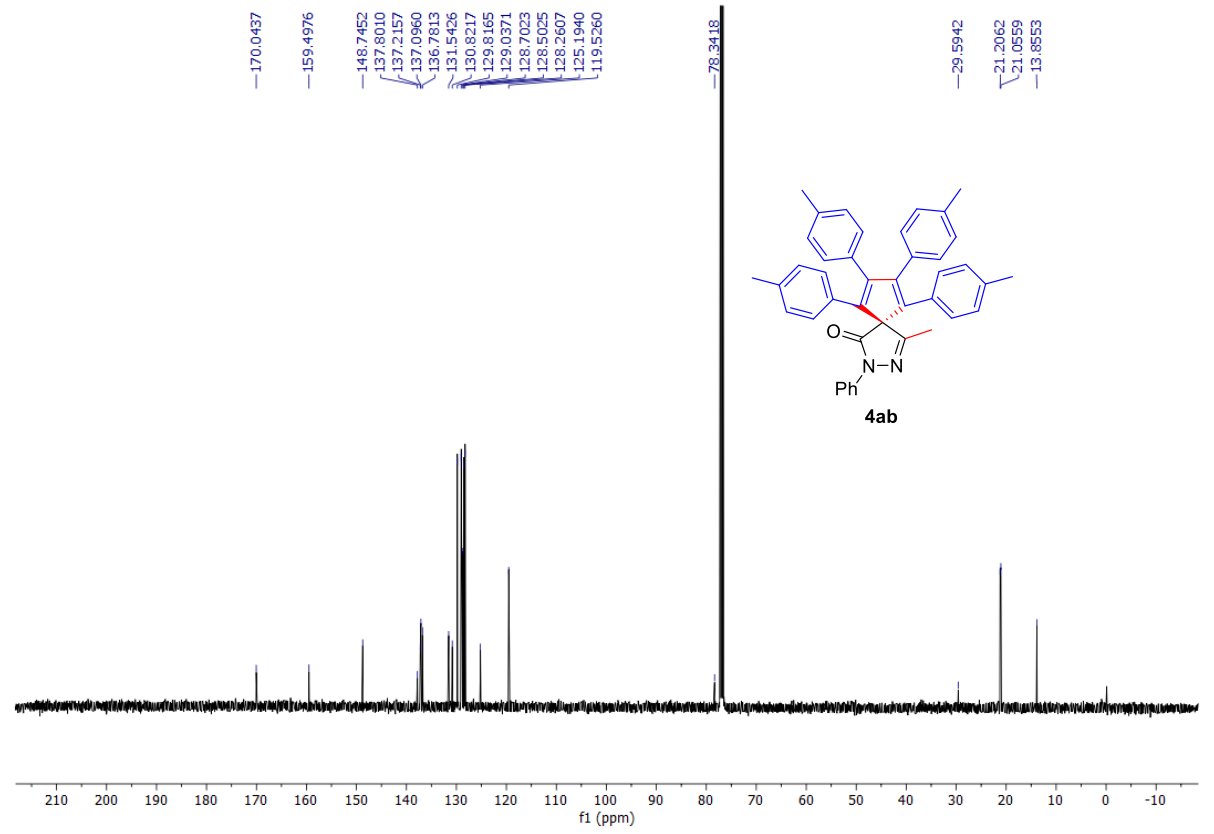

7.6929
7.6757
7.3712
7.3676
7.3637
7.3526
7.3510
7.3391
7.3356
7.3317
7.1907
7.1885
7.1863
7.1839
7.1813
7.1784
7.1736
7.1666
7.1615
7.1588
7.1549
7.1521
7.1494
7.1326
7.1297
7.1201
7.1167
7.1104
7.1056
7.1006
7.0965
7.0879
7.0339
7.0306
7.0236
7.0211
7.0206
7.0160
7.0149
6.9703
6.9688
6.9548
6.9521
2.0774
O
N–N
Ph
4aa
2.05
2.11
13.33
4.12
4.20
3.00
f1 (ppm)


169.6084
158.7732
149.1470
137.9922
137.6799
134.2503
133.4721
129.9307
128.7457
128.4869
128.3635
127.8413
127.5924
127.3444
125.3770
119.5953
78.5135
29.6033
14.0039
O
N–N
Ph
4aa
f1 (ppm)

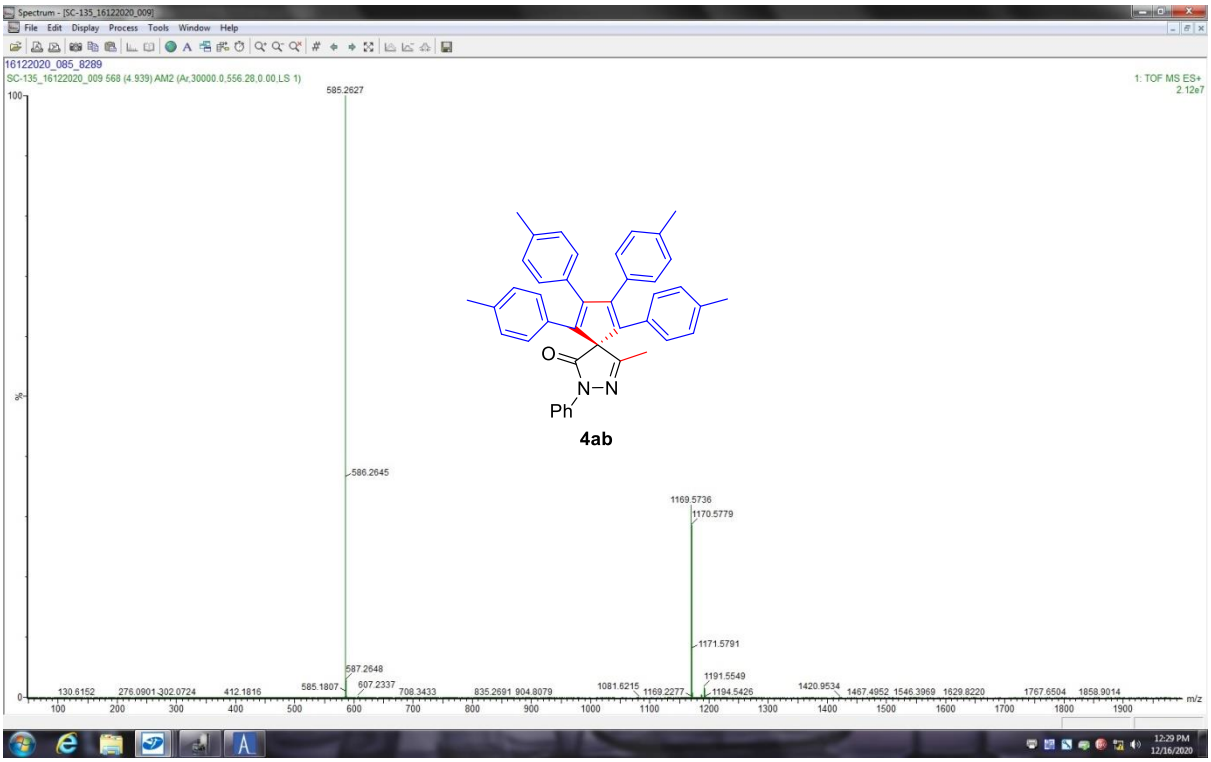

Spectrum - [SC-132_12072019_022]
File Edit Display Process Tools Window Help
12072019_297_5329
SC-132_12072019_022 160 (4.123) AM2 (Ar,30000.0,556.42,0.00,LS 1)
1: TOF MS ES+
1.82e7
529.2198
530.2247
1057.4480
1058.4507
1059.4543
531.2305
529.1597
529.1058
1057.1354
1082.4349
1168.9773
1303.7059
1380.9299
1469.5518
124.0840
145.0802
166.0690
289.0982
355.1414
423.1689
574.2753
652.3108
713.1763
733.4570
%
m/z
O
N–N
Ph
4aa
2:49 PM
7/16/2019

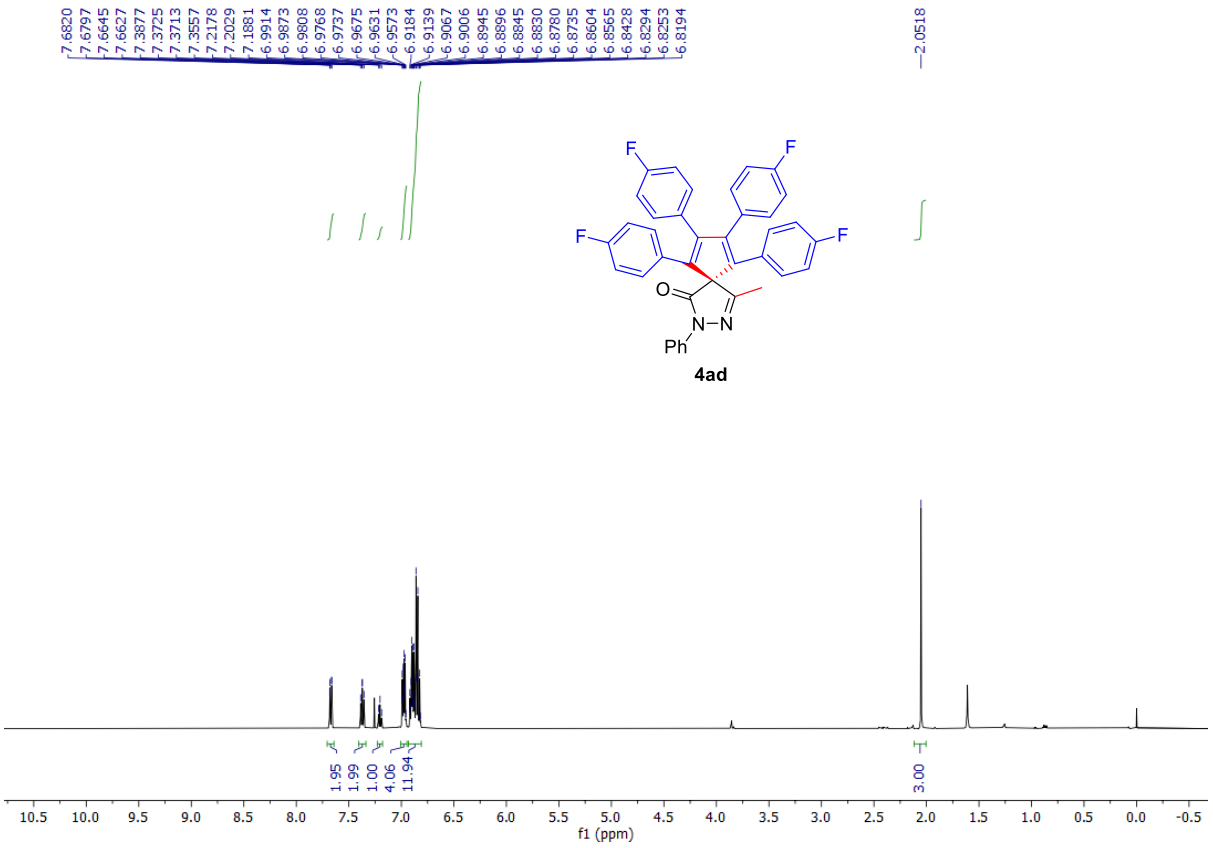

33678
Name of Sample: SC-135
Spectrum No :33678
7.7261
7.7238
7.7086
7.7069
7.3782
7.3743
7.3632
7.3614
7.3497
7.3462
7.1920
7.1772
7.1623
6.9346
6.9188
6.9079
6.8958
6.8860
6.8802
6.8781
6.8421
6.8260
2.2720
2.2092
2.1939
2.0369
O
N–N
Ph
2.08
2.09
1.10
12.27
4.10
6.03
6.07
3.00
f1 (ppm)

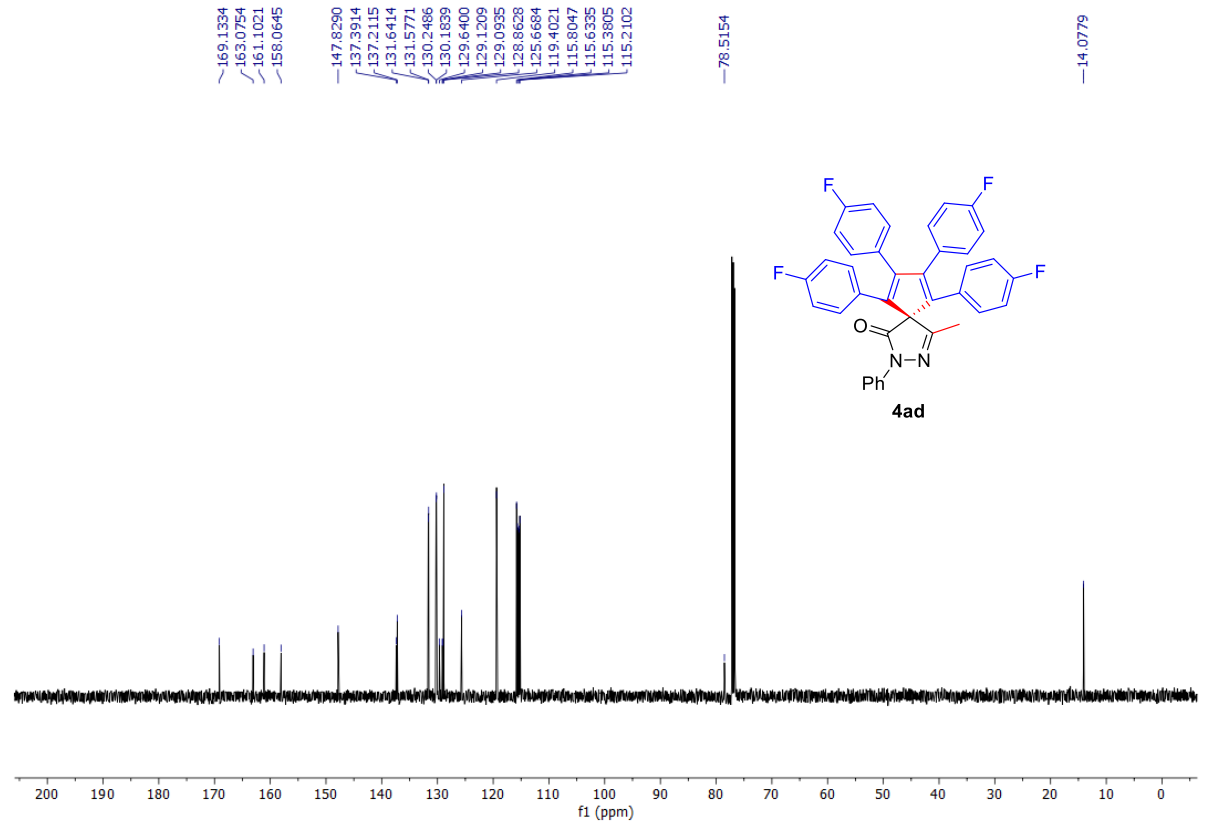
4ab

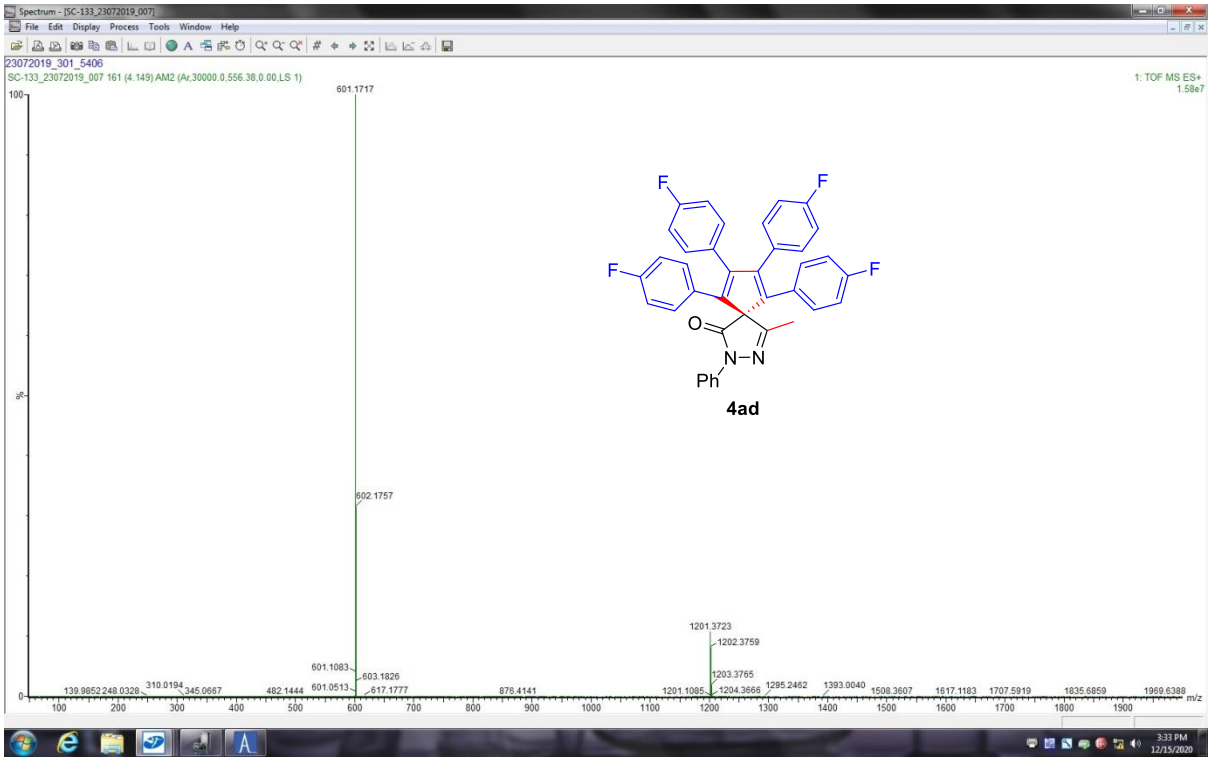

170.0437
159.4976
148.7452
137.8010
137.2157
137.0960
136.7813
131.5426
130.8217
129.8165
129.0371
128.7023
128.5025
128.2607
125.1940
119.5260
78.3418
29.5942
21.2062
21.0559
13.8553
O
N–N
Ph
f1 (ppm)

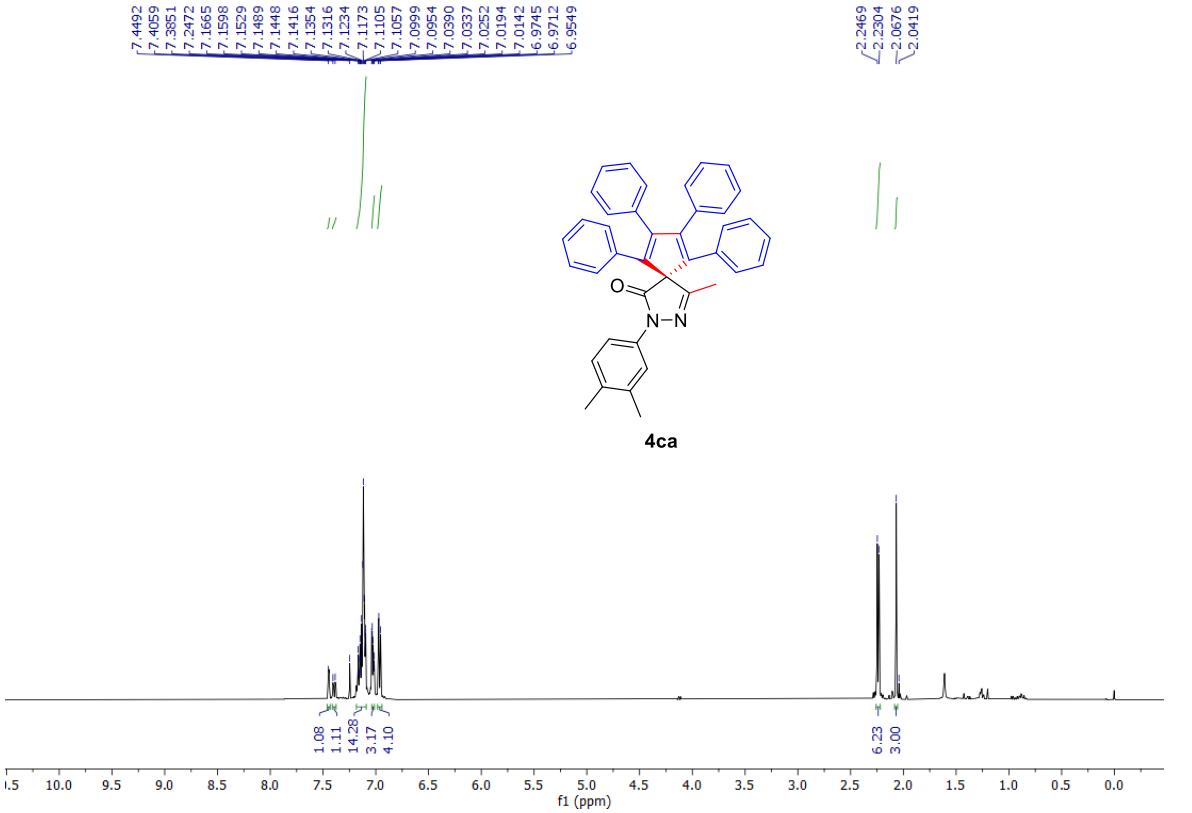
4ab


Spectrum - [SC-135_16122020_009]
File Edit Display Process Tools Window Help
16122020_085_8289
SC-135_16122020_009 568 (4.939) AM2 (Ar,30000.0,556.28,0.00,LS 1)
1: TOF MS ES+
2.12e7
585.2627
586.2645
1169.5736
1170.5779
1171.5791
587.2648
1191.5549
607.2337
585.1807
130.6152
276.0901
302.0724
412.1816
708.3433
835.2691
904.8079
1081.6215
1169.2277
1194.5426
1420.9534
1467.4952
1546.3969
1629.8220
1767.6504
1858.9014
m/z
O
N–N
Ph
4ab
12:29 PM
12/16/2020

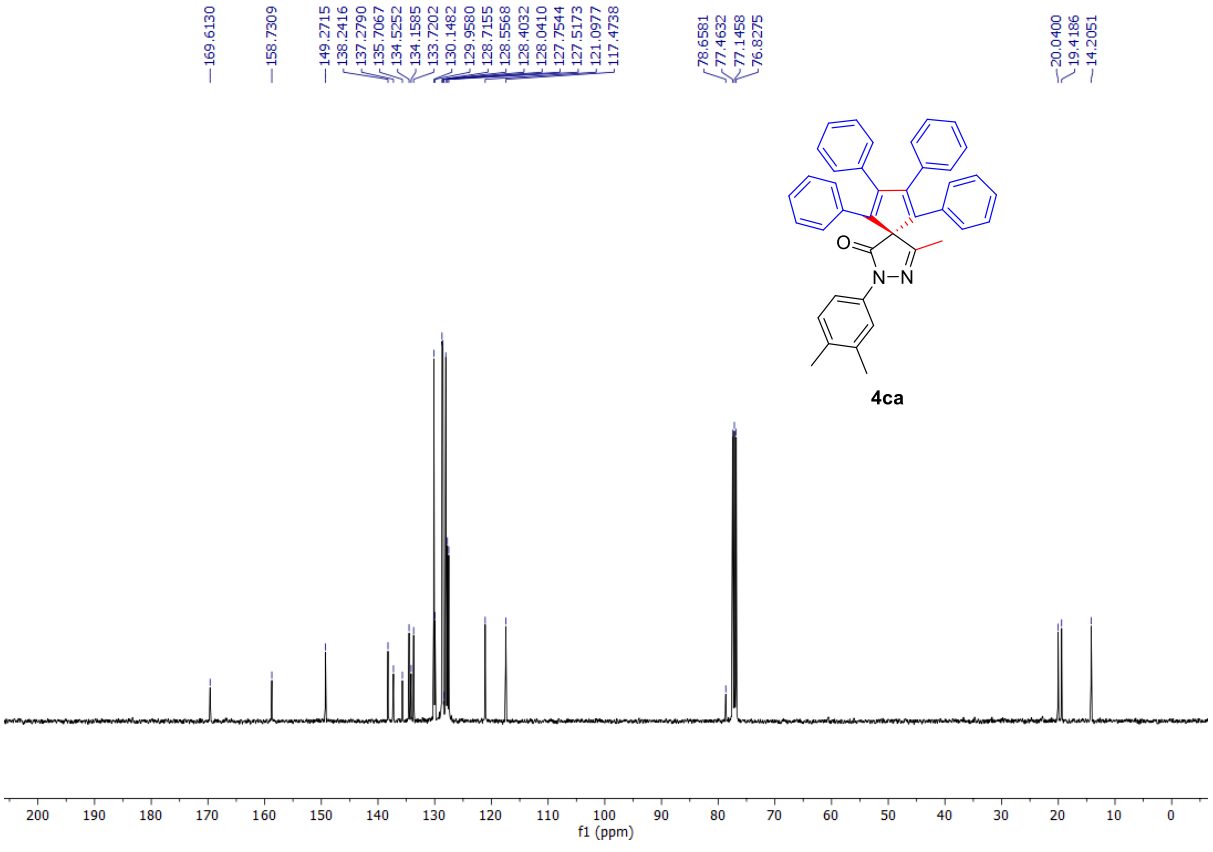

7.6820
7.6797
7.6645
7.6627
7.3877
7.3725
7.3713
7.3557
7.2178
7.2029
7.1881
6.9914
6.9873
6.9808
6.9768
6.9737
6.9675
6.9631
6.9573
6.9184
6.9139
6.9067
6.9006
6.8945
6.8896
6.8845
6.8830
6.8780
6.8735
6.8604
6.8565
6.8428
6.8294
6.8253
6.8194
2.0518
F
F
F
F
O
N–N
Ph
4ad
1.95
1.99
1.00
4.06
11.94
3.00
f1 (ppm)


169.1334
163.0754
161.1021
158.0645
147.8290
137.3914
137.2115
131.6414
131.5771
130.2486
130.1839
129.6400
129.1209
129.0935
128.8628
125.6684
119.4021
115.8047
115.6335
115.3805
115.2102
78.5154
14.0779
F
F
F
F
O
N–N
Ph
4ad
f1 (ppm)

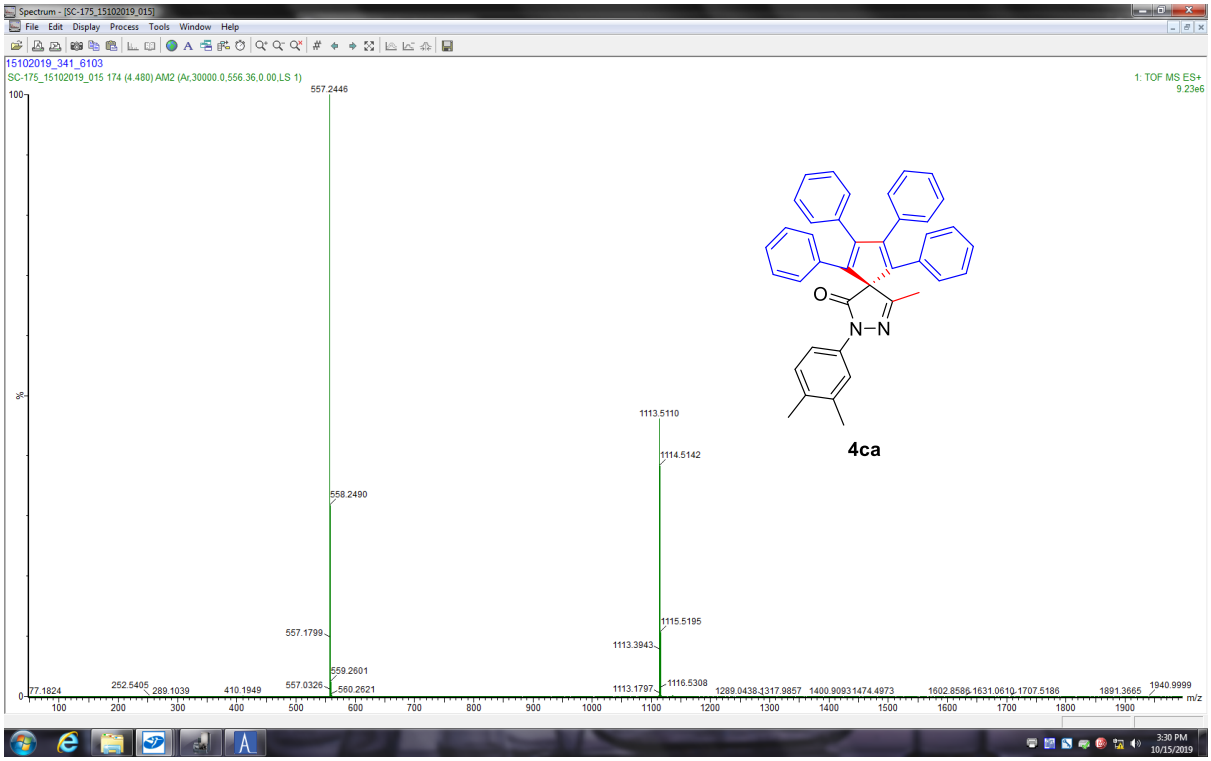

Spectrum - [SC-133_23072019_007]
File Edit Display Process Tools Window Help
23072019_301_5406
SC-133_23072019_007 161 (4.149) AM2 (Ar,30000.0,556.38,0.00,LS 1)
1: TOF MS ES+
1.58e7
601.1717
602.1757
1201.3723
1202.3759
1203.3765
601.1083
603.1826
601.0513
617.1777
139.9852 248.0328 310.0194 345.0667 482.1444 876.4141 1201.1085 1204.3666 1295.2462 1393.0040 1508.3607 1617.1183 1707.5919 1835.6859 1969.6388
m/z
F
F
F
F
O
N–N
Ph
4ad
3:33 PM
12/15/2020

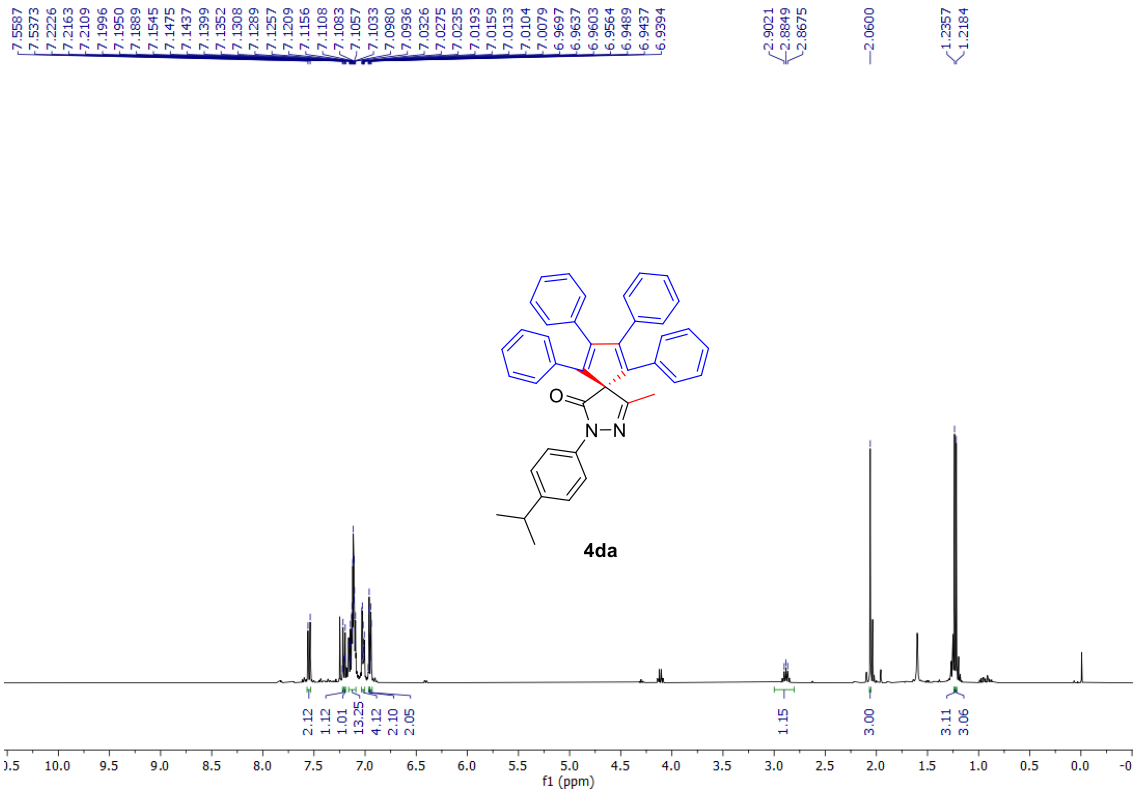

7.4492
7.4059
7.3851
7.2472
7.1665
7.1598
7.1529
7.1489
7.1448
7.1416
7.1354
7.1316
7.1234
7.1173
7.1105
7.1057
7.0999
7.0954
7.0390
7.0337
7.0252
7.0194
7.0142
6.9745
6.9712
6.9549
2.2469
2.2304
2.0676
2.0419
O
N–N
1.08
1.11
14.28
3.17
4.10
6.23
3.00
f1 (ppm)

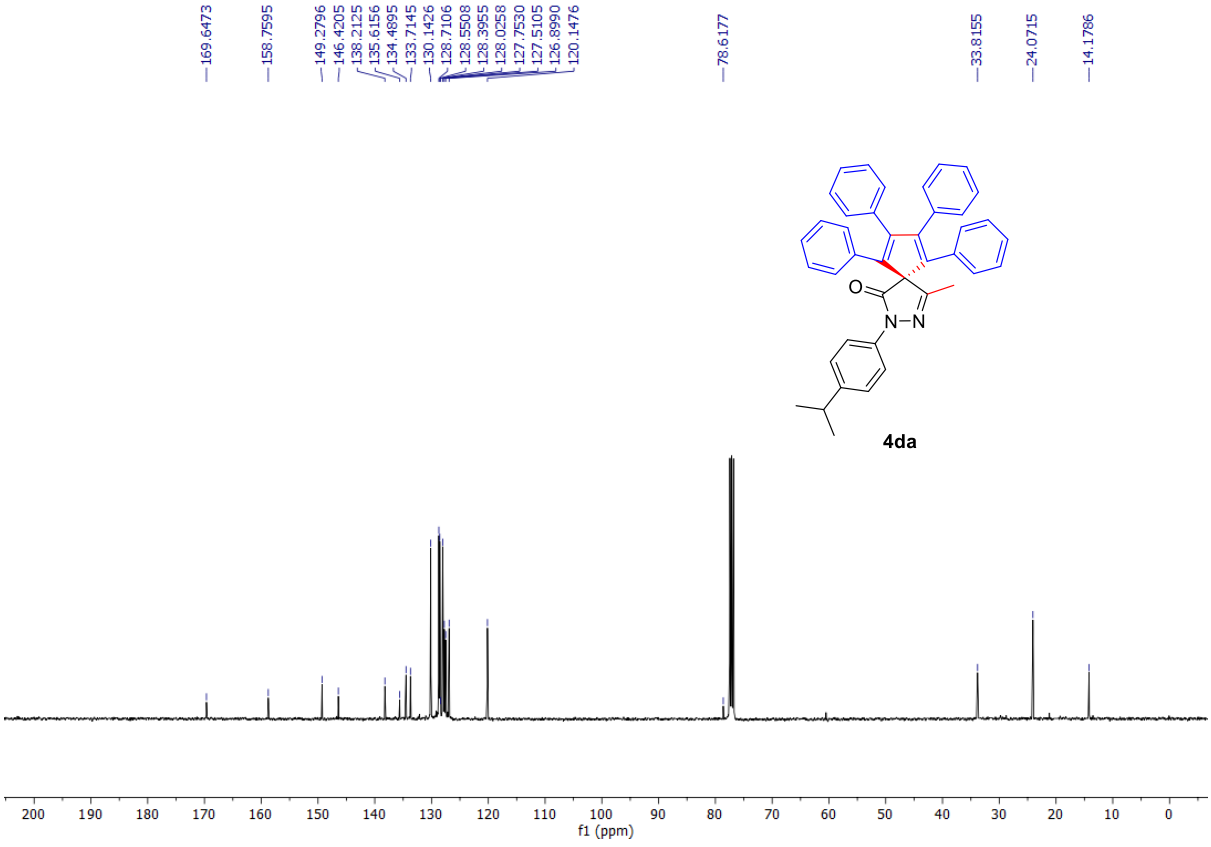
4ca

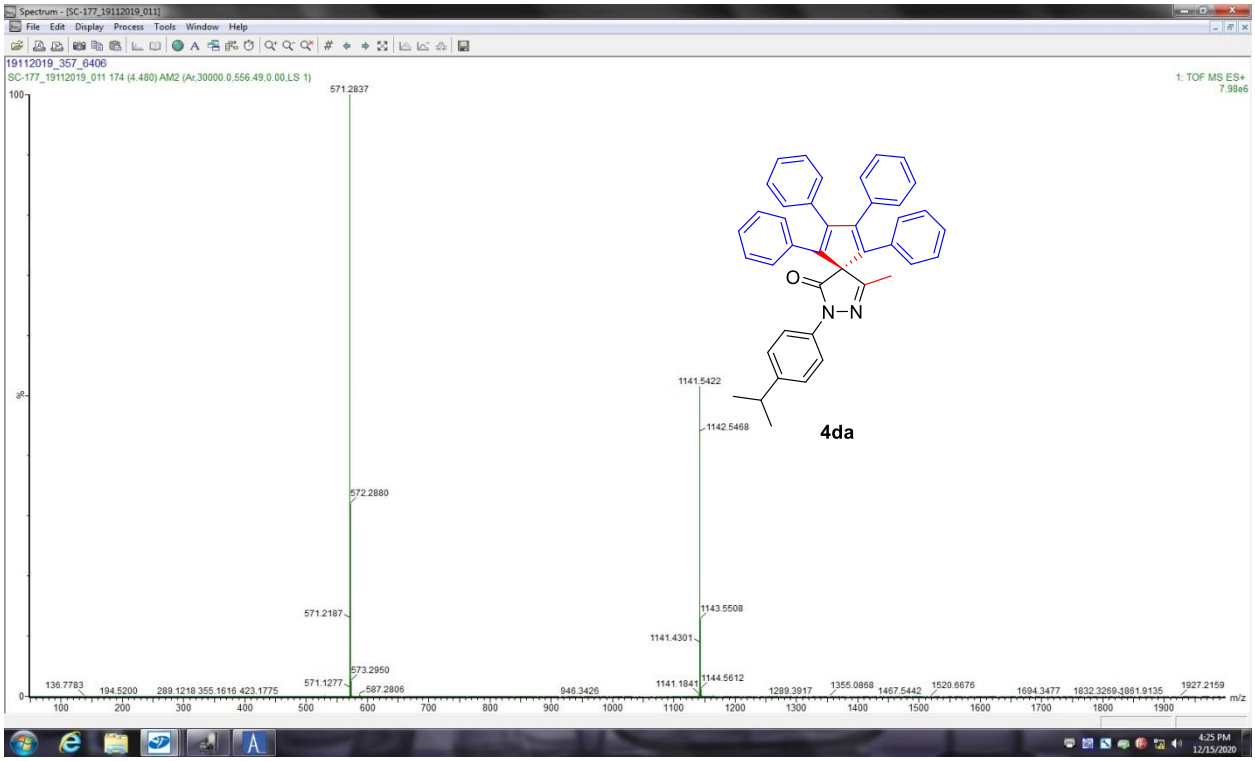

169.6130
158.7309
149.2715
138.2416
137.2790
135.7067
134.5252
134.1585
133.7202
130.1482
129.9580
128.7155
128.5568
128.4032
128.0410
127.7544
127.5173
121.0977
117.4738
78.6581
77.4632
77.1458
76.8275
20.0400
19.4186
14.2051
O
N–N
f1 (ppm)

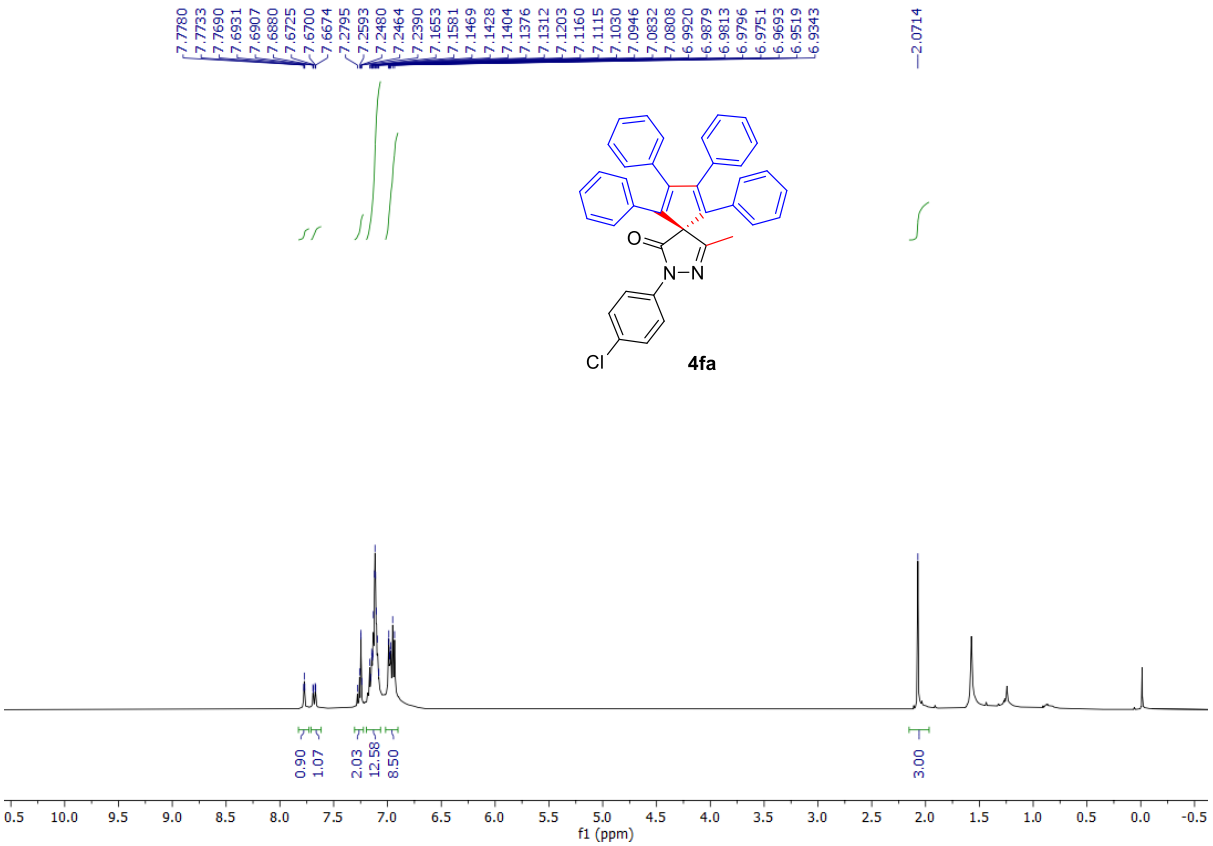
4ca

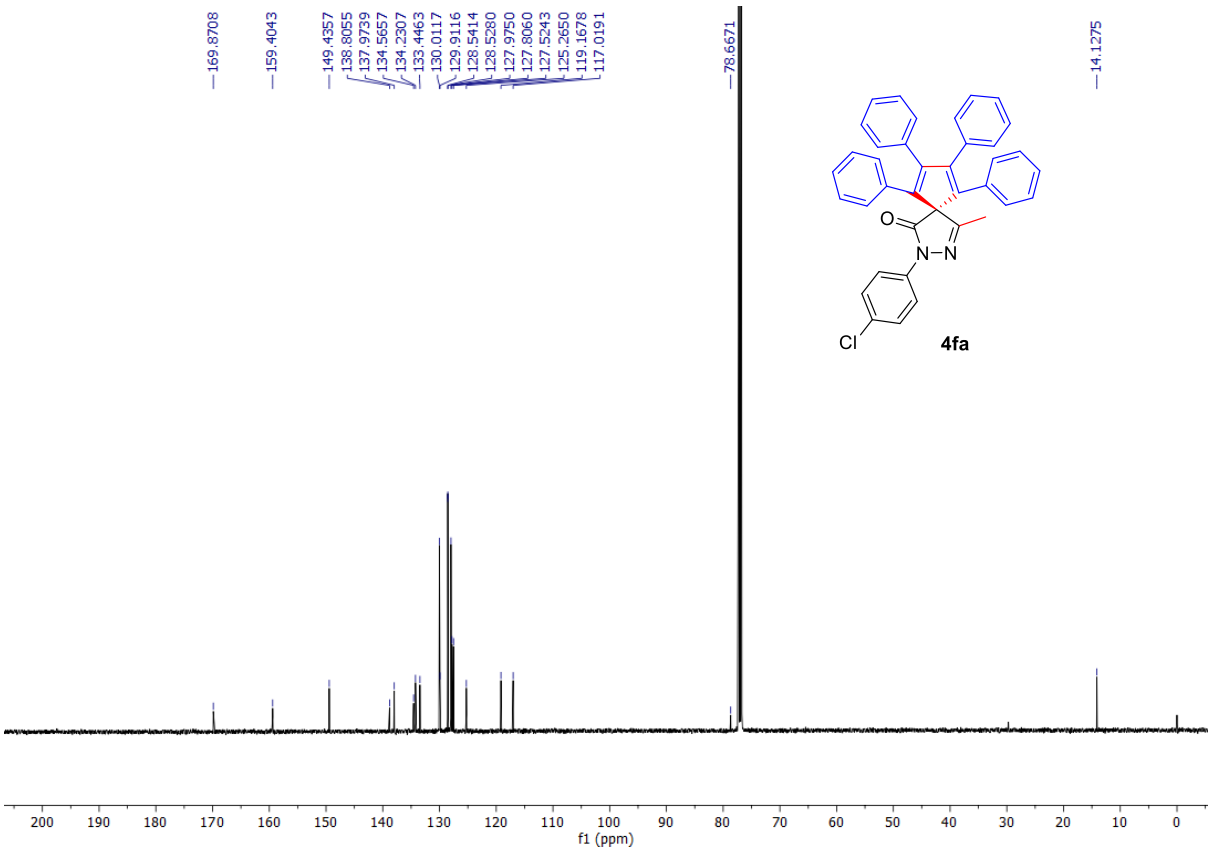

Spectrum - [SC-175_15102019_015]
File Edit Display Process Tools Window Help
15102019_341_6103
SC-175_15102019_015 174 (4.480) AM2 (Ar,30000.0,556.36,0.00,LS 1)
1: TOF MS ES+
9.23e6
100
%
0
557.2446
558.2490
557.1799
559.2601
557.0326
560.2621
1113.5110
1114.5142
1115.5195
1113.3943
1116.5308
1113.1797
77.1824
252.5405
289.1039
410.1949
1289.0438
1317.9857
1400.9093
1474.4973
1602.8586
1631.0610
1707.5186
1891.3665
1940.9999
m/z
O
N–N
4ca
3:30 PM
10/15/2019

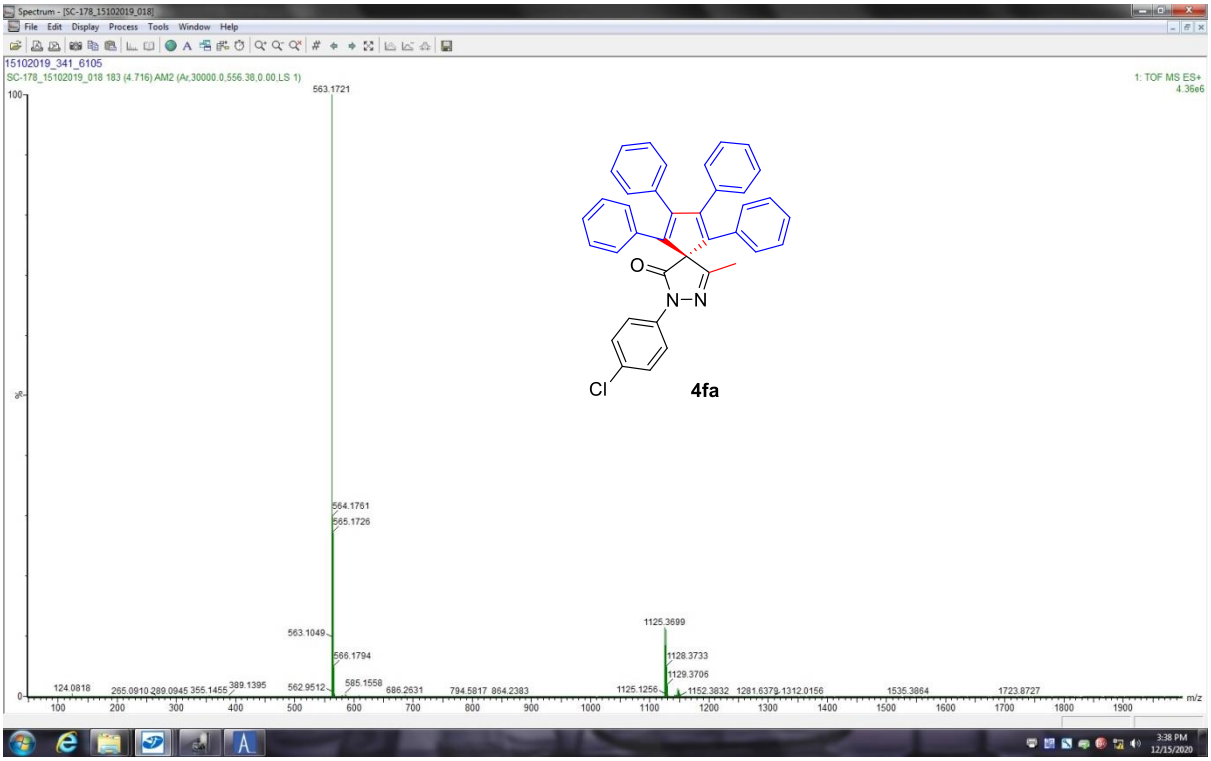

7.5587
7.5373
7.2226
7.2163
7.2109
7.1996
7.1950
7.1889
7.1545
7.1475
7.1437
7.1399
7.1352
7.1308
7.1289
7.1257
7.1209
7.1156
7.1108
7.1083
7.1057
7.1033
7.0980
7.0936
7.0326
7.0275
7.0235
7.0193
7.0159
7.0133
7.0104
7.0079
6.9697
6.9637
6.9603
6.9564
6.9489
6.9437
6.9394
2.9021
2.8849
2.8675
2.0600
1.2357
1.2184
O
N–N
4da
2.12
1.12
1.01
13.25
4.12
2.10
2.05
1.15
3.00
3.11
3.06
f1 (ppm)

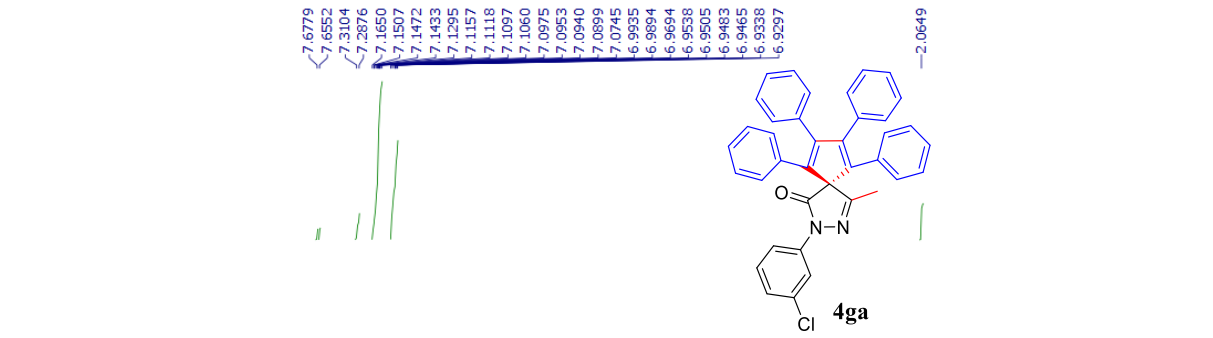

169.6473
158.7595
149.2796
146.4205
138.2125
135.6156
134.4895
133.7145
130.1426
128.7106
128.5508
128.3955
128.0258
127.7530
127.5105
126.8990
120.1476
78.6177
33.8155
24.0715
14.1786
O
N–N
4da
f1 (ppm)

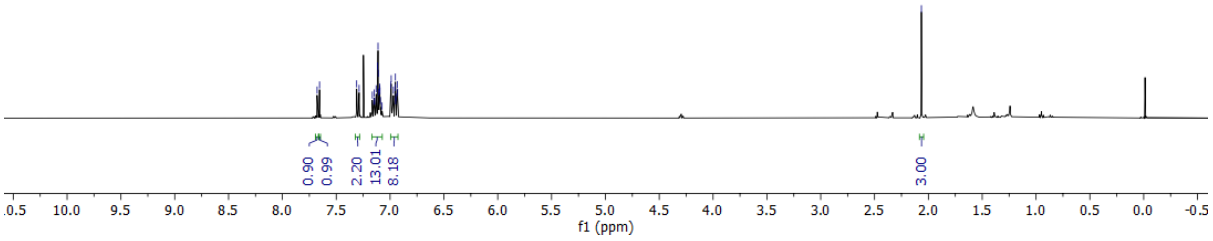

Spectrum - [SC-177_19112019_011]
File Edit Display Process Tools Window Help
19112019_357_6406
SC-177_19112019_011 174 (4.480) AM2 (Ar,30000.0,556.49,0.00,LS 1)
1: TOF MS ES+
7.98e6
571.2837
572.2880
571.2187
573.2950
571.1277
587.2806
1141.5422
1142.5468
1143.5508
1141.4301
1144.5612
1141.1841
136.7783
194.5200
289.1218
355.1616
423.1775
946.3426
1289.3917
1355.0868
1467.5442
1520.6676
1694.3477
1832.3269
1861.9135
1927.2159
4da
4:25 PM
12/15/2020

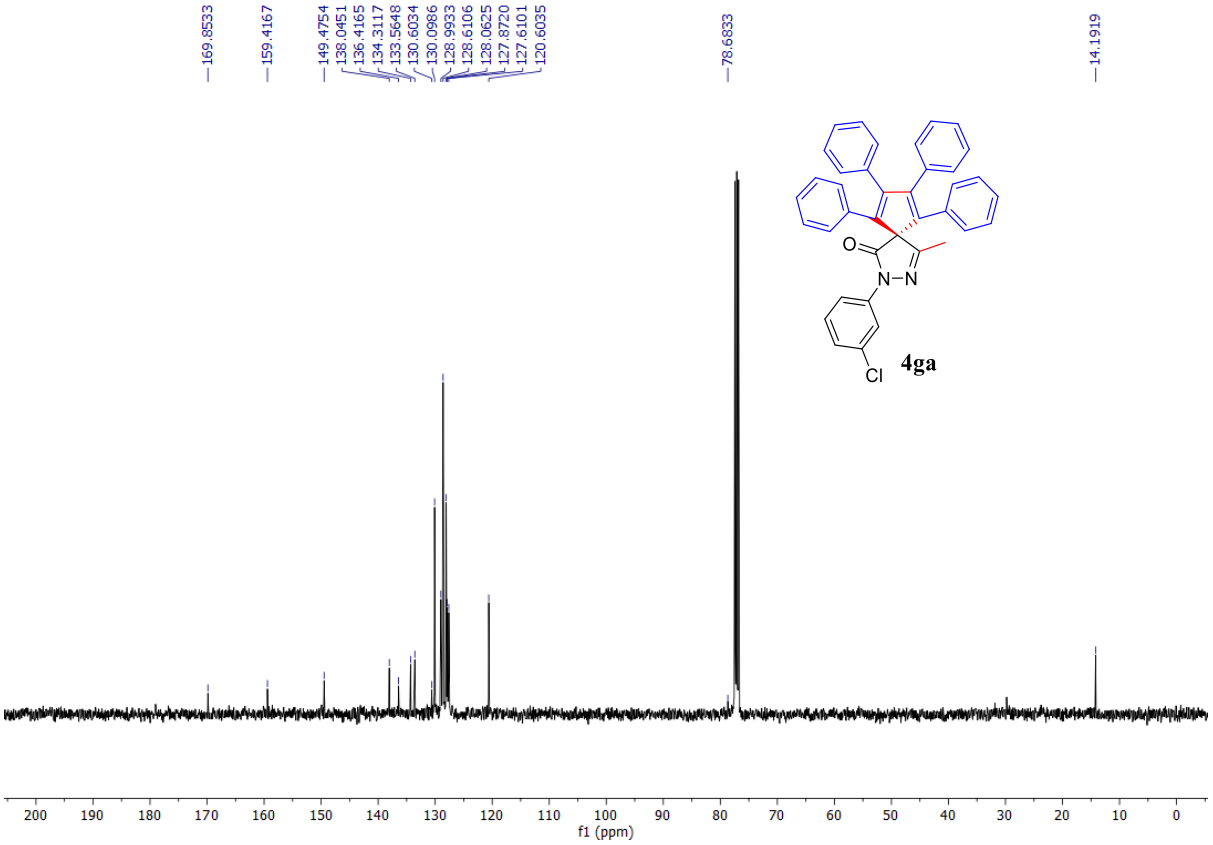

7.7780
7.7733
7.7690
7.6931
7.6907
7.6880
7.6725
7.6700
7.6674
7.2795
7.2593
7.2480
7.2464
7.2390
7.1653
7.1581
7.1469
7.1428
7.1404
7.1376
7.1312
7.1203
7.1160
7.1115
7.1030
7.0946
7.0832
7.0808
6.9920
6.9879
6.9813
6.9796
6.9751
6.9693
6.9519
6.9343
2.0714
O
N–N
Cl
4fa
0.90
1.07
2.03
12.58
8.50
3.00
f1 (ppm)

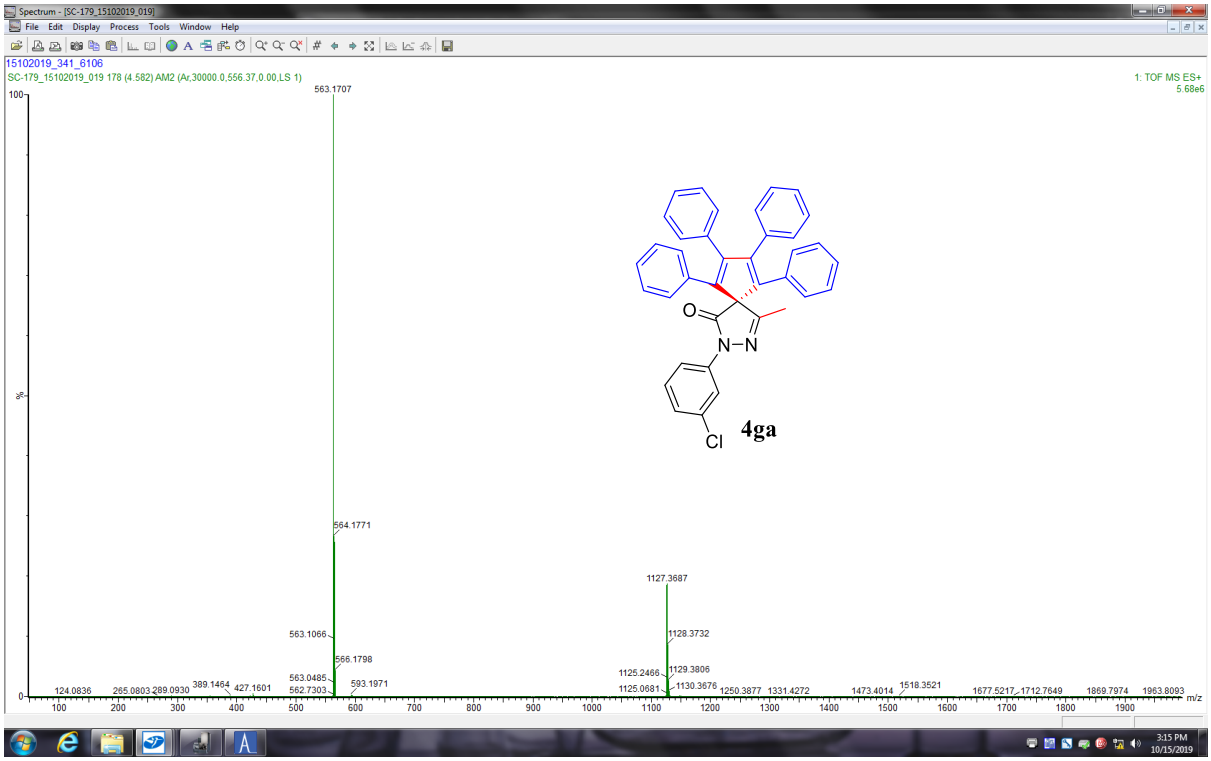

169.8708
159.4043
149.4357
138.8055
137.9739
134.5657
134.2307
133.4463
130.0117
129.9116
128.5414
128.5280
127.9750
127.8060
127.5243
125.2650
119.1678
117.0191
78.6671
14.1275
O
N–N
Cl
4fa
f1 (ppm)


Spectrum - [SC-178_15102019_018]
File Edit Display Process Tools Window Help
15102019_341_6105
SC-178_15102019_018 183 (4.716) AM2 (Ar,30000.0,556.38,0.00,LS 1)
1: TOF MS ES+
4.36e6
100
%
0
563.1721
564.1761
565.1726
563.1049
566.1794
1125.3699
1128.3733
1129.3706
124.0818
265.0910 289.0945 355.1455
389.1395
562.9512
585.1558
686.2631
794.5817 864.2383
1125.1256
1152.3832 1281.6379 1312.0156
1535.3864
1723.8727
m/z
100 200 300 400 500 600 700 800 900 1000 1100 1200 1300 1400 1500 1600 1700 1800 1900
O
N–N
Cl
4fa
3:38 PM
12/15/2020

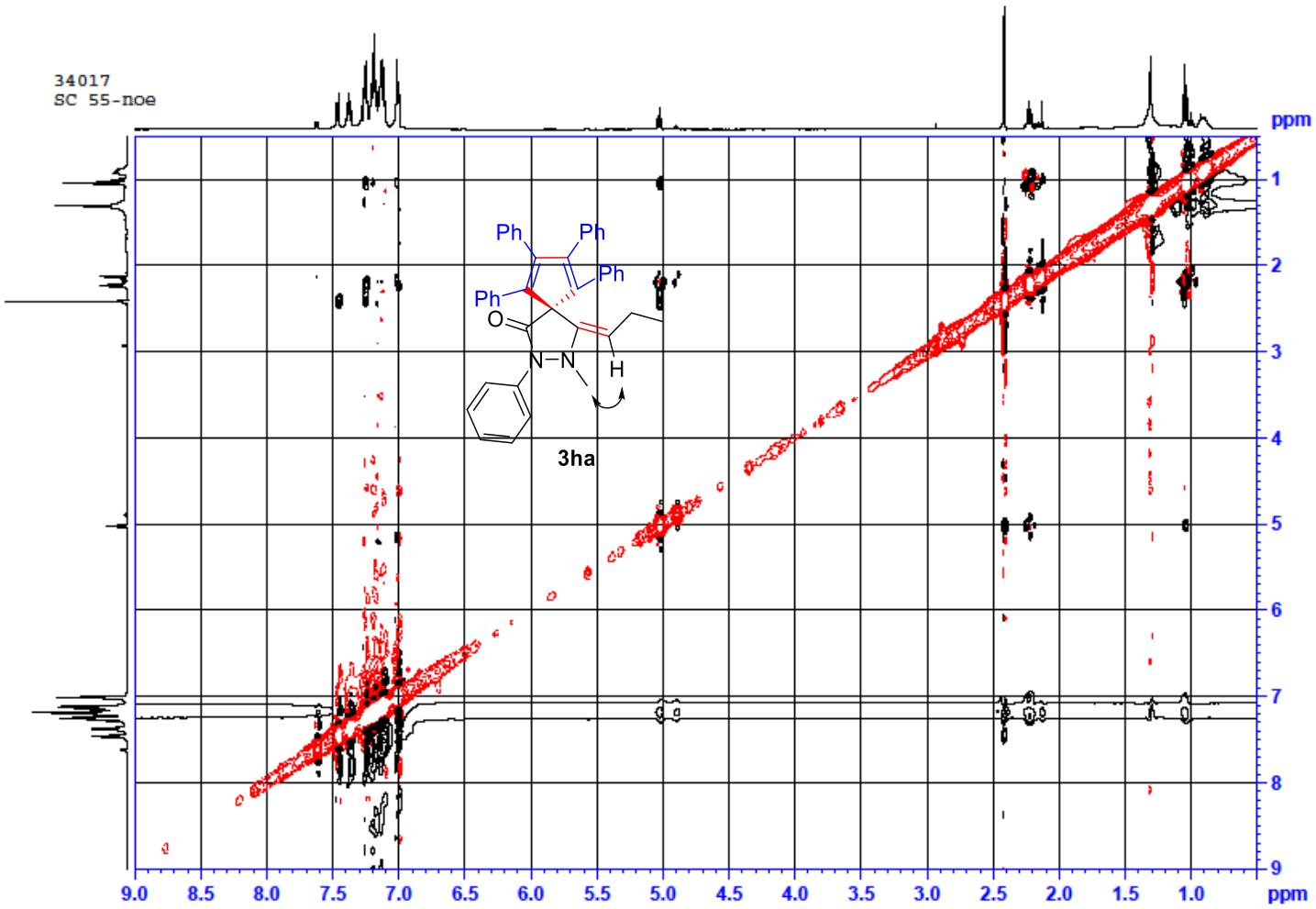

7.6779
7.6552
7.3104
7.2876
7.1650
7.1507
7.1472
7.1433
7.1295
7.1157
7.1118
7.1097
7.1060
7.0975
7.0953
7.0940
7.0899
7.0745
6.9935
6.9894
6.9694
6.9538
6.9505
6.9483
6.9465
6.9338
6.9297
2.0649
O
N–N
Cl
4ga


0.90
0.99
2.20
13.01
8.18
3.00
f1 (ppm)

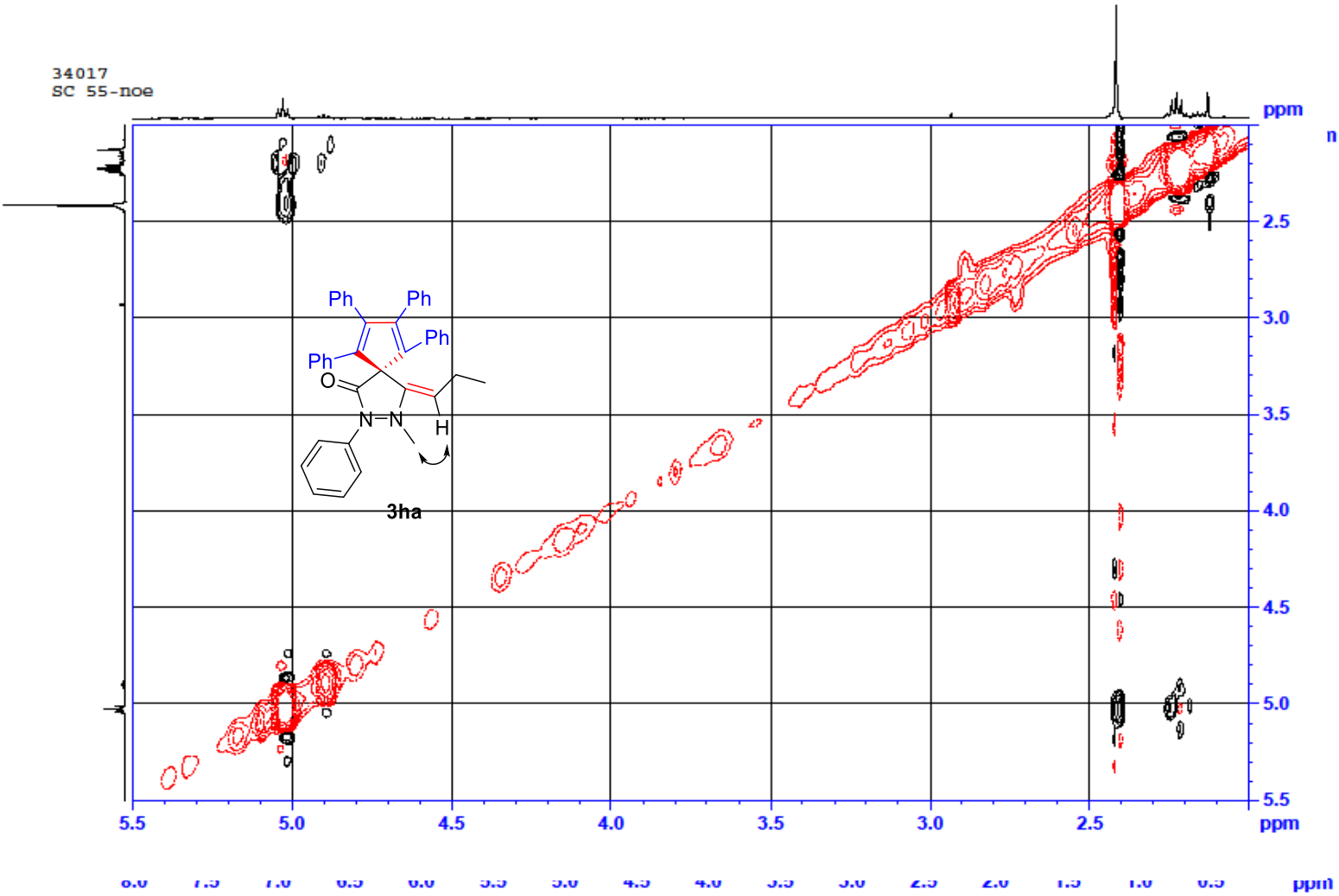

169.8533
159.4167
149.4754
138.0451
136.4165
134.3117
133.5648
130.6034
130.0986
128.9933
128.6106
128.0625
127.8720
127.6101
120.6035
78.6833
14.1919
O
N–N
Cl
4ga
f1 (ppm)


Spectrum - [SC-179_15102019_019]
File Edit Display Process Tools Window Help
15102019_341_6106
SC-179_15102019_019 178 (4.582) AM2 (Ar,30000.0,556.37,0.00,LS 1)
1: TOF MS ES+
5.68e6
100
%
0
563.1707
564.1771
1127.3687
1128.3732
563.1066
566.1798
1129.3806
563.0485
1125.2466
562.7303
593.1971
1125.0681
1130.3676
124.0836
265.0803
289.0930
389.1464
427.1601
1250.3877
1331.4272
1473.4014
1518.3521
1677.5217
1712.7649
1869.7974
1963.8093
100 200 300 400 500 600 700 800 900 1000 1100 1200 1300 1400 1500 1600 1700 1800 1900
m/z
O
N–N
Cl
4ga
3:15 PM
10/15/2019

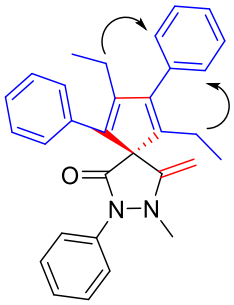
NOE of compound **3ha**



Expanded form of NOE of **3ha**:

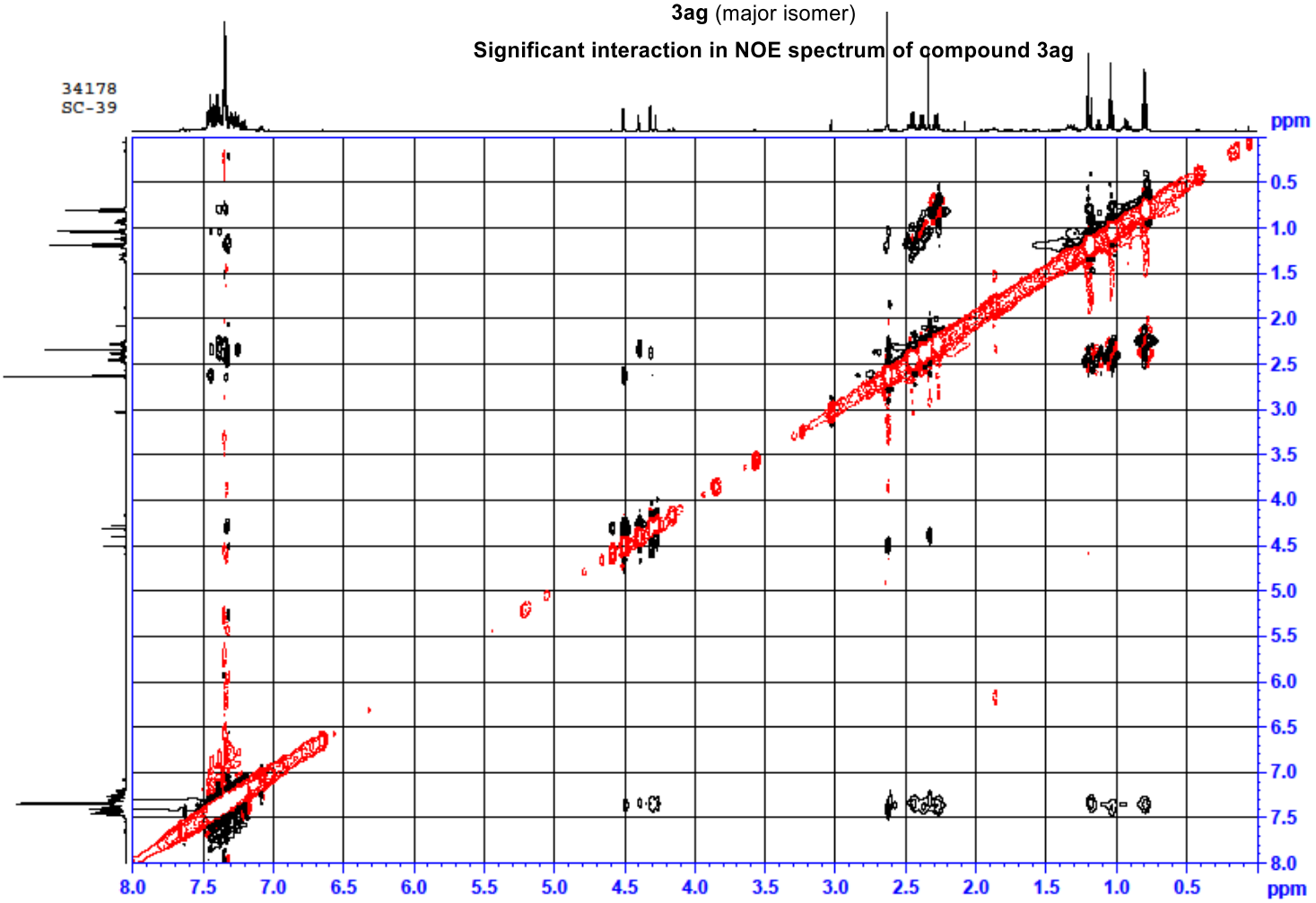


NOE of **3ag**:

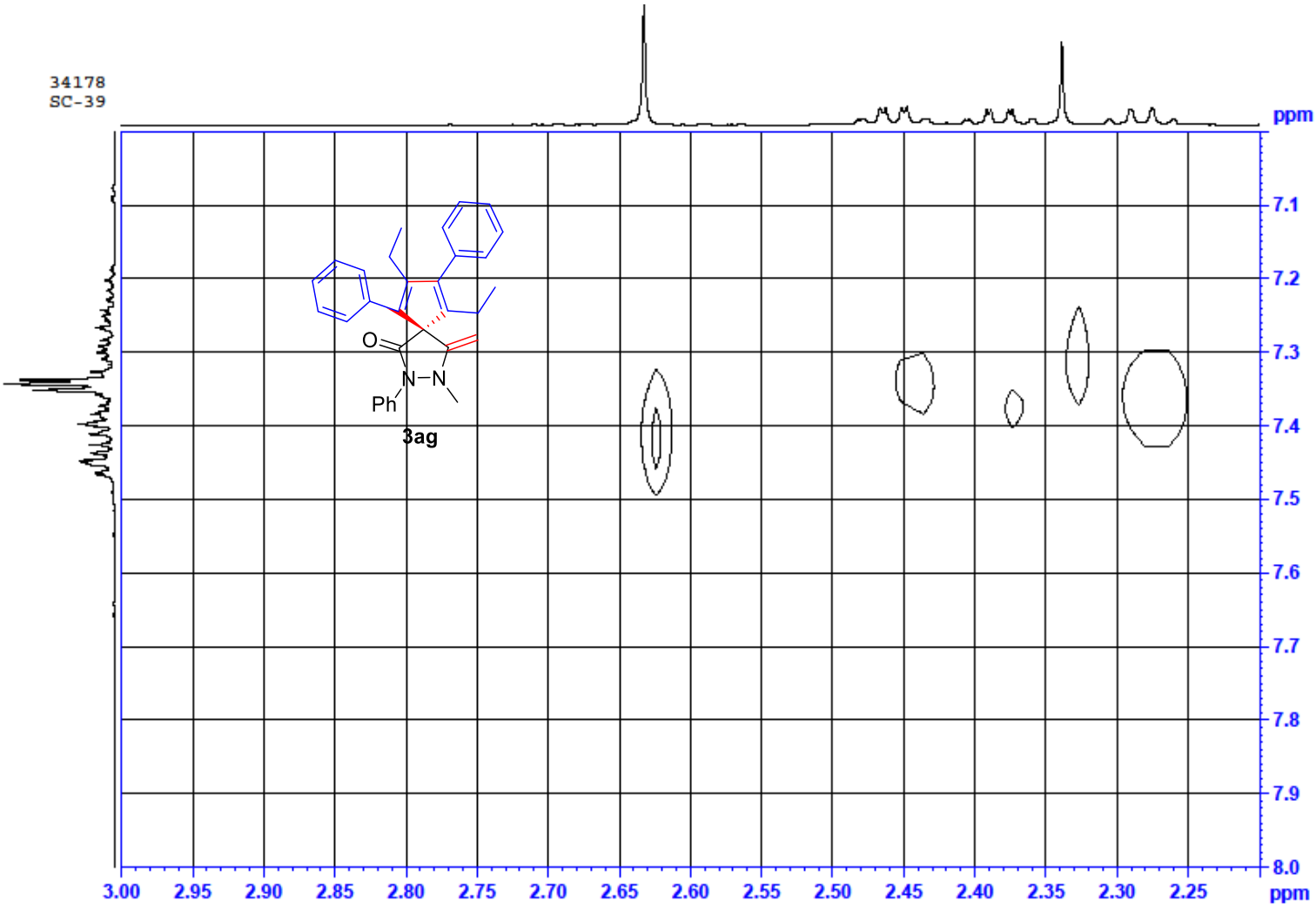


3ag (major isomer)

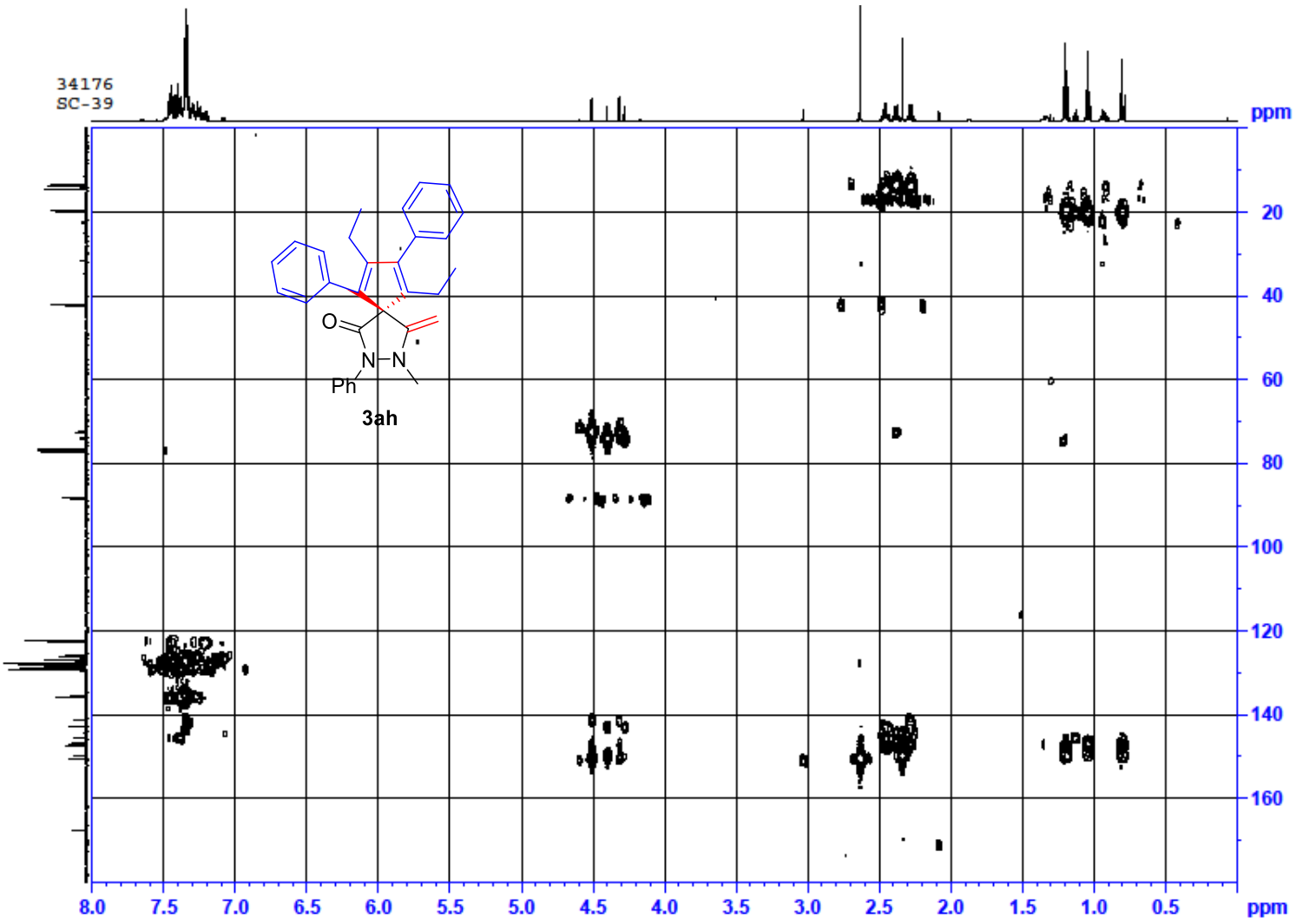
Significant interaction in NOE spectrum of compound 3ag

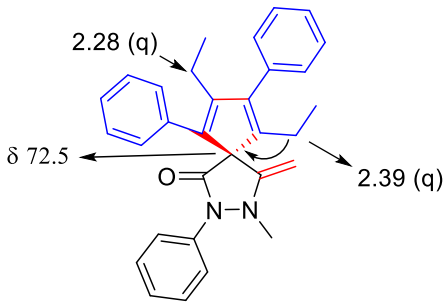


NOE of **3ag** (Expanded form):



HMBC of **3ah**:

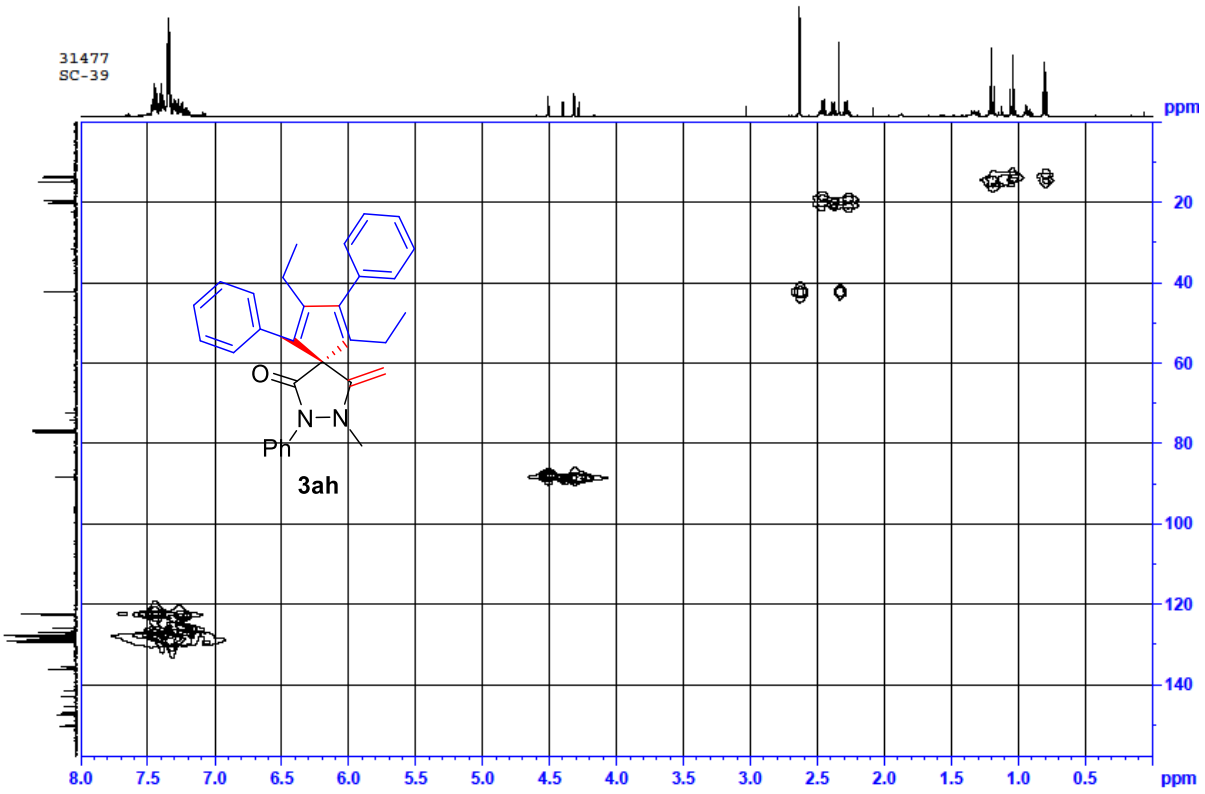




3ah (major isomer)

Significant interaction in HMBC spectrum of compound 3ah

HMQC of **3ah**:



X-Ray crystallographic data of compound 3aa: Empirical Formula- $C_{39}H_{30}N_2O$, M = 542.65, triclinic, Space group P-1, a = 10.9996(6) Å, b = 12.1270(6) Å, c = 23.4345(12) Å, V = 3028.0(3) $Å^3$, Z = 4, T = 100 K, ρcalcd = 1.190 g/cm^3 , 2Θmax. = 28.819º, Refinement of 759 parameters on 7364 independent reflections with wR_2 = 0.1920 and S = 0.937. The crystal structure has been deposited at the Cambridge Crystallographic Data Centre (CCDC 1944638). The data can be obtained free of charge via the Internet at www.ccdc.cam.ac.uk/data_request.

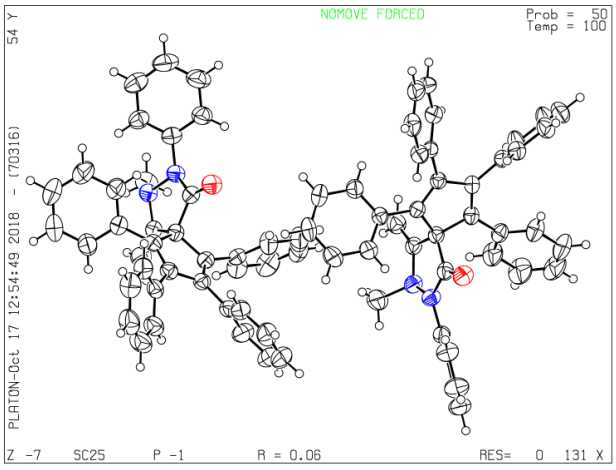


Fig. S2 X-Ray Structure of Compound **3aa**

X-Ray crystallographic data of compound 4aa: Empirical Formula- $C_{38}H_{28}N_2O$, M = 528.62, orthorhombic, Space group P-21, a = 10.6306 (8) Å, b = 15.1263(11) Å, c = 17.9884(14) Å, V = 2892.6(4) $Å^3$, Z = 4, T = 296(2) K, ρcalcd = 1.214 g/cm^3 , 2Θmax. = 25.000°, Refinement of 371 parameters on 5081 independent reflections with wR_2 = 0.1127 and S = 1.024. The crystal structure has been deposited at the Cambridge Crystallographic Data Centre (CCDC-2079413). The data can be obtained free of charge via the Internet at www.ccdc.cam.ac.uk/data_request.

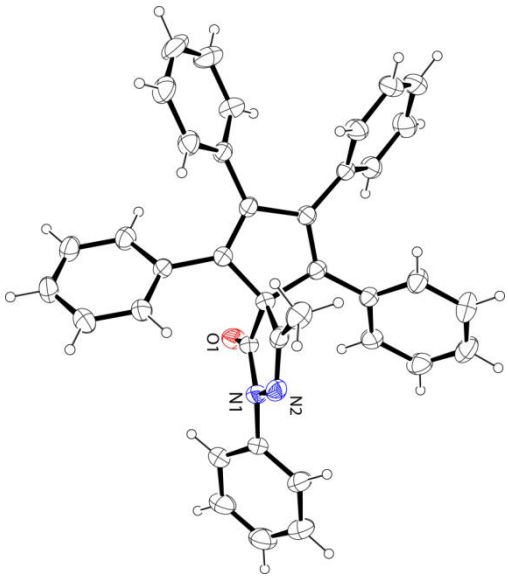


Fig. S1 X-Ray Structure of Compound **4aa**

3276
PPS_D2O_2ND