Electronic Supplementary Material (ESI) for Chemical Science.

# Contents

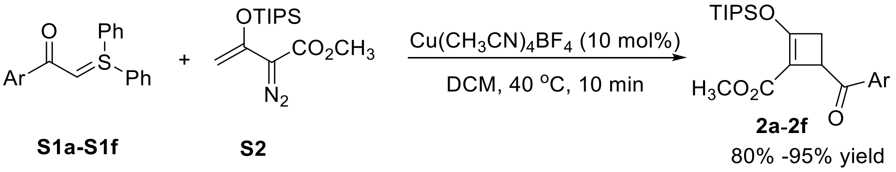
## 1. General information

All reactions, unless noted, were performed in oven-dried (120 °C) glassware with magnetic stirring under an inert atmosphere of dry nitrogen. Analytical thin layer chromatography (TLC) was carried out using EM Science silica gel 60 F254 plates; visualization was accomplished with UV light (254 nm). Column chromatography was performed on CombiFlash® Rf200 and Rf+ purification systems using normal phase disposable columns. $^{1}$H, $^{13}$C, $^{19}$F NMR spectra were recorded on a Bruker spectrometer (300 or 500 MHz). Chemical shifts were reported in ppm downfield from tetramethylsilane (TMS) with the solvent resonance as the internal standard ($CDCl_3$, $\delta = 7.26$). Spectra were reported as follows: chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, comp = composite of magnetically non-equivalent protons, dd = doublet of doublets), coupling constants (Hz), integration and assignment. $^{13}$C NMR spectra were collected on Bruker instruments (75 or 126 MHz) with complete proton decoupling. Chemical shifts are reported in ppm from the tetramethylsilane with the solvent resonance as internal standard ($CDCl_3$, $\delta = 77.0$). High-resolution mass spectra (HRMS) were performed on a Bruker MicroTOF-ESI mass spectrometer with an ESI resource using CsI or LTQ ESI positive ion calibration solution as the standard. Enantioselectivities were determined by HPLC analysis at 25 °C using an Agilent 1260 Infinity HPLC System equipped with an G1311B quaternary pump, G1315D diode array detector, G1329B auto-sampler, G1316A thermostated column compartment and G1170A valve drive. For instrument control and data processing, Agilent OpenLAB CDS ChemStation Edition for LC & LC/MS Systems (Rev. C.01.07 [26]) software was used. The Chiralpak AD-H column was obtained from Daicel Chiral Technologies. Tetrahydrofuran, dichloromethane, chloroform, and toluene were purified using a JC-Meyer solvent purification system. Optical rotations were reported as follows: $[a]_D^{23}$ (*c*: g/100 mL, in DCM).

## 2. Preparation of Reactants

1*H*-Isochromene acetals (**1**)[1], donor-acceptor cyclobutenes (**2**)[2], donor-acceptor cycloprpenes (**4**)[3], siloxyalkynes (**6**)[4], donor-acceptor azetine **9**[5] and other metallo-vinyl carbenes cycloaddition products (**10** and **11**)[6] were prepared by reported methods.

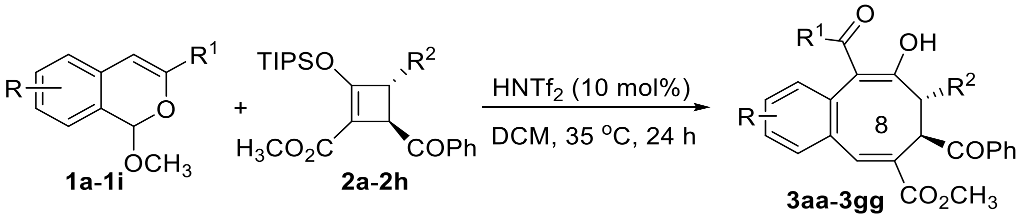
**Figure 1.** General procedure for the synthesis of Donor-Acceptor Cyclobutenes.



The modified procedure for the synthesis of donor-acceptor cyclobutenes **(2a-2f)** is described: To a solution of sulfur ylide (**S1a-S1f**, 3.0 mmol) and $Cu(CH_3CN)_4BF_4$ (94.3 mg, 0.3 mmol,10 mol% ) in 10 mL $CH_2Cl_2$ at 40 °C was slowly added a solution of enoldiazo compounds **S2** (3.6 mmol, 1.2 equiv.) in 3 mL $CH_2Cl_2$ over 5 minutes. The resulting solution was stirred at 40 °C for 10 min, after which the crude product was purified by flash chromatography (hexane/ethyl acetate = 19/1) to give donor-acceptor cyclobutenes **(2a-2f)** in excellent yield.

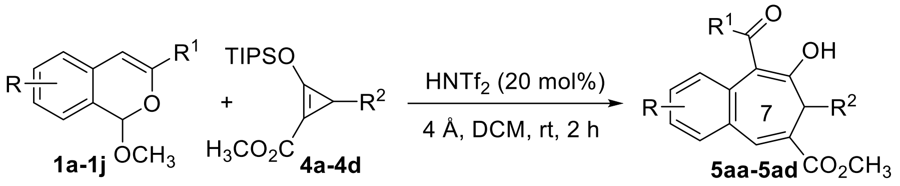
## 3. General procedure for the catalyzed [4+4]-, [4+3]- and [4+2]-cycloaddition reactions.

**Figure 2.** General procedure for the catalyzed [4+4]-cycloaddition reactions.



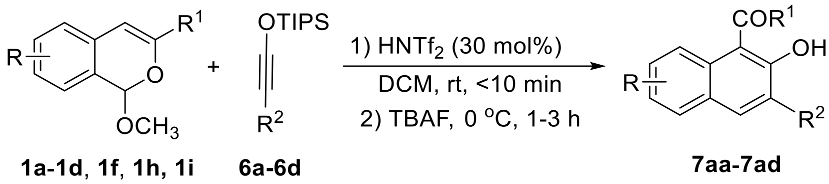
The donor-acceptor cyclobutene (**2a-2h**) (0.13 mmol, 1.3 equiv.) was dissolved in dry $CH_2Cl_2$ (1 mL), after which a solution of $HNTf_2$ (10 mol%) in dry $CH_2Cl_2$ (0.1 mL) was added slowly. The mixture was stirred at 35 °C for 5 min, then a solution of acetal compounds (**1a-1i**) (0.1 mmol, 1.0 equiv.) in 1 mL $CH_2Cl_2$ was added over 30 minutes. The reaction solution was stirred at the same temperature for 24 h, and the progress of the reaction was monitored by TLC. After complete reaction of the acetal substrate, the reaction solution was subjected to flash chromatography on silica gel with a 5:1 (v/v) mixture of hexane:ethyl acetate as the eluent to afford the desired products **3aa-3gg**.

**Figure 3.** General procedure for the catalyzed [4+3]-cycloaddition reactions.



The acetal compound (**1a-1j**) (0.2 mmol, 1.0 equiv.) and 4 Å molecular sieves (50 mg) were dissolved in dry $CH_2Cl_2$ (1 mL), and a solution of $HNTf_2$ (20 mol%) in dry $CH_2Cl_2$ (0.4 mL) was added slowly, after which a solution of donor-acceptor cyclopropene (**4a-4d**) (0.24 mmol, 1.2 equiv.) in dry $CH_2Cl_2$ (1.0 mL) was added over 5 min. The reaction solution was stirred at room temperature for 2 h, and the progress of the reaction was monitored by TLC. After complete reaction of the acetal substrate, the reaction solution was subjected to flash chromatography on silica gel with a 9:1 (v/v) mixture of hexane:ethyl acetate as the eluent to afford the desired product (**5aa-5ad)**.

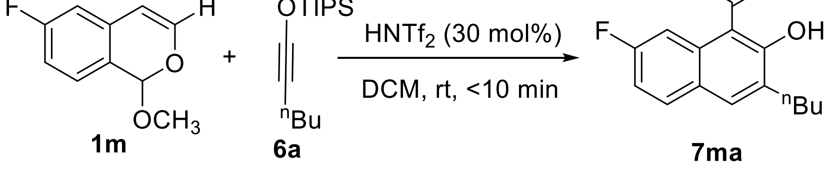
**Figure 4.** General procedure for the catalyzed [4+2]-cycloaddition reactions.



Acetal compound (**1a-1d, 1f, 1h** and **1i)** (0.2 mmol, 1.0 equiv.) and siloxyalkynes **6a-6d** (0.3 mmol, 1.5 equiv.) were dissolved in dry $CH_2Cl_2$ (2 mL), and a solution of $HNTf_2$ (20 mol%) in dry $CH_2Cl_2$ (0.4 mL) was added slowly, after which another solution of siloxyalkynes (**6a-6d**) (0.1 mmol, 0.5 equiv.) in dry $CH_2Cl_2$ (0.5 mL) was added in the reaction solution, then $HNTf_2$ (10 mol%) was slowly added to the reaction solution. The progress of the reaction was monitored by TLC.

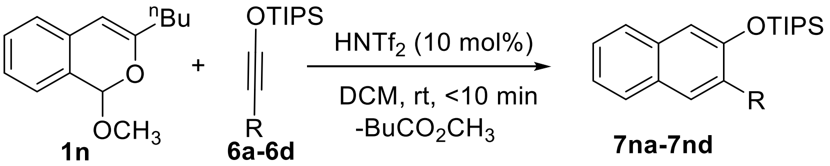
After complete reaction of the acetal substrate (<10 min), the reaction solution was cooled to 0 °C, and TBAF (0.4 mmol, 2.0 equiv., 1.0 M in THF) was added. The reaction solution was then stirred at 0 °C for 1-3 h, and the progress of the reaction was monitored by TLC. Upon completion of the reaction the solvent was removed, and the residue was subjected to flash chromatography on silica gel with a 9:1 (v/v) mixture of hexane:ethyl acetate as the eluent to afford the desired products **7aa-7ad**.

**Figure 5.** General procedure for the catalyzed [4+2]-cycloaddition reaction of **1m** with **6a**.



Acetal compound **1m** (36 mg, 0.2 mmol, 1.0 equiv.) and siloxyalkyne **6a** (76.2 mg, 0.3 mmol, 1.5 equiv.) were dissolved in dry $CH_2Cl_2$ (2 mL), and a solution of $HNTf_2$ (20 mol%) in dry $CH_2Cl_2$ (0.4 mL) was added slowly. Then another solution of siloxyalkyne **6a** (25.4 mg, 0.1 mmol, 0.5 equiv.) in dry $CH_2Cl_2$ (0.5 mL) was added in the reaction solution, after which $HNTf_2$ (10 mol%) was slowly added. The progress of the reaction was monitored by TLC. After complete reaction of the acetal substrate (<10 min), the reaction solution was subjected to flash chromatography on silica gel with a 10:1 (v/v) mixture of hexane: $CH_2Cl_2$ as the eluent to afford the desired products **7ma**.

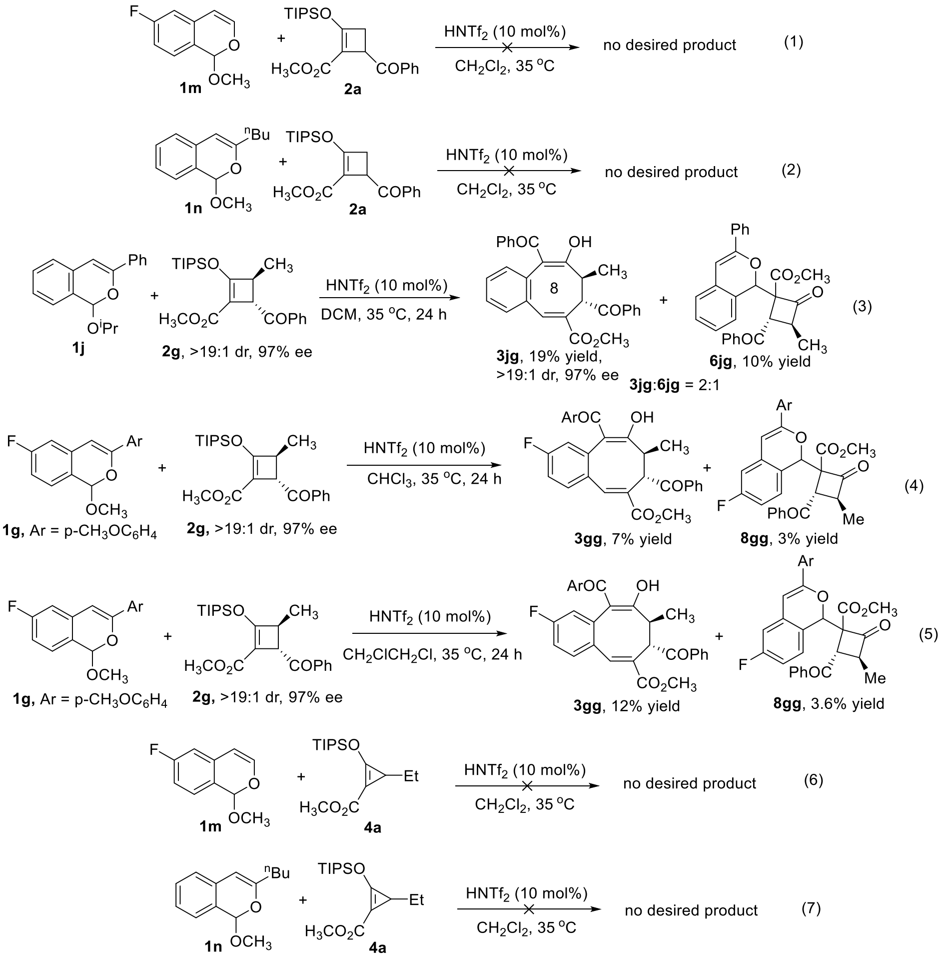
**Figure 6.** General procedure for the catalyzed [4+2]-cycloaddition reactions of **1n** with siloxyalkynes **6a-6d**.



Acetal compound **1n** (43.6 mg, 0.2 mmol, 1.0 equiv.) and siloxyalkynes **6a-6d** (0.3 mmol, 1.5 equiv.) were dissolved in dry $CH_2Cl_2$ (2 mL), and a solution of $HNTf_2$ (10 mol%) in dry $CH_2Cl_2$ (0.2 mL) was added slowly. The progress of the reaction was monitored by TLC. After complete reaction of acetal substrate (<10 min), the reaction solution was subjected to flash chromatography on silica gel with a 19:1 (v/v) mixture of hexane: ethyl acetate as the eluent to afford the desired products **7na-7nd**.

## 4. Constraints of these Brønsted acid catalyzed cycloadditions of of benzopyrylium.

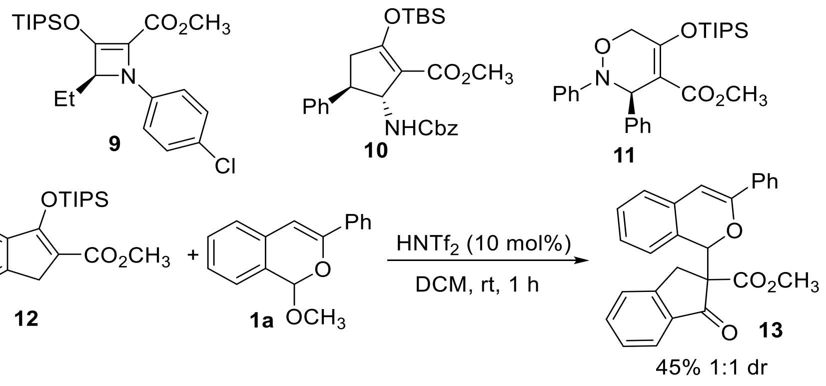
**Figure 7.** Constraints of these Brønsted acid catalyzed cycloadditions**.**



Acetal compounds **1m** and **1n** were employed in [4+4]-cycloaddition reactions with **2a** but did not produce any of the desired products. Spectral analysis showed that mostly starting material remained [Eq(1-2)]. The isopropyl acetal substrate **1j,** which forms the bulky 2-propanol nucleophile, failed to suppress the competing desilylation pathway [Eq(3)]. When $CHCl_3$ and $CH_2ClCH_2Cl$ were used as solvent, the [4+4] cycloaddition reaction was inefficient, and the desired product was isolated in only 7% and 12% yields [Eq(4-5)]. The reaction between acetal compounds **1m** and **1n** and donor-acceptor cyclopropene **4a** did not produce any of the desired products. Spectral analysis showed that mostly starting material remained [Eq(6-7)].

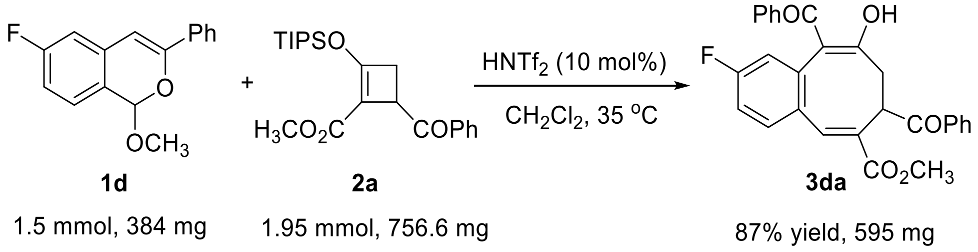
Other constraints were noted in our evaluation of this methodology (Figure 1). As expected, nitrogen-containing donor-acceptor azetine (**9**) and other metallovinylcarbenes cycloaddition products (**10** and **11**) were unreactive, and the reactants were recovered. In addition, compound **12** reacted with acetal (**1a**), giving only the direct addition product **13** in good yield, which suggests unfavorable competition for cycloaddition from desilylation.

**Figure 8.** Observed other reaction constraints.



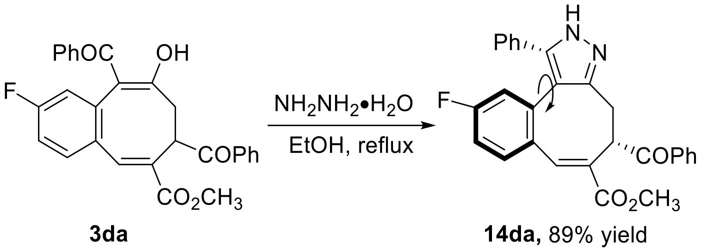
## 5. General procedure for large scale reaction, further transformations and discussion.

**Figure 9.** General procedure for large scale reaction of **1d** with **2a**.



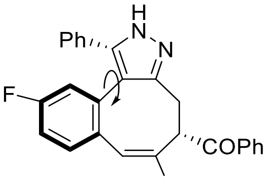
Donor-acceptor cyclobutene **2a** (756.6 mg, 1.95 mmol, 1.3 equiv.) was dissolved in dry $CH_2Cl_2$ (10 mL), after which a solution of $HNTf_2$ (10 mol%) in dry $CH_2Cl_2$ (1.5 mL) was added slowly. The solution was stirred at 35 °C for 5 min, then a solution of acetal compounds **1d** (384 mg, 1.5 mmol, 1.0 equiv.) in 5 mL $CH_2Cl_2$ was added over 30 minutes. The reaction solution was stirred at same temperature for 24 h, and the progress of the reaction was monitored by TLC. After complete reaction of the acetal substrate, the reaction solution was subjected to flash chromatography on silica gel with a 5:1 (v/v) mixture of hexane:ethyl acetate as the eluent to afford the desired product **3da** in 87% yield.

**Figure 10.** General procedure for further transformation of **3da** with Hydrazine.



A screw-capped 25-mL vial equipped with a magnetic stirring bar was loaded with compound **3da** (0.15 mmol) and anhydrous ethanol (2.5 mL). Hydrazine hydrate (45 wt. % $N_2H_4$, 0.225 mmol, 1.5 equiv.) in anhydrous ethanol (2.5 mL) was added in one portion at room temperature, and the reaction solution was stirred at 90 °C for 1 h. The progress of the reaction was monitored by TLC. After complete conversion of starting material **3da**, the solvent was evaporated, and the residue was purified by column chromatography on silica gel with a 2:1 (v/v) mixture of hexane:ethyl acetate as the eluent to afford pyrazole **14da**.

**Methyl (*E*)-5-Benzoyl-10-fluoro-1-phenyl-4,5-dihydro-2*H*-benzo[3,4]-cycloocta[1,2-*c*]pyrazole-6-carboxylate.**



**14da**

White solid (60 mg, 89% yield), 0.2 mmol scale reaction. m.p. 138 – 139 °C.

Major rotamer:

**$^1$H NMR** (500 MHz, chloroform-*d*) δ 11.57 (s, 1H), 8.05 (s, 1H), 7.60 (d, *J* = 7.5 Hz, 2H), 7.51 – 7.48 (comp., 2H), 7.38 (t, *J* = 7.5 Hz, 2H), 7.28 – 7.23 (comp., 3H), 7.18 – 7.13 (comp., 3H), 6.81 (dd, *J* = 10.0, 2.5 Hz, 1H), 4.51 (dd, *J* = 10.0, 6.0 Hz, 1H), 3.61 – 3.53 (comp., 5H).

**$^{13}$C NMR** (126 MHz, chloroform-*d*) δ 197.98, 165.46, 162.55 (d, *J* = 254 Hz, 1C), 142.14, 136.63, 135.95 (d, *J* = 9 Hz, 1C), 132.66, 131.17, 129.05, 128.98, 128.49, 128.39, 128.00, 127.89, 119.93 (d, *J* = 21 Hz, 1C), 114.62 (d, *J* = 21 Hz, 1C), 114.63, 52.04, 44.54, 25.91.

**$^{19}$F NMR** (470.5 MHz, chloroform-*d*) δ -112.2 (m, 1F).

Minor rotamer:

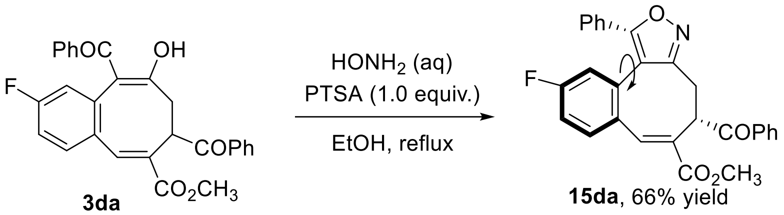
**$^1$H NMR** (500 MHz, chloroform-*d*) δ 7.90 (s, 1H), 7.65 – 7.58 (m, 1H), 7.52 – 7.48 (comp, 2H), 7.39 – 7.36 (m, 1H), 7.33 – 7.23 (comp, 3H) 7.19 – 7.13 (comp, 3H), 6.73 (t, *J* = 8.5 Hz, 1H), 6.61 (d, *J* = 8.5 Hz, 2H), 4.92 (t, *J* = 5.5 Hz, 1H), 3.88 (s, 3H), 3.45 (dd, *J* = 15.5, 5.5 Hz, 1H), 3.03 (dd, *J* = 15.5, 5.5 Hz, 1H).

**$^{13}$C NMR** (126 MHz, chloroform-*d*) δ 197.76, 167.37, 162.38 (d, *J* = 250 Hz, 1C), 142.28, 135.53, 133.37, 131.83, 130.13, 128.30, 128.18, 128.09, 118.16 (d, *J* = 21 Hz, 1C), 113.89 (d, *J* = 21 Hz, 1C), 52.78, 45.76, 25.47.

**$^{19}$F NMR** (470.5 MHz, chloroform-*d*) δ -112.6 (m, 1F).

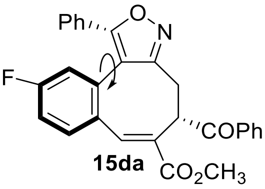
**HRMS (ESI)** scaled for $[M+H]^+$: $C_{28}H_{22}FN_2O_3$, m/z: 453.1609, observed: 453.1598.

**Figure 11.** General procedure for further transformation of **3da** with Hydroxylamine.



A screw-capped 25 mL vial equipped with a magnetic stirring bar was loaded with compound **3da** (0.1 mmol), *p*-toluenesulfonic acid monohydrate (PTSA·$H_2O$, 0.1 mmol) and anhydrous ethanol (2.5 mL). Hydroxylamine (50% wt. in water, 0.3 mmol) in anhydrous ethanol (2.5 mL) was added in one portion at room temperature, and the reaction solution was stirred at 90 °C for 3 days. After that, hydroxylamine (50% wt. in water, 0.3 mmol) in anhydrous ethanol (2.5 mL) was added again, and the reaction solution was stirred at 90 °C for an additional 3 days. Solvents were evaporated, and the residue was purified by column chromatography on silica gel with a 3:1 (v/v) mixture of hexane:ethyl acetate as the eluent to afford pyrazole **15da**.

**Methyl (*E*)-5-Benzoyl-10-fluoro-1-phenyl-4,5-dihydrobenzo[3,4]-cycloocta[1,2-*c*]isoxazole-6-carboxylate.**



**15da**

White solid (30 mg, 66% yield), 0.1 mmol scale reaction. m.p. 218 – 219 °C.

Major rotamer:

**$^1$H NMR** (500 MHz, chloroform-*d*) δ 7.97 (s, 1H), 7.64 (d, *J* = 7.2 Hz, 1H), 7.59 – 7.53 (comp., 2H), 7.51 (t, *J* = 7.0 Hz, 2H), 7.56 – 7.54 (comp., 3H), 7.36 – 7.29 (comp, 3H), 7.27 – 7.22 (comp., 1H), 7.03 (dd, *J* = 9.5, 2.5 Hz, 1H), 4.42 (dd, *J* = 12.5, 5.5 Hz, 1H), 3.75 (dd, *J* = 17.0, 12.5 Hz, 1H), 3.59 (s, 3H), 3.44 (dd, *J* = 17.0, 5.5 Hz, 1H).

**$^{13}$C NMR** (126 MHz, chloroform-*d*) δ 197.07, 167.20, 164.92, 162.80 (d, *J* = 254 Hz, 1C), 160.53, 141.02, 136.67, 135.70, 133.08, 132.66, 131.38 (d, *J* = 9 Hz, 1C), 130.13, 128.73, 128.42, 127.82, 127.51, 119.26 (d, *J* = 21 Hz, 1C), 116.25 (d, *J* = 21 Hz, 1C), 113.36, 52.10, 44.16, 25.10.

**$^{19}$F NMR** (470.5 MHz, chloroform-*d*) δ -110.9 (m, 1F).

Minor rotamer:

**$^1$H NMR** (500 MHz, chloroform-*d*) δ 7.86 (s, 1H), 6.93 (td, *J* = 8.5, 2.5 Hz, 1H), 6.88 (dd, *J* = 8.5, 2.5 Hz, 1H), 6.77 (dd, *J* = 8.5, 5.5 Hz, 1H), 5.11 (dd, *J* = 7.0, 5.0 Hz, 1H), 3.86 (s, 3H), 3.55 (dd, *J* = 16.0, 5.0 Hz, 1H), 3.35 (dd, *J* = 16.0, 5.0 Hz, 1H).

**$^{13}$C NMR** (126 MHz, chloroform-*d*) δ 197.36, 166.91, 165.97, 162.60 (d, *J* = 254 Hz, 1C), 161.09, 141.23, 135.21, 133.21, 130.88, 128.39, 128.34, 127.16, 127.04, 117.78, 117.69 (d, *J* = 22 Hz, 1C), 115.49 (d, *J* = 22 Hz, 1C), 114.00, 52.88, 45.45, 23.25.

**$^{19}$F NMR** (470.5 MHz, chloroform-*d*) δ -111.5 (m, 1F).

**HRMS (ESI)** scaled for $[M+H]^+$: $C_{28}H_{21}FNO_4$, m/z: 454.1449, observed: 454.1431.

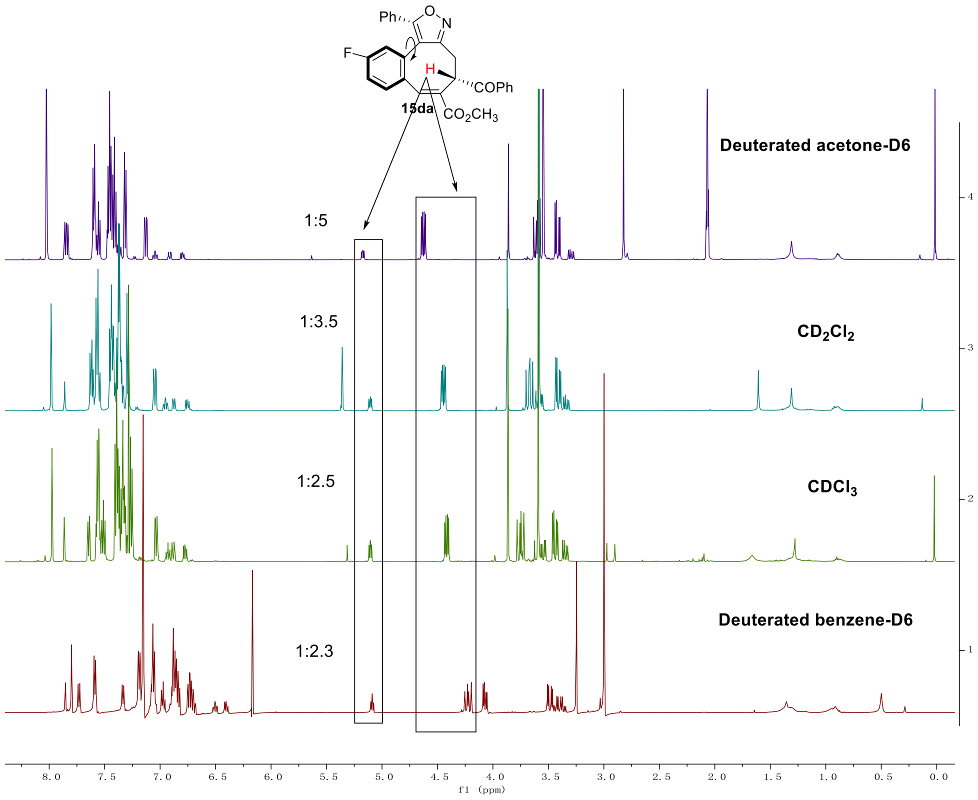


**Figure 12.** NMR spectra of compound **15da** in different deuterated solvents.

**Discussion 1.** The ratio of the proton NMR signals are different in different deuterated solvents, indicating that rotamers exists in solution of product **15da**.

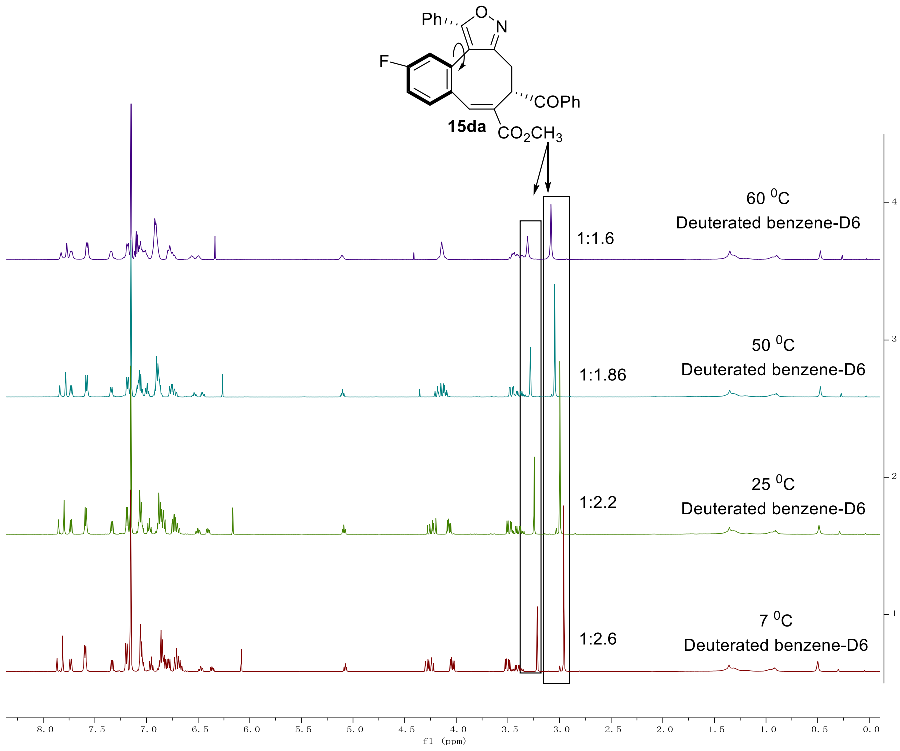


**Figure 13.** The NMR spectra of compound **15da** in different temperatures.

**Discussion 2.** The ratio of the proton NMR spectra reversibly change at different temperatures, indicating the existence of rotamers.

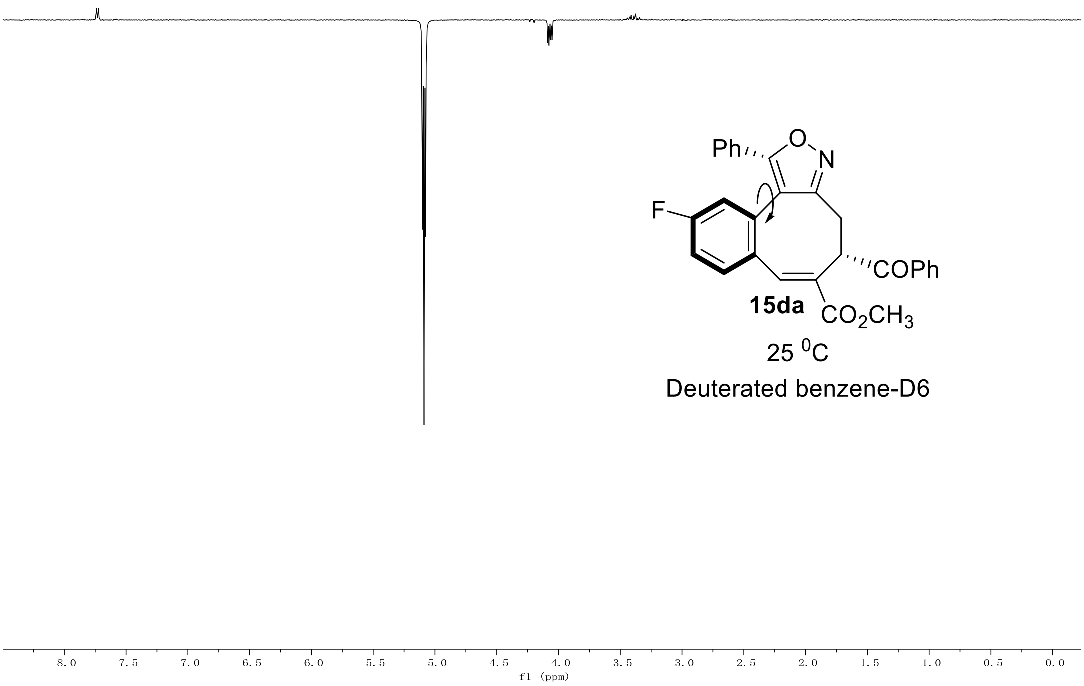
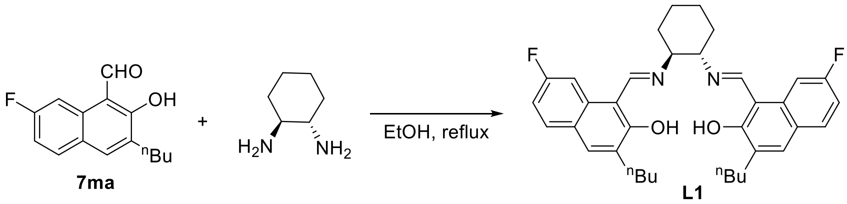


**Figure 14.** The 1D- gradient NOE spectra experiment of **15da**.

## 6. General procedure for the synthesis of salen type ligands L1 and L2

**Figure 15.** General procedure for the synthesis of salen type ligand **L1.**



**7ma**

**L1**

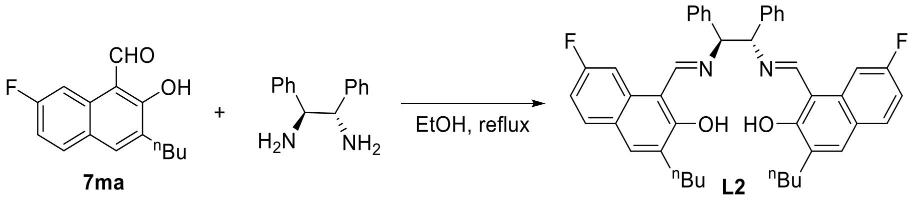
**1,1'-((1*E*,1'*E*)-(((1*S*,2*S*)-Cyclohexane-1,2-diyl)bis(azanylylidene))bis(methanylylidene))bis(3-butyl-7-fluoronaphthalen-2-ol)**

To a solution of (*S*,*S*)-1,2-cyclohexanediamine (57 mg, 0.5 mmol, 1.0 equiv.) in EtOH (5 mL) was added a solution of **7ma** (270.6, 1.1 mmol, 2.1 equiv.) in EtOH (5 mL). The suspension was refluxed for 12 h at which time a yellow solution was evident. The mixture was cooled to room temperature, and the solvent was removed. The reaction mixture was purified by flash chromatography on silica gel (15% EtOAc/hexanes) to give **L1** (151 mg, 53%) as an amorphous yellow solid: mp 60 – 61 °C.

**$^1$H NMR** (500 MHz, chloroform-*d*) δ 14.63 (s, 2H), 8.46 (s, 2H), 7.32 (dd, *J* = 8.5, 6.0 Hz, 2H), 7.26 (s, 2H), 7.22 (dd, *J* = 11.5, 2.5 Hz, 2H), 6.83 (td, *J* = 8.5, 2.5 Hz, 2H), 3.45 – 3.29 (m, 2H), 2.71 – 2.65 (m, 2H), 2.57 – 2.51 (m, 2H), 2.24 (d, *J* = 14.0 Hz, 2H), 1.96 (d, *J* = 8.5 Hz, 2H), 1.85 – 1.70 (m, 2H), 1.66 – 1.55 (m, 4H), 1.55 – 1.39 (comp., 6H), 0.97 (t, *J* = 7.5 Hz, 6H).

**$^{13}$C NMR** (126 MHz, chloroform-*d*) δ 174.27, 161.92 (d, *J* = 245 Hz, 1C), 158.76, 134.84, 134.00, 133.92, 130.19 (d, *J* = 9 Hz, 1C), 123.04, 111.35 (d, *J* = 24 Hz, 1C), 106.04 (d, *J* = 3.9 Hz, 1C), 102.90 (d, *J* = 24 Hz, 1C), 68.55, 32.44, 31.04, 29.53, 24.38, 22.81, 14.02.
**$^{19}$F NMR** (470.5 MHz, chloroform-*d*) δ -113.1 (m, 1F).
**HRMS (ESI)** scaled for $[M+H]^+$:$C_{36}H_{41}F_2N_2O_2$, m/z: 571.3131, observed: 571.3114.
**$[\alpha]_D^{23}$** = +460.98 (*c* 0.31, $CH_2Cl_2$).

**Figure 16.** General procedure for the synthesis of salen type ligand **L2.**

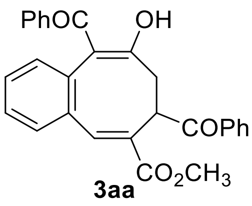


**1,1'-(1*E*,1'*E*)-[(1*S*,2*S*)-1,2-Diphenylethane-1,2-diyl)bis(azanylylidene))bis(methanylylidene)]-bis(3-butyl-7-fluoronaphthalen-2-ol)**

To a solution of (*S*,*S*)-1,2-diphenylethylenediaine (40.3 mg, 0.19 mmol, 1.0 equiv.) in EtOH (5 mL) was added a solution of **7ma** (93.5 mg, 0.38 mmol, 2 equiv.) in EtOH (5 mL). The suspension was refluxed for 12 h at which time a yellow solution was evident. The mixture was cooled to room temperature, and the solvent was removed. The crude mixture was purified by flash chromatography on silica gel (35% EtOAc/hexanes) to give **L2** (94 mg, 74%) as an amorphous yellow solid: mp 65 – 66 °C.
**$^1$H NMR** (500 MHz, chloroform-*d*) δ 15.41 (s, 2H), 8.82 (s, 2H), 7.45 – 7.38 (comp., 4H), 7.34 (s, 2H), 7.32 – 7.25 (comp., 10H), 6.93 (td, *J* = 8.5, 2.5 Hz, 2H), 4.85 (s, 2H), 2.73 – 2.57 (m, 4H), 1.69 – 1.52 (m, 4H), 1.47 – 1.40 (m, 4H), 0.99 (t, *J* = 7.5 Hz, 6H).
**$^{13}$C NMR** (126 MHz, chloroform-*d*) δ 169.12, 161.76 (d, *J* = 245 Hz, 1C), 160.84, 137.97, 133.43, 133.34, 133.16, 130.33 (d, *J* = 9.7 Hz, 1C), 128.72, 128.09, 127.76, 123.63, 111.96 (d, *J* = 24 Hz, 1C), 107.07 (d, *J* = 4 Hz, 1C), 103.31 (d, *J* = 24 Hz, 1C), 77.95, 30.96, 29.41, 22.74, 14.05.
**$^{19}$F NMR** (470.5 MHz, chloroform-*d*) δ -113.1 (m, 1F).
**HRMS (ESI)** scaled for; $[M+H]^+$:$C_{44}H_{43}F_2N_2O_2$, m/z: 669.3293, observed:669.3284.
**$[\alpha]_D^{23}$** = +134.44 (*c* 0.30, $CH_2Cl_2$).

## 7. Analytical and spectral characterization data for reaction products

### Methyl (5*E*, 9*Z*)-7,10-Dibenzoyl-9-hydroxy-7,8-dihydrobenzo[8]-annulene-6-carboxylate.



**3aa**

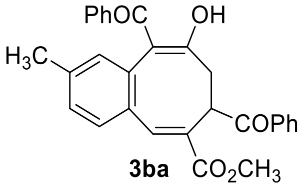
Colorless oil (33 mg, 76% yield), 0.1 mmol scale reaction.
**$^1$H NMR** (500 MHz, chloroform-*d*) δ 8.32 (s, 1H), 8.11 (d, *J* = 7.5 Hz, 2H), 7.62 (t, *J* = 7.5 Hz, 1H), 7.53 – 7.52 (comp, 3H), 7.34 – 7.31 (comp, 2H), 7.25 – 7.20 (comp, 4H), 7.04 (t, *J* = 7.5 Hz, 1H), 6.77

(d, *J* = 7.5 Hz, 1H), 5.27 (dd, *J* = 12.5, 4.5 Hz, 1H), 3.74 (s, 3H), 2.95 (t, *J* = 12.5 Hz, 1H), 2.50 (dd, *J* = 12.5, 4.5 Hz, 1H).

**$^{13}$C NMR** (126 MHz, chloroform-*d*) δ 198.2, 192.2, 186.7, 167.6, 142.3, 135.9, 135.8, 135.1, 133.9, 133.5, 132.2, 131.1, 130.7, 129.9, 129.3, 128.9, 128.8, 128.0, 127.8, 127.7, 52.5, 46.9, 37.0.

**HRMS (ESI)** scaled for [M+H]$^+$:$C_{28}H_{23}O_5$, m/z: 439.1540, observed: 439.1541.

### Methyl (5*E*, 9*Z*)-7,10-Dibenzoyl-9-hydroxy-2-methyl-7,8-dihydro-benzo[8]annulene-6-carboxylate.



**3ba**

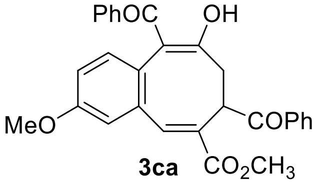
Colorless oil (29.4 mg, 65% yield), 0.1 mmol scale reaction.

**$^1$H NMR** (500 MHz, chloroform-*d*) δ 8.31 (s, 1H), 8.12 (d, *J* = 8.0 Hz, 2H), 7.62 (t, *J* = 7.5 Hz, 1H), 7.53 (t, *J* = 7.5 Hz, 2H), 7.43 (d, *J* = 8.0 Hz, 1H), 7.35 (t, *J* = 7.0 Hz, 1H), 7.28 – 7.19 (comp, 4H), 7.15 (d, *J* = 8.0 Hz, 1H), 6.59 (s, 1H), 5.26 (dd, *J* = 12.5, 4.5 Hz, 1H), 3.73 (s, 3H), 2.98 (t, *J* = 12.5 Hz, 1H), 2.50 (dd, *J* = 12.5, 4.5 Hz, 1H), 2.10 (s, 3H).

**$^{13}$C NMR** (126 MHz, chloroform-*d*) δ 198.3, 192.2, 186.6, 167.8, 142.5, 138.0, 135.9, 135.1, 133.7, 133.4, 132.9, 132.7, 131.0 , 130.2, 129.9, 129.3, 128.9, 128.8, 128.6, 127.8, 112.8, 52.5, 47.0, 37.0, 20.9.

**HRMS (ESI)** scaled for [M+H]$^+$:$C_{29}H_{25}O_5$, m/z: 453.1697, observed: 453.1698.

### Methyl (5*E*, 9*Z*)-7,10-Dibenzoyl-9-hydroxy-3-methoxy-7,8-dihydrobenzo[8]annulene-6-carboxylate.



**3ca**

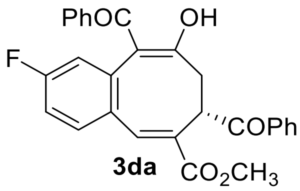
Colorless oil (26 mg, 55% yield), 0.1 mmol scale reaction.

**$^1$H NMR** (500 MHz, chloroform-*d*) δ 8.29 (s, 1H), 8.12 (d, *J* = 7.5 Hz, 2H), 7.63 (t, *J* = 7.5 Hz, 1H), 7.54 (t, *J* = 7.5 Hz, 2H), 7.35 (t, *J* = 7.0 Hz, 1H), 7.29 – 7.22 (comp, 5H), 7.06 (s, 1H), 6.67 (d, *J* = 8.5 Hz, 1H), 6.61 (d, *J* = 8.5 Hz, 1H), 5.28 (dd, *J* = 12.5, 4.5 Hz, 1H), 3.85 (s, 3H), 3.75 (s, 3H), 3.00 (t, *J* = 12.5 Hz, 1H), 2.51 (dd, *J* = 12.5, 4.5 Hz, 1H).

**$^{13}$C NMR** (126 MHz, chloroform-*d*) δ 198.2, 192.5, 186.4, 167.7, 158.9, 142.1, 136.8, 136.0, 135.1, 133.5, 133.3, 131.0, 130.7, 129.4, 129.0, 128.8, 127.9, 126.2, 114.8, 113.9, 112.3, 55.4, 52.5, 47.1, 37.0.

**HRMS (ESI)** scaled for [M+H]$^+$:$C_{29}H_{25}O_6$, m/z: 469.1646, observed: 469.1651.

### Methyl (*S*, 5*E*, 9*Z*)-7,10-Dibenzoyl-2-fluoro-9-hydroxy-7,8-dihydro-benzo[8]annulene-6-carboxylate.



**3da**

White solid (64 mg, 81% yield, 80% ee), 0.2 mmol scale reaction. m.p. 171 – 172 ºC.

Optical purity determined by HPLC analysis [Daicel chiralpak ADH, *n*-hexane/*i*-PrOH = 75/25, 1.0 mL/min, λ = 254 nm, $t_1$ = 9.10 min, $t_2$ = 19.63 min].

**$^1$H NMR** (500 MHz, chloroform-*d*) δ 8.27 (s, 1H), 8.11 (d, *J* = 8.5 Hz, 2H), 7.63 (t, *J* = 7.5 Hz, 1H), 7.56 – 7.49 (comp, 3H), 7.42 – 7.36 (m, 1H), 7.28 – 7.19 (comp, 4H), 7.06 (td, *J* = 8.5, 2.5 Hz, 1H), 6.49 (dd, *J* = 9.5, 2.5 Hz, 1H), 5.28 (dd, *J* = 13.5, 4.5 Hz, 1H), 3.74 (s, 3H), 2.92 (t, *J* = 12.0 Hz, 1H), 2.53 (dd, *J* = 12.0, 4.5 Hz, 1H).

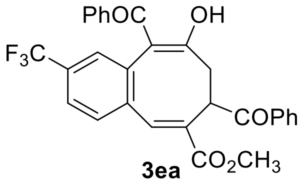
**$^{13}$C NMR** (126 MHz, chloroform-*d*) δ 198.02, 192.00, 187.00, 167.49, 161.70 (d, *J* = 254 Hz, 1C), 141.27, 136.31 (d, *J* = 8.4 Hz, 1C), 135.48, 134.99, 133.58, 131.81, 131.74, 131.42, 131.03, 129.20, 128.98, 128.78, 128.03, 118.74 (d, *J* = 21 Hz, 1C), 115.21 (d, *J* = 21 Hz, 1C), 112.06, 52.57, 46.75, 37.04.

**$^{19}$F NMR** (470.5 MHz, chloroform-*d*) δ -113.0 (m, 1F).

**HRMS (ESI)** scaled for $[M+H]^+$:$C_{28}H_{22}FO_5$, m/z: 457.1446, observed: 457.1453.

**$[\alpha]_D^{23}$** = +55.4 (*c* 0.43, $CH_2Cl_2$).

### Methyl (5*E*, 9*Z*)-7,10-Dibenzoyl-9-hydroxy-2-(trifluoromethyl)-7,8-dihydrobenzo[8]annulene-6-carboxylate.



**3ea**

Colorless oil (25.3 mg, 50% yield), 0.1 mmol scale reaction.

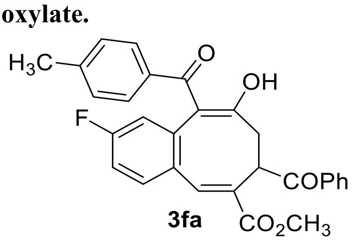
**$^1$H NMR** (500 MHz, chloroform-*d*) δ 8.30 (s, 1H), 8.11 (d, *J* = 8.0 Hz, 2H), 7.82 (s, 1H), 7.64 (t, *J* = 7.5 Hz, 2H), 7.55 (t, *J* = 7.5 Hz, 2H), 7.26 - 7.20 (m, 5H), 6.90 (d, *J* = 8.0 Hz, 1H), 5.30 (dd, *J* = 12.5, 4.5 Hz, 1H), 3.76 (s, 3H), 2.87 (t, *J* = 12.5 Hz, 1H), 2.55 (dd, *J* = 12.5, 4.5 Hz, 1H).

**$^{13}$C NMR** (126 MHz, chloroform-*d*) δ 197.71, 191.69, 187.58, 167.22, 140.47, 137.85, 136.39, 135.47, 134.86, 133.65, 132.85, 132.28, 131.48, 130.00 (q, *J* = 32 Hz, 1C), 129.23, 129.00, 128.80, 128.07, 126.91 (q, *J* = 3.6 Hz, 1C), 123.62 (q, *J* = 271 Hz, 1C), 124.50 (q, *J* = 3.6 Hz, 1C), 111.89, 52.69, 46.75, 36.81.

**$^{19}$F NMR** (470.5 MHz, chloroform-*d*) δ -63.2 (s, 1F).

**HRMS (ESI)** scaled for $[M+H]^+$:$C_{29}H_{22}F_3O_5$, m/z: 507.1414, observed: 507.1422.

### Methyl (5*E*, 9*Z*)-7-Benzoyl-2-fluoro-9-hydroxy-10-(4-methyl-benzoyl)-7,8-dihydrobenzo[8]annulene-6-carboxylate.



**3fa**

Colorless oil (40 mg, 85% yield), 0.1 mmol scale reaction.

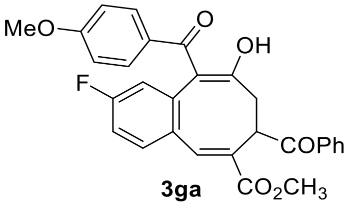
**$^1$H NMR** (500 MHz, chloroform-*d*) δ 8.26 (s, 1H), 8.11 (d, *J* = 7.5 Hz, 2H), 7.63 (t, *J* = 7.5 Hz, 1H), 7.58 – 7.47 (comp, 3H), 7.14 (d, *J* = 8.0 Hz, 2H), 7.05 (d, *J* = 8.0 Hz, 3H), 6.52 (dd, *J* = 9.5 Hz, 4.5, 1H), 5.26 (dd, *J* = 12.5, 4.5 Hz, 1H), 3.74 (s, 3H), 2.91 (t, *J* = 12.5 Hz, 1H), 2.51 (dd, *J* = 12.5, 4.5 Hz, 1H), 2.34 (s, 3H).

**$^{13}$C NMR** (126 MHz, chloroform-*d*) δ 198.11, 191.63, 186.97, 167.52, 161.69 (d, *J* = 254 Hz, 1C), 142.17, 141.30, 136.56 (d, *J* = 8.4 Hz, 1C), 135.00, 133.55, 132.62, 131.94, 131.75, 131.68, 130.99, 129.38, 128.96, 128.78, 128.75, 118.75 (d, *J* = 21 Hz, 1C), 115.14 (d, *J* = 21 Hz, 1C), 111.79, 52.54, 46.77, 37.01, 21.55.

**$^{19}$F NMR** (470.5 MHz, chloroform-*d*) δ -113.1 (m, 1F).

**HRMS (ESI)** scaled for $[M+H]^+$:$C_{29}H_{24}FO_5$, m/z: 471.1602, observed: 471.1602.

**Methyl (5*E*, 9*Z*)-7-Benzoyl-2-fluoro-9-hydroxy-10-(4-methoxy-benzoyl)-7,8-dihydrobenzo[8]annulene-6-carboxylate**.



**3ga**

Colorless oil (41 mg, 84% yield), 0.1 mmol scale reaction.

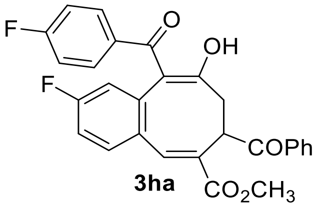
**$^1$H NMR** (500 MHz, chloroform-*d*) δ 8.25 (s, 1H), 8.11 (d, *J* = 7.5 Hz, 2H), 7.63 (t, *J* = 7.5 Hz, 1H), 7.58 – 7.50 (comp, 3H), 7.23 (d, *J* = 8.5 Hz, 2H), 7.08 (td, *J* = 8.5, 2.5 Hz, 1H), 6.75 (d, *J* = 9.0 Hz, 2H), 6.56 (dd, *J* = 9.0, 2.5 Hz, 1H), 5.26 (dd, *J* = 12.5, 4.5 Hz, 1H), 3.82 (s, 3H), 3.73 (s, 3H), 2.90 (t, *J* = 12.5 Hz, 1H), 2.50 (dd, *J* = 12.5, 4.5 Hz, 1H).

**$^{13}$C NMR** (126 MHz, chloroform-*d*) δ 198.14, 190.80, 186.52, 167.52, 162.21, 161.75 (d, *J* = 254 Hz, 1C), 141.21, 136.80 (d, *J* = 8.4 Hz, 1C), 135.01, 133.53, 131.92, 131.81, 131.74, 131.60, 131.06, 128.95, 128.77, 127.74, 118.74 (d, *J* = 21 Hz, 1C), 115.17 (d, *J* = 21 Hz, 1C), 113.40, 111.34, 55.34, 52.52, 46.80, 36.88.

**$^{19}$F NMR** (470.5 MHz, chloroform-*d*) δ -113.0 (m, 1F).

**HRMS (ESI)** scaled for $[M+H]^+$:$C_{29}H_{24}FO_6$, m/z: 487.1551, observed: 487.1553.

**Methyl (5*E*, 9*Z*)-7-Benzoyl-2-fluoro-10-(4-fluorobenzoyl)-9-hy-droxy-7,8-dihydrobenzo[8]annulene-6-carboxylate.**



**3ha**

Colorless oil (37 mg, 78% yield), 0.1 mmol scale reaction.

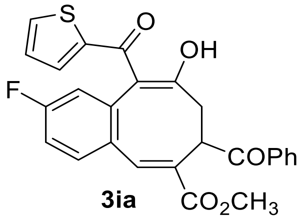
**$^1$H NMR** (500 MHz, chloroform-*d*) δ 8.25 (s, 1H), 8.10 (d, *J* = 7.5 Hz, 2H), 7.64 (t, *J* = 7.5 Hz, 1H), 7.55 -7.51 (comp, 3H), 7.26 -7.24 (comp, 2H), 7.09 (td, *J* = 8.0, 2.5 Hz, 1H), 6.95 (t, *J* = 9.0 Hz, 2H), 6.51 (dd, *J* = 9.0, 2.5 Hz, 1H), 5.27 (dd, *J* = 12.5, 4.5 Hz, 1H), 3.74 (s, 3H), 2.91 (t, *J* = 12.5 Hz, 1H), 2.53 (dd, *J* = 12.5, 4.5 Hz, 1H).

**$^{13}$C NMR** (126 MHz, chloroform-*d*) δ 197.94, 191.64, 185.92, 167.44,165.39 (d, *J* = 254 Hz, 1C), 161.75(d, $J$ = 254 Hz, 1C), 141.06, 136.15 (d, $J$ = 8.4 Hz, 1C), 134.93, 133.61, 131.97, 131.91, 131.78, 131.70, 131.14, 128.98, 128.77, 118.67 (d, $J$ = 21 Hz, 1C), 115.41(d, $J$ = 21 Hz, 1C), 115.30 (d, $J$ = 21 Hz, 1C), 52.59, 46.71, 36.93.

**$^{19}$F NMR** (470.5 MHz, chloroform-*d*) δ -106.8 (m, 1F), -112.7 (m, 1F).

**HRMS (ESI)** scaled for $[M+H]^+$:$C_{28}H_{21}F_2O_5$, m/z: 475.1352, observed: 475.1350.

**Methyl (5*E*, 9*Z*)-7-Benzoyl-2-fluoro-9-hydroxy-10-(thiophene-2-car-bonyl)-7,8-dihydrobenzo[8]annulene-6-carboxylate.**



**3ia**

Colorless oil (40 mg, 87% yield), 0.1 mmol scale reaction.

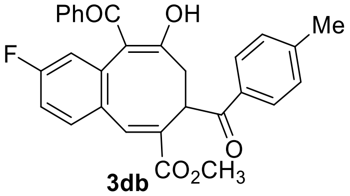
**$^1$H NMR** (500 MHz, chloroform-*d*) δ 8.17 (s, 1H), 8.09 (d, $J$ = 7.5 Hz, 2H), 7.63 (t, $J$ = 7.5 Hz, 1H), 7.60 – 7.49 (comp, 4H), 7.22 (td, $J$ = 8.5, 2.5 Hz, 1H), 6.96 (d, $J$ = 8.5 Hz, 3H), 5.24 (dd, $J$ = 12.5, 4.5 Hz, 1H), 3.70 (s, 3H), 2.85 (t, $J$ = 12.5 Hz, 1H), 2.51 (dd, $J$ = 12.5, 4.5 Hz, 1H).

**$^{13}$C NMR** (126 MHz, chloroform-*d*) δ 198.05, 188.64, 160.93, 167.48, 161.92 (d, $J$ = 254 Hz, 1C), 141.09, 139.86, 135.27 (d, $J$ = 8.4 Hz, 1C), 133.97, 133.81, 133.57, 132.54, 131.97, 131.90, 130.84, 128.96, 128.77, 127.80, 119.18 (d, $J$ = 21 Hz, 1C), 116.16 (d, $J$ = 21 Hz, 1C), 110.47, 56.70, 46.80, 36.59.

**$^{19}$F NMR** (470.5 MHz, chloroform-*d*) δ -112.6 (m, 1F).

**HRMS (ESI)** scaled for $[M+H]^+$:$C_{26}H_{20}FO_5S$, m/z: 463.1010, observed: 463.1011.

**Methyl (5*E*, 9*Z*)-10-Benzoyl-2-fluoro-9-hydroxy-7-(4-methyl-benzoyl)-7,8-dihydrobenzo[8]annulene-6-carboxylate.**



**3db**

Colorless oil (38 mg, 81% yield), 0.1 mmol scale reaction.

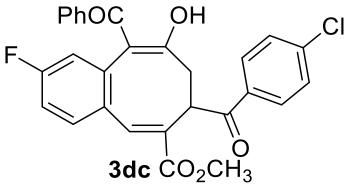
**$^1$H NMR** (500 MHz, chloroform-*d*) δ 8.25 (s, 1H), 8.01 (d, $J$ = 8.5 Hz, 2H), 7.51 (dd, $J$ = 8.5, 6.0 Hz, 1H), 7.39 – 7.36 (m, 1H), 7.33 (d, $J$ = 8.0 Hz, 2H), 7.28 – 7.22 (comp, 4H), 7.05 (td, $J$ = 8.5, 2.5 Hz, 1H), 6.49 (dd, $J$ = 9.0, 3.0 Hz, 1H), 5.25 (dd, $J$ = 13.5, 4.5 Hz, 1H), 3.73 (s, 3H), 2.92 (t, $J$ = 12.0 Hz, 1H), 2.52 (dd, $J$ = 12.0, 4.5 Hz, 1H), 2.45 (s, 3H).

**$^{13}$C NMR** (126 MHz, chloroform-*d*) δ 197.59, 192.12, 186.97, 167.50, 161.67 (d, $J$ = 254 Hz, 1C), 144.53, 141.19, 136.30 (d, $J$ = 8.4 Hz, 1C), 135.50, 132.38, 132.03, 132.01, 131.79, 131.72, 131.39, 131.13, 129.66, 129.20, 128.93, 128.02, 118.71 (d, $J$ = 21 Hz, 1C), 115.19 (d, $J$ = 21 Hz, 1C), 112.07, 52.54, 46.59, 37.20, 21.72.

**$^{19}$F NMR** (470.5 MHz, chloroform-*d*) δ -113.2 (m, 1F).

**HRMS (ESI)** scaled for $[M+H]^+$:$C_{29}H_{24}FO_5$, m/z: 471.1602, observed: 471.1609.

### Methyl (5*E*, 9*Z*)-10-Benzoyl-7-(4-chlorobenzoyl)-2-fluoro-9-hy-droxy-7,8-dihydrobenzo[8]annulene-6-carboxylate.



**3dc**

Colorless oil (33 mg, 67% yield), 0.1 mmol scale reaction.

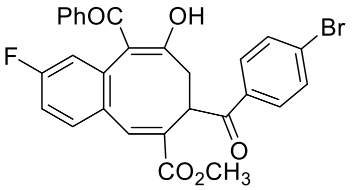
**$^1$H NMR** (500 MHz, chloroform-*d*) δ 8.26 (s, 1H), 8.05 (d, *J* = 8.5 Hz, 2H), 7.52 (d, *J* = 8.5 Hz, 3H), 7.38 (d, *J* = 8.5 Hz, 1H), 7.29 – 7.21 (comp, 5H), 7.06 (td, *J* = 8.5, 2.5 Hz, 1H), 6.50 (dd, *J* = 9.5, 2.5 Hz, 1H), 5.20 (dd, *J* = 12.5, 4.5 Hz, 1H), 3.75 (s, 3H), 2.93 (t, *J* = 12.5 Hz, 1H), 2.47 (dd, *J* = 12.5, 4.5 Hz, 1H).

**$^{13}$C NMR** (126 MHz, chloroform-*d*) δ 196.92, 191.76, 187.01, 167.43, 161.73 (d, *J* = 254 Hz, 1C), 141.37, 140.12, 136.29 (d, *J* = 8.4 Hz, 1C), 135.40, 133.33, 131.80, 131.73, 131.46, 130.76, 130.20, 129.30, 129.20, 128.04, 118.79 (d, *J* = 21 Hz, 1C), 115.26 (d, *J* = 21 Hz, 1C), 52.60, 46.72, 36.94.

**$^{19}$F NMR** (470.5 MHz, chloroform-*d*) δ -112.8 (m, 1F).

**HRMS (ESI)** scaled for $[M+H]^+$:$C_{28}H_{21}ClFO_5$, m/z: 491.1056, observed: 491.1063.

### Methyl (5*E*, 9*Z*)-10-Benzoyl-7-(4-bromobenzoyl)-2-fluoro-9-hy-droxy-7,8-dihydrobenzo[8]annulene-6-carboxylate.



**3dd**

Colorless oil (38 mg, 72% yield), 0.1 mmol scale reaction.

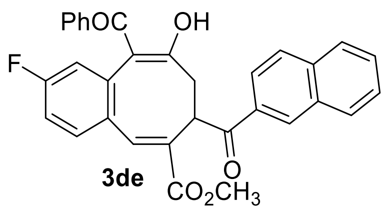
**$^1$H NMR** (500 MHz, chloroform-*d*) δ 8.26 (s, 1H), 7.97 (d, *J* = 8.5 Hz, 2H), 7.68 (d, *J* = 8.5 Hz, 2H), 7.50 (dd, *J* = 8.5, 6.0 Hz, 1H), 7.39 (t, *J* = 7.0 Hz, 1H), 7.27 – 7.22 (comp, 5H), 7.06 (td, *J* = 8.5, 3.0 Hz, 1H), 6.50 (dd, *J* = 9.0, 3.0 Hz, 1H), 5.19 (dd, *J* = 12.5, 4.5 Hz, 1H), 3.75 (s, 3H), 2.93 (t, *J* = 12.5 Hz, 1H), 2.47 (dd, *J* = 12.5, 4.5 Hz, 1H).

**$^{13}$C NMR** (126 MHz, chloroform-*d*) δ 197.14, 191.74, 187.02, 167.43, 161.73 (d, *J* = 254 Hz, 1C), 141.39, 136.29 (d, *J* = 8.4 Hz, 1C), 135.39, 133.74, 132.31, 131.80, 131.74, 131.48, 130.73, 130.29, 129.20, 128.90, 128.05, 118.80 (d, *J* = 21 Hz, 1C), 115.26 (d, *J* = 21 Hz, 1C), 52.62, 46.70, 36.91.

**$^{19}$F NMR** (470.5 MHz, chloroform-*d*) δ -112.8 (m, 1F).

**HRMS (ESI)** scaled for $[M+H]^+$:$C_{28}H_{21}BrFO_5$, m/z: 535.0551, observed: 535.0561.

### Methyl (5*E*, 9*Z*)-7-(2-Naphthoyl)-10-benzoyl-2-fluoro-9-hydroxy-7,8-dihydrobenzo[8]annulene-6-carboxylate.



**3de**

Colorless oil (43 mg, 85% yield), 0.1 mmol scale reaction.

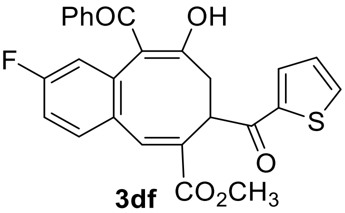
**$^1$H NMR** (500 MHz, chloroform-*d*) δ 8.29 (s, 1H), 8.27 - 8.23 (comp, 2H), 8.04 (d, *J* = 8.0 Hz, 1H), 7.95 – 7.86 (m, 1H), 7.61 (t, *J* = 8.0 Hz, 1H), 7.58 – 7.50 (comp, 3H), 7.39 (t, *J* = 7.0 Hz, 1H), 7.31 – 7.21 (comp, 5H), 7.11 (td, *J* = 8.0, 2.5 Hz, 1H), 6.51 (dd, *J* = 9.5, 2.5 Hz, 1H), 5.25 (dd, *J* = 12.5, 4.5 Hz, 1H), 3.78 (s, 3H), 2.99 (t, *J* = 12.5 Hz, 1H), 2.49 (dd, *J* = 12.5, 4.5 Hz, 1H).

**$^{13}$C NMR** (126 MHz, chloroform-*d*) δ 200.92, 192.34, 186.66, 167.60, 161.76 (d, *J* = 254 Hz, 1C), 141.33, 136.42 (d, *J* = 8.4 Hz, 1C), 135.43, 134.57, 133.90, 132.82, 132.03, 132.01, 131.76, 131.69, 131.41, 130.92, 130.63, 129.19, 128.48, 128.03, 127.91, 127.57, 126.52, 125.26, 124.67, 118.78 (d, *J* = 21 Hz, 1C), 115.26 (d, *J* = 21 Hz, 1C), 112.12, 52.61, 50.81, 36.67.

**$^{19}$F NMR** (470.5 MHz, chloroform-*d*) δ -112.9 (m, 1F).

**HRMS (ESI)** scaled for $[M+H]^+$:$C_{32}H_{24}FO_5$, m/z: 507.1602, observed: 507.1608.

### Methyl (5*E*, 9*Z*)-10-Benzoyl-2-fluoro-9-hydroxy-7-(thiophene-2-car-bonyl)-7,8-dihydrobenzo[8]annulene-6-carboxylate.



**3df**

Colorless oil (47 mg, 51% yield), 0.2 mmol scale reaction.

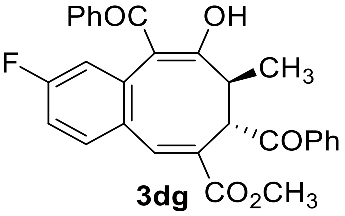
**$^1$H NMR** (500 MHz, chloroform-*d*) δ 8.17 (s, 1H), 8.08 (d, *J* = 8.5 Hz, 2H), 7.64 – 7.48 (comp, 5H), 7.21 (td, *J* = 8.5, 2.5 Hz, 1H), 7.00 – 6.86 (comp, 3H), 5.25 (dd, *J* = 13.5, 4.5 Hz, 1H), 3.69 (s, 3H), 2.85 (t, *J* = 12.5 Hz, 1H), 2.51 (dd, *J* = 12.0, 4.5 Hz, 1H).

**$^{13}$C NMR** (126 MHz, Chloroform-*d*) δ 198.02, 188.66, 179.43, 167.47, 161.91 (d, *J* = 254 Hz, 1C), 141.07, 139.85, 135.27(d, *J* = 8.4 Hz, 1C), 134.98, 133.97, 133.84, 133.57, 132.52, 131.98, 131.91, 130.86, 128.96, 128.77, 127.81, 119.18 (d, *J* = 21 Hz, 1C), 116.15 (d, *J* = 21 Hz, 1C), 110.47, 52.52, 46.81, 36.58.

**$^{19}$F NMR** (470.5 MHz, chloroform-*d*) δ -113.0 (m, 1F).

**HRMS (ESI)** scaled for $[M+H]^+$:$C_{26}H_{20}FO_5S$, m/z: 463.1010, observed: 463.1021.

### Methyl (5*E*, 7*S*, 8*S*, 9*Z*)-7,10-Dibenzoyl-2-fluoro-9-hydroxy-8-methyl-7,8-dihydrobenzo[8]annulene-6-carboxylate.



**3dg**

Colorless oil (21 mg, 45% yield, >19:1 dr, 97% ee), 0.1 mmol scale reaction.

Optical purity determined by HPLC analysis [Daicel chiralpak ADH, *n*-hexane/*i*-PrOH = 80/20, 1.0 mL/min, λ = 254 nm, $t_1$ = 4.67 min, $t_2$ = 5.44 min].

**$^1$H NMR** (500 MHz, chloroform-*d*) δ 8.11 (d, *J* = 7.5 Hz, 2H), 8.08 (s, 1H), 7.59 (t, *J* = 7.5 Hz, 1H), 7.50 (t, *J* = 7.5 Hz, 2H), 7.42 (dd, *J* = 8.5, 6.0 Hz, 1H), 7.37 – 7.32 (m, 1H), 7.25 – 7.17 (comp, 4H), 7.07 (td, *J* = 8.5, 2.5 Hz, 1H), 6.50 (dd, *J* = 9.5, 2.5 Hz, 1H), 5.02 (d, *J* = 11.5 Hz, 1H), 3.67 (s, 3H), 3.46 (dq, *J* = 11.5, 6.5 Hz, 1H), 0.95 (d, *J* = 6.5 Hz, 3H).

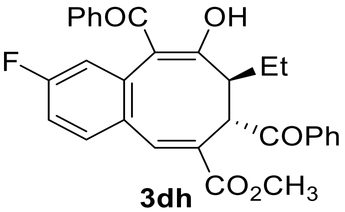
**$^{13}$C NMR** (126 MHz, chloroform-*d*) δ 199.32, 197.86, 184.12, 167.35, 161.93(d, *J* = 254 Hz, 1C), 141.75, 137.41, 136.08 (d, *J* = 8.4 Hz, 1C), 135.32, 133.53, 133.03, 131.99, 131.13, 130.75, 130.68, 129.13, 129.10, 128.70, 127.98, 118.44 (d, *J* = 21 Hz, 1C), 115.18 (d, *J* = 21 Hz, 1C), 52.45, 51.26, 41.30, 15.52.

**$^{19}$F NMR** (470.5 MHz, chloroform-*d*) δ -113.0 (m, 1F).

**HRMS (ESI)** scaled for $[M+H]^+$:$C_{29}H_{24}FO_5$, m/z: 471.1602, observed: 471.1616.

**$[\alpha]_D^{23}$** = +146.3 (*c* 0.61, $CH_2Cl_2$).

### Methyl (5*E*, 7*S*, 8*S*, 9*Z*)-7,10-Dibenzoyl-8-ethyl-2-fluoro-9-hydroxy-7,8-dihydrobenzo[8]annulene-6-carboxylate.



**3dh**

Colorless oil (17 mg, 35% yield, >19:1 dr, 90% ee), 0.1 mmol scale reaction.

Optical purity determined by HPLC analysis [Daicel chiralpak ADH, *n*-hexane/*i*-PrOH = 80/20, 1.0 mL/min, λ = 254 nm, $t_1$ = 4.93 min, $t_2$ = 6.90 min].

**$^1$H NMR** (500 MHz, chloroform-*d*) δ 8.13 (d, *J* = 7.5 Hz, 2H), 8.10 (s, 1H), 7.62 (t, *J* = 7.5 Hz, 1H), 7.52 (t, *J* = 7.5 Hz, 2H), 7.45 (dd, *J* = 8.5, 6.0 Hz, 1H), 7.38 (t, *J* = 7.3 Hz, 1H), 7.28 – 7.19 (comp, 4H), 7.10 (td, *J* = 8.5, 2.5 Hz, 1H), 6.53 (dd, *J* = 9.5, 2.5 Hz, 1H), 5.07 (d, *J* = 11.5 Hz, 1H), 3.68 (s, 3H), 3.35 (td, *J* = 11.5, 3.0 Hz, 1H), 1.85 – 1.77 (m, 1H), 1.08 – 1.03 (m, 1H), 0.67 (t, *J* = 7.5 Hz, 3H).

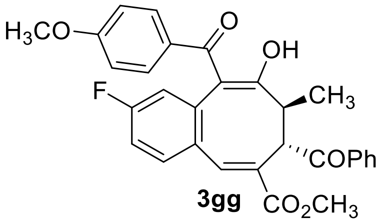
**$^{13}$C NMR** (126 MHz, chloroform-*d*) δ 199.36, 196.69, 184.44, 167.35, 162.02 (d, *J* = 254 Hz, 1C), 141.73, 137.30, 136.25 (d, *J* = 8.4 Hz, 1C), 135.38, 133.53, 133.07, 132.03, 131.14, 130.77, 130.70, 129.08, 128.70, 127.96, 118.15 (d, *J* = 21 Hz, 1C), 115.18 (d, *J* = 21 Hz, 1C), 52.43, 50.16, 48.74, 23.66, 12.09.

**$^{19}$F NMR** (470.5 MHz, chloroform-*d*) δ -113.0 (m, 1F).

**HRMS (ESI)** scaled for $[M+H]^+$:$C_{30}H_{26}FO_5$, m/z: 485.1759, observed: 485.1775.

**$[\alpha]_D^{23}$** = +327.7 (*c* 0.14, $CH_2Cl_2$).

### Methyl (5*E*, 7*S*, 8*S*, 9*Z*)-7-Benzoyl-2-fluoro-9-hydroxy-10-(4-methoxybenzoyl)-8-methyl-7,8-dihydrobenzo[8]annulene-6-carboxylate.



**3gg**

Colorless oil (25 mg, 50% yield, >19:1 dr, 97% ee), 0.1 mmol scale reaction.

Optical purity determined by HPLC analysis [Daicel chiralpak ADH, *n*-hexane/*i*-PrOH = 95/5, 1.0 mL/min, λ = 254 nm, $t_1$ = 13.59 min, $t_2$ = 17.50 min].

**$^1$H NMR** (500 MHz, chloroform-*d*) δ 8.13 (d, *J* = 8.5 Hz, 2H), 8.09 (s, 1H), 7.61 (t, *J* = 7.5 Hz, 1H), 7.52 (t, *J* = 7.5 Hz, 2H), 7.46 (dd, *J* = 8.5, 6.0 Hz, 1H), 7.20 – 7.18 (comp, 2H), 7.11 (td, *J* = 8.5, 2.5 Hz, 1H), 6.76 – 6,73 (comp, 2H), 6.60 (dd, *J* = 9.5, 2.5 Hz, 1H), 5.04 (d, *J* = 11.5 Hz, 1H), 3.82 (s, 3H), 3.68 (s, 3H), 3.50 – 3.39 (m, 1H), 0.96 (d, *J* = 6.5 Hz, 3H).

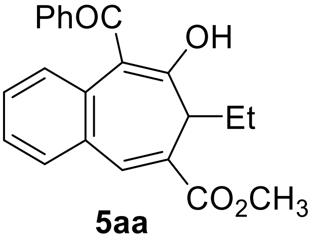
**$^{13}$C NMR** (126 MHz, chloroform-*d*) δ 199.50, 196.55, 183.96, 167.39,161.99 (d, *J* = 254 Hz, 1C), 161.96, 141.69, 137.46, 136.53 (d, *J* = 8.4 Hz, 1C), 133.49, 133.00, 132.06, 131.41, 130.79, 130.72, 129.12, 128.67, 127.62, 118.42 (d, *J* = 21 Hz, 1C), 115.14 (d, *J* = 21 Hz, 1C), 113.36, 110.99, 55.32, 52.40, 51.25 , 41.07, 15.53.

**$^{19}$F NMR** (470.5 MHz, chloroform-*d*) δ -112.9 (m, 1F).

**HRMS (ESI)** scaled for $[M+H]^+$: $C_{30}H_{26}FO_6$, m/z: 501.1708, observed: 501.1686.

**$[\alpha]_D^{23}$** = +384.0 (*c* 0.30, $CH_2Cl_2$).

**Methyl 9-Benzoyl-7-ethyl-8-hydroxy-7*H*-benzo-[7]annulene-6-carboxylate.**



**5aa**

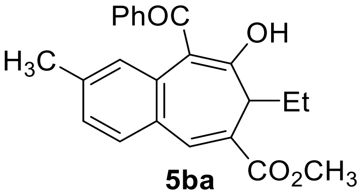
Pale yellow oil (49.5 mg, 71% yield), 0.2 mmol scale reaction.

**$^1$H NMR** (300 MHz, chloroform-*d*) δ 7.99 (s, 1H), 7.42 (d, *J* = 7.5 Hz, 1H), 7.35 – 7.29 (m, 1H), 7.22 – 7.11 (comp, 5H), 6.92 (t, *J* = 7.0 Hz, 1H), 6.78 (d, *J* = 7.8 Hz, 1H), 4.13 – 4.03 (m, 1H), 3.89 (s, 3H), 1.32 – 1.13 (m, 2H), 0.82 (t, *J* = 7.5 Hz, 3H).

**$^{13}$C NMR** (75 MHz, Chloroform-*d*) δ 196.3, 189.0, 166.9, 138.8, 133.2, 132.0, 130.7, 129.7, 129.6, 127.8, 127.7, 126.1, 52.5, 49.9, 17.7, 12.2.

**HRMS (ESI)** scaled for $[M+H]^+$:$C_{22}H_{21}O_4$, m/z: 349.1434, observed: 349.1437.

**Methyl 9-Benzoyl-7-ethyl-8-hydroxy-2-methyl-7*H*-benzo[7]-annulene-6-carboxylate.**



**5ba**

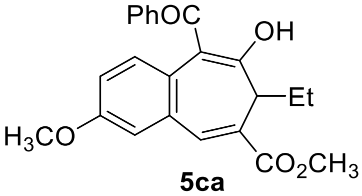
Pale yellow oil (58 mg, 80% yield), 0.2 mmol scale reaction.

**$^1$H NMR** (500 MHz, chloroform-*d*) δ 7.95 (s, 1H), 7.33 – 7.28 (comp, 2H), 7.18 (t, *J* = 7.5 Hz, 2H), 7.12 (d, *J* = 7.5 Hz, 2H), 6.99 (d, *J* = 7.5 Hz, 1H), 6.56 (s, 1H), 4.13 – 4.03 (m, 1H), 3.88 (s, 3H), 1.98 (s, 3H), 1.33 – 1.28 (m, 1H), 1.20 – 1.17 (m, 1H), 0.82 (t, *J* = 7.5 Hz, 3H).

**$^{13}$C NMR** (126 MHz, chloroform-*d*) δ 195.9, 189.5, 167.0, 138.9, 137.8, 134.0, 130.8, 130.5, 129.8, 129.4, 127.7, 127.0, 52.4, 49.9, 21.0, 17.7, 12.2.

**HRMS (ESI)** scaled for $[M+H]^+$:$C_{23}H_{23}O_4$, m/z: 363.1591, observed: 363.1594.

**Methyl 9-Benzoyl-7-ethyl-8-hydroxy-3-methoxy-7*H*-benzo[7]-annulene-6-carboxylate**.



**5ca**

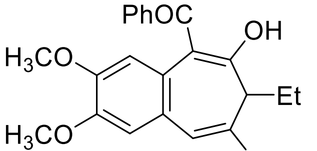
Pale yellow oil (60 mg, 79% yield), 0.2 mmol scale reaction.

**$^1$H NMR** (500 MHz, chloroform-*d*) δ 7.93 (s, 1H), 7.33 – 7.29 (m, 1H), 7.20 (t, *J* = 7.5 Hz, 2H), 7.15 (d, *J* = 7.5 Hz, 2H), 6.92 (s, 1H), 6.68 (d, *J* = 8.6 Hz, 1H), 6.51 (dd, *J* = 8.5, 3.0 Hz, 1H), 4.09 – 4.06 (m, 1H), 3.88 (s, 3H), 3.80 (s, 3H), 1.32 – 1.27 (m, 1H), 1.25 – 1.17 (m, 1H), 0.82 (t, *J* = 7.5 Hz, 3H).

**$^{13}$C NMR** (126 MHz, chloroform-*d*) δ 196.6, 188.0, 166.9, 157.5, 138.7, 134.4, 132.2, 130.5, 129.6, 127.8, 114.6, 113.5, 55.3, 52.5, 50.2, 20.9, 12.3.

**HRMS (ESI)** scaled for $[M+H]^+$:$C_{23}H_{23}O_5$, m/z: 379.1540, observed: 379.1540.

**Methyl 9-Benzoyl-7-ethyl-8-hydroxy-2,3-dimethoxy-7*H*-benzo-[7]annulene-6-carboxylate.**



**5ja**

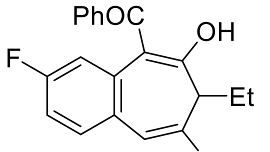
Pale yellow oil (66 mg, 81% yield), 0.2 mmol scale reaction.

**$^1$H NMR** (500 MHz, chloroform-*d*) δ 7.90 (s, 1H), 7.32 (t, *J* = 7.5 Hz, 1H), 7.22 (t, *J* = 7.5 Hz, 2H), 7.16 (d, *J* = 7.5 Hz, 2H), 6.86 (s, 1H), 6.17 (s, 1H), 4.11 – 4.06 (m, 1H), 3.91 (s, 3H), 3.88 (s, 3H), 3.26 (s, 3H), 1.36 – 1.29 (m, 1H), 1.23 (s, 1H), 0.83 (t, *J* = 7.5 Hz, 3H).

**$^{13}$C NMR** (126 MHz, chloroform-*d*) δ 195.5, 189.5, 167.0, 148.1, 138.6, 130.5, 129.7, 129.2, 128.0, 116.37, 111.6, 55.8, 55.4, 49.8, 20.5, 17.9, 12.2.

**HRMS (ESI)** scaled for $[M+H]^+$:$C_{24}H_{25}O_6$, m/z: 409.1646, observed: 409.1645.

**Methyl 9-Benzoyl-7-ethyl-2-fluoro-8-hydroxy-7*H*-benzo[7]annulene-6-carboxylate.**



**5da**

Pale yellow oil (57 mg, 78% yield), 0.2 mmol scale reaction.

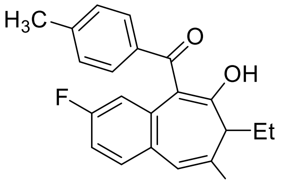
**$^1$H NMR** (500 MHz, chloroform-*d*) δ 7.94 (s, 1H), 7.39 (t, *J* = 7.5 Hz, 1H), 7.35 (d, *J* = 7.5 Hz, 1H), 7.23 (t, *J* = 7.5 Hz, 2H), 7.15 (d, *J* = 7.5 Hz, 2H), 6.89 (t, *J* = 7.5 Hz, 1H), 6.47 (d, *J* = 10.0 Hz, 1H), 4.15 – 4.03 (m, 1H), 3.89 (s, 3H), 1.30 – 1.27 (m, 1H), 1.23 – 1.16 (m, 1H), 0.83 (t, *J* = 7.5 Hz, 3H).

**$^{13}$C NMR** (126 MHz, chloroform-*d*) δ 195.89, 191.57, 166.76, 161.32 (d, *J* = 254 Hz, 1C), 137.73, 131.74, 131.65, 131.09, 129.40, 128.03, 119.57 (d, *J* = 22 Hz, 1C), 113.61(d, *J* = 22 Hz, 1C), 52.54, 49.73, 20.89, 12.18.

**$^{19}$F NMR** (470.5 MHz, chloroform-*d*) δ -111.7 (m, 1F).

**HRMS (ESI)** scaled for $[M+H]^+$:$C_{22}H_{20}FO_4$, m/z: 367.1340, observed: 367.1339.

**Methyl 7-Ethyl-2-fluoro-8-hydroxy-9-(4-methylbenzoyl)-7*H*-benzo[7]annulene-6-carboxylate.**



**5fa**

Pale yellow oil (57 mg, 75% yield), 0.2 mmol scale reaction.

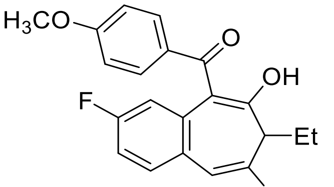
**$^1$H NMR** (500 MHz, chloroform-*d*) δ 7.94 (s, 1H), 7.43 – 7.36 (m, 1H), 7.03 (comp, 4H), 6.90 (t, *J* = 8.0 Hz, 1H), 6.51 (d, *J* = 11.5 Hz, 1H), 4.13 – 4.02 (m, 1H), 3.88 (s, 3H), 2.33 (s, 3H), 1.30 – 1.24 (m, 1H), 1.23 –1.16 (m, 1H), 0.83 (t, *J* = 7.5 Hz, 3H).

**$^{13}$C NMR** (126 MHz, chloroform-*d*) δ 195.43, 189.85, 166.78, 161.31 (d, *J* = 250 Hz, 1C), 141.76, 137.72, 131.71, 131.68, 131.61, 129.56, 128.73, 119.57 (d, *J* = 22 Hz, 1C), 113.51 (d, *J* = 22 Hz, 1C), 52.51, 49.65, 21.50, 20.90, 12.18.

**$^{19}$F NMR** (470.5 MHz, chloroform-*d*) δ -111.8 (m, 1F).

**HRMS (ESI)** scaled for $[M+H]^+$:$C_{23}H_{22}FO_4$, m/z: 381.1497, observed: 381.1499.

**Methyl 7-Ethyl-2-fluoro-8-hydroxy-9-(4-methoxybenzoyl)-7*H*-benzo[7]annulene-6-carboxylate.**



**5ga**

Pale yellow oil (61 mg, 78% yield), 0.2 mmol scale reaction.

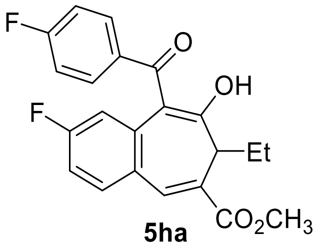
**$^1$H NMR** (500 MHz, chloroform-*d*) δ 7.93 (s, 1H), 7.44 – 7.38 (m, 1H), 7.12 (d, *J* = 8.5 Hz, 2H), 6.91 (t, *J* = 8.5 Hz, 1H), 6.72 (d, *J* = 9.0 Hz, 2H), 6.55 (d, *J* = 10.0 Hz, 1H), 4.11 – 4.01 (m, 1H), 3.88 (s, 3H), 3.80 (s, 3H), 1.27 – 1.22 (m, 1H), 1.21 – 1.15 (m, 1H), 0.82 (t, *J* = 7.5 Hz, 3H).

**$^{13}$C NMR** (126 MHz, chloroform-*d*) δ 194.66, 189.52, 166.78, 161.37 (d, *J* = 250 Hz, 1C), 137.63, 131.88, 131.69, 119.51(d, *J* = 22 Hz, 1C), 113.50 (d, *J* = 22 Hz, 1C), 113.36, 55.31, 52.50, 49.40, 20.90, 12.17.

**$^{19}$F NMR** (470.5 MHz, chloroform-*d*) δ -111.7 (m, 1F).

**HRMS (ESI)** scaled for $[M+H]^+$:$C_{23}H_{22}FO_5$, m/z: 397.1446, observed: 397.1449.

**Methyl 7-Ethyl-2-fluoro-9-(4-fluorobenzoyl)-8-hydroxy-7*H*-benzo[7]annulene-6-carboxylate.**



**5ha**

Pale yellow oil (46 mg, 60% yield), 0.2 mmol scale reaction.

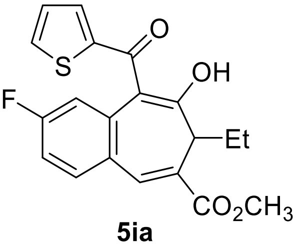
**$^1$H NMR** (500 MHz, chloroform-*d*) δ 7.93 (s, 1H), 7.44 – 7.37 (m, 1H), 7.20 – 7.12 (comp, 2H), 6.95 – 6.88 (comp, 3H), 6.48 (d, *J* = 9.5 Hz, 1H), 4.15 – 4.02 (m, 1H), 3.88 (s, 3H), 1.29 – 1.23 (m, 1H), 1.22 – 1.15 (m, 1H), 0.82 (t, *J* = 7.5 Hz, 3H).

**$^{13}$C NMR** (126 MHz, chloroform-*d*) δ 195.52, 188.64, 166.68, 164.17 (d, *J* = 254 Hz, 1C), 161.36 (d, *J* = 254 Hz, 1C), 137.58, 131.92, 131.84, 119.48 (d, *J* = 22 Hz, 1C), 115.26 (d, *J* = 22 Hz, 1C), 113.78 (d, *J* = 22 Hz, 1C), 52.55, 49.54, 20.92, 12.15.

**$^{19}$F NMR** (470.5 MHz, chloroform-*d*) δ -107.2 (m, 1F), -111.5 (m, 1F).

**HRMS (ESI)** scaled for $[M+H]^+$:$C_{22}H_{19}F_2O_4$, m/z: 385.1246, observed: 385.1249.

**Methyl 7-Ethyl-2-fluoro-8-hydroxy-9-(thiophene-2-carbonyl)-7*H*-benzo[7]annulene-6-carboxylate.**



**5ia**

Pale yellow oil (33.5 mg, 45% yield), 0.2 mmol scale reaction.

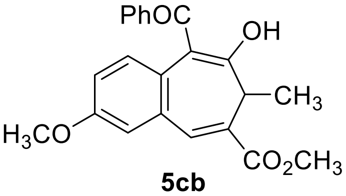
**$^1$H NMR** (500 MHz, chloroform-*d*) δ 7.92 (s, 1H), 7.49 (d, *J* = 5.0 Hz, 1H), 7.48 – 7.44 (m, 1H), 7.03 (t, *J* = 8.5 Hz, 1H), 6.95 (d, *J* = 8.5 Hz, 1H), 6.90 – 6.85 (m, 1H), 6.76 (d, *J* = 5.0 Hz, 1H), 4.06 – 3.99 (m, 1H), 3.87 (s, 3H), 1.28 – 1.22 (m, 1H), 1.17 – 1.12 (m, 1H), 0.82 (t, *J* = 7.5 Hz, 3H).

**$^{13}$C NMR** (126 MHz, chloroform-*d*) δ 192.19, 182.51, 166.69, 161.36 (d, *J* = 250 Hz, 1C), 137.43, 133.51, 132.81, 132.43, 131.68 (d, *J* = 9 Hz, 1C), 127.42, 119.70 (d, *J* = 21 Hz, 1C), 114.32 (d, *J* = 21 Hz, 1C), 109.61, 52.52, 48.69, 20.87, 12.16.

**$^{19}$F NMR** (470.5 MHz, chloroform-*d*) δ -111.5 (m, 1F).

**HRMS (ESI)** scaled for $[M+H]^+$:$C_{20}H_{18}FO_4S$, m/z: 373.0904, observed: 373.0907.

**Methyl 9-Benzoyl-8-hydroxy-3-methoxy-7-methyl-7*H*-benzo[7]-annulene-6-carboxylate**.

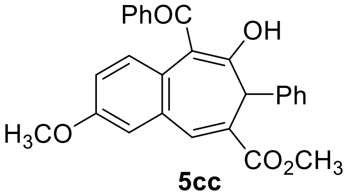


**5cb**

Pale yellow oil (59 mg, 81% yield), 0.2 mmol scale reaction.

**$^1$H NMR** (500 MHz, chloroform-*d*) δ 7.88 (s, 1H), 7.31 (t, *J* = 7.5 Hz, 1H), 7.20 (t, *J* = 7.5 Hz, 2H), 7.16 (d, *J* = 7.5 Hz, 2H), 6.93 (d, *J* = 2.5 Hz, 1H), 6.70 (d, *J* = 9.0 Hz, 1H), 6.53 (dd, *J* = 9.0, 2.5 Hz, 1H), 4.35 – 4.15 (m, 1H), 3.88 (s, 3H), 3.80 (s, 3H), 1.03 – 0.68 (m, 3H).
**$^{13}$C NMR** (126 MHz, chloroform-*d*) δ 191.10, 188.02, 166.68, 157.57, 134.47, 130.54, 129.61, 127.84, 114.70, 55.28, 52.42.
**HRMS (ESI)** scaled for $[M+H]^+$:$C_{22}H_{21}O_5$, m/z: 365.1384, observed: 365.1388.

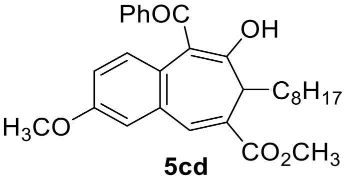
**Methyl 9-Benzoyl-8-hydroxy-3-methoxy-7-phenyl-7*H*-benzo[7]-annulene-6-carboxylate**.



**5cc**

Pale yellow oil (58.8 mg, 69% yield), 0.2 mmol scale reaction.
**$^1$H NMR** (300 MHz, chloroform-*d*) δ 8.19 (s, 1H), 7.32 – 7.28 (m, 1H), 7.23 – 7.10 (comp, 4H), 7.04 – 6.89 (comp, 5H), 6.81 (d, *J* = 2.5 Hz, 1H), 6.38 (d, *J* = 8.5 Hz, 1H), 6.25 (dd, *J* = 8.5, 2.5 Hz, 1H), 3.94 (s, 3H), 3.71 (s, 3H).
**$^{13}$C NMR** (75 MHz, chloroform-*d*) δ 196.5, 186.7, 166.9, 157.4, 140.9, 136.4, 135.2, 134.4, 134.2, 130.7, 130.6, 129.6, 127.9, 127.8, 126.7, 126.5, 126.2, 114.5, 112.9, 55.2, 52.8.
**HRMS (ESI)** scaled for $[M+H]^+$:$C_{27}H_{23}O_5$, m/z: 427.1540, observed: 427.1545.

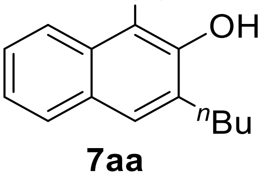
**Methyl 9-Benzoyl-8-hydroxy-3-methoxy-7-octyl-7*H*-benzo[7]-annulene-6-carboxylate**.



**5cd**

Pale yellow oil (58 mg, 63% yield), 0.2 mmol scale reaction.
**$^1$H NMR** (500 MHz, chloroform-*d*) δ 7.93 (s, 1H), 7.31 (t, *J* = 7.5 Hz, 1H), 7.23 – 7.12 (comp, 4H), 6.92 (s, 1H), 6.67 (d, *J* = 8.5 Hz, 1H), 6.51 (d, *J* = 11.0 Hz, 1H), 4.17 – 4.11 (m, 1H), 3.88 (s, 3H), 3.80 (s, 3H), 1.26 – 1.11 (m, 14H), 0.86 (t, *J* = 7.5 Hz, 3H).
**$^{13}$C NMR** (126 MHz, chloroform-*d*) δ 196.73, 187.81, 166.90,157.52, 138.72, 137.04, 134.51, 134.41, 132.42, 130.52, 129.58, 127.81, 126.78, 114.56, 113.47, 110.75, 55.25, 52.51, 48.69, 31.79, 29.14, 29.09, 29.03, 27.68, 27.47, 22.60, 14.08.
**HRMS (ESI)** scaled for $[M+H]^+$:$C_{29}H_{35}O_5$, m/z: 463.2479, observed: 463.2488.

**(3-Butyl-2-hydroxynaphthalen-1-yl)(phenyl)methanone**.



**7aa**

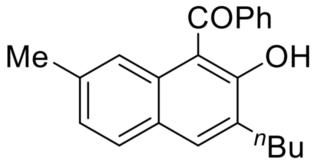
Yellow oil (52 mg, 86% yield), 0.2 mmol scale reaction.

**$^1$H NMR** (500 MHz, chloroform-*d*) δ 11.84 (s, 1H), 7.81 (s, 1H), 7.72 (d, *J* = 7.5 Hz, 1H), 7.69 – 7.63 (m, 2H), 7.61 – 7.54 (m, 1H), 7.43 (t, *J* = 8.0 Hz, 2H), 7.27 (t, *J* = 7.5 Hz, 2H), 7.15 – 7.09 (m, 1H), 2.94 – 2.83 (m, 2H), 1.85 – 1.73 (m, 2H), 1.55 – 1.47 (m, 2H), 1.04 (t, *J* = 7.5 Hz, 3H).

**$^{13}$C NMR** (126 MHz, chloroform-*d*) δ 200.9, 161.2, 140.7, 135.0, 132.5, 129.4, 128.5, 128.2, 128.0, 126.1, 125.7, 123.6, 113.7, 31.5, 30.1, 22.7, 14.1.

**HRMS (ESI)** scaled for $[M+H]^+$: $C_{21}H_{21}O_2$, m/z: 305.1536, observed: 305.1538.

**(3-Butyl-2-hydroxy-7-methylnaphthalen-1-yl)(phenyl)methanone.**



**7ba**

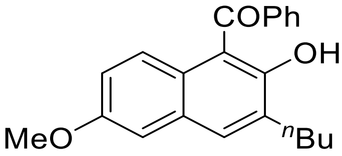
Yellow oil (60 mg, 94% yield), 0.2 mmol scale reaction.

**$^1$H NMR** (500 MHz, chloroform-*d*) δ 11.92 (s, 1H), 7.76 (s, 1H), 7.65 (d, *J* = 7.5 Hz, 2H), 7.61 (d, *J* = 8.0 Hz, 1H), 7.58 (t, *J* = 7.5 Hz, 1H), 7.43 (t, *J* = 7.5 Hz, 2H), 7.10 (d, *J* = 8.0 Hz, 1H), 7.01 (s, 1H), 2.91 – 2.82 (m, 2H), 2.16 (s, 3H), 1.83 – 1.73 (m, 2H), 1.54 – 1.46 (h, *J* = 7.5 Hz, 2H), 1.03 (t, *J* = 7.4 Hz, 3H).

**$^{13}$C NMR** (126 MHz, chloroform-*d*) δ 201.0, 161.4, 140.7, 135.4, 134.9, 132.3, 131.5, 131.3, 129.4, 128.4, 127.8, 126.3, 125.8, 125.5, 113.3, 31.5, 30.0, 22.7, 21.9, 14.1.

**HRMS (ESI)** scaled for $[M+H]^+$: $C_{22}H_{23}O_2$, m/z: 319.1693, observed: 319.1706.

**(3-Butyl-2-hydroxy-6-methoxynaphthalen-1-yl)(phenyl)methanone.**



**7ca**

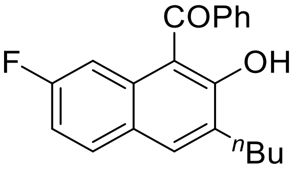
Yellow oil (64 mg, 96% yield), 0.2 mmol scale reaction.

**$^1$H NMR** (500 MHz, chloroform-*d*) δ 11.53 (s, 1H), 7.71 (s, 1H), 7.64 (d, *J* = 9.0 Hz, 2H), 7.57 (t, *J* = 8.0 Hz, 1H), 7.42 (t, *J* = 8.0 Hz, 2H), 7.16 (d, *J* = 9.0 Hz, 1H), 7.08 (d, *J* = 3.0 Hz, 1H), 6.79 (dd, *J* = 9.0, 2.5 Hz, 1H), 3.89 (s, 3H), 2.91 – 2.82 (m, 2H), 1.81 – 1.70 (m, 2H), 1.51 – 1.47 (m, 2H), 1.02 (t, *J* = 7.5 Hz, 3H).

**$^{13}$C NMR** (126 MHz, chloroform-*d*) δ 200.8, 159.3, 155.7, 140.7, 133.9, 132.9, 132.5, 129.4, 129.2, 128.6, 127.5, 126.1, 117.4, 114.0, 106.8, 55.2, 31.5, 30.1, 22.7, 14.1.

**HRMS (ESI)** scaled for $[M+H]^+$: $C_{22}H_{23}O_3$, m/z: 335.1642, observed: 335.1629.

**(3-Butyl-7-fluoro-2-hydroxynaphthalen-1-yl)(phenyl)methanone.**



**7da**

Yellow oil (48.3 mg, 75% yield), 0.2 mmol scale reaction.

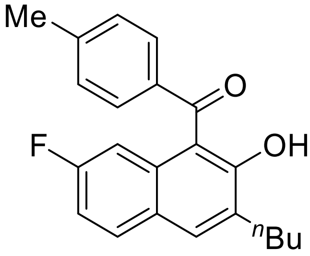
**$^{1}$H NMR** (500 MHz, chloroform-*d*) δ 12.00 (s, 1H), 7.77 (s, 1H), 7.69 (dd, *J* = 9.0, 6.0 Hz, 1H), 7.66 – 7.62 (m, 2H), 7.60 (t, *J* = 7.5 Hz, 1H), 7.45 (t, *J* = 7.5 Hz, 2H), 7.03 (td, *J* = 7.5, 2.5 Hz, 1H), 6.85 (dd, *J* = 12.0, 2.5 Hz, 1H), 2.92 – 2.80 (m, 2H), 1.78 – 1.72 (m, 2H), 1.51 – 1.48 (m, 2H), 1.02 (t, *J* = 7.5 Hz, 3H).

**$^{13}$C NMR** (126 MHz, chloroform-*d*) δ 200.67, 162.26, 160.39 (d, *J* = 245 Hz, 1C), 140.12, 134.80, 132.76, 132.51 (d, *J* = 9 Hz, 1C), 131.79, 130.23, 130.16, 129.30, 128.70, 125.05, 113.31 (d, *J* = 21 Hz, 1C), 110.51 (d, *J* = 21 Hz, 1C), 31.43, 29.90, 22.68, 14.03.

**$^{19}$F NMR** (470.5 MHz, chloroform-*d*) δ -112.6 (m, 1F).

**HRMS (ESI)** scaled for $[M+H]^+$: $C_{21}H_{20}FO_2$, m/z: 323.1442, observed: 323.1441.

**(3-Butyl-7-fluoro-2-hydroxynaphthalen-1-yl)(p-tolyl)methanone**.



**7fa**

Yellow oil (53 mg, 79% yield), 0.2 mmol scale reaction.

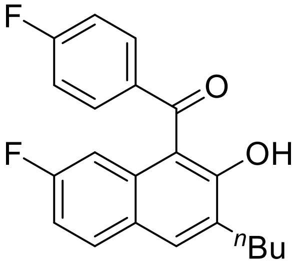
**$^{1}$H NMR** (500 MHz, chloroform-*d*) δ 11.75 (s, 1H), 7.76 (s, 1H), 7.69 (dd, *J* = 9.0, 6.0 Hz, 1H), 7.55 (d, *J* = 8.0 Hz, 2H), 7.24 (d, *J* = 8.0 Hz, 2H), 7.03 (td, *J* = 8.5, 2.5 Hz, 1H), 6.92 (dd, *J* = 12.0, 2.5 Hz, 1H), 2.90 – 2.80 (m, 2H), 2.46 (s, 3H), 1.80 – 1.70 (m, 2H), 1.52 – 1.44 (m, 2H), 1.01 (t, *J* = 7.5 Hz, 3H).

**$^{13}$C NMR** (126 MHz, chloroform-*d*) δ 200.28, 161.63, 160.46 (d, *J* = 245 Hz, 1C), 143.77 , 137.30, 134.39, 132.53 (d, *J* = 9 Hz, 1C), 131.72, 130.14, 130.06, 129.61, 129.37, 125.04, 113.26 (d, *J* = 21 Hz, 1C), 110.49 (d, *J* = 21 Hz, 1C), 31.44, 29.92, 22.67, 21.75, 14.02.

**$^{19}$F NMR** (470.5 MHz, chloroform-*d*) δ -111.8 (m, 1F).

**HRMS (ESI)** scaled for $[M+H]^+$: $C_{22}H_{22}FO_2$, m/z: 337.1598, observed: 337.1613.

**(3-Butyl-7-fluoro-2-hydroxynaphthalen-1-yl)(4-fluorophenyl)-methanone**.



**7ha**

Yellow oil (56 mg, 83% yield), 0.2 mmol scale reaction.

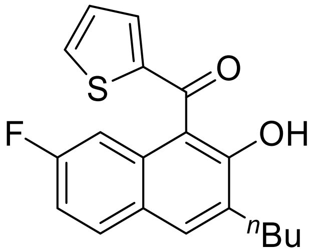
**$^1$H NMR** (500 MHz, chloroform-*d*) δ 11.68 (s, 1H), 7.77 (s, 1H), 7.72 – 7.65 (m, 3H), 7.13 (t, *J* = 8.5 Hz, 2H), 7.05 (ddd, *J* = 12.0, 8.5, 2.5 Hz, 1H), 6.87 (dd, *J* = 12.0, 2.5 Hz, 1H), 2.89 – 2.78 (comp, 2H), 1.77 –1.71 (m, 2H), 1.52 – 1.44 (m, 2H), 1.01 (t, *J* = 7.5 Hz, 3H).

**$^{13}$C NMR** (126 MHz, chloroform-*d*) δ 198.87, 165.52 (d, *J* = 255 Hz, 1C), 161.87, 160.56 (d, *J* = 245 Hz, 1C), 136.11, 134.76, 132.35, 132.28, 132.16, 132.09, 131.80, 130.32 (d, *J* = 9 Hz, 1C), 125.07, 115.92 (d, *J* = 21 Hz, 1C), 113.44 (d, *J* = 21 Hz, 1C), 110.34 (d, *J* = 21 Hz, 1C), 31.42, 29.89, 22.66, 14.01.

**$^{19}$F NMR** (470.5 MHz, chloroform-*d*) δ-104.9 (m, 1F), -112.3 (m, 1F).

**HRMS (ESI)** scaled for $[M+H]^+$: $C_{21}H_{19}F_2O_2$, m/z: 341.1348, observed: 341.1363.

**(3-Butyl-7-fluoro-2-hydroxynaphthalen-1-yl)(thiophen-2-yl)methanone.**



**7ia**

Yellow oil (40.6 mg, 62% yield), 0.2 mmol scale reaction.

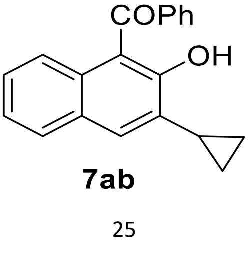
**$^1$H NMR** (500 MHz, chloroform-*d*) δ 10.41 (s, 1H), 7.76 (dd, *J* = 5.0, 1.0 Hz, 1H), 7.74 (s, 1H), 7.71 (dd, *J* = 9.0, 6.0 Hz, 1H), 7.41 (dd, *J* = 4.0, 1.0 Hz, 1H), 7.37 (dd, *J* = 12.0, 2.5 Hz, 1H), 7.10 – 7.06 (comp, 2H), 2.88 – 2.79 (m, 2H), 1.80 – 1.67 (m, 2H), 1.50 – 1.43 (m, 2H), 1.00 (t, *J* = 7.5 Hz, 3H).

**$^{13}$C NMR** (126 MHz, chloroform-*d*) δ 190.81, 160.40 (d, *J* = 245 Hz, 1C), 159.16, 144.51, 135.59, 134.91, 133.73, 132.0 (d, *J* = 9 Hz, 1C), 131.59, 130.00 (d, *J* = 9 Hz, 1C), 128.16, 125.28, 113.64 (d, *J* = 21 Hz, 1C), 110.15 (d, *J* = 21 Hz, 1C), 31.46, 29.99, 22.65, 14.01.

**$^{19}$F NMR** (470.5 MHz, chloroform-*d*) δ -110.5 (m, 1F).

**HRMS (ESI)** scaled for $[M+H]^+$: $C_{19}H_{18}FO_2S$, m/z: 329.1006, observed: 329.1021.

**(3-Cyclopropyl-2-hydroxynaphthalen-1-yl)(phenyl)methanone.**



**7ab**

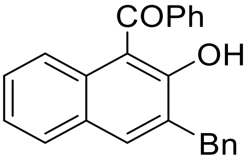
Yellow oil (46 mg, 80% yield), 0.2 mmol scale reaction.

**$^1$H NMR** (500 MHz, chloroform-*d*) δ 11.48 (s, 1H), 7.70 – 7.66 (comp, 3H), 7.61 – 7.55 (comp, 2H), 7.43 (t, *J* = 8.0 Hz, 2H), 7.31 – 7.23 (comp, 2H), 7.12 (ddd, *J* = 8.4, 6.9, 1.4 Hz, 1H), 2.38 – 2.33 (m, 1H), 1.15 – 1.08 (m, 2H), 0.89 – 0.84 (m, 2H).

**$^{13}$C NMR** (126 MHz, chloroform-*d*) δ 200.7, 160.8, 140.4, 133.1, 132.6, 131.0, 130.7, 129.5, 128.5, 128.2, 128.0, 125.9, 125.8, 123.7, 114.0, 10.0, 7.5.

**HRMS (ESI)** scaled for $[M+H]^+$: $C_{20}H_{17}O_2$, m/z: 289.1223, observed: 289.1237.

### (3-benzyl-2-hydroxynaphthalen-1-yl)(phenyl)methanone.



**7ac**

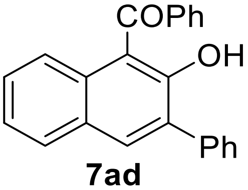
Yellow solid (57 mg, 85% yield), 0.2 mmol scale reaction.

**$^1$H NMR** (500 MHz, chloroform-d) δ 11.79 (s, 1H), 7.70 (s, 1H), 7.68 (d, *J* = 8.0 Hz, 1H), 7.66 – 7.62 (comp., 2H), 7.58 (t, *J* = 7.5 Hz, 1H), 7.43 (t, *J* = 7.5 Hz, 2H), 7.39 – 7.34 (comp., 4H), 7.26 (dd, J = 15.0, 8.0 Hz, 3H), 7.12 (t, *J* = 7.5 Hz, 1H), 4.23 (s, 2H).

**$^{13}$C NMR** (126 MHz, chloroform-d) δ 200.8, 160.7, 140.5, 139.7, 135.7, 132.6, 131.5, 131.1, 129.4, 129.2, 128.5, 128.52, 128.2, 128.1, 126.3, 126.1, 126.0, 123.7, 36.1.

**HRMS (ESI)** scaled for [M+H]+: $C_{24}H_{19}O_2$, m/z: 339.1380, observed: 339.1387.

### (2-Hydroxy-3-phenylnaphthalen-1-yl)(phenyl)methanone.



**7ad**

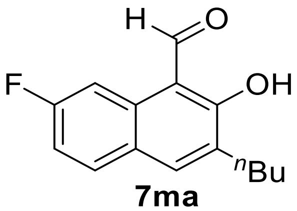
Yellow oil (22 mg, 35% yield), 0.2 mmol scale reaction.

**$^1$H NMR** (500 MHz, chloroform-*d*) δ 11.11 (s, 1H), 8.00 (s, 1H), 7.82 (d, *J* = 8.0 Hz, 1H), 7.76 – 7.70 (comp, 4H), 7.61 (t, *J* = 7.5 Hz, 1H), 7.55 – 7.51 (comp, 2H), 7.46 (td, *J* = 7.5, 1.5 Hz, 3H), 7.38 – 7.31 (m, 2H), 7.23 – 7.20 (m, 1H).

**$^{13}$C NMR** (126 MHz, chloroform-*d*) δ 200.5, 158.3, 140.2, 136.8, 135.8, 132.8, 132.0, 131.6, 129.6, 128.6, 128.5, 128.3, 128.0, 126.7, 125.9, 124.0, 115.2.

**HRMS (ESI)** scaled for $[M+H]^+$: $C_{23}H_{17}O_2$, m/z: 325.1223, observed: 325.1234.

### 3-butyl-7-fluoro-2-hydroxy-1-naphthaldehyde.



**7ma**

White solid (31 mg, 61% yield), 0.2 mmol scale reaction.

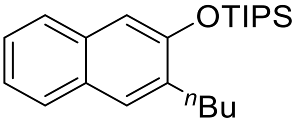
**$^{1}$H NMR** (500 MHz, chloroform-*d*) δ 13.61 (s, 1H), 10.64 (s, 1H), 7.89 (dd, *J* = 11.0, 2.5 Hz, 1H), 7.78 (s, 1H), 7.73 (dd, *J* = 9.0, 6.0 Hz, 1H), 7.17 (td, *J* = 8.0, 2.5 Hz, 1H), 2.83 – 2.69 (m, 2H), 1.76 – 1.65 (m, 2H), 1.48 – 1.41 (m, 2H), 0.99 (t, *J* = 7.5 Hz, 3H).

**$^{13}$C NMR** (126 MHz, chloroform-*d*) δ 192.79, 165.20, 162.40 (d, *J* = 245 Hz, 1C), 137.16, 133.2 (d, *J* = 9 Hz, 1C), 131.74, 131.19, 131.11, 124.52, 113.90 (d, *J* = 21 Hz, 1C), 110.60, 103.12 (d, *J* = 21 Hz, 1C), 31.25, 29.17, 22.58, 13.96.

**$^{19}$F NMR** (470.5 MHz, chloroform-*d*) δ -113.0 (m, 1F).

**HRMS (ESI)** scaled for $[M+H]^+$: $C_{15}H_{16}FO_2$, m/z: 247.1129, observed: 247.1133.

**((3-butylnaphthalen-2-yl)oxy)triisopropylsilane.**



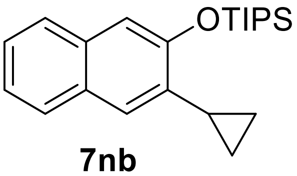
**7na**

Colorless oil (65 mg, 91% yield), 0.2 mmol scale reaction.

**$^{1}$H NMR** (500 MHz, chloroform-*d*) δ 7.76 (dd, *J* = 8.0, 1.0 Hz, 1H), 7.69 (dd, *J* = 8.0, 1.0 Hz, 1H), 7.63 (s, 1H), 7.40 (ddd, *J* = 8.0, 7.0, 1.0 Hz, 1H), 7.34 (ddd, *J* = 8.0, 7.0, 1.0 Hz, 1H), 7.17 (s, 1H), 2.89 – 2.81 (m, 2H), 1.78 – 1.69 (m, 2H), 1.51 – 1.42 (m, 5H), 1.22 (d, *J* = 7.5 Hz, 18H), 1.02 (t, *J* = 7.5 Hz, 3H).

**$^{13}$C NMR** (126 MHz, chloroform-*d*) δ 153.0, 135.0, 133.3, 129.1, 128.2, 127.0, 126.1, 123.4, 112.4, 32.3, 31.2, 22.8, 18.2, 13.2. The spectra is consist with previous report.[4]

**((3-cyclopropylnaphthalen-2-yl)oxy)triisopropylsilane.**



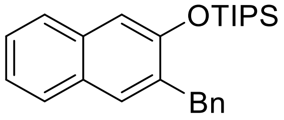
**7nb**

Colorless oil (62.5 mg, 92% yield), 0.2 mmol scale reaction.

**$^{1}$H NMR** (500 MHz, chloroform-*d*) δ 7.72 (d, *J* = 8.0 Hz, 1H), 7.68 (d, *J* = 8.0 Hz, 1H), 7.39 (ddd, *J* = 8.0, 7.0, 1.0 Hz, 1H), 7.35 (s, 1H), 7.34 – 7.31 (m, 1H), 7.18 (s, 1H), 2.42 – 2.32 (m, 1H), 1.53 – 1.43 (m, 3H), 1.23 (d, *J* = 7.5 Hz, 18H), 1.07 – 1.01 (m, 2H), 0.85 – 0.77 (m, 2H).

**$^{13}$C NMR** (126 MHz, chloroform-*d*) δ 153.8, 135.9, 132.9, 129.1, 127.1, 126.0, 125.1, 123.7, 123.5, 112.4, 18.2, 13.1, 10.9, 8.0. The spectra is consist with previous report.[4]

### ((3-Benzylnaphthalen-2-yl)oxy)triisopropylsilane.



**7nc**

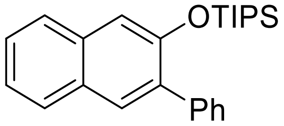
Colorless oil (74mg, 96% yield), 0.2 mmol scale reaction.

**$^1$H NMR** (500 MHz, chloroform-*d*) δ 7.76 – 7.71 (m, 2H), 7.52 (s, 1H), 7.44 (t, *J* = 7.5 Hz, 1H), 7.39 – 7.33 (comp, 3H), 7.32 – 7.28 (comp, 3H), 7.24 (s, 1H), 4.26 (s, 2H), 1.51 – 1.40 (m, 3H), 1.22 –1.19 (m, 18H).

**$^{13}$C NMR** (126 MHz, chloroform-*d*) δ 152.9, 140.7, 133.2, 129.4, 129.1, 129.0, 128.4, 127.3, 126.1, 126.0, 125.5, 123.6, 112.5, 36.9, 18.2, 13.2.

**HRMS (ESI)** scaled for $[M+H]^+$: $C_{26}H_{35}OSi$, m/z: 391.2452, observed: 391.2448.

### Triisopropyl((3-phenylnaphthalen-2-yl)oxy)silane.



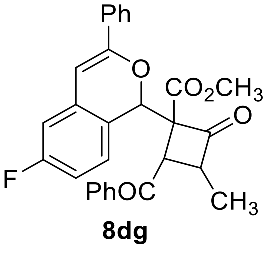
**7nd**

Colorless oil (18.8 mg, 25% yield), 0.2 mmol scale reaction.

**$^1$H NMR** (300 MHz, chloroform-*d*) δ 7.85 – 7.78 (comp, 2H), 7.73 (s, 1H), 7.64 – 7.59 (comp, 2H), 7.50 – 7.42 (comp, 3H), 7.41 – 7.33 (comp, 2H), 7.29 (s, 1H), 1.33 – 1.20 (m, 3H), 1.04 (d, *J* = 7.5 Hz, 18H).

**$^{13}$C NMR** (75 MHz, chloroform-*d*) δ 151.8, 139.1, 135.0, 134.0, 130.0, 129.1, 127.8, 127.0, 126.2, 126.0, 123.9, 113.9, 17.9, 13.0. The spectra is consist with previous report.[4]

### Methyl 2-Benzoyl-1-(6-fluoro-3-phenyl-1H-isochromen-1-yl)-3-methyl-4-oxocyclobutane-1-carboxylate.



**8dg**

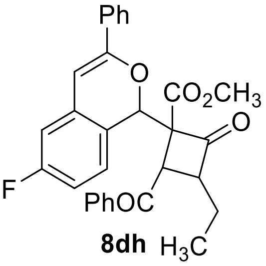
Colorless oil (10.8 mg, 23% yield, 5:1 dr).

Major isomer: **$^1$H NMR** (500 MHz, chloroform-*d*) δ 8.05 (d, *J* = 7.5 Hz, 2H), 7.78 – 7.71 (comp., 2H), 7.52 (t, *J* = 7.5 Hz, 2H), 7.44 - 7.39 (comp., 2H), 7.24 (s, 1H), 7.09 – 7.01 (comp., 2H), 6.96 – 6.85 (comp., 2H), 6.47 (s, 1H), 6.08 (s, 1H), 4.45 (d, *J* = 8.8 Hz, 1H), 4.20 – 4.05 (m, 1H), 3.63 (s, 3H), 0.90 (d, *J* = 7.5 Hz, 3H).

**$^{13}$C NMR** (126 MHz, Chloroform-*d*) δ 201.67, 197.10, 167.26, 163.20 (d, *J* = 245 Hz), 151.18, 137.09, 133.64, 133.22, 129.45, 128.87, 128.71, 128.46, 128.3, 128.30, 127.84, 127.14, 127.06, 124.90, 124.43, 113.78 (d, *J* = 21 Hz), 111.22 (d, *J* = 21 Hz), 102.39, 76.10, 55.11, 52.93, 45.50, 12.63.

**HRMS (ESI)** scaled for [M+H]$^+$: $C_{29}H_{24}FO_5$, m/z: 471.1608, observed: 471.19.1607.

**Methyl 2-Benzoyl-1-(6-fluoro-3-phenyl-1H-isochromen-1-yl)-3-methyl-4-oxocyclobutane-1-carboxylate.**



**8dh**

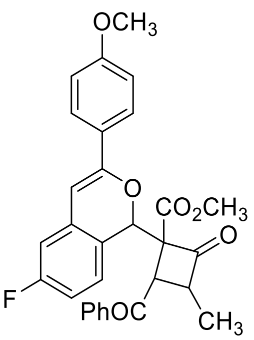
Colorless oil (8.4 mg, 18% yield, 5:1 dr).

Major isomer: **$^1$H NMR** (500 MHz, Chloroform-*d*) δ 8.06 (d, *J* = 7.5 Hz, 2H), 7.74 – 7.72 (comp, 2H), 7.66 – 7.61 (m, 1H), 7.53 – 7.50 (comp, 2H), 7.44 – 7.39 (comp, 3H), 7.25 – 7.22 (m, 1H), 7.09 – 7.07 (m, 1H), 6.93 – 6.85 (m, 2H), 6.45 (s, 1H), 6.07 (s, 1H), 4.49 (d, *J* = 9.0 Hz, 1H), 4.12 – 4.04 (m, 1H), 3.62 (s, 3H), 1.51 – 1.43 (m, 1H), 1.17 – 1.07 (m, 1H), 0.71 (t, *J* = 7.5 Hz, 3H).

**$^{13}$C NMR** (126 MHz, Chloroform-*d*) δ 201.16, 197.37, 162.26, 160.42 (d, *J* = 245 Hz), 129.42, 128.85, 128.66, 128.46, 128.35, 127.84, 124.90, 124.42, 113.74(d, *J* = 21 Hz),, 111.18 (d, *J* = 21 Hz), 102.26, 76.20, 61.85, 52.93, 46.94, 43.57, 21.45, 11.19.

**HRMS (ESI)** scaled for [M+H]$^+$: $C_{30}H_{26}FO_5$, m/z: 485.1764, observed: 485.1760.

**Methyl 2-benzoyl-1-(6-fluoro-3-(4-methoxyphenyl)-1H-isochromen-1-yl)-3-methyl-4-oxocyclobutane-1-carboxylate**.



**8gg**

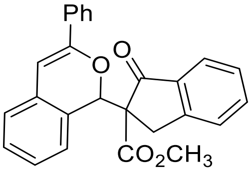
Colorless oil (6 mg, 12% yield).

Major isomer: **$^1$H NMR** (500 MHz, chloroform-*d*) δ 8.04 (d, *J* = 7.5 Hz, 2H), 7.68 (d, *J* = 9.0 Hz, 2H), 7.62 (t, *J* = 7.5 Hz, 1H), 7.52 (t, *J* = 7.5 Hz, 2H), 7.45 – 7.38 (m, 1H), 7.01 (dd, *J* = 8.4, 5.5 Hz, 1H), 6.96 – 6.92 (comp, 2H), 6.91 – 6.82 (comp, 2H), 6.34 (s, 1H), 6.07 (s, 1H), 4.43 (d, *J* = 8.5 Hz, 1H), 4.19 – 4.07 (m, 1H), 3.86 (s, 3H), 3.63 (s, 3H), 0.90 (d, *J* = 7.5 Hz, 3H).

**$^{13}$C NMR** (126 MHz, chloroform-*d*) δ 201.71, 200.06, 164.20, 162.55 (d, *J* = 245 Hz), 151.24, 137.12, 133.57, 128.82, 128.34, 126.04, 114.09, 113.29 (d, $J$ = 21 Hz), 110.85 (d, $J$ = 21 Hz), 100.67, 76.13, 55.35; 55.16; 52.89; 45.50; 12.68.

**HRMS (ESI)** scaled for $[M+H]^+$: $C_{30}H_{26}FO_6$, m/z: 501.1708, observed: 501.1686.

**Methyl 1-oxo-2-(3-phenyl-1H-isochromen-1-yl)-2,3-dihydro-1H-indene-2-carboxylate.**



**13**

Colorless oil (17 mg, 45% yield, 1:1 dr), 0.1 mmol scale reaction.

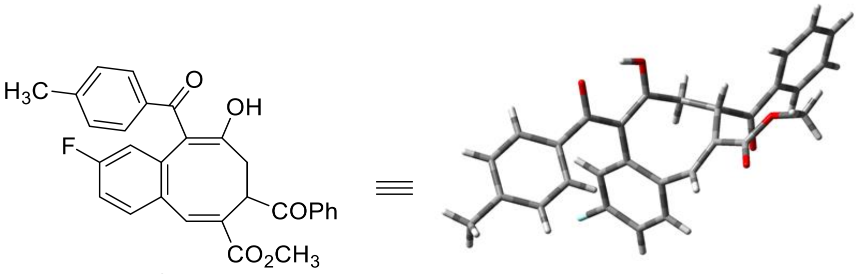
**13** was reported as 1:1 mixture spectrum:

**$^1$H NMR** (500 MHz, chloroform-*d*) δ 7.91 (d, $J$ = 7.5 Hz, 1H), 7.73 (d, $J$ = 7.5 Hz, 1H), 7.66 – 7.62 (comp., 2H), 7.57 (td, $J$ = 7.5, 1.0 Hz, 1H), 7.52 – 7.47 (m, 1H), 7.45 (d, $J$ = 7.5 Hz, 1H), 7.43 – 7.37 (comp., 4H), 7.35 – 7.29 (comp., 5H), 7.25 – 7.19 (comp., 4H), 7.16 (tt, $J$ = 7.5, 2.5 Hz, 2H), 7.07 (d, $J$ = 7.5 Hz, 1H), 7.01 (d, $J$ = 7.5 Hz, 1H), 6.99 – 6.95 (comp, 2H), 6.70 (s, 1H), 6.40 (s, 1H), 6.37 (s, 1H), 6.35 (s, 1H), 4.04 (d, $J$ = 17.5 Hz, 1H), 3.92 (d, $J$ = 17.5 Hz, 1H), 3.92 (s, 3H), 3.84 (s, 3H), 3.69 (d, $J$ = 17.3 Hz, 1H), 3.42 (d, $J$ = 17.3 Hz, 1H).

**$^{13}$C NMR** (126 MHz, chloroform-*d*) δ 199.22, 198.48, 168.88, 168.12, 154.48, 154.37, 153.45, 151.99, 135.5, 135.4, 134.85, 134.75, 133.83, 133.04, 131.49, 129.02, 128.85, 128.76, 128.53, 128.37, 128.15, 127.63, 127.44, 127.00, 126.78, 126.33, 126.18, 125.79, 125.08, 124.84, 124.67, 124.39, 124.33, 123.50, 101.01, 99.89, 80.14, 79.77, 70.24, 65.15, 53.43, 53.32, 33.24, 31.68.

**HRMS (ESI)** scaled for $[M+H]^+$: $C_{26}H_{21}O_4$, m/z: 419.1254, observed: 419.1261.

## 8. X-ray crystal structure of the product 3fa, 7ma and 15da



Single crystals of $C_{29}H_{22}FO_5$ were prepared by slow evaporation of a EA/hexane solution. A suitable colorless plate-like crystal with dimensions of 0.021 mm × 0.107 mm × 0.141 mm, was mounted in paratone oil onto a nylon loop. All data were collected at 100.0(1) K, using a XtaLAB Synergy/ Dualflex, HyPix fitted with CuKα radiation (λ = 1.54184 Å). Data collection and unit cell refinement were performed using *CrysAlisPro* software.[1] The total number of data were measured in the 6.76° < 2θ < 144.8°, using ω scans. Data processing and absorption correction, giving minimum and maximum transmission factors (0.769, 1.000) were accomplished with *CrysAlisPro*[1] and *SCALE3 ABSPACK*[2], respectively. The structure, using Olex2[3], was solved with the ShelXT[4] structure solution program using direct methods and refined (on $F^2$) with the ShelXL[5] refinement package using full-matrix, least-squares techniques. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atom positions were determined by geometry and refined by a riding model.

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[1] CrysAlisPro 1.171.40.63a (Rigaku Oxford Diffraction, 2019)

[2] SCALE3 ABSPACK -An Oxford Diffraction program(1.0.4,gui:1.0.3) (C) 2005 Oxford Diffraction Ltd.

[3] O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard, H. Puschmann, *J. Appl. Cryst.* 2009, **42**, 339.

[4] G. M. Sheldrick, *Acta Cryst.* 2015, **A71**, 3.

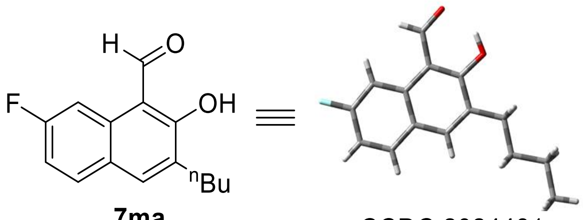
[5] G. M. Sheldrick, *Acta Cryst.* 2008, **A64**, 112.

***Table S1:*** Crystallographic data and structure refinement for **3fa**

| Identification code | **3fa** |
|---|---|
| Empirical formula | $C_{29}H_{22}FO_5$ |
| Formula weight | 469.46 |
| Crystal system | Monoclinic |
| Space group | $P2_1$ |
| $a$ (Å) | 9.9631(3) |
| $b$ (Å) | 9.1494(2) |
| $c$ (Å) | 13.3605(4) |
| $\alpha$ (°) | 90 |
| $\beta$ (°) | 102.001(3) |
| $\gamma$ (°) | 90 |
| Volume (Å$^3$) | 1191.28(6) |
| Z | 2 |
| ρ (calc.) | 1.309 |
| λ | 1.54184 |
| Temp. (K) | 100.0(1) |
| F(000) | 490 |
| μ (mm$^{-1}$) | 0.779 |
| $T_{min}$, $T_{max}$ | 0.769, 1.000 |
| $2\theta_{range}$ (°) | 6.76 to 144.8 |
| Reflections collected | 14112 |
| Independent reflections | 4208 [R(int) = 0.0406] |
| Completeness | 99.9% |
| Data / restraints / parameters | 4208/ 1 /319 |
| Observed data [I > 2σ(I)] | 3887 |
| $wR(F^2$ all data) | 0.1190 |
| $R(F$ obsd data) | 0.0482 |
| Goodness-of-fit on $F^2$ | 1.04 |
| largest diff. peak and hole (e Å$^{-3}$) | 0.45 / -0.24 |

$$wR_2 = \{ \Sigma [w(F_o^2 - F_c^2)^2] / \Sigma [w(F_o^2)^2] \}^{1/2}$$

$$R_1 = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|$$



**7ma**

CCDC 2024481

Single crystals of $C_{15}H_{15}FO_2$ were prepared by slow evaporation of a dichloromethane and hexane solution. A suitable colorless block-like crystal, with dimensions of 0.175 mm × 0.104 mm × 0.072 mm, was mounted in paratone oil onto a nylon loop. All data were collected at 100.0(1) K, using a XtaLAB Synergy/ Dualflex, HyPix fitted with CuKα radiation ($\lambda = 1.54184$ Å). Data collection and unit cell refinement were performed using *CrysAlisPro* software.[1] The total number of data were measured in the $9.27° < 2\theta < 152.5°$, using $\omega$ scans. Data processing and absorption correction, giving minimum and maximum transmission factors (0.600, 1.000) were accomplished with *CrysAlisPro*[6] and *SCALE3 ABSPACK*[7], respectively. The structure, using Olex2[8], was solved with the ShelXT[9] structure solution program using direct methods and refined (on $F^2$) with the ShelXL[10] refinement package using full-matrix, least-squares techniques. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atom positions were determined by geometry and refined by a riding model.

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[1] CrysAlisPro 1.171.40.63a (Rigaku Oxford Diffraction, 2019)

[7] SCALE3 ABSPACK -An Oxford Diffraction program(1.0.4,gui:1.0.3) (C) 2005 Oxford Diffraction Ltd.

[8] O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard, H. Puschmann, *J. Appl. Cryst.* 2009, **42**, 339.

[9] G. M. Sheldrick, *Acta Cryst.* 2015, **A71**, 3.

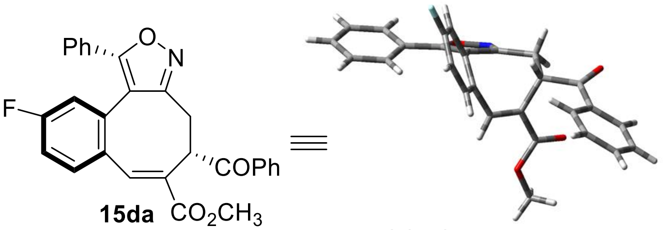
[10] G. M. Sheldrick, *Acta Cryst.* 2008, **A64**, 112.

***Table S2:*** Crystallographic data and structure refinement for **7ma**

| Identification code | **7ma** |
|---|---|
| Empirical formula | $C_{15}H_{15}FO_2$ |
| Formula weight | 246.27 |
| Crystal system | Monoclinic |
| Space group | $P2_1/n$ |
| $a$ (Å) | 7.3867(2) |
| $b$ (Å) | 19.0785(5) |
| $c$ (Å) | 9.3357(2) |
| $\alpha$ (°) | 90 |
| $\beta$ (°) | 111.972(3) |
| $\gamma$ (°) | 90 |
| Volume (Å$^3$) | 1220.09(6) |
| Z | 4 |
| ρ (calc.) | 1.341 |
| λ | 1.54184 |
| Temp. (K) | 100.0(1) |
| F(000) | 520 |
| μ (mm$^{-1}$) | 0.808 |
| $T_{min}$, $T_{max}$ | 0.600, 1.000 |
| $2\theta_{range}$ (°) | 9.27 to 152.5 |
| Reflections collected | 13853 |
| Independent reflections | 2429<br>[R(int) = 0.0414] |
| Completeness | 99.8% |
| Data / restraints / parameters | 2429/ 0 /165 |
| Observed data [I > 2σ(I)] | 2122 |
| $wR$($F^2$ all data) | 0.1096 |
| $R$($F$ obsd data) | 0.0415 |
| Goodness-of-fit on $F^2$ | 1.09 |
| largest diff. peak and hole (e Å$^{-3}$) | 0.21 / -0.32 |

$$wR_2 = \{ \Sigma [w(F_o^2 - F_c^2)^2] / \Sigma [w(F_o^2)^2] \}^{1/2}$$

$$R_1 = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|$$



**15da**

CCDC 2024482

Single crystals of $C_{28}H_{21}FNO_4$ were prepared by slow evaporation of a dichloromethane and hexane solution. A suitable colorless plank-like crystal, with dimensions of 0.369 mm × 0.180 mm × 0.058 mm, was mounted in paratone oil onto a nylon loop. All data were collected at 100.0(1) K, using a XtaLAB Synergy/ Dualflex, HyPix fitted with CuKα radiation ($\lambda$ = 1.54184 Å). Data collection and unit cell refinement were performed using *CrysAlisPro* software.[1] The total number of data were measured in the $7.29° < 2\theta < 153.4°$, using ω scans. Data processing and absorption correction, giving minimum and maximum transmission factors (0.437, 1.000) were accomplished with *CrysAlisPro*[11] and *SCALE3 ABSPACK*[12], respectively. The structure, using Olex2[13], was solved with the ShelXT[14] structure solution program using direct methods and refined (on $F^2$) with the ShelXL[15] refinement package using full-matrix, least-squares techniques. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atom positions were determined by geometry and refined by a riding model.

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[1] CrysAlisPro 1.171.40.63a (Rigaku Oxford Diffraction, 2019)

[12] SCALE3 ABSPACK -An Oxford Diffraction program(1.0.4,gui:1.0.3) (C) 2005 Oxford Diffraction Ltd.

[13] O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard, H. Puschmann, *J. Appl. Cryst.* 2009, **42**, 339.

[14] G. M. Sheldrick, *Acta Cryst.* 2015, **A71**, 3.

[15] G. M. Sheldrick, *Acta Cryst.* 2008, **A64**, 112.

***Table S3:*** Crystallographic data and structure refinement for **15da**

| Identification code | **15da** |
|---|---|
| Empirical formula | $C_{28}H_{21}FNO_4$ |
| Formula weight | 454.46 |
| Crystal system | Monoclinic |
| Space group | $P2_1/c$ |
| $a$ (Å) | 12.28538(14) |
| $b$ (Å) | 20.3181(2) |
| $c$ (Å) | 8.91344(10) |
| $\alpha$ (°) | 90 |
| $\beta$ (°) | 99.0372(11) |
| $\gamma$ (°) | 90 |
| Volume (Å$^3$) | 2197.31(4) |
| Z | 4 |
| ρ (calc.) | 1.374 |
| λ | 1.54184 |
| Temp. (K) | 100.0(1) |
| F(000) | 948 |
| μ (mm$^{-1}$) | 0.804 |
| $T_{min}$, $T_{max}$ | 0.437, 1.000 |
| $2\theta_{range}$ (°) | 7.29 to 153.4 |
| Reflections collected | 21382 |
| Independent reflections | 4485 [R(int) = 0.0402] |
| Completeness | 99.9% |
| Data / restraints / parameters | 4485/ 0 /308 |
| Observed data [I > 2σ(I)] | 4040 |
| $wR(F^2$ all data) | 0.1051 |
| $R(F$ obsd data) | 0.0383 |
| Goodness-of-fit on $F^2$ | 1.05 |
| largest diff. peak and hole (e Å$^{-3}$) | 0.29 / -0.78 |

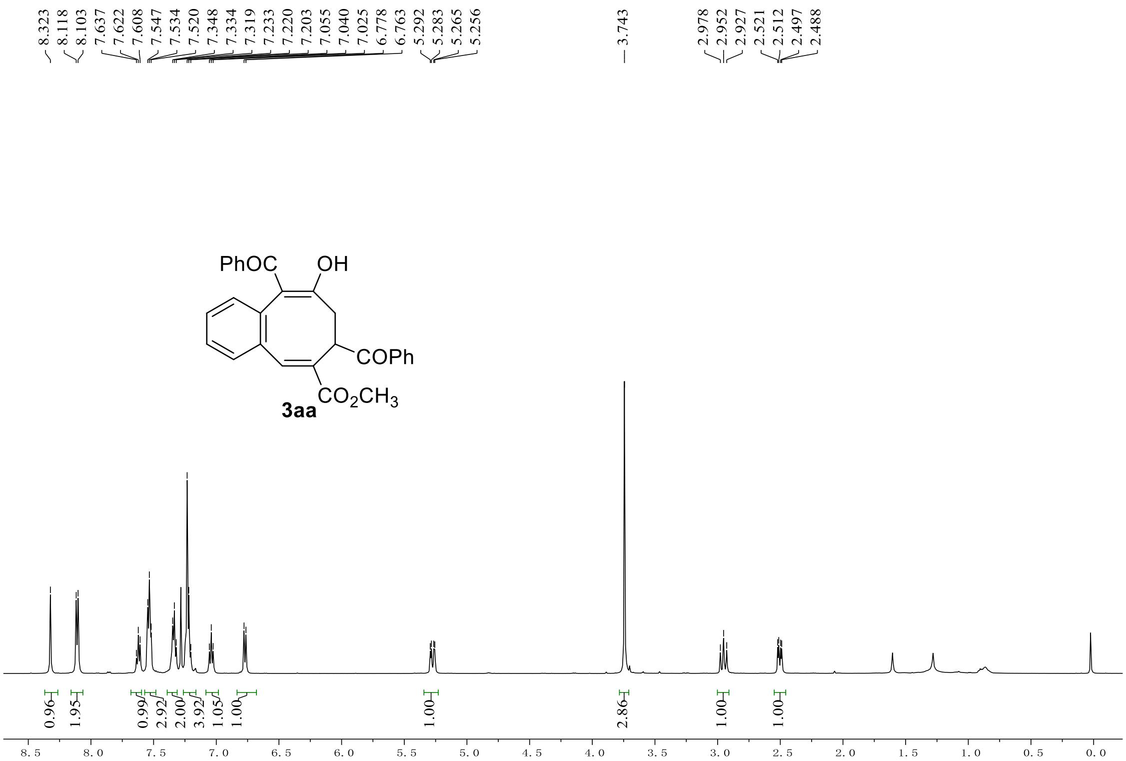
$wR_2 = \{ \Sigma [w(Fo2 – Fc2)2] / \Sigma [w(Fo2)2] \}1/2$

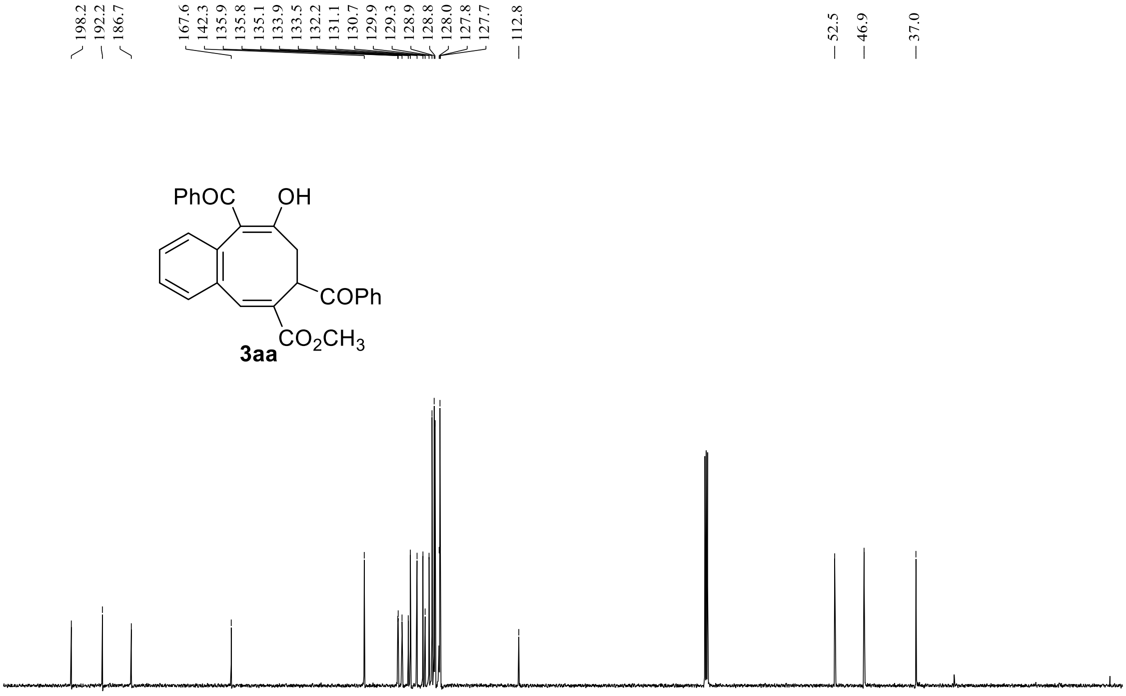
$R_1 = \Sigma ||Fo| – |Fc|| / \Sigma |Fo|$

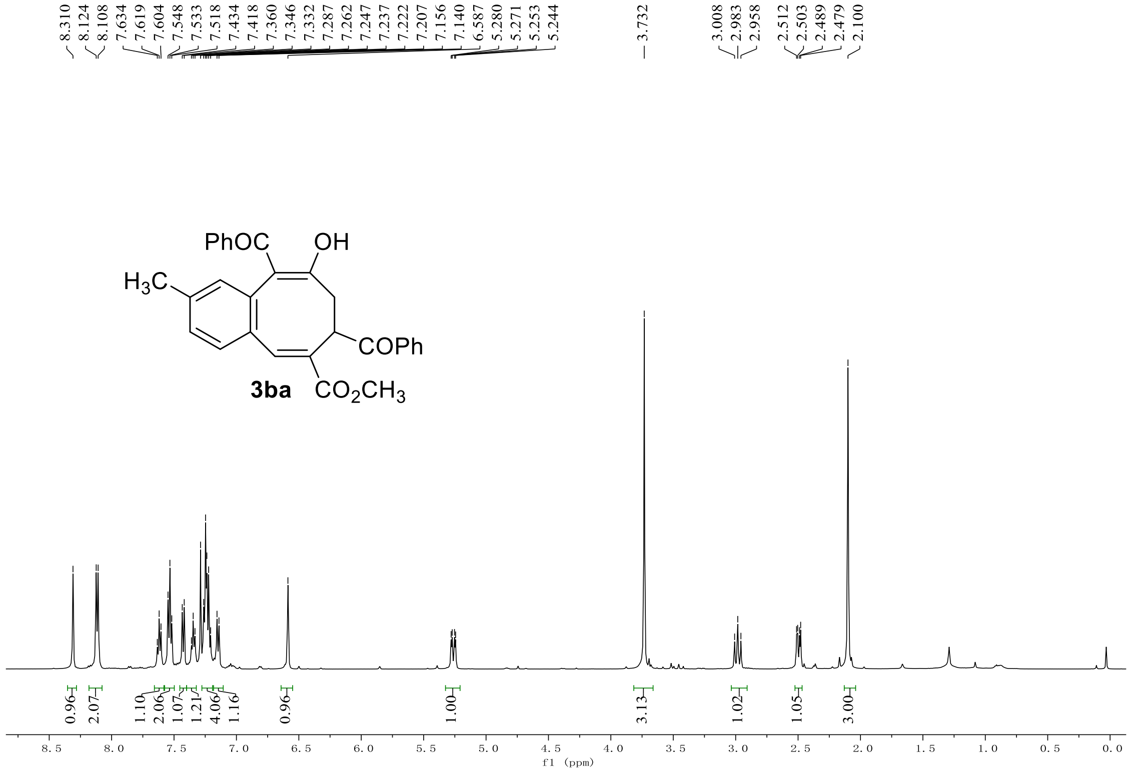
## 9. References

1. (a) N. T. Patil, Y. Yamamoto, *J. Org. Chem.* 2004, **69**, 5139. (b) H. Qian, W. X. Zhao, Z. B. Wang, J. W. Sun, *J. Am. Chem. Soc.* 2015, **137**, 560.
2. (a) Y. M. Deng, L. A. Massey, P. Y. Zavalij, M. P. Doyle, *Angew. Chem. Int. Ed.* 2017, **56**, 7479. (b) K. Dong, K. O. Marichev, X. Xu, M. P. Doyle, *Synlett* 2019, **30**, 1457. (c) R. Wang, K. O. Marichev, K. Y. Dong, J. A. Jensen, M. P. Doyle, *J. Org. Chem.* 2020, **85**, 9475.
3. Y. M. Deng, C. Jing, M. P. Doyle, *Chem. Commun.* 2015, **51**, 12924.
4. (a) R. F. Sweis, M. P. Schramm, S. A. Kozmin, *J. Am. Chem. Soc.* 2004, **126**, 7442. (b) Y. E. Türkmen, T. J. Montavon, S. A. Kozmin, V. H. Rawal, *J. Am. Chem. Soc.* 2012, **134**, 9062.
5. (a) K. O. Marichev, K. Wang, K. Dong, N. Greco, L. A. Massey, Y. Deng, H. Arman, M. P. Doyle, *Angew. Chem. Int. Ed.* 2019, **58**, 16188. (b) K. O. Marichev, K. Dong, L. A. Massey, Y. Deng, L.; Wang, K. De Angelis, H. Arman, M. P. Doyle, *Nature Communications* 2019**, 10**, 5328.
6. Q. Q. Chen, Y. M. Deng, M. Lankelma, M. P. Doyle, *Chem. Soc. Rev.* 2017**, 46**, 5425.

## 10. NMR spectrum of products



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7.262
7.247
7.237
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7.207
7.156
7.140
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5.280
5.271
5.253
5.244
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3.008
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OH
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COPh
3ba
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2.07
1.10
2.06
1.07
1.21
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1.16
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1.00
3.13
1.02
1.05
3.00
8.5
8.0
7.5
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6.5
6.0
5.5
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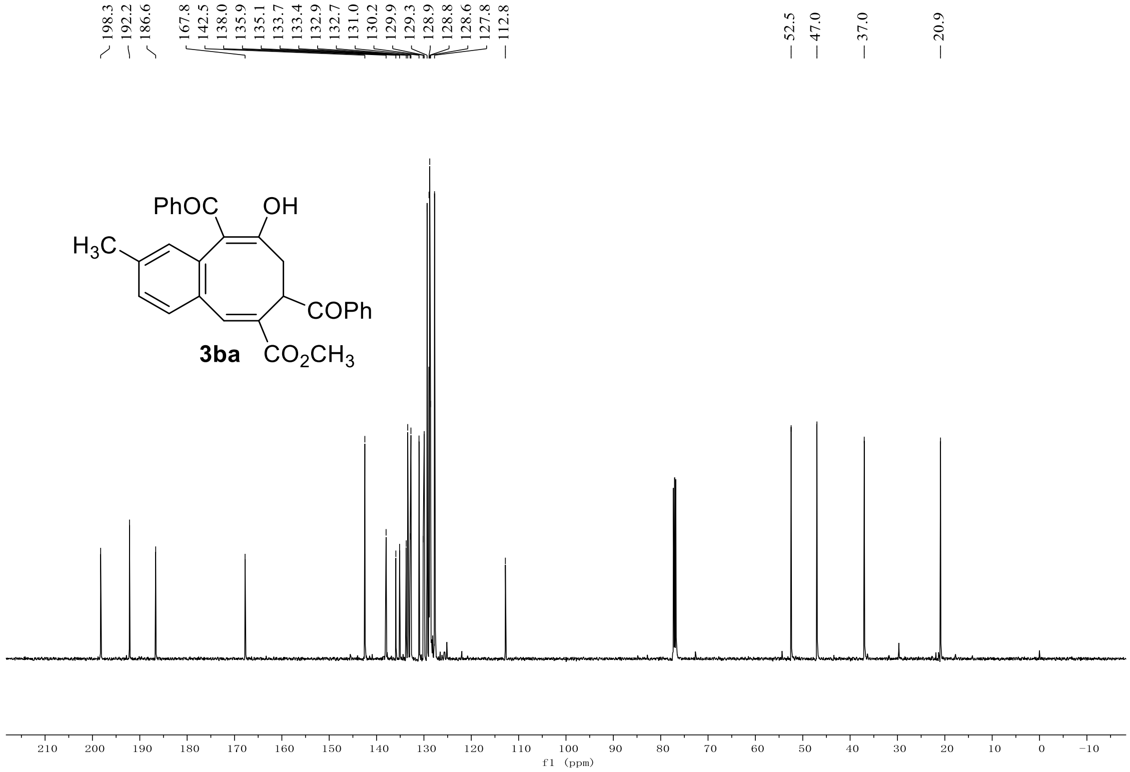
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130.2
129.9
129.3
128.9
128.8
128.6
127.8
112.8
52.5
47.0
37.0
20.9
PhOC
OH
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COPh
3ba
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200
190
180
170
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120
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100
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40
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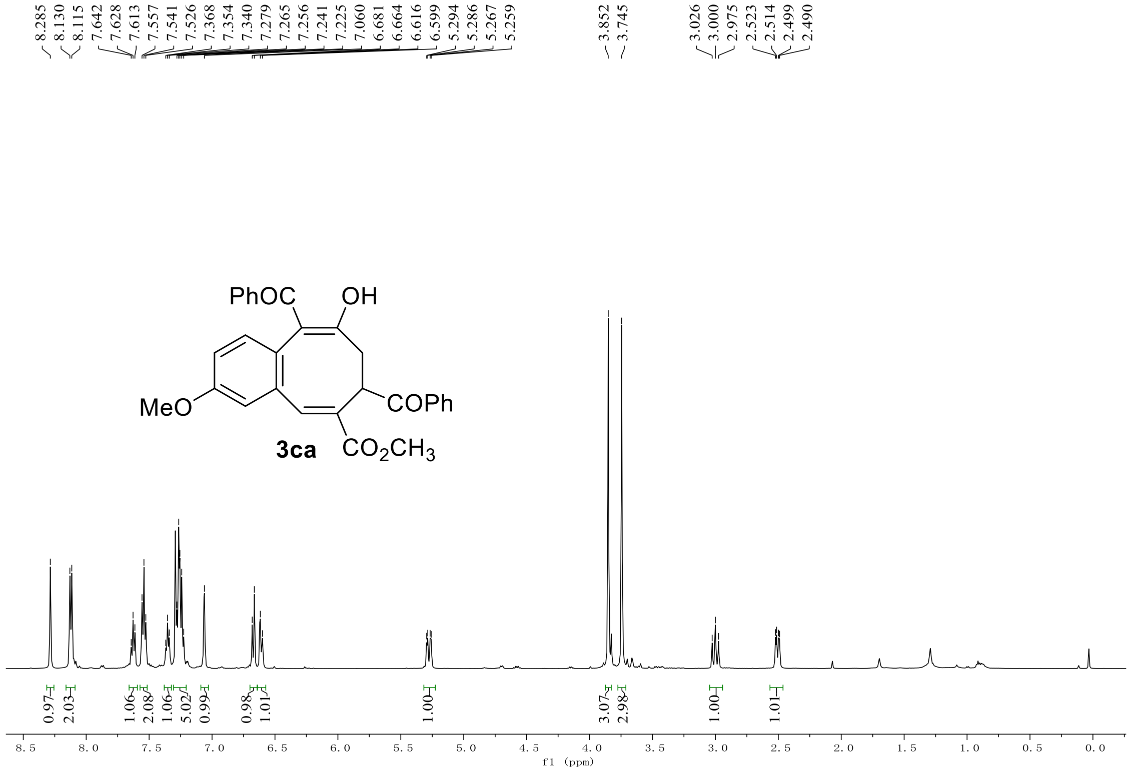
f1 (ppm)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7.225
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6.664
6.616
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5.267
5.259
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2.490
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MeO
COPh
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1.00
1.01
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7.0
6.5
6.0
5.5
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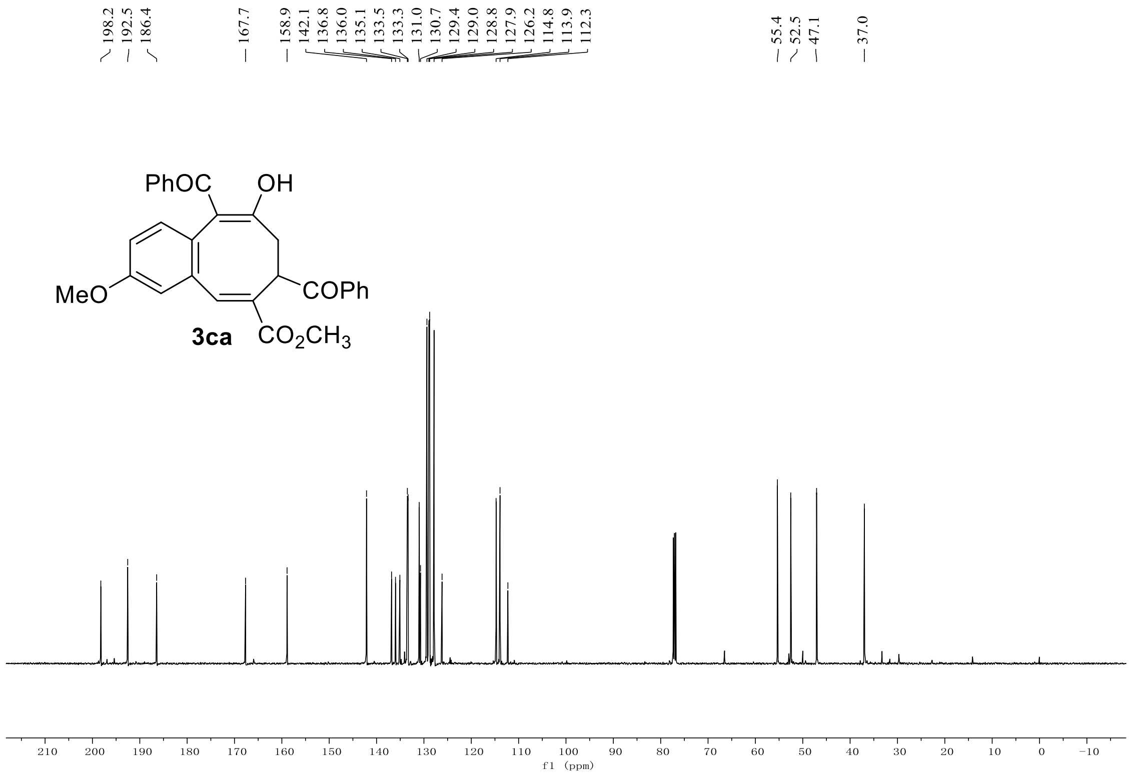
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127.9
126.2
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113.9
112.3
55.4
52.5
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37.0
PhOC
OH
MeO
COPh
3ca
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210
200
190
180
170
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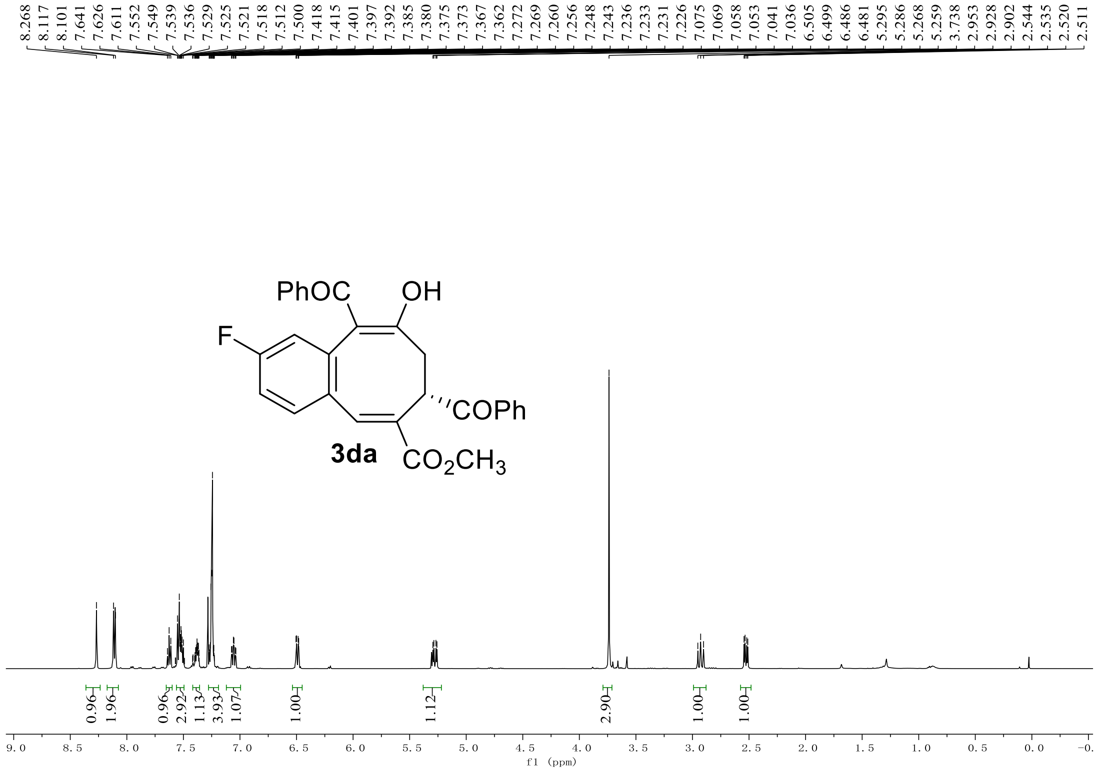
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7.518
7.512
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7.401
7.397
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7.272
7.269
7.260
7.256
7.248
7.243
7.236
7.233
7.231
7.226
7.075
7.069
7.058
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7.041
7.036
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6.499
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6.481
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2.928
2.902
2.544
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2.511
PhOC
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F
COPh
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0.96
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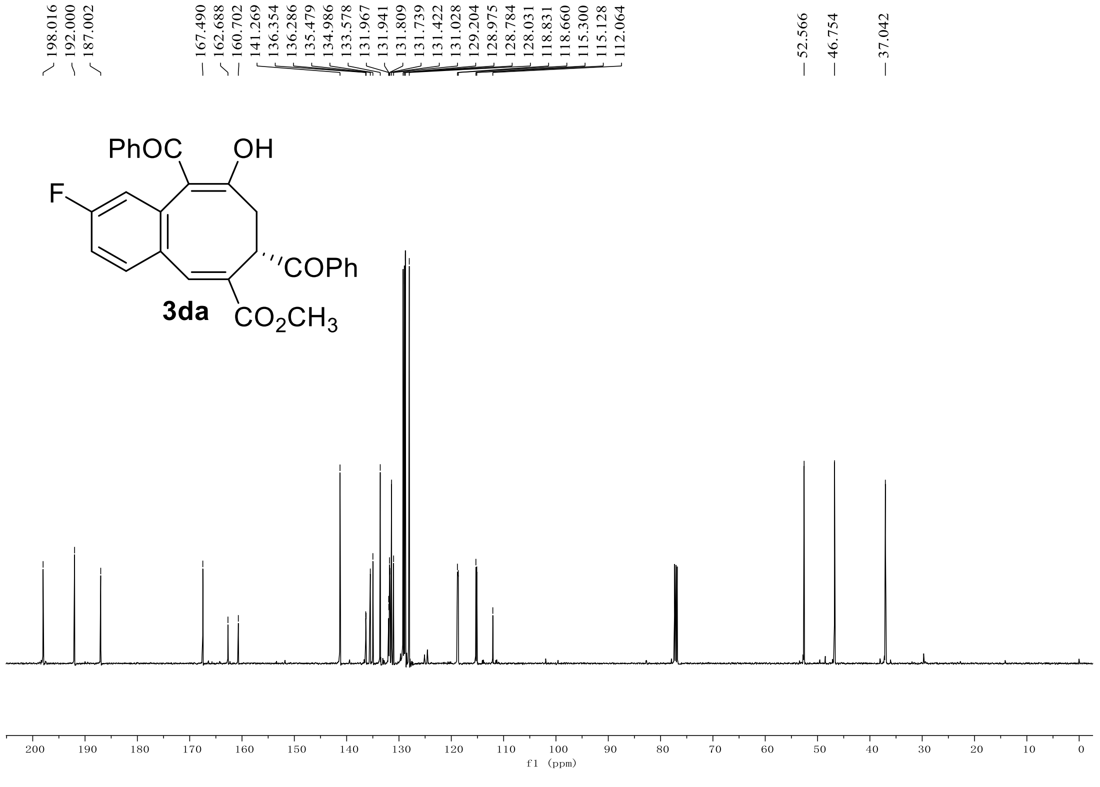
f1 (ppm)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52.566
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37.042
PhOC
OH
F
COPh
3da
$CO_2CH_3$
200
190
180
170
160
150
140
130
120
110
100
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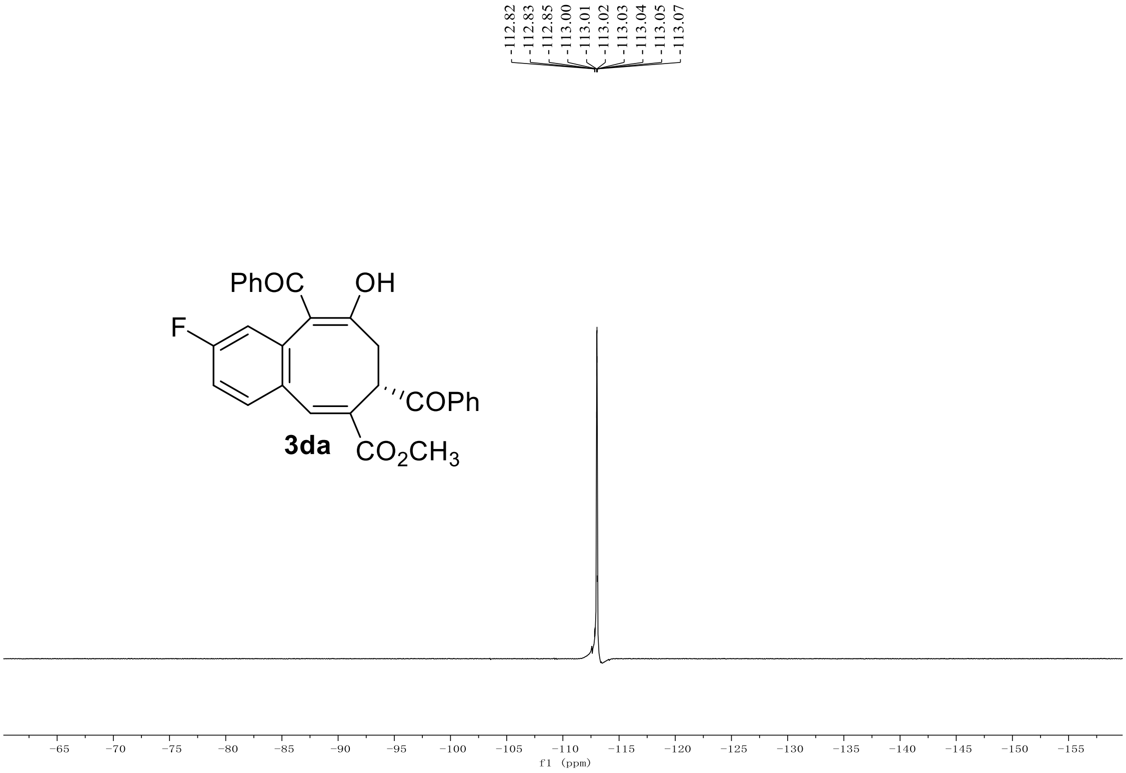
f1 (ppm)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F
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−75
−80
−85
−90
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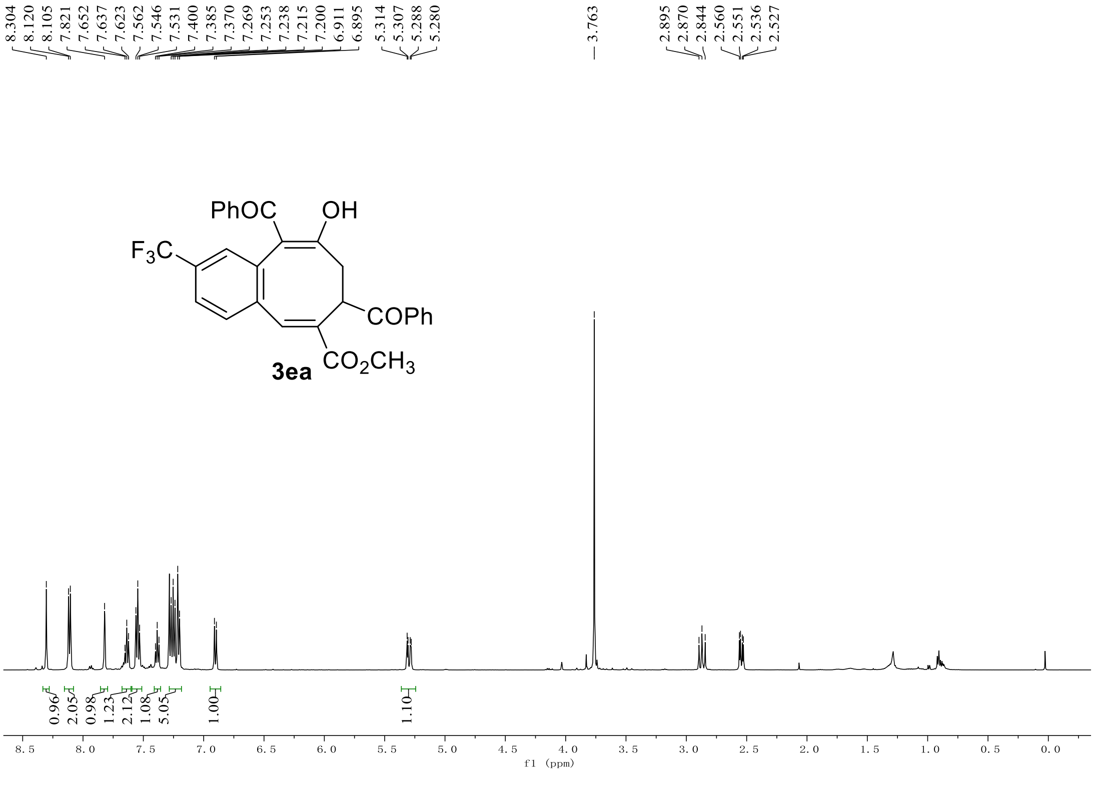
−155
f1 (ppm)

**3da**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$F_3C$
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$CO_2CH_3$
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7.0
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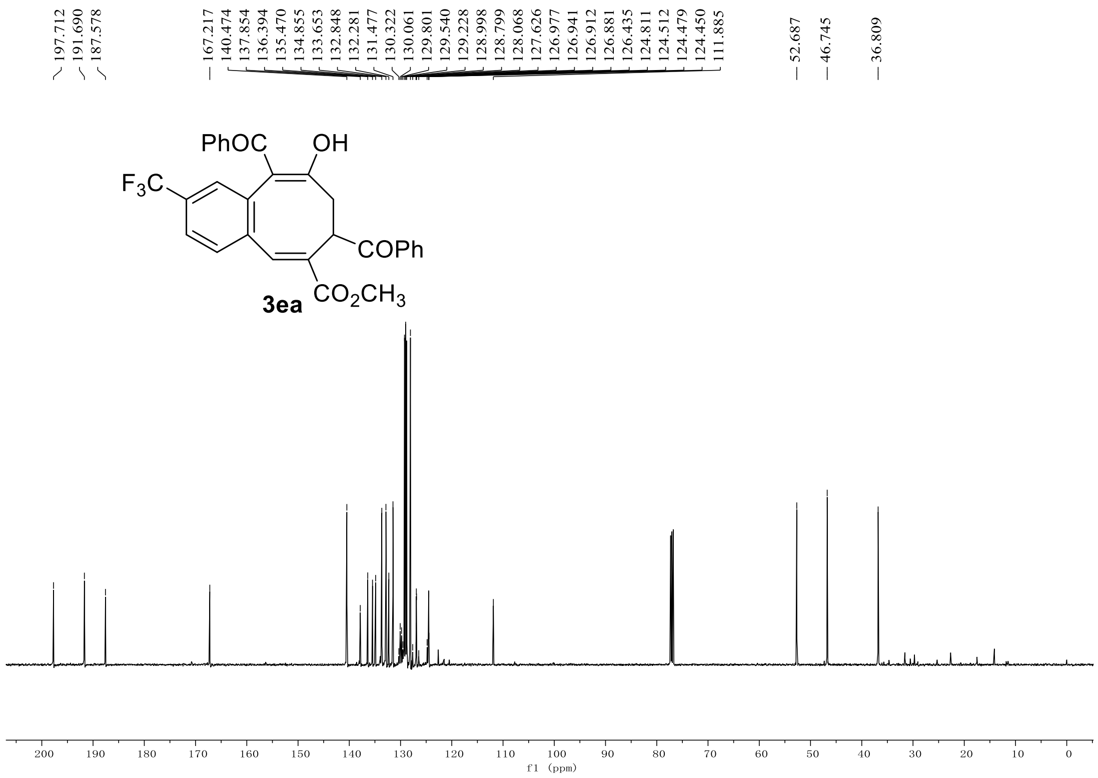
f1 (ppm)

**3ea**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COPh
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50
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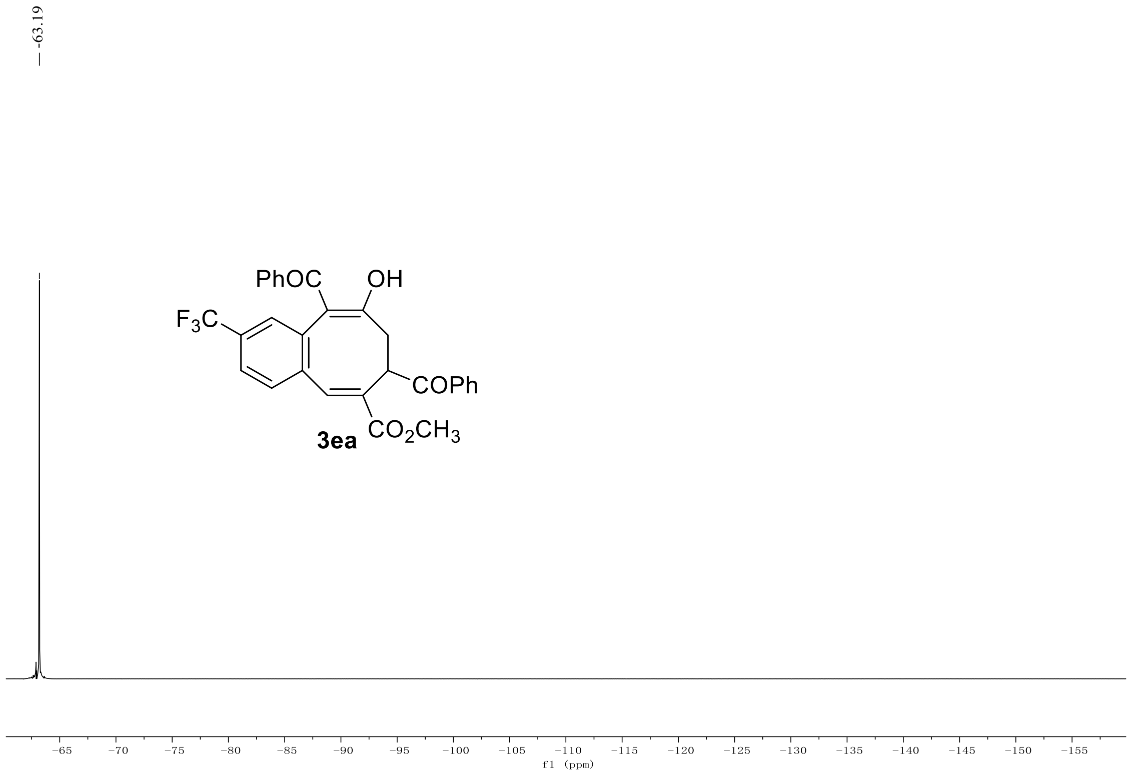
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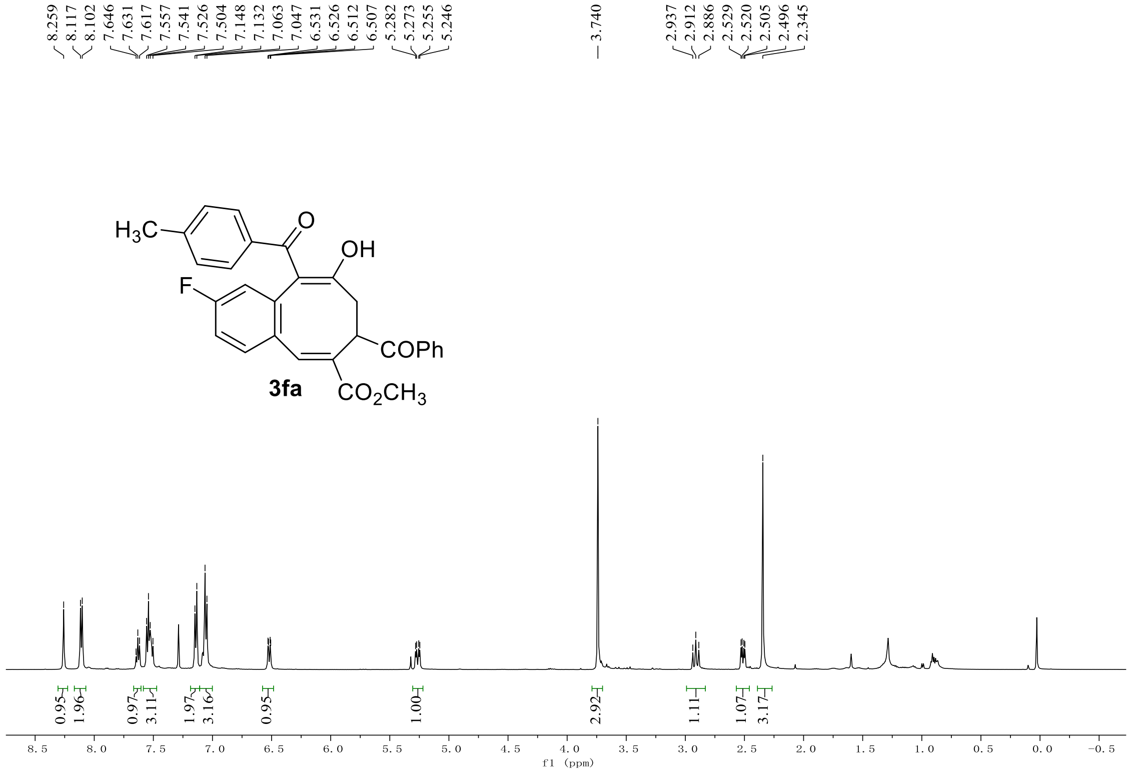
f1 (ppm)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2.520
2.505
2.496
2.345
$H_3C$
O
OH
F
COPh
$CO_2CH_3$
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0.97
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1.97
3.16
0.95
1.00
2.92
1.11
1.07
3.17
8.5
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7.5
7.0
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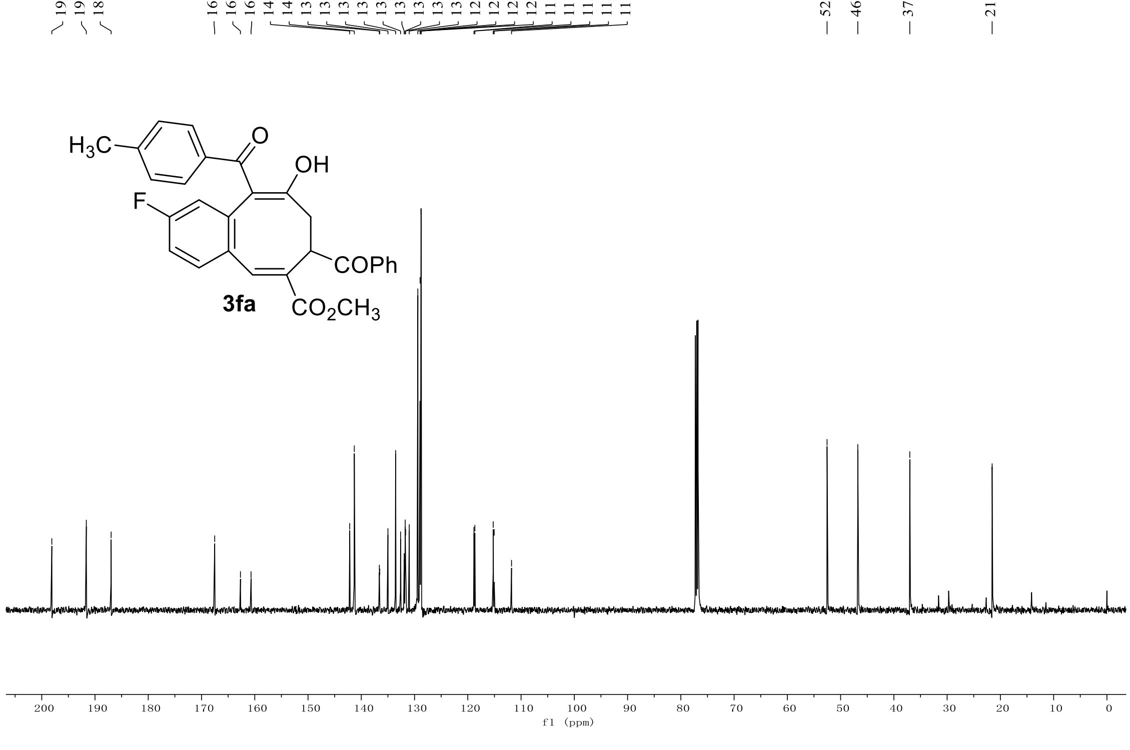
f1 (ppm)

**3fa**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52.544
46.772
37.011
21.548
$H_3C$
O
OH
F
COPh
$CO_2CH_3$
200
190
180
170
160
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110
100
90
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70
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50
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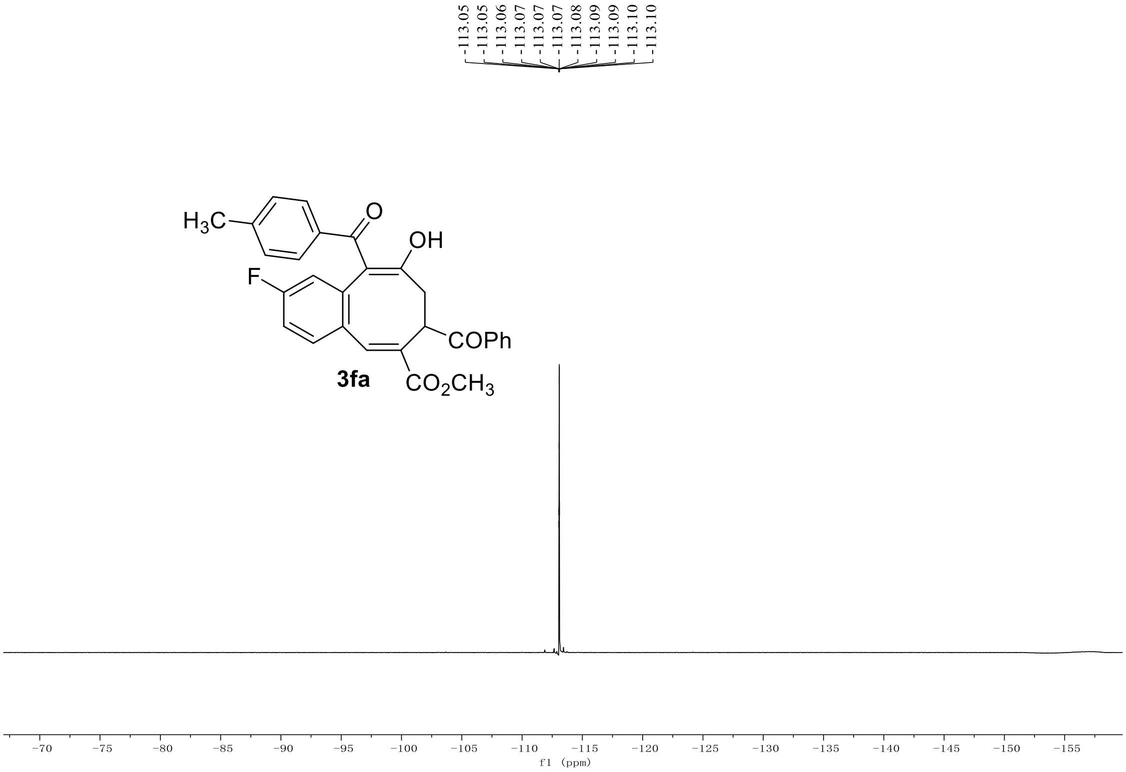
30
20
10
0
f1 (ppm)

**3fa**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COPh
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3fa
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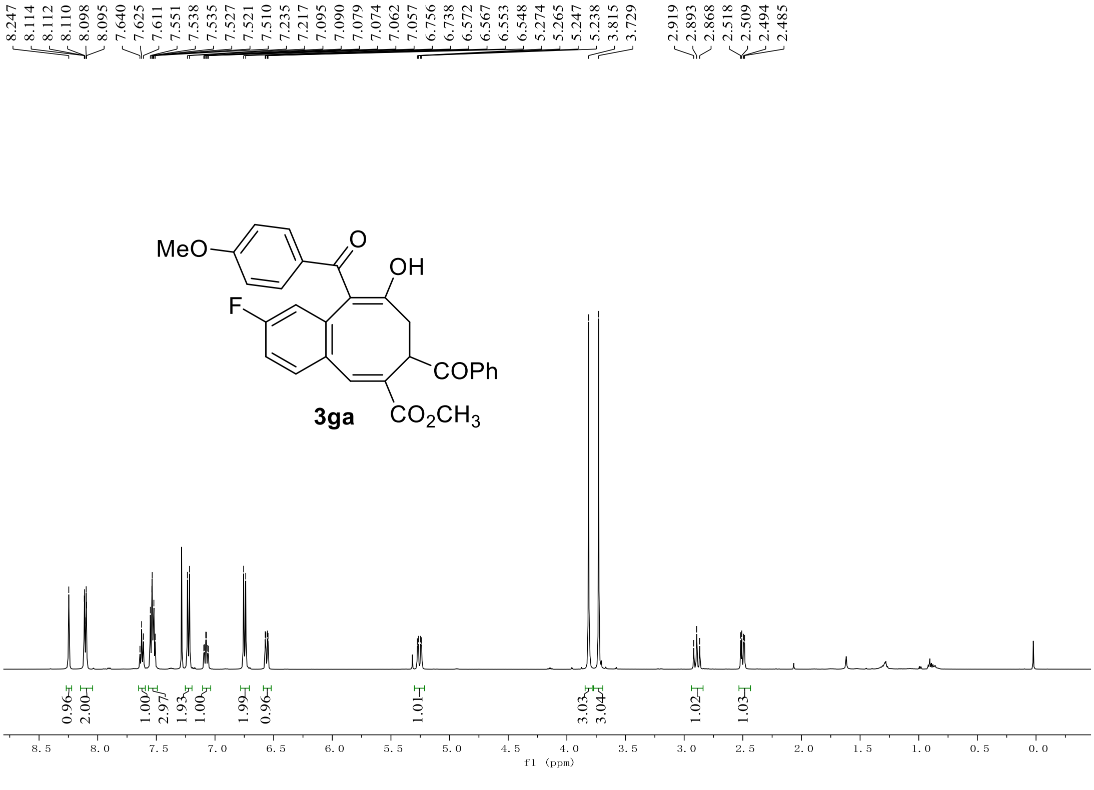
−155
f1 (ppm)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1.02
1.03
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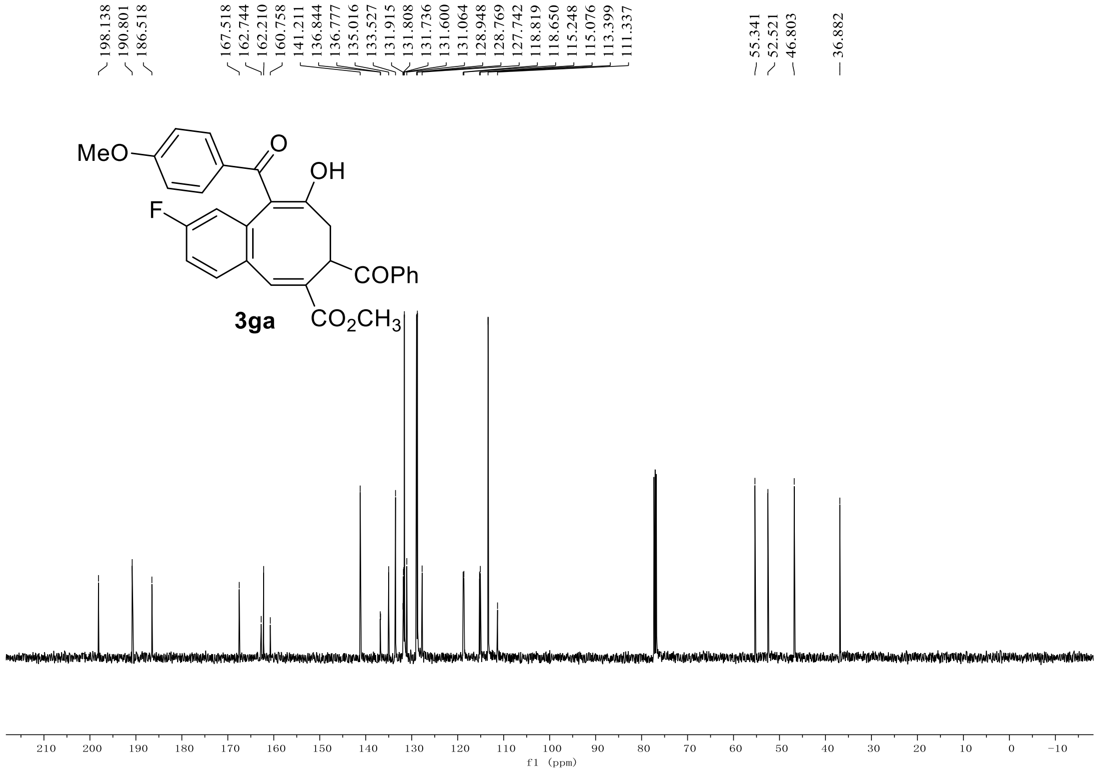
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131.064
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128.769
127.742
118.819
118.650
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115.076
113.399
111.337
55.341
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46.803
36.882
MeO
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OH
F
COPh
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210
200
190
180
170
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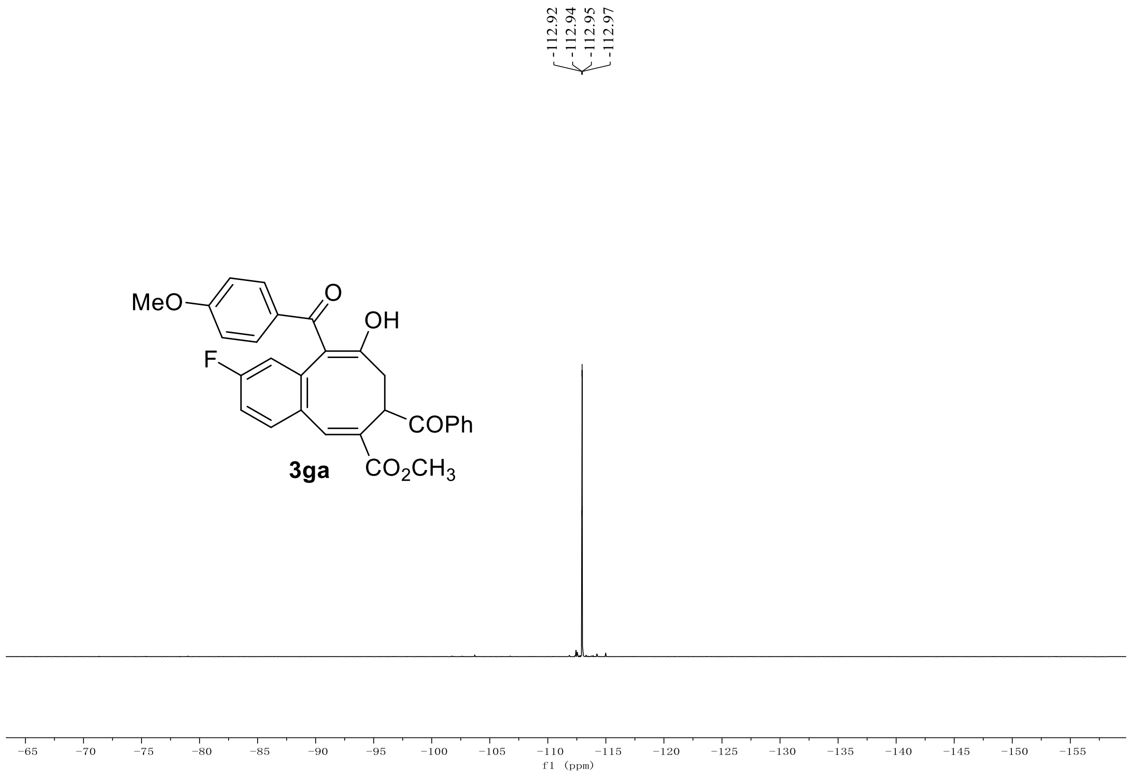
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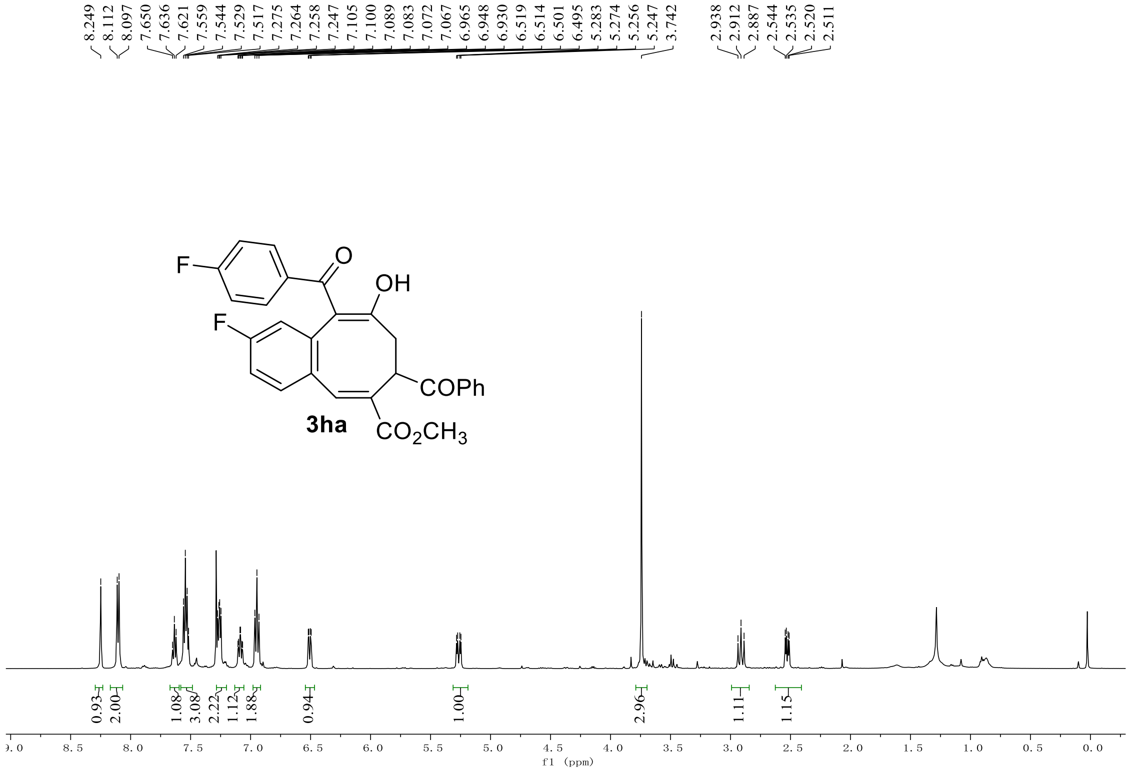
f1 (ppm)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COPh
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3.08
2.22
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8.0
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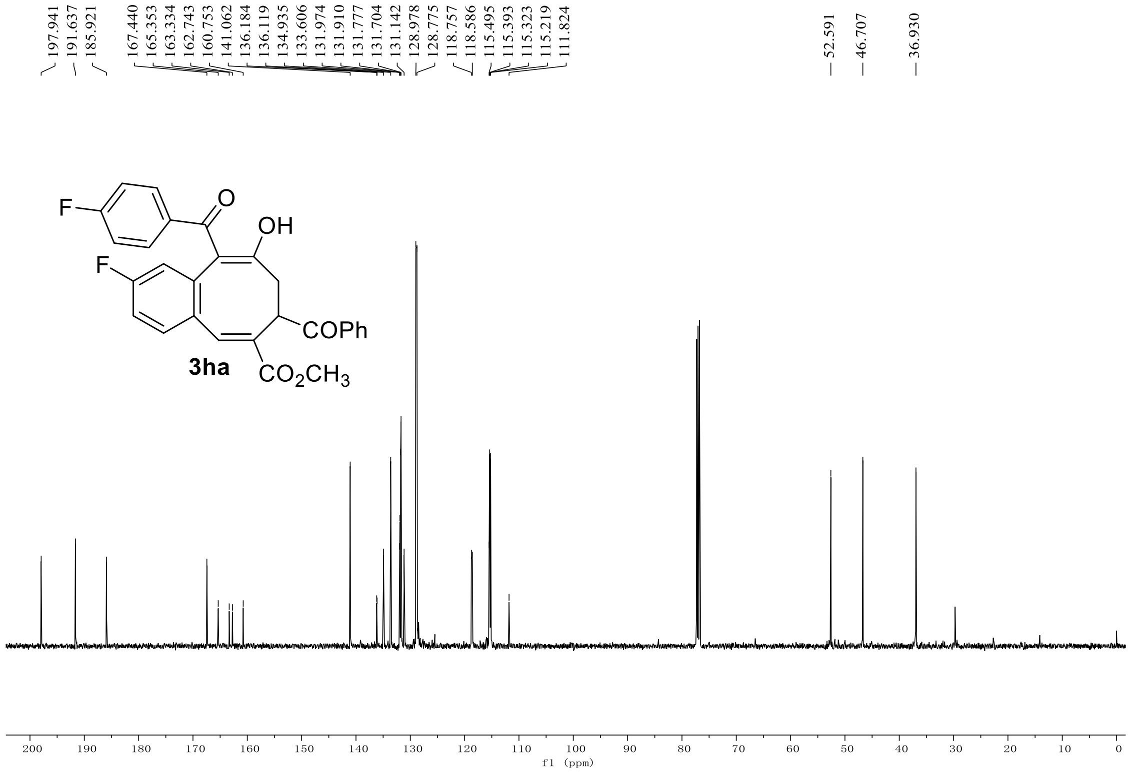
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F
O
OH
F
COPh
3ha
CO2CH3
200
190
180
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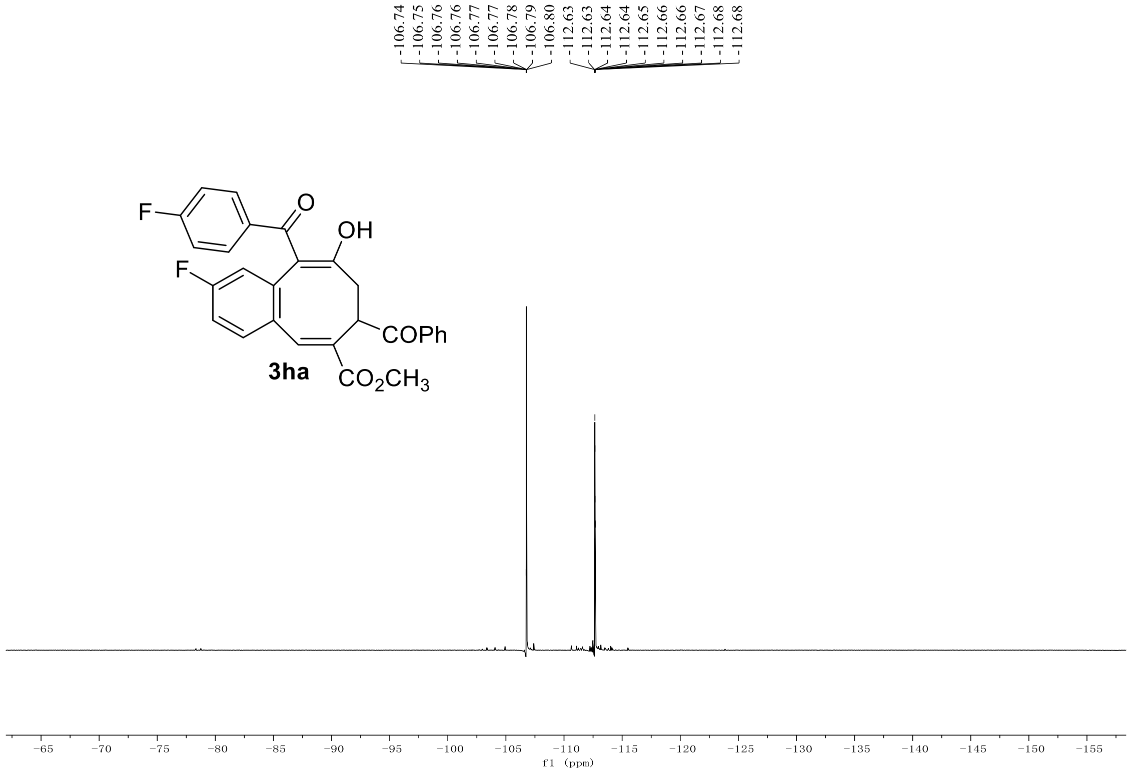
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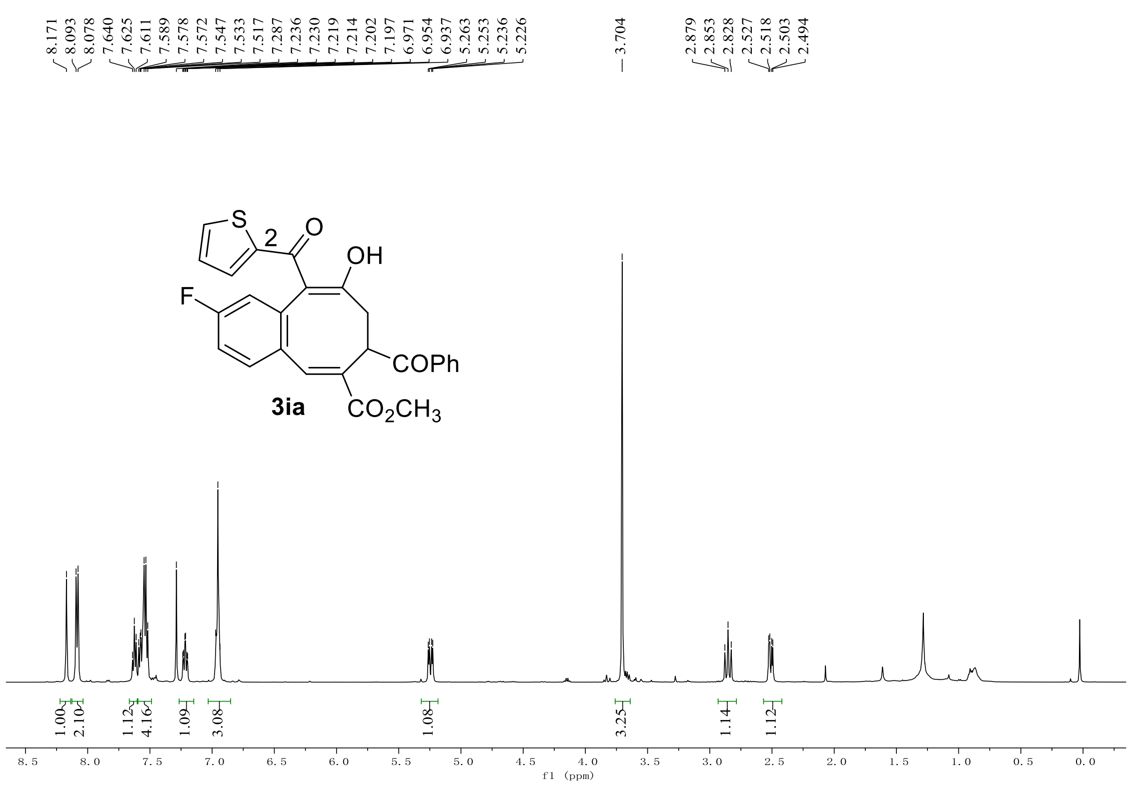
f1 (ppm)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8.093
8.078
7.640
7.625
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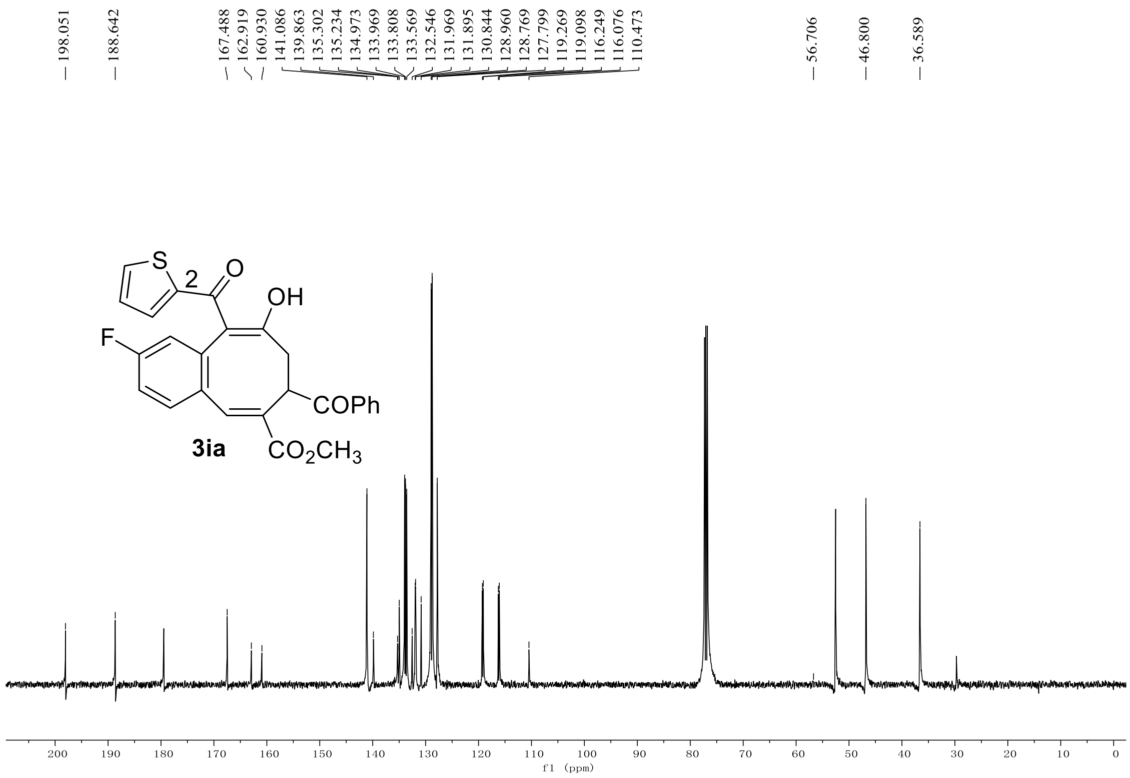
7.589
7.578
7.572
7.547
7.533
7.517
7.287
7.236
7.230
7.219
7.214
7.202
7.197
6.971
6.954
6.937
5.263
5.253
5.236
5.226
3.704
2.879
2.853
2.828
2.527
2.518
2.503
2.494
S
2
O
OH
F
COPh
3ia
CO2CH3
1.00
2.10
1.12
4.16
1.09
3.08
1.08
3.25
1.14
1.12
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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167.488
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160.930
141.086
139.863
135.302
135.234
134.973
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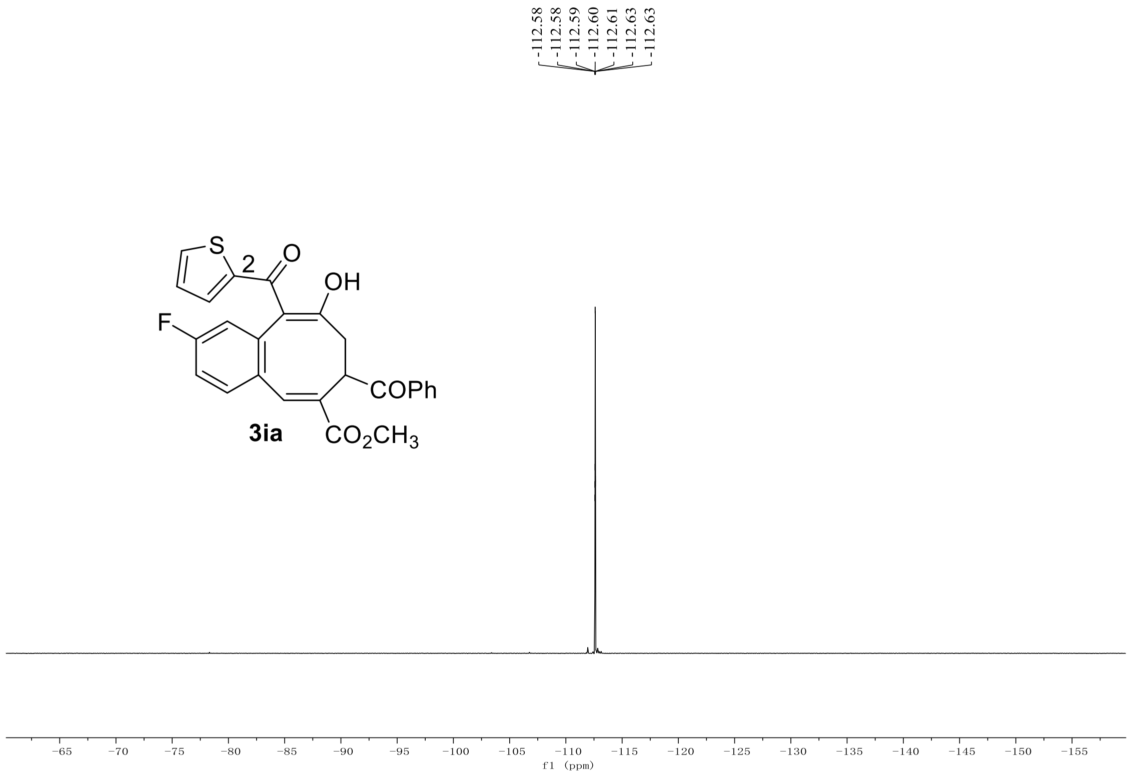
133.808
133.569
132.546
131.969
131.895
130.844
128.960
128.769
127.799
119.269
119.098
116.249
116.076
110.473
56.706
46.800
36.589
S
2
O
OH
F
COPh
3ia
$CO_2CH_3$
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


-112.58
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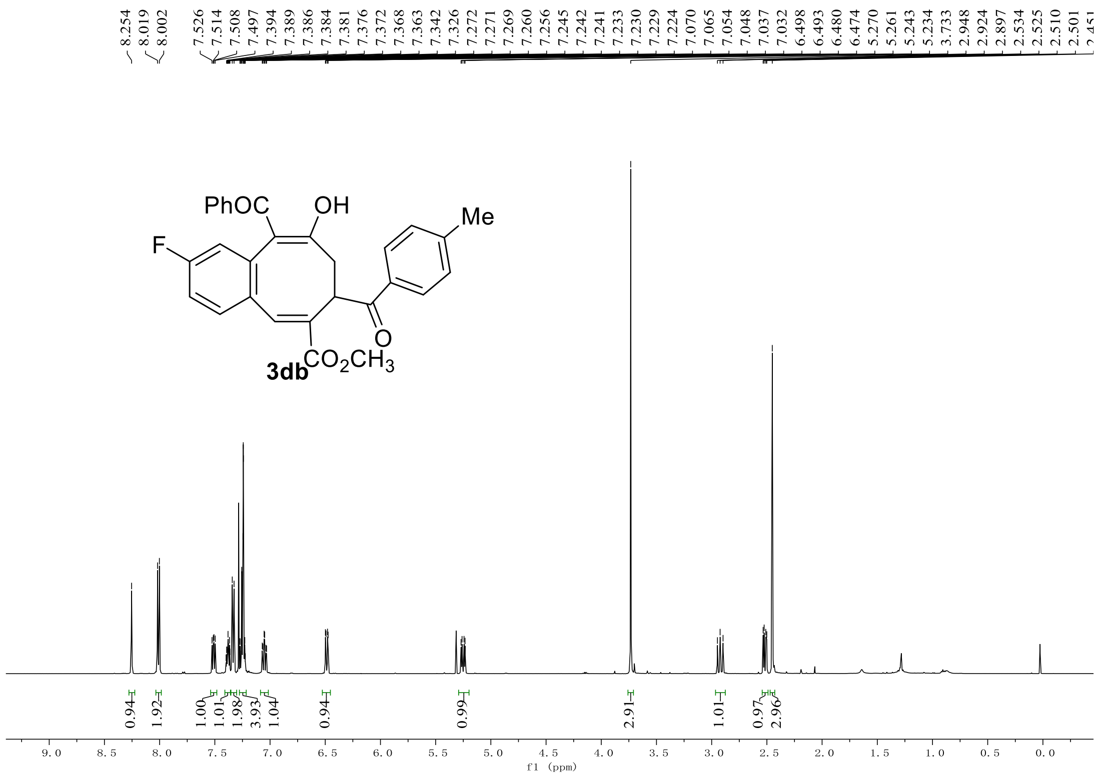
-112.59
-112.60
-112.61
-112.63
-112.63
S
2
O
OH
F
COPh
3ia
$CO_2CH_3$
−65
−70
−75
−80
−85
−90
−95
−100
−105
−110
−115
−120
−125
−130
−135
−140
−145
−150
−155
f1 (ppm)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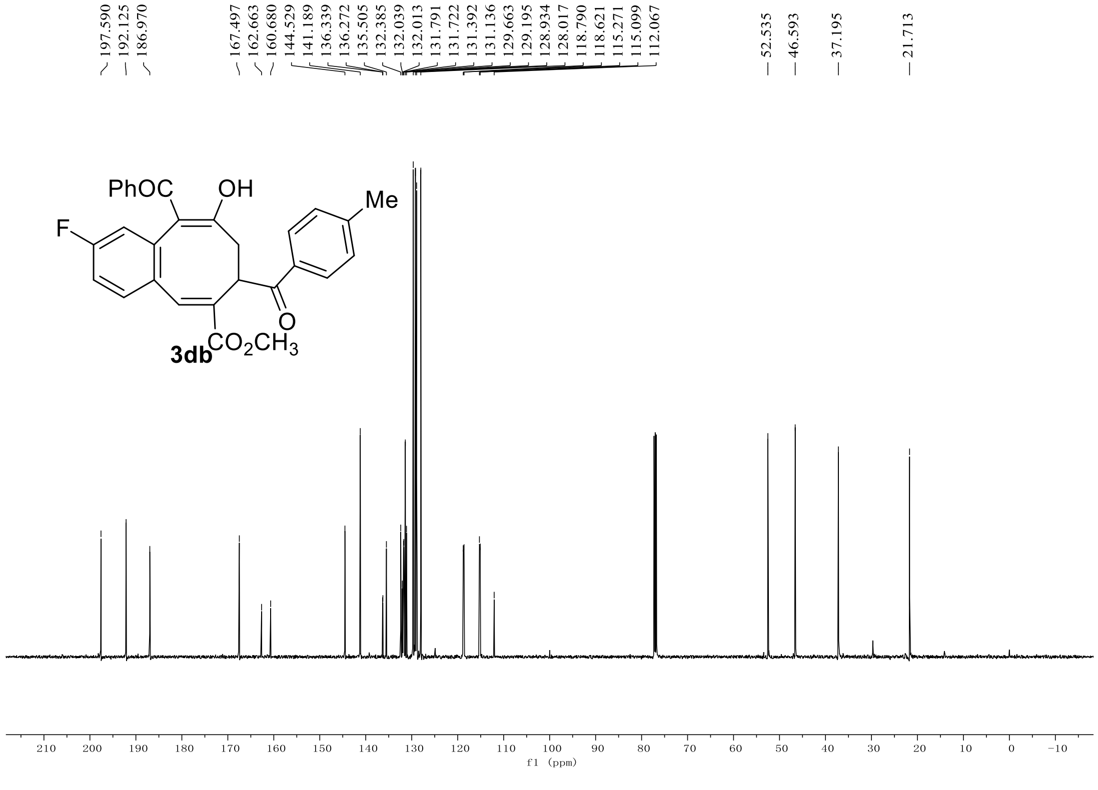
8.019
8.002
7.526
7.514
7.508
7.497
7.394
7.389
7.386
7.384
7.381
7.376
7.372
7.368
7.363
7.342
7.326
7.272
7.271
7.269
7.260
7.256
7.245
7.242
7.241
7.233
7.230
7.229
7.224
7.070
7.065
7.054
7.048
7.037
7.032
6.498
6.493
6.480
6.474
5.270
5.261
5.243
5.234
3.733
2.948
2.924
2.897
2.534
2.525
2.510
2.501
2.451
PhOC
OH
Me
F
O
$CO_2CH_3$
0.94
1.92
1.00
1.01
1.98
3.93
1.04
0.94
0.99
2.91
1.01
0.97
2.96
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)


**3db**
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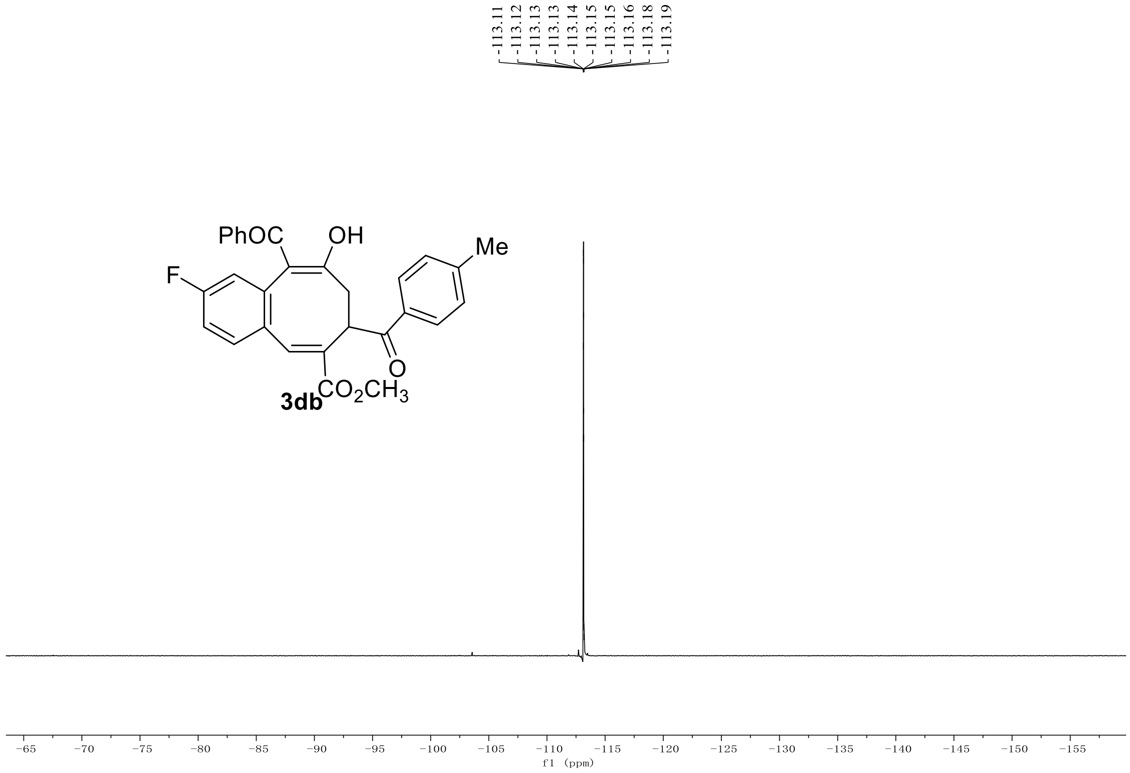
192.125
186.970
167.497
162.663
160.680
144.529
141.189
136.339
136.272
135.505
132.385
132.039
132.013
131.791
131.722
131.392
131.136
129.663
129.195
128.934
128.017
118.790
118.621
115.271
115.099
112.067
52.535
46.593
37.195
21.713
PhOC
OH
Me
F
O
$CO_2CH_3$
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)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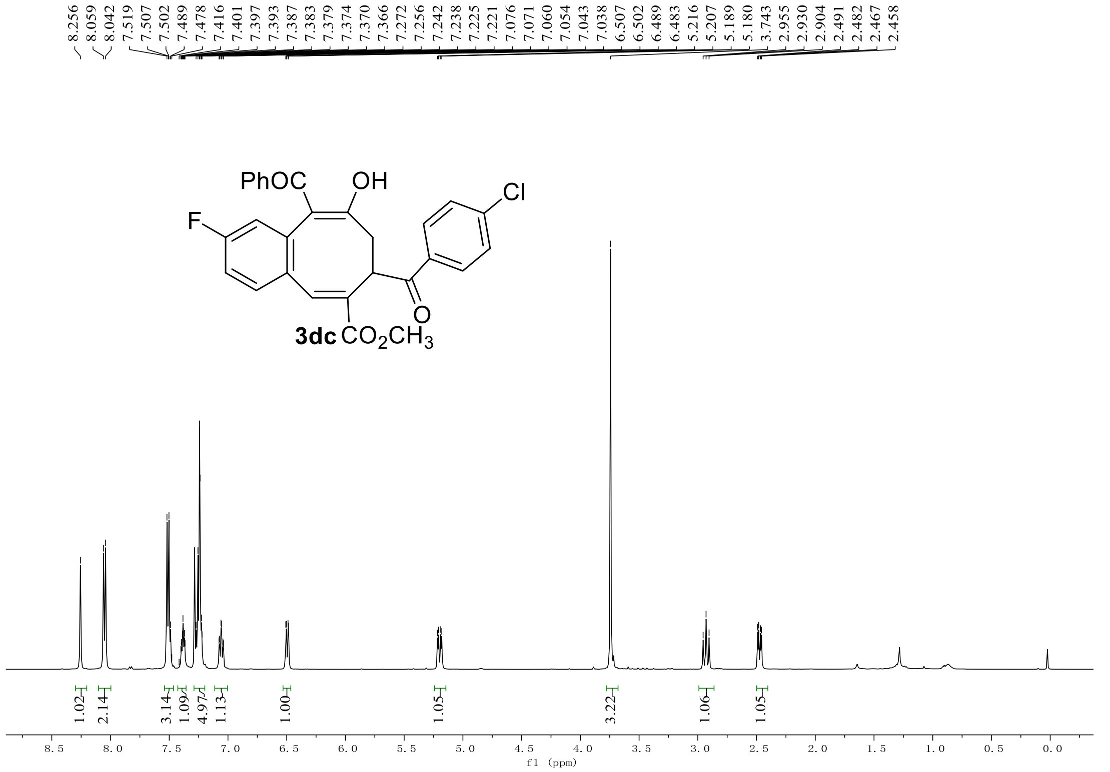
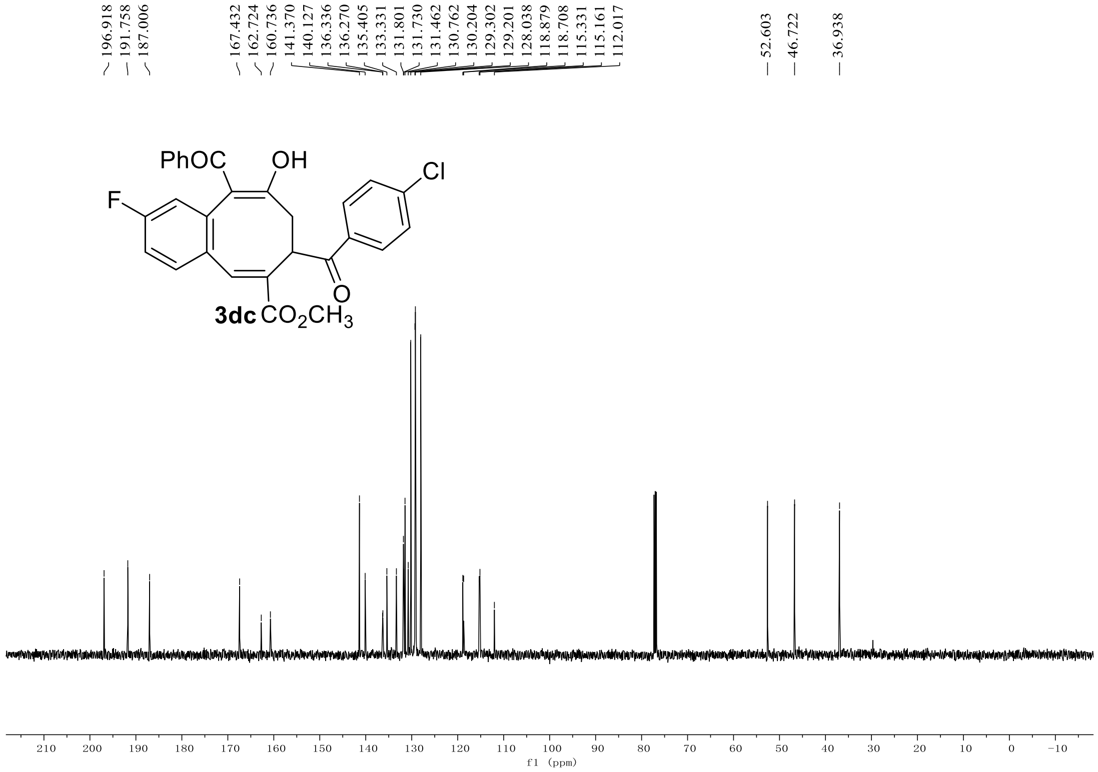
-113.12
-113.13
-113.13
-113.14
-113.15
-113.15
-113.16
-113.18
-113.19
PhOC
OH
Me
F
O
$CO_2CH_3$
-65
-70
-75
-80
-85
-90
-95
-100
-105
-110
-115
-120
-125
-130
-135
-140
-145
-150
-155
f1 (ppm)

**3db**


8.256
8.059
8.042
7.519
7.507
7.502
7.489
7.478
7.416
7.401
7.397
7.393
7.387
7.383
7.379
7.374
7.370
7.366
7.272
7.256
7.242
7.238
7.225
7.221
7.076
7.071
7.060
7.054
7.043
7.038
6.507
6.502
6.489
6.483
5.216
5.207
5.189
5.180
3.743
2.955
2.930
2.904
2.491
2.482
2.467
2.458
PhOC
OH
Cl
F
O
$CO_2CH_3$
1.02
2.14
3.14
1.09
4.97
1.13
1.00
1.05
3.22
1.06
1.05
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)

**3dc**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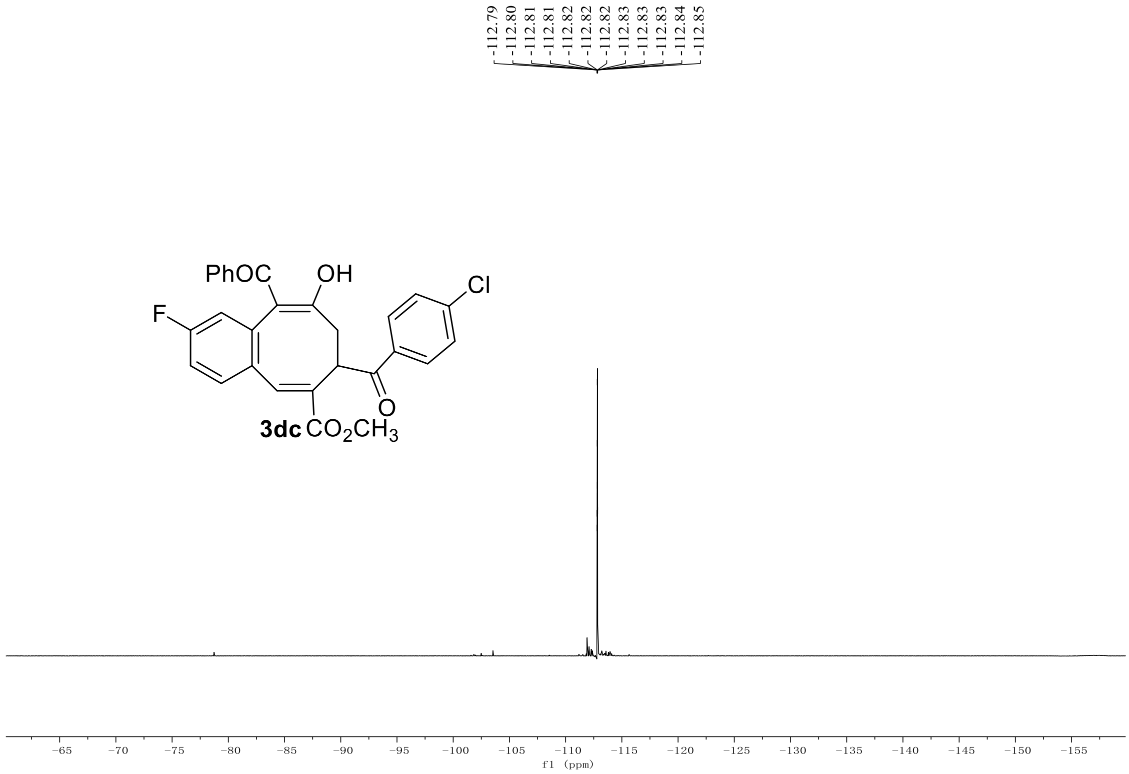
187.006
167.432
162.724
160.736
141.370
140.127
136.336
136.270
135.405
133.331
131.801
131.730
131.462
130.762
130.204
129.302
129.201
128.038
118.879
118.708
115.331
115.161
112.017
52.603
46.722
36.938
PhOC
OH
F
Cl
O
3dc
$CO_2CH_3$
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)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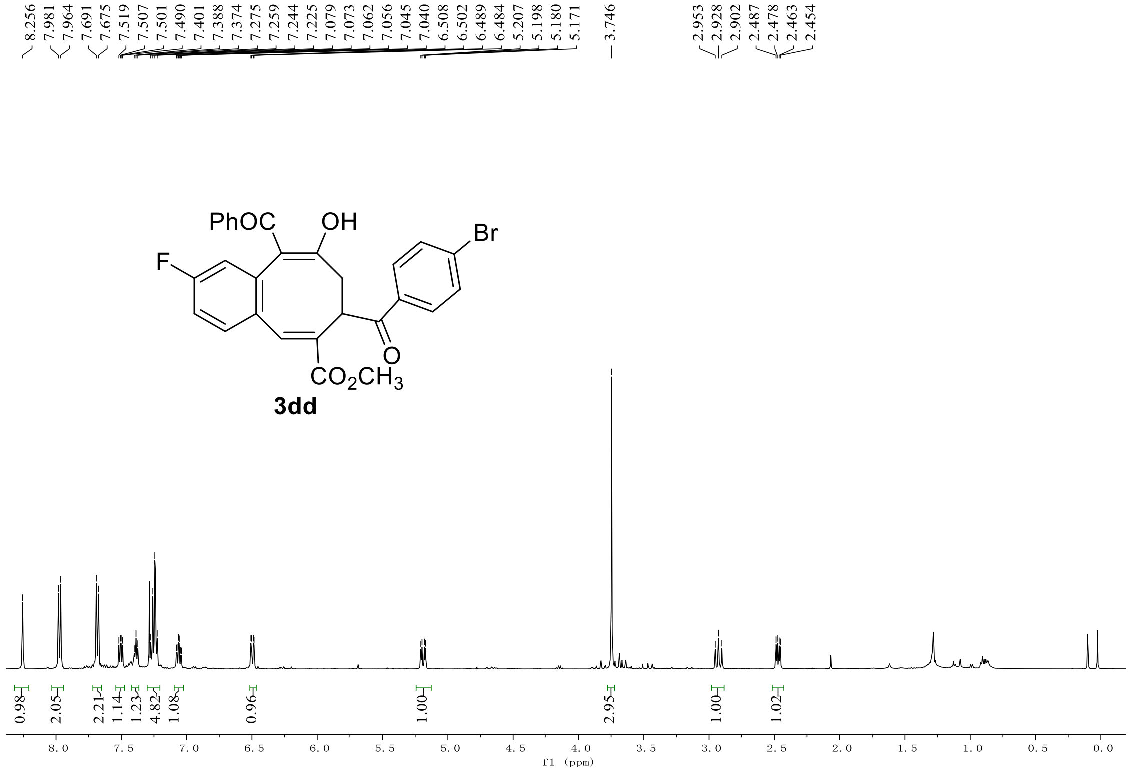
-112.80
-112.81
-112.81
-112.82
-112.82
-112.82
-112.83
-112.83
-112.83
-112.84
-112.85
PhOC
OH
F
Cl
O
3dc
$CO_2CH_3$
−65
−70
−75
−80
−85
−90
−95
−100
−105
−110
−115
−120
−125
−130
−135
−140
−145
−150
−155
f1 (ppm)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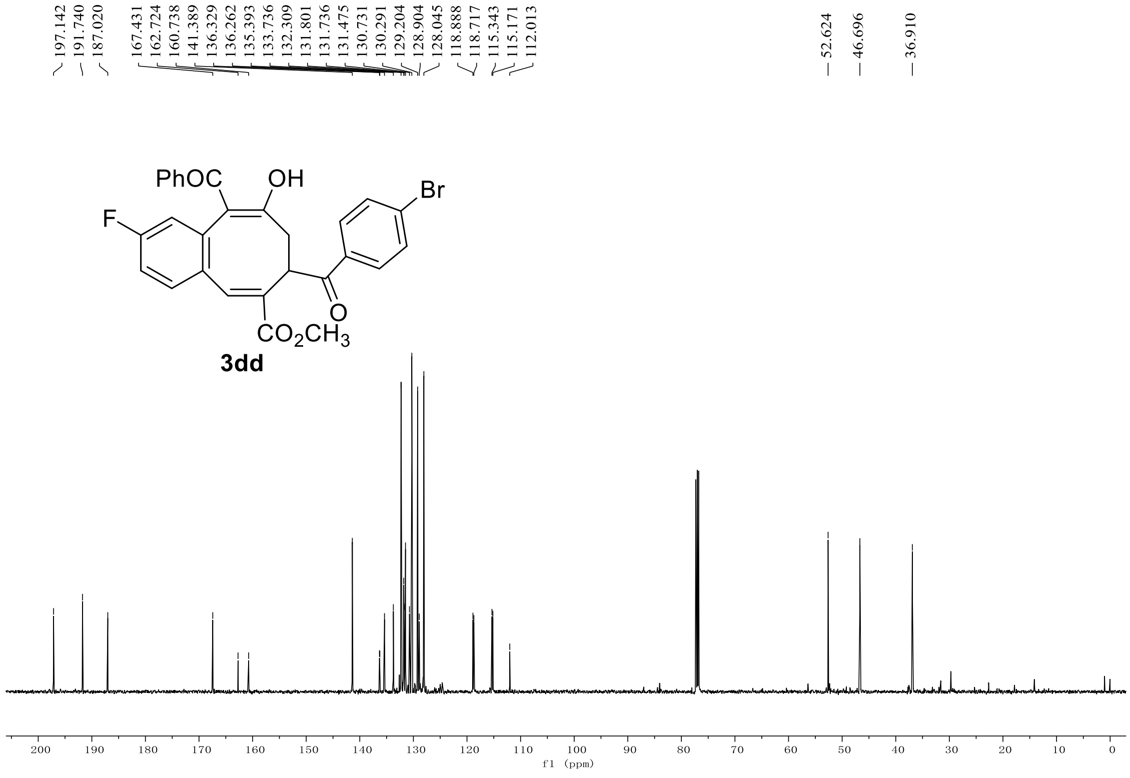
7.981
7.964
7.691
7.675
7.519
7.507
7.501
7.490
7.401
7.388
7.374
7.275
7.259
7.244
7.225
7.079
7.073
7.062
7.056
7.045
7.040
6.508
6.502
6.489
6.484
5.207
5.198
5.180
5.171
3.746
2.953
2.928
2.902
2.487
2.478
2.463
2.454
PhOC
OH
Br
F
O
CO2CH3
3dd
0.98
2.05
2.21
1.14
1.23
4.82
1.08
0.96
1.00
2.95
1.00
1.02
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)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136.329
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135.393
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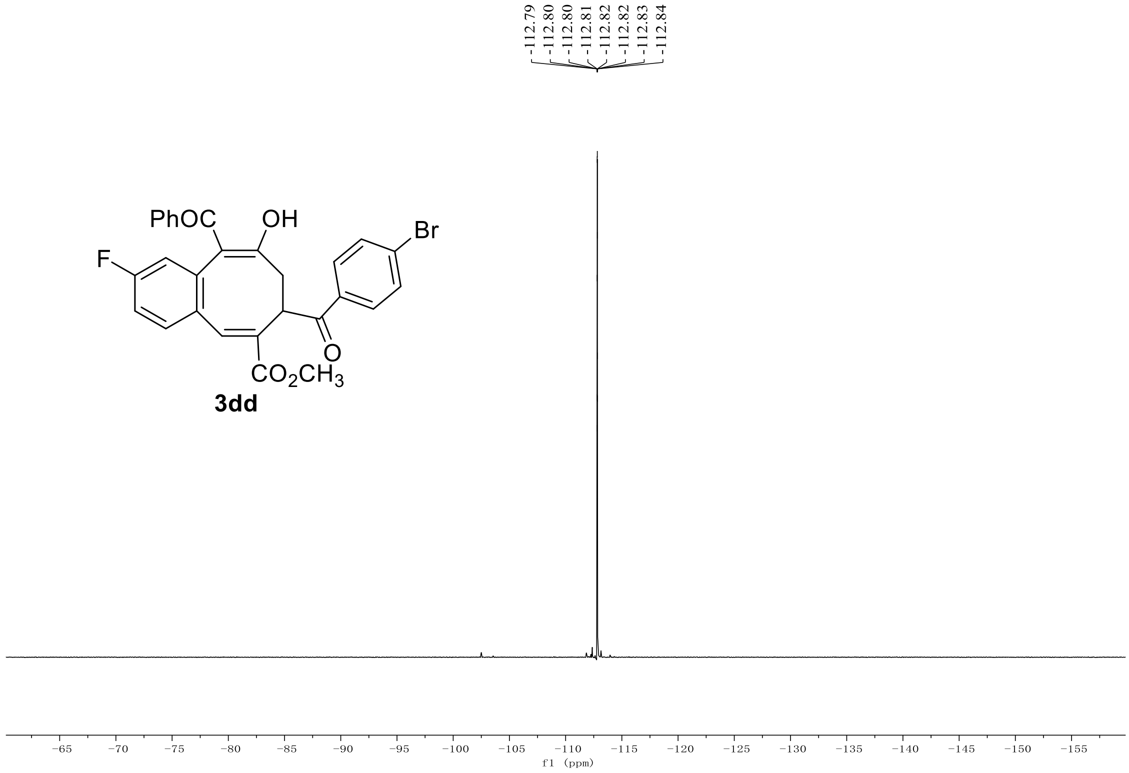
132.309
131.801
131.736
131.475
130.731
130.291
129.204
128.904
128.045
118.888
118.717
115.343
115.171
112.013
52.624
46.696
36.910
PhOC
OH
Br
F
O
CO2CH3
3dd
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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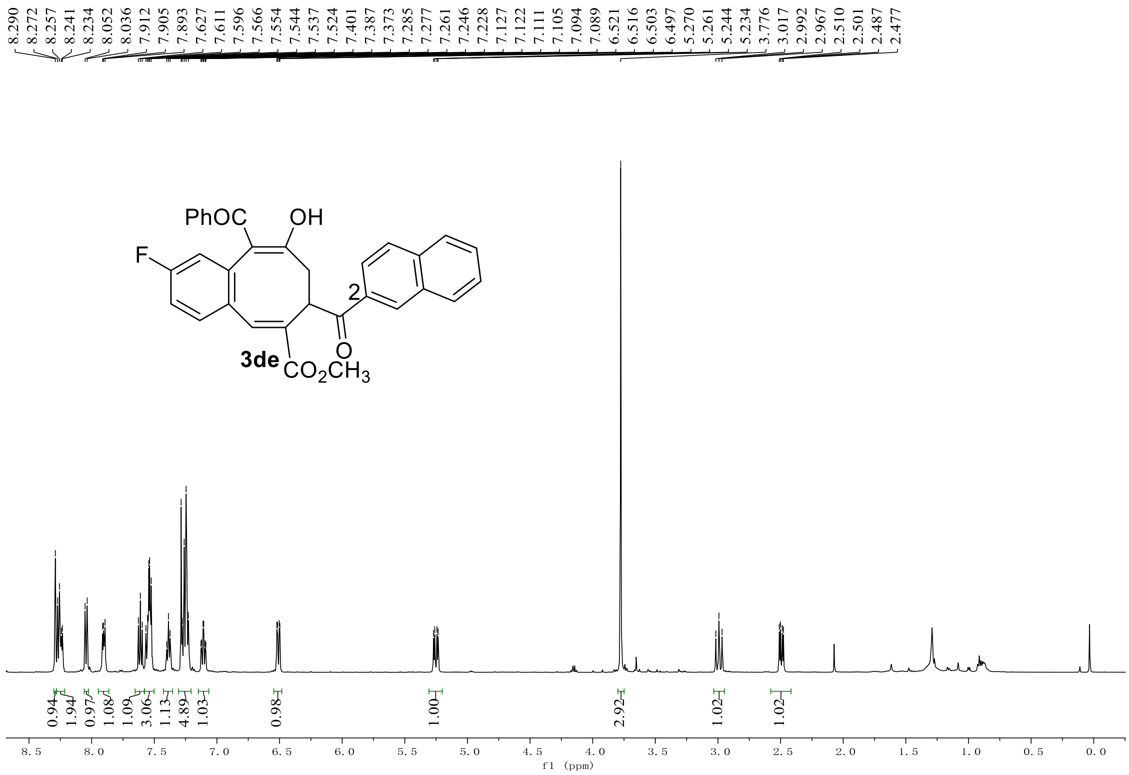
-112.80
-112.80
-112.81
-112.82
-112.82
-112.83
-112.84
PhOC
OH
F
Br
O
CO2CH3
3dd
-65
-70
-75
-80
-85
-90
-95
-100
-105
-110
-115
-120
-125
-130
-135
-140
-145
-150
-155
f1 (ppm)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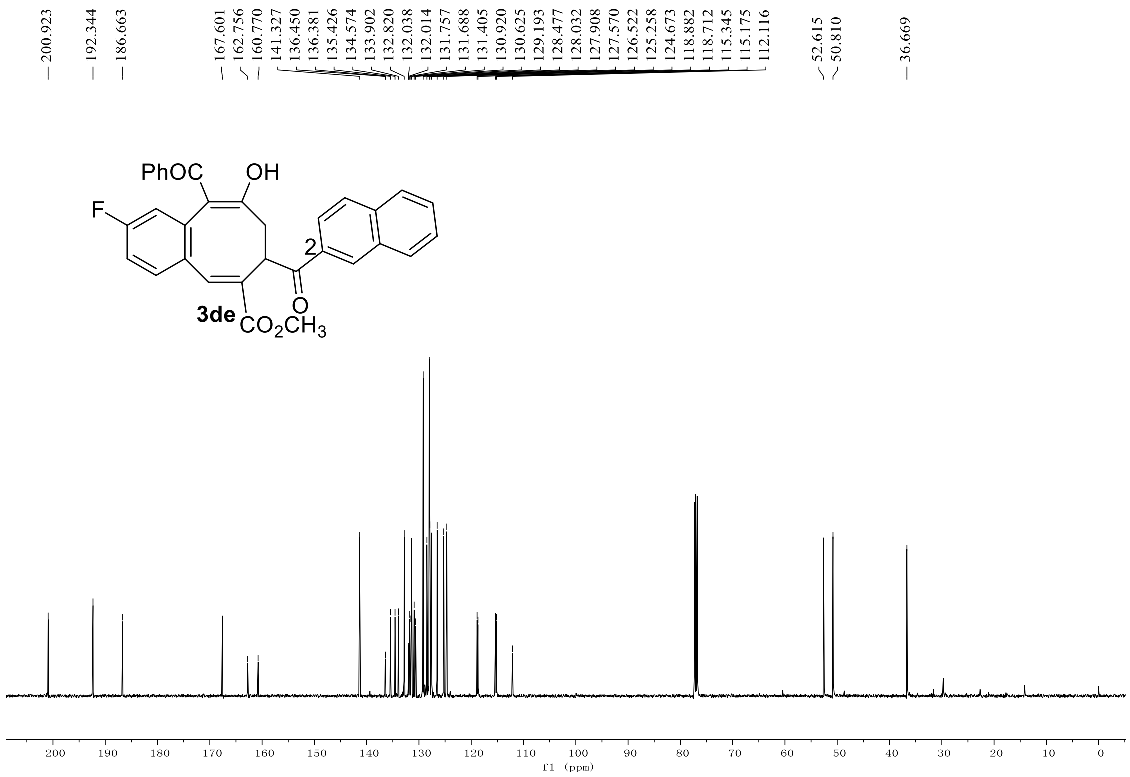
8.036
7.912
7.905
7.893
7.627
7.611
7.596
7.566
7.554
7.544
7.537
7.524
7.401
7.387
7.373
7.285
7.277
7.261
7.246
7.228
7.127
7.122
7.111
7.105
7.094
7.089
6.521
6.516
6.503
6.497
5.270
5.261
5.244
5.234
3.776
3.017
2.992
2.967
2.510
2.501
2.487
2.477
PhOC
OH
F
2
O
3de
CO2CH3
0.94
1.94
0.97
1.08
1.09
3.06
1.13
4.89
1.03
0.98
1.00
2.92
1.02
1.02
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)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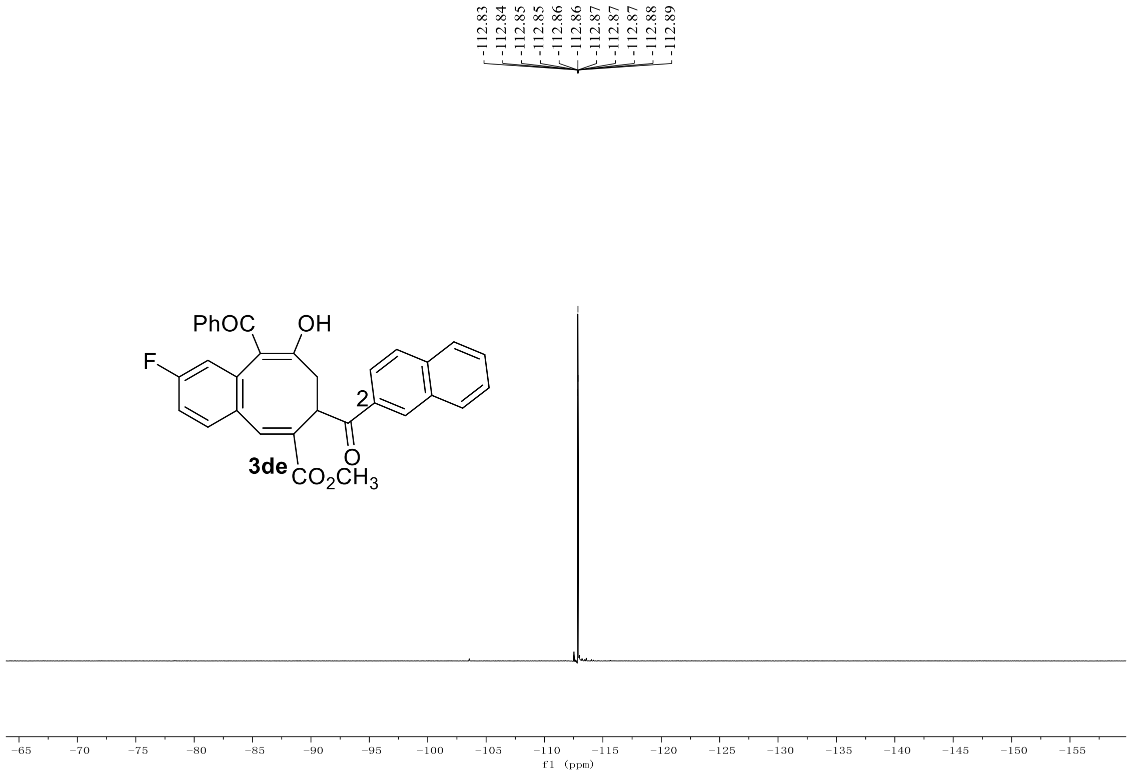
132.820
132.038
132.014
131.757
131.688
131.405
130.920
130.625
129.193
128.477
128.032
127.908
127.570
126.522
125.258
124.673
118.882
118.712
115.345
115.175
112.116
52.615
50.810
36.669
PhOC
OH
F
2
O
3de
CO2CH3
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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-112.85
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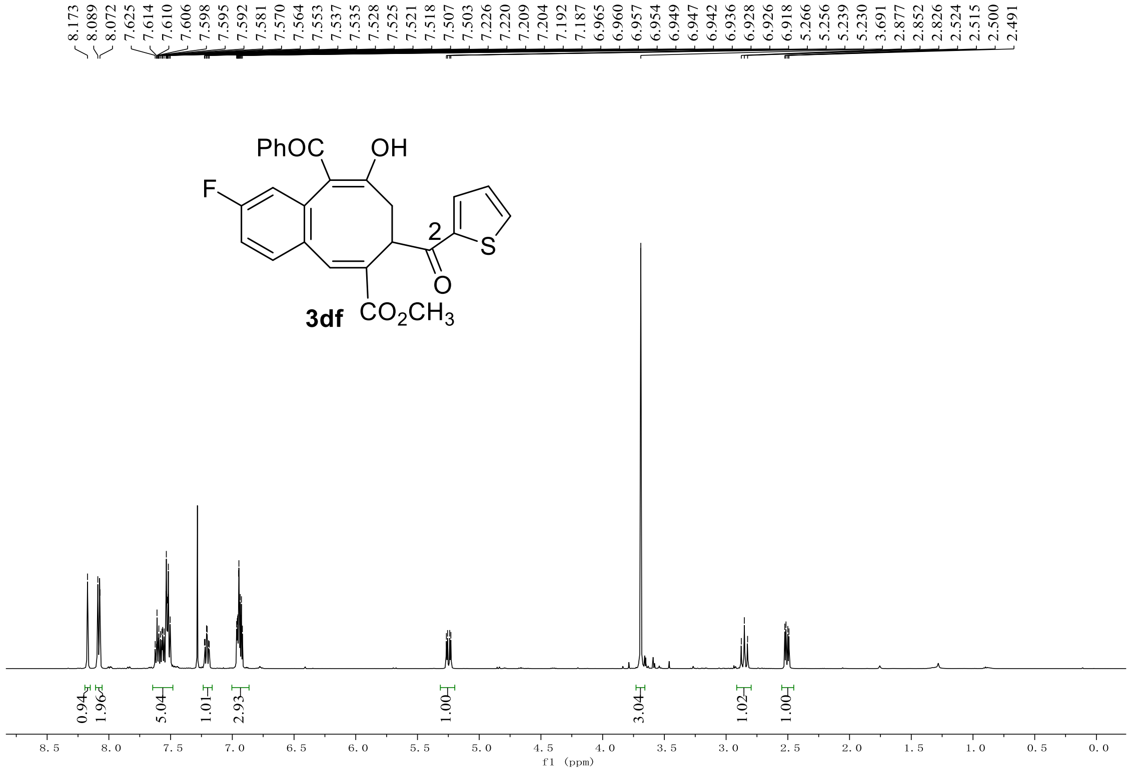
-112.87
-112.87
-112.87
-112.88
-112.89
PhOC
OH
F
2
O
3de
CO2CH3
−65
−70
−75
−80
−85
−90
−95
−100
−105
−110
−115
−120
−125
−130
−135
−140
−145
−150
−155
f1 (ppm)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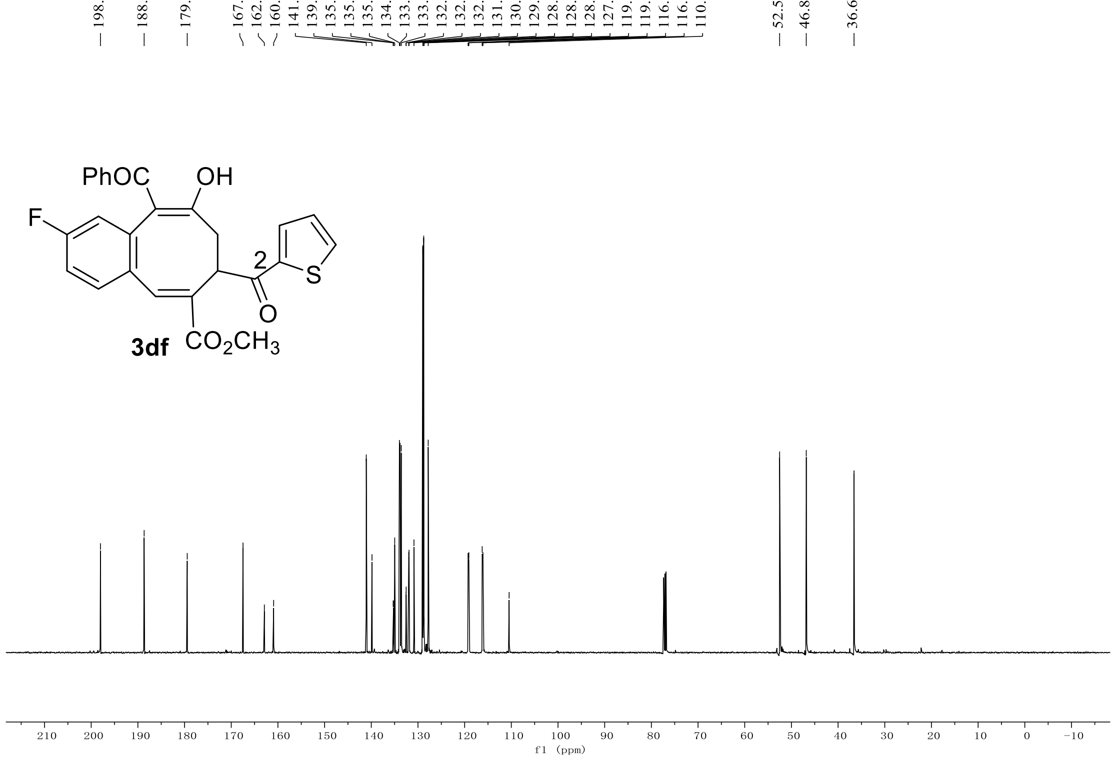
8.072
7.625
7.614
7.610
7.606
7.598
7.595
7.592
7.581
7.570
7.564
7.553
7.537
7.535
7.528
7.525
7.521
7.518
7.507
7.503
7.226
7.220
7.209
7.204
7.192
7.187
6.965
6.960
6.957
6.954
6.949
6.947
6.942
6.936
6.928
6.926
6.918
5.266
5.256
5.239
5.230
3.691
2.877
2.852
2.826
2.524
2.515
2.500
2.491
PhOC
OH
F
2
S
O
3df
$CO_2CH_3$
0.94
1.96
5.04
1.01
2.93
1.00
3.04
1.02
1.00
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)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179.4
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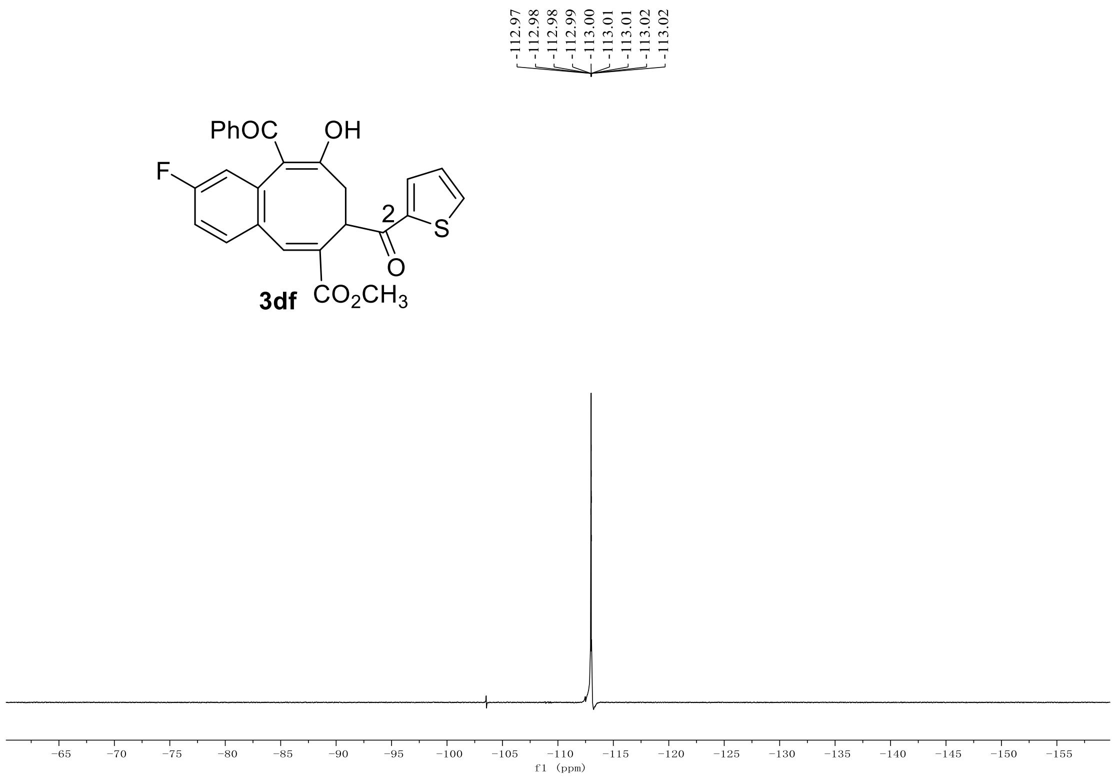
162.9
160.9
141.1
139.8
135.3
135.2
135.0
134.0
133.8
133.6
132.6
132.5
132.0
131.9
130.9
129.0
128.8
128.7
128.7
127.8
119.3
119.1
116.2
116.1
110.5
52.5
46.8
36.6
PhOC
OH
F
2
S
O
3df
$CO_2CH_3$
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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-112.98
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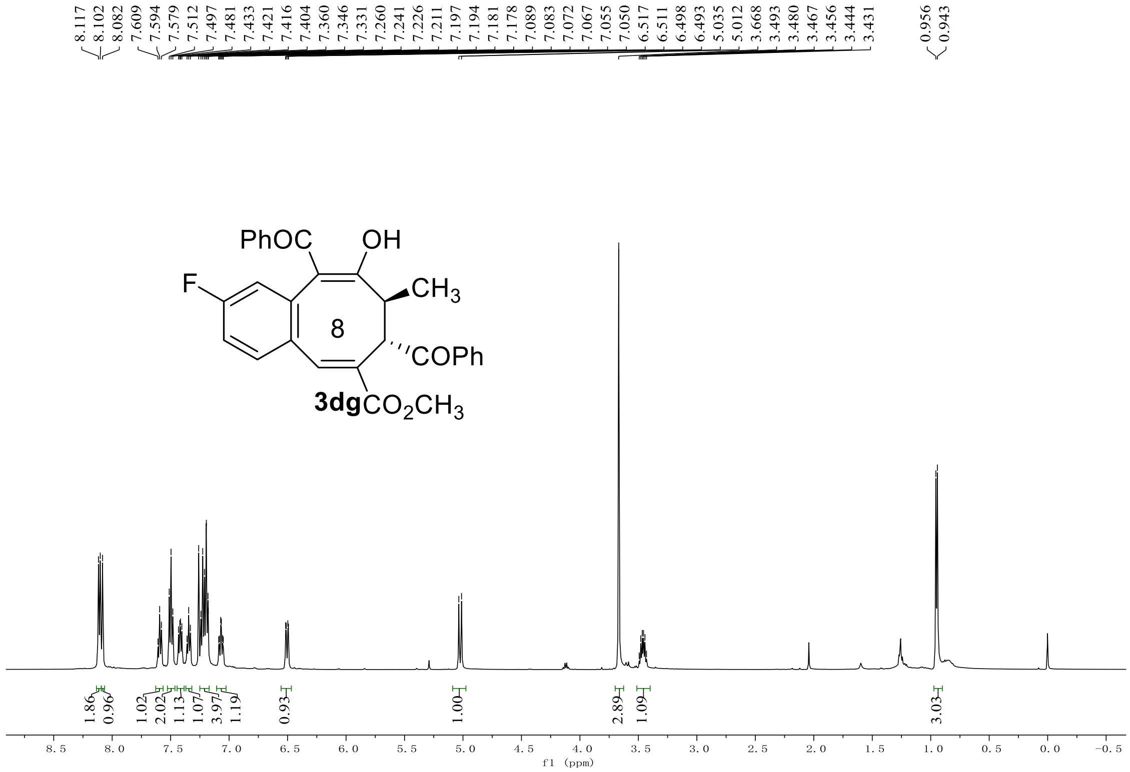
-113.00
-113.01
-113.01
-113.02
-113.02
PhOC
OH
F
2
S
O
3df
CO$_2$CH$_3$
-65
-70
-75
-80
-85
-90
-95
-100
-105
-110
-115
-120
-125
-130
-135
-140
-145
-150
-155
f1 (ppm)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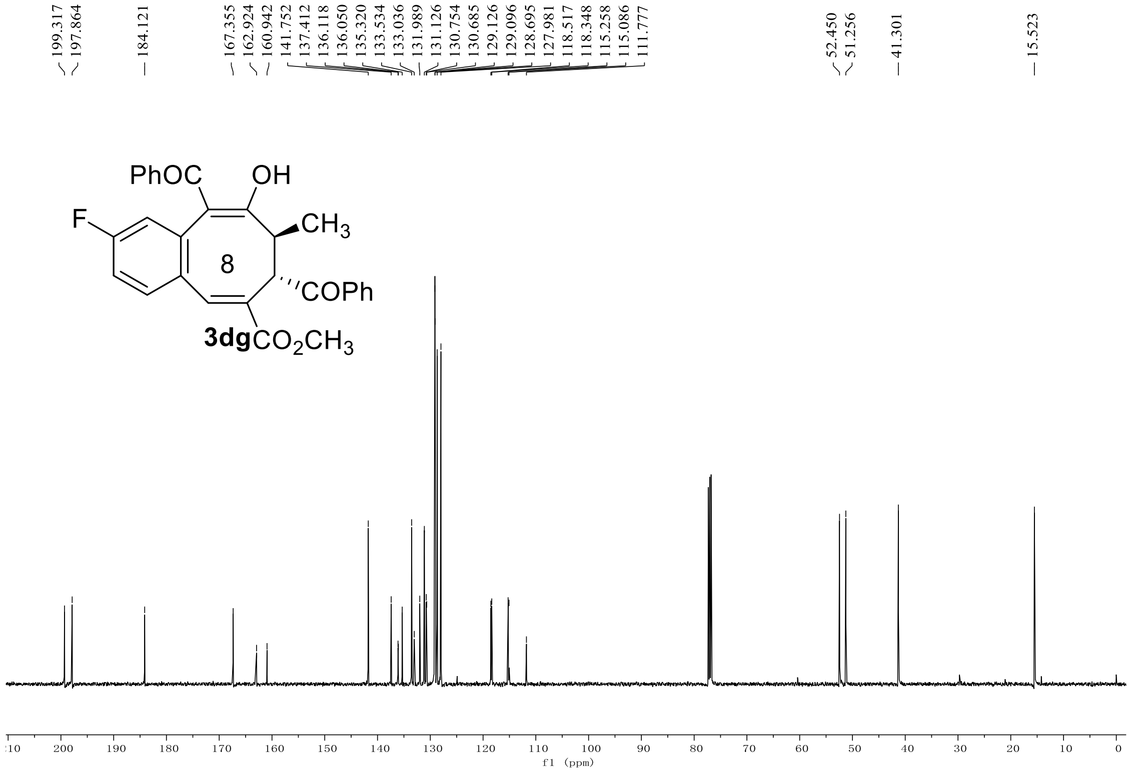
7.579
7.512
7.497
7.481
7.433
7.421
7.416
7.404
7.360
7.346
7.331
7.260
7.241
7.226
7.211
7.197
7.194
7.181
7.178
7.089
7.083
7.072
7.067
7.055
7.050
6.517
6.511
6.498
6.493
5.035
5.012
3.668
3.493
3.480
3.467
3.456
3.444
3.431
0.956
0.943
PhOC
OH
F
CH$_3$
8
COPh
3dg
CO$_2$CH$_3$
1.86
0.96
1.02
2.02
1.13
1.07
3.97
1.19
0.93
1.00
2.89
1.09
3.03
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)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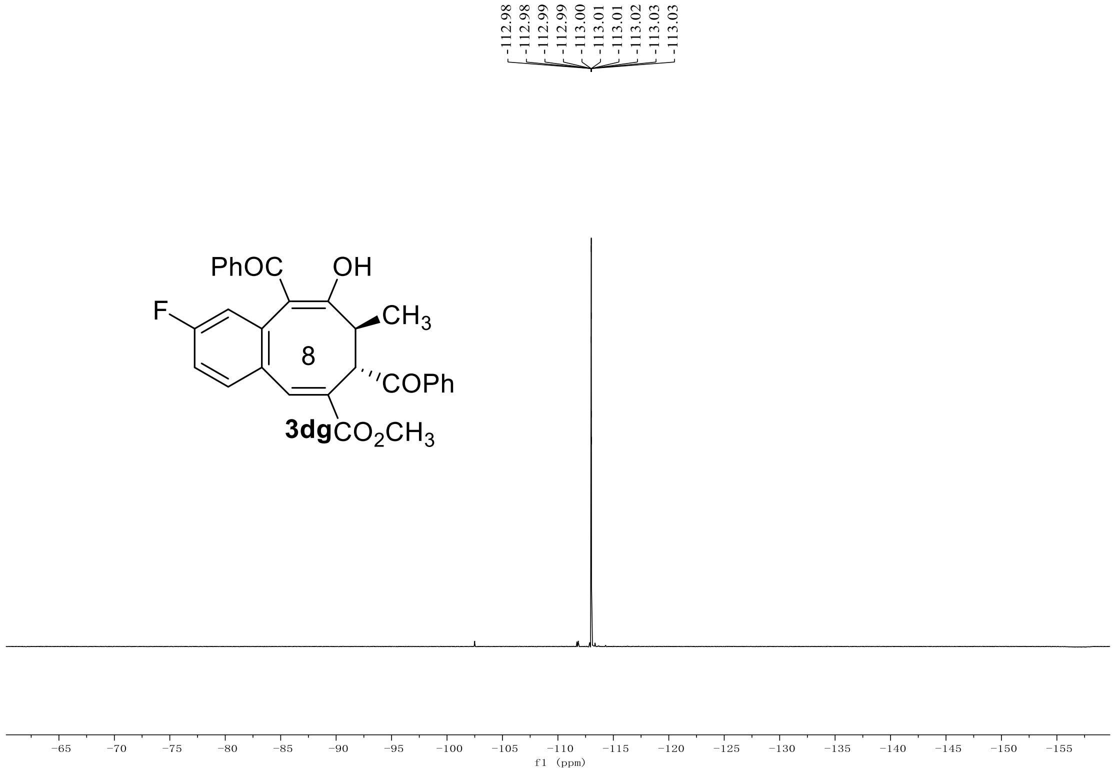
162.924
160.942
141.752
137.412
136.118
136.050
135.320
133.534
133.036
131.989
131.126
130.754
130.685
129.126
129.096
128.695
127.981
118.517
118.348
115.258
115.086
111.777
52.450
51.256
41.301
15.523
PhOC
OH
F
CH3
8
COPh
3dg
CO2CH3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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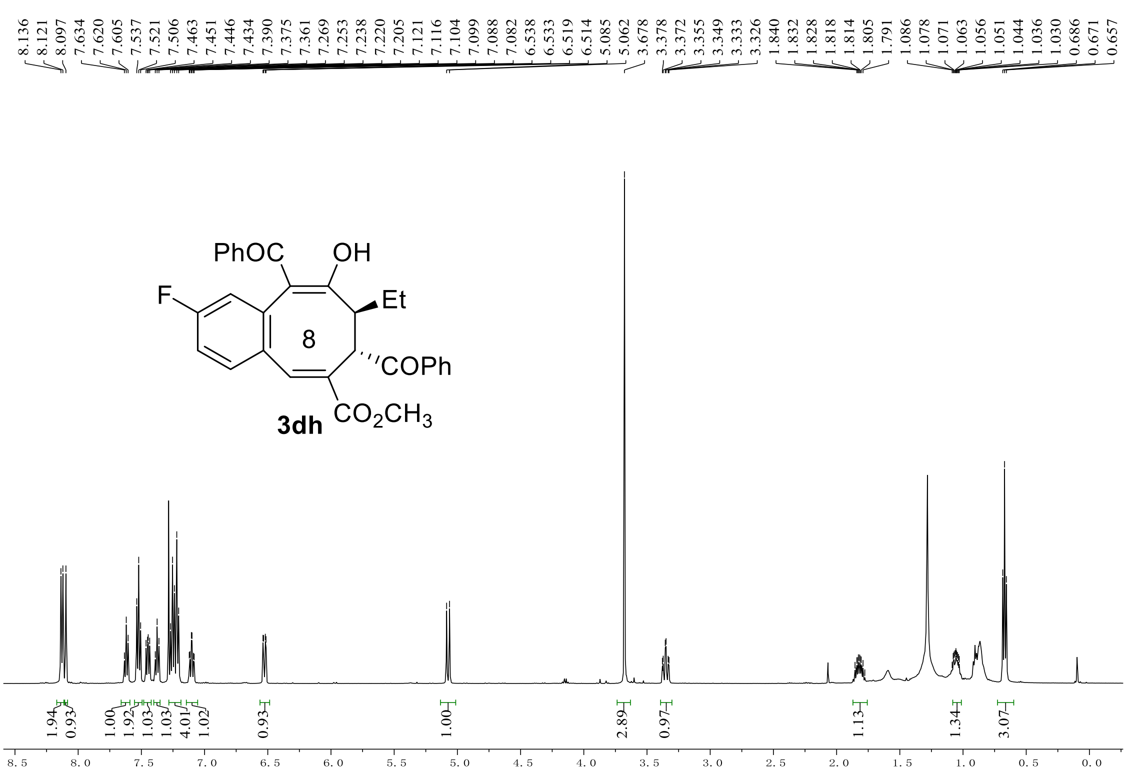
-112.98
-112.99
-112.99
-113.00
-113.01
-113.01
-113.02
-113.03
-113.03
PhOC
OH
F
CH3
8
COPh
3dg
CO2CH3
-65
-70
-75
-80
-85
-90
-95
-100
-105
-110
-115
-120
-125
-130
-135
-140
-145
-150
-155
f1 (ppm)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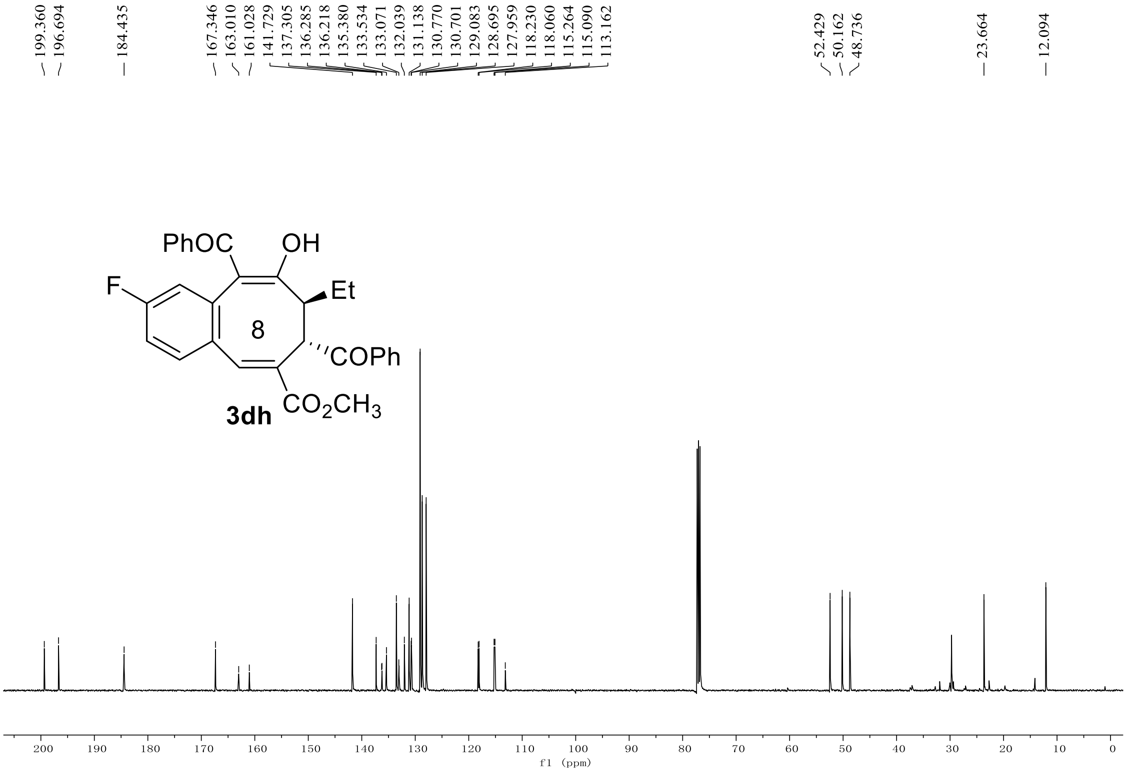
8.121
8.097
7.634
7.620
7.605
7.537
7.521
7.506
7.463
7.451
7.446
7.434
7.390
7.375
7.361
7.269
7.253
7.238
7.220
7.205
7.121
7.116
7.104
7.099
7.088
7.082
6.538
6.533
6.519
6.514
5.085
5.062
3.678
3.378
3.372
3.355
3.349
3.333
3.326
1.840
1.832
1.828
1.818
1.814
1.805
1.791
1.086
1.078
1.071
1.063
1.056
1.051
1.044
1.036
1.030
0.686
0.671
0.657
PhOC
OH
F
Et
8
COPh
CO2CH3
3dh
1.94
0.93
1.00
1.92
1.03
1.03
4.01
1.02
0.93
1.00
2.89
0.97
1.13
1.34
3.07
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)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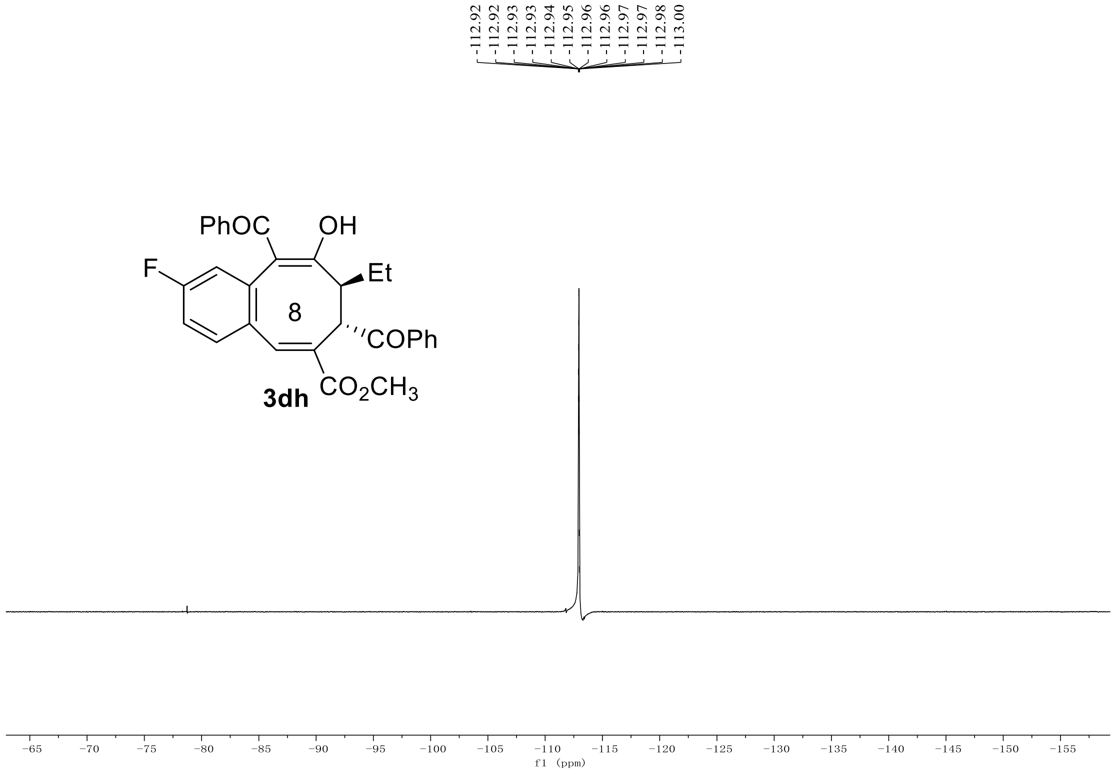
161.028
141.729
137.305
136.285
136.218
135.380
133.534
133.071
132.039
131.138
130.770
130.701
129.083
128.695
127.959
118.230
118.060
115.264
115.090
113.162
52.429
50.162
48.736
23.664
12.094
PhOC
OH
F
Et
8
COPh
CO2CH3
3dh
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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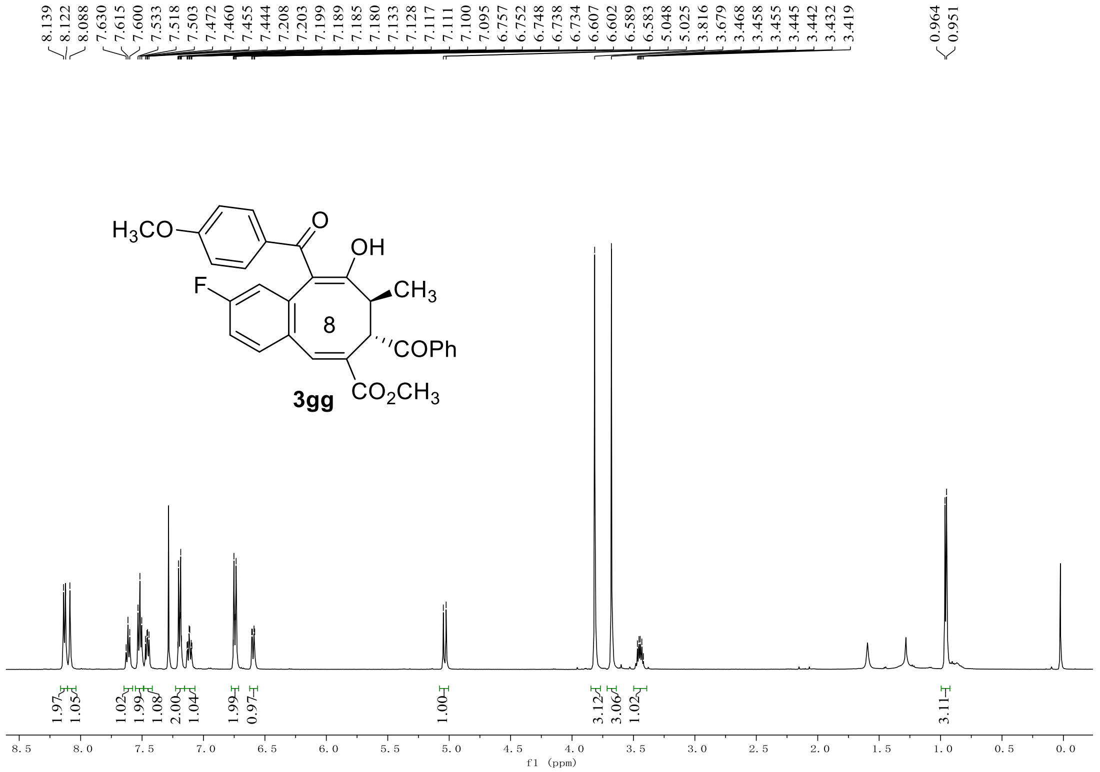
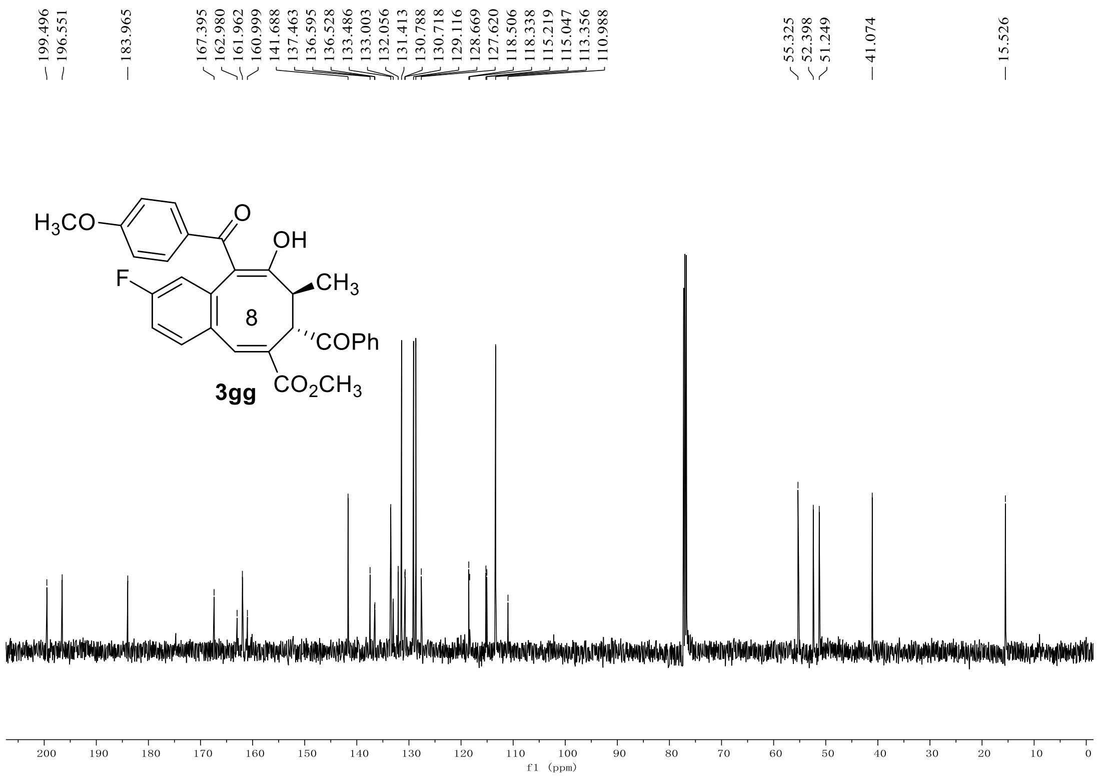
-112.92
-112.93
-112.93
-112.94
-112.95
-112.96
-112.96
-112.97
-112.97
-112.98
-113.00
PhOC
OH
F
Et
8
COPh
$CO_2CH_3$
3dh
−65 −70 −75 −80 −85 −90 −95 −100 −105 −110 −115 −120 −125 −130 −135 −140 −145 −150 −155
f1 (ppm)


8.139
8.122
8.088
7.630
7.615
7.600
7.533
7.518
7.503
7.472
7.460
7.455
7.444
7.208
7.203
7.199
7.189
7.185
7.180
7.133
7.128
7.117
7.111
7.100
7.095
6.757
6.752
6.748
6.738
6.734
6.607
6.602
6.589
6.583
5.048
5.025
3.816
3.679
3.468
3.458
3.455
3.445
3.442
3.432
3.419
0.964
0.951
$H_3CO$
O
OH
F
$CH_3$
8
COPh
$CO_2CH_3$
3gg
1.97
1.05
1.02
1.99
1.08
2.00
1.04
1.99
0.97
1.00
3.12
3.06
1.02
3.11
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)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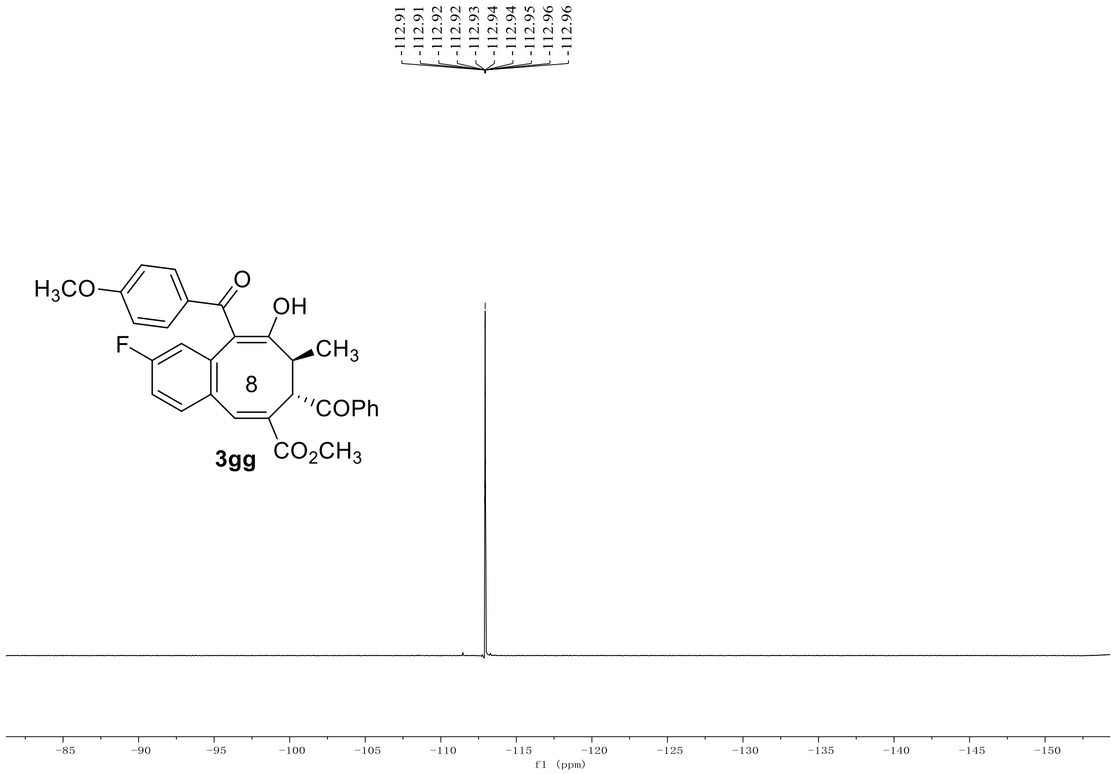
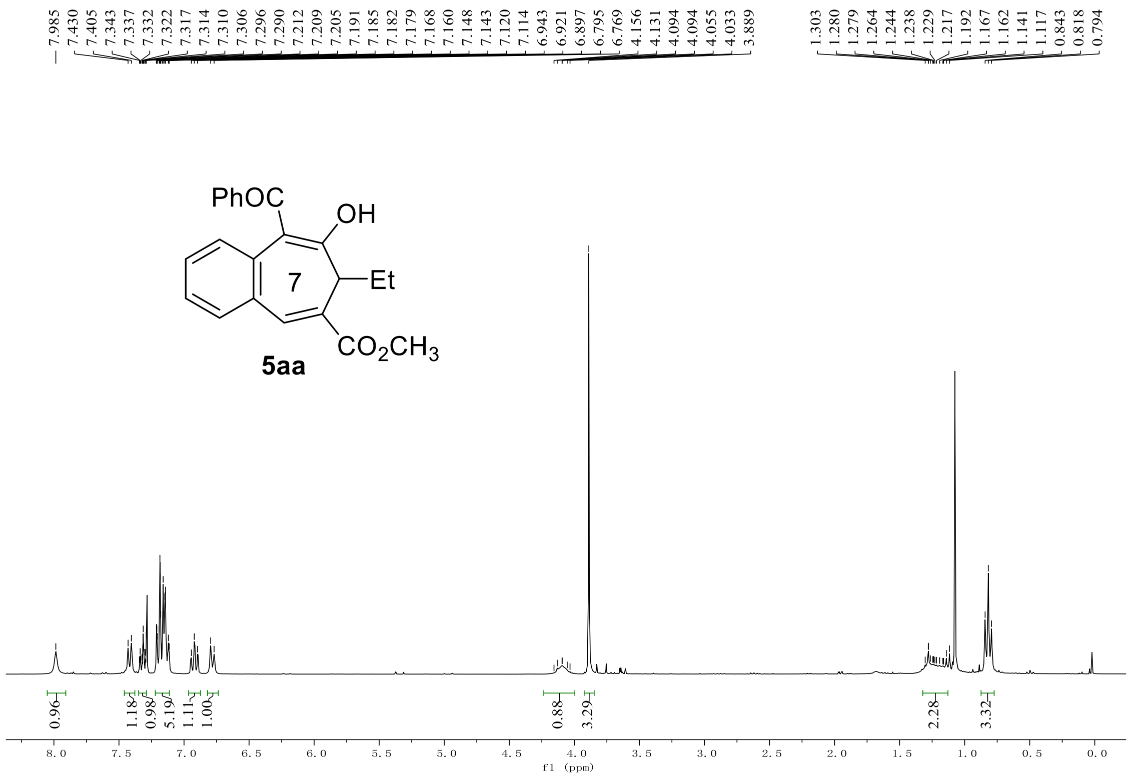
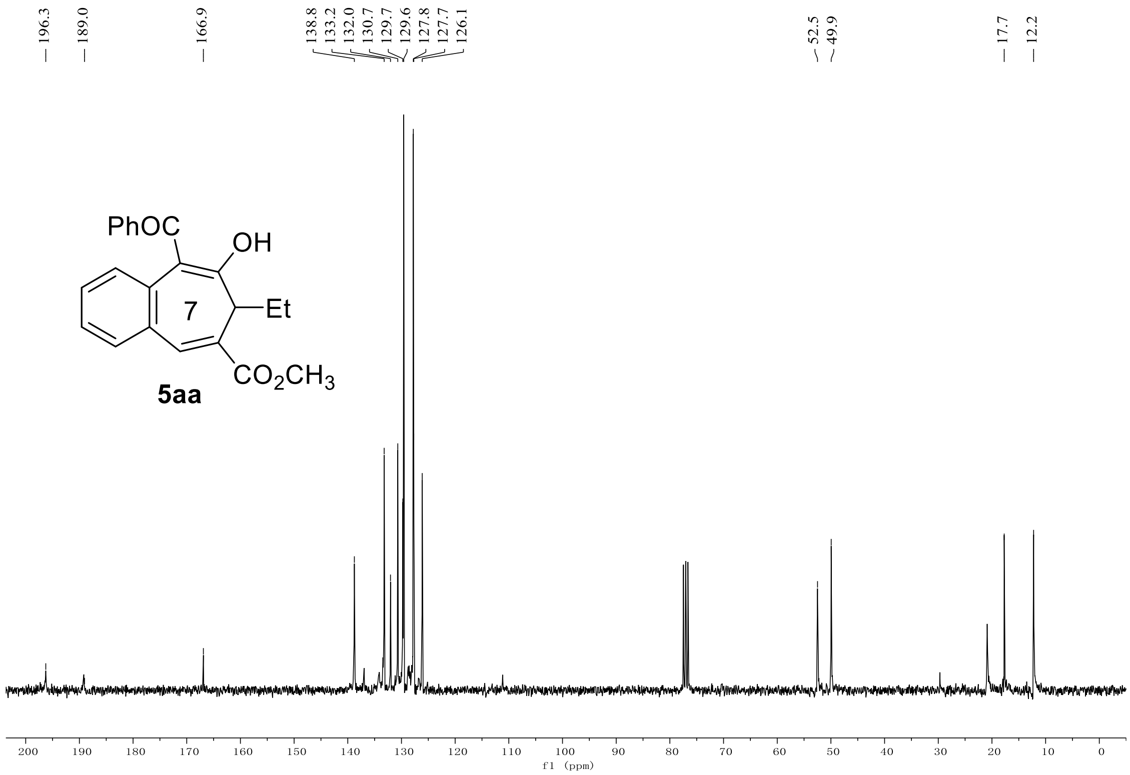
161.962
160.999
141.688
137.463
136.595
136.528
133.486
133.003
132.056
131.413
130.788
130.718
129.116
128.669
127.620
118.506
118.338
115.219
115.047
113.356
110.988
55.325
52.398
51.249
41.074
15.526
H3CO
O
OH
F
CH3
8
COPh
CO2CH3
3gg
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


-112.91
-112.91
-112.92
-112.92
-112.93
-112.94
-112.94
-112.95
-112.96
-112.96
H3CO
O
OH
F
CH3
8
COPh
CO2CH3
3gg
-85
-90
-95
-100
-105
-110
-115
-120
-125
-130
-135
-140
-145
-150
f1 (ppm)


7.985
7.430
7.405
7.343
7.337
7.332
7.322
7.317
7.314
7.310
7.306
7.296
7.290
7.212
7.209
7.205
7.191
7.185
7.182
7.179
7.168
7.160
7.148
7.143
7.120
7.114
6.943
6.921
6.897
6.795
6.769
4.156
4.131
4.094
4.094
4.055
4.033
3.889
1.303
1.280
1.279
1.264
1.244
1.238
1.229
1.217
1.192
1.167
1.162
1.141
1.117
0.843
0.818
0.794
PhOC
OH
7
Et
CO2CH3
5aa
0.96
1.18
0.98
5.19
1.11
1.00
0.88
3.29
2.28
3.32
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)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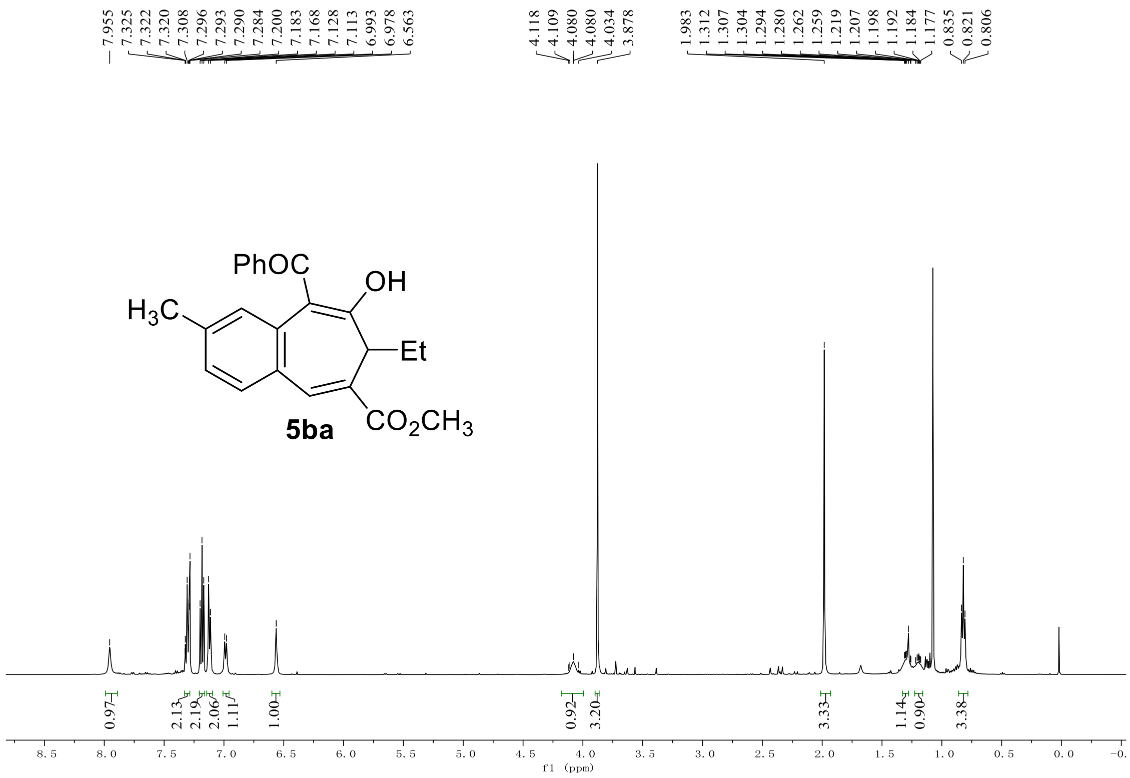
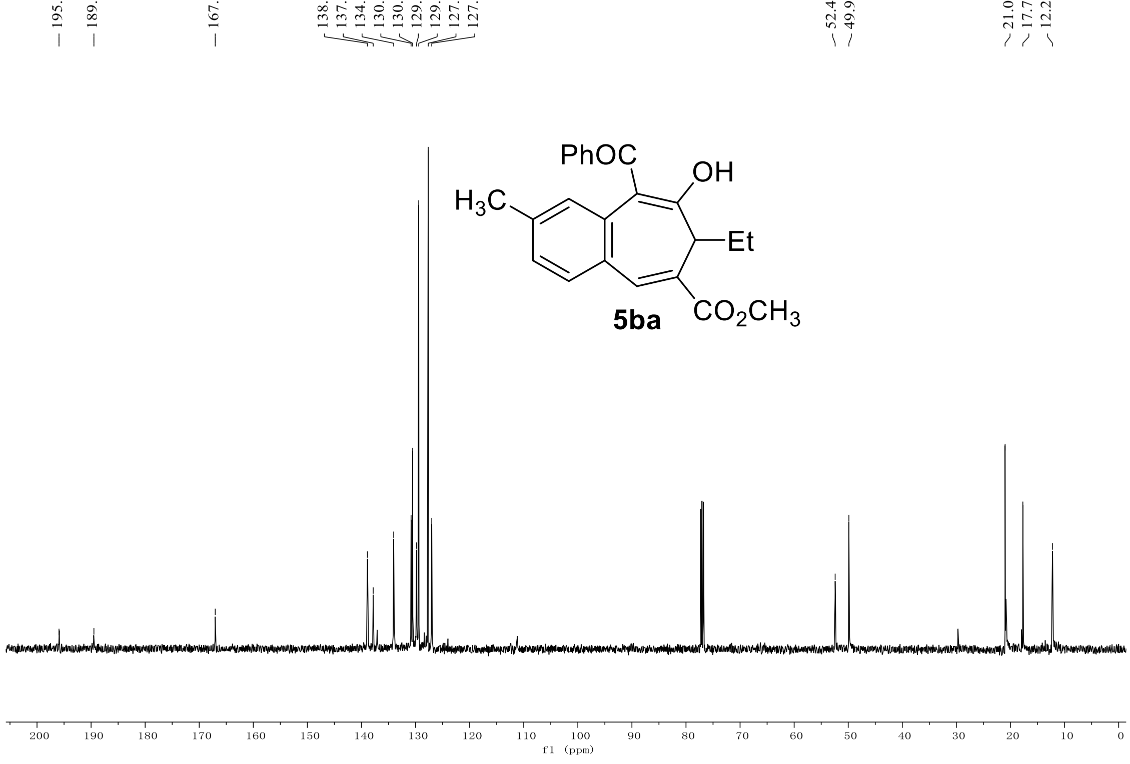
166.9
138.8
133.2
132.0
130.7
129.7
129.6
127.8
127.7
126.1
52.5
49.9
17.7
12.2
PhOC
OH
7
Et
CO2CH3
5aa
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.955
7.325
7.322
7.320
7.308
7.296
7.293
7.290
7.284
7.200
7.183
7.168
7.128
7.113
6.993
6.978
6.563
4.118
4.109
4.080
4.080
4.034
3.878
1.983
1.312
1.307
1.304
1.294
1.280
1.262
1.259
1.219
1.207
1.198
1.192
1.184
1.177
0.835
0.821
0.806
PhOC
OH
$H_3C$
Et
$CO_2CH_3$
5ba
0.97
2.13
2.19
2.06
1.11
1.00
0.92
3.20
3.33
1.14
0.90
3.38
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.
f1 (ppm)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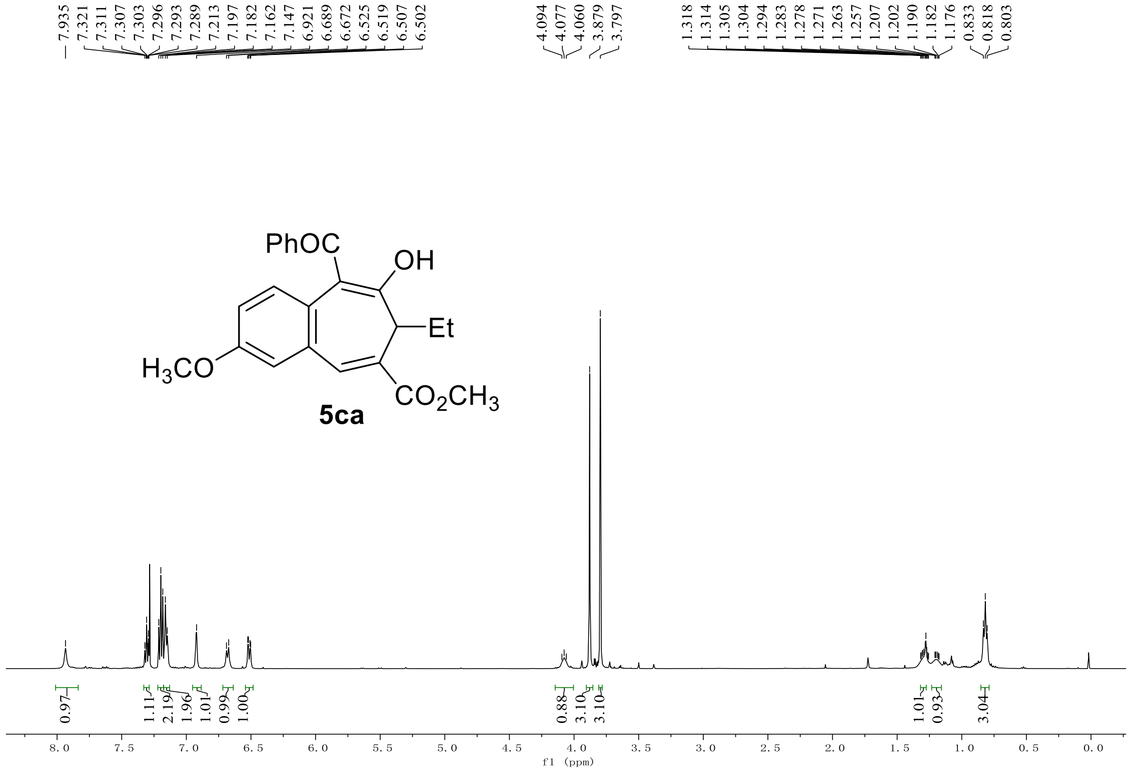
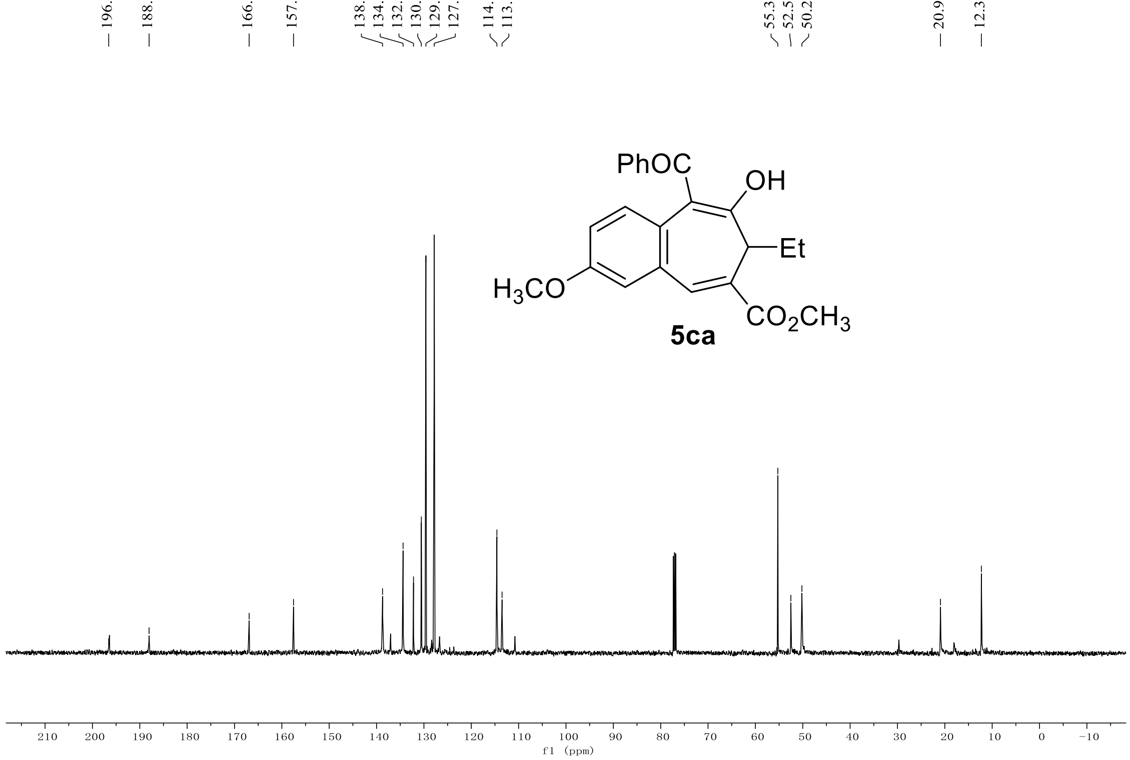
137.8
134.0
130.8
130.5
129.8
129.4
127.7
127.0
52.4
49.9
21.0
17.7
12.2
PhOC
OH
$H_3C$
Et
$CO_2CH_3$
5ba
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.935
7.321
7.311
7.307
7.303
7.296
7.293
7.289
7.213
7.197
7.182
7.162
7.147
6.921
6.689
6.672
6.525
6.519
6.507
6.502
4.094
4.077
4.060
3.879
3.797
1.318
1.314
1.305
1.304
1.294
1.283
1.278
1.271
1.263
1.257
1.207
1.202
1.190
1.182
1.176
0.833
0.818
0.803
PhOC
OH
Et
H3CO
CO2CH3
5ca
0.97
1.11
2.19
1.96
1.01
0.99
1.00
0.88
3.10
3.10
1.01
0.93
3.04
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)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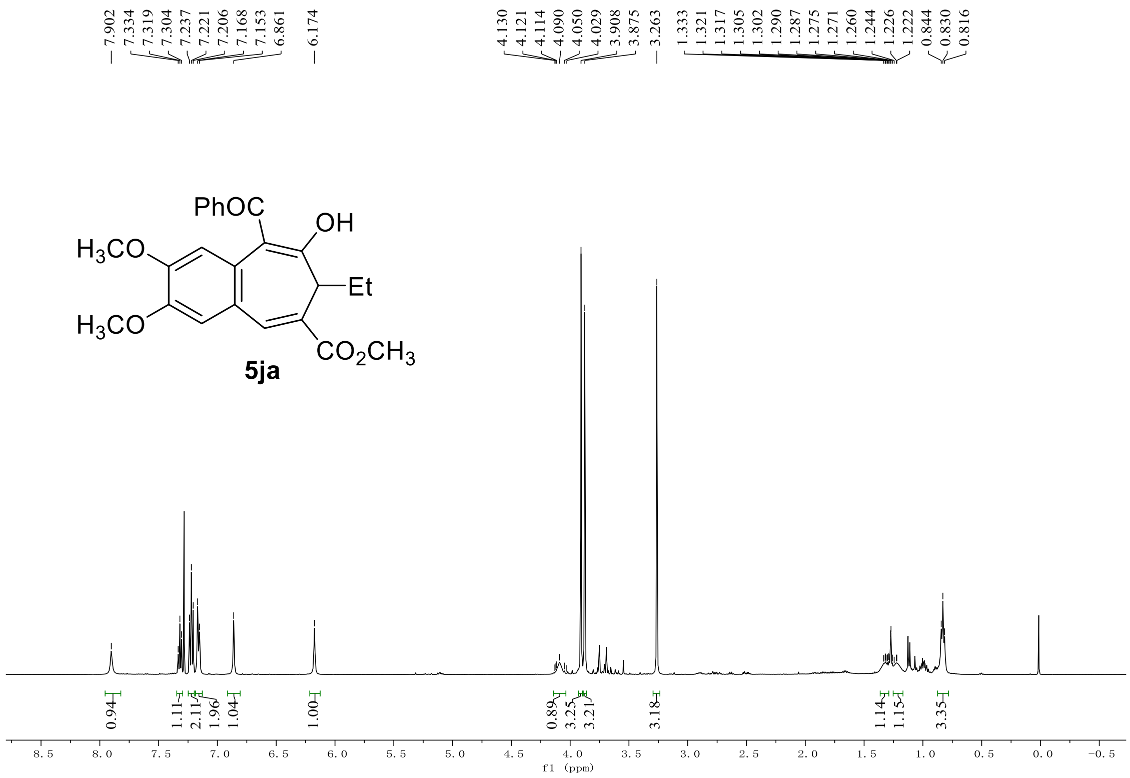
166.9
157.5
138.7
134.4
132.2
130.5
129.6
127.8
114.6
113.5
55.3
52.5
50.2
20.9
12.3
PhOC
OH
Et
H3CO
CO2CH3
5ca
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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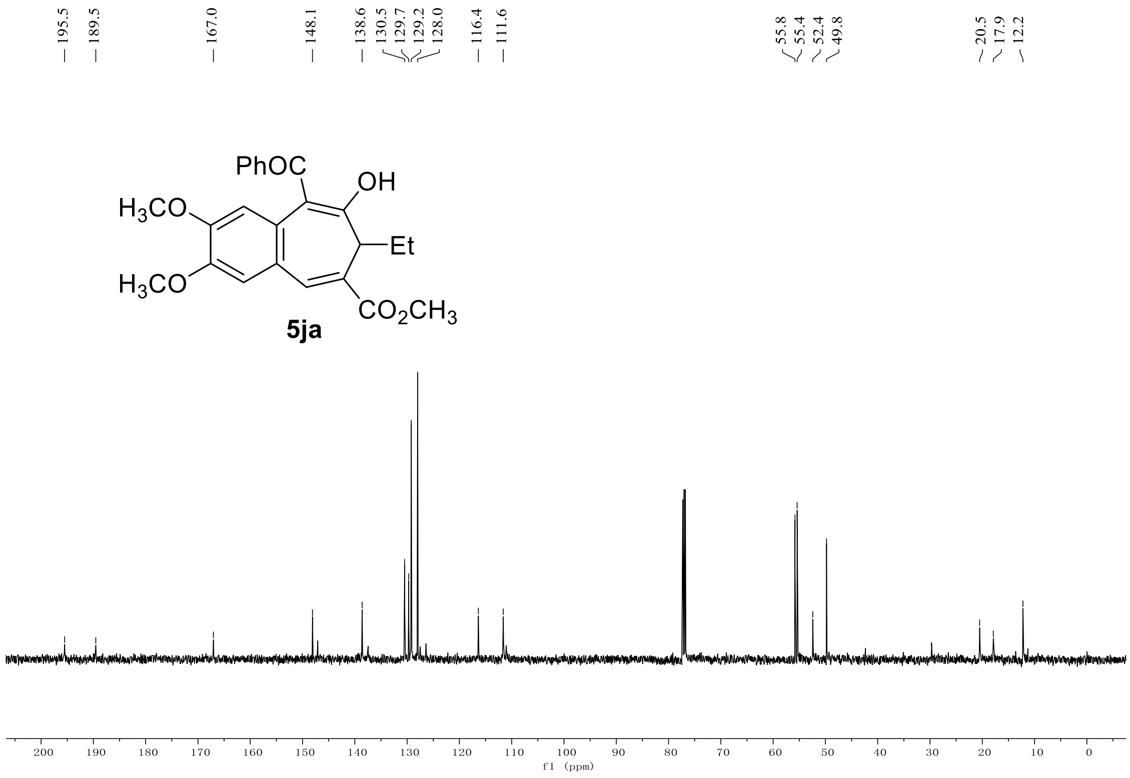
7.304
7.237
7.221
7.206
7.168
7.153
6.861
6.174
4.130
4.121
4.114
4.090
4.050
4.029
3.908
3.875
3.263
1.333
1.321
1.317
1.305
1.302
1.290
1.287
1.275
1.271
1.260
1.244
1.226
1.222
0.844
0.830
0.816
PhOC
OH
H3CO
H3CO
Et
CO2CH3
5ja
0.94
1.11
2.11
1.96
1.04
1.00
0.89
3.25
3.21
3.18
1.14
1.15
3.35
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)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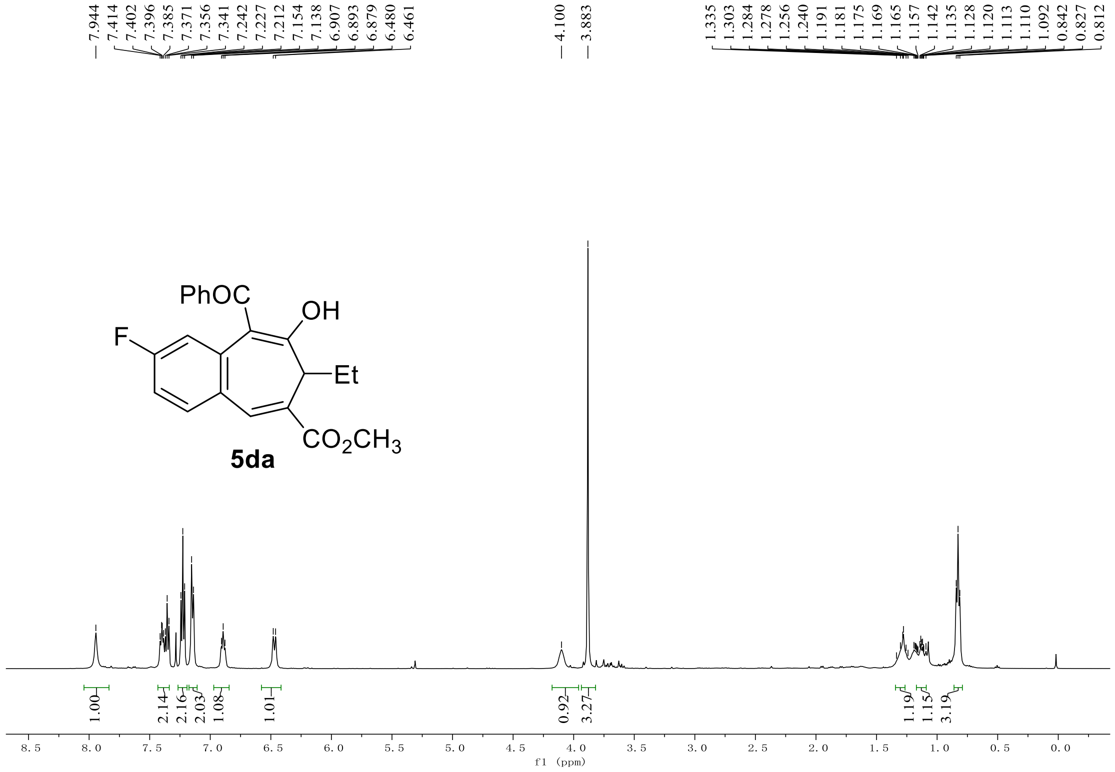
130.5
129.7
129.2
128.0
116.4
111.6
55.8
55.4
52.4
49.8
20.5
17.9
12.2
PhOC
OH
H3CO
H3CO
Et
CO2CH3
5ja
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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7.402
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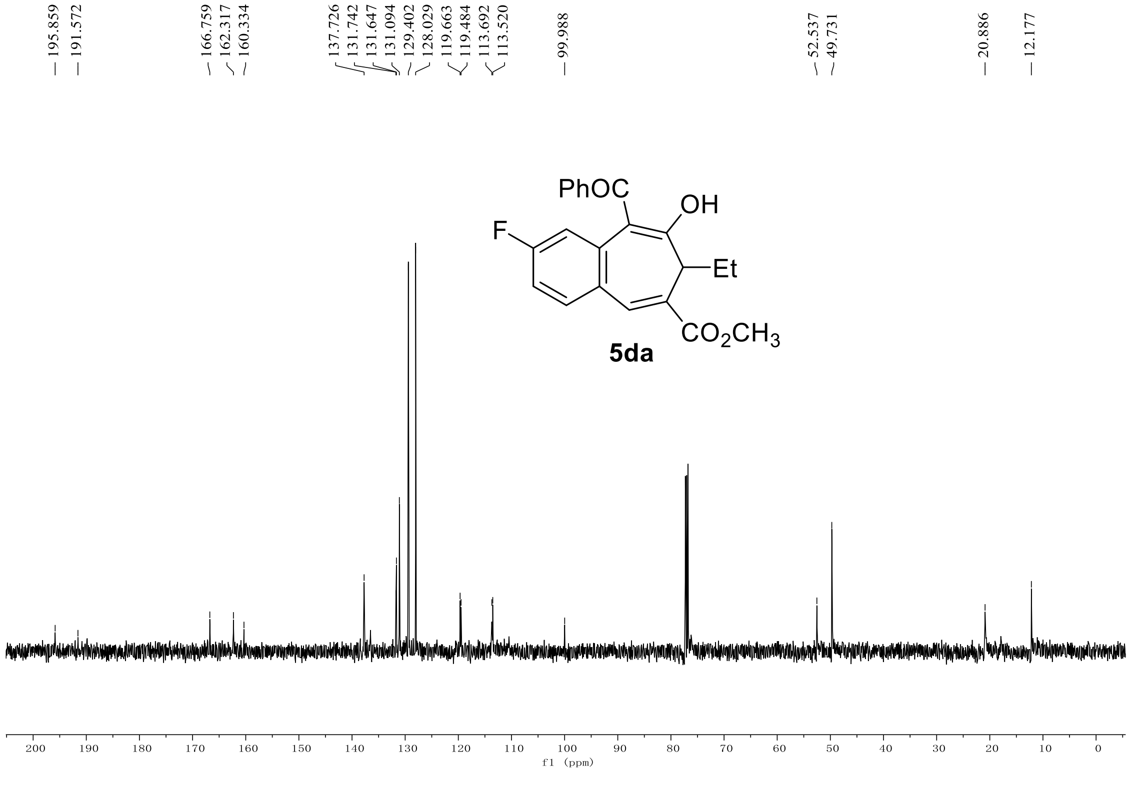
7.371
7.356
7.341
7.242
7.227
7.212
7.154
7.138
6.907
6.893
6.879
6.480
6.461
4.100
3.883
1.335
1.303
1.284
1.278
1.256
1.240
1.191
1.181
1.175
1.169
1.165
1.157
1.142
1.135
1.128
1.120
1.113
1.110
1.092
0.842
0.827
0.812
PhOC
OH
F
Et
CO2CH3
5da
1.00
2.14
2.16
2.03
1.08
1.01
0.92
3.27
1.19
1.15
3.19
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)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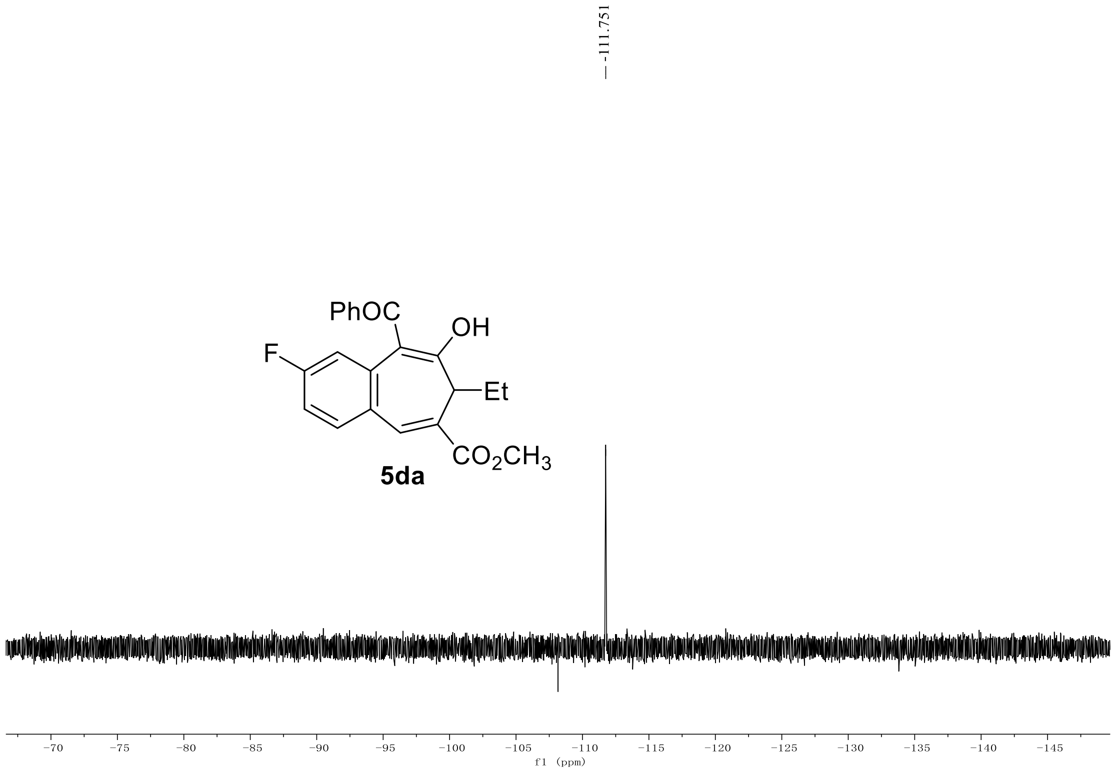
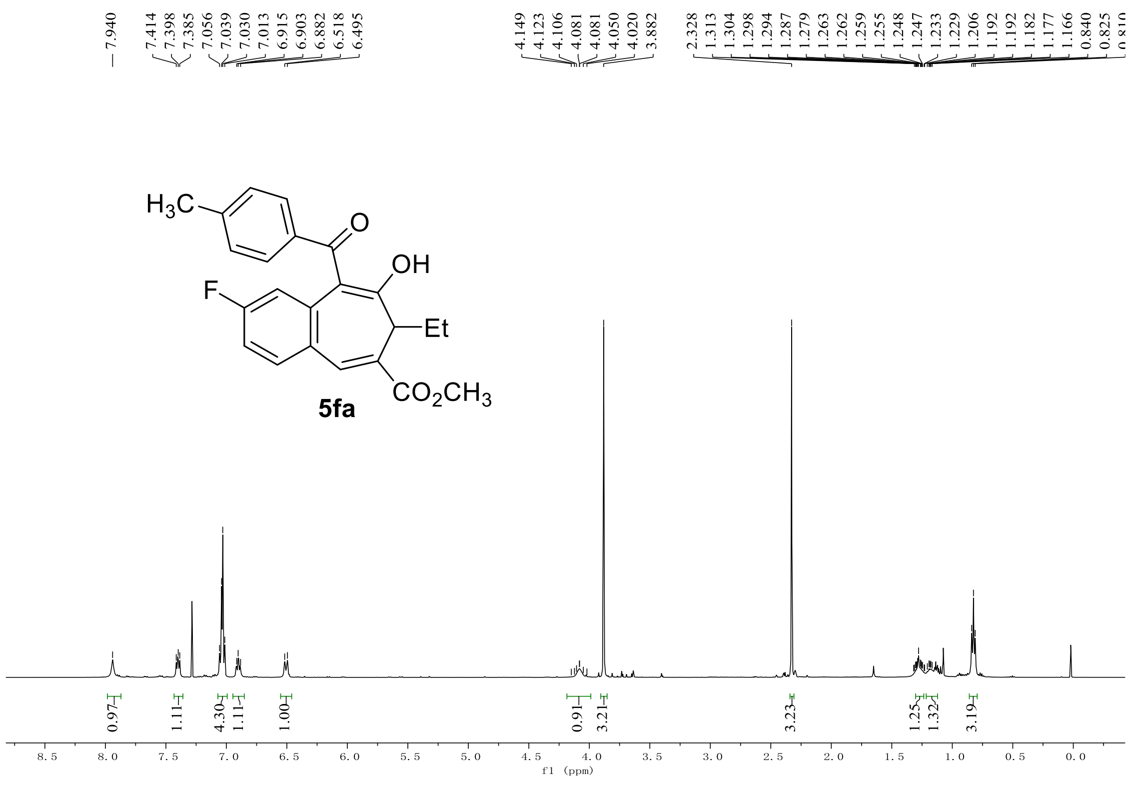
137.726
131.742
131.647
131.094
129.402
128.029
119.663
119.484
113.692
113.520
99.988
52.537
49.731
20.886
12.177
PhOC
OH
F
Et
CO2CH3
5da
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


-111.751
PhOC
OH
F
Et
CO2CH3
5da
−70
−75
−80
−85
−90
−95
−100
−105
−110
−115
−120
−125
−130
−135
−140
−145
f1 (ppm)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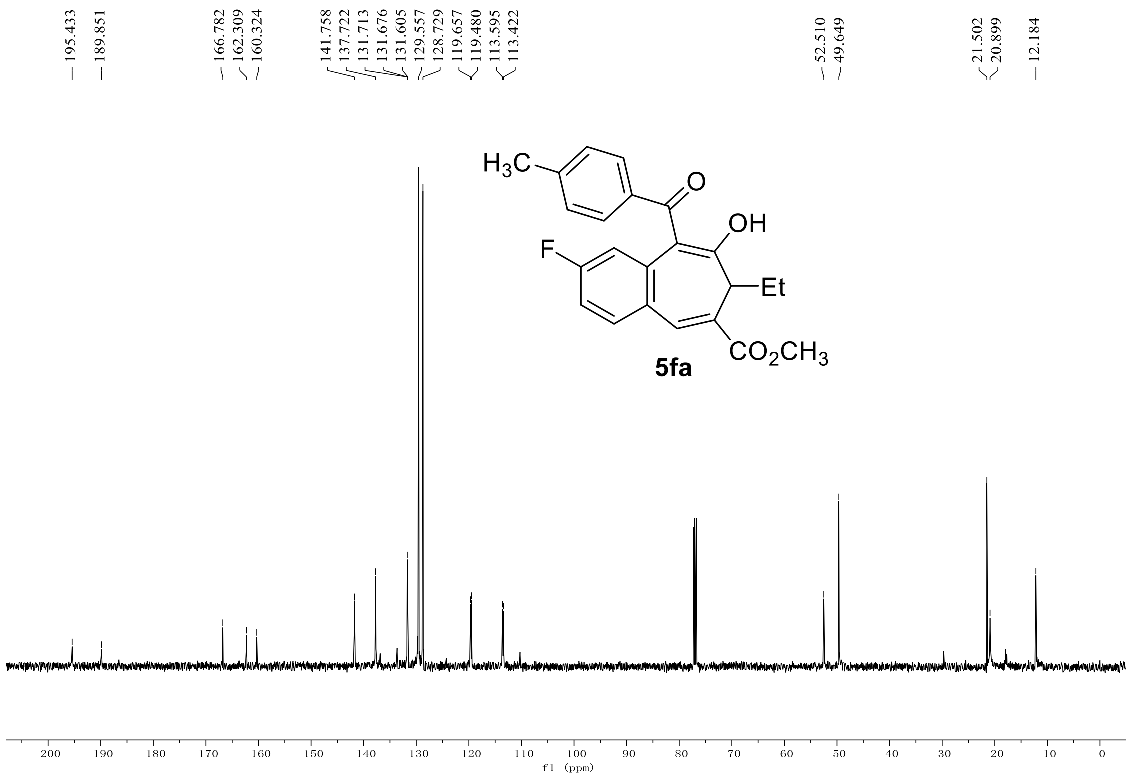
7.385
7.056
7.039
7.030
7.013
6.915
6.903
6.882
6.518
6.495
4.149
4.123
4.106
4.081
4.081
4.050
4.020
3.882
2.328
1.313
1.304
1.298
1.294
1.287
1.279
1.263
1.262
1.259
1.255
1.248
1.247
1.233
1.229
1.206
1.192
1.192
1.182
1.177
1.166
0.840
0.825
0.810
H3C
O
OH
F
Et
CO2CH3
5fa
0.97
1.11
4.30
1.11
1.00
0.91
3.21
3.23
1.25
1.32
3.19
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)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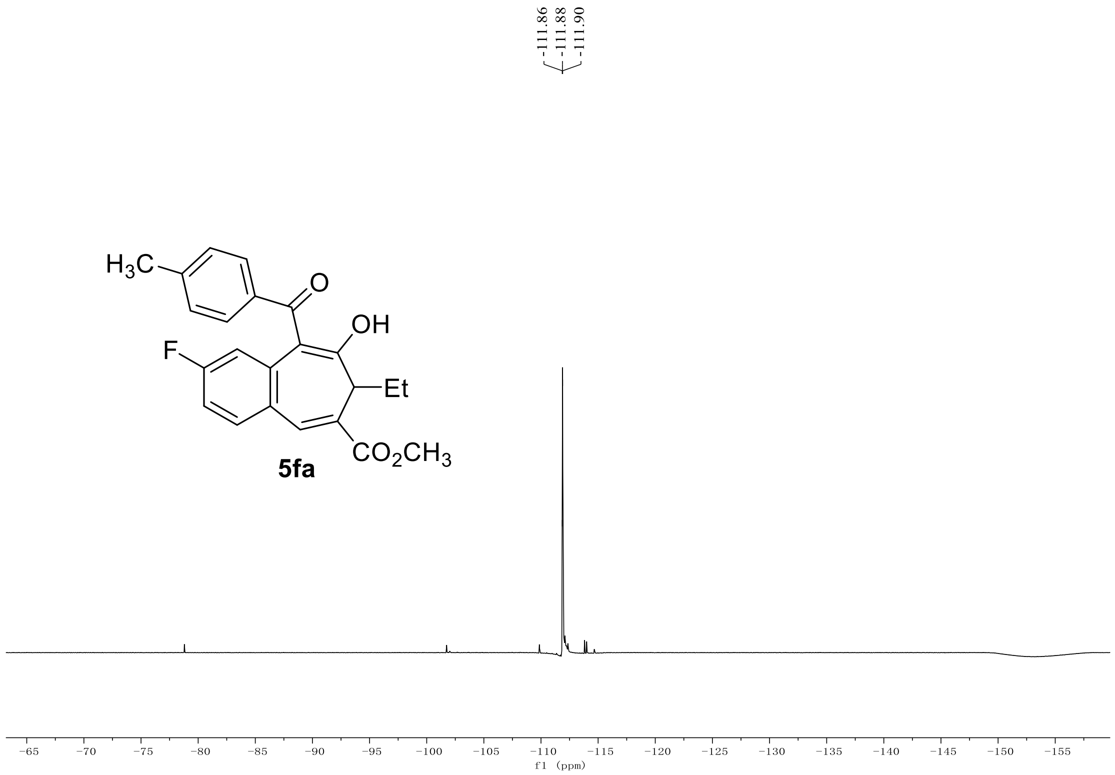
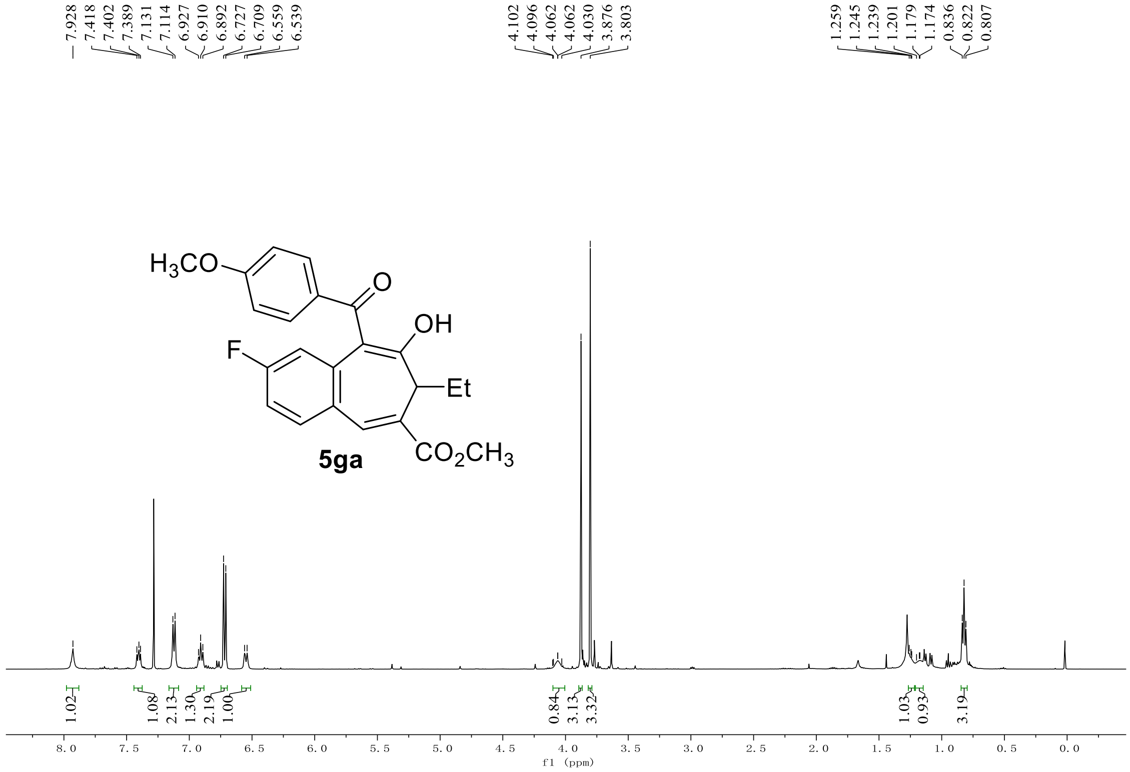
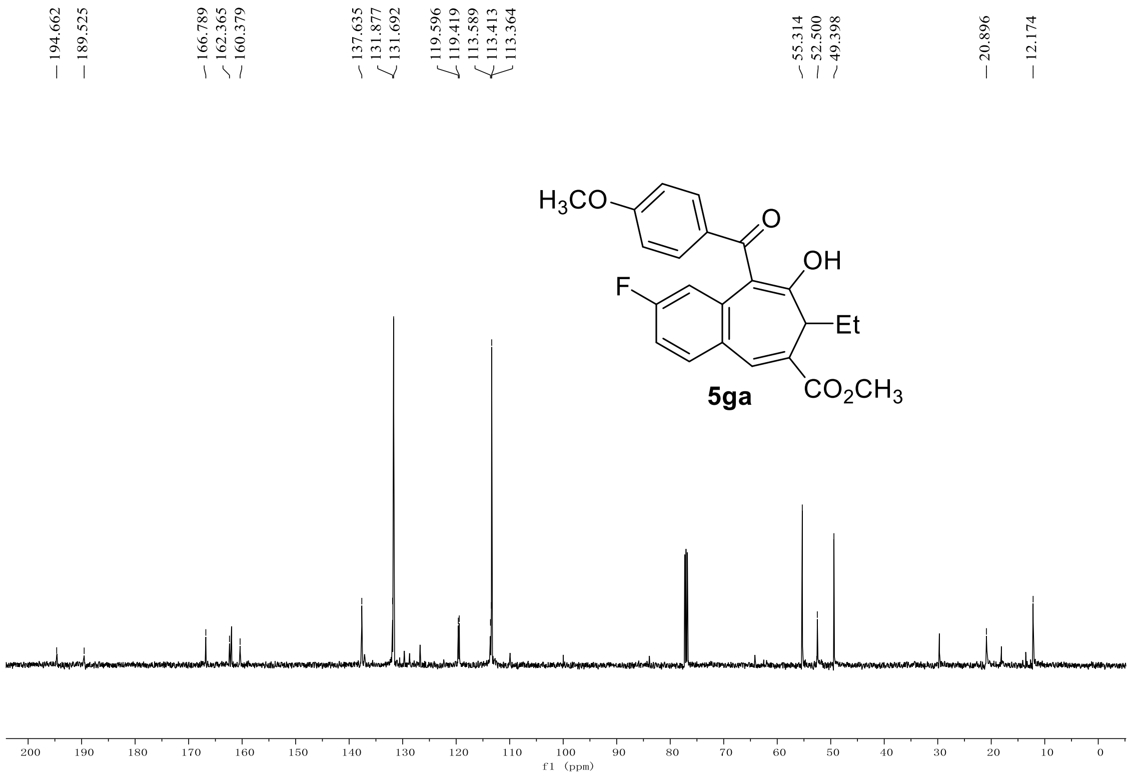
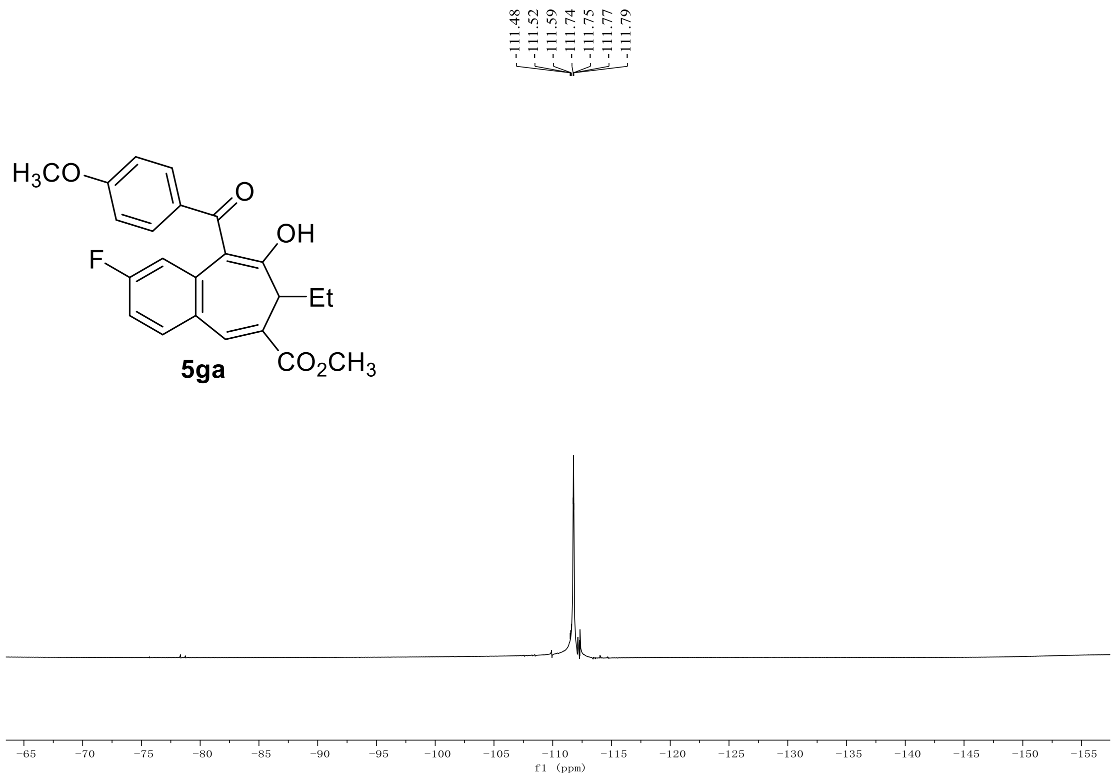
137.722
131.713
131.676
131.605
129.557
128.729
119.657
119.480
113.595
113.422
52.510
49.649
21.502
20.899
12.184
$H_3C$
O
OH
F
Et
$CO_2CH_3$
5fa
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

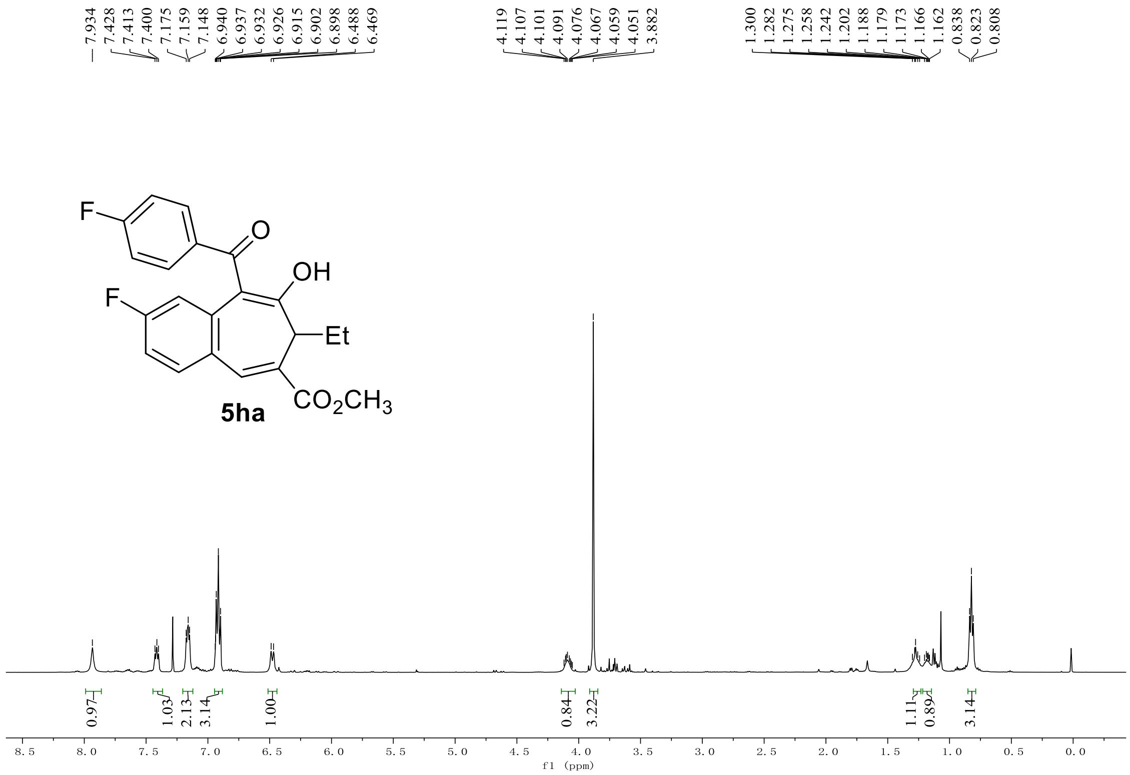

-111.86
-111.88
-111.90
$H_3C$
O
OH
F
Et
$CO_2CH_3$
5fa
-65
-70
-75
-80
-85
-90
-95
-100
-105
-110
-115
-120
-125
-130
-135
-140
-145
-150
-155
f1 (ppm)


7.928
7.418
7.402
7.389
7.131
7.114
6.927
6.910
6.892
6.727
6.709
6.559
6.539
4.102
4.096
4.062
4.062
4.030
3.876
3.803
1.259
1.245
1.239
1.201
1.179
1.174
0.836
0.822
0.807
H3CO
O
OH
F
Et
CO2CH3
5ga
1.02
1.08
2.13
1.30
2.19
1.00
0.84
3.13
3.32
1.03
0.93
3.19
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)

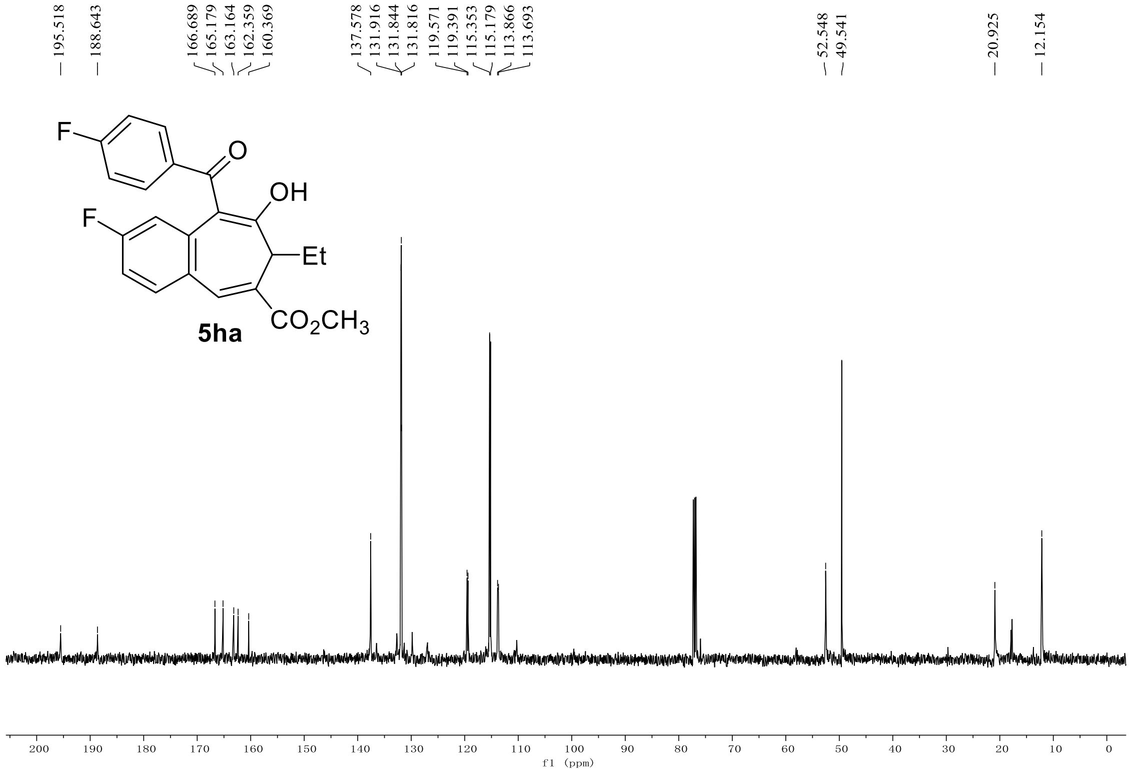

194.662
189.525
166.789
162.365
160.379
137.635
131.877
131.692
119.596
119.419
113.589
113.413
113.364
55.314
52.500
49.398
20.896
12.174
H3CO
O
OH
F
Et
CO2CH3
5ga
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

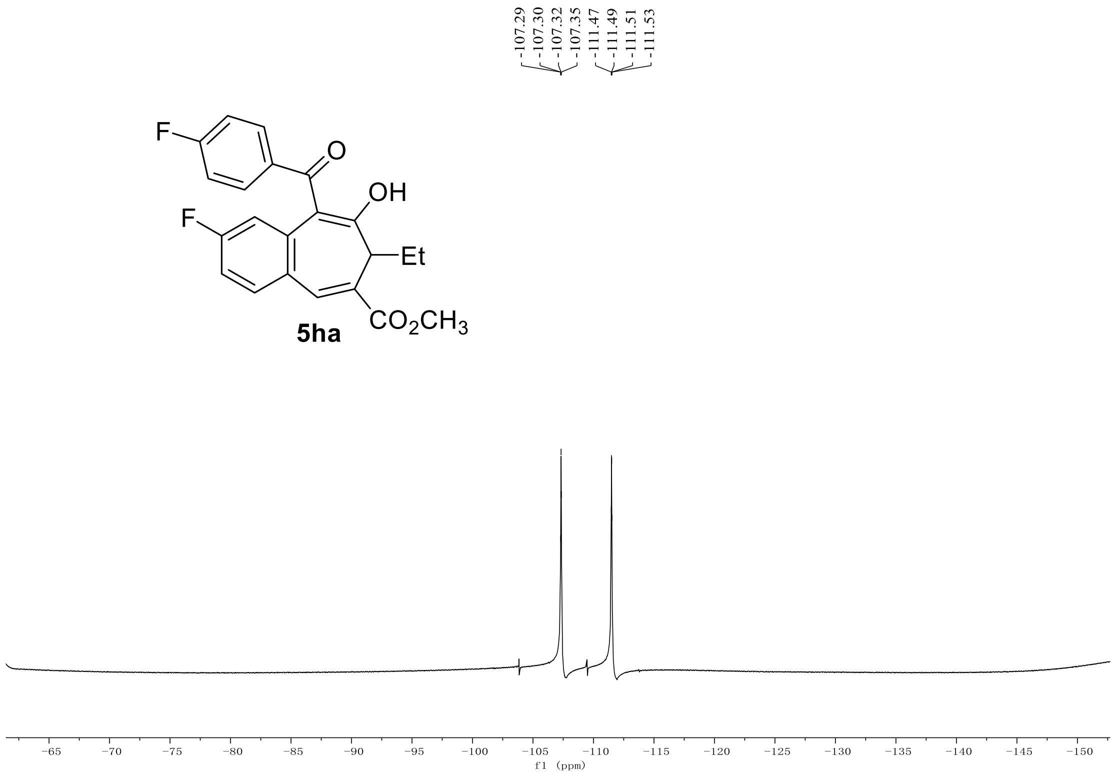

-111.48
-111.52
-111.59
-111.74
-111.75
-111.77
-111.79
H3CO
O
OH
F
Et
CO2CH3
−65 −70 −75 −80 −85 −90 −95 −100 −105 −110 −115 −120 −125 −130 −135 −140 −145 −150 −155
f1 (ppm)

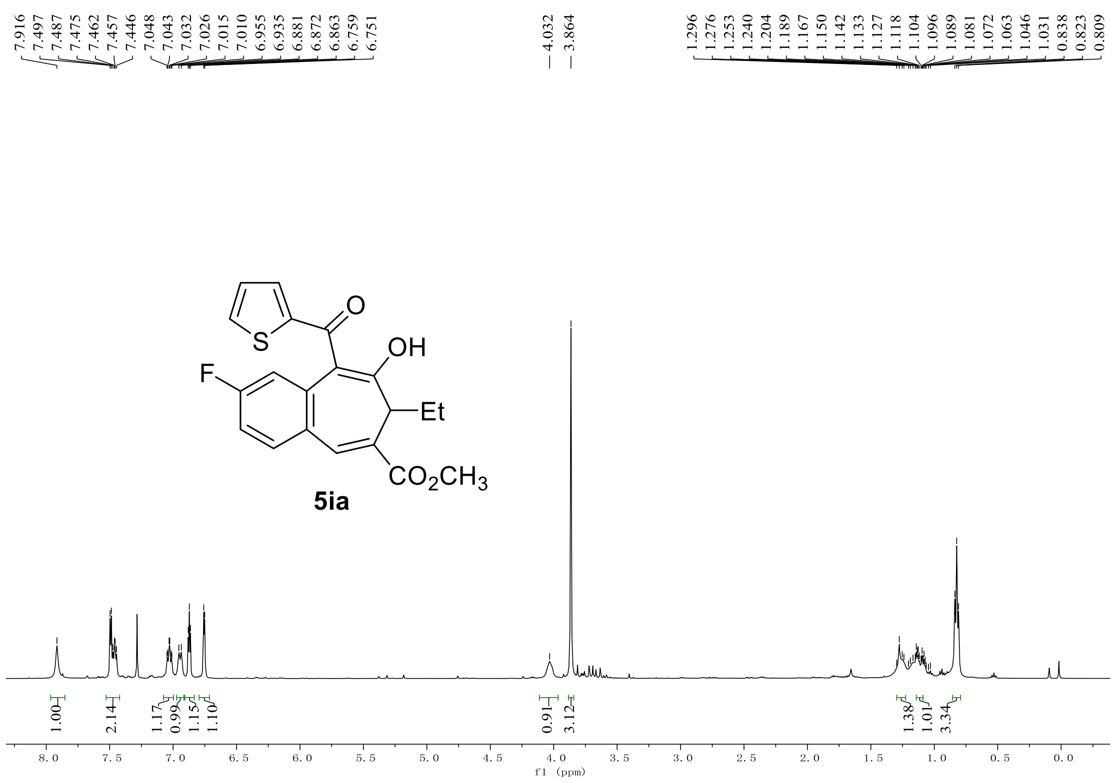
**5ga**


7.934
7.428
7.413
7.400
7.175
7.159
7.148
6.940
6.937
6.932
6.926
6.915
6.902
6.898
6.488
6.469
4.119
4.107
4.101
4.091
4.076
4.067
4.059
4.051
3.882
1.300
1.282
1.275
1.258
1.242
1.202
1.188
1.179
1.173
1.166
1.162
0.838
0.823
0.808
F
O
OH
F
Et
CO2CH3
0.97
1.03
2.13
3.14
1.00
0.84
3.22
1.11
0.89
3.14
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)

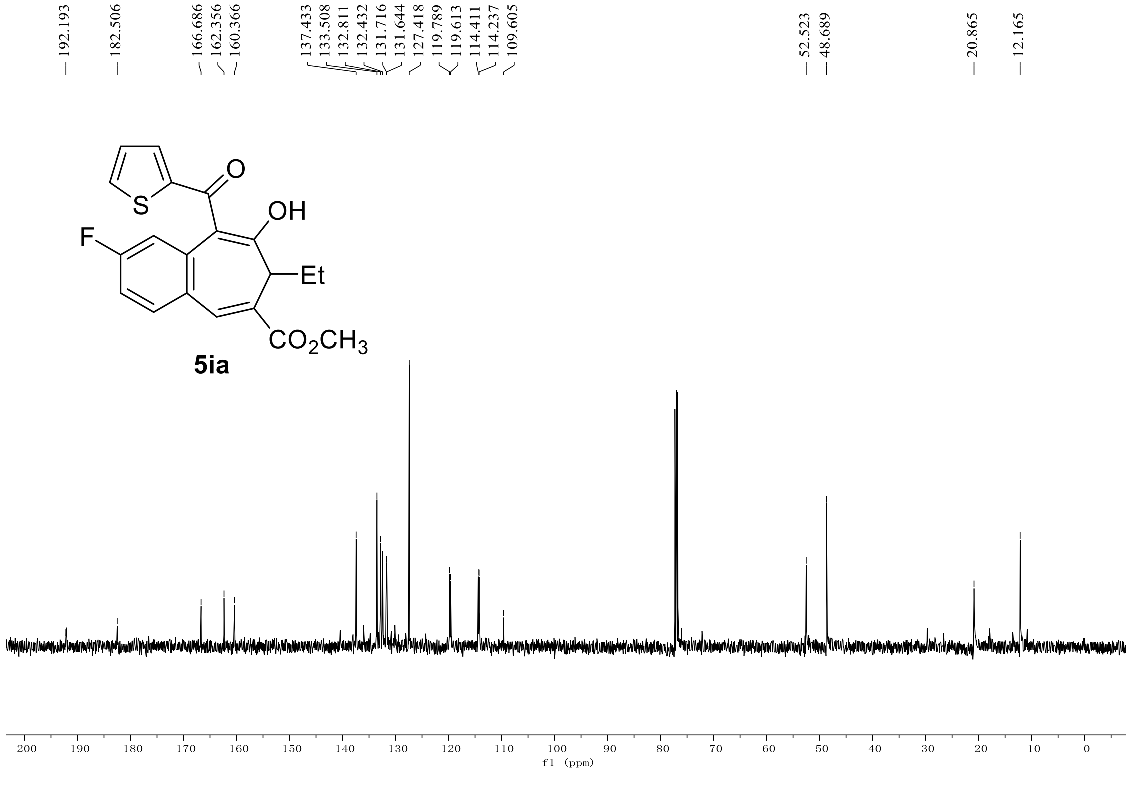
**5ha**


195.518
188.643
166.689
165.179
163.164
162.359
160.369
137.578
131.916
131.844
131.816
119.571
119.391
115.353
115.179
113.866
113.693
52.548
49.541
20.925
12.154
F
O
OH
F
Et
CO2CH3
5ha
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

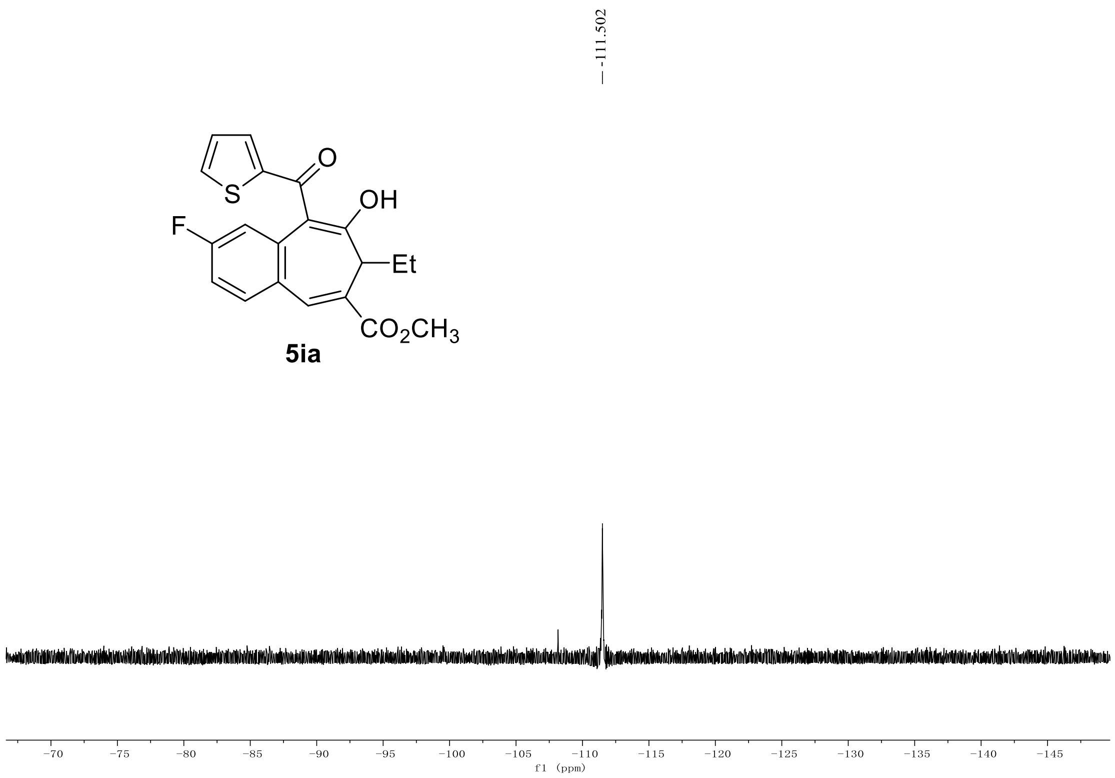

-107.29
-107.30
-107.32
-107.35
-111.47
-111.49
-111.51
-111.53
F
O
OH
F
Et
CO2CH3
5ha
−65 −70 −75 −80 −85 −90 −95 −100 −105 −110 −115 −120 −125 −130 −135 −140 −145 −150
f1 (ppm)


7.916
7.497
7.487
7.475
7.462
7.457
7.446
7.048
7.043
7.032
7.026
7.015
7.010
6.955
6.935
6.881
6.872
6.863
6.759
6.751
4.032
3.864
1.296
1.276
1.253
1.240
1.204
1.189
1.167
1.150
1.142
1.133
1.127
1.118
1.104
1.096
1.089
1.081
1.072
1.063
1.046
1.031
0.838
0.823
0.809
F
S
O
OH
Et
$CO_2CH_3$
1.00
2.14
1.17
0.99
1.15
1.10
0.91
3.12
1.38
1.01
3.34
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)

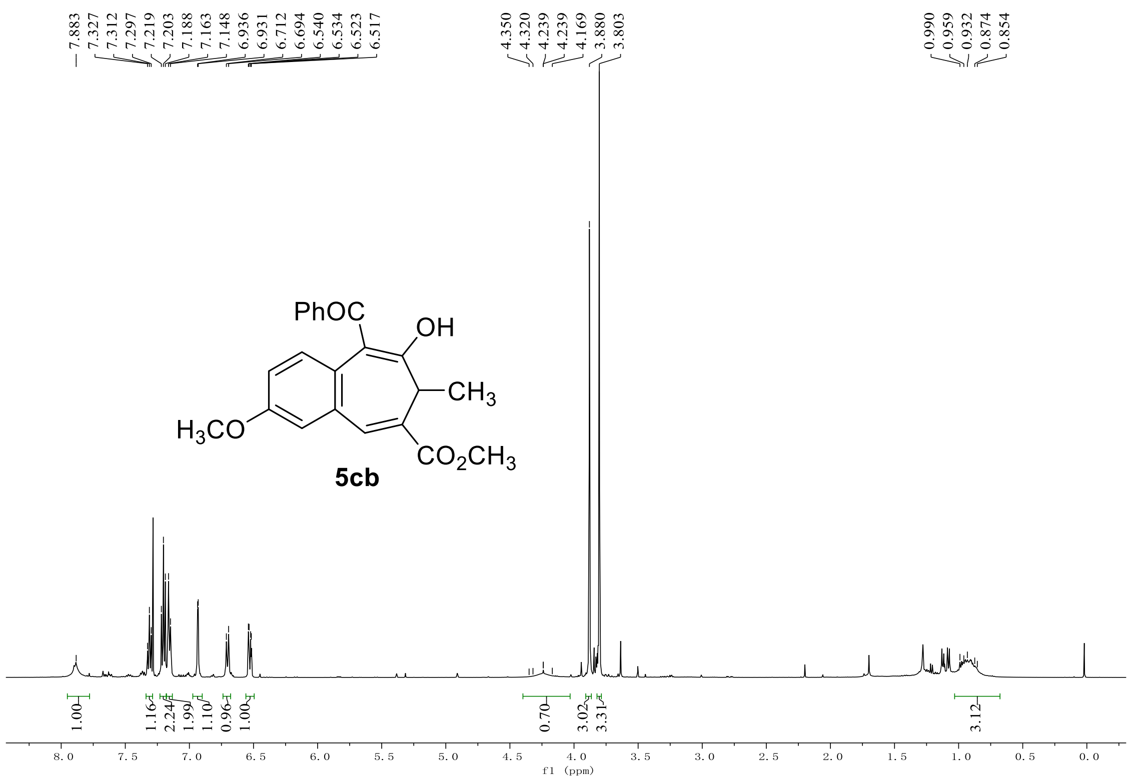
**5ia**


192.193
182.506
166.686
162.356
160.366
137.433
133.508
132.811
132.432
131.716
131.644
127.418
119.789
119.613
114.411
114.237
109.605
52.523
48.689
20.865
12.165
F
S
O
OH
Et
$CO_2CH_3$
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

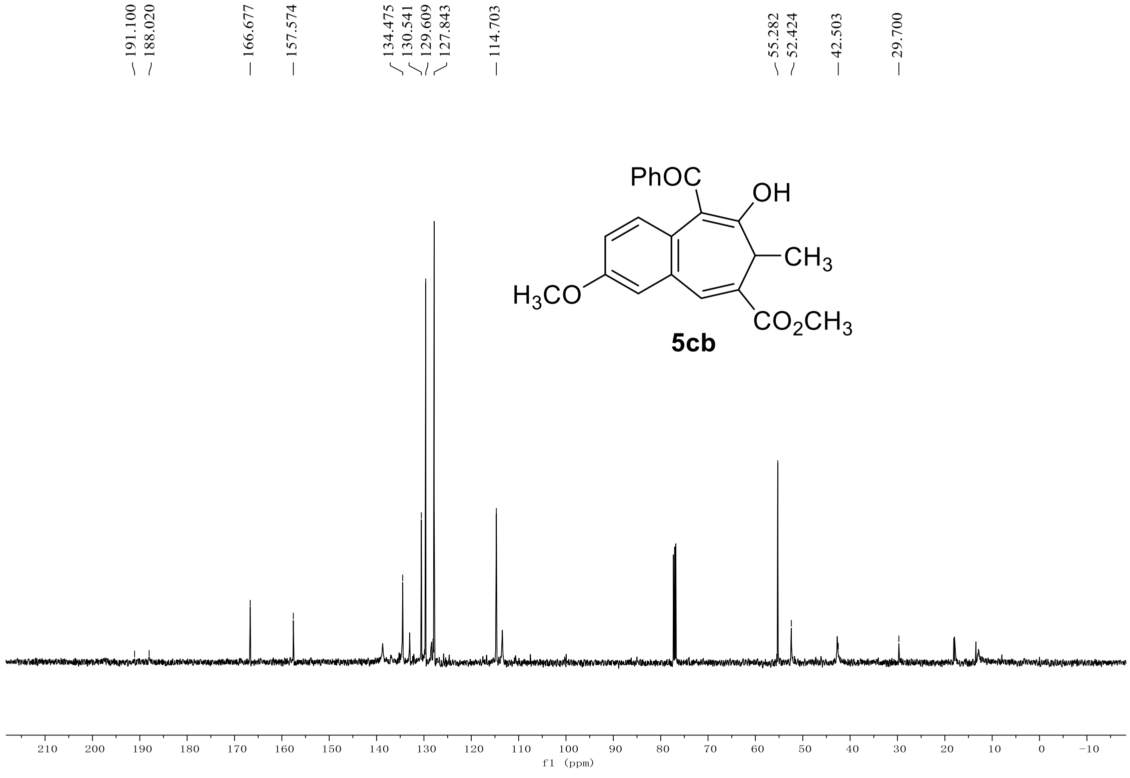
**5ia**

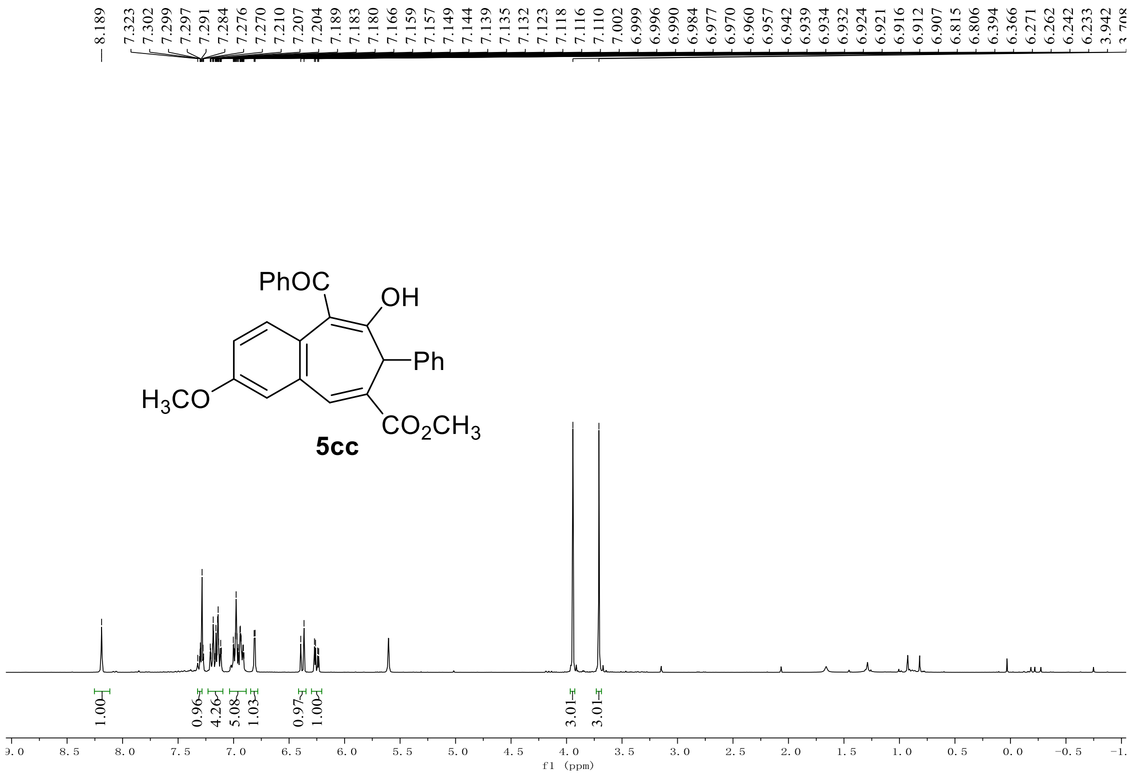

-111.502
O
S
OH
F
Et
CO2CH3
−70
−75
−80
−85
−90
−95
−100
−105
−110
−115
−120
−125
−130
−135
−140
−145
f1 (ppm)

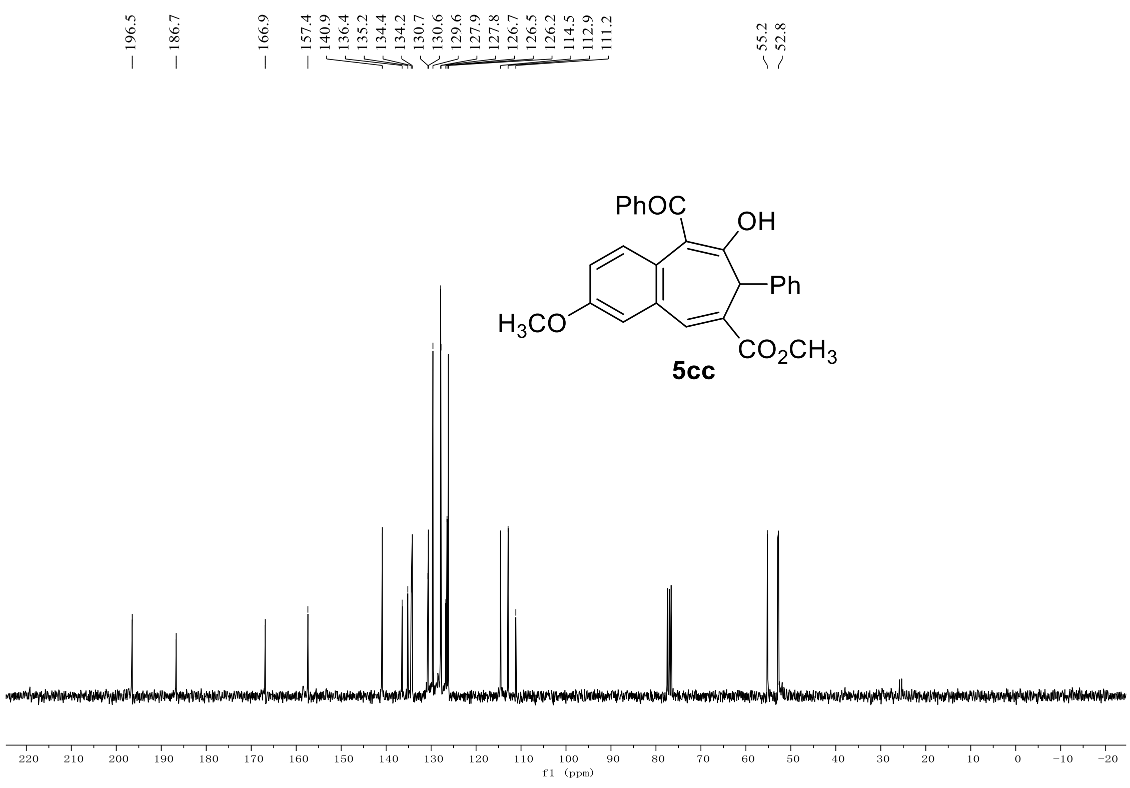
**5ia**


7.883
7.327
7.312
7.297
7.219
7.203
7.188
7.163
7.148
6.936
6.931
6.712
6.694
6.540
6.534
6.523
6.517
4.350
4.320
4.239
4.239
4.169
3.880
3.803
0.990
0.959
0.932
0.874
0.854
PhOC
OH
CH3
H3CO
CO2CH3
1.00
1.16
2.24
1.99
1.10
0.96
1.00
0.70
3.02
3.31
3.12
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)

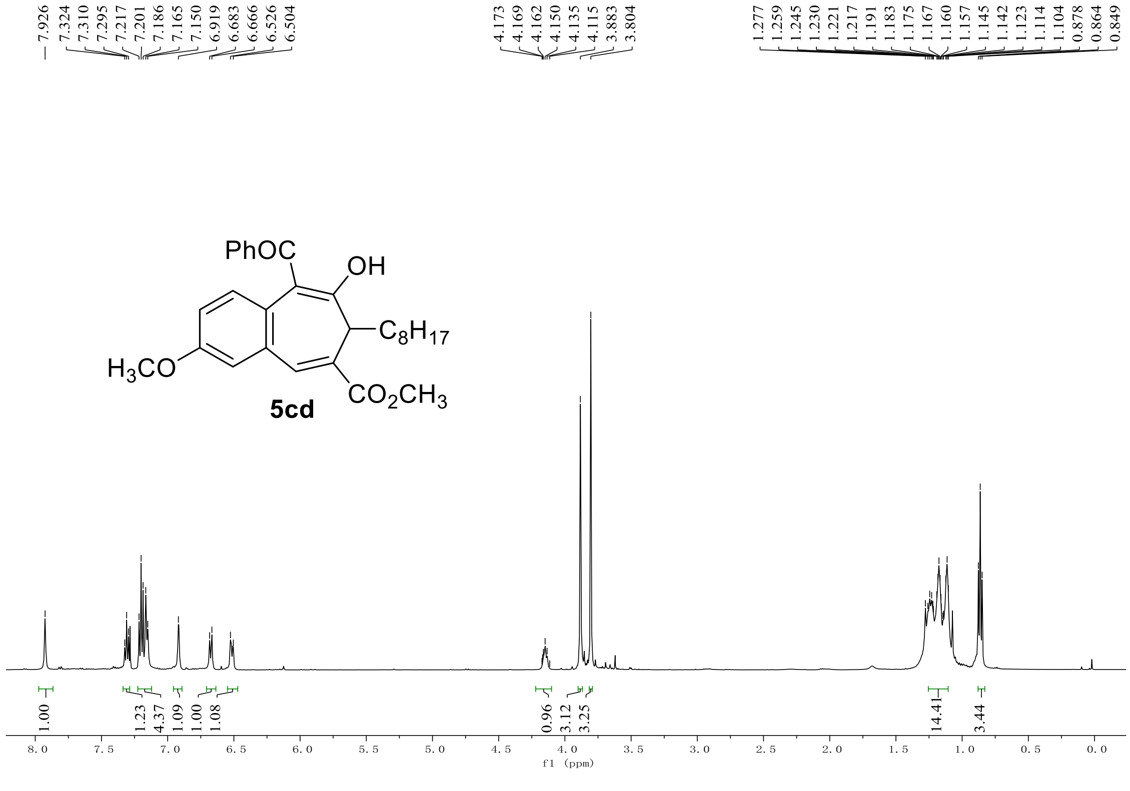
**5cb**


191.100
188.020
166.677
157.574
134.475
130.541
129.609
127.843
114.703
55.282
52.424
42.503
29.700
PhOC
OH
CH3
H3CO
CO2CH3
5cb
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

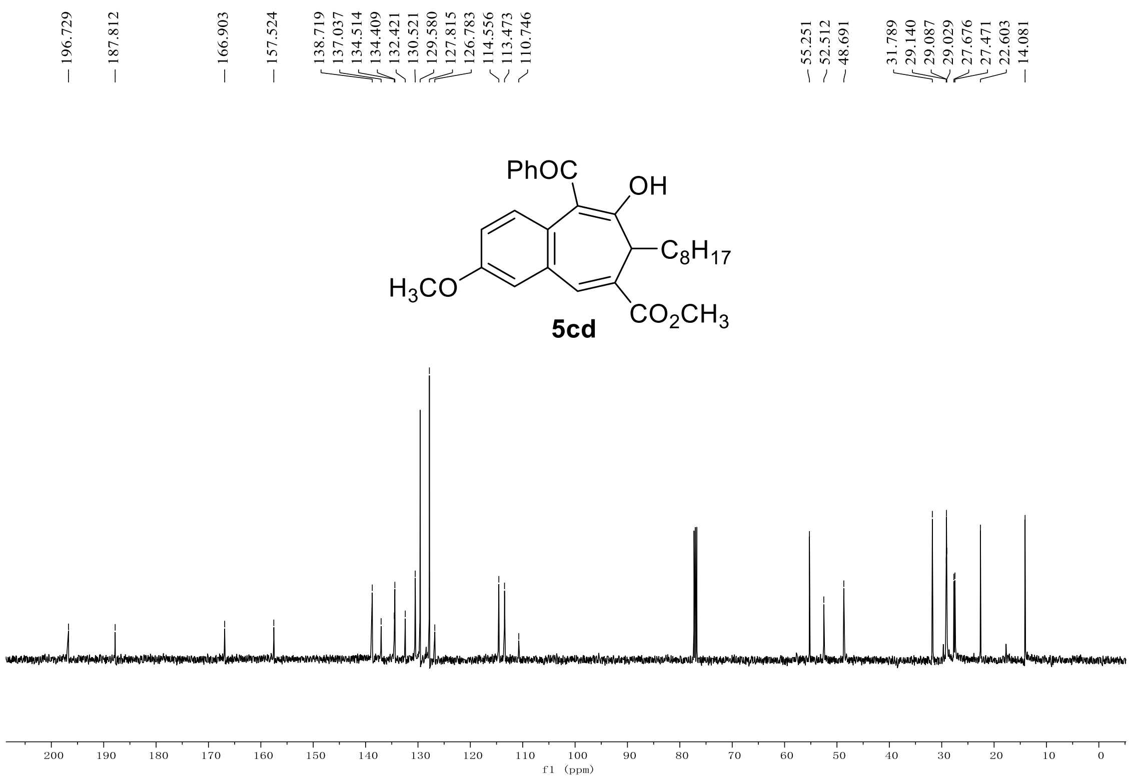

8.189
7.323
7.302
7.299
7.297
7.291
7.284
7.276
7.270
7.210
7.207
7.204
7.189
7.183
7.180
7.166
7.159
7.157
7.149
7.144
7.139
7.135
7.132
7.123
7.118
7.116
7.110
7.002
6.999
6.996
6.990
6.984
6.977
6.970
6.960
6.957
6.942
6.939
6.934
6.932
6.924
6.921
6.916
6.912
6.907
6.815
6.806
6.394
6.366
6.271
6.262
6.242
6.233
3.942
3.708
PhOC
OH
Ph
H3CO
CO2CH3
5cc
1.00
0.96
4.26
5.08
1.03
0.97
1.00
3.01
3.01
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0.5
f1 (ppm)


196.5
186.7
166.9
157.4
140.9
136.4
135.2
134.4
134.2
130.7
130.6
129.6
127.9
127.8
126.7
126.5
126.2
114.5
112.9
111.2
55.2
52.8
PhOC
OH
Ph
H3CO
CO2CH3
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)

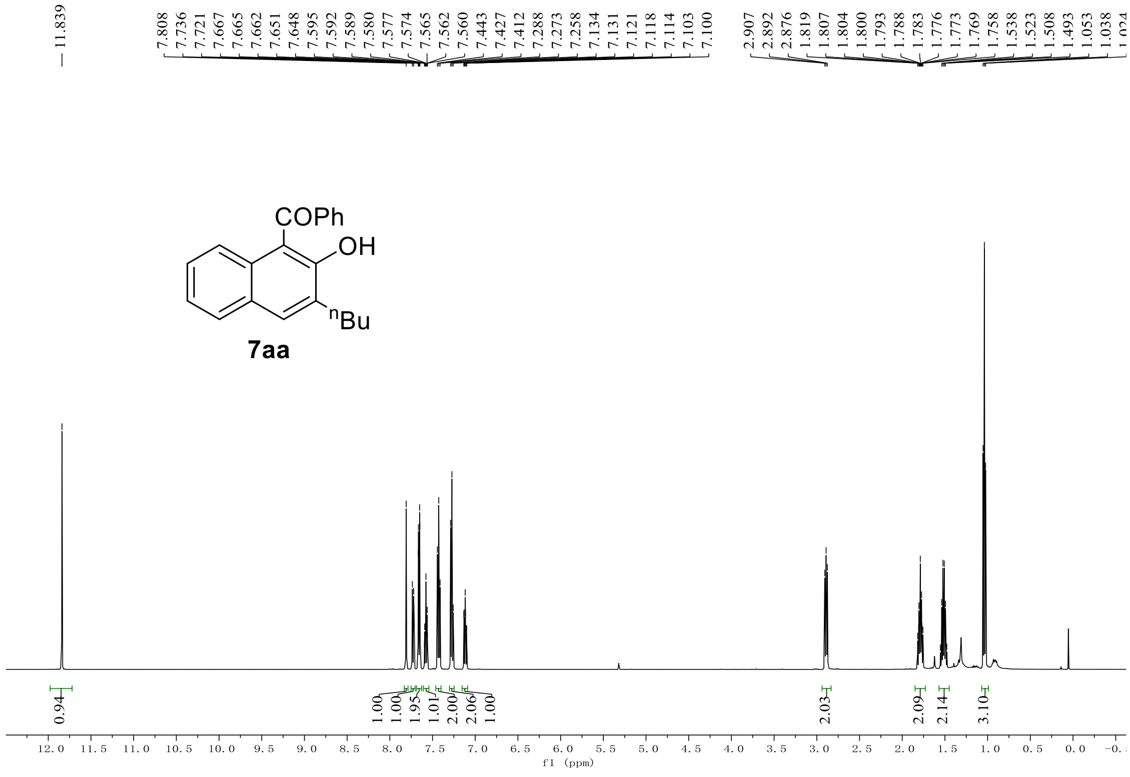
**5cc**


7.926
7.324
7.310
7.295
7.217
7.201
7.186
7.165
7.150
6.919
6.683
6.666
6.526
6.504
4.173
4.169
4.162
4.150
4.135
4.115
3.883
3.804
1.277
1.259
1.245
1.230
1.221
1.217
1.191
1.183
1.175
1.167
1.160
1.157
1.145
1.142
1.123
1.114
1.104
0.878
0.864
0.849
PhOC
OH
C8H17
H3CO
CO2CH3
1.00
1.23
4.37
1.09
1.00
1.08
0.96
3.12
3.25
14.41
3.44
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)

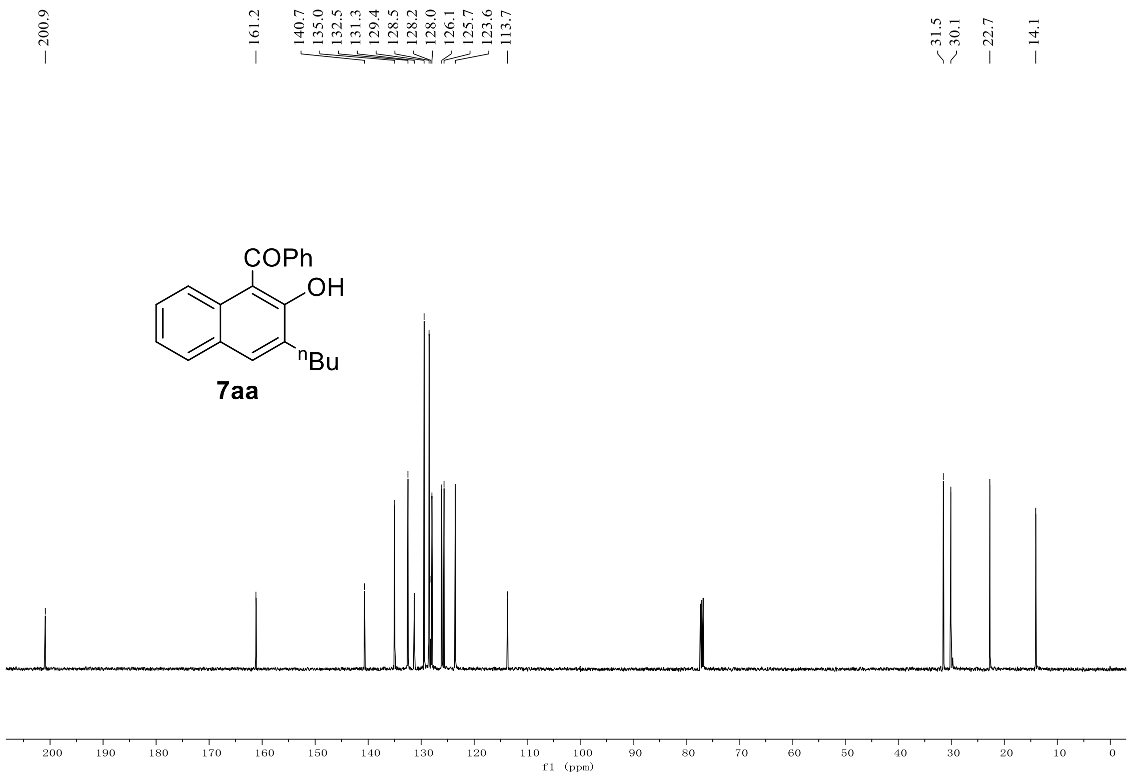
**5cd**


196.729
187.812
166.903
157.524
138.719
137.037
134.514
134.409
132.421
130.521
129.580
127.815
126.783
114.556
113.473
110.746
55.251
52.512
48.691
31.789
29.140
29.087
29.029
27.676
27.471
22.603
14.081
PhOC
OH
$C_8H_{17}$
$H_3CO$
$CO_2CH_3$
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

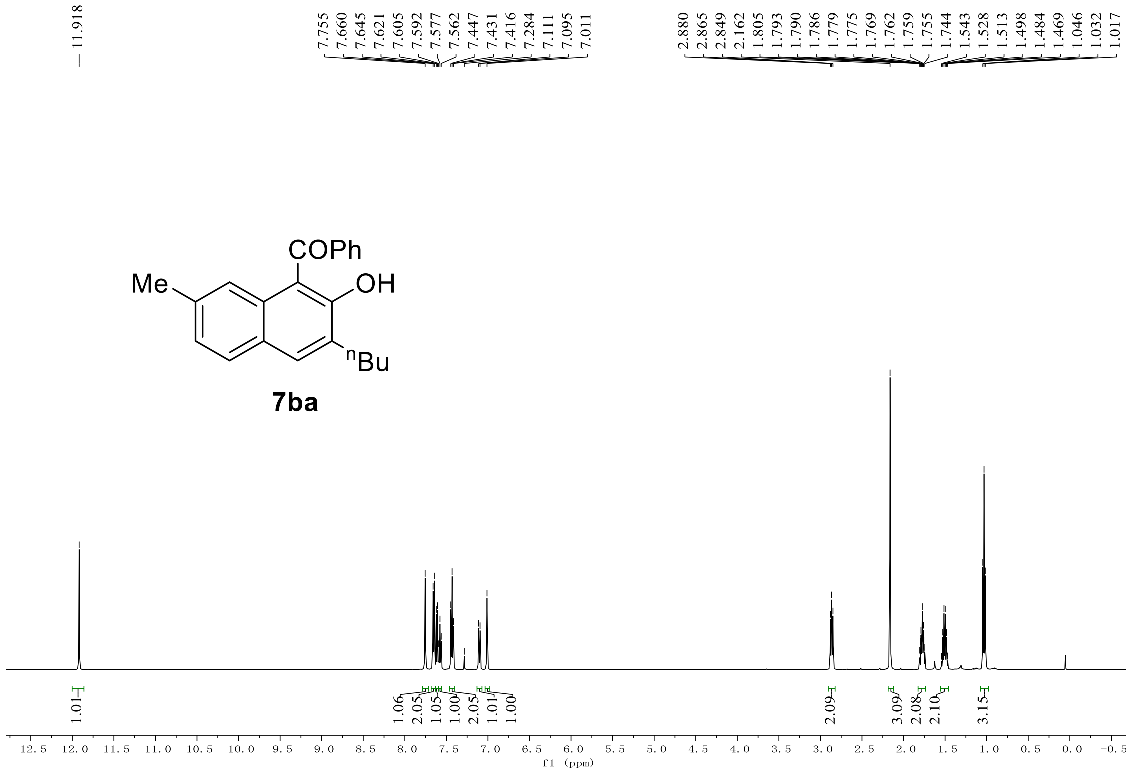
**5cd**


11.839
7.808
7.736
7.721
7.667
7.665
7.662
7.651
7.648
7.595
7.592
7.589
7.580
7.577
7.574
7.565
7.562
7.560
7.443
7.427
7.412
7.288
7.273
7.258
7.134
7.131
7.121
7.118
7.114
7.103
7.100
2.907
2.892
2.876
1.819
1.807
1.804
1.800
1.793
1.788
1.783
1.776
1.773
1.769
1.758
1.538
1.523
1.508
1.493
1.053
1.038
COPh
OH
$^nBu$
0.94
1.00
1.00
1.95
1.01
2.00
2.06
1.00
2.03
2.09
2.14
3.10
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

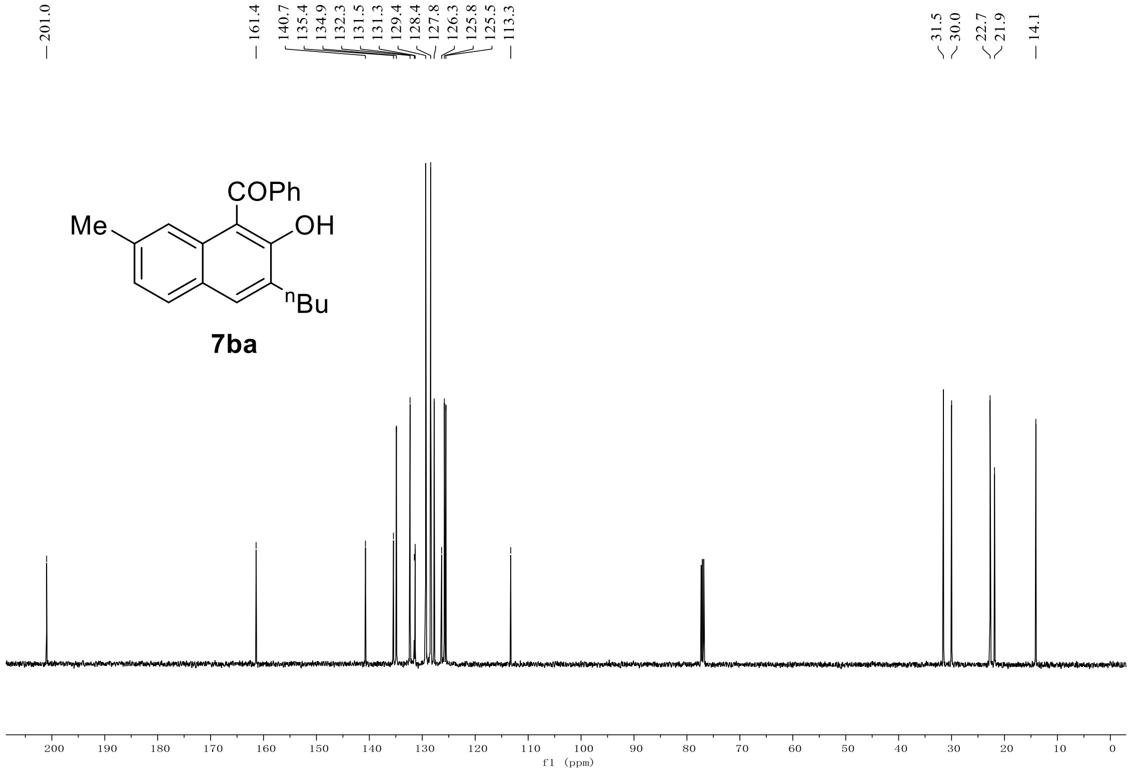
**7aa**


200.9
161.2
140.7
135.0
132.5
131.3
129.4
128.5
128.2
128.0
126.1
125.7
123.6
113.7
31.5
30.1
22.7
14.1
COPh
OH
$^n$Bu
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

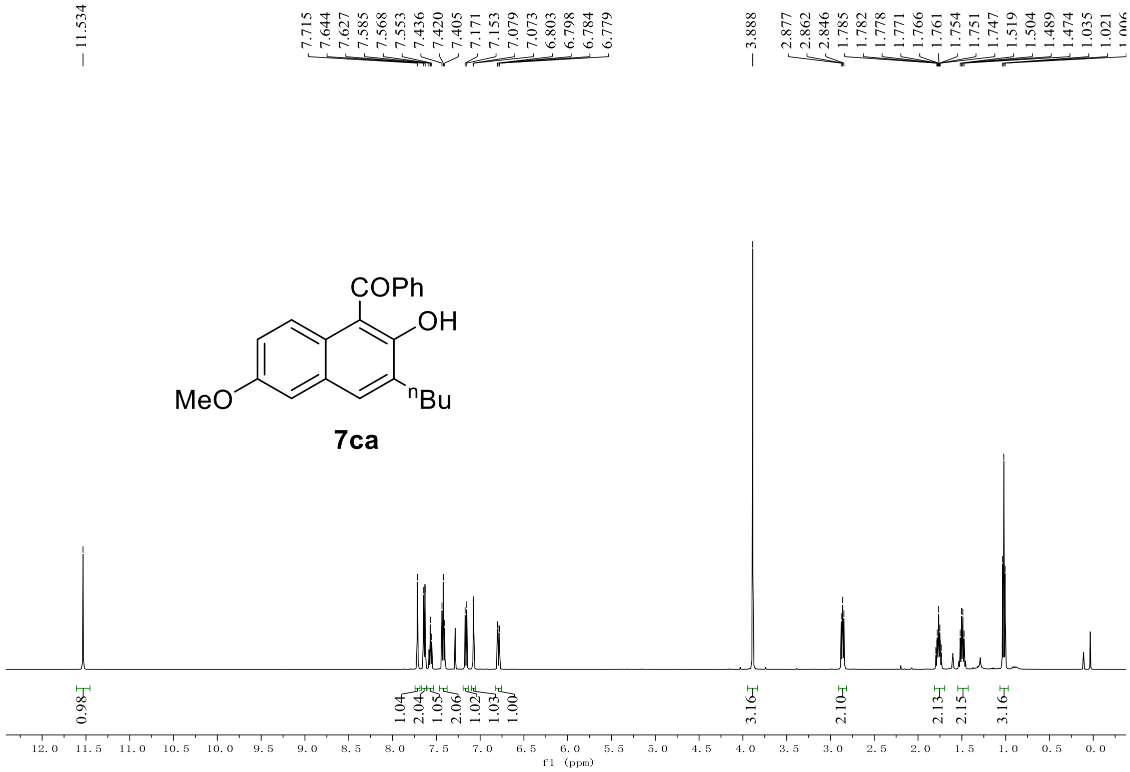
**7aa**


11.918
7.755
7.660
7.645
7.621
7.605
7.592
7.577
7.562
7.447
7.431
7.416
7.284
7.111
7.095
7.011
2.880
2.865
2.849
2.162
1.805
1.793
1.790
1.786
1.779
1.775
1.769
1.762
1.759
1.755
1.744
1.543
1.528
1.513
1.498
1.484
1.469
1.046
1.032
1.017
COPh
Me
OH
$^n$Bu
1.01
1.06
2.05
1.05
1.00
2.05
1.01
1.00
2.09
3.09
2.08
2.10
3.15
12.5
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

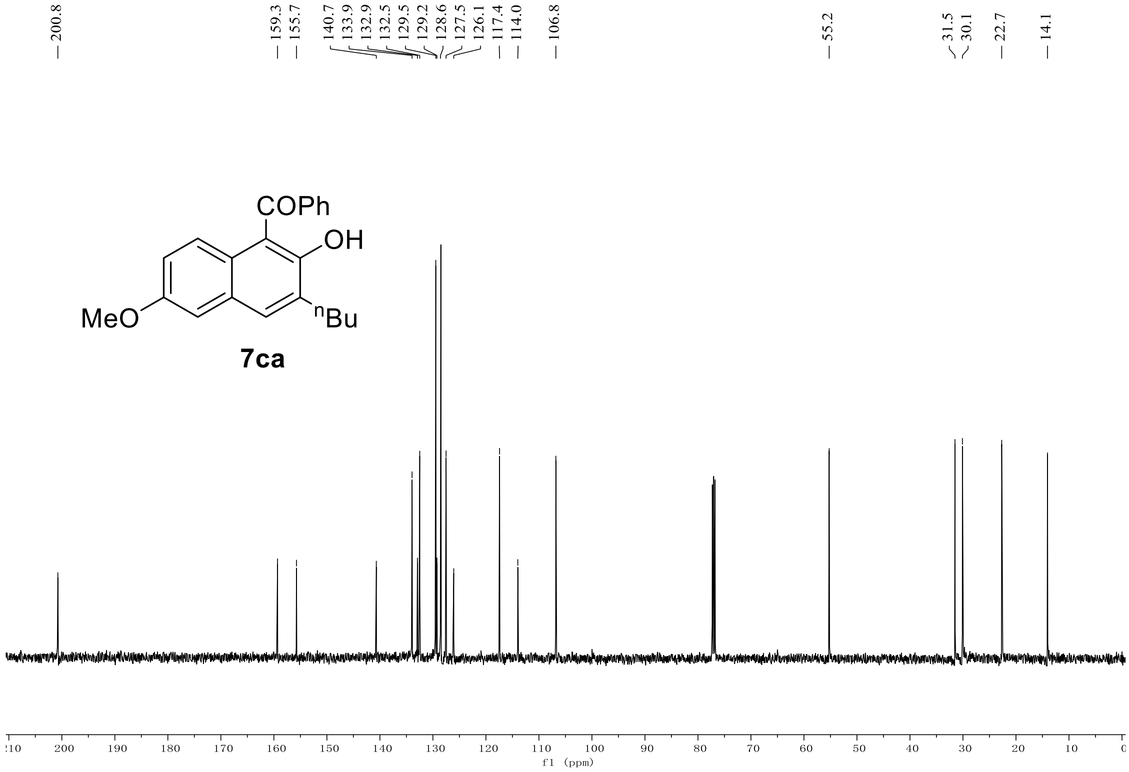
**7ba**


201.0
161.4
140.7
135.4
134.9
132.3
131.5
131.3
129.4
128.4
127.8
126.3
125.8
125.5
113.3
31.5
30.0
22.7
21.9
14.1
COPh
OH
Me
nBu
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

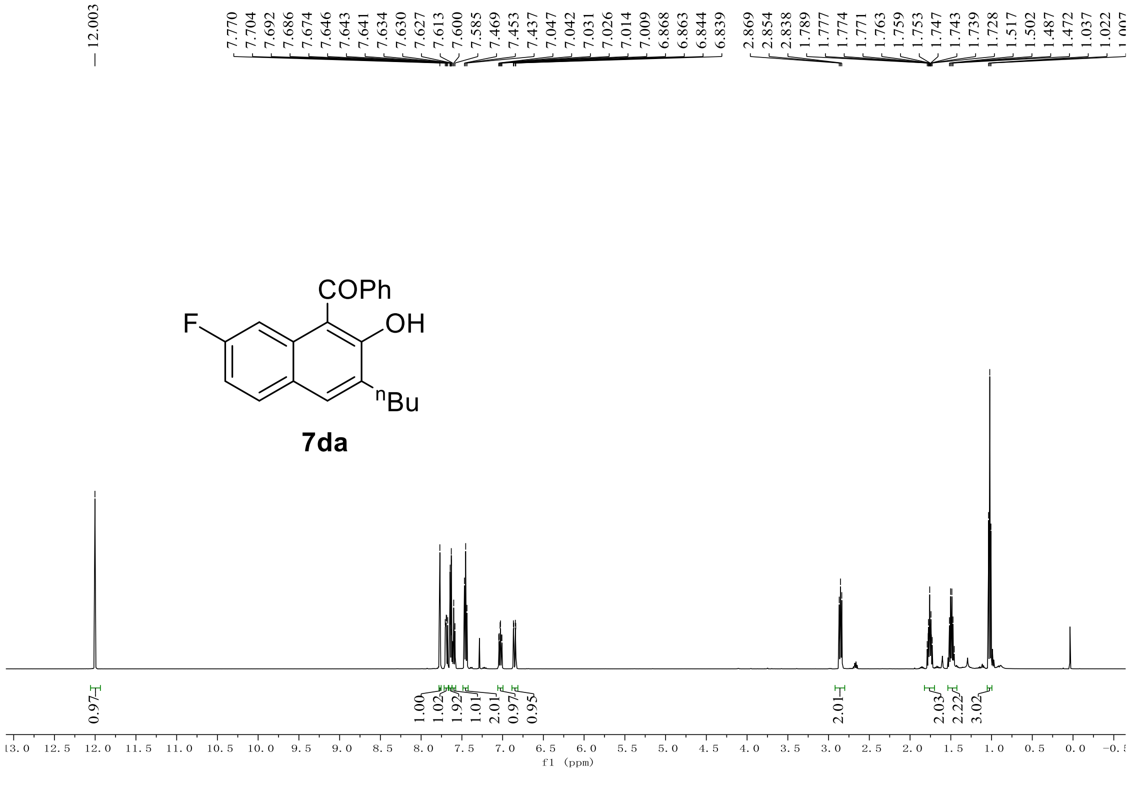
**7ba**


11.534
7.715
7.644
7.627
7.585
7.568
7.553
7.436
7.420
7.405
7.171
7.153
7.079
7.073
6.803
6.798
6.784
6.779
3.888
2.877
2.862
2.846
1.785
1.782
1.778
1.771
1.766
1.761
1.754
1.751
1.747
1.519
1.504
1.489
1.474
1.035
1.021
COPh
OH
MeO
nBu
0.98
1.04
2.04
1.05
2.06
1.02
1.03
1.00
3.16
2.10
2.13
2.15
3.16
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

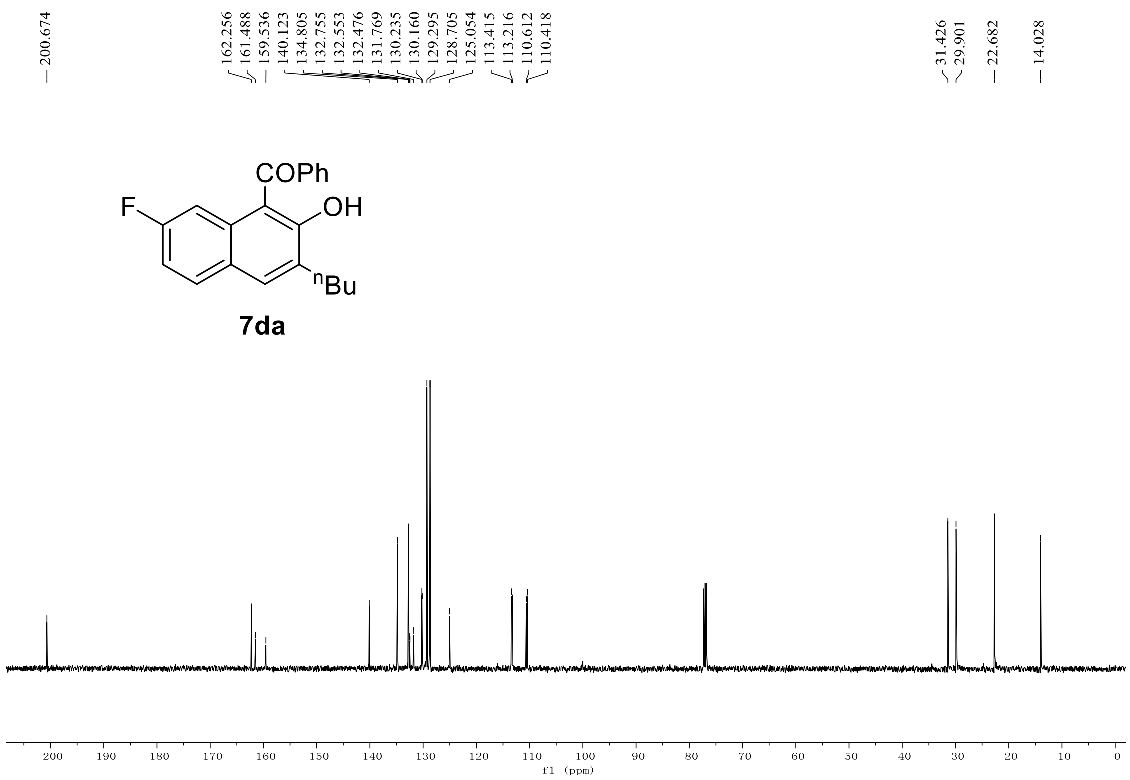
**7ca**

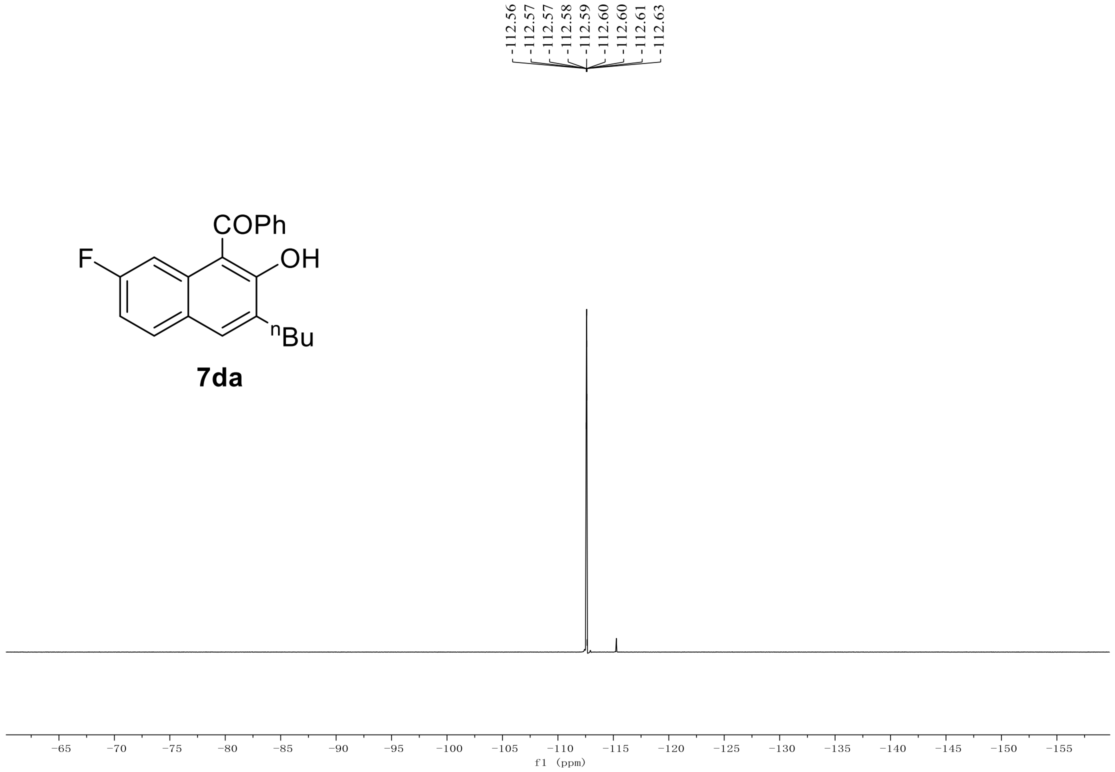

200.8
159.3
155.7
140.7
133.9
132.9
132.5
129.5
129.2
128.6
127.5
126.1
117.4
114.0
106.8
55.2
31.5
30.1
22.7
14.1
COPh
OH
MeO
nBu
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

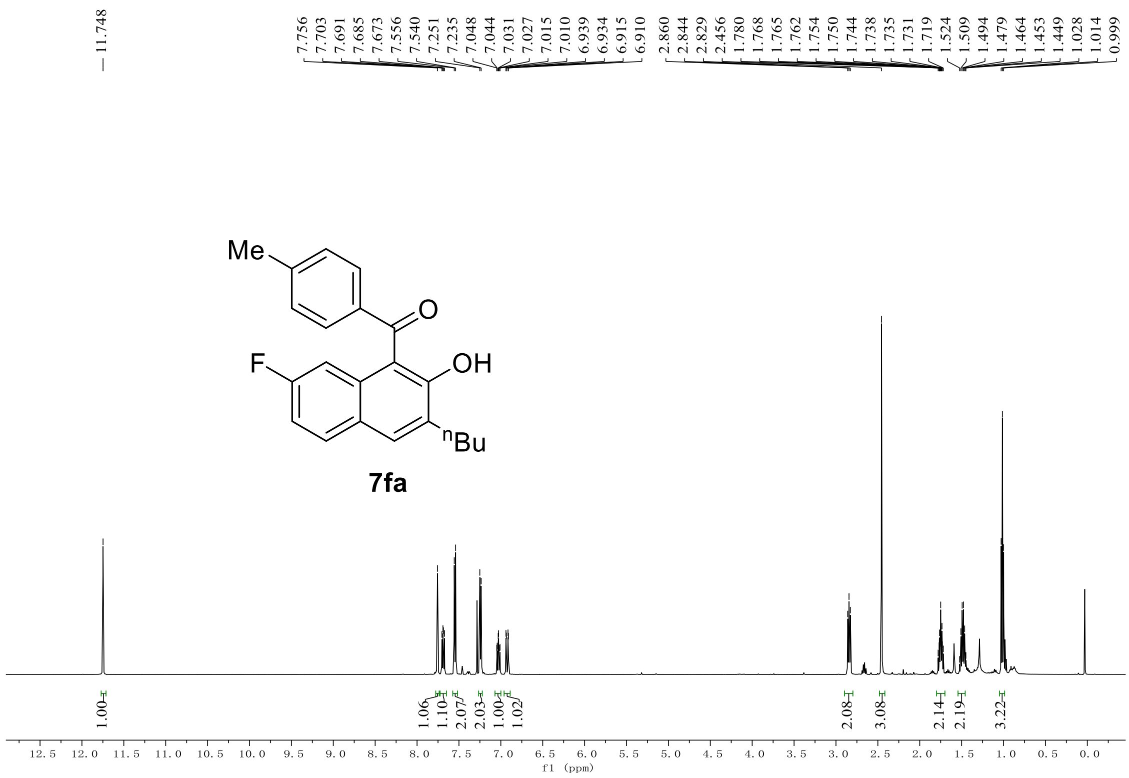
**7ca**


12.003
7.770
7.704
7.692
7.686
7.674
7.646
7.643
7.641
7.634
7.630
7.627
7.613
7.600
7.585
7.469
7.453
7.437
7.047
7.042
7.031
7.026
7.014
7.009
6.868
6.863
6.844
6.839
2.869
2.854
2.838
1.789
1.777
1.774
1.771
1.763
1.759
1.753
1.747
1.743
1.739
1.728
1.517
1.502
1.487
1.472
1.037
1.022
COPh
F
OH
nBu
0.97
1.00
1.02
1.92
1.01
2.01
0.97
0.95
2.01
2.03
2.22
3.02
13.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

**7da**


200.674
162.256
161.488
159.536
140.123
134.805
132.755
132.553
132.476
131.769
130.235
130.160
129.295
128.705
125.054
113.415
113.216
110.612
110.418
31.426
29.901
22.682
14.028
COPh
F
OH
nBu
7da
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


-112.56
-112.57
-112.57
-112.58
-112.59
-112.60
-112.60
-112.61
-112.63
COPh
F
OH
nBu
7da
−65
−70
−75
−80
−85
−90
−95
−100
−105
−110
−115
−120
−125
−130
−135
−140
−145
−150
−155
f1 (ppm)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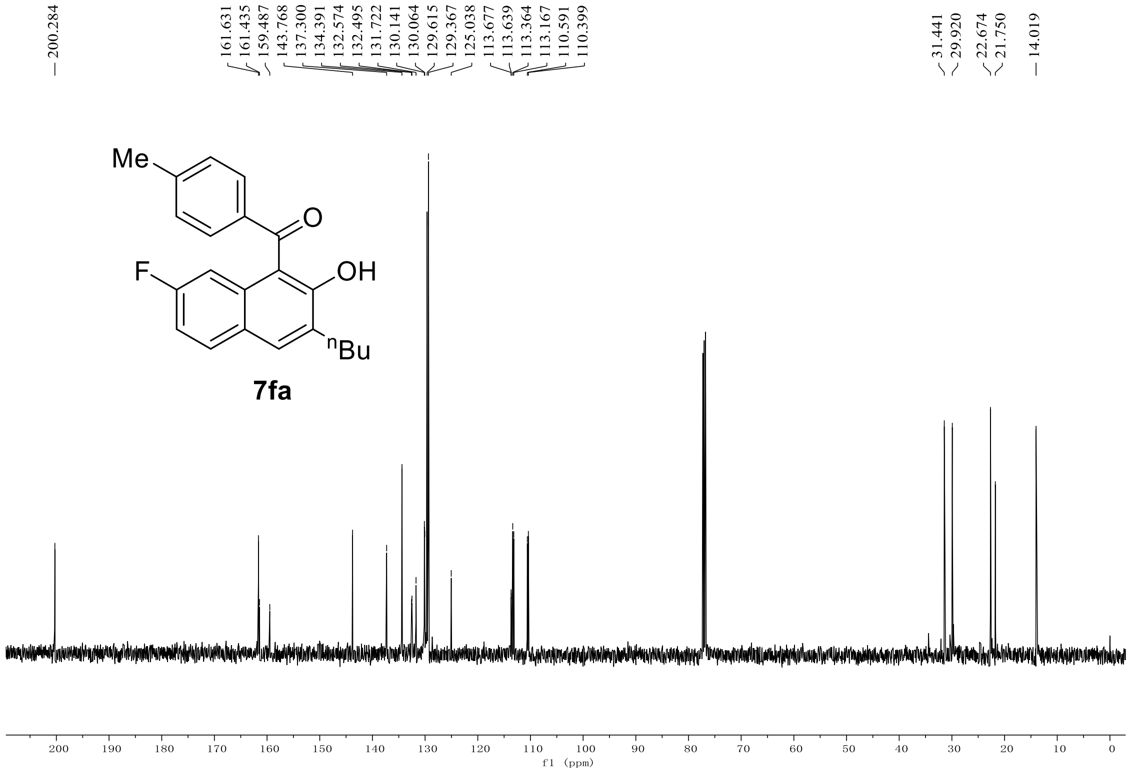
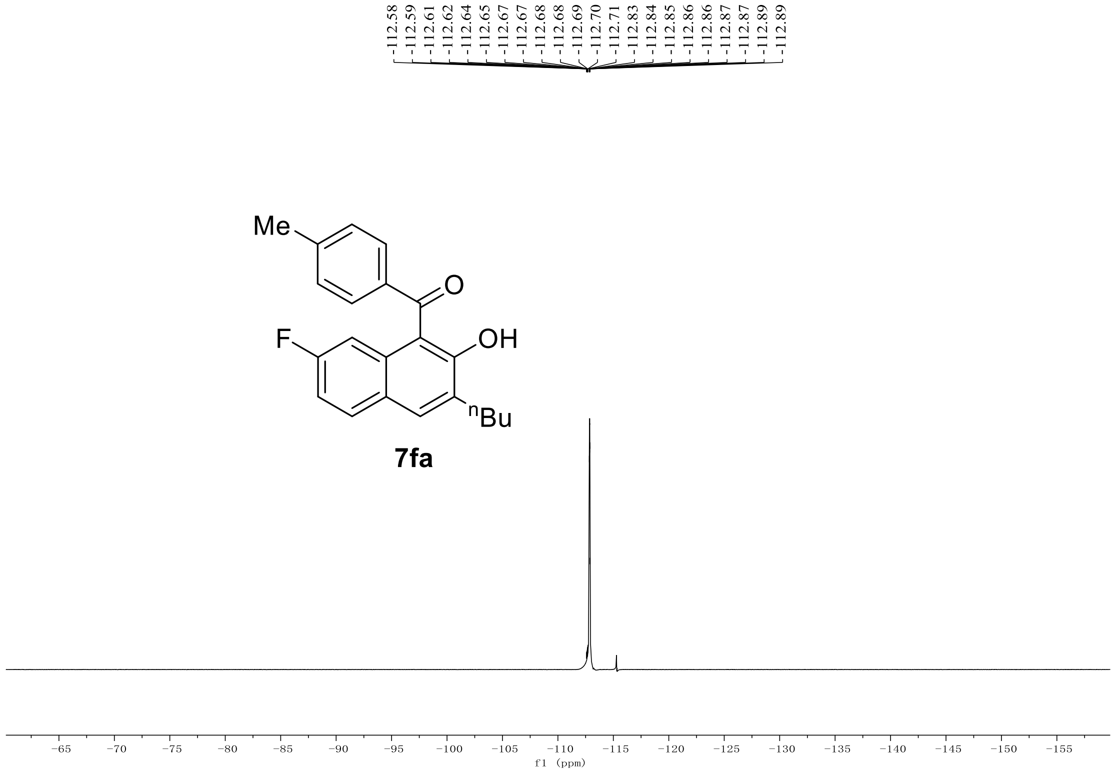
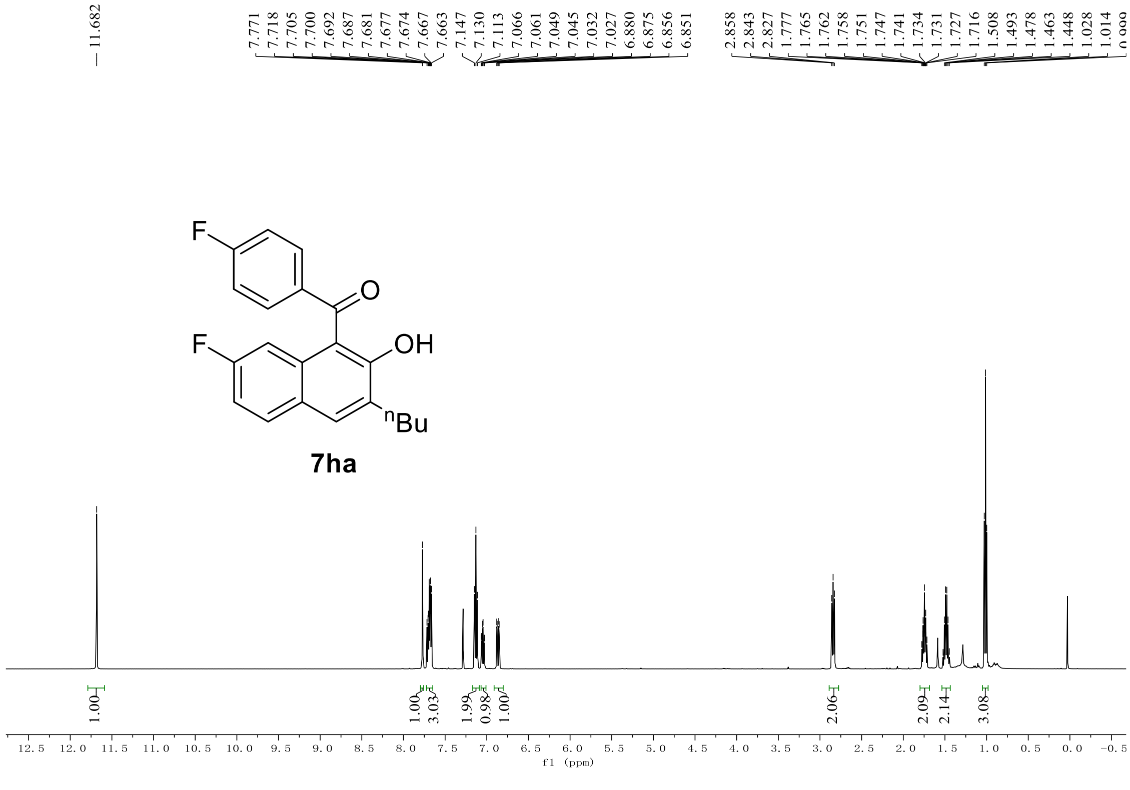
7.756
7.703
7.691
7.685
7.673
7.556
7.540
7.251
7.235
7.048
7.044
7.031
7.027
7.015
7.010
6.939
6.934
6.915
6.910
2.860
2.844
2.829
2.456
1.780
1.768
1.765
1.762
1.754
1.750
1.744
1.738
1.735
1.731
1.719
1.524
1.509
1.494
1.479
1.464
1.453
1.449
1.028
1.014
0.999
Me
O
F
OH
nBu
7fa
1.00
1.06
1.10
2.07
2.03
1.00
1.02
2.08
3.08
2.14
2.19
3.22
12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

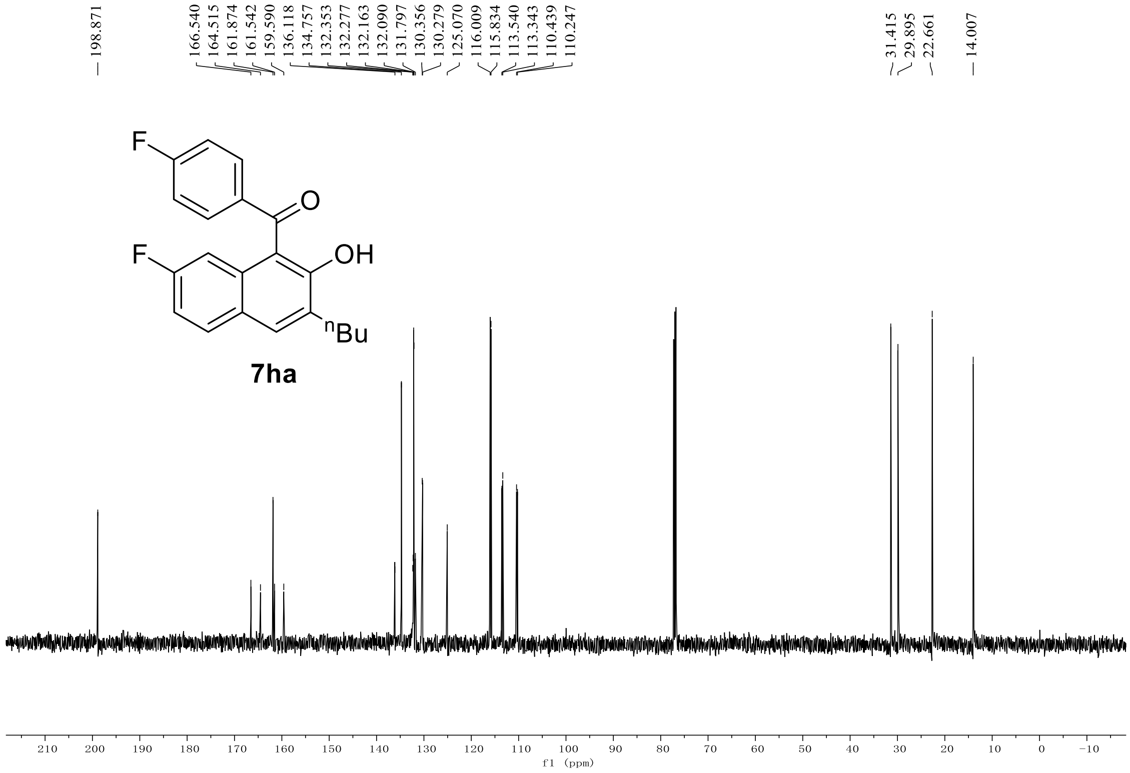

200.284
161.631
161.435
159.487
143.768
137.300
134.391
132.574
132.495
131.722
130.141
130.064
129.615
129.367
125.038
113.677
113.639
113.364
113.167
110.591
110.399
31.441
29.920
22.674
21.750
14.019
Me
O
F
OH
nBu
7fa
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


-112.58
-112.59
-112.61
-112.62
-112.64
-112.65
-112.67
-112.67
-112.68
-112.68
-112.69
-112.70
-112.71
-112.83
-112.84
-112.85
-112.86
-112.86
-112.87
-112.87
-112.89
-112.89
Me
O
F
OH
nBu
-65
-70
-75
-80
-85
-90
-95
-100
-105
-110
-115
-120
-125
-130
-135
-140
-145
-150
-155
f1 (ppm)

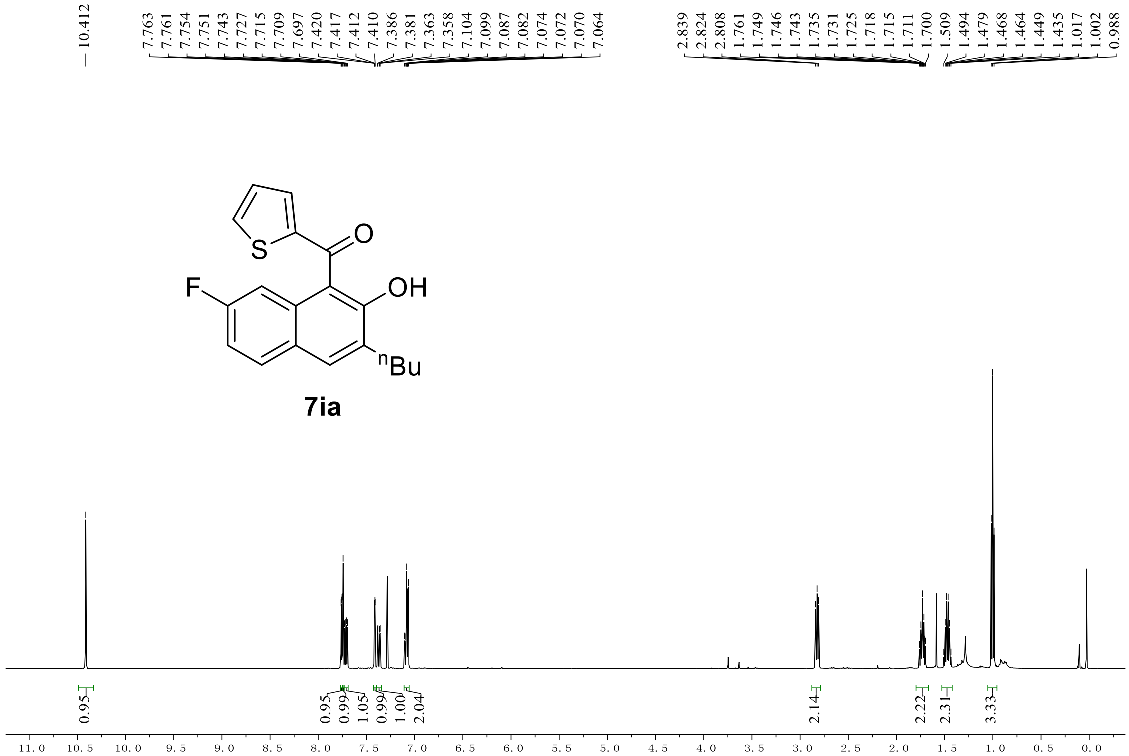
**7fa**

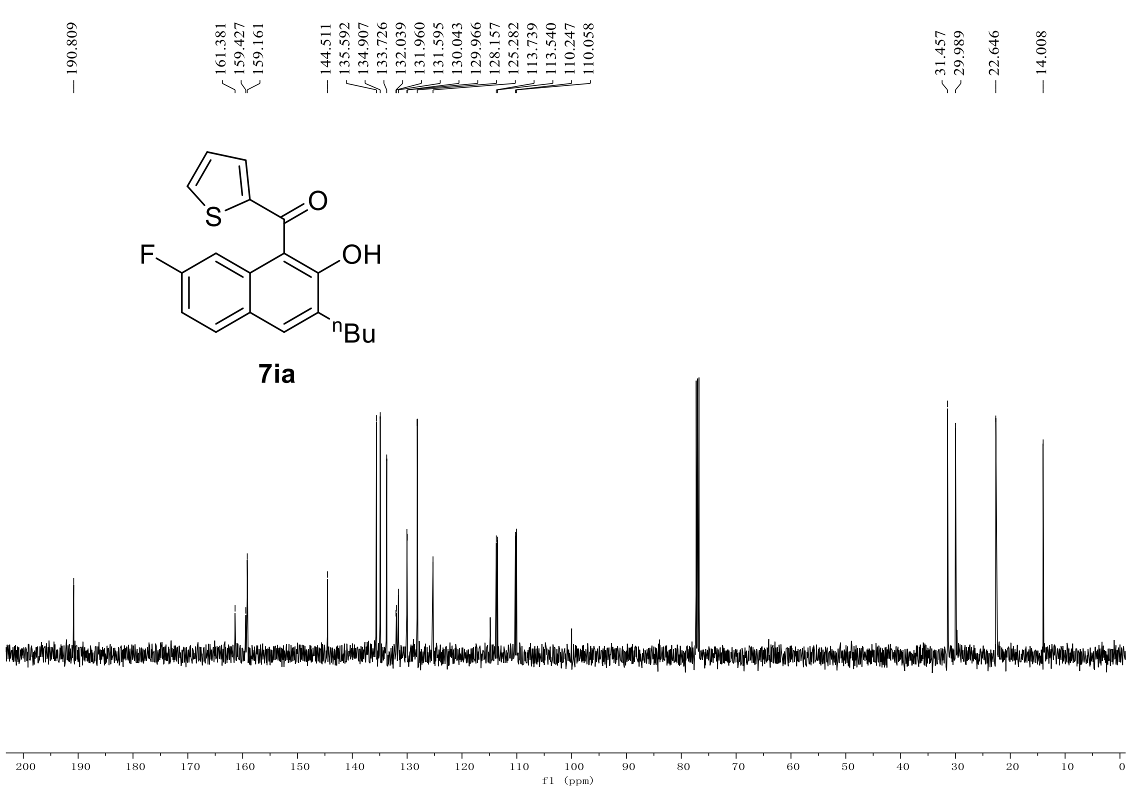

11.682
7.771
7.718
7.705
7.700
7.692
7.687
7.681
7.677
7.674
7.667
7.663
7.147
7.130
7.113
7.066
7.061
7.049
7.045
7.032
7.027
6.880
6.875
6.856
6.851
2.858
2.843
2.827
1.777
1.765
1.762
1.758
1.751
1.747
1.741
1.734
1.731
1.727
1.716
1.508
1.493
1.478
1.463
1.448
1.028
1.014
0.999
F
O
F
OH
nBu
1.00
1.00
3.03
1.99
0.98
1.00
2.06
2.09
2.14
3.08
12.5
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

**7ha**


198.871
166.540
164.515
161.874
161.542
159.590
136.118
134.757
132.353
132.277
132.163
132.090
131.797
130.356
130.279
125.070
116.009
115.834
113.540
113.343
110.439
110.247
31.415
29.895
22.661
14.007
F
O
F
OH
nBu
7ha
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)


-104.94
-104.95
-104.96
-104.96
-104.97
-104.97
-104.98
-104.98
-104.99
-105.00
-112.29
-112.31
-112.31
-112.32
-112.32
-112.33
-112.34
-112.35
F
O
F
OH
nBu
7ha
−65
−70
−75
−80
−85
−90
−95
−100
−105
−110
−115
−120
−125
−130
−135
−140
−145
−150
−155
f1 (ppm)


10.412
7.763
7.761
7.754
7.751
7.743
7.727
7.715
7.709
7.697
7.420
7.417
7.412
7.410
7.386
7.381
7.363
7.358
7.104
7.099
7.087
7.082
7.074
7.072
7.070
7.064
2.839
2.824
2.808
1.761
1.749
1.746
1.743
1.735
1.731
1.725
1.718
1.715
1.711
1.700
1.509
1.494
1.479
1.468
1.464
1.449
1.435
1.017
1.002
0.988
S
O
F
OH
nBu
7ia
0.95
0.95
0.99
1.05
0.99
1.00
2.04
2.14
2.22
2.31
3.33
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


190.809
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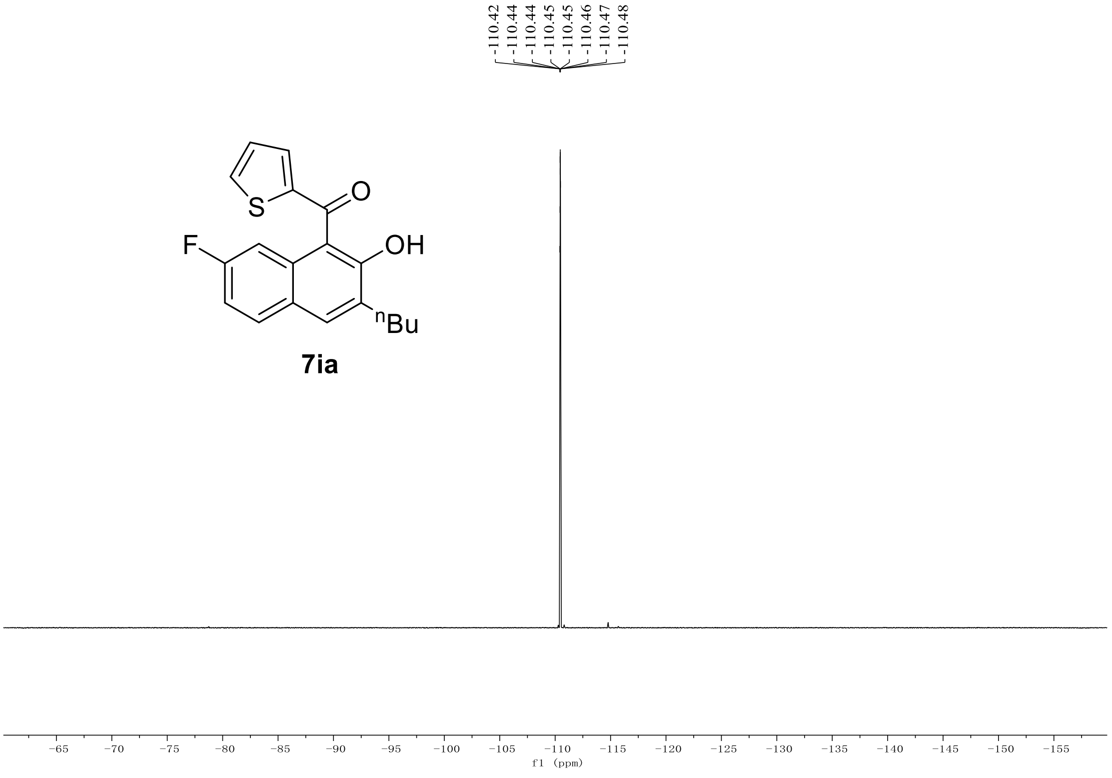
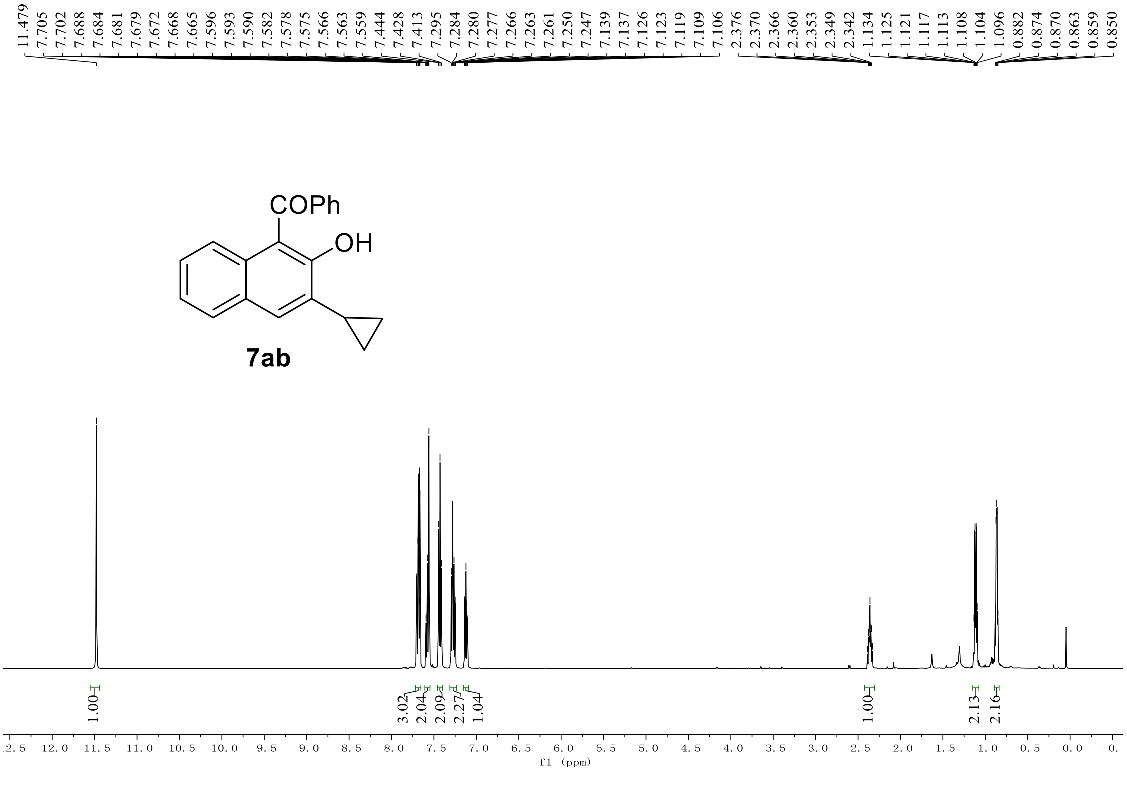
159.427
159.161
144.511
135.592
134.907
133.726
132.039
131.960
131.595
130.043
129.966
128.157
125.282
113.739
113.540
110.247
110.058
31.457
29.989
22.646
14.008
S
O
F
OH
nBu
7ia
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


-110.42
-110.44
-110.44
-110.45
-110.45
-110.46
-110.47
-110.48
S
O
F
OH
nBu
7ia
-65
-70
-75
-80
-85
-90
-95
-100
-105
-110
-115
-120
-125
-130
-135
-140
-145
-150
-155
f1 (ppm)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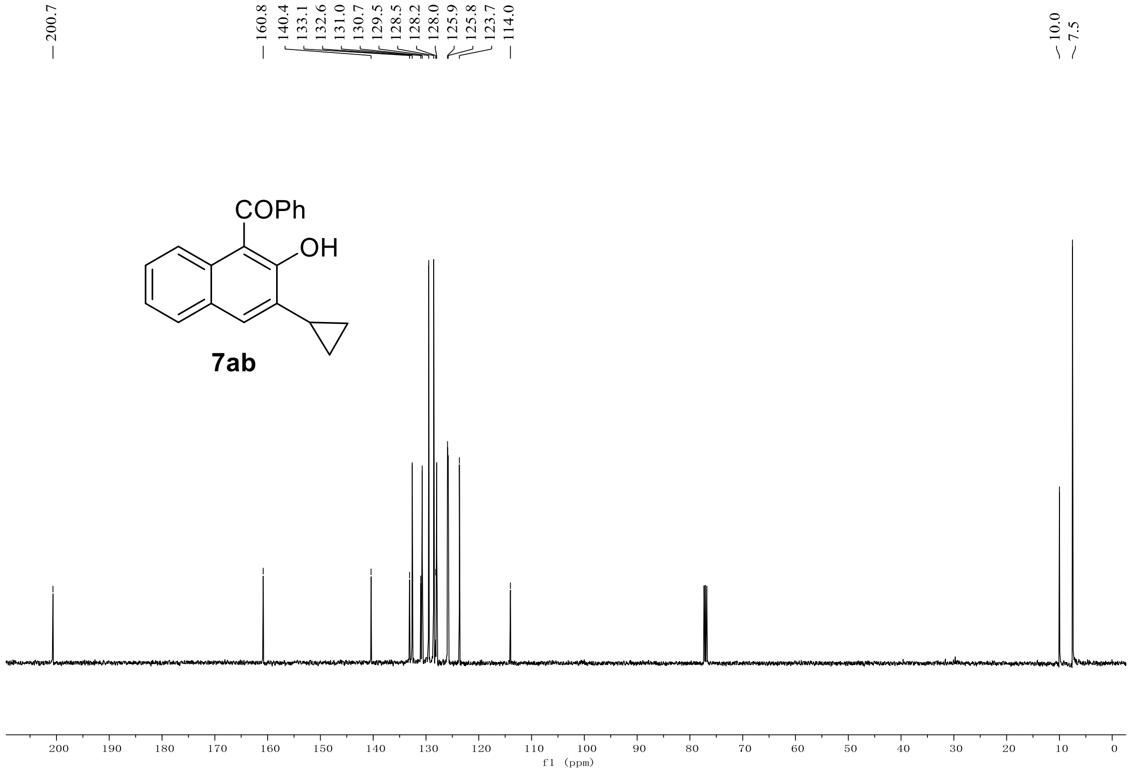
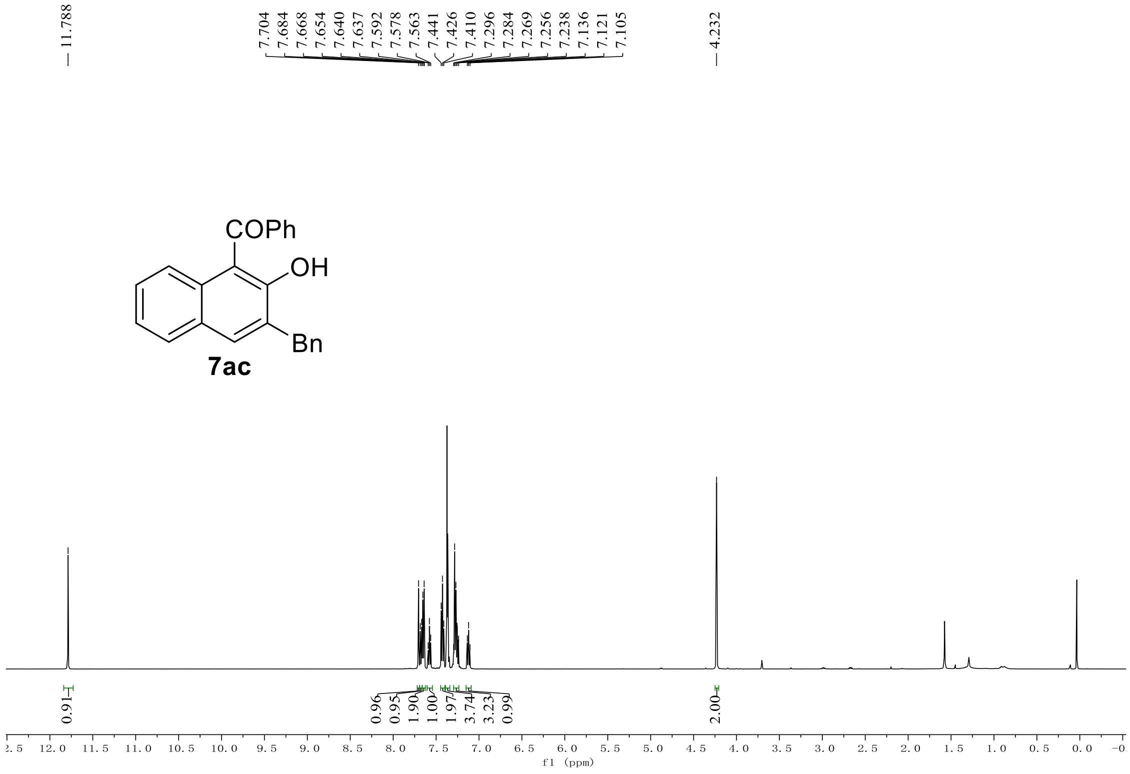
7.702
7.688
7.684
7.681
7.679
7.672
7.668
7.665
7.596
7.593
7.590
7.582
7.578
7.575
7.566
7.563
7.559
7.444
7.428
7.413
7.295
7.284
7.280
7.277
7.266
7.263
7.261
7.250
7.247
7.139
7.137
7.126
7.123
7.119
7.109
7.106
2.376
2.370
2.366
2.360
2.353
2.349
2.342
1.134
1.125
1.121
1.117
1.113
1.108
1.104
1.096
0.882
0.874
0.870
0.863
0.859
0.850
COPh
OH
7ab
1.00
3.02
2.04
2.09
2.27
1.04
1.00
2.13
2.16
2.5
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


200.7
160.8
140.4
133.1
132.6
131.0
130.7
129.5
128.5
128.2
128.0
125.9
125.8
123.7
114.0
10.0
7.5
COPh
OH
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

**7ab**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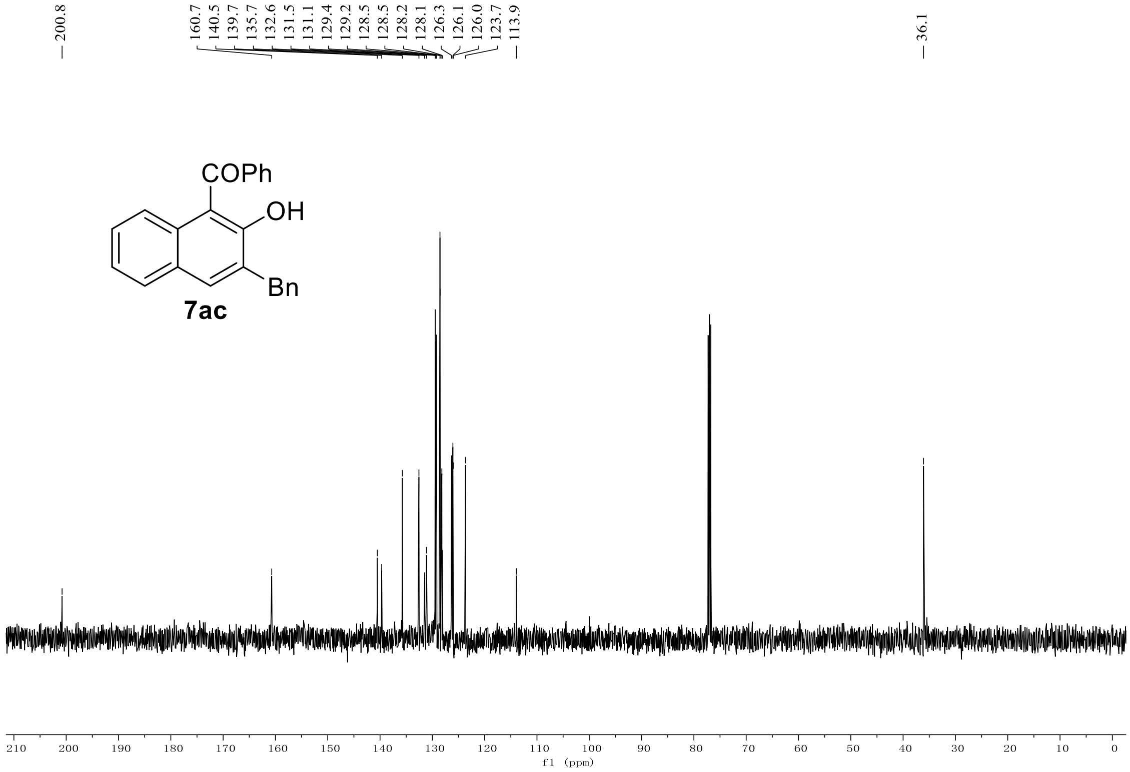
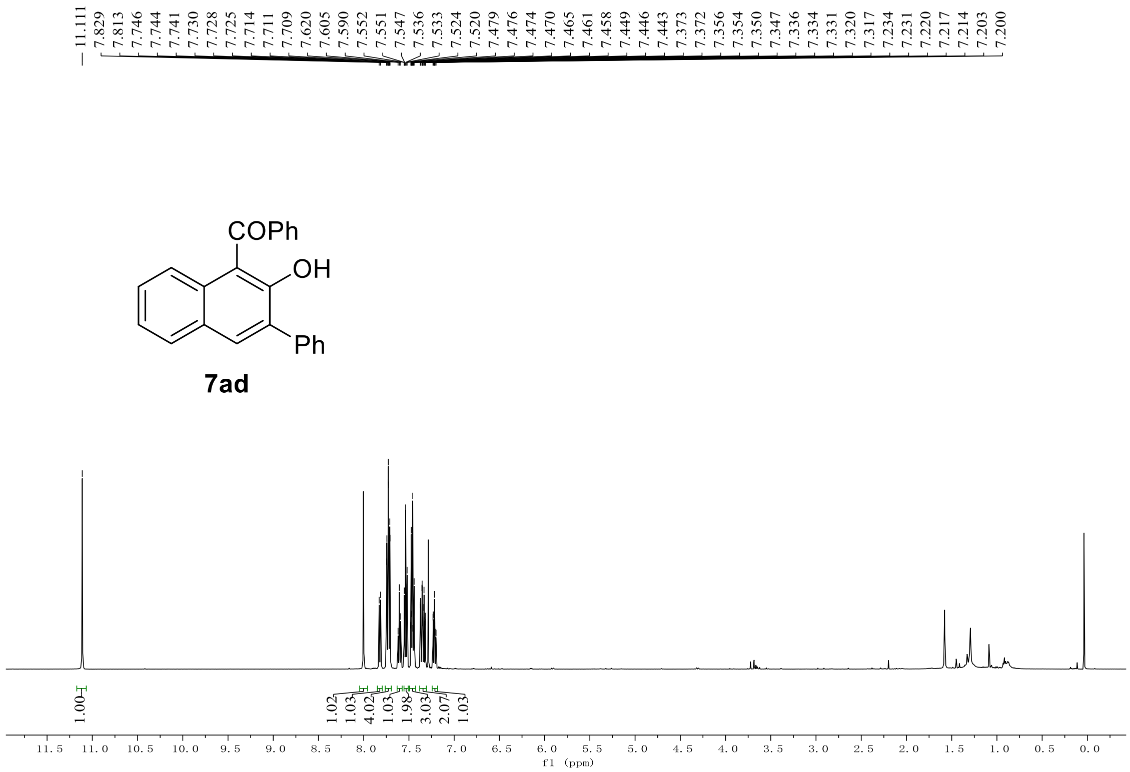
7.704
7.684
7.668
7.654
7.640
7.637
7.592
7.578
7.563
7.441
7.426
7.410
7.296
7.284
7.269
7.256
7.238
7.136
7.121
7.105
4.232
COPh
OH
Bn
0.91
0.96
0.95
1.90
1.00
1.97
3.74
3.23
0.99
2.00
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

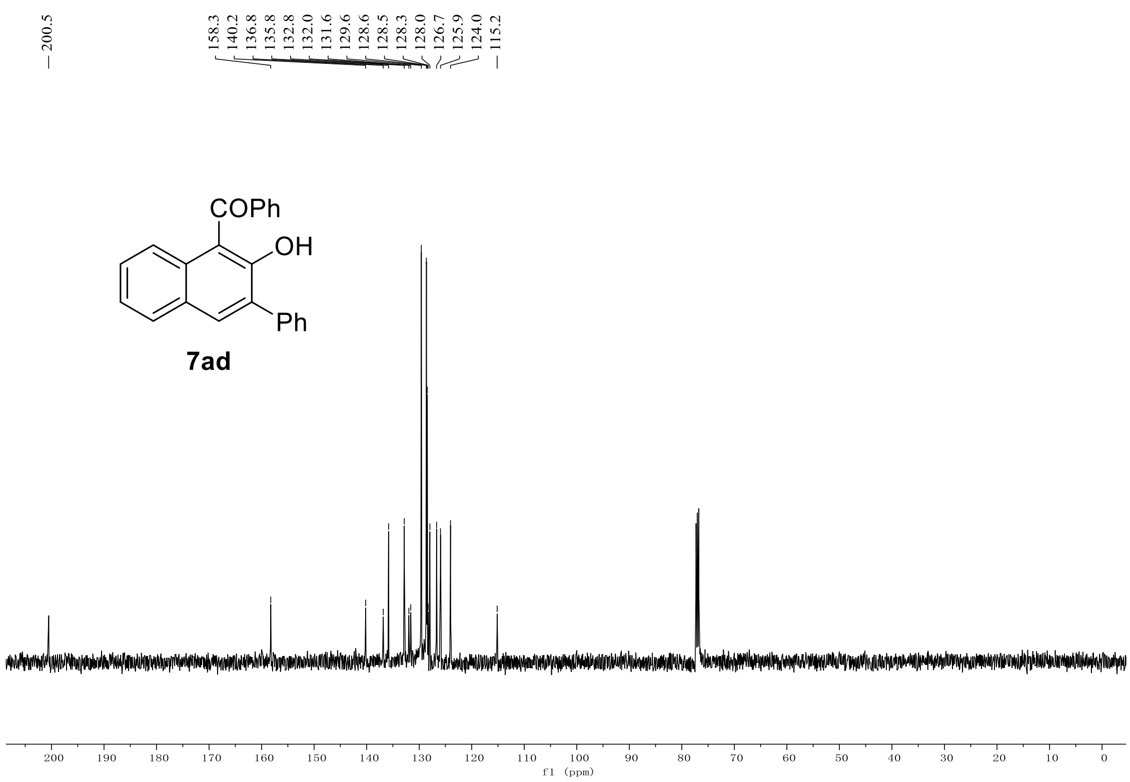
**7ac**

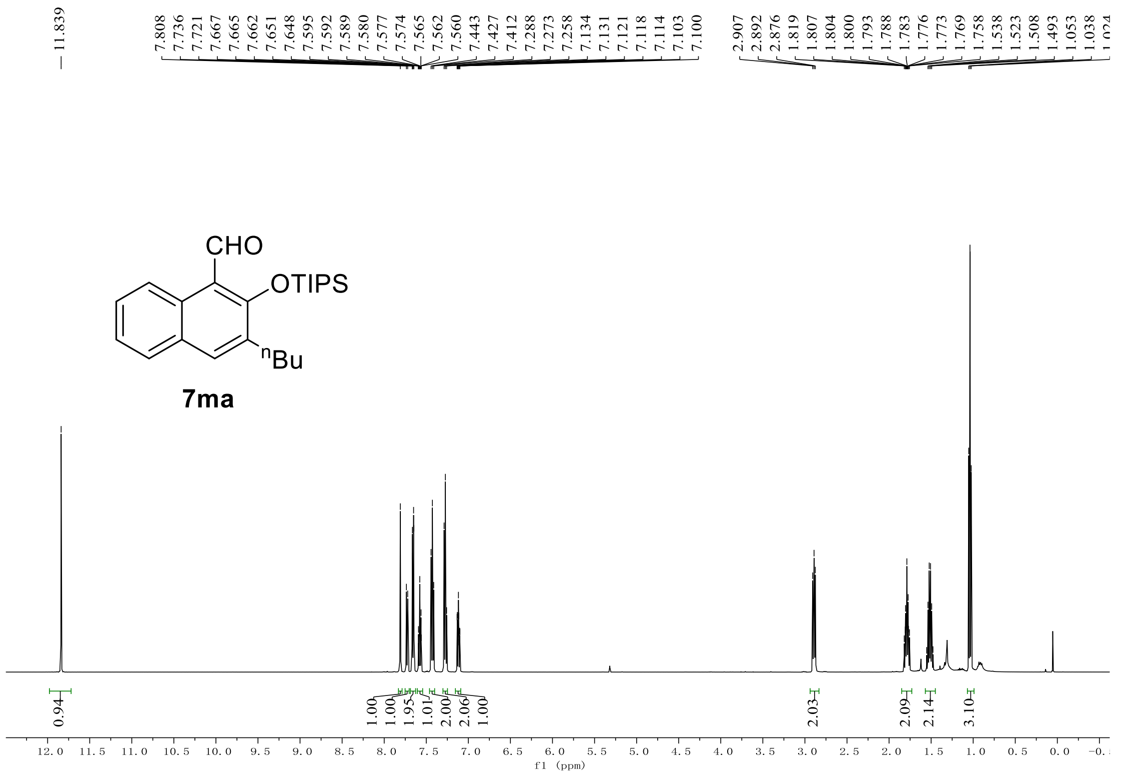

200.8
160.7
140.5
139.7
135.7
132.6
131.5
131.1
129.4
129.2
128.5
128.5
128.2
128.1
126.3
126.1
126.0
123.7
113.9
36.1
COPh
OH
Bn
f1 (ppm)

**7ac**


11.111
7.829
7.813
7.746
7.744
7.741
7.730
7.728
7.725
7.714
7.711
7.709
7.620
7.605
7.590
7.552
7.551
7.547
7.536
7.533
7.524
7.520
7.479
7.476
7.474
7.470
7.465
7.461
7.458
7.449
7.446
7.443
7.373
7.372
7.356
7.354
7.350
7.347
7.336
7.334
7.331
7.320
7.317
7.234
7.231
7.220
7.217
7.214
7.203
7.200
COPh
OH
Ph
1.00
1.02
1.03
4.02
1.03
1.98
3.03
2.07
1.03
f1 (ppm)

**7ad**


200.5
158.3
140.2
136.8
135.8
132.8
132.0
131.6
129.6
128.6
128.5
128.3
128.0
126.7
125.9
124.0
115.2
COPh
OH
Ph
7ad
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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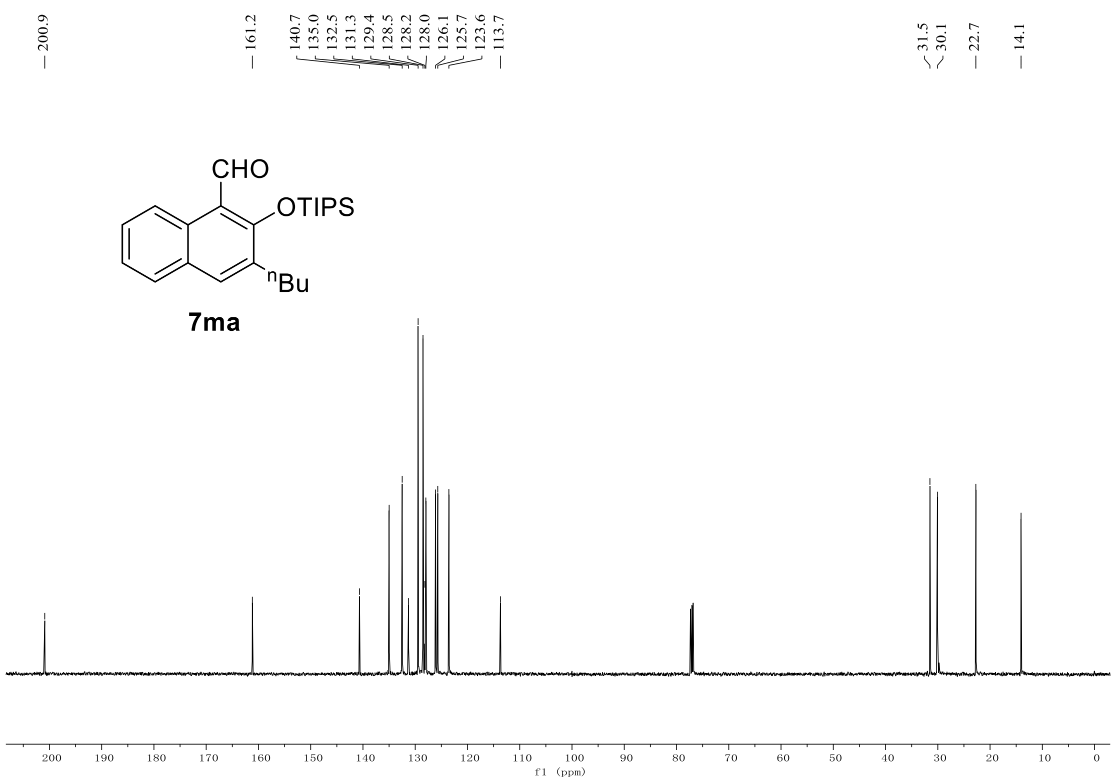
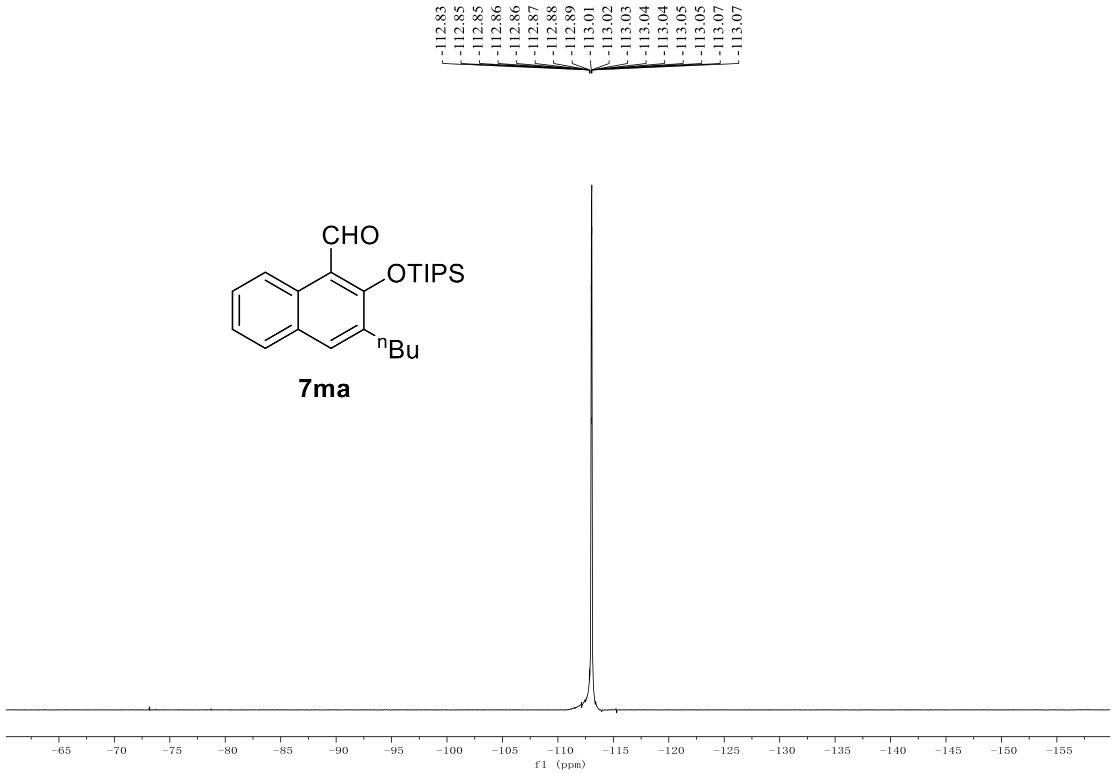
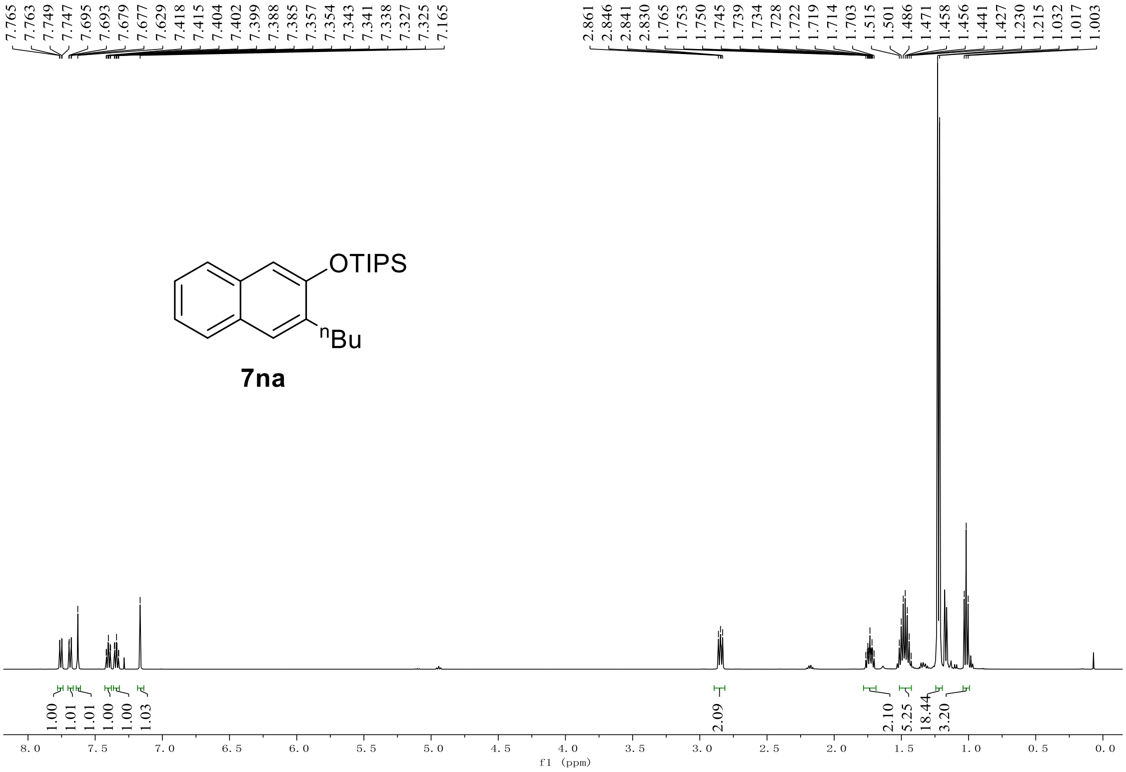
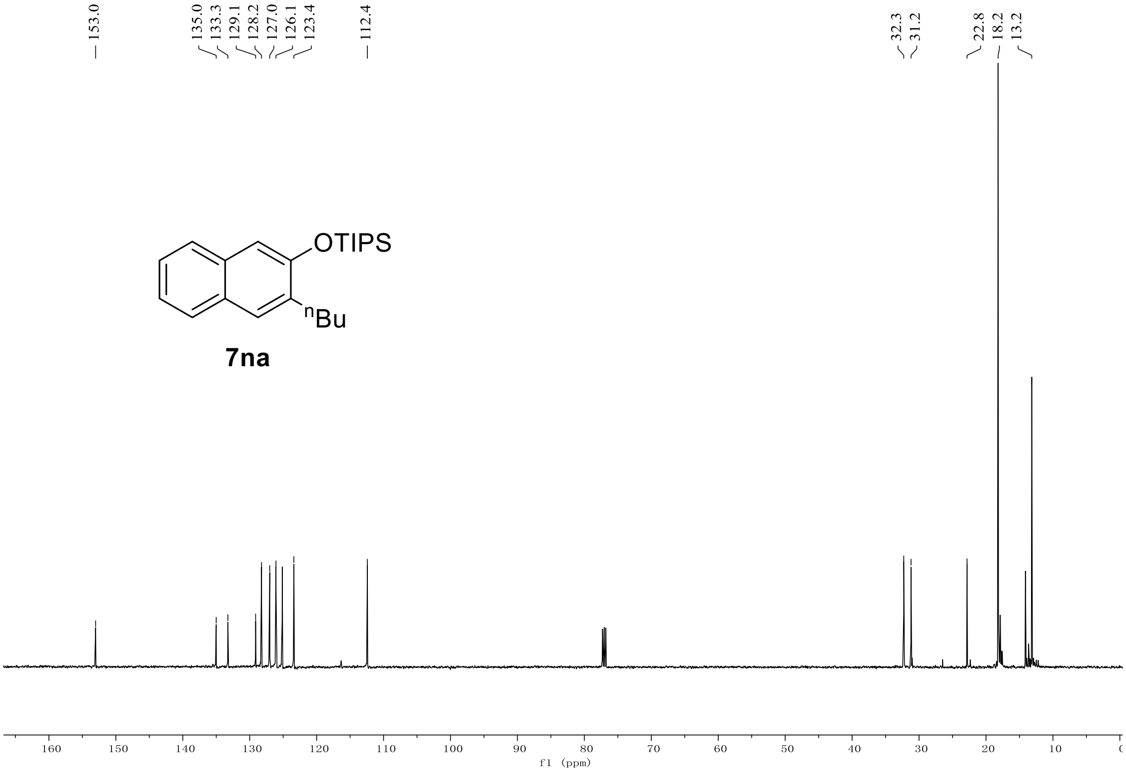
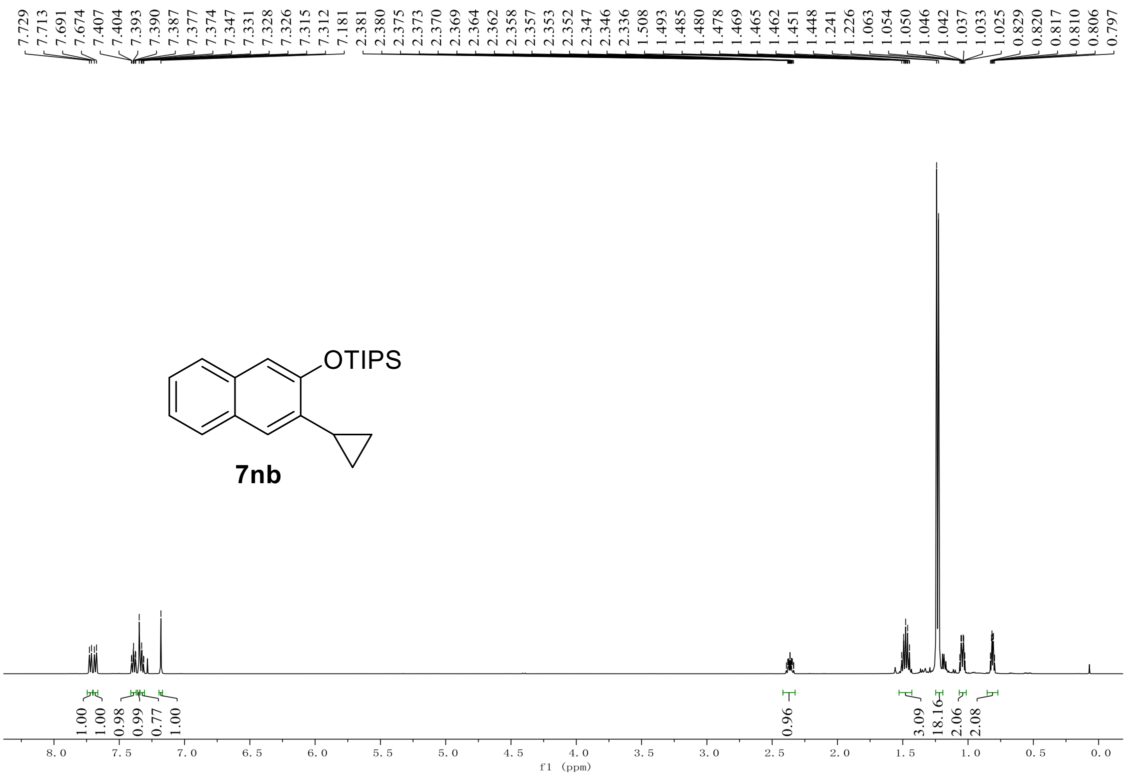
7.662
7.651
7.648
7.595
7.592
7.589
7.580
7.577
7.574
7.565
7.562
7.560
7.443
7.427
7.412
7.288
7.273
7.258
7.134
7.131
7.121
7.118
7.114
7.103
7.100
2.907
2.892
2.876
1.819
1.807
1.804
1.800
1.793
1.788
1.783
1.776
1.773
1.769
1.758
1.538
1.523
1.508
1.493
1.053
1.038
1.024
CHO
OTIPS
$^n$Bu
7ma
0.94
1.00
1.00
1.95
1.01
2.00
2.06
1.00
2.03
2.09
2.14
3.10
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


200.9
161.2
140.7
135.0
132.5
131.3
129.4
128.5
128.2
128.0
126.1
125.7
123.6
113.7
31.5
30.1
22.7
14.1
CHO
OTIPS
nBu
7ma
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


-112.83
-112.85
-112.85
-112.86
-112.86
-112.87
-112.88
-112.89
-113.01
-113.02
-113.03
-113.04
-113.05
-113.05
-113.07
-113.07
CHO
OTIPS
nBu
7ma
-65 -70 -75 -80 -85 -90 -95 -100 -105 -110 -115 -120 -125 -130 -135 -140 -145 -150 -155
f1 (ppm)


7.765
7.763
7.749
7.747
7.695
7.693
7.679
7.677
7.629
7.418
7.415
7.404
7.402
7.399
7.388
7.385
7.357
7.354
7.343
7.341
7.338
7.327
7.325
7.165
2.861
2.846
2.841
2.830
1.765
1.753
1.750
1.745
1.739
1.734
1.728
1.722
1.719
1.714
1.703
1.515
1.501
1.486
1.471
1.458
1.456
1.441
1.427
1.230
1.215
1.032
1.017
1.003
OTIPS
nBu
7na
1.00
1.01
1.01
1.00
1.00
1.03
2.09
2.10
5.25
18.44
3.20
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)


153.0
135.0
133.3
129.1
128.2
127.0
126.1
123.4
112.4
32.3
31.2
22.8
18.2
13.2
OTIPS
nBu
7na
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.729
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7.674
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7.404
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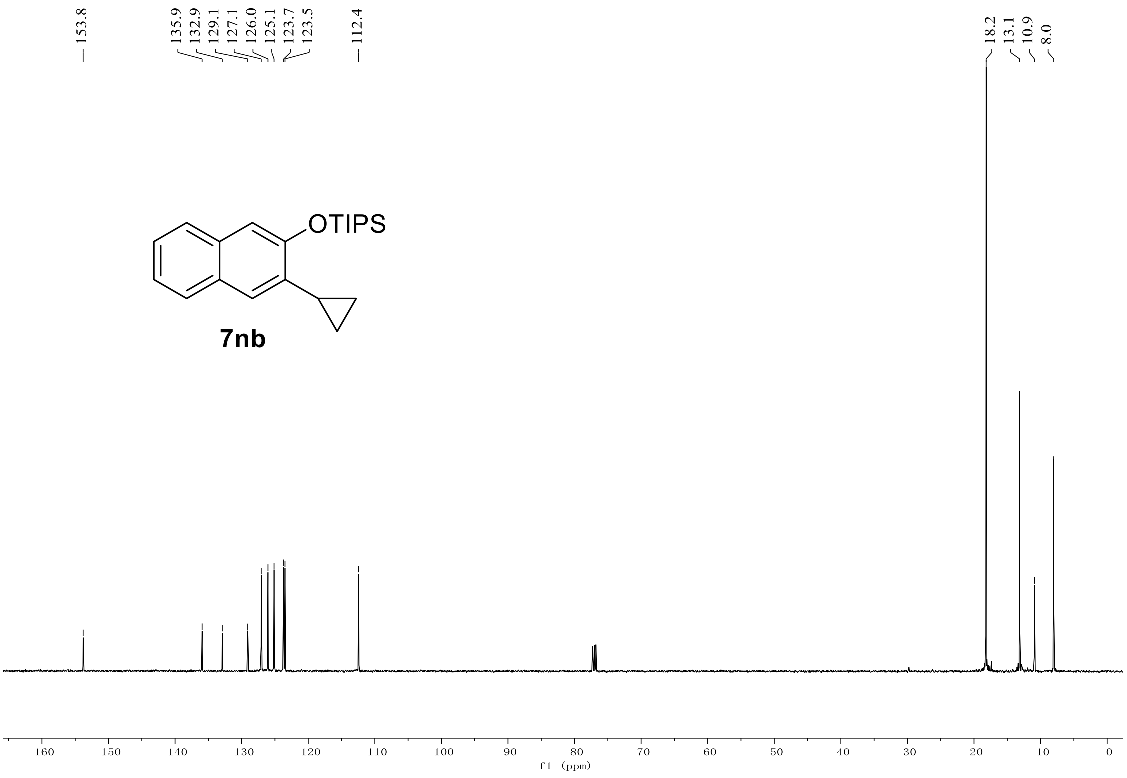
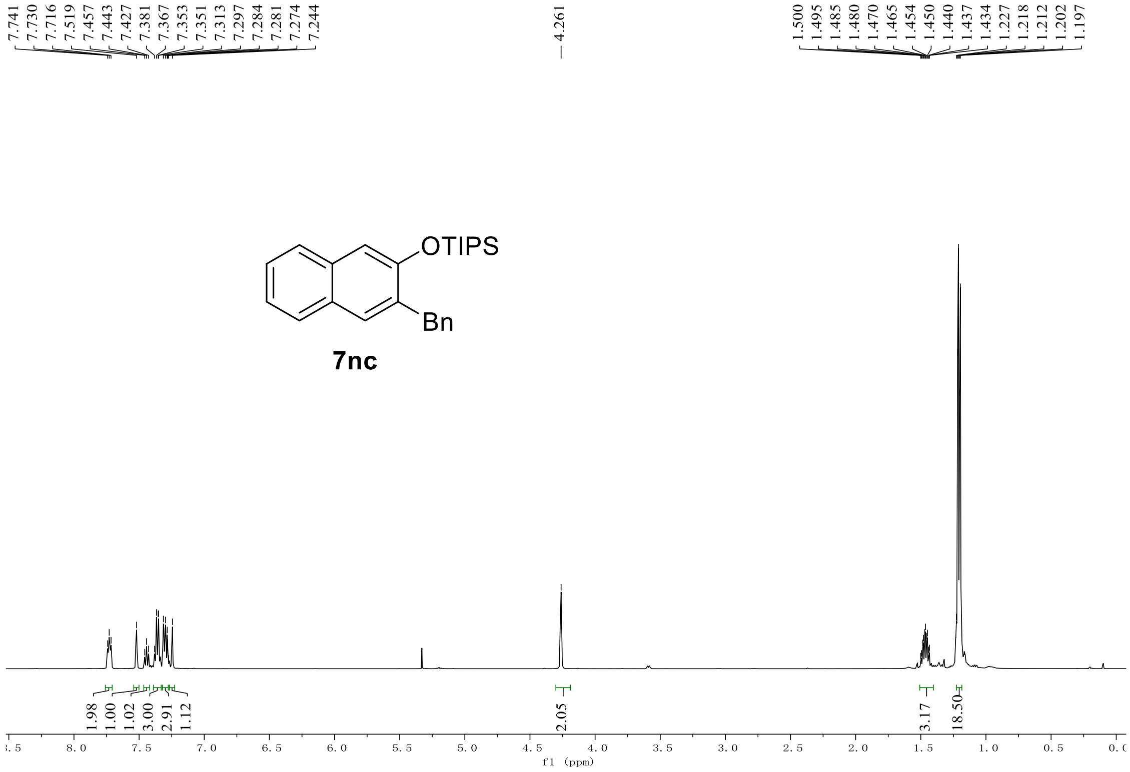
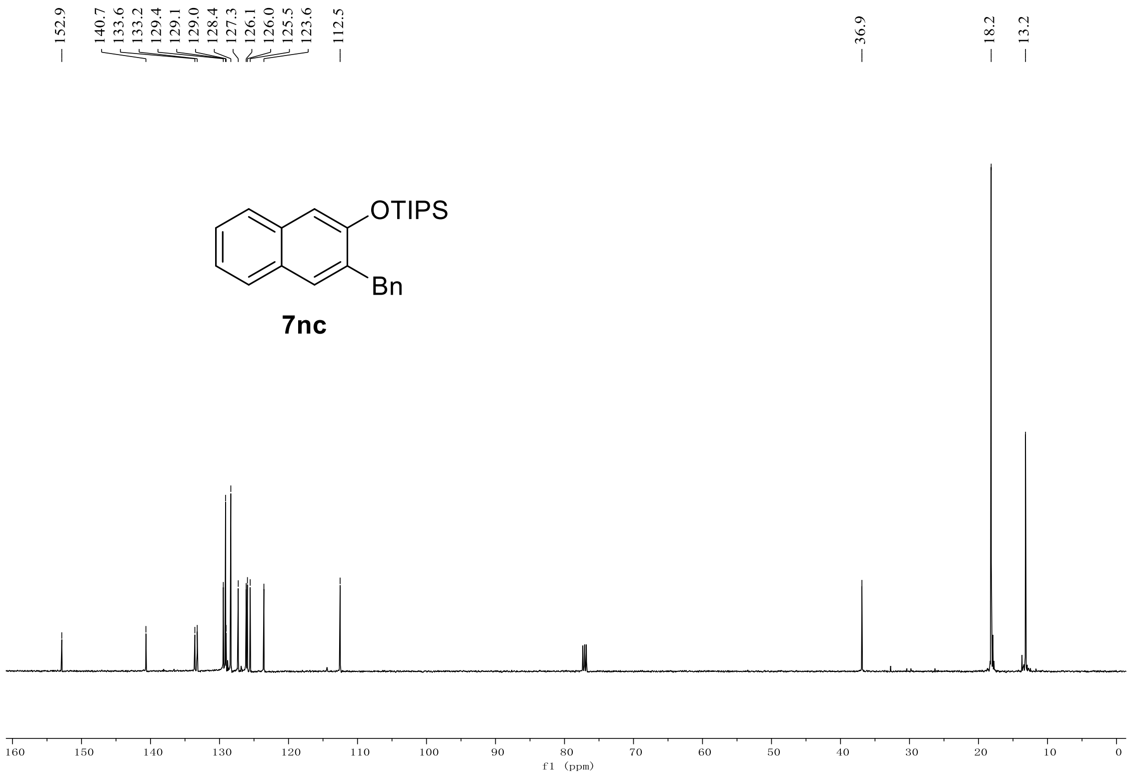
7.390
7.387
7.377
7.374
7.347
7.331
7.328
7.326
7.315
7.312
7.181
2.381
2.380
2.375
2.373
2.370
2.369
2.364
2.362
2.358
2.357
2.353
2.352
2.347
2.346
2.336
1.508
1.493
1.485
1.480
1.478
1.469
1.465
1.462
1.451
1.448
1.241
1.226
1.063
1.054
1.050
1.046
1.042
1.037
1.033
1.025
0.829
0.820
0.817
0.810
0.806
0.797
OTIPS
1.00
1.00
0.98
0.99
0.77
1.00
0.96
3.09
18.16
2.06
2.08
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)

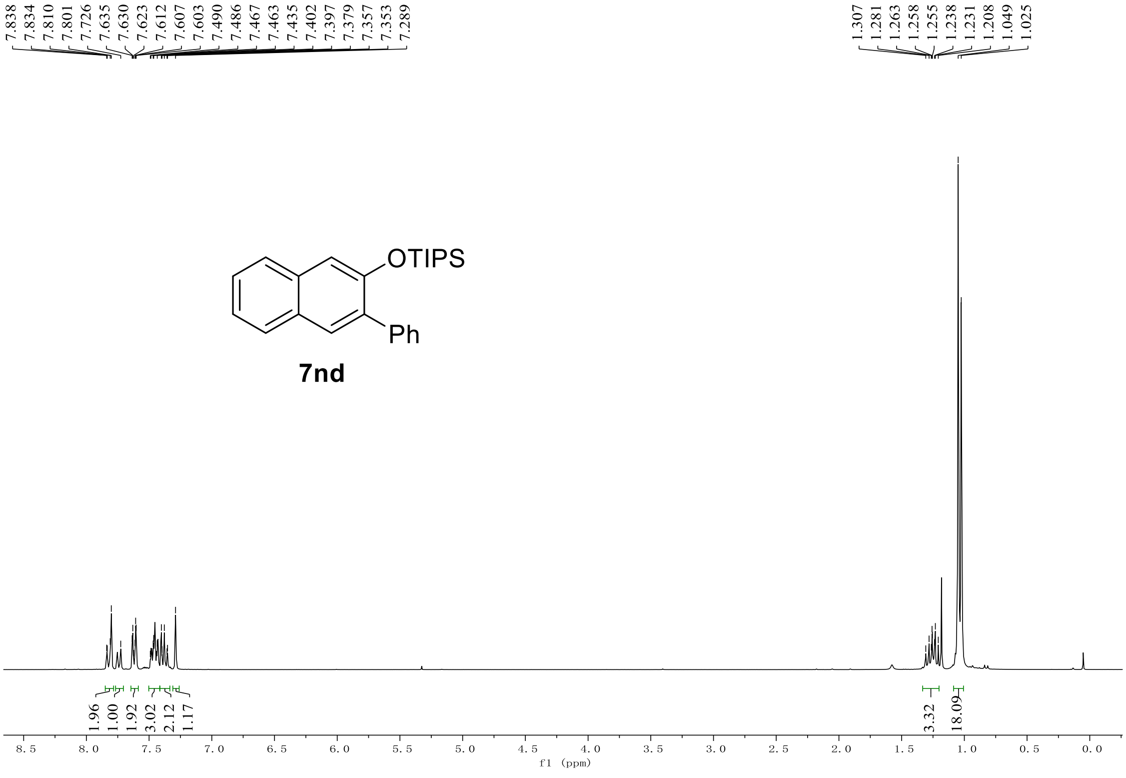
**7nb**

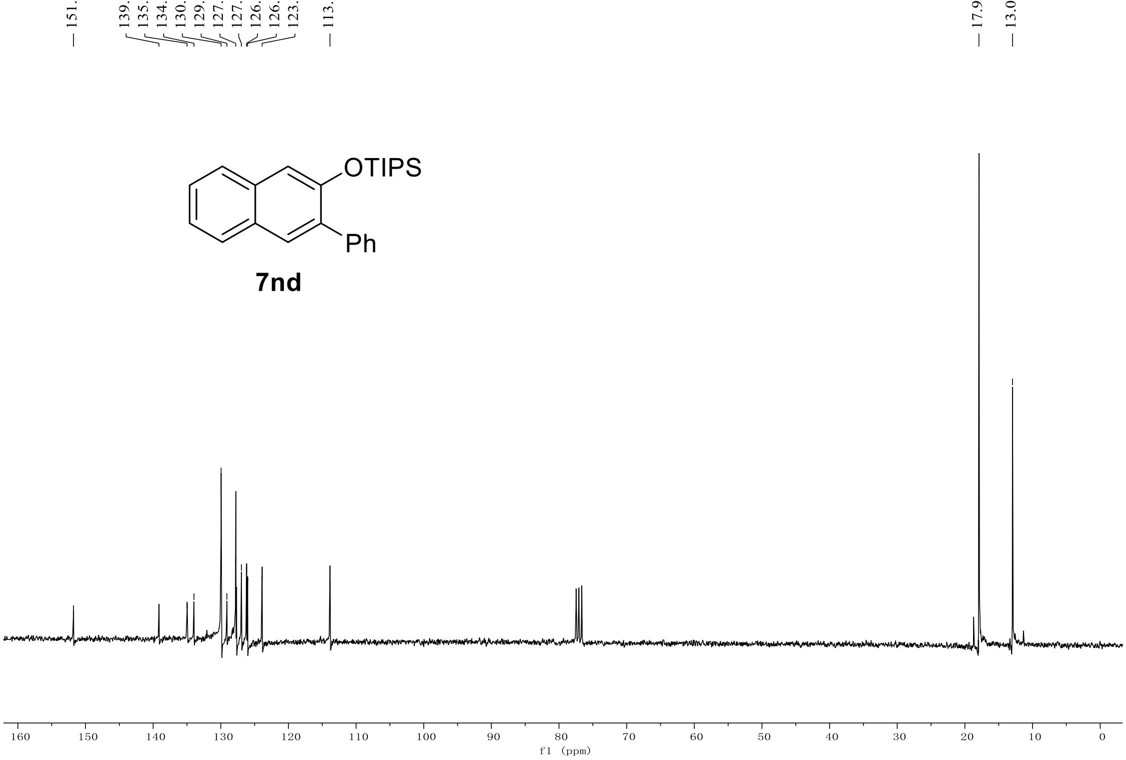

153.8
135.9
132.9
129.1
127.1
126.0
125.1
123.7
123.5
112.4
18.2
13.1
10.9
8.0
OTIPS
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

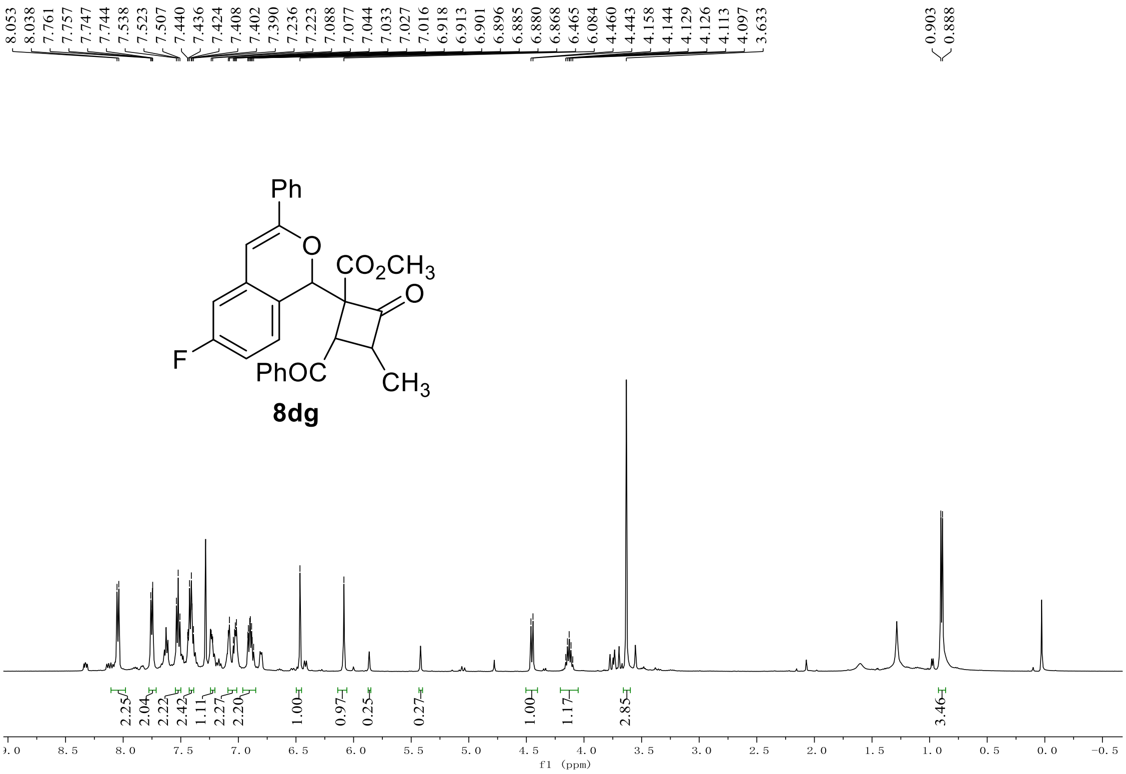
**7nb**

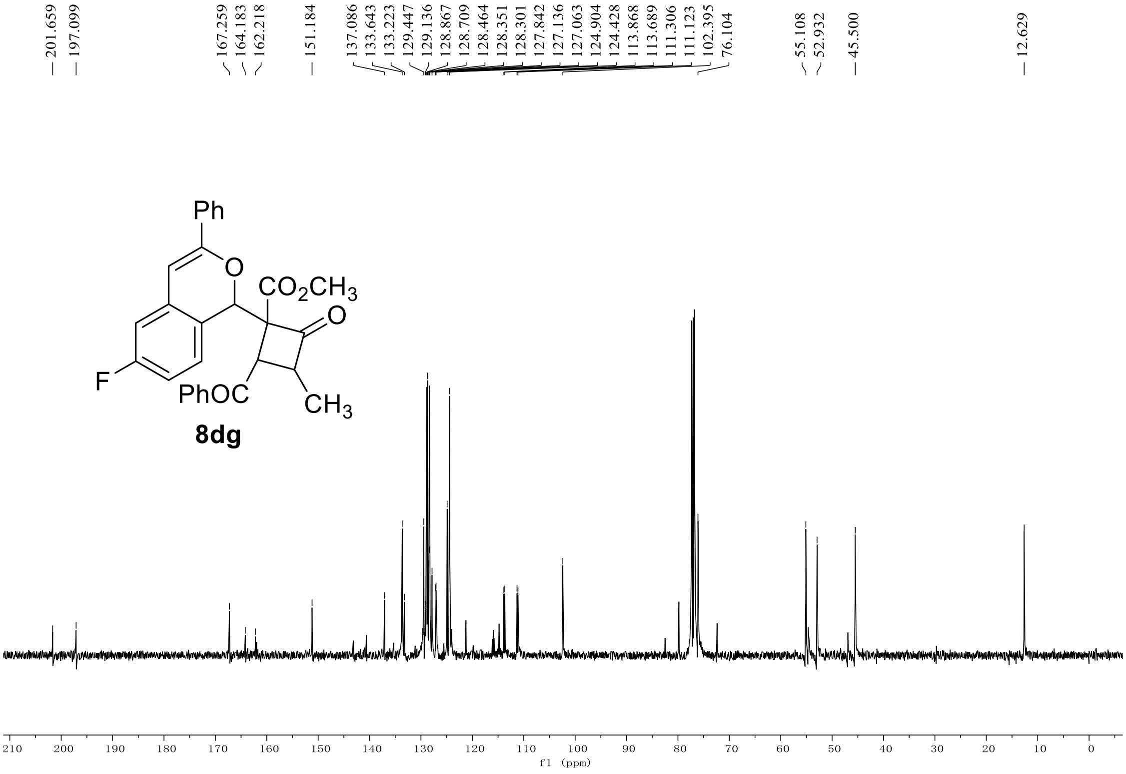

7.741
7.730
7.716
7.519
7.457
7.443
7.427
7.381
7.367
7.353
7.351
7.313
7.297
7.284
7.281
7.274
7.244
4.261
1.500
1.495
1.485
1.480
1.470
1.465
1.454
1.450
1.440
1.437
1.434
1.227
1.218
1.212
1.202
1.197
OTIPS
Bn
7nc
1.98
1.00
1.02
3.00
2.91
1.12
2.05
3.17
18.50
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

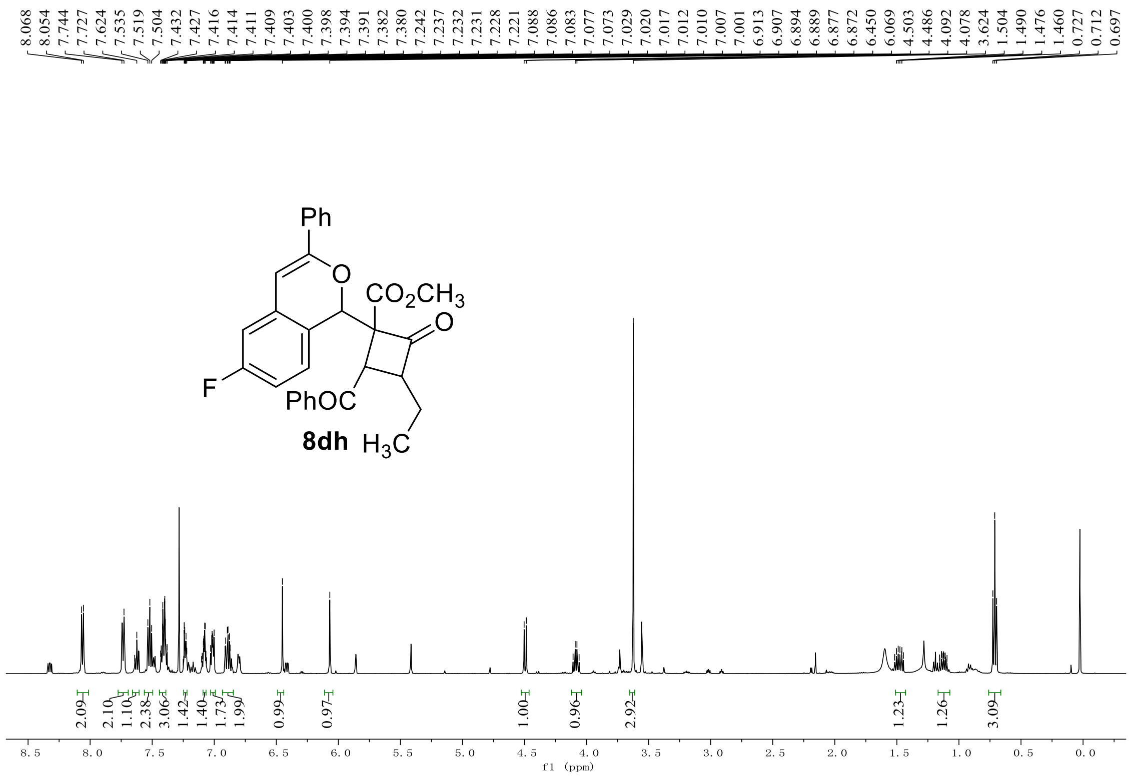

152.9
140.7
133.6
133.2
129.4
129.1
129.0
128.4
127.3
126.1
126.0
125.5
123.6
112.5
36.9
18.2
13.2
OTIPS
Bn
7nc
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

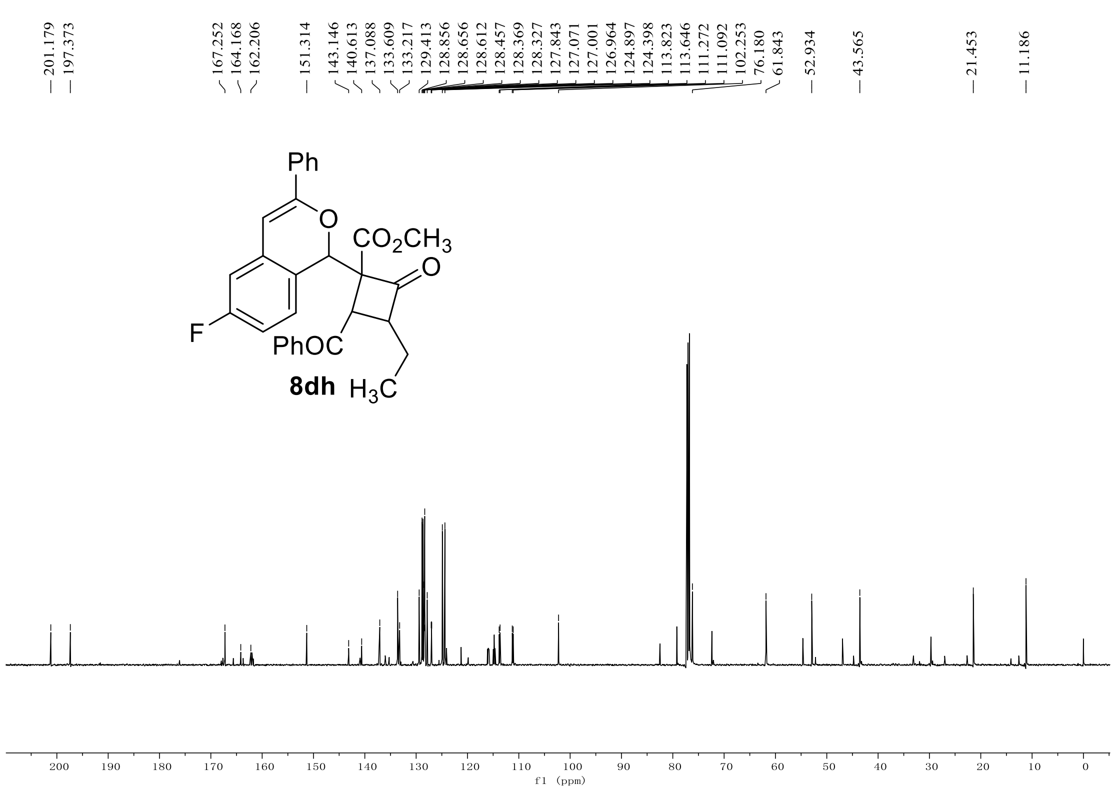

7.838
7.834
7.810
7.801
7.726
7.635
7.630
7.623
7.612
7.607
7.603
7.490
7.486
7.467
7.463
7.435
7.402
7.397
7.379
7.357
7.353
7.289
1.307
1.281
1.263
1.258
1.255
1.238
1.231
1.208
1.049
1.025
OTIPS
Ph
7nd
1.96
1.00
1.92
3.02
2.12
1.17
3.32
18.09
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

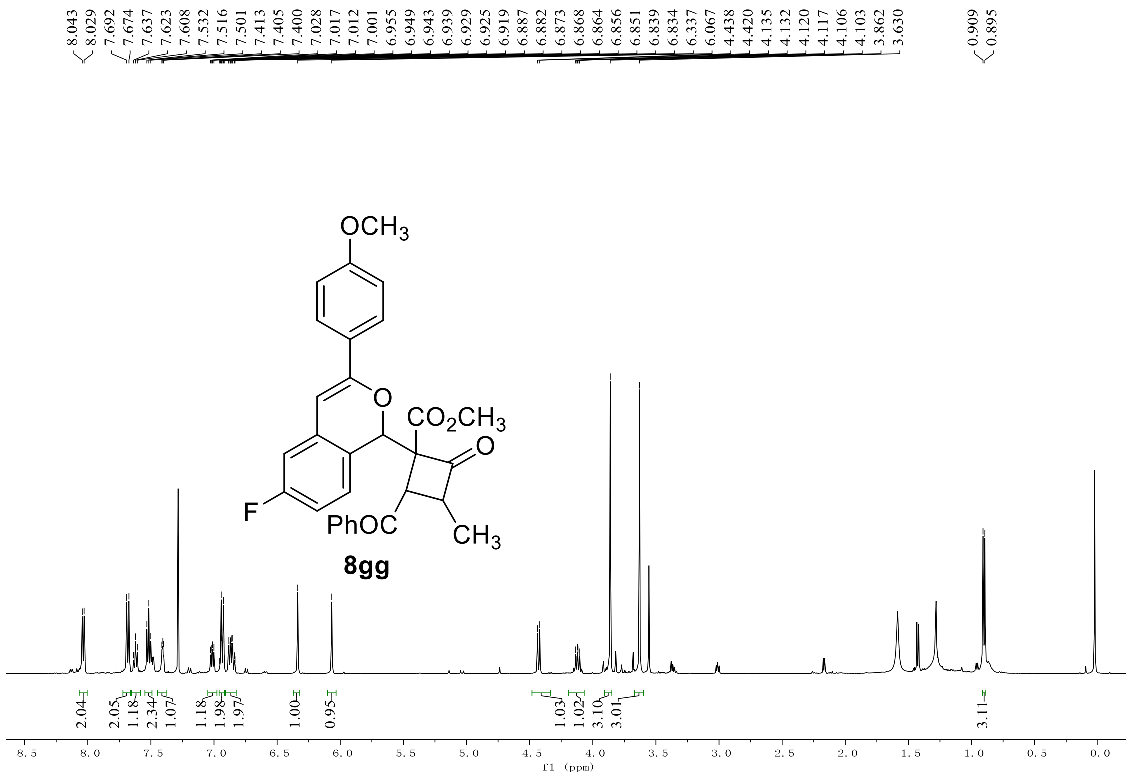

151.8
139.1
135.0
134.0
130.0
129.1
127.8
127.0
126.2
126.0
123.9
113.9
17.9
13.0
OTIPS
Ph
7nd
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

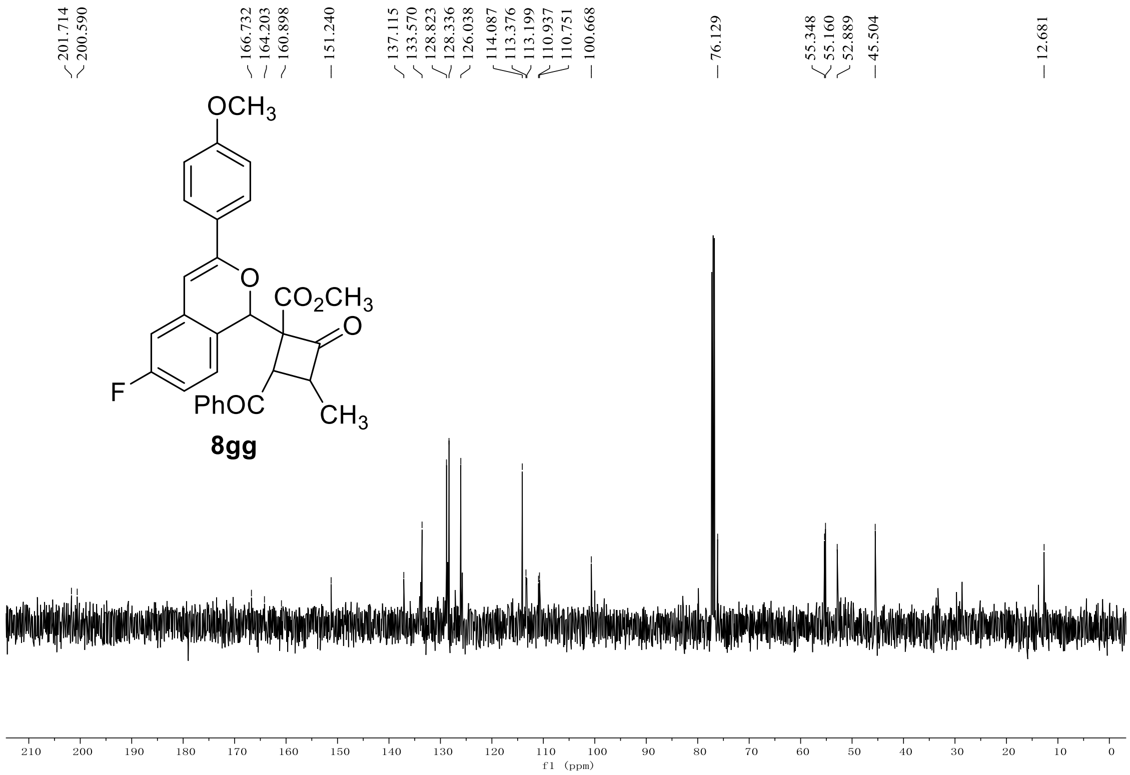

8.053
8.038
7.761
7.757
7.747
7.744
7.538
7.523
7.507
7.440
7.436
7.424
7.408
7.402
7.390
7.236
7.223
7.088
7.077
7.044
7.033
7.027
7.016
6.918
6.913
6.901
6.896
6.885
6.880
6.868
6.465
6.084
4.460
4.443
4.158
4.144
4.129
4.126
4.113
4.097
3.633
0.903
0.888
Ph
O
CO2CH3
O
F
PhOC
CH3
8dg
2.25
2.04
2.22
2.42
1.11
2.27
2.20
1.00
0.97
0.25
0.27
1.00
1.17
2.85
3.46
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

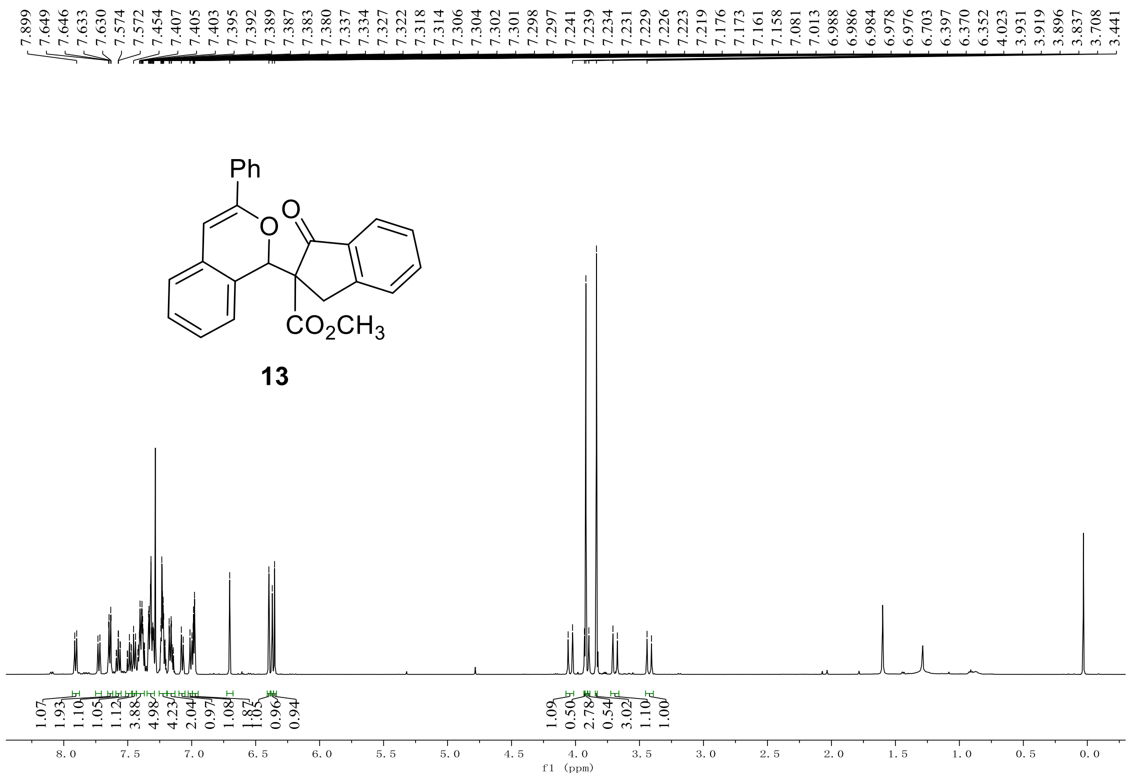

201.659
197.099
167.259
164.183
162.218
151.184
137.086
133.643
133.223
129.447
129.136
128.867
128.709
128.464
128.351
128.301
127.842
127.136
127.063
124.904
124.428
113.868
113.689
111.306
111.123
102.395
76.104
55.108
52.932
45.500
12.629
Ph
O
CO2CH3
O
F
PhOC
CH3
8dg
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


8.068
8.054
7.744
7.727
7.624
7.535
7.519
7.504
7.432
7.427
7.416
7.414
7.411
7.409
7.403
7.400
7.398
7.394
7.391
7.382
7.380
7.242
7.237
7.232
7.231
7.228
7.221
7.088
7.086
7.083
7.077
7.073
7.029
7.020
7.017
7.012
7.010
7.007
7.001
6.913
6.907
6.894
6.889
6.877
6.872
6.450
6.069
4.503
4.486
4.092
4.078
3.624
1.504
1.490
1.476
1.460
0.727
0.712
0.697
Ph
O
CO2CH3
O
F
PhOC
8dh
H3C
2.09
2.10
1.10
2.38
3.06
1.42
1.40
1.73
1.99
0.99
0.97
1.00
0.96
2.92
1.23
1.26
3.09
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)

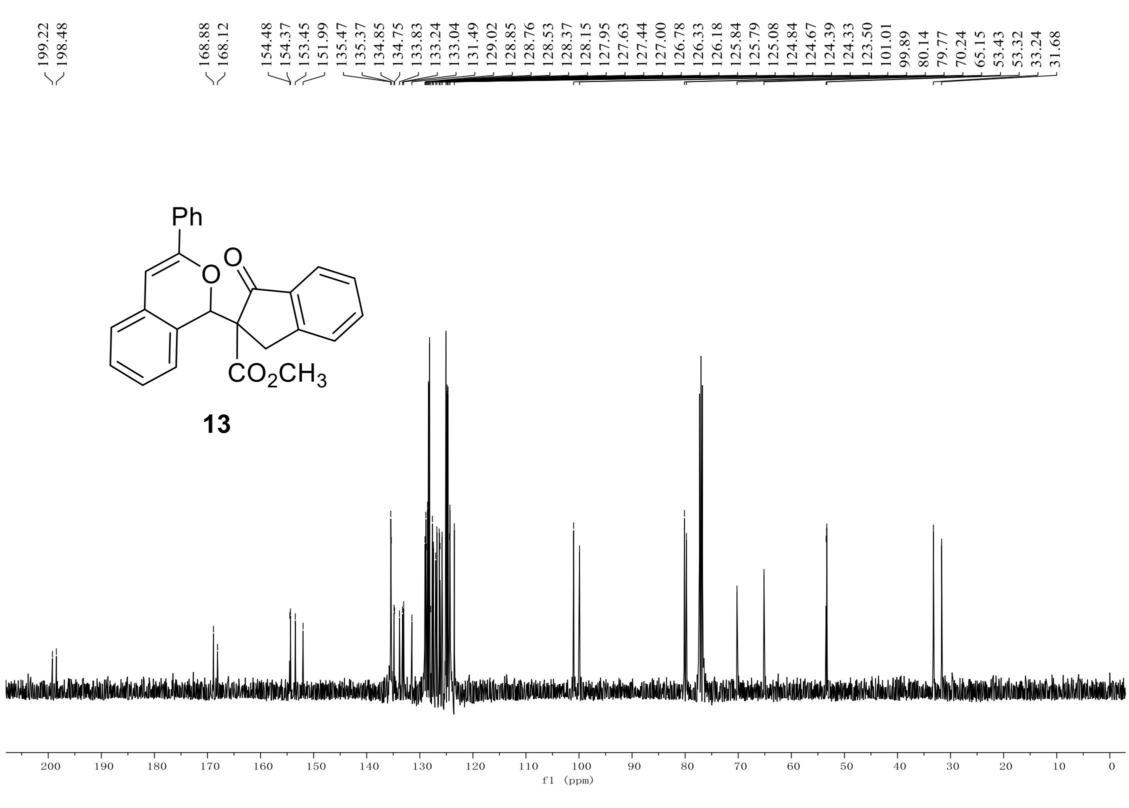

201.179
197.373
167.252
164.168
162.206
151.314
143.146
140.613
137.088
133.609
133.217
129.413
128.856
128.656
128.612
128.457
128.369
128.327
127.843
127.071
127.001
126.964
124.897
124.398
113.823
113.646
111.272
111.092
102.253
76.180
61.843
52.934
43.565
21.453
11.186
Ph
O
CO2CH3
O
F
PhOC
8dh
H3C
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


8.043
8.029
7.692
7.674
7.637
7.623
7.608
7.532
7.516
7.501
7.413
7.405
7.400
7.028
7.017
7.012
7.001
6.955
6.949
6.943
6.939
6.929
6.925
6.919
6.887
6.882
6.873
6.868
6.864
6.856
6.851
6.839
6.834
6.337
6.067
4.438
4.420
4.135
4.132
4.120
4.117
4.106
4.103
3.862
3.630
0.909
0.895
OCH3
O
CO2CH3
O
F
PhOC
CH3
8gg
2.04
2.05
1.18
2.34
1.07
1.18
1.98
1.97
1.00
0.95
1.03
1.02
3.10
3.01
3.11
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)

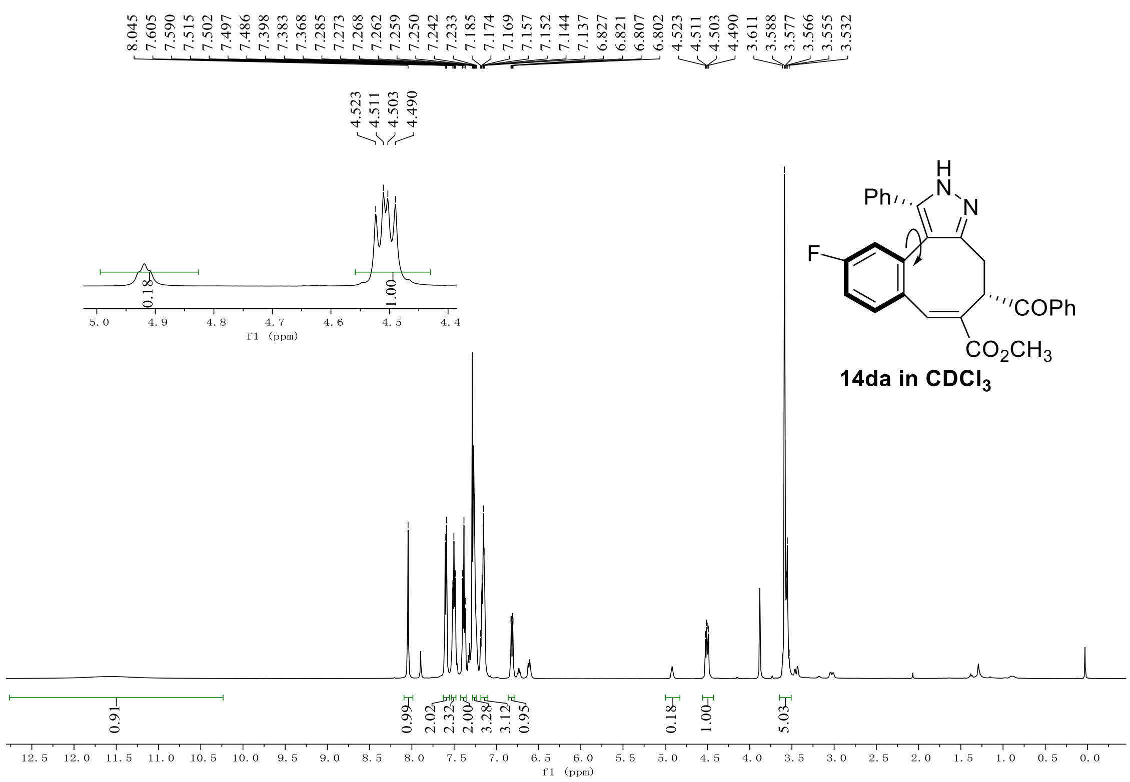

201.714
200.590
166.732
164.203
160.898
151.240
137.115
133.570
128.823
128.336
126.038
114.087
113.376
113.199
110.937
110.751
100.668
76.129
55.348
55.160
52.889
45.504
12.681
OCH3
O
CO2CH3
O
F
PhOC
CH3
8gg
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.899
7.649
7.646
7.633
7.630
7.574
7.572
7.454
7.407
7.405
7.403
7.395
7.392
7.389
7.387
7.383
7.380
7.337
7.334
7.327
7.322
7.318
7.314
7.306
7.304
7.302
7.301
7.298
7.297
7.241
7.239
7.234
7.231
7.229
7.226
7.223
7.219
7.176
7.173
7.161
7.158
7.081
7.013
6.988
6.986
6.984
6.978
6.976
6.703
6.397
6.370
6.352
4.023
3.931
3.919
3.896
3.837
3.708
3.441
Ph
O
O
$CO_2CH_3$
1.07
1.93
1.10
1.05
1.12
3.88
4.98
4.23
2.04
0.97
1.08
1.87
1.05
0.96
0.94
1.09
0.50
2.78
0.54
3.02
1.10
1.00
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)

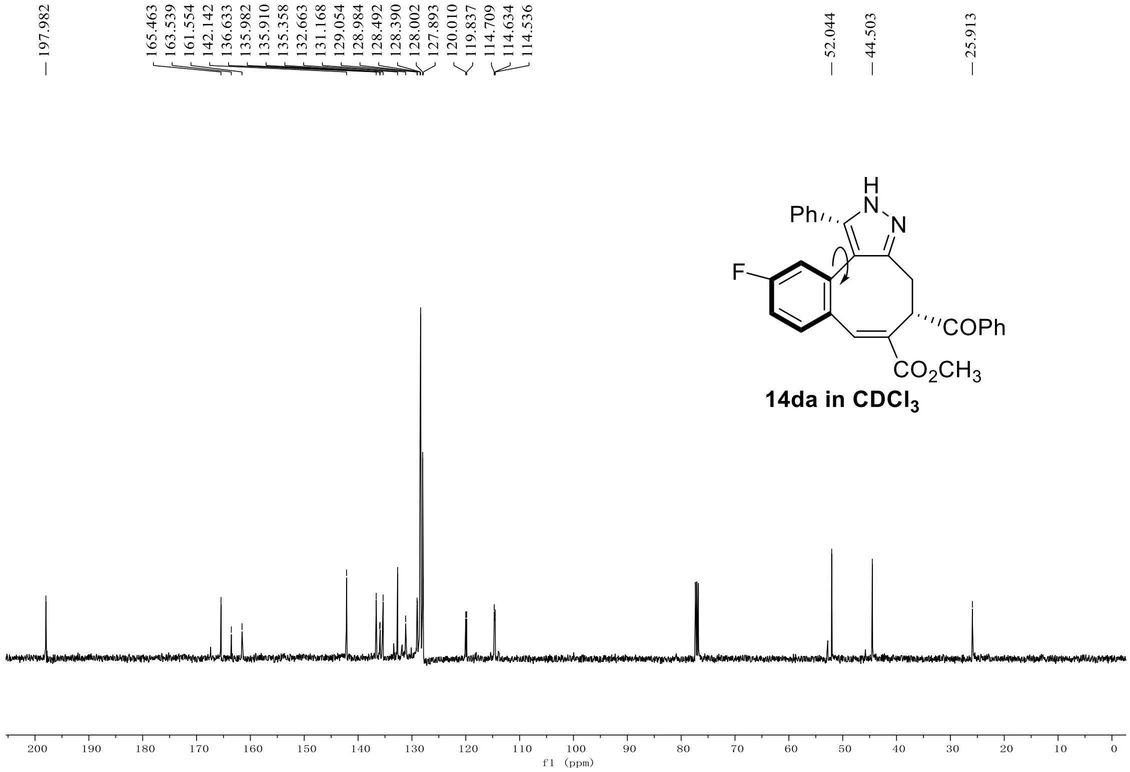
**13**


199.22
198.48
168.88
168.12
154.48
154.37
153.45
151.99
135.47
135.37
134.85
134.75
133.83
133.24
133.04
131.49
129.02
128.85
128.76
128.53
128.37
128.15
127.95
127.63
127.44
127.00
126.78
126.33
126.18
125.84
125.79
125.08
124.84
124.67
124.39
124.33
123.50
101.01
99.89
80.14
79.77
70.24
65.15
53.43
53.32
33.24
31.68
Ph
O
O
$CO_2CH_3$
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

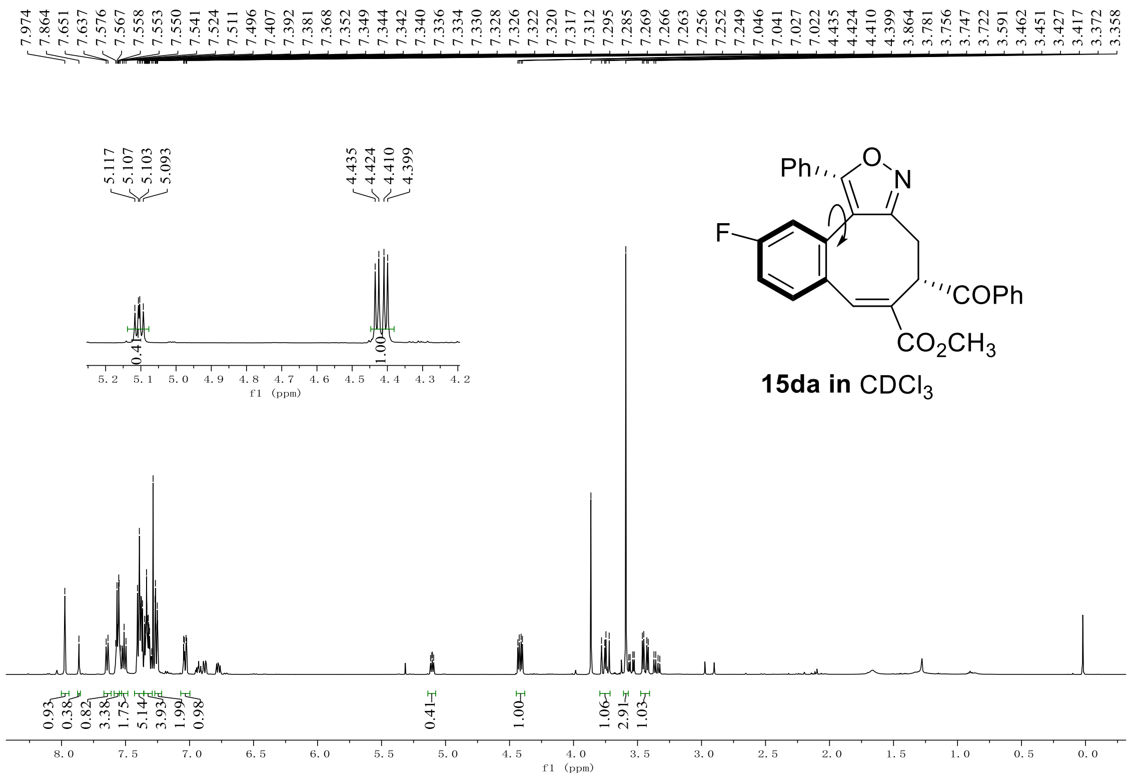
**13**



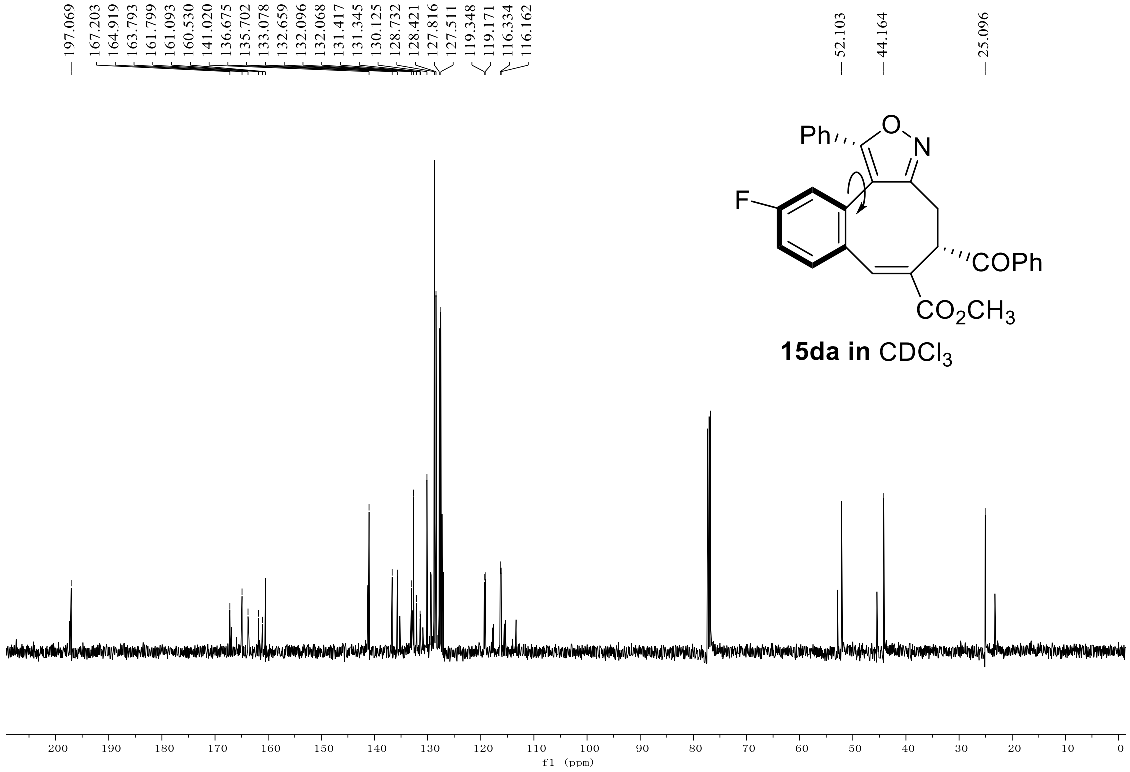
**14da in CDCl$_3$**



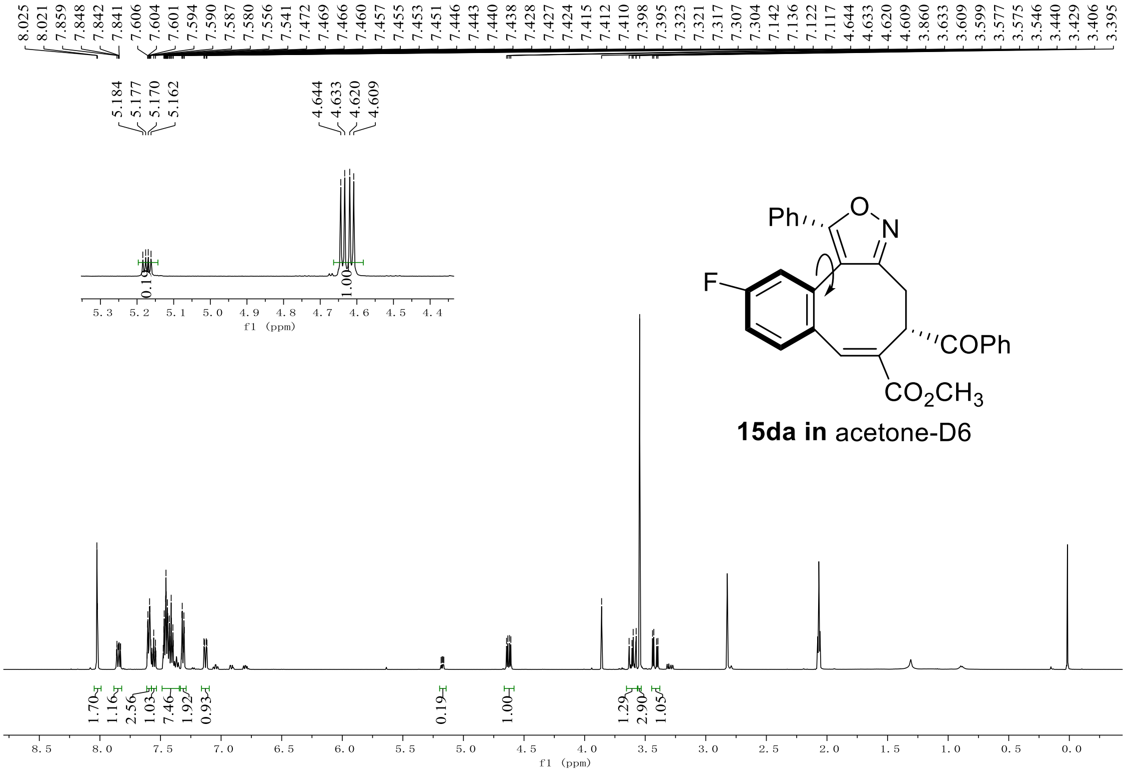
**14da in CDCl$_3$**



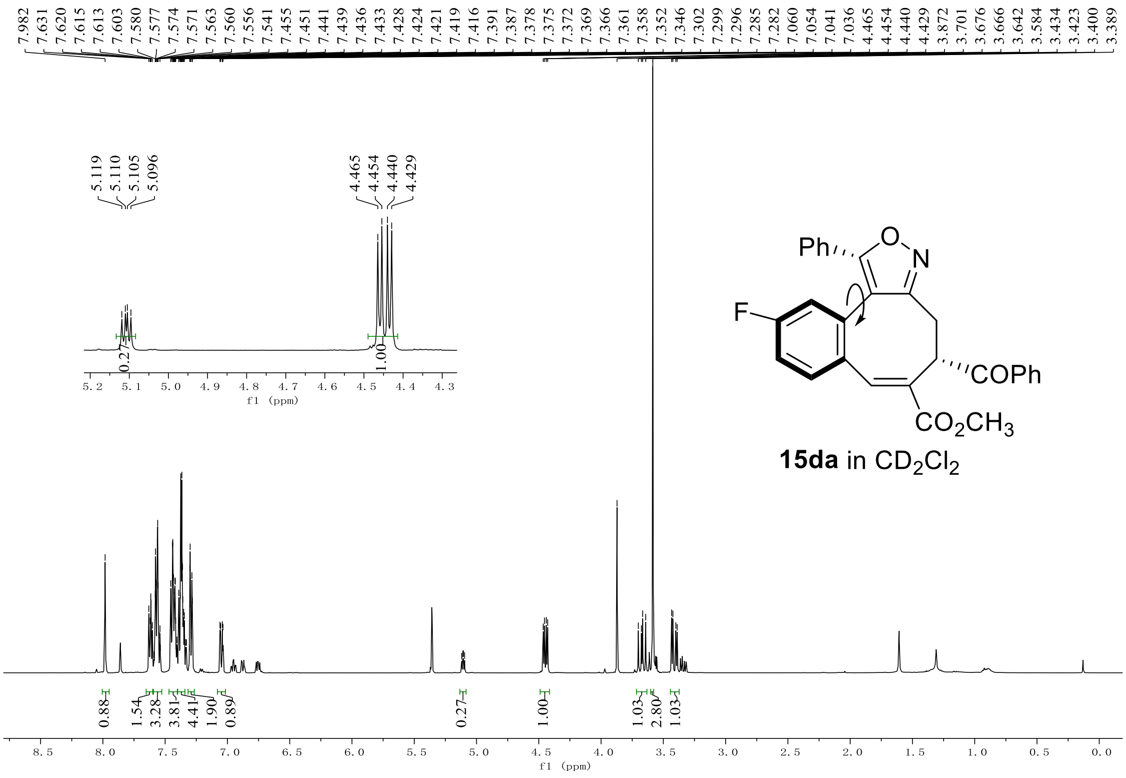
**15da in** CDCl$_3$



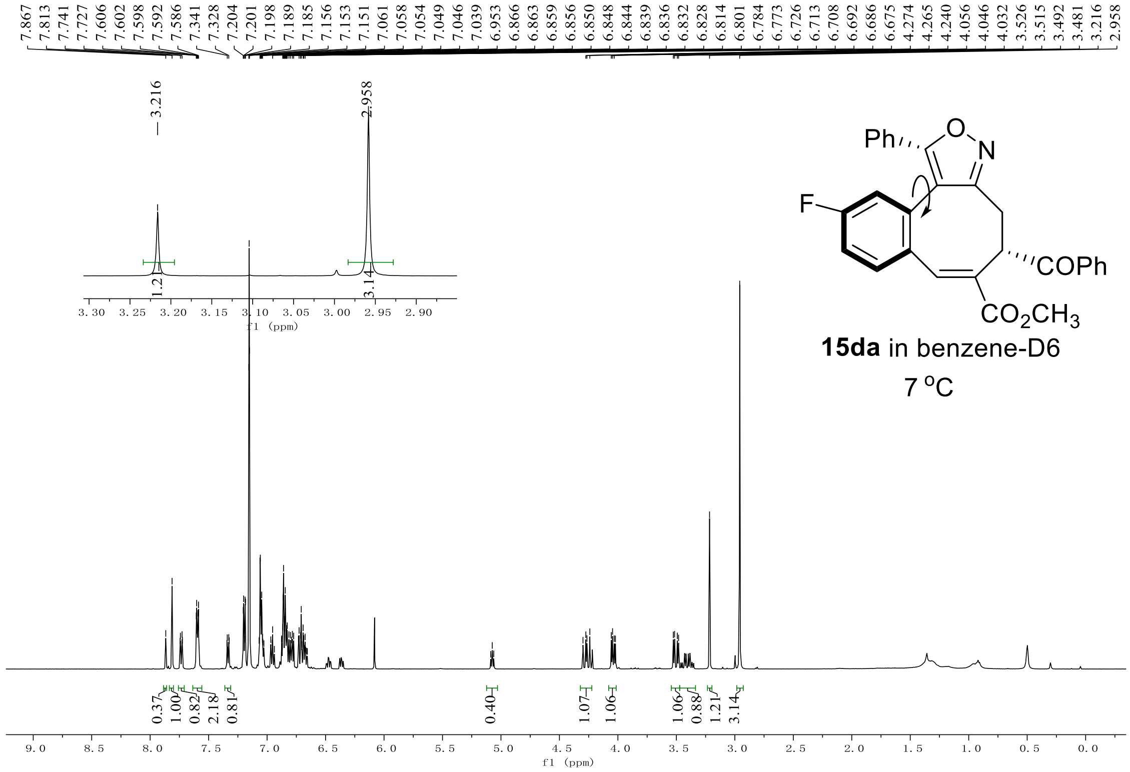
**15da in** CDCl$_3$



**15da in** acetone-D6

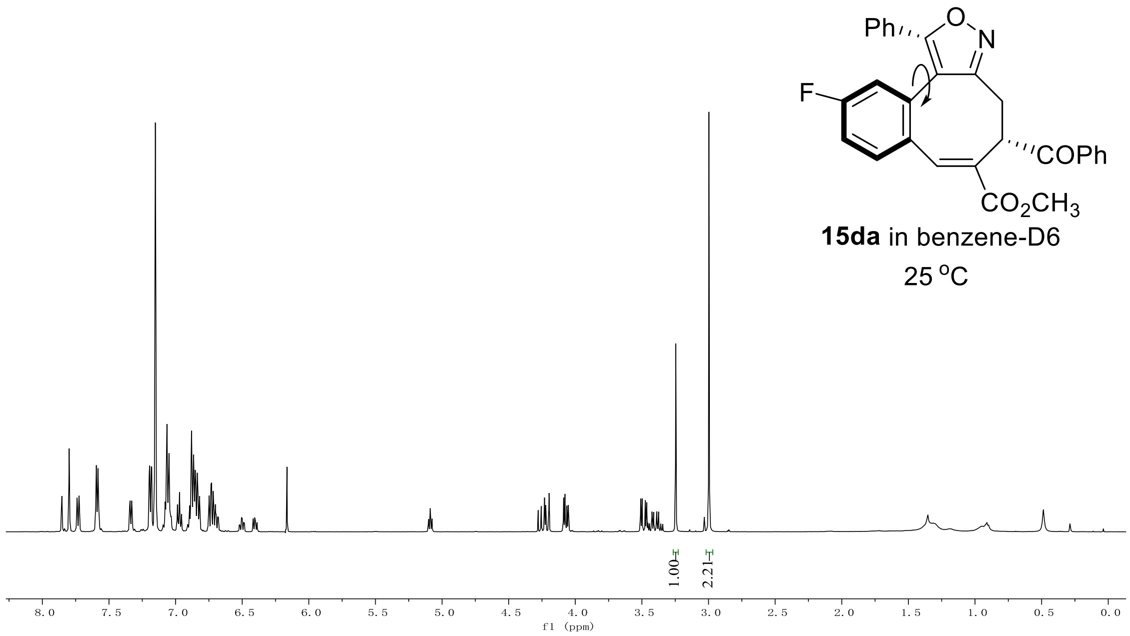


**15da** in CD$_2$Cl$_2$



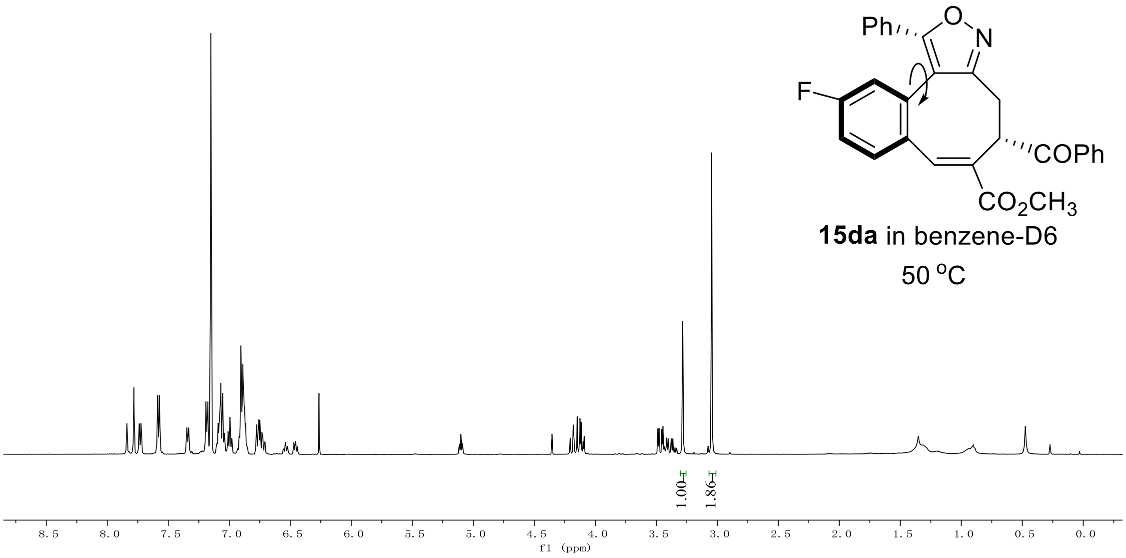
**15da** in benzene-D6

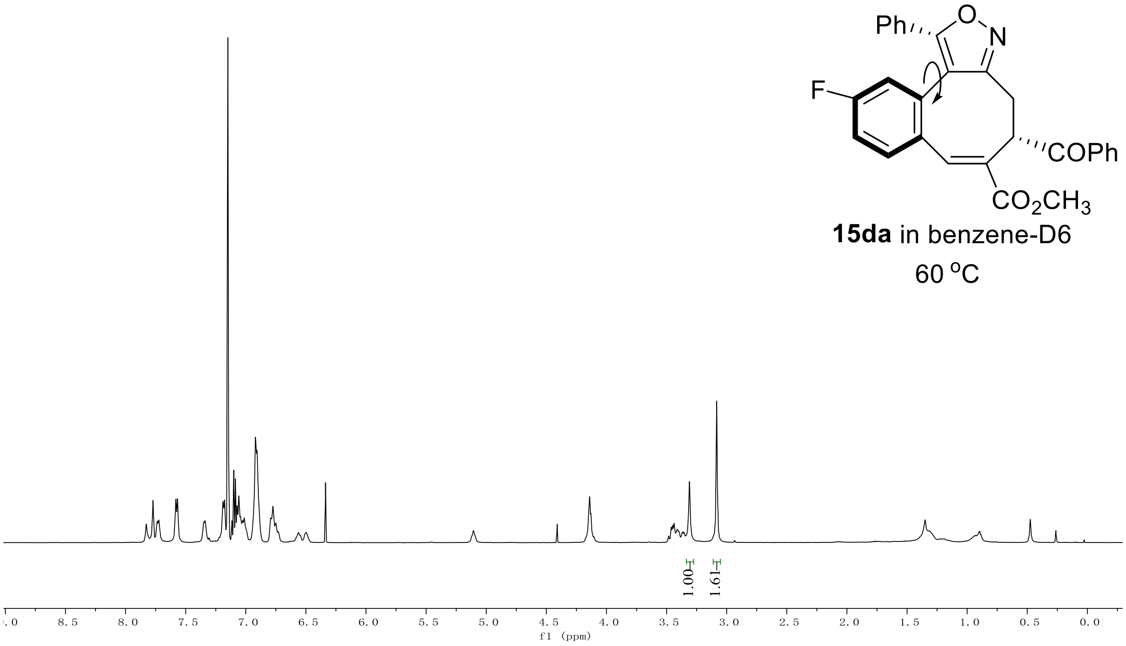
7 °C

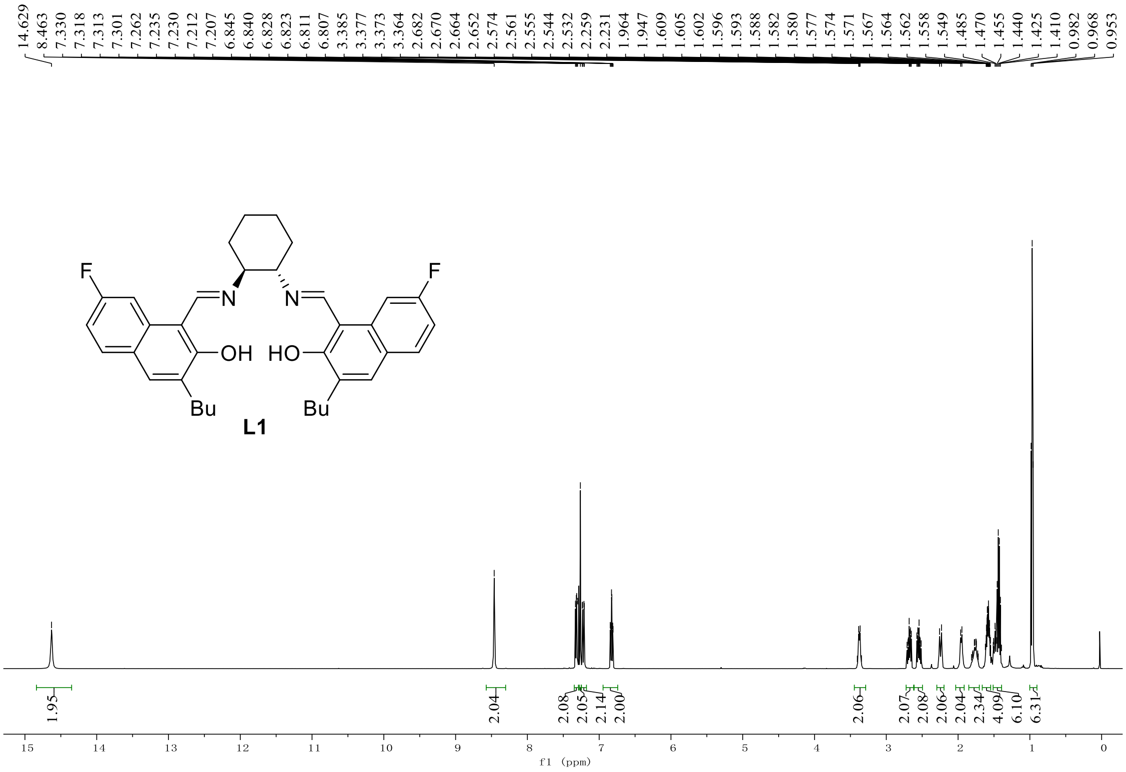


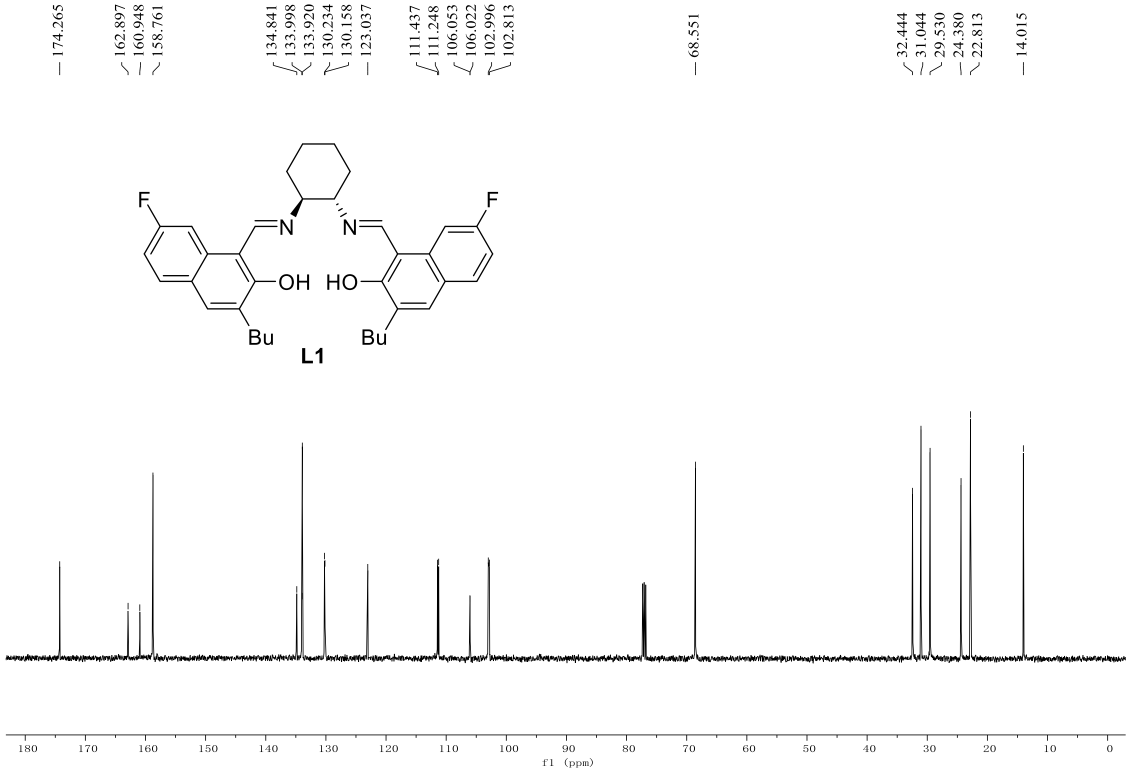
**15da** in benzene-D6

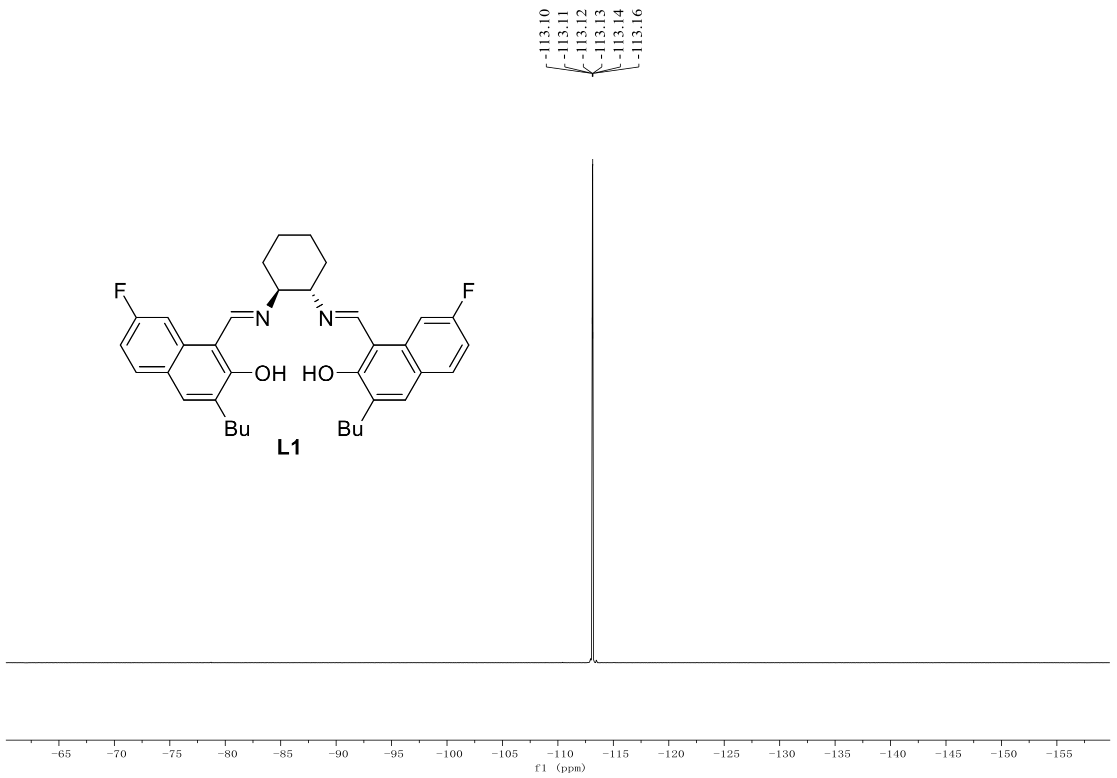
25 °C


Ph
O
N
F
COPh
CO2CH3
**15da** in benzene-D6
50 °C
1.00
1.86
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)


Ph
O
N
F
COPh
CO2CH3
**15da** in benzene-D6
60 °C
1.00
1.61
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)

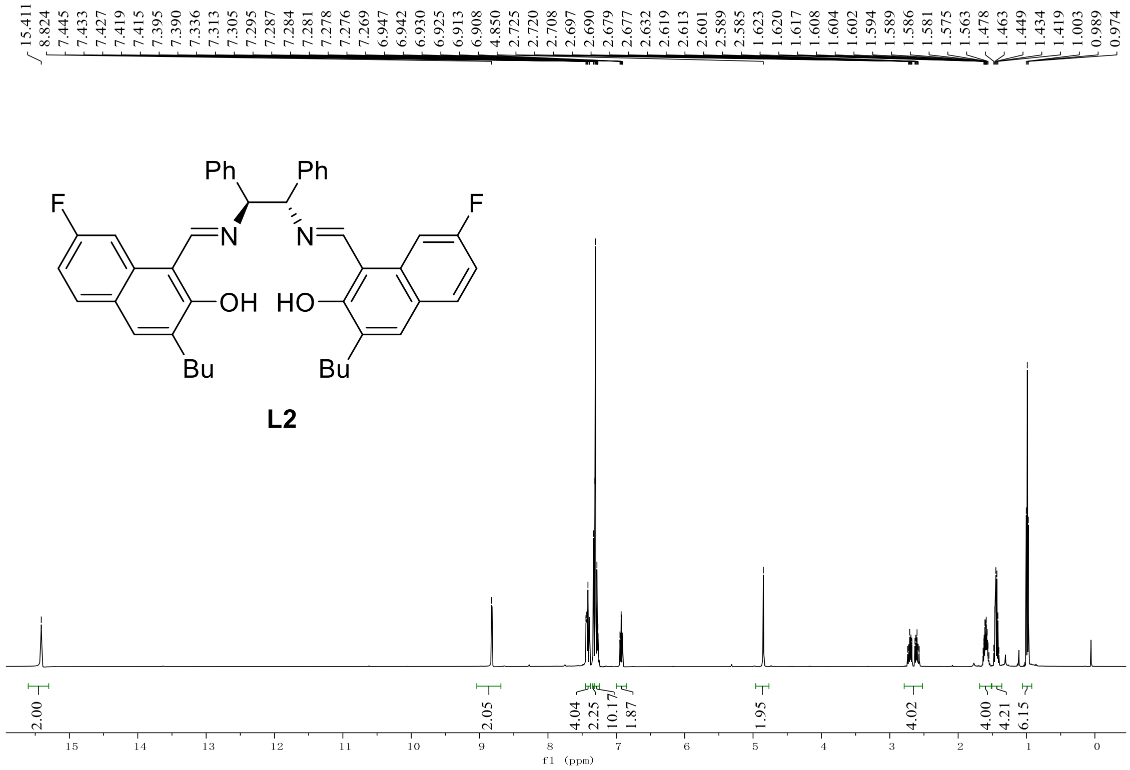

14.629
8.463
7.330
7.318
7.313
7.301
7.262
7.235
7.230
7.212
7.207
6.845
6.840
6.828
6.823
6.811
6.807
3.385
3.377
3.373
3.364
2.682
2.670
2.664
2.652
2.574
2.561
2.555
2.544
2.532
2.259
2.231
1.964
1.947
1.609
1.605
1.602
1.596
1.593
1.588
1.582
1.580
1.577
1.574
1.571
1.567
1.564
1.562
1.558
1.549
1.485
1.470
1.455
1.440
1.425
1.410
0.982
0.968
0.953
F
N
N
F
OH
HO
Bu
Bu
L1
1.95
2.04
2.08
2.05
2.14
2.00
2.06
2.07
2.08
2.06
2.04
2.34
4.09
6.10
6.31
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)


174.265
162.897
160.948
158.761
134.841
133.998
133.920
130.234
130.158
123.037
111.437
111.248
106.053
106.022
102.996
102.813
68.551
32.444
31.044
29.530
24.380
22.813
14.015
F
N
N
F
OH
HO
Bu
Bu
L1
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



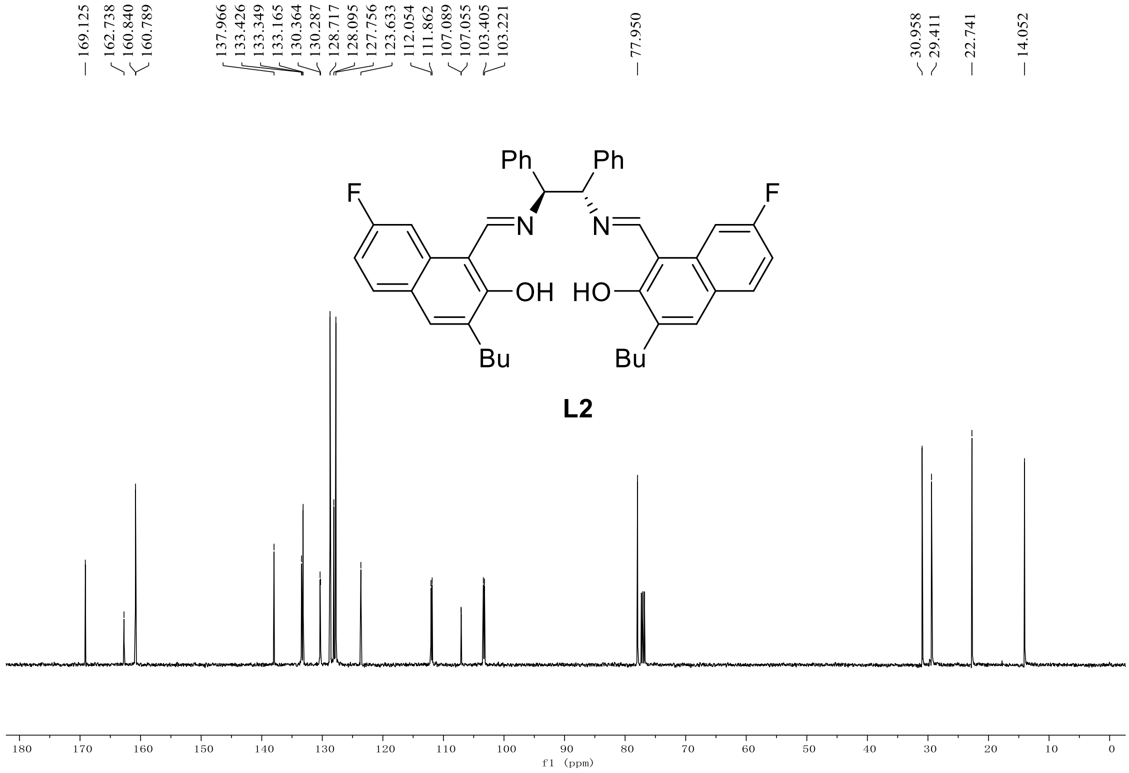
**L1**

-113.10
-113.11
-113.12
-113.13
-113.14
-113.16
F
N
N
F
OH
HO
Bu
Bu
-65
-70
-75
-80
-85
-90
-95
-100
-105
-110
-115
-120
-125
-130
-135
-140
-145
-150
-155
f1 (ppm)



**L2**

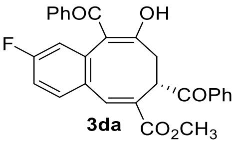
15.411
8.824
7.445
7.433
7.427
7.419
7.415
7.395
7.390
7.336
7.313
7.305
7.295
7.287
7.284
7.281
7.278
7.276
7.269
6.947
6.942
6.930
6.925
6.913
6.908
4.850
2.725
2.720
2.708
2.697
2.690
2.679
2.677
2.632
2.619
2.613
2.601
2.589
2.585
1.623
1.620
1.617
1.608
1.604
1.602
1.594
1.589
1.586
1.581
1.575
1.563
1.478
1.463
1.449
1.434
1.419
1.003
0.989
0.974
Ph
Ph
F
F
N
N
OH
HO
Bu
Bu
2.00
2.05
4.04
2.25
10.17
1.87
1.95
4.02
4.00
4.21
6.15
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)


169.125
162.738
160.840
160.789
137.966
133.426
133.349
133.165
130.364
130.287
128.717
128.095
127.756
123.633
112.054
111.862
107.089
107.055
103.405
103.221
77.950
30.958
29.411
22.741
14.052
Ph
Ph
F
F
N
N
OH
HO
Bu
Bu
L2
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

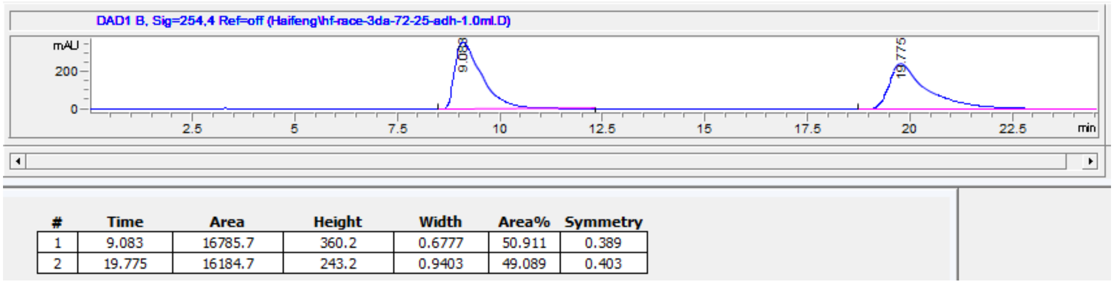

-113.05
-113.06
-113.06
-113.07
-113.08
-113.08
-113.09
-113.10
-113.12
Ph
Ph
F
F
N
N
OH
HO
Bu
Bu
L2
−65
−70
−75
−80
−85
−90
−95
−100
−105
−110
−115
−120
−125
−130
−135
−140
−145
−150
−155
f1 (ppm)

## 11. HPLC spectra of products

*Chiral HPLC of racemic* **3da**

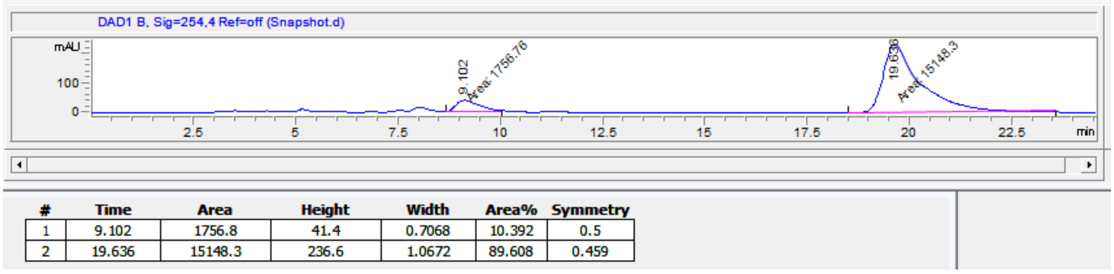


**3da**



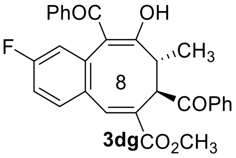
| # | Time | Area | Height | Width | Area% | Symmetry |
|---|---|---|---|---|---|---|
| 1 | 9.083 | 16785.7 | 360.2 | 0.6777 | 50.911 | 0.389 |
| 2 | 19.775 | 16184.7 | 243.2 | 0.9403 | 49.089 | 0.403 |

*Chiral HPLC of chiral* **3da**

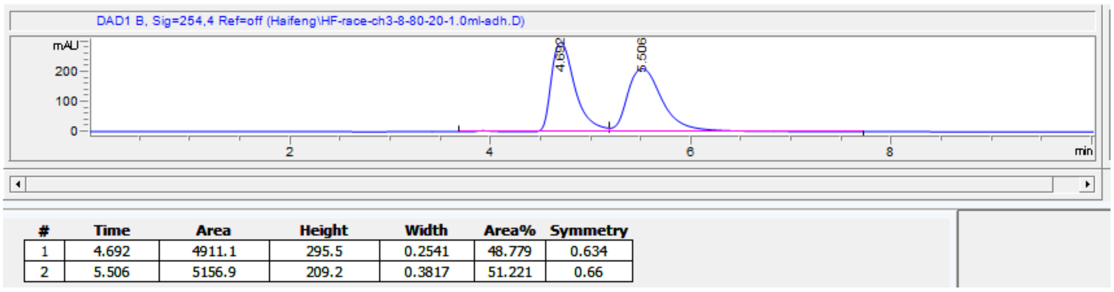


| # | Time | Area | Height | Width | Area% | Symmetry |
|---|---|---|---|---|---|---|
| 1 | 9.102 | 1756.8 | 41.4 | 0.7068 | 10.392 | 0.5 |
| 2 | 19.636 | 15148.3 | 236.6 | 1.0672 | 89.608 | 0.459 |

*Chiral HPLC of racemic* **3dg**

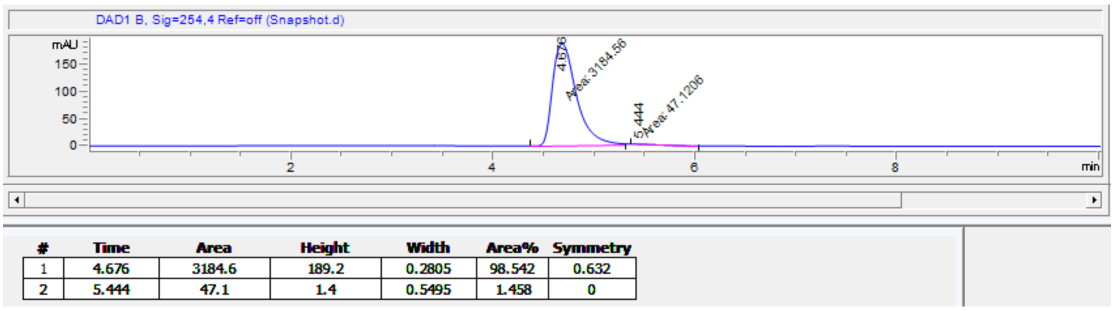


**3dg**



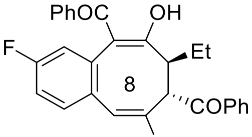
| # | Time | Area | Height | Width | Area% | Symmetry |
|---|---|---|---|---|---|---|
| 1 | 4.692 | 4911.1 | 295.5 | 0.2541 | 48.779 | 0.634 |
| 2 | 5.506 | 5156.9 | 209.2 | 0.3817 | 51.221 | 0.66 |

*Chiral HPLC of chiral* **3dg**

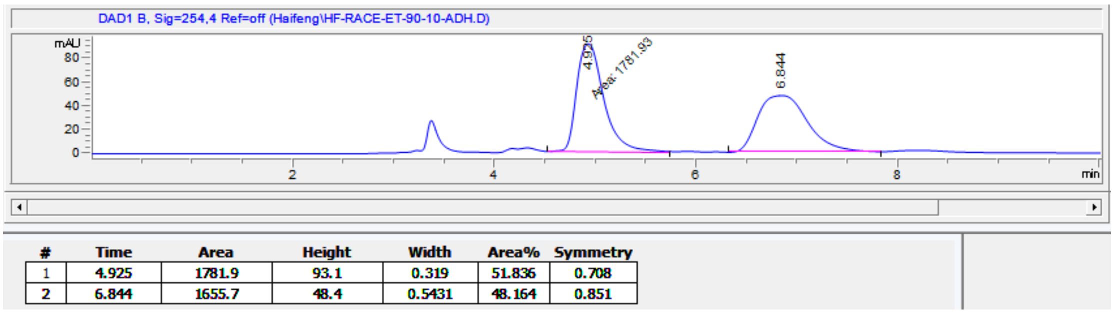


| # | Time | Area | Height | Width | Area% | Symmetry |
|---|---|---|---|---|---|---|
| 1 | 4.676 | 3184.6 | 189.2 | 0.2805 | 98.542 | 0.632 |
| 2 | 5.444 | 47.1 | 1.4 | 0.5495 | 1.458 | 0 |

*Chiral HPLC of racemic* **3dh**



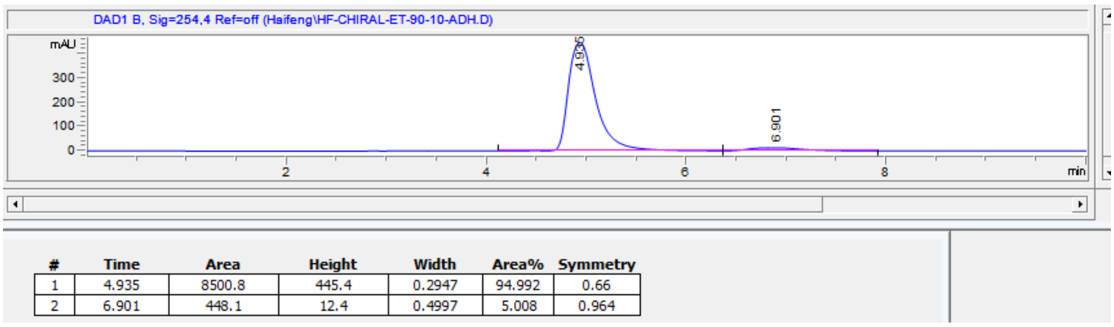
**3dh**



DAD1 B, Sig=254,4 Ref=off (Haifeng\HF-RACE-ET-90-10-ADH.D)

| # | Time | Area | Height | Width | Area% | Symmetry |
|---|---|---|---|---|---|---|
| 1 | 4.925 | 1781.9 | 93.1 | 0.319 | 51.836 | 0.708 |
| 2 | 6.844 | 1655.7 | 48.4 | 0.5431 | 48.164 | 0.851 |

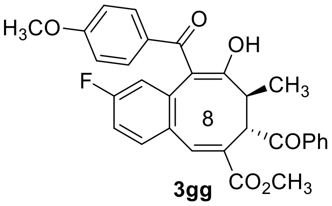
*Chiral HPLC of chiral* **3dh**



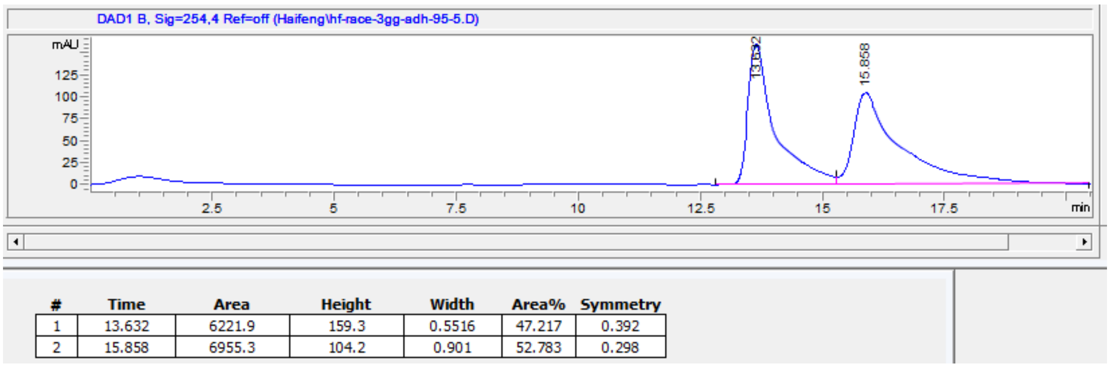
DAD1 B, Sig=254,4 Ref=off (Haifeng\HF-CHIRAL-ET-90-10-ADH.D)

| # | Time | Area | Height | Width | Area% | Symmetry |
|---|---|---|---|---|---|---|
| 1 | 4.935 | 8500.8 | 445.4 | 0.2947 | 94.992 | 0.66 |
| 2 | 6.901 | 448.1 | 12.4 | 0.4997 | 5.008 | 0.964 |

*Chiral HPLC of racemic* **3gg**



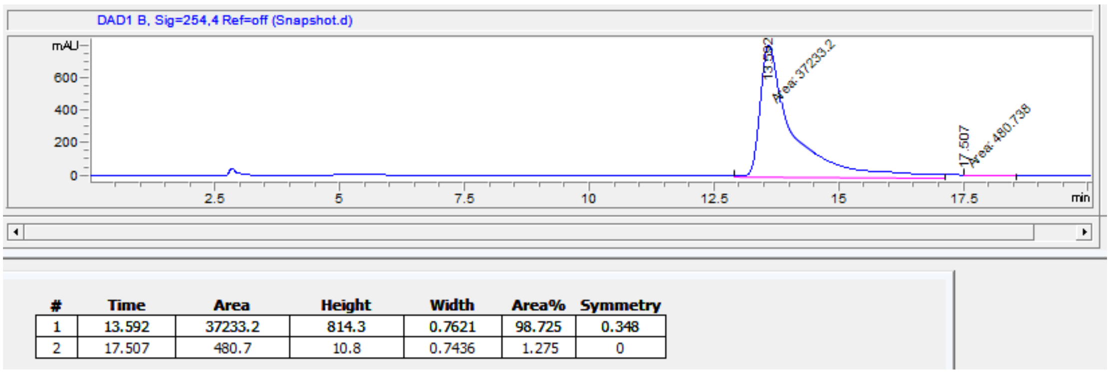
**3gg**



DAD1 B, Sig=254,4 Ref=off (Haifeng\hf-race-3gg-adh-95-5.D)

| # | Time | Area | Height | Width | Area% | Symmetry |
|---|---|---|---|---|---|---|
| 1 | 13.632 | 6221.9 | 159.3 | 0.5516 | 47.217 | 0.392 |
| 2 | 15.858 | 6955.3 | 104.2 | 0.901 | 52.783 | 0.298 |

*Chiral HPLC of chiral* **3gg**



| # | Time | Area | Height | Width | Area% | Symmetry |
|---|---|---|---|---|---|---|
| 1 | 13.592 | 37233.2 | 814.3 | 0.7621 | 98.725 | 0.348 |
| 2 | 17.507 | 480.7 | 10.8 | 0.7436 | 1.275 | 0 |