Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Pd(II)-Catalyzed Denitrative Alkyne Annulation Reaction for the Synthesis of Cyclopenta[*b*]chromanes

Pratiksha Bhorali,[†] Deep J. Kalita,[†] Babulal Das[‡] and Sanjib Gogoi[*†]

[†]Applied Organic Chemistry, Chemical Sciences & Technology Division, CSIR-North East Institute of Science and Technology, Jorhat-785006, Academy of Scientific and Innovative Research (AcSIR), Ghaziabad-201002, India, Email: skgogoi1@gmail.com, sanjibgogoi@neist.res.in

[‡]Department of Chemistry, Indian Institute of Technology Guwahati, Guwahati 781039, India

Supporting Information

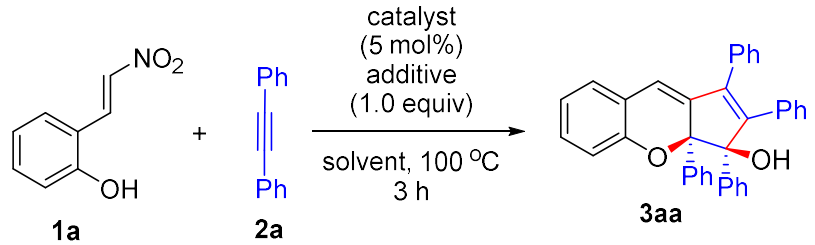
1. General Information

All the commercially available reagents were used as received. Melting points were measured with a Buchi B-540 melting point apparatus and are uncorrected. All experiments were monitored by thin layer chromatography. TLC was performed on Merck TLC Silica gel 60 F_{254} precoated plates. Column chromatography was performed on silica gel (100-200 mesh, Merck). All the heating reactions were performed on oil bath. NMR spectra were recorded on Bruker Avance III 500 or 400 MHz FTNMR spectrometer using tetramethylsilane (TMS) as an internal standard. HRMS data were recorded by mass analyzer of model - Xevo G2-XS Q-TOF, Make-Waters, Software-MassLynx V 4.1.

2. Reaction Procedure

2.1. General procedure for the synthesis of 2-hydroxy nitrostyrenes: A solution of nitromethane (5 mL), NH_4OAc (1.0 mmol) and acetic acid (2.0 mL) was stirred at 90 ^oC for 15 minutes. Then, salicyldehyde (5 mmol) was added into this mixture. The reaction mixture was then refluxed for 3 hours. After cooling to room temperature, the mixture was extracted with dichloromethane (25 mL × 2). The organic layer was washed with brine and dried over anhydrous Na_2SO_4. The solvent was removed under vacuum and the obtained crude product was purified by silica gel (100–200 mesh) column chromatography using EtOAc/Hexane (1: 10) as the eluant.

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



1a **2a** **3aa**

entry	catalyst	additive	solvent	**3aa**[b] (%)
1	$[RhCp^*Cl_2]_2$	$Cu(OAc)_2.H_2O$	xylene	0
2	$[IrCp^*Cl_2]_2$	$Cu(OAc)_2.H_2O$	xylene	0
3	$[\{RuCl_2(p\text{-cymene})\}_2]$	$Cu(OAc)_2.H_2O$	xylene	0
4	$Pd(OAc)_2$	$Cu(OAc)_2.H_2O$	xylene	85
5	$Pd(OAc)_2$	AgOAc	xylene	0
6	$Pd(OAc)_2$	NaOAc	xylene	49
7	$Pd(OAc)_2$	CsOAc	xylene	34
8	$Pd(OAc)_2$	$Cu(OAc)_2.H_2O$	dioxane	0
9	$Pd(OAc)_2$	$Cu(OAc)_2.H_2O$	DMF	0
10	$Pd(OAc)_2$	$Cu(OAc)_2.H_2O$	DMSO	0
11	$Pd(OAc)_2$	$Cu(OAc)_2.H_2O$	^{t}AmOH	60
12	$Pd(OAc)_2$	$Cu(OAc)_2.H_2O$	toluene	76
13	$Pd(OAc)_2$	$Cu(OAc)_2.H_2O$	PhCl	68
14	$Pd(OAc)_2$	$Cu(OAc)_2.H_2O$	DCE	19
15	$Pd(OAc)_2$	$Cu(OAc)_2.H_2O$	MeCN	11
16[c]	$Pd(OAc)_2$	$Cu(OAc)_2.H_2O$	xylene	81
17[d]	$Pd(OAc)_2$	$Cu(OAc)_2.H_2O$	xylene	60
18[e]	$Pd(OAc)_2$	$Cu(OAc)_2.H_2O$	xylene	82

[a]Reaction conditions: **1a** (0.25 mmol), **2a** (0.50 mmol), catalyst (5.0 mol%), additive (0.25 mmol) and solvent (3.0 mL) at 100 °C under air for 3 h; unless otherwise mentioned. [b]Isolated yields. [c]Temperature 120 °C. [d]Temperature 80 °C. [e]Time 10 h.

2.2. General procedure for the synthesis of cyclopenta[*b*]chromanes: A mixture of 2-hydroxy nitrostyrene (0.25 mmol), diphenyl acetylene (0.50 mmol, 2.0 equiv.), $Pd(OAc)_2$ (5 mol%), $Cu(OAc)_2.H_2O$ (0.25 mmol) in xylene (3.0 mL) was stirred at 100 ^oC for 3 hours. The solvent was removed under vacuum and the crude reaction mixture was poured into water and extracted with dichloromethane (25 mL × 2). Then the organic layer was washed with brine and dried over anhydrous Na_2SO_4. The solvent was removed under vacuum and the obtained crude product was purified by silica gel (100–200 mesh) column chromatography using EtOAc/Hexane as the eluant to afford cyclopenta[*b*]chromane derivatives.

2.3. General procedure for the synthesis of cyclopentenones: A mixture of cyclopenta[*b*]chromane (0.1 mmol), $In(OTf)_3$ (10 mol%) in chlorobenzene (3.0 mL) was stirred at 50 ^oC for 2 hours. The solvent was removed under vacuum and the crude reaction mixture was poured into water and extracted with dichloromethane (25 mL × 2). Then the organic layer was washed with brine and dried over anhydrous Na_2SO_4. The solvent was removed under vacuum and the obtained crude product was purified by silica gel (100–200 mesh) column chromatography using EtOAc/Hexane as the eluant to afford the cyclopentenones.

3. Measurement of fluorescence quantum yield (Φ_F):

Fluorescence quantum yields (Φ_F) of the compounds were calculated using quinine sulfate (in 0.5 M H_2SO_4 solution) as a standard (Φ_F = 0.54). Emission spectra of these compounds were recorded from 370 to 680 nm with excitation at 350 nm. Absorbance (optical density, OD) of all these samples were recorded at 350 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 samples and the reference, OD_{ref} and OD_{sample} are the absorbances of the reference and the sample which were measured at the excitation wavelength; n_{sample} and n_{ref} are the refractive indices of the sample and the reference in solution.

$$\Phi F = \Phi ref\ (Asample/\ Aref\ )\ x\ (\ ODref/\ ODsample)\ x\ (\ nref/\ nsample)^2 \qquad (1)$$

Sl. No	Compound	λ_{max} (nm)	λ_{em} (nm)	Φ_F
1	**3aa**	350	441	0.16
2	**3ad**	350	452	0.14
3	**3af**	355	452	0.20
4	**3ca**	355	442	0.36
5	**3da**	352	450	0.12

6	**3ea**	333	452	0.12
7	**3ha**	357	442	0.17
8	**3ka**	357	441	0.17

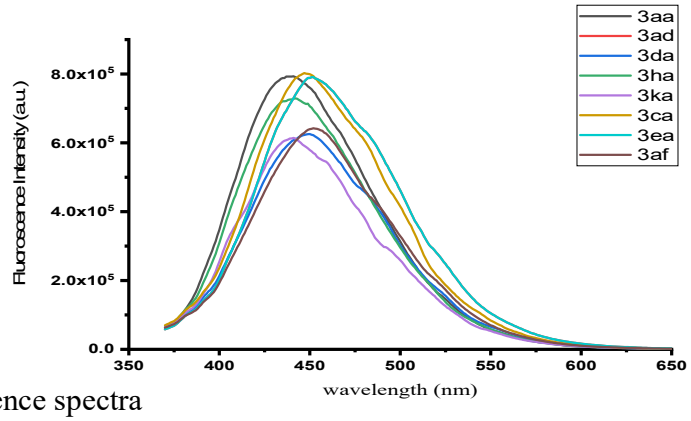
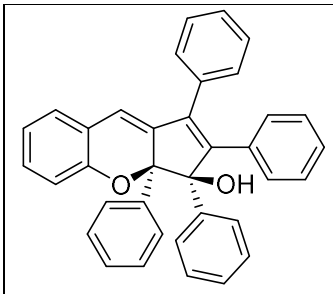


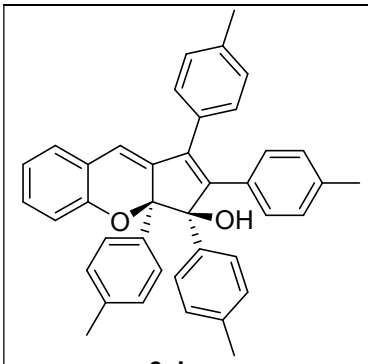
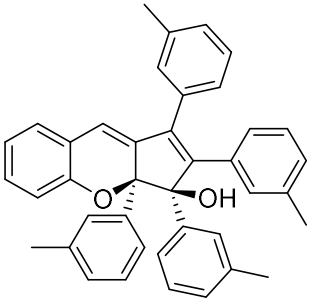
Figure 1. Fluorescence spectra

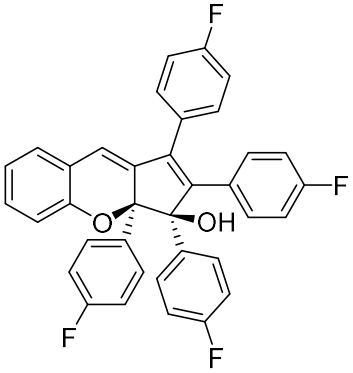
4. Spectral and Analytical Data:

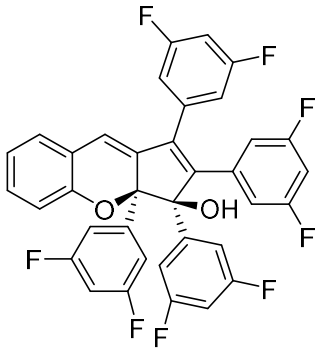
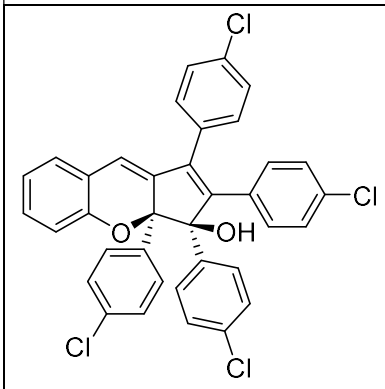


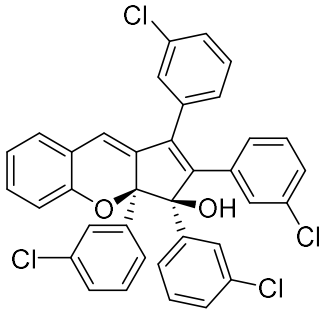
3aa

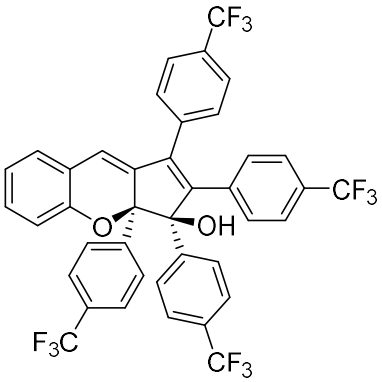
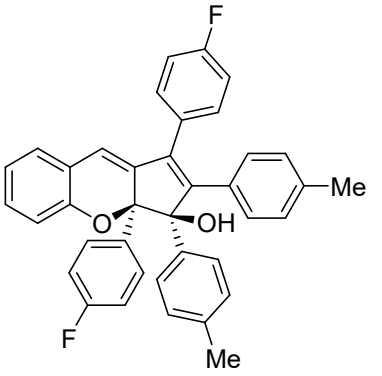
1,2,3,3a-tetraphenyl-3,3a-dihydrocyclopenta[*b*]chromen-3-ol (3aa): Following the general procedure **2.2**, the reaction was carried out by heating a mixture of 2-hydroxynitrostyrene **1a** (41 mg, 0.25 mmol), alkyne **2a** (89 mg, 0.50 mmol), [$Pd(OAc)_2$] (3 mg, 5 mol%) and $Cu(OAc)_2.H_2O$ (50 mg, 0.25 mmol) in xylene (3.0 mL) at 100 ^oC for 3 h under air to afford the title compound. The product was purified by flash column chromatography on silica gel (3% EtOAc in hexane); 81% yield (pale yellow solid, 99 mg); mp 176-178 ^oC. ^1H NMR (400 MHz, $CDCl_3$) δ 7.53–7.50 (m, 2H), 7.45–7.39 (m, 3H), 7.24–7.20 (m, 3H), 7.15–6.92 (m, 11H), 6.87–6.80 (m, 5H), 6.56 (s, 1H), 4.97 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.9, 148.0, 144.5, 142.2, 139.9, 139.7, 134.6, 134.0, 129.9, 129.8, 128.9, 128.8, 128.5, 128.2, 127.7, 127.6, 127.5, 127.4, 127.3, 127.1, 126.6, 126.3, 124.0, 122.6, 117.7, 117.6, 90.1, 87.5. HRMS Calcd (ESI) m/z for $C_{36}H_{26}O_2$: $[M–OH]^+$ 473.1905, found: 473.1902.

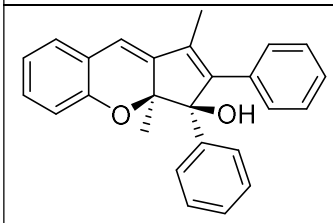
 **3ab**	**1,2,3,3a-tetra-*p*-tolyl-3,3a-dihydrocyclopenta[*b*]chromen-3-ol (3ab):** Following the general procedure **2.2**, the reaction was carried out by heating a mixture of 2-hydroxynitrostyrene **1a** (41 mg, 0.25 mmol), alkyne **2b** (103 mg, 0.50 mmol), [$Pd(OAc)_2$] (3 mg, 5 mol%) and $Cu(OAc)_2.H_2O$ (50 mg, 0.25 mmol) in xylene (3.0 mL) at 100 ^oC for 3 h under air to afford the title compound. The product was purified by flash column chromatography on silica gel (3% EtOAc in hexane); 83% yield (pale yellow solid, 113 mg); mp 133-135 ^oC. ^1H NMR (400 MHz, $CDCl_3$) δ 7.40 (d, J = 8.0 Hz, 2H), 7.24 (d, J = 7.8 Hz, 2H), 7.10 (d, J = 8.2 Hz, 2H), 7.06–6.94 (m, 5H), 6.83–6.79 (m, 3H), 6.75–6.64 (m, 6H), 6.52 (s, 1H), 4.88 (s, 1H), 2.43 (s, 3H), 2.17 (s, 3H), 2.13 (s, 3H), 2.12 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.0, 147.9, 145.1, 141.4, 138.1, 137.0, 136.9, 136.7, 135.5, 131.9, 131.3, 129.8, 129.7, 129.5, 128.5, 128.4, 128.1, 127.7, 127.5, 127.3, 127.2, 124.2, 122.4, 117.7, 116.9, 89.9, 87.6, 21.6, 21.4, 21.1, 21.0. HRMS Calcd (ESI) m/z for $C_{40}H_{34}O_2$: $[M–OH]^+$ 529.2531, found: 529.2528.
 **3ac**	**1,2,3,3a-tetra-*m*-tolyl-3,3a-dihydrocyclopenta[*b*]chromen-3-ol (3ac):** Following the general procedure **2.2**, the reaction was carried out by heating a mixture of 2-hydroxynitrostyrene **1a** (41 mg, 0.25 mmol), alkyne **2c** (103 mg, 0.50 mmol), [$Pd(OAc)_2$] (3 mg, 5 mol%) and $Cu(OAc)_2.H_2O$ (50 mg, 0.25 mmol) in xylene (3.0 mL) at 100 ^oC for 3 h under air to afford the title compound. The product was purified by flash column chromatography on silica gel (3% EtOAc in hexane); 71% yield (pale yellow solid, 97 mg); mp 98-100 ^oC. ^1H NMR (400 MHz, $CDCl_3$) δ 7.33–7.28 (m, 3H), 7.21–7.19 (m, 1H), 7.07–6.96 (m, 6H), 6.90–6.80 (m, 5H), 6.75–6.57 (m, 5H), 6.53 (s, 1H), 4.90 (s, 1H), 2.38 (s, 3H), 2.06 (s, 3H), 2.04 (s, 3H), 2.01 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.0, 148.0, 144.7,

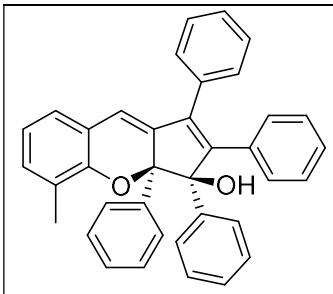
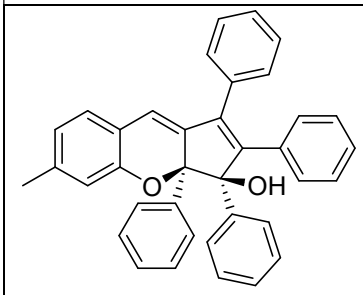
	142.1, 139.8, 138.3, 136.9, 136.4, 135.9, 134.7, 134.2, 130.3, 129.1, 128.9, 128.6, 128.1, 127.9, 127.4, 127.0, 126.8, 126.7, 126.3, 125.2, 124.6, 124.2, 122.5, 117.7, 117.2, 90.1, 87.5, 21.7, 21.5, 21.3. HRMS Calcd (ESI) m/z for $C_{40}H_{34}O_2$: $[M–OH]^+$ 529.2531, found: 529.2529.
 **3ad**	**1,2,3,3a-tetrakis(4-fluorophenyl)-3,3a-dihydrocyclopenta[*b*]chromen-3-ol (3ad):** Following the general procedure **2.2**, the reaction was carried out by heating a mixture of 2-hydroxynitrostyrene **1a** (41 mg, 0.25 mmol), alkyne **2d** (107 mg, 0.50 mmol), $[Pd(OAc)_2]$ (3 mg, 5 mol%) and $Cu(OAc)_2.H_2O$ (50 mg, 0.25 mmol) in xylene (3.0 mL) at 100 ^oC for 3 h under air to afford the title compound. The product was purified by flash column chromatography on silica gel (3% EtOAc in hexane); 79% yield (white solid, 111 mg); mp 211-213 ^oC. ^1H NMR (400 MHz, $CDCl_3$) δ 7.47–7.43 (m, 2H), 7.17 –7.07 (m, 7H), 7.01–6.98 (m, 3H), 6.89–6.85 (m, 1H), 6.75–6.59 (m, 7H), 6.56 (s, 1H), 4.93 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.9 (d, J = 248), 162.2 (d, J = 247), 162.1 (d, J = 246), 161.6 (d, J = 245), 152.6, 146.9, 143.7, 140.9, 135.4, 135.3, 135.3, 131.6, 131.6, 131.5, 130.2 (d, J = 4), 129.4 (d, J = 4), 129.8, 129.7, 129.3, 129.2, 127.6, 123.7, 122.9, 118.0, 117.9 (d, J = 29), 116.2 (d, J = 22), 115.1 (d, J = 21), 114.4 (d, J = 22), 113.9 (d, J = 21), 89.6, 86.8. ^{19}F NMR ($CDCl_3$, 376 MHz): −111.9,−112.6,−114.1,−115.7. HRMS Calcd (ESI) m/z for $C_{36}H_{22}F_4O_2$: $[M–OH]^+$ 545.1527, found: 545.1526.

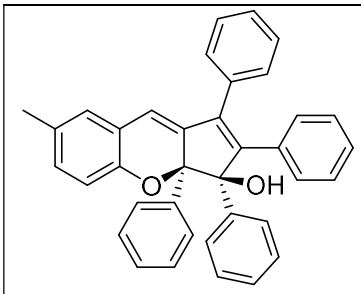
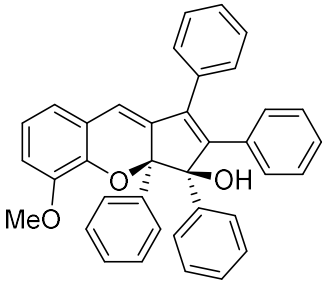
 **3ae**	**1,2,3,3a-tetrakis(3,5-difluorophenyl)-3,3a-dihydrocyclopenta[*b*]chromen-3-ol (3ae):** Following the general procedure **2.2**, the reaction was carried out by heating a mixture of 2-hydroxynitrostyrene **1a** (41 mg, 0.25 mmol), alkyne **2e** (125 mg, 0.50 mmol), [$Pd(OAc)_2$] (3 mg, 5 mol%) and $Cu(OAc)_2.H_2O$ (50 mg, 0.25 mmol) in xylene (3.0 mL) at 100 ^oC for 3 h under air to afford the title compound. The product was purified by flash column chromatography on silica gel (3% EtOAc in hexane); 73% yield (pale yellow sticky solid, 115 mg). ^1H NMR (500 MHz, $CDCl_3$) δ 7.20–7.17 (m, 1H), 7.08–7.05 (m, 2H), 6.97–6.75 (m, 7H), 6.63–6.48 (m, 7H), 4.98 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.6 (d, *J* = 249 Hz), 163.5 (d, *J* = 250 Hz), 162.8 (d, *J* = 247 Hz), 162.7 (d, *J* = 248 Hz), 162.5 (d, *J* = 247 Hz), 162.4 (d, *J* = 247 Hz), 152.2, 145.5, 143.2, 143.1, 141.7, 140.8, 136.3, 135.5, 130.4, 128.3, 123.6, 122.8, 120.3, 117.9, 112.6 (d, *J* = 26 Hz), 112.5 (d, *J* = 12 Hz), 112.3 (d, *J* = 26 Hz), 112.2 (d, *J* = 12 Hz), 111.1 (d, *J* = 23 Hz), 110.8 (d, *J* = 28 Hz), 105.2 (d, *J* = 25 Hz), 105.0 (d, *J* = 25 Hz), 104.5 (d, *J* = 26 Hz), 104.2 (d, *J* = 26 Hz), 104.0 (d, *J* = 26 Hz), 103.8 (d, *J* = 26 Hz), 103.2 (d, *J* = 25 Hz), 102.9 (d, *J* = 25 Hz), 89.4, 86.1. ^{19}F NMR ($CDCl_3$, 376 MHz): −107.3,−108.6,−109.0. HRMS Calcd (ESI) m/z for $C_{36}H_{18}F_8O_2$: $[M–OH]^+$ 617.1152, found: 617.1148.
 **3af**	**1,2,3,3a-tetrakis(4-chlorophenyl)-3,3a-dihydrocyclopenta[*b*]chromen-3-ol (3af):** Following the general procedure **2.2**, the reaction was carried out by heating a mixture of 2-hydroxynitrostyrene **1a** (41 mg, 0.25 mmol), alkyne **2f** (123 mg, 0.50 mmol), [$Pd(OAc)_2$] (3 mg, 5 mol%) and $Cu(OAc)_2.H_2O$ (50 mg, 0.25 mmol) in xylene (3.0 mL) at 100 ^oC for 3 h under air to afford the title compound. The product was purified by flash column chromatography on silica gel (3%

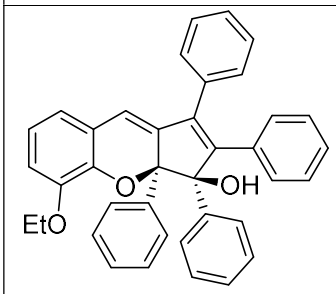
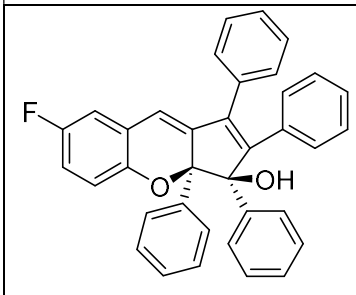
	EtOAc in hexane); 85% yield (white solid, 133 mg); mp 183-185 ^{o}C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.44–7.39 (m, 4H), 7.11–7.09 (m, 3H), 7.02–6.96 (m, 8H), 6.90–6.74 (m, 5H), 6.57 (s, 1H), 4.94 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.5, 146.8, 143.1, 141.3, 137.9, 137.8, 134.9, 133.8, 133.7, 132.8, 132.4, 131.7, 131.1, 130.9, 129.5, 129.4, 128.8, 128.4, 127.8, 127.7, 127.2, 123.5, 123.1, 118.6, 117.7, 89.5, 86.8.
 **3ag**	**1,2,3,3a-tetrakis(3-chlorophenyl)-3,3a-dihydrocyclopenta [*b*]chromen-3-ol (3ag):** Following the general procedure **2.2**, the reaction was carried out by heating a mixture of 2-hydroxynitrostyrene **1a** (41 mg, 0.25 mmol), alkyne **2g** (123 mg, 0.50 mmol), [$Pd(OAc)_2$] (3 mg, 5 mol%) and $Cu(OAc)_2.H_2O$ (50 mg, 0.25 mmol) in xylene (3.0 mL) at 100 ^{o}C for 3 h under air to afford the title compound. The product was purified by flash column chromatography on silica gel (3% EtOAc in hexane); 61% yield (yellow sticky, 95 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (t, *J* = 1.8 Hz, 1H), 7.44–7.28 (m, 4H), 7.21 (t, *J* = 1.8 Hz, 1H), 7.15–7.03 (m, 7H), 7.01–6.88 (m, 6H), 6.78–7.74 (m, 1H), 6.59 (s, 1H), 4.95 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.4, 146.5, 142.4, 141.8, 141.4, 135.6, 134.9, 133.9, 133.5, 130.5, 129.7, 129.4, 129.3, 129.2, 128.7, 128.2, 128.1, 127.9, 127.8, 127.2, 123.4, 123.2, 119.1, 117.9, 89.6, 86.7. HRMS Calcd (ESI) m/z for $C_{36}H_{22}Cl_4O_2$: $[M–OH]^+$ 609.0347, found: 609.0345.

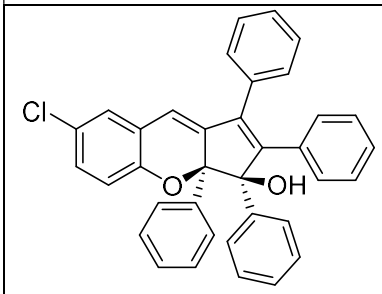
 **3ah**	**1,2,3,3a-tetrakis(4-(trifluoromethyl)phenyl)-3,3a-dihydrocyclopenta[*b*]chromen-3-ol (3ah):** Following the general procedure **2.2**, the reaction was carried out by heating a mixture of 2-hydroxynitrostyrene **1a** (41 mg, 0.25 mmol), alkyne **2h** (157 mg, 0.50 mmol), [$Pd(OAc)_2$] (3 mg, 5 mol%) and $Cu(OAc)_2.H_2O$ (50 mg, 0.25 mmol) in xylene (3.0 mL) at 100 ^oC for 3 h under air to afford the title compound. The product was purified by flash column chromatography on silica gel (3% EtOAc in hexane); 56% yield (pale yellow sticky solid, 106 mg). ^1H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, *J* = 8.6 Hz, 2H), 7.60 (d, *J* = 7.9 Hz, 2H), 7.39–7.31 (m, 4H), 7.24–7.11 (m, 7H), 7.06–7.02 (m, 3H), 6.94–6.90 (m, 2H), 6.62 (s, 1H), 5.09 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.3, 146.5, 143.3, 142.9, 142.6, 142.1, 137.2, 136.7, 130.1, 129.4 (d, *J* = 32 Hz), 128.2, 128.1, 127.5, 126.3 (d, *J* = 3 Hz), 125.3 (d, *J* = 4 Hz), 124.5 (d, *J* = 3 Hz), 124.1, 123.5, 123.2, 123.0 (d, *J* = 272 Hz) 119.8, 117.8, 89.9, 86.9.
 **3ai**	**2,3-bis(4-fluorophenyl)-1,3a-di-*p*-tolyl-3,3a-dihydrocyclo penta[*b*]chromen-3-ol (3ai, mixture of isomers 2:2:1:1):** Following the general procedure **2.2**, the reaction was carried out by heating a mixture of 2-hydroxynitrostyrene **1a** (41 mg, 0.25 mmol), alkyne **2i** (105 mg, 0.25 mmol), [$Pd(OAc)_2$] (3 mg, 5 mol%) and $Cu(OAc)_2.H_2O$ (50 mg, 0.50 mmol) in xylene (3.0 mL) at 100 ^oC for 3 h under air to afford the title compound. The product was purified by flash column chromatography on silica gel (3% EtOAc in hexane); 54% yield (yellow solid, 76 mg); mp 97-99 ^oC. ^1H NMR (400 MHz, $CDCl_3$) δ 7.49–7.35 (m, 2H), 7.25– 6.96 (m, 9H), 6.87–6.63 (m, 8H), 6.56–6.52 (m, 2H), 4.99– 4.80 (bs, 1H), 2.43 (s, 2H), 2.18 (s, 1H), 2.14 (s, 1H), 2.12 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.0 (d, *J* = 246 Hz), 152.9, 152.7, 144.3, 142.1,

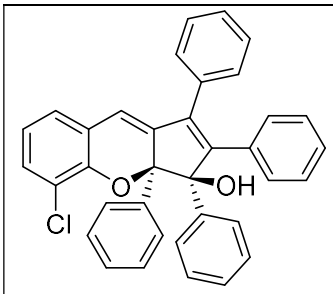
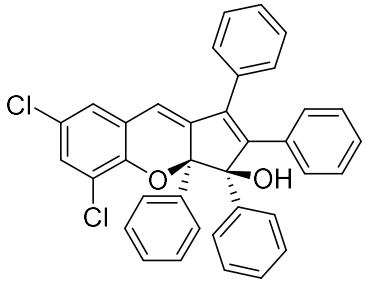
	141.8, 138.6, 137.6, 137.2, 136.6, 136.4, 136.1, 135.7, 131.6, 131.5, 130.8, 129.7, 129.3, 128.9, 128.6, 128.0, 127.6, 123.8, 122.7 (d, J = 7 Hz), 117.7, 117.2, 116.1, 115.9, 115.0 (d, J = 21 Hz), 114.8 (d, J = 21 Hz), 114.2, 113.9, 113.6 (d, J = 21 Hz), 113.4 (d, J = 21 Hz), 89.8, 89.6, 87.0, 21.6, 21.4, 21.1, 14.2. ^{19}F NMR ($CDCl_3$, 376 MHz): −112.6,−113.5,−114.9,−116.6. HRMS Calcd (ESI) m/z for $C_{38}H_{28}F_2O_2$: $[M–OH]^+$ 537.2030, found: 537.2031.
 **3aj**	**1,3-dimethyl-2,3a-diphenyl-3,3a-dihydrocyclopenta[*b*]chromen-3-ol (3aj, mixture 4.9:1):** Following the general procedure **2.2**, the reaction was carried out by heating a mixture of 2-hydroxynitrostyrene **1a** (41 mg, 0.25 mmol), alkyne **2j** (58 mg, 0.50 mmol), $[Pd(OAc)_2]$ (3 mg, 5 mol%) and $Cu(OAc)_2.H_2O$ (50 mg, 0.25 mmol) in xylene (3.0 mL) at 100 ^oC for 3 h under air to afford the title compound. The product was purified by flash column chromatography on silica gel (2 % EtOAc in hexane 71% yield (pale yellow liquid, 65 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.52–7.41 (m, 8H), 7.37–7.33 (m, 1H), 7.24–7.04 (m, 3H), 6.96–6.91 (m, 2H), 6.25 (s, 0.17H), 6.23 (s, 0.83H), 4.56–4.53 (m, 0.17H), 4.43 (s, 0.83H), 1.93 (s, 2.5H), 1.64 (s, 0.5H), 1.28 (s, 0.5H), 0.99 (s, 2.5H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.7, 146.5, 144.9, 139.8, 139.5, 134.0, 132.5, 130.4, 129.2, 128.6, 128.4, 128.3, 128.0, 127.9, 127.6, 127.2, 126.5, 124.9, 124.2, 123.5, 122.3, 119.3, 117.5, 112.9, 111.2, 87.2, 83.5, 83.2, 73.6, 42.0, 29.8, 21.6, 12.6. HRMS Calcd (ESI) m/z for $C_{26}H_{22}O_2$: $[M–OH]^+$ 349.1592, found: 349.1587.
	5-methyl-1,2,3,3a-tetraphenyl-3,3a-dihydrocyclopenta[*b*] chromen-3-ol (3ba): Following the general procedure **2.2**, the reaction was carried out by heating a mixture of 2-hydroxynitrostyrene **1b** (45 mg, 0.25 mmol), alkyne **2a** (89 mg,

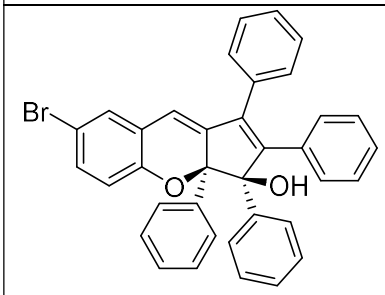
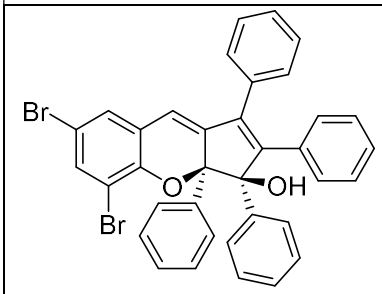
 **3ba**	0.50 mmol), [$Pd(OAc)_2$] (3 mg, 5 mol%) and $Cu(OAc)_2.H_2O$ (50 mg, 0.25 mmol) in xylene (3.0 mL) at 100 ^oC for 3 h under air to afford the title compound. The product was purified by flash column chromatography on silica gel (3% EtOAc in hexane); 73% yield (white solid, 92 mg); mp 194-196 ^oC. ^1H NMR (400 MHz, $CDCl_3$) δ 7.45–7.43 (m, 2H), 7.37–7.31 (m, 3H), 7.16–7.04 (m, 4H), 6.93–6.73 (m, 13H), 6.67–6.64 (m, 1H), 6.48 (s, 1H), 4.99 (s, 1H), 2.30 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.9, 147.7, 143.9, 142.1, 140.1, 140.0, 134.7, 134.1, 130.5, 129.9, 129.8, 128.5, 128.1, 127.7, 127.4, 127.3, 127.3, 127.1, 126.7, 126.3, 126.2, 125.3, 123.5, 122.1, 117.9, 90.2, 87.7, 15.9. HRMS Calcd (ESI) m/z for $C_{37}H_{28}O_2$: $[M–OH]^+$ 487.2062, found: 487.2060.
 **3ca**	**6-methyl-1,2,3,3a-tetraphenyl-3,3a-dihydrocyclopenta[*b*] chromen-3-ol (3ca):** Following the general procedure **2.2**, the reaction was carried out by heating a mixture of 2-hydroxynitrostyrene **1c** (45 mg, 0.25 mmol), alkyne **2a** (89 mg, 0.50 mmol), [$Pd(OAc)_2$] (3 mg, 5 mol%) and $Cu(OAc)_2.H_2O$ (50 mg, 0.25 mmol) in xylene (3.0 mL) at 100 ^oC for 3 h under air to afford the title compound. The product was purified by flash column chromatography on silica gel (3% EtOAc in hexane); 80% yield (pale yellow solid, 101 mg); mp 196-198 ^oC. ^1H NMR (400 MHz, $CDCl_3$) δ 7.55–7.52 (m, 2H), 7.46–7.40 (m, 3H), 7.37–7.29 (m, 1H), 7.24–7.16 (m, 4H), 7.01–6.84 (m, 12H), 6.67–6.65 (m, 1H), 6.55 (s, 1H), 4.99 (s, 1H), 2.26 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.8, 147.3, 143.4, 142.2, 140.0, 139.8, 139.3, 134.7, 134.1, 129.9, 129.8, 128.8, 128.4, 128.2, 127.7, 127.6, 127.3, 127.2, 127.1, 126.6, 126.2, 123.4, 121.3, 118.3, 117.7, 90.1, 87.6, 21.6. HRMS Calcd (ESI) m/z for $C_{37}H_{28}O_2$: $[M–OH]^+$ 487.2062, found: 487.2058.

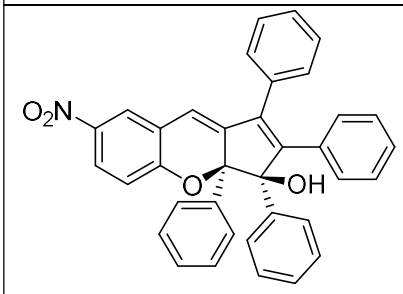
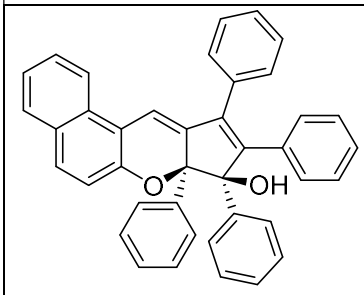
 **3da**	**7-methyl-1,2,3,3a-tetraphenyl-3,3a-dihydrocyclopenta[*b*] chromen-3-ol (3da):** Following the general procedure **2.2**, the reaction was carried out by heating a mixture of 2-hydroxynitrostyrene **1d** (45 mg, 0.50 mmol), alkyne **2a** (89 mg, 0.25 mmol), $[Pd(OAc)_2]$ (3 mg, 5 mol%) and $Cu(OAc)_2.H_2O$ (50 mg, 0.25 mmol) in xylene (3.0 mL) at 100 ^oC for 3 h under air to afford the title compound. The product was purified by flash column chromatography on silica gel (3% EtOAc in hexane); 83% yield (pale yellow solid, 104 mg); mp 186-188 ^oC. ^1H NMR (400 MHz, $CDCl_3$) δ 7.55–7.53 (m, 2H), 7.47–7.41 (m, 3H), 7.25–7.16 (m, 3H), 7.03–6.79 (m, 15H), 6.55 (s, 1H), 5.05 (s, 1H), 2.17 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.7, 147.8, 144.6, 142.2, 139.9, 139.8, 134.7, 134.0, 131.7, 129.9, 129.8, 129.4, 128.8, 128.4, 128.2, 127.9, 127.7, 127.5, 127.4, 127.2, 127.1, 126.6, 126.2, 123.7, 117.7, 117.4, 90.0, 87.5, 20.7. HRMS Calcd (ESI) m/z for $C_{37}H_{28}O_2$: $[M–OH]^+$ 487.2062, found: 487.2061.
 **3ea**	**5-methoxy-1,2,3,3a-tetraphenyl-3,3a-dihydrocyclopenta[*b*] chromen-3-ol (3ea):** Following the general procedure **2.2**, the reaction was carried out by heating a mixture of 2-hydroxynitrostyrene **1e** (48 mg, 0.25 mmol), alkyne **2a** (89 mg, 0.50 mmol), $[Pd(OAc)_2]$ (3 mg, 5 mol%) and $Cu(OAc)_2.H_2O$ (50 mg, 0.25 mmol) in xylene (3.0 mL) at 100 ^oC for 3 h under air to afford the title compound. The product was purified by flash column chromatography on silica gel (4% EtOAc in hexane); 75% yield (pale yellow solid, 98 mg); mp 216-218 ^oC. ^1H NMR (400 MHz, $CDCl_3$) δ 7.55–7.52 (m, 2H), 7.46–7.40 (m, 3H), 7.26–7.23 (m, 4H), 7.02–6.84 (m, 11H), 6.80–6.75 (m, 1H), 6.72–6.69 (m, 1H), 6.62–6.59 (m, 1H), 6.56 (s, 1H), 5.12 (s, 1H), 3.88 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.2, 148.1, 145.1, 142.1, 141.8, 139.9, 139.8, 134.7, 134.0,

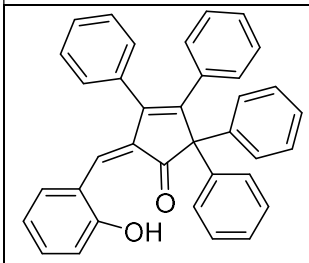
	129.9, 129.8, 128.4, 128.2, 127.7, 127.4, 127.2, 127.1, 126.6, 126.1, 124.9, 122.2, 119.6, 117.6, 112.1, 90.1, 87.7, 56.2. HRMS Calcd (ESI) m/z for $C_{37}H_{28}O_3$: $[M–OH]^+$ 503.2011, found: 503.2010.
 **3fa**	**5-ethoxy-1,2,3,3a-tetraphenyl-3,3a-dihydrocyclopenta[*b*] chromen-3-ol (3fa):** Following the general procedure **2.2**, the reaction was carried out by heating a mixture of 2-hydroxynitrostyrene **1f** (52 mg, 0.25 mmol), alkyne **2a** (89 mg, 0.50 mmol), $[Pd(OAc)_2]$ (3 mg, 5 mol%) and $Cu(OAc)_2.H_2O$ (50 mg, 0.25 mmol) in xylene (3.0 mL) at 100 ^oC for 3 h under air to afford the title compound. The product was purified by flash column chromatography on silica gel (4% EtOAc in hexane); 60% yield (yellow solid, 80 mg); mp 182-184 ^oC. ^1H NMR (400 MHz, $CDCl_3$) δ 7.55–7.52 (m, 2H), 7.46–7.40 (m, 3H), 7.25–7.23 (m, 3H), 7.03–6.84 (m, 12H), 6.78–6.70 (m, 2H), 6.62–6.59 (m, 1H), 6.55 (s, 1H), 5.16 (s, 1H), 4.23–4.02 (m, 2H), 1.49 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.4, 148.0, 145.0, 142.2, 140.0, 139.9, 138.8, 135.3, 134.7, 134.0, 129.9, 129.8, 128.8, 128.4, 128.2, 128.1, 127.7, 127.4, 127.2, 127.0, 126.6, 126.1, 125.0, 123.7, 122.2, 120.3, 119.7, 117.6, 114.4, 114.0, 90.1, 87.6, 65.1, 64.9, 15.2, 14.9. HRMS Calcd (ESI) m/z for $C_{38}H_{30}O_3$: $[M–OH]^+$ 517.2168, found: 517.2165.
 **3ga**	**7-fluoro-1,2,3,3a-tetraphenyl-3,3a-dihydrocyclopenta[*b*] chromen-3-ol (3ga):** Following the general procedure **2.2**, the reaction was carried out by heating a mixture of 2-hydroxynitrostyrene **1g** (46 mg, 0.25 mmol), alkyne **2a** (89 mg, 0.50 mmol), $[Pd(OAc)_2]$ (3 mg, 5 mol%) and $Cu(OAc)_2.H_2O$ (50 mg, 0.25 mmol) in xylene (3.0 mL) at 100 ^oC for 3 h under air to afford the title compound. The product was purified by flash column chromatography on silica gel (3% EtOAc in

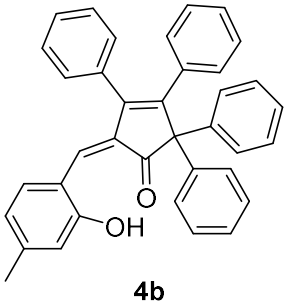
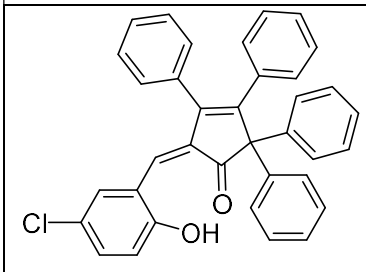
	hexane); 70% yield (yellow solid, 89 mg); mp 107-109 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.52–7.50 (m, 2H), 7.46–7.41 (m, 3H), 7.23–7.21 (m, 3H), 7.13–6.94 (m, 8H), 6.90–6.72 (m, 6H), 6.69–6.67 (m, 1H), 6.51 (s, 1H), 4.93 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.2 (d, *J* = 238 Hz), 148.9, 148.7, 146.1, 141.8, 139.5, 139.4, 134.4, 133.8, 129.8, 128.9, 128.6, 128.1, 127.7, 127.6, 127.5, 127.4, 127.2, 126.7, 126.4, 125.0 (d, *J* = 8 Hz), 118.3 (d, *J* = 8 Hz), 116.8, 114.9 (d, *J* = 24 Hz), 113.4 (d, *J* = 23 Hz), 90.0, 87.7. ^{19}F NMR ($CDCl_3$, 376 MHz): −121.3. HRMS Calcd (ESI) m/z for $C_{36}H_{25}FO_2$: $[M–OH]^+$ 491.1811, found: 491.1815.
 **3ha**	**7-chloro-1,2,3,3a-tetraphenyl-3,3a-dihydrocyclopenta[*b*] chromen-3-ol (3ha):** Following the general procedure **2.2**, the reaction was carried out by heating a mixture of 2-hydroxynitrostyrene **1h** (50 mg, 0.25 mmol), alkyne **2a** (89 mg, 0.50 mmol), $[Pd(OAc)_2]$ (3 mg, 5 mol%) and $Cu(OAc)_2.H_2O$ (50 mg, 0.25 mmol) in xylene (3.0 mL) at 100 °C for 3 h under air to afford the title compound. The product was purified by flash column chromatography on silica gel (3% EtOAc in hexane); 79% yield (pale yellow solid, 104 mg); mp 204-206 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52–7.49 (m, 2H), 7.47–7.41 (m, 3H), 7.24–7.21 (m, 2H), 7.13–6.93 (m, 12H), 6.90–6.88 (m, 1H), 6.86–6.82 (m, 3H), 6.50 (s, 1H), 4.85 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.4, 148.9, 145.9, 141.9, 139.4, 134.4, 133.7, 129.8, 128.9, 128.6, 128.4, 128.1, 127.8, 127.7, 127.5, 127.4, 127.2, 126.9, 126.7, 126.4, 125.5, 118.9, 116.6, 90.0, 87.8. HRMS Calcd (ESI) m/z for $C_{36}H_{25}ClO_2$: $[M–OH]^+$ 507.1516, found: 507.1514.

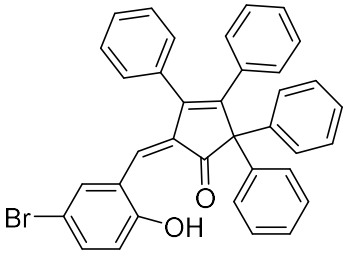
 **3ia**	**5-chloro-1,2,3,3a-tetraphenyl-3,3a-dihydrocyclopenta[*b*] chromen-3-ol (3ia):** Following the general procedure **2.2**, the reaction was carried out by heating a mixture of 2-hydroxynitrostyrene **1i** (50 mg, 0.25 mmol), alkyne **2a** (89 mg, 0.50 mmol), [$Pd(OAc)_2$] (3 mg, 5 mol%) and $Cu(OAc)_2.H_2O$ (50 mg, 0.25 mmol) in xylene (3.0 mL) at 100 ^oC for 3 h under air to afford the title compound. The product was purified by flash column chromatography on silica gel (3% EtOAc in hexane); 69% yield (pale yellow solid, 91 mg); mp 173-175 ^oC. ^1H NMR (500 MHz, $CDCl_3$) δ 7.51 (d, *J* = 7.1 Hz, 2H), 7.46–7.41 (m, 3H), 7.26–7.22 (m, 4H), 7.12–7.10 (m, 1H), 7.04–6.75 (m, 13H), 6.55 (s, 1H), 4.94 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.7, 145.5, 141.9, 139.5, 139.4, 134.4, 133.8, 129.8, 129.2, 128.9, 128.6, 128.1, 127.8, 127.7, 127.5, 127.3, 126.8, 126.4, 125.8, 125.6, 122.9, 116.9, 90.1, 88.4. HRMS Calcd (ESI) m/z for $C_{36}H_{25}ClO_2$: $[M–OH]^+$ 507.1516, found: 507.1513.
 **3ja**	**5,7-dichloro-1,2,3,3a-tetraphenyl-3,3a-dihydrocyclopenta [*b*]chromen-3-ol (3ja):** Following the general procedure **2.2**, the reaction was carried out by heating a mixture of 2-hydroxynitrostyrene **1j** (58 mg, 0.25 mmol), alkyne **2a** (89 mg, 0.50 mmol), [$Pd(OAc)_2$] (3 mg, 5 mol%) and $Cu(OAc)_2.H_2O$ (50 mg, 0.25 mmol) in xylene (3.0 mL) at 100 ^oC for 3 h under air to afford the title compound. The product was purified by flash column chromatography on silica gel (3% EtOAc in hexane); 66% yield (yellow solid, 92 mg); mp 99-101 ^oC. ^1H NMR (500 MHz, $CDCl_3$) δ 7.50–7.49 (m, 2H), 7.46–7.43 (m, 3H), 7.24–7.09 (m, 7H), 7.05–6.95 (m, 6H), 6.92–6.90 (m, 1H), 6.87–6.85 (m, 3H), 6.48 (s, 1H), 4.82 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.6, 147.3, 146.9, 141.7, 139.2, 138.9, 134.2, 133.5, 129.9, 129.8, 129.0, 128.7, 128.5, 128.0, 127.9, 127.8,

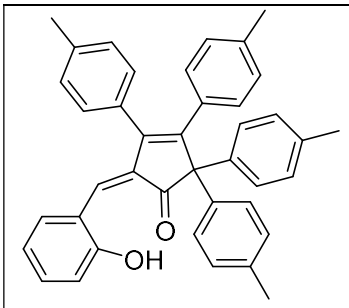
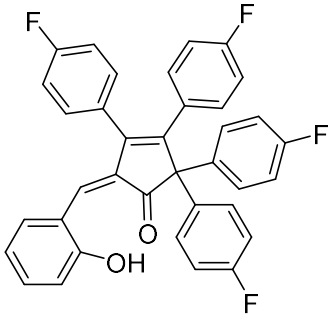
	127.7, 127.3, 127.2, 126.8, 126.6, 126.5, 125.4, 123.4, 115.9, 90.0, 88.6. HRMS Calcd (ESI) m/z for $C_{36}H_{24}Cl_2O_2$: $[M–OH]^+$ 541.1126, found: 541.1125.
 **3ka**	**7-bromo-1,2,3,3a-tetraphenyl-3,3a-dihydrocyclopenta[*b*] chromen-3-ol (3ka):** Following the general procedure **2.2**, the reaction was carried out by heating a mixture of 2-hydroxynitrostyrene **1k** (61 mg, 0.25 mmol), alkyne **2a** (89 mg, 0.50 mmol), $[Pd(OAc)_2]$ (3 mg, 5 mol%) and $Cu(OAc)_2.H_2O$ (50 mg, 0.25 mmol) in xylene (3.0 mL) at 100 ^oC for 3 h under air to afford the title compound. The product was purified by flash column chromatography on silica gel (3% EtOAc in hexane); 70% yield (yellow solid, 100 mg); mp 237-239 ^oC. ^1H NMR (400 MHz, $CDCl_3$) δ 7.52–7.49 (m, 2H), 7.46–7.42 (m, 3H), 7.25–7.22 (m, 2H), 7.15–7.09 (m, 4H), 7.04–6.92 (m, 7H), 6.90 (d, *J* = 8.5 Hz, 2H), 6.86–6.83 (m, 3H), 6.50 (s, 1H), 4.85 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.9, 148.9, 145.9, 141.8, 139.4, 139.4, 134.4, 133.7, 131.3, 129.8, 128.9, 128.6, 128.1, 127.7, 127.6, 127.5, 127.2, 126.7, 126.4, 125.9, 119.4, 116.5, 114.8, 90.0, 87.8.
 **3la**	**5,7-dibromo-1,2,3,3a-tetraphenyl-3,3a-dihydrocyclopenta [*b*]chromen-3-ol (3la):** Following the general procedure **2.2**, the reaction was carried out by heating a mixture of 2-hydroxynitrostyrene **1l** (80 mg, 0.25 mmol), alkyne **2a** (89 mg, 0.50 mmol), $[Pd(OAc)_2]$ (3 mg, 5 mol%) and $Cu(OAc)_2.H_2O$ (50 mg, 0.25 mmol) in xylene (3.0 mL) at 100 ^oC for 3 h under air to afford the title compound. The product was purified by flash column chromatography on silica gel (3% EtOAc in hexane); 69% yield (yellow solid, 112 mg); mp 191-194 ^oC. ^1H NMR (400 MHz, $CDCl_3$) δ 7.51–7.48 (m, 2H), 7.46–7.42 (m, 3H), 7.38 (d, *J* = 2.2 Hz, 1H), 7.24–7.17 (m, 5H), 7.05–6.97 (m, 7H), 6.91–6.89 (m, 1H), 6.87–6.83 (m, 3H), 6.47 (s, 1H),

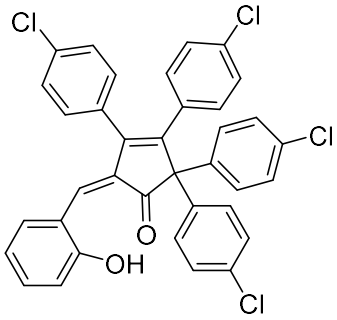
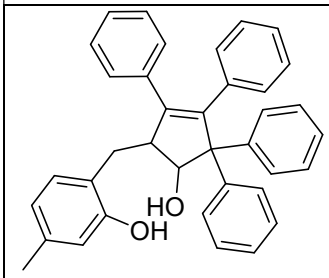
	4.83 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.6, 148.9, 146.7, 141.6, 139.2, 138.9, 134.2, 133.8, 133.5, 129.9, 129.8, 128.9, 128.7, 128.0, 127.9, 127.8, 127.7, 127.3, 127.0, 126.8, 126.5, 115.9, 114.8, 112.5, 90.1, 88.9. HRMS Calcd (ESI) m/z for $C_{36}H_{24}Br_2O_2$: $[M–OH]^+$ 629.0116, found: 629.0110.
 3ma	**7-nitro-1,2,3,3a-tetraphenyl-3,3a-dihydrocyclopenta[*b*]chromen-3-ol (3ma):** Following the general procedure **2.2**, the reaction was carried out by heating a mixture of 2-hydroxynitrostyrene **1m** (52 mg, 0.25 mmol), alkyne **2a** (89 mg, 0.50 mmol), $[Pd(OAc)_2]$ (3 mg, 5 mol%) and $Cu(OAc)_2.H_2O$ (50 mg, 0.25 mmol) in xylene (3.0 mL) at 100 °C for 3 h under air to afford the title compound. The product was purified by flash column chromatography on silica gel (4% EtOAc in hexane); 85% yield (pale yellow solid, 114 mg); mp 210-221 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.90–7.88 (m, 1H), 7.80 (d, *J* = 2.85 Hz, 1H), 7.52–7.43 (m, 5H), 7.25–7.24 (m, 2H), 7.11–6.83 (m, 14H), 6.56 (s, 1H), 4.61 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.2, 149.6, 146.6, 142.8, 141.6, 139.1, 138.8, 134.0, 133.3, 129.8, 129.7, 129.0, 128.8, 128.0, 127.9, 127.8, 127.7, 127.4, 127.3, 126.8, 126.6, 124.4, 124.3, 122.7, 90.1, 88.7. HRMS Calcd (ESI) m/z for $C_{36}H_{25}NO_4$: $[M–OH]^+$ 518.1756, found: 518.1753.
 3na	**7a,8,9,10-tetraphenyl-7a,8-dihydrobenzo[*f*]cyclopenta[*b*]chromen-8-ol (3na):** Following the general procedure **2.2**, the reaction was carried out by heating a mixture of 2-hydroxynitrostyrene **1n** (54 mg, 0.25 mmol), alkynes **2a** (89 mg, 0.50 mmol), $[Pd(OAc)_2]$ (3 mg, 5 mol%) and $Cu(OAc)_2.H_2O$ (50 mg, 0.25 mmol) in xylene (3.0 mL) at 100 °C for 3 h under air to afford the title compound. The product was purified by flash column chromatography on silica gel (3% EtOAc in hexane); 74% yield (pale yellow solid,

	99 mg); mp 240-243 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.87–7.82 (m, 1H), 7.75–7.57 (m, 5H), 7.51–7.37 (m, 4H), 7.29–7.18 (m, 7H), 7.02–6.84 (m, 10H), 5.06 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.1, 147.9, 143.8, 142.5, 139.9, 139.8, 134.7, 134.2, 130.3, 130.0, 129.9, 129.8, 129.3, 129.0, 128.6, 128.2, 127.7, 127.5, 127.4, 127.3, 127.1, 126.7, 126.6, 126.3, 124.3, 122.4, 121.8, 118.8, 117.7, 113.7, 90.4, 87.8. HRMS Calcd (ESI) m/z for $C_{40}H_{28}O_2$: $[M–OH]^+$ 523.2062, found: 523.2061.
 **4a**	**5-(2-hydroxybenzylidene)-2,2,3,4-tetraphenylcyclopent-3-en-1-one (4a, *E*:*Z* = 1:3):** Following the general procedure **2.3**, the reaction was carried out by heating a mixture of chromene derivative **3aa** (49 mg, 0.1 mmol), $In(OTf)_3$ (6 mg, 10 mol%) in chlorobenzene (3.0 mL) at 50 °C for 2 h under air to afford the title compound. The product was purified by flash column chromatography on silica gel (6% EtOAc in hexane); 89% yield (sticky yellow solid, 43 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.53 (s, 0.25H), 7.46 (d, *J* = 7.4 Hz, 4H), 7.40 (d, *J* = 4.3 Hz, 2H), 7.37–7.35 (m, 1H), 7.30 (t, *J* = 7.5 Hz, 4H), 7.27–7.20 (m, 3H), 7.00–6.84 (m, 9H), 6.55 (d, *J* = 8.2 Hz, 0.25H), 6.44 (d, *J* = 7.6 Hz, 0.25H), 6.29 (t, *J* = 7.5 Hz, 0.25H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 208.5, 155.9, 145.6, 144.5, 140.1, 139.8, 136.8, 134.9, 134.8, 133.4, 132.8, 131.7, 130.7, 130.5, 130.2, 129.9, 129.8, 129.7, 128.9, 128.4, 128.3, 128.2, 127.7, 127.5, 127.4, 127.4, 127.3, 124.5, 121.5, 120.8, 119.5, 119.3, 115.0, 71.4. HRMS Calcd (ESI) m/z for $C_{36}H_{26}O_2$: $[M+H]^+$ 491.2011, found: 491.2010.

 **4b**	**5-(2-hydroxy-4-methylbenzylidene)-2,2,3,4-tetraphenylcyclopent-3-en-1-one (4b, *E*:*Z* = 1:4):** Following the general procedure **2.3**, the reaction was carried out by heating a mixture of chromene derivative **3ca** (50 mg, 0.1 mmol), $In(OTf)_3$ (6 mg, 10 mol%) in chlorobenzene (3.0 mL) at 50 ^oC for 2 h under air to afford the title compound. The product was purified by flash column chromatography on silica gel (6% EtOAc in hexane); 85% yield (yellow solid, 43 mg); mp 120-125 ^oC. ^1H NMR (500 MHz, $CDCl_3$) δ 7.51 (s, 1H), 7.48 (s, 0.25H), 7.45–7.43 (m, 3H), 7.39–7.37 (m, 3H), 7.35–7.33 (m, 1H), 7.30–7.24 (m, 8H), 7.20 (d, *J* = 8.0 Hz, 1H), 6.99–6.91 (m, 3H), 6.87–6.84 (m, 2H), 6.79 (s, 1H), 6.68 (d, *J* = 8.9 Hz, 1H), 6.37 (s, 0.25H), 6.31 (d, *J* = 7.9 Hz, 0.25H), 6.31 (d, *J* = 7.4 Hz, 0.25H), 2.28 (s, 2.25H), 2.12 (s, 0.75H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 208.5, 155.9, 145.9, 145.8, 143.8, 142.8, 140.2, 140.0, 139.9, 135.8, 135.1, 134.9, 134.8, 133.4, 133.2, 130.7, 130.4, 130.4, 130.2, 130.2, 129.9 129.8, 129.7, 128.9, 128.4, 128.3, 128.2, 128.1, 127.7, 127.5, 127.4, 127.3, 127.2, 121.8, 121.6, 119.9, 119.7, 119.5, 118.6, 115.6, 71.4, 71.3, 21.4. HRMS Calcd (ESI) m/z for $C_{37}H_{28}O_2$: $[M+H]^+$ 505.2168, found: 505.2166.
 **4c**	**5-(5-chloro-2-hydroxybenzylidene)-2,2,3,4-tetraphenylcyclopent-3-en-1-one (4c, *E*:*Z* = 1:1.5):** Following the general procedure **2.3**, the reaction was carried out by heating a mixture of chromen derivatives **3ha** (53 mg, 0.1 mmol), $In(OTf)_3$ (6 mg, 10 mol%) in chlorobenzene (3.0 mL) at 50 ^oC for 2 h under air to afford the title compound. The product was purified by flash column chromatography on silica gel (6% EtOAc in hexane); 76% yield (yellow solid, 40 mg); mp 159-161 ^oC. ^1H NMR (500 MHz, $CDCl_3$) δ 7.51 (d, *J* = 6.4, 0.40H), 7.44–7.42 (m, 3H), 7.39–7.36 (m, 3H), 7.30–7.26 (m,

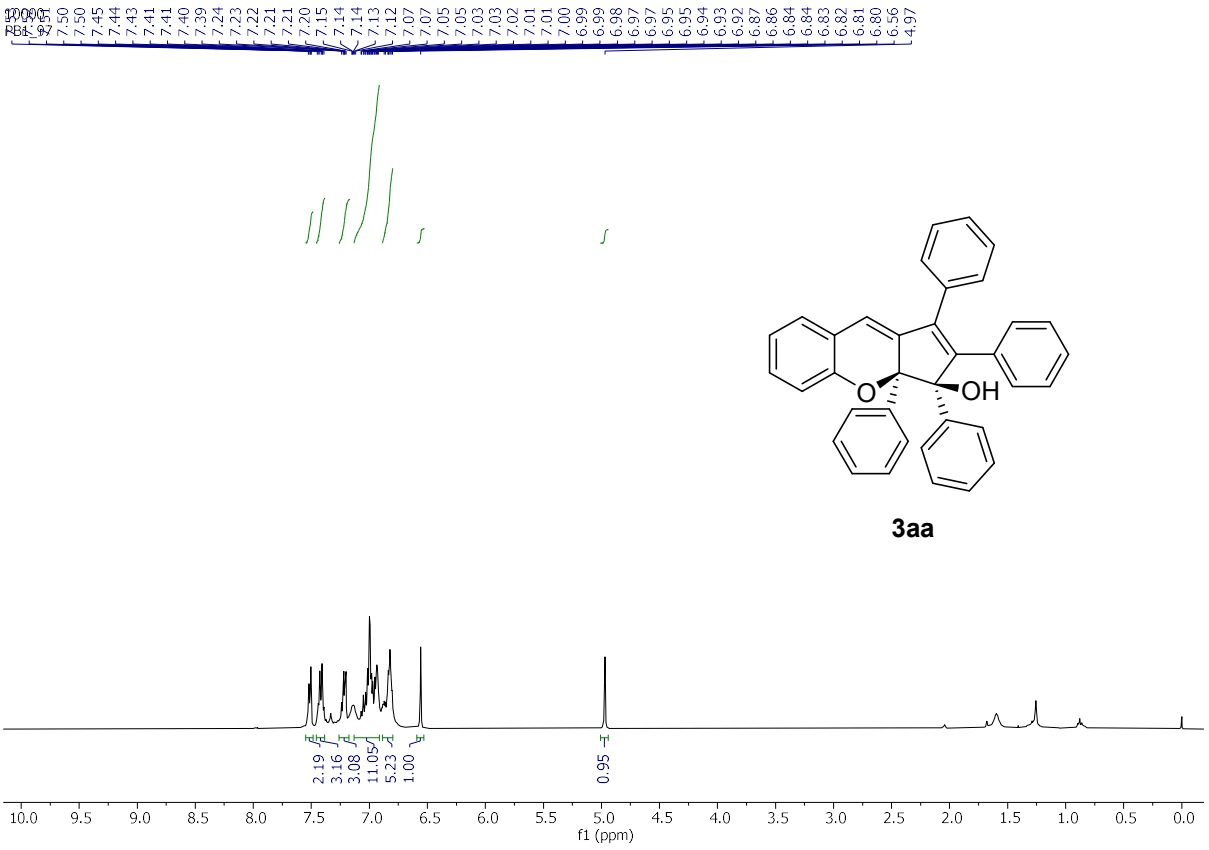
	7H), 7.20–6.83 (m, 9H), 6.73 (s, 0.60H), 6.52–6.49 (m, 0.60H), 6.36 (s, 0.40H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 208.6, 205.1, 154.4, 152.7, 149.4, 145.4, 145.3, 139.9, 139.5, 138.0, 137.6, 134.6, 134.5, 132.2, 131.1, 130.8, 130.5, 130.4, 130.1, 129.8, 129.7, 129.5, 129.4, 129.1, 128.7, 128.6, 128.5, 128.4, 128.1, 127.8, 127.7, 127.6, 127.5, 127.4, 127.0, 126.2, 125.9, 125.6, 124.3, 123.6, 122.8, 120.9, 116.2, 114.9, 71.5, 71.4. HRMS Calcd (ESI) m/z for $C_{36}H_{25}ClO_2$: $[M+H]^+$ 525.1621, found: 525.1619.
 **4d**	**5-(5-bromo-2-hydroxybenzylidene)-2,2,3,4-tetraphenylcyclopent-3-en-1-one (4d, *E*:*Z* = 1:3):** Following the general procedure **2.3**, the reaction was carried out by heating a mixture of chromene derivative **3ka** (56 mg, 0.1 mmol), $In(OTf)_3$ (6 mg, 10 mol%) in chlorobenzene (3.0 mL) at 50 ^{o}C for 2 h under air to afford the title compound. The product was purified by flash column chromatography on silica gel (6% EtOAc in hexane); 75% yield (yellow solid, 43 mg); mp 160-163 ^{o}C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.53 (s, 0.25H),7.47–7.43 (m, 5H), 7.40–7.33 (m, 3H), 7.31–7.28 (m, 4H), 7.25 (d, *J* = 7.1 Hz, 3H), 7.08–6.93 (m, 4H), 6.92–6.84 (m, 3H), 6.78– 6.76 (m, 1H), 6.46–6.43 (m, 0.75H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 208.5, 205.4, 154.8, 153.4, 149.3, 145.4, 145.3, 141.9, 139.9, 139.5, 138.0, 137.3, 135.1, 134.7, 134.6, 134.5, 133.9, 133.7, 132.5, 130.7, 130.6, 130.5, 130.1, 129.8, 129.4, 129.1, 128.5, 128.4, 128.2, 128.0, 127.9, 127.7, 127.6, 127.5, 127.4, 126.4, 123.3, 121.1, 116.6, 112.8, 111.4, 71.5, 71.4. HRMS Calcd (ESI) m/z for $C_{36}H_{25}BrO_2$: $[M+H]^+$ 569.1116, found: 569.1111.

 **4e**	**5-(2-hydroxybenzylidene)-2,2,3,4-tetra-*p*-tolylcyclopent-3-en-1-one (4e, *E*:*Z* = 1:4):** Following the general procedure **2.3**, the reaction was carried out by heating a mixture of chromene derivative **3ab** (55 mg, 0.1 mmol), $In(OTf)_3$ (6 mg, 10 mol%) in chlorobenzene (3.0 mL) at 50 ^oC for 2 h under air to afford the title compound. The product was purified by flash column chromatography on silica gel (6% EtOAc in hexane); 69% yield (sticky yellow solid, 38 mg). ^1H NMR (500 MHz, $CDCl_3$) δ 7.57 (s, 0.8H), 7.42–7.38 (m, 0.40H), 7.33 (d, *J* = 7.9 Hz, 3H), 7.28–7.20 (m, 5.2H), 7.12–7.08 (m, 4H), 6.95 (d, *J* = 8.3 Hz, 1H), 6.85–6.71 (m, 7H), 6.52 (d, *J* = 8.2 Hz, 0.20H), 6.43 (d, *J* = 7.7 Hz, 0.20H), 6.30 (t, *J* = 7.6 Hz, 0.20H) 2.39 (s, 3H), 2.31 (s, 6H), 2.14 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 209.7, 156.0, 144.8, 144.2, 137.9, 137.3, 137.1, 136.9, 133.6, 132.3, 132.2, 131.8, 131.4, 131.3, 130.8, 130.4, 130.0, 129.8, 129.7, 129.1, 129.0, 128.3, 128.2, 128.1, 125.1, 120.8, 120.0, 70.6, 21.5, 21.3, 21.2. HRMS Calcd (ESI) m/z for $C_{40}H_{34}O_2$: $[M+H]^+$ 547.2637, found: 547.2623.
 **4f**	**2,2,3,4-tetrakis(4-fluorophenyl)-5-(2-hydroxybenzylidene)cyclopent-3-en-1-one (4f, *E*:*Z* = 1:2):** Following the general procedure **2.3**, the reaction was carried out by heating a mixture of chromene derivative **3ad** (56 mg, 0.1 mmol), $In(OTf)_3$ (6 mg, 10 mol%) in chlorobenzene (3.0 mL) at 50 ^oC for 2 h under air to afford the title compound. The product was purified by flash column chromatography on silica gel (6% EtOAc in hexane); 86% yield (sticky yellow solid, 48 mg). ^1H NMR (500 MHz, $CDCl_3$) δ 7.60–7.56 (m, 0.35H), 7.51–7.44 (m, 0.7H), 7.36–7.33 (m, 4.2H), 7.24–7.21 (m, 0.7H), 7.13–7.08 (m, 1H), 7.03–6.84 (m, 8H), 6.84–6.61 (m, 5H), 6.57 (d, *J* = 8.2 Hz, 0.35H), 6.43–6.34 (m, 0.7H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 206.9, 162.6 (d, *J* = 247 Hz), 162.2

	(d, *J* = 246 Hz), 162.1 (d, *J* = 246 Hz), 159.0 (d, *J* = 246 Hz), 155.7, 145.0, 143.2, 141.6, 135.9, 135.5, 135.3, 133.3, 133.2, 132.9, 132.3, 132.2, 132.1, 132.0, 131.9, 131.7, 131.3, 131.2, 131.0, 130.4, 130.1, 127.8, 123.7, 121.2, 120.9, 119.5, 118.8, 116.4, 116.2, 115.6 (d, *J* = 21 Hz), 115.5 (d, *J* = 21 Hz), 115.0 (d, *J* = 21 Hz), 114.9 (d, *J* = 21 Hz), 70.1. HRMS Calcd (ESI) m/z for $C_{36}H_{22}F_4O_2$: $[M+H]^+$ 563.1634, found: 563.1630.
 **4g**	**2,2,3,4-tetrakis(4-chlorophenyl)-5-(2-hydroxybenzylidene)cyclopent-3-en-1-one (4g, *E*:*Z* = 1:2.3):** Following the general procedure **2.3**, the reaction was carried out by heating a mixture of chromene derivative **3af** (63 mg, 0.1 mmol), $In(OTf)_3$ (6 mg, 10 mol%) in chlorobenzene (3.0 mL) at 50 ^oC for 2 h under air to afford the title compound. The product was purified by flash column chromatography on silica gel (6% EtOAc in hexane); 79% yield (sticky yellow solid, 50 mg). ^1H NMR (500 MHz, $CDCl_3$) δ 7.55 (s, 0.30H), 7.49 (d, *J* = 7.8 Hz, 0.60H), 7.39–7.09 (m, 12H), 7.00–6.83 (m, 5.2H), 6.74–6.69 (m, 2H), 6.57–6.53 (m, 0.30H), 6.39–6.32 (m, 0.60H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 205.8, 155.7, 153.8, 145.5, 142.5, 137.9, 137.8, 135.6, 134.6, 133.9, 133.8, 133.6, 133.1, 132.7, 132.6, 132.3, 131.7, 131.4, 130.9, 130.8, 130.5, 129.8, 129.6, 128.9, 128.3, 128.2, 128.1, 123.5, 121.2, 120.9, 119.6, 118.5, 115.1, 70.3. HRMS Calcd (ESI) m/z for $C_{36}H_{22}Cl_4O_2$: $[M+H]^+$ 627.0452, found: 627.0449.
 **4h**	**2-((5-hydroxy-2,3,4,4-tetraphenylcyclopent-2-en-1-yl)methyl)phenol (4h):** The reaction was carried out by reacting **4b** (50 mg, 0.1 mmol) with $NaBH_4$ (6 mg, 1.5 equiv.) and cerium(III)chloride (5 mg, 20 mol%) in methanol (3.0 mL) at room temperature for 4 hours under air. The product was purified by silica gel flash column chromatography (10% EtOAc in hexane); 90% yield (yellow liquid, 46 mg). ^1H NMR

	(400 MHz, $CDCl_3$) δ 7.53–7.50 (m, 2H), 7.38–7.27 (m, 10H), 7.24–7.17 (m, 3H), 6.94–6.84 (m, 5H), 6.62–6.52 (m, 3H), 4.98 (d, *J* = 6.0 Hz, 1H), 3.40–3.35 (m, 1H), 2.73 (dd, *J* = 14.5, 10.2 Hz, 1H), 2.39 (dd, *J* = 14.5, 3.1 Hz, 1H), 2.22 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.5, 143.9, 142.2, 141.7, 139.8, 137.7, 137.2, 136.2, 131.4, 130.7, 129.8, 129.7, 128.5, 128.1, 127.9, 127.6, 127.5, 127.4, 126.8, 126.5, 124.4, 121.3, 117.6, 80.3, 69.2, 54.7, 27.5, 21.1. HRMS Calcd (ESI) m/z for $C_{37}H_{32}O_2$: $[M–OH]^+$ 491.2375, found: 491.2372.

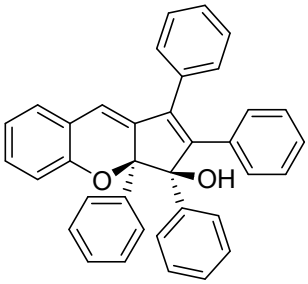
5. NMR Spectra and HRMS of Synthesized Compounds:



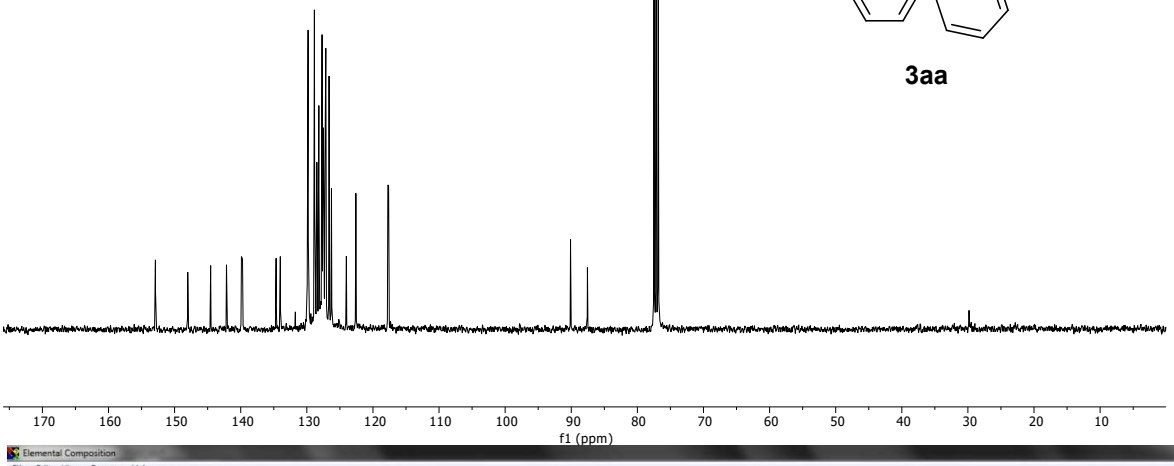
3aa

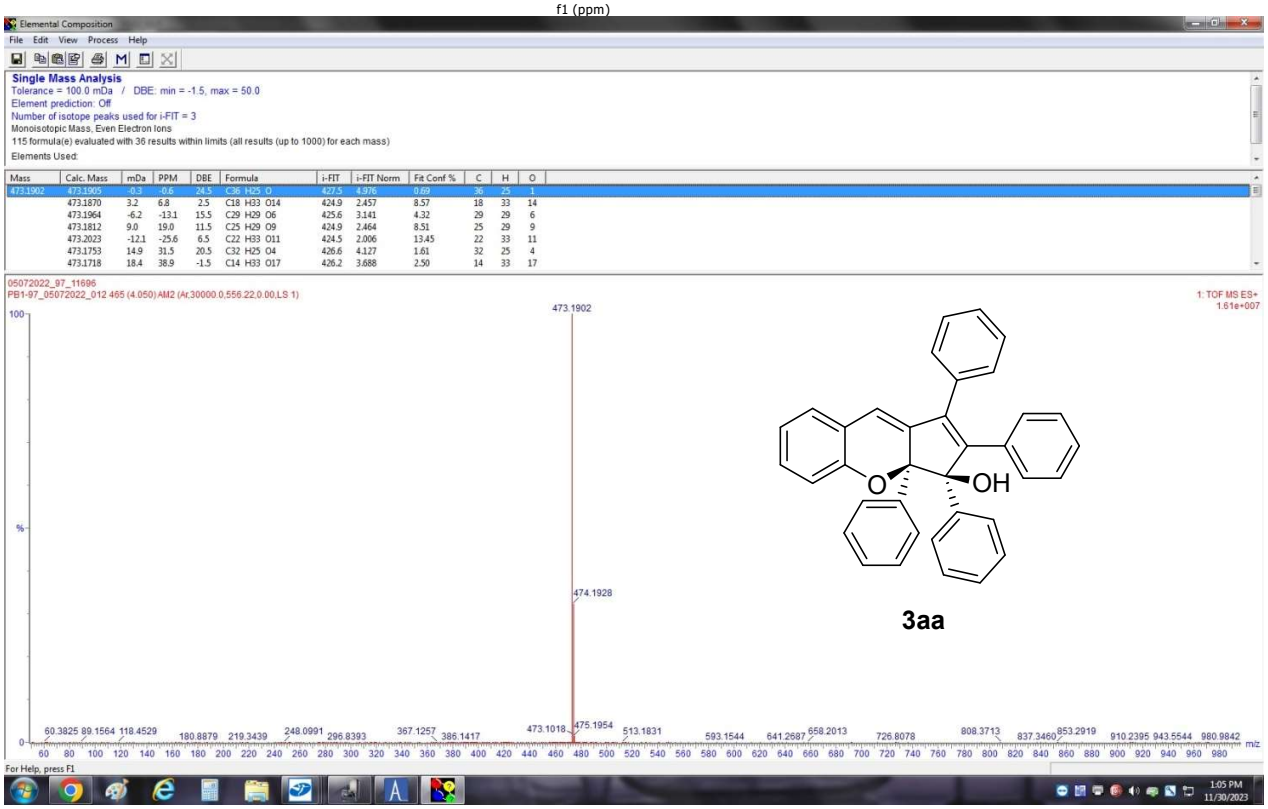
10030
PB1_97

152.91
148.01
144.55
142.15
139.89
139.73
134.65
134.01
129.89
129.81
128.85
128.82
128.48
128.18
127.70
127.56
127.49
127.45
127.26
127.13
126.63
126.27
124.02
122.59
117.74
117.63
90.11
87.55
77.48
77.16
76.84

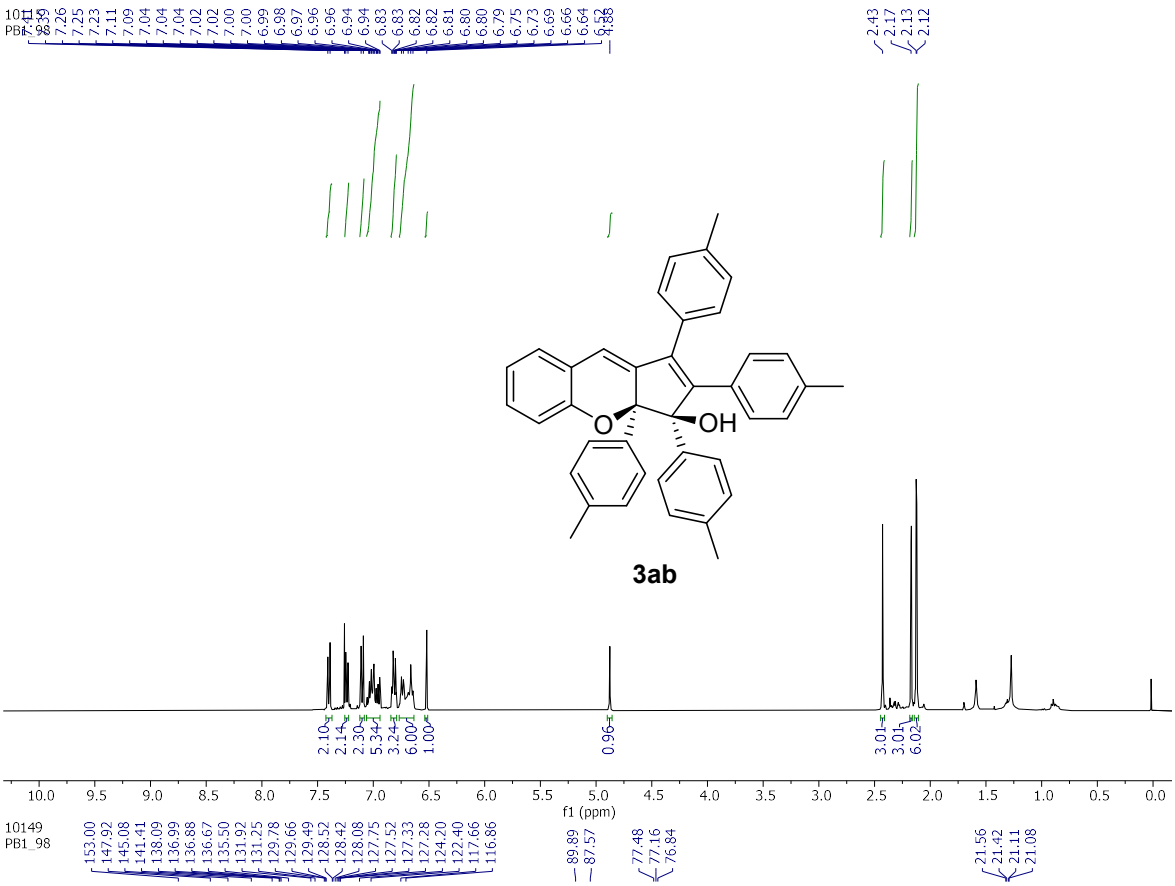


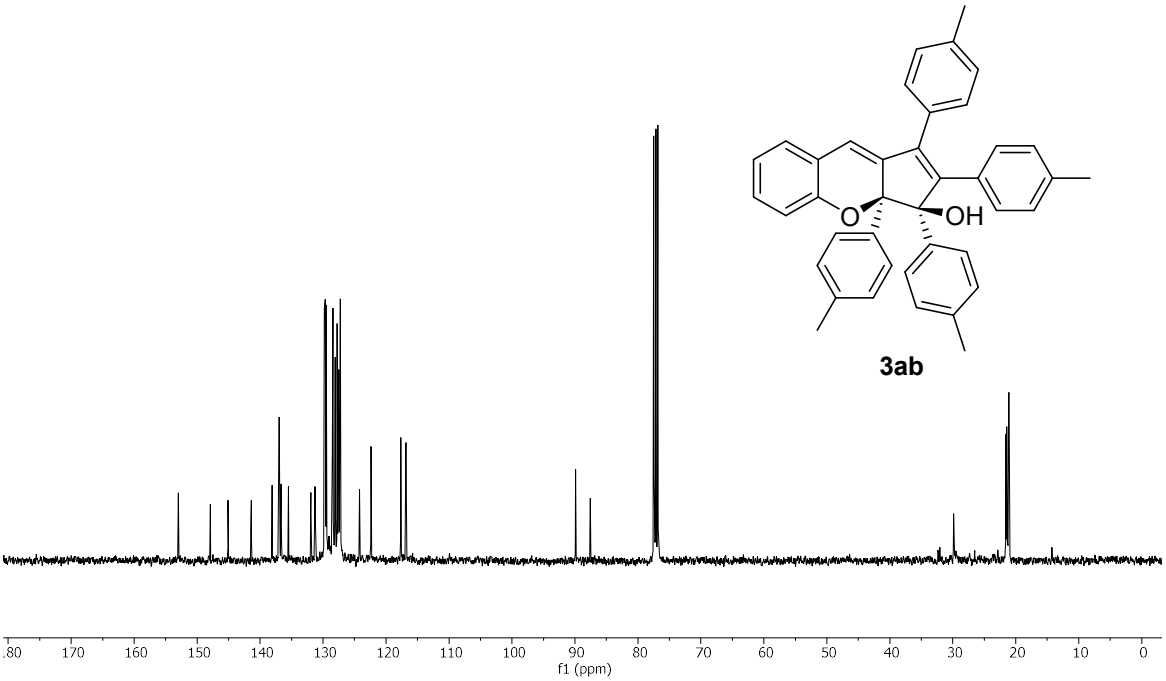
3aa

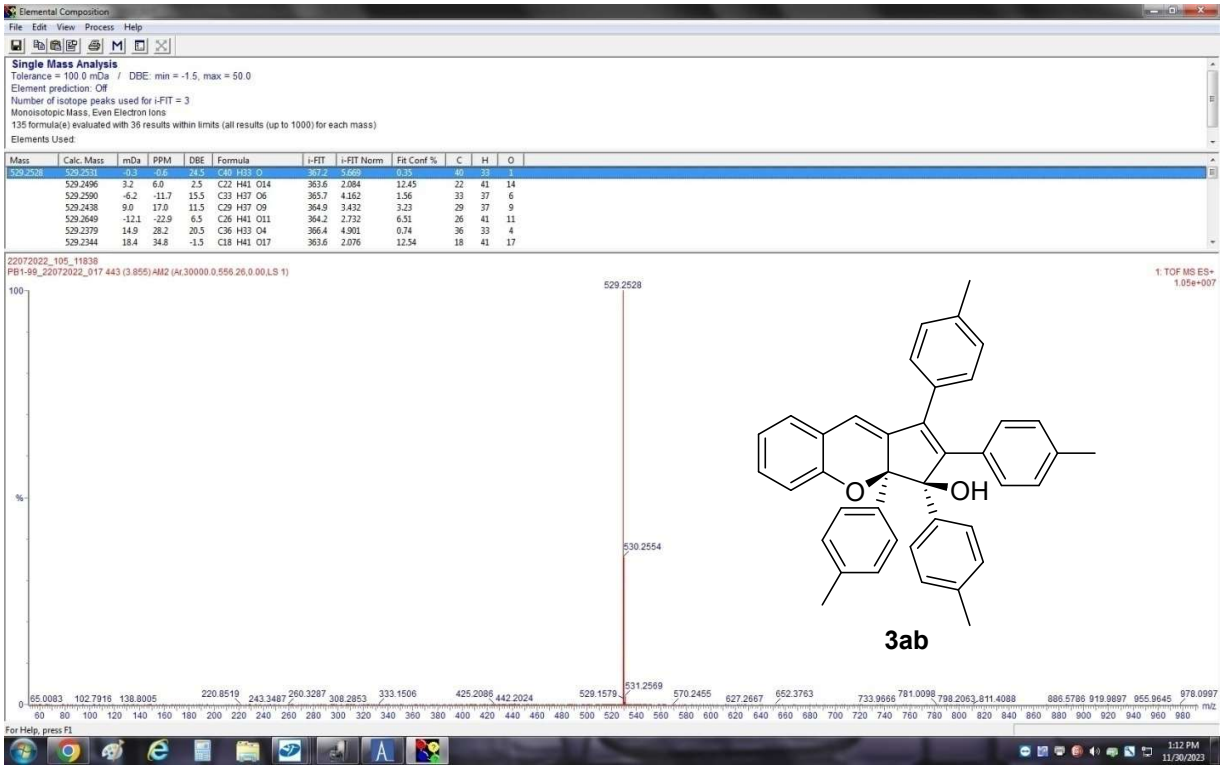


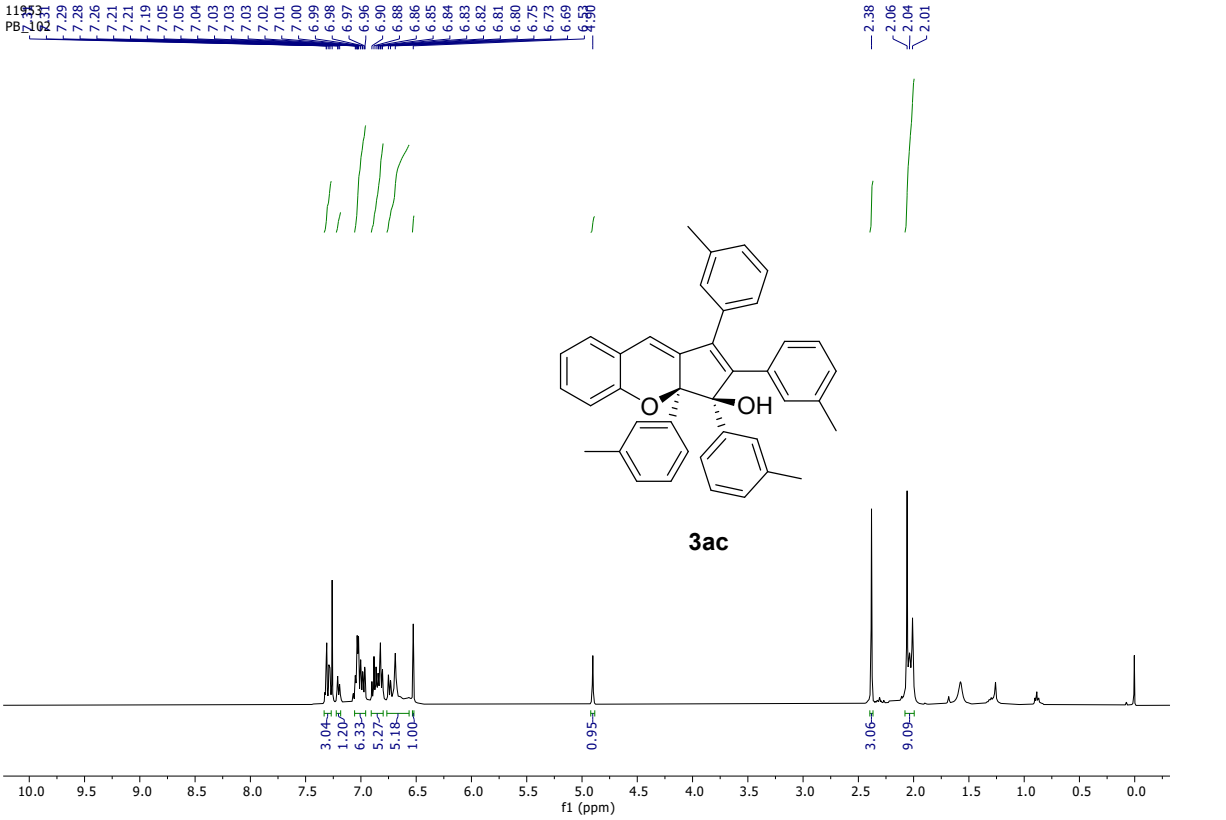


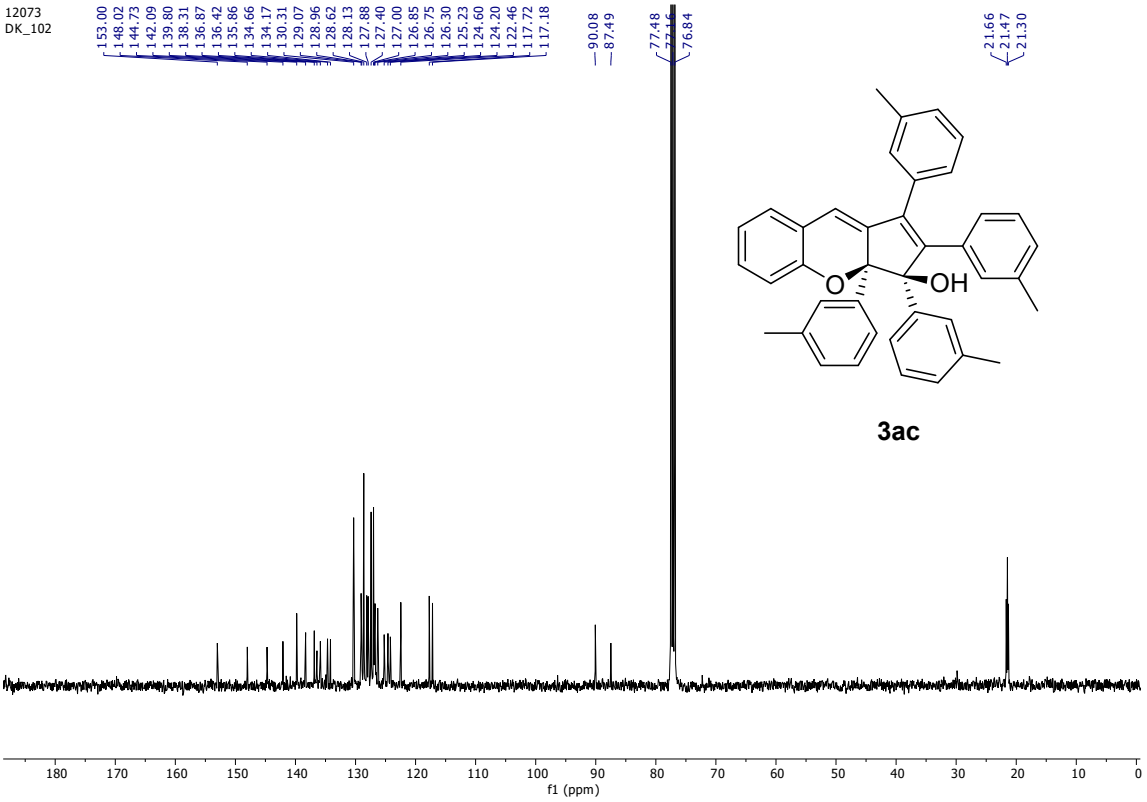
3aa

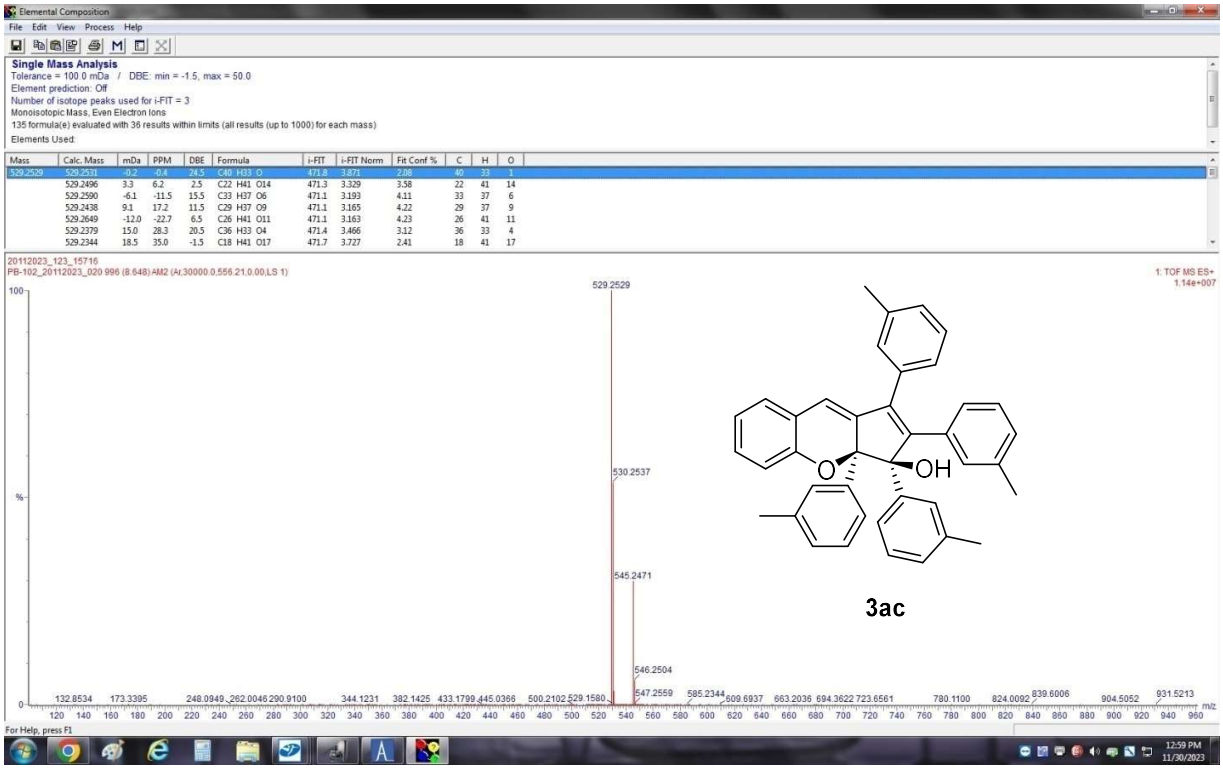

OH
3ab
f1 (ppm)

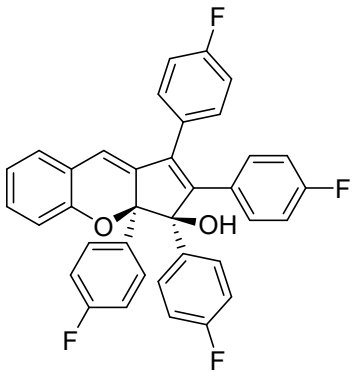

OH
3ab
f1 (ppm)


Elemental Composition
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
135 formula(e) evaluated with 36 results within limits (all results (up to 1000) for each mass)
Elements Used:
529.2528
530.2554
531.2569
O
OH
3ab

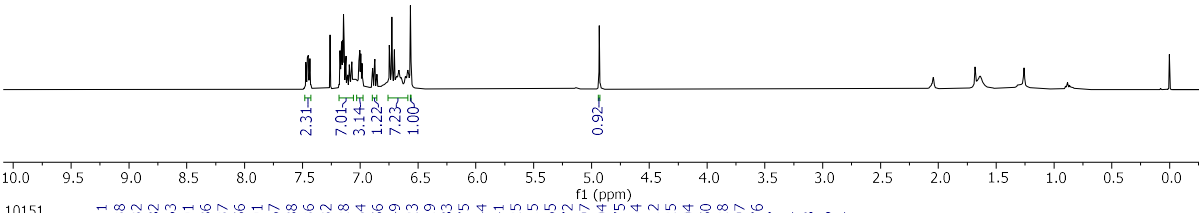

11953
PB-102
O
OH
3ac
f1 (ppm)


12073
DK_102
153.00
148.02
144.73
142.09
139.80
138.31
136.87
136.42
135.86
134.66
134.17
130.31
129.07
128.96
128.62
128.13
127.88
127.40
127.00
126.85
126.75
126.30
125.23
124.60
124.20
122.46
117.72
117.18
90.08
87.49
77.48
77.16
76.84
21.66
21.47
21.30
O
OH
3ac
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

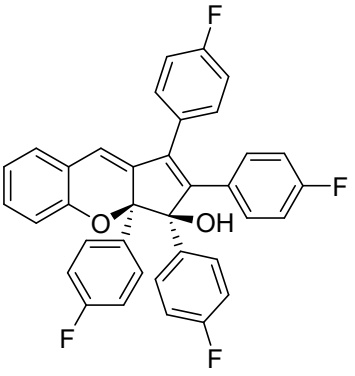

Elemental Composition
File Edit View Process Help
Single Mass Analysis
Tolerance = 100.0 mDa / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3
Monoisotopic Mass, Even Electron Ions
135 formula(e) evaluated with 36 results within limits (all results (up to 1000) for each mass)
Elements Used:
Mass Calc. Mass mDa PPM DBE Formula i-FIT i-FIT Norm Fit Conf % C H O
529.2529 529.2531 -0.2 -0.4 24.5 C40 H33 O 471.8 3.371 2.08 40 33 1
529.2496 3.3 6.2 2.5 C22 H41 O14 471.3 3.329 3.58 22 41 14
529.2590 -6.1 -11.5 15.5 C33 H37 O6 471.1 3.193 4.11 33 37 6
529.2438 9.1 17.2 11.5 C29 H37 O9 471.1 3.165 4.22 29 37 9
529.2649 -12.0 -22.7 6.5 C26 H41 O11 471.1 3.163 4.23 26 41 11
529.2379 15.0 28.3 20.5 C36 H33 O4 471.4 3.466 3.12 36 33 4
529.2344 18.5 35.0 -1.5 C18 H41 O17 471.7 3.727 2.41 18 41 17
20112023_123_15716
PB-102_20112023_020 996 (8.648) AM2 (Ar,30000.0,556.21,0.00,LS 1)
1: TOF MS ES+
1.14e+007
529.2529
530.2537
545.2471
546.2504
547.2559
O
OH
3ac
For Help, press F1


F
F
O
OH
F
F

3ad

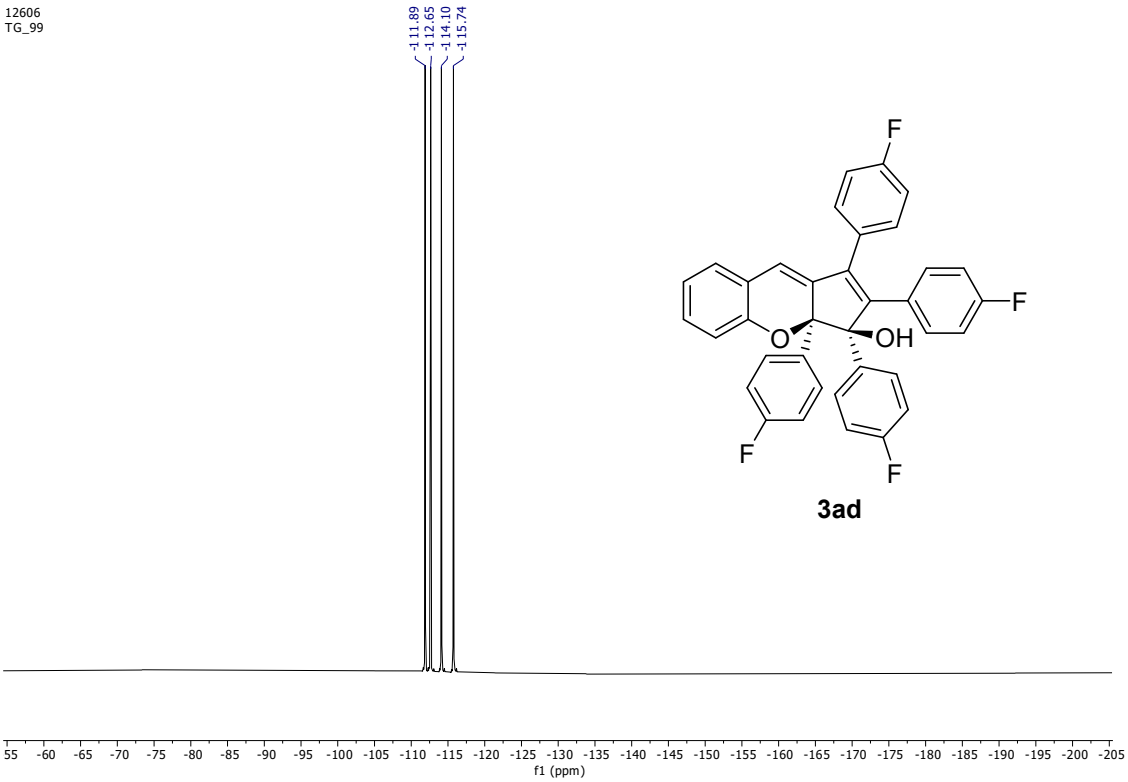

2.31
7.01
3.14
1.22
7.23
1.00
0.92
f1 (ppm)


10151
PB1_99

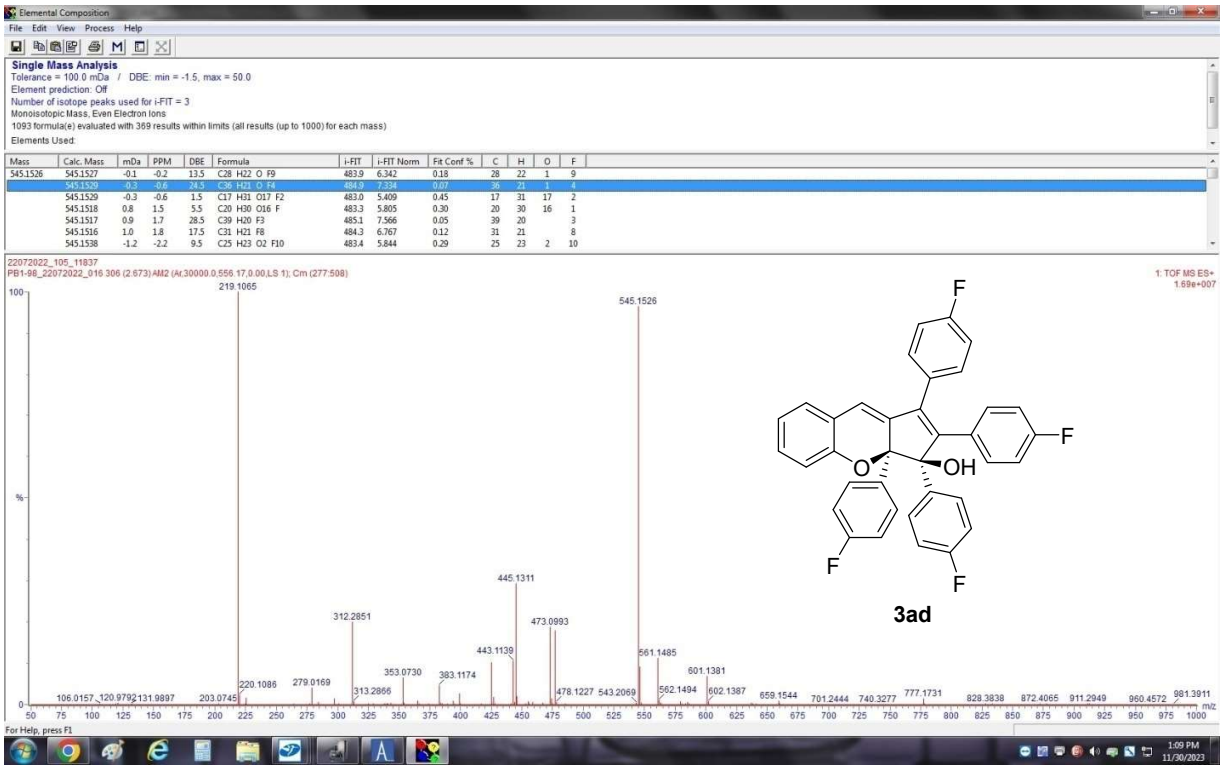

F
F
O
OH
F
F

3ad

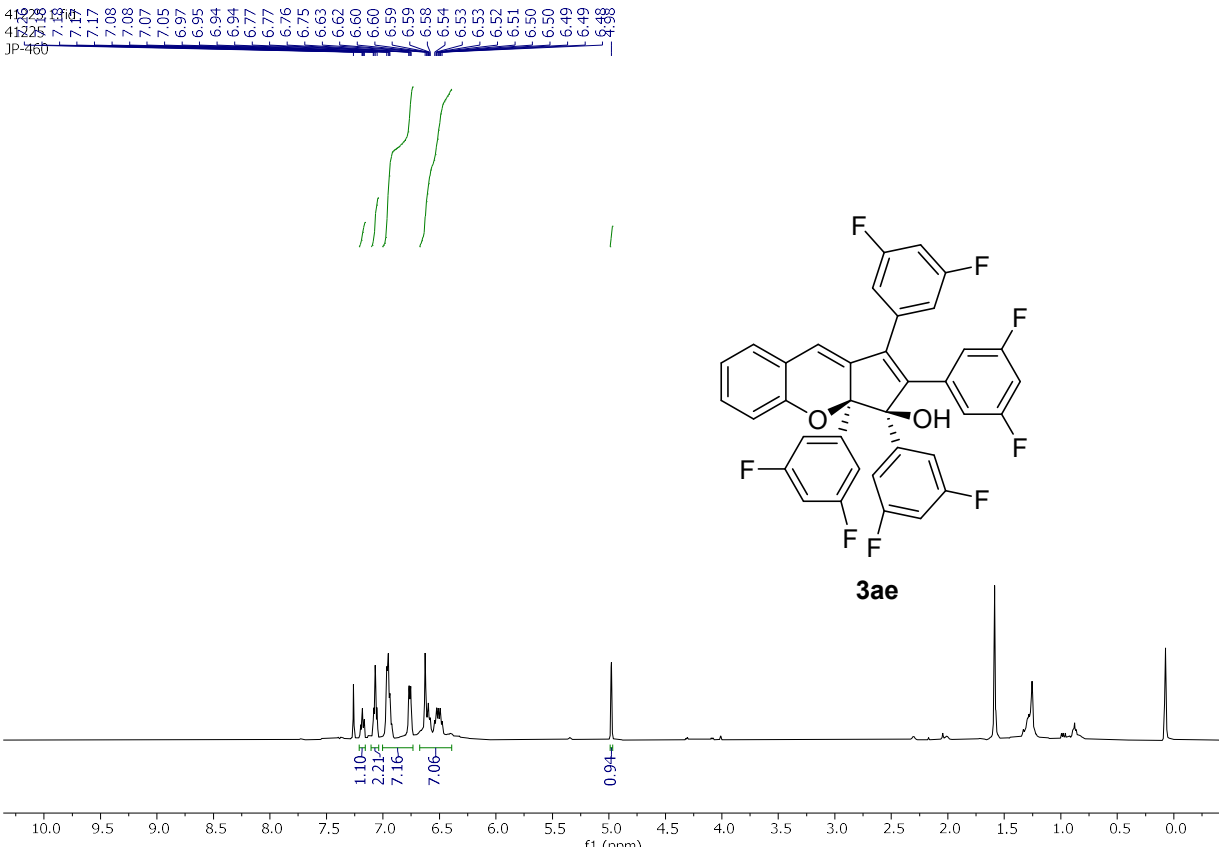
f1 (ppm)


12606
TG_99
-111.89
-112.65
-114.10
-115.74
F
F
O
OH
F
F
F
55 -60 -65 -70 -75 -80 -85 -90 -95 -100 -105 -110 -115 -120 -125 -130 -135 -140 -145 -150 -155 -160 -165 -170 -175 -180 -185 -190 -195 -200 -205
f1 (ppm)

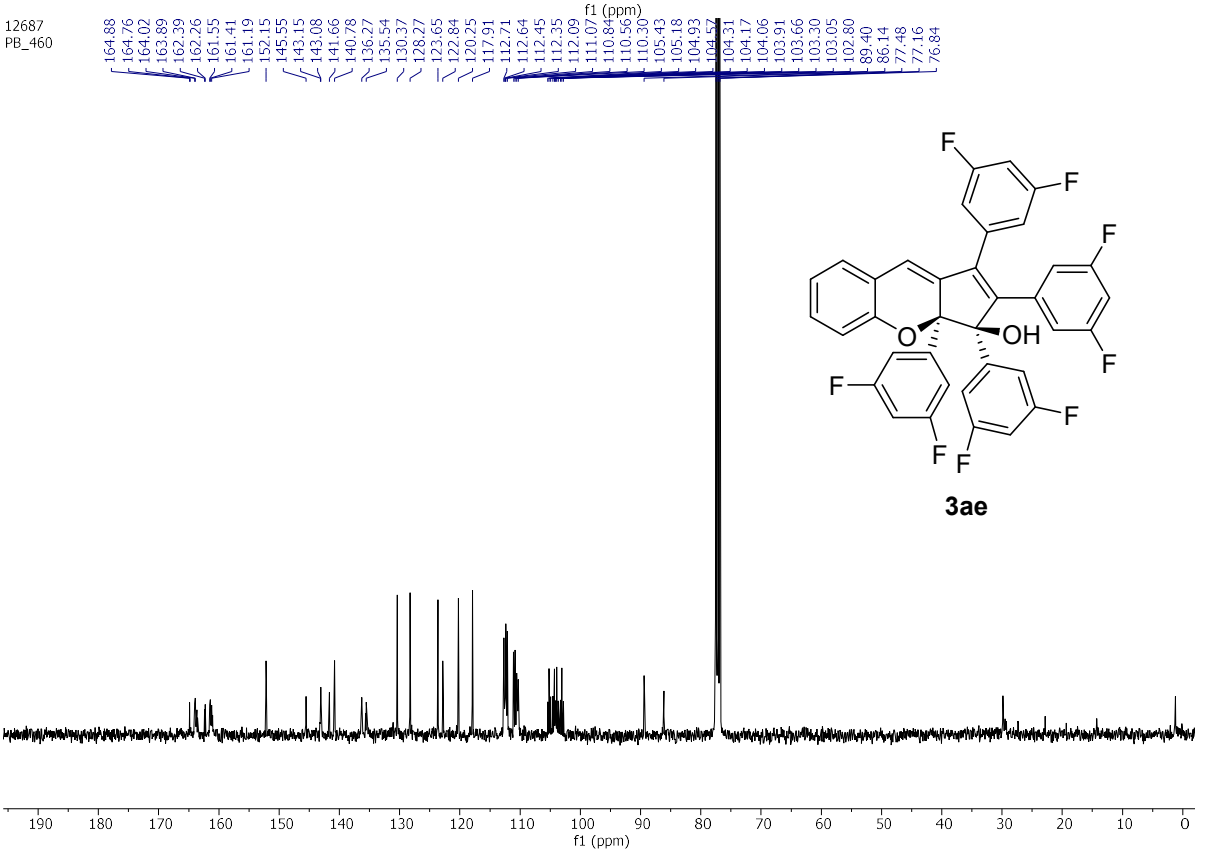
3ad


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
1093 formula(e) evaluated with 369 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 O F
545.1526 545.1527 -0.1 -0.2 13.5 C28 H22 O F9 483.9 6.342 0.18 28 22 1 9
545.1529 -0.3 -0.6 24.5 C36 H21 O F4 484.9 7.334 0.07 36 21 1 4
545.1529 -0.3 -0.6 1.5 C17 H31 O17 F2 483.0 5.409 0.45 17 31 17 2
545.1518 0.8 1.5 5.5 C20 H30 O16 F 483.3 5.805 0.30 20 30 16 1
545.1517 0.9 1.7 28.5 C39 H20 F3 485.1 7.566 0.05 39 20 3
545.1516 1.0 1.8 17.5 C31 H21 F8 484.3 6.767 0.12 31 21 8
545.1538 -1.2 -2.2 9.5 C25 H23 O2 F10 483.4 5.844 0.29 25 23 2 10
22072022_105_11837
PB1-98_22072022_016 306 (2.673) AM2 (Ar,30000.0,556.17,0.00,LS 1); Cm (277:508)
1: TOF MS ES+
1.69e+007
100
%
0
219.1065
545.1526
445.1311
312.2851
473.0993
443.1139
561.1485
601.1381
353.0730
383.1174
220.1086
279.0169
313.2866
478.1227
543.2069
562.1494
602.1387
659.1544
701.2444
740.3277
777.1731
828.3838
872.4065
911.2949
960.4572
981.3911
106.0157
120.0792
131.9897
203.0745
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
m/z
For Help, press F1
1:09 PM
11/30/2023
F
F
O
OH
F
F
F

3ad

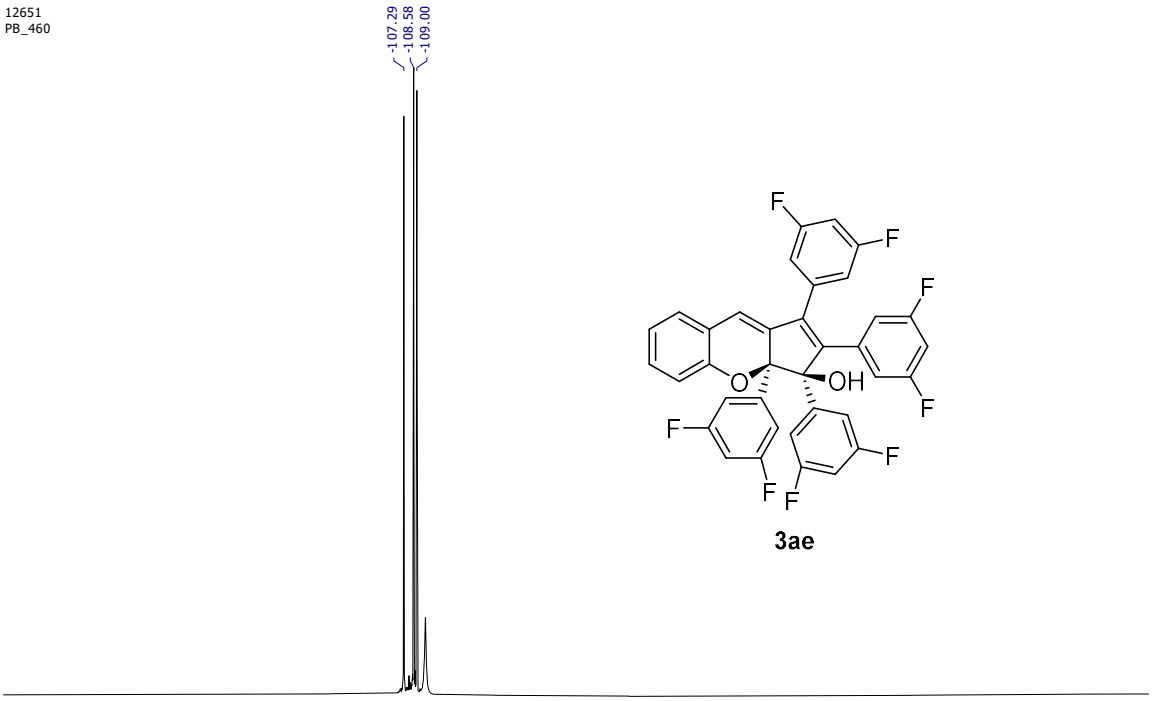


3ae

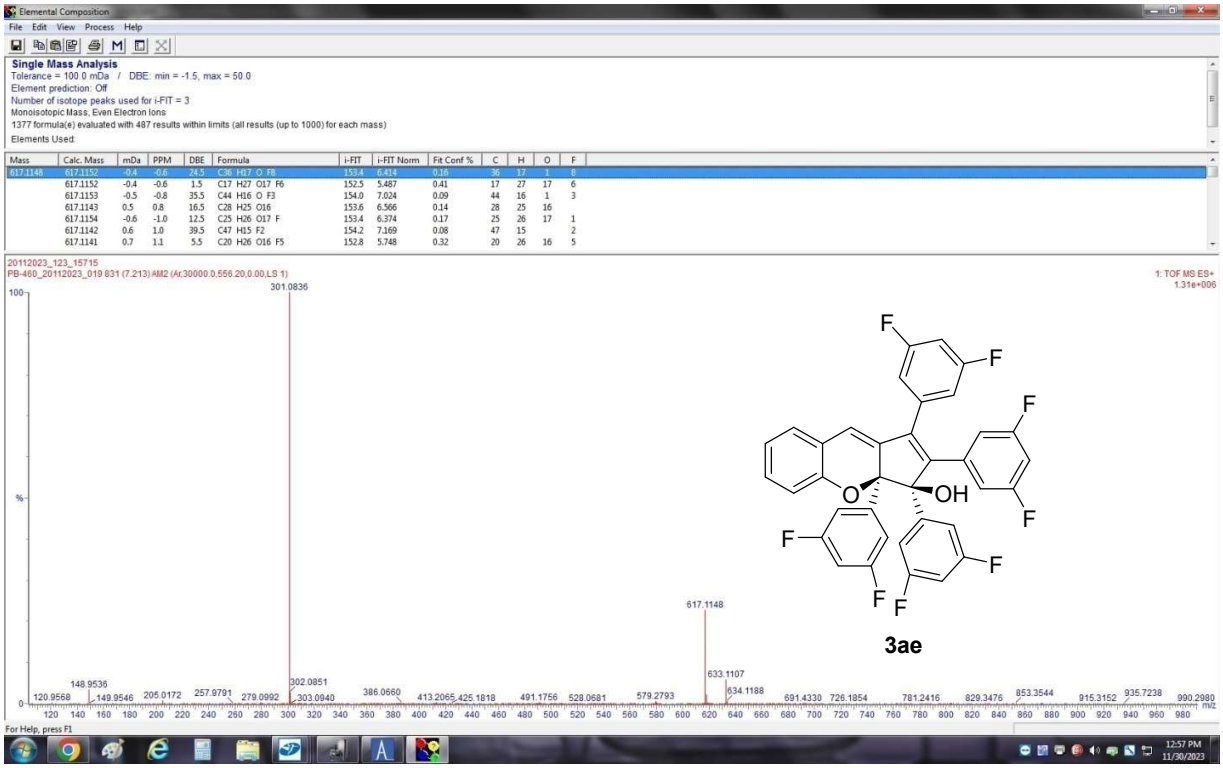


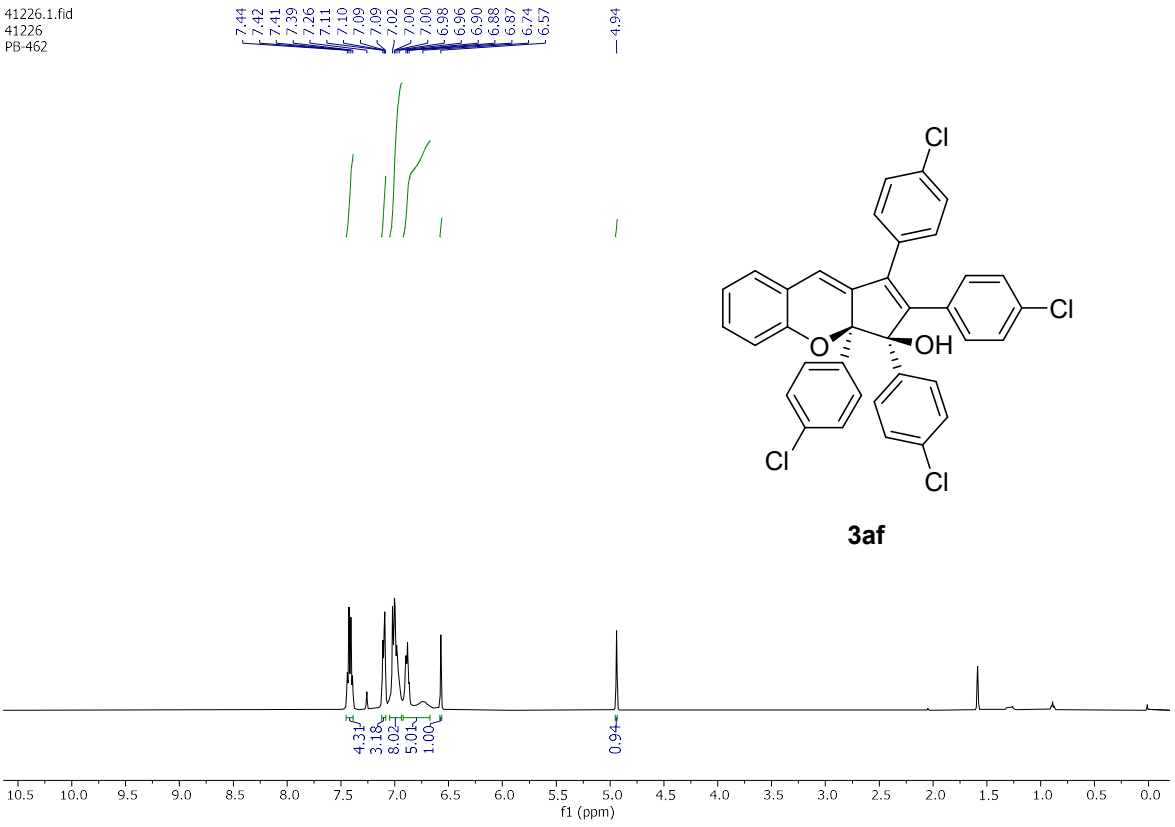
3ae

12651
PB_460

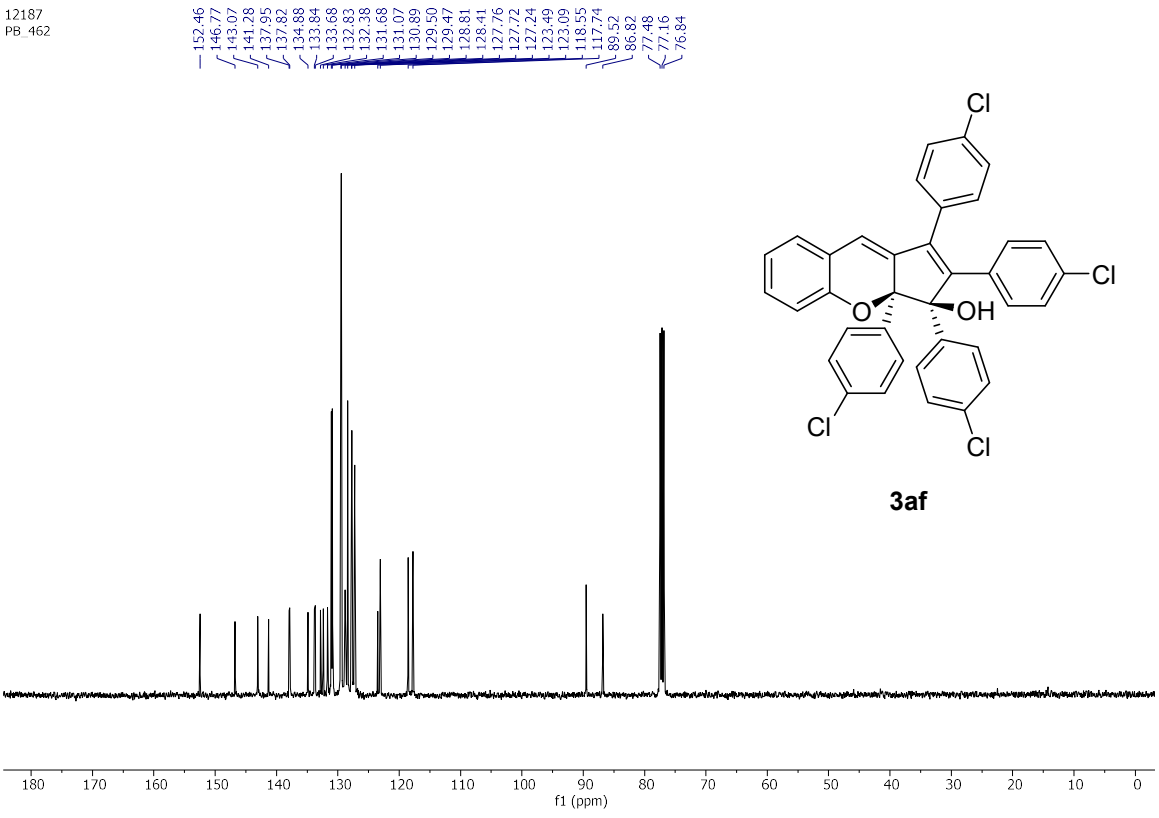


3ae

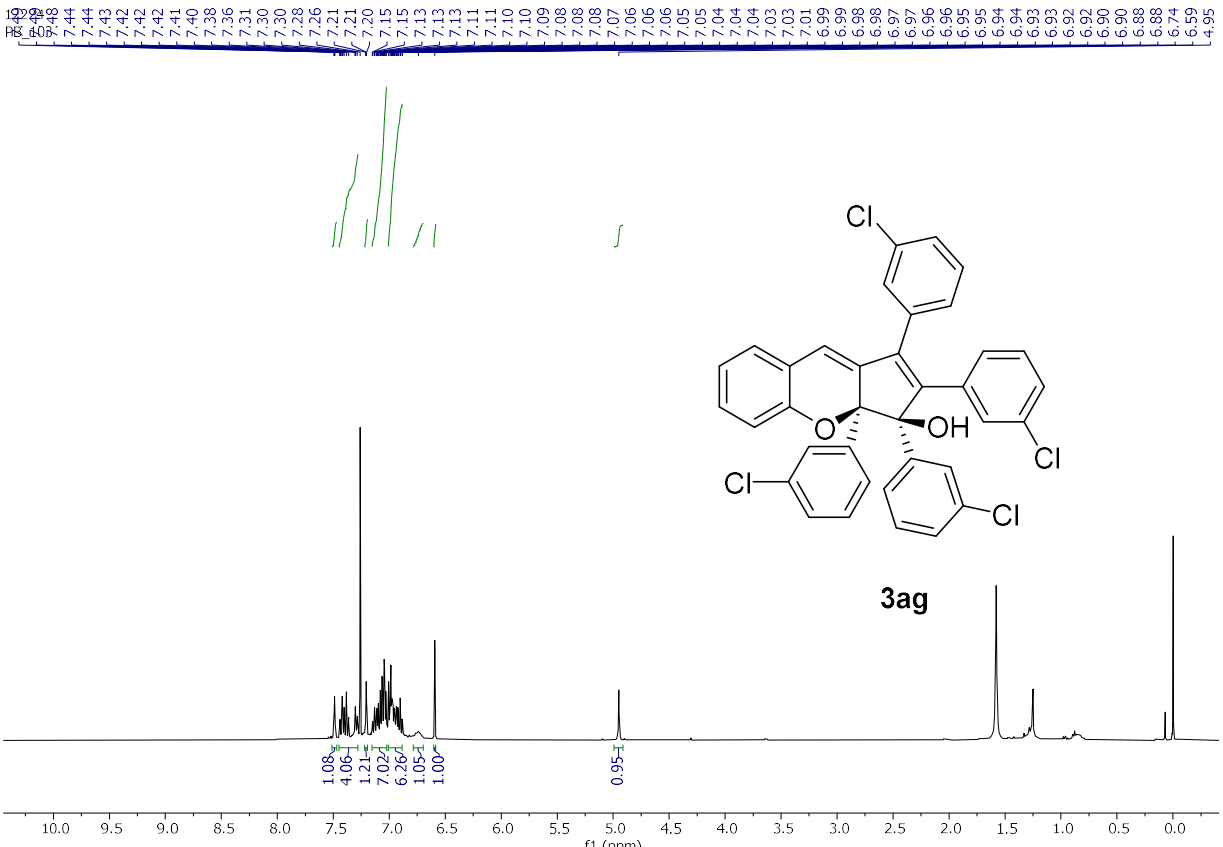


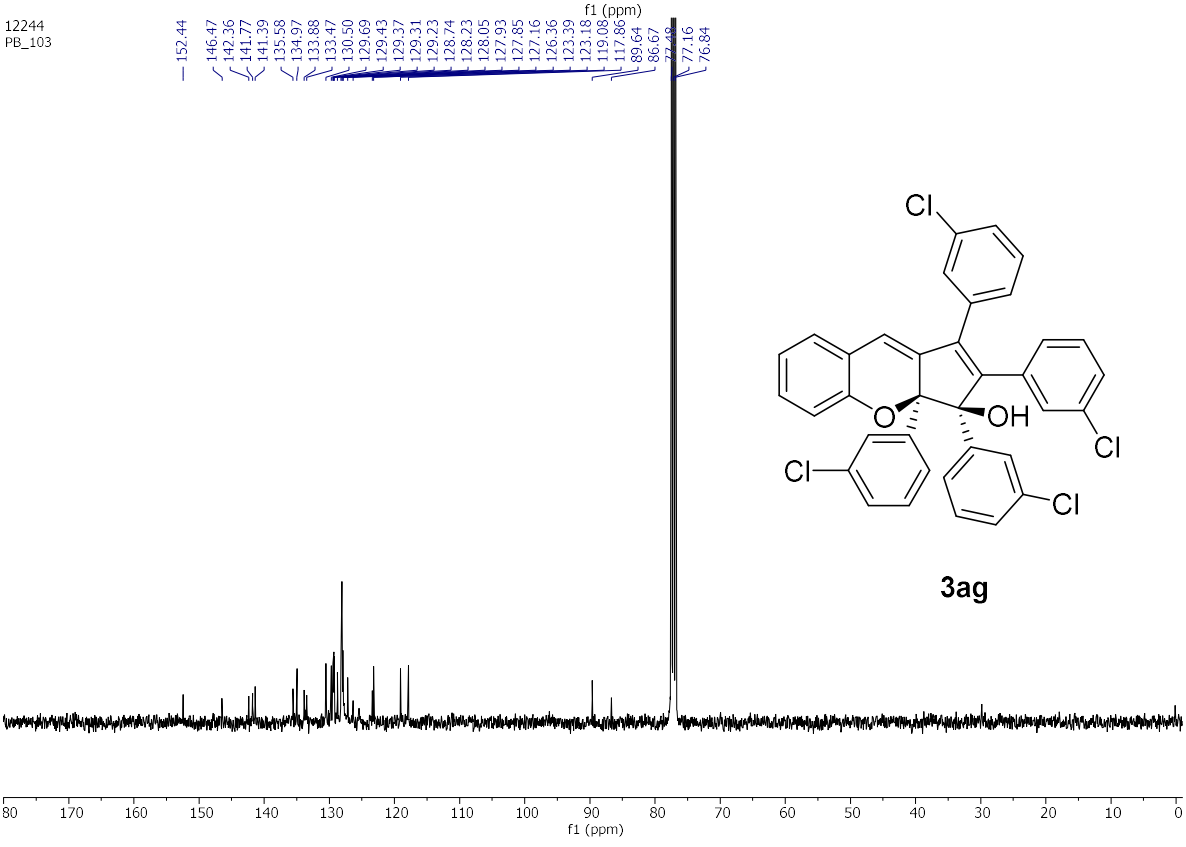

41226.1.fid
41226
PB-462
7.44
7.42
7.41
7.39
7.26
7.11
7.10
7.09
7.09
7.02
7.00
7.00
6.98
6.96
6.90
6.88
6.87
6.74
6.57
4.94
Cl
Cl
O
OH
Cl
Cl
4.31
3.18
8.02
5.01
1.00
0.94
f1 (ppm)

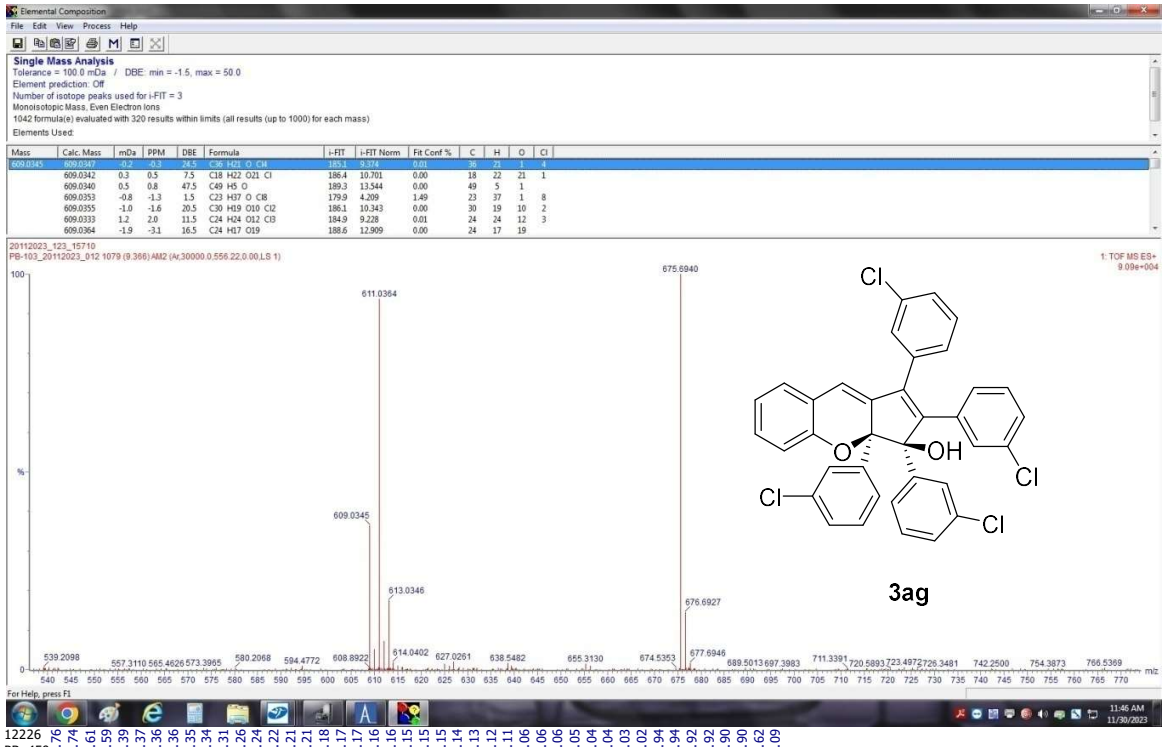
3af

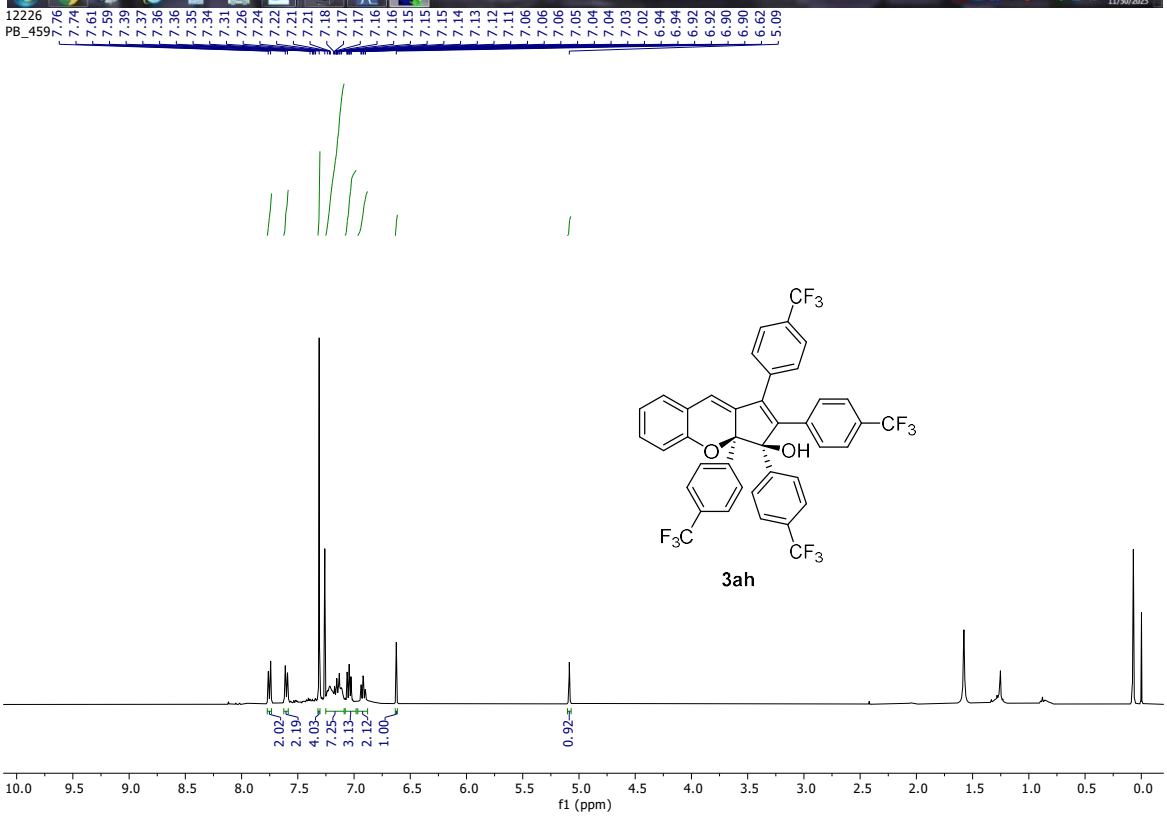

12187
PB_462
152.46
146.77
143.07
141.28
137.95
137.82
134.88
133.84
133.68
132.83
132.38
131.68
131.07
130.89
129.50
129.47
128.81
128.41
127.76
127.72
127.24
123.49
123.09
118.55
117.74
89.52
86.82
77.48
77.16
76.84
Cl
Cl
O
OH
Cl
Cl
f1 (ppm)

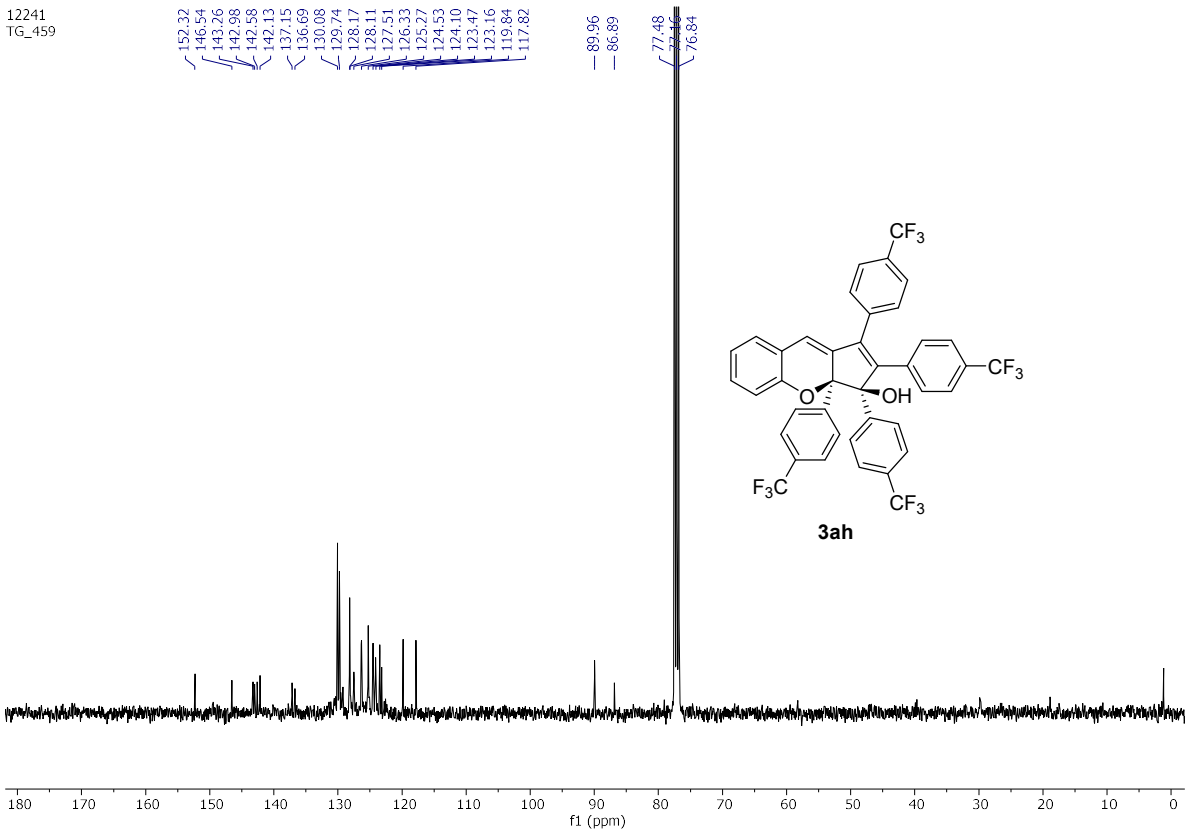
3af

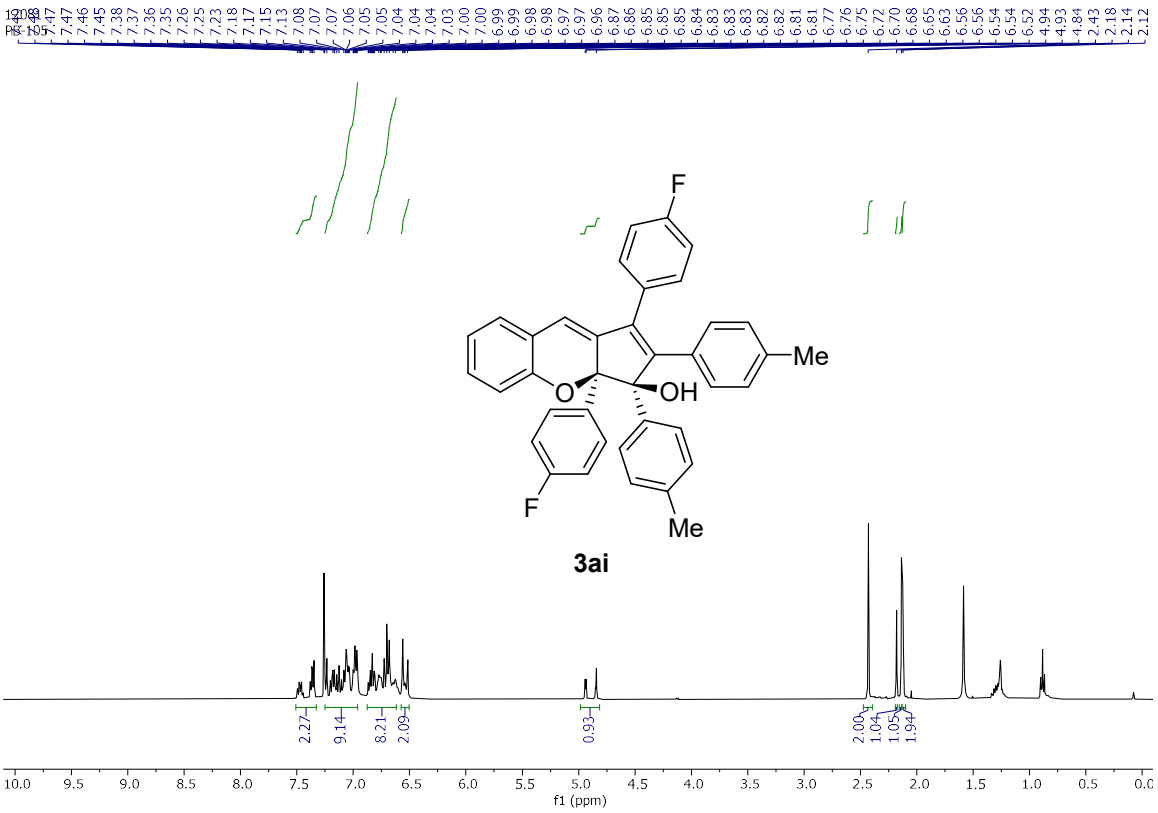

Cl
O
OH
Cl
Cl
Cl
3ag
f1 (ppm)

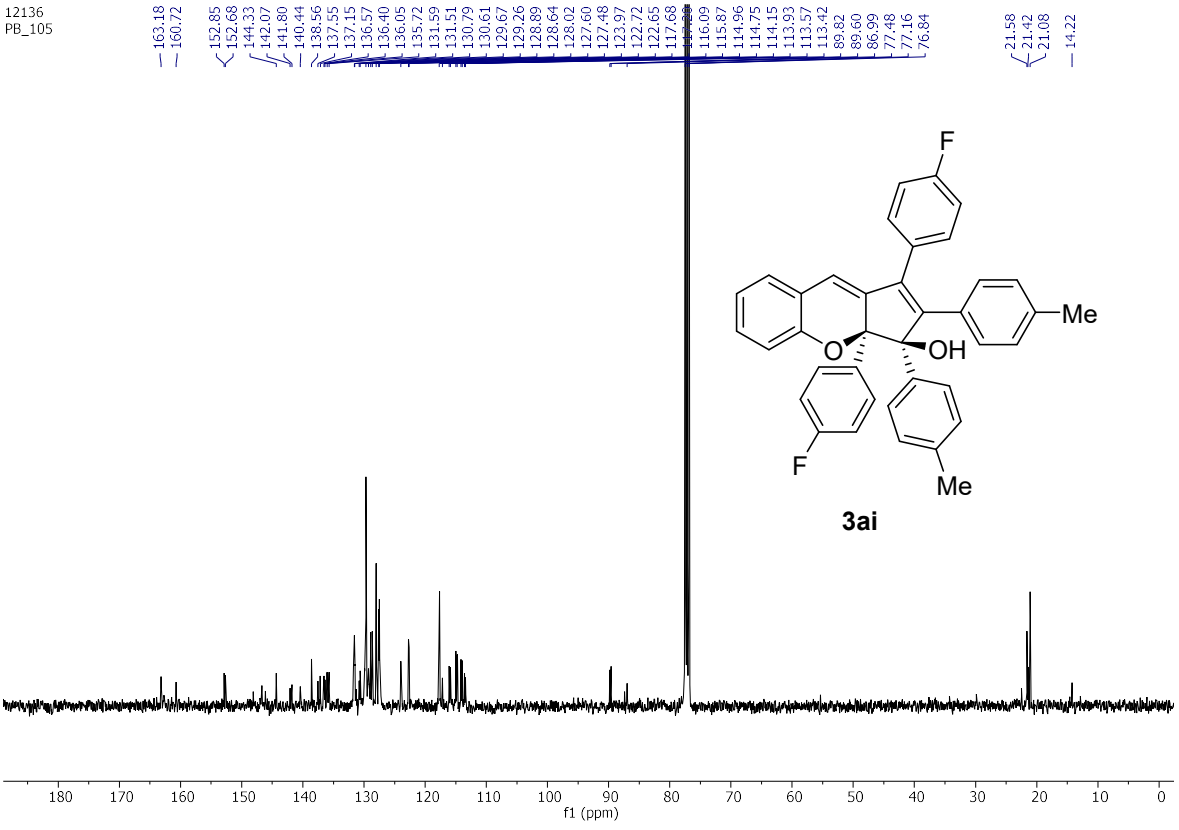

12244
PB_103
Cl
O
OH
Cl
Cl
Cl
3ag
f1 (ppm)


Elemental Composition
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
1042 formula(e) evaluated with 320 results within limits (all results (up to 1000) for each mass)
Elements Used:
609.0345
611.0364
675.6940
613.0346
676.6927
Cl
OH
O
3ag

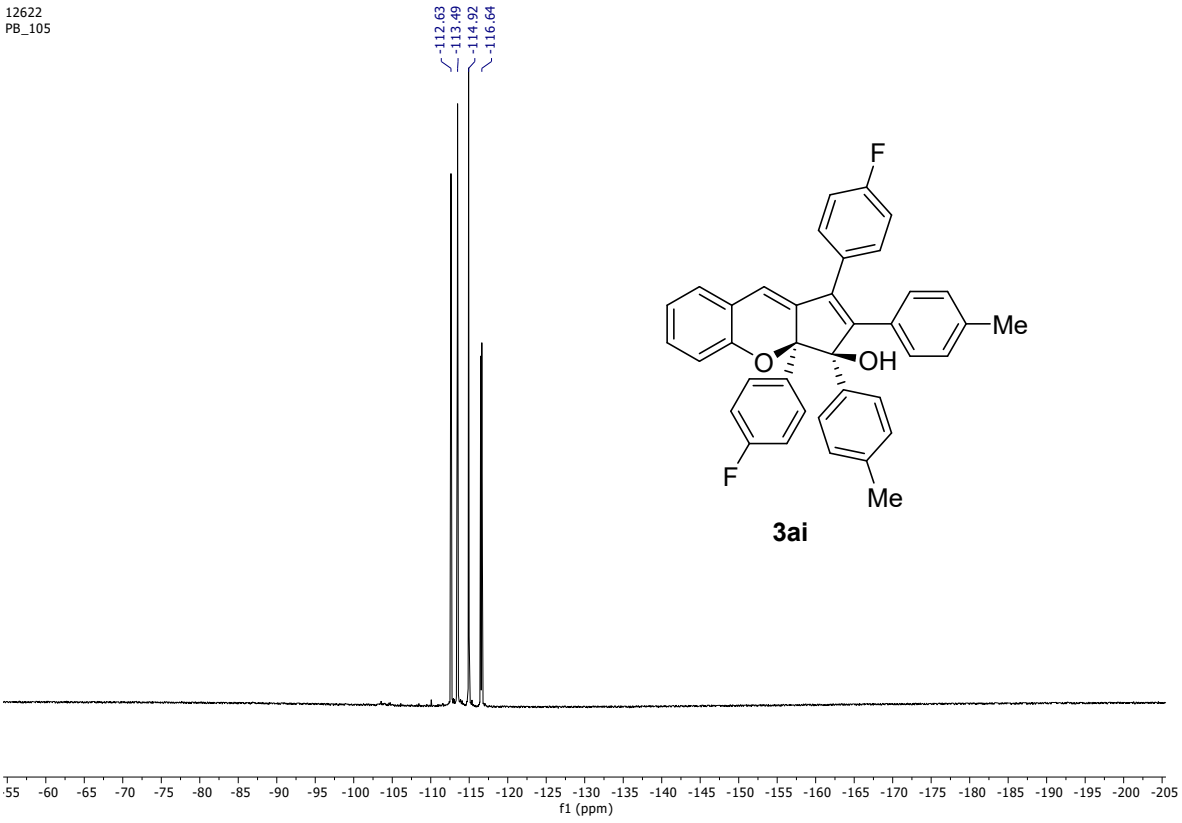

12226
PB_459
CF3
OH
O
F3C
3ah
2.02
2.19
4.03
7.25
3.13
2.12
1.00
0.92
f1 (ppm)


12241
TG_459
152.32
146.54
143.26
142.98
142.58
142.13
137.15
136.69
130.08
129.74
128.17
128.11
127.51
126.33
125.27
124.53
124.10
123.47
123.16
119.84
117.82
89.96
86.89
77.48
76.84
CF3
CF3
O
OH
F3C
CF3
3ah
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

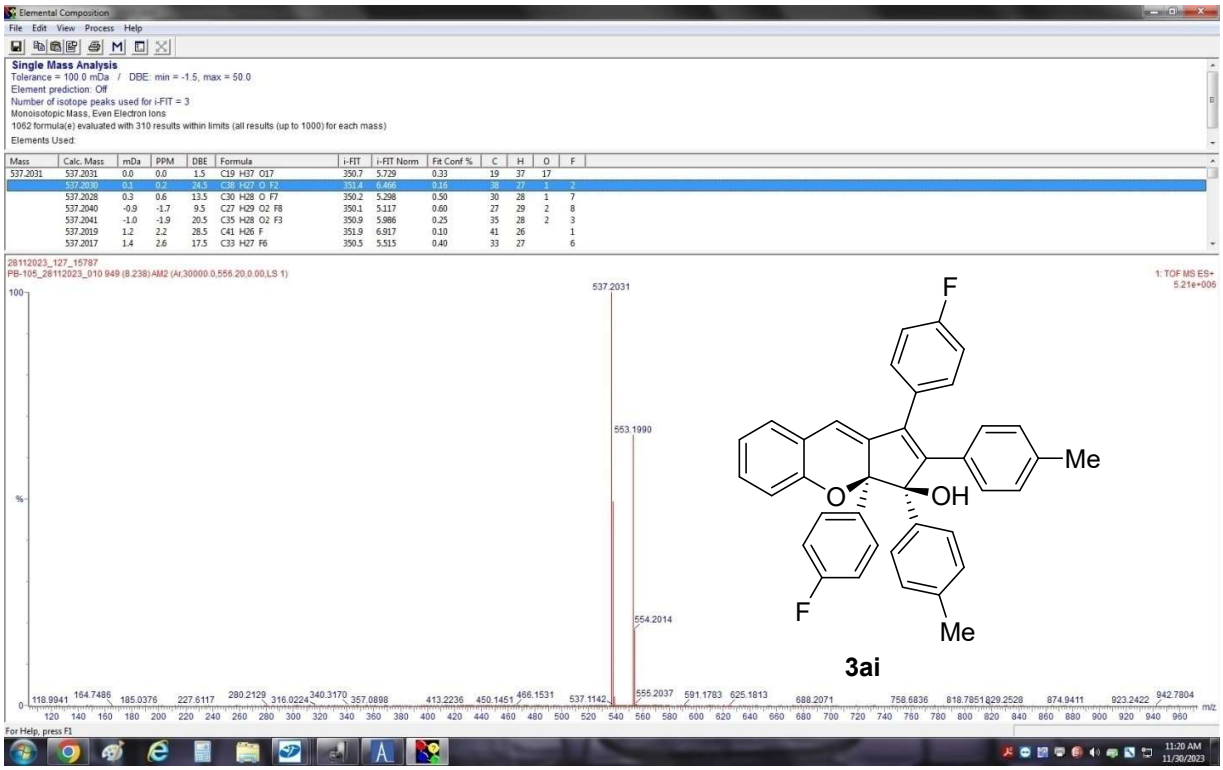

F
Me
O
OH
F
Me
3ai
2.27
9.14
8.21
2.09
0.93
2.00
1.04
1.05
1.94
f1 (ppm)


12136
PB_105
F
Me
O
OH
F
Me
3ai
f1 (ppm)

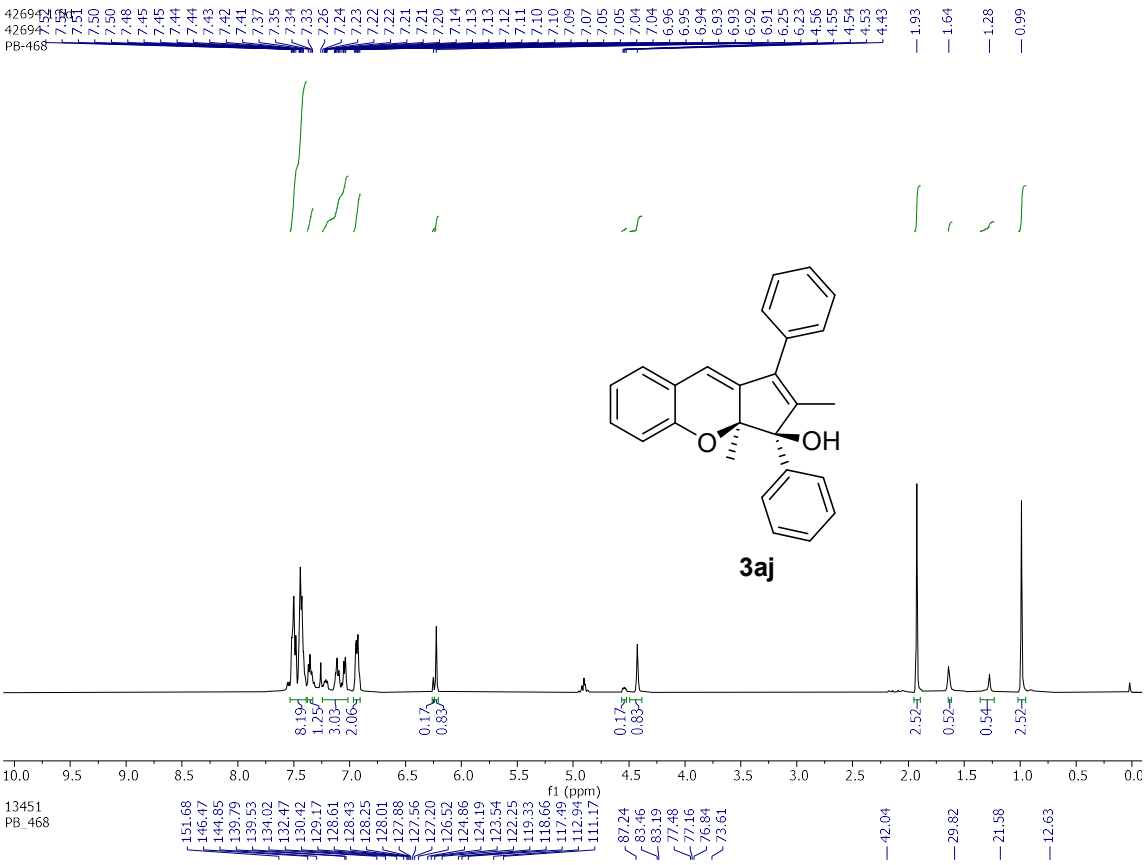
12622
PB_105

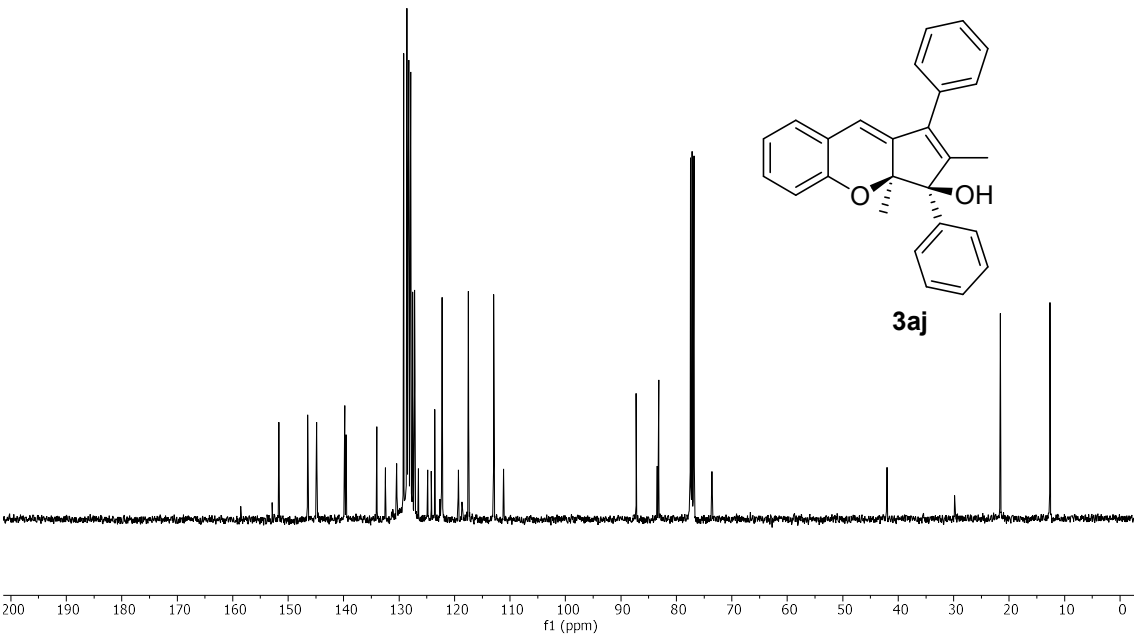


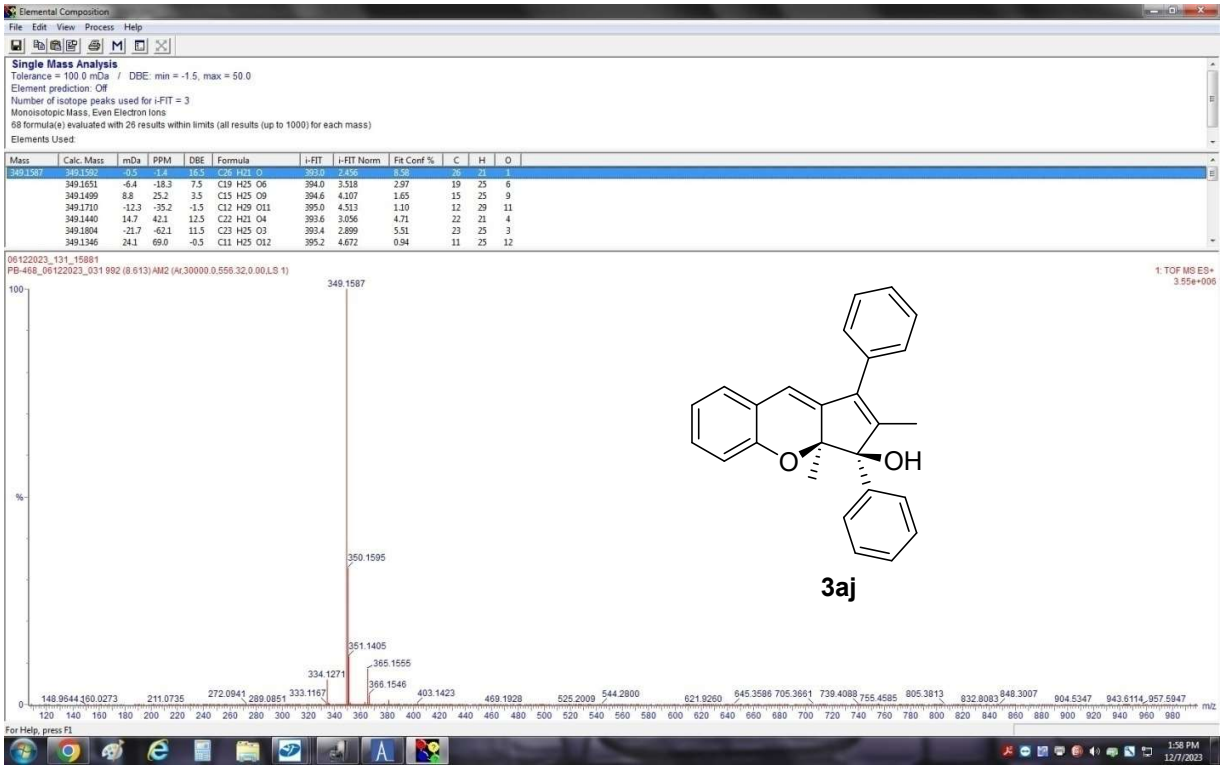
3ai

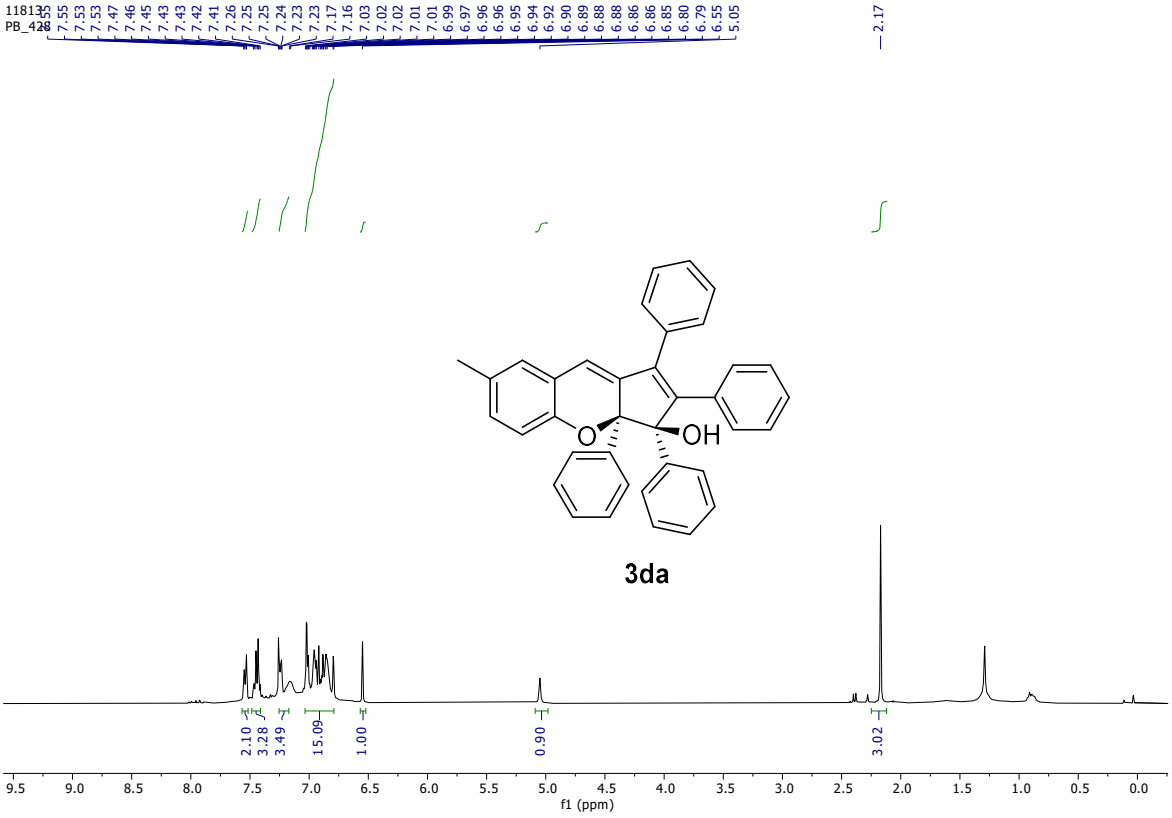


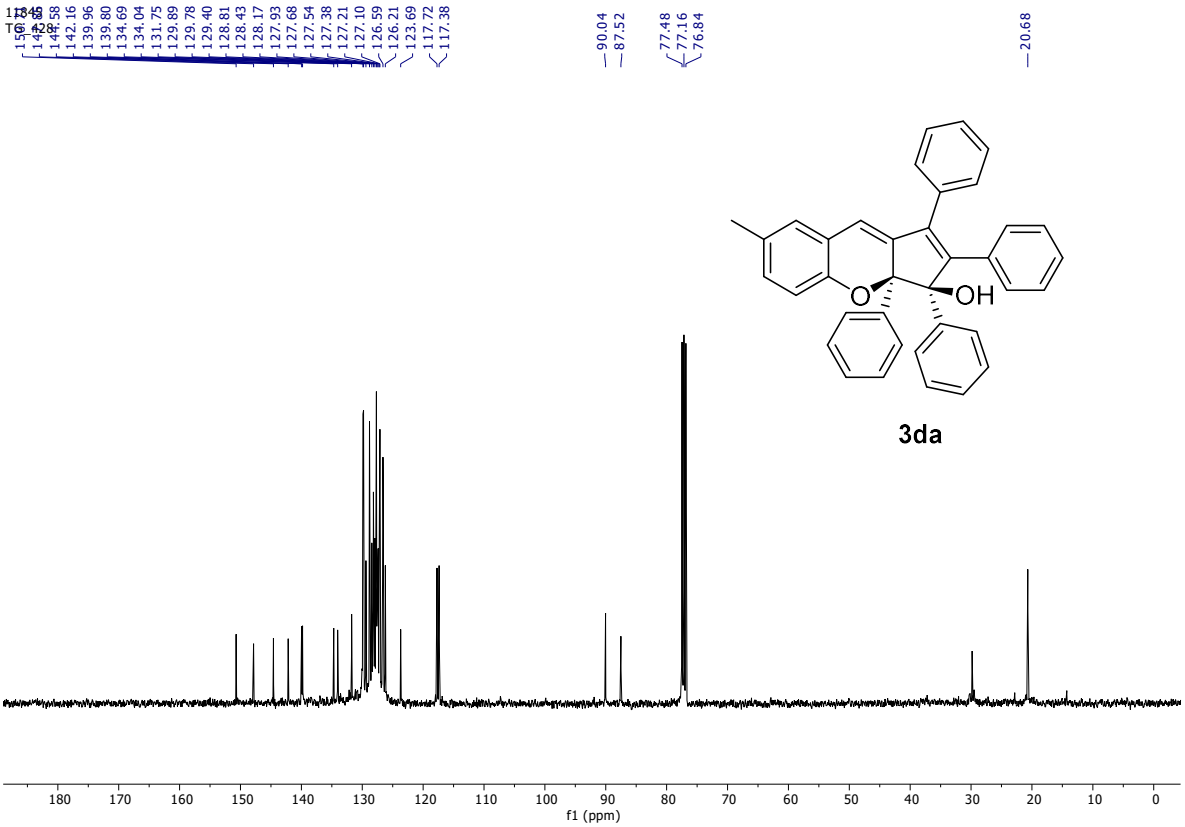
3ai

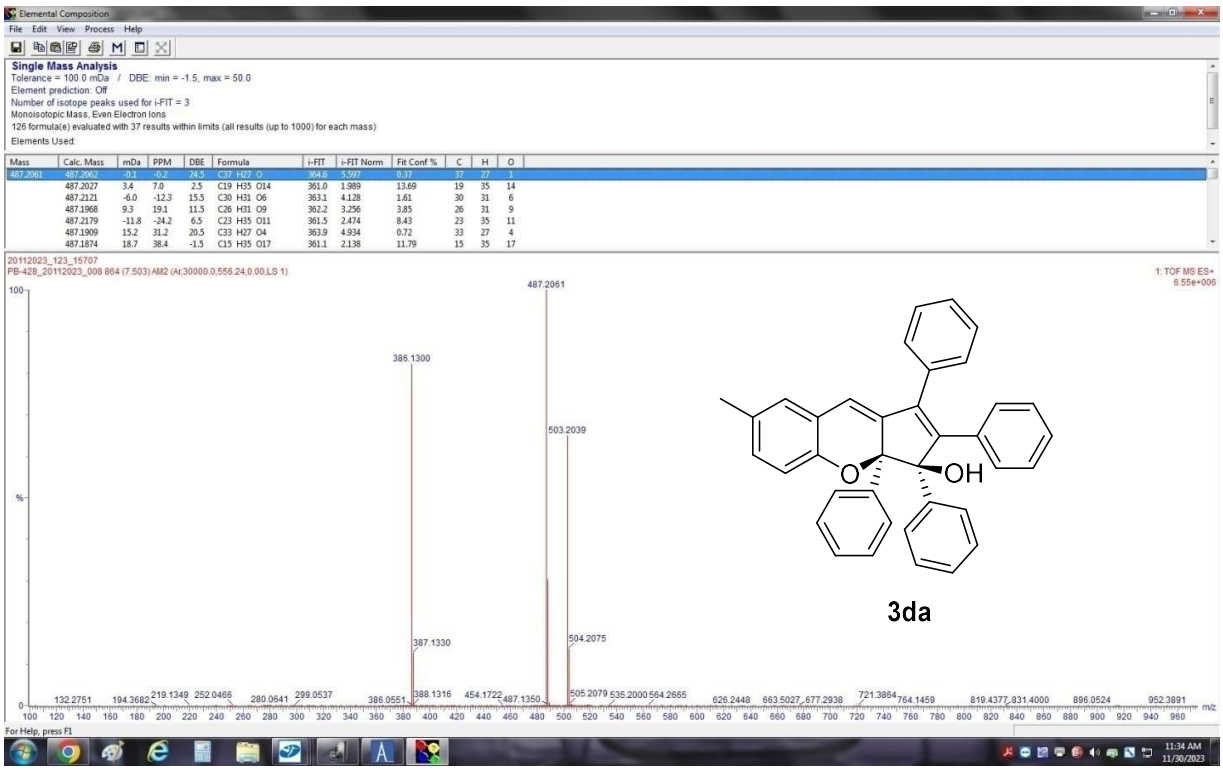

OH
3aj
f1 (ppm)

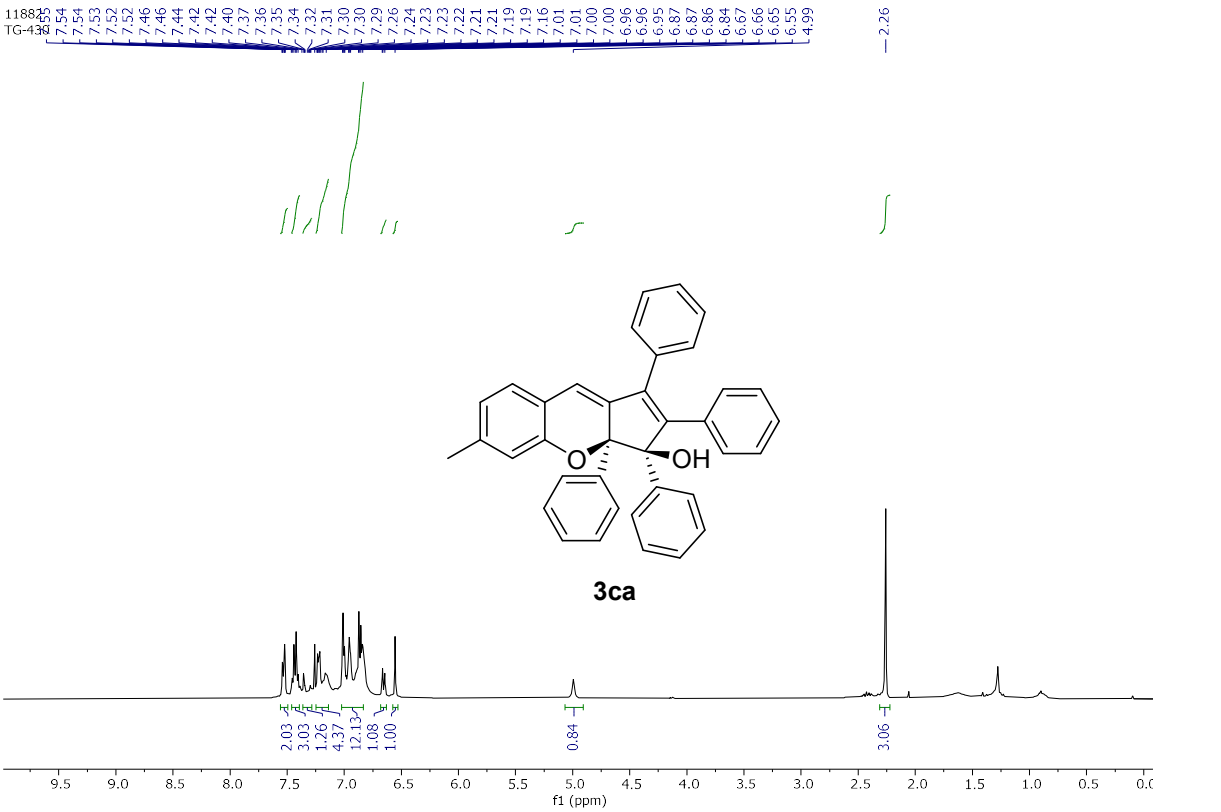

OH
3aj
f1 (ppm)

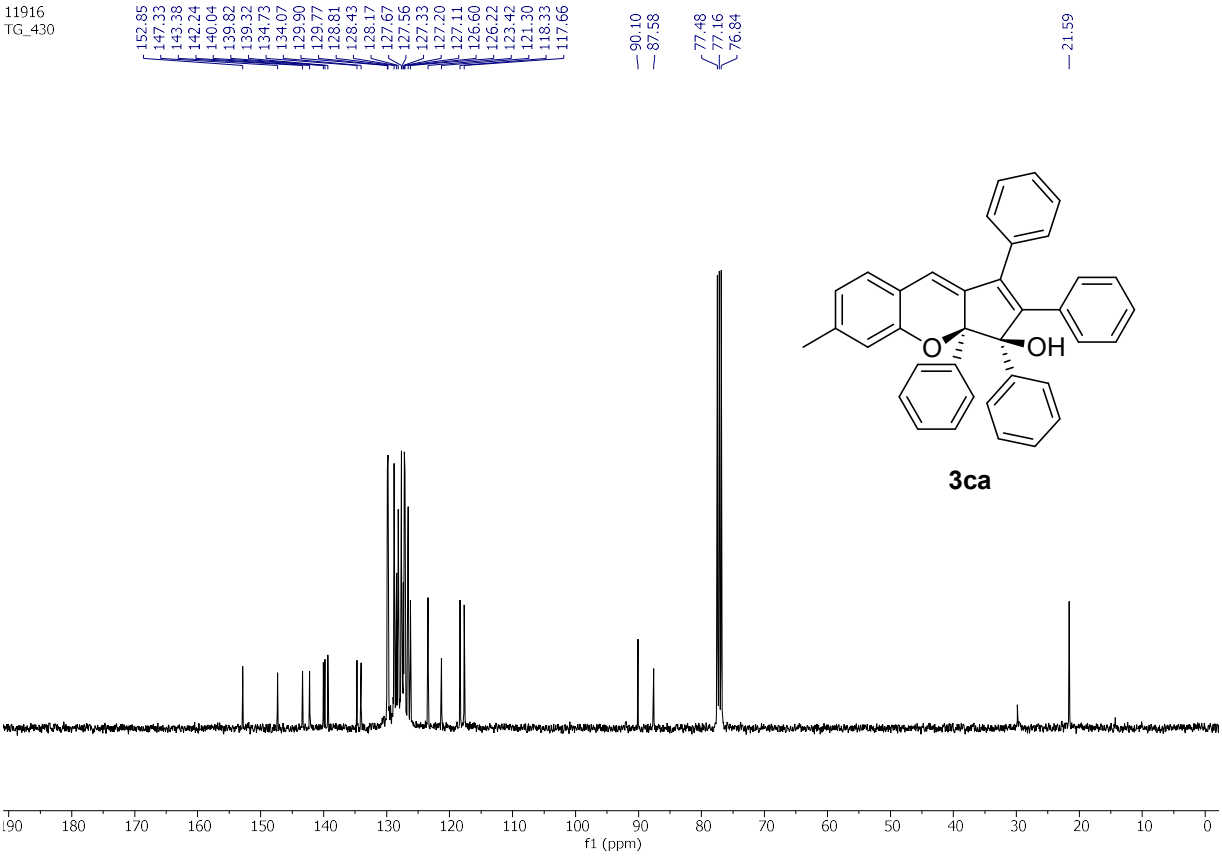

Elemental Composition
Single Mass Analysis
Tolerance = 100.0 mDa / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3
Monoisotopic Mass, Even Electron Ions
68 formula(e) evaluated with 26 results within limits (all results (up to 1000) for each mass)
Elements Used:
Mass Calc. Mass mDa PPM DBE Formula i-FIT i-FIT Norm Fit Conf % C H O
349.1587 349.1592 -0.5 -1.4 16.5 C26 H21 O 393.0 2.456 8.58 26 21 1
349.1651 -6.4 -18.3 7.5 C19 H25 O6 394.0 3.518 2.97 19 25 6
349.1499 8.8 25.2 3.5 C15 H25 O9 394.6 4.107 1.65 15 25 9
349.1710 -12.3 -35.2 -1.5 C12 H29 O11 395.0 4.513 1.10 12 29 11
349.1440 14.7 42.1 12.5 C22 H21 O4 393.6 3.056 4.71 22 21 4
349.1804 -21.7 -62.1 11.5 C23 H25 O3 393.4 2.899 5.51 23 25 3
349.1346 24.1 69.0 -0.5 C11 H25 O12 395.2 4.672 0.94 11 25 12
06122023_131_15881
PB-468_06122023_031 992 (8.613) AM2 (Ar,30000.0,556.32,0.00,LS 1)
1: TOF MS ES+
3.55e+006
349.1587
350.1595
351.1405
365.1555
366.1546
334.1271
OH
3aj

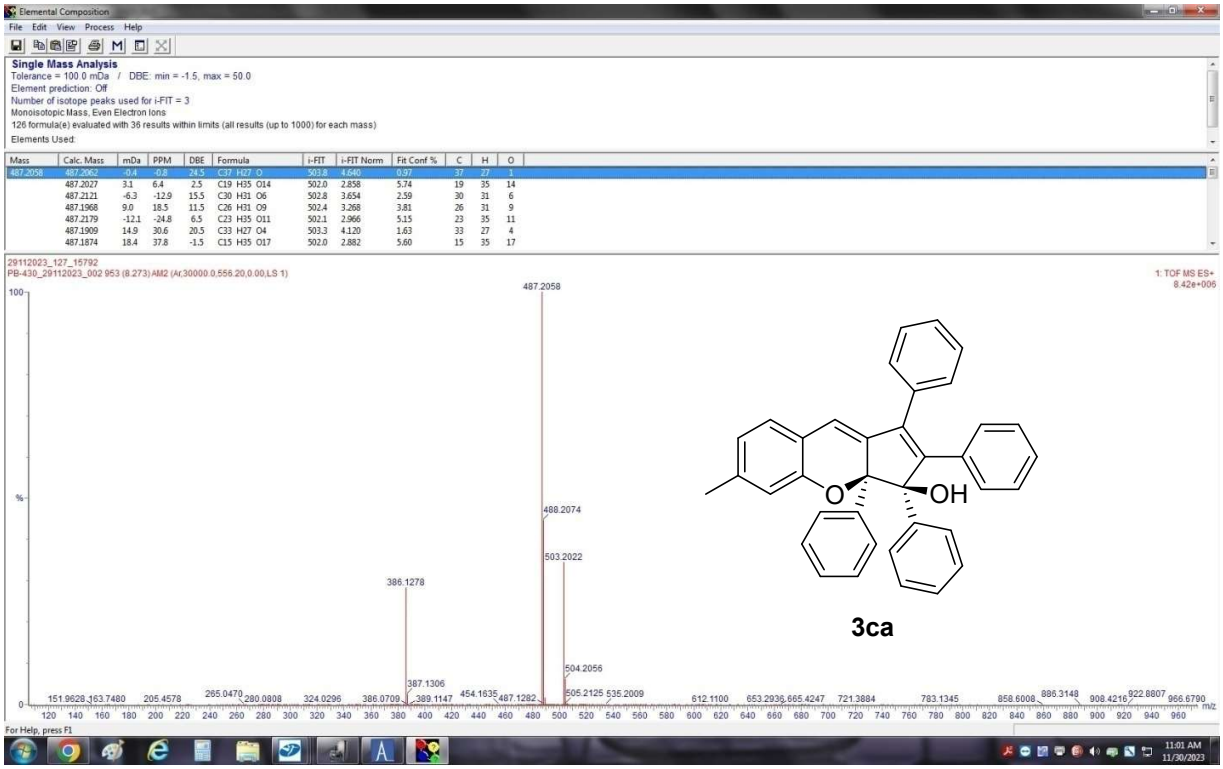

11813
PB_428
OH
3da
2.10
3.28
3.49
15.09
1.00
0.90
3.02
f1 (ppm)

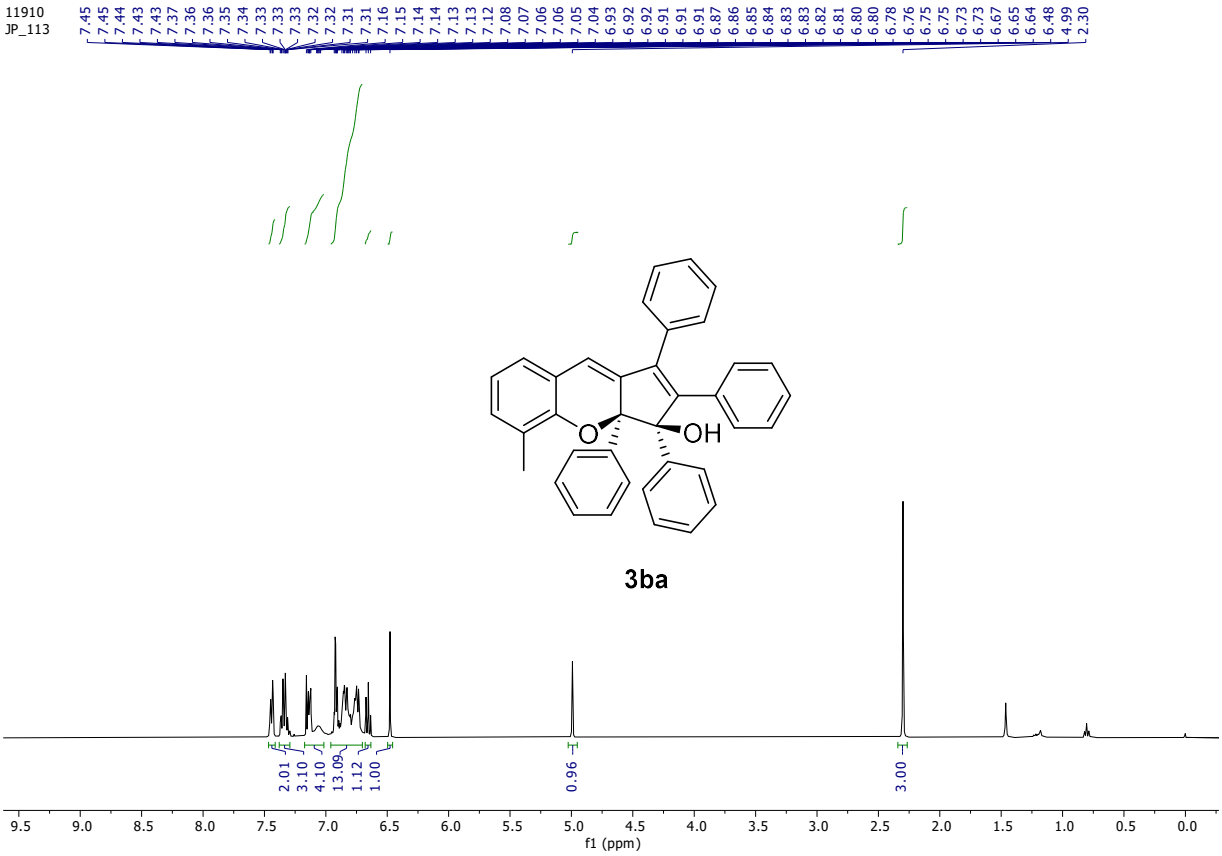

150.45
147.38
144.38
142.16
139.96
139.80
134.69
134.04
131.75
129.89
129.78
129.40
128.81
128.43
128.17
127.93
127.68
127.54
127.38
127.21
127.10
126.59
126.21
123.69
117.72
117.38
90.04
87.52
77.48
77.16
76.84
20.68
O
OH
3da
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


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
126 formula(e) evaluated with 37 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 O
487.2061 487.2062 -0.1 -0.2 14.5 C31 H27 O 364.6 1.507 0.01 31 27 1
487.2027 3.4 7.0 2.5 C19 H35 O14 361.0 1.989 13.69 19 35 14
487.2121 -6.0 -12.3 15.5 C30 H31 O6 363.1 4.128 1.61 30 31 6
487.1968 9.3 19.1 11.5 C26 H31 O9 362.2 3.256 3.85 26 31 9
487.2179 -11.8 -24.2 6.5 C23 H35 O11 361.5 2.474 8.43 23 35 11
487.1909 15.2 31.2 20.5 C33 H27 O4 363.9 4.934 0.72 33 27 4
487.1874 18.7 38.4 -1.5 C15 H35 O17 361.1 2.138 11.79 15 35 17
20112023_123_15707
PB-428_20112023_008 864 (7.503) AM2 (Ar,30000.0,556.24,0.00,LS 1)
1: TOF MS ES+
6.55e+006
100
%
0
487.2061
386.1300
503.2039
387.1330
504.2075
132.2751 194.3682 219.1349 252.0466 280.0641 299.0537 386.0551 388.1316 454.1722 487.1350 505.2079 535.2000 564.2665 626.2448 663.5027 677.2938 721.3864 764.1459 819.4377 831.4000 896.0524 952.3891
m/z
O
OH
3da
For Help, press F1
11:34 AM
11/30/2023


11882
TG-430
7.55
7.54
7.54
7.53
7.52
7.52
7.46
7.46
7.44
7.42
7.42
7.40
7.37
7.36
7.35
7.34
7.32
7.31
7.30
7.30
7.29
7.26
7.24
7.23
7.23
7.22
7.21
7.21
7.19
7.19
7.16
7.01
7.01
7.00
7.00
6.96
6.96
6.95
6.87
6.87
6.86
6.84
6.67
6.66
6.65
6.55
4.99
2.26
O
OH
3ca
2.03
3.03
1.26
4.37
12.13
1.08
1.00
0.84
3.06
f1 (ppm)

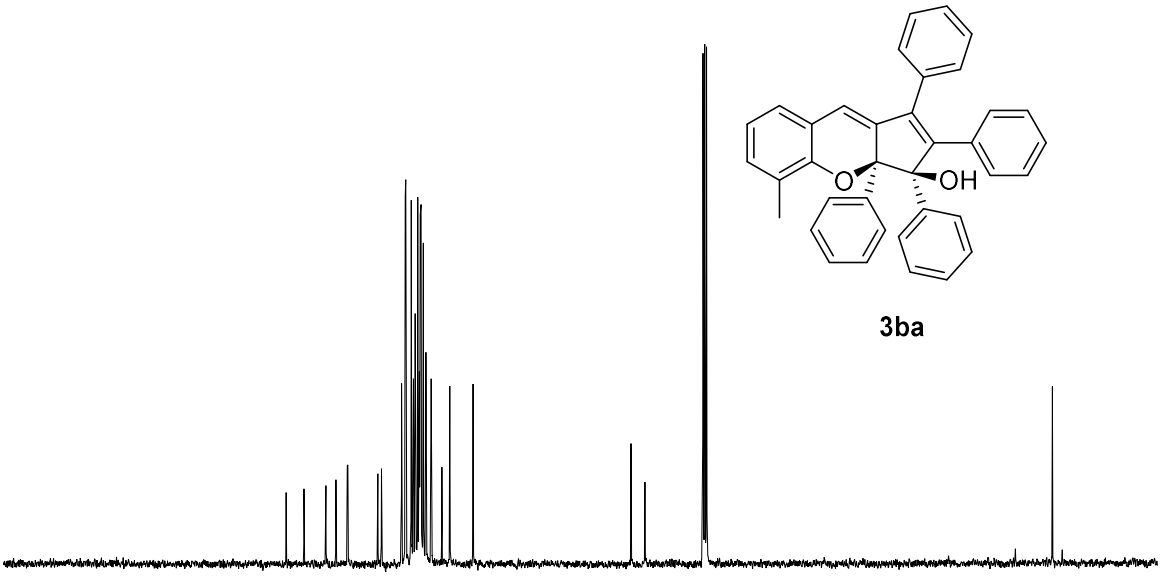

11916
TG_430
152.85
147.33
143.38
142.24
140.04
139.82
139.32
134.73
134.07
129.90
129.77
128.81
128.43
128.17
127.67
127.56
127.33
127.20
127.11
126.60
126.22
123.42
121.30
118.33
117.66
90.10
87.58
77.48
77.16
76.84
21.59
O
OH
3ca
f1 (ppm)


Elemental Composition
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
126 formula(e) evaluated with 36 results within limits (all results (up to 1000) for each mass)
Elements Used:
487.2058
488.2074
503.2022
386.1278
387.1306
504.2056
O
OH
3ca

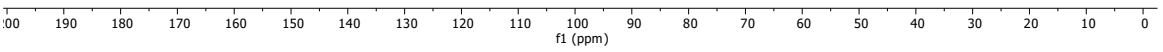

11910
JP_113
O
OH
3ba
2.01
3.10
4.10
13.09
1.12
1.00
0.96
3.00
f1 (ppm)

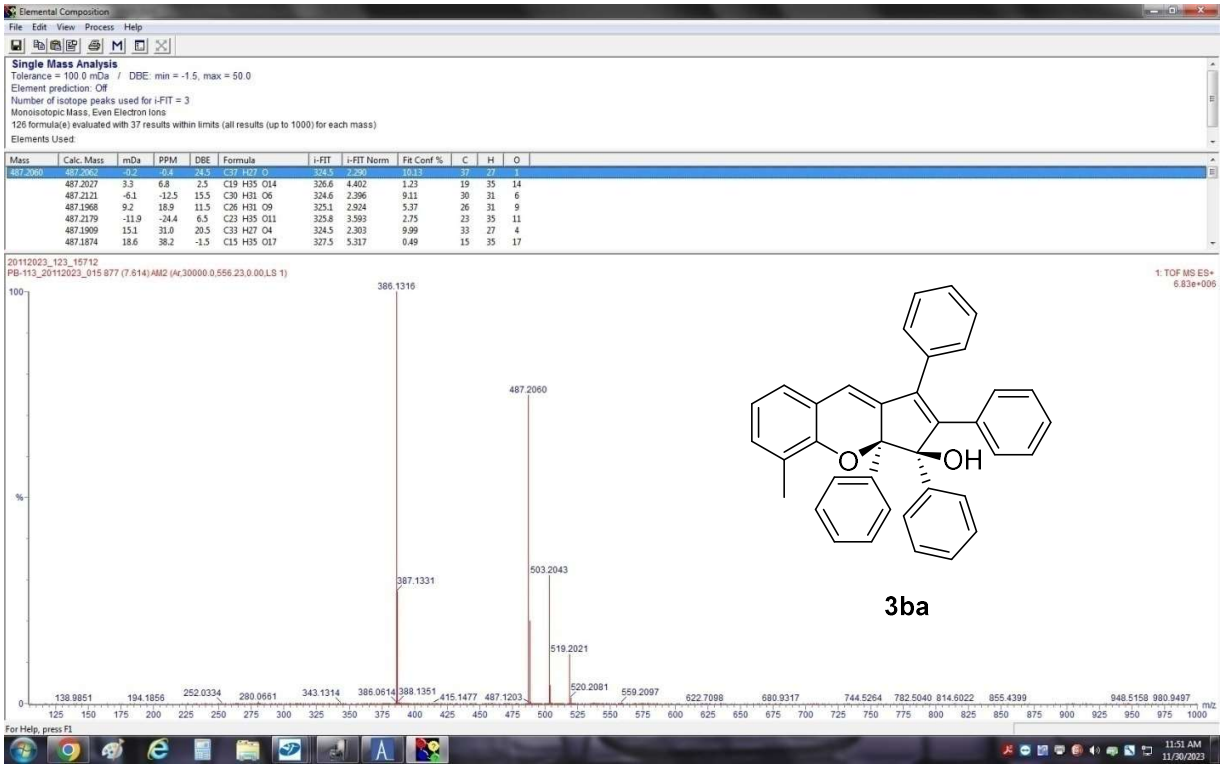
11892
PB_113

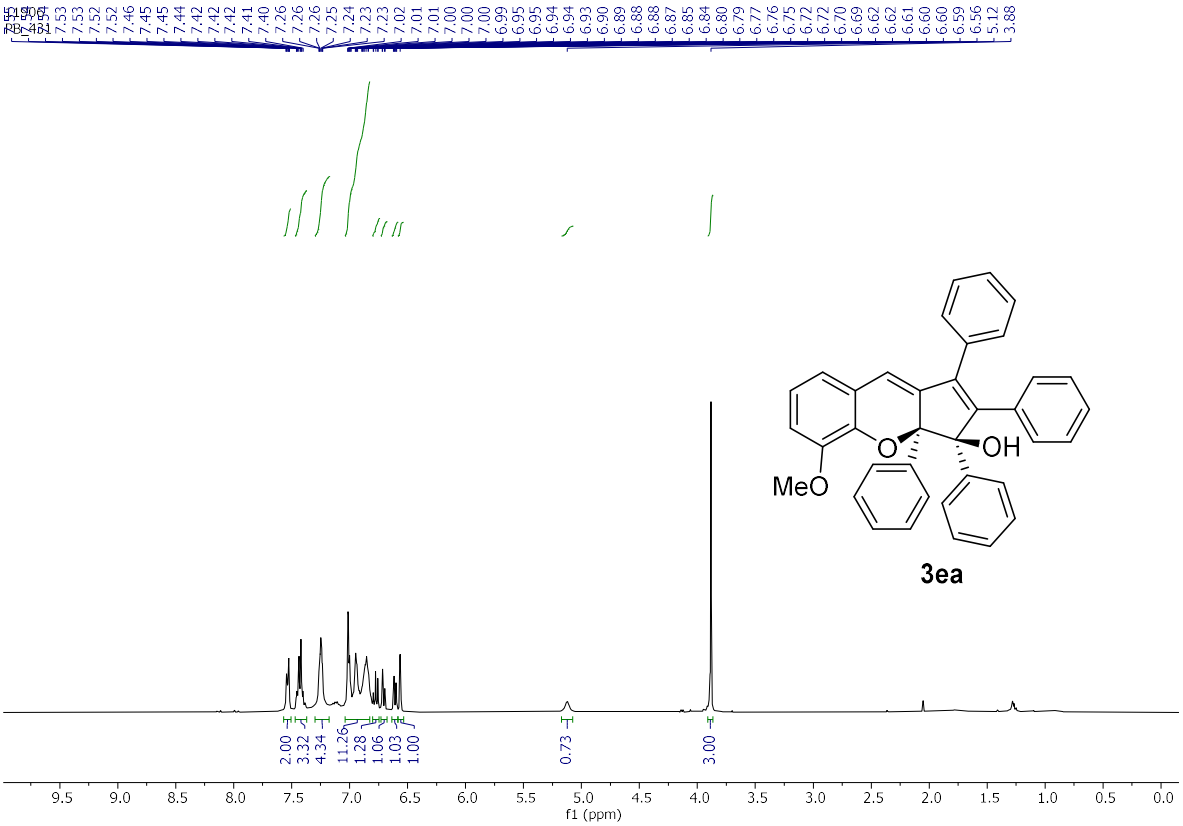
150.86
147.72
143.86
142.10
140.10
139.99
134.72
134.08
130.54
129.90
129.80
128.84
128.45
128.14
127.69
127.39
127.30
127.26
127.11
126.71
126.26
126.23
125.33
123.45
122.05
117.96
90.15
87.69
77.48
77.16
76.84
15.96

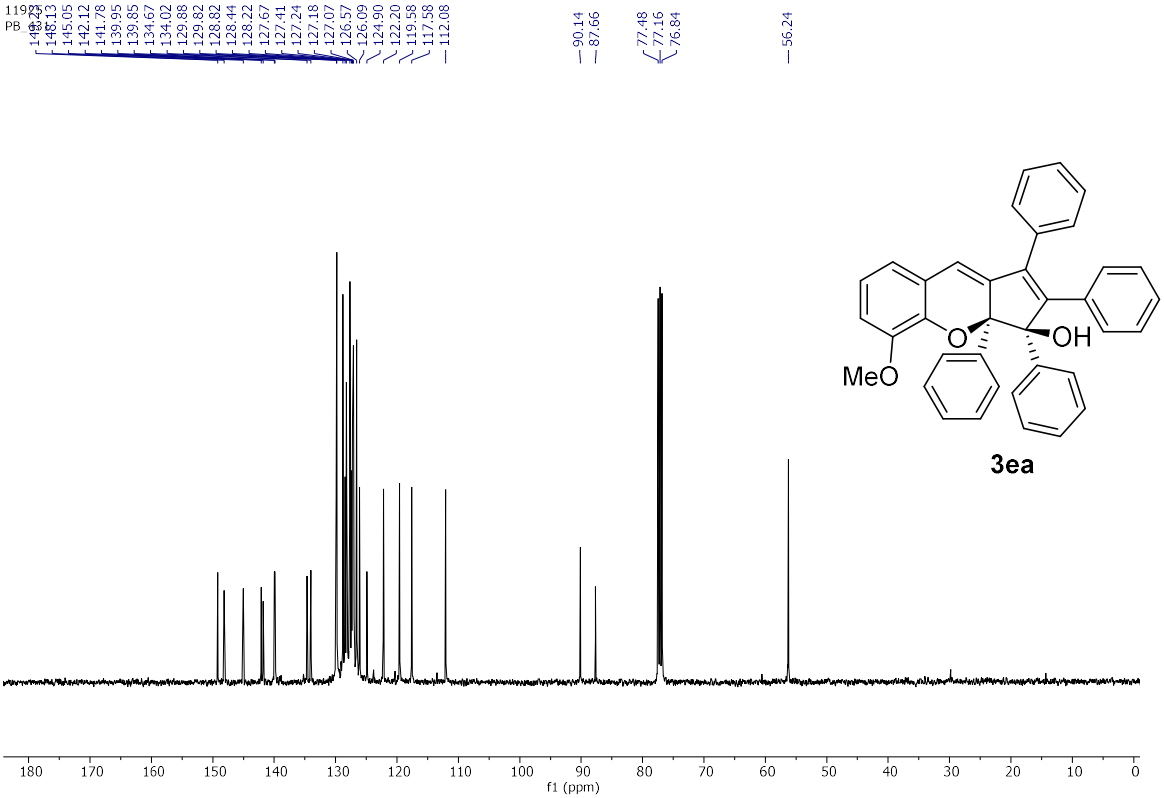


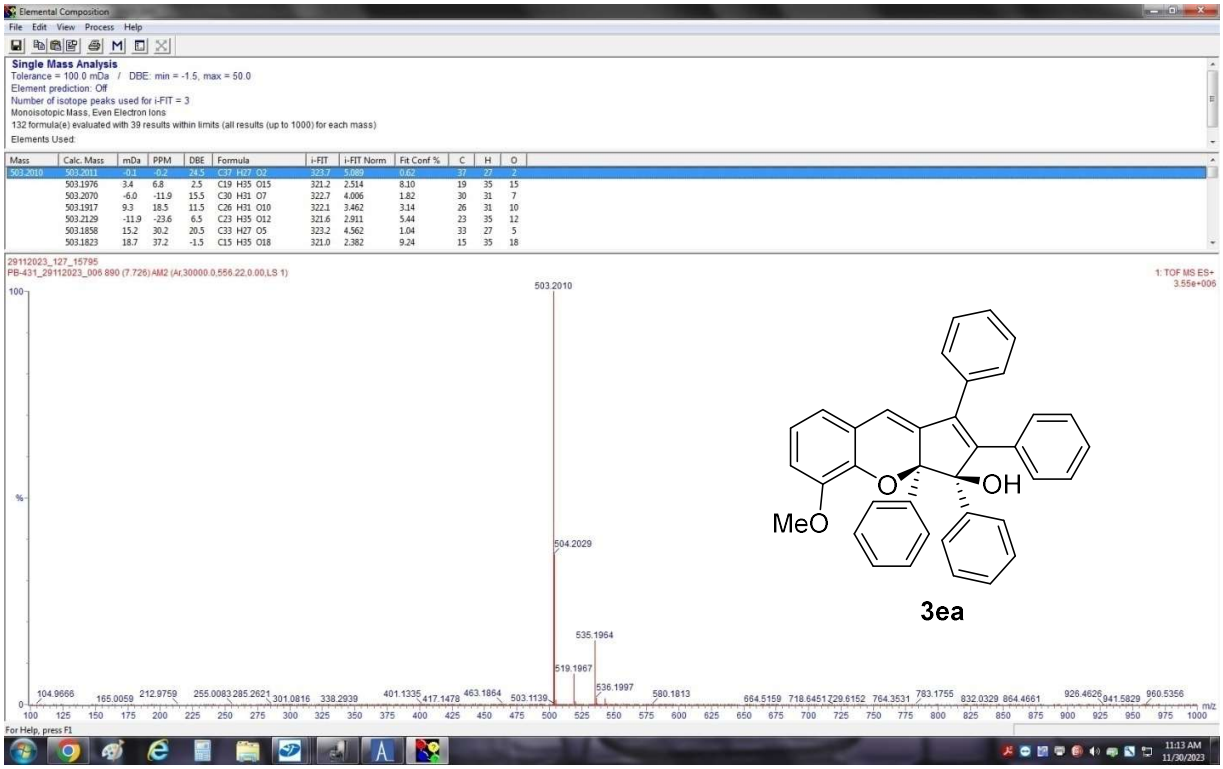
3ba

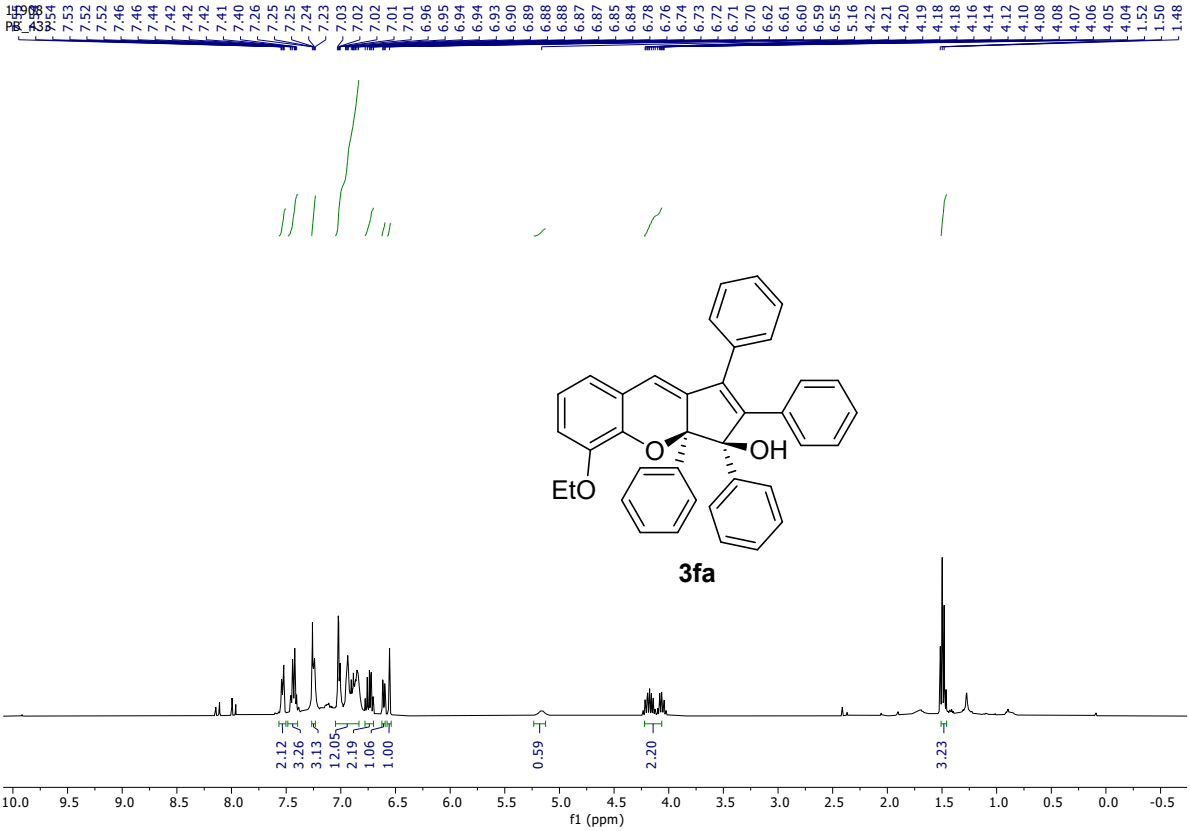


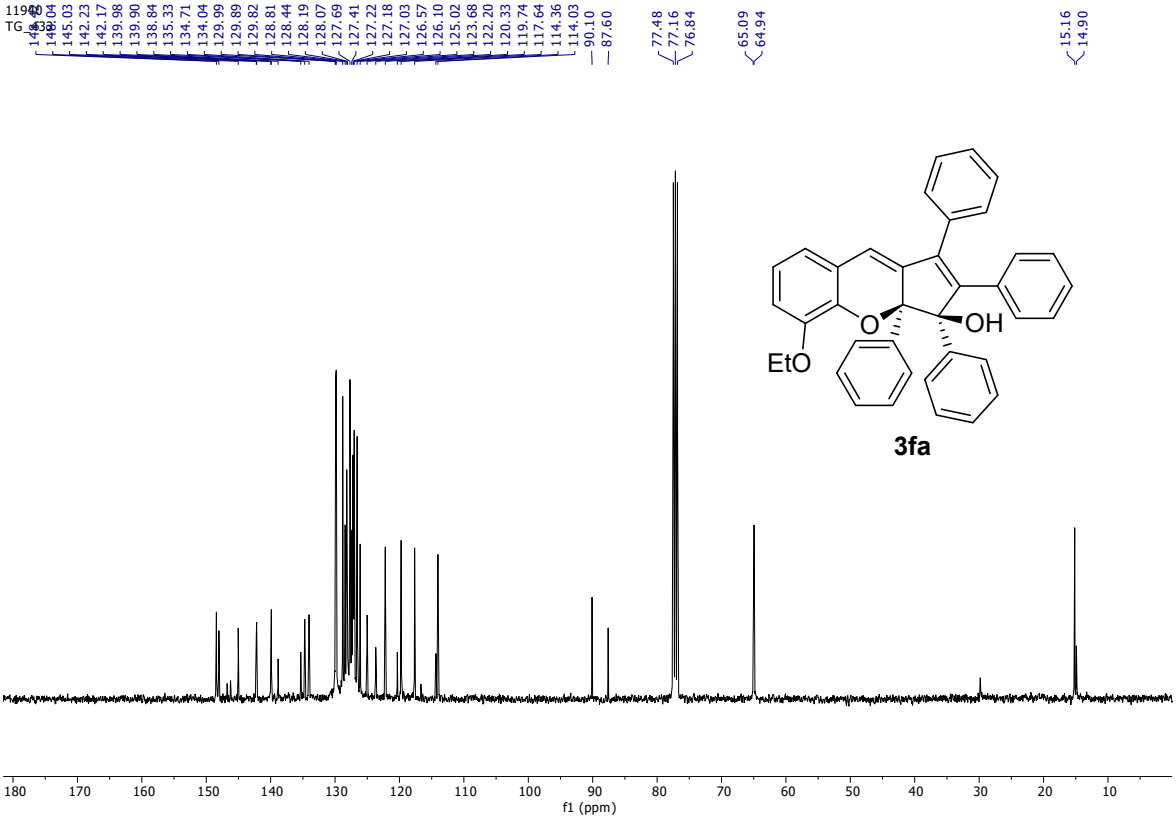


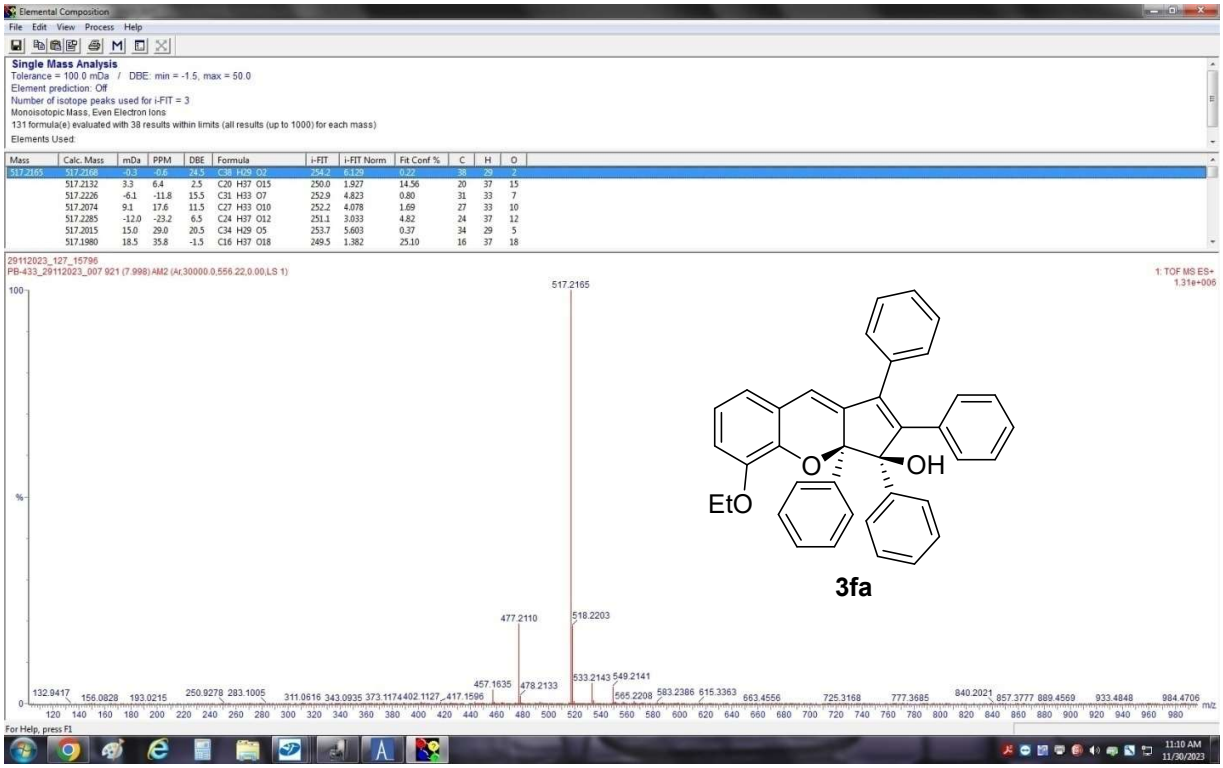

MeO
O
OH
3ea
2.00
3.32
4.34
11.26
1.28
1.06
1.03
1.00
0.73
3.00
f1 (ppm)


MeO
O
OH
3ea
f1 (ppm)

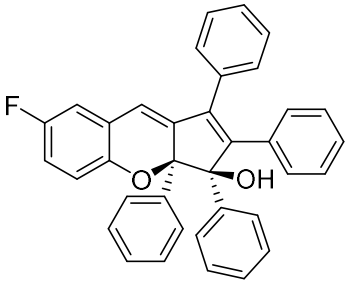

Elemental Composition
Single Mass Analysis
Tolerance = 100.0 mDa / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3
Monoisotopic Mass, Even Electron Ions
132 formula(e) evaluated with 39 results within limits (all results (up to 1000) for each mass)
Elements Used:
503.2010
504.2029
535.1964
519.1967
536.1997
MeO
OH
3ea


EtO
OH
3fa
f1 (ppm)

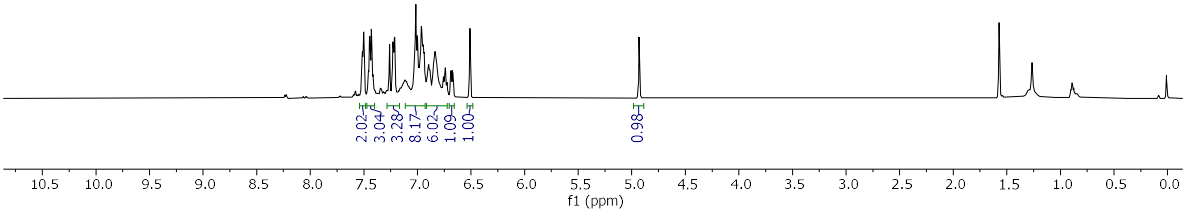

11940
TG_633
145.03
142.23
142.17
139.98
139.90
138.84
135.33
134.71
134.04
129.99
129.89
129.82
128.81
128.44
128.19
128.07
127.69
127.41
127.22
127.18
127.03
126.57
126.10
125.02
123.68
122.20
120.33
119.74
117.64
114.36
114.03
90.10
87.60
77.48
77.16
76.84
65.09
64.94
15.16
14.90
O
OH
EtO
3fa
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

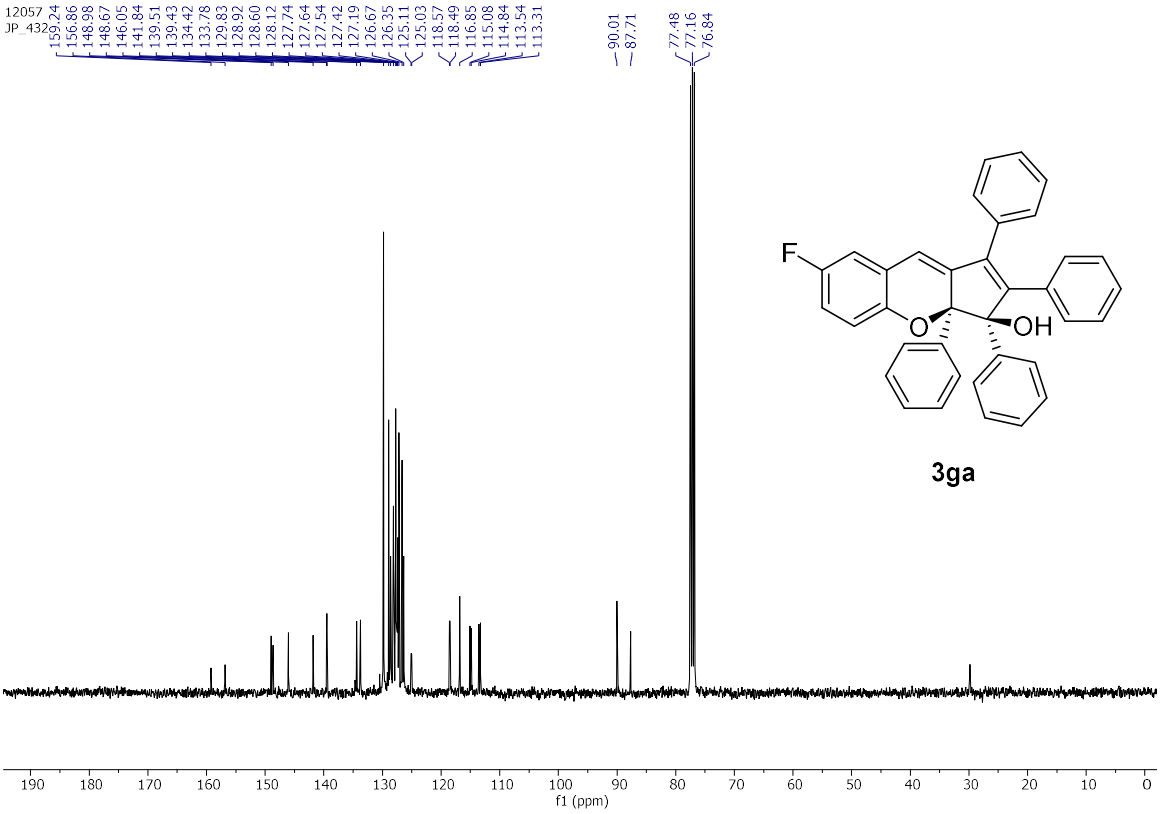

Elemental Composition
File Edit View Process Help
Single Mass Analysis
Tolerance = 100.0 mDa / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3
Monoisotopic Mass, Even Electron Ions
131 formula(e) evaluated with 38 results within limits (all results (up to 1000) for each mass)
Elements Used:
Mass Calc. Mass mDa PPM DBE Formula i-FIT i-FIT Norm Fit Conf % C H O
517.2165 517.2168 -0.3 -0.6 24.5 C38 H29 O2 254.2 6.129 0.22 38 29 2
517.2132 3.3 6.4 2.5 C20 H37 O15 250.0 1.927 14.56 20 37 15
517.2226 -6.1 -11.8 15.5 C31 H33 O7 252.9 4.823 0.80 31 33 7
517.2074 9.1 17.6 11.5 C27 H33 O10 252.2 4.078 1.69 27 33 10
517.2285 -12.0 -23.2 6.5 C24 H37 O12 251.1 3.033 4.82 24 37 12
517.2015 15.0 29.0 20.5 C34 H29 O5 253.7 5.603 0.37 34 29 5
517.1980 18.5 35.8 -1.5 C16 H37 O18 249.5 1.382 25.10 16 37 18
29112023_127_15796
PB-433_29112023_007 921 (7.998) AM2 (Ar,30000.0,556.22,0.00,LS 1)
1: TOF MS ES+
1.31e+006
517.2165
477.2110
518.2203
457.1635
478.2133
533.2143
549.2141
O
OH
EtO
3fa
For Help, press F1
11:10 AM
11/30/2023


PB-43L


F
O
OH

3ga

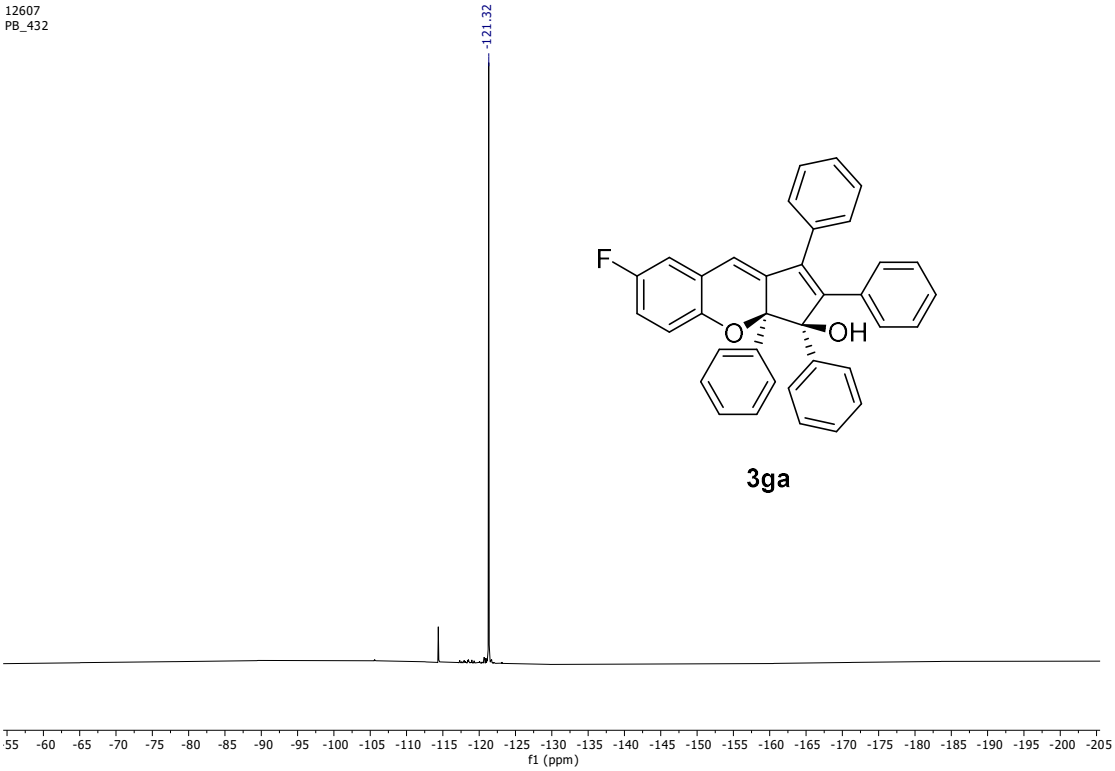

2.02
3.04
3.28
8.17
6.02
1.09
1.00
0.98
f1 (ppm)


12057
JP_432
f1 (ppm)

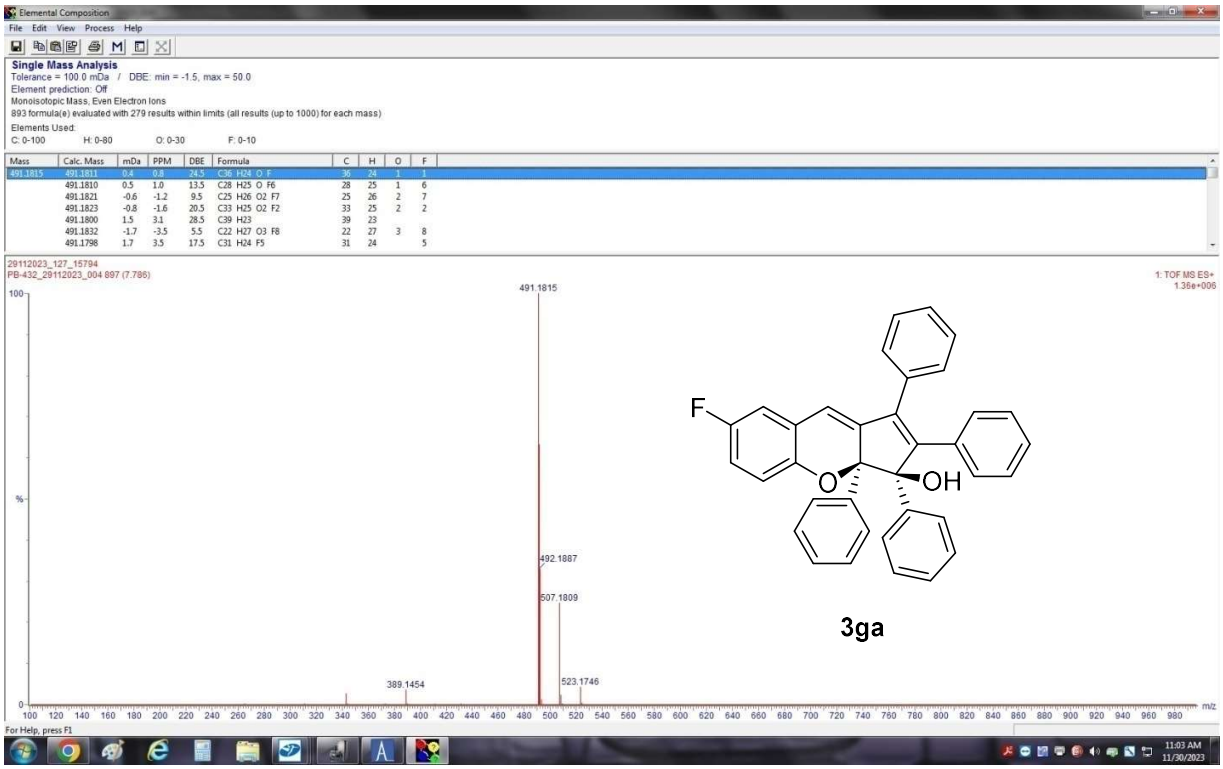
F
O
OH

3ga

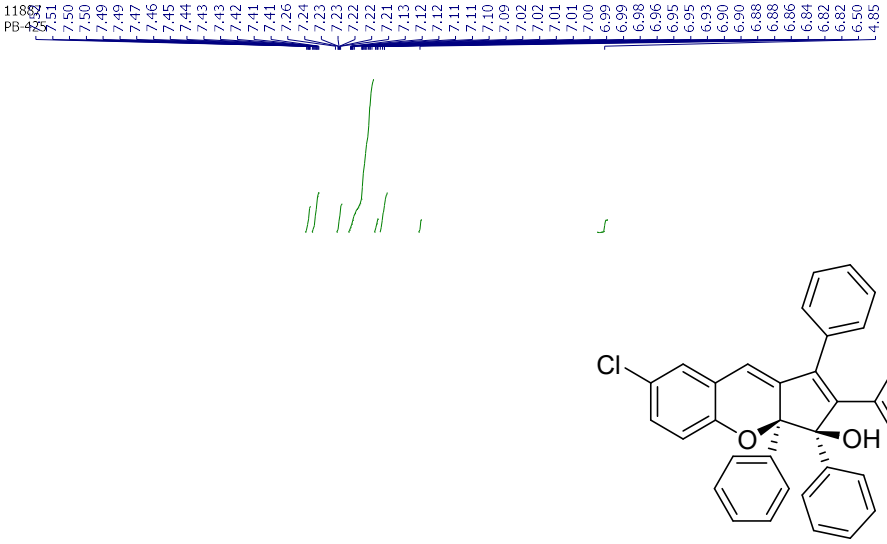
12607
PB_432



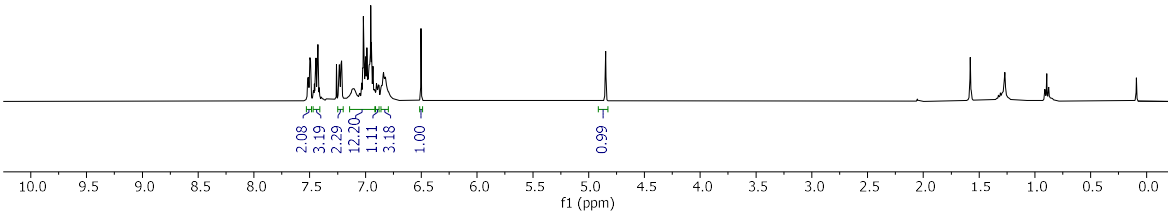
3ga

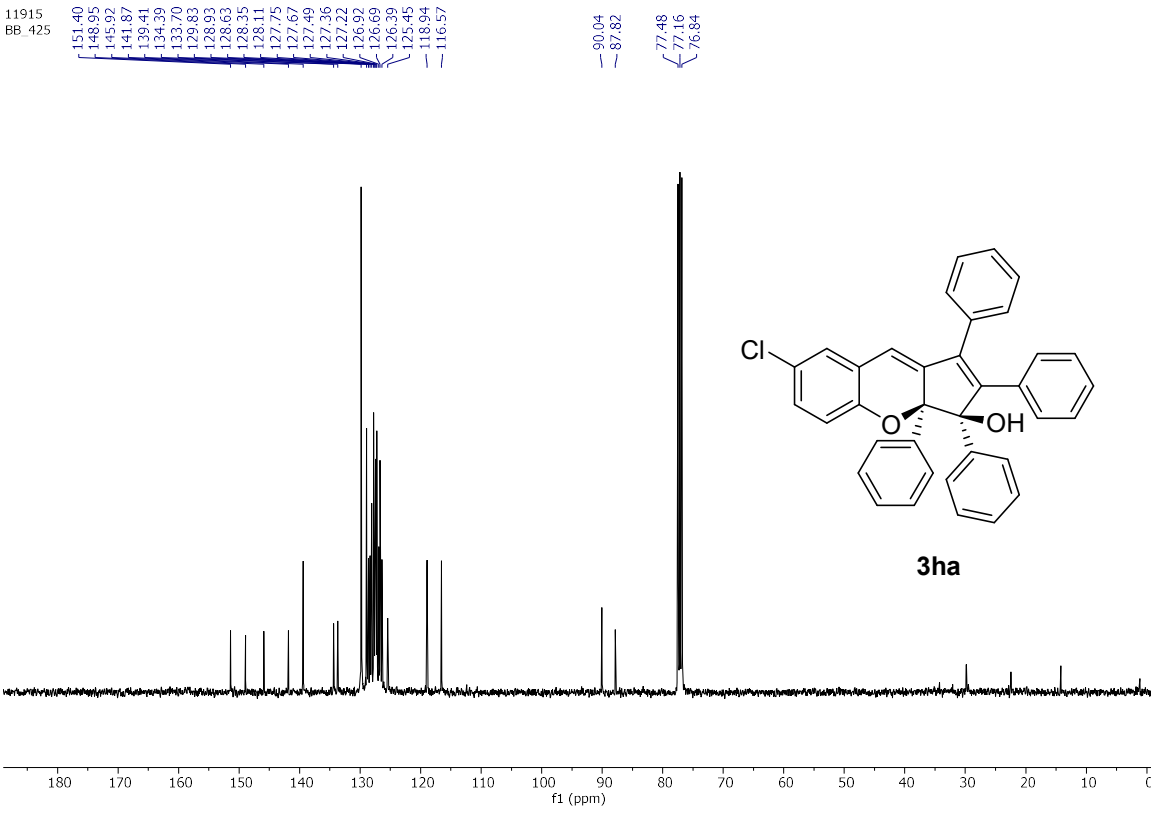


3ga

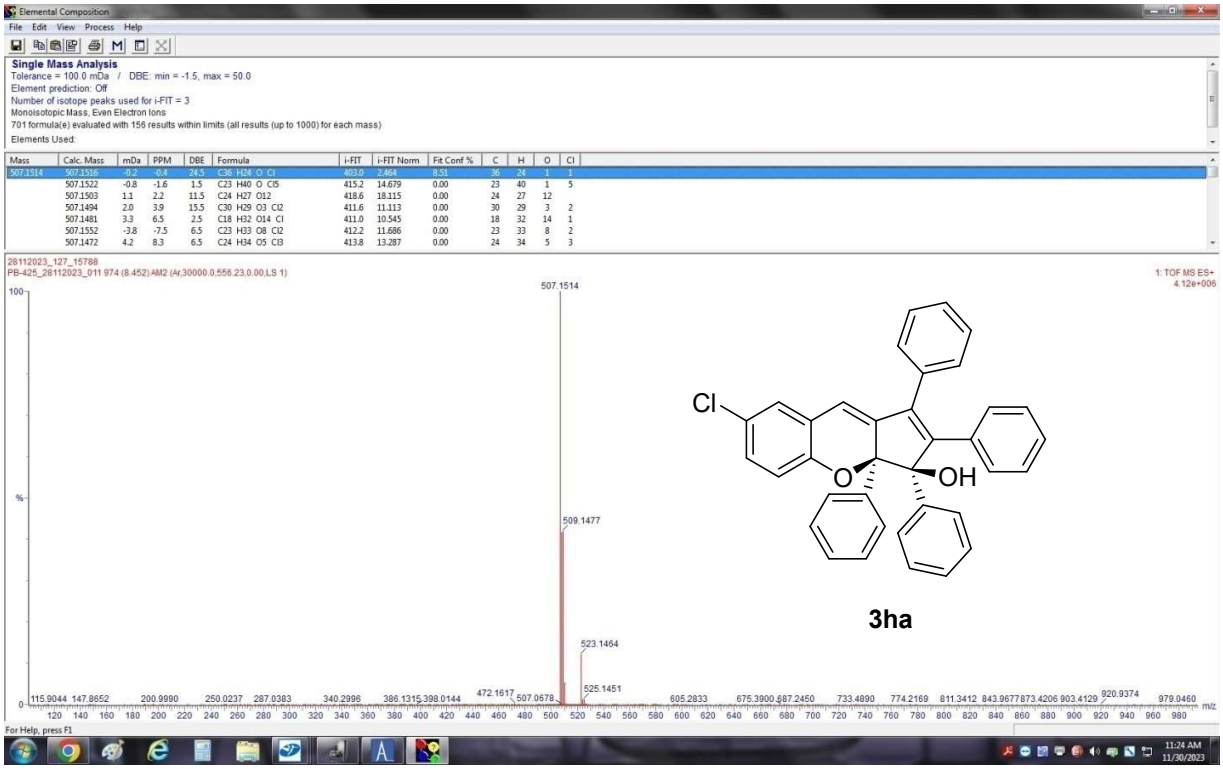


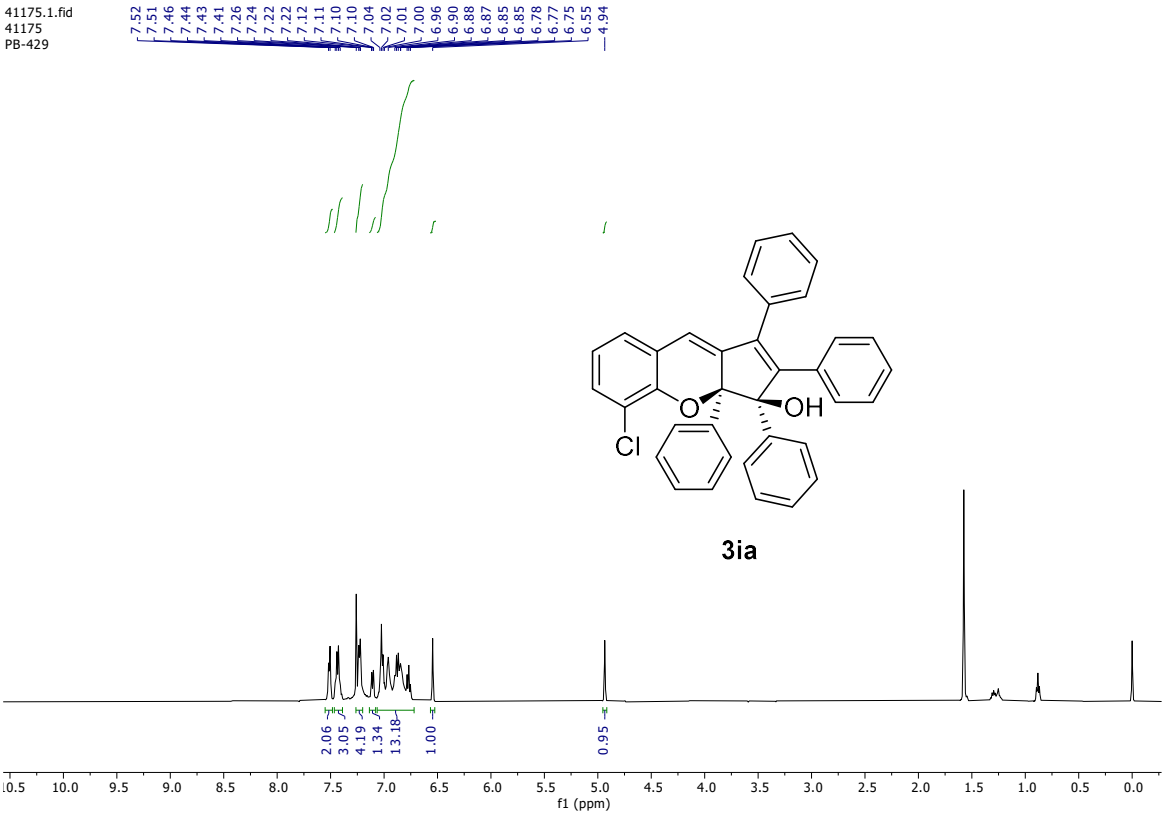
3ha

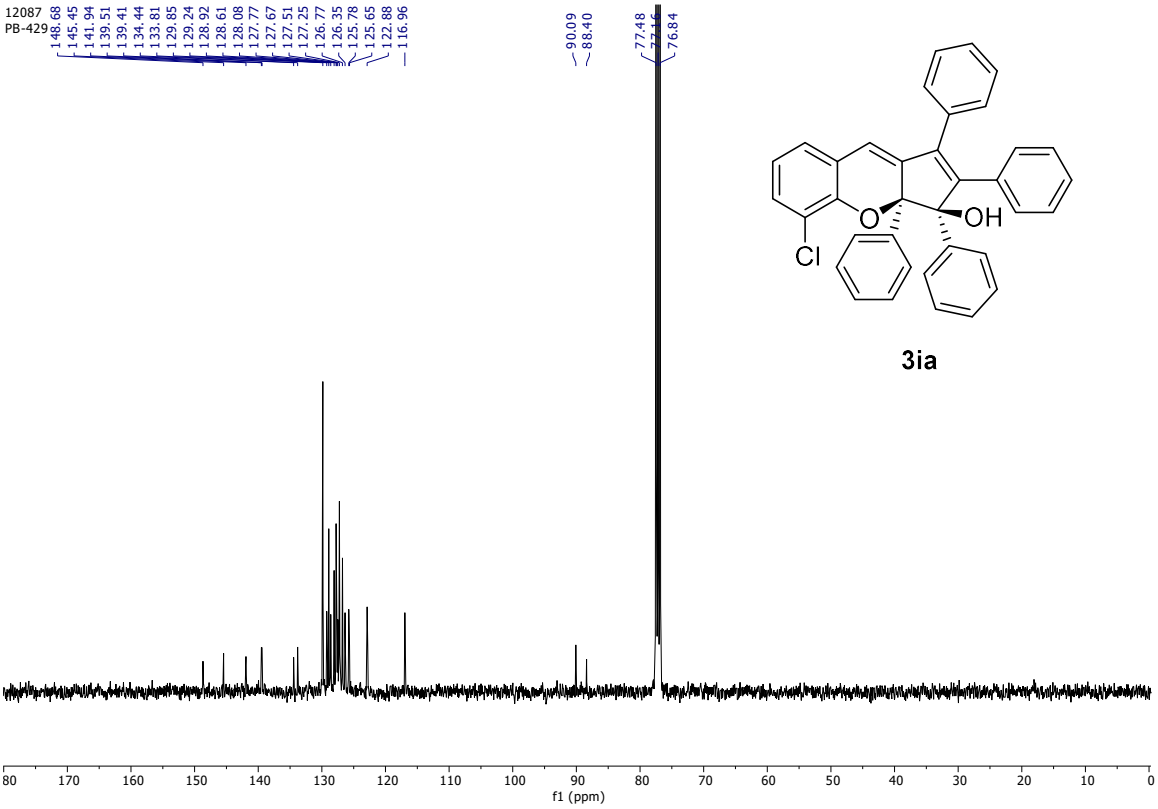




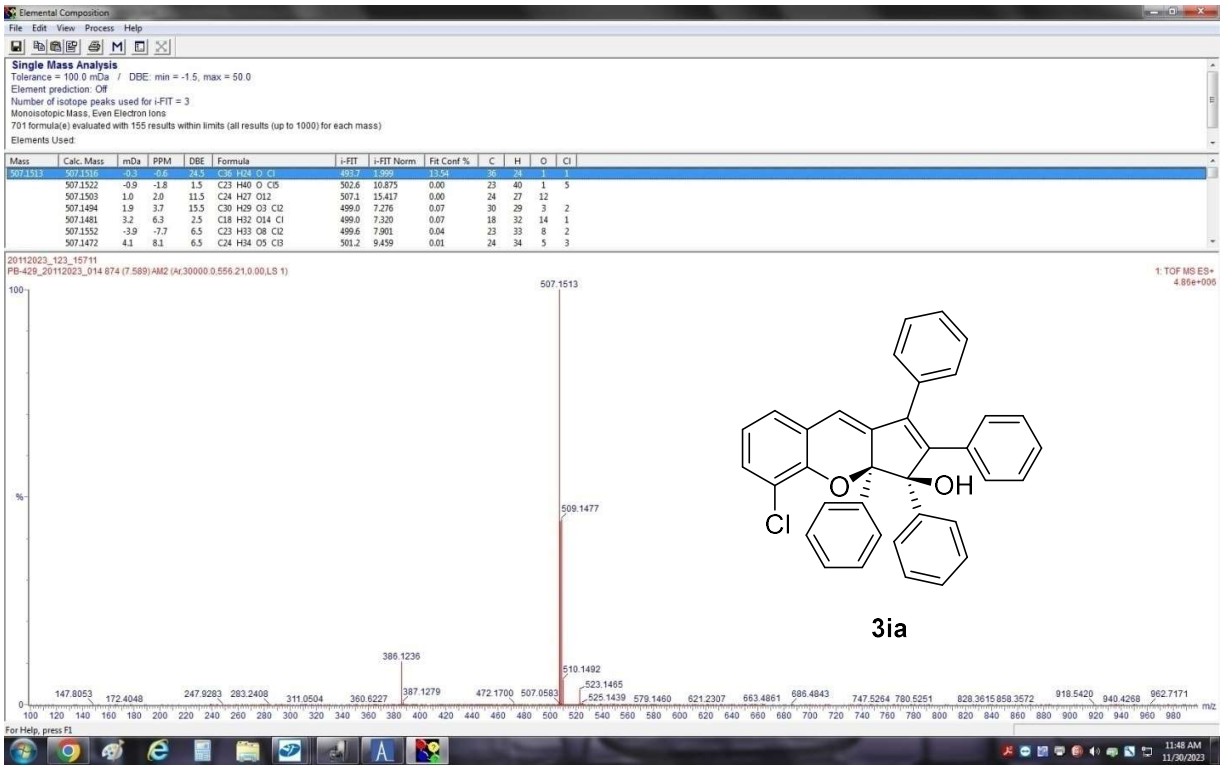
3ha

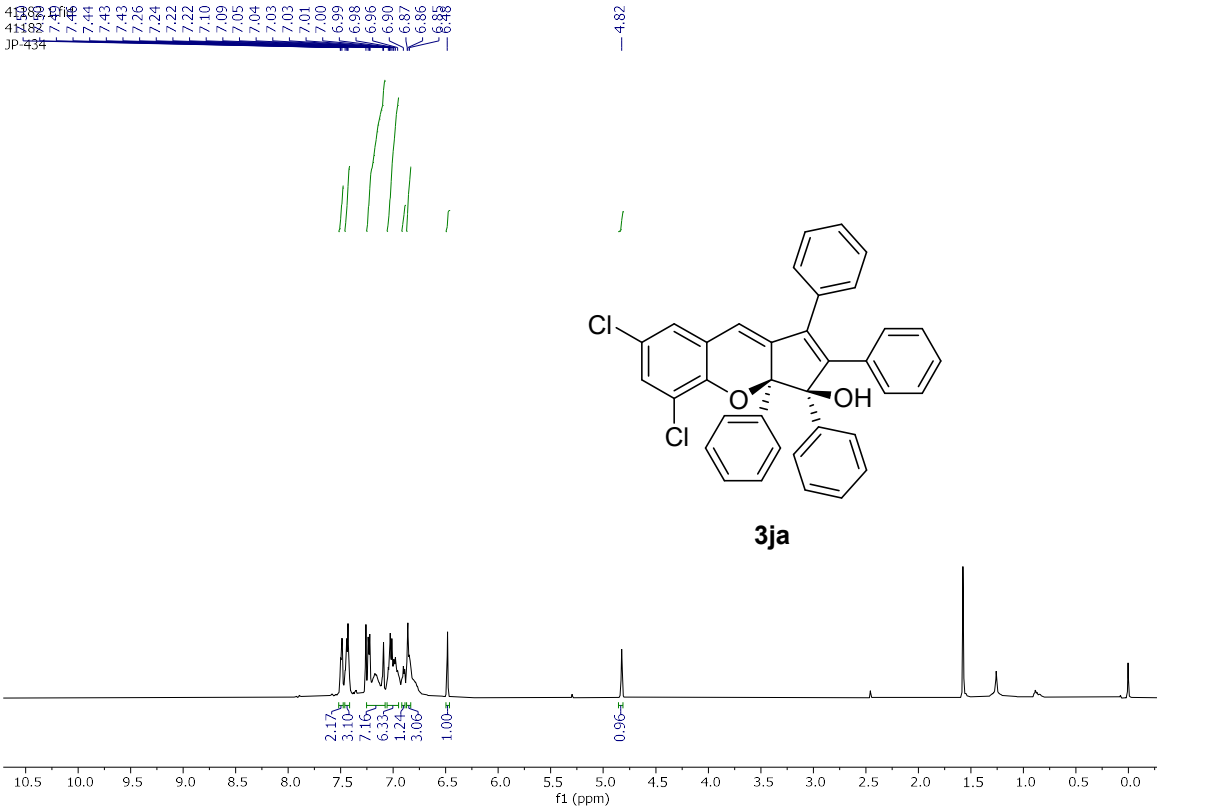

Elemental Composition
Single Mass Analysis
Tolerance = 100.0 mDa / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3
Monoisotopic Mass, Even Electron Ions
701 formula(e) evaluated with 156 results within limits (all results (up to 1000) for each mass)
Elements Used:
507.1514
509.1477
523.1464
525.1451
Cl
O
OH
3ha

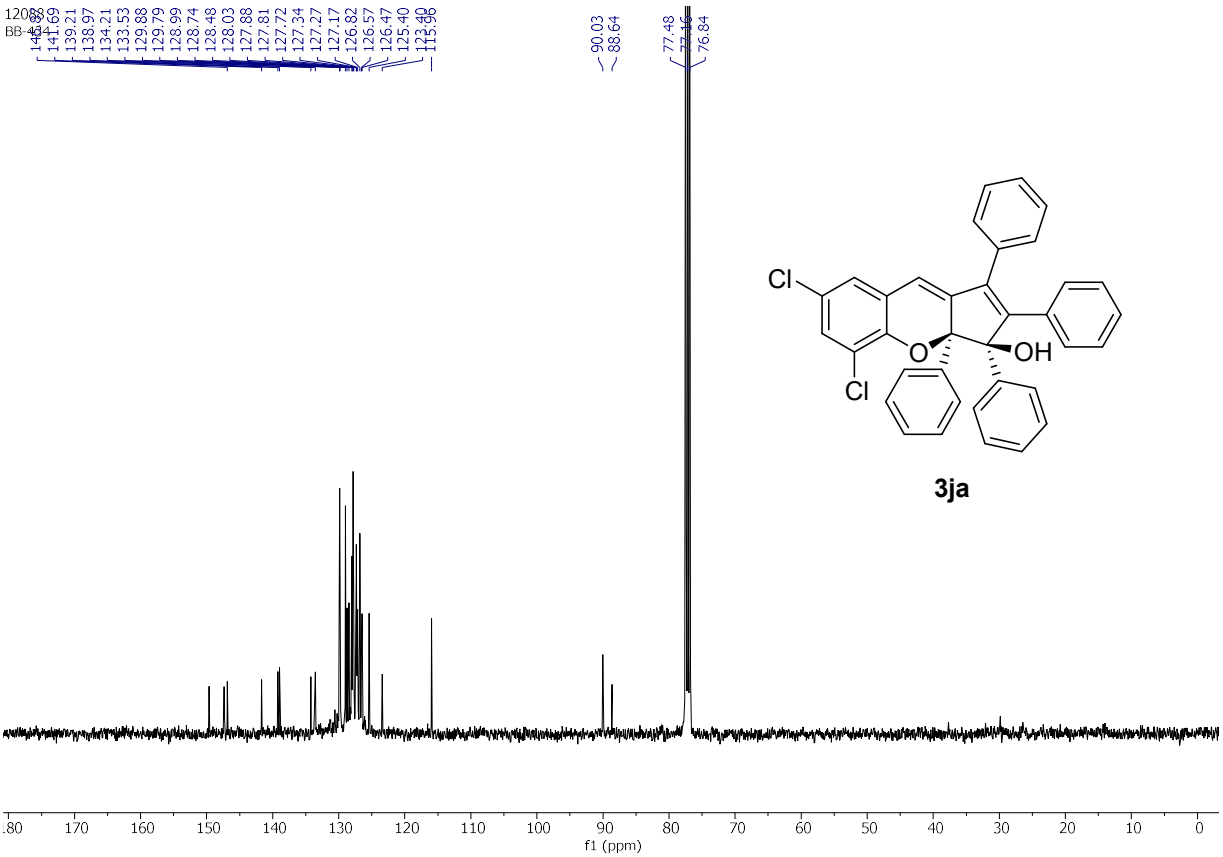

41175.1.fid
41175
PB-429
Cl
O
OH
3ia
f1 (ppm)

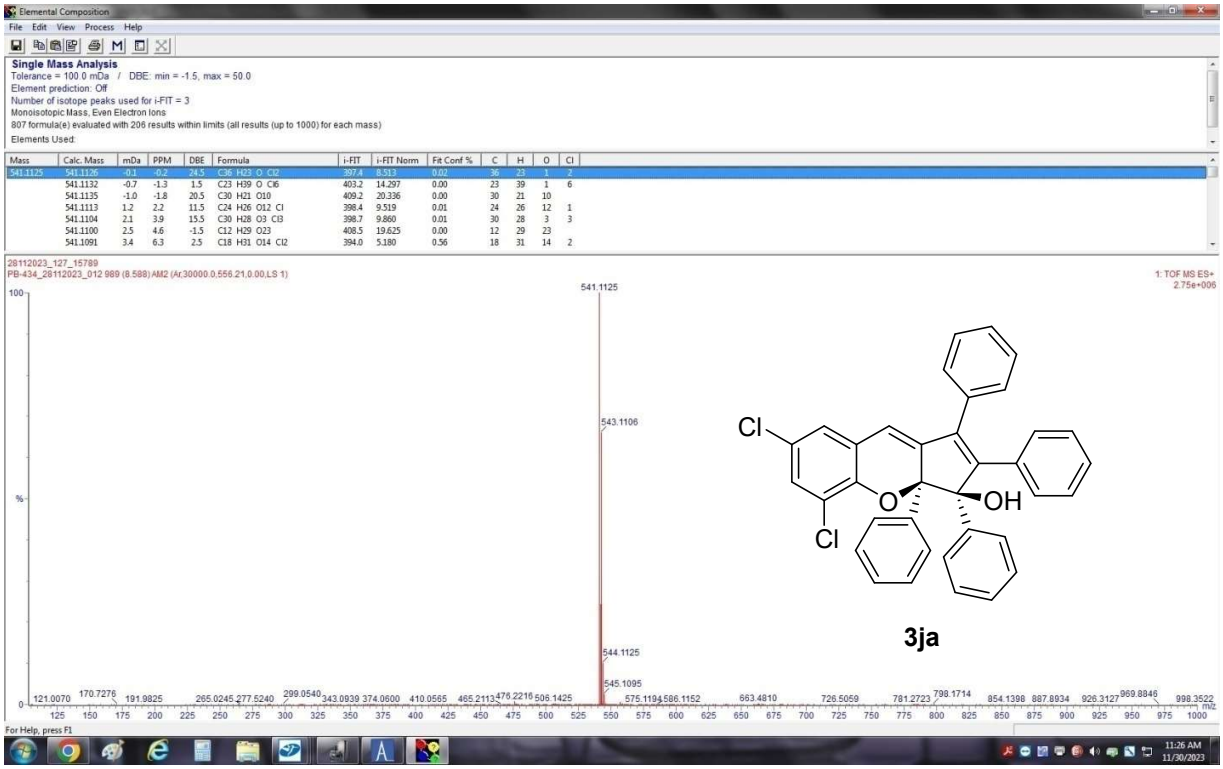

12087
PB-429
148.68
145.45
141.94
139.51
139.41
134.44
133.81
129.85
129.24
128.92
128.61
128.08
127.77
127.67
127.51
127.25
126.77
126.35
125.78
125.65
122.88
116.96
90.09
88.40
77.48
77.16
76.84
O
OH
Cl
f1 (ppm)

3ia


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
701 formula(e) evaluated with 155 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 O Cl
507.1513 507.1516 -0.3 -0.6 24.5 C36 H24 O Cl 493.7 1.999 13.54 36 24 1 1
507.1522 -0.9 -1.8 1.5 C23 H40 O Cl5 502.6 10.875 0.00 23 40 1 5
507.1503 1.0 2.0 11.5 C24 H27 O12 507.1 15.417 0.00 24 27 12
507.1494 1.9 3.7 15.5 C30 H29 O3 Cl2 499.0 7.276 0.07 30 29 3 2
507.1481 3.2 6.3 2.5 C18 H32 O14 Cl 499.0 7.320 0.07 18 32 14 1
507.1552 -3.9 -7.7 6.5 C23 H33 O8 Cl2 499.6 7.901 0.04 23 33 8 2
507.1472 4.1 8.1 6.5 C24 H34 O5 Cl3 501.2 9.459 0.01 24 34 5 3
20112023_123_15711
PB-429_20112023_014 874 (7.589) AM2 (Ar,30000.0,556.21,0.00,LS 1)
1: TOF MS ES+
4.85e+006
507.1513
509.1477
386.1236
510.1492
523.1465
O
OH
Cl
3ia
For Help, press F1
11:48 AM
11/30/2023

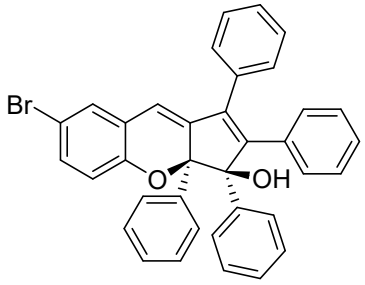

Cl
O
OH
Cl
3ja
f1 (ppm)


Cl
O
OH
Cl
3ja
f1 (ppm)

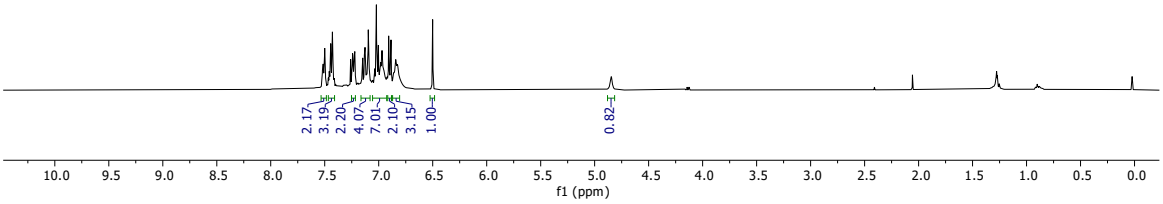


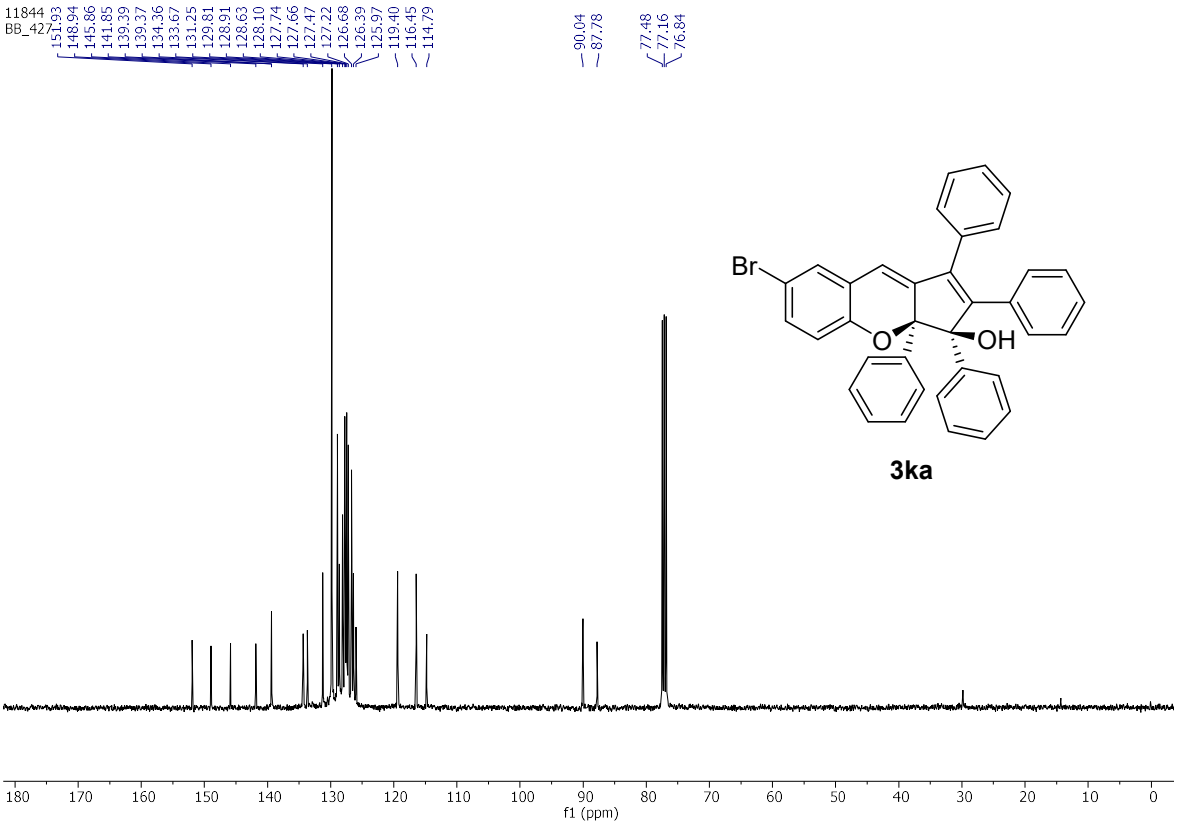
3ja

11812
PB_427

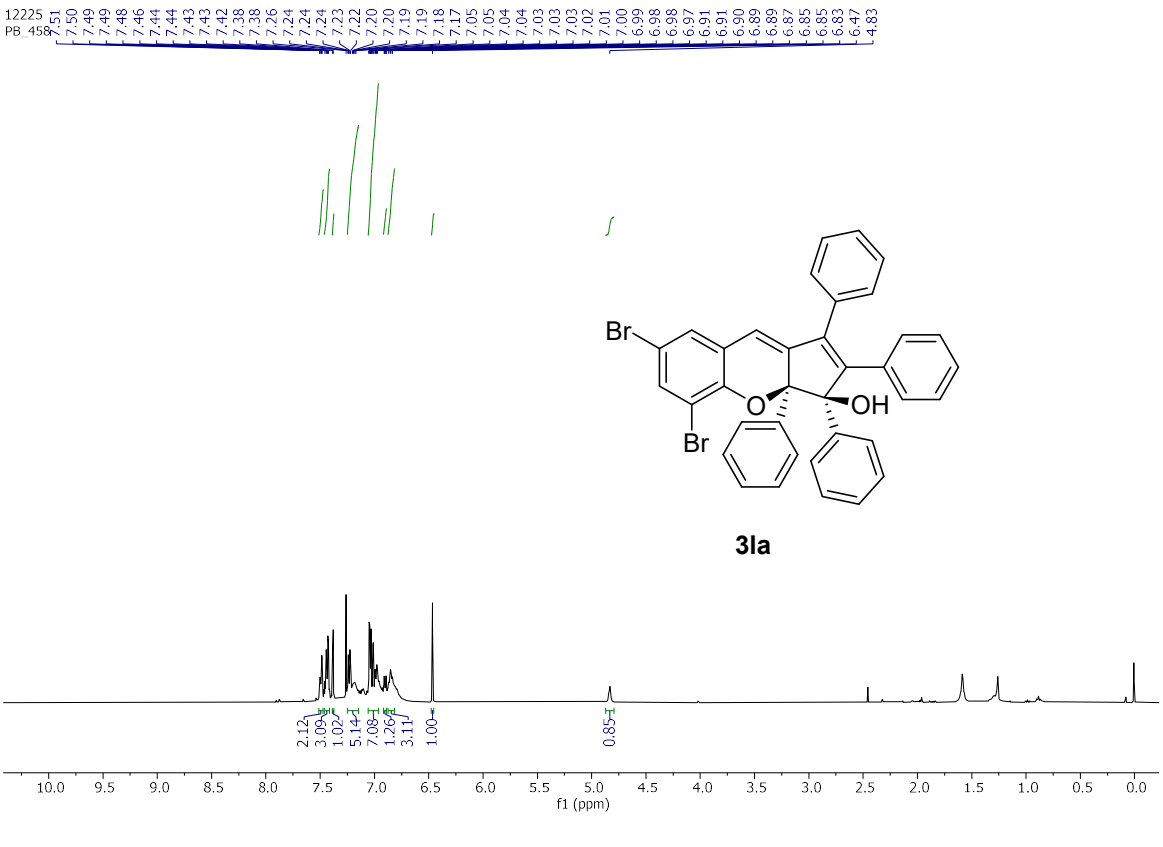


3ka

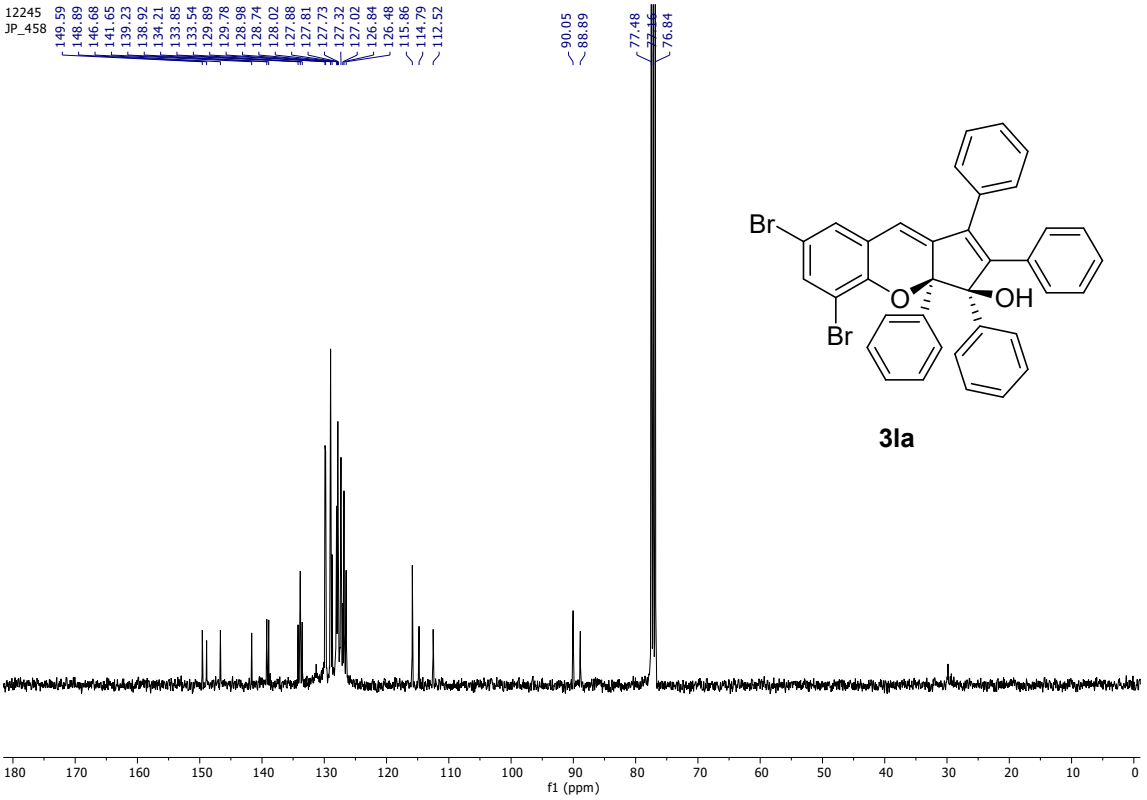


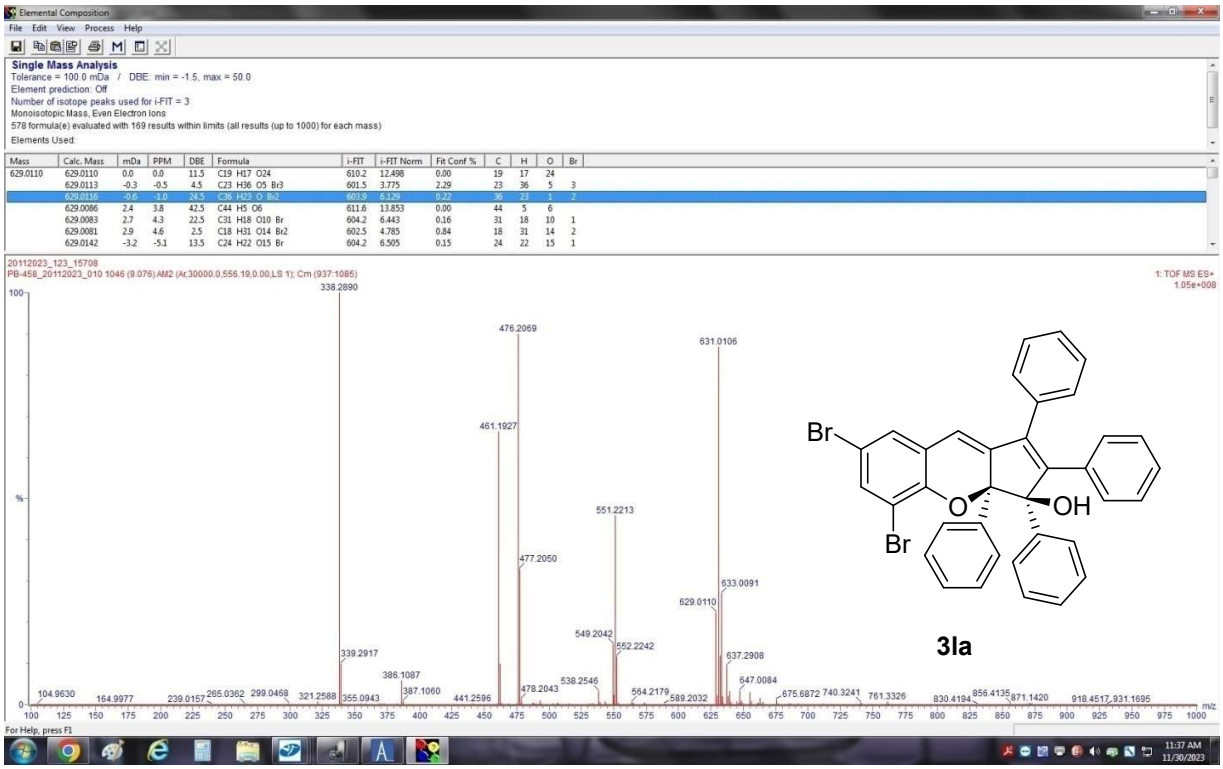

11844
BB_427
151.93
148.94
145.86
141.85
139.39
139.37
134.36
133.67
131.25
129.81
128.91
128.63
128.10
127.74
127.66
127.47
127.22
126.68
126.39
125.97
119.40
116.45
114.79
90.04
87.78
77.48
77.16
76.84
Br
O
OH
f1 (ppm)

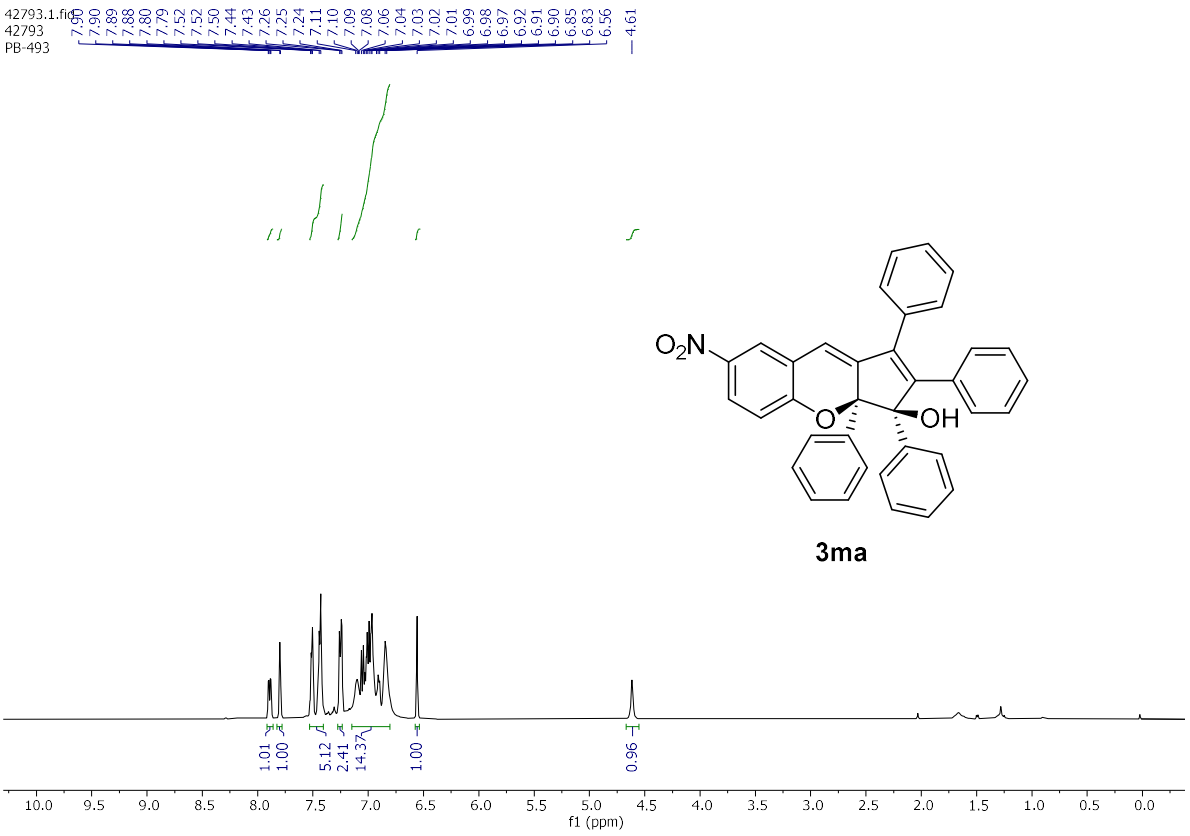
3ka


12225
PB_458
7.51
7.50
7.49
7.49
7.48
7.46
7.44
7.44
7.43
7.43
7.42
7.38
7.38
7.26
7.24
7.24
7.23
7.22
7.20
7.20
7.19
7.19
7.18
7.17
7.05
7.05
7.04
7.04
7.03
7.03
7.03
7.02
7.01
7.00
6.99
6.98
6.98
6.97
6.91
6.91
6.90
6.89
6.87
6.85
6.85
6.83
6.47
4.83
Br
O
OH
Br
2.12
3.05
1.02
5.14
7.08
1.26
3.11
1.00
0.85
f1 (ppm)

3la

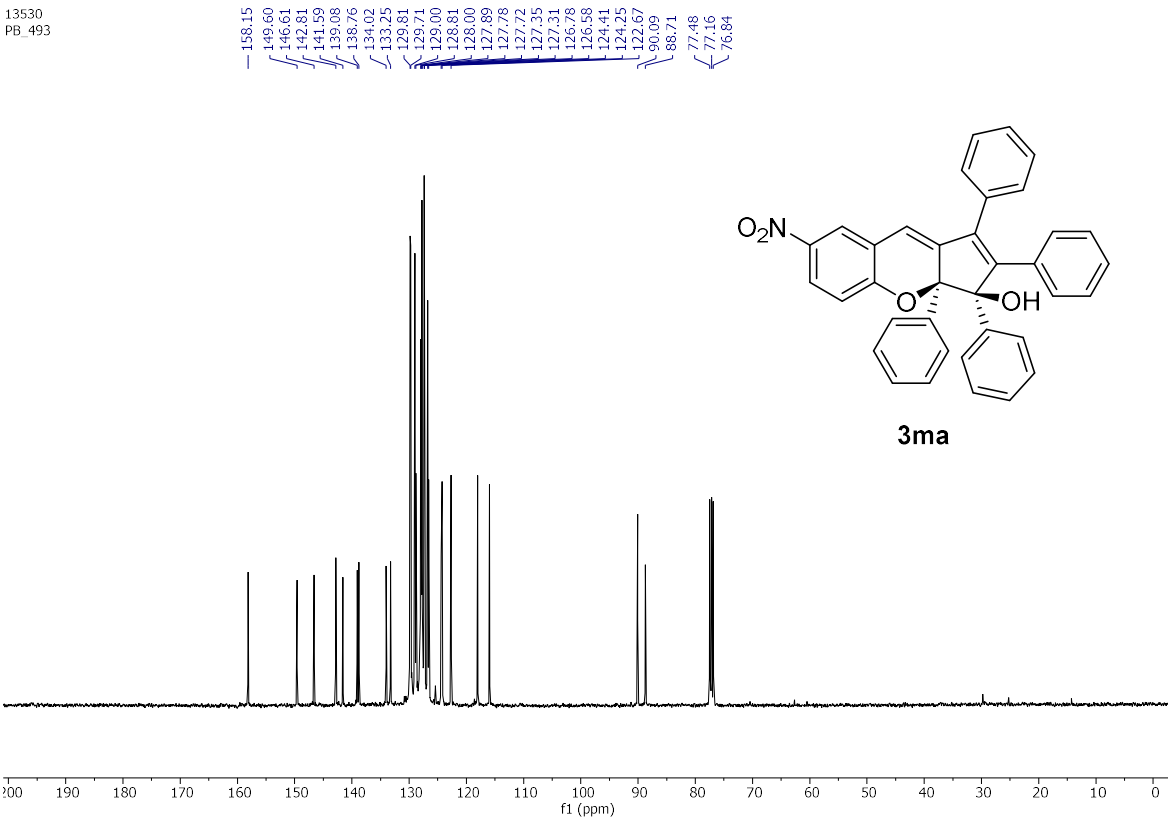

12245
JP_458
149.59
148.89
146.68
141.65
139.23
138.92
134.21
133.85
133.54
129.89
129.78
128.98
128.74
128.02
127.88
127.81
127.73
127.32
127.02
126.84
126.48
115.86
114.79
112.52
90.05
88.89
77.48
76.84
Br
O
OH
Br
3la
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


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
578 formula(e) evaluated with 169 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 | O | Br
629.0110 | 629.0110 | 0.0 | 0.0 | 11.5 | C19 H17 O24 | 610.2 | 12.498 | 0.00 | 19 | 17 | 24
629.0113 | -0.3 | -0.5 | 4.5 | C23 H36 O5 Br3 | 601.5 | 3.775 | 2.29 | 23 | 36 | 5 | 3
629.0116 | -0.6 | -1.0 | 24.5 | C36 H23 O Br2 | 603.9 | 6.129 | 0.22 | 36 | 23 | 1 | 2
629.0086 | 2.4 | 3.8 | 42.5 | C44 H5 O6 | 611.6 | 13.853 | 0.00 | 44 | 5 | 6
629.0083 | 2.7 | 4.3 | 22.5 | C31 H18 O10 Br | 604.2 | 6.443 | 0.16 | 31 | 18 | 10 | 1
629.0081 | 2.9 | 4.6 | 2.5 | C18 H31 O14 Br2 | 602.5 | 4.785 | 0.84 | 18 | 31 | 14 | 2
629.0142 | -3.2 | -5.1 | 13.5 | C24 H22 O15 Br | 604.2 | 6.505 | 0.15 | 24 | 22 | 15 | 1
20112023_123_15708
PB-458_20112023_010 1046 (9.076) AM2 (Ar,30000.0,556.19,0.00,LS 1); Cm (937:1085)
1: TOF MS ES+
1.05e+008
338.2890
476.2069
631.0106
461.1927
551.2213
477.2050
633.0091
629.0110
549.2042
552.2242
339.2917
637.2908
386.1087
647.0084
387.1060
538.2546
478.2043
564.2179
589.2032
441.2596
355.0943
321.2588
299.0468
265.0362
239.0157
164.9977
104.9630
675.6872
740.3241
761.3326
830.4194
956.4135
871.1420
918.4517
931.1695
m/z
Br
O
OH
Br
3la
For Help, press F1
11:37 AM
11/30/2023


42793.1.fid
42793
PB-493
7.90
7.90
7.89
7.88
7.80
7.79
7.52
7.52
7.50
7.44
7.43
7.26
7.25
7.24
7.11
7.10
7.09
7.08
7.06
7.04
7.03
7.02
7.01
6.99
6.98
6.97
6.92
6.91
6.90
6.85
6.83
6.56
4.61
1.01
1.00
5.12
2.41
14.37
1.00
0.96
f1 (ppm)

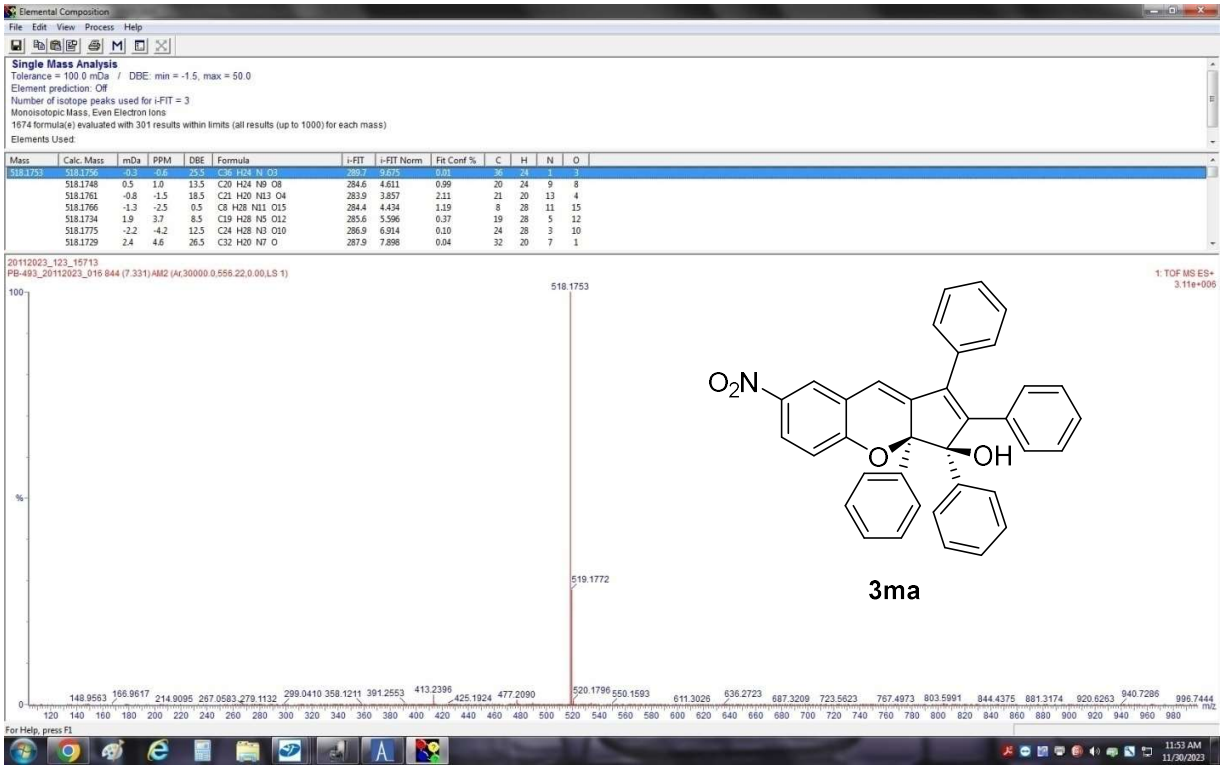
O2N
O
OH

3ma

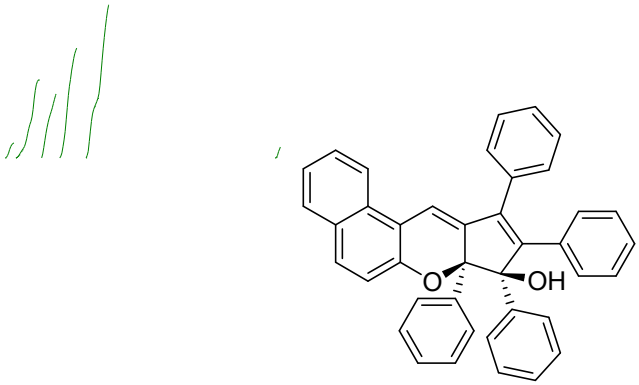

13530
PB_493
158.15
149.60
146.61
142.81
141.59
139.08
138.76
134.02
133.25
129.81
129.71
129.00
128.81
128.00
127.89
127.78
127.72
127.35
127.31
126.78
126.58
124.41
124.25
122.67
90.09
88.71
77.48
77.16
76.84
f1 (ppm)

O2N
O
OH

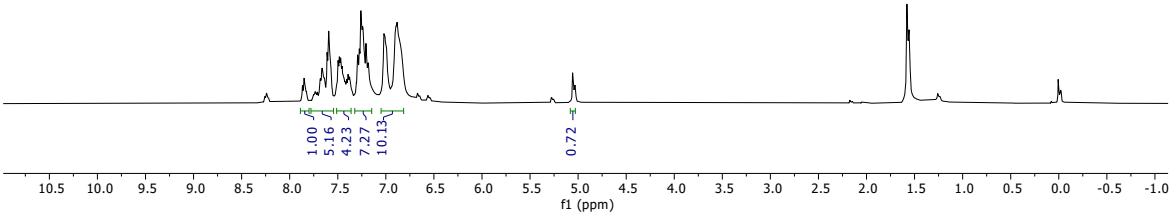
3ma

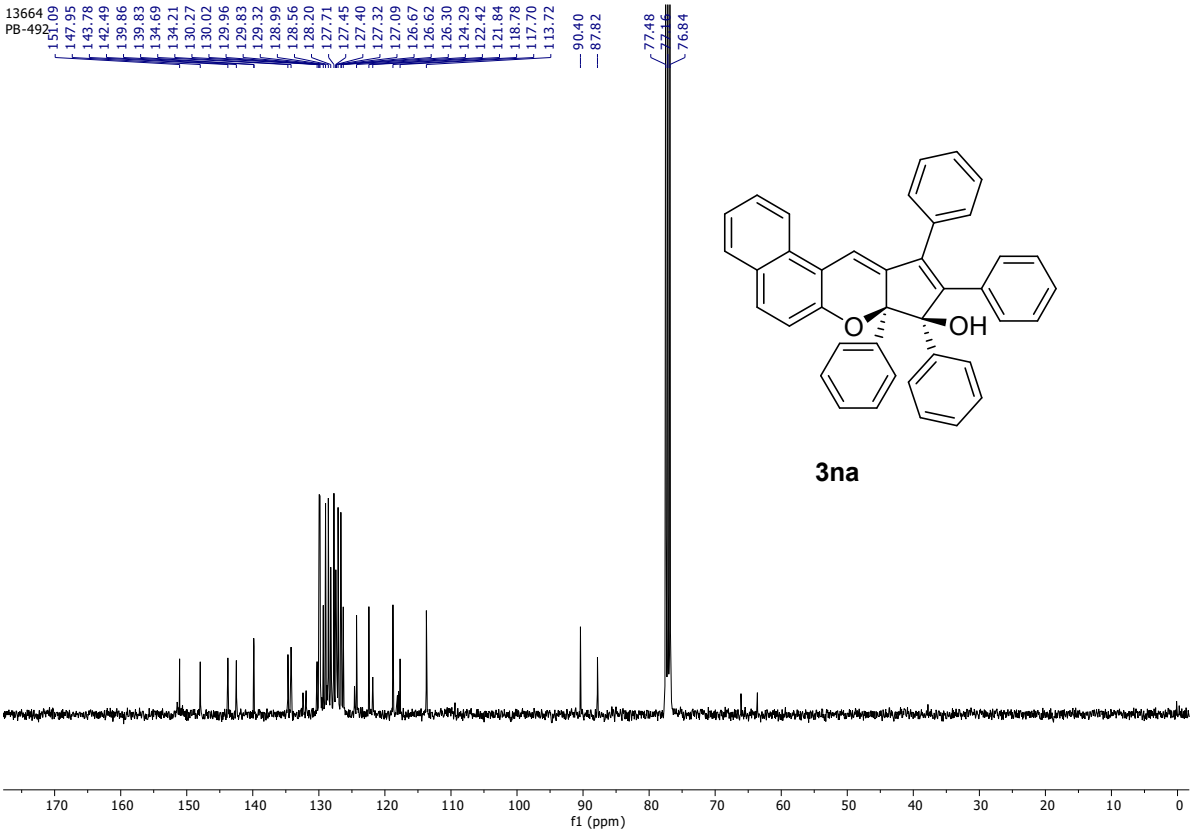

Elemental Composition
Single Mass Analysis
Tolerance = 100.0 mDa / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3
Monoisotopic Mass, Even Electron Ions
1674 formula(e) evaluated with 301 results within limits (all results (up to 1000) for each mass)
Elements Used:
518.1753
519.1772
520.1796
O2N
OH
O

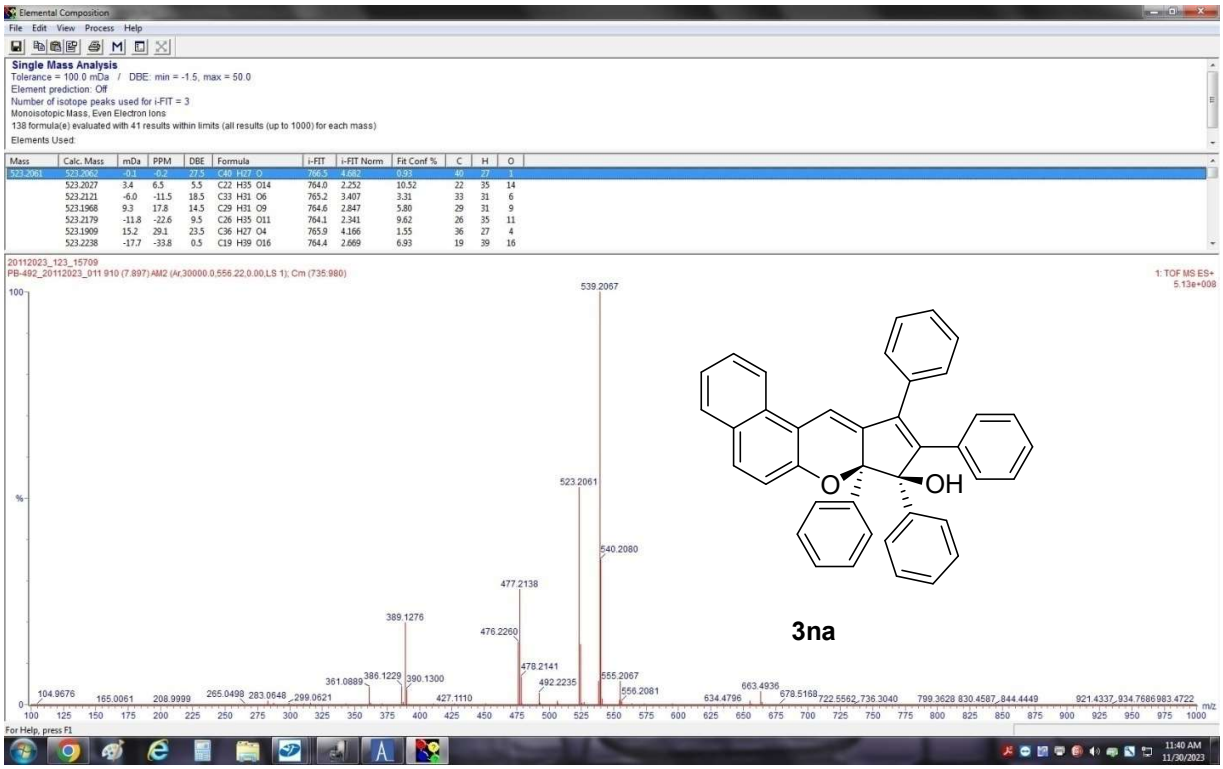
3ma

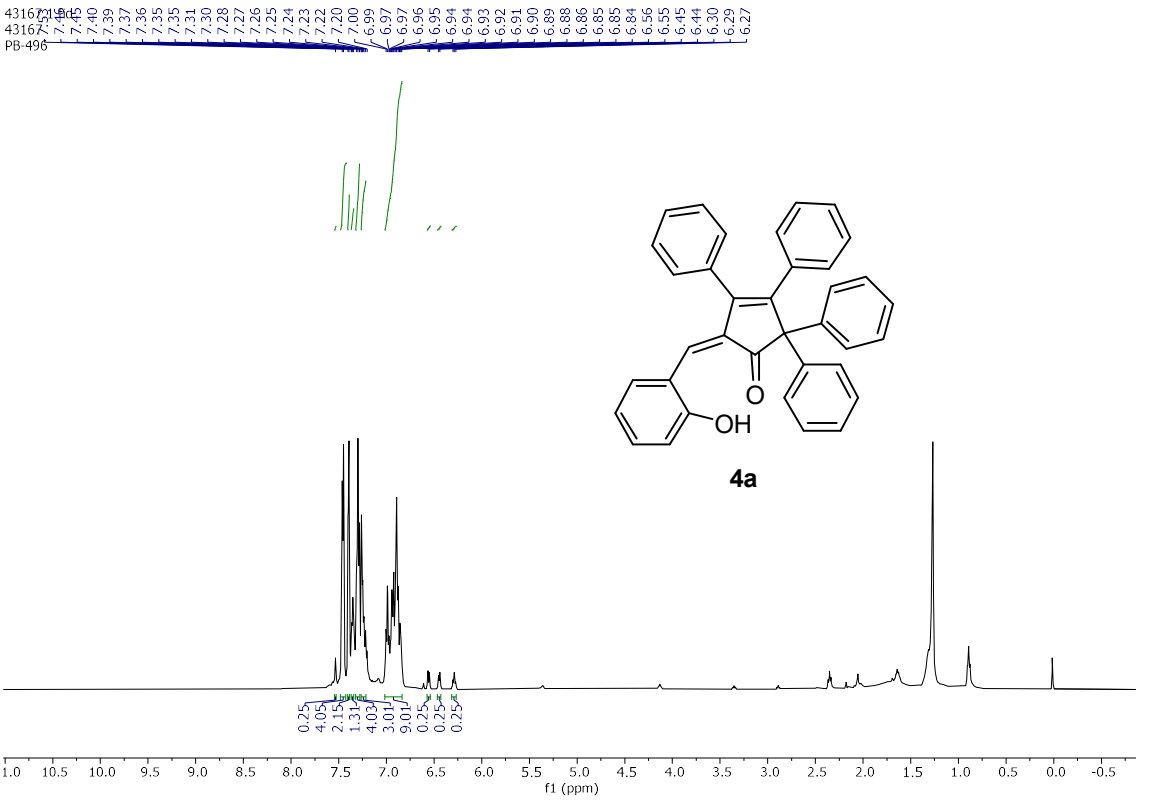

O
OH

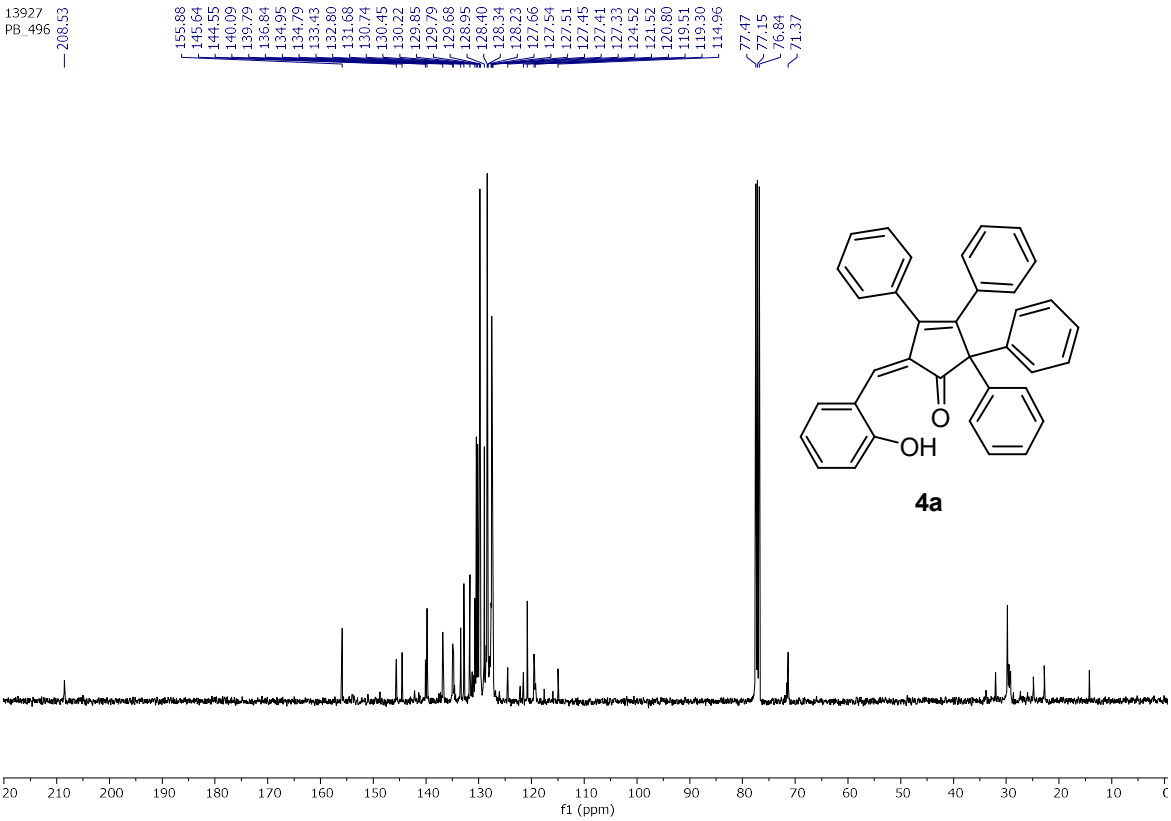
3na

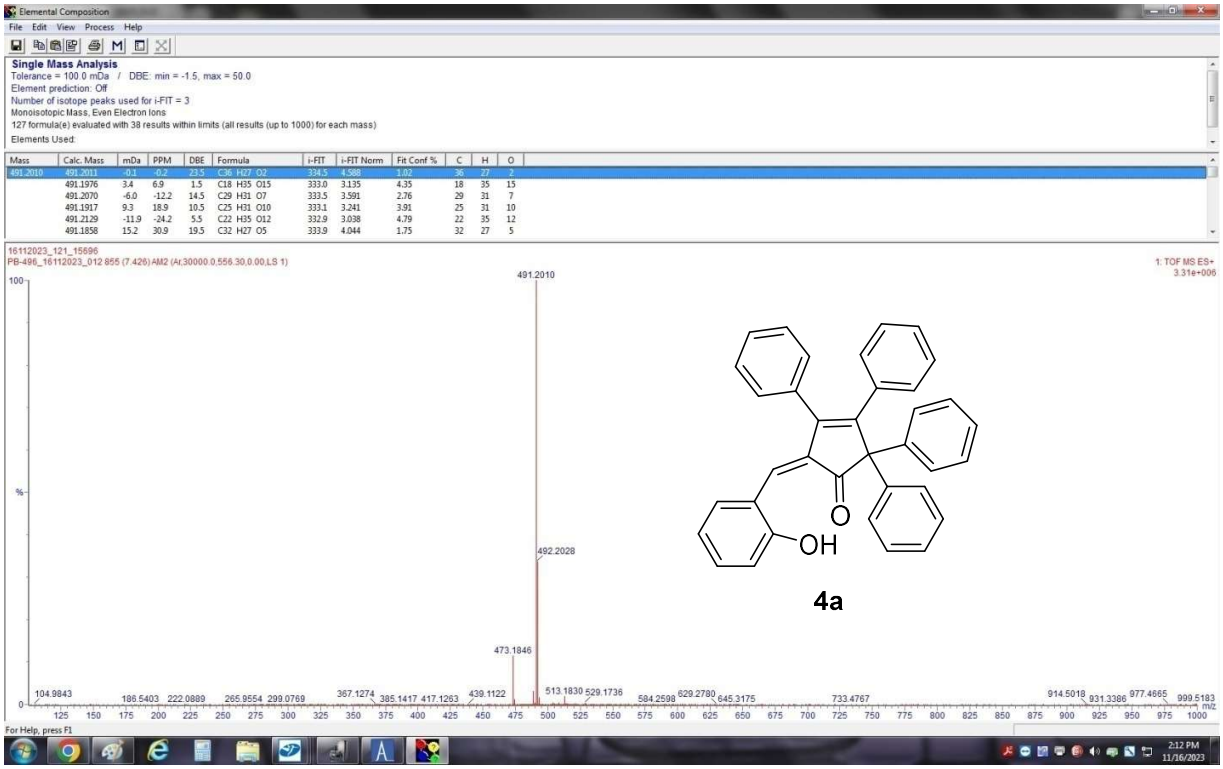

1.00
5.16
4.23
7.27
10.13
0.72
f1 (ppm)


13664
PB-492
151.09
147.95
143.78
142.49
139.86
139.83
134.69
134.21
130.27
130.02
129.96
129.83
129.32
128.99
128.56
128.20
127.71
127.45
127.40
127.32
127.09
126.67
126.62
126.30
124.29
122.42
121.84
118.78
117.70
113.72
90.40
87.82
77.48
77.16
76.84
O
OH
3na
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
138 formula(e) evaluated with 41 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 O
523.2061 523.2062 -0.1 -0.2 27.5 C40 H27 O 766.5 4.682 0.93 40 27 1
523.2027 3.4 6.5 5.5 C22 H35 O14 764.0 2.252 10.52 22 35 14
523.2121 -6.0 -11.5 18.5 C33 H31 O6 765.2 3.407 3.31 33 31 6
523.1968 9.3 17.8 14.5 C29 H31 O9 764.6 2.847 5.80 29 31 9
523.2179 -11.8 -22.6 9.5 C26 H35 O11 764.1 2.341 9.62 26 35 11
523.1909 15.2 29.1 23.5 C36 H27 O4 765.9 4.166 1.55 36 27 4
523.2238 -17.7 -33.8 0.5 C19 H39 O16 764.4 2.669 6.93 19 39 16
20112023_123_15709
PB-492_20112023_011 910 (7.897) AM2 (Ar,30000.0,556.22,0.00,LS 1); Cm (735:980)
1: TOF MS ES+
5.13e+008
100
%
0
539.2067
523.2061
540.2080
477.2138
389.1276
476.2260
478.2141
492.2235
555.2067
556.2081
361.0889
386.1229
390.1300
427.1110
104.9676
165.0061
208.9999
265.0498
283.0648
299.0621
634.4796
663.4936
678.5168
722.5562
736.3040
799.3628
830.4587
844.4449
921.4337
934.7686
983.4722
O
OH
3na
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
m/z
For Help, press F1
11:40 AM
11/30/2023

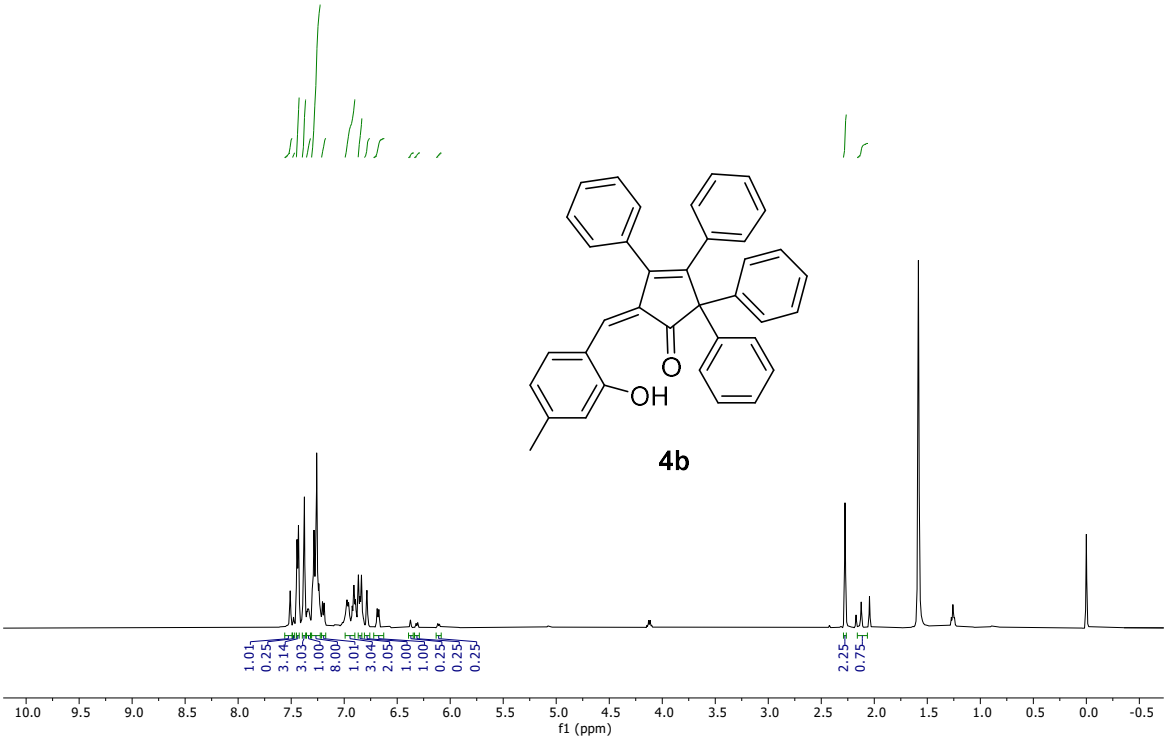

PB-496
O
OH
4a
f1 (ppm)


PB_496
O
OH
4a
f1 (ppm)


Elemental Composition
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
127 formula(e) evaluated with 38 results within limits (all results (up to 1000) for each mass)
Elements Used:
491.2010
492.2028
473.1846
OH
O

4a


pb-503

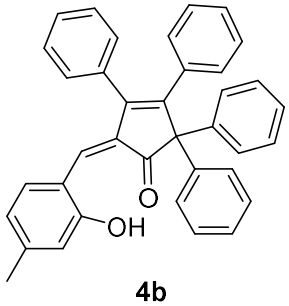

OH
O
f1 (ppm)

4b

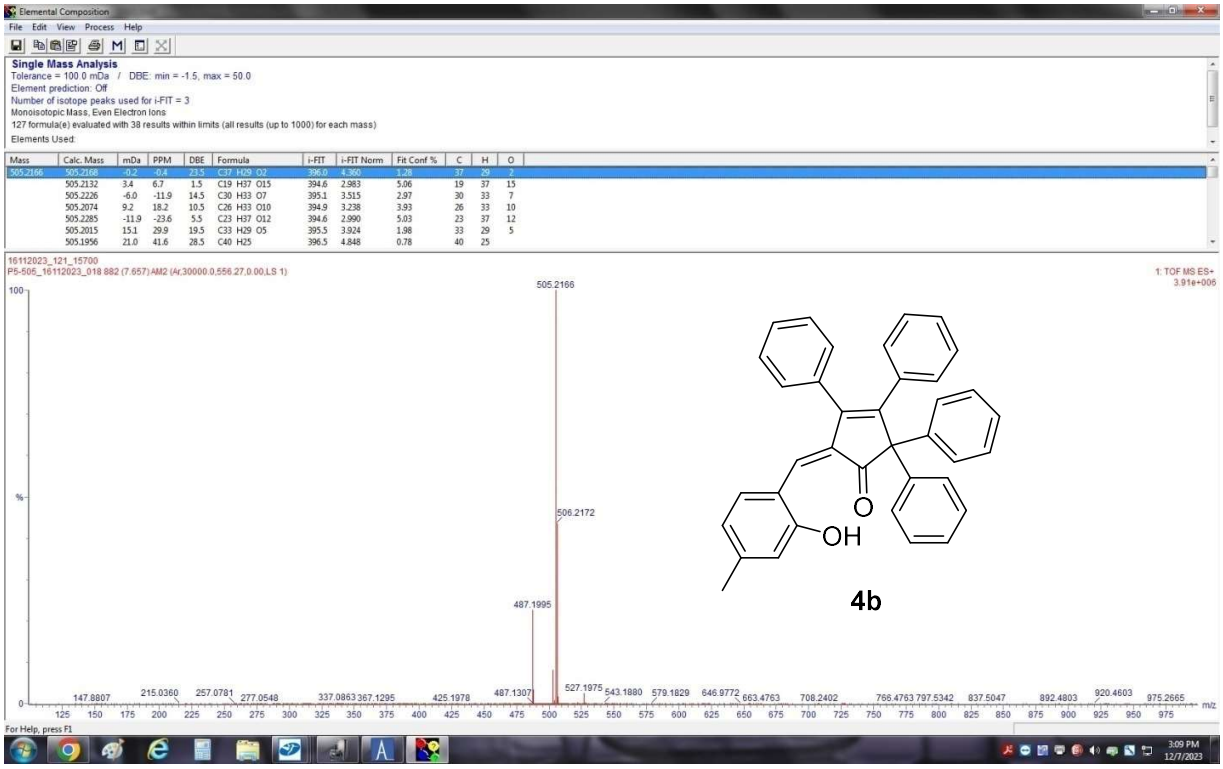
13887
PB_503

208.47

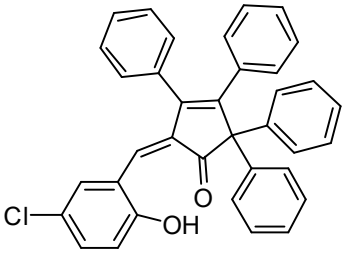
155.93
145.88
145.82
143.79
142.85
140.19
139.95
139.89
135.79
135.08
134.94
134.88
133.44
133.28
130.72
130.44
130.40
130.24
130.20
129.86
129.80
129.75
128.93
128.89
128.38
128.34
128.26
128.14
127.74
127.49
127.45
127.29
127.15
121.79
121.65
119.93
119.71
119.50
118.61
115.61
77.48
77.16
76.84
71.40
71.36
21.43



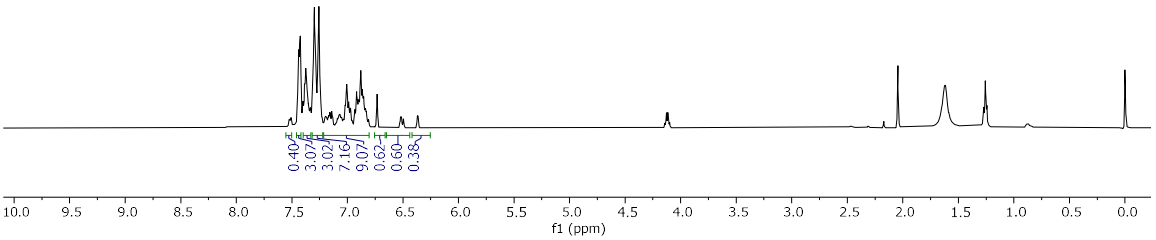
4b

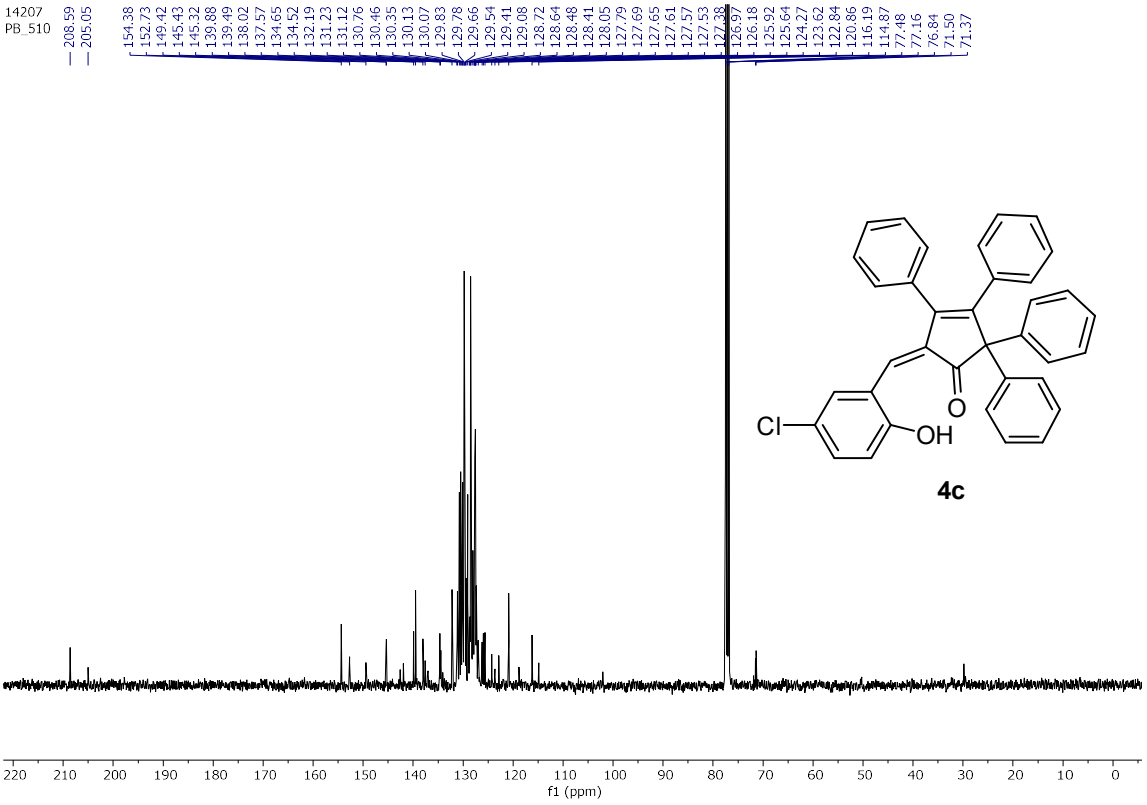



BB-510


Cl
OH
O

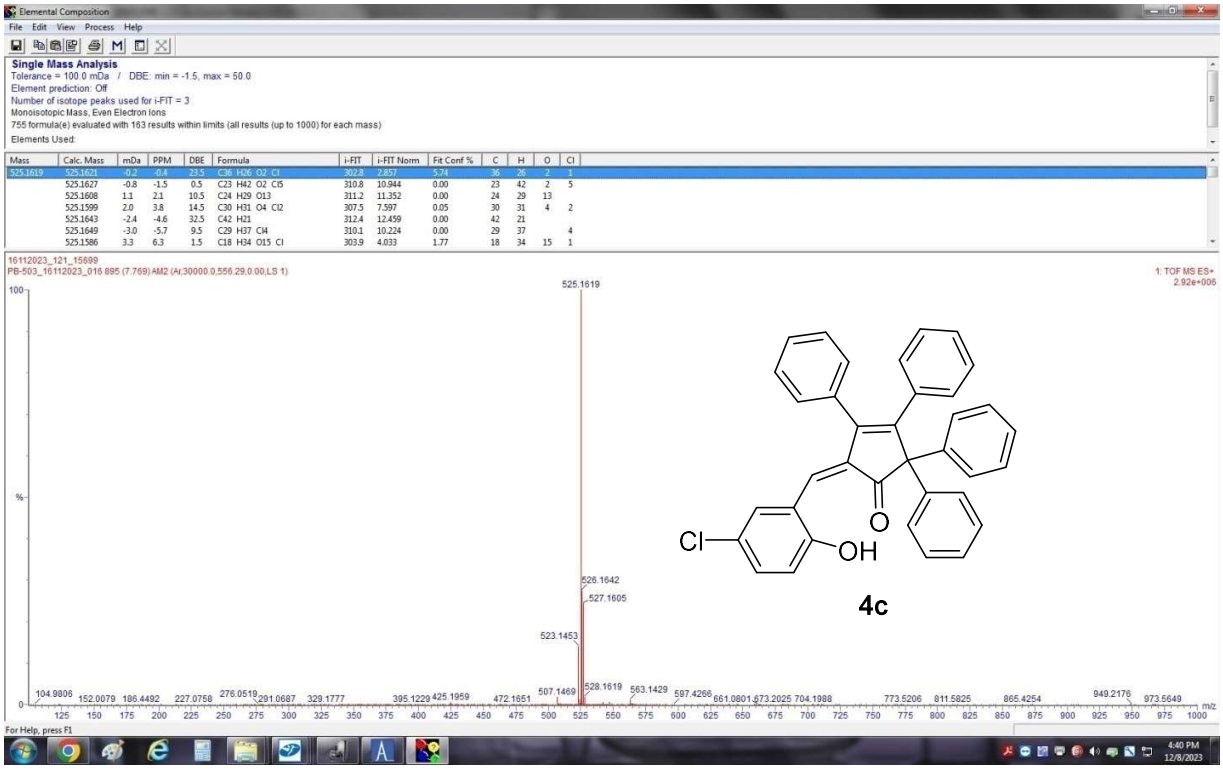
4c


0.40
3.07
3.02
7.16
9.07
0.62
0.60
0.38
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
f1 (ppm)

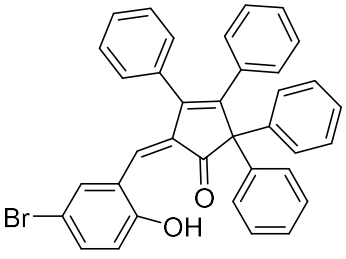

14207
PB_510
208.59
205.05
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

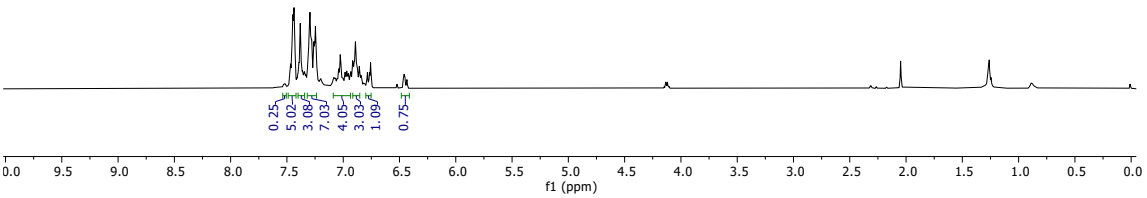
Cl
OH
O

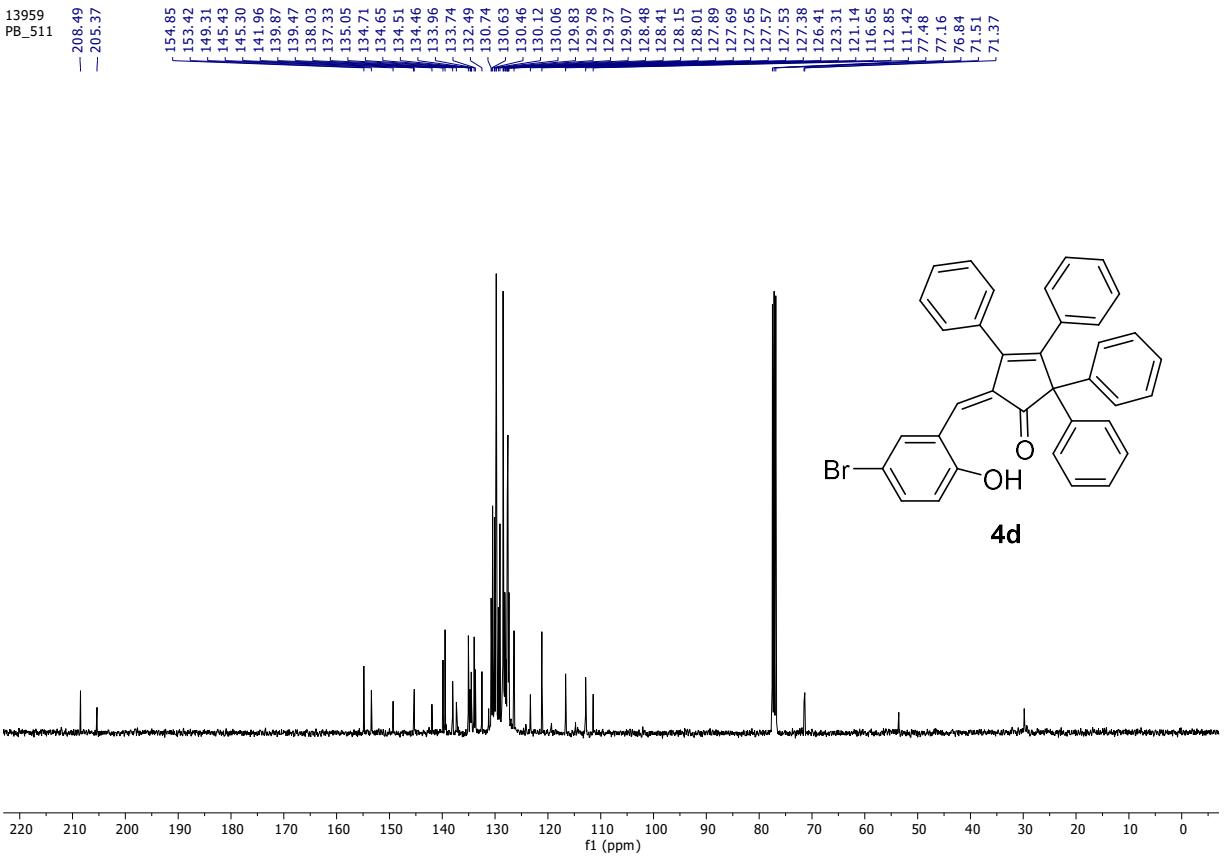
4c

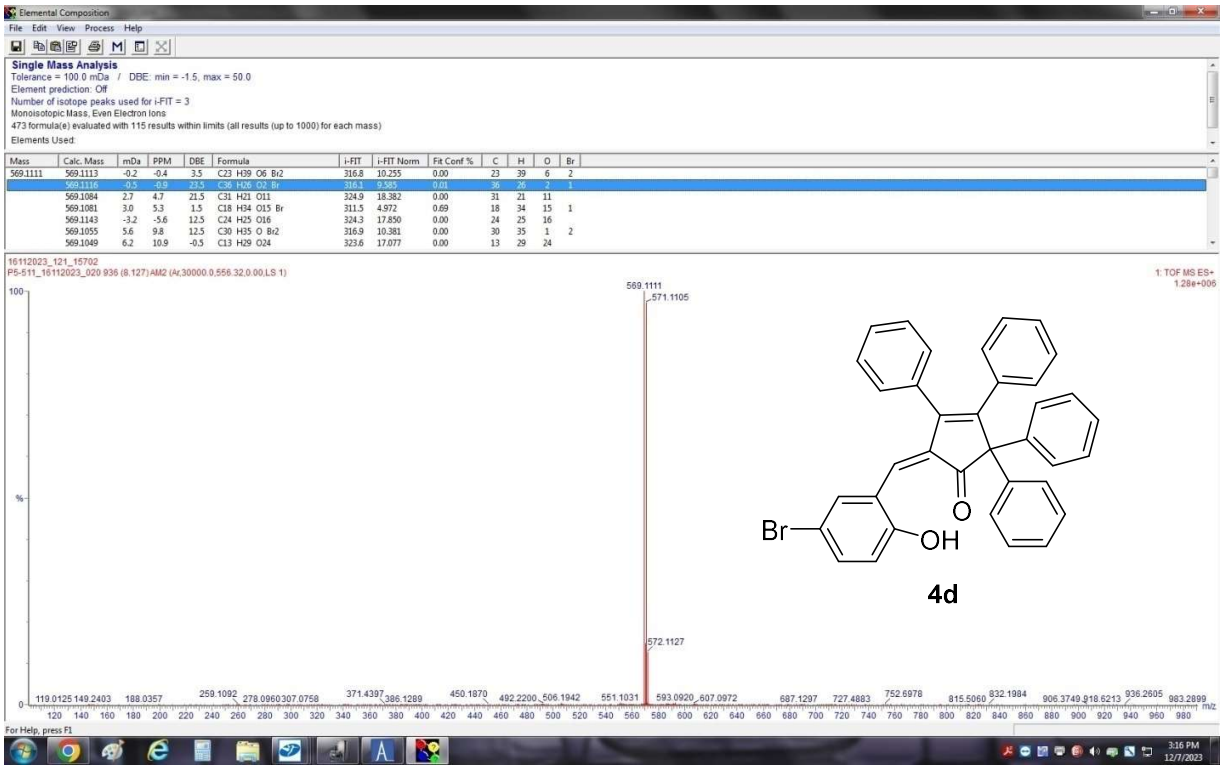

Elemental Composition
Single Mass Analysis
Tolerance = 100.0 mDa / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3
Monoisotopic Mass, Even Electron Ions
755 formula(e) evaluated with 163 results within limits (all results (up to 1000) for each mass)
Elements Used:
525.1619
526.1642
527.1605
523.1453
Cl
OH
O
4c

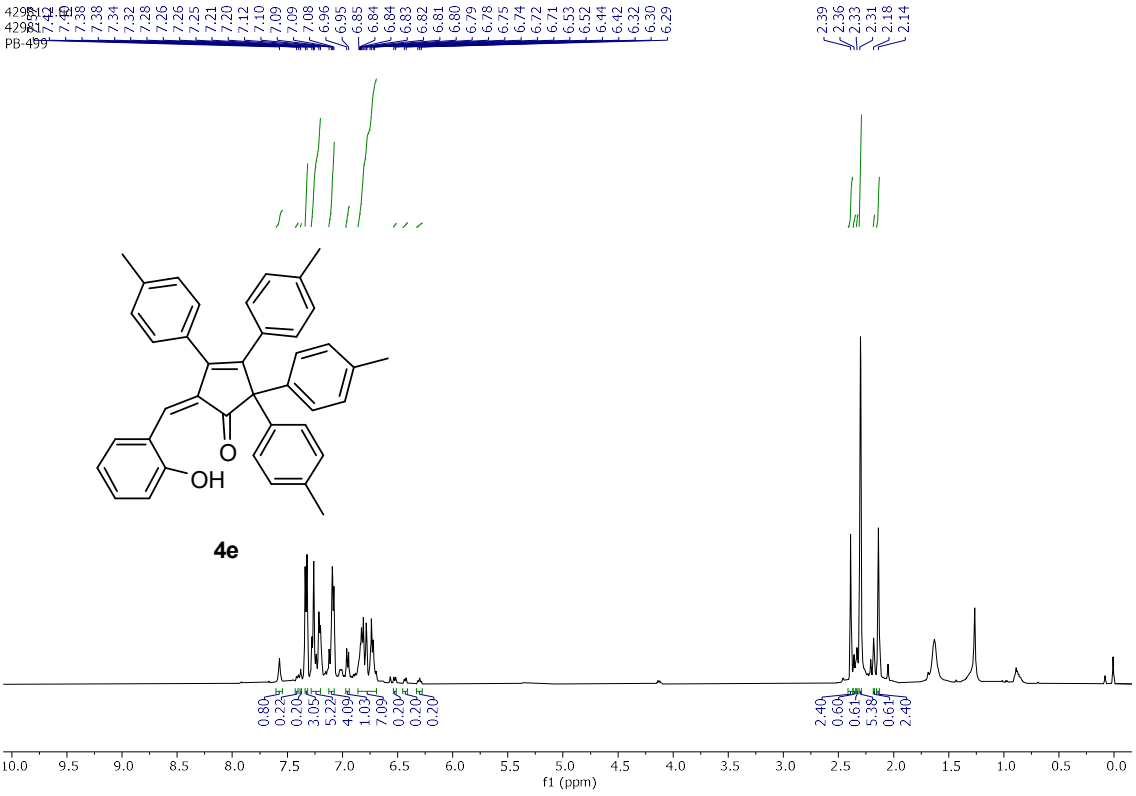

SH-511

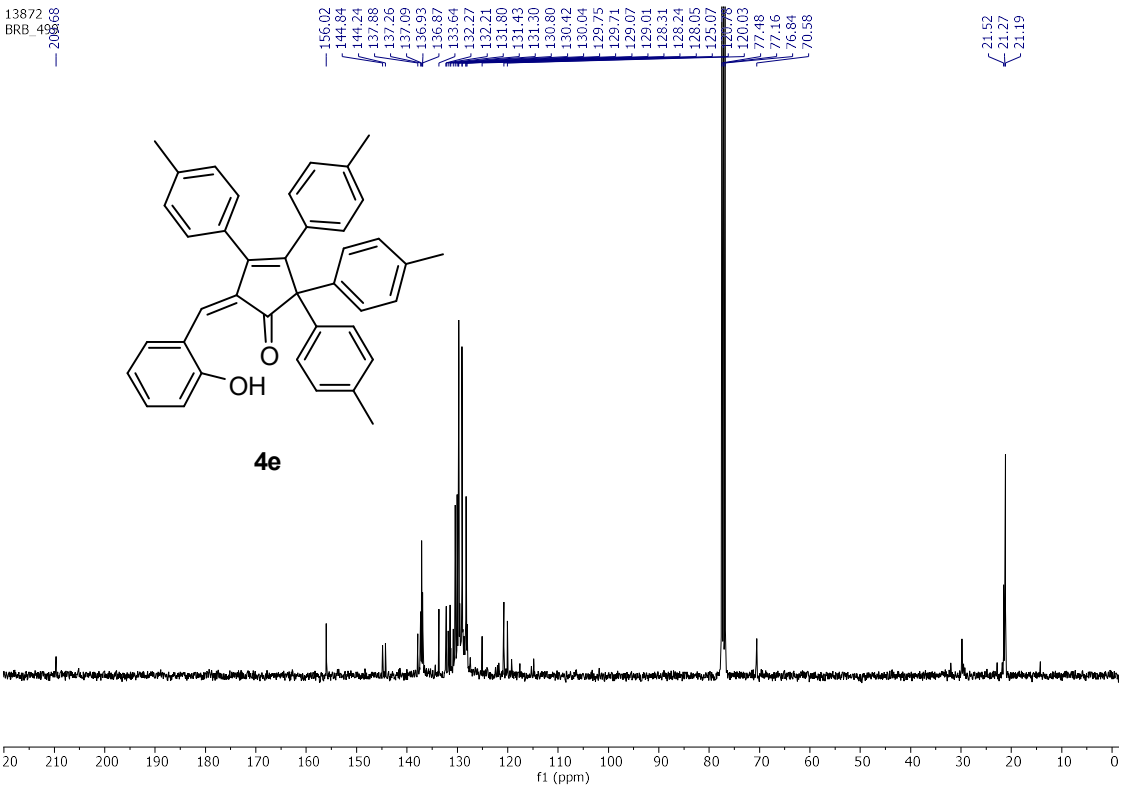

Br
OH
O
4d

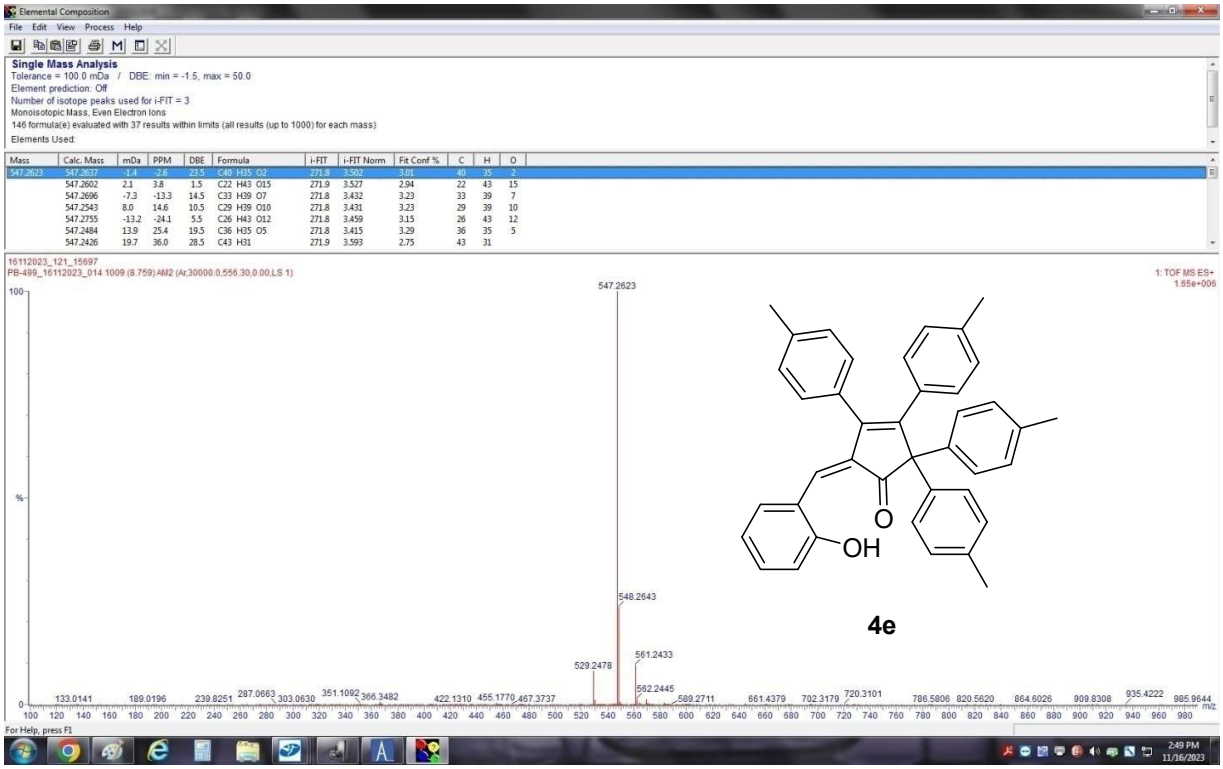

f1 (ppm)


13959
PB_511
208.49
205.37
154.85
153.42
149.31
145.43
145.30
141.96
139.87
139.47
138.03
137.33
135.05
134.71
134.65
134.51
134.46
133.96
133.74
132.49
130.74
130.63
130.46
130.12
130.06
129.83
129.78
129.37
129.07
128.48
128.41
128.15
128.01
127.89
127.69
127.65
127.57
127.53
127.38
126.41
123.31
121.14
116.65
112.85
111.42
77.48
77.16
76.84
71.51
71.37
Br
OH
O
4d
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

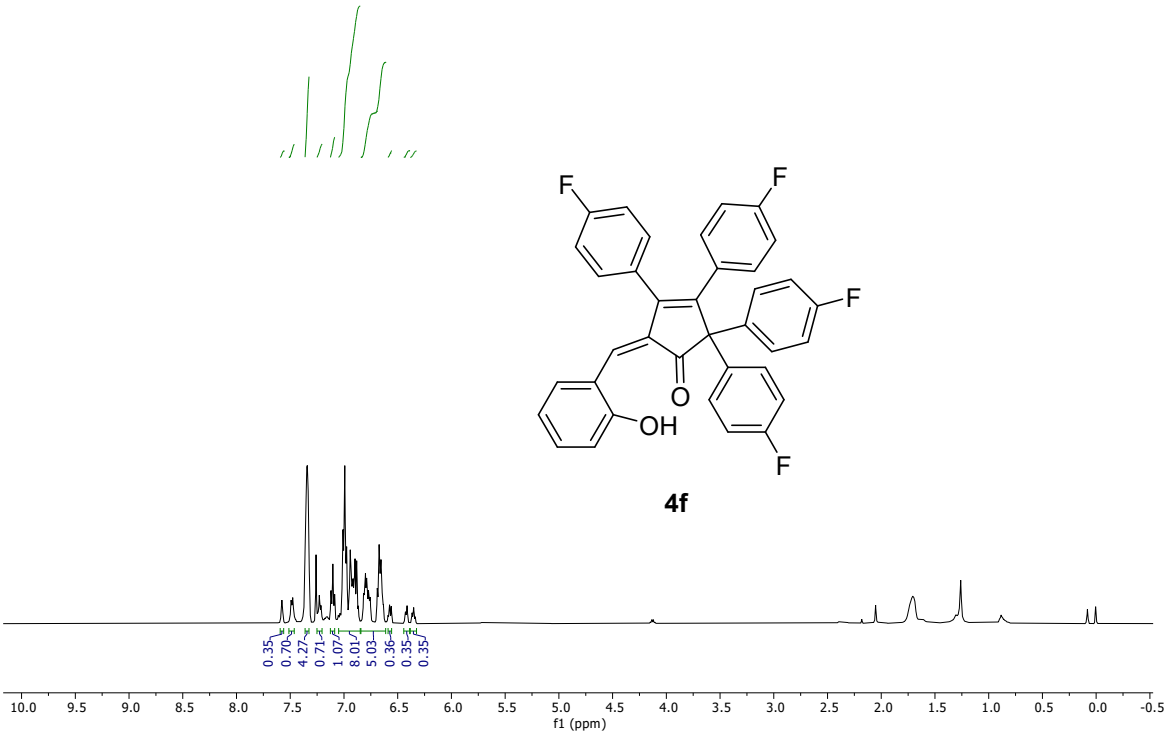

Elemental Composition
File Edit View Process Help
Single Mass Analysis
Tolerance = 100.0 mDa / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3
Monoisotopic Mass, Even Electron Ions
473 formula(e) evaluated with 115 results within limits (all results (up to 1000) for each mass)
Elements Used:
Mass Calc. Mass mDa PPM DBE Formula i-FIT i-FIT Norm Fit Conf % C H O Br
569.1111 569.1113 -0.2 -0.4 23.5 C33 H39 O6 Br2 316.8 10.255 0.00 23 39 6 2
569.1116 0.3 0.9 23.5 C36 H26 O2 Br 316.1 9.585 0.01 36 26 2 1
569.1084 2.7 4.7 21.5 C31 H21 O11 324.9 18.382 0.00 31 21 11
569.1081 3.0 5.3 1.5 C18 H34 O15 Br 311.5 4.972 0.69 18 34 15 1
569.1143 -3.2 -5.6 12.5 C24 H25 O16 324.3 17.850 0.00 24 25 16
569.1055 5.6 9.8 12.5 C30 H35 O Br2 316.9 10.381 0.00 30 35 1 2
569.1049 6.2 10.9 -0.5 C13 H29 O24 323.6 17.077 0.00 13 29 24
16112023_121_15702
P5-511_16112023_020 936 (8.127) AM2 (Ar,30000.0,556.32,0.00,LS 1)
1: TOF MS ES+
1.29e+006
569.1111
571.1105
572.1127
Br
OH
O
4d
For Help, press F1
3:16 PM
12/7/2023


PB-499
7.42
7.38
7.34
7.32
7.28
7.26
7.25
7.21
7.20
7.12
7.10
7.09
7.09
7.08
6.96
6.95
6.85
6.84
6.84
6.83
6.82
6.81
6.80
6.79
6.78
6.75
6.74
6.72
6.71
6.53
6.52
6.44
6.42
6.32
6.30
6.29
2.39
2.36
2.33
2.31
2.18
2.14
O
OH
4e
0.80
0.23
0.20
3.05
5.22
4.09
1.03
7.09
0.20
0.20
0.20
2.40
0.60
0.61
5.38
0.61
2.40
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
f1 (ppm)

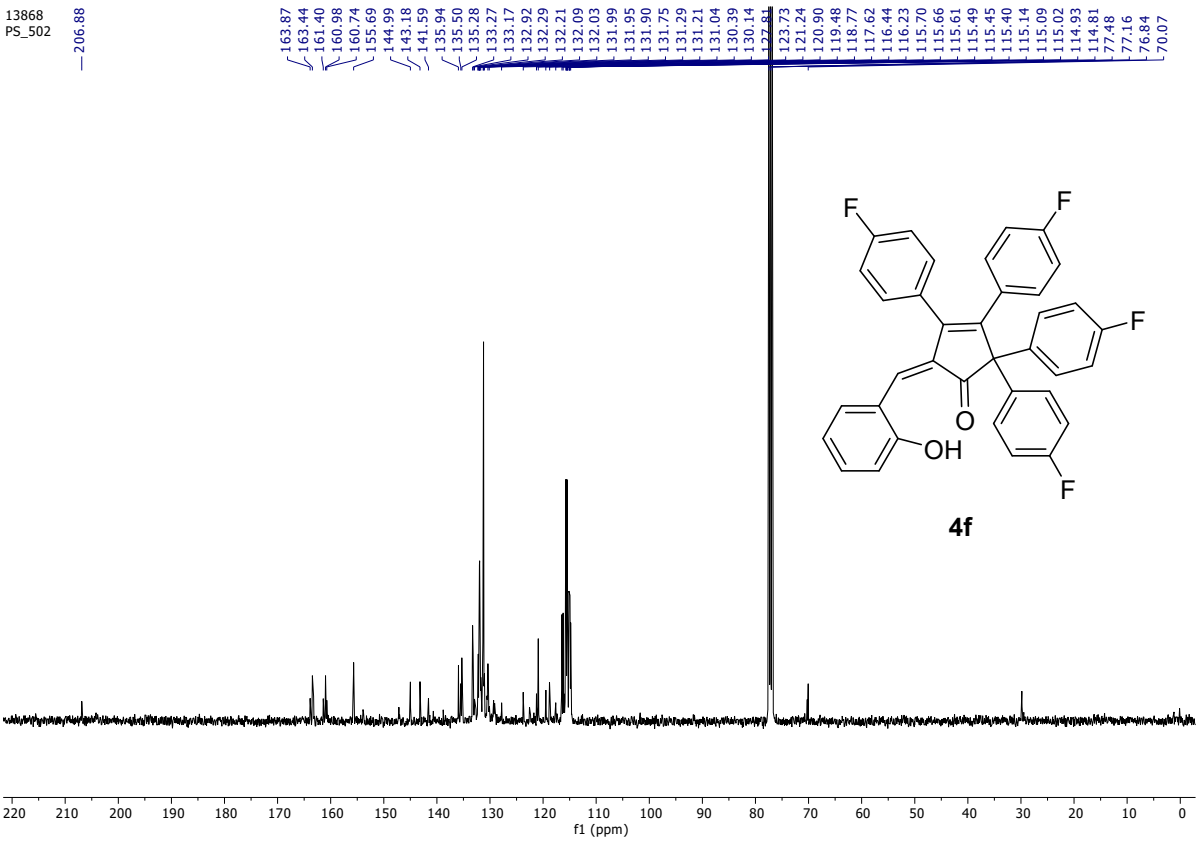

13872
BRB_499
209.68
156.02
144.84
144.24
137.88
137.26
137.09
136.93
136.87
133.64
132.27
132.21
131.80
131.43
131.30
130.80
130.42
130.04
129.75
129.71
129.07
129.01
128.31
128.24
128.05
125.07
120.03
77.48
77.16
76.84
70.58
21.52
21.27
21.19
O
OH
4e
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

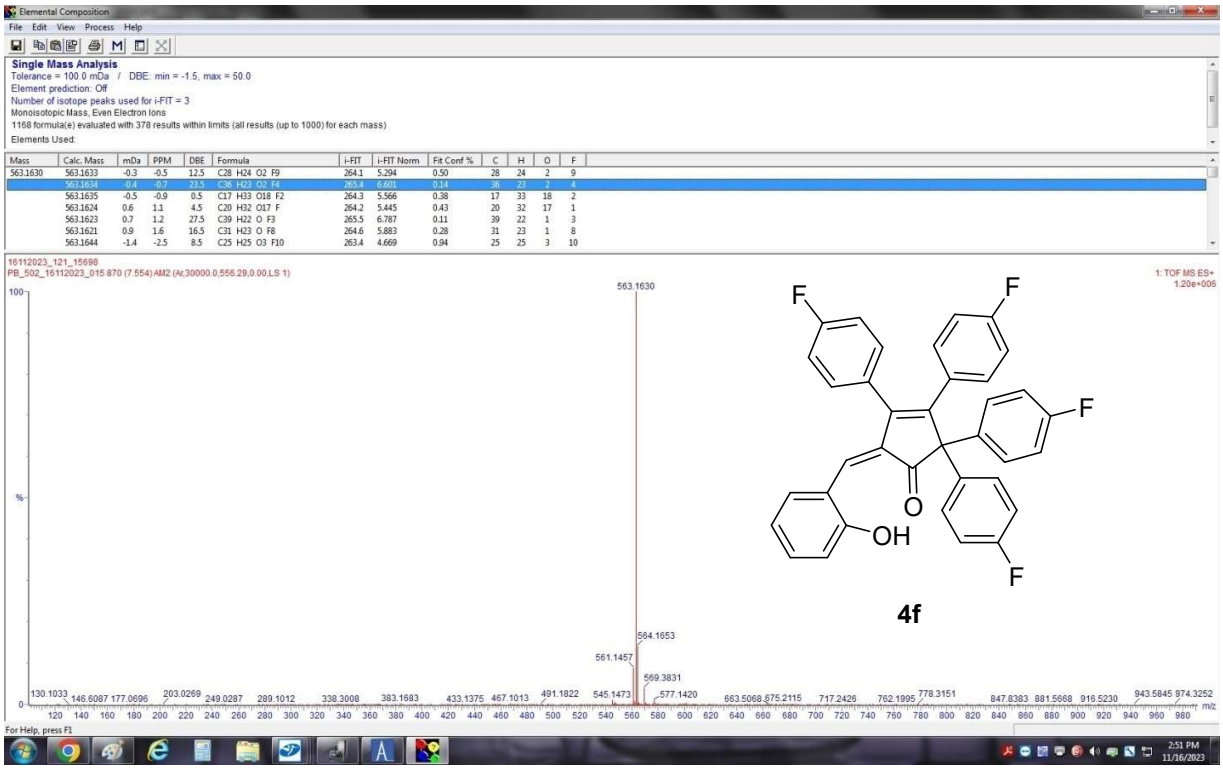

Elemental Composition
Single Mass Analysis
Tolerance = 100.0 mDa / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3
Monoisotopic Mass, Even Electron Ions
146 formula(e) evaluated with 37 results within limits (all results (up to 1000) for each mass)
Elements Used:
547.2623
548.2643
561.2433
529.2478
562.2445
O
OH

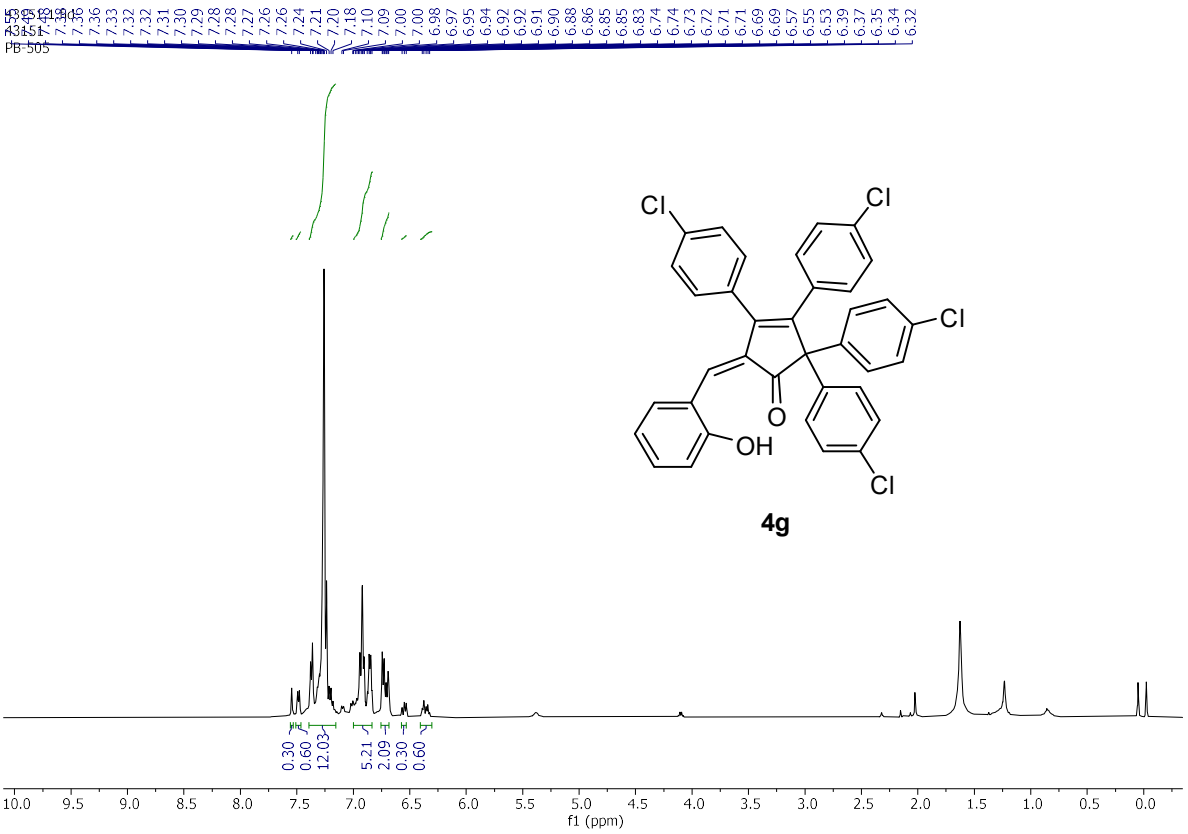
4e

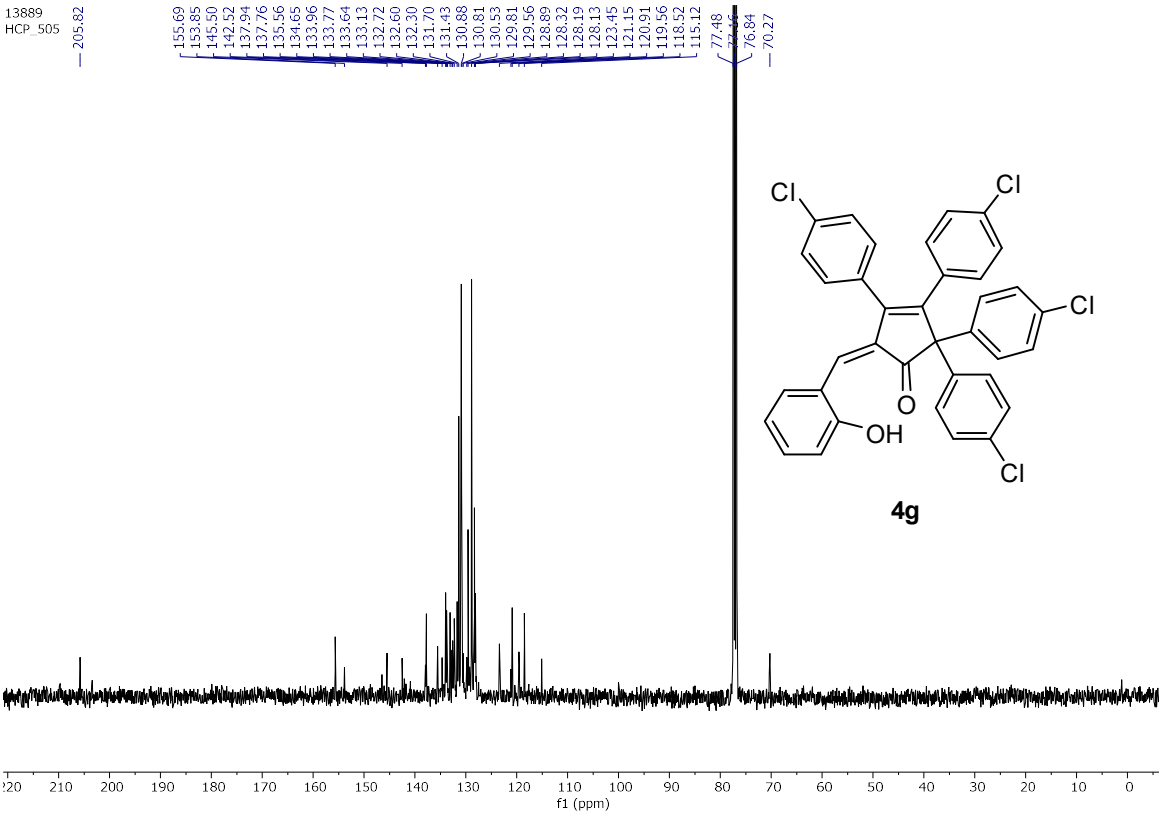

F
F
F
F
O
OH
f1 (ppm)

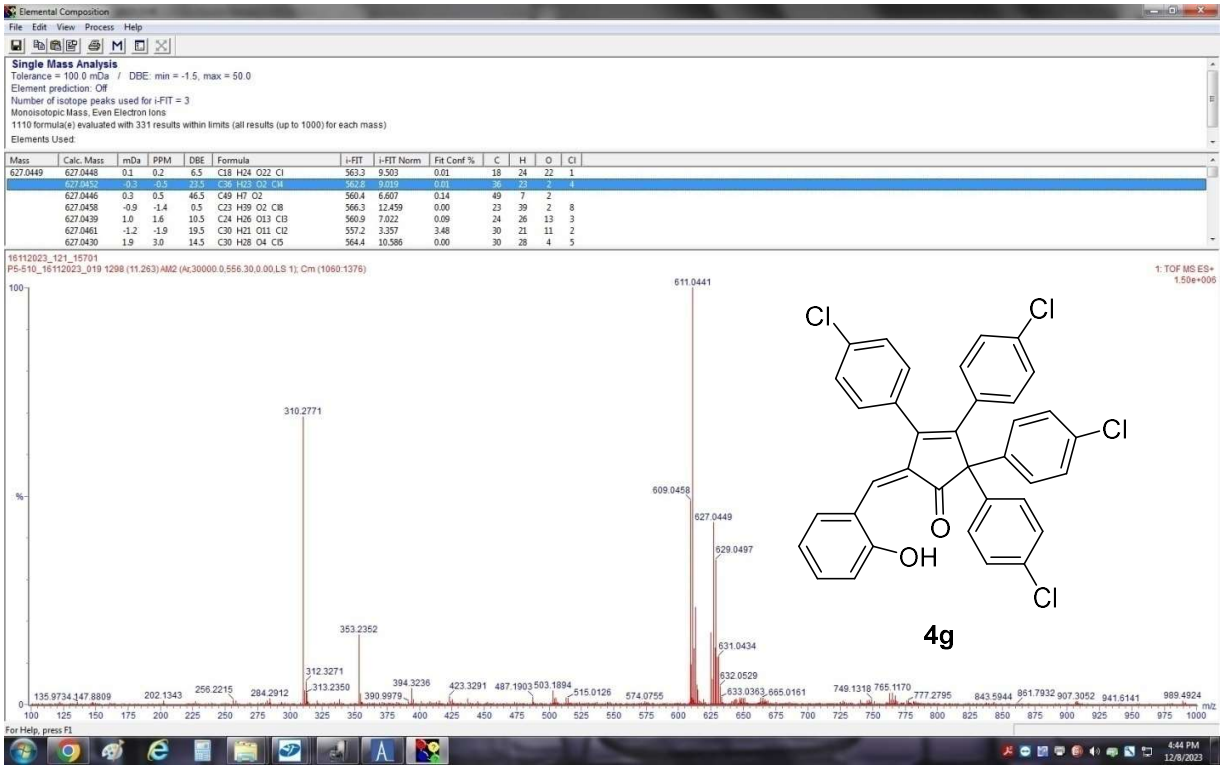
4f

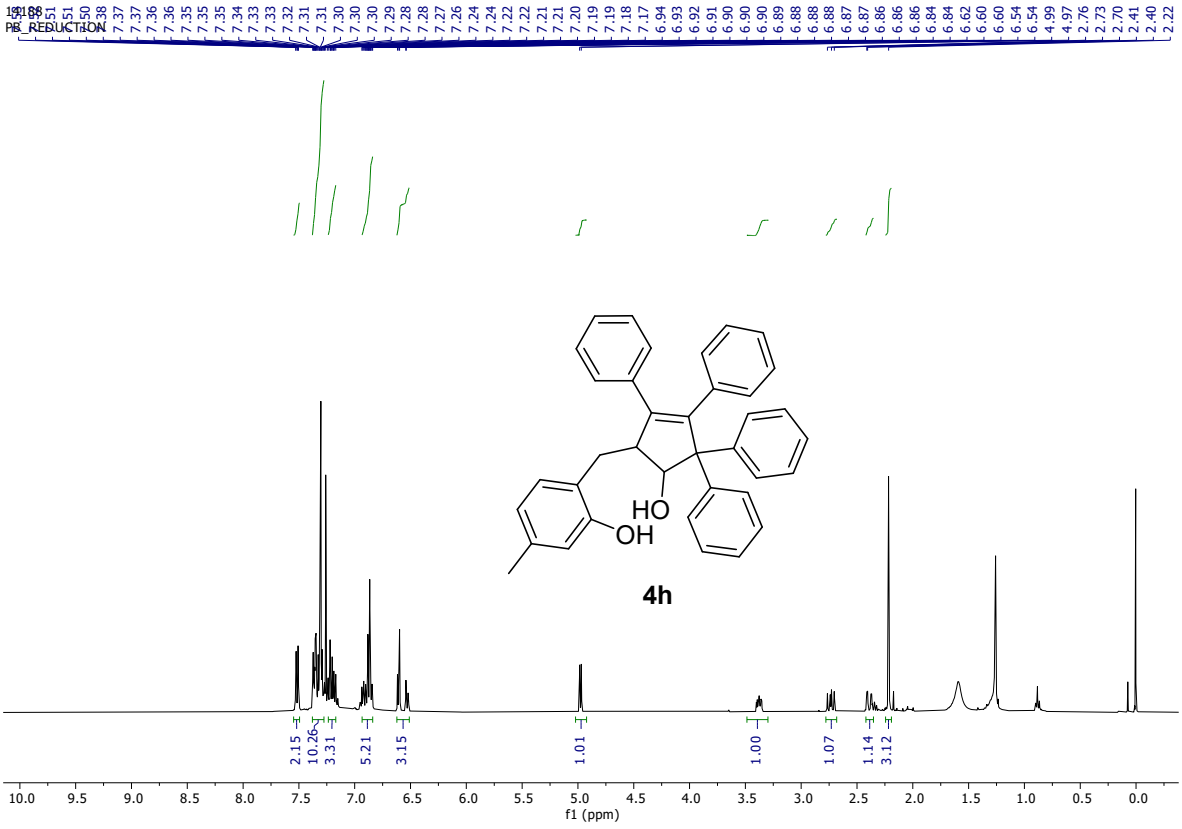

13868
PS_502
206.88
163.87
163.44
161.40
160.98
160.74
155.69
144.99
143.18
141.59
135.94
135.50
135.28
133.27
133.17
132.92
132.29
132.21
132.09
132.03
131.99
131.95
131.90
131.75
131.29
131.21
131.04
130.39
130.14
127.81
123.73
121.24
120.90
119.48
118.77
117.62
116.44
116.23
115.70
115.66
115.61
115.49
115.45
115.40
115.14
115.09
115.02
114.93
114.81
77.48
77.16
76.84
70.07
F
F
F
O
OH
F
4f
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

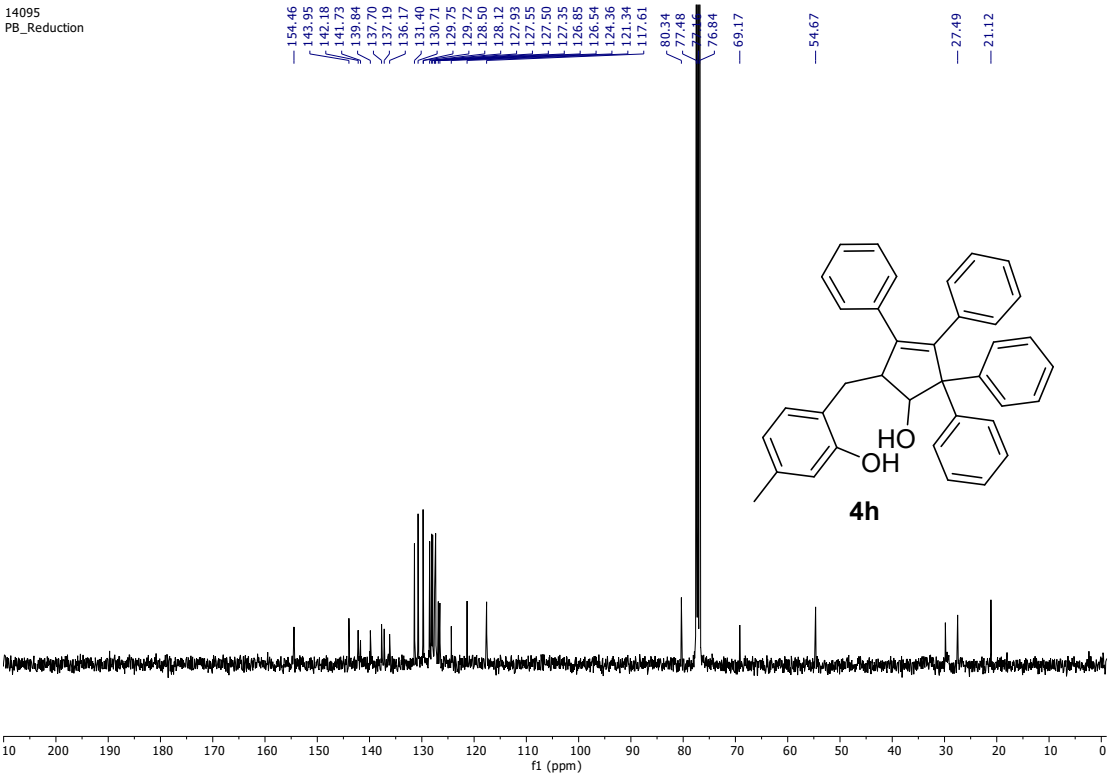

Elemental Composition
File Edit View Process Help
Single Mass Analysis
Tolerance = 100.0 mDa / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3
Monoisotopic Mass, Even Electron Ions
1168 formula(e) evaluated with 378 results within limits (all results (up to 1000) for each mass)
Elements Used:
Mass Calc. Mass mDa PPM DBE Formula i-FIT i-FIT Norm Fit Conf % C H O F
563.1630 563.1633 -0.3 -0.5 12.5 C28 H24 O2 F9 264.1 5.294 0.50 28 24 2 9
563.1634 -0.4 -0.7 23.5 C36 H23 O2 F4 265.4 6.601 0.14 36 23 2 4
563.1635 -0.5 -0.9 0.5 C17 H33 O18 F2 264.3 5.566 0.38 17 33 18 2
563.1624 0.6 1.1 4.5 C20 H32 O17 F 264.2 5.445 0.43 20 32 17 1
563.1623 0.7 1.2 27.5 C39 H22 O F3 265.5 6.787 0.11 39 22 1 3
563.1621 0.9 1.6 16.5 C31 H23 O F8 264.6 5.883 0.28 31 23 1 8
563.1644 -1.4 -2.5 8.5 C25 H25 O3 F10 263.4 4.669 0.94 25 25 3 10
16112023_121_15698
PB_502_16112023_015 870 (7.554) AM2 (Ar,30000.0,556.29,0.00,LS 1)
1: TOF MS ES+
1.20e+006
100
%
0
563.1630
564.1653
561.1457
569.3831
130.1033
146.6087
177.0696
203.0269
249.0287
289.1012
338.3008
383.1683
433.1375
467.1013
491.1822
545.1473
577.1420
663.5068
675.2115
717.2426
762.1995
778.3151
847.8383
881.5668
916.5230
943.5845
974.3252
m/z
F
F
F
O
OH
F
4f
For Help, press F1
2:51 PM
11/16/2023

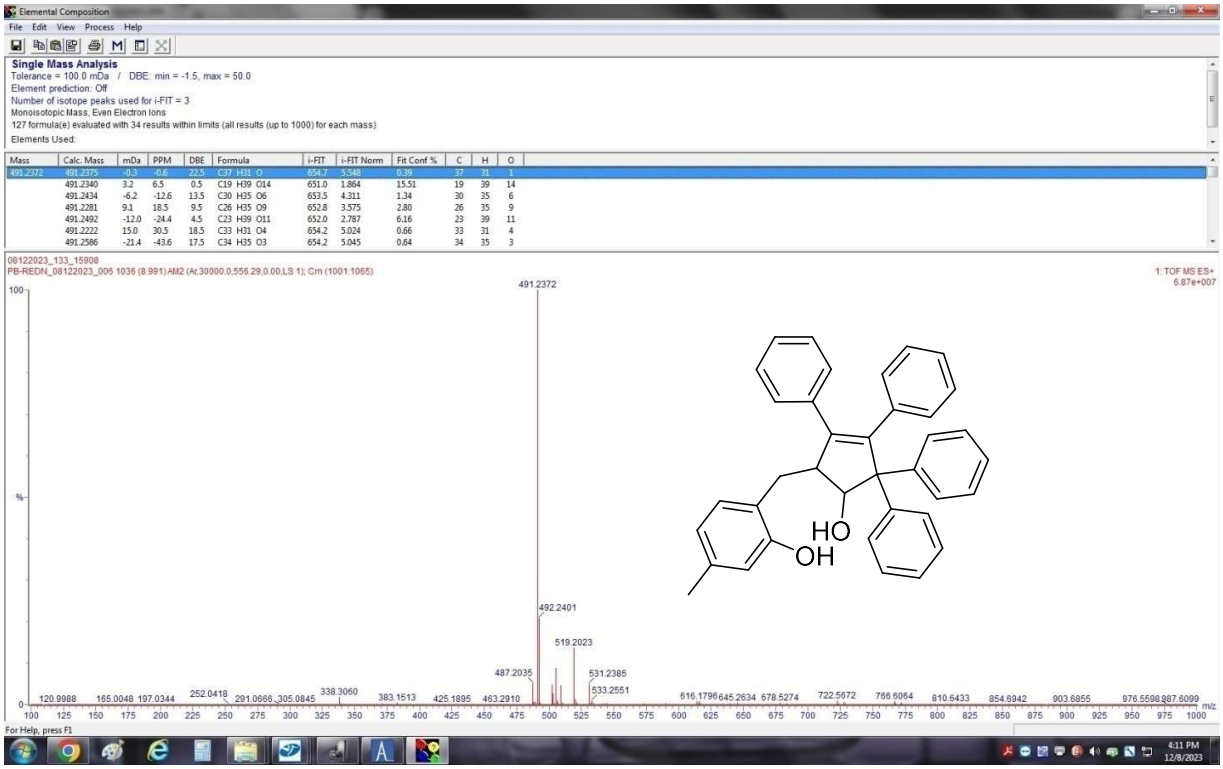

PB-505
Cl
Cl
Cl
Cl
O
OH
4g
0.30
0.60
12.03
5.21
2.09
0.30
0.60
f1 (ppm)


13889
HCP_505
205.82
155.69
153.85
145.50
142.52
137.94
137.76
135.56
134.65
133.96
133.77
133.64
133.13
132.72
132.60
132.30
131.70
131.43
130.88
130.81
130.53
129.81
129.56
128.89
128.32
128.19
128.13
123.45
121.15
120.91
119.56
118.52
115.12
77.48
76.84
70.27
Cl
Cl
Cl
Cl
O
OH
4g
f1 (ppm)


Elemental Composition
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
1110 formula(e) evaluated with 331 results within limits (all results (up to 1000) for each mass)
Elements Used:
611.0441
310.2771
609.0458
627.0449
629.0497
353.2352
631.0434
312.3271
313.2350
394.3236
423.3291
487.1903
503.1894
515.0126
574.0755
390.9979
Cl
Cl
Cl
Cl
O
OH
4g

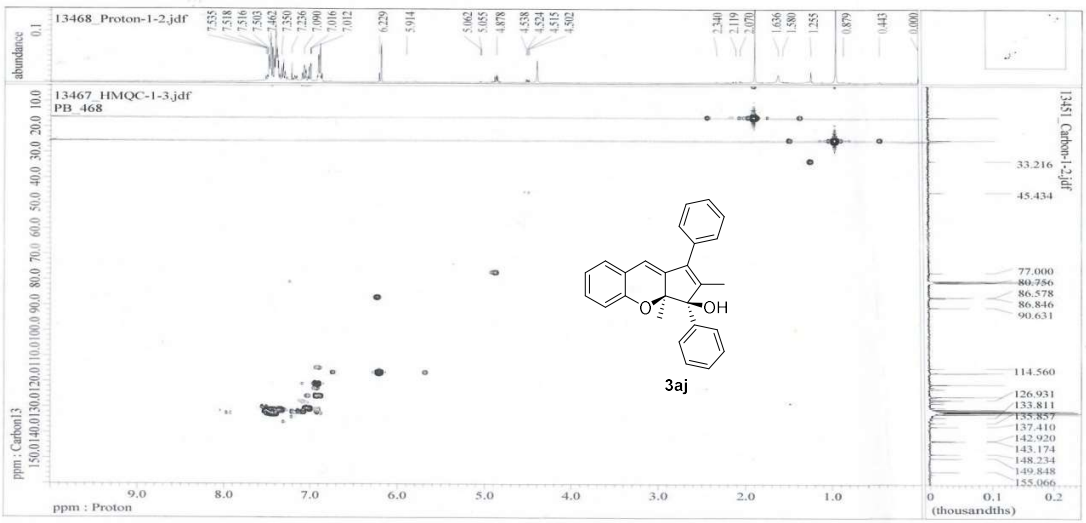

PIS_REDUCTION
HO
OH
4h
2.15
10.26
3.31
5.21
3.15
1.01
1.00
1.07
1.14
3.12
f1 (ppm)


14095
PB_Reduction
154.46
143.95
142.18
141.73
139.84
137.70
137.19
136.17
131.40
130.71
129.75
129.72
128.50
128.12
127.93
127.55
127.50
127.35
126.85
126.54
124.36
121.34
117.61
80.34
77.48
77.16
76.84
69.17
54.67
27.49
21.12
HO
OH
4h
f1 (ppm)

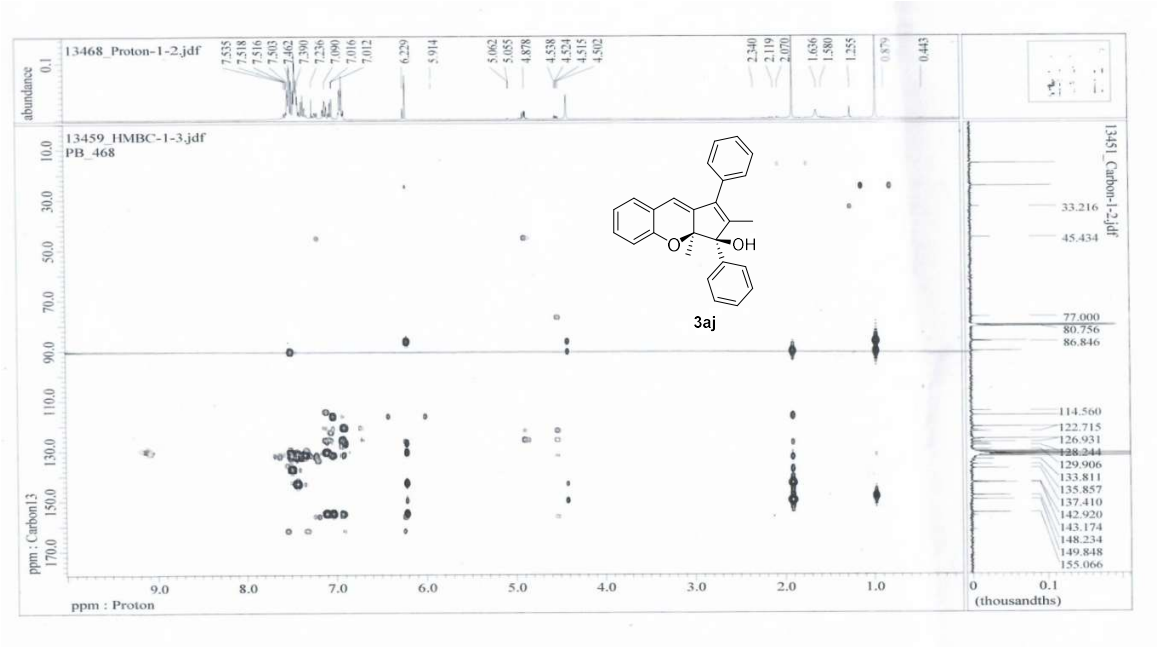

Elemental Composition
File Edit View Process Help
Single Mass Analysis
Tolerance = 100.0 mDa / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3
Monoisotopic Mass, Even Electron Ions
127 formula(e) evaluated with 34 results within limits (all results (up to 1000) for each mass)
Elements Used:
Mass Calc. Mass mDa PPM DBE Formula i-FIT i-FIT Norm Fit Conf % C H O
491.2372 491.2375 -0.3 -0.6 22.5 C37 H31 O 654.7 5.548 0.39 37 31 1
491.2340 3.2 6.5 0.5 C19 H39 O14 651.0 1.864 15.51 19 39 14
491.2434 -6.2 -12.6 13.5 C30 H35 O6 653.5 4.311 1.34 30 35 6
491.2281 9.1 18.5 9.5 C26 H35 O9 652.8 3.575 2.80 26 35 9
491.2492 -12.0 -24.4 4.5 C23 H39 O11 652.0 2.787 6.16 23 39 11
491.2222 15.0 30.5 18.5 C33 H31 O4 654.2 5.024 0.66 33 31 4
491.2586 -21.4 -43.6 17.5 C34 H35 O3 654.2 5.045 0.64 34 35 3
08122023_133_15908
PB-REDN_08122023_006 1036 (8.991) AM2 (Ar,30000.0,556.29,0.00,LS 1); Cm (1001:1065)
1: TOF MS ES+
6.87e+007
491.2372
492.2401
519.2023
487.2035
531.2385
533.2551
HO
OH
For Help, press F1

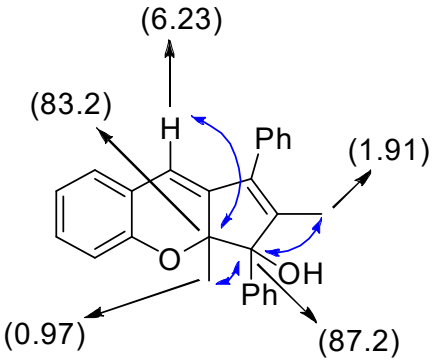
Structure determination of 3aj

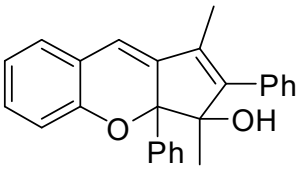
HMQC spectrum of 3aj



HMBC spectrum of 3aj

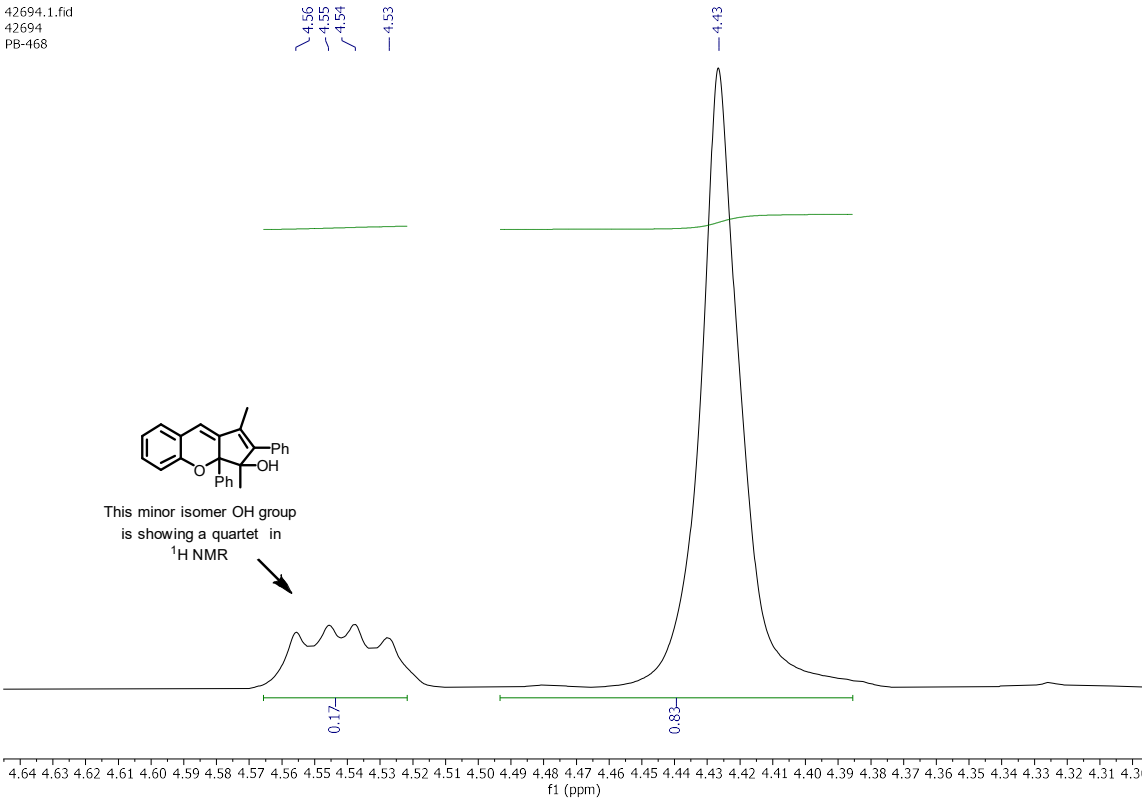






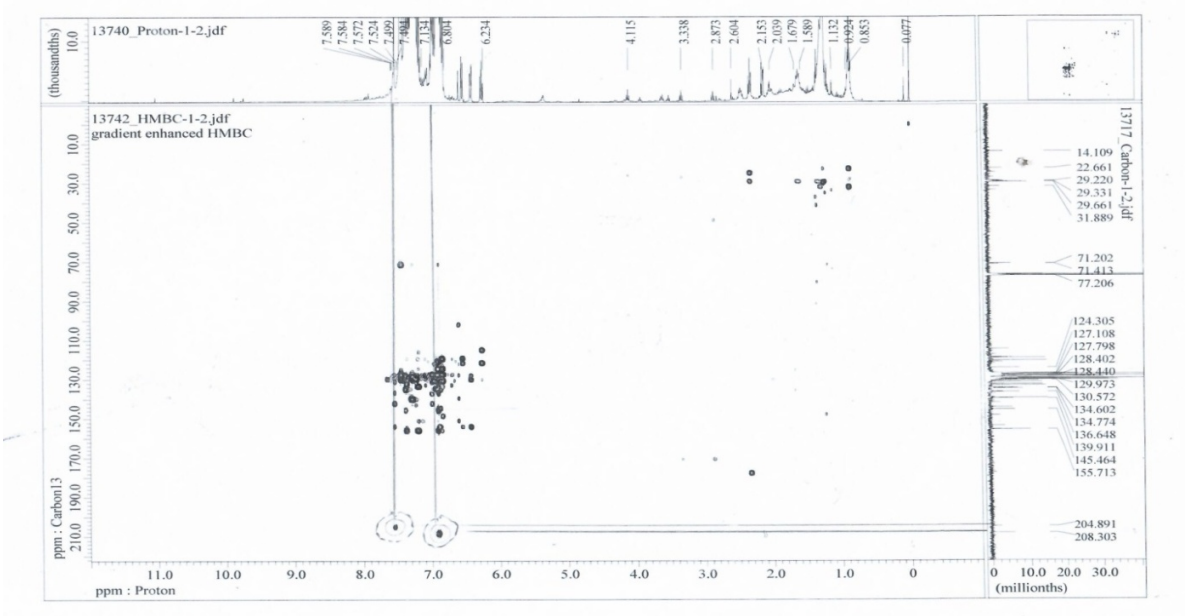
(In this minor isomer OH group is showing a quartet in ^{1}H NMR at δ 4.54)

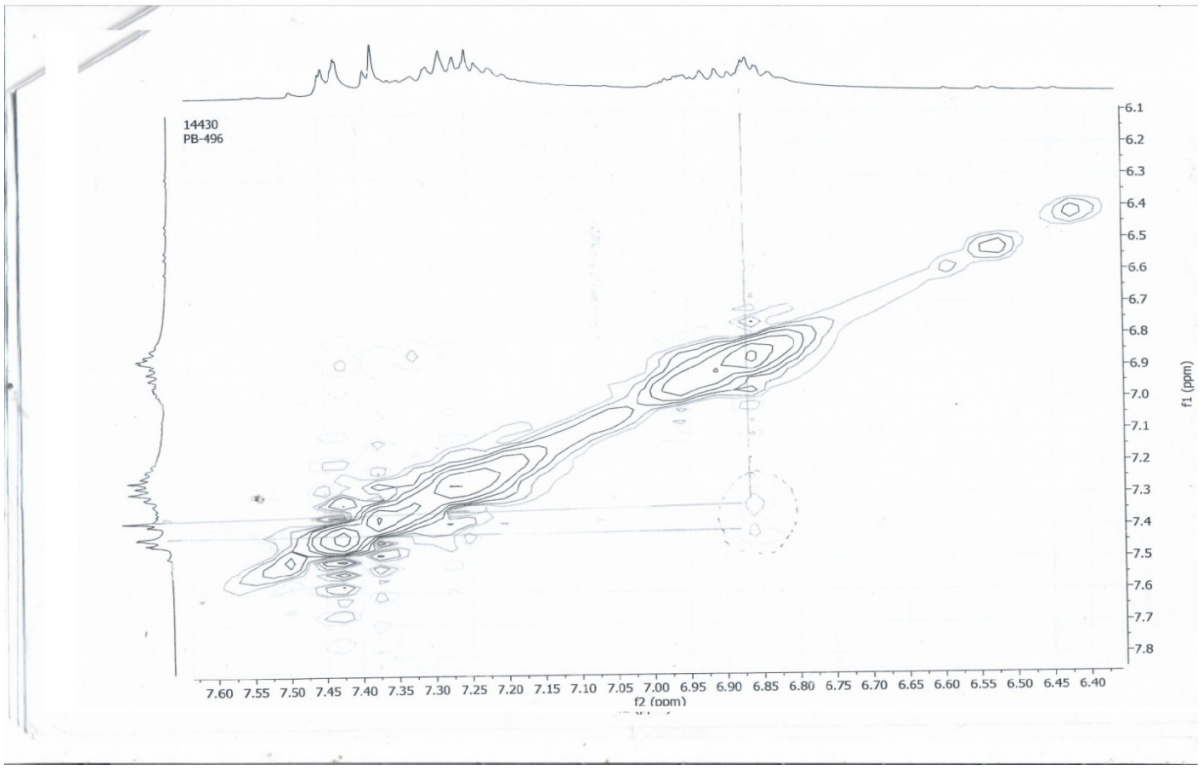
Figure 2. Major correlations in HMBC of **3aj**



Structure determination of 4a

HMBC and NOE spectra of 4a





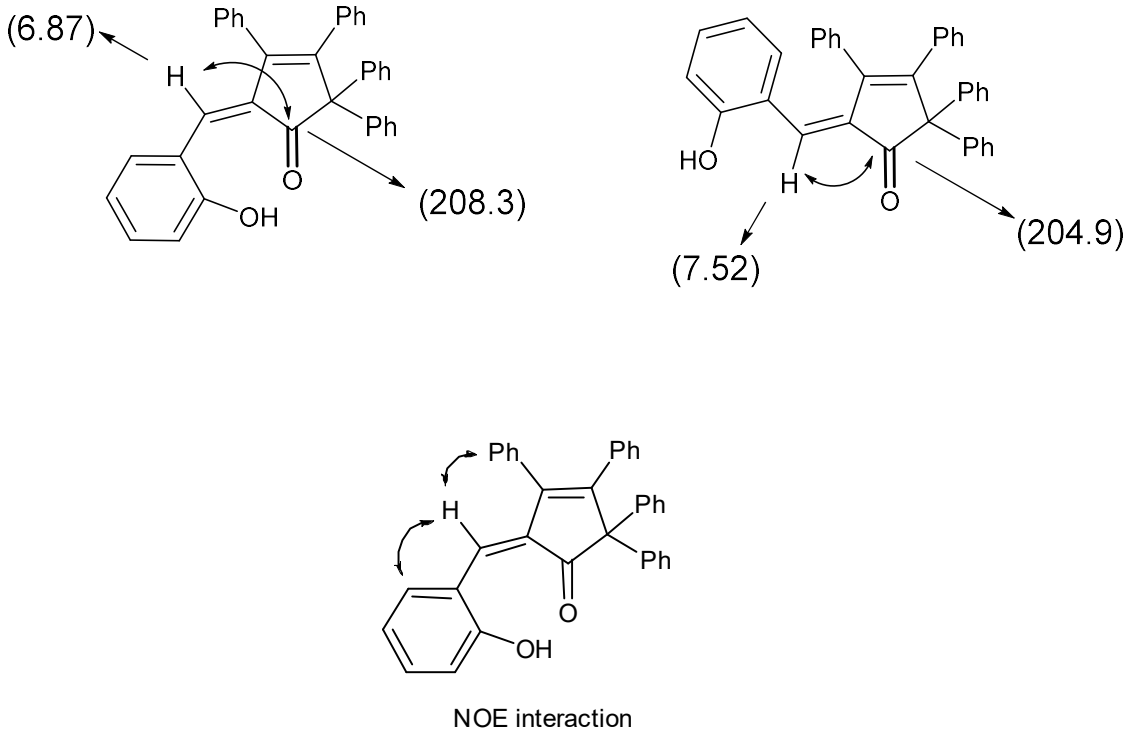
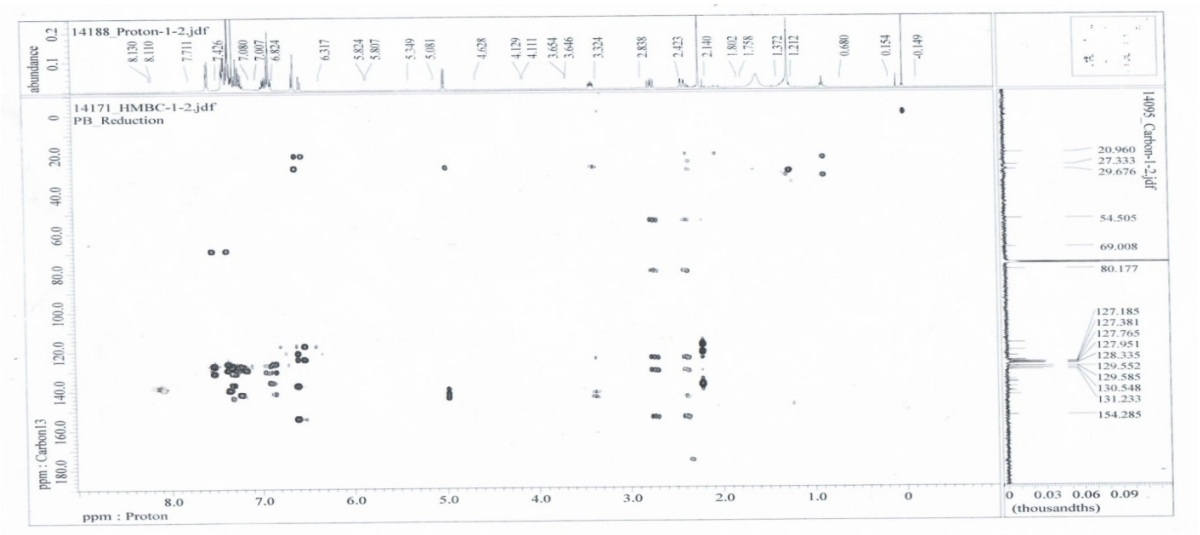
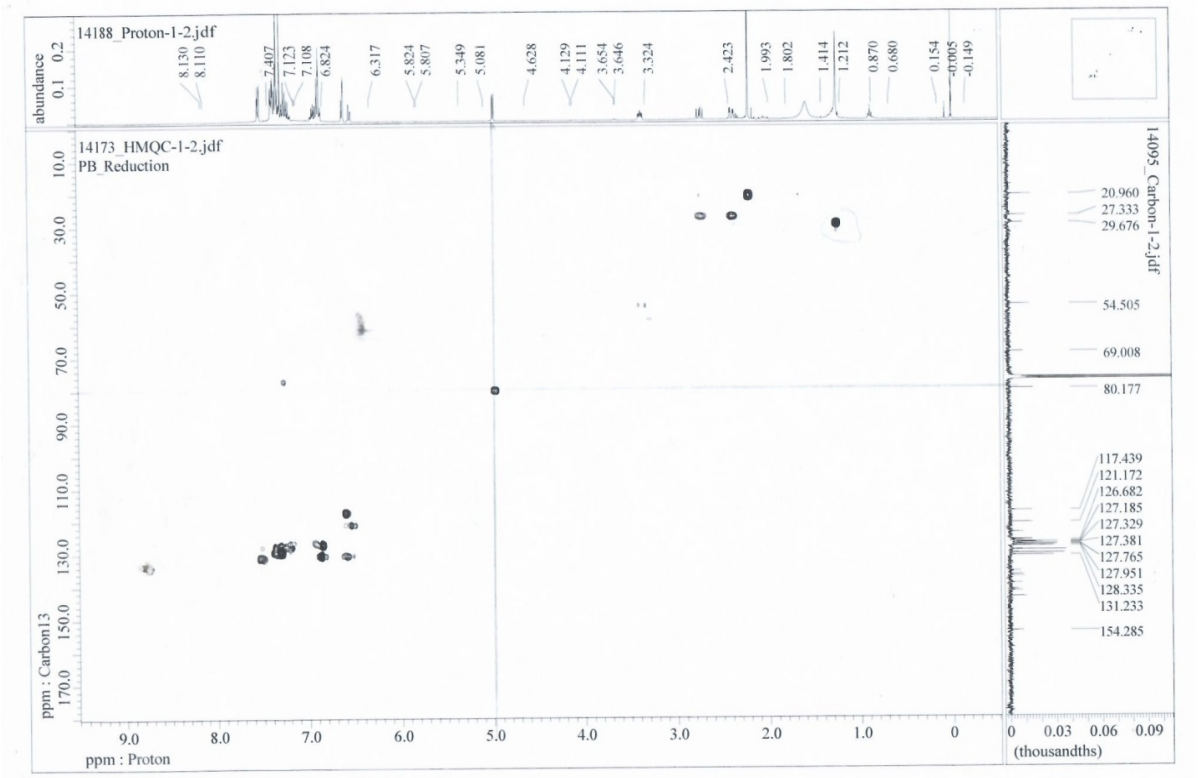


Figure 3. Major HMBC and NOE interactions of **4a**

HMBC and HMQC spectra of 4h





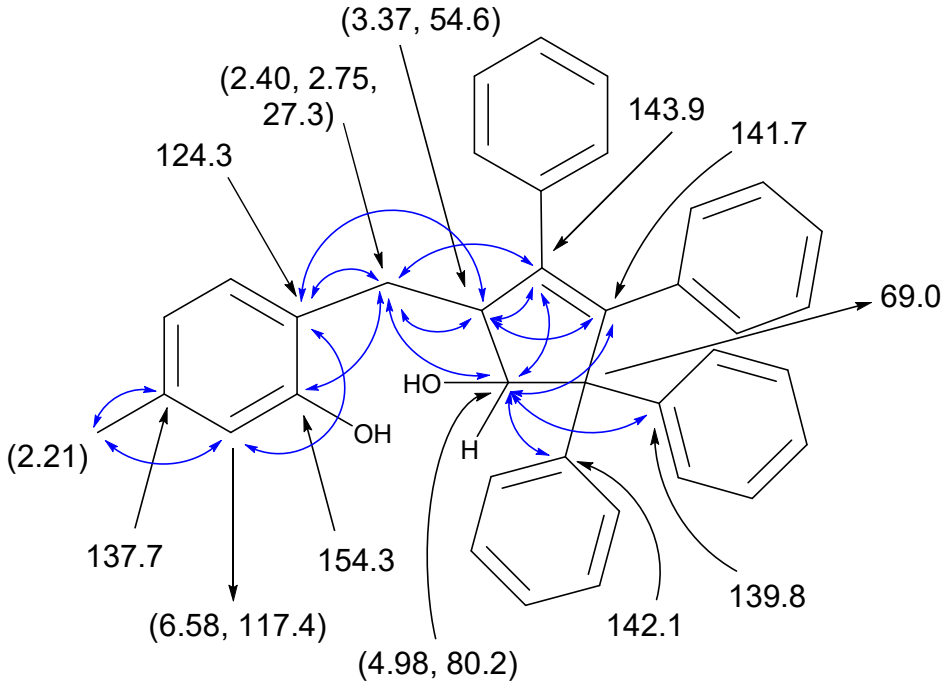
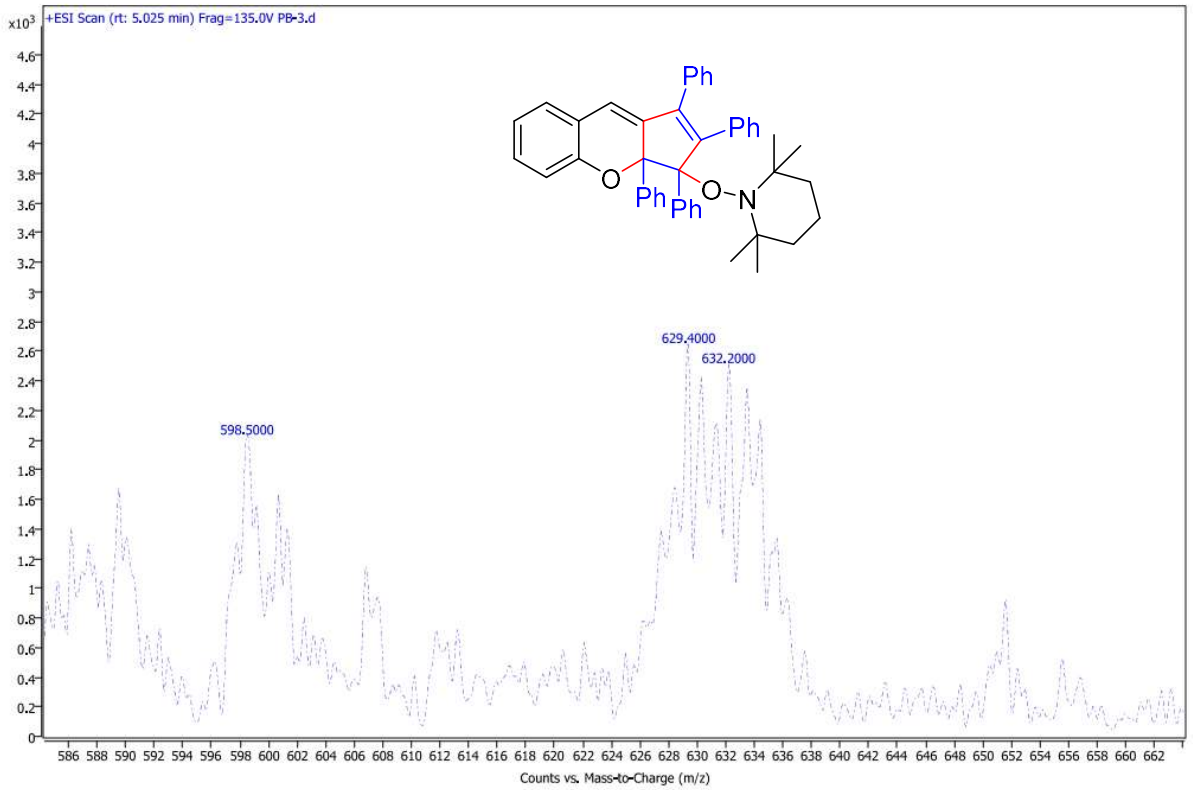


Figure 4. Significant correlations in HMBC of **4h**

User Spectrum Plot Report

Agilent Trusted Answers



Generated at 16:46 on 13-03-2024