Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Synthesis of 2-Chromanone-fused [3.2.0] Bicycles through a Phosphine-mediated Tandem [3+2] Cyclization/Intramolecular Wittig Reaction

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Supporting Information

1. General Information S2

2. Representative Procedure for Tandem [3+2] Cyclization/Intramolecular Wittig Reaction

2.1 Synthesis of 2-Chromanone-Fused [3.2.0] Bicycles **3** S3

2.2 Synthesis of Fluorinated Bicyclo[3.2.0] Heptenone **5** S3

2.3 Optimization of the Reaction Conditions S4

3. General Procedure for the Synthesis of Bicyclo[3.2.0] Heptenone Derivatives

3.1 Synthesis of Product **6** S5

3.2 Synthesis of Compound **7** S5

3.3 Synthesis of Compounds **8** and **9** S6

4. Characterization Data of Products (**3a-3n**, **5a-5l**, **6-9**) S7

5. NMR Spectras of Products S20

6. X-Ray Diffraction of compound

6.1 X-Ray Diffraction of **3a** S60

6.2 X-Ray Diffraction of **5a** S65

6.3 X-Ray Diffraction of **9** S71

1. General Information

All the starting materials were obtained from commercial sources and were used without further purification unless otherwise stated. Toluene, THF and Et_2O were dried and distilled from sodium benzophenone prior to use. $CHCl_3$ and CH_2Cl_2 were distilled from CaH_2 prior to use. Dioxane was dried and distilled from Na prior to use. Melting points of solid products were measured using a Shanghai YDWG WRS-2A. ^1H and ^{13}C NMR spectra were recorded on a AMX500 (500 MHz) or AMX400 (400 MHz) spectrometer. Chemical shifts were reported in parts per million (ppm), and the residual solvent peak was used as an internal reference: proton (chloroform δ 7.26), carbon (chloroform δ 77.0). Multiplicity was indicated as follows: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), dd (doublet of doublet). Coupling constants were reported in Hertz (Hz). All high-resolution mass spectra were obtained on a Finnigan/MAT 95XL-T spectrometer. For thin layer chromatography (TLC), Merck pre-coated TLC plates (Merck 60 F254) were used, and compounds were visualized with a UV light at 254 nm. Flash chromatographic separations were performed on Merck 60 (0.040 - 0.063 mm) mesh silica gel. *S*ubstituted 3-carbaldehyde coumarins **1**[1], 2,2,2-trifluoroacetaldehyde coumarins **4**[2] and ynones **2**[3] were prepared according to the literature reported methods.

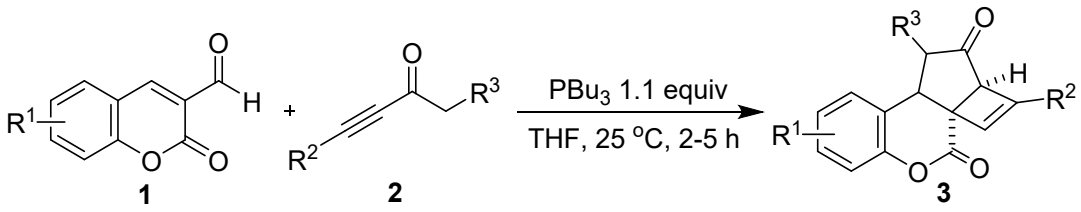
1. L. Floreková, R. Flašík, H Stankovičová and A. Gáplovský, *Synth. Commun.*, 2011, **41**(10), 1514.

2. H. Li, L. Cai, J. Li, Y. Hu, P. Zhou and J. Zhang, *Dyes and Pigments,* 2011, **91**(3), 309

3. M. Yamaguchi, K. Shibato, S. FuJiwara and I. Hirao, *Synth.*, **1986**, 421.

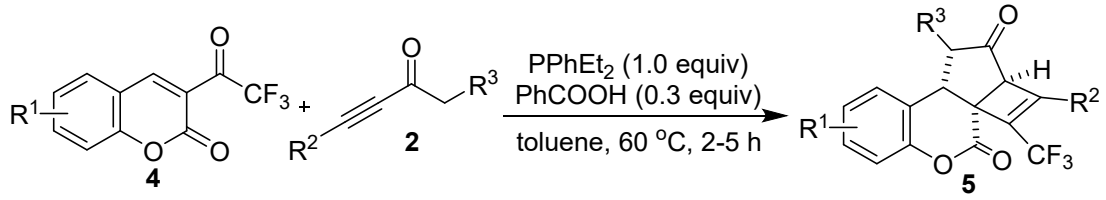
2. Representative Procedure for Tandem [3+2] Cyclization/Intramolecular Wittig Reaction

2.1 Synthesis of 2-Chromanone-fused [3.2.0] Bicycles 3



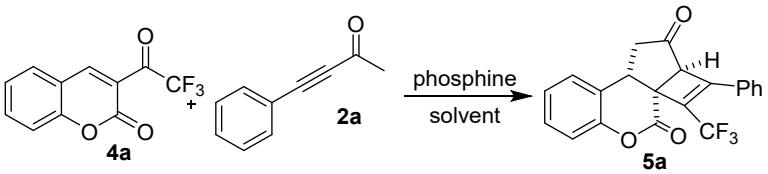
To a flame-dried round bottle flask with a magnetic stirring bar was added 3-carbaldehyde coumarin **1** (0.24 mmol, 1.2 equiv), PBu_3 (0.22 mmol, 1.1 equiv), followed by the addition of anhydrous THF (4 mL). Ynone **2** (0.2 mmol, 1.0 equiv) was then added. The reaction solution was stirred under nitrogen atmosphere at room temperature for 2-5 h until the disappearing of starting material **2** (monitored by TLC). The solvent was then removed *in vacuo* and the resulting residue was purified by column chromatography on silica gel (hexane/EtOAc = 15:1 to 5:1) to afford the corresponding products **3** (48 - 61% yield).

2.2 Synthesis of Fluorinated Bicyclo[3.2.0] Heptenone 5



To a solution of 2,2,2-trifluoroacetaldehyde coumarin **4** (0.2 mmol, 1.0 equiv) and ynone **2** (0.40 mmol, 2.0 equiv) in toluene (2 mL) was added PPh_2Et (0.2 mmol, 1.0 equiv), followed by the addition of PhCOOH (0.06 mmol, 0.3 equiv). The resulting mixture was stirred under nitrogen atmosphere at 60 °C for 2-4 h. Upon completion of the reaction, the solvent was removed *in vacuo* and the residue was purified by column chromatography on silica gel (hexane/EtOAc = 20:1 to 3:1) to afford cyclization adduct **5** (36 - 87% yields).

2.3 <u>Optimization of the Reaction Conditions</u>[a]

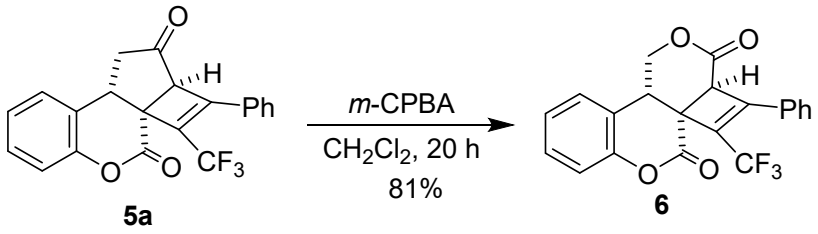


entry	phosphine	additive	solvent	temp. °C	time (h)	yield (%)[b]
1	Ph_2PCH_3	PhCOOH	CH_2Cl_2	RT	17	39
2	Ph_2PCH_3	PhCOOH	THF	RT	17	43
3	Ph_2PCH_3	PhCOOH	CH_3CN	RT	17	56
4	Ph_2PCH_3	PhCOOH	EtOH	RT	20	14
5	Ph_2PCH_3	PhCOOH	Toluene	RT	17	61
6	Bu_3P	PhCOOH	Toluene	RT	20	61
7	Ph_3P	PhCOOH	Toluene	RT	20	32
8	$PhPEt_2$	PhCOOH	Toluene	RT	15	64
9	$PhPEt_2$	PhCOOH	Toluene	40	8	78
10	$PhPEt_2$	PhCOOH	Toluene	60	2	87
11	$PhPEt_2$	PhCOOH	Toluene	80	1.5	82
12	Ph_2PCH_3	PhCOOH	Toluene	60	2	84
13	PCy_3	PhCOOH	Toluene	60	2	0
14	DPPE	PhCOOH	Toluene	60	2	47
15	P(*p*-OMePh)$_3$	PhCOOH	Toluene	60	2	56
16	P(*p*-FPh)$_3$	PhCOOH	Toluene	60	2	52
17	$PhPEt_2$	PhCOOH	Toluene (0.3 mL)	60	30	28
18	$PhPEt_2$	PhCOOH	Toluene (0.5 mL)	60	30	37
19	$PhPEt_2$	PhCOOH	Toluene (0.7 mL)	60	30	46
20	$PhPEt_2$	\	Toluene	60	30	34
21	$PhPEt_2$	PhOH	Toluene	60	2	48
22	$PhPEt_2$	CH_3COOH	Toluene	60	2	54
23	$PhPEt_2$	4-FPhCOOH	Toluene	60	18	52
24	$PhPEt_2$	4-NO_2PhCOOH	Toluene	60	23	5

[a] Reaction conditions: **4a** (0.20 mmol), **2a** (0.40 mmol), phosphine (0.20 mmol) and acid additive (0.06 mmol) in solvent (2.0 mL); [b] Isolated yields.

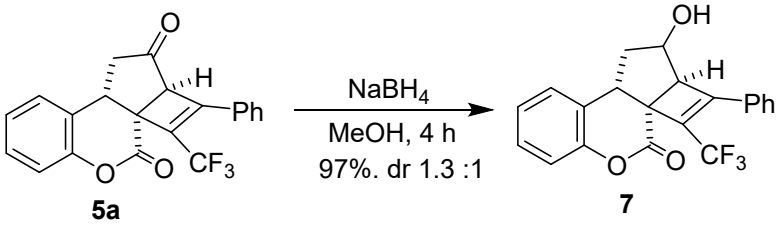
3. General Procedure for the Synthesis of Bicyclo[3.2.0] Heptenone Derivatives

3.1 Synthesis of Product 6



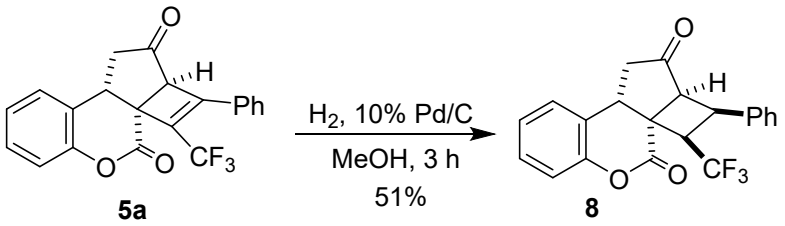
To a solution of product **5a** (50 mg, 0.135 mmol) in CH_2Cl_2 (0.6 mL) was added 85% *m*-CPBA (65.79 mg, 0.324 mmol) at 0 ^oC, then the resulting mixture was stirred at rt overnight. Upon the reaction finished, the reaction mixture was quenched with 10% K_2CO_3 solution and a saturated aqueous solution of $Na_2S_2O_3$. The aqueous layer was extracted two times with CH_2Cl_2. The combined organic layer was dried over Na_2SO_4, filtrated and concentrated under reduced pressure. Purification by silica gel column chromatography (Hexane/EtOAc = 10:1) gave 42.3 mg (81% yield) of lactone **6**.

3.2 Synthesis of Compound 7

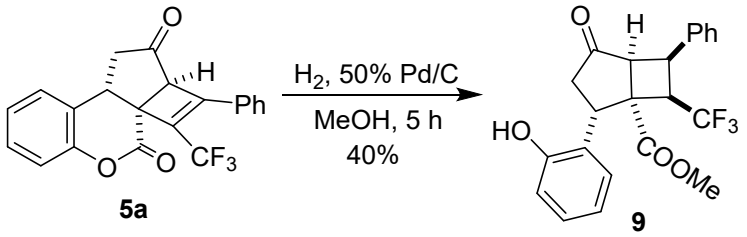


To a solution of product **5a** (37 mg, 0.1 mmol) in MeOH (1 mL) was added $NaBH_4$ (2.5 equiv) at room temperature under nitrogen, then the resulting mixture was allowed to stirred for 4 h. The reaction mixture was quenched with 6 M aqueous HCl 2 mL. The aqueous layer was then extracted two times with CH_2Cl_2. The combined organic layer was dried over Na_2CO_3, filtrated and concentrated under reduced pressure. Purification by silica gel column chromatography (Hexane/EtOAc = 10:1) gave 48.8 mg (97% yield) of product **7**.

3.3 <u>Synthesis of Compounds 8 and 9</u>



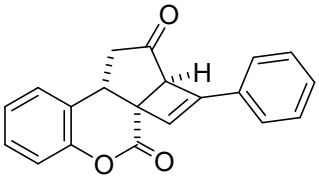
A solution of **5a** (0.135 mmol, 50 mg) in 1 mL of MeOH (previously degassed with nitrogen) was hydrogenated in the presence of 10% Pd/C (5 mg) at room temperature. Once **5a** was fully consumed as determined by TLC, Pd/C was removed by filtration, and the filtrate was concentrated. The crude product was purified by column chromatography on silica gel (Hexane/EtOAc = 30:1 to 10:1) to afford **8** as a white solid (25.6 mg, 51% yield).



A solution of **5a** (0.135 mmol, 50 mg) in 1 mL of MeOH (previously degassed with nitrogen) was hydrogenated in the presence of 50% Pd/C (25 mg) at room temperature. Once **5a** was full-y consumed as determined by TLC, Pd/C was removed by filtration, and the filtrate was concentrated. The crude product was purified by column chromatography on silica gel (Hexane/EtOAc = 30:1 to 10:1) to afford **9** as a white solid (21.8 mg, 40% yield).

4. Characterization Data of Products (3a-3n, 5a-5l, 6-9)

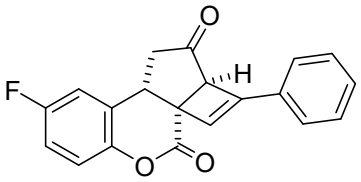
Analytical data of **3a:**



3a

61% yield; a white solid; Mp: 118.6 ~ 119.8 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.48 (d, *J* = 7.1 Hz, 2H), 7.40 - 7.34 (m, 3H), 7.31 (t, *J* = 7.7 Hz, 1H), 7.24 - 7.17 (m, 2H), 7.07 (d, *J* = 8.2 Hz, 1H), 6.72 (s, 1H), 3.93 (d, *J* = 7.6 Hz, 1H), 3.78 (s, 1H), 3.60 (dd, *J* = 17.5, 7.7 Hz, 1H), 2.77 (d, *J* = 17.5 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 209.1, 166.3, 149.4, 146.9, 130.0, 128.8, 128.5, 127.8, 127.7, 127.0, 124.5, 124.4, 119.7, 116.5, 56.7, 49.6, 40.3, 34.6; HRMS calcd for $C_{20}H_{15}O_3$ $[M+H]^+$ = 303.1016, found = 303.1024.

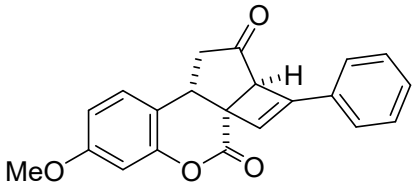
Analytical data of **3b:**



3b

56% yield; a white solid; Mp: 168.6 ~ 170.8 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.48 (dd, *J* = 7.7, 1.5 Hz, 2H), 7.37 (d, *J* = 7.6 Hz, 3H), 7.07 - 7.02 (m, 2H), 6.94 (dd, *J* = 8.8, 2.4 Hz, 1H), 6.71 (d, *J* = 1.1 Hz, 1H), 3.92 (d, *J* = 7.7 Hz, 1H), 3.78 (s, 1H), 3.61 (dd, *J* = 17.5, 7.8 Hz, 1H), 2.69 (d, *J* = 17.5 Hz, 1H); ^{19}F NMR (471 MHz, $CDCl_3$) δ -116.34; ^{13}C NMR (126 MHz, $CDCl_3$) δ 209.6, 166.9, 148.1, 146.4, 130.9, 129.8, 128.7, 127.7, 125.5, 119.0 (d, *J* = 8.4 Hz), 116.8, 116.6, 115.3, 115.1, 57.6, 50.1, 41.3, 35.8; HRMS calcd for $C_{20}H_{14}FO_3$ $[M+H]^+$ = 321.0921, found = 321.0942.

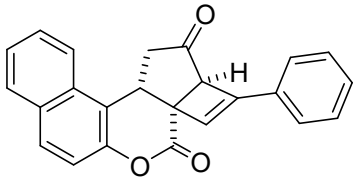
Analytical data of **3c:**



3c

52% yield; a white solid; Mp: 171.2 ~ 174.5 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.49 - 7.46 (m, 2H), 7.39 - 7.33 (m, 3H), 7.12 (d, *J* = 8.7 Hz, 1H), 6.75 (dd, *J* = 8.7, 2.6 Hz, 1H), 6.71 (d, *J* = 1.4 Hz, 1H), 6.59 (d, *J* = 2.6 Hz, 1H), 3.85 (d, *J* = 7.3 Hz, 1H), 3.80 (s, 3H), 3.75 (d, *J* = 1.2 Hz, 1H), 3.57 - 3.52 (m, 1H), 2.70 (d, *J* = 17.4 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 210.4, 167.5, 160.4, 151.1, 147.8, 131.0, 129.7, 129.6, 128.7, 127.9, 125.5, 112.3, 112.1, 102.3, 57.6, 55.6, 50.7, 41.2, 35.1; HRMS calcd for $C_{21}H_{17}O_4$ $[M+H]^+$ = 333.1121, found = 333.1133.

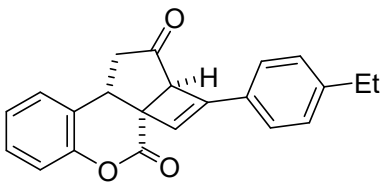
Analytical data of **3d:**



3d

44% yield; a white solid; Mp: 210.8 ~ 213.6 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.87 (d, *J* = 8.0 Hz, 1H), 7.81 (d, *J* = 9.0 Hz, 1H), 7.65 (d, *J* = 8.4 Hz, 1H), 7.59 - 7.54 (m, 3H), 7.51 - 7.47 (m, 1H), 7.41 - 7.37 (m, 2H), 7.21 (d, *J* = 8.9 Hz, 1H), 6.85 (s, 1H), 4.43 (dd, *J* = 8.9, 2.8 Hz, 1H), 4.04 (s, 1H), 3.81 - 3.76 (m, 1H), 2.95 - 2.91 (m, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 210.0, 167.6, 148.1, 147.8, 131.6, 131.2, 131.0, 130.5, 129.8, 129.3, 129.1, 128.7, 127.4, 125.6, 125.3, 123.4, 117.6, 114.6, 50.75, 45.8, 35.5, 29.7; HRMS calcd for $C_{22}H_{17}O_3$ $[M+H]^+$ = 353.1172, found = 353.1193.

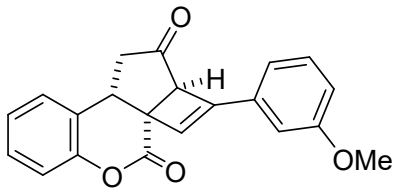
Analytical data of **3e:**



3e

55% yield; a white solid; Mp: 198.8 ~ 200.1 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40 (d, *J* = 8.1 Hz, 2H), 7.30 (t, *J* = 7.8 Hz, 1H), 7.24 -7.19 (m, 4H), 7.07 (d, *J* = 8.1 Hz, 1H), 6.65 (d, *J* = 1.1 Hz, 1H), 3.92 (d, *J* = 7.6 Hz, 1H), 3.76 (s, 1H), 3.60 (dd, *J* = 17.5, 7.7 Hz, 1H), 2.75 (d, *J* = 17.4 Hz, 1H), 2.67 - 2.61 (m, 2H), 1.23 (d, *J* = 7.6 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 210.4, 167.5, 150.4, 147.9, 146.3, 129.5, 128.8, 128.6, 128.2, 126.8, 125.6, 125.4, 117.5, 57.7, 50.6, 41.3, 35.7, 28.9, 15.4; HRMS calcd for $C_{22}H_{19}O_3$ $[M+H]^+$ = 331.1329, found = 331.1321.

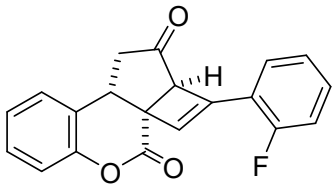
Analytical data of **3f:**



3f

54% yield; a white solid; Mp: 182.8 ~ 185.1 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33 - 7.27 (m, 2H), 7.24 (d, *J* = 7.5 Hz, 1H), 7.20 (d, *J* = 7.4 Hz, 1H), 7.07 (d, *J* = 8.0 Hz, 2H), 7.00 (s, 1H), 6.90 (dd, *J* = 8.2, 2.2 Hz, 1H), 6.72 (s, 1H), 3.93 (d, *J* = 7.6 Hz, 1H), 3.82 (s, 3H), 3.76 (s, 1H), 3.59 (dd, *J* = 17.5, 7.7 Hz, 1H), 2.77 (d, *J* = 17.4 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 210.1, 167.3, 159.8, 150.4, 147.8, 132.3, 129.8, 129.6, 128.8, 128.3, 125.4, 120.7, 118.1, 117.5, 115.9, 110.3, 57.7, 55.3, 50.6, 41.3, 35.6; HRMS calcd for $C_{21}H_{17}O_4$ $[M+H]^+$ = 333.1121, found = 333.11129.

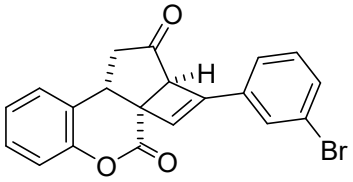
Analytical data of **3g:**



3g

38% yield; a white solid; Mp: 172.6 ~ 175.3 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.30 - 7.22 (m, 2H), 7.17 - 7.10 (m, 4H), 7.03 - 6.95 (m, 2H), 6.69 (d, *J* = 1.2 Hz, 1H), 3.87 (d, *J* = 7.5 Hz, 1H), 3.69 (s, 1H), 3.51 (dd, *J* = 17.6, 7.7 Hz, 1H), 2.72 (d, *J* = 17.6 Hz, 1H); ^{19}F NMR (471 MHz, $CDCl_3$) δ -112.10; ^{13}C NMR (126 MHz, $CDCl_3$) δ 209.8, 167.1, 150.3, 146.8, 130.4 (d, *J* = 8.1 Hz), 130.0, 129.7, 129.6, 128.8, 125.5, 121.3, 120.5, 117.5, 116.8, 112.3, 112.2, 57.6, 50.7, 41.3, 35.5; HRMS calcd for $C_{20}H_{14}FO_3$ $[M+H]^+$ = 321.0921, found = 321.0919.

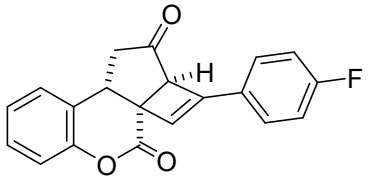
Analytical data of **3h:**



3h

50% yield; a white solid; Mp: 183.2 ~ 187.6 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.64 (t, *J* = 1.7 Hz, 1H), 7.49 - 7.45 (m, 1H), 7.38 (d, *J* = 7.8 Hz, 1H), 7.31 (dd, *J* = 11.2, 4.1 Hz, 1H), 7.25 - 7.16 (m, 3H), 7.08 (dd, *J* = 8.2, 0.8 Hz, 1H), 6.76 (d, *J* = 1.4 Hz, 1H), 3.94 (d, *J* = 7.5 Hz, 1H), 3.75 (d, *J* = 1.2 Hz, 1H), 3.60 - 3.55 (m, 1H), 2.79 (d, *J* = 17.6 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 209.7, 167.1, 150.3, 146.5, 132.9, 132.7, 130.3, 129.8, 129.7, 128.8, 128.4, 125.5, 124.2, 122.9, 120.5, 117.5, 57.6, 50.8, 41.3, 35.5; HRMS calcd for $C_{20}H_{14}BrO_3$ $[M+H]^+$ = 381.0121, found = 381.0138.

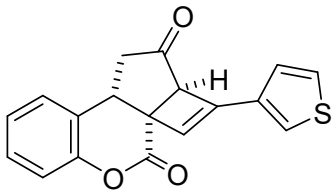
Analytical data of **3i:**



3i

58% yield; a white solid; Mp: 132.8 ~ 136.7 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.47 (dd, *J* = 8.5, 5.4 Hz, 2H), 7.31 (t, *J* = 7.3 Hz, 1H), 7.24 - 7.18 (m, 2H), 7.06 (t, *J* = 8.9 Hz, 3H), 6.66 (s, 1H), 3.93 (d, *J* = 7.5 Hz, 1H), 3.75 (s, 1H), 3.59 (dd, *J* = 17.6, 7.6 Hz, 1H), 2.78 (d, *J* = 17.5 Hz, 1H); ^{19}F NMR (471 MHz, $CDCl_3$) δ -109.91; ^{13}C NMR (126 MHz, $CDCl_3$) δ 210.2, 167.3, 164.5, 162.5, 150.3, 146.8, 129.6, 128.8, 127.6, 127.5, 127.4 (d, *J* = 2.6 Hz), 125.5, 120.6, 117.5, 116.0, 115.8, 57.7, 50.6, 41.4, 35.6; HRMS calcd for $C_{20}H_{14}FO_3$ $[M+H]^+$ = 321.0921, found = 321.0929.

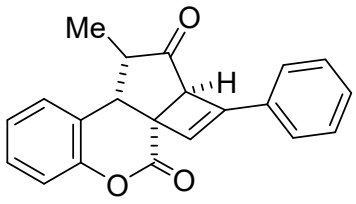
Analytical data of **3j:**



3j

41% yield; a white solid; Mp: 127.2 ~ 130.2 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36 (d, *J* = 5.0 Hz, 1H), 7.30 (t, *J* = 7.7 Hz, 1H), 7.24 - 7.17 (m, 2H), 7.14 (d, *J* = 3.5 Hz, 1H), 7.07 (d, *J* = 8.1 Hz, 1H), 7.04 - 6.93 (m, 1H), 6.45 (s, 1H), 3.93 (d, *J* = 7.6 Hz, 1H), 3.72 (s, 1H), 3.63 (dd, *J* = 17.6, 7.7 Hz, 1H), 2.78 (d, *J* = 17.4 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 209.6, 167.2, 150.3, 141.7, 129.6, 128.8, 127.9, 127.7, 127.6, 125.8, 125.4, 120.6, 117.5, 58.3, 51.5, 41.3, 35.9; HRMS calcd for $C_{18}H_{13}O_3S$ $[M+H]^+$ = 309.0580, found = 309.0577.

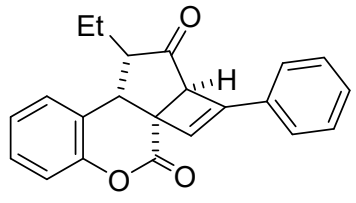
Analytical data of **3k:**



3k

48% yield; a white solid; Mp: 169.0 ~ 172.1 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.59 (dd, *J* = 8.1, 1.3 Hz, 2H), 7.42 - 7.29 (m, 4H), 7.21 - 7,18 (m, 2H), 7.12 (d, *J* = 8.0 Hz, 1H), 6.77 (s, 1H), 4.23 (d, *J* = 1.9 Hz, 1H), 3.46 (d, *J* = 8.5 Hz, 1H), 3.00 - 2.97 (m, 1H), 1.41 (d, *J* = 7.2 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 209.9, 168.3, 149.9, 148.9, 131.9, 131.4, 129.6, 129.2, 128.8, 128.6, 125.8, 125.1, 121.8, 117.6, 59.7, 58.1, 48.9, 45.5, 16.9; HRMS calcd for $C_{21}H_{17}O_3$ $[M+H]^+$ = 317.1172, found = 317.1179.

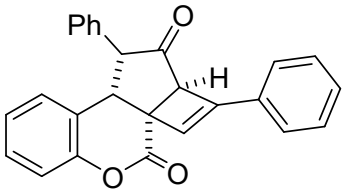
Analytical data of **3l:**



3l

51% yield; a white solid; Mp: 174.2 ~ 176.9 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.62 - 7.49 (m, 2H), 7.40 - 7.27 (m, 4H), 7.23 - 7.13 (m, 2H), 7.07 (d, *J* = 8.3 Hz, 1H), 6.75 (s, 1H), 4.06 (d, *J* = 1.5 Hz, 1H), 3.68 (d, *J* = 4.2 Hz, 1H), 2.94 - 2.77 (m, 1H), 1.96 - 1.82 (m, 2H), 1.06 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 211.3, 167.8, 150.0, 147.6, 131.2, 130.7, 129.6, 129.1, 128.8, 128.6, 125.6, 125.3, 122.2, 117.5, 63.0, 60.2, 49.5, 41.3, 28.5, 12.6; HRMS calcd for $C_{22}H_{19}O_3$ $[M+H]^+$ = 331.1329, found = 331.1330.

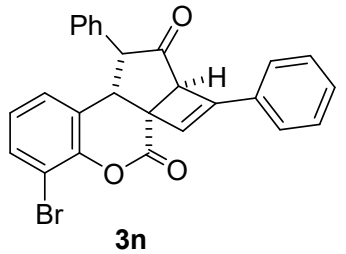
Analytical data of **3m:**



3m

59% yield; a white solid; Mp: 209.2 ~ 211.9 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.60 (d, *J* = 6.8 Hz, 2H), 7.38 (d, *J* = 7.5 Hz, 3H), 7.32 - 7.28 (m, 4H), 7.13 (d, *J* = 8.2 Hz, 1H), 7.08 (d, *J* = 6.9 Hz, 2H), 7.02 (t, *J* = 7.5 Hz, 1H), 6.80 (s, 1H), 6.69 (d, *J* = 7.4 Hz, 1H), 4.40 (d, *J* = 4.8 Hz, 1H), 4.16 (d, *J* = 9.1 Hz, 1H), 4.00 (d, *J* = 9.2 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 206.7, 168.1, 149.7, 148.0, 136.7, 131.9, 131.3, 129.7, 129.3, 129.0, 128.7, 128.6, 127.7, 125.9, 125.0, 121.4, 117.5, 69.8, 60.0, 48.5, 46.1; HRMS calcd for $C_{26}H_{19}O_3$ $[M+H]^+$ = 379.1329, found = 379.1324.

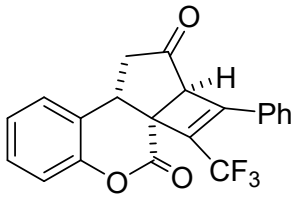
Analytical data of **3n:**



3n

60% yield; a white solid; Mp: 198.4 ~ 200.7 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.61 (d, *J* = 7.5 Hz, 2H), 7.53 (d, *J* = 7.9 Hz, 1H), 7.42 - 7.28 (m, 6H), 7.06 (d, *J* = 7.3 Hz, 2H), 6.86 (t, *J* = 7.8 Hz, 1H), 6.80 (s, 1H), 6.56 (d, *J* = 7.7 Hz, 1H), 4.43 (s, 1H), 4.13 (d, *J* = 9.8 Hz, 1H), 3.98 (d, *J* = 9.8 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 206.0, 167.0, 148.4, 146.7, 136.2, 133.2, 131.6, 131.2, 129.8, 129.0, 128.8, 128.6, 127.9, 127.8, 126.0, 125.5, 123.1, 111.2, 100.0, 70.1, 60.0, 48.4, 46.7; HRMS calcd for $C_{26}H_{18}BrO_3$ $[M+H]^+$ = 457.0434, found = 457.0456.

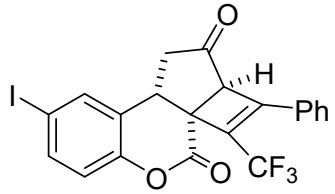
Analytical data of **5a:**



5a

87% yield; a white solid; Mp: 158.9 ~ 159.5 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.65 (d, *J* = 7.2 Hz, 2H), 7.46 (q, *J* = 6.2 Hz, 3H), 7.34 (t, *J* = 7.5 Hz, 1H), 7.24 (dd, *J* = 11.2, 7.5 Hz, 2H), 7.10 (d, *J* = 8.1 Hz, 1H), 4.11 (d, *J* = 7.5 Hz, 1H), 3.76 (s, 1H), 3.53 (dd, *J* = 17.6, 7.6 Hz, 1H), 2.88 (d, *J* = 17.6 Hz, 1H); ^{19}F NMR (471 MHz, $CDCl_3$) δ -61.81; ^{13}C NMR(126 MHz, $CDCl_3$) δ 207.5, 165.1, 150.1, 148.93, 148.88, 131.7, 129.9, 129.1, 128.8, 128.31, 128.30, 125.7, 125.6 (q, *J* = 37.8 Hz), 120.8 (q, *J* = 272.0 Hz), 119.7, 117.7, 55.7, 51.8, 41.1, 34.6; HRMS calcd for $C_{21}H_{14}F_3O_3$ $[M+H]^+$ = 371.0890, found = 371.0904.

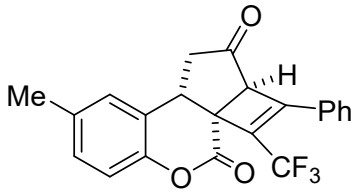
Analytical data of **5b:**



5b

36% yield; a yellow solid; Mp: 212.6 ~ 215.0 °C; ^{1}H NMR(500 MHz, $CDCl_3$) δ 7.72 - 7.60 (m, 3H), 7.55 (s, 1H), 7.52 - 7.42 (m, 3H), 6.85 (d, *J* = 8.6 Hz, 1H), 4.08 (d, *J* = 7.6 Hz, 1H), 3.84 - 3.68 (m, 1H), 3.53 (dd, *J* = 17.7, 7.7 Hz, 1H), 2.82 (d, *J* = 17.7 Hz, 1H); ^{19}F NMR (471 MHz, $CDCl_3$) δ - 61.81; ^{13}C NMR(126 MHz, $CDCl_3$) δ 206.8, 164.4, 150.0, 149.1, 138.9, 137.6, 131.9, 129.1, 128.6, 128.34, 128.33, 125.3 (q, *J* = 39.1 Hz), 122.2, 120.7 (q, *J* = 270.1 Hz), 119.7, 100.0, 88.7, 55.7, 51.3, 41.1, 34.4; HRMS calcd for $C_{21}H_{13}F_3IO_3$ $[M+H]^+$ = 496.9856, found = 496.9867.

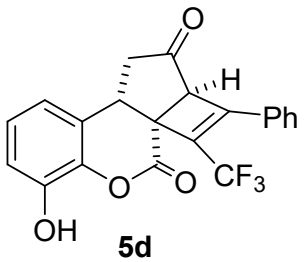
Analytical data of **5c:**



5c

65% yield; a white solid; Mp: 199.2 ~ 200 °C; ^{1}H NMR(500 MHz, $CDCl_3$) δ 7.64 (dd, *J* = 7.7, 1.7 Hz, 2H), 7.53 - 7.38 (m, 3H), 7.12 (d, *J* = 8.1 Hz, 1H), 7.03 - 6.90 (m, 2H), 4.06 (d, *J* = 7.5 Hz, 1H), 3.74 (s, 1H), 3.51 (dd, *J* = 17.7, 7.4 Hz, 1H), 2.87 (d, *J* = 17.6 Hz, 1H), 2.34 (s, 3H); ^{19}F NMR (471 MHz, $CDCl_3$) δ -61.83; ^{13}C NMR(126 MHz, $CDCl_3$) δ 207.6, 165.2, 148.9, 148.8, 148.0, 135.4, 131.7, 130.5, 129.1, 129.0, 128.8, 128.3, 125.7 (q, *J* = 37.8 Hz), 120.8 (q, *J* = 272.2 Hz), 119.2, 117.4, 55.7, 51.8, 41.1, 34.6, 20.9; HRMS calcd for $C_{22}H_{16}F_3O_3$ $[M+H]^+$ = 385.1046, found = 385.1048.

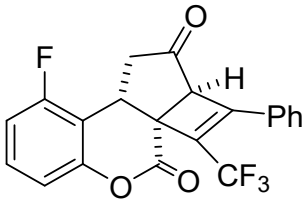
Analytical data of **5d:**



5d

50% yield; a white solid; Mp: 160.3 ~ 162.5 °C; ^{1}H NMR(500 MHz, $CDCl_3$) δ 7.75 - 7.59 (m, 2H), 7.53 - 7.40 (m, 3H), 7.11 (t, *J* = 8.0 Hz, 1H), 6.97 (d, *J* = 8.1 Hz, 1H), 6.76 (d, *J* = 7.9 Hz, 1H), 5.79 (s, 1H), 4.12 (d, *J* = 7.6 Hz, 1H), 3.86 - 3.74 (m, 1H), 3.54 - 3.49 (m, 1H), 2.87 (d, *J* = 17.7 Hz, 1H); ^{19}F NMR (471 MHz, $CDCl_3$) δ -61.82; ^{13}C NMR (126 MHz, $CDCl_3$) δ 207.0, 164.2, 144.1, 137.7, 131.8, 129.1, 128.6, 128.4, 126.0, 120.7 (q, *J* = 272.2 Hz), 120.6, 119.4, 116.4, 55.8, 51.8, 41.0, 34.8; HRMS calcd for $C_{21}H_{14}F_3O_4$ $[M+H]^+$ = 387.0839, found = 387.0831.

Analytical data of **5e:**

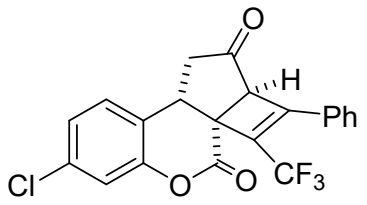


5e

87% yield, a brown solid; Mp: 189.0 ~ 191.0 °C; ^{1}H NMR(500 MHz, $CDCl_3$) δ 7.68 - 7.63 (m, 2H), 7.51 - 7.43 (m, 3H), 7.35 - 7.30 (m, 1H), 6.92 (d, *J* = 8.4 Hz, 2H), 4.20 (d, *J* = 8.3 Hz, 1H), 3.86 (s, 1H), 3.54 (dd, *J* = 18.6, 8.4 Hz, 1H), 3.06 - 3.01 (m, 1H); ^{19}F NMR (471 MHz, $CDCl_3$) δ -61.71, -110.37; ^{13}C NMR(126 MHz, $CDCl_3$) δ 207.6, 164.5, 150.7, 149.4, 143.5, 131.8, 130.5, 129.1, 128.4 (d, *J* = 2.5 Hz), 128.3, 127.2, 125.7 (q, *J* = 37.1 Hz), 120.7 (q, *J* = 272.2 Hz), 113.3 (d, *J* = 3.4 Hz),

112.5, 109.5, 56.8, 50.9, 41.9, 32.2; HRMS calcd for $C_{21}H_{13}F_4O_3$ $[M+H]^+$ = 389.0795, found = 389.0791.

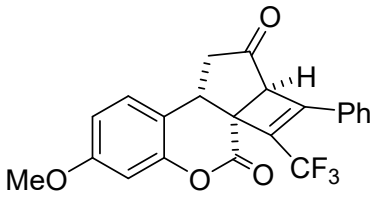
Analytical data of **5f:**



5f

40% yield; a white solid; Mp: 151.0 ~ 153.5 °C; ^{1}H NMR(500 MHz, $CDCl_3$) δ 7.66 - 7.61 (m, 2H), 7.49 - 7.43 (m, 3H), 7.23 - 7.16 (m, 2H), 7.12 (d, *J* = 1.9 Hz, 1H), 4.07 (d, *J* = 7.3 Hz, 1H), 3.76 (s, 1H), 3.53 (dd, *J* = 17.6, 7.5 Hz, 1H), 2.82 (d, *J* = 17.6 Hz, 1H); ^{19}F NMR (471 MHz, $CDCl_3$) δ -61.81; ^{13}C NMR(126 MHz, $CDCl_3$) δ 206.8, 164.4, 150.5, 149.0, 143.5, 135.3, 131.8, 129.8, 129.1, 128.6, 128.3, 126.0, 125.3 (q, *J* = 39.1 Hz), 120.7 (q, *J* = 272.2 Hz), 118.3, 118.0, 55.6, 51.5, 41.0, 34.4; HRMS calcd for $C_{21}H_{13}ClF_3O_3$ $[M+H]^+$ = 405.0500, found = 405.0502.

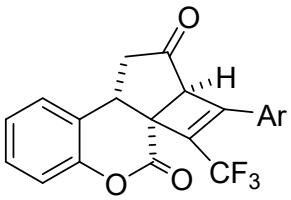
Analytical data of **5g:**



5g

71% yield; a white solid; Mp: 149.1 ~ 152.4 °C; ^{1}H NMR(500 MHz, $CDCl_3$) δ 7.61 - 7.55 (m, 2H), 7.46 - 7.33 (m, 3H), 7.05 (dd, *J* = 8.7, 0.6 Hz, 1H), 6.70 (dd, *J* = 8.7, 2.6 Hz, 1H), 6.54 (d, *J* = 2.6 Hz, 1H), 3.96 (d, *J* = 7.2 Hz, 1H), 3.74 (s, 3H), 3.70 - 3.64 (m, 1H), 3.43 - 3.38 (m, 1H), 2.74 (d, *J* = 17.5 Hz, 1H); ^{19}F NMR (471 MHz, $CDCl_3$) δ -61.81; ^{13}C NMR(126 MHz, $CDCl_3$) δ 207.6, 165.2, 160.7, 150.9, 148.9, 148.8, 131.7, 129.5, 129.1, 128.8, 128.3 (d, *J* = 2.1 Hz), 125.6 (q, *J* = 37.8 Hz), 120.8 (q, *J* = 272.2 Hz), 112.4, 111.2, 102.4, 55.6, 51.9, 41.0, 34.1, 29.7; HRMS calcd for $C_{21}H_{16}F_3O_4$ $[M+H]^+$ = 401.0995, found = 401.1001.

Analytical data of **5h:**

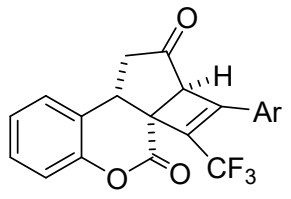


Ar = 4-OMePh

5h

71% yield; a white solid; Mp: 154.6 ~ 157.0 °C; ^{1}H NMR(500 MHz, $CDCl_3$) δ 7.63 - 7.45 (m, 2H), 7.24 (dd, *J* = 7.1, 1.1 Hz, 1H), 7.18 -7.08 (m, 2H), 7.05 - 6.97 (m, 1H), 6.93 - 6.83 (m, 2H), 4.01 (d, *J* = 7.5 Hz, 1H), 3.77 (s, 3H), 3.69 - 3.61 (m, 1H), 3.48 - 3.43 (m, 1H), 2.77 (d, *J* = 17.6 Hz, 1H); ^{19}F NMR (471 MHz, $CDCl_3$) δ -61.60; ^{13}C NMR(126 MHz, $CDCl_3$) δ 207.8, 165.3, 162.2, 150.1, 148.4, 148.3, 130.3, 129.9, 128.8, 125.7, 121.6, 122.2 (q, *J* = 37.8 Hz), 121.0 (q, *J* = 270.9 Hz), 119.6, 117.6, 114.5, 55.7, 55.5, 51.6, 41.2, 34.8; HRMS calcd for $C_{22}H_{16}F_3O_4$ $[M+H]^+$ = 401.0995, found = 401.1012.

Analytical data of **5i:**

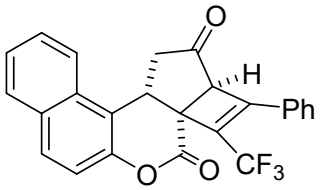


Ar=4-BrPh

5i

54% yield; a white solid; Mp: 136.3 ~ 139.2 °C; ^{1}H NMR(500 MHz, $CDCl_3$) δ ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.64 (dd, *J* = 7.9, 1.7 Hz, 1H), 7.61 - 7.56 (m, 1H), 7.50 - 7.44 (m, 2H), 7.43 - 7.39 (m, 1H), 7.37 - 7.32 (m, 1H), 7.25 - 7.23 (m, 1H), 7.10 (d, *J* = 8.1 Hz, 1H), 4.11 (d, *J* = 7.5 Hz, 1H), 3.83 - 3.68 (m, 1H), 3.56 - 3.48 (m, 1H), 2.88 (dd, *J* = 17.7, 5.9 Hz, 1H); ^{19}F NMR (471 MHz, $CDCl_3$) δ -61.81; ^{13}C NMR (126 MHz, $CDCl_3$) δ 207.4, 165.1, 150.1, 141.9, 132.5, 132.3, 129.6, 129.1, 128.8, 128.3, 127.6, 126.6 (q, *J* = 35.3 Hz), 125.7, 120.8 (q, *J* = 270.9 Hz), 119.7, 117.7(d, *J* = 3.7 Hz), 55.7, 41.1, 34.6, 27.7; HRMS calcd for $C_{21}H_{13}BrF_3O_3$ $[M+H]^+$ = 448.9995, found = 449.0032.

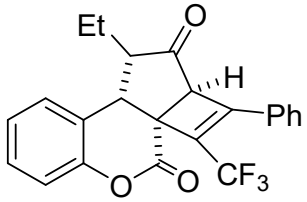
Analytical data of **5j:**



5j

41% yield; a white solid; Mp: 176.7 ~ 179.0 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.88 (d, *J* = 8.1 Hz, 1H), 7.83 (d, *J* = 9.0 Hz, 1H), 7.71 (dd, *J* = 7.7, 1.8 Hz, 2H), 7.67 (d, *J* = 8.5 Hz, 1H), 7.62 - 7.57 (m, 1H), 7.54 - 7.50 (m, 1H), 7.48 (t, *J* = 6.4 Hz, 3H), 7.23 (d, *J* = 8.9 Hz, 1H), 4.59 (dd, *J* = 8.7, 2.9 Hz, 1H), 4.02 (s, 1H), 3.75 (dd, *J* = 18.5, 8.1 Hz, 1H), 3.05 - 3.01 (m, 1H); ^{19}F NMR (471 MHz, $CDCl_3$) δ -61.49; ^{13}C NMR (126 MHz, $CDCl_3$) δ 207.3, 165.3, 149.2, 147.6, 131.8, 131.7, 130.9, 130.8, 129.4, 129.1, 128.9, 128.4, 127.6, 126.7 (q, *J* = 37.8 Hz), 125.5, 123.3, 120.9 (q, *J* = 272.2 Hz), 117.6, 113.7, 58.3, 51.6, 45.7, 34.5; HRMS calcd for $C_{25}H_{16}F_3O_3$ $[M+H]^+$ = 421.1046, found = 421.1012.

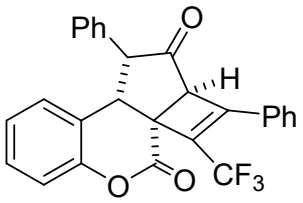
Analytical data of **5k:**



5k

66% yield; a light green solid; Mp: 132.4 ~ 134.0 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.70 (dd, *J* = 7.5, 1.9 Hz, 2H), 7.51 - 7.42 (m, 3H), 7.36 - 7.29 (m, 1H), 7.24 - 7.15 (m, 2H), 7.10 (d, *J* = 8.2 Hz, 1H), 4.07 - 3.97 (m, 1H), 3.84 (d, *J* = 4.1 Hz, 1H), 2.97 - 2.78 (m, 1H), 1.99 - 1.80 (m, 2H), 1.08 (t, *J* = 7.4 Hz, 3H); ^{19}F NMR (471 MHz, $CDCl_3$) δ -61.56; ^{13}C NMR(126 MHz, $CDCl_3$) δ 209.3, 165.7, 149.7, 149.20, 149.15, 131.6, 129.5, 129.0, 128.9, 128.8, 128.5, 128.0 (q, *J* = 37.8 Hz), 125.6, 121.3, 120.8 (q, *J* = 272.0 Hz), 117.7, 62.7, 58.1, 50.2, 40.2, 27.4, 12.3; HRMS calcd for $C_{22}H_{18}F_3O_3$ $[M+H]^+$ = 399.1203, found = 399.1221.

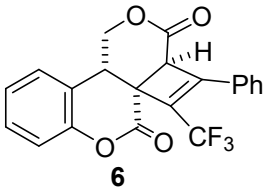
Analytical data of **5l:**



5l

60% yield; a white solid; Mp: 152.9 ~ 154.7 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (dd, *J* = 7.4, 2.0 Hz, 2H), 7.51 - 7.44 (m, 3H), 7.33 (d, *J* = 6.9 Hz, 4H), 7.15 (d, *J* = 8.0 Hz, 1H), 7.09 - 6.96 (m, 3H), 6.68 (d, *J* = 7.6 Hz, 1H), 4.36 (dd, *J* = 2.7, 1.6 Hz, 1H), 4.20 (d, *J* = 9.5 Hz, 1H), 4.11 (d, *J* = 9.5 Hz, 1H); ^{19}F NMR (471 MHz, $CDCl_3$) δ -62.04; ^{13}C NMR(126 MHz, $CDCl_3$) δ 206.4, 164.0, 149.1, 147.90, 147.85, 130.7, 128.9, 128.1, 127.7, 127.28, 127.26, 124.7, 124.6 (q, *J* = 37.8 Hz), 119.8 (q, *J* = 272.2 Hz), 118.6, 116.6, 50.8, 40.1, 33.6, 28.7; HRMS calcd for $C_{27}H_{18}F_3O_3$ $[M+H]^+$ = 447.1203, found = 447.1232.

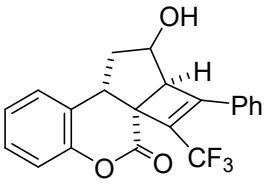
Analytical data of **6:**



6

81% yield; a white solid; Mp: 194.4 ~ 196.2 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.69 - 7.63 (m, 2H), 7.53 - 7.45 (m, 3H), 7.40 (t, *J* = 7.8 Hz, 1H), 7.34 (d, *J* = 7.7 Hz, 1H), 7.24 (dd, *J* = 7.6, 0.8 Hz, 1H), 7.17 (d, *J* = 8.2 Hz, 1H), 5.55 (d, *J* = 2.0 Hz, 1H), 3.98 (t, *J* = 4.4 Hz, 1H), 3.27 (dd, *J* = 17.1, 5.3 Hz, 1H), 2.96 (dd, *J* = 17.1, 4.0 Hz, 1H); ^{19}F NMR (471 MHz, $CDCl_3$) δ -61.55; ^{13}C NMR(126 MHz, $CDCl_3$) δ 166.9, 166.0, 150.3, 132.2, 130.4, 129.3, 128.7, 127.3, 126.9, 126.1, 120.8 (q, *J* = 272.2 Hz), 120.0, 119.2, 117.6, 74.9, 50.9, 33.0, 31.5; HRM*S* calcd for $C_{21}H_{14}F_3O_4$ $[M+H]^+$ = 387.0839, found = 387.0848.

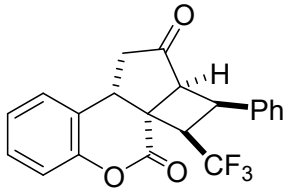
Analytical data of **7:**



7

97% yield; a white solid; Mp: 100.0 ~ 103.1 °C; the ^{1}H NMR analysis of the crude reaction mixture gave 1.3 :1 d.r.; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.72 (dd, *J* = 6.5, 3.2 Hz, 2H), 7.70 - 7.65 (m, 2H), 7.42 - 7.38 (m, 6H), 7.21 - 7.12 (m, 4H), 7.03 - 6.94 (m, 2H), 6.87 (d, *J* = 8.1 Hz, 1H), 6.84 (d, *J* = 8.1 Hz, 1H), 5.49 (d, *J* = 3.1 Hz, 1H), 5.43 (s, 1H), 4.14 - 3.97 (m, 2H), 3.85 (dd, *J* = 6.8, 3.1 Hz, 1H), 3.77 (d, *J* = 3.9 Hz, 1H), 3.52 (d, *J* = 6.1 Hz, 1H), 3.47 (d, *J* = 6.8 Hz, 2H), 3.37 (d, *J* = 4.0 Hz, 1H), 2.50 - 2.38 (m, 2H), 2.31 (dd, *J* = 12.4, 6.0 Hz, 1H), 2.25 - 2.15 (m, 1H); ^{19}F NMR (471 MHz, $CDCl_3$) δ -59.78, -60.50; ^{13}C NMR(126 MHz, $CDCl_3$, major) δ 150.3, 149.3, 149.2, 131.3, 130.4, 128.8, 128.7, 128.6, 127.9, 126.8 (q, *J* = 35.3 Hz), 124.7, 122.3, 121.4 (q, *J* = 273.4 Hz), 117.8, 92.9, 69.9, 55.6, 50.3, 46.0, 39.0; HRMS calcd for $C_{21}H_{16}F_3O_3$ $[M+H]^+$ = 373.1046, found = 373.1021.

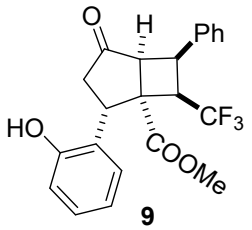
Analytical data of **8:**



8

51% yield; a white solid; Mp: 263.3 ~ 267.0 °C; ^{1}H NMR (500 MHz, DMSO) δ 7.49 - 7.33 (m, 6H), 7.31 (t, *J* = 7.1 Hz, 1H), 7.27 - 7.24 (m, 1H), 7.17 (d, *J* = 8.1 Hz, 1H), 4.61 (t, *J* = 9.5 Hz, 1H), 4.46 (dd, *J* = 13.4, 7.9 Hz, 1H), 4.18 (d, *J* = 10.1 Hz, 1H), 4.07 - 3.95 (m, 1H), 2.93 - 2.81 (m, 2H); ^{19}F NMR (471 MHz, DMSO) δ -61.94; ^{13}C NMR(126 MHz, DMSO) δ 212.5, 165.4, 150.2, 135.7, 130.6, 129.7, 128.7, 128.0, 127.8, 125.4, 121.8 (q, *J* = 265.9 Hz), 120.8, 119.7, 117.1, 100.0, 51.1, 50.7, 48.1, 43.5, 41.9, 37.9; HRMS calcd for $C_{27}H_{16}F_3O_3$ $[M+H]^+$ = 373.1046, found = 373.1077.

Analytical data of **9:**

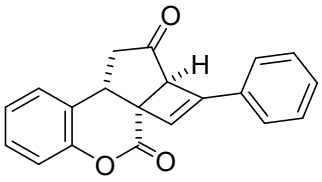


9

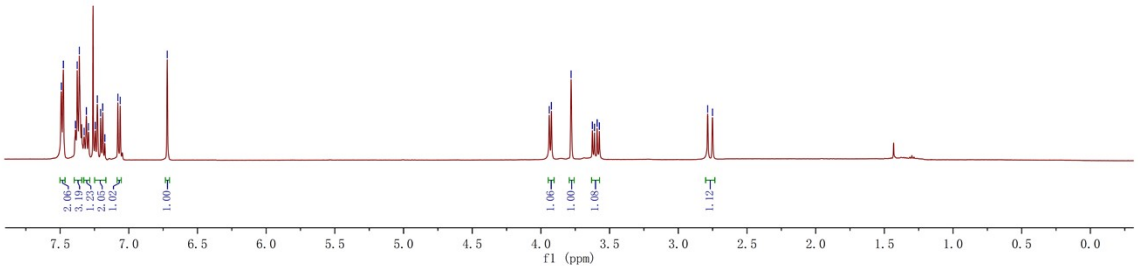
40% yield; a white solid; Mp: 203.6 ~ 206.8 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.23 - 7.16 (m, 5H), 7.12 - 6.91 (m, 2H), 6.76 (t, *J* = 7.5 Hz, 1H), 6.59 (d, *J* = 8.3 Hz, 1H), 5.97 (s, 1H), 4.24 (t, *J* = 11.5 Hz, 1H), 4.03 (d, *J* = 8.8 Hz, 1H), 3.87 (d, *J* = 11.2 Hz, 1H), 3.83 - 3.65 (m, 1H), 3.33 (dd, *J* = 19.7, 10.3

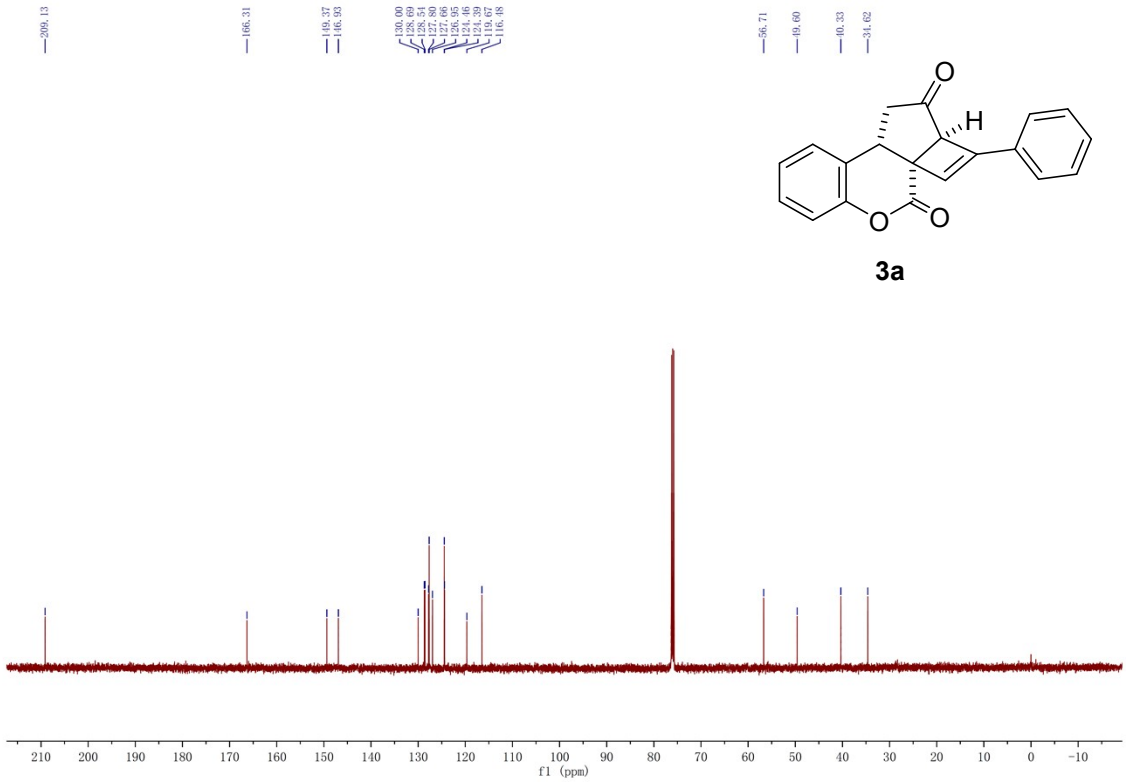
Hz, 1H), 3.19 (s, 3H), 2.84 (d, *J* = 19.9 Hz, 1H); ^{19}F NMR (471 MHz, $CDCl_3$) δ -60.56; ^{13}C NMR(126 MHz, $CDCl_3$) δ 218.0, 172.9, 153.5, 134.1, 131.4, 129.6, 128.9, 128.7, 128.2, 127.7, 126.9 (q, *J* =278.5 Hz), 120.4, 116.3, 55.2, 53.2, 52.1, 50.1 (d, *J* = 27.7 Hz), 47.0, 42.7, 39.6; HRMS calcd for $C_{22}H_{20}F_3O_4$ $[M+H]^+$ = 405.1308, found = 405.1325.

5. NMR *Spectra* of the Products



3a

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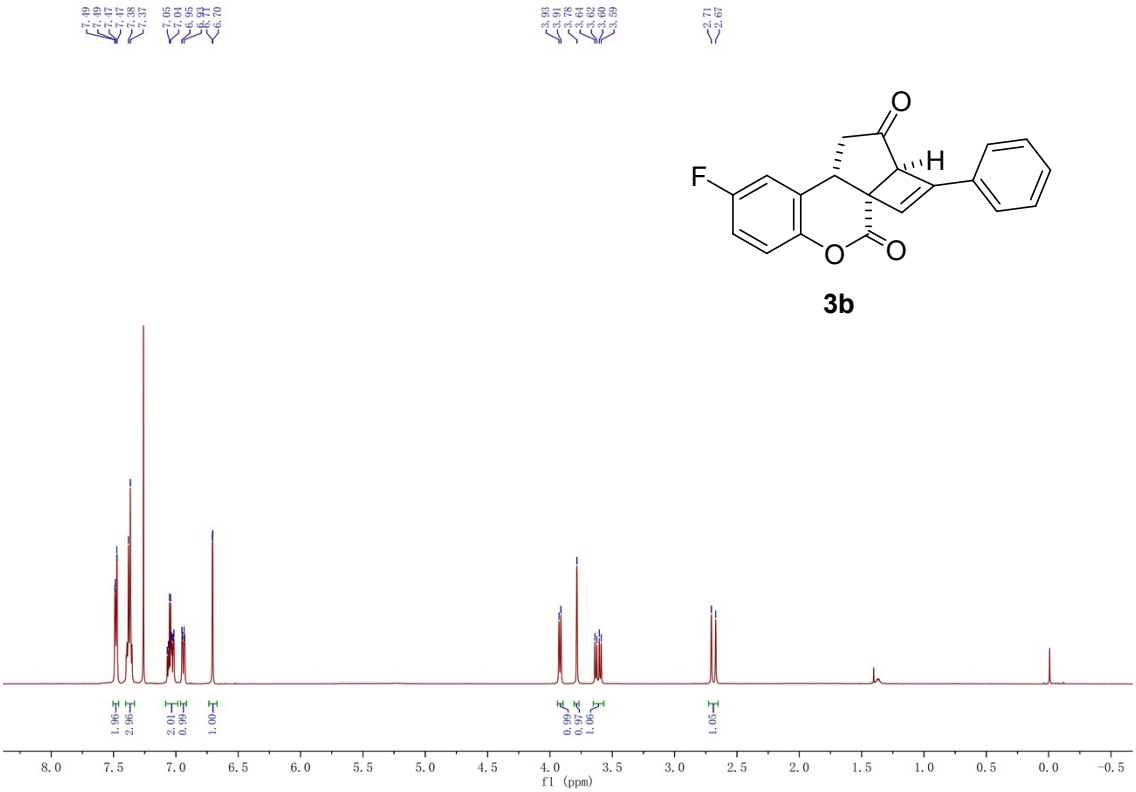
149.37
146.93
130.00
128.69
128.51
128.30
127.66
126.95
124.46
124.39
118.67
116.48
56.71
49.60
40.33
34.62
O
H
O
O
3a
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)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7.49
7.47
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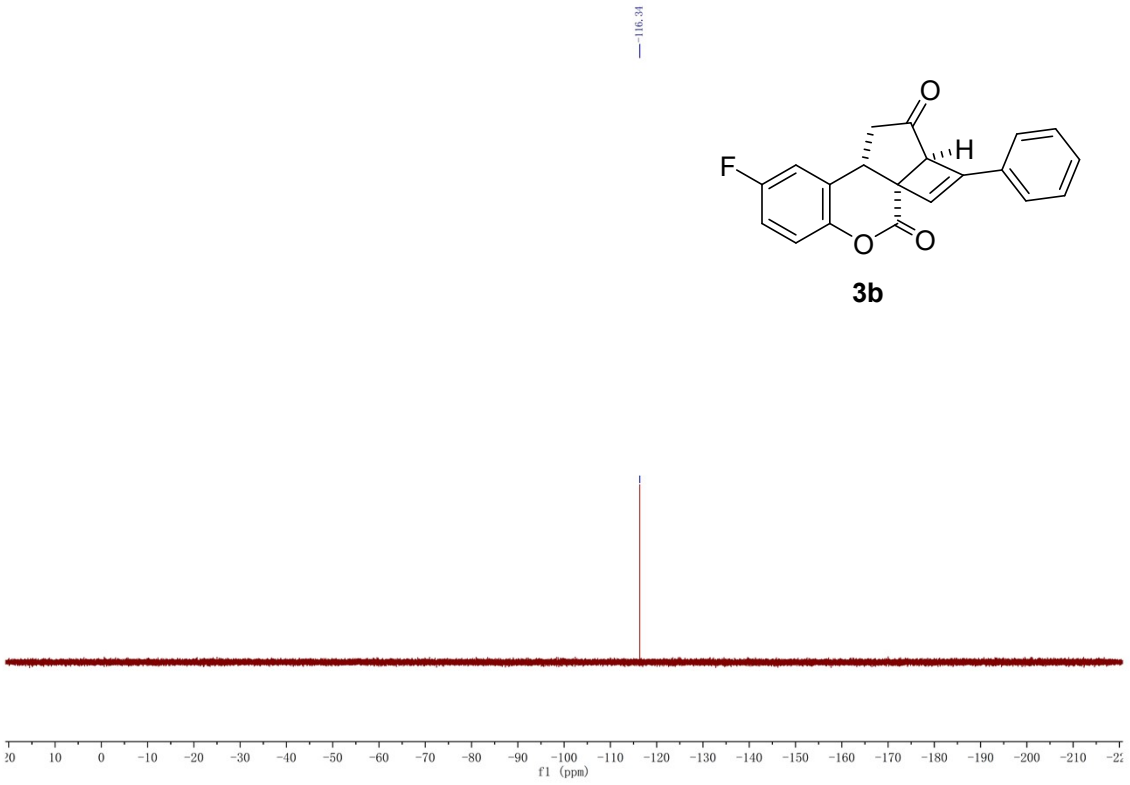
7.37
7.05
7.04
6.95
6.94
6.71
6.70
3.93
3.91
3.78
3.64
3.62
3.60
3.59
2.71
2.67
O
H
F
O
O
3b
1.96
2.96
2.01
0.99
1.00
0.99
0.97
1.06
1.05
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5
f1 (ppm)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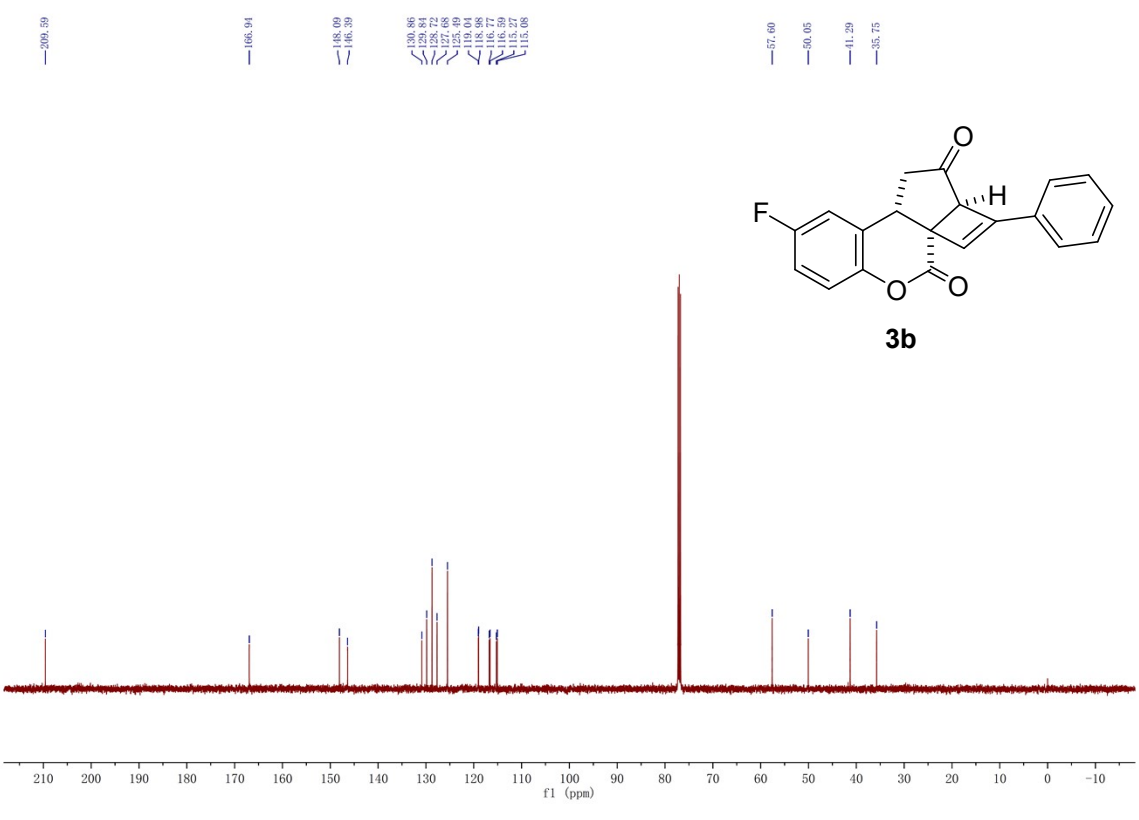
O
H
F
O
O
f1 (ppm)

3b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146.39
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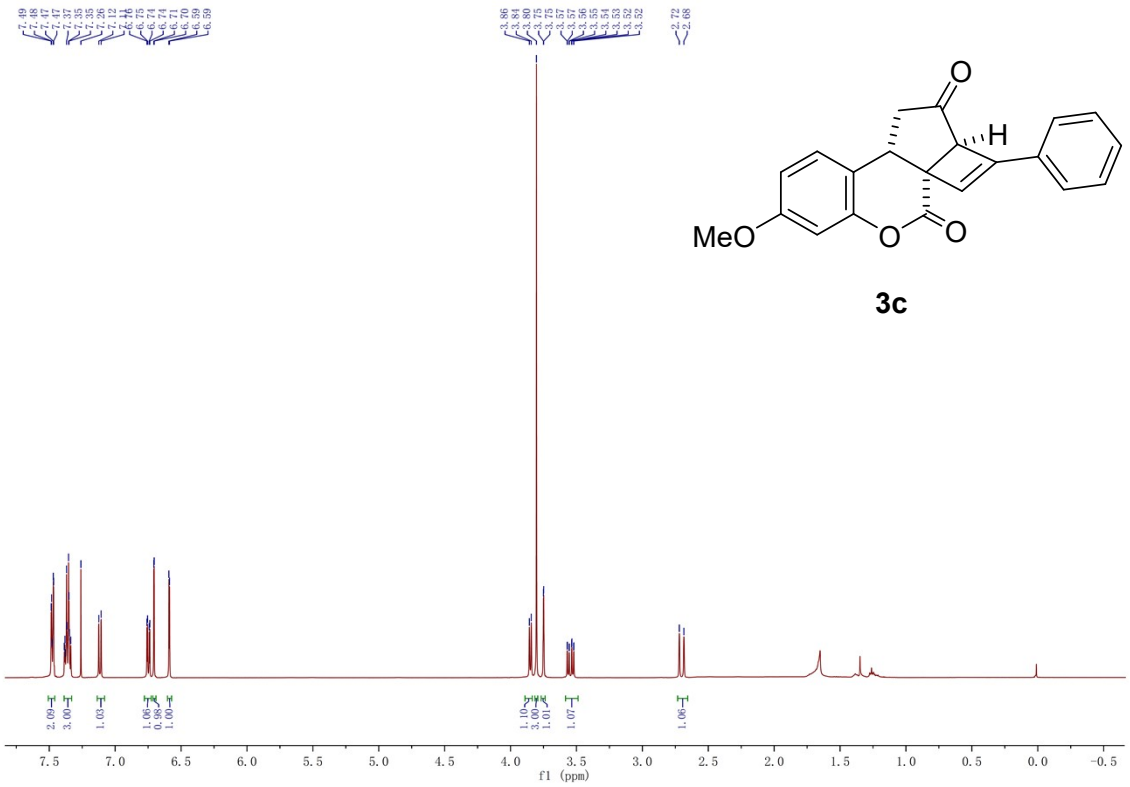
129.84
128.72
127.68
125.49
119.04
118.98
118.77
116.59
115.27
115.08
57.60
50.05
41.29
35.75
O
H
F
O
O
f1 (ppm)

3b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7.47
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7.35
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7.26
7.12
7.11
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6.75
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6.71
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3.56
3.55
3.54
3.53
3.52
3.52
2.72
2.68
2.09
3.00
1.63
1.06
0.98
1.00
1.10
3.00
1.01
1.07
1.06
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
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1.0
0.5
0.0
-0.5
f1 (ppm)

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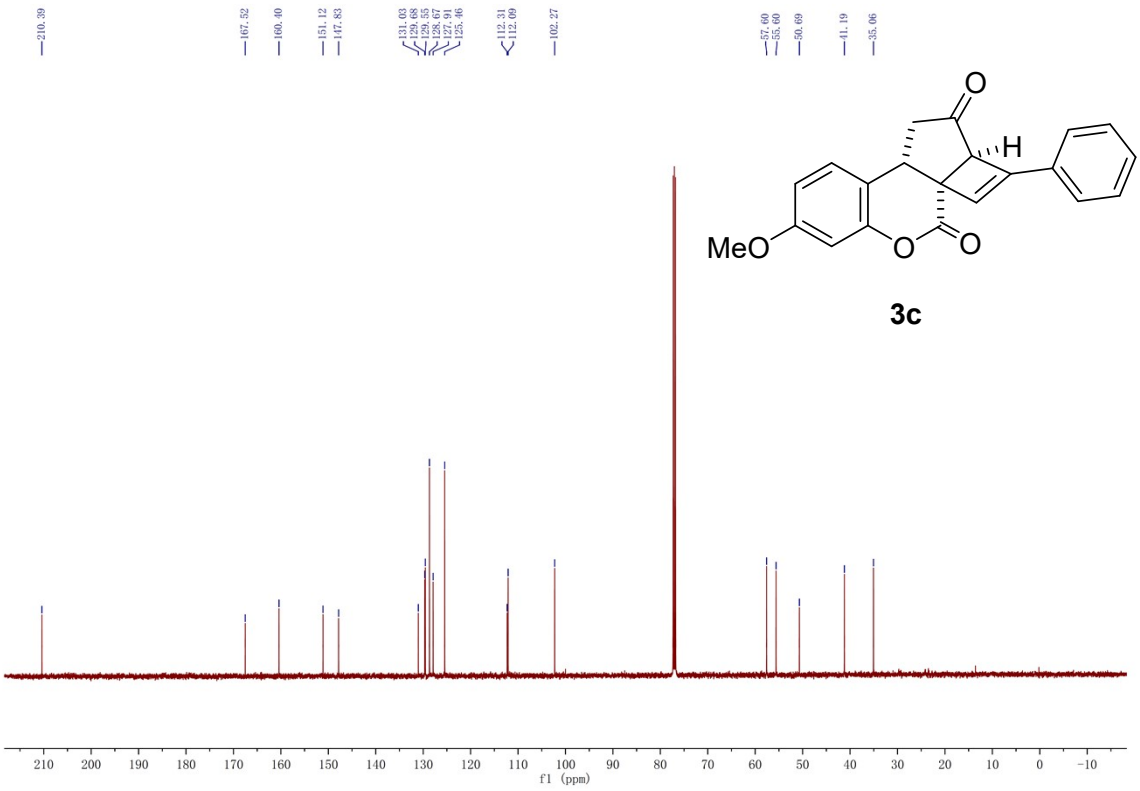
H
MeO
O
O

3c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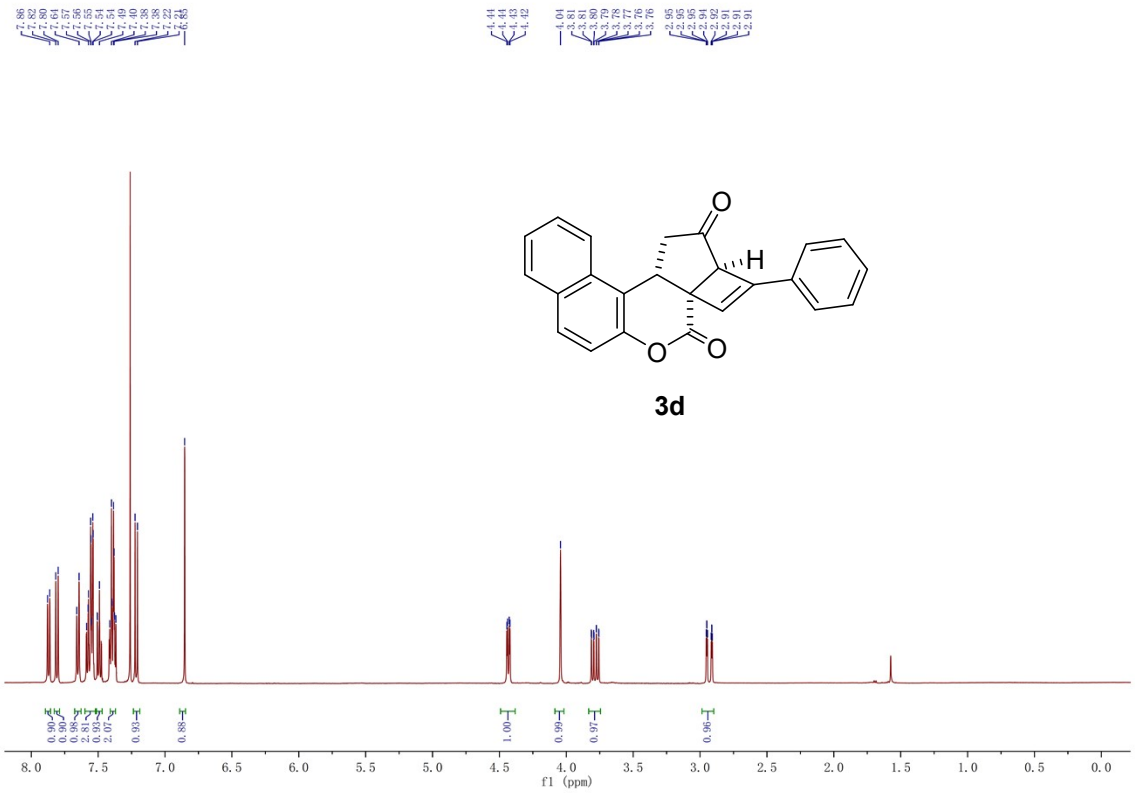
128.67
127.91
125.46
112.31
112.09
102.27
57.60
55.60
50.69
41.19
35.06
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

O
H
MeO
O
O

3c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3.76
3.76
2.95
2.95
2.94
2.92
2.91
2.91
2.91
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H
O
O
3d
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0.90
0.98
0.81
0.93
2.07
0.93
0.88
1.00
0.99
0.97
0.96
8.0
7.5
7.0
6.5
6.0
5.5
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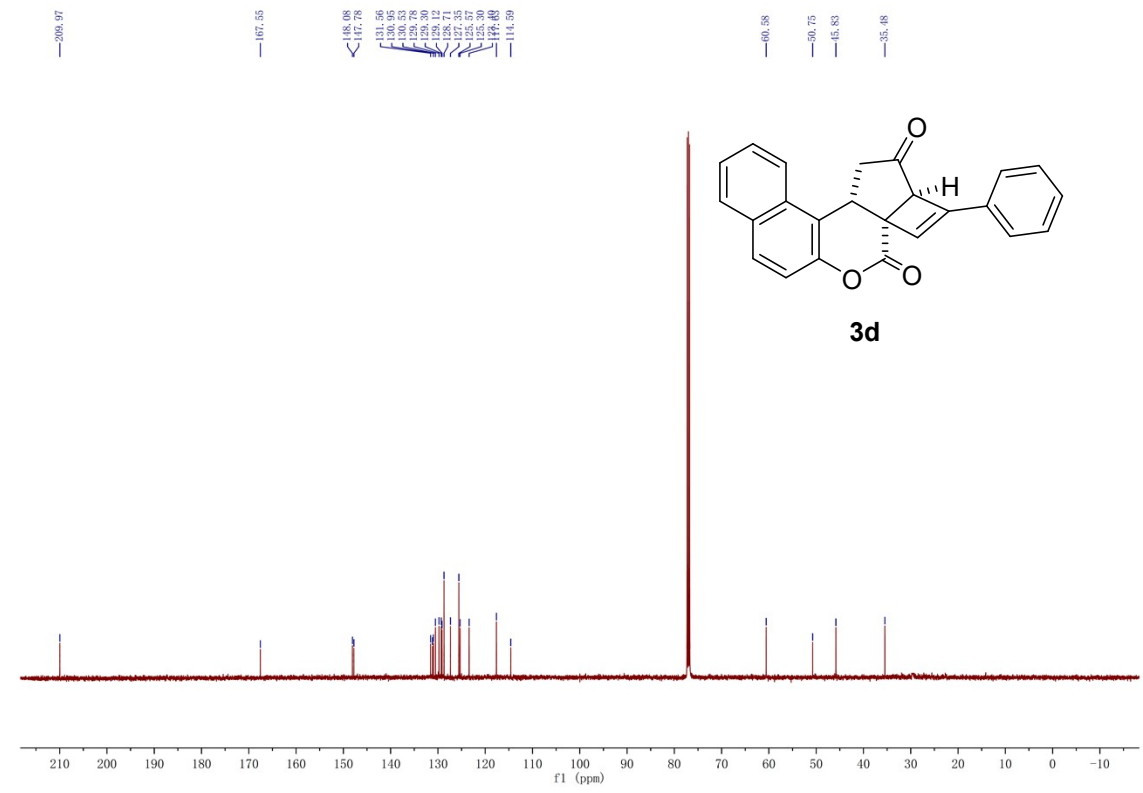
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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130.95
130.53
129.78
129.30
129.12
128.71
127.35
125.57
125.30
114.59
60.58
50.75
45.83
35.48
O
H
O
O
3d
210
200
190
180
170
160
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120
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80
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40
30
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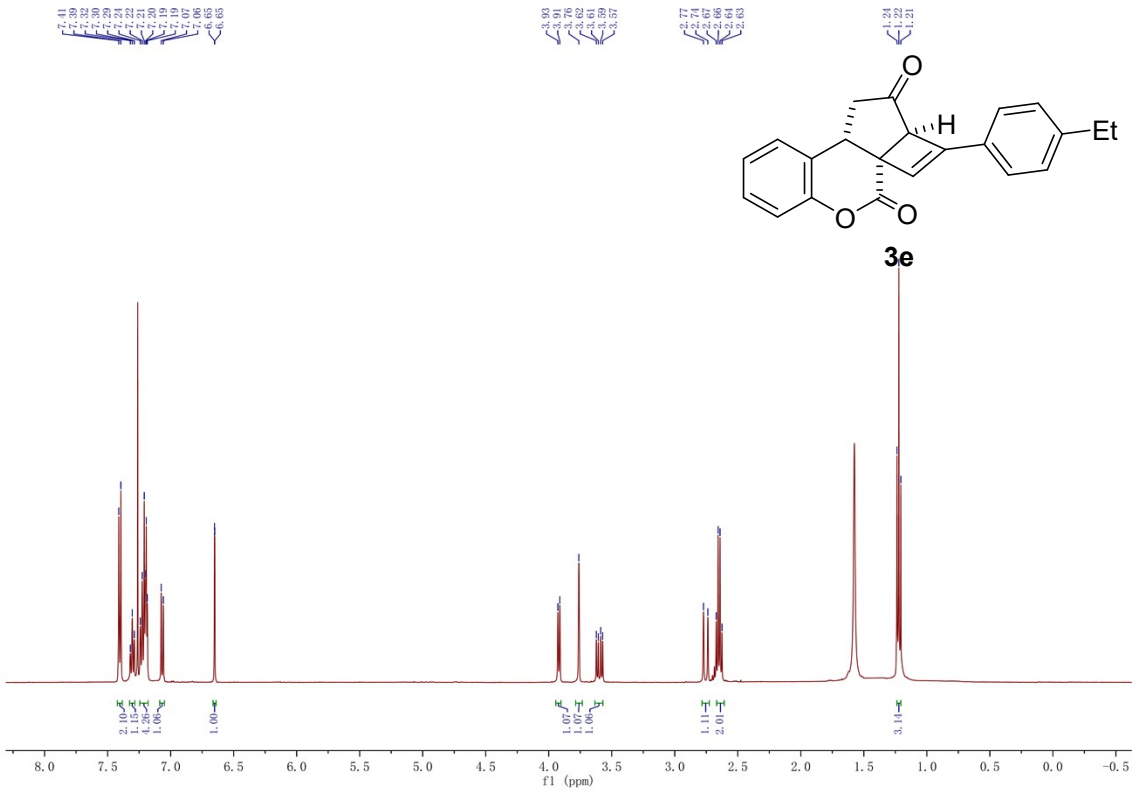
10
0
-10
f1 (ppm)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3.61
3.59
3.57
2.77
2.74
2.67
2.66
2.64
2.63
1.24
1.22
1.21
O
H
Et
O
O
3e
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1.15
1.94
1.06
1.00
1.00
1.07
1.07
1.06
1.11
2.01
3.14
8.0
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7.0
6.5
6.0
5.5
5.0
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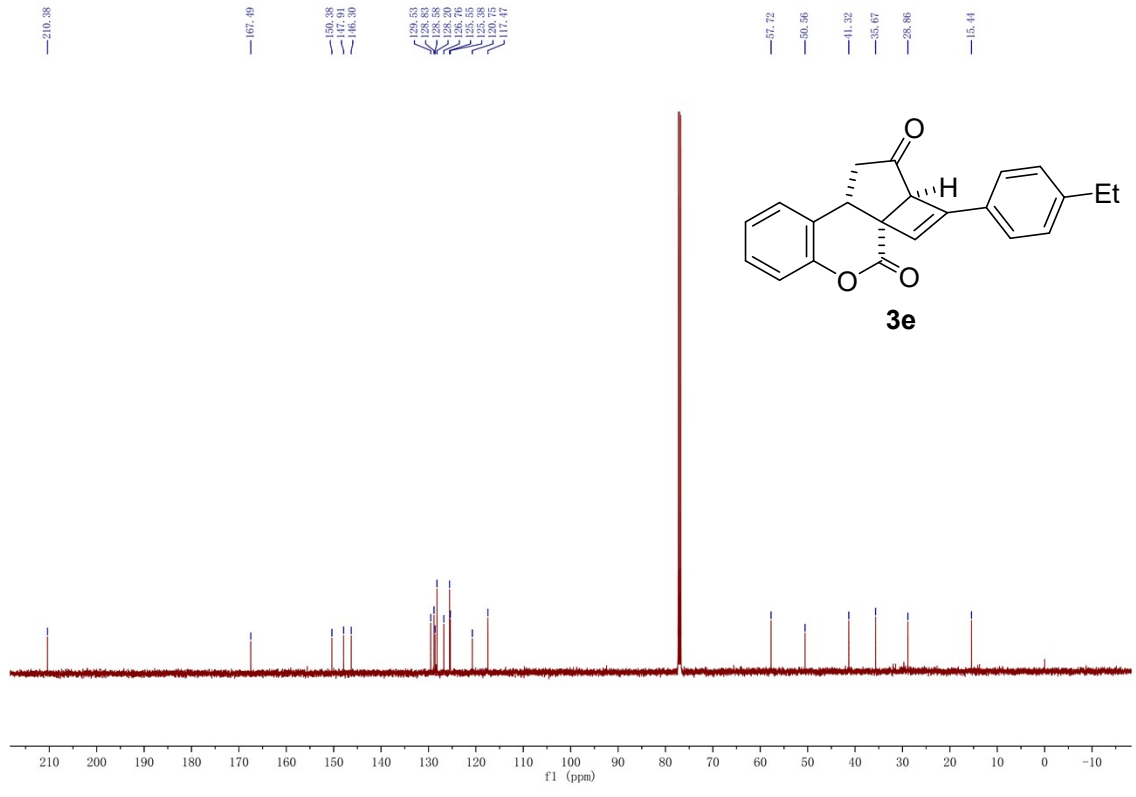
f1 (ppm)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128.58
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125.55
125.38
120.75
117.47
57.72
50.56
41.32
35.67
28.86
15.44
O
H
Et
O
O
3e
210
200
190
180
170
160
150
140
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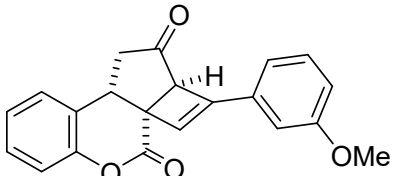
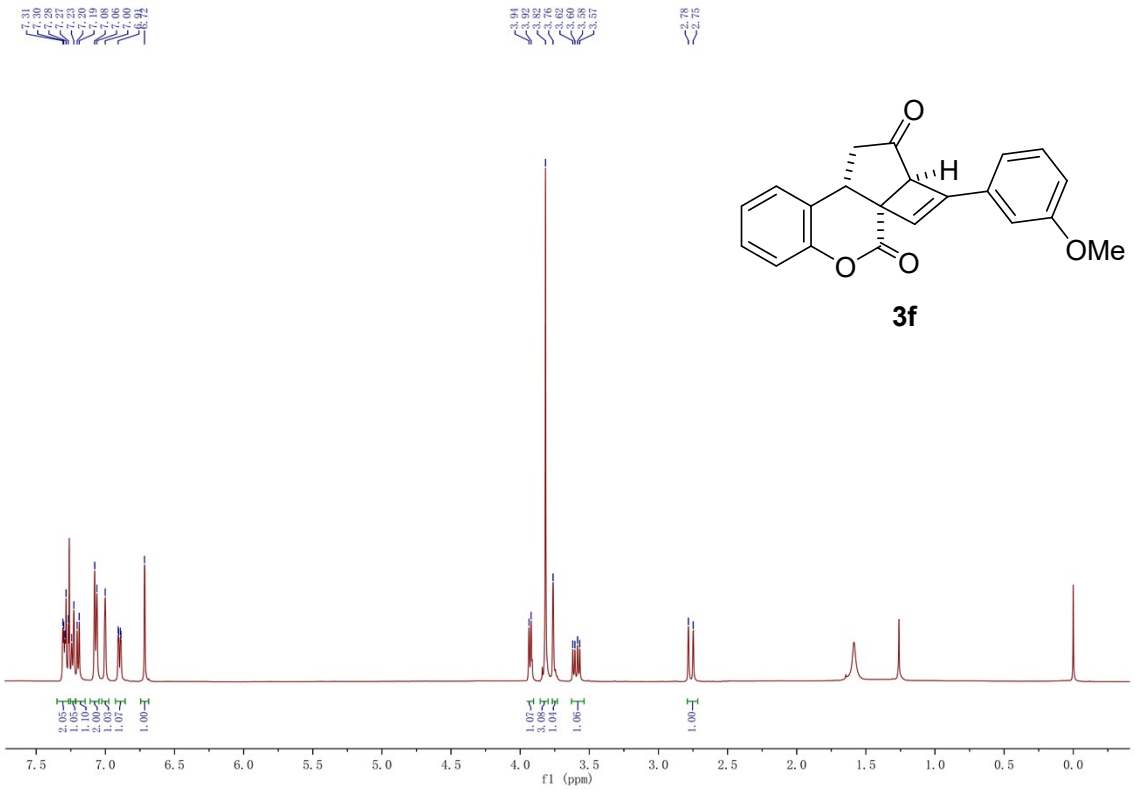
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)


O
H
OMe
O
O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7.08
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7.00
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H
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O
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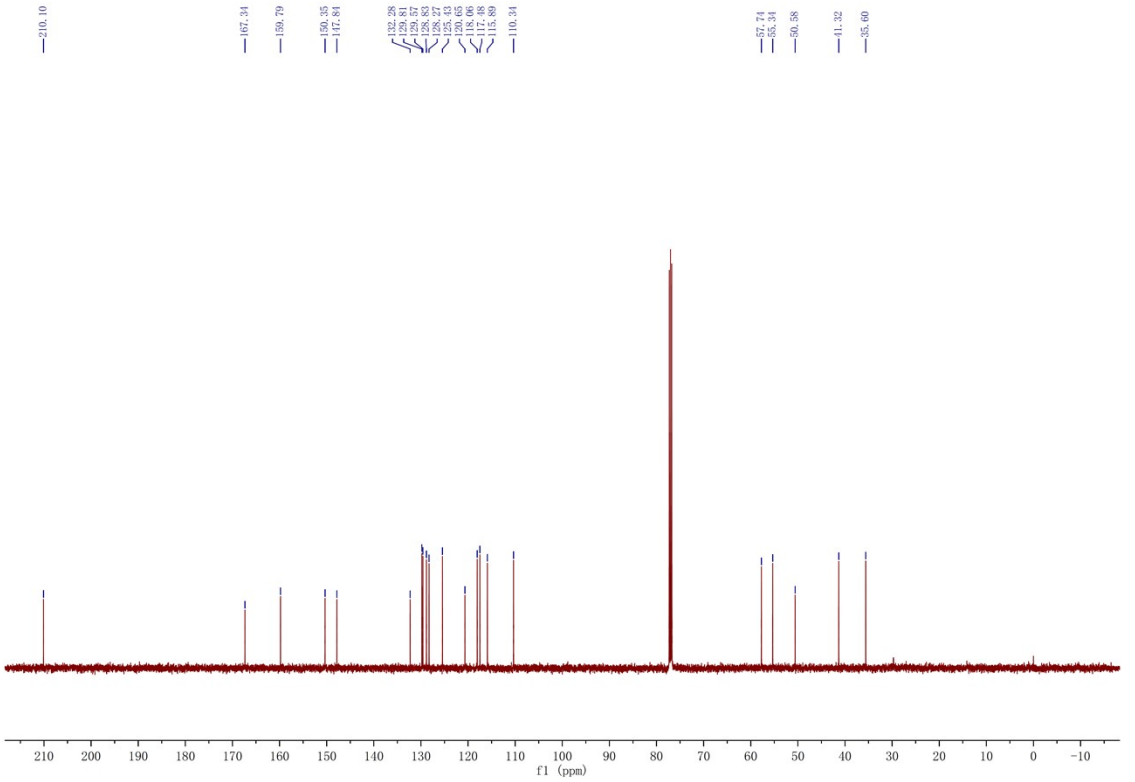
1.01
1.06
1.00
f1 (ppm)

3f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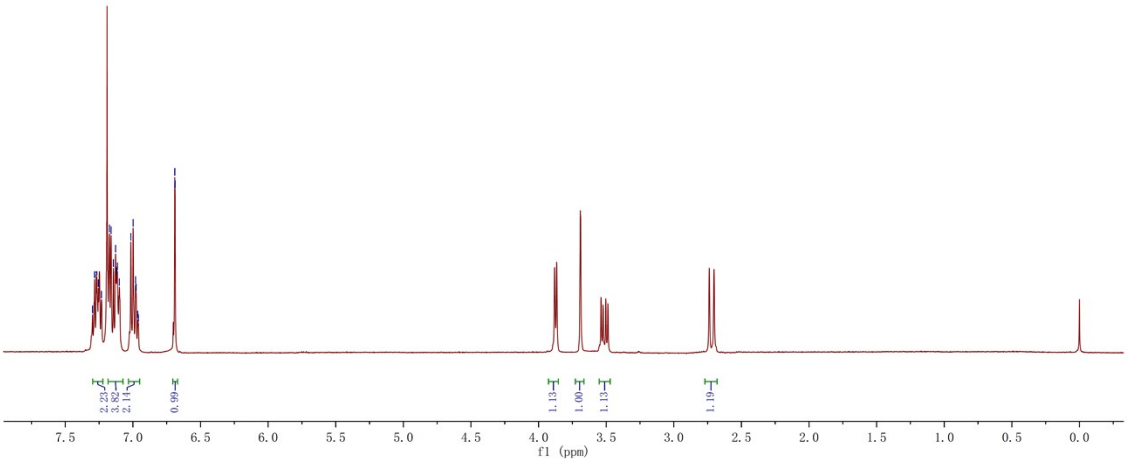
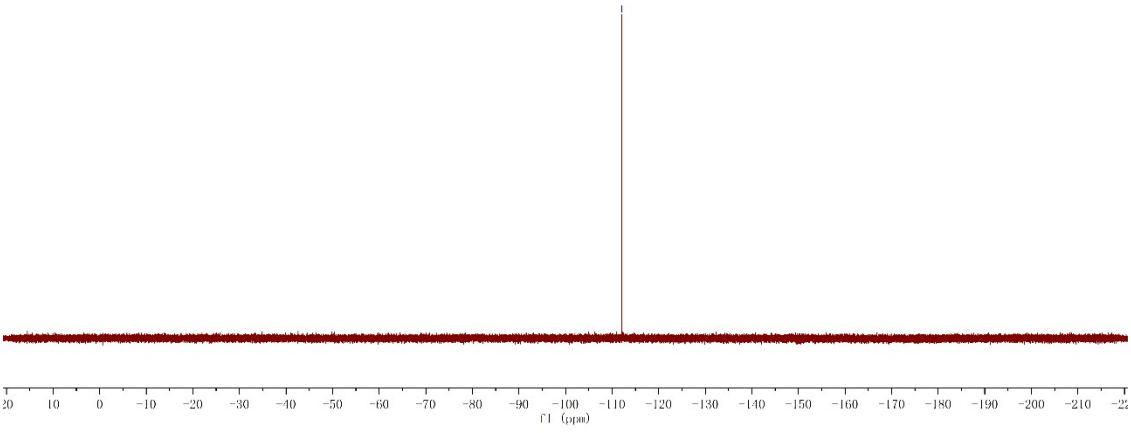
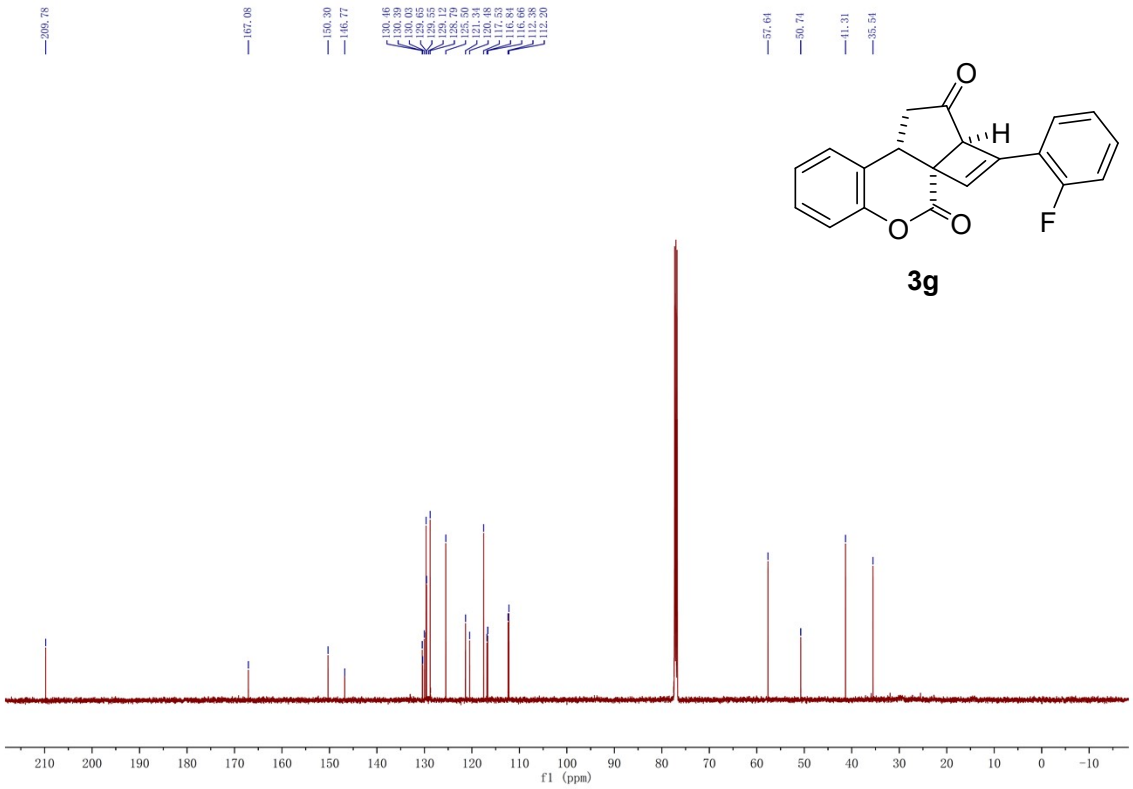
117.48
115.89
110.34
67.74
65.34
50.58
41.32
35.60
f1 (ppm)


3g
3g


f1 (ppm)


f1 (ppm)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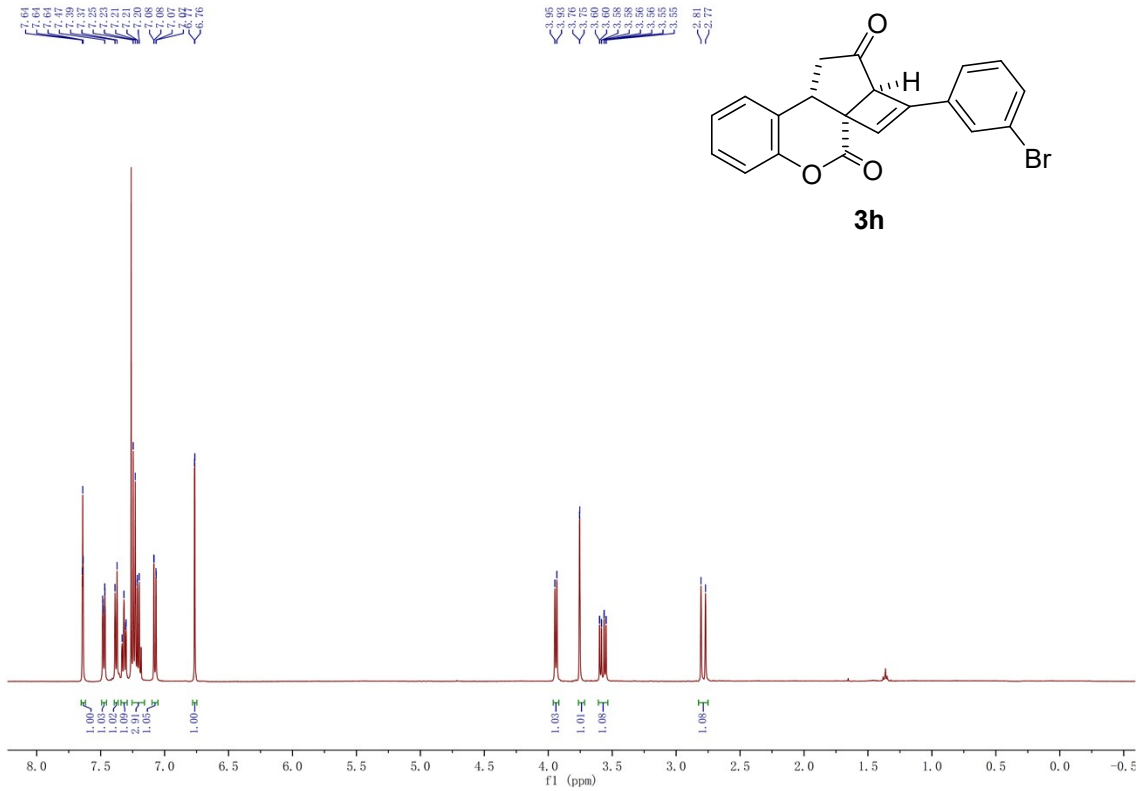
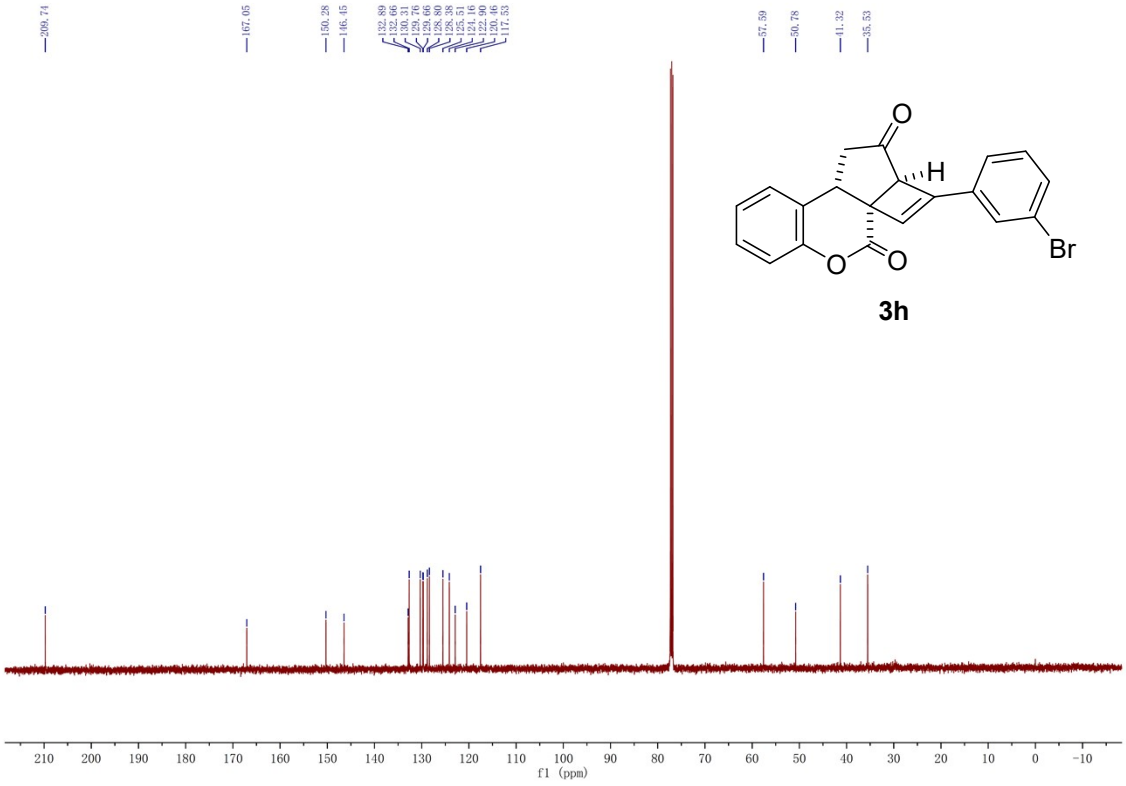
167.08
150.30
146.77
130.46
130.39
130.03
129.65
129.55
129.12
128.79
125.69
121.34
120.48
117.53
116.84
116.66
112.58
112.20
57.64
50.74
41.31
35.54
O
H
O
O
F

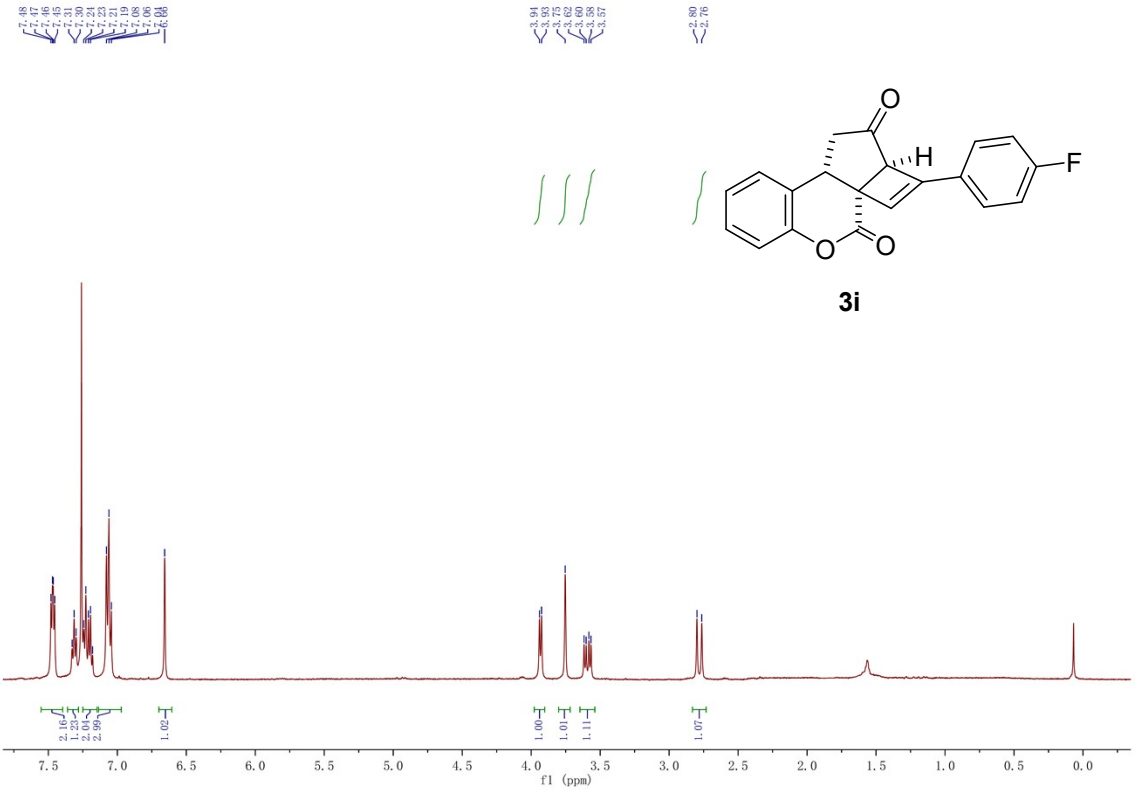
3g


7.64
7.64
7.64
7.47
7.47
7.39
7.37
7.25
7.23
7.21
7.21
7.20
7.08
7.08
7.07
6.77
6.76
3.95
3.93
3.76
3.75
3.60
3.60
3.58
3.56
3.56
3.55
3.55
2.81
2.77
O
H
O
O
Br

3h


209.74
167.05
150.28
146.45
132.89
132.66
132.31
130.31
129.76
129.66
128.80
128.38
125.51
124.16
122.90
120.46
117.53
57.59
50.78
41.32
35.53
O
H
Br
O
O
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)

3h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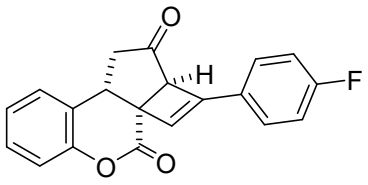
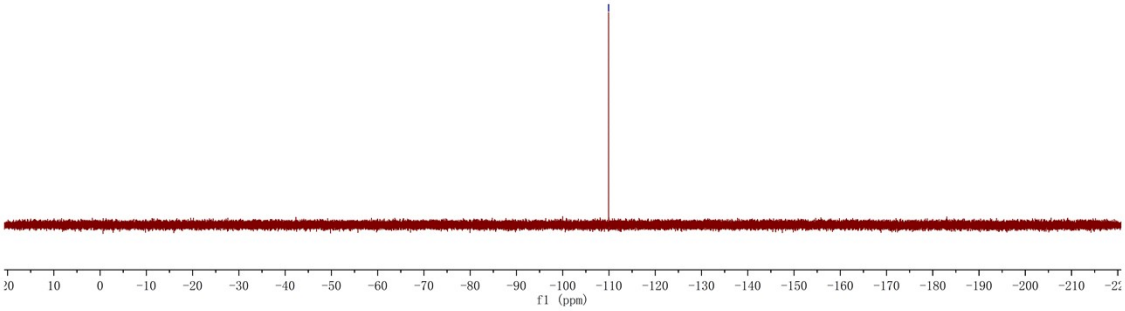
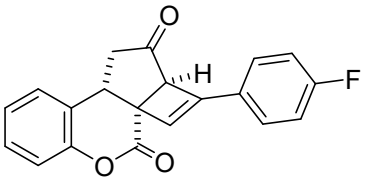
7.47
7.46
7.45
7.31
7.30
7.24
7.23
7.21
7.19
7.08
7.06
3.94
3.93
3.75
3.62
3.60
3.58
3.57
2.80
2.76
O
H
F
O
O
2.10
1.23
2.14
2.09
1.02
1.00
1.01
1.11
1.07
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

3i

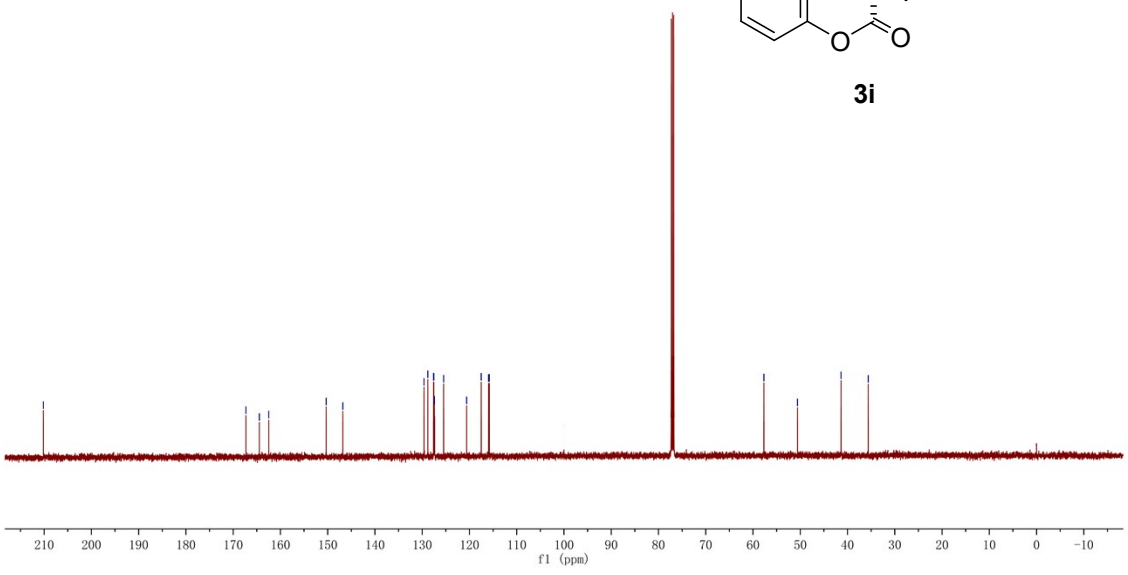

O
H
F
O
O

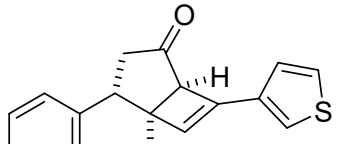
3i


-109.92
f1 (ppm)

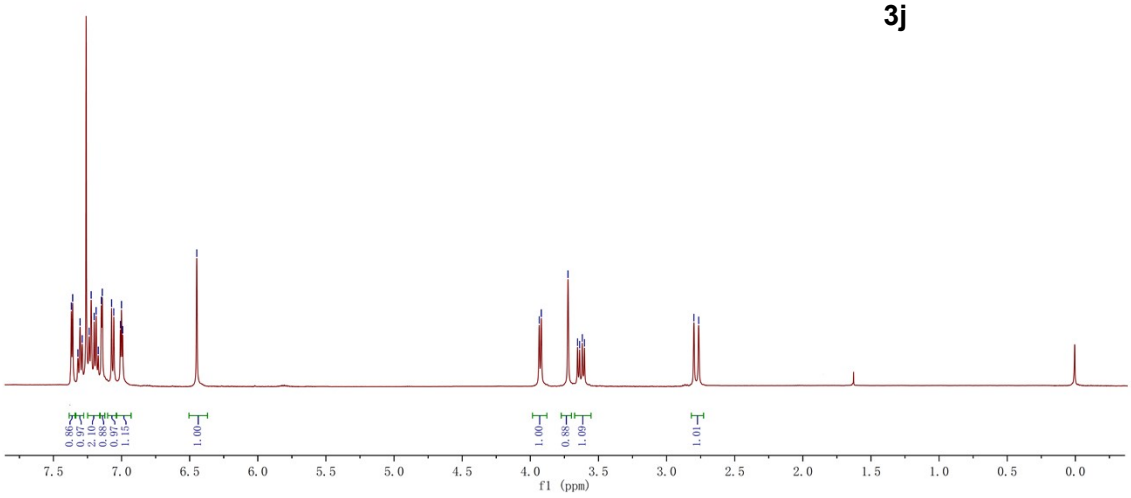

O
H
F
O
O

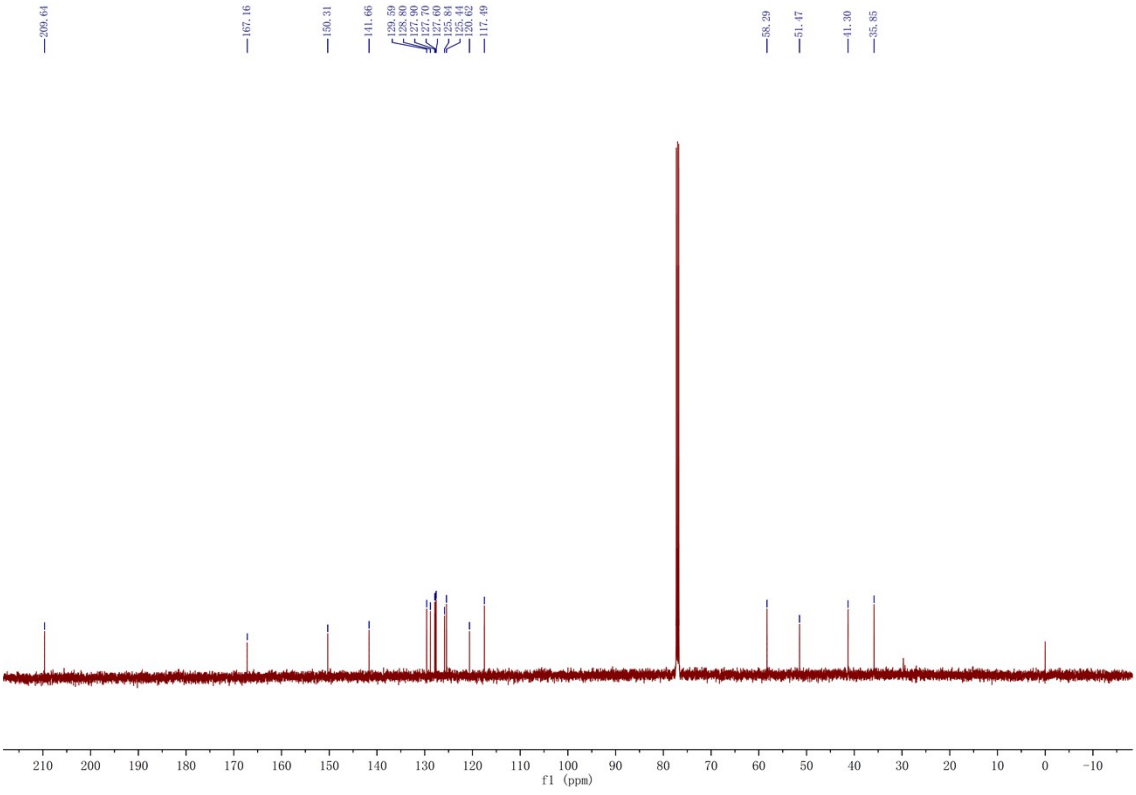
3i

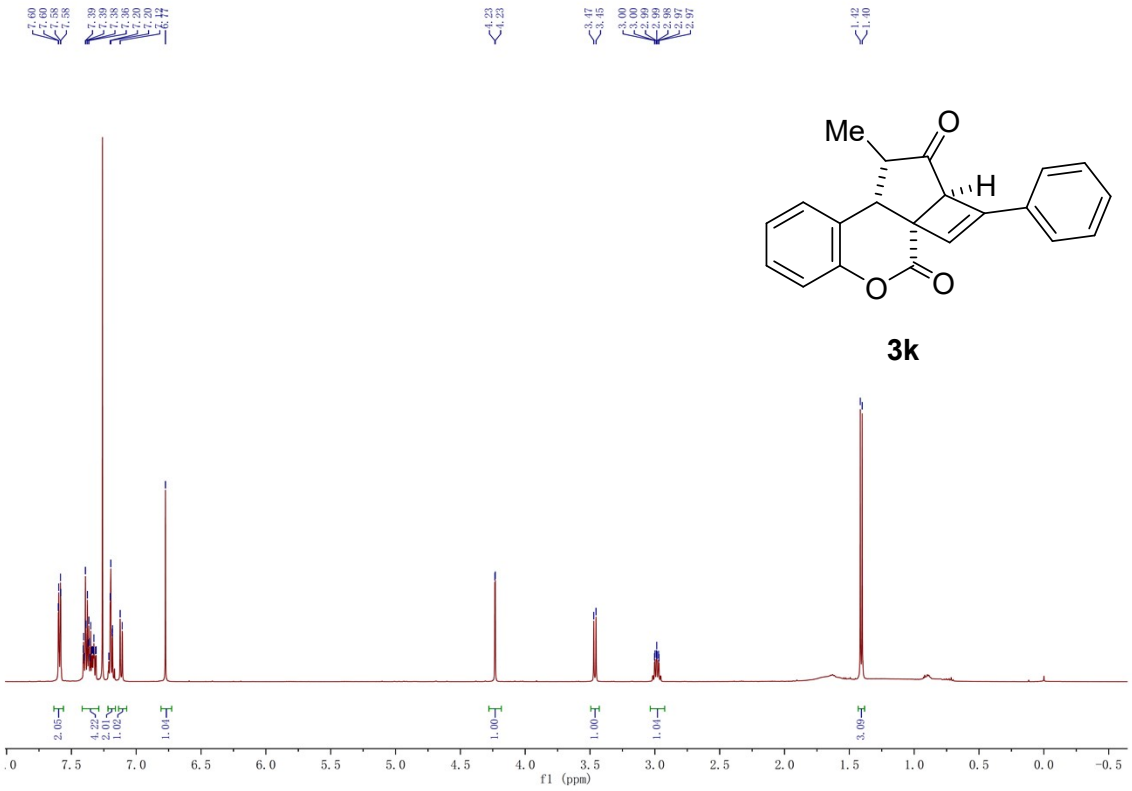

210.16
167.30
164.46
162.47
150.32
146.80
129.62
128.81
128.60
127.53
127.44
127.42
125.47
120.60
117.51
115.96
115.79
57.69
50.58
41.36
35.61
f1 (ppm)


O
H
S

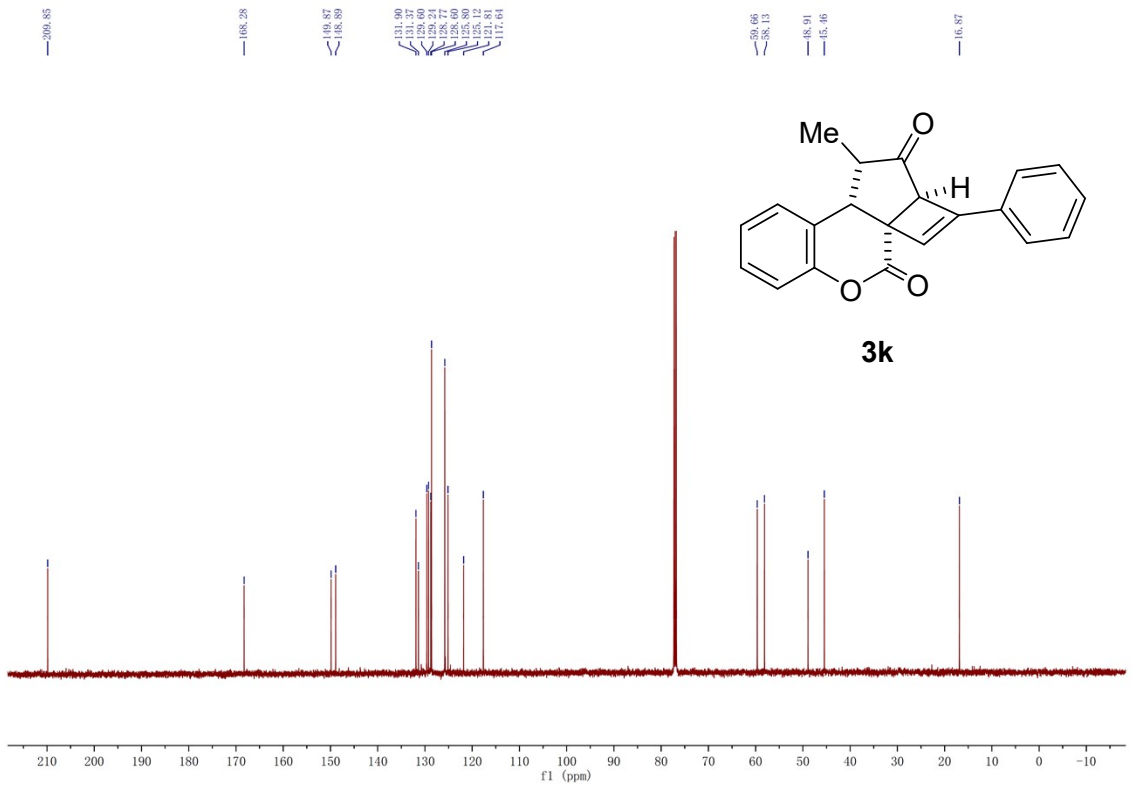
3j



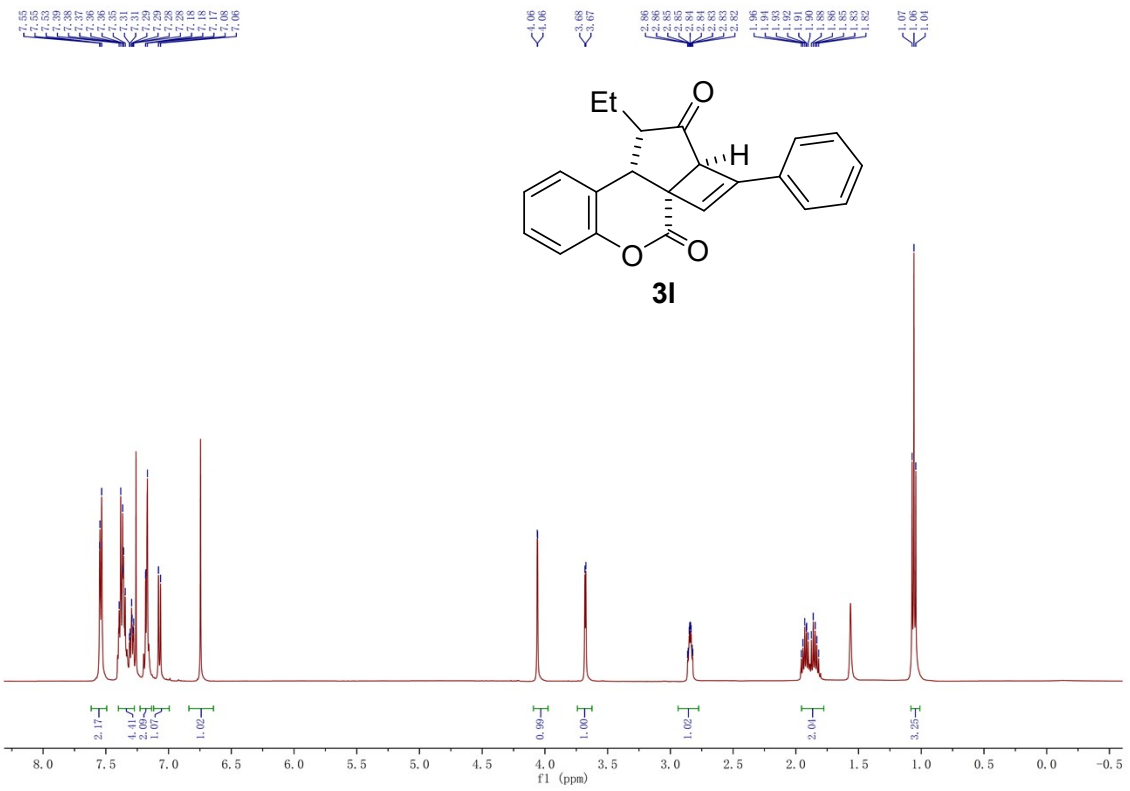


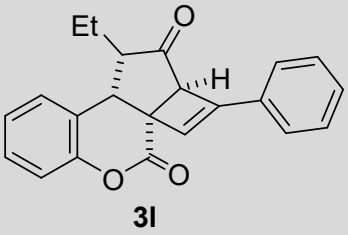


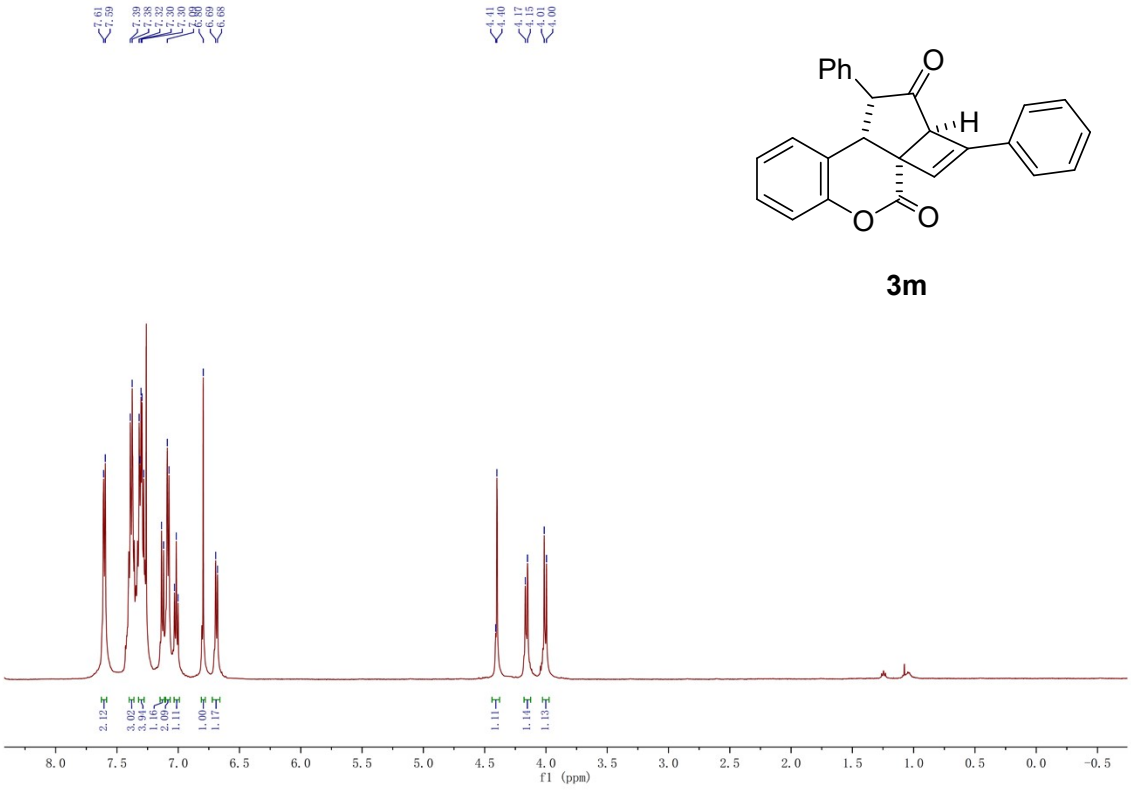
3k



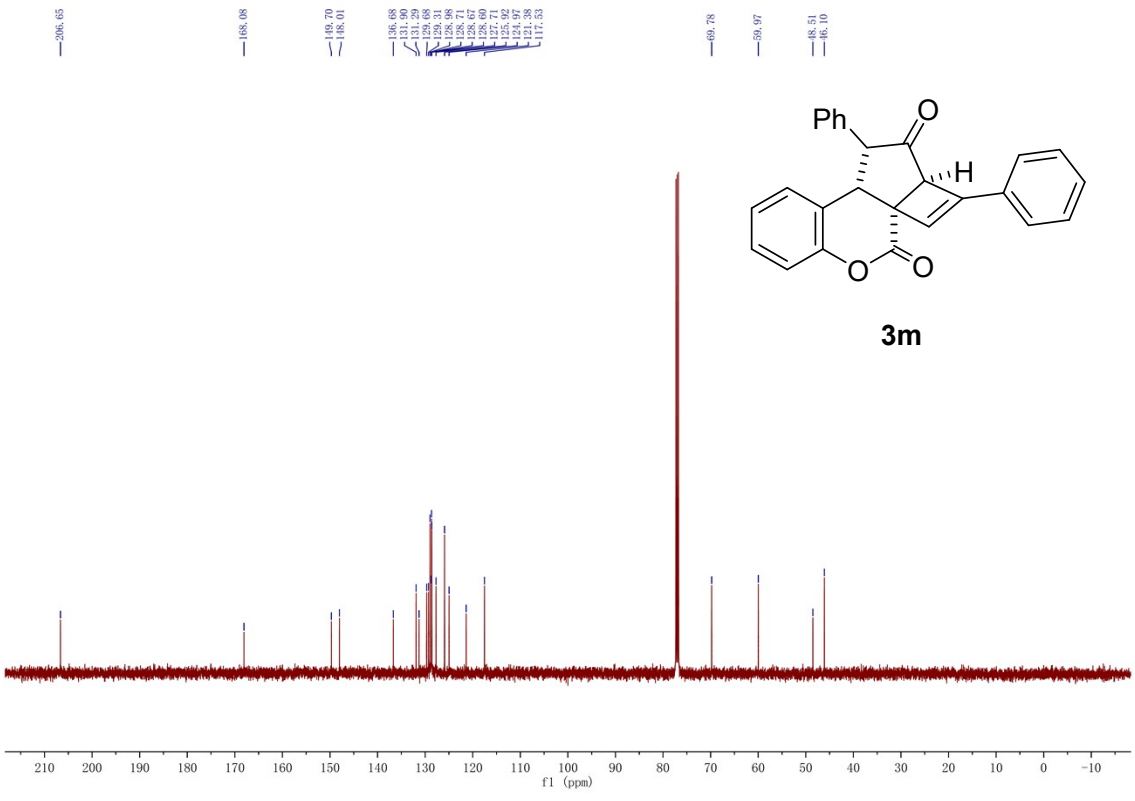
3k


Et
O
H
O
O
3l
f1 (ppm)

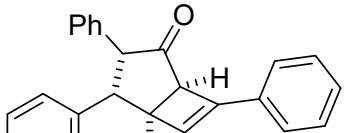

Et
O
H
O
O
3l

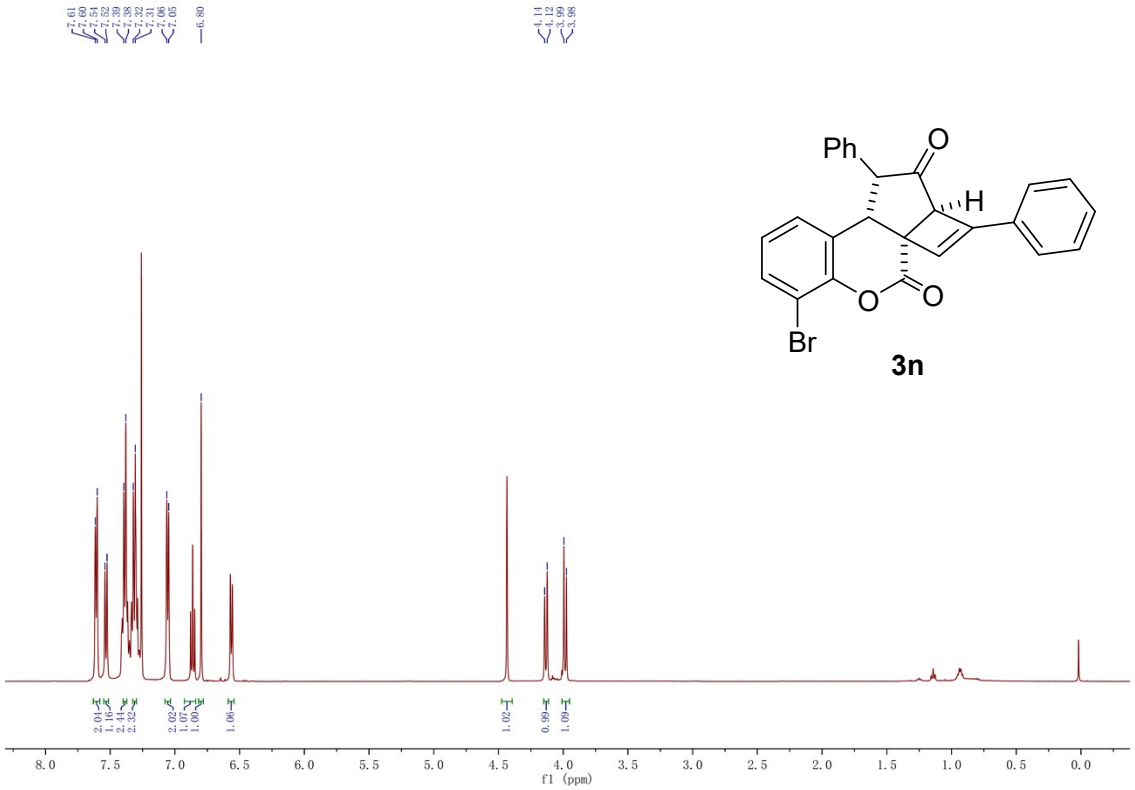

7.61
7.59
7.39
7.38
7.32
7.30
7.30
7.09
6.69
6.68
4.41
4.40
4.17
4.15
4.01
4.00
Ph
O
H
O
O
2.12
3.02
3.04
1.46
2.09
1.11
1.00
1.17
1.11
1.14
1.13
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

3m

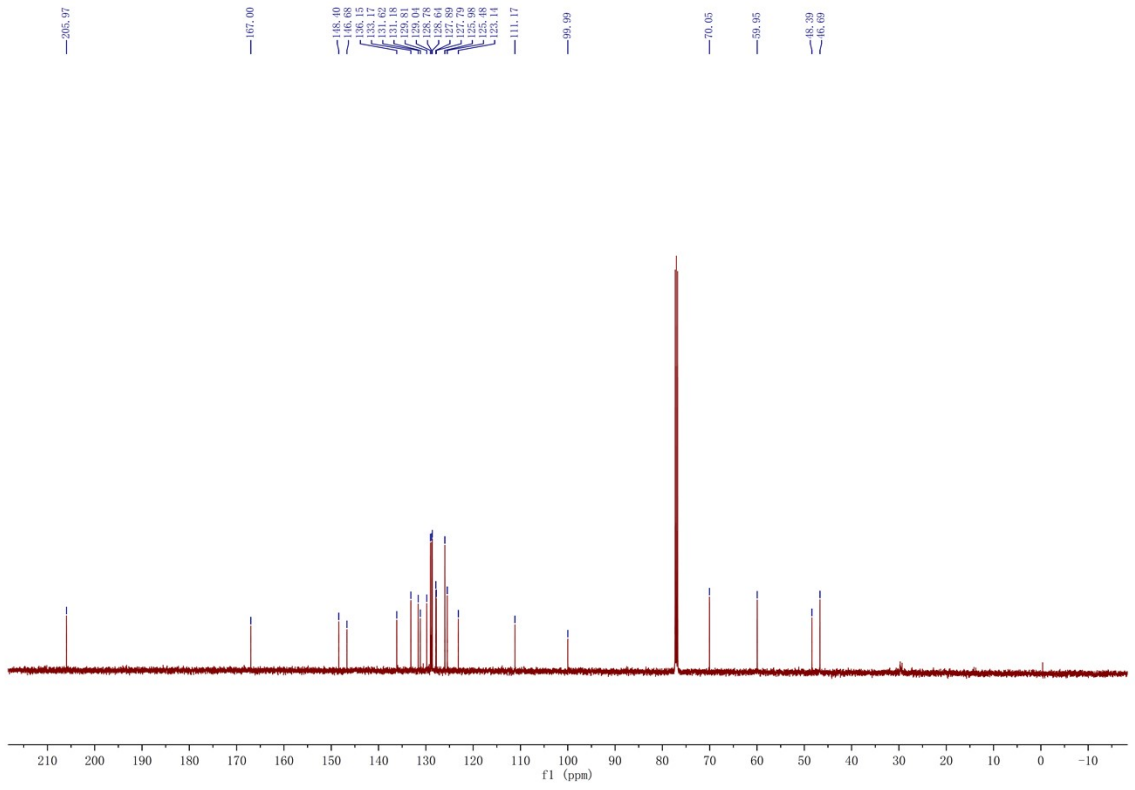

206.65
168.08
149.70
148.01
136.68
131.90
131.29
129.68
129.31
128.98
128.71
128.67
128.60
127.71
125.92
124.97
121.38
117.53
69.78
59.97
48.51
46.10
Ph
O
H
O
O
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

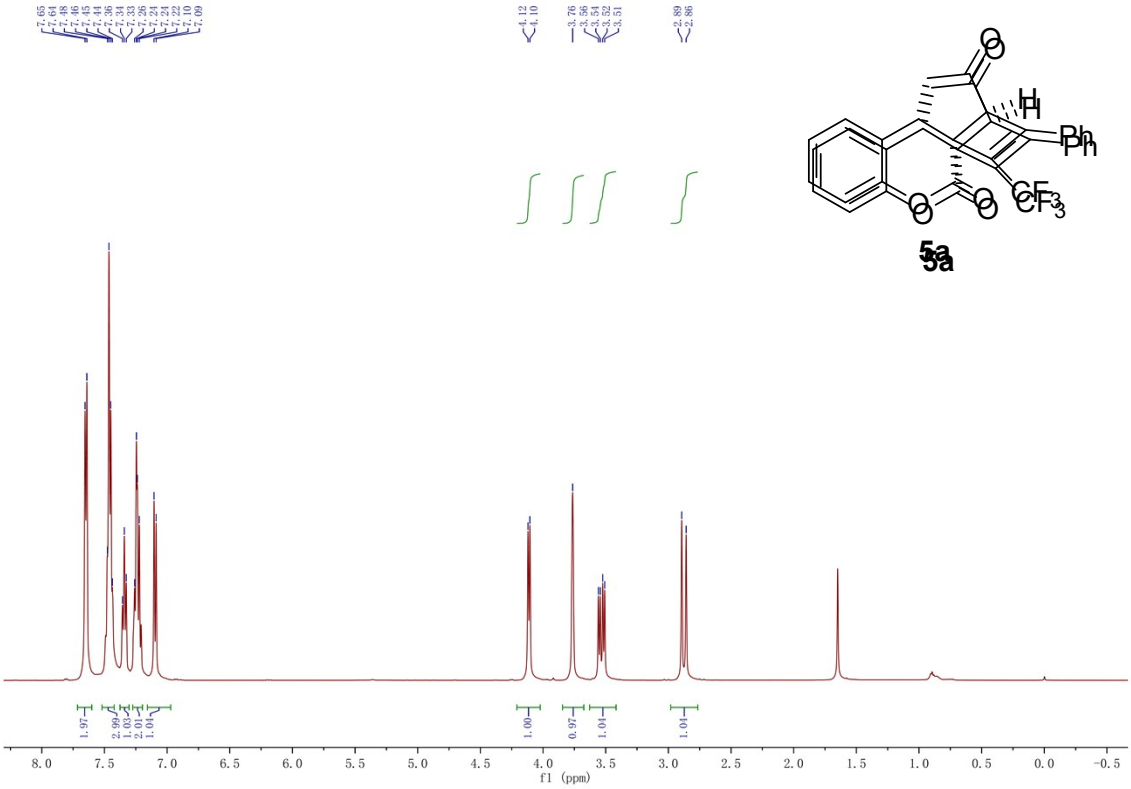
3m

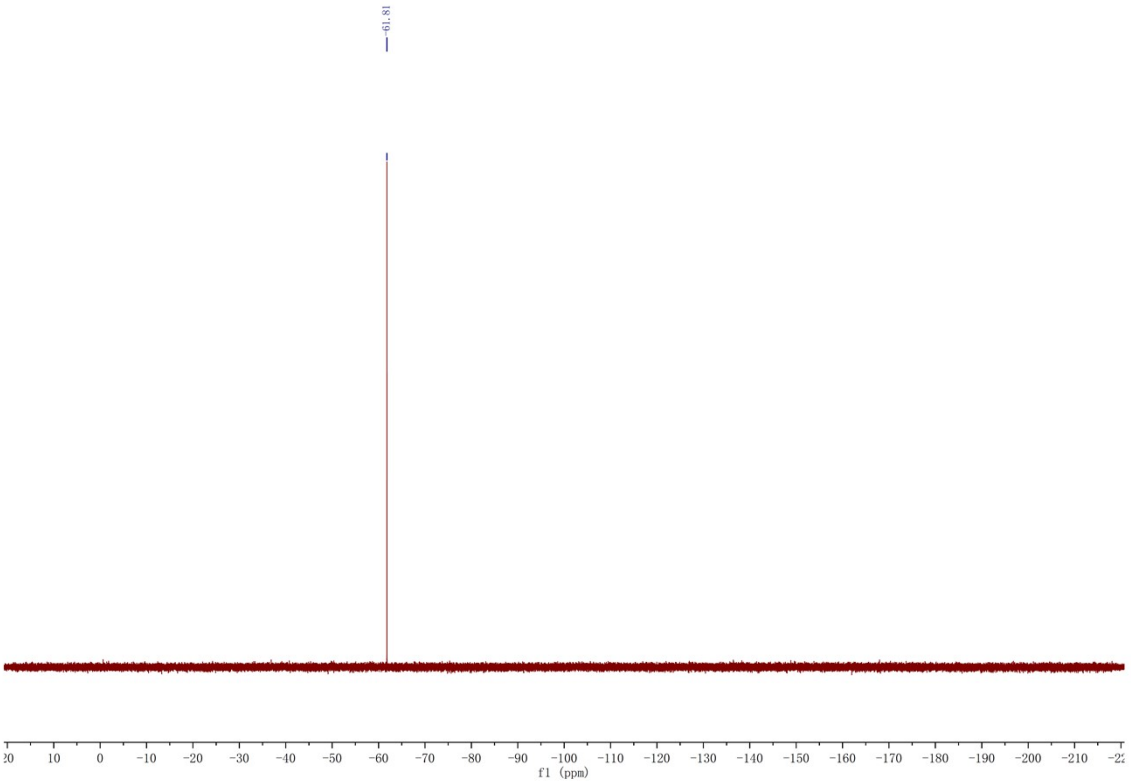

Ph
O
H

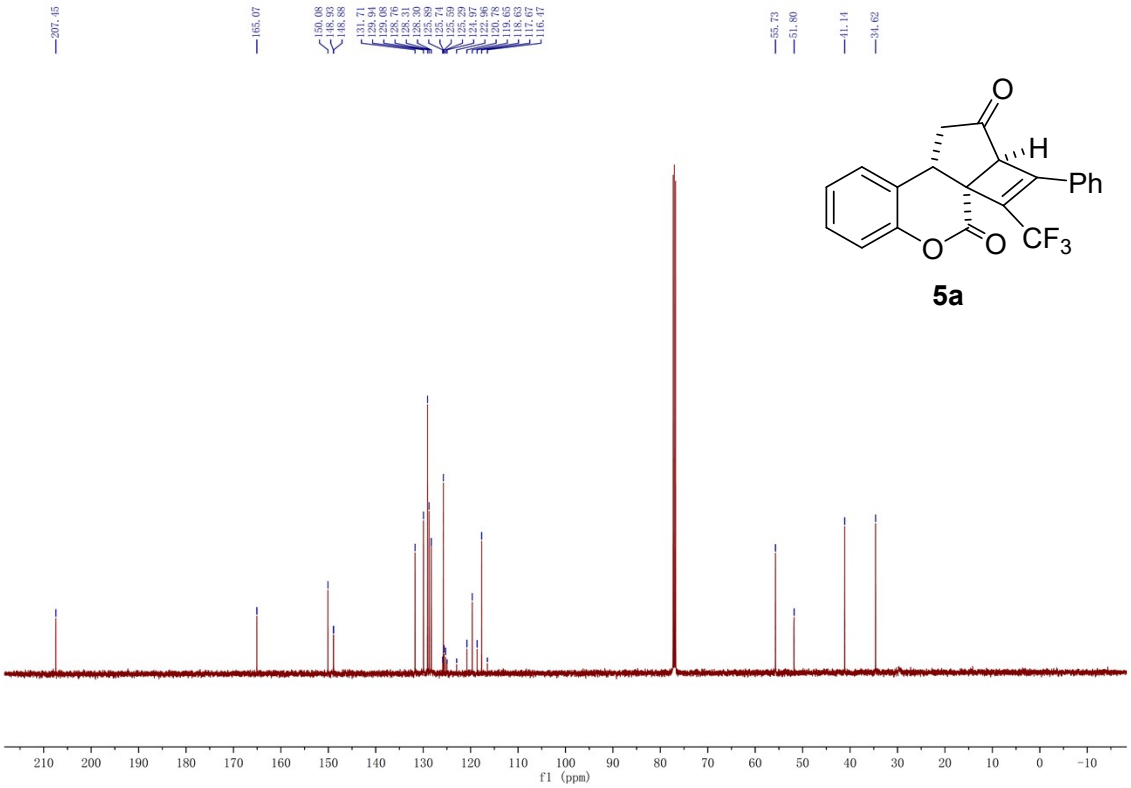

7.61
7.60
7.54
7.52
7.39
7.38
7.32
7.31
7.06
7.05
6.80
4.14
4.12
4.00
3.99
3.98
Ph
O
H
O
O
Br
2.01
1.16
2.44
2.32
2.02
1.07
1.00
1.06
1.02
0.99
1.09
f1 (ppm)

3n


205.97
167.00
148.40
146.68
136.15
133.17
131.62
131.18
129.81
129.04
128.78
128.64
128.59
127.79
125.98
125.48
123.14
111.17
99.99
70.05
59.95
48.39
46.69
f1 (ppm)

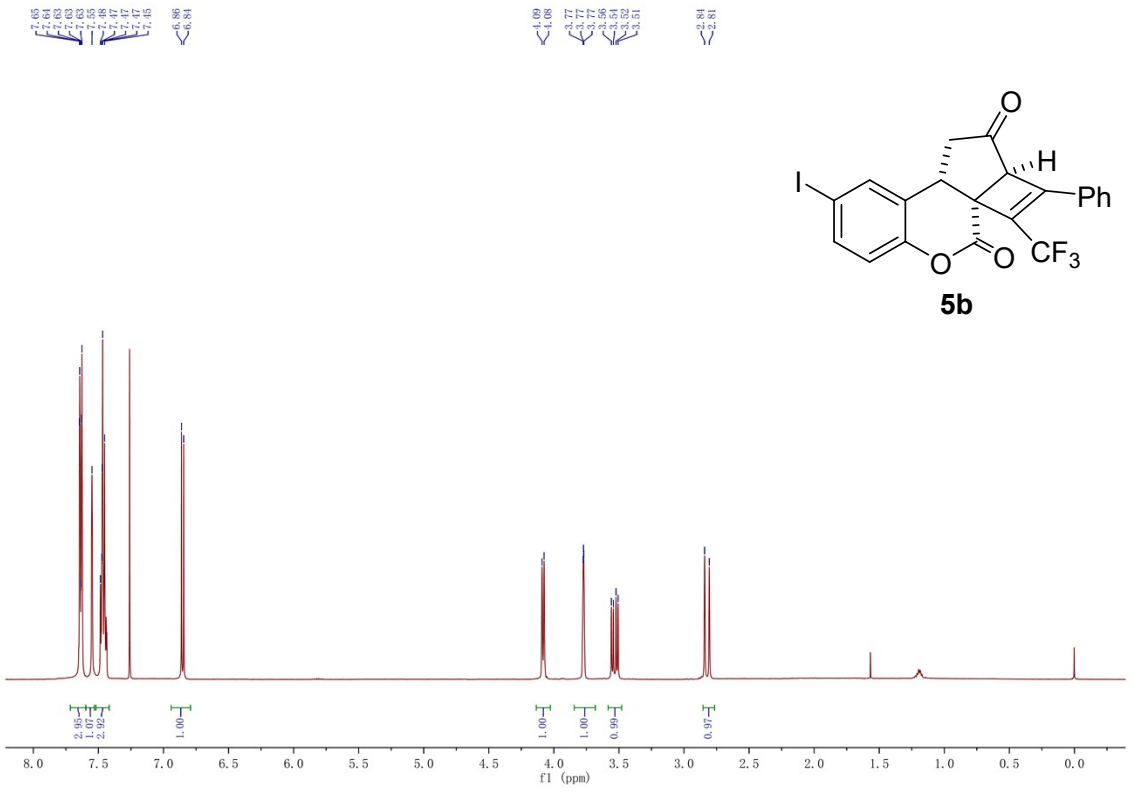

7.65
7.64
7.48
7.46
7.45
7.44
7.36
7.34
7.33
7.26
7.24
7.24
7.22
7.10
7.09
4.12
4.10
3.76
3.56
3.54
3.52
3.51
2.89
2.86
O
H
Ph
Ph
CF3
O
O
5a
1.97
2.99
2.02
2.01
1.04
1.00
0.97
1.04
1.04
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


-61.81
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)


207.45
165.07
150.08
148.93
148.88
131.71
129.94
129.68
128.76
128.31
128.30
125.89
125.74
125.39
125.29
124.97
122.96
120.78
119.65
118.63
117.67
116.47
55.73
51.80
41.14
34.62
f1 (ppm)

O
H
Ph
CF3
O
O

5a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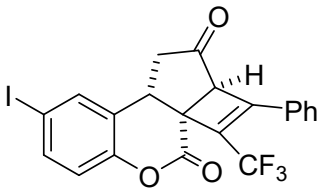
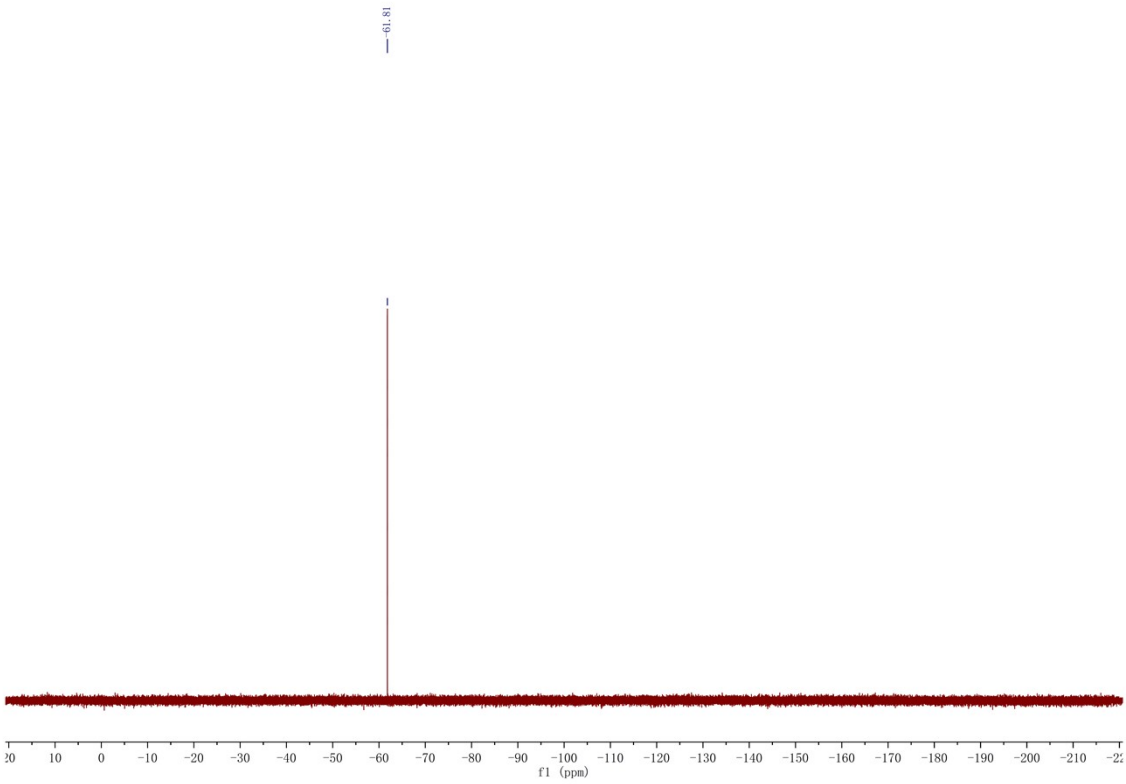
7.64
7.63
7.63
7.63
7.55
7.48
7.47
7.47
7.47
7.45
6.86
6.84
4.09
4.08
3.77
3.77
3.77
3.56
3.54
3.52
3.51
2.84
2.81
2.95
1.07
2.92
1.00
1.00
1.00
0.99
0.97
f1 (ppm)

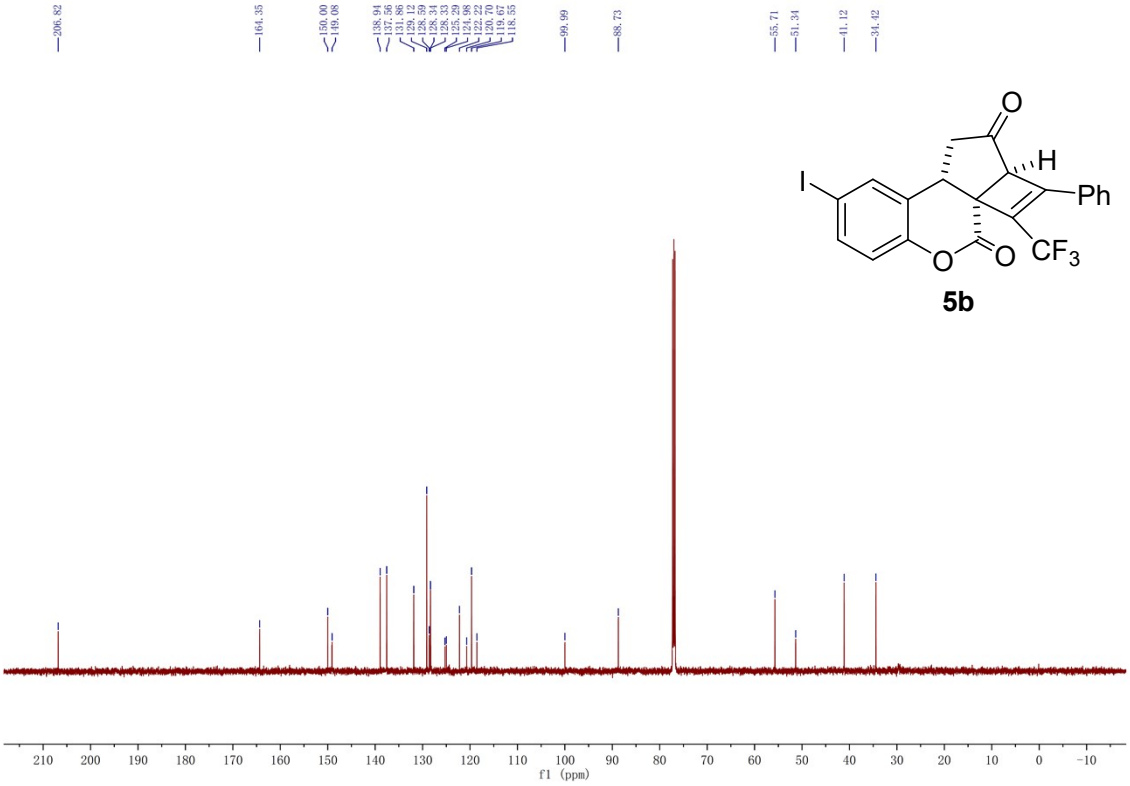
O
H
I
Ph
CF3
O
O

5b


O
H
I
Ph
CF3
O
O

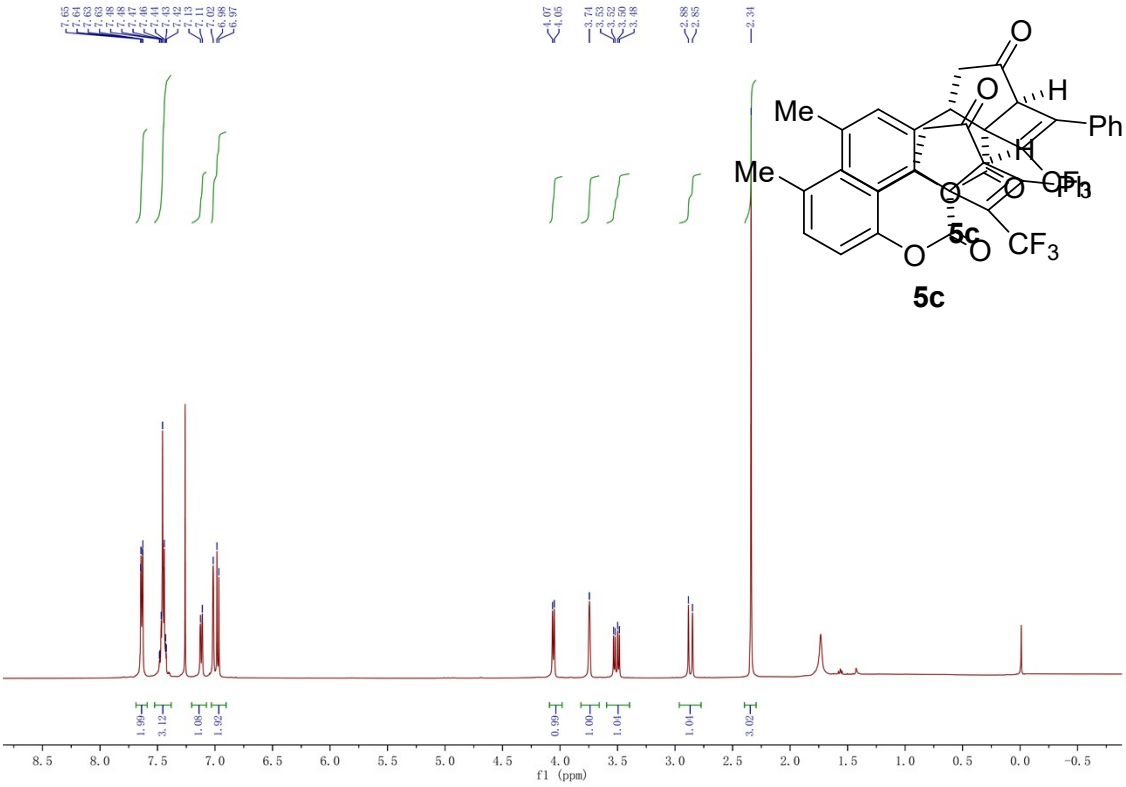
5b


61.81
f1 (ppm)


206.82
164.35
150.00
149.08
138.94
137.56
131.86
129.12
128.59
128.34
128.33
125.29
124.98
122.22
120.70
119.67
118.55
99.99
88.73
55.71
51.34
41.12
34.42
f1 (ppm)

O
H
I
Ph
O
O
CF3

5b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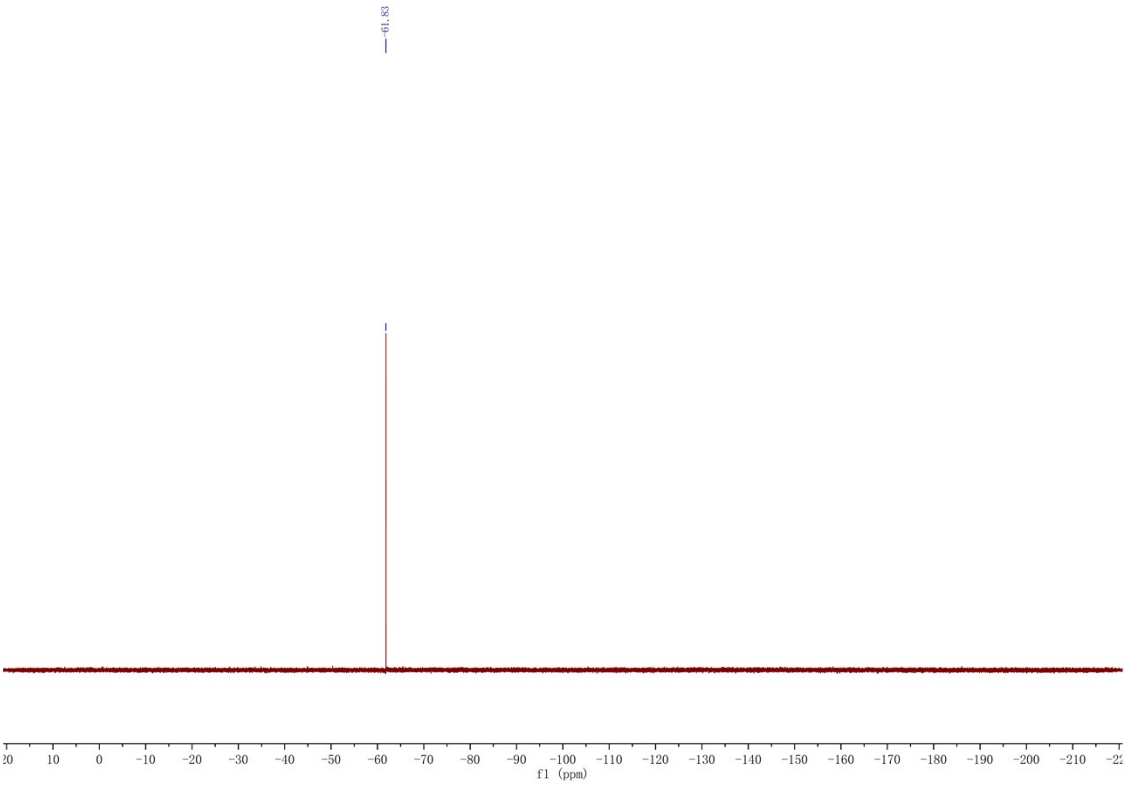
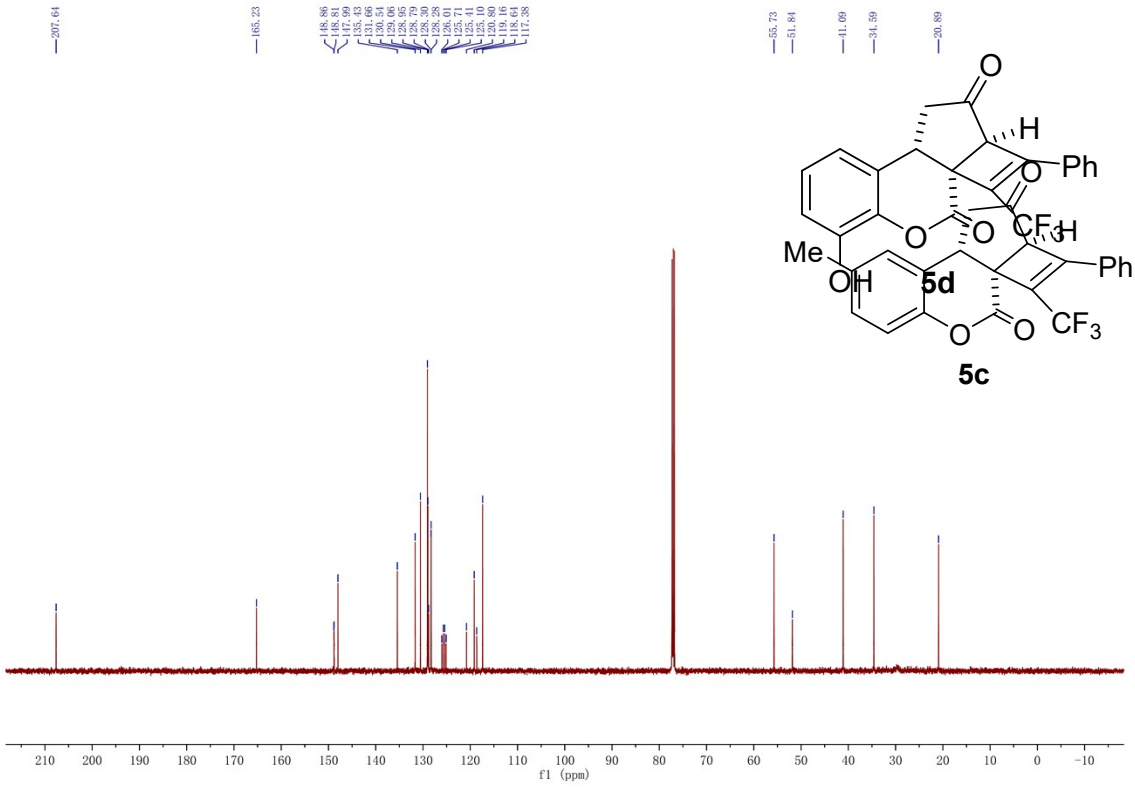
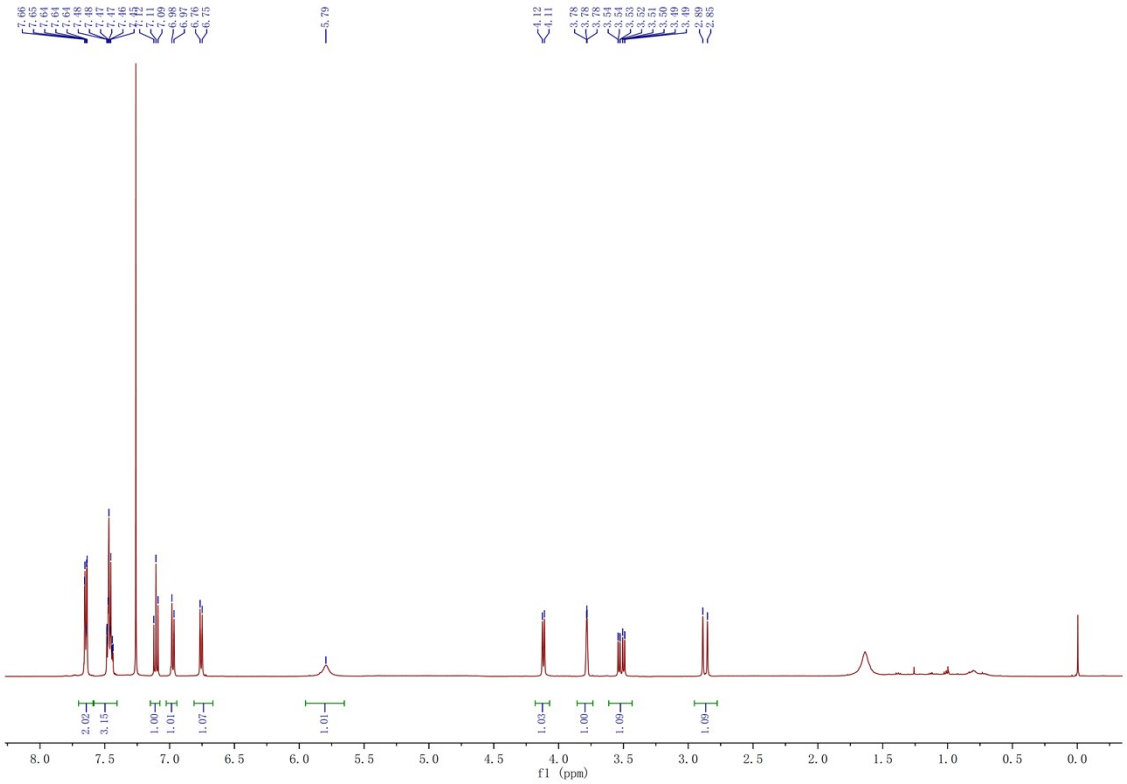
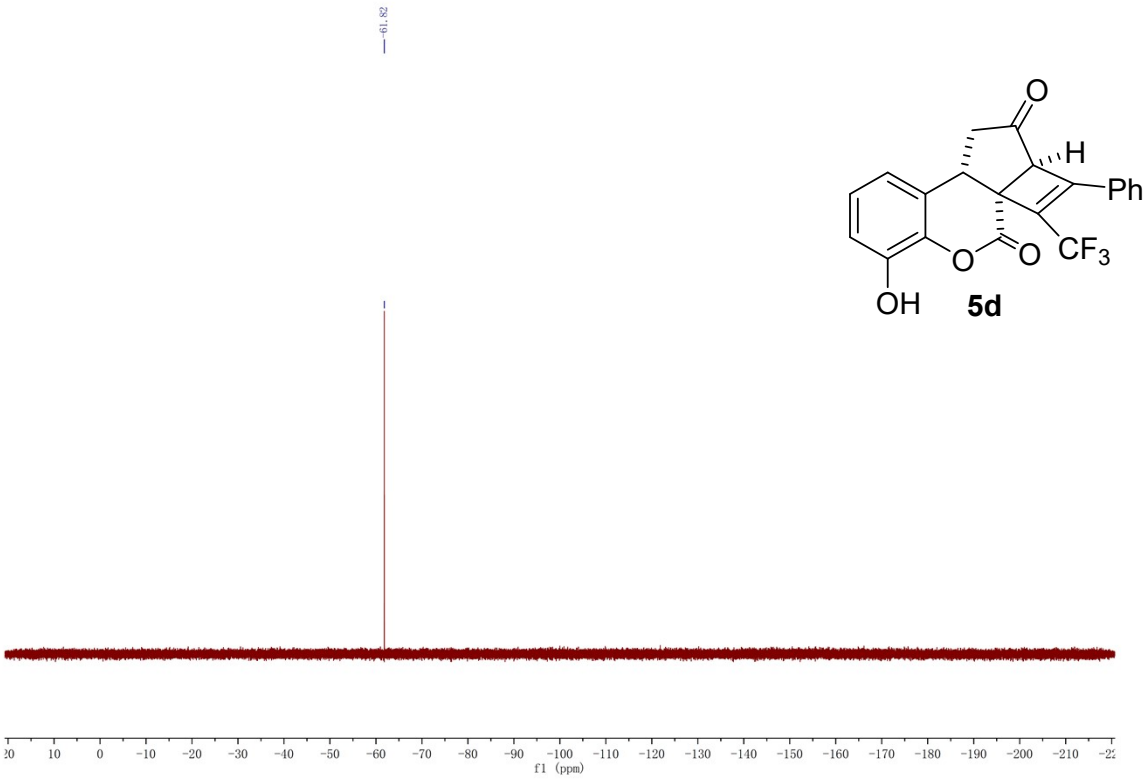
7.64
7.63
7.63
7.48
7.47
7.46
7.44
7.43
7.42
7.13
7.11
7.02
6.98
6.97
4.07
4.05
3.74
3.53
3.52
3.50
3.48
2.88
2.85
2.34
Me
Me
O
O
H
Ph
H
O
O
O
CF3
O
O
5c
1.99
3.12
1.08
1.92
0.99
1.00
1.01
1.01
3.02
f1 (ppm)

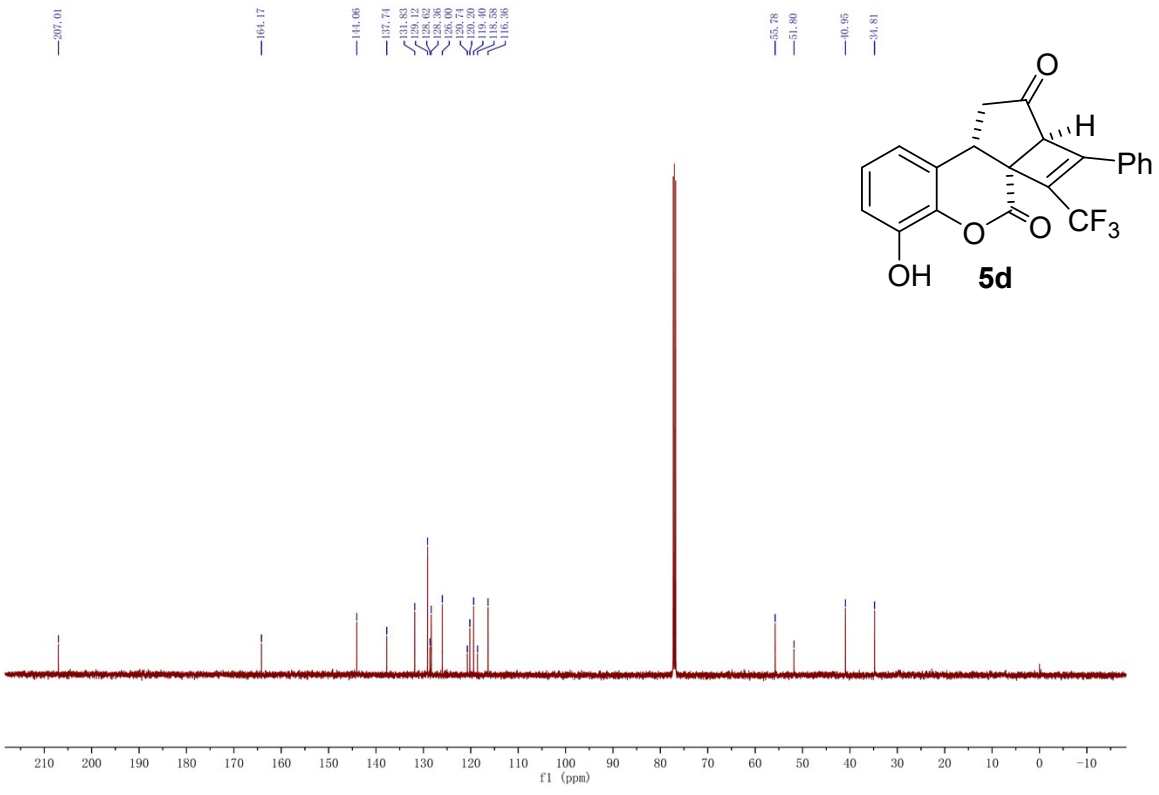
5c

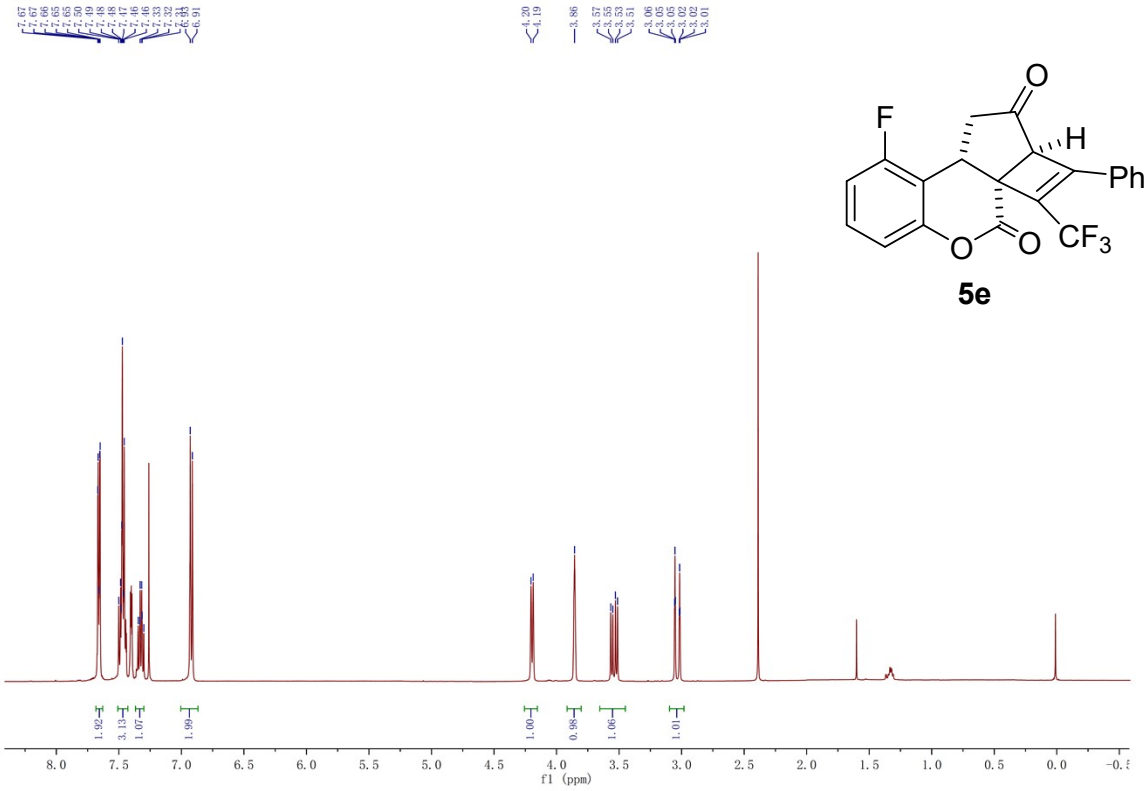

-61.83
f1 (ppm)

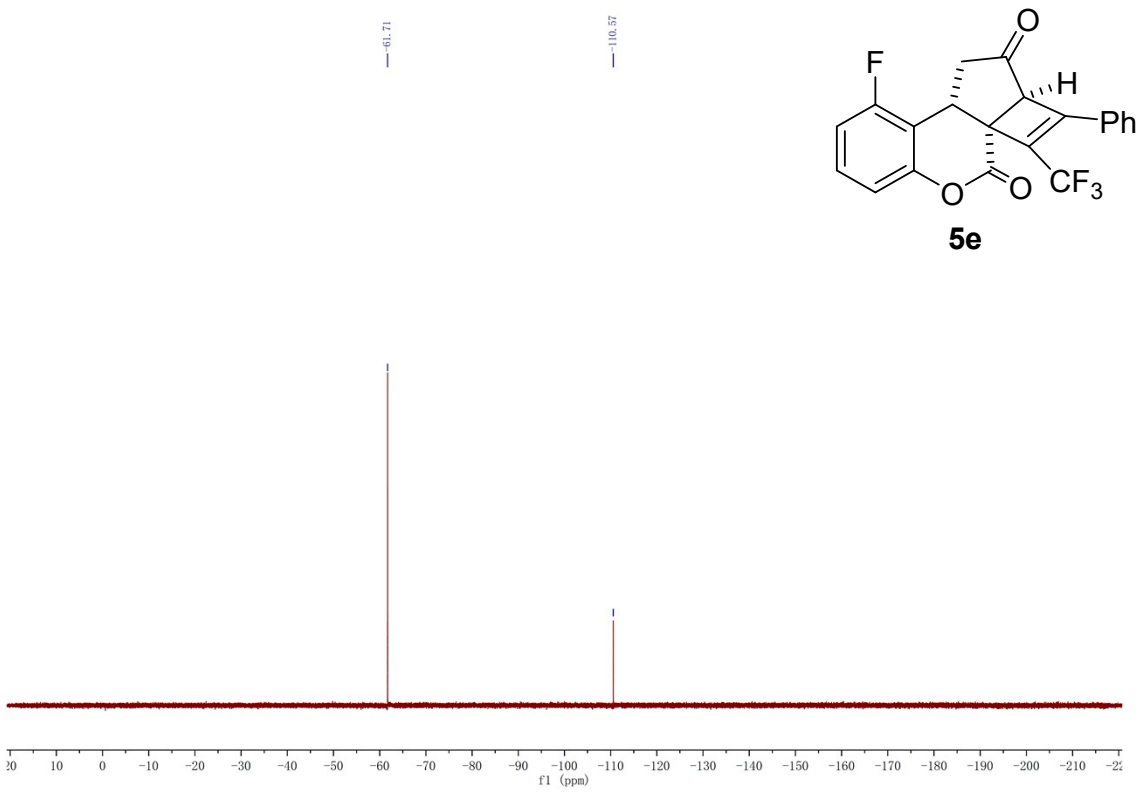

207.64
165.23
148.86
148.81
147.99
135.43
131.66
130.54
129.86
128.95
128.79
128.30
128.28
126.01
125.71
125.41
125.10
120.80
119.16
118.64
117.38
55.73
51.84
41.09
34.59
20.89
O
H
Ph
O
O
O
CF3
H
Me
OH
5d
Ph
O
O
CF3
5c
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

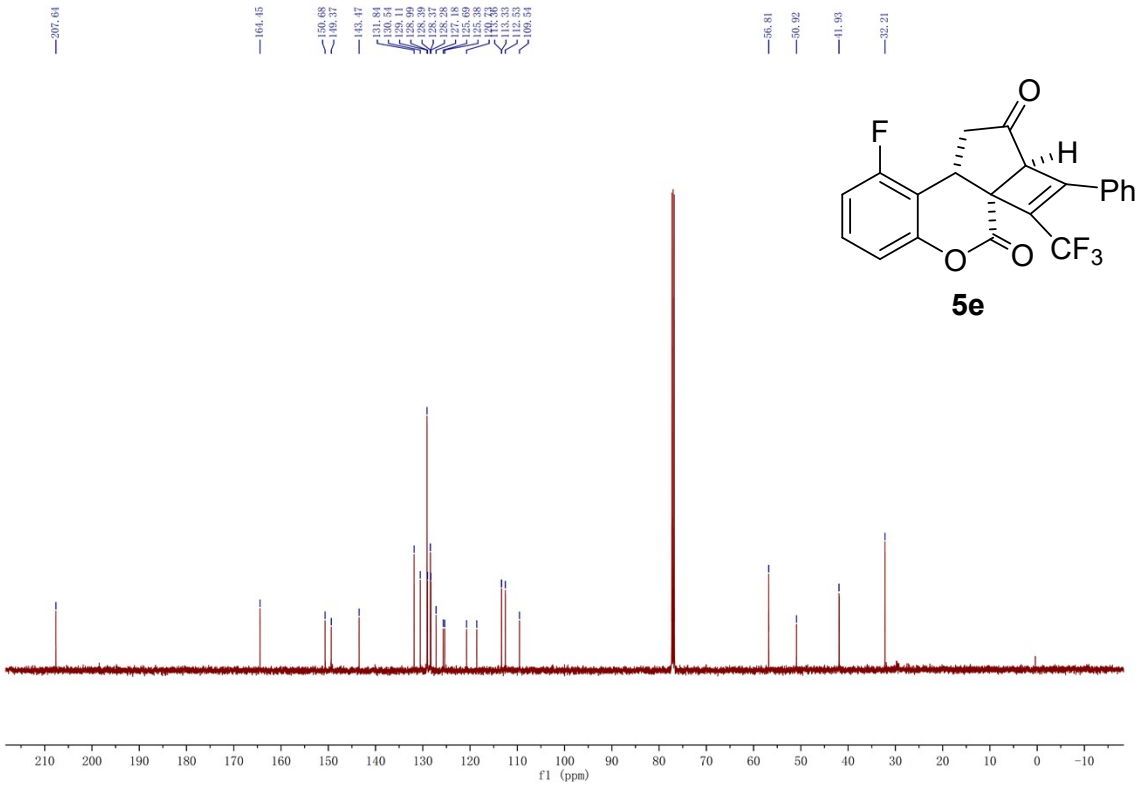

7.66
7.65
7.64
7.64
7.64
7.48
7.48
7.47
7.47
7.46
7.11
7.09
6.98
6.97
6.76
6.75
5.79
4.12
4.11
3.78
3.78
3.54
3.54
3.53
3.52
3.51
3.50
3.49
3.49
2.89
2.85
2.02
3.15
1.00
1.01
1.07
1.01
1.03
1.00
1.09
1.09
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


61.82
O
H
Ph
CF3
O
O
OH
5d
f1 (ppm)


207.01
164.17
144.06
137.74
131.83
129.12
128.62
128.36
126.60
120.71
120.20
119.40
118.38
116.36
55.78
51.80
40.95
34.81
O
H
Ph
CF3
O
O
OH
5d
f1 (ppm)

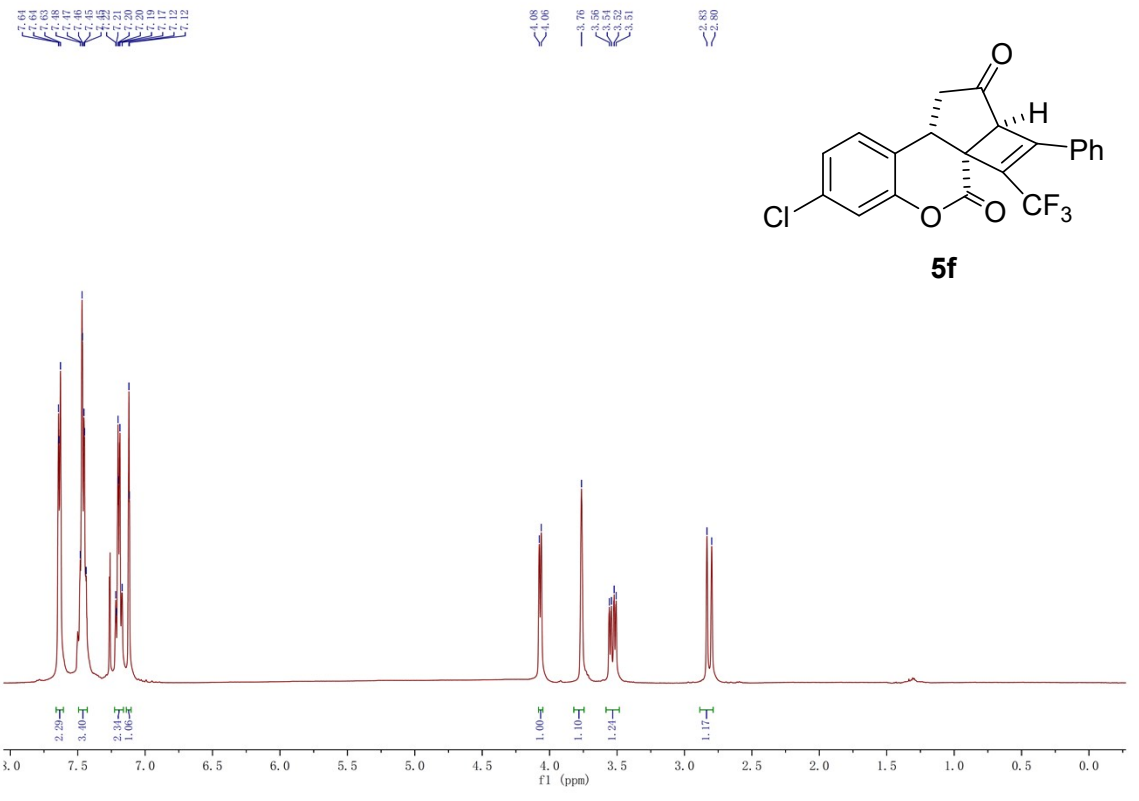

F
O
H
Ph
CF3
O
O
5e
f1 (ppm)


F
O
H
Ph
CF3
O
O
5e
f1 (ppm)


207.64
164.45
150.68
149.37
143.47
131.84
130.54
129.11
128.99
128.59
128.37
128.28
127.18
125.69
125.38
124.44
123.36
113.33
112.53
109.54
56.81
50.92
41.93
32.21
f1 (ppm)

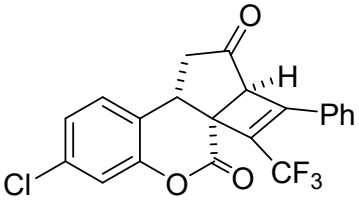
O
F
H
Ph
O
O
CF3

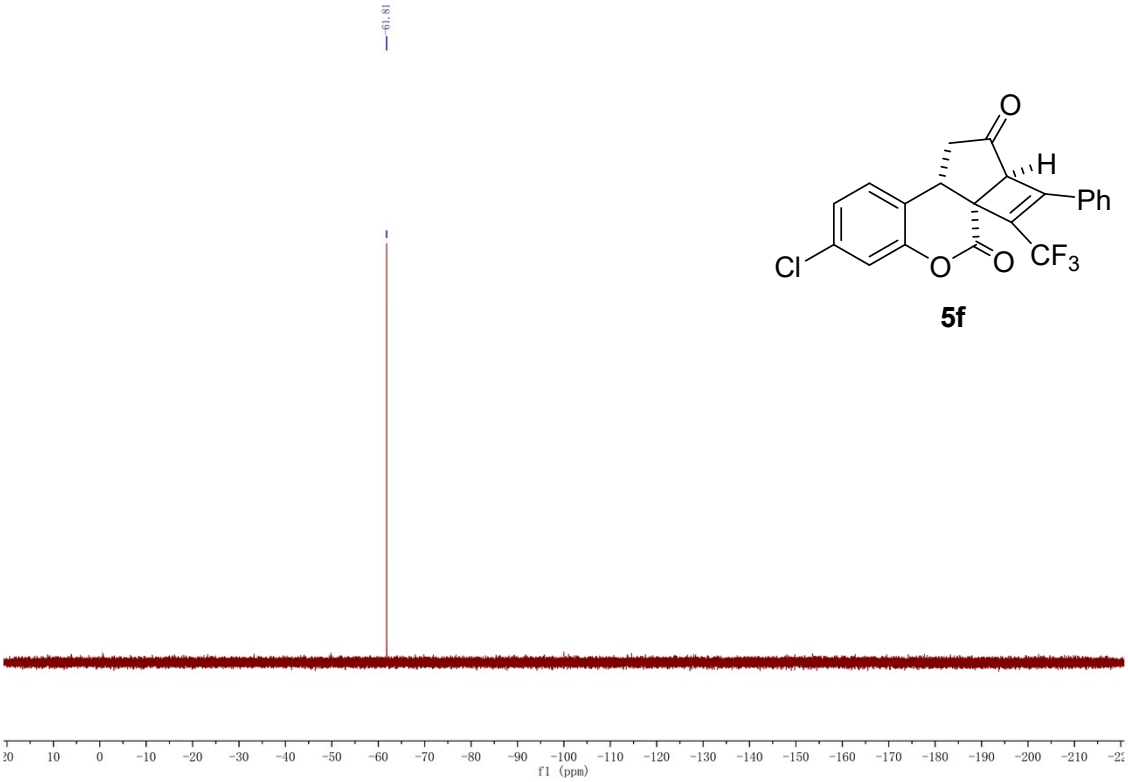
5e


7.64
7.64
7.63
7.63
7.48
7.47
7.46
7.45
7.45
7.44
7.21
7.20
7.20
7.19
7.17
7.12
7.12
4.08
4.06
3.76
3.56
3.54
3.52
3.51
2.83
2.80
2.29
3.40
2.34
1.06
1.00
1.10
1.24
1.17
f1 (ppm)

O
H
Ph
Cl
O
O
CF3

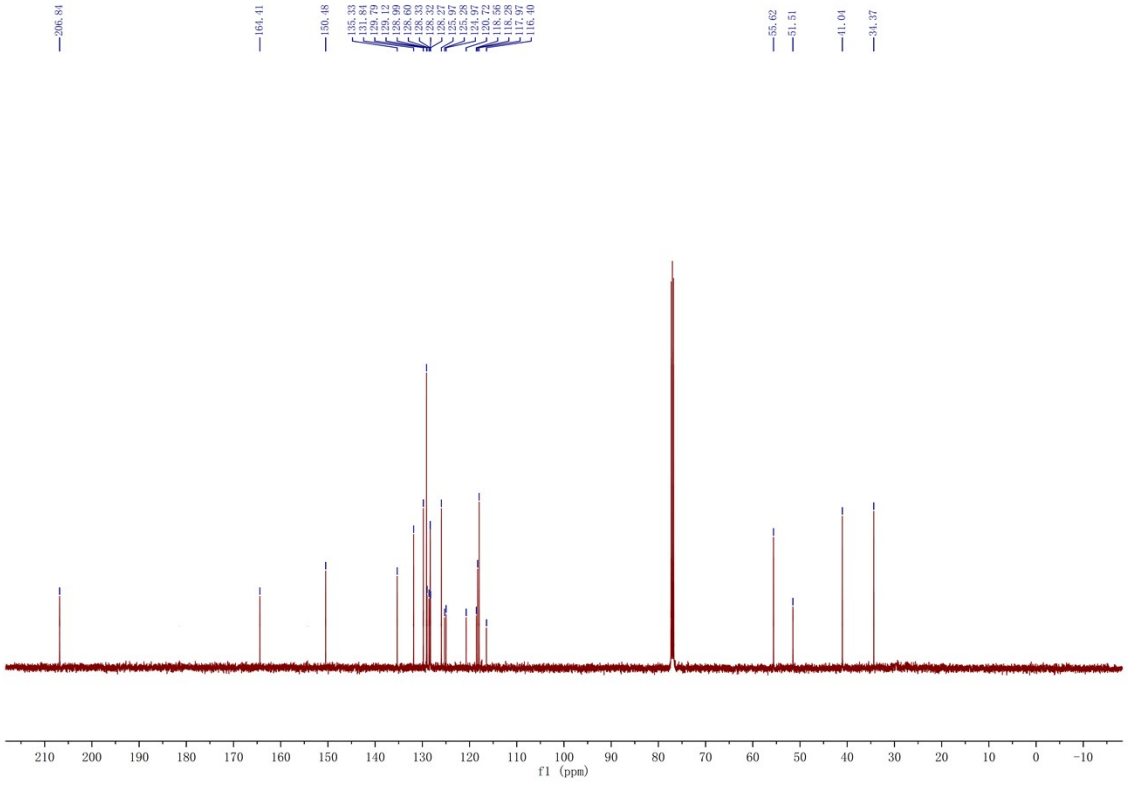
5f

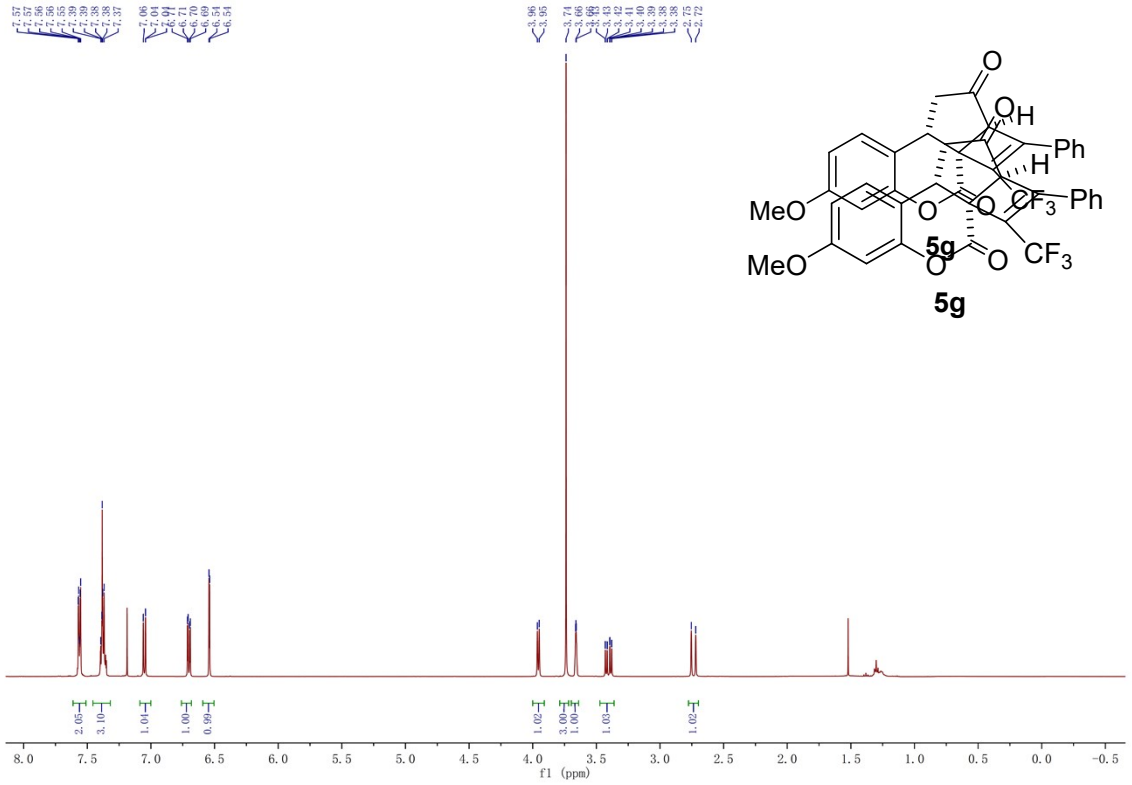

O
H
Ph
Cl
O
O
CF3


-61.81
f1 (ppm)

O
H
Ph
Cl
O
O
CF3

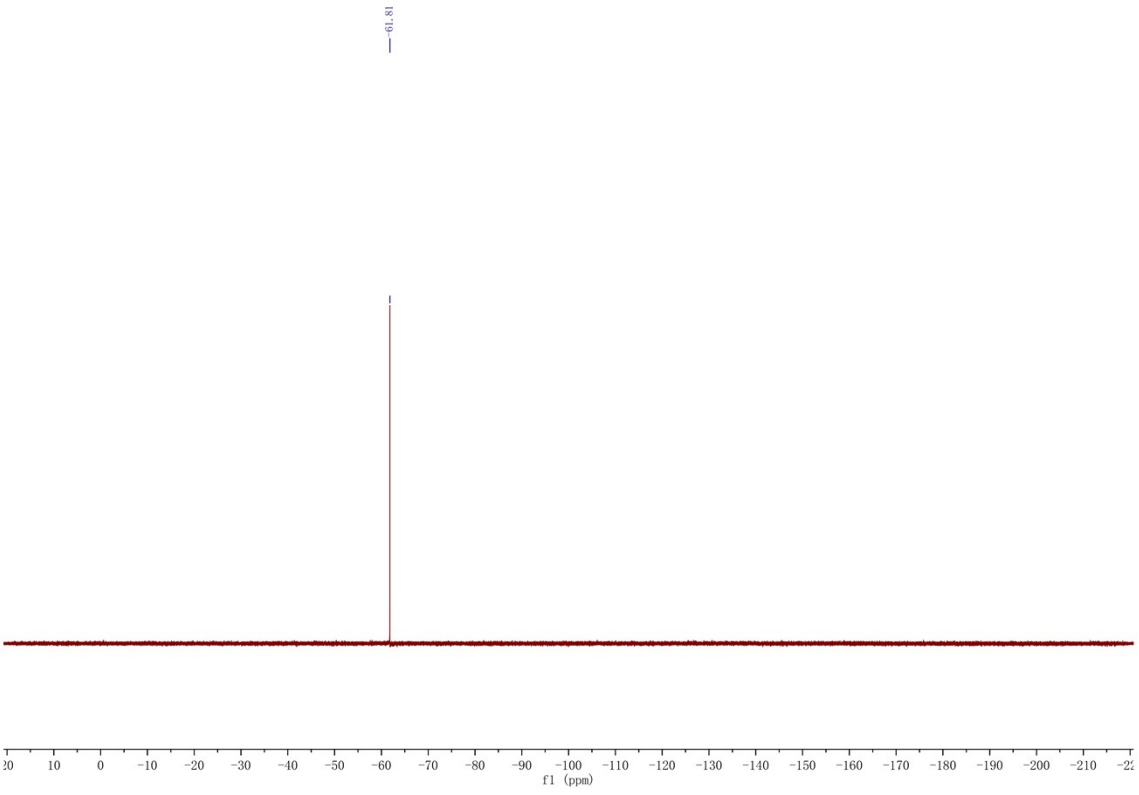
5f

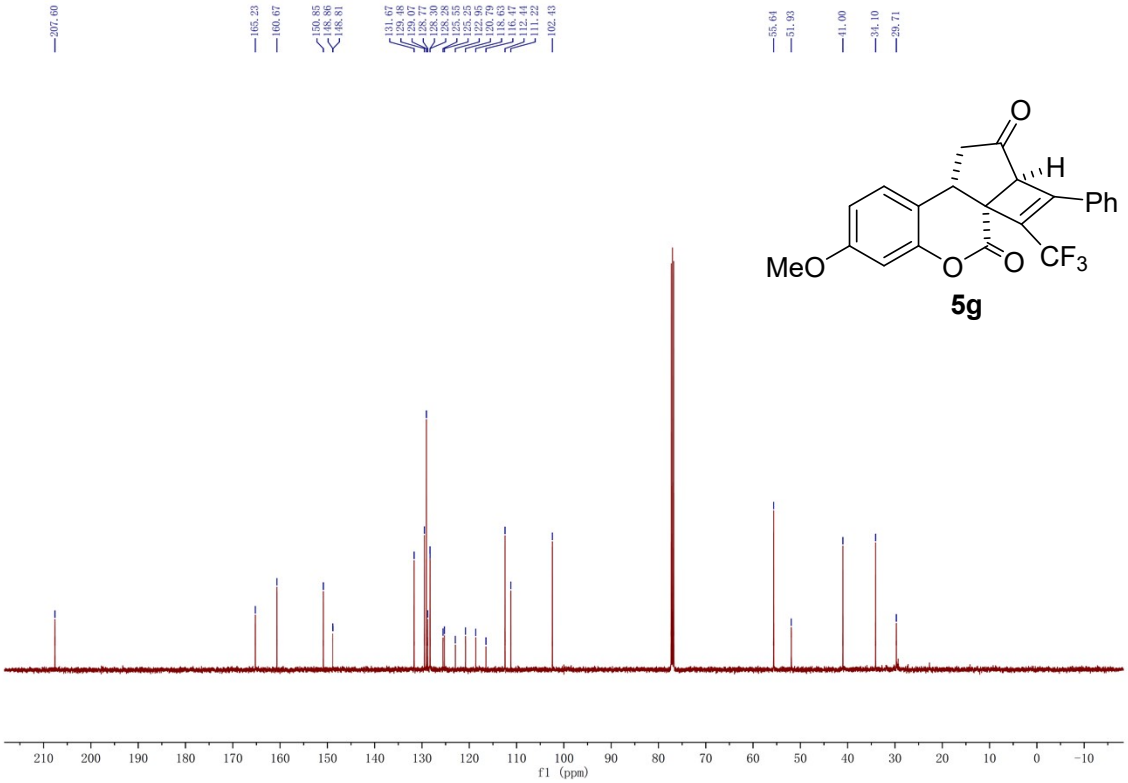

206.84
164.41
150.48
135.33
131.84
129.79
129.12
128.99
128.69
128.53
128.32
128.27
125.97
125.38
124.57
120.72
118.56
118.28
117.97
116.40
55.62
51.51
41.04
34.37
f1 (ppm)

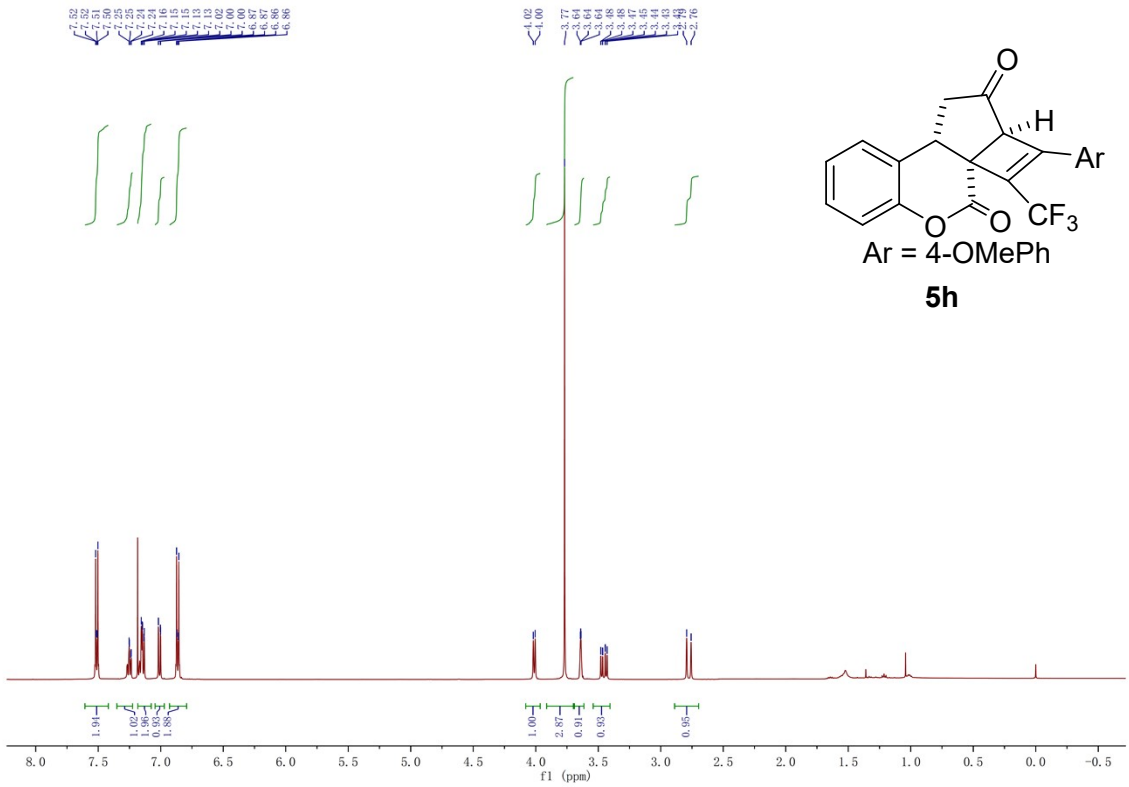

7.57
7.57
7.56
7.56
7.55
7.39
7.39
7.38
7.38
7.37
7.06
7.01
6.71
6.70
6.69
6.54
6.54
3.96
3.95
3.74
3.66
3.43
3.42
3.41
3.40
3.39
3.38
3.38
2.75
2.72
2.05
3.10
1.01
1.00
0.99
1.02
3.00
1.00
1.03
1.02
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

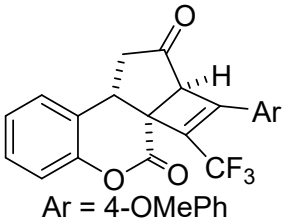
O
OH
Ph
H
MeO
O
O
CF3
Ph
5g
MeO
O
O
CF3

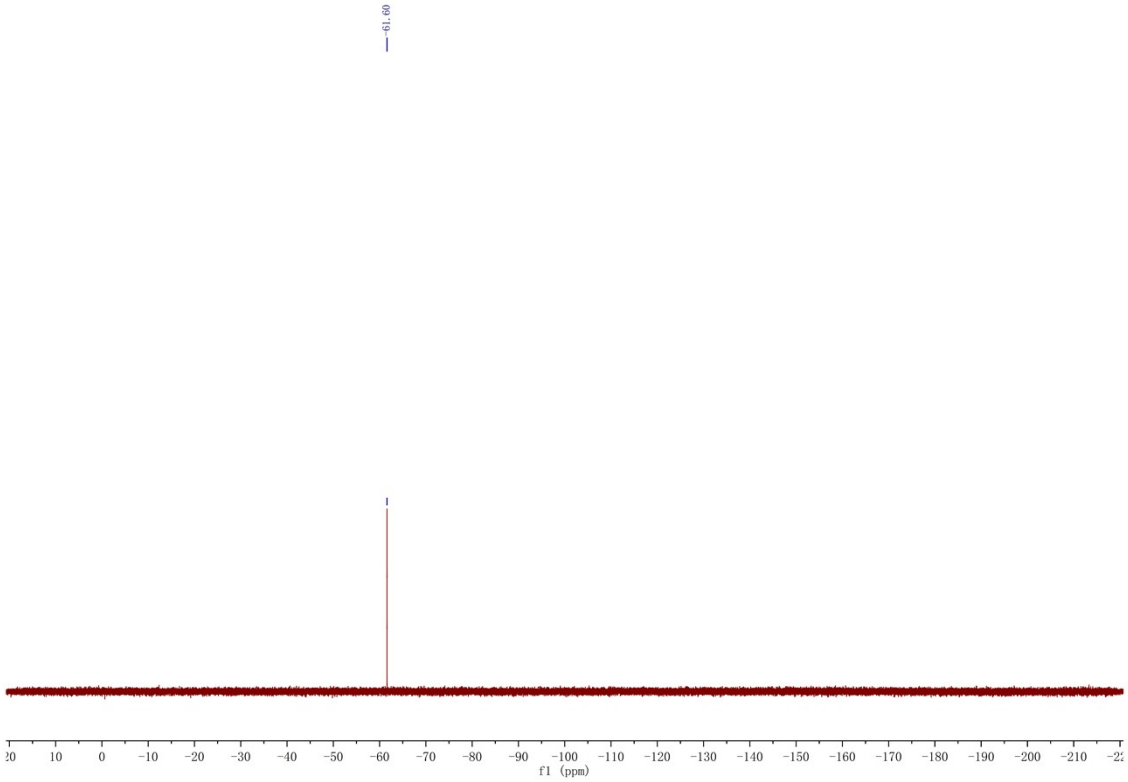
5g

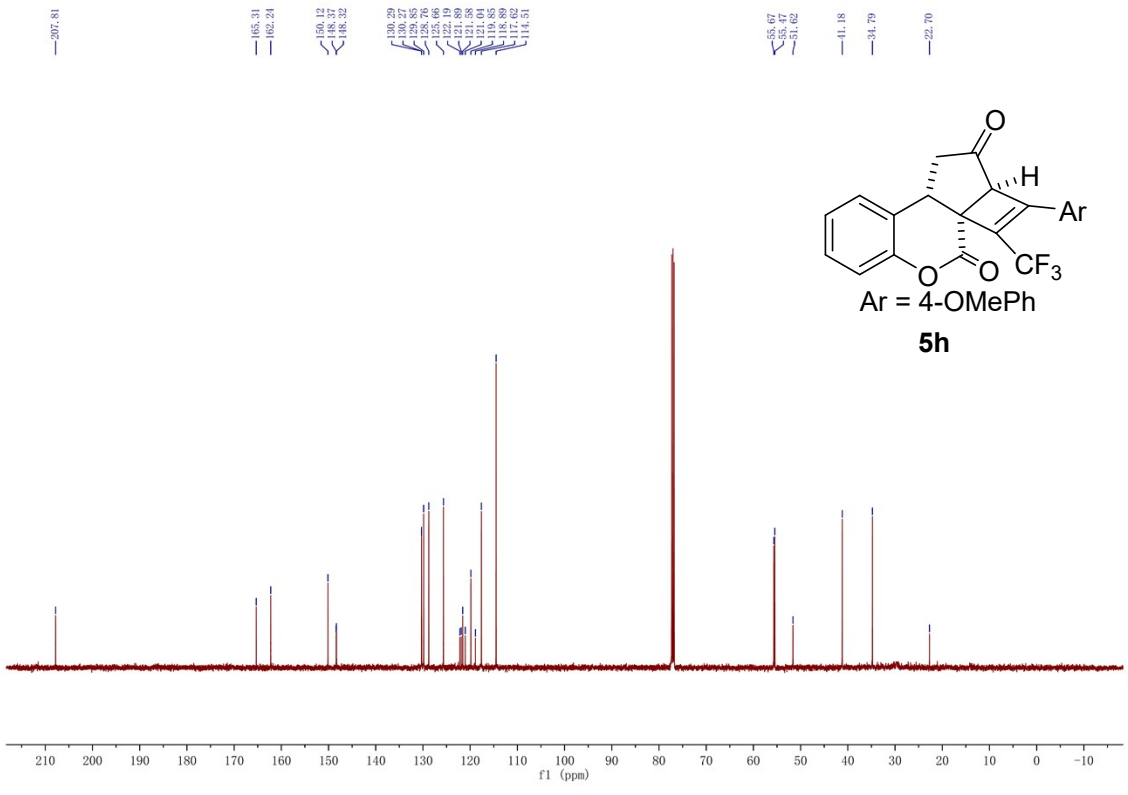

-61.81
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)


207.60
165.23
160.67
150.85
148.86
148.81
131.67
129.48
129.07
128.77
128.30
128.28
125.55
125.25
122.95
120.79
118.63
116.47
112.44
111.22
102.43
55.64
51.93
41.00
34.10
29.71
O
H
Ph
MeO
O
O
CF3
5g
f1 (ppm)


7.52
7.52
7.51
7.50
7.25
7.24
7.24
7.16
7.15
7.13
7.13
7.02
7.00
7.00
6.87
6.86
6.86
4.02
4.00
3.77
3.64
3.64
3.48
3.47
3.45
3.44
3.43
2.76
1.94
1.02
1.96
0.93
1.88
1.00
2.87
0.91
0.93
0.95
O
H
Ar
O
O
CF3
Ar = 4-OMePh
5h
f1 (ppm)


O
H
Ar
O
O
CF3
Ar = 4-OMePh

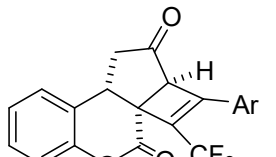

-61.60
f1 (ppm)

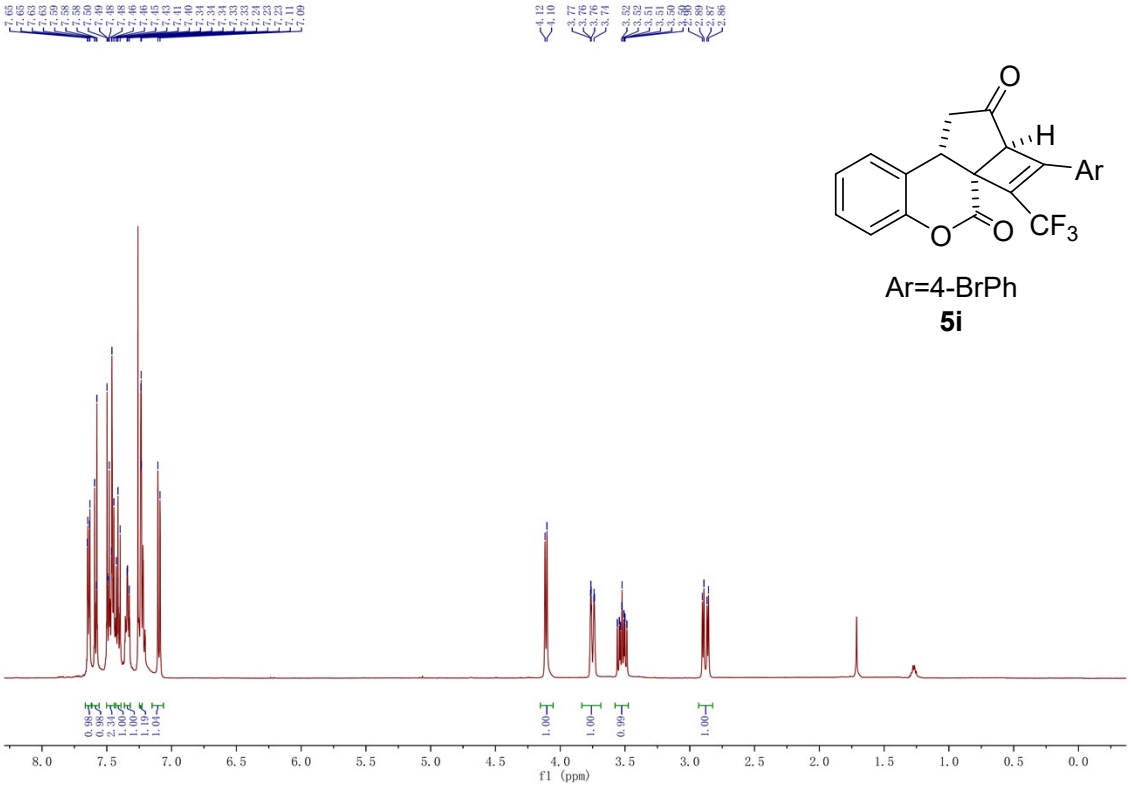

207.81
165.31
162.24
150.12
148.37
148.32
130.29
130.27
129.85
128.76
125.66
122.19
121.89
121.38
121.04
119.85
118.89
117.62
114.51
55.67
55.47
51.62
41.18
34.79
22.70
f1 (ppm)

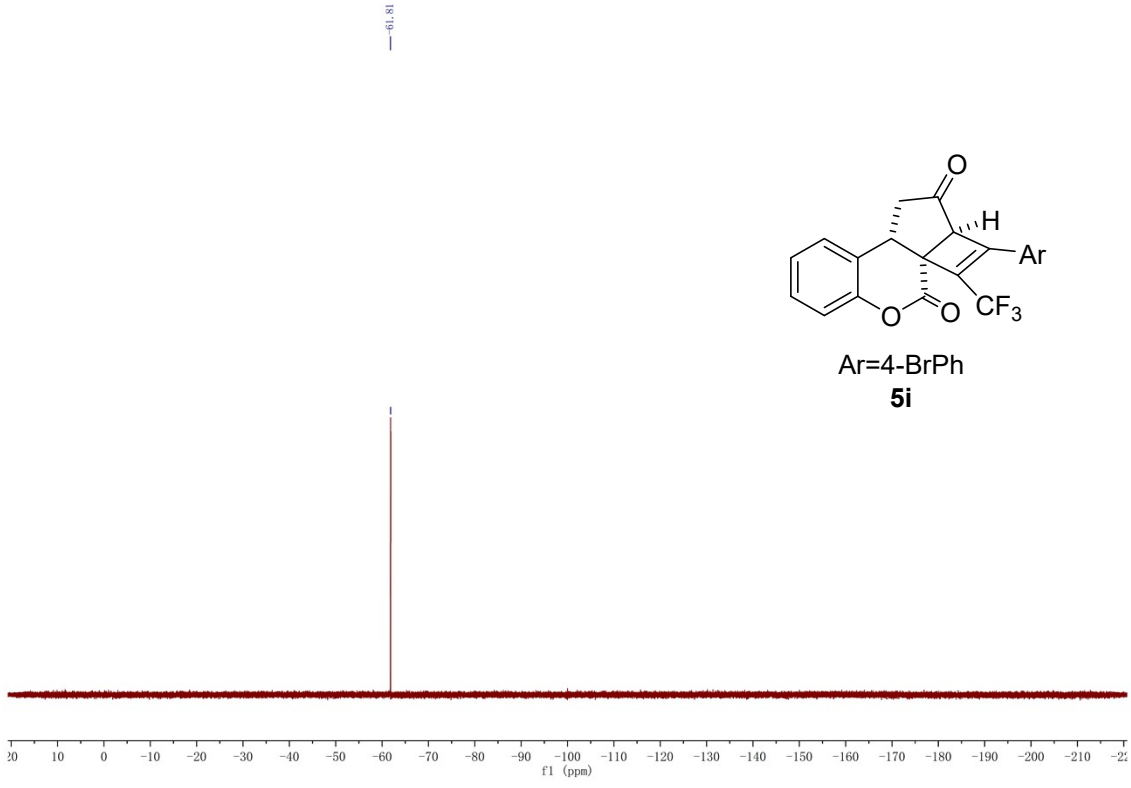
O
H
Ar
O
O
CF3

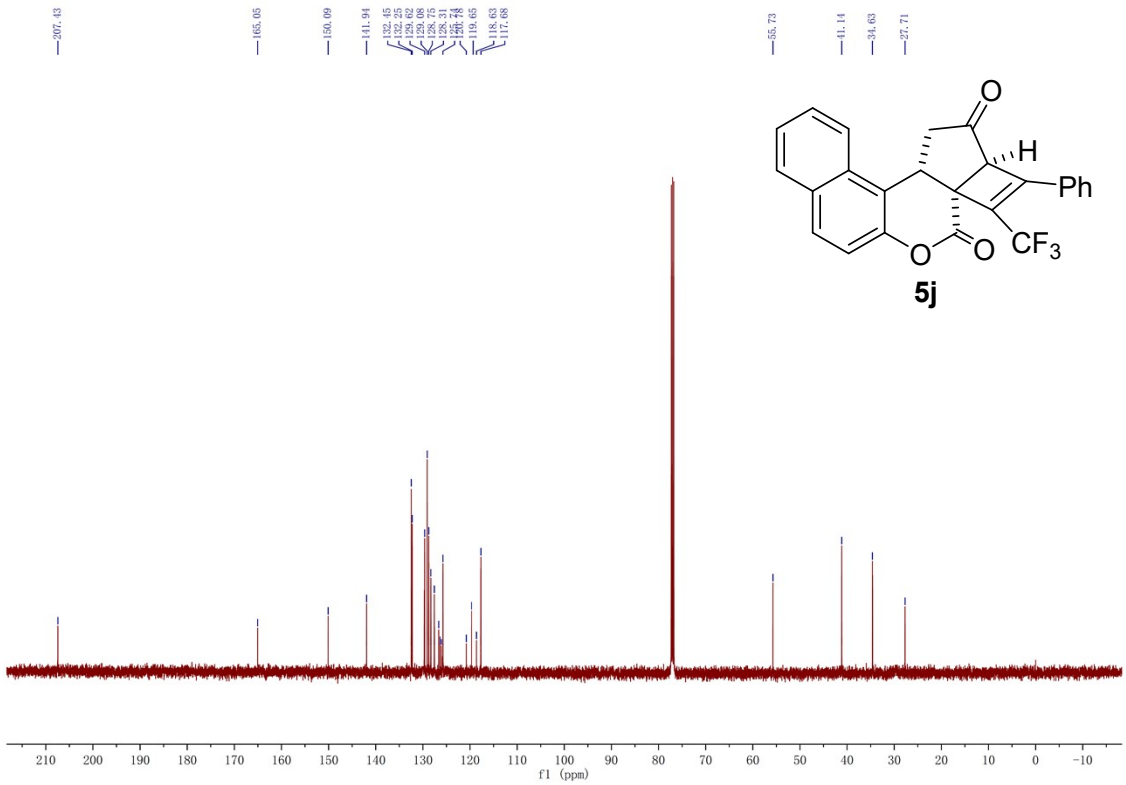
Ar = 4-OMePh

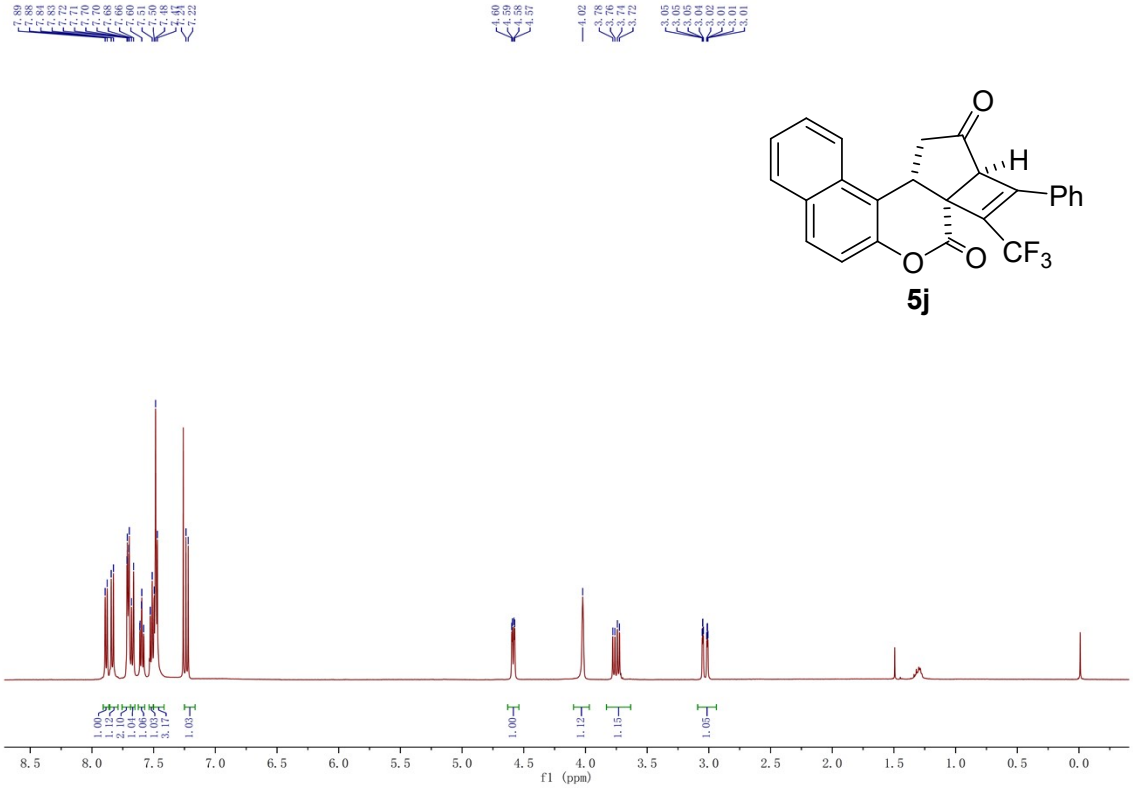
5h

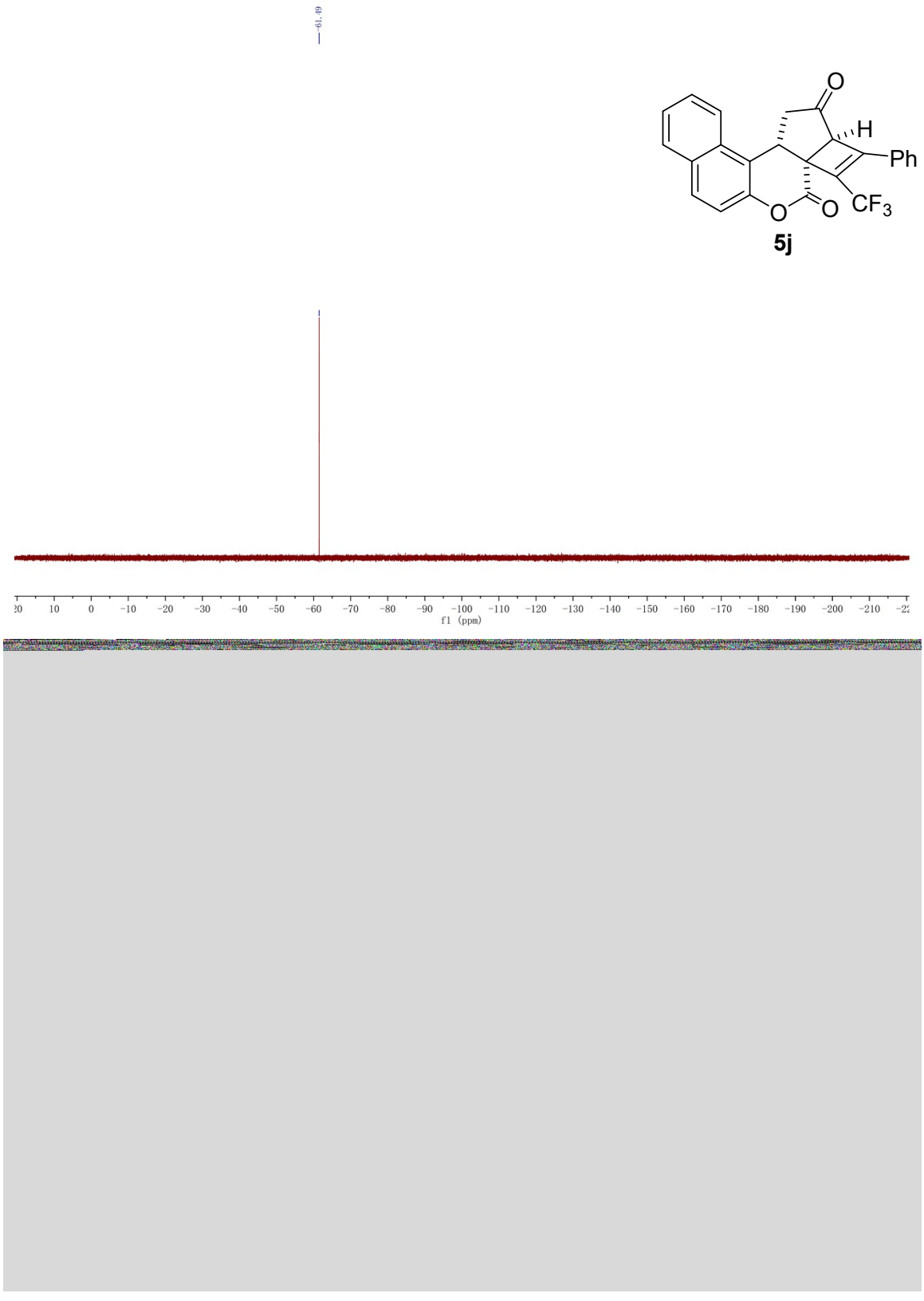

O
H
Ar

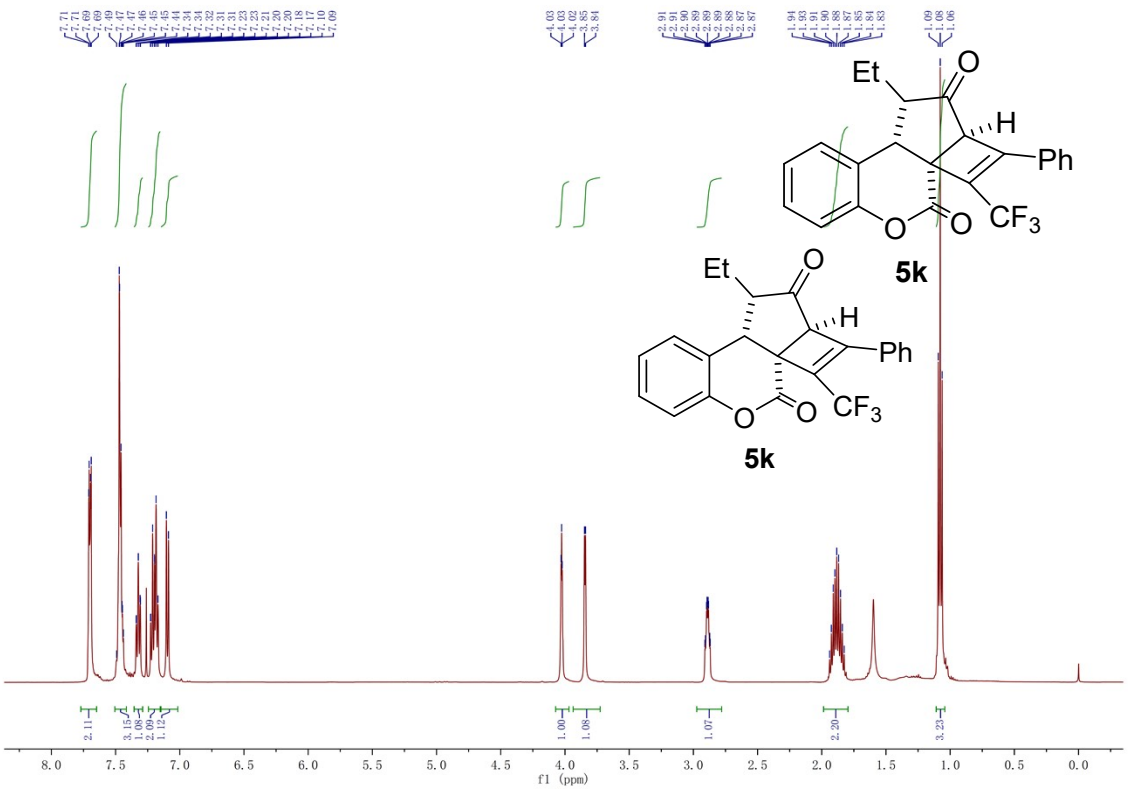

O
H
Ar
O
O
CF3
Ar=4-BrPh
5i
f1 (ppm)

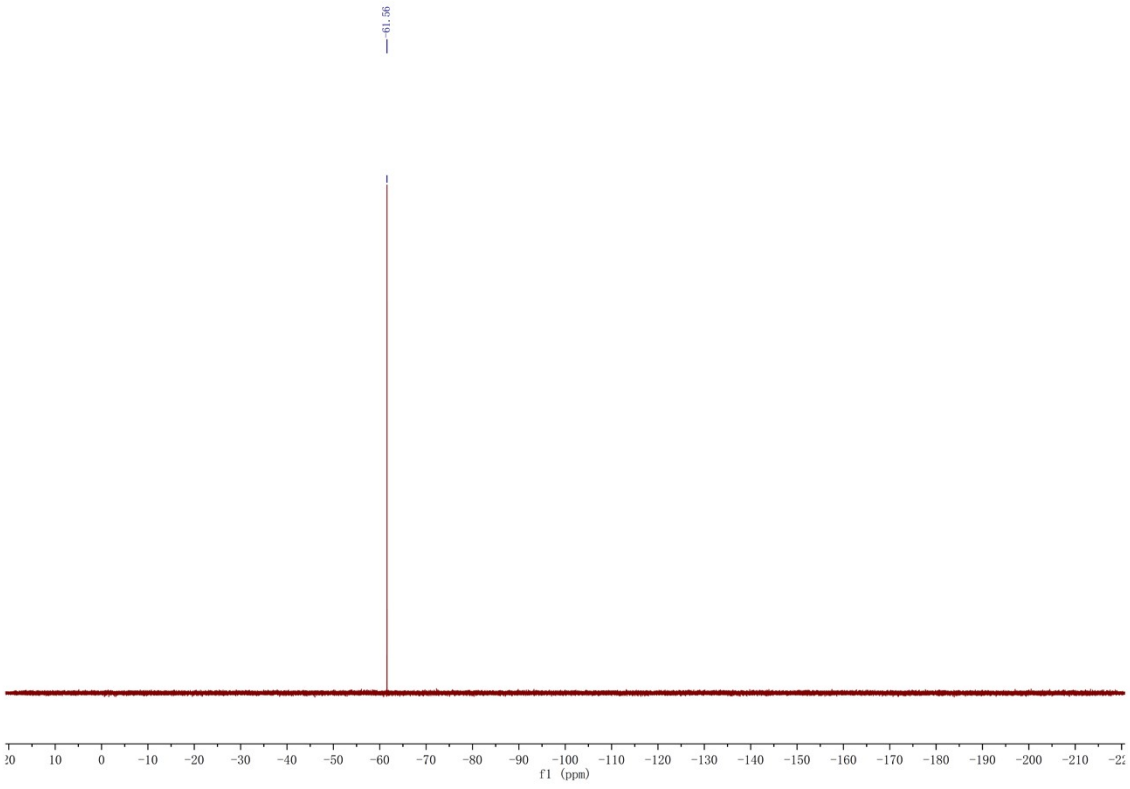

-61.81
O
H
Ar
O
O
CF3
Ar=4-BrPh
5i
f1 (ppm)

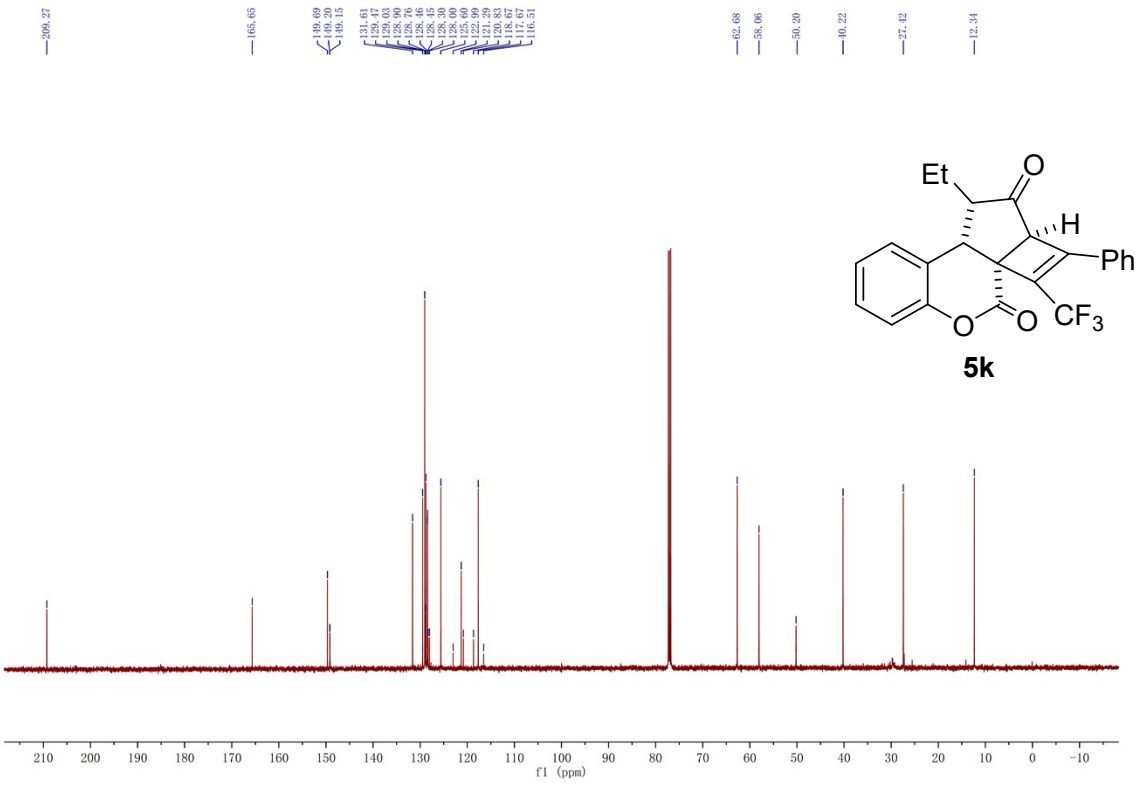

207.43
165.05
150.09
141.94
132.45
132.25
129.62
129.08
128.75
128.31
119.65
118.63
117.68
55.73
41.14
34.63
27.71
O
H
Ph
CF3
O
O
5j
f1 (ppm)

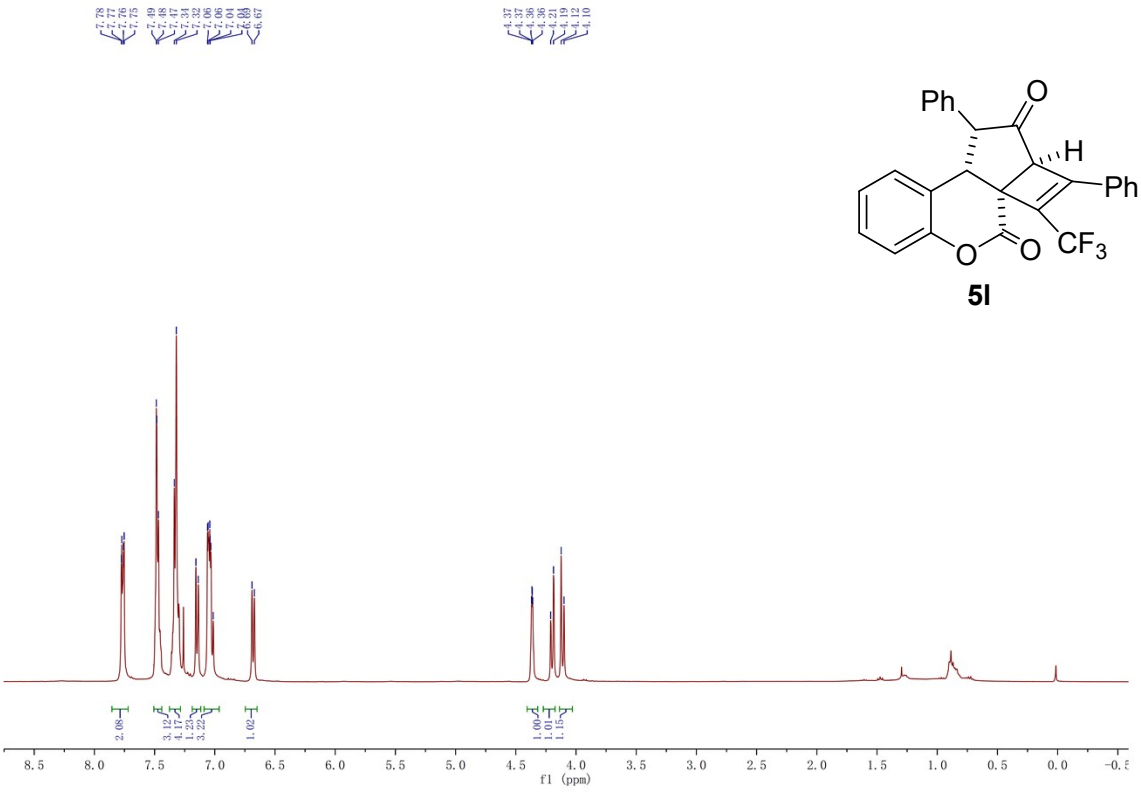

7.89
7.88
7.84
7.83
7.72
7.71
7.70
7.70
7.68
7.66
7.60
7.51
7.50
7.49
7.48
7.44
7.43
7.22
4.60
4.59
4.58
4.57
4.02
3.78
3.76
3.74
3.72
3.05
3.05
3.04
3.04
3.02
3.01
3.01
3.01
O
H
Ph
CF3
O
O
5j
f1 (ppm)

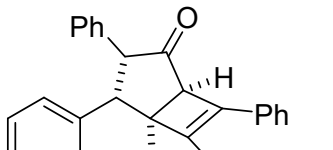

-61.49
O
H
Ph
CF3
O
O
5j
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

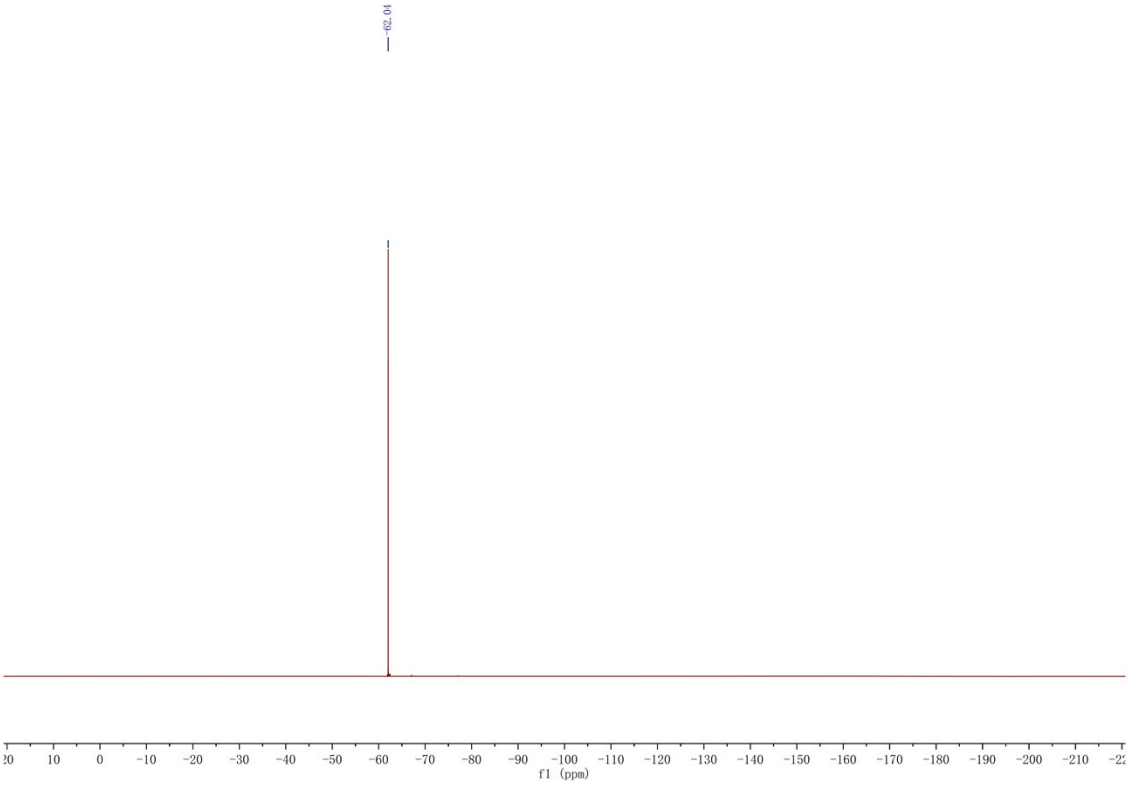

Et
O
H
Ph
CF3
O
O
5k
Et
O
H
Ph
CF3
O
O
5k
f1 (ppm)

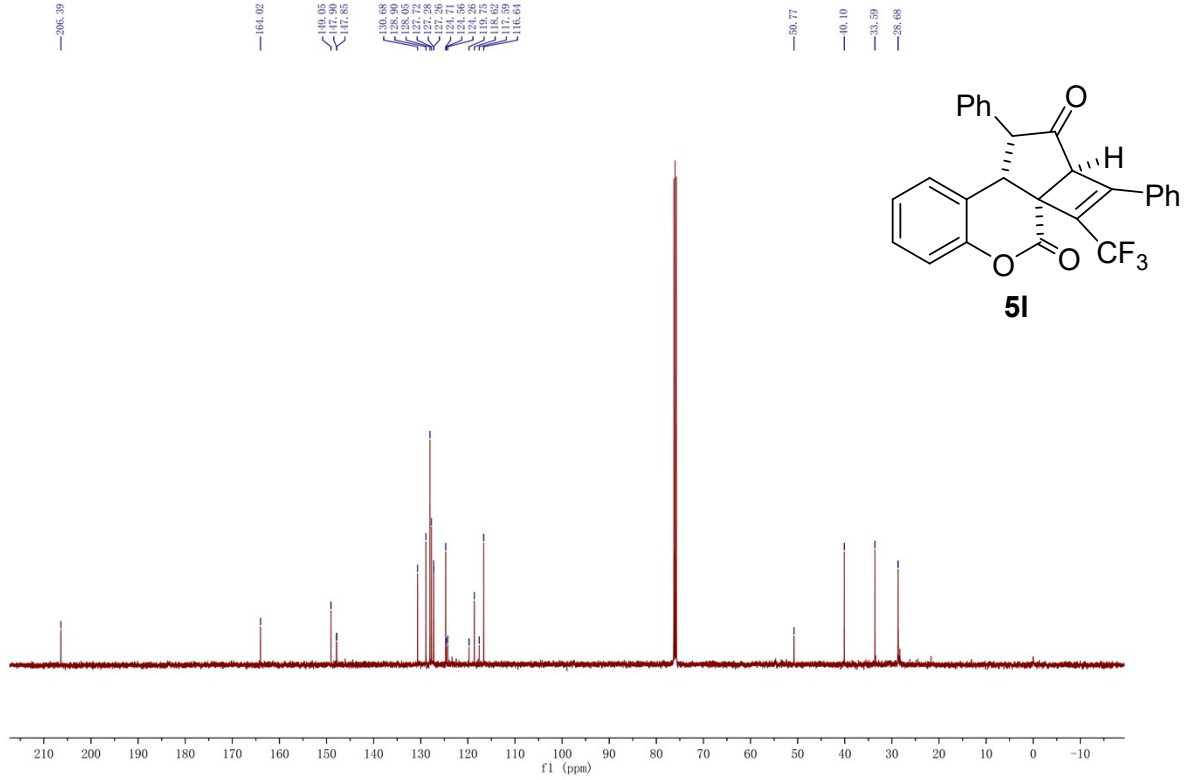

-61.56
f1 (ppm)


209.27
165.65
149.69
149.20
149.15
131.61
129.47
129.03
128.90
128.76
128.46
128.45
128.30
128.00
125.69
122.99
121.29
120.83
118.67
117.67
116.51
62.68
58.06
50.20
40.22
27.42
12.34
Et
O
H
Ph
O
O
CF3
5k
f1 (ppm)


7.78
7.77
7.76
7.75
7.49
7.48
7.47
7.34
7.32
7.06
7.06
7.04
6.68
6.67
4.37
4.37
4.36
4.36
4.21
4.19
4.12
4.10
Ph
O
H
Ph
O
O
CF3
5l
2.08
3.12
4.17
1.23
3.22
1.02
1.00
1.01
1.15
f1 (ppm)

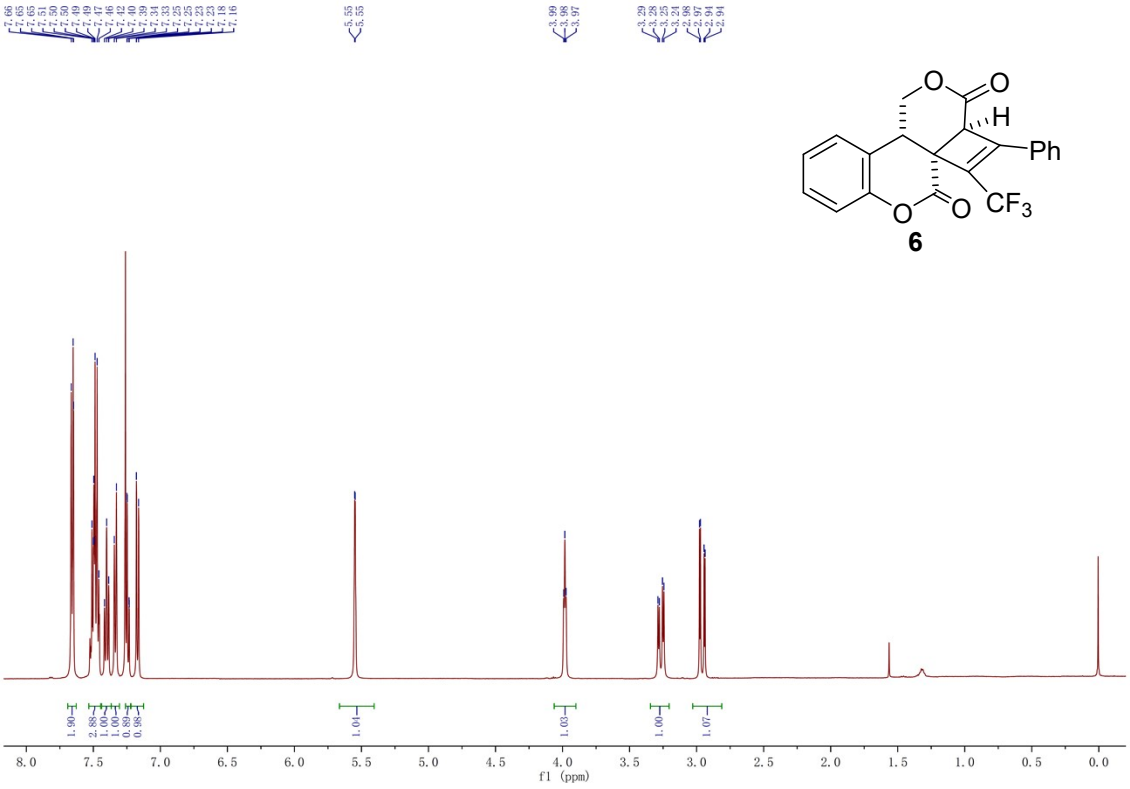

Ph
O
H
Ph

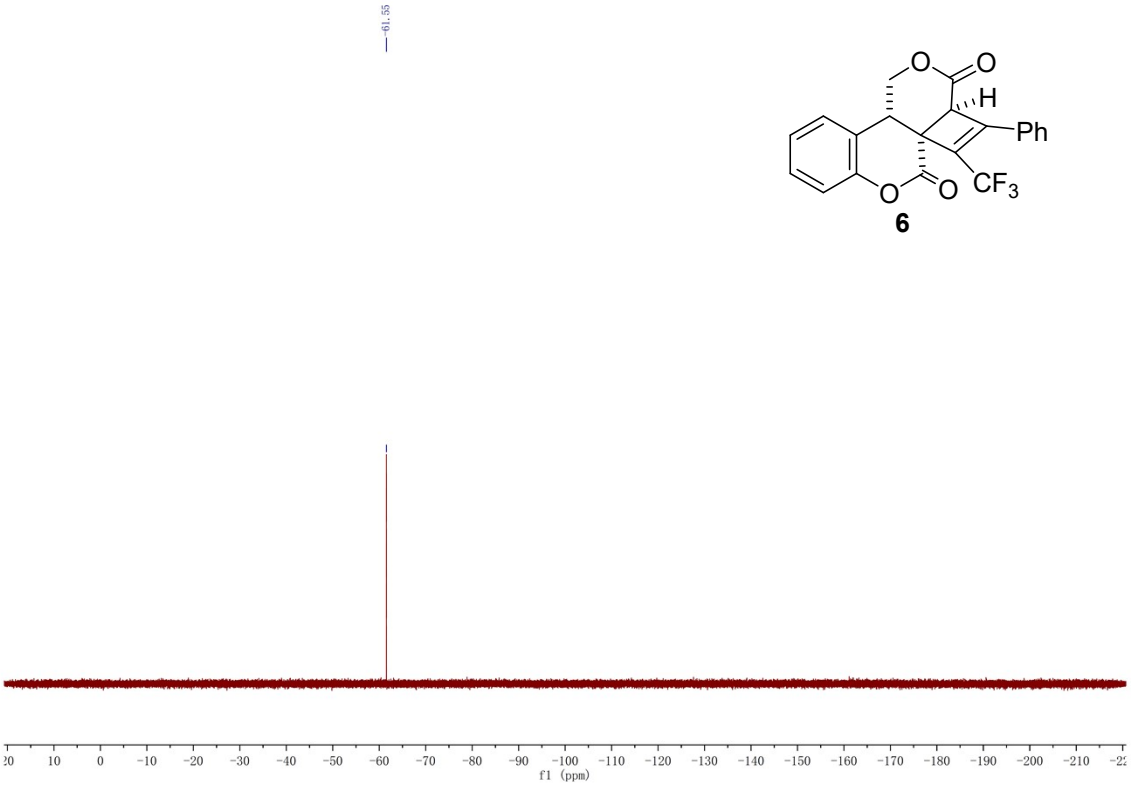

-62.04
f1 (ppm)

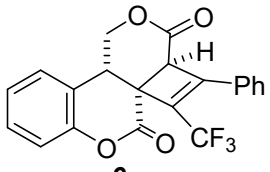

206.39
164.02
149.05
147.90
147.85
130.68
128.90
128.85
127.72
127.28
127.26
124.71
124.68
124.26
119.75
118.62
117.89
116.64
50.77
40.10
33.59
28.68
f1 (ppm)

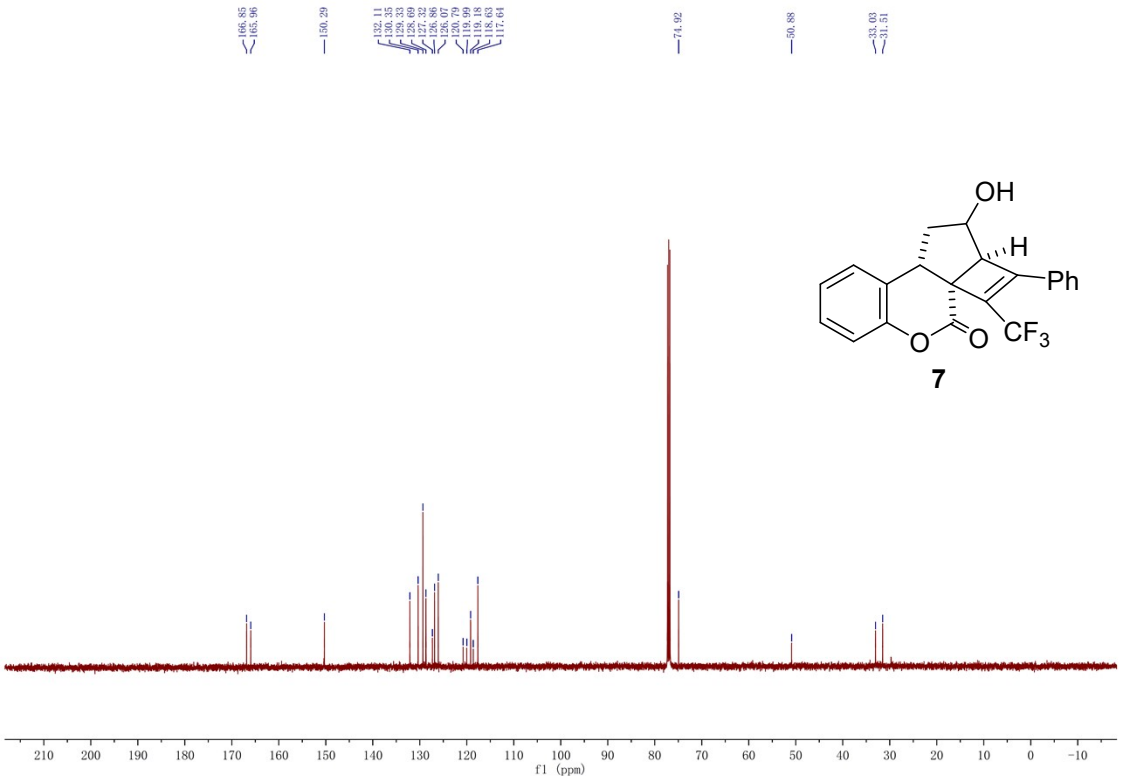
Ph
O
H
Ph
CF3
O
O

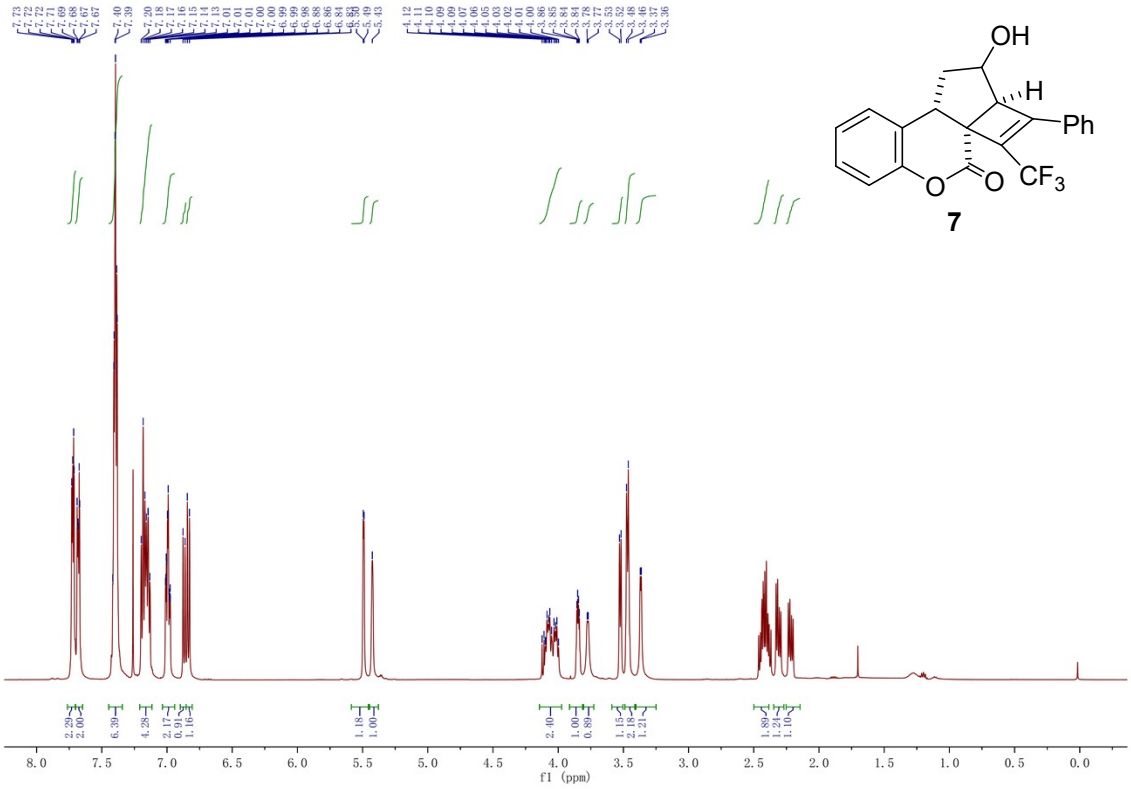
5l

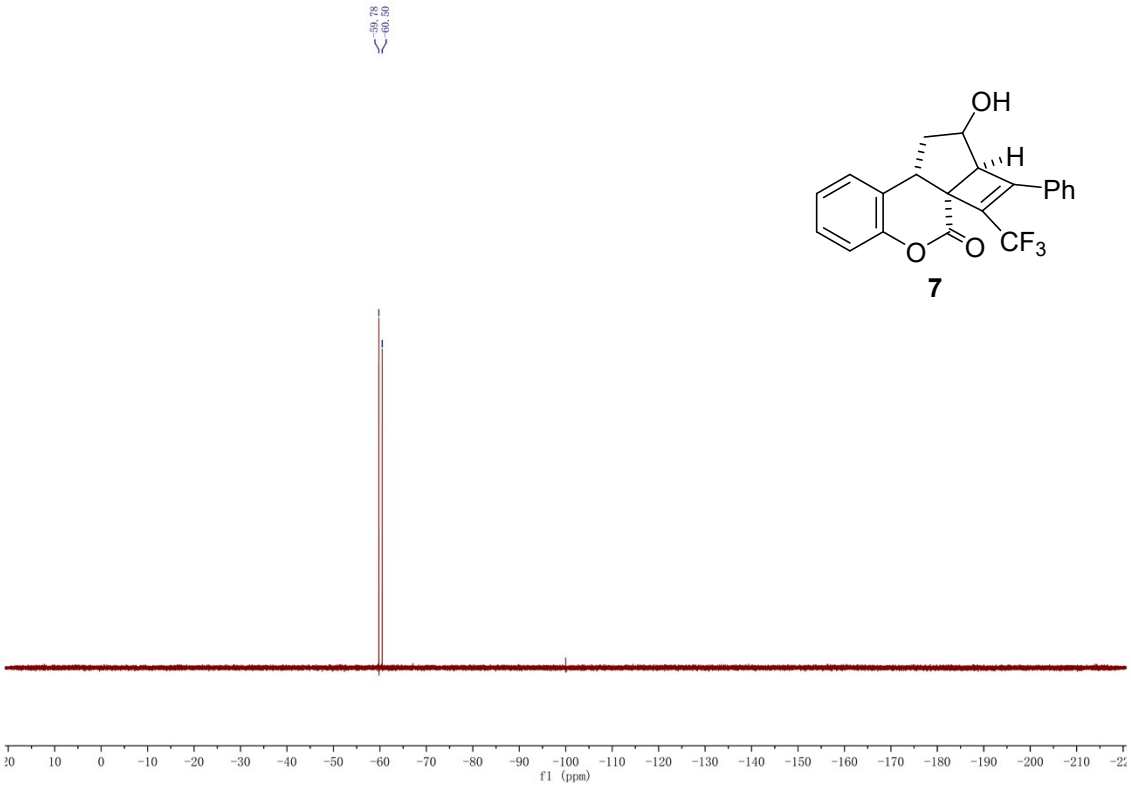

7.66
7.65
7.65
7.51
7.50
7.50
7.49
7.49
7.47
7.46
7.46
7.42
7.40
7.39
7.34
7.33
7.25
7.25
7.23
7.23
7.18
7.16
5.55
5.53
3.99
3.98
3.97
3.29
3.28
3.25
3.24
2.98
2.97
2.94
2.94
O
O
H
Ph
O
O
CF3
6
1.90
2.88
1.00
1.00
0.89
0.98
1.04
1.03
1.00
1.07
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


-61.55
O
O
H
Ph
O
O
CF3
6
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

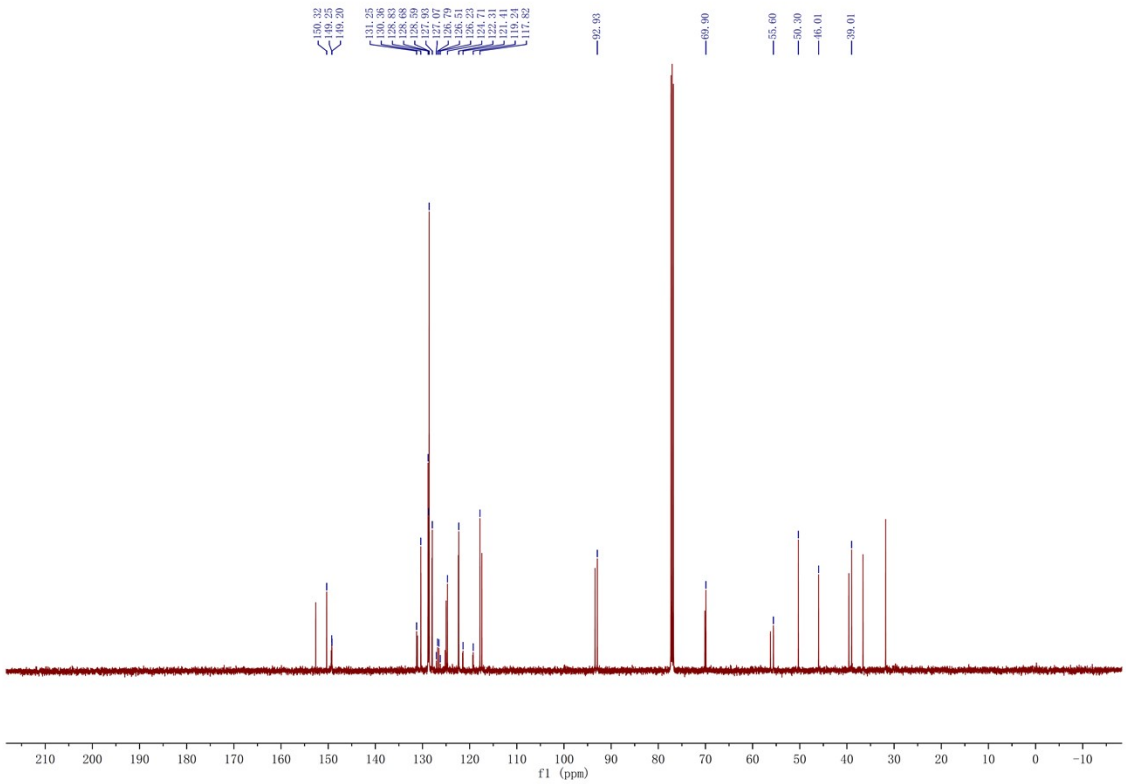

O
O
H
Ph
O
O
CF3

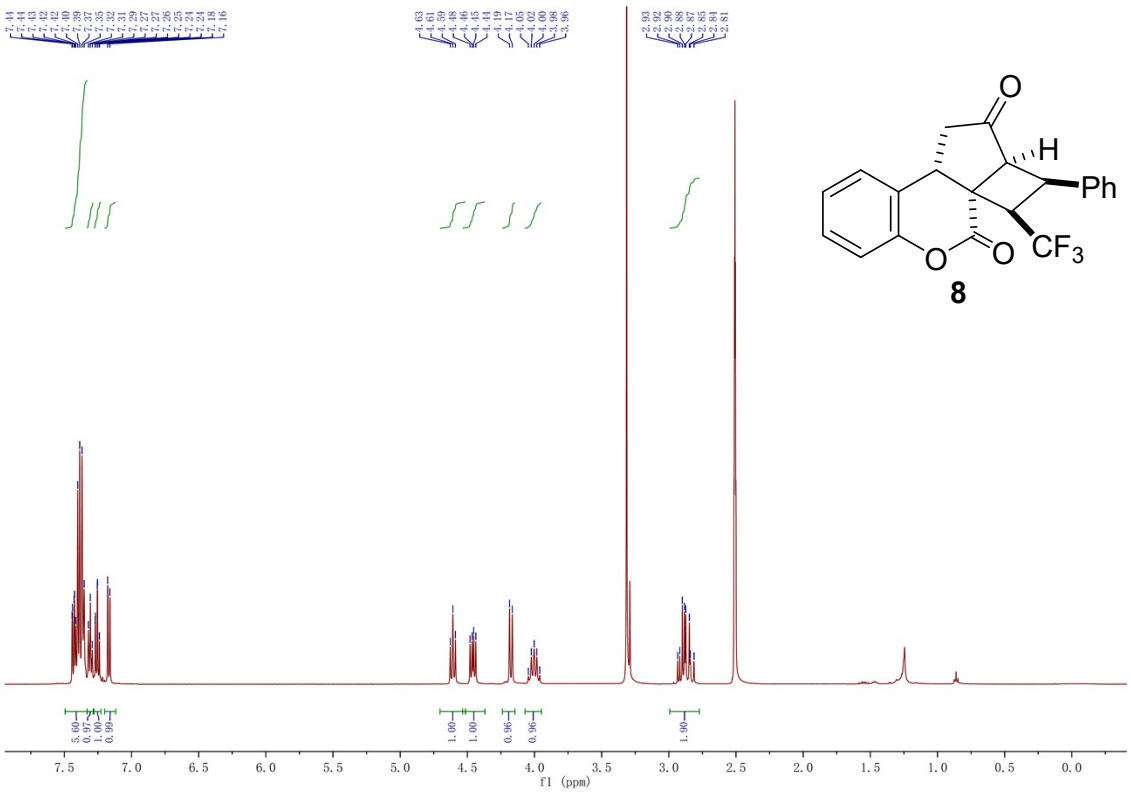

166.85
165.96
150.29
132.11
130.35
129.33
128.69
127.32
126.98
126.07
120.79
119.99
119.18
118.63
117.64
74.92
50.88
33.03
31.51
OH
H
Ph
CF3
O
O
7
f1 (ppm)


OH
H
Ph
CF3
O
O
7
f1 (ppm)


-59.78
-60.50
OH
H
Ph
CF3
O
O
f1 (ppm)

7


150.32
149.25
149.20
131.25
130.36
128.83
128.68
128.59
127.93
127.07
126.79
126.51
126.23
124.71
122.31
121.41
119.24
117.82
92.93
69.90
55.60
50.30
46.01
39.01
f1 (ppm)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7.24
7.24
7.18
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4.59
4.48
4.46
4.45
4.44
4.19
4.17
4.05
4.02
4.00
3.98
3.96
2.93
2.92
2.90
2.88
2.87
2.85
2.84
2.81
5.60
0.97
1.00
0.99
1.00
1.00
0.96
0.96
1.90
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
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f1 (ppm)
O
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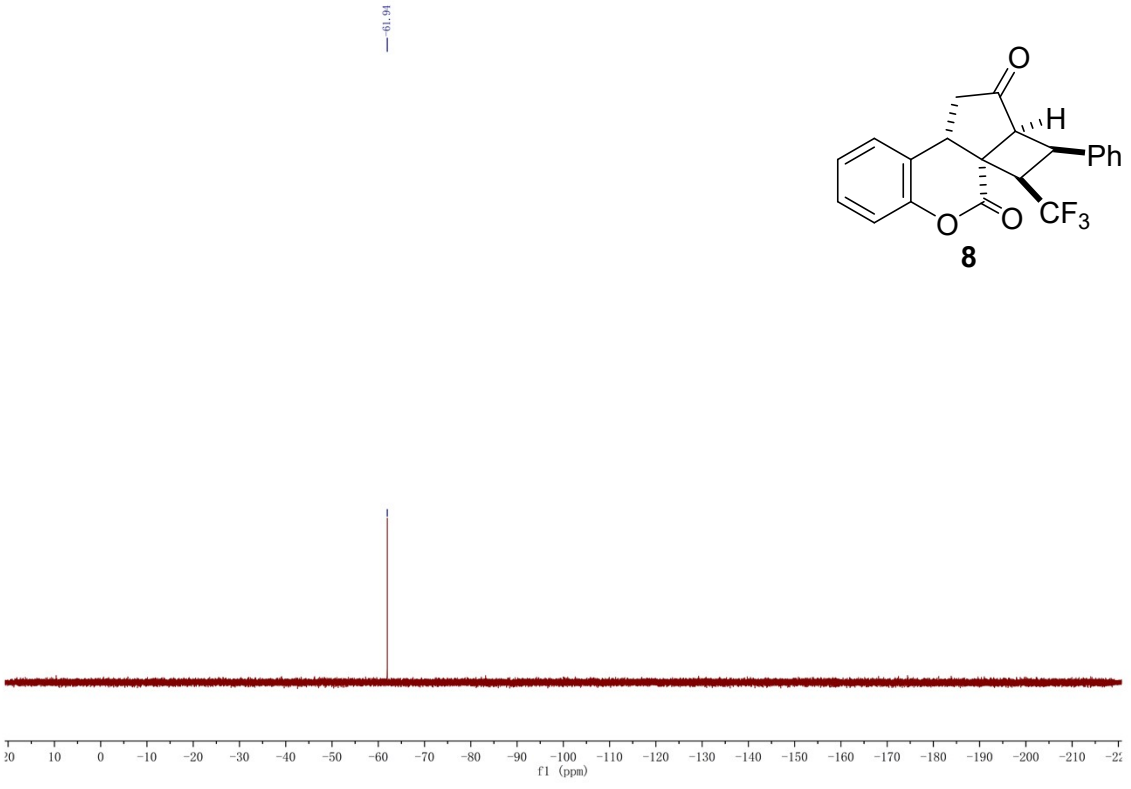
Ph
CF3
O
O

8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-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
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-120
-130
-140
-150
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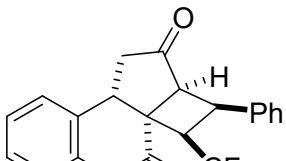
-170
-180
-190
-200
-210
f1 (ppm)
O
H
Ph
CF3
O
O

8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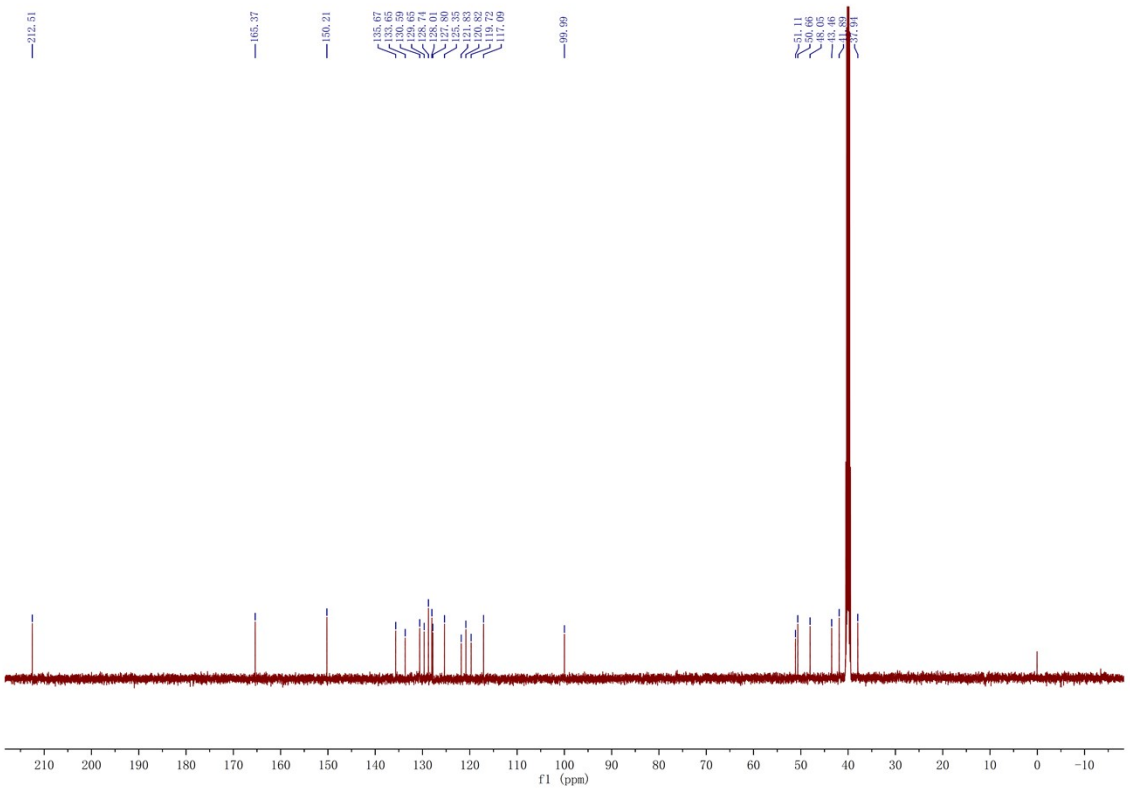
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135.67
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120.92
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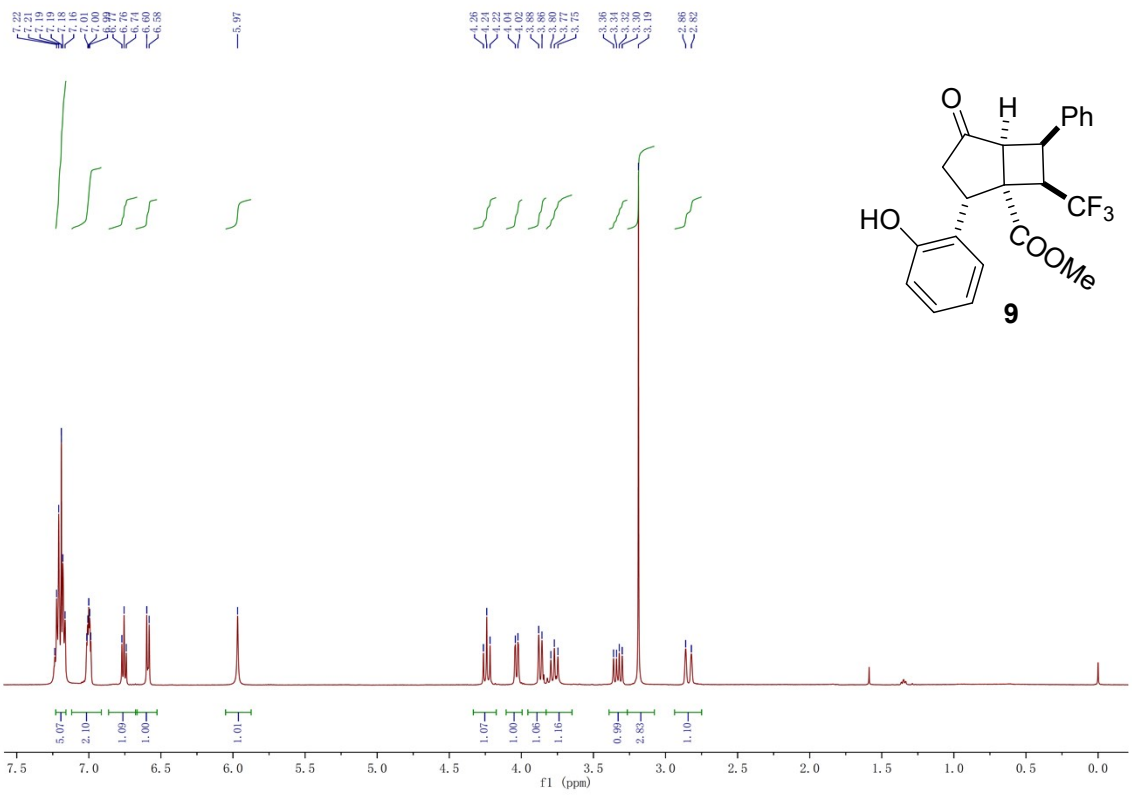
117.09
99.99
51.11
50.66
48.05
43.46
41.69
37.91
f1 (ppm)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7.16
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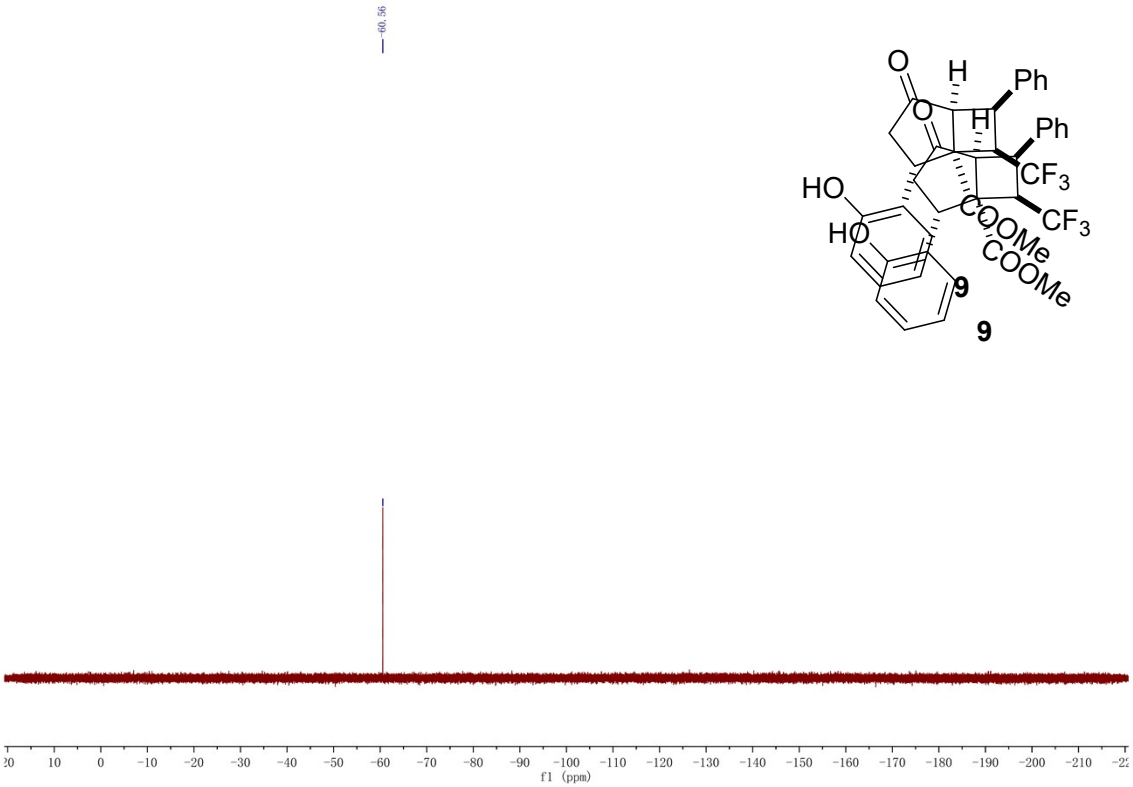
6.99
6.98
6.76
6.74
6.60
6.58
5.97
4.26
4.24
4.22
4.04
4.02
3.88
3.86
3.80
3.77
3.75
3.36
3.34
3.32
3.30
3.19
2.86
2.82
5.07
2.10
1.09
1.00
1.01
1.07
1.00
1.06
1.16
0.99
2.83
1.10
f1 (ppm)

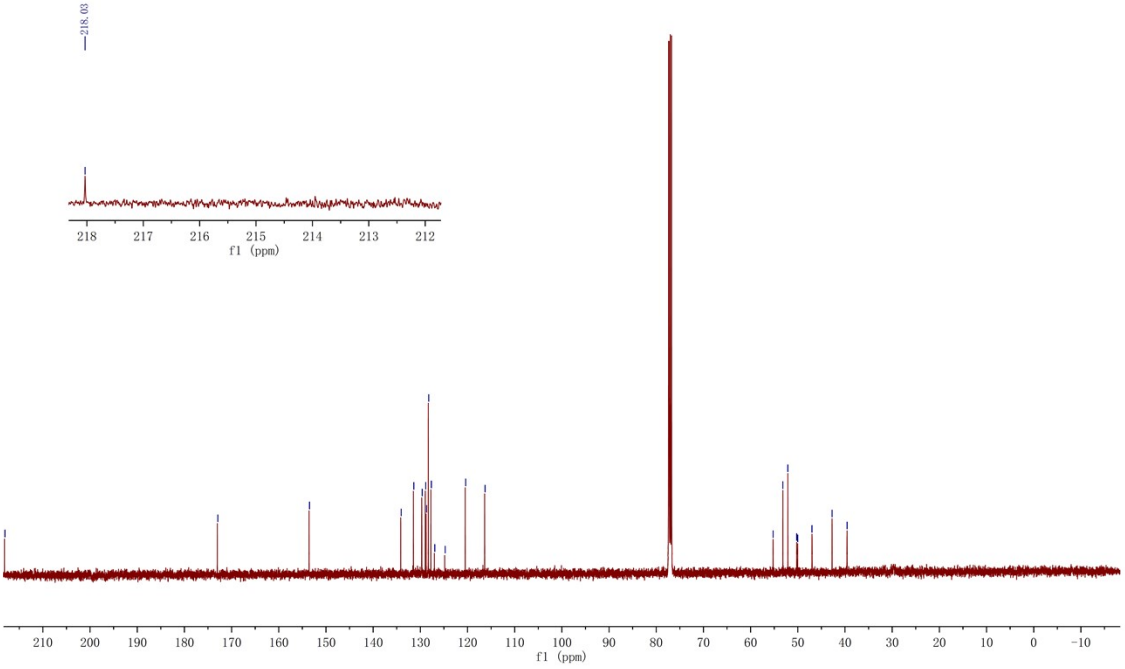
O
H
Ph
CF3
HO
COOMe

9


-60.56
f1 (ppm)

O
H
Ph
O
H
Ph
CF3
HO
HO
CF3
COOMe
COOMe
9

9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128.67
128.21
127.67
126.93
124.72
120.39
116.27
55.23
53.16
52.10
50.24
50.02
47.09
42.74
39.55
218.63
f1 (ppm)
f1 (ppm)

6. X-Ray Diffraction of compound

Experimental:

Crystal structure determination for compound was selected and carried out using a 'Bruker APEX-II CCD' diffractometer. The crystal was kept at 170.0 K during data collection. Using Olex2[1], the structure was solved with the ShelXT[2] structure solution program using Intrinsic Phasing and refined with the ShelXL[3] refinement package using Least Squares minimisation.

6.1 X-Ray Diffraction of 3a

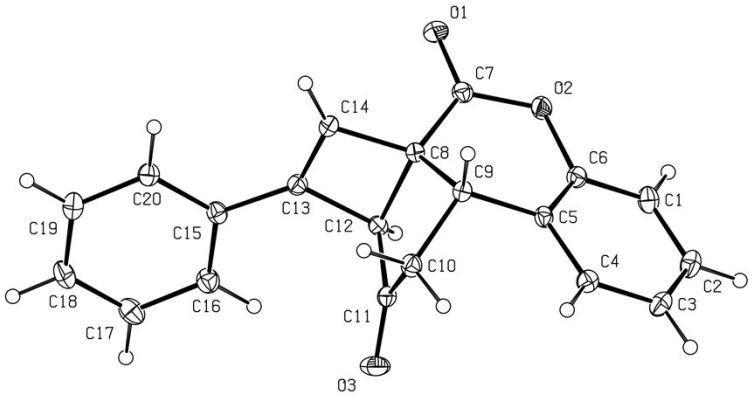

Figure S1. ORTEP drawing with thermal ellipsoids drawn to the 50 % level

Crystal structure determination of 3a

Crystal Data for $C_{20}H_{14}O_3$ (*M* =302.31 g/mol): orthorhombic, space group $P2_12_12_1$ (no. 19), *a* = 6.932(2) Å, *b* = 11.065(4) Å, *c* = 19.212(7) Å, *V* = 1473.5(8) Å^3, *Z* = 4, *T* = 170.01 K, μ(MoKα) = 0.091 mm^{-1}, *Dcalc* = 1.363 g/cm^3, 18145 reflections measured (5.616° ≤ 2Θ ≤ 54.976°), 3362 unique (R_{int} = 0.0292, R_{sigma} = 0.0196) which were used in all calculations. The final R_1 was 0.0306 (I > 2σ(I)) and wR_2 was 0.0766 (all data).

4. Dolomanov, O. V., Bourhis, L. J., Gildea, R. J., Howard, J. A. K. & Puschmann, H. (2009), J. Appl. Cryst. 42, 339-341.
5. Sheldrick, G.M. (2015). Acta Cryst. A71, 3-8.
6. Sheldrick, G.M. (2015). Acta Cryst. C71, 3-8.

Table S1. Crystal data and structure refinement for 3a.

Identification code	190320_CP_315_0m
Empirical formula	$C_{20}H_{14}O_3$
Formula weight	302.31
Temperature/K	170.01
Crystal system	orthorhombic
Space group	$P2_12_12_1$
a/Å	6.932(2)
b/Å	11.065(4)

c/Å	19.212(7)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	1473.5(8)
Z	4
ρ_{calc}g/cm^3	1.363
μ/mm^{-1}	0.091
F(000)	632.0
Crystal size/mm^3	0.29 × 0.18 × 0.12
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.616 to 54.976
Index ranges	-8 ≤ h ≤ 9, -14 ≤ k ≤ 14, -24 ≤ l ≤ 24
Reflections collected	18145
Independent reflections	3362 [R_{int} = 0.0292, R_{sigma} = 0.0196]
Data/restraints/parameters	3362/0/208
Goodness-of-fit on F^2	1.042
Final R indexes [I>=2σ (I)]	R_1 = 0.0306, wR_2 = 0.0749
Final R indexes [all data]	R_1 = 0.0327, wR_2 = 0.0766
Largest diff. peak/hole / e Å^{-3}	0.19/-0.19
Flack parameter	0.5(3)

Table S2. Bond lengths [Å] and angles [°] for 3a.

Bond lengths---

O1	C7	1.197(2)
O2	C6	1.399(2)
O2	C7	1.356(2)
O3	C11	1.207(2)
C1	C2	1.388(3)
C1	C6	1.384(2)
C2	C3	1.385(3)
C3	C4	1.392(3)
C4	C5	1.395(2)
C5	C6	1.388(2)
C5	C9	1.522(2)
C7	C8	1.505(2)
C8	C9	1.550(2)
C8	C12	1.585(2)
C8	C14	1.519(2)
C9	C10	1.540(2)
C10	C11	1.515(3)

C11	C12	1.521(2)
C12	C13	1.529(2)
C13	C14	1.337(2)
C13	C15	1.465(2)
C15	C16	1.395(3)
C15	C20	1.399(3)
C16	C17	1.396(3)
C17	C18	1.385(3)
C18	C19	1.387(3)
C19	C20	1.389(3)

Angles----------

C7	O2	C6	120.48(13)
C6	C1	C2	118.62(17)
C3	C2	C1	120.02(17)
C2	C3	C4	120.06(17)
C3	C4	C5	121.23(16)
C4	C5	C9	123.19(15)
C6	C5	C4	116.85(15)
C6	C5	C9	119.93(15)
C1	C6	O2	114.83(15)
C1	C6	C5	123.17(16)
C5	C6	O2	121.92(15)
O1	C7	O2	117.59(15)
O1	C7	C8	124.98(16)
O2	C7	C8	117.44(14)
C7	C8	C9	114.37(14)
C7	C8	C12	116.21(14)
C7	C8	C14	112.40(14)
C9	C8	C12	105.19(13)
C14	C8	C9	119.73(14)
C14	C8	C12	85.50(12)
C5	C9	C8	107.43(13)
C5	C9	C10	110.18(14)
C10	C9	C8	102.73(13)
C11	C10	C9	102.88(14)
O3	C11	C10	126.09(17)
O3	C11	C12	124.95(17)
C10	C11	C12	108.96(14)
C11	C12	C8	103.93(13)
C11	C12	C13	108.83(13)

C13	C12	C8	85.04(12)
C14	C13	C12	94.46(14)
C14	C13	C15	136.83(17)
C15	C13	C12	128.25(15)
C13	C14	C8	94.73(14)
C16	C15	C13	120.06(16)
C16	C15	C20	119.21(15)
C20	C15	C13	120.65(16)
C15	C16	C17	120.38(18)
C18	C17	C16	119.87(18)
C17	C18	C19	120.04(16)
C18	C19	C20	120.44(18)
C19	C20	C15	120.01(17)

Table S3. Torsion angles [°] for 3a

O1	C7	C8	C9	-143.32(17)
O1	C7	C8	C12	93.8(2)
O1	C7	C8	C14	-2.5(2)
O2	C7	C8	C9	36.3(2)
O2	C7	C8	C12	-86.67(18)
O2	C7	C8	C14	177.12(14)
O3	C11	C12	C8	-170.15(17)
O3	C11	C12	C13	100.4(2)
C1	C2	C3	C4	1.4(3)
C2	C1	C6	O2	174.99(16)
C2	C1	C6	C5	-2.0(3)
C2	C3	C4	C5	-1.5(3)
C3	C4	C5	C6	-0.1(2)
C3	C4	C5	C9	178.15(16)
C4	C5	C6	O2	-174.87(15)
C4	C5	C6	C1	1.9(2)
C4	C5	C9	C8	-151.52(16)
C4	C5	C9	C10	-40.3(2)
C5	C9	C10	C11	-73.85(16)
C6	O2	C7	O1	179.08(16)
C6	O2	C7	C8	-0.5(2)
C6	C1	C2	C3	0.3(3)
C6	C5	C9	C8	26.7(2)
C6	C5	C9	C10	137.88(16)
C7	O2	C6	C1	160.64(15)

C7	O2	C6	C5	-22.4(2)
C7	C8	C9	C5	-46.76(19)
C7	C8	C9	C10	-162.97(14)
C7	C8	C12	C11	142.51(15)
C7	C8	C12	C13	-109.29(15)
C7	C8	C14	C13	112.54(16)
C8	C9	C10	C11	40.37(17)
C8	C12	C13	C14	-3.97(13)
C8	C12	C13	C15	-177.20(17)
C9	C5	C6	O2	6.8(2)
C9	C5	C6	C1	-176.46(16)
C9	C8	C12	C11	14.90(17)
C9	C8	C12	C13	123.10(13)
C9	C8	C14	C13	-108.92(16)
C9	C10	C11	O3	148.63(18)
C9	C10	C11	C12	-32.16(17)
C10	C11	C12	C8	10.63(17)
C10	C11	C12	C13	-78.83(16)
C11	C12	C13	C14	99.08(15)
C11	C12	C13	C15	-74.2(2)
C12	C8	C9	C5	81.95(15)
C12	C8	C9	C10	-34.26(17)
C12	C8	C14	C13	-3.99(13)
C12	C13	C14	C8	4.14(14)
C12	C13	C15	C16	-7.3(3)
C12	C13	C15	C20	169.38(16)
C13	C15	C16	C17	175.09(18)
C13	C15	C20	C19	-174.27(16)
C14	C8	C9	C5	175.46(14)
C14	C8	C9	C10	59.25(19)
C14	C8	C12	C11	-104.70(14)
C14	C8	C12	C13	3.49(12)
C14	C13	C15	C16	-177.4(2)
C14	C13	C15	C20	-0.7(3)
C15	C13	C14	C8	176.4(2)
C15	C16	C17	C18	-0.4(3)
C16	C15	C20	C19	2.4(3)
C16	C17	C18	C19	1.7(3)
C17	C18	C19	C20	-0.9(3)
C18	C19	C20	C15	-1.2(3)
C20	C15	C16	C17	-1.6(3)

6.2 X-Ray Diffraction of 5a

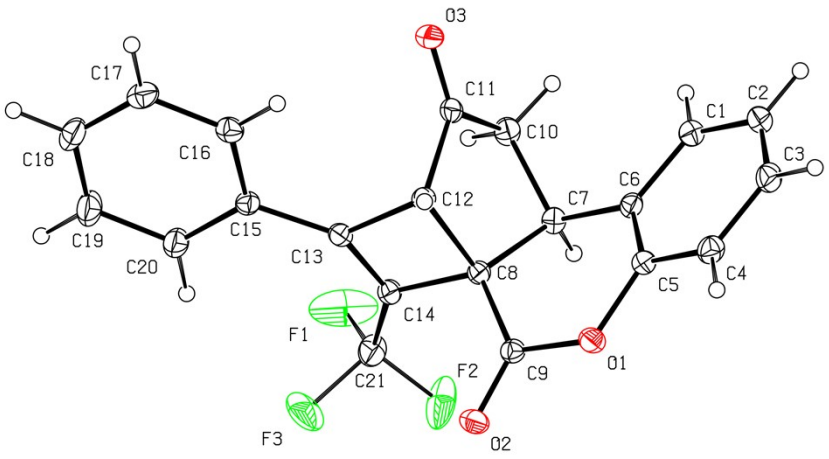

Figure S2. ORTEP drawing with thermal ellipsoids drawn to the 50 % level

Crystal structure determination of 5a

Crystal Data for $C_{21}H_{13}F_3O_3$ (*M* =370.31 g/mol): triclinic, space group P-1 (no. 2), *a* = 8.411(4) Å, *b* = 9.622(4) Å, *c* = 11.004(4) Å, *α* = 82.333(14)°, *β* = 70.00(2)°, *γ* = 79.92(2)°, *V* = 821.4(6) Å^3, *Z* = 2, *T* = 170.0 K, μ(MoKα) = 0.122 mm^{-1}, *Dcalc* = 1.497 g/cm^3, 10186 reflections measured (5.204° ≤ 2Θ ≤ 54.114°), 3600 unique (R_{int} = 0.0220, R_{sigma} = 0.0285) which were used in all calculations. The final R_1 was 0.0436 (I > 2σ(I)) and wR_2 was 0.1083 (all data).

Table S4. Crystal data and structure refinement for 5a.

Identification code	200717_FJF_044_DJ_0m
Empirical formula	$C_{21}H_{13}F_3O_3$
Formula weight	370.31
Temperature/K	170.0
Crystal system	triclinic
Space group	P-1
a/Å	8.411(4)
b/Å	9.622(4)

c/Å	11.004(4)
α/°	82.333(14)
β/°	70.00(2)
γ/°	79.92(2)
Volume/Å^3	821.4(6)
Z	2
ρ_{calc}g/cm^3	1.497
μ/mm^{-1}	0.122
F(000)	380.0
Crystal size/mm^3	0.46 × 0.36 × 0.29
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.204 to 54.114
Index ranges	-10 ≤ h ≤ 10, -12 ≤ k ≤ 12, -14 ≤ l ≤ 14
Reflections collected	10186
Independent reflections	3600 [R_{int} = 0.0220, R_{sigma} = 0.0285]
Data/restraints/parameters	3600/87/272
Goodness-of-fit on F^2	1.043
Final R indexes [I>=2σ (I)]	R_1 = 0.0436, wR_2 = 0.1056
Final R indexes [all data]	R_1 = 0.0465, wR_2 = 0.1083
Largest diff. peak/hole / e Å^{-3}	0.48/-0.38

Table S5. Bond lengths [Å] and angles [°] for 5a.

Bond lengths---

O1	C5	1.4014(17)
O1	C9	1.3575(17)
O2	C9	1.2015(17)
O3	C11	1.2085(18)
C1	C2	1.393(2)
C1	C6	1.3997(19)
C2	C3	1.386(2)
C3	C4	1.384(2)
C4	C5	1.3903(19)
C5	C6	1.3901(19)
C6	C7	1.5209(18)
C7	C8	1.5512(18)
C7	C10	1.5359(19)
C8	C9	1.5097(18)
C8	C12	1.5844(19)
C8	C14	1.5210(18)
C10	C11	1.516(2)
C11	C12	1.5312(18)

C12	C13	1.5308(18)
C13	C14	1.3512(19)
C13	C15	1.4624(19)
C14	C21	1.490(2)
C15	C16	1.402(2)
C15	C20	1.398(2)
C16	C17	1.392(2)
C17	C18	1.383(2)
C18	C19	1.389(3)
C19	C20	1.389(2)
C21	F1	1.283(2)
C21	F2	1.308(3)
C21	F3	1.377(2)
C21	F1A	1.433(5)
C21	F2A	1.224(6)
C21	F3A	1.245(5)

Angles----------

C9	O1	C5	120.66(10)
C2	C1	C6	121.29(14)
C3	C2	C1	120.19(14)
C4	C3	C2	119.93(14)
C3	C4	C5	118.92(14)
C4	C5	O1	114.72(12)
C6	C5	O1	122.25(12)
C6	C5	C4	122.97(13)
C1	C6	C7	123.00(12)
C5	C6	C1	116.68(13)
C5	C6	C7	120.30(12)
C6	C7	C8	107.76(10)
C6	C7	C10	110.74(11)
C10	C7	C8	102.61(11)
C7	C8	C12	105.72(10)
C9	C8	C7	114.31(11)
C9	C8	C12	115.88(10)
C9	C8	C14	112.68(11)
C14	C8	C7	119.93(11)
C14	C8	C12	84.66(9)
O1	C9	C8	117.30(11)
O2	C9	O1	117.90(12)
O2	C9	C8	124.80(12)

C11	C10	C7	103.89(11)
O3	C11	C10	126.40(13)
O3	C11	C12	124.62(13)
C10	C11	C12	108.95(11)
C11	C12	C8	103.65(10)
C13	C12	C8	86.37(10)
C13	C12	C11	108.14(10)
C14	C13	C12	92.86(11)
C14	C13	C15	139.48(12)
C15	C13	C12	127.40(12)
C13	C14	C8	95.69(11)
C13	C14	C21	135.88(13)
C21	C14	C8	128.25(12)
C16	C15	C13	118.75(12)
C20	C15	C13	122.52(12)
C20	C15	C16	118.73(13)
C17	C16	C15	120.42(14)
C18	C17	C16	120.40(14)
C17	C18	C19	119.49(14)
C18	C19	C20	120.71(15)
C19	C20	C15	120.22(14)
F1	C21	C14	113.98(15)
F1	C21	F2	113.6(2)
F1	C21	F3	103.5(2)
F2	C21	C14	111.38(17)
F2	C21	F3	102.21(19)
F3	C21	C14	111.24(14)
F1A	C21	C14	104.9(2)
F2A	C21	C14	117.3(4)
F2A	C21	F1A	96.7(5)
F2A	C21	F3A	112.4(6)
F3A	C21	C14	118.2(3)
F3A	C21	F1A	103.3(5)

Table S6. Torsion angles [°] for 5a

O1	C5	C6	C1	-175.63(12)
O1	C5	C6	C7	5.89(19)
O3	C11	C12	C8	-173.77(12)

O3	C11	C12	C13	95.60(15)
C1	C2	C3	C4	1.0(2)
C1	C6	C7	C8	-153.24(12)
C1	C6	C7	C10	-41.75(17)
C2	C1	C6	C5	-0.7(2)
C2	C1	C6	C7	177.75(13)
C2	C3	C4	C5	-0.3(2)
C3	C4	C5	O1	176.27(12)
C3	C4	C5	C6	-1.0(2)
C4	C5	C6	C1	1.5(2)
C4	C5	C6	C7	-177.02(12)
C5	O1	C9	O2	174.72(12)
C5	O1	C9	C8	-5.86(17)
C5	C6	C7	C8	25.14(16)
C5	C6	C7	C10	136.63(12)
C6	C1	C2	C3	-0.5(2)
C6	C7	C8	C9	-45.89(14)
C6	C7	C8	C12	82.78(12)
C6	C7	C8	C14	175.67(11)
C6	C7	C10	C11	-75.89(13)
C7	C8	C9	O1	38.81(16)
C7	C8	C9	O2	-141.82(13)
C7	C8	C12	C11	16.24(12)
C7	C8	C12	C13	124.03(10)
C7	C8	C14	C13	-110.10(13)
C7	C8	C14	C21	65.53(19)
C7	C10	C11	O3	152.25(13)
C7	C10	C11	C12	-29.82(14)
C8	C7	C10	C11	38.88(13)
C8	C12	C13	C14	-4.95(10)
C8	C12	C13	C15	-179.95(13)
C8	C14	C21	F1	-115.4(3)
C8	C14	C21	F2	14.7(3)
C8	C14	C21	F3	127.99(18)
C8	C14	C21	F1A	-61.4(4)
C8	C14	C21	F2A	44.4(6)
C8	C14	C21	F3A	-175.8(6)
C9	O1	C5	C4	165.07(12)
C9	O1	C5	C6	-17.62(19)
C9	C8	C12	C11	143.97(11)
C9	C8	C12	C13	-108.24(12)
C9	C8	C14	C13	110.84(12)

C9	C8	C14	C21	-73.52(18)
C10	C7	C8	C9	-162.81(11)
C10	C7	C8	C12	-34.14(12)
C10	C7	C8	C14	58.76(14)
C10	C11	C12	C8	8.25(13)
C10	C11	C12	C13	-82.38(13)
C11	C12	C13	C14	98.23(12)
C11	C12	C13	C15	-76.77(16)
C12	C8	C9	O1	-84.54(14)
C12	C8	C9	O2	94.83(16)
C12	C8	C14	C13	-5.02(10)
C12	C8	C14	C21	170.62(15)
C12	C13	C14	C8	5.18(10)
C12	C13	C14	C21	-169.90(17)
C12	C13	C15	C16	2.31(19)
C12	C13	C15	C20	-178.36(13)
C13	C14	C21	F1	58.4(3)
C13	C14	C21	F2	-171.6(2)
C13	C14	C21	F3	-58.3(2)
C13	C14	C21	F1A	112.3(4)
C13	C14	C21	F2A	-141.8(6)
C13	C14	C21	F3A	-2.0(6)
C13	C15	C16	C17	177.13(12)
C13	C15	C20	C19	-177.88(14)
C14	C8	C9	O1	-179.75(11)
C14	C8	C9	O2	-0.37(18)
C14	C8	C12	C11	-103.38(10)
C14	C8	C12	C13	4.41(9)
C14	C13	C15	C16	-169.99(16)
C14	C13	C15	C20	9.3(3)
C15	C13	C14	C8	179.06(16)
C15	C13	C14	C21	4.0(3)
C15	C16	C17	C18	1.4(2)
C16	C15	C20	C19	1.4(2)
C16	C17	C18	C19	0.3(2)
C17	C18	C19	C20	-1.1(3)
C18	C19	C20	C15	0.2(3)
C20	C15	C16	C17	-2.2(2)

6.3 X-Ray Diffraction of 9

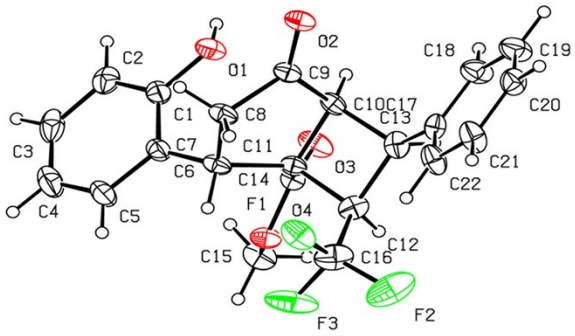

Figure S3. ORTEP drawing with thermal ellipsoids drawn to the 50 % level

Crystal structure determination of 9

Crystal Data for $C_{22}H_{19}F_3O_4$ (*M* =404.37 g/mol): triclinic, space group P-1 (no. 2), *a* = 12.2823(12) Å, *b* = 14.0355(14) Å, *c* = 19.007(2) Å, *α* = 83.638(4)°, *β* = 73.089(4)°, *γ* = 65.017(4)°, *V* = 2841.3(5) Å^3, *Z* = 6, *T* = 170.0 K, μ(MoKα) = 0.116 mm^{-1}, *Dcalc* = 1.418 g/cm^3, 53908 reflections measured (3.932° ≤ 2Θ ≤ 54.424°), 12491 unique (R_{int} = 0.0783, R_{sigma} = 0.0655) which were used in all calculations. The final R_1 was 0.0692 (I > 2σ(I)) and wR_2 was 0.2011 (all data).

Table S7. Crystal data and structure refinement for 9

Identification code	mo_210430_FJF_130_DJ_0m
Empirical formula	$C_{22}H_{19}F_3O_4$
Formula weight	404.37
Temperature/K	170.0
Crystal system	triclinic
Space group	P-1
a/Å	12.2823(12)
b/Å	14.0355(14)
c/Å	19.007(2)

α/°	83.638(4)
β/°	73.089(4)
γ/°	65.017(4)
Volume/Å^3	2841.3(5)
Z	6
ρ_{calc}g/cm^3	1.418
μ/mm^{-1}	0.116
F(000)	1260.0
Crystal size/mm^3	0.16 × 0.08 × 0.06
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	3.932 to 54.424
Index ranges	-15 ≤ h ≤ 15, -18 ≤ k ≤ 17, -24 ≤ l ≤ 24
Reflections collected	53908
Independent reflections	12491 [R_{int} = 0.0783, R_{sigma} = 0.0655]
Data/restraints/parameters	12491/195/845
Goodness-of-fit on F^2	1.039
Final R indexes [I>=2σ (I)]	R_1 = 0.0692, wR_2 = 0.1750
Final R indexes [all data]	R_1 = 0.1034, wR_2 = 0.2011
Largest diff. peak/hole / e Å^{-3}	0.70/-0.43

Table S8. Bond lengths [Å] and angles [°] for 9

Bond lengths---

F1	C16	1.348(4)
F2	C16	1.343(4)
F3	C16	1.340(4)
O1	C1	1.364(3)
O2	C9	1.224(3)
O3	C14	1.193(3)
O4	C14	1.336(3)
O4	C15	1.453(3)
C1	C2	1.386(4)
C1	C6	1.397(4)
C2	C3	1.399(5)
C3	C4	1.376(6)
C4	C5	1.377(5)
C5	C6	1.391(4)
C6	C7	1.517(4)
C7	C8	1.544(4)
C7	C11	1.577(4)
C8	C9	1.512(4)
C9	C10	1.506(4)

C10	C11	1.542(3)
C10	C13	1.566(4)
C11	C12	1.578(4)
C11	C14	1.507(4)
C12	C13	1.561(4)
C12	C16	1.490(5)
C13	C17	1.524(5)
C13	C17A	1.510(14)
C17	C18	1.386(6)
C17	C22	1.387(5)
C18	C19	1.379(6)
C19	C20	1.374(7)
C20	C21	1.372(6)
C21	C22	1.389(5)
C17A	C18A	1.376(16)
C17A	C22A	1.391(16)
C18A	C19A	1.377(16)
C19A	C20A	1.358(17)
C20A	C21A	1.368(16)
C21A	C22A	1.388(14)
F4	C38	1.340(4)
F5	C38	1.336(3)
F6	C38	1.349(3)
O5	C23	1.373(3)
O6	C31	1.227(3)
O7	C36	1.196(3)
O8	C36	1.333(3)
O8	C37	1.452(3)
C23	C24	1.392(4)
C23	C28	1.395(4)
C24	C25	1.386(4)
C25	C26	1.377(5)
C26	C27	1.385(4)
C27	C28	1.394(4)
C28	C29	1.521(4)
C29	C30	1.544(3)
C29	C33	1.576(4)
C30	C31	1.512(4)
C31	C32	1.508(4)
C32	C33	1.545(3)
C32	C35	1.563(3)
C33	C34	1.580(3)
C33	C36	1.512(3)

C34	C35	1.575(3)
C34	C38	1.496(4)
C35	C39	1.512(3)
C39	C40	1.396(4)
C39	C44	1.393(4)
C40	C41	1.390(4)
C41	C42	1.386(4)
C42	C43	1.377(4)
C43	C44	1.385(4)
F7	C60	1.351(4)
F8	C60	1.343(4)
F9	C60	1.341(4)
O9	C45	1.368(3)
O10	C53	1.222(3)
O11	C58	1.194(3)
O12	C58	1.344(3)
O12	C59	1.447(3)
C45	C46	1.389(4)
C45	C50	1.396(4)
C46	C47	1.394(4)
C47	C48	1.382(5)
C48	C49	1.375(4)
C49	C50	1.392(4)
C50	C51	1.516(4)
C51	C52	1.547(4)
C51	C55	1.574(4)
C52	C53	1.505(4)
C53	C54	1.512(4)
C54	C55	1.542(3)
C54	C57	1.563(4)
C55	C56	1.579(4)
C55	C58	1.516(4)
C56	C57	1.572(4)
C56	C60	1.494(4)
C57	C61	1.506(4)
C61	C62	1.389(4)
C61	C66	1.394(4)
C62	C63	1.390(4)
C63	C64	1.375(4)
C64	C65	1.383(4)
C65	C66	1.388(4)

Angles----------

C14	O4	C15	116.1(2)
O1	C1	C2	122.4(3)
O1	C1	C6	116.3(3)
C2	C1	C6	121.3(3)
C1	C2	C3	119.0(3)
C4	C3	C2	120.2(3)
C3	C4	C5	120.1(3)
C4	C5	C6	121.3(4)
C1	C6	C7	121.3(2)
C5	C6	C1	118.0(3)
C5	C6	C7	120.7(3)
C6	C7	C8	113.6(2)
C6	C7	C11	113.3(2)
C8	C7	C11	104.2(2)
C9	C8	C7	107.3(2)
O2	C9	C8	124.1(3)
O2	C9	C10	125.3(3)
C10	C9	C8	110.5(2)
C9	C10	C11	105.9(2)
C9	C10	C13	115.3(2)
C11	C10	C13	91.0(2)
C7	C11	C12	118.7(2)
C10	C11	C7	108.2(2)
C10	C11	C12	89.4(2)
C14	C11	C7	113.6(2)
C14	C11	C10	115.5(2)
C14	C11	C12	109.4(2)
C13	C12	C11	89.9(2)
C16	C12	C11	119.6(3)
C16	C12	C13	125.0(3)
C12	C13	C10	89.1(2)
C17	C13	C10	121.4(3)
C17	C13	C12	127.3(3)
C17A	C13	C10	109.9(11)
C17A	C13	C12	139.7(8)
O3	C14	O4	124.0(3)
O3	C14	C11	125.4(2)
O4	C14	C11	110.6(2)
F1	C16	C12	116.1(3)
F2	C16	F1	106.7(3)
F2	C16	C12	112.0(4)

F3	C16	F1	105.8(3)
F3	C16	F2	105.7(3)
F3	C16	C12	109.8(3)
C18	C17	C13	114.4(4)
C18	C17	C22	117.9(4)
C22	C17	C13	127.7(4)
C19	C18	C17	121.2(5)
C20	C19	C18	120.7(5)
C21	C20	C19	118.7(4)
C20	C21	C22	121.2(4)
C17	C22	C21	120.3(4)
C18A	C17A	C13	118.0(14)
C18A	C17A	C22A	119.8(14)
C22A	C17A	C13	122.2(13)
C17A	C18A	C19A	120.1(17)
C20A	C19A	C18A	119.0(18)
C19A	C20A	C21A	122.2(17)
C20A	C21A	C22A	118.5(15)
C21A	C22A	C17A	119.5(13)
C36	O8	C37	115.8(2)
O5	C23	C24	121.3(2)
O5	C23	C28	117.1(2)
C24	C23	C28	121.7(2)
C25	C24	C23	119.1(3)
C26	C25	C24	120.4(3)
C25	C26	C27	119.9(3)
C26	C27	C28	121.5(3)
C23	C28	C29	121.4(2)
C27	C28	C23	117.4(3)
C27	C28	C29	121.2(2)
C28	C29	C30	113.6(2)
C28	C29	C33	111.7(2)
C30	C29	C33	104.48(19)
C31	C30	C29	107.3(2)
O6	C31	C30	124.2(2)
O6	C31	C32	124.3(2)
C32	C31	C30	111.5(2)
C31	C32	C33	105.0(2)
C31	C32	C35	117.8(2)
C33	C32	C35	90.58(18)
C29	C33	C34	121.3(2)

C32	C33	C29	108.3(2)
C32	C33	C34	89.48(17)
C36	C33	C29	113.0(2)
C36	C33	C32	115.0(2)
C36	C33	C34	107.9(2)
C35	C34	C33	88.89(18)
C38	C34	C33	119.6(2)
C38	C34	C35	121.3(2)
C32	C35	C34	89.02(18)
C39	C35	C32	122.5(2)
C39	C35	C34	127.0(2)
O7	C36	O8	124.2(2)
O7	C36	C33	124.9(2)
O8	C36	C33	110.9(2)
F4	C38	F6	105.5(2)
F4	C38	C34	116.1(2)
F5	C38	F4	106.1(2)
F5	C38	F6	107.0(2)
F5	C38	C34	110.6(3)
F6	C38	C34	111.0(2)
C40	C39	C35	124.5(2)
C44	C39	C35	117.7(2)
C44	C39	C40	117.8(2)
C41	C40	C39	120.6(3)
C42	C41	C40	120.3(3)
C43	C42	C41	119.9(3)
C42	C43	C44	119.7(3)
C43	C44	C39	121.8(3)
C58	O12	C59	115.6(2)
O9	C45	C46	121.9(3)
O9	C45	C50	116.9(2)
C46	C45	C50	121.2(3)
C45	C46	C47	119.2(3)
C48	C47	C46	120.3(3)
C49	C48	C47	119.7(3)
C48	C49	C50	121.6(3)
C45	C50	C51	121.7(2)
C49	C50	C45	117.9(3)
C49	C50	C51	120.3(3)
C50	C51	C52	113.3(2)
C50	C51	C55	111.6(2)

C52	C51	C55	105.0(2)
C53	C52	C51	107.1(2)
O10	C53	C52	124.3(3)
O10	C53	C54	124.4(2)
C52	C53	C54	111.3(2)
C53	C54	C55	105.6(2)
C53	C54	C57	118.2(2)
C55	C54	C57	90.7(2)
C51	C55	C56	120.9(2)
C54	C55	C51	107.9(2)
C54	C55	C56	89.58(19)
C58	C55	C51	112.7(2)
C58	C55	C54	114.9(2)
C58	C55	C56	109.1(2)
C57	C56	C55	89.04(19)
C60	C56	C55	120.3(2)
C60	C56	C57	121.6(2)
C54	C57	C56	89.08(19)
C61	C57	C54	123.0(2)
C61	C57	C56	125.4(2)
O11	C58	O12	124.6(2)
O11	C58	C55	125.3(2)
O12	C58	C55	110.2(2)
F7	C60	C56	115.3(3)
F8	C60	F7	105.8(3)
F8	C60	C56	110.7(2)
F9	C60	F7	106.5(2)
F9	C60	F8	107.2(3)
F9	C60	C56	111.0(3)
C62	C61	C57	118.0(3)
C62	C61	C66	117.9(3)
C66	C61	C57	124.1(2)
C61	C62	C63	121.4(3)
C64	C63	C62	119.8(3)
C63	C64	C65	119.9(3)
C64	C65	C66	120.3(3)
C65	C66	C61	120.7(3)

Table S9. Torsion angles [°] for 9

O1	C1	C2	C3	-176.6(3)
O1	C1	C6	C5	175.6(3)
O1	C1	C6	C7	-4.8(4)
O2	C9	C10	C11	-177.2(3)
O2	C9	C10	C13	83.8(3)
C1	C2	C3	C4	1.2(5)
C1	C6	C7	C8	60.1(4)
C1	C6	C7	C11	-58.5(3)
C2	C1	C6	C5	-2.0(4)
C2	C1	C6	C7	177.5(3)
C2	C3	C4	C5	-2.2(5)
C3	C4	C5	C6	1.0(5)
C4	C5	C6	C1	1.1(5)
C4	C5	C6	C7	-178.5(3)
C5	C6	C7	C8	-120.3(3)
C5	C6	C7	C11	121.0(3)
C6	C1	C2	C3	0.9(4)
C6	C7	C8	C9	-104.3(3)
C6	C7	C11	C10	106.3(2)
C6	C7	C11	C12	-154.1(2)
C6	C7	C11	C14	-23.4(3)
C7	C8	C9	O2	165.8(3)
C7	C8	C9	C10	-14.8(3)
C7	C11	C12	C13	-116.3(2)
C7	C11	C12	C16	14.9(4)
C7	C11	C14	O3	120.4(3)
C7	C11	C14	O4	-62.4(3)
C8	C7	C11	C10	-17.7(3)
C8	C7	C11	C12	81.9(3)
C8	C7	C11	C14	-147.3(2)
C8	C9	C10	C11	3.3(3)
C8	C9	C10	C13	-95.6(3)
C9	C10	C11	C7	9.2(3)
C9	C10	C11	C12	-111.0(2)
C9	C10	C11	C14	137.7(2)
C9	C10	C13	C12	102.4(2)
C9	C10	C13	C17	-32.2(4)
C9	C10	C13	C17A	-41.3(8)
C10	C11	C12	C13	-5.8(2)
C10	C11	C12	C16	125.4(3)
C10	C11	C14	O3	-5.5(4)
C10	C11	C14	O4	171.7(2)
C10	C13	C17	C18	-71.4(5)

C10	C13	C17	C22	110.6(5)
C10	C13	C17A	C18A	-105(2)
C10	C13	C17A	C22A	78(2)
C11	C7	C8	C9	19.5(3)
C11	C10	C13	C12	-5.8(2)
C11	C10	C13	C17	-140.4(3)
C11	C10	C13	C17A	-149.5(8)
C11	C12	C13	C10	5.7(2)
C11	C12	C13	C17	135.8(3)
C11	C12	C13	C17A	126.2(16)
C11	C12	C16	F1	-58.5(4)
C11	C12	C16	F2	178.6(3)
C11	C12	C16	F3	61.5(4)
C12	C11	C14	O3	-104.4(3)
C12	C11	C14	O4	72.8(3)
C12	C13	C17	C18	172.3(4)
C12	C13	C17	C22	-5.8(7)
C12	C13	C17A	C18A	140.9(17)
C12	C13	C17A	C22A	-36(3)
C13	C10	C11	C7	125.9(2)
C13	C10	C11	C12	5.8(2)
C13	C10	C11	C14	-105.5(2)
C13	C12	C16	F1	54.8(5)
C13	C12	C16	F2	-68.1(4)
C13	C12	C16	F3	174.8(3)
C13	C17	C18	C19	-178.9(5)
C13	C17	C22	C21	178.8(4)
C13	C17A	C18A	C19A	-172(2)
C13	C17A	C22A	C21A	168.8(18)
C14	C11	C12	C13	111.1(2)
C14	C11	C12	C16	-117.7(3)
C15	O4	C14	O3	-4.7(4)
C15	O4	C14	C11	178.0(2)
C16	C12	C13	C10	-121.3(3)
C16	C12	C13	C17	8.9(5)
C16	C12	C13	C17A	-0.8(17)
C17	C18	C19	C20	-0.3(9)
C18	C17	C22	C21	0.8(7)
C18	C19	C20	C21	1.3(9)
C19	C20	C21	C22	-1.2(8)
C20	C21	C22	C17	0.1(7)
C22	C17	C18	C19	-0.7(8)
C17A	C18A	C19A	C20A	3(4)

C18A	C17A	C22A	C21A	-8(4)
C18A	C19A	C20A	C21A	-10(4)
C19A	C20A	C21A	C22A	7(4)
C20A	C21A	C22A	C17A	2(3)
C22A	C17A	C18A	C19A	5(4)
O5	C23	C24	C25	-178.6(3)
O5	C23	C28	C27	178.4(2)
O5	C23	C28	C29	-3.3(4)
O6	C31	C32	C33	175.1(2)
O6	C31	C32	C35	76.3(3)
C23	C24	C25	C26	0.5(5)
C23	C28	C29	C30	54.0(3)
C23	C28	C29	C33	-63.8(3)
C24	C23	C28	C27	-0.6(4)
C24	C23	C28	C29	177.7(3)
C24	C25	C26	C27	-1.0(5)
C25	C26	C27	C28	0.8(5)
C26	C27	C28	C23	0.0(4)
C26	C27	C28	C29	-178.3(3)
C27	C28	C29	C30	-127.7(3)
C27	C28	C29	C33	114.4(3)
C28	C23	C24	C25	0.3(4)
C28	C29	C30	C31	-106.2(2)
C28	C29	C33	C32	104.2(2)
C28	C29	C33	C34	-154.9(2)
C28	C29	C33	C36	-24.5(3)
C29	C30	C31	O6	172.9(2)
C29	C30	C31	C32	-7.3(3)
C29	C33	C34	C35	-122.0(2)
C29	C33	C34	C38	3.8(3)
C29	C33	C36	O7	112.9(3)
C29	C33	C36	O8	-67.9(3)
C30	C29	C33	C32	-19.0(3)
C30	C29	C33	C34	81.9(3)
C30	C29	C33	C36	-147.6(2)
C30	C31	C32	C33	-4.7(3)
C30	C31	C32	C35	-103.5(2)
C31	C32	C33	C29	14.7(2)
C31	C32	C33	C34	-108.2(2)
C31	C32	C33	C36	142.2(2)
C31	C32	C35	C34	96.4(2)
C31	C32	C35	C39	-38.2(3)
C32	C33	C34	C35	-10.76(19)

C32	C33	C34	C38	115.1(2)
C32	C33	C36	O7	-12.1(4)
C32	C33	C36	O8	167.0(2)
C32	C35	C39	C40	57.5(4)
C32	C35	C39	C44	-119.6(3)
C33	C29	C30	C31	15.8(3)
C33	C32	C35	C34	-10.88(19)
C33	C32	C35	C39	-145.5(2)
C33	C34	C35	C32	10.64(18)
C33	C34	C35	C39	141.9(3)
C33	C34	C38	F4	-54.8(3)
C33	C34	C38	F5	-175.8(2)
C33	C34	C38	F6	65.6(3)
C34	C33	C36	O7	-110.2(3)
C34	C33	C36	O8	68.9(3)
C34	C35	C39	C40	-59.5(4)
C34	C35	C39	C44	123.4(3)
C35	C32	C33	C29	133.8(2)
C35	C32	C33	C34	10.85(19)
C35	C32	C33	C36	-98.8(2)
C35	C34	C38	F4	53.7(4)
C35	C34	C38	F5	-67.2(3)
C35	C34	C38	F6	174.2(2)
C35	C39	C40	C41	-177.9(3)
C35	C39	C44	C43	177.8(2)
C36	C33	C34	C35	105.4(2)
C36	C33	C34	C38	-128.7(2)
C37	O8	C36	O7	-2.4(4)
C37	O8	C36	C33	178.4(2)
C38	C34	C35	C32	-113.8(3)
C38	C34	C35	C39	17.5(4)
C39	C40	C41	C42	0.5(5)
C40	C39	C44	C43	0.6(4)
C40	C41	C42	C43	0.1(5)
C41	C42	C43	C44	-0.3(4)
C42	C43	C44	C39	0.0(4)
C44	C39	C40	C41	-0.8(4)
O9	C45	C46	C47	177.3(3)
O9	C45	C50	C49	-176.6(2)
O9	C45	C50	C51	5.8(4)
O10	C53	C54	C55	-177.7(3)
O10	C53	C54	C57	-78.1(3)
C45	C46	C47	C48	-0.3(5)

C45	C50	C51	C52	-56.4(3)
C45	C50	C51	C55	61.9(3)
C46	C45	C50	C49	2.6(4)
C46	C45	C50	C51	-175.0(3)
C46	C47	C48	C49	1.5(5)
C47	C48	C49	C50	-0.7(5)
C48	C49	C50	C45	-1.3(4)
C48	C49	C50	C51	176.4(3)
C49	C50	C51	C52	126.1(3)
C49	C50	C51	C55	-115.7(3)
C50	C45	C46	C47	-1.8(4)
C50	C51	C52	C53	106.1(3)
C50	C51	C55	C54	-105.7(2)
C50	C51	C55	C56	153.7(2)
C50	C51	C55	C58	22.2(3)
C51	C52	C53	O10	-171.2(3)
C51	C52	C53	C54	8.9(3)
C51	C55	C56	C57	120.2(2)
C51	C55	C56	C60	-6.4(4)
C51	C55	C58	O11	-114.7(3)
C51	C55	C58	O12	66.2(3)
C52	C51	C55	C54	17.5(3)
C52	C51	C55	C56	-83.1(3)
C52	C51	C55	C58	145.4(2)
C52	C53	C54	C55	2.2(3)
C52	C53	C54	C57	101.7(3)
C53	C54	C55	C51	-12.3(3)
C53	C54	C55	C56	110.2(2)
C53	C54	C55	C58	-138.9(2)
C53	C54	C57	C56	-98.7(2)
C53	C54	C57	C61	34.1(4)
C54	C55	C56	C57	9.4(2)
C54	C55	C56	C60	-117.2(3)
C54	C55	C58	O11	9.4(4)
C54	C55	C58	O12	-169.6(2)
C54	C57	C61	C62	125.9(3)
C54	C57	C61	C66	-53.7(4)
C55	C51	C52	C53	-15.9(3)
C55	C54	C57	C56	9.5(2)
C55	C54	C57	C61	142.3(3)
C55	C56	C57	C54	-9.28(19)
C55	C56	C57	C61	-140.3(3)
C55	C56	C60	F7	51.8(4)

C55	C56	C60	F8	-68.2(4)
C55	C56	C60	F9	172.9(2)
C56	C55	C58	O11	108.2(3)
C56	C55	C58	O12	-70.9(3)
C56	C57	C61	C62	-118.2(3)
C56	C57	C61	C66	62.3(4)
C57	C54	C55	C51	-132.0(2)
C57	C54	C55	C56	-9.5(2)
C57	C54	C55	C58	101.4(2)
C57	C56	C60	F7	-57.9(4)
C57	C56	C60	F8	-177.9(3)
C57	C56	C60	F9	63.2(4)
C57	C61	C62	C63	179.1(3)
C57	C61	C66	C65	-179.2(3)
C58	C55	C56	C57	-106.8(2)
C58	C55	C56	C60	126.5(3)
C59	O12	C58	O11	7.6(4)
C59	O12	C58	C55	-173.3(2)
C60	C56	C57	C54	116.3(3)
C60	C56	C57	C61	-14.7(4)
C61	C62	C63	C64	0.3(5)
C62	C61	C66	C65	1.3(5)
C62	C63	C64	C65	0.7(5)
C63	C64	C65	C66	-0.8(6)
C64	C65	C66	C61	-0.2(6)
C66	C61	C62	C63	-1.3(5)