Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

Ru(II)-Catalyzed Cascade *cis* Carbohalogenation and Cyclization of Alkyne-tethered Cyclohexadienones for Tetrasubstituted Alkenes

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Contents

1. General methods

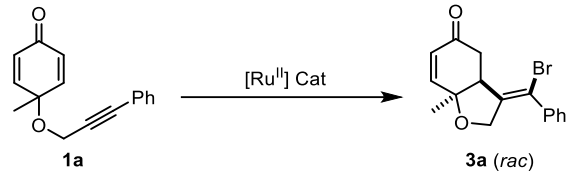
All reactions and manipulations involving air-sensitive compounds were performed using standard Schlenk techniques. Melting points were measured on an SGW$_{@}$X-4B apparatus and uncorrected. ^{1}H, ^{13}C and ^{19}F NMR spectra were recorded on Bruker AV400 or JNM-ECZ400S/L1 400 MHz spectrometers. Chemical shifts (δ values) were reported in ppm with internal TMS (^{1}H NMR), $CDCl_3$ (^{13}C NMR), DMSO-d_6 (^{13}C NMR) or external CF_3CO_2H (^{19}F NMR) as references, respectively. HRMS (ESI) were determined on Agilent Technologies 6224 TOF LC/MS. IR spectra were measured on a NICOLET iS10 spectrometer. Single crystal X-ray diffraction date was recorded on Bruker D8 Venture or Bruker SMART CCD diffractometers. Column chromatography was performed on silica gel (200-300 mesh) using a mixture of petroleum ether (60-90 ºC)/ethyl acetate as the eluent.

2. Synthesis of substrates

Alkyne-tethered cyclohexadienones **1** were synthesized according to the literature[1, 2] and all data were in agreement with those reported[1, 2].

3. Optimization of reaction conditions

Table S1 Optimization of the reaction conditions of *cis* carbobromination[a]

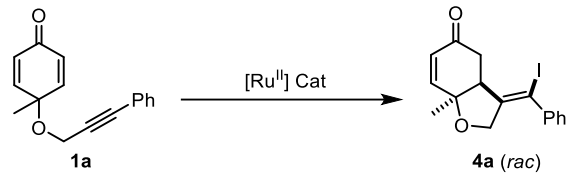


1a **3a** (*rac*)

Entry	catalyst	solvent	halide source	yield **3a**[f] (%)
1[b]	[$RuCl_2$(*p*-cymene)]$_2$	Toluene	$^{n}Et_4NBr$	73 (>20:1)
2	Ru(OAc)$_2$(*p*-cymene)	Toluene	$^{n}Et_4NBr$	83 (>20:1)
3	Ru(OAc)$_2$(*p*-cymene)	Toluene	$^{n}Bu_4NBr$	85 (>20:1)
4	Ru(OAc)$_2$(*p*-cymene)	Toluene	$^{n}Heptyl_4NBr$	81 (>20:1)
5[c]	Ru(OAc)$_2$(*p*-cymene)	Toluene	$^{n}Bu_4NBr$	79 (>20:1)
6[d]	Ru(OAc)$_2$(*p*-cymene)	Toluene	$^{n}Bu_4NBr$	76 (>20:1)
7[e]	Ru(OAc)$_2$(*p*-cymene)	Toluene	$^{n}Bu_4NBr$	66 (>20:1)
8	Ru(OAc)$_2$(*p*-cymene)	Dioxane	$^{n}Bu_4NBr$	52 (>20:1)
9	Ru(OAc)$_2$(*p*-cymene)	MeCN	$^{n}Bu_4NBr$	NR
10	Ru(OAc)$_2$(*p*-cymene)	THF	$^{n}Bu_4NBr$	86 (>20:1)
11	Ru(OAc)$_2$(*p*-cymene)	PhCl	$^{n}Bu_4NBr$	91 (>20:1)
12	Ru(OAc)$_2$(*p*-cymene)	EtOH	$^{n}Bu_4NB$	49 (>20:1)

[a] Reaction conditions: $Ru(OAc)_2$(*p*-cymene) (10 mol%), **1a** (0.1 mmol), halide source (2.0 equiv), HOAc (20.0 equiv), solvent (1.0 mL) at 100 °C under N_2 for 24 h; [b] $[RuCl_2(p\text{-cymene})]_2$ (5 mol%); [c] HOAc (10.0 equiv); [d] ^{n}Bu$_4$NBr (1.5 equiv); [e] ^{n}Bu$_4$NBr (3.0 equiv); [f] All *E*/*Z* ratios were determinded by ^{1}H NMR.

Table S2 Optimization of the reaction conditions of *cis* carboiodination[a]

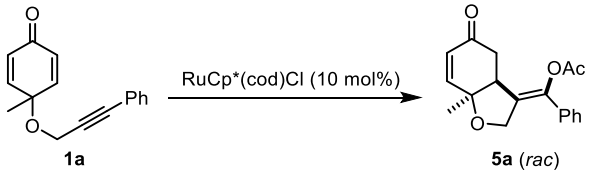


1a **4a** (*rac*)

Entry	catalyst	solvent	halide source	yield **4a**[f] (%)
1[b]	$[RuI_2(p\text{-cymene})]_2$	Toluene	^{n}Et$_4$NI	53 (>20:1)
2[b]	$[RuI_2(p\text{-cymene})]_2$	Toluene	^{n}Bu$_4$NI	72 (>20:1)
3[b]	$[RuI_2(p\text{-cymene})]_2$	Toluene	^{n}Heptyl$_4$NI	67 (>20:1)
4	$Ru(OAc)_2$(p-cymene)	Toluene	^{n}Bu$_4$NI	91 (>20:1)
5[c]	$Ru(OAc)_2$(p-cymene)	Toluene	^{n}Bu$_4$NI	58 (>20:1)
6[d]	$Ru(OAc)_2$(p-cymene)	Toluene	^{n}Bu$_4$NI	79 (>20:1)
7[e]	$Ru(OAc)_2$(p-cymene)	Toluene	^{n}Bu$_4$NI	75 (>20:1)
8	$Ru(OAc)_2$(p-cymene)	Dioxane	^{n}Bu$_4$NI	80 (>20:1)
9	$Ru(OAc)_2$(p-cymene)	MeCN	^{n}Bu$_4$NI	NR
10	$Ru(OAc)_2$(p-cymene)	THF	^{n}Bu$_4$NI	74 (>20:1)
11	$Ru(OAc)_2$(p-cymene)	PhCl	^{n}Bu$_4$NI	74 (>20:1)

[a] Reaction conditions: Catalyst (10 mol%), **1a** (0.1 mmol), halide source (2.0 equiv), HOAc (20.0 equiv), solvent (1.0 mL) at 100 °C under N_2 for 48 h; [b] $[RuI_2(p\text{-cymene})]_2$ (5 mol%); [c] HOAc (10.0 equiv); [d] ^{n}Bu$_4$NI (1.5 equiv); [e] ^{n}Bu$_4$NI (3.0 equiv); [f] All *E*/*Z* ratios were determinded by ^{1}H NMR.

Table S3 Optimization of the reaction conditions of *cis* carbooxygenation[a]



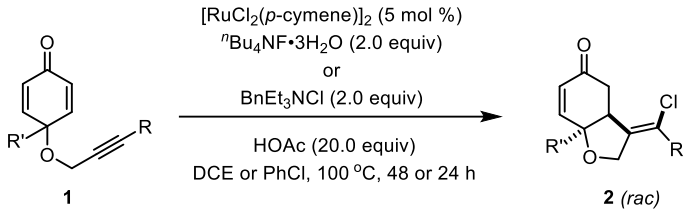
1a **5a** (*rac*)

Entry	Solvent	Additive	T (°C)	yield **5a**[d] (%)
1	DCE	AgOAc	40	53 (>20:1)
2	DCE	AgOAc	60	90 (>20:1)
3	DCE	AgOAc	80	80 (>20:1)
4	PhCl	AgOAc	60	77 (>20:1)
5	Dioxane	AgOAc	60	88 (>20:1)
6	MeCN	AgOAc	60	11 (>20:1)
7	Toluene	AgOAc	60	41 (>20:1)
8	EtOH	AgOAc	60	17 (>20:1)
9	THF	AgOAc	60	92 (>20:1)
10[b]	THF	AgOAc	60	83 (>20:1)
11[c]	THF	AgOAc	60	80 (>20:1)
12	THF	NaOAc	60	79 (>20:1)

[a] Reaction conditions: RuCp*(cod)Cl (10 mol%), **1a** (0.1 mmol), additive (0.5 equiv), HOAc (20.0 equiv), solvent (1.0 mL) at 60 ℃ under N_2 for 15 h; [b] AgOAc (0.2 equiv); [c] HOAc (10.0 equiv); [d] All *E*/*Z* ratios were determinded by ^{1}H NMR.

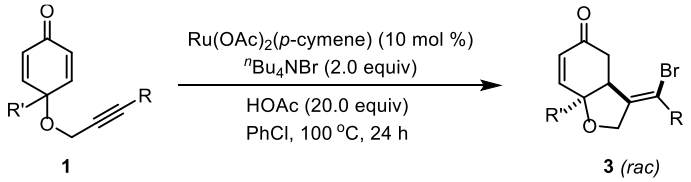
4. General procedure for the *cis* Carbohalogenation

a) General procedure for the *cis* carbochlorination



A sealed tube (25 mL) charged with a stir bar was added $[RuCl_2(p\text{-cymene})]_2$ (6.2 mg, 0.01 mmol, 5 mol%), alkynes **1** (0.20 mmol, 1.0 equiv) and ^{n}Bu$_4$NF·3H$_2$O (126.2 mg, 0.40 mmol, 2.0 equiv) or $BnEt_3NCl$ (91.1 mg, 0.40 mmol, 2.0 equiv). The tube was purged three times by vacuum and N_2, then anhydrous DCE (4.0 mL, 0.05 M) or PhCl (4.0 mL,0.05 M) was added. At last, glacial HOAc (229 μL, 4.0 mmol, 20.0 equiv) was added and the resulted mixture was stirred and heated at 100 ℃ in an oil bath for 48 or 24 h. Upon completion, the reaction mixture was cooled to room temperature, and quenched with aqueous saturated $NaHCO_3$ and then extracted with EtOAc (20 mL × 3), and then dried over anhydrous Na_2SO_4, filtered and concentrated in vacuo. The residue was purified by column chromatography using petroleum ether/ethyl acetate mixture as the eluent, which afforded the carbochlorination products **2**.

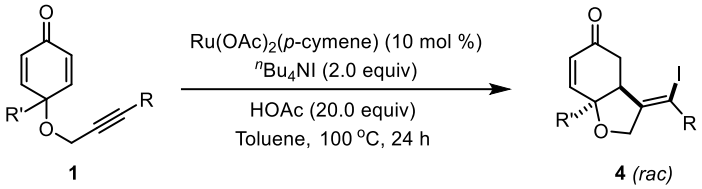
b) General procedure for the *cis* carbobromination



A sealed tube (25 mL) charged with a stir bar was added $Ru(OAc)_2(p\text{-cymene})$ (7.1 mg, 0.02 mmol, 10 mol%), alkynes **1** (0.20 mmol, 1.0 equiv) and ^{n}Bu$_4$NBr (128.9 mg, 0.40 mmol, 2.0 equiv). The tube was purged three times by vacuum and N_2, then anhydrous PhCl (2.0 mL, 0.1 M) was added. At last, glacial HOAc (229 μL, 4.0 mmol, 20.0 equiv)

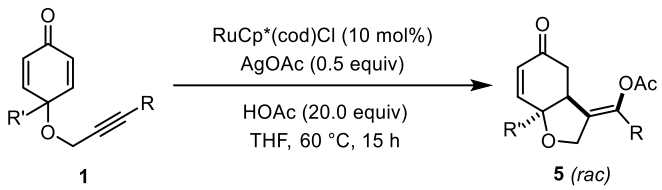
was added and the resulted mixture was stirred and heated at 100 ℃ in an oil bath for 24 h. Upon completion, the reaction mixture was cooled to room temperature, and quenched with aqueous saturated $NaHCO_3$ and then extracted with EtOAc (20 mL × 3), and then dried over anhydrous Na_2SO_4, filtered and concentrated in vacuo. The residue was purified by column chromatography using petroleum ether/ethyl acetate mixture as the eluent, which afforded carbobromination products **3**.

c) General procedure for the *cis* carboiodination



A sealed tube (25 mL) charged with a stir bar was added [$Ru(OAc)_2$(*p*-cymene)] (7.1 mg, 0.02 mmol, 10 mol%), alkynes **1** (0.20 mmol, 1.0 equiv) and $^{n}Bu_4NI$ (147.7 mg, 0.40 mmol, 2.0 equiv). The tube was purged three times by vacuum and N_2, then anhydrous toluene (2.0 mL, 0.1 M) was added. At last, glacial HOAc (229 μL, 4.0 mmol, 20.0 equiv) was added and the resulted mixture was stirred and heated at 100 ℃ in an oil bath for 48 h. Upon completion, the reaction mixture was cooled to room temperature, and quenched with aqueous saturated $NaHCO_3$ and then extracted with EtOAc (20 mL × 3), and then dried over anhydrous Na_2SO_4, filtered and concentrated in vacuo. The residue was purified by column chromatography using petroleum ether/ethyl acetate mixture as eluent, which afforded carboiodination products **4**.

d) General procedure for the *cis* carbooxygenation



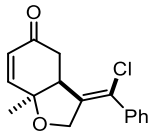
A sealed tube (25 mL) charged with a stir bar was added RuCp*(cod)Cl (7.6 mg, 0.02 mmol, 10 mol%), alkynes **1** (0.20 mmol, 1.0 equiv) and AgOAc (16.7 mg, 0.1 mmol, 0.5 equiv). The tube was purged three times by vacuum and N_2, then anhydrous THF

(2.0 mL, 0.1 M) was added. At last, glacial HOAc (229 μL, 4.0 mmol, 20.0 equiv) was added and the resulted mixture was stirred and heated at 60 ℃ in an oil bath for 15 h. Upon completion, the reaction mixture was cooled to room temperature, and quenched with aqueous saturated $NaHCO_3$ and then extracted with EtOAc (20 mL × 3), and then dried over anhydrous Na_2SO_4, filtered and concentrated in vacuo. The residue was purified by column chromatography using petroleum ether/ethyl acetate mixture as eluent, which afforded carbooxygenation products **5**.

5. Characterization data

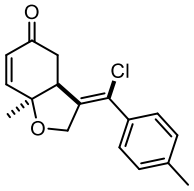
a) Characterization data for compounds 2

(*E*)-3-(chloro(phenyl)methylene)-7a-methyl-2,3,3a,7a-tetrahydrobenzofuran-5(4*H*)-one, 2a



Light yellow solid, 47.2 mg, 86% yield, PE : EtOAc = 5:1, M.p. 79 – 81 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.30 (m, 3H), 7.30 – 7.28 (m, 2H), 6.56 (dd, *J* = 10.1, 0.8 Hz, 1H), 6.14 (d, *J* = 10.1 Hz, 1H), 4.38 (dd, *J* = 13.2, 1.9 Hz, 1H), 4.23 (d, *J* = 13.1 Hz, 1H), 3.33 – 3.28 (m, 2H), 2.74 – 2.68 (m, 1H), 1.55 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.4, 149.8, 139.0, 137.8, 130.4, 129.1, 128.5, 127.9, 126.4, 79.8, 69.6, 49.1, 36.4, 24.0 ppm; FTIR (neat) υ 3027, 1680, 1489, 1091, 1009, 766 cm^{-1}; HRMS (ESI) m/z: Calcd. For $C_{16}H_{16}ClO_2^+$: 275.0833, Found: 275.0831 ($M+H^+$).

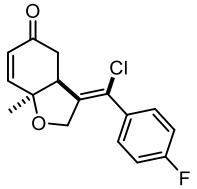
(*E*)-3-(chloro(*p*-tolyl)methylene)-7a-methyl-2,3,3a,7a-tetrahydrobenzofuran-5(*4H*)-one, 2b



Light yellow semisolid, 52.5 mg, 91% yield, PE : EtOAc = 5:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21 – 7.13 (m, 4H), 6.55 (d, *J* = 10.5 Hz, 1H), 6.13 (d, *J* = 10.5 Hz, 1H), 4.37

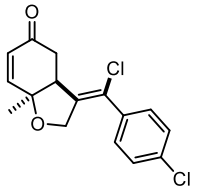
(dd, *J* = 13.1, 1.8 Hz, 1H), 4.22 (d, *J* = 13.1 Hz, 1H), 3.33 – 3.27 (m, 2H), 2.70 (dd, *J* = 17.9, 7.5 Hz, 1H), 2.35 (s, 3H), 1.54 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.5, 149.8, 139.1, 138.3, 135.0, 130.4, 129.1, 127.8, 126.5, 79.7, 69.6, 49.0, 36.3, 24.0, 21.3 ppm; FTIR (neat) υ 2846, 1677, 1450, 1121, 1045, 809, 717 cm^{-1}; HRMS (ESI) m/z: Calcd. $C_{17}H_{18}ClO_2^+$: 289.0990, Found: 289.0974 ($M+H^+$).

(*E*)-3-(chloro(4-fluorophenyl)methylene)-7a-methyl-2,3,3a,7a-tetrahydrobenzo-furan-5(*4H*)-one, 2c



Light yellow semisolid, 29.8 mg, 51% yield, PE : EtOAc = 5:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 – 7.26 (m, 2H), 7.07 – 7.01 (m, 2H), 6.55 (dd, *J* = 10.3, 1.0 Hz, 1H), 6.14 (d, *J* = 10.3 Hz, 1H), 4.34 (dd, *J* = 13.1, 2.0 Hz, 1H), 4.19 (d, *J* = 13.1 Hz, 1H), 3.32 – 3.29 (m, 2H), 2.70 (dd, *J* = 17.7, 7.3 Hz, 1H), 1.55 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.3, 162.8 (d, *J* = 249.6 Hz), 149.8, 139.2, 134.0 (d, *J* = 2.9 Hz), 130.5, 129.9 (d, *J* = 8.5 Hz), 125.4, 115.6 (d, *J* = 21.7 Hz), 79.9, 69.5, 49.1, 36.3, 24.0 ppm; ^{19}F NMR (376 MHz, $CDCl_3$) δ -111.1 ppm; FTIR (neat) υ 2924, 1682, 1600, 1506, 1229, 1091, 834 cm^{-1}; HRMS (ESI) m/z: Calcd. For $C_{16}H_{14}ClFO_2Na^+$: 315.0559, Found: 315.0570 ($M+Na^+$).

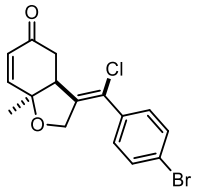
(*E*)-3-(chloro(4-chlorophenyl)methylene)-7a-methyl-2,3,3a,7a-tetrahydrobenzo-furan-5(*4H*)-one, 2d



Light yellow solide, 47.5 mg, 77% yield, PE : EtOAc = 5:1, M.p. 97 – 99 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 (d, *J* = 8.5 Hz, 2H), 7.23 (d, *J* = 8.5 Hz, 2H), 6.56 (d, *J* = 10.8 Hz, 1H), 6.14 (d, *J* = 10.8 Hz, 1H), 4.35 (dd, *J* = 13.2, 1.9 Hz, 1H), 4.20 (d, *J* = 13.2 Hz, 1H), 3.33 – 3.28 (m, 2H), 2.70 (dd, *J* = 17.6, 7.3 Hz, 1H), 1.55 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.3, 149.8, 139.8, 136.2, 135.0, 130.5, 129.3, 128.8,

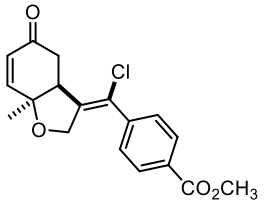
125.3, 79.9, 69.5, 49.2, 36.3, 24.0 ppm; FTIR (neat) υ 2920, 1681, 1488, 1091, 1042, 858, 745 cm^{-1}; HRMS (ESI) m/z: Calcd. For $C_{16}H_{14}Cl_2O_2Na^+$: 331.0263, Found: 331.0275 ($M+Na^+$).

(*E*)-3-((4-bromophenyl)chloromethylene)-7a-methyl-2,3,3a,7a-tetrahydrobenzofuran-5(*4H*)-one, 2e



Light yellow solid, 50 mg, 71% yield, PE : EtOAc = 5:1, M.p. 99 – 101 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 7.50 – 7.47 (m, 2H), 7.18 – 7.15 (m, 2H), 6.55 (dd, *J* = 10.3, 0.9 Hz, 1H), 6.14 (d, *J* = 10.3 Hz, 1H), 4.34 (dd, *J* = 13.2, 2.0 Hz, 1H), 4.19 (d, *J* = 13.2 Hz, 1H), 3.33 – 3.28 (m, 2H), 2.70 (dd, *J* = 17.7, 7.3 Hz, 1H), 1.55 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.3, 149.8, 139.8, 136.7, 131.7, 130.5, 129.5, 125.3, 123.3, 79.9, 69.5, 49.2, 36.3, 23.9 ppm; FTIR (neat) υ 3336, 2921, 1678, 1478, 1388, 1092, 1011, 835, cm^{-1}; HRMS (ESI) m/z: Calcd. For $C_{16}H_{15}BrClNO_2^+$: 352.9939, Found: 352.9947 ($M+H^+$).

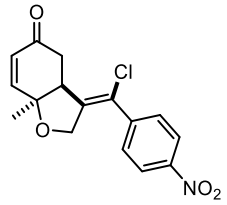
(*E*)-methyl 4-(chloro(7a-methyl-5-oxo-3a,4,5,7a-tetrahydrobenzofuran-3(*2H*)-ylidene)methyl)benzoate, 2f



Off-white solide, 49.8 mg, 75% yield, PE : EtOAc = 5:1, M.p. 118 – 119 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 8.03 – 8.01 (m, 2H), 7.38 – 7.36 (m, 2H), 6.57 (d, *J* = 10.2 Hz, 1H), 6.15 (d, *J* = 10.2 Hz, 1H), 4.39 (dd, *J* = 13.3, 1.8 Hz, 1H), 4.22 (d, *J* = 13.3 Hz, 1H), 3.93 (s, 3H), 3.34 – 3.29 (m, 2H), 2.76 – 2.70 (m, 1H), 1.56 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.1, 166.4, 149.7, 141.9, 140.9, 130.5, 129.7, 127.9, 125.3, 79.8, 69.4, 52.4, 49.3, 36.3, 23.9 ppm; FTIR (neat) υ 2918, 1720, 1665, 1276, 1078, 864, 769, cm^{-1}; HRMS (ESI) m/z: Calcd. For $C_{18}H_{18}ClO_4^+$: 333.0888, Found: 333.0894 ($M+H^+$).

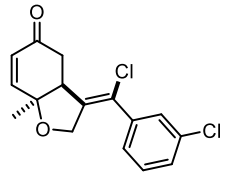
(*E*)-3-(chloro(4-nitrophenyl)methylene)-7a-methyl-2,3,3a,7a-tetrahydrobenzo-

furan-5(*4H*)-one, 2g



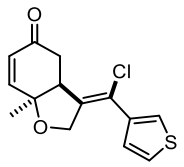
Light yellow solid, 40.8 mg, 64% yield, PE : EtOAc = 5:1, M.p. 189 – 190 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24 – 8.21 (m, 2H), 7.49 – 7.47 (m, 2H), 6.57 (dd, *J* = 10.3, 0.9 Hz, 1H), 6.17 (d, *J* = 10.3 Hz, 1H), 4.39 (dd, *J* = 13.3, 1.9 Hz, 1H), 4.22 (d, *J* = 13.3 Hz, 1H), 3.35 – 3.30 (m, 2H), 2.77 – 2.70 (m, 1H), 1.58 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.8, 149.6, 147.8, 143.8, 142.7, 130.6, 128.9, 124.2, 123.8, 80.0, 69.4, 49.6, 36.3, 23.9 ppm; FTIR (neat) υ 2918, 1680, 1508, 1345, 1117, 1012, 864 cm^{-1}; HRMS (ESI) m/z: Calcd. For $C_{16}H_{14}ClNO_4Na^+$: 342.0504, Found: 342.0516 ($M+Na^+$).

(*E*)-3-(chloro(3-chlorophenyl)methylene)-7a-methyl-2,3,3a,7a-tetrahydrobenzo-furan-5(*4H*)-one, 2h



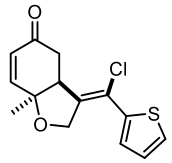
Yellow liquid, 31.4 mg, 51% yield, PE : EtOAc = 5:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 – 7.27 (m, 2H), 7.16 (dt, *J* = 6.6, 1.9 Hz, 1H), 6.56 (d, *J* = 10.3 Hz, 1H), 6.15 (d, *J* = 10.3 Hz, 1H), 4.36 (dd, *J* = 13.2, 1.8 Hz, 1H), 4.22 (d, *J* = 13.2 Hz, 1H), 3.31 – 3.27 (m, 2H), 2.71 (dd, *J* = 18.3, 7.8 Hz, 1H), 1.55 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.2, 149.8, 140.4, 139.5, 134.5, 130.5, 129.8, 129.3, 128.1, 126.1, 124.9, 79.9, 69.5, 49.2, 36.3, 24.0 ppm; FTIR (neat) υ 3359, 2928, 1681, 1565, 1411, 1217, 1041, 868, 785 cm^{-1}; HRMS (ESI) m/z: Calcd. For $C_{16}H_{14}Cl_2O_2Na^+$: 331.0263, Found: 331.0276 ($M+Na^+$).

(*E*)-3-(chloro(thiophen-3-yl)methylene)-7a-methyl-2,3,3a,7a-tetrahydrobenzo-furan-5(*4H*)-one, 2i



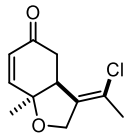
Light yellow semisolid, 25.8 mg, 46% yield, PE : EtOAc = 5:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 (dd, *J* = 5.0, 3.0 Hz, 1H), 7.25 (dd, *J* = 2.9, 1.1 Hz, 1H), 7.09 (dd, *J* = 5.1, 1.2 Hz, 1H), 6.59 (d, *J* = 10.2 Hz, 1H), 6.12 (d, *J* = 10.2 Hz, 1H), 4.46 (s, 2H), 3.34 (t, *J* = 5.5 Hz, 1H), 3.21 (dd, *J* = 16.7, 5.5 Hz, 1H), 2.72 (dd, *J* = 16.7, 6.3 Hz, 1H), 1.53 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.5, 149.5, 138.6, 138.3, 130.4, 127.0, 126.0, 124.7, 121.6, 79.5, 69.8, 49.3, 36.5, 24.1 ppm; FTIR (neat) υ 3055, 1682, 1420, 1264, 1041, 895, 731 cm^{-1}; HRMS (ESI) m/z: Calcd. For $C_{14}H_{13}ClSO_2Na^+$: 303.0217, Found: 303.0207 ($M+Na^+$).

(*E*)-3-(chloro(thiophen-2-yl)methylene)-7a-methyl-2,3,3a,7a-tetrahydrobenzo-furan-5(*4H*)-one, 2j



Red-brown semisolid, 37.6 mg, 67% yield, PE : EtOAc = 5:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 (dd, *J* = 5.1, 1.2 Hz, 1H), 7.07 (dd, *J* = 3.8, 0.9 Hz, 1H), 7.03 (dd, *J* = 5.1, 3.8 Hz, 1H), 6.60 (d, *J* = 10.2 Hz, 1H), 6.11 (d, *J* = 10.2 Hz, 1H), 4.61 (d, *J* = 13.8 Hz, 1H), 4.53 (dd, *J* = 13.8, 2.1 Hz, 1H), 3.38 (td, *J* = 6.3, 1.8 Hz, 1H), 3.12 (dd, *J* = 16.6, 6.3 Hz, 1H), 2.73 (dd, *J* = 16.6, 6.2 Hz, 1H), 1.52 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.3, 149.1, 140.4, 138.5, 130.3, 127.5, 127.4, 127.2, 120.0, 79.4, 69.9, 49.9, 36.5, 24.2 ppm; FTIR (neat) υ 3055, 1680, 1414, 1264, 1040, 816, 732 cm^{-1}; HRMS (ESI) m/z: Calcd. For $C_{14}H_{13}ClO_2SNa^+$: 303.0217, Found: 303.0228 ($M+Na^+$).

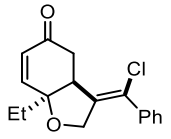
(*E*)-3-(1-chloroethylidene)-7a-methyl-2,3,3a,7a-tetrahydrobenzofuran-5(*4H*)-one, 2k



Light yellow liquid, 33.1 mg, 78% yield, PE : EtOAc = 5:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.54 (d, *J* = 10.2 Hz, 1H), 6.04 (d, *J* = 10.2 Hz, 1H), 4.41 (d, *J* = 12.8 Hz, 1H), 4.24 (d, *J* = 12.8 Hz, 1H), 3.17 – 3.11 (m, 2H), 2.62 (dd, *J* = 18.3, 7.7 Hz, 1H), 2.00 (s, 3H), 1.48 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.8, 149.6, 135.8, 130.1, 123.0,

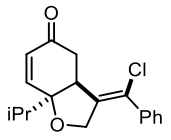
80.1, 68.9, 48.1, 36.6, 23.90, 23.88 ppm; FTIR (neat) υ 2987, 1702, 1609, 1499, 1264, 896, 731 cm^{-1}; HRMS (ESI) m/z: Calcd. For $C_{11}H_{14}ClO_2^+$: 213.0677, Found: 213.0696 ($M+H^+$).

(*E*)-3-(chloro(phenyl)methylene)-7a-ethyl-2,3,3a,7a-tetrahydrobenzofuran-5(*4H*)-one, 2l



Light yellow liquid, 37.4 mg, 65% yield, PE : EtOAc = 5:1. ^1H NMR (400 MHz, $CDCl_3$) δ 7.35 – 7.28 (m, 5H), 6.58 (dd, *J* = 10.2, 0.8 Hz, 1H), 6.21 (d, *J* = 10.2 Hz, 1H), 4.37 (dd, *J* = 13.1, 2.1 Hz, 1H), 4.21 (d, *J* = 13.1 Hz, 1H), 3.42 – 3.39 (m, 1H), 3.27 (dd, *J* = 16.9, 4.2 Hz, 1H), 2.70 (dd, *J* = 16.9, 6.8 Hz, 1H), 1.87 – 1.83 (m, 2H), 1.05 (t, *J* = 7.5 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.7, 148.9, 139.5, 137.8, 131.3, 129.1, 128.5, 127.9, 126.3, 82.2, 69.3, 46.8, 36.9, 30.8, 8.3 ppm; FTIR (neat) υ 2934, 1682, 1491, 1381, 1054, 858, 758 cm^{-1}; HRMS (ESI) m/z: Calcd. For $C_{17}H_{18}ClO_2^+$: 289.0990, Found: 289.0984 ($M+H^+$).

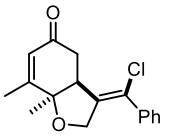
(*E*)-3-(chloro(phenyl)methylene)-7a-isopropyl-2,3,3a,7a-tetrahydrobenzofuran-5(*4H*)-one, 2m



Light yellow liquid, 52.5 mg, 87% yield, PE : EtOAc = 5:1. ^1H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.32 (m, 3H), 7.30 – 7.26 (m, 2H), 6.57 (dd, *J* = 10.4, 0.8 Hz, 1H), 6.27 (d, *J* = 10.4 Hz, 1H), 4.33 (dd, *J* = 12.9, 1.9 Hz, 1H), 4.19 (d, *J* = 12.9 Hz, 1H), 3.48 – 3.46 (m, 1H), 3.23 (dd, *J* = 17.2, 3.6 Hz, 1H), 2.70 (dd, *J* = 17.2, 7.2 Hz, 1H), 2.12 – 2.04 (m, 1H), 1.05 (dd, *J* = 11.5, 6.9 Hz, 6H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.9, 147.6, 140.2, 137.8, 132.0, 129.1, 128.4, 128.0, 126.1, 84.3, 68.8, 44.8, 37.9, 35.7, 17.5, 17.1 ppm; FTIR (neat) υ 3058, 1683, 1464, 1386, 1221, 1053, 888, 786 cm^{-1}; HRMS (ESI) m/z: Calcd. For $C_{18}H_{20}ClO_2^+$: 303.1146, Found: 303.1144 ($M+H^+$).

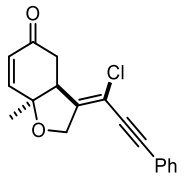
(*E*)-3-(chloro(phenyl)methylene)-7,7a-dimethyl-2,3,3a,7a-tetrahydrobenzo-

furan-5(*4H*)-one, 2n



Off-white solid, 46.7 mg, 81% yield, PE : EtOAc = 5:1, M.p. 103 – 104 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.27 (m, 5H), 6.04 (s, 1H), 4.22 – 4.14 (m, 2H), 3.44 (dd, *J* = 17.1, 3.5 Hz, 1H), 3.29 – 3.28 (m, 1H), 2.68 (dd, *J* = 17.1, 6.4 Hz, 1H), 2.00 (s, 3H), 1.57 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.8, 160.2, 138.8, 138.0, 129.3, 129.0, 128.5, 127.9, 126.3, 82.3, 69.6, 50.1, 36.1, 22.5, 18.2 ppm; FTIR (neat) υ 2919, 1667, 1443, 1171, 1098, 1021, 760 cm^{-1}; HRMS (ESI) m/z: Calcd. For $C_{17}H_{18}ClO_2^+$: 289.0990, Found: 289.0991 ($M+H^+$).

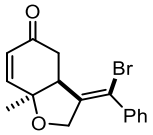
(*E*)-3-(1-chloro-3-phenylprop-2-yn-1-ylidene)-7a-methyl-2,3,3a,7a-tetrahydroben zofuran-5(4*H*)-one, 2o



Light yellow liquid, 25.2 mg, 42% yield, PE : EtOAc = 5:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 – 7.43 (m, 2H), 7.37 – 7.32 (m, 3H), 6.58 (d, *J* = 10.3 Hz, 2H), 6.08 (d, *J* = 10.2 Hz, 2H), 4.64 (d, *J* = 14.6 Hz, 1H), 4.43 (dd, *J* = 14.6, 2.2 Hz, 1H), 3.28 – 3.19 (m, 2H), 2.67 (dd, *J* = 16.0, 5.4 Hz, 1H), 1.53 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.7, 149.5, 148.2, 131.8, 130.3, 129.5, 128.6, 121.6, 106.7, 95.1, 84.0, 80.8, 70.6, 48.9, 36.1, 23.8 ppm; FTIR (neat) υ 2912, 1687, 1375, 1245, 1095, 903, 723 cm^{-1}; HRMS (ESI) m/z: Calcd. For $C_{18}H_{15}ClNaO_2^+$: 321.0653, Found: 321.0659 ($M+Na^+$)

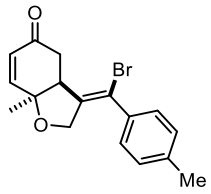
b) Characterization data for compounds 3

(*E*)-3-(bromo(phenyl)methylene)-7a-methyl-2,3,3a,7a-tetrahydrobenzofuran-5(*4H*)-one, 3a



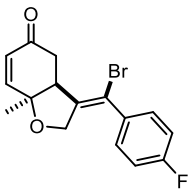
Light yellow semisolid, 58.3 mg, 91% yield, PE : EtOAc = 5:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.26 (m, 5H), 6.56 (dd, *J* = 10.2, 0.7 Hz, 1H), 6.14 (d, *J* = 10.2 Hz, 1H), 4.32 (dd, *J* = 13.2, 1.7 Hz, 1H), 4.16 (d, *J* = 13.2 Hz, 1H), 3.31 – 3.25 (m, 2H), 2.71 (td, *J* = 8.4, 5.6 Hz, 1H), 1.54 (s, 3H) ppm; ^{13}C NMR (400 MHz, $CDCl_3$) δ 197.4, 149.6, 142.1, 139.5, 130.3, 129.1, 128.5, 128.3, 116.7, 79.5, 69.8, 50.7, 36.5, 24.3 ppm; FTIR (neat) υ 3358, 2920, 1678, 1444, 1091, 1007, 854 cm^{-1}; HRMS (ESI) m/z: Calcd. For $C_{16}H_{15}BrO_2^+$: 341.0148, Found: 341.0158 ($M+Na^+$).

(*E*)-3-(bromo(*p*-tolyl)methylene)-7a-methyl-2,3,3a,7a-tetrahydrobenzofuran-5(*4H*)-one, 3b



Off-white solide, 60.4 mg, 91% yield, PE : EtOAc = 5:1, M.p. 106 – 108 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.18 – 7.12 (m, 4H), 6.56 (d, *J* = 10.2 Hz, 1H), 6.13 (d, *J* = 10.2 Hz, 1H), 4.32 (dd, *J* = 13.2, 1.6 Hz, 1H), 4.16 (d, *J* = 13.2 Hz, 1H), 3.30 – 3.23 (m, 2H), 2.70 (dt, *J* = 14.6, 4.3 Hz, 1H), 2.34 (s, 3H), 1.53 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.4, 149.6, 141.5, 139.1, 136.6, 130.3, 129.1, 128.2, 116.9, 79.5, 69.8, 50.7, 36.4, 24.2, 21.3 ppm; FTIR (neat) υ 2923, 1696, 1406, 1370, 1279, 1069, 1026, 951, 865, 781 cm^{-1}; HRMS (ESI) m/z: Calcd. For $C_{17}H_{18}BrO_2^+$: 333.0485, Found: 333.0484 ($M+H^+$).

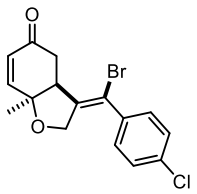
(*E*)-3-(bromo(4-fluorophenyl)methylene)-7a-methyl-2,3,3a,7a-tetrahydrobenzo-furan-5(*4H*)-one, 3c



Light yellow liquid, 41.0 mg, 61% yield, PE : EtOAc = 5:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 – 7.25 (m, 2H), 7.05 – 7.00 (m, 2H), 6.56 (d, *J* = 10.2 Hz, 1H), 6.14 (d, *J* = 10.2 Hz, 1H), 4.29 (dd, *J* = 13.2, 1.8 Hz, 1H), 4.13 (d, *J* = 13.2 Hz, 1H), 3.30 – 3.24 (m, 2H), 2.70 (dd, *J* = 16.0, 5.7 Hz, 1H), 1.54 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.3,

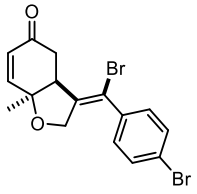
162.7 (d, *J* = 249.9 Hz), 149.5, 142.5, 135.6 (d, *J* = 3.1 Hz), 130.4, 130.3 (d, *J* = 8.5 Hz), 115.6 (d, *J* = 21.9 Hz), 79.7, 69.7, 50.7, 36.4, 24.2 ppm; ^{19}F NMR (376 MHz, $CDCl_3$) δ -111.2 ppm; FTIR (neat) υ 2972, 1680, 1504, 1228, 1088, 1012, 857, 720 cm^{-1}; HRMS (ESI) m/z: Calcd. For $C_{16}H_{15}BrFO_2^+$: 337.0234, Found: 337.0236 ($M+H^+$).

(*E*)-3-(bromo(4-chlorophenyl)methylene)-7a-methyl-2,3,3a,7a-tetrahydrobenzofuran-5(4*H*)-one, 3d



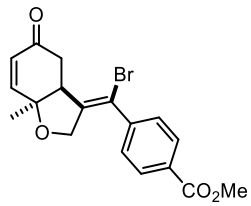
Off-white solid, 50.0 mg, 71% yield, PE : EtOAc = 5:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 – 7.28 (m, 2H), 7.25 – 7.17 (m, 2H), 6.53 (dd, *J* = 10.2, 0.8 Hz, 1H), 6.11 (d, *J* = 10.2 Hz, 1H), 4.27 (dd, *J* = 13.2, 1.8 Hz, 1H), 4.11 (d, *J* = 13.2 Hz, 1H), 3.29 – 3.20 (m, 2H), 2.68 (dd, *J* = 15.9, 5.6 Hz, 1H), 1.52 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.2, 149.5, 142.9, 137.9, 135.0, 130.4, 129.7, 128.8, 115.3, 79.7, 69.7, 50.8, 36.4, 24.2 ppm; FTIR (neat) υ 2968, 1690, 1486, 1279, 1070, 1030, 951, 865, 761 cm^{-1}; HRMS (ESI) m/z: Calcd. For $C_{16}H_{14}BrClO_2Na^+$: 374.9758, Found: 374.9770 ($M+Na^+$).

(*E*)-3-(bromo(4-bromophenyl)methylene)-7a-methyl-2,3,3a,7a-tetrahydrobenzofuran-5(*4H*)-one, 3e



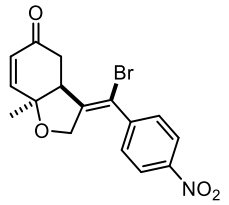
Light yellow solid, 62.9 mg, 79% yield, PE : EtOAc = 5:1, M.p. 129 – 131 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 – 7.45 (m, 2H), 7.17 – 7.13 (m, 2H), 6.55 (dd, *J* = 10.3, 0.7 Hz), 6.13 (d, *J* = 10.3 Hz, 1H), 4.29 (dd, *J* = 13.2, 1.8 Hz, 1H), 4.13 (d, *J* = 13.2 Hz, 1H), 3.30 – 3.23 (m, 2H), 2.70 (dd, *J* = 15.8, 5.5 Hz, 1H), 1.54 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.1, 149.5, 142.9, 138.3, 131.7, 130.4, 129.9, 123.2, 115.3, 79.6, 69.7, 50.7, 36.3, 24.2 ppm; FTIR (neat) υ 2924, 1696, 1482, 1391, 1279, 1068, 1027, 951, 863, 759 cm^{-1}; HRMS (ESI) m/z: Calcd. For $C_{16}H_{14}Br_2O_2Na^+$: 418.9253, Found: 418.9256 ($M+Na^+$).

(*E*)-methyl 4-(bromo(7a-methyl-5-oxo-3a,4,5,7a-tetrahydrobenzofuran-3(2*H*) -ylidene)methyl)benzoate, 3f



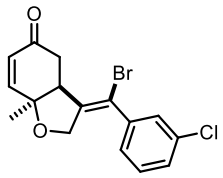
Off-white solid, 59.4 mg, 79% yield, PE : EtOAc = 5:1, M.p. 103 – 105 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 – 7.99 (m, 2H), 7.37 – 7.35 (m, 2H), 6.57 (d, *J* = 10.3 Hz, 1H), 6.15 (d, *J* = 10.3 Hz, 1H), 4.33 (dd, *J* = 13.3, 1.7 Hz, 1H), 4.14 (d, *J* = 13.3 Hz, 1H), 3.92 (s, 3H), 3.31 – 3.27 (m, 2H), 2.75 – 2.69 (m, 1H), 1.55 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.1, 166.4, 149.5, 143.7, 143.6, 130.5, 130.4, 129.8, 128.4, 115.4, 79.6, 69.7, 52.4, 50.9, 36.3, 24.2 ppm; FTIR (neat) υ 2850, 1720, 1671, 1434, 1279, 1110, 1015, 965, 841, 764 cm^{-1}; HRMS (ESI) m/z: Calcd. For $C_{18}H_{18}BrO_4^+$: 377.0383, Found: 377.0390 ($M+H^+$).

(*E*)-3-(bromo(4-nitrophenyl)methylene)-7a-methyl-2,3,3a,7a-tetrahydrobenzo furan-5(4*H*)-one, 3g



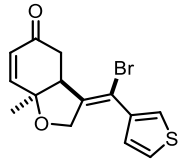
Off-white solid, 52.3 mg, 72% yield, PE : EtOAc = 5:1, M.p. 178 – 180 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23 – 8.19 (m, 2H), 7.48 – 7.46 (m, 2H), 6.58 (dd, *J* = 10.2, 0.5 Hz, 1H), 6.16 (d, *J* = 10.2 Hz, 1H), 4.33 (dd, *J* = 13.3, 1.7 Hz, 1H), 4.14 (d, *J* = 13.3 Hz, 1H), 3.33 – 3.27 (m, 2H), 2.73 (dd, *J* = 18.4, 8.1 Hz, 1H), 1.57 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.8, 149.4, 147.7, 145.41, 145.37, 130.5, 129.4, 123.8, 113.7, 79.8, 69.6, 51.0, 36.3, 24.1 ppm; FTIR (neat) υ 2962, 1678, 1591, 1506, 1343, 1259, 1088, 1010, 840, 798, 753 cm^{-1}; HRMS (ESI) m/z: Calcd. For $C_{16}H_{15}BrNO_4^+$: 364.0179, Found: 364.0170 ($M+H^+$).

(*E*)-3-(bromo(3-chlorophenyl)methylene)-7a-methyl-2,3,3a,7a-tetrahydrobenzo furan-5(4*H*)-one, 3h



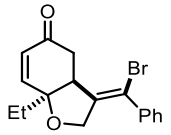
Off-white solid, 46.6 mg, 66% yield, PE : EtOAc = 5:1, M.p. 123 – 125 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 – 7.27 (m, 3H), 7.16 – 7.13 (m, 1H), 6.56 (d, *J* = 10.3 Hz, 1H), 6.14 (d, *J* = 10.3 Hz, 1H), 4.31 (d, *J* = 13.3 Hz, 1H), 4.15 (d, *J* = 13.3 Hz, 1H), 3.30 – 3.23 (m, 2H), 2.74 – 2.67 (m, 1H), 1.54 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.1, 149.5, 143.5, 141.1, 134.4, 130.4, 129.8, 129.2, 128.5, 126.5, 114.8, 79.64, 69.7, 50.8, 36.3, 24.2 ppm; FTIR (neat) υ 3055, 2978, 1681, 1564, 1412, 1265, 1091, 897 cm^{-1}; HRMS (ESI) m/z: Calcd. For $C_{16}H_{14}BrClNO_2Na^+$: 374.9758, Found: 374.9766 ($M+Na^+$).

(*E*)-3-(bromo(thiophen-3-yl)methylene)-7a-methyl-2,3,3a,7a-tetrahydrobenzo furan-5(4*H*)-one, 3i



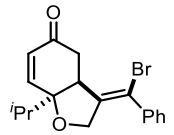
Reddish brown semi-solid, 44.4 mg, 64% yield, PE : EtOAc = 5:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 (dd, *J* = 5.1, 3.0 Hz, 1H), 7.22 (dd, *J* = 3.0, 1.3 Hz, 1H), 7.10 (dd, *J* = 5.1, 1.3 Hz, 1H), 6.58 (dd, *J* = 10.2, 0.6 Hz, 1H), 6.12 (d, *J* = 10.2 Hz, 1H), 4.43 (dd, *J* = 13.3, 1.8 Hz, 1H), 4.37 (d, *J* = 13.3 Hz, 1H), 3.27 (td, *J* = 5.9, 1.0 Hz, 1H), 3.19 (dd, *J* = 16.5, 5.9 Hz, 1H), 2.72 (dd, *J* = 16.5, 6.2 Hz, 1H), 1.52 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.4, 149.4, 141.7, 139.8, 130.3, 127.7, 125.9, 125.0, 111.3, 79.2, 70.0, 51.1, 36.5, 24.3 ppm; FTIR (neat) υ 3355, 2969, 1675, 1410, 1371, 1137, 1069, 1020, 953, 885, 837, 800, 751 cm^{-1}; HRMS (ESI) m/z: Calcd. For $C_{14}H_{13}BrNaO_2S^+$: 346.9712, Found: 346.9723 ($M+Na^+$).

(*E*)-3-(bromo(phenyl)methylene)-7a-ethyl-2,3,3a,7a-tetrahydrobenzofuran-5(4*H*)-one, 3j



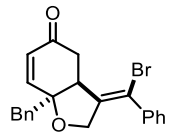
Off-white solid, 50.3 mg, 76% yield, PE : EtOAc = 5:1, M.p. 75 – 76 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 – 7.26 (m, 5H), 6.58 (dd, *J* = 10.4, 0.6 Hz, 1H), 6.20 (d, *J* = 10.4 Hz, 1H), 4.32 (dd, *J* = 13.1, 1.9 Hz, 1H), 4.14 (d, *J* = 13.1 Hz, 1H), 3.34 – 3.31 (m, 1H), 3.24 (dd, *J* = 16.8, 5.0 Hz, 1H), 2.71 (dd, *J* = 16.8, 6.7 Hz, 1H), 1.85 (q, *J* = 7.6 Hz, 2H), 1.03 (t, *J* = 7.6 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.6, 148.6, 142.6, 139.4, 131.2, 129.0, 128.5, 128.4, 116.6, 82.0, 69.5, 48.5, 37.0, 30.9, 8.3 ppm; FTIR (neat) υ 3355, 2965, 1681, 1444, 1385, 1079, 1015, 867, 760 cm^{-1}; HRMS (ESI) m/z: Calcd. For $C_{17}H_{17}BrNaO_2^+$: 355.0304, Found: 355.0314 ($M+Na^+$).

(*E*)-3-(bromo(phenyl)methylene)-7a-isopropyl-2,3,3a,7a-tetrahydrobenzofuran-5(4*H*)-one, 3k



Off-white solid, 46.5 mg, 67% yield, PE : EtOAc = 5:1, M.p. 75 – 76 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 – 7.26 (m, 5H), 6.58 (d, *J* = 10.4 Hz, 2H), 6.27 (d, *J* = 10.4 Hz, 2H), 4.27 (dd, *J* = 12.9, 1.8 Hz, 1H), 4.12 (d, *J* = 12.9 Hz, 1H), 3.40 – 3.38 (m, 1H), 3.22 (dd, *J* = 17.1, 4.2 Hz, 1H), 2.70 (dd, *J* = 17.1, 7.2 Hz, 1H), 2.09 – 2.04 (m, 1H), 1.06 (d, *J* = 7.0 Hz, 3H), 1.03 (d, *J* = 6.9 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.9, 147.4, 143.2, 139.3, 132.0, 129.0, 128.5, 116.7, 84.2, 69.1, 46.6, 38.0, 35.6, 17.5, 17.2 ppm; FTIR (neat) υ 2965, 1676, 1445, 1387, 1119, 1058, 866, 785 cm^{-1}; HRMS (ESI) m/z: Calcd. For $C_{18}H_{20}BrO_2^+$: 347.0641, Found: 347.0640 ($M+H^+$).

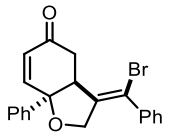
(*E*)-7a-benzyl-3-(bromo(phenyl)methylene)-2,3,3a,7a-tetrahydrobenzofuran-5(4*H*)-one, 3l



Light yellow liquid, 49.8 mg, 63% yield, PE : EtOAc = 5:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 – 7.22 (m, 10H), 6.55 (d, *J* = 10.4 Hz, 1H), 6.14 (d, *J* = 10.3 Hz, 1H), 4.32 (dd, *J* = 13.1, 1.9 Hz, 1H), 4.16 (d, *J* = 13.1 Hz, 1H), 3.41 – 3.38 (m, 1H), 3.16 –3.11 (m, 2H), 3.05 (d, *J* = 13.6 Hz, 1H), 2.31 (dd, *J* = 16.8, 6.7 Hz, 1H) ppm; ^{13}C NMR (100

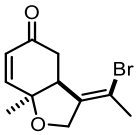
MHz, $CDCl_3$) δ 197.4, 148.2, 142.0, 139.3, 135.2, 131.1, 130.4, 129.0, 128.6, 128.5, 128.4, 127.3, 116.7, 82.0, 69.7, 48.9, 44.7, 36.6 ppm; FTIR (neat) υ 2920, 1682, 1492, 1443, 1170, 1042, 1014, 848, 759 cm^{-1}; HRMS (ESI) m/z: Calcd. For $C_{22}H_{19}BrNaO_2^+$: 417.0461, Found: 417.0468 ($M+Na^+$).

(*E*)-3-(bromo(phenyl)methylene)-7a-phenyl-2,3,3a,7a-tetrahydrobenzofuran-5(4*H*)-one, 3m



Off-white semi-solid, 38.8 mg, 51% yield, PE : EtOAc = 5:1. ^1H NMR (400 MHz, $CDCl_3$) δ 7.49 – 7.46 (m, 2H), 7.44 – 7.40 (m, 2H), 7.38 – 7.30 (m, 4H), 7.28 – 7.25 (m, 2H), 6.62 (d, *J* = 10.2 Hz, 1H), 6.32 (d, *J* = 10.2 Hz, 1H), 4.50 (dd, *J* = 13.2, 2.0 Hz, 1H), 4.35 (d, *J* = 13.2 Hz, 1H), 3.58 – 3.55 (m, 1H), 3.32 (dd, *J* = 16.7, 5.2 Hz, 1H), 2.84 (dd, *J* = 16.8, 6.4 Hz, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.4, 147.9, 141.6, 141.0, 139.3, 130.8, 129.1, 129.0, 128.5, 128.4, 125.3, 116.6, 83.2, 70.1, 52.4, 36.3 ppm; FTIR (neat) υ 2918, 2850, 1686, 1445, 1261, 1019, 797, 762 cm^{-1}; HRMS (ESI) m/z: Calcd. For $C_{21}H_{18}BrO_2^+$: 381.0485, Found: 381.0493 ($M+H^+$).

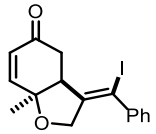
(*E*)-3-(1-bromoethylidene)-7a-methyl-2,3,3a,7a-tetrahydrobenzofuran-5(4*H*)-one, 3n



Light yellow liquid, 40.0 mg, 78% yield, PE : EtOAc = 5:1. ^1H NMR (400 MHz, $CDCl_3$) δ 6.56 (d, *J* = 10.2 Hz, 1H), 6.05 (d, *J* = 10.2 Hz, 1H), 4.42 (d, *J* = 12.8 Hz, 1H), 4.28 (d, *J* = 12.8 Hz, 1H), 3.08 – 3.02 (m, 2H), 2.64 (dd, *J* = 18.8, 8.3 Hz, 1H), 2.19 (s, 3H), 1.47 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.7, 149.1, 139.1, 130.1, 113.3, 79.6, 69.0, 49.9, 36.7, 26.3, 24.2 ppm; FTIR (neat) υ 2944, 2830, 1450, 1374, 1275, 1167, 1022, 824 cm^{-1}; HRMS (ESI) m/z: Calcd. For $C_{11}H_{14}BrO_2^+$: 257.0172, Found: 257.0178 ($M+H^+$).

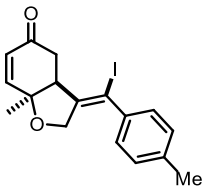
c) Characterization data for compounds 4

(*E*)-3-(iodo(phenyl)methylene)-7a-methyl-2,3,3a,7a-tetrahydrobenzofuran-5(4*H*)-one, 4a



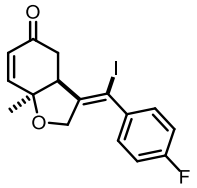
Light yellow solid, 66.6 mg, 91% yield, PE : EtOAc = 5:1, M.p. 72 – 74 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 – 7.22 (m, 5H), 6.58 (d, *J* = 10.2 Hz, 1H), 6.12 (d, *J* = 10.2 Hz, 1H), 4.37 (dd, *J* = 13.5, 1.5 Hz, 1H), 4.17 (d, *J* = 13.4 Hz, 1H), 3.16 – 3.10 (m, 2H), 2.73 (dd, *J* = 18.9, 8.7 Hz, 1H), 1.52 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.3, 149.3, 148.5, 142.8 130.2, 128.7, 128.6, 128.2, 92.0, 78.9, 69.3, 53.6, 36.8, 24.6 ppm; FTIR (neat) υ 2924, 1679, 1443, 1370, 1279, 1070, 1024, 952, 852, 722 cm^{-1}; HRMS (ESI) m/z: Calcd. For $C_{16}H_{16}IO_2^+$: 367.0189, Found: 367.0199 ($M+H^+$).

(*E*)-3-(iodo(p-tolyl)methylene)-7a-methyl-2,3,3a,7a-tetrahydrobenzofuran-5(4*H*)-one, 4b



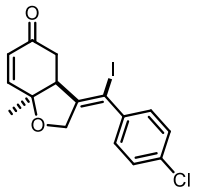
Off-white solid, 69.2 mg, 91% yield, PE : EtOAc = 5:1, M.p. 150 – 152. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.14 – 7.11 (m, 4H), 6.57 (d, *J* = 10.2 Hz, 1H), 6.12 (d, *J* = 10.2 Hz, 1H), 4.37 (dd, *J* = 13.4, 1.6 Hz, 1H), 4.17 (d, *J* = 13.4 Hz, 1H), 3.15 – 3.09 (m, 2H), 2.72 (dd, *J* = 18.4, 8.3 Hz, 1H), 2.33 (s, 3H), 1.51 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.3, 149.3, 147.9, 139.9, 138.7, 130.1, 129.2, 128.1, 92.4, 78.8, 69.3, 53.6, 36.8, 24.6, 21.3 ppm; FTIR (neat) υ 2922, 1685, 1370, 1278, 1069, 1022, 952, 857, 777 cm^{-1}; HRMS (ESI) m/z: Calcd. For $C_{17}H_{18}IO_2^+$: 381.0346, Found: 381.0346 ($M+H^+$).

(*E*)-3-((4-fluorophenyl)iodomethylene)-7a-methyl-2,3,3a,7a-tetrahydrobenzo-furan-5(4*H*)-one, 4c



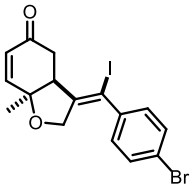
Light yellow solid, 49.2 mg, 64% yield, PE : EtOAc = 5:1, M.p. 118 – 120 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 – 7.20 (m, 2H), 7.02 – 6.98 (m, 2H), 6.57 (d, *J* = 10.2 Hz, 1H), 6.12 (d, *J* = 10.2 Hz, 1H), 4.34 (dd, *J* = 13.4, 1.7 Hz, 1H), 4.15 (d, *J* = 13.4 Hz, 1H), 3.16 – 3.12 (m, 2H), 2.71 (dd, *J* = 18.3, 8.2 Hz, 1H), 1.52 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.1, 162.4 (d, *J* = 249.2 Hz), 149.2, 149.0, 138.9 (d, *J* = 3.1 Hz), 130.1 (d, *J* = 14.4 Hz), 130.0, 115.6 (d, *J* = 21.7 Hz), 90.5, 79.0, 69.2, 53.6, 36.7, 24.5 ppm; ^{19}F NMR (376 MHz, $CDCl_3$) δ -111.8 ppm; FTIR (neat) υ 2926, 1687, 1504, 1372, 1278, 1229, 1070, 1028, 952, 862, 735 cm^{-1}; HRMS (ESI) m/z: Calcd. For $C_{16}H_{15}INO_4^+$: 406.9915, Found: 406.9924 ($M+Na^+$).

(*E*)-3-((4-chlorophenyl)iodomethylene)-7a-methyl-2,3,3a,7a-tetrahydrobenzo-furan-5(4*H*)-one, 4d



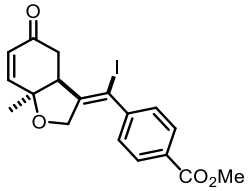
Off-white solid, 58.4 mg, 73% yield, PE : EtOAc = 5:1, M.p. 172 – 174 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 – 7.25 (m, 2H), 7.16 – 7.13 (m, 2H), 6.55 (d, *J* = 10.2 Hz, 1H), 6.10 (d, *J* = 10.2 Hz, 1H), 4.31 (dd, *J* = 13.5, 1.6 Hz, 1H), 4.13 (d, *J* = 13.5 Hz, 1H), 3.14 – 3.08 (m, 2H), 2.69 (dd, *J* = 18.3, 8.2 Hz, 1H), 1.49 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.1, 149.3, 149.2, 141.2, 134.5, 130.2, 129.5, 128.8, 90.2, 79.0, 69.2, 53.6, 36.7, 24.5 ppm; FTIR (neat) υ 2924, 1689, 1484, 1370, 1279, 1209, 1070, 1025, 952, 893, 854, 821, 744 cm^{-1}; HRMS (ESI) m/z: Calcd. For $C_{16}H_{14}ClINaO_2^+$: 422.9619, Found: 422.9620 ($M+Na^+$).

(*E*)-3-((4-bromophenyl)iodomethylene)-7a-methyl-2,3,3a,7a-tetrahydrobenzo-furan-5(4*H*)-one, 4e



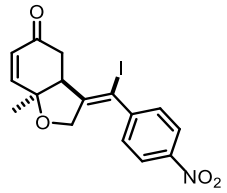
Light yellow solid, 59.6 mg, 67% yield, PE : EtOAc = 5:1, M.p. 174 – 176 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 – 7.43 (m, 2H), 7.12 – 7.09 (m, 2H), 6.57 (d, *J* = 10.2 Hz, 1H), 6.12 (d, *J* = 10.2 Hz, 1H), 4.33 (dd, *J* = 13.5, 1.6 Hz, 1H), 4.15 (d, *J* = 13.5 Hz, 1H), 3.16 – 3.10 (m, 2H), 2.71 (dd, *J* = 18.4, 8.3 Hz, 1H), 1.52 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.1, 149.3, 149.2, 141.7, 131.7, 130.2, 129.8, 122.8, 90.2, 79.0, 69.2, 53.6, 36.7, 24.5 ppm; FTIR (neat) υ 2922, 1686, 1481, 1390, 1330, 1278, 1052, 1023, 952, 892, 852, 818 cm^{-1}; HRMS (ESI) m/z: Calcd. For $C_{16}H_{15}BrIO_2^+$: 444.9295, Found: 444.9304 ($M+H^+$).

(*E*)-Methyl 4-(iodo(7a-methyl-5-oxo-3a,4,5,7a-tetrahydrobenzofuran-3(2*H*)-ylidene)methyl)benzoate, 4f



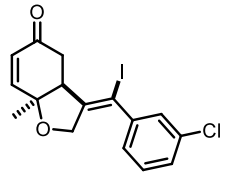
Off-white solid, 61.1 mg, 72% yield, PE : EtOAc = 5:1, M.p. 129 – 131 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, *J* = 8.4 Hz, 2H), 7.30 (d, *J* = 8.4 Hz, 2H), 6.58 (d, *J* = 10.2 Hz, 1H), 6.13 (d, *J* = 10.2 Hz, 1H), 4.36 (dd, *J* = 13.5, 1.6 Hz, 1H), 4.14 (d, *J* = 13.5 Hz, 1H), 3.92 (s, 3H), 3.16 – 3.13 (m, 2H), 2.73 (dd, *J* = 18.3, 8.3 Hz, 1H), 1.53 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.9, 166.3, 149.8, 149.1, 146.9, 130.2, 130.2, 129.8, 128.2, 90.1, 79.0, 69.2, 53.6, 52.34, 36.6, 24.5 ppm; FTIR (neat) υ 2927, 1723, 1682, 1434, 1278, 1109, 1017, 955, 857, 729 cm^{-1}; HRMS (ESI) m/z: Calcd. For $C_{18}H_{17}INaO_4^+$: 447.0064, Found: 447.0076 ($M+Na^+$).

(*E*)-3-(iodo(4-nitrophenyl)methylene)-7a-methyl-2,3,3a,7a-tetrahydrobenzofuran-5(4*H*)-one, 4g



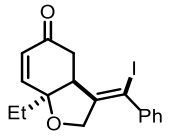
Light yellow solid, 60.0 mg, 73% yield, PE : EtOAc = 5:1, M.p. 163 – 165 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 – 8.18 (m, 2H), 7.43 – 7.40 (m, 2H), 6.58 (d, *J* = 10.3 Hz, 1H), 6.15 (d, *J* = 10.3 Hz, 1H), 4.35 (dd, *J* = 13.6, 1.7 Hz, 1H), 4.14 (d, *J* = 13.6 Hz, 1H), 3.19 – 3.14 (m, 2H), 2.73 (dd, *J* = 18.2, 8.1 Hz, 1H), 1.55 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.7, 151.2, 149.1, 148.8, 147.5, 130.3, 129.3, 123.9, 88.1, 79.2, 69.2, 53.6, 36.5, 24.4 ppm; FTIR (neat) υ 2921, 1686, 1510, 1342, 1276, 1110, 1027, 830, 729 cm^{-1}; HRMS (ESI) m/z: Calcd. For $C_{16}H_{15}INO_4^+$: 412.0040, Found: 412.0051 ($M+H^+$).

(*E*)-3-((3-chlorophenyl)iodomethylene)-7a-methyl-2,3,3a,7a-tetrahydrobenzo-furan-5(4*H*)-one, 4h



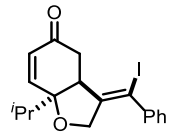
Light yellow semi-solid, 51.2 mg, 64% yield, PE : EtOAc = 5:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 – 7.22 (m, 3H), 7.12 – 7.09 (m, 1H), 6.58 (d, *J* = 10.2 Hz, 1H), 6.13 (d, *J* = 10.2 Hz, 1H), 4.35 (dd, *J* = 13.6, 1.6 Hz, 1H), 4.17 (d, *J* = 13.6 Hz, 1H), 3.15 – 3.09 (m, 2H), 2.72 (dd, *J* = 18.4, 8.3 Hz, 1H), 1.52 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.0, 149.7, 149.1, 144.3, 134.3, 130.2, 129.9, 128.8, 128.2, 126.3, 89.4, 79.0, 69.2, 53.6, 36.6, 24.5 ppm; FTIR (neat) υ 2971, 1679, 1562, 1408, 1278, 1174, 1115, 1040, 907, 727 cm^{-1}; HRMS (ESI) m/z: Calcd. For $C_{16}H_{15}ClIO_2^+$: 400.9800, Found: 400.9808 ($M+H^+$).

(*E*)-7a-ethyl-3-(iodo(phenyl)methylene)-2,3,3a,7a-tetrahydrobenzofuran-5(4*H*)-one, 4i



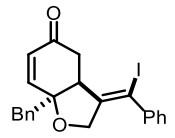
Light yellow liquid, 56.2 mg, 74% yield, PE : EtOAc = 5:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 – 7.22 (m, 5H), 6.59 (d, *J* = 10.3 Hz, 1H), 6.19 (d, *J* = 10.3 Hz, 1H), 4.37 (dd, *J* = 13.4, 1.7 Hz, 1H), 4.14 (d, *J* = 13.3 Hz, 1H), 3.21 (td, *J* = 6.5, 1.4 Hz, 1H), 3.08 (dd, *J* = 16.6, 6.4 Hz, 1H), 2.73 (dd, *J* = 16.6, 6.7 Hz, 1H), 1.82 (q, *J* = 7.5 Hz, 2H), 1.02 (t, *J* = 7.6 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.5, 148.9, 148.2, 142.7, 131.1, 128.7, 128.5, 128.2, 92.1, 81.4, 68.9, 51.5, 37.3, 31.0, 8.4 ppm; FTIR (neat) υ 2927, 1681, 1442, 1384, 1173, 1033, 932, 857, 757 cm^{-1}; HRMS (ESI) m/z: Calcd. For $C_{17}H_{18}IO_2^+$: 381.0346, Found: 381.0356 ($M+H^+$).

(*E*)-3-(iodo(phenyl)methylene)-7a-isopropyl-2,3,3a,7a-tetrahydrobenzofuran--5(4*H*)-one, 4j



Off-white solid, 29.9 mg, 38% yield, PE : EtOAc = 5:1, 87 – 89 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 – 7.21 (m, 5H), 6.59 (d, *J* = 10.4 Hz, 1H), 6.25 (d, *J* = 10.4 Hz, 1H), 4.31 (dd, *J* = 13.1, 1.7 Hz, 1H), 4.12 (d, *J* = 13.1 Hz, 1H), 3.29 – 3.26 (m, 1H), 3.08 (dd, *J* = 16.9, 5.4 Hz, 1H), 2.72 (dd, *J* = 16.9, 7.2 Hz, 1H), 2.06 (hept, *J* = 6.9 Hz, 1H), 1.03 (dd, *J* = 15.9, 6.9 Hz, 6H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.7, 149.4, 147.0, 142.6, 131.8, 128.7, 128.5, 128.4, 92.5, 83.7, 68.6, 49.8, 38.4, 35.5, 17.32, 17.26 ppm; FTIR (neat) υ 2962, 1676, 1386, 1274, 1116, 1017, 857, 760 cm^{-1}; HRMS (ESI) m/z: Calcd. For $C_{18}H_{19}INaO_2^+$: 417.0322, Found: 417.0332 ($M+Na^+$).

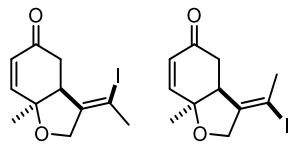
(*E*)-7a-benzyl-3-(iodo(phenyl)methylene)-2,3,3a,7a-tetrahydrobenzofuran-5(4*H*)-one, 4k



Light yellow semi-solid, 34.3 mg, 39% yield, PE : EtOAc = 5:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 – 7.24 (m, 8H), 7.18 – 7.16 (m, 2H), 6.59 (d, *J* = 10.3 Hz, 1H), 6.12 (d, *J* = 10.3 Hz, 1H), 4.39 (dd, *J* = 13.4, 1.7 Hz, 1H), 4.18 (d, *J* = 13.4 Hz, 1H), 3.31 (td, *J* = 6.6, 1.4 Hz, 1H), 3.12 (d, *J* = 13.7 Hz, 1H), 3.03 (d, *J* = 13.7 Hz, 1H), 2.97 (dd, *J* =

16.6, 6.7 Hz, 1H), 2.42 (dd, *J* = 16.6, 6.6 Hz, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.4, 148.3, 148.0, 142.6, 135.2, 130.9, 130.5, 128.7, 128.5, 128.2, 127.4, 92.2, 81.4, 69.2, 51.8, 45.0, 36.9 ppm; FTIR (neat) υ 2915, 1681, 1492, 1386, 1265, 1043, 810 cm^{-1}; HRMS (ESI) m/z: Calcd. For $C_{22}H_{20}IO_2^+$: 443.0502, Found: 443.0512 ($M+H^+$).

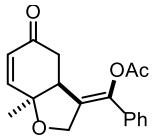
3-(1-iodoethylidene)-7a-methyl-2,3,3a,7a-tetrahydrobenzofuran-5(4H)-one, (*E*)-4l and (*Z*)- 4l



Following the general procedure, **4l** was isolated by silica gel flash chromatography (petroleum ether/ethyl acetate = 5:1) as a *E*/*Z* mixture (*E*/*Z* = 3/1), Light yellow liquid, 38 mg, 63% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.59 (d, *J* = 10.2 Hz, 1H), 6.59 (d, *J* = 10.2 Hz, 0.32H), 6.05 (d, *J* = 10.2 Hz, 1H), 6.04 (d, *J* = 10.2 Hz, 0.32H), 4.51 (d, *J* = 13.1 Hz, 1H), 4.45 – 4.41 (m, 1H), 4.28 (dd, *J* = 13.9, 1.3 Hz, 0.35H), 4.25 – 4.21 (m, 0.33H), 3.13 – 3.09 (m, 0.35H), 2.97 – 2.94 (m, 1H), 2.84 (dd, *J* = 16.2, 8.4 Hz, 1H), 2.76 – 2.71 (m, 0.31H), 2.68 (dd, *J* = 16.2, 6.0 Hz, 1H), 2.58 – 2.54 (m, 0.33H), 2.54 – 2.53 (m, 1H), 2.40 (d, *J* = 1.3 Hz, 3H), 1.44 (s, 4H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.6, (197.2), (149.5), 148.6, 145.5, (145.2), 130.0, (129.7), (88.8), 87.9, (81.2), 78.7, (77.0), 68.3, 53.2, (48.0), (38.2), 37.0, 30.7, (30.0), 24.6, (24.3) ppm; FTIR (neat) υ 2923, 1677, 1449, 1372, 1284, 1182, 1089, 805 cm^{-1}; HRMS (ESI) m/z: Calcd. For $C_{11}H_{14}IO_2^+$: 305.0033, Found: 305.0042 ($M+H^+$).

d) Characterization data for compounds 5

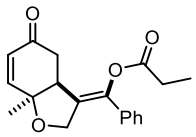
(*E*)-(7a-methyl-5-oxo-3a,4,5,7a-tetrahydrobenzofuran-3(2*H*)-ylidene)(phenyl) methyl acetate, 5a



Yellow-brown liquid, 54.8 mg, 92% yield, PE : EtOAc = 2:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.30 (m, 3H), 7.22 – 7.19 (m, 2H), 6.58 (dd, *J* = 10.2, 1.1 Hz, 1H),

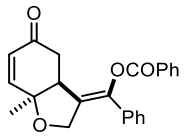
6.08 (d, *J* = 10.3 Hz, 1H), 4.49 (s, 2H), 3.20 (t, *J* = 4.8 Hz, 1H), 2.88 (dd, *J* = 16.6, 4.8 Hz, 1H), 2.64 (dd, *J* = 16.6, 6.0 Hz, 1H), 2.26 (s, 3H), 1.51 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.0, 168.7, 150.2, 140.7, 135.0, 130.1, 130.0, 128.8, 128.6, 126.7, 79.7, 68.2, 47.1, 37.0, 23.6, 20.9 ppm; FTIR (neat) υ 2970, 1758, 1446, 1372, 1197, 1027, 891, 773 cm^{-1}; HRMS (ESI) m/z: Calcd. For $C_{18}H_{18}O_4Na^+$: 321.1097, Found: 321.1105 ($M+Na^+$).

((*E*)-7a-methyl-5-oxo-3a,4,5,7a-tetrahydrobenzofuran-3(2*H*)-ylidene)(phenyl)methyl propionate, 5a'



Light yellow liquid, 50.2 mg, 80% yield, PE : EtOAc = 2:1. ^{1}H NMR (400 MHz, $CDCl_3$) ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 – 7.29 (m, 3H), 7.21 – 7.19 (m, 2H), 6.58 (dd, *J* = 10.3, 1.1 Hz, 1H), 6.07 (d, *J* = 10.3 Hz, 1H), 4.50 (d, *J* = 1.3 Hz, 2H), 3.21 – 3.18 (m, 1H), 2.87 (dd, *J* = 16.6, 4.9 Hz, 1H), 2.62 (dd, *J* = 16.6, 6.0 Hz, 1H), 2.55 (q, *J* = 7.6 Hz, 2H), 1.51 (s, 3H), 1.23 (t, *J* = 7.6 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.0, 172.1, 150.2, 140.8, 135.1, 130.1, 130.0, 128.7, 128.6, 126.7, 79.6, 68.2, 47.1, 37.1, 27.6, 23.7, 9.2 ppm; FTIR (neat) υ 2956, 1746, 1675, 1434, 1356, 1021, 776 cm^{-1}; HRMS (ESI) m/z: Calcd. For $C_{19}H_{20}NaO_4^+$: 335.1254, Found: 335.1251 ($M+Na^+$).

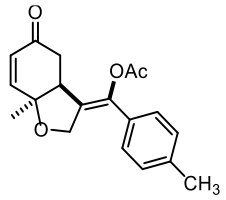
((*E*)-7a-methyl-5-oxo-3a,4,5,7a-tetrahydrobenzofuran-3(2*H*)-ylidene)(phenyl)methyl benzoate, 5a''



Light yellow liquid, 58.4 mg, 81% yield, PE : EtOAc = 2:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 – 8.19 (m, 2H), 7.67 – 7.63 (m, 1H), 7.54 – 7.50 (m, 2H), 7.36 – 7.26 (m, 5H), 6.58 (dd, *J* = 10.3, 1.2 Hz, 1H), 6.08 (dd, *J* = 10.2, 0.7 Hz, 1H), 4.62 (dd, *J* = 13.3, 0.5 Hz, 1H), 4.55 (dd, *J* = 13.3, 2.1 Hz, 1H), 3.28 – 3.26 (m, 1H), 2.94 (ddd, *J* = 16.7, 4.6, 0.8 Hz, 1H), 2.58 (dd, *J* = 16.7, 5.9 Hz, 1H), 1.52 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.1, 164.3, 150.3, 140.8, 134.9, 134.0, 130.4, 130.4, 130.2, 128.9, 128.9,

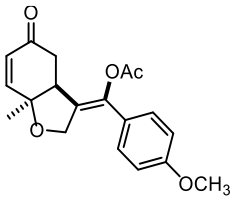
128.8, 128.7, 126.7, 79.8, 68.3, 47.4, 37.2, 23.5 ppm; FTIR (neat) υ 2927, 1733, 1682, 1450, 1244, 1094, 712 cm^{-1}; HRMS (ESI) m/z: Calcd. For $C_{23}H_{20}NaO_4^+$: 383.1254, Found: 383.1250 ($M+Na^+$).

(*E*)-(7a-methyl-5-oxo-3a,4,5,7a-tetrahydrobenzofuran-3(2*H*)-ylidene)(*p*-tolyl) methyl acetate, 5b



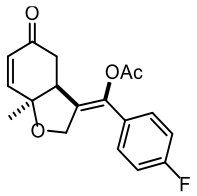
Light yellow solid, 58.0 mg, 93% yield, PE : EtOAc = 2:1, M.p. 96 – 97 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 7.15 (d, *J* = 8.1 Hz, 2H), 7.09 (d, *J* = 8.3 Hz, 2H), 6.58 (dd, *J* = 10.2, 1.1 Hz, 1H), 6.07 (d, *J* = 10.2 Hz, 1H), 4.48 (s, 2H), 3.2 – 3.18 (m, 1H), 2.87 (dd, *J* = 16.7, 4.8 Hz, 1H), 2.63 (dd, *J* = 16.6, 6.0 Hz, 1H), 2.33 (s, 3H), 2.24 (s, 3H), 1.50 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.1, 168.7, 150.2, 140.8, 138.8, 132.1, 130.1, 129.3, 126.6, 79.6, 68.2, 47.0, 37.1, 23.6, 21.4, 21.0 ppm; FTIR (neat) υ 2921, 1755, 1690, 1369, 1279, 1200, 1079, 1027, 889, 818 cm^{-1}; HRMS (ESI) m/z: Calcd. For $C_{19}H_{20}NaO_4^+$: 335.1254, Found: 335.1256 ($M+Na^+$).

(*E*)-(4-methoxyphenyl)(7a-methyl-5-oxo-3a,4,5,7a-tetrahydrobenzofuran-3(2*H*) -ylidene)methyl acetate, 5c



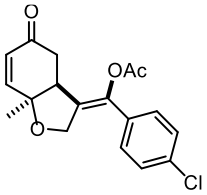
Light yellow solid, 46.6 mg, 71% yield, PE : EtOAc = 2:1, M.p. 105 – 107 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 7.14 (d, *J* = 8.5 Hz, 2H), 6.86 (d, *J* = 8.6 Hz, 2H), 6.57 (d, *J* = 10.3 Hz, 1H), 6.07 (d, *J* = 10.2 Hz, 1H), 4.47 (s, 2H), 3.79 (s, 3H), 3.18 (t, *J* = 5.2 Hz, 1H), 2.87 (dd, *J* = 16.6, 4.7 Hz, 1H), 2.62 (dd, *J* = 16.6, 5.9 Hz, 1H), 2.24 (s, 3H), 1.50 (s, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.1, 168.7, 159.7, 150.2, 140.6, 130.1, 128.5, 128.1, 127.4, 113.9, 79.6, 68.2, 55.4, 47.0, 37.0, 23.6, 21.0 ppm; FTIR (neat) υ 2929, 1753, 1680, 1606, 1511, 1444, 1370, 1206, 1175, 1097, 1030, 869 cm^{-1}; HRMS (ESI) m/z: Calcd. For $C_{19}H_{20}NaO_5^+$: 351.1203, Found: 351.1209 ($M+Na^+$).

(*E*)-(4-fluorophenyl)(7a-methyl-5-oxo-3a,4,5,7a-tetrahydrobenzofuran-3(2*H*) -ylidene)methyl acetate, 5d



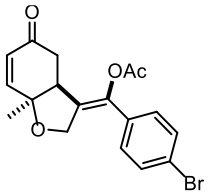
Light yellow solid, 53.1 mg, 84% yield, PE : EtOAc = 2:1, M.p. 77 – 79 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 – 7.17 (m, 2H), 7.06 – 7.00 (m, 2H), 6.57 (dd, *J* = 10.2, 1.1 Hz, 1H), 6.08 (d, *J* = 10.2 Hz, 1H), 4.43 (d, *J* = 1.1 Hz, 2H), 3.19 (t, *J* = 4.7 Hz, 1H), 2.87 (dd, *J* = 16.6, 4.6 Hz, 1H), 2.64 (dd, *J* = 16.6, 5.9 Hz, 1H), 2.25 (s, 3H), 1.51 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.8, 168.6, 162.6 (d, *J* = 249.3 Hz), 150.2, 139.9, 131.2 (d, *J* = 3.2 Hz), 130.2, 130.0, 128.7 (d, *J* = 8.4 Hz), 115.7 (d, *J* = 21.9 Hz), 79.8, 68.0, 47.1, 37.0, 23.5, 20.9 ppm; ^{19}F NMR (376 MHz, $CDCl_3$) δ -111.4 ppm; FTIR (neat) υ 2921, 1750, 1669, 1508, 1370, 1200, 1129, 1097, 1061, 1044, 1017, 836, 793 cm^{-1}; HRMS (ESI) m/z: Calcd. For $C_{18}H_{17}FNaO_4^+$: 339.1003, Found: 339.1008 ($M+Na^+$).

(*E*)-(4-chlorophenyl)(7a-methyl-5-oxo-3a,4,5,7a-tetrahydrobenzofuran-3(2*H*) -ylidene)methyl acetate, 5e



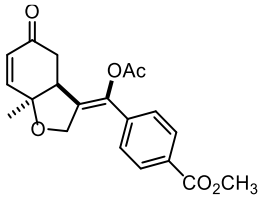
White solid, 51.8 mg, 78% yield, PE : EtOAc = 2:1, M.p. 138 – 139 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 – 7.30 (m, 2H), 7.16 – 7.12 (m, 2H), 6.57 (dd, *J* = 10.3, 1.2 Hz, 1H), 6.08 (d, *J* = 10.3 Hz, 1H), 4.44 (d, *J* = 1.2 Hz, 2H), 3.20 – 3.17 (m, 1H), 2.87 (dd, *J* = 16.7, 4.6 Hz, 1H), 2.64 (dd, *J* = 16.7, 6.0 Hz, 1H), 2.25 (s, 3H), 1.51 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.8, 168.6, 150.1, 139.8, 134.6, 133.5, 130.7, 130.2, 128.9, 128.1, 79.8, 68.0, 47.2, 37.0, 23.5, 20.9 ppm; FTIR (neat) υ 2979, 2845, 1761, 1682, 1493, 1371, 1192, 1094, 1037, 872, 828 cm^{-1}; HRMS (ESI) m/z: Calcd. For $C_{18}H_{17}ClNaO_4^+$: 355.0708, Found: 355.0714 ($M+Na^+$).

(*E*)-(4-bromophenyl)(7a-methyl-5-oxo-3a,4,5,7a-tetrahydrobenzofuran-3(2*H*) -ylidene)methyl acetate, 5f



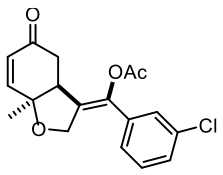
Light yellow solid, 63.2 mg, 84% yield, PE : EtOAc = 2:1, M.p. 152 – 154 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 – 7.45 (m, 2H), 7.09 – 7.06 (m, 2H), 6.57 (dd, *J* = 10.3, 1.2 Hz, 1H), 6.08 (dd, *J* = 10.3, 0.5 Hz, 1H), 4.44 (d, *J* = 1.2 Hz, 2H), 3.20 – 3.17 (m, 1H), 2.86 (dd, *J* = 16.7, 4.6 Hz, 1H), 2.64 (dd, *J* = 16.6, 6.0 Hz, 1H), 2.25 (s, 3H), 1.51 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.7, 168.6, 150.1, 139.8, 133.9, 131.8, 130.8, 130.2, 128.3, 122.9, 79.8, 68.0, 47.2, 36.9, 23.5, 20.9 ppm; FTIR (neat) υ 2923, 1756, 1680, 1490, 1371, 1193, 1093, 1038, 871, 825 cm^{-1}; HRMS (ESI) m/z: Calcd. For $C_{18}H_{17}BrNaO_4^+$: 399.0202, Found: 399.0209 ($M+Na^+$).

(*E*)-methyl 4-(acetoxy(7a-methyl-5-oxo-3a,4,5,7a-tetrahydrobenzofuran-3(2*H*) -ylidene)methyl)benzoate, 5g



White solid, 50.8 mg, 71% yield, PE : EtOAc = 2:1, M.p. 152 – 154 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 – 8.00 (m, 2H), 7.28 – 7.26 (m, 2H), 6.59 (dd, *J* = 10.3, 1.1 Hz, 1H), 6.09 (d, *J* = 10.2 Hz, 1H), 4.54 – 4.46 (m, 2H), 3.92 (s, 3H), 3.22 (t, *J* = 5.2 Hz, 1H), 2.88 (dd, *J* = 16.6, 4.6 Hz, 1H), 2.66 (dd, *J* = 16.6, 6.0 Hz, 1H), 2.28 (s, 3H), 1.52 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.6, 168.5, 166.4, 150.1, 139.9, 139.2, 132.2, 130.2, 130.1, 129.8, 126.5, 79.7, 68.0, 52.3, 47.3, 37.0, 23.5, 20.8 ppm; FTIR (neat) υ 2835, 1764, 1715, 1701, 1376, 1286, 1202, 1113, 1094, 1016, 862, 752 cm^{-1}; HRMS (ESI) m/z: Calcd. For $C_{20}H_{20}NaO_6^+$: 379.1152, Found:379.1154 ($M+Na^+$).

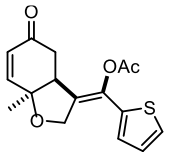
(*E*)-(3-chlorophenyl)(7a-methyl-5-oxo-3a,4,5,7a-tetrahydrobenzofuran-3(2*H*) -ylidene)methyl acetate, 5h



Light yellow solid, 43.8 mg, 66% yield, PE : EtOAc = 2:1, M.p. 113 – 115 °C. ^{1}H NMR

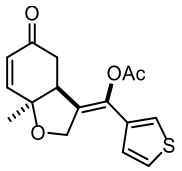
(400 MHz, $CDCl_3$) δ 7.29 – 7.27 (m, 2H), 7.19 – 7.18 (m, 1H), 7.10 – 7.08 (m, 1H), 6.58 (dd, *J* = 10.3, 1.2 Hz, 1H), 6.09 (dd, *J* = 10.2, 0.5 Hz, 1H), 4.47 (d, *J* = 1.3 Hz, 2H), 3.20 – 3.18 (m, 1H), 2.86 (dd, *J* = 16.7, 4.7 Hz, 1H), 2.64 (dd, *J* = 16.6, 6.0 Hz, 1H), 2.26 (s, 3H), 1.52 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.7, 168.6, 150.1, 139.4, 136.8, 134.6, 131.4, 130.2, 129.9, 128.9, 126.8, 125.0, 79.8, 68.0, 47.2, 37.0, 23.5, 20.9 ppm; FTIR (neat) υ 2926, 1754, 1678, 1593, 1562, 1476, 1371, 1175, 1037, 880, 726 cm^{-1}; HRMS (ESI) m/z: Calcd. For $C_{18}H_{17}ClNaO_4^+$: 355.0708, Found: 355.0708 ($M+Na^+$).

(*E*)-(7a-methyl-5-oxo-3a,4,5,7a-tetrahydrobenzofuran-3(2*H*)-ylidene)(thiophen-2-yl)methyl acetate, 5i



Red-brown solid, 53.2 mg, 88% yield, PE : EtOAc = 2:1, M.p. 84 – 87 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 7.32 (dd, *J* = 5.1, 1.1 Hz, 1H), 7.03 (dd, *J* = 5.1, 3.7 Hz, 1H), 6.89 (dd, *J* = 3.7, 0.6 Hz, 1H), 6.60 (dd, *J* = 10.3, 1.1 Hz, 1H), 6.05 (dd, *J* = 10.3, 0.6 Hz, 1H), 4.73 (d, *J* = 13.8 Hz, 1H), 4.51 (dd, *J* = 13.8, 2.4 Hz, 1H), 3.17 (td, *J* = 4.9, 1.1 Hz, 1H), 2.90 (ddd, *J* = 16.6, 5.1, 0.7 Hz, 1H), 2.61 (dd, *J* = 16.6, 5.8 Hz, 1H), 2.31 (s, 3H), 1.51 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.0, 168.5, 150.2, 137.6, 135.5, 130.1, 129.6, 127.6, 126.3, 125.5, 80.0, 68.5, 47.6, 36.9, 23.4, 20.9 ppm; FTIR (neat) υ 2926, 1750, 1685, 1418, 1371, 1192, 1090, 1042, 1005, 837, 718 cm^{-1}; HRMS (ESI) m/z: Calcd. For $C_{16}H_{16}NaSO_4^+$: 327.0662, Found: 327.0664 ($M+Na^+$).

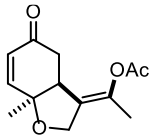
(*E*)-(7a-methyl-5-oxo-3a,4,5,7a-tetrahydrobenzofuran-3(2*H*)-ylidene)(thiophen-3-yl)methyl acetate, 5j



Light yellow solid, 43.9 mg, 72% yield, PE : EtOAc = 2:1, M.p. 86 – 88 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 7.31 (dd, *J* = 5.1, 3.0 Hz, 1H), 7.11 (dd, *J* = 3.0, 1.2 Hz, 1H), 6.95 (dd, *J* = 5.1, 1.3 Hz, 1H), 6.58 (dd, *J* = 10.2, 1.1 Hz, 1H), 6.05 (dd, *J* = 10.2, 0.5 Hz,

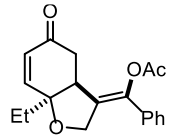
1H), 4.64 (d, *J* = 13.5 Hz, 1H), 4.50 (dd, *J* = 13.3, 2.3 Hz, 1H), 3.16 (td, *J* = 4.9, 1.0 Hz, 1H), 2.89 (ddd, *J* = 16.5, 5.0, 0.5 Hz, 1H), 2.62 (dd, *J* = 16.6, 5.8 Hz, 1H), 2.29 (s, 3H), 1.51 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.0, 168.6, 150.1, 136.7, 136.0, 130.1, 129.4, 126.3, 125.6, 123.2, 79.8, 68.3, 47.3, 37.0, 23.5, 20.9 ppm; FTIR (neat) υ 2971, 1758, 1678, 1370, 1187, 1097, 1037, 885, 846, 782, 733 cm^{-1}; HRMS (ESI) m/z: Calcd. For $C_{16}H_{16}NaSO_4^+$: 327.0662, Found: 327.0664 ($M+Na^+$).

(*E*)-1-(7a-methyl-5-oxo-3a,4,5,7a-tetrahydrobenzofuran-3(2*H*)-ylidene)ethyl acetate, 5k



Light yellow liquid, 34.0 mg, 72% yield, PE : EtOAc = 2:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.53 (dd, *J* = 10.3, 1.4 Hz, 1H), 6.00 (dd, *J* = 10.2, 0.9 Hz, 1H), 4.44 – 4.40 (m, 1H), 4.23 – 4.19 (m, 1H), 3.00 – 2.97 (m, 1H), 2.90 (ddd, *J* = 16.5, 4.2, 0.9 Hz, 1H), 2.54 (dd, *J* = 16.5, 5.6 Hz, 1H), 2.18 (s, 3H), 1.79 – 1.78 (m, 3H), 1.48 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.4, 168.7, 150.6, 139.0, 129.9, 126.5, 80.6, 67.7, 46.2, 37.0, 23.2, 21.0, 18.1 ppm; FTIR (neat) υ 3359, 2929, 1719, 1679, 1498, 1374, 1187, 1156, 1016, 939, 868 cm^{-1}; HRMS (ESI) m/z: Calcd. For $C_{13}H_{14}O_4Na^+$: 259.0941, Found: 259.0946 ($M+Na^+$).

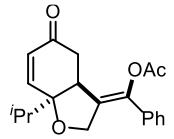
(*E*)-(7a-ethyl-5-oxo-3a,4,5,7a-tetrahydrobenzofuran-3(2*H*)-ylidene)(phenyl) methyl acetate, 5l



Light yellow liquid, 56.9 mg, 92% yield, PE : EtOAc = 2:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.27 (m, 3H), 7.21 – 7.19 (m, 2H), 6.61 (dd, *J* = 10.3, 1.0 Hz, 1H), 6.14 (d, *J* = 10.2 Hz, 1H), 4.51 (dd, *J* = 13.2, 2.0 Hz, 1H), 4.46 (d, *J* = 13.2 Hz, 1H), 3.27 (dd, *J* = 5.8, 5.1 Hz, 1H), 2.86 (dd, *J* = 16.7, 5.0 Hz, 1H), 2.63 (dd, *J* = 16.7, 6.2 Hz, 1H), 2.25 (s, 3H), 1.84 – 1.79 (m, 2H), 1.02 (t, *J* = 7.5 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.2, 168.7, 149.3, 140.7, 134.9, 130.9, 130.5, 128.7, 128.6, 126.6, 82.0, 67.9, 44.6,

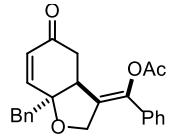
37.4, 30.1, 20.9, 8.2 ppm; FTIR (neat) υ 2969, 1758, 1682, 1370, 1200, 1030, 895 cm^{-1}; HRMS (ESI) m/z: Calcd. For $C_{19}H_{20}NaO_4^+$: 335.1254, Found: 335.1258 ($M+Na^+$).

(*E*)-(7a-isopropyl-5-oxo-3a,4,5,7a-tetrahydrobenzofuran-3(2*H*)-ylidene)(phenyl) methyl acetate, 5m



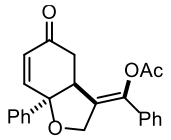
Light yellow solid, 54.8 mg, 84% yield, PE : EtOAc = 2:1, M.p. 84 – 86 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.29 (m, 3H), 7.20 – 7.17 (m, 2H), 6.61 (dd, *J* = 10.4, 1.0 Hz, 1H), 6.22 (d, *J* = 10.5 Hz, 1H), 4.49 (dd, *J* = 13.1, 1.9 Hz, 1H), 4.42 (d, *J* = 13.1 Hz, 1H), 3.36 (t, *J* = 5.5 Hz, 1H), 2.83 (dd, *J* = 17.0, 4.5 Hz, 1H), 2.64 (dd, *J* = 17.0, 6.7 Hz, 1H), 2.26 (s, 3H), 2.09 – 2.03 (m, 1H), 1.06 (d, *J* = 7.0 Hz, 3H), 1.01 (d, *J* = 6.9 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.5, 168.7, 148.0, 140.5, 134.9, 131.8, 131.3, 128.7, 128.6, 126.6, 84.1, 67.6, 42.5, 38.2, 35.0, 21.0, 17.4, 17.3 ppm; FTIR (neat) υ 2924, 1754, 1682, 1493, 1368, 1200, 1043, 899, 785 cm^{-1}; HRMS (ESI) m/z: Calcd. For $C_{20}H_{22}NaO_4^+$: 349.1410, Found: 349.1414 ($M+Na^+$).

(*E*)-(7a-benzyl-5-oxo-3a,4,5,7a-tetrahydrobenzofuran-3(2*H*)-ylidene)(phenyl) methyl acetate, 5n



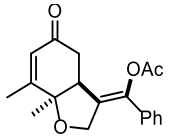
Light yellow liquid, 68.8 mg, 92% yield, PE : EtOAc = 2:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 – 7.27 (m, 5H), 7.26 – 7.23 (m, 3H), 7.20 – 7.17 (m, 2H), 6.54 (dd, *J* = 10.3, 1.2 Hz, 1H), 6.09 (d, *J* = 10.4 Hz, 1H), 4.49 (d, *J* = 1.5 Hz, 2H), 3.31 (t, *J* = 4.7 Hz, 1H), 3.09 (dd, *J* = 33.7, 13.8 Hz, 2H), 2.76 (dd, *J* = 16.8, 4.4 Hz, 1H), 2.31 (dd, *J* = 16.8, 6.1 Hz, 1H), 2.23 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.9, 168.7, 148.9, 140.8, 135.3, 135.0, 131.0, 130.4, 129.8, 128.8, 128.6, 128.5, 127.2, 126.6, 82.0, 68.0, 45.2, 43.8, 37.0, 20.9 ppm; FTIR (neat) υ 3029, 2917, 1762, 1683, 1495, 1369, 1201, 1038, 897 cm^{-1}; HRMS (ESI) m/z: Calcd. For $C_{24}H_{22}NaO_4^+$: 397.1410, Found: 397.1411 ($M+H^+$).

(*E*)-(5-oxo-7a-phenyl-3a,4,5,7a-tetrahydrobenzofuran-3(2*H*)-ylidene)(phenyl) methyl acetate, 5o



White solid, 71.5 mg, 99% yield, PE : EtOAc = 2:1, M.p. 62 – 64 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 – 7.46 (m, 2H), 7.42 – 7.28 (m, 6H), 7.22 – 7.20 (m, 2H), 6.66 (dd, *J* = 10.2, 1.3 Hz, 1H), 6.31 (dd, *J* = 10.3, 0.5 Hz, 1H), 4.72 – 4.68 (m, 2H), 3.47 (t, *J* = 5.1 Hz, 1H), 2.90 (ddd, *J* = 16.7, 4.4, 0.6 Hz, 1H), 2.70 (dd, *J* = 16.7, 5.9 Hz, 1H), 2.20 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.0, 168.6, 148.2, 140.6, 140.2, 134.9, 131.1, 129.5, 128.9, 128.8, 128.6, 128.5, 126.7, 125.4, 83.5, 68.6, 49.1, 36.6, 20.9 ppm; FTIR (neat) υ 2851, 1757, 1686, 1369, 1201, 1042, 897, 761 cm^{-1}; HRMS (ESI) m/z: Calcd. For $C_{23}H_{20}NaO_4^+$: 383.1254, Found: 383.1264 ($M+Na^+$).

(*E*)-(7,7a-dimethyl-5-oxo-3a,4,5,7a-tetrahydrobenzofuran-3(2*H*)-ylidene)(phenyl) methyl acetate, 5p



Off-white solid, 44.3 mg, 71% yield, PE:EtOAc = 2:1, M.p. 148 – 150 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.27 (m, 3H), 7.20 – 7.17 (m, 2H), 5.98 – 5.97 (m, 1H), 4.45 (d, *J* = 13.5 Hz, 1H), 4.29 (dd, *J* = 13.2, 2.3 Hz, 1H), 3.19 – 3.16 (m, 1H), 2.95 (ddd, *J* = 16.9, 3.6, 0.8 Hz, 1H), 2.64 (dd, *J* = 16.9, 6.0 Hz, 1H), 2.26 (s, 3H), 1.98 (d, *J* = 1.3 Hz, 3H), 1.54 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.2, 168.7, 160.8, 140.6, 135.1, 129.8, 128.9, 128.7, 128.6, 126.7, 82.2, 68.0, 48.3, 36.7, 22.2, 21.0, 18.1 ppm; FTIR (neat) υ 2918, 1752, 1660, 1444, 1367, 1216, 1112, 1062, 1020, 909, 779, cm^{-1}; HRMS (ESI) m/z: Calcd. For $C_{19}H_{20}NaO_4^+$: 335.1254, Found: 335.1258 ($M+Na^+$).

6. Determination the configuration of product 2a and 3n via NOE

To confirm the relative configuration of the carbon-carbon double bond in product **2a**, a 2D-NOE spectrum was then collected as shown in Figure *S1*. The NOE signal is found between the H atom of methylene group (-OCH_2-) and the H atom of the phenyl ring,

which confirmed the relative configuration of the carbon-carbon double bond in product **2a** as drawn in Figure *S1*

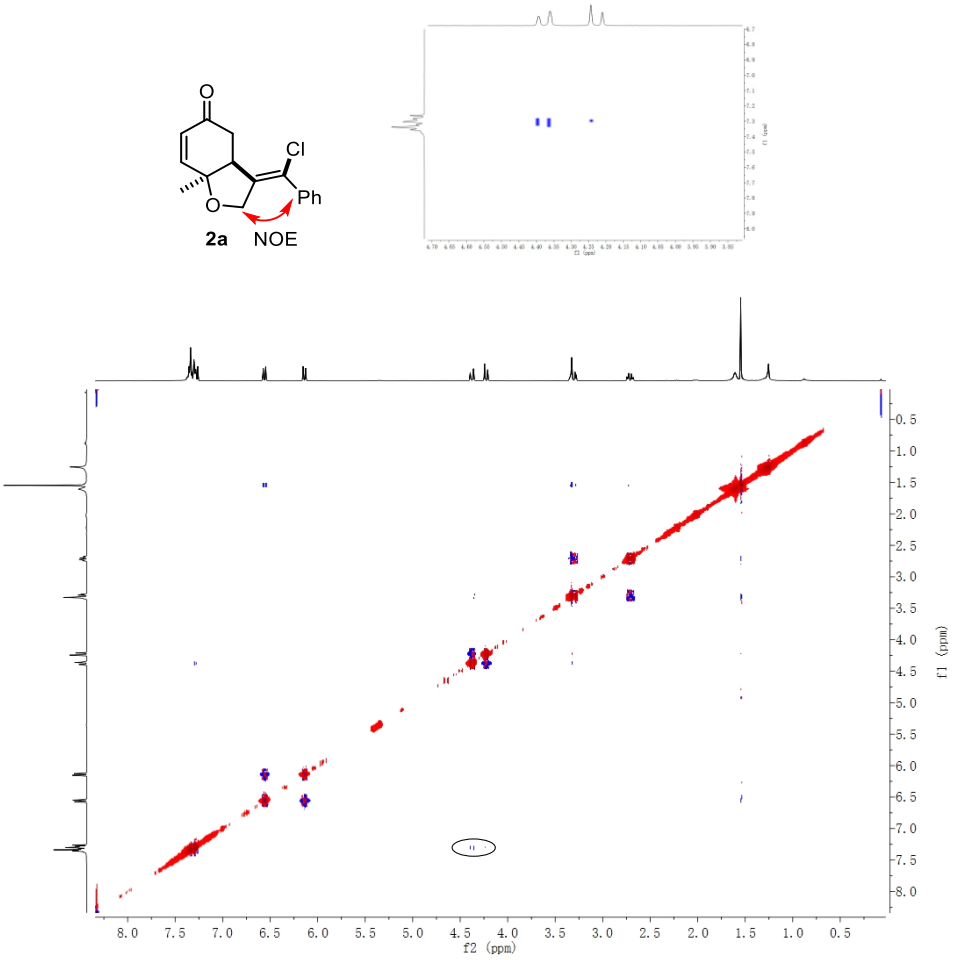
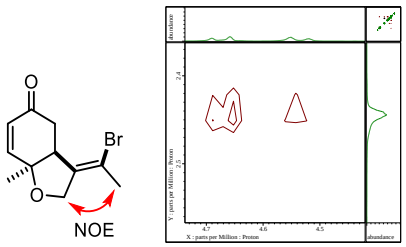


Figure S1 2D-NOE spectrum of product **2a**



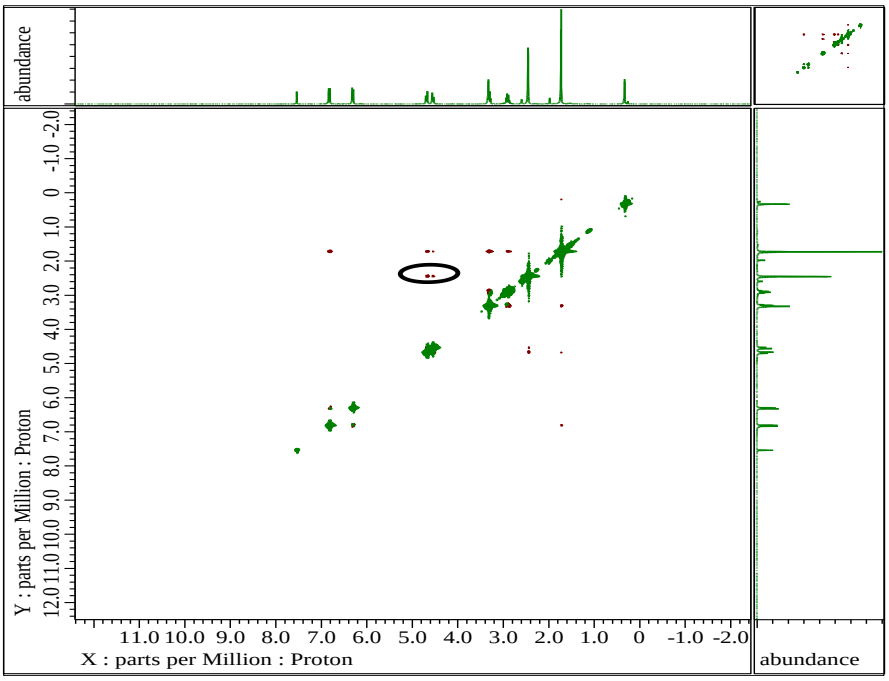


Figure S2 2D-NOE spectrum of product **3n**

To confirm the relative configuration of the carbon-carbon double bond in product **3n**, a 2D-NOE spectrum was then collected as shown in Figure *S2*. The NOE signal is found between the H atom of methylene group (-OCH_2-) and the H atom of methyl group on double bond, which confirmed the relative configuration of the carbon-carbon double bond in product **3n** as drawn in Figure *S2*

7. Scale-up synthesis and synthetic transformations

7.1 General procedure for Scale-up synthesis of compound 2a

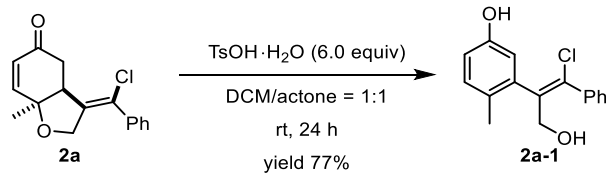
A sealed Schlenk tube (250 mL) charged with a stir bar was added $[RuCl_2(p\text{-cymene})]_2$ (153 mg, 0.25 mmol, 5 mol%), alkynes **1** (1.19 g, 5.0 mmol, 1.0 equiv), and then $^{n}Bu_4NF{\cdot}3H_2O$ (3.16 g, 10.0 mmol, 2.0 equiv). The tube was purged three times by vacuum and N_2, then anhydrous DCE (100 mL, 0.05 M) was added. At last, glacial HOAc (5.7 mL, 100.0 mmol, 20.0 equiv) was added and the resulted mixture was stirred and heated at 100 ℃ in an oil bath for 48. Upon completion, the reaction mixture was cooled to room temperature, and quenched with aqueous saturated $NaHCO_3$ and then extracted with EtOAc (100 mL × 3), and then dried over anhydrous Na_2SO_4, filtered and concentrated in vacuo. The residue was purified by column chromatography using

petroleum ether/ethyl acetate mixture as eluent, affording product **2a** with 71% yield.

7.2 General procedure for Scale-up synthesis of compound 5a

A sealed Schlenk tube (100 mL) charged with a stir bar was added RuCp*(cod)Cl (76 mg, 0.2 mmol, 10 mol%), 1, 6-enyne **1** (476 mg, 2.0 mmol, 1.0 equiv) and AgOAc (167 mg, 1.0 mmol, 0.5 equiv). The tube was purged three times by vacuum and N_2, then anhydrous THF (20.0 mL, 0.1 M) was added. At last, glacial HOAc (2.3 mL, 40.0 mmol, 20.0 equiv) was added and the resulted mixture was stirred and heated at 60 ℃ in an oil bath for 15 h. Upon completion, the reaction mixture was cooled to room temperature, and quenched with aqueous saturated $NaHCO_3$ and then extracted with EtOAc (40 mL × 3), and then dried over anhydrous Na_2SO_4, filtered and concentrated in vacuo. The residue was purified by column chromatography using petroleum ether/ethyl acetate mixture as eluent, affording product **5a** with 83% yield.

7.3 Procedure for synthesis of compound 2a-1

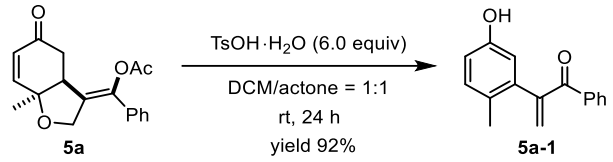


A sealed tube (25 mL) charged with a stir bar was added **2a** (54.8 mg, 0.2 mmol) and *p*-toluenesulfonic acid monohydrate (228.2 mg, 1.2 mmol) and DCM/acetone (2.0 mL, 1/1, v/v). The mixture was stirred 24 h at room temperature. Then it was quenched by aqueous saturated $NaHCO_3$ (30 mL), extracted with EtOAc (20 mL × 3), dried over anhydrous Na_2SO_4, filtered and concentrated in vacuo. The residue was purified by flash column chromatography (petroleum ether/EtOAc = 2/1) to afford **2a-1**.[3]

White solid, 42.2 mg, 77% yield, PE : EtOAc = 2:1, M.p. 101 – 103 ℃. ^{1}H NMR (400 MHz, DMSO-*d*$_6$) δ 9.17 (s, 1H), 7.56 – 7.53 (m, 2H), 7.49 – 7.41 (m, 3H), 7.03 (d, *J* = 8.1 Hz, 1H), 6.64 – 6.59 (m, 2H), 4.96 (t, *J* = 5.5 Hz, 1H), 4.07 (dd, *J* = 11.8, 5.3 Hz, 1H), 4.00 (dd, *J* = 11.8, 5.7 Hz, 1H), 2.19 (s, 3H) ppm; ^{13}C NMR (400 MHz, DMSO-*d*$_6$) δ 155.0, 140.0, 139.3, 137.5, 130.54, 130.49, 128.9, 128.4, 125.4, 115.1, 114.2, 62.4, 18.1 ppm; FTIR (neat) υ 3349, 3175, 1606, 1452, 1234, 1019, 888, 736 cm^{-1}; HRMS

(ESI) m/z: Calcd. For $C_{16}H_{15}ClO_2Na^+$: 297.0653, Found: 297.0657 ($M+Na^+$).

7.4 Procedure for synthesis of compound 5a-1

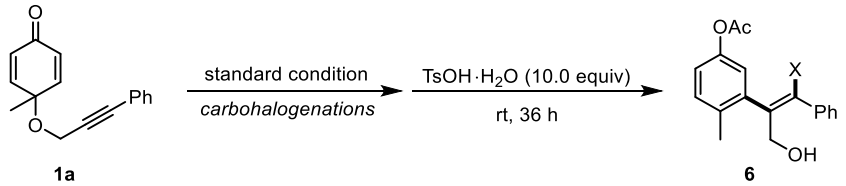


A sealed tube (25 mL) charged with a stir bar was added **5a** (59.6 mg, 0.2 mmol) and *p*-toluenesulfonic acid monohydrate (228.2 mg, 1.2 mmol) and DCM/acetone (2.0 mL, 1/1, v/v). The mixture was stirred 24 h at room temperature. Then it was quenched by aqueous saturated $NaHCO_3$ (30 mL), extracted with EtOAc (20 mL × 3), dried over anhydrous Na_2SO_4, filtered and concentrated in vacuo. The residue was purified by flash column chromatography (petroleum ether/EtOAc = 2/1) to afford **5a-1**. [3]

2-(5-hydroxy-2-methylphenyl)-1-phenylprop-2-en-1-one, 5a-1[4]

Colorless liquid, 43.6 mg, 92% yield, PE : EtOAc = 5:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 – 7.88 (m, 2H), 7.58 – 7.54 (m, 1H), 7.46 – 7.42 (m, 2H), 6.98 (d, *J* = 8.2 Hz, 1H), 6.73 (d, *J* = 2.7 Hz, 1H), 6.69 (dd, *J* = 8.2, 2.7 Hz, 1H), 5.98 (dd, *J* = 17.7, 1.0 Hz, 2H), 5.73 (s, 1H), 2.10 (s, 3H) ppm; ^{13}C NMR (400 MHz, $CDCl_3$) δ 197.1, 154.0, 149.0, 139.2, 137.20, 132.9, 131.4, 130.0, 128.5, 128.4, 127.5, 117.0, 115.6, 19.6 ppm.

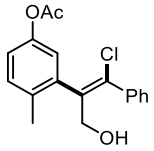
7.5 Procedure for synthesis of compound 6



Following the general procedure of the above carbohalogenations, *p*-toluenesulfonic acid monohydrate (380 mg, 2.0 mmol, 10.0 equiv) was directly added into the reaction mixture after it was cooled to room temperature, and the resulted mixture was stirred at room temperature for 48 h. Upon completion, the reaction mixture was quenched with aqueous saturated $NaHCO_3$ and extracted with EtOAc (20 mL × 3), and then dried over anhydrous Na_2SO_4, then filtered and concentrated in vacuo. The residue was purified by column chromatography using petroleum ether/ethyl acetate mixture as the eluent to

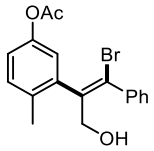
afford product **6**.

(*E*)-3-(1-chloro-3-hydroxy-1-phenylprop-1-en-2-yl)-4-methylphenyl acetate, 6a



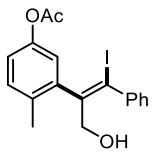
Colorless liquid, 41.2 mg, 65% yield, PE : EtOAc = 5:1. ^{1}H NMR (400 MHz,$CDCl_3$) δ 7.49 – 7.46 (m, 2H), 7.44 – 7.39 (m, 3H), 7.12 (d, *J* = 8.2 Hz, 1H), 6.74 (dd, *J* = 8.2, 2.7 Hz, 1H), 6.67 (d, *J* = 2.7 Hz, 1H), 4.99 (bs, 1H), 4.74 (d, *J* = 12.0 Hz, 1H), 4.69 (d, *J* = 12.0 Hz, 1H), 2.29 (s, 3H), 1.94 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.8, 153.7, 139.1, 137.5, 135.7, 133.3, 131.3, 129.4, 129.0, 128.7, 128.2, 115.2, 115.1, 65.4, 20.9, 18.4 ppm; FTIR (neat) υ 2925, 1734, 1445, 1377, 1230, 1028, 743, 697 cm^{-1}; HRMS (ESI) m/z: Calcd. For $C_{18}H_{17}ClO_3Na^+$:339.0758, Found: 339.0772 ($M+Na^+$).

(*E*)-3-(1-bromo-3-hydroxy-1-phenylprop-1-en-2-yl)-4-methylphenyl acetate, 6b



Colorless liquid, 43.8 mg, 61% yield, PE : EtOAc = 5:1. ^{1}H NMR (400 MHz,$CDCl_3$) δ 7.46 – 7.34 (m, 5H), 7.11 (d, *J* = 8.2 Hz, 1H), 6.74 (dd, *J* = 8.2, 2.7 Hz, 1H), 6.66 (d, *J* = 2.7 Hz, 1H), 5.28 (bs, 1H), 4.69 (d, *J* = 12.1 Hz, 1H), 4.64 (d, *J* = 12.0 Hz, 1H), 2.30 (s, 3H), 1.92 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.9, 153.7, 140.8, 139.1, 136.6, 131.3, 129.2, 129.0, 128.6, 127.8, 127.6, 115.1, 65.0, 20.9, 18.4 ppm; FTIR (neat) υ 2971, 1669,1495, 1378, 1083, 876, 730 cm^{-1}; HRMS (ESI) m/z: Calcd. For $C_{18}H_{17}BrO_3Na^+$: 383.0253, Found: 383.0234 ($M+Na^+$).

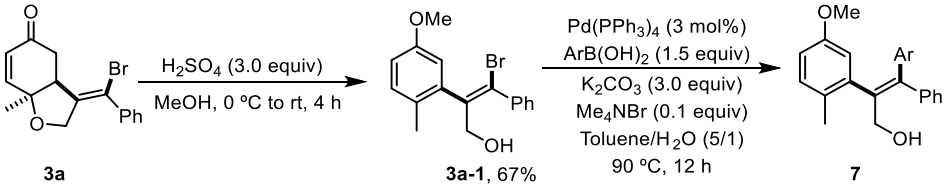
(*E*)-3-(3-hydroxy-1-iodo-1-phenylprop-1-en-2-yl)-4-methylphenyl acetate, 6c



Colorless liquid, 43.1 mg, 53% yield, PE : EtOAc = 5:1. ^{1}H NMR (400 MHz,$CDCl_3$) δ 7.38 – 7.37 (m, 4H), 7.34 – 7.28 (m, 1H), 7.12 (d, *J* = 8.2 Hz, 1H), 6.75 (dd, *J* = 8.2, 2.7 Hz, 1H), 6.61 (d, *J* = 2.7 Hz, 1H), 5.07 (bs, 1H), 4.66 (d, *J* = 12.1 Hz, 1H), 4.61 (d,

J = 12.1 Hz), 2.30 (s, 3H), 1.90 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.7, 153.7, 144.1, 143.1, 142.6, 131.5, 128.8, 128.6, 128.5, 127.4, 115.22, 115.19, 106.9, 63.3, 20.9, 18.4 ppm; FTIR (neat) υ 2923, 1599, 1498, 1230, 1176, 1024, 825 cm^{-1}; HRMS (ESI) m/z: Calcd. For $C_{18}H_{17}IO_3Na^+$: 431.0115, Found: 431.0097 ($M+Na^+$).

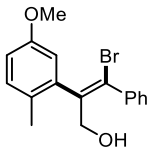
6.6 Procedure for synthesis of compound 7



A sealed tube (25 mL) charged with a stir bar was added **3a** (95.7 mg, 0.3 mmol, 1.0 equiv) and MeOH (8.0 mL), then followed by conc. H_2SO_4 (45 μL, 0.9 mmol, 3.0 equiv) at 0 ℃. The reaction mixture was stirred at room temperature for 4 h and quenched with aqueous saturated $NaHCO_3$, which was extracted with EtOAc (30 mL× 3). The organic phase was combined, dried with anhydrous Na_2SO_4, and then evaporated under reduced pressure. The residue was purified by silica gel chromatography to afford the product **3a-1** in 67% yield.[5]

A sealed tube (25 mL) charged with a stir bar was added $Pd(PPh_3)_4$ (6.9 mg, 0.006 mmol, 3 mol%), **3a-1** (66.5 mg, 0.20 mmol, 1.0 equiv) and Me_4NBr (3.1 mg, 0.02 mmol, 0.1 equiv). The tube was purged three times by vacuum and N_2, then anhydrous toulene (2.0 mL, 0.1 M) and 2 mol/L K_2CO_3 (0.4 mL) was added. The resulted mixture was heated at 90 ℃ in an oil bath and stirred for 12 h. Upon completion, the reaction mixture was cooled to room temperature, and extracted with EtOAc (20 mL × 3), and then dried over anhydrous Na_2SO_4, filtered and concentrated in vacuo. The residue was purified by column chromatography using petroleum ether/ethyl acetate mixture as eluent to afford product **7**[6].

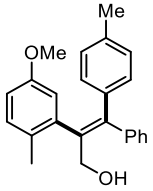
(*E*)-3-bromo-2-(5-methoxy-2-methylphenyl)-3-phenylprop-2-en-1-ol, 3a-1



Colorless liquid, 66.8 mg, 67%, PE : EtOAc = 5:1. ^{1}H NMR (400 MHz,$CDCl_3$) δ 7.50

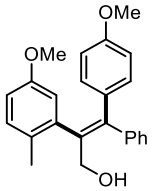
– 7.48 (m, 2H), 7.43 – 7.33 (m, 3H), 7.19 (d, *J* = 8.4 Hz, 1H), 6.83 (dd, *J* = 8.4, 2.7 Hz, 1H), 6.74 (d, *J* = 2.7 Hz, 1H), 4.25 (d, *J* = 12.3 Hz, 1H), 4.17 (d, *J* = 12.3 Hz, 1H), 3.82 (s, 3H), 2.32 (s, 3H), 1.53 (bs, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.8, 141.1, 140.7, 139.4, 131.4, 129.1, 129.0, 128.5, 127.9, 125.0, 113.8, 113.5, 63.9, 55.5, 18.4 ppm; FTIR (neat) υ 2921, 1743, 1603, 1495, 1407, 1290, 1216, 1045 cm^{-1}; HRMS (ESI) m/z: Calcd. For $C_{17}H_{21}BrNO_2^+$: 350.0750, Found: 350.0732 ($M+NH_4^+$).

(*E*)-2-(5-methoxy-2-methylphenyl)-3-phenyl-3-(*p*-tolyl)prop-2-en-1-ol, 7a



Colorless liquid, 56.4 mg, 82% yield, PE : EtOAc = 5:1. ^{1}H NMR (400 MHz,$CDCl_3$) δ 7.39 – 7.28 (m, 5H), 6.97 (d, *J* = 8.4 Hz, 1H), 6.84 – 6.79 (m, 5H), 6.69 (dd, *J* = 8.4, 2.8 Hz, 1H), 4.40 (dd, *J* = 12.0, 5.5 Hz, 1H), 4.31 (dd, *J* = 12.0, 6.6 Hz, 1H), 3.77 (s, 3H), 2.19 (s, 3H), 2.07 (s, 3H), 1.45 (t, *J* = 6.3 Hz, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.6, 142.8, 142.2, 140.6, 139.0, 136.8, 136.4, 131.3, 129.9, 129.8, 128.7, 128.4, 128.3, 127.4, 115.4, 112.9, 65.7, 55.4, 21.3, 19.0 ppm; FTIR (neat) υ 2869, 1643, 1497, 1406, 1225, 1051, 887 cm^{-1}; HRMS (ESI) m/z: Calcd. For $C_{24}H_{25}O_2^+$:345.1849, Found: 345.1856 ($M+H^+$).

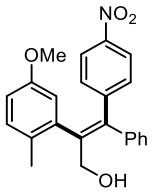
(*E*)-2-(5-methoxy-2-methylphenyl)-3-(4-methoxyphenyl)-3-phenylprop-2-en-1-ol, 7b



Colorless liquid, 62.8 mg, 87% yield, PE : EtOAc = 5:1. ^{1}H NMR (400 MHz,$CDCl_3$) δ 7.39 – 7.28 (m, 5H), 6.96 (d, *J* = 8.4 Hz, 1H), 6.84 – 6.81 (m, 2H), 6.68 (dd, *J* = 8.4, 2.8 Hz, 1H), 6.57 – 6.53 (m, 2H), 4.39 (d, *J* = 12.0 Hz, 1H), 4.29 (d, *J* = 12.0 Hz, 1H), 3.77 (s, 3H), 3.67 (s, 3H), 2.05 (s, 3H), 1.50 (bs, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.2, 157.6, 142.4, 142.2, 140.7, 136.3, 134.4, 131.4, 131.2, 129.9, 128.7, 128.4, 127.4, 115.3, 112.8, 112.8, 65.8, 55.4, 55.1, 19.0 ppm; FTIR (neat) 2886, 1740, 1382,

1316, 1232, 1087, 881 cm^{-1}; HRMS (ESI) m/z: Calcd. For $C_{24}H_{25}O_3^+$:361.1798, Found: 361.1801 ($M+H^+$).

(*E*)-2-(5-methoxy-2-methylphenyl)-3-(4-nitrophenyl)-3-phenylprop-2-en-1-ol, 7c



Colorless liquid, 54.6 mg, 73% yield, PE : EtOAc = 5:1. ^1H NMR (400 MHz,$CDCl_3$) δ 7.91 – 7.87 (m, 2H), 7.43 – 7.31 (m, 5H), 7.11 – 7.07 (m, 2H), 6.99 (d, *J* = 8.4 Hz, 1H), 6.80 (d, *J* = 2.7 Hz, 1H), 6.72 (dd, *J* = 8.4, 2.7 Hz, 1H), 4.44 (dd, *J* = 12.2, 4.6 Hz, 1H), 4.36 (dd, *J* = 12.1, 5.5 Hz, 1H), 3.77 (s, 3H), 2.08 (s, 3H), 1.52 (t, *J* = 5.6 Hz, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.8, 148.9, 146.3, 140.9, 140.5, 140.4, 139.3, 131.7, 130.7, 129.9, 128.8, 128.2, 128.1, 122.9, 115.5, 113.3, 65.3, 55.5, 18.9 ppm; FTIR (neat) 2920, 2320, 2079, 1644, 1510, 1344, 1053, 858 ppm; HRMS (ESI) m/z: Calcd. For $C_{23}H_{22}NO_4^+$: 376.1543, Found: 376.1544 ($M+H^+$).

8. Crystal structural data

8.1 Crystal structural data 2g

Single crystal of compound **2g** was obtained by recrystallization from ethyl acetate and petroleum ether. The structure was shown in *Figure S3*. X-ray diffractional data and the refinement were shown in *Table S4*.

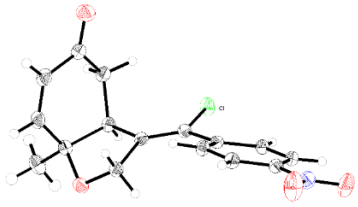


Figure S3 X-ray single crystal structure of **2g**. Displacement ellipsoids are drawn at the 25% probability level.

Table S4 Crystal data and structure refinement for substrate **2g**

	2g
Empirical formula	$C_{32}H_{28}Cl_2N_2O_8$
Formula weight	639.46
Temperature	300.0 K

Wavelength	0.71073 Å
Crystal system space group	triclinic P-1
Unit cell dimensions	a = 8.7268 (3) Å, b = 8.8198(3) Å, c = 9.8887(3) Å, α = 94.7650(10)° β = 107.4040(10)° γ = 93.8140(10)°
Volume	720.42(4) $Å^3$
Z, Calculated density	1, 1.474 Mg/m^3
Absorption coefficient	0.283 mm^{-1}
F(000)	332.0
Crystal size	0.26 × 0.24 × 0.2 mm^3
Theta range for data collection	4.342 to 55.012 °
Limiting indices	-11 ⩽ h ⩽ 11, -11 ⩽ k ⩽ 11, -12 ⩽ l ⩽ 12
Reflections collected / unique	17022 /3325 [R_{int} = 0.0295, R_{sigma} = 0.0228]
Completeness to theta = 29.00	100 %
Data / restraints / parameters	3325/0/200
Goodness-of-fit on F^2	1.059
Final R indices [I>2sigma(I)]	R_1 = 0.0380, wR_2 = 0.0962
R indices (all data)	R_1 = 0.0437, wR_2 = 0.1010
Largest diff. peak and hole	0.21 and -0.34e·$Å^{-3}$

CIF files of **2g** can be obtained from the Cambridge Crystallographic Data Centre using deposition numbers 2083884. Copies of the data can be obtained, free of charge, on application to the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [e-mail: deposit@ccdc.cam.ac.uk, fax: +44 (1223) 336 033].

8.2 Crystal structural data 3g

Single crystal of compound **3g** was obtained by recrystallization from ethyl acetate and petroleum ether. The structure was shown in *Figure S4*. X-ray diffractional data and the refinement were shown in *Table S5*.

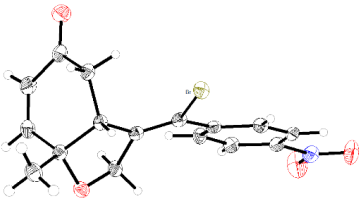


Figure S4 X-ray single crystal structure of **3g**. Displacement ellipsoids are drawn at the 50% probability level.

Table S5 Crystal data and structure refinement for substrate **3g**

	3g
Empirical formula	$C_{32}H_{28}Br_2N_2O_8$
Formula weight	728.38
Temperature	296.15 K
Wavelength	0.71073 Å
Crystal system space group	triclinic P-1
Unit cell dimensions	a = 8.708(2) Å, b = 8.801(2) Å, c = 9.811(3) Å, α = 93.879(4)° β = 106.094(3)° γ = 92.492(3)°
Volume	719.3(3) $Å^3$
Z, Calculated density	1, 1.681 Mg/m^3
Absorption coefficient	2.876 mm^{-1}
F(000)	368.0
Crystal size	0.26 × 0.24 × -0.2 mm^3
Theta range for data collection	4.336 to 51.124 °
Limiting indices	-10 ⩽ h ⩽ 10, -10 ⩽ k ⩽ 10, -11 ⩽ l ⩽ 11
Reflections collected / unique	7121/2668 [R_{int} = 0.0255, R_{sigma} = 0.0293]
Completeness to theta = 29.00	100 %
Data / restraints / parameters	2668/0/200
Goodness-of-fit on F^2	1.045
Final R indices [I>2sigma(I)]	R_1 = 0.0265, wR_2 = 0.0692
R indices (all data)	R_1 = 0.0317, wR_2 = 0.0715
Largest diff. peak and hole	0.69/-0.52 e·$Å^{-3}$

CIF files of **3g** can be obtained from the Cambridge Crystallographic Data Centre using deposition numbers 2105850. Copies of the data can be obtained, free of charge, on application to the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [e-mail: deposit@ccdc.cam.ac.uk, fax: +44 (1223) 336 033].

8.3 Crystal structural data 4e

Single crystal of compound **4e** was obtained by recrystallization from ethyl acetate and petroleum ether. The structure was shown in *Figure S5*. X-ray diffractional data and the refinement were shown in *Table S6*.

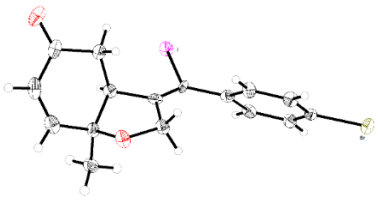


Figure S5 X-ray single crystal structure of **4e**. Displacement ellipsoids are drawn at the 50% probability level.

Table S6 Crystal data and structure refinement for substrate **4e**

	4e
Empirical formula	$C_{128}H_{112}Br_8I_8O_{16}$
Formula weight	3560.65
Temperature	296.15K
Wavelength	0.71073 Å
Crystal system space group	orthorhombic Pbca
Unit cell dimensions	a = 10.6516(15) Å, b = 8.2155(12) Å, c = 34.902(5) Å, α = 90° β = 90° γ = 90°
Volume	3054.2(8) $Å^3$
Z, Calculated density	1, 1.936 Mg/m^3
Absorption coefficient	4.712 mm^{-1}
F(000)	1712.0
Crystal size	0.26 × 0.22 × 0.2 mm^3
Theta range for data collection	4.48 to 50.924 °

Limiting indices	-12 ⩽ h ⩽ 12, -9 ⩽ k ⩽ 9, -41 ⩽ l ⩽ 33
Reflections collected / unique	17202/2691 [R_{int} = 0.0272, R_{sigma} = 0.0218]
Completeness to theta = 29.00	96%
Data / restraints / parameters	2691/0/182
Goodness-of-fit on F^2	1.239
Final R indices [I>2sigma(I)]	R_1 = 0.0356, wR_2 = 0.0760
R indices (all data)	R_1 = 0.0416, wR_2 = 0.0777
Largest diff. peak and hole	0.95/-1.01 e·Å^{-3}

CIF files of **4e** can be obtained from the Cambridge Crystallographic Data Centre using deposition numbers 2111667. Copies of the data can be obtained, free of charge, on application to the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [e-mail: deposit@ccdc.cam.ac.uk, fax: +44 (1223) 336 033].

8.4 Crystal structural data 5e

Single crystal of compound **5e** was obtained by recrystallization from ethyl acetate and petroleum ether. The structures were shown in *Figure S6*. X-ray diffractional data and the refinement were shown in *Table S7*.

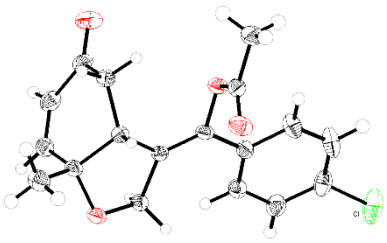


Figure S6 X-ray single crystal structure of **5e**. Displacement ellipsoids are drawn at the 25% probability level.

Table S7 Crystal data and structure refinement for substrate **5e**

	5e
Empirical formula	$C_{144}H_{136}Cl_8O_{36}$
Formula weight	2662.12
Temperature	300.0 K
Wavelength	0.71073 Å

Crystal system space group	monoclinic C2/c
Unit cell dimensions	a = 32.6039(12) Å, b = 7.5419(3) Å, c = 13.9954(4)Å, α = 90° β = 110(10)° γ = 90°
Volume	3222.6(2)Å^3
Z, Calculated density	1, 1.372 Mg/m^3
Absorption coefficient	0.255 mm^{-1}
F(000)	1392.0
Crystal size	0.26 × 0.24 ×-0.2 mm^3
Theta range for data collection	5.564 to 54.99 °
Limiting indices	-42 ⩽ h ⩽ 41, -9 ⩽ k ⩽ 9, -18 ⩽ l ⩽ 18
Reflections collected / unique	18713/3690 [R_{int} = 0.0613, R_{sigma} = 0.0409]
Completeness to theta = 29.00	100%
Data / restraints / parameters	3690/0/210
Goodness-of-fit on F^2	1.025
Final R indices [I>2sigma(I)]	R_1 = 0.0514, wR_2 = 0.1110
R indices (all data)	R_1 = 0.0914, wR_2 = 0.1350
Largest diff. peak and hole	0.27/-0.32 e·Å^{-3}

CIF files of **5e** can be obtained from the Cambridge Crystallographic Data Centre using deposition numbers 2155999. Copies of the data can be obtained, free of charge, on application to the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [e-mail: deposit@ccdc.cam.ac.uk, fax: +44 (1223) 336 033].

9. References

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selective cascade dihalogenation of alkyne-tethered cyclohexadienones via Umpolung of palladium enolate. *Chem. Commun*. **2019**, *55*, 13442.

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(4) Nair, A. M., Halder I., Sharma R., and Volla, C. M. R. Water Mediated rearrangement of alkynyl cyclohexadienones: access tometa-alkenylated phenols. *Org. Lett.* **2021**, *23*, 1840.

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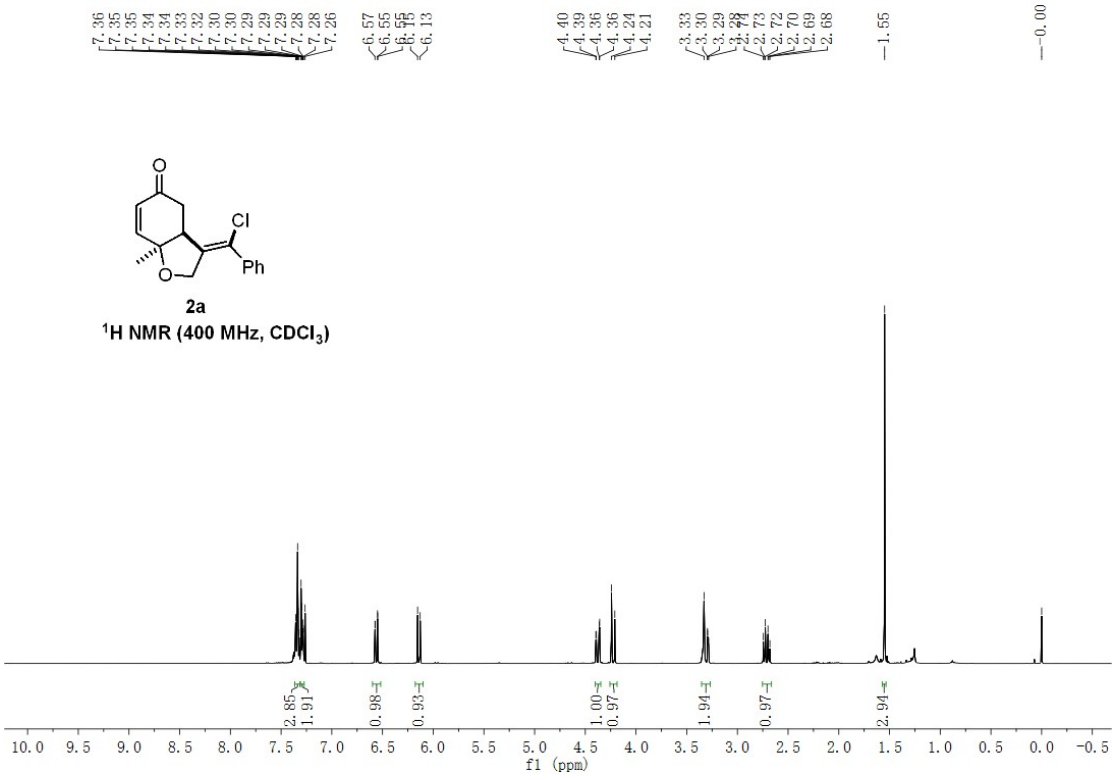
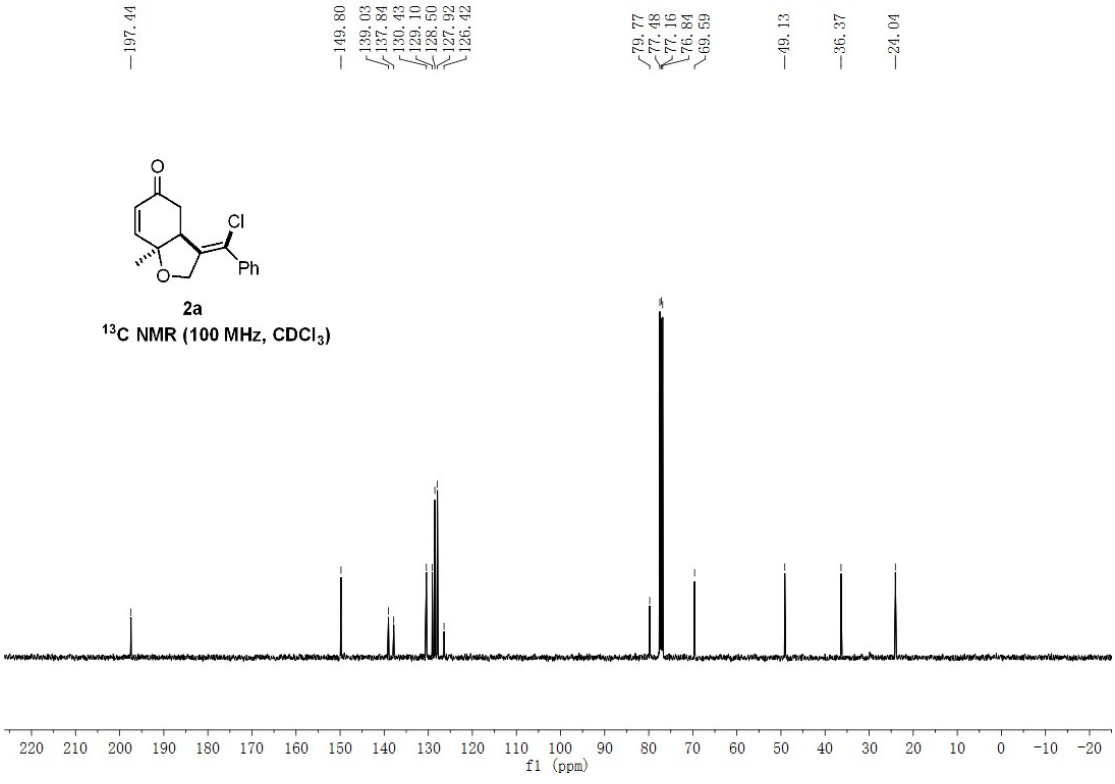
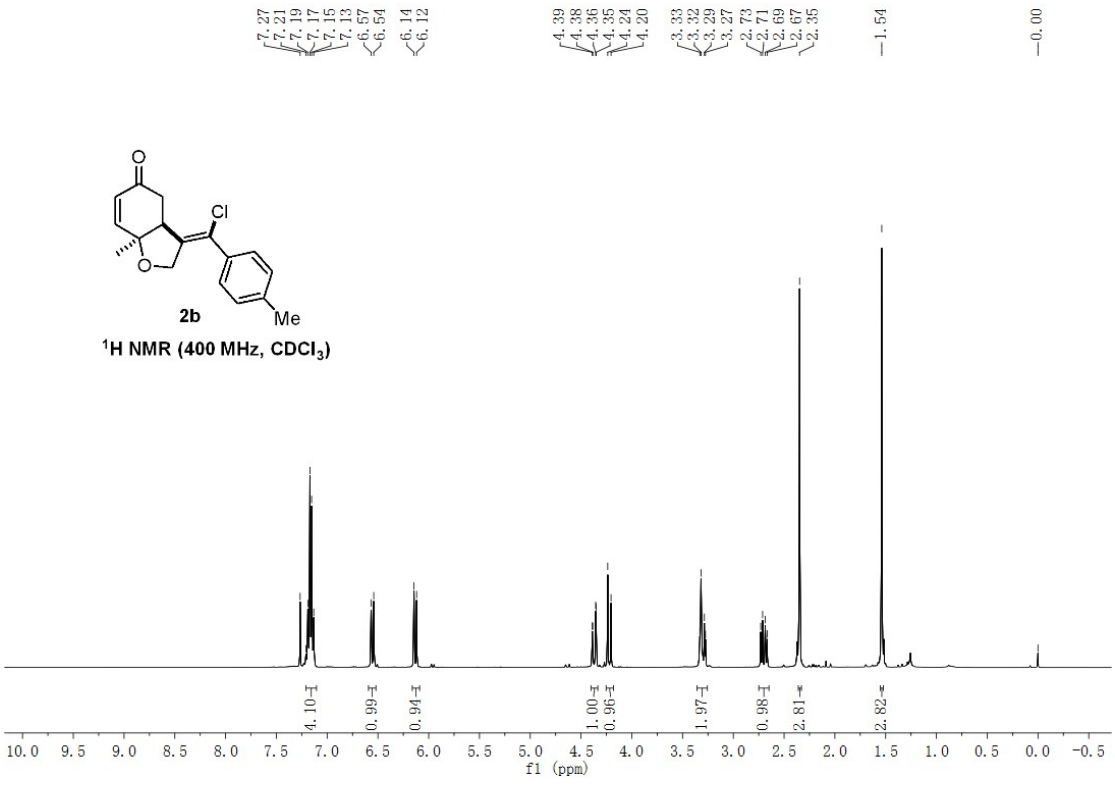
(6) Qin, M. M.; Wu, Z. B.; Zhang, J. R.; Xing, X. Y.; Zhu, L. N.; Zhong, Y. Q.; Guo, Y. R.; Zhao; G. J.; The aggregation-induced emission of Methyl-bis-(4-triphenylvinylbenzyl)-amine in solution with torsional and locked stacking effects. *J. Mol. Liq.* **2021**, *339*, 116626.

10. NMR spectra of new compounds







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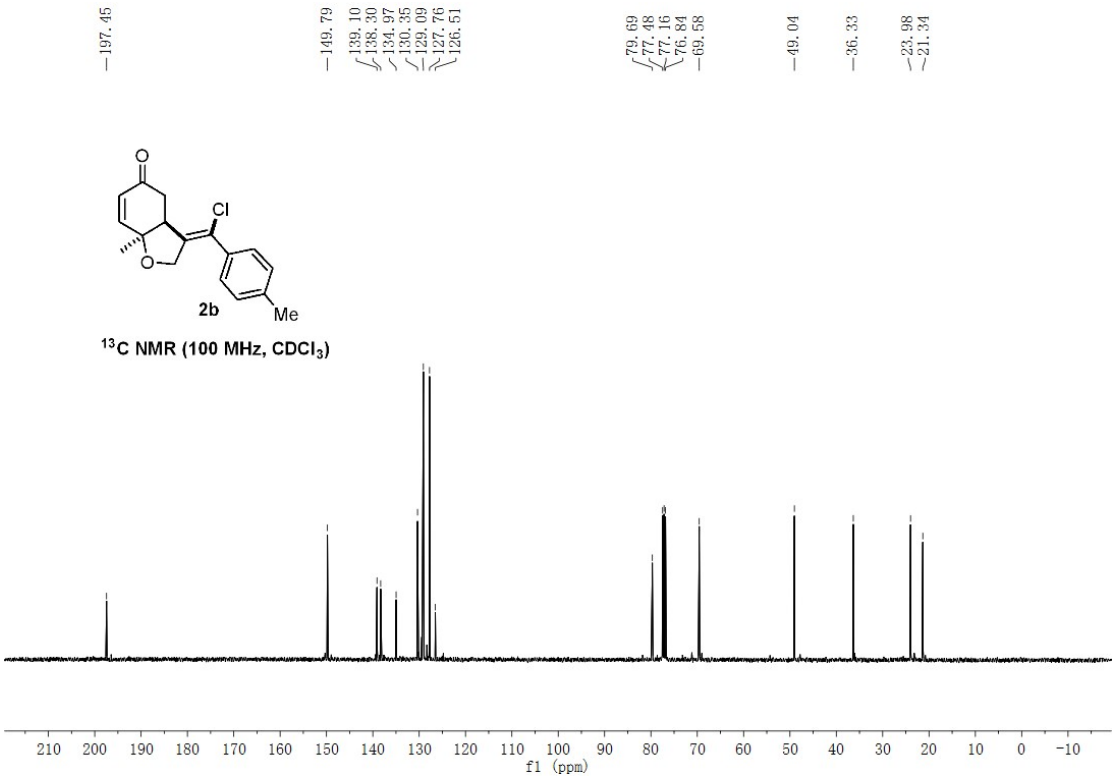
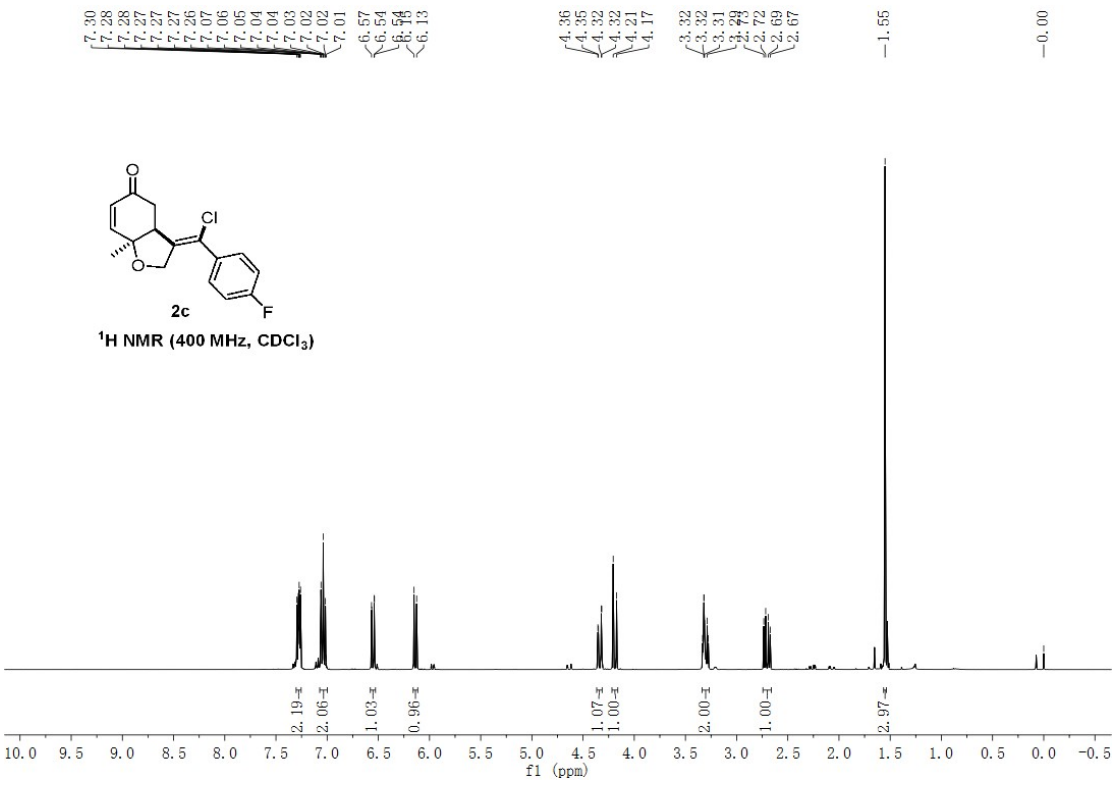


^{13}C NMR (100 MHz, $CDCl_3$)



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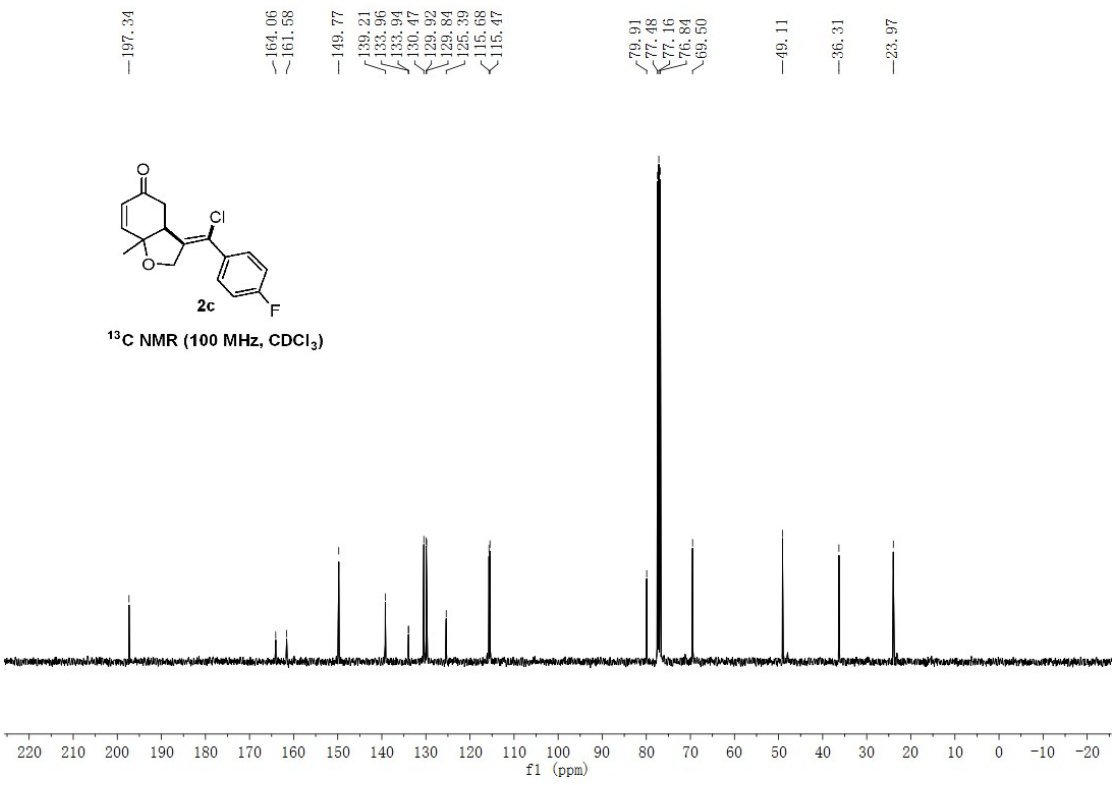

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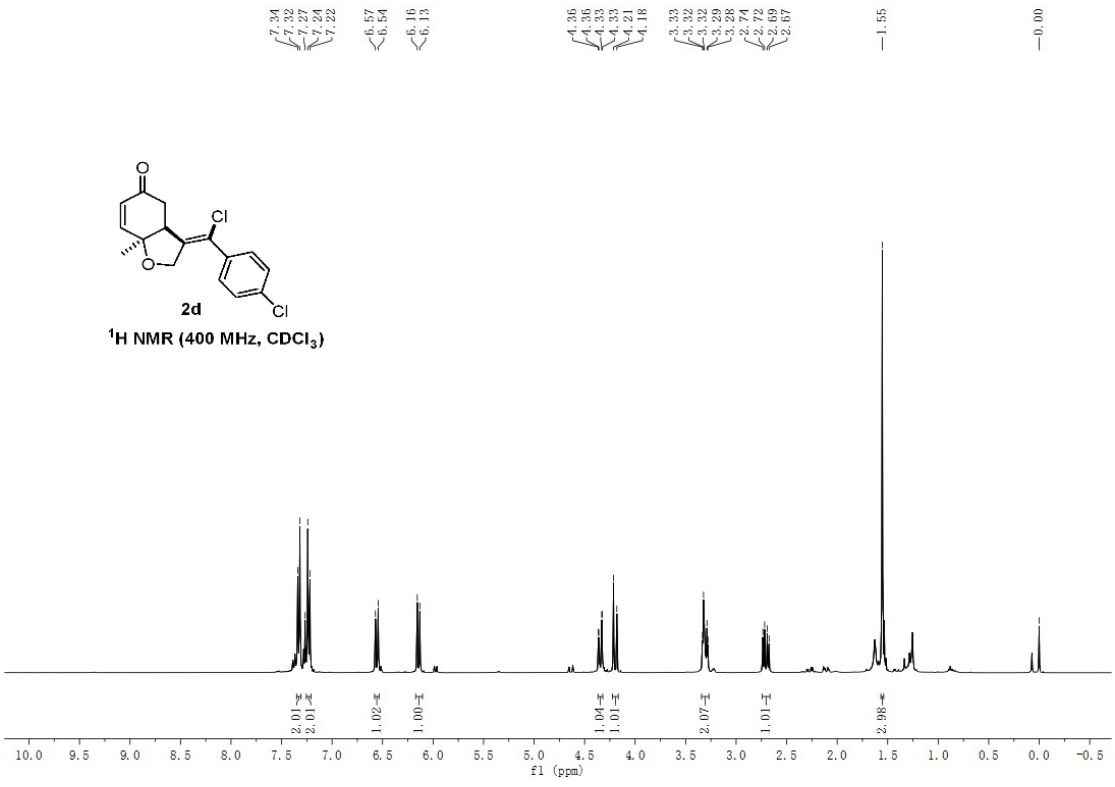

2d

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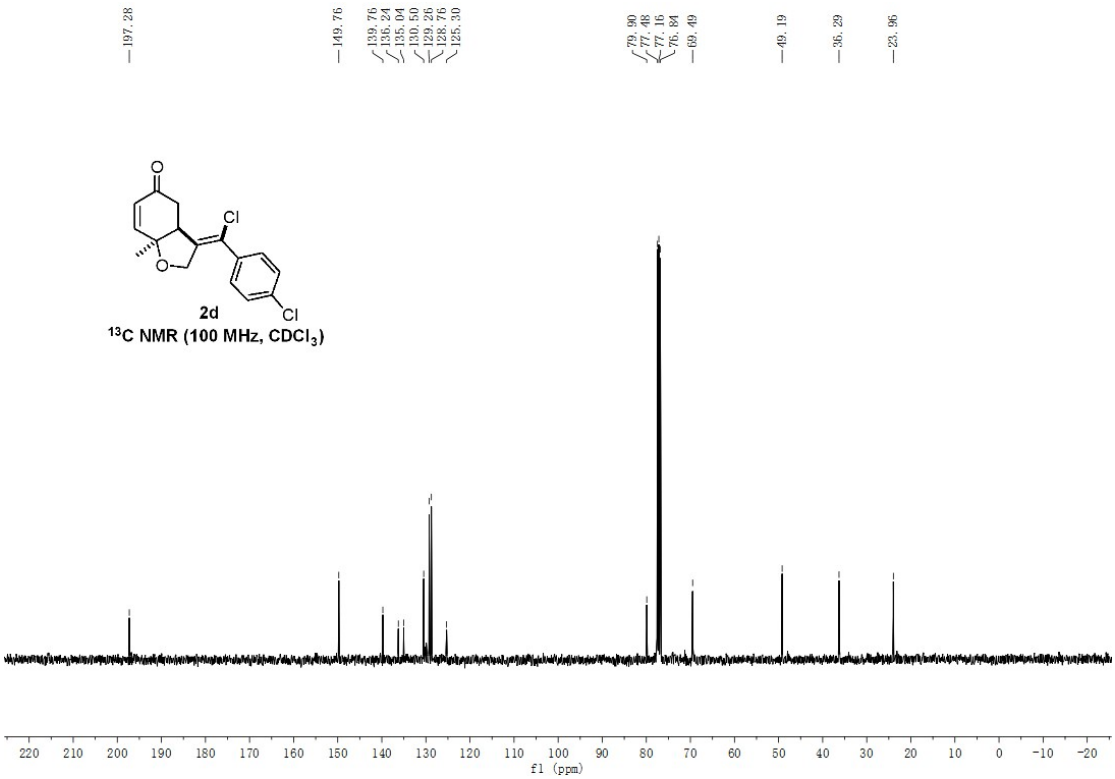
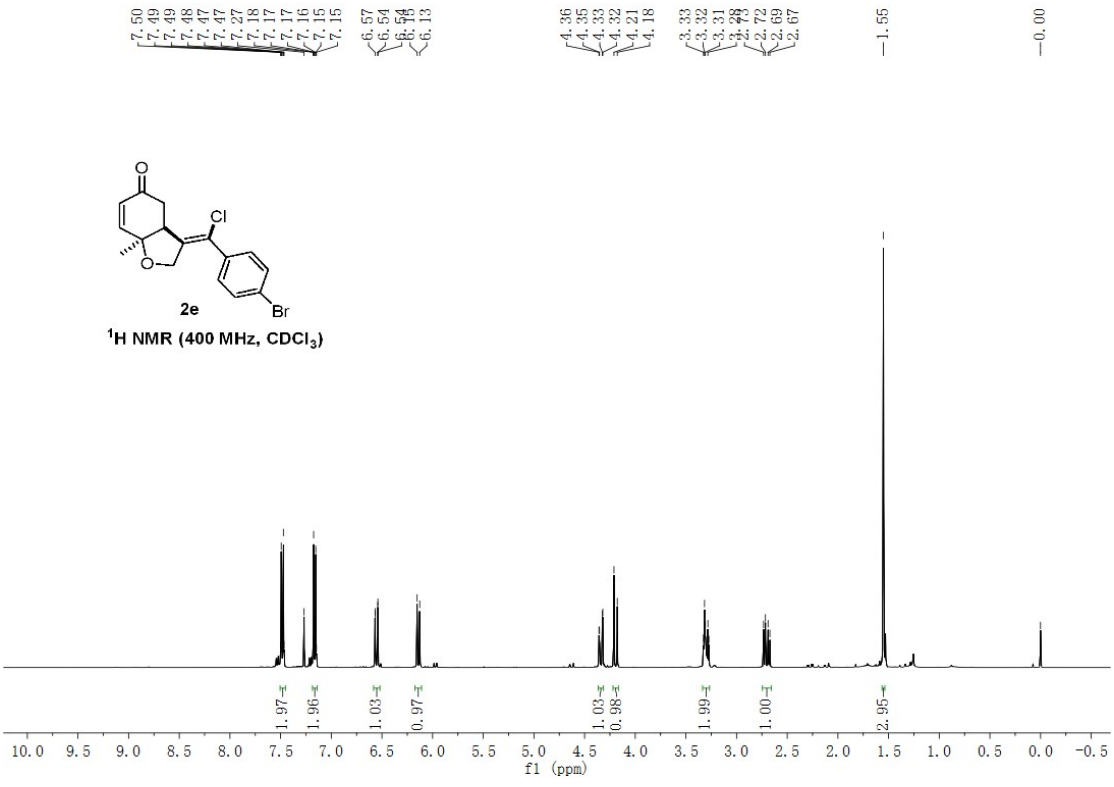


^{13}C NMR (100 MHz, $CDCl_3$)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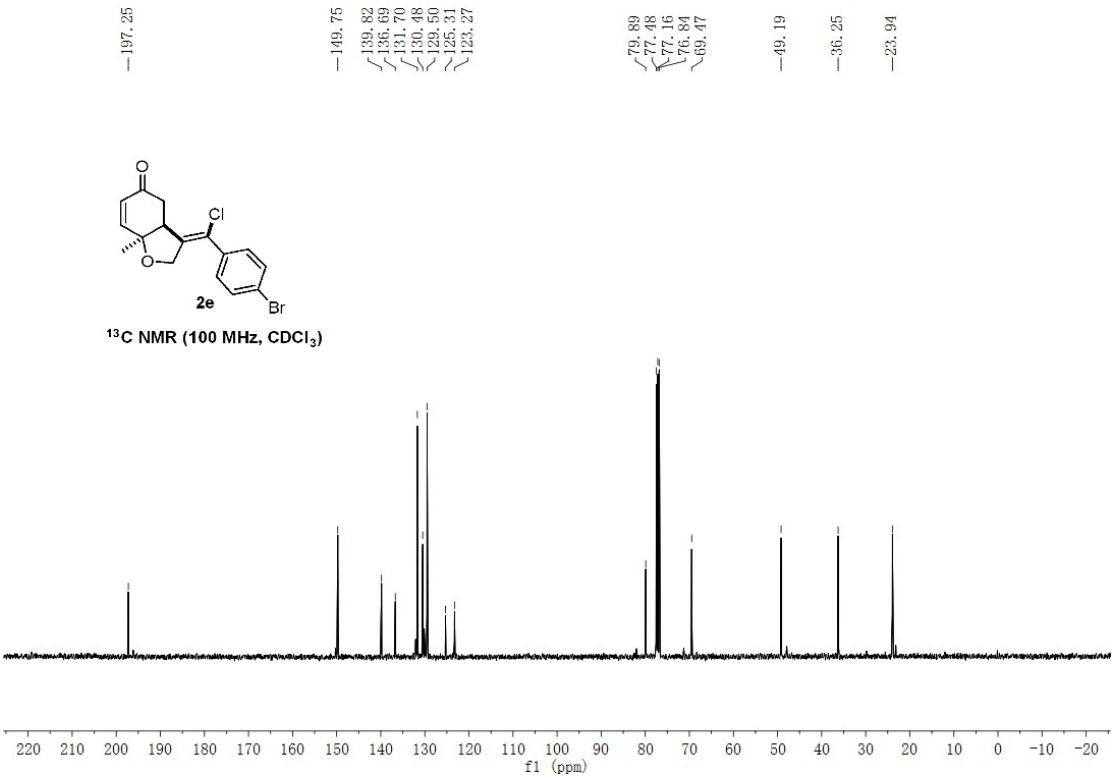
7.49
7.48
7.47
7.47
7.27
7.18
7.17
7.17
7.16
7.15
7.15
6.57
6.54
6.54
6.13
4.36
4.35
4.33
4.32
4.21
4.18
3.33
3.32
3.31
2.72
2.69
2.67
1.55
0.00
O
Cl
O
Br
2e
1H NMR (400 MHz, CDCl3)
1.97
1.96
1.03
0.97
1.03
0.98
1.99
1.00
2.95
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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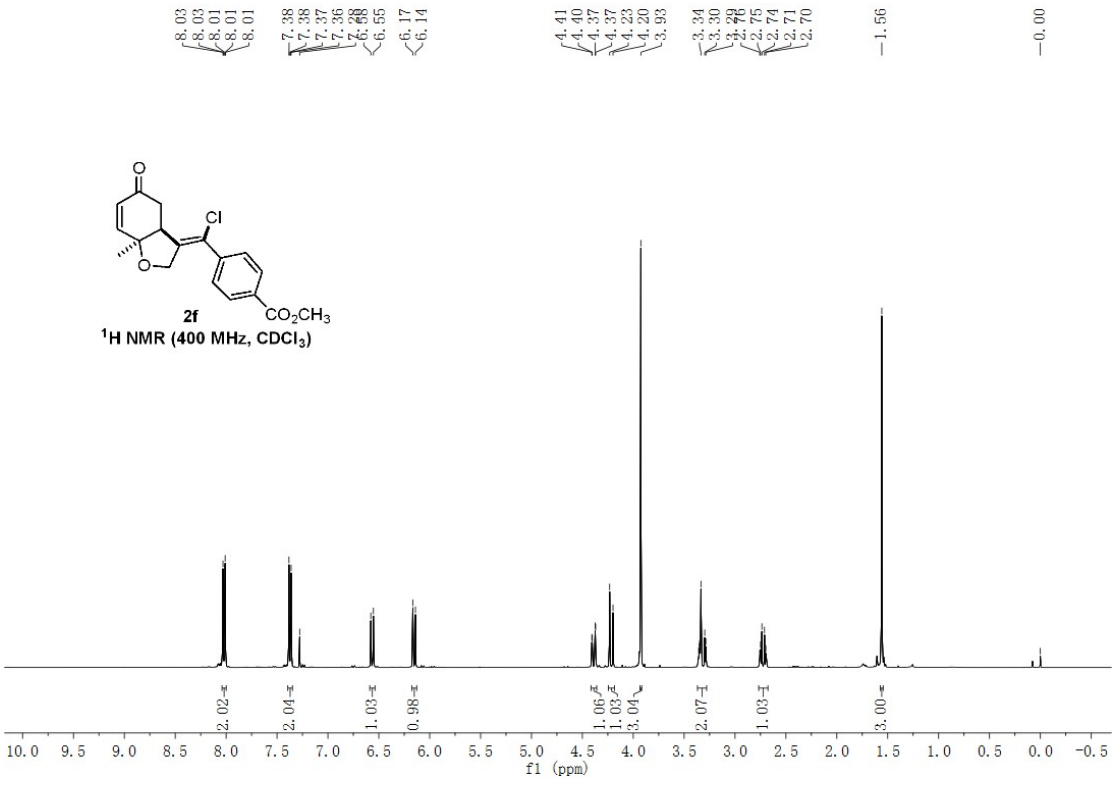
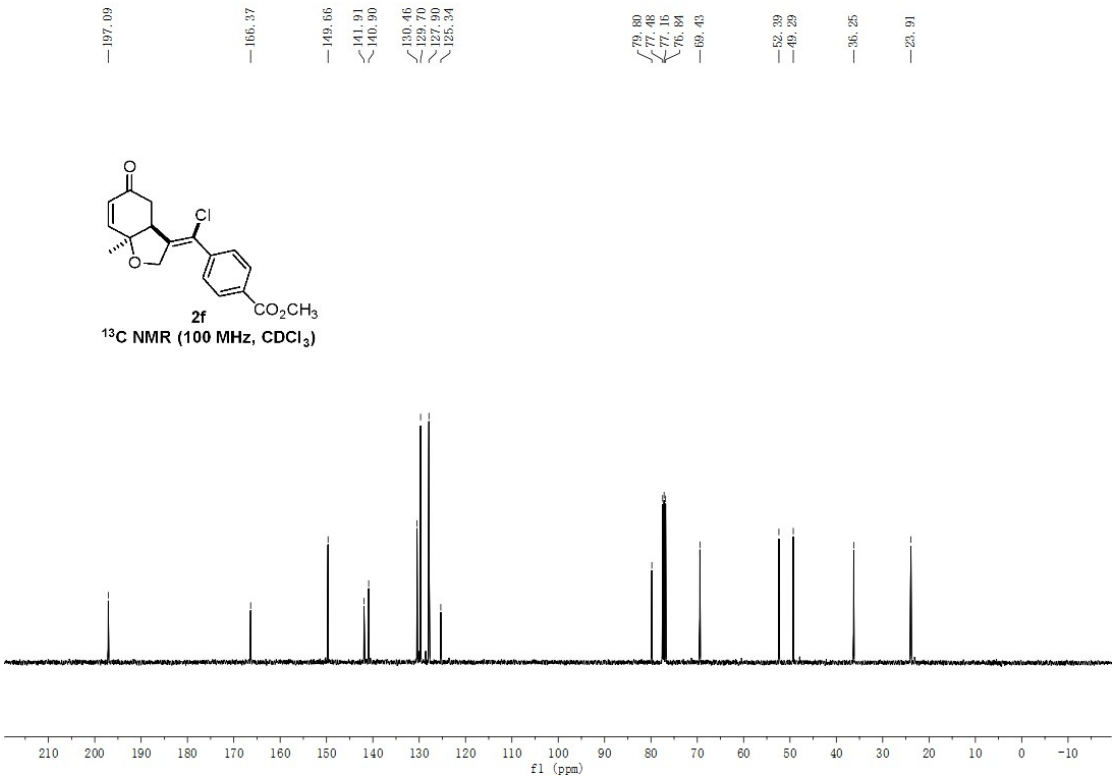
139.82
136.69
131.70
130.48
129.50
125.31
123.27
79.89
77.48
77.16
76.84
69.47
49.19
36.25
23.94
O
Cl
O
Br
2e
13C NMR (100 MHz, CDCl3)
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)



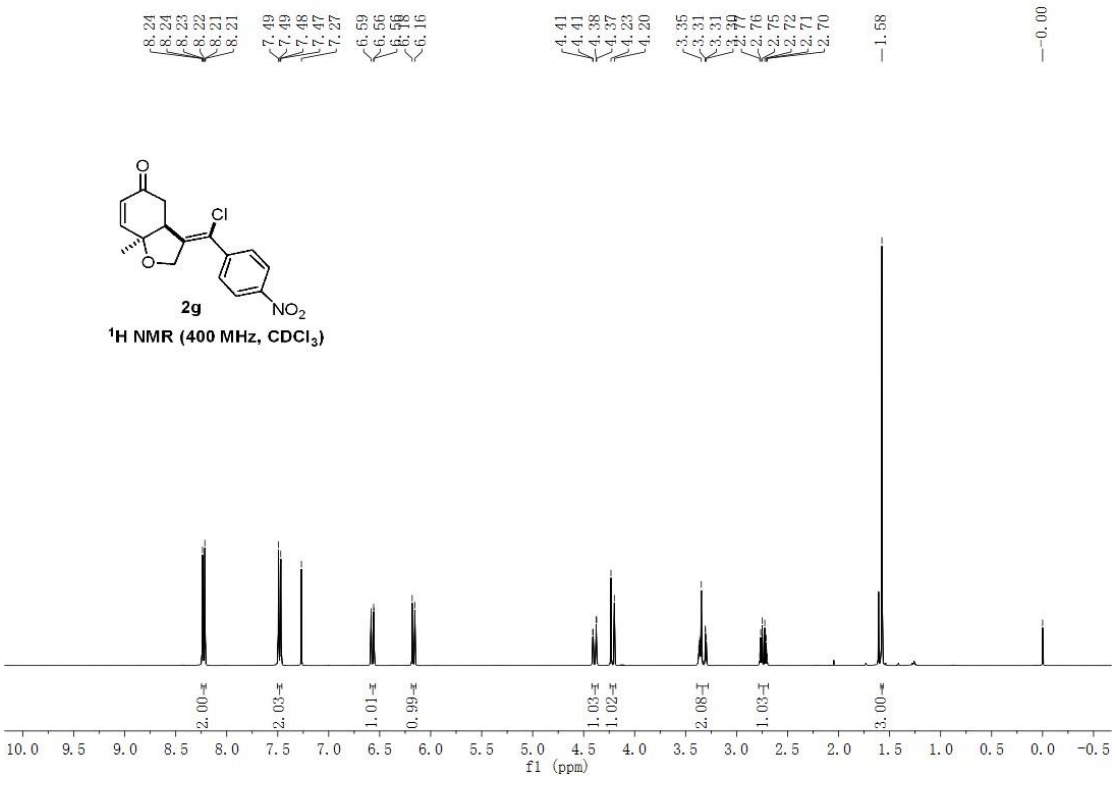
2f

^{1}H NMR (400 MHz, $CDCl_3$)



2f

^{13}C NMR (100 MHz, $CDCl_3$)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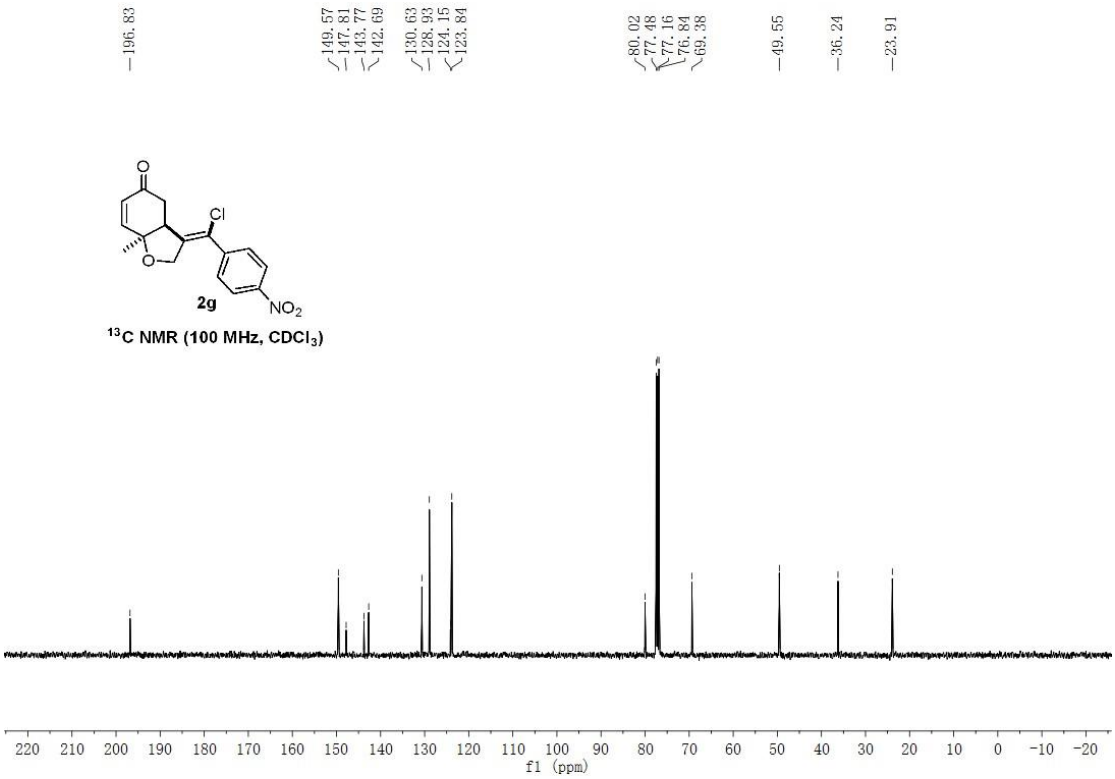
8.24
8.23
8.22
8.21
8.21
7.49
7.49
7.48
7.47
7.27
6.59
6.56
6.16
4.41
4.41
4.38
4.37
4.23
4.20
3.35
3.31
3.31
2.76
2.75
2.72
2.71
2.70
1.58
0.00
O
Cl
O
NO2
2g
1H NMR (400 MHz, CDCl3)
2.00
2.03
1.01
0.99
1.03
1.02
2.08
1.03
3.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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123.84
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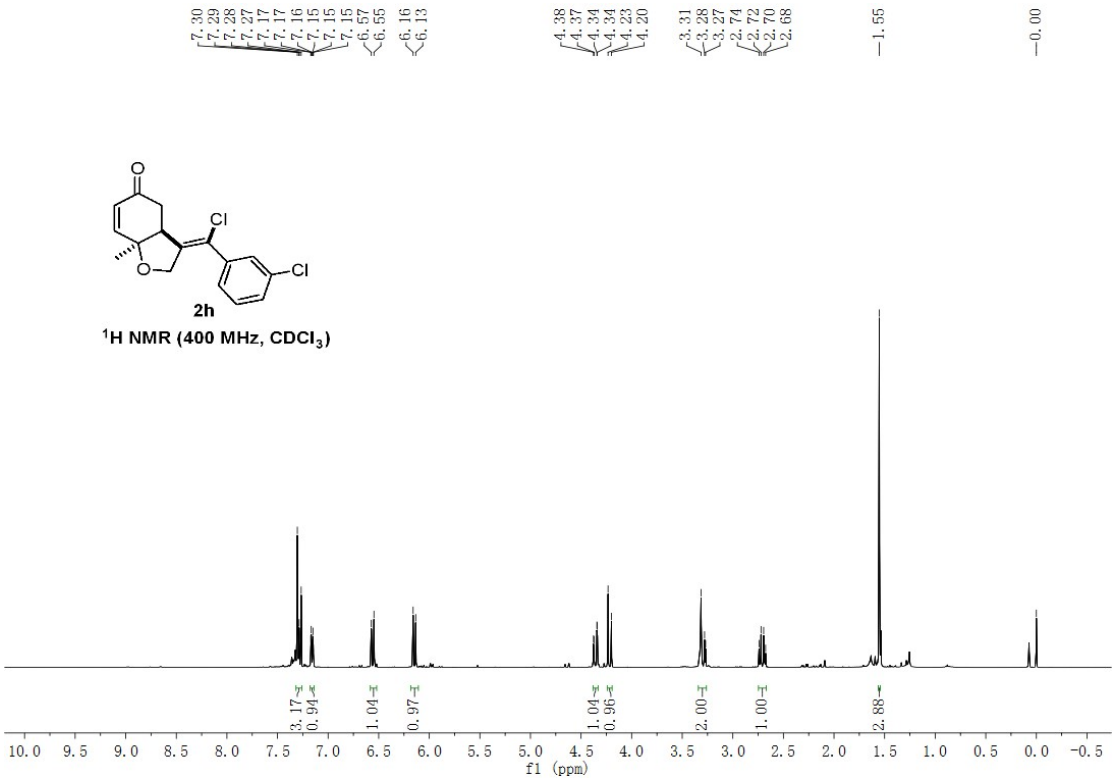
77.48
77.16
76.84
69.38
49.55
36.24
23.91
O
Cl
O
NO2
2g
13C NMR (100 MHz, CDCl3)
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)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7.17
7.16
7.15
7.15
7.15
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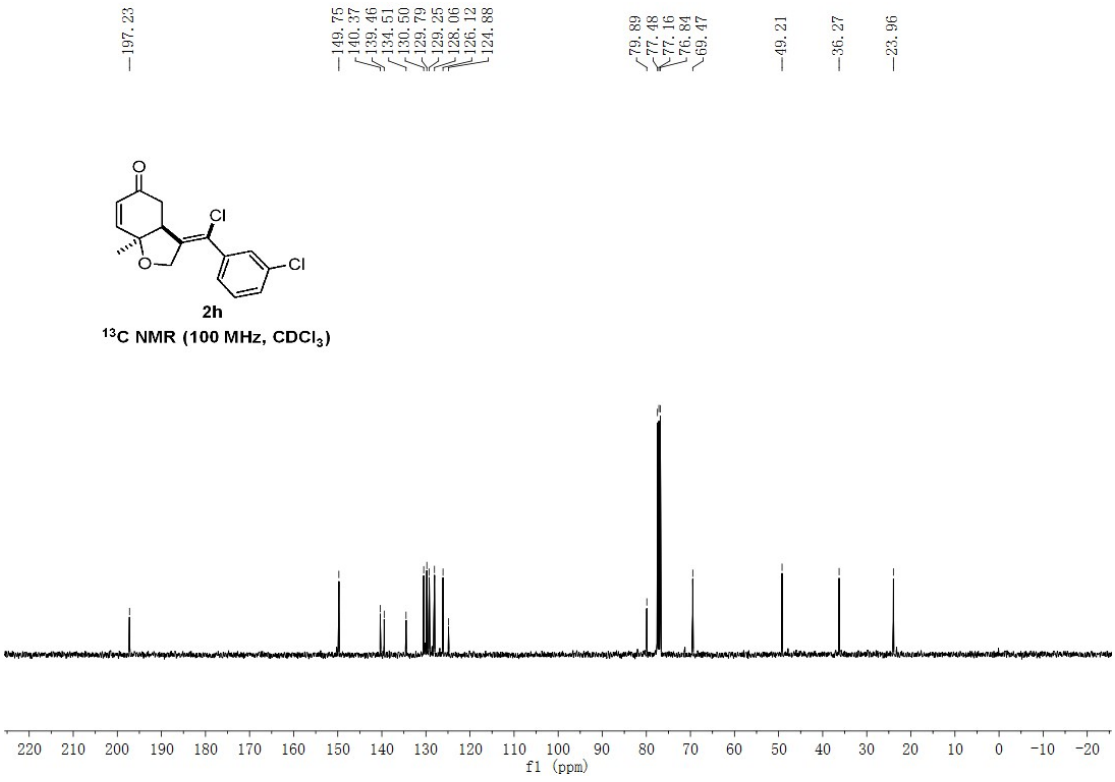
6.55
6.16
6.13
4.38
4.37
4.34
4.34
4.23
4.20
3.31
3.28
3.27
2.74
2.72
2.70
2.68
1.55
0.00
O
Cl
O
Cl
2h
1H NMR (400 MHz, CDCl3)
3.17
0.94
1.04
0.97
1.04
0.96
2.00
1.00
2.88
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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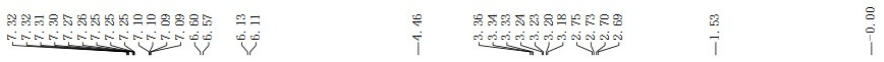
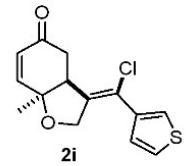
134.51
130.50
129.79
129.25
128.06
126.12
124.88
79.89
77.48
77.16
76.84
69.47
49.21
36.27
23.96
O
Cl
O
Cl
2h
13C NMR (100 MHz, CDCl3)
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)





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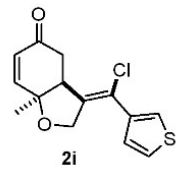
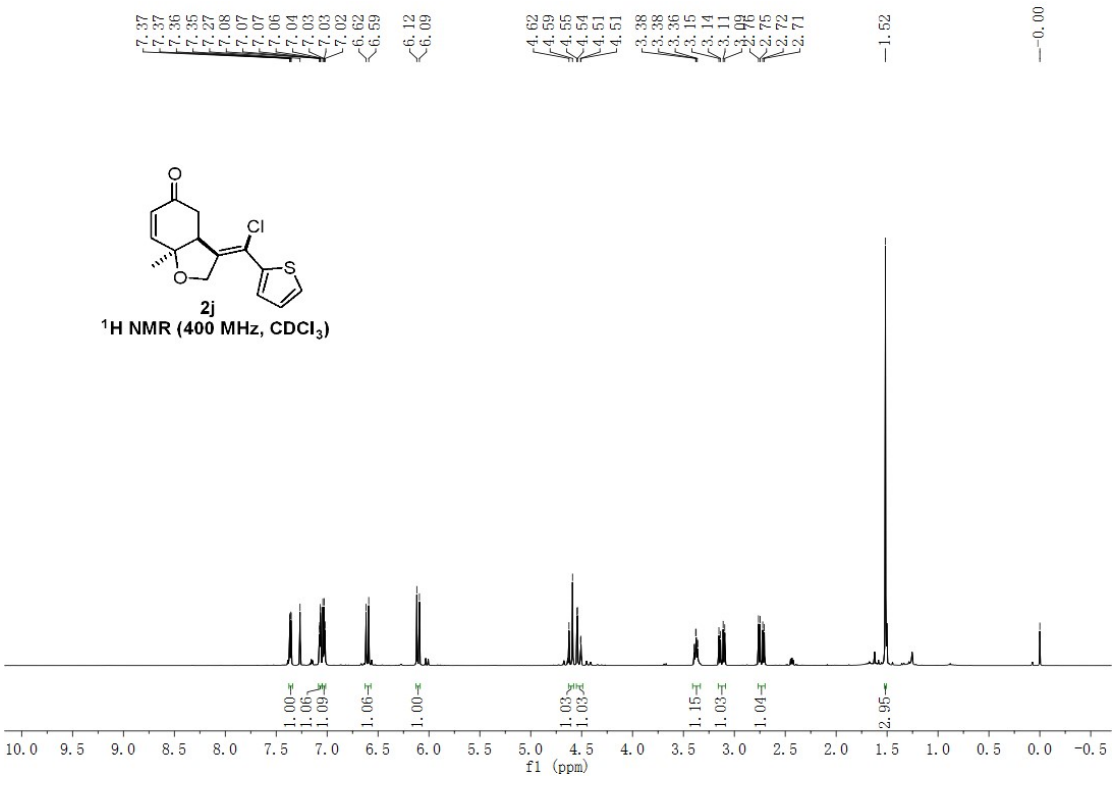
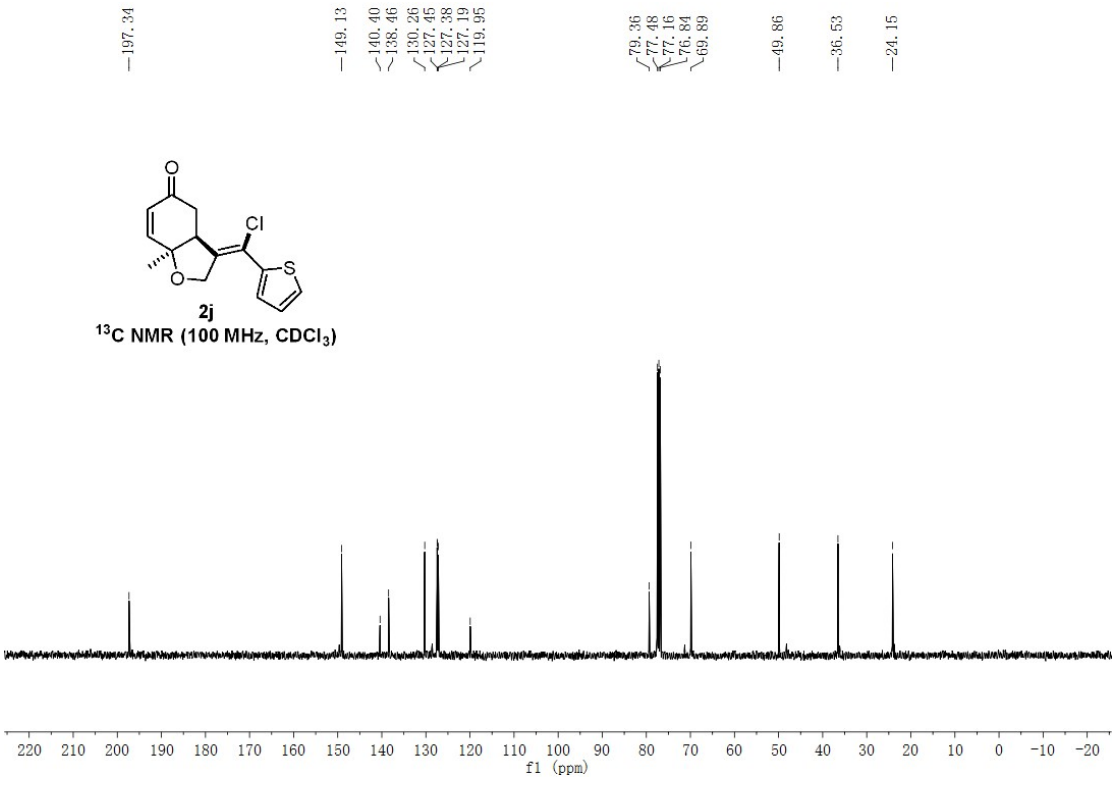
^{1}H NMR (400 MHz, $CDCl_3$)



2i

^{13}C NMR (100 MHz, $CDCl_3$)


7.37
7.37
7.36
7.35
7.27
7.08
7.07
7.07
7.06
7.04
7.03
7.03
7.02
6.62
6.59
6.12
6.09
4.62
4.59
4.55
4.54
4.51
4.51
3.38
3.38
3.36
3.15
3.14
3.11
2.76
2.75
2.72
2.71
1.52
0.00
Cl
S
O
O
2j
^{1}H NMR (400 MHz, CDCl$_3$)
1.00
1.06
1.09
1.06
1.00
1.03
1.03
1.15
1.03
1.04
2.95
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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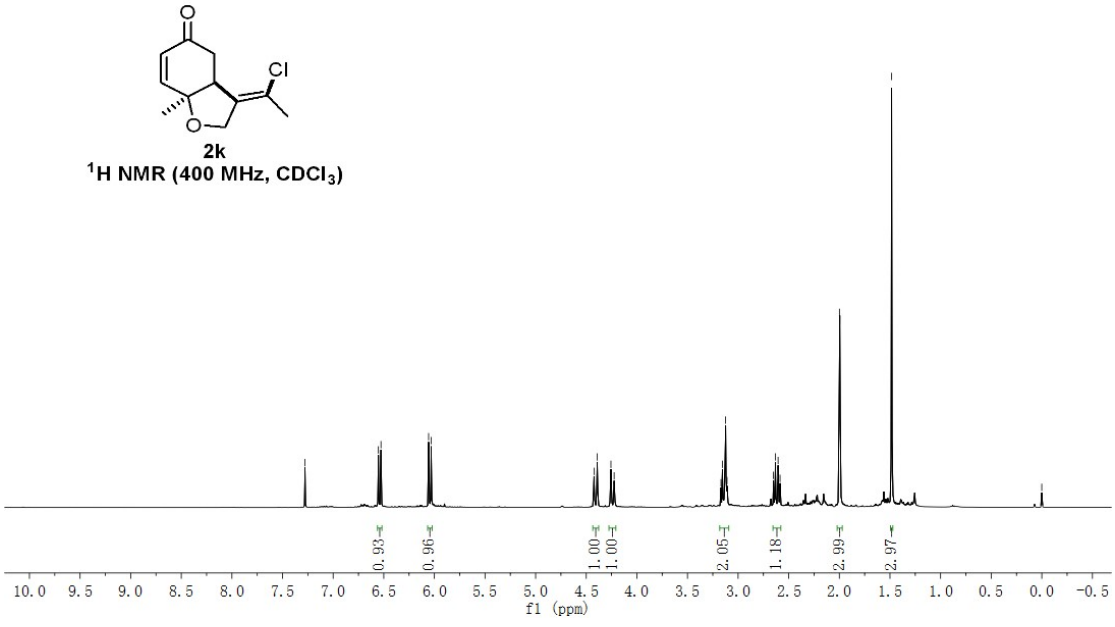
127.38
127.19
119.95
79.36
77.48
77.16
76.84
69.89
49.86
36.53
24.15
Cl
S
O
O
2j
^{13}C NMR (100 MHz, CDCl$_3$)
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)



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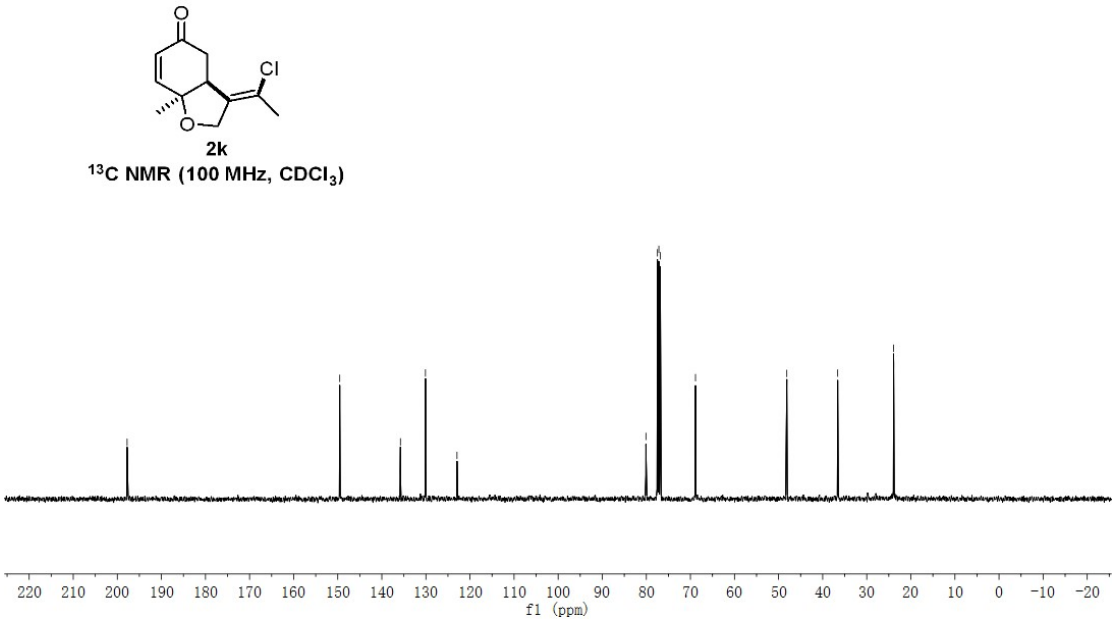

2k

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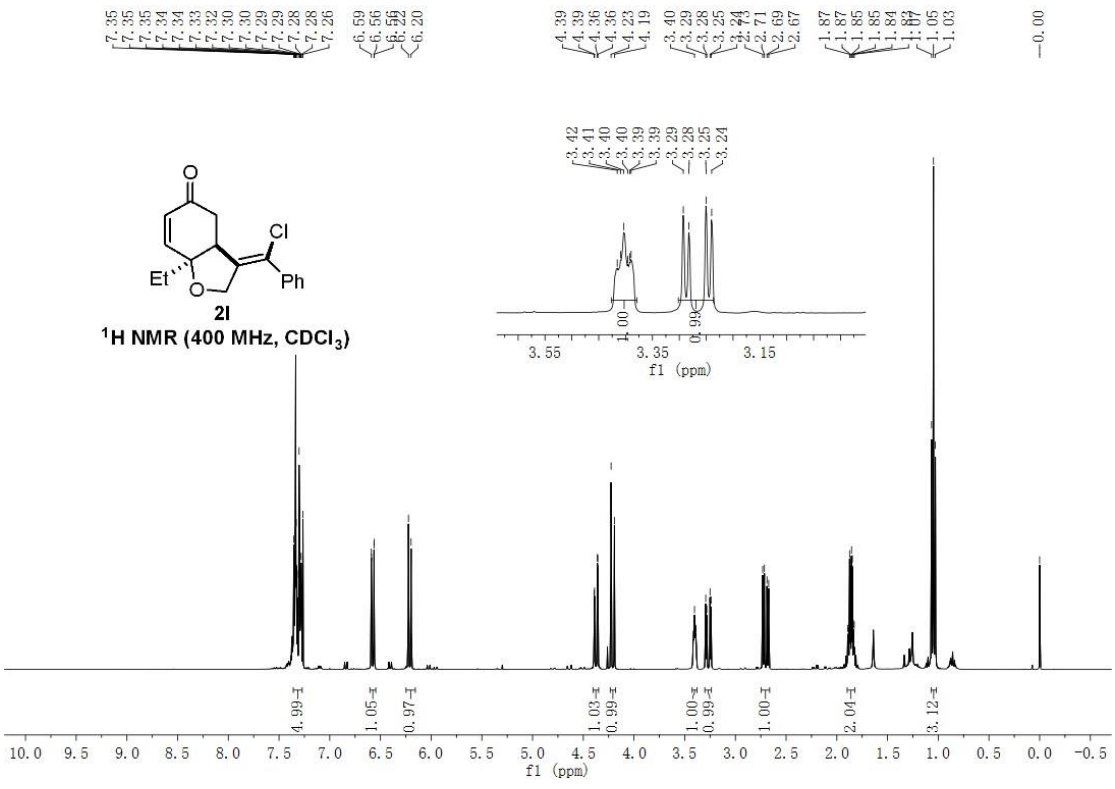
2l
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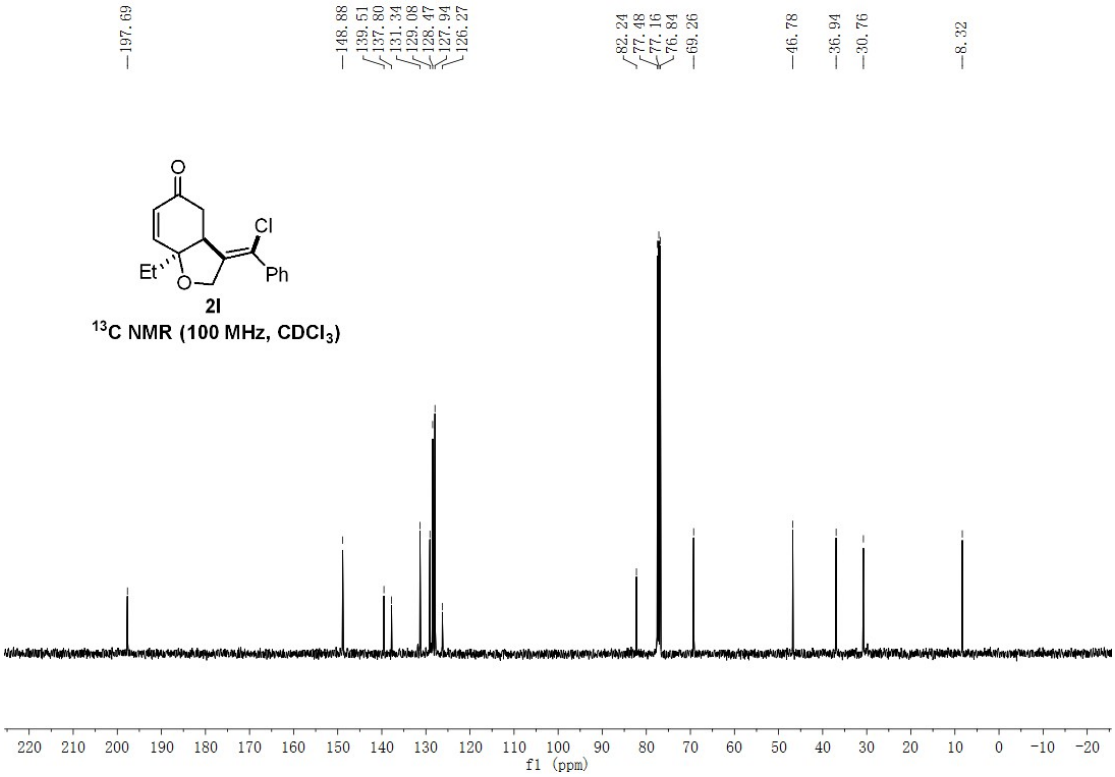
f1 (ppm)


2l
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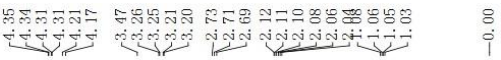
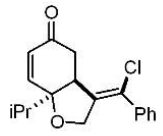
f1 (ppm)





2m

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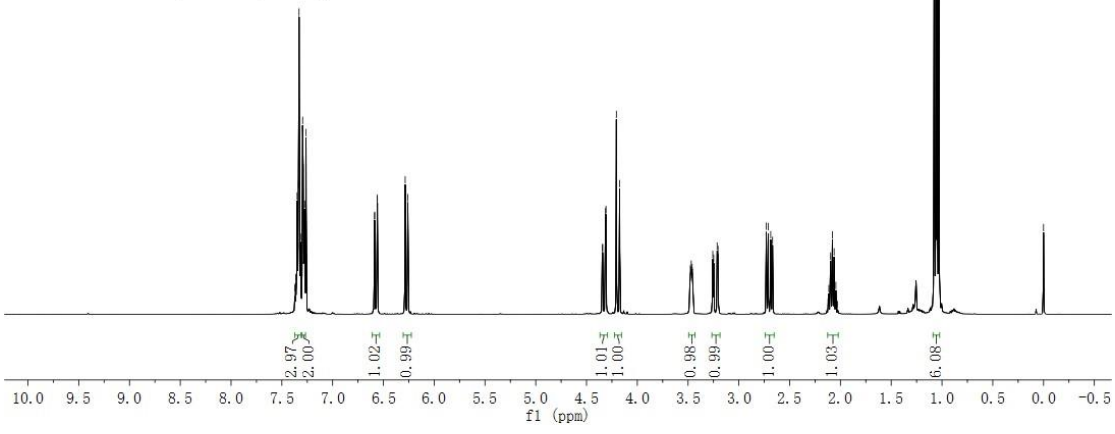

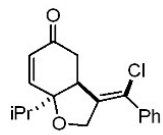

2m

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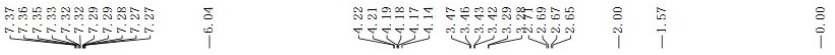
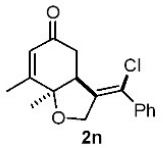
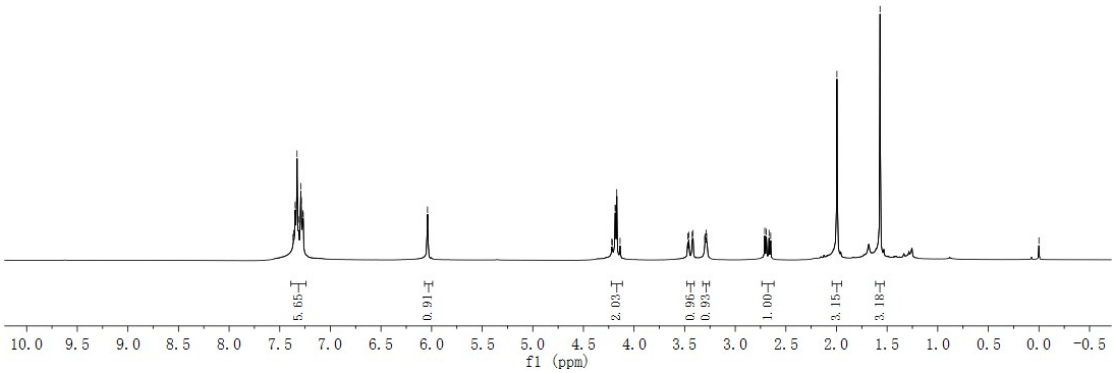
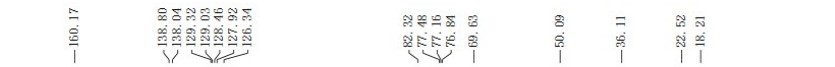


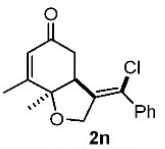


2n

^{1}H NMR (400 MHz, $CDCl_3$)







2n

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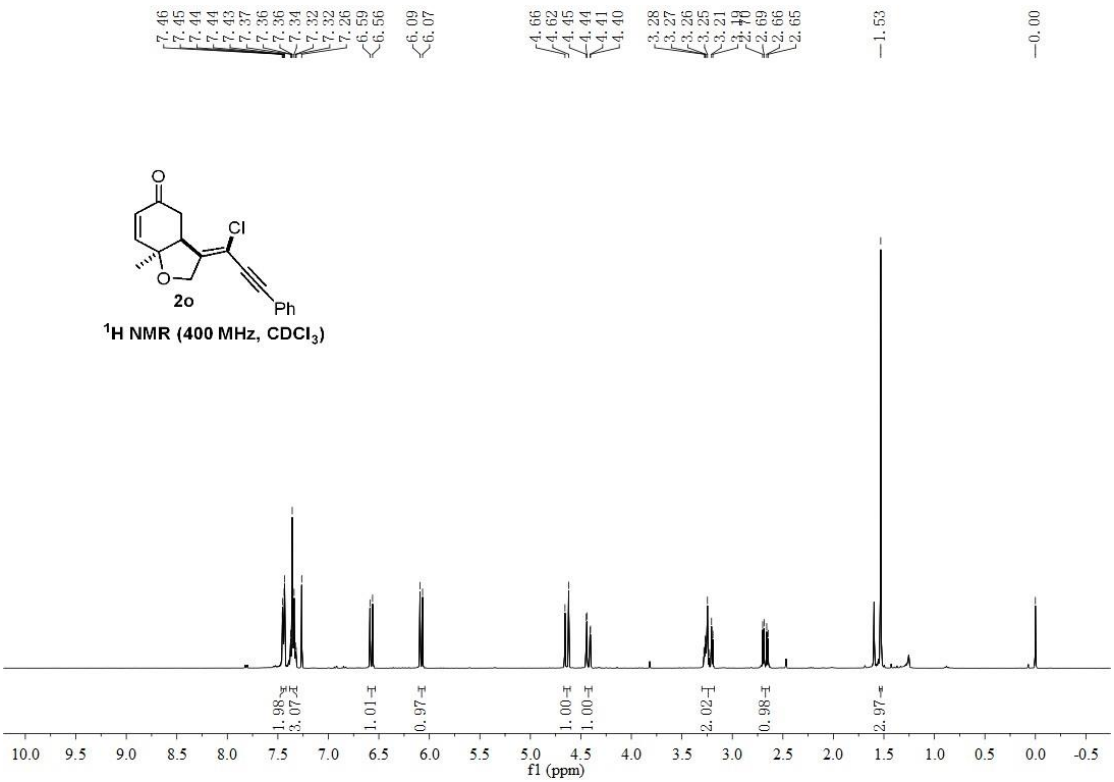

2o

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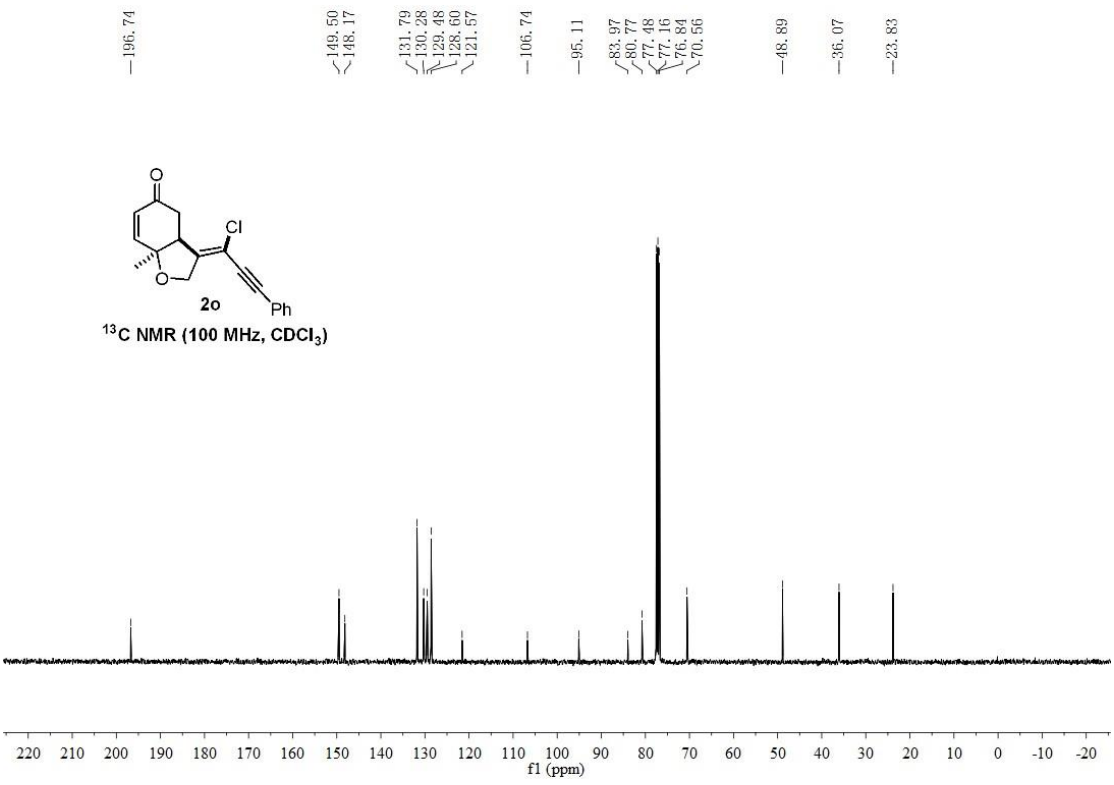
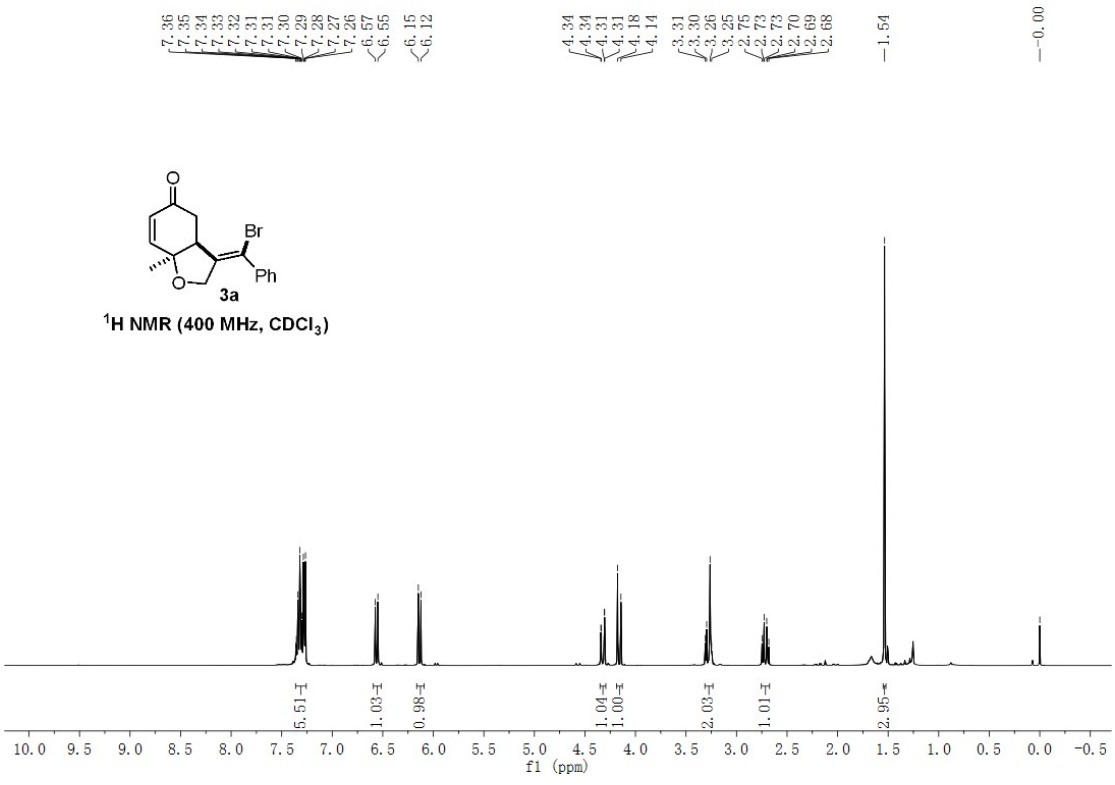
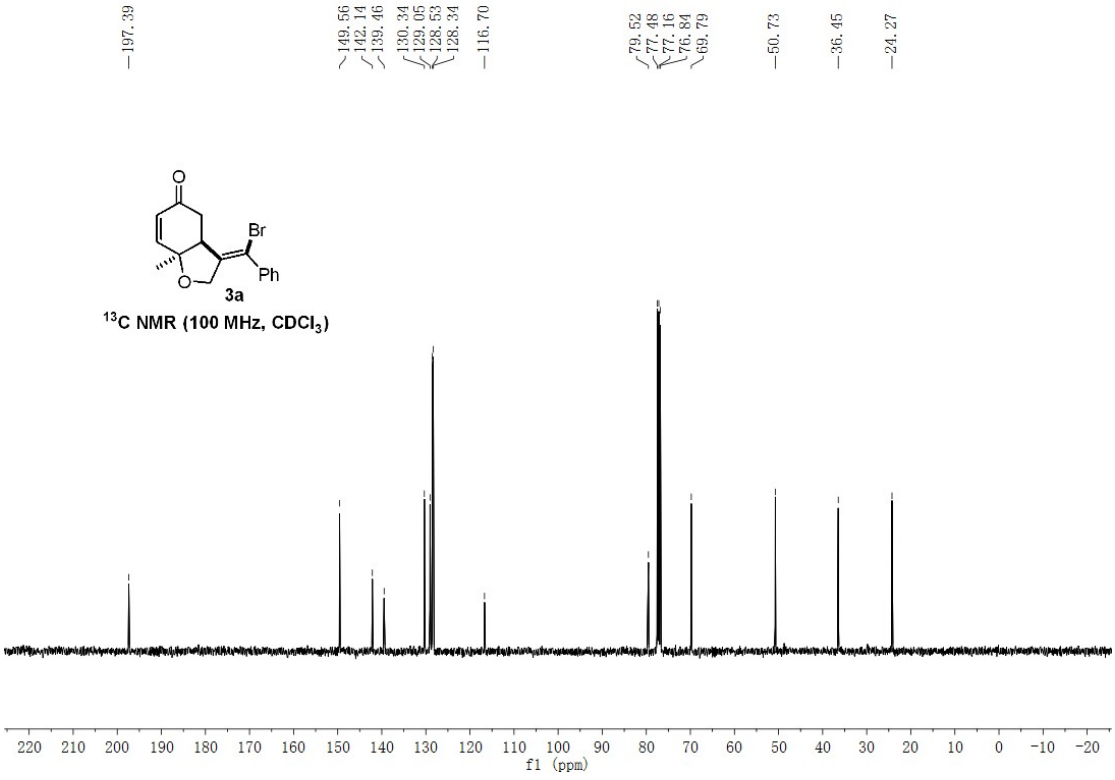
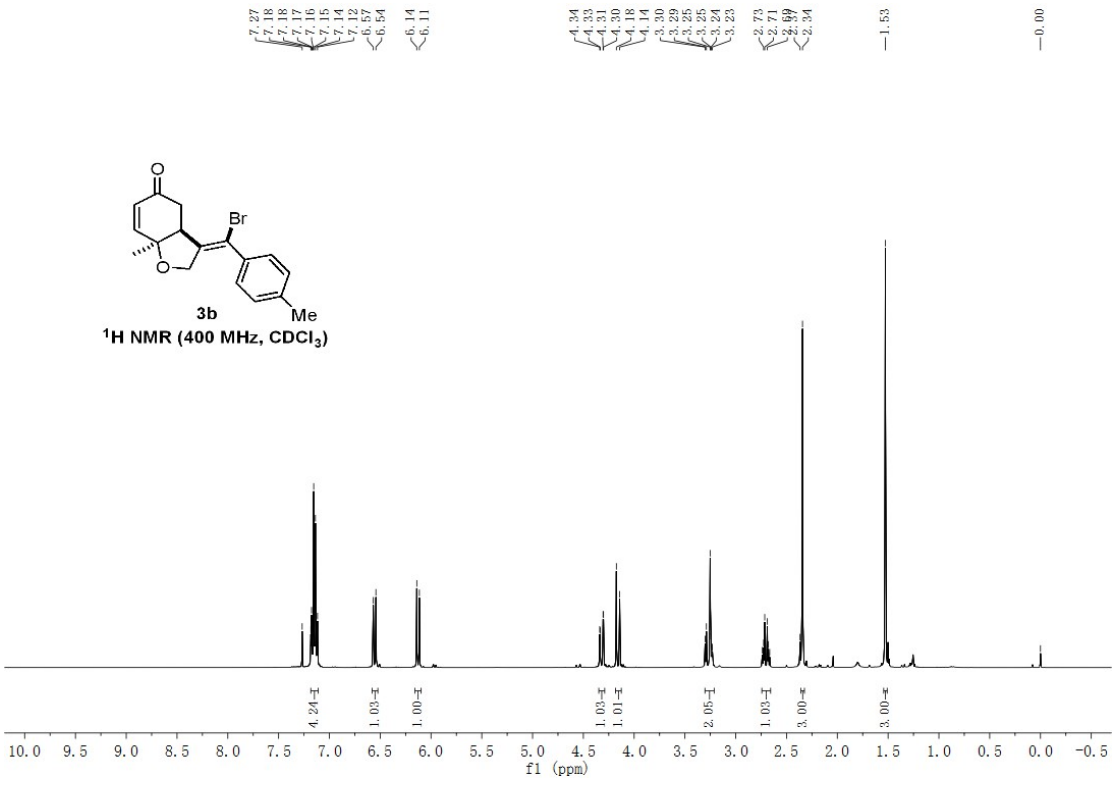


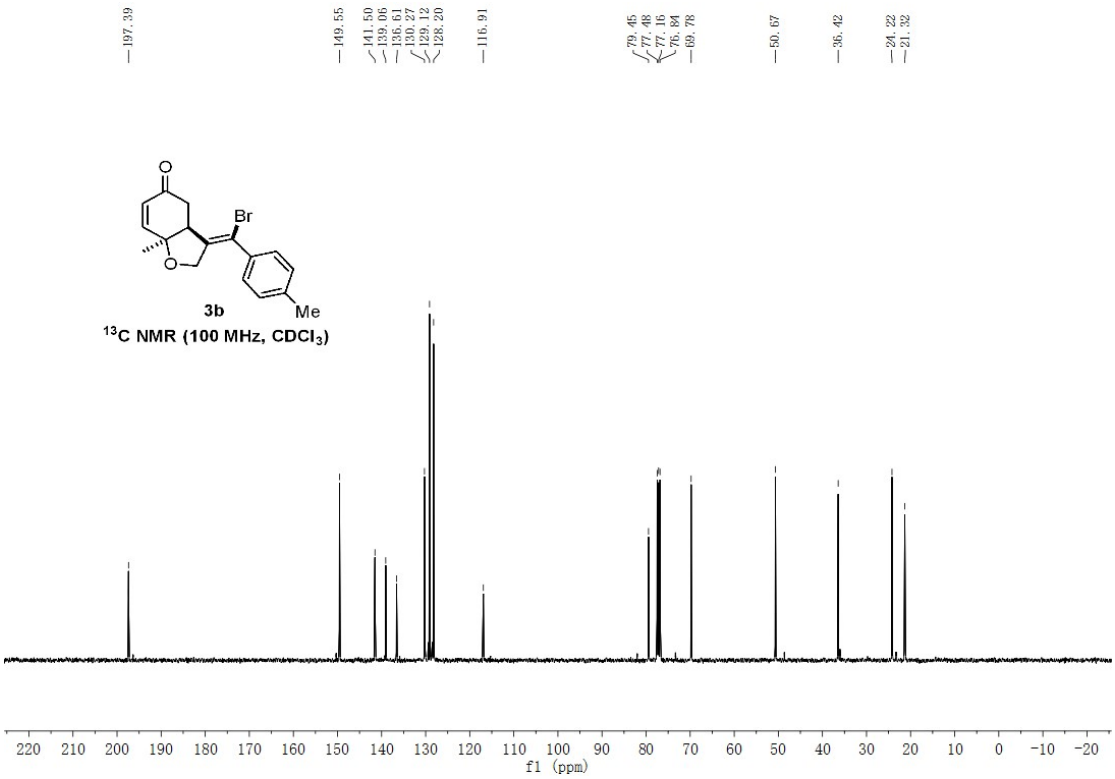
2o

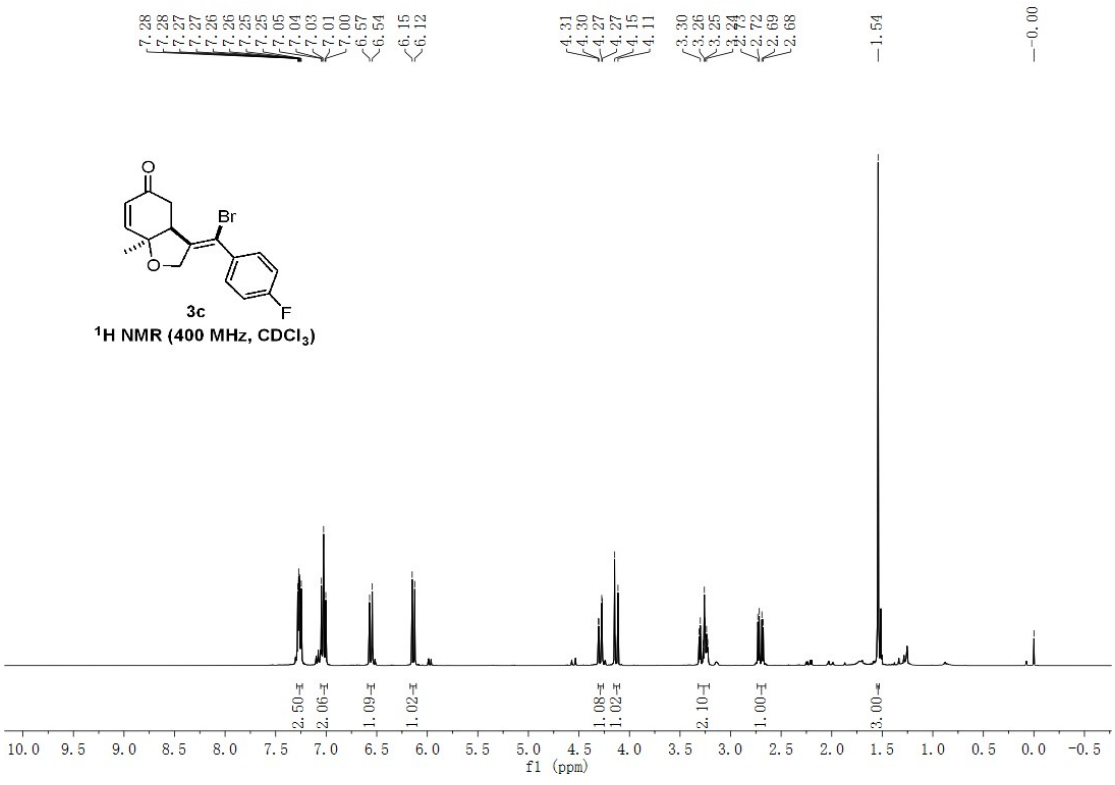
^{13}C NMR (100 MHz, $CDCl_3$)

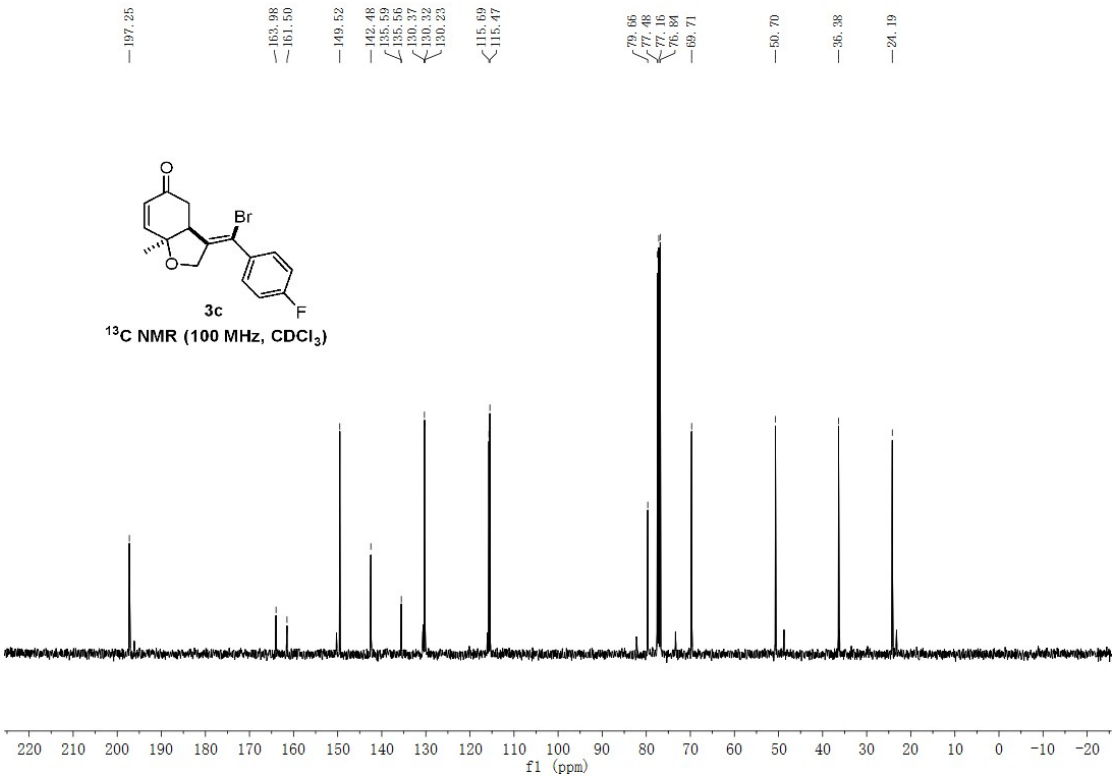

7.36
7.35
7.34
7.33
7.32
7.31
7.31
7.30
7.29
7.28
7.27
7.26
6.57
6.55
6.15
6.12
4.34
4.34
4.31
4.31
4.18
4.14
3.31
3.30
3.26
3.25
2.75
2.73
2.73
2.70
2.69
2.68
1.54
0.00
O
Br
Ph
3a
1H NMR (400 MHz, CDCl3)
5.51
1.03
0.98
1.04
1.00
2.03
1.01
2.95
f1 (ppm)

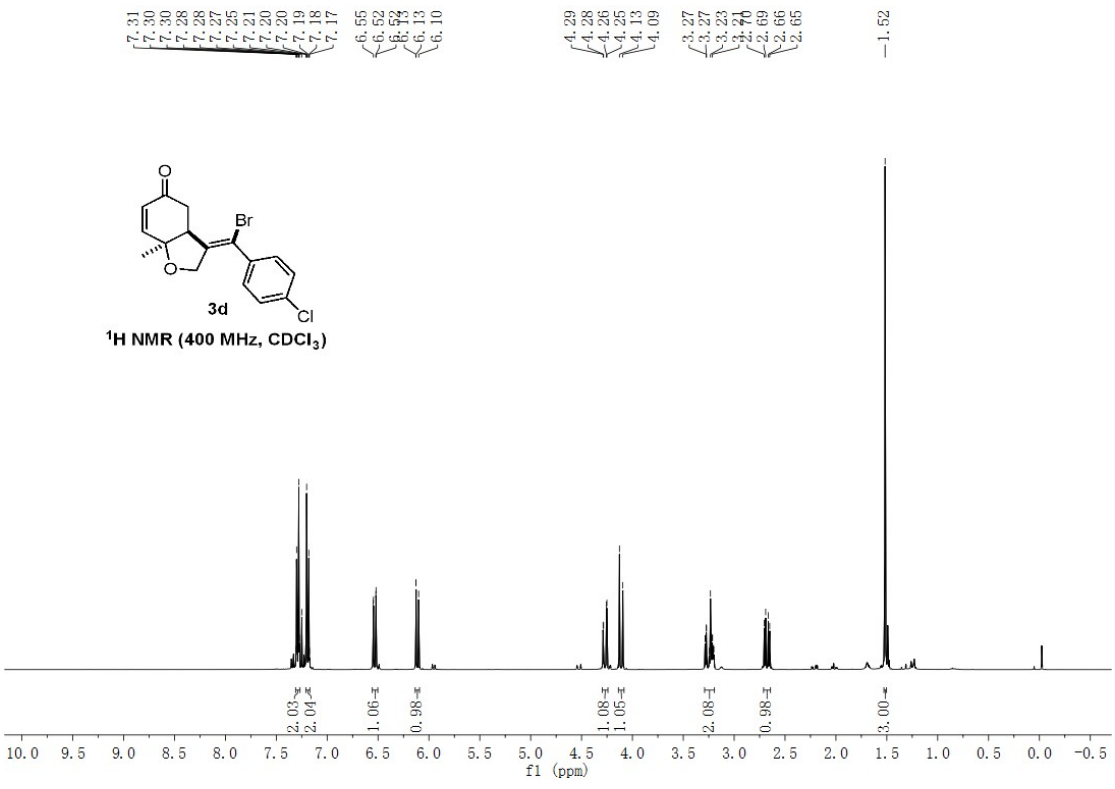

197.39
149.56
142.14
139.46
130.34
129.05
128.53
128.34
116.70
79.52
77.48
77.16
76.84
69.79
50.73
36.45
24.27
O
Br
Ph
3a
13C NMR (100 MHz, CDCl3)
f1 (ppm)

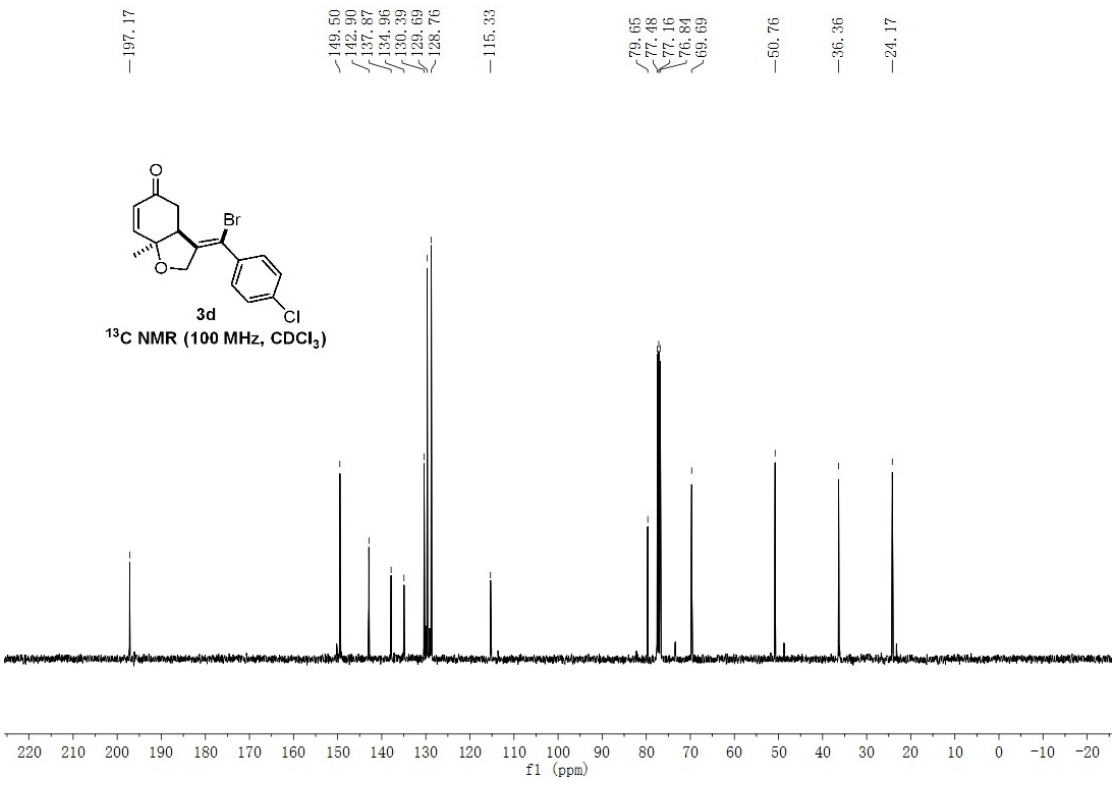

Br
Me
3b
^{1}H NMR (400 MHz, CDCl$_3$)
f1 (ppm)

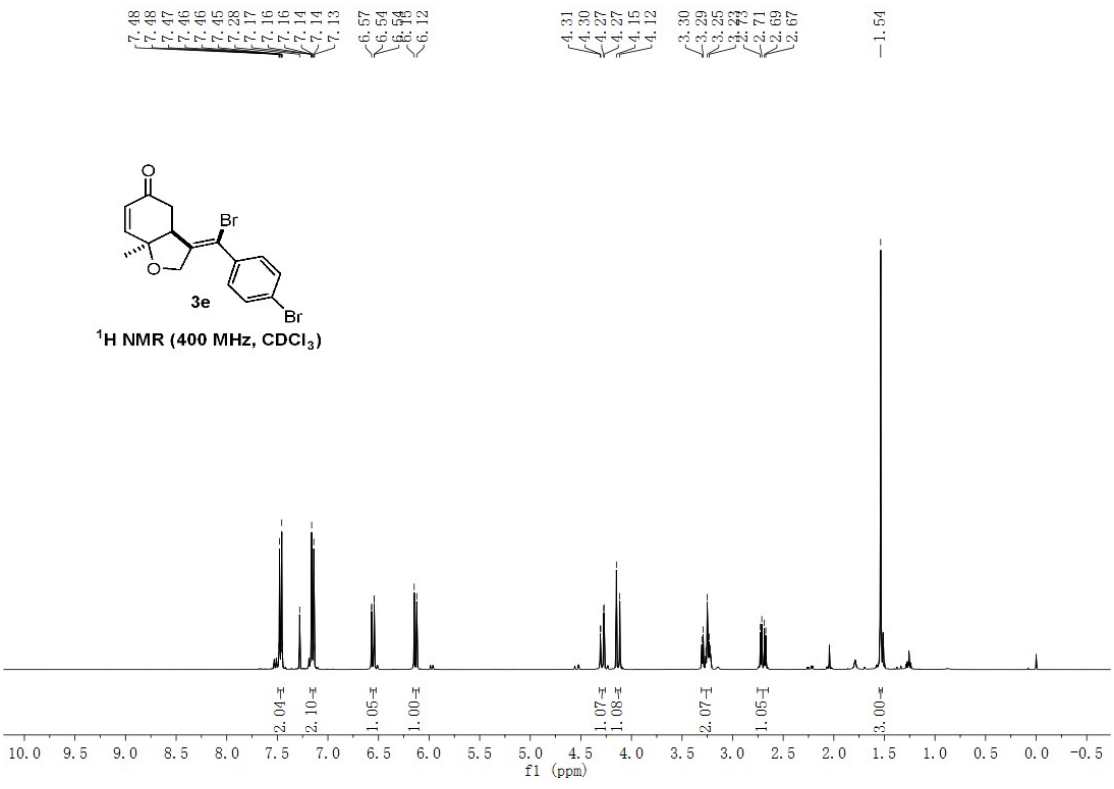

Br
Me
3b
^{13}C NMR (100 MHz, CDCl$_3$)
f1 (ppm)


7.28
7.28
7.27
7.27
7.26
7.26
7.25
7.25
7.05
7.04
7.03
7.01
7.00
6.57
6.54
6.15
6.12
4.31
4.30
4.27
4.27
4.15
4.11
3.30
3.26
3.25
2.72
2.69
2.68
1.54
0.00
O
Br
O
F
3c
^{1}H NMR (400 MHz, CDCl$_3$)
2.50
2.06
1.09
1.02
1.08
1.02
2.10
1.00
3.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

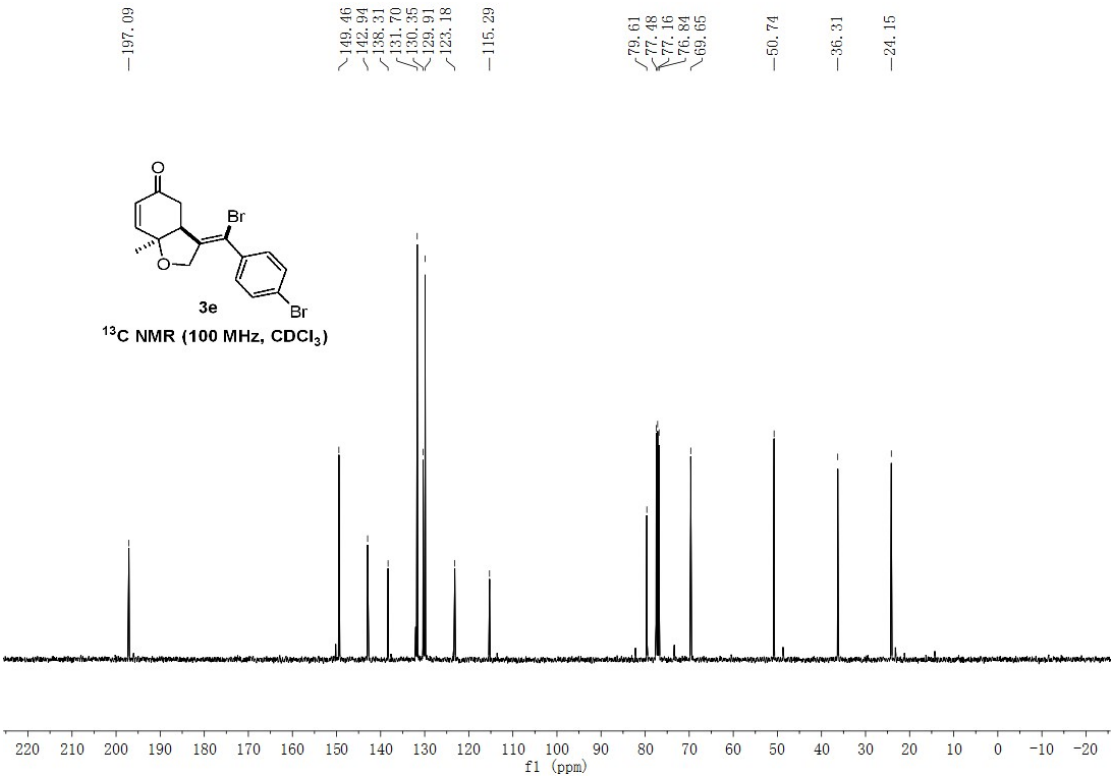

197.25
163.98
161.50
149.52
142.48
135.59
135.56
130.37
130.32
130.23
115.69
115.47
79.66
77.48
77.15
76.84
69.71
50.70
36.38
24.19
O
Br
O
F
3c
^{13}C NMR (100 MHz, CDCl$_3$)
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)


7.31
7.30
7.28
7.28
7.27
7.25
7.21
7.20
7.20
7.19
7.18
7.17
6.55
6.52
6.13
6.10
4.29
4.28
4.26
4.25
4.13
4.09
3.27
3.27
3.23
2.69
2.66
2.65
1.52
O
Br
O
Cl
3d
1H NMR (400 MHz, CDCl3)
2.03
2.04
1.06
0.98
1.08
1.05
2.08
0.98
3.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

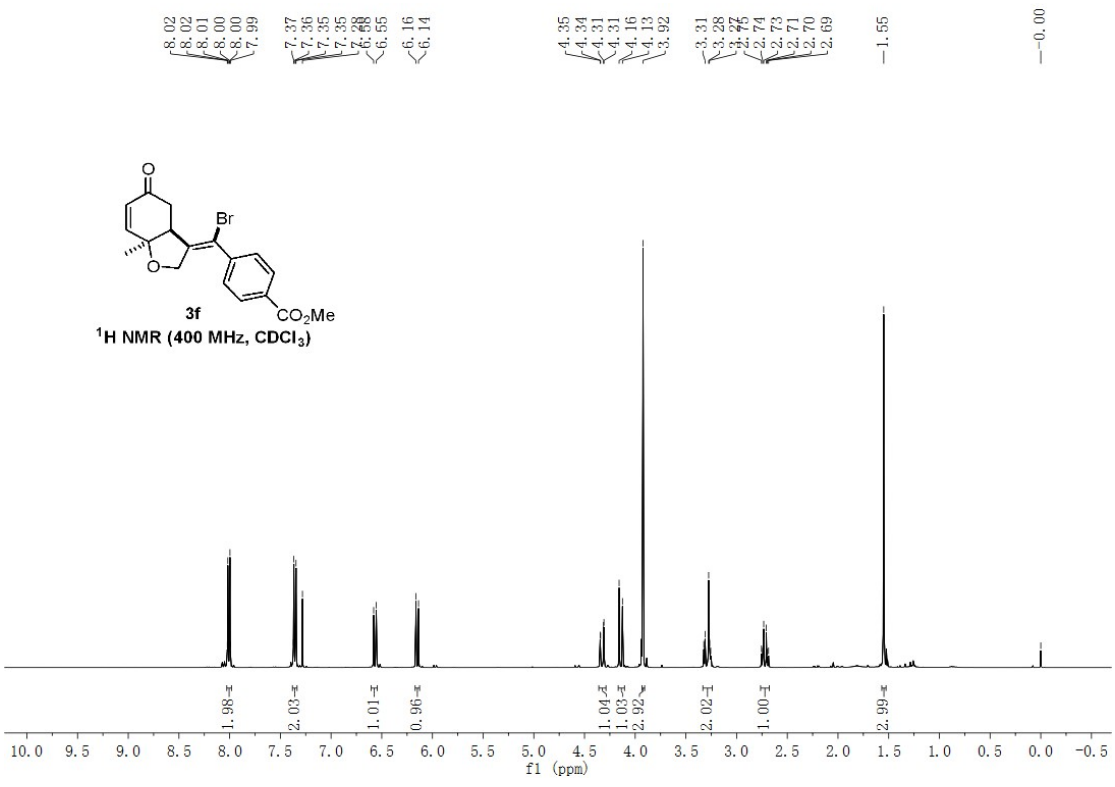

197.17
149.50
142.90
137.87
134.96
130.39
129.69
128.76
115.33
79.65
77.48
77.16
76.84
69.69
50.76
36.36
24.17
O
Br
O
Cl
3d
13C NMR (100 MHz, CDCl3)
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)

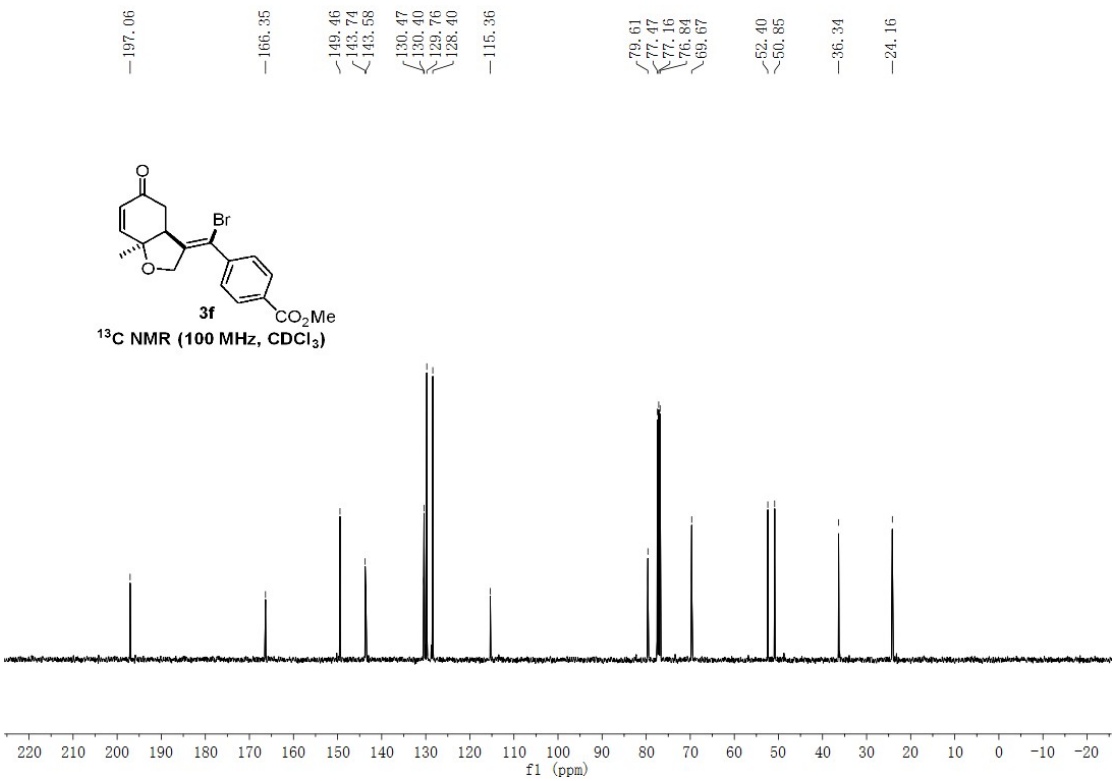


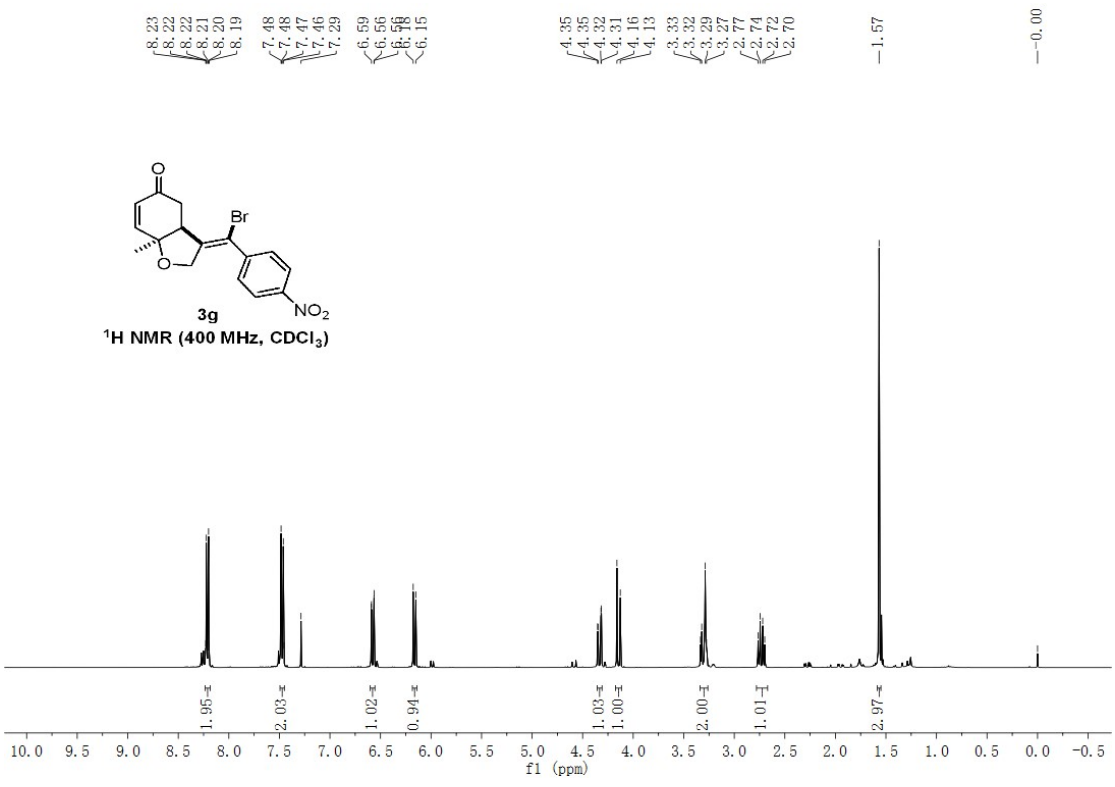
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (100 MHz, $CDCl_3$)

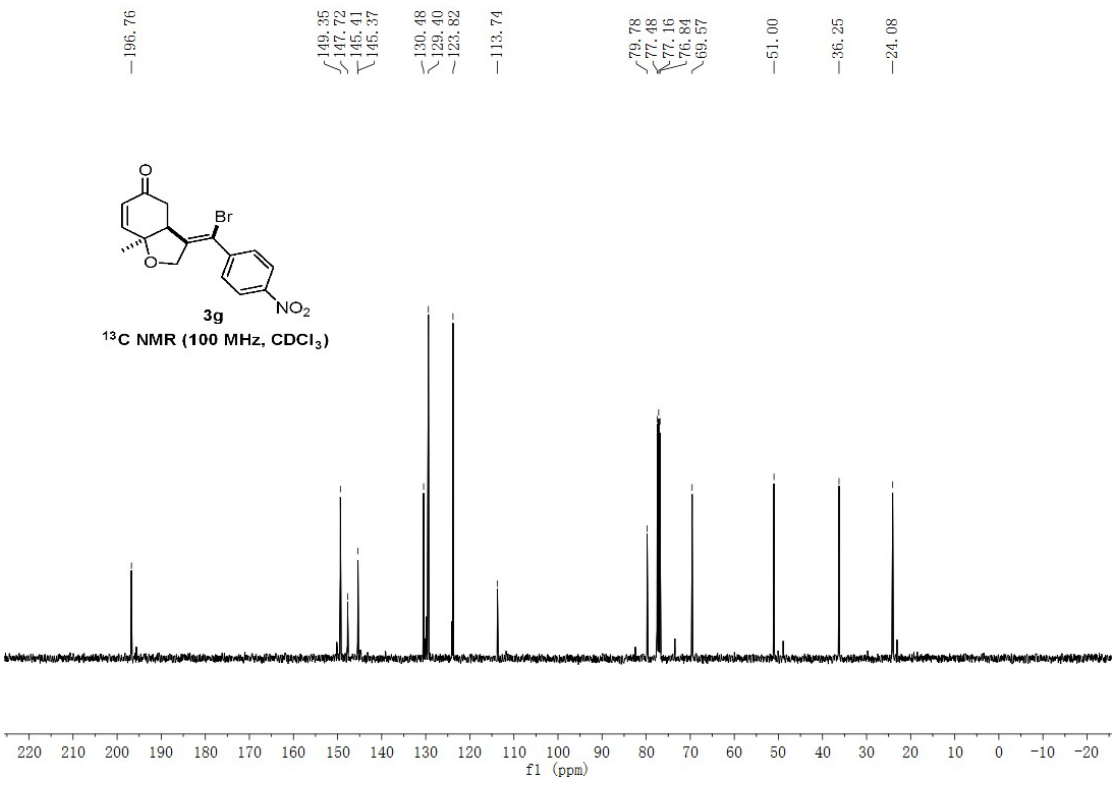

8.02
8.02
8.01
8.00
8.00
7.99
7.37
7.36
7.35
7.35
6.55
6.16
6.14
4.35
4.34
4.31
4.31
4.16
4.13
3.92
3.31
3.28
2.74
2.73
2.71
2.70
2.69
1.55
0.00
Br
O
CO2Me
3f
1H NMR (400 MHz, CDCl3)
1.98
2.03
1.01
0.96
1.04
1.03
2.92
2.02
1.00
2.99
f1 (ppm)


197.06
166.35
149.46
143.74
143.58
130.47
130.40
129.76
128.40
115.36
79.61
77.47
77.16
76.84
69.67
52.40
50.85
36.34
24.16
Br
O
CO2Me
3f
13C NMR (100 MHz, CDCl3)
f1 (ppm)



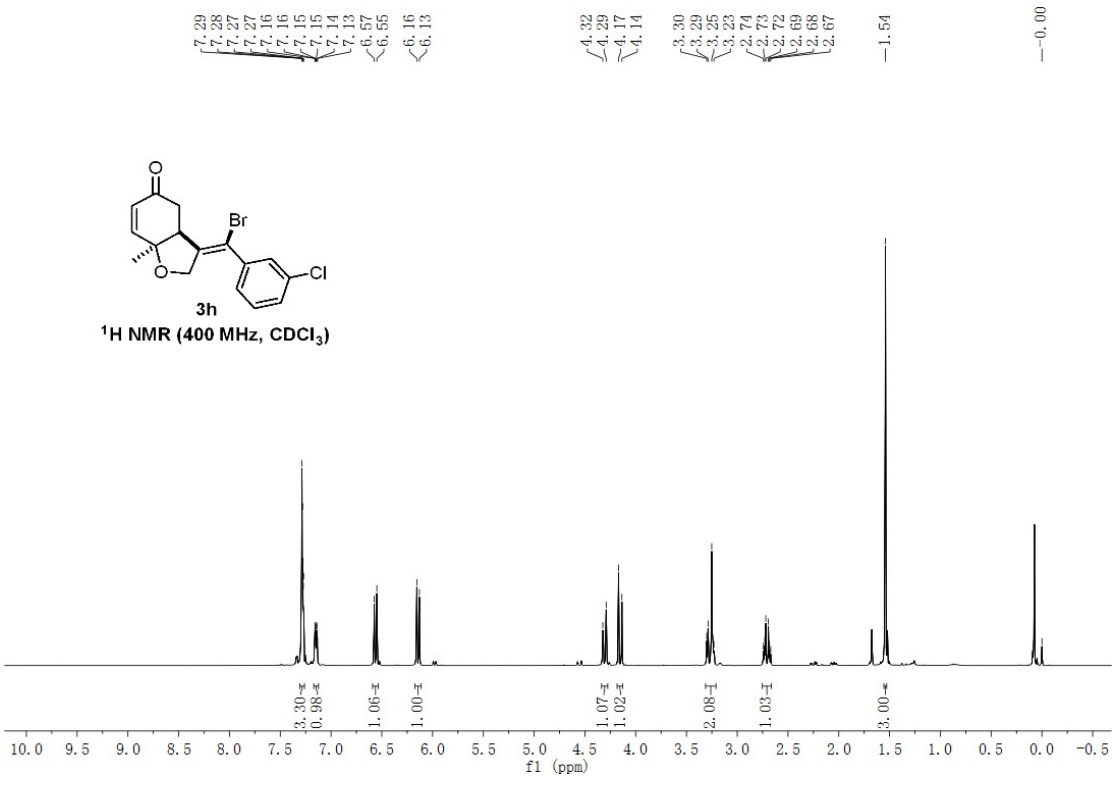
3g

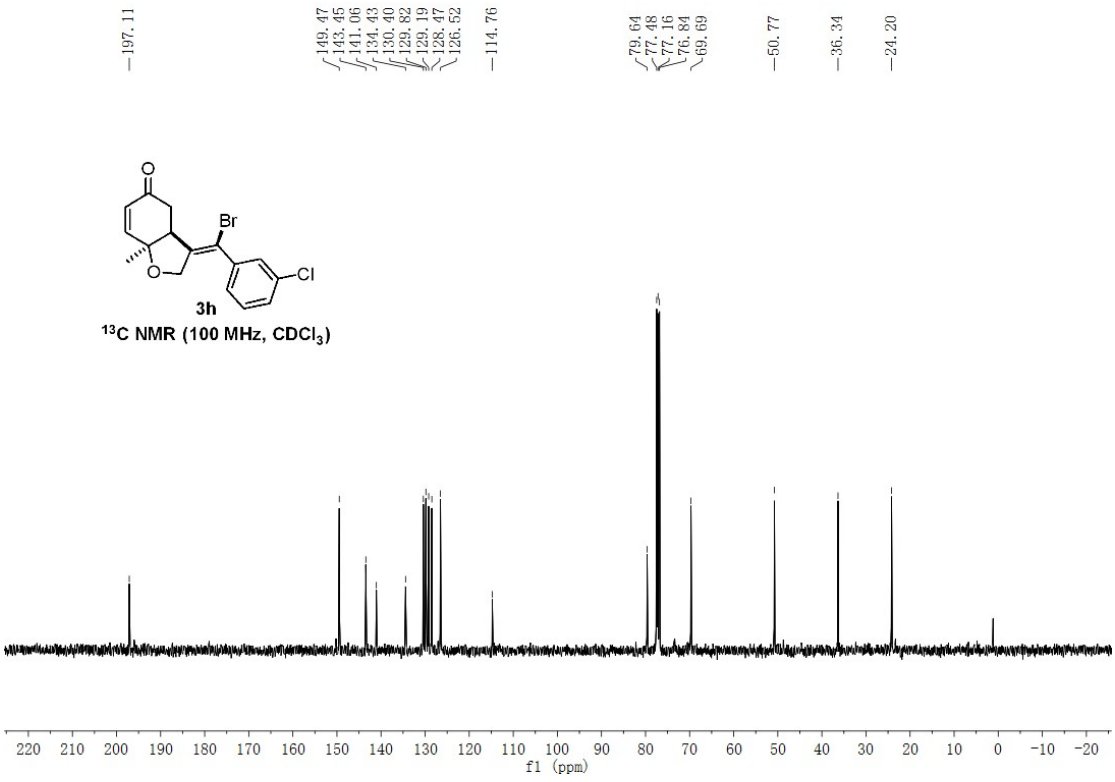
^{1}H NMR (400 MHz, $CDCl_3$)

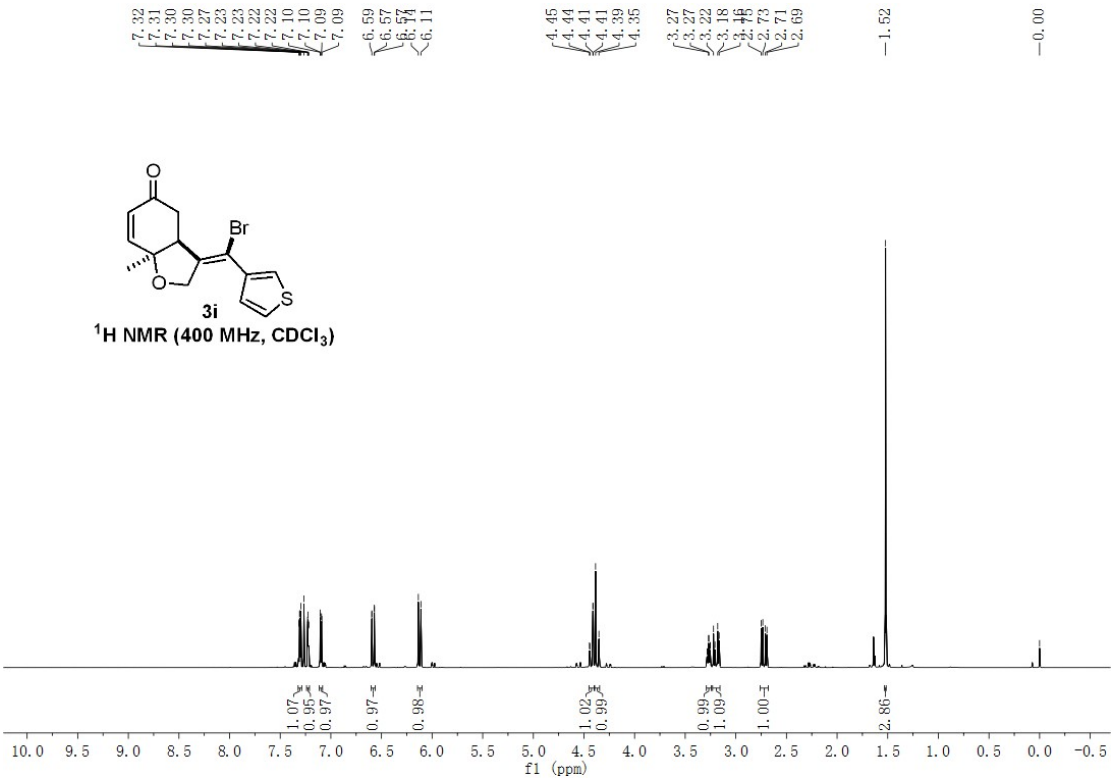


3g

^{13}C NMR (100 MHz, $CDCl_3$)

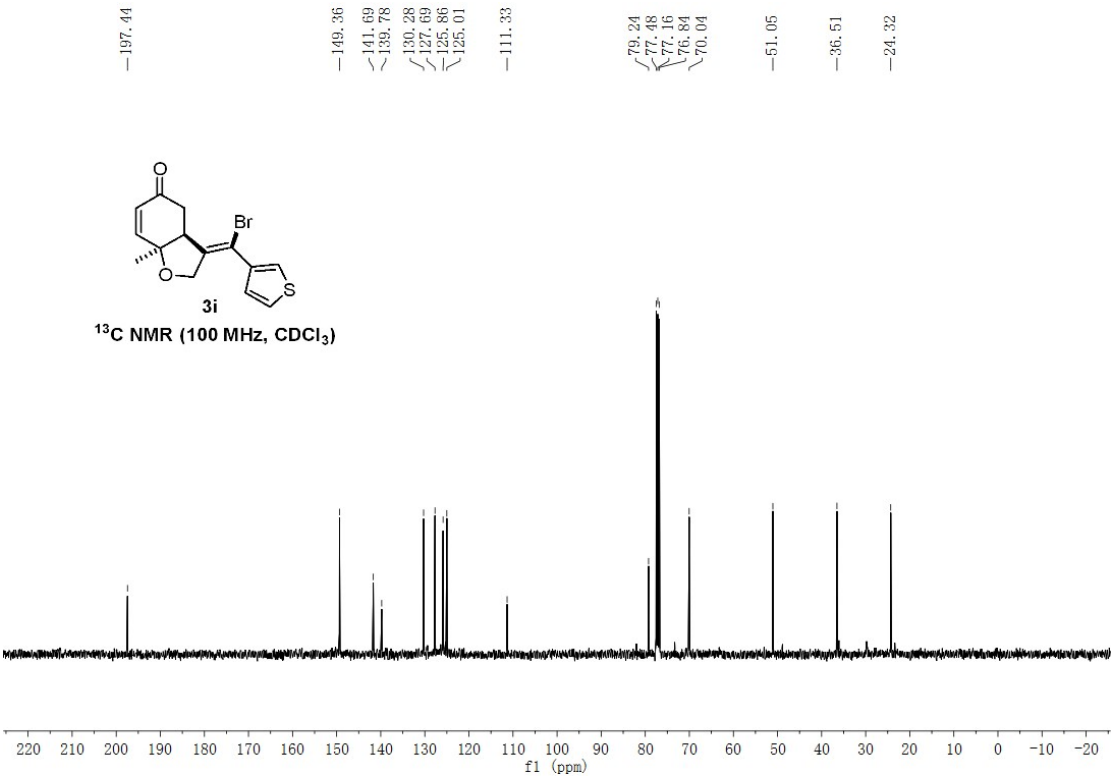

7.29
7.28
7.27
7.27
7.16
7.16
7.15
7.15
7.14
7.13
6.57
6.55
6.16
6.13
4.32
4.29
4.17
4.14
3.30
3.29
3.25
3.23
2.74
2.73
2.72
2.69
2.68
2.67
1.54
0.00
Br
Cl
3h
^{1}H NMR (400 MHz, CDCl$_3$)
3.30
0.98
1.06
1.00
1.07
1.02
2.08
1.03
3.00
f1 (ppm)


197.11
149.47
143.45
141.06
134.43
130.40
129.82
129.19
128.47
126.52
114.76
79.64
77.48
77.16
76.84
69.69
50.77
36.34
24.20
Br
Cl
3h
^{13}C NMR (100 MHz, CDCl$_3$)
f1 (ppm)



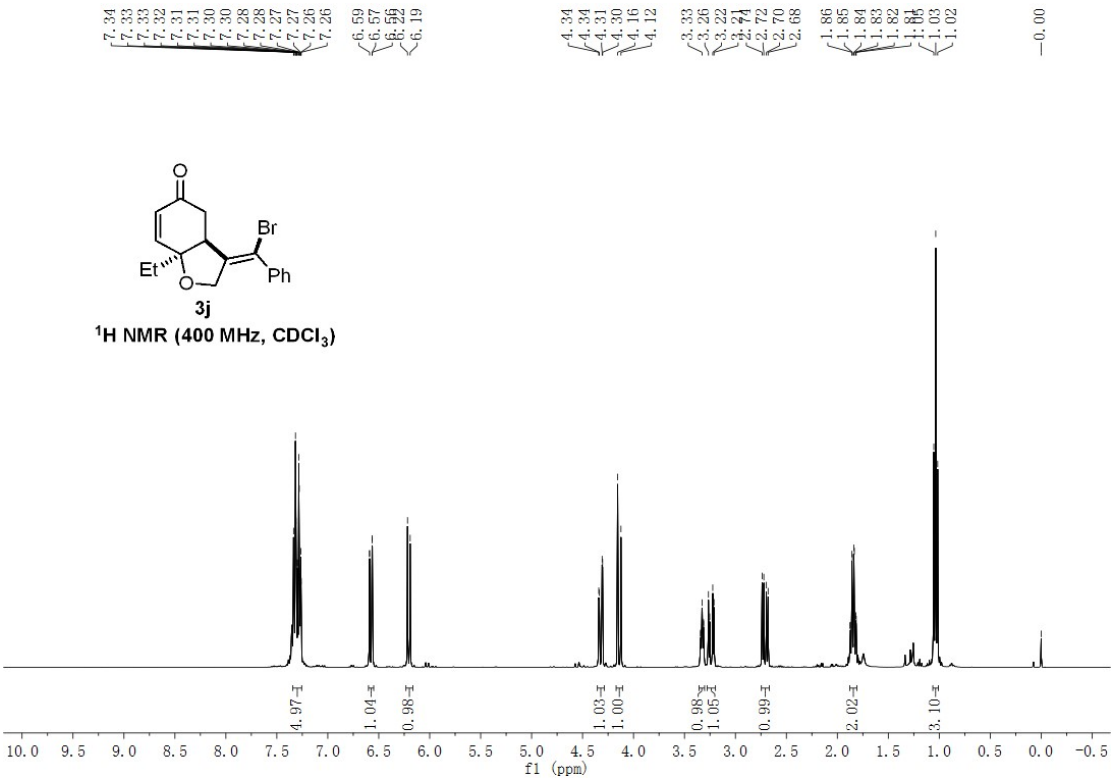
3i

^{1}H NMR (400 MHz, $CDCl_3$)



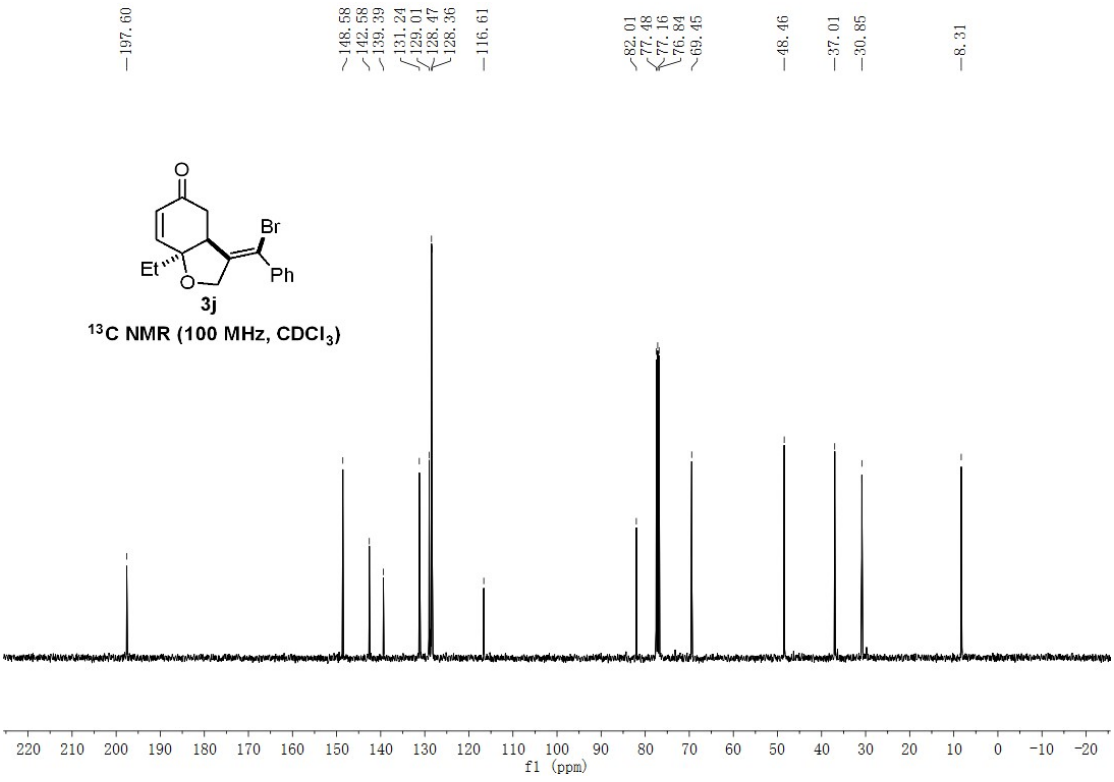
3i

^{13}C NMR (100 MHz, $CDCl_3$)



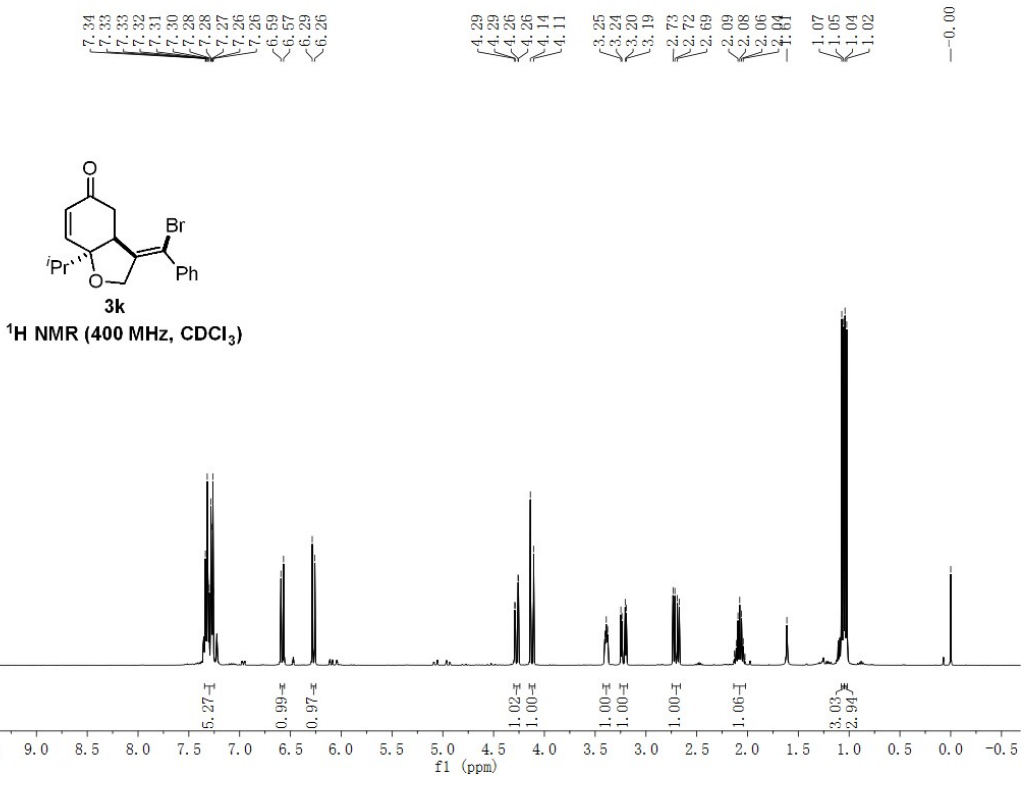
3j

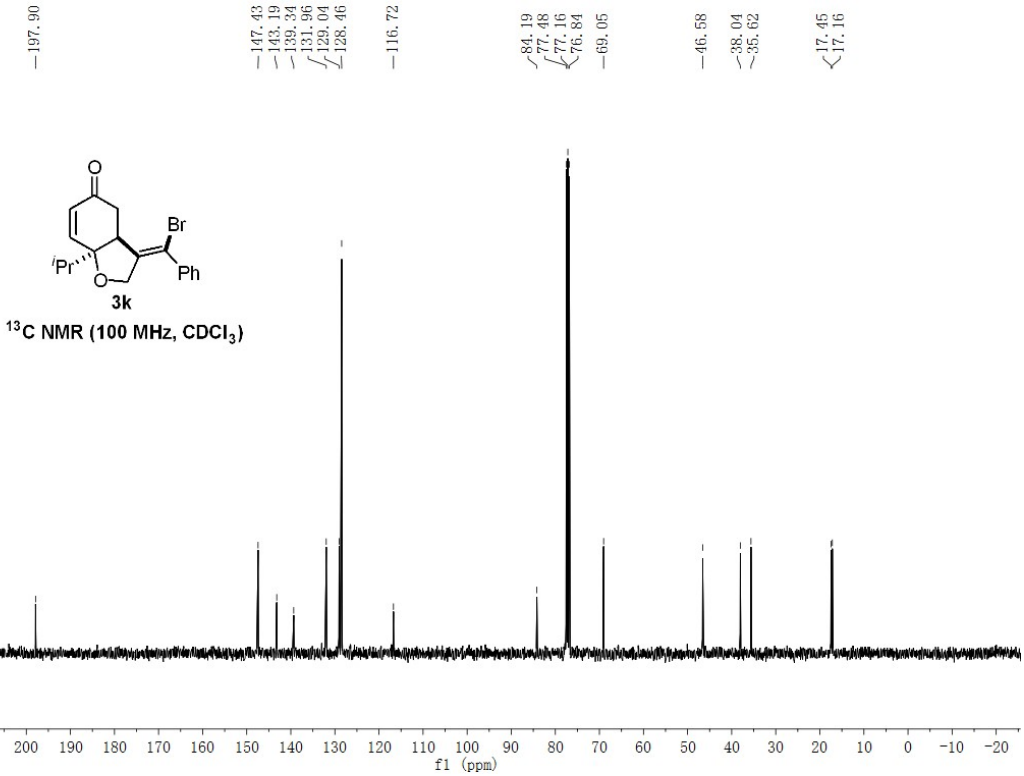
^{1}H NMR (400 MHz, $CDCl_3$)

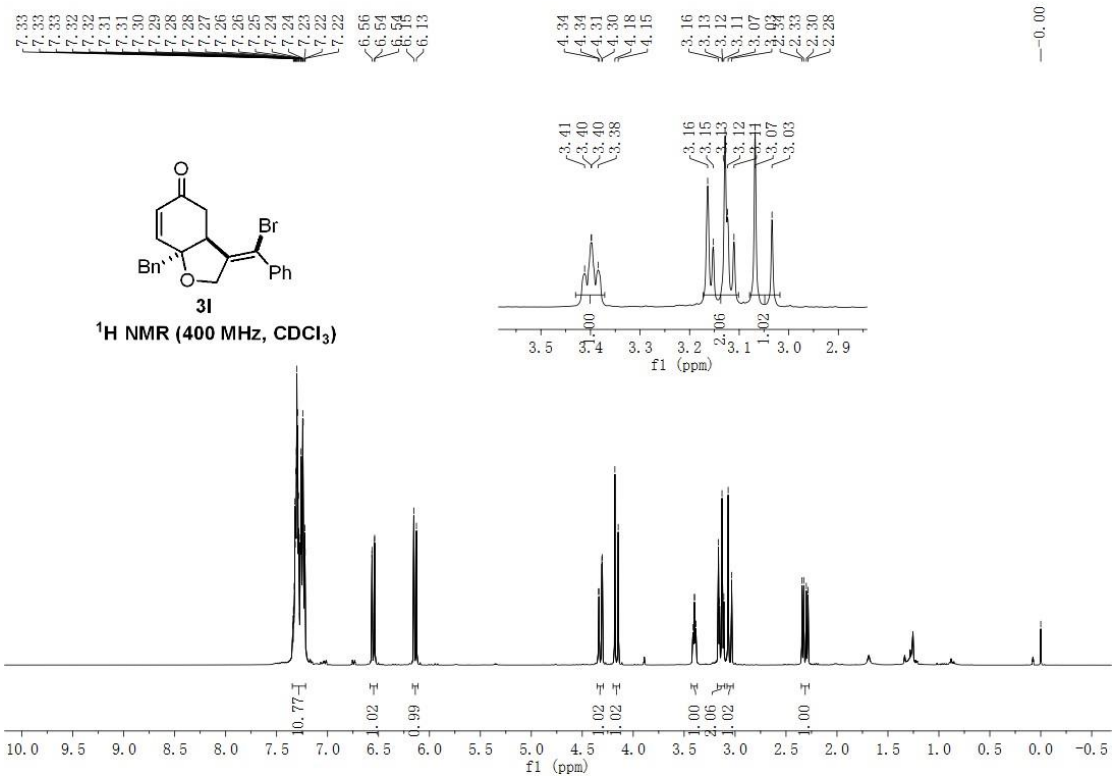


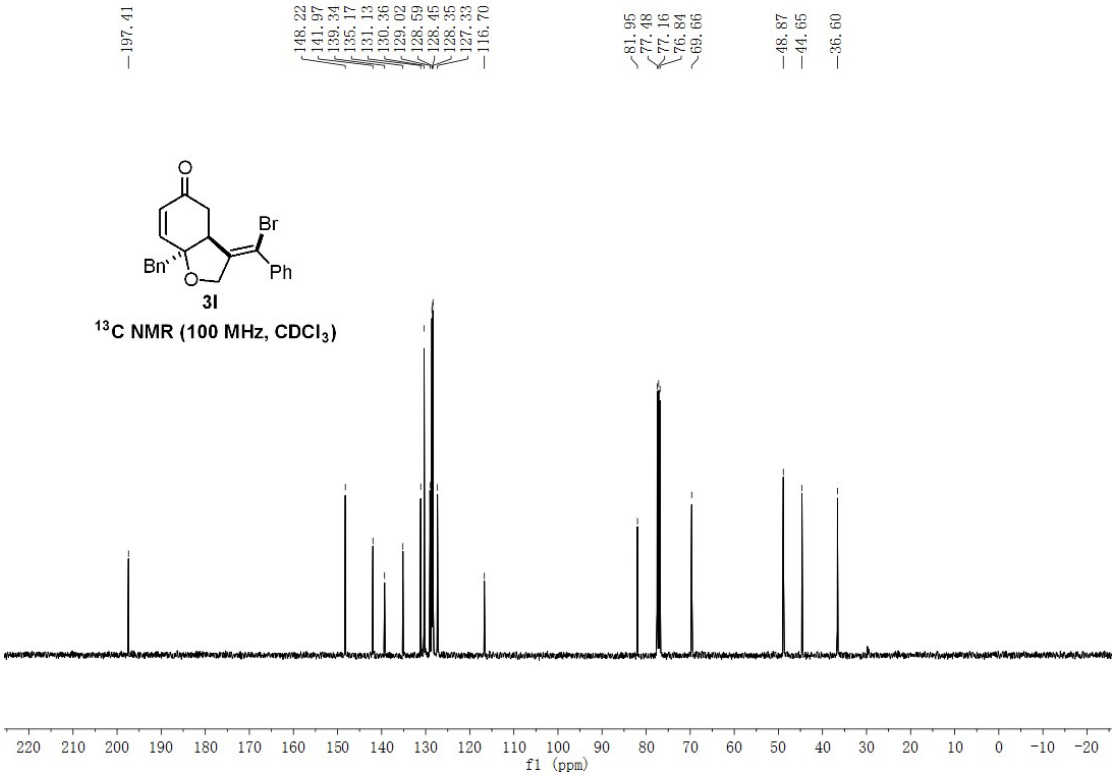
3j

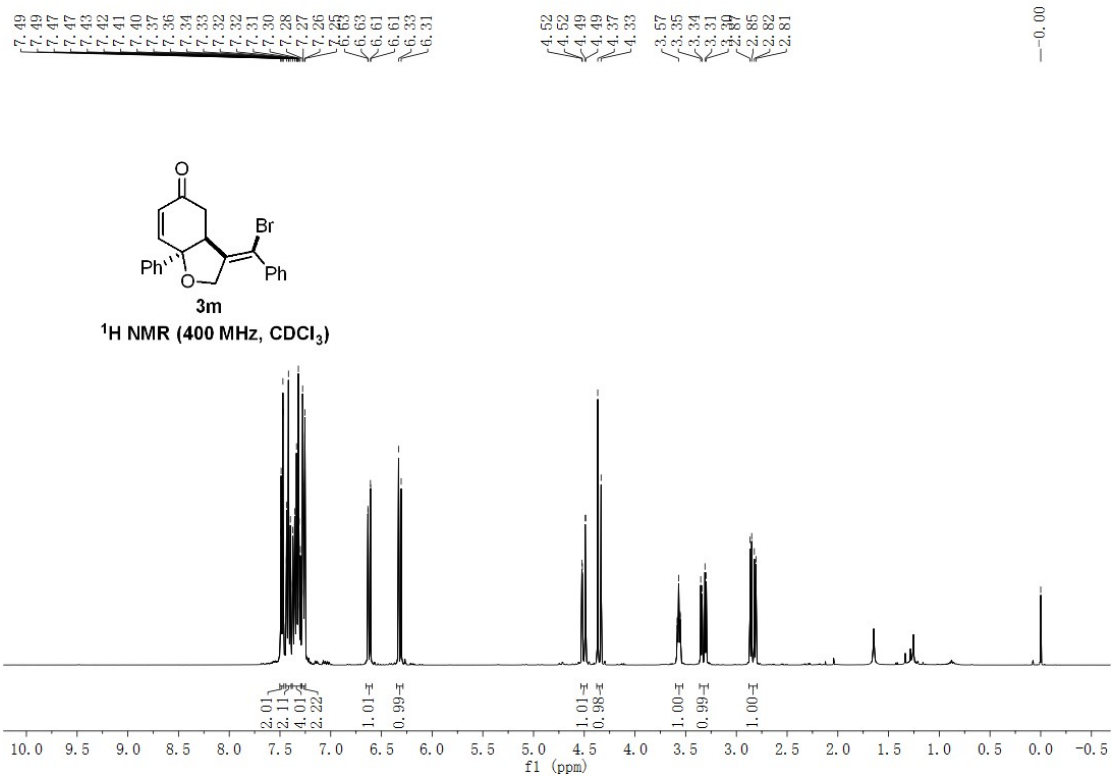
^{13}C NMR (100 MHz, $CDCl_3$)

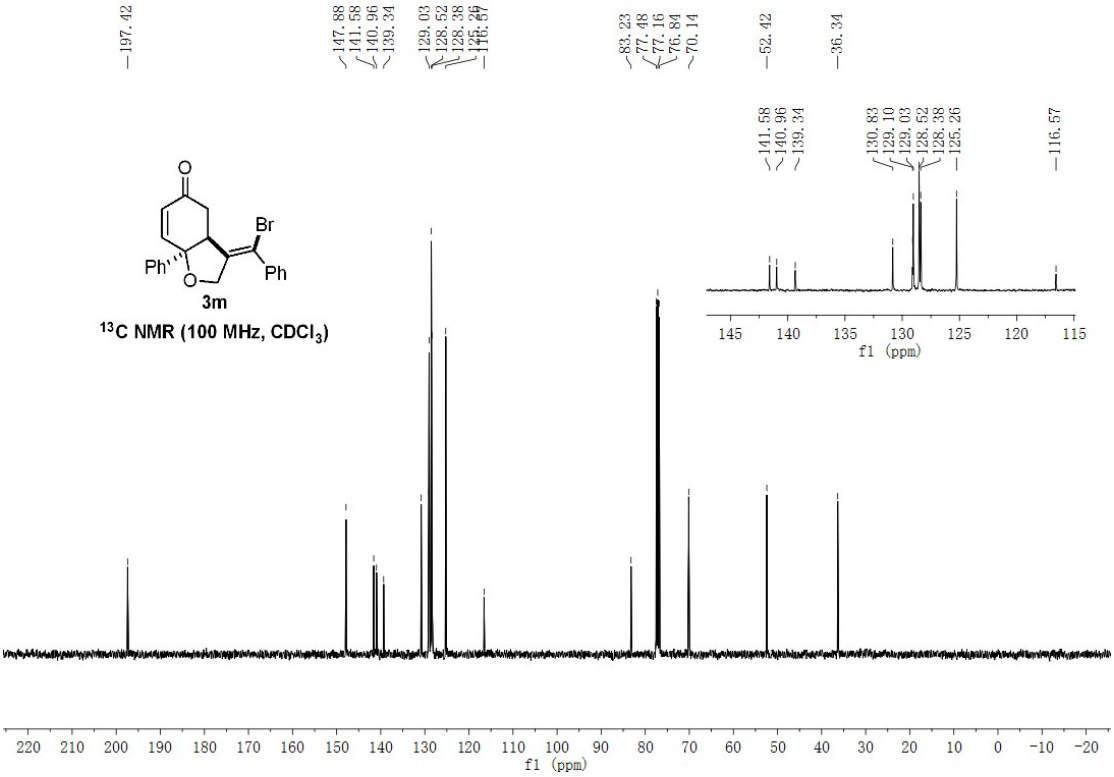

7.34
7.33
7.32
7.31
7.30
7.28
7.28
7.27
7.26
7.26
6.59
6.57
6.29
6.26
4.29
4.29
4.26
4.26
4.14
4.11
3.25
3.24
3.20
3.19
2.73
2.72
2.69
2.09
2.08
2.06
1.81
1.07
1.05
1.04
1.02
0.00
O
Br
iPr
O
Ph
3k
1H NMR (400 MHz, CDCl3)
5.27
0.99
0.97
1.02
1.00
1.00
1.00
1.00
1.06
3.03
2.94
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

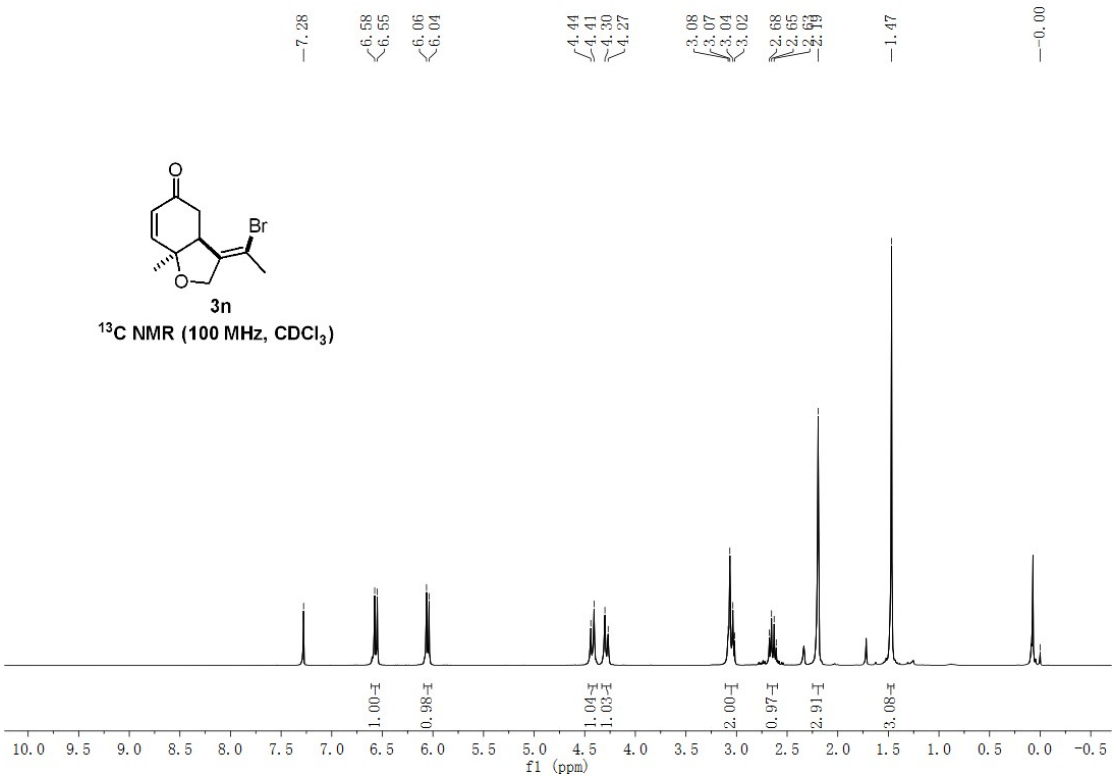

197.90
147.43
143.19
139.34
131.96
129.04
128.46
116.72
84.19
77.48
77.16
76.84
69.05
46.58
38.04
35.62
17.45
17.16
O
Br
iPr
O
Ph
3k
13C NMR (100 MHz, CDCl3)
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)


Br
Bn
Ph
O
3l
^{1}H NMR (400 MHz, CDCl$_3$)
f1 (ppm)


Br
Bn
Ph
O
3l
^{13}C NMR (100 MHz, CDCl$_3$)
f1 (ppm)

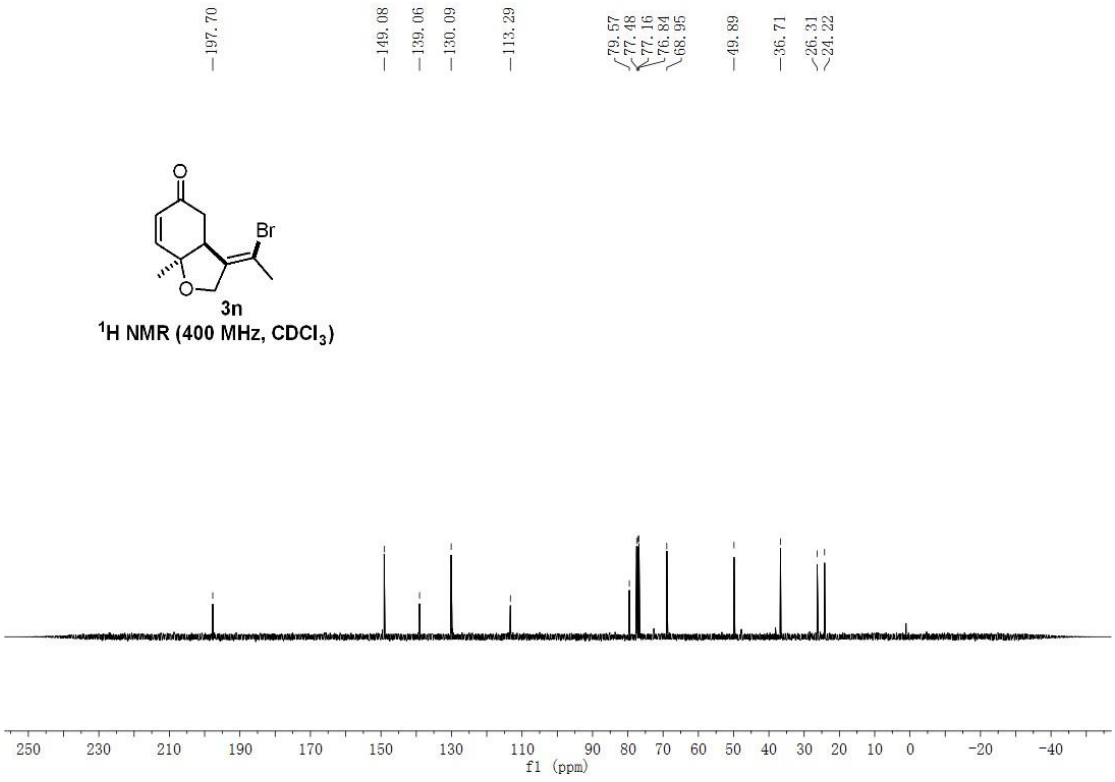

7.49
7.49
7.47
7.47
7.43
7.42
7.41
7.40
7.37
7.36
7.34
7.33
7.32
7.32
7.31
7.30
7.28
7.27
7.26
7.25
6.63
6.63
6.61
6.61
6.33
6.31
4.52
4.52
4.49
4.49
4.37
4.33
3.57
3.35
3.34
3.31
3.30
2.87
2.85
2.82
2.81
0.00
O
Br
Ph
Ph
O
3m
1H NMR (400 MHz, CDCl3)
2.01
2.11
4.01
2.22
1.01
0.99
1.01
0.98
1.00
0.99
1.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


197.42
147.88
141.58
140.96
139.34
129.03
128.52
128.38
125.26
116.57
83.23
77.48
77.16
76.84
70.14
52.42
36.34
141.58
140.96
139.34
130.83
129.10
129.03
128.52
128.38
125.26
116.57
145 140 135 130 125 120 115
f1 (ppm)
O
Br
Ph
Ph
O
3m
13C NMR (100 MHz, CDCl3)
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)



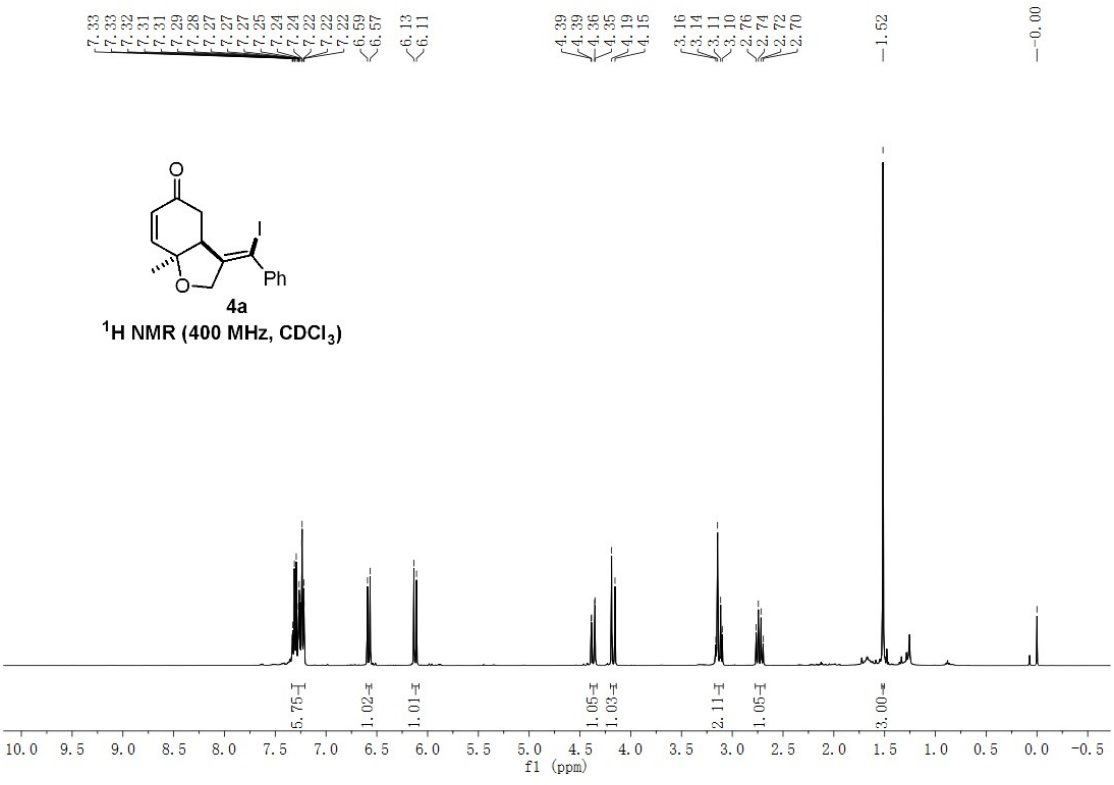
3n

^{13}C NMR (100 MHz, $CDCl_3$)



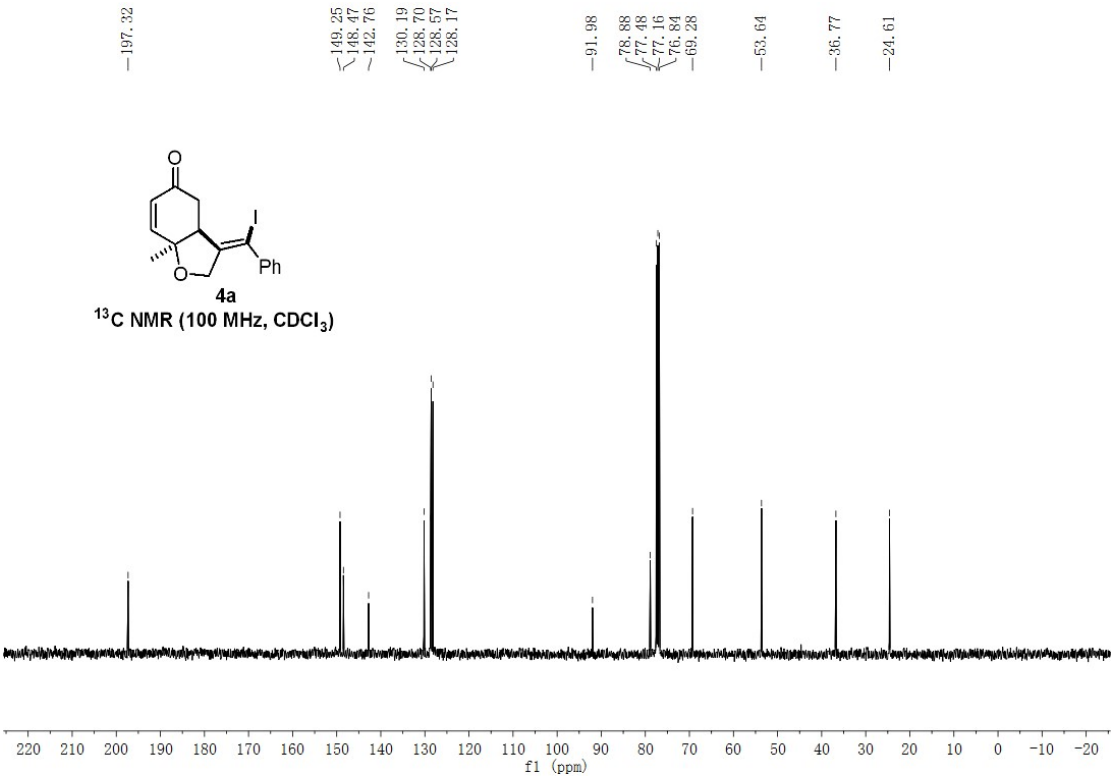
3n

^{1}H NMR (400 MHz, $CDCl_3$)



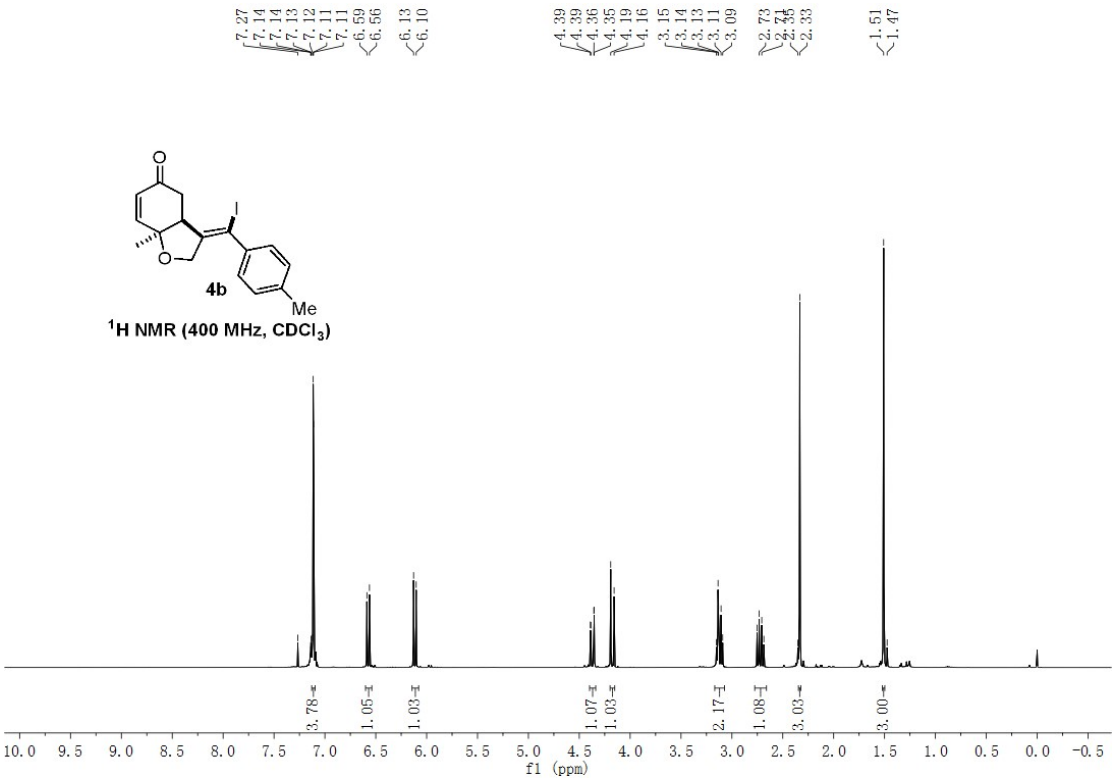
4a

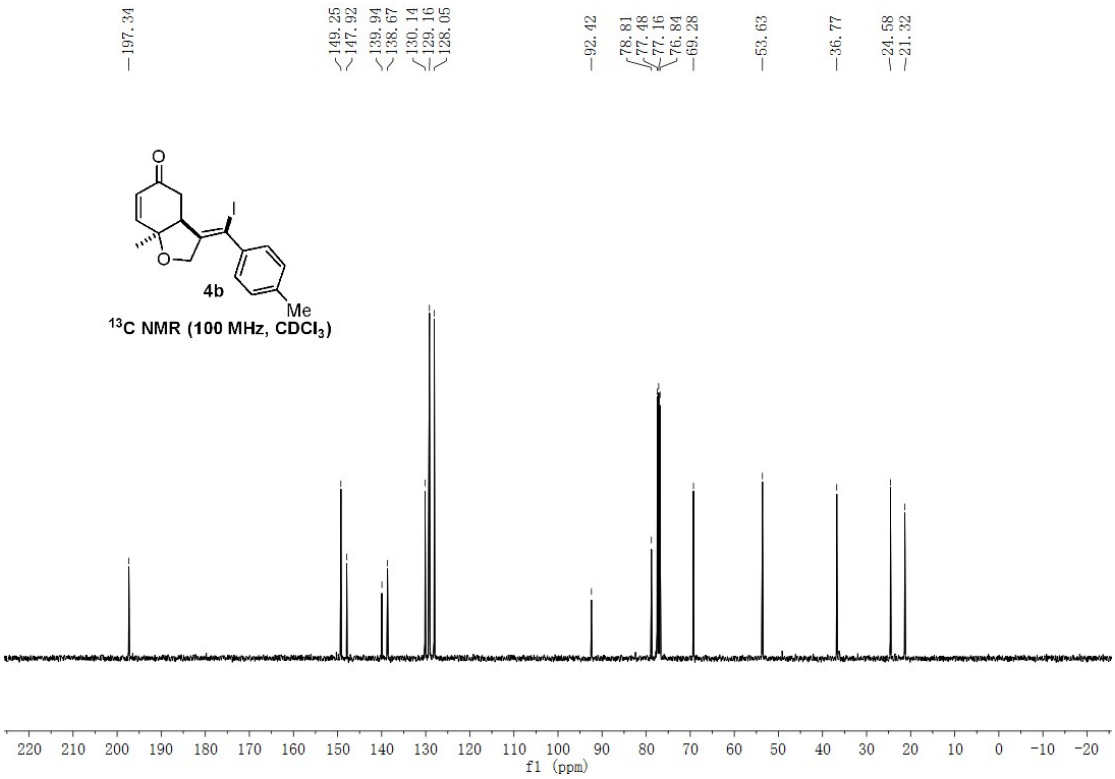
^{1}H NMR (400 MHz, $CDCl_3$)

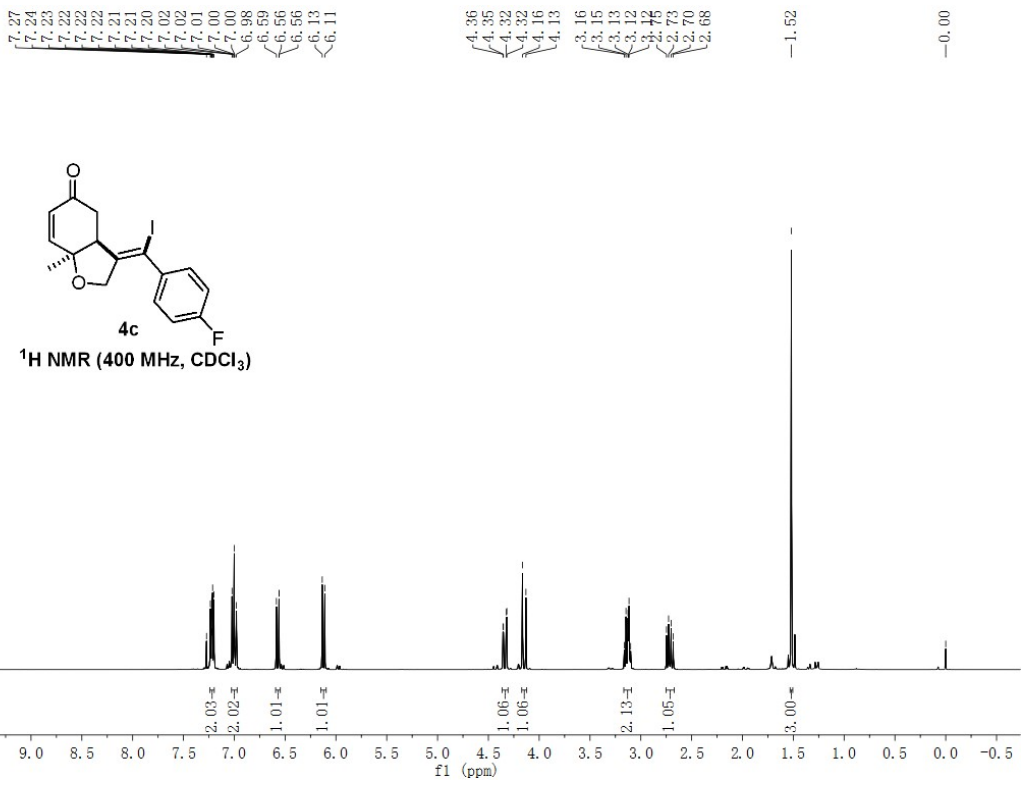


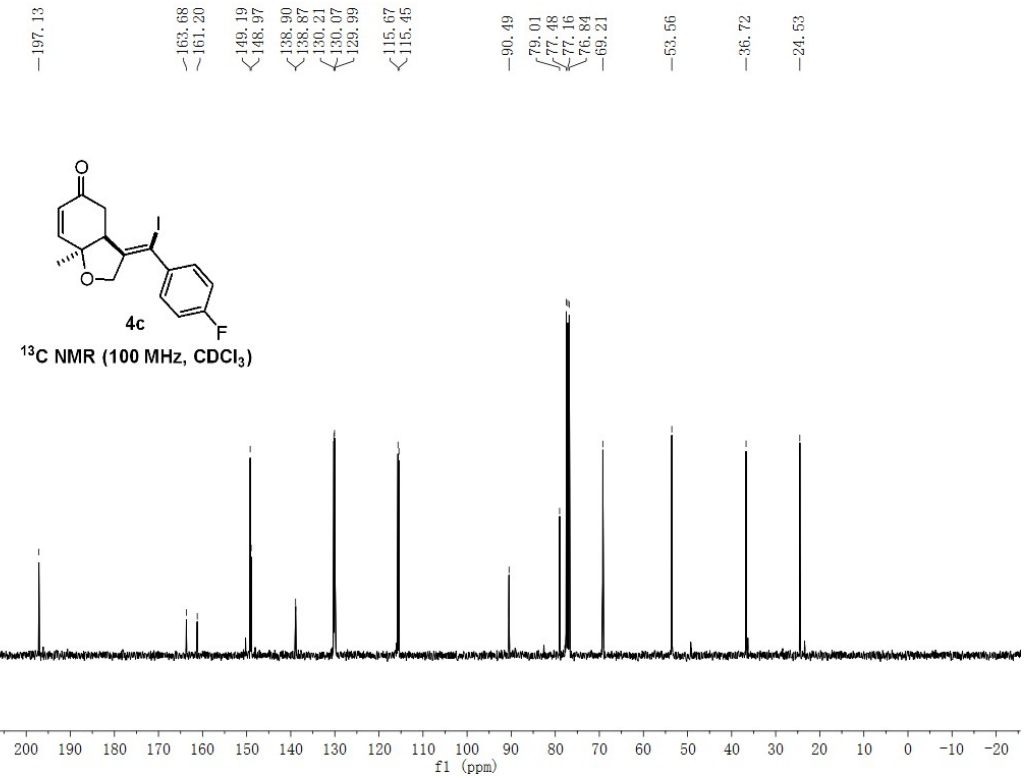
4a

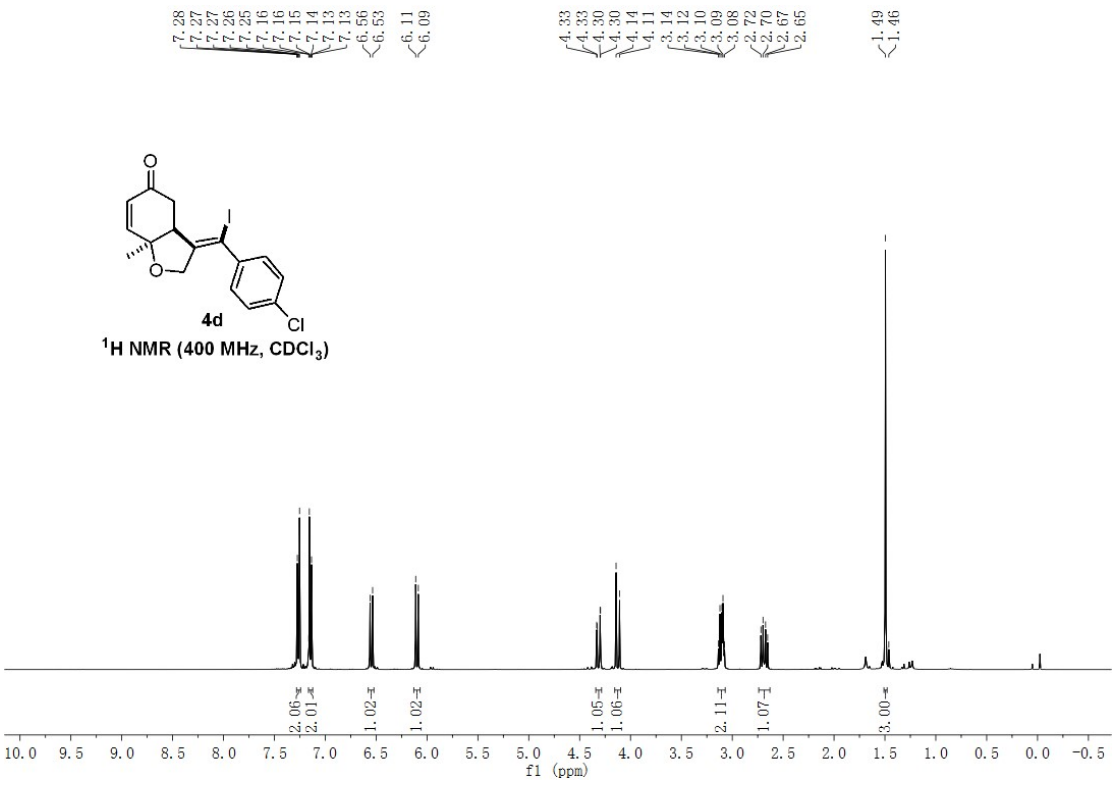
^{13}C NMR (100 MHz, $CDCl_3$)

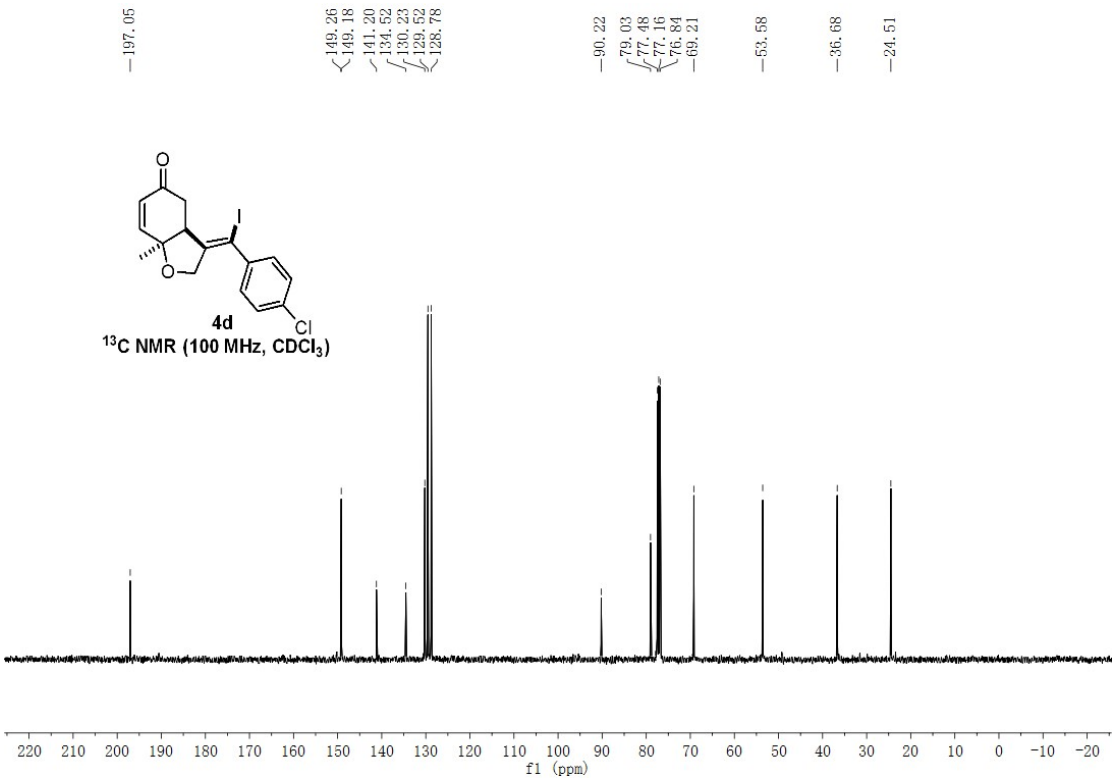

7.27
7.14
7.14
7.13
7.12
7.11
7.11
6.59
6.56
6.13
6.10
4.39
4.39
4.36
4.35
4.19
4.16
3.15
3.14
3.13
3.11
3.09
2.73
2.71
2.35
2.33
1.51
1.47
O
O
I
Me
4b
^{1}H NMR (400 MHz, CDCl$_3$)
3.78
1.05
1.03
1.07
1.03
2.17
1.08
3.03
3.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

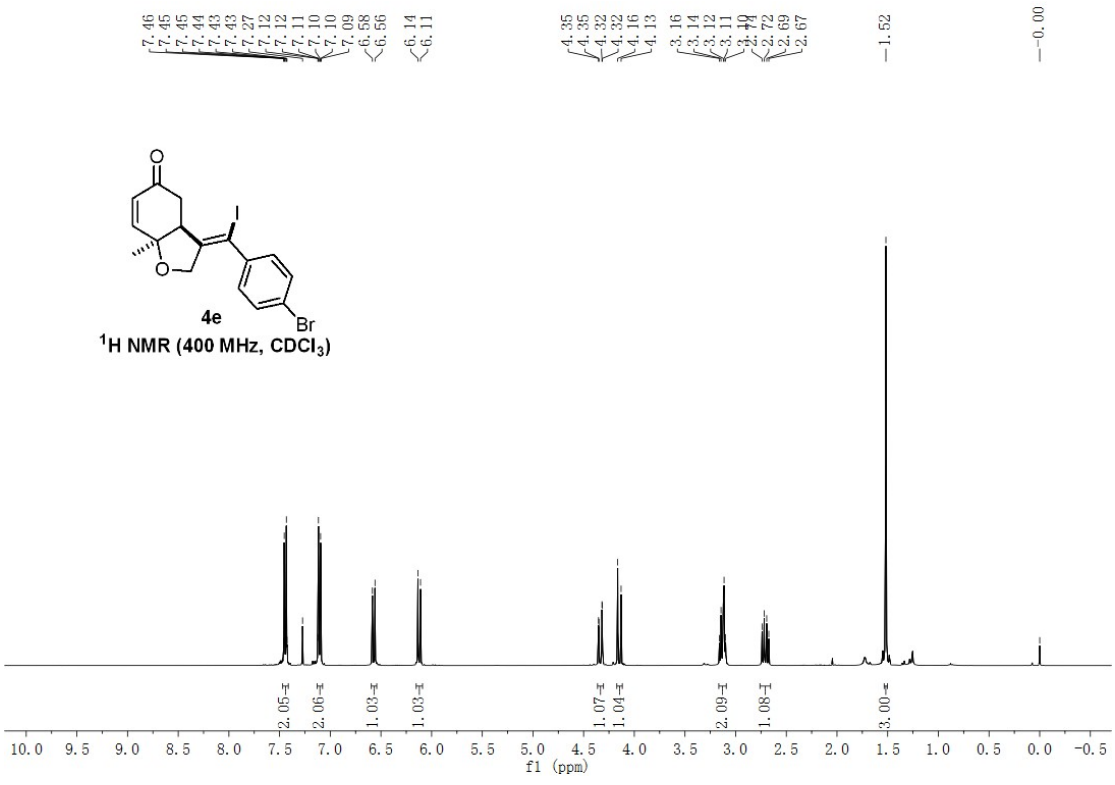

197.34
149.25
147.92
139.94
138.67
130.14
129.16
128.05
92.42
78.81
77.48
77.16
76.84
69.28
53.63
36.77
24.58
21.32
O
O
I
Me
4b
^{13}C NMR (100 MHz, CDCl$_3$)
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)

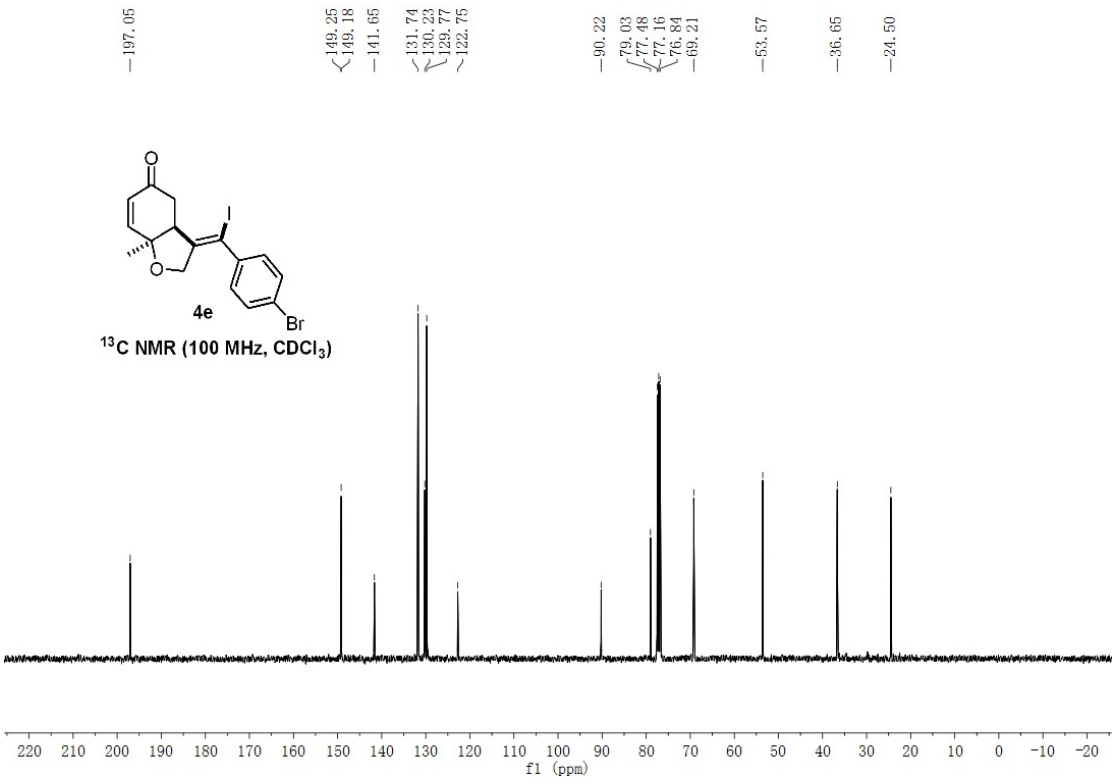

7.27
7.24
7.23
7.22
7.22
7.22
7.21
7.21
7.20
7.02
7.02
7.01
7.00
7.00
6.98
6.59
6.56
6.56
6.13
6.11
4.36
4.35
4.32
4.32
4.16
4.13
3.16
3.15
3.13
3.12
2.75
2.73
2.70
2.68
1.52
0.00
O
I
O
F
4c
^{1}H NMR (400 MHz, CDCl$_3$)
2.03
2.02
1.01
1.01
1.06
1.06
2.13
1.05
3.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

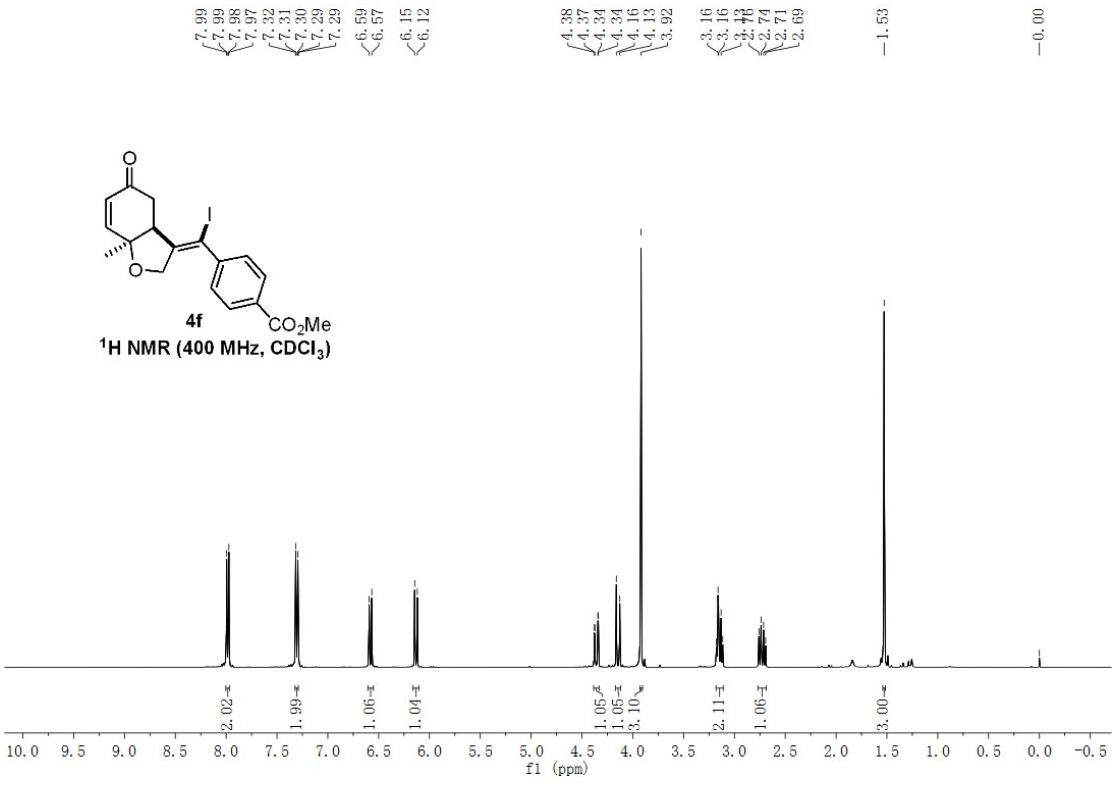

197.13
163.68
161.20
149.19
148.97
138.90
138.87
130.21
130.07
129.99
115.67
115.45
90.49
79.01
77.48
77.16
76.84
69.21
53.56
36.72
24.53
O
I
O
F
4c
^{13}C NMR (100 MHz, CDCl$_3$)
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)

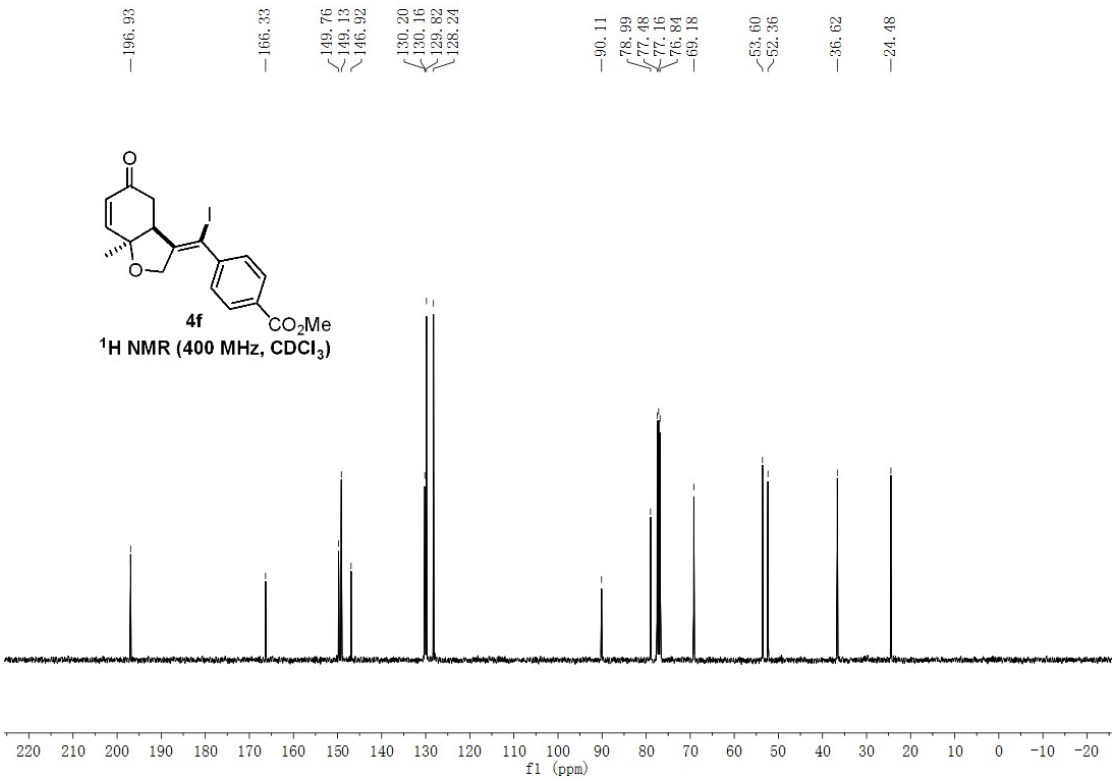

7.28
7.27
7.27
7.26
7.25
7.16
7.16
7.15
7.14
7.13
7.13
6.56
6.53
6.11
6.09
4.33
4.33
4.30
4.30
4.14
4.11
3.14
3.12
3.10
3.09
3.08
2.72
2.70
2.67
2.65
1.49
1.46
O
I
O
Cl
4d
^{1}H NMR (400 MHz, CDCl$_3$)
2.06
2.01
1.02
1.02
1.05
1.06
2.11
1.07
3.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

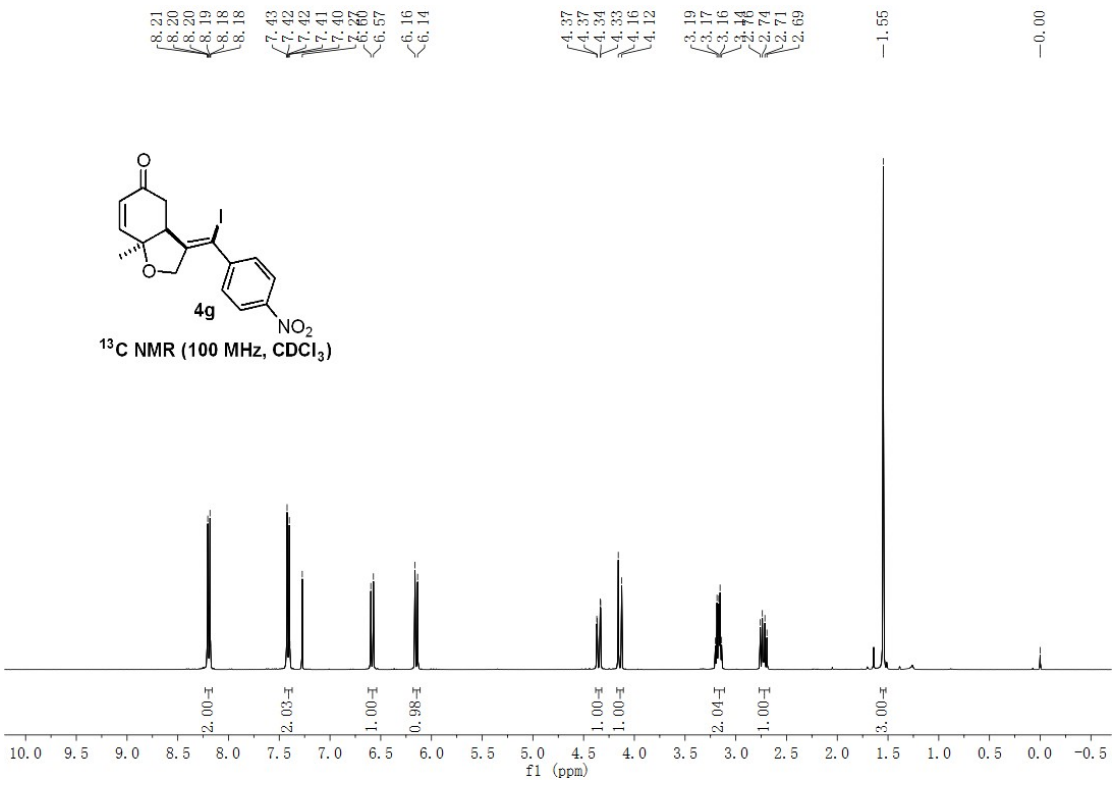

197.05
149.26
149.18
141.20
134.52
130.23
129.52
128.78
90.22
79.03
77.48
77.16
76.84
69.21
53.58
36.68
24.51
O
I
O
Cl
4d
^{13}C NMR (100 MHz, CDCl$_3$)
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)

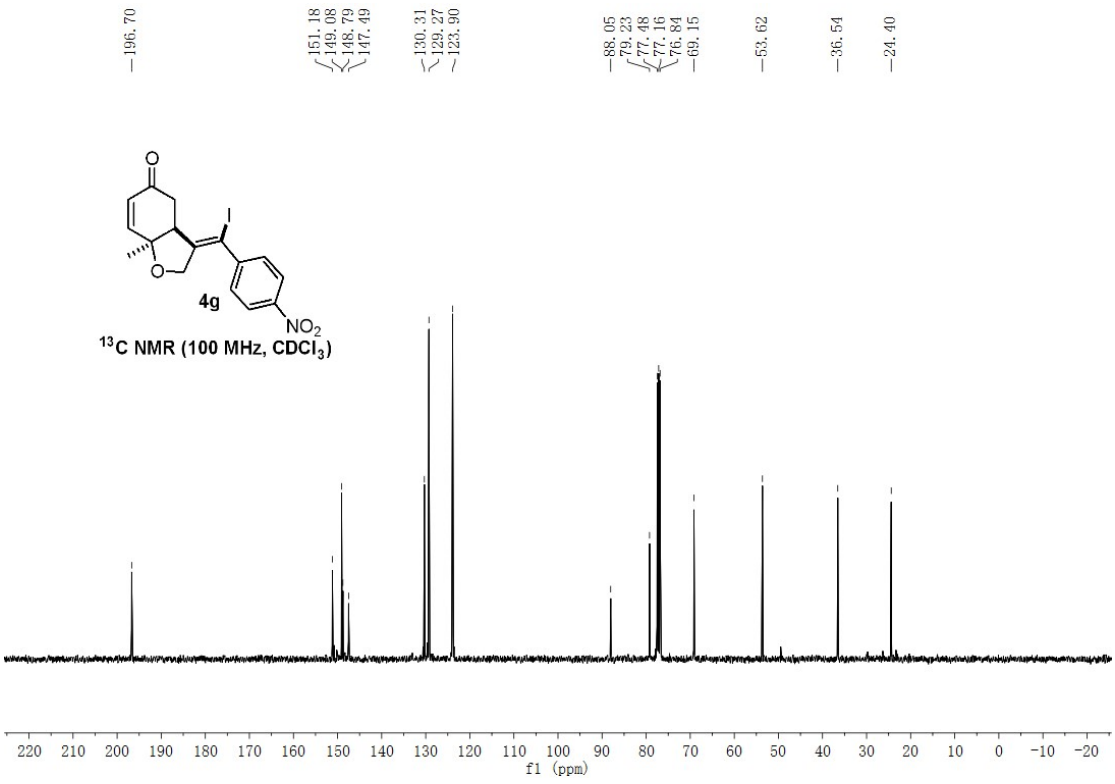

7.46
7.45
7.45
7.44
7.43
7.43
7.27
7.12
7.12
7.11
7.10
7.10
7.09
6.58
6.56
6.14
6.11
4.35
4.35
4.32
4.32
4.16
4.13
3.16
3.14
3.12
3.11
2.72
2.69
2.67
1.52
0.00
O
O
I
Br
4e
^{1}H NMR (400 MHz, CDCl$_3$)
2.05
2.06
1.03
1.03
1.07
1.04
2.09
1.08
3.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

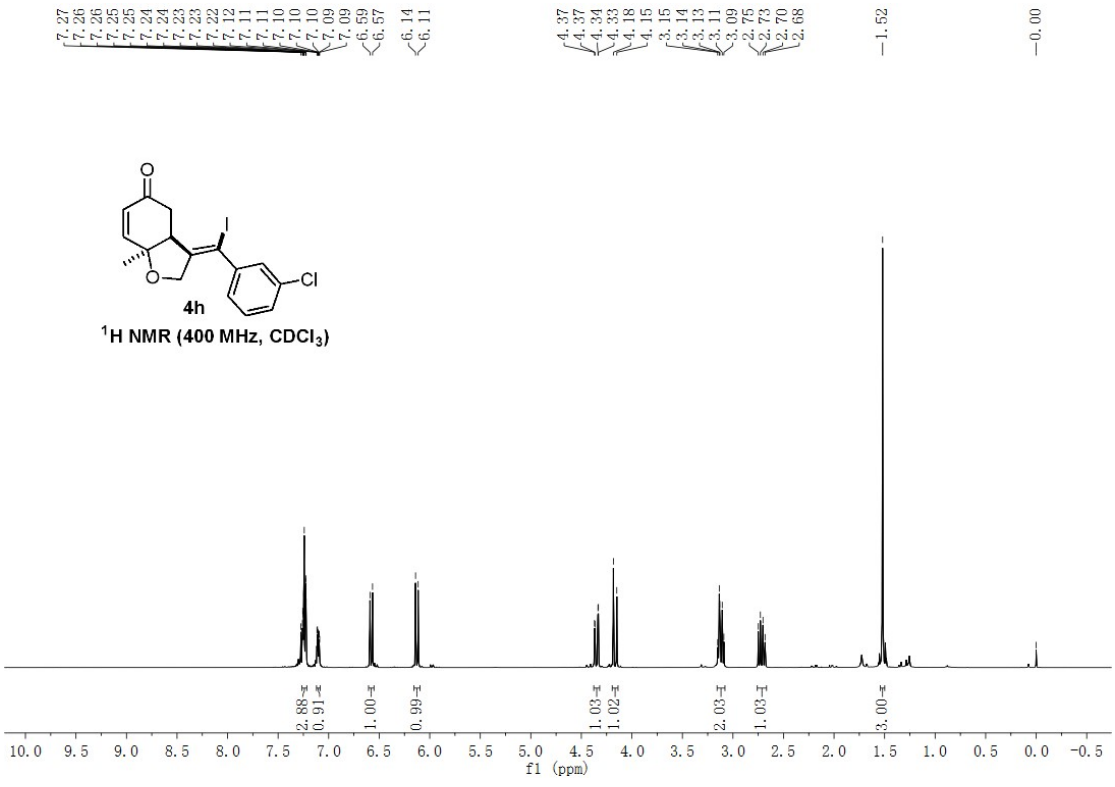

197.05
149.25
149.18
141.65
131.74
130.23
129.77
122.75
90.22
79.03
77.48
77.16
76.84
69.21
53.57
36.65
24.50
O
O
I
Br
4e
^{13}C NMR (100 MHz, CDCl$_3$)
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)

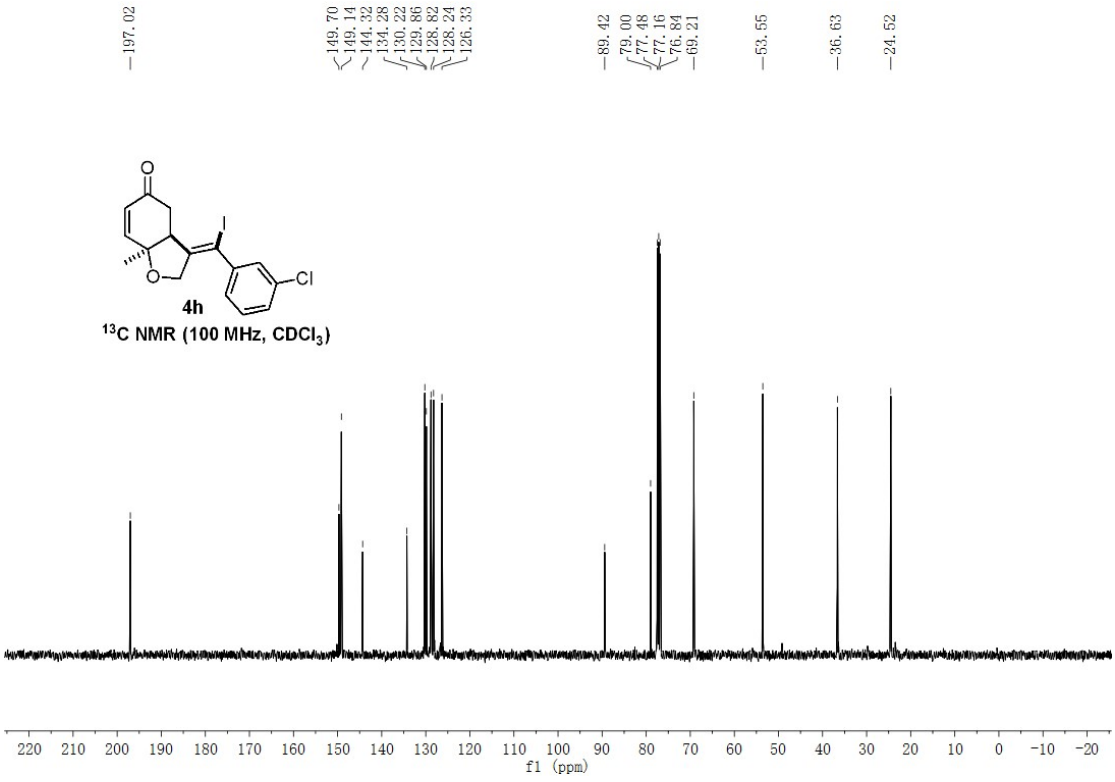

7.99
7.99
7.98
7.97
7.32
7.31
7.30
7.29
7.29
6.59
6.57
6.15
6.12
4.38
4.37
4.34
4.34
4.16
4.13
3.92
3.16
3.16
2.74
2.71
2.69
1.53
0.00
O
I
O
4f
CO2Me
1H NMR (400 MHz, CDCl3)
2.02
1.99
1.06
1.04
1.05
1.05
3.10
2.11
1.06
3.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

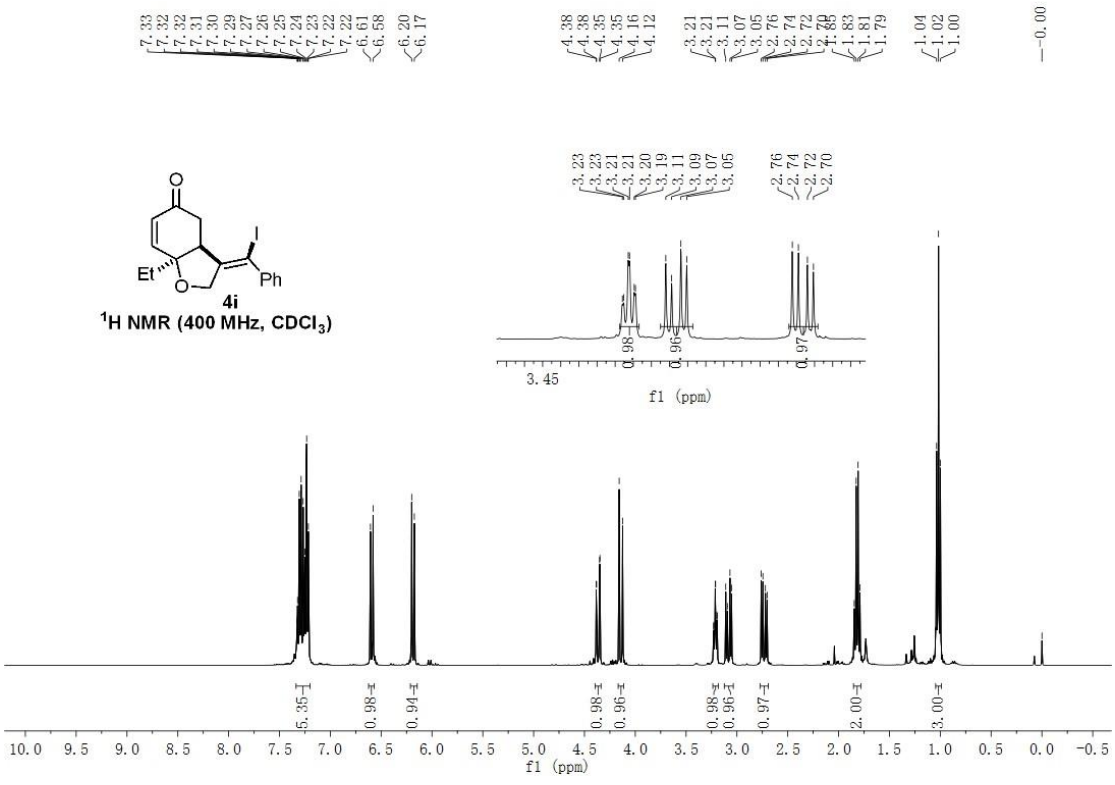

196.93
166.33
149.76
149.13
146.92
130.20
130.16
129.82
128.24
90.11
78.99
77.48
77.16
76.84
69.18
53.60
52.36
36.62
24.48
O
I
O
4f
CO2Me
1H NMR (400 MHz, CDCl3)
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)

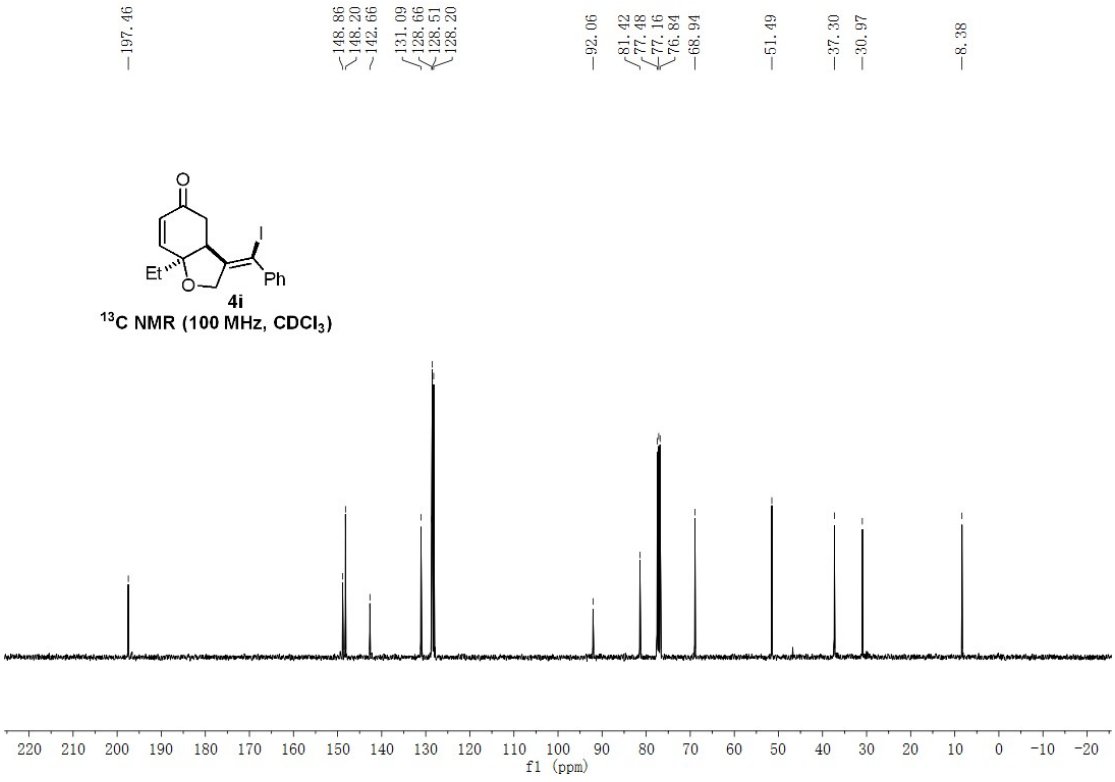

8.21
8.20
8.20
8.19
8.18
8.18
7.43
7.42
7.42
7.41
7.40
6.57
6.16
6.14
4.37
4.37
4.34
4.33
4.16
4.12
3.19
3.17
3.16
2.74
2.71
2.69
1.55
0.00
4g
NO2
13C NMR (100 MHz, CDCl3)
2.00
2.03
1.00
0.98
1.00
1.00
2.04
1.00
3.00
f1 (ppm)

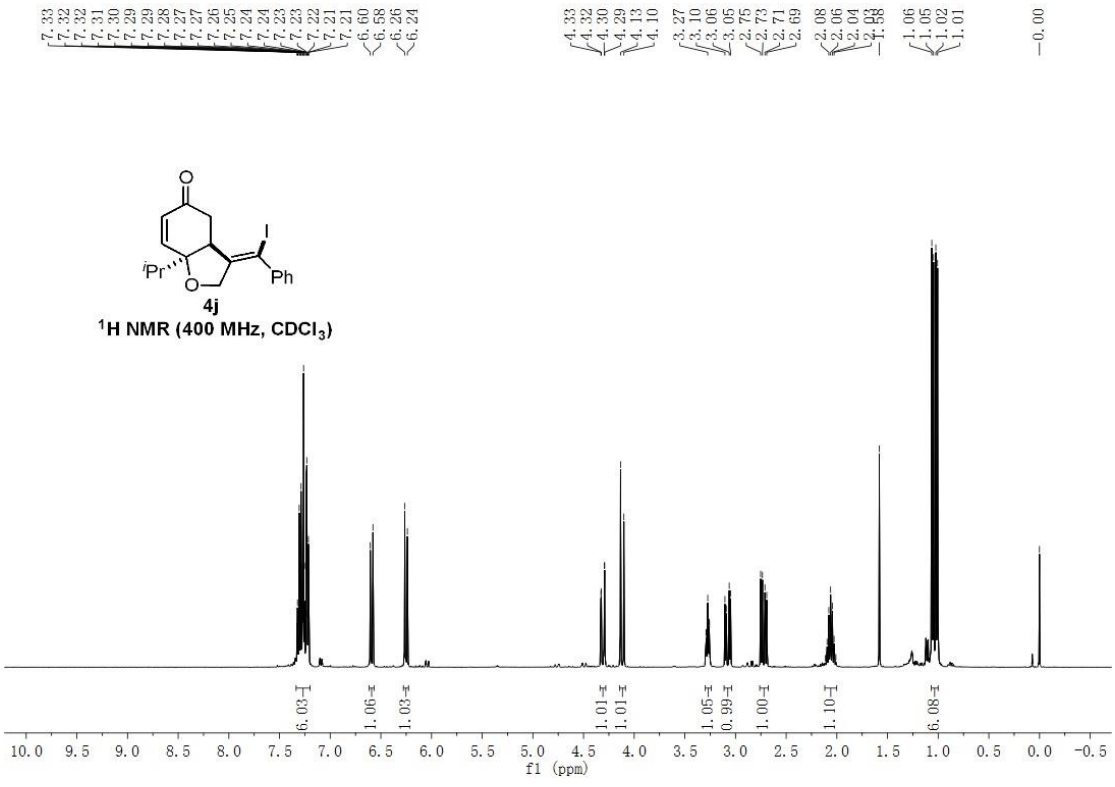

196.70
151.18
149.08
148.79
147.49
130.31
129.27
123.90
88.05
79.23
77.48
77.16
76.84
69.15
53.62
36.54
24.40
4g
NO2
13C NMR (100 MHz, CDCl3)
f1 (ppm)

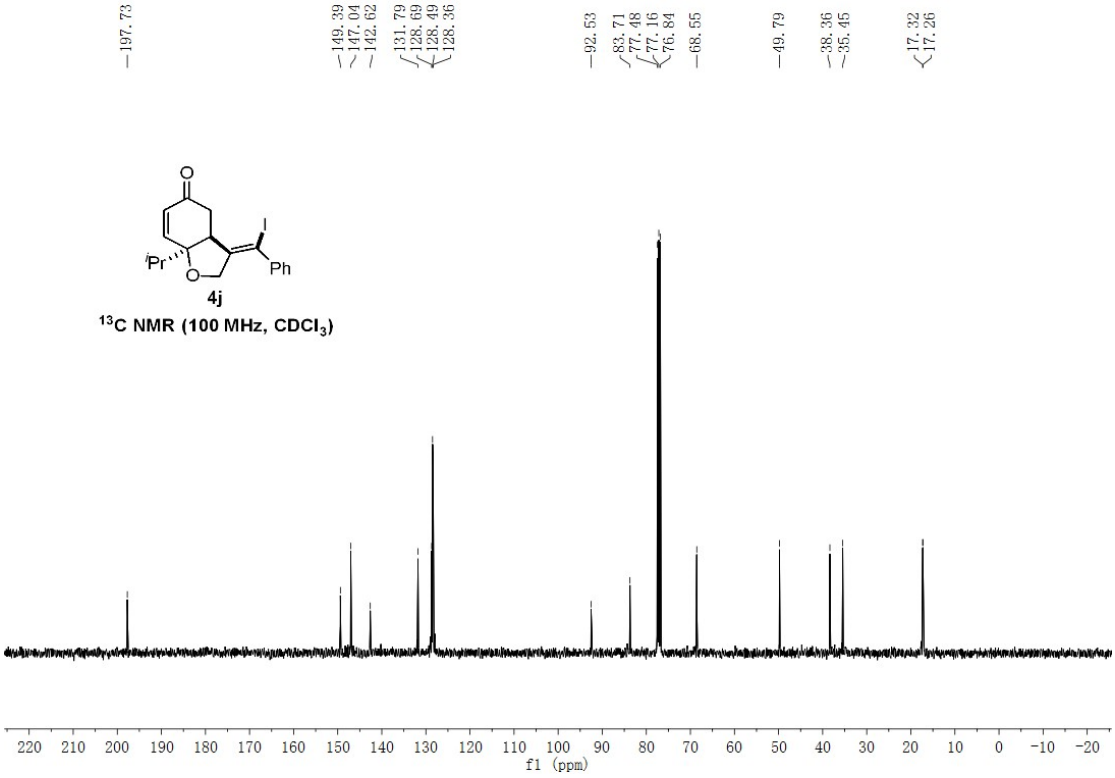

7.27
7.26
7.26
7.25
7.25
7.24
7.24
7.23
7.23
7.22
7.12
7.11
7.11
7.10
7.10
7.10
7.09
7.09
6.59
6.57
6.14
6.11
4.37
4.37
4.34
4.33
4.18
4.15
3.15
3.14
3.13
3.11
3.09
2.75
2.73
2.70
2.68
1.52
0.00
O
I
Cl
4h
^{1}H NMR (400 MHz, CDCl$_3$)
2.88
0.91
1.00
0.99
1.03
1.02
2.03
1.03
3.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

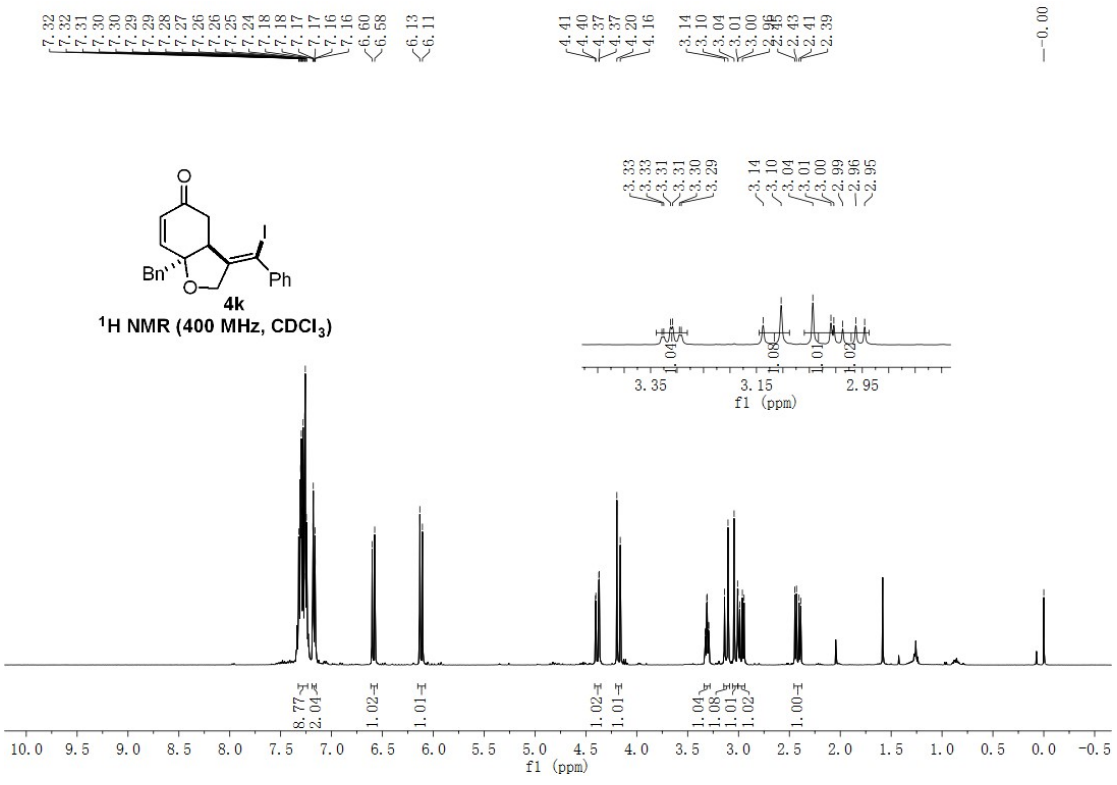

197.02
149.70
149.14
144.32
134.28
130.22
129.86
128.82
128.24
126.33
89.42
79.00
77.48
77.16
76.84
69.21
53.55
36.63
24.52
O
I
Cl
4h
^{13}C NMR (100 MHz, CDCl$_3$)
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)

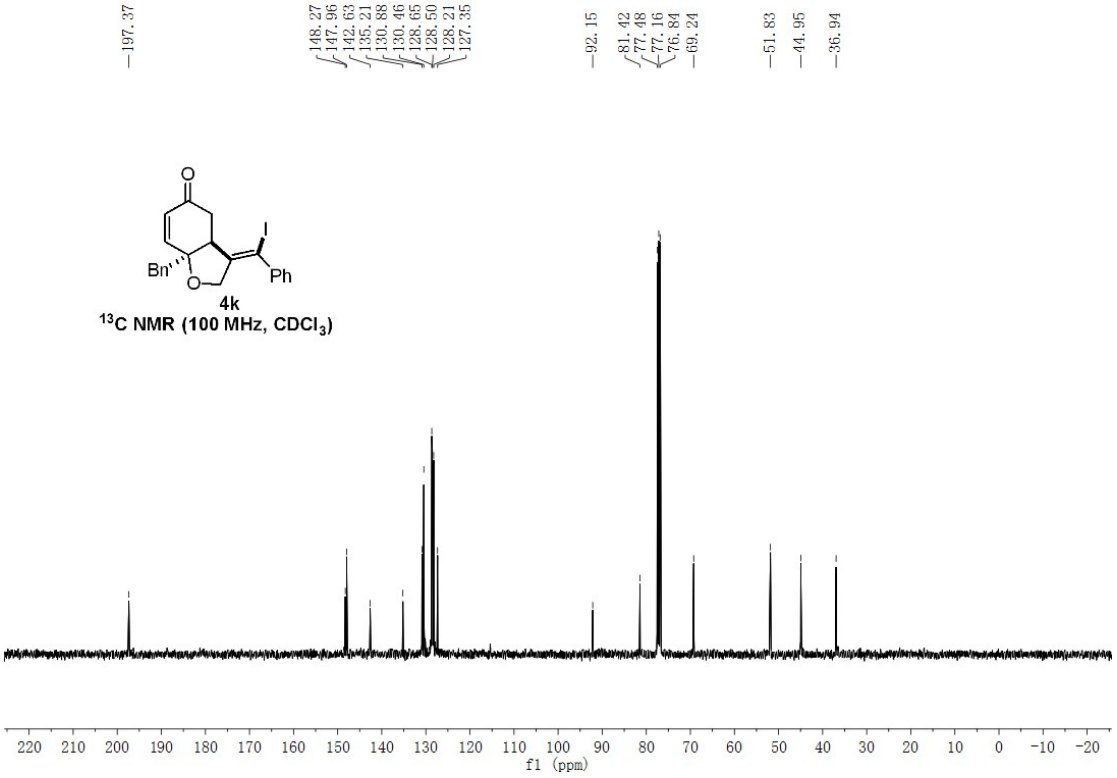

7.33 7.32 7.32 7.31 7.30 7.29 7.27 7.26 7.25 7.24 7.23 7.22 7.22 6.61 6.58 6.20 6.17
4.38 4.38 4.35 4.35 4.16 4.12
3.21 3.21 3.11 3.07 3.05 2.76 2.74 2.72 2.70 1.85 1.83 1.81 1.79
1.04 1.02 1.00
0.00
O
I
Et
O
Ph
4i
1H NMR (400 MHz, CDCl3)
3.23 3.23 3.21 3.21 3.20 3.19 3.11 3.09 3.07 3.05
2.76 2.74 2.72 2.70
0.98 0.96 0.97
3.45
f1 (ppm)
5.35 0.98 0.94 0.98 0.96 0.98 0.96 0.97 2.00 3.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

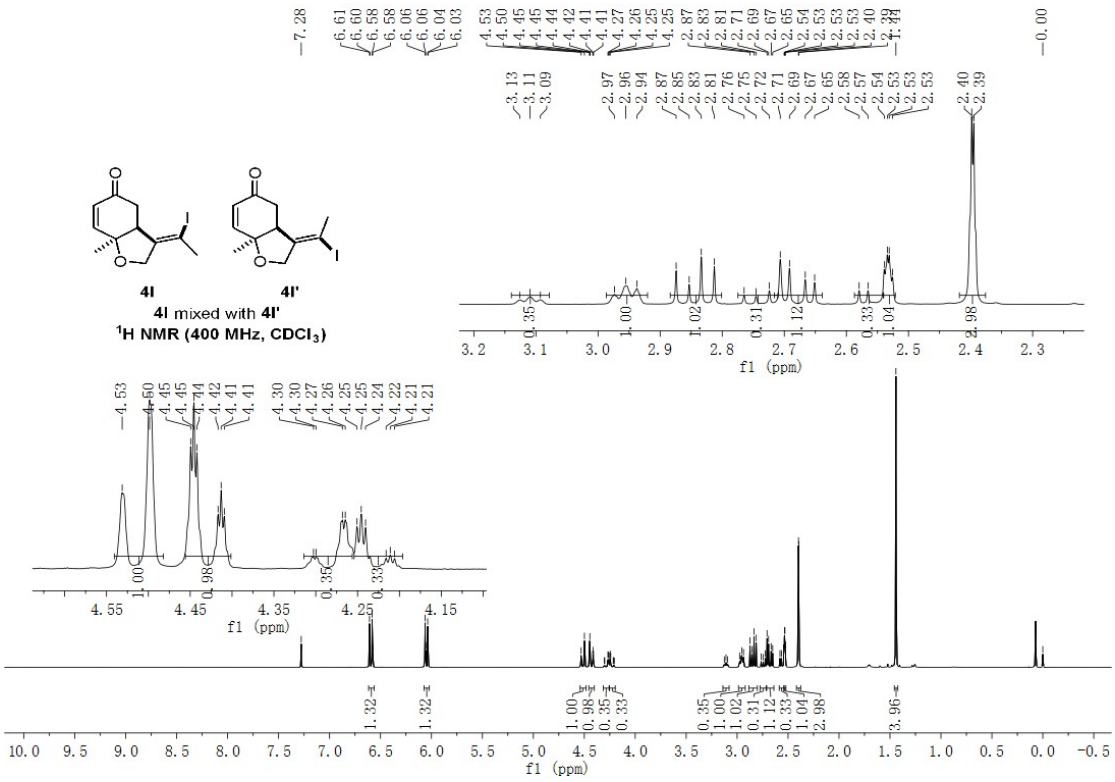

197.46
148.86 148.20 142.66 131.09 128.66 128.51 128.20
92.06
81.42 77.48 77.16 76.84 68.94
51.49
37.30 30.97
8.38
O
I
Et
O
Ph
4i
13C NMR (100 MHz, CDCl3)
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)

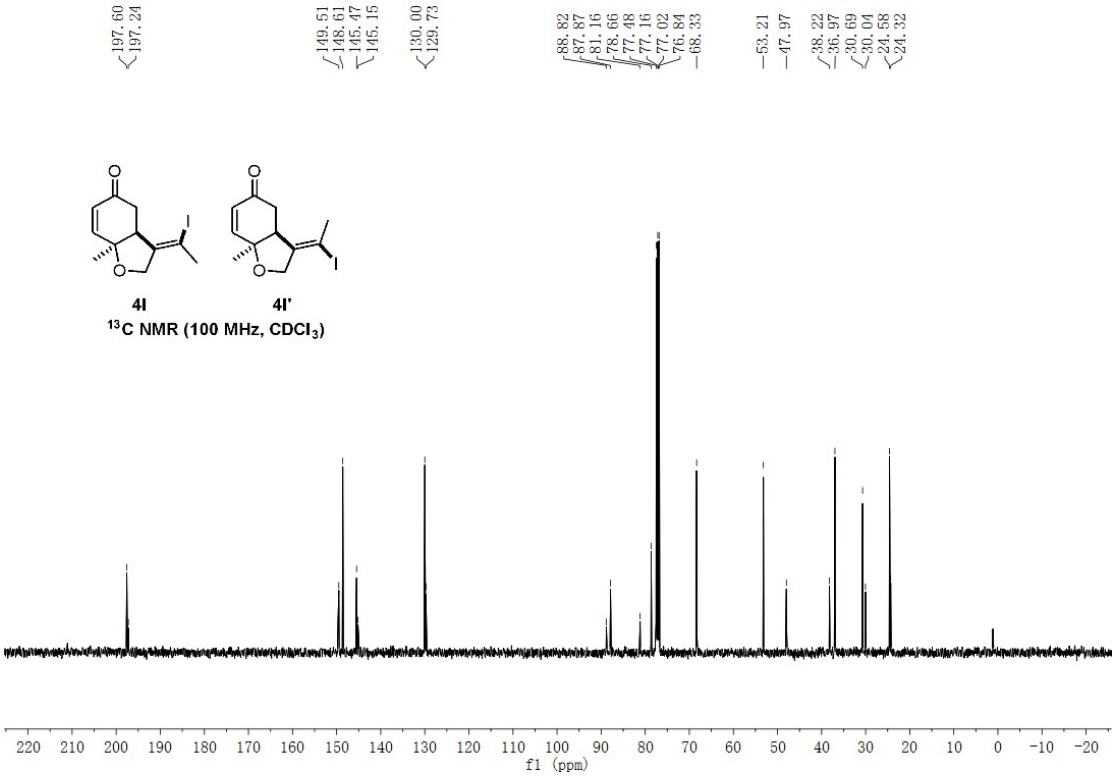

7.33 7.32 7.32 7.31 7.30 7.29 7.29 7.28 7.27 7.27 7.26 7.25 7.24 7.24 7.23 7.23 7.22 7.21 7.21 6.60 6.58 6.26 6.24
4.33 4.32 4.30 4.29 4.13 4.10 3.27 3.10 3.06 3.05 2.75 2.73 2.71 2.69 2.08 2.06 2.04 2.03 1.58 1.06 1.05 1.02 1.01 0.00
iPr
O
I
Ph
4j
1H NMR (400 MHz, CDCl3)
6.03 1.06 1.03 1.01 1.01 1.05 0.99 1.00 1.10 6.08
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

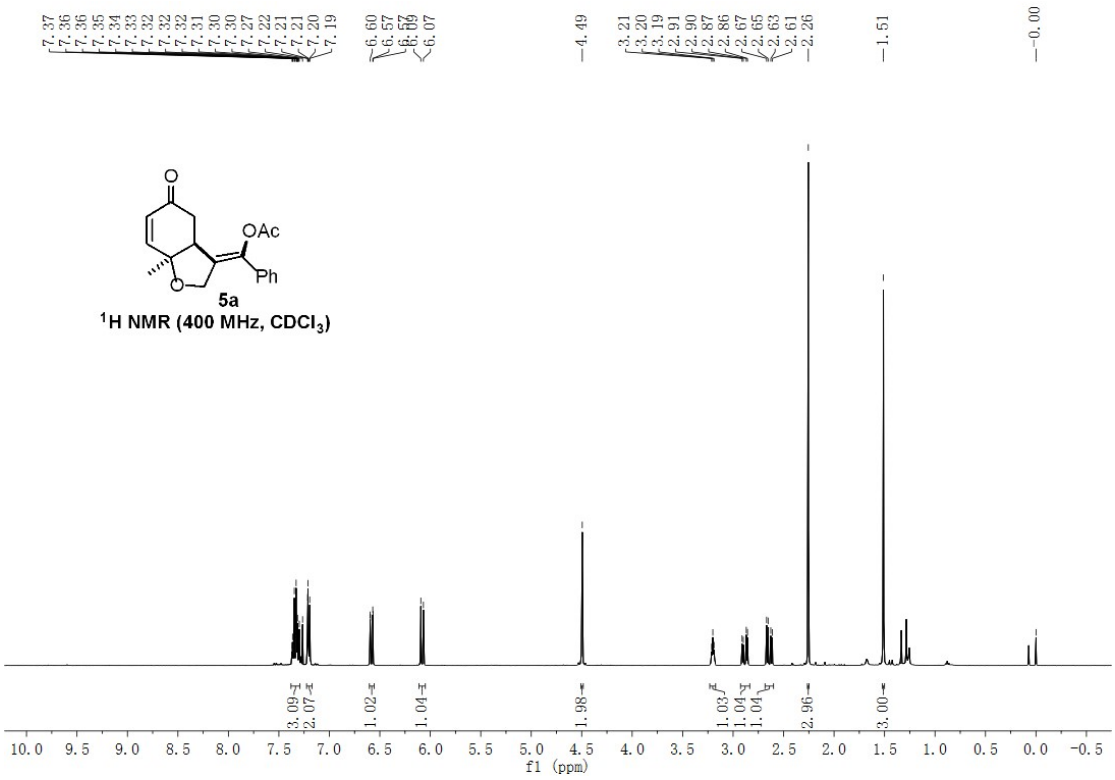

197.73
149.39 147.04 142.62 131.79 128.69 128.49 128.36 92.53 83.71 77.48 77.16 76.84 68.55 49.79 38.36 35.45 17.32 17.26
iPr
O
I
Ph
4j
13C NMR (100 MHz, CDCl3)
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)

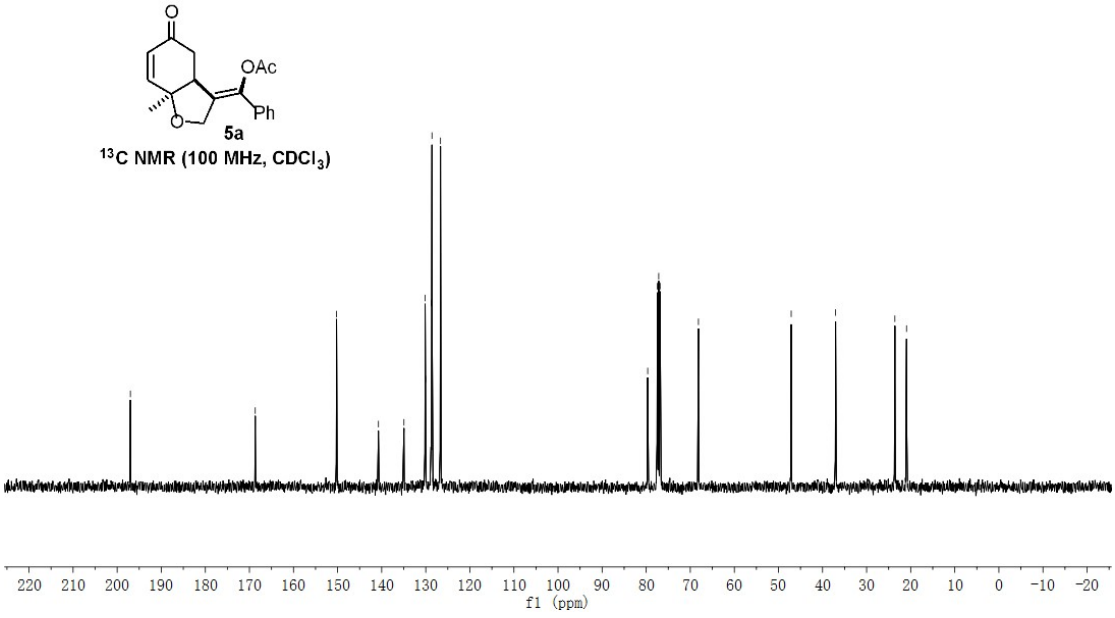

4k
^{1}H NMR (400 MHz, CDCl$_3$)
f1 (ppm)

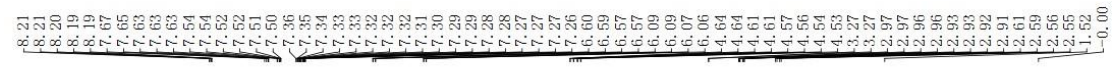

4k
^{13}C NMR (100 MHz, CDCl$_3$)
f1 (ppm)

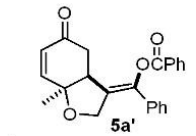

4l
4l'
4l mixed with 4l'
^{1}H NMR (400 MHz, $CDCl_3$)
f1 (ppm)


4l
4l'
^{13}C NMR (100 MHz, $CDCl_3$)
f1 (ppm)


OAc
Ph
5a
1H NMR (400 MHz, CDCl3)
f1 (ppm)

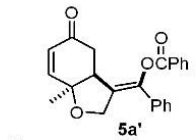

OAc
Ph
5a
13C NMR (100 MHz, CDCl3)
f1 (ppm)





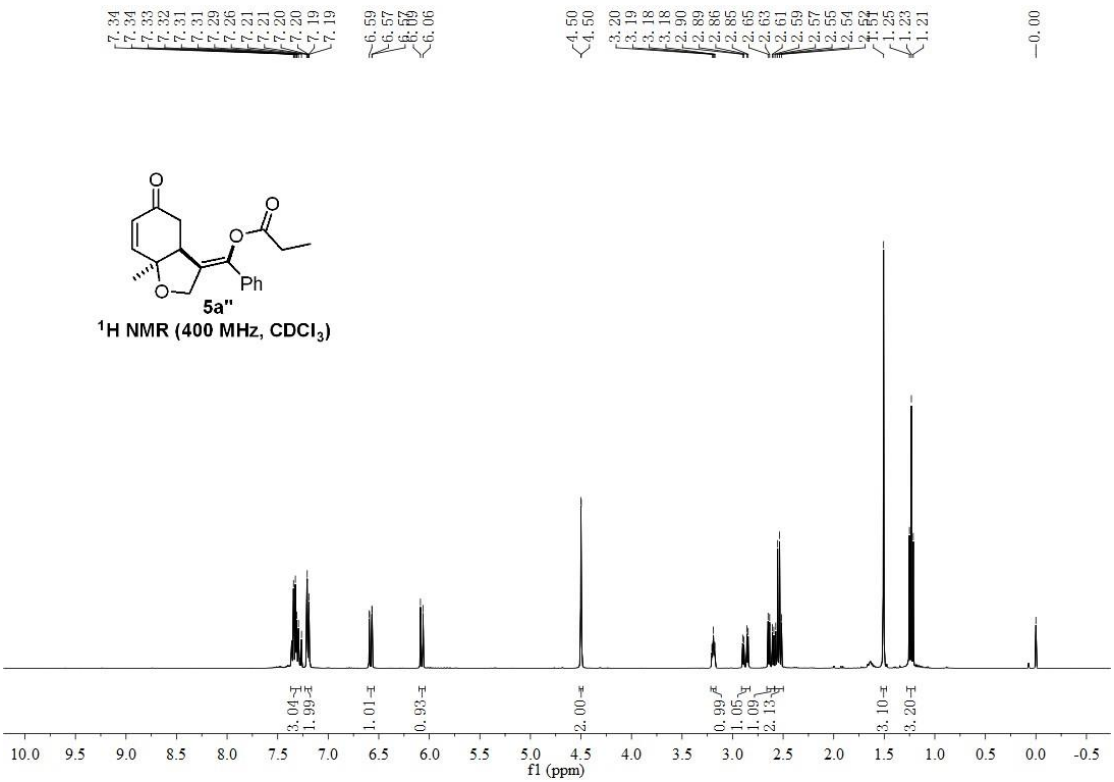
5a'

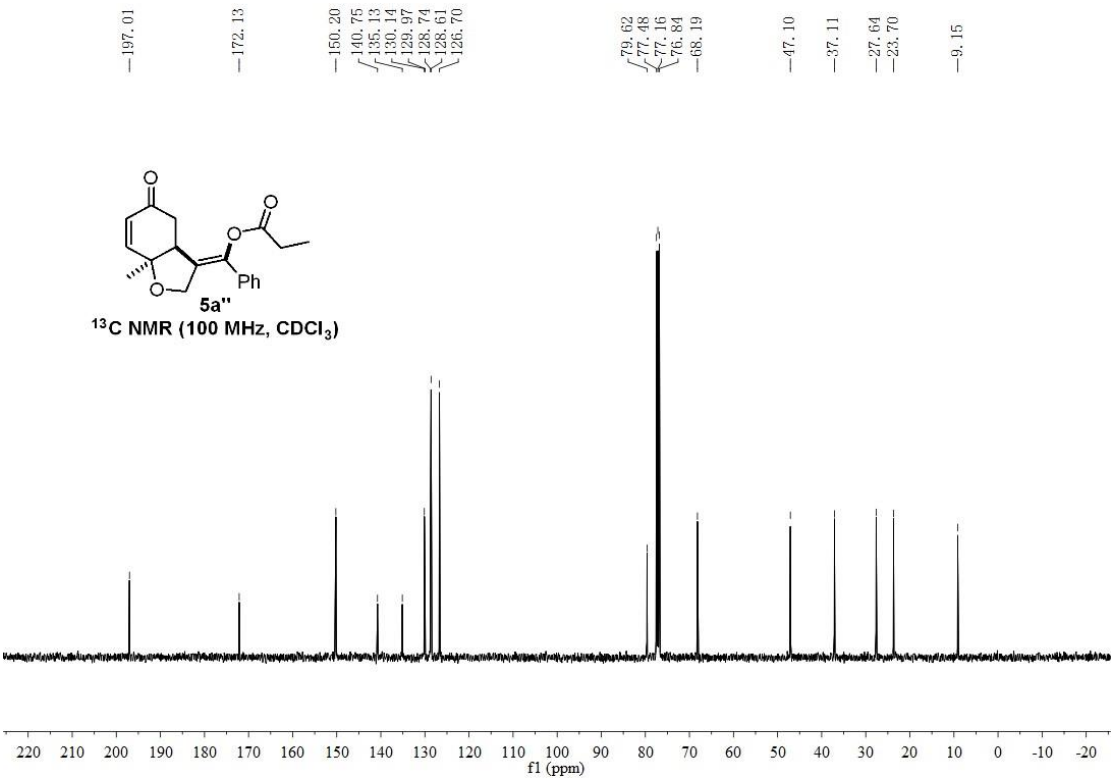
^{1}H NMR (400 MHz, $CDCl_3$)

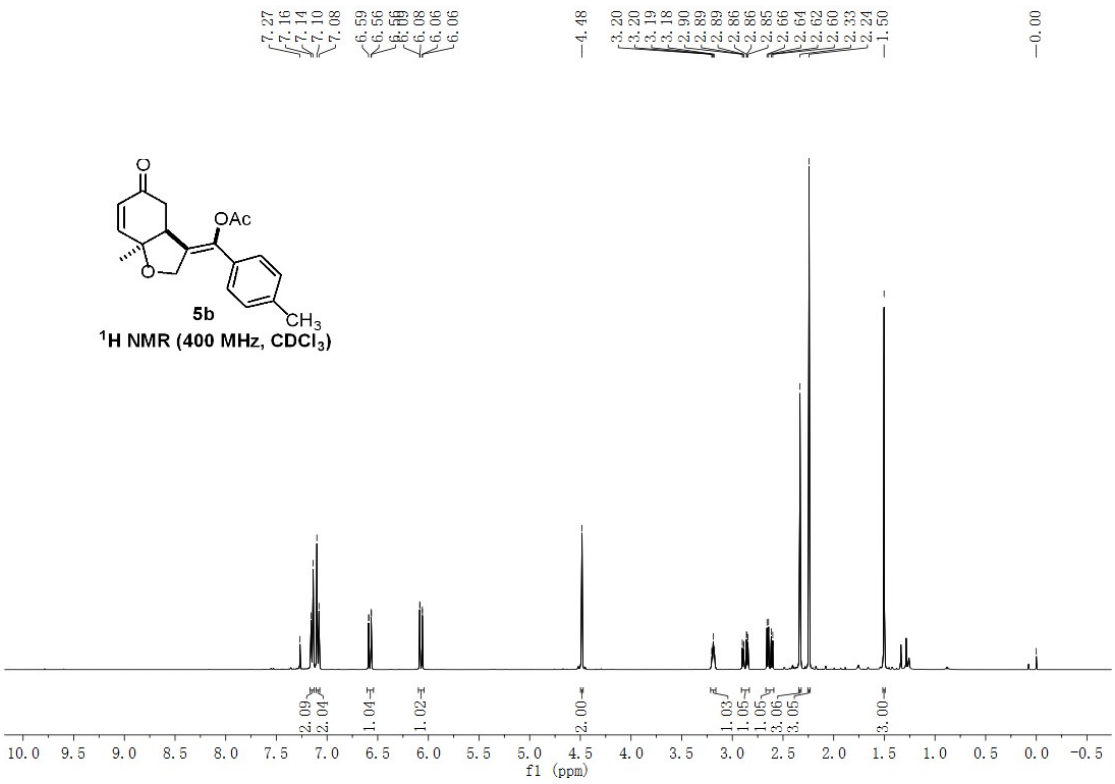


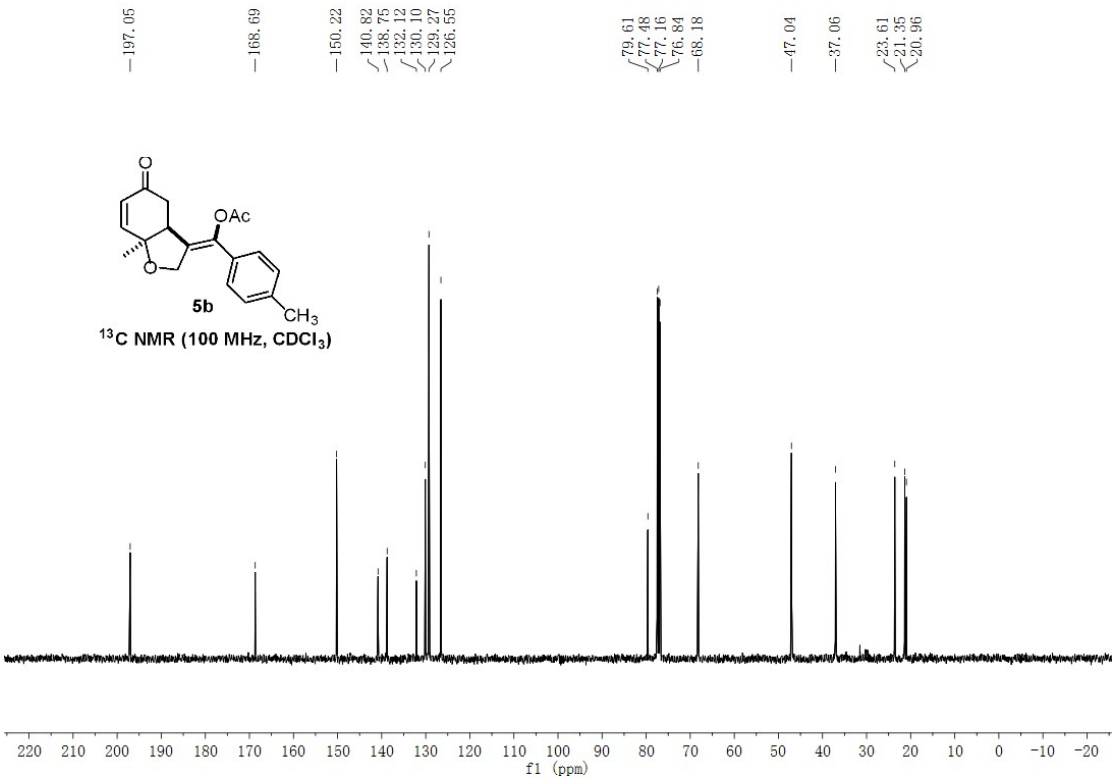
5a'

^{13}C NMR (100 MHz, $CDCl_3$)


7.34
7.34
7.33
7.32
7.31
7.31
7.29
7.26
7.21
7.21
7.20
7.20
7.19
7.19
6.59
6.57
6.57
6.09
6.06
4.50
4.50
3.20
3.19
3.18
3.18
2.90
2.89
2.86
2.85
2.65
2.63
2.61
2.59
2.57
2.55
2.54
1.51
1.25
1.23
1.21
0.00
O
O
O
Ph
5a''
1H NMR (400 MHz, CDCl3)
3.04
1.99
1.01
0.93
2.00
0.99
1.05
1.09
2.13
3.10
3.20
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


197.01
172.13
150.20
140.75
135.13
130.14
129.97
128.74
128.61
126.70
79.62
77.48
77.16
76.84
68.19
47.10
37.11
27.64
23.70
9.15
O
O
O
Ph
5a''
13C NMR (100 MHz, CDCl3)
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)


7.27
7.16
7.14
7.10
7.08
6.59
6.56
6.08
6.06
6.06
4.48
3.20
3.20
3.19
3.18
2.90
2.89
2.89
2.86
2.86
2.85
2.66
2.64
2.62
2.60
2.33
2.24
1.50
0.00
OAc
CH3
5b
1H NMR (400 MHz, CDCl3)
2.09
2.04
1.04
1.02
2.00
1.03
1.05
1.05
3.06
3.05
3.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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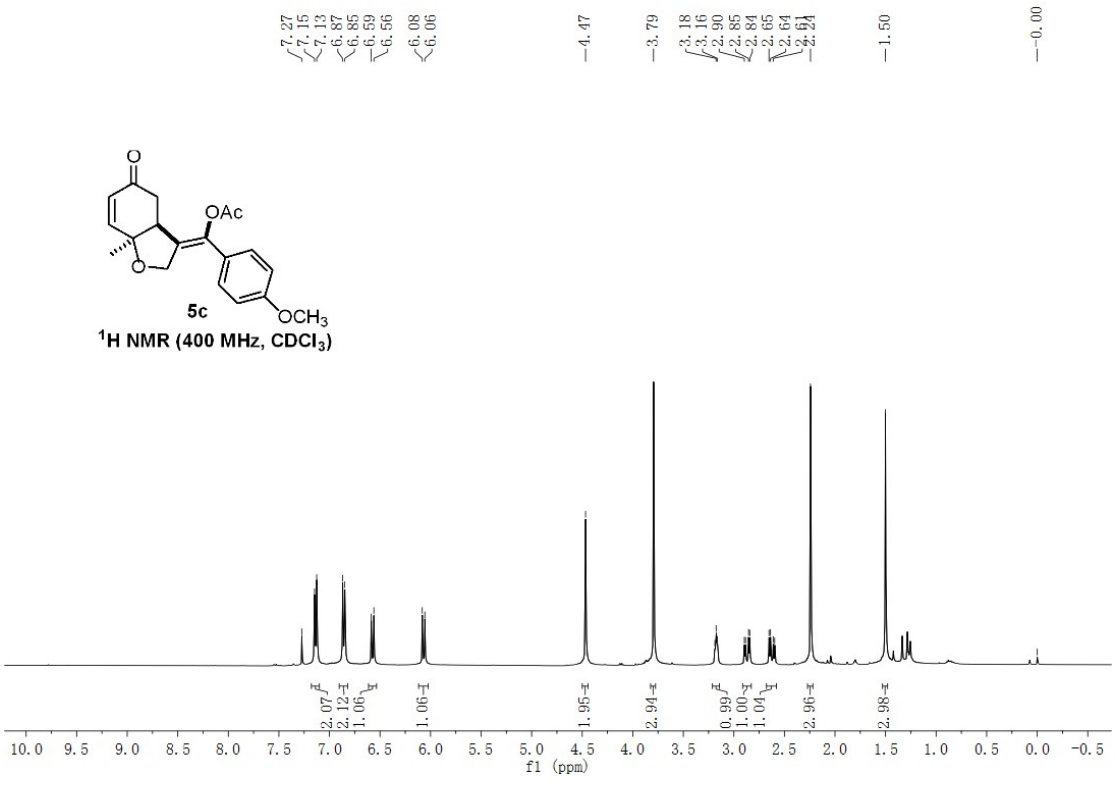
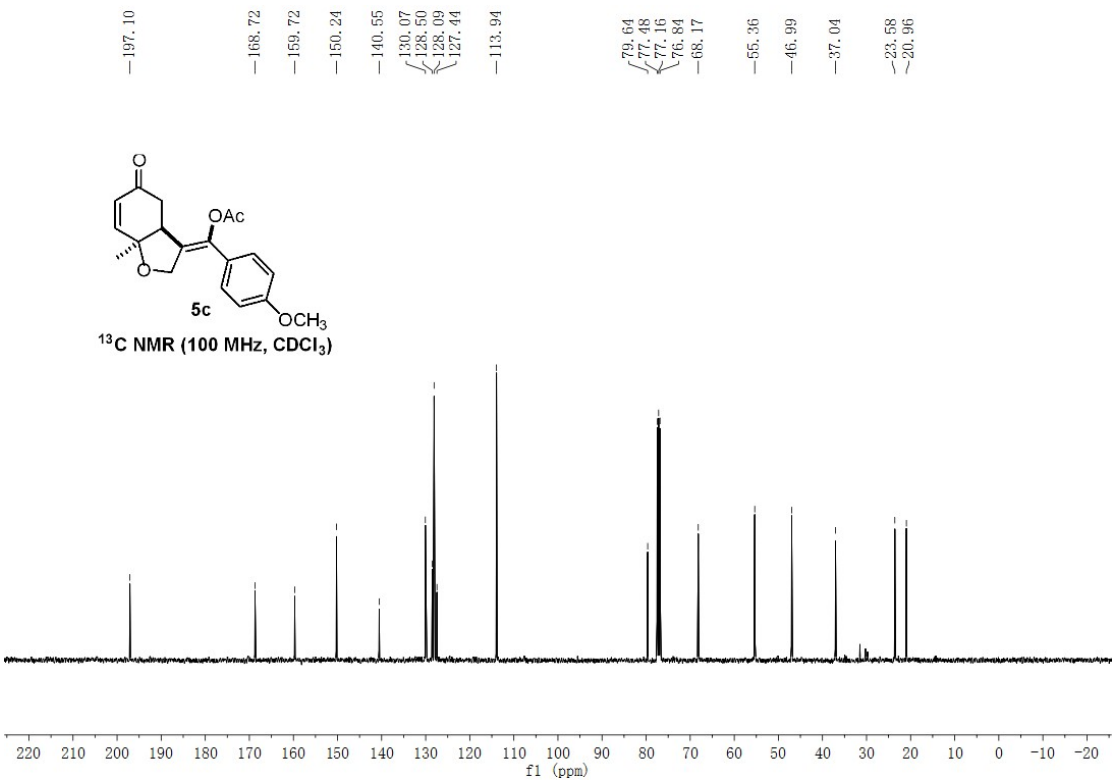
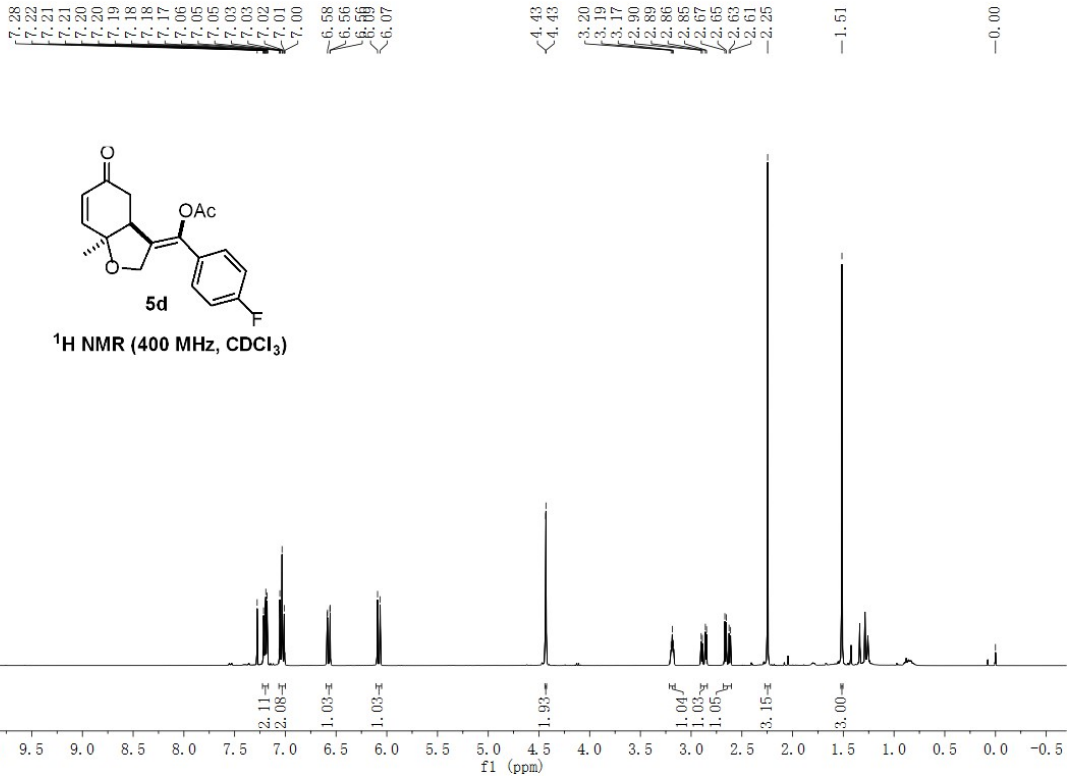
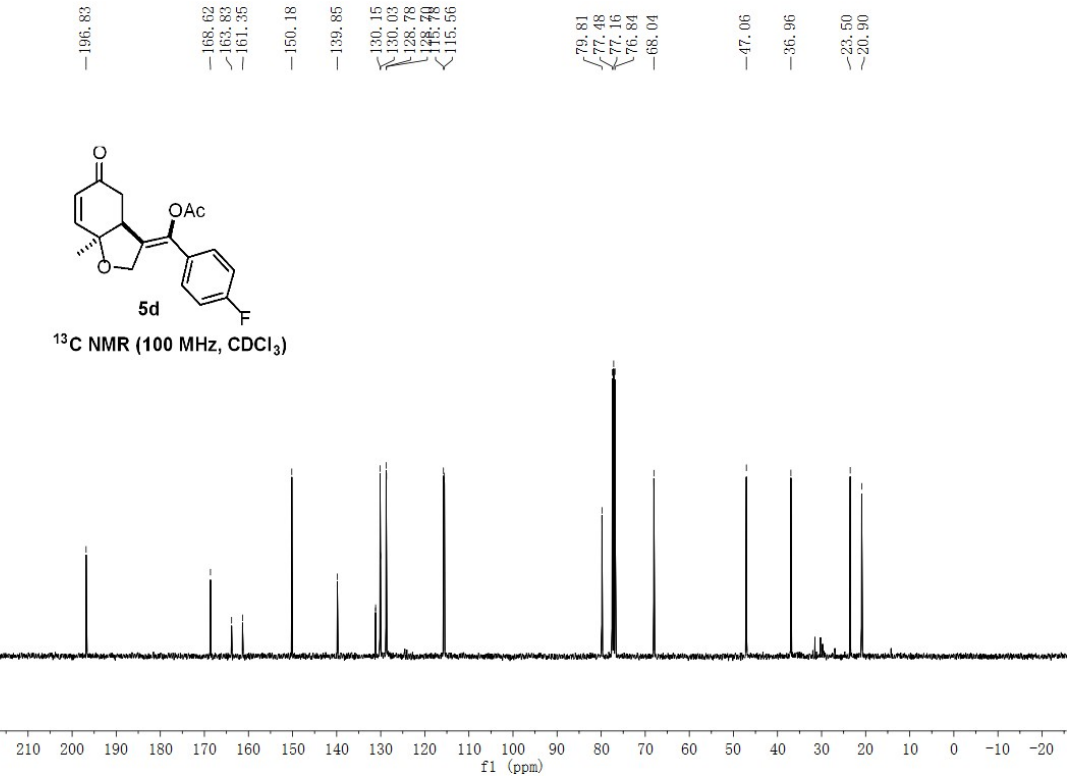
168.69
150.22
140.82
138.75
132.12
130.10
129.27
126.55
79.61
77.48
77.16
76.84
68.18
47.04
37.06
23.61
21.35
20.96
OAc
CH3
5b
13C NMR (100 MHz, CDCl3)
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)


7.27
7.15
7.13
6.87
6.85
6.59
6.56
6.08
6.06
4.47
3.79
3.18
3.16
2.90
2.85
2.84
2.65
2.64
1.50
0.00
OAc
OCH3
5c
1H NMR (400 MHz, CDCl3)
2.07
2.12
1.06
1.06
1.95
2.94
0.99
1.00
1.04
2.96
2.98
f1 (ppm)

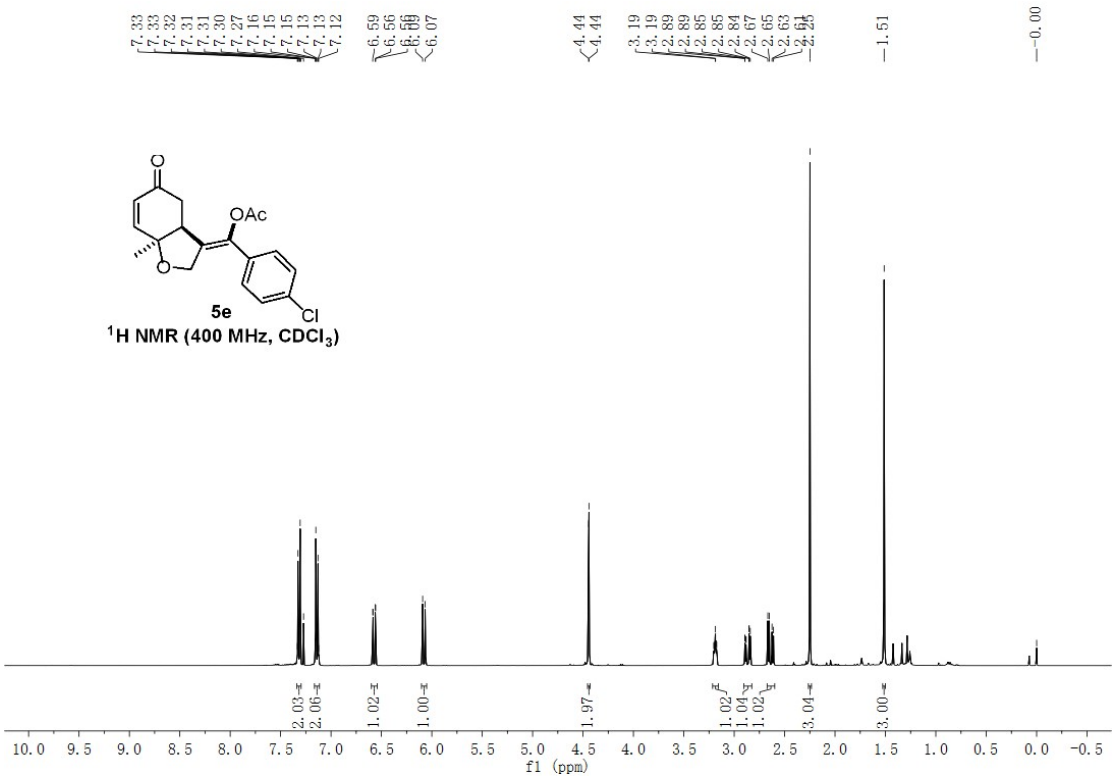

197.10
168.72
159.72
150.24
140.55
130.07
128.50
128.09
127.44
113.94
79.64
77.48
77.16
76.84
68.17
55.36
46.99
37.04
23.58
20.96
OAc
OCH3
5c
13C NMR (100 MHz, CDCl3)
f1 (ppm)



^{1}H NMR (400 MHz, $CDCl_3$)

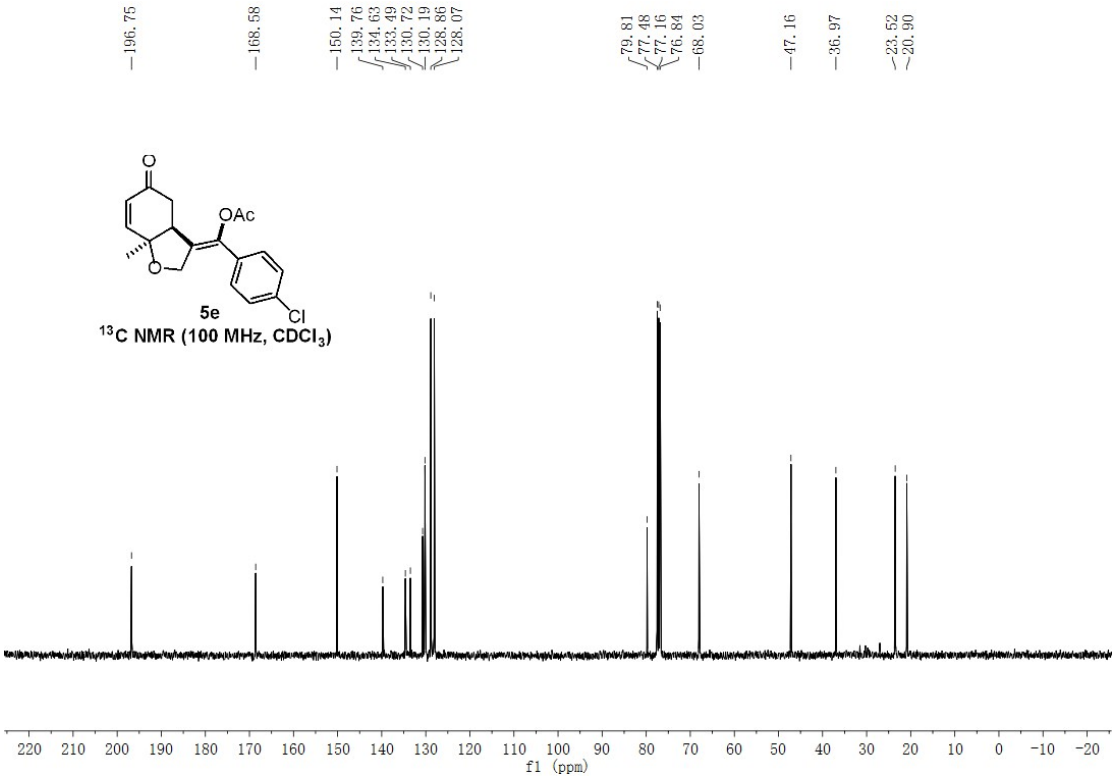


^{13}C NMR (100 MHz, $CDCl_3$)



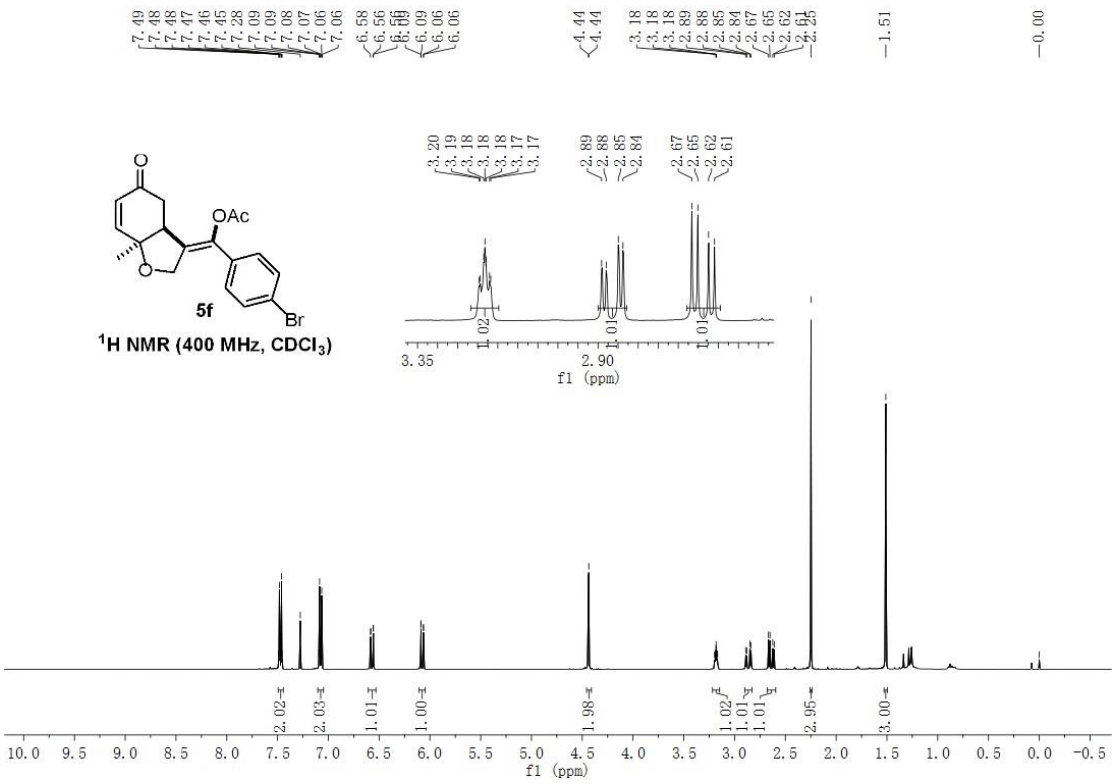
5e

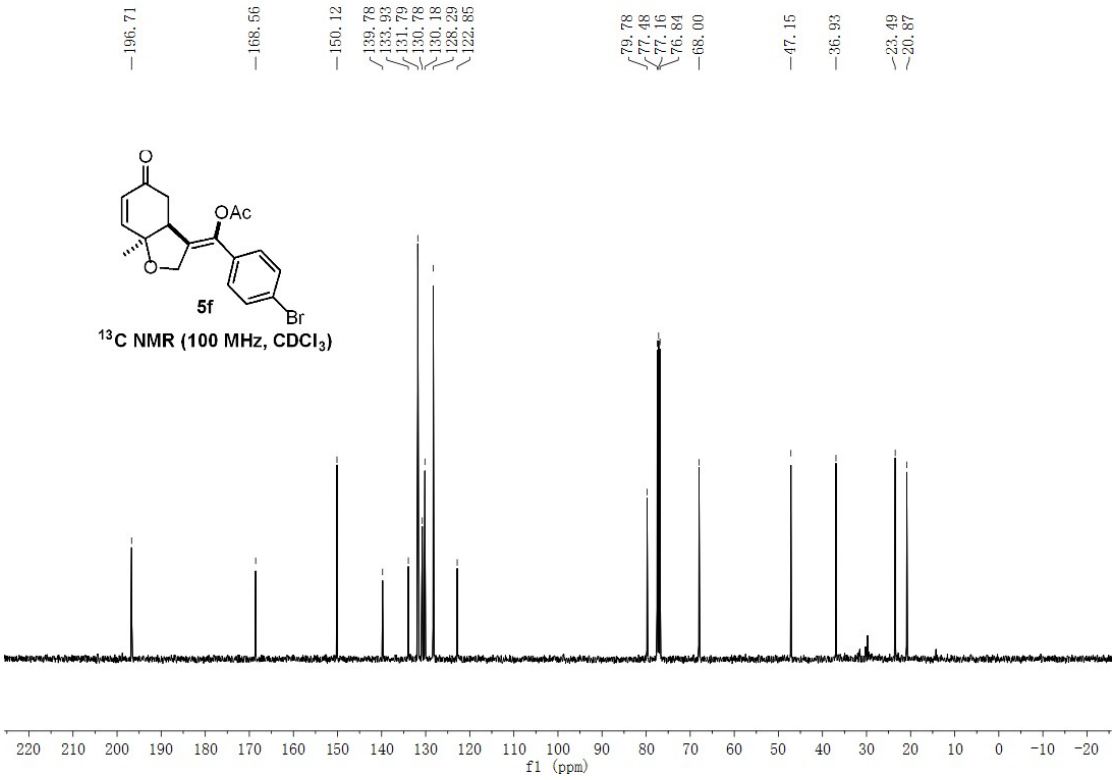
^{1}H NMR (400 MHz, $CDCl_3$)

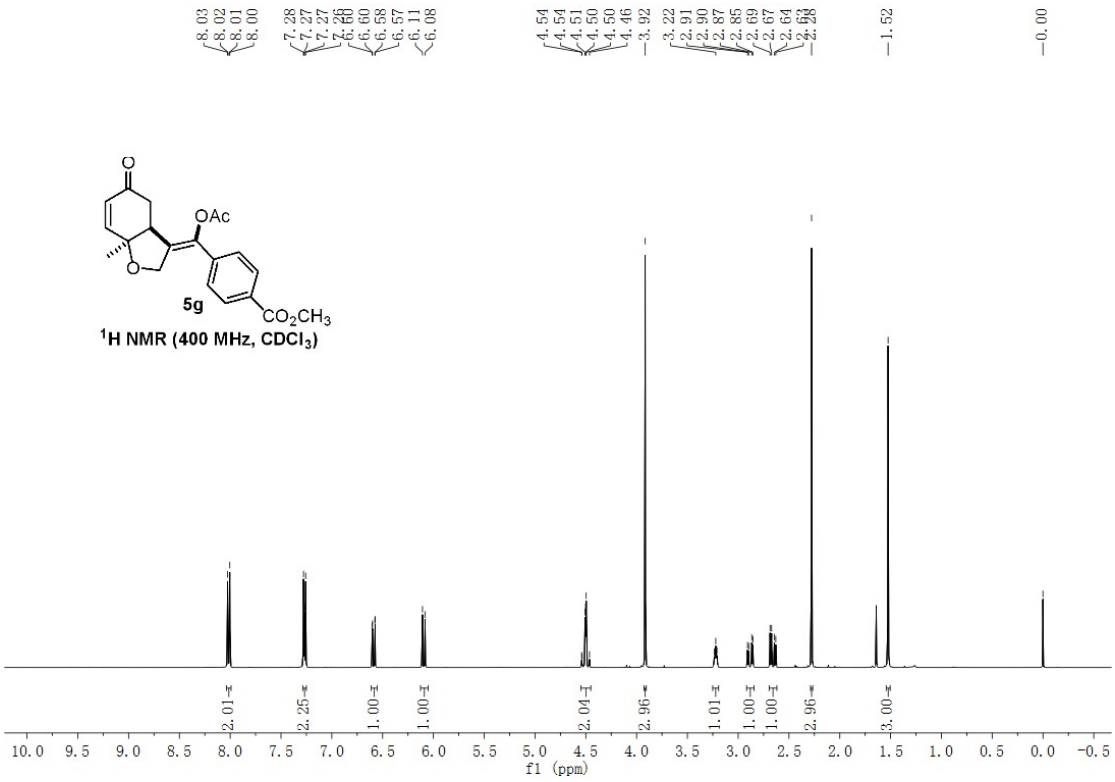


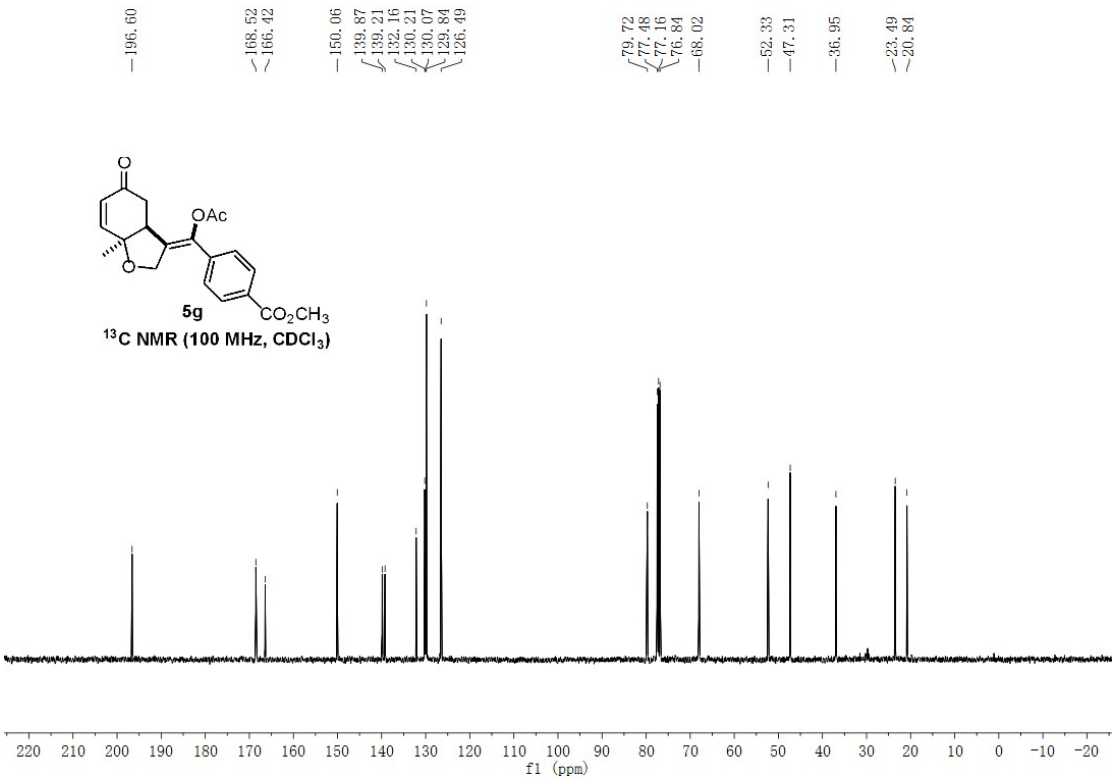
5e

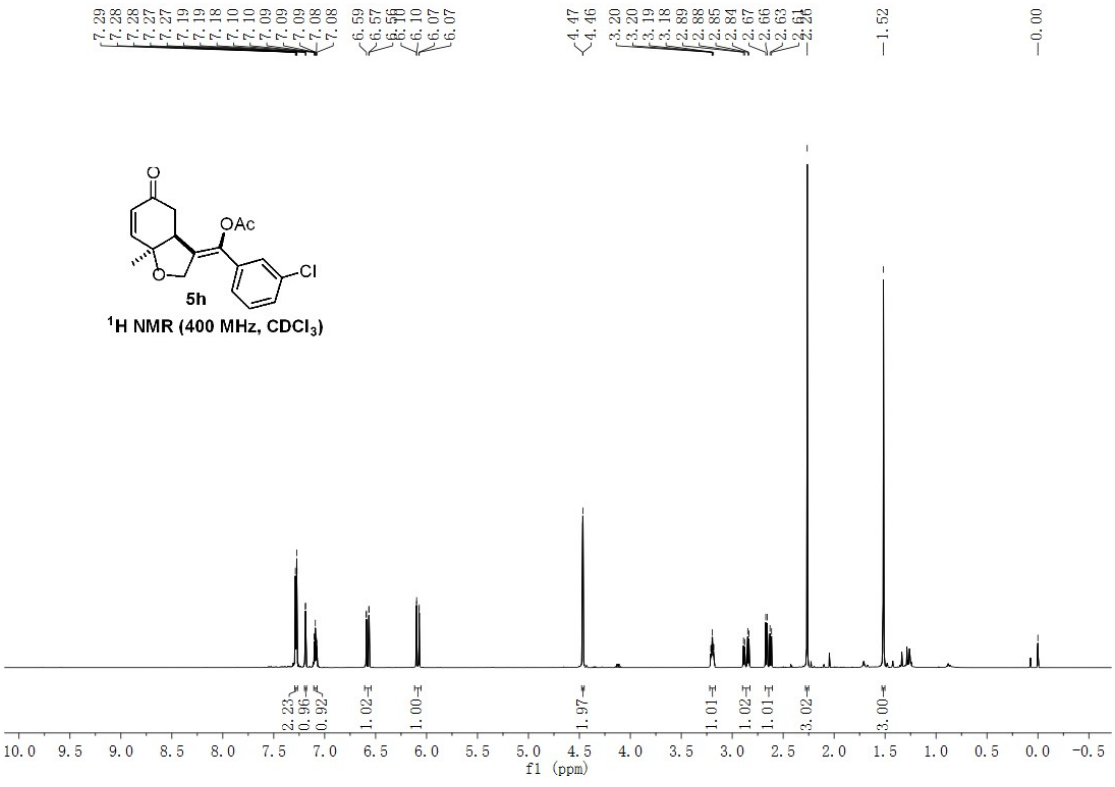
^{13}C NMR (100 MHz, $CDCl_3$)

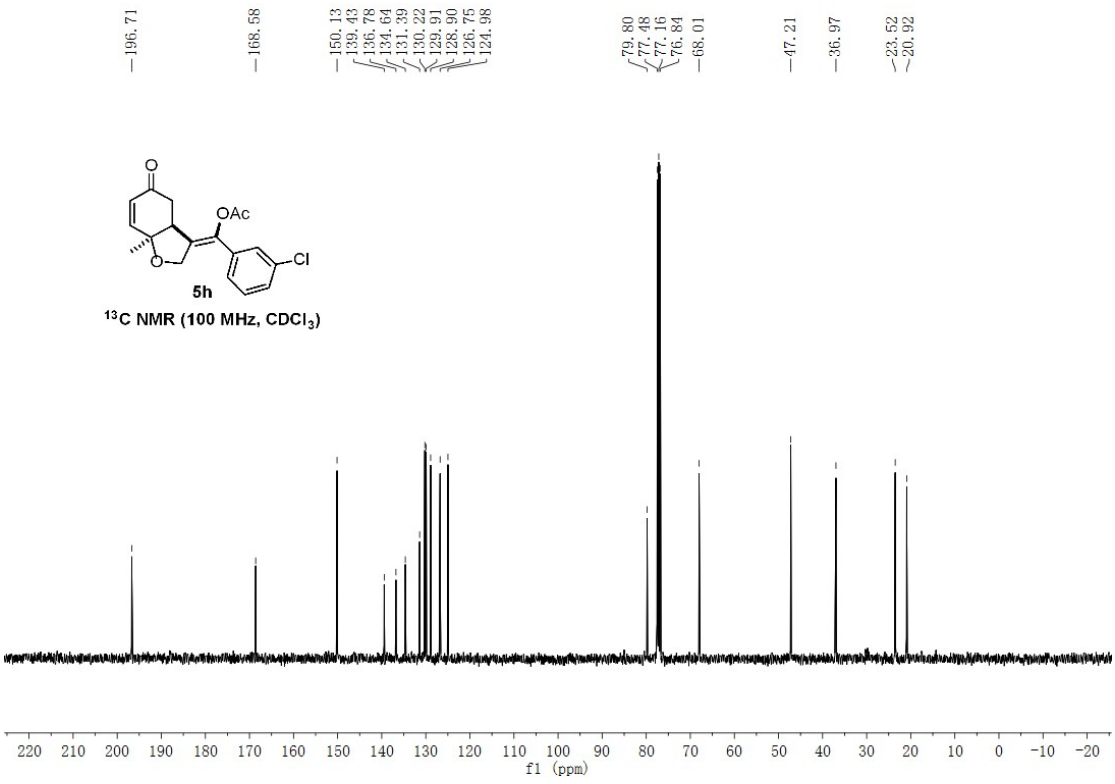

5f
^{1}H NMR (400 MHz, CDCl$_3$)
f1 (ppm)


5f
^{13}C NMR (100 MHz, CDCl$_3$)
f1 (ppm)


8.03
8.02
8.01
8.00
7.28
7.27
7.27
6.60
6.58
6.57
6.11
6.08
4.54
4.54
4.51
4.50
4.50
4.46
3.92
3.22
2.91
2.90
2.87
2.85
2.69
2.67
2.64
1.52
0.00
OAc
5g
CO2CH3
1H NMR (400 MHz, CDCl3)
2.01
2.25
1.00
1.00
2.04
2.96
1.01
1.00
1.00
2.96
3.00
f1 (ppm)


196.60
168.52
166.42
150.06
139.87
139.21
132.16
130.21
130.07
129.84
126.49
79.72
77.48
77.16
76.84
68.02
52.33
47.31
36.95
23.49
20.84
OAc
5g
CO2CH3
13C NMR (100 MHz, CDCl3)
f1 (ppm)


7.29
7.28
7.28
7.27
7.27
7.19
7.19
7.18
7.10
7.10
7.09
7.09
7.09
7.08
7.08
6.59
6.57
6.56
6.10
6.07
6.07
4.47
4.46
3.20
3.20
3.19
3.18
2.89
2.88
2.85
2.84
2.67
2.66
2.63
2.61
1.52
0.00
O
OAc
Cl
5h
1H NMR (400 MHz, CDCl3)
2.23
0.96
0.92
1.02
1.00
1.97
1.01
1.02
1.01
3.02
3.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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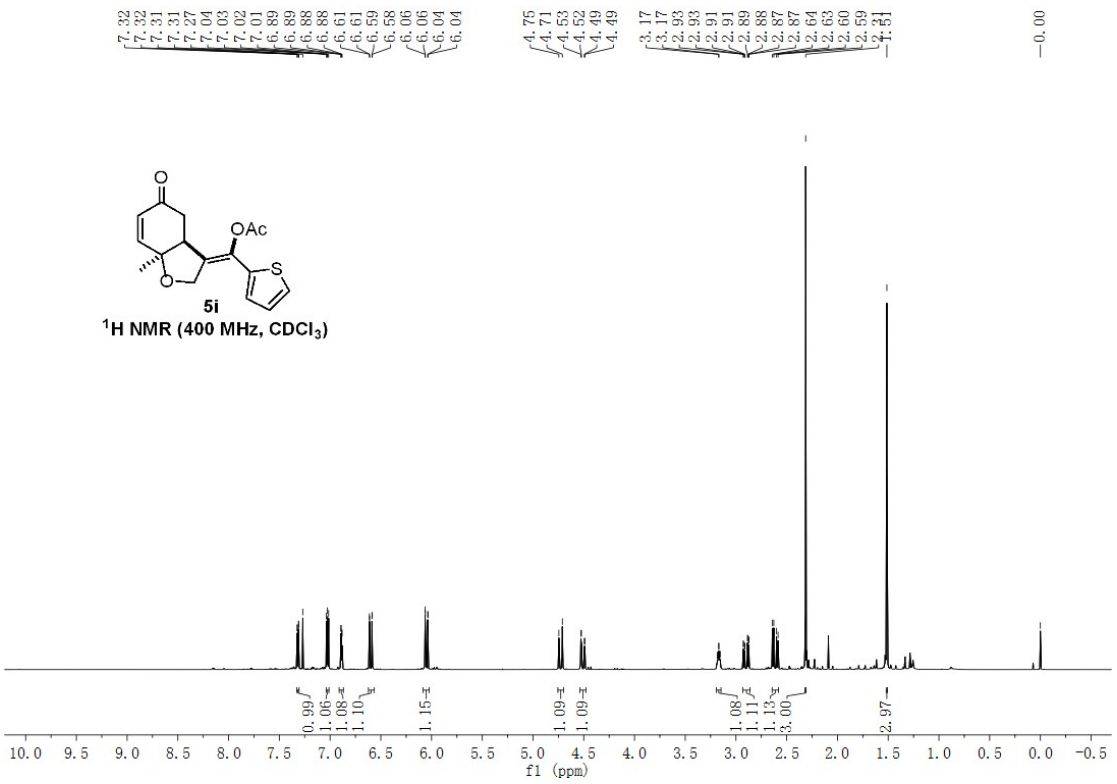
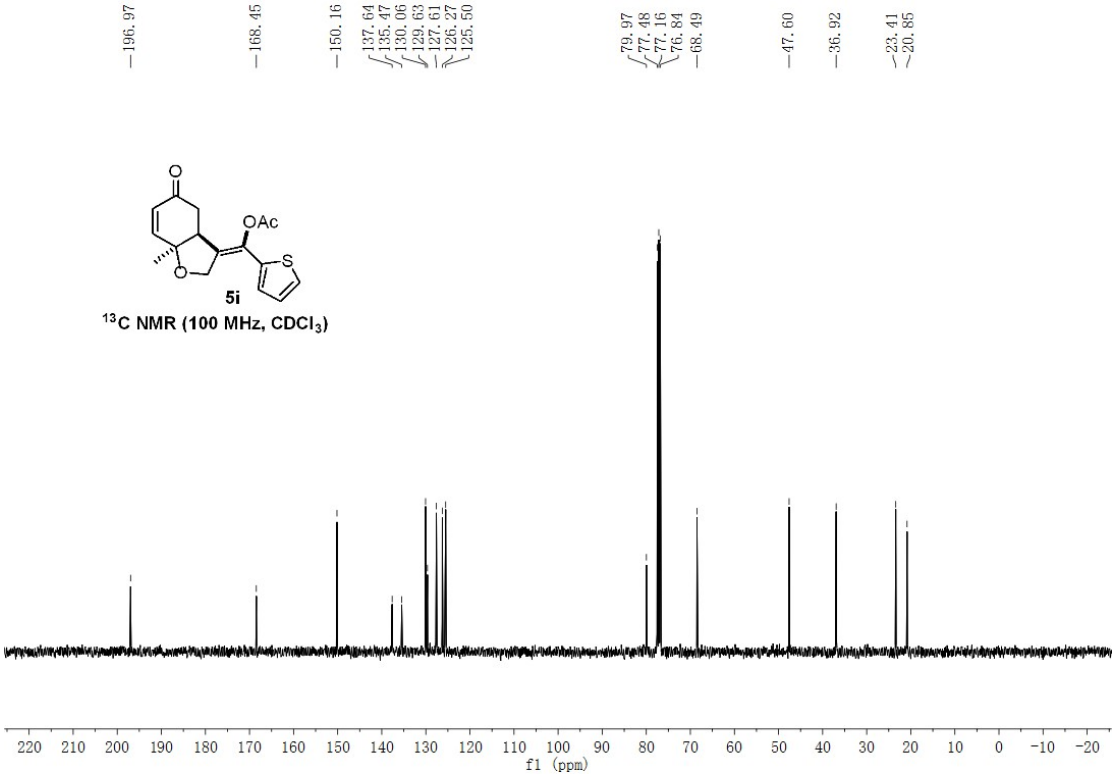
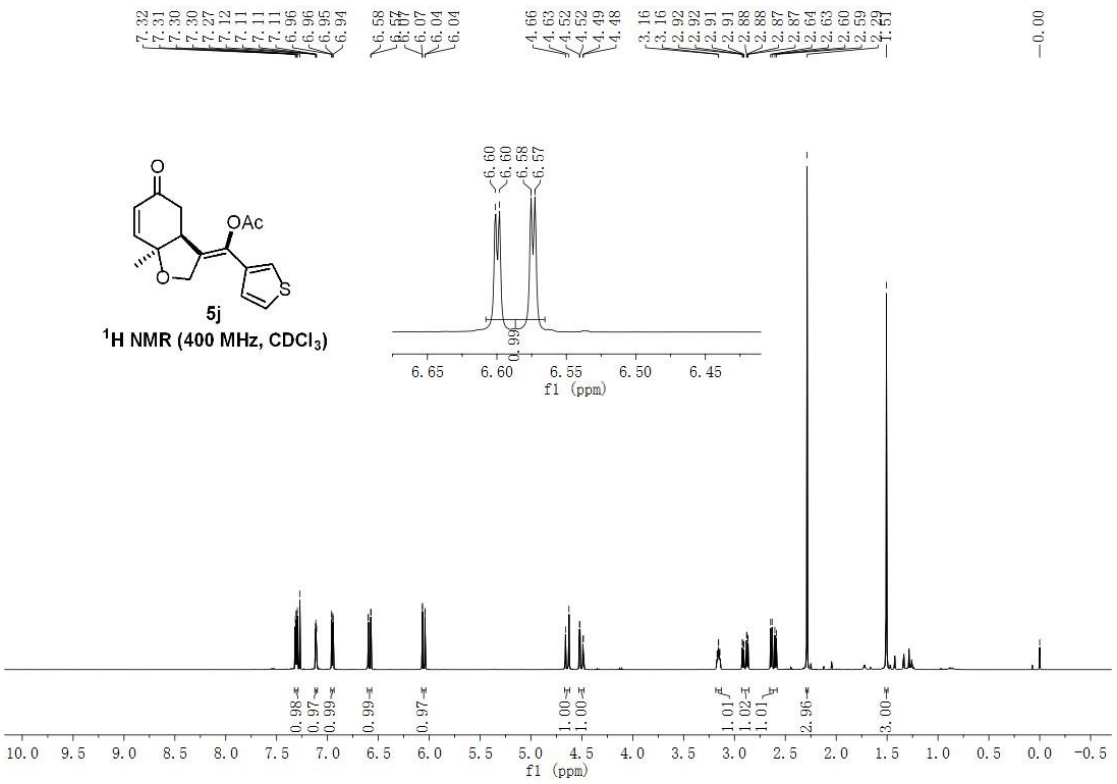
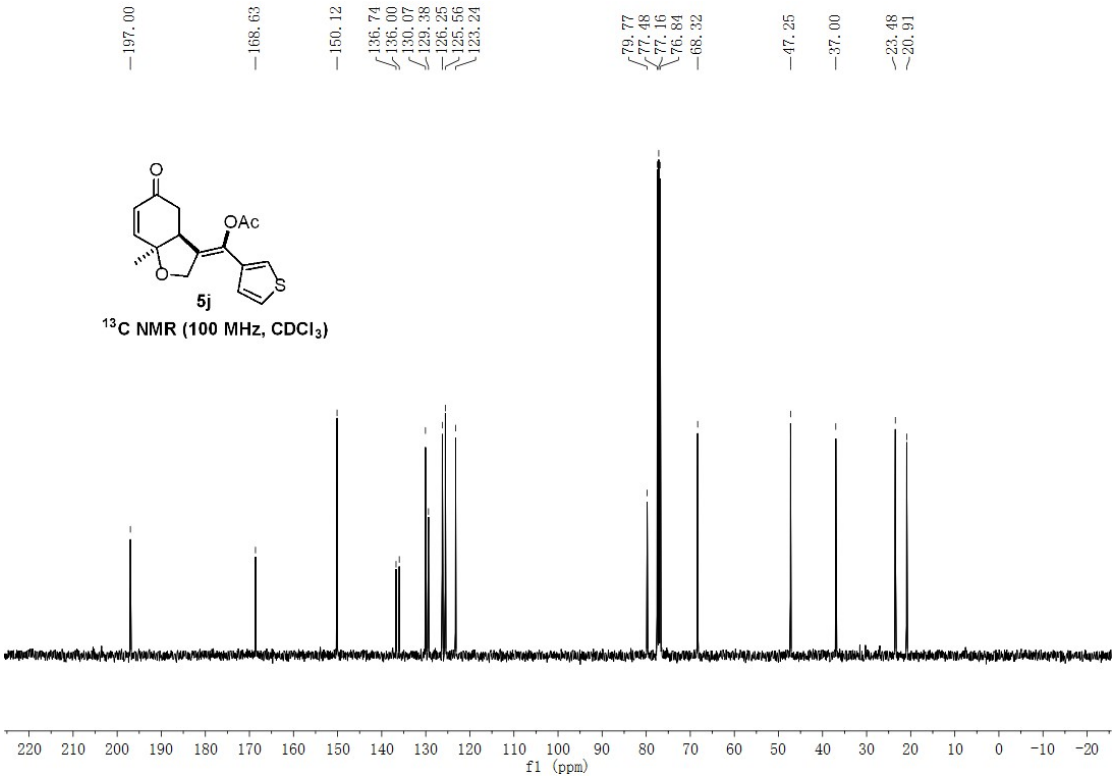
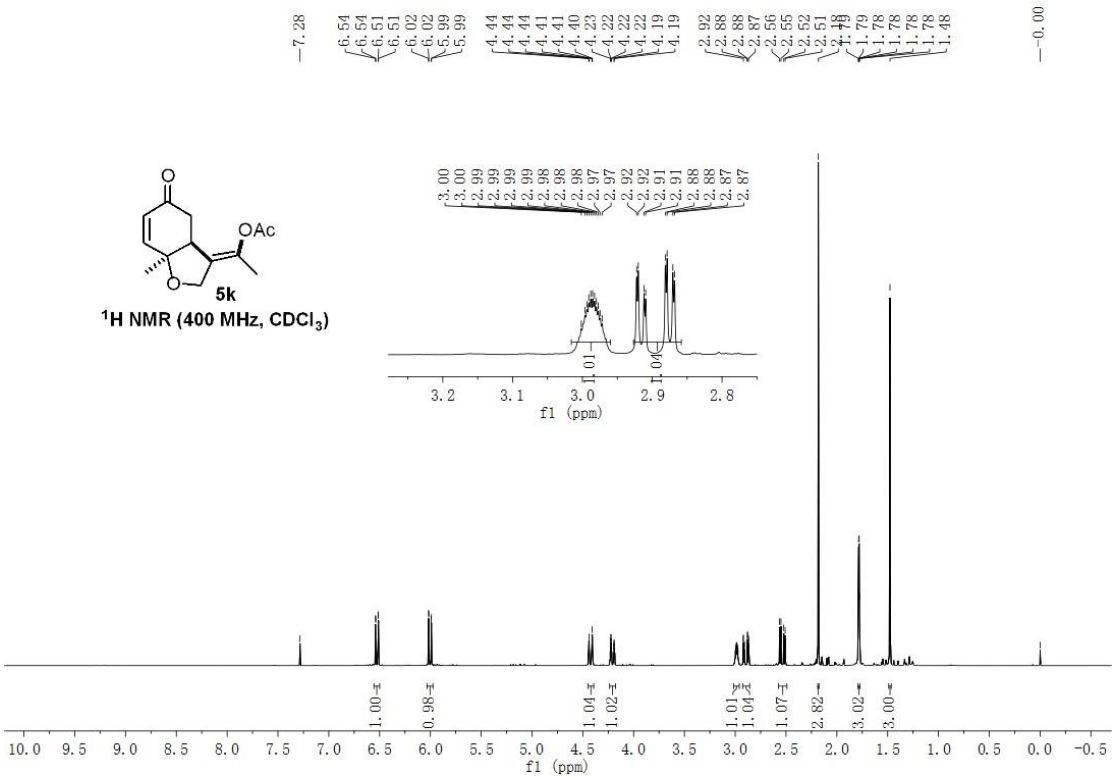
168.58
150.13
139.43
136.78
134.64
131.39
130.22
129.91
128.90
126.75
124.98
79.80
77.48
77.16
76.84
68.01
47.21
36.97
23.52
20.92
O
OAc
Cl
5h
13C NMR (100 MHz, CDCl3)
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)

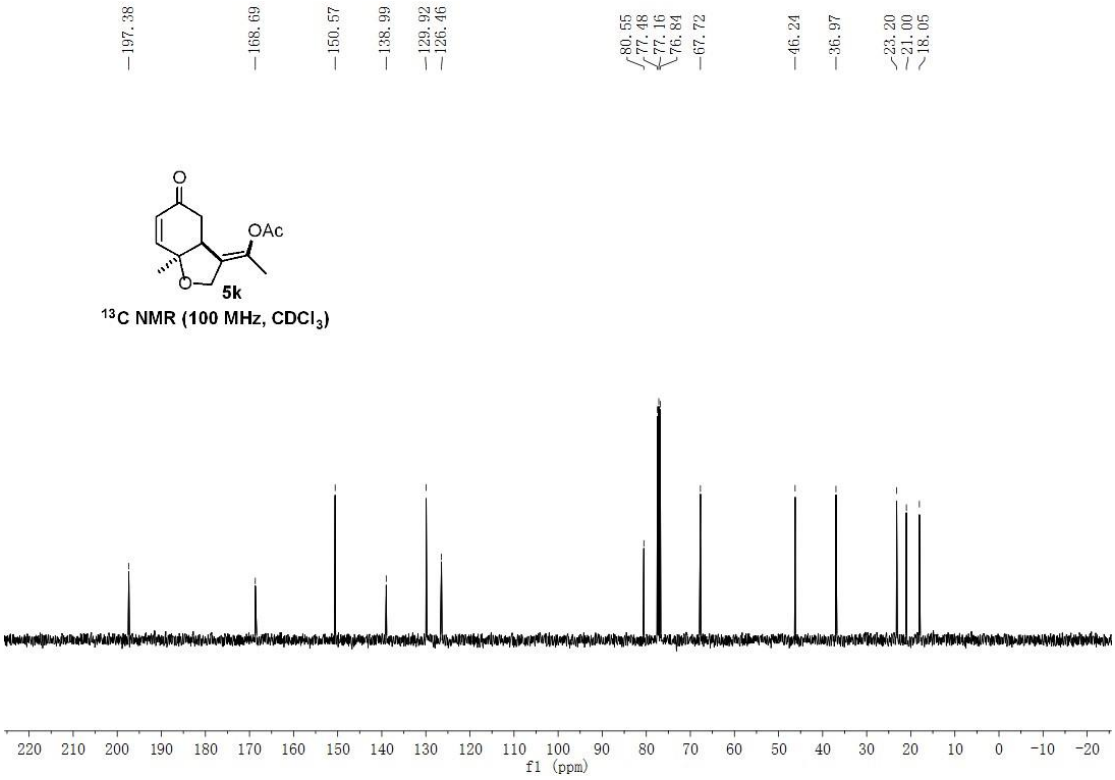

OAc
S
5i
^{1}H NMR (400 MHz, CDCl$_3$)
f1 (ppm)


OAc
S
5i
^{13}C NMR (100 MHz, CDCl$_3$)
f1 (ppm)


OAc
S
5j
^{1}H NMR (400 MHz, CDCl$_3$)
f1 (ppm)


OAc
S
5j
^{13}C NMR (100 MHz, CDCl$_3$)
f1 (ppm)


7.28
6.54
6.54
6.51
6.51
6.02
6.02
5.99
5.99
4.44
4.44
4.44
4.41
4.41
4.40
4.23
4.22
4.22
4.22
4.19
4.19
2.92
2.88
2.88
2.87
2.56
2.55
2.52
2.51
1.79
1.79
1.78
1.78
1.78
1.78
1.48
0.00
OAc
5k
1H NMR (400 MHz, CDCl3)
3.00
3.00
2.99
2.99
2.99
2.99
2.98
2.98
2.98
2.97
2.97
2.92
2.92
2.91
2.91
2.88
2.88
2.87
2.87
1.01
1.04
3.2
3.1
3.0
2.9
2.8
f1 (ppm)
1.00
0.98
1.04
1.02
1.01
1.04
1.07
2.82
3.02
3.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)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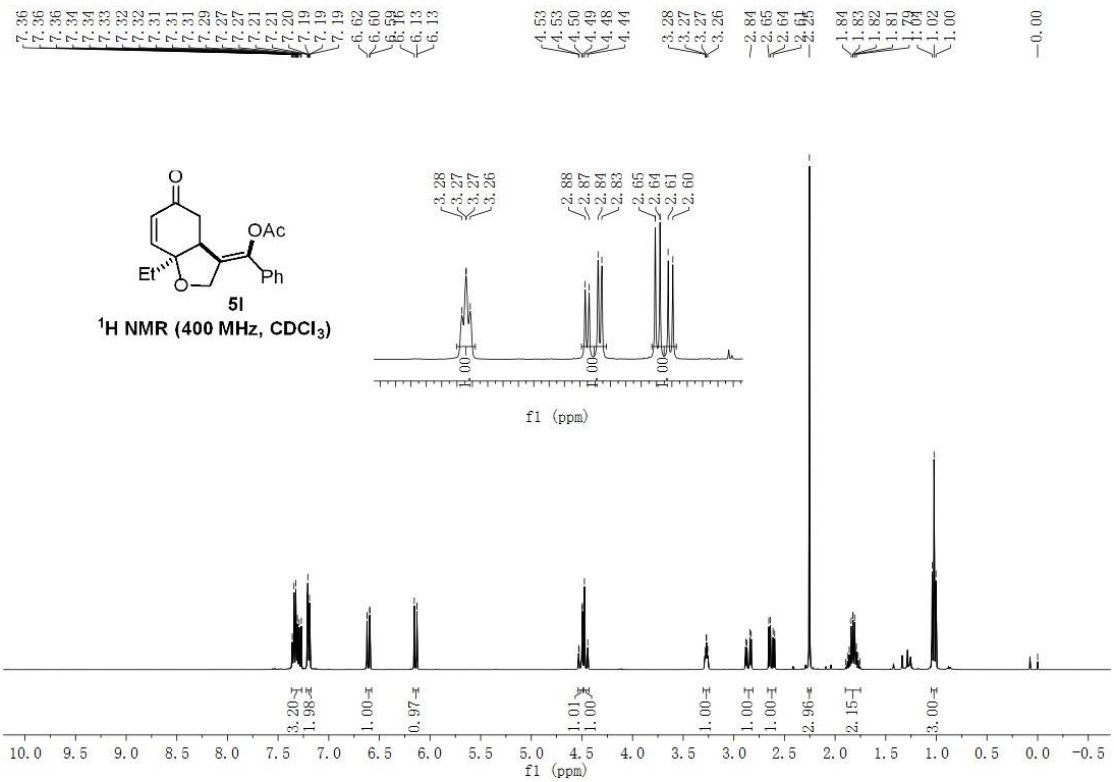
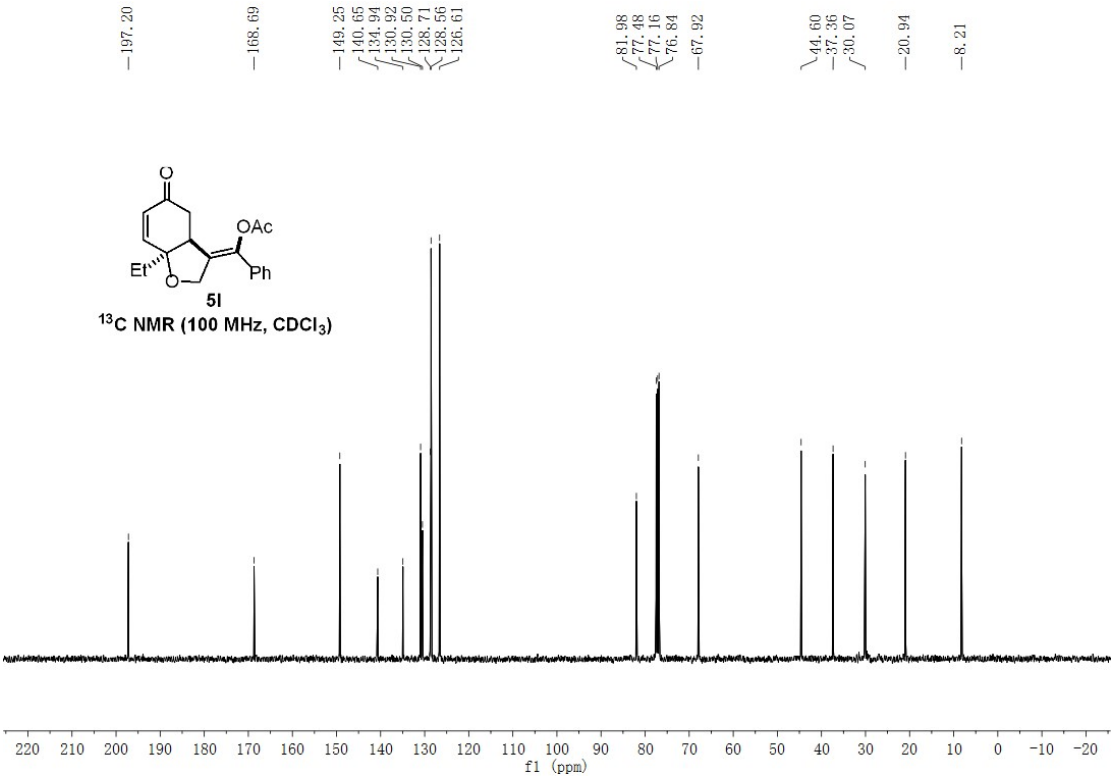
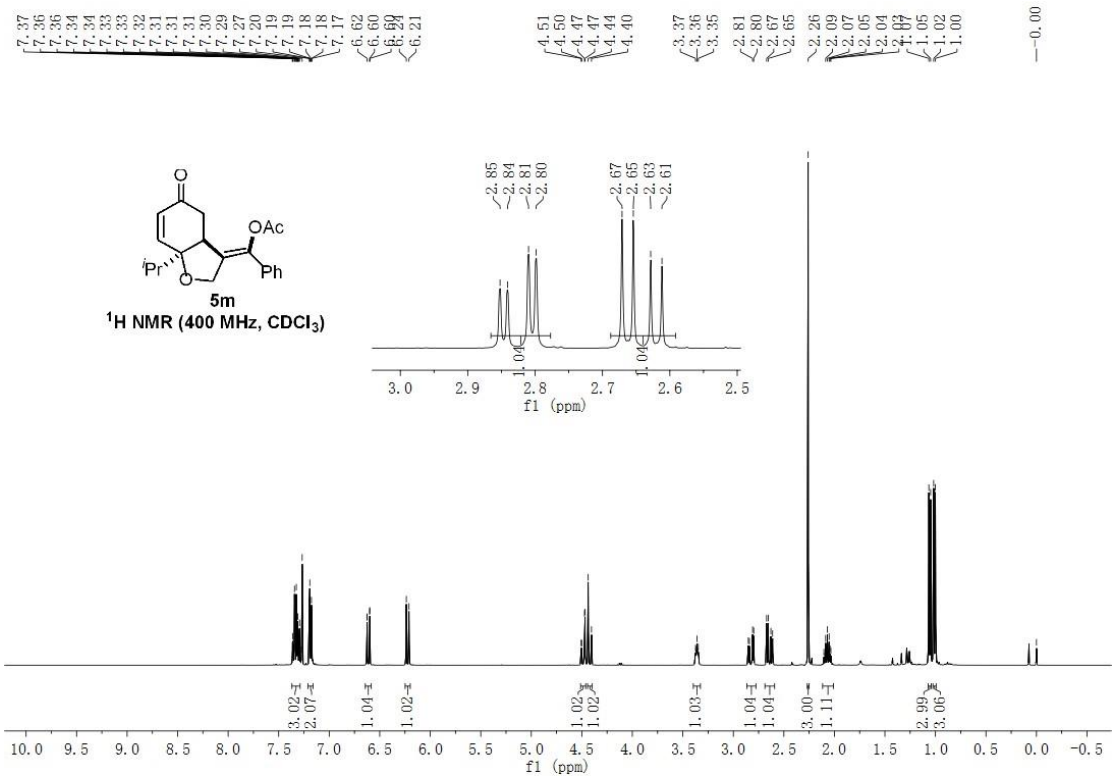
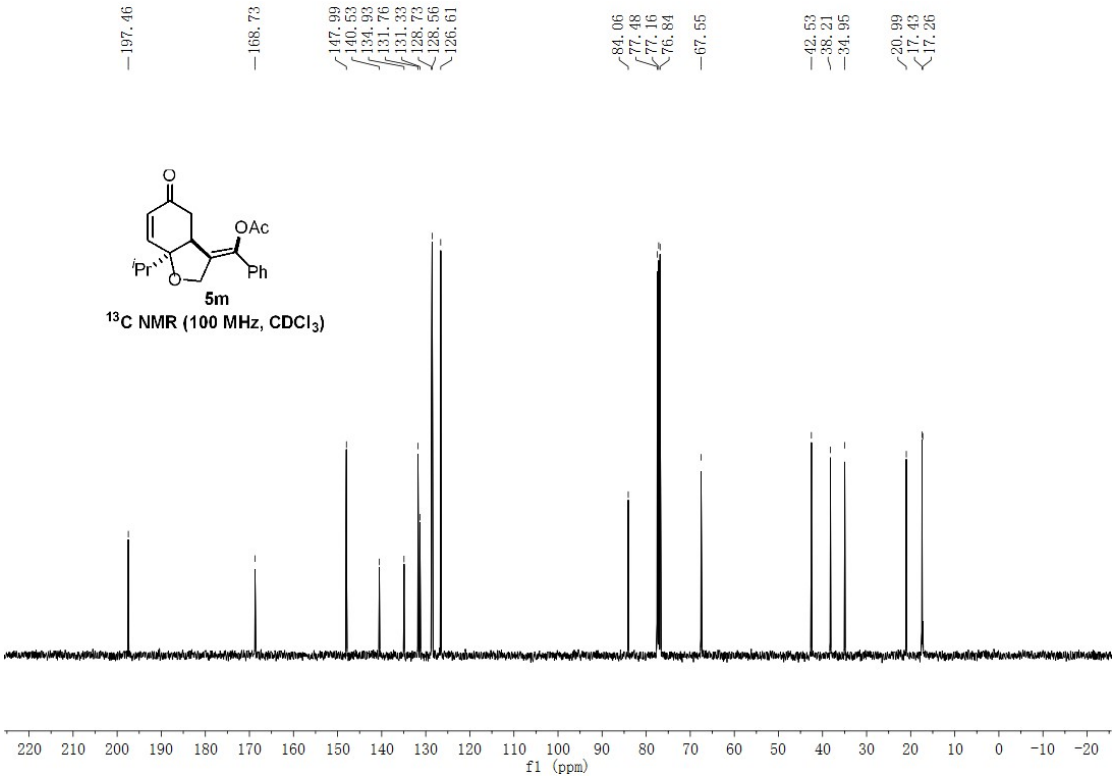
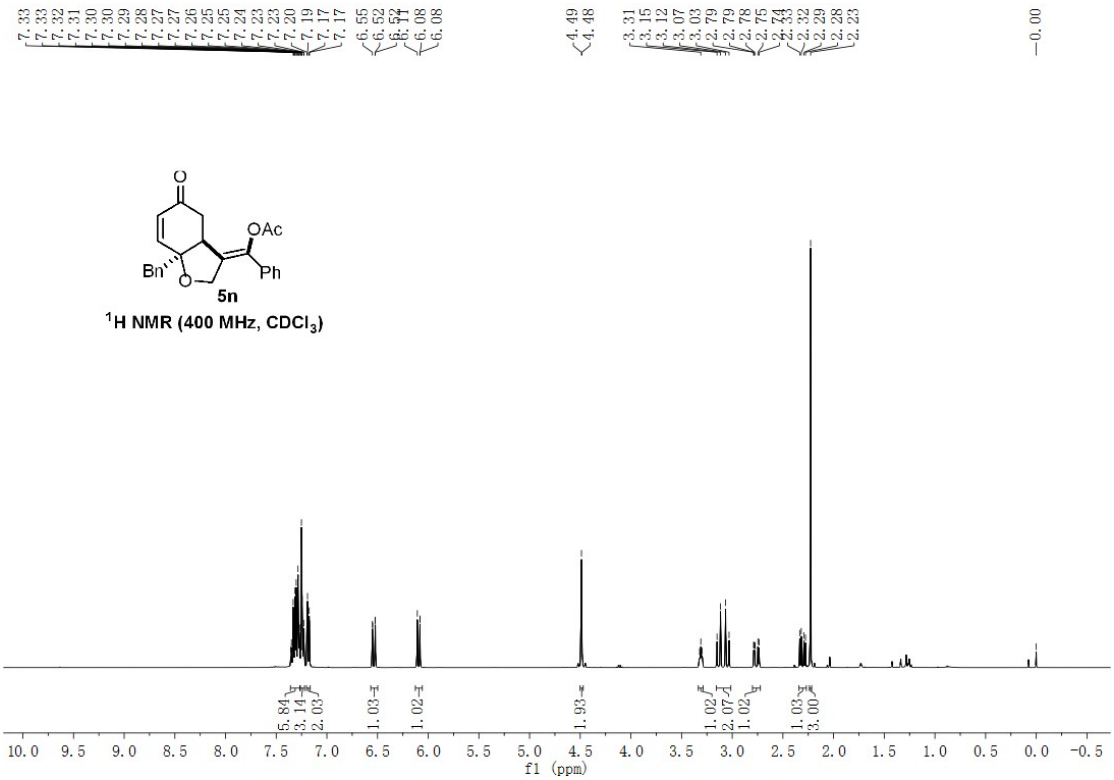
168.69
150.57
138.99
129.92
126.46
80.55
77.48
77.16
76.84
67.72
46.24
36.97
23.20
21.00
18.05
OAc
5k
13C NMR (100 MHz, CDCl3)
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
f1 (ppm)


OAc
Et
Ph
5l
^{1}H NMR (400 MHz, CDCl$_3$)
f1 (ppm)


OAc
Et
Ph
5l
^{13}C NMR (100 MHz, CDCl$_3$)
f1 (ppm)

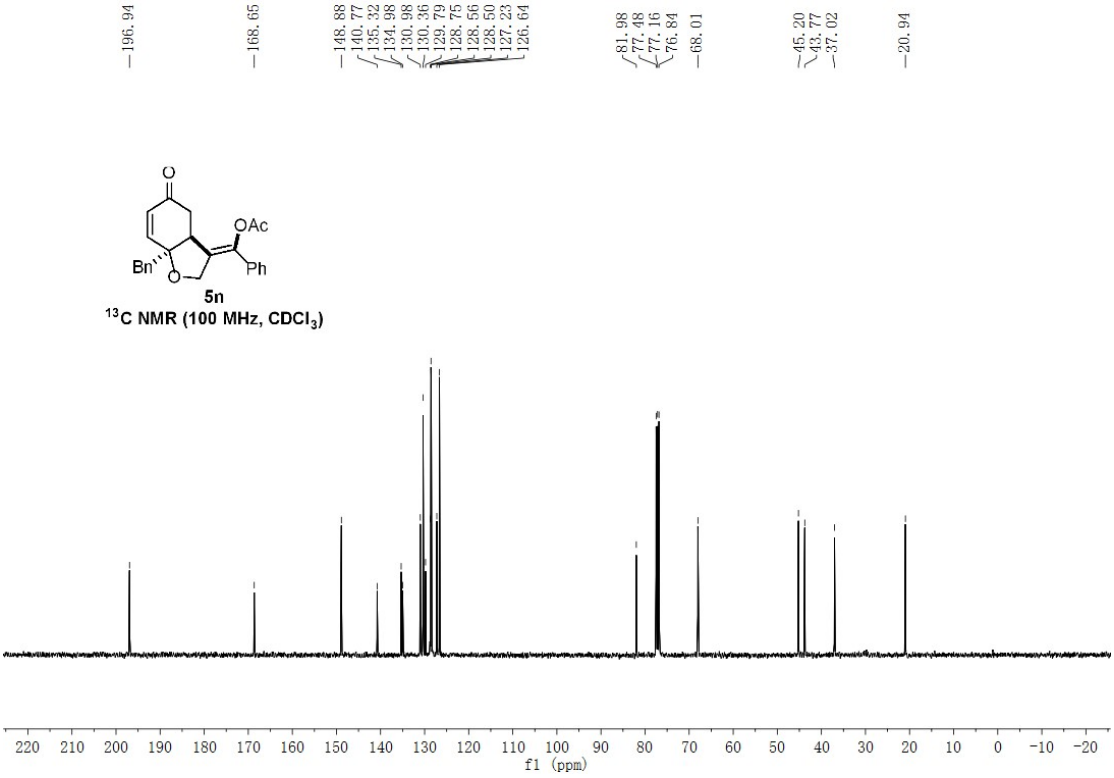

5m
^{1}H NMR (400 MHz, CDCl$_3$)
f1 (ppm)


5m
^{13}C NMR (100 MHz, CDCl$_3$)
f1 (ppm)



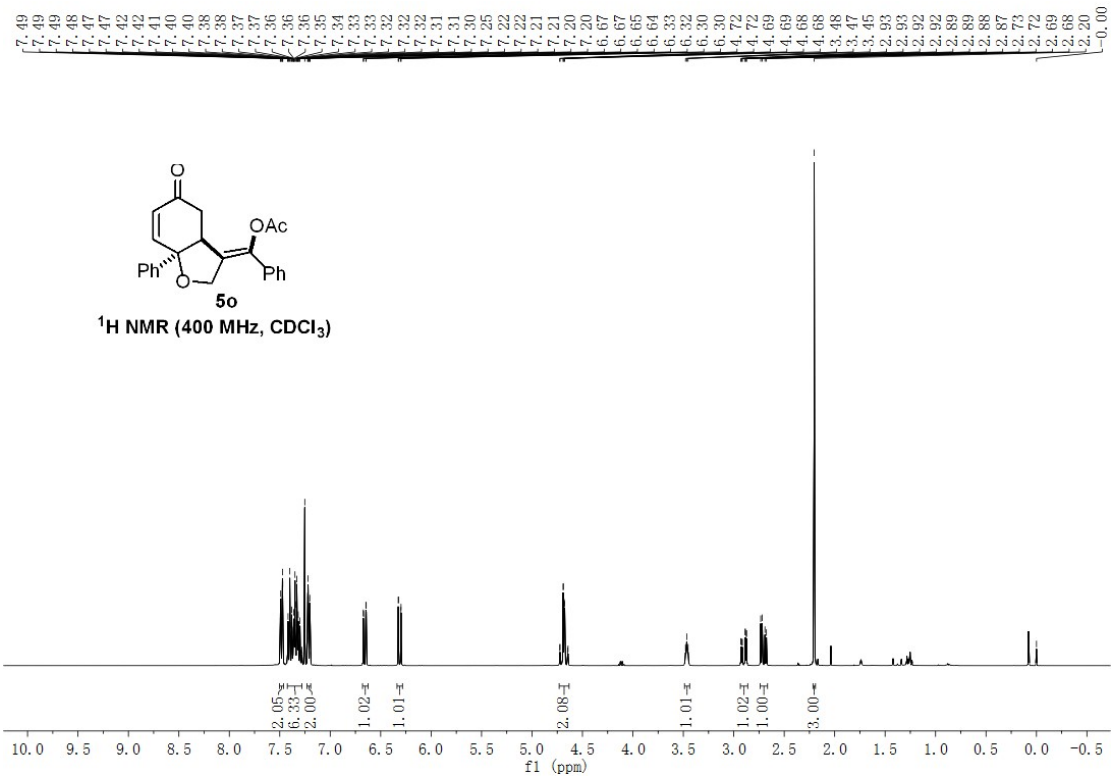
5n

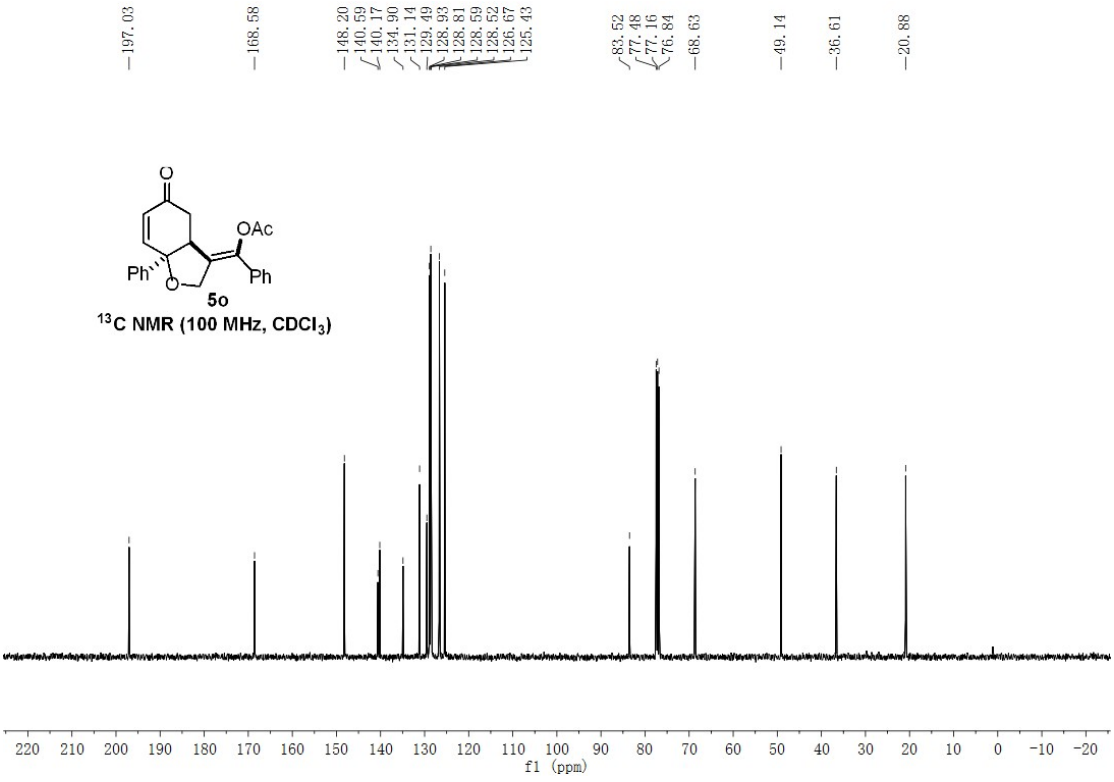
^{1}H NMR (400 MHz, $CDCl_3$)

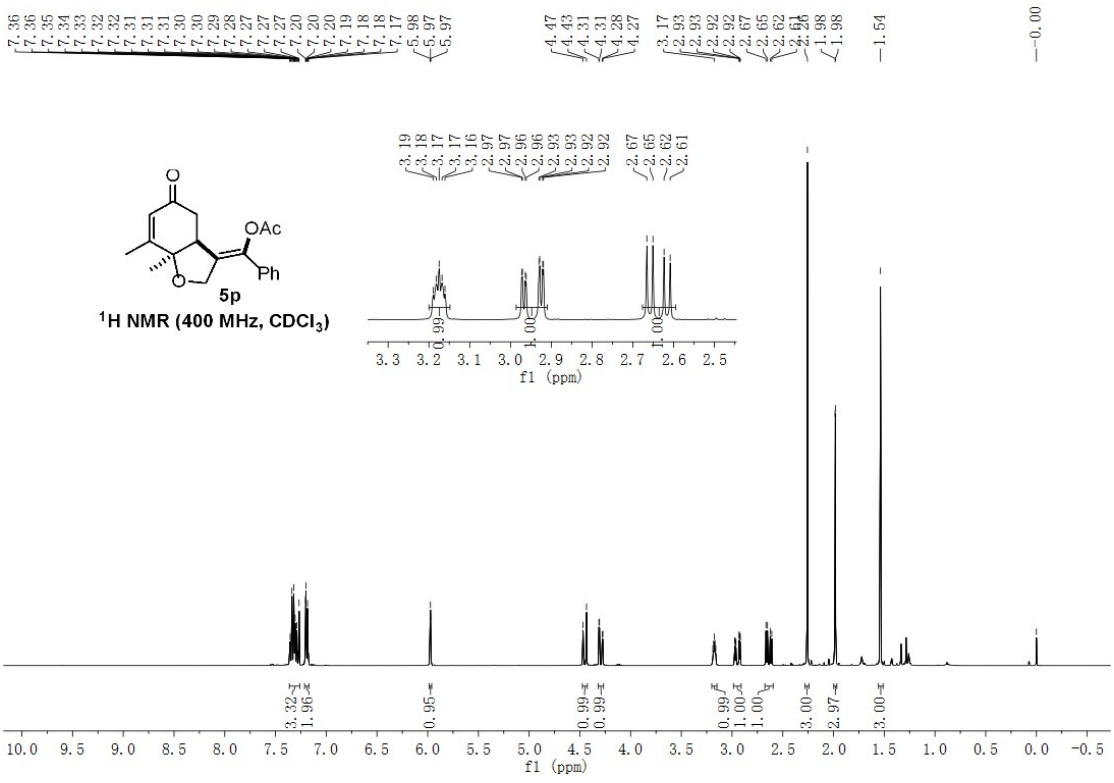


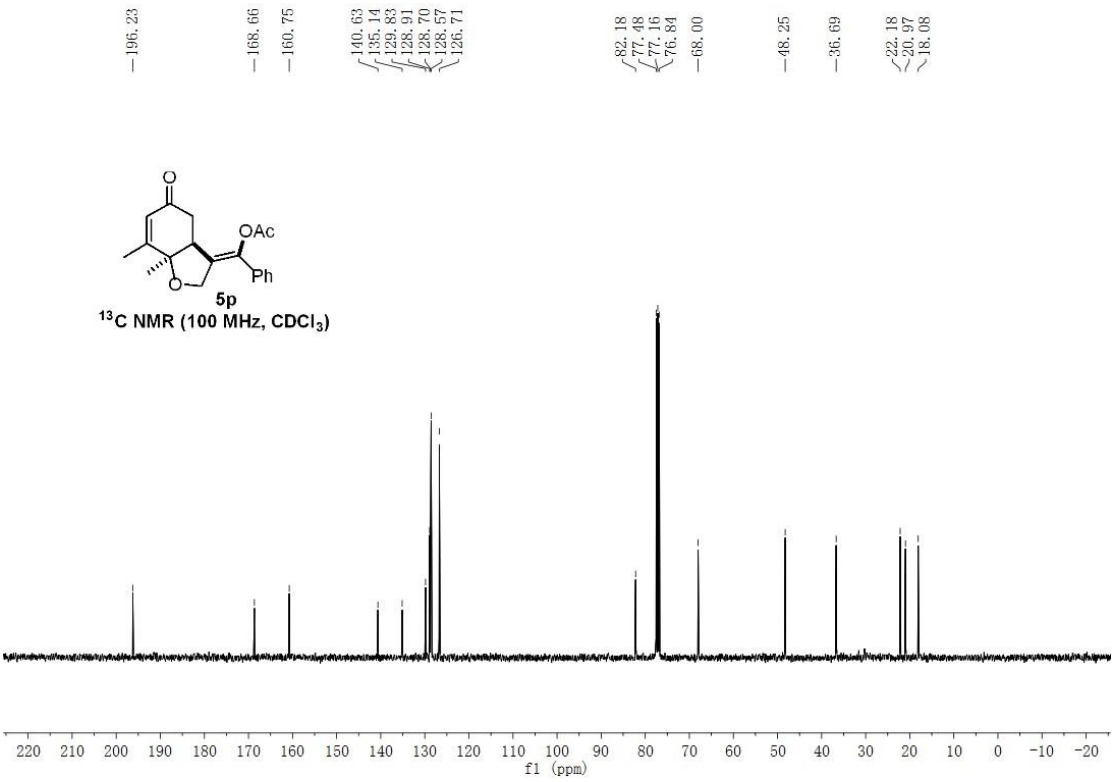
5n

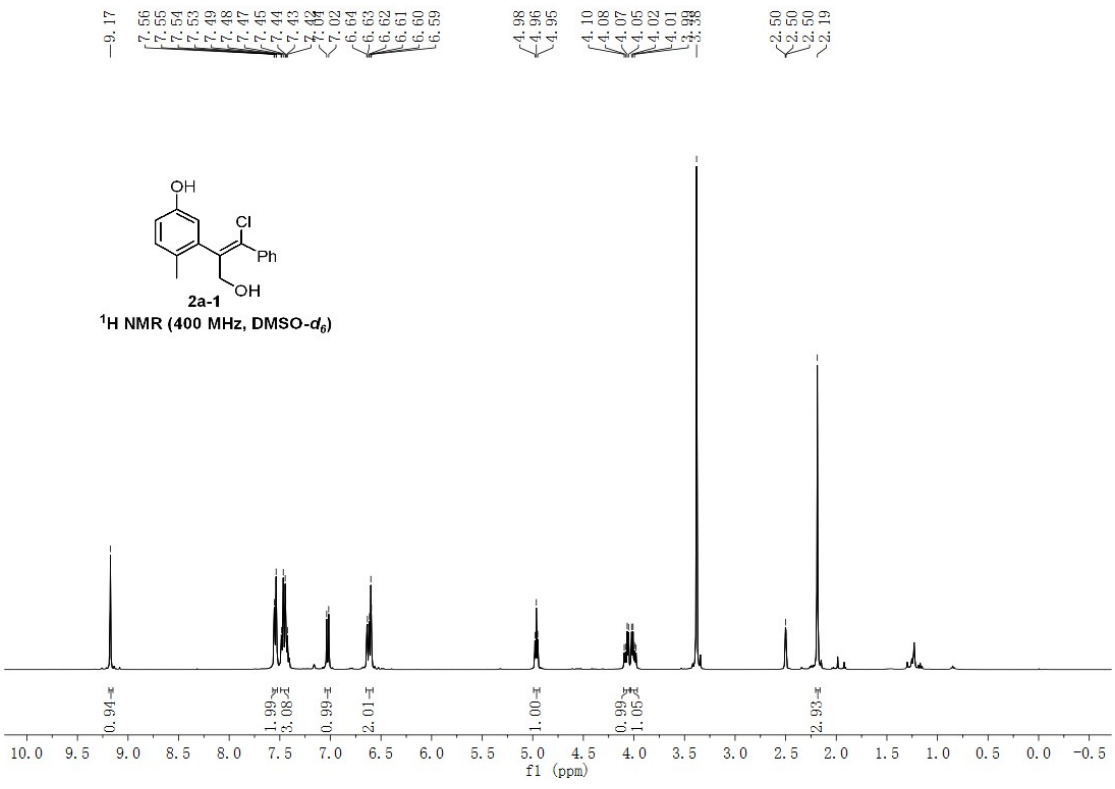
^{13}C NMR (100 MHz, $CDCl_3$)


OAc
Ph
Ph
O
5o
^{1}H NMR (400 MHz, CDCl$_3$)
f1 (ppm)


OAc
Ph
Ph
O
5o
^{13}C NMR (100 MHz, CDCl$_3$)
f1 (ppm)

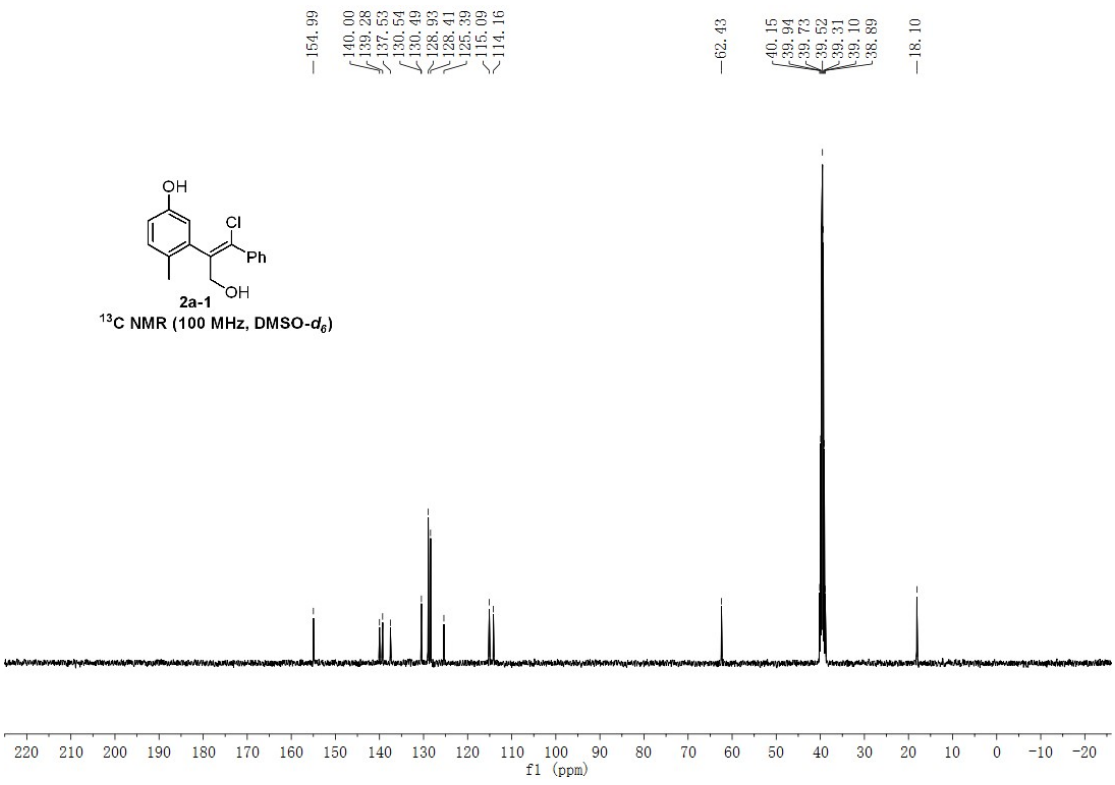

OAc
Ph
5p
^{1}H NMR (400 MHz, CDCl$_3$)


OAc
Ph
5p
^{13}C NMR (100 MHz, CDCl$_3$)



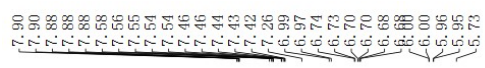
2a-1

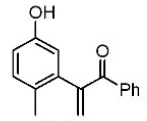
^{1}H NMR (400 MHz, DMSO-d_6)



2a-1

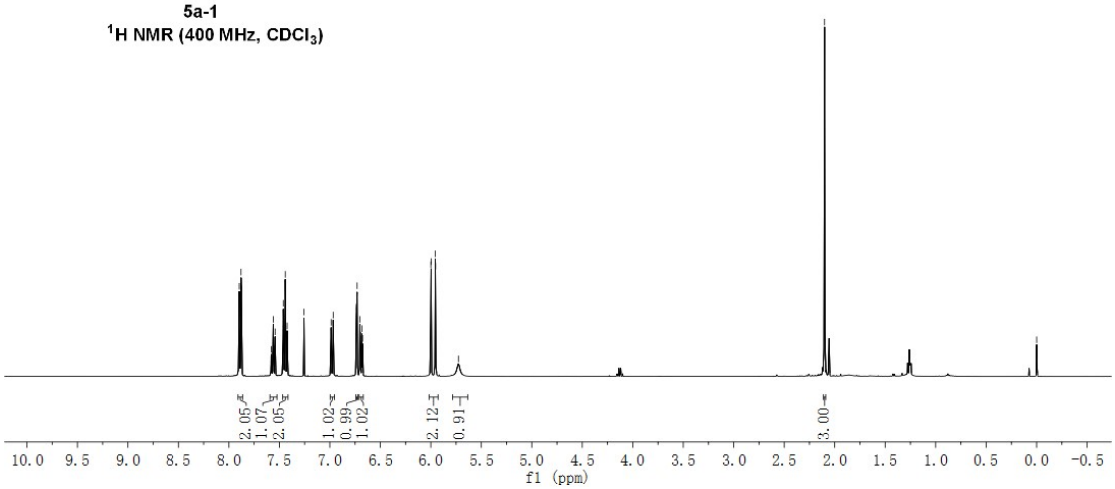
^{13}C NMR (100 MHz, DMSO-d_6)

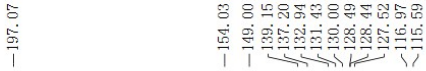


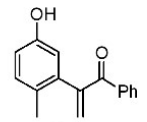


5a-1

^{1}H NMR (400 MHz, $CDCl_3$)

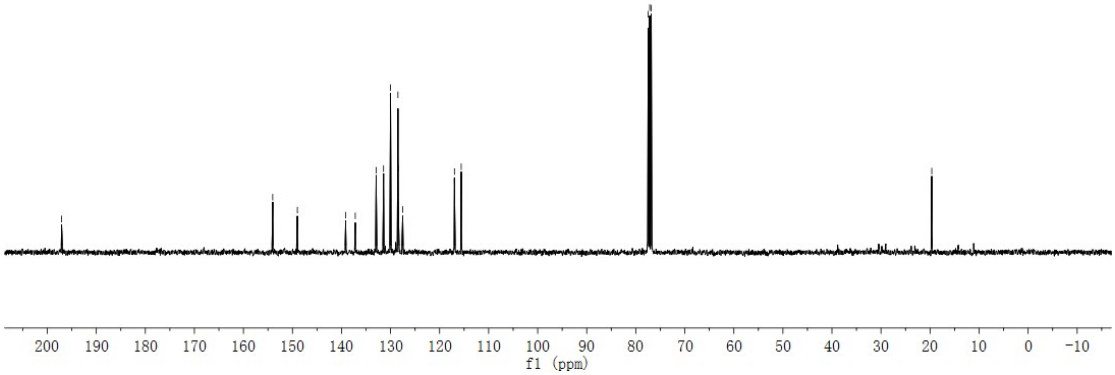


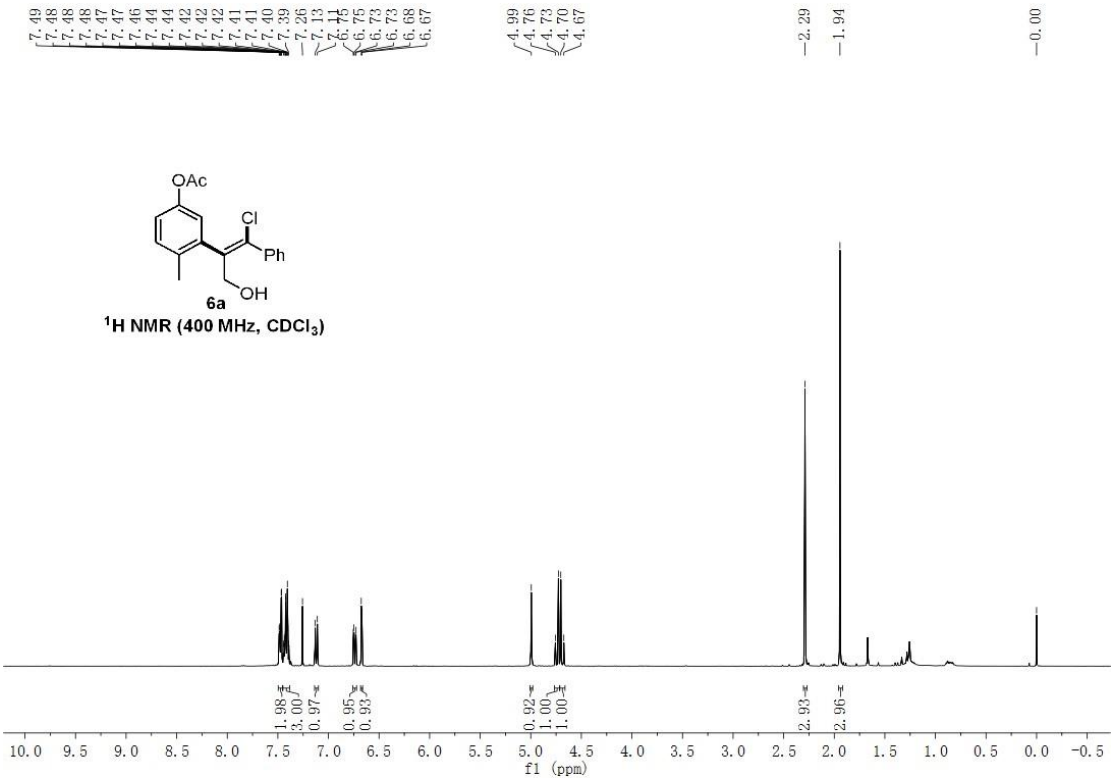


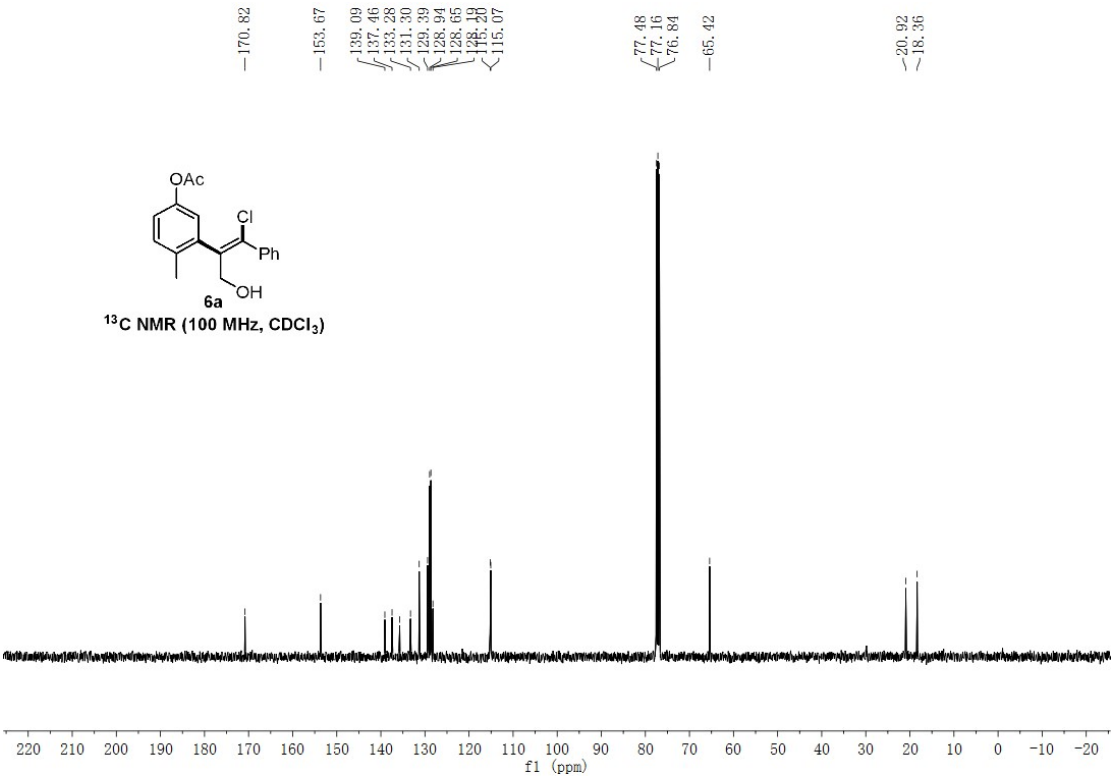


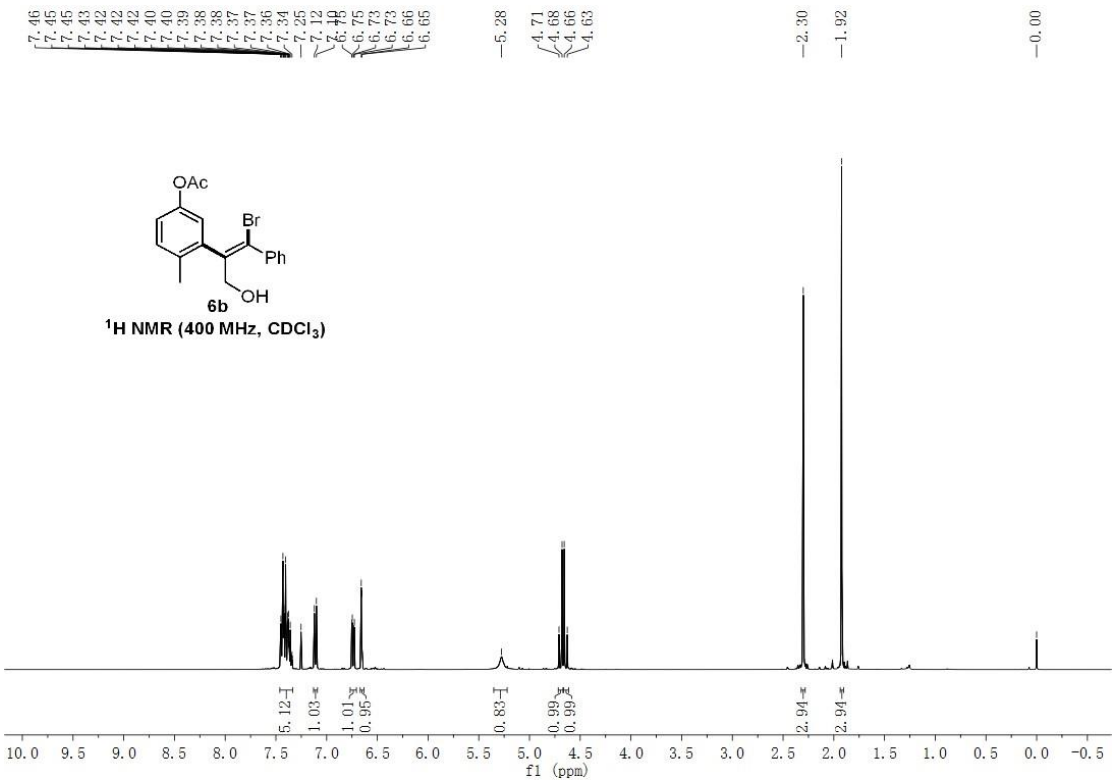
5a-1

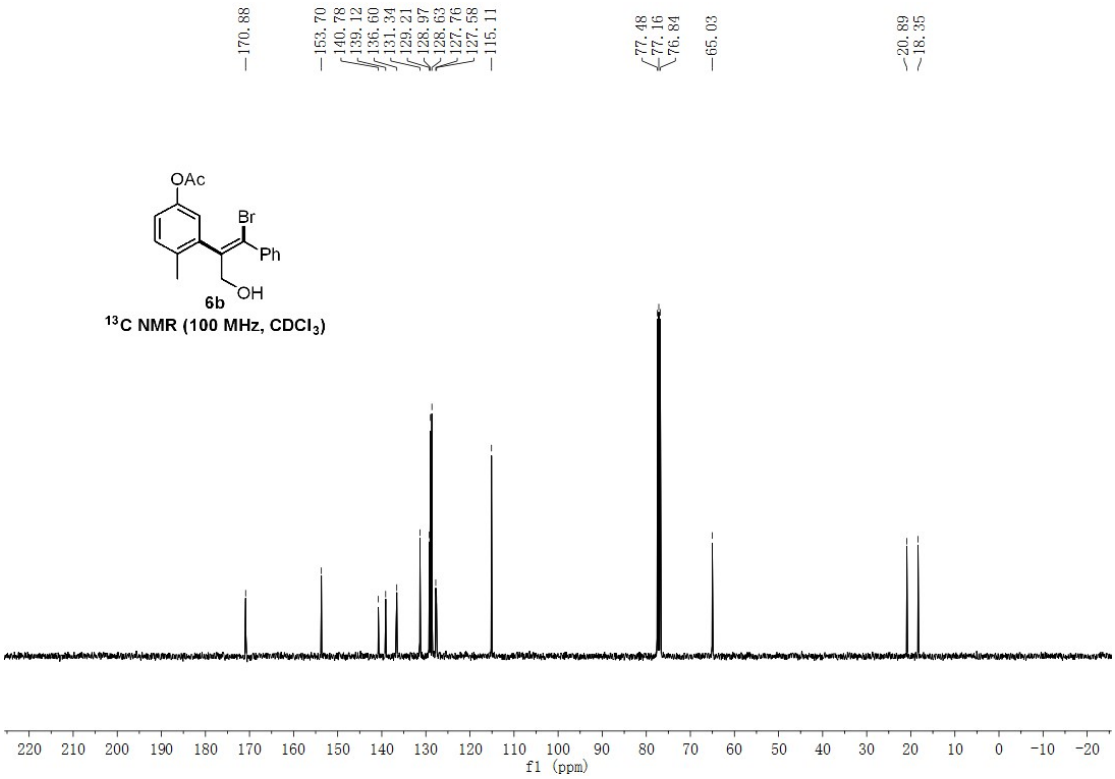
^{13}C NMR (100 MHz, $CDCl_3$)

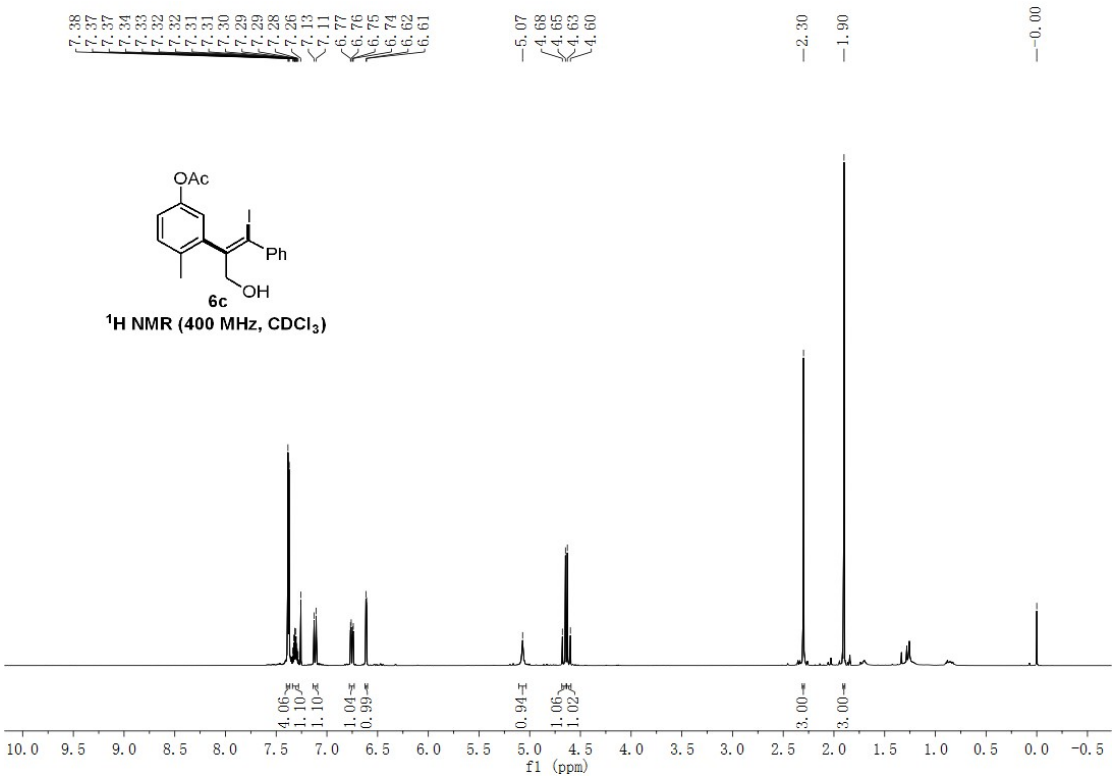



7.49
7.48
7.48
7.48
7.47
7.47
7.46
7.44
7.44
7.42
7.42
7.42
7.41
7.41
7.40
7.39
7.26
7.13
6.75
6.75
6.73
6.73
6.68
6.67
4.99
4.76
4.73
4.70
4.67
2.29
1.94
0.00
OAc
Cl
Ph
OH
6a
1H NMR (400 MHz, CDCl3)
1.98
3.00
0.97
0.95
0.93
0.92
1.00
1.00
2.93
2.96
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

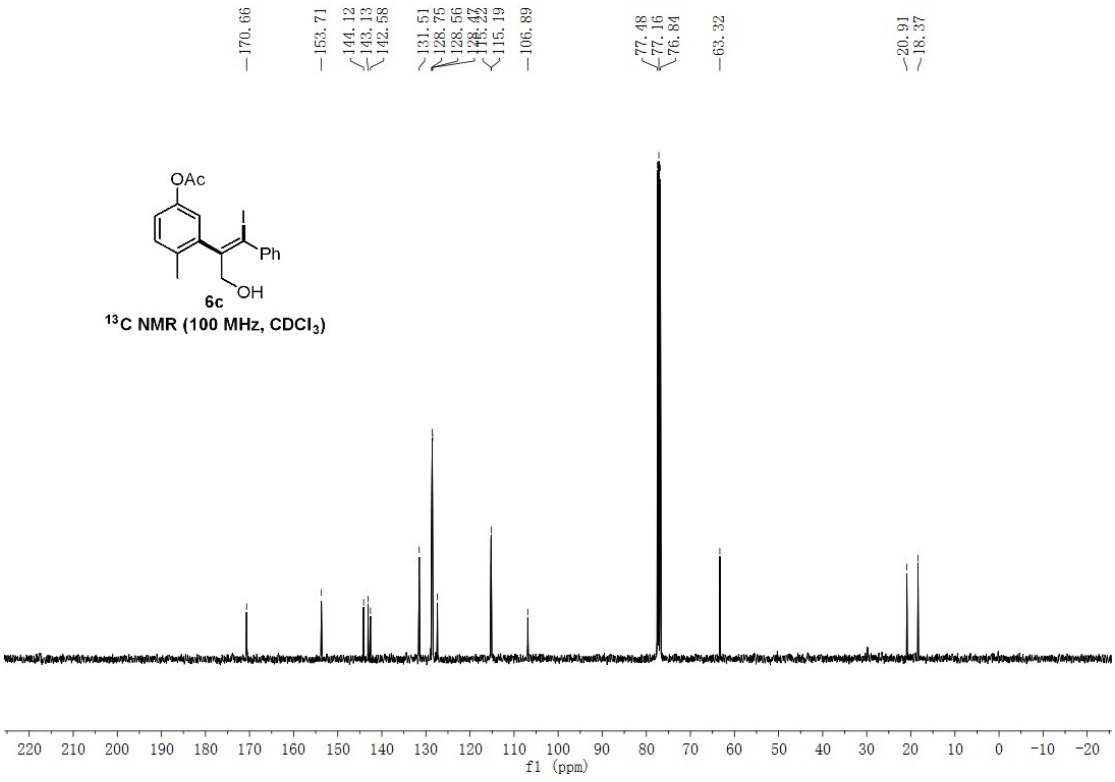

170.82
153.67
139.09
137.46
133.28
131.30
129.39
128.94
128.65
128.19
125.20
115.07
77.48
77.16
76.84
65.42
20.92
18.36
OAc
Cl
Ph
OH
6a
13C NMR (100 MHz, CDCl3)
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)


7.46
7.45
7.45
7.43
7.42
7.42
7.42
7.40
7.40
7.39
7.38
7.38
7.37
7.37
7.36
7.34
7.25
7.12
6.75
6.73
6.66
6.65
5.28
4.71
4.68
4.66
4.63
2.30
1.92
0.00
OAc
Br
Ph
OH
6b
^{1}H NMR (400 MHz, CDCl$_3$)
5.12
1.03
1.01
0.95
0.83
0.99
0.99
2.94
2.94
f1 (ppm)

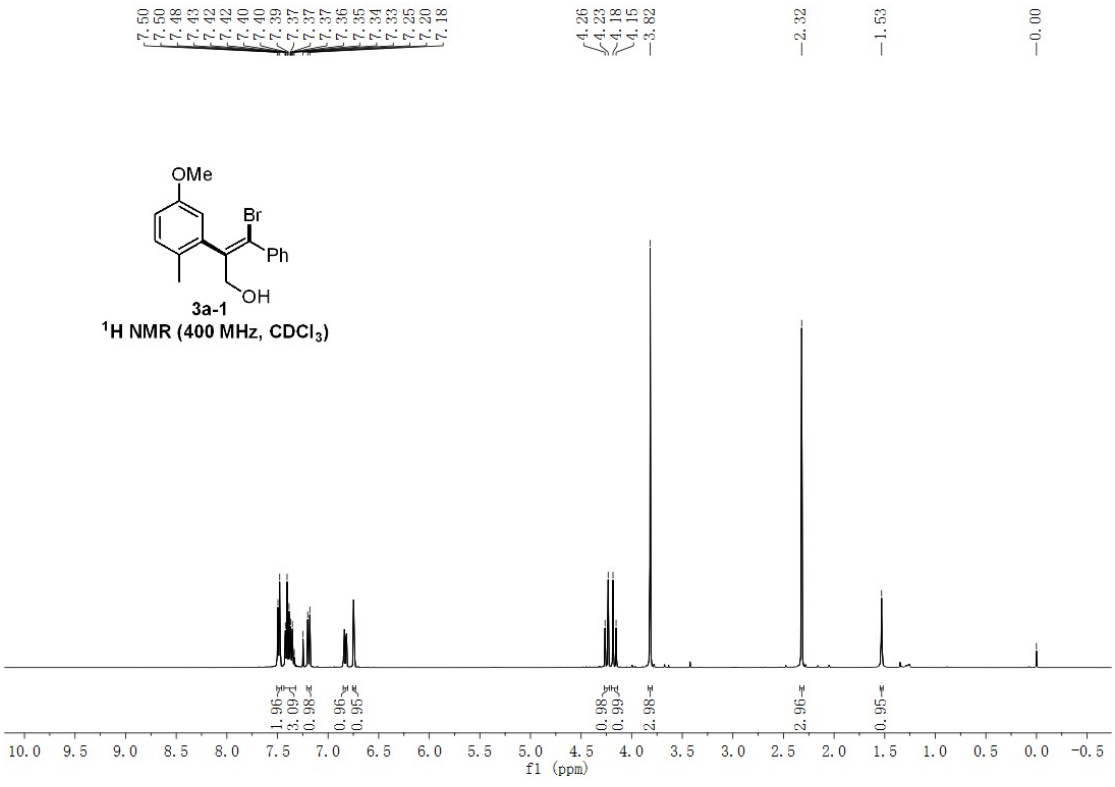

170.88
153.70
140.78
139.12
136.60
131.34
129.21
128.97
128.63
127.76
127.58
115.11
77.48
77.16
76.84
65.03
20.89
18.35
OAc
Br
Ph
OH
6b
^{13}C NMR (100 MHz, CDCl$_3$)
f1 (ppm)



^{1}H NMR (400 MHz, $CDCl_3$)

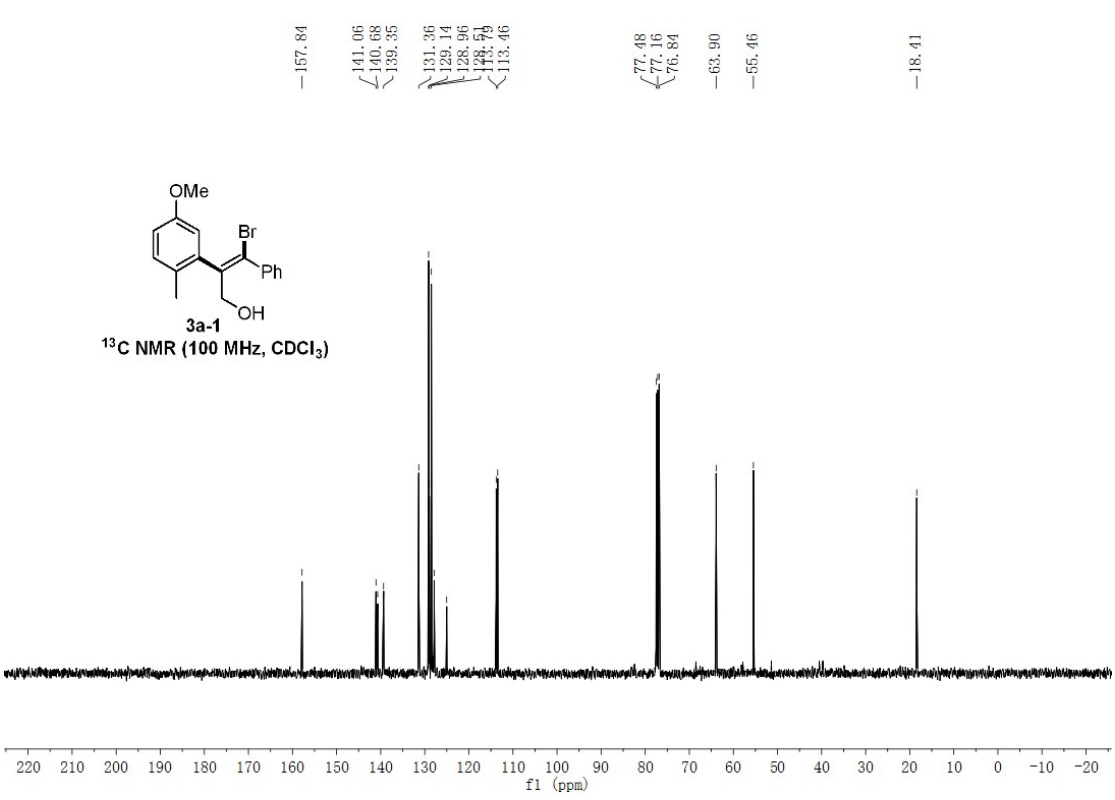


^{13}C NMR (100 MHz, $CDCl_3$)



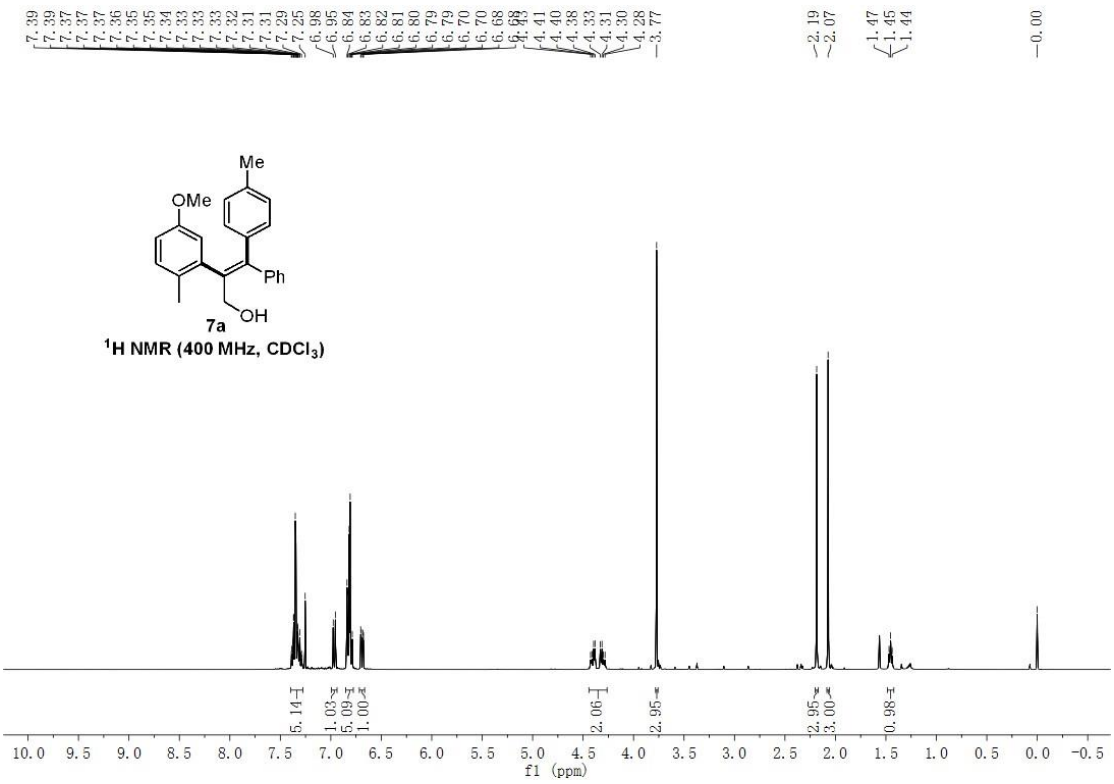
3a-1

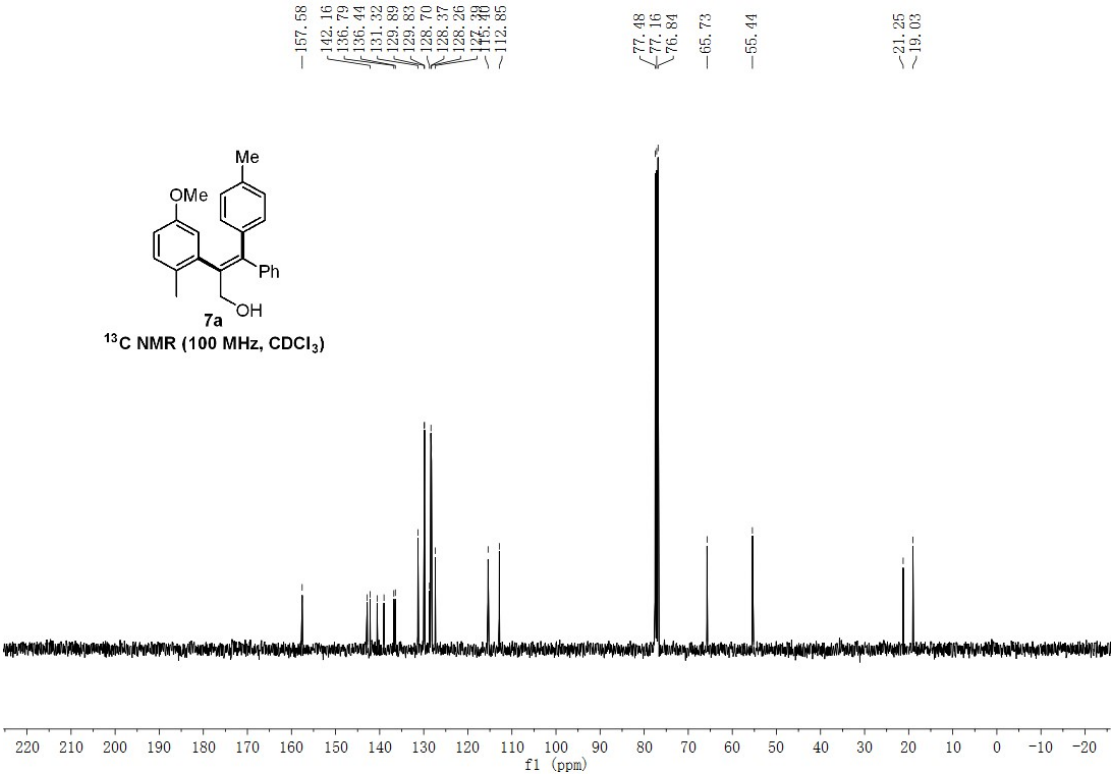
^{1}H NMR (400 MHz, $CDCl_3$)

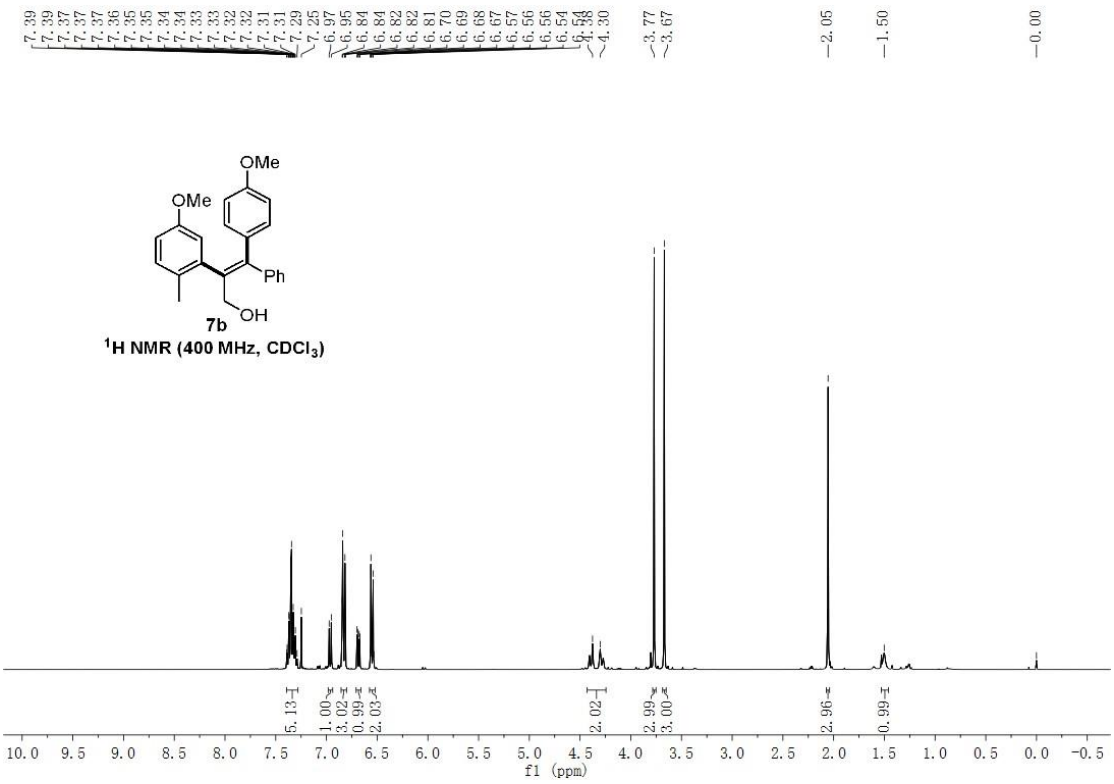


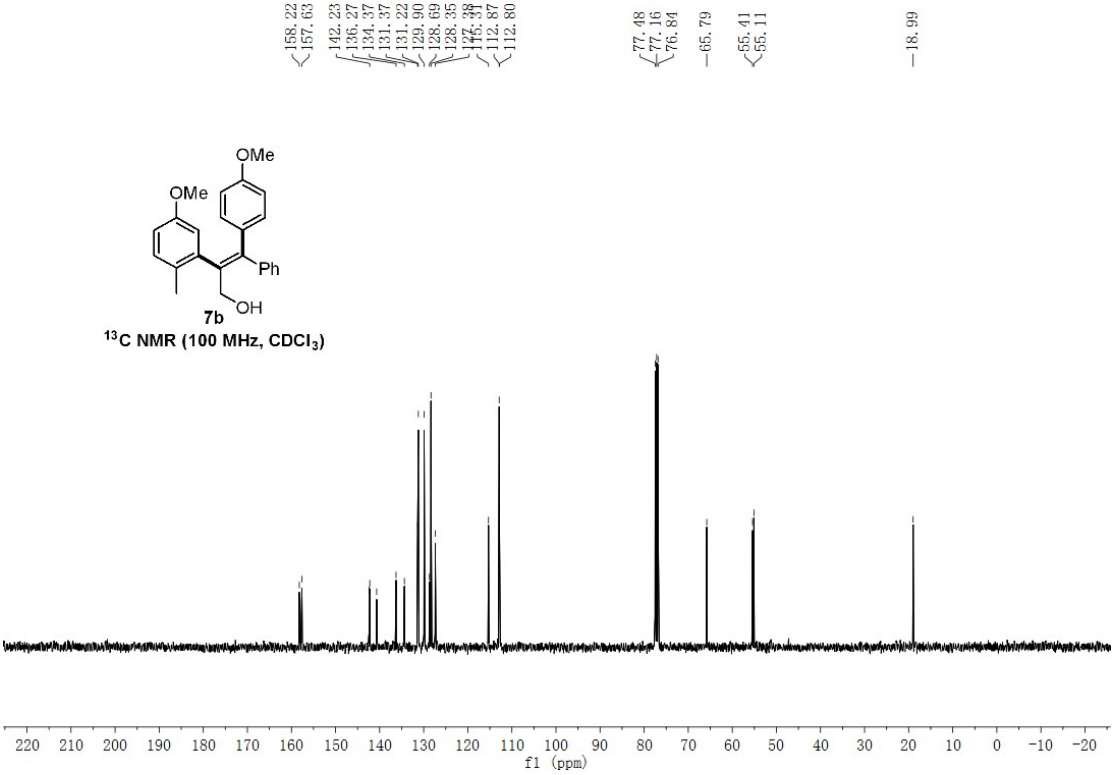
3a-1

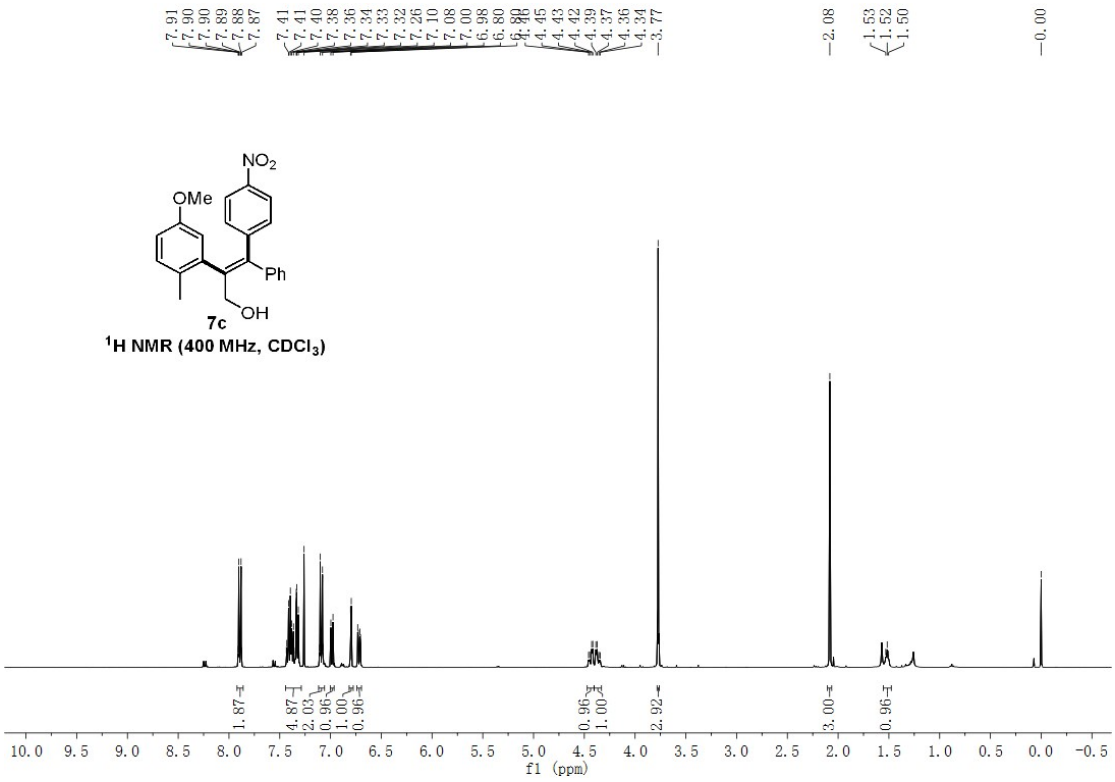
^{13}C NMR (100 MHz, $CDCl_3$)

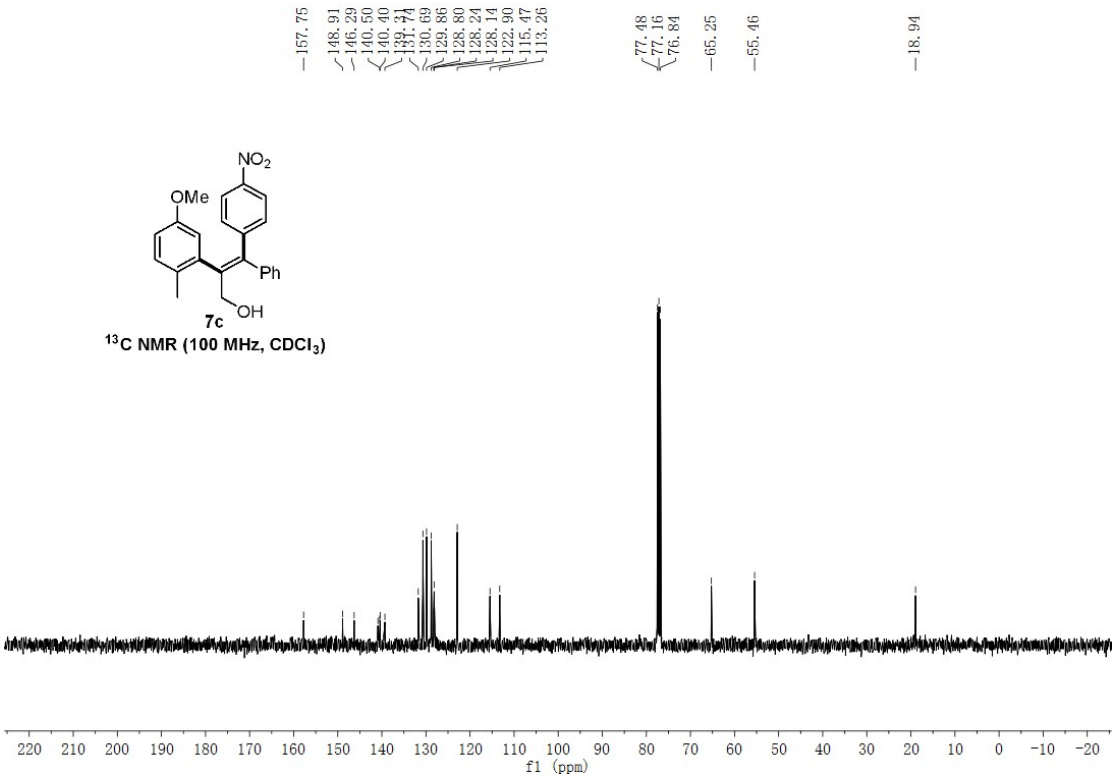

Me
OMe
Ph
OH
7a
^{1}H NMR (400 MHz, CDCl$_3$)
f1 (ppm)


Me
OMe
Ph
OH
7a
^{13}C NMR (100 MHz, CDCl$_3$)
f1 (ppm)


OMe
OMe
Ph
OH
7b
1H NMR (400 MHz, CDCl3)
f1 (ppm)


OMe
OMe
Ph
OH
7b
13C NMR (100 MHz, CDCl3)
f1 (ppm)


7.91
7.90
7.90
7.89
7.88
7.87
7.41
7.41
7.40
7.38
7.36
7.34
7.33
7.32
7.26
7.10
7.08
7.00
6.98
6.80
4.45
4.43
4.42
4.39
4.37
4.36
4.34
3.77
2.08
1.53
1.52
1.50
0.00
NO2
OMe
Ph
OH
7c
1H NMR (400 MHz, CDCl3)
1.87
4.87
2.03
0.96
1.00
0.96
0.96
1.00
2.92
3.00
0.96
f1 (ppm)


157.75
148.91
146.29
140.50
140.40
131.74
130.69
129.86
128.80
128.24
128.14
122.90
115.47
113.26
77.48
77.16
76.84
65.25
55.46
18.94
NO2
OMe
Ph
OH
7c
13C NMR (100 MHz, CDCl3)
f1 (ppm)