Supporting Information

Rh_2(II)-Catalyzed Enantioselective Intramolecular Büchner Reaction and Aromatic Substitution of Donor-Donor Carbenes

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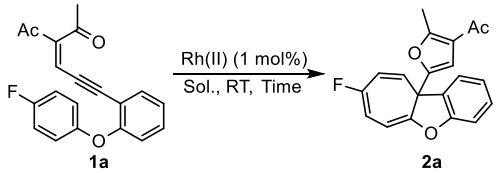
1. General information.

All reactions were conducted under dry N_2 atmosphere in schlenk tube. Catalysts were commercial available. Commercially obtained reagents were used without purification. Reaction starting materials were prepared as depicted in the literature.

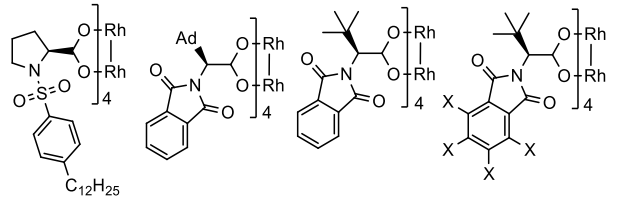
^1H, ^{13}C NMR spectra were recorded on a Bruker AVANCE 400 (400 MHz for ^1H; 100 MHz for ^{13}C) and Bruker AVANCE 500 (500 MHz for ^1H; 126 MHz for ^{13}C), ^1H NMR and ^{13}C NMR chemical shifts were determined relative to internal standard TMS at δ 0.0. Chemical shifts (δ) are reported in ppm, and coupling constants (*J*) are in Hertz(Hz). The following abbreviations were used to explain the multiplicities: s = singlet, d =doublet, t = triplet, q = quartet, m = multiplet, br = broad. Infrared (IR) spectra are recorded on a Nicolet 210 spectrophotometer and were recorded in potassium bromide (KBr) pellet. Mass spectra (MS) were obtained using ESI mass spectrometer. Enantiomeric ratios were determined by HPLC, using a chiralcel OD-H column with hexane and *i*-PrOH as solvents.

2. Table S1. Optimization of Büchner reaction conditions.[a]



Entry	Rh(II)	Sol.	Time	Yield (%)[b]	ee (%)[c]
1	$Rh_2(Opiv)_4$	DCM	3 h	94	-
2	$Rh_2(5S\text{-}MEPY)_4$	DCM	4 h	trace	-
3	$Rh_2(R\text{-}DOSP)_4$	DCM	4 h	99	racemic
4	$Rh_2(S\text{-}PTTL)_4$	DCM	12 h	97	6
5	$Rh_2(S\text{-}PTAD)_4$	DCM	12 h	91	29
6	$Rh_2(S\text{-}TFPTTL)_4$	DCM	4 h	99	-20
7	$Rh_2(S\text{-}TCPTTL)_4$	DCM	4 h	99	73
8	$Rh_2(S\text{-}BTPCP)_4$	DCM	2 h	99	83
9	$Rh_2(S\text{-}BTPCP)_4$	Toluene	4 h	99	60
10	$Rh_2(S\text{-}BTPCP)_4$	$CHCl_3$	8 h	99	70
11	$Rh_2(S\text{-}BTPCP)_4$	DCE	2 h	99	92
12[d]	**$Rh_2(S\text{-}BTPCP)_4$**	**DCE**	**30 h**	**99**	**96**
13[e]	$Rh_2(S\text{-}BTPCP)_4$	DCE	53 h	99	96

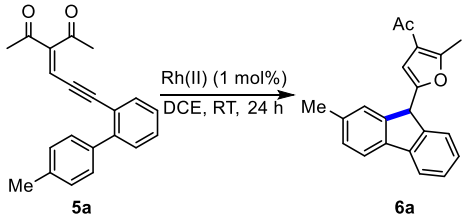
[a] The reaction was performed in DCE under N_2, **1a** = 0.2 mmol, [**1a**] = 0.1 M，1 mol% Rh(II). [b] isolated yield. [c] The ee value of **2a** was determined by HPLC using a chiral stationary phase. [d] -20 °C. [e] -20 °C, 0.5 mol% $Rh_2(S\text{-}BTPCP)_4$.



$Rh_2(S\text{-}DOSP)_4$ $Rh_2(S\text{-}PTAD)_4$ $Rh_2(S\text{-}PTTL)_4$ X= Cl: $Rh_2(S\text{-}TCPTTL)_4$ X= F: $Rh_2(S\text{-}TFPTTL)_4$

$Rh_2(S\text{-}BPTTL)_4$ $Rh_2(S\text{-}NTTL)_4$ $Rh_2(S\text{-}BTPCP)_4$ $Rh_2(5S\text{-}MEPY)_4$

3. Table S2. Optimization of aromatic substitution conditions.[a]



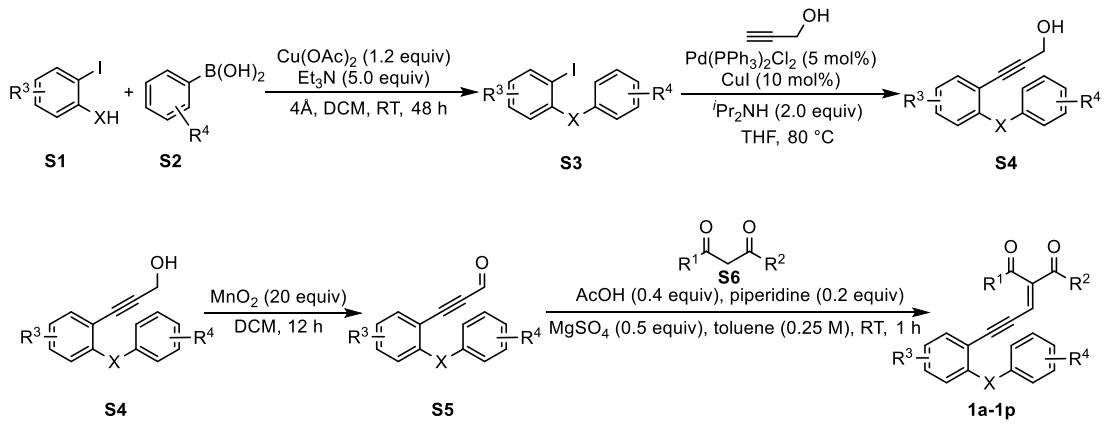
5a **6a**

Entry	Rh(II)	Sol.	Time	Yield[b] (%)	ee[c] (%)
1	$Rh_2(OPiv)_4$	DCE	12 h	95%	-
2[d]	ZnI_2	DCE	3 h	99%	-
3	Rh_2(S-DOSP)$_4$	DCE	12 h	99	-35
4	Rh_2(S-PTAD)$_4$	DCE	24 h	99	52
5	Rh_2(S-PTTL)$_4$	DCE	12 h	99	91
6	Rh_2(S-TCPTTL)$_4$	DCE	12 h	57	53
7	Rh_2(S-TFPTTL)$_4$	DCE	12 h	20	35
8	Rh_2(S-BPTTL)$_4$	DCE	48 h	67	70
9	Rh_2(S-NTTL)$_4$	DCE	48 h	94	86
10	Rh_2(5S-MEPY)$_4$	DCE	24 h	N.R.	-
11	Rh_2(S-BTPCP)$_4$	DCE	24 h	93	96
12	**Rh_2(S-BTPCP)$_4$**	**DCM**	**24 h**	**95**	**97**
13	Rh_2(S-BTPCP)$_4$	Toluene	24 h	33	60
14	Rh_2(S-BTPCP)$_4$	$CHCl_3$	24 h	80	92

[a] The reaction was performed in DCE under N_2, **1a** = 0.2 mmol, [**1a**] = 0.1 M, [b] isolated yield. [c] The *ee* value of **2a** was determined by HPLC using a chiral stationary phase. [d] ZnI_2: 10 mol%.

4. General procedure for preparation of enynones.

Scheme S1. general procedure for preparation of *N*-allyl enynones 1a – 1p.



Typical procedure for preparation of S3[1]

A mixture of 2-iodophenol or N-methyl-2-iodoaniline **S1** (5 mmol), arylboronic acid **S2** (7.5 mmol, 1.5 equiv), anhydrous $Cu(OAc)_2$ (6 mmol, 1.2 equiv, 1.09 g), triethylamine (25 mmol, 5.0 equiv, 3.5 mL) and powdered 4Å molecular sieves (1.0 g) in anhydrous DCM (40 mL) was stirred at room temperature for 48 h. The reaction was monitored by TLC and then the reaction mixture was filtered through a plug of silica gel and the filtrate was concentrated in vacuo. Purification by silica gel chromatography (petroleum ether) afforded chromatographically and spectroscopically pure product **S3**.

Typical procedure for preparation of S5[2]

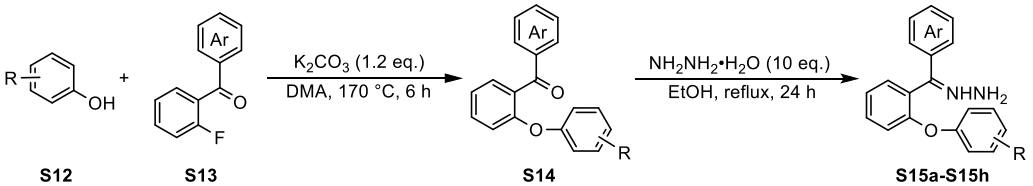
Under nitrogen atmosphere, a mixture of **S3** (3 mmol, 1.0 eq.), CuI (10 mol%), $Pd(PPh3)_2Cl_2$ (5 mol%) were added to a schlenk tube, $^iPr_2NH$ (2.0 equiv) and THF (12 mL) as co-solvent was added to the reaction mixture, then propargyl alcohol (6 mmol, 2.0 eq) was added slowly. The reaction was stirred for 12 h at 80 °C. The mixture was diluted with H_2O, and extracted with CH_2Cl_2. The extract was dried over $MgSO_4$ and evaporated under reduced pressure. The residue was purified by chromatography on silica gel with petroleum ether/ethyl acetate (5:1) as the eluent to afford **S4**.

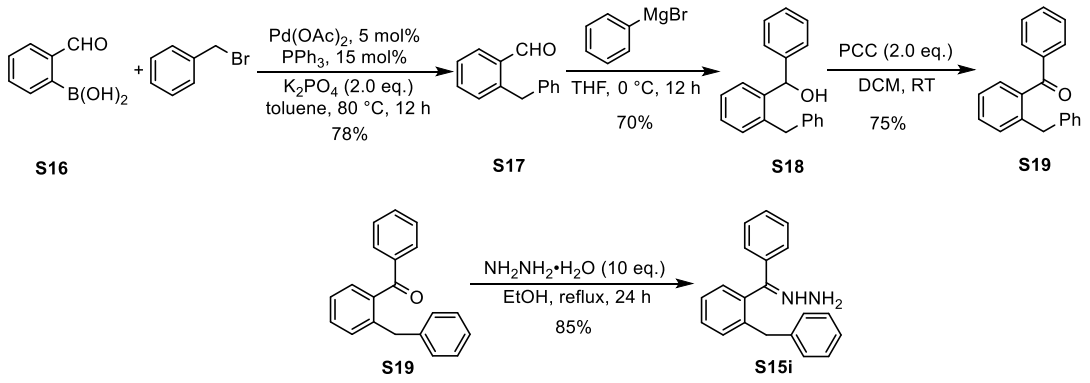
To a solution of **S4** (2.0 mmol, 1.0 eq.) in DCM (0.5 M) at room temperature was added MnO_2 (20 eq.). The resulting mixture was stirred overnight and monitored by TLC. After **S4** was completely consumed, filtered and concentrated under reduced pressure. Purification of the crude product by flash column chromatography (silica gel, petroleum ether/AcOEt = 10:1) gave **S5**.

Typical procedure for preparation of enynones 1a – 1p[2]

S5 (1.0 eq), AcOH (0.4 eq.), piperidine (0.2 eq.) and $MgSO_4$ (0.5 eq.) were added to a solution of **S6** (1.2 eq) in toluene at room temperature. The reaction was stirred at room temperature and monitored by TLC for 1 h. The reaction mixture was extracted with ethyl acetate and water. Combined organic layers were washed with brine and dried over $MgSO_4$. Filtered and concentrated under reduced pressure. The resulting residue was purified by flash column chromatography (silica gel, petroleum ether/AcOEt = 10:1) to yield **1a** – **1p**.

General procedure for preparation of Donor-Donor hydrazones S15a-S15i.





Typical procedure for preparation of S14[4]

To a solution of 2-Fluorobenzophenone **S13** (5.00 mmol, 1.0 equiv) in DMA (10 mL), phenol **S12** (6 mmol, 1.2 equiv) and anhydrous K_2CO_3 (6 mmol, 828 mg, 1.2 equiv) were added. The resulting mixture was stirred and slowly heated to 170 °C. After reacted for 6 h and cooling to room temperature the reaction mixture was poured into H_2O (20 mL) and the aqueous layer was extracted with DCM (3×20 mL). After drying over Na_2SO4, filtration and concentration in vacuo, the desired 2-phenoxybenzophenone **S14** was obtained through flash column chromatography (silica gel, petroleum ether/AcOEt = 30:1).

Typical procedure for preparation of hydrazones S15a-S15h[5]

To a 25 mL Schlenk tube containing a magnetic stirring bar and compound 2-phenoxybenzophenone **S14** (4.0 mmol) in ethanol (10 ml), was added $N_2H_4{\cdot}H_2O$ (2.0 g, 40 mmol). The solution was stirred under refluxing for 24 hours, the solvent was evaporated under reduced pressure and the resulting crude product extracted with ethyl acetate (3×15 mL). The combined organic layers were dried over Na_2SO_4, filtration and concentration in vacuo, the desired hydrazones **S15a-S15h** was obtained through flash column chromatography (silica gel, petroleum ether/AcOEt = 10:1).

Typical procedure for preparation of S17[6]

To a 50 mL Schlenk tube containing a magnetic stirring bar, a solution of benzyl bromide (10.0 mmol, 1.7 g, 1.0 equiv) in toluene (20 mL) were added $Pd(OAc)_2$ (112 mg, 5 mol%), PPh_3 (393 mg, 15 mol%), K_3PO_4 (4.2 g, 2.0 equiv) and 2-formylbenzeneboronic acid **S16** (1.8 g, 1.2 equiv). After stirring at 80 °C for 12 h, the reaction mixture was filtered through a pad of silica gel. Concentrated in vacuo, the desired 2-benzylbenzaldehyde **S17** was obtained through flash column chromatography (silica gel, petroleum ether/AcOEt = 50:1).

Typical procedure for preparation of S18

To a 50 mL Schlenk tube containing a magnetic stirring bar, a solution of 2-benzylbenzaldehyde **S17** (8.0 mmol) in THF (10 mL) was added under 0 °C. Phenylmagnesium bromide (1.5 equiv) in 10 mL THF was added dropwise. The reaction was stirred under 0 °C for 12 h. Upon completion, the saturated NH_4Cl (20 mL) was added to quench the reaction, the resulting solution was extracted with EtOAc (20 mL×3). The combined organic layers were dried over Na_2SO_4, filtration and concentration in vacuo, the desired product **S18** was obtained through flash column chromatography (silica gel, petroleum ether/AcOEt = 5:1).

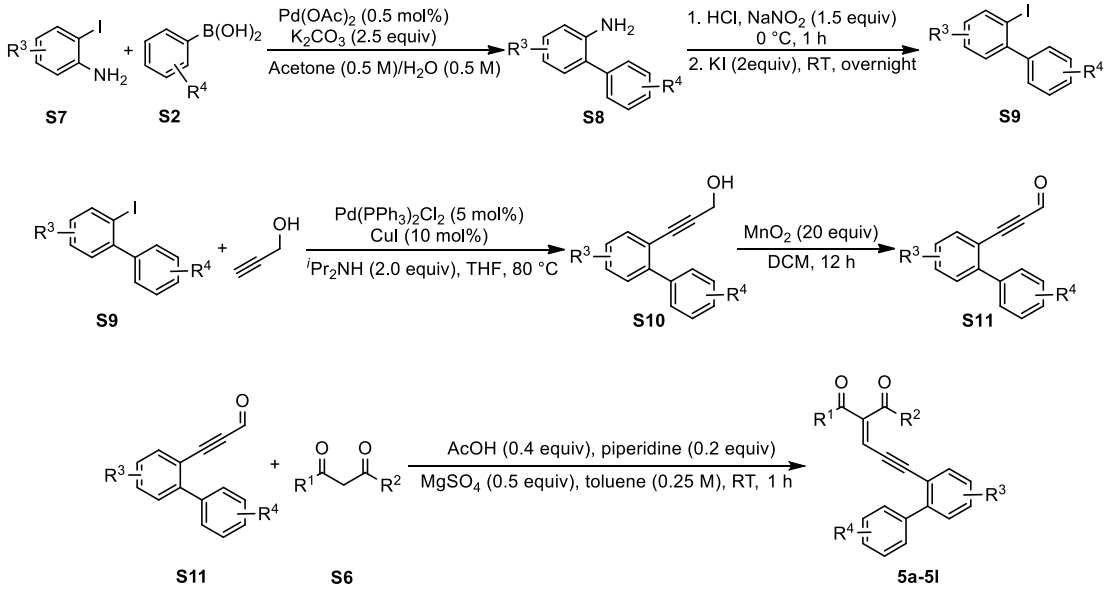
Typical procedure for preparation of S19

To a solution of **S18** (5.0 mmol, 1.0 eq.) in DCM (0.1 M) at room temperature was added PCC (2.0 equiv). The resulting mixture was stirred and monitored by TLC. After **S18** was completely consumed, filtered and concentrated under reduced pressure. the desired product **S19** was obtained through flash column chromatography (silica gel, petroleum ether/AcOEt = 20:1).

Typical procedure for preparation of hydrazones S15i

The desired hydrazones **S15i** was obtained through the corresponding procedure for the synthesis of hydrazones **S15a-S15h**.

Scheme S2. general procedure for preparation of *N*-allyl enynones 5a – 5l.



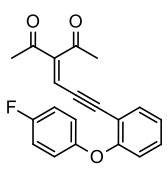
Typical procedure for preparation of S9[3]**.**

To a solution of substituted 2-iodoaniline **S7** (5.0 mmol) in acetone (8 mL) and water (10 mL) was added substituted phenylboronic acid **S2** (6.0 mmol, 1.2 equiv), and K_2CO_3 (1.73 g, 12.5 mmol, 2.5 equiv). A solution of $Pd(OAc)_2$ (5.6 mg, 0.025 mmol, 0.5 mol %) in acetone (2.0 mL) was then introduced to the reaction mixture via a syringe. After the reaction mixture was stirred at 70 °C overnight, it was allowed to cool to room temperature. The reaction mixture was extracted with EtOAc (3×20 mL), and the combined organic phases were washed with 50 mL of water. The organic phases were dried over anhydrous Na_2SO_4, and concentrated in vacuo. The crude product was purified by silica gel column chromatography (petroleum ether) to give the corresponding substituted 2-aminobiphenyls **S8**.

A solution of concn. HCl (36-38%; 2.3 mL, 6.5 mmol) in water (8.5 mL) was added slowly to the prepared 2-aminobiphenyl **S8** (5.0 mmol) with stirring. An aqueous solution of $NaNO_2$ (20%; 2.59 g, 7.5 mmol) was added to the reaction mixture at 0 °C within 10 min and stirred for 1 h at the same temperature. An aqueous solution of KI (1.66 g, 10.0 mmol) in water (10.0 mL) was added and the reaction mixture was stirred at room temperature overnight. EtOAc (30 mL) was added to the reaction mixture and the organic phase was treated with saturated $NaHSO_3$ to decolorize. The aqueous phase was extracted with EtOAc (3×20 mL). The combined organic phases were dried over anhydrous Na_2SO_4 and concentrated in vacuo. The crude product was purified by silica gel column chromatography (petroleum ether unless otherwise noted) to give the desired 2-iodobiphenyls **S9**.

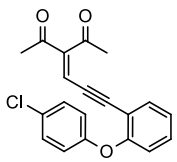
Typical procedure for preparation of enynones 5a – 5l

The procedure for the synthesis of enynones **5a-5l** from **S9** was similar with the synthesis of **1a-1p** from **S3** described above.

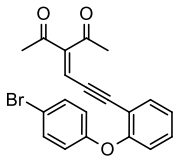


3-(3-(2-(4-Fluorophenoxy)phenyl)prop-2-yn-1-ylidene)pentane-2,4-dione (1a) Yield: 65%, yellow oil, R_f = 0.3 (petroleum ether/AcOEt = 10:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (d, J = 7.7 Hz, 1H), 7.36 – 7.30 (m, 1H), 7.12 – 7.02 (m, 3H), 7.01 – 6.96 (m, 2H), 6.95 (d, J = 1.9 Hz, 1H), 6.81 (d, J = 8.4 Hz, 1H), 2.51 (s, 3H), 2.33 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -118.9. ^{13}C NMR (101 MHz, $CDCl_3$) δ 200.9, 195.6, 159.2 (d, J = 242.8 Hz), 158.8, 152.0 (d, J = 2.6 Hz), 149.1, 134.1, 131.7, 123.2, 122.2, 120.7 (d, J = 8.4

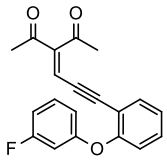
Hz), 117.3, 116.5 (d, J = 23.5 Hz), 113.3, 103.0, 89.7, 31.0, 27.6. IR (KBr, cm^{-1}) 3065, 2954, 1711, 1686, 1570, 1500, 1447, 1365, 1214, 1092, 952, 847, 758. HRMS (ESI) ($[M+H]^+$) Calcd. for $[C_{20}H_{16}FO_3]^+$: 323.1078, Found. 323.1081.



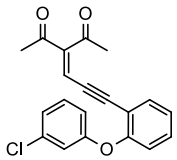
3-(3-(2-(4-Chlorophenoxy)phenyl)prop-2-yn-1-ylidene)pentane-2,4-dione (1b) Yield: 63%, yellow oil, R_f = 0.3 (petroleum ether/AcOEt = 10:1). ^1H NMR (400 MHz, $CDCl_3$) δ 7.52 (d, J = 7.7 Hz, 1H), 7.39 – 7.28 (m, 3H), 7.13 (t, J = 7.7 Hz, 1H), 6.97 – 6.85 (m, 4H), 2.48 (s, 3H), 2.33 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 200.8, 195.5, 158.0, 155.1, 149.2, 134.2, 131.8, 129.9, 129.0, 123.7, 122.1, 120.1, 118.3, 113.9, 102.7, 89.7, 30.9, 27.6. IR (KBr, cm^{-1}) 3031, 1711, 1570, 1482, 1445, 1363, 1236, 1168, 956, 872, 760. HRMS (ESI) ($[M+H]^+$) Calcd. for $[C_{20}H_{16}ClO_3]^+$: 339.0782, Found. 339.0784.



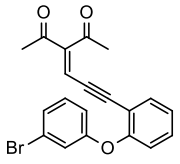
3-(3-(2-(4-Bromophenoxy)phenyl)prop-2-yn-1-ylidene)pentane-2,4-dione (1c) Yield: 62%, yellow oil, R_f = 0.3 (petroleum ether/AcOEt = 10:1). ^1H NMR (400 MHz, $CDCl_3$) δ 7.52 (dd, J = 7.8, 1.9 Hz, 1H), 7.48 – 7.42 (m, 2H), 7.39 – 7.32 (m, 1H), 7.13 (t, J = 7.6 Hz, 1H), 6.93 – 6.85 (m, 4H), 2.47 (s, 3H), 2.33 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 200.8, 195.5, 157.8, 155.7, 149.2, 134.2, 132.9, 131.8, 123.8, 122.0, 120.5, 118.4, 116.5, 114.0, 102.6, 89.7, 30.9, 27.6. IR (KBr, cm^{-1}) 3031, 1711, 1693, 1571, 1480, 1444, 1367, 1233, 1170, 1066, 957, 871, 760. HRMS (ESI) ($[M+H]^+$) Calcd. for $[C_{20}H_{16}BrO_3]^+$: 383.0277, Found. 383.0279.



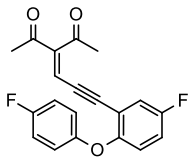
3-(3-(2-(3-Fluorophenoxy)phenyl)prop-2-yn-1-ylidene)pentane-2,4-dione (1d) Yield: 55%, yellow oil, R_f = 0.3 (petroleum ether/AcOEt = 10:1). ^1H NMR (400 MHz, $CDCl_3$) δ 7.56 – 7.50 (m, 1H), 7.42 – 7.35 (m, 1H), 7.32 – 7.26 (m, 1H), 7.19 – 7.13 (m, 1H), 6.95 (dd, J = 8.4, 2.4 Hz, 1H), 6.90 (s, 1H), 6.84 (t, J = 8.6 Hz, 1H), 6.78 (d, J = 8.5 Hz, 1H), 6.72 – 6.67 (m, 1H), 2.47 (s, 3H), 2.32 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -110.5. ^{13}C NMR (101 MHz, $CDCl_3$) δ 200.8, 195.6, 163.5 (d, J = 247.2 Hz), 158.0 (d, J = 10.5 Hz), 157.4, 149.1, 134.2, 131.8, 130.7 (d, J = 9.6 Hz), 124.1, 122.0, 119.1, 114.3, 114.1 (d, J = 3.0 Hz), 110.6 (d, J = 21.1 Hz), 106.2 (d, J = 24.6 Hz), 102.5, 89.7, 30.9, 27.6. IR (KBr, cm^{-1}) 3031, 1711, 1572, 1482, 1444, 1367, 1244, 1124, 959, 865, 771. HRMS (ESI) ($[M+Na]^+$) Calcd. for $[C_{20}H_{15}FNaO_3]^+$: 345.0897, Found. 345.0901.



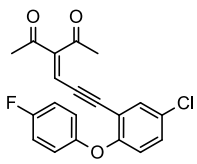
3-(3-(2-(3-Chlorophenoxy)phenyl)prop-2-yn-1-ylidene)pentane-2,4-dione (1e) Yield: 57%, yellow oil, R_f = 0.3 (petroleum ether/AcOEt = 10:1). ^1H NMR (400 MHz, $CDCl_3$) δ 7.53 (d, J = 7.3 Hz, 1H), 7.38 (t, J = 8.1 Hz, 1H), 7.31 – 7.24 (m, 1H), 7.19 – 7.08 (m, 2H), 6.97 (s, 1H), 6.95 – 6.85 (m, 3H), 2.47 (s, 3H), 2.33 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 200.8, 195.6, 157.4, 157.4, 149.2, 135.2, 134.3, 131.8, 130.7, 124.1, 123.9, 122.0, 119.0, 118.9, 116.8, 114.3, 102.5, 89.7, 30.9, 27.6. IR (KBr, cm^{-1}) 3029, 1712, 1577, 1473, 1443, 1361, 1231, 1108, 952, 908, 768. HRMS (ESI) ($[M+Na]^+$) Calcd. for $[C_{20}H_{15}ClNaO_3]^+$: 361.0602, Found. 361.0602.



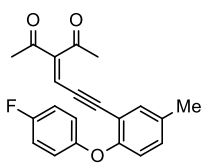
3-(3-(2-(3-Bromophenoxy)phenyl)prop-2-yn-1-ylidene)pentane-2,4-dione (1f) Yield: 57%, yellow oil, R_f = 0.3 (petroleum ether/AcOEt = 10:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (d, J = 7.3 Hz, 1H), 7.38 (t, J = 7.9 Hz, 1H), 7.30 – 7.19 (m, 2H), 7.18 – 7.09 (m, 2H), 6.91 (dd, J = 11.8, 5.3 Hz, 3H), 2.47 (s, 3H), 2.33 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 200.8, 195.6, 157.5, 157.4, 149.2, 134.3, 131.8, 131.0, 126.9, 124.1, 123.0, 122.0, 121.8, 119.0, 117.3, 114.2, 102.5, 89.8, 31.0, 27.6. IR (KBr, cm^{-1}) 3029, 1712, 1576, 1469, 1445, 1363, 1229, 1109, 953, 896, 765. HRMS (ESI) ([M+Na]$^+$) Calcd. for $[C_{20}H_{15}BrNaO_3]^+$: 405.0097, Found. 405.0091.



3-(3-(5-Fluoro-2-(4-fluorophenoxy)phenyl)prop-2-yn-1-ylidene)pentane-2,4-dione (1g) Yield: 53%, yellow oil, R_f = 0.3 (petroleum ether/AcOEt = 10:1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.20 (dd, J = 8.2, 3.1 Hz, 1H), 7.05 (dd, J = 9.3, 7.7 Hz, 3H), 6.95 (dd, J = 9.1, 4.4 Hz, 2H), 6.89 (s, 1H), 6.81 (dd, J = 9.1, 4.6 Hz, 1H), 2.47 (s, 3H), 2.34 (s, 3H). ^{19}F NMR (471 MHz, CDCl3) δ -119.0, -119.1. ^{13}C NMR (126 MHz, $CDCl_3$) δ 200.7, 195.4, 159.1 (d, J = 242.7 Hz), 157.9 (d, J = 244.1 Hz), 154.8 (d, J = 2.6 Hz), 152.5 (d, J = 2.6 Hz), 149.7, 121.4, 120.1 (d, J = 8.3 Hz), 120.0 (d, J = 24.7 Hz), 119.3 (d, J = 8.6 Hz), 118.7 (d, J = 23.3 Hz), 116.6 (d, J = 23.5 Hz), 114.8 (d, J = 9.7 Hz), 101.0 (d, J = 3.0 Hz), 90.0, 30.9, 27.6. IR (KBr, cm^{-1}) 3051, 1767, 1712, 1575, 1484, 1422, 1364, 1205, 1091, 947, 845. HRMS (ESI) ([M+Na]$^+$) Calcd. for $[C_{20}H_{14}F_2NaO_3]^+$: 363.0803, Found. 363.0799.

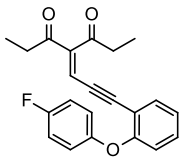


3-(3-(5-Chloro-2-(4-fluorophenoxy)phenyl)prop-2-yn-1-ylidene)pentane-2,4-dione (1h) Yield: 52%, yellow oil, R_f = 0.3 (petroleum ether/AcOEt = 10:1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.47 (d, J = 2.5 Hz, 1H), 7.30 – 7.25 (m, 1H), 7.07 (t, J = 8.5 Hz, 2H), 7.01 – 6.96 (m, 2H), 6.91 (s, 1H), 6.74 (d, J = 8.8 Hz, 1H), 2.49 (s, 3H), 2.34 (s, 3H). ^{19}F NMR (471 MHz, $CDCl_3$) δ -118.3. ^{13}C NMR (126 MHz, $CDCl_3$) δ 200.8, 195.5, 159.4 (d, J = 243.5 Hz), 157.5, 151.7 (d, J = 2.8 Hz), 149.7, 133.3, 131.6, 128.1, 121.4, 120.8 (d, J = 8.3 Hz), 118.4, 116.7 (d, J = 23.5 Hz), 114.7, 100.9, 90.2, 30.9, 27.6. IR (KBr, cm^{-1}) 3031, 1712, 1688, 1569, 1501, 1477, 1423, 1364, 1250, 1214, 1092, 958, 827, 782. HRMS (ESI) ([M+Na]$^+$) Calcd. for $[C_{20}H_{14}ClFNaO_3]^+$: 379.0508, Found. 379.0510.

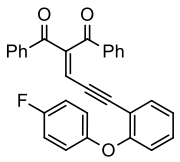


3-(3-(2-(4-Fluorophenoxy)-5-methylphenyl)prop-2-yn-1-ylidene)pentane-2,4-dione (1i) Yield: 63%, yellow oil, R_f = 0.3 (petroleum ether/AcOEt = 10:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 (s, 1H), 7.14 (d, J = 8.5 Hz, 1H), 7.03 (t, J = 8.7 Hz, 2H), 6.98 – 6.90 (m, 3H), 6.74 (d, J = 8.4 Hz, 1H), 2.49 (s, 3H), 2.32 (d, J = 4.1 Hz, 6H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -119.6. ^{13}C NMR (101 MHz, $CDCl_3$) δ 201.0, 195.6, 158.9 (d, J = 242.0 Hz), 156.5, 152.6 (d, J = 2.3 Hz), 148.9, 134.3, 133.1, 132.6, 122.4, 120.1 (d, J = 8.3 Hz), 117.9, 116.4 (d, J = 23.4 Hz), 113.3, 103.3, 89.4, 31.0, 27.6, 20.4. IR (KBr, cm^{-1}) 3029, 2924, 1710, 1690, 1568,

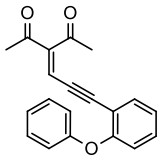
1495, 1424, 1364, 1246, 1215, 1133, 961, 832. HRMS (ESI) ([M+Na]$^+$) Calcd. for [$C_{21}H_{17}FNaO_3$]$^+$: 359.1054, Found. 359.1049.



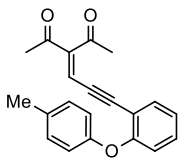
4-(3-(2-(4-Fluorophenoxy)phenyl)prop-2-yn-1-ylidene)heptane-3,5-dione (1j) Yield: 62%, yellow oil, R_f = 0.3 (petroleum ether/AcOEt = 10:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (d, J = 7.7 Hz, 1H), 7.31 (t, J = 8.0 Hz, 1H), 7.10 – 7.03 (m, 3H), 6.99 (dd, J = 9.2, 4.0 Hz, 2H), 6.89 (s, 1H), 6.78 (d, J = 8.3 Hz, 1H), 2.87 (q, J = 7.2 Hz, 2H), 2.64 (q, J = 7.2 Hz, 2H), 1.10 (t, J = 7.2 Hz, 3H), 1.04 (t, J = 7.2 Hz, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -118.9. ^{13}C NMR (101 MHz, $CDCl_3$) δ 204.7, 198.3, 159.2 (d, J = 242.8 Hz), 158.0, 152.1 (d, J = 2.9 Hz), 149.4, 134.1, 131.5, 123.1, 120.9 (d, J = 8.2 Hz), 120.3, 117.2, 116.5 (d, J = 23.5 Hz), 113.3, 101.3, 89.4, 36.7, 32.9, 7.9, 7.5. IR (KBr, cm^{-1}) 2981, 2938, 1711, 1570, 1501, 1447, 1371, 1260, 1211, 1039, 966, 848, 756. HRMS (ESI) ([M+Na]$^+$) Calcd. for [$C_{22}H_{19}FNaO_3$]$^+$: 373.1210, Found. 373.1205.



2-(3-(2-(4-Fluorophenoxy)phenyl)prop-2-yn-1-ylidene)-1,3-diphenylpropane-1,3-dione (1k) Yield: 51%, yellow oil, R_f = 0.3 (petroleum ether/AcOEt = 10:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, J = 8.2 Hz, 2H), 7.80 (d, J = 8.1 Hz, 2H), 7.52 (dt, J = 12.7, 7.4 Hz, 2H), 7.41 (dt, J = 14.5, 7.6 Hz, 4H), 7.21 (t, J = 7.9 Hz, 1H), 7.04 – 6.90 (m, 5H), 6.87 – 6.82 (m, 2H), 6.68 (d, J = 8.4 Hz, 1H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -119.2. ^{13}C NMR (101 MHz, $CDCl_3$) δ 194.0, 192.9, 159.1 (d, J = 242.1 Hz), 157.9, 152.1 (d, J = 2.5 Hz), 147.9, 136.8, 136.3, 134.2, 133.7, 132.9, 131.3, 129.6, 129.3, 128.7, 128.6, 124.3, 122.9, 120.9 (d, J = 8.3 Hz), 117.2, 116.3 (d, J = 23.4 Hz), 113.3, 102.1, 89.5. IR (KBr, cm^{-1}) 3061, 2957, 2925, 1710, 1679, 1574, 1500, 1446, 1357, 1261, 1213, 1116, 971, 850, 733. HRMS (ESI) ([M+Na]$^+$) Calcd. for [$C_{30}H_{19}FNaO_3$]$^+$: 469.1210, Found. 469.1206.

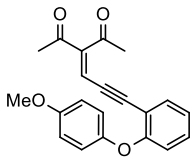


3-(3-(2-Phenoxyphenyl)prop-2-yn-1-ylidene)pentane-2,4-dione (1l) Yield: 57%, yellow oil, R_f = 0.3 (petroleum ether/AcOEt = 10:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (d, J = 7.7 Hz, 1H), 7.39 – 7.29 (m, 3H), 7.12 (dt, J = 21.0, 7.5 Hz, 2H), 7.01 (d, J = 8.0 Hz, 2H), 6.94 (s, 1H), 6.87 (d, J = 8.4 Hz, 1H), 2.49 (s, 3H), 2.32 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 201.0, 195.7, 158.6, 156.3, 148.9, 134.1, 131.7, 129.9, 124.0, 123.2, 122.4, 119.1, 118.1, 113.7, 103.3, 89.6, 31.0, 27.7. IR (KBr, cm^{-1}) 3032, 1712, 1682, 1576, 1483, 1445, 1363, 1233, 1162, 1022, 953, 871, 755. HRMS (ESI) ([M+Na]$^+$) Calcd. for [$C_{20}H_{16}NaO_3$]$^+$: 327.0992, Found. 327.0988.

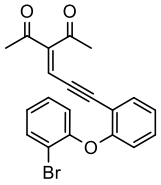


3-(3-(2-(*p*-Tolyloxy)phenyl)prop-2-yn-1-ylidene)pentane-2,4-dione (1m) Yield: 57%, yellow oil, R_f = 0.3 (petroleum ether/AcOEt = 10:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 (d, J = 7.7 Hz, 1H), 7.29 (q, J = 6.9, 6.1 Hz, 1H), 7.16 (d, J = 8.8 Hz, 2H), 7.05 (t, J = 7.4 Hz, 1H), 6.97 (s, 1H), 6.91 (d, J = 8.4 Hz, 2H), 6.81 (d, J = 8.5 Hz, 1H), 2.53 (s, 3H), 2.34 (d, J = 4.7 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 201.1, 195.7, 159.2, 153.8, 148.8, 134.0, 133.8, 131.7, 130.4, 122.8, 122.6, 119.3, 117.3, 113.2, 103.6, 89.6, 31.0, 27.7,

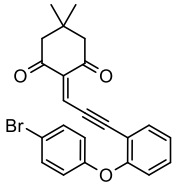
20.8. IR (KBr, cm^{-1}) 3031, 1710, 1684, 1573, 1501, 1481, 1444, 1361, 1233, 1024, 958, 854, 752. HRMS (ESI) ($[M+Na]^+$) Calcd. for $[C_{21}H_{18}NaO_3]^+$: 341.1148, Found. 341.1143.



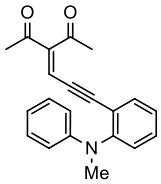
3-(3-(2-(4-Methoxyphenoxy)phenyl)prop-2-yn-1-ylidene)pentane-2,4-dione (1n) Yield: 55%, yellow oil, R_f = 0.3 (petroleum ether/AcOEt = 10:1). ^1H NMR (400 MHz, $CDCl_3$) δ 7.49 (d, J = 7.4 Hz, 1H), 7.28 (t, J = 7.6 Hz, 1H), 7.06 – 6.95 (m, 4H), 6.90 (d, J = 6.9 Hz, 2H), 6.75 (d, J = 8.4 Hz, 1H), 3.81 (s, 3H), 2.55 (s, 3H), 2.34 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 201.1, 195.7, 159.9, 156.4, 149.2, 148.8, 134.0, 131.7, 122.6, 122.4, 121.0, 116.4, 115.0, 112.6, 103.7, 89.6, 55.7, 31.0, 27.7. IR (KBr, cm^{-1}) 3012, 2955, 1712, 1683, 1576, 1480, 1446, 1357, 1235, 1031, 958, 856, 751. HRMS (ESI) ($[M+Na]^+$) Calcd. for $[C_{21}H_{18}NaO_4]^+$: 357.1097, Found. 357.1095.



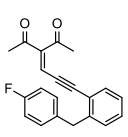
3-(3-(2-(2-Bromophenoxy)phenyl)prop-2-yn-1-ylidene)pentane-2,4-dione (1o) Yield: 87%, yellow oil, R_f = 0.3 (petroleum ether/AcOEt = 10:1). ^1H NMR (500 MHz, Chloroform-d) δ 7.65 (dd, J = 7.9, 1.5 Hz, 1H), 7.53 (dd, J = 7.7, 1.6 Hz, 1H), 7.37 – 7.25 (m, 2H), 7.09 (ddd, J = 13.7, 8.2, 6.9 Hz, 2H), 6.98 (d, J = 8.9 Hz, 2H), 6.71 (d, J = 8.3 Hz, 1H), 2.54 (s, 3H), 2.34 (s, 3H). ^{13}C NMR (126 MHz, Chloroform-d) δ 201.01, 195.73, 158.12, 152.74, 148.91, 134.18, 134.04, 131.71, 128.93, 125.89, 123.35, 122.37, 121.16, 116.89, 115.07, 113.10, 102.96, 89.88, 31.13, 27.75. IR (KBr, cm^{-1}) 3027, 1708, 1681, 1576, 1480, 1363, 1235, 1021, 960, 851, 746. HRMS (ESI) ($[M+Na]^+$) Calcd. for $[C_{20}H_{16}BrNaO_3]^+$: 383.0277, Found. 383.0270.



2-(3-(2-(4-Bromophenoxy)phenyl)prop-2-yn-1-ylidene)-5,5-dimethylcyclohexane-1,3-dione (1p) Yield: 12%, yellow oil, R_f = 0.3 (petroleum ether/AcOEt = 10:1). ^1H NMR (500 MHz, Chloroform-d) δ 7.75 (dd, J = 7.8, 1.7 Hz, 1H), 7.46 (d, J = 8.8 Hz, 1H), 7.41 (d, J = 8.7 Hz, 1H), 7.29 (d, J = 5.5 Hz, 2H), 7.19 – 7.15 (m, 1H), 6.95 (d, J = 8.7 Hz, 2H), 6.82 (d, J = 8.5 Hz, 1H), 2.57 (s, 4H), 1.10 (s, 6H). ^{13}C NMR (126 MHz, Chloroform-d) δ 196.4, 195.1, 158.5, 156.0, 138.6, 135.6, 132.7, 132.4, 129.6, 123.9, 120.7, 118.6, 116.3, 114.6, 108.6, 94.8, 53.1, 52.2, 31.5, 30.0, 28.6. HRMS (ESI) ($[M+Na]^+$) Calcd. for $[C_{23}H_{19}BrNaO_3]^+$: 445.0410, Found. 445.0411.

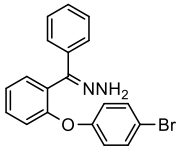


3-(3-(2-(Methyl(phenyl)amino)phenyl)prop-2-yn-1-ylidene)pentane-2,4-dione (1q) Yield: 33%, yellow oil, R_f = 0.3 (petroleum ether/AcOEt = 10:1). ^1H NMR (400 MHz, $CDCl_3$) δ 7.51 (d, J = 7.7 Hz, 1H), 7.39 (d, J = 8.1 Hz, 1H), 7.24 – 7.15 (m, 4H), 6.82 – 6.76 (m, 2H), 6.72 (d, J = 8.1 Hz, 2H), 3.28 (s, 3H), 2.31 (s, 3H), 2.28 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 201.0, 195.5, 151.4, 149.0, 148.8, 134.5, 131.6, 129.0, 127.3, 125.1, 122.2, 120.0, 118.9, 115.6, 105.2, 89.7, 40.2, 30.8, 27.4. IR (KBr, cm^{-1}) 3029, 2954, 1711, 1575, 1500, 1483, 1446, 1366, 1231, 1129, 973, 858, 749. HRMS (ESI) ($[M+Na]^+$) Calcd. for $[C_{21}H_{19}NNaO_3]^+$: 340.1308, Found. 340.1309.

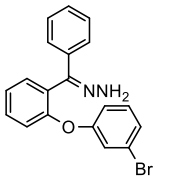


3-(3-(2-(4-Fluorobenzyl)phenyl)prop-2-yn-1-ylidene)pentane-2,4-dione (1r) Yield: 88%, yellow oil, R_f = 0.3 (petroleum ether/AcOEt = 10:1). ^1H NMR (500 MHz, Chloroform-d) δ 7.50 (d, J = 7.7 Hz, 1H), 7.35 (t, J = 7.6 Hz, 1H), 7.24 (t, J = 7.8 Hz, 1H), 7.19 – 7.12 (m, 3H), 6.98 (t, J = 8.7 Hz, 2H), 6.93 (s, 1H), 4.13 (s,

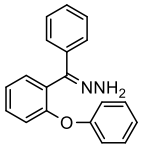
2H), 2.46 (s, 3H), 2.37 (s, 3H). ^{19}F NMR (471 MHz, Chloroform-d) δ -116.87. ^{13}C NMR (126 MHz, Chloroform-d) δ 200.8, 195.6, 161.5 (d, J_{C-F} = 244.3 Hz), 149.4, 143.7, 135.7 (d, J_{C-F} = 3.2 Hz), 133.2, 130.5, 130.2 (d, J_{C-F} = 7.8 Hz), 129.7, 126.6, 122.0, 121.4, 115.3 (d, J_{C-F} = 21.3 Hz), 105.8, 88.8, 39.2, 30.9, 27.2. HRMS (ESI) ([M+H]$^+$) Calcd. for $[C_{21}H_{18}FO_2]^+$: 321.1285, Found. 321.1286.



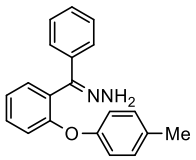
((2-(4-Bromophenoxy)phenyl)(phenyl)methylene)hydrazine (S15a) Yield: 87%, yellow oil, R_f = 0.25 (petroleum ether/AcOEt = 5:1). *E*/*Z* = 81:19. ^{1}H NMR (500 MHz, Chloroform-d) δ 7.54 – 7.41 (m, 2H), 7.43 – 7.22 (m, 8H), 7.06 (d, J = 8.2 Hz, 1H), 6.81 (d, J = 8.8 Hz, 2H), 5.53 (br, 2H). ^{13}C NMR (126 MHz, Chloroform-d) δ 155.7, 154.6, 145.8, 138.0, 132.6, 131.0, 130.7, 128.1, 128.1, 126.0, 124.5, 120.9, 119.2, 118.8, 116.2. IR (KBr, cm^{-1}) 3416, 3059, 1576, 1480, 1442, 1328 1233, 1091, 1066, 832, 754. HRMS (ESI) ([M+H]$^+$) Calcd. for $[C_{19}H_{16}BrN_2O]^+$: 367.0441, Found. 367.0438.



((2-(3-Bromophenoxy)phenyl)(phenyl)methylene)hydrazine (S15b) Yield: 82%, yellow oil, R_f = 0.25 (petroleum ether/AcOEt = 5:1). *E*/*Z* = 80:20. ^{1}H NMR (500 MHz, Chloroform-d) δ 7.50 – 7.45 (m, 2H), 7.34 – 7.26 (m, 6H), 7.18 (dt, J = 7.9, 1.1 Hz, 1H), 7.11 (dd, J = 8.2, 2.1 Hz, 2H), 7.06 (t, J = 2.1 Hz, 1H), 6.86 (dd, J = 8.2, 2.3 Hz, 1H), 5.54 (br, 2H). ^{13}C NMR (126 MHz, Chloroform-d) δ 157.4, 154.2, 145.7, 137.9, 131.1, 130.8, 130.7, 128.1, 128.1, 126.6, 126.0, 124.7, 124.4, 122.6, 122.2, 119.7, 117.7. IR (KBr, cm^{-1}) 3417, 3061, 1577, 1472, 1438, 1227, 1060, 946, 890, 761. HRMS (ESI) ([M+H]$^+$) Calcd. for $[C_{19}H_{16}BrN_2O]^+$: 367.0441, Found. 367.0442.

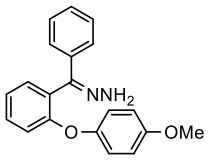


((2-Phenoxyphenyl)(phenyl)methylene)hydrazine (S15c) Yield: 93%, yellow oil, R_f = 0.25 (petroleum ether/AcOEt = 5:1). *E*/*Z* = 76:24. ^{1}H NMR (500 MHz, Chloroform-d) δ 7.58 – 7.52 (m, 2H), 7.43 (ddd, J = 8.9, 7.2, 1.9 Hz, 1H), 7.35 – 7.26 (m, 8H), 7.12 – 7.05 (m, 2H), 6.99 – 6.94 (m, 2H), 5.57 (br, 2H). ^{13}C NMR (126 MHz, Chloroform-d) δ 156.4, 155.1, 146.2, 138.2, 130.9, 130.6, 129.7, 128.1, 128.0, 126.1, 123.9, 123.8, 119.5, 118.8, 117.4. IR (KBr, cm^{-1}) 3416, 3056, 1587, 1484, 1443, 1329, 1235, 1067, 948, 869, 746. HRMS (ESI) ([M+H]$^+$) Calcd. for $[C_{19}H_{17}N_2O]^+$: 289.1335, Found. 289.1336.

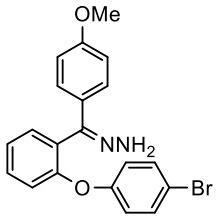


(Phenyl(2-(p-tolyloxy)phenyl)methylene)hydrazine (S15d) Yield: 91%, yellow oil, R_f = 0.25 (petroleum ether/AcOEt = 5:1). *E*/*Z* = 86:14. ^{1}H NMR (500 MHz, Chloroform-d) δ 7.61 – 7.52 (m, 2H), 7.41 (ddd, J = 8.6, 7.3, 1.9 Hz, 1H), 7.36 – 7.27 (m, 4H), 7.24 (td, J = 7.4, 1.1 Hz, 1H), 7.10 (d, J = 8.3 Hz, 2H), 7.03 (dd, J = 8.4, 1.1 Hz, 1H), 6.87 (d, J = 8.5 Hz, 2H), 5.58 (br, 2H), 2.33 (s, 3H). ^{13}C NMR (126 MHz, Chloroform-d) δ 155.6, 154.0, 146.4, 138.3, 133.4, 130.8, 130.5, 130.2, 128.1, 128.0, 126.1, 123.55, 123.50, 119.6, 118.2, 20.8. IR (KBr, cm^{-1}) 3418, 3029, 2949, 1589, 1492, 1444, 1237, 946, 832, 763. HRMS (ESI) ([M+H]$^+$)

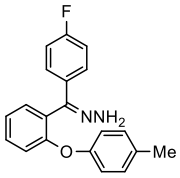
Calcd. for $[C_{20}H_{19}N_2O]^+$: 303.1492, Found. 303.1493.



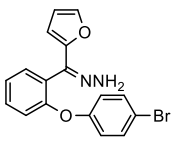
((2-(4-Methoxyphenoxy)phenyl)(phenyl)methylene)hydrazine (S15e) Yield: 94%, yellow oil, R_f = 0.25 (petroleum ether/AcOEt = 5:1). *E*/*Z* = 65:35. ^{1}H NMR (500 MHz, Chloroform-d) δ 7.57 – 7.53 (m, 2H), 7.40 – 7.36 (m, 1H), 7.35 – 7.25 (m, 4H), 7.21 (td, J = 7.4, 1.1 Hz, 1H), 6.90 (d, J = 9.1 Hz, 2H), 6.83 (d, J = 9.1 Hz, 2H), 6.74 (d, J = 9.0 Hz, 1H), 5.56 (br, 2H), 3.78 (s, 3H). ^{13}C NMR (126 MHz, Chloroform-d) δ 156.2, 149.5, 146.5, 138.2, 130.7, 130.5, 128.7, 128.2, 128.1, 126.1, 123.2, 121.2, 119.3, 117.4, 114.8, 55.6. IR (KBr, cm^{-1}) 3406, 3058, 2947, 1593, 1495, 1447, 1226, 1033, 948, 840, 764. HRMS (ESI) ([M+H]$^+$) Calcd. for $[C_{20}H_{19}N_2O_2]^+$: 319.1441, Found. 319.1442.



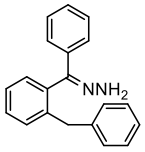
((2-(4-Bromophenoxy)phenyl)(4-methoxyphenyl)methylene)hydrazine (S15f) Yield: 83%, yellow oil, R_f = 0.25 (petroleum ether/AcOEt = 5:1). *E*/*Z* = 85:15. ^{1}H NMR (500 MHz, Chloroform-d) δ 7.46 – 7.40 (m, 3H), 7.38 – 7.34 (m, 2H), 7.32 – 7.28 (m, 2H), 7.06 (d, J = 8.2 Hz, 1H), 6.82 (dd, J = 11.1, 8.9 Hz, 4H), 5.33 (br, 2H), 3.81 (s, 3H). ^{13}C NMR (126 MHz, Chloroform-d) δ 159.7, 155.8, 154.5, 146.1, 132.5, 131.0, 130.8, 130.6, 127.3, 124.5, 124.4, 120.9, 119.3, 116.2, 113.6, 55.3. IR (KBr, cm^{-1}) 3414, 3055, 2941, 1603, 1478, 1445, 1240, 1166, 1025, 832, 749. HRMS (ESI) ([M+H]$^+$) Calcd. for $[C_{20}H_{18}BrN_2O_2]^+$: 397.0546, Found. 397.0547.



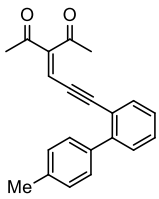
(*E*)-((4-Fluorophenyl)(2-(p-tolyloxy)phenyl)methylene)hydrazine (S15g) Yield: 62%, yellow oil, R_f = 0.25 (petroleum ether/AcOEt = 5:1). ^{1}H NMR (500 MHz, Chloroform-d) δ 7.52 (ddd, J = 8.7, 5.3, 1.5 Hz, 2H), 7.41 (ddd, J = 8.7, 7.2, 2.0 Hz, 1H), 7.30 – 7.22 (m, 2H), 7.09 (d, J = 8.2 Hz, 2H), 7.04 – 6.96 (m, 3H), 6.87 – 6.81 (m, 2H), 5.53 (br, 2H), 2.32 (s, 3H). ^{19}F NMR (471 MHz, Chloroform-d) δ -114.27. ^{13}C NMR (126 MHz, Chloroform-d) δ 162.8 (d, J = 247.2 Hz), 155.5, 153.9, 145.5, 134.5 (d, J = 3.1 Hz), 133.5, 130.7 (d, J = 3.8 Hz), 130.2, 127.8 (d, J = 8.1 Hz), 123.6, 123.2, 119.5, 118.3, 115.1, 114.9, 20.7. IR (KBr, cm^{-1}) 3411, 3051, 2944, 1600, 1498, 1444, 1233, 1158, 834, 752. HRMS (ESI) ([M+H]$^+$) Calcd. for $[C_{20}H_{18}FN_2O]^+$: 321.1398, Found. 321.1399.



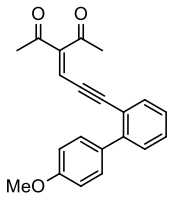
(*Z*)-((2-(4-Bromophenoxy)phenyl)(furan-2-yl)methylene)hydrazine (S15h) Yield: 53%, yellow oil, R_f = 0.25 (petroleum ether/AcOEt = 5:1). ^{1}H NMR (500 MHz, Chloroform-d) δ 7.45 (ddd, J = 8.2, 7.3, 1.8 Hz, 1H), 7.43 – 7.34 (m, 4H), 7.31 – 7.25 (m, 1H), 7.05 (dd, J = 8.2, 1.1 Hz, 1H), 6.87 – 6.79 (m, 2H), 6.35 (dd, J = 3.4, 1.8 Hz, 1H), 6.13 (dd, J = 3.3, 0.9 Hz, 1H), 5.53 (s, 2H). ^{13}C NMR (126 MHz, Chloroform-d) δ 155.8, 154.4, 152.2, 142.9, 138.0, 132.6, 131.2, 131.0, 124.5, 122.6, 120.6, 119.3, 116.2, 111.1, 109.2. IR (KBr, cm^{-1}) 3414, 3055, 2946, 1574, 1480, 1442, 1234, 1155, 1066, 969, 745. HRMS (ESI) ([M+H]$^+$) Calcd. for $[C_{17}H_{14}BrN_2O_2]^+$: 357.0233, Found. 357.0234.



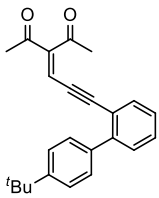
((2-Benzylphenyl)(phenyl)methylene)hydrazine (S15i) Yield: 78%, yellow oil, R_f = 0.25 (petroleum ether/AcOEt = 5:1). *E*/*Z* = 96:4. ^{1}H NMR (500 MHz, Chloroform-d) δ 7.50 (dt, J = 7.3, 1.8 Hz, 2H), 7.42 (pd, J = 7.4, 1.7 Hz, 2H), 7.37 – 7.29 (m, 4H), 7.27 – 7.16 (m, 4H), 7.15 – 7.10 (m, 2H), 5.23 (br, 2H), 3.83 (s, 2H). ^{13}C NMR (126 MHz, Chloroform-d) δ 148.9, 140.4, 140.0, 138.0, 132.5, 130.6, 129.4, 129.3, 129.2, 128.4, 128.3, 128.1, 127.3, 126.1, 126.0, 39.1. IR (KBr, cm^{-1}) 3416, 3024, 2942, 1573, 1488, 1443, 1169, 739, 696. HRMS (ESI) ([M+H]$^+$) Calcd. for $[C_{20}H_{19}N_2]^+$: 287.1543, Found. 287.1544.



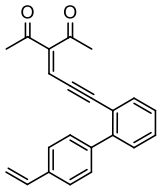
3-(3-(4'-Methyl-[1,1'-biphenyl]-2-yl)prop-2-yn-1-ylidene)pentane-2,4-dione (5a) Yield: 71%, yellow oil, R_f = 0.3 (petroleum ether/AcOEt = 10:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (d, J = 7.7 Hz, 1H), 7.35 (d, J = 7.4 Hz, 1H), 7.30 (d, J = 8.0 Hz, 3H), 7.24 (t, J = 7.5 Hz, 1H), 7.15 (d, J = 7.7 Hz, 2H), 6.77 (s, 1H), 2.33 (s, 3H), 2.21 (s, 3H), 2.12 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 201.0, 195.6, 148.7, 144.8, 137.8, 137.1, 133.8, 130.3, 129.8, 129.1, 129.0, 127.1, 122.4, 120.1, 107.5, 87.7, 30.6, 27.5, 21.2. IR (KBr, cm^{-1}) 3023, 2921, 1711, 1669, 1570, 1476, 1419, 1361, 1243, 1176, 953, 822, 762. HRMS (ESI) ([M+H]$^+$) Calcd. for $[C_{21}H_{19}O_2]^+$: 303.1380, Found. 303.1384.



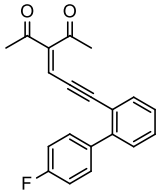
3-(3-(4'-Methoxy-[1,1'-biphenyl]-2-yl)prop-2-yn-1-ylidene)pentane-2,4-dione (5b) Yield: 69%, yellow oil, R_f = 0.3 (petroleum ether/AcOEt = 10:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (d, J = 7.6 Hz, 1H), 7.46 – 7.41 (m, 3H), 7.38 (d, J = 6.7 Hz, 1H), 7.31 (t, J = 7.5 Hz, 1H), 6.99 – 6.95 (m, 3H), 6.86 (s, 1H), 3.87 (s, 3H), 2.30 (s, 3H), 2.23 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 201.0, 195.6, 159.5, 148.7, 144.5, 133.8, 132.3, 130.3, 130.3, 129.67, 126.9, 122.3, 120.0, 113.8, 107.6, 87.7, 55.4, 30.6, 27.5. IR (KBr, cm^{-1}) 3004, 2959, 2837, 1710, 1664, 1576, 1516, 1474, 1419, 1371, 1248, 1178, 1035, 958, 835, 763. HRMS (ESI) ([M+H]$^+$) Calcd. for $[C_{21}H_{19}O_3]^+$: 319.1329, Found. 319.1327.



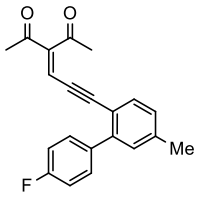
3-(3-(4'-(tert-Butyl)-[1,1'-biphenyl]-2-yl)prop-2-yn-1-ylidene)pentane-2,4-dione (5c) Yield: 68%, yellow oil, R_f = 0.3 (petroleum ether/AcOEt = 10:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (d, J = 7.6 Hz, 1H), 7.48 – 7.38 (m, 6H), 7.32 (td, J = 7.5, 1.6 Hz, 1H), 6.88 (s, 1H), 2.29 (s, 3H), 2.12 (s, 3H), 1.38 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 200.9, 195.6, 150.9, 148.6, 144.6, 137.0, 133.9, 130.3, 129.9, 128.8, 127.0, 125.3, 122.4, 120.1, 107.6, 87.8, 34.7, 31.4, 30.5, 27.6. IR (KBr, cm^{-1}) 3027, 2961, 2869, 1710, 1690, 1570, 1516, 1476, 1363, 1243, 1174, 1054, 955, 837, 763. HRMS (ESI) ([M+Na]$^+$) Calcd. for $[C_{24}H_{24}NaO_2]^+$: 367.1669, Found. 367.1673.



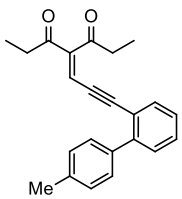
3-(3-(4'-Vinyl-[1,1'-biphenyl]-2-yl)prop-2-yn-1-ylidene)pentane-2,4-dione (5d) Yield: 67%, yellow oil, R_f = 0.3 (petroleum ether/AcOEt = 10:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (d, *J* = 7.7 Hz, 1H), 7.49 – 7.43 (m, 5H), 7.40 (d, *J* = 7.5 Hz, 1H), 7.33 (t, *J* = 7.5 Hz, 1H), 6.84 (s, 1H), 6.77 (dd, J = 17.6, 10.9 Hz, 1H), 5.83 (d, J = 17.6 Hz, 1H), 5.31 (d, J = 10.9 Hz, 1H), 2.29 (s, 3H), 2.19 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 201.0, 195.6, 148.9, 144.3, 139.3, 137.2, 136.3, 133.9, 130.4, 129.7, 129.3, 127.3, 126.2, 122.1, 120.1, 114.5, 107.0, 87.8, 30.6, 27.4. IR (KBr, cm^{-1}) 3026, 2943, 2837, 1710, 1691, 1576, 1476, 1370, 1244, 1176, 957, 845, 763. HRMS (ESI) ($[M+H]^+$) Calcd. for $[C_{22}H_{19}O_2]^+$: 315.1380, Found. 315.1382.



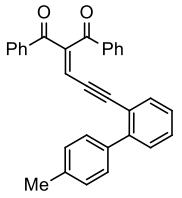
3-(3-(4'-Fluoro-[1,1'-biphenyl]-2-yl)prop-2-yn-1-ylidene)pentane-2,4-dione (5e) Yield: 55%, yellow oil, R_f = 0.3 (petroleum ether/AcOEt = 10:1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.58 (dd, J = 7.7, 1.4 Hz, 1H), 7.48 – 7.44 (m, 3H), 7.36 (ddd, J = 14.8, 7.5, 1.3 Hz, 2H), 7.16 – 7.10 (m, 2H), 6.82 (s, 1H), 2.31 (s, 3H), 2.25 (s, 3H). ^{19}F NMR (471 MHz, $CDCl_3$) δ -114.2. ^{13}C NMR (126 MHz, $CDCl_3$) δ 200.8, 195.5, 162.6 (d, J = 247.5 Hz), 149.1, 143.6, 135.93 (d, J = 3.5 Hz), 133.82, 130.80 (d, J = 8.2 Hz), 130.36, 129.72, 127.40, 121.91, 120.14, 115.29 (d, J = 21.6 Hz), 106.61, 87.79, 30.61, 27.37. IR (KBr, cm^{-1}) 3029, 2927, 1711, 1692, 1576, 1477, 1370, 1242, 1176, 1054, 958, 840, 763. HRMS (ESI) ($[M+Na]^+$) Calcd. for $[C_{20}H_{15}FNaO_2]^+$: 329.0948, Found. 329.0943.



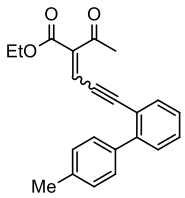
3-(3-(4'-Fluoro-5-methyl-[1,1'-biphenyl]-2-yl)prop-2-yn-1-ylidene)pentane-2,4-dione (5f) Yield: 68%, yellow oil, R_f = 0.3 (petroleum ether/AcOEt = 10:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 – 7.41 (m, 3H), 7.21 – 7.08 (m, 4H), 6.83 (s, 1H), 2.41 (s, 3H), 2.30 (s, 3H), 2.24 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -114.4. ^{13}C NMR (101 MHz, $CDCl_3$) δ 200.9, 195.5, 162.6 (d, J = 247.2 Hz), 148.6, 143.5, 141.0, 136.0 (d, J = 3.2 Hz), 133.8, 130.8 (d, J = 8.1 Hz), 130.5, 128.3, 122.3, 117.2, 115.2 (d, J = 21.4 Hz), 107.4, 87.5, 30.6, 27.4, 21.6. IR (KBr, cm^{-1}) 3026, 2925, 1711, 1692, 1575, 1511, 1488, 1370, 1224, 1176, 1024, 959, 837. HRMS (ESI) ($[M+Na]^+$) Calcd. for $[C_{21}H_{17}FNaO_2]^+$: 343.1105, Found. 343.1100.



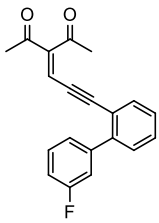
4-(3-(4'-Methyl-[1,1'-biphenyl]-2-yl)prop-2-yn-1-ylidene)heptane-3,5-dione (5g) Yield: 77%, yellow oil, R_f = 0.3 (petroleum ether/AcOEt = 10:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (d, J = 7.7 Hz, 1H), 7.34 – 7.27 (m, 4H), 7.20 (t, J = 7.4 Hz, 1H), 7.13 (d, J = 7.9 Hz, 2H), 6.71 (s, 1H), 2.48 (dq, J = 17.3, 7.2 Hz, 4H), 2.31 (s, 3H), 0.97 (t, J = 7.2 Hz, 3H), 0.86 (t, J = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 204.6, 198.4, 149.0, 144.5, 137.7, 137.0, 133.8, 130.2, 129.8, 129.0, 129.0, 127.0, 120.5, 120.1, 105.9, 87.5, 36.6, 32.8, 21.3, 8.0, 7.5. IR (KBr, cm^{-1}) 3025, 2979, 2937, 1709, 1691, 1577, 1476, 1375, 1206, 1115, 1043, 967, 821, 762. HRMS (ESI) ($[M+Na]^+$) Calcd. for $[C_{23}H_{22}NaO_2]^+$: 353.1512, Found. 353.1511.



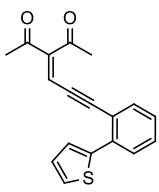
2-(3-(4'-Methyl-[1,1'-biphenyl]-2-yl)prop-2-yn-1-ylidene)-1,3-diphenylpropane-1,3-dione (5h) Yield: 63%, yellow oil, R_f = 0.3 (petroleum ether/AcOEt = 10:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, J = 7.4 Hz, 2H), 7.82 (d, J = 7.8 Hz, 2H), 7.60 – 7.41 (m, 6H), 7.37 – 7.33 (m, 4H), 7.18 (d, J = 7.6 Hz, 3H), 7.10 (d, J = 7.7 Hz, 1H), 6.92 (s, 1H), 2.40 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 194.1, 193.0, 147.6, 144.3, 137.5, 136.9, 136.9, 136.4, 134.0, 133.8, 133.0, 130.1, 129.7, 129.6, 129.3, 129.0, 128.9, 128.8, 128.7, 126.8, 124.8, 120.0, 106.8, 87.8, 21.3. IR (KBr, cm^{-1}) 3068, 3026, 2933, 1712, 1676, 1576, 1446, 1357, 1260, 1118, 970, 761. HRMS (ESI) ($[M+Na]^+$) Calcd. for $[C_{31}H_{22}NaO_2]^+$: 449.1512, Found. 449.1510.



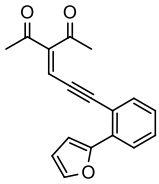
Ethyl 2-acetyl-5-(4'-methyl-[1,1'-biphenyl]-2-yl)pent-2-en-4-ynoate (5i) Yield: 74%, *E*/*Z* = 1.25:1, yellow oil, R_f = 0.3 (petroleum ether/AcOEt = 10:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (dd, J = 7.6, 3.6 Hz, 1H), 7.35 – 7.28 (m, 4H), 7.19 (dd, J = 9.8, 4.6 Hz, 1H), 7.13 (d, J = 7.9 Hz, 2H), 6.82 (d, J = 2.6 Hz, 1H), 4.10 (dq, J = 28.1, 7.1 Hz, 2H), 2.30 (s, 3H), 2.25 (s, 1H), 2.13 (s, 2H), 1.16 (dt, J = 14.2, 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 198.7, 194.0, 165.3, 163.9, 144.7, 144.5, 141.9, 140.8, 137.6, 137.1, 137.0, 133.9, 130.2, 130.2, 129.8, 129.7, 129.0, 127.0, 127.0, 124.7, 123.0, 120.2, 106.9, 105.4, 88.0, 87.4, 61.6, 61.5, 30.2, 27.6, 21.2, 14.2, 14.1. IR (KBr, cm^{-1}) 3022, 2983, 1716, 1581, 1475, 1368, 1248, 1061, 952, 822, 761. HRMS (ESI) ($[M+Na]^+$) Calcd. for $[C_{22}H_{20}NaO_3]^+$: 355.1305, Found. 355.1309.



3-(3-(3'-Fluoro-[1,1'-biphenyl]-2-yl)prop-2-yn-1-ylidene)pentane-2,4-dione (5j) Yield: 59%, yellow oil, R_f = 0.3 (petroleum ether/AcOEt = 10:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (d, J = 7.5 Hz, 1H), 7.46 (q, J = 6.9, 5.9 Hz, 1H), 7.38 (q, J = 8.5, 7.9 Hz, 3H), 7.27 (d, J = 7.6 Hz, 1H), 7.20 (d, J = 9.7 Hz, 1H), 7.13 – 7.06 (m, 1H), 6.83 (s, 1H), 2.30 (s, 3H), 2.24 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -113.0. ^{13}C NMR (101 MHz, $CDCl_3$) δ 200.8, 195.5, 162.6 (d, J = 246.2 Hz), 149.2, 143.2 (d, J = 2.0 Hz), 142.1 (d, J = 7.8 Hz), 133.9, 130.4, 129.9 (d, J = 8.3 Hz), 129.7, 127.8, 125.0 (d, J = 2.9 Hz), 121.9, 120.1, 116.1 (d, J = 22.0 Hz), 114.8 (d, J = 21.0 Hz), 106.3, 88.0, 30.6, 27.4. IR (KBr, cm^{-1}) 3063, 2924, 1711, 1691, 1581, 1473, 1371, 1246, 1180, 1023, 959, 879, 763. HRMS (ESI) ($[M+Na]^+$) Calcd. for $[C_{20}H_{15}FNaO_2]^+$: 329.0948, Found. 329.0944.



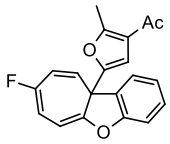
3-(3-(2-(Thiophen-2-yl)phenyl)prop-2-yn-1-ylidene)pentane-2,4-dione (5k) Yield: 66%, yellow oil, R_f = 0.3 (petroleum ether/AcOEt = 10:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (d, J = 7.9 Hz, 2H), 7.45 – 7.35 (m, 3H), 7.28 (t, J = 8.0 Hz, 1H), 7.12 (t, J = 4.3 Hz, 1H), 6.93 (s, 1H), 2.38 (s, 3H), 2.33 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 201.0, 195.6, 149.2, 141.2, 136.9, 134.3, 130.4, 129.5, 127.7, 127.4, 127.3, 126.5, 122.1, 119.4, 106.9, 89.0, 30.8, 27.4. IR (KBr, cm^{-1}) 3026, 2954, 1710, 1667, 1574, 1476, 1369, 1243, 1175, 1022, 953, 851, 761. HRMS (ESI) ($[M+Na]^+$) Calcd. for $[C_{18}H_{14}NaO_2S]^+$: 317.0607, Found. 317.0603.



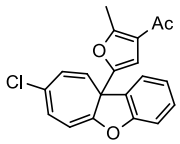
3-(3-(2-(Furan-2-yl)phenyl)prop-2-yn-1-ylidene)pentane-2,4-dione (5l) Yield: 68%, yellow oil, R_f = 0.3 (petroleum ether/AcOEt = 10:1). ^{1}H NMR (400 MHz, Chloroform-d) δ 7.81 (d, J = 8.0 Hz, 1H), 7.53 – 7.50 (m, 2H), 7.43 (t, J = 7.7 Hz, 1H), 7.24 (t, J = 7.5 Hz, 1H), 7.11 (d, J = 3.4 Hz, 1H), 6.99 (s, 1H), 6.53 (s, 1H), 2.50 (s, 3H), 2.37 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 201.0, 195.5, 151.4, 149.4, 142.6, 134.4, 132.5, 130.4, 126.9, 126.0, 121.9, 116.7, 111.9, 110.0, 106.9, 89.0, 31.0, 27.3. IR (KBr, cm^{-1}) 3028, 2924, 1709, 1666, 1579, 1496, 1372, 1244, 1176, 1008, 956, 762. HRMS (ESI) ($[M+H]^+$) Calcd. for $[C_{18}H_{15}O_3]^+$: 279.1016, Found. 279.1018.

5. General procedure for Büchner reaction.

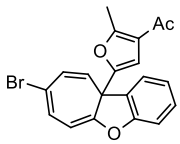
Under N_2 atmosphere, to a solution of enynones **1** (0.2 mmol) in dry DCE (0.1 M) at -20 °C, Rh_2(S-BTPCP)$_4$ (0.01 eq. the catalyst was dissolved in DCE) were added. The reaction mixture was then stirred for 30 hours at -20 °C. After the reaction was completed, the reaction mixture was filtered through short silica gel, and then the solvent was removed under reduced pressure. The crude aromatic substitution product was purified by flash column chromatography (silica gel, petroleum ether/AcOEt = 10:1) to yield **2a** – **2p** (the products were stored in fridge and keep in dark place with aluminum foil).



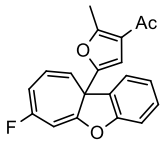
1-(5-(8-Fluoro-10a*H*-cyclohepta[*b*]benzofuran-10a-yl)-2-methylfuran-3-yl)ethanone (2a) Yield: 99%, yellow oil, R_f = 0.3 (petroleum ether/AcOEt = 10:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 (d, J = 7.6 Hz, 1H), 7.24 (t, J = 7.9 Hz, 1H), 7.03 (t, J = 7.7 Hz, 1H), 6.97 (d, J = 8.1 Hz, 1H), 6.32 (t, J = 9.6 Hz, 1H), 6.17 – 6.06 (m, 3H), 5.65 – 5.57 (m, 1H), 2.35 (s, 3H), 2.21 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -105.3. ^{13}C NMR (101 MHz, CDCl3) δ 194.0, 158.6, 157.8 (d, J = 238.2 Hz), 156.1, 149.3 (d, J = 3.2 Hz), 148.5, 130.9, 129.4, 124.0, 123.2, 121.9 (d, J = 12.7 Hz), 121.7, 121.4 (d, J = 19.4 Hz), 110.3, 107.6 (d, J = 29.9 Hz), 107.3, 97.4 (d, J = 11.4 Hz), 51.6, 29.0, 14.5. IR (KBr, cm^{-1}) 3035, 2922, 1711, 1661, 1570, 1483, 1363 1244, 1017, 951, 847, 758. HRMS (ESI) ([M+H]$^+$) Calcd. for $[C_{20}H_{16}FO_3]^+$: 323.1078, Found. 323.1080. HPLC: OD-H column, 95:5 hexane:isopropanol, 1.00 mL/min, t_R = major: 7.2 min, minor: 6.8 min. 96% ee. $[\alpha]_D^{24}$ -132.3° (c 0.83, CH_2Cl_2).



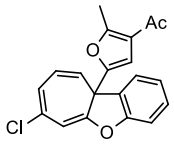
1-(5-(8-Chloro-10a*H*-cyclohepta[*b*]benzofuran-10a-yl)-2-methylfuran-3-yl)ethanone (2b) Yield: 97%, yellow oil, R_f = 0.3 (petroleum ether/AcOEt = 10:1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38 – 7.30 (m, 2H), 7.12 (t, J = 7.5 Hz, 1H), 7.08 (d, J = 8.1 Hz, 1H), 6.77 (d, J = 7.4 Hz, 1H), 6.53 (d, J = 10.0 Hz, 1H), 6.20 (s, 1H), 6.15 (d, J = 7.5 Hz, 1H), 5.45 (d, J = 10.0 Hz, 1H), 2.40 (s, 3H), 2.32 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 194.1, 158.7, 156.2, 153.4, 147.8, 130.7, 130.6, 129.5, 128.5, 124.0, 123.5, 121.4, 120.7, 118.5, 110.4, 107.7, 100.4, 51.8, 29.1, 14.5. IR (KBr, cm^{-1}) 3058, 2926, 1762, 1715, 1672, 1584, 1486, 1450, 1334, 1241, 1093, 935, 839, 759. HRMS (ESI) ([M+H]$^+$) Calcd. for $[C_{20}H_{16}ClO_3]^+$: 339.0782, Found. 339.0787. HPLC: OD-H column, 99:1 hexane:isopropanol, 1.00 mL/min, t_R = major: 11.8 min, minor: 10.8 min. 98% ee. $[\alpha]_D^{24}$ -128.2° (c 1.17, CH_2Cl_2).



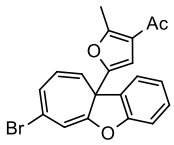
1-(5-(8-Bromo-10a*H*-cyclohepta[*b*]benzofuran-10a-yl)-2-methylfuran-3-yl)ethanone (2c) Yield: 99%, yellow oil, R_f = 0.3 (petroleum ether/AcOEt = 10:1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38 (d, J = 7.5 Hz, 1H), 7.33 (t, J = 7.9 Hz, 1H), 7.12 (t, J = 7.3 Hz, 1H), 7.07 (d, J = 8.1 Hz, 1H), 6.62 – 6.55 (m, 1H), 6.41 (d, J = 10.0 Hz, 1H), 6.27 – 6.17 (m, 2H), 5.55 (d, J = 10.0 Hz, 1H), 2.41 (s, 3H), 2.31 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 194.0, 158.6, 156.1, 152.7, 148.1, 130.8, 129.5, 129.4, 128.7, 125.0, 124.0, 123.4, 121.5, 120.8, 110.4, 107.5, 99.6, 51.7, 29.1, 14.5. IR (KBr, cm^{-1}) 3035, 2931, 1772, 1714, 1581, 1484, 1449, 1334, 1241, 1148, 1009, 933, 837, 758. HRMS (ESI) ([M+H]$^+$) Calcd. for $[C_{20}H_{16}BrO_3]^+$: 383.0277, Found. 383.0278. HPLC: OD-H column, 99:1 hexane:isopropanol, 1.00 mL/min, t_R = major: 11.8 min, minor: 11.2 min. 98% ee. $[\alpha]_D^{24}$ -114.3° (c 1.33, CH_2Cl_2).



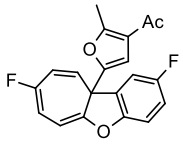
1-(5-(7-Fluoro-10a*H*-cyclohepta[*b*]benzofuran-10a-yl)-2-methylfuran-3-yl)ethanone (2d) Yield: 95%, yellow oil, R_f = 0.3 (petroleum ether/AcOEt = 10:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (d, J = 7.6 Hz, 1H), 7.33 (t, J = 7.7 Hz, 1H), 7.16 – 7.07 (m, 2H), 6.38 – 6.26 (m, 2H), 6.19 (s, 1H), 6.10 (dd, J = 17.2, 7.0 Hz, 1H), 5.42 (d, J = 9.8 Hz, 1H), 2.42 (s, 3H), 2.30 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -97.8. ^{13}C NMR (101 MHz, $CDCl_3$) δ 194.0, 157.7, 157.2 (d, J = 265.8 Hz), 154.0 (d, J = 19.0 Hz), 148.2, 131.2, 129.3, 124.6 (d, J = 11.9 Hz), 124.0, 123.7, 121.6, 119.4, 116.8 (d, J = 2.6 Hz), 110.4, 107.4, 106.6 (d, J = 28.5 Hz), 96.2 (d, J = 41.2 Hz), 52.3, 29.1, 14.5. IR (KBr, cm^{-1}) 3030, 2921, 1710, 1663, 1578, 1482, 1359 1241, 956, 855, 761. HRMS (ESI) ($[M+H]^+$) Calcd. for $[C_{20}H_{16}FO_3]^+$: 323.1078, Found. 323.1077. HPLC: OD-H column, 99:1 hexane:isopropanol, 1.00 mL/min, t_R = major: 13.5 min, minor: 9.1 min. 90% ee. $[\alpha]_D^{24}$ -95.6° (c 1.5, CH_2Cl_2).



1-(5-(7-Chloro-10a*H*-cyclohepta[*b*]benzofuran-10a-yl)-2-methylfuran-3-yl)ethanone (2e) Yield: 92%, yellow oil, R_f = 0.3 (petroleum ether/AcOEt = 10:1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.47 (dd, J = 7.6, 1.3 Hz, 1H), 7.32 (td, J = 7.8, 1.4 Hz, 1H), 7.13 (t, J = 7.6 Hz, 1H), 7.08 (d, J = 8.2 Hz, 1H), 6.50 (dd, J = 7.0, 1.4 Hz, 1H), 6.37 (s, 1H), 6.29 (dd, J = 9.6, 7.0 Hz, 1H), 6.15 (s, 1H), 5.56 (d, J = 9.7 Hz, 1H), 2.44 (s, 3H), 2.30 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 194.0, 158.5, 155.9, 152.8, 148.1, 132.1, 131.0, 129.4, 125.8, 124.1, 124.0, 123.6, 121.5, 120.2, 110.5, 107.2, 103.8, 52.0, 29.1, 14.5. IR (KBr, cm^{-1}) 2924, 2887, 1712, 1668, 1582, 1483, 1449, 1336, 1241, 1022, 955, 847, 758. HRMS (ESI) ($[M+Na]^+$) Calcd. for $[C_{20}H_{15}ClNaO_3]^+$: 361.0602, Found. 361.0597. HPLC: OD-H column, 99:1 hexane:isopropanol, 1.00 mL/min, t_R = major: 12.85 min, minor: 9.0 min. 89% ee. $[\alpha]_D^{24}$ -100.7° (c 1.5, CH_2Cl_2).

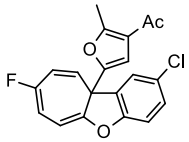


1-(5-(7-Bromo-10a*H*-cyclohepta[*b*]benzofuran-10a-yl)-2-methylfuran-3-yl)ethanone (2f) Yield: 97%, yellow oil, R_f = 0.3 (petroleum ether/AcOEt = 10:1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.49 (d, J = 7.6 Hz, 1H), 7.32 (td, J = 7.8, 1.3 Hz, 1H), 7.14 (td, J = 7.5, 1.0 Hz, 1H), 7.07 (d, J = 8.1 Hz, 1H), 6.71 (d, J = 6.9 Hz, 1H), 6.50 (s, 1H), 6.21 (dd, J = 9.6, 6.9 Hz, 1H), 6.15 (s, 1H), 5.61 (d, J = 9.6 Hz, 1H), 2.45 (s, 3H), 2.31 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 194.1, 158.5, 155.8, 152.5, 147.9, 130.9, 129.4, 127.7, 126.4, 124.1, 123.6, 121.4, 121.2, 121.0, 110.5, 107.3, 106.0, 52.1, 29.1, 14.5. IR (KBr, cm^{-1}) 3031, 2928, 1710, 1579, 1480, 1446, 1332, 1237, 1145, 1022, 956, 848, 754. HRMS (ESI) ($[M+Na]^+$) Calcd. for $[C_{20}H_{15}BrNaO_3]^+$: 405.0097, Found. 405.0093. HPLC: OD-H column, 99:1 hexane:isopropanol, 1.00 mL/min, t_R = major: 12.7 min, minor: 9.3 min. 90% ee. $[\alpha]_D^{24}$ -91.5° (c 1.2, CH_2Cl_2).

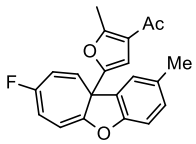


1-(5-(2,8-Difluoro-10a*H*-cyclohepta[*b*]benzofuran-10a-yl)-2-methylfuran-3-yl)ethanone (2g) Yield: 99%, yellow oil, R_f = 0.3 (petroleum ether/AcOEt = 10:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.13 (d, J = 7.5 Hz, 1H), 7.05 – 6.93 (m, 2H), 6.44 – 6.37 (m, 1H), 6.24 – 6.11 (m, 3H), 5.64 (dd, J = 10.3,

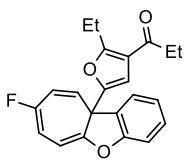
4.6 Hz, 1H), 2.44 (s, 3H), 2.29 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -105.1, -119.6. ^{13}C NMR (101 MHz, $CDCl_3$) δ 193.6, 158.9 (d, J = 241.6 Hz), 158.6, 157.7 (d, J = 238.9 Hz), 152.1 (d, J = 1.5 Hz), 149.5 (d, J = 3.4 Hz), 147.9, 132.1 (d, J = 8.4 Hz), 121.9, 121.6 (d, J = 9.8 Hz), 121.1 (d, J = 13.1 Hz), 116.1 (d, J = 24.7 Hz), 111.2 (d, J = 25.4 Hz), 110.9 (d, J = 8.5 Hz), 107.62 (d, J = 30.0 Hz), 107.6, 97.7 (d, J = 11.5 Hz), 52.0, 28.9, 14.4. IR (KBr, cm^{-1}) 2975, 2930, 1710, 1481, 1372, 1303, 1235, 1159, 952, 818. HRMS (ESI) ($[M+Na]^+$) Calcd. for $[C_{20}H_{14}F_2NaO_3]^+$: 363.0803, Found. 363.0803. HPLC: OD-H column, 99:1 hexane:isopropanol, 1.00 mL/min, t_R = major: 12.3 min, minor: 10.5 min. 97% ee. $[\alpha]_D^{24}$ -114.9° (c 0.8, CH_2Cl_2).



1-(5-(2-Chloro-8-fluoro-10a*H*-cyclohepta[*b*]benzofuran-10a-yl)-2-methylfuran-3-yl)ethanone (2h) Yield: 92%, yellow oil, R_f = 0.3 (petroleum ether/AcOEt = 10:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (s, 1H), 7.27 (d, J = 8.3 Hz, 1H), 6.97 (d, J = 8.6 Hz, 1H), 6.44 – 6.37 (m, 1H), 6.24 – 6.11 (m, 3H), 5.65 (dd, J = 10.4, 5.1 Hz, 1H), 2.44 (s, 3H), 2.29 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -104.7. ^{13}C NMR (126 MHz, $CDCl_3$) δ 193.8, 158.8, 157.8 (d, J = 239.0 Hz), 154.7, 149.1 (d, J = 3.3 Hz), 147.8, 132.5, 129.5, 128.1, 124.3, 122.0, 121.6 (d, J = 12.0 Hz), 121.2 (d, J = 12.8 Hz), 111.4, 107.64, 107.6 (d, J = 30.0 Hz), 97.9 (d, J = 11.5 Hz), 51.7, 29.1, 14.6. IR (KBr, cm^{-1}) 2973, 2933, 2887, 1466, 1376, 1306, 1160, 1130, 952, 817. HRMS (ESI) ($[M+Na]^+$) Calcd. for $[C_{20}H_{14}ClFNaO_3]^+$: 379.0508, Found. 379.0512. HPLC: OD-H column, 99:1 hexane:isopropanol, 1.00 mL/min, t_R = major: 10.7 min, minor: 9.8 min. 96% ee. $[\alpha]_D^{24}$ -125.2° (c 0.5, CH_2Cl_2).

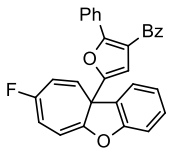


1-(5-(8-Fluoro-2-methyl-10a*H*-cyclohepta[*b*]benzofuran-10a-yl)-2-methylfuran-3-yl)ethanone (2i) Yield: 99%, yellow oil, R_f = 0.3 (petroleum ether/AcOEt = 10:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21 (s, 1H), 7.10 (d, J = 8.4 Hz, 1H), 6.93 (d, J = 8.1 Hz, 1H), 6.39 (t, J = 9.6 Hz, 1H), 6.23 – 6.11 (m, 3H), 5.66 (dd, J = 10.7, 4.5 Hz, 1H), 2.43 (s, 3H), 2.35 (s, 3H), 2.30 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -105.7. ^{13}C NMR (101 MHz, $CDCl_3$) δ 194.0, 158.5, 157.7 (d, J = 238.0 Hz), 154.1, 149.7 (d, J = 3.8 Hz), 148.7, 132.8, 130.8, 129.9, 124.3, 121.8 (d, J = 12.6 Hz), 121.6 (d, J = 8.5 Hz), 121.3, 109.9, 107.6 (d, J = 29.7 Hz), 107.2, 97.2 (d, J = 11.6 Hz), 51.7, 29.1, 21.0, 14.6. IR (KBr, cm^{-1}) 2972, 2933, 2886, 1768, 1704, 1465, 1377, 1306, 1160, 1129, 951, 817. HRMS (ESI) ($[M+Na]^+$) Calcd. for $[C_{21}H_{17}FNaO_3]^+$: 359.1054, Found. 359.1060. HPLC: OD-H column, 99:1 hexane:isopropanol, 1.00 mL/min, t_R = major: 9.3 min, minor: 8.8 min. 97% ee. $[\alpha]_D^{24}$ -127.2° (c 1.0, CH_2Cl_2).

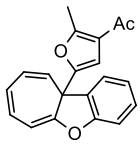


1-(2-Ethyl-5-(8-fluoro-10a*H*-cyclohepta[*b*]benzofuran-10a-yl)furan-3-yl)propan-1-one (2j) Yield: 95%, yellow oil, R_f = 0.3 (petroleum ether/AcOEt = 10:1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.46 (dd, J = 7.5, 1.2 Hz, 1H), 7.31 (td, J = 7.8, 1.3 Hz, 1H), 7.11 (t, J = 7.5 Hz, 1H), 7.05 (d, J = 8.1 Hz, 1H), 6.43 – 6.34 (m, 1H), 6.23 – 6.15 (m, 2H), 6.13 (s, 1H), 5.70 (dd, J = 10.3, 4.6 Hz, 1H), 2.86 (ddq, J = 30.1,

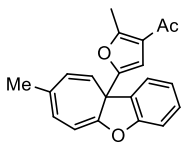
15.1, 7.5 Hz, 2H), 2.67 – 2.56 (m, 2H), 1.09 (dt, J = 11.8, 7.4 Hz, 6H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -105.3. ^{13}C NMR (126 MHz, $CDCl_3$) δ 196.9, 163.3, 157.8 (d, J = 238.1 Hz), 156.1, 149.2 (d, J = 3.3 Hz), 148.4, 130.9, 129.4, 124.0, 123.2, 122.2 (d, J = 12.9 Hz), 121.4 (d, J = 36.1 Hz), 119.9, 110.3, 107.5 (d, J = 30.0 Hz), 106.8, 97.4 (d, J = 11.6 Hz), 51.6, 34.3, 21.7, 11.8, 7.7. IR (KBr, cm^{-1}) 2975, 2888, 1706, 1552, 1464, 1376, 1305, 1242, 1159, 1130, 951, 817, 756. HRMS (ESI) ($[M+Na]^+$) Calcd. for $[C_{22}H_{19}FNaO_3]^+$: 373.1210, Found. 373.1205. HPLC: OD-H column, 99:1 hexane:isopropanol, 1.00 mL/min, t_R = major: 7.2 min, minor: 6.6 min. 90% ee. $[\alpha]_D^{24}$ -88.7° (c 0.8, CH_2Cl_2).



(5-(8-Fluoro-10a*H*-cyclohepta[*b*]benzofuran-10a-yl)-2-phenylfuran-3-yl)(phenyl)methanone (2k) Yield: 98%, yellow oil, R_f = 0.3 (petroleum ether/AcOEt = 10:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, J = 7.7 Hz, 2H), 7.60 – 7.52 (m, 3H), 7.48 (t, J = 7.4 Hz, 1H), 7.39 – 7.30 (m, 3H), 7.26 – 7.21 (m, 3H), 7.13 (t, J = 7.5 Hz, 1H), 7.06 (d, J = 8.1 Hz, 1H), 6.41 (t, J = 9.5 Hz, 1H), 6.29 – 6.19 (m, 3H), 5.75 (dd, J = 10.4, 4.6 Hz, 1H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -105.1. ^{13}C NMR (126 MHz, $CDCl_3$) δ 191.4, 157.9 (d, J = 238.4 Hz), 156.2, 155.8, 149.5, 149.3 (d, J = 3.3 Hz), 137.9, 132.9, 130.6, 129.7, 129.6, 129.5, 129.0, 128.3, 128.2, 127.3, 124.2, 123.3, 122.1 (d, J = 12.9 Hz), 121.6 (d, J = 36.0 Hz), 120.8, 111.0, 110.4, 107.8 (d, J = 29.9 Hz), 97.6 (d, J = 11.6 Hz), 51.8. IR (KBr, cm^{-1}) 2923, 1712, 1543, 1486, 1452, 1268, 1158, 1136, 978, 838, 758. HRMS (ESI) ($[M+Na]^+$) Calcd. for $[C_{30}H_{19}FNaO_3]^+$: 469.1210, Found. 469.1204. HPLC: OD-H column, 99:1 hexane:isopropanol, 1.00 mL/min, t_R = major: 11.8 min, minor: 8.4 min. 62% ee. $[\alpha]_D^{24}$ -57.1° (c 1.1, CH_2Cl_2).



1-(5-(10a*H*-cyclohepta[*b*]benzofuran-10a-yl)-2-methylfuran-3-yl)ethanone (2l) Yield: 91%, yellow oil, R_f = 0.3 (petroleum ether/AcOEt = 10:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (d, J = 7.5 Hz, 1H), 7.30 (t, J = 7.9 Hz, 1H), 7.14 – 7.03 (m, 2H), 6.47 – 6.30 (m, 4H), 6.10 (s, 1H), 5.54 (d, J = 9.6 Hz, 1H), 2.41 (s, 3H), 2.28 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 194.1, 158.2, 156.1, 151.8, 148.8, 131.7, 129.1, 127.2, 126.3, 125.3, 124.0, 123.1, 121.5, 119.3, 110.2, 107.1, 101.2, 51.9, 29.0, 14.6. IR (KBr, cm^{-1}) 2978, 2885, 1711, 1576, 1482, 1373, 1244, 1160, 955, 818, 757. HRMS (ESI) ($[M+Na]^+$) Calcd. for $[C_{20}H_{16}NaO_3]^+$: 327.0992, Found. 327.0986. HPLC: OD-H column, 99:1 hexane:isopropanol, 1.00 mL/min, t_R = major: 12.3 min, minor: 11.8 min. 94% ee. $[\alpha]_D^{24}$ -64.5° (c 0.67, CH_2Cl_2).



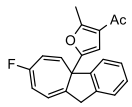
1-(2-Methyl-5-(8-methyl-10a*H*-cyclohepta[*b*]benzofuran-10a-yl)furan-3-yl)ethanone (2m) Yield: 89%, yellow oil, R_f = 0.3 (petroleum ether/AcOEt = 10:1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38 (d, J = 7.5 Hz, 1H), 7.29 (t, J = 7.8 Hz, 1H), 7.11 – 7.02 (m, 2H), 6.22 (d, J = 9.9 Hz, 1H), 6.20 – 6.14 (m, 2H), 6.10 (s, 1H), 5.51 (d, J = 9.8 Hz, 1H), 2.40 (s, 3H), 2.29 (s, 3H), 2.01 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 194.1, 158.2, 156.3, 150.9, 149.6, 134.0, 131.6, 130.3, 129.1, 124.0, 123.1, 122.9, 121.5, 119.2, 110.1, 106.8, 100.5, 51.3, 29.0, 24.2, 14.5. IR (KBr, cm^{-1}) 2975, 2934, 2888, 1710, 1467, 1376, 1247, 1160, 952, 817, 755. HRMS (ESI) ($[M+Na]^+$) Calcd. for

$[C_{21}H_{18}NaO_3]^+$: 341.1148, Found. 341.1144. HPLC: OD-H column, 99:1 hexane:isopropanol, 1.00 mL/min, t_R = major: 16.4 min, minor: 11.2 min. 75% ee. $[\alpha]_D^{24}$ -69.0° (c 1.2, CH_2Cl_2).

1-(2-Methyl-5-(8-methyl-10a*H*-cyclohepta[*b*]benzofuran-10a-yl)furan-3-yl)ethanone (2o) Yield: 94%, yellow oil, R_f = 0.3 (petroleum ether/AcOEt = 10:1). ^{1}H NMR (500 MHz, Chloroform-d) δ 7.38 (dd, J = 7.6, 1.3 Hz, 1H), 7.34 (td, J = 7.9, 1.4 Hz, 1H), 7.18 (d, J = 8.1 Hz, 1H), 7.14 (td, J = 7.5, 1.0 Hz, 1H), 6.53 (dd, J = 11.6, 0.9 Hz, 1H), 6.42 (dd, J = 9.8, 6.3 Hz, 1H), 6.28 (dd, J = 11.6, 6.3 Hz, 1H), 6.13 (s, 1H), 5.61 (d, J = 9.7 Hz, 1H), 2.41 (s, 3H), 2.29 (s, 3H). ^{13}C NMR (126 MHz, Chloroform-d) δ 193.9, 158.5, 155.5, 148.6, 147.7, 131.8, 129.7, 129.4, 126.9, 125.7, 124.0, 123.8, 121.9, 121.6, 110.8, 107.6, 94.4, 51.8, 29.1, 14.6. HRMS (ESI) ($[M+H]^+$) Calcd. for $[C_{20}H_{16}BrO_3]^+$: 383.0277, Found. 383.0269. HPLC: OD-H column, 99:1 hexane:isopropanol, 1.00 mL/min, t_R = major: 13.0 min, minor: 17.99 min. 70% ee. $[\alpha]_D^{24}$ -61.0° (c 1.1, CH_2Cl_2).

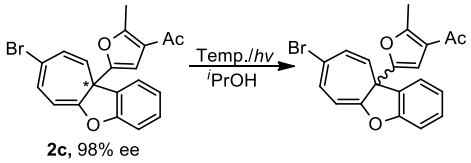
2-(8-Bromo-10aH-cyclohepta[b]benzofuran-10a-yl)-6,6-dimethyl-6,7-dihydrobenzofuran-4(5H)-one (2p) Yield: 85%, yellow oil, R_f = 0.3 (petroleum ether/AcOEt = 10:1). ^{1}H NMR (500 MHz, Chloroform-d) δ 7.42 (d, J = 7.6 Hz, 1H), 7.35 (t, J = 7.9 Hz, 1H), 7.15 (t, J = 7.6 Hz, 1H), 7.10 (d, J = 8.1 Hz, 1H), 6.80 (d, J = 7.5 Hz, 1H), 6.53 (d, J = 10.0 Hz, 1H), 6.28 (s, 1H), 6.19 (d, J = 7.6 Hz, 1H), 5.48 (d, J = 9.9 Hz, 1H), 2.61 (s, 2H), 2.30 (s, 2H), 1.09 (s, 3H), 1.06 (s, 3H). ^{13}C NMR (126 MHz, Chloroform-d) δ 193.8, 166.4, 156.1, 152.9, 151.2, 130.7, 130.7, 129.5, 128.7, 124.0, 123.5, 120.6, 120.0, 118.4, 110.4, 103.4, 100.7, 51.94, 51.90, 37.3, 35.1, 28.8, 28.3. HRMS (ESI) ($[M+Na]^+$) Calcd. for $[C_{23}H_{19}BrNaO_3]^+$: 445.0410, Found. 445.0401. HPLC: MD(2) column, 98:2 hexane:isopropanol, 0.80 mL/min, t_R = major: 18.2 min, minor: 17.4 min. 92% ee.

1-(2-Methyl-5-(5-methyl-5,10a-dihydrocyclohepta[*b*]indol-10a-yl)furan-3-yl)ethanone (2q) Yield: 25% (81% yield catalyzed by $Rh_2(TFA)_4$ and no C-H insertion product was detected), yellow oil, R_f = 0.3 (petroleum ether/AcOEt = 10:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (d, J = 7.4 Hz, 1H), 7.30 – 7.23 (m, 1H), 6.94 (t, J = 7.5 Hz, 1H), 6.74 (d, J = 7.9 Hz, 1H), 6.54 (dd, J = 11.0, 7.3 Hz, 1H), 6.36 (dd, J = 9.8, 6.5 Hz, 1H), 6.09 (dd, J = 11.0, 6.5 Hz, 1H), 6.03 (s, 1H), 5.75 (d, J = 7.4 Hz, 1H), 5.49 (d, J = 9.7 Hz, 1H), 3.26 (s, 3H), 2.41 (s, 3H), 2.26 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 194.2, 157.7, 149.7, 145.5, 143.6, 133.7, 128.6, 128.5, 126.7, 123.8, 121.4, 120.3, 120.2, 113.4, 107.0, 106.8, 95.2, 52.7, 30.3, 29.0, 14.6. IR (KBr, cm^{-1}) 3032, 2974, 2887, 1708, 1483, 1377, 1245, 1160, 1130, 951, 817, 756. HRMS (ESI) ($[M+Na]^+$) Calcd. for $[C_{21}H_{19}NNaO_2]^+$: 340.1308, Found. 340.1308. HPLC: OD-H column, 99:1 hexane:isopropanol, 1.00 mL/min, t_R = major: 19.5 min, minor: 30.0 min. 76% ee. $[\alpha]_D^{24}$ -44.8° (c 0.5, CH_2Cl_2).



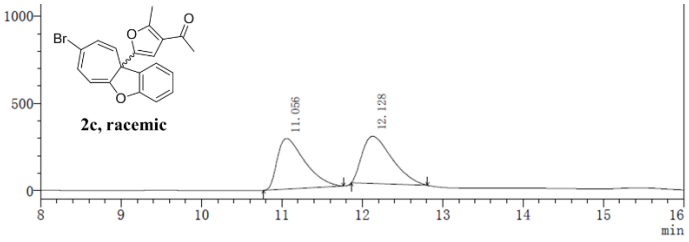
1-(5-(7-Fluorobenzo[a]azulen-4b(10H)-yl)-2-methylfuran-3-yl)ethan-1-one (2r) Yield: 60%, yellow oil, R_f = 0.4 (petroleum ether/AcOEt = 5:1). ^{1}H NMR (500 MHz, Chloroform-d) δ 7.45 – 7.39 (m, 1H), 7.35 – 7.30 (m, 3H), 6.46 – 6.42 (m, 1H), 6.35 (ddd, J = 10.3, 8.2, 2.0 Hz, 1H), 6.24 (ddd, J = 17.2, 7.4, 1.9 Hz, 1H), 6.18 (s, 1H), 5.66 (dd, J = 10.4, 5.1 Hz, 1H), 4.24 (d, J = 21.9 Hz, 1H), 3.99 (d, J = 21.9 Hz, 1H), 2.44 (s, 3H), 2.34 (s, 3H). ^{19}F NMR (471 MHz, Chloroform-d) δ -102.88. ^{13}C NMR (126 MHz, Chloroform-d) δ 194.31, 160.50 (d, J_{C-F} = 242.8 Hz), 157.9, 151.8, 147.0, 140.0, 137.8 (d, J_{C-F} = 3.3 Hz), 129.5 (d, J_{C-F} = 13.4 Hz), 127.8 (d, J_{C-F} = 21.9 Hz), 124.6, 124.3, 121.5, 121.0, 120.7, 117.5 (d, J_{C-F} = 11.4 Hz), 110.1 (d, J_{C-F} = 26.9 Hz), 106.6, 55.5, 38.6, 29.0, 14.6. HRMS (ESI) ($[M+H]^+$) Calcd. for $[C_{21}H_{18}FO_2]^+$: 321.1285, Found. 321.1287. HPLC: MD(2) column, 99:1 hexane:isopropanol, 1.00 mL/min, t_R = major: 10.8 min, minor: 10.0 min. 82% ee.

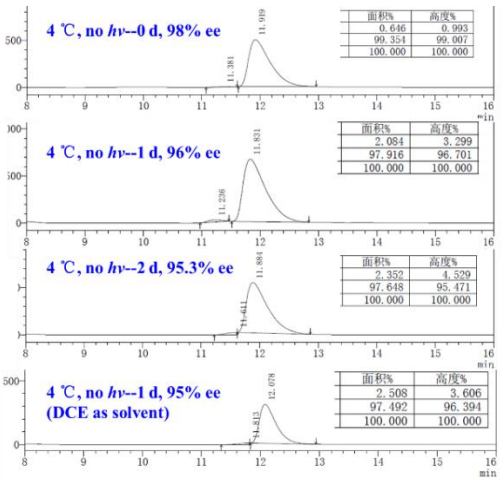
6. Table S3. racemization control experiments of 2c

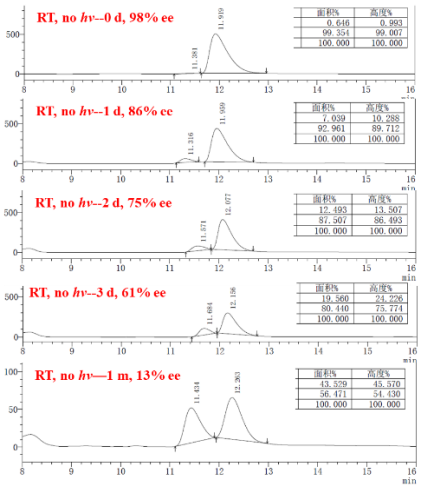


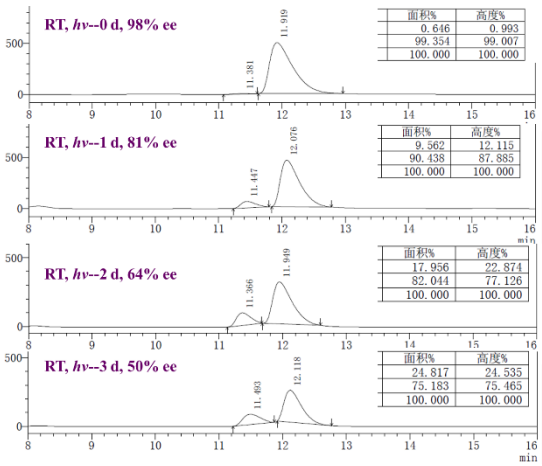
2c, 98% ee

Time	ee			
	4 °C, no *hv*	4 °C, no *hv* (DCE)	RT, no *hv*	RT, *hv*
0d	98%	98%	98%	98%
1d	96%	96%	86%	81%
2d	95.3%	95%	75%	64%
3d	94%	93.5%	61%	50%
1m	-	-	13%	-

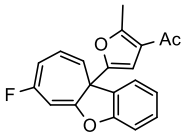




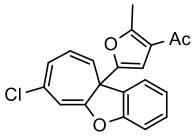




7. Table S4: the racemization of 7-substutited products with room temperature and dark condition.

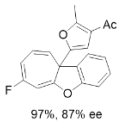


2d

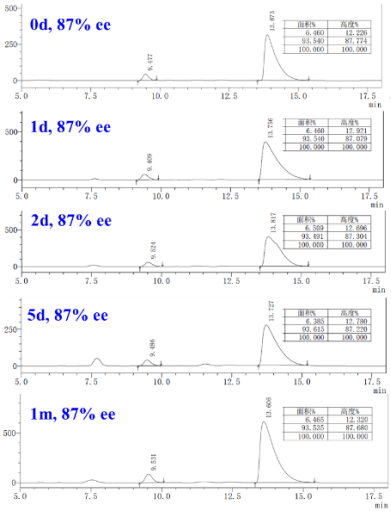


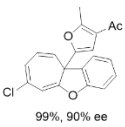
2e

Time	**2d**	**2e**
0 d	87% ee	88% ee
1 d	87% ee	88% ee
2 d	87% ee	88% ee
5 d	87% ee	88% ee
1 month	87% ee[a]	88% ee[a]

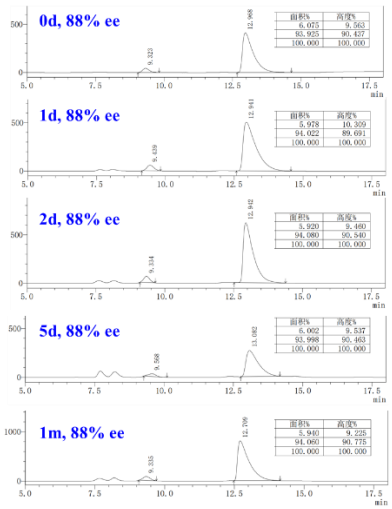


97%, 87% ee

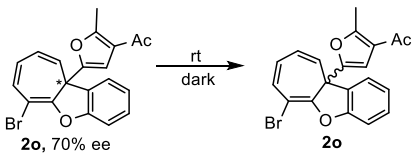




99%, 90% ee



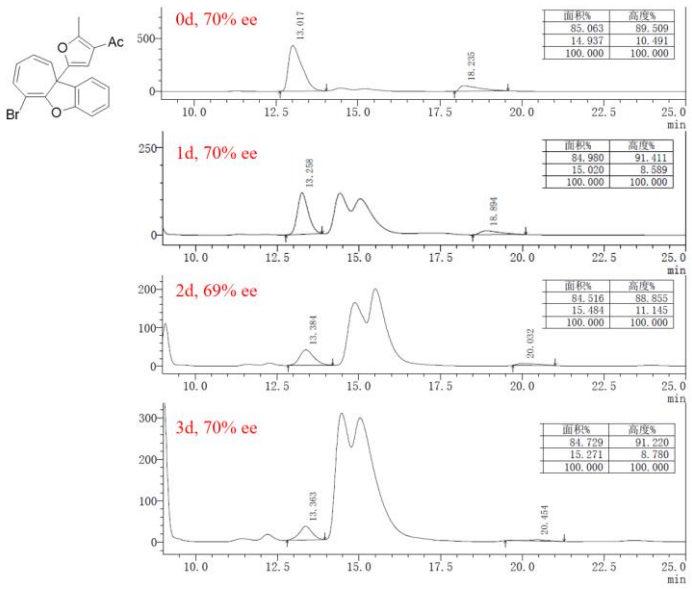
8. Scheme S3. the racemization of product 2o with room temperature and dark condition.



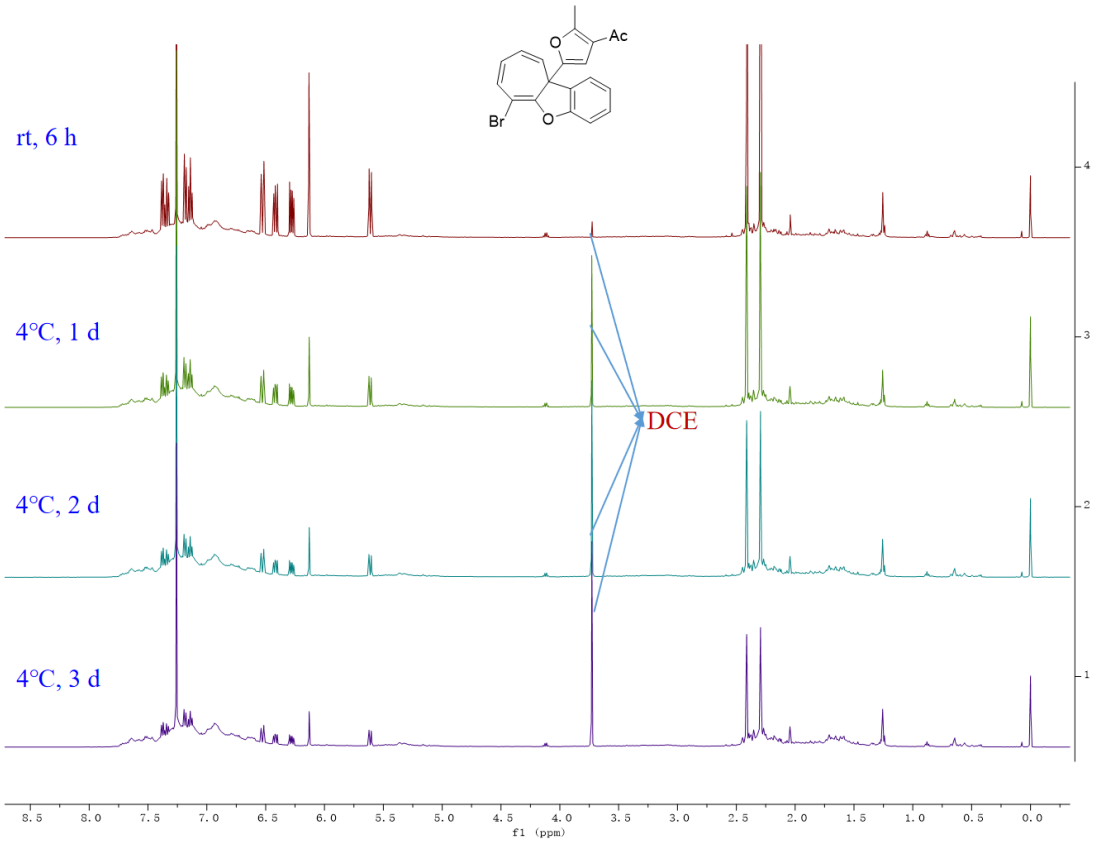
2o, 70% ee

2o

Just prepared: 70% ee
one day: 70% ee
two days: 69% ee
three days: 70% ee

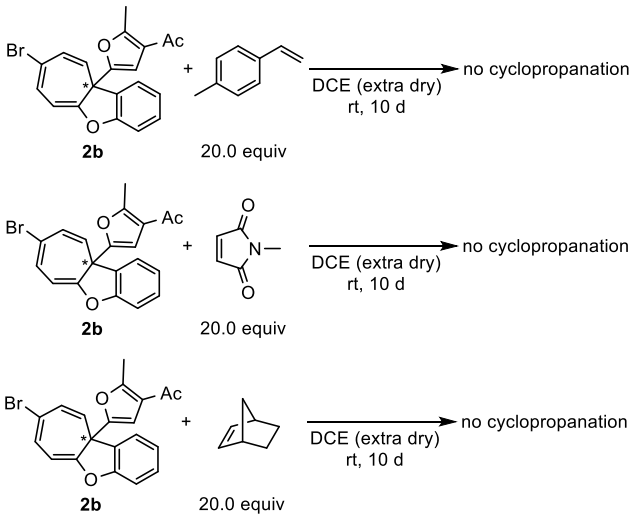


9. Scheme S4. the decomposition of product 2o was monitored by ^{1}H NMR spectrum.



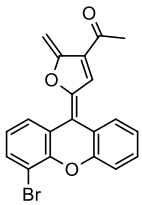
10. Trap of free carbene intermediate through cyclopropanation with 2c and alkenes.

In a solution of extra dry DCM (2 mL), Büchner product **2c** (0.2 mmol) was dissolved and then the excess alkenes were added. The reaction mixture was stirred at room temperature for 10 days. The reaction was monitored by TLC and no cyclopropanation was detected.



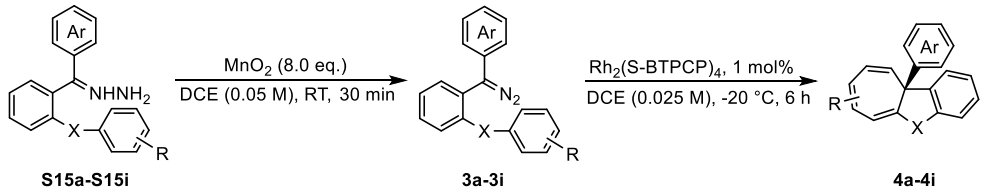
11. Trap of radical intermediate with 2o and TEMPO.

In a solution of extra dry DCM (2 mL), Büchner product **2o** (0.2 mmol) was dissolved and then the TEMPO (4.0 equiv, 0.8 mmol) were added. The reaction mixture was stirred at room temperature for 36 h. The reaction was monitored by TLC, after the substrate **2o** was completely transformed, the reaction mixture was filtered through short silica gel, and then the solvent was removed under reduced pressure. The crude product was purified by flash column chromatography (silica gel, petroleum ether/AcOEt = 10:1) to yield **9** (52%).



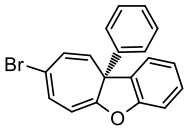
1-(5-(4-Bromo-9H-xanthen-9-ylidene)-2-methylene-2,5-dihydrofuran-3-yl)ethan-1-one (9) Yield: 52%, yellow oil, R_f = 0.25 (petroleum ether/AcOEt = 10:1). ^{1}H NMR (500 MHz, Chloroform-d) δ 7.75 (d, J = 8.0 Hz, 1H), 7.47 (t, J = 7.5 Hz, 1H), 7.35 (t, J = 7.8 Hz, 3H), 7.29 (t, J = 7.7 Hz, 1H), 7.13 (t, J = 7.5 Hz, 1H), 6.93 (d, J = 7.8 Hz, 1H), 5.24 (s, 1H), 4.70 (s, 1H), 2.65 (s, 3H). ^{13}C NMR (126 MHz, Chloroform-d) δ 190.3, 157.0, 154.7, 149.6, 145.7, 133.4, 132.0, 131.8, 130.6, 127.9, 127.8, 125.4, 125.4, 124.4, 122.2, 116.6, 111.9, 106.5, 87.1, 30.9. IR (KBr, cm^{-1}) 2971, 1709, 1481, 1376, 1242, 1158, 1132, 950, 815, 754. HRMS (ESI) ([M+H]$^+$) Calcd. for $[C_{20}H_{14}BrO_3]^+$: 381.0121, Found. 381.0126.

12. General procedure for Büchner reaction with donor-donor diazo compounds as carbene precursors.

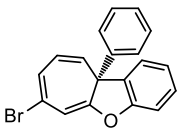


S15a-S15i **3a-3i** **4a-4i**

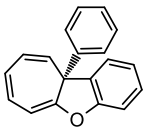
To a 25 mL oven-dried flask containing a magnetic stirring bar hydrazones **S15a**-**S15i** (0.2 mmol) in dry DCE (4.0 ml), was added MnO_2 (141 mg, 8.0 eq) slowly, after consumption of the material in 30 minutes, the reaction mixture was filtered through alumina. The crude diazo compounds **3a**-**3i** were used for next step without purification. To a solution in dry DCE (4 mL, 0.05 M) at -20 °C, Rh_2(S-BTPCP)$_4$ (0.01 eq. the catalyst was dissolved in DCE) were added. Then the diazo compounds **3a**-**3i** in dry DCE (4 ml, 0.05 M) was added slowly for 1 hour under -20 °C. The reaction mixture was then stirred for 6 hours at -20 °C. After the reaction was completed, the reaction mixture was filtered through short silica gel, and then the solvent was removed under reduced pressure. The crude aromatic substitution product was purified by flash column chromatography (silica gel, petroleum ether/AcOEt = 50:1) to yield **4a** – **4i**.



8-Bromo-10a-phenyl-10a*H*-cyclohepta[*b*]benzofuran (4a) Yield: 89%, R_f = 0.5 (petroleum ether/AcOEt = 50:1). ^{1}H NMR (500 MHz, Chloroform-d) δ 7.30 – 7.26 (m, 1H), 7.24 (dd, J = 7.6, 1.3 Hz, 1H), 7.21 – 7.14 (m, 5H), 7.11 (d, J = 8.1 Hz, 1H), 7.07 (td, J = 7.5, 1.0 Hz, 1H), 6.70 (d, J = 7.4 Hz, 1H), 6.62 (d, J = 9.9 Hz, 1H), 6.22 (d, J = 7.4 Hz, 1H), 5.66 (d, J = 10.0 Hz, 1H). ^{13}C NMR (126 MHz, Chloroform-d) δ 157.2, 155.5, 141.0, 134.8, 129.9, 128.9, 128.7, 127.9, 127.1, 125.8, 124.0, 123.5, 123.3, 118.5, 110.2, 99.7, 56.4. IR (KBr, cm^{-1}) 2973, 2889, 1465, 1378, 1154, 952, 815, 704. HRMS (ESI) ([M+H]$^+$) Calcd. for [$C_{19}H_{14}BrO$]$^+$: 337.0223, Found. 337.0222. HPLC: OD-H column, 99:1 hexane:isopropanol, 1.00 mL/min, t_R = major: 5.6 min, minor: 6.3 min. 99.3% ee. $[\alpha]_D^{23}$ -77.3° (c 0.9, CH_2Cl_2).

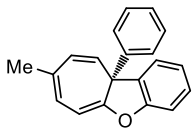


7-Bromo-10a-phenyl-10a*H*-cyclohepta[*b*]benzofuran (4b) Yield: 96%, R_f = 0.5 (petroleum ether/AcOEt = 50:1). ^{1}H NMR (500 MHz, Chloroform-d) δ 7.33 – 7.25 (m, 4H), 7.24 – 7.15 (m, 3H), 7.13 – 7.06 (m, 2H), 6.63 (dd, J = 6.7, 1.2 Hz, 1H), 6.59 (s, 1H), 6.31 (dd, J = 9.6, 6.7 Hz, 1H), 5.83 (d, J = 9.6 Hz, 1H). ^{13}C NMR (126 MHz, Chloroform-d) δ 156.3, 155.3, 141.1, 134.7, 128.7, 128.0, 127.1, 126.0, 125.7, 123.9, 123.7, 123.6, 121.4, 110.3, 105.2, 56.8. IR (KBr, cm^{-1}) 2973, 2888, 1465, 1379, 1307, 1156, 952, 880, 817. HRMS (ESI) ([M+H]$^+$) Calcd. for [$C_{19}H_{14}BrO$]$^+$: 337.0223, Found. 337.0222. HPLC: OD-H column, 99:1 hexane:isopropanol, 1.00 mL/min, t_R = major: 5.6 min, minor: 6.1 min. 98% ee. $[\alpha]_D^{23}$ -70.1° (c 0.8, CH_2Cl_2).

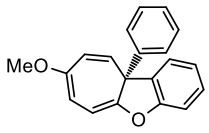


10a-Phenyl-10a*H*-cyclohepta[*b*]benzofuran (4c) Yield: 95%, R_f = 0.5 (petroleum ether/AcOEt = 50:1). ^{1}H NMR (500 MHz, Chloroform-d) δ 7.31 – 7.25 (m, 4H), 7.20 – 7.09 (m, 4H), 7.06 (t, J = 7.5 Hz, 1H), 6.51 (dd, J = 9.7, 6.2 Hz, 1H), 6.43 (d, J = 6.8 Hz, 1H), 6.37 (dd, J = 10.9, 6.8 Hz, 1H), 6.29 (dd, J = 10.9, 6.2 Hz, 1H), 5.78 (d, J = 9.7 Hz, 1H). ^{13}C NMR (126 MHz, Chloroform-d) δ 155.6, 155.5, 141.9, 135.5, 128.4, 127.6, 126.7, 126.6, 126.5, 126.0, 125.5, 124.0, 123.1, 122.1, 110.1, 100.4, 56.4. IR (KBr, cm^{-1}) 2975, 2890, 1465, 1379, 1249,

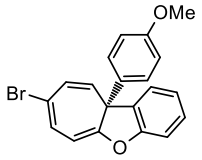
1153, 953, 818, 690. HRMS (ESI) ([M+H]$^+$) Calcd. for $[C_{19}H_{15}O]^+$: 259.1117, Found. 259.1118. HPLC: OD-H column, 99:1 hexane:isopropanol, 1.00 mL/min, t_R = major: 5.6 min, minor: 6.2 min. 99% ee. $[\alpha]_D^{23}$ -88.5° (c 1.0, CH_2Cl_2).



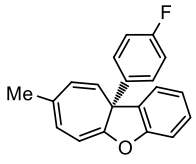
8-Methyl-10a-phenyl-10a*H*-cyclohepta[*b*]benzofuran (4d) Yield: 97%, R_f = 0.5 (petroleum ether/AcOEt = 50:1). ^{1}H NMR (500 MHz, Chloroform-d) δ 7.22 – 7.16 (m, 4H), 7.12 – 7.01 (m, 4H), 6.97 (t, J = 7.5 Hz, 1H), 6.27 (d, J = 9.9 Hz, 1H), 6.20 (d, J = 7.0 Hz, 1H), 6.04 (d, J = 7.0 Hz, 1H), 5.68 (d, J = 9.9 Hz, 1H), 1.87 (s, 3H). ^{13}C NMR (126 MHz, Chloroform-d) δ 155.8, 154.9, 142.5, 135.6, 134.2, 129.7, 128.3, 127.6, 126.6, 125.9, 124.0, 123.4, 122.9, 121.9, 110.0, 99.8, 55.9, 24.0. IR (KBr, cm^{-1}) 2975, 2889, 1466, 1377, 1309, 1157, 953, 818, 690. HRMS (ESI) ([M+H]$^+$) Calcd. for $[C_{20}H_{17}O]^+$: 273.1274, Found. 273.1275. HPLC: OD-H column, 99:1 hexane:isopropanol, 1.00 mL/min, t_R = major: 4.7 min, minor: 7.1 min. 96% ee. $[\alpha]_D^{23}$ -67.1° (c 0.8, CH_2Cl_2).



8-Methoxy-10a-phenyl-10a*H*-cyclohepta[*b*]benzofuran (4e) Yield: 91%, R_f = 0.5 (petroleum ether/AcOEt = 50:1). ^{1}H NMR (500 MHz, Chloroform-d) δ 7.26 – 7.22 (m, 4H), 7.19 – 7.14 (m, 2H), 7.14 – 7.10 (m, 1H), 7.07 – 6.99 (m, 2H), 6.36 (dd, J = 10.3, 1.8 Hz, 1H), 6.24 (d, J = 7.6 Hz, 1H), 5.92 (d, J = 10.3 Hz, 1H), 5.57 (dd, J = 7.7, 1.7 Hz, 1H), 3.48 (s, 3H). ^{13}C NMR (126 MHz, Chloroform-d) δ 155.8, 155.7, 152.5, 142.3, 135.2, 128.4, 127.7, 126.7, 125.9, 125.3, 124.1, 124.0, 122.8, 109.9, 100.9, 97.9, 55.5, 55.2. IR (KBr, cm^{-1}) 2976, 2888, 1465, 1379, 1154, 952, 819, 692. HRMS (ESI) ([M+H]$^+$) Calcd. for $[C_{20}H_{17}O_2]^+$: 289.1223, Found. 289.1224. HPLC: OD-H column, 99:1 hexane:isopropanol, 1.00 mL/min, t_R = major: 6.6 min, minor: 7.7 min. 96% ee. $[\alpha]_D^{23}$ -73.6° (c 1.0, CH_2Cl_2).

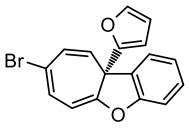


8-Bromo-10a-(4-methoxyphenyl)-10a*H*-cyclohepta[*b*]benzofuran (4f) Yield: 84%, R_f = 0.5 (petroleum ether/AcOEt = 50:1). ^{1}H NMR (500 MHz, Chloroform-d) δ 7.24 – 7.21 (m, 1H), 7.18 (dd, J = 7.5, 1.3 Hz, 1H), 7.08 – 7.00 (m, 4H), 6.70 – 6.63 (m, 3H), 6.56 (d, J = 10.0 Hz, 1H), 6.15 (d, J = 7.4 Hz, 1H), 5.59 (d, J = 10.0 Hz, 1H), 3.70 (s, 3H). ^{13}C NMR (126 MHz, Chloroform-d) δ 158.5, 157.4, 155.4, 135.0, 132.9, 129.9, 128.8, 128.6, 126.9, 123.9, 123.5, 123.4, 118.4, 113.3, 110.2, 99.6, 55.8, 55.1. IR (KBr, cm^{-1}) 2974, 2889, 1465, 1380, 1308, 1155, 952, 817, 646. HRMS (ESI) ([M+H]$^+$) Calcd. for $[C_{20}H_{16}BrO_2]^+$: 367.0328, Found. 367.0329. HPLC: OD-H column, 99:1 hexane:isopropanol, 1.00 mL/min, t_R = major: 7.8 min, minor: 8.8 min. 99.2% ee. $[\alpha]_D^{23}$ -89.4° (c 0.8, CH_2Cl_2).

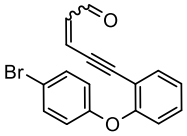


10a-(4-Fluorophenyl)-8-methyl-10a*H*-cyclohepta[*b*]benzofuran (4g) Yield: 99%, R_f = 0.5 (petroleum ether/AcOEt = 50:1). ^{1}H NMR (500 MHz, Chloroform-d) δ 7.26 – 7.18 (m, 1H), 7.22 – 7.09 (m, 3H), 7.06 – 6.96 (m, 2H), 6.79 (td, J = 8.7, 2.1 Hz, 2H), 6.27 (dd, J = 9.9, 1.8 Hz, 1H), 6.20 (dd, J = 7.0, 1.9 Hz, 1H), 6.06 (d, J = 7.1 Hz, 1H), 5.66 (dd, J = 9.9, 1.9 Hz, 1H), 1.89 (s, 3H). ^{19}F

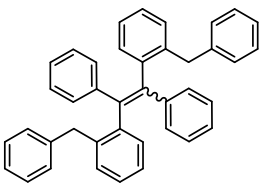
NMR (471 MHz, Chloroform-d) δ -116.4. ^{13}C NMR (126 MHz, Chloroform-d) δ 161.4 (d, J = 244.6 Hz), 155.7, 154.8, 138.1 (d, J = 3.2 Hz), 135.3, 134.2, 129.8, 128.5, 127.4 (d, J = 8.1 Hz), 123.9, 123.4, 123.0, 121.7, 114.4 (d, J = 21.4 Hz), 110.0, 99.8, 55.2, 24.0. IR (KBr, cm^{-1}) 2976, 2888, 1465, 1377, 1310, 1154, 953, 817. HRMS (ESI) ([M+H]$^+$) Calcd. for $[C_{20}H_{16}FO]^+$: 291.1180, Found. 291.1181. HPLC: OD-H column, 99:1 hexane:isopropanol, 1.00 mL/min, t_R = major: 4.7 min, minor: 6.3 min. 99.5% ee. $[\alpha]_D^{23}$ -88.1° (c 0.7, CH_2Cl_2)



8-Bromo-10a-(furan-2-yl)-10a*H*-cyclohepta[*b*]benzofuran (4h) Yield: 24%, R_f = 0.5 (petroleum ether/AcOEt = 50:1). ^{1}H NMR (500 MHz, Chloroform-d) δ 7.36 (dd, J = 7.6, 1.3 Hz, 1H), 7.30 (td, J = 7.8, 1.4 Hz, 1H), 7.18 (d, J = 1.6 Hz, 1H), 7.13 – 7.04 (m, 2H), 6.75 (d, J = 7.6 Hz, 1H), 6.51 (d, J = 10.1 Hz, 1H), 6.18 – 6.11 (m, 2H), 5.99 (dd, J = 3.4, 0.9 Hz, 1H), 5.48 (d, J = 10.0 Hz, 1H). ^{13}C NMR (126 MHz, Chloroform-d) δ 156.1, 153.8, 150.1, 142.6, 131.3, 130.3, 129.3, 128.5, 124.0, 123.4, 121.1, 118.4, 110.3, 109.7, 107.1, 100.2, 52.1. IR (KBr, cm^{-1}) 2976, 2888, 1464, 1378, 1249, 1153, 954. HRMS (ESI) ([M+H]$^+$) Calcd. for $[C_{17}H_{12}BrO_2]^+$: 327.0015, Found. 327.0016. HPLC: OD-H column, 99:1 hexane:isopropanol, 1.00 mL/min, t_R = major: 5.6 min, minor: 6.0 min. 22% ee. $[\alpha]_D^{23}$ -27.4° (c 0.5, CH_2Cl_2).

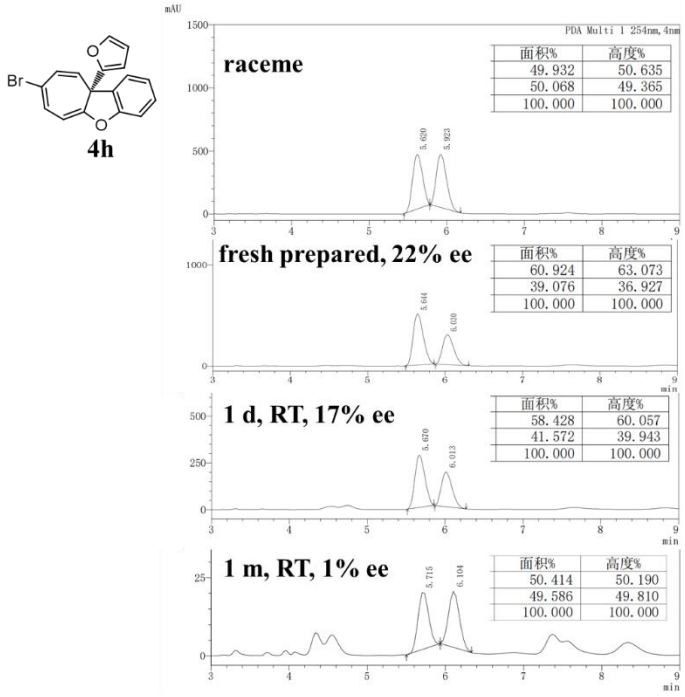


5-(2-(4-Bromophenoxy)phenyl)pent-2-en-4-ynal (4h') Yield: 55%, *Z*/*E* = 93:7. R_f = 0.5 (petroleum ether/AcOEt = 10:1). ^{1}H NMR (500 MHz, Chloroform-d) δ 10.05 (d, J = 8.3 Hz, 1H), 7.55 (dd, J = 7.7, 1.7 Hz, 1H), 7.48 – 7.42 (m, 2H), 7.37 (ddd, J = 8.9, 7.5, 1.7 Hz, 1H), 7.16 (td, J = 7.6, 1.1 Hz, 1H), 6.94 (dd, J = 8.4, 1.1 Hz, 1H), 6.91 – 6.84 (m, 2H), 6.78 (d, J = 10.8 Hz, 1H), 6.26 (dd, J = 10.8, 8.3 Hz, 1H). ^{13}C NMR (126 MHz, Chloroform-d) δ 192.1, 157.5, 156.1, 137.5, 134.0, 132.8, 131.4, 128.4, 124.0, 120.0, 119.1, 116.1, 114.4, 96.7, 88.8. IR (KBr, cm^{-1}) 3029, 1710, 1691, 1573, 1477, 1365, 1233, 1168, 1061, 953, 874, 761. HRMS (ESI) ([M+H]$^+$) Calcd. for $[C_{17}H_{12}BrO_2]^+$: 327.0015, Found. 327.0016.



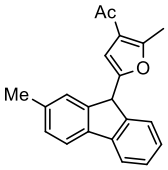
1,2-bis(2-benzylphenyl)-1,2-diphenylethene (4i') Yield: 87%, *E*/*Z* = 90:10. R_f = 0.7 (petroleum ether). ^{1}H NMR (500 MHz, Chloroform-d) δ 7.46 (dd, J = 5.4, 3.0 Hz, 5H), 7.39 – 7.34 (m, 5H), 7.07 (dd, J = 8.0, 6.4 Hz, 7H), 7.05 – 7.00 (m, 4H), 6.99 – 6.93 (m, 7H), 5.25 (s, 4H). ^{13}C NMR (126 MHz, Chloroform-d) δ 145.8, 138.9, 128.6, 128.1, 127.6, 126.1, 124.1 54.9. HRMS (ESI) ([M+H]$^+$) Calcd. for $[C_{40}H_{33}]^+$: 437.2264, Found. 437.2274.

13. The racemization of product 4i at room temperature.

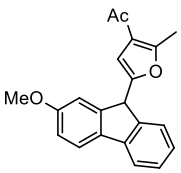


14. General procedure for aromatic substitution reaction.

Under nitrogen atmosphere, to a solution of enynones **5** (0.2 mmol) in dry DCM (0.1 M), Rh_2(S-BTPCP)$_4$ (0.01 eq. the catalyst was dissolved in DCM) were added. The reaction mixture was then stirred for 24 hours at room temperature. After the reaction was completed, the reaction mixture was filtered through short silica gel, and then the solvent was removed under reduced pressure. The crude aromatic substitution product was purified by flash column chromatography (silica gel, petroleum ether/AcOEt = 10:1) to yield **6a** – **6l**.

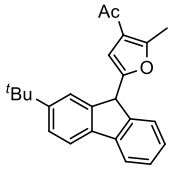


1-(2-Methyl-5-(2-methyl-9H-fluoren-9-yl)furan-3-yl)ethanone (6a) Yield: 95%, yellow oil, R_f = 0.3 (petroleum ether/AcOEt = 10:1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.75 (d, J = 7.6 Hz, 1H), 7.68 (d, J = 7.8 Hz, 1H), 7.56 – 7.53 (m, 1H), 7.43 – 7.37 (m, 2H), 7.30 (td, J = 7.5, 1.1 Hz, 1H), 7.24 (d, J = 7.9 Hz, 1H), 6.23 (s, 1H), 5.10 (s, 1H), 2.58 (s, 3H), 2.43 (s, 3H), 2.32 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 193.2, 157.2, 151.1, 142.9, 142.5, 140.0, 137.2, 136.4, 127.7, 126.8, 125.9, 124.8, 124.1, 121.0, 118.9, 118.8, 105.3, 45.9, 28.1, 20.7, 13.5. IR (KBr, cm^{-1}) 2976, 2931, 1716, 1561, 1448, 1373, 1232, 1134, 952, 863, 758. HRMS (ESI) ([M+H]$^+$) Calcd. for $[C_{21}H_{19}O_2]^+$: 303.1380, Found. 303.1382. HPLC: OD-H column, 99:1 hexane:isopropanol, 1.00 mL/min, t_R = major: 11.9 min, minor: 15.3 min. 97% ee. $[\alpha]_D^{24}$ -81.4° (c 1.17, CH_2Cl_2).

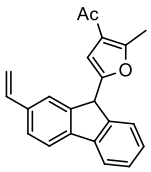


1-(5-(2-Methoxy-9H-fluoren-9-yl)-2-methylfuran-3-yl)ethanone (6b) Yield: 95%, yellow oil, R_f = 0.3 (petroleum ether/AcOEt = 10:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (dd, J = 7.9, 3.0 Hz, 2H), 7.44 (d, J = 7.5 Hz, 1H), 7.30 (t, J = 7.5 Hz, 1H), 7.20 – 7.13 (m, 1H), 7.07 – 7.00 (m, 1H), 6.88 (dd, J = 8.4, 2.3 Hz, 1H), 6.15 (s, 1H), 5.00 (s, 1H), 3.77 (s, 3H), 2.49 (s, 3H), 2.22 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 194.2, 159.7, 158.3, 152.0, 145.5, 143.2, 140.9, 133.9, 128.0, 126.3, 125.1, 122.1, 120.9, 119.4, 113.8, 111.1,

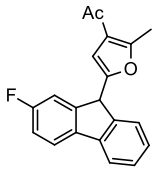
106.4, 55.6, 47.1, 29.1, 14.5. IR (KBr, cm^{-1}) 2973, 2932, 2888, 1711, 1672, 1564, 1463, 1376, 1305, 1160, 1130, 951, 817, 765. HRMS (ESI) ($[M+H]^+$) Calcd. for $[C_{21}H_{19}O_3]^+$: 319.1329, Found. 319.1331. HPLC: OD-H column, 99:1 hexane:isopropanol, 1.00 mL/min, t_R = major: 20.9 min, minor: 22.9 min. 95% ee. $[\alpha]_D^{24}$ -73.1° (c 0.67, CH_2Cl_2).



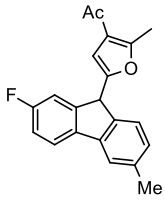
1-(5-(2-(*tert*-Butyl)-9H-fluoren-9-yl)-2-methylfuran-3-yl)ethanone (6c) Yield: 96%, yellow oil, R_f = 0.3 (petroleum ether/AcOEt = 10:1). ^1H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, J = 7.6 Hz, 1H), 7.70 (d, J = 8.0 Hz, 1H), 7.61 (s, 1H), 7.55 (d, J = 7.5 Hz, 1H), 7.46 (d, J = 8.0 Hz, 1H), 7.39 (t, J = 7.4 Hz, 1H), 7.29 (t, J = 7.5 Hz, 1H), 6.20 (s, 1H), 5.10 (s, 1H), 2.58 (s, 3H), 2.30 (s, 3H), 1.37 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 194.2, 158.2, 152.3, 150.9, 143.7, 143.6, 141.0, 138.3, 127.9, 126.9, 125.2, 125.1, 122.2, 122.1, 119.9, 119.7, 106.3, 47.1, 35.0, 31.6, 29.1, 14.5. IR (KBr, cm^{-1}) 2974, 2889, 1709, 1561, 1465, 1375, 1305, 1159, 1130, 951, 818, 743. HRMS (ESI) ($[M+H]^+$) Calcd. for $[C_{24}H_{25}O_2]^+$: 345.1849, Found. 345.1851. HPLC: OD-H column, 99:1 hexane:isopropanol, 1.00 mL/min, t_R = major: 7.46 min, minor: 6.95 min. 91% ee. $[\alpha]_D^{24}$ -52.7° (c 0.33, CH_2Cl_2).



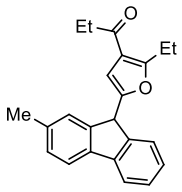
1-(2-Methyl-5-(2-vinyl-9H-fluoren-9-yl)furan-3-yl)ethanone (6d) Yield: 99%, yellow oil, R_f = 0.3 (petroleum ether/AcOEt = 10:1). ^1H NMR (400 MHz, $CDCl_3$) δ 7.73 (dd, J = 14.5, 7.7 Hz, 2H), 7.59 (s, 1H), 7.54 (d, J = 7.5 Hz, 1H), 7.45 (d, J = 7.9 Hz, 1H), 7.40 (t, J = 7.4 Hz, 1H), 7.31 (t, J = 7.4 Hz, 1H), 6.77 (dd, J = 17.6, 10.9 Hz, 1H), 6.23 (s, 1H), 5.77 (d, J = 17.6 Hz, 1H), 5.25 (d, J = 10.9 Hz, 1H), 5.11 (s, 1H), 2.56 (s, 3H), 2.29 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 194.1, 158.3, 151.8, 144.1, 144.0, 140.7, 140.7, 137.1, 136.9, 128.0, 127.4, 126.4, 125.3, 122.9, 122.1, 120.2, 120.2, 113.8, 106.5, 47.0, 29.1, 14.5. IR (KBr, cm^{-1}) 2973, 2933, 2887, 1708, 1571, 1465, 1417, 1377, 1306, 1160, 1130, 951, 817. HRMS (ESI) ($[M+Na]^+$) Calcd. for $[C_{22}H_{18}NaO_2]^+$: 337.1199, Found. 337.1192. HPLC: OD-H column, 99:1 hexane:isopropanol, 1.00 mL/min, t_R = major: 12.6 min, minor: 13.4 min. 98% ee. $[\alpha]_D^{24}$ -125.7° (c 1.5, CH_2Cl_2).



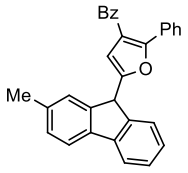
1-(5-(2-Fluoro-9H-fluoren-9-yl)-2-methylfuran-3-yl)ethanone (6e) Yield: 93%, yellow oil, R_f = 0.3 (petroleum ether/AcOEt = 10:1). ^1H NMR (500 MHz, $CDCl_3$) δ 7.75 – 7.70 (m, 2H), 7.55 (d, J = 7.6 Hz, 1H), 7.42 (t, J = 7.5 Hz, 1H), 7.34 – 7.26 (m, 2H), 7.12 (td, J = 8.8, 2.5 Hz, 1H), 6.24 (s, 1H), 5.11 (s, 1H), 2.58 (s, 3H), 2.32 (s, 3H). ^{19}F NMR (471 MHz, $CDCl_3$) δ -114.2. ^{13}C NMR (126 MHz, $CDCl_3$) δ 194.2, 162.6 (d, J = 246.0 Hz), 158.5, 151.2, 145.7 (d, J = 8.4 Hz), 143.4, 140.1, 136.9 (d, J = 2.4 Hz), 128.1, 127.1, 125.3, 122.1, 121.2 (d, J = 8.8 Hz), 119.9, 115.2 (d, J = 23.1 Hz), 112.7 (d, J = 23.4 Hz), 106.6, 47.0, 29.1, 14.5. IR (KBr, cm^{-1}) 2973, 2934, 1710, 1571, 1466, 1374, 1307, 1164, 1092, 954, 853, 744. HRMS (ESI) ($[M+Na]^+$) Calcd. for $[C_{20}H_{15}FNaO_2]^+$: 329.0948, Found. 329.0944. HPLC: OD-H column, 99:1 hexane:isopropanol, 1.00 mL/min, t_R = major: 13.2 min, minor: 10.3 min. 61% ee. $[\alpha]_D^{24}$ -85.5° (c 1.5, CH_2Cl_2).



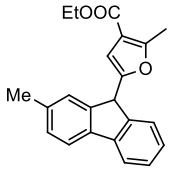
1-(5-(2-Fluoro-6-methyl-9H-fluoren-9-yl)-2-methylfuran-3-yl)ethanone (6f) Yield: 76%, yellow oil, R_f = 0.3 (petroleum ether/AcOEt = 10:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (dd, J = 8.4, 5.0 Hz, 1H), 7.53 (s, 1H), 7.42 (d, J = 7.7 Hz, 1H), 7.24 (s, 1H), 7.15 – 7.05 (m, 2H), 6.22 (s, 1H), 5.05 (s, 1H), 2.56 (s, 3H), 2.44 (s, 3H), 2.31 (s, 3H). ^{19}F NMR (471 MHz, $CDCl_3$) δ -114.4. ^{13}C NMR (101 MHz, $CDCl_3$) δ 194.1, 162.5 (d, J = 245.5 Hz), 158.4, 151.6, 146.1 (d, J = 8.3 Hz), 140.6 (d, J = 2.0 Hz), 140.3, 138.0, 136.9 (d, J = 2.5 Hz), 128.0, 124.9, 122.1, 121.0 (d, J = 8.9 Hz), 120.5, 115.1 (d, J = 22.9 Hz), 112.7 (d, J = 23.3 Hz), 106.5, 46.7, 29.1, 21.6, 14.5. IR (KBr, cm^{-1}) 2971, 2930, 2885, 1711, 1565, 1449, 1372, 1310, 1233, 1137, 957, 849, 741. HRMS (ESI) ($[M+Na]^+$) Calcd. for $[C_{21}H_{17}FNaO_2]^+$: 343.1105, Found. 343.1100. HPLC: OD-H column, 99:1 hexane:isopropanol, 1.00 mL/min, t_R = major: 11.6 min, minor: 9.6 min. 87% ee. $[\alpha]_D^{24}$ -88.0° (c 1.17, CH_2Cl_2).



1-(2-Ethyl-5-(2-methyl-9H-fluoren-9-yl)furan-3-yl)propan-1-one (6g) Yield: 99%, yellow oil, R_f = 0.3 (petroleum ether/AcOEt = 10:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (d, J = 7.5 Hz, 1H), 7.54 (d, J = 7.7 Hz, 1H), 7.46 (d, J = 7.5 Hz, 1H), 7.32 – 7.24 (m, 2H), 7.18 (t, J = 7.4 Hz, 1H), 7.10 (d, J = 7.4 Hz, 1H), 6.03 (s, 1H), 4.99 (s, 1H), 2.94 (q, J = 7.5 Hz, 2H), 2.49 (q, J = 7.3 Hz, 2H), 2.31 (s, 3H), 1.17 (t, J = 7.5 Hz, 3H), 0.97 (t, J = 7.3 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.1, 163.0, 152.2, 144.0, 143.6, 141.1, 138.3, 137.4, 128.8, 127.9, 126.9, 126.0, 125.3, 120.6, 119.9, 119.9, 105.5, 47.0, 34.4, 21.8, 21.7, 12.1, 7.8. IR (KBr, cm^{-1}) 2975, 2890, 1712, 1557, 1459, 1373, 1247, 1157, 1132, 952, 821, 766. HRMS (ESI) ($[M+H]^+$) Calcd. for $[C_{23}H_{23}O_2]^+$: 331.1693, Found. 331.1696. HPLC: OD-H column, 99:1 hexane:isopropanol, 1.00 mL/min, t_R = major: 7.2 min, minor: 8.2 min. 98% ee. $[\alpha]_D^{24}$ -102.1° (c 0.67, CH_2Cl_2).

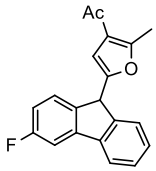


(5-(2-Methyl-9H-fluoren-9-yl)-2-phenylfuran-3-yl)(phenyl)methanone (6h) Yield: 95%, yellow oil, R_f = 0.3 (petroleum ether/AcOEt = 10:1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.80 – 7.73 (m, 3H), 7.70 – 7.65 (m, 4H), 7.49 (s, 1H), 7.46 – 7.38 (m, 2H), 7.34 – 7.26 (m, 6H), 7.23 (t, J = 3.9 Hz, 1H), 6.28 (s, 1H), 5.24 (s, 1H), 2.43 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 191.9, 155.6, 153.5, 143.6, 143.3, 141.2, 138.5, 138.0, 137.5, 132.8, 130.0, 129.8, 128.9, 128.9, 128.4, 128.3, 128.0, 127.5, 127.0, 126.1, 125.4, 121.7, 120.0, 119.9, 109.6, 47.1, 21.8. IR (KBr, cm^{-1}) 2974, 2888, 1711, 1560, 1466, 1375, 1306, 1160, 1130, 951, 818, 693. HRMS (ESI) ($[M+H]^+$) Calcd. for $[C_{31}H_{23}O_2]^+$: 427.1693, Found. 427.1694. HPLC: OD-H column, 99:1 hexane:isopropanol, 1.00 mL/min, t_R = major: 14.3 min, minor: 18.2 min. 98% ee. $[\alpha]_D^{24}$ -146.7° (c 1.17, CH_2Cl_2).

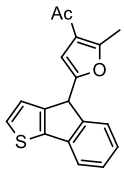


Ethyl 2-methyl-5-(2-methyl-9H-fluoren-9-yl)furan-3-carboxylate (6i) Yield: 97%, yellow oil, R_f = 0.3 (petroleum ether/AcOEt = 10:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, J = 7.5 Hz, 1H), 7.64 (d, J = 7.7 Hz, 1H), 7.52 (d, J = 7.5 Hz, 1H), 7.40 – 7.33 (m, 2H), 7.27 (t, J = 7.4 Hz, 1H), 7.23 – 7.17 (m,

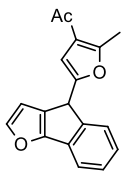
1H), 6.29 (s, 1H), 5.06 (s, 1H), 4.22 (q, J = 7.1 Hz, 2H), 2.54 (s, 3H), 2.40 (s, 3H), 1.28 (t, J = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.2, 159.0, 152.1, 144.0, 143.7, 141.1, 138.3, 137.3, 128.7, 127.8, 126.9, 125.9, 125.2, 119.9, 119.8, 114.1, 106.7, 60.0, 47.0, 21.7, 14.4, 13.9. IR (KBr, cm^{-1}) 2975, 2889, 1711, 1563, 1465, 1375, 1248, 1158, 1131, 1078, 951, 820. HRMS (ESI) ($[M+H]^+$) Calcd. for $[C_{22}H_{21}O_3]^+$: 333.1485, Found. 333.1490. HPLC: OD-H column, 99:1 hexane:isopropanol, 1.00 mL/min, t_R = major: 7.4 min, minor: 9.2 min. 97% ee. $[\alpha]_D^{24}$ -94.4° (c 0.5, CH_2Cl_2).



1-(5-(3-Fluoro-9H-fluoren-9-yl)-2-methylfuran-3-yl)ethanone (6j) Yield: 91%, yellow oil, R_f = 0.3 (petroleum ether/AcOEt = 10:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, J = 7.6 Hz, 1H), 7.57 (d, J = 7.5 Hz, 1H), 7.51 (dd, J = 8.4, 5.1 Hz, 1H), 7.46 – 7.40 (m, 2H), 7.36 (t, J = 7.4 Hz, 1H), 7.02 (td, J = 8.7, 2.3 Hz, 1H), 6.21 (s, 1H), 5.09 (s, 1H), 2.57 (s, 3H), 2.30 (s, 4H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -114.5. ^{13}C NMR (101 MHz, $CDCl_3$) δ 194.0, 163.2 (d, J = 244.9 Hz), 158.3, 151.6, 144.5, 143.0 (d, J = 9.0 Hz), 140.1, 139.0, 128.1 (d, J = 5.4 Hz), 126.3 (d, J = 9.0 Hz), 125.4, 122.1, 120.4, 114.3 (d, J = 23.1 Hz), 107.3 (d, J = 23.3 Hz), 106.4, 46.5, 29.1, 14.5. IR (KBr, cm^{-1}) 2975, 2931, 1751, 1698, 1595, 1465, 1362, 1200, 1162, 1089, 949, 818, 766. HRMS (ESI) ($[M+H]^+$) Calcd. for $[C_{20}H_{16}FO_2]^+$: 307.1129, Found. 307.1133. HPLC: OD-H column, 99:1 hexane:isopropanol, 1.00 mL/min, t_R = major: 13.6 min, minor: 15.3 min. 95% ee. $[\alpha]_D^{24}$ -102.2° (c 1.17, CH_2Cl_2).



1-(5-(4H-indeno[1,2-b]thiophen-4-yl)-2-methylfuran-3-yl)ethanone (6k) Yield: 99%, yellow oil, R_f = 0.25 (petroleum ether/AcOEt = 10:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (d, J = 7.5 Hz, 1H), 7.47 (d, J = 7.5 Hz, 1H), 7.37 – 7.31 (m, 2H), 7.25 – 7.19 (m, 1H), 7.15 (d, J = 4.9 Hz, 1H), 6.19 (s, 1H), 4.94 (s, 1H), 2.57 (s, 3H), 2.30 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 194.2, 158.3, 150.9, 147.4, 146.5, 143.4, 137.9, 128.0, 127.95, 125.6, 125.3, 122.6, 122.1, 119.2, 106.1, 44.4, 29.1, 14.5. IR (KBr, cm^{-1}) 3027, 2924, 1710, 1666, 1574, 1476, 1423, 1370, 1243, 1175, 1023, 953, 851, 762. HRMS (ESI) ($[M+H]^+$) Calcd. for $[C_{18}H_{15}O_2S]^+$: 295.0787, Found. 295.0785. HPLC: OD-H column, 95:5 hexane:isopropanol, 1.00 mL/min, t_R = major: 8.8 min, minor: 12.5 min. 96% ee. $[\alpha]_D^{24}$ -118.2° (c 1.17, CH_2Cl_2).

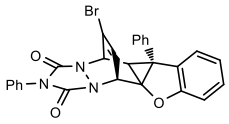


1-(5-(4H-indeno[1,2-b]furan-4-yl)-2-methylfuran-3-yl)ethanone (6l) Yield: 99%, yellow oil, R_f = 0.3 (petroleum ether/AcOEt = 10:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (d, J = 7.9 Hz, 2H), 7.40 (d, J = 7.5 Hz, 1H), 7.26 (t, J = 7.5 Hz, 1H), 7.12 (t, J = 7.5 Hz, 1H), 6.55 (s, 1H), 6.15 (s, 1H), 4.69 (s, 1H), 2.50 (s, 3H), 2.23 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 194.1, 159.4, 158.2, 150.7, 147.1, 146.3, 132.5, 128.6, 127.8, 125.6, 125.3, 122.0, 116.9, 108.6, 106.0, 40.2, 29.1, 14.5. IR (KBr, cm^{-1}) 3029, 2928, 1710, 1665, 1572, 1426, 1373 1243, 1175, 1008, 956, 856, 761. HRMS (ESI) ($[M+H]^+$) Calcd. for $[C_{18}H_{15}O_3]^+$: 279.1016, Found. 279.1019. HPLC: OD-H column, 99:1 hexane:isopropanol, 1.00 mL/min, t_R = major: 11.9 min, minor: 19.8 min. 99% ee. $[\alpha]_D^{24}$ -124.6° (c 1.17,

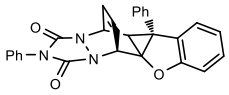
CH_2Cl_2).

15. [4+2] cycloaddition of cycloheptatriene 4 with PTAD.

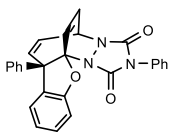
To a solution of **4** (0.10 mmol, 1.0 equiv.) in ethyl acetate (1.0 mL) was added the PTAD (0.105 mmol, 18.4mg). The reaction mixture was stirred at room temperature and monitored by TLC. After the reaction was completed, the solvent was removed in vacuo and the crude product was directly purified by flash chromatography.



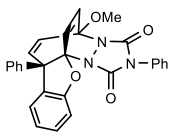
(5b*R*)-14-Bromo-2,5b-diphenyl-5a,5b-dihydro-1*H*,5*H*,11*H*-5,11-ethenobenzofuro[2',3':1,3]cyclopropa[1,2-*d*][1,2,4]triazolo[1,2-*a*]pyridazine-1,3(2*H*)-dione (10a) Yield: 68%, > 95:5 dr, white solid, R_f = 0.45 (petroleum ether/AcOEt = 5:1). ^{1}H NMR (500 MHz, Chloroform-d) δ 7.49 – 7.44 (m, 6H), 7.42 – 7.37 (m, 1H), 7.33 (q, J = 3.1 Hz, 2H), 7.24 (t, J = 7.7 Hz, 1H), 6.96 – 6.89 (m, 2H), 6.83 (d, J = 7.6 Hz, 1H), 6.14 (dd, J = 6.7, 2.3 Hz, 1H), 5.77 (d, J = 6.7 Hz, 1H), 5.59 (dd, J = 4.8, 2.4 Hz, 1H), 1.52 (d, J = 4.8 Hz, 1H). ^{13}C NMR (126 MHz, Chloroform-d) δ 156.8, 156.3, 156.2, 134.2, 132.9, 131.0, 130.7, 129.6, 129.2, 129.2, 129.1, 128.6, 128.6, 127.7, 127.1, 125.5, 124.7, 121.8, 117.7, 111.1, 72.8, 62.3, 57.8, 46.4, 20.6. HRMS (ESI) ([M+Na]$^+$) Calcd. for $[C_{27}H_{18}BrNaN_3O_3]^+$: 534.0424, Found. 534.0424. HPLC: OD-H column, 90:10 hexane:isopropanol, 1.00 mL/min, t_R = major: 26.2 min, minor: 30.965 min. 99% ee.



(5b*R*)-2,5b-Diphenyl-5a,5b-dihydro-1*H*,5*H*,11*H*-5,11-ethenobenzofuro[2',3':1,3]cyclopropa[1,2-*d*][1,2,4]triazolo[1,2-*a*]pyridazine-1,3(2H)-dione (10b) Yield: 36%, > 95:5 dr, red oil, R_f = 0.45 (petroleum ether/AcOEt = 5:1). ^{1}H NMR (500 MHz, Chloroform-d) δ 7.50 – 7.36 (m, 6H), 7.31 (dd, J = 6.1, 2.9 Hz, 2H), 7.26 – 7.21 (m, 2H), 7.06 (d, J = 8.1 Hz, 1H), 6.96 (dt, J = 6.5, 2.0 Hz, 1H), 6.91 (td, J = 7.5, 1.0 Hz, 1H), 6.80 (dd, J = 7.6, 1.3 Hz, 1H), 5.88 (ddd, J = 8.0, 6.1, 1.8 Hz, 1H), 5.73 (dd, J = 6.3, 1.4 Hz, 1H), 5.67 (ddd, J = 7.6, 5.7, 1.5 Hz, 1H), 5.56 (ddd, J = 5.9, 4.6, 1.8 Hz, 1H), 1.49 (d, J = 4.6 Hz, 1H). ^{13}C NMR (126 MHz, Chloroform-d) δ 156.7, 156.6, 156.2, 135.6, 133.4, 131.2, 130.8, 129.4, 129.2, 128.9, 128.8, 128.4, 127.9, 127.6, 125.6, 125.3, 124.7, 121.6, 111.1, 73.4, 55.9, 53.9, 46.1, 19.8. HRMS (ESI) ([M+H]$^+$) Calcd. for $[C_{27}H_{20}N_3O_3]^+$: 434.1499, Found. 434.1499. HPLC: MD(2) column, 80:20 hexane:isopropanol, 0.50 mL/min, t_R = major: 36.6 min, minor: 41.9 min. 99% ee.



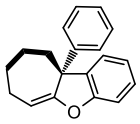
(7a*R*)-2,7a-diphenyl-5,7a-dihydro-1*H*-5,12a-ethenobenzofuro[2,3-*c*][1,2,4]triazolo[1,2-*a*][1,2]diazepine-1,3(2*H*)-dione (11a) Yield: 57%, > 95:5 dr, white solid, R_f = 0.25 (petroleum ether/AcOEt = 5:1). ^{1}H NMR (500 MHz, Chloroform-d) δ 7.46 – 7.39 (m, 5H), 7.38 – 7.32 (m, 2H), 7.27 – 7.22 (m, 3H), 7.21 – 7.14 (m, 2H), 7.07 – 6.99 (m, 2H), 6.62 (dd, J = 9.4, 6.9 Hz, 1H), 6.50 (dd, J = 10.8, 7.8 Hz, 1H), 6.42 (d, J = 10.8 Hz, 1H), 6.03 (d, J = 9.4 Hz, 1H), 5.35 (t, J = 7.3 Hz, 1H). ^{13}C NMR (126 MHz, Chloroform-d) δ 159.7, 150.3, 149.9, 136.1, 133.4, 131.4, 130.4, 130.1, 129.8, 129.5, 129.3, 129.0, 128.2, 128.0, 126.1, 123.9, 123.5, 123.4, 113.0, 104.8, 64.4, 47.8. HRMS (ESI) ([M+H]$^+$) Calcd. for $[C_{27}H_{20}N_3O_3]^+$: 434.1499, Found. 434.1495. HPLC: MD(2) column, 80:20 hexane:isopropanol, 0.50 mL/min, t_R = major: 45.7 min, minor: 58.6 min. > 99% ee.



(7a*R*)-5-Methoxy-2,7a-diphenyl-5,7a-dihydro-1*H*-5,12a-ethenobenzofuro[2,3-*c*][1,2,4]triazolo[1,2-*a*][1,2]diazepine-1,3(2*H*)-dione (11b) Yield: 49%, > 95:5 dr, white solid, R_f = 0.25 (petroleum ether/AcOEt = 4:1). ^{1}H NMR (500 MHz, Chloroform-d) δ 7.45 (t, J = 7.8 Hz, 2H), 7.38 (dd, J = 8.0, 6.0 Hz, 3H), 7.31 – 7.20 (m, 7H), 7.13 (d, J = 8.1 Hz, 1H), 7.02 (t, J = 7.5 Hz, 1H), 6.70 (d, J = 11.8 Hz, 1H), 5.76 (dd, J = 11.9, 2.0 Hz, 1H), 5.66 (d, J = 7.3 Hz, 1H), 5.33 (dd, J = 7.5, 1.9 Hz, 1H), 3.46 (s, 3H). ^{13}C NMR (126 MHz, Chloroform-d) δ 157.4, 156.3, 155.8, 150.2, 138.0, 132.7, 131.3, 129.8, 129.2, 128.98, 128.97, 128.5, 128.1, 127.5, 126.3, 125.7, 123.6, 123.5, 112.8, 101.3, 95.0, 64.8, 60.2, 55.0. HRMS (ESI) ([M+H]$^+$) Calcd. for $[C_{28}H_{22}N_3O_4]^+$: 464.1605, Found. 464.1598. HPLC: MD(2) column, 80:20 hexane:isopropanol, 0.50 mL/min, t_R = major: 25.3 min, minor: 24.7 min. > 99% ee.

16. Hydrogenation of cycloheptatriene 4c.

A suspension of Pd/C 10% (10 mg) and **4c** (25.8 mg, 0.1 mmol) in ethyl acetate (3.0 mL) was stirred at room temperature under 1 atm hydrogen atmosphere. After being stirred 3 hours, the mixture was filtrated through a pad of Celite and the filtration was concentrated in vacuo, the residue was purified by column chromatography on silica gel to afford the desired the product **12** in 94% yield (24.6 mg, 98% ee).

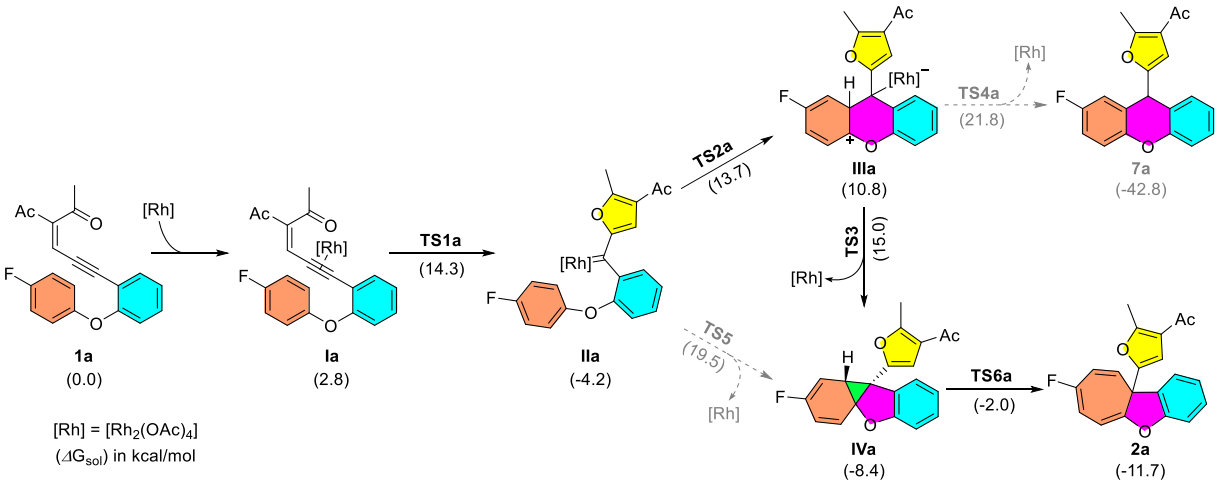


(*R*)-10a-phenyl-8,9,10,10a-tetrahydro-7*H*-cyclohepta[*b*]benzofuran (12) Yield: 94%, white solid, R_f = 0.7 (petroleum ether). ^{1}H NMR (500 MHz, Chloroform-d) δ 7.64 – 7.55 (m, 2H), 7.38 (t, J = 7.8 Hz, 2H), 7.26 – 7.21 (m, 1H), 7.19 (dd, J = 7.5, 1.4 Hz, 1H), 7.11 (td, J = 7.8, 1.4 Hz, 1H), 6.92 – 6.81 (m, 2H), 5.82 (dd, J = 9.3, 4.8 Hz, 1H), 2.80 (ddd, J = 14.1, 5.3, 2.3 Hz, 1H), 2.14 – 1.90 (m, 4H), 1.71 (dddt, J = 18.7, 10.7, 5.3, 2.8 Hz, 2H), 1.54 – 1.43 (m, 1H). ^{13}C NMR (126 MHz, Chloroform-d) δ 163.8, 155.9, 141.7, 135.8, 129.0, 128.1, 126.4, 126.2, 123.1, 121.6, 109.3, 104.0, 56.2, 36.6, 28.0, 27.3, 23.9. HRMS (ESI) ([M+Na]$^+$) Calcd. for $[C_{19}H_{18}NaO]^+$: 285.1250, Found. 285.1251. HPLC: MD(2) column, 99.2:0.8 hexane:isopropanol, 0.40 mL/min, t_R = major: 11.6 min, minor: 11.4 min. 98% ee.

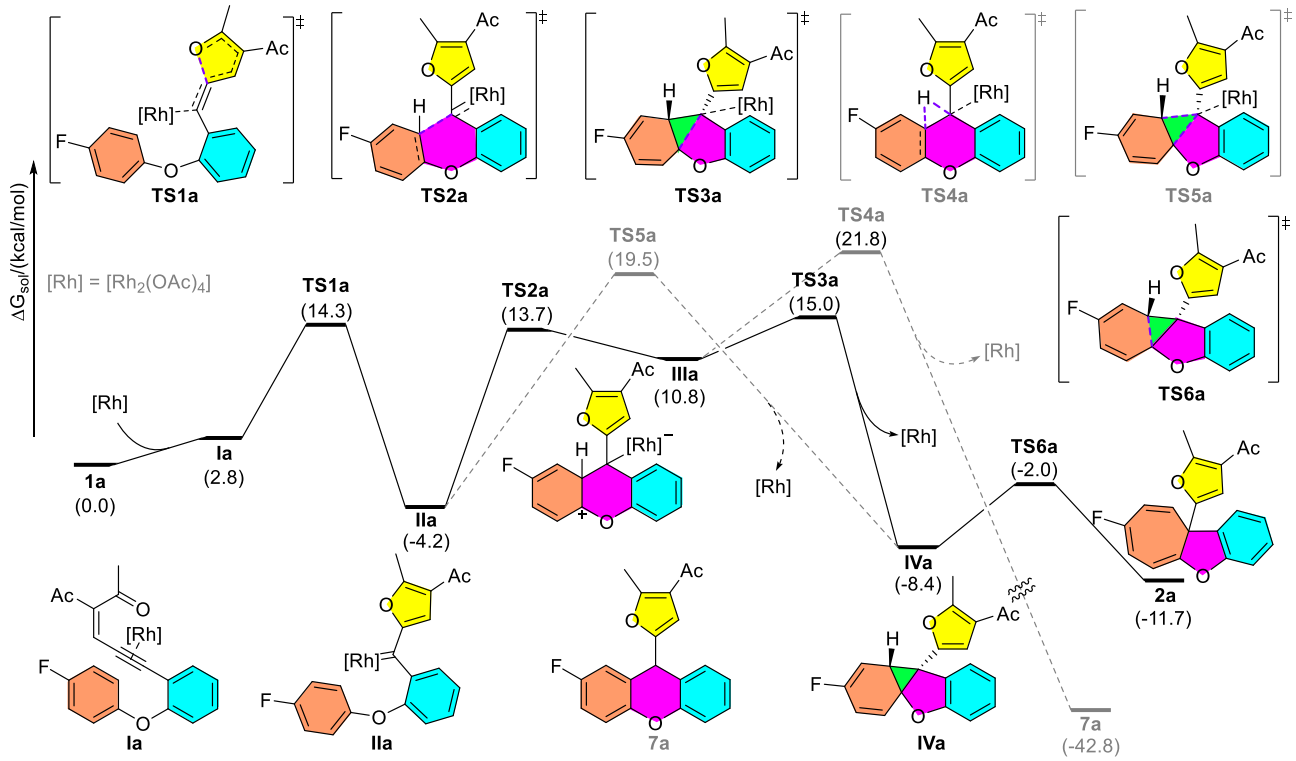
17. Computational details

All of the calculations were performed with Gaussian 16 program.[7] The hybrid B3LYP functional in conjunction with the def2SVP basis sets,[8-9] was applied for the optimization of all stationary points in gas phase. Empirical dispersion was included using the D3 version of Grimme's dispersion with Becke-Johnson damping.[10] Frequency calculations were performed at the same level to confirm whether each stationary point was either a minimum or a transition structure. All the thermochemistry data were obtained at 253.15 K. Single point energy calculations were carried out with Truhlar's M06 functional with def2TZVP basis set for all atoms in dichloroethane with SMD solvent model.[11-12] $Rh_2(OAc)_4$ was used as the catalyst model during the investigation of reaction mechanism to reduce the computation cost. For each stationary point, the free energy corrections were calculated using Grimme's quasiharmonic approximation with GoodVibes.[13] Computed structures were illustrated using CYLView.[14]

1. DFT studies on Rh_2(II)-catalyzed Büchner reaction of enynones.



Scheme S1. Plausible reaction pathways of Rh_2(II)-catalyzed Büchner reaction of enynone 1a. If not otherwise noted, relative Gibbs free energies computed at 253.15 K with M06/def2TZVP-SMD(dichloroethane)//B3LYP-D3(BJ)/def2SVP theoretical level are reported in kcal/mol.



Scheme S2. Free energy profiles of Rh_2(II)-catalyzed Büchner reaction pathways of enynone 1a.

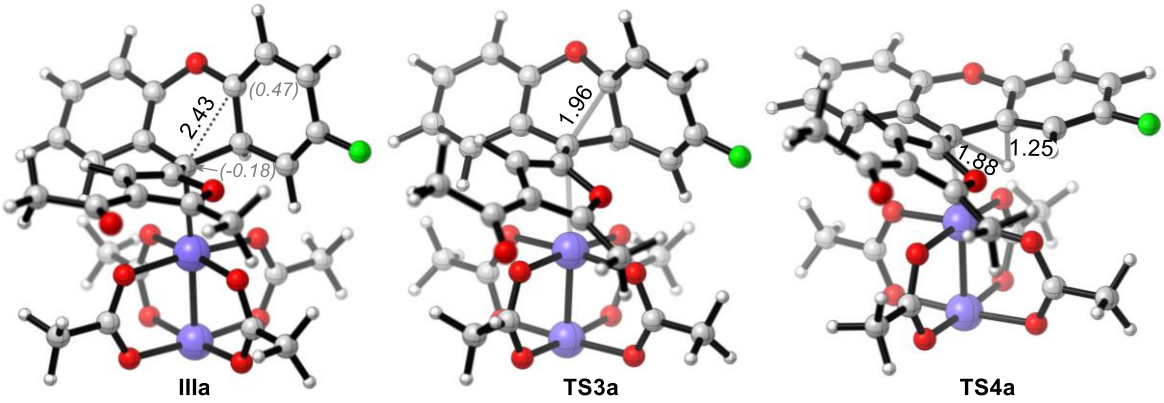
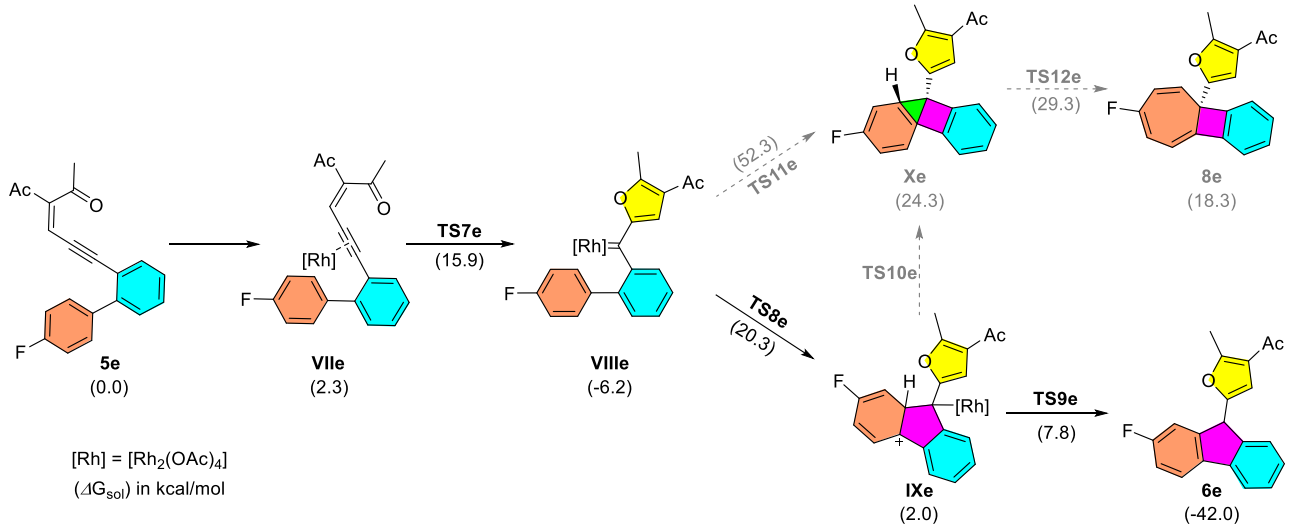


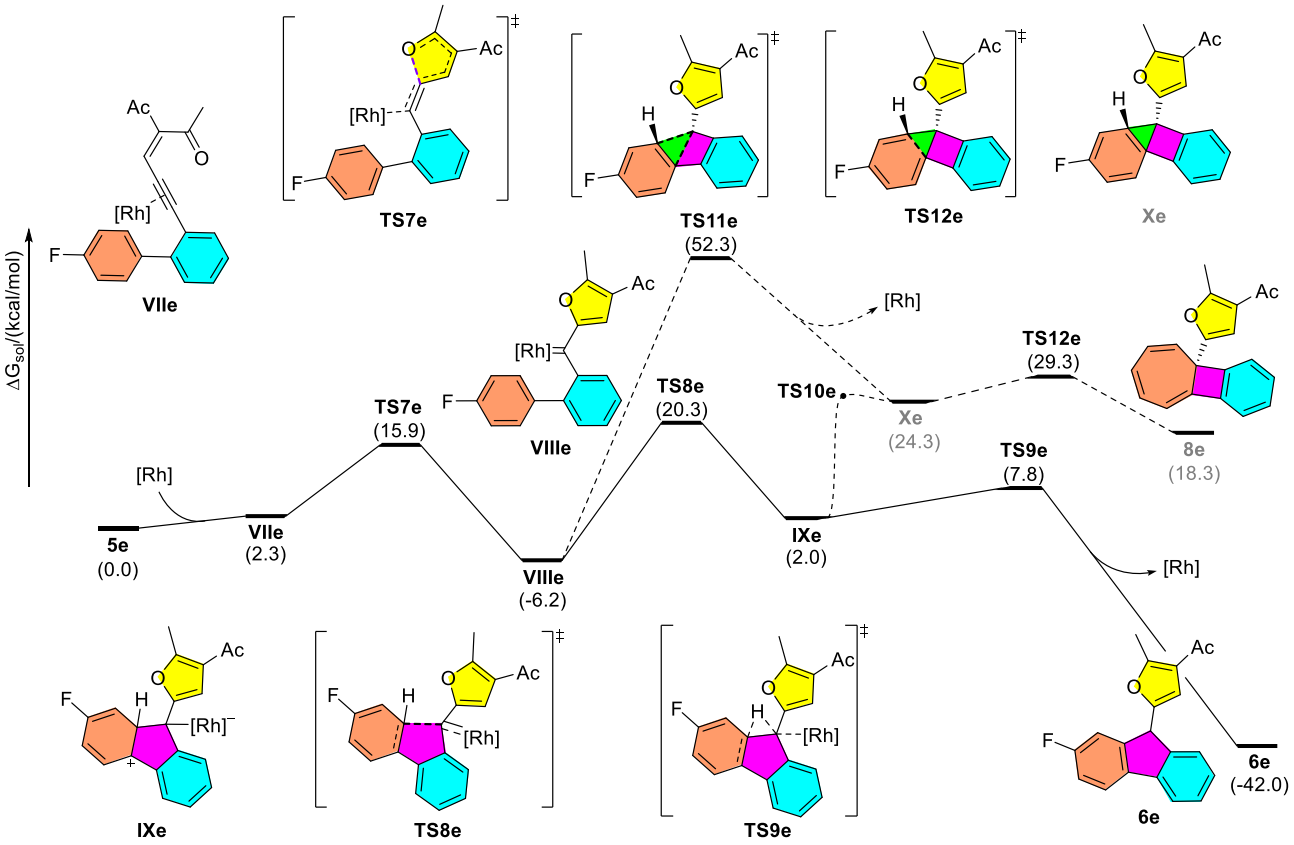
Figure S1. Optimized structures of important stationary points. NBO charge is present in brackets. And distance is given at angstrom.

Based on our experimental observations and DFT calculations, the plausible reaction mechanism was proposed. The reaction starts with the coordination of rhodium catalyst with alkyne moiety, followed by a 5-*exo-dig* cyclization to afford rhodium carbene intermediate **IIa**. Then, electrophilic addition of carbene to phenyl ring leads to the formation of intermediate **IIIa**. Due to the breaking of aromatic system, intermediate **IIIa** is highly unstable, and the free energy increased by 15.0 kcal/mol related to carbene **IIa**. From intermediate **IIIa**, there is a competition between ring closure and [1,2]-H shift. The ring-closure step is favored with a low free energy barrier of 4.2 kcal/mol, which could be possibly contributed to the close distance and attractive electrostatic interaction between two carbons of the forming bond in intermediate **IIIa**. Moreover, there is a smaller distortion energy penalty to overcome during the ring-closure step, as the structure of **TS3a** is closer to that of intermediate **IIIa** than the [1,2]-H shift transition state structure of **TS4a**. Moreover, a concerted cyclopropanation step *via* **TS5a** was also considered, but the free energy barrier, 23.7 kcal/mol is higher than the ring-closure step by 4.5 kcal/mol.

2. DFT studies on Rh_2(II)-catalyzed aromatic substitution reaction of enyones.



Scheme S3. Plausible reaction pathways of Rh_2(II)-catalyzed aromatic substitution reaction of enyone 5e. After extensive optimization, we ultimately found that TS10e could not be located.



Scheme S4. Free energy profiles of Rh_2(II)-catalyzed aromatic substitution reaction of enyone 5e.

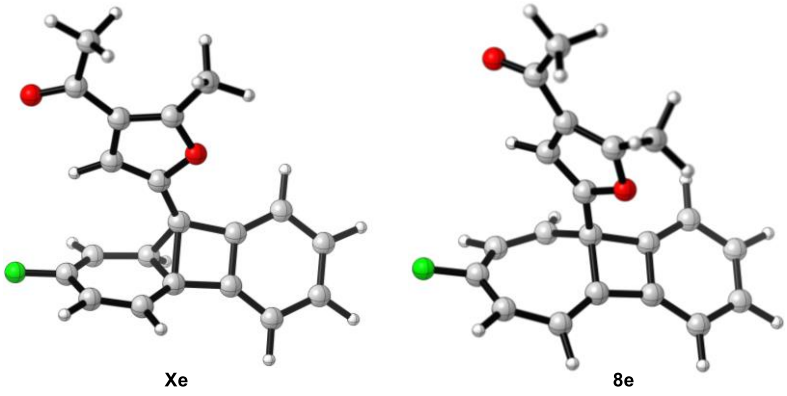


Figure S1. Optimized structures of selected stationary points.

For Rh(II)-catalyzed transformation of enynone **5e**, the possible Büchner reaction is impossible, as the corresponding product **8e** is even higher in free energy than reactant **5e** by 18.3 kcal/mol. This could be contributed to the high ring strain

of the fused cyclobutene in structures **Xe** and **8e**. However, the aromatic substitution process *via* **TS9e** is more favorable due the release of this high ring strain.

3 **Tables of energies and other thermodynamic parameters.**

Table S1

Index	E_{ele}	E_{ele}(SP)	ZPE	H	G(T)	qh-G(T)
1a	-1095.87583	-1096.29686	0.29546	-1095.56312	-1095.62384	-1095.61806
[Rh_2]	-1134.67797	-1135.13924	0.21028	-1134.45046	-1134.50769	-1134.50398
Ia	-2230.60765	-2231.45456	0.50765	-2230.06551	-2230.16119	-2230.15298
TS1a	-2230.58192	-2231.43429	0.50617	-2230.04159	-2230.13881	-2230.12920
IIa	-2230.61504	-2231.46800	0.50965	-2230.07166	-2230.16703	-2230.15812
TS2a	-2230.59493	-2231.43922	0.50844	-2230.05323	-2230.14605	-2230.13822
IIIa	-2230.59969	-2231.44415	0.50904	-2230.05716	-2230.15048	-2230.14261
TS3a	-2230.59295	-2231.43823	0.50924	-2230.05065	-2230.14283	-2230.13514
IVa	-1095.89761	-1096.31675	0.29878	-1095.58337	-1095.63580	-1095.63327
TS4a	-2230.57899	-2231.42253	0.50437	-2230.04139	-2230.13368	-2230.12613
TS5a	-2230.58567	-2231.43022	0.50788	-2230.04470	-2230.13590	-2230.12878
TS6a	-1095.88968	-1096.30560	0.29751	-1095.57693	-1095.62860	-1095.62633
2a	-1095.91075	-1096.32204	0.29880	-1095.59631	-1095.64882	-1095.64642
7a	-1095.96323	-1096.37285	0.30033	-1095.64739	-1095.70046	-1095.69763

Table S2

Index	E_{ele}	E_{ele}(SP)	ZPE	H	G(T)	qh-G(T)
5e	-1020.72428	-1021.08524	0.29160	-1020.41629	-1020.47294	-1020.46869
VIIe	-2155.45219	-2156.24324	0.50368	-2154.91493	-2155.00748	-2155.00021
TS7e	-2155.43685	-2156.22220	0.50331	-2154.90085	-2154.99123	-2154.98419
VIIIe	-2155.46761	-2156.25844	0.50560	-2154.92897	-2155.02244	-2155.01393
TS8e	-2155.41961	-2156.21431	0.50294	-2154.88406	-2154.97582	-2154.96785
IXe	-2155.45028	-2156.24398	0.50451	-2154.91251	-2155.00736	-2154.99810
TS9e	-2155.44470	-2156.23263	0.50071	-2154.91160	-2155.00168	-2154.99458
6e	-1020.80159	-1021.15834	0.29575	-1020.49095	-1020.54252	-1020.53988
TS11e	-2155.37720	-2156.16366	0.50277	-2154.84184	-2154.93229	-2154.92506

Xe	-1020.68359	-1021.04999	0.29312	-1020.37534	-1020.42692	-1020.42447
TS12e	-1020.67645	-1021.04099	0.29198	-1020.36955	-1020.42104	-1020.41844
8e	-1020.70062	-1021.05969	0.29331	-1020.39205	-1020.44398	-1020.44144

Notes: E_{ele}, ZPE, H, G(T), and qh-G(T) were the electronic energies, zero-point energies, sum of electronic and thermal ethalpies, sum of electronic and thermal free energies, and sum of electronic and thermal free energies using Grimme's quasiharmonic approximation, respectively, which were given at the B3LYP-D3(BJ)/def2SVP level. E_{ele}(SP) were electronic energies with solvent correction at the M06/def2TZVP-SMD(dichloroethane) level.

9.5 Coordinates of all stationary points.

1a

C	0.223343	1.710976	0.001690
C	1.568811	1.257857	0.000681
C	2.622029	2.177551	-0.002096
C	2.346144	3.546529	-0.003460
C	1.027369	4.014327	-0.002059
C	-0.021846	3.100809	0.000263
C	-0.846764	0.782426	0.004961
O	1.745658	-0.089083	0.002965
C	3.021640	-0.619638	-0.001891
C	3.642284	-0.907251	-1.219175
C	4.910489	-1.490538	-1.226319
C	5.531664	-1.773867	-0.011276
C	4.918671	-1.492586	1.208371
C	3.650454	-0.909233	1.210686
F	6.748348	-2.333626	-0.015819
C	-1.805851	0.023540	0.010309
C	-2.829385	-0.933247	0.021087
C	-4.190441	-0.791359	0.006628
C	-4.908933	0.517312	-0.065301
O	-6.090122	0.567426	-0.363636
C	-4.158916	1.801978	0.229711
O	-4.323068	-3.156136	0.000604
C	-4.947716	-2.111175	0.026997
C	-6.454491	-2.131897	0.108781
H	3.651953	1.821437	-0.003136
H	3.177196	4.255736	-0.005783
H	0.821700	5.086225	-0.003176
H	-1.058194	3.443094	0.001699
H	3.123754	-0.677028	-2.151326
H	5.422055	-1.732902	-2.159192
H	5.436532	-1.736455	2.137371
H	3.138213	-0.680420	2.146652
H	-2.496494	-1.980571	0.028643
H	-3.558696	1.730850	1.148235
H	-3.462023	2.030799	-0.591457
H	-4.896686	2.610295	0.312380
H	-6.772620	-3.173514	0.245484
H	-6.820625	-1.499687	0.930710
H	-6.892275	-1.707973	-0.805748

[Rh_2]

Rh	-0.003812	-0.004932	1.188560
Rh	-0.004708	-0.003925	-1.188152
O	1.437811	1.444398	1.126476
O	1.436394	1.445906	-1.125220
O	1.443830	-1.445610	-1.127166
O	-1.453814	1.436944	-1.124141
O	-1.445115	-1.452729	-1.125633
O	-1.444644	-1.453311	1.126103
O	1.444124	-1.446924	1.124543
O	-1.452576	1.436521	1.127576
C	-1.861124	1.854429	0.002132
C	1.853811	1.854058	0.000739
C	1.859978	-1.855916	-0.001714
C	-1.861803	-1.861761	0.000276

C	-2.963394	-2.889155	-0.001065
C	-2.887559	2.957018	0.000745
C	2.954291	2.882909	-0.001442
C	2.959410	-2.885815	-0.000695
H	2.935787	-3.472124	-0.927911
H	2.870688	-3.535342	0.879817
H	3.927947	-2.362892	0.056380
H	2.856771	3.541291	-0.874526
H	3.921412	2.359536	-0.075602
H	2.941764	3.459922	0.931742
H	-2.361627	3.922918	-0.071147
H	-3.545313	2.862487	-0.873132
H	-3.465481	2.944259	0.933369
H	-2.883961	-3.530959	-0.888035
H	-3.930898	-2.362980	-0.044214
H	-2.933393	-3.483734	0.920743

Ia

C	-1.447898	-1.002396	2.559714
C	-2.786488	-0.914040	2.120619
C	-3.615940	-2.036322	2.143179
C	-3.120139	-3.250379	2.620082
C	-1.799268	-3.350167	3.077464
C	-0.968731	-2.235361	3.046782
C	-0.579554	0.108583	2.388154
O	-3.243193	0.308215	1.712892
C	-3.893223	0.425097	0.501547
C	-3.362183	-0.153094	-0.655670
C	-3.999690	0.053105	-1.879424
C	-5.147415	0.843533	-1.926805
C	-5.674090	1.431918	-0.779390
C	-5.041398	1.216417	0.447307
F	-5.755263	1.045150	-3.105165
C	0.113575	1.109226	2.221520
C	0.942235	2.249497	2.154904
C	0.780666	3.383169	1.421266
C	-0.348878	3.621134	0.466517
O	-0.139672	4.245799	-0.561284
C	-1.714005	3.064119	0.770106
O	2.981587	4.035355	2.014473
C	1.930198	4.366511	1.496006
C	1.744750	5.763124	0.954312
H	-4.644511	-1.945895	1.790139
H	-3.773749	-4.125658	2.641955
H	-1.418116	-4.303918	3.447657
H	0.077601	-2.302785	3.345870
H	-2.441324	-0.730888	-0.584825
H	-3.610317	-0.380921	-2.802372
H	-6.571919	2.047293	-0.856602
H	-5.422966	1.663622	1.366385
H	1.891835	2.179738	2.697702
H	-1.739042	2.028053	0.408357
H	-1.947941	3.046998	1.842644
H	-2.462698	3.641770	0.211984
H	2.583530	6.384721	1.292060
H	1.706905	5.727223	-0.143689
H	0.785628	6.195015	1.279716
Rh	0.927141	-0.421227	0.279127

Rh	1.969549	-1.291492	-1.694884
O	-0.595630	-1.764433	-0.077615
O	0.458712	-2.668350	-1.845117
O	0.868955	0.062578	-2.778470
O	2.996473	-2.582373	-0.478378
O	3.444143	0.101196	-1.476223
O	2.552050	0.808803	0.460055
O	-0.021411	0.935630	-0.907101
O	1.926688	-1.846301	1.364511
C	2.748464	-2.605380	0.762342
C	-0.497379	-2.608147	-1.023198
C	0.131810	0.891308	-2.170567
C	3.440441	0.836808	-0.445474
C	4.579848	1.802720	-0.259909
C	3.460114	-3.643910	1.591849
C	-1.639739	-3.578179	-1.180837
C	-0.651063	1.895171	-2.970998
H	-0.336679	1.887193	-4.021288
H	-0.526070	2.892358	-2.523296
H	-1.720524	1.639733	-2.900526
H	-1.319371	-4.464961	-1.741548
H	-2.447906	-3.081210	-1.742261
H	-2.037414	-3.850738	-0.194034
H	2.862180	-4.569793	1.580038
H	4.443250	-3.867671	1.158149
H	3.557165	-3.305614	2.631369
H	4.811785	2.289017	-1.217746
H	5.472949	1.235926	0.048616
H	4.334347	2.544072	0.510774

TS1a

C	1.035464	-1.905082	-0.877354
C	2.191289	-2.352645	-0.196856
C	2.597569	-3.686480	-0.290779
C	1.869250	-4.580137	-1.076748
C	0.715253	-4.155135	-1.745302
C	0.287797	-2.836284	-1.623961
C	0.616310	-0.528762	-0.762707
O	2.812806	-1.472712	0.644517
C	4.171050	-1.306590	0.663199
C	4.705202	-0.723866	1.817309
C	6.069980	-0.442123	1.892511
C	6.887663	-0.755859	0.809525
C	6.367689	-1.337744	-0.344484
C	5.001331	-1.610844	-0.421888
F	8.202789	-0.488995	0.877156
C	1.153759	0.637411	-0.795801
C	1.163461	2.011998	-0.608377
C	2.330460	2.734687	-0.725016
C	3.448047	1.863112	-1.100269
O	3.168925	0.667601	-1.277640
C	4.877988	2.299565	-1.269535
O	1.187629	4.730974	-0.257575
C	2.261687	4.205718	-0.499302
C	3.518563	5.049299	-0.567301
H	3.478957	-4.015984	0.261504
H	2.195568	-5.620329	-1.149571
H	0.139222	-4.860306	-2.348098

H	-0.626052	-2.489499	-2.105448
H	4.032710	-0.488083	2.643541
H	6.508319	0.011985	2.782898
H	7.035655	-1.562336	-1.178053
H	4.577132	-2.030660	-1.333161
H	0.216499	2.499492	-0.375158
H	4.972334	3.060864	-2.057687
H	5.257561	2.740381	-0.335964
H	5.485927	1.423506	-1.525143
H	3.248407	6.088673	-0.344010
H	4.272674	4.702595	0.155401
H	3.975077	5.000094	-1.567816
Rh	-1.448965	-0.090078	-0.157458
Rh	-3.721247	0.192189	0.647923
O	-1.425636	-1.878805	0.848998
O	-3.573202	-1.666589	1.499611
O	-2.924047	1.043287	2.337140
O	-4.374414	-0.667526	-1.094869
O	-3.727537	2.047147	-0.237035
O	-1.669988	1.727325	-1.090950
O	-0.825322	0.888779	1.531124
O	-2.264810	-1.016749	-1.808347
C	-3.528692	-1.097269	-1.926332
C	-2.474549	-2.287008	1.436824
C	-1.679156	1.235552	2.408542
C	-2.720091	2.421914	-0.895155
C	-2.721181	3.803141	-1.499401
C	-4.046038	-1.796192	-3.159655
C	-2.374088	-3.620410	2.135513
C	-1.136200	1.945636	3.623391
H	-1.936800	2.146033	4.345138
H	-0.673079	2.892662	3.305597
H	-0.347561	1.333247	4.084916
H	-3.372346	-4.010219	2.369142
H	-1.812001	-3.484883	3.073372
H	-1.811288	-4.327731	1.510721
H	-3.929215	-2.883475	-3.022913
H	-5.108045	-1.569495	-3.313578
H	-3.452264	-1.503204	-4.036419
H	-3.651184	4.331814	-1.259313
H	-2.603381	3.722762	-2.590712
H	-1.852480	4.362600	-1.117850

IIa

C	0.914586	-1.881747	-0.797157
C	2.034151	-2.354636	-0.070714
C	2.390176	-3.704547	-0.095161
C	1.665244	-4.598840	-0.883991
C	0.558107	-4.153271	-1.615001
C	0.167552	-2.820081	-1.541873
C	0.465089	-0.498177	-0.691712
O	2.672322	-1.473055	0.767132
C	4.025314	-1.280849	0.746311
C	4.541080	-0.484403	1.777297
C	5.902955	-0.188526	1.821306
C	6.742600	-0.698576	0.831901
C	6.242413	-1.485105	-0.201351
C	4.875911	-1.773349	-0.251039

F	8.055901	-0.420645	0.874355
C	1.373573	0.556506	-0.816139
C	1.289540	1.902493	-0.474565
C	2.545390	2.497461	-0.737937
C	3.348149	1.481905	-1.271468
O	2.665208	0.339560	-1.320827
C	4.752442	1.426834	-1.750973
O	1.940953	4.643205	-0.032057
C	2.829976	3.926753	-0.450563
C	4.230343	4.458206	-0.675438
H	3.229681	-4.046887	0.511975
H	1.954001	-5.652309	-0.907397
H	-0.018161	-4.856198	-2.220311
H	-0.722820	-2.465075	-2.059758
H	3.854078	-0.101438	2.533441
H	6.324015	0.426920	2.618264
H	6.924456	-1.860792	-0.966269
H	4.474758	-2.367542	-1.071074
H	0.420944	2.387596	-0.049758
H	5.024891	2.324608	-2.319913
H	5.442589	1.340449	-0.895069
H	4.892216	0.538144	-2.378766
H	4.281496	5.490287	-0.306927
H	4.980783	3.838749	-0.160071
H	4.476091	4.448590	-1.750035
Rh	-1.437604	-0.094600	-0.163160
Rh	-3.718175	0.399348	0.617559
O	-1.557222	-1.841367	0.904605
O	-3.664949	-1.413595	1.590596
O	-2.870170	1.313408	2.252283
O	-4.414375	-0.539952	-1.071183
O	-3.577261	2.179505	-0.411684
O	-1.511475	1.690746	-1.175082
O	-0.781878	0.910134	1.503065
O	-2.326941	-1.020285	-1.776990
C	-3.597214	-1.045721	-1.882228
C	-2.626721	-2.124840	1.534952
C	-1.618059	1.392943	2.336669
C	-2.532874	2.446803	-1.060159
C	-2.443264	3.778779	-1.764741
C	-4.146362	-1.772082	-3.086754
C	-2.616701	-3.430789	2.292914
C	-1.022225	2.129577	3.511582
H	-1.810106	2.462878	4.197347
H	-0.455478	2.998147	3.141577
H	-0.311581	1.473138	4.035332
H	-3.626845	-3.686403	2.634875
H	-1.950010	-3.330335	3.163969
H	-2.206837	-4.227269	1.655660
H	-3.983486	-2.853664	-2.954573
H	-5.220128	-1.578252	-3.196175
H	-3.602126	-1.462929	-3.990466
H	-3.369234	4.350459	-1.631111
H	-2.248116	3.615265	-2.835180
H	-1.588854	4.343281	-1.359418

TS2a

C	-1.215547	2.286948	-0.220850

C	-1.679926	3.359324	0.561532	H	-2.306522	-3.947959	-0.476940
C	-1.666647	4.679834	0.106584	H	-0.161124	1.610853	2.249159
C	-1.242745	4.947149	-1.192056	H	-0.244701	-0.811240	2.855988
C	-0.856463	3.890839	-2.027670	H	-4.476612	-0.444230	3.501598
C	-0.843470	2.584853	-1.547407	H	-4.422872	1.938210	2.663991
C	-1.095973	0.896287	0.292315	H	-6.301985	-0.640680	-3.636887
C	-2.310487	1.868495	2.253808	H	-5.850166	0.534410	-2.353414
O	-2.317702	3.123831	1.765675	H	-4.703511	0.183935	-3.658711
C	-2.132034	0.020446	-0.192223	F	-2.425885	-1.993370	3.676472
C	-3.163090	0.203954	-1.091304	Rh	0.925954	0.045566	0.040521
C	-3.769938	-1.073791	-1.311301	Rh	3.105357	-0.928646	-0.497211
C	-3.078803	-1.962181	-0.491852	O	1.656856	1.790495	-0.763492
O	-2.112333	-1.310239	0.162534	O	3.628468	0.865026	-1.341557
C	-3.226961	-3.406969	-0.201014	O	3.744412	-0.239955	1.336110
C	-1.115914	1.083517	2.196700	O	2.297206	-1.540643	-2.284527
C	-1.154536	-0.218064	2.812555	O	2.467983	-2.674473	0.380723
C	-2.352248	-0.734812	3.215033	O	0.464300	-1.774164	0.880731
C	-3.546451	0.020939	3.169430	O	1.725268	0.625379	1.840797
C	-3.520268	1.327836	2.707490	O	0.299999	-0.604412	-1.809567
O	-5.353886	-2.534933	-2.287471	C	1.097358	-1.262034	-2.552414
C	-4.901614	-1.405774	-2.202931	C	2.818255	1.830482	-1.274457
C	-5.479199	-0.263925	-3.016632	C	2.951431	0.378505	2.092607
H	-2.030086	5.466482	0.769690	C	1.307325	-2.723562	0.871668
H	-1.235364	5.975614	-1.559543	C	0.852259	-4.029019	1.479923
H	-0.543500	4.089492	-3.055094	C	0.529591	-1.779778	-3.852068
H	-0.506336	1.763404	-2.178608	C	3.266720	3.165965	-1.816595
H	-3.428127	1.152747	-1.548403	C	3.485968	0.905870	3.401558
H	-3.377291	-3.556690	0.881279	H	2.729905	0.800091	4.191715
H	-4.077020	-3.809287	-0.762226	H	3.701583	1.980392	3.285629

H	4.412328	0.386422	3.675609
H	3.735749	3.736217	-0.998329
H	2.402400	3.738670	-2.177871
H	4.011666	3.025940	-2.610364
H	0.022528	-2.738326	-3.654790
H	-0.217079	-1.079668	-4.249676
H	1.332490	-1.953823	-4.579344
H	0.497210	-4.687021	0.669959
H	0.023768	-3.858073	2.179566
H	1.692525	-4.532282	1.976608

IIIa

C	-1.216659	1.952381	-1.333025
C	-1.655317	3.285848	-1.203759
C	-1.500927	4.241609	-2.212248
C	-0.938341	3.852288	-3.421766
C	-0.562208	2.512570	-3.614885
C	-0.702879	1.581309	-2.593211
C	-1.310148	1.043371	-0.173245
C	-2.507967	2.839626	0.934364
O	-2.440452	3.641335	-0.124761
C	-2.173763	-0.106604	-0.344322
C	-2.677956	-0.741883	-1.458907
C	-3.270538	-1.970139	-1.010431
C	-3.124152	-1.984873	0.369066
O	-2.478990	-0.868531	0.758406
C	-3.527490	-2.934802	1.430545
C	-1.400470	1.892939	1.175221
C	-1.547848	1.099440	2.421955
C	-2.653075	1.220132	3.191089
C	-3.725613	2.104020	2.865273
C	-3.650203	2.906848	1.741841
O	-4.401053	-4.024276	-1.345092
C	-3.902608	-3.022406	-1.831485
C	-3.890300	-2.803103	-3.332810
H	-1.858643	5.257840	-2.039067
H	-0.808946	4.583794	-4.222221
H	-0.130371	2.201280	-4.568760
H	-0.355777	0.557528	-2.724297
H	-2.600638	-0.383487	-2.479306
H	-4.158214	-2.431816	2.182692
H	-4.075665	-3.769226	0.979648
H	-2.636699	-3.315918	1.957381
H	-0.443846	2.445607	1.210369
H	-0.757282	0.396543	2.676394
H	-4.600531	2.123241	3.517853
H	-4.453466	3.593142	1.470277
H	-4.378841	-3.651541	-3.828022
H	-4.414016	-1.868793	-3.592329
H	-2.854618	-2.703790	-3.696920
F	-2.798061	0.481083	4.303029
Rh	0.828782	0.062046	0.063105
Rh	3.021798	-0.993635	0.215034
O	1.708828	1.432208	-1.189622
O	3.703020	0.382894	-1.144769
O	3.440541	0.315449	1.744942
O	2.444007	-2.232162	-1.319234
O	2.214600	-2.313603	1.563800

O	0.173623	-1.372085	1.389952
O	1.392736	1.252305	1.642479
O	0.446905	-1.203590	-1.514043
C	1.309648	-2.076357	-1.848321
C	2.923767	1.299511	-1.530942
C	2.566060	1.138991	2.125621
C	0.987465	-2.234256	1.846974
C	0.415759	-3.269168	2.785967
C	0.924677	-2.989647	-2.987198
C	3.480751	2.353038	-2.457078
C	2.934914	2.100289	3.228843
H	2.074511	2.264227	3.892110
H	3.200231	3.069608	2.776459
H	3.797632	1.725990	3.793424
H	3.818331	3.209723	-1.851434
H	2.696373	2.709029	-3.138380
H	4.341441	1.959797	-3.012758
H	-0.066490	-3.423560	-2.789047
H	0.847642	-2.397814	-3.912850
H	1.670639	-3.782113	-3.120161
H	-0.035145	-4.074883	2.183973
H	-0.375268	-2.825430	3.405417
H	1.206560	-3.702614	3.410827

TS3a

C	-1.851836	2.123212	-0.828476
C	-2.401099	3.356940	-0.435827
C	-2.418320	4.477383	-1.263238
C	-1.922062	4.338975	-2.560278
C	-1.431924	3.101576	-3.005329
C	-1.394479	2.001216	-2.150348
C	-1.831798	1.088453	0.217685
C	-2.860525	2.191302	1.477049
O	-3.036139	3.351290	0.778796
C	-2.320880	-0.230265	-0.094372
C	-2.924283	-0.731876	-1.223955
C	-2.912879	-2.163146	-1.101219
C	-2.341886	-2.435181	0.133175
O	-2.014183	-1.280822	0.735814
C	-2.036443	-3.683068	0.869504
C	-1.502060	1.632627	1.646645
C	-1.376102	0.677030	2.773343
C	-2.481314	0.168180	3.349943
C	-3.815226	0.598449	3.019894
C	-3.989619	1.621918	2.130959
O	-3.153164	-4.359042	-1.943310
C	-3.350088	-3.162360	-2.092307
C	-4.035808	-2.631439	-3.336352
H	-2.849111	5.412862	-0.903246
H	-1.935644	5.196923	-3.236240
H	-1.059066	3.001451	-4.027206
H	-0.974718	1.051672	-2.479991
H	-3.278383	-0.143143	-2.064175
H	-2.439043	-3.634290	1.894148
H	-2.451816	-4.541307	0.330533
H	-0.943698	-3.806810	0.956605
H	-0.682855	2.358818	1.598884
H	-0.384192	0.352234	3.077529

H	-4.657502	0.121058	3.522673
H	-4.975379	2.027230	1.898323
H	-4.343628	-3.472857	-3.969639
H	-4.912171	-2.019369	-3.069698
H	-3.346929	-1.980018	-3.899037
F	-2.379710	-0.771898	4.305637
Rh	0.852844	0.196917	0.085832
Rh	3.072371	-0.654516	-0.200973
O	1.298526	1.591586	-1.338334
O	3.311280	0.670540	-1.742004
O	3.699066	0.780912	1.124106
O	2.294536	-2.051750	-1.485873
O	2.748774	-1.940078	1.354698
O	0.618278	-1.241470	1.535905
O	1.590186	1.473379	1.510517
O	0.248199	-1.125684	-1.349031
C	1.066212	-1.994698	-1.785129
C	2.403508	1.527155	-1.956422
C	2.846962	1.516621	1.700203
C	1.595458	-1.972277	1.876562
C	1.352162	-2.976688	2.974290
C	0.507227	-3.031698	-2.724543
C	2.663866	2.573850	-3.008682
C	3.357062	2.554070	2.666989
H	2.636115	2.700553	3.482222
H	3.459955	3.510918	2.129785
H	4.340122	2.264854	3.058734
H	3.283220	3.369885	-2.564731
H	1.718907	3.013535	-3.351486
H	3.226801	2.137347	-3.844599
H	-0.311659	-3.573714	-2.227066
H	0.072873	-2.527696	-3.601227
H	1.288270	-3.731664	-3.043449
H	1.245287	-3.975392	2.521132
H	0.433932	-2.730495	3.522113
H	2.217163	-3.011958	3.650828

IVa

C	-2.113671	-0.689693	-0.484451
C	-3.187671	-0.152104	0.239225
C	-4.431502	-0.770284	0.289807
C	-4.573484	-1.982525	-0.399631
C	-3.505272	-2.545422	-1.109610
C	-2.262288	-1.898788	-1.156511
C	-0.941595	0.224754	-0.342450
C	-1.529108	1.330491	0.559001
O	-2.861199	1.009493	0.883577
C	0.405830	-0.322133	-0.154645
C	1.593873	-0.195740	-0.809746
C	2.548385	-1.019580	-0.106387
C	1.852588	-1.594669	0.942447
O	0.569063	-1.173554	0.913863
C	2.240288	-2.530112	2.025465
C	-1.187059	1.624532	-0.920531
C	-0.101661	2.589224	-1.144784
C	0.634610	3.040150	-0.107689
C	0.315865	2.764852	1.275382
C	-0.763800	2.014385	1.594710

O	4.702101	-1.942641	0.238153
C	3.980635	-1.209909	-0.417615
C	4.521661	-0.436839	-1.605704
H	-5.251694	-0.328005	0.857039
H	-5.536239	-2.498393	-0.375429
H	-3.643010	-3.493748	-1.633186
H	-1.423585	-2.330227	-1.707427
H	1.774058	0.423146	-1.683257
H	3.303067	-2.774847	1.920603
H	2.058940	-2.077334	3.014388
H	1.641067	-3.454331	1.973096
H	-2.024395	1.664662	-1.623013
H	0.084966	2.970044	-2.150373
H	0.926159	3.245989	2.041663
H	-1.099658	1.891179	2.625758
H	5.589463	-0.658361	-1.725846
H	3.980177	-0.712217	-2.525380
H	4.380566	0.646312	-1.458413
F	1.664519	3.877356	-0.314742

TS4a

C	-0.841355	2.113037	-1.427043
C	0.037365	3.207640	-1.518938
C	0.347073	3.821867	-2.726141
C	-0.210113	3.337498	-3.912876
C	-1.053736	2.227307	-3.865410
C	-1.350003	1.622626	-2.643085
C	-1.089833	1.462406	-0.124280
C	0.390790	3.304420	0.829517
O	0.689068	3.722521	-0.410228
C	-2.347829	0.746634	0.066901
C	-3.506090	0.626071	-0.660956
C	-4.337115	-0.338494	0.014625
C	-3.627474	-0.736826	1.131601
O	-2.453246	-0.074513	1.168481
C	-3.893053	-1.699588	2.226068
C	-0.455920	2.152516	1.061347
C	-0.817464	1.898258	2.438050
C	-0.193608	2.588278	3.454219
C	0.707917	3.627364	3.209329
C	0.984797	3.983321	1.888194
O	-6.273596	-1.682468	0.236319
C	-5.668814	-0.830132	-0.393593
C	-6.256621	-0.224350	-1.654125
H	1.030945	4.672004	-2.715253
H	0.029350	3.818423	-4.863513
H	-1.471718	1.812804	-4.785454
H	-1.945790	0.712920	-2.627966
H	-3.752301	1.171056	-1.564858
H	-3.901957	-1.190590	3.204790
H	-4.863838	-2.177620	2.054218
H	-3.100441	-2.465921	2.261958
H	0.412463	1.253422	0.981208
H	-1.488081	1.079377	2.673032
H	1.177450	4.143182	4.048055
H	1.650875	4.814444	1.653241
H	-7.242520	-0.666828	-1.843770
H	-6.352440	0.868610	-1.550020

H	-5.594441	-0.409975	-2.515431
F	-0.464680	2.251690	4.725802
Rh	0.626877	-0.221360	-0.082935
Rh	2.182084	-2.116250	-0.173015
O	1.020382	0.054645	-2.068873
O	2.376844	-1.742884	-2.184489
O	3.711265	-0.793101	0.202825
O	0.552675	-3.317673	-0.534183
O	1.892714	-2.363040	1.850241
O	0.376975	-0.697317	1.910208
O	2.291815	0.954169	0.322295
O	-0.842687	-1.548515	-0.582562
C	-0.584995	-2.791414	-0.670882
C	1.793470	-0.743087	-2.687291
C	3.453504	0.426633	0.362571
C	1.058607	-1.631538	2.444726
C	0.800059	-1.880023	3.910226
C	-1.750726	-3.690680	-0.999270
C	2.047586	-0.433904	-4.141396
C	4.597705	1.378560	0.606146
H	4.369951	2.014726	1.473630
H	4.701709	2.040286	-0.267953
H	5.532155	0.827636	0.765476
H	2.989052	0.133929	-4.217189
H	1.235853	0.182021	-4.548804
H	2.167751	-1.365036	-4.710969
H	-2.690334	-3.245968	-0.645333
H	-1.810983	-3.800139	-2.094282
H	-1.595849	-4.687065	-0.565509
H	-0.093147	-2.518906	4.004261
H	0.591672	-0.931443	4.423839
H	1.651063	-2.399125	4.368431

TS5a

Rh	0.840524	-0.103760	0.055130
Rh	2.674720	-1.669949	-0.267182
O	1.991294	1.257413	-0.952082
O	3.649035	-0.220086	-1.332788
O	-0.131526	-1.610886	1.084866
O	1.592621	-3.038303	0.824830
O	3.507342	-0.933591	1.458051
O	1.763325	0.450109	1.808680
O	0.094257	-0.781256	-1.740380
O	1.737951	-2.305282	-1.976813
C	3.120462	0.925959	-1.422151
C	0.682491	-1.723512	-2.355363
C	2.885563	-0.058651	2.121367
C	0.442614	-2.736053	1.240007
C	3.500748	0.404390	3.419484
H	3.134288	-0.242827	4.233230
H	4.593654	0.313100	3.377039
H	3.199585	1.437308	3.637364
C	3.906585	2.007304	-2.120230
H	3.240497	2.822212	-2.430210
H	4.651173	2.408639	-1.413922
H	4.449350	1.586759	-2.977572
C	-0.350919	-3.803247	1.955887
H	-0.944499	-3.359045	2.766710

H	-1.050585	-4.261449	1.237675
H	0.313712	-4.585317	2.343050
C	0.069082	-2.159800	-3.663533
H	0.431768	-3.155647	-3.946566
H	-1.026970	-2.147936	-3.588367
H	0.360899	-1.440603	-4.445808
C	-0.984373	1.366139	0.101874
C	-0.440155	2.601765	-0.458379
C	0.944763	4.464052	0.325347
C	-1.109809	1.889554	1.766042
C	-2.444425	2.489571	1.607621
C	-1.030730	0.805483	2.739106
C	-3.576148	1.769513	1.926605
H	-2.509897	3.445422	1.087866
C	-2.155876	0.101433	3.052701
H	-0.041379	0.523871	3.092984
C	-3.411186	0.534068	2.555498
H	-4.578884	2.122666	1.682255
H	-2.119806	-0.789574	3.681055
O	-0.063695	2.830873	1.819653
C	1.084610	4.872598	-1.010334
C	0.464000	4.168053	-2.048824
C	-0.304632	3.029543	-1.781552
H	-0.765357	2.457102	-2.586134
H	0.583679	4.508117	-3.079938
H	1.677833	5.761671	-1.236807
H	1.410956	5.007268	1.148514
C	0.174159	3.339723	0.571027
C	-2.054779	0.622540	-0.471563
C	-2.645739	-0.573413	-0.117605
O	-2.775808	1.167128	-1.523071
C	-3.768882	-0.763188	-0.984929
H	-2.237405	-1.257498	0.615700
C	-3.784538	0.330607	-1.839087
C	-4.655587	0.705351	-2.977092
H	-5.461888	-0.031003	-3.068480
H	-5.075378	1.714165	-2.831858
H	-4.073887	0.725495	-3.914362
C	-4.732656	-1.883929	-0.962555
C	-4.552214	-2.889093	0.158970
H	-3.554602	-3.354550	0.103995
H	-4.619133	-2.379912	1.133986
H	-5.326863	-3.662302	0.085022
O	-5.632318	-1.992838	-1.778081
F	-4.482361	-0.217334	2.813662

TS6a

C	-2.107787	-0.763650	-0.194273
C	-3.103752	-0.250830	0.642284
C	-4.283053	-0.936418	0.903579
C	-4.435948	-2.190725	0.295175
C	-3.444144	-2.723796	-0.537907
C	-2.264247	-2.008415	-0.791342
C	-0.992650	0.248762	-0.252033
C	-1.512512	1.315494	0.662845
O	-2.769625	0.978325	1.150207
C	0.395421	-0.253112	-0.139967
C	1.306501	-0.332259	0.865943

C	2.477643	-0.972751	0.311919
C	2.177718	-1.236893	-1.011949
O	0.923484	-0.803292	-1.281739
C	2.935977	-1.865156	-2.120087
C	-1.280346	1.397677	-1.189951
C	-0.317943	2.375870	-1.535838
C	0.548760	2.931157	-0.620089
C	0.314032	2.944321	0.771462
C	-0.761385	2.299407	1.344271
O	4.680246	-1.834441	0.438954
C	3.750980	-1.277208	0.998467
C	3.850915	-0.856370	2.452583
H	-5.045752	-0.513647	1.558823
H	-5.348294	-2.762588	0.479783
H	-3.591935	-3.704274	-0.995168
H	-1.483929	-2.412552	-1.439170
H	1.167272	0.037358	1.877106
H	3.927849	-2.151375	-1.752977
H	2.410759	-2.759422	-2.495315
H	3.040536	-1.165334	-2.965666
H	-2.170154	1.282844	-1.813777
H	-0.321238	2.787103	-2.548744
H	0.924790	3.625986	1.367246
H	-1.106828	2.575509	2.342781
H	4.838103	-1.133698	2.842757
H	3.704625	0.231680	2.549923
H	3.064555	-1.344191	3.051271
F	1.532412	3.734583	-1.072089

2a

C	-2.067101	-0.465884	-0.593907
C	-2.987532	-0.375352	0.449966
C	-4.125936	-1.168325	0.516564
C	-4.320246	-2.086564	-0.524446
C	-3.405316	-2.196244	-1.579625
C	-2.263122	-1.383103	-1.618461
C	-0.945349	0.530211	-0.328316
C	-1.462826	1.165739	0.968617
O	-2.637550	0.581248	1.370094
C	-0.850785	1.615841	-1.380179
C	-0.080426	2.719362	-1.247113
C	0.610072	3.138242	-0.055537
C	0.253654	2.919630	1.240242
C	-0.871946	2.147090	1.686319
C	0.374930	-0.165053	-0.124657
C	1.591279	-0.109573	-0.731582
C	2.431051	-1.076737	-0.059598
C	1.642011	-1.651975	0.919260
O	0.405333	-1.102167	0.874950
F	1.646733	3.973586	-0.290272
C	1.889042	-2.692786	1.945402
O	4.468026	-2.234625	0.286530
C	3.848525	-1.389407	-0.337504
C	4.509038	-0.596444	-1.449639
H	-4.829310	-1.073110	1.344712
H	-5.203332	-2.729475	-0.508248
H	-3.581015	-2.923679	-2.374737
H	-1.537459	-1.473207	-2.430373

H	-1.431668	1.471860	-2.294418
H	0.021150	3.399073	-2.099325
H	0.829427	3.466998	1.991447
H	-1.298856	2.379820	2.664962
H	1.864004	0.550121	-1.548857
H	2.925312	-3.037839	1.858380
H	1.715846	-2.290165	2.957243
H	1.202390	-3.544720	1.808726
H	5.552848	-0.918154	-1.553042
H	3.977172	-0.750188	-2.402683
H	4.472310	0.482720	-1.228766

7a

C	-0.977381	-1.669594	-0.773054
C	-1.711854	-2.005668	0.371223
C	-1.948012	-3.343237	0.710998
C	-1.451414	-4.357999	-0.103035
C	-0.728143	-4.042608	-1.260431
C	-0.496598	-2.706291	-1.583094
C	-0.648908	-0.221177	-1.063272
C	-2.316768	0.241543	0.778454
O	-2.237069	-1.058145	1.205203
C	0.769394	0.078861	-0.662363
C	1.699840	-0.580418	0.080335
C	2.860081	0.281199	0.147785
C	2.535266	1.416183	-0.570522
O	1.275900	1.289793	-1.058833
C	3.267922	2.664949	-0.888850
C	-1.615721	0.704525	-0.342481
C	-1.769748	2.041257	-0.728251
C	-2.598294	2.881429	0.005775
C	-3.287719	2.427426	1.129685
C	-3.146585	1.095611	1.512138
O	5.063954	0.817233	0.831215
C	4.141390	0.019570	0.837211
C	4.257866	-1.306656	1.564672
H	-2.526981	-3.557788	1.610710
H	-1.636636	-5.401464	0.161856
H	-0.344215	-4.836464	-1.904220
H	0.083253	-2.449216	-2.473427
H	1.574674	-1.563448	0.524588
H	2.724101	3.544136	-0.504969
H	4.261992	2.618708	-0.430307
H	3.370026	2.791421	-1.979632
H	-0.731964	-0.037044	-2.148787
H	-1.226492	2.437525	-1.587234
H	-3.928878	3.115341	1.682922
H	-3.677839	0.694382	2.376474
H	5.249696	-1.379589	2.028006
H	3.478625	-1.391478	2.339513
H	4.111167	-2.145888	0.865488
F	-2.734499	4.161820	-0.373245

5e

C	1.169742	1.789044	-0.046546
C	2.487541	1.248674	-0.045000
C	3.568292	2.143512	-0.022298
C	3.374241	3.525016	-0.013603

C	2.078616	4.052697	-0.028306
C	0.988278	3.190382	-0.044197
C	0.019577	0.955565	-0.004696
C	2.740636	-0.212651	-0.053248
C	2.079551	-1.068621	-0.952440
C	2.337586	-2.438422	-0.964393
C	3.265760	-2.958410	-0.064952
C	3.942358	-2.141154	0.837001
C	3.677173	-0.771931	0.834241
F	3.515086	-4.273882	-0.069398
C	-1.004281	0.288805	0.044776
C	-2.096833	-0.587731	0.098902
C	-3.441976	-0.342943	0.073673
C	-4.056987	1.013350	-0.061508
O	-5.225054	1.138906	-0.386515
C	-3.216160	2.247764	0.200520
O	-3.759780	-2.688481	0.145782
C	-4.300430	-1.597737	0.148362
C	-5.801744	-1.494103	0.257723
H	4.582985	1.740608	-0.035539
H	4.238561	4.193071	-0.005407
H	1.921453	5.133322	-0.026016
H	-0.029473	3.584636	-0.042257
H	1.365328	-0.655969	-1.665547
H	1.834821	-3.108470	-1.663743
H	4.658007	-2.584944	1.531034
H	4.189873	-0.127157	1.551000
H	-1.842381	-1.655556	0.153873
H	-2.626389	2.161152	1.124431
H	-2.501829	2.399751	-0.623580
H	-3.892446	3.110553	0.253148
H	-6.199040	-2.499034	0.450070
H	-6.099436	-0.796582	1.054220
H	-6.222789	-1.080466	-0.669318

VIIe

C	1.775685	0.767711	2.489534
C	3.014445	1.095027	1.872156
C	4.190785	0.612010	2.460263
C	4.157821	-0.172006	3.615171
C	2.934570	-0.500754	4.209264
C	1.750468	-0.036020	3.645633
C	0.550022	1.182410	1.900312
C	3.060332	1.842898	0.592859
C	2.343926	3.035690	0.400638
C	2.325365	3.673394	-0.838624
C	3.036883	3.110450	-1.893023
C	3.787128	1.949611	-1.731786
C	3.793556	1.323525	-0.486763
F	2.989094	3.693613	-3.101712
C	-0.492687	1.646115	1.440380
C	-1.542116	2.435785	0.931393
C	-2.885627	2.319741	1.108064
C	-3.533534	1.217963	1.886903
O	-4.669840	0.863109	1.618173
C	-2.771327	0.538863	3.000673
O	-3.153807	4.141154	-0.379617
C	-3.712701	3.340518	0.347213

C	-5.212644	3.379442	0.513776
H	5.149545	0.865654	2.003083
H	5.092670	-0.528251	4.054414
H	2.906331	-1.120963	5.107608
H	0.783772	-0.302596	4.075183
H	1.791560	3.474068	1.232100
H	1.761800	4.593633	-1.000257
H	4.339714	1.543173	-2.580606
H	4.346419	0.392838	-0.358143
H	-1.231501	3.229528	0.239243
H	-2.106903	-0.228763	2.572954
H	-2.148752	1.237952	3.575842
H	-3.500075	0.042247	3.655113
H	-5.585192	4.301863	0.050082
H	-5.665353	2.500451	0.033353
H	-5.506208	3.326127	1.572087
Rh	-0.386413	-2.266261	-1.519522
Rh	-0.198588	-0.451553	0.043926
O	1.554434	-2.769281	-1.133446
O	1.762858	-1.031009	0.275906
O	0.323397	0.756913	-1.519947
O	-0.739463	-1.760746	1.528841
O	-2.187180	-0.105896	-0.325391
O	-2.324603	-1.734337	-1.864670
O	0.228274	-0.962373	-2.973309
O	-0.997143	-3.441580	0.050137
C	-1.050194	-2.954211	1.214267
C	2.210378	-2.052316	-0.325222
C	0.436486	0.252462	-2.679755
C	-2.818665	-0.782011	-1.197040
C	-4.248001	-0.387415	-1.450926
C	-1.553740	-3.838806	2.325804
C	3.649066	-2.426003	-0.071348
C	0.878090	1.165454	-3.793511
H	0.731668	2.216687	-3.521508
H	0.335699	0.916872	-4.715676
H	1.950865	1.000811	-3.977771
H	4.016175	-1.944620	0.843489
H	4.256359	-2.091899	-0.927835
H	3.745039	-3.518230	-0.004656
H	-1.006449	-3.629035	3.254680
H	-2.616816	-3.606302	2.500763
H	-1.464553	-4.896142	2.047995
H	-4.251410	0.557391	-2.018354
H	-4.754962	-0.198004	-0.494290
H	-4.764267	-1.160177	-2.032900

TS7e

C	0.772512	-2.397788	-0.970970
C	1.793982	-2.961913	-0.155150
C	1.856550	-4.358125	-0.042568
C	0.951167	-5.185608	-0.708146
C	-0.059321	-4.623165	-1.492818
C	-0.160416	-3.238967	-1.604775
C	0.653787	-0.964451	-1.142122
C	2.778561	-2.109515	0.555526
C	2.367435	-0.975197	1.276545
C	3.301713	-0.073140	1.785118

C	4.655548	-0.336247	1.602764	Rh	-3.113107	0.867302	0.812261
C	5.099890	-1.493810	0.972198	O	-1.126753	-1.490554	1.127247
C	4.153370	-2.373582	0.445701	O	-2.869073	-0.589274	2.237337
F	5.564214	0.577465	2.009324	O	-1.858355	2.127967	1.845119
C	1.399839	0.039988	-1.441139	O	-4.244366	-0.422618	-0.307634
C	1.705163	1.387680	-1.268276	O	-3.221751	2.273092	-0.679761
C	3.020638	1.785741	-1.210894	O	-1.316539	1.539721	-1.633245
C	3.913088	0.672570	-1.546953	O	-0.037800	1.175534	0.929675
O	3.361174	-0.408566	-1.807451	O	-2.444210	-1.128791	-1.466151
C	5.411629	0.759351	-1.625456	C	-3.687762	-1.119327	-1.200621
O	2.393695	3.939272	-0.521821	C	-1.960854	-1.452911	2.086308
C	3.312680	3.161191	-0.723995	C	-0.613378	2.032096	1.678574
C	4.735800	3.561640	-0.395860	C	-2.305942	2.336985	-1.544642
H	2.624520	-4.797952	0.597697	C	-2.351614	3.463919	-2.545200
H	1.025473	-6.270235	-0.599383	C	-4.555037	-2.038544	-2.024866
H	-0.779758	-5.263823	-2.006502	C	-1.862349	-2.561040	3.104573
H	-0.964337	-2.780011	-2.179068	C	0.294332	3.001121	2.391285
H	1.306542	-0.774758	1.416858	H	-0.285628	3.692371	3.013868
H	2.987570	0.834844	2.301592	H	0.878174	3.556613	1.640159
H	6.170994	-1.669992	0.859743	H	1.007151	2.441565	3.016244
H	4.489067	-3.247021	-0.116505	H	-2.340594	-2.262369	4.045654
H	0.889815	2.089197	-1.097797	H	-0.811156	-2.835813	3.264383
H	5.720534	1.562344	-2.311053	H	-2.384707	-3.446541	2.707747
H	5.837335	0.980765	-0.637021	H	-4.291459	-3.082038	-1.791278
H	5.802751	-0.201632	-1.979061	H	-5.616210	-1.868419	-1.807812
H	4.723767	4.584724	-0.000485	H	-4.350751	-1.878714	-3.093555
H	5.159634	2.880832	0.359571	H	-3.343324	3.932045	-2.553317
H	5.385275	3.521216	-1.282682	H	-2.085167	3.092578	-3.544381
Rh	-1.154619	-0.022056	-0.309174	H	-1.600030	4.216988	-2.257815

VIIIe

C	-0.875706	2.160776	-1.056201
C	-1.933686	2.787359	-0.335943
C	-2.123108	4.168361	-0.489699
C	-1.305486	4.927349	-1.327618
C	-0.250123	4.315094	-2.009750
C	-0.021450	2.950912	-1.852560
C	-0.619437	0.721916	-1.002997
C	-2.800034	2.025539	0.596306
C	-2.249140	1.100790	1.500836
C	-3.068496	0.327224	2.322980
C	-4.448437	0.495790	2.255165
C	-5.027084	1.426591	1.393918
C	-4.196436	2.185226	0.568198
F	-5.242991	-0.253181	3.036244
C	-1.647930	-0.186998	-1.263385
C	-1.751565	-1.557599	-1.042956
C	-3.097837	-1.930998	-1.254299
C	-3.763624	-0.760925	-1.644941
O	-2.913421	0.260825	-1.670648
C	-5.175169	-0.440536	-1.976777
O	-2.820604	-4.162052	-0.612937
C	-3.593480	-3.309318	-1.005826
C	-5.059041	-3.615664	-1.230850
H	-2.914377	4.657009	0.083385
H	-1.477621	6.001725	-1.427307
H	0.407237	4.905407	-2.652327
H	0.818202	2.464387	-2.347492
H	-1.167881	0.983615	1.564423
H	-2.648230	-0.404904	3.013678
H	-6.112872	1.538219	1.375330
H	-4.640988	2.889975	-0.137669
H	-0.943811	-2.204639	-0.727457
H	-5.636760	-1.211651	-2.606712
H	-5.767278	-0.356207	-1.049243
H	-5.217885	0.527932	-2.492065
H	-5.249974	-4.660430	-0.956199
H	-5.696567	-2.952293	-0.625178
H	-5.330629	-3.461018	-2.287717
Rh	1.133788	0.036948	-0.275150
Rh	3.191811	-0.785318	0.794555
O	0.120213	-1.069654	1.130337
O	2.001157	-1.894150	2.056836
O	3.145719	-2.338506	-0.557321
O	3.056209	0.833061	2.062063
O	4.242862	0.361380	-0.544821
O	2.361212	1.036361	-1.588729
O	1.218021	-1.619978	-1.485373
O	1.206059	1.617369	1.034561
C	2.131201	1.673115	1.910494
C	0.751918	-1.814676	1.952562
C	2.189836	-2.439061	-1.369297
C	3.625800	1.004067	-1.432953
C	4.431772	1.824635	-2.410917
C	2.108552	2.879204	2.817751
C	-0.108307	-2.656403	2.863258
C	2.151930	-3.639636	-2.283321

H	3.093625	-4.198305	-2.224722
H	1.955785	-3.317132	-3.315896
H	1.318458	-4.292267	-1.977992
H	0.510507	-3.339238	3.457201
H	-0.835887	-3.220612	2.260493
H	-0.677495	-1.996018	3.536079
H	1.074928	3.117356	3.104059
H	2.731772	2.705710	3.703525
H	2.507169	3.743420	2.262454
H	5.505514	1.687478	-2.236661
H	4.166267	2.886883	-2.295487
H	4.171717	1.530789	-3.438704

TS8e

C	1.207126	-1.950009	-1.218372
C	1.973834	-2.987993	-0.626802
C	2.265616	-4.170186	-1.326892
C	1.781340	-4.316826	-2.621835
C	1.025973	-3.286945	-3.214807
C	0.723824	-2.114993	-2.522989
C	1.035515	-0.729257	-0.381524
C	2.421785	-2.564703	0.680302
C	1.615328	-1.470571	1.165273
C	2.107503	-0.668714	2.251326
C	3.294798	-1.018860	2.837926
C	4.029244	-2.156225	2.421818
C	3.597152	-2.930255	1.352772
F	3.787863	-0.305751	3.859421
C	1.997780	0.345023	-0.619953
C	1.936360	1.710007	-0.598759
C	3.261489	2.205862	-0.836827
C	4.072465	1.089844	-0.976361
O	3.321832	-0.023852	-0.846260
C	5.520474	0.869142	-1.246234
O	2.698579	4.478439	-0.780566
C	3.578849	3.647000	-0.914964
C	5.015864	4.065115	-1.166727
H	2.853340	-4.962701	-0.857407
H	1.987417	-5.230746	-3.183262
H	0.672609	-3.407757	-4.241948
H	0.131875	-1.326371	-2.983090
H	0.548266	-1.749890	1.345940
H	1.516193	0.179908	2.597694
H	4.961764	-2.383603	2.943368
H	4.208385	-3.761453	0.995785
H	1.049961	2.308311	-0.441062
H	5.810703	1.235586	-2.244355
H	6.155645	1.385650	-0.510589
H	5.735974	-0.206813	-1.199810
H	5.066073	5.160527	-1.204810
H	5.676776	3.695389	-0.366403
H	5.386669	3.646462	-2.115794
Rh	-0.960661	-0.054718	-0.102968
Rh	-3.240717	0.711178	0.426004
O	-1.241330	-1.539680	1.289924
O	-3.319640	-0.842581	1.793759
O	-2.392698	1.938046	1.850085
O	-3.912459	-0.560519	-1.041389

O	-2.956964	2.195488	-0.965558
O	-0.879508	1.470500	-1.467447
O	-0.309909	1.194506	1.406641
O	-1.821184	-1.250164	-1.537125
C	-3.082808	-1.243601	-1.699138
C	-2.343206	-1.613766	1.940521
C	-1.148688	1.926150	2.030475
C	-1.863922	2.270161	-1.588078
C	-1.669228	3.408667	-2.559943
C	-3.619302	-2.115610	-2.810348
C	-2.441784	-2.730498	2.950230
C	-0.568076	2.845680	3.078844
H	-1.343045	3.505453	3.486615
H	0.245838	3.438261	2.635322
H	-0.132956	2.243463	3.892201
H	-3.411329	-2.703128	3.461156
H	-1.626357	-2.635573	3.683614
H	-2.312329	-3.696412	2.438594
H	-2.961049	-2.978866	-2.973576
H	-4.642801	-2.438577	-2.580054
H	-3.647815	-1.521290	-3.738267
H	-2.572383	4.027612	-2.618404
H	-1.418429	3.006050	-3.552725
H	-0.813304	4.018278	-2.230296

IXe

C	1.439828	-0.507222	2.202779
C	0.186996	0.167344	2.532345
C	-0.721382	-0.427065	3.458932
C	-0.425103	-1.658595	3.977418
C	0.770251	-2.360212	3.600788
C	1.681029	-1.814977	2.733760
C	2.207648	0.308747	1.367648
C	0.146322	1.412377	1.874686
C	1.409128	1.546963	1.053728
C	1.943432	2.943316	0.962960
C	1.105048	3.962325	1.242951
C	-0.227560	3.795266	1.777449
C	-0.677918	2.553357	2.119071
F	1.503254	5.234494	1.060640
C	3.418115	-0.003833	0.683199
C	4.157912	0.664652	-0.267766
C	5.242568	-0.193486	-0.640433
C	5.106450	-1.343865	0.119661
O	4.012936	-1.229415	0.907730
C	5.874358	-2.612360	0.252159
O	6.176984	1.249313	-2.227928
C	6.253692	0.177365	-1.656663
C	7.370789	-0.799998	-1.965726
H	-1.648037	0.087846	3.716774
H	-1.113335	-2.131176	4.682131
H	0.953503	-3.350111	4.026007
H	2.589527	-2.349350	2.461644
H	1.103927	1.311483	0.007064
H	2.937789	3.145380	0.565557
H	-0.824386	4.693073	1.945727
H	-1.648557	2.421567	2.599384
H	3.970556	1.644710	-0.694021

H	5.949486	-3.144944	-0.708518
H	6.901275	-2.432385	0.608113
H	5.370768	-3.269946	0.973192
H	8.028057	-0.359358	-2.725664
H	7.955573	-1.028432	-1.060599
H	6.964306	-1.752769	-2.341053
Rh	-1.343659	0.043389	0.182733
Rh	-2.583390	-0.738306	-1.724383
O	-1.093911	1.815066	-0.828624
O	-2.308554	1.100851	-2.583454
O	-0.807632	-1.373383	-2.542475
O	-4.272398	-0.050788	-0.786941
O	-2.789435	-2.545360	-0.788661
O	-1.662163	-1.805161	1.014592
O	0.340568	-0.665820	-0.741595
O	-3.109205	0.705868	0.990506
C	-4.184890	0.508495	0.344143
C	-1.624592	1.970246	-1.971781
C	0.259805	-1.208369	-1.888034
C	-2.293726	-2.692009	0.366679
C	-2.489607	-4.020592	1.053162
C	-5.469511	0.948641	1.000853
C	-1.441943	3.315908	-2.625694
C	1.552310	-1.710354	-2.480200
H	1.813146	-2.662475	-1.990634
H	2.361401	-0.996526	-2.269450
H	1.446553	-1.879198	-3.558739
H	-2.173517	4.017058	-2.192622
H	-1.614035	3.247461	-3.706867
H	-0.438058	3.705661	-2.409650
H	-5.289158	1.807891	1.659675
H	-6.224110	1.187753	0.240691
H	-5.850605	0.116763	1.615359
H	-2.718910	-4.804192	0.320435
H	-3.335173	-3.932345	1.754279
H	-1.594319	-4.274361	1.636626

TS9e

C	-0.490628	2.360887	1.640880
C	-1.784628	2.861470	1.284224
C	-2.765971	3.047027	2.276698
C	-2.452261	2.758788	3.596313
C	-1.172485	2.268093	3.947566
C	-0.196746	2.057760	2.986789
C	0.302819	2.186695	0.446140
C	-1.843367	3.040734	-0.138604
C	-0.579697	2.596400	-0.698621
C	-0.294457	2.842604	-2.078539
C	-1.324818	3.322396	-2.856030
C	-2.599431	3.651827	-2.347895
C	-2.848750	3.519316	-0.987615
F	-1.110981	3.508619	-4.168603
C	1.707927	1.910618	0.337952
C	2.527541	1.583274	-0.713049
C	3.796657	1.225943	-0.155299
C	3.681746	1.397296	1.215627
O	2.429133	1.804897	1.507232
C	4.597755	1.227789	2.376238

O	4.733993	0.415818	-2.142127
C	4.905846	0.682370	-0.963935
C	6.246287	0.439346	-0.298670
H	-3.758925	3.415023	2.008626
H	-3.202060	2.907702	4.377186
H	-0.955634	2.044064	4.994798
H	0.779365	1.657158	3.253101
H	-0.652917	1.306441	-0.574609
H	0.663138	2.603098	-2.533756
H	-3.356629	4.024643	-3.038910
H	-3.816633	3.816958	-0.578323
H	2.265082	1.498549	-1.759432
H	4.886307	0.173253	2.514026
H	5.524133	1.809539	2.256874
H	4.091195	1.564906	3.290468
H	6.959793	0.084270	-1.052651
H	6.627630	1.359060	0.172196
H	6.151725	-0.318393	0.495907
Rh	-0.464819	-0.430670	0.000533
Rh	-0.734786	-2.811841	-0.234528
O	-2.181887	-0.235242	-1.112608
O	-2.358268	-2.458744	-1.427790
O	0.520116	-2.720534	-1.858582
O	-1.943451	-2.736208	1.427473
O	0.918081	-3.045646	0.959377
O	1.213105	-0.818732	1.107135
O	0.655795	-0.478686	-1.712272
O	-1.603861	-0.522442	1.687094
C	-2.104507	-1.635766	2.033355
C	-2.744921	-1.266477	-1.594095
C	0.952524	-1.596214	-2.244108
C	1.550172	-2.020394	1.338808
C	2.832016	-2.221549	2.108043
C	-2.937599	-1.645348	3.289678
C	-3.997725	-1.042944	-2.401660
C	1.900975	-1.546595	-3.412412
H	2.123107	-2.556565	-3.776636
H	2.825544	-1.031520	-3.105997
H	1.447719	-0.949221	-4.218412
H	-4.074822	-1.796459	-3.196455
H	-4.008981	-0.027430	-2.817112
H	-4.867722	-1.160462	-1.735398
H	-3.231830	-0.623636	3.559890
H	-3.818137	-2.287714	3.151430
H	-2.336064	-2.074903	4.106766
H	2.917068	-3.256855	2.459108
H	2.875565	-1.518331	2.951191
H	3.676359	-1.995697	1.437156

6e

C	-1.233436	-1.541361	-0.594003
C	-2.451860	-1.217381	0.038569
C	-3.282253	-2.230484	0.525401
C	-2.878472	-3.561925	0.379412
C	-1.663106	-3.878205	-0.241324
C	-0.830337	-2.863797	-0.733356
C	-0.521101	-0.272226	-1.050746
C	-2.592824	0.245321	0.065420

C	-1.460825	0.819139	-0.550808
C	-1.309427	2.197011	-0.643403
C	-2.325256	2.994033	-0.111922
C	-3.460667	2.454059	0.495219
C	-3.597287	1.066001	0.586627
F	-2.205417	4.328433	-0.185961
C	0.886036	-0.142464	-0.574962
C	2.086880	-0.022203	-1.202727
C	3.089597	0.060828	-0.168502
C	2.408382	-0.016255	1.032102
O	1.082207	-0.138721	0.782771
C	2.796219	0.005419	2.470231
O	4.933925	0.246834	-1.598128
C	4.533991	0.199158	-0.448696
C	5.497895	0.279514	0.720064
H	-4.228733	-1.990445	1.015597
H	-3.516482	-4.364513	0.757121
H	-1.362113	-4.923615	-0.341643
H	0.121355	-3.106934	-1.212777
H	-0.481154	-0.245887	-2.153595
H	-0.434869	2.660623	-1.103768
H	-4.219204	3.131382	0.891175
H	-4.479909	0.636054	1.065230
H	2.281678	0.007818	-2.271276
H	3.474217	-0.824629	2.723104
H	3.307196	0.942383	2.741518
H	1.892467	-0.086463	3.087354
H	6.519176	0.379243	0.331624
H	5.263393	1.142350	1.363552
H	5.429783	-0.623248	1.347720

TS11e

C	-0.269106	2.685077	-1.373355
C	-0.248816	3.557310	-0.263562
C	0.530711	4.693887	-0.218158
C	1.359575	4.914834	-1.340958
C	1.341913	4.051678	-2.448098
C	0.512367	2.917998	-2.502603
C	-1.200704	1.754716	-0.739586
C	-1.357959	2.788024	0.463002
C	-1.335943	2.338747	1.875902
C	-2.479641	1.884918	2.442404
C	-3.720989	1.979776	1.723038
C	-3.852019	2.720128	0.563778
C	-2.695197	3.216493	-0.038190
F	-4.800079	1.441814	2.302676
C	-1.907379	0.567186	-1.013348
C	-2.612670	-0.295632	-0.182791
C	-3.125624	-1.337882	-1.014026
C	-2.697636	-1.057437	-2.303703
O	-2.004394	0.101201	-2.314577
C	-2.795294	-1.803704	-3.577209
O	-4.067199	-3.491264	-1.308235
C	-3.812402	-2.559692	-0.559662
C	-4.146849	-2.621215	0.918612
H	0.539718	5.377097	0.634288
H	2.030753	5.777138	-1.350885
H	1.996892	4.271875	-3.295314

H	0.513867	2.247851	-3.361709
H	-0.380075	2.299780	2.394939
H	-2.500807	1.455743	3.446045
H	-4.843686	2.891410	0.141496
H	-2.736605	3.846607	-0.925062
H	-2.602737	-0.262949	0.897491
H	-3.486291	-2.644751	-3.452691
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H	-4.709462	-1.729070	1.236134
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Rh	2.478357	-1.492736	0.693210
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O	1.514146	-1.859882	2.464855
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O	3.290118	0.221920	1.467603
O	3.345220	-1.049019	-1.104850
O	1.580979	0.210185	-1.714898
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O	1.444826	1.401171	0.949793
C	2.612384	1.289345	1.434078
C	0.336742	-1.430369	2.630032
C	0.484145	-2.998886	-0.744732
C	2.732048	-0.286192	-1.907595
C	3.416514	0.082761	-3.198891
C	3.215985	2.536296	2.028267
C	-0.373590	-1.813118	3.904263
C	-0.121733	-4.210279	-1.406551
H	0.230789	-4.249648	-2.450234
H	-1.217536	-4.134248	-1.419948
H	0.204226	-5.127213	-0.899391
H	-1.091529	-1.033607	4.191246
H	0.350759	-1.995969	4.708041
H	-0.933035	-2.745890	3.725181
H	2.708521	2.759964	2.980350
H	4.287509	2.397853	2.215834
H	3.040998	3.384326	1.350934
H	4.378515	-0.434608	-3.292811
H	3.570722	1.172653	-3.218089
H	2.761671	-0.170454	-4.045742

Xe

C	-2.124363	-0.898493	-0.495395
C	-2.898466	-0.067508	0.329184
C	-4.156678	-0.428204	0.773258
C	-4.616913	-1.698838	0.357993
C	-3.840744	-2.530650	-0.454472
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C	-1.865671	1.026547	0.378802
C	-1.455931	1.409480	-1.068167
C	-0.547495	2.569235	-1.158960
C	-0.031507	3.125939	-0.041846
C	-0.395319	2.737766	1.298738
C	-1.341987	1.778767	1.488956
F	0.824283	4.154816	-0.139491

C	0.425654	-0.317159	-0.389540
C	1.645720	0.299948	-0.460849
C	2.630444	-0.681833	-0.090905
C	1.936589	-1.844120	0.190858
O	0.612781	-1.621814	0.016908
C	2.309565	-3.222213	0.616345
O	4.496409	0.711851	-0.338940
C	4.080372	-0.395533	-0.050433
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H	-4.761014	0.203862	1.427875
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H	-4.234098	-3.509291	-0.740522
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H	-0.333051	3.013671	-2.131949
H	0.048910	3.287923	2.129368
H	-1.706340	1.544353	2.491482
H	1.865389	1.325090	-0.733614
H	2.957032	-3.719301	-0.123345
H	2.849017	-3.221452	1.576286
H	1.396950	-3.821741	0.734819
H	6.058201	-1.122680	0.327287
H	4.801582	-1.866828	1.371603
H	4.941236	-2.368897	-0.323703

TS12e

C	-2.135586	-0.857050	-0.615179
C	-2.900470	-0.169987	0.344679
C	-4.170039	-0.588723	0.714220
C	-4.633700	-1.762759	0.085297
C	-3.864003	-2.450785	-0.861893
C	-2.579345	-2.004217	-1.242950
C	-0.981189	0.145945	-0.530129
C	-1.838919	0.854263	0.545033
C	-1.341491	1.448280	-1.148085
C	-0.541420	2.620419	-1.046973
C	0.046928	3.017550	0.132891
C	-0.354436	2.586049	1.419139
C	-1.379014	1.675843	1.591407
F	0.889145	4.066364	0.098272
C	0.411772	-0.268682	-0.324494
C	1.612880	0.090612	-0.855538
C	2.611619	-0.725176	-0.213879
C	1.932108	-1.532915	0.680739
O	0.609583	-1.255737	0.612911
C	2.322474	-2.590180	1.654987
O	4.453365	0.150123	-1.365428
C	4.054249	-0.633158	-0.522945
C	5.018392	-1.531756	0.229149
H	-4.777858	-0.070387	1.458970
H	-5.620017	-2.153509	0.347761
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H	-0.487505	3.306360	-1.896135
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H	-1.877484	1.603956	2.561601
H	1.808088	0.851738	-1.604233

H	2.836519	-3.430635	1.163227
H	2.999286	-2.199924	2.431264
H	1.419895	-2.976762	2.147002
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8e

C	-2.079255	-0.726582	-0.711900
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C	-3.845943	-1.077070	0.945296
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C	-1.007437	1.542554	-1.478560
C	-0.535086	2.756595	-1.122557
C	-0.140497	3.178238	0.206240
C	-0.592689	2.759970	1.420736
C	-1.555863	1.709994	1.644126
F	0.686880	4.244625	0.192107
C	0.382414	-0.156479	-0.321692
C	1.618890	0.195855	-0.768790
C	2.555096	-0.719396	-0.164650
C	1.804358	-1.574297	0.621563
O	0.497556	-1.233768	0.522400
C	2.104325	-2.733045	1.508581
O	4.481283	0.170059	-1.156457
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H	1.166312	-3.106484	1.940873
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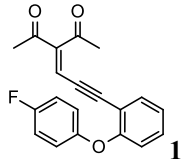
H	4.805188	-1.584881	1.392559
H	4.623745	-2.702925	0.027695

18. Reference.

1. a) D. M. T. Chan, K. L. Monaco, R.-P. Wang, M. P. Winters, Tetrahedron Lett., **1998**, 39, 2933; b) J. W. Lockner, D. D. Dixon, R. Risgaard, P. S. Baran, *Org. Lett.*, **2011**, *13*, 5628.
2. a) D. Zhu, J. Ma, K. Luo, H. Fu, L. Zhang, S. Zhu, *Angew. Chem. Int. Ed*., **2016**, *55*, 8452; b) D. Zhu, L. Chen, H. Zhang, Z. Ma, H. Jiang, S. Zhu, *Angew. Chem. Int. Ed.*, **2018**, *57*, 12405.
3. G. Shi, D. Chen, H. Jiang, Y. Zhang, Y. Zhang, *Org. Lett.*, **2016**, *18*, 2958.
4. Z. Liu, H. Tan, L. Wang, T. Fu, Y. Xia, Y. Zhang, J. Wang, *Angew. Chem. Int. Ed*., **2015**, *54*, 3056.
5. C. Soldi, K. N. Lamb, R. A. Squitieri, M. G.-Lopez, M. J. D. Maso, J. T. Shaw, *J. Am. Chem. Soc.*, **2014**, *136*, 15142.
6. T. Fujita, I. Takahashi, M. Hayashi, J. Wang, K. Fuchibe, J. Ichikawa, *Eur. J. Org. Chem.*, **2017**, 262.
7. Gaussian 16, Revision C.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2016.
8. (a) A. D. Becke, *J. Chem. Phys.*, **1993**, *98*, 5648-5652; (b) C. Lee, W. Yang, R. G. Parr, *Phys. Rev. B*, **1988**, *37*, 785-789.
9. (a) F. Weigend and R. Ahlrichs, *Phys. Chem. Chem. Phys.*, **2005**, *7*, 3297-3305. (b) F. Weigend, *Phys. Chem. Chem. Phys.*, **2006**, *8*, 1057-1065.
10. S. Grimme, S. Ehrlich, L. Goerigk, *J. Comp. Chem.*, **2011**, *32*, 1456-1465.
11. Y. Zhao and D. G. Truhlar, *Theor. Chem. Acc.*, **2008**, *120*, 215-241.
12. A. V. Marenich, C. J. Cramer, D. G. Truhlar, *J. Phys. Chem. B*, **2009**, *113*, 6378-6396.
13. G. Luchini, J. V. Alegre-Requena, I. Funes-Ardoiz, R. S. Paton, *F1000Research*, **2020**, *9*, 291.
14. CYLview20, C. Y. Legault, Université de Sherbrooke, 2020 (http://www.cylview.org).

19. Spectra of NMR



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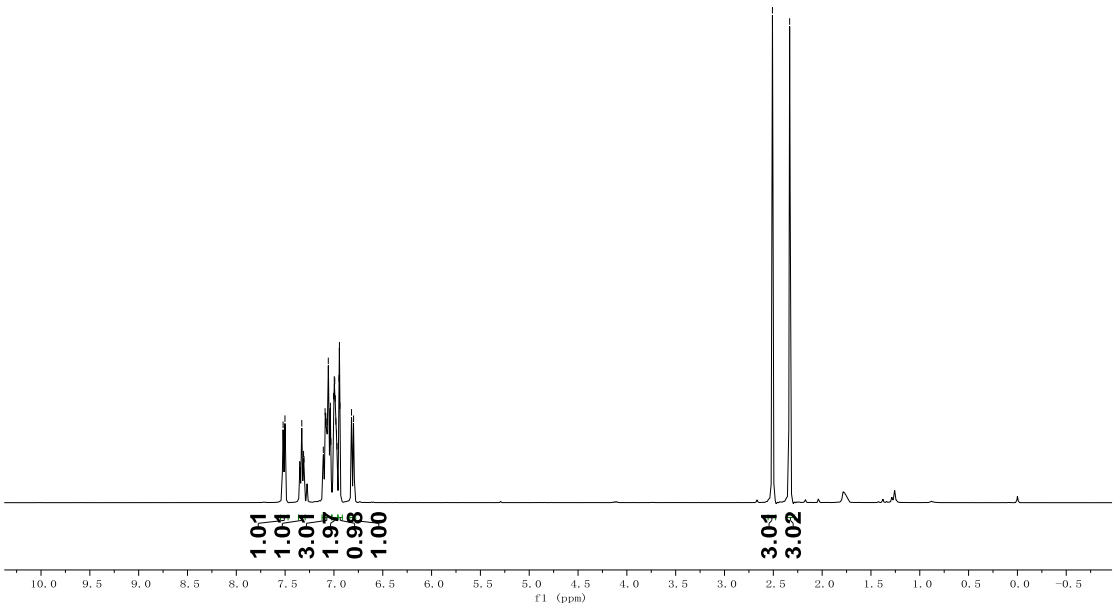

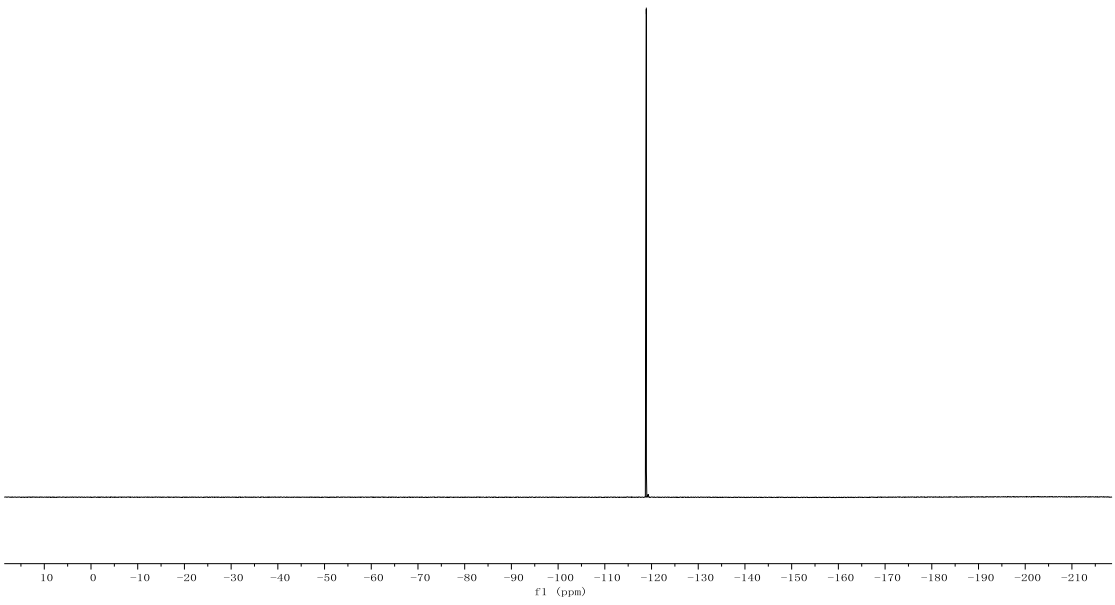

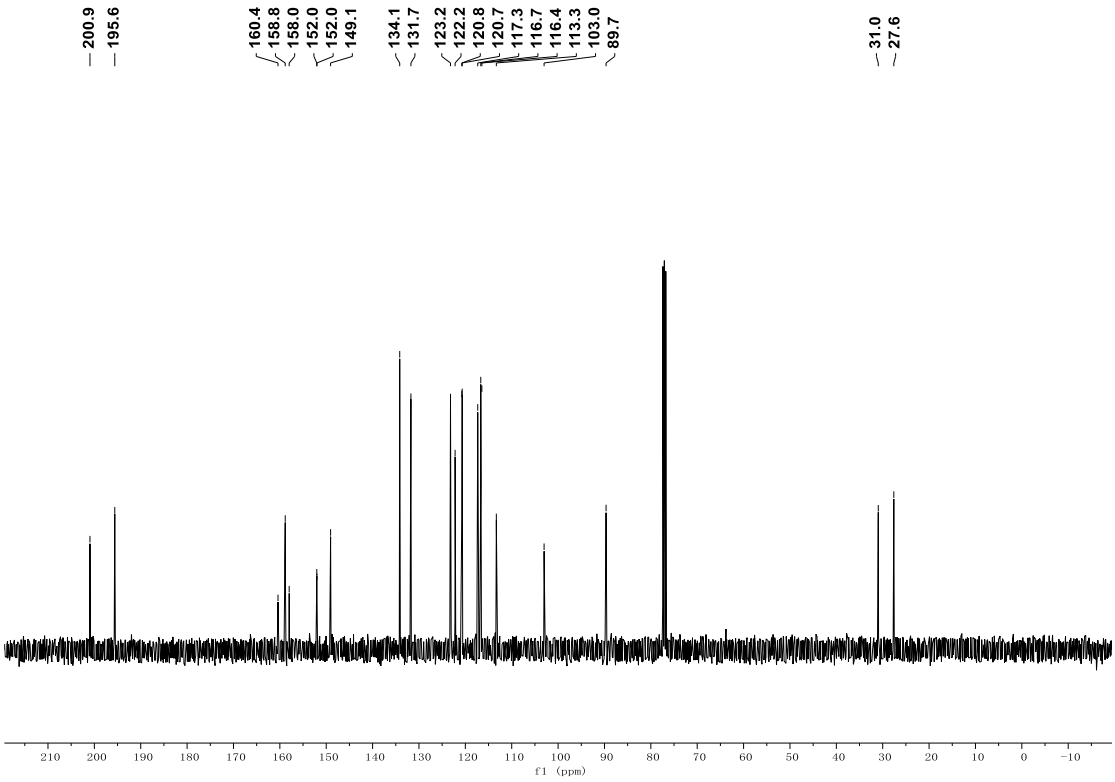
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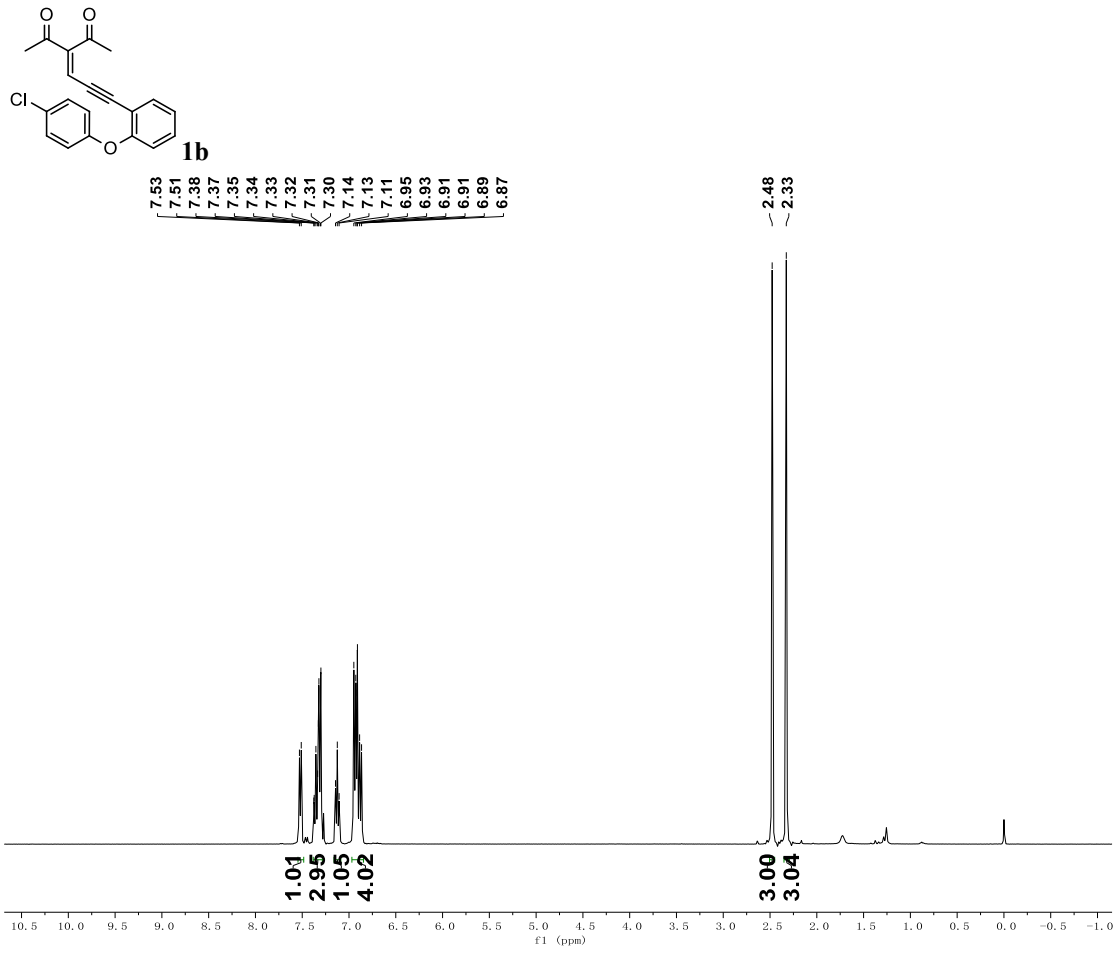
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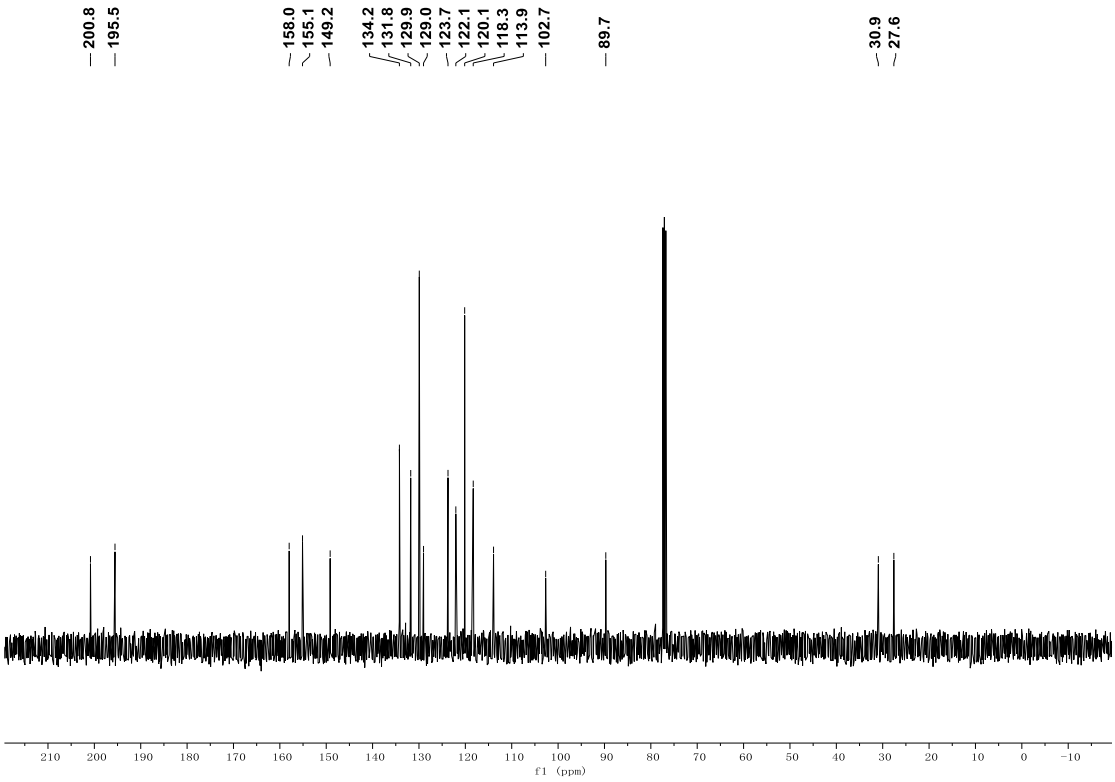
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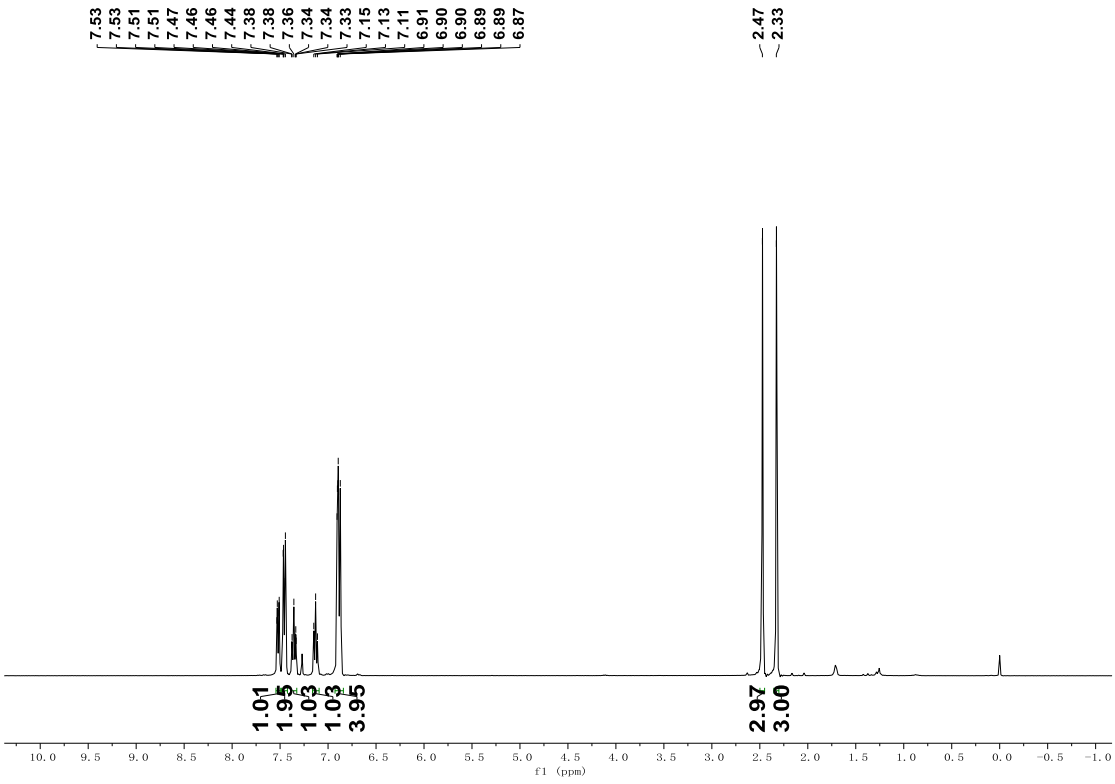
f1 (ppm)


O
O
Br
O

1c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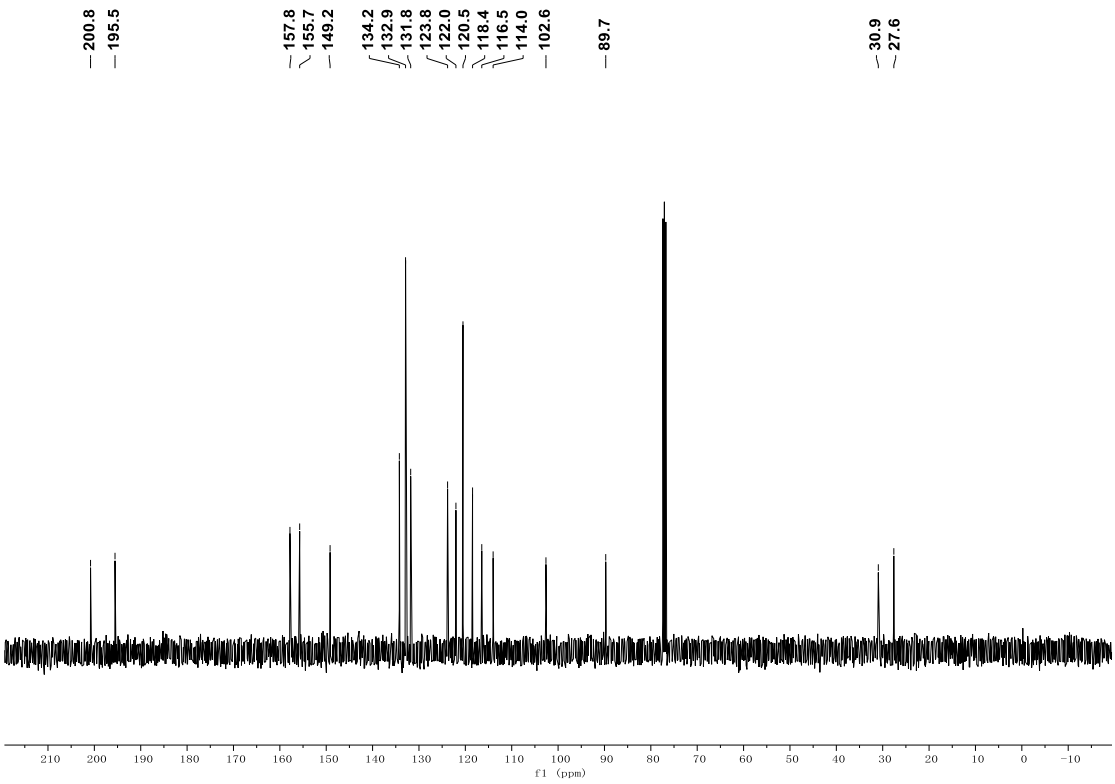
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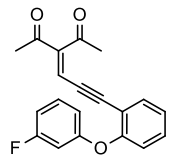
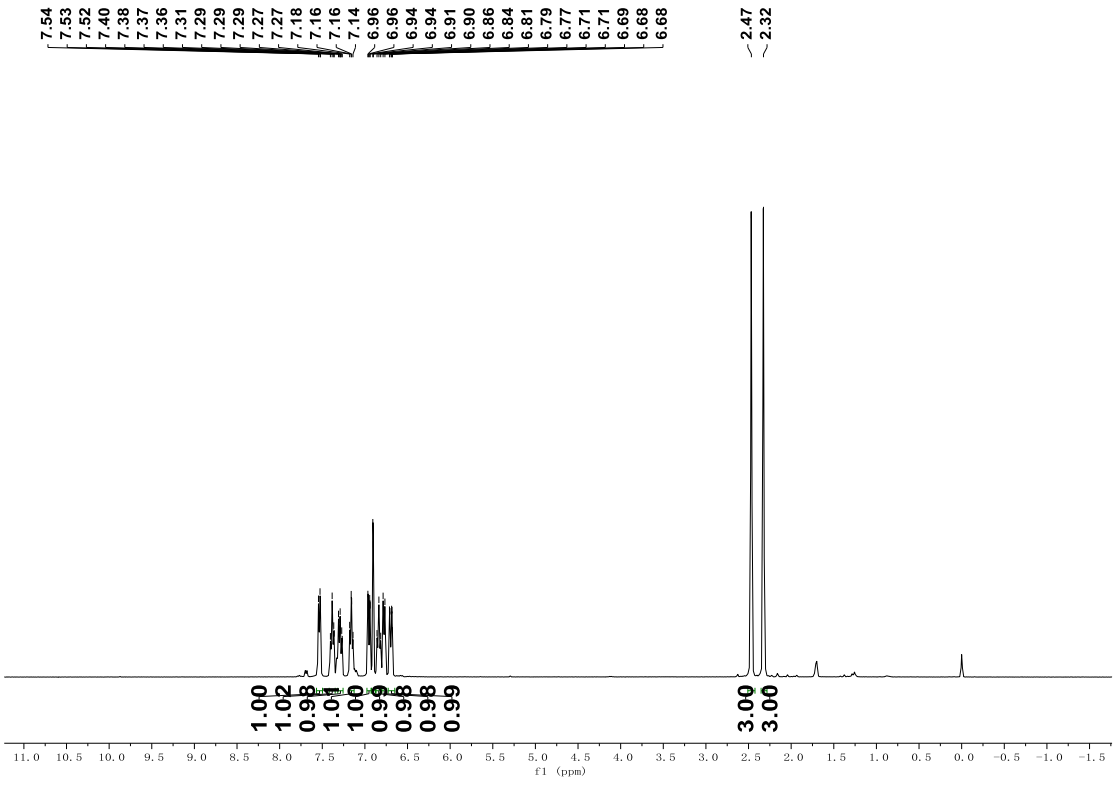

O
O
F
O

1d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7.14
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6.96
6.94
6.94
6.91
6.90
6.86
6.84
6.81
6.79
6.77
6.71
6.71
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6.68
6.68
2.47
2.32
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0.99
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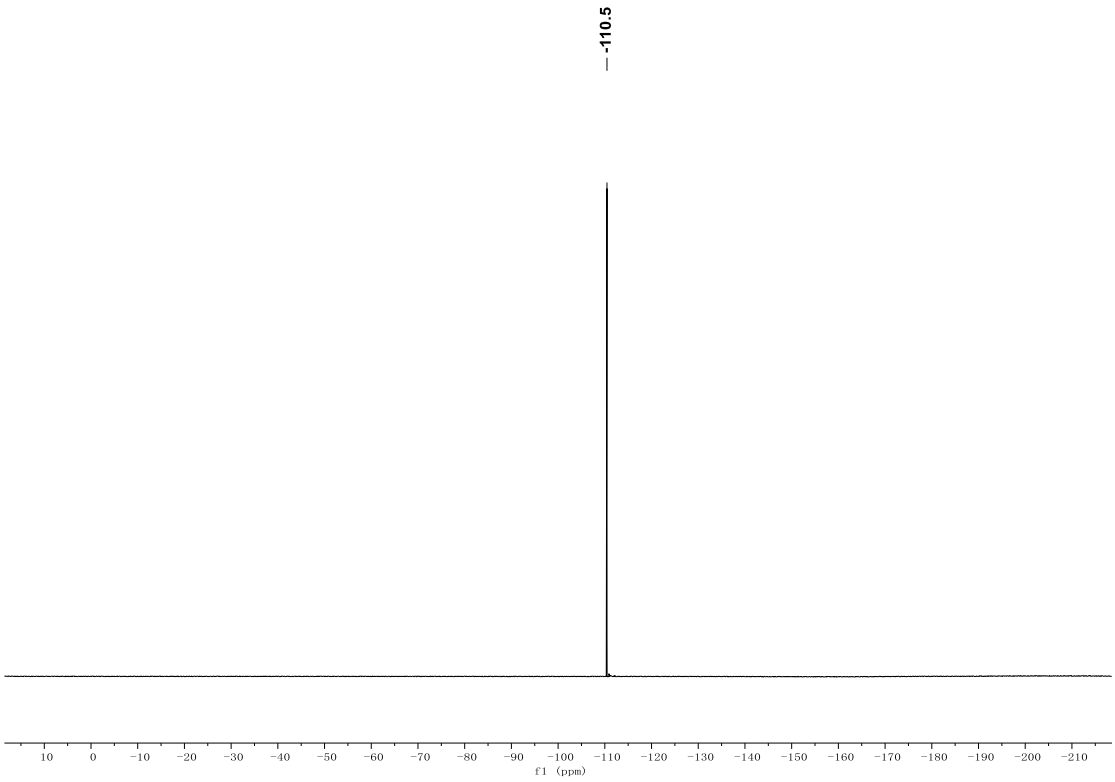
3.00
f1 (ppm)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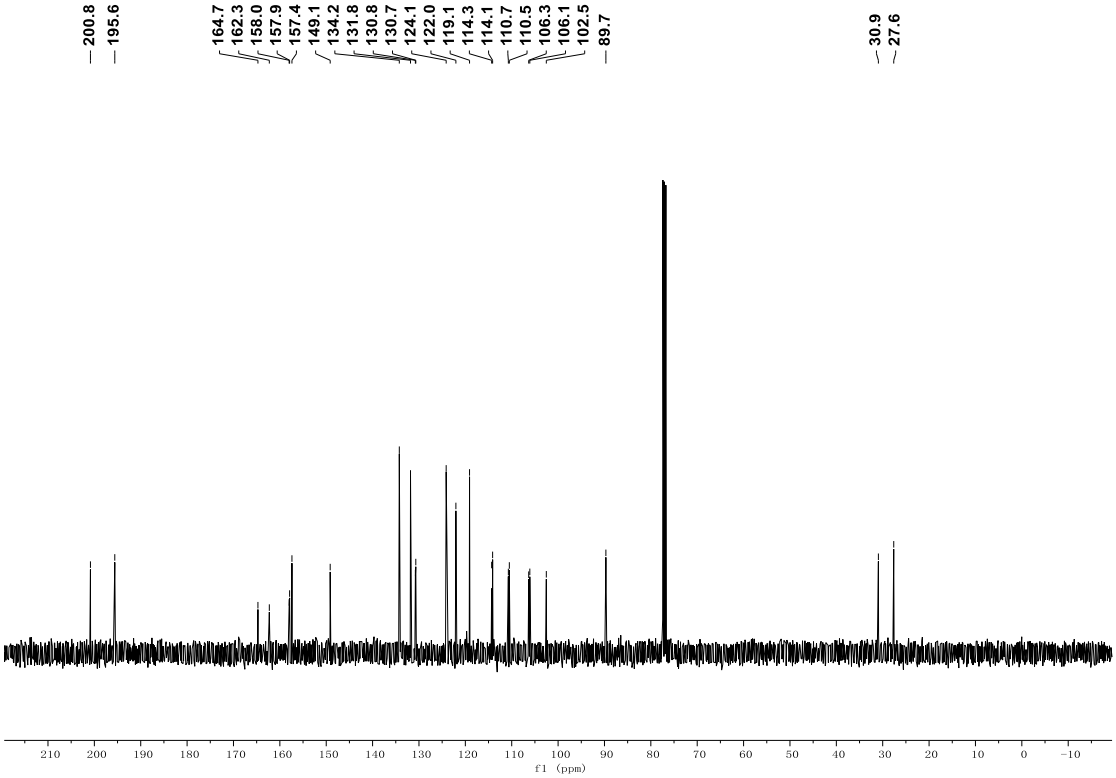
f1 (ppm)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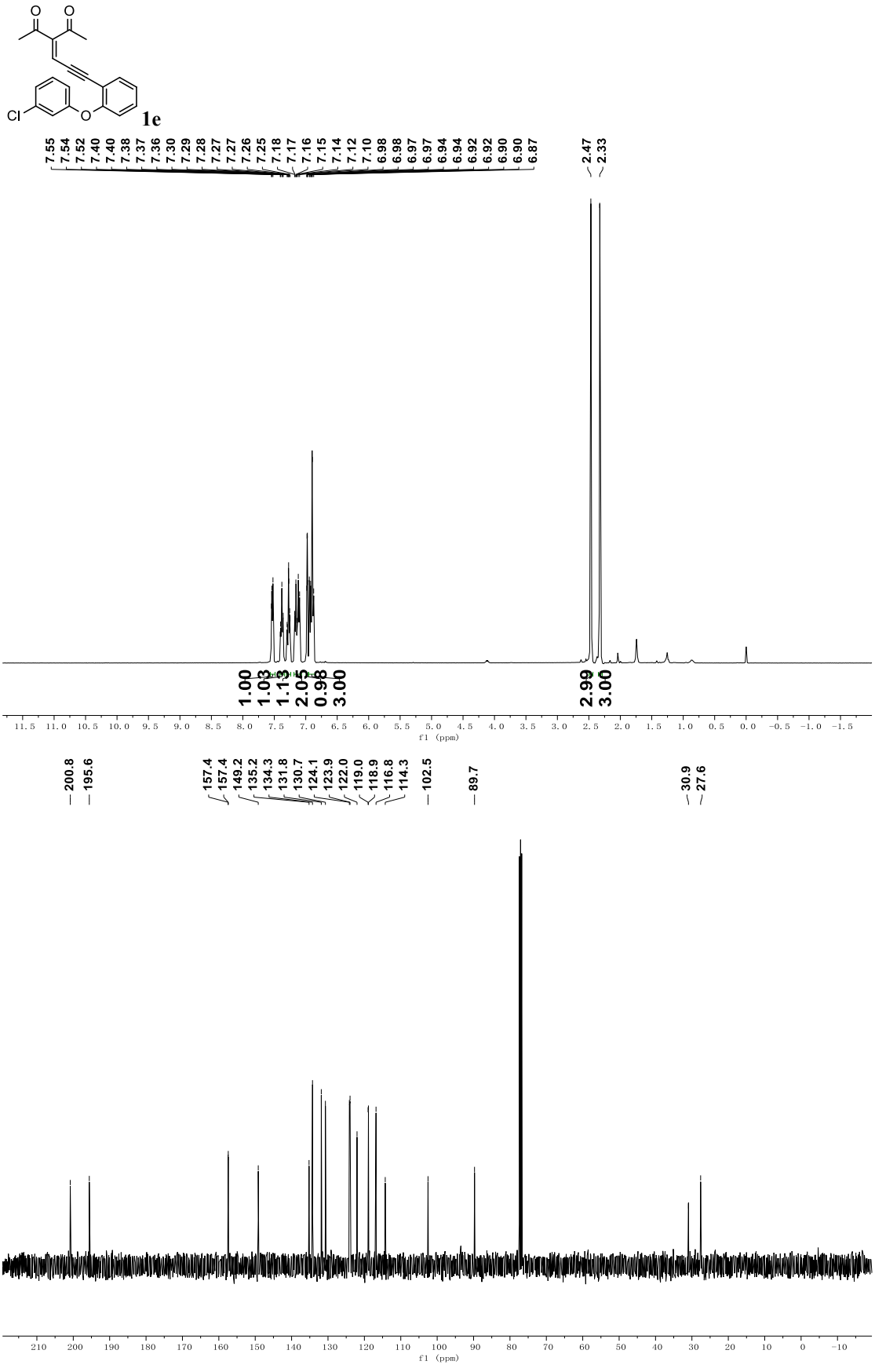
124.1
122.0
119.1
114.3
114.1
110.7
110.5
106.3
106.1
102.5
89.7
30.9
27.6
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)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7.14
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7.10
6.98
6.98
6.97
6.97
6.94
6.94
6.92
6.92
6.90
6.90
6.87
2.47
2.33
1.00
1.03
1.13
2.05
0.98
3.00
2.99
3.00
f1 (ppm)
200.8
195.6
157.4
157.4
149.2
135.2
134.3
131.8
130.7
124.1
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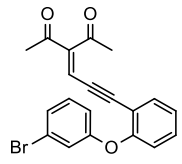
27.6
f1 (ppm)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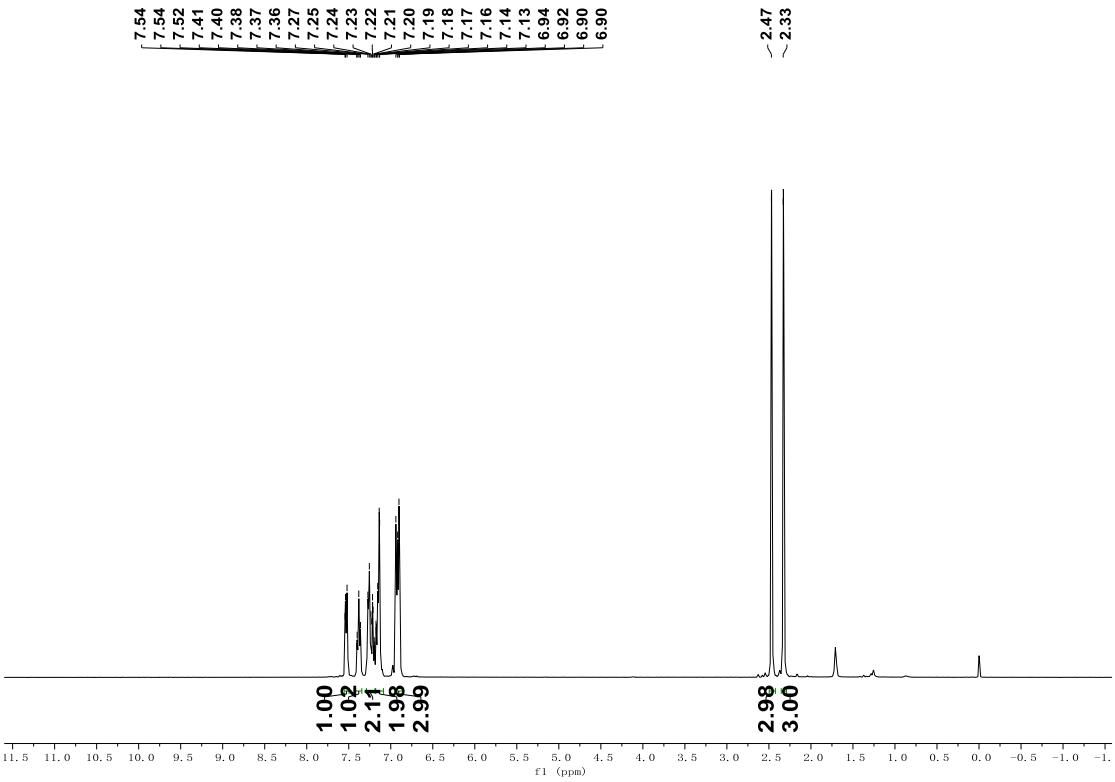
Br
O

1f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7.19
7.18
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7.14
7.13
6.94
6.92
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6.90
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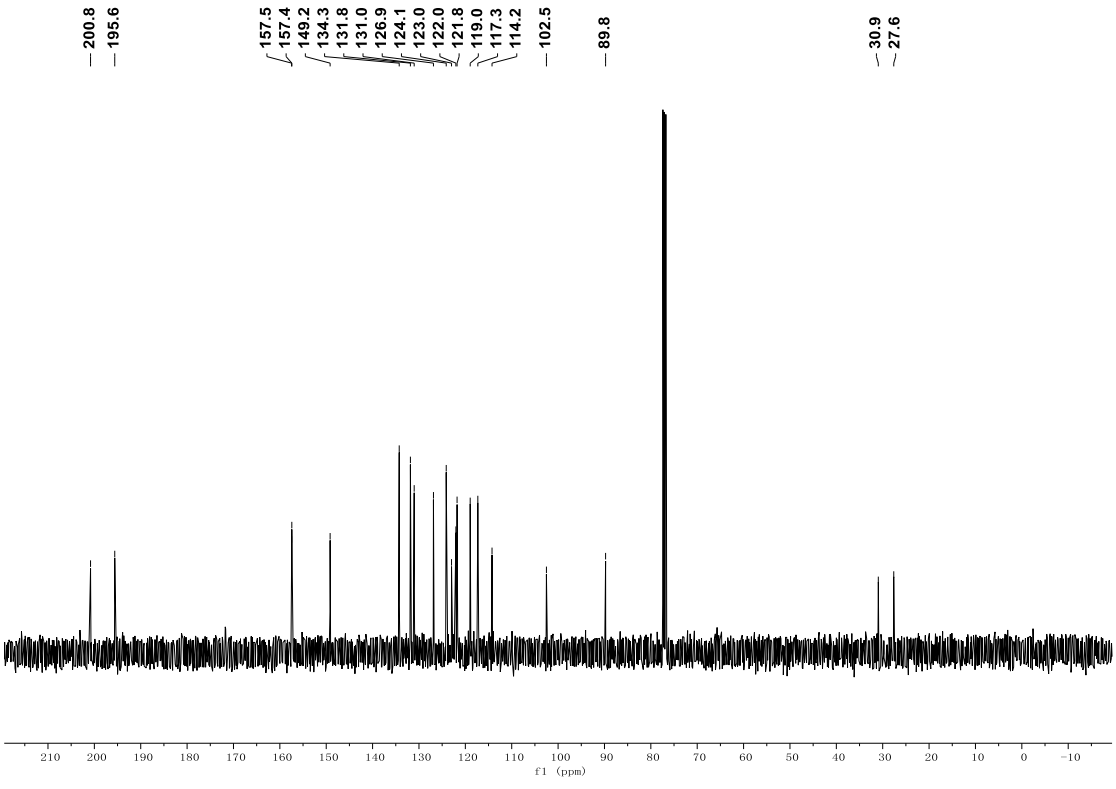
1.98
2.99
2.98
3.00
f1 (ppm)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126.9
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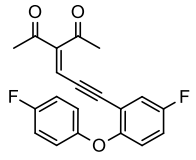
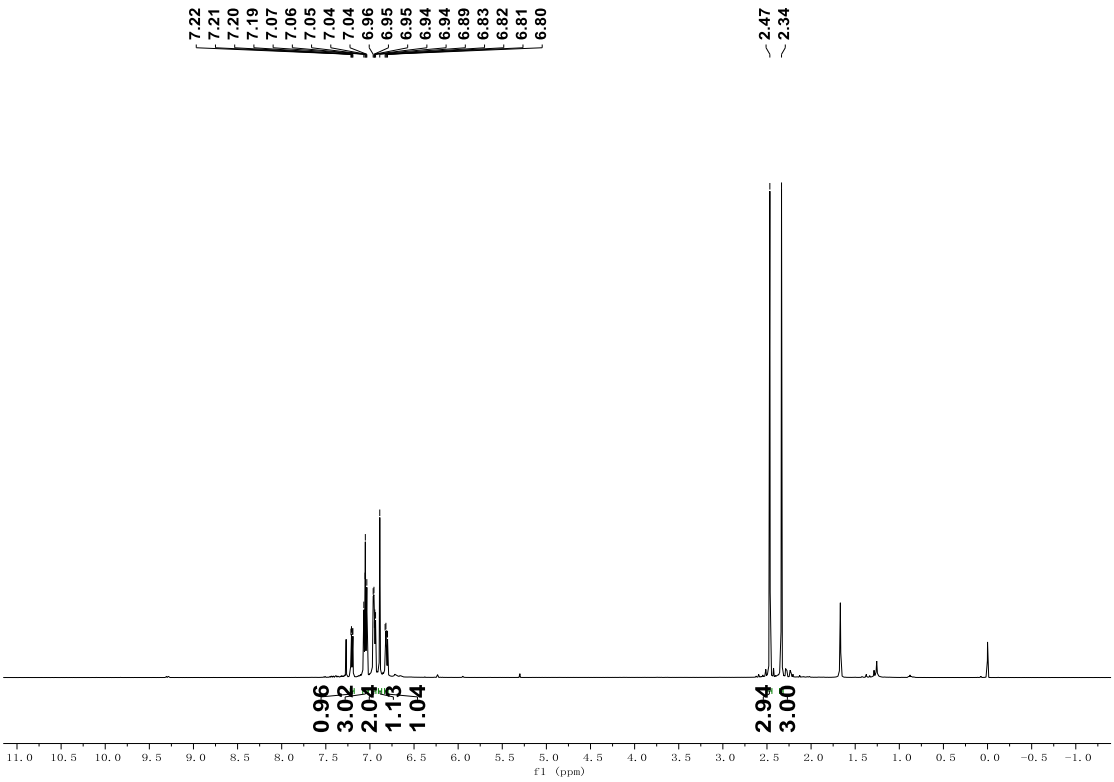
119.0
117.3
114.2
102.5
89.8
30.9
27.6
f1 (ppm)


O
O
F
F
O

1g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7.19
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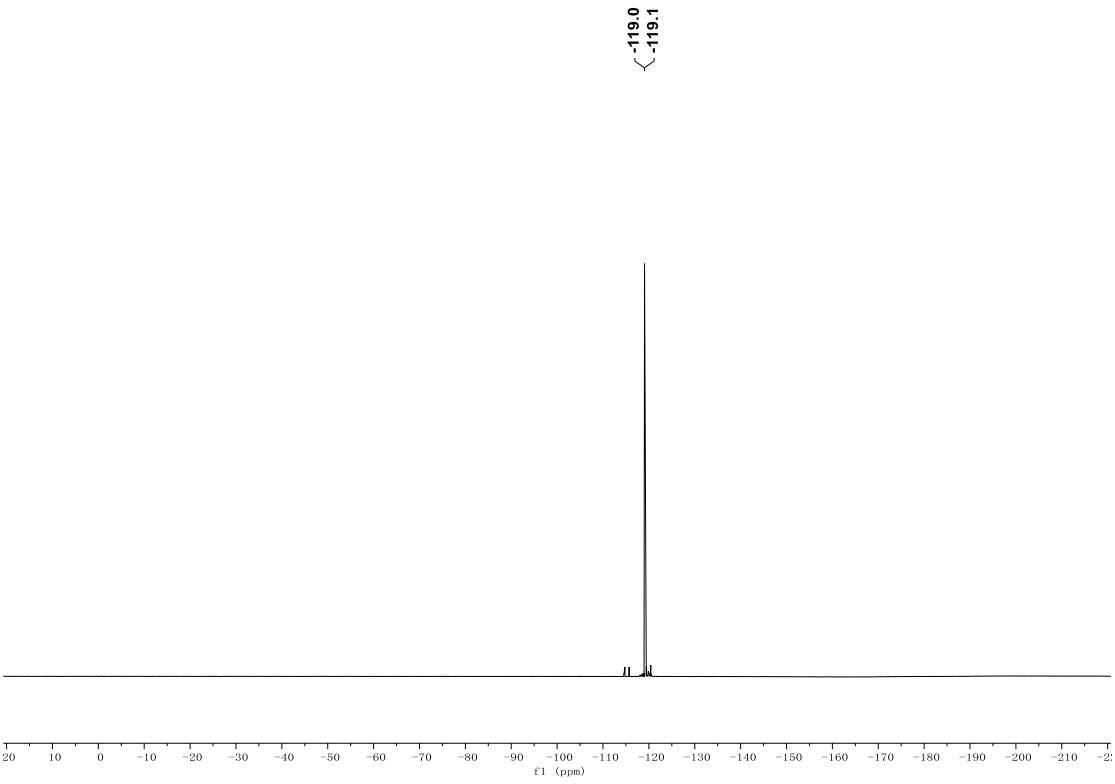
7.06
7.05
7.04
7.04
6.96
6.95
6.95
6.94
6.94
6.89
6.83
6.82
6.81
6.80
2.47
2.34
0.96
3.02
2.04
1.13
1.04
2.94
3.00
f1 (ppm)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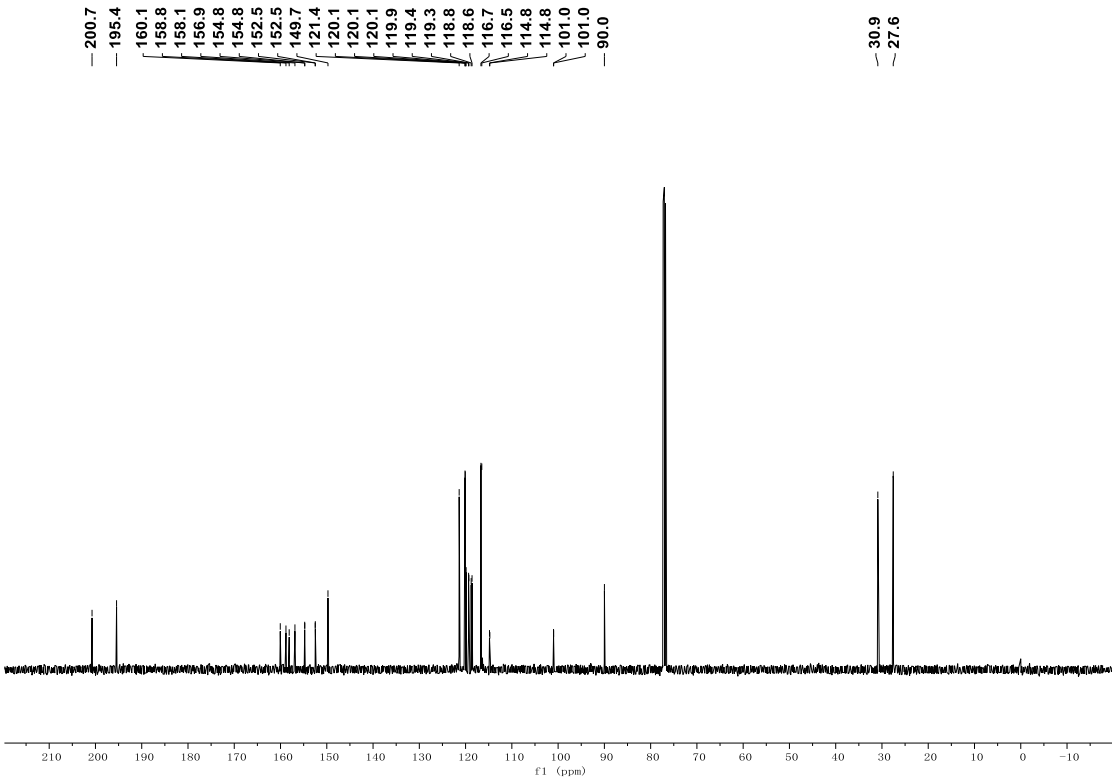
-119.1
f1 (ppm)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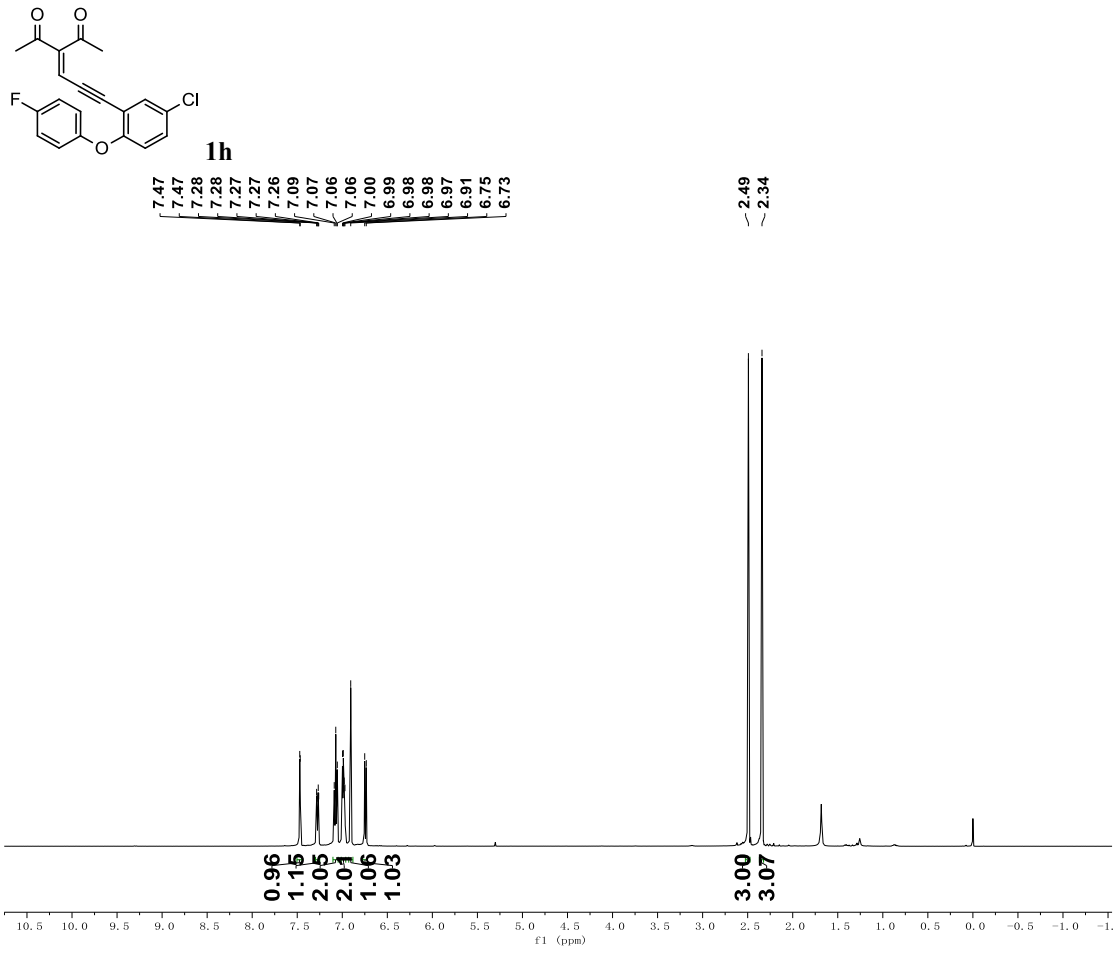
158.1
156.9
154.8
154.8
152.5
152.5
149.7
121.4
120.1
120.1
119.9
119.4
119.3
118.8
118.6
116.7
116.5
114.8
114.8
101.0
101.0
90.0
30.9
27.6
f1 (ppm)


O
O
F
Cl
O
1h
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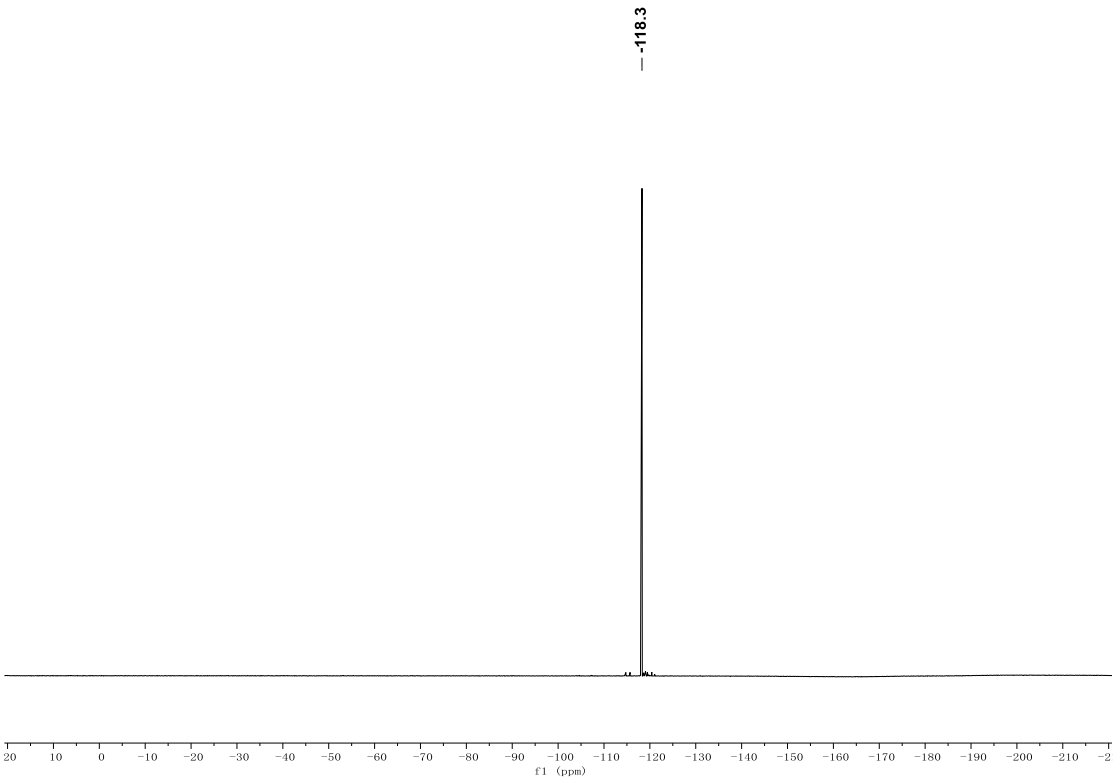
7.27
7.27
7.26
7.09
7.07
7.06
7.06
7.00
6.99
6.98
6.98
6.97
6.91
6.75
6.73
2.49
2.34
0.96
1.15
2.05
2.04
1.06
1.03
3.00
3.07
f1 (ppm)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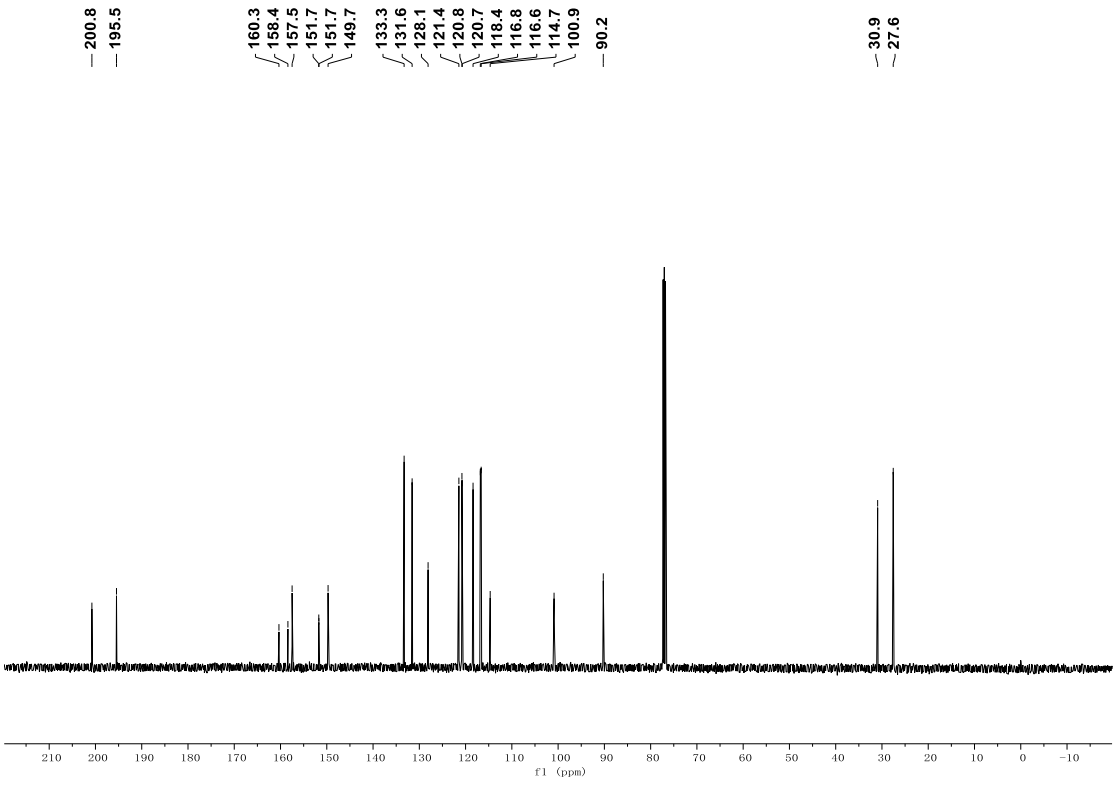
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149.7
133.3
131.6
128.1
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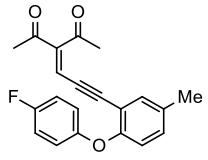
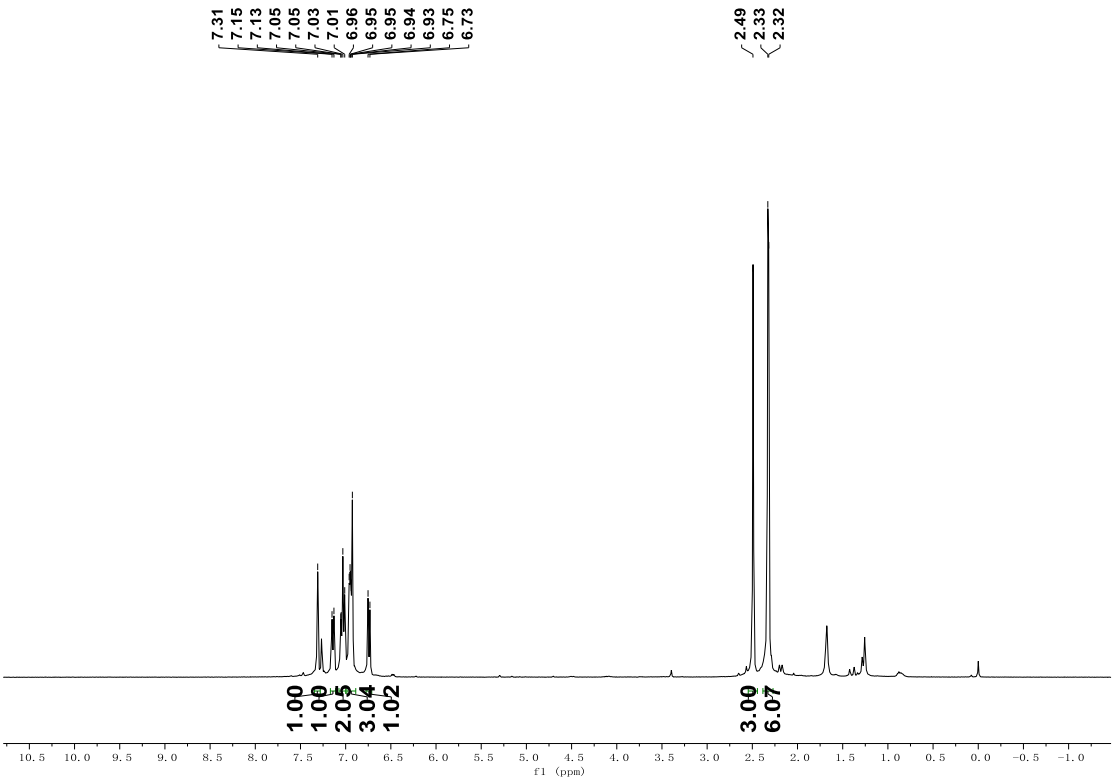
100.9
90.2
30.9
27.6
f1 (ppm)


O
O
F
Me
O

1i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7.05
7.03
7.01
6.96
6.95
6.95
6.94
6.93
6.75
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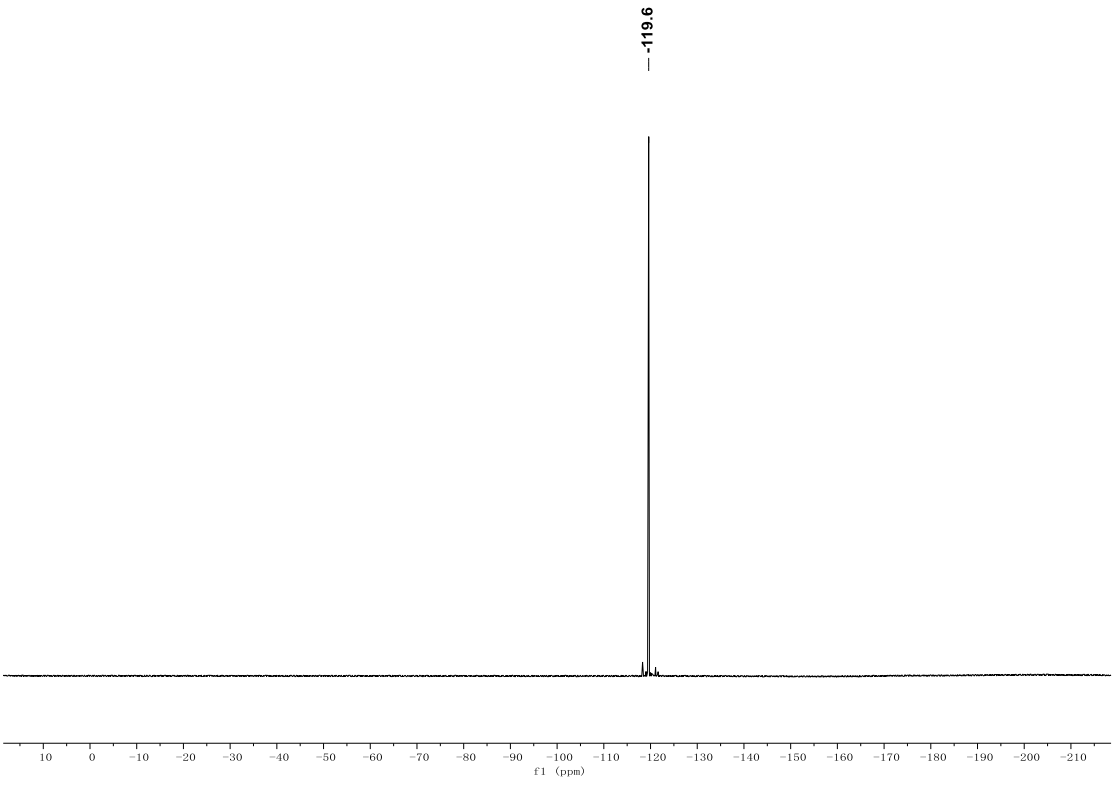
3.04
1.02
3.00
6.07
f1 (ppm)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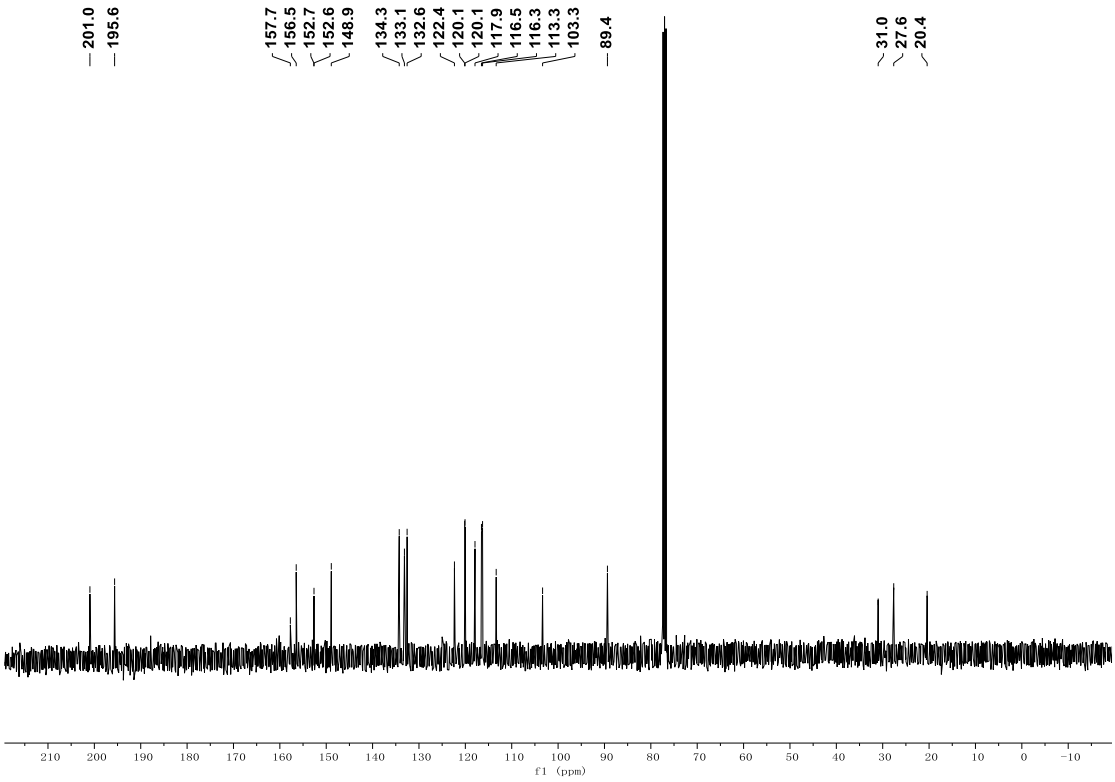
f1 (ppm)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156.5
152.7
152.6
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134.3
133.1
132.6
122.4
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120.1
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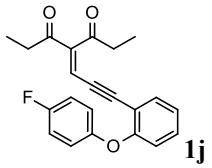
116.5
116.3
113.3
103.3
89.4
31.0
27.6
20.4
f1 (ppm)


O
O
F
O

1j


7.49
7.47
7.33
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7.29
7.08
7.07
7.06
7.04
7.01
7.00
6.99
6.98
6.97
6.89
6.79
6.77
2.90
2.88
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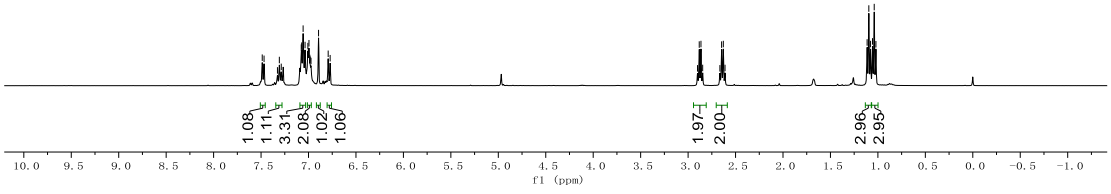
2.65
2.63
2.61
1.11
1.10
1.08
1.06
1.04
1.02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3.31
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1.02
1.06
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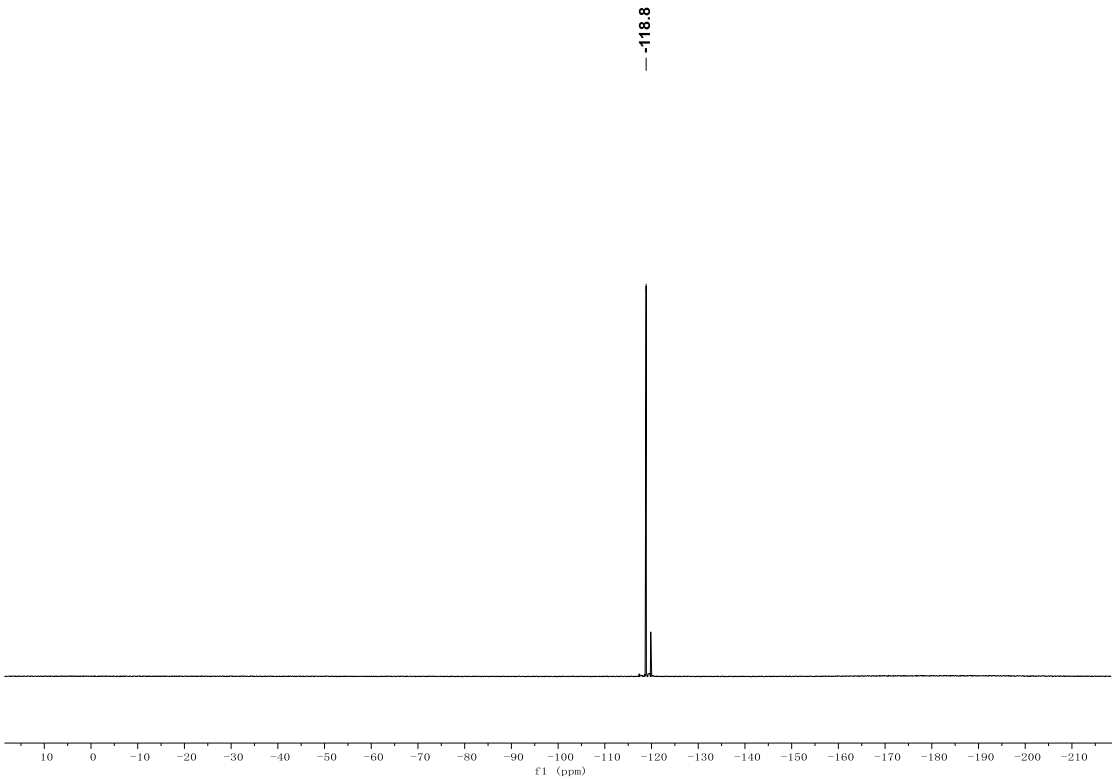
2.00
2.96
2.95
f1 (ppm)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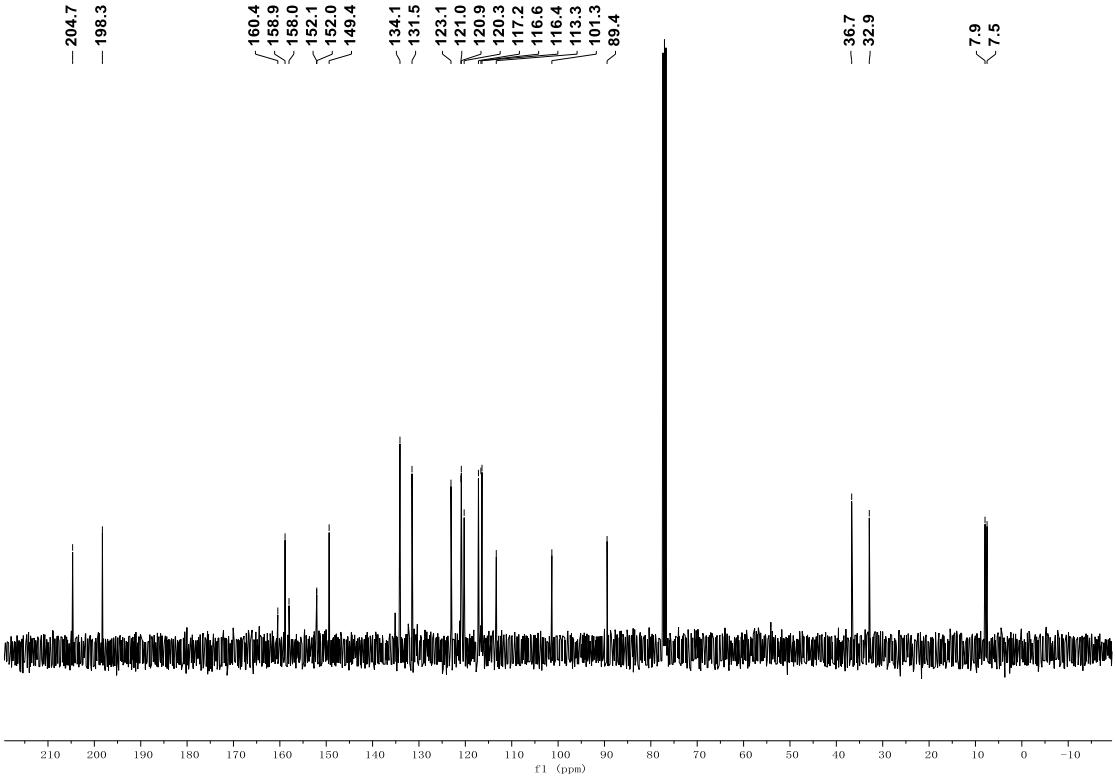
f1 (ppm)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152.0
149.4
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131.5
123.1
121.0
120.9
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117.2
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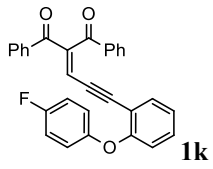
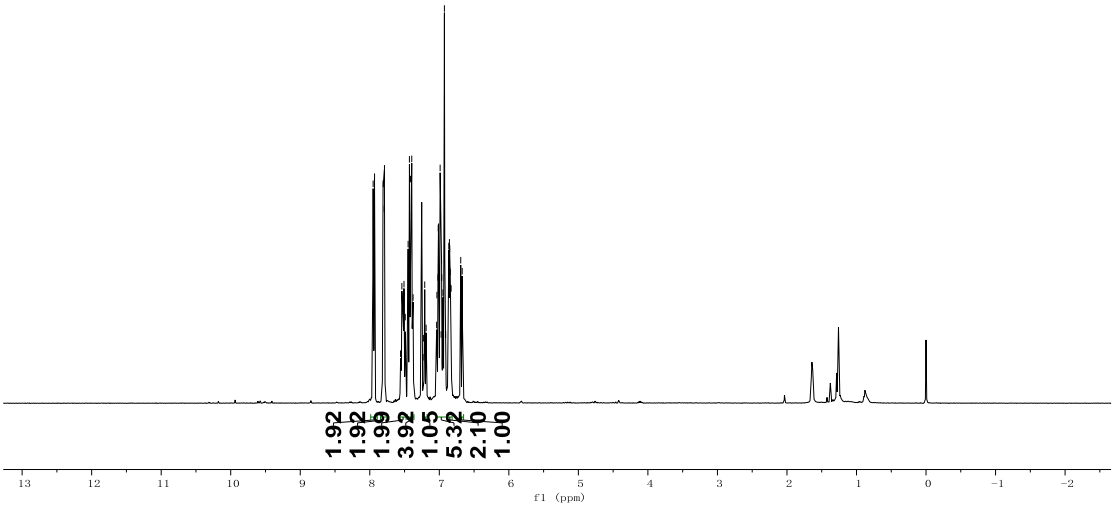
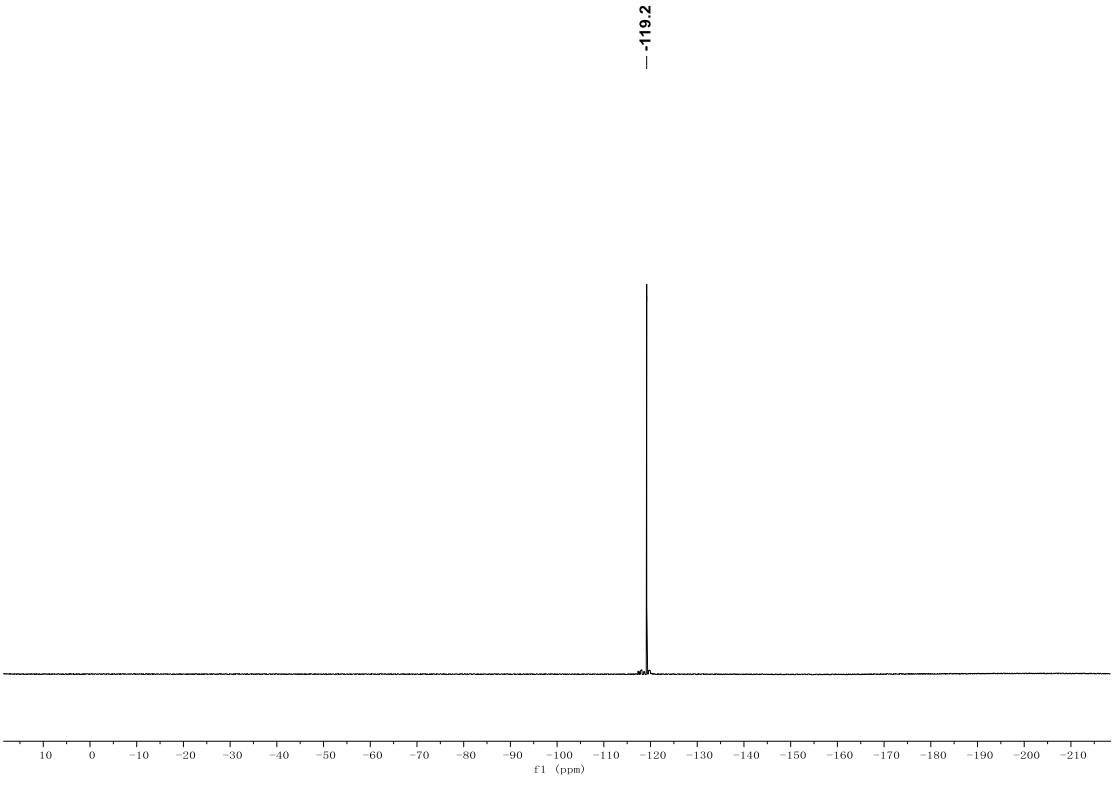
116.4
113.3
101.3
89.4
36.7
32.9
7.9
7.5
f1 (ppm)

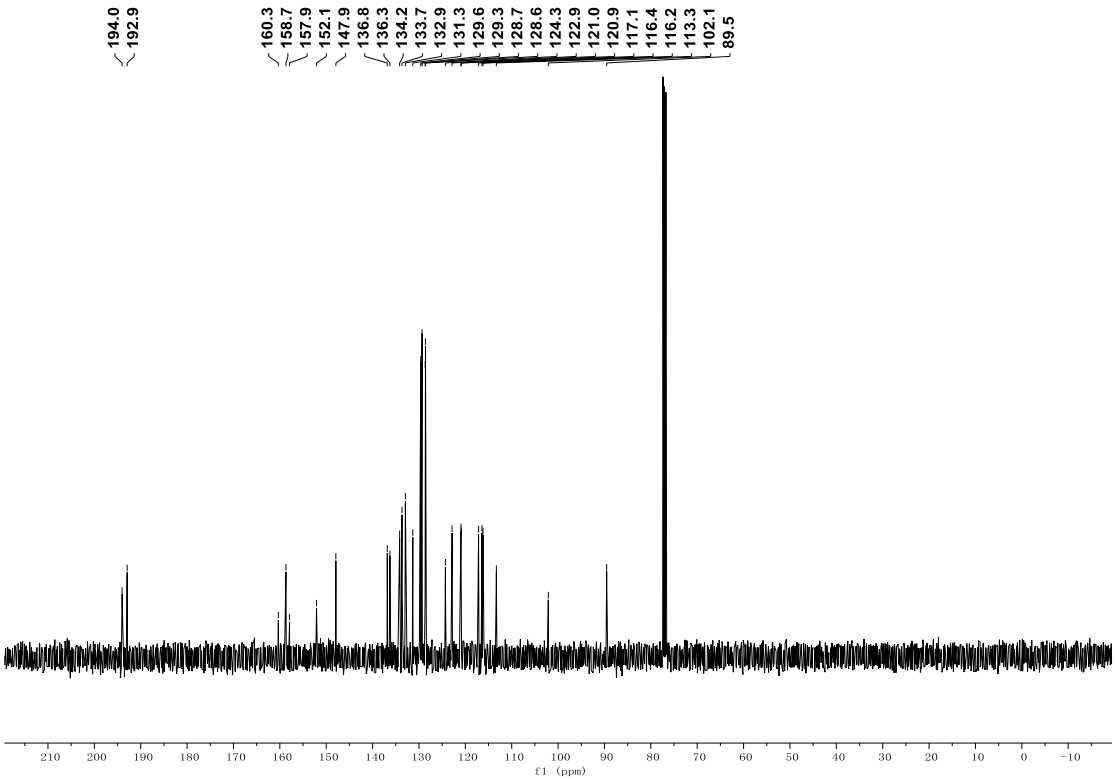


1k

7.95 7.94 7.93 7.81 7.79 7.79 7.56 7.54 7.52 7.51 7.49 7.45 7.43 7.41 7.40 7.38 7.23 7.23 7.21 7.19 7.19 7.04 7.03 7.02 7.02 7.01 7.01 6.99 6.97 6.97 6.96 6.95 6.93 6.91 6.86 6.85 6.85 6.84 6.84 6.83 6.69 6.67



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131.3
129.6
129.3
128.7
128.6
124.3
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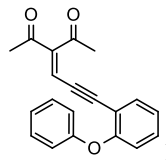
121.0
120.9
117.1
116.4
116.2
113.3
102.1
89.5
f1 (ppm)



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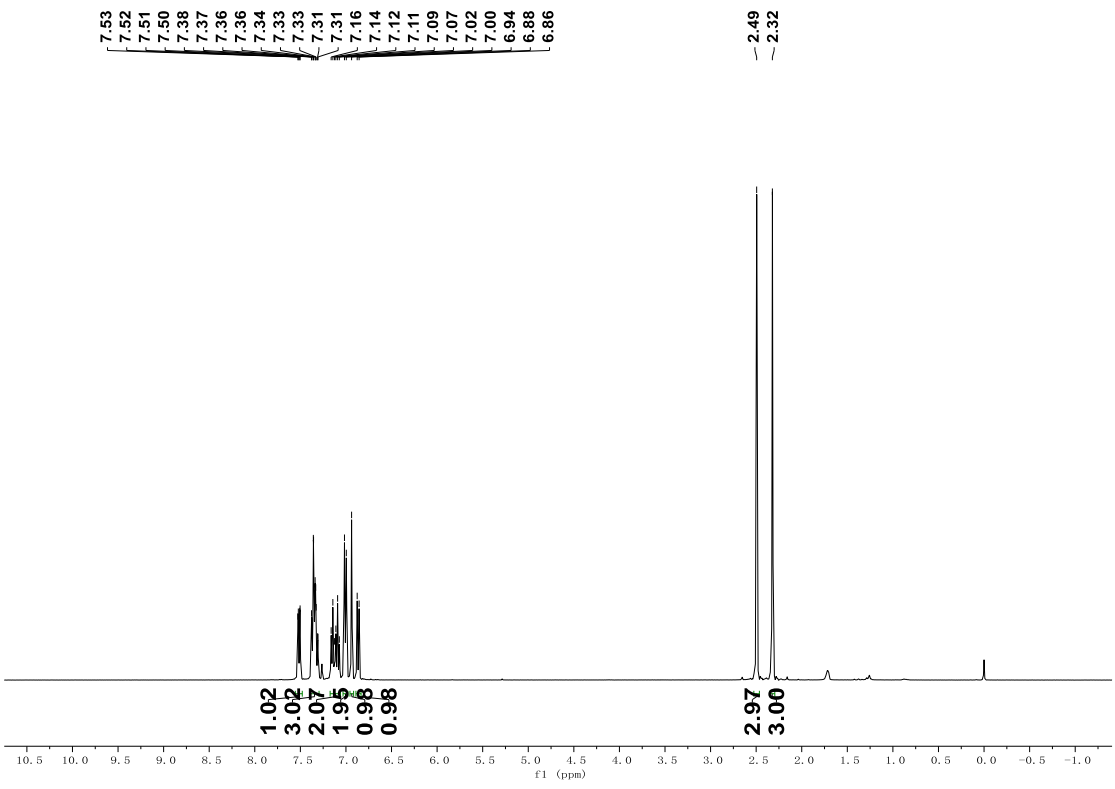
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7.14
7.12
7.11
7.09
7.07
7.02
7.00
6.94
6.88
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3.02
2.07
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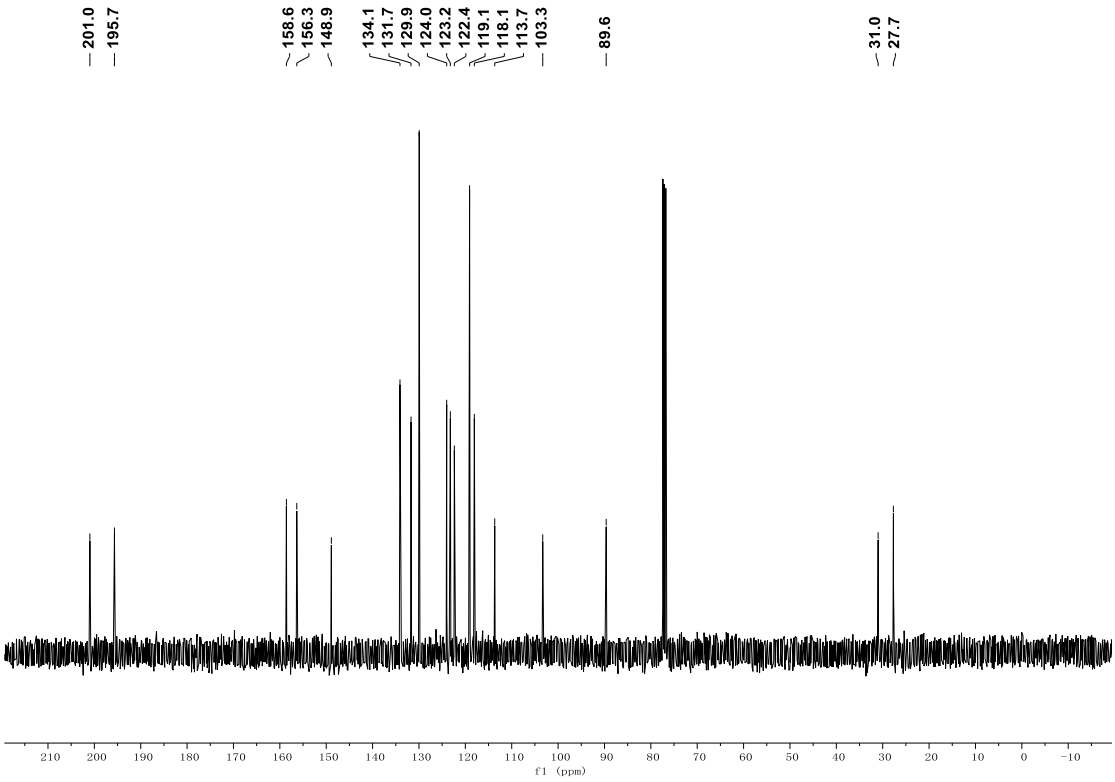
0.98
2.97
3.00
f1 (ppm)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122.4
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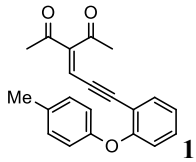
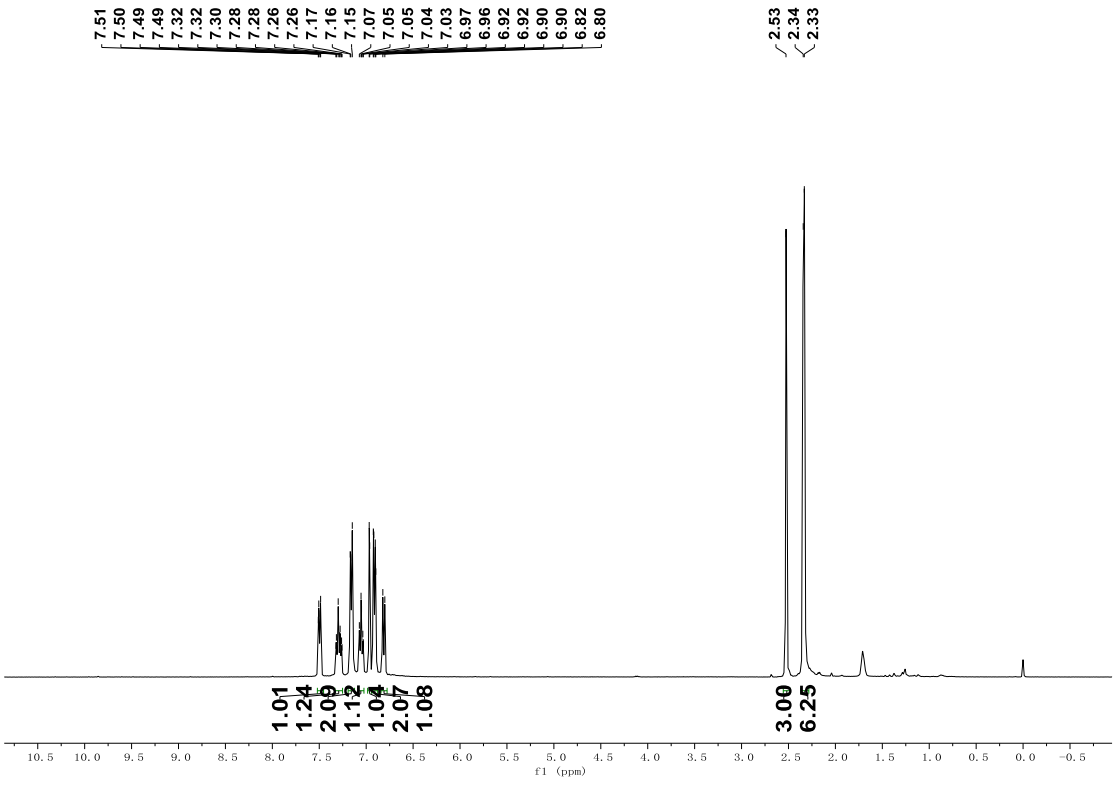
118.1
113.7
103.3
89.6
31.0
27.7
f1 (ppm)


O
O
Me
O

1m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7.05
7.05
7.04
7.03
6.97
6.96
6.92
6.92
6.90
6.90
6.82
6.80
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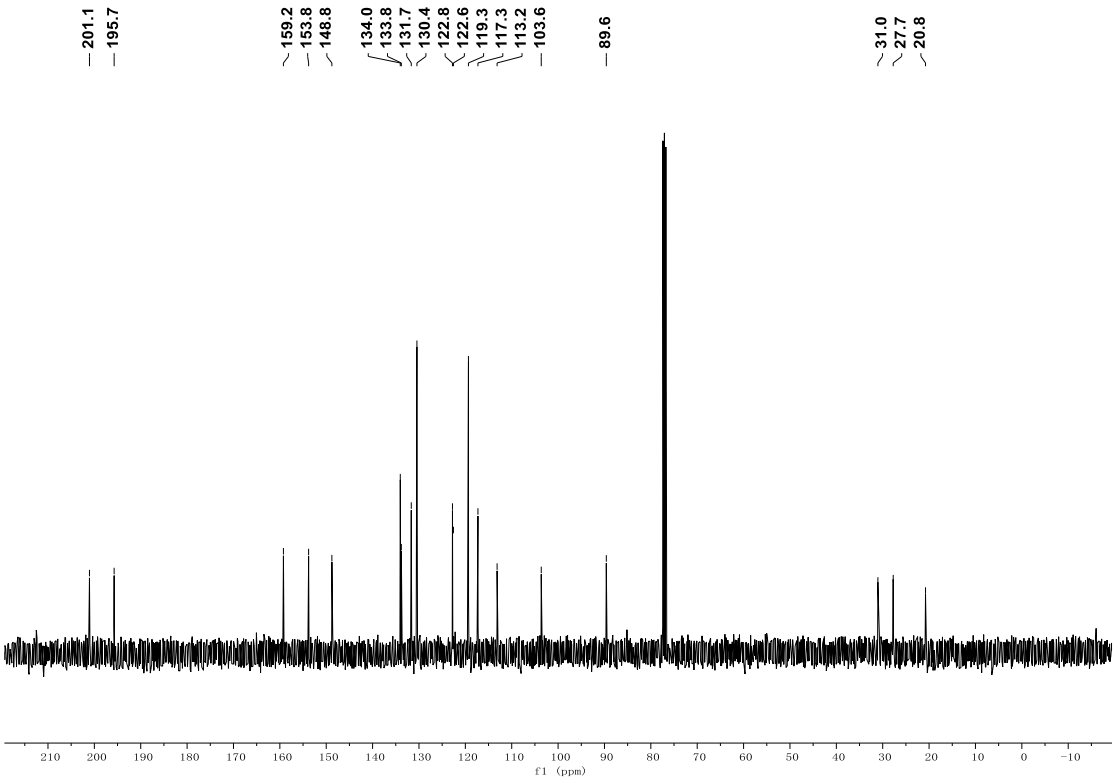
1.04
2.07
1.08
3.00
6.25
f1 (ppm)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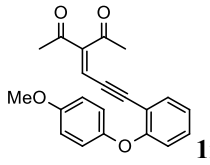
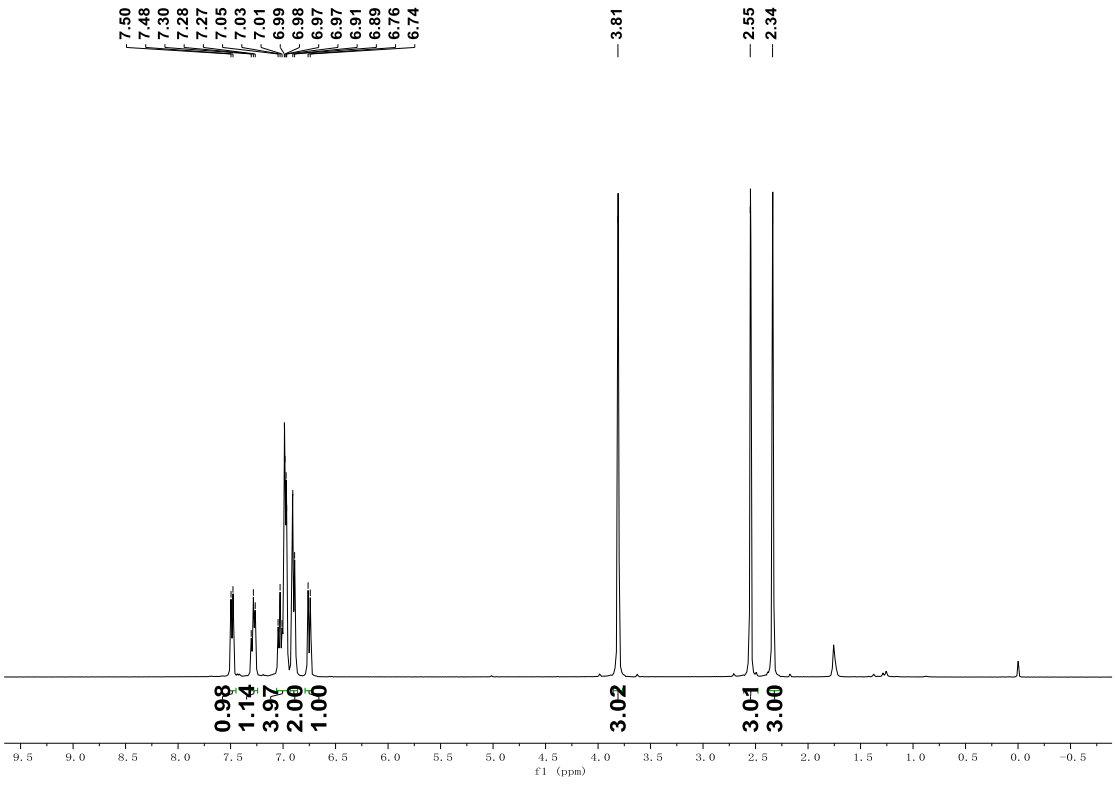
153.8
148.8
134.0
133.8
131.7
130.4
122.8
122.6
119.3
117.3
113.2
103.6
89.6
31.0
27.7
20.8
f1 (ppm)


O
O
MeO
O

1n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7.05
7.03
7.01
6.99
6.98
6.97
6.97
6.91
6.89
6.76
6.74
3.81
2.55
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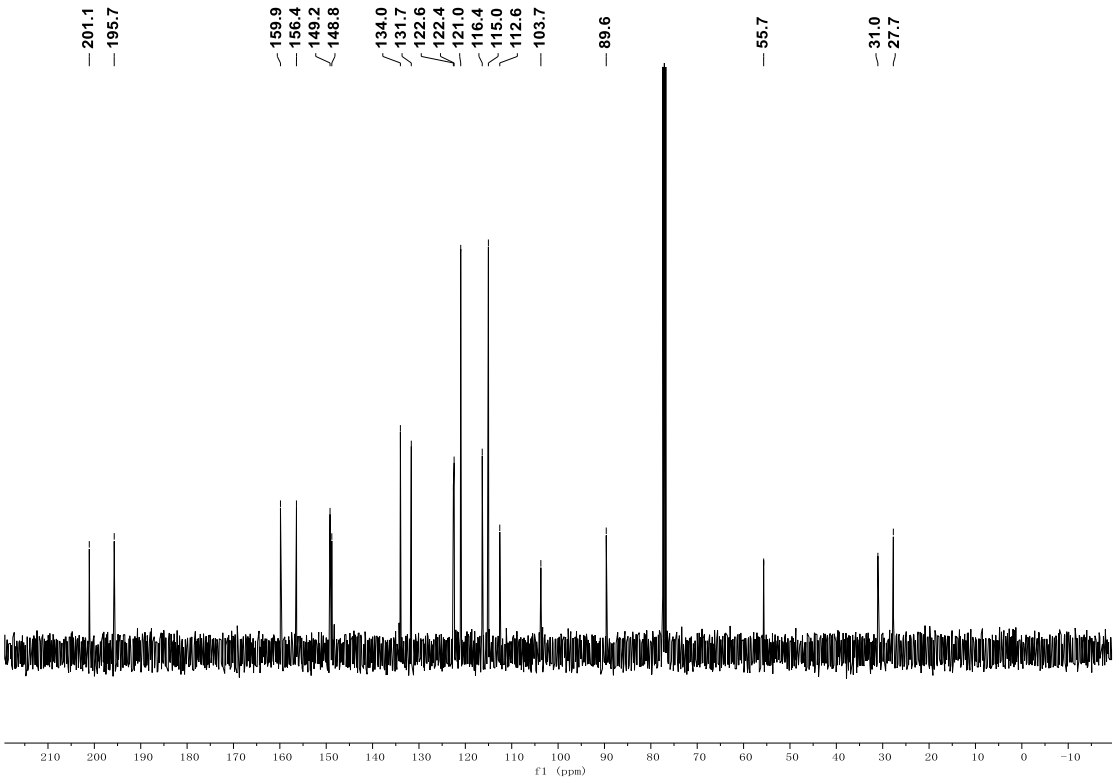
0.98
1.14
3.97
2.06
1.00
3.02
3.01
3.00
f1 (ppm)


201.1
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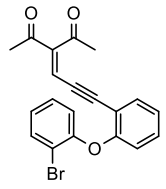
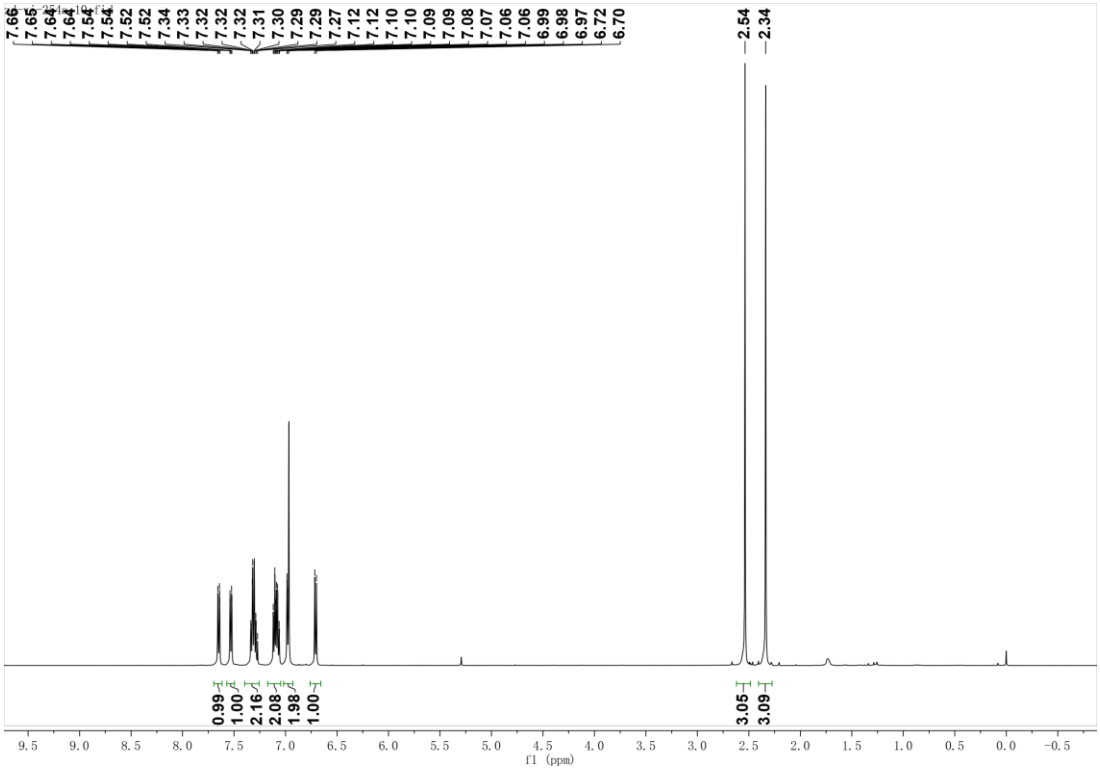
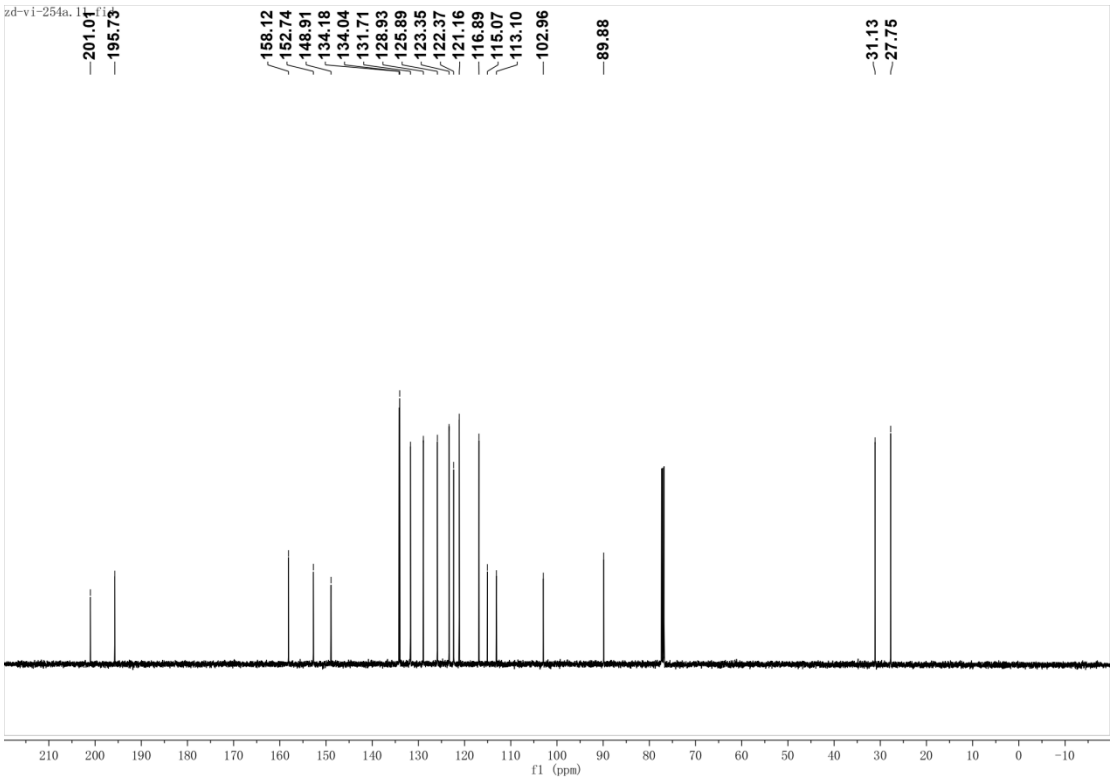
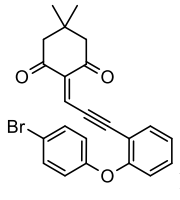
122.4
121.0
116.4
115.0
112.6
103.7
89.6
55.7
31.0
27.7
f1 (ppm)


O
O
Br

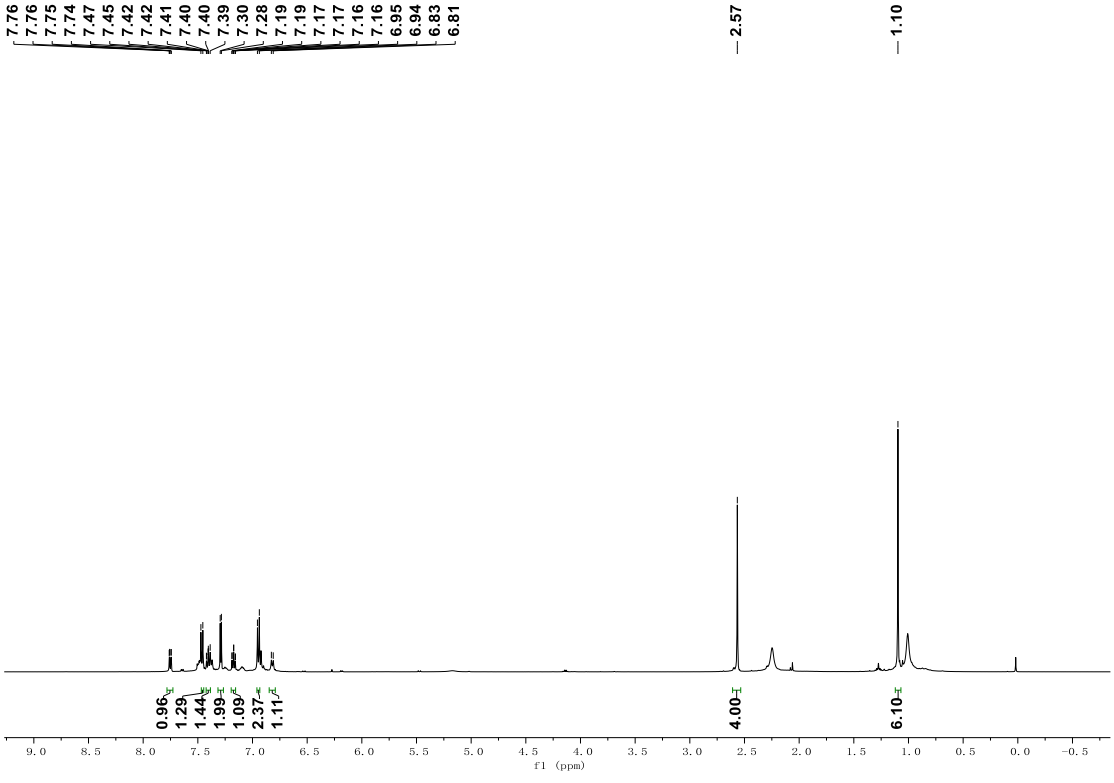
1o

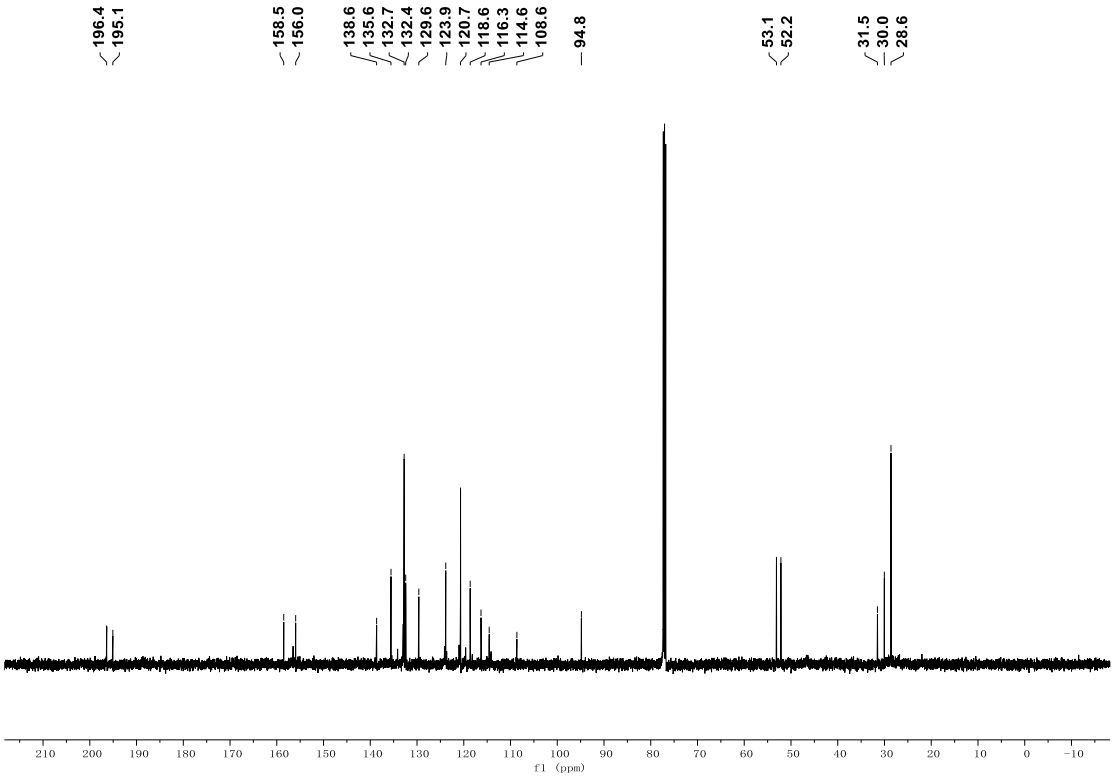

7.66
7.65
7.64
7.64
7.54
7.54
7.52
7.52
7.34
7.33
7.32
7.32
7.32
7.31
7.30
7.29
7.29
7.27
7.12
7.12
7.10
7.10
7.09
7.09
7.08
7.07
7.06
7.06
6.99
6.98
6.97
6.72
6.70
2.54
2.34
0.99
1.00
2.16
2.08
1.98
1.00
3.05
3.09
f1 (ppm)

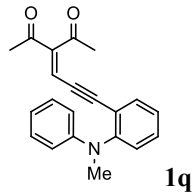

201.01
195.73
158.12
152.74
148.91
134.18
134.04
131.71
128.93
125.89
123.35
122.37
121.16
116.89
115.07
113.10
102.96
89.88
31.13
27.75
f1 (ppm)


O
O
Br
O

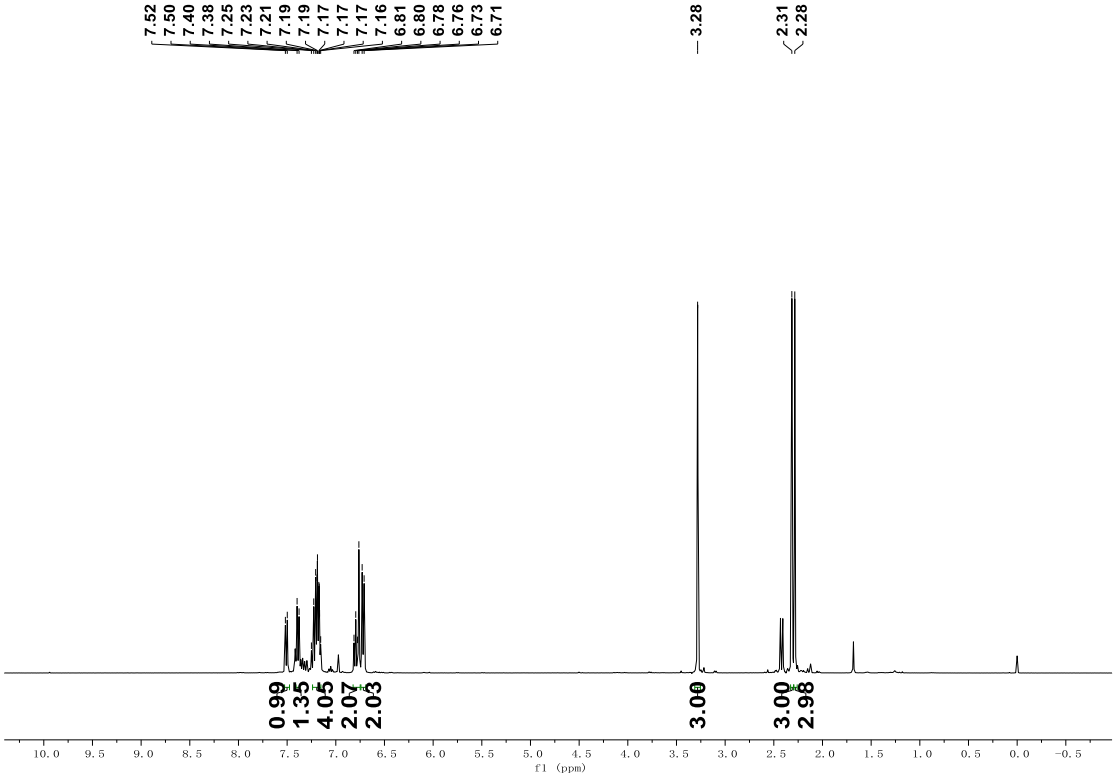
1p

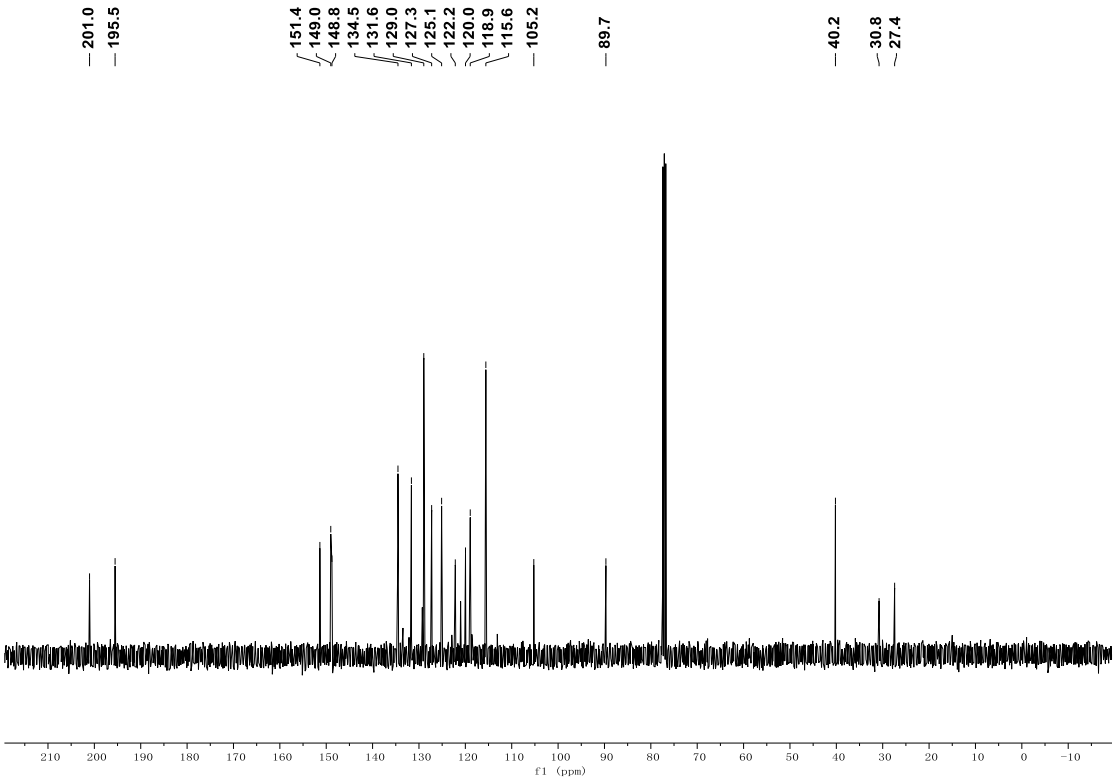

7.76
7.76
7.75
7.74
7.47
7.45
7.42
7.42
7.41
7.40
7.40
7.39
7.30
7.28
7.19
7.19
7.17
7.17
7.16
7.16
6.95
6.94
6.83
6.81
2.57
1.10
0.96
1.29
1.44
1.99
1.09
2.37
1.11
4.00
6.10
f1 (ppm)

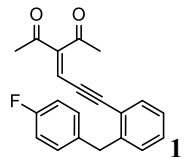

196.4
195.1
158.5
156.0
138.6
135.6
132.7
132.4
129.6
123.9
120.7
118.6
116.3
114.6
108.6
94.8
53.1
52.2
31.5
30.0
28.6
f1 (ppm)


O
O
N
Me

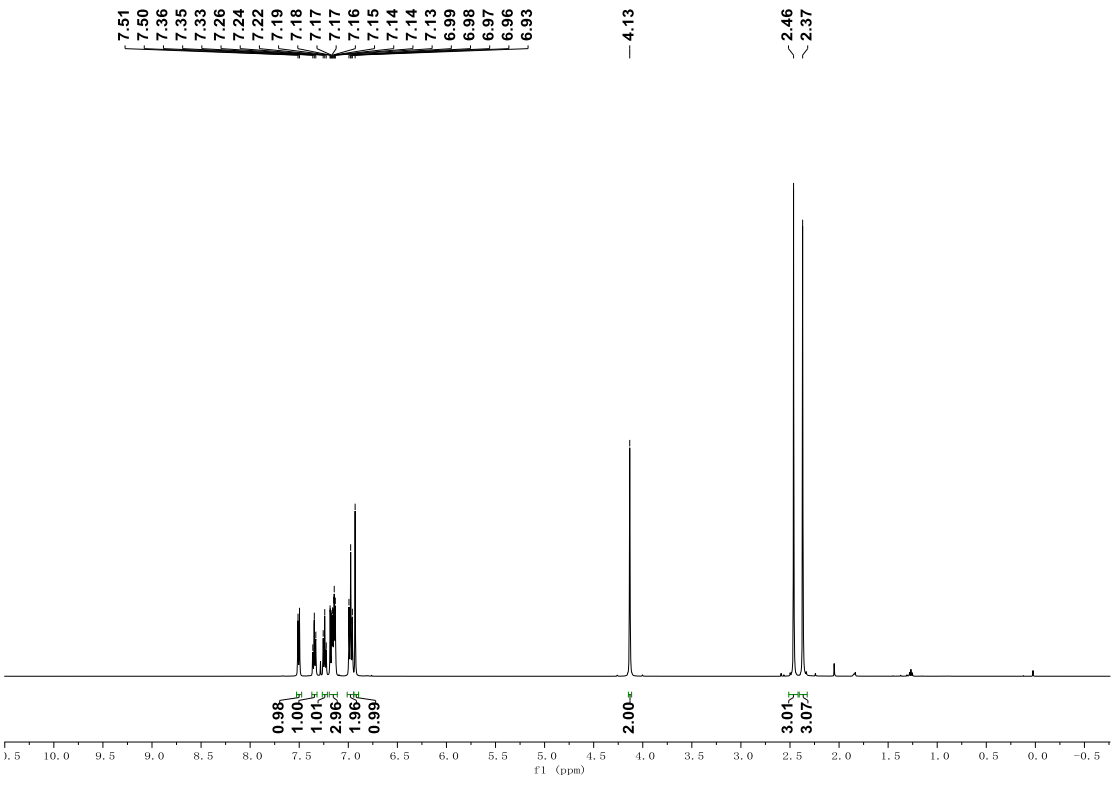
1q

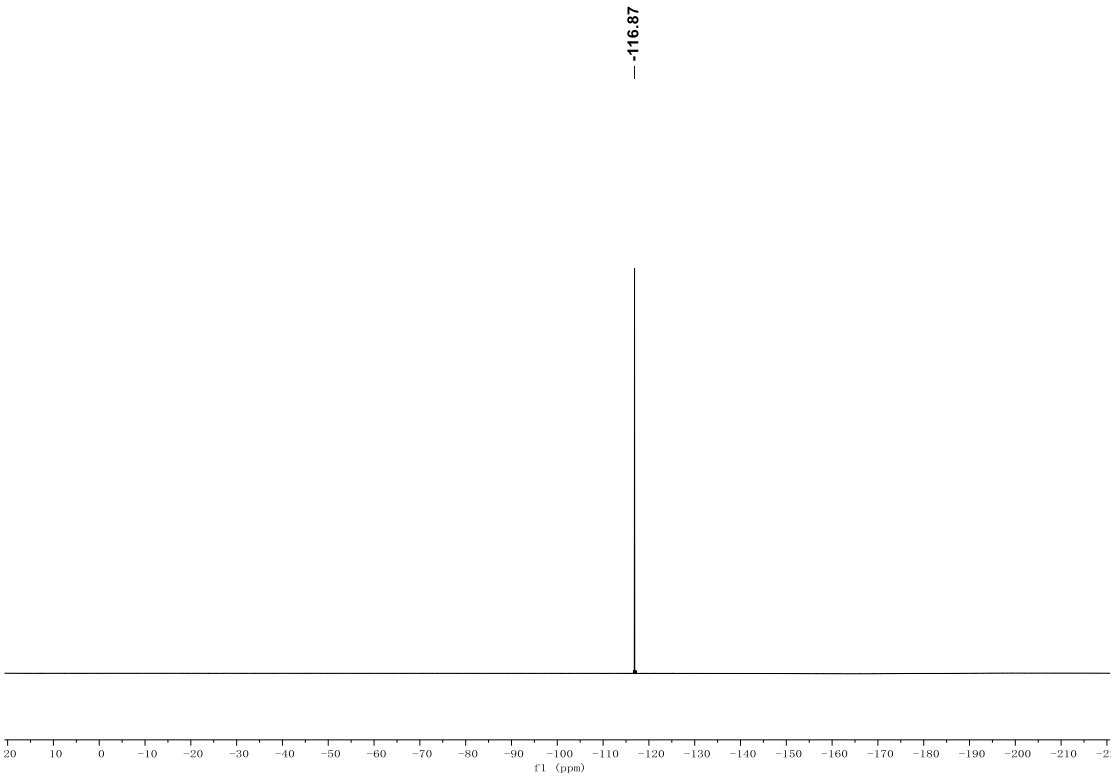

7.52
7.50
7.40
7.38
7.25
7.23
7.21
7.19
7.19
7.17
7.17
7.17
7.16
6.81
6.80
6.78
6.76
6.73
6.71
3.28
2.31
2.28
0.99
1.35
4.05
2.07
2.03
3.00
3.00
2.98
f1 (ppm)

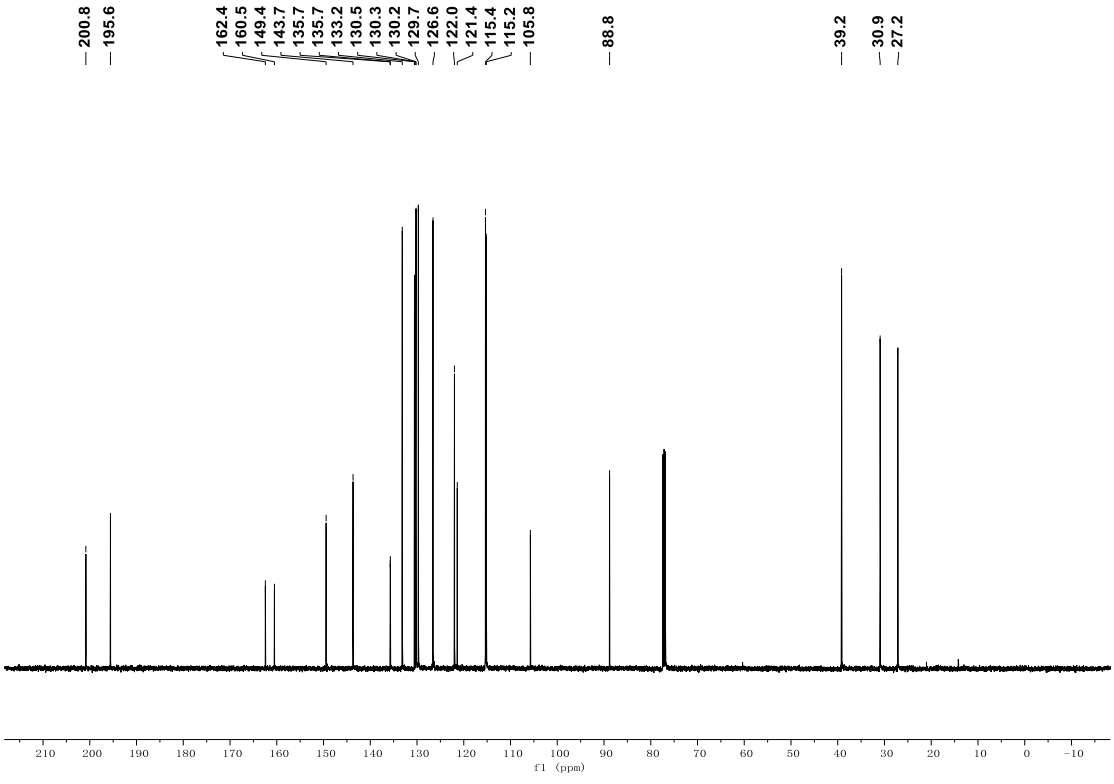

201.0
195.5
151.4
149.0
148.8
134.5
131.6
129.0
127.3
125.1
122.2
120.0
118.9
115.6
105.2
89.7
40.2
30.8
27.4
f1 (ppm)

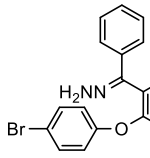

O
O
F

1r


7.51
7.50
7.36
7.35
7.33
7.26
7.24
7.22
7.19
7.18
7.17
7.17
7.16
7.15
7.14
7.14
7.13
6.99
6.98
6.97
6.96
6.93
4.13
2.46
2.37
0.98
1.00
1.01
2.96
1.96
0.99
2.00
3.01
3.07
f1 (ppm)

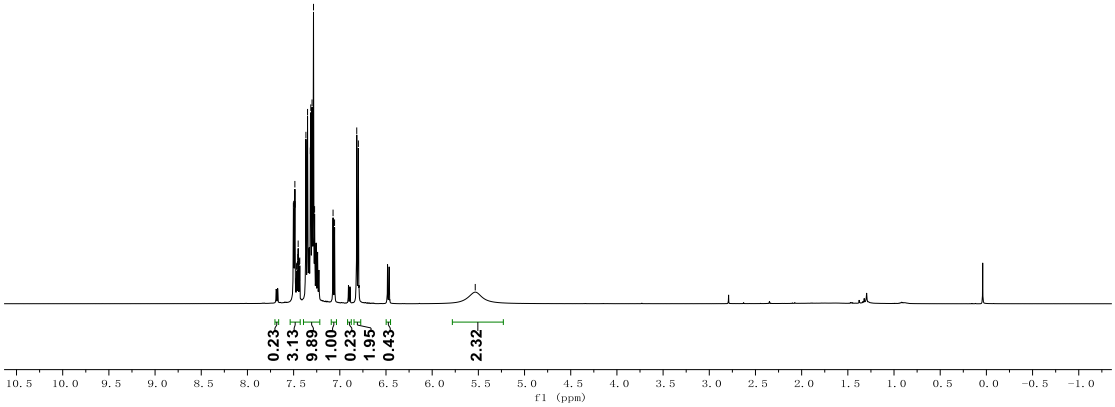

-116.87
f1 (ppm)


200.8
195.6
162.4
160.5
149.4
143.7
135.7
135.7
133.2
130.5
130.3
130.2
129.7
126.6
122.0
121.4
115.4
115.2
105.8
88.8
39.2
30.9
27.2
f1 (ppm)

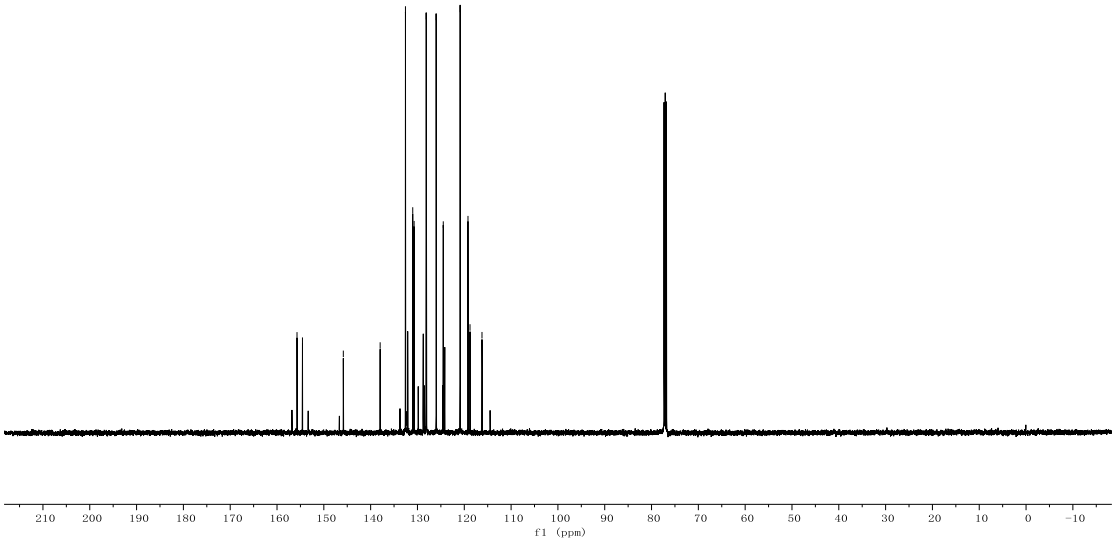


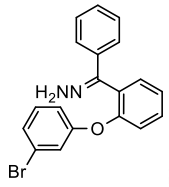
S15a

7.50 7.50 7.49 7.49 7.49 7.48 7.45 7.45 7.45 7.44 7.43 7.37 7.35 7.35 7.32 7.31 7.30 7.29 7.28 7.27 7.07 7.06 6.82 6.80 5.33

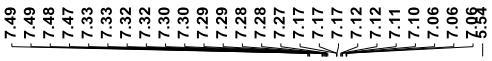


155.7 154.6 145.8 138.0 132.6 131.0 130.7 128.1 128.1 126.0 124.5 120.9 119.2 118.8 116.2




H2NN
O
Br

S15b


7.49
7.49
7.48
7.47
7.33
7.32
7.32
7.30
7.30
7.29
7.29
7.28
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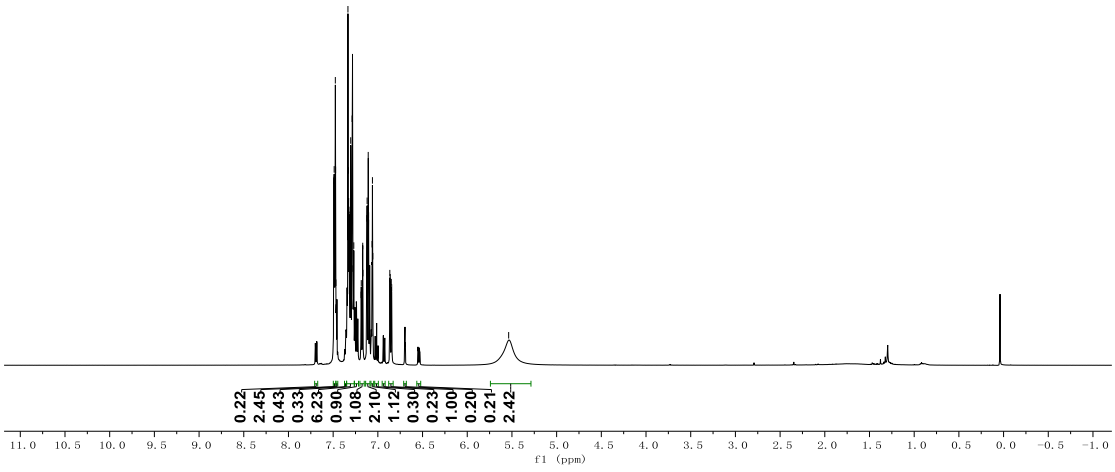
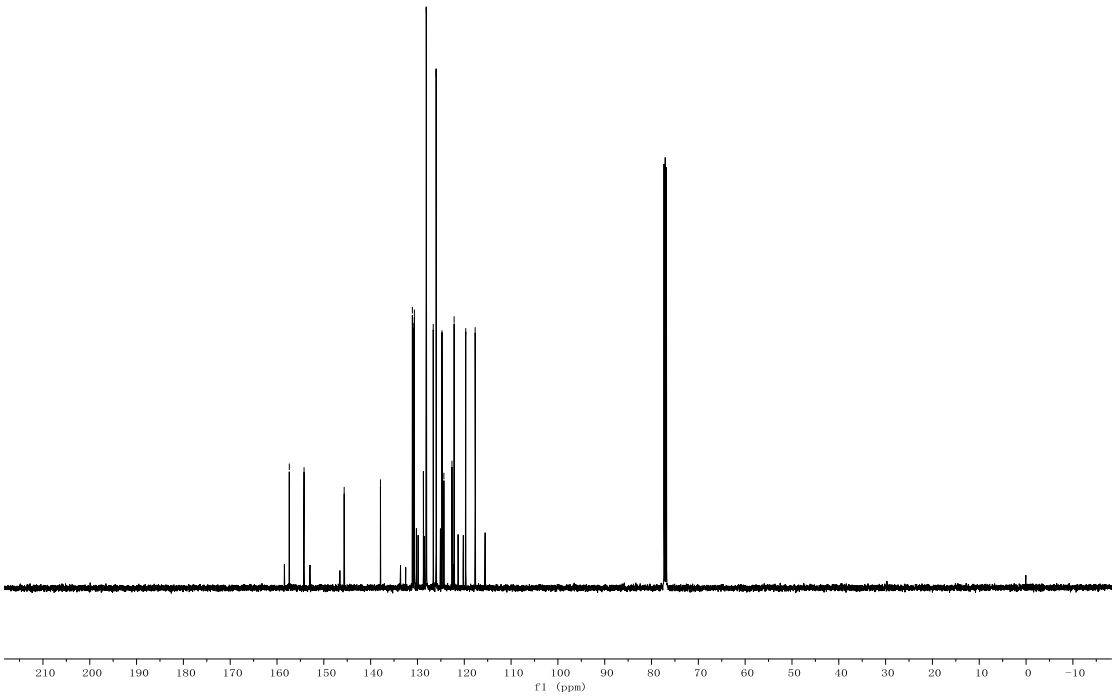
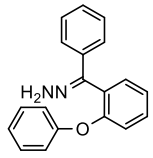
7.12
7.11
7.10
7.06
7.06
5.54


0.22
2.45
0.43
0.33
6.23
0.90
1.08
2.10
1.12
0.30
0.23
1.00
0.20
0.21
2.42
f1 (ppm)

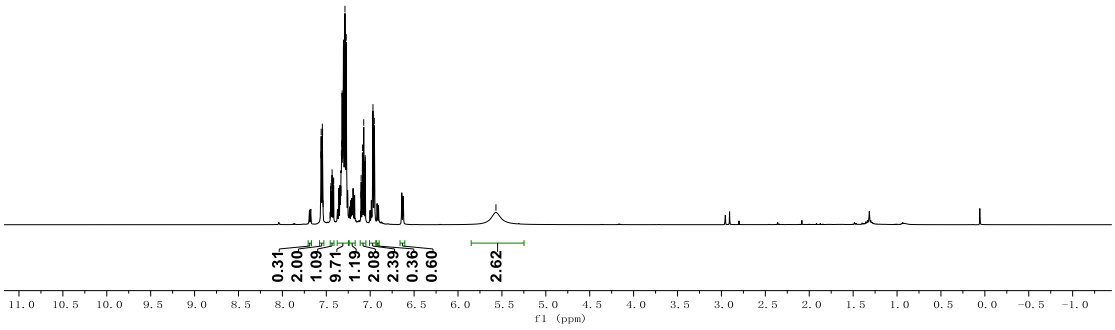

157.4
154.2
145.7
137.9
131.1
130.8
130.7
128.1
128.1
126.6
126.0
124.8
124.4
122.6
122.2
119.7
117.7


f1 (ppm)

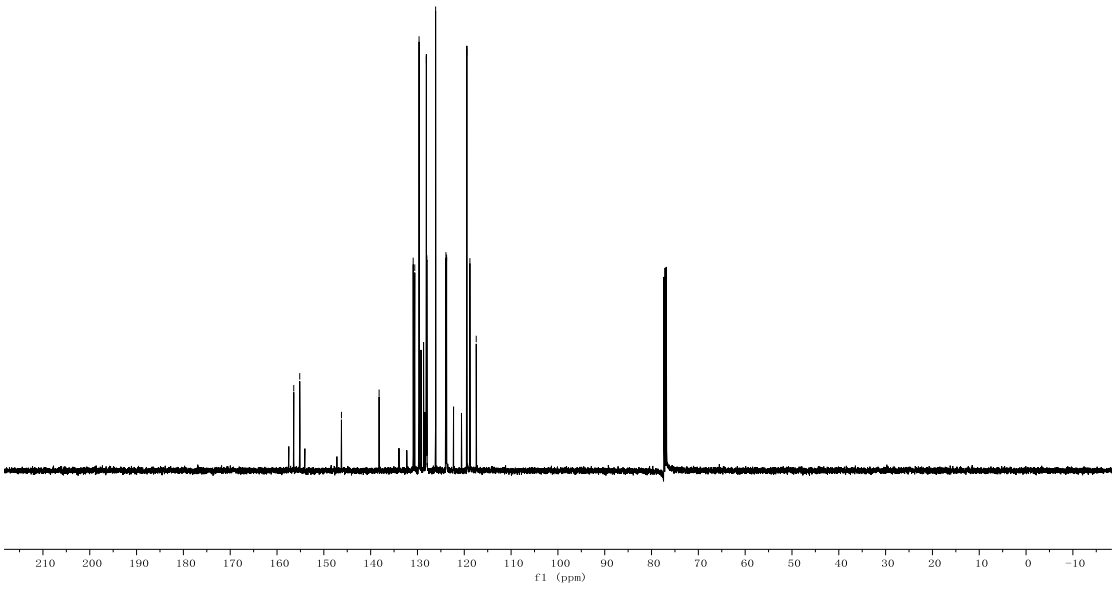


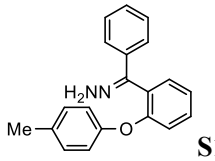
S15c

7.56 7.56 7.55 7.55 7.54 7.54 7.54 7.46 7.45 7.45 7.44 7.43 7.43 7.42 7.42 7.33 7.32 7.32 7.31 7.31 7.30 7.30 7.30 7.29 7.29 7.29 7.28 7.28 7.28 7.27 7.27 7.11 7.11 7.10 7.10 7.09 7.09 7.09 7.07 7.06 7.06 6.97 6.97 6.96 6.96 6.96 6.95 6.95 5.57

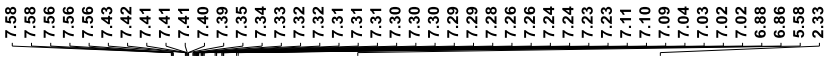


156.4 155.1 146.2 138.2 130.9 130.6 129.7 128.1 128.0 126.1 123.9 123.8 119.5 118.8 117.4




H2NN
Me
O

S15d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7.58
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7.56
7.56
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7.41
7.41
7.41
7.40
7.39
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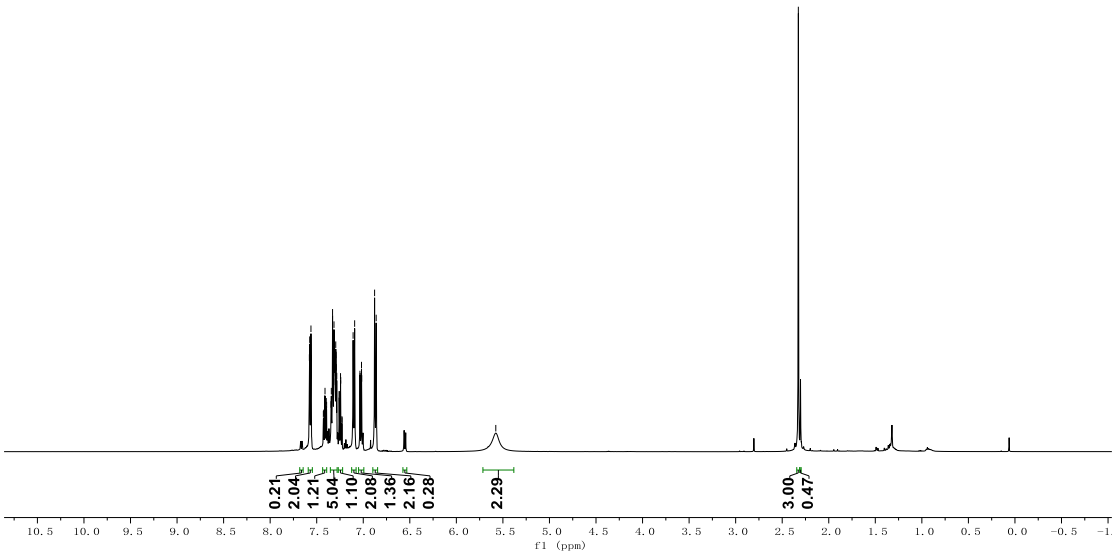
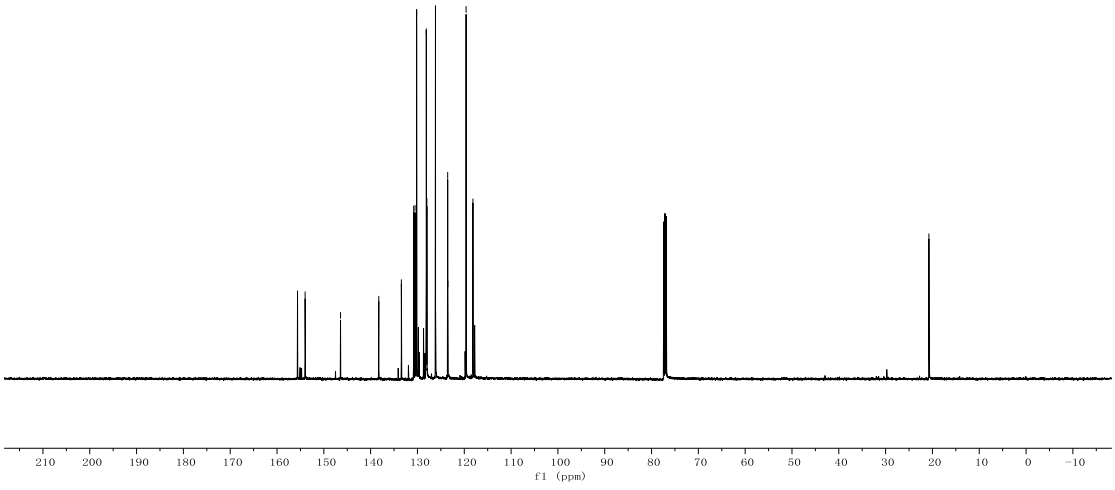
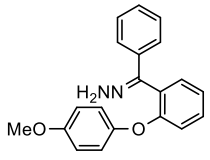
7.34
7.33
7.32
7.32
7.31
7.31
7.31
7.30
7.30
7.30
7.29
7.29
7.28
7.26
7.26
7.24
7.24
7.23
7.23
7.11
7.10
7.09
7.04
7.03
7.02
7.02
6.88
6.86
5.58
2.33

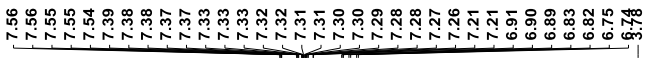

0.21
2.04
1.21
5.04
1.10
2.08
1.36
2.16
0.28
2.29
3.00
0.47
f1 (ppm)

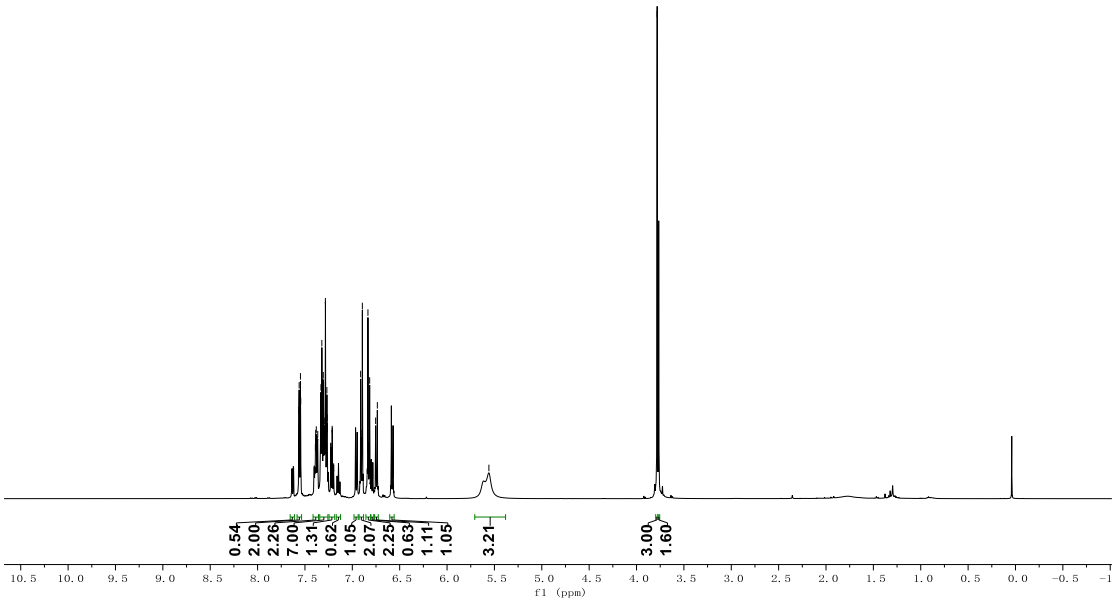

155.6
154.0
146.4
138.3
133.4
130.8
130.5
130.2
128.1
128.0
126.1
123.5
123.5
119.6
118.2
20.8

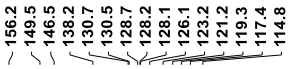

f1 (ppm)


H2NN
MeO
O

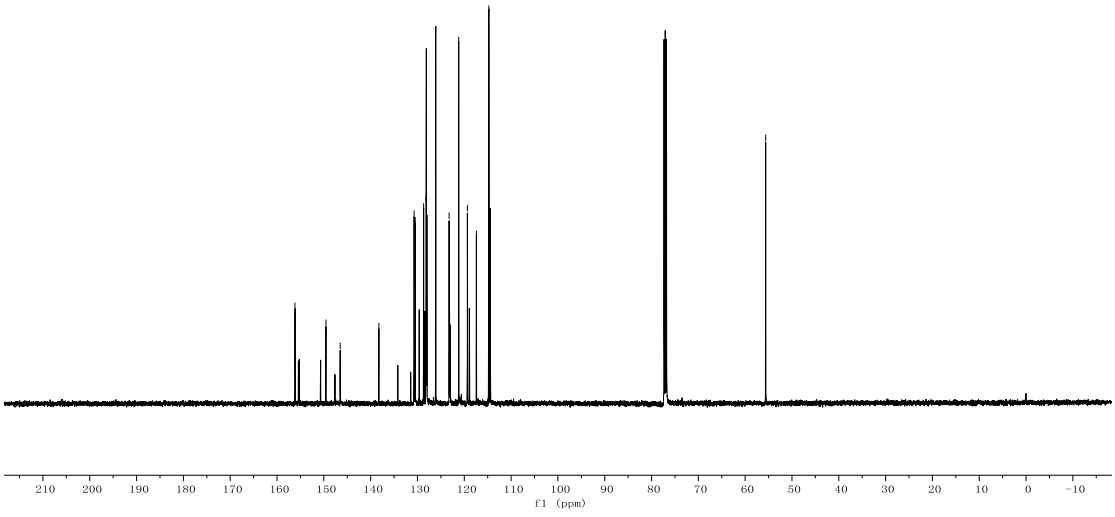
S15e

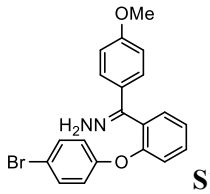

7.56
7.56
7.55
7.55
7.54
7.39
7.38
7.38
7.37
7.37
7.33
7.33
7.32
7.31
7.31
7.30
7.30
7.29
7.28
7.28
7.27
7.26
7.21
7.21
6.91
6.90
6.89
6.83
6.82
6.75
6.74
3.78


0.54
2.00
2.26
7.00
1.31
0.62
1.05
2.07
2.25
0.63
1.11
1.05
3.21
3.00
1.60
f1 (ppm)


156.2
149.5
146.5
138.2
130.7
130.5
128.7
128.2
128.1
126.1
123.2
121.2
119.3
117.4
114.8

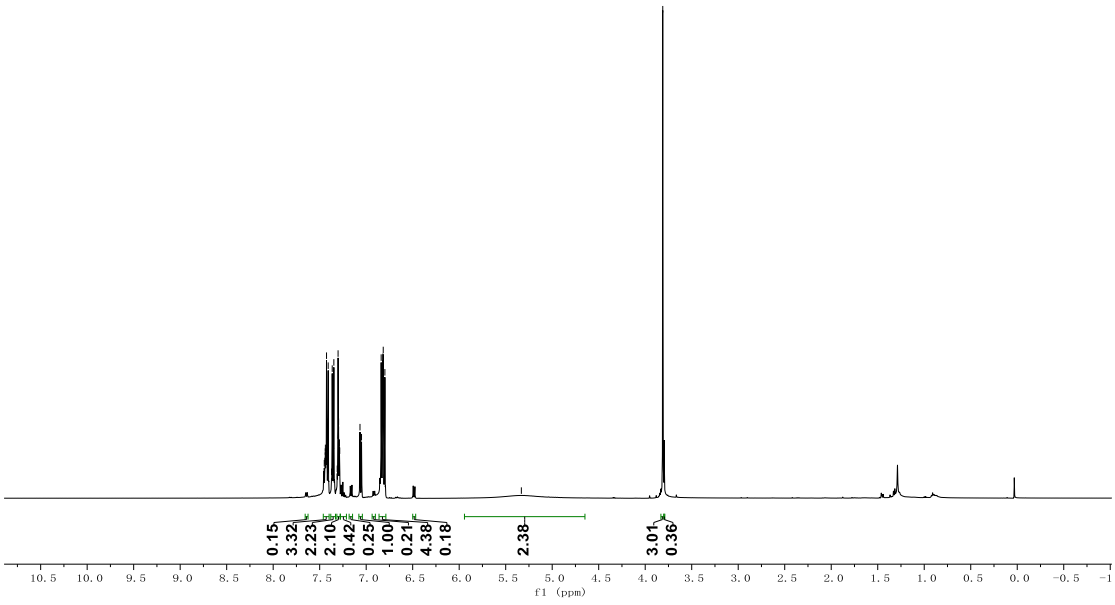

55.6


f1 (ppm)

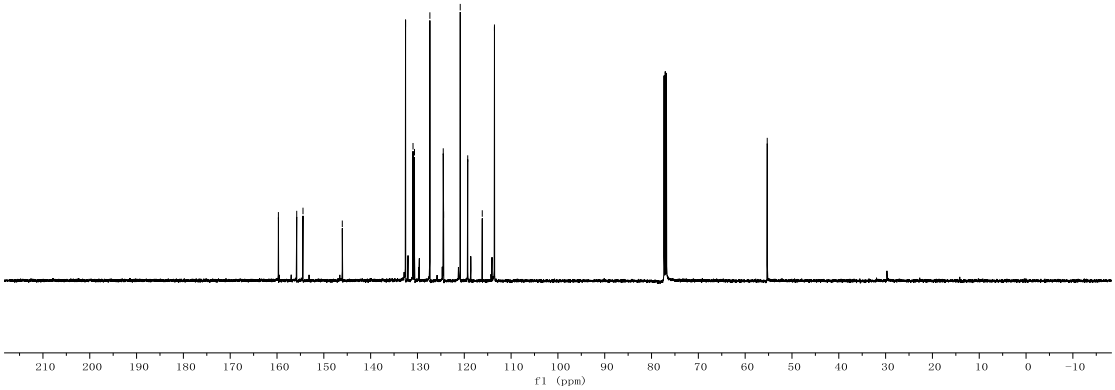

OMe
H2NN
Br
O

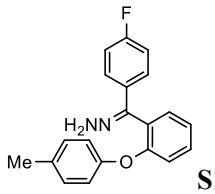
S15f


7.45
7.44
7.44
7.44
7.43
7.43
7.43
7.42
7.41
7.41
7.37
7.36
7.35
7.35
7.31
7.30
7.30
7.29
7.29
7.28
7.07
7.05
6.84
6.82
6.82
6.80
5.33
3.81


0.15
3.32
2.23
2.10
0.42
0.25
1.00
0.21
4.38
0.18
2.38
3.01
0.36
f1 (ppm)

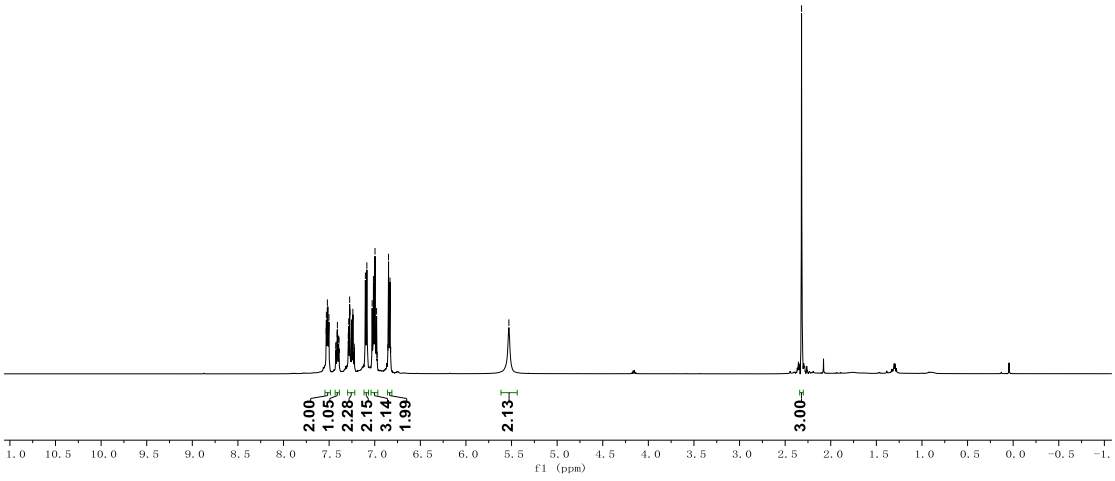

159.7
155.8
154.5
146.1
132.5
131.0
130.8
130.6
127.3
124.5
124.4
120.9
119.3
116.2
113.6
55.3

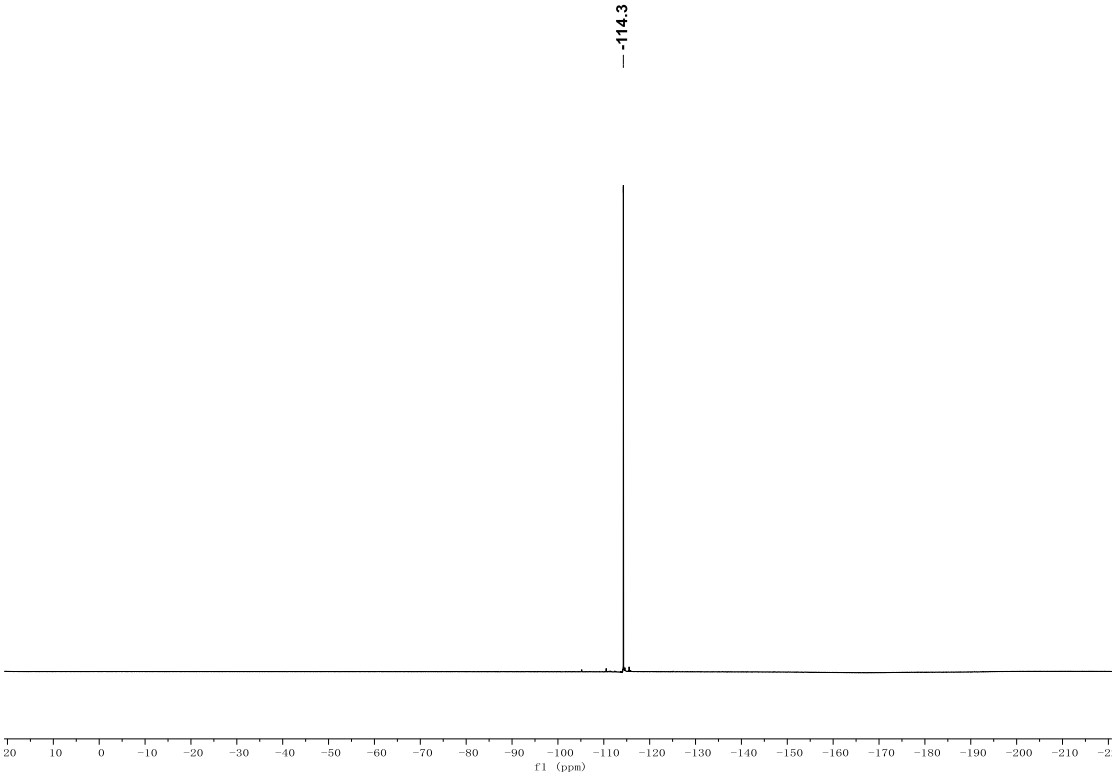

f1 (ppm)

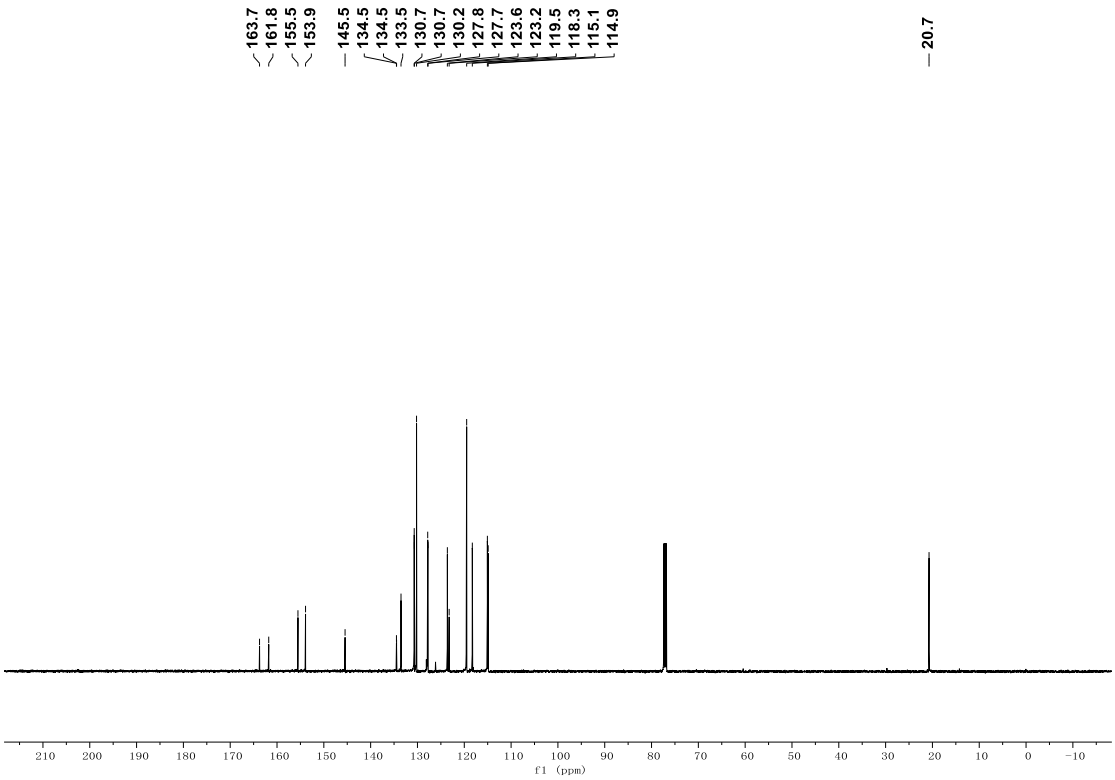


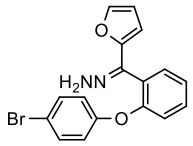
S15g

7.53 7.53 7.53 7.52 7.52 7.51 7.51 7.51 7.50 7.43 7.42 7.41 7.41 7.41 7.40 7.39 7.29 7.29 7.27 7.27 7.25 7.25 7.24 7.24 7.22 7.22 7.10 7.09 7.03 7.02 7.01 7.01 7.00 7.00 6.99 6.98 6.98 6.97 6.86 6.85 6.84 6.83 6.82 5.53 2.32



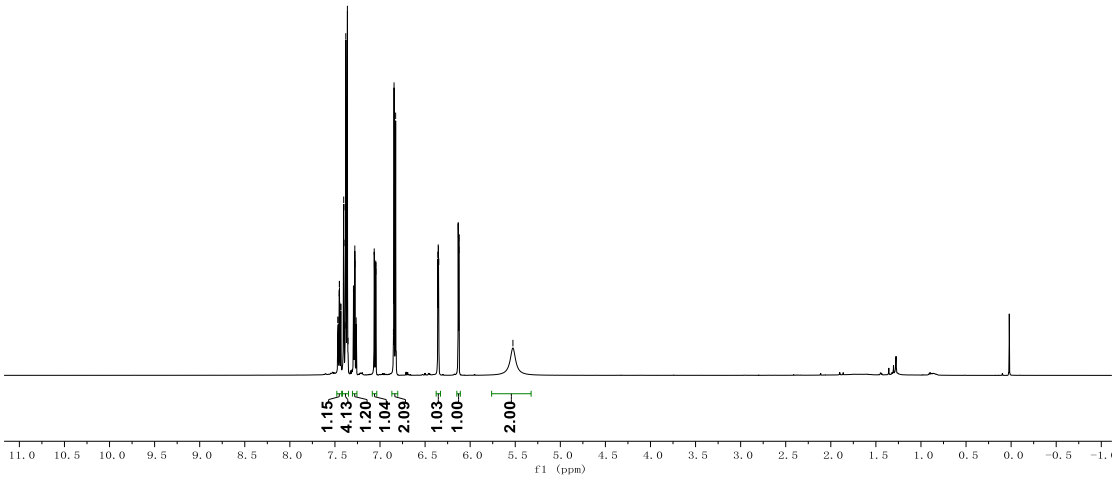


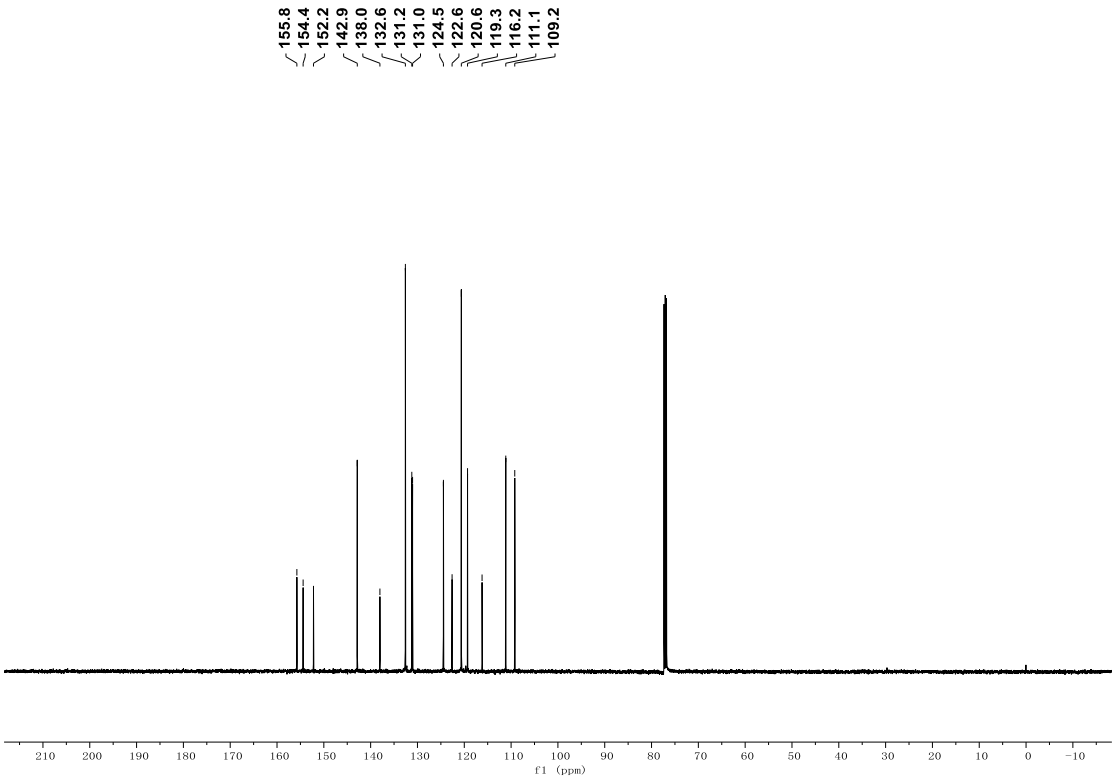

163.7
161.8
155.5
153.9
145.5
134.5
133.5
130.7
130.7
130.2
127.8
127.7
123.6
123.2
119.5
118.3
115.1
114.9
20.7
f1 (ppm)

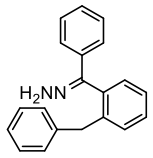

O
H2NN
Br
O

S15h

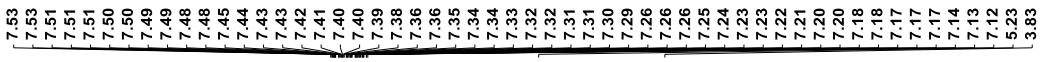

7.45
7.45
7.40
7.40
7.40
7.40
7.38
7.38
7.37
7.36
7.29
7.28
7.06
7.06
7.05
7.05
6.84
6.84
6.83
6.83
6.36
6.35
6.35
6.13
6.13
6.12
5.53


1.15
4.13
1.20
1.04
2.09
1.03
1.00
2.00
f1 (ppm)


155.8
154.4
152.2
142.9
138.0
132.6
131.2
131.0
124.5
122.6
120.6
119.3
116.2
111.1
109.2
f1 (ppm)


H2NN

S15i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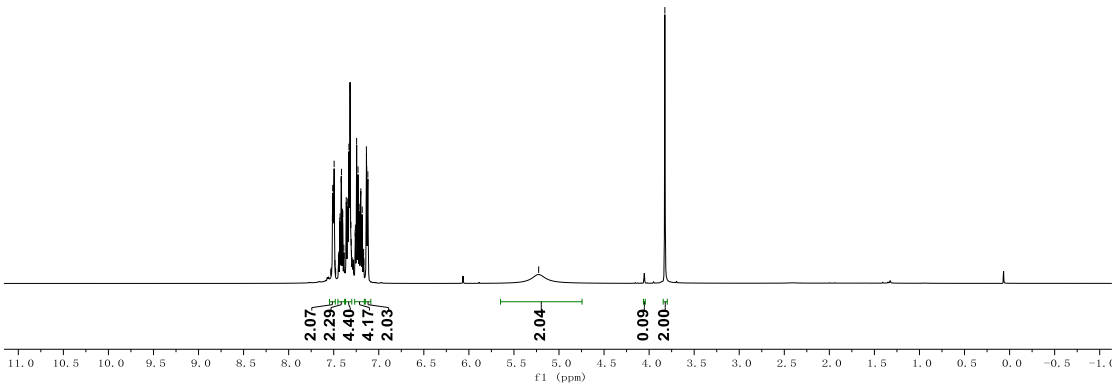
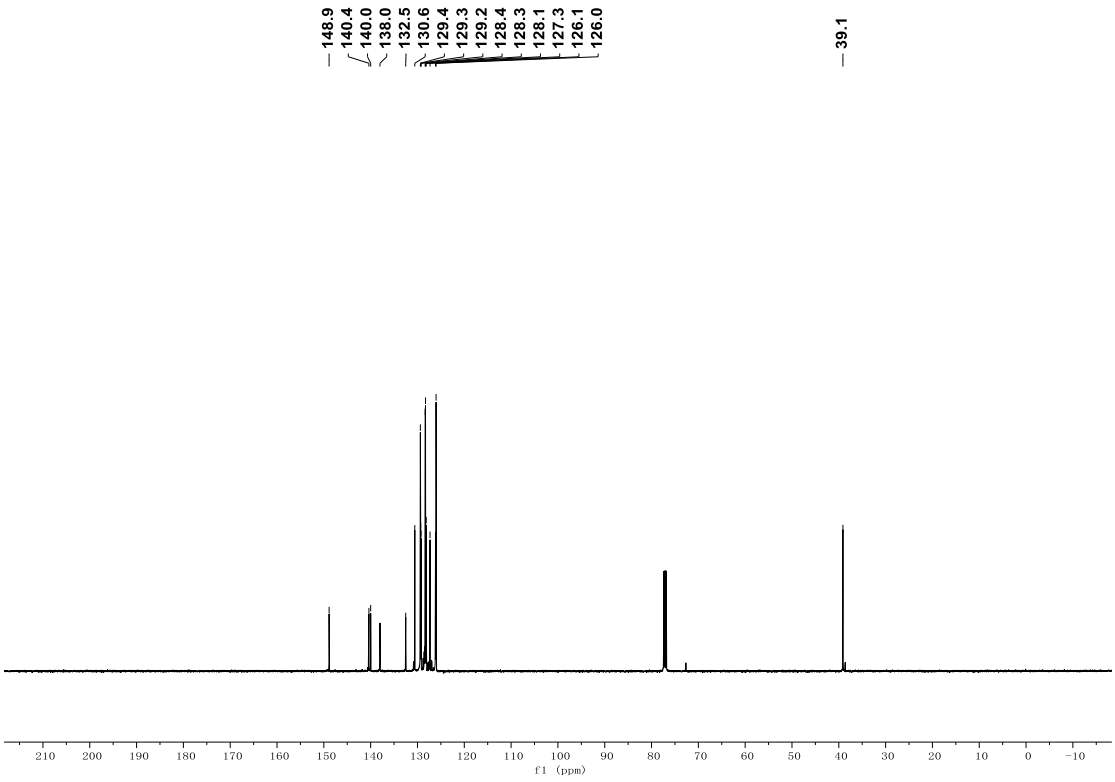
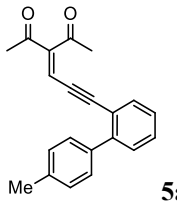
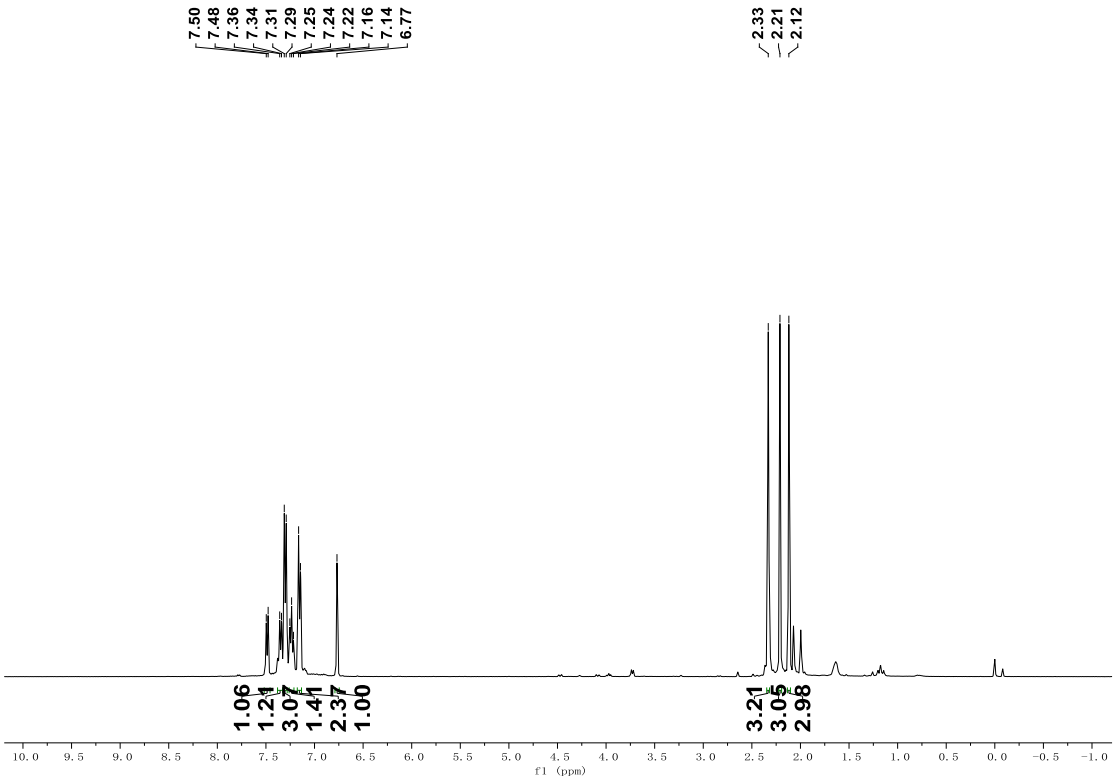
7.53
7.51
7.51
7.51
7.50
7.50
7.49
7.49
7.48
7.48
7.45
7.44
7.43
7.43
7.42
7.41
7.40
7.40
7.39
7.38
7.36
7.36
7.35
7.34
7.34
7.33
7.32
7.32
7.31
7.31
7.30
7.29
7.26
7.26
7.26
7.25
7.24
7.23
7.23
7.22
7.21
7.20
7.20
7.18
7.18
7.17
7.17
7.17
7.14
7.13
7.12
5.23
3.83

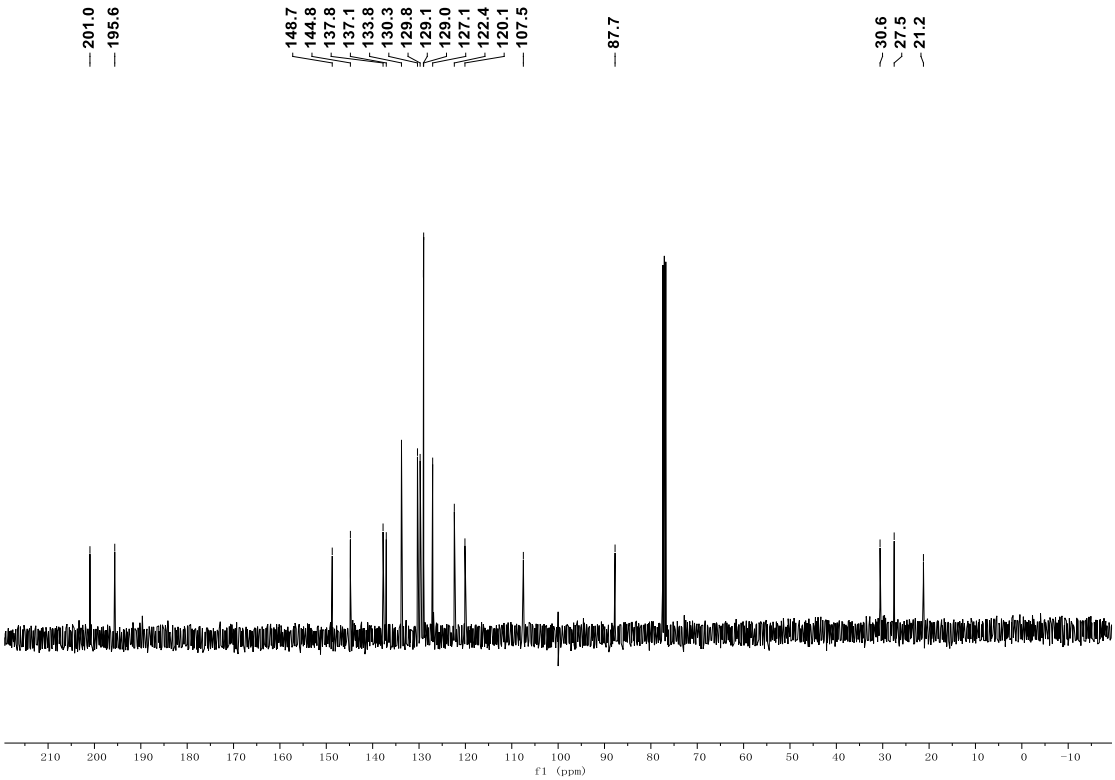

2.07
2.29
4.40
4.17
2.03
2.04
0.09
2.00
f1 (ppm)

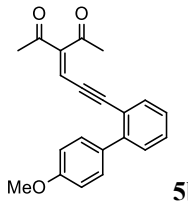

148.9
140.4
140.0
138.0
132.5
130.6
129.4
129.3
129.2
128.4
128.3
128.1
127.3
126.1
126.0
39.1
f1 (ppm)


O
O
Me

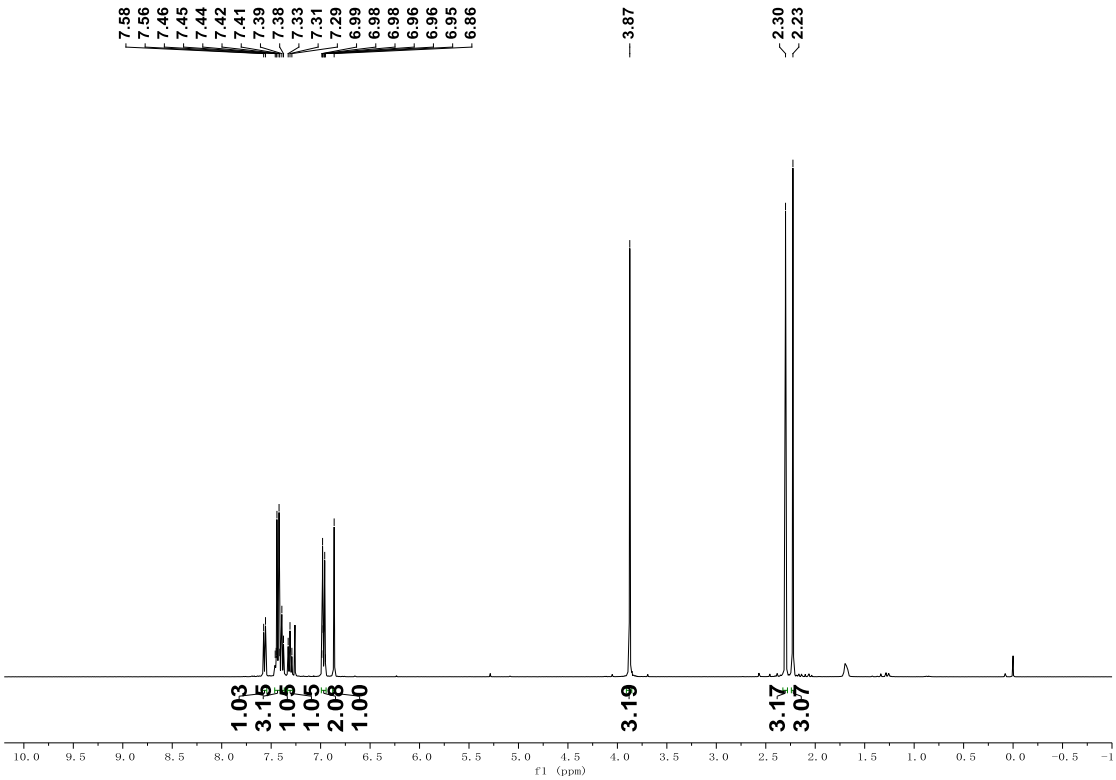
5a

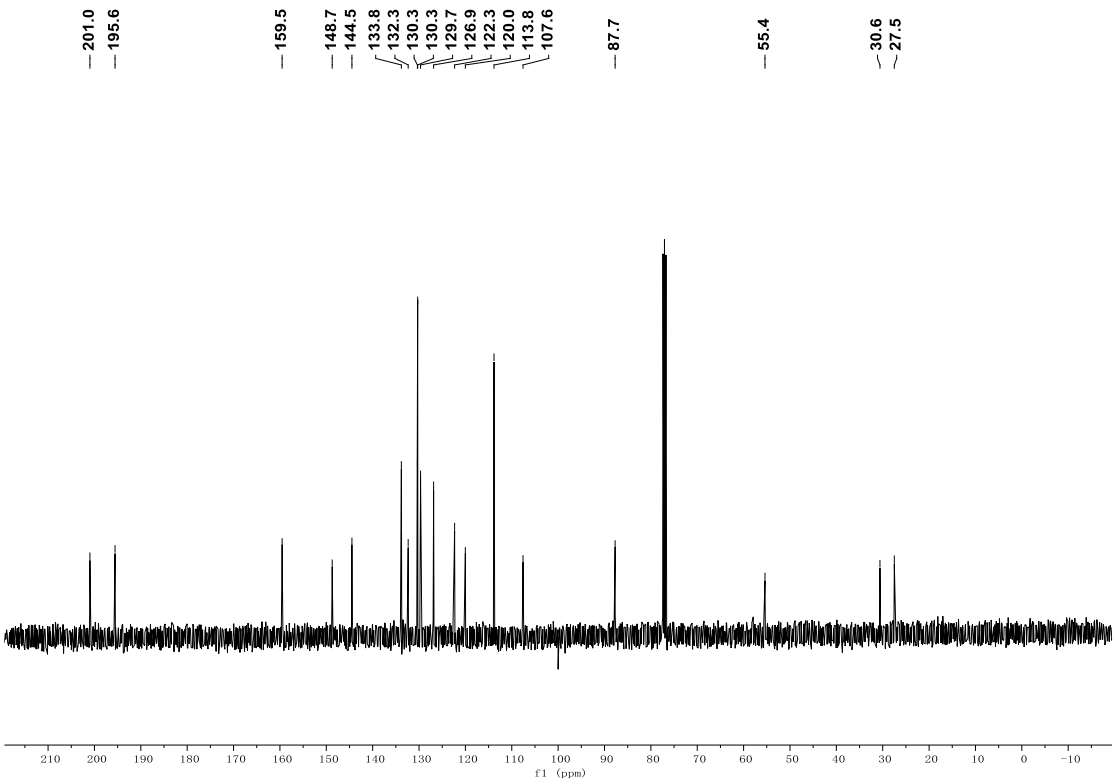

7.50
7.48
7.36
7.34
7.31
7.29
7.25
7.24
7.22
7.16
7.14
6.77
2.33
2.21
2.12
1.06
1.21
3.07
1.41
2.37
1.00
3.21
3.05
2.98
f1 (ppm)

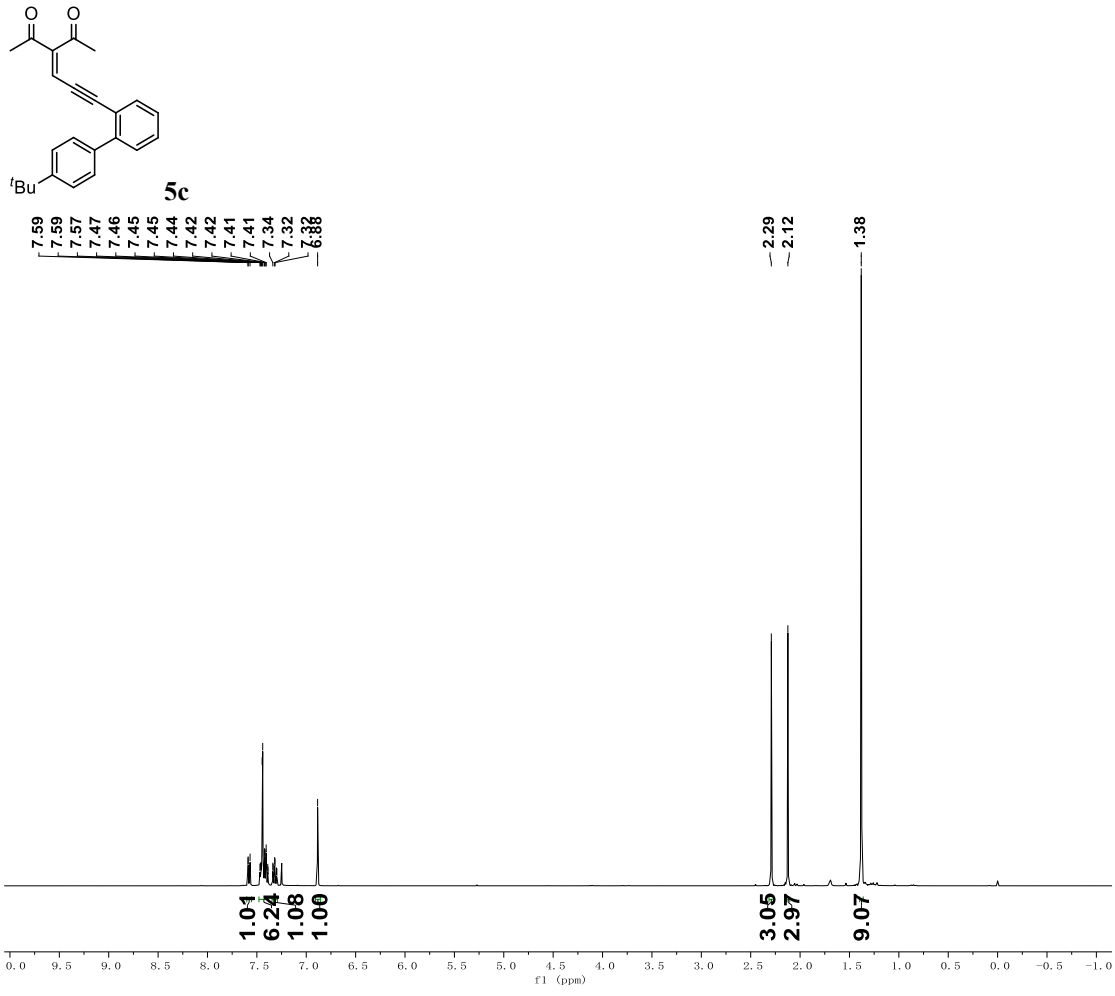

201.0
195.6
148.7
144.8
137.8
137.1
133.8
130.3
129.8
129.1
129.0
127.1
122.4
120.1
107.5
87.7
30.6
27.5
21.2
f1 (ppm)

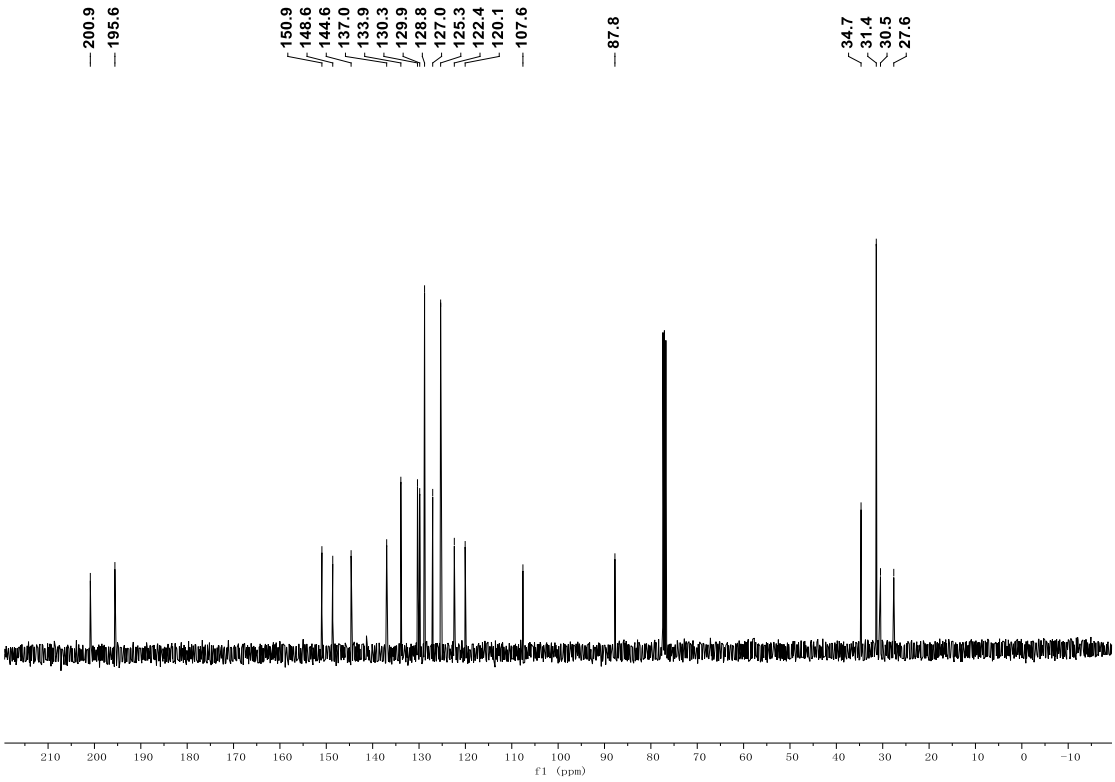

O
O
MeO

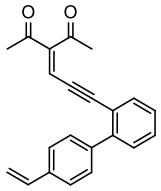
5b


7.58
7.56
7.46
7.45
7.44
7.42
7.41
7.39
7.38
7.33
7.31
7.29
6.99
6.98
6.98
6.96
6.96
6.95
6.86
3.87
2.30
2.23
1.03
3.15
1.05
1.05
2.08
1.00
3.19
3.17
3.07
f1 (ppm)

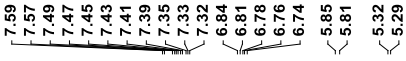

201.0
195.6
159.5
148.7
144.5
133.8
132.3
130.3
130.3
129.7
126.9
122.3
120.0
113.8
107.6
87.7
55.4
30.6
27.5
f1 (ppm)

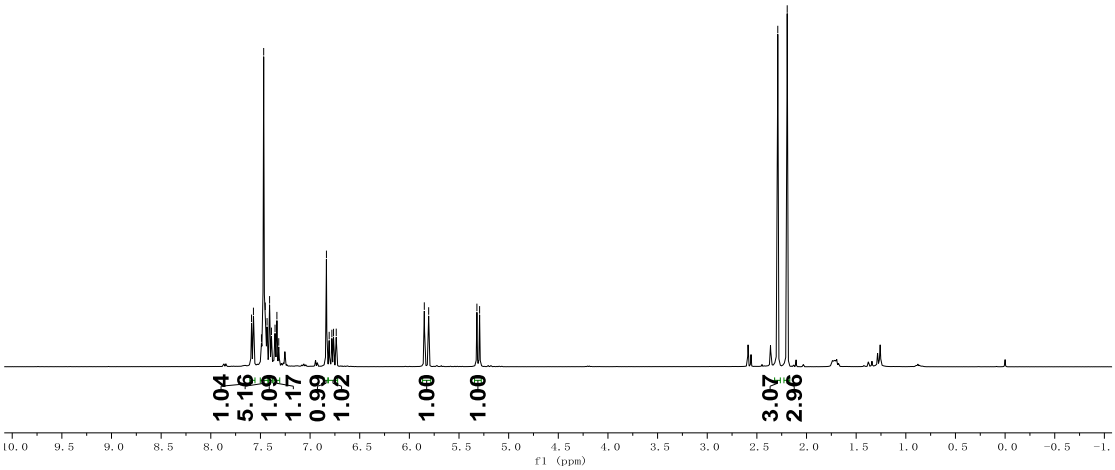

5c
7.59
7.59
7.57
7.47
7.46
7.45
7.45
7.44
7.42
7.42
7.41
7.41
7.34
7.32
2.29
2.12
1.38
1.01
6.24
1.08
1.00
3.05
2.97
9.07
f1 (ppm)


200.9
195.6
150.9
148.6
144.6
137.0
133.9
130.3
129.9
128.8
127.0
125.3
122.4
120.1
107.6
87.8
34.7
31.4
30.5
27.6
f1 (ppm)



5d


7.59
7.57
7.49
7.47
7.45
7.43
7.41
7.39
7.35
7.33
7.32
6.84
6.81
6.78
6.76
6.74
5.85
5.81
5.32
5.29
2.29
2.19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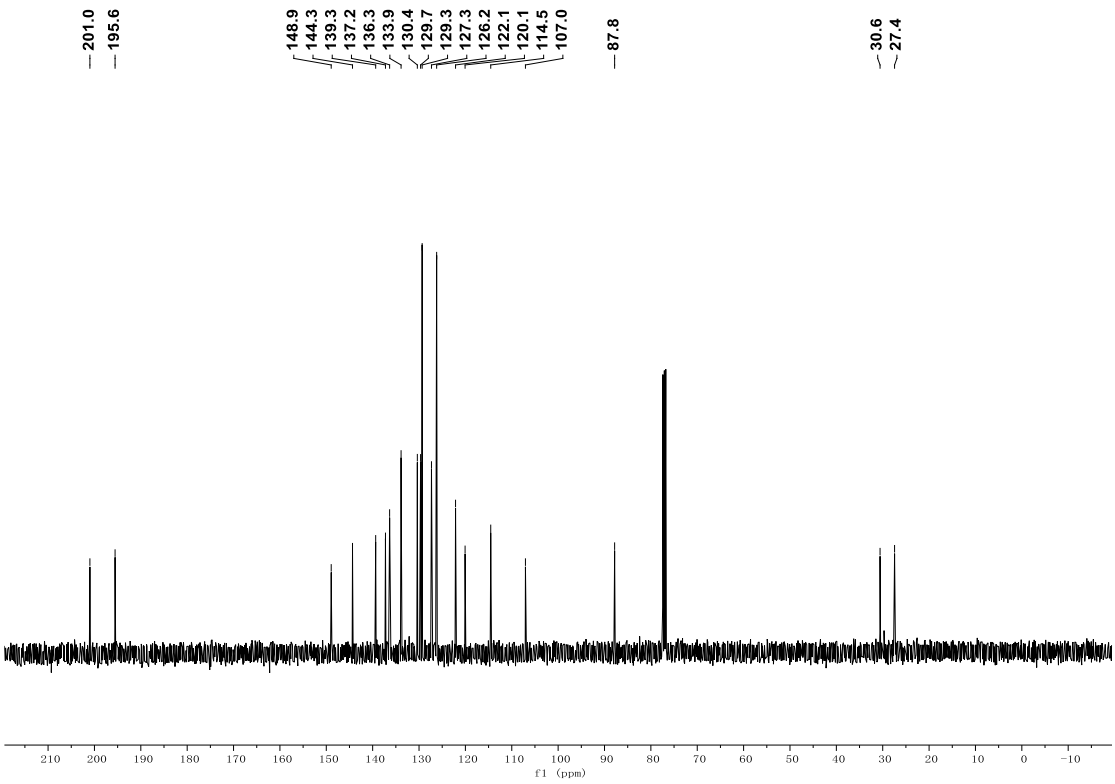
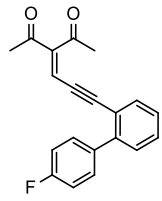
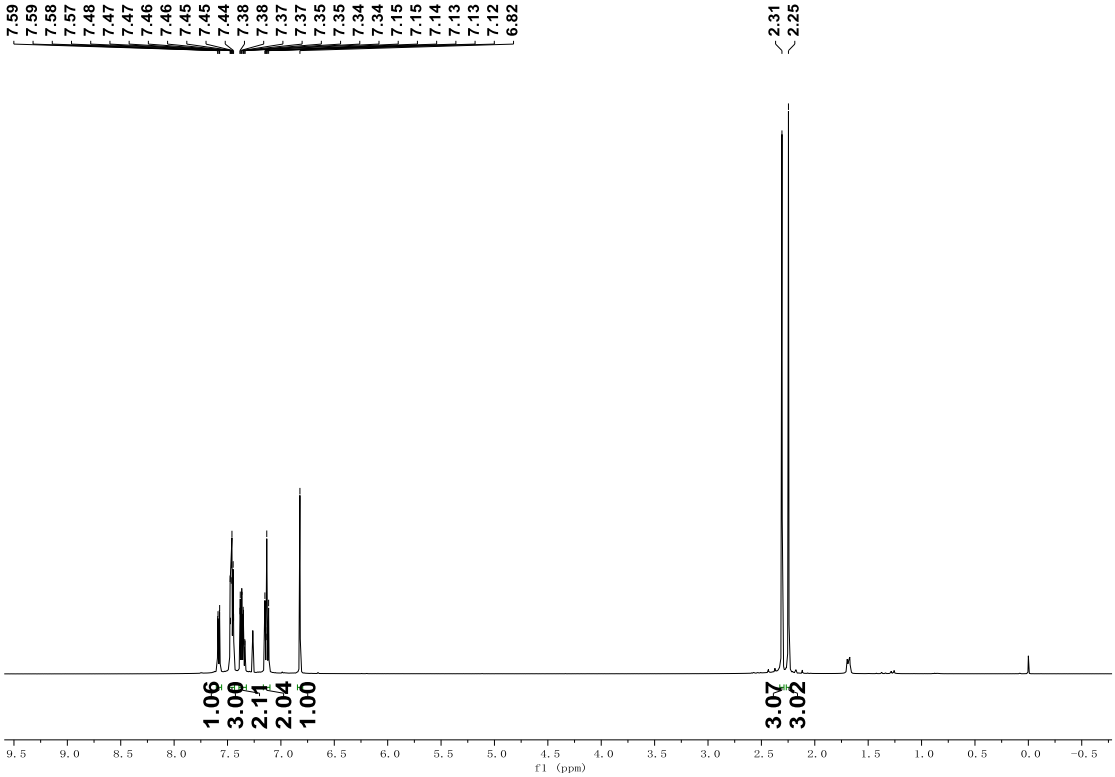
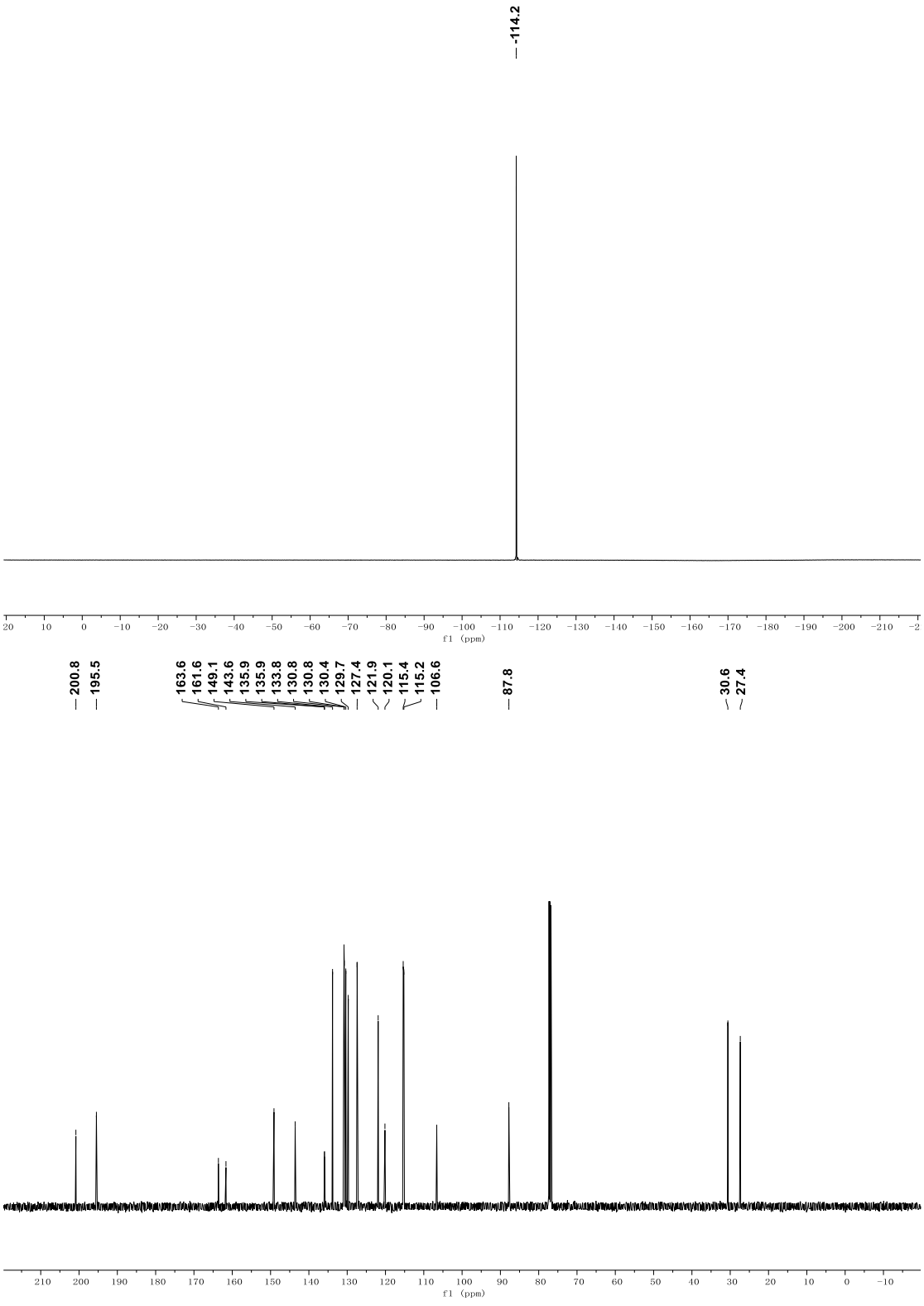
1.03
1.17
0.99
1.02
1.00
1.00
3.07
2.96
f1 (ppm)

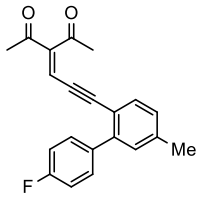

201.0
195.6
148.9
144.3
139.3
137.2
136.3
133.9
130.4
129.7
129.3
127.3
126.2
122.1
120.1
114.5
107.0
87.8
30.6
27.4
f1 (ppm)


O
O
F

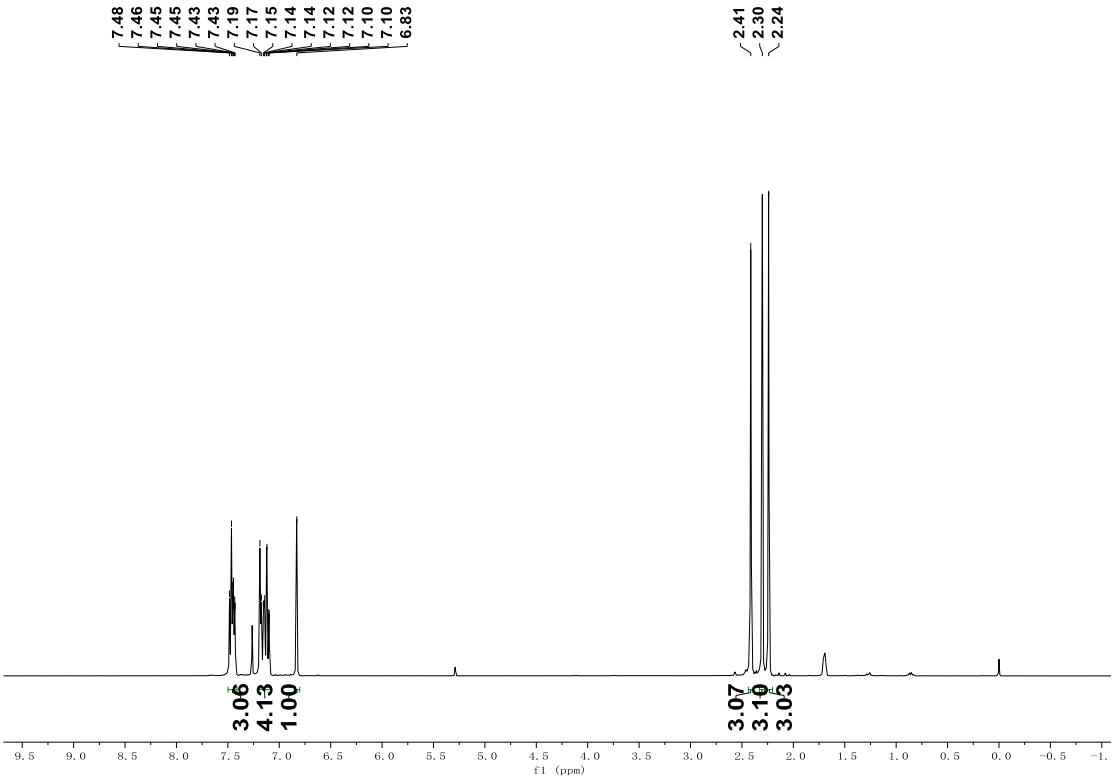
5e


7.59
7.59
7.58
7.57
7.48
7.47
7.47
7.46
7.46
7.45
7.45
7.44
7.38
7.38
7.37
7.37
7.35
7.35
7.34
7.34
7.15
7.15
7.14
7.13
7.13
7.12
6.82
2.31
2.25
1.06
3.00
2.11
2.04
1.00
3.07
3.02
f1 (ppm)


-114.2
f1 (ppm)
200.8
195.5
163.6
161.6
149.1
143.6
135.9
135.9
133.8
130.8
130.8
130.4
129.7
127.4
121.9
120.1
115.4
115.2
106.6
87.8
30.6
27.4
f1 (ppm)


O
O
Me
F

5f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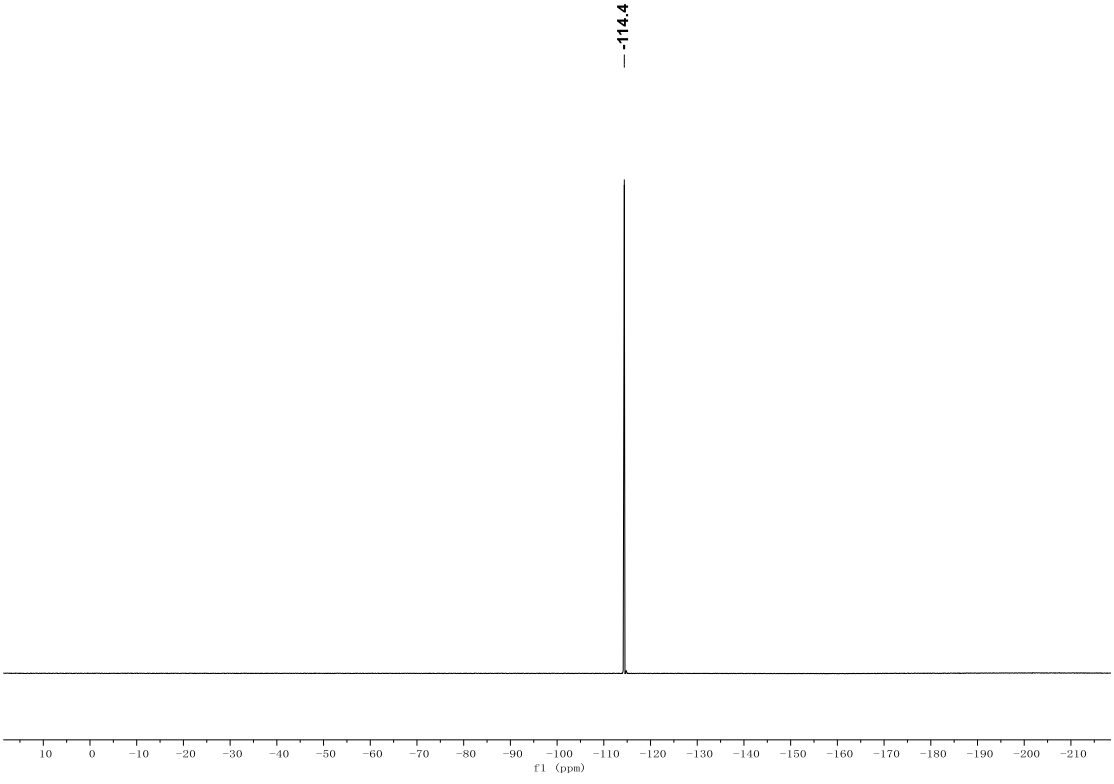
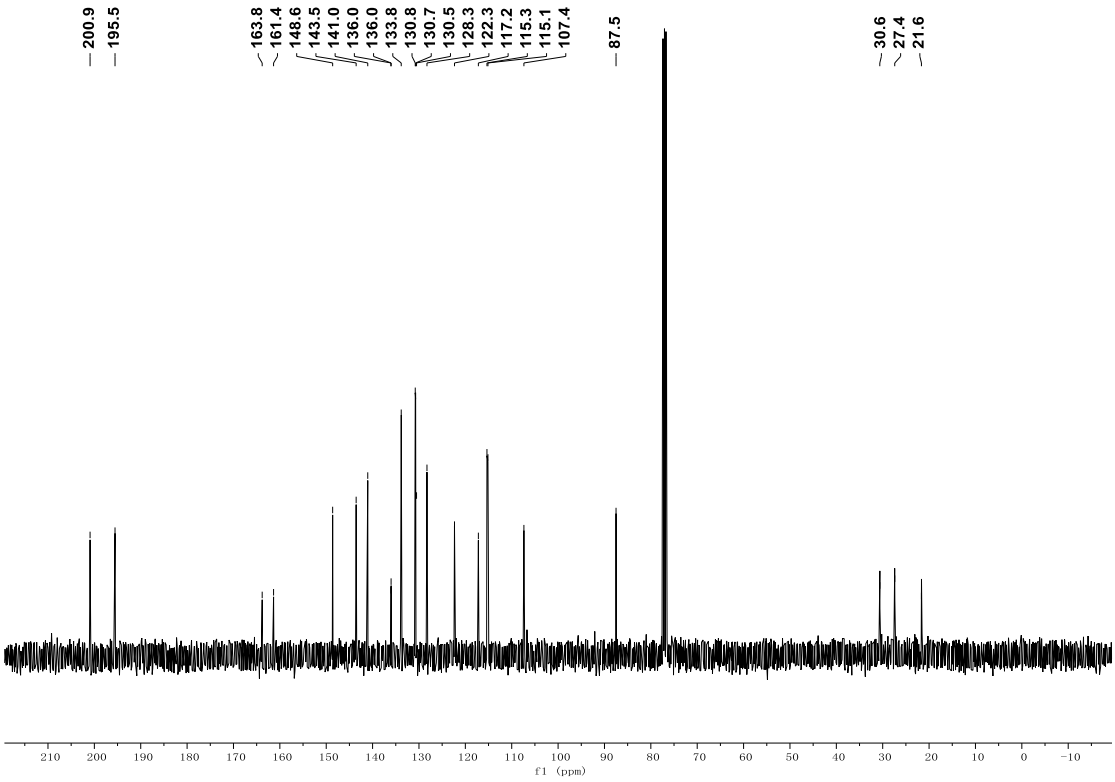
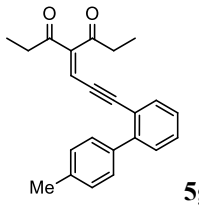
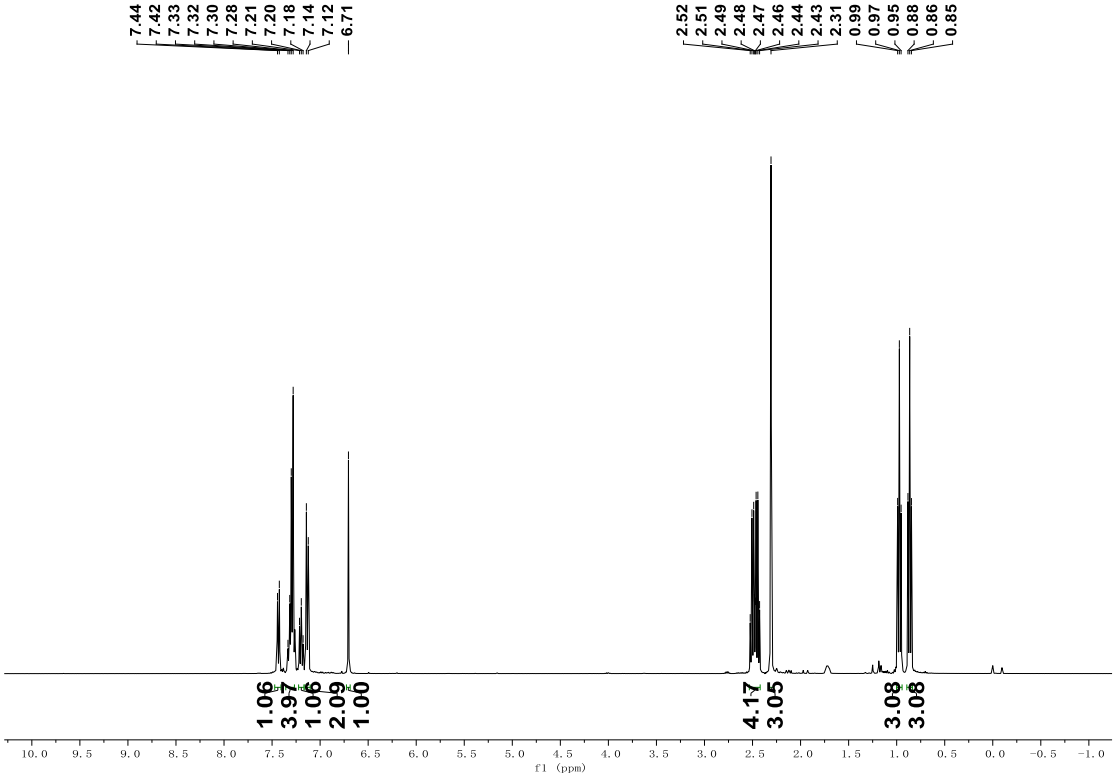
7.45
7.43
7.43
7.19
7.17
7.15
7.14
7.14
7.12
7.12
7.10
7.10
6.83
2.41
2.30
2.24
3.06
4.13
1.00
3.07
3.10
3.03
f1 (ppm)


-114.4
f1 (ppm)


200.9
195.5
163.8
161.4
148.6
143.5
141.0
136.0
136.0
133.8
130.8
130.7
130.5
128.3
122.3
117.2
115.3
115.1
107.4
87.5
30.6
27.4
21.6
f1 (ppm)


O
O
Me

5g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7.42
7.33
7.32
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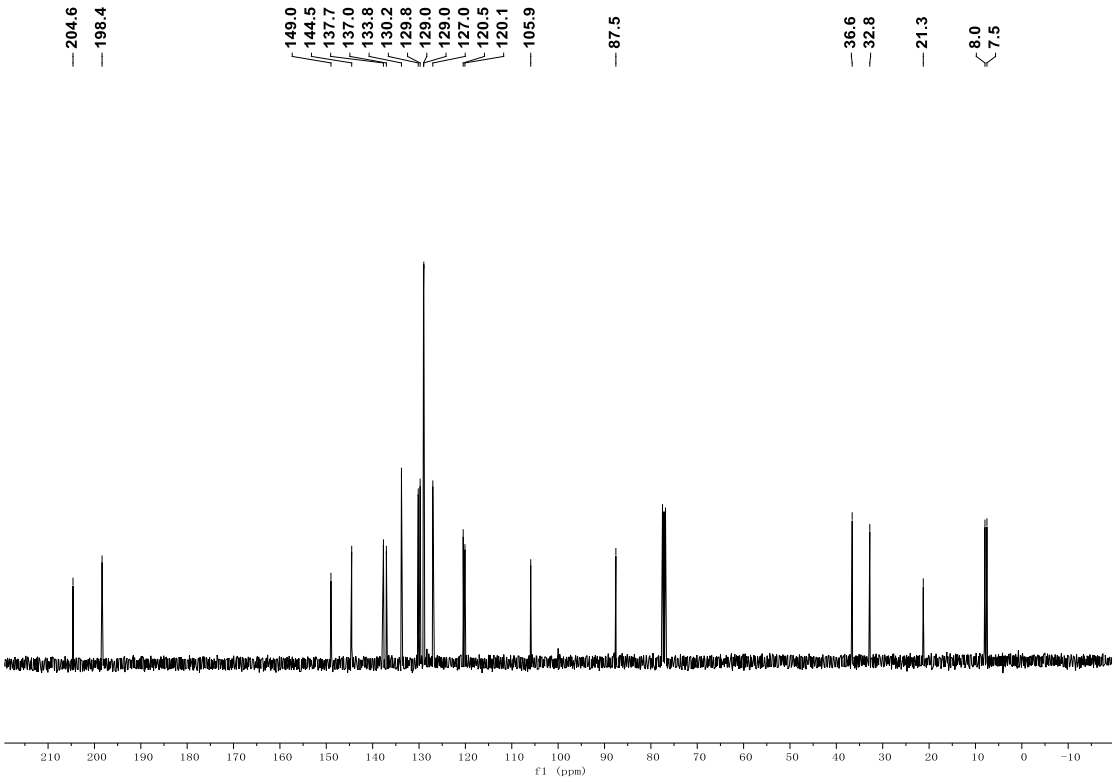
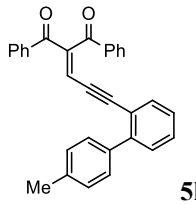
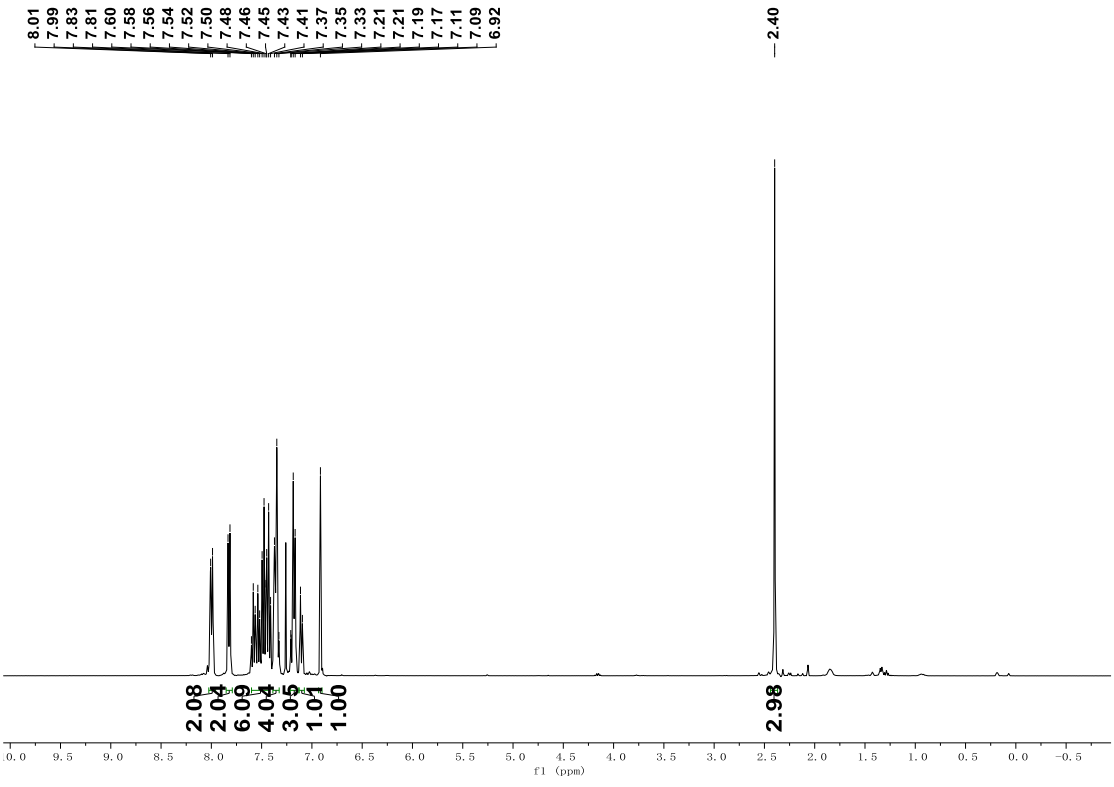
7.28
7.21
7.20
7.18
7.14
7.12
6.71
2.52
2.51
2.49
2.48
2.47
2.46
2.44
2.43
2.31
0.99
0.97
0.95
0.88
0.86
0.85
1.06
3.97
1.06
2.09
1.00
4.17
3.05
3.08
3.08
f1 (ppm)


204.6
198.4
149.0
144.5
137.7
137.0
133.8
130.2
129.8
129.0
129.0
127.0
120.5
120.1
105.9
87.5
36.6
32.8
21.3
8.0
7.5
f1 (ppm)


O
O
Ph
Ph
Me

5h


8.01
7.99
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7.81
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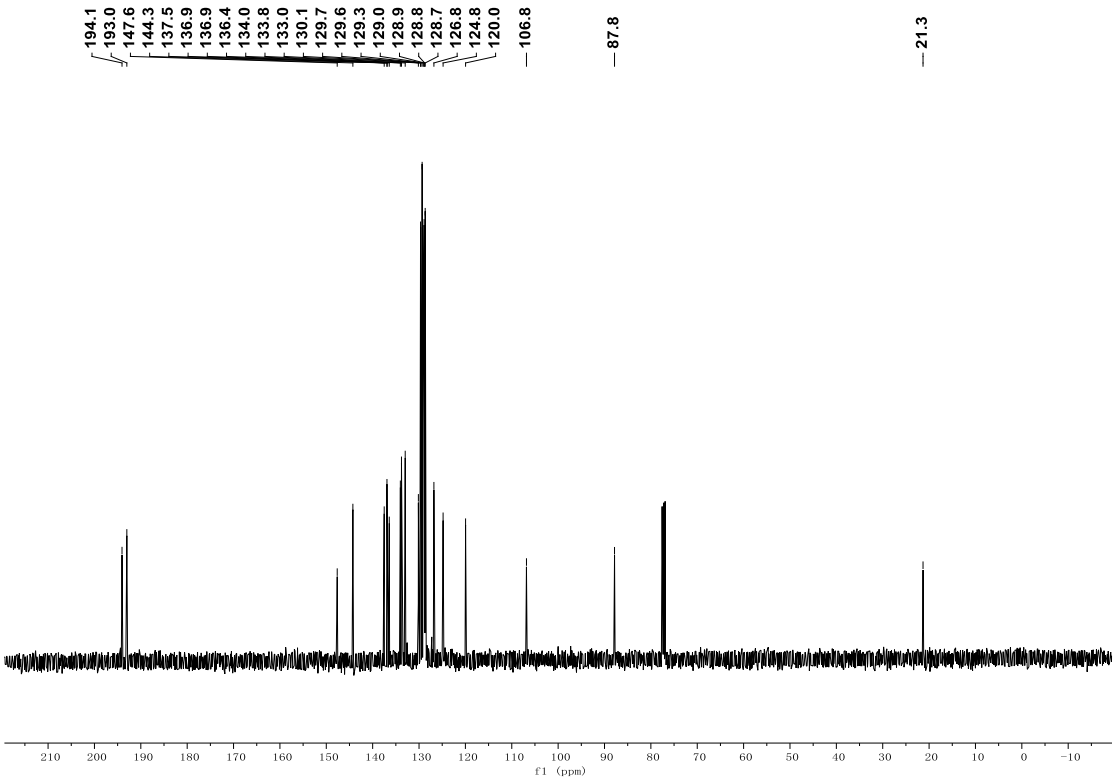
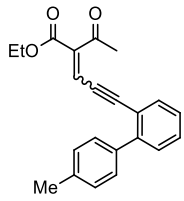
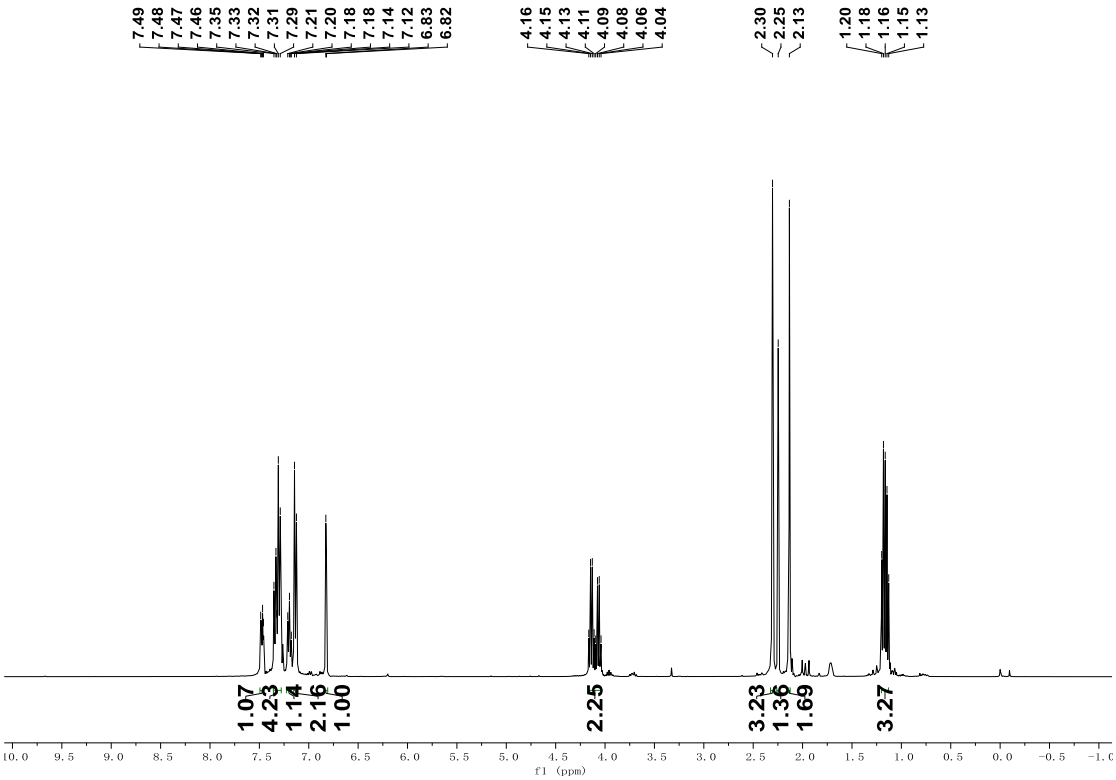
7.58
7.56
7.54
7.52
7.50
7.48
7.46
7.45
7.43
7.41
7.37
7.35
7.33
7.21
7.21
7.19
7.17
7.11
7.09
6.92
2.40
2.08
2.04
6.09
4.04
3.05
1.01
1.00
2.98
f1 (ppm)


194.1
193.0
147.6
144.3
137.5
136.9
136.9
136.4
134.0
133.8
133.0
130.1
129.7
129.6
129.3
129.0
128.9
128.8
128.7
126.8
124.8
120.0
106.8
87.8
21.3
f1 (ppm)


O
O
EtO
Me

5i (*E*/*Z* = 1.25:1)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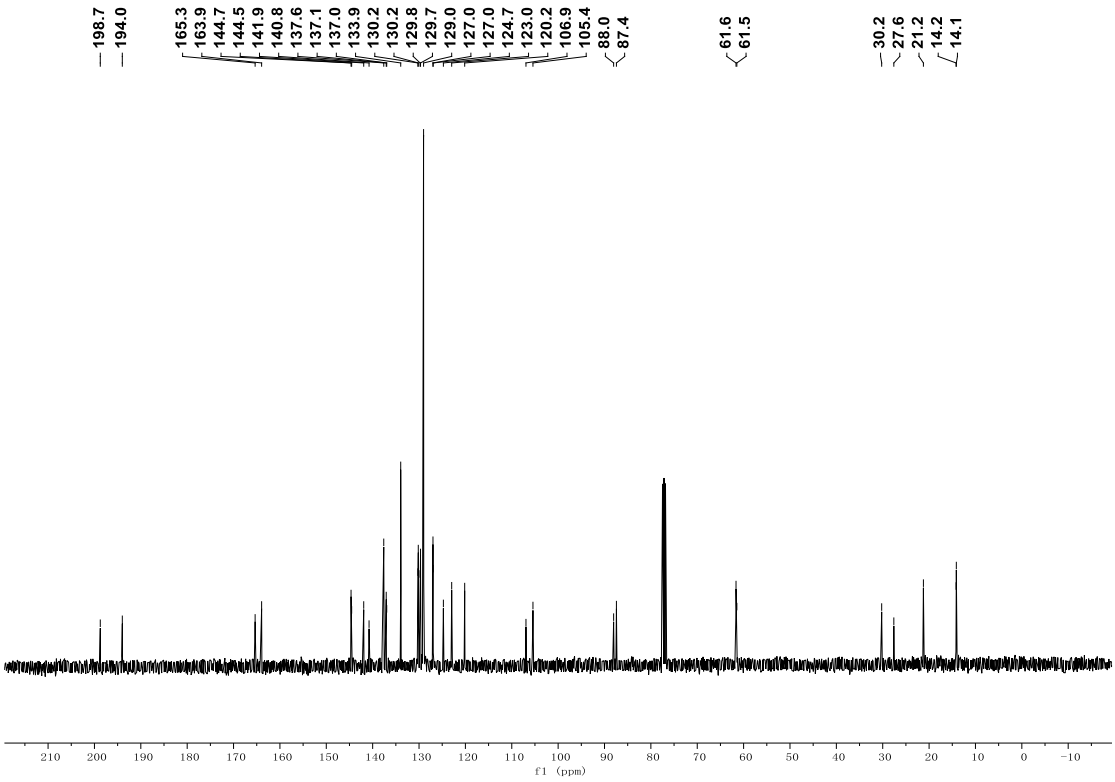
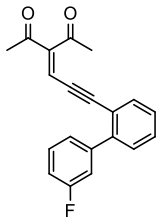
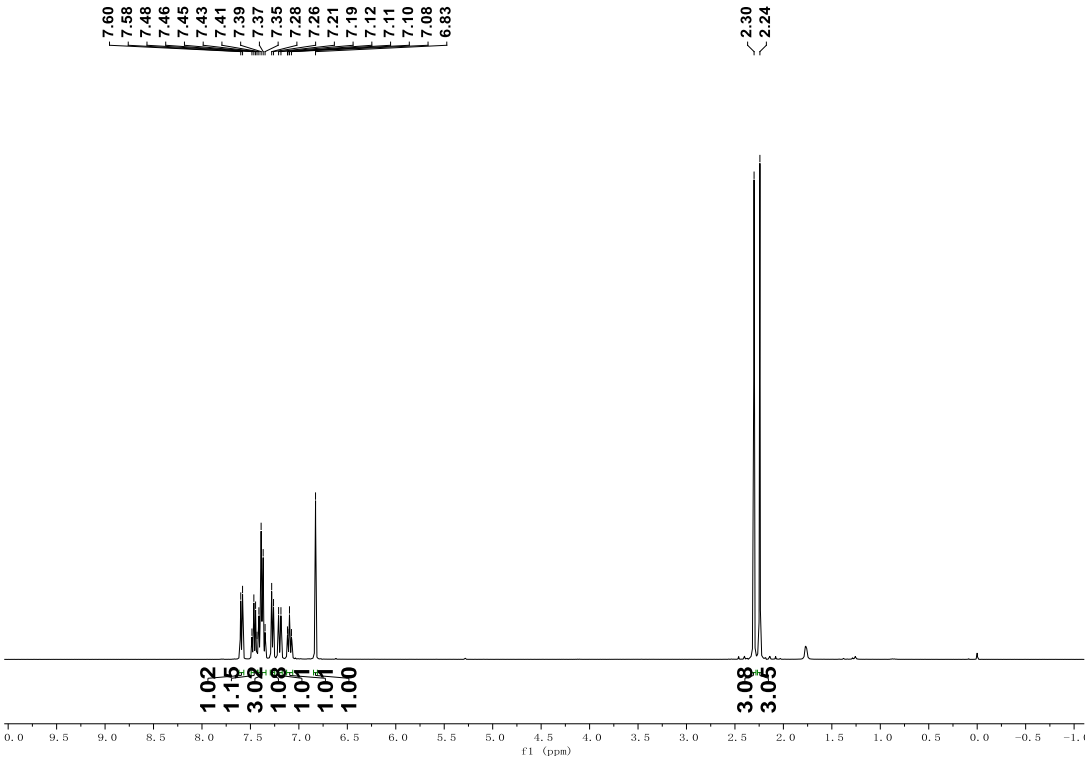
7.47
7.46
7.35
7.33
7.32
7.31
7.29
7.21
7.20
7.18
7.18
7.14
7.12
6.83
6.82
4.16
4.15
4.13
4.11
4.09
4.08
4.06
4.04
2.30
2.25
2.13
1.20
1.18
1.16
1.15
1.13
1.07
4.23
1.14
2.16
1.00
2.25
3.23
1.36
1.69
3.27
f1 (ppm)


198.7
194.0
165.3
163.9
144.7
144.5
141.9
140.8
137.6
137.1
137.0
133.9
130.2
130.2
129.8
129.7
129.0
127.0
127.0
124.7
123.0
120.2
106.9
105.4
88.0
87.4
61.6
61.5
30.2
27.6
21.2
14.2
14.1
f1 (ppm)



5j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7.48
7.46
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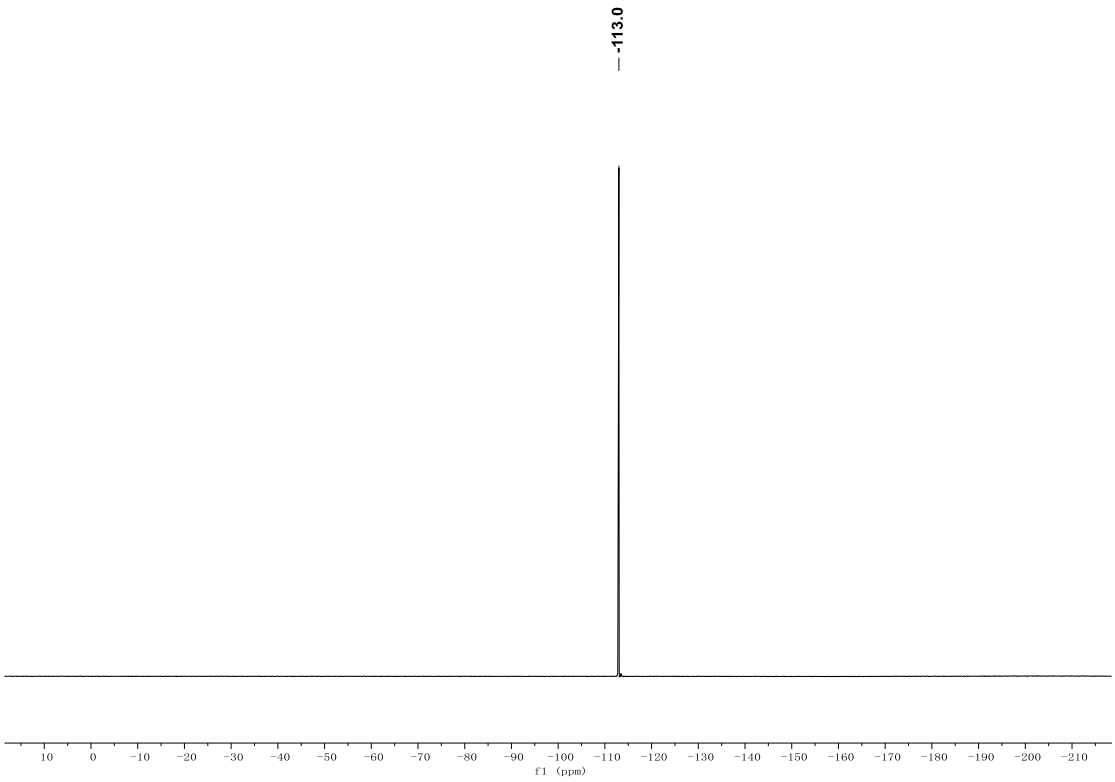
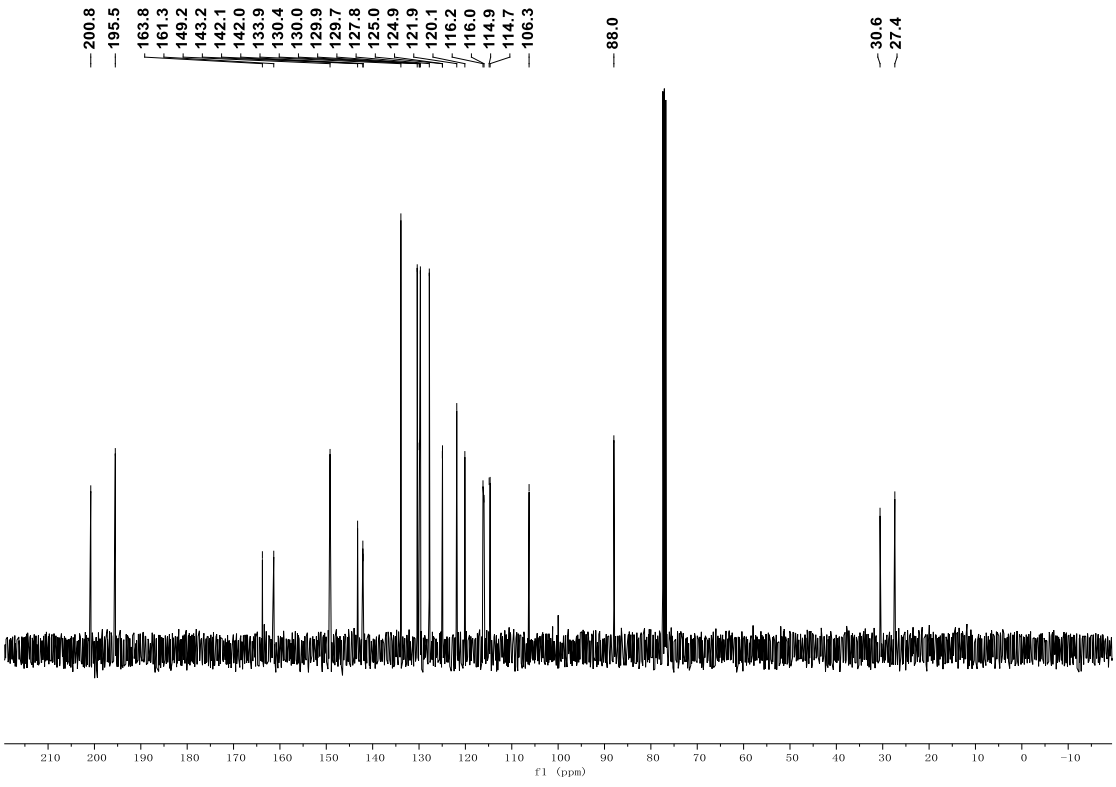
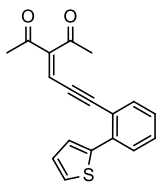
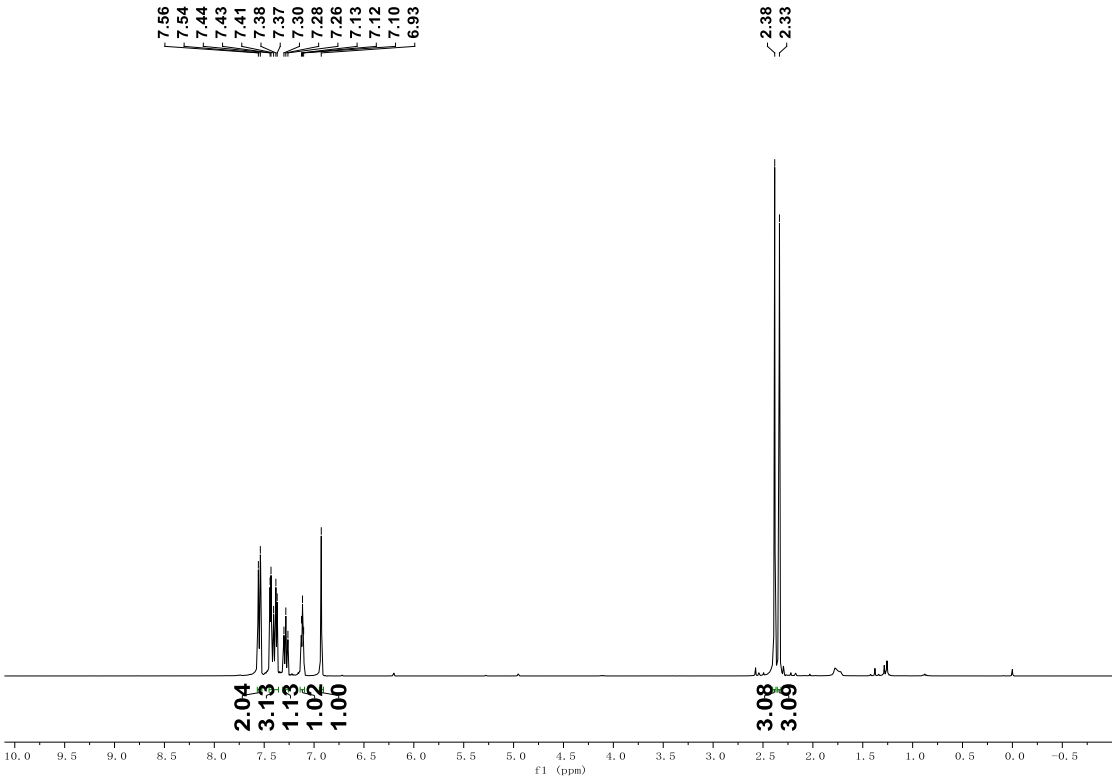
7.43
7.41
7.39
7.37
7.35
7.28
7.26
7.21
7.19
7.12
7.11
7.10
7.08
6.83
2.30
2.24
1.02
1.15
3.02
1.08
1.01
1.01
1.00
3.08
3.05
f1 (ppm)

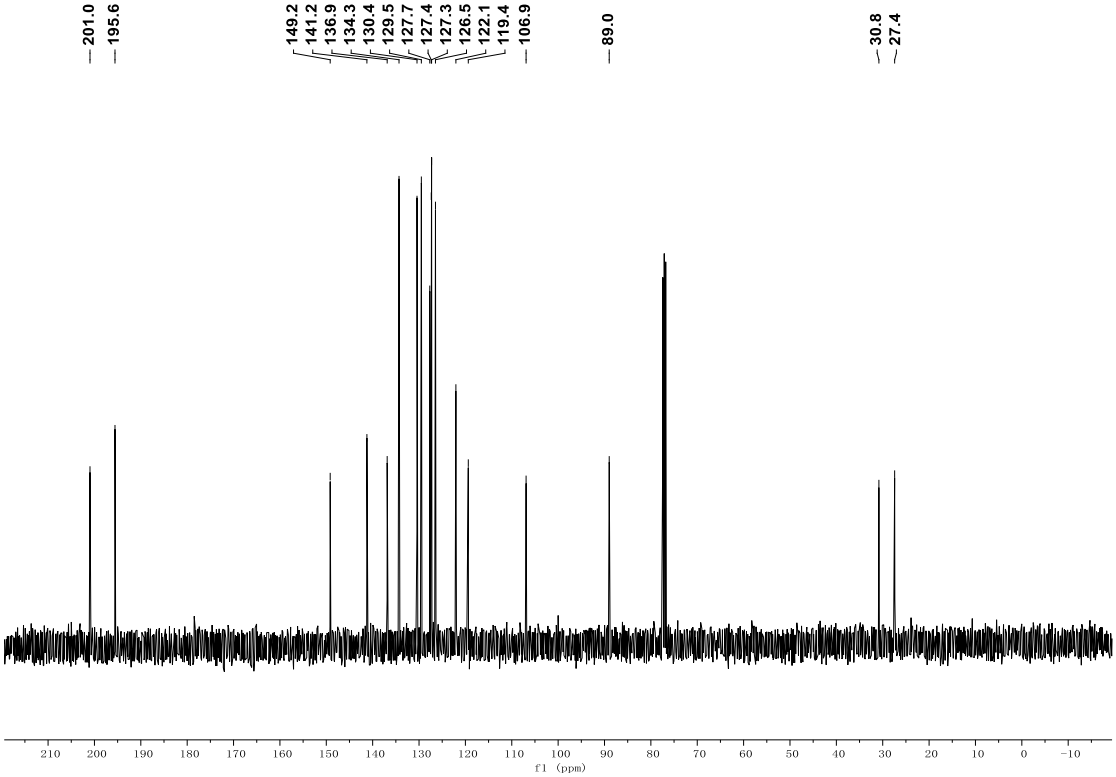

-113.0
f1 (ppm)

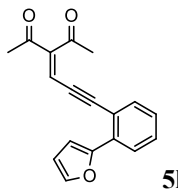

200.8
195.5
163.8
161.3
149.2
143.2
142.1
142.0
133.9
130.4
130.0
129.9
129.7
127.8
125.0
124.9
121.9
120.1
116.2
116.0
114.9
114.7
106.3
88.0
30.6
27.4
f1 (ppm)



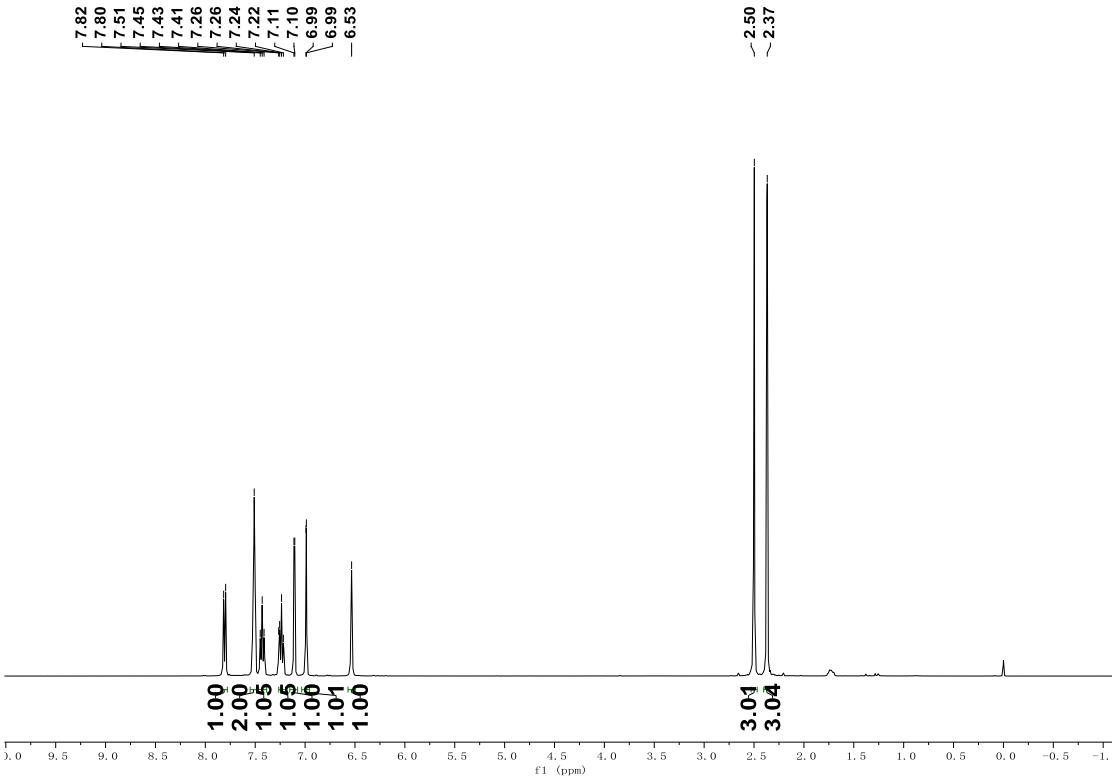
5k


7.56
7.54
7.44
7.43
7.41
7.38
7.37
7.30
7.28
7.26
7.13
7.12
7.10
6.93
2.38
2.33
2.04
3.13
1.13
1.02
1.00
3.08
3.09
f1 (ppm)


201.0
195.6
149.2
141.2
136.9
134.3
130.4
129.5
127.7
127.4
127.3
126.5
122.1
119.4
106.9
89.0
30.8
27.4
f1 (ppm)



5l


7.82
7.80
7.51
7.45
7.43
7.41
7.26
7.24
7.22
7.11
7.10
6.99
6.99
6.53
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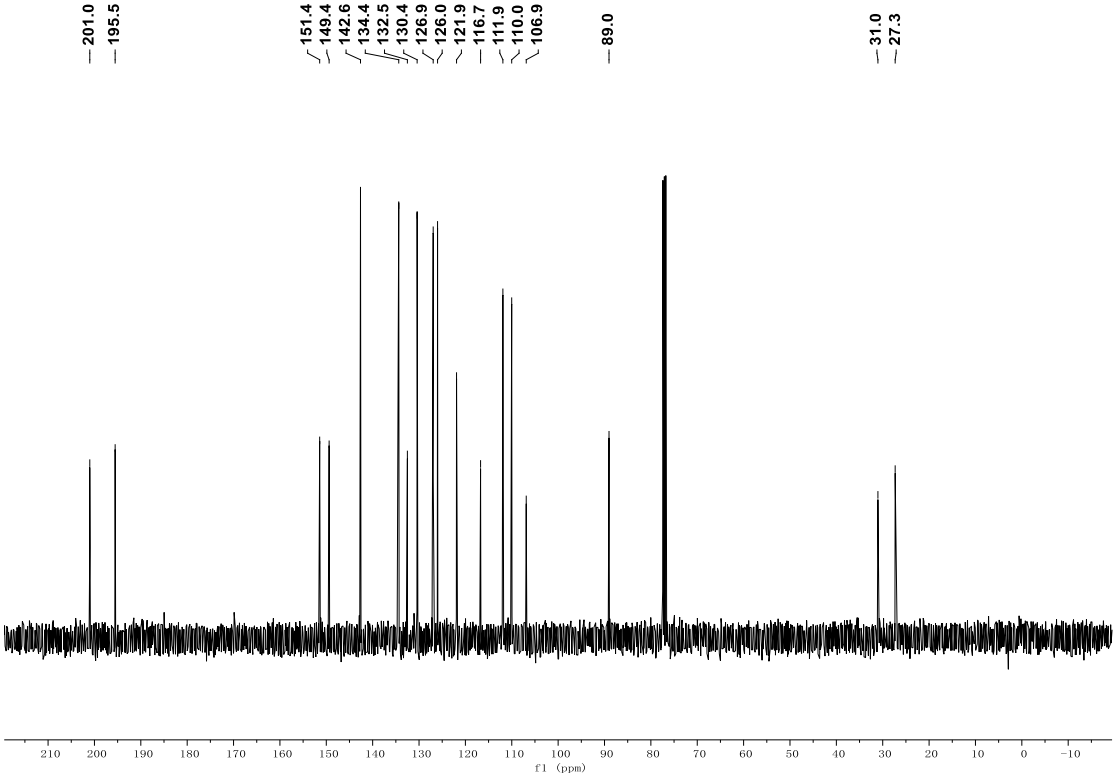
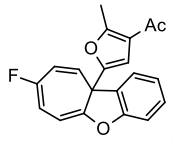
2.00
1.05
1.05
1.00
1.01
1.00
3.01
3.04
f1 (ppm)


201.0
195.5
151.4
149.4
142.6
134.4
132.5
130.4
126.9
126.0
121.9
116.7
111.9
110.0
106.9
89.0
31.0
27.3
f1 (ppm)


Ac
O
F
O

2a


7.37
7.35
7.26
7.24
7.22
7.05
7.03
7.01
6.98
6.96
6.35
6.32
6.30
6.13
6.11
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6.07
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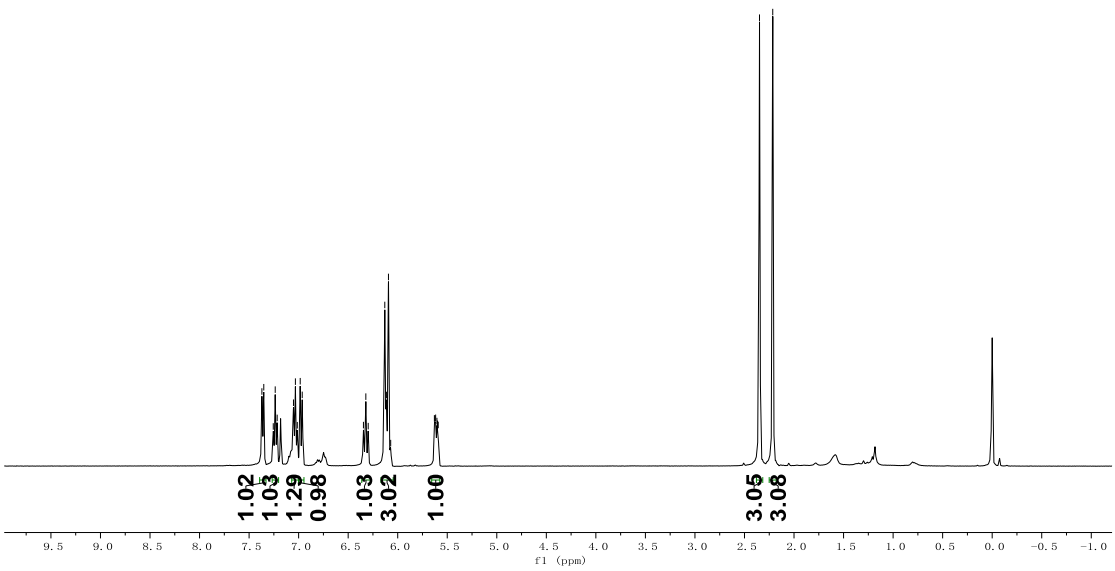
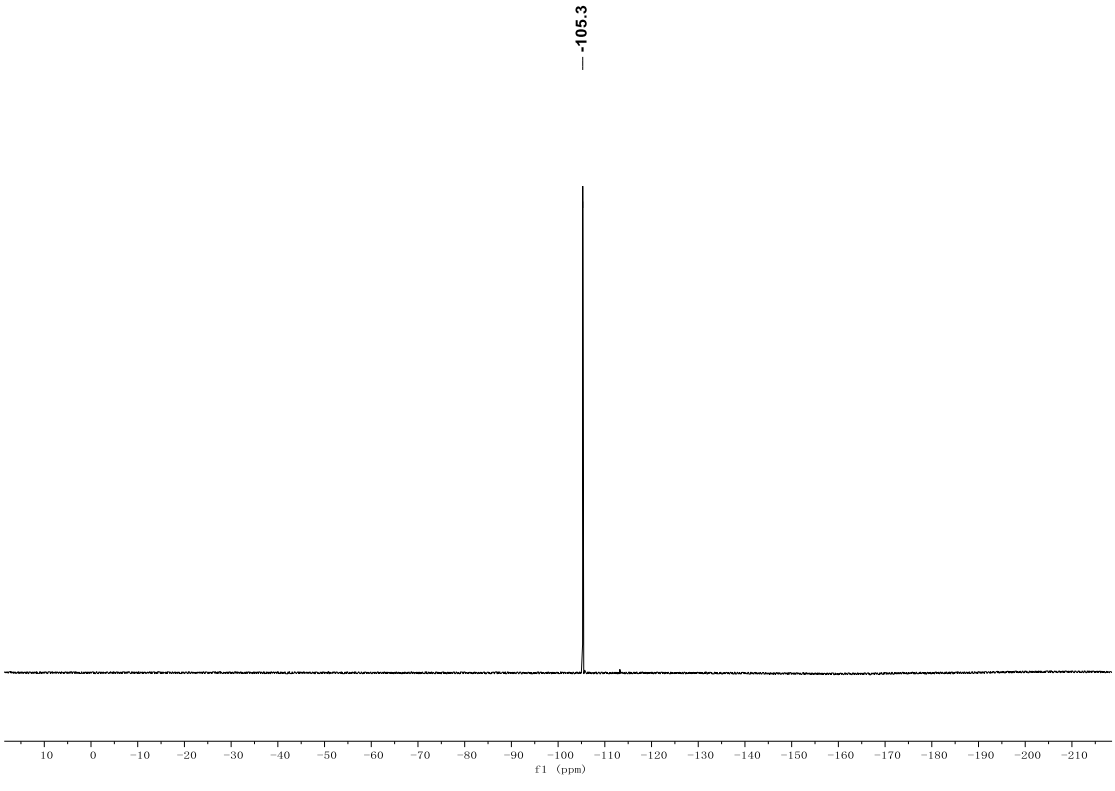
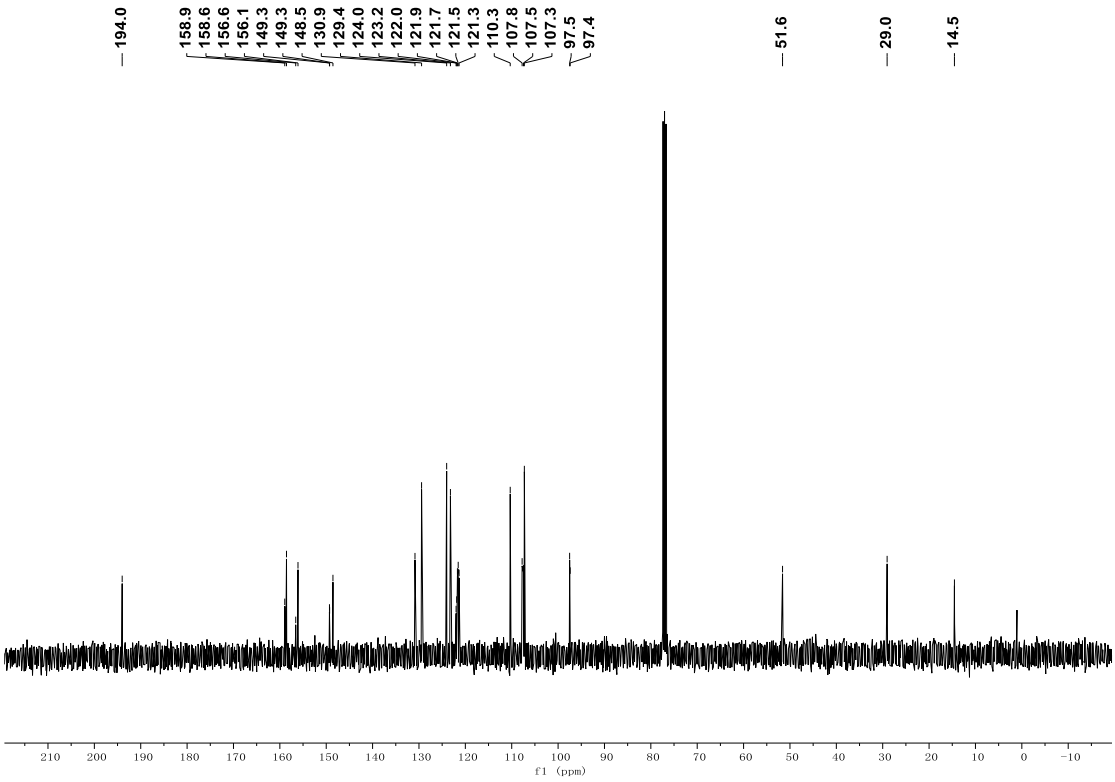
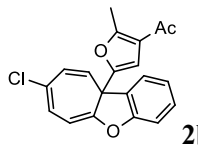
5.62
5.62
5.60
5.60
5.59


2.35
2.21

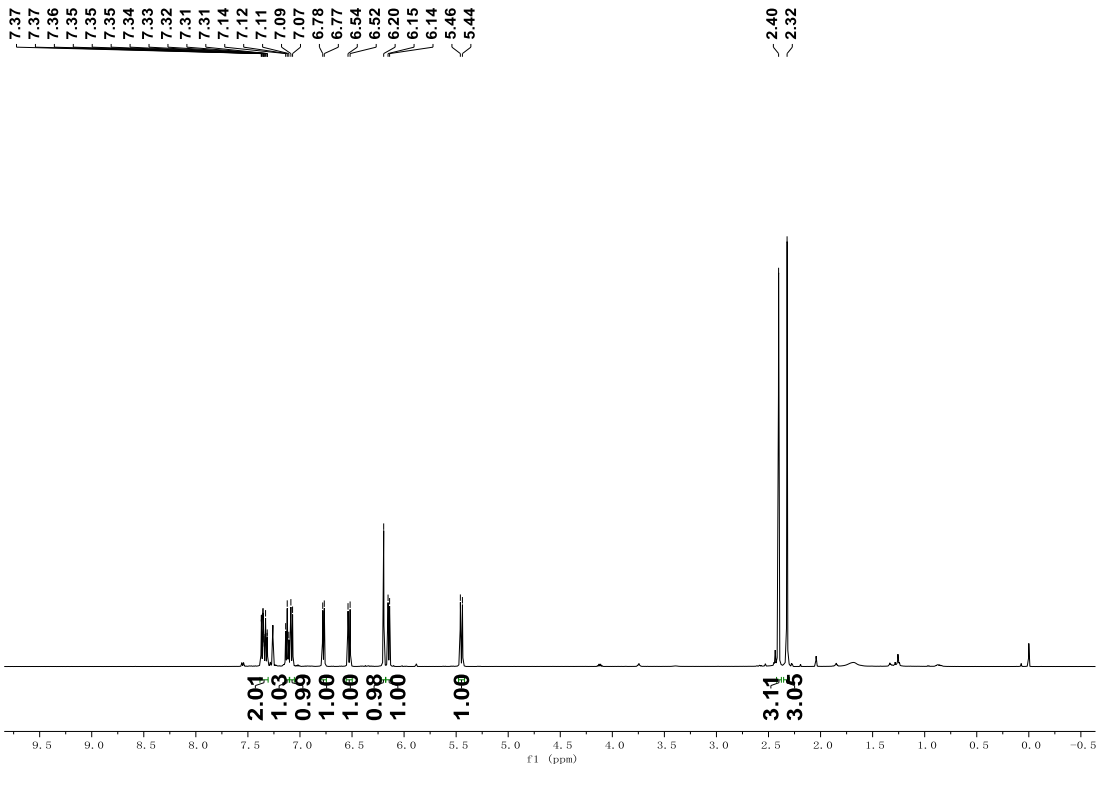

1.02
1.03
1.29
0.98
1.03
3.02
1.00
3.05
3.08
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

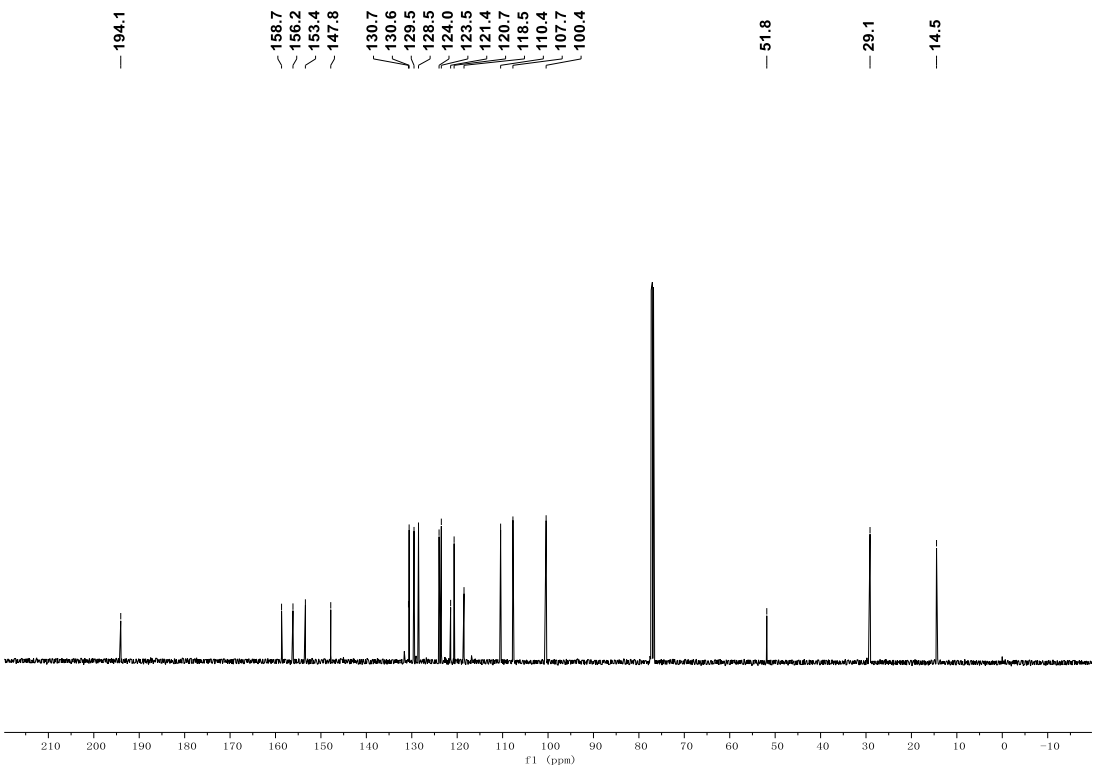

-105.3
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

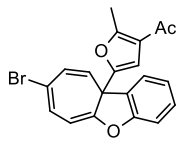

194.0
158.9
158.6
156.6
156.1
149.3
149.3
148.5
130.9
129.4
124.0
123.2
122.0
121.9
121.7
121.5
121.3
110.3
107.8
107.5
107.3
97.5
97.4
51.6
29.0
14.5
f1 (ppm)


Ac
O
Cl
O

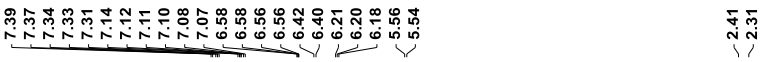
2b

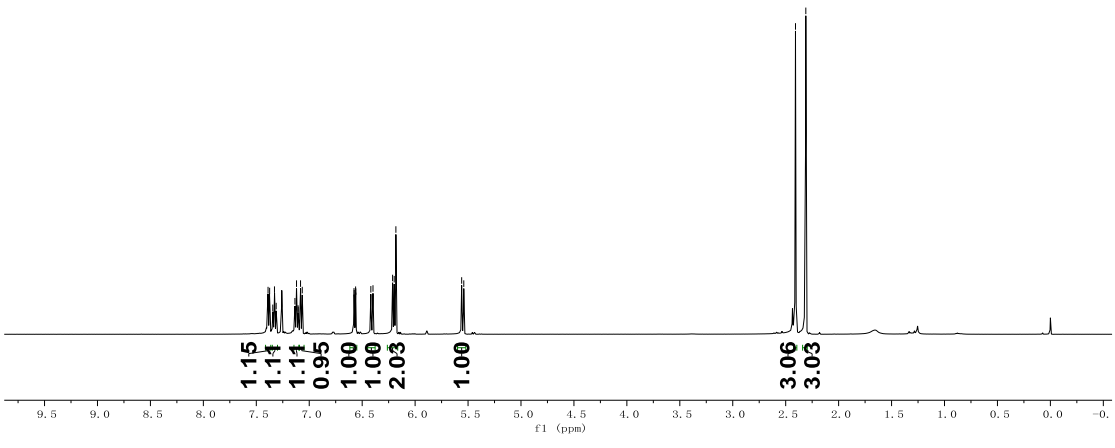

7.37
7.37
7.36
7.35
7.35
7.35
7.34
7.33
7.32
7.31
7.31
7.14
7.12
7.11
7.09
7.07
6.78
6.77
6.54
6.52
6.20
6.15
6.14
5.46
5.44
2.40
2.32
2.01
1.03
0.99
1.00
1.00
0.98
1.00
1.00
3.11
3.05
f1 (ppm)

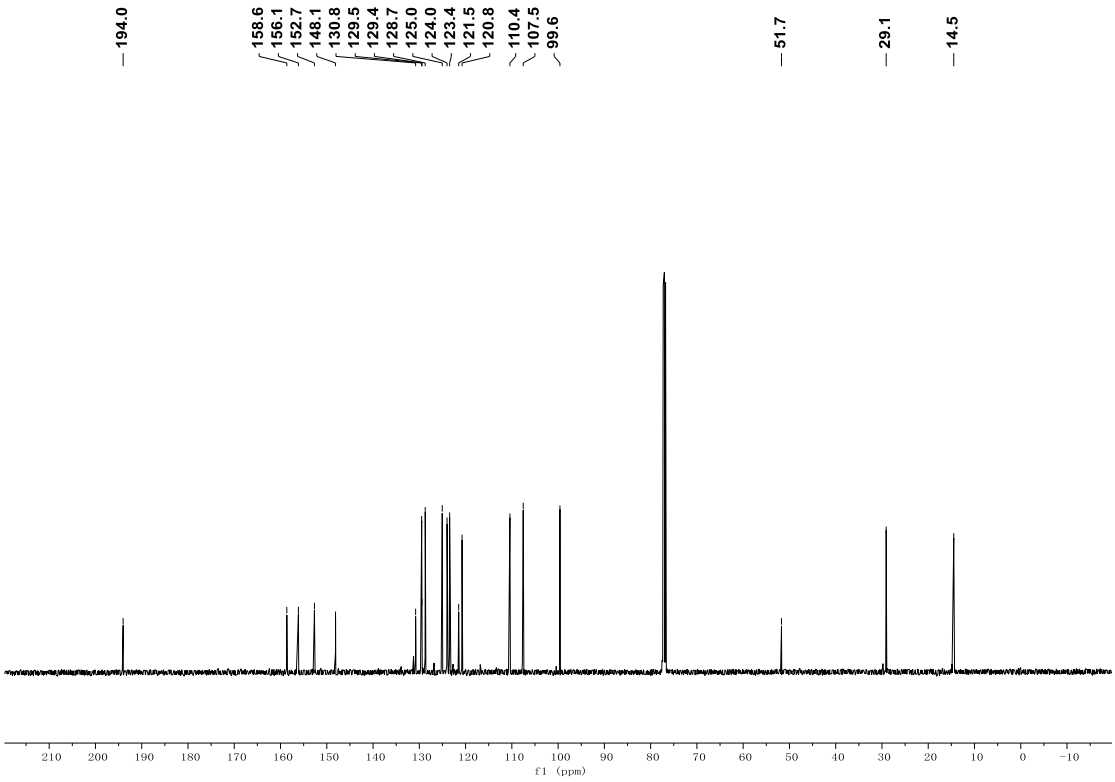

194.1
158.7
156.2
153.4
147.8
130.7
130.6
129.5
128.5
124.0
123.5
121.4
120.7
118.5
110.4
107.7
100.4
51.8
29.1
14.5
f1 (ppm)

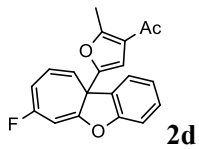

Ac
Br
O
O

2c

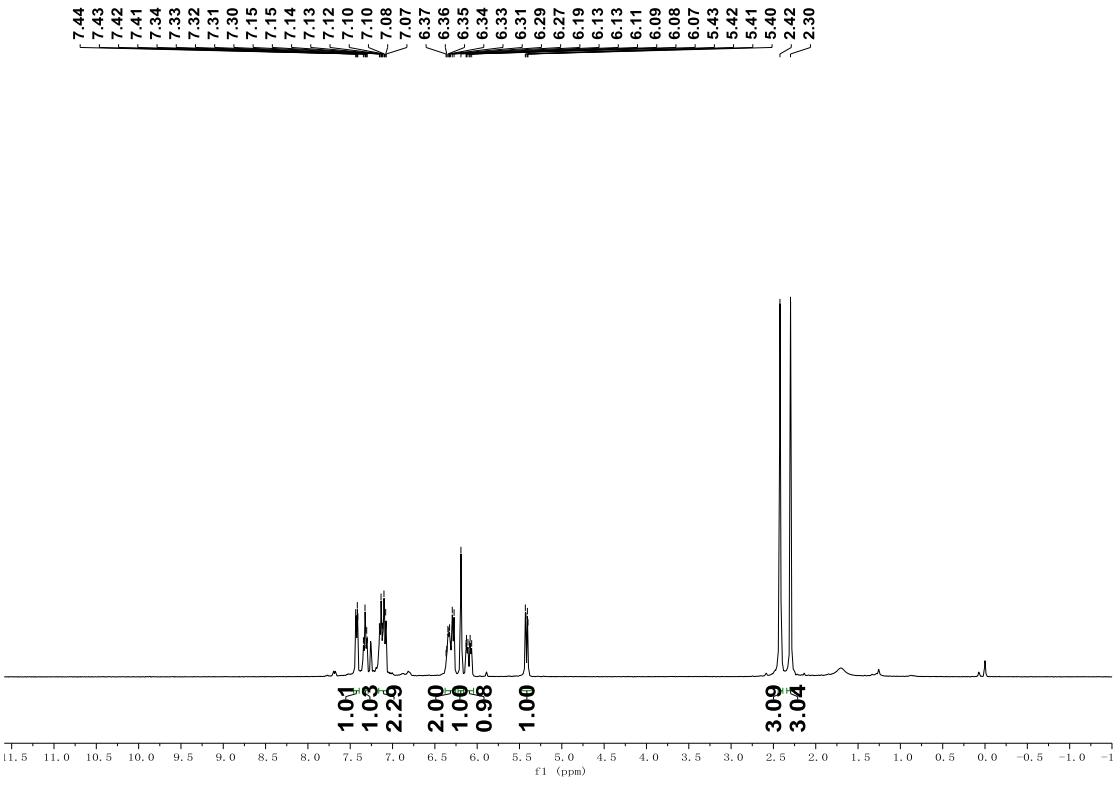

7.39
7.37
7.34
7.33
7.31
7.14
7.12
7.11
7.10
7.08
7.07
6.58
6.58
6.56
6.56
6.42
6.40
6.21
6.20
6.18
5.56
5.54
2.41
2.31


1.15
1.14
1.11
0.95
1.00
1.00
2.03
1.00
3.06
3.03
f1 (ppm)


194.0
158.6
156.1
152.7
148.1
130.8
129.5
129.4
128.7
125.0
124.0
123.4
121.5
120.8
110.4
107.5
99.6
51.7
29.1
14.5
f1 (ppm)


Ac
O
F
O

2d


7.44
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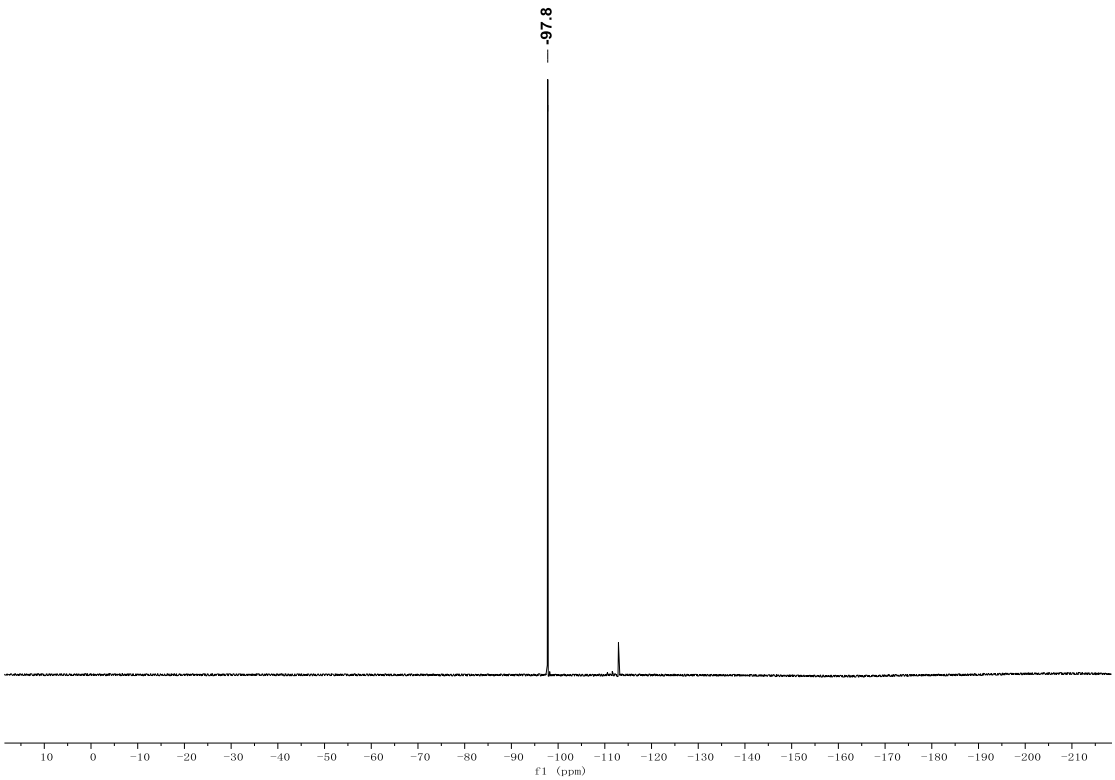
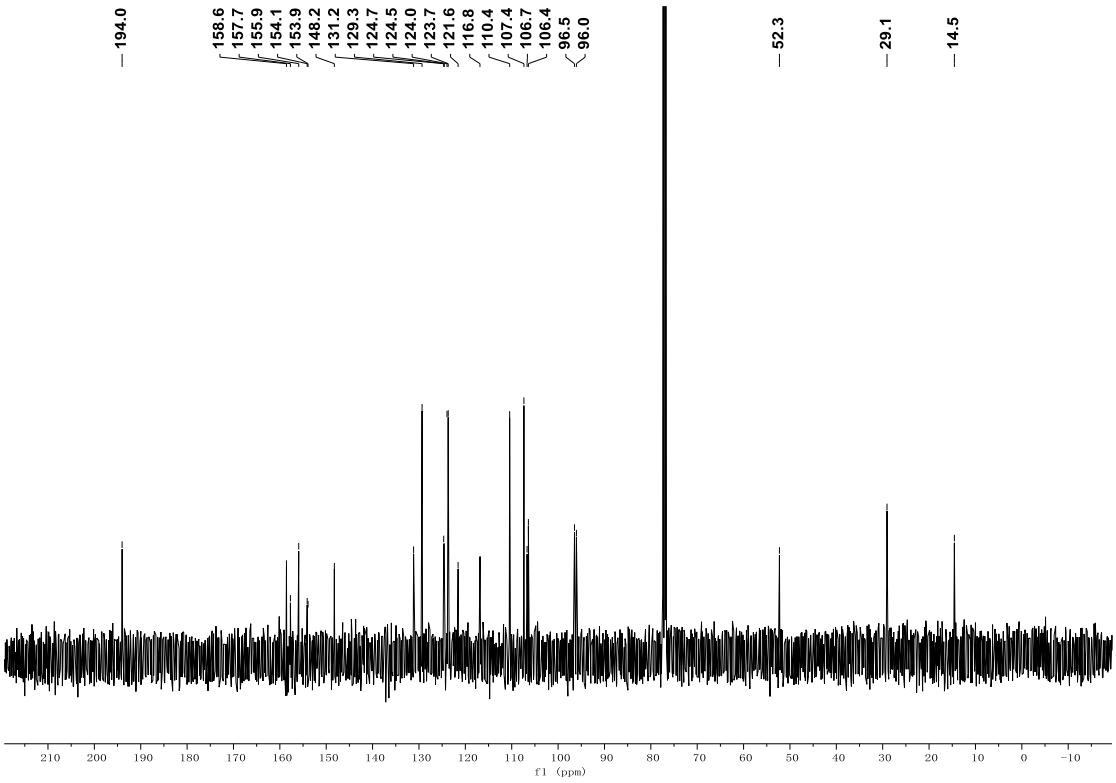
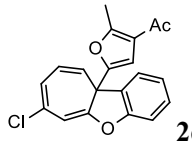
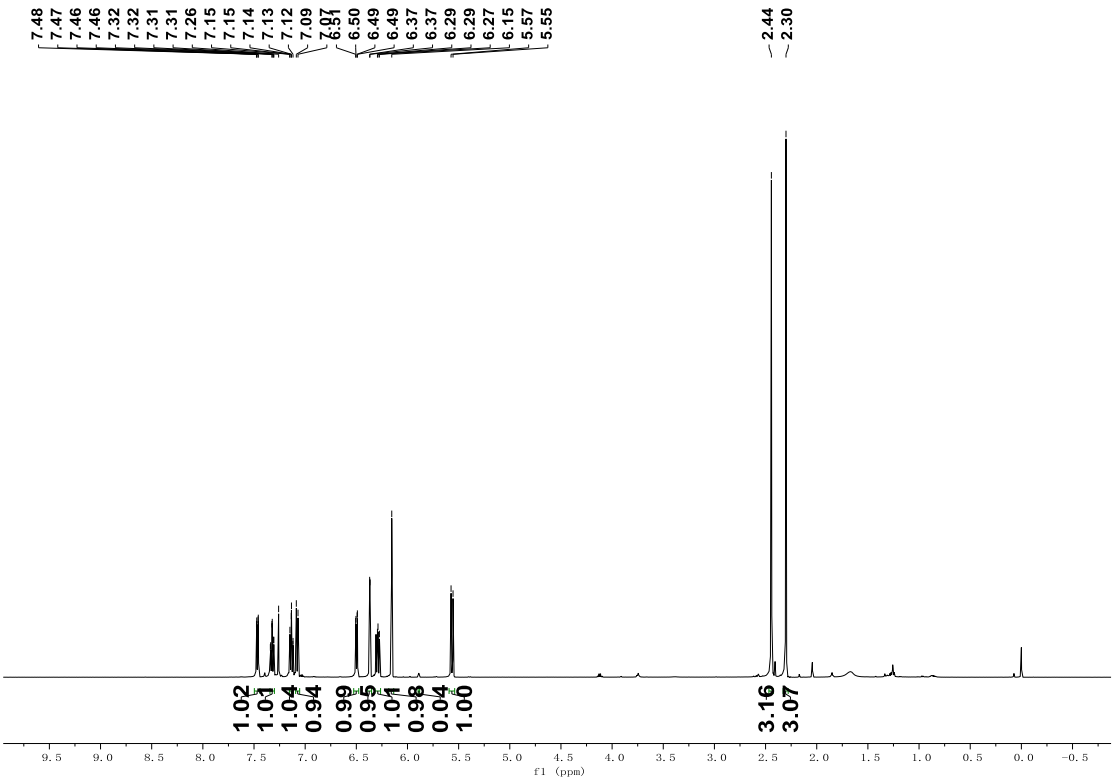
7.42
7.41
7.34
7.33
7.32
7.31
7.30
7.15
7.15
7.14
7.13
7.12
7.10
7.10
7.08
7.07
6.37
6.36
6.35
6.34
6.33
6.31
6.29
6.27
6.19
6.13
6.13
6.11
6.09
6.08
6.07
5.43
5.42
5.41
5.40
2.42
2.30
1.01
1.03
2.29
2.00
1.00
0.98
1.00
3.09
3.04
f1 (ppm)


-97.8
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)


194.0
158.6
157.7
155.9
154.1
153.9
148.2
131.2
129.3
124.7
124.5
124.0
123.7
121.6
116.8
110.4
107.4
106.7
106.4
96.5
96.0
52.3
29.1
14.5
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)


Ac
O
Cl
O

2e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7.46
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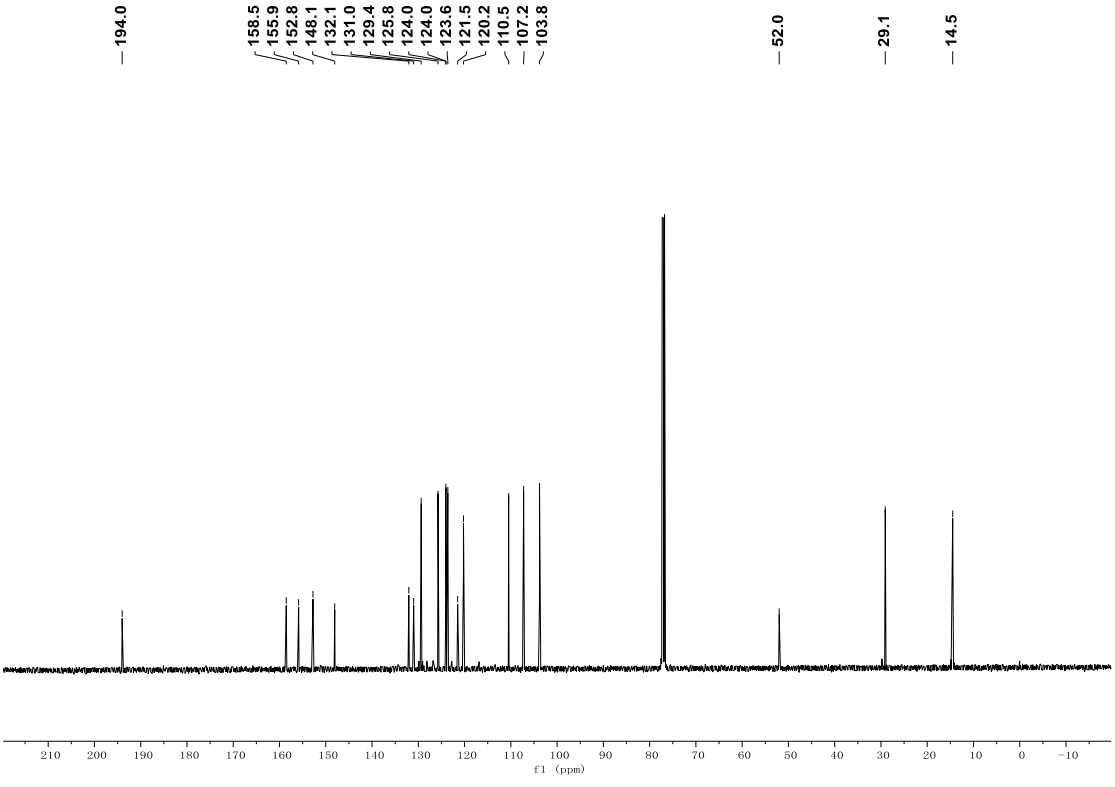
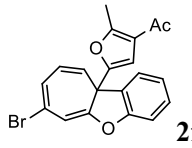
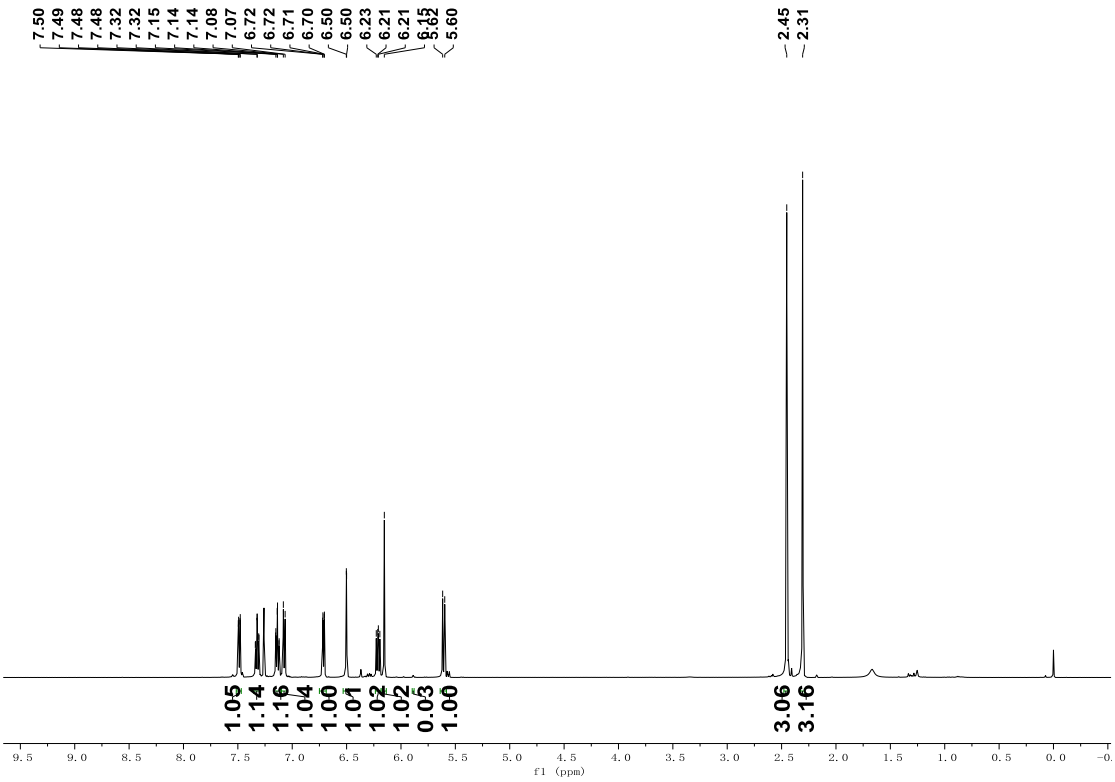
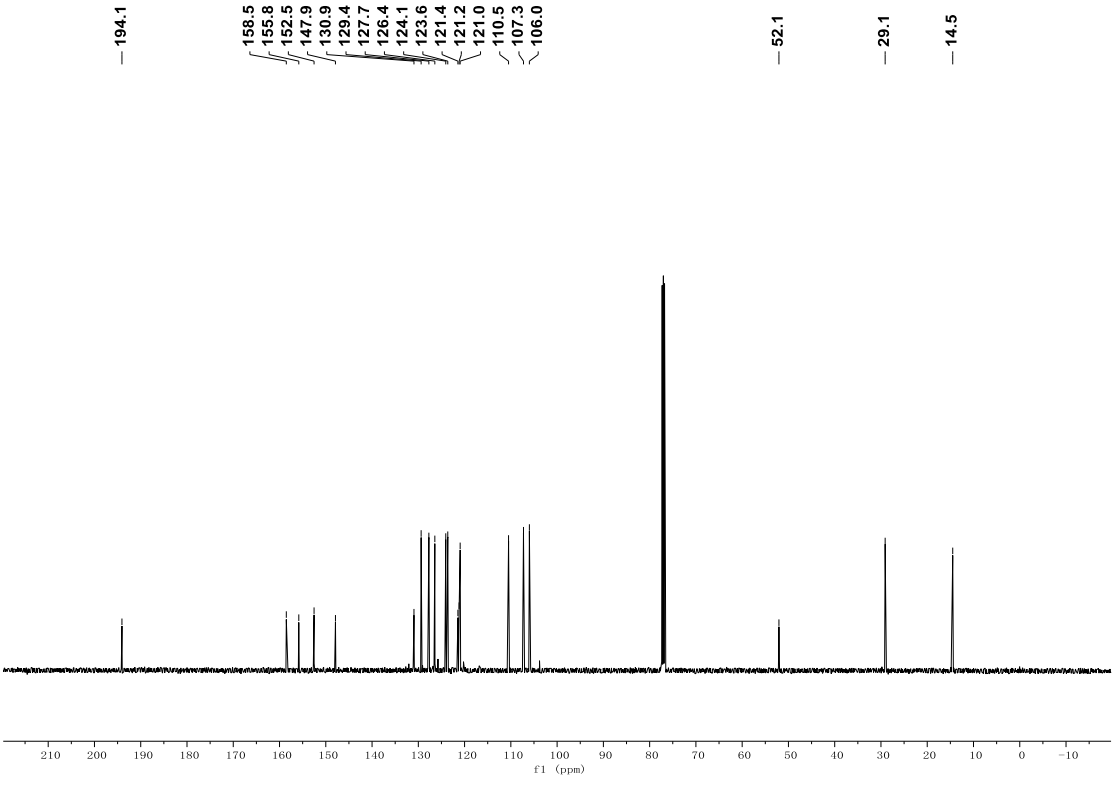
7.32
7.31
7.31
7.26
7.15
7.15
7.14
7.13
7.12
7.09
7.07
6.51
6.50
6.49
6.49
6.37
6.37
6.29
6.29
6.27
6.15
5.57
5.55
2.44
2.30
1.02
1.01
1.04
0.94
0.99
0.95
1.01
0.98
0.04
1.00
3.16
3.07
f1 (ppm)

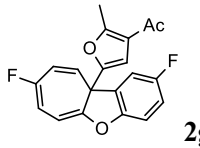

194.0
158.5
155.9
152.8
148.1
132.1
131.0
129.4
125.8
124.0
124.0
123.6
121.5
120.2
110.5
107.2
103.8
52.0
29.1
14.5
f1 (ppm)


Ac
O
Br
O

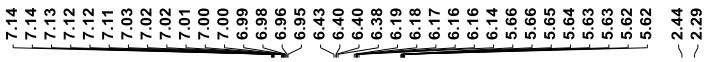
2f

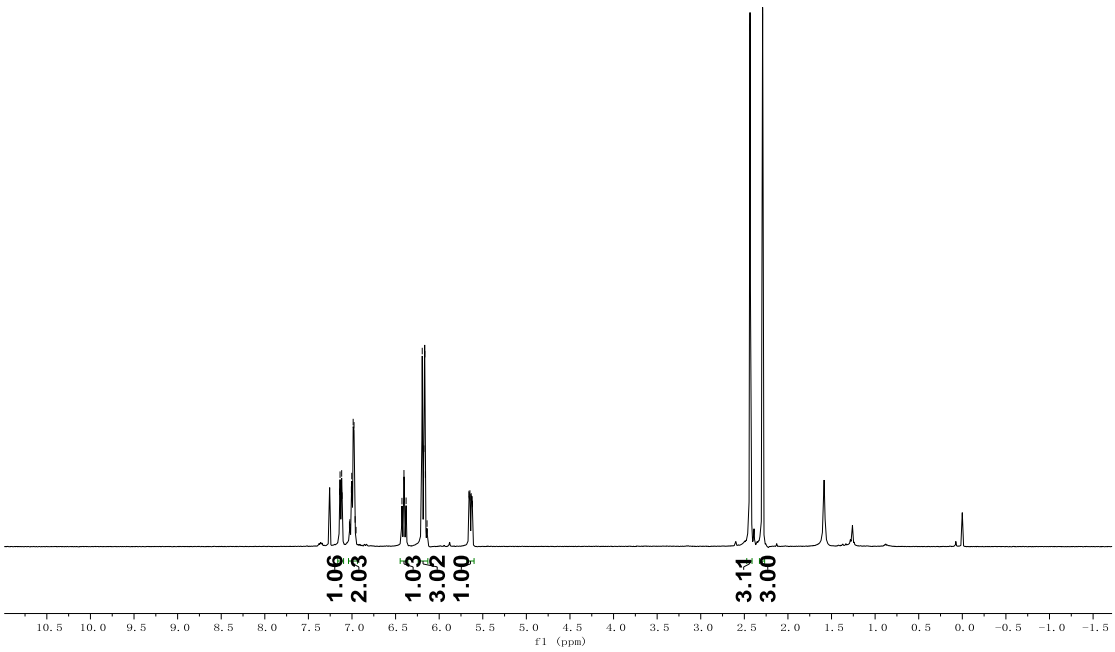

7.50
7.49
7.48
7.48
7.32
7.15
7.14
7.14
7.08
7.07
6.72
6.72
6.71
6.70
6.50
6.50
6.23
6.21
6.21
6.15
6.02
5.60
2.45
2.31
1.05
1.14
1.16
1.04
1.00
1.01
1.02
1.02
0.03
1.00
3.06
3.16
f1 (ppm)

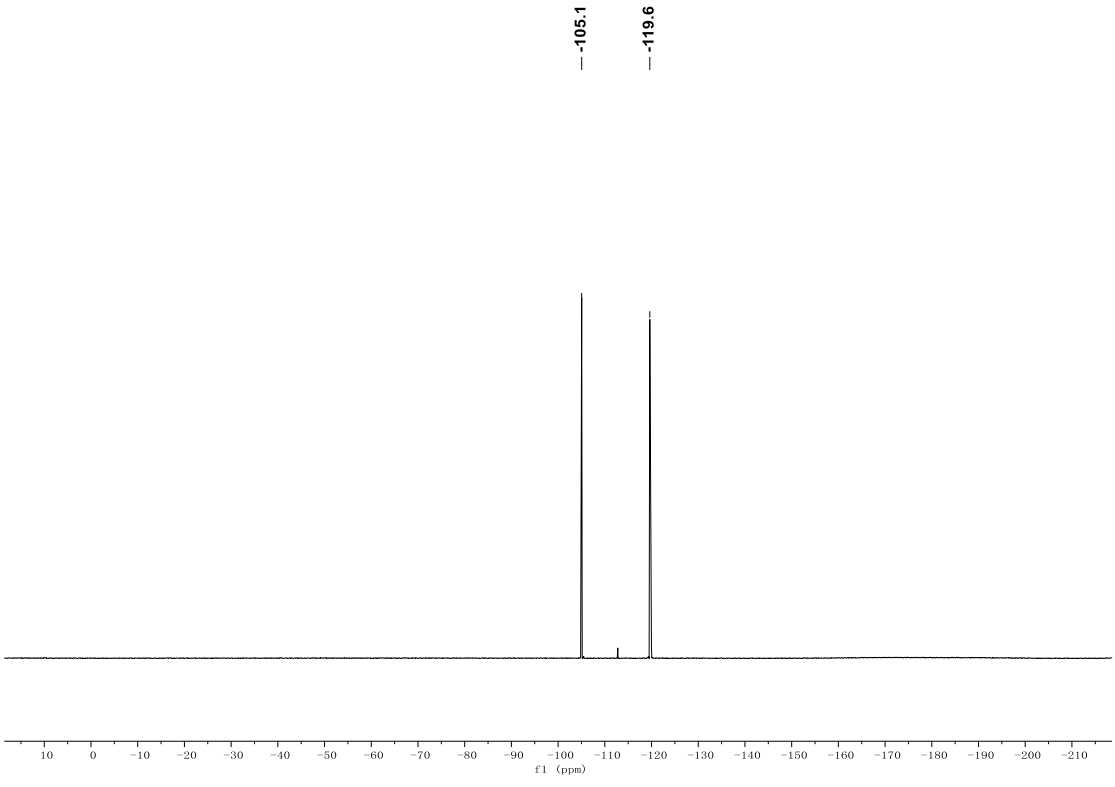

194.1
158.5
155.8
152.5
147.9
130.9
129.4
127.7
126.4
124.1
123.6
121.4
121.2
121.0
110.5
107.3
106.0
52.1
29.1
14.5
f1 (ppm)

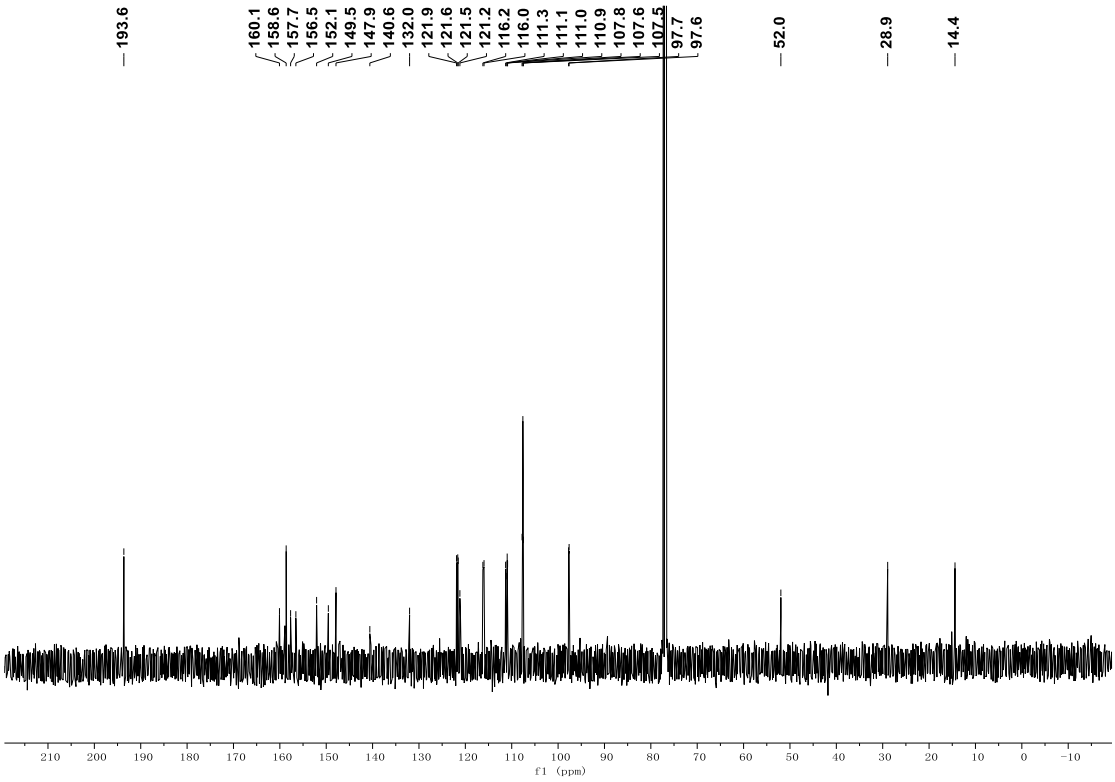

Ac
O
F
F
O

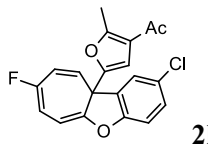
2g


7.14
7.14
7.13
7.12
7.12
7.11
7.03
7.02
7.02
7.01
7.00
7.00
6.99
6.98
6.96
6.95
6.43
6.40
6.40
6.38
6.19
6.18
6.17
6.16
6.16
6.14
5.66
5.66
5.65
5.64
5.63
5.63
5.62
5.62
2.44
2.29

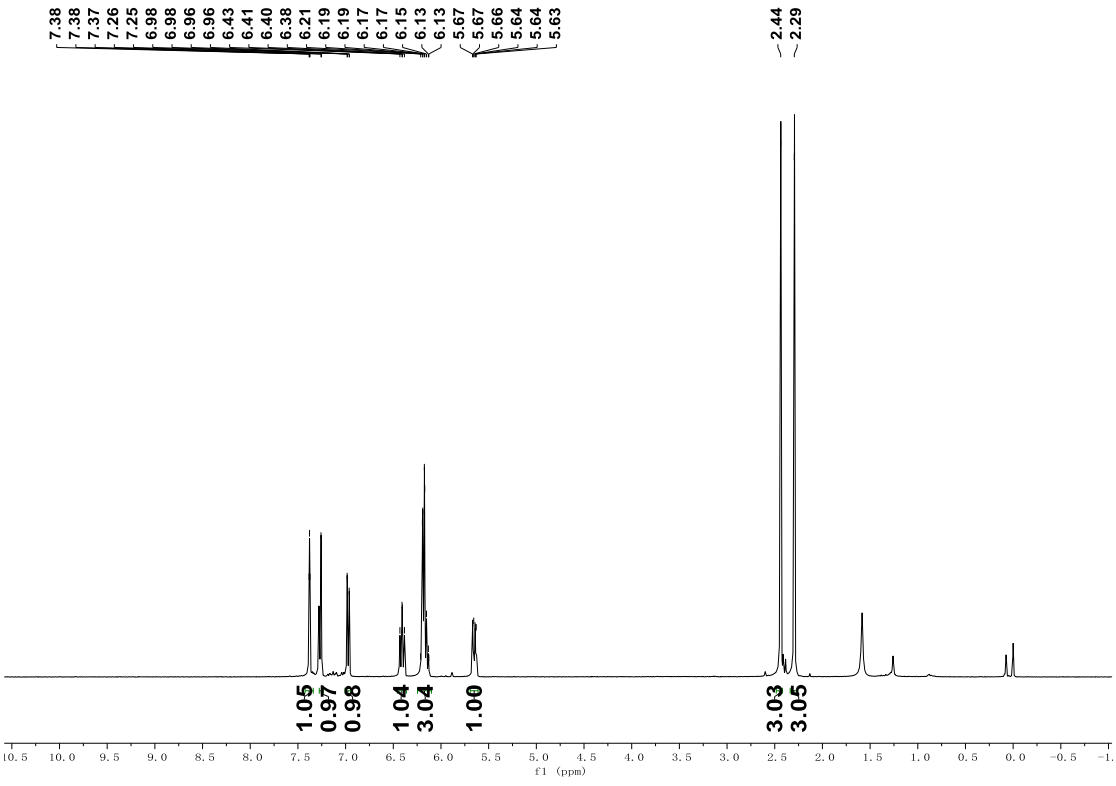

1.06
2.03
1.03
3.02
1.00
3.11
3.00
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0 -1.5
f1 (ppm)

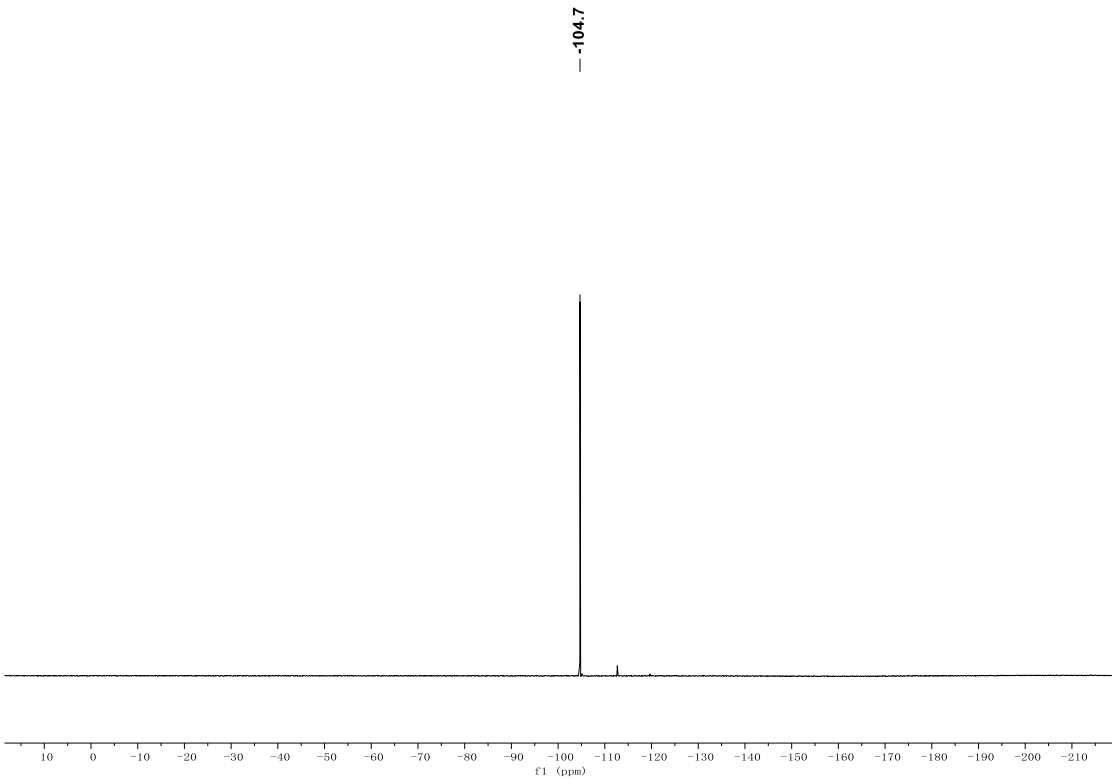

-105.1
-119.6
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

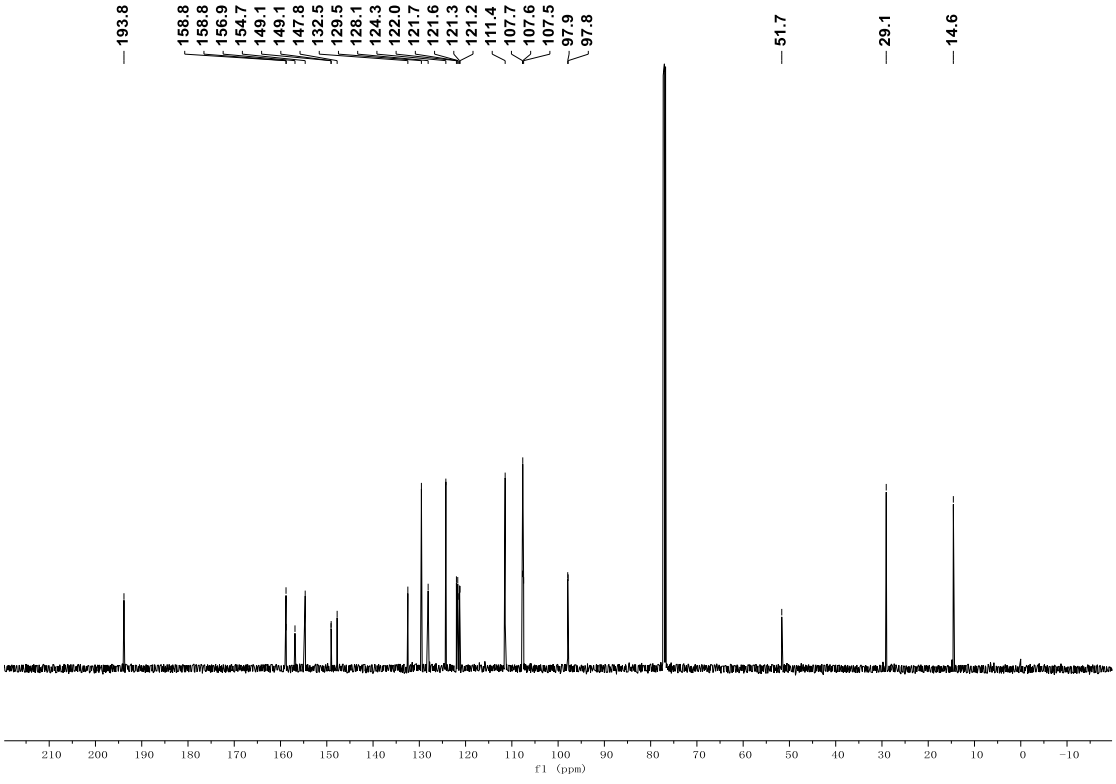

193.6
160.1
158.6
157.7
156.5
152.1
149.5
147.9
140.6
132.0
121.9
121.6
121.5
121.2
116.2
116.0
111.3
111.1
111.0
110.9
107.8
107.6
107.5
97.7
97.6
52.0
28.9
14.4
f1 (ppm)

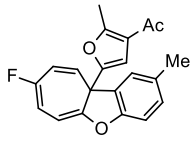

Ac
O
Cl
F
O

2h


7.38
7.38
7.37
7.26
7.25
6.98
6.98
6.96
6.96
6.43
6.41
6.40
6.38
6.21
6.19
6.19
6.17
6.17
6.15
6.13
6.13
5.67
5.67
5.66
5.64
5.64
5.63
2.44
2.29
1.05
0.97
0.98
1.04
3.04
1.00
3.03
3.05
f1 (ppm)


-104.7
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)

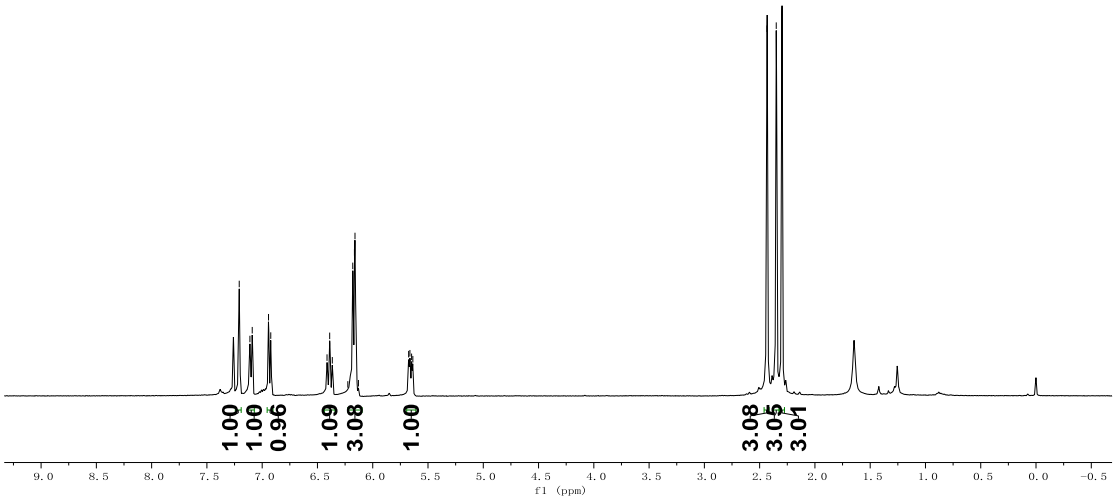

193.8
158.8
158.8
156.9
154.7
149.1
149.1
147.8
132.5
129.5
128.1
124.3
122.0
121.7
121.6
121.3
121.2
111.4
107.7
107.6
107.5
97.9
97.8
51.7
29.1
14.6
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

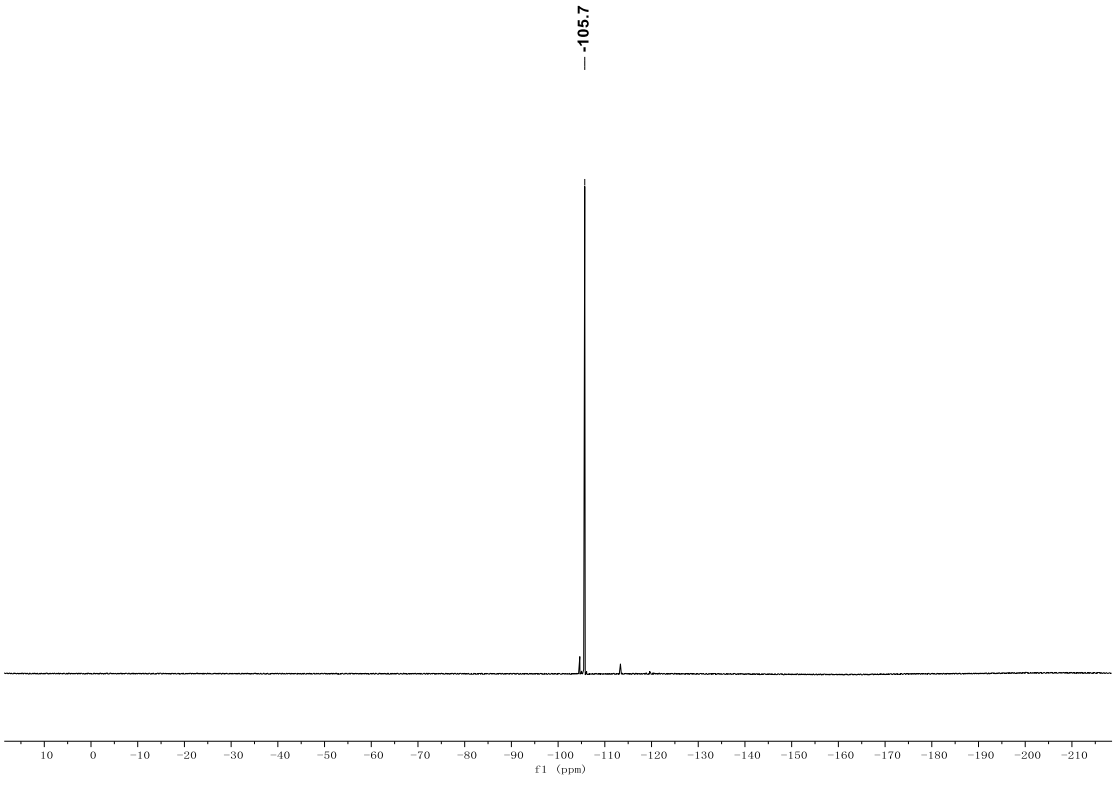

Ac
O
Me
F
O

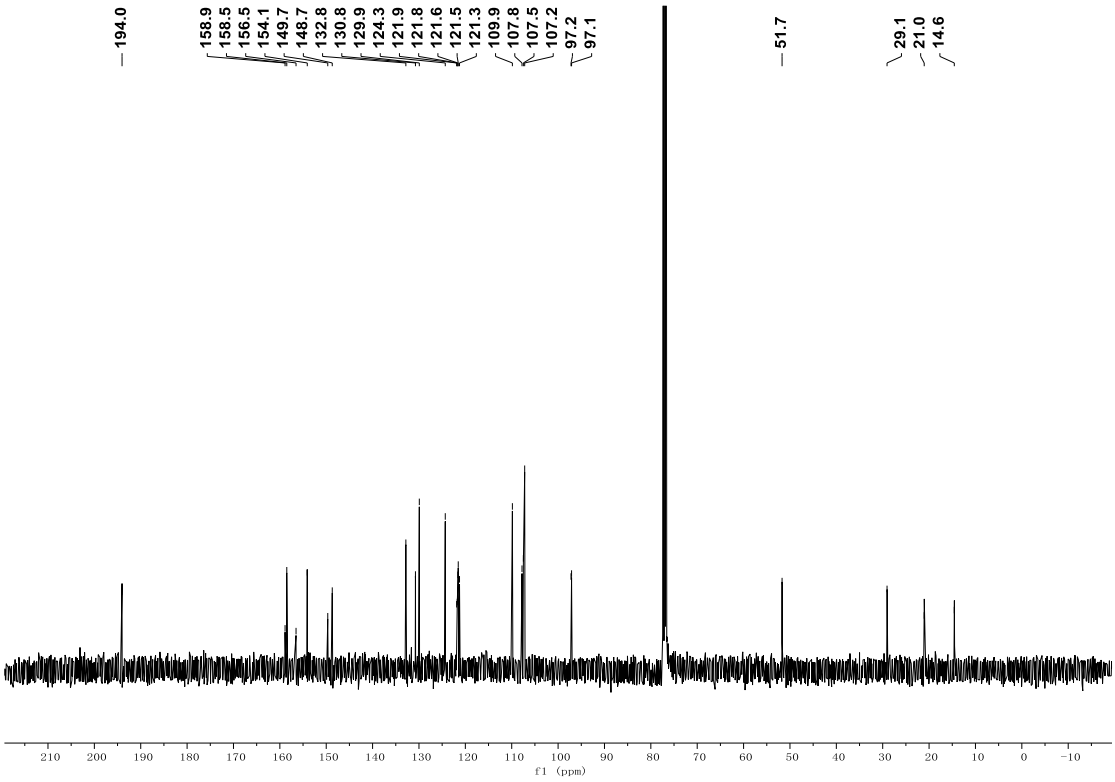
2i


7.21
7.11
7.09
6.94
6.92
6.41
6.39
6.37
6.23
6.18
6.17
6.16
6.13
5.68
5.66
5.65
5.64


2.43
2.35
2.30


1.00
1.00
0.96
1.09
3.08
1.00
3.08
3.05
3.01
f1 (ppm)


-105.7
f1 (ppm)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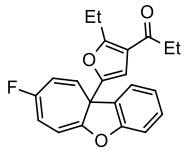
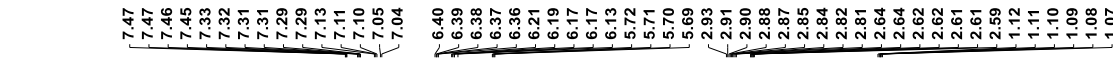
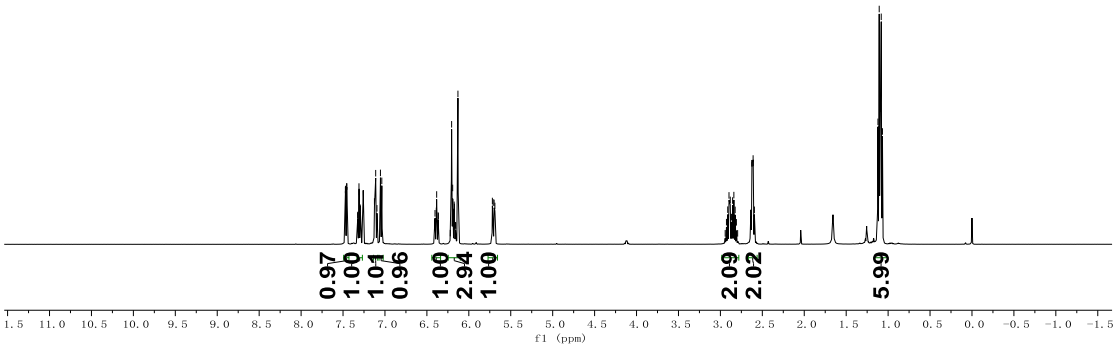
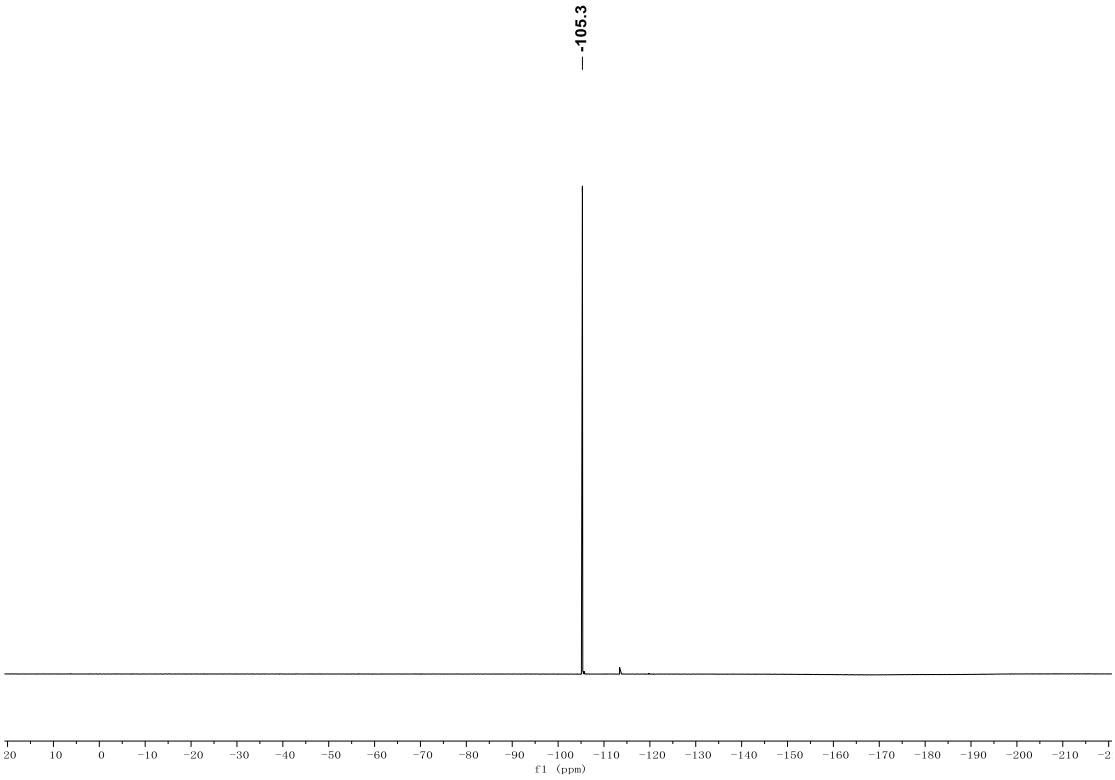
158.9
158.5
156.5
154.1
149.7
148.7
132.8
130.8
129.9
124.3
121.9
121.8
121.6
121.5
121.3
109.9
107.8
107.5
107.2
97.2
97.1
51.7
29.1
21.0
14.6
f1 (ppm)

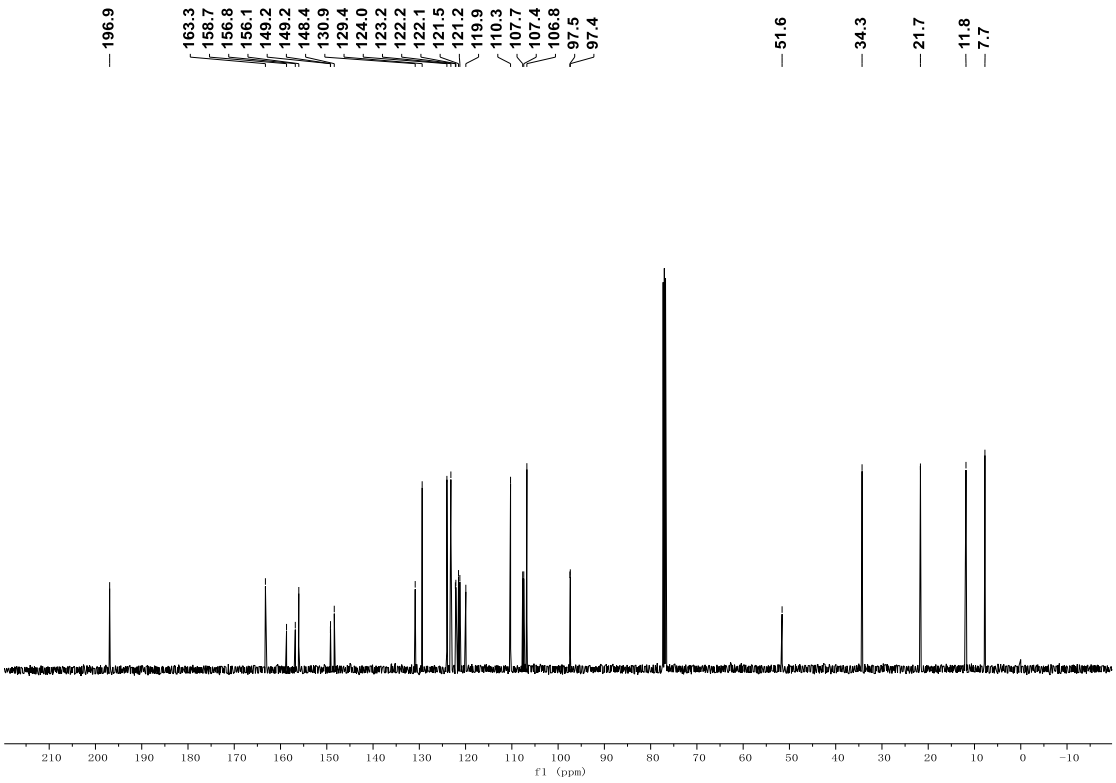

Et
O
Et
O
F
O

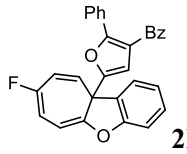
2j


7.47
7.47
7.46
7.45
7.33
7.32
7.31
7.31
7.29
7.29
7.13
7.11
7.10
7.05
7.04
6.40
6.39
6.38
6.37
6.36
6.21
6.19
6.17
6.17
6.13
5.72
5.71
5.70
5.69
2.93
2.91
2.90
2.88
2.87
2.85
2.84
2.82
2.81
2.64
2.64
2.62
2.62
2.61
2.61
2.59
1.12
1.11
1.10
1.09
1.08


0.97
1.05
1.01
0.96
1.00
2.94
1.00
2.09
2.02
5.99
f1 (ppm)

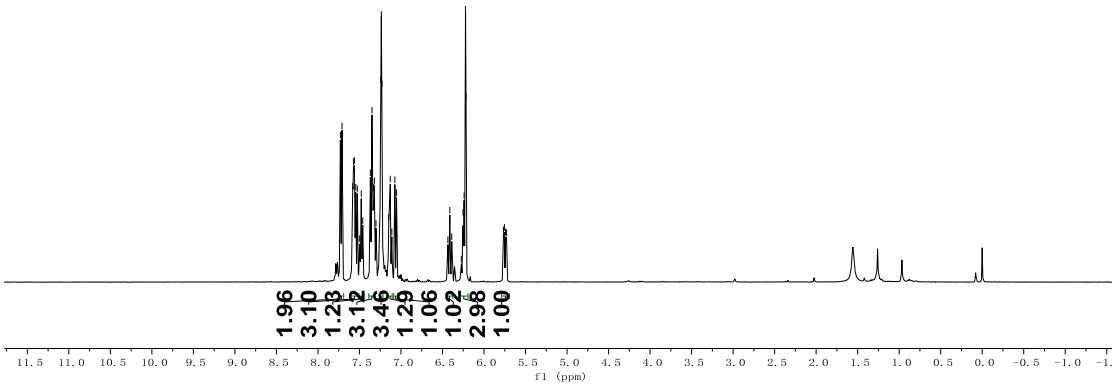

-105.3
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -2
f1 (ppm)

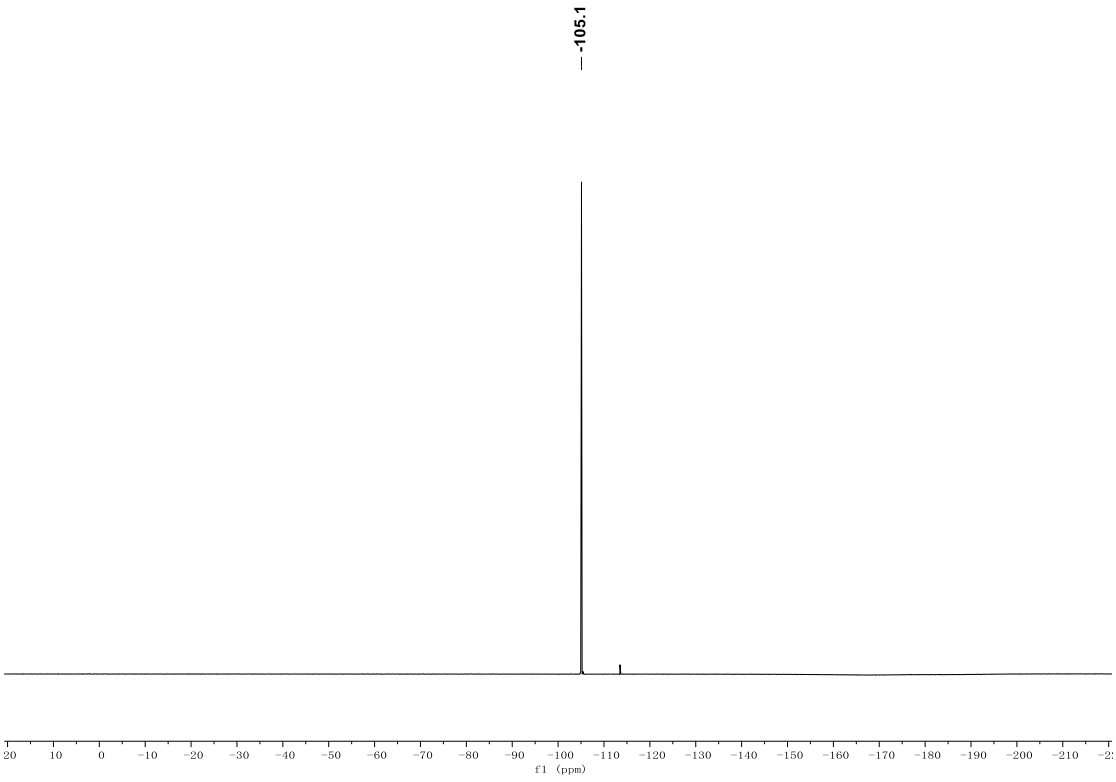

196.9
163.3
158.7
156.8
156.1
149.2
149.2
148.4
130.9
129.4
124.0
123.2
122.2
122.1
121.5
121.2
119.9
110.3
107.7
107.4
106.8
97.5
97.4
51.6
34.3
21.7
11.8
7.7
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

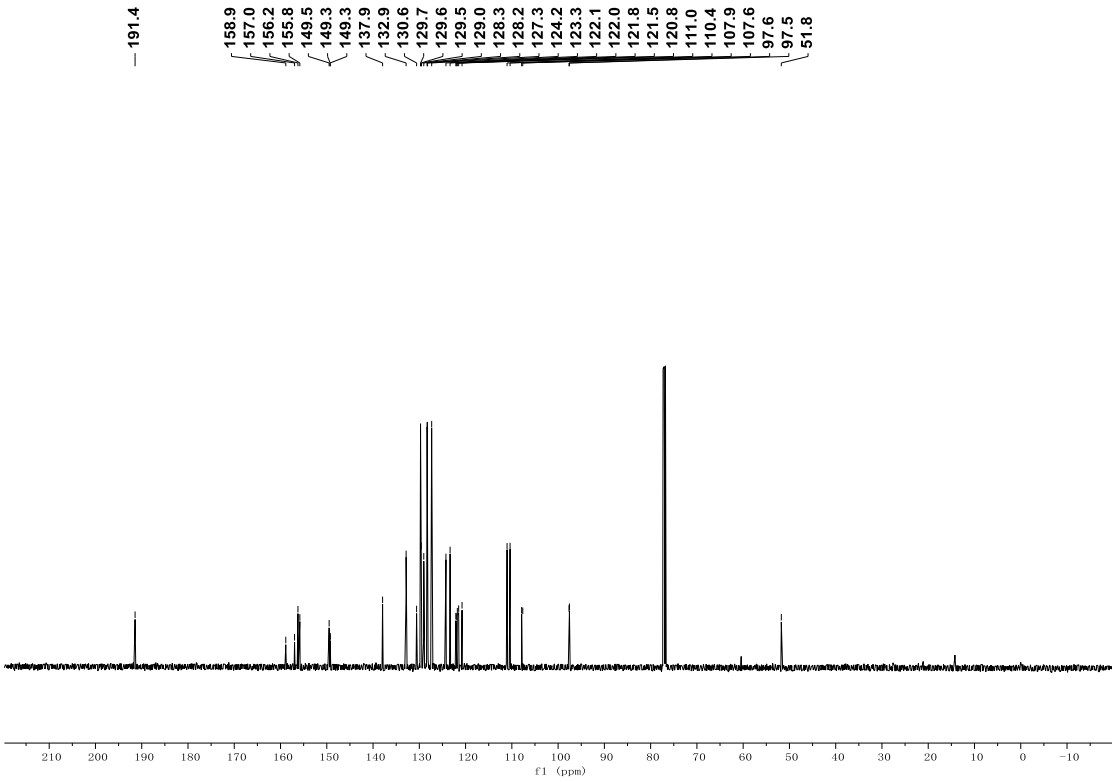

Ph
Bz
O
F
O

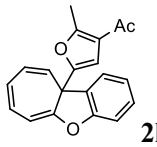
2k


7.73
7.71
7.58
7.57
7.56
7.54
7.53
7.48
7.46
7.37
7.35
7.33
7.32
7.30
7.24
7.24
7.23
7.15
7.13
7.07
7.05
6.41
6.39
6.27
6.25
6.24
6.22
6.22
5.77
5.75
5.74
5.73

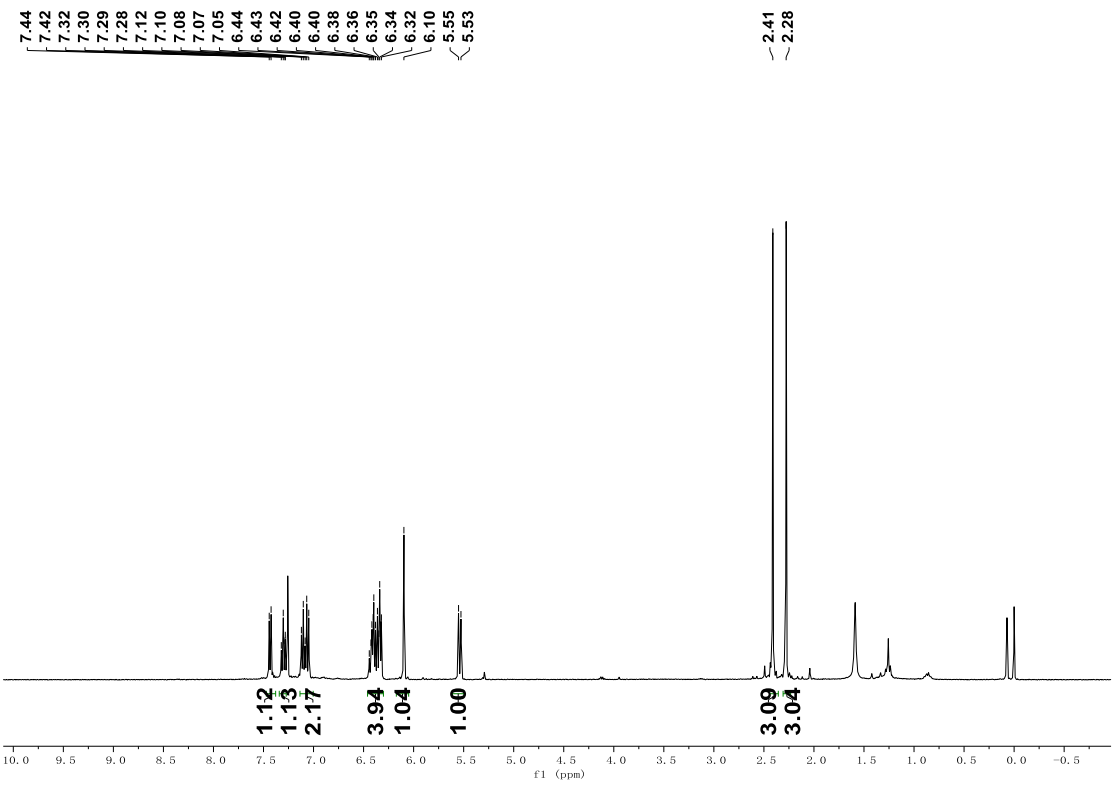

1.96
3.10
1.23
3.12
3.46
1.29
1.06
1.02
2.98
1.00
f1 (ppm)

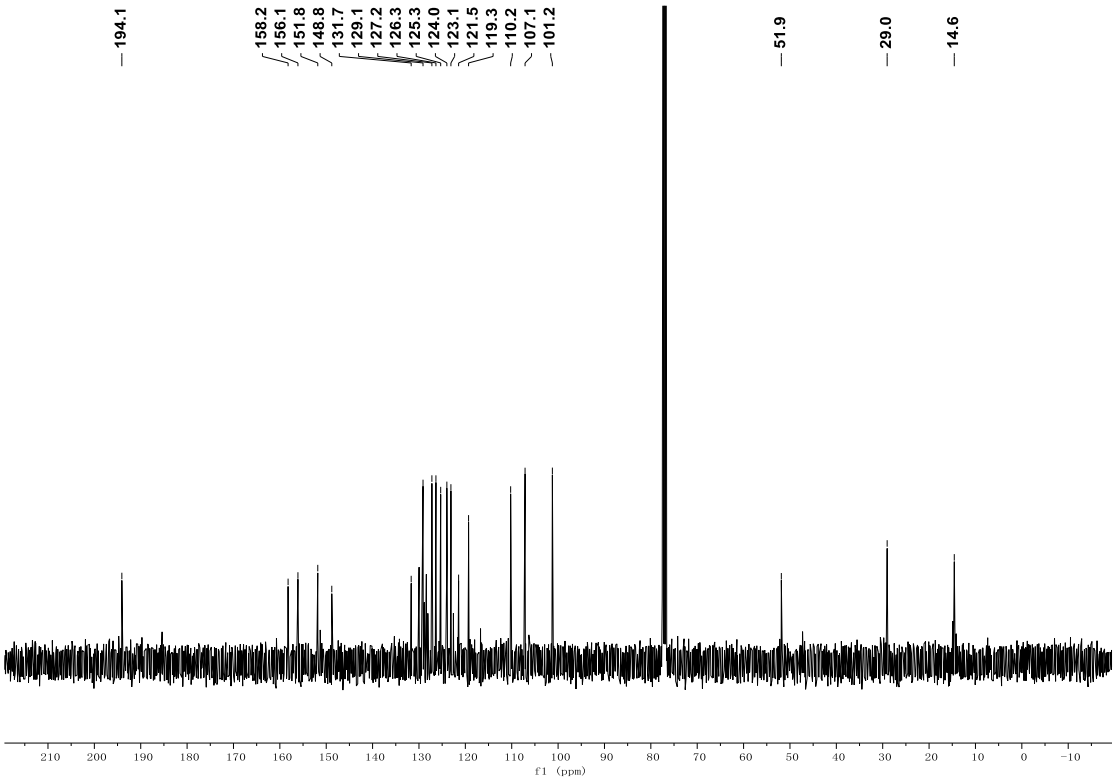

-105.1
f1 (ppm)

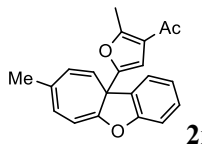

191.4
158.9
157.0
156.2
155.8
149.5
149.3
149.3
137.9
132.9
130.6
129.7
129.6
129.5
129.0
128.3
128.2
127.3
124.2
123.3
122.1
122.0
121.8
121.5
120.8
111.0
110.4
107.9
107.6
97.6
97.5
51.8
f1 (ppm)


Ac
O
O

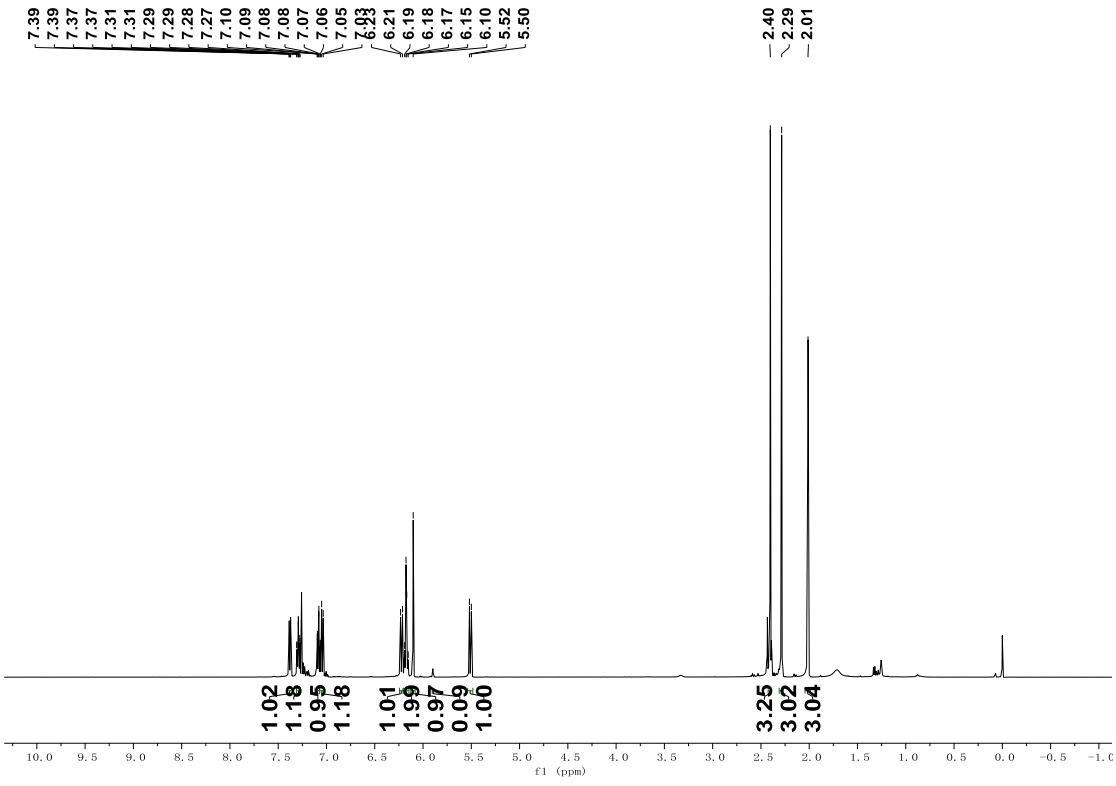
2l

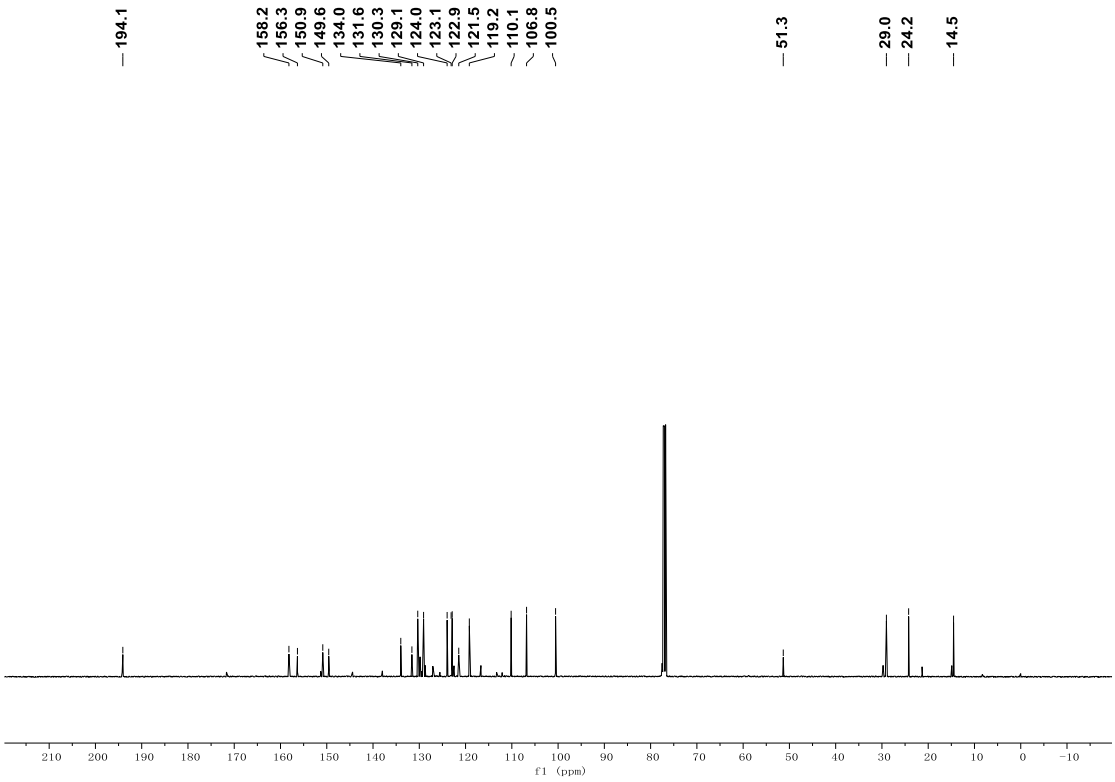

7.44
7.42
7.32
7.30
7.29
7.28
7.12
7.10
7.08
7.07
7.05
6.44
6.43
6.42
6.40
6.40
6.38
6.36
6.35
6.34
6.32
6.10
5.55
5.53
2.41
2.28
1.12
1.13
2.17
3.94
1.04
1.00
3.09
3.04
f1 (ppm)

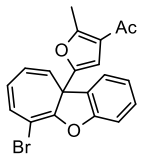

194.1
158.2
156.1
151.8
148.8
131.7
129.1
127.2
126.3
125.3
124.0
123.1
121.5
119.3
110.2
107.1
101.2
51.9
29.0
14.6
f1 (ppm)


Ac
Me
O
O

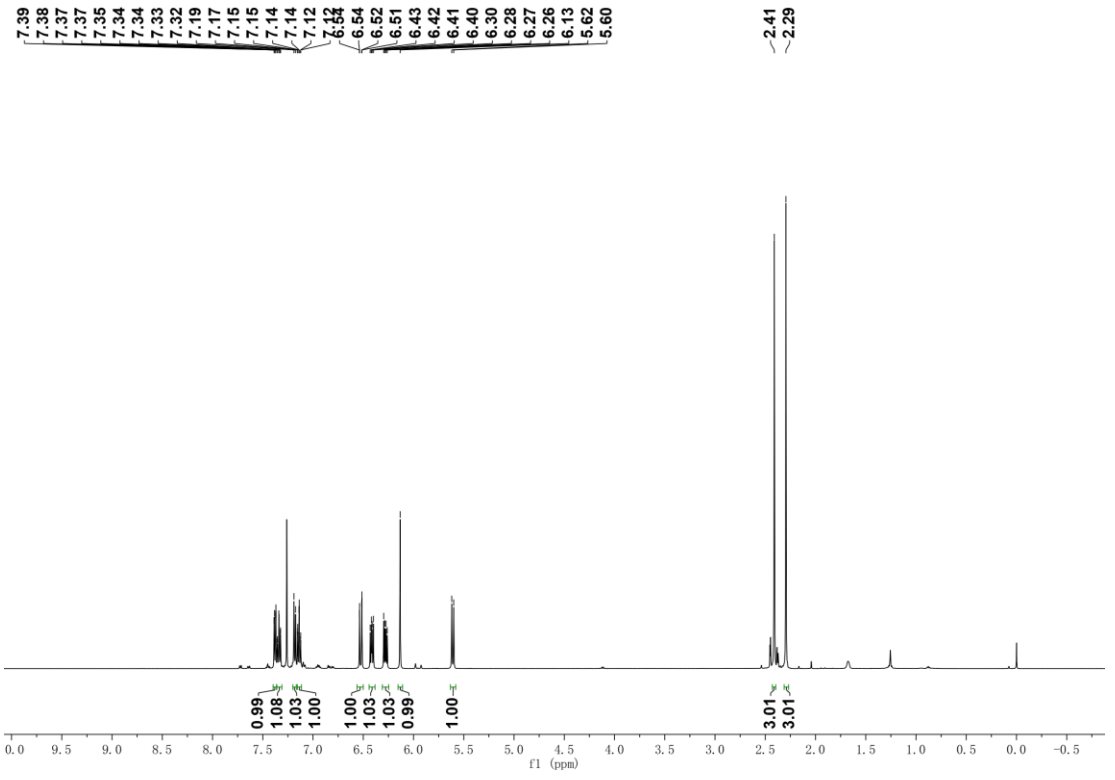
2m

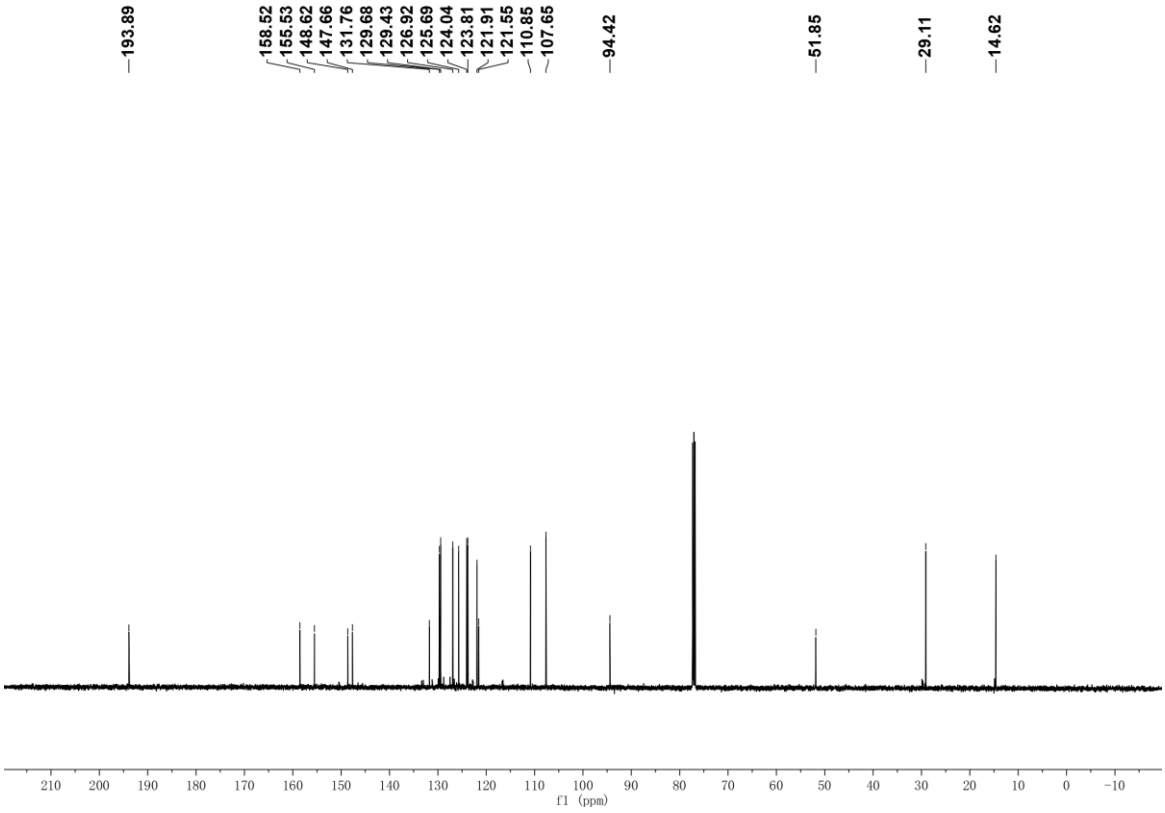

7.39
7.39
7.37
7.37
7.31
7.31
7.29
7.29
7.28
7.27
7.10
7.09
7.08
7.08
7.07
7.06
7.05
6.23
6.21
6.19
6.18
6.17
6.15
6.10
5.52
5.50
2.40
2.29
2.01
1.02
1.13
0.95
1.18
1.01
1.99
0.97
0.09
1.00
3.25
3.02
3.04
f1 (ppm)

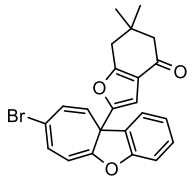

194.1
158.2
156.3
150.9
149.6
134.0
131.6
130.3
129.1
124.0
123.1
122.9
121.5
119.2
110.1
106.8
100.5
51.3
29.0
24.2
14.5
f1 (ppm)


Ac
O
O
Br

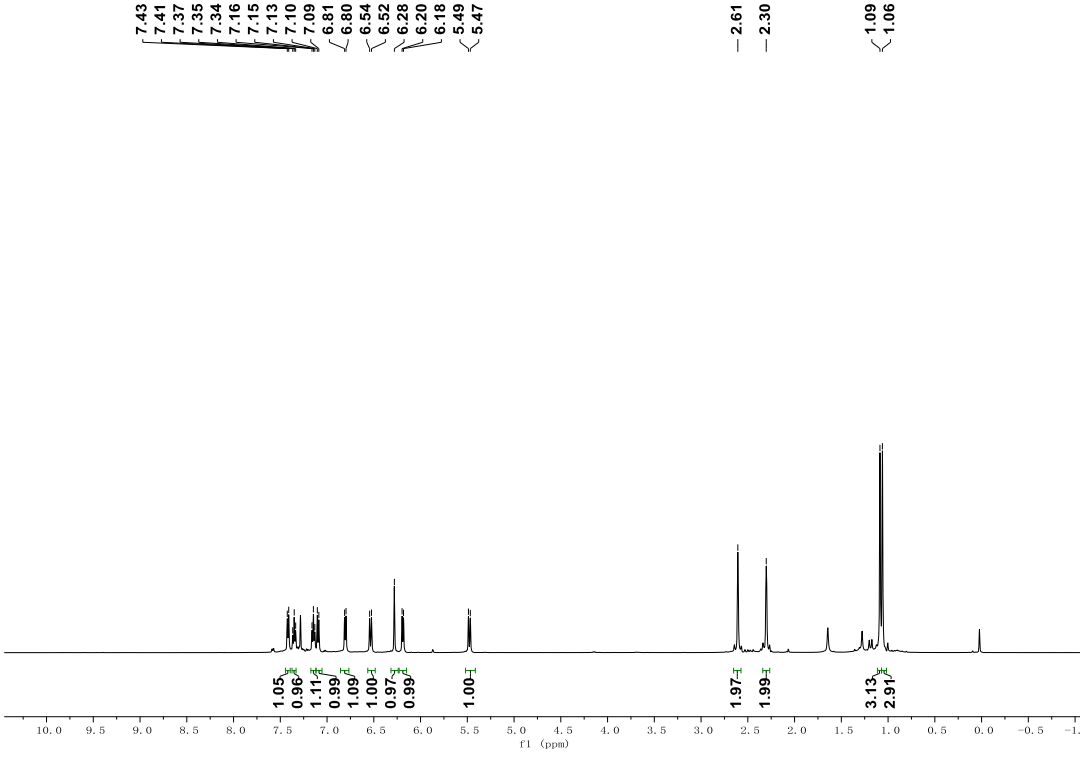
2o

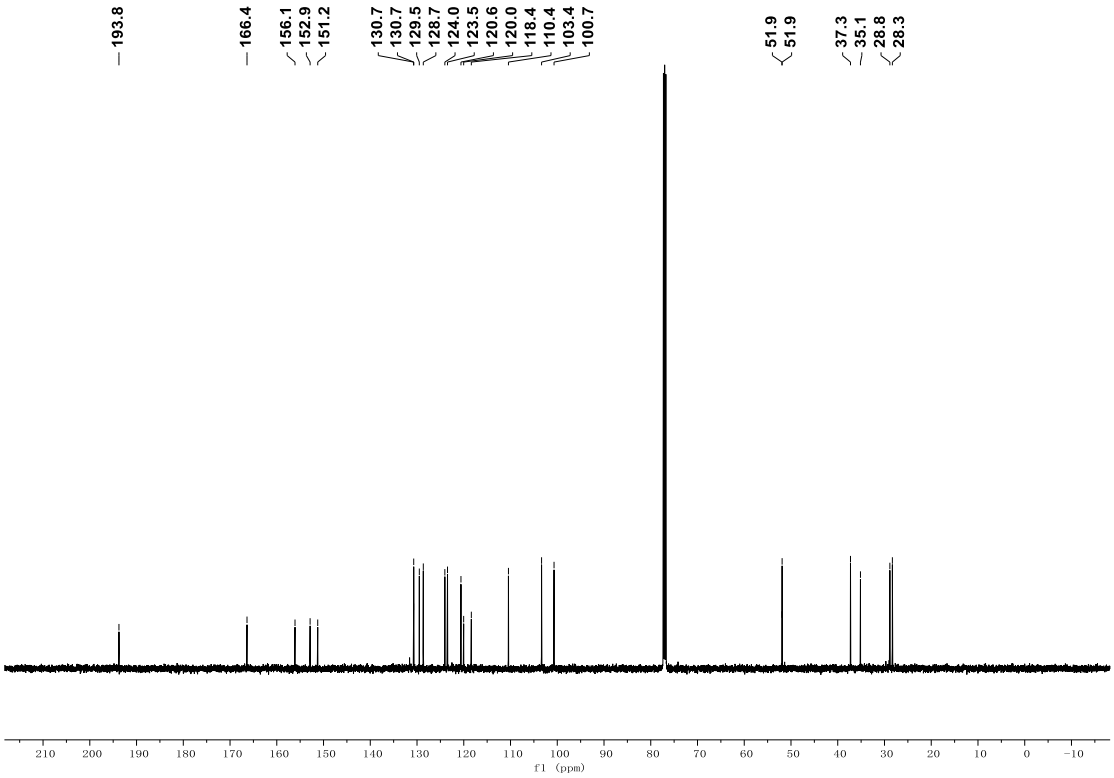

7.39
7.38
7.37
7.37
7.35
7.34
7.34
7.33
7.32
7.19
7.17
7.15
7.15
7.14
7.14
7.12
6.54
6.52
6.51
6.43
6.42
6.41
6.40
6.30
6.28
6.27
6.26
6.13
5.62
5.60
2.41
2.29
0.99
1.08
1.03
1.00
1.00
1.03
1.03
0.99
1.00
3.01
3.01
f1 (ppm)

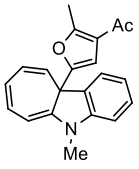

193.89
158.52
155.53
148.62
147.66
131.76
129.68
129.43
126.92
125.69
124.04
123.81
121.91
121.55
110.85
107.65
94.42
51.85
29.11
14.62
f1 (ppm)


Br
O
O
O

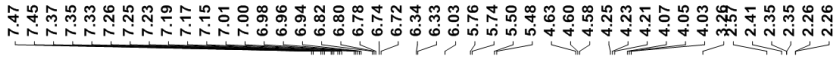
2p


7.43
7.41
7.37
7.35
7.34
7.16
7.15
7.13
7.10
7.09
6.81
6.80
6.54
6.52
6.28
6.20
6.18
5.49
5.47
2.61
2.30
1.09
1.06
1.05
0.96
1.11
0.99
1.09
1.00
0.97
0.99
1.00
1.97
1.99
3.13
2.91
f1 (ppm)

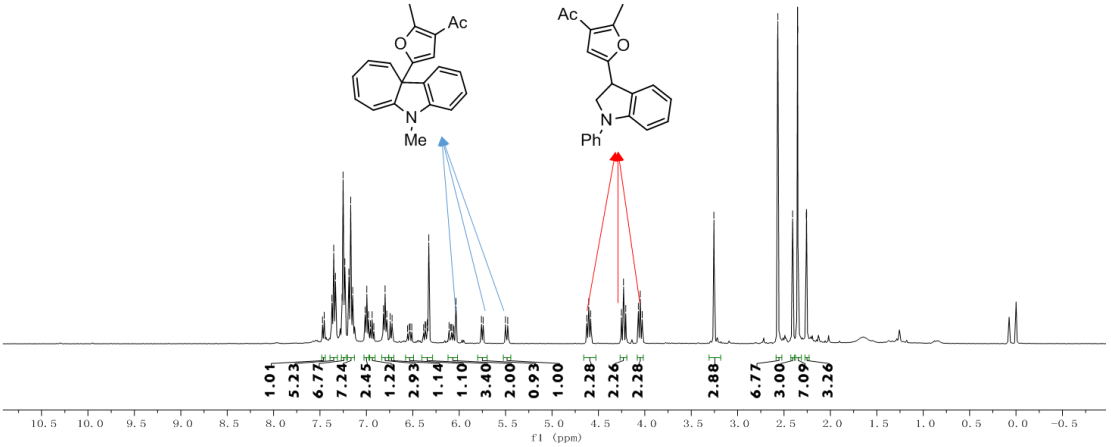


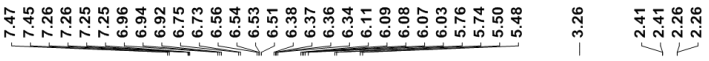


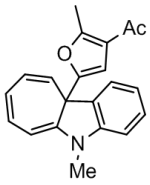
2q [catalyzed by Rh_2(S-BTPCP)$_4$ and Rh_2(TFA)$_4$]



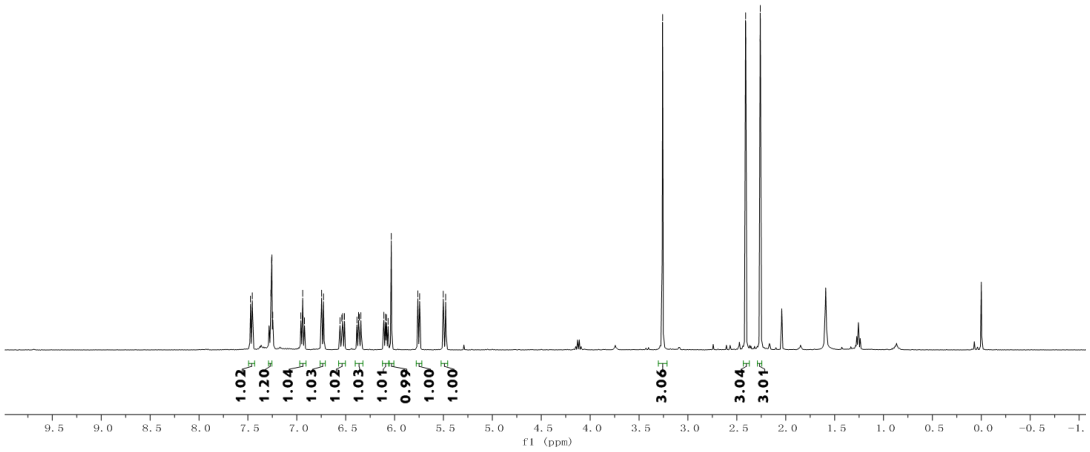
catalyzed by Rh_2(S-BTPCP)$_4$

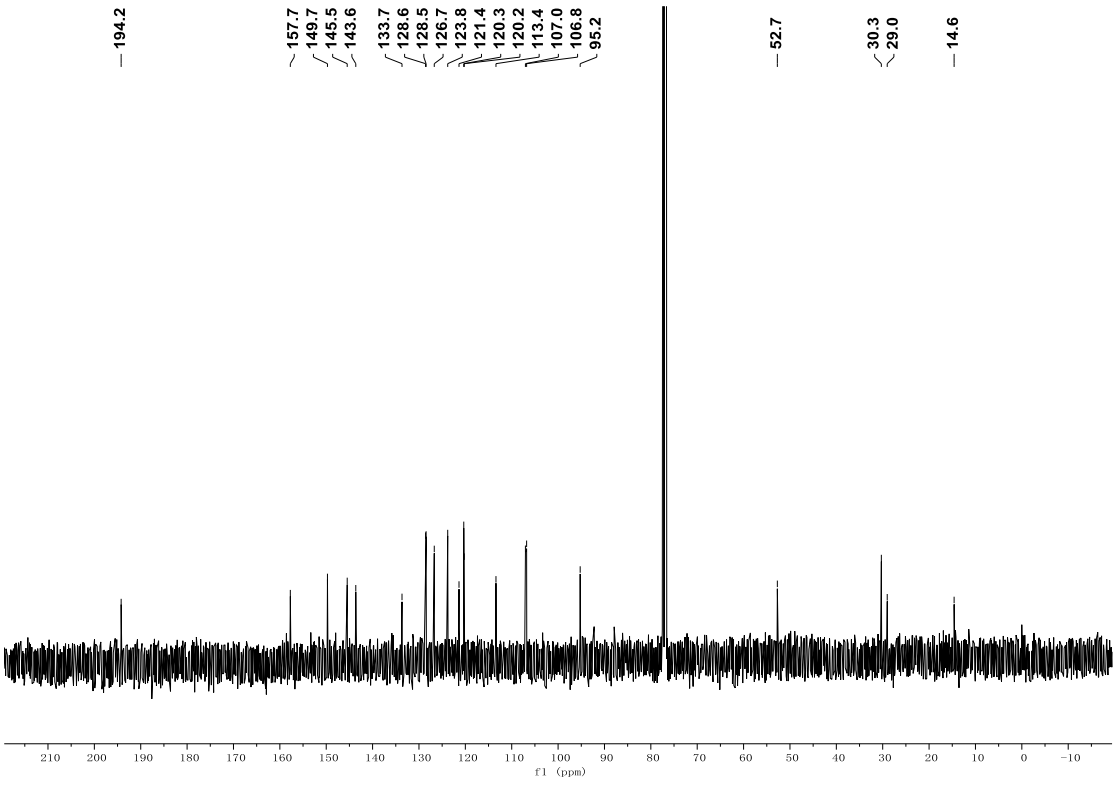


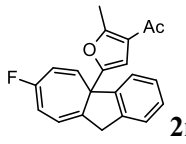




catalyzed by $Rh_2(TFA)_4$

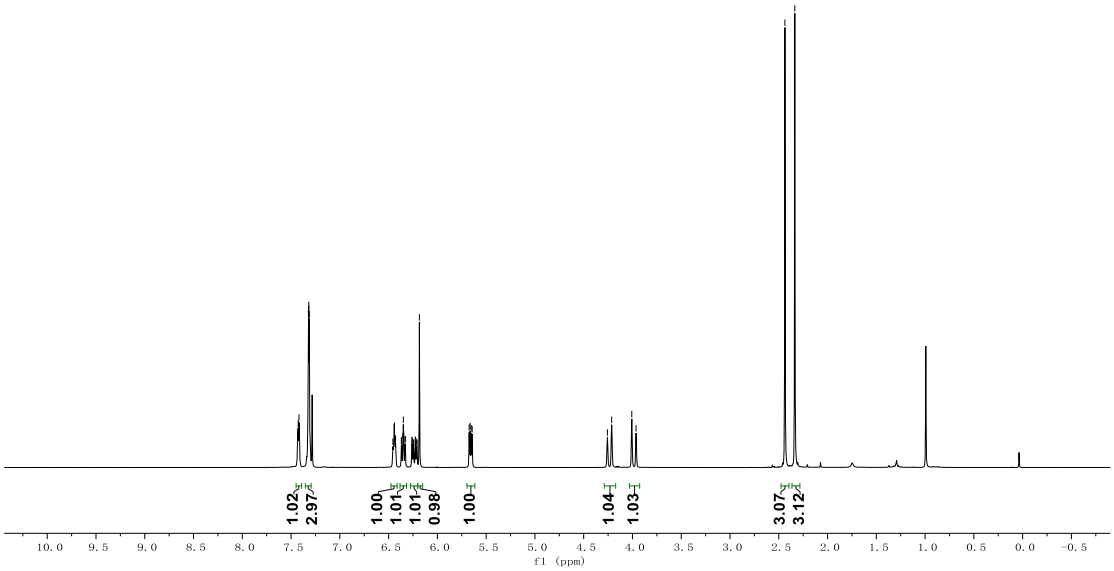


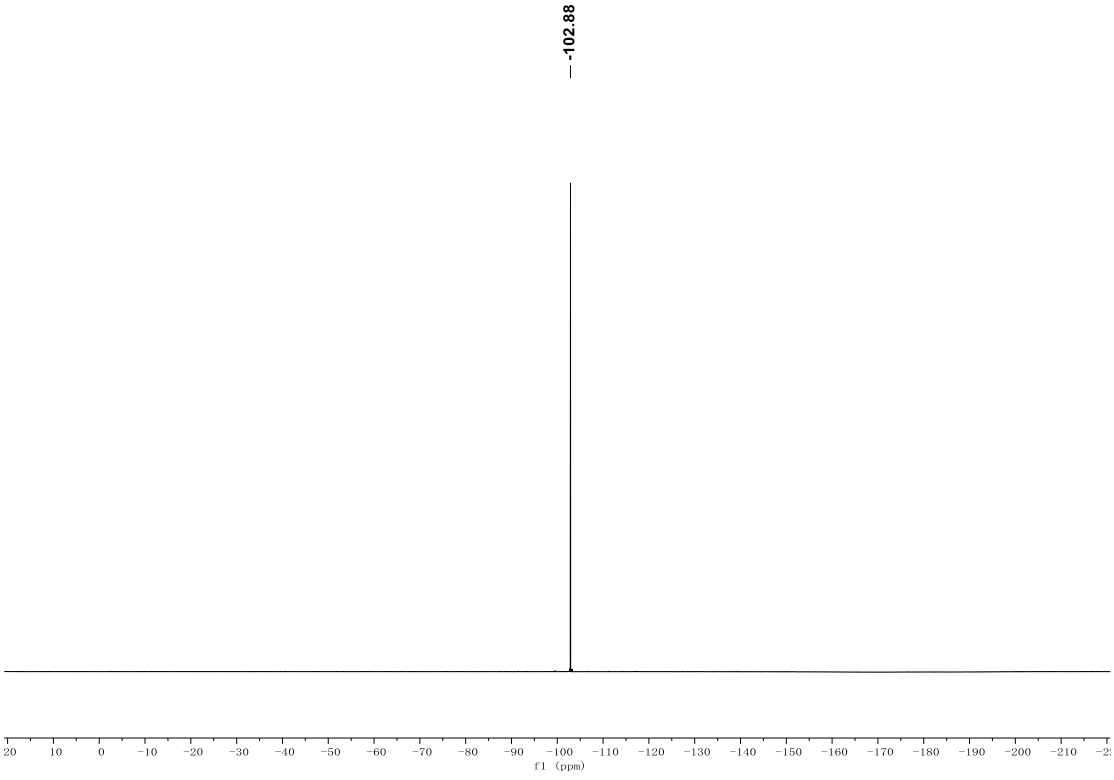


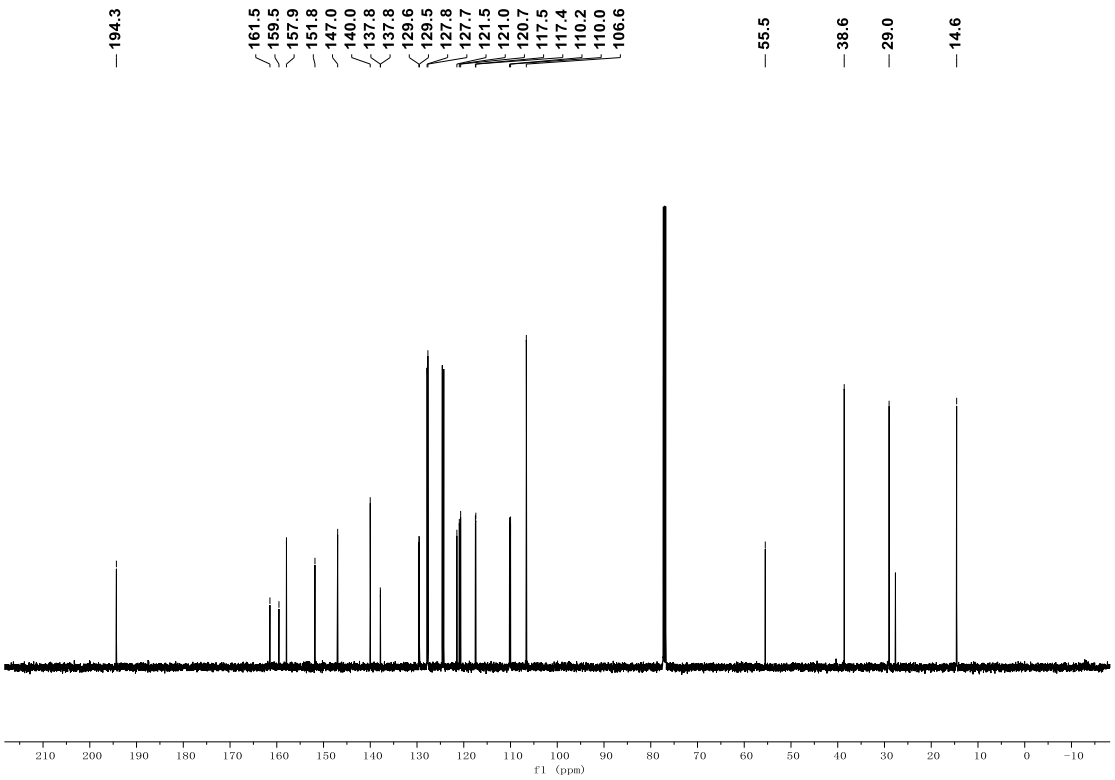


2r

7.43 7.43 7.43 7.42 7.41 7.32 7.32 7.31 6.46 6.44 6.44 6.43 6.43 6.37 6.37 6.35 6.35 6.34 6.33 6.33 6.26 6.26 6.25 6.24 6.23 6.22 6.21 6.21 6.18 5.67 5.66 5.65 5.64 4.26 4.21 4.01 3.96 2.44 2.34



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161.5
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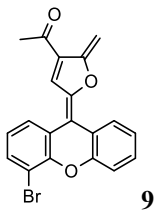
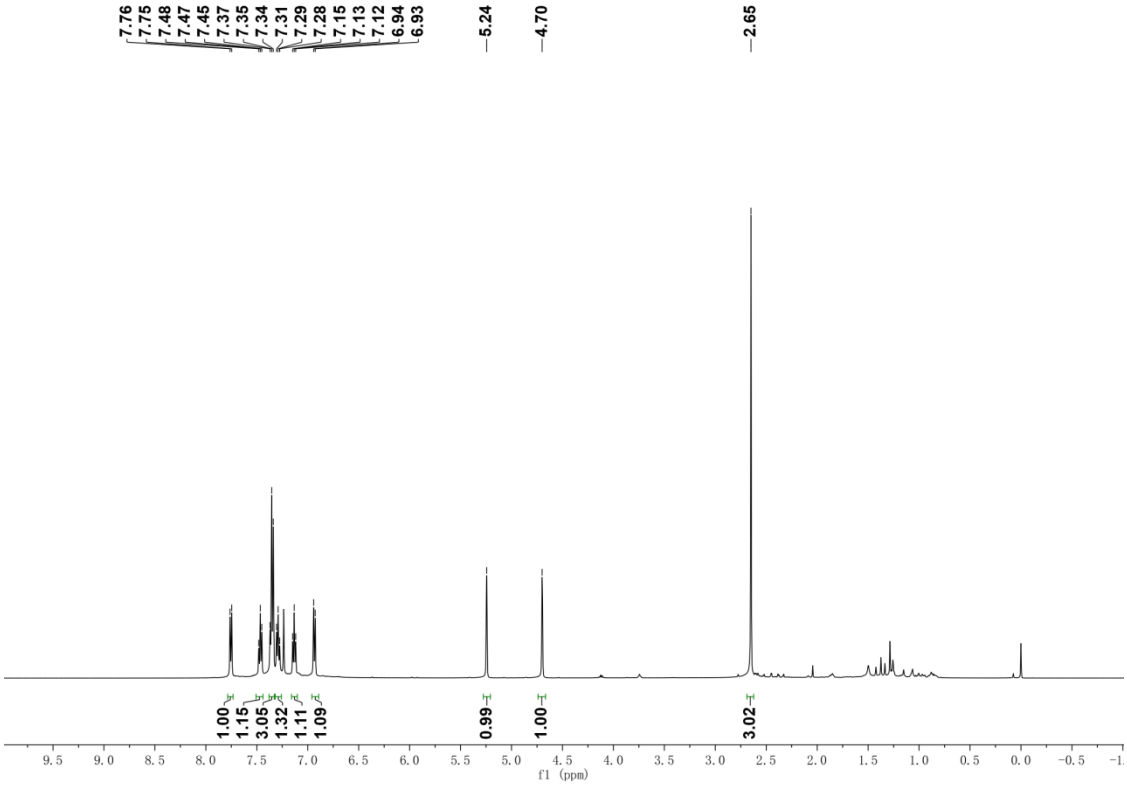
157.9
151.8
147.0
140.0
137.8
137.8
129.6
129.5
127.8
127.7
121.5
121.0
120.7
117.5
117.4
110.2
110.0
106.6
55.5
38.6
29.0
14.6
f1 (ppm)


O
O
O
Br

9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7.75
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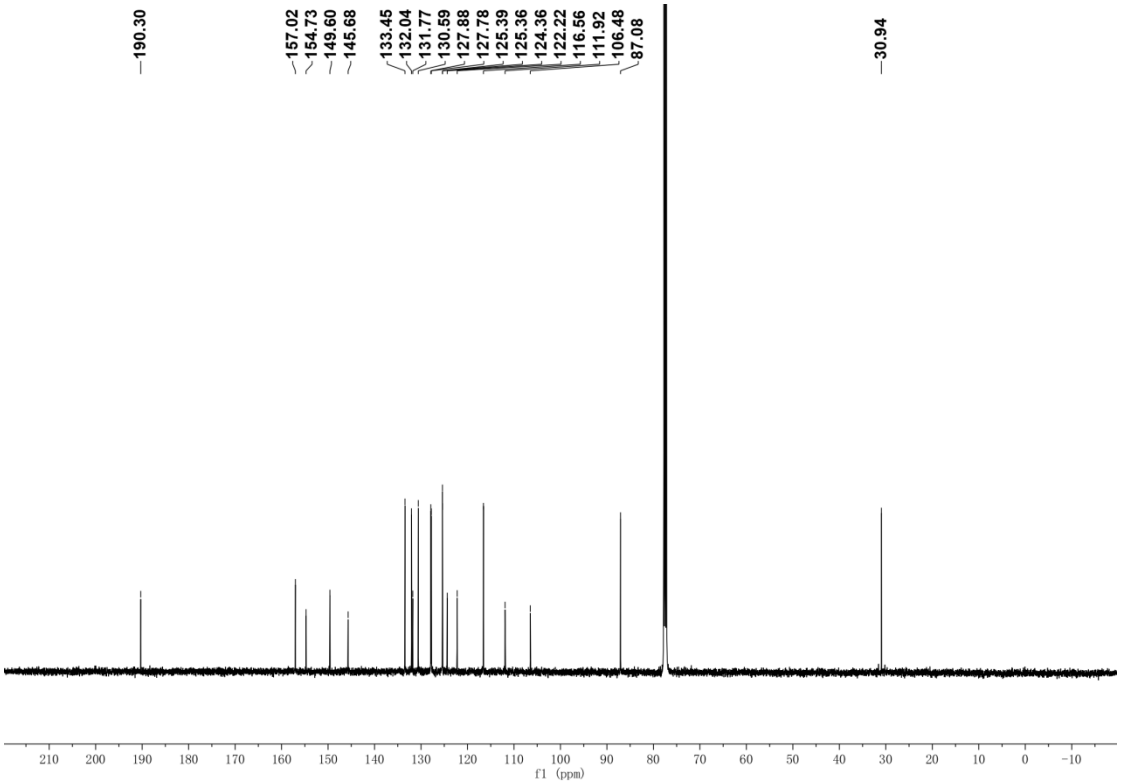
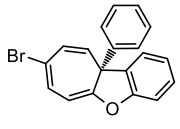
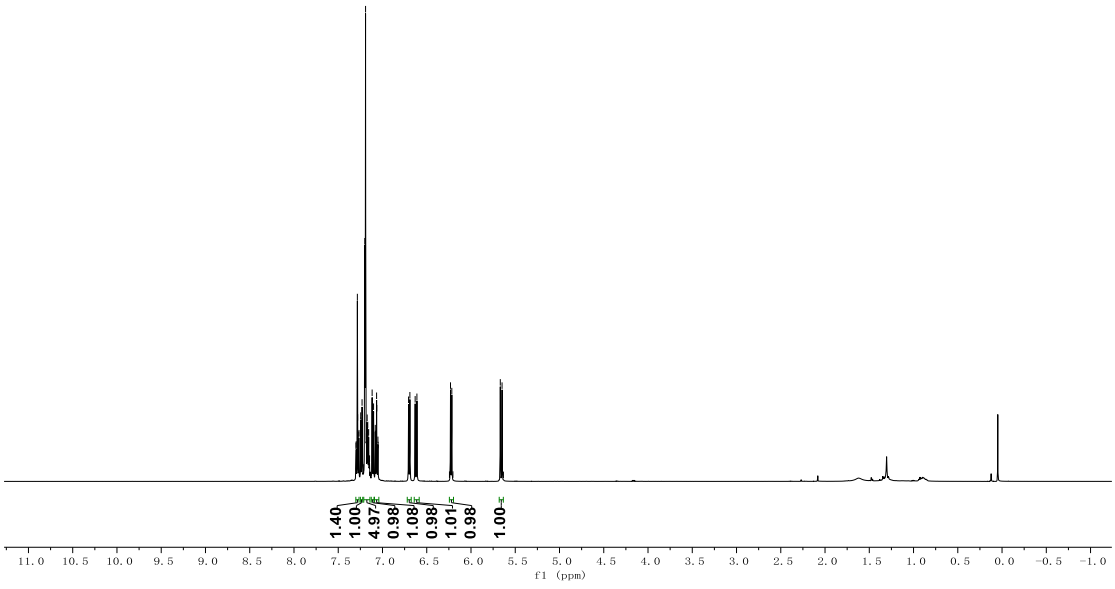
7.47
7.45
7.37
7.35
7.34
7.31
7.29
7.28
7.15
7.13
7.12
6.94
6.93
5.24
4.70
2.65
1.00
1.15
3.05
1.32
1.11
1.09
0.99
1.00
3.02
f1 (ppm)


190.30
157.02
154.73
149.60
145.68
133.45
132.04
131.77
130.59
127.88
127.78
125.39
125.36
124.36
122.22
116.56
111.92
106.48
87.08
30.94
f1 (ppm)


Br
O

4a


7.28
7.28
7.27
7.25
7.24
7.23
7.23
7.20
7.19
7.17
7.17
7.16
7.12
7.10
7.08
7.08
7.07
7.06
6.71
6.69
6.63
6.61
6.23
6.22
5.67
5.65
5.63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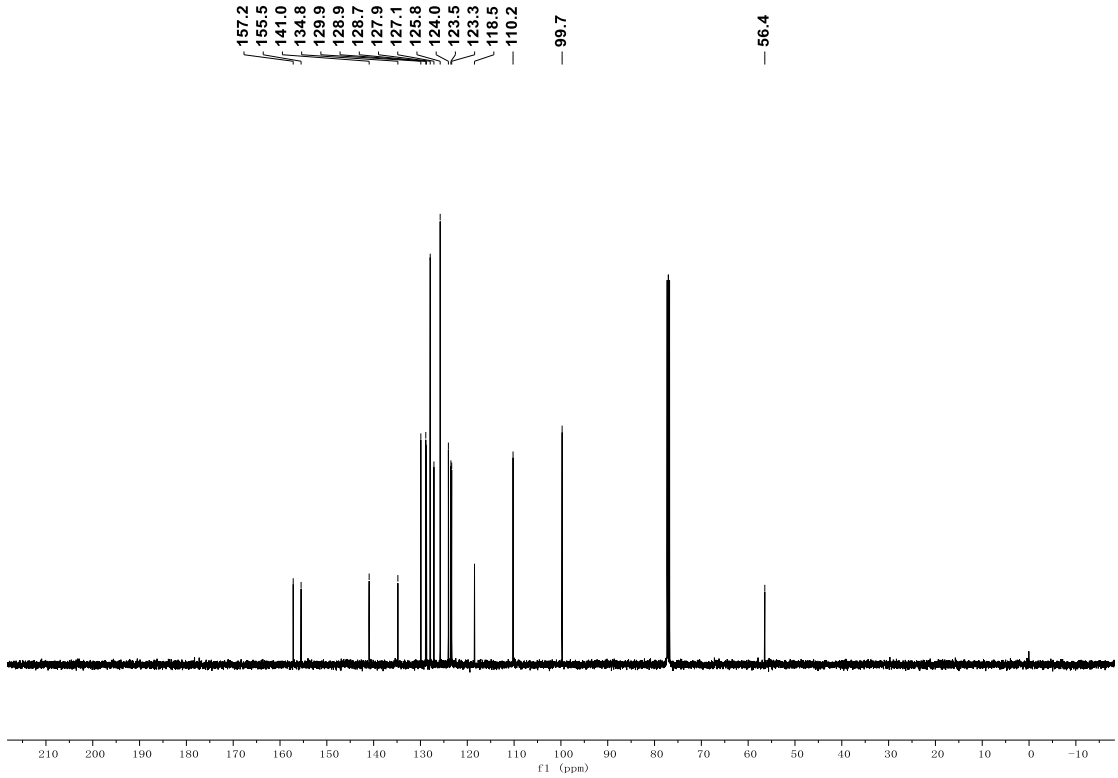
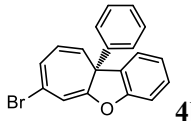
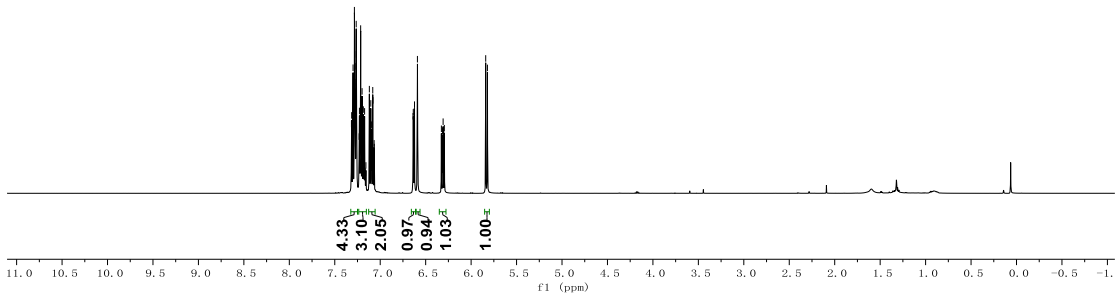
0.98
1.08
0.98
1.01
0.98
1.00
f1 (ppm)

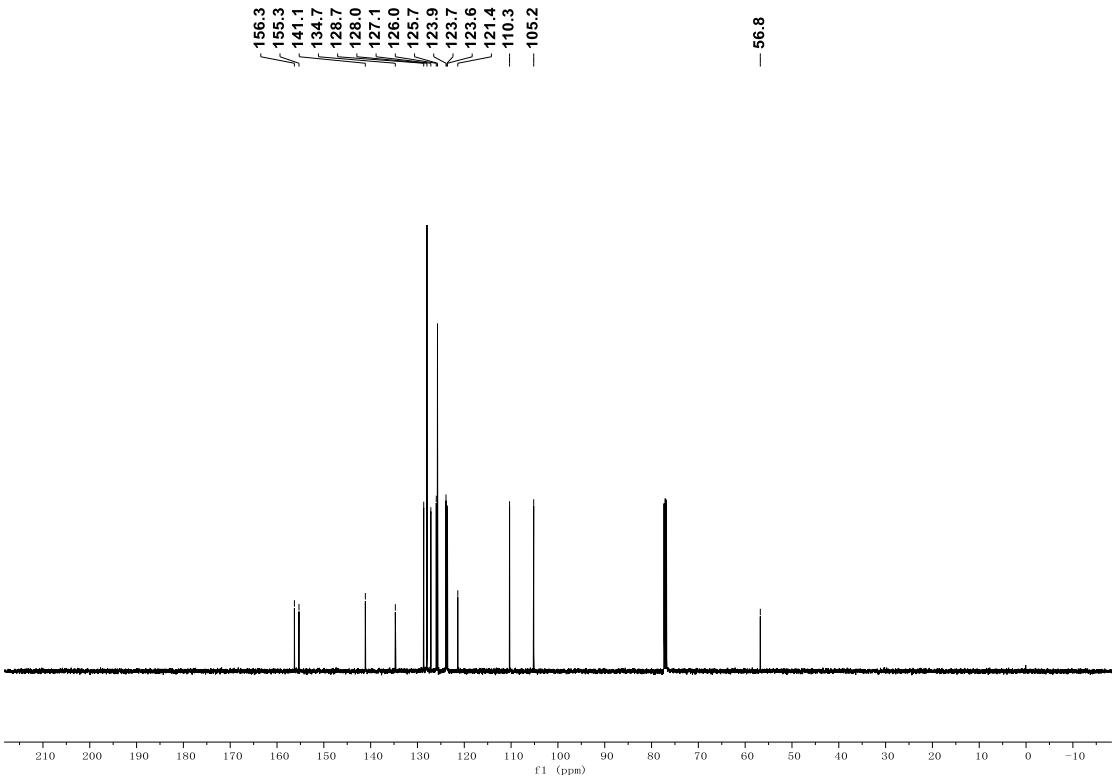

157.2
155.5
141.0
134.8
129.9
128.9
128.7
127.9
127.1
125.8
124.0
123.5
123.3
118.5
110.2
99.7
56.4
f1 (ppm)

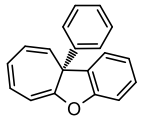

Br
O

4b


7.32
7.31
7.30
7.30
7.28
7.28
7.28
7.27
7.26
7.26
7.23
7.22
7.21
7.20
7.19
7.17
7.12
7.10
7.08
7.08
6.64
6.63
6.62
6.59
6.33
6.31
6.31
6.29
5.84
5.82


4.33
3.10
2.05
0.97
0.94
1.03
1.00
f1 (ppm)


156.3
155.3
141.1
134.7
128.7
128.0
127.1
126.0
125.7
123.9
123.7
123.6
121.4
110.3
105.2
56.8
f1 (ppm)



4c


7.31
7.30
7.29
7.29
7.28
7.27
7.27
7.26
7.25
7.25
7.19
7.17
7.17
7.16
7.16
7.15
7.13
7.11
7.10
7.05
6.53
6.52
6.51
6.50
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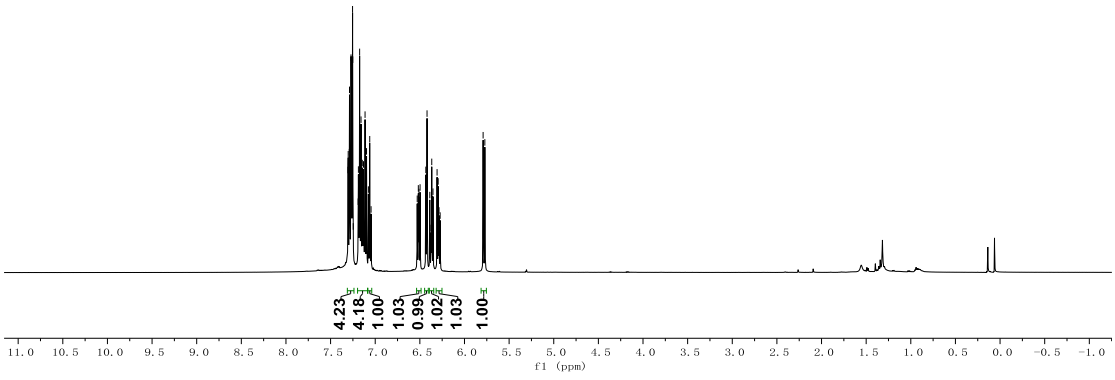
6.31
6.29
6.29
6.27
5.79
5.77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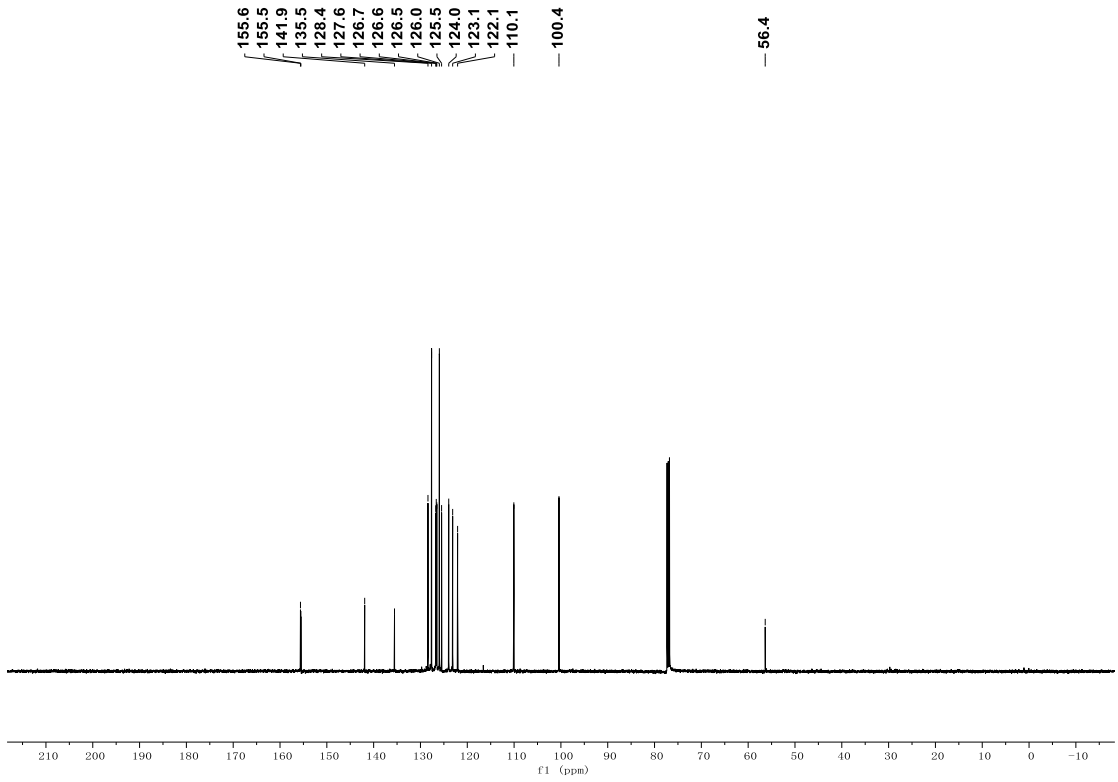
4.18
1.00
1.03
0.99
1.02
1.03
1.00
f1 (ppm)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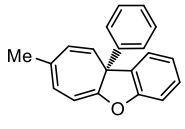
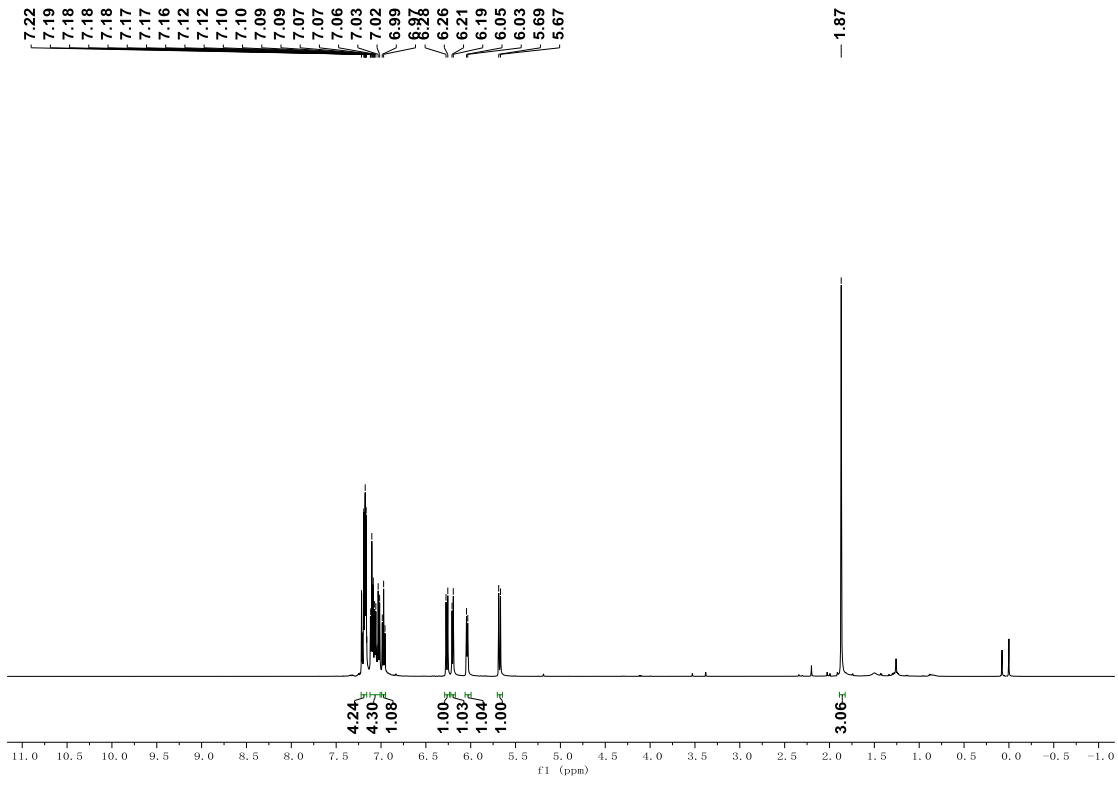
155.5
141.9
135.5
128.4
127.6
126.7
126.6
126.5
126.0
125.5
124.0
123.1
122.1
110.1
100.4
56.4
f1 (ppm)


Me
O

4d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7.12
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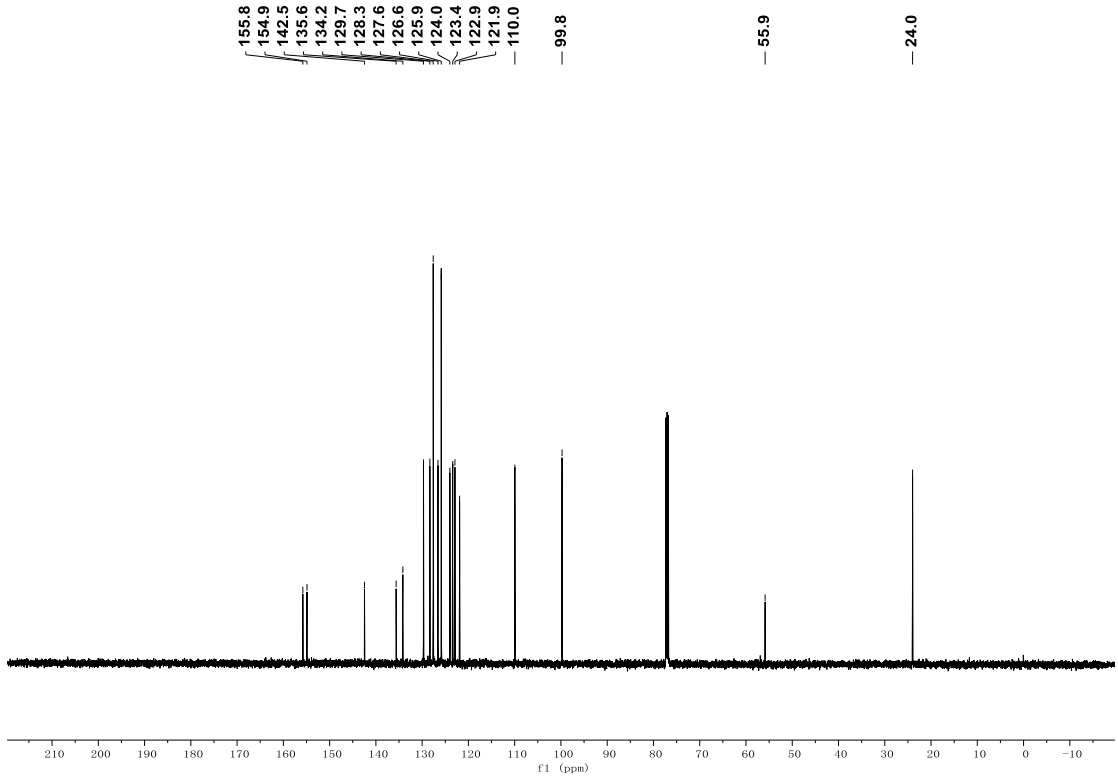
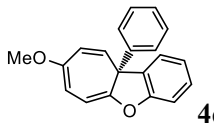
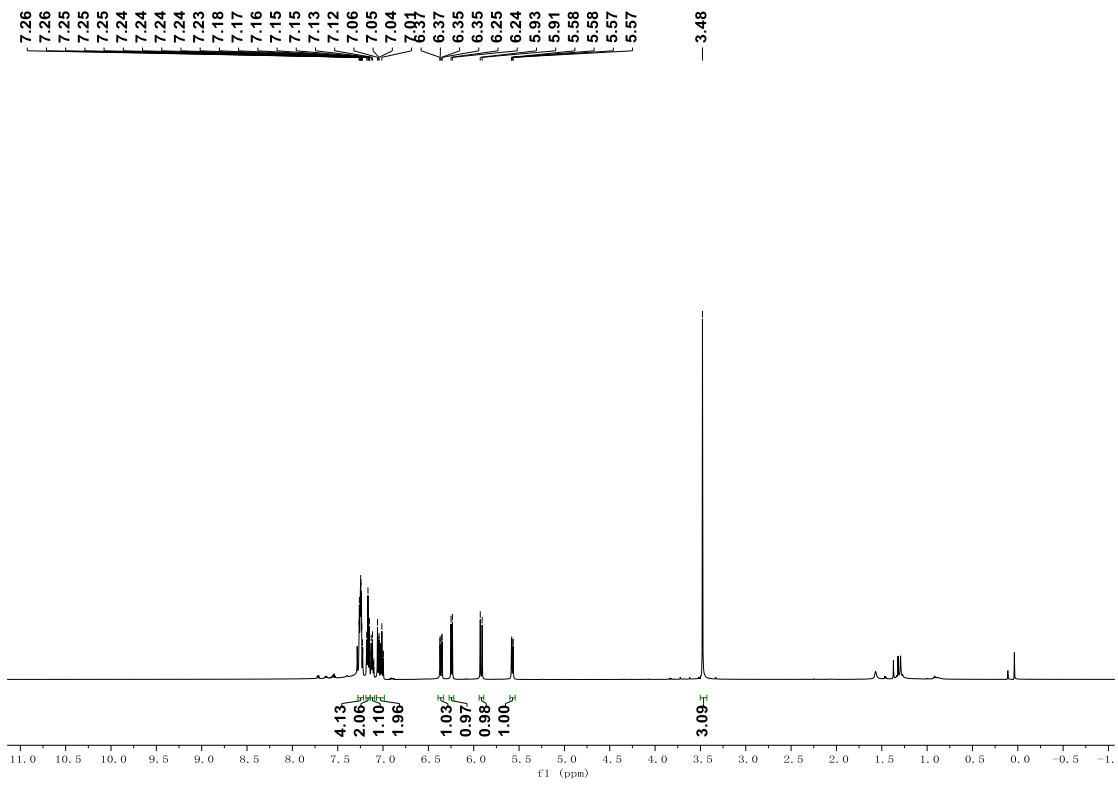
7.10
7.09
7.09
7.07
7.07
7.06
7.03
7.02
6.99
6.97
6.28
6.26
6.21
6.19
6.05
6.03
5.69
5.67
1.87
4.24
4.30
1.08
1.00
1.03
1.04
1.00
3.06
f1 (ppm)


155.8
154.9
142.5
135.6
134.2
129.7
128.3
127.6
126.6
125.9
124.0
123.4
122.9
121.9
110.0
99.8
55.9
24.0
f1 (ppm)


MeO
O

4e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7.25
7.25
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7.24
7.24
7.24
7.24
7.23
7.18
7.17
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7.15
7.13
7.12
7.06
7.05
7.04
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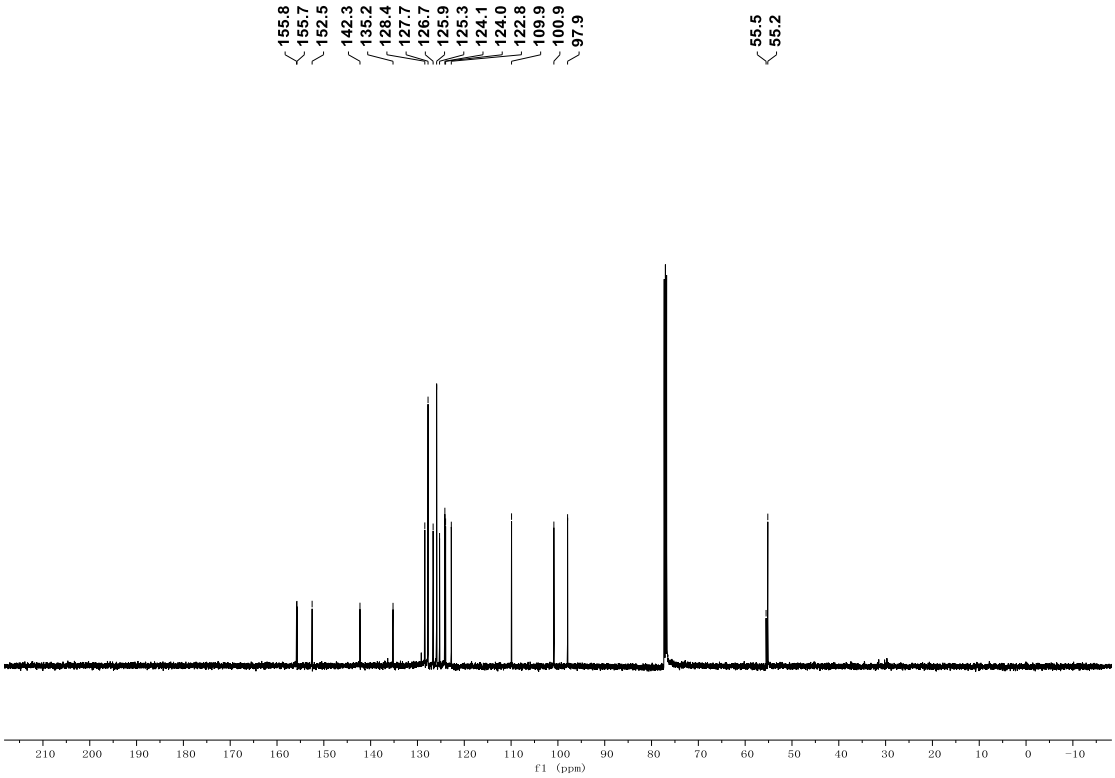
6.37
6.35
6.35
6.25
6.24
5.93
5.91
5.58
5.58
5.57
5.57
3.48
4.13
2.06
1.10
1.96
1.03
0.97
0.98
1.00
3.09
f1 (ppm)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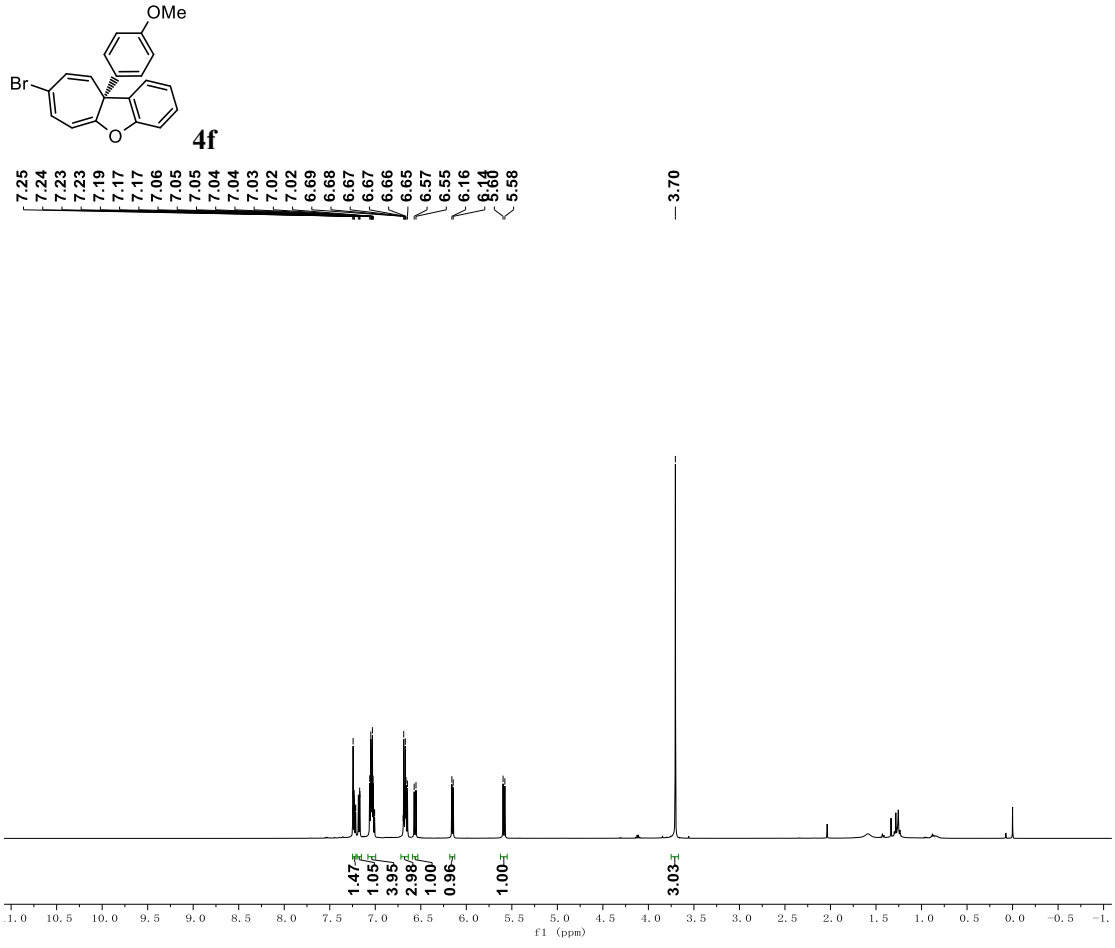
155.7
152.5
142.3
135.2
128.4
127.7
126.7
125.9
125.3
124.1
124.0
122.8
109.9
100.9
97.9
55.5
55.2
f1 (ppm)


OMe
Br
O
4f
7.25
7.24
7.23
7.23
7.19
7.17
7.17
7.06
7.05
7.05
7.04
7.04
7.03
7.02
7.02
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6.66
6.65
6.57
6.55
6.16
6.14
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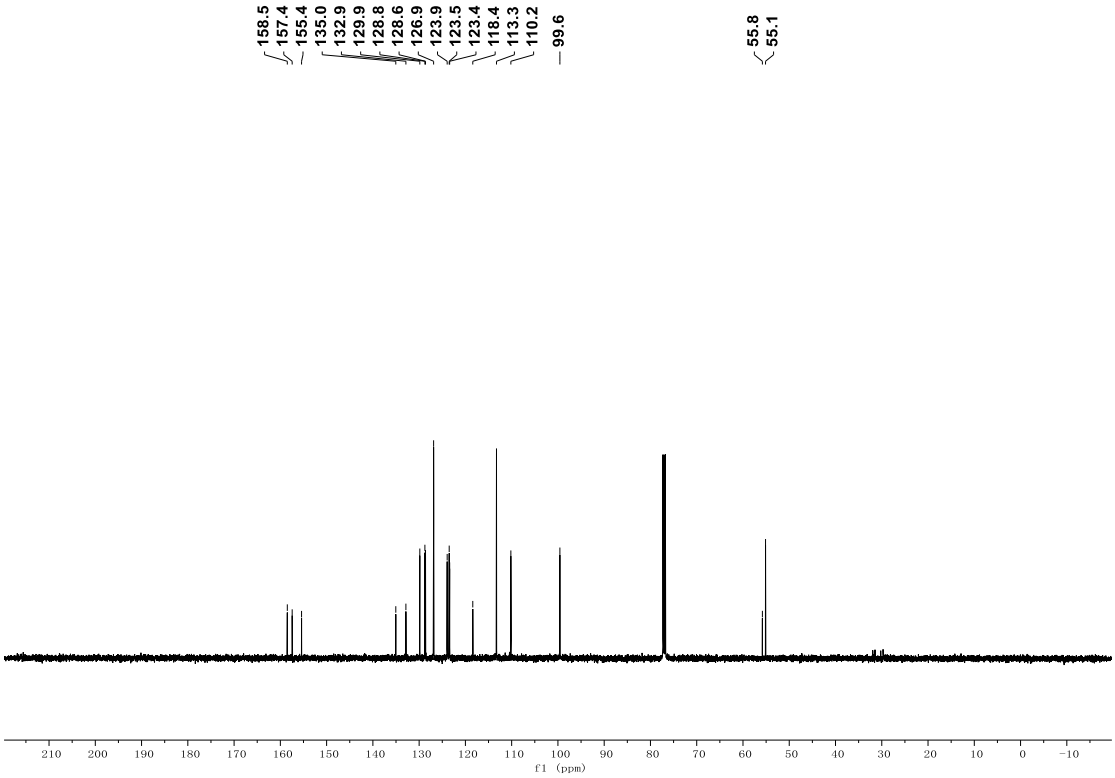
5.58
3.70
1.47
1.05
3.95
2.98
1.00
0.96
1.00
3.03
f1 (ppm)


158.5
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155.4
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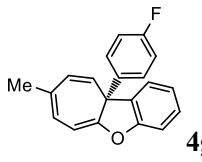
132.9
129.9
128.8
128.6
126.9
123.9
123.5
123.4
118.4
113.3
110.2
99.6
55.8
55.1
f1 (ppm)


F
Me
O

4g


7.24
7.24
7.23
7.23
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7.18
7.18
7.17
7.17
7.16
7.16
7.15
7.15
7.14
7.14
7.13
7.13
7.12
7.12
7.04
7.04
7.03
7.02
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7.01
7.00
7.00
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6.81
6.80
6.79
6.79
6.79
6.78
6.77
6.28
6.28
6.26
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6.21
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6.20
6.19
6.06
6.05
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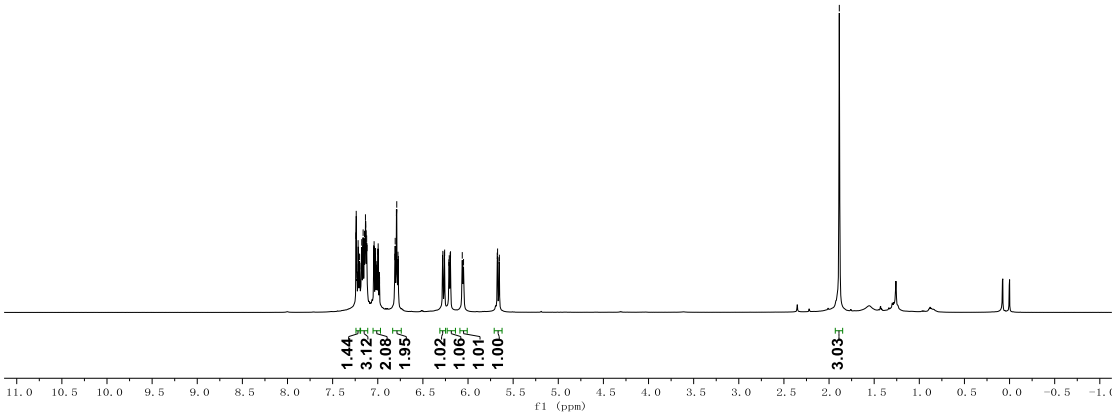
5.67
5.66
5.65
1.89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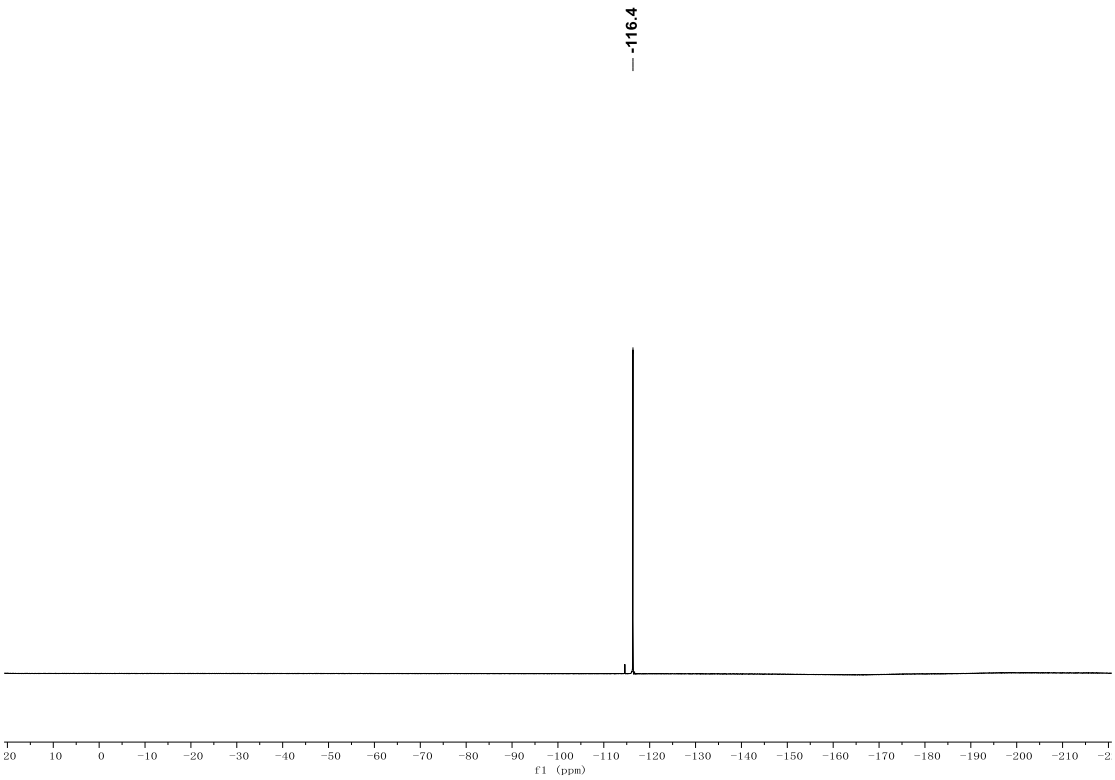
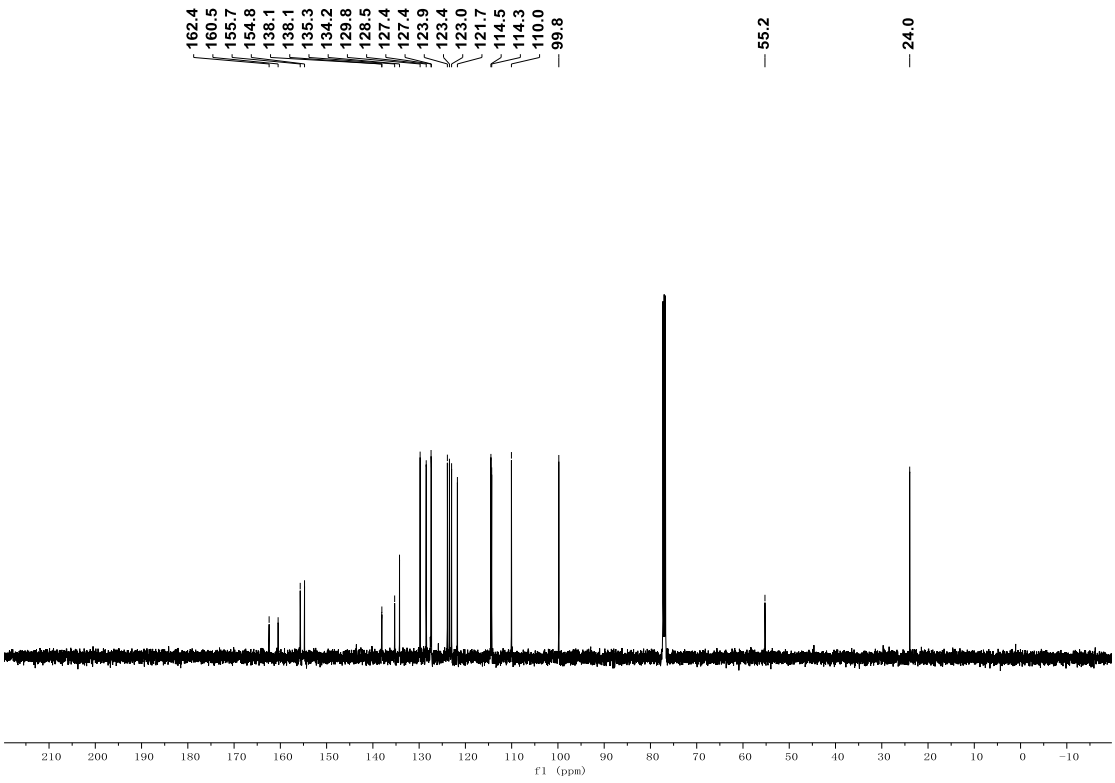
1.02
1.06
1.01
1.00
3.03
f1 (ppm)


-116.4
20 10 0 −10 −20 −30 −40 −50 −60 −70 −80 −90 −100 −110 −120 −130 −140 −150 −160 −170 −180 −190 −200 −210 −2
f1 (ppm)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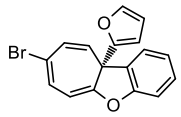
160.5
155.7
154.8
138.1
138.1
135.3
134.2
129.8
128.5
127.4
127.4
123.9
123.4
123.0
121.7
114.5
114.3
110.0
99.8
55.2
24.0
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)


Br
O
O

4h


7.37
7.35
7.35
7.31
7.30
7.18
7.18
7.18
7.10
7.10
7.08
7.06
6.76
6.74
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6.15
6.13
6.00
6.00
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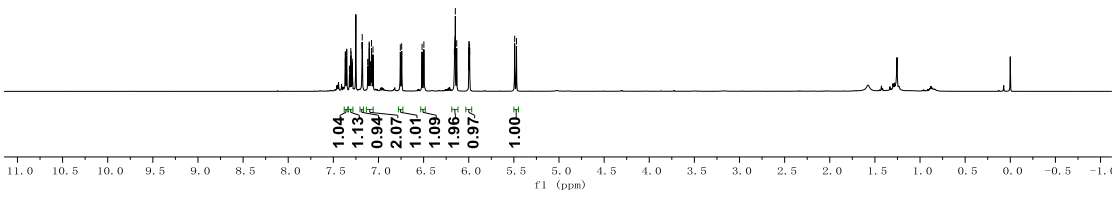
5.49
5.47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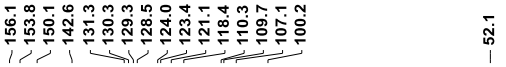
1.13
0.94
2.07
1.01
1.09
1.96
0.97
1.00
f1 (ppm)


156.1
153.8
150.1
142.6
131.3
130.3
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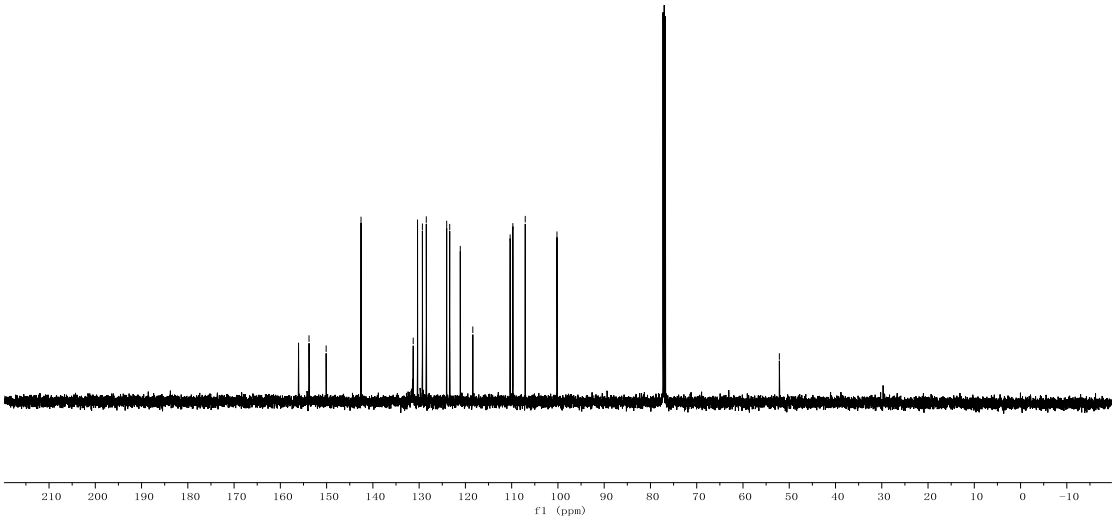
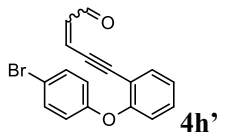
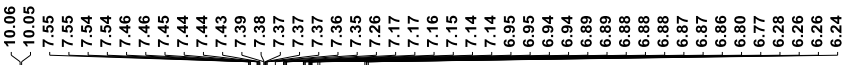
128.5
124.0
123.4
121.1
118.4
110.3
109.7
107.1
100.2
52.1


f1 (ppm)


O
Br
O

4h’


10.06
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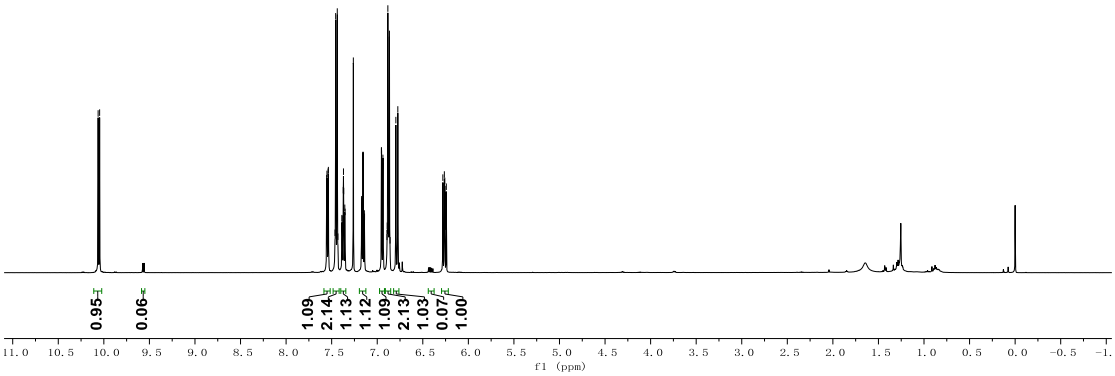
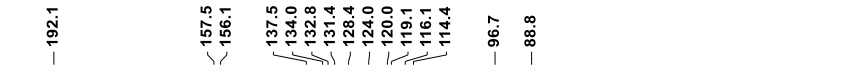
6.26
6.26
6.24


0.95
0.06
1.09
2.14
1.13
1.12
1.09
2.13
1.03
0.07
1.00
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5 −1.
f1 (ppm)


192.1
157.5
156.1
137.5
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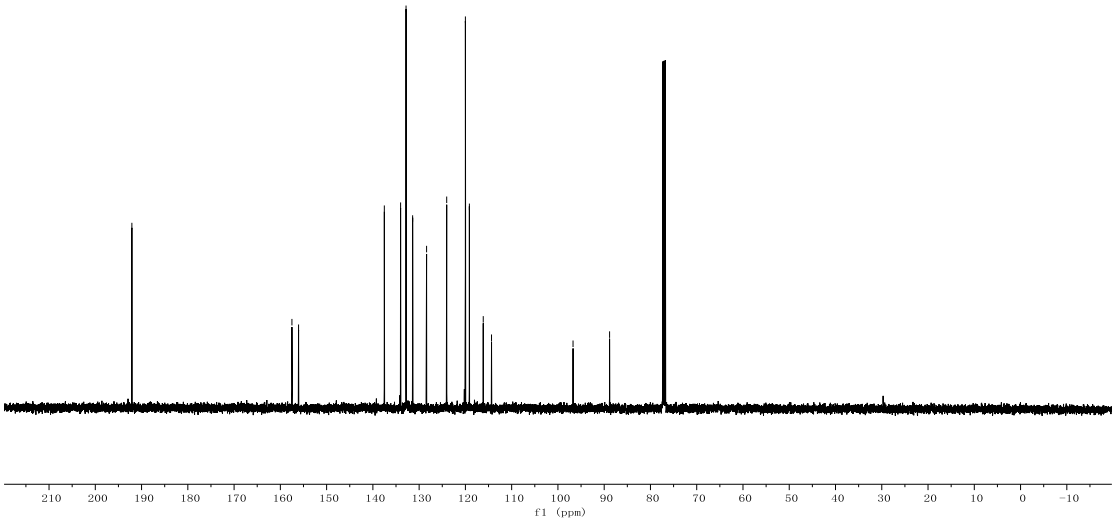
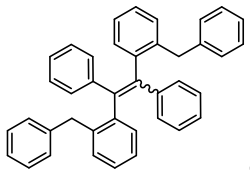
132.8
131.4
128.4
124.0
120.0
119.1
116.1
114.4
96.7
88.8


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)



4i'


7.47
7.46
7.45
7.45
7.39
7.38
7.38
7.37
7.36
7.36
7.35
7.09
7.08
7.07
7.07
7.06
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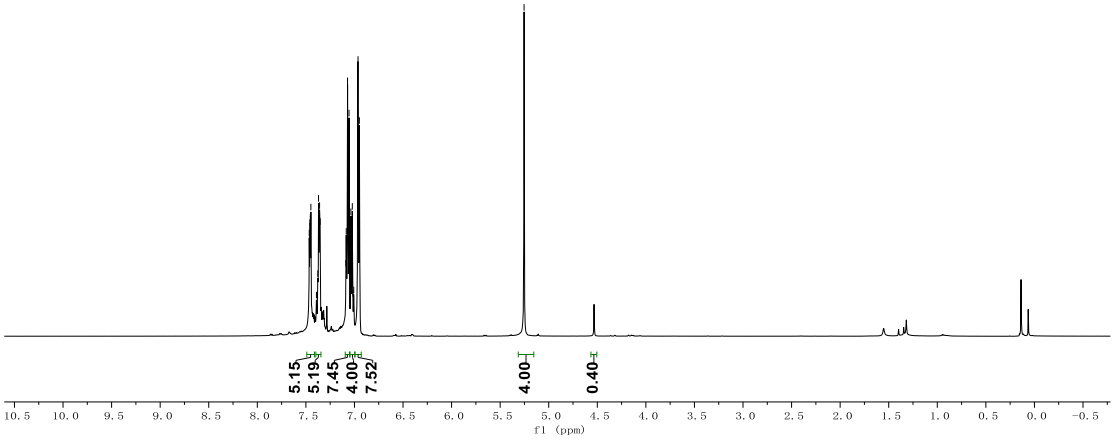
7.04
7.03
7.03
7.02
7.02
7.01
6.97
6.96
6.95
5.25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5.19
7.45
4.00
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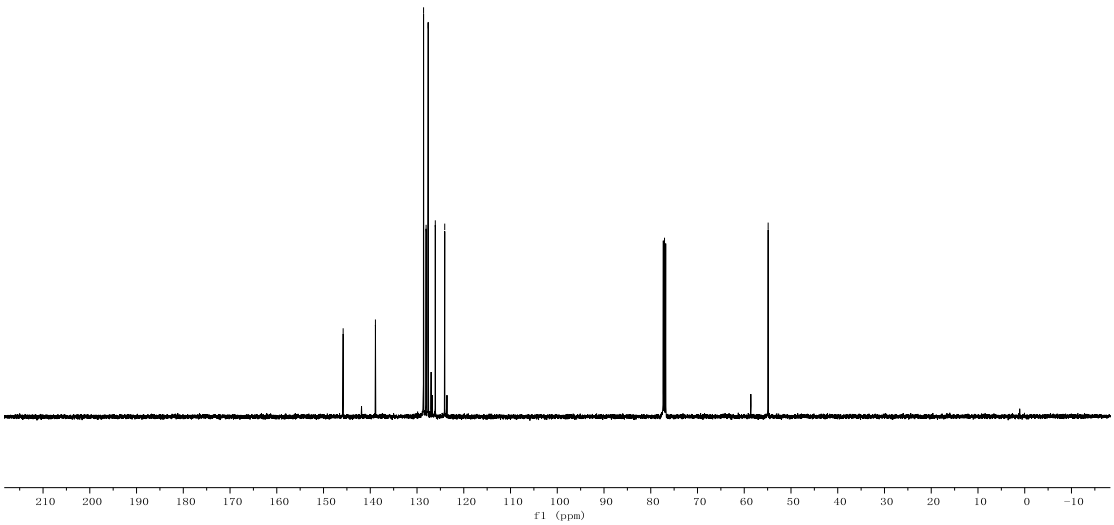
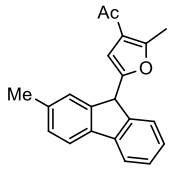
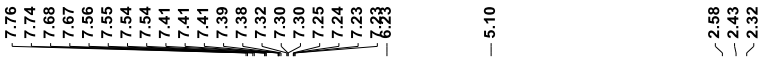
4.00
0.40
f1 (ppm)


145.8
138.9
128.6
128.1
127.6
126.1
124.1
54.9


f1 (ppm)


Ac
O
Me

6a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7.67
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7.54
7.54
7.41
7.41
7.41
7.39
7.38
7.32
7.30
7.30
7.25
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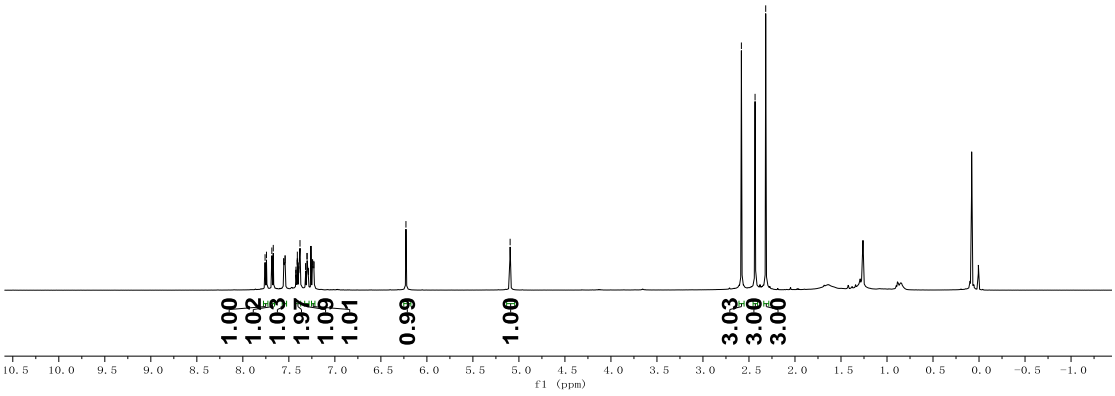
7.23
7.23
6.23
5.10
2.58
2.43
2.32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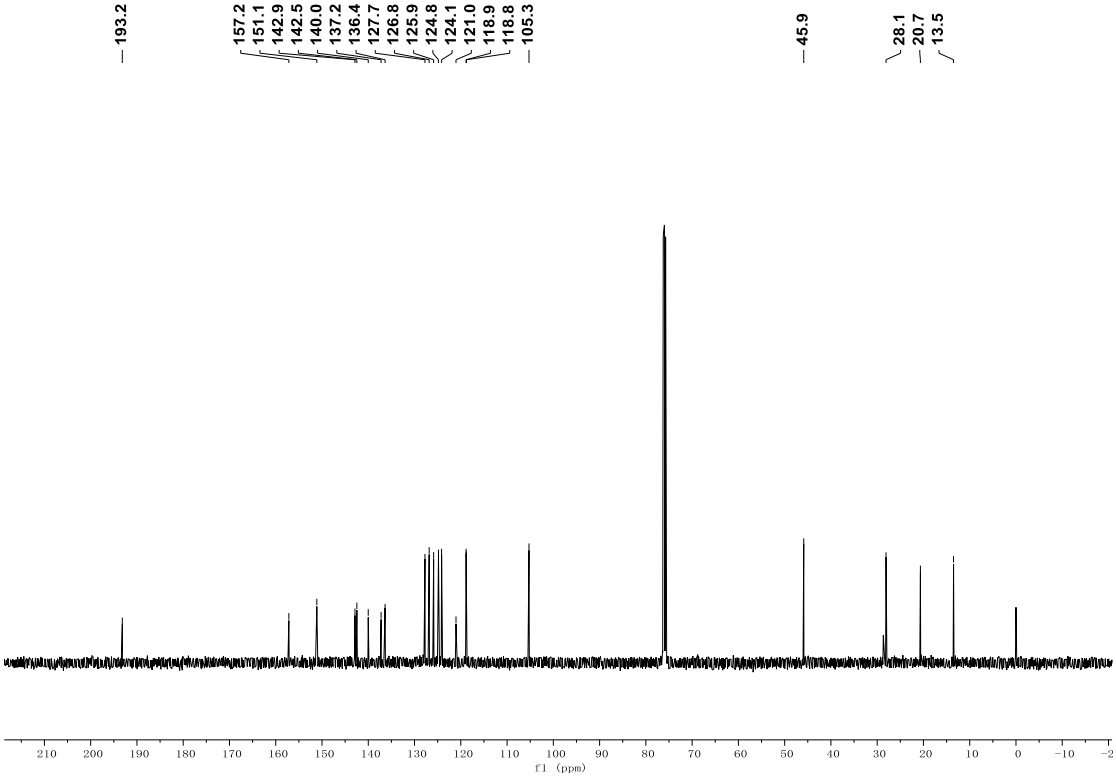
1.01
0.99
1.00
3.03
3.00
3.00
f1 (ppm)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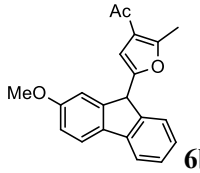
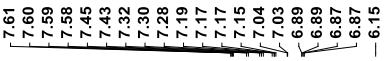
157.2
151.1
142.9
142.5
140.0
137.2
136.4
127.7
126.8
125.9
124.8
124.1
121.0
118.9
118.8
105.3
45.9
28.1
20.7
13.5
f1 (ppm)


Ac
O
MeO

6b


7.61
7.60
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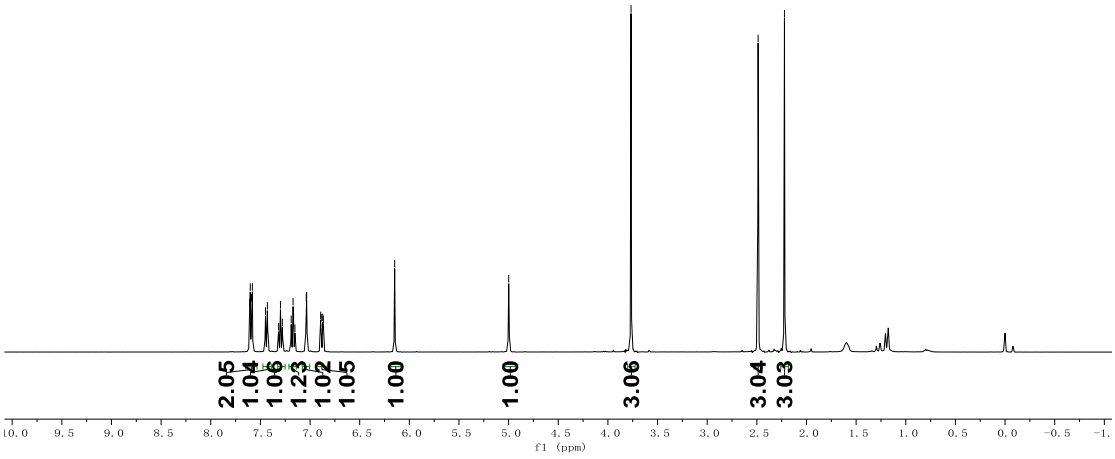
7.58
7.45
7.43
7.32
7.30
7.28
7.19
7.17
7.17
7.15
7.04
7.03
6.89
6.89
6.87
6.87
6.15
5.00
3.77
2.49
2.22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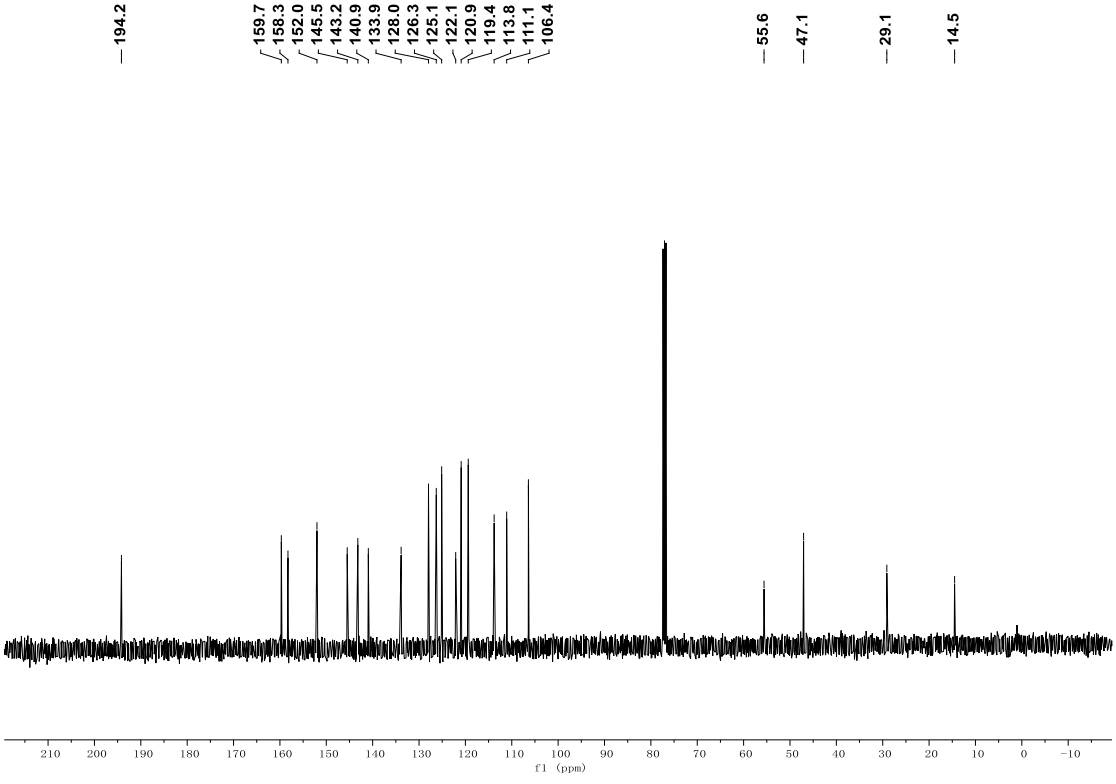
1.23
1.02
1.05
1.00
1.00
3.06
3.04
3.03
f1 (ppm)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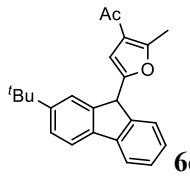
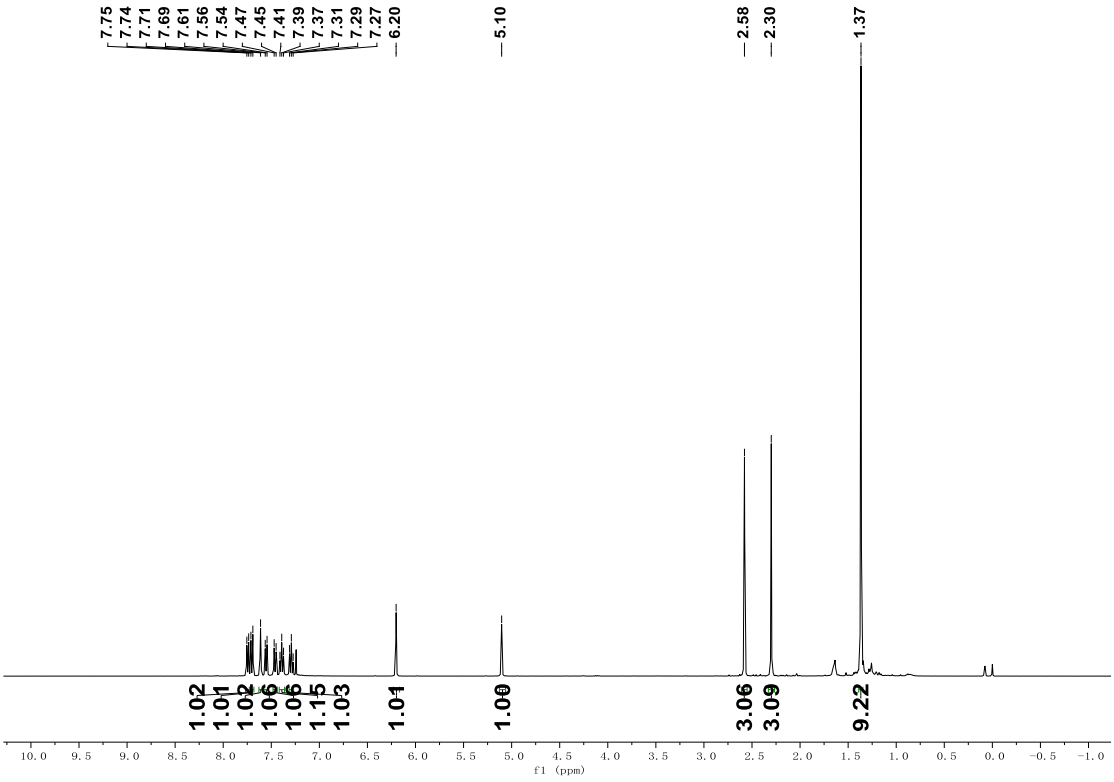
159.7
158.3
152.0
145.5
143.2
140.9
133.9
128.0
126.3
125.1
122.1
120.9
119.4
113.8
111.1
106.4
55.6
47.1
29.1
14.5
f1 (ppm)


Ac
O
tBu

6c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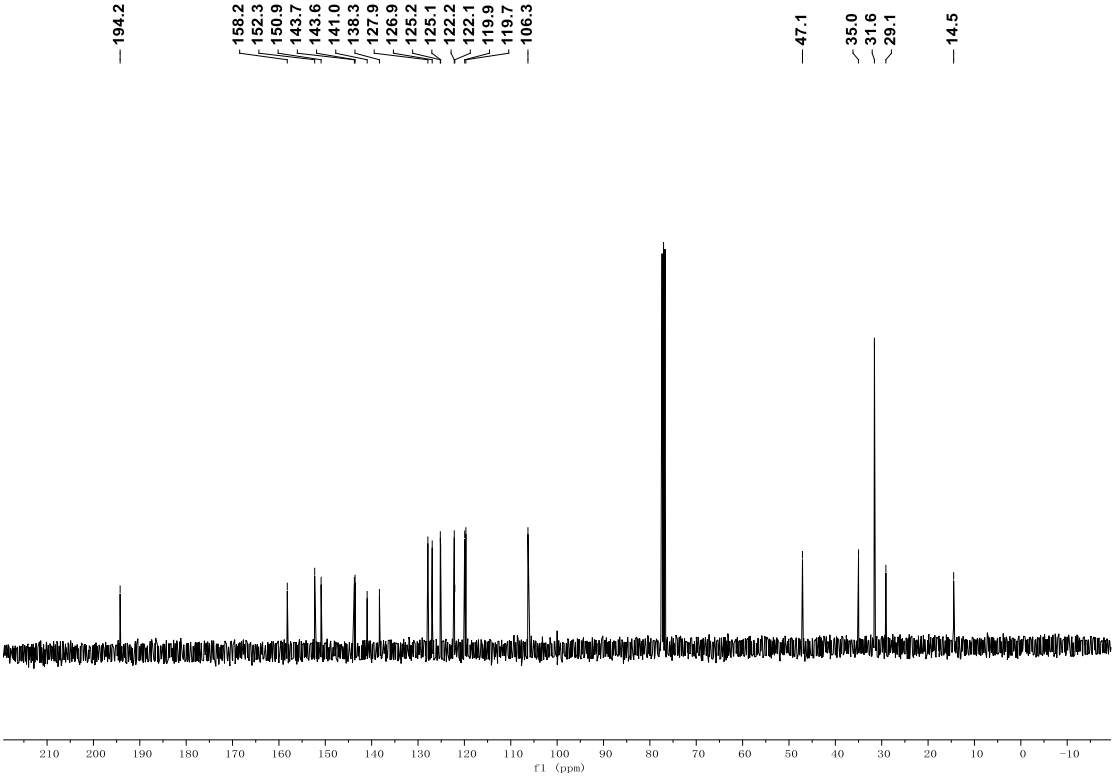
7.39
7.37
7.31
7.29
7.27
6.20
5.10
2.58
2.30
1.37
1.02
1.01
1.02
1.05
1.15
1.03
1.01
1.00
3.06
3.09
9.22
f1 (ppm)


194.2
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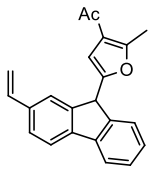
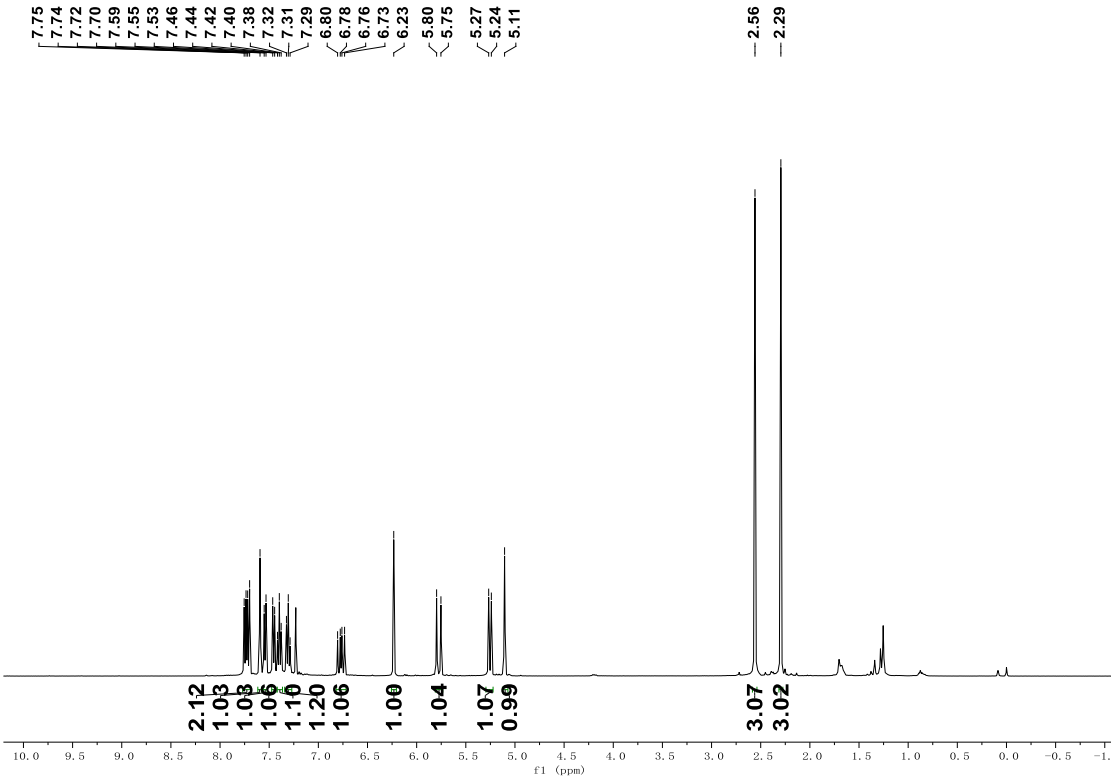
152.3
150.9
143.7
143.6
141.0
138.3
127.9
126.9
125.2
125.1
122.2
122.1
119.9
119.7
106.3
47.1
35.0
31.6
29.1
14.5
f1 (ppm)


Ac
O

6d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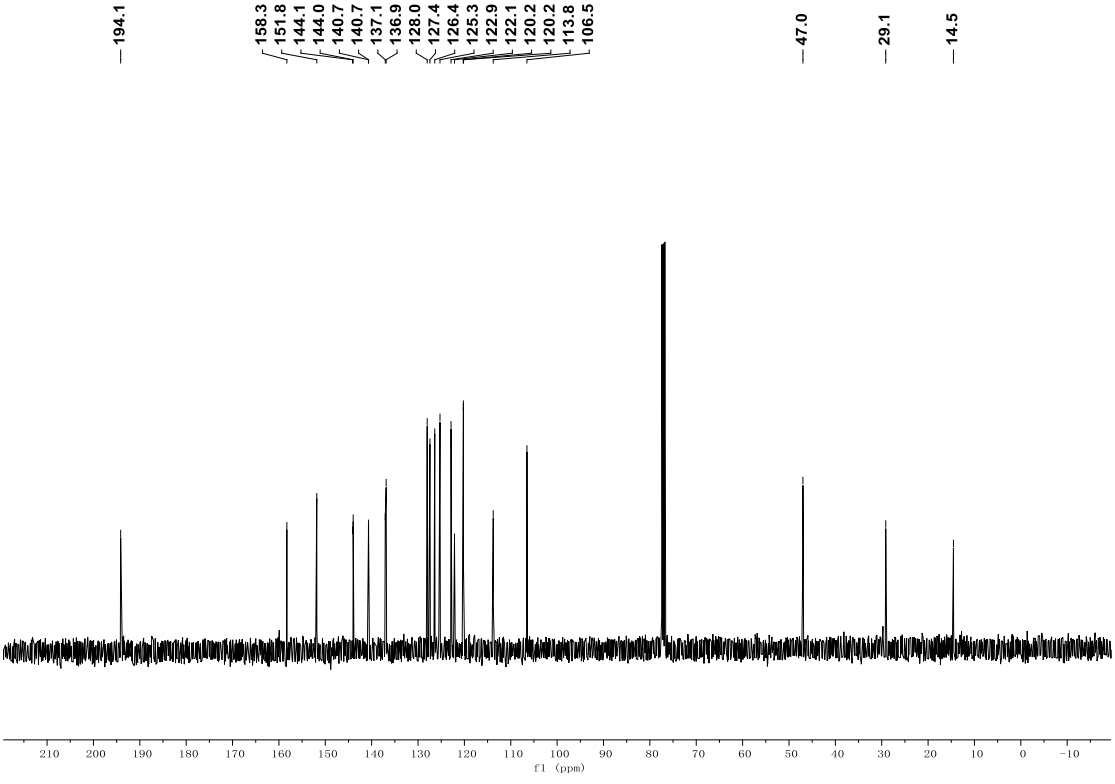
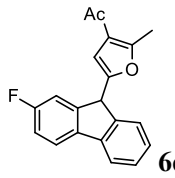
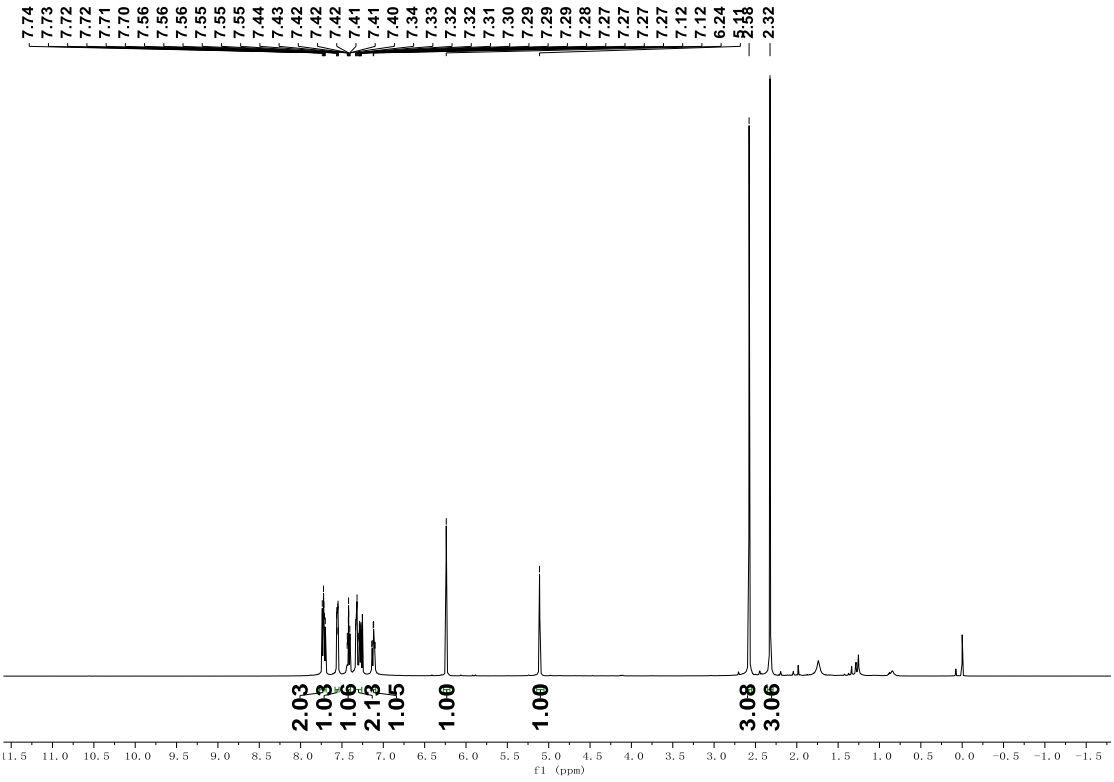
7.42
7.40
7.38
7.32
7.31
7.29
6.80
6.78
6.76
6.73
6.23
5.80
5.75
5.27
5.24
5.11
2.56
2.29
2.12
1.03
1.03
1.06
1.10
1.20
1.06
1.00
1.04
1.07
0.99
3.07
3.02
f1 (ppm)


194.1
158.3
151.8
144.1
144.0
140.7
140.7
137.1
136.9
128.0
127.4
126.4
125.3
122.9
122.1
120.2
120.2
113.8
106.5
47.0
29.1
14.5
f1 (ppm)


Ac
O
F

6e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7.70
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7.56
7.55
7.55
7.55
7.44
7.43
7.42
7.42
7.42
7.41
7.41
7.40
7.34
7.33
7.32
7.32
7.31
7.30
7.29
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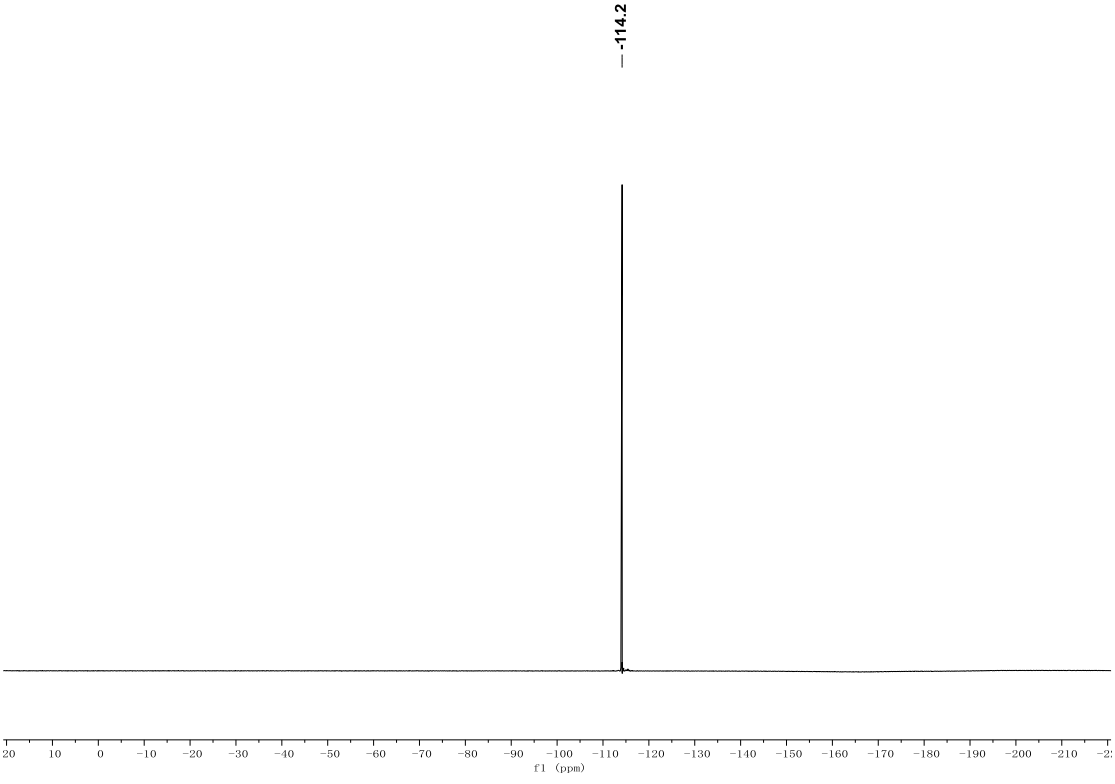
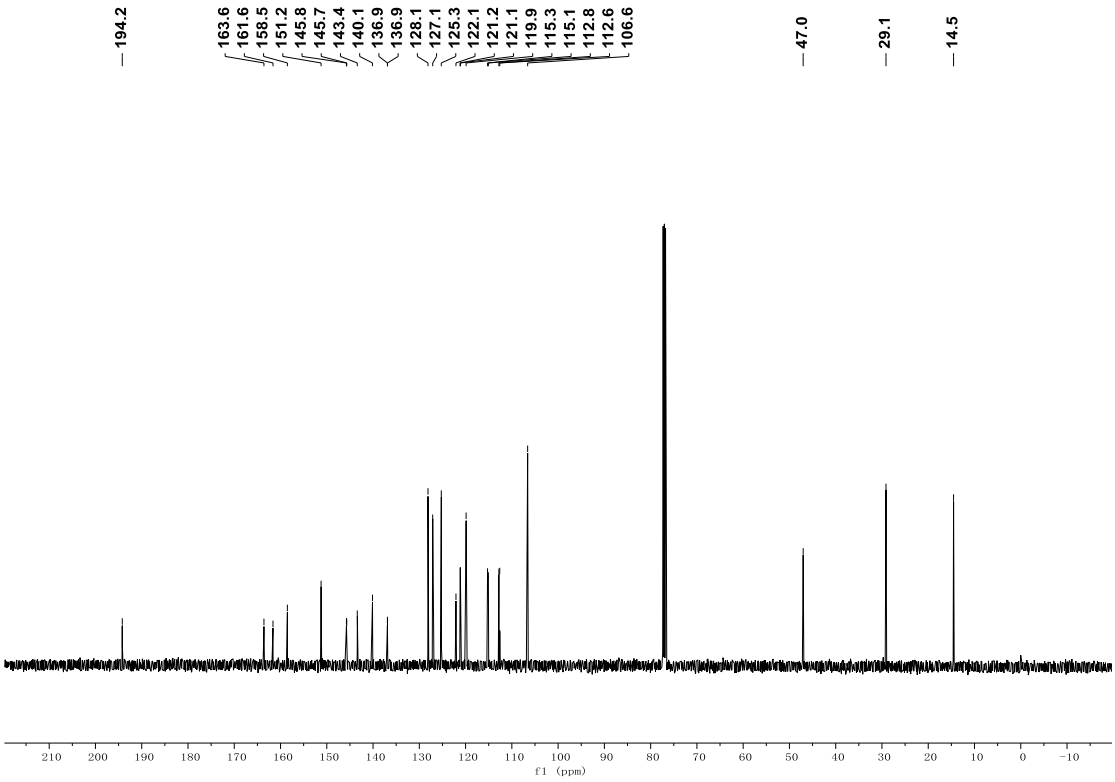
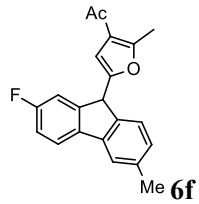
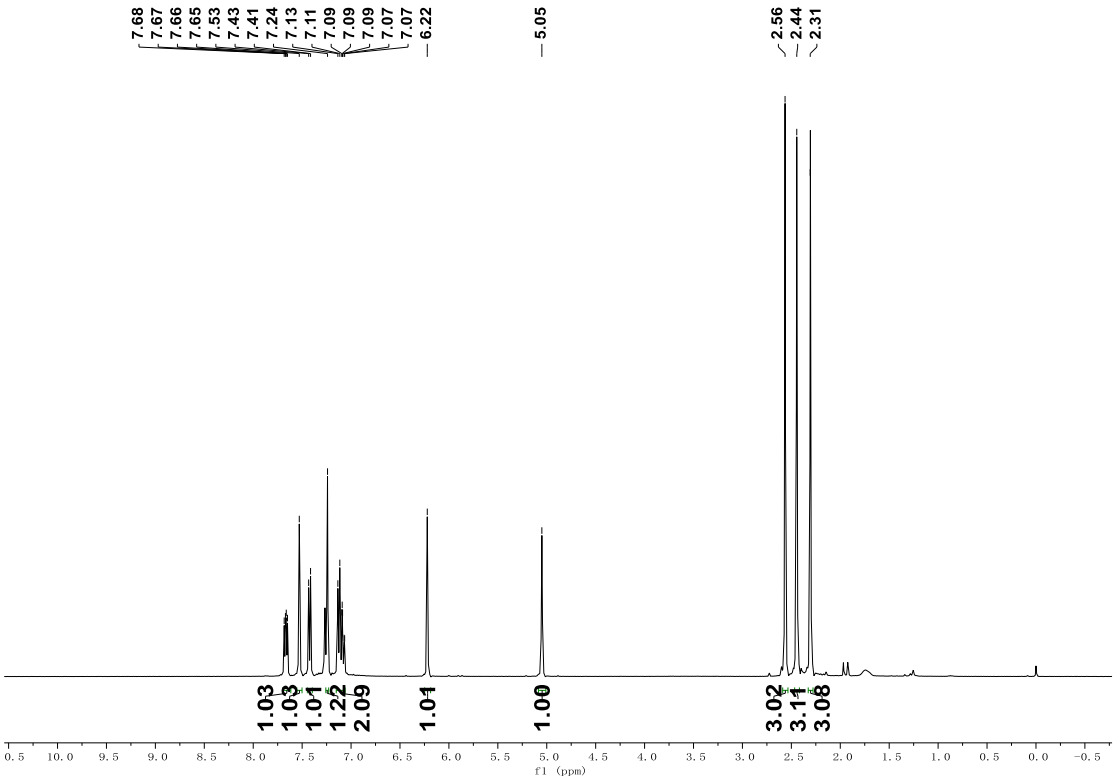
1.00
1.00
3.08
3.06
f1 (ppm)


-114.2
f1 (ppm)


194.2
163.6
161.6
158.5
151.2
145.8
145.7
143.4
140.1
136.9
136.9
128.1
127.1
125.3
122.1
121.2
121.1
119.9
115.3
115.1
112.8
112.6
106.6
47.0
29.1
14.5
f1 (ppm)


Ac
O
F
Me

6f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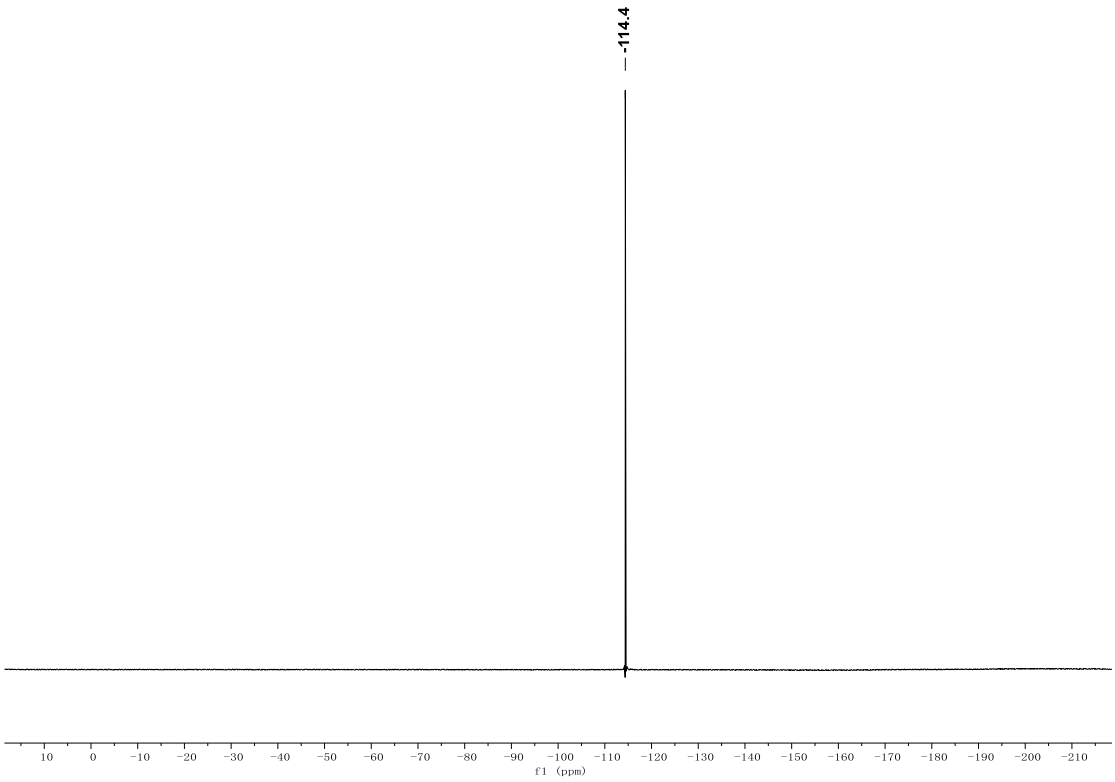
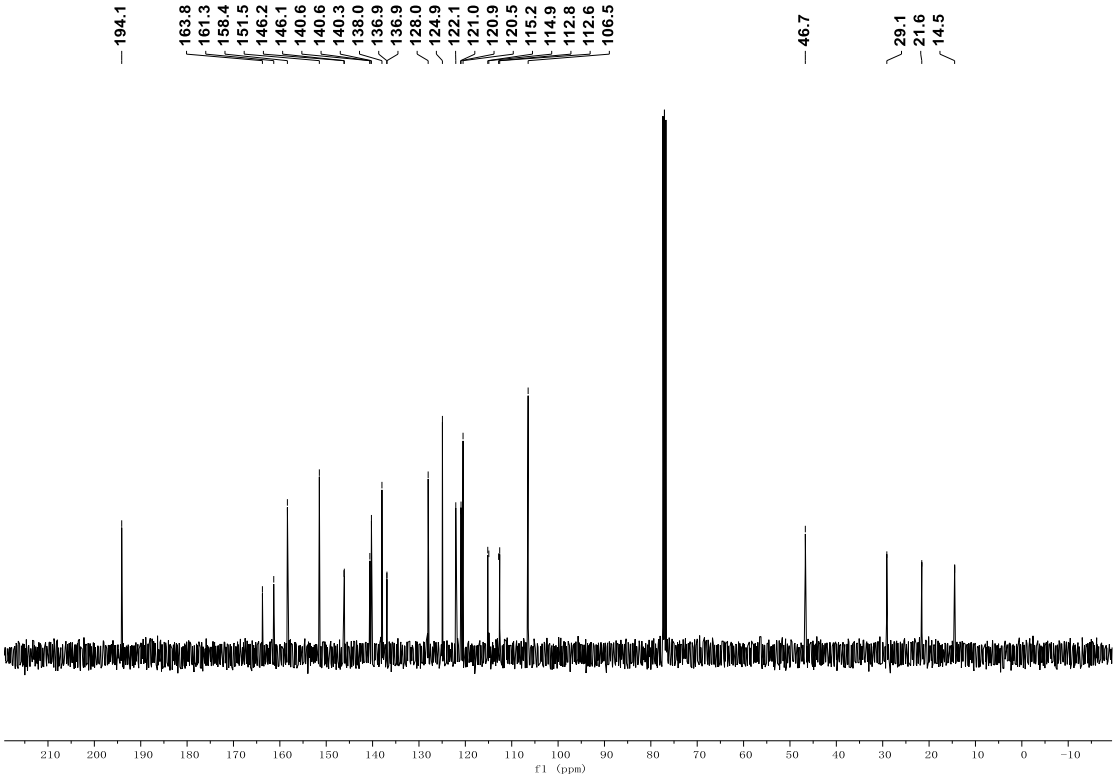
7.43
7.41
7.24
7.13
7.11
7.09
7.09
7.09
7.07
7.07
6.22
5.05
2.56
2.44
2.31
1.03
1.03
1.01
1.22
2.09
1.01
1.00
3.02
3.11
3.08
f1 (ppm)


-114.4
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)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161.3
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146.1
140.6
140.6
140.3
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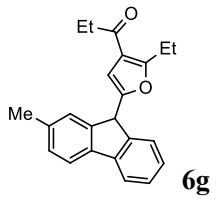
136.9
136.9
128.0
124.9
122.1
121.0
120.9
120.5
115.2
114.9
112.8
112.6
106.5
46.7
29.1
21.6
14.5
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)


Et
O
Et
O
Me

6g


7.62
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7.53
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7.25
7.20
7.18
7.16
7.11
7.09
6.03
4.99
2.96
2.94
2.93
2.91
2.52
2.50
2.48
2.46
2.31
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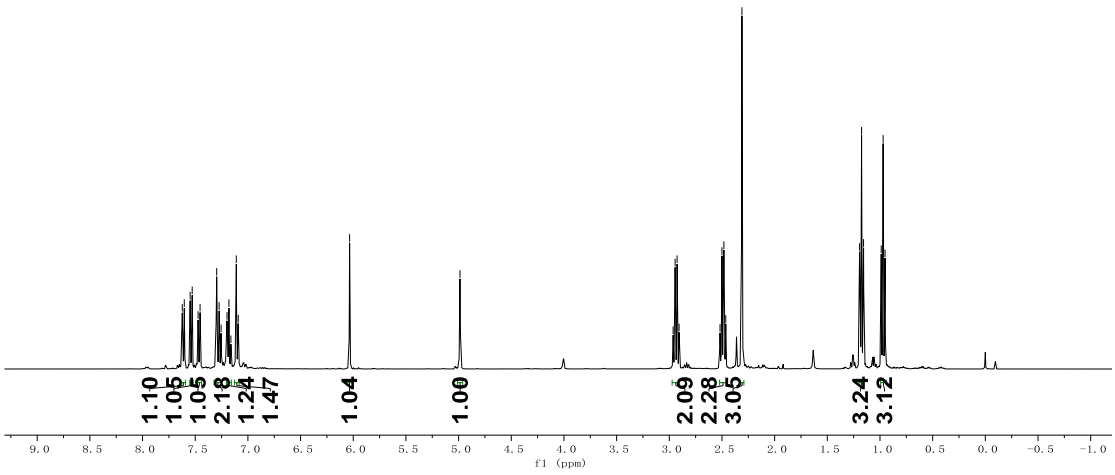
1.17
1.16
0.99
0.97
0.95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2.09
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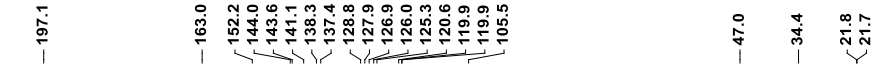
3.24
3.12
f1 (ppm)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152.2
144.0
143.6
141.1
138.3
137.4
128.8
127.9
126.9
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119.9
119.9
105.5
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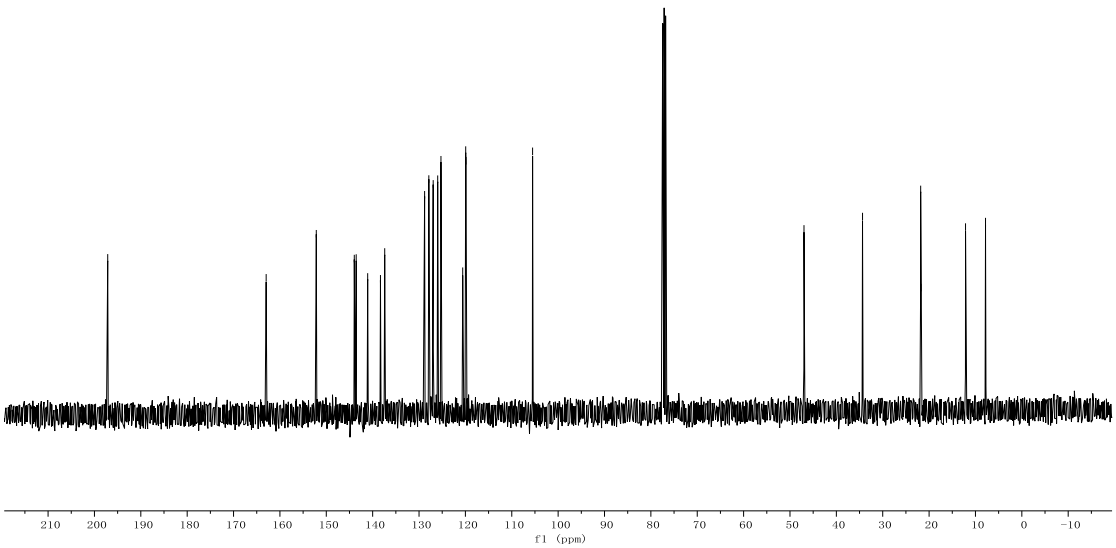
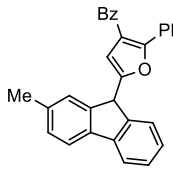
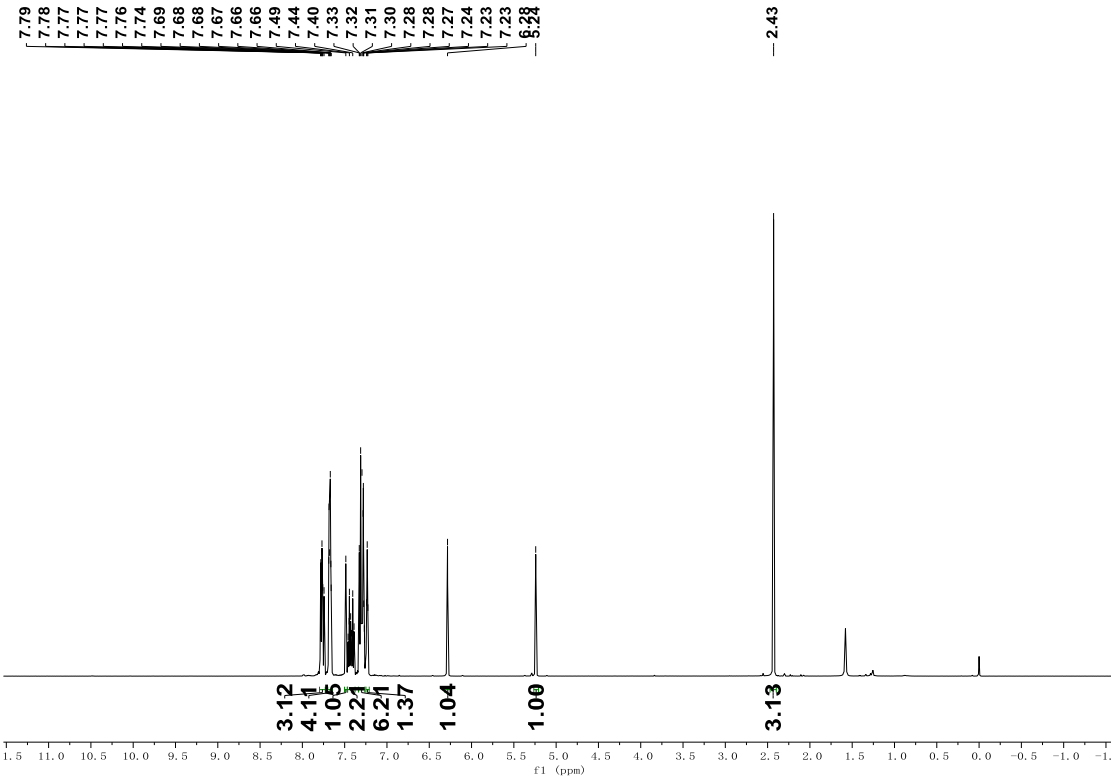
34.4
21.8
21.7
12.1
7.8


f1 (ppm)


Bz
Ph
O
Me

6h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7.24
7.23
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4.11
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2.21
6.21
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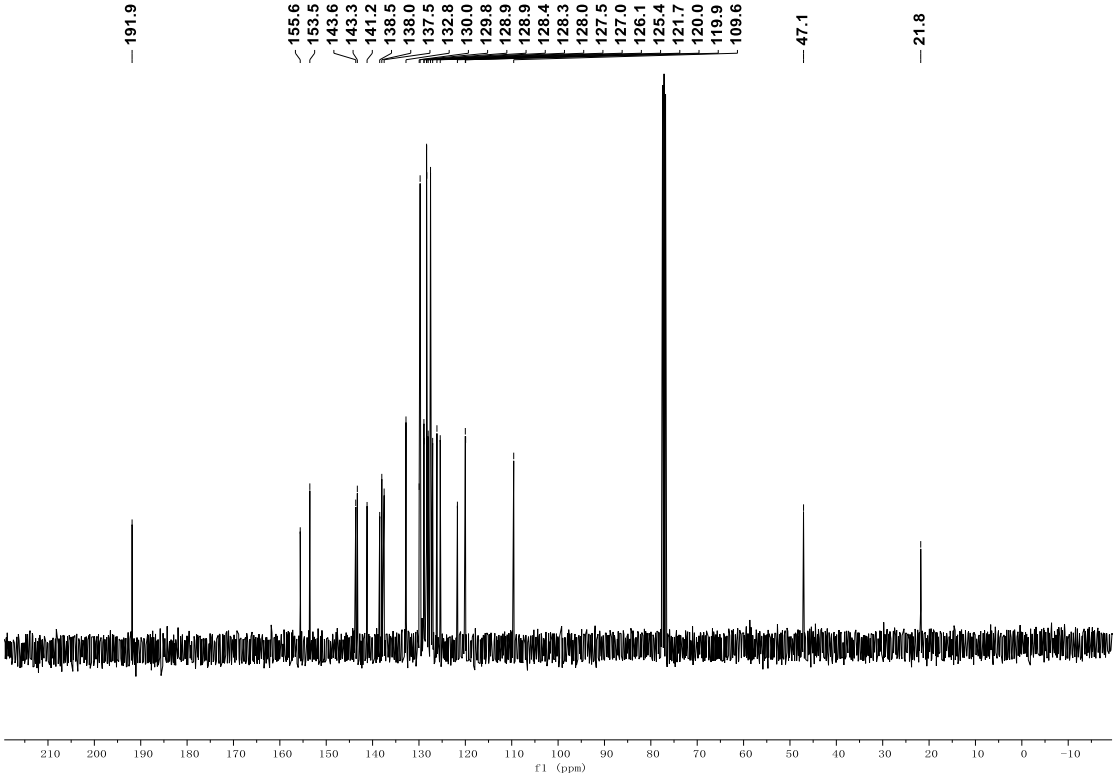
1.04
1.00
3.13
f1 (ppm)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143.6
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132.8
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129.8
128.9
128.9
128.4
128.3
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127.5
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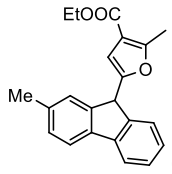
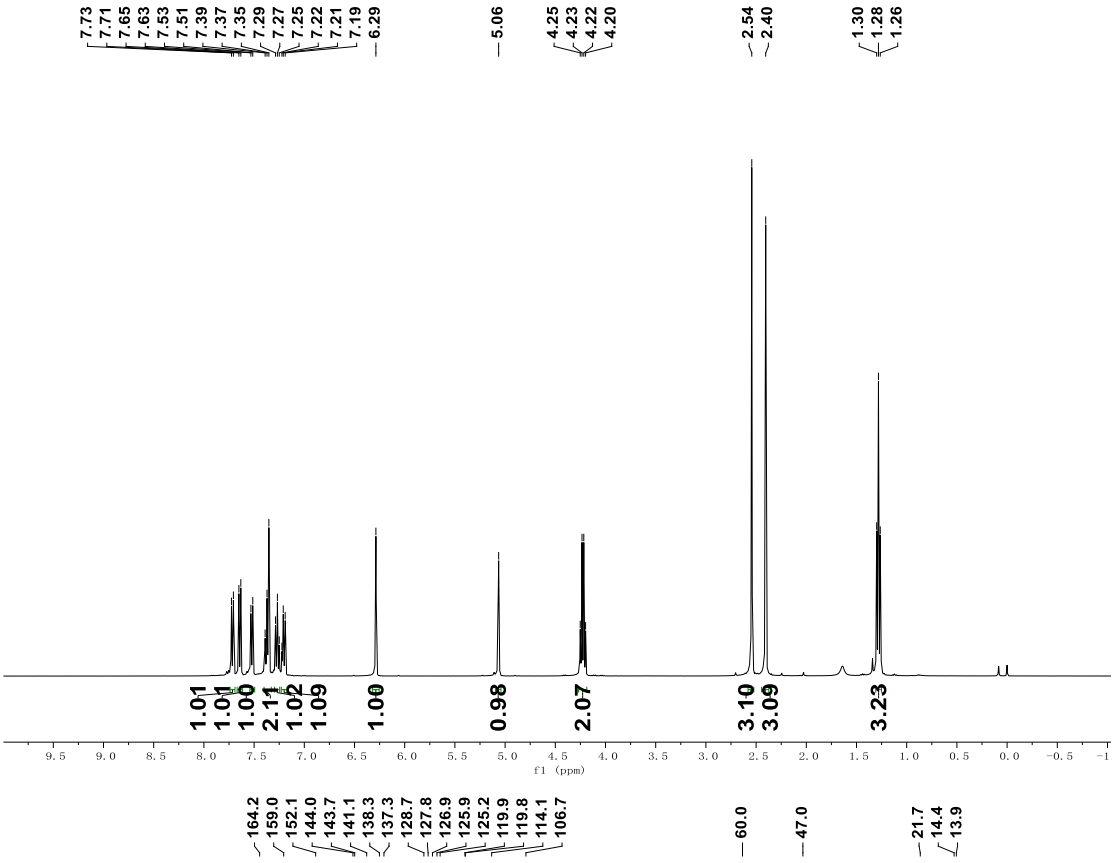
126.1
125.4
121.7
120.0
119.9
109.6
47.1
21.8
f1 (ppm)


EtOOC
Me
O

6i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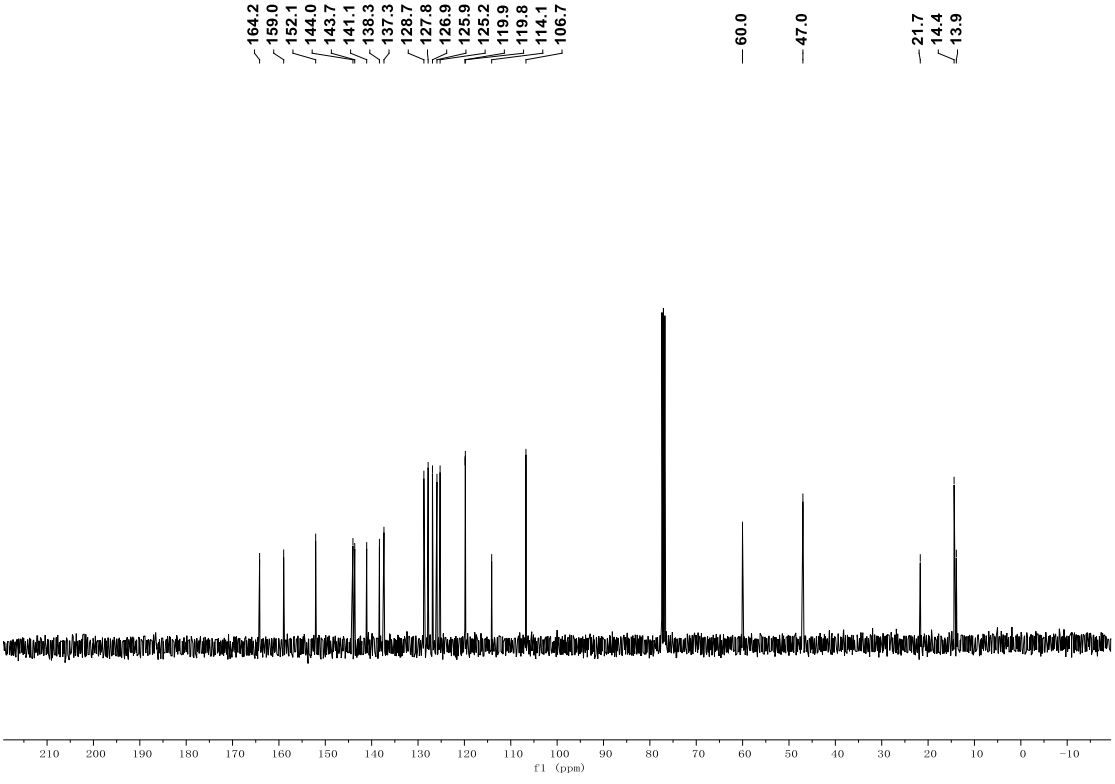
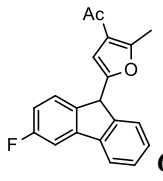
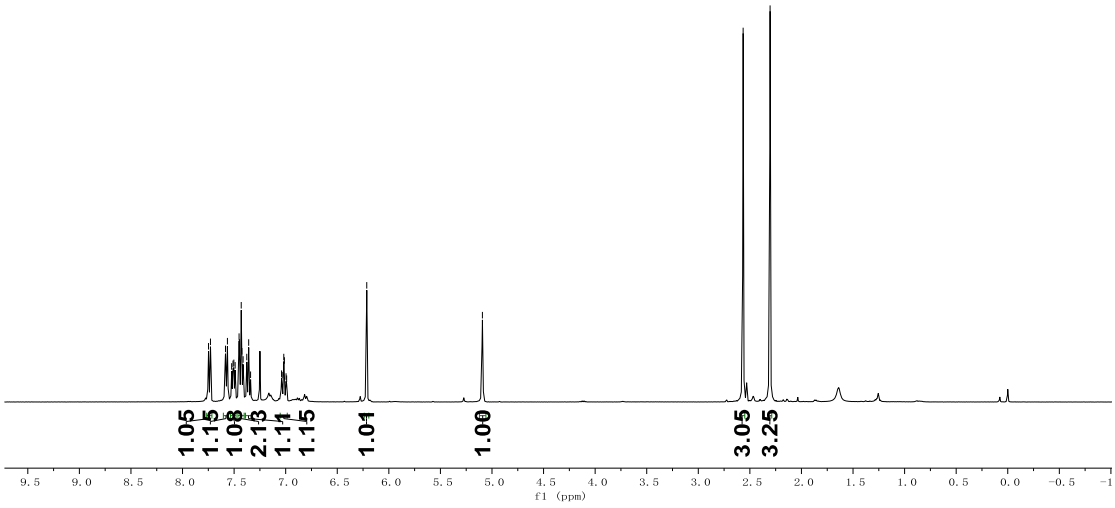
7.63
7.53
7.51
7.39
7.37
7.35
7.29
7.27
7.25
7.22
7.21
7.19
6.29
5.06
4.25
4.23
4.22
4.20
2.54
2.40
1.30
1.28
1.26
1.01
1.01
1.00
2.11
1.02
1.09
1.00
0.98
2.07
3.10
3.09
3.23
f1 (ppm)

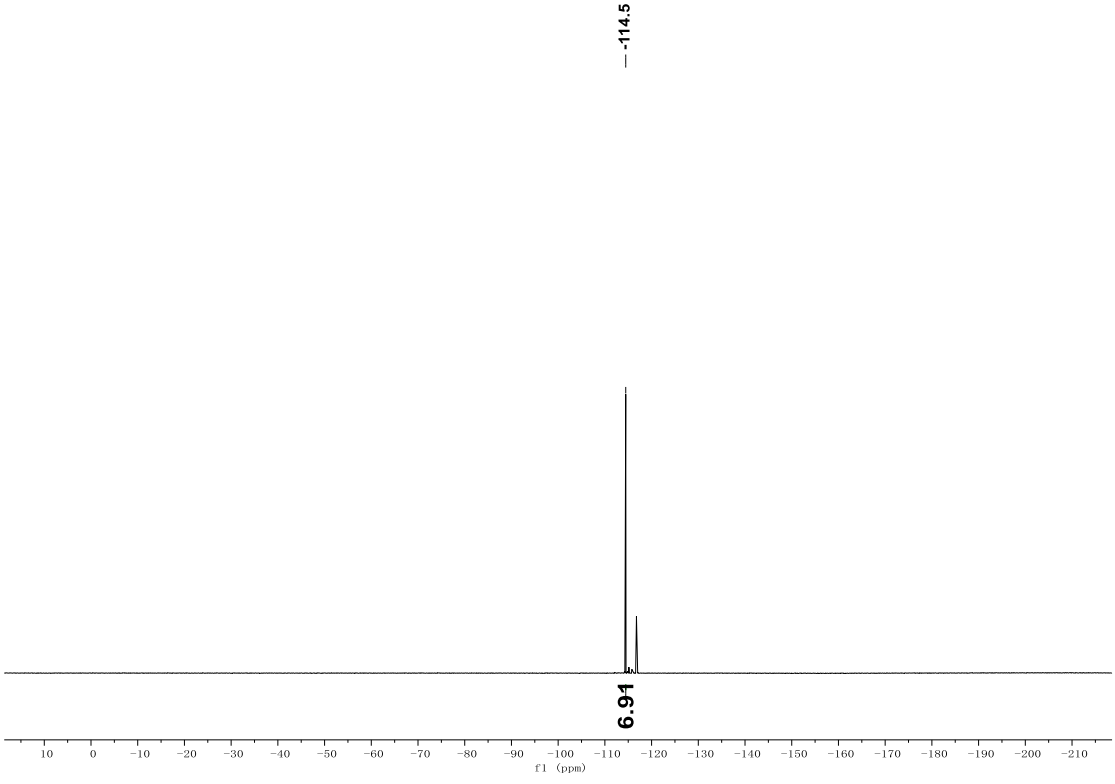

164.2
159.0
152.1
144.0
143.7
141.1
138.3
137.3
128.7
127.8
126.9
125.9
125.2
119.9
119.8
114.1
106.7
60.0
47.0
21.7
14.4
13.9
f1 (ppm)

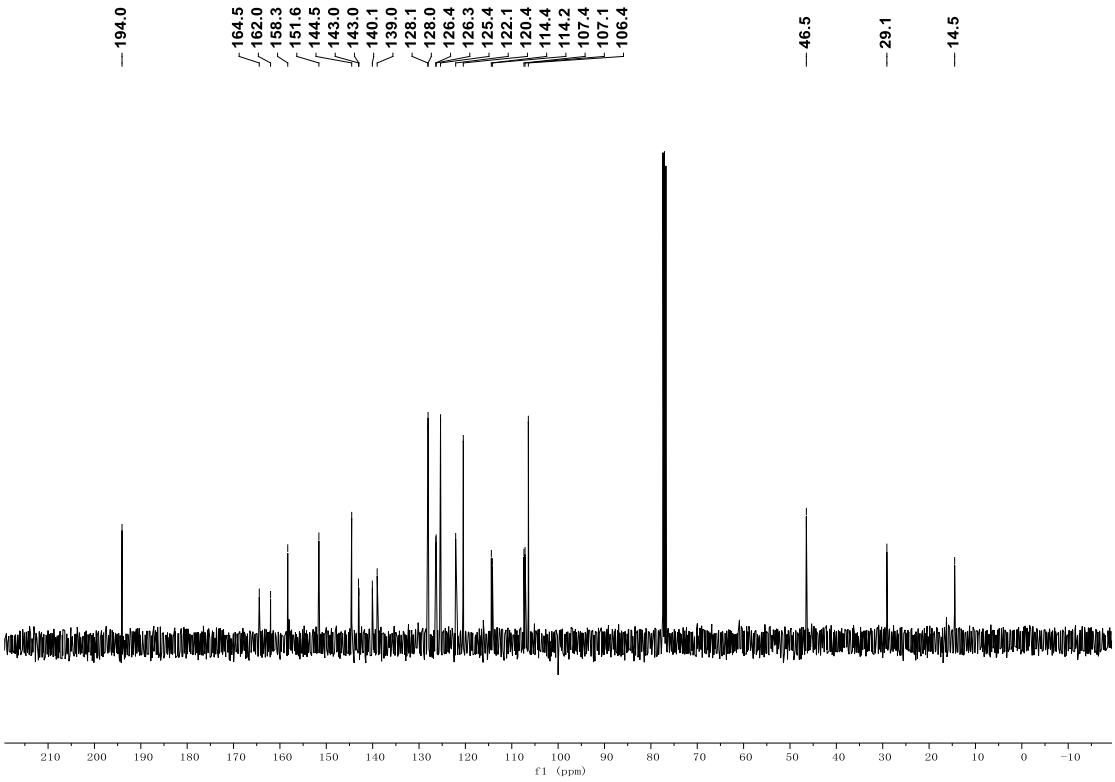

Ac
O
F

6j


7.75
7.73
7.58
7.56
7.52
7.51
7.50
7.49
7.45
7.45
7.43
7.42
7.41
7.38
7.36
7.04
7.02
6.21
5.09
2.57
2.30


1.05
1.15
1.00
2.13
1.11
1.15
1.01
1.00
3.05
3.25
f1 (ppm)


-114.5
6.91
f1 (ppm)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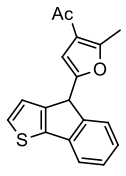
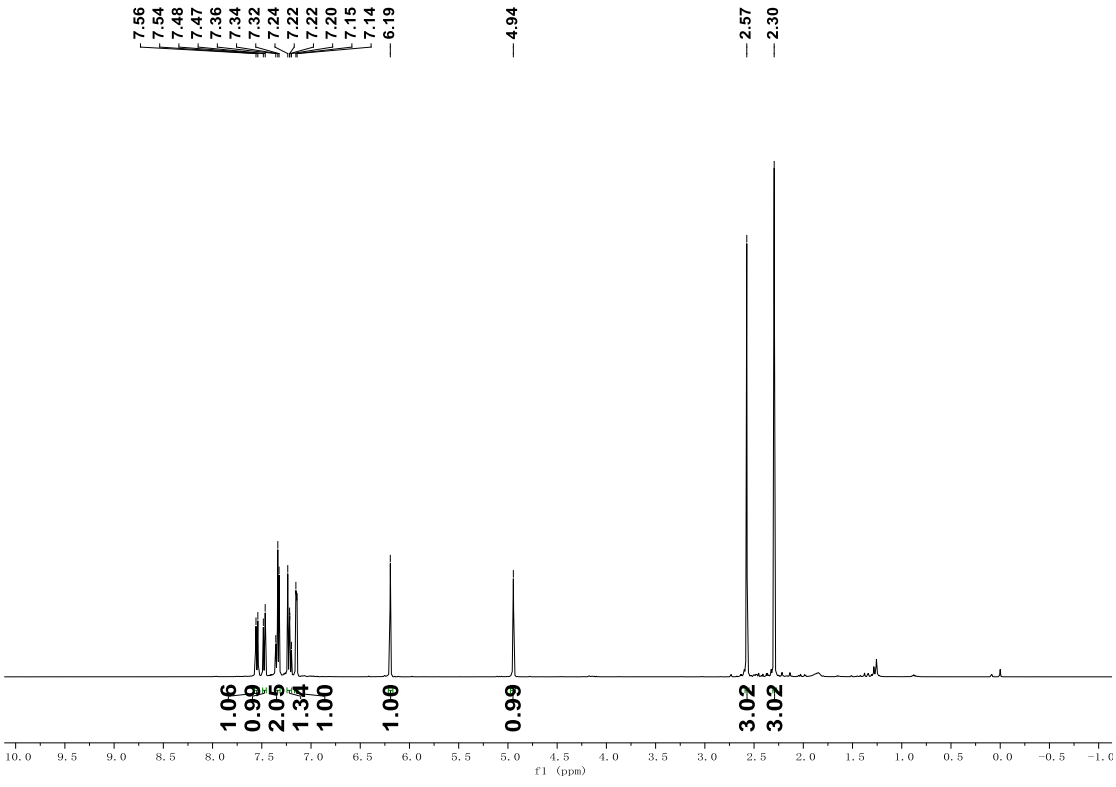
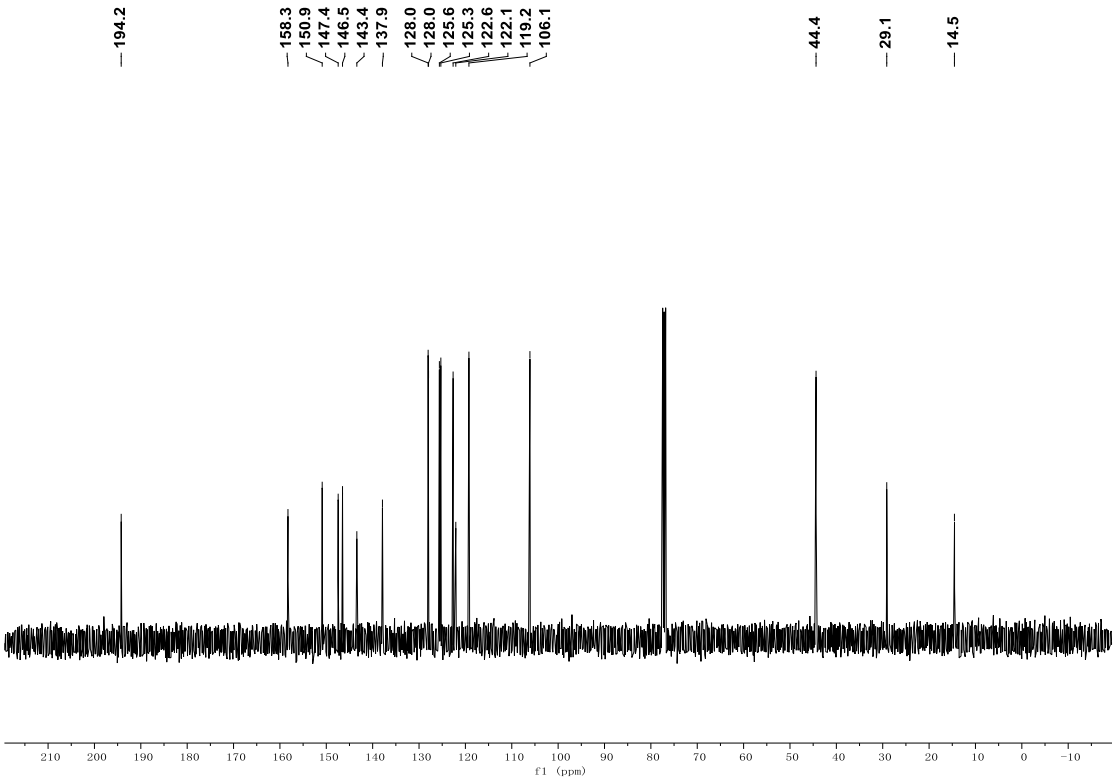
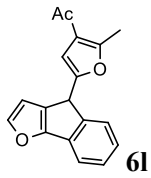
162.0
158.3
151.6
144.5
143.0
143.0
140.1
139.0
128.1
128.0
126.4
126.3
125.4
122.1
120.4
114.4
114.2
107.4
107.1
106.4
46.5
29.1
14.5
f1 (ppm)


Ac
O
S

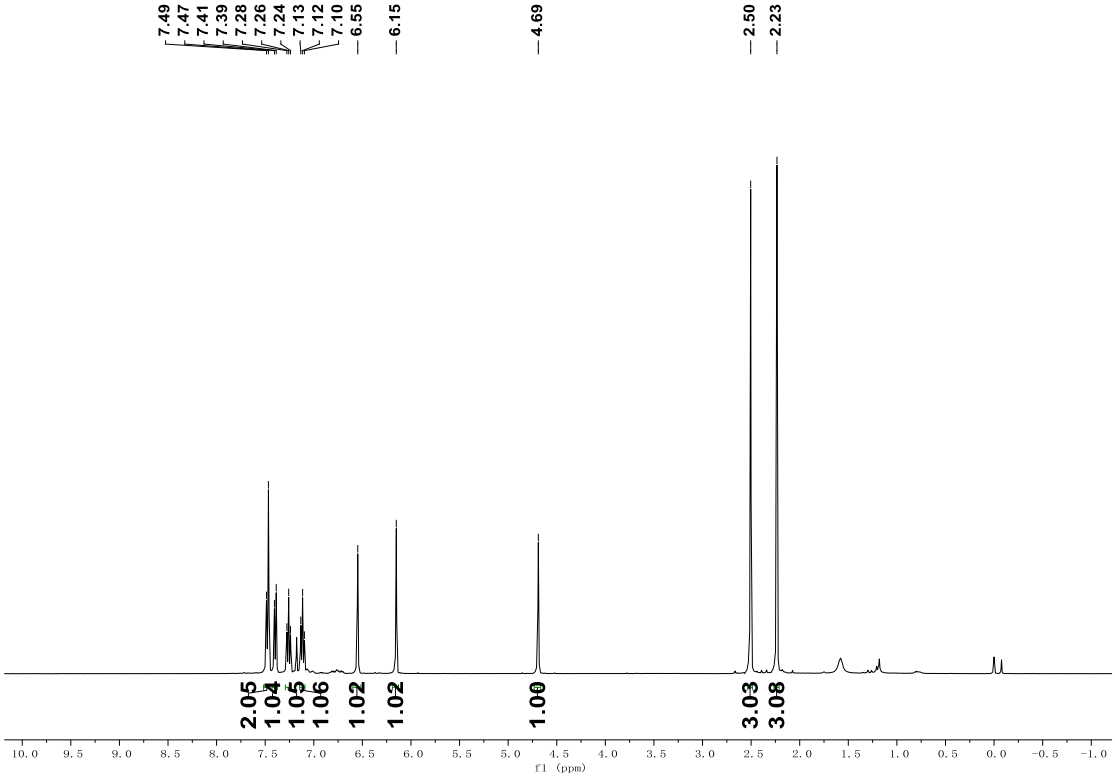
6k

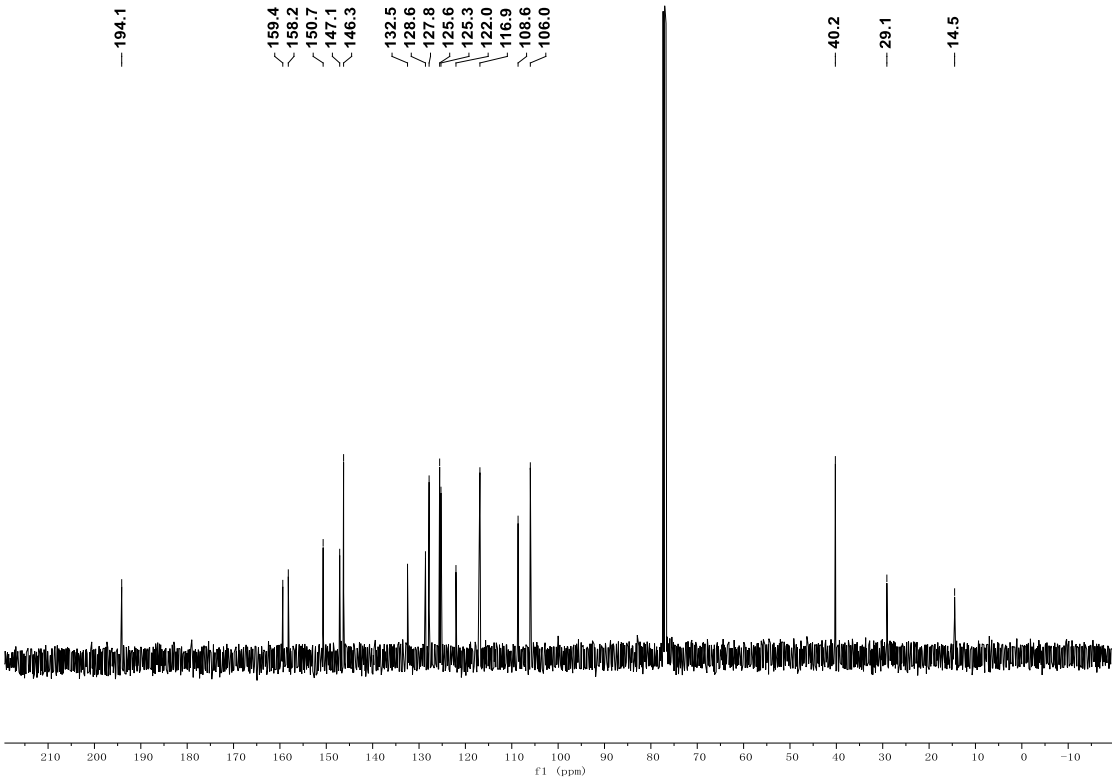

7.56
7.54
7.48
7.47
7.36
7.34
7.32
7.24
7.22
7.22
7.20
7.15
7.14
6.19
4.94
2.57
2.30
1.06
0.99
2.05
1.34
1.00
1.00
0.99
3.02
3.02
f1 (ppm)

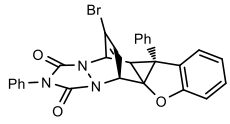

194.2
158.3
150.9
147.4
146.5
143.4
137.9
128.0
128.0
125.6
125.3
122.6
122.1
119.2
106.1
44.4
29.1
14.5
f1 (ppm)


Ac
O
O

6l

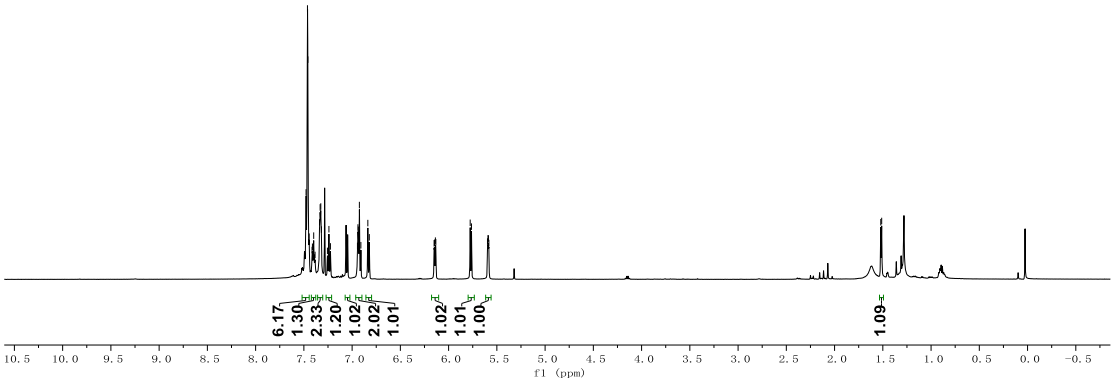

7.49
7.47
7.41
7.39
7.28
7.26
7.24
7.13
7.12
7.10
6.55
6.15
4.69
2.50
2.23
2.05
1.04
1.05
1.06
1.02
1.02
1.00
3.03
3.08
f1 (ppm)

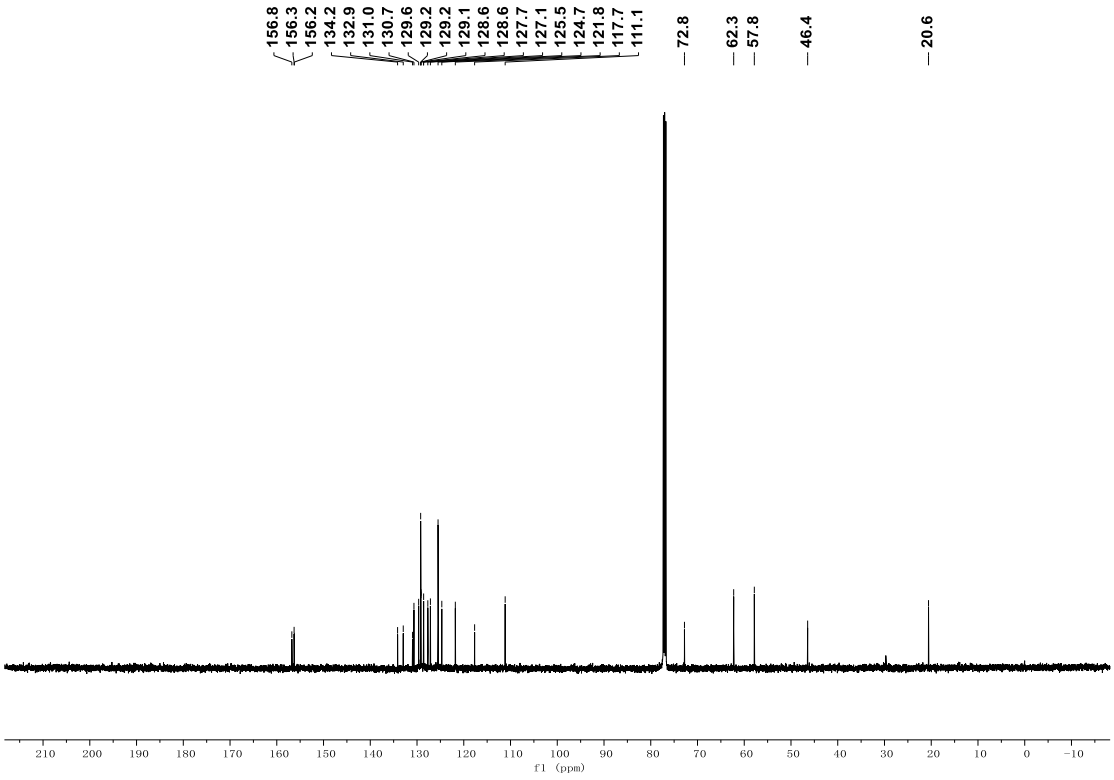

194.1
159.4
158.2
150.7
147.1
146.3
132.5
128.6
127.8
125.6
125.3
122.0
116.9
108.6
106.0
40.2
29.1
14.5
f1 (ppm)

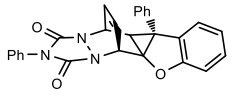

Br
Ph
O
N
Ph
N
O
O

10a

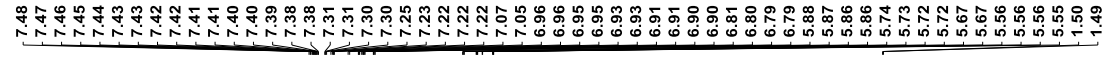

7.48
7.46
7.46
7.45
7.42
7.41
7.40
7.34
7.33
7.32
7.32
7.24
7.22
6.94
6.94
6.92
6.91
6.84
6.82
6.15
6.14
6.13
5.78
5.76
5.60
5.59
5.59
5.58
1.52
1.51


6.17
1.30
2.33
1.20
1.02
2.02
1.01
1.02
1.01
1.00
1.09
f1 (ppm)


156.8
156.3
156.2
134.2
132.9
131.0
130.7
129.6
129.2
129.2
129.1
128.6
128.6
127.7
127.1
125.5
124.7
121.8
117.7
111.1
72.8
62.3
57.8
46.4
20.6
f1 (ppm)


O
N
Ph
N
N
O
Ph
O

10b


7.48
7.47
7.46
7.45
7.44
7.43
7.43
7.42
7.42
7.41
7.41
7.40
7.40
7.39
7.38
7.38
7.31
7.31
7.30
7.30
7.25
7.23
7.22
7.22
7.22
7.07
7.05
6.96
6.96
6.95
6.95
6.93
6.93
6.91
6.91
6.90
6.90
6.81
6.80
6.79
6.79
5.88
5.87
5.86
5.86
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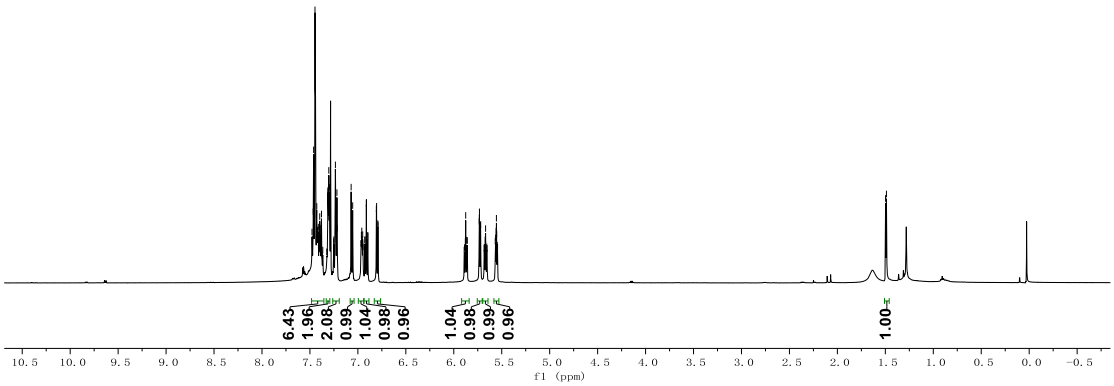
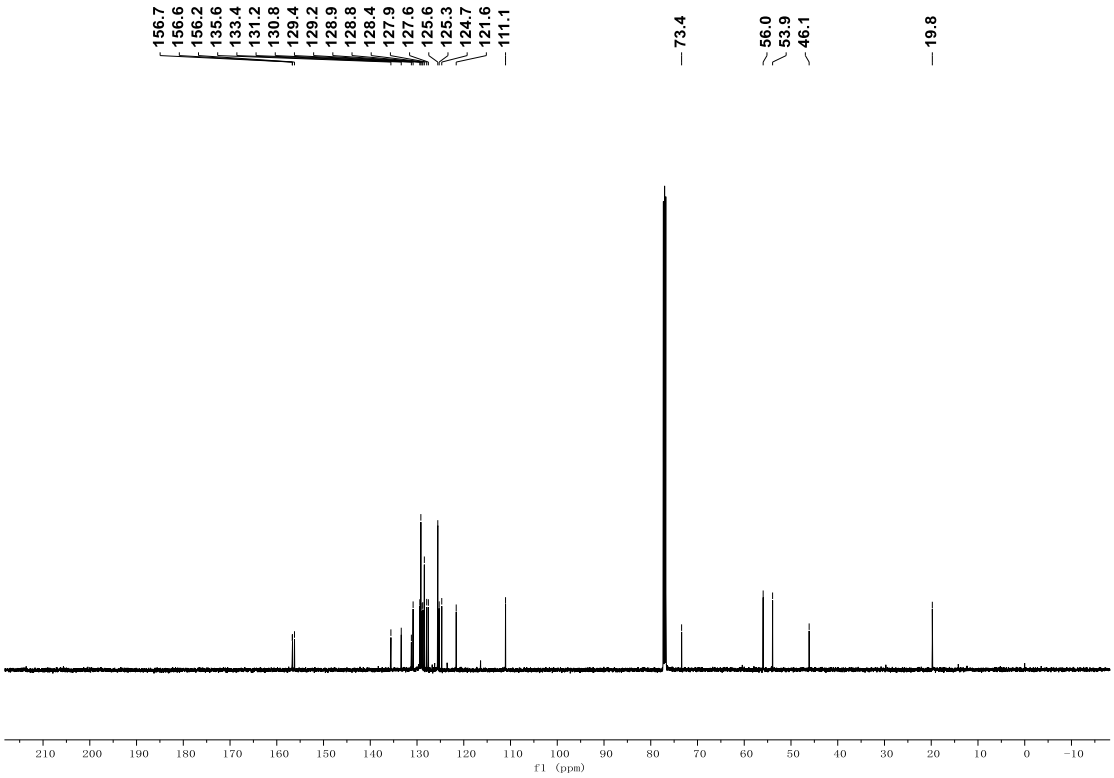
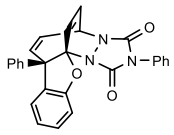
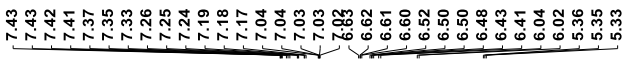
5.56
5.56
5.56
5.55
1.50
1.49

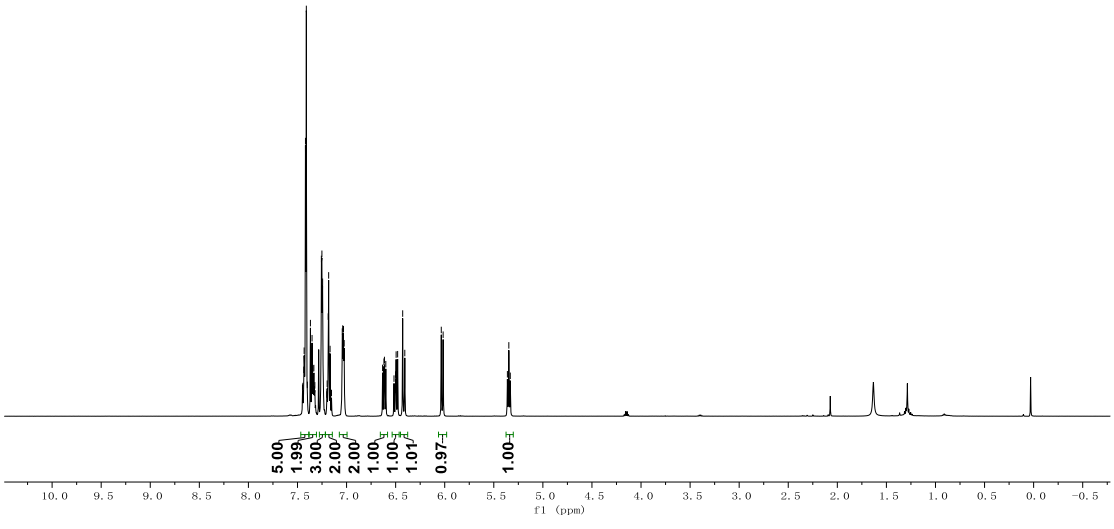

6.43
1.96
2.08
0.99
1.04
0.98
0.96
1.04
0.98
0.99
0.96
1.00
f1 (ppm)

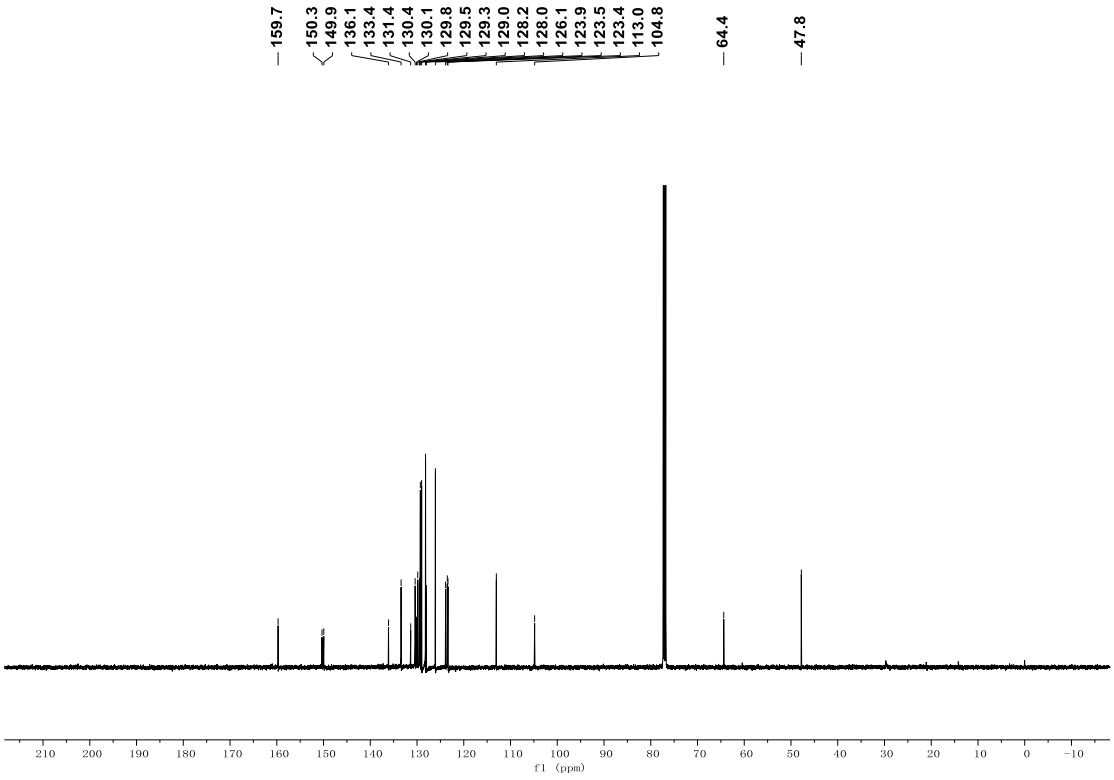

156.7
156.6
156.2
135.6
133.4
131.2
130.8
129.4
129.2
128.9
128.8
128.4
127.9
127.6
125.6
125.3
124.7
121.6
111.1
73.4
56.0
53.9
46.1
19.8
f1 (ppm)

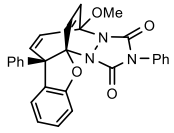

Ph
N
O
N
N
Ph
O
O

11a

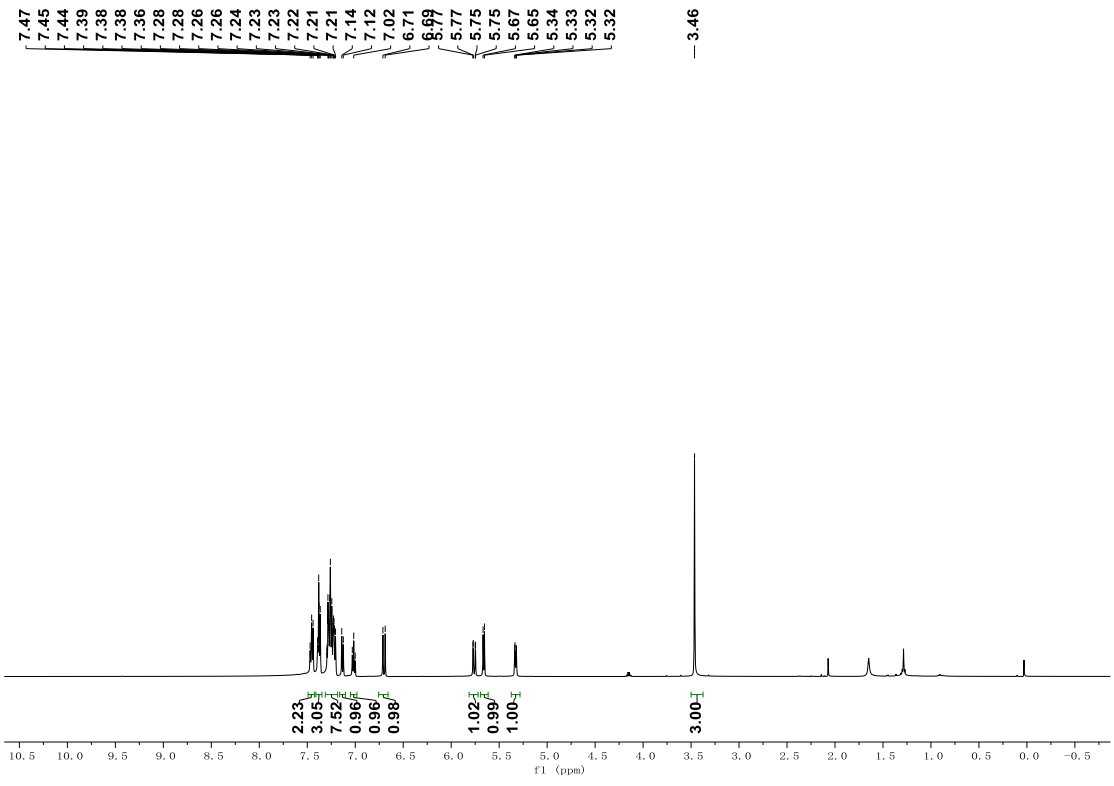

7.43
7.43
7.42
7.41
7.37
7.35
7.33
7.26
7.25
7.24
7.19
7.18
7.17
7.04
7.04
7.03
7.03
7.02
6.63
6.62
6.61
6.60
6.52
6.50
6.50
6.48
6.43
6.41
6.04
6.02
5.36
5.35
5.33

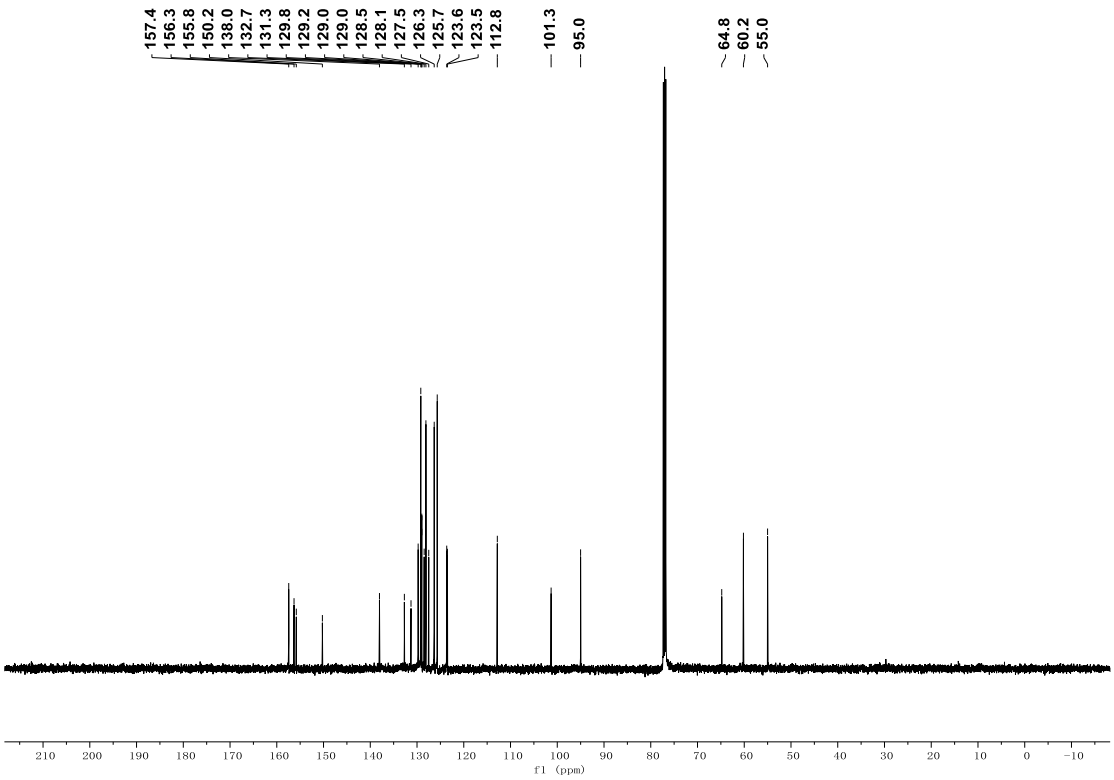

5.00
1.99
3.00
2.00
2.00
1.00
1.00
1.01
0.97
1.00
f1 (ppm)

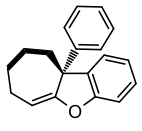

159.7
150.3
149.9
136.1
133.4
131.4
130.4
130.1
129.8
129.5
129.3
129.0
128.2
128.0
126.1
123.9
123.5
123.4
113.0
104.8
64.4
47.8
f1 (ppm)


OMe
Ph
N
O
N
N
Ph
O
O

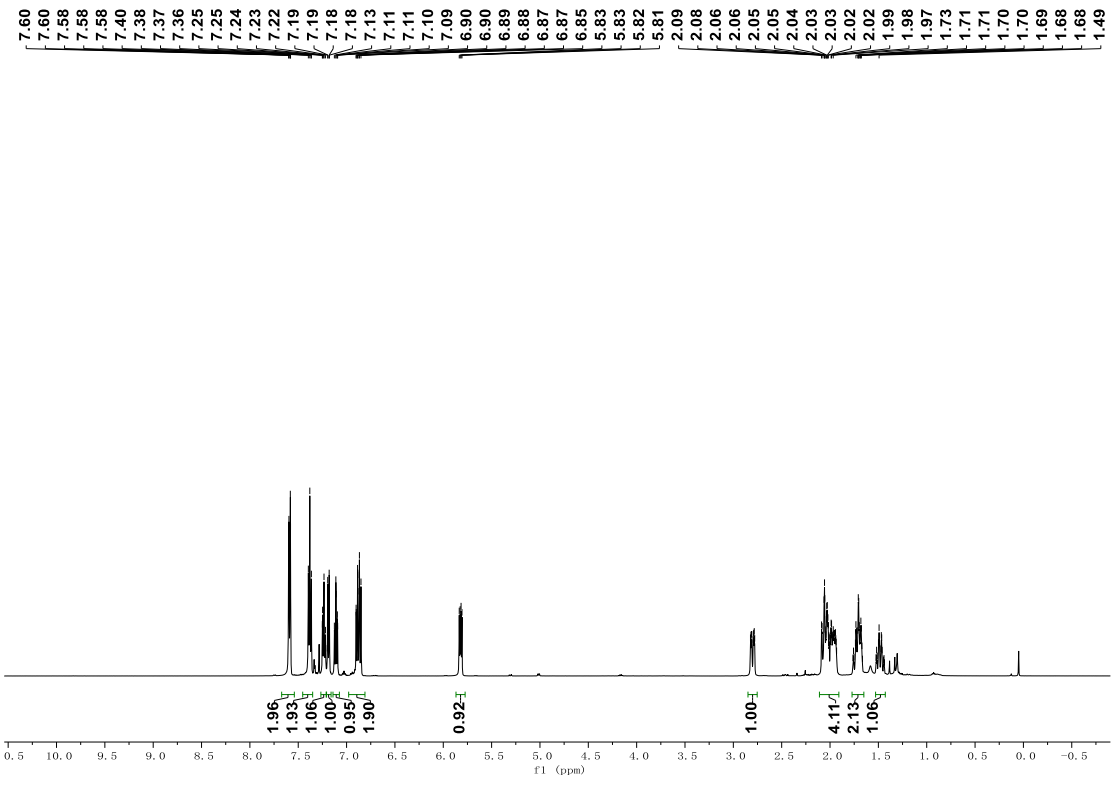
11b

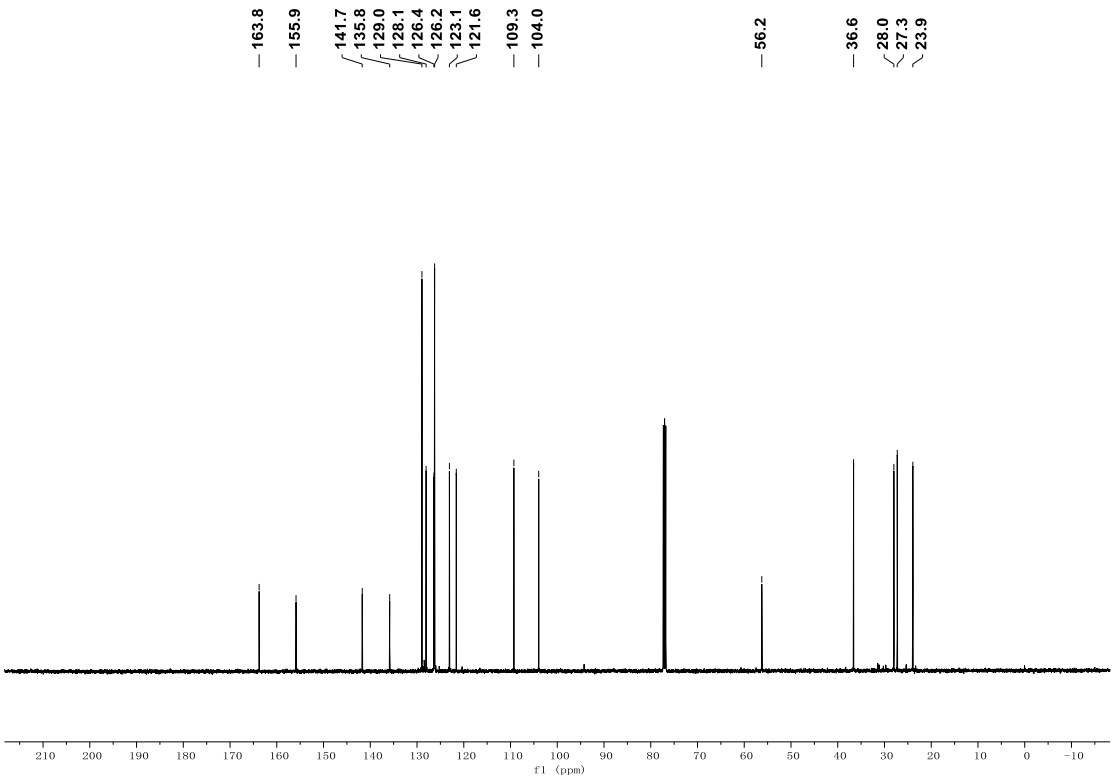

7.47
7.45
7.44
7.39
7.38
7.38
7.36
7.28
7.28
7.26
7.26
7.24
7.23
7.23
7.22
7.21
7.21
7.14
7.12
7.02
6.71
6.69
5.77
5.77
5.75
5.75
5.67
5.65
5.34
5.33
5.32
5.32
3.46
2.23
3.05
7.52
0.96
0.96
0.98
1.02
0.99
1.00
3.00
f1 (ppm)


157.4
156.3
155.8
150.2
138.0
132.7
131.3
129.8
129.2
129.0
129.0
128.5
128.1
127.5
126.3
125.7
123.6
123.5
112.8
101.3
95.0
64.8
60.2
55.0
f1 (ppm)

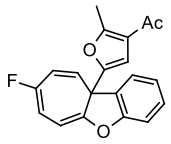


12

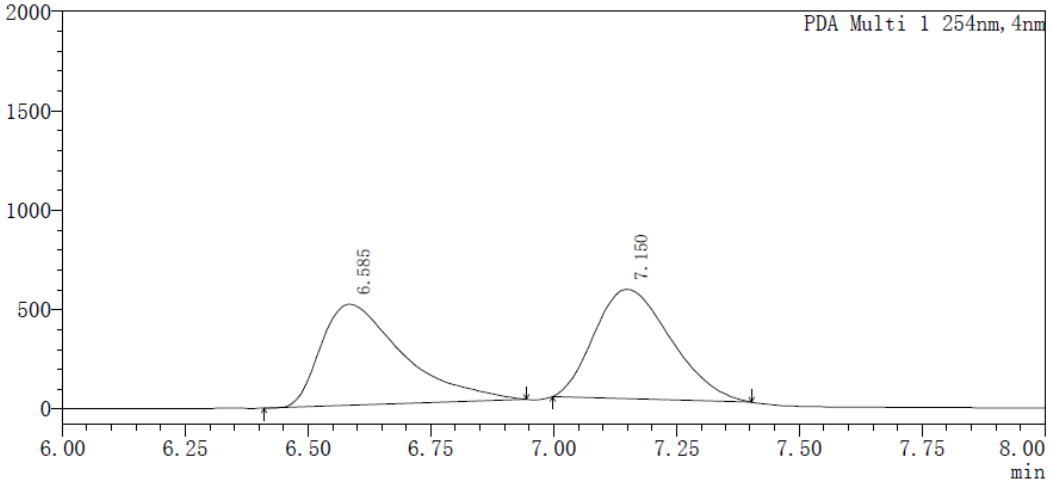

7.60
7.60
7.58
7.58
7.58
7.40
7.38
7.37
7.36
7.25
7.25
7.24
7.23
7.22
7.19
7.19
7.18
7.18
7.13
7.11
7.11
7.10
7.09
6.90
6.90
6.89
6.88
6.87
6.87
6.85
5.83
5.83
5.82
5.81
2.09
2.08
2.06
2.06
2.05
2.05
2.04
2.03
2.03
2.02
2.02
1.99
1.98
1.97
1.73
1.71
1.71
1.70
1.70
1.69
1.68
1.68
1.49
1.96
1.93
1.06
1.00
0.95
1.90
0.92
1.00
4.11
2.13
1.06
f1 (ppm)


163.8
155.9
141.7
135.8
129.0
128.1
126.4
126.2
123.1
121.6
109.3
104.0
56.2
36.6
28.0
27.3
23.9
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)

20. Data of HPLC



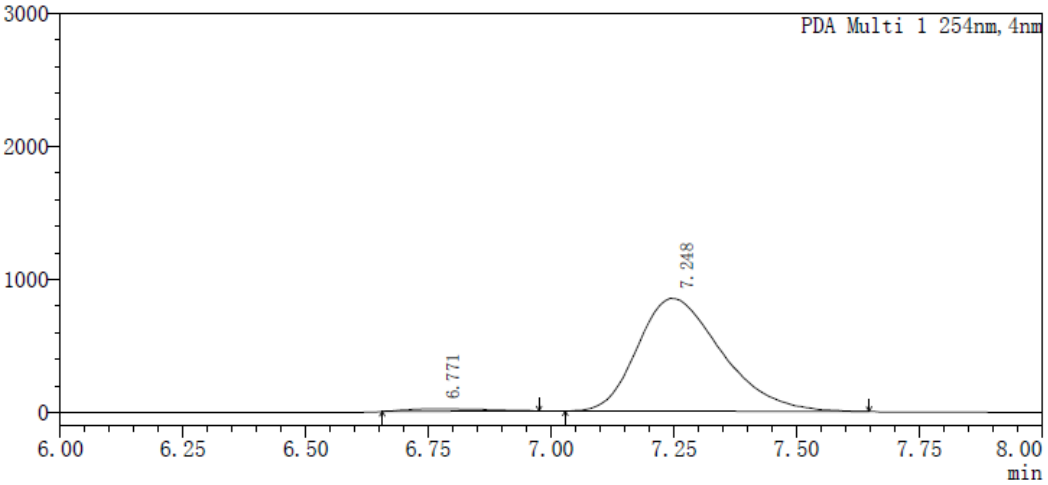
2a



〈峰表〉

PDA Ch1 254nm

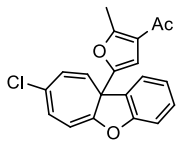
峰号	保留时间	面积	高度	化合物名	面积%	高度%
1	6.585	5924618	508908		49.816	48.014
2	7.150	5968344	551000		50.184	51.986
总计		11892962	1059908		100.000	100.000



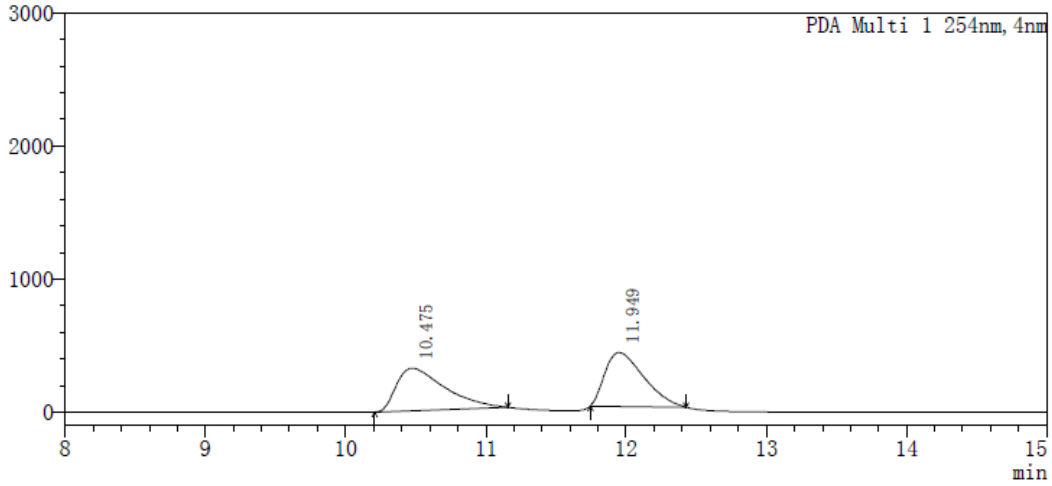
〈峰表〉

PDA Ch1 254nm

峰号	保留时间	面积	高度	化合物名	面积%	高度%
1	6.771	202297	18612		1.964	2.152
2	7.248	10096260	846142		98.036	97.848
总计		10298557	864754		100.000	100.000



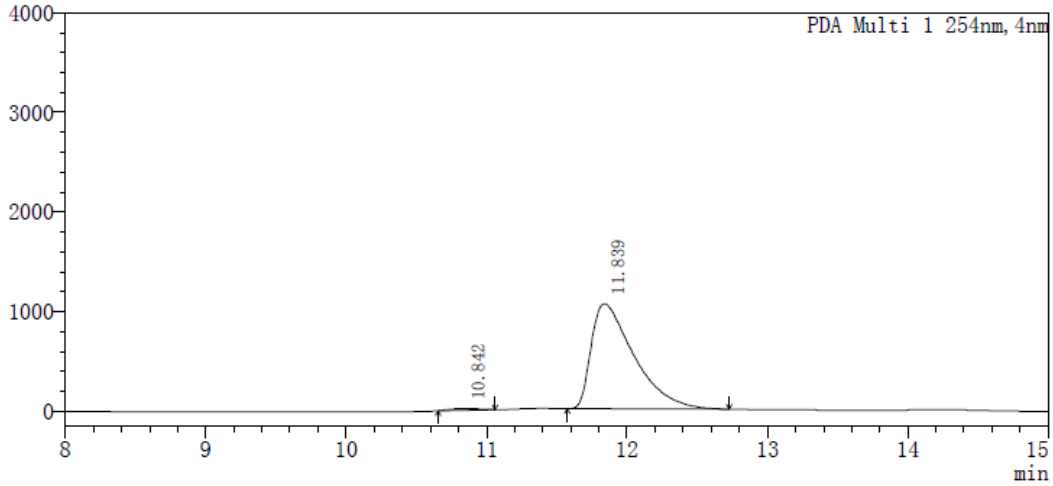
2b



〈峰表〉

PDA Ch1 254nm

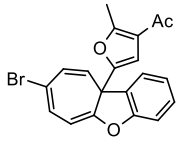
峰号	保留时间	面积	高度	化合物名	面积%	高度%
1	10.475	7690956	319043		49.680	44.160
2	11.949	7789968	403431		50.320	55.840
总计		15480924	722474		100.000	100.000



〈峰表〉

PDA Ch1 254nm

峰号	保留时间	面积	高度	化合物名	面积%	高度%
1	10.842	232053	15616		1.026	1.459
2	11.839	22388679	1054883		98.974	98.541
总计		22620732	1070499		100.000	100.000



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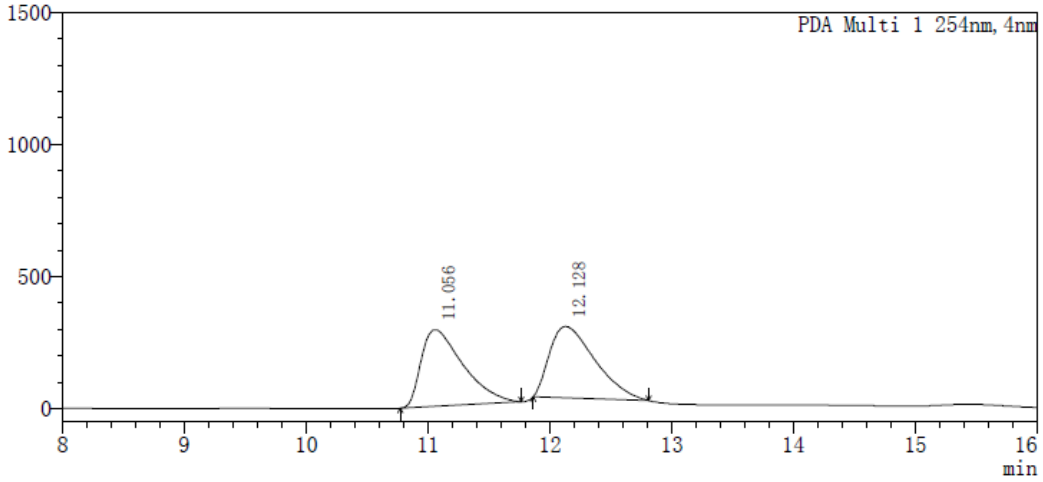
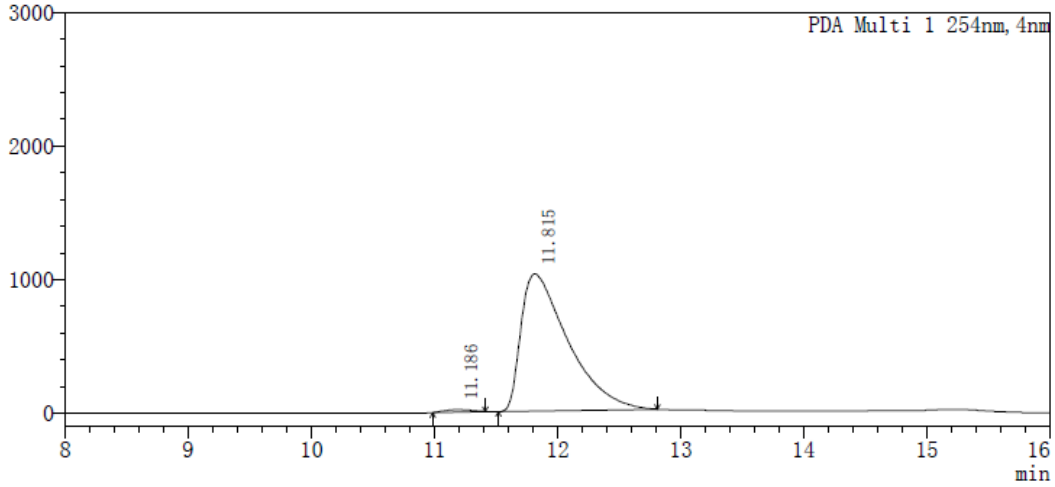


〈峰表〉

PDA Ch1 254nm

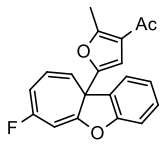
峰号	保留时间	面积	高度	化合物名	面积%	高度%
1	11.056	6963614	290291		49.729	51.749
2	12.128	7039482	270666		50.271	48.251
总计		14003096	560957		100.000	100.000



〈峰表〉

PDA Ch1 254nm

峰号	保留时间	面积	高度	化合物名	面积%	高度%
1	11.186	270703	17964		0.978	1.718
2	11.815	27417314	1027428		99.022	98.282
总计		27688016	1045392		100.000	100.000



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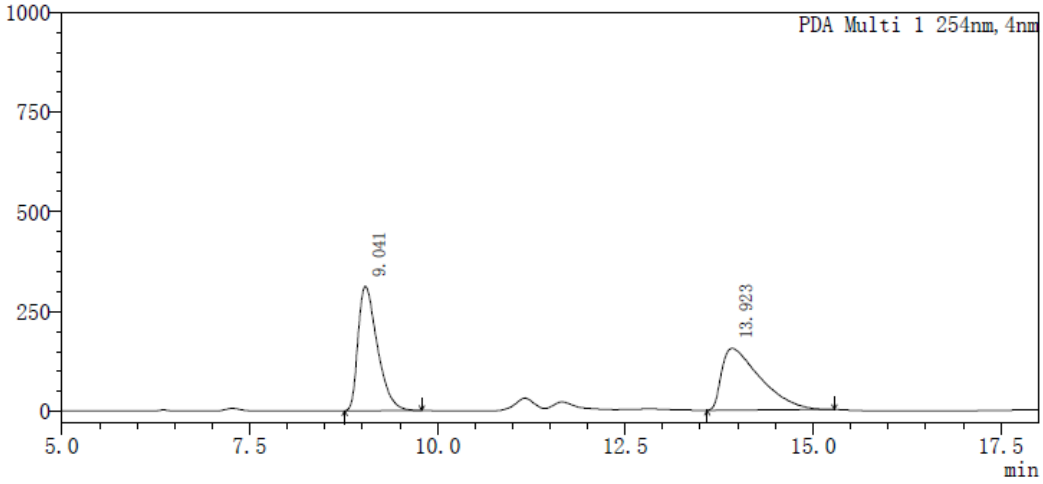
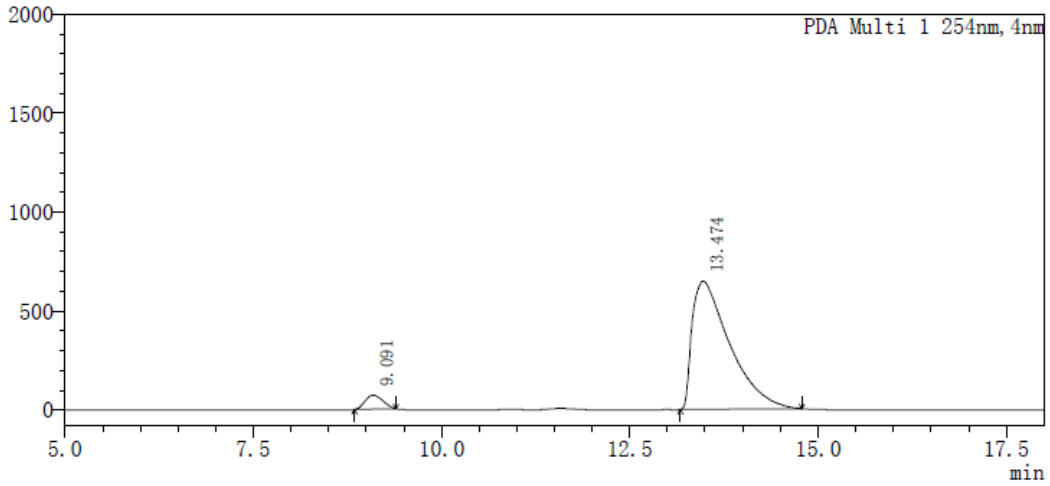


〈峰表〉

PDA Ch1 254nm

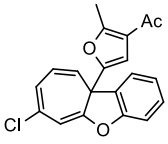
峰号	保留时间	面积	高度	化合物名	面积%	高度%
1	9.041	5596521	311889		50.255	66.753
2	13.923	5539822	155337		49.745	33.247
总计		11136343	467225		100.000	100.000



〈峰表〉

PDA Ch1 254nm

峰号	保留时间	面积	高度	化合物名	面积%	高度%
1	9.091	1163235	70702		4.920	9.832
2	13.474	22479278	648370		95.080	90.168
总计		23642513	719072		100.000	100.000



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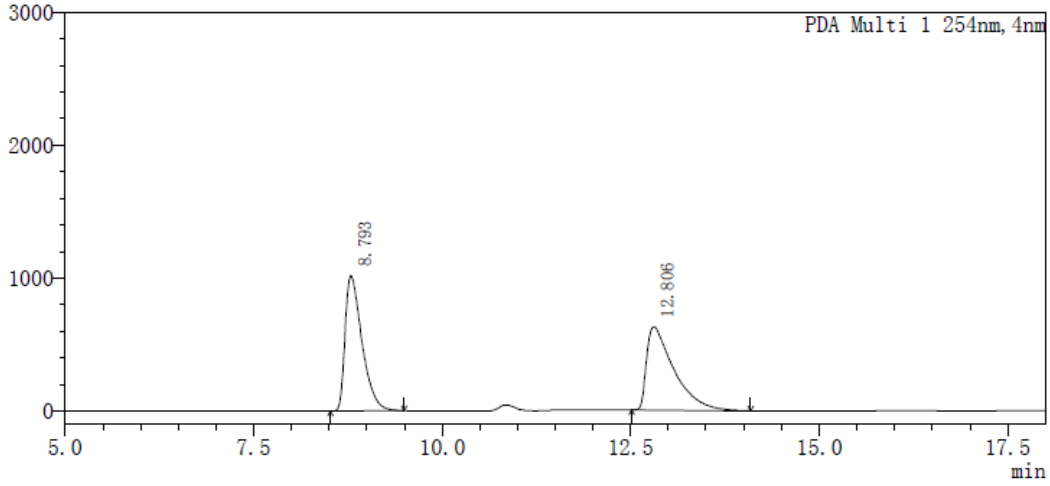
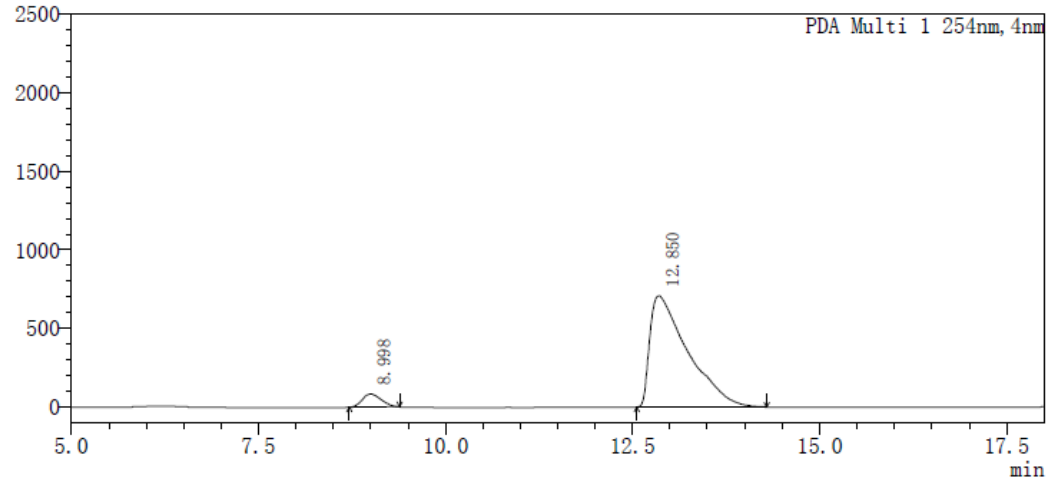


〈峰表〉

PDA Ch1 254nm

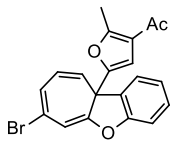
峰号	保留时间	面积	高度	化合物名	面积%	高度%
1	8.793	15876381	1016350		50.205	61.885
2	12.806	15746983	625980		49.795	38.115
总计		31623364	1642330		100.000	100.000



〈峰表〉

PDA Ch1 254nm

峰号	保留时间	面积	高度	化合物名	面积%	高度%
1	8.998	1463115	82498		5.555	10.451
2	12.850	24876275	706889		94.445	89.549
总计		26339390	789387		100.000	100.000



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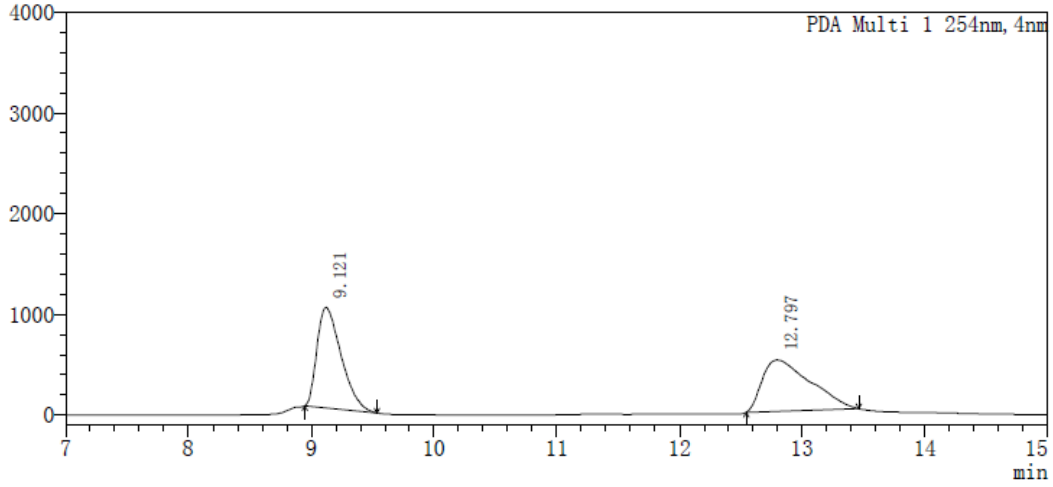
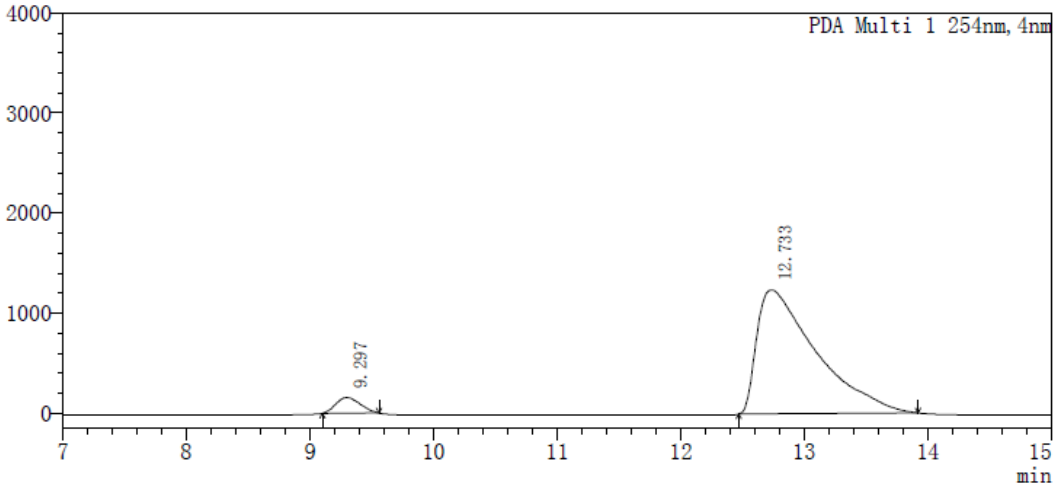


〈峰表〉

PDA Ch1 254nm

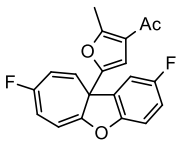
峰号	保留时间	面积	高度	化合物名	面积%	高度%
1	9.121	13649733	996078		49.692	66.255
2	12.797	13818669	507332		50.308	33.745
总计		27468401	1503409		100.000	100.000



〈峰表〉

PDA Ch1 254nm

峰号	保留时间	面积	高度	化合物名	面积%	高度%
1	9.297	2122820	155440		4.885	11.150
2	12.733	41330739	1238675		95.115	88.850
总计		43453559	1394115		100.000	100.000



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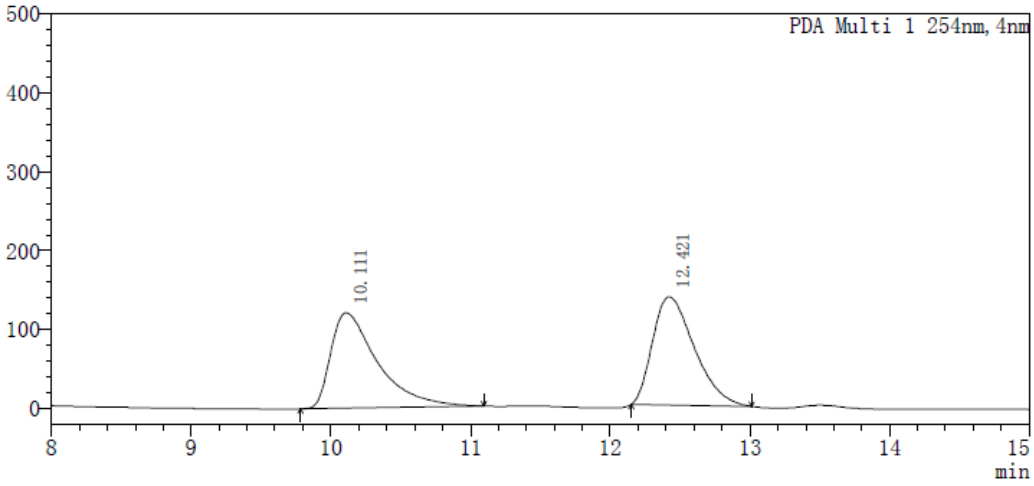
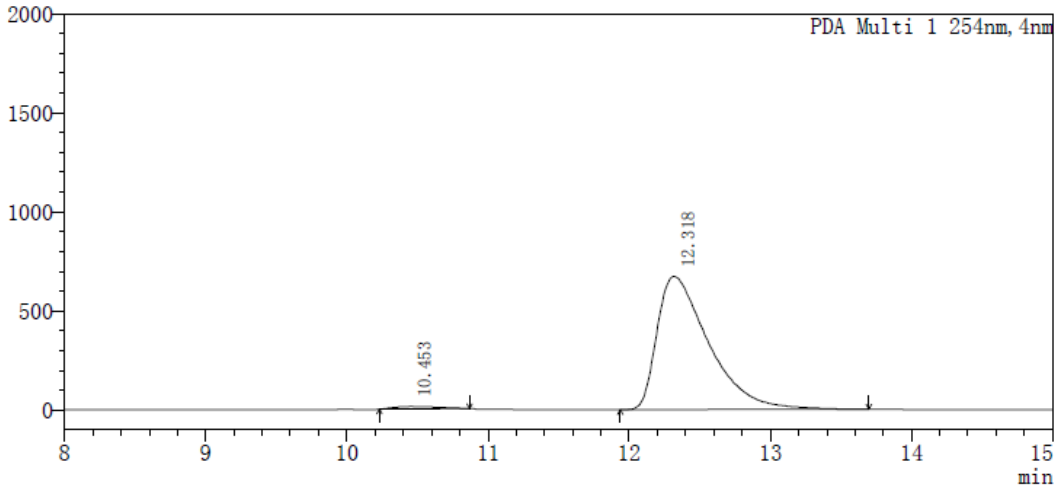


〈峰表〉

PDA Ch1 254nm

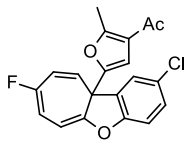
峰号	保留时间	面积	高度	化合物名	面积%	高度%
1	10.111	2818837	120678		49.752	46.866
2	12.421	2846928	136817		50.248	53.134
总计		5665765	257495		100.000	100.000



〈峰表〉

PDA Ch1 254nm

峰号	保留时间	面积	高度	化合物名	面积%	高度%
1	10.453	265352	12066		1.529	1.763
2	12.318	17085696	672533		98.471	98.237
总计		17351048	684599		100.000	100.000



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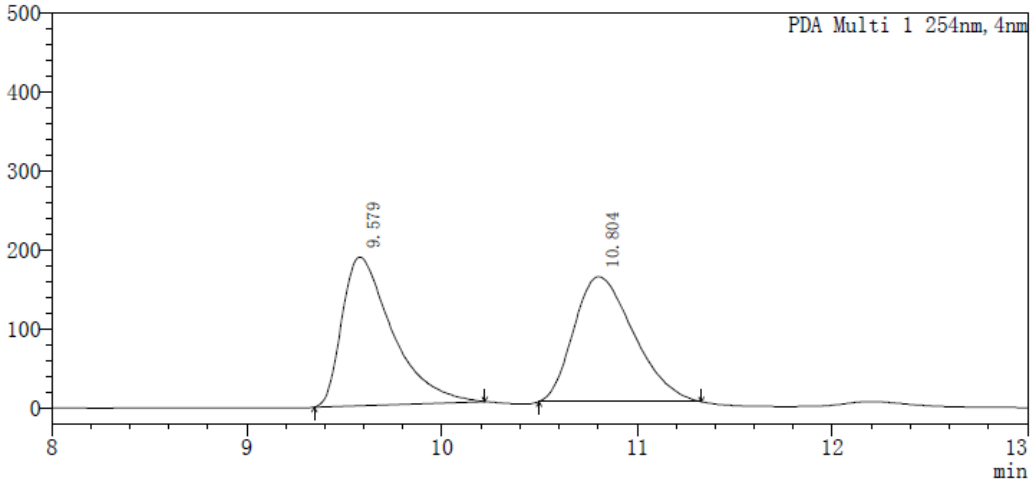
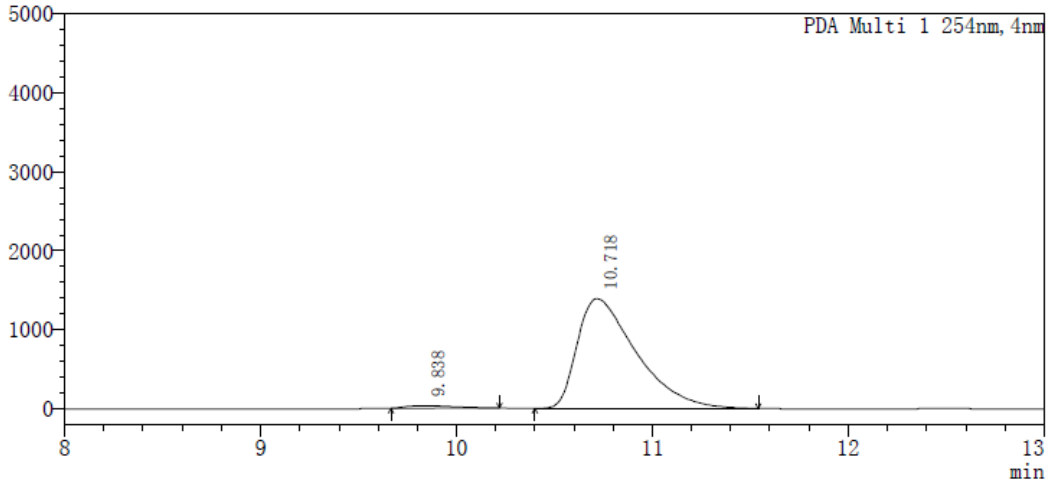


〈峰表〉

PDA Ch1 254nm

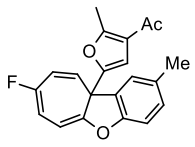
峰号	保留时间	面积	高度	化合物名	面积%	高度%
1	9.579	3380453	187989		49.934	54.274
2	10.804	3389375	158379		50.066	45.726
总计		6769827	346368		100.000	100.000



〈峰表〉

PDA Ch1 254nm

峰号	保留时间	面积	高度	化合物名	面积%	高度%
1	9.838	552976	34077		1.869	2.399
2	10.718	29033764	1386579		98.131	97.601
总计		29586740	1420656		100.000	100.000



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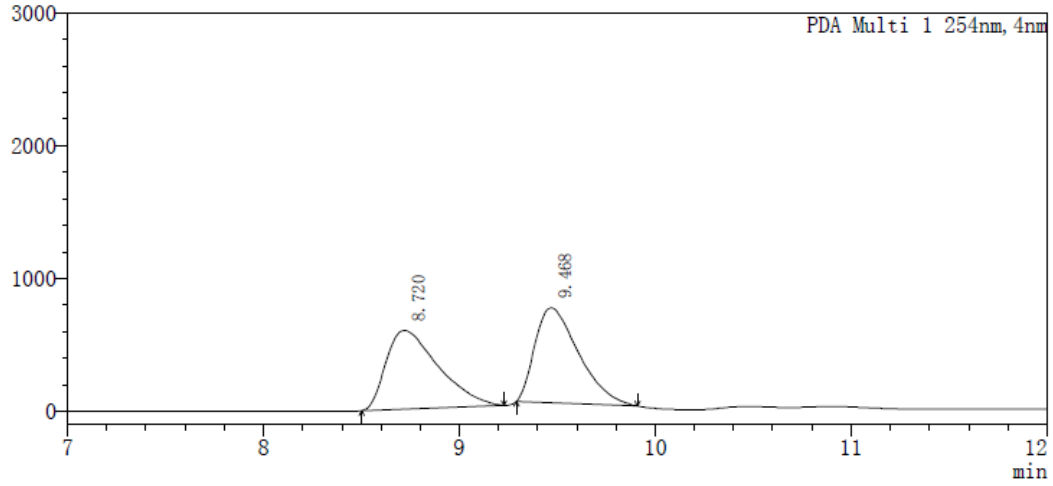
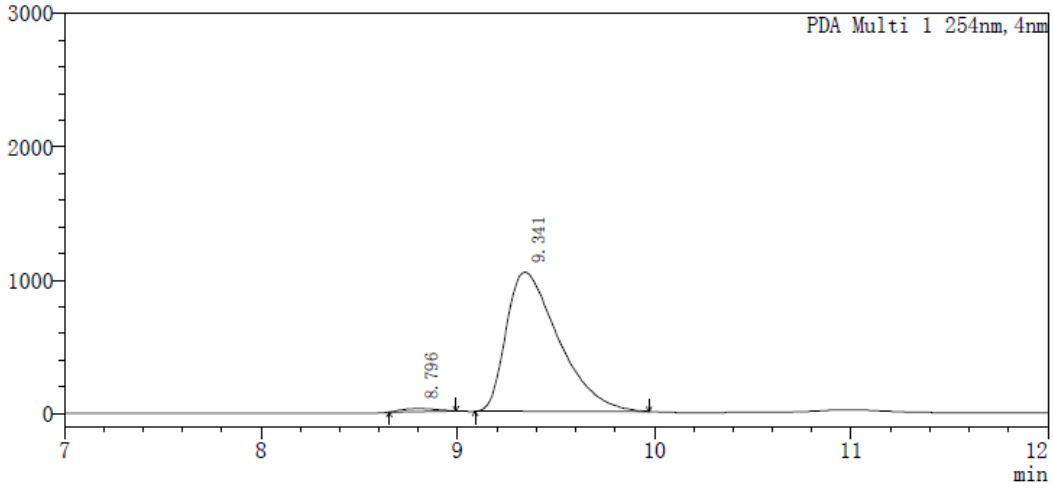


〈峰表〉

PDA Ch1 254nm

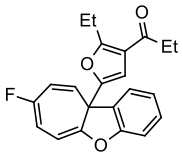
峰号	保留时间	面积	高度	化合物名	面积%	高度%
1	8.720	10958318	591396		49.626	45.303
2	9.468	11123301	714029		50.374	54.697
总计		22081619	1305424		100.000	100.000



〈峰表〉

PDA Ch1 254nm

峰号	保留时间	面积	高度	化合物名	面积%	高度%
1	8.796	272419	22686		1.388	2.127
2	9.341	19361338	1043999		98.612	97.873
总计		19633756	1066684		100.000	100.000



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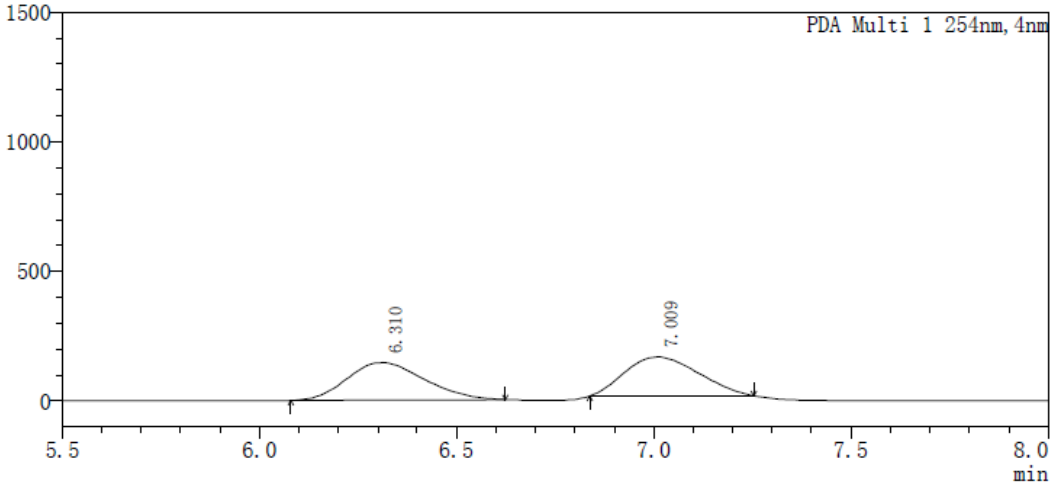
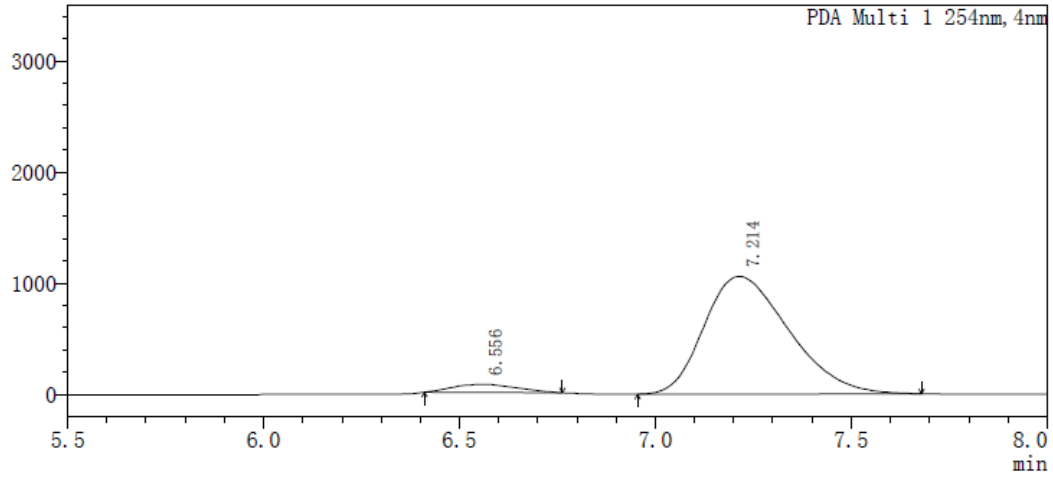


〈峰表〉

PDA Ch1 254nm

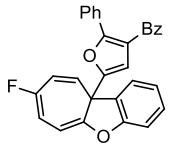
峰号	保留时间	面积	高度	化合物名	面积%	高度%
1	6.310	1977886	144565		50.285	49.013
2	7.009	1955450	150385		49.715	50.987
总计		3933336	294949		100.000	100.000



〈峰表〉

PDA Ch1 254nm

峰号	保留时间	面积	高度	化合物名	面积%	高度%
1	6.556	846283	72988		5.041	6.458
2	7.214	15940130	1057273		94.959	93.542
总计		16786413	1130262		100.000	100.000



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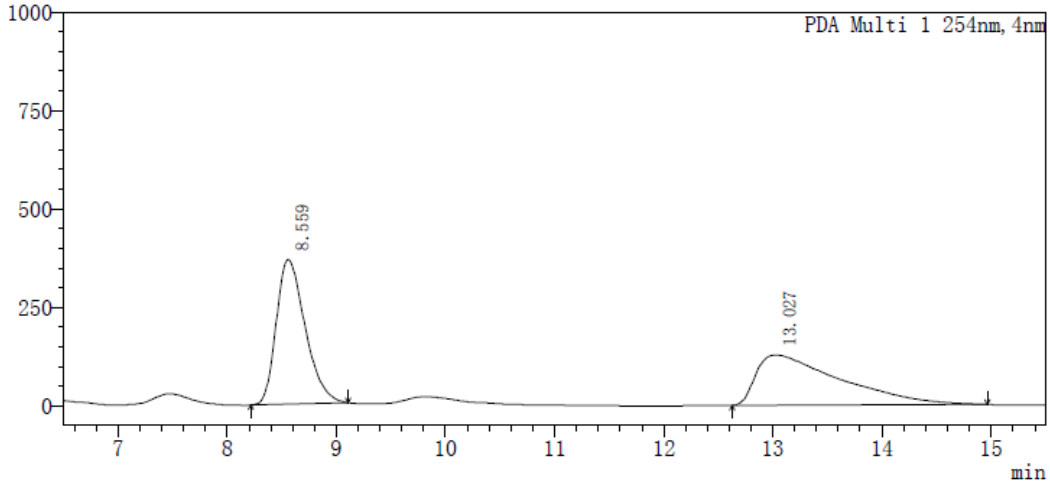
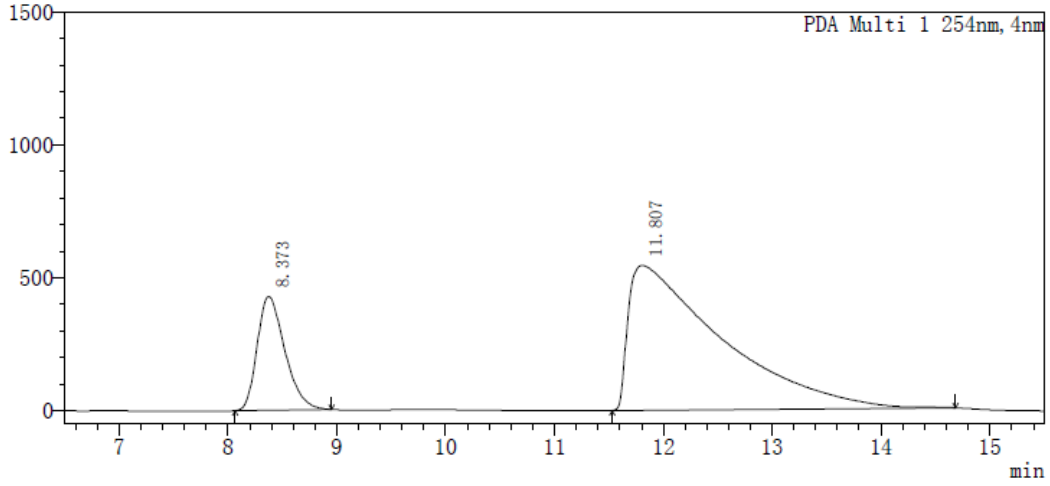


〈峰表〉

PDA Ch1 254nm

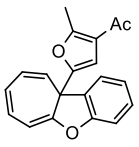
峰号	保留时间	面积	高度	化合物名	面积%	高度%
1	8.559	6779700	367581		49.842	74.261
2	13.027	6822812	127405		50.158	25.739
总计		13602512	494986		100.000	100.000



〈峰表〉

PDA Ch1 254nm

峰号	保留时间	面积	高度	化合物名	面积%	高度%
1	8.373	7586281	428071		19.024	44.006
2	11.807	32291010	544681		80.976	55.994
总计		39877291	972753		100.000	100.000



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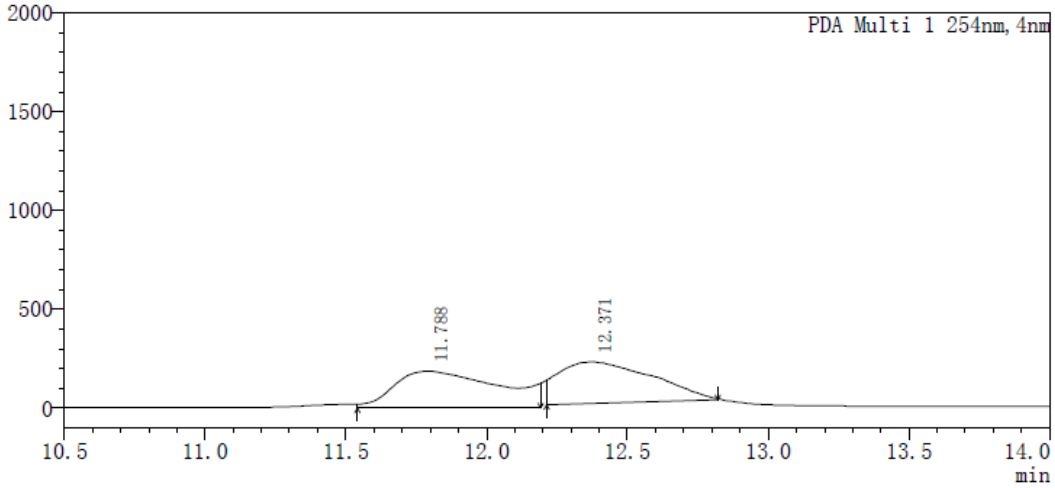
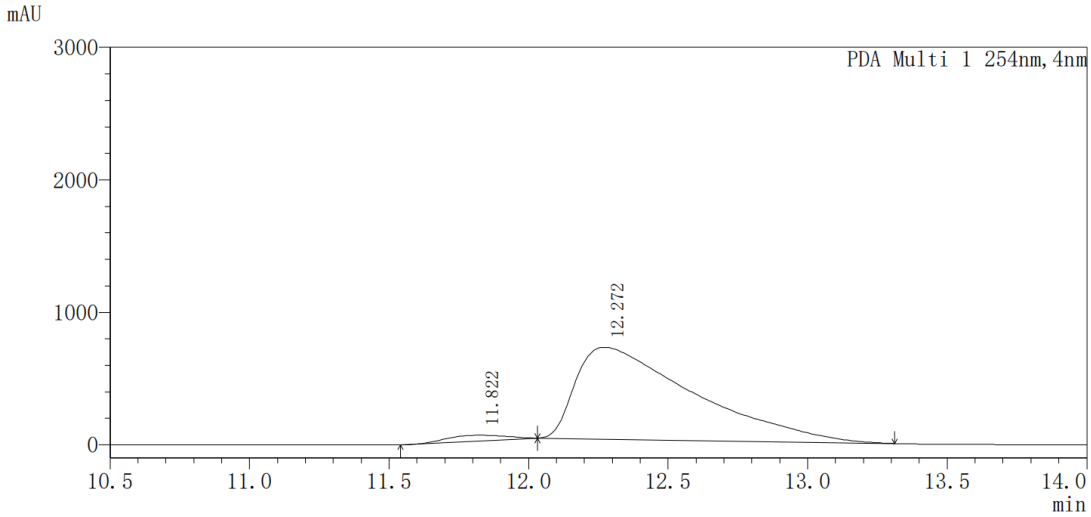


〈峰表〉

PDA Ch1 254nm

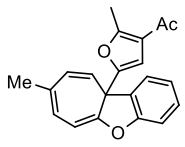
峰号	保留时间	面积	高度	化合物名	面积%	高度%
1	11.788	4875208	186102		50.187	47.027
2	12.371	4838782	209632		49.813	52.973
总计		9713989	395734		100.000	100.000



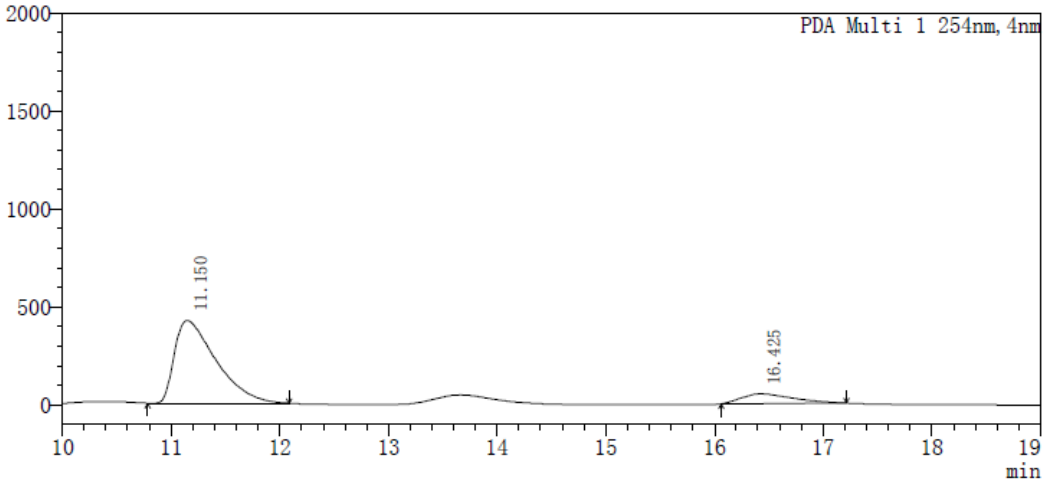
〈峰表〉

PDA Ch1 254nm

峰号	保留时间	面积	高度	化合物名	面积%	高度%
1	11.822	651763	43430		3.088	5.894
2	12.272	20453331	693430		96.912	94.106
总计		21105094	736860		100.000	100.000



2l (The racemic sample can't be obtained from $Rh_2(OPiv)_4$ and other Rh(II)-catalyzed conditions, the enantiomers was identified from UV spectrum with Shimadzu LabSolutions)

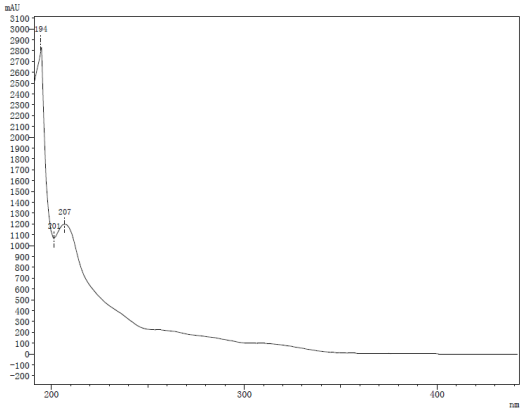


〈峰表〉

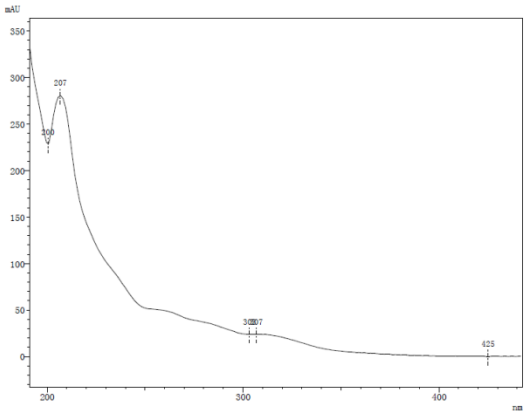
PDA Ch1 254nm

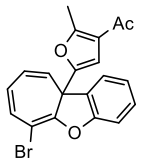
峰号	保留时间	面积	高度	化合物名	面积%	高度%
1	11.150	11257463	422156		87.441	89.485
2	16.425	1616895	49605		12.559	10.515
总计		12874358	471761		100.000	100.000

The major enantiomer's UV spectrum



The minor enantiomer's UV spectrum





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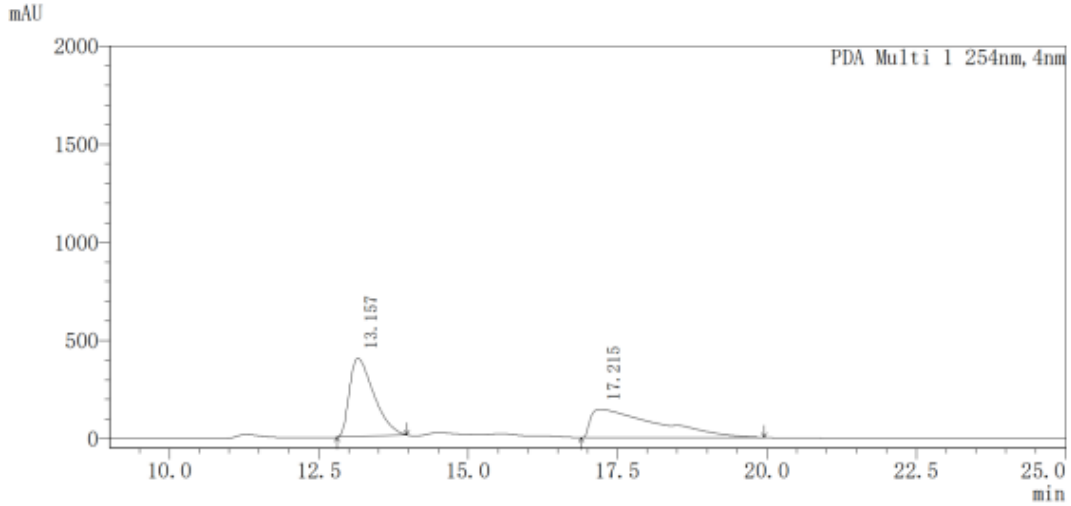
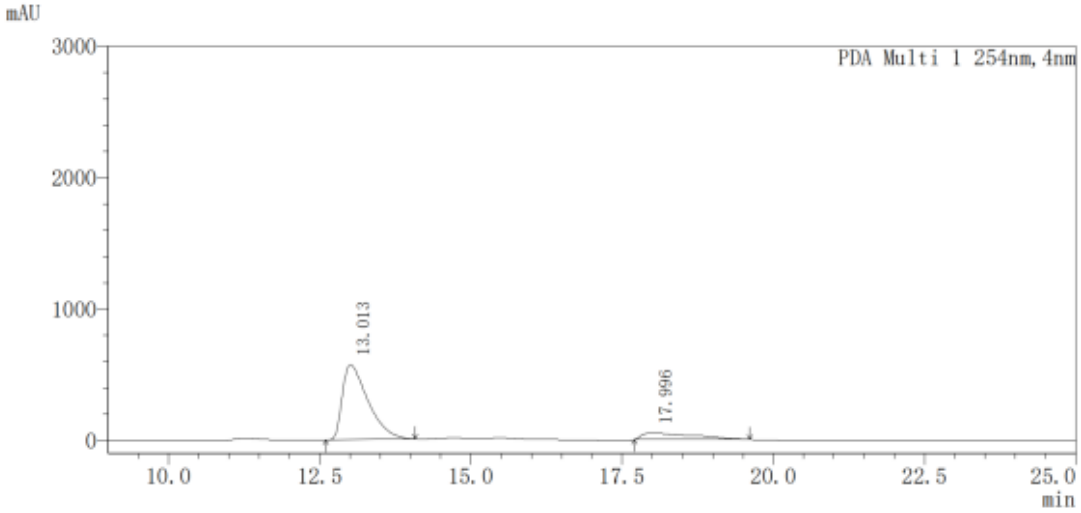


〈峰表〉

PDA Ch1 254nm

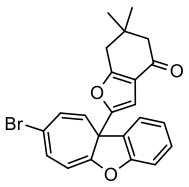
峰号	保留时间	面积	高度	化合物名	面积%	高度%
1	13.157	11292744	398509		50.330	73.504
2	17.215	11144744	143649		49.670	26.496
总计		22437488	542158		100.000	100.000



〈峰表〉

PDA Ch1 254nm

峰号	保留时间	面积	高度	化合物名	面积%	高度%
1	13.013	16852688	569364		84.952	92.124
2	17.996	2985136	48680		15.048	7.876
总计		19837824	618044		100.000	100.000



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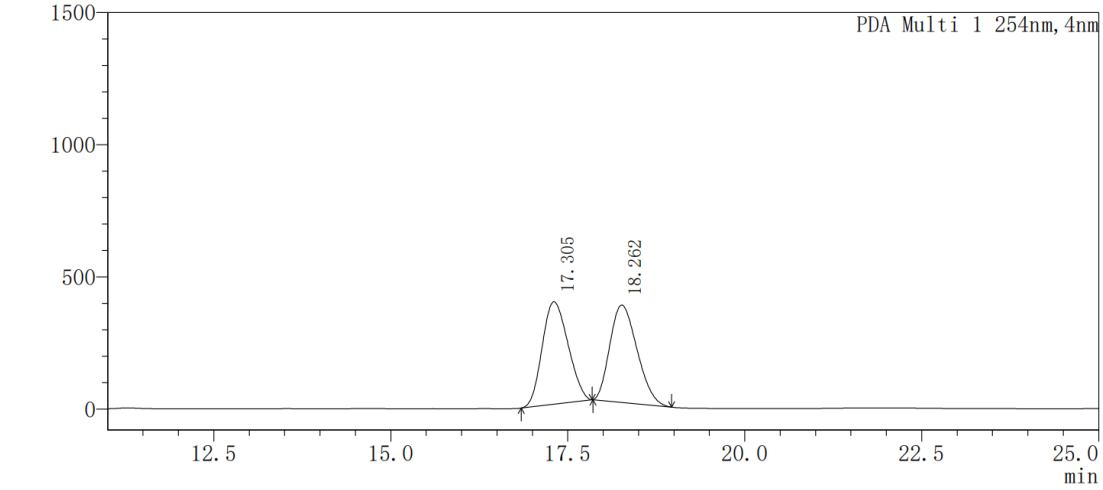

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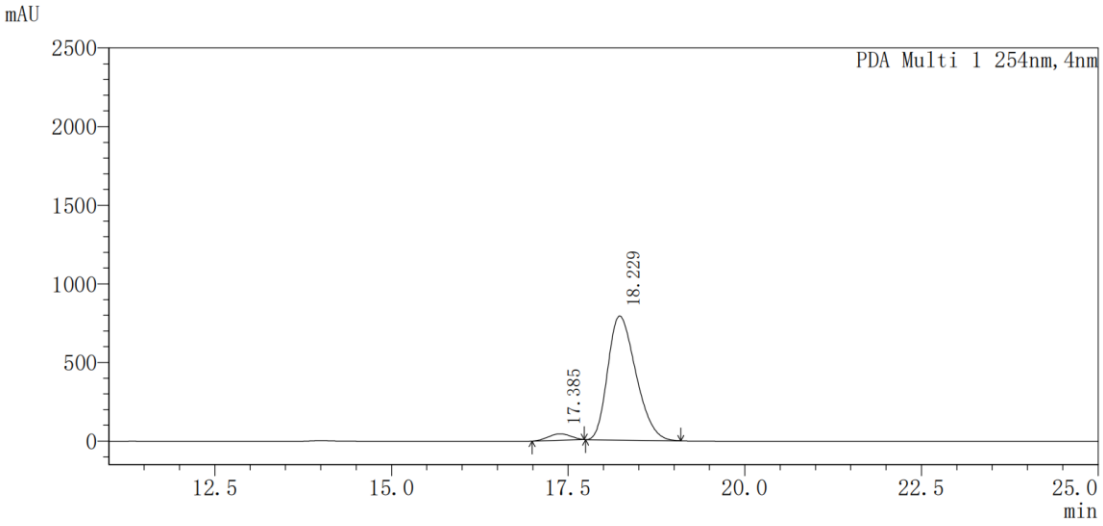
PDA Ch1 254nm

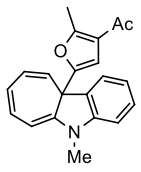
峰号	保留时间	面积	高度	面积%	高度%
1	17.305	9865361	387918	50.024	51.267
2	18.262	9855760	368742	49.976	48.733
总计		19721121	756660	100.000	100.000



<峰表>

PDA Ch1 254nm

峰号	保留时间	面积	高度	面积%	高度%
1	17.385	904571	41037	3.972	4.941
2	18.229	21868019	789584	96.028	95.059
总计		22772590	830620	100.000	100.000



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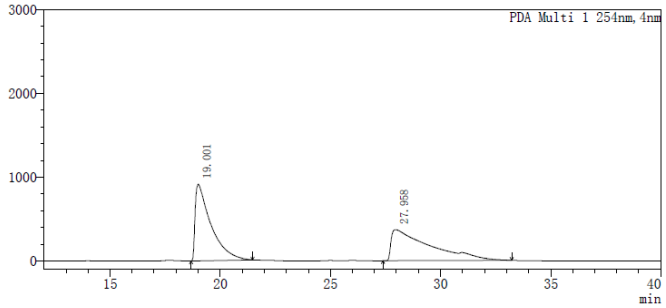
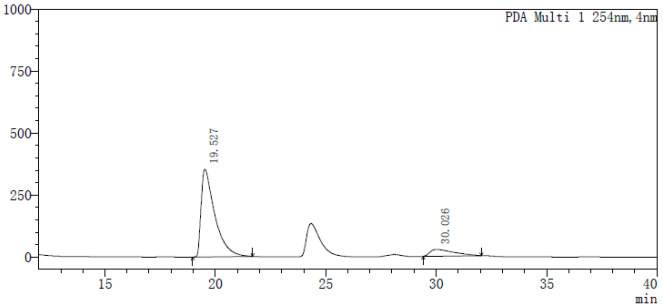


〈峰表〉

PDA Ch1 254nm

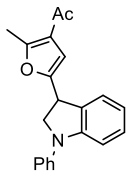
峰号	保留时间	面积	高度	化合物名	面积%	高度%
1	19.001	45389411	911802		49.930	71.022
2	27.958	45515894	372034		50.070	28.978
总计		90905305	1283837		100.000	100.000



〈峰表〉

PDA Ch1 254nm

峰号	保留时间	面积	高度	化合物名	面积%	高度%
1	19.527	15189725	353982		87.989	92.837
2	30.026	2073524	27311		12.011	7.163
总计		17263250	381293		100.000	100.000



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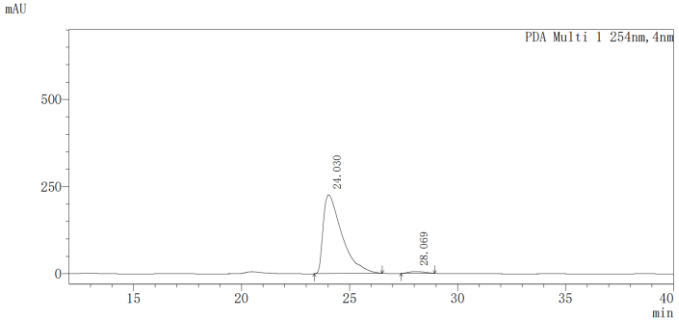
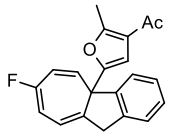


〈峰表〉

PDA Ch1 254nm

峰号	保留时间	面积	高度	化合物名	面积%	高度%
1	24.030	13605323	226222		98.047	97.675
2	28.069	270939	5386		1.953	2.325
总计		13876262	231608		100.000	100.000



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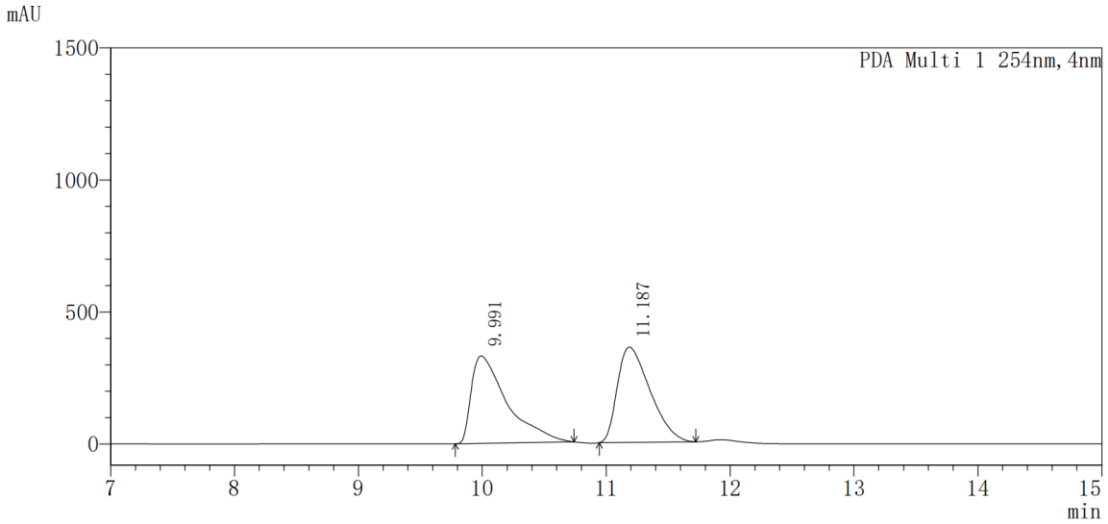
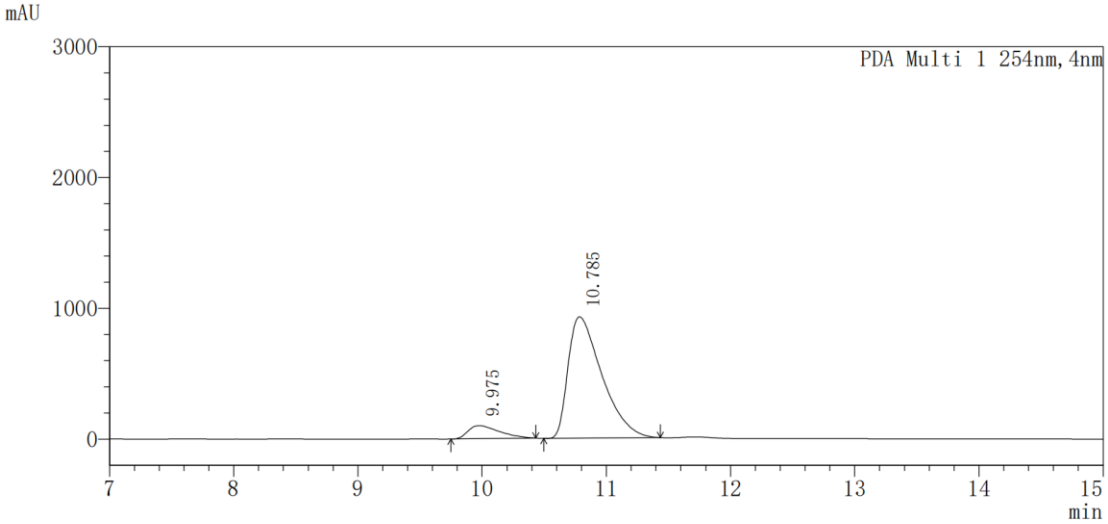


〈峰表〉

PDA Ch1 254nm

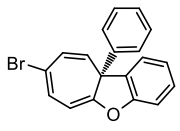
峰号	保留时间	面积	高度	面积%	高度%
1	9.991	6661087	330800	50.152	47.823
2	11.187	6620724	360916	49.848	52.177
总计		13281811	691716	100.000	100.000



〈峰表〉

PDA Ch1 254nm

峰号	保留时间	面积	高度	面积%	高度%
1	9.975	1755350	100187	9.083	9.732
2	10.785	17570567	929234	90.917	90.268
总计		19325917	1029421	100.000	100.000



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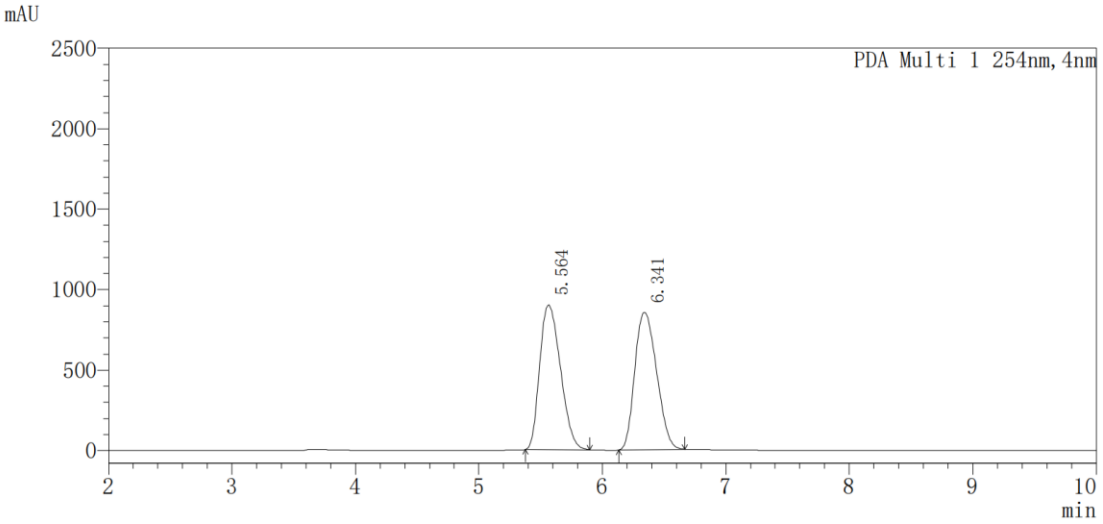
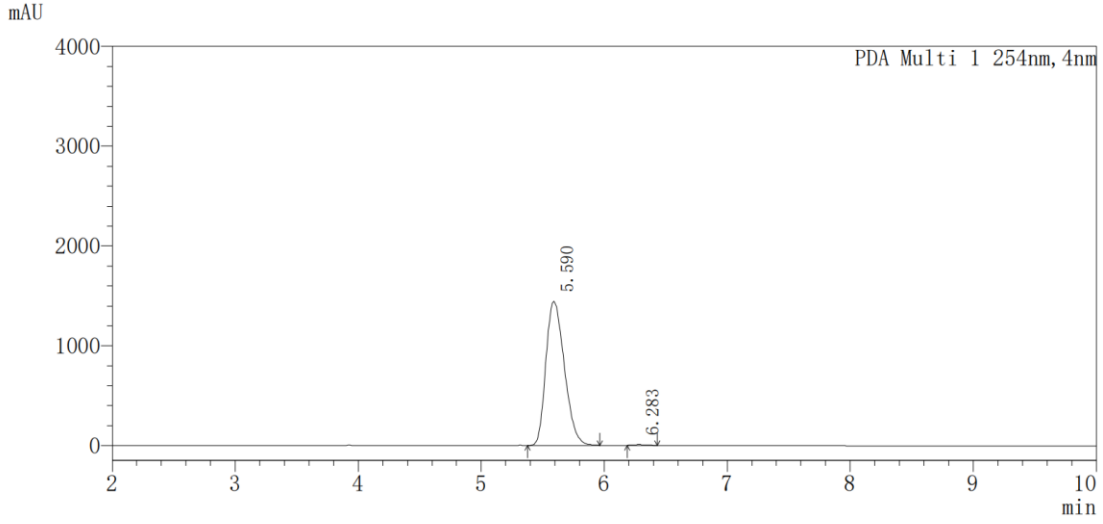


〈峰表〉

PDA Ch1 254nm

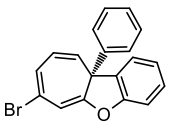
峰号	保留时间	面积	高度	化合物名	面积%	高度%
1	5.564	10520614	898587	RT:5.564	50.065	51.274
2	6.341	10493203	853928	RT:6.341	49.935	48.726
总计		21013817	1752515		100.000	100.000



〈峰表〉

PDA Ch1 254nm

峰号	保留时间	面积	高度	化合物名	面积%	高度%
1	5.590	15051313	1442522		99.684	99.573
2	6.283	47691	6188		0.316	0.427
总计		15099004	1448709		100.000	100.000



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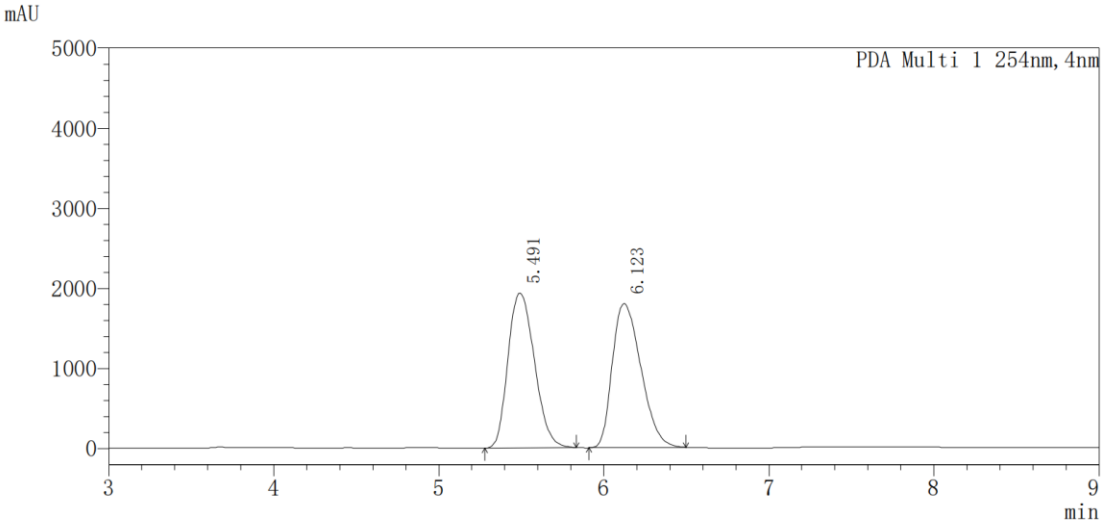
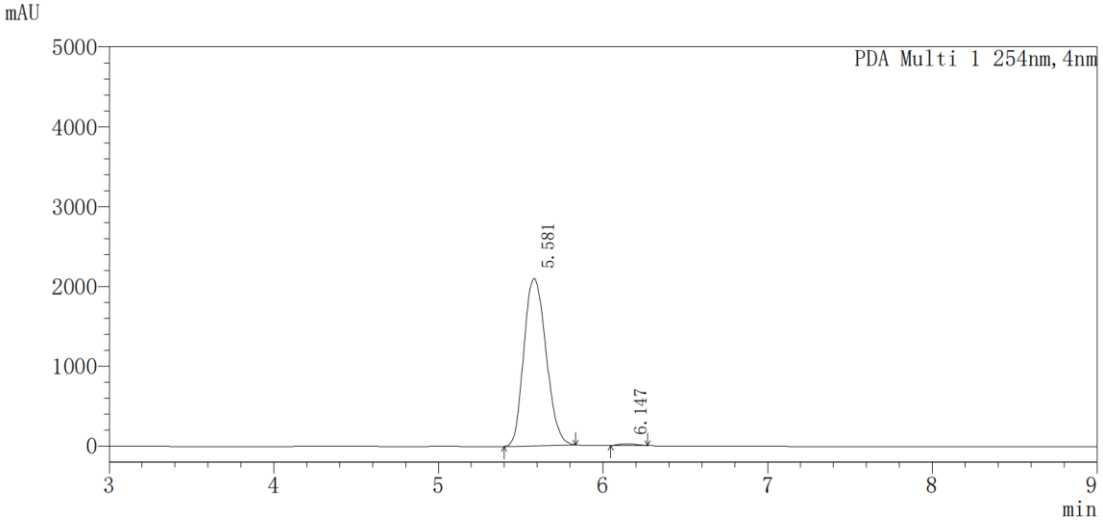


〈峰表〉

PDA Ch1 254nm

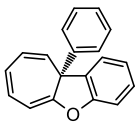
峰号	保留时间	面积	高度	化合物名	面积%	高度%
1	5.491	21573911	1934085		49.859	51.843
2	6.123	21696110	1796598		50.141	48.157
总计		43270021	3730684		100.000	100.000



〈峰表〉

PDA Ch1 254nm

峰号	保留时间	面积	高度	化合物名	面积%	高度%
1	5.581	19624092	2097919		99.149	98.861
2	6.147	168391	24178		0.851	1.139
总计		19792483	2122096		100.000	100.000



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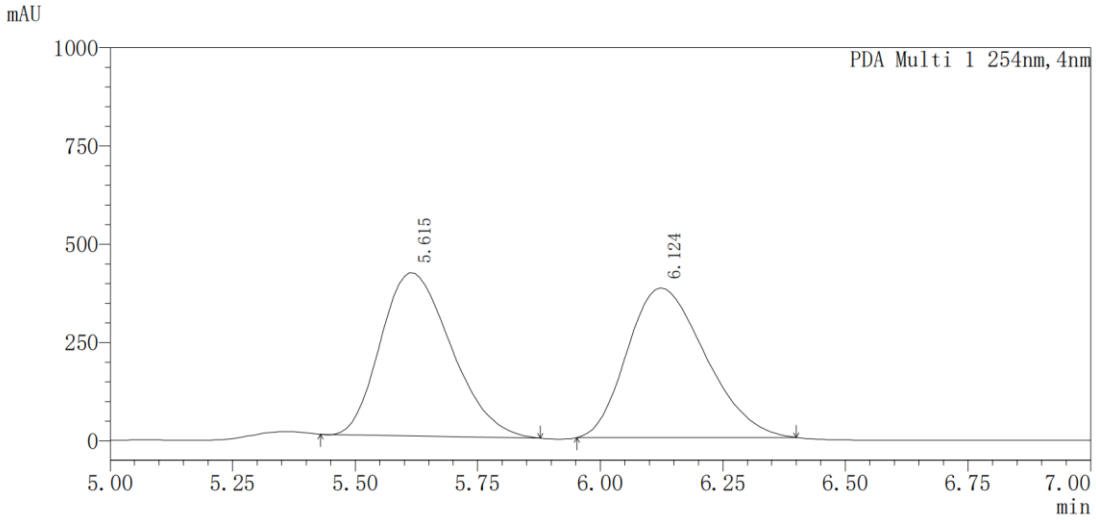
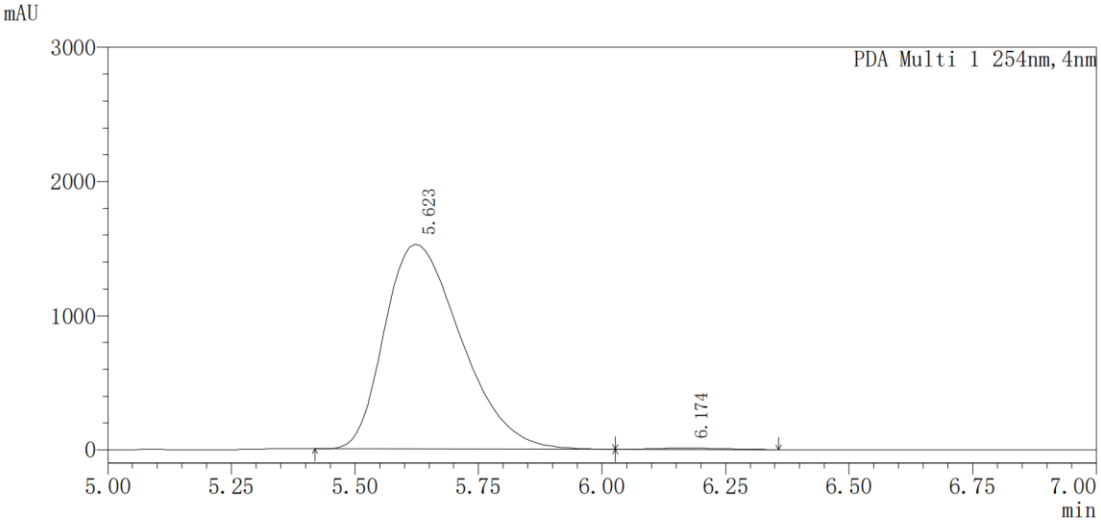


〈峰表〉

PDA Ch1 254nm

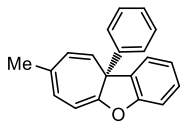
峰号	保留时间	面积	标记	化合物名	面积%
1	5.615	4157142	M		49.616
2	6.124	4221538	M		50.384
总计		8378680			100.000



〈峰表〉

PDA Ch1 254nm

峰号	保留时间	面积	标记	化合物名	面积%
1	5.623	16426522	M		99.485
2	6.174	85063	M		0.515
总计		16511585			100.000



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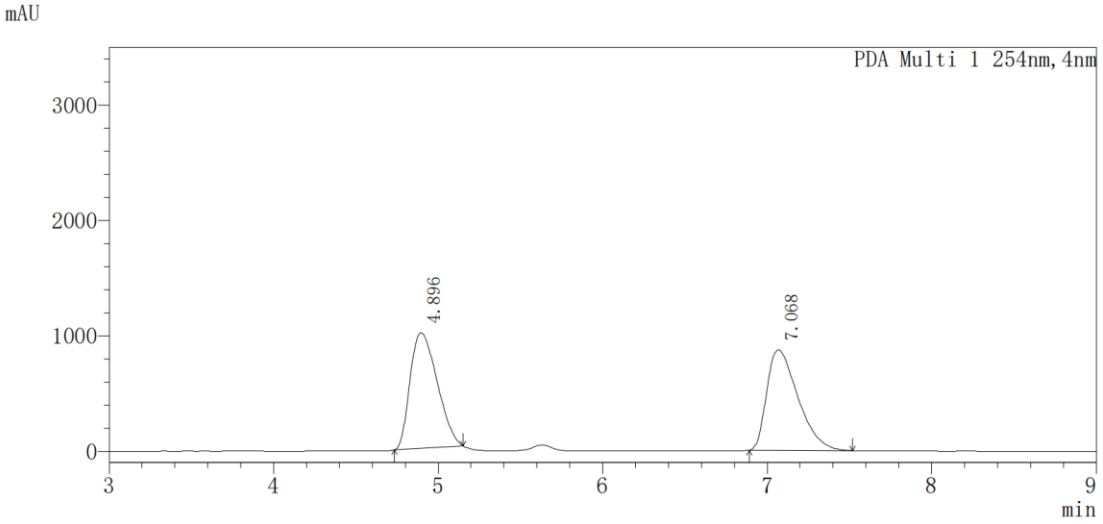
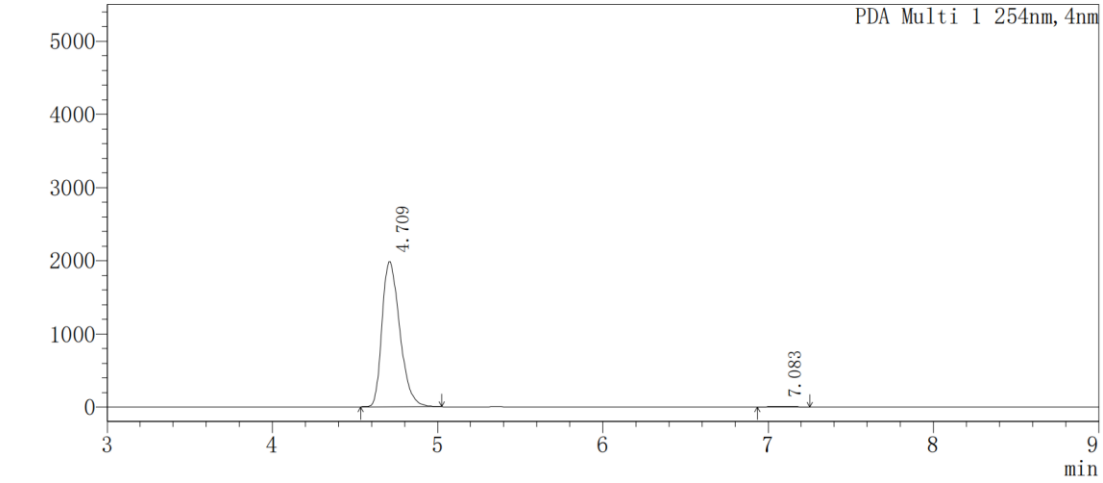


〈峰表〉

PDA Ch1 254nm

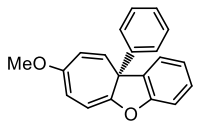
峰号	保留时间	面积	高度	化合物名	面积%	高度%
1	4.896	11468549	1001384		49.982	53.482
2	7.068	11477026	870982		50.018	46.518
总计		22945575	1872367		100.000	100.000



〈峰表〉

PDA Ch1 254nm

峰号	保留时间	面积	高度	化合物名	面积%	高度%
1	4.709	14833266	1981040		99.569	99.692
2	7.083	64144	6115		0.431	0.308
总计		14897409	1987155		100.000	100.000



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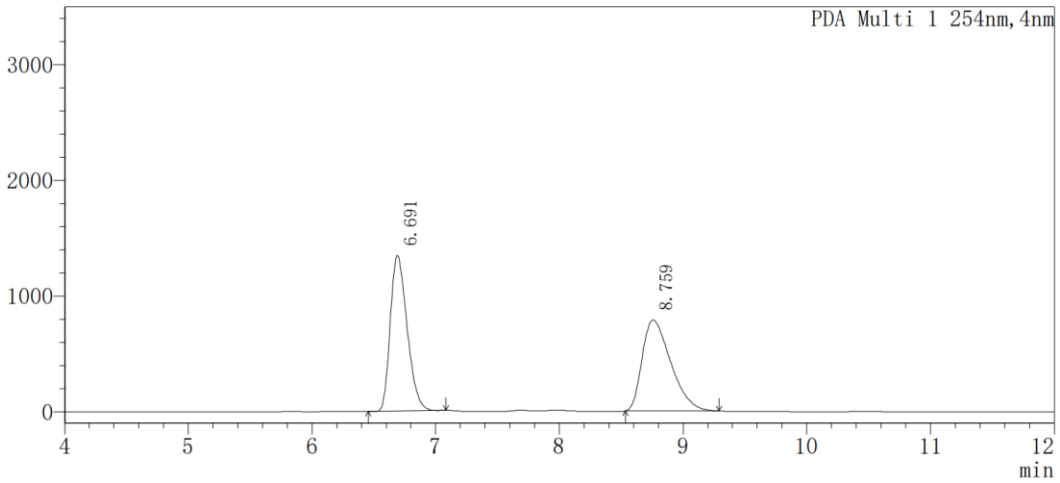
mAU

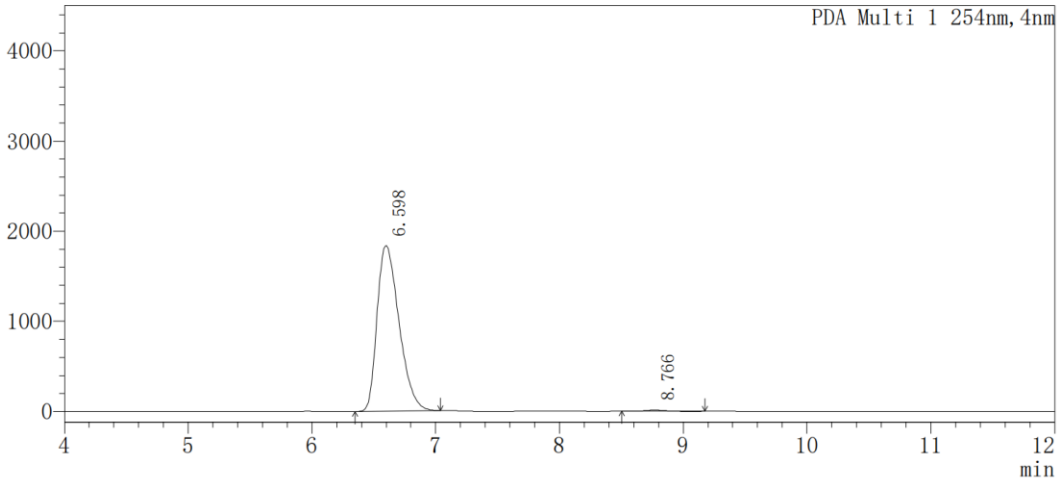


〈峰表〉

PDA Ch1 254nm

峰号	保留时间	面积	高度	化合物名	面积%	高度%
1	6.691	12785057	1345697		50.258	63.137
2	8.759	12653596	785683		49.742	36.863
总计		25438653	2131380		100.000	100.000

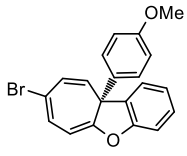
mAU



〈峰表〉

PDA Ch1 254nm

峰号	保留时间	面积	高度	化合物名	面积%	高度%
1	6.598	22613097	1833895		99.510	99.313
2	8.766	111298	12681		0.490	0.687
总计		22724396	1846576		100.000	100.000



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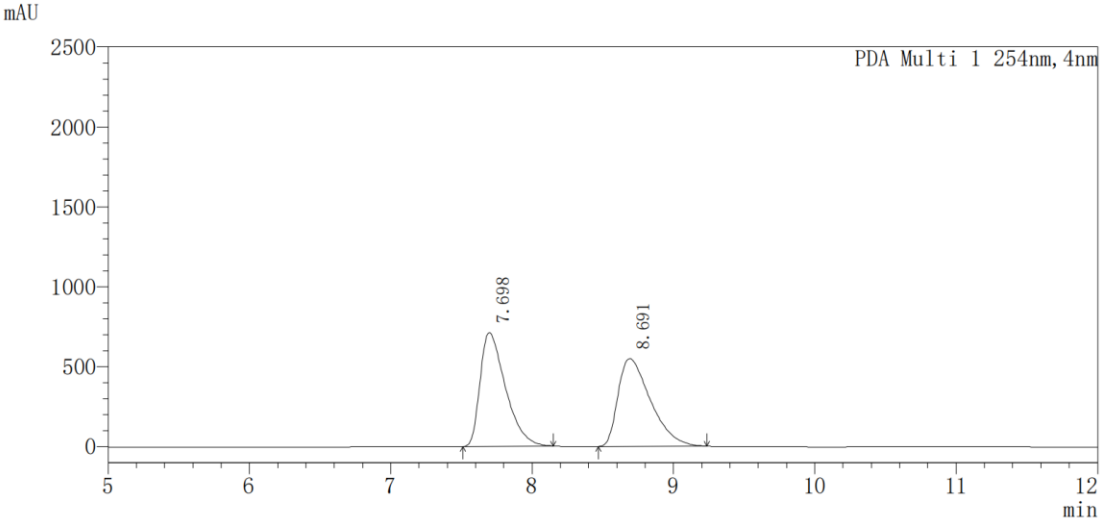
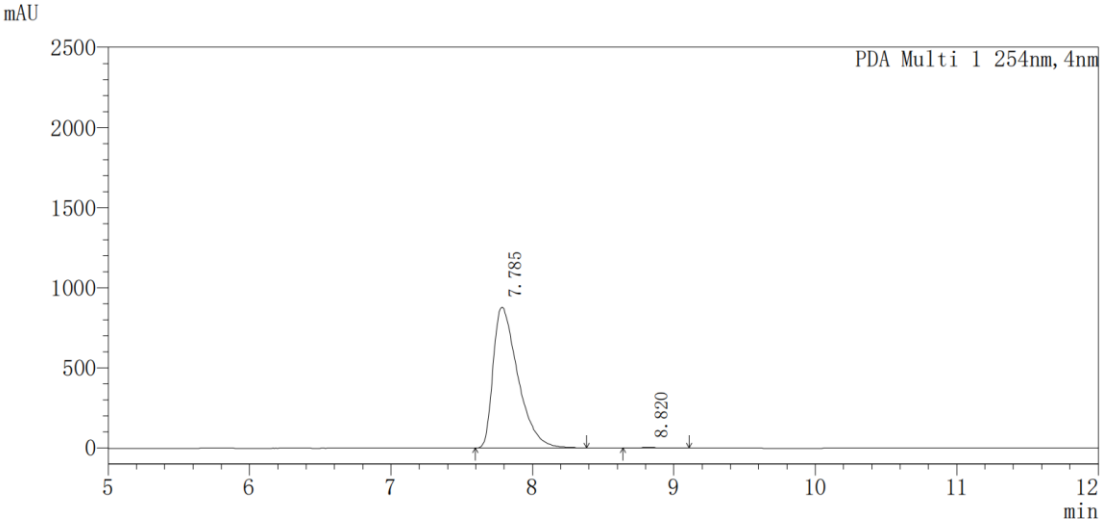


〈峰表〉

PDA Ch1 254nm

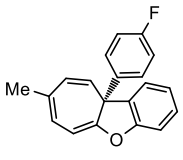
峰号	保留时间	面积	高度	化合物名	面积%	高度%
1	7.698	8892840	710953		50.268	56.423
2	8.691	8798034	549081		49.732	43.577
总计		17690874	1260034		100.000	100.000



〈峰表〉

PDA Ch1 254nm

峰号	保留时间	面积	高度	化合物名	面积%	高度%
1	7.785	10643986	878591		99.622	99.643
2	8.820	40379	3146		0.378	0.357
总计		10684365	881737		100.000	100.000



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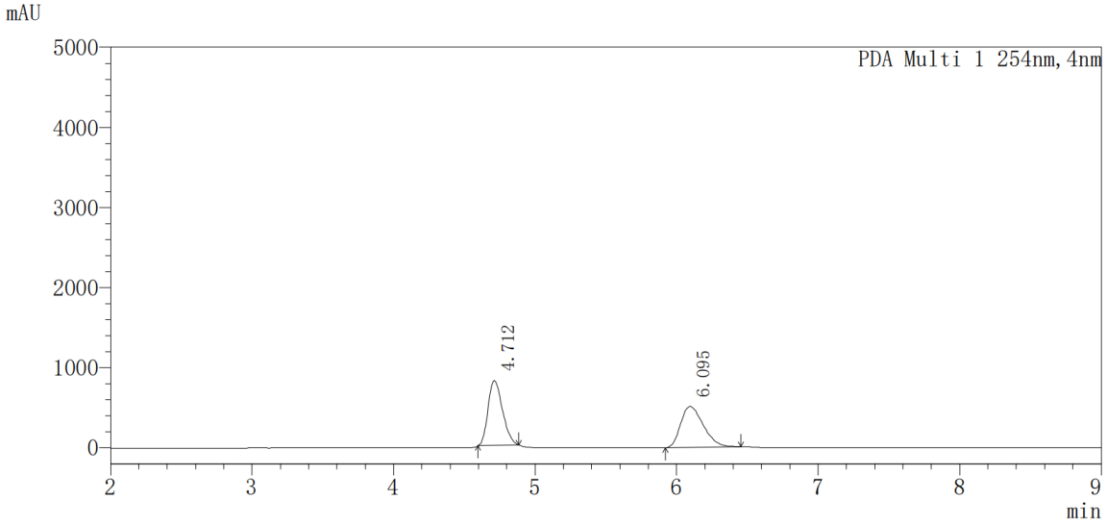
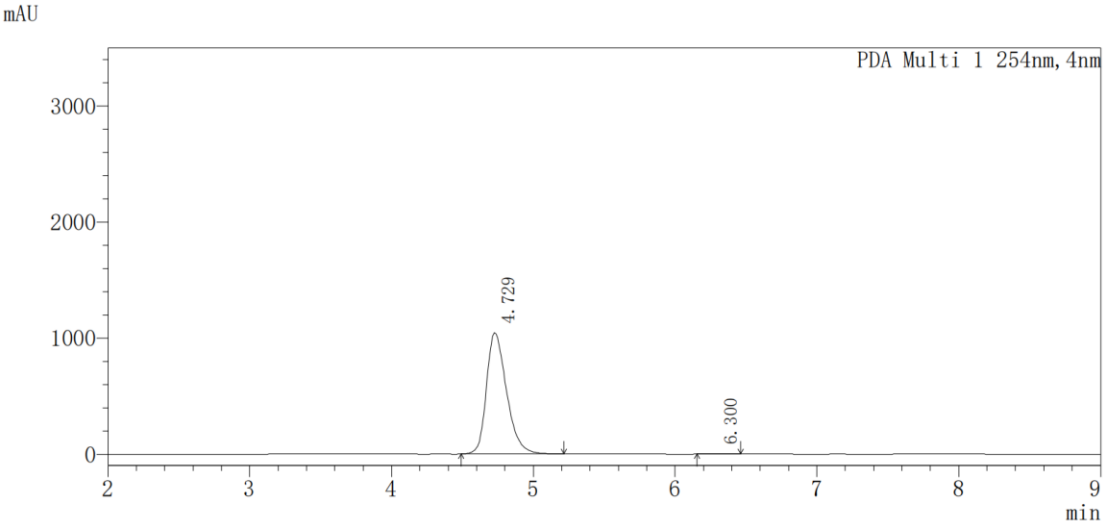


〈峰表〉

PDA Ch1 254nm

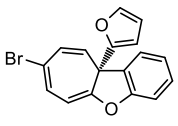
峰号	保留时间	面积	高度	化合物名	面积%	高度%
1	4.712	5736005	813774		50.362	61.480
2	6.095	5653642	509862		49.638	38.520
总计		11389647	1323636		100.000	100.000



〈峰表〉

PDA Ch1 254nm

峰号	保留时间	面积	高度	化合物名	面积%	高度%
1	4.729	10286591	1043973		99.755	99.752
2	6.300	25281	2598		0.245	0.248
总计		10311871	1046571		100.000	100.000



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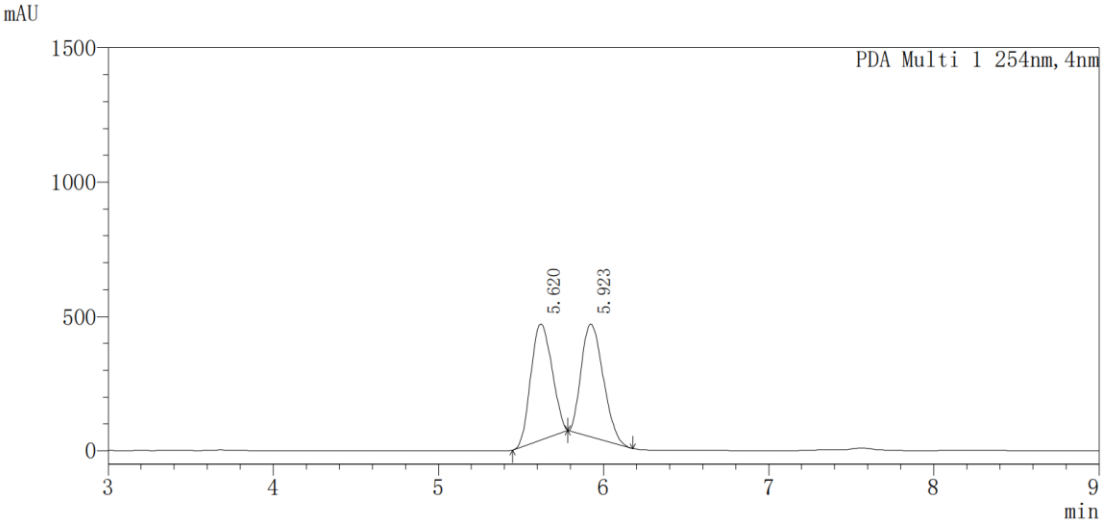
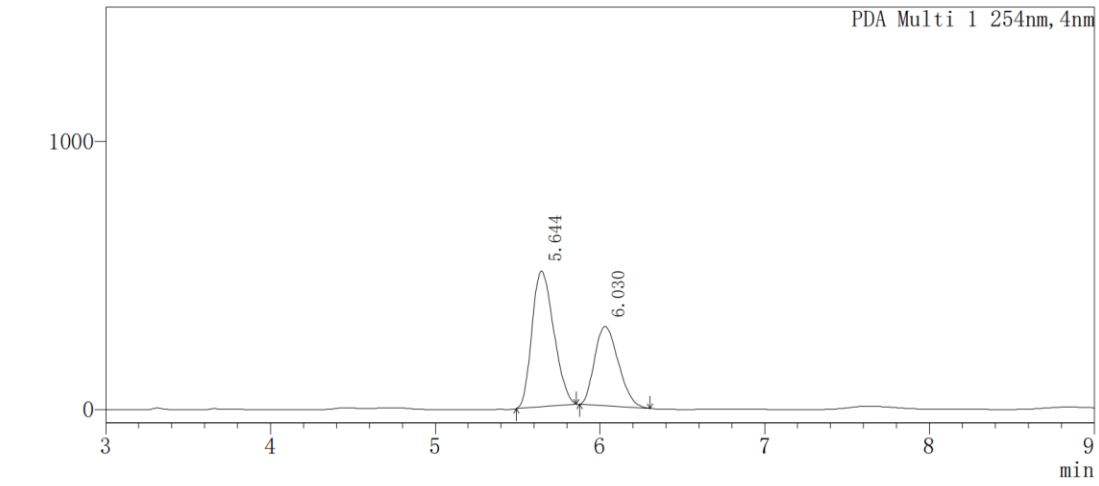


〈峰表〉

PDA Ch1 254nm

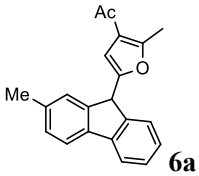
峰号	保留时间	面积	高度	化合物名	面积%	高度%
1	5.620	3841098	431512		49.932	50.635
2	5.923	3851526	420687		50.068	49.365
总计		7692623	852199		100.000	100.000



〈峰表〉

PDA Ch1 254nm

峰号	保留时间	面积	高度	化合物名	面积%	高度%
1	5.644	4638783	506053		60.924	63.073
2	6.030	2975238	296270		39.076	36.927
总计		7614021	802324		100.000	100.000



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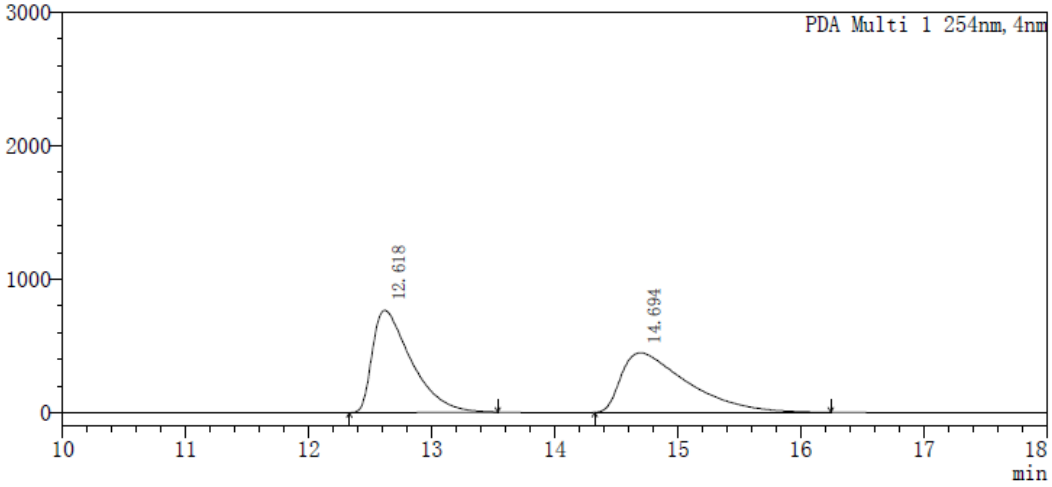
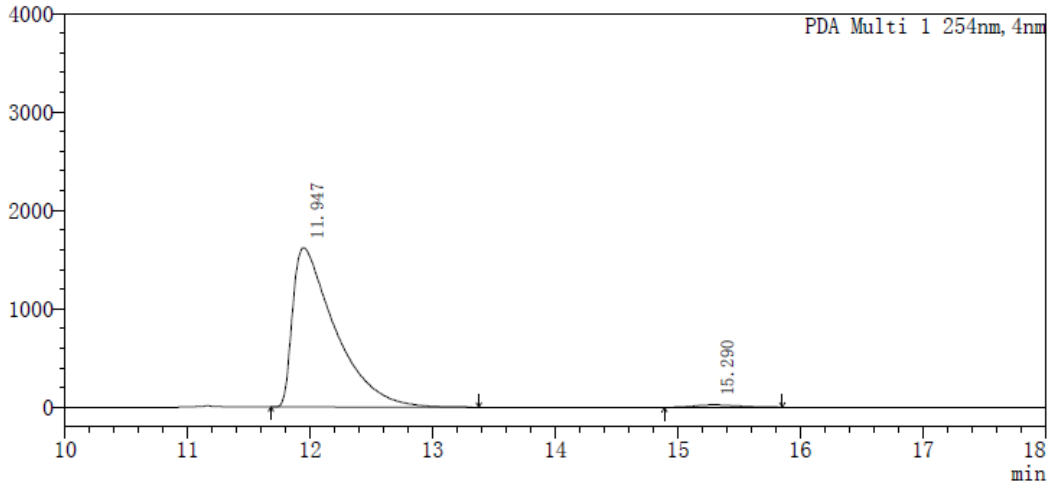


〈峰表〉

PDA Ch1 254nm

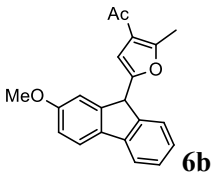
峰号	保留时间	面积	高度	化合物名	面积%	高度%
1	12.618	16846981	764471		50.237	63.161
2	14.694	16688124	445879		49.763	36.839
总计		33535104	1210350		100.000	100.000



〈峰表〉

PDA Ch1 254nm

峰号	保留时间	面积	高度	化合物名	面积%	高度%
1	11.947	39167726	1620756		98.477	98.509
2	15.290	605673	24531		1.523	1.491
总计		39773399	1645286		100.000	100.000



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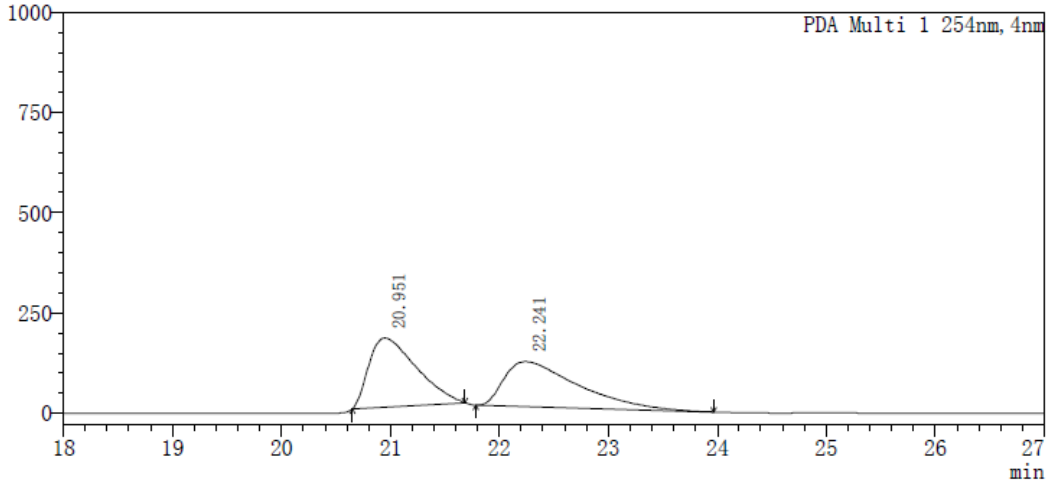
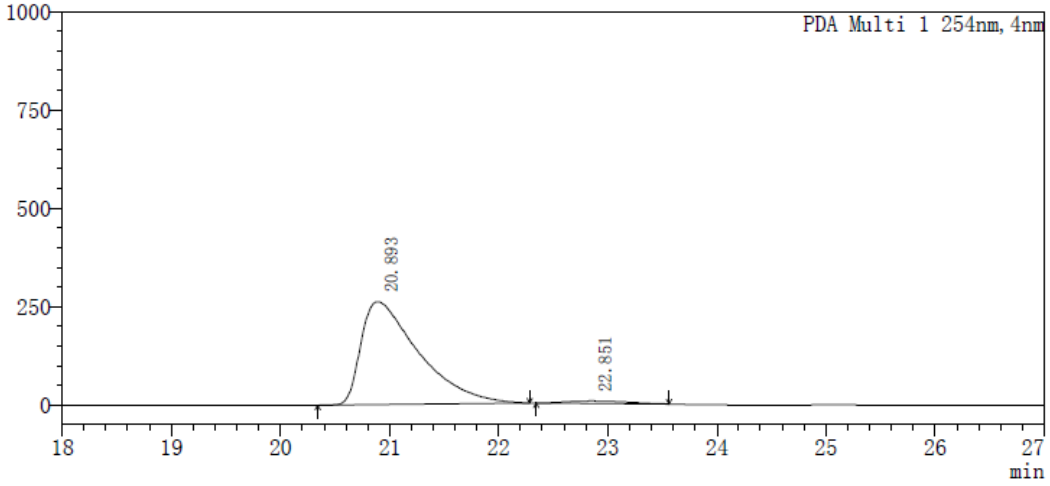


〈峰表〉

PDA Ch1 254nm

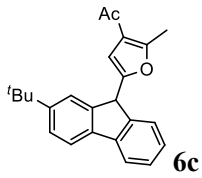
峰号	保留时间	面积	高度	化合物名	面积%	高度%
1	20.951	5223228	172092		49.677	60.506
2	22.241	5291161	112329		50.323	39.494
总计		10514389	284421		100.000	100.000



〈峰表〉

PDA Ch1 254nm

峰号	保留时间	面积	高度	化合物名	面积%	高度%
1	20.893	9608376	261690		97.593	97.738
2	22.851	237018	6057		2.407	2.262
总计		9845393	267748		100.000	100.000



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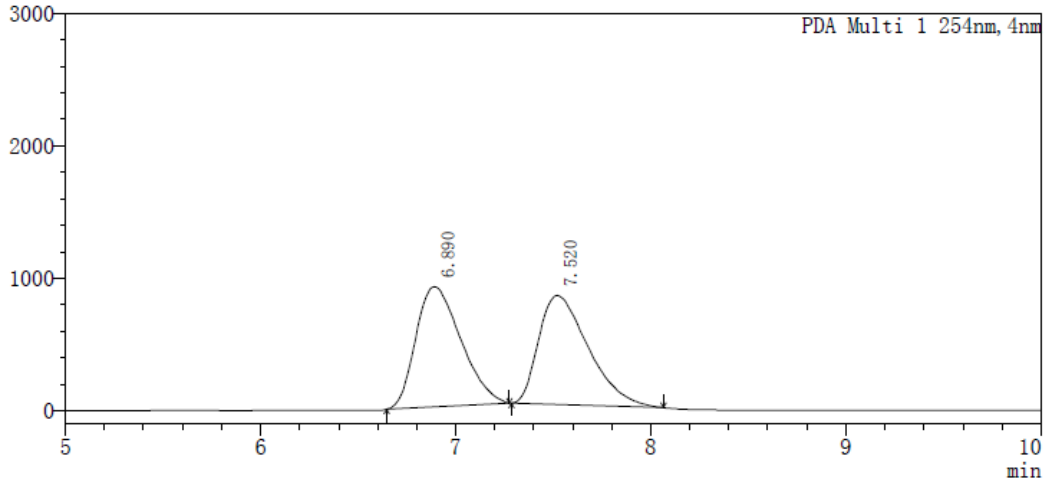
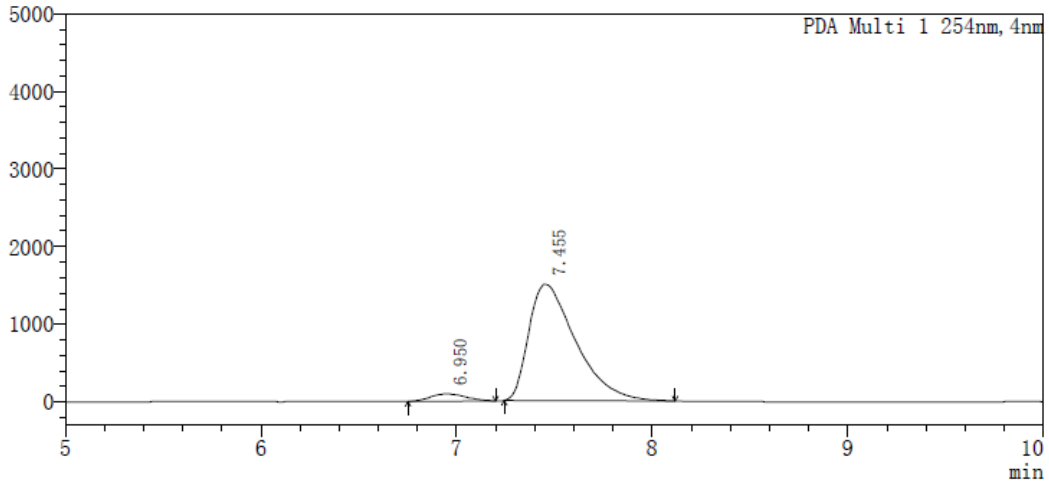


〈峰表〉

PDA Ch1 254nm

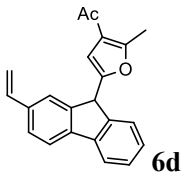
峰号	保留时间	面积	高度	化合物名	面积%	高度%
1	6.890	14551899	907034		50.010	52.485
2	7.520	14546075	821145		49.990	47.515
总计		29097973	1728178		100.000	100.000



〈峰表〉

PDA Ch1 254nm

峰号	保留时间	面积	高度	化合物名	面积%	高度%
1	6.950	1204013	94488		4.578	5.923
2	7.455	25098842	1500726		95.422	94.077
总计		26302855	1595214		100.000	100.000



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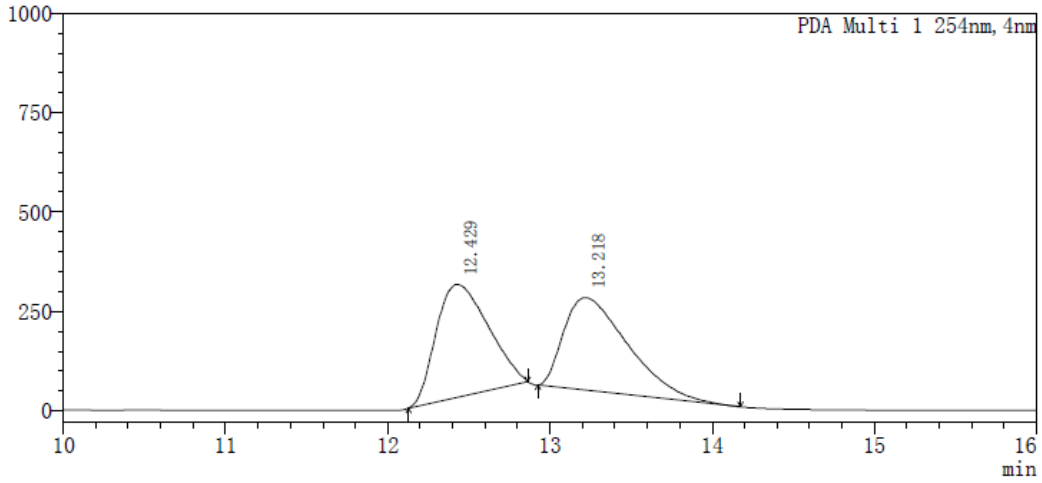
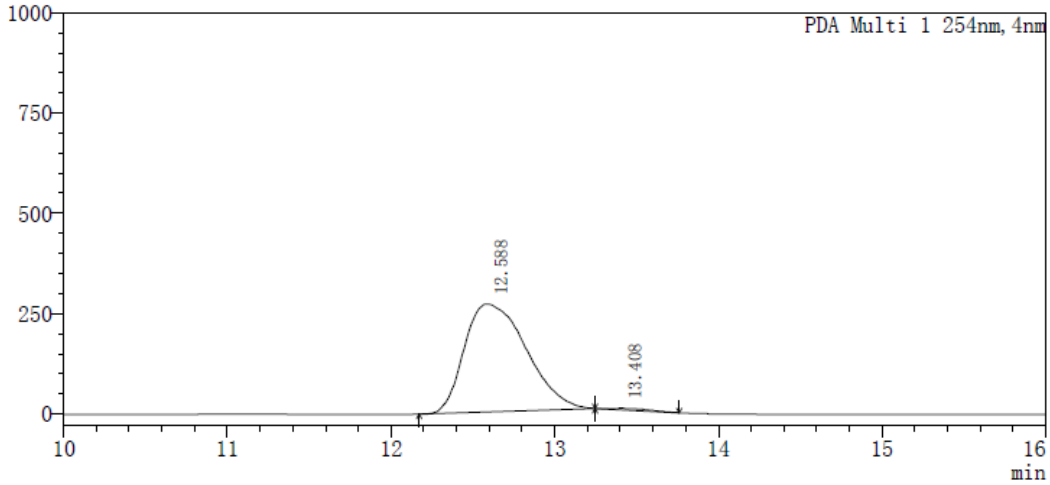


〈峰表〉

PDA Ch1 254nm

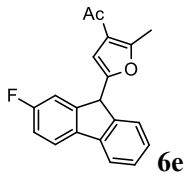
峰号	保留时间	面积	高度	化合物名	面积%	高度%
1	12.429	6334331	283978		49.658	54.951
2	13.218	6421708	232807		50.342	45.049
总计		12756039	516785		100.000	100.000



〈峰表〉

PDA Ch1 254nm

峰号	保留时间	面积	高度	化合物名	面积%	高度%
1	12.588	7076919	269331		99.087	98.628
2	13.408	65209	3746		0.913	1.372
总计		7142128	273077		100.000	100.000



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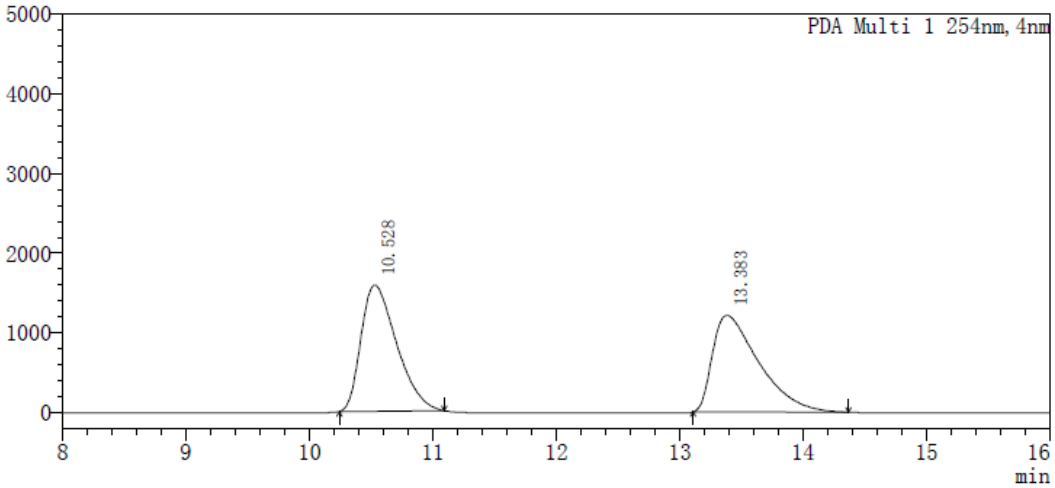
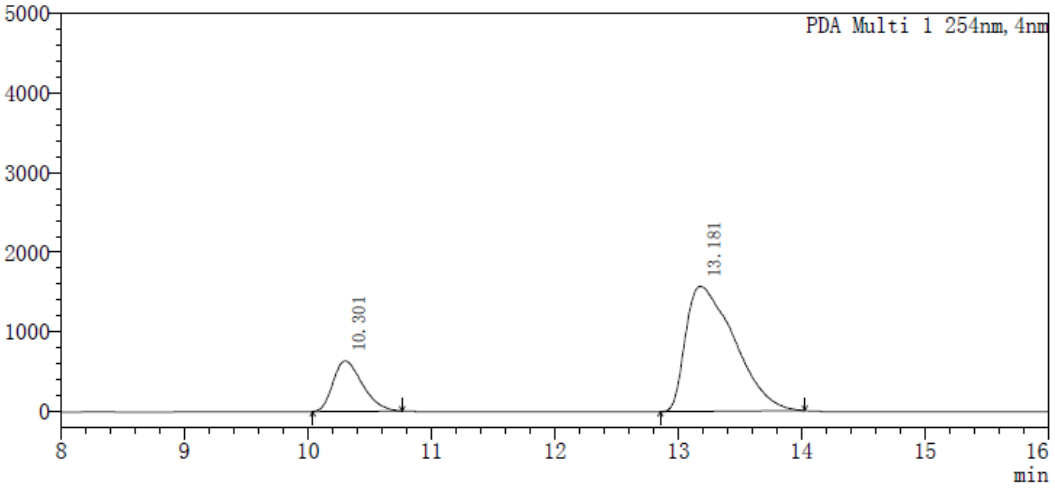


〈峰表〉

PDA Ch1 254nm

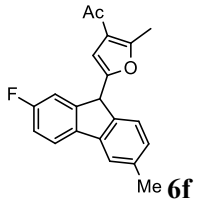
峰号	保留时间	面积	高度	化合物名	面积%	高度%
1	10.528	31742770	1581265		50.044	56.607
2	13.383	31687064	1212156		49.956	43.393
总计		63429834	2793420		100.000	100.000



〈峰表〉

PDA Ch1 254nm

峰号	保留时间	面积	高度	化合物名	面积%	高度%
1	10.301	10437922	631541		19.467	28.714
2	13.181	43181893	1567886		80.533	71.286
总计		53619815	2199427		100.000	100.000



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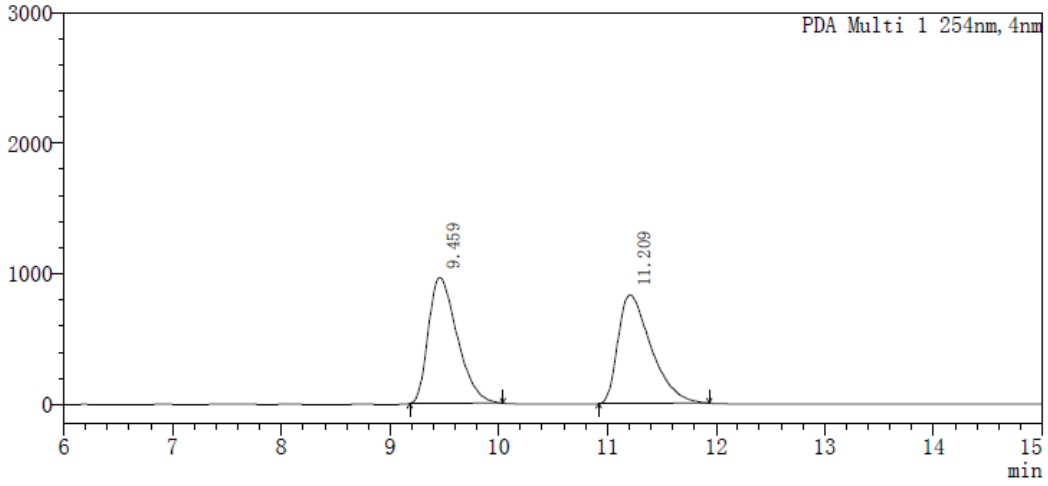
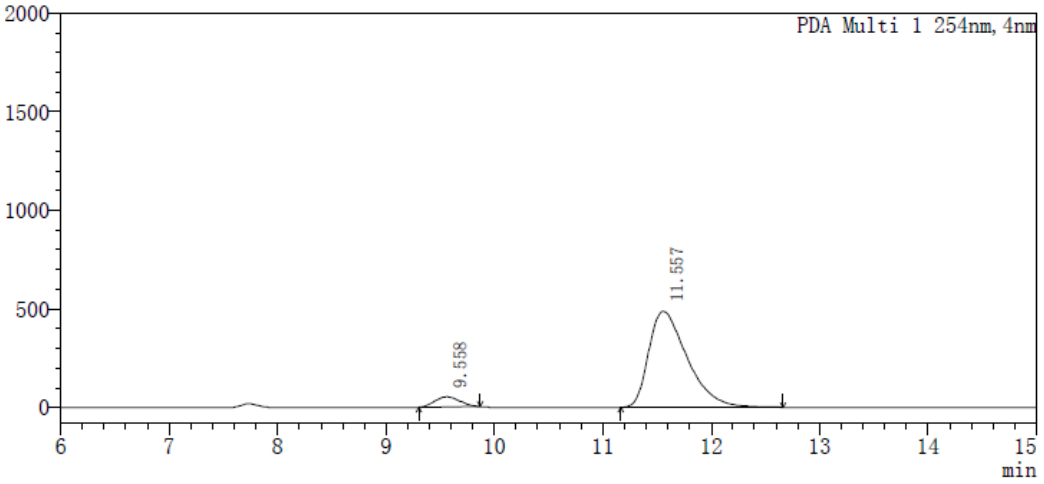


〈峰表〉

PDA Ch1 254nm

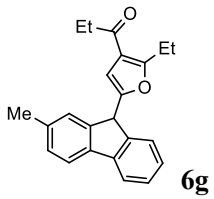
峰号	保留时间	面积	高度	化合物名	面积%	高度%
1	9.459	17783809	962660		50.246	53.653
2	11.209	17609946	831572		49.754	46.347
总计		35393755	1794232		100.000	100.000



〈峰表〉

PDA Ch1 254nm

峰号	保留时间	面积	高度	化合物名	面积%	高度%
1	9.558	829074	51369		6.449	9.547
2	11.557	12026722	486719		93.551	90.453
总计		12855795	538087		100.000	100.000



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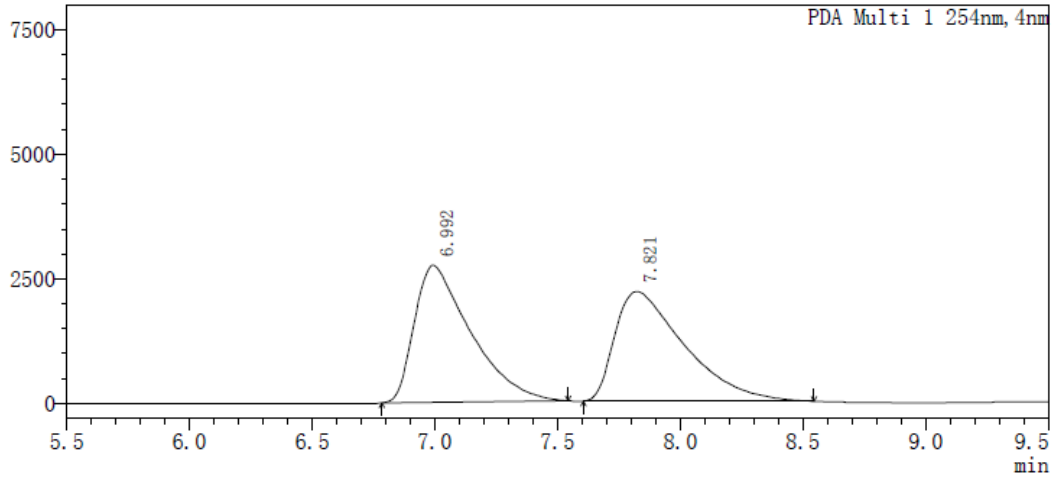
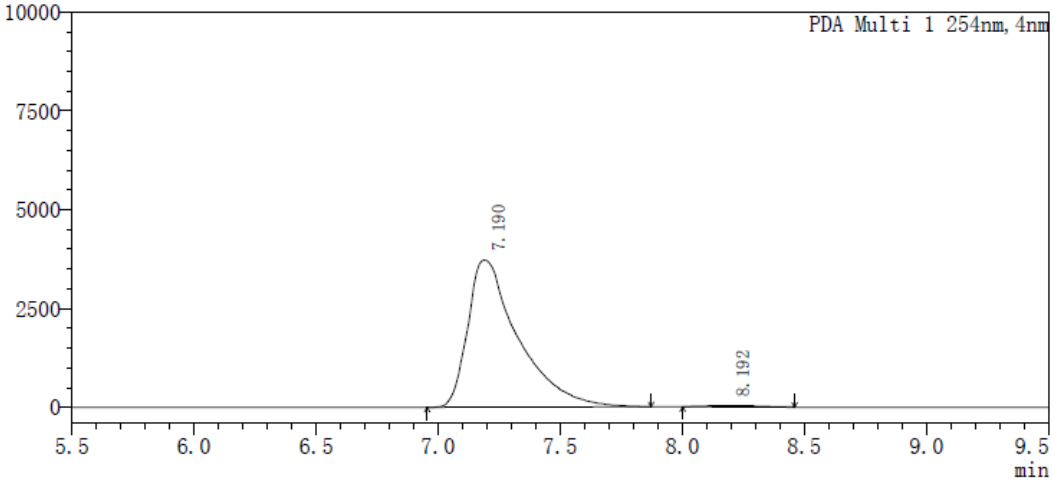


〈峰表〉

PDA Ch1 254nm

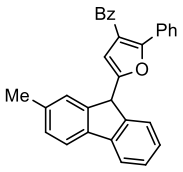
峰号	保留时间	面积	高度	化合物名	面积%	高度%
1	6.992	43896140	2747402		50.359	55.533
2	7.821	43269678	2199947		49.641	44.467
总计		87165818	4947349		100.000	100.000



〈峰表〉

PDA Ch1 254nm

峰号	保留时间	面积	高度	化合物名	面积%	高度%
1	7.190	53384828	3719318		98.984	99.020
2	8.192	548113	36809		1.016	0.980
总计		53932941	3756126		100.000	100.000



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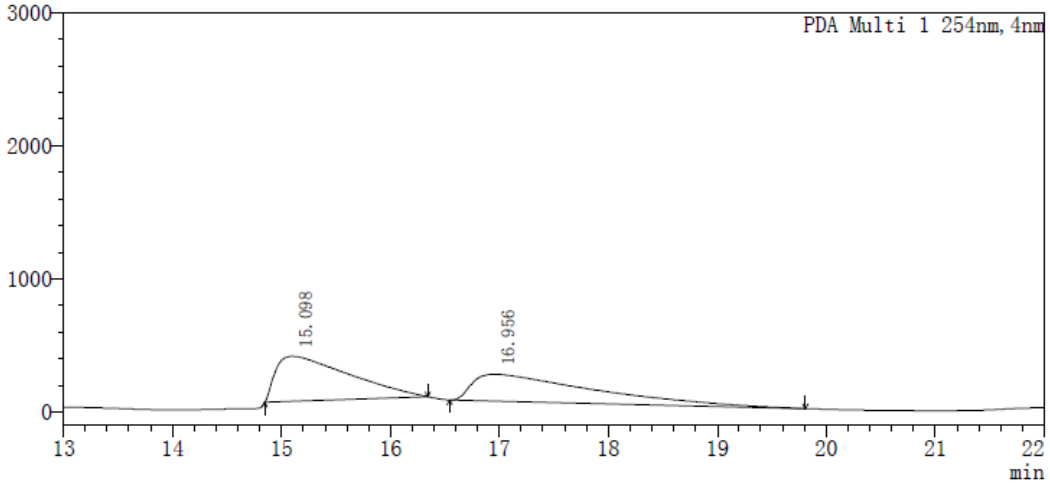
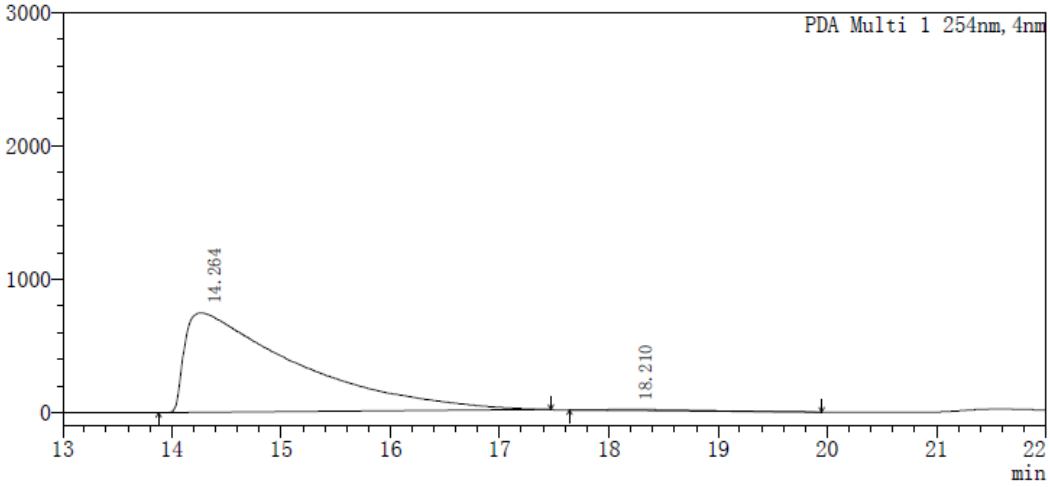


〈峰表〉

PDA Ch1 254nm

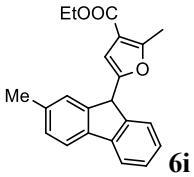
峰号	保留时间	面积	高度	化合物名	面积%	高度%
1	15.098	15795906	338740		50.387	62.702
2	16.956	15553312	201495		49.613	37.298
总计		31349217	540235		100.000	100.000



〈峰表〉

PDA Ch1 254nm

峰号	保留时间	面积	高度	化合物名	面积%	高度%
1	14.264	52822874	743697		99.194	99.090
2	18.210	428964	6829		0.806	0.910
总计		53251837	750526		100.000	100.000



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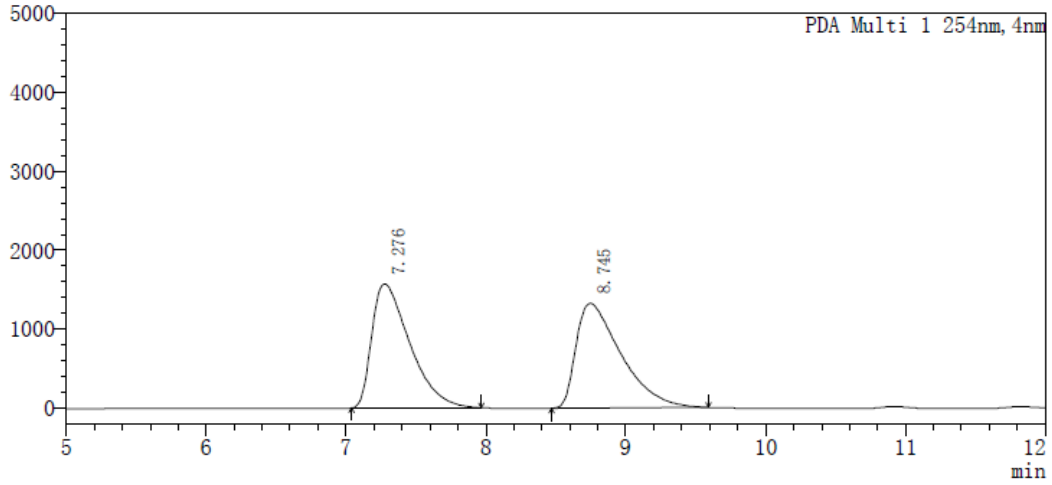
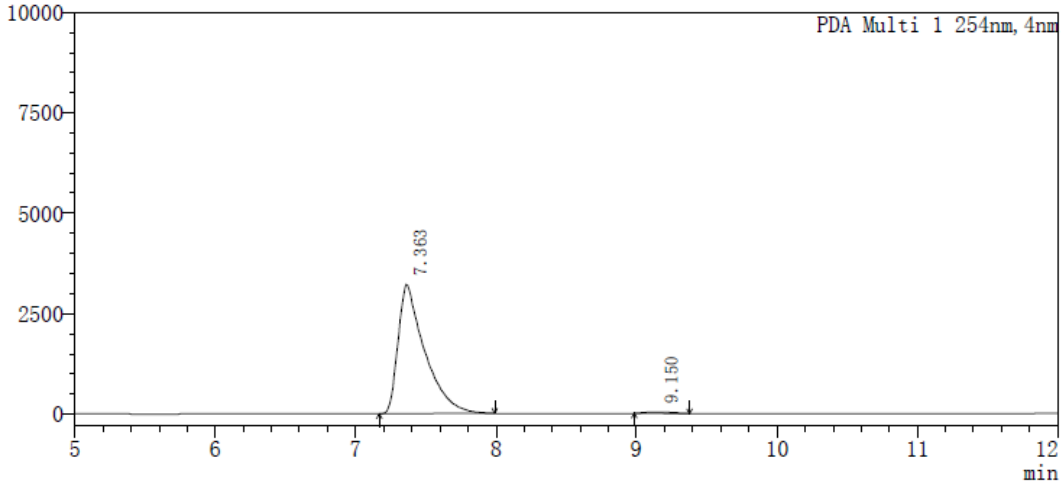


〈峰表〉

PDA Ch1 254nm

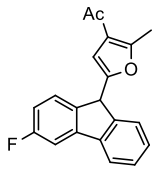
峰号	保留时间	面积	高度	化合物名	面积%	高度%
1	7.276	29607740	1568146		50.005	54.255
2	8.745	29601968	1322159		49.995	45.745
总计		59209708	2890305		100.000	100.000



〈峰表〉

PDA Ch1 254nm

峰号	保留时间	面积	高度	化合物名	面积%	高度%
1	7.363	42428434	3219757		98.855	98.865
2	9.150	491315	36965		1.145	1.135
总计		42919750	3256722		100.000	100.000



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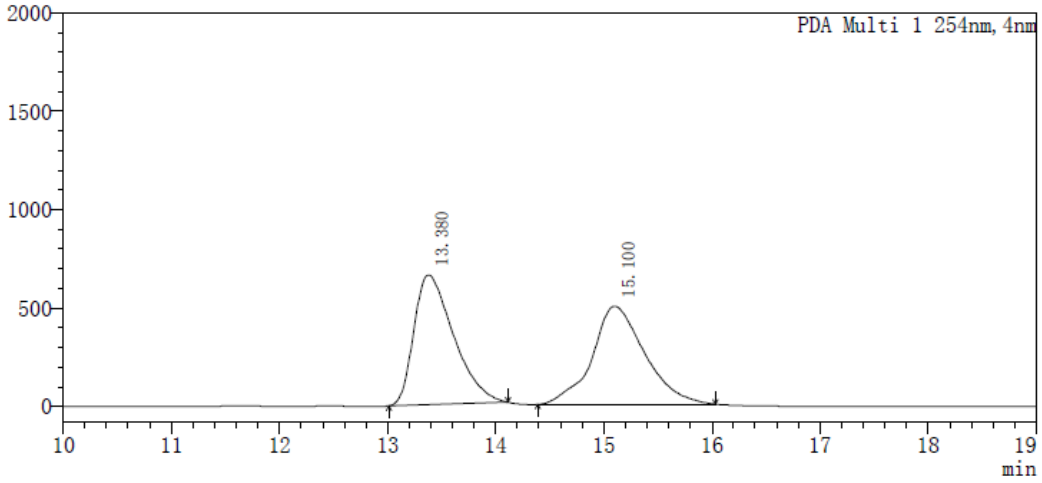
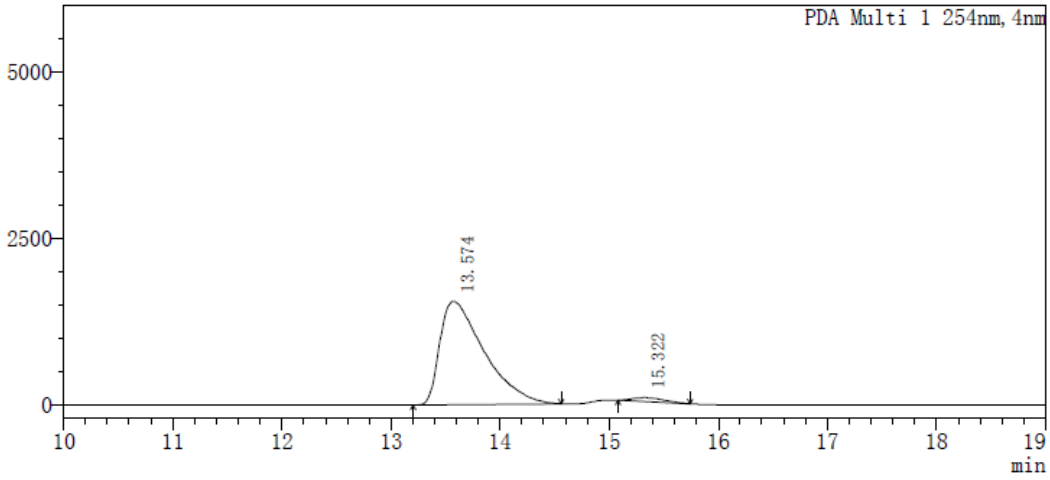


〈峰表〉

PDA Ch1 254nm

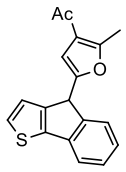
峰号	保留时间	面积	高度	化合物名	面积%	高度%
1	13.380	16773609	657593		49.856	56.948
2	15.100	16870375	497137		50.144	43.052
总计		33643984	1154730		100.000	100.000



〈峰表〉

PDA Ch1 254nm

峰号	保留时间	面积	高度	化合物名	面积%	高度%
1	13.574	43730114	1549584		97.452	96.447
2	15.322	1143154	57081		2.548	3.553
总计		44873268	1606665		100.000	100.000



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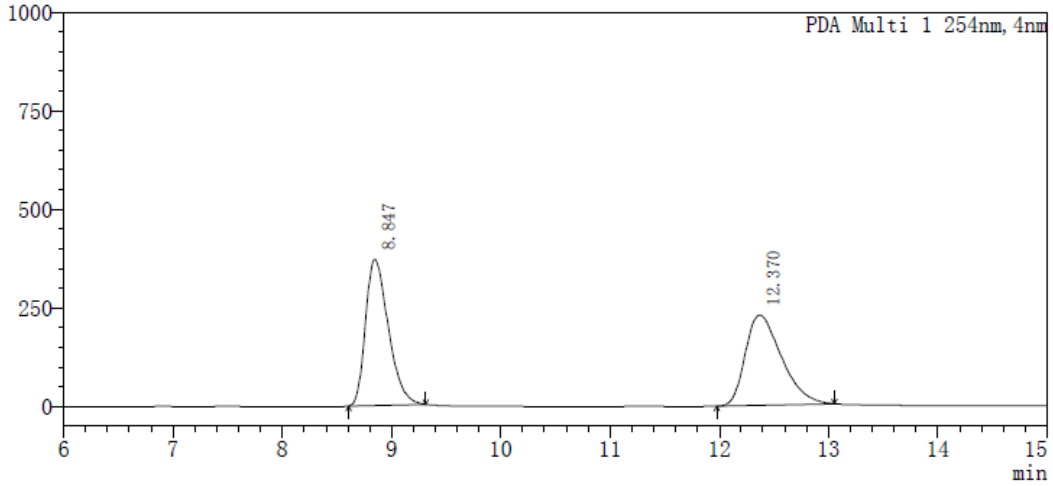
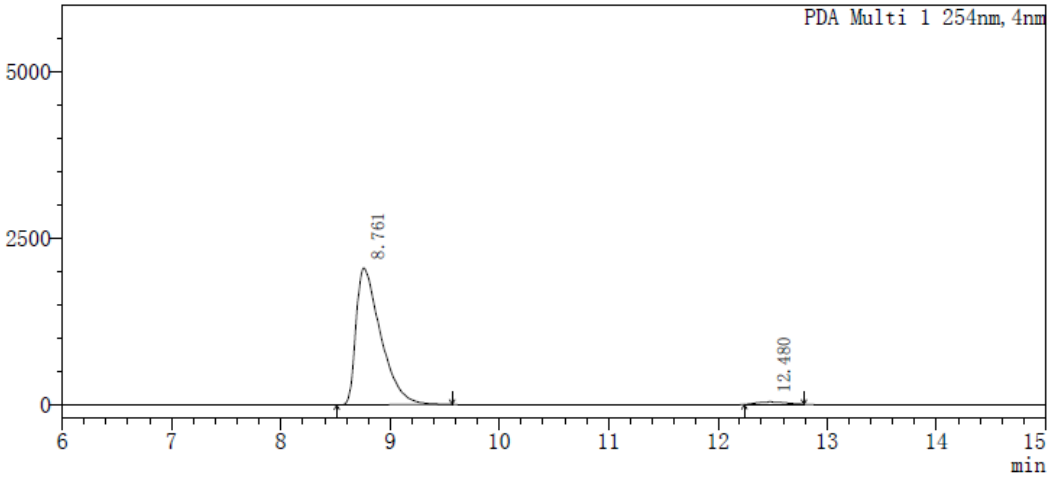


〈峰表〉

PDA Ch1 254nm

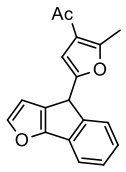
峰号	保留时间	面积	高度	化合物名	面积%	高度%
1	8.847	5381753	371024		50.486	61.783
2	12.370	5278065	229500		49.514	38.217
总计		10659818	600524		100.000	100.000



〈峰表〉

PDA Ch1 254nm

峰号	保留时间	面积	高度	化合物名	面积%	高度%
1	8.761	32326458	2049509		98.001	98.247
2	12.480	659442	36563		1.999	1.753
总计		32985899	2086072		100.000	100.000



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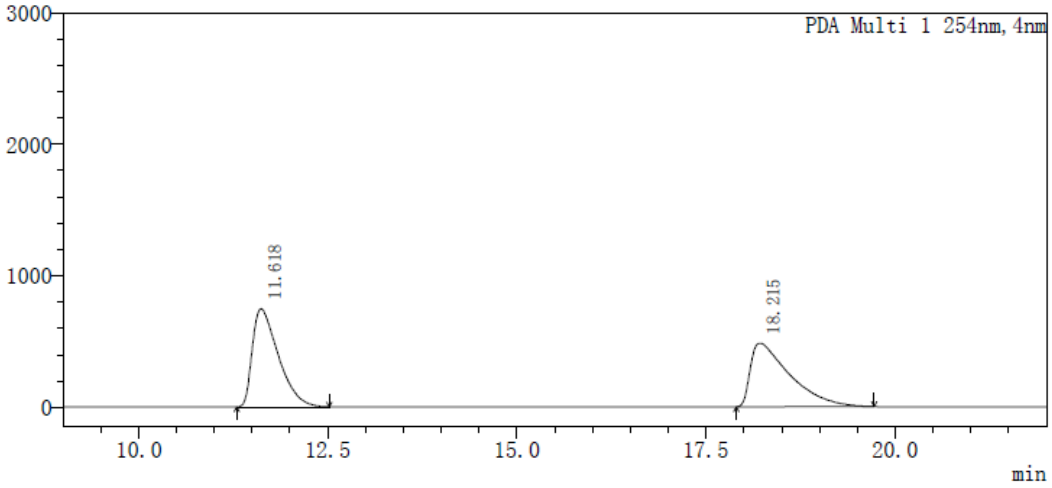
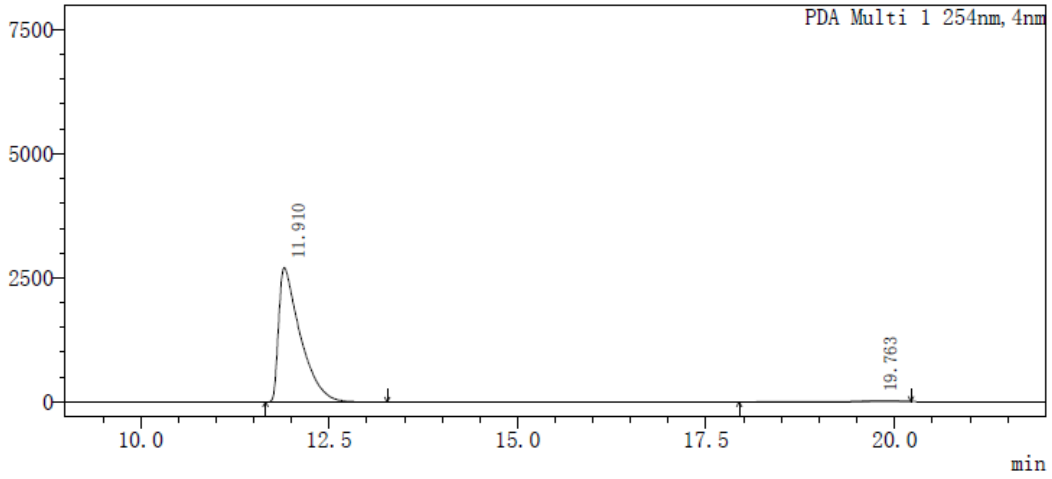


〈峰表〉

PDA Ch1 254nm

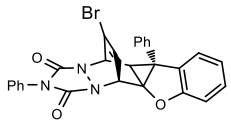
峰号	保留时间	面积	高度	化合物名	面积%	高度%
1	11.618	17849740	746353		50.432	60.646
2	18.215	17543763	484322		49.568	39.354
总计		35393504	1230675		100.000	100.000



〈峰表〉

PDA Ch1 254nm

峰号	保留时间	面积	高度	化合物名	面积%	高度%
1	11.910	54095626	2701619		99.488	99.356
2	19.763	278481	17522		0.512	0.644
总计		54374107	2719141		100.000	100.000



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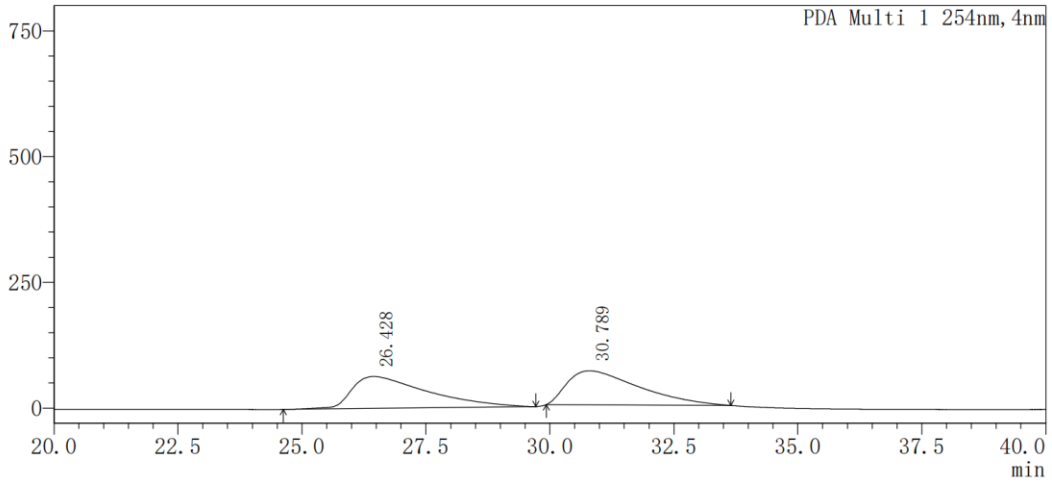
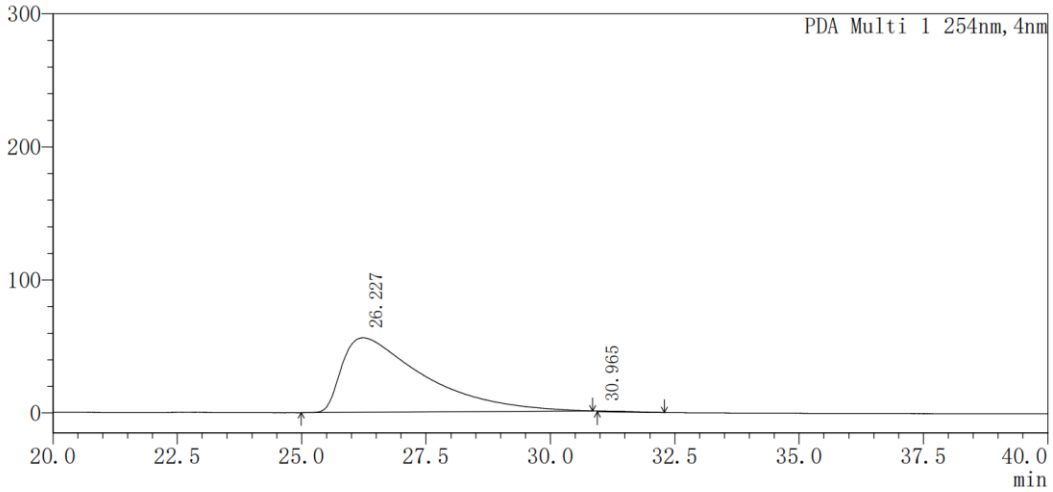


〈峰表〉

PDA Ch1 254nm

峰号	保留时间	面积	高度	面积%	高度%
1	26.428	6723481	63339	49.552	48.359
2	30.789	6844931	67639	50.448	51.641
总计		13568412	130977	100.000	100.000

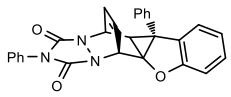
mAU



〈峰表〉

PDA Ch1 254nm

峰号	保留时间	面积	高度	面积%	高度%
1	26.227	6425231	56103	99.527	98.939
2	30.965	30546	601	0.473	1.061
总计		6455777	56704	100.000	100.000



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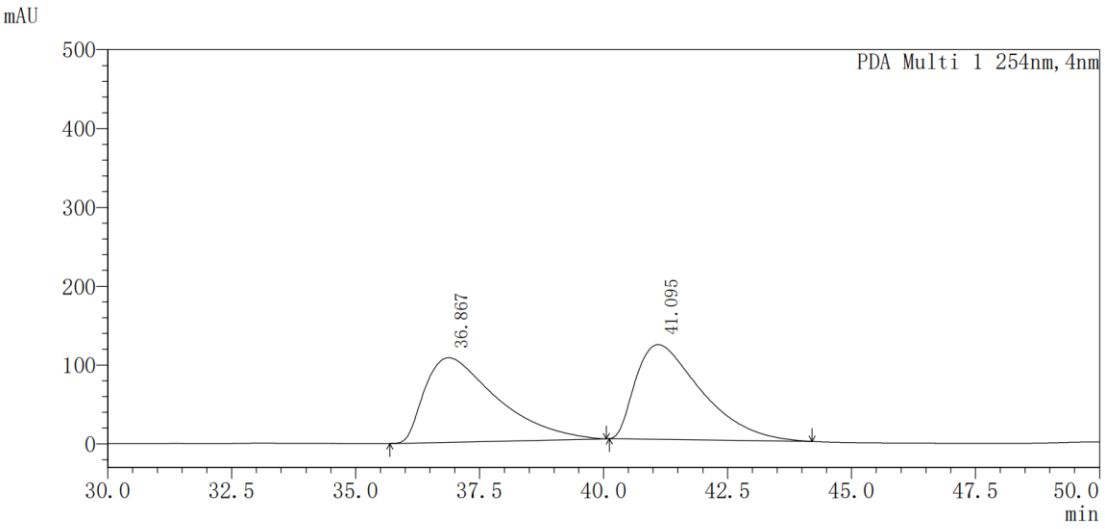
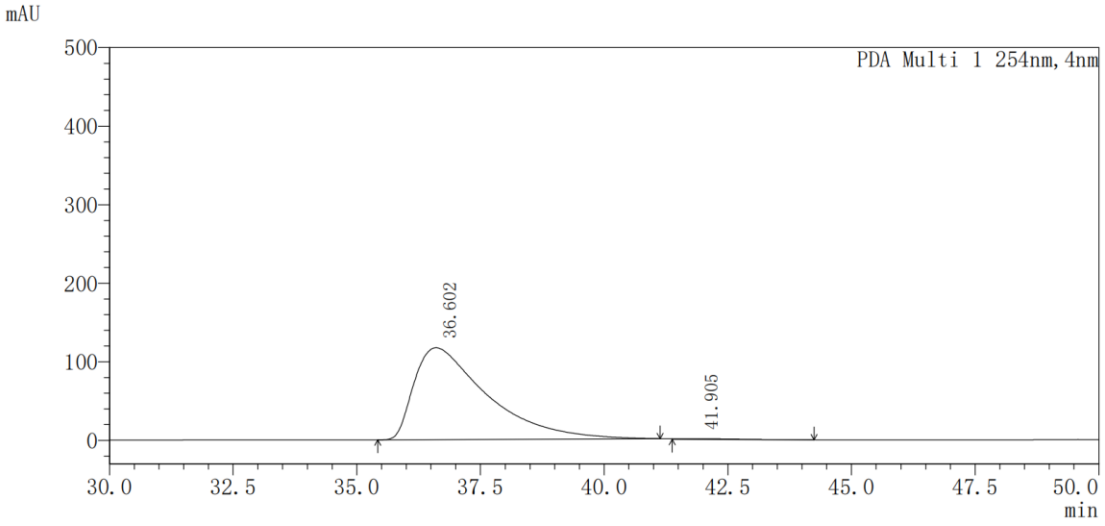


〈峰表〉

PDA Ch1 254nm

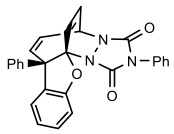
峰号	保留时间	面积	高度	面积%	高度%
1	36.867	10878011	107290	49.533	47.155
2	41.095	11082954	120237	50.467	52.845
总计		21960965	227526	100.000	100.000



〈峰表〉

PDA Ch1 254nm

峰号	保留时间	面积	高度	面积%	高度%
1	36.602	11997841	116955	99.414	99.344
2	41.905	70767	772	0.586	0.656
总计		12068608	117727	100.000	100.000



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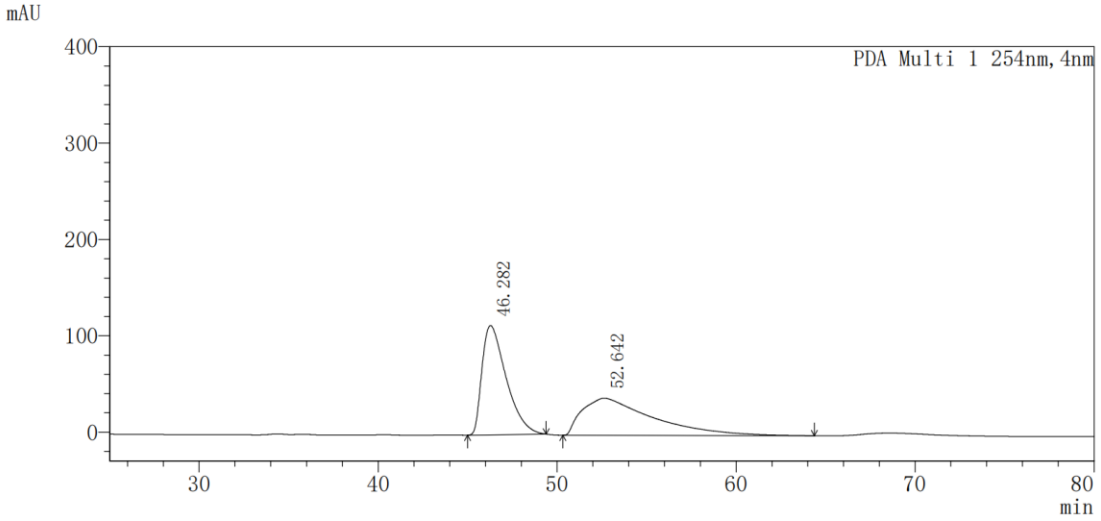
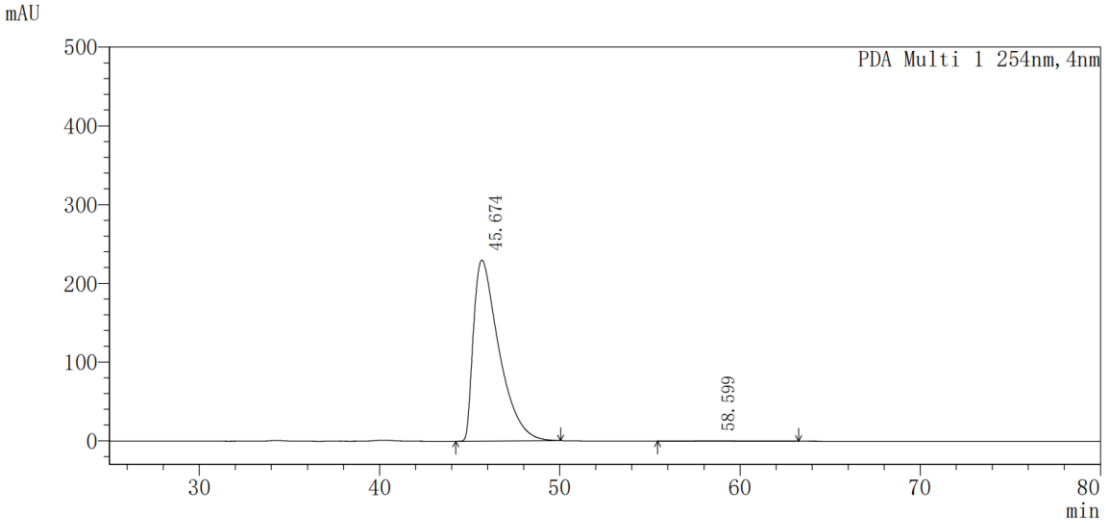


〈峰表〉

PDA Ch1 254nm

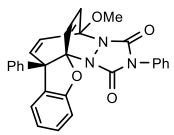
峰号	保留时间	面积	高度	面积%	高度%
1	46.282	10659504	113358	50.291	74.650
2	52.642	10536147	38495	49.709	25.350
总计		21195651	151853	100.000	100.000



〈峰表〉

PDA Ch1 254nm

峰号	保留时间	面积	高度	面积%	高度%
1	45.674	22664478	230094	99.615	99.816
2	58.599	87508	423	0.385	0.184
总计		22751986	230517	100.000	100.000



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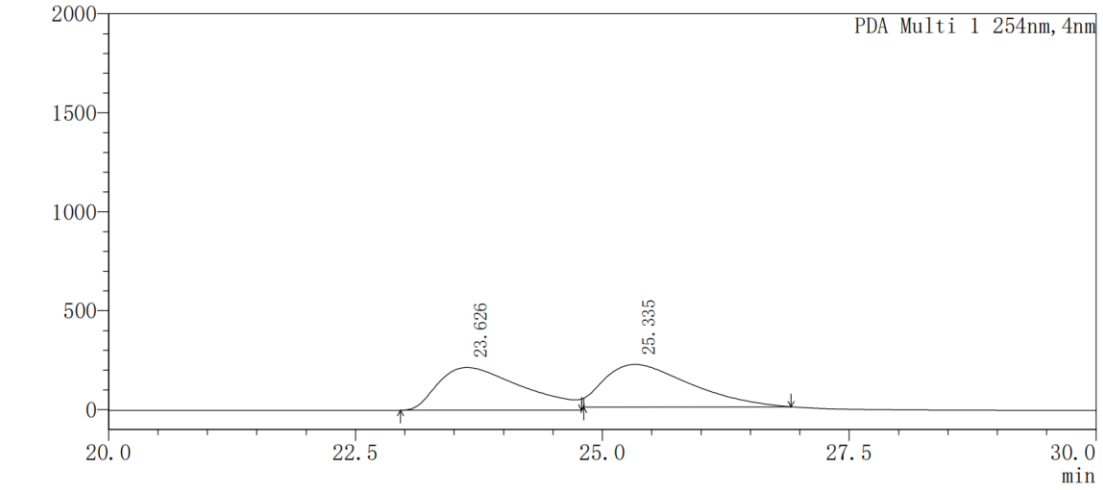
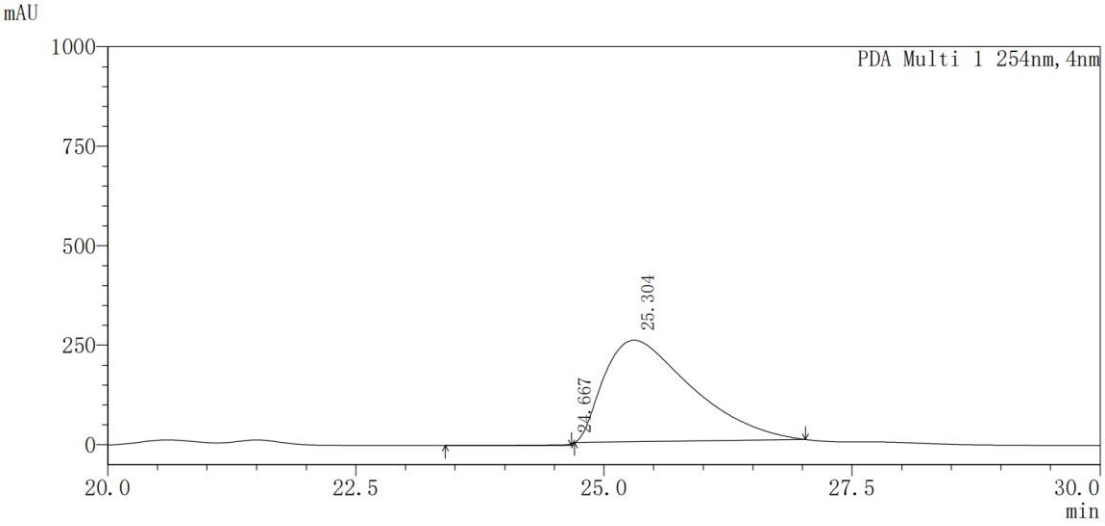


〈峰表〉

PDA Ch1 254nm

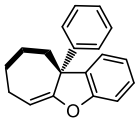
峰号	保留时间	面积	高度	面积%	高度%
1	23.626	12945635	215385	49.405	49.976
2	25.335	13257243	215592	50.595	50.024
总计		26202878	430977	100.000	100.000



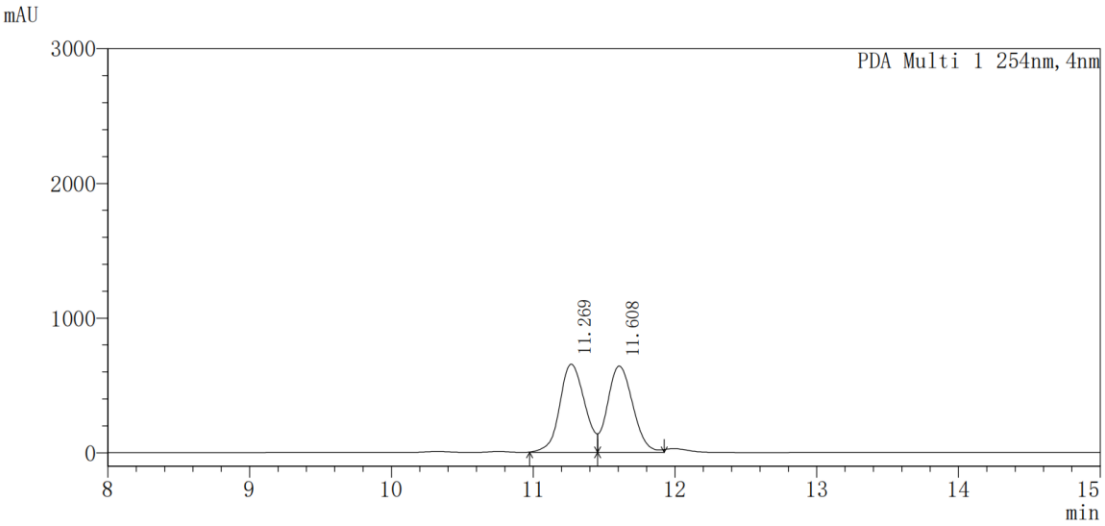
〈峰表〉

PDA Ch1 254nm

峰号	保留时间	面积	高度	面积%	高度%
1	24.667	52310	3761	0.331	1.452
2	25.304	15754694	255204	99.669	98.548
总计		15807004	258966	100.000	100.000



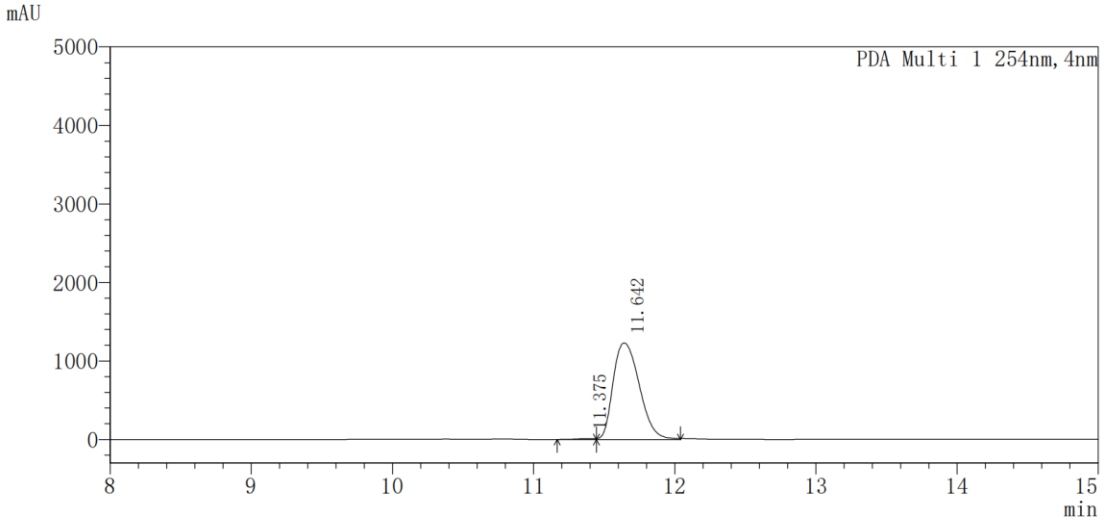
12



〈峰表〉

PDA Ch1 254nm

峰号	保留时间	面积	高度	面积%	高度%
1	11.269	8069011	654119	50.523	50.485
2	11.608	7902077	641553	49.477	49.515
总计		15971088	1295672	100.000	100.000



〈峰表〉

PDA Ch1 254nm

峰号	保留时间	面积	高度	面积%	高度%
1	11.375	96914	10119	0.606	0.816
2	11.642	15884787	1229933	99.394	99.184
总计		15981701	1240052	100.000	100.000