Electronic Supplementary Information

Access to Phosphorous-containing Cyclopenta[*b*]benzofuranols via Peptide-phosphonium Salt-promoted Serendipitous Cascade Reaction

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1. General information

All the starting materials were obtained from commercial sources and used without further purification unless otherwise stated. ^{1}H NMR, ^{13}C NMR, ^{31}P NMR and ^{19}F NMR spectra were recorded at ambient temperature in $CDCl_3$ on Bruker Avance III HD 400 spectrometer. The chemical shifts were given in parts permillion (ppm), and the residual solvent peak was used as an internal reference ($CDCl_3$: δ 7.26 ppm ^{1}H; δ 77.16 ppm ^{13}C). Multiplicity was indicated as follows: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), dd (doublet of doublet). Coupling constants (*J*) were reported in Hertz (Hz). High resolution mass spectra were obtained on a Thermo LTQ mass spectrometer. For thin layer chromatography (TLC), Merck pre-coated TLC plates (Merck 60 F254) were used, and compounds were visualized with a UV light at 254 nm. Further visualization was achieved by staining with iodine, or ceric ammonium molybdate followed by heating on a hot plate. Flash chromatographic separations were performed on Merck 60 (0.040-0.063 mm) mesh silica gel. Enantiomeric excess was determined by HPLC analysis using chiral column described below in detail.

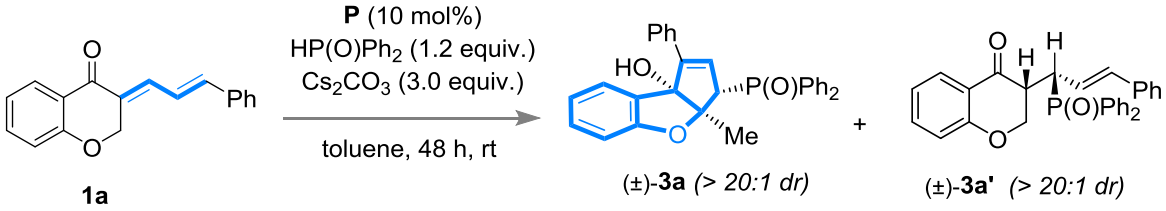
All phosphonium salt catalysts used in this study were prepared by following the procedures reported in the literatures.[1] All conjugated diene benzopyranone compounds **1** were synthesized following the methods reported in the literature.[2, 3]

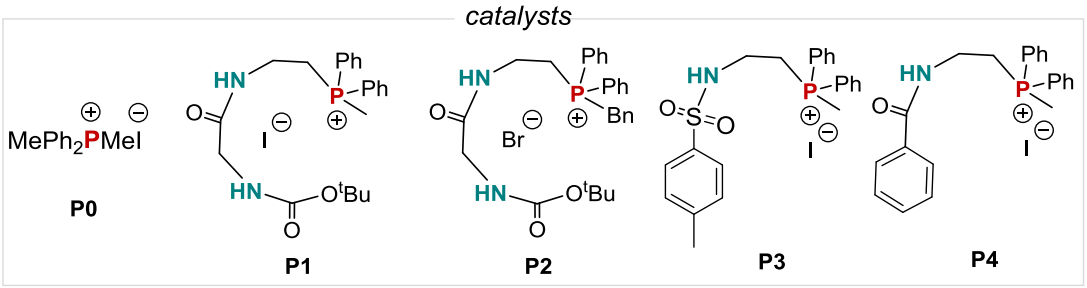
The configurations of products (±)-**3** were determined by X-ray crystallographic analysis of the single crystal of (±)-**3a** (CCDC 2171783). The configurations of (±)-**3'** and (±)-**4** were also determined by X-ray crystallographic analysis of the single crystal of (±)-**3a'** (CCDC 2171785) and (±)-**4** (CCDC 2207797).

Of note, the diastereomeric values of the tricyclic phosphorous products (**3**) and addition products (**3'**) were all >20:1 in this study, due to the following: *(a)* the origin of this complete diastereoselectivities of products **3** was attributed to the inherent steric hindrance and intramolecular H-bonding effect; *(b)* addition products **3'** are in *cis*-forms including two stereoisomers of (*2R, 3R)* and (*2S, 3S*), while the other two stereoisomers are *trans*-forms. The products **3'** can be synthesized from the *trans*-enantiomers under basic conditions through enolation process, due to the inherent steric hindrance of the stereoisomers. At the completion of the reaction, the *trans*-enantiomers have already been transformed.

2. Optimization of reaction conditions

***Table S1*:** Initial studies.[a,b]

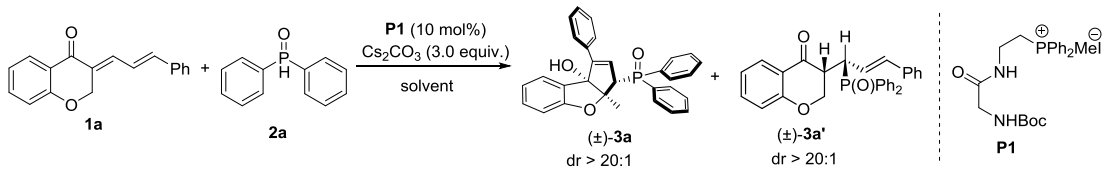




entry	cat.	yield of (±)-3a	yield of (±)-3a'
1	--	0	32
2	**P0**	5	40
3	**P1**	**15**	**63**
4	**P2**	12	62
5	**P3**	11	54
6	**P4**	10	56

[a] Reaction conditions: **1a** (26.2 mg, 0.10 mmol), **2a** (24.2 mg, 0.12 mmol), Cs_2CO_3 (97.8 mg, 0.30 mmol) and **P** (10 mol%) in solvent (2.5 mL) at room temperature for 48 h. [b] Isolated yields.

***Table S2*:** Screening of the solvents.[a,f]

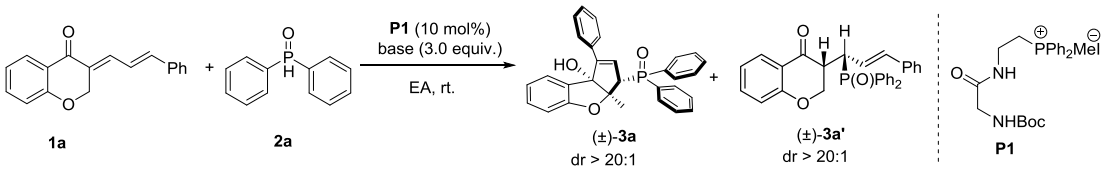


Entry	base	solvent	Conv. (%)[b]	time	yield (%) of (±)-**3a**	yield (%) of (±)-**3a'**
1	Cs_2CO_3	toluene	>95%	2 d	15	63

2	Cs_2CO_3	Et_2O	>95%	2 d	trace	72
3	Cs_2CO_3	dioxane	>95%	2 d	0	68
4	Cs_2CO_3	THF	>95%	2 d	10	23
5	Cs_2CO_3	EtOH	messy	2 d	n.d.	n.d.
6	Cs_2CO_3	MeOH	messy	2 d	n.d.	n.d.
7	Cs_2CO_3	H_2O	N.R.	2 d	0	0
8	Cs_2CO_3	CH_3CN	>95%	2 d	10	48
9	**Cs_2CO_3**	**EA**	>95%	**1 d**	38	0
10[c]	Cs_2CO_3	EA	>95%	16 h	36	0
11[d]	Cs_2CO_3	EA	60	1 d	33	0
12[e]	Cs_2CO_3	EA	12	1 d	trace	trace

[a] Reaction conditions: **1a** (26.2 mg, 0.10 mmol), **2a** (24.2 mg, 0.12 mmol), Cs_2CO_3 (97.8 mg, 0.30 mmol) and **P1** (10 mol%) in solvent (2.5 mL) at room temperature. [b] conversion was determined by crude ^{1}H NMR. [c] The reaction temperature was 35 ^{o}C. [d] The reaction temperature was 50^{o}C. [e] The reaction temperature was 70 ^{o}C. [f] Isolated yields.

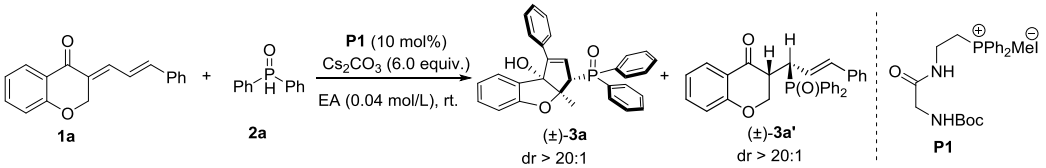
***Table S3*:** Screening of the bases.[a,e]



Entry	base	Conv. (%)[b]	time	yield (%) of (±)-**3a**	yield (%) of (±)-**3a'**
1	Cs_2CO_3	>95%	1 d	38	0
2	KOH	messy	2 h	n.d.	n.d.
3	NaOH	>95%	12 h	26	0
4	K_3PO_4	<5%	2 d	0	0
5	DIPEA	messy	2 d	0	0
6	DBU	messy	2 d	0	0
7[c]	**Cs_2CO_3**	**>95%**	**18 h**	**40**	**0**
8[d]	Cs_2CO_3	>95%	18 h	36	0

[a] Reaction conditions: **1a** (26.2 mg, 0.10 mmol), **2a** (24.2 mg, 0.12 mmol), Cs_2CO_3 (97.8 mg, 0.30 mmol) and **P1** (10 mol%) in solvent (2.5 mL) at room temperature. [b] Conversion was determined by crude ^{1}H NMR. [c] Cs_2CO_3 (195.6 mg, 0.60 mmol). [d] Cs_2CO_3 (293.4 mg, 0.90 mmol). [e] Isolated yields.

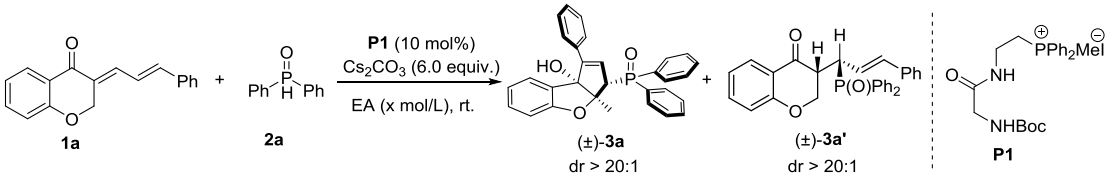
***Table S4*:** Screening of equivalent of **2a**.[a,c]



Entry	**2a**	time	Conv. (%)[b]	yield (%)(±)-**3a**	yield (%)(±)-**3a'**
1	1.2 equiv.	18 h	>95%	40	0
2	1.5 equiv.	18 h	>95%	45	0
3	2.0 equiv.	18 h	>95%	46	0

[a] Reaction conditions: **1a** (26.2 mg, 0.10 mmol), **2a** (x mmol), Cs_2CO_3 (0.60 mmol) and **P1** (10 mol%) in solvent (2.5 mL) at room temperature. [b] Conversion was determined by crude ^{1}H NMR. [c] Isolated yields.

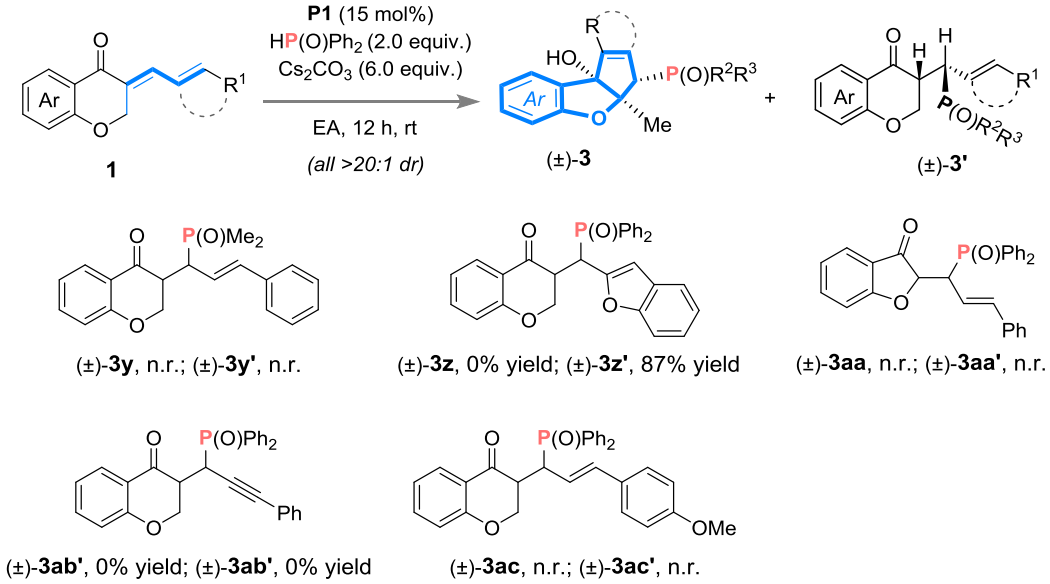
***Table S5*:** Screening of reaction concentration and loading of catalyst.[a,d]



Entry	EA	time	Conv. (%)[b]	yield (%)(±)-**3a**	yield (%)(±)-**3a'**
1	2.5 mL	18 h	>95%	46	0
2	1.25 mL	18 h	>95%	42	0
3	0.625 mL	18 h	>95%	38	0
4	5.0 mL	18 h	>95%	37	0
5[b]	2.5 mL	12 h	>95%	53	0
6[c]	2.5 mL	12 h	>95%	53	0

[a] Reaction conditions: **1a** (26.2 mg, 0.10 mmol), **2a** (40.4 mg, 0.20 mmol), Cs_2CO_3 (0.30 mmol) and **P1** (10 mol%) in solvent (2.5 mL) at room temperature. [b] Conversion was determined by ^1H crude NMR. [b] The loading of **P1** was 15 mol%. [c] The loading of **P1** was 20 mol%.[d] Isolated yields.

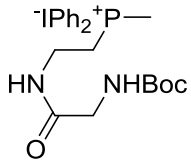
***Table S6*:** Substrates limitation.[a,b]



[a] Reaction conditions: **1** (0.10 mmol), **2** (0.20 mmol), Cs_2CO_3 (0.60 mmol) and **P1** (0.015 mmol) in EA (2.5 mL) for 12 h at room temperature. [b] Isolated yields.

3. Preparation of the catalyst

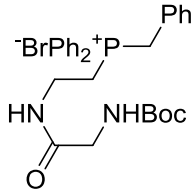
All the phosphonium salt catalysts **P0-P1** were prepared by the previuosly reported procedures.[1] The **P0** catalyst is known compounds, and its characterization data were in agreement with those reported in the literature.[2] Unknown compounds **P1, P2, P3,** and **P4** were fully characterized.



(2-(2-((tert-butoxycarbonyl)amino)acetamido)ethyl)(methyl)diphenylphosphonium iodide (P1)

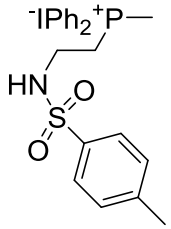
A yellow solid; m.p. = 143-145 ^oC; ^1H NMR (400 MHz, $CDCl_3$) δ 7.94 (t, J = 4.9 Hz, 1H), 7.81 (dd, J = 13.0, 7.4 Hz, 4H), 7.70-7.63 (m, 2H), 7.62-7.54 (m, 4H), 5.33

(s, 1H), 3.74-3.58 (m, 2H), 3.55-3.46 (m, 2H), 3.46-3.35 (m, 2H), 5.33 (s, 1H), 3.73-3.57 (m, 2H), 3.55-3.46 (m, 2H), 3.43 (d, *J* = 4.2 Hz, 2H), 2.80 (d, *J* = 13.7 Hz, 3H), 1.31 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.6, 155.9, 134.8, 132.4 (d, *J* = 10.3 Hz), 130.2 (d, *J* = 12.5 Hz), 119.0 (d, *J* = 85.3 Hz), 79.8, 43.7, 32.8, 28.3, 23.4 (d, *J* = 50.9 Hz), 8.3 (d, *J* = 53.8 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 21.99; HRMS (ESI) calcd for $C_{22}H_{30}N_2O_3P$ $[M-I]^+$ 401.1989; found 401.1989.



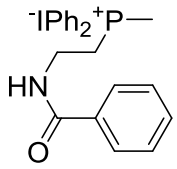
benzyl(2-(2-((tert-butoxycarbonyl)amino)acetamido)ethyl)diphenylphosphonium bromide (P2）

A white solid; m.p. = 178-179 °C; ^{1}H NMR (400 MHz, DMSO-d6) δ 8.28-8.10 (m, 1H), 7.93-7.81 (m, 6H), 7.77-7.67 (m, 4H), 7.30-7.18 (m, 3H), 7.06-6.90 (m, 3H), 4.76 (d, *J* = 15.6 Hz, 2H), 3.42 (d, *J* = 5.8 Hz, 2H), 3.33 (s, 1H), 3.31-3.21 (m, 2H), 3.17-3.01 (m, 2H), 1.37 (s, 9H); ^{13}C NMR (100 MHz, DMSO-d6) δ 170.0, 155.7, 134.8, 133.4 (d, *J* = 9.6 Hz), 130.3 (d, *J* = 5.0 Hz), 129.8 (d, *J* = 12.2 Hz), 128.8, 128.1 (d, *J* = 4.1 Hz), 127.9 (d, *J* = 2.7 Hz), 117.8, 117.0, 79.2, 78.2, 43.3, 32.3, 28.2, 19.0 (d, *J* = 47.3 Hz),; ^{31}P NMR (162 MHz, DMSO-d6) δ 23.74; HRMS (ESI) calcd for $C_{28}H_{34}N_2O_3P$ $[M-Br]^+$ 477.2302; found 477.2304.



methyl(2-((4-methylphenyl)sulfonamido)ethyl)diphenylphosphonium iodide (**P3**)

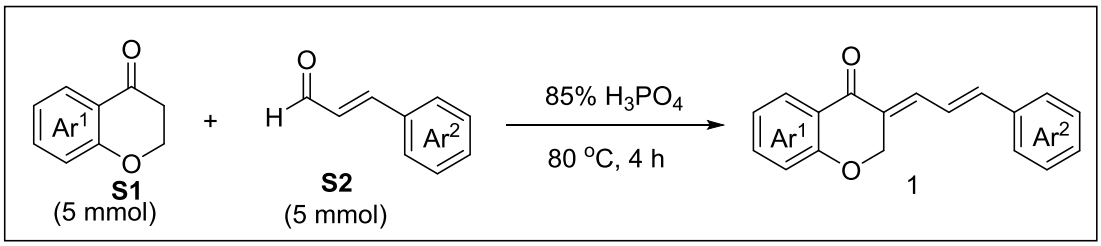
A yellow solid; m.p. = 88-90 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87-7.78 (m, 4H), 7.77-7.67 (m, 4H), 7.67-7.57 (m, 4H), 7.21 (d, *J* = 8.0 Hz, 2H), 7.06 (t, *J* = 6.2 Hz, 1H), 3.64-3.51 (m, 2H), 3.35-3.20 (m, 2H), 2.81 (d, *J* = 13.8 Hz, 3H), 2.33 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.7, 135.7, 135.0 (d, *J* = 2.8 Hz), 132.6 (d, *J* = 10.1 Hz), 130.5 (d, *J* = 12.6 Hz), 129.9, 127.4, 119.1 (d, *J* = 85.6 Hz), 37.0, 24.2 (d, *J* = 52.9 Hz), 21.6, 9.5 (d, *J* = 49.5 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 22.65; HRMS (ESI) calcd for $C_{21}H_{22}NO_2PS$ $[M-I]^+$ 383.1103; found 383.1110.



(2-benzamidoethyl)(methyl)diphenylphosphonium iodide (P4)

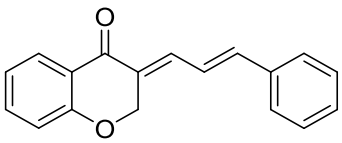
A yellow solid; m.p. = 172-174 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26 (t, J = 5.8 Hz, 1H), 7.86-7.71 (m, 6H), 7.60-7.47 (m, 6H), 7.47 (t, J = 7.4 Hz, 1H), 7.26 (t, J = 8.3 Hz, 2H), 4.05-3.91 (m, 2H), 3.75-3.64 (m, 2H), 2.87 (d, J = 13.7 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.7, 134.7 (d, J = 3.0 Hz), 132.4, 132.2 (d, J = 10.2 Hz), 131.8, 130.3 (d, J = 12.5 Hz), 128.2, 127.6, 119.3 (d, J = 85.3 Hz), 33.5, 23.8 (d, J = 50.8 Hz), 8.4 (d, J = 54.3 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 21.63; HRMS (ESI) calcd for $C_{22}H_{23}NOP$ $[M-I]^+$ 348.1512; found 348.1510.

4. **Preparation of the substrate:** phenylallylidene chroman-4-one **1**



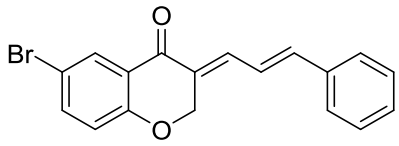
All the phenylallylidene chroman-4-one **1** used in this article were synthesised according to the literature.[4] The unknown compounds are **1c**, **1d**, **1e**, **1f**, **1g**, **1i**, **1j**, **1k**, **1l**, **1m**, **1n**, **1o**, **1v**, **1w**, **1x**, **1z**, **1aa**, **1ab**, and **1ac**, and all of them were fully characterized.

Characterization of unknown substrates



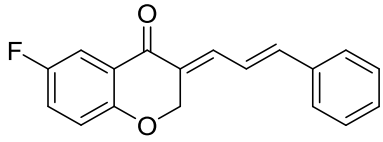
(*E*)-3-((*E*)-3-phenylallylidene)chroman-4-one (1a)

A yellow solid; 1.02 g, 78% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (dd, J = 7.8, 1.6 Hz, 1H), 7.56-7.45 (m, 4H), 7.42-7.31 (m, 3H), 7.13-6.97 (m, 4H), 5.26 (d, J = 1.6 Hz, 2H); HRMS (ESI) m/z calcd for $C_{18}H_{15}O_2$ $[M+H]^+$ 263.1067; found 263.1068.



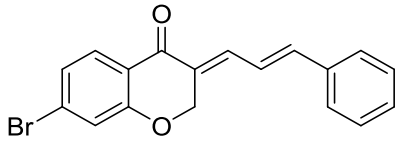
(*E*)-6-bromo-3-((*E*)-3-phenylallylidene)chroman-4-one (1c)

A yellow solid; 1.29 g, 76% yield; m.p. = 165-167 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (d, *J* = 6.3 Hz, 1H), 7.56-7.47 (m, 4H), 7.42-7.34 (m, 3H), 7.13-7.06 (m, 1H), 7.04-6.94 (m, 1H), 6.89 (d, *J* = 8.8 Hz, 1H), 5.25 (d, *J* = 1.5 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 180.8, 160.4, 144.1, 138.2, 137.0, 136.0, 130.4, 129.8, 129.1, 128.2, 127.7, 123.8, 121.5, 120.1, 114.7, 67.2; HRMS (ESI) m/z calcd for $C_{18}H_{14}O_2Br$ $[M+H]^+$ 341.0172; found 341.0175.



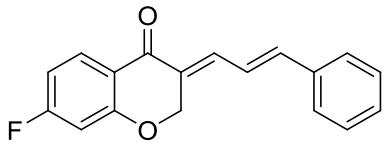
(*E*)-6-fluoro-3-((*E*)-3-phenylallylidene)chroman-4-one (1d)

A yellow solid; 1.06 g, 76% yield; m.p. = 148-150 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (dd, *J* = 8.4, 3.2 Hz, 1H), 7.55-7.48 (m, 3H), 7.42-7.34 (m, 3H), 7.22-7.16 (m, 1H), 7.10 (d, *J* = 15.3 Hz, 1H), 7.02 (d, *J* = 11.6 Hz, 1H), 7.00-6.95 (m, 1H), 5.24 (d, *J* = 2.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 181.2, 157.6 (d, *J* = 1.3 Hz), 157.6 (d, *J* = 240.5 Hz), 143.9, 136.7, 135.9, 129.7, 129.0, 128.4, 127.5, 123.1 (d, *J* = 6.9 Hz), 123.0 (d, *J* = 24.1 Hz), 121.5, 119.5 (d, *J* = 7.2 Hz), 112.9 (d, *J* = 23.6 Hz), 67.1; ^{19}F NMR (376 MHz, $CDCl_3$) δ -120.86; HRMS (ESI) m/z calcd for $C_{18}H_{14}FO_2$ $[M+H]^+$ 281.0972; found 281.0972.



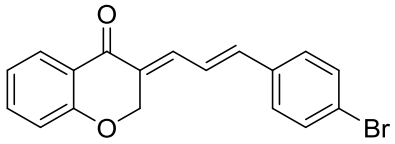
(*E*)-6-bromo-3-((*E*)-3-phenylallylidene)chroman-4-one (1e)

A yellow solid; 1.28 g, 75% yield; m.p. = 163-165 ^{o}C;^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, *J* = 5.8 Hz, 1H), 7.55-7.48 (m, 3H), 7.42-7.33 (m, 3H), 7.22-7.18 (m, 2H), 7.10 (d, *J* = 10.2 Hz, 1H), 6.99 (d, *J* = 7.9, 2.3 Hz, 1H), 5.27 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 181.3, 161.7, 144.0, 136.8, 136.0, 130.1, 129.8, 129.3, 129.1, 128.4, 127.7, 125.6, 121.6, 121.4, 121.2, 67.5; HRMS (ESI) m/z calcd for $C_{18}H_{14}O_2Br$ $[M+H]^+$ 341.0172; found 341.0175.



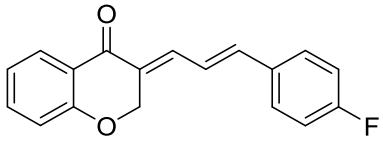
(*E*)-7-fluoro-3-((E)-3-phenylallylidene)chroman-4-one (1f)

A yellow solid; 1.09 g, 78% yield; m.p. = 149-151 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (dd, *J* = 8.8, 6.6 Hz, 1H), 7.53-7.48 (m, 3H), 7.41-7.34 (m, 3H), 7.10-7.07 (m, 1H), 7.02-6.95 (m, 1H), 6.80-6.75 (m, 1H), 6.68 (dd, *J* = 9.8, 2.4 Hz, 1H), 5.28 (d, *J* = 1.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 180.8, 167.4 (d, *J* = 254.3 Hz), 163.2 (d, *J* = 13.8 Hz), 143.7, 136.5, 136.1, 130.5 (d, *J* = 11.4 Hz), 129.8, 129.1, 128.4, 127.6, 121.6, 119.3, 110.4 (d, *J* = 22.5 Hz), 104.8 (d, *J* = 24.3 Hz), 67.6; ^{19}F NMR (565 MHz, $CDCl_3$) δ -101.02; HRMS (ESI) m/z calcd for $C_{18}H_{14}FO_2$ $[M+H]^+$ 281.0972; found 281.0972.



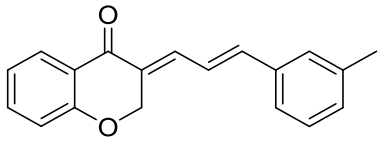
(*E*)-3-((*E*)-3-(4-bromophenyl)allylidene)chroman-4-one (1g)

A yellow solid; 1.36 g, 80% yield; m.p. = 168-169 ^{o}C;^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (dd, *J* = 7.9, 1.6 Hz, 1H), 7.54-7.44 (m, 4H), 7.40-7.35 (m, 2H), 7.10-7.04 (m, 1H), 7.02-6.96 (m, 3H), 5.25 (d, *J* = 1.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 181.0, 161.5, 141.9, 135.8, 135.6, 135.1, 132.2, 129.8, 128.9, 128.0, 123.7, 122.5, 122.3, 122.1, 118.0, 67.1; HRMS (ESI) m/z calcd for $C_{18}H_{14}O_2Br$ $[M+H]^+$ 341.0172; found = 341.0175.



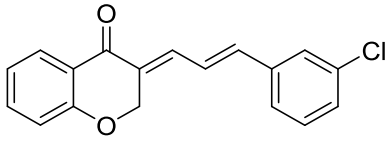
(*E*)-3-((*E*)-3-(4-fluorophenyl)allylidene)chroman-4-one (1i)

A yellow solid; 1.13 g, 81% yield; m.p. = 120-122 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (dd, *J* = 7.8, 1.7 Hz, 1H), 7.55-7.43 (m, 4H), 7.12-6.87 (m. 6H), 5.25 (d, *J* = 1.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 182.1, 163.5 (d, *J* = 249.2 Hz), 161.5, 142.0, 135.9, 135.8, 132.4, 129.4, 129.3, 128.0, 122.5, 122.1, 121.5 (d, *J* = 2.4 Hz), 118.0, 116.3, 116.1, 67.1; HRMS (ESI) m/z calcd for $C_{18}H_{14}FO_2$ $[M+H]^+$ 281.0972; found 281.0969.



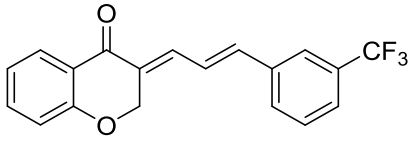
(*E*)-3-((*E*)-3-(m-tolyl)allylidene)chroman-4-one (1j)

A yellow solid; 1.05 g, 76% yield; m.p. = 99-100 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (dd, *J* = 7.9, 1.8 Hz, 1H), 7.51-7.45 (m, 2H), 7.34-7.32 (m, 2H), 7.29 (d, *J* = 7.5 Hz, 1H), 7.16 (d, *J* = 7.4 Hz, 1H), 7.08-6.98 (m, 4H), 5.27 (d, *J* = 1.8 Hz, 2H), 2.38 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 182.1, 161.5, 143.7, 138.7, 136.3, 136.1, 135.7, 130.5, 129.0, 128.9, 128.3, 128.0, 124.8, 122.6, 122.0, 121.6, 118.0, 67.1, 21.5; HRMS (ESI) m/z calcd for $C_{19}H_{17}O_2$ $[M+H]^+$ 277.1223; found 277.1223.



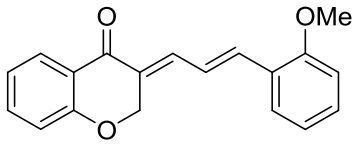
(*E*)-3-((*E*)-3-(3-chlorophenyl)allylidene)chroman-4-one (1k)

A yellow solid; 1.20 g, 81% yield; m.p. = 138-140 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (dd, *J* = 7.9, 1.8 Hz, 1H), 7.50 (d, *J* = 1.6 Hz, 1H), 7.49-7.45 (m, 2H), 7.38-7.36 (m, 1H), 7.32-7.30 (m, 2H), 7.09-7.04 (m, 1H), 7.01-6.98 (m, 3H), 5.26 (d, *J* = 1.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 182.0, 161.6, 141.5, 138.0, 135.9, 135.4, 135.1, 130.3, 130.2, 129.4, 128.1, 127.2, 125.8, 123.0, 122.4, 122.1, 118.1, 67.1; HRMS (ESI) m/z calcd for $C_{18}H_{14}O_2Cl$ $[M+H]^+$ 297.0677; found 297.0678.



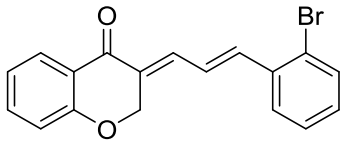
(*E*)-3-((*E*)-3-(3-(trifluoromethyl)phenyl)allylidene)chroman-4-one (1l)

A yellow solid; 1.39 g, 84% yield; m.p. = 154-156 ^{o}C;^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (dd, *J* = 7.8, 1.8 Hz, 1H), 7.8 (s, 1H), 7.7 (d, *J* = 7.9 Hz, 1H), 7.6 (d, *J* = 7.7 Hz, 1H), 7.53-7.46 (m, 3H), 7.10-7.06 (m, 3H), 7.0 (d, *J* = 8.3 Hz, 1H), 5.28 (d, *J* = 1.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 182.0, 161.6, 141.2, 136.9, 136.0, 135.2, 131.7, 131.4, 130.6 (d, *J* = 4.4 Hz), 129.6, 128.1, 126.7 (q, *J* = 256.0 Hz),125.9 (d, *J* = 3.9 Hz), 123.9 (d, *J* = 3.8 Hz), 123.4, 122.4, 122.1, 118.1, 67.1; ^{19}F NMR (376 MHz, CDCl3) δ -62.83; HRMS (ESI) m/z calcd for $C_{19}H_{14}O_2F_3$ $[M+H]^+$ 331.0940; found 331.0940.



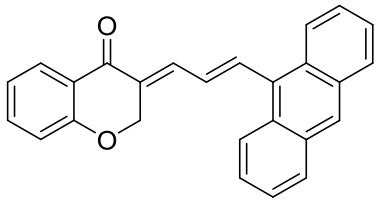
(*E*)-3-((*E*)-3-(2-methoxyphenyl)allylidene)chroman-4-one (1m)

A yellow solid; 1.15 g, 79% yield; m.p. = 105-106 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (dd, *J* = 7.9, 1.8 Hz, 1H), 7.54-7.50 (m, 2H), 7.48-7.38 (m, 2H), 7.32-7.28 (m, 1H), 7.11-7.07 (m, 2H), 6.99-6.96 (m, 2H), 6.90 (dd, *J* = 7.9, 1.8 Hz, 1H), 5.24 (d, *J* = 1.4 Hz, 2H), 3.88 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 182.0, 161.5, 157.8, 138.9, 137.2, 135.5, 130.8, 128.4, 128.0, 125.1, 122.6, 122.4, 121.8, 120.9, 117.9, 111.2, 67.1, 55.6; HRMS (ESI) m/z calcd for $C_{19}H_{17}O_3$ $[M+H]^+$ 293.1172; found 293.1178.



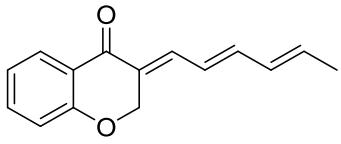
(*E*)-3-((*E*)-3-(2-bromophenyl)allylidene)chroman-4-one (1n)

A yellow solid; 1.33 g, 78% yield; m.p. = 148-150 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (dd, *J* = 7.9, 1.8 Hz, 1H), 7.65 (dd, *J* = 7.8, 1.7 Hz, 1H), 7.60 (dd, *J* = 8.0, 1.3 Hz, 1H), 7.56-7.51 (m, 1H), 7.50-7.47 (m, 1H), 7.46-7.43 (m, 1H), 7.35-7.30 (m, 1H), 7.20-7.15 (m, 1H), 7.08-7.03 (m, 1H), 7.00-6.91 (m, 2H), 5.25 (d, *J* = 1.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 182.0, 161.5, 141.4, 135.9, 135.8, 135.6, 133.6, 130.5, 130.2, 128.1, 127.8, 127.3, 125.0, 124.1, 122.5, 122.1, 118.0, 67.0; HRMS (ESI) m/z calcd for $C_{18}H_{14}O_2Br$ $[M+H]^+$ 341.0172; found 341.0172.



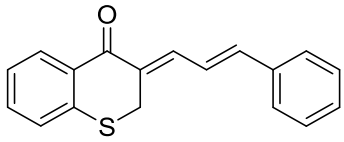
(*E*)-3-((*E*)-3-(anthracen-9-yl)allylidene)chroman-4-one (1o)

A yellow solid; 1.38 g, 76% yield; m.p. = 107-109 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.49 (s, 1H), 8.10-7.95 (m, 4H), 7.80 (dd, *J* = 8.1, 1.8 Hz, 1H), 7.60 (d, *J* = 11.1 Hz, 1H), 7.50-7.41 (m, 5H), 7.16-7.06 (m, 1H), 7.02-6.90 (m, 3H), 5.31 (d, *J* = 1.5 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 182.0, 161.5, 151.9, 138.3, 135.8, 131.9, 131.4, 131.0, 129.7, 129.6, 129.0, 128.0, 127.9, 127.1, 126.2, 125.8, 125.4, 122.3, 122.0, 117.9, 67.0; HRMS (ESI) m/z calcd for $C_{26}H_{19}O_2$ $[M+H]^+$ 363.1380; found 363.1380.



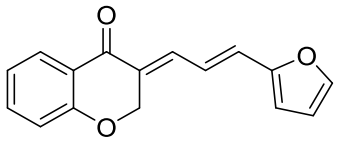
(*E*)-3-((2*E*,4*E*)-hexa-2,4-dien-1-ylidene)chroman-4-one (1v)

A yellow solid; 780.6 mg, 69% yield; m.p. = 94-96 ^{o}C;^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (dd, *J* = 7.9, 1.8 Hz, 1H), 7.49-7.40 (m, 1H), 7.37-7.30 (m, 1H), 7.07-7.00 (m, 1H), 6.95 (d, *J* = 8.3 Hz, 1H), 6.69 (dd, *J* = 14.6, 10.8 Hz, 1H), 6.36-6.18 (m, 2H), 6.08-5.96 (m 1H), 5.15 (s, 2H), 1.84 (d, *J* = 8.4 Hz, 3H) ; ^{13}C NMR (100 MHz, $CDCl_3$) δ 182.0, 161.4, 144.1, 136.8, 136.4, 131.6, 128.1, 127.9, 123.3, 122.6, 121.9, 117.9, 67.0, 18.8; HRMS (ESI) m/z calcd for $C_{15}H_{15}O_2$ $[M+H]^+$ 227.1067; found 227.1067.



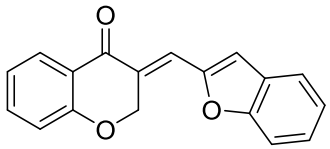
(*E*)-3-((*E*)-3-phenylallylidene)thiochroman-4-one (1w)

A yellow solid; 1.14 g, 82% yield; m.p. = 101-103 ^{o}C;^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (dd, *J* = 7.9, 1.1 Hz, 1H), 7.51-7.42 (m, 3H), 7.37-7.25 (m. 5H), 7.23-7.17 (m, 1H), 7.09-7.00 (m, 2H), 4.01 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 185.3, 142.6, 141.0, 136.8, 136.2, 132.8, 130.9, 130.4, 129.4, 128.9, 127.9, 127.4, 125.8, 122.5, 28.8; HRMS (ESI) m/z calcd for $C_{18}H_{15}OS$ $[M+H]^+$ 279.0838; found 279.0839.



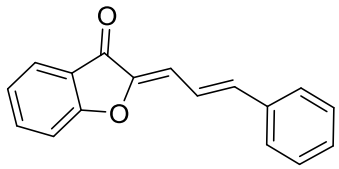
(*E*)-3-((*E*)-3-(furan-2-yl)allylidene)chroman-4-one (1x)

A yellow solid; 883 mg, 70% yield; m.p. = 138-140 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.52-7.38 (m, 3H), 7.08-7.02 (m, 1H), 6.97 (d, *J* = 8.3 Hz, 1H), 6.94-6.78 (m, 2H), 6.58 (d, *J* = 3.3 Hz, 1H), 6.48-6.44 (m, 1H), 5.23(s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 181.9, 161.5, 152.4, 144.3, 135.6, 129.3, 129.1, 128.0, 122.5, 121.9, 120.1, 118.0, 113.2, 112.6, 67.1; HRMS (ESI) m/z calcd for $C_{16}H_{13}O_3$ $[M+H]^+$ 253.0859; found 253.0859.



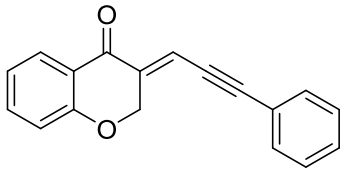
(*E*)-3-(benzofuran-2-ylmethylene)chroman-4-one (1z)

A yellow solid; 1.09 g, 79% yield; m.p. = 114-116 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (dd, *J* = 7.9, 1.8 Hz, 1H), 7.60-7.56 (m, 2H), 7.50-7.43 (m, 2H), 7.38-7.33 (m, 1H), 7.24-7.22 (m, 1H), 7.06-6.97 (m, 3H), 5.71 (d, *J* = 1.9 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 181.4, 161.6, 156.0, 152.7, 135.8, 127.9, 126.8, 123.7, 122.1, 122.0, 121.9, 118.0, 114.5, 111.5, 68.1; HRMS (ESI) m/z calcd for $C_{18}H_{13}O_3$ $[M+H]^+$ 277.0859, found 277.0856.



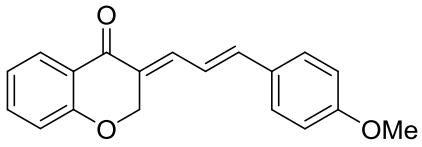
(*Z*)-2-((*E*)-3-phenylallylidene)benzofuran-3(2H)-one (1aa)

A yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (d, *J* = 5.9 Hz, 1H), 7.53-7.47 (m, 1H), 7.43 (d, *J* = 6.9 Hz, 2H), 7.29-7.19 (m, 4H), 7.18-7.12 (m, 1H), 7.09-7.03 (m, 1H), 6.89 (d, *J* = 15.8 Hz, 1H), 6.67 (d, *J* = 11.5 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 183.8, 165.5, 147.5, 141.5, 136.7, 136.3, 129.4, 128.9, 127.5, 124.5, 123.3, 122.5, 120.7, 114.4, 112.8; HRMS (ESI) m/z calcd for $C_{17}H_{13}O_2$ $[M+H]^+$ 249.0910, found 249.0910.



(*E*)-3-(3-phenylprop-2-yn-1-ylidene)chroman-4-one (1ab)

A yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, *J* = 2.6 Hz, 1H), 7.54-7.51(m, 2H), 7.42-7.35 (m, 4H), 7.09 (s, 1H), 7.01 (d, *J* = 11.6 Hz, 1H), 6.95 (d, *J* = 8.7 Hz, 1H), 5.26 (d, *J* = 1.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 181.0, 160.0, 144.1, 137.0, 136.0, 135.5, 129.9, 129.1, 129.0, 128.3, 127.9, 127.7, 127.5, 127.3, 123.4, 121.6, 119.7, 67.3; HRMS (ESI) m/z calcd for $C_{18}H_{13}O_2Br$ $[M+H]^+$ 457.1363, found 457.1365.

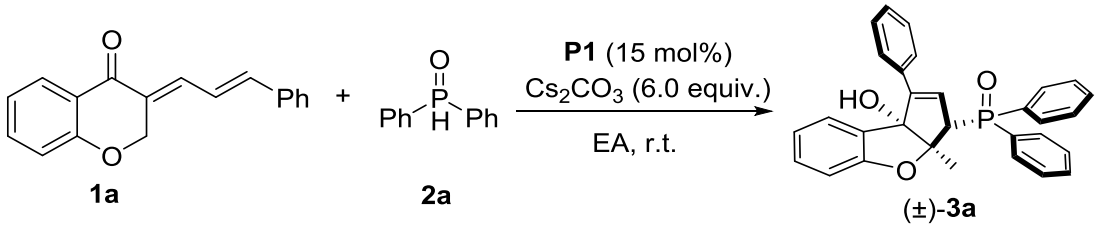


(*E*)-3-((*E*)-3-(4-methoxyphenyl)allylidene)chroman-4-one (1ac)

A yellow solid; 1.15 g, 79% yield; m.p. = 108-110 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (dd, *J* = 7.9, 1.8 Hz, 1H), 7.51-7.44 (m, 4H), 7.07-6.05 (m, 3H), 6.92-6.85 (m,

3H), 5.24(d, *J* = 1.7 Hz, 2H), 3.8 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ182.0, 161.5, 161.0, 143.3, 136.7, 135.5, 129.2, 129.0, 128.0, 122.6, 122.0, 119.7, 118.0, 114.5, 67.1, 55.5; HRMS (ESI) m/z calcd for $C_{19}H_{17}O_3$ $[M+H]^+$ 293.1172; found 293.1174.

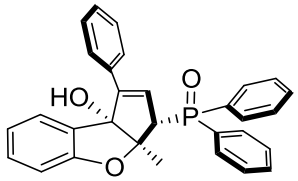
5. Representative procedure for this reaction



1a **2a** (±)-**3a**

To a solution of EA (2.5 mL) were added conjugated diene benzopyranone compounds **1a** (0.10 mmol, 1.0 equiv.), **2a** (0.20 mmol. 2.0 equiv.), Cs_2CO_3 (0.60 mmol, 6.0 equiv.) and **P1** (0.15 equiv.). The reaction mixture was stirred at room temperature for 12 h. The solvent was evaporated to give the crude product, which was directly purified by silica gel chromatography (Petroleum ether/ethy acetate = 3:1) to afford the desired product **3a.**

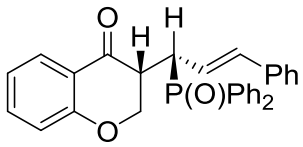
6. Characterization of the products (±)-3



((3*S,3*a**S**,8*b**S**)-8b-hydroxy-3a-methyl-1-phenyl-3a,8b-dihydro-3H-cyclopenta[*b*]benzofuran-3-yl)diphenylphosphine oxide ((±)-3a)**

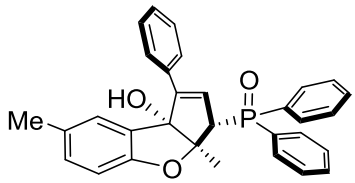
A white solid; 24.6 mg, 53% yield; m.p. = 178-181 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05-7.96 (m, 2H), 7.78-7.69 (m, 2H), 7.62-7.56 (m, 5H), 7.52-7.42 (m, 3H), 7.30-7.22 (m, 3H), 7.05 (td, *J* = 7.6, 1.4 Hz, 1H), 6.75 (td, *J* = 7.6, 0.9 Hz, 1H), 6.66 (d, *J* = 8.0 Hz, 1H), 5.57 (t, *J* = 3.1 Hz, 1H), 5.22 (s, 1H), 4.22 (dd, *J* = 5.2, 2.9 Hz, 1H), 1.31 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.6, 149.1 (d, *J* = 10.0 Hz), 134.3 (d, *J* = 3.4 Hz), 132.8 (d, *J* = 16.5 Hz), 132.3 (d, *J* = 2.8 Hz), 132.1 (d, *J* = 2.6 Hz), 130.8 (d, *J* = 15.3 Hz), 130.8 (d, *J* = 2.7 Hz), 129.3, 129.1, 129.1, 128.9, 128.1, 128.0, 127.6 (d, *J* = 2.3

Hz), 125.7, 122.2 (d, *J* = 8.7 Hz), 121.1, 110.2, 99.2 (d, *J* = 3.7 Hz), 92.9, 52.0 (d, *J* = 64.7 Hz), 18.1; ^{31}P NMR (162 MHz, $CDCl_3$) δ 29.59; HRMS (ESI) m/z calcd for $C_{30}H_{26}O_3P$ $[M+H]^+$ 465.1614; found 465.1609.



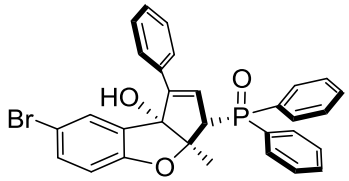
(*R)-3-((*S**,*E*)-1-(diphenylphosphoryl)-3-phenylallyl)chroman-4-one ((±)-3a')**

A white solid; m.p. = 173-175 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01-7.91 (m, 2H), 7.87-7.77 (m, 3H), 7.54-7.47 (m, 3H), 7.44-7.36 (m, 4H), 7.24-7.12 (m, 5H), 6.97-6.91 (m, 1H), 6.90 (d, *J* = 8.4 Hz, 1H), 6.58 (dd, *J* = 15.7, 3.2 Hz, 1H), 6.28-6.16 (m, 1H), 5.31 (dd, *J* = 11.4,, 5.4 Hz, 1H), 4.58-4.45 (m, 2H), 3.30-3.17 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.3 (d, *J* = 13.2 Hz), 161.8, 138.1 (d, *J* = 12.0 Hz), 136.3 (d, *J* = 1.6 Hz), 136.2, 132.3, 132.2 (d, *J* = 2.6 Hz), 131.8 (d, *J* = 3.0 Hz), 131.3, 131.1 (d, *J* = 2.8 Hz), 131.0 (d, *J* = 2.8 Hz), 130.9, 129.2 (d, *J* = 11.3 Hz), 128.6 (d, *J* = 11.7 Hz), 128.5, 127.7 (d, *J* = 45.1 Hz), 126.4, 121.4, 120.8 (d, *J* = 1.4 Hz), 118.8 (d, *J* = 6.1 Hz), 118.0, 68.7, 46.1, 39.4 (d, *J* = 71.7 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 34.32; HRMS (ESI) m/z calcd for $C_{30}H_{26}O_3P$ $[M+H]^+$ 465.1614; found 465.1614.



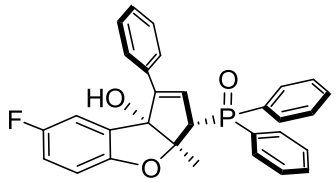
((3*S,3*aS**,8*bS**)-8b-hydroxy-3a,7-dimethyl-1-phenyl-3a,8b-dihydro-3H-cyclopenta[*b*]benzofuran-3-yl)diphenylphosphine oxide ((±)-3b)**

A white solid; 25.8 mg, 54% yield; m.p. = 153-155 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04-7.95 (m, 2H), 7.77-7.70 (m, 2H), 7.63-7.54 (m, 5H), 7.49-7.40 (m, 3H), 7.28-7.23 (m, 3H), 7.12 (d, *J* = 1.8 Hz, 1H), 6.84 (dd, *J* = 8.1, 1.1 Hz, 1H), 6.56 (d, *J* = 8.1 Hz, 1H), 5.60 (t, *J* = 3.1 Hz, 1H), 5.21 (s, 1H), 4.23 (dd, *J* = 5.3, 3.0 Hz, 1H), 2.14 (s, 3H), 1.31 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.6 , 149.1 (d, *J* = 9.9 Hz), 134.3 (d, *J* = 3.4 Hz), 132.9 (d, *J* = 15.7 Hz), 132.3 (d, *J* = 2.8 Hz), 132.1 (d, *J* = 2.7 Hz), 132.0, 131.8, 130.8 (d, *J* = 7.0 Hz), 130.8 (d, *J* = 7.1 Hz), 130.4, 129.5, 129.2 (d, *J* = 11.6 Hz), 129.0 (d, *J* = 11.8 Hz), 128.1, 128.9, 127.6 (d, *J* = 2.2 Hz), 126.2, 122.2 (d, *J* = 8.7 Hz), 109.7, 99.2 (d, *J* = 3.6 Hz), 92.9 (d, *J* = 1.8 Hz), 52.0 (d, *J* = 64.5 Hz), 20.9, 18.0; ^{31}P NMR (162 MHz, $CDCl_3$) δ 29.61; HRMS (ESI) m/z calcd for $C_{31}H_{28}O_3P$ $[M+H]^+$ 479.1771; found 479.1778.



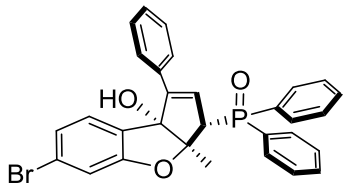
((3*S,3*aS**,8*bS**)-7-bromo-8b-hydroxy-3a-methyl-1-phenyl-3a,8b-dihydro-3H-cyclopenta[*b*]benzofuran-3-yl)diphenylphosphine oxide ((±)-3c)**

A white solid; 29.9 mg, 55% yield; m.p. = 141-143 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03-7.95 (m, 2H), 7.76-7.67 (m, 2H), 7.61-7.53 (m, 5H), 7.51-7.41 (m, 4H), 7.38 (d, *J* = 2.1 Hz, 1H), 7.30-7.26 (m, 2H), 7.14 (dd, *J* = 8.5, 2.2 Hz, 1H), 6.53 (d, *J* = 8.5 Hz, 1H), 5.59 (t, *J* = 3.1 Hz, 1H), 5.29 (s, 1H), 4.20 (dd, *J* = 5.3, 2.9 Hz, 1H), 1.28 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.8 , 148.7 (d, *J* = 10.0 Hz), 133.9 (d, *J* = 3.4 Hz), 132.7, 132.6 (d, *J* = 5.0 Hz), 132.4 (d, *J* = 2.7 Hz), 132.3 (d, *J* = 2.9 Hz), 132.0, 131.9, 131.6 (d, *J* = 23.2 Hz), 130.9 (d, *J* = 5.1 Hz), 130.8 (d, *J* = 5.4 Hz), 130.7, 129.8, 129.3 (d, *J* = 11.7 Hz), 129.0 (d, *J* = 12.1 Hz), 128.8, 128.7, 128.4, 128.3, 127.4 (d, *J* = 2.3 Hz), 122.7 (d, *J* = 8.8 Hz), 113.0, 111.9, 100.1 (d, *J* = 3.7 Hz), 92.7, 51.9 (d, *J* = 64.2 Hz), 18.0; ^{31}P NMR (162 MHz, $CDCl_3$) δ 29.60; HRMS (ESI) m/z calcd for $C_{30}H_{25}BrO_3P$ $[M+H]^+$ 543.0719; found 543.0723.



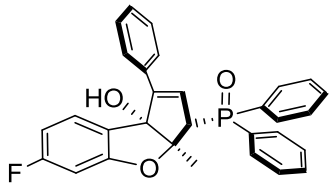
((3*S,3*aS**,8*bS**)-7-fluoro-8b-hydroxy-3a-methyl-1-phenyl-3a,8b-dihydro-3H-cyclopenta[*b*]benzofuran-3-yl)diphenylphosphine oxide ((±)-3d)**

A white solid; 26.0 mg, 54% yield; m.p. = 145-146 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05-7.96 (m, 2H), 7.78-7.68 (m, 2H), 7.64-7.54 (m, 5H), 7.52-7.40 (m, 3H), 7.32-7.21 (m, 3H), 7.01 (dd, *J* = 7.9, 2.7 Hz, 1H), 6.72 (td, *J* = 8.8, 2.8 Hz, 1H), 6.57 (dd, *J* = 8.7, 4.0 Hz, 1H), 5.62 (s, 1H), 5.37 (s, 1H), 4.28-4.20 (m, 1H), 1.32 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.6 (d, *J* = 236.8 Hz), 154.6, 148.7 (d, *J* = 10.0 Hz), 134.1 (d, *J* = 3.0 Hz), 132.6 (d, *J* = 5.0 Hz), 132.4 (d, *J* = 2.8 Hz), 132.2 (d, *J* = 2.9 Hz), 131.9 (d, *J* = 10.4 Hz), 131.6 (d, *J* = 22.3 Hz), 130.9 (d, *J* = 5.4 Hz), 130.8 (d, *J* = 5.8 Hz), 129.2 (d, *J* = 21.6 Hz), 129.0 (d, *J* = 21.5 Hz), 128.7 (d, *J* = 13.2 Hz), 128.3, 128.2, 127.4 (d, *J* = 2.2 Hz), 122.7 (d, *J* = 8.6 Hz), 115.4 (d, *J* = 24.4 Hz), 112.8 (d, *J* = 24.8 Hz), 110.5 (d, *J* = 8.5 Hz), 100.0 (d, *J* = 3.9 Hz), 92.8, 52.0 (d, *J* = 64.3 Hz), 17.9; ^{31}P NMR (162 MHz, $CDCl_3$) δ 29.67; ^{19}F NMR (376 MHz, $CDCl_3$) δ -122.89; HRMS (ESI) m/z calcd for $C_{30}H_{24}FNaO_3P$ $[M+Na]^+$ 505.1339; found 505.1340.



((3*S,3*aS**,8*bS**)-6-bromo-8b-hydroxy-3a-methyl-1-phenyl-3a,8b-dihydro-3H-cyclopenta[*b*]benzofuran-3-yl)diphenylphosphine oxide ((±)-3e)**

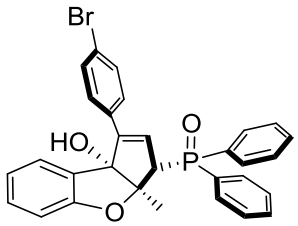
A white solid; 31.5 mg, 58% yield; m.p. = 136-138 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04-7.95 (m, 2H), 7.76-7.68 (m, 2H), 7.61-7.54 (m, 5H), 7.49-7.41 (m, 3H), 7.32-7.26 (m, 2H), 6.99 (dd, *J* = 7.9, 2.7 Hz, 1H), 6.72 (td, *J* = 8.8, 2.8 Hz, 1H), 6.56 (dd, *J* = 8.8, 4.0 Hz, 1H), 5.60 (t, *J* = 3.2 Hz, 1H), 5.30 (s, 1H), 4.21 (dd, *J* = 5.3, 2.9 Hz, 1H), 1.30 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.8 , 156.5, 154.6, 148.7 (d, *J* = 9.4 Hz), 134.1 (d, *J* = 3.5 Hz), 132.7 (d, *J* = 15.7 Hz), 132.4 (d, *J* = 2.7 Hz), 132.2 (d, *J* = 2.7 Hz), 131.7 (d, *J* = 22.6 Hz), 130.9 (d, *J* = 5.5 Hz), 130.8 (d, *J* = 5.8 Hz), 129.3 (d, *J* = 11.6 Hz), 129.0 (d, *J* = 12.0 Hz), 128.3, 128.2, 127.5 (d, *J* = 2.2 Hz), 122.7 (d, *J* = 8.7 Hz), 115.4 (d, *J* = 24.4 Hz), 112.9 (d, *J* = 25.2 Hz), 110.5 (d, *J* = 8.4 Hz), 100.0 (d, *J* = 3.7 Hz), 92.8, 52.0 (d, *J* = 64.2 Hz), 17.9; ^{31}P NMR (162 MHz, $CDCl_3$) δ 29.61; HRMS (ESI) m/z calcd for $C_{30}H_{25}BrO_3P$ $[M+H]^+$ 543.0719; found 543.0719.



((3*S,3*aS**,8*bS**)-6-fluoro-8b-hydroxy-3a-methyl-1-phenyl-3a,8b-dihydro-3H-cyclopenta[*b*]benzofuran-3-yl)diphenylphosphine oxide ((±)-3f)**

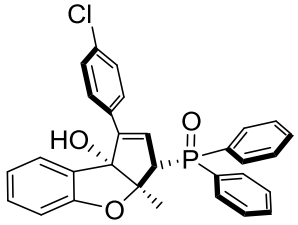
A white solid; 27.5 mg, 57% yield; m.p. = 147-148 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05-7.97 (m, 2H), 7.94-7.87 (m, 1H), 7.77-7.70 (m, 2H), 7.60-7.56 (m, 4H), 7.49-7.43 (m, 3H), 7.30-7.23 (m, 2H), 7.23-7.16 (m, 2H), 6.48-6.40 (m, 1H), 6.38 (dd, *J* = 9.3, 2.2 Hz, 1H), 5.57 (t, *J* = 3.0 Hz, 1H), 5.25 (s, 1H), 4.21 (dd, *J* = 5.2, 2.8 Hz, 1H), 1.31 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.7 (d, *J* = 243.3 Hz), 162.5, 159.8 (d, *J* = 13.1 Hz), 149.0 (d, *J* = 9.8 Hz), 134.1 (d, *J* = 3.4 Hz), 132.6, 132.4 (d, *J* = 2.8 Hz), 132.2 (d, *J* = 2.6 Hz), 131.9 (d, *J* = 10.3 Hz), 130.9 (d, *J* = 4.0 Hz), 130.8 (d, *J* = 4.3 Hz), 129.3 (d, *J* = 11.7 Hz), 129.0 (d, *J* = 11.9 Hz), 128.7 (d, *J* = 13.3 Hz), 128.2, 128.1, 127.5 (d, *J* = 2.3 Hz), 126.2 (d, *J* = 10.5 Hz), 124.4 (d, *J* = 69.4 Hz), 122.1 (d, *J* = 8.6 Hz), 120.9 (d, *J* = 4.8 Hz), 107.8 (d, *J* = 22.6 Hz), 100.4 (d, *J* = 3.8 Hz), 98.8 (d, *J* = 26.3 Hz), 92.3, 51.9 (d, *J* = 64.5 Hz), 18.1; ^{31}P NMR (162 MHz, $CDCl_3$) δ 29.61; ^{19}F NMR (376 MHz,

$CDCl_3$) δ -112.50; HRMS (ESI) m/z calcd for $C_{30}H_{25}FO_3P$ $[M+H]^+$ 483.1520; found 483.1521.



((3*S,3*aS**,8*bS**)-1-(4-bromophenyl)-8b-hydroxy-3a-methyl-3a,8b-dihydro-3H-cyclopenta[*b*]benzofuran-3-yl)diphenylphosphine oxide ((±)-3g)**

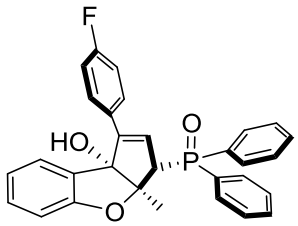
A white solid; 29.9 mg, 55% yield; m.p. = 160-161 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06-7.95 (m, 2H), 7.76-7.67 (m, 2H), 7.64-7.54 (m, 3H), 7.54-7.42 (m, 5H), 7.40-7.35 (m, 2H), 7.27-7.24 (m, 1H), 7.10-7.03 (m, 1H), 6.77 (td, *J* = 7.4, 0.6 Hz, 1H), 6.66 (d, *J* = 8.0 Hz, 1H), 5.56 (t, *J* = 3.1 Hz, 1H), 5.27 (s, 1H), 4.20 (dd, *J* = 5.2, 2.9 Hz, 1H), 1.29 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.6, 148.1 (d, *J* = 9.8 Hz), 133.2 (d, *J* = 3.5 Hz), 132.7 (d, *J* = 6.2 Hz), 132.4 (d, *J* = 2.8 Hz), 132.2 (d, *J* = 2.7 Hz), 132.0 (d, *J* =13.1 Hz), 131.4, 130.9 (d, *J* = 9.1 Hz), 130.8 (d, *J* = 9.3 Hz), 129.3, 129.2, 129.2 (d, *J* = 2.4 Hz), 129.1 (d, *J* = 12.0 Hz), 127.9, 125.6, 122.8 (d, *J* = 8.7 Hz), 122.2, 121.3, 110.3, 99.1 (d, *J* = 3.7 Hz), 92.7, 52.1 (d, *J* = 64.2 Hz), 18.0; ^{31}P NMR (162 MHz, $CDCl_3$) δ 29.70; HRMS (ESI) m/z calcd for $C_{30}H_{25}BrO_3P$ $[M+H]^+$ 543.0719; found 543.0719.



((3*S,3*aS**,8*bS**)-1-(4-chlorophenyl)-8b-hydroxy-3a-methyl-3a,8b-dihydro-3H-cyclopenta[*b*]benzofuran-3-yl)diphenylphosphine oxide ((±)-3h)**

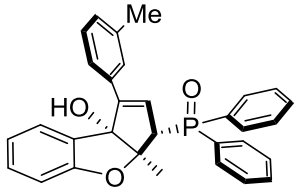
A white solid; 27.4 mg, 55% yield; m.p. = 168-170 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05-7.95 (m, 2H), 7.77-7.67 (m, 2H), 7.62-7.55 (m, 3H), 7.55-7.51 (m, 2H), 7.51-7.42 (m, 3H), 7.28-7.20 (m, 3H), 7.06 (td, *J* = 7.9, 1.3 Hz, 1H), 6.76 (t, *J* = 7.5 Hz, 1H), 6.66 (d, *J* = 8.0 Hz, 1H), 5.55 (t, *J* = 3.0 Hz, 1H), 5.45-5.15 (m, 1H), 4.21 (dd, *J* = 5.4, 2.9 Hz, 1H), 1.29 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.6 , 148.1 (d, *J* = 9.9 Hz), 133.9, 132.7 (d, *J* = 3.4 Hz), 132.7 (d, *J* = 6.3 Hz), 132.4 (d, *J* = 2.6 Hz), 132.2 (d, *J* = 2.8 Hz), 131.7 (d, *J* = 13.0 Hz), 130.9 (d, *J* = 9.0 Hz), 130.8 (d, *J* = 9.4 Hz), 129.3, 129.2, 129.1 (d, *J* = 11.9 Hz), 128.9 (d, *J* = 2.3 Hz), 128.4, 127.9, 125.6, 122.7 (d, *J* = 8.7 Hz), 121.2, 110.3, 99.1 (d, *J* = 3.6 Hz), 92.8, 52.1 (d, *J* = 64.3 Hz), 18.0; ^{31}P NMR (162 MHz,

$CDCl_3$) δ 29.75; HRMS (ESI) m/z calcd for $C_{30}H_{25}ClO_3P$ $[M+H]^+$ 499.1224, found 499.1226.



((3*S,3*aS**,8*bS**)-1-(4-fluorophenyl)-8b-hydroxy-3a-methyl-3a,8b-dihydro-3H-cyclopenta[*b*]benzofuran-3-yl)diphenylphosphine oxide ((±)-3i)**

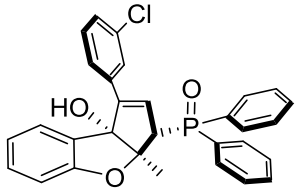
A white solid; 28.0 mg, 58% yield; m.p. = 176-178 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04-7.96 (m, 2H), 7.76-7.68 (m, 2H), 7.61-7.53 (m, 5H), 7.51-7.42 (m, 3H), 7.27-7.23 (m, 1H), 7.06 (t, *J* = 7.6 Hz, 1H), 6.97-6.91 (m, 2H), 6.76 (t, *J* = 7.4 Hz, 1H), 6.67 (d, *J* = 8.0 Hz, 1H), 5.52 (t, *J* = 3.2 Hz, 1H), 5.25 (s, 1H), 4.22 (dd, *J* = 5.2, 2.9 Hz, 1H), 1.20 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.7 (d, *J* = 245.5 Hz), 158.7, 148.2 (d, *J* = 9.9 Hz), 132.8 (d, *J* = 8.5 Hz), 132.4 (d, *J* = 2.8 Hz), 132.2 (d, *J* = 2.8 Hz), 130.9 (d, *J* = 9.1 Hz), 132.8 (d, *J* = 8.8 Hz), 129.4 (d, *J* = 2.3 Hz), 129.3, 129.3 (d, *J* = 2.2 Hz), 129.2 (d, *J* = 2.5 Hz), 129.1 (d, *J* = 12.0 Hz), 128.0, 125.6, 122.1 (d, *J* = 8.7 Hz), 121.4, 115.1 (d, *J* = 21.1 Hz), 110.3, 99.1 (d, *J* = 3.6 Hz), 92.8 (d, *J* = 2.2 Hz), 51.9 (d, *J* = 64.3 Hz), 18.0; ^{31}P NMR (162 MHz, $CDCl_3$) δ 29.71; ^{19}F NMR (376 MHz, $CDCl_3$) δ -113.82; HRMS (ESI) m/z calcd for $C_{30}H_{25}FO_3P$ $[M+H]^+$ 483.1520, found 483.1521.



((3*S,3*aS**,8*bS**)-8b-hydroxy-3a-methyl-1-(m-tolyl)-3a,8b-dihydro-3H-cyclopenta[*b*]benzofuran-3-yl)diphenylphosphine oxide ((±)-3j)**

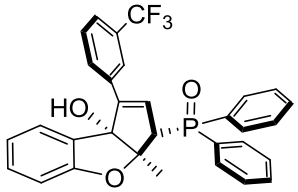
A white solid; 26.8 mg, 56% yield; m.p. = 158-161 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06-7.96 (m, 2H), 7.78-7.70 (m, 2H), 7.62-7.54 (m, 3H), 7.54-7.36 (m, 5H), 7.29 (dd, *J* = 7.4, 1.1 Hz, 1H), 7.15 (t, *J* = 7.6 Hz, 1H), 7.08-7.02 (m, 2H), 6.76 (td, *J* = 7.4, 0.8 Hz, 1H), 6.67 (d, *J* = 8.0 Hz, 1H), 5.57 (t, *J* = 3.0 Hz, 1H), 5.21 (s, 1H), 4.23 (dd, *J* = 5.2, 2.9 Hz, 1H), 2.29 (s, 3H), 1.31 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.6 , 149.3 (d, *J* = 9.9 Hz), 137.6, 134.2 (d, *J* = 3.4 Hz), 132.9 (d, *J* = 18.1 Hz), 132.3 (d, *J* = 2.8 Hz), 132.1 (d, *J* = 2.7 Hz), 131.9 (d, *J* = 25.2 Hz), 130.8 (dd, *J* = 8.9, 4.9 Hz), 129.1 (dd, *J* = 20.3, 11.6 Hz), 128.9 (d, *J* = 23.3 Hz), 128.3 (d, *J* = 2.2 Hz), 128.2, 128.0, 125.8, 124.7 (d, *J* = 2.2 Hz), 122.0 (d, *J* = 8.7 Hz), 121.1, 110.2, 99.2 (d, *J* = 3.7 Hz), 92.9, 52.0 (d, *J*

= 64.7 Hz), 21.6, 18.1; ^{31}P NMR (162 MHz, $CDCl_3$) δ 29.60; HRMS (ESI) m/z calcd for $C_{31}H_{28}O_3P$ $[M+H]^+$ 479.1771, found 479.1771.



((3*S,3*aS**,8*bS**)-7-bromo-8b-hydroxy-3a-methyl-1-phenyl-3a,8b-dihydro-3H-cyclopenta[*b*]benzofuran-3-yl)diphenylphosphine oxide ((±)-3k)**

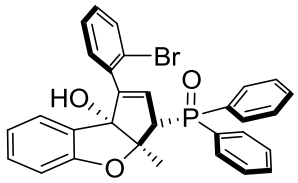
A white solid; 28.4 mg, 57% yield; m.p. = 165-167 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04-7.96 (m, 2H), 7.76-7.69 (m, 2H), 7.63-7.42 (m, 9H), 7.22-7.18 (m, 2H), 7.07 (td, *J* = 7.8, 1.3 Hz, 1H), 6.77 (td, *J* = 7.5, 1.0 Hz, 1H), 6.66 (d, *J* = 8.0 Hz, 1H), 5.60 (t, *J* = 3.1 Hz, 1H), 5.29 (s, 1H), 4.23 (dd, *J* = 5.4, 2.9 Hz, 1H), 1.29 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.5 , 147.8 (d, *J* = 10.0 Hz), 136.0 (d, *J* = 3.0 Hz), 133.0, 132.5 (d, *J* = 13.1 Hz), 132.3 (d, *J* = 2.7 Hz), 132.1 (d, *J* = 2.7 Hz), 131.8 (d, *J* = 10.4 Hz), 131.5 (d, *J* = 20.2 Hz), 130.7 (d, *J* = 9.4 Hz), 130.6 (d, *J* = 9.4 Hz), 129.3 (d, *J* = 13.1 Hz), 129.1 (d, *J* = 2.6 Hz), (d, *J* = 12.0 Hz), 128.6 (d, *J* = 13.5 Hz), 128.0, 127.8, 127.5 (d, *J* = 2.3 Hz), 125.6 (d, *J* = 2.2 Hz), 125.5, 123.3 (d, *J* = 8.7 Hz), 121.2, 110.2, 99.0 (d, *J* = 3.7 Hz), 92.6 (d, *J* = 2.1 Hz), 52.0 (d, *J* = 64.2 Hz), 17.9; ^{31}P NMR (162 MHz, $CDCl_3$) δ 29.72; HRMS (ESI) m/z calcd for $C_{30}H_{25}ClO_3P$ $[M+H]^+$ 499.1224; found 499.1226.



((3*S,3*aS**,8*bS**)-8b-hydroxy-3a-methyl-1-(3-(trifluoromethyl)phenyl)-3a,8b-dihydro-3H-cyclopenta[*b*]benzofuran-3-yl)diphenylphosphine oxide ((±)-3l)**

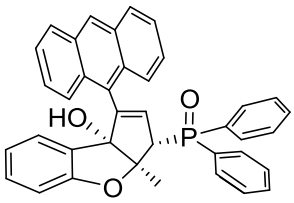
A white solid; 33.6 mg, 63% yield; m.p. = 189-191 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05-7.95 (m, 2H), 7.85-7.77 (m, 2H), 7.77-7.69 (m, 2H), 7.63-7.56 (m, 3H), 7.53-7.43 (m, 4H), 7.38 (td, *J* = 7.8 Hz, 1H), 7.27-7.22 (m, 1H), 7.07 (td, *J* = 7.8, 1.3 Hz, 1H), 6.77 (d, *J* = 7.4, 0.6 Hz, 1H), 6.67 (d, *J* = 8.0 Hz, 1H), 5.66 (t, *J* = 3.1 Hz, 1H), 5.36 (s, 1H), 4.25 (dd, *J* = 5.4, 3.0 Hz, 1H), 1.30 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.7, 147.8 (d, *J* = 9.7 Hz), 135.0 (d, *J* = 2.8 Hz), 132.6 (d, *J* = 2.9 Hz), 132.5 (d, *J* = 38.8 Hz), 132.3 (d, *J* = 2.6 Hz), 131.9 (d, *J* = 10.3 Hz), 131.6 (d, *J* = 17.2 Hz), 130.8 (d, *J* = 10.5 Hz), 130.7 (d, *J* = 9.4 Hz), 129.8, 129.3 (d, *J* = 5.9 Hz), 129.2 (d, *J* = 4.1 Hz), 128.9 (d, *J* = 28.2 Hz), 128.7, 127.8，125.5，124.7 (d, *J* =10.4 Hz), 124.4, 124.2 (q, *J* = 271.0 Hz), 123.7 (d, *J* = 8.7 Hz), 121.3, 120.9 (d, *J* = 4.7 Hz), 110.4, 99.1 (d, *J* = 3.6 Hz), 92.7 (d, *J*

= 1.8 Hz), 52.1 (d, *J* = 63.9 Hz), 18.0; ^{31}P NMR (162 MHz, $CDCl_3$) δ 29.82; ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.62; HRMS (ESI) m/z calcd for $C_{31}H_{25}F_3O_3P$ $[M+H]^+$ 533.1488; found 533.1490.



((3*S,3*aS**,8*bS**)-1-(2-bromophenyl)-8b-hydroxy-3a-methyl-3a,8b-dihydro-3H-cyclopenta[*b*]benzofuran-3-yl)diphenylphosphine oxide ((±)-3n)**

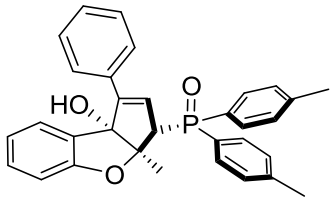
A white solid; 26.0 mg, 48% yield; m.p. = 240-241 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07-7.97 (m, 2H), 7.83-7.73 (m, 2H), 7.63-7.56 (m, 3H), 7.48-7.38 (m, 4H), 7.25-7.19 (m, 2H), 7.15-7.05 (m, 2H), 6.78-6.68 (m, 3H), 5.47 (t, *J* = 2.8 Hz, 1H), 5.12 (s, 1H), 4.29 (dd, *J* = 5.0, 3.0 Hz, 1H), 1.33 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.0, 147.5 (d, *J* = 10.1 Hz), 132.9, 132.7, 132.5, 132.4 (d, *J* = 2.7 Hz), 132.2 (d, *J* = 2.6 Hz), 131.2 (d, *J* = 3.3 Hz), 130.9 (d, *J* = 0.9 Hz), 130.8 (d, *J* = 1.2 Hz), 129.3 (d, *J* = 1.1 Hz), 129.2, 129.1 (d, *J* = 2.4 Hz), 129.0, 127.2, 126.5, 126.1 (d, *J* = 8.2 Hz), 125.0, 121.2, 110.1, 98.1 (d, *J* = 3.7 Hz), 93.7 (d, *J* = 2.4 Hz), 52.2 (d, *J* = 64.0 Hz), 18.1; ^{31}P NMR (162 MHz, $CDCl_3$) δ 29.45; HRMS (ESI) m/z calcd for $C_{30}H_{25}BrO_3P$ $[M+H]^+$ 543.0719; found 543.0723.



((3*S,3*aS**,8*bS**)-1-(anthracen-9-yl)-8b-hydroxy-3a-methyl-3a,8b-dihydro-3H-cyclopenta[*b*]benzofuran-3-yl)diphenylphosphine oxide ((±)-3o)**

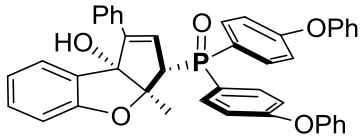
A white solid; 26.6 mg, 46% yield; m.p. = 189-190 ^{o}C ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.93 (d, *J* = 9.0, 0.6 Hz, 1H), 8.19-8.07 (m, 2H), 7.99 (d, *J* = 8.5 Hz, 1H), 7.95-7.85 (m, 2H), 7.80 (d, *J* = 8.6 Hz, 1H), 7.75-7.69 (m, 1H), 7.68-7.61 (m, 3H), 7.57-7.49 (m, 1H), 7.43-7.33 (m, 3H), 7.20-7.12 (m, 1H), 7.07-6.98 (m, 1H), 6.80 (d, *J* = 8.0 Hz, 1H), 6.75-6.66 (m, 2H), 6.28 (td, *J* = 7.4, 0.8 Hz, 1H), 6.10 (d, *J* = 7.4, 1.0 Hz, 1H), 5.64 (t, *J* = 2.8 Hz, 1H), 5.20 (s, 1H), 4.50 (dd, *J* = 4.4, 2.8 Hz, 1H), 1.45 (s, 3H);^{13}C NMR (100 MHz, $CDCl_3$) δ 159.0, 146.9 (d, *J* = 10.0 Hz), 132.9, 134.4 (d, *J* = 38.9 Hz), 132.3 (d, *J* = 38.8 Hz), 131.8 (d, *J* = 16.9 Hz), 131.6 (d, *J* = 20.3 Hz), 131.3,

130.9 (d, *J* = 9.0 Hz), 130.8 (d, *J* = 9.1 Hz), 129.4 (d, *J* = 11.7Hz), 129.2 (d, *J* = 4.8 Hz), 129.0, 128.2 (d, *J* = 18.3 Hz), 127.9 (d, *J* = 8.3 Hz), 127.5, 126.9, 125.7 (d, *J* = 20.5 Hz), 125.4 (d, *J* = 9.6 Hz), 122.4 (d, *J* = 27.5 Hz), 121.4, 109.9, 98.5 (d, *J* = 3.8 Hz), 95.4, 52.8 (d, *J* = 60.4 Hz), 18.6; ^{31}P NMR (162 MHz, $CDCl_3$) δ 30.66; HRMS (ESI) m/z calcd for $C_{39}H_{32}O_3P$ $[M+H]^+$ 579.2084; found 579.2080.



((3*S,3*aS**,8*bS**)-8b-hydroxy-3a-methyl-1-phenyl-3a,8b-dihydro-3H-cyclopenta[*b*]benzofuran-3-yl)di-p-tolylphosphine oxide ((±)-3p)**

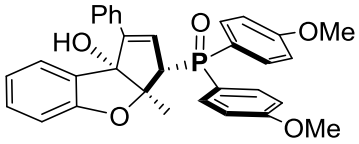
A white solid; 30.0 mg, 61% yield; m.p. = 163-165 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (dd, *J* = 11.2, 8.1 Hz, 2H), 7.66-7.57 (m, 4H), 7.37 (dd, *J* = 8.0, 2.6 Hz, 2H), 7.32 (dd, *J* = 7.5, 1.0 Hz, 1H), 7.29-7.18 (m, 5H), 7.05 (td, *J* = 7.9, 1.4 Hz, 1H), 6.75 (td, *J* = 7.4, 0.7 Hz, 1H), 6.68 (d, *J* = 8.0 Hz, 1H), 5.62 (d, *J* = 3.1 Hz, 1H), 5.37 (s, 1H), 4.22 (dd, *J* =5.5, 2.9 Hz, 1H), 2.42 (s, 3H), 2.34 (s, 3H), 1.35 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.7, 148.8 (d, *J* = 9.9 Hz), 142.7 (d, *J* = 2.8 Hz), 142.5 (d, *J* = 2.7 Hz), 134.4 (d, *J* = 3.2 Hz), 130.8 (d, *J* = 1.4 Hz), 130.7 (d, *J* = 1.9 Hz), 129.9 (d, *J* = 12.1 Hz), 129.7 (d, *J* = 8.0 Hz), 129.7 (d, *J* = 12.3 Hz), 128.9, 128.7 (d, *J* = 15.2 Hz), 128.2, 128.0, 127.9, 127.6 (d, *J* = 2.1 Hz), 125.7, 122.5 (d, *J* = 8.7 Hz), 121.0, 110.1, 99.2 (d, *J* = 3.6 Hz), 92.8 (d, *J* = 1.9 Hz), 52.1 (d, *J* = 64.4 Hz), 21.6 (d, *J* = 10.2 Hz), 18.0; ^{31}P NMR (162 MHz, $CDCl_3$) δ 30.15; HRMS (ESI) m/z calcd for $C_{32}H_{30}O_3P$ $[M+H]^+$ 493.1927; found 493.1929.



((3*S,3*aS**,8*bS**)-8b-hydroxy-3a-methyl-1-phenyl-3a,8b-dihydro-3H-cyclopenta[*b*]benzofuran-3-yl)bis(4-phenoxyphenyl)phosphine oxide ((±)-3q)**

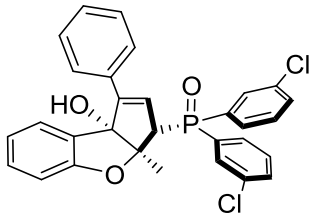
A white solid; 40.8mg, 63% yield; m.p. = 181-183 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.63 (dd, *J* = 10.6, 8.6 Hz, 1H), 7.70-7.58 (m, 4H), 7.45-7.34 (m, 4H), 7.32-7.18 (m, 6H), 7.14 (d, *J* = 8.6, 2.0 Hz, 2H), 7.09 (d, *J* = 8.3 Hz, 2H), 7.07-6.98 (m, 5H), 6.76 (t, *J*

= 7.4 Hz, 1H), 6.67 (d, *J* = 8.0 Hz, 1H), 5.64 (d, *J* = 2.8 Hz, 1H), 5.24 (s, 1H), 4.16 (dd, *J* = 4.9, 2.8 Hz, 1H), 1.35 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.4 (d, *J* = 2.9 Hz), 161.3 (d, *J* = 2.8 Hz), 158.6, 155.3 (d, *J* = 4.5 Hz), 149.1 (d, *J* = 9.8 Hz), 134.4 (d, *J* = 3.3 Hz), 132.8 (d, *J* = 10.5 Hz), 130.2 (d, *J* = 6.3 Hz), 129.1, 128.1, 128.0, 127.6 (d, *J* = 1.9 Hz), 126.2, 125.7, 125.2 (d, *J* = 8.1 Hz), 124.9 (d, *J* = 7.3 Hz), 122.3 (d, *J* = 8.7 Hz), 121.1, 120.4 (d, *J* = 1.3 Hz), 118.1 (d, *J* = 12.6 Hz), 117.9 (d, *J* = 12.7 Hz), 110.2, 99.2 (d, *J* = 3.5 Hz), 92.8, 52.2 (d, *J* = 65.3 Hz), 18.1; ^{31}P NMR (162 MHz, $CDCl_3$) δ 29.50; HRMS (ESI) m/z calcd for $C_{42}H_{34}O_5P$ $[M+H]^+$ 649.2138; found 649.2140.



((3*S,3*aS**,8*bS**)-8b-hydroxy-3a-methyl-1-phenyl-3a,8b-dihydro-3H-cyclopenta[*b*]benzofuran-3-yl)bis(4-methoxyphenyl)phosphine oxide ((±)-3r)**

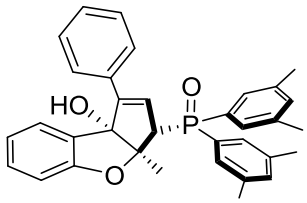
A white solid; 32.5 mg, 62% yield; m.p. = 175-177 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (dd, *J* = 10.7, 8.7 Hz, 2H), 7.64-7.56 (m, 4H), 7.32-7.20 (m, 5H), 7.07 (d, *J* = 8.8, 2.0 Hz, 2H), 7.03 (dd, *J* = 7.6, 1.0 Hz, 1H), 6.92 (dd, *J* = 8.7, 2.1 Hz, 2H), 6.74 (td, *J* = 7.4, 0.7 Hz, 1H), 6.65 (d, *J* = 8.0 Hz, 1H), 5.58 (t, *J* = 3.0 Hz, 1H), 5.31 (s, 1H), 4.11 (dd, *J* = 5.4, 2.9 Hz, 1H), 3.87 (s, 3H), 3.80 (s, 3H), 1.31 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.7 (d, *J* = 2.5 Hz), 162.5 (d, *J* = 2.6 Hz), 158.7, 148.7 (d, *J* = 9.7 Hz), 134.5, 132.7 (d, *J* = 4.1 Hz), 132.6 (d, *J* = 3.5 Hz), 129.0, 128.3, 128.1, 127.9, 127.6 (d, *J* = 1.9 Hz), 125.8, 124.2 (d, *J* = 16.7 Hz), 123.1 (d, *J* = 9.8 Hz), 122.6 (d, *J* = 8.7 Hz), 121.1, 114.8 (d, *J* = 12.5 Hz), 114.5 (d, *J* = 12.9 Hz), 110.2, 99.3, 92.8, 55.51 (d, *J* = 8.2 Hz), 52.3 (d, *J* = 65.2 Hz), 18.1;^{31}P NMR (162 MHz, $CDCl_3$) δ 29.92; HRMS (ESI) m/z calcd for $C_{32}H_{30}O_5P$ $[M+H]^+$ 525.1825; found 525.1829.



bis(3-chlorophenyl)((3*S,3*aS**,8*bS**)-8b-hydroxy-3a-methyl-1-phenyl-3a,8b-dihydro-3H-cyclopenta[*b*]benzofuran-3-yl)phosphine oxide ((±)-3s)**

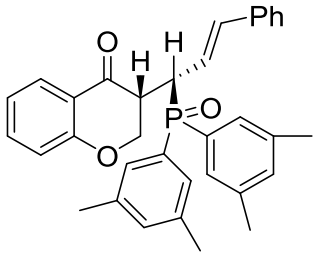
A white solid; 30.9 mg, 58% yield; m.p. = 178-180 ^{o}C; ^{1}H NMR (400 MHz, DMSO-d6) δ 8.31 (s, 1H), 8.19 (d, *J* = 11.4 Hz, 1H), 8.11 (dd, *J* = 10.7, 7.4 Hz, 1H),

8.01 (d, *J* = 11.4 Hz, 1H), 7.95 (dd, *J* = 10.6, 7.6 Hz, 1H), 7.76-7.69 (m, 3H), 7.69-7.61 (m, 2H), 7.57 (td, *J* = 7.7, 3.2 Hz, 1H), 7.35-7.23 (m, 3H), 7.18 (d, *J* = 7.4 Hz, 1H), 7.11 (t, *J* =7.5 Hz, 1H), 6.80-6.71 (m, 2H), 5.86 (s, 1H), 5.74 (t, *J* = 3.3 Hz, 1H), 4.88 (dd, *J* = 8.8, 2.5 Hz, 1H),1.27 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d6) δ 158.1, 147.2 (d, *J* = 10.8 Hz), 136.4, 135.5 (d, *J* = 5.3 Hz), 134.6, 134.2 (d, *J* = 9.2 Hz), 132.1 (d, *J* = 9.3 Hz), 133.6 (d, *J* = 3.2 Hz), 132.2 (d, *J* = 10.8, 2.4 Hz), 131.3 (d, *J* = 12.5 Hz), 131.1 (d, *J* = 12.4 Hz), 130.0 (d, *J* = 3.2 Hz), 129.9 (d, *J* = 3.1 Hz), 129.4, 129.3 (d, *J* = 6.3 Hz), 129.2 (d, *J* = 6.9 Hz), 128.6 (d, *J* = 1.5 Hz), 128.2, 128.0, 127.2 (d, *J* = 0.9 Hz), 125.2, 122.8 (d, *J* = 7.0 Hz), 120.6, 110.2, 99.0, 92.8, 79.2, 51.9 (d, *J* = 66.9 Hz), 18.2; ^{31}P NMR (162 MHz, DMSO-d6) δ 26.03; HRMS (ESI) m/z calcd for $C_{30}H_{24}Cl_2O_3P$ $[M+H]^+$ 533.0835; found 533.0836.



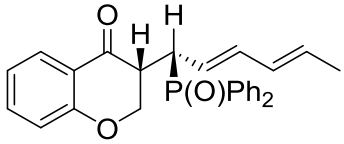
bis(3,5-dimethylphenyl)((3*S,3*aS**,8*bS**)-8b-hydroxy-3a-methyl-1-phenyl-3a,8b-dihydro-3H-cyclopenta[*b*]benzofuran-3-yl)phosphine oxide ((±)-3t)**

A white solid; 32.3 mg, 62% yield; m.p. = 150-151 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62-7.57 (m, 3H), 7.57 (s, 1H), 7.34 (d, *J* = 11.8 Hz, 2H), 7.31 (dd, *J* = 7.6, 0.8 Hz, 1H), 7.28-7.20 (m, 3H), 7.18 (s, 1H), 7.09 (s, 1H), 7.05 (td, *J* = 7.9, 1.3 Hz, 1H), 6.79-6.72 (m, 1H), 6.67 (d, *J* = 8.0 Hz, 1H), 5.62 (d, *J* = 3.0 Hz, 1H), 5.24 (s, 1H), 4.24 (dd, *J* =5.4, 2.8 Hz, 1H), 2.41 (s, 6H), 2.31 (s, 6H), 1.33 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.7, 148.8 (d, *J* = 9.8 Hz), 138.9 (d, *J* = 12.3 Hz), 138.7 (d, *J* = 12.5 Hz),134.4 (d, *J* = 3.3 Hz), 134.0 (d, *J* = 2.7 Hz), 133.8 (d, *J* = 2.7 Hz), 132.9 (d, *J* = 27.4 Hz), 132.0 (d, *J* = 34.3 Hz), 129.0, 128.3 (d, *J* = 6.4 Hz), 128.2 (d, *J* = 4.0 Hz), 128.1 (d, *J* = 6.3 Hz), 128.0 (d, *J* = 16.2 Hz), 127.6 (d, *J* = 2.1 Hz), 125.8, 122.7 (d, *J* = 8.5 Hz), 121.1, 110.1, 99.3 (d, *J* = 3.6 Hz), 92.8, 51.7 (d, *J* = 63.8 Hz), 21.6, 21.5, 18.1; ^{31}P NMR (162 MHz, $CDCl_3$) δ 29.91; HRMS (ESI) m/z calcd for $C_{34}H_{34}O_3P$ $[M+H]^+$ 521.2240; found 521.2242.



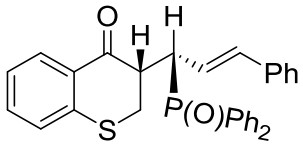
(*R)-3-((*S**,*E*)-1-(bis(3,5-dimethylphenyl)phosphoryl)-3-phenylallyl)chroman-4-one ((±)-3t')**

A light yellow solid; m.p. = 131-132 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (dd, *J* = 7.9, 1.6 Hz, 1H), 7.53 (d, *J* = 11.2 Hz, 1H), 7.43-7.35 (m, 3H), 7.23-7.15 (m, 5H), 7.13 (s, 1H), 7.02 (s, 1H), 6.98-6.92 (m, 1H), 6.91 (d, *J* = 8.3 Hz, 1H), 6.56 (dd, *J* = 15.7, 3.2 Hz, 1H), 6.27-6.14 (m, 1H), 5.31 (dd, *J* = 11.3, 5.4 Hz, 1H), 4.50 (dd, *J* = 13.1, 11.5 Hz, 1H), 4.47-4.41 (m, 1H), 3.30-3.17 (m, 1H), 2.35 (s, 6H), 2.26 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.6 (d, *J* = 13.0 Hz), 162.0, 138.9 (d, *J* = 11.9 Hz), 138.2 (d, *J* = 12.3 Hz), 137.9 (d, *J* = 12.0 Hz), 136.6 (d, *J* = 1.6 Hz), 136.2, 134.0 (d, *J* = 2.8 Hz), 133.6 (d, *J* = 2.9 Hz), 131.9 (d, *J* = 46.5 Hz), 131.0 (d, *J* = 41.7 Hz), 128.7 (d, *J* = 8.7 Hz), 128.6 (d, *J* = 8.7 Hz), 128.5, 127.7 (d, *J* = 29.8 Hz), 126.5, 121.4, 120.9, 119.3 (d, *J* = 6.1 Hz), 118.1, 68.8, 46.2, 39.5 (d, *J* = 71.0 Hz), 21.4 (d, *J* = 13.3 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 34.92; HRMS (ESI) m/z calcd for $C_{34}H_{34}O_3P$ $[M+H]^+$ 521.2240; found 521.2241.



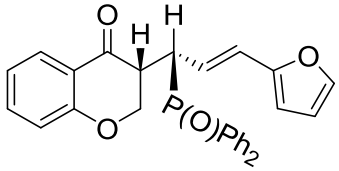
(*R)-3-((*S**,2*E*,4*E*)-1-(diphenylphosphoryl)hexa-2,4-dien-1-yl)chroman-4-one ((±)-3v')**

A white solid; 35.1 mg, 82% yield; m.p. = 140-141 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93-7.81 (m, 3H), 7.83-7.70 (m, 2H), 7.53-7.38 (m, 7H), 7.00-6.93 (m, 1H), 6.90 (d, *J* = 8.4 Hz, 1H), 6.24-6.10 (m, 1H), 5.82 (dd, *J* = 15.0, 11.2 Hz, 1H), 5.62-5.44 (m, 2H), 5.20 (dd, *J* = 11.4, 5.4 Hz, 1H), 4.41 (dd, *J* = 13.4 11.4 Hz, 1H), 4.38-4.31 (m, 2H), 3.20-3.06 (m, 1H), 1.63 (d, *J* = 6.7 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.5 (d, *J* = 13.3 Hz), 162.0, 138.7 (d, *J* = 12.1 Hz), 136.2, 132.5, 132.2 (d, *J* = 2.7 Hz), 131.8 (d, *J* = 2.7 Hz), 131.2 (d, *J* = 8.7 Hz), 132.1 (d, *J* = 8.6 Hz), 130.9 (d, *J* = 2.4 Hz), 130.7 (d, *J* = 2.6 Hz), 129.2 (d, *J* = 11.2 Hz), 128.6 (d, *J* = 11.6 Hz), 127.6, 121.4, 120.9, 118.8 (d, *J* = 6.5 Hz), 118.1, 68.8, 46.0, 38.9 (d, *J* = 72.2 Hz), 18.1; ^{31}P NMR (162 MHz, $CDCl_3$) δ 34.41; HRMS (ESI) m/zcalcd for $C_{27}H_{26}O_3P$ $[M+H]^+$ 429.1614; found 429.1620.



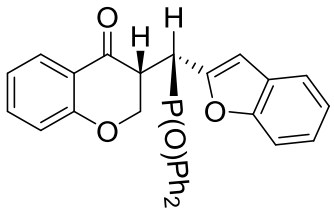
(*R)-3-((*S**,*E*)-1-(diphenylphosphoryl)-3-phenylallyl)thiochroman-4-one ((±)-3w')**

A white solid; 46.1 mg, 96% yield; m.p. = 168-170 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (dd, *J* = 8.0 Hz, 1H), 7.96-7.88 (m, 2H), 7.85-7.76 (m, 2H), 7.56-7.46 (m, 3H), 7.46-7.37 (m, 3H), 7.34-7.28 (m, 1H), 7.24-7.15 (m, 6H), 7.11 (t, *J* = 7.7 Hz, 1H), 6.62 (dd, *J* = 15.8, 3.2 Hz, 1H), 6.36-6.24 (m, 1H), 4.60 (dd, *J* = 9.8, 7.1 Hz, 1H), 3.91 (dd, *J* = 13.2, 3.7 Hz, 1H), 3.47 (t, *J* = 13.6 Hz, 1H), 3.31-3.18 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.9 (d, *J* = 13.2 Hz), 142.4, 138.0 (d, *J* = 12.2 Hz), 136.6, 133.4, 132.3 (d, *J* = 45.3 Hz), 132.2 (d, *J* = 2.7 Hz), 131.9 (d, *J* = 2.6 Hz), 131.8 (d, *J* = 82.2 Hz), 131.2 (d, *J* = 6.8 Hz), 131.1 (d, *J* = 6.8 Hz), 130.7, 130.1, 129.2 (d, *J* = 11.3 Hz), 128.6 (d, *J* = 11.7 Hz), 128.5, 127.9 (d, *J* = 15.7 Hz), 126.5, 125.0, 119.2 (d, *J* = 6.3 Hz), 49.2, 41.0 (d, *J* = 71.9 Hz), 28.8; ^{31}P NMR (162 MHz, $CDCl_3$) δ 34.82; HRMS (ESI) m/z calcd for $C_{30}H_{26}O_2PS$ $[M+H]^+$ 481.1386; found 481.1389.



(*R)-3-((*S**,*E*)-1-(diphenylphosphoryl)-3-(furan-2-yl)allyl)chroman-4-one ((±)-3x')**

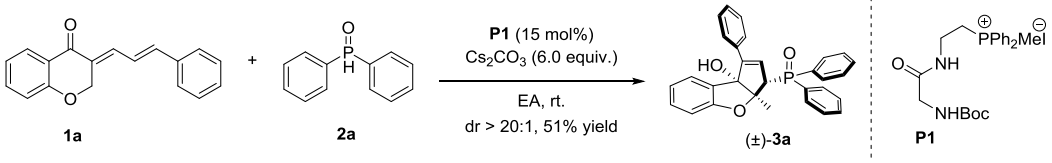
A white solid; 39.5 mg, 87% yield; m.p. = 139-141 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96-7.87 (m, 2H), 7.86-7.75 (m, 3H),7.53-7.46 (m, 3H), 7.45-7.37 (m, 4H), 7.23-7.20 (m, 1H), 6.98-6.92 (m, 1H), 6.90 (d, *J* = 8.3 Hz, 1H), 6.39 (dd, *J* = 15.6, 3.1 Hz, 1H), 6.25 (dd, *J* = 3.3, 1.8 Hz, 1H), 6.19-6.11 (m, 1H), 6.09 (d, *J* = 3.2 Hz, 1H), 5.27 (dd, *J* = 11.4, 5.5 Hz, 1H), 4.52-5.41 (m, 2H), 3.26-3.15 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.4 (d, *J* = 13.2 Hz), 162.0, 151.8 (d, *J* = 2.2 Hz), 142.3, 136.2, 132.2 (d, *J* = 2.7 Hz), 131.9 (d, *J* = 2.8 Hz), 131.2 (d, *J* = 38.1 Hz), 131.2 (d, *J* = 8.8 Hz), 131.2 (d, *J* = 33.2 Hz), 131.1 (d, *J* = 8.7 Hz), 129.2 (d, *J* = 11.3 Hz), 128.7 (d, *J* = 11.7 Hz), 127.5, 126.0 (d, *J* = 12.4 Hz), 121.4, 120.8, 118.1, 117.2 (d, *J* = 6.2 Hz), 111.3, 108.7 (d, *J* = 6.4 Hz), 68.7, 46.1, 39.0 (d, *J* = 72.0 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 33.97; HRMS (ESI) m/z calcd for $C_{28}H_{24}O_4P$ $[M+H]^+$ 455.1407; found 455.1400.



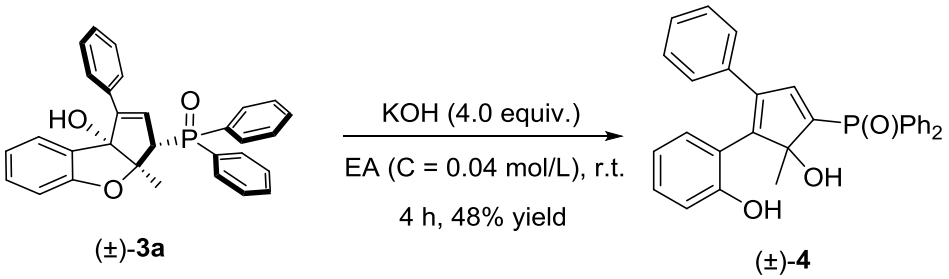
(*R)-3-((*R**)-benzofuran-2-yl(diphenylphosphoryl)methyl)chroman-4-one ((±)-3z')**

A white solid; 41.6 mg, 87% yield; m.p. = 142-144 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04-7.94 (m, 2H), 7.80 (dd, *J* = 7.9, 1.8 Hz, 1H), 7.79-7.71 (m, 2H), 7.54-7.48 (m, 3H), 7.42-7.34 (m, 3H), 7.34-7.27 (m, 3H), 7.19-7.13 (m, 1H), 7.13-7.07 (m, 1H), 6.96-6.91 (m, 1H), 6.86 (dd, *J* = 8.4, 1.0 Hz, 1H), 6.81 (d, *J* = 1.0 Hz, 1H), 5.35 (dd, *J* = 11.4, 5.4 Hz, 1H), 5.57 (dd, *J* = 10.2, 1.5 Hz, 1H), 4.09 (dd, *J* = 13.6, 11.5 Hz, 1H), 3.45-3.33 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.9, 162.0, 154.7, 149.5 (d, *J* = 2.6 Hz), 136.3, 132.4 (d, *J* = 2.6 Hz), 132.0, 132.0 (d, *J* = 2.7 Hz), 131.6, 132.1 (d, *J* = 8.8 Hz), 131.0, 130.7 (d, *J* = 9.1 Hz), 130.6, 129.3 (d, *J* = 11.6 Hz), 128.6 (d, *J* = 12.0 Hz), 127.9, 127.6, 123.5 (d, *J* = 140.2 Hz), 121.2 (d, *J* = 48.4 Hz), 120.4, 118.0, 111.3, 108.6 (d, *J* = 5.1 Hz), 69.5, 45.1, 35.3 (d, *J* = 70.9 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 31.93; HRMS (ESI) m/z calcd for $C_{30}H_{24}O_4P$ $[M+H]^+$ 479.1407, found 479.1410.

7. Procedure for gram-scale synthesis of 3a and its transformation



To a flask (250 mL) with a magnetic stirring bar were added **1a** (1.00 g, 3.81 mmol), **2a** (1.54 g, 7.62 mmol), phosphonium salt **P1** (302 mg, 0.57 mmol) and Cs_2CO_3 (7.40 g, 22.86 mmol), followed by the addition of EA (40 mL). The reaction mixture was stirred at room temperature for 12 h. Until completion, the reaction mixture was concentrated. Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 3:1) afforded the prodcut (±)-**3a** as a white solid (902.6 mg, 51% yield, >20:1 *dr*).



(±)-**3a** (±)-**4**

To a solution of EA (2.5 mL) were (±)-**3a** (0.10 mmol), and KOH (0.40 mmol). The reaction mixture was stirred at room temperature for 4 h. The solvent was evaporated to give the crude product, which was directly purified by silica gel chromatography to provide the desired product (±)-**4** as a light yellow solid.

A yellow solid; 23.7 mg, 48% yield; m.p. = 174-176 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.30 (s, 1H), 7.96-7.88 (m, 2H), 7.70-7.62 (m, 3H), 7.62-7.58 (m, 2H), 7.53 (dd, *J* = 7.8, 1.6 Hz, 1H), 7.48-7.42 (m, 2H), 7.21-7.15 (m, 6H), 7.05-6.99 (m, 1H), 6.73 (d, *J* = 8.9 Hz, 1H), 6.69 (dd, *J* = 7.7, 1.6 Hz, 1H), 6.64-6.58 (m, 1H), 3.76-3.72 (m, 1H), 1.34 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.9, 151.3, 145.7 (d, *J* = 10.9 Hz), 141.0 (d, *J* = 109.8 Hz), 139.2 (d, *J* = 14.9 Hz), 134.2, 132.8, 132.6, 131.7 (d, *J* = 5.6 Hz), 131.6 (d, *J* = 5.0 Hz), 130.4, 128.9 (d, *J* = 8.3 Hz), 128.8 (d, *J* = 8.4 Hz), 128.6 (d, *J* = 33.5 Hz), 128.0, 127.2, 121.0, 119.6, 118.2, 90.04 (d, *J* = 8.6 Hz), 68.0, 24.9 (d, *J* = 159.4 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 27.96; HRMS (ESI) m/z calcd for $C_{30}H_{26}O_3P$ $[M+H]^+$ 465.1614, found 465.1617.

8. Determination of configuration of the products (±)-3', (±)-3, (±)-4

A. The configurations of products **(±)-3'** were assigned by X-ray crystallographic analysis of (±)-**3a'**. CCDC 2171785 contains the supplementary crystallographic data of (±)-**3a'** for this paper. This data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

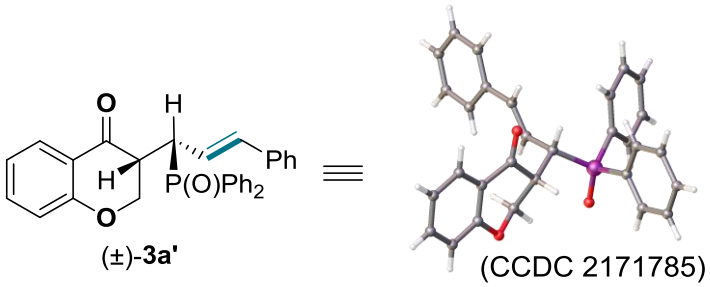


Figure S1. X-ray structure of (±)-**3a'**.

Table S7. Crystal data and structure refinement for (±)-**3a'**. The ellipsoid contour % probability level is 50%.

Identification code	**(±)-3a'**
Empirical formula	$C_{30}H_{25}O_3P$
Formula weight	464.47
Temperature/K	252.0
Crystal system	triclinic
Space group	*P*-1
a/Å	10.560(2)
b/Å	10.831(2)
c/Å	11.869(2)
α/°	68.716(6)
β/°	78.861(6)
γ/°	85.017(6)
Volume/Å^3	1240.9(4)
Z	2
ρ_{calc}g/cm^3	1.243
μ/mm^{-1}	0.140
F(000)	488.0
Crystal size/mm^3	0.25 × 0.23 × 0.11
Radiation	Mo*K*α (λ = 0.71073)
2θ range for data collection/°	3.74 to 55.24
Index ranges	-13 ≤ h ≤ 13, -14 ≤ k ≤ 14, -15 ≤ l ≤ 15
Reflections collected	41898
Independent reflections	5754 [R_{int} = 0.0853, R_{sigma} = 0.0574]
Data/restraints/parameters	5754/0/307
Goodness-of-fit on F^2	1.023
Final R indexes [I>=2σ (I)]	R_1 = 0.0486, wR_2 = 0.1169
Final R indexes [all data]	R_1 = 0.0731, wR_2 = 0.1331
Largest diff. peak/hole / e Å^{-3}	0.28/-0.22

B. The configurations of products **3** were assigned by X-ray crystallographic analysis of (±)-**3a**. CCDC 2171783 contains the supplementary crystallographic data of (±)-**3a** for this paper. This data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

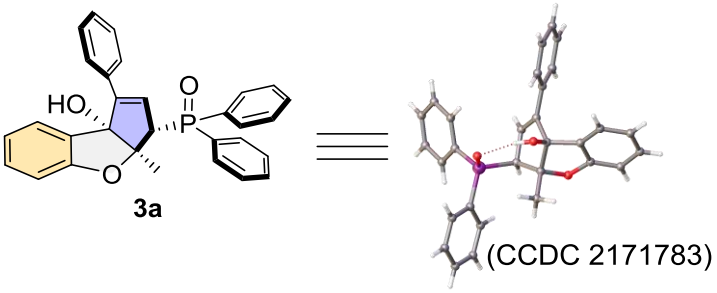


Figure S2. X-ray structure of (±)-**3a**.

Table S8. Crystal data and structure refinement for (±)-**3a**. The ellipsoid contour % probability level is 50%.

Identification code	**(±)-3a**
Empirical formula	$C_{30}H_{25}O_3P$
Formula weight	464.47
Temperature/K	304.0
Crystal system	monoclinic
Space group	*C*2/c
a/Å	44.9718(11)
b/Å	6.84850(10)
c/Å	18.4695(4)
α/ °	90
β/ °	114.1240(10)
γ/ °	90
Volume/Å^3	5191.60(19)
Z	4
ρ_{calc}g/cm^3	1.297
μ/mm^{-1}	0.239
F(000)	2120.0
Crystal size/mm^3	0.34 × 0.23 × 0.08
Radiation	Mo*K*α (λ = 0.71073)
2θ range for data collection/ °	3.97 to 55.008
Index ranges	-58 ≤ h ≤ 58, -8 ≤ k ≤ 8, -23 ≤ l ≤ 23
Reflections collected	37050
Independent reflections	5946 [Rint = 0.0585, Rsigma = 0.0376]
Data/restraints/parameters	5946/0/323

Goodness-of-fit on F^2	1.029
Final R indexes [I>=2σ (I)]	R1 = 0.0483, wR2 = 0.1228
Final R indexes [all data]	R1 = 0.0696, wR2 = 0.1387
Largest diff. peak/hole / e Å^{-3}	0.58/-0.63

C. The configurations of products **4** were assigned by X-ray crystallographic analysis. CCDC 2207797 contains the supplementary crystallographic data of **4** for this paper. This data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif

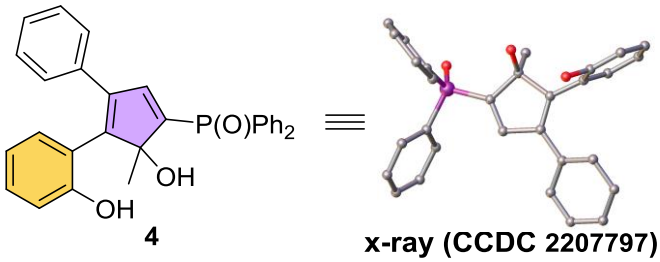


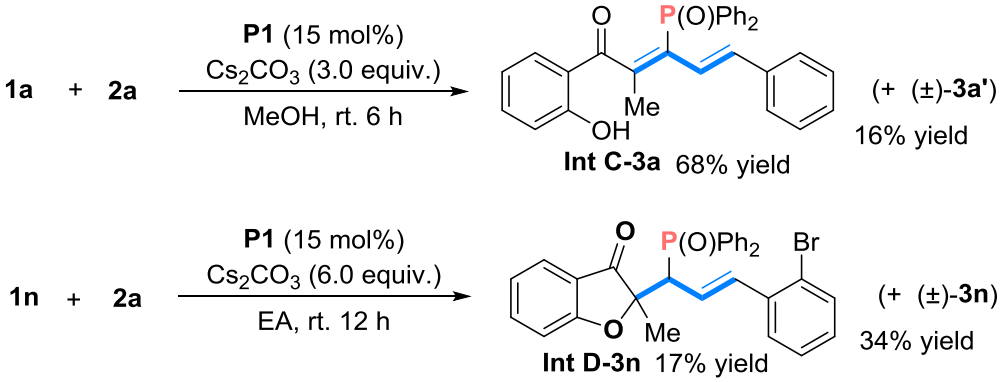
Table S9. Crystal data and structure refinement for (±)-**4**. The ellipsoid contour % probability level is 50%.

Identification code	**(±)-4**
Empirical formula	$C_{30}H_{25}O_3P$
Formula weight	464.47
Temperature/K	173(2)
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	9.2171(2)
b/Å	17.9048(6)
c/Å	14.5888(4)
α/°	90
β/°	99.2740(10)
γ/°	90
Volume/Å^3	2376.13(12)
Z	4
ρ_{calc}g/cm^3	1.298
μ/mm^{-1}	0.146
F(000)	976.0
Crystal size/mm^3	0.220 × 0.333 × 0.381
Radiation	Mo$K\alpha$ (λ = 0.71073)
2θ range for data collection/°	2.45 to 27.46
Index ranges	-11 ≤ h ≤ 11, -22 ≤ k ≤ 23, -18 ≤ l ≤ 16
Reflections collected	17751
Independent reflections	5930 [Rint = 0.0343, Rsigma = 0.0422]
Data/restraints/parameters	5409/3/321

Goodness-of-fit on F^2	1.049
Final *R* indexes [*I*>=2σ (I)]	R1 = 0.0584, wR2 = 0.1381
Final *R* indexes [all data]	R1 = 0.0806, wR2 = 0.1533
Largest diff. peak/hole / e Å^{-3}	0.612/-0.343

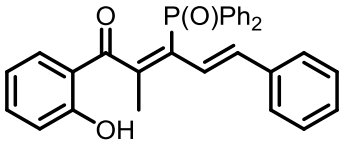
9. Mechanistic studies and proposed reaction process

A. The preparation of intermediate **Int C-3a** and **Int D-3n**



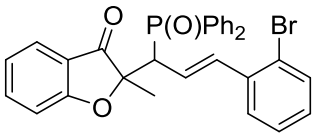
[a] Reaction conditions: **1** (26.2 mg, 0.10 mmol), **2a** (0.20 mmol), Cs_2CO_3 (0.60 mmol) and **P1** (15 mol%) in solvent (2.5 mL) at room temperature. [b] Isolated yields.

(2*Z*,4*E*)-3-(diphenylphosphoryl)-1-(2-hydroxyphenyl)-2-methyl-5-phenylpenta-2,4-dien-1-one （Int C-3a）



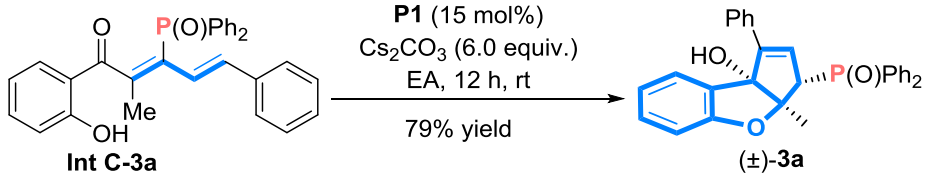
A yellow solid; 31.5 mg, 68% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.65 (s, 1H), 7.61-7.50 (m, 5H), 7.50-7.41 (m, 4H), 7.39-7.30 (m, 5H), 7.24-7.17 (m, 3H), 6.98 (dd, *J* = 8.4, 0.6 Hz, 1H), 6.92-6.86 (m, 1H), 6.86-6.81 (m, 2H), 1.91 (d, *J* = 2.5 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.3, 151.1, 136.1, 135.2 (d, *J* = 9.8 Hz), 132.8, 132.7, 132.1 (d, *J* = 2.7 Hz), 131.7, 130.2, 128.9, 128.6 (d, *J* = 1.2 Hz), 128.2 (d, *J* = 11.9 Hz), 128.0 (d, *J* = 1.8 Hz), 119.5, 118.9, 118.5, 21.3 (d, *J* = 11.4 Hz); ^{31}P NMR (162 MHz, CDCl3) δ 25.38; HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{30}H_{26}O_3P$ 465.1614; found 465.1614.

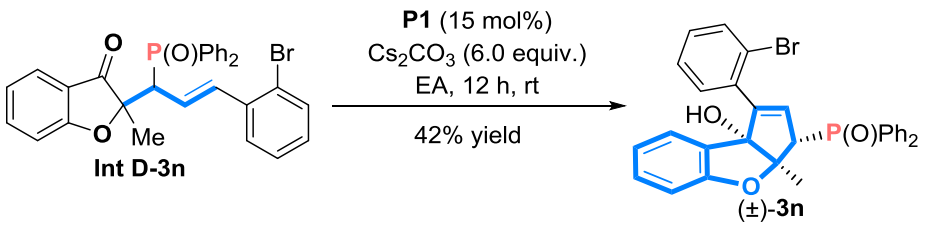
(*E*)-2-(3-(2-bromophenyl)-1-(diphenylphosphoryl)allyl)-2-methylbenzofuran-3(2H)-one (Int D-3n)



A yellow solid; 9.3 mg, 17% yield; m.p. = 241-243 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (dd, *J* = 7.5, 1.0 Hz), 7.70-7.54 (m, 6H), 7.50-7.32 (m, 7H), 7.21 (td, *J* = 7.8, 1.5 Hz, 1H), 7.14 (dd, *J* = 7.7, 1.6 Hz, 1H), 7.04-6.97 (m, 1H), 6.27 (d, *J* = 8.0 Hz, 1H), 6.17 (dd, *J* = 10.8, 3.0 Hz, 1H), 5.01 (t, *J* = 2.8 Hz, 1H), 1.74 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.27, 148.5 (d, *J* = 10.7 Hz), 142.1 (d, *J* = 97.9 Hz), 136.0, 133.6, 132.1, 132.0 (d, *J* = 2.7 Hz), 132.0, 131.9 (d, *J* = 4.5 Hz), 131.8, 131.7 (d, *J* = 10.0 Hz), 130.9, 129.6 (d, *J* = 31.4 Hz), 128.6 (d, *J* = 12.1 Hz), 128.4 (d, *J* = 12.5 Hz), 127.9, 127.3, 125.2, 121.6, 111.6, 101.1 (d, *J* = 6.5 Hz), 88.2 (d, *J* = 7.9 Hz), 59.3 (d, *J* = 12.9 Hz), 20.6; ^{31}P NMR (162 MHz, $CDCl_3$) δ 23.33; HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{30}H_{25}BrO_3P$ 543.0719, found = 543.0725.

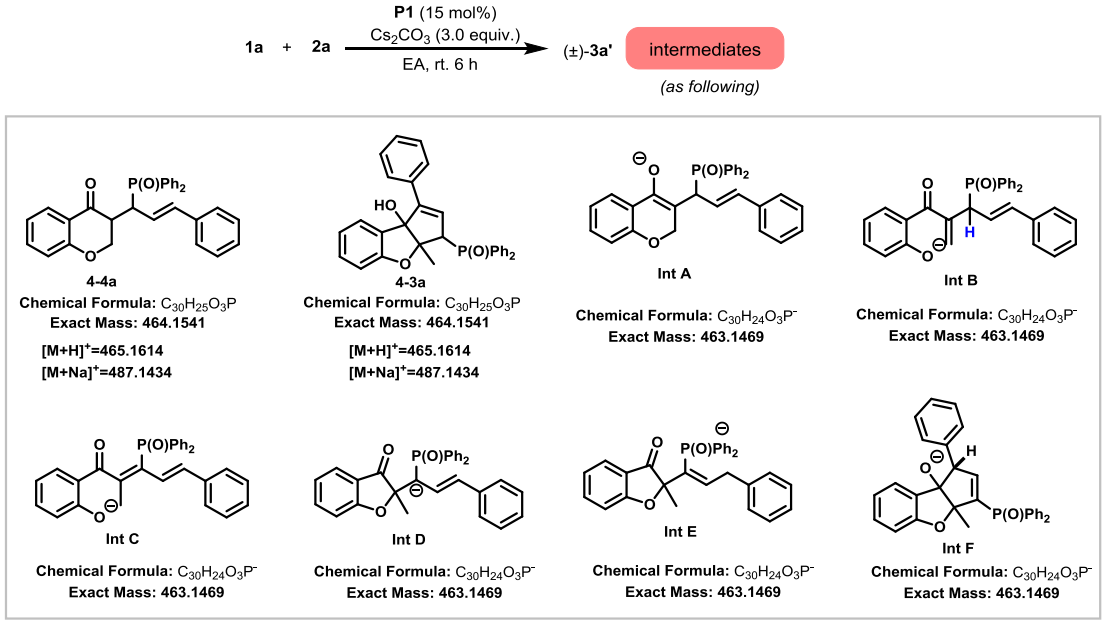
B. The control experiments of isolated **Int C-3a** and **Int D-3n**





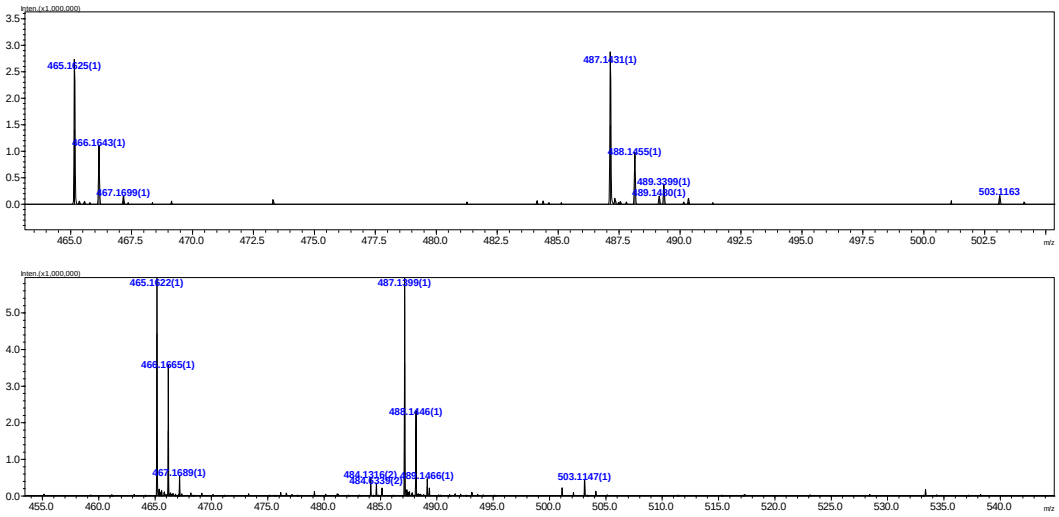
The intermediates **Int C-3a** and **Int D-3n** were used as the substrates under the optimized reaction condition, and the corresponding tricyclic products (±)-**3a** and (±)-**3n** were obtained.

C. The *in-situ* HRMS testing of the reaction mixture

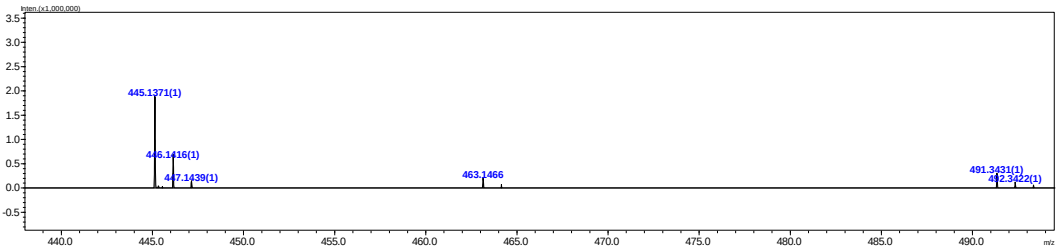


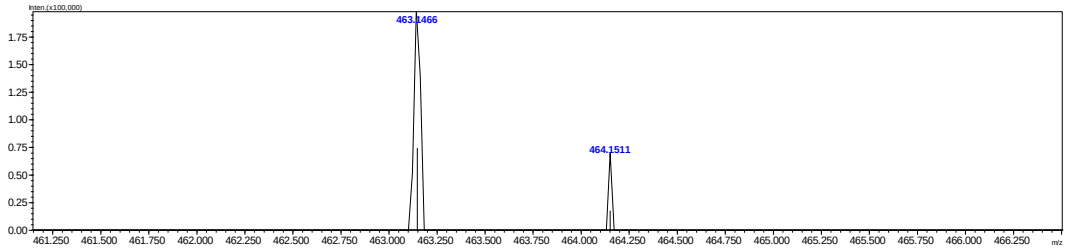
We tested the reaction mixture of the above reaction. The negative HRMS testing showed the favorable results.

(+)

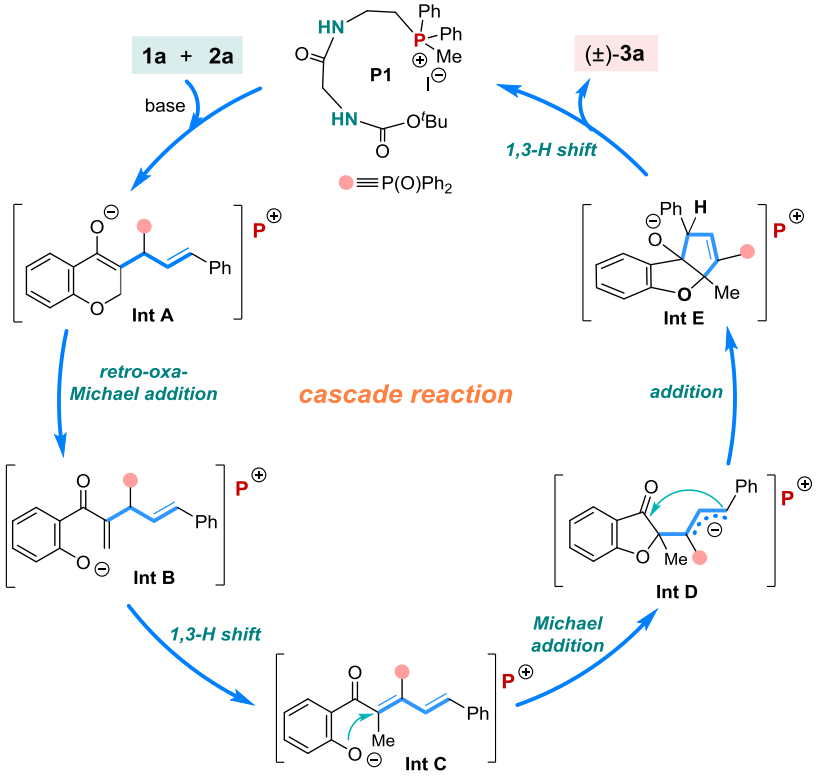


(-)





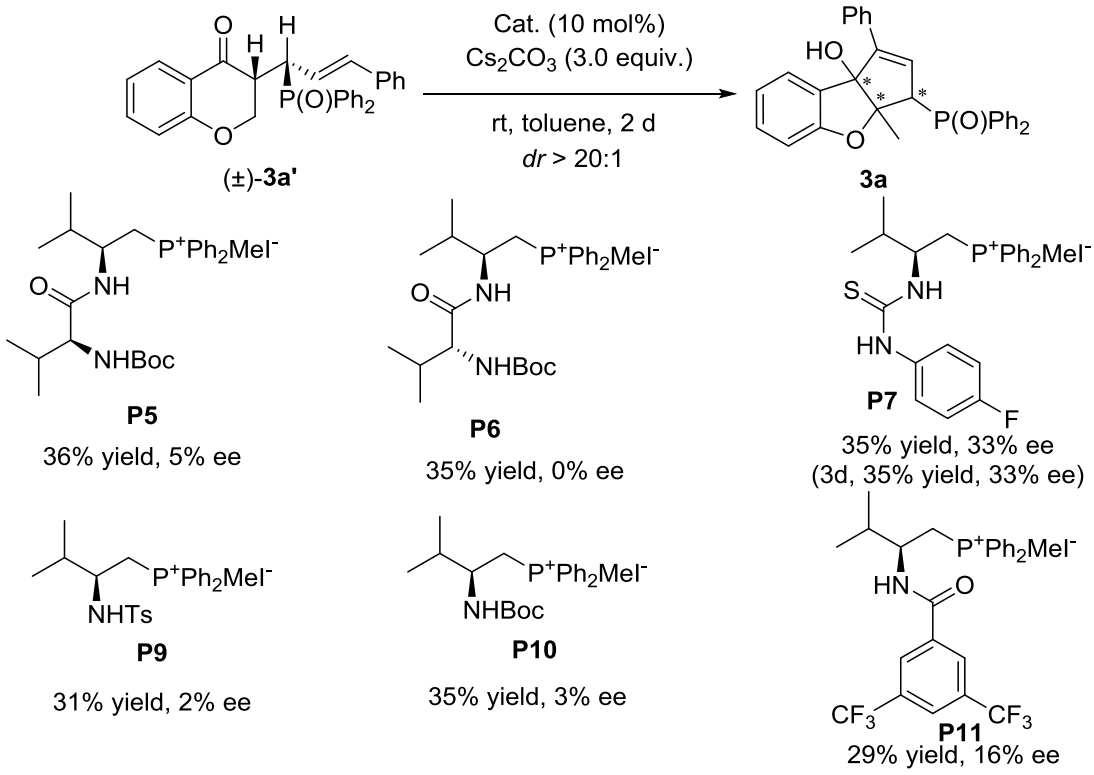
D. Proposed reaction process



Of note, the whole process was accelerated by the bifunctional phosphonium salt **P1**, which non-covalently interact with the intermediates by ion-pairing and double hydrogen-bonding interactions. The **Int A** was opened up under basic condition by hydrolysis and went quickly to **Int B** by dehydration, followed by a 1,3-H shift process to a more stable intermediate **Int C**, which distinguished with a large conjugation structure Then the nucleophilic negative phenoxy of **Int C** attacked the α-carbon of carbonyl, as the result of steric hinderance to form the benzofuran skeleton **Int D**. Subsequently, 1,3-H shift occurred and thus afforded the intermediate **Int E**, which then went through an intramolecular aldol reaction for accessing to important intermediate of cyclopenta[*b*]benzofuran **Int F**. This intermediate finally was transformed into the targeting product **3a** via 1,3-H shift process.

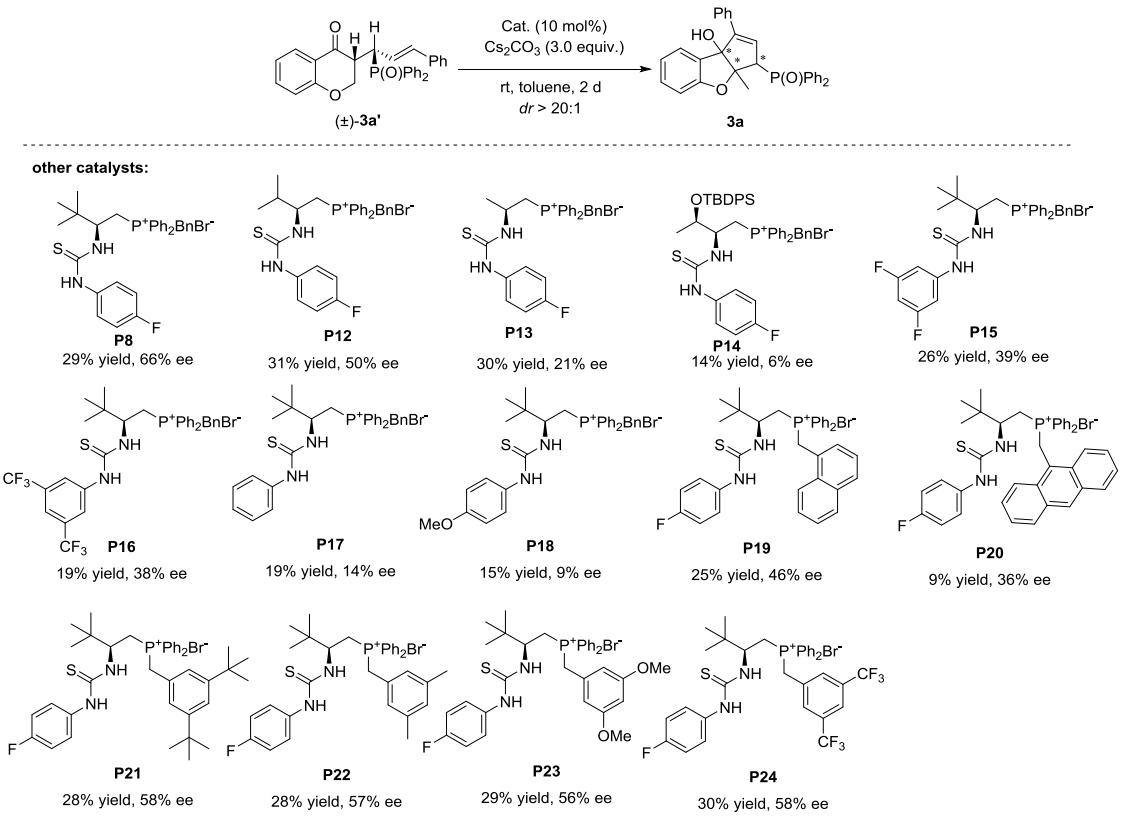
10.Reaction optimization for accessing to the chiral product 3

***Table S10*:** Catalytic Asymmetric Synthesis of **3a**: screening of the types of the catalysts.[a,b]



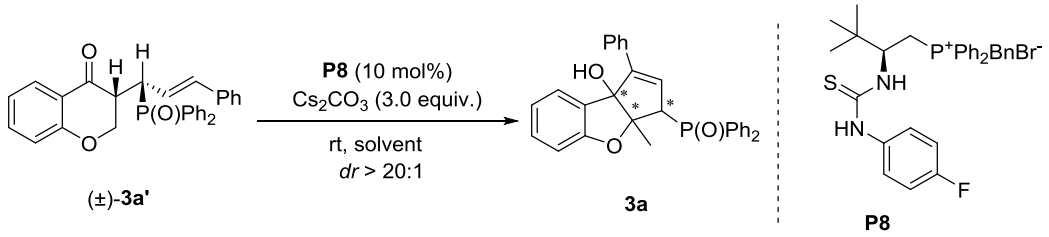
[a] Reaction conditions: **3a'** (46.5 mg, 0.10 mmol), Cs_2CO_3 (97.8 mg, 0.30 mmol) and cat (0.01 mmol) in toluene (2.5 mL) at room temperature. [b] Isolated yields.

***Table S11*:** Catalytic Asymmetric Synthesis of **3a**: screening of the other catalysts.[a,b]



[a] Reaction conditions: **3a'** (46.5 mg, 0.10 mmol), Cs_2CO_3 (97.8 mg, 0.30 mmol) and cat (0.01 mmol) in toluene (2.5 mL) at room temperature. [b] Isolated yields.

***Table S12*:** Screening of solvents.[a,b]

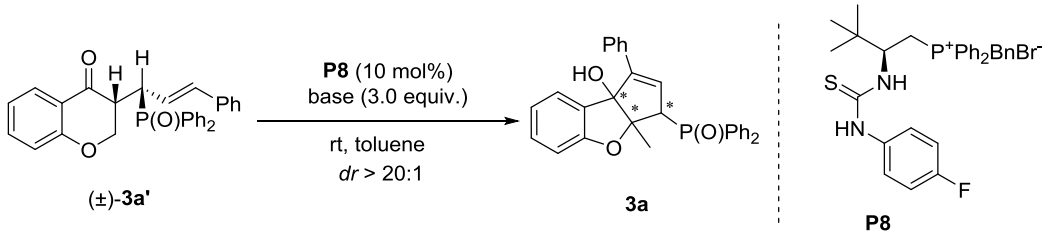


entry	solvent	time	yield	ee
1	Toluene	2 d	29%	66%
2	Mesitylene	2 d	28%	63%
3	Cl-Ph	2 d	27%	66%
4	Br-Ph	2 d	27%	62%
5	CF_3-Ph	2 d	24%	52%
6	NO_2-Ph	2 d	74%	10%
7	$CHCl_3$	2 d	10%	53%
8	CH_2Cl_2	2 d	31%	21%
9	CCl_4	2 d	trace	-
10	DCE	2 d	21%	8%

11	EA	2 d	58%	45%
12	acetone	2 d	81%	2%
13	DMF	2 d	-	-
14	CH_3CN	2 d	43%	6%
15	Dioxane	2 d	83%	0%
16	Et_2O	2 d	22%	15%
17	PhOMe	2 d	49%	44%
18	PE(30-60 ^oC)	2 d	NR	-
19	Hexane	2 d	NR	-
20	Pentane	2 d	NR	-
21	cyclopentane	2 d	NR	0%
22	Xylene	2 d	29	50%
23	Hex/tol=1:1	2 d	26	19%

[a] Reaction conditions: **3a'** (46.5 mg, 0.10 mmol), Cs_2CO_3 (97.8 mg, 0.30 mmol) and **P8** (0.01 mmol) in solvent (2.5 mL) at room temperature. [b] Isolated yields.

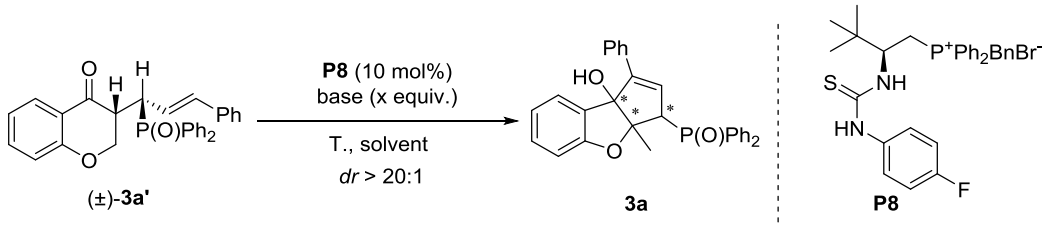
***Table S13*:** Screening of bases.[a,b]



entry	base	time	yield	ee
1	Et_3N	2 d	trace	-
2	DBU	2 d	20%	4%
3	DABCO	2 d	trace	-
4	DMAP	2 d	trace	-
5	DIPEA	2 d	trace	-
6	Cs_2CO_3	2 d	29%	66%
7	K_2CO_3	2 d	trace	-
8	Na_2CO_3	2 d	trace	-
9	K_3PO_4	2 d	Trace	-
10	$K_3PO_4 \cdot 3H_2O$	2 d	trace	-
11	KOH	15 h	58%	0%
12	Cs_2CO_3 (6.0 equiv.)	26 h	60%	10%
13	Cs_2CO_3 (8.0 equiv.)	16 h	59%	7%

[a] Reaction conditions: **3a'** (46.5 mg, 0.10 mmol), base (x equiv.) and **P8** (0.01 mmol) in toluene (2.5 mL) at room temperature. [b] Isolated yields.

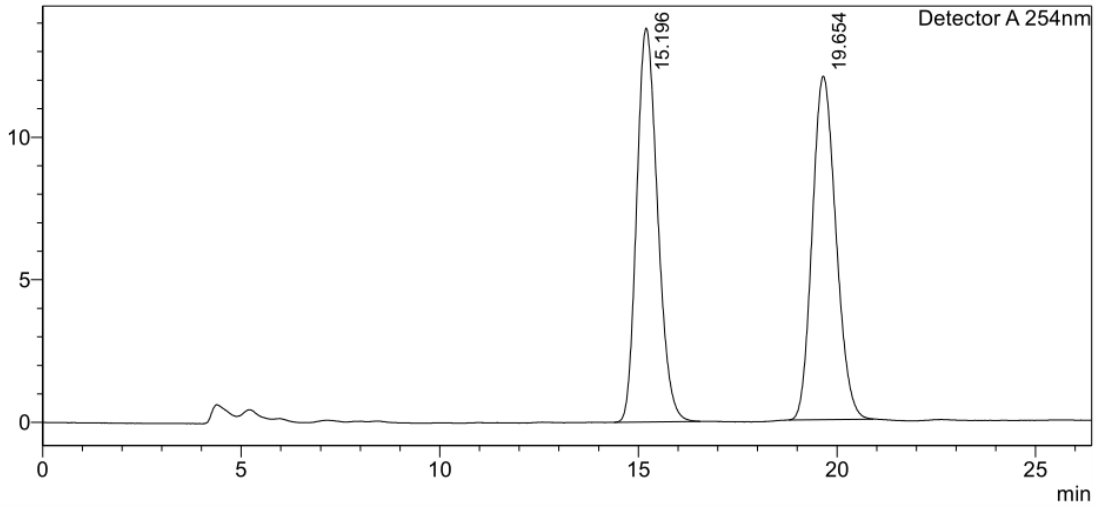
***Table S14*:** Screening of temperature.[a,b]



entry	base (equiv.)	Solvent	Temp.	time	yield	ee
1	3.0	Toluene	0 °C	2 d	trace	-
2	3.0	EA	0 °C	2 d	trace	-
3	6.0	Toluene	0 °C	2 d	trace	-
4	6.0	EA	0 °C	2 d	trace	-
5	3.0	Toluene	40 °C	2 d	33%	30%
6	2.0	Toluene	40 °C	2 d	10%	55%

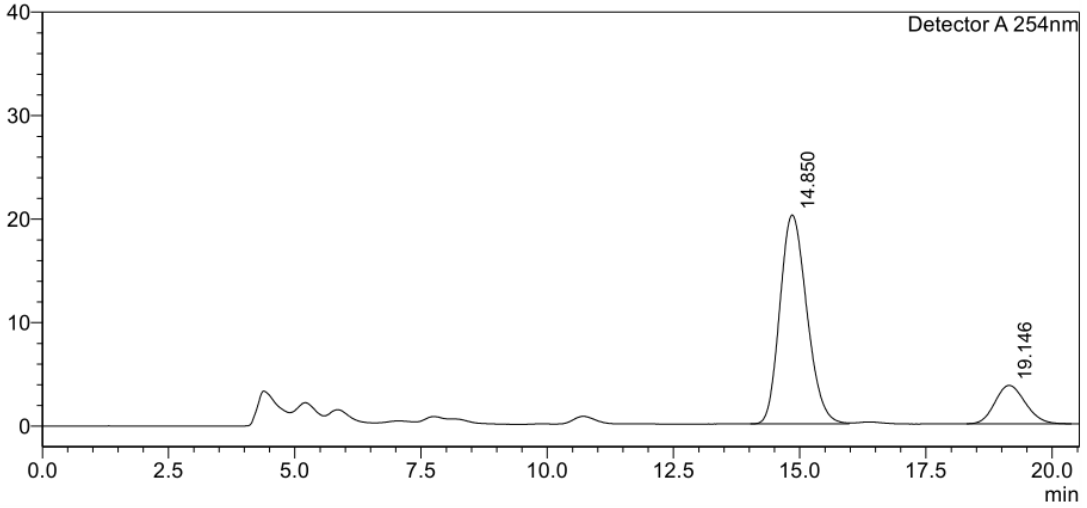
[a] Reaction conditions: **3a'** (46.5 mg, 0.10 mmol), Cs_2CO_3 (x equiv.) and **P8** (0.01 mmol) in solvent (2.5 mL) at room temperature. [b] Isolated yields.

The best chiral condition of **3a** we've got yet : **(±)-3a**' (46.5 mg, 0.10 mmol), Cs_2CO_3 (3.0 equiv.) and **P8** (0.01 mmol) in toluene (2.5 mL) at room temperature for 2d. The ee value was 66%, t_R (minor) = 19.146 min, t_R (major) = 14.850 min (HPLC condition: Chiralpak IE column, λ = 254 nm, T = 25 °C, 30% *i*-PrOH/n-Hexane, flow rate = 1.0 mL/min).



Detector A 254nm

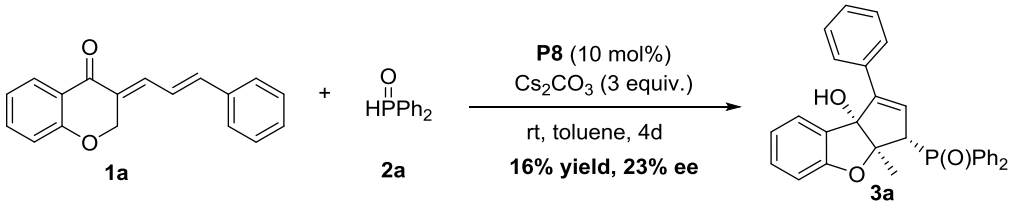
Peak#	Ret. Time	Height	Height%	Area	Area%
1	15.196	13809	53.411	505288	50.297
2	19.654	12045	46.589	499324	49.703
Total		25854	100.000	1004612	100.000



Detector A 254nm

Peak#	Ret. Time	Height	Height%	Area	Area%
1	14.850	20191	84.477	752346	82.851
2	19.146	3710	15.523	155728	17.149
Total		23901	100.000	908074	100.000

***Table S15*:** Asymmetric reaction from **1a** and **2a**.



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

[a] Reaction conditions: **1a** (0.10 mmol), 2a (0.12 mmol), Cs_2CO_3 (3.0 equiv.) and **P8** (0.01 mmol) in toluene (2.5 mL) at room temperature.

We have employed **1a** and **2a** as the starting materials under the standard reaction condition in the presence of chiral phosphonium salts **P8** to investigate the chiral induction. As a result, the chiral target **3a** was obtained only in 16% yield and 23% ee unfortunately, which possibly was due to the low reaction activity and the complicated process of the reaction.

11. References

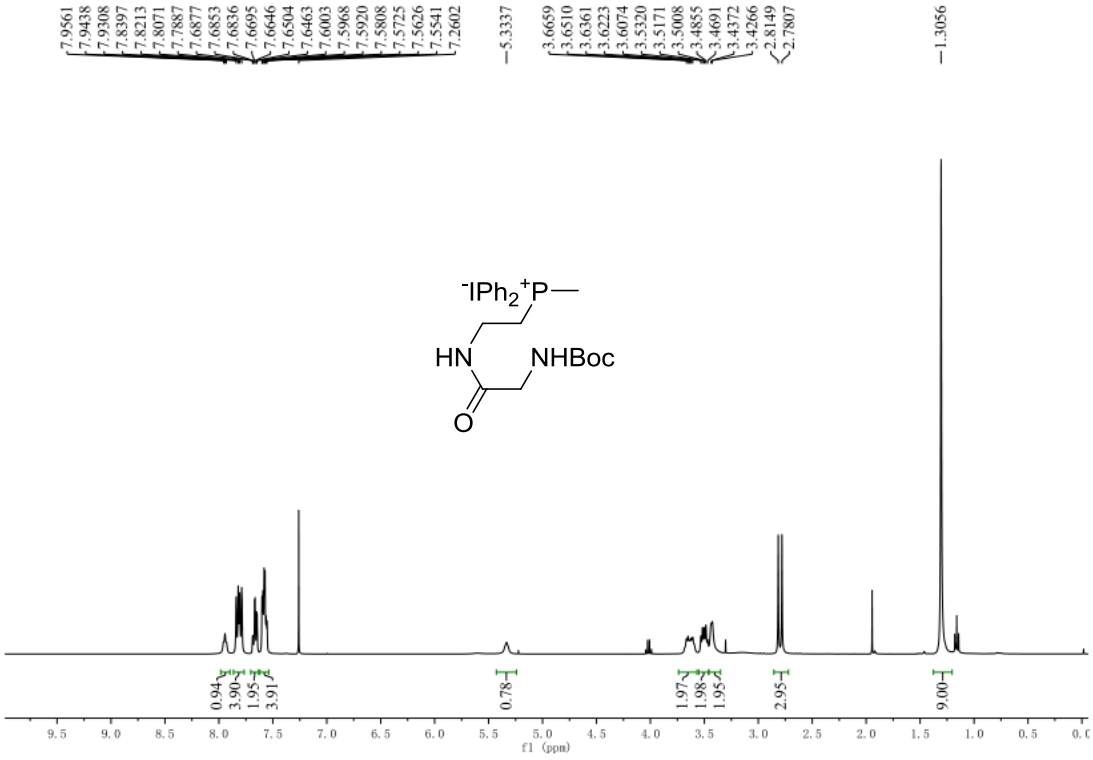
[1] (*a*) X. Han, Y. Wang, F. Zhong, and Y. Lu, *J. Am. Chem. Soc.* 2011, **133**, 1726-1729; (*b*) X. Han, F. Zhong, Y. Wang, and Y. Lu, *Angew. Chem. Int. Ed.* 2012, **51**, 767-770; (*c*) F. Zhong, X. Han, Y. Wang, and Y. Lu, *Chem. Sci.* 2012, **3**, 1231-1234; (*d*) F. Zhong, X. Han, Y. Wang, and Y. Lu, *Angew. Chem. Int. Ed*. 2011, **50**, 7837-7841; (*e*) F. Zhong, J. Luo, G.-Y. Chen, X. Dou, and Y. Lu, *J. Am. Chem. Soc.* 2012, **134**, 10222-10227; (*f*) F. Zhong, X. Dou, X. Han, W. Yao, Q. Zhu, Y. Meng, and Y. Lu, *Angew. Chem. Int. Ed.* 2013, **52**, 943-947.

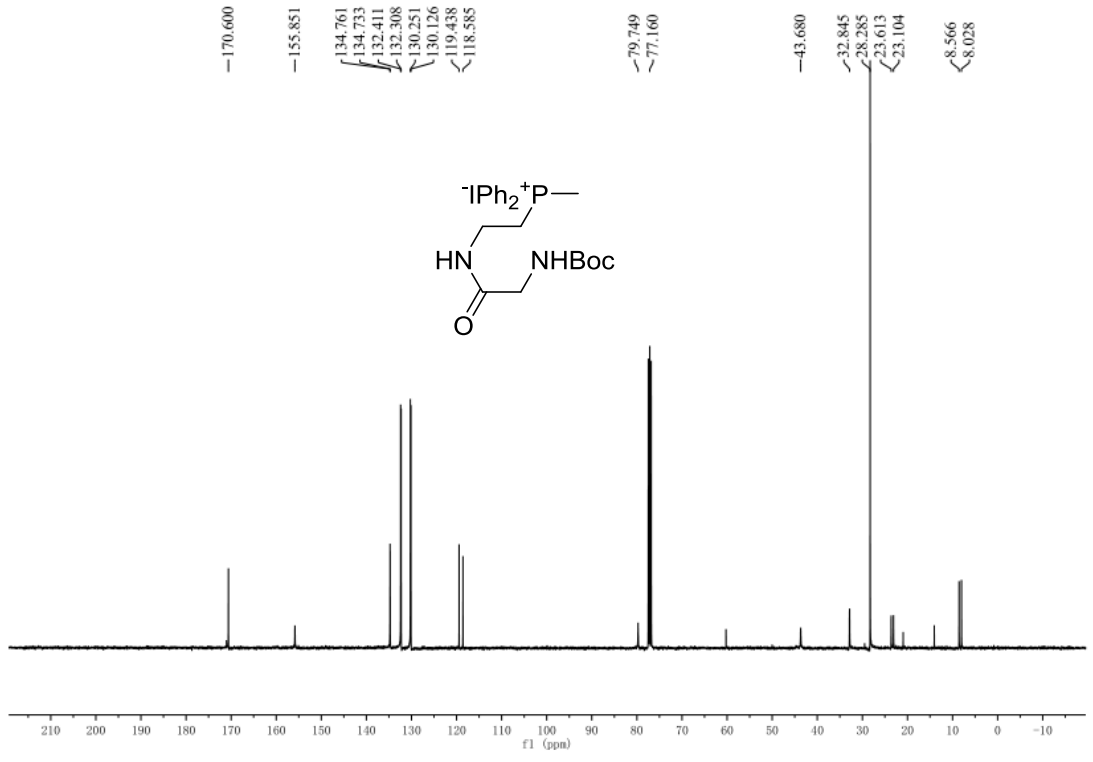
[2] (*a*) J.-H. Wu, J. Pan, J. Du, X. Wang, C. Jiang, and T. Wang, *Org. Lett.* 2020, **22**, 395-399; (*b*) D. Lu, J.-H. Wu, J. Pan, X. Chen, X. Ren, and T. Wang, *Chem. Commun.* 2020, **56**, 11231-11234; (*c*) L. Zhu, X. Ren, Z. Liao, J. Pan, C. Jiang, and T. Wang, *Org. Lett.* 2019, **21**, 8667-8672.

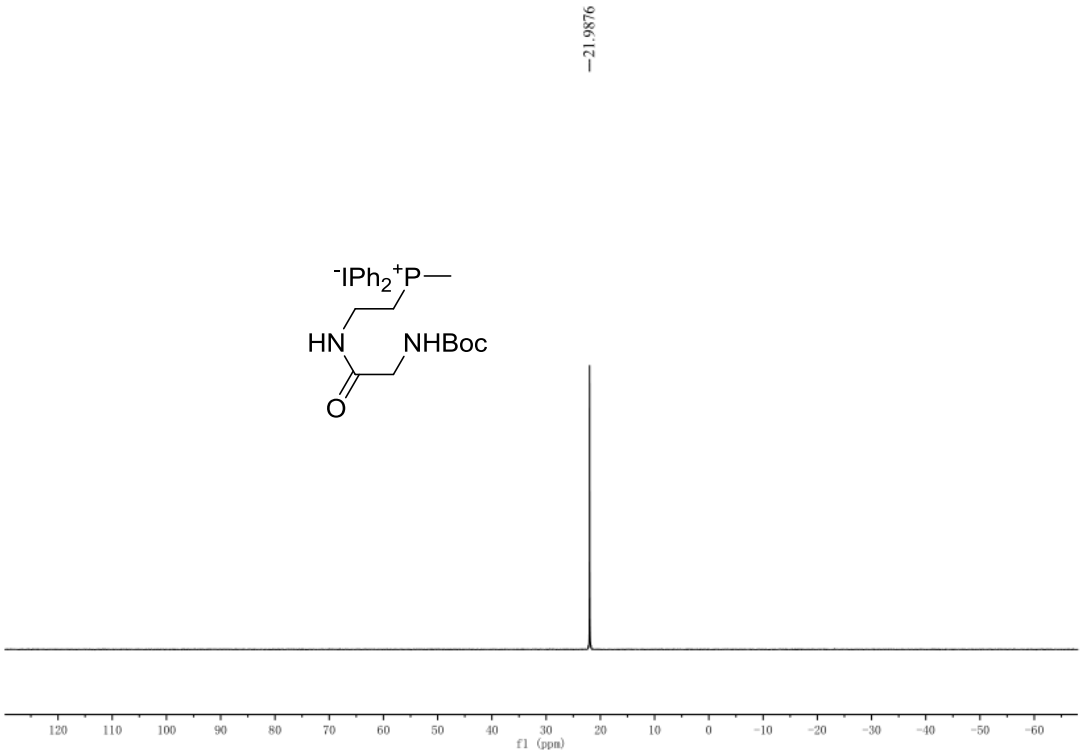
[3] (*a*) K. M. Dawood, and T. Fuchigami, *J. Org. Chem.* 2001, **66**, 7691; (*b*) D. Basavaiah, M. Bakthadoss, and S. Pandiaraju, *Chem. Commum.* 1998, *1639*; (c) F. Fournier, J. Berthelot, A. M. Pavard, N. Ronzani and J. J. Basselier, *Eur. J. Med. Chem.* 1981, **16**, 48.

[4] C. Conti, L. P. Monaco, and N. Desideri, *Bioorg. Med. Chem.* 2011, **19**, 7357-7364.

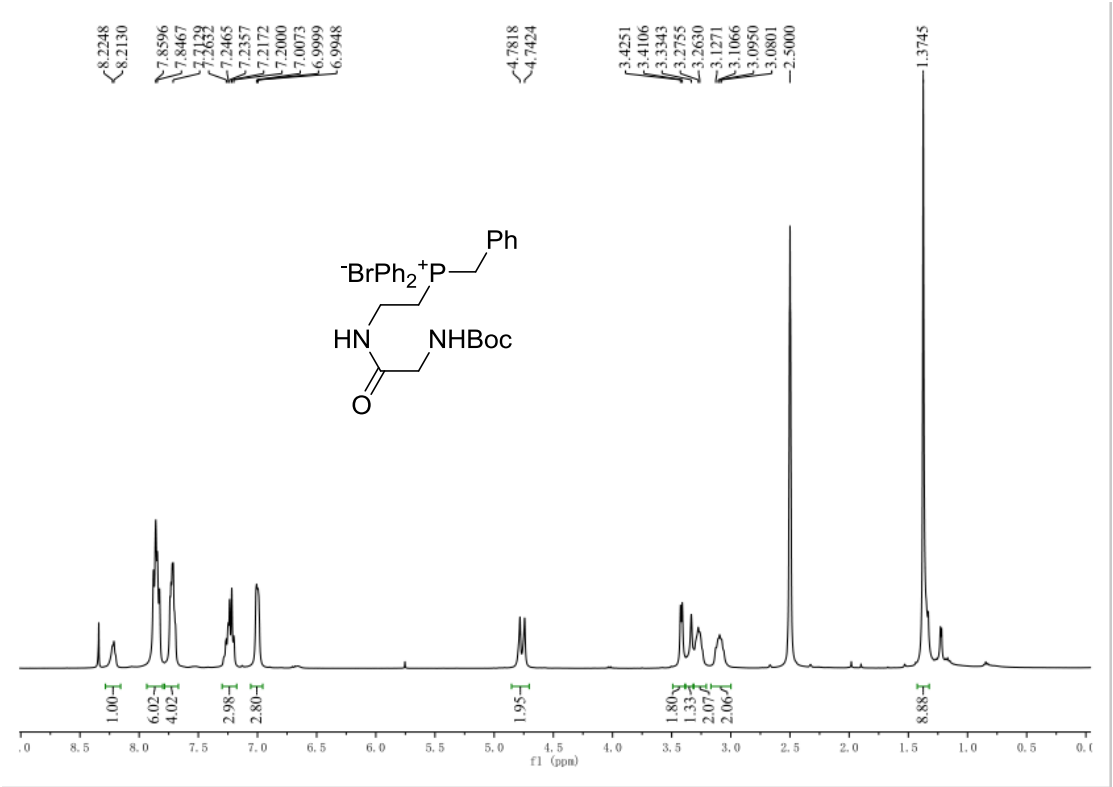
12. NMR spectra of the products

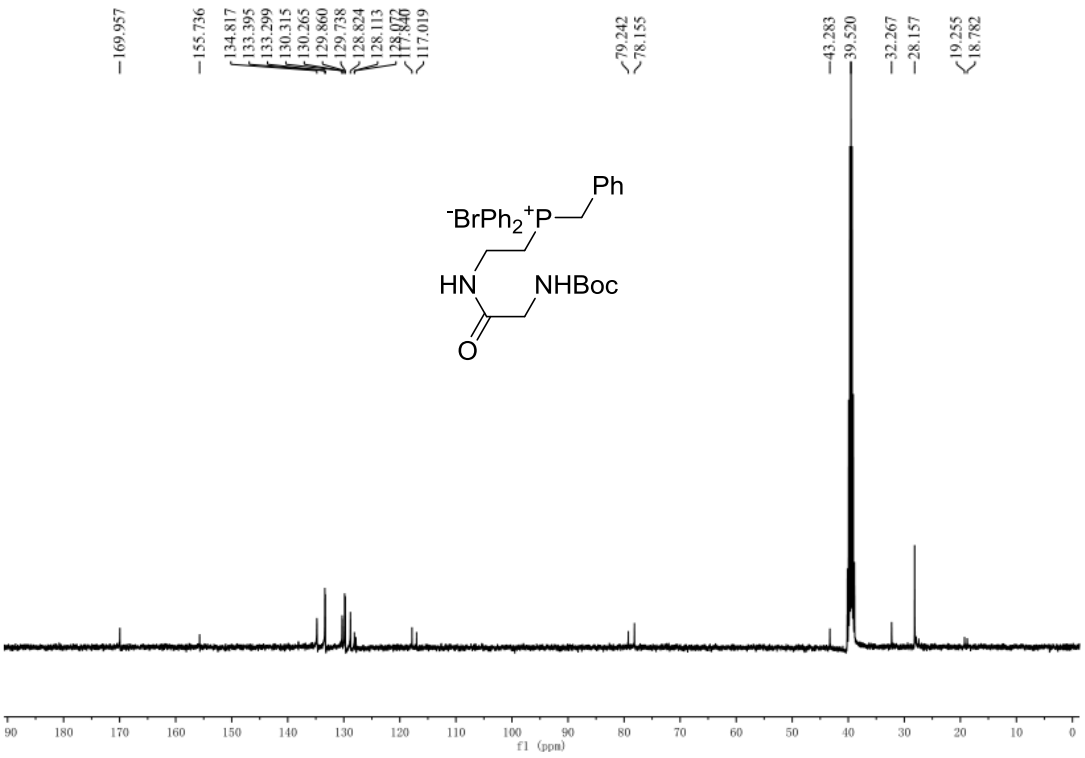


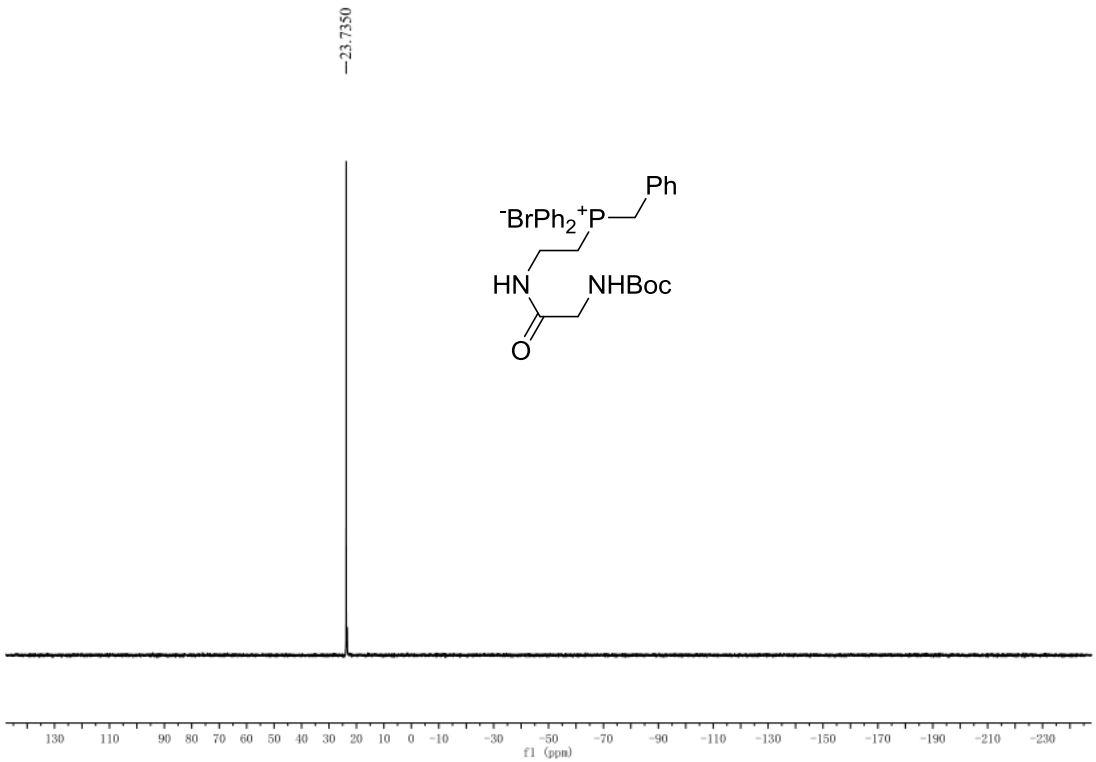




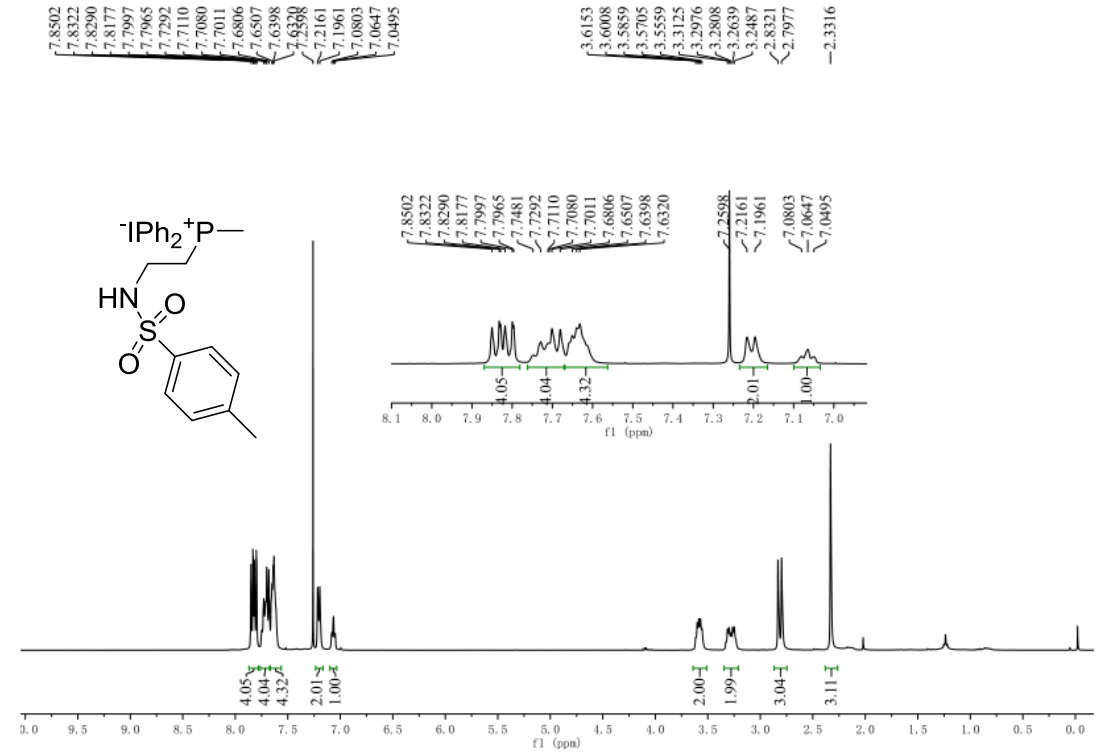
^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$),^{31}P NMR (162 MHz, $CDCl_3$) of **P1**







^{1}H NMR (400 MHz, DMSO-d6), ^{13}C NMR (100 MHz, DMSO-d6), ^{31}P NMR (162 MHz, DMSO-d6) of **P2**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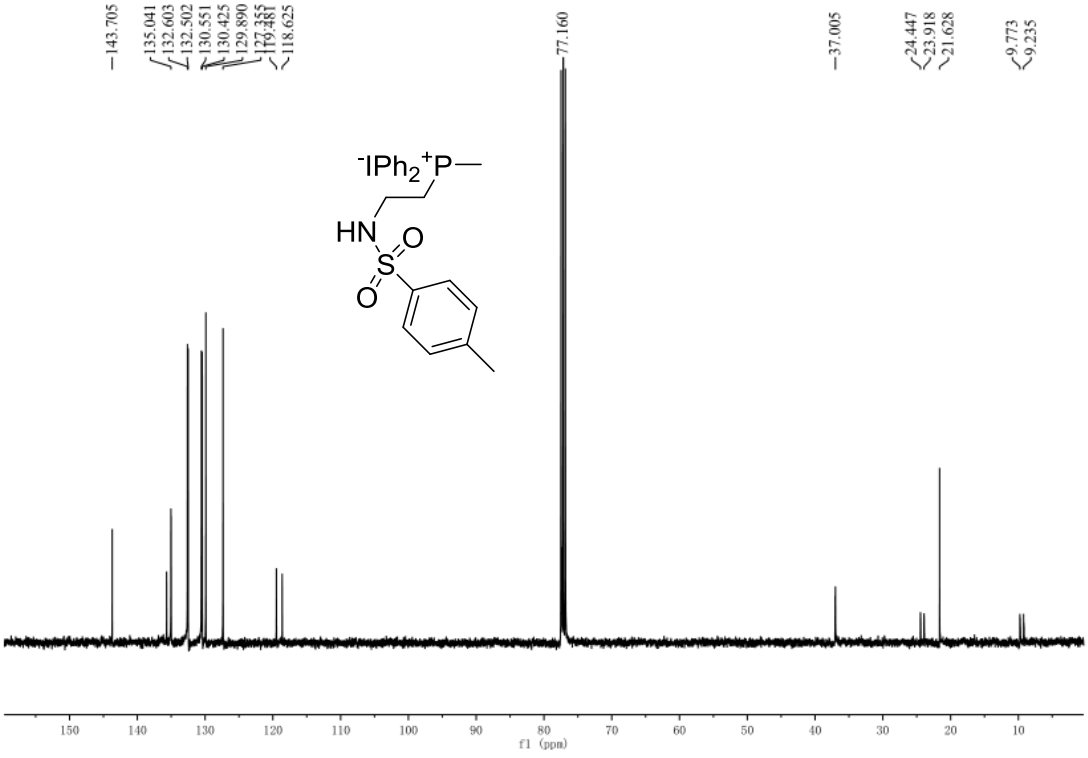
7.8290
7.8177
7.7997
7.7965
7.7292
7.7110
7.7080
7.7011
7.6806
7.6507
7.6398
7.6320
7.2161
7.1961
7.0803
7.0647
7.0495
3.6153
3.6008
3.5859
3.5705
3.5559
3.3125
3.2976
3.2808
3.2639
3.2487
2.8321
2.7977
2.3316
HN
O
S
O
4.05
4.04
4.32
2.01
1.00
2.00
1.99
3.04
3.11
f1 (ppm)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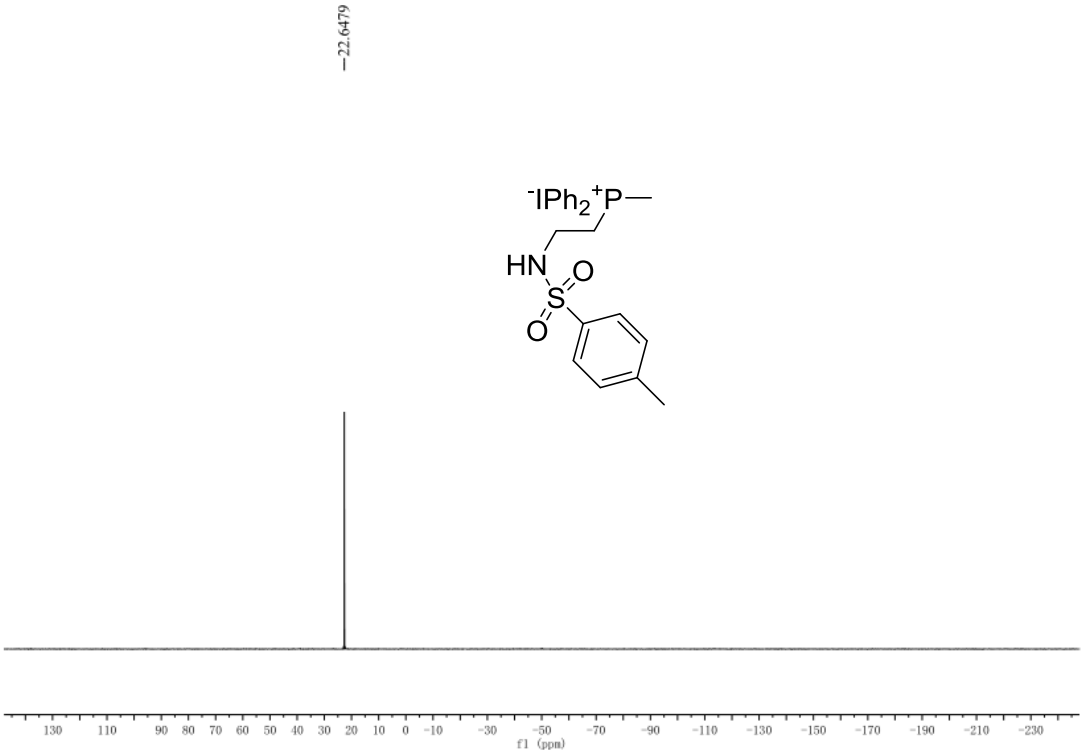
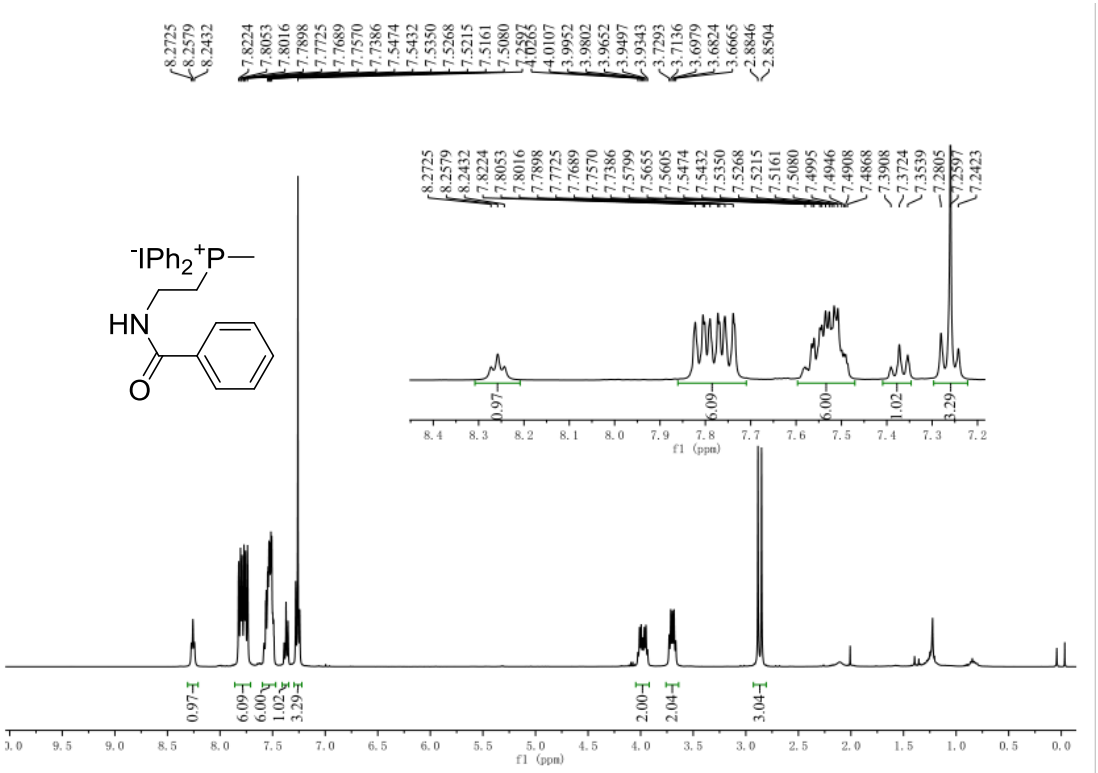
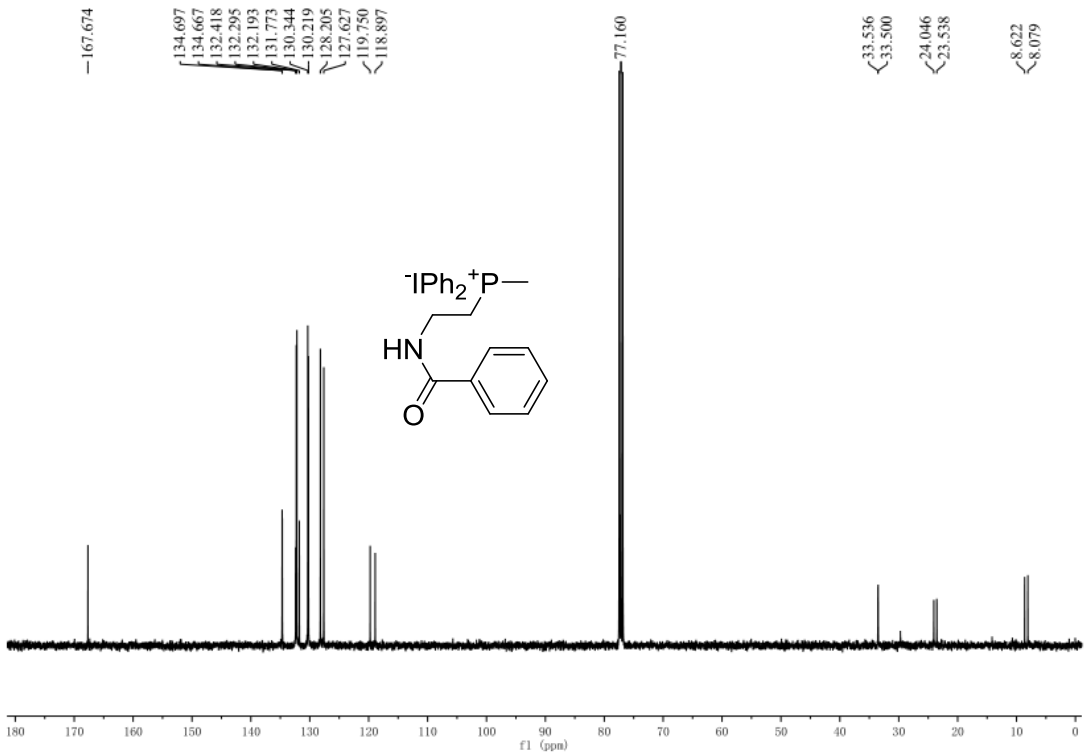
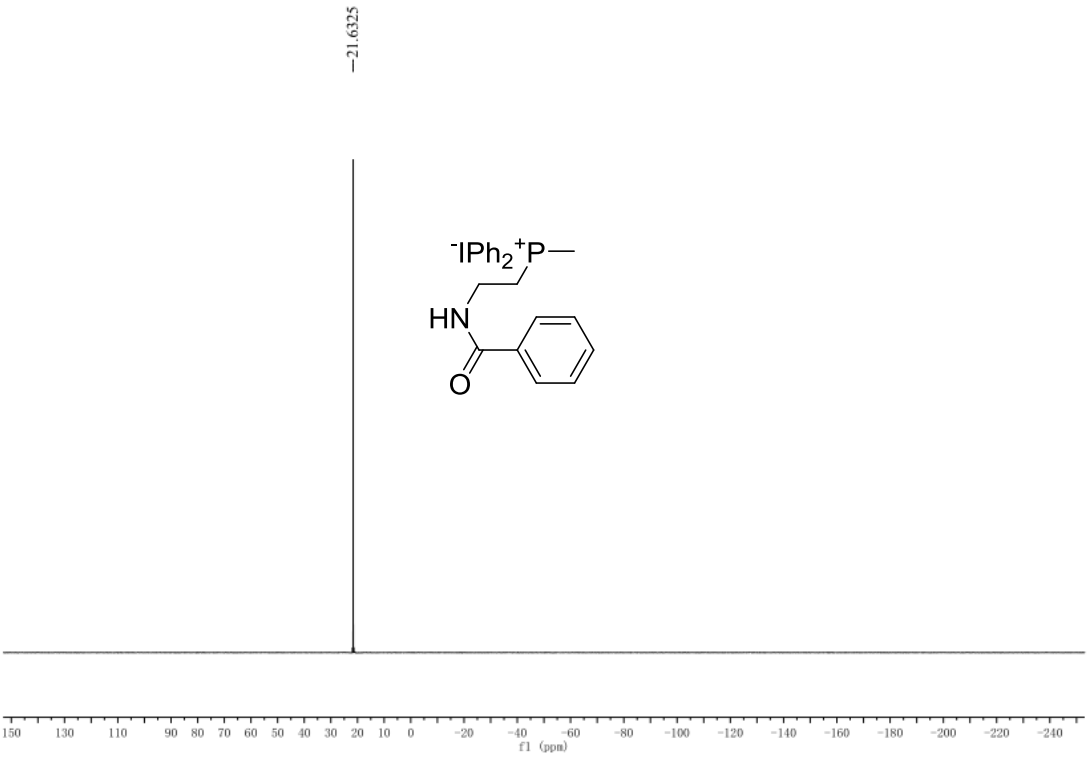
9.235
HN
O
S
O
f1 (ppm)



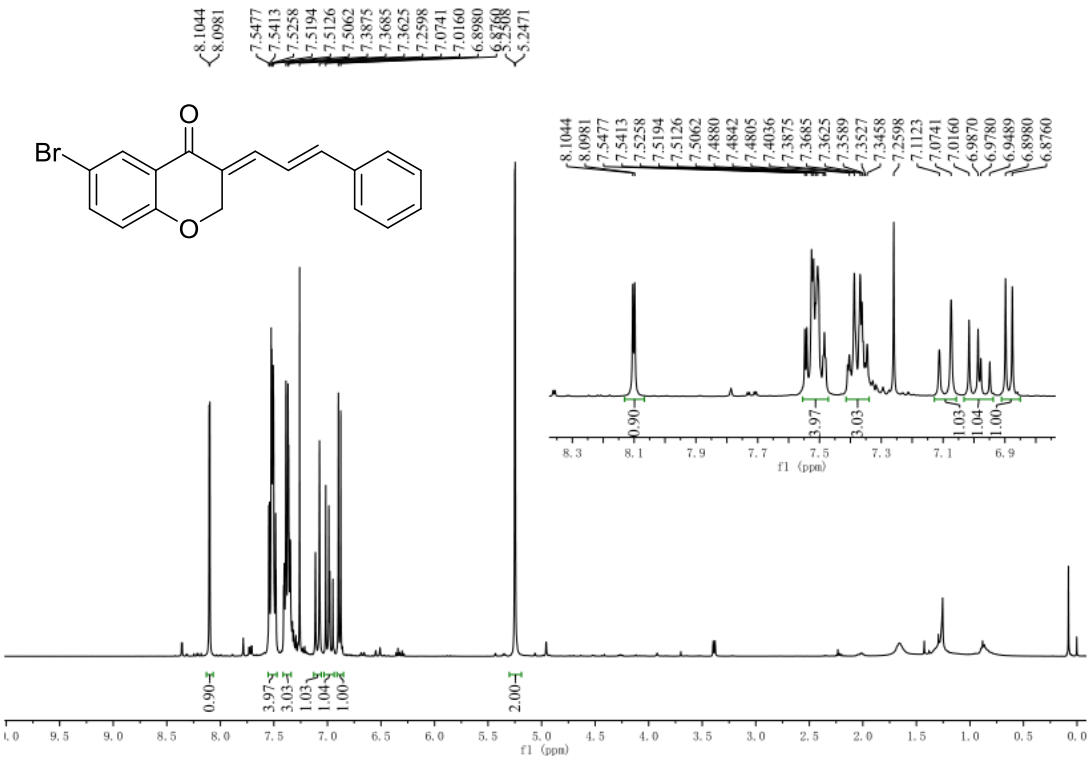
^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$),^{31}P NMR (162 MHz, $CDCl_3$) of **P3**

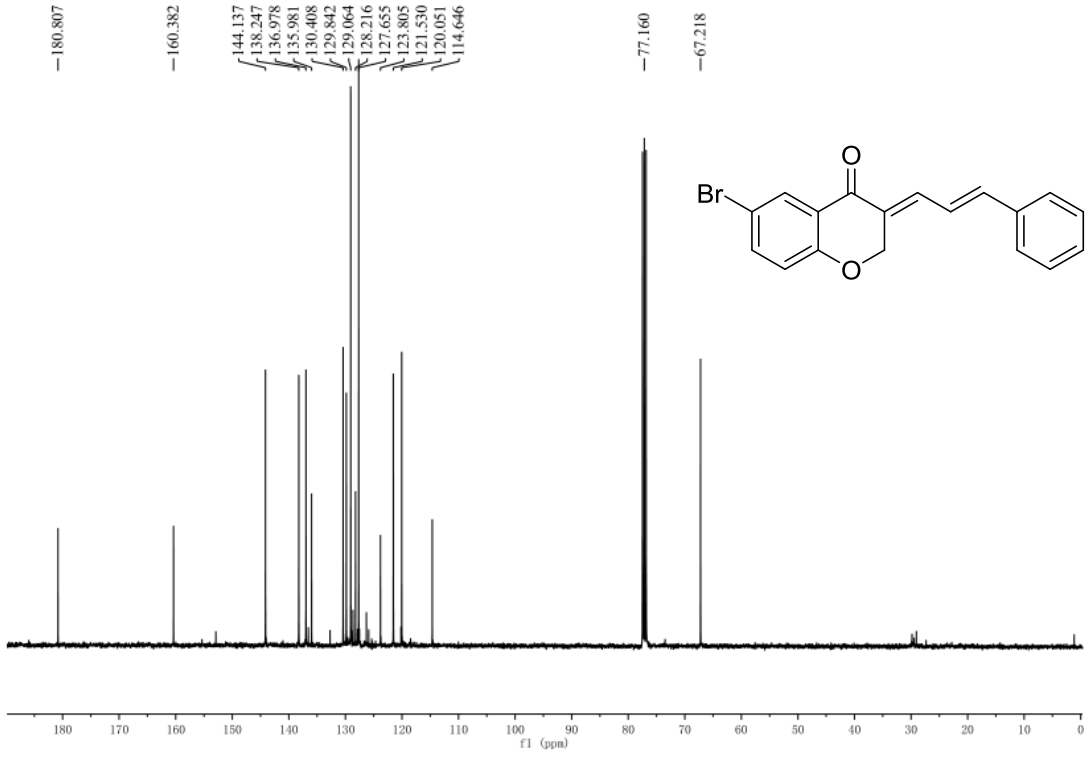




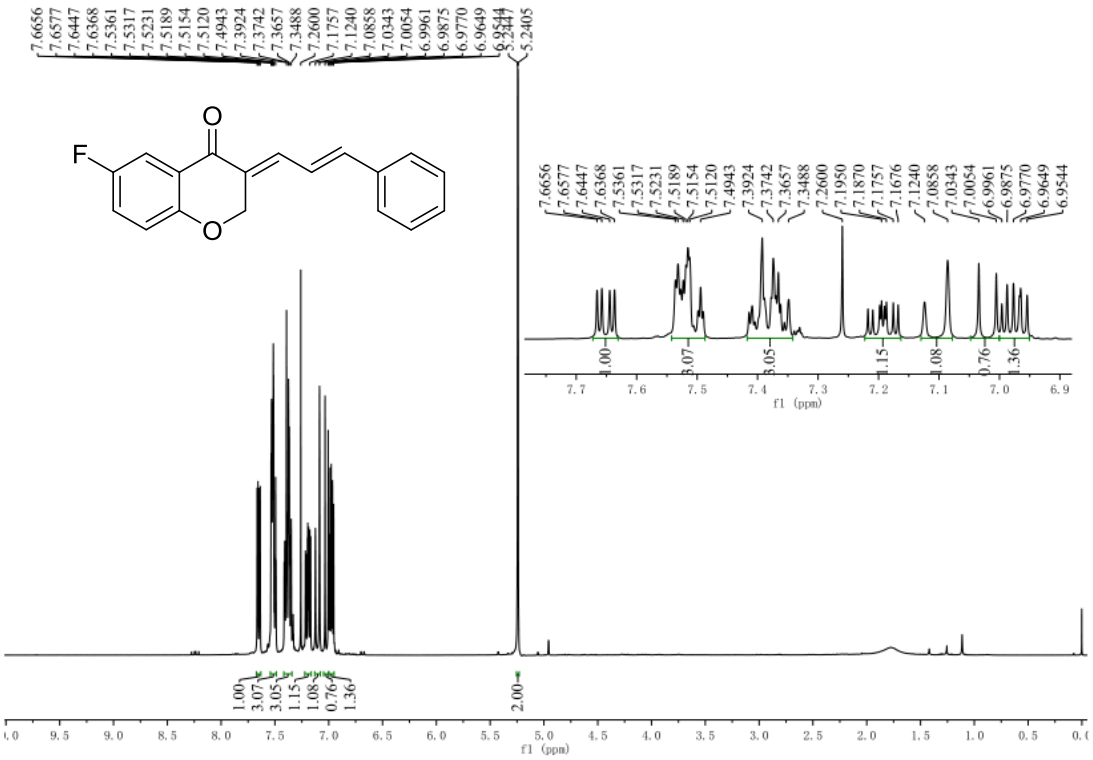


^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$),^{31}P NMR (162 MHz, $CDCl_3$) of **P4**





^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) of **1c**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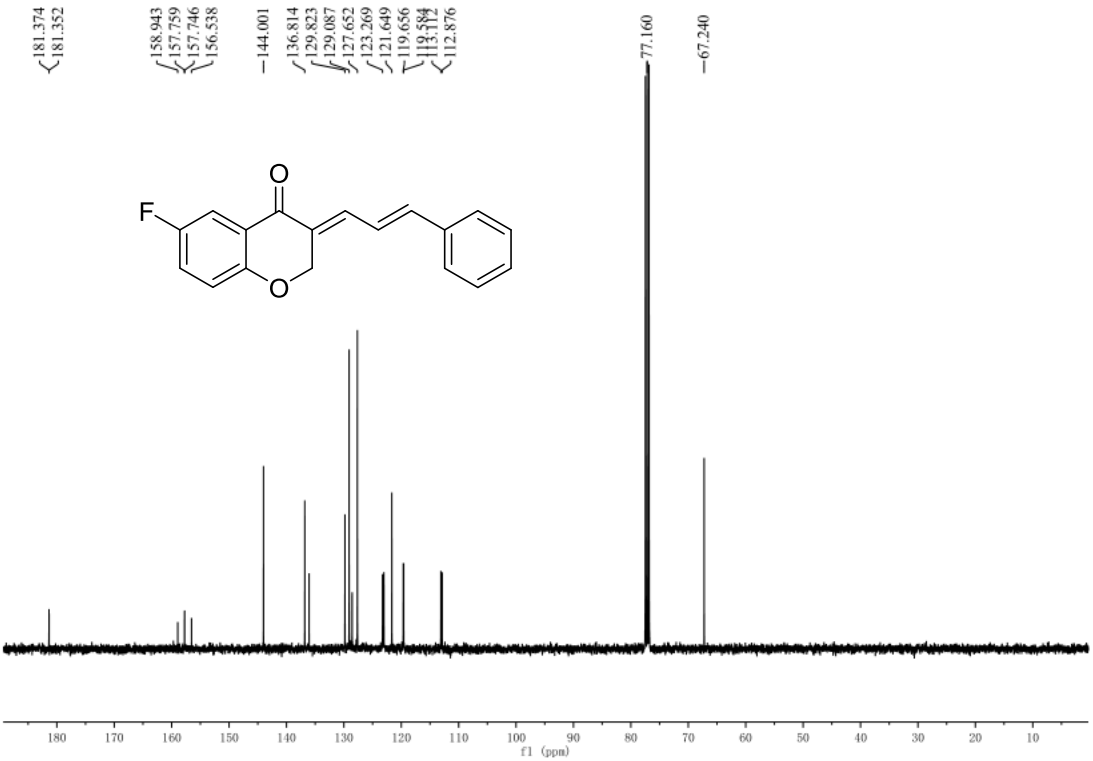
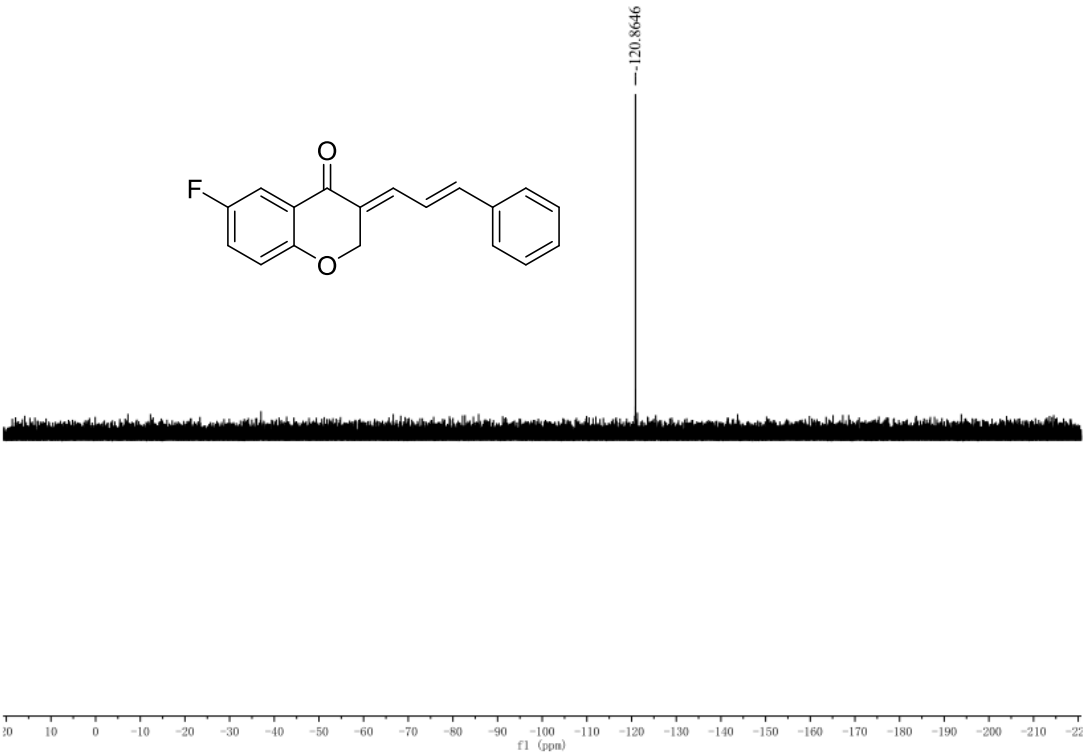
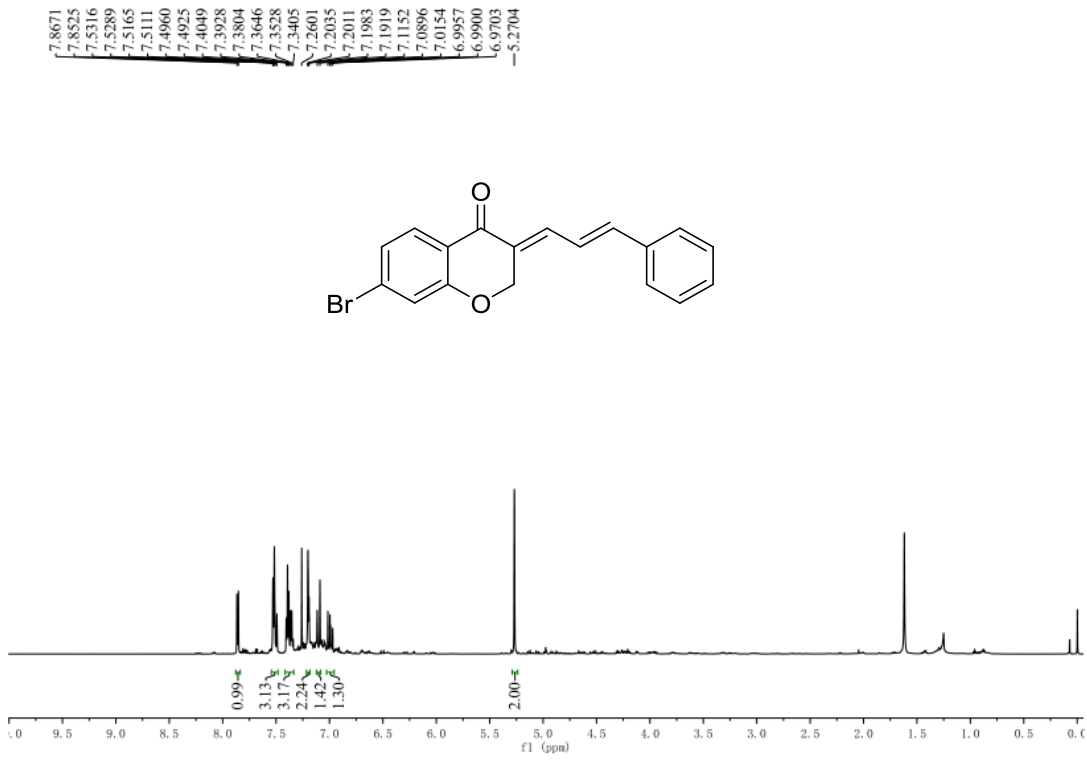
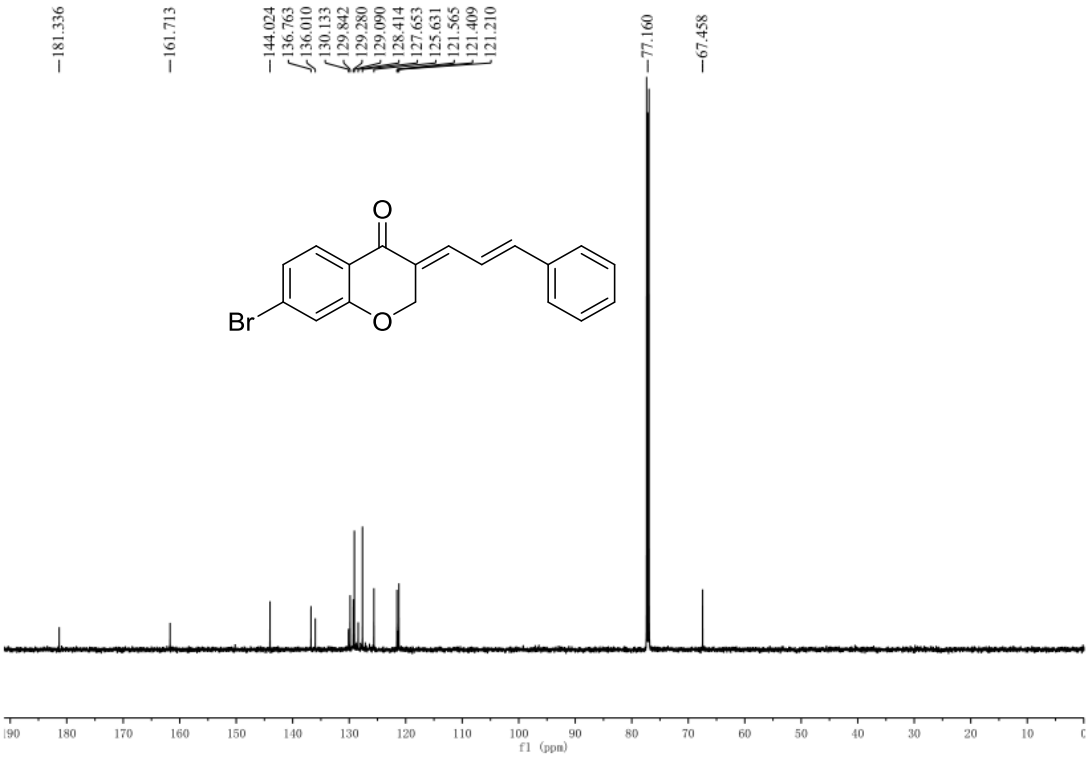
7.6577
7.6447
7.6368
7.5361
7.5317
7.5231
7.5189
7.5154
7.5120
7.4943
7.3924
7.3742
7.3657
7.3488
7.2600
7.1757
7.1240
7.0858
7.0343
7.0054
6.9961
6.9875
6.9770
6.9649
6.9544
5.2447
5.2405
F
O
O
1.00
3.07
3.05
1.15
1.08
0.76
1.36
2.00
f1 (ppm)


181.374
181.352
158.943
157.759
157.746
156.538
144.001
136.814
129.823
129.087
127.652
123.269
121.649
119.656
112.876
77.160
67.240
F
O
O
f1 (ppm)

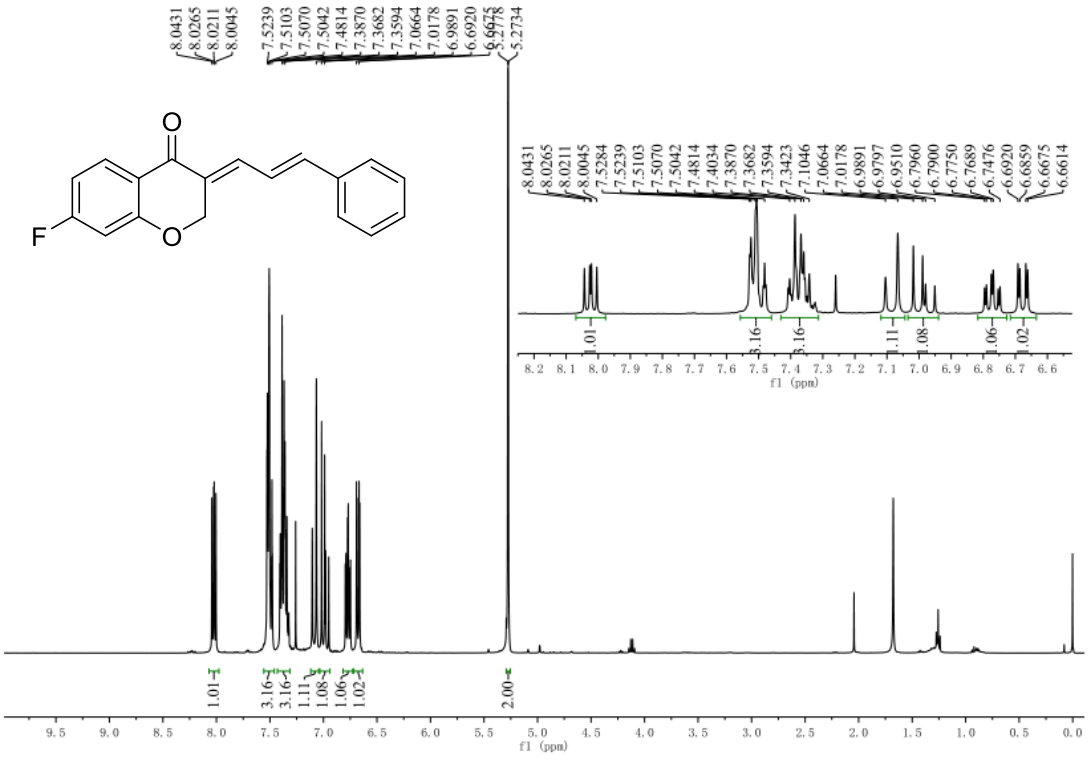


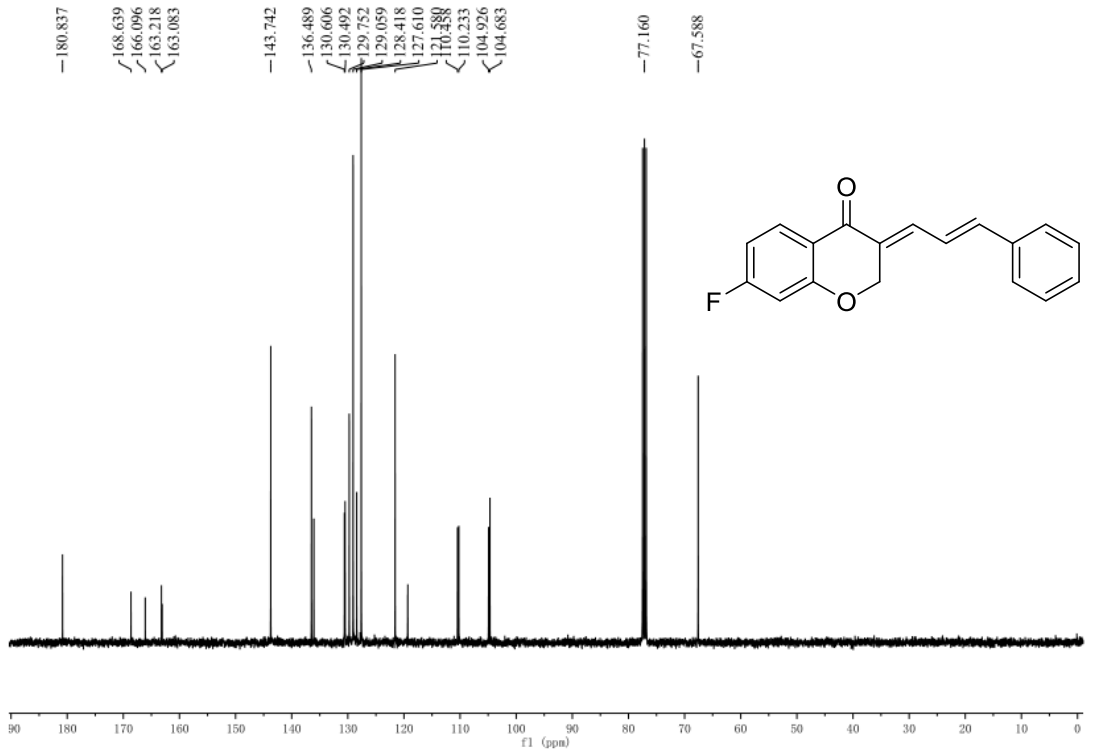
^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$), ^{19}F NMR (376 MHz, $CDCl_3$) of **1d**

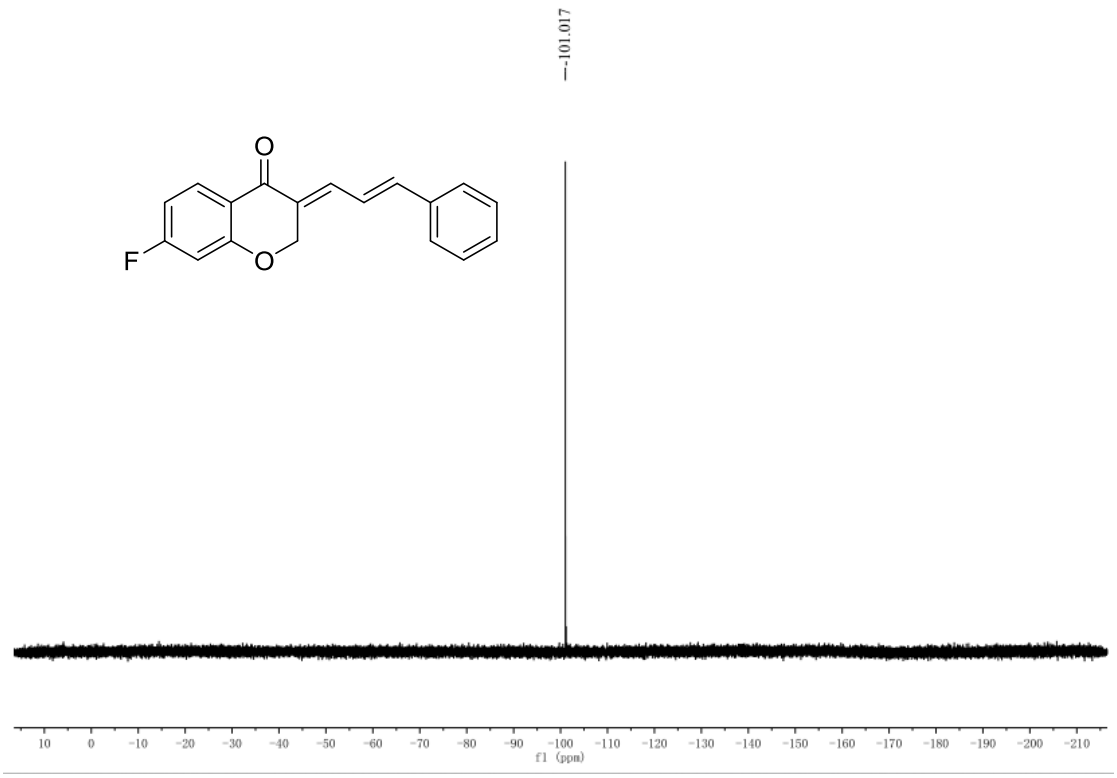




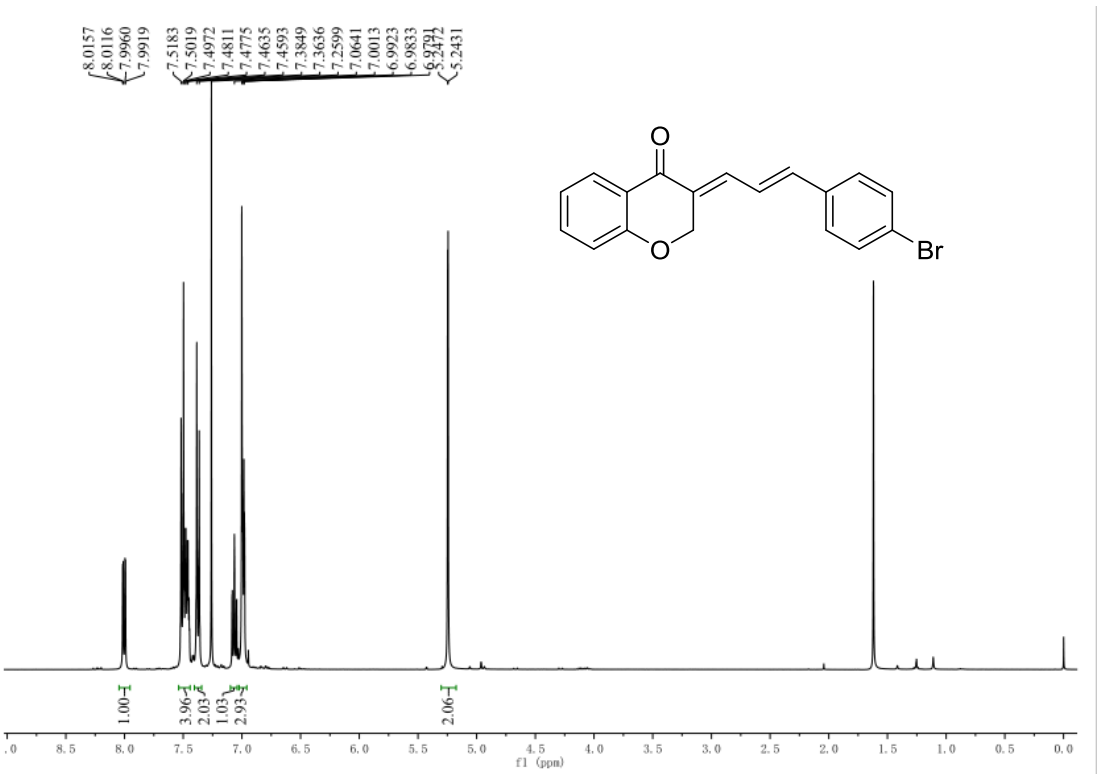
^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) of **1e**

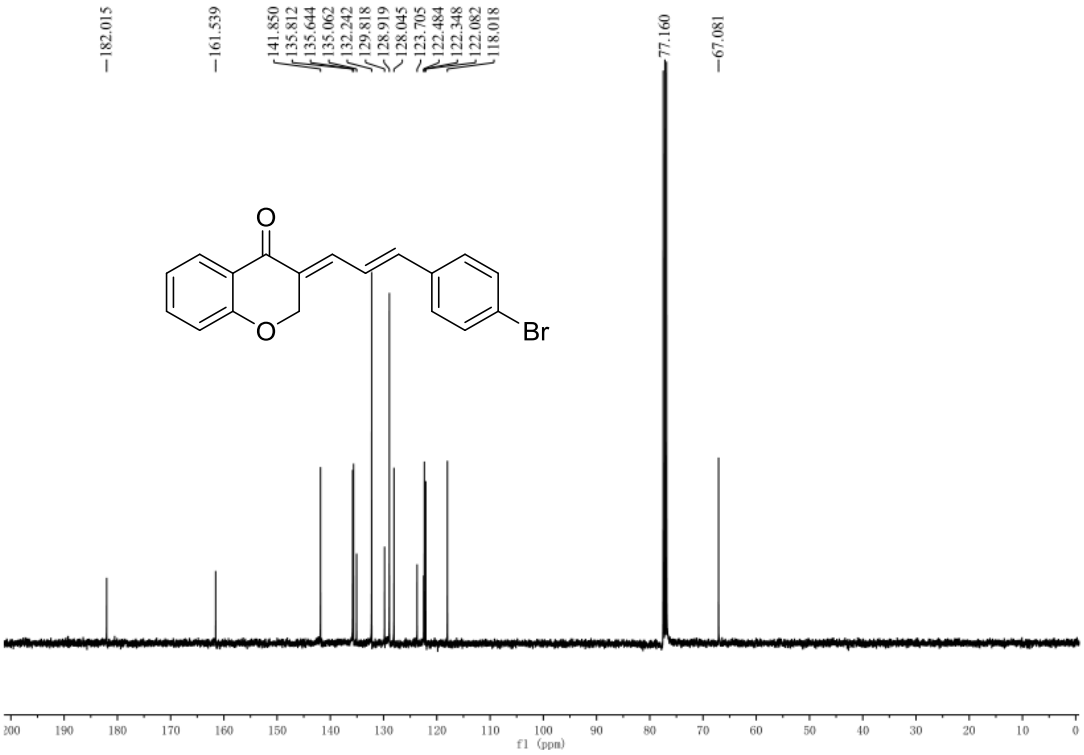




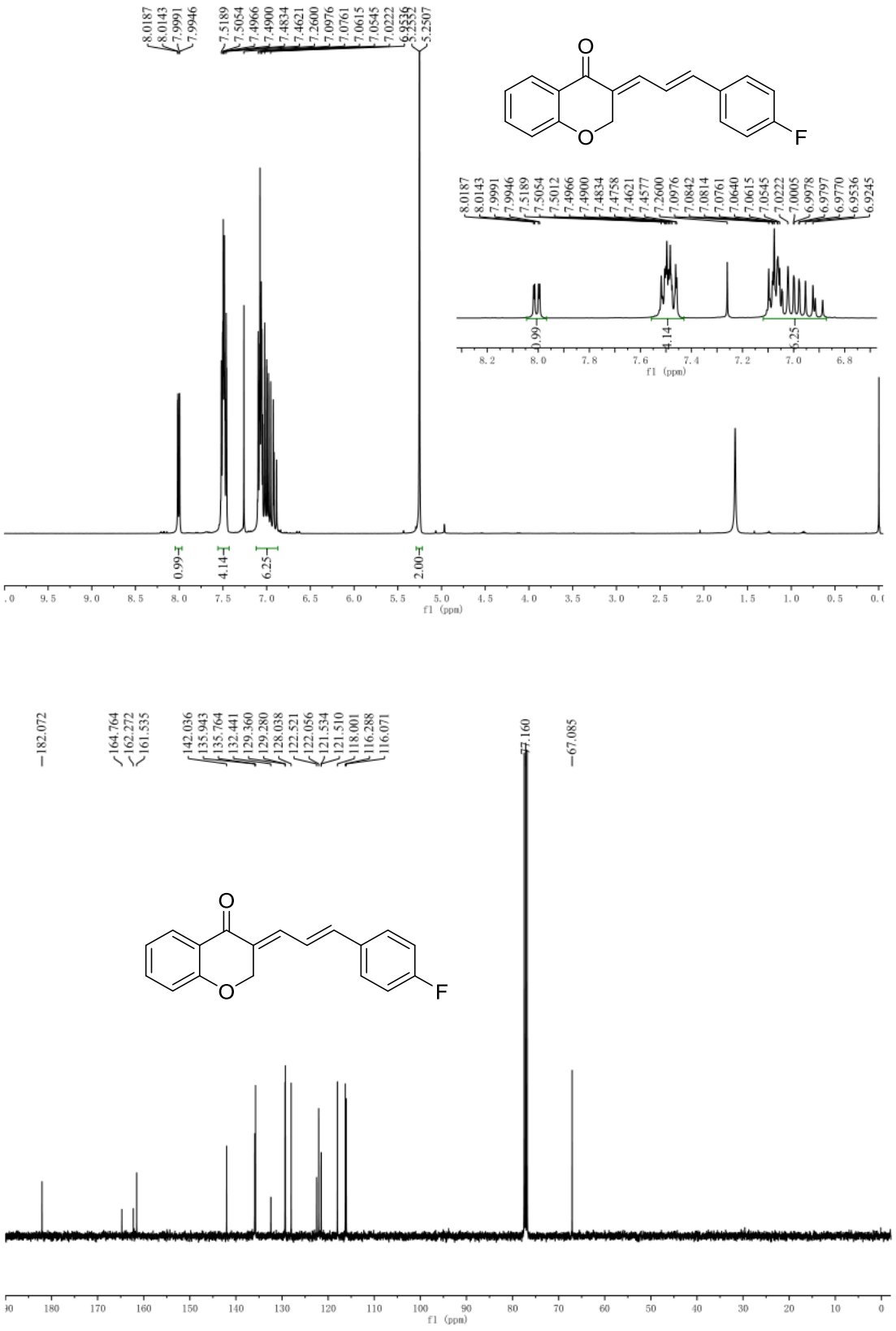


^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$), ^{19}F NMR (376 MHz, $CDCl_3$) of **1f**

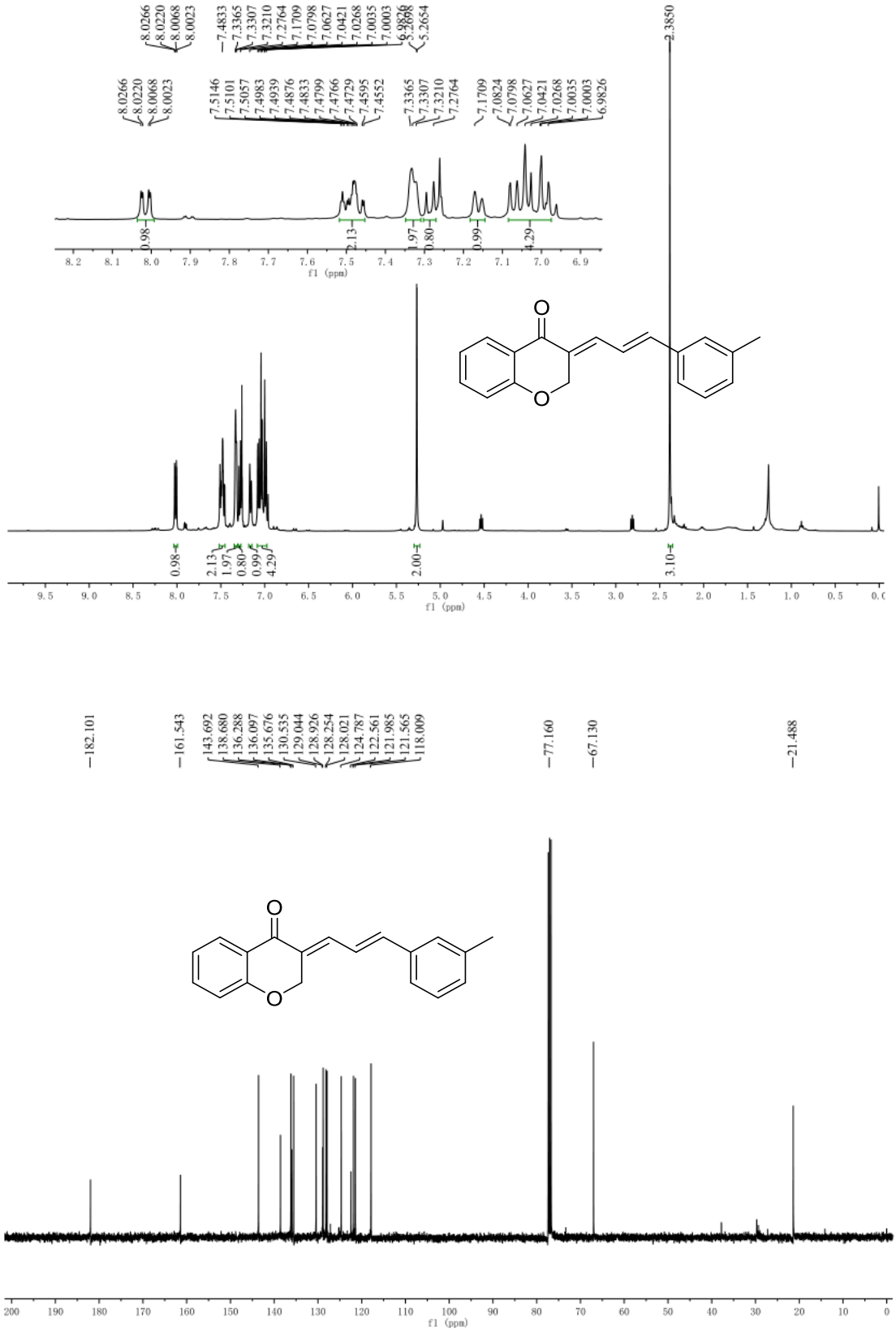




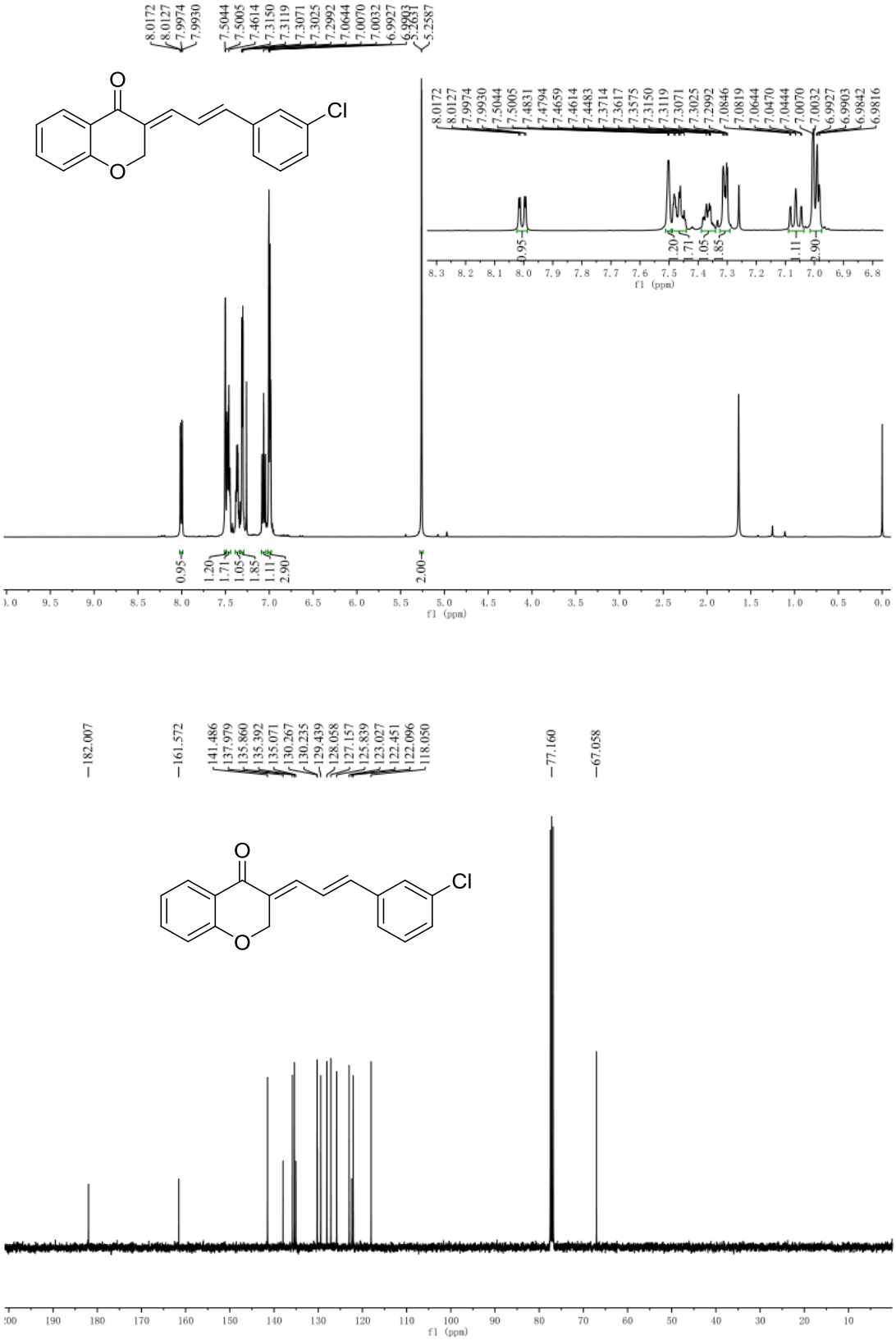
^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) of **1g**



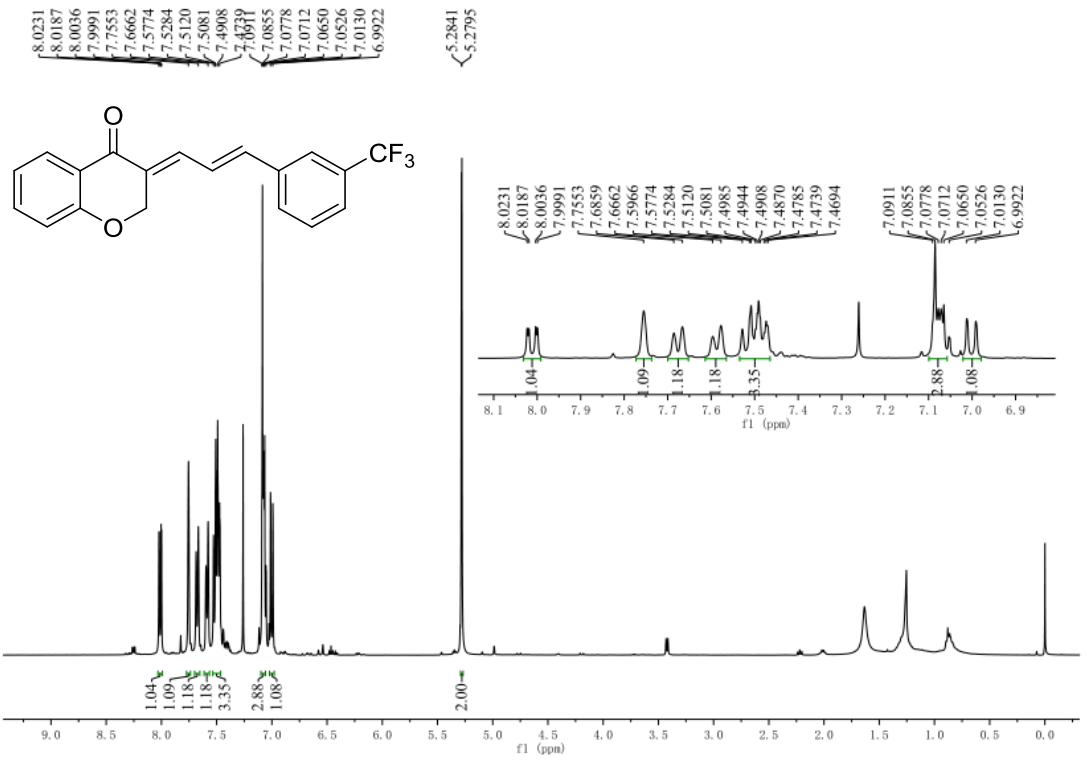
^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) of **1i**

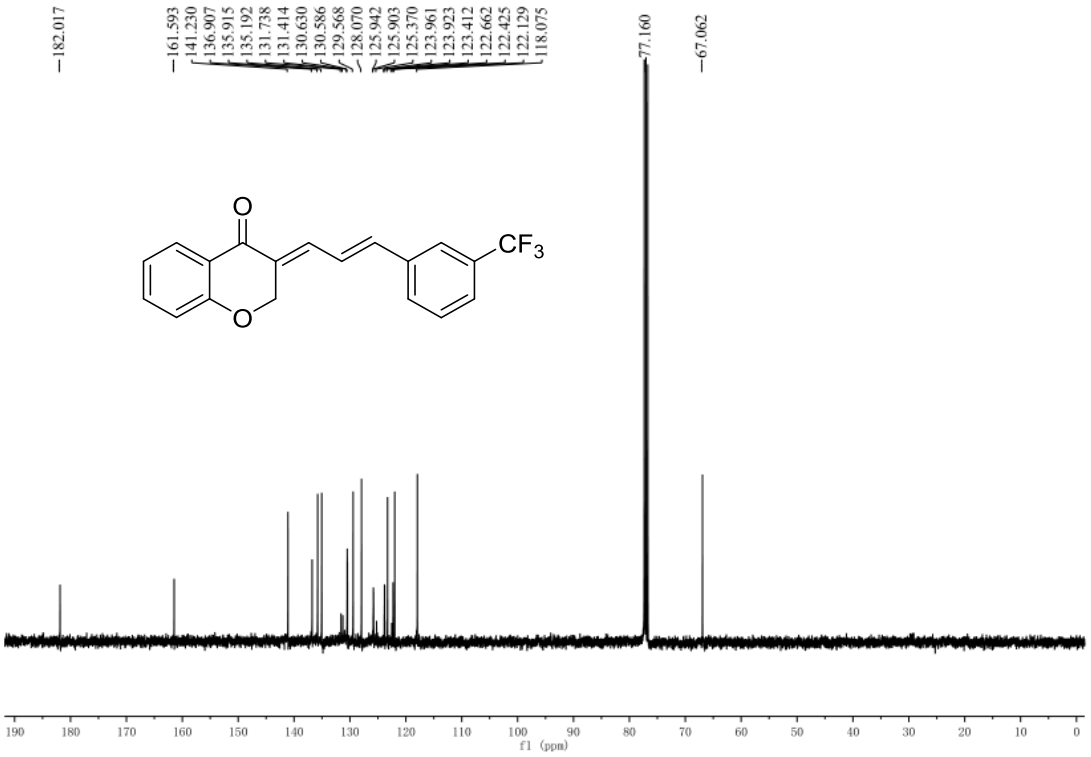


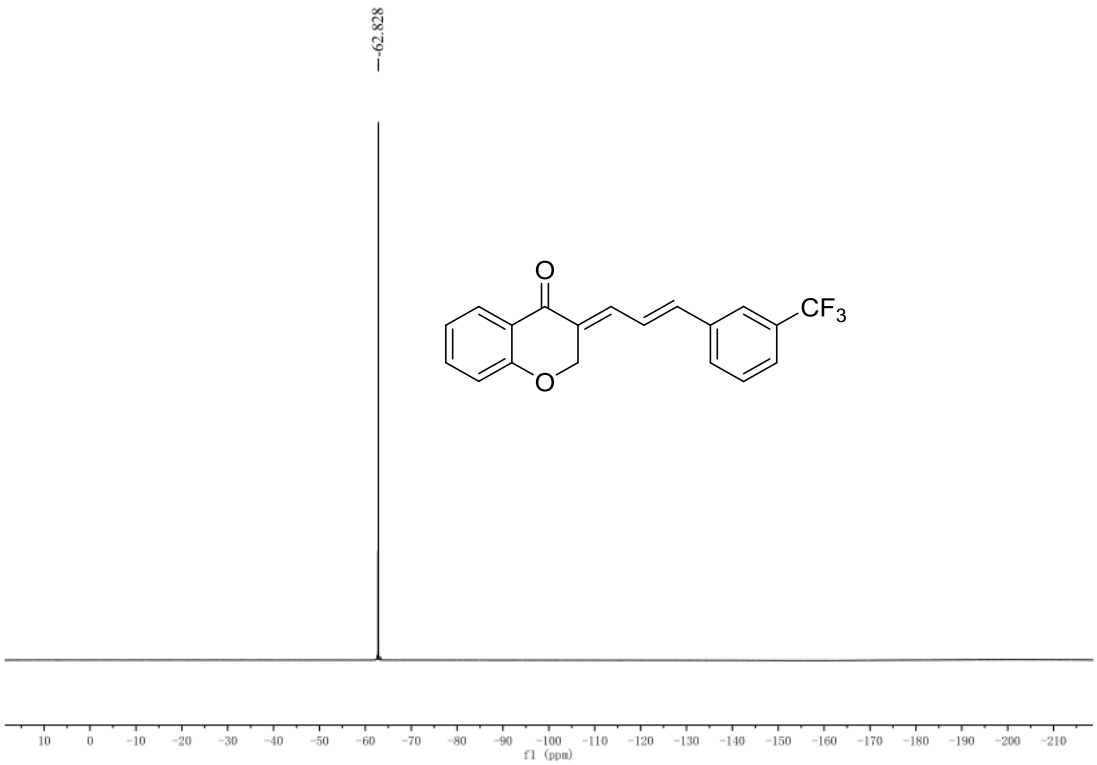
^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) of **1j**



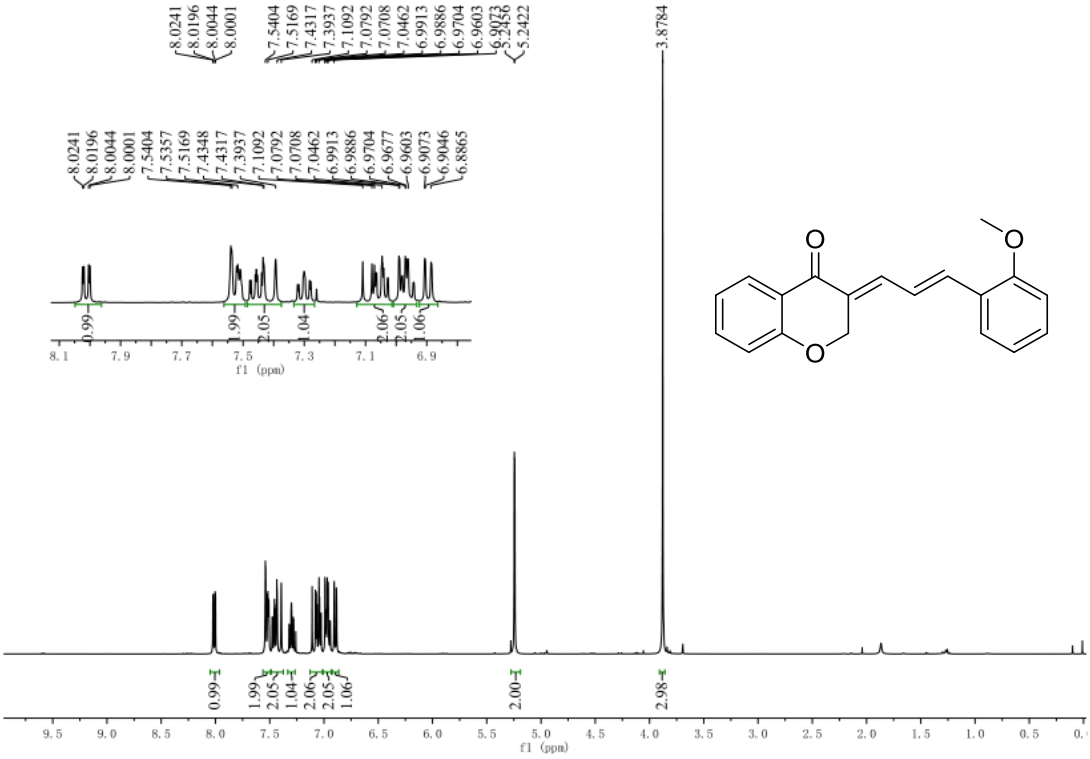
^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) of **1k**

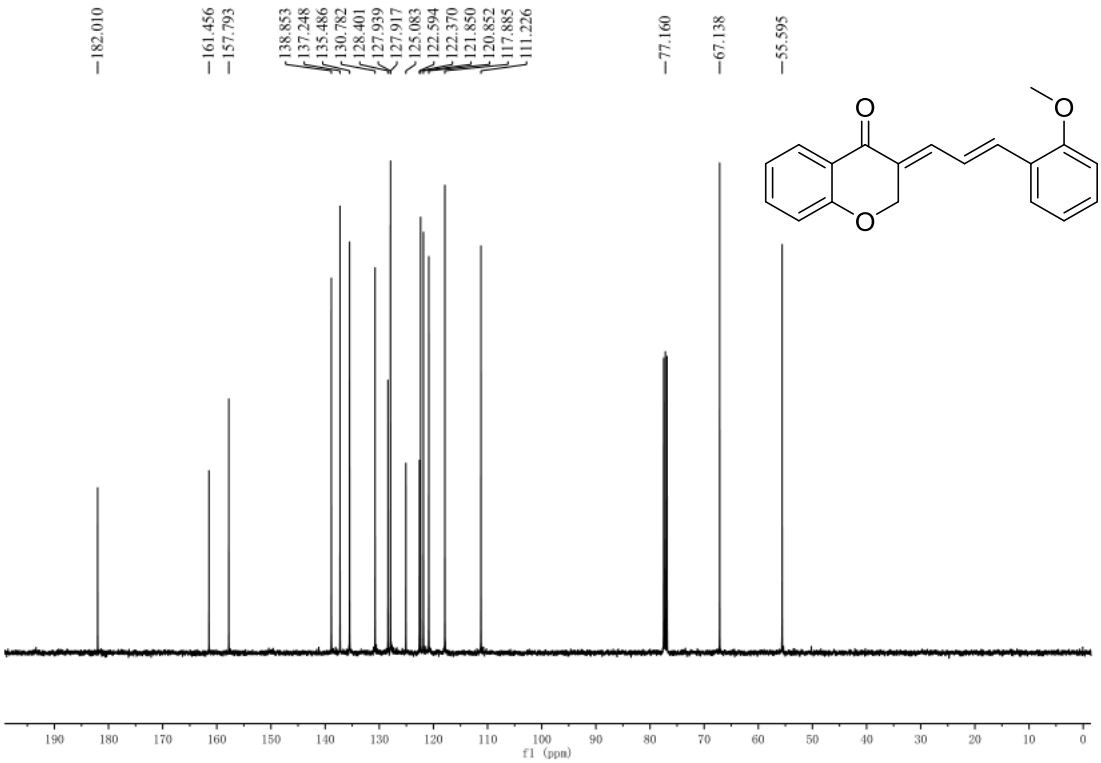

8.0231
8.0187
8.0036
7.9991
7.7553
7.6662
7.5774
7.5284
7.5120
7.5081
7.4908
7.4739
7.0911
7.0855
7.0778
7.0712
7.0650
7.0526
7.0130
6.9922
5.2841
5.2795
O
O
CF3
1.04
1.09
1.18
1.18
3.35
2.88
1.08
2.00
f1 (ppm)


182.017
161.593
141.230
136.907
135.915
135.192
131.738
131.414
130.630
130.586
129.568
128.070
125.942
125.903
125.370
123.961
123.923
123.412
122.662
122.425
122.129
118.075
77.160
67.062
O
O
CF3
f1 (ppm)

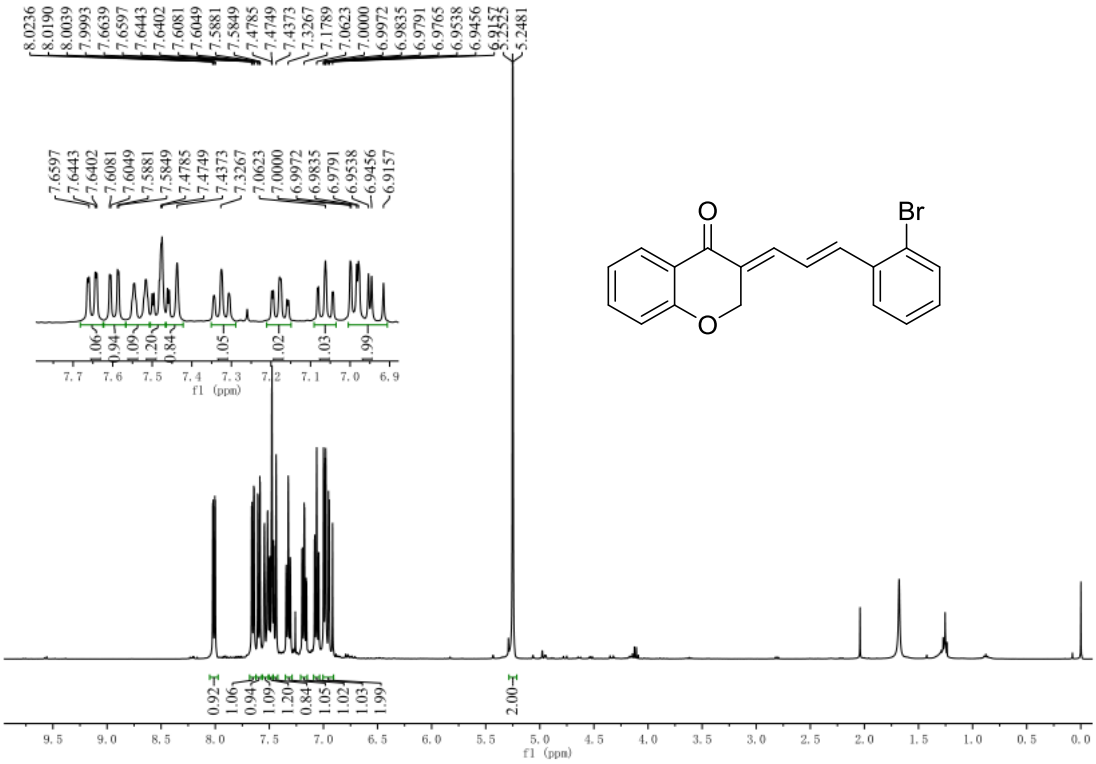


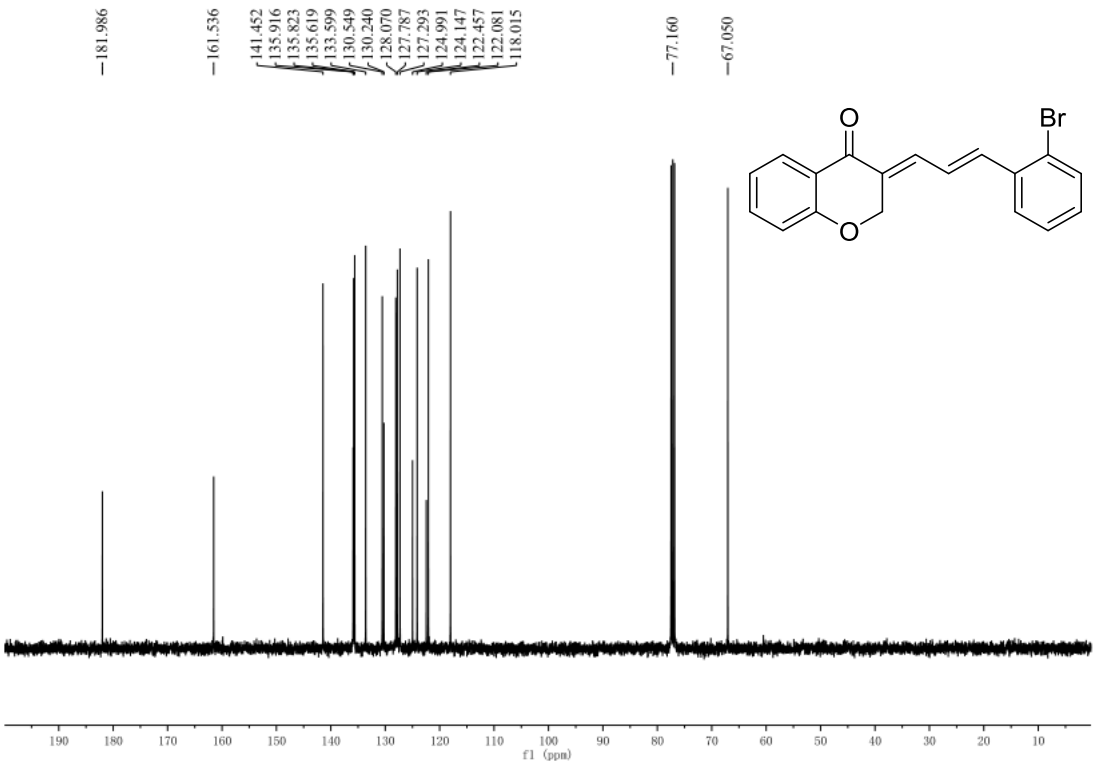
^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$), ^{19}F NMR (376 MHz, $CDCl_3$) of **1l**



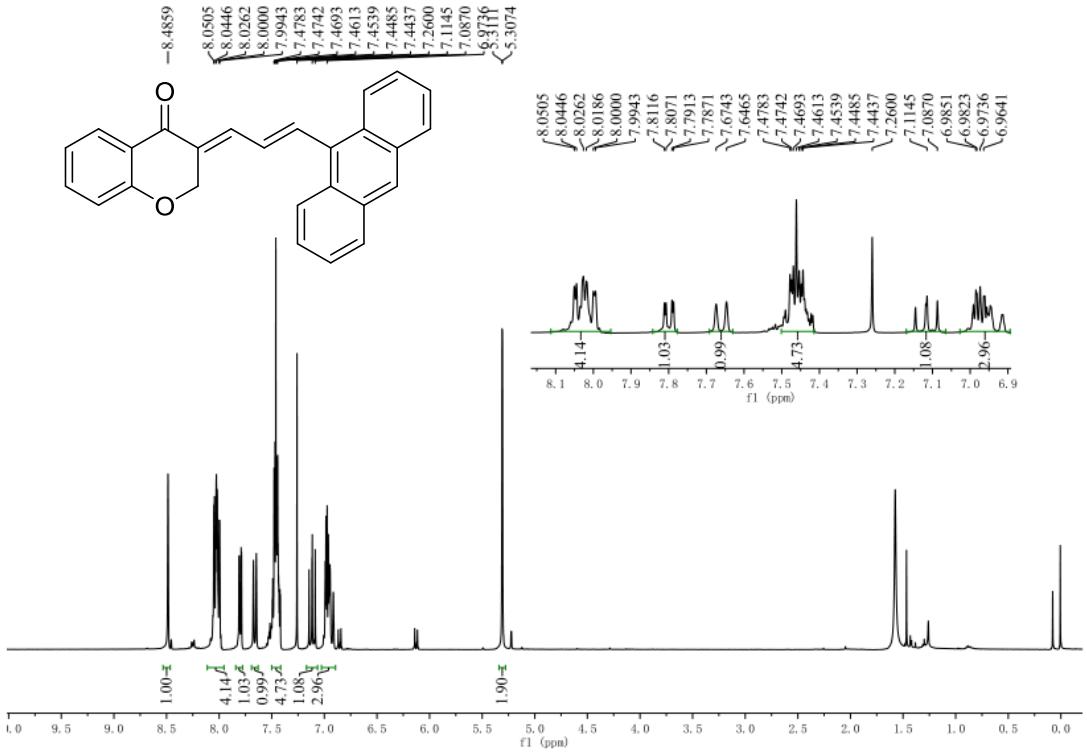


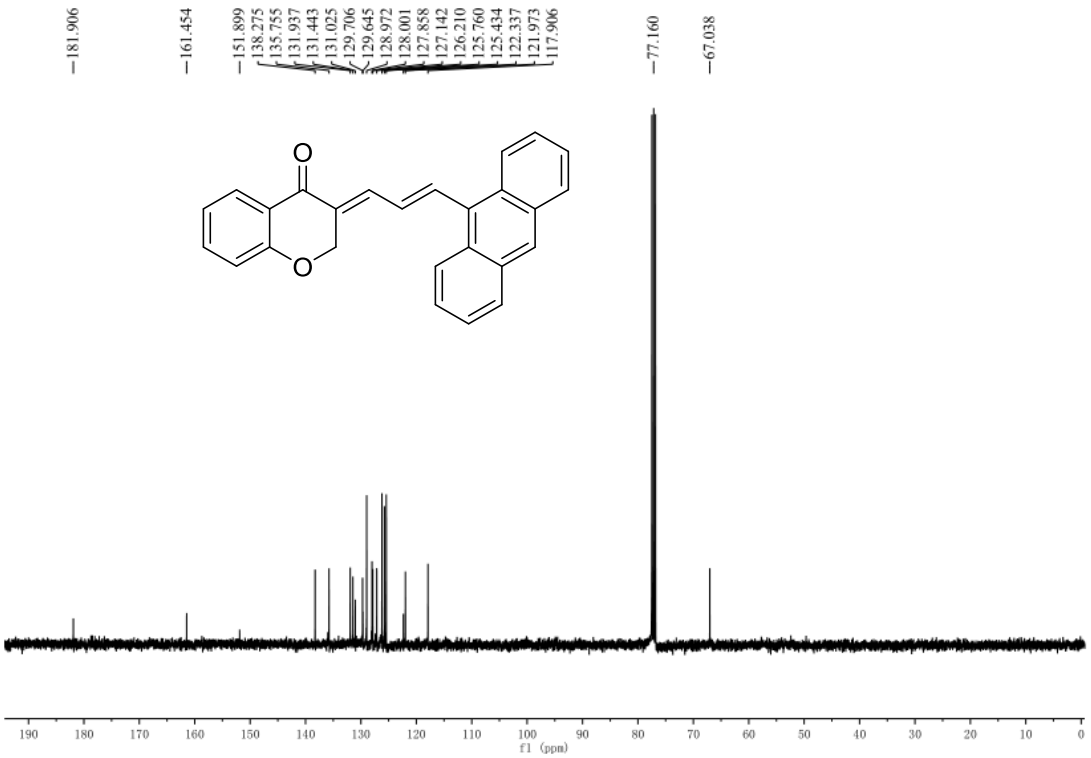
^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) of **1m**



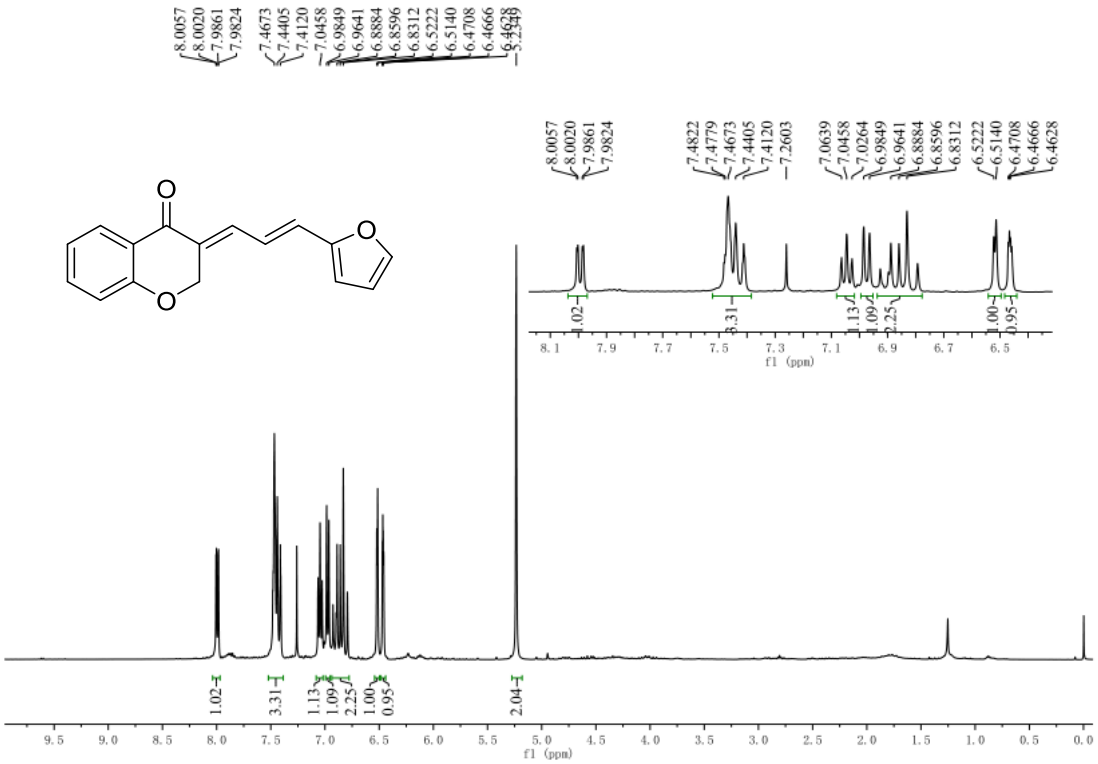


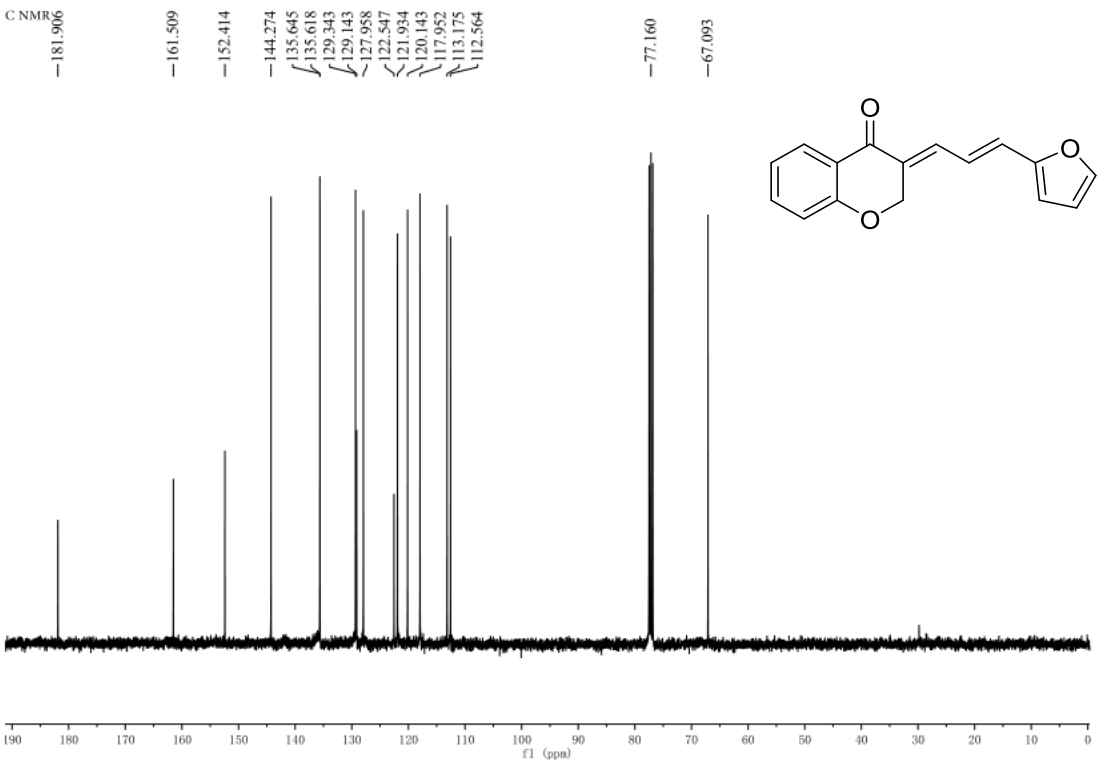
^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) of **1n**



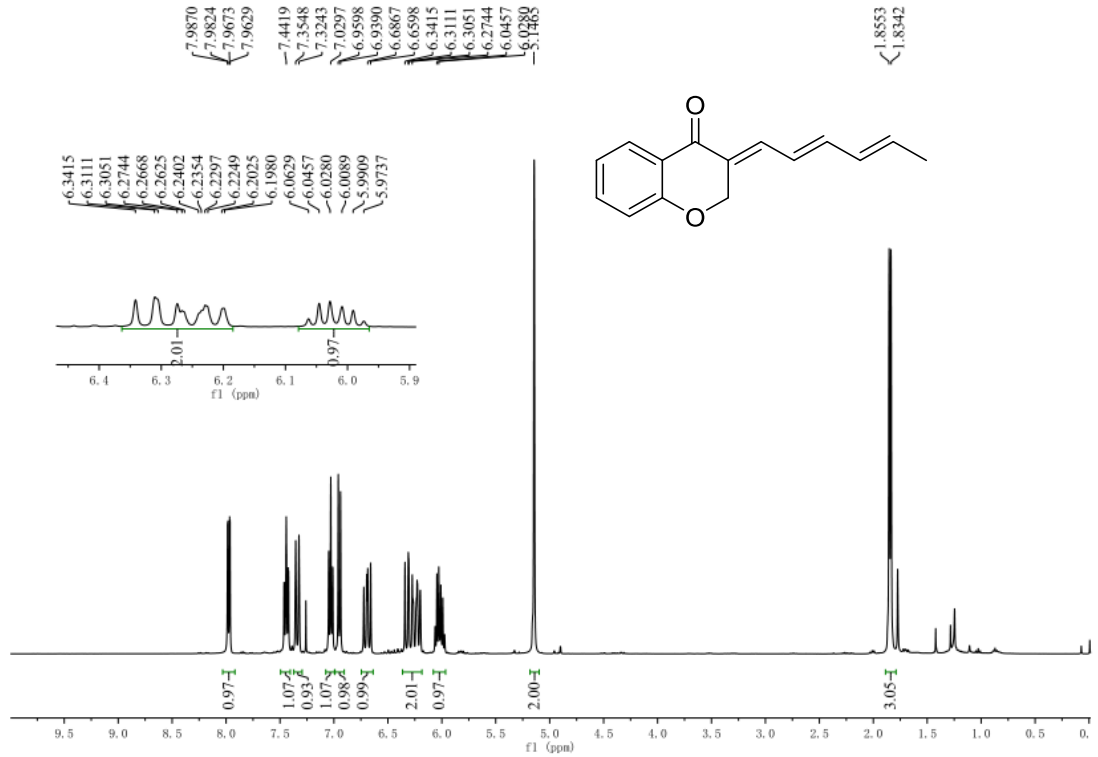


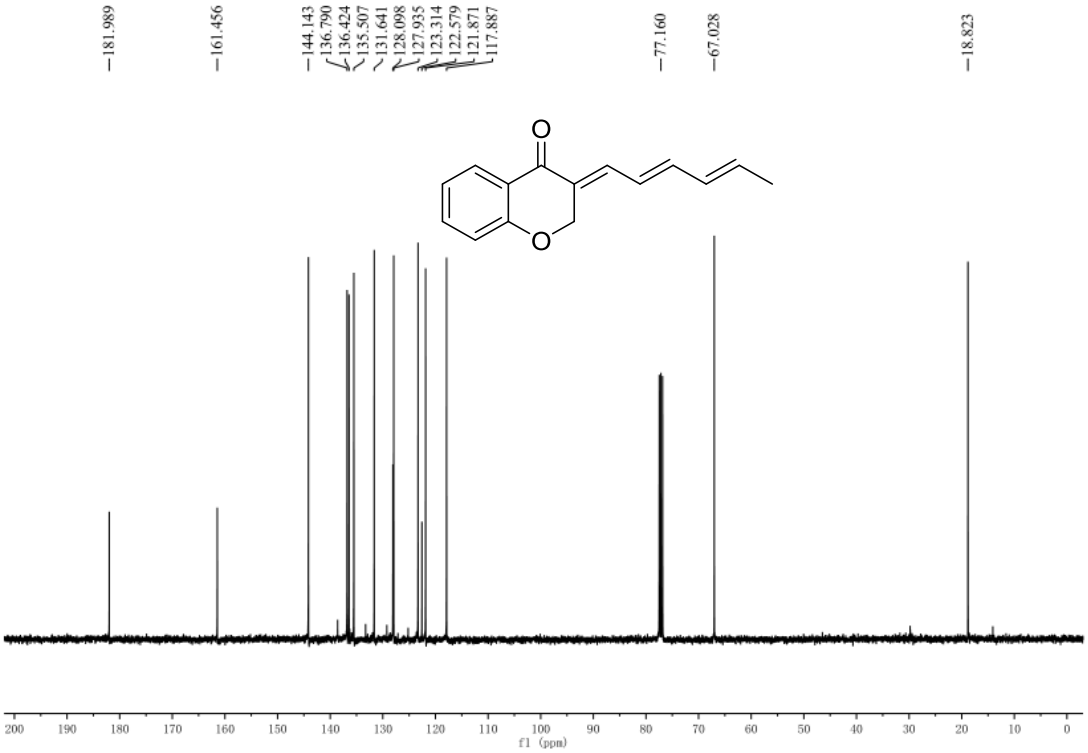
^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) of **1o**



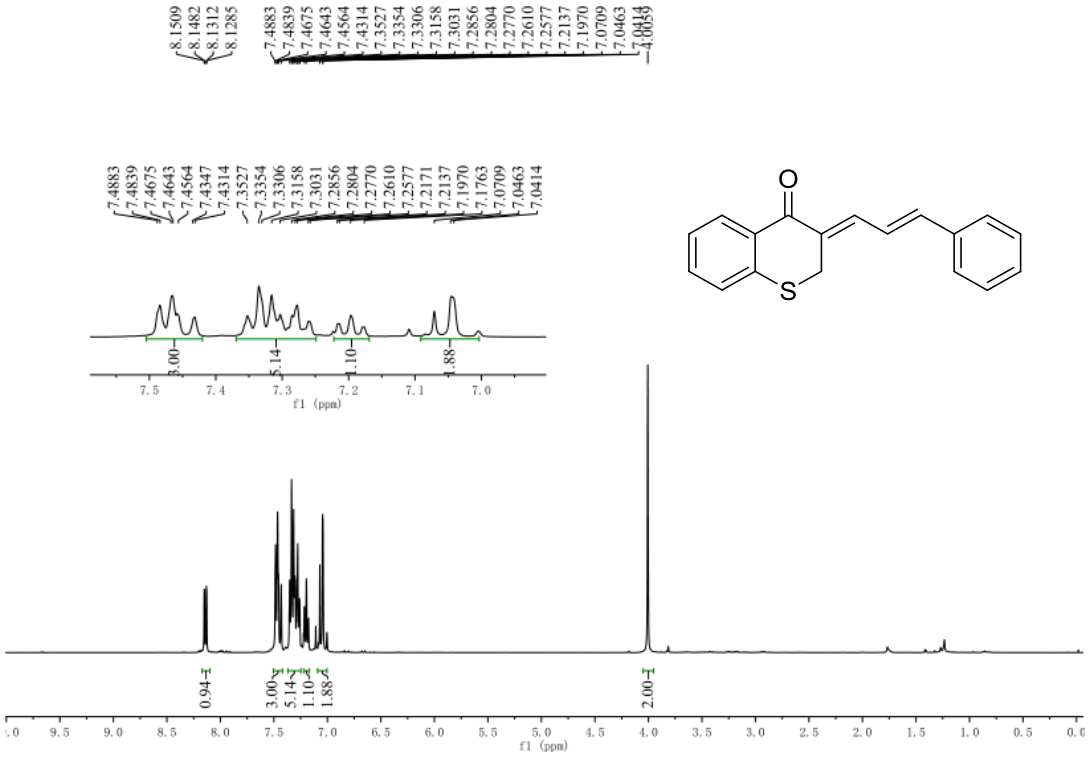


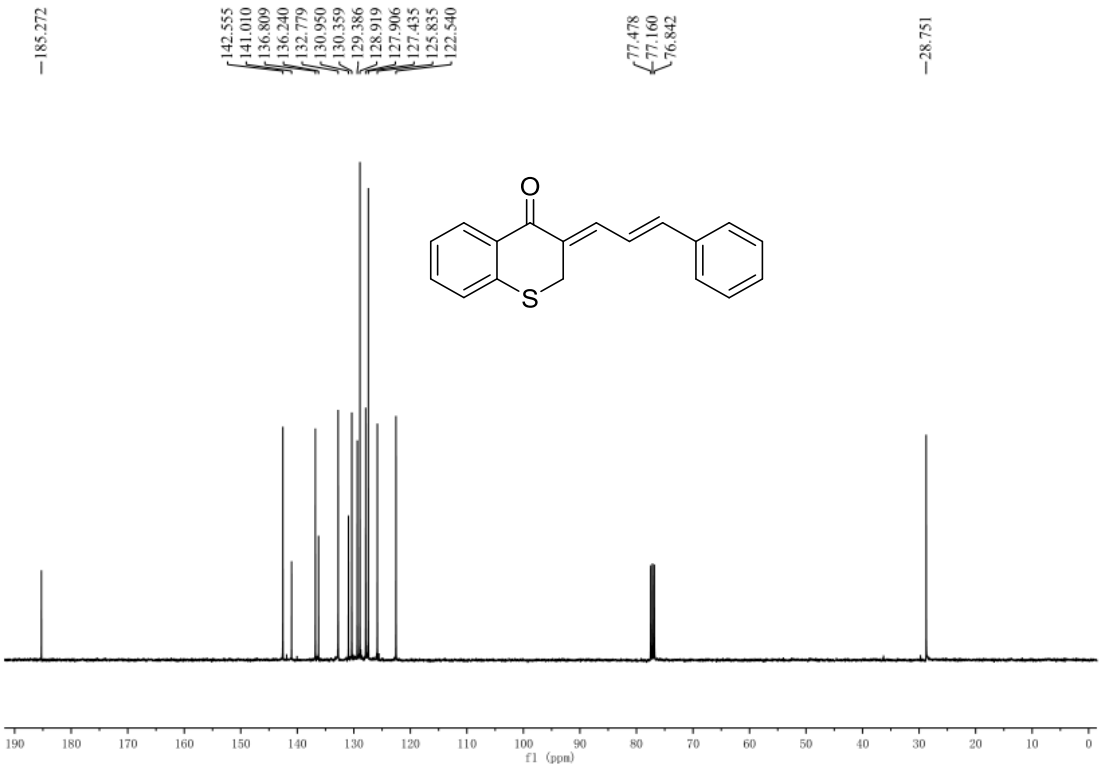
^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) of **1x**



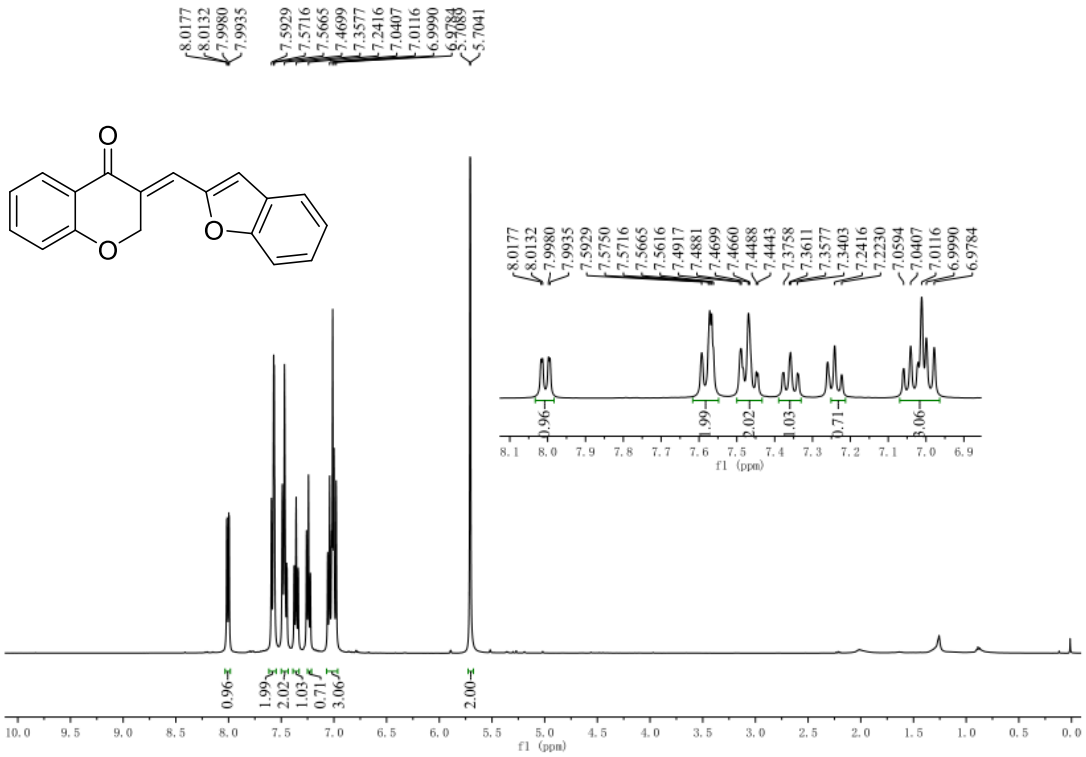


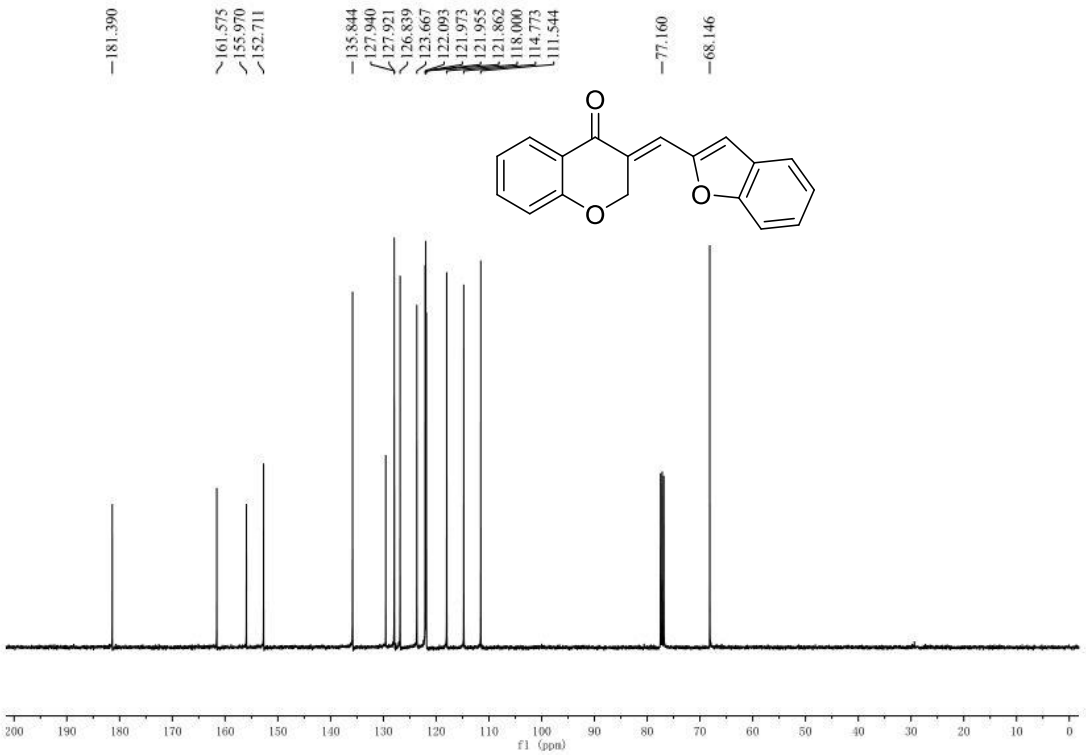
^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) of **1v**



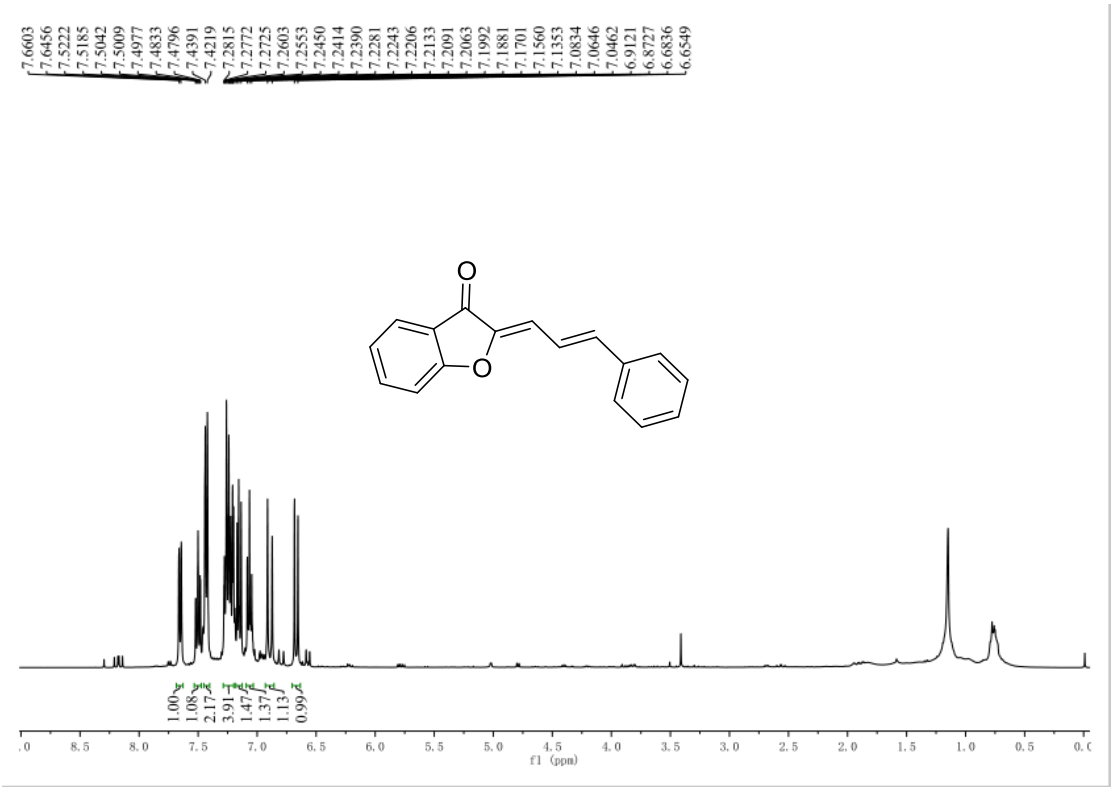


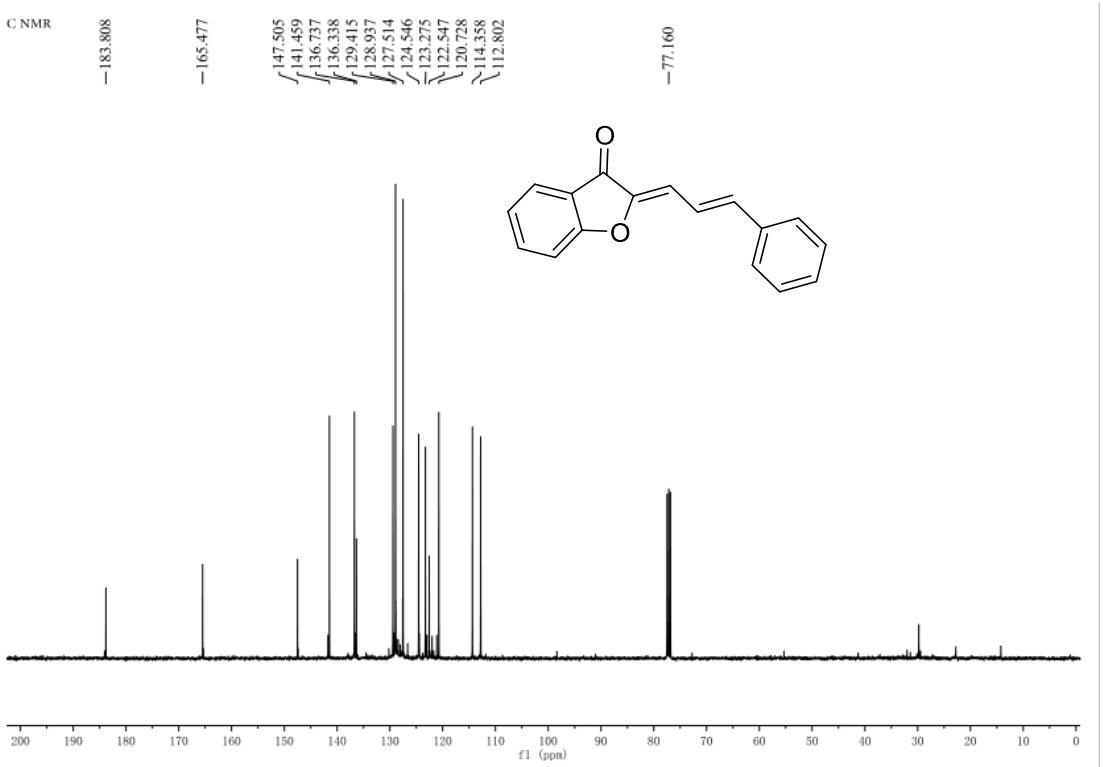
^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) of **1w**



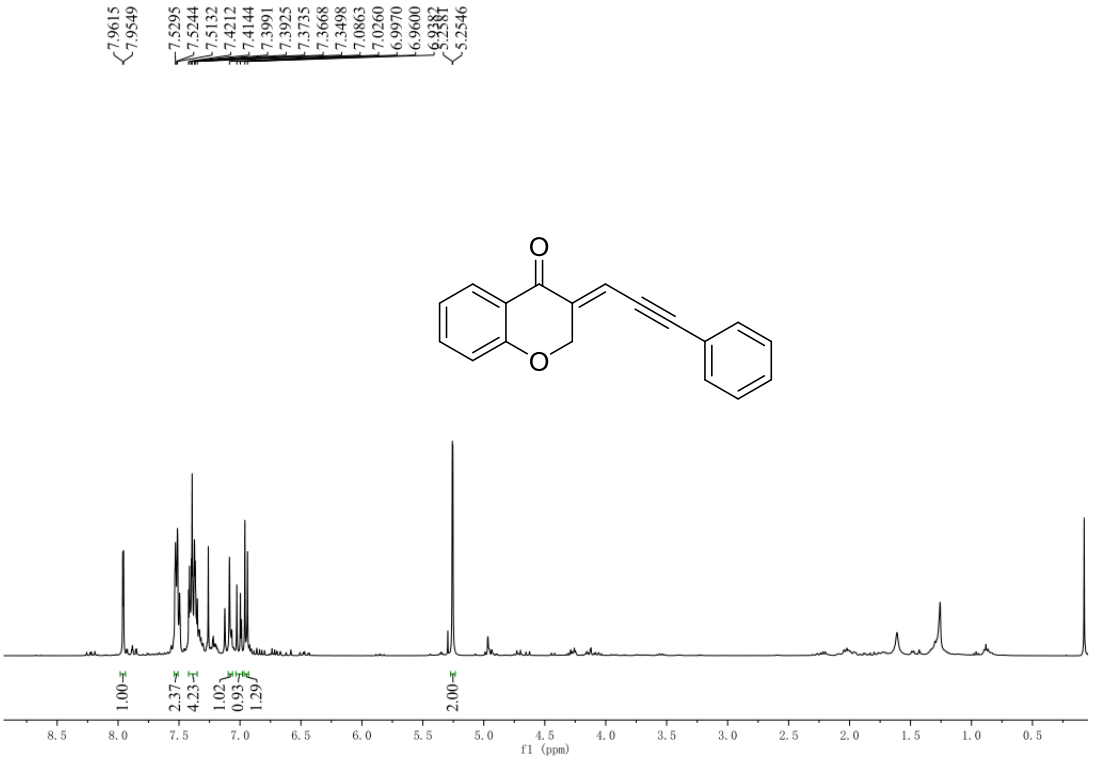


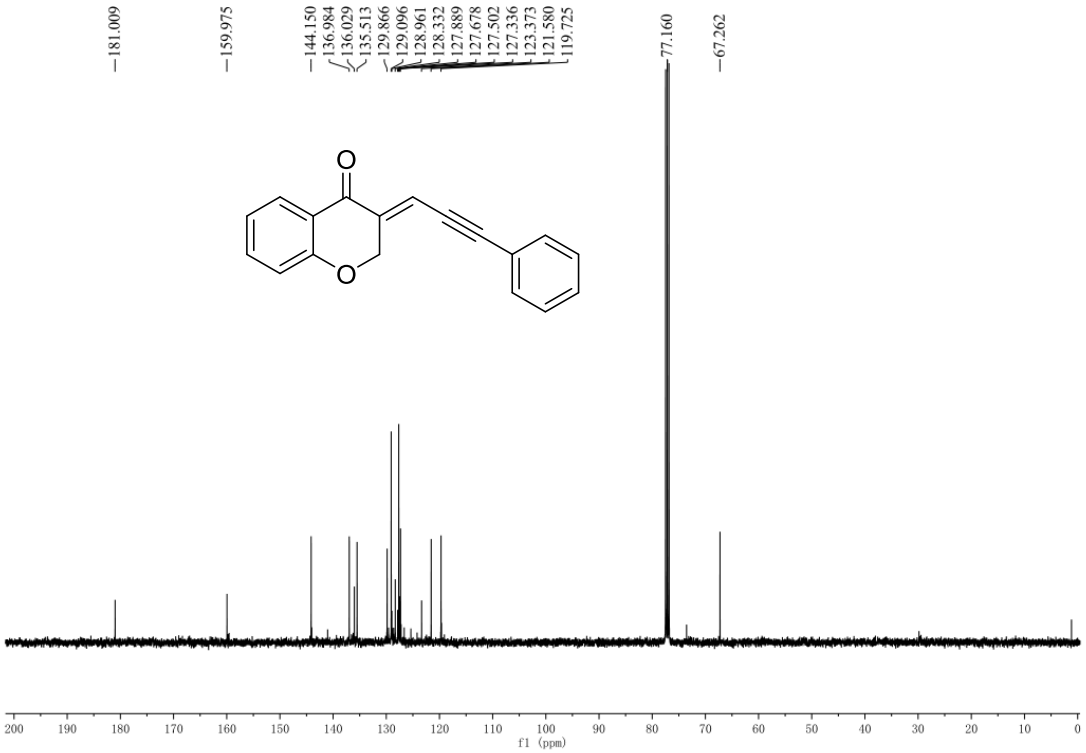
^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) of **1z**



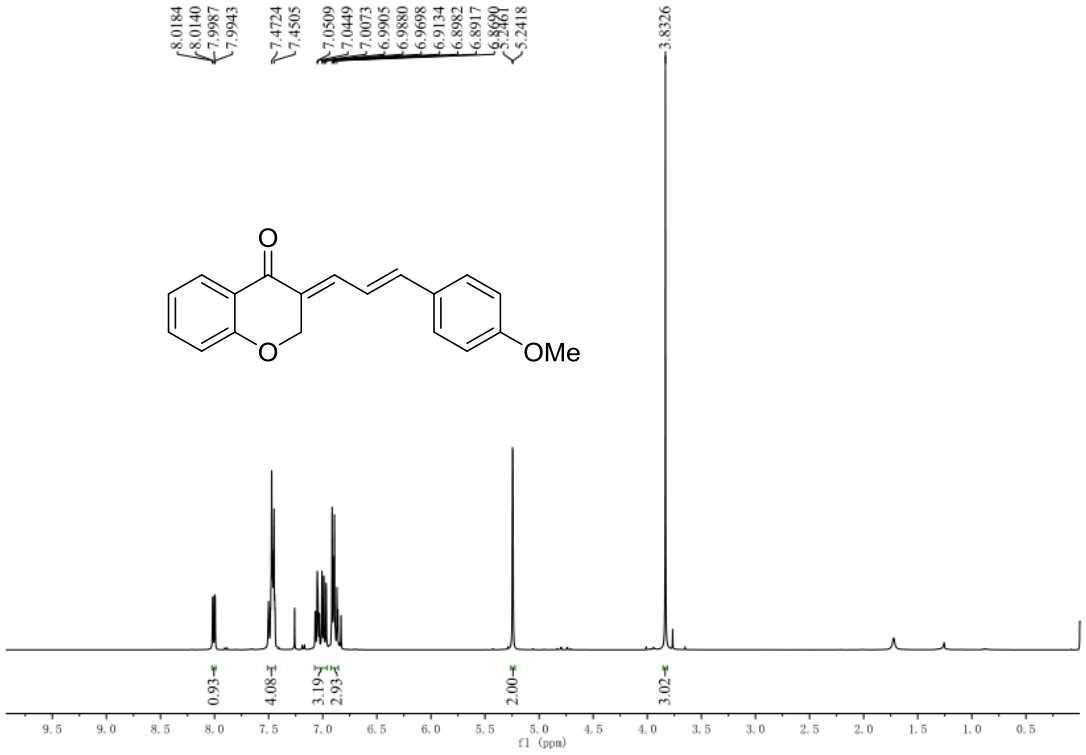


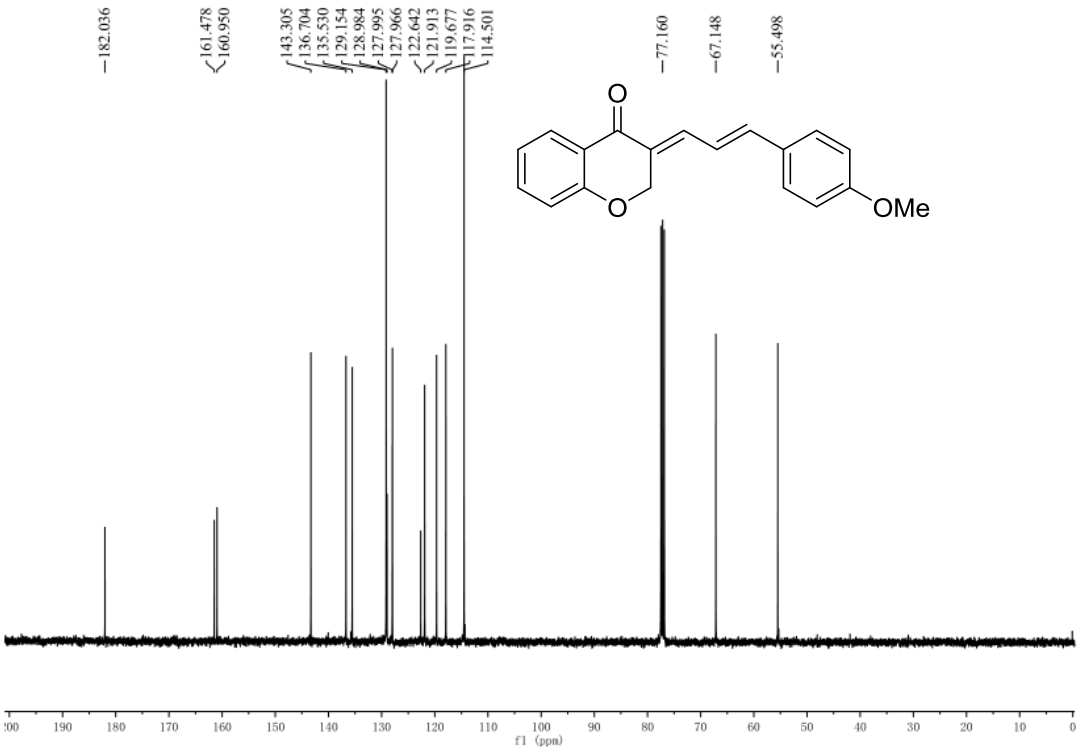
^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) of **1aa**



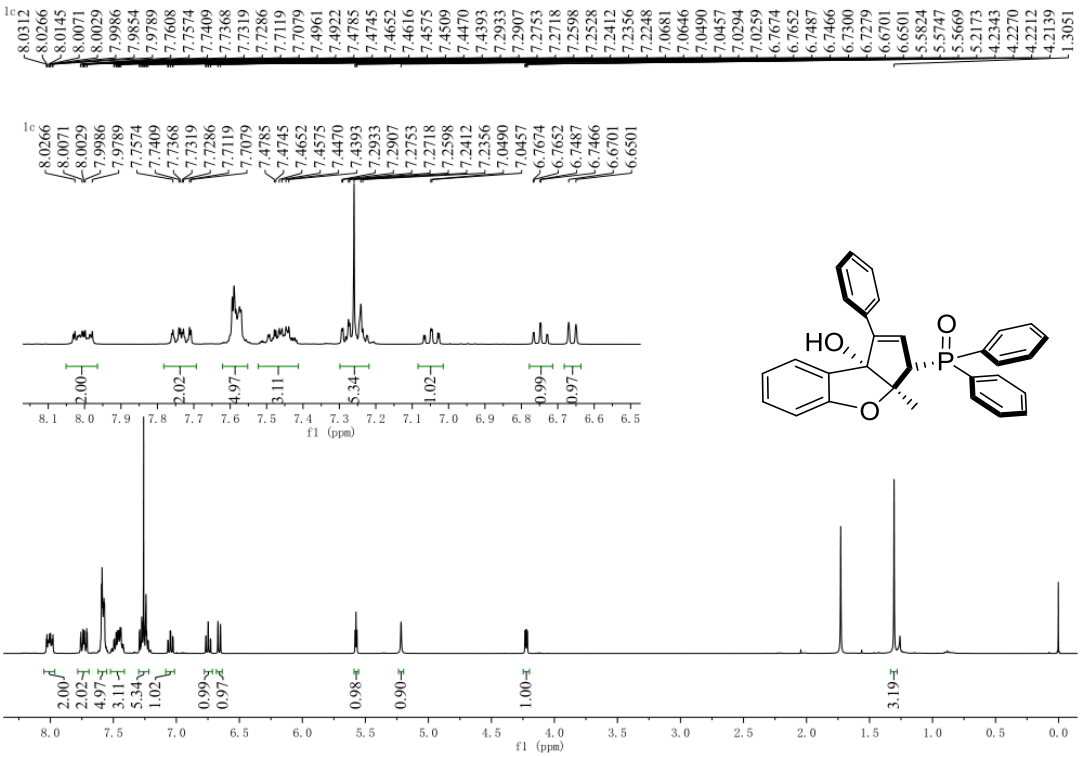


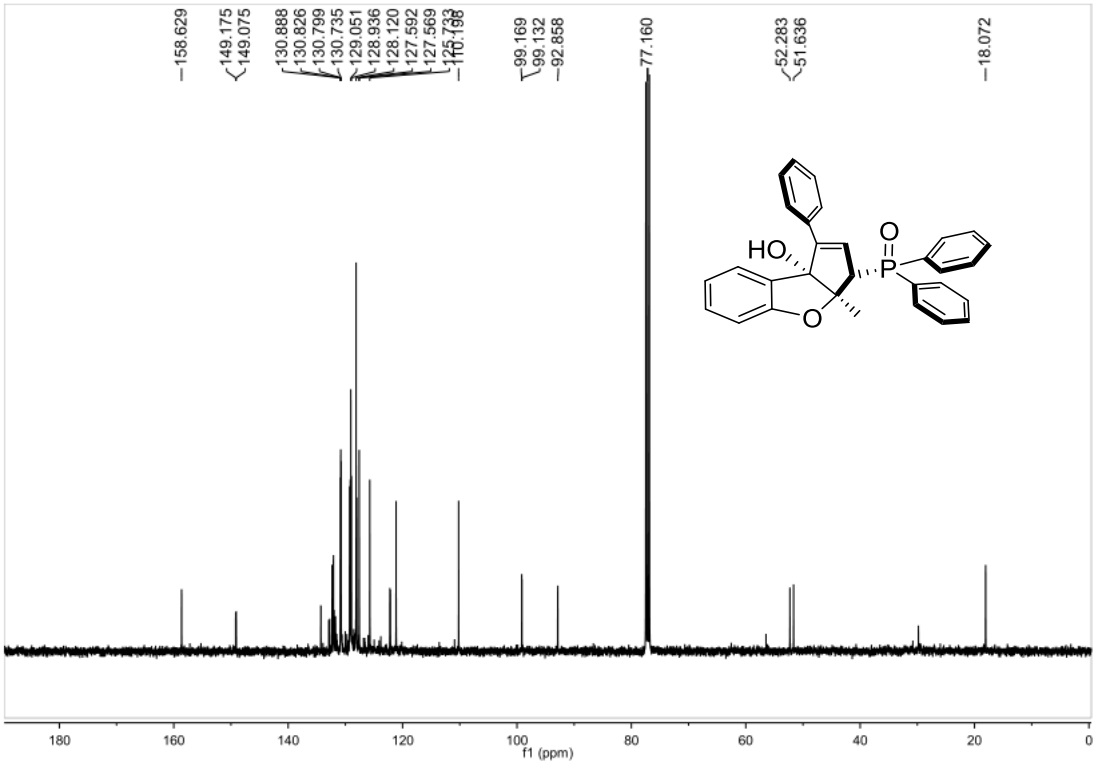
^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) of **1ab**

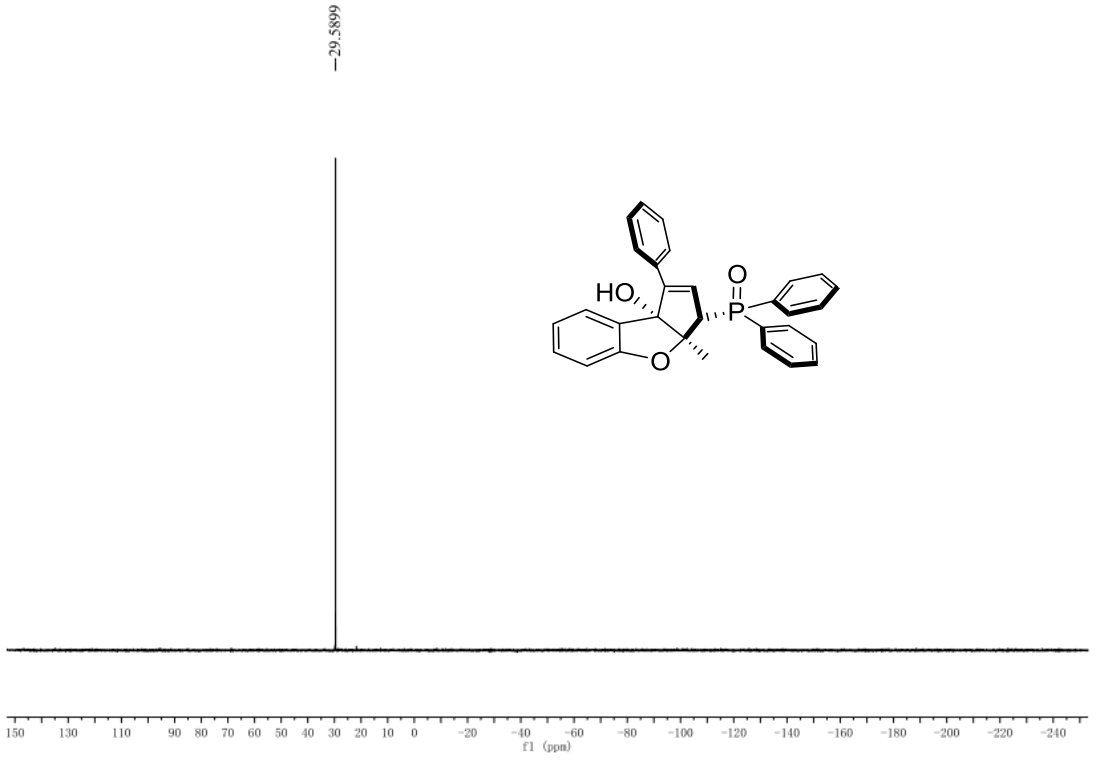




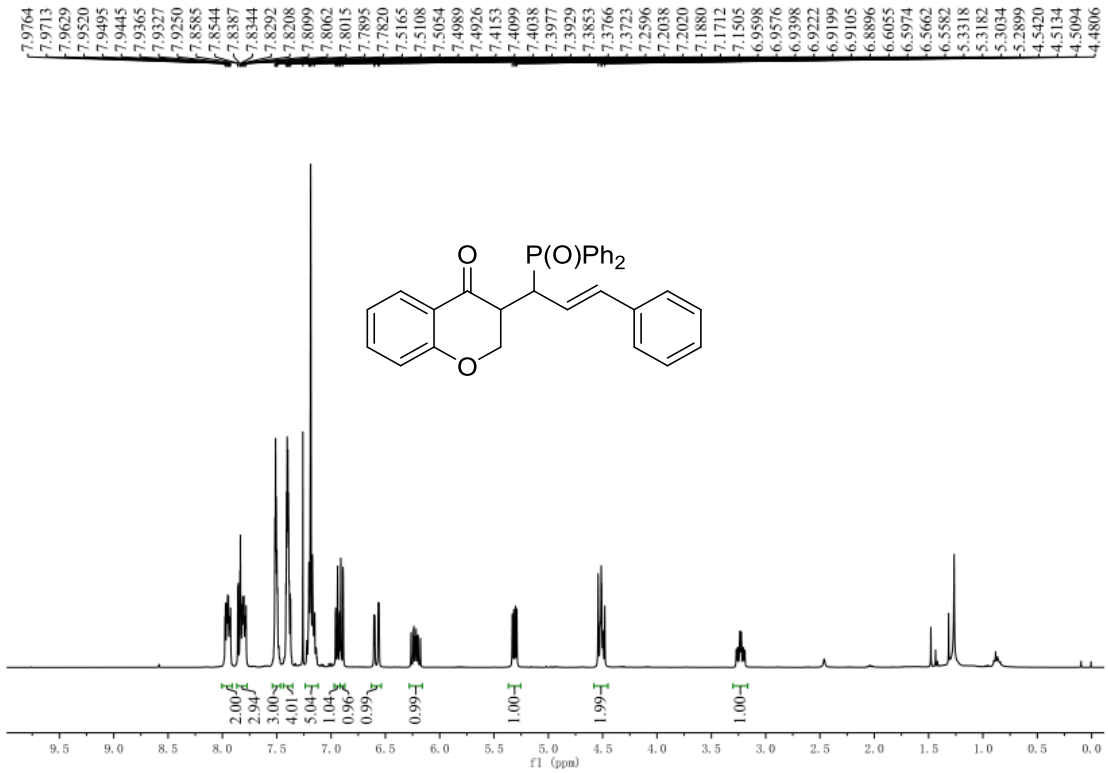
^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) of **1ac**







^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$),^{31}P NMR (162 MHz, $CDCl_3$) of (±)−**3a**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7.9713
7.9629
7.9520
7.9495
7.9445
7.9365
7.9327
7.9250
7.8585
7.8544
7.8387
7.8344
7.8292
7.8208
7.8099
7.8062
7.8015
7.7895
7.7820
7.5165
7.5108
7.5054
7.4989
7.4926
7.4153
7.4099
7.4038
7.3977
7.3929
7.3853
7.3766
7.3723
7.2596
7.2038
7.2020
7.1880
7.1712
7.1505
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6.9576
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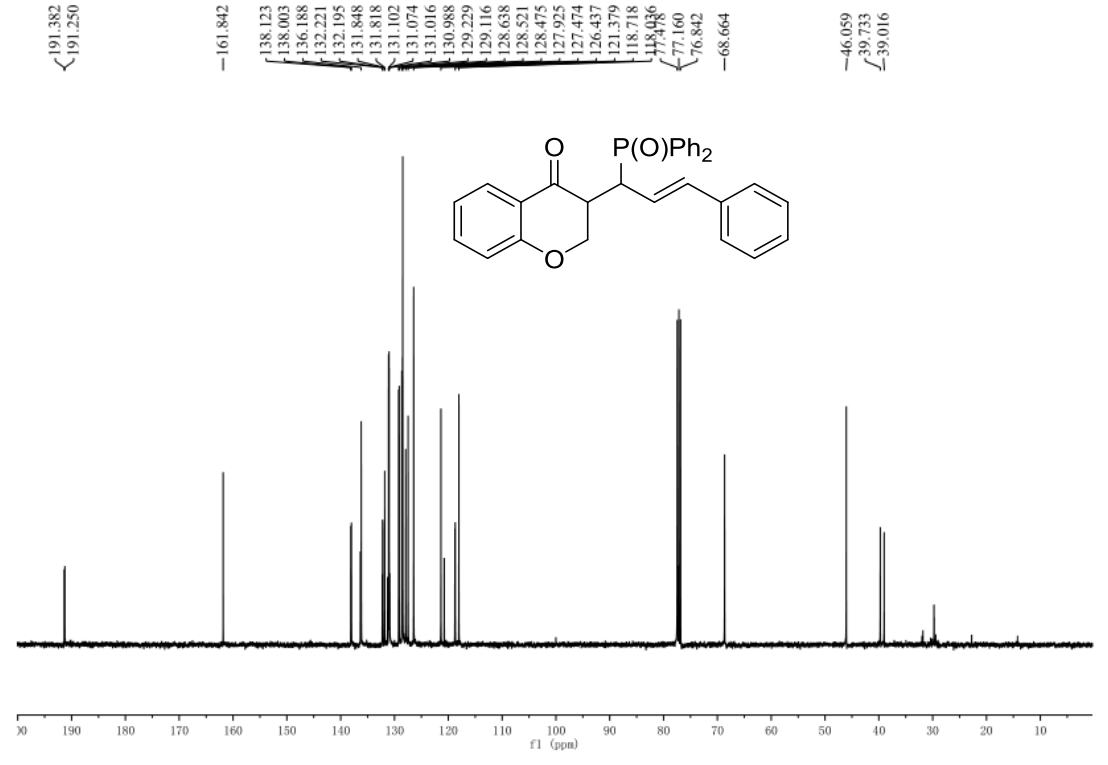
6.9199
6.9105
6.8896
6.6055
6.5974
6.5662
6.5582
5.3318
5.3182
5.3034
5.2899
4.5420
4.5134
4.5094
4.4806
O
P(O)Ph2
O
2.00
2.94
3.00
4.01
5.04
1.04
0.96
0.99
0.99
1.00
1.99
1.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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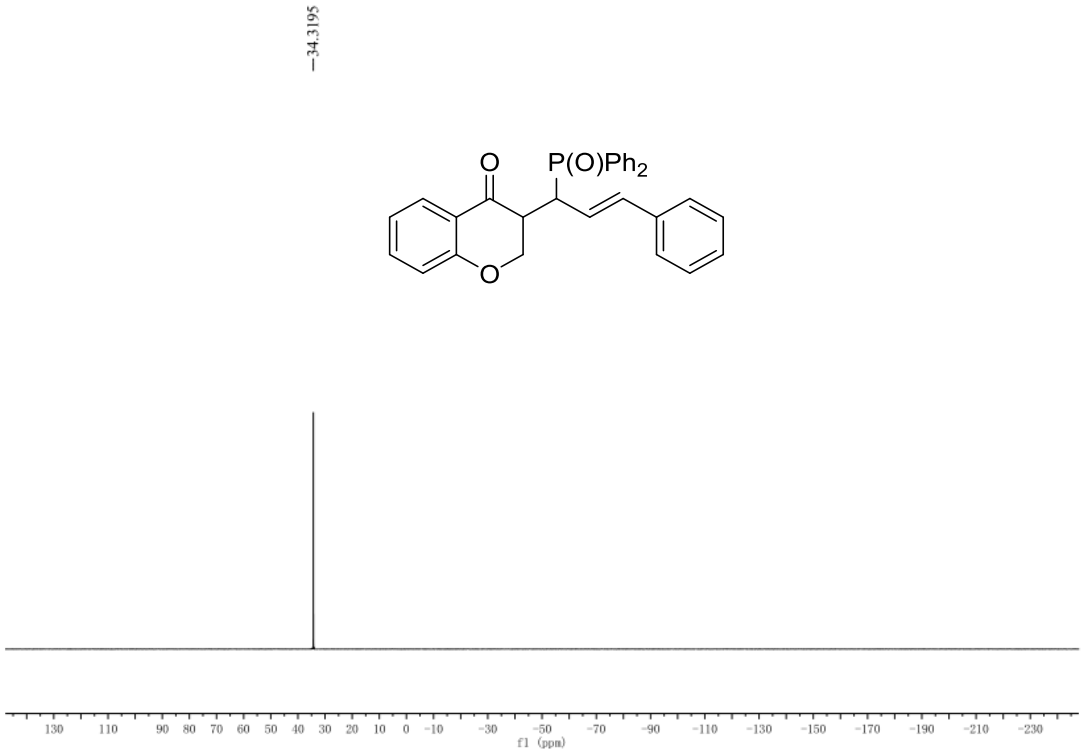
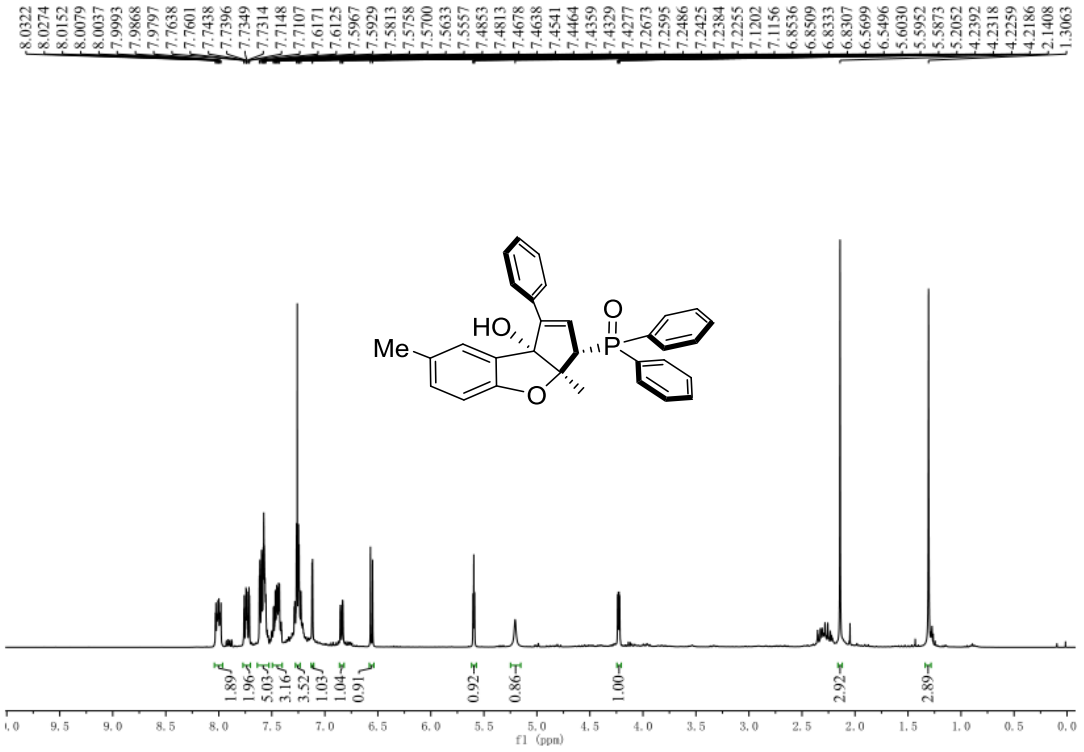
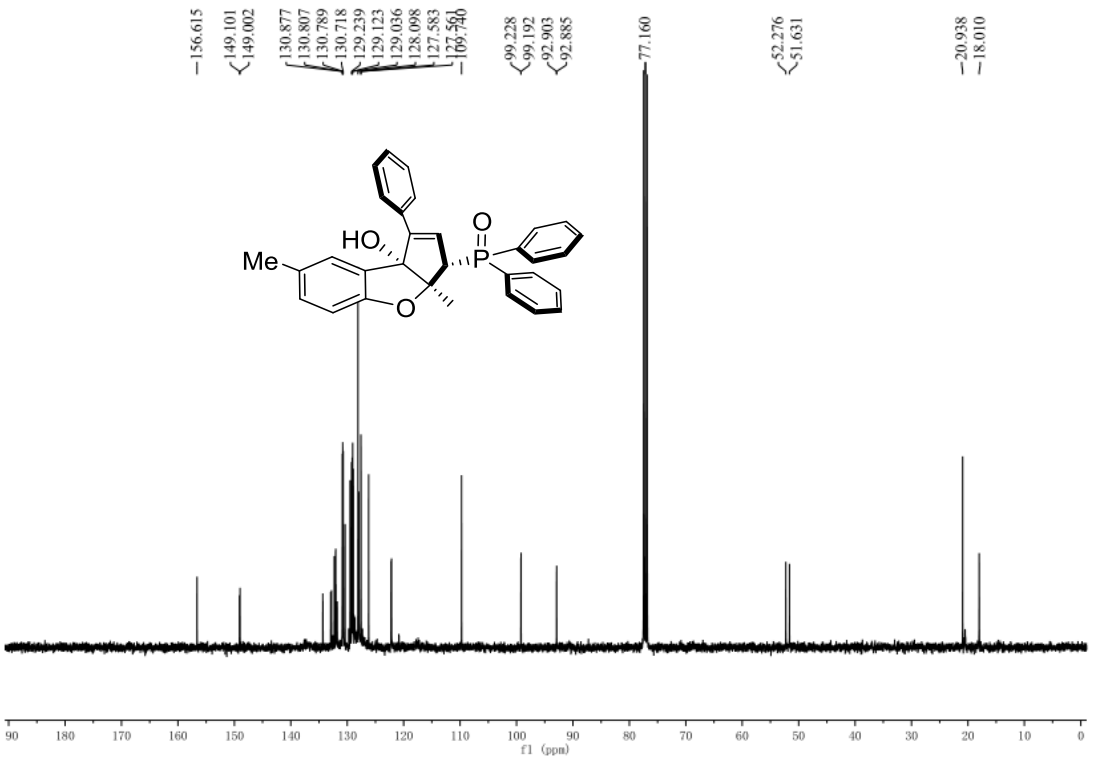
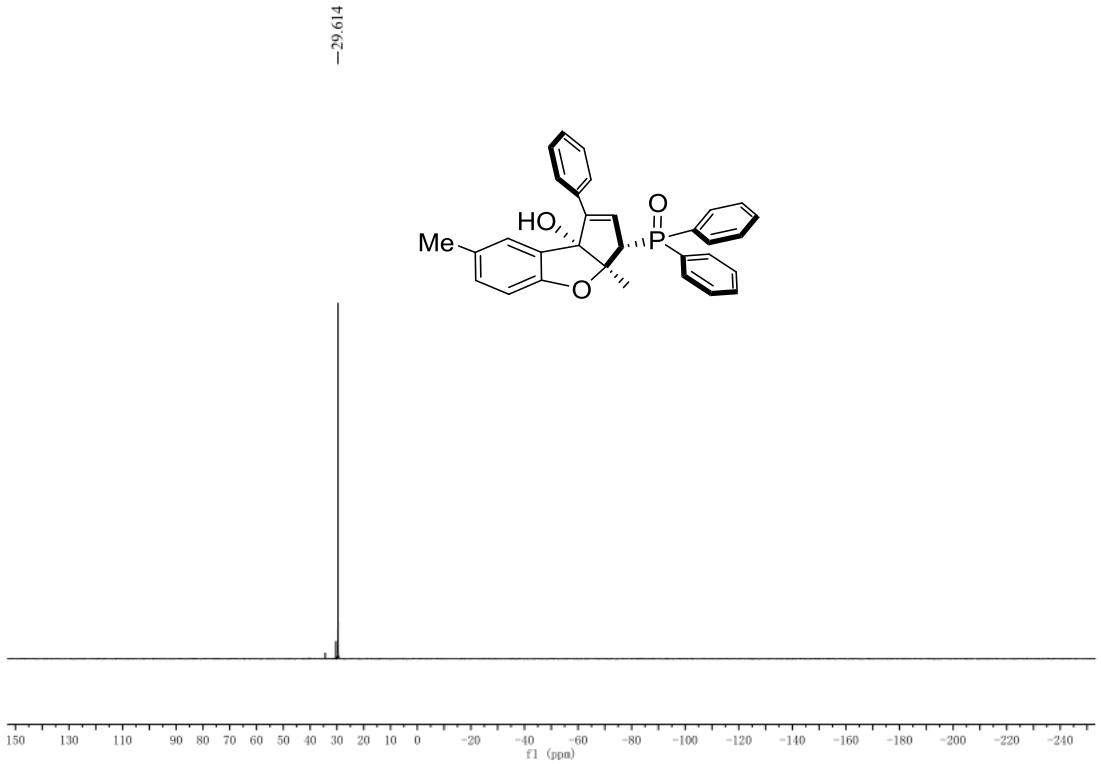
191.250
161.842
138.123
138.003
136.188
132.221
132.195
131.848
131.818
131.102
131.074
131.016
130.988
129.229
129.116
128.638
128.521
128.475
127.925
127.474
126.437
121.379
118.718
118.036
77.478
77.160
76.842
68.664
46.059
39.733
39.016
O
P(O)Ph2
O
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)



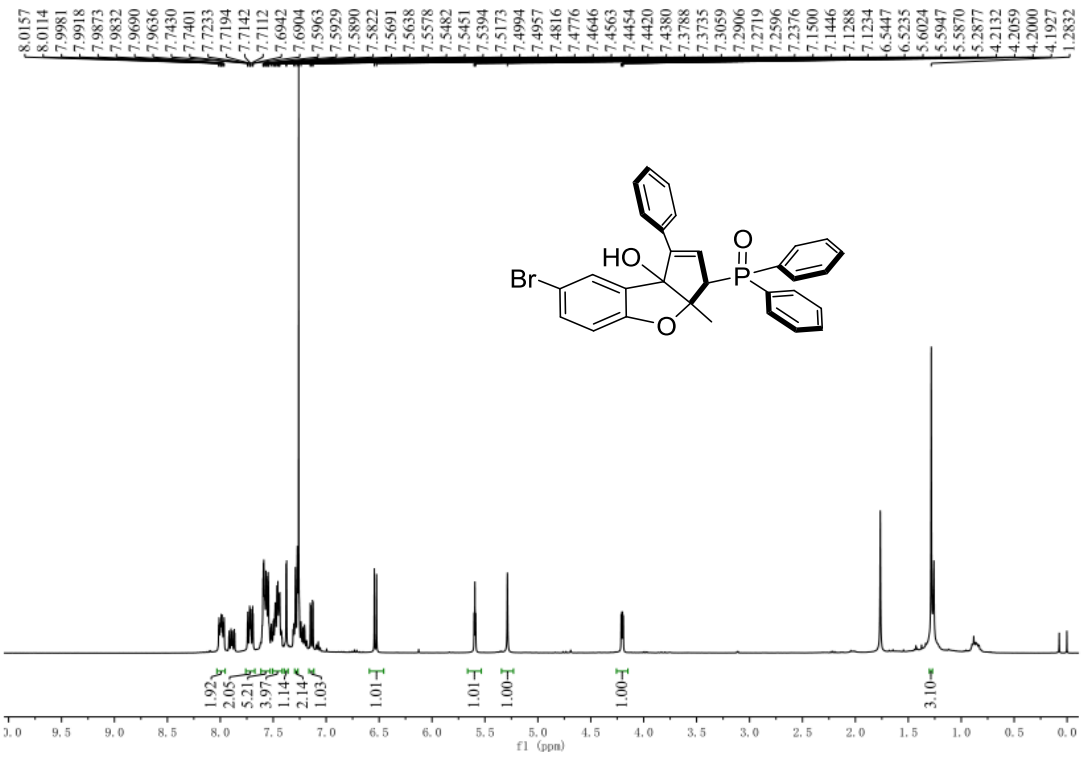
^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$),^{31}P NMR (162 MHz, $CDCl_3$) of (±)−**3a'**

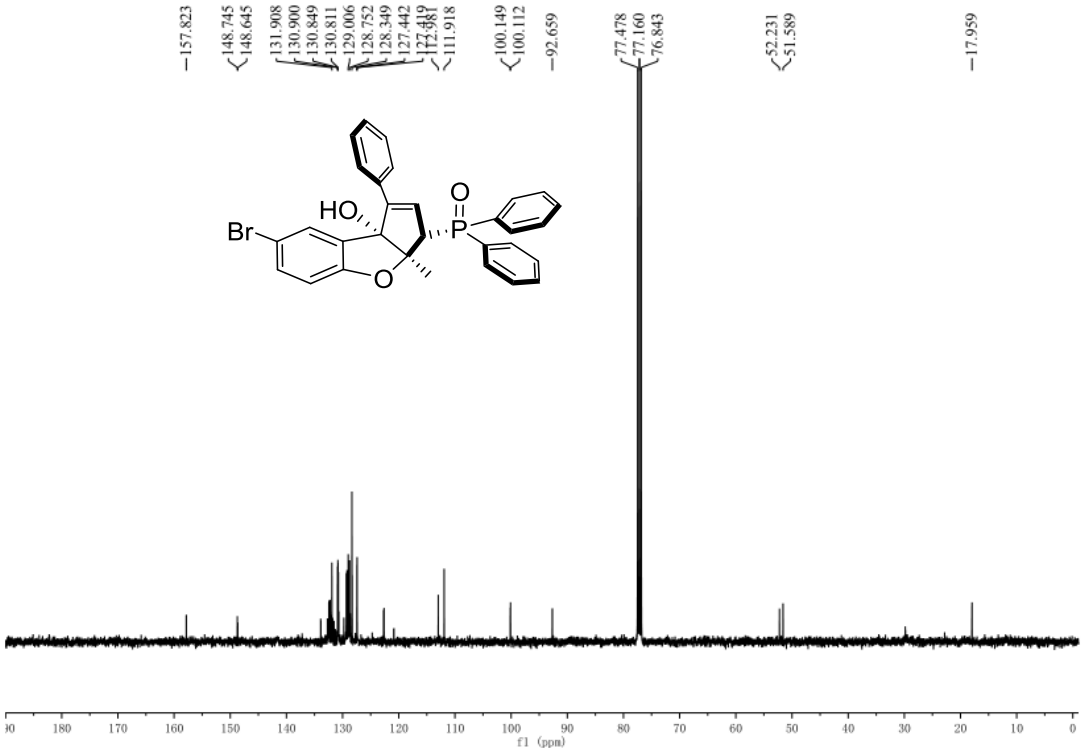


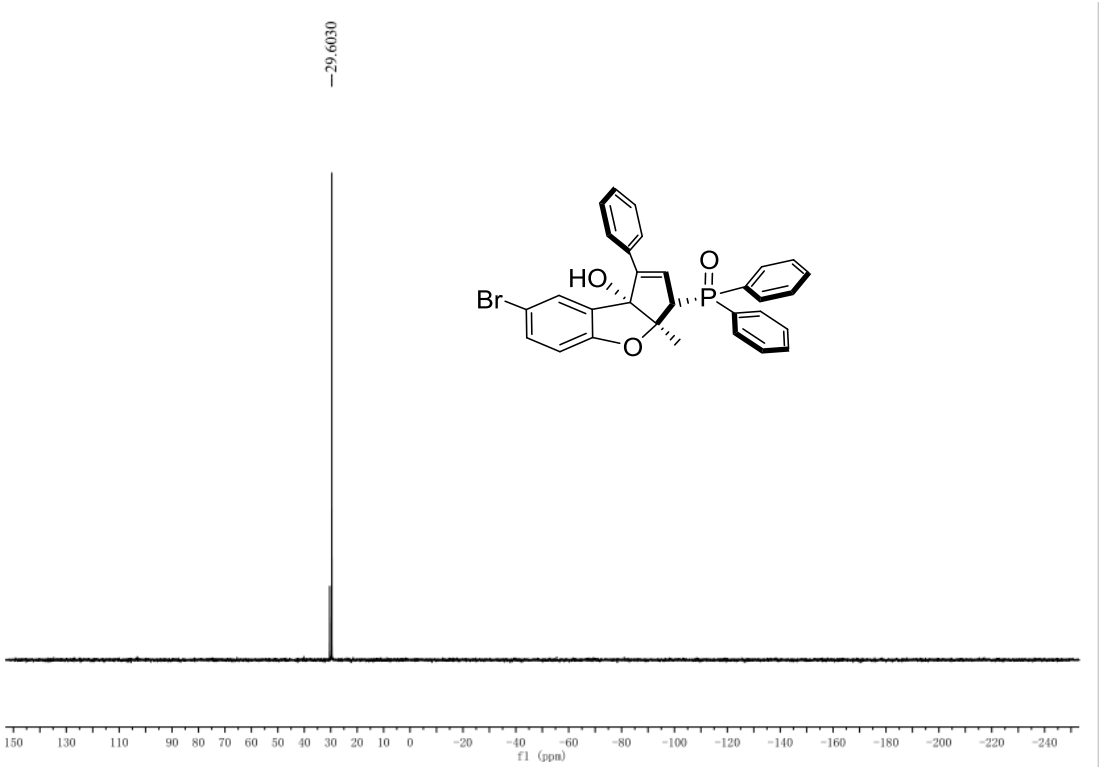




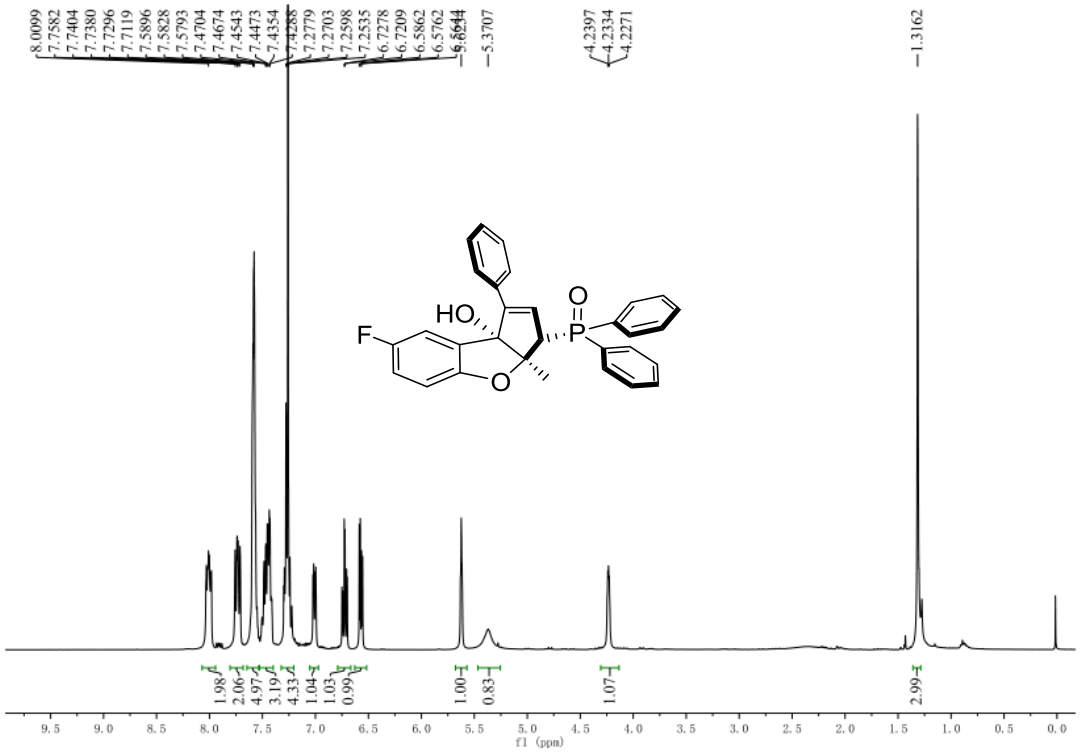
^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$),^{31}P NMR (162 MHz, $CDCl_3$) of **3b**

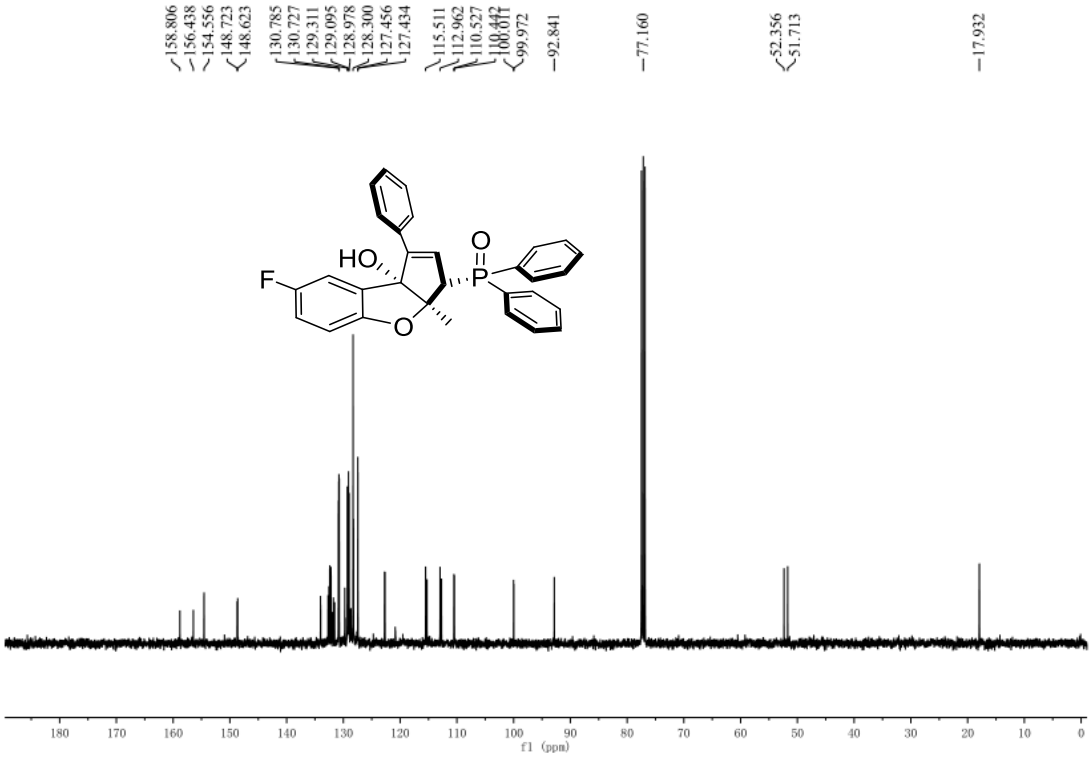

HO
Br
O
P
O
f1 (ppm)


HO
Br
O
P
O
f1 (ppm)



^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$),^{31}P NMR (162 MHz, $CDCl_3$) of **3c**

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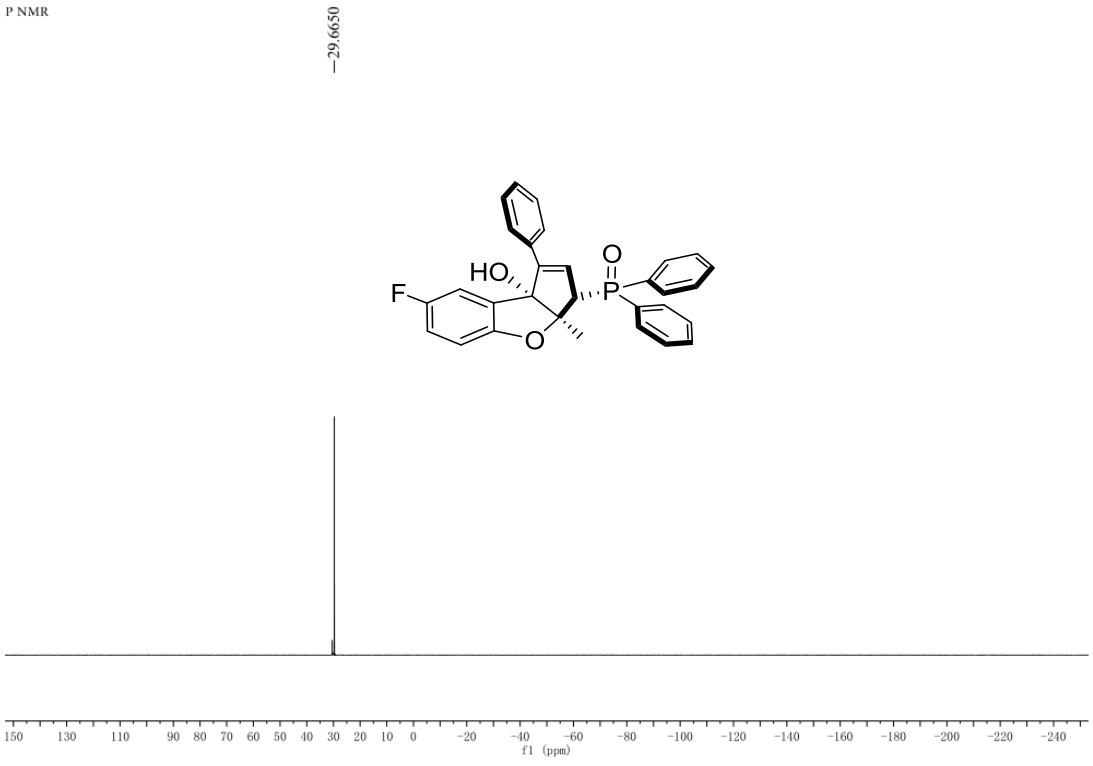
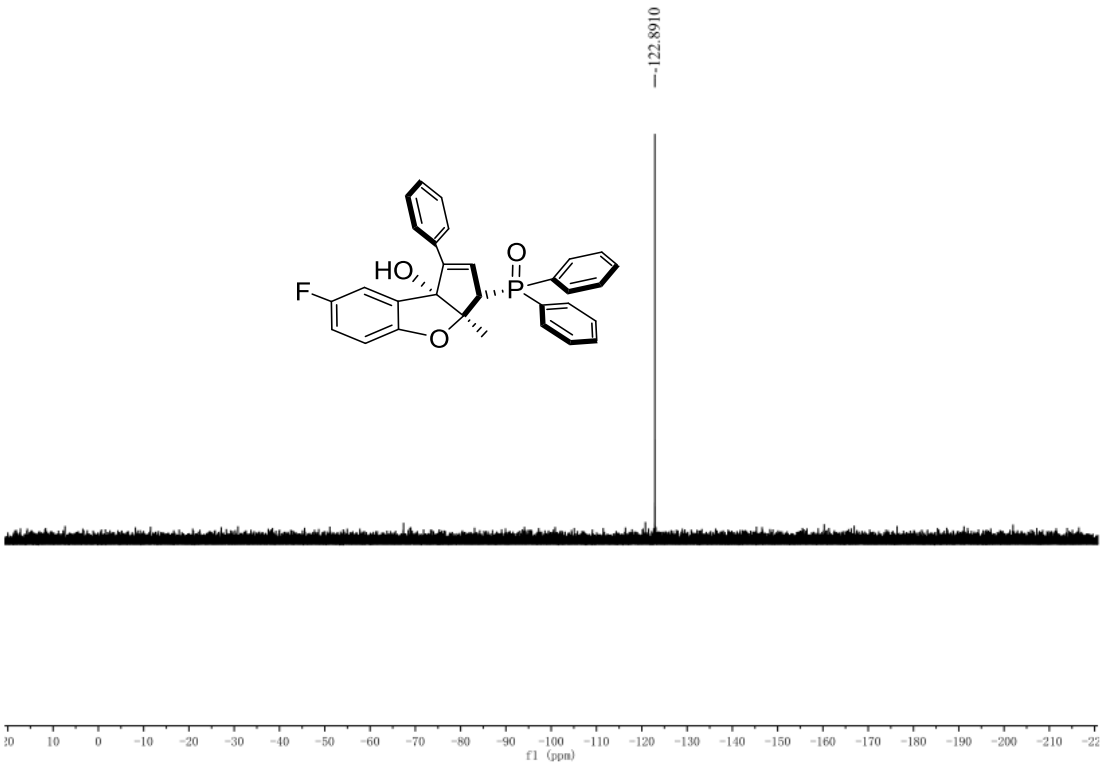
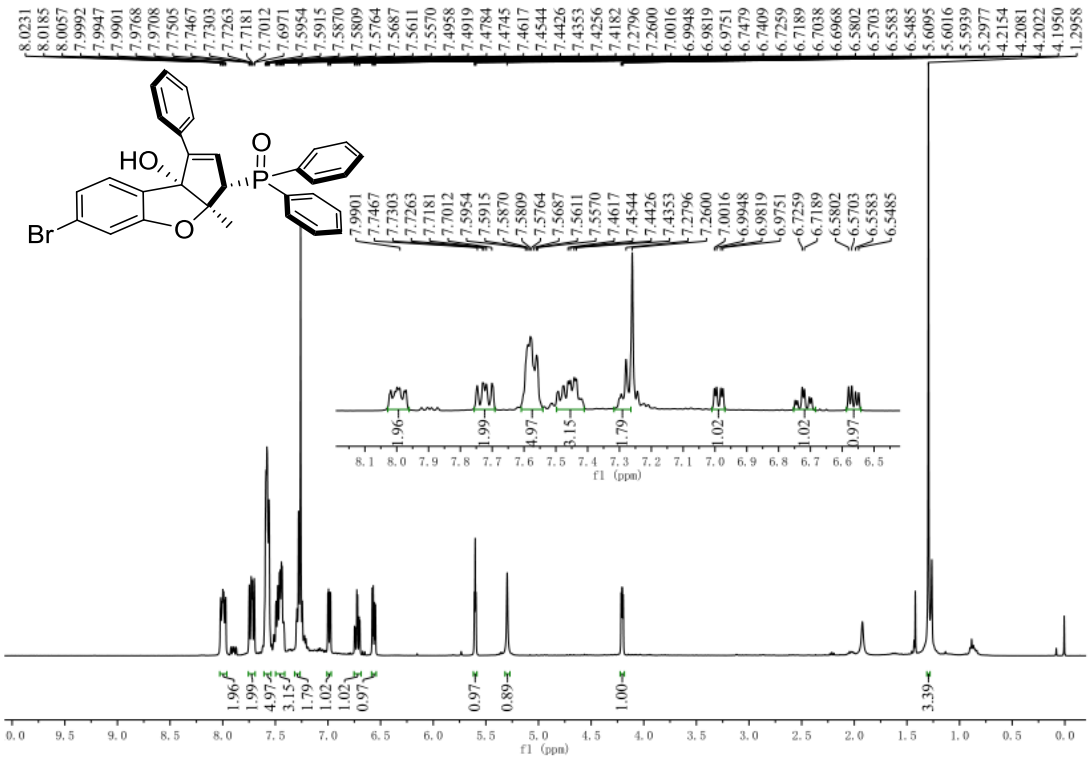
156.438
154.556
148.723
148.623
130.785
130.727
129.311
129.095
128.978
128.300
127.456
127.434
115.511
112.962
110.527
99.972
92.841
77.160
52.356
51.713
17.932
HO
F
O
P
O
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

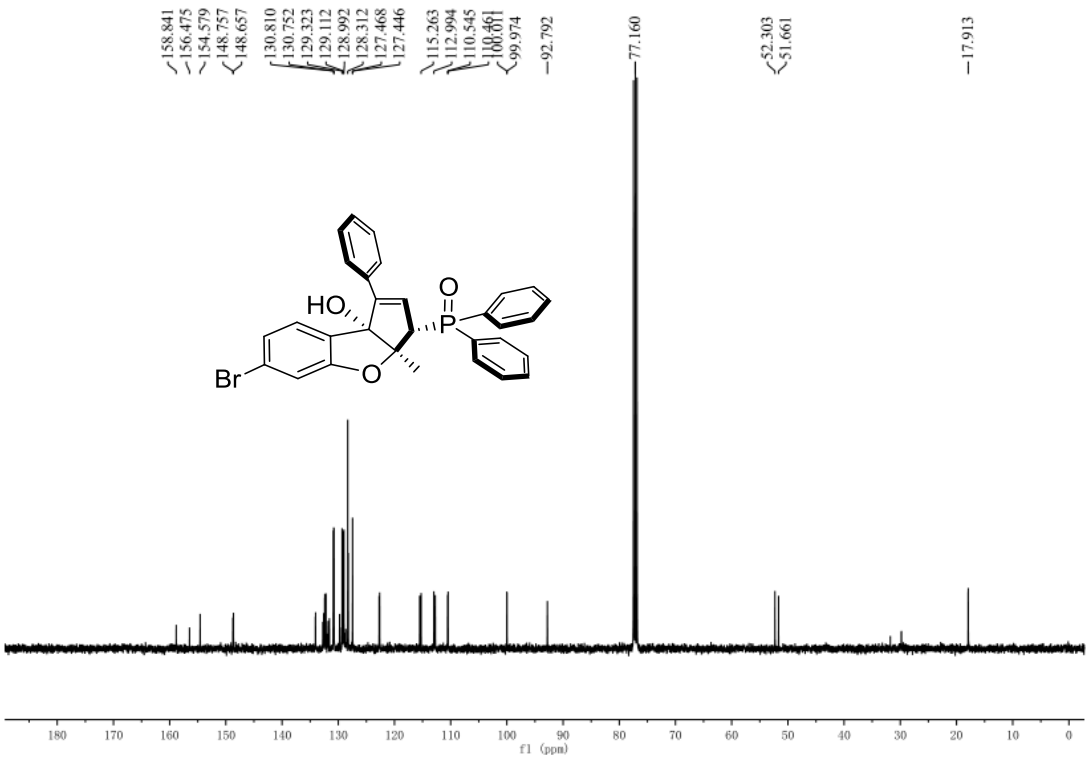
P NMR

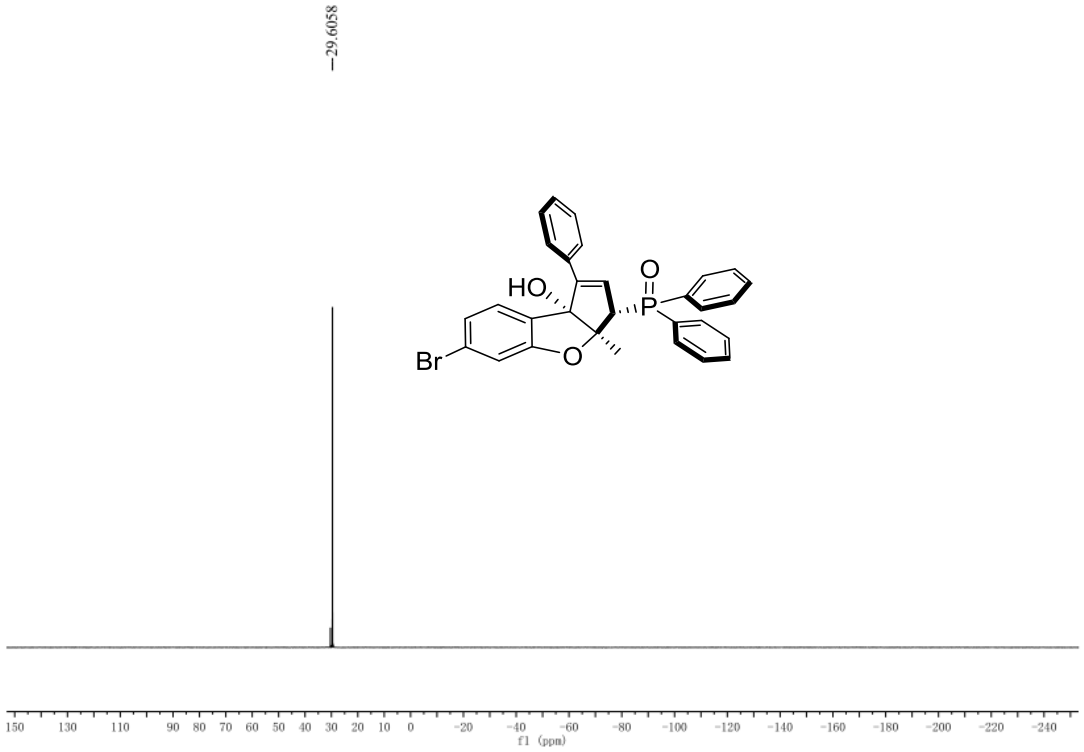

29.6650
HO
F
O
P
O
150 130 110 90 80 70 60 50 40 30 20 10 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 -220 -240
f1 (ppm)



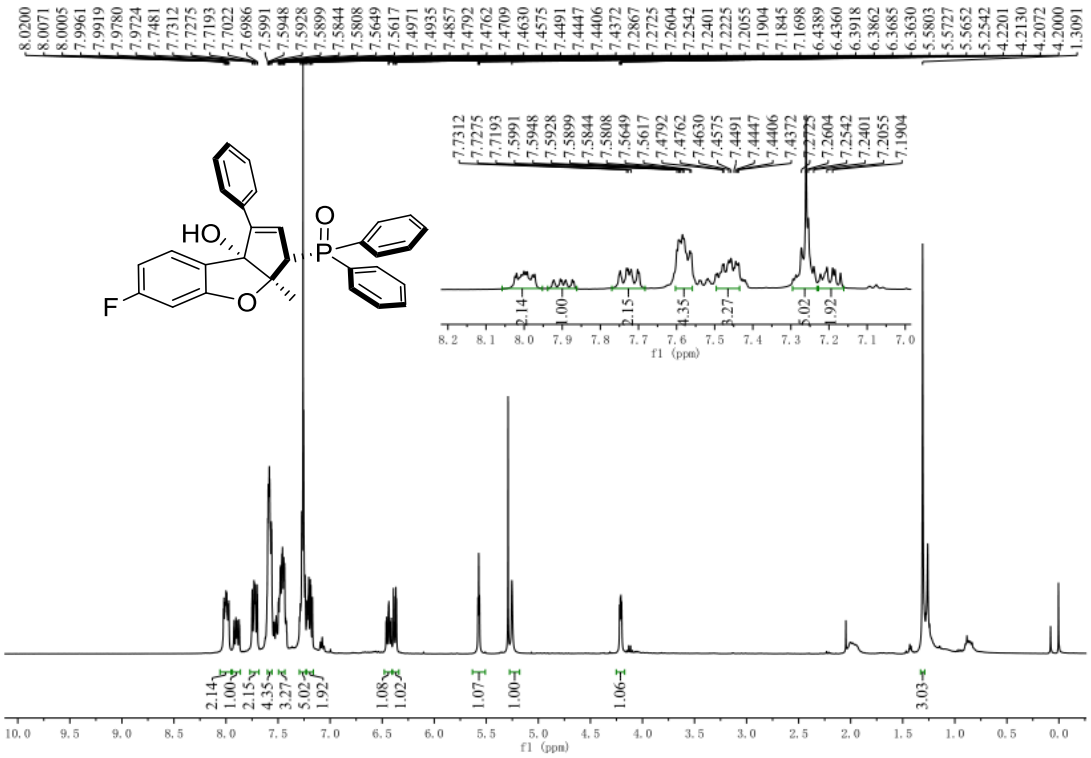
^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$),^{31}P NMR (162 MHz, $CDCl_3$), ^{19}F NMR (376 MHz, $CDCl_3$) of **3d**

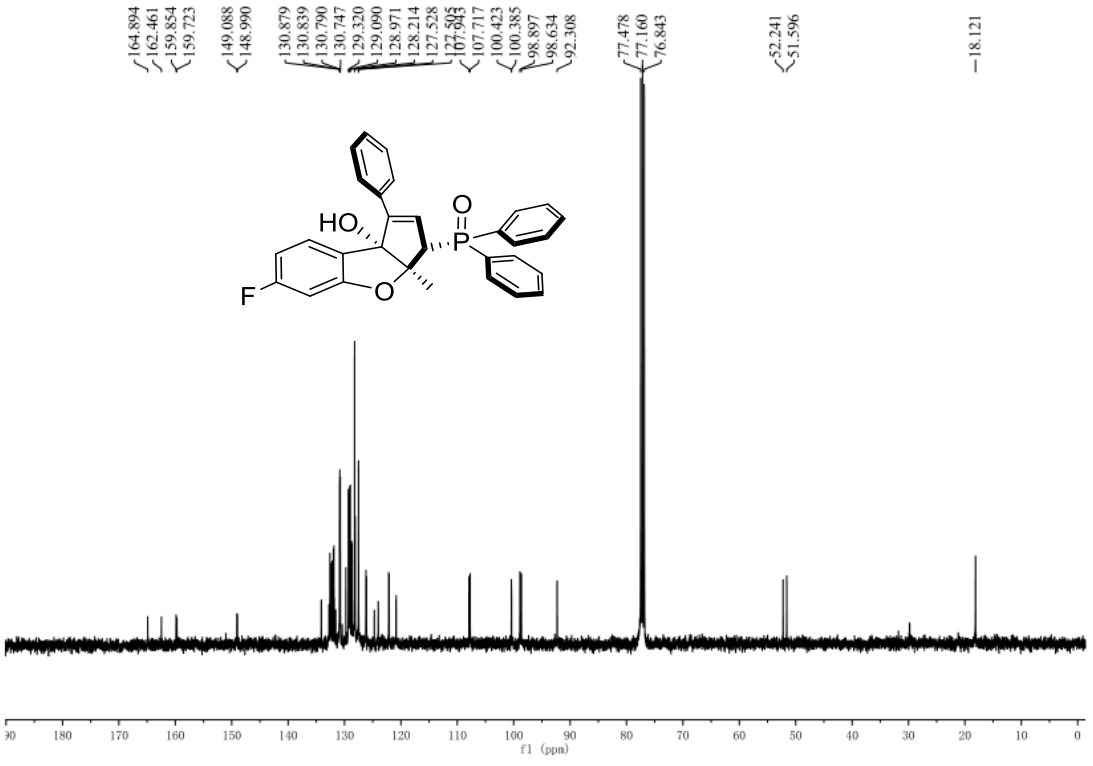


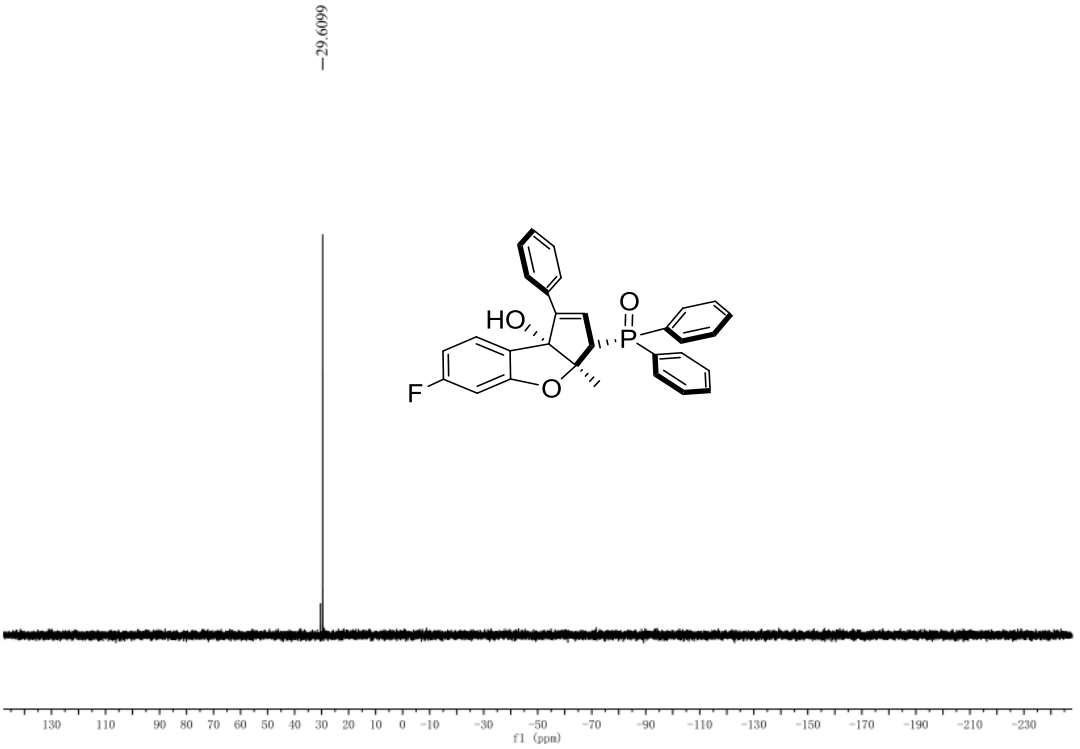


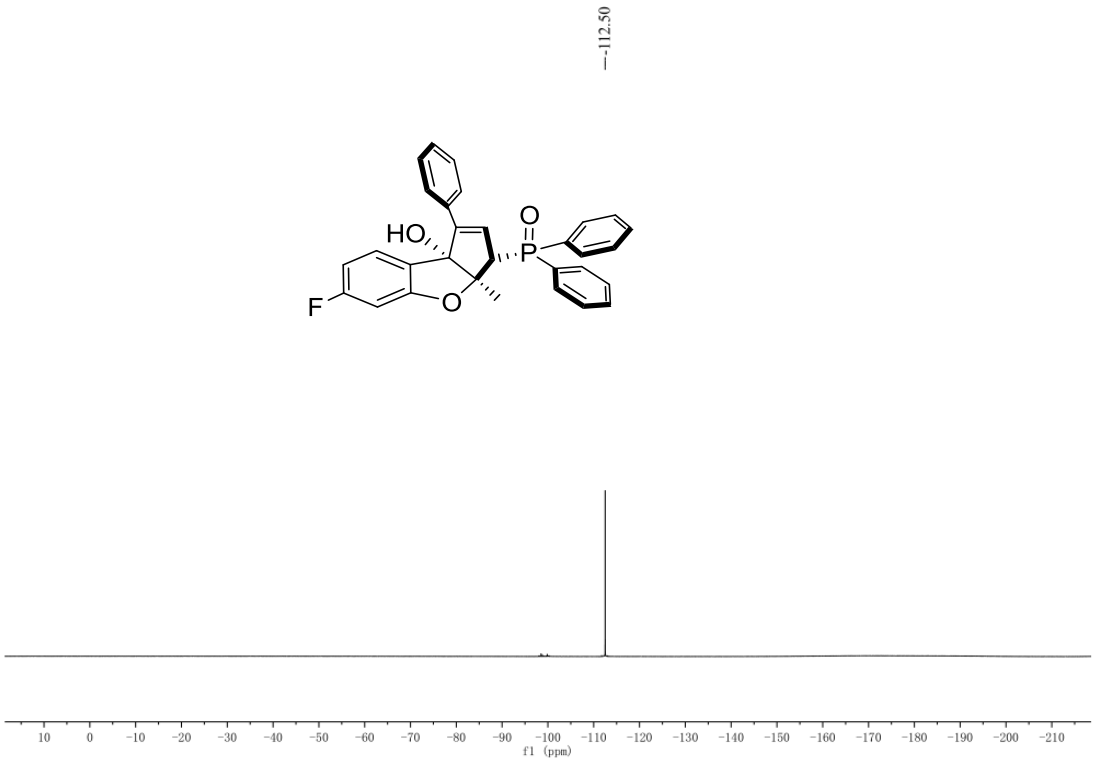


^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$),^{31}P NMR (162 MHz, $CDCl_3$) of **3e**

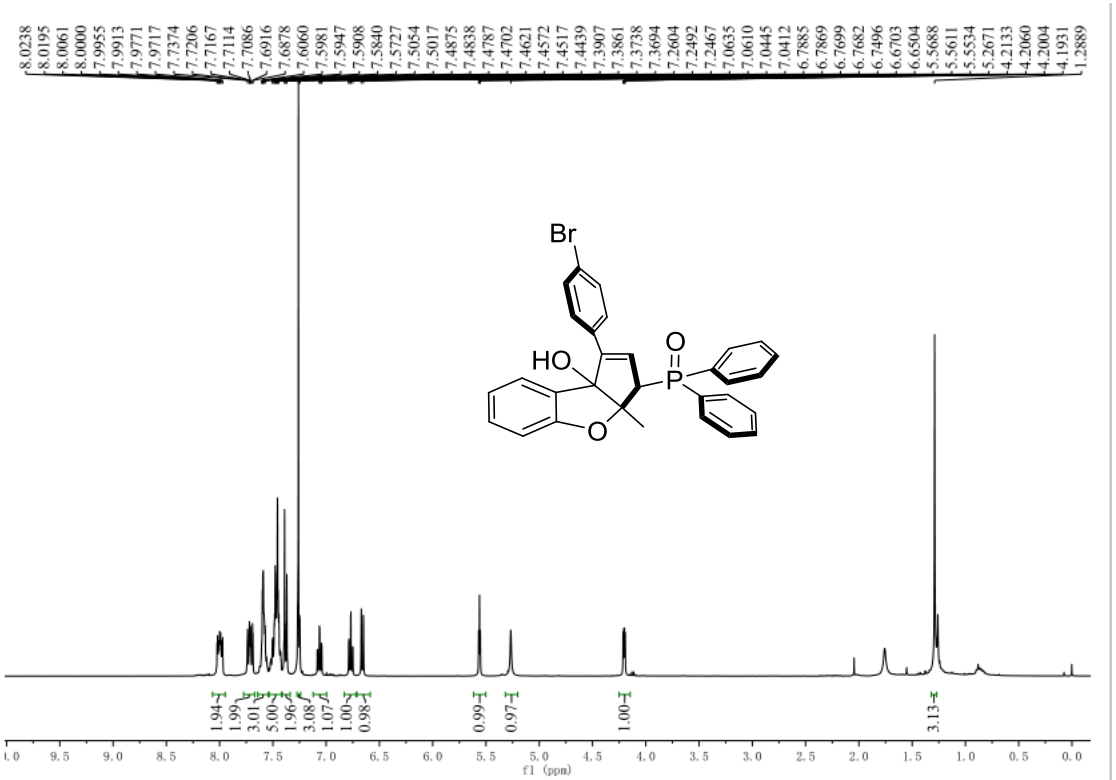

HO
O
P
F
O
f1 (ppm)

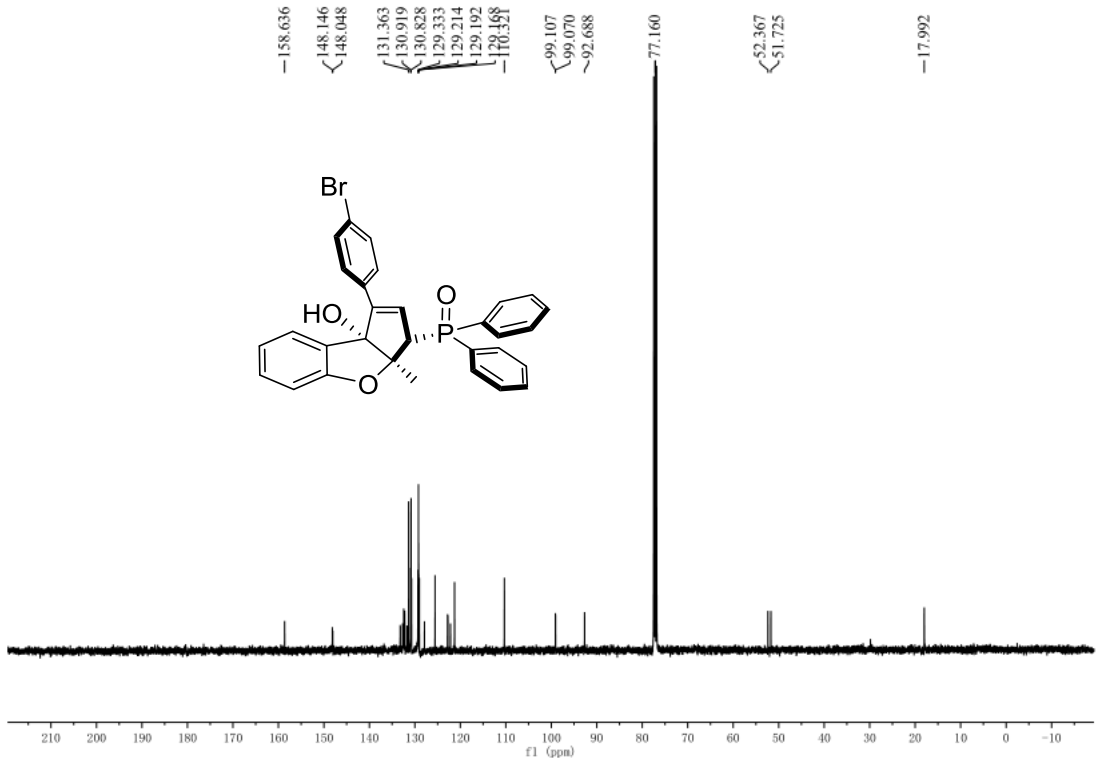

HO
O
P
F
O
f1 (ppm)

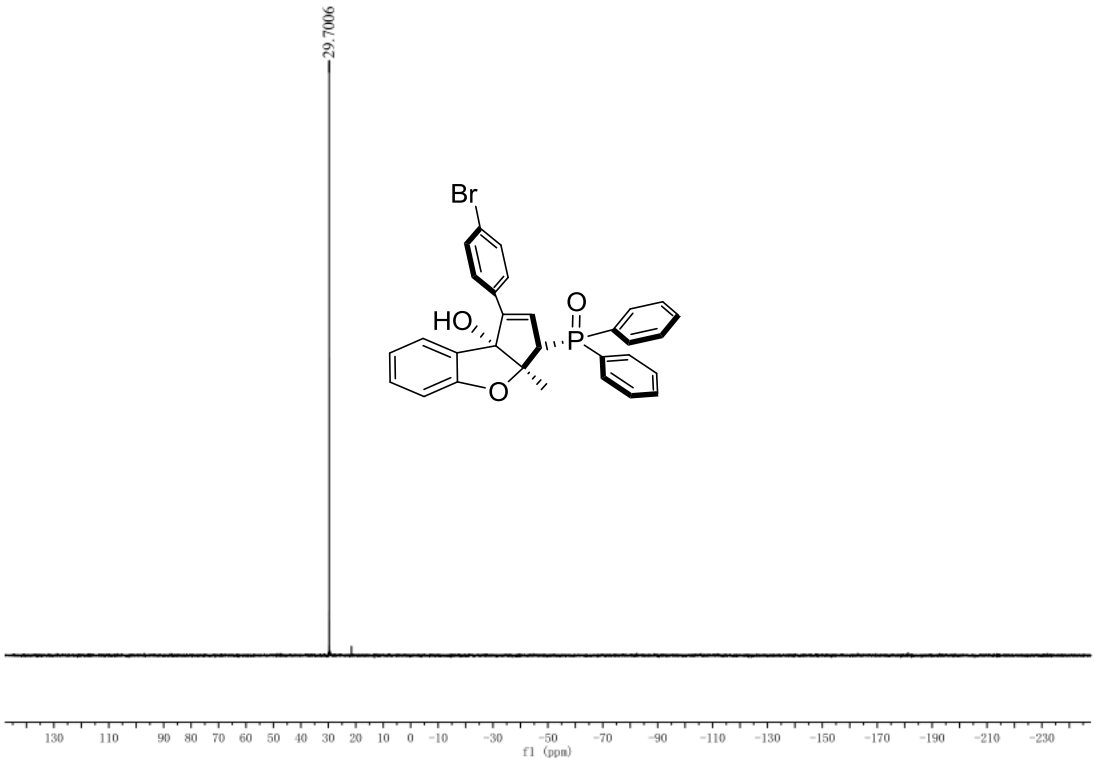




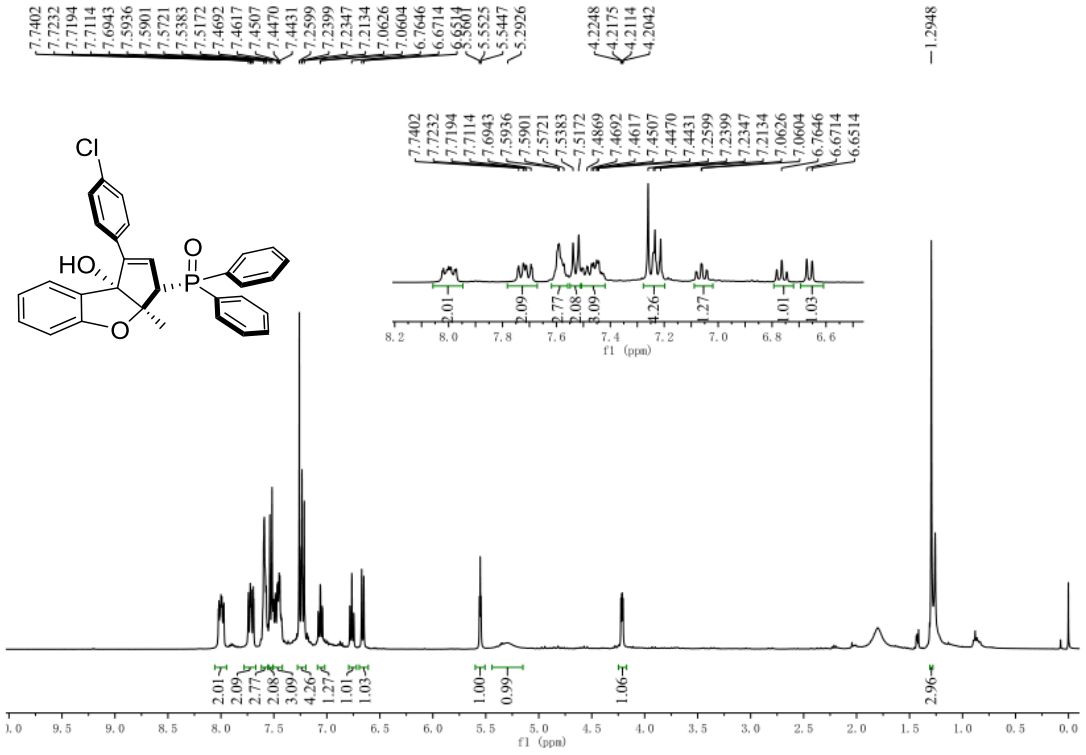
^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$), ^{31}P NMR (162 MHz, $CDCl_3$), ^{19}F NMR (376 MHz, $CDCl_3$) of **3f**

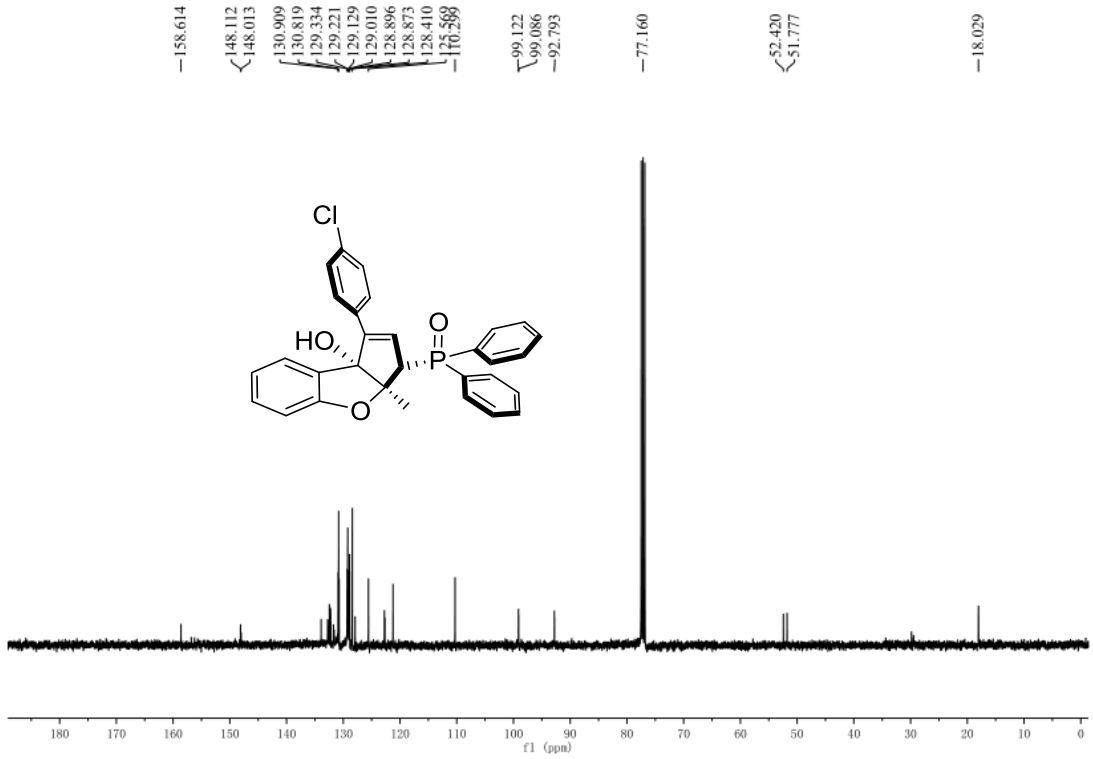

Br
HO
O
P
O
f1 (ppm)

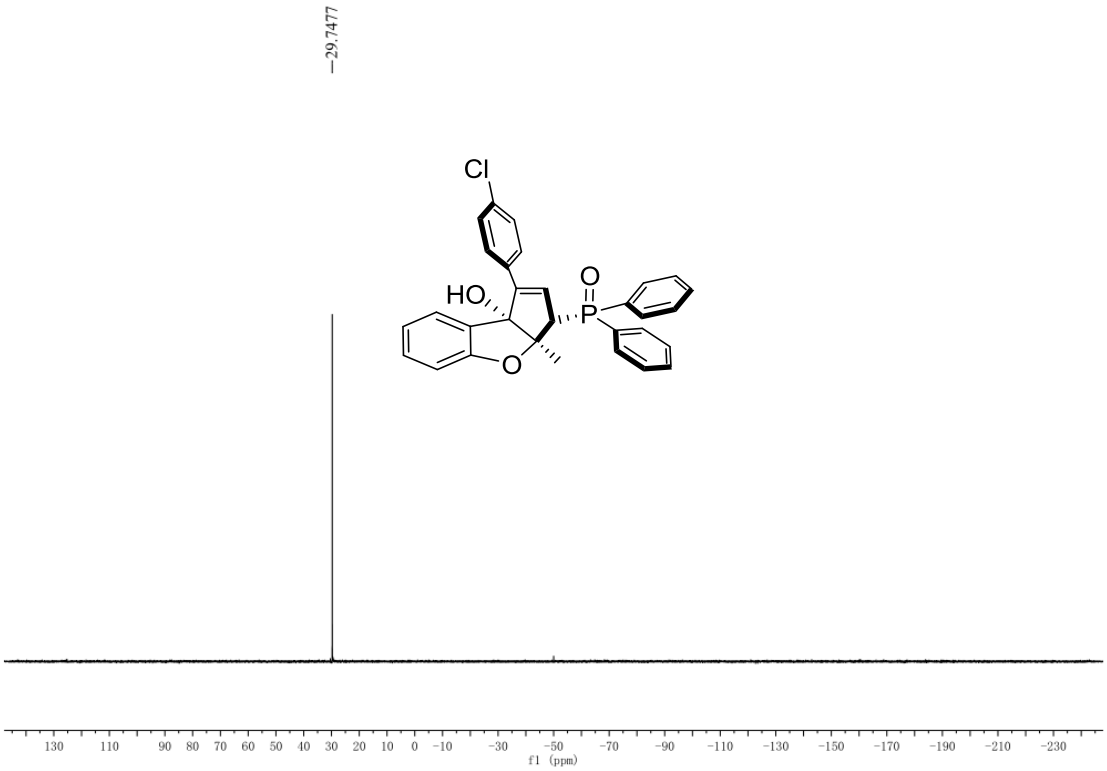

Br
HO
O
P
O
f1 (ppm)



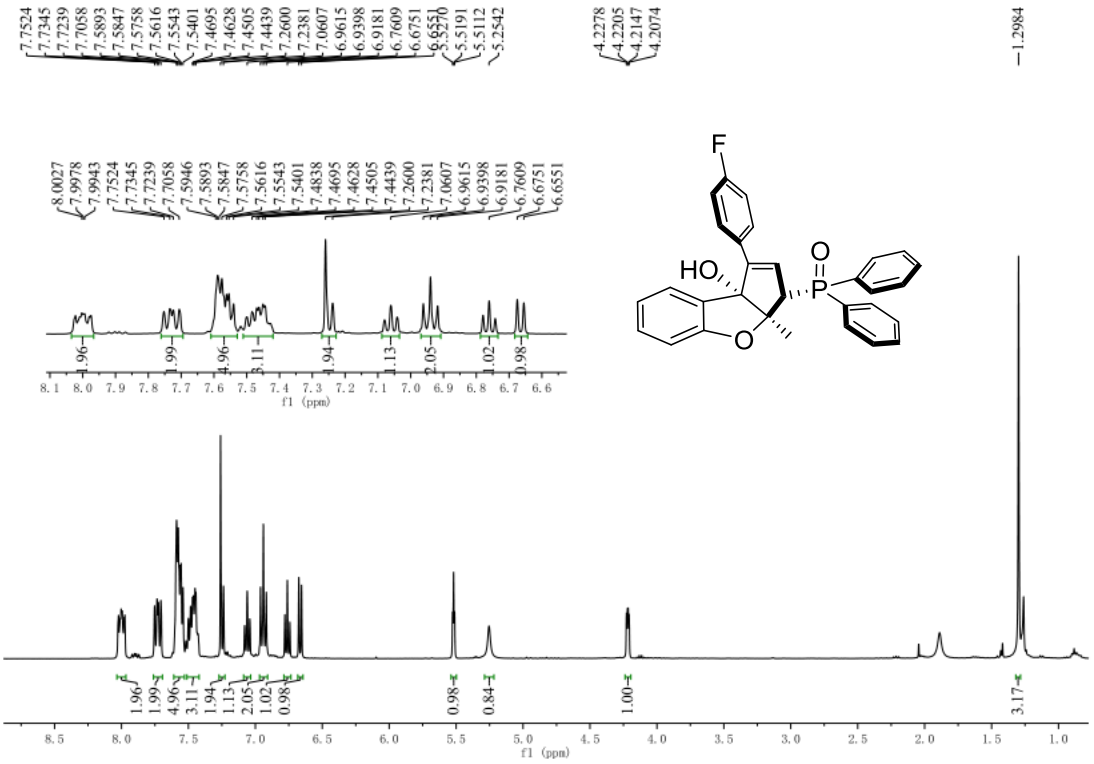
^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$),^{31}P NMR (162 MHz, $CDCl_3$) of **3g**

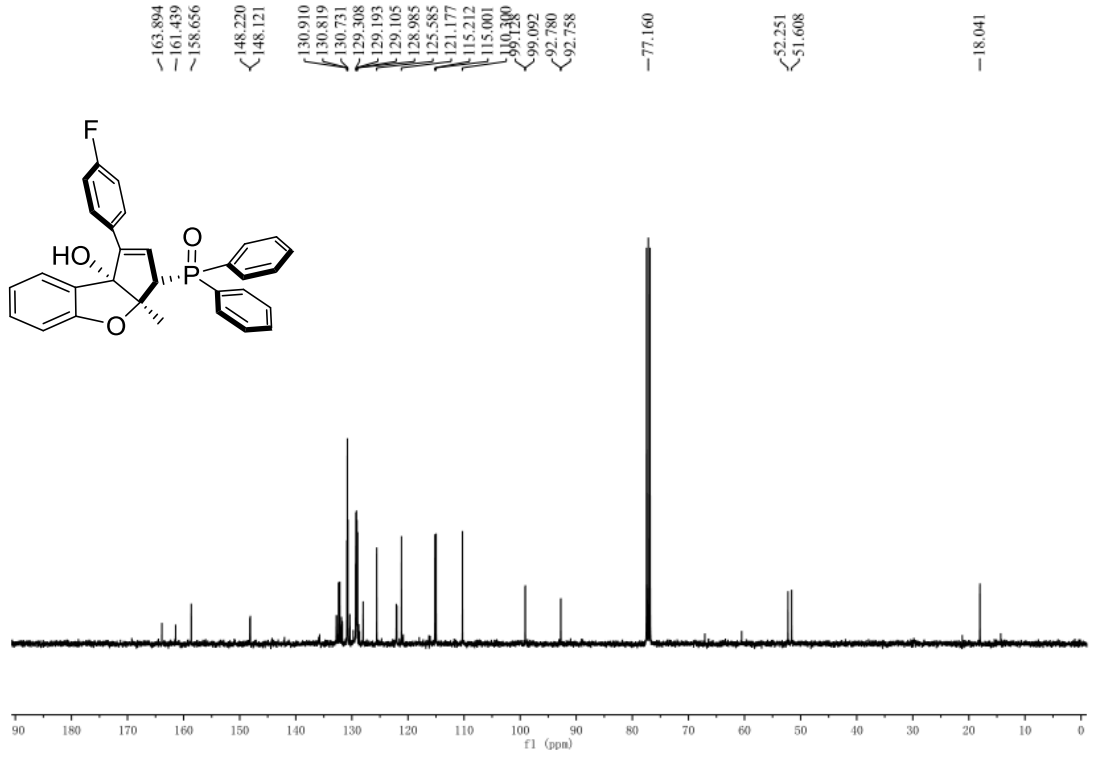


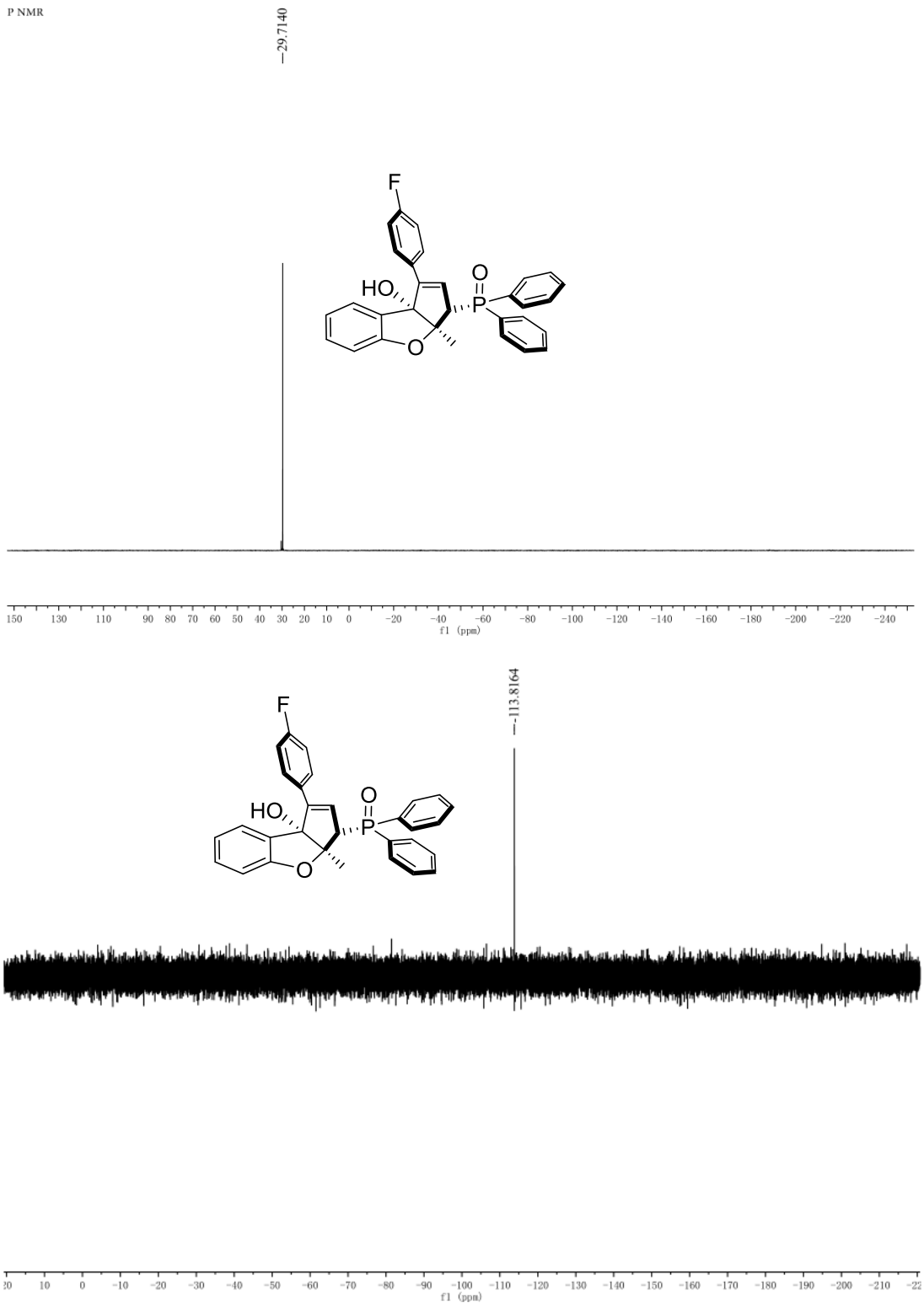




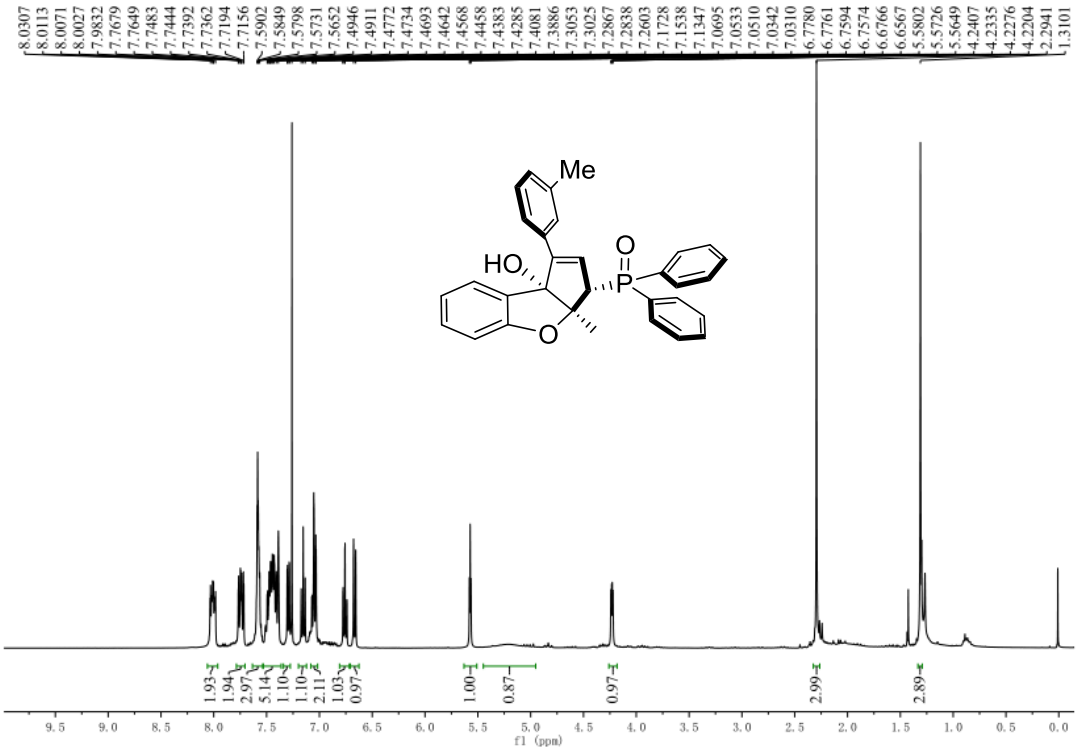
^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$), ^{31}P NMR (162 MHz, $CDCl_3$) of **3h**

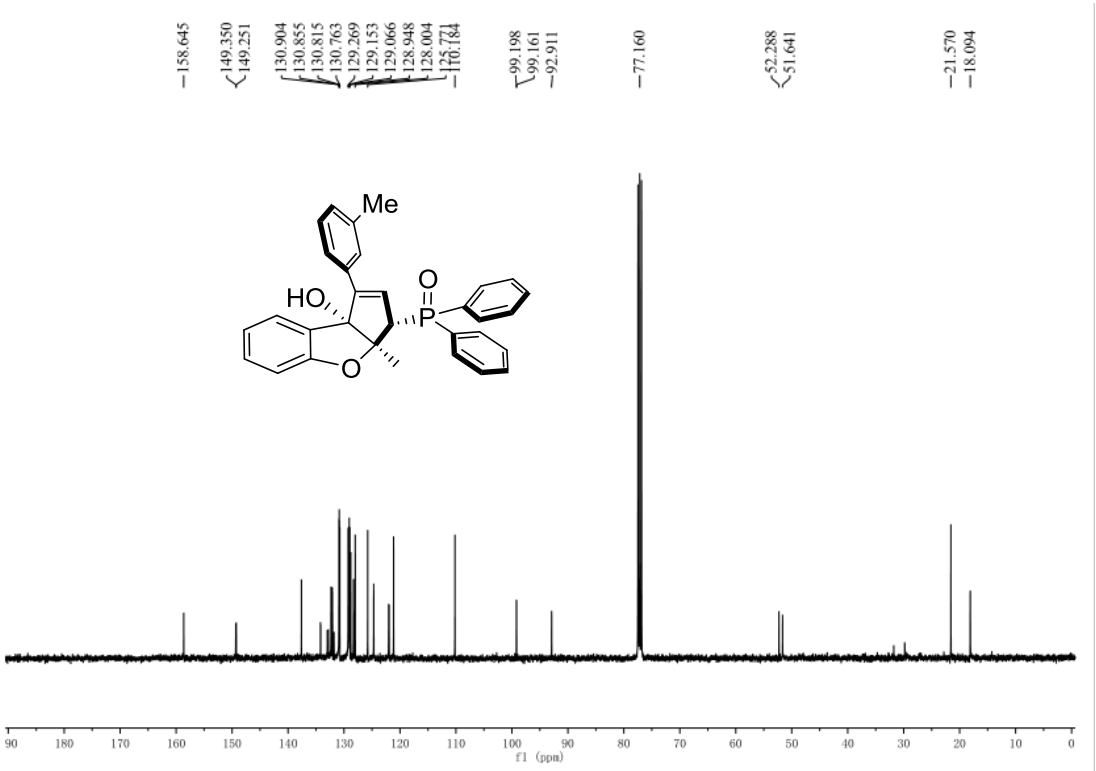

F
HO
O
P
O

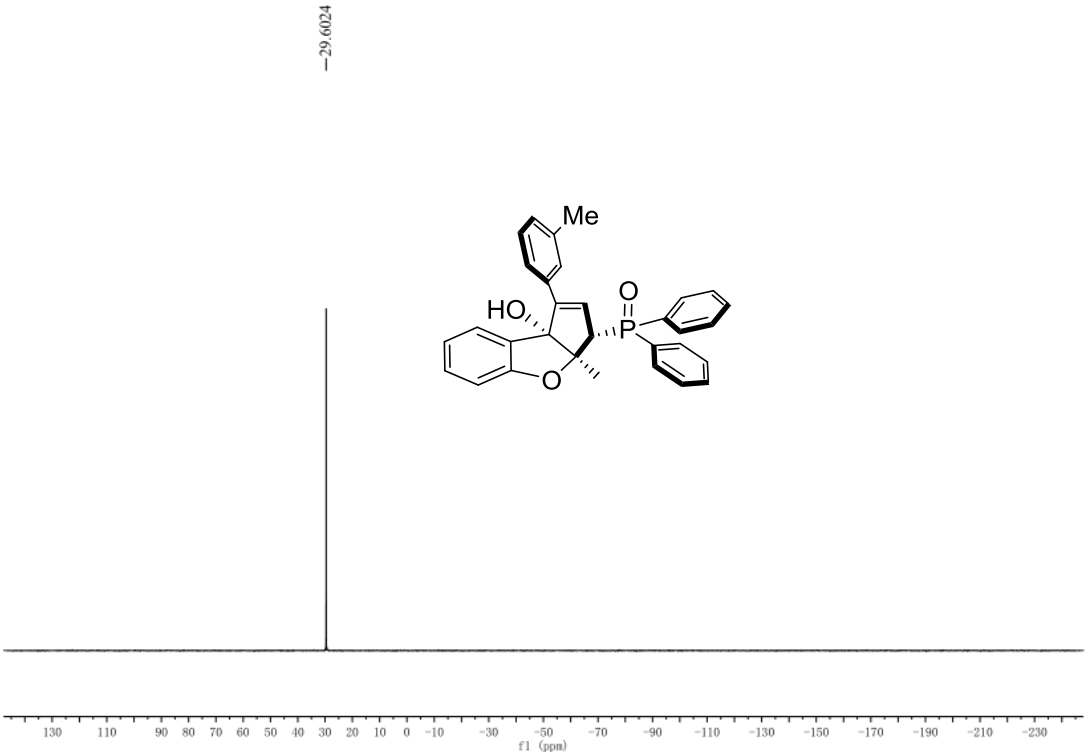

F
HO
O
P
O



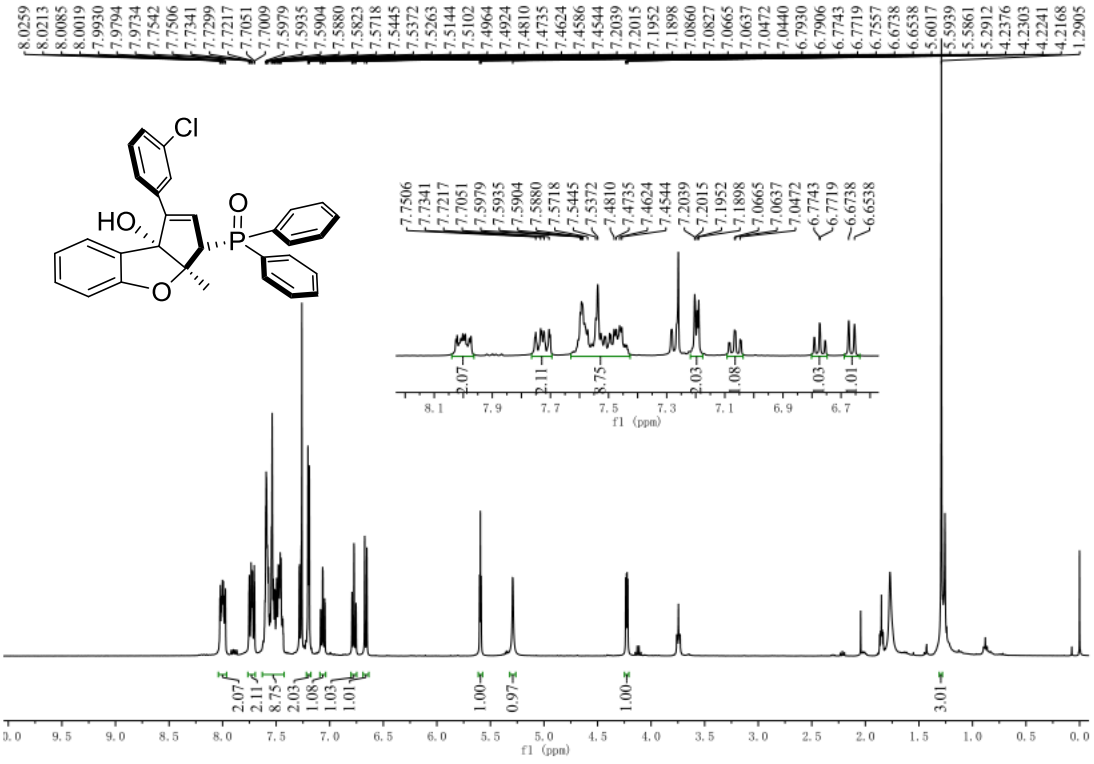
^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$), ^{31}P NMR (162 MHz, $CDCl_3$), ^{19}F NMR (376 MHz, $CDCl_3$) of **3i**

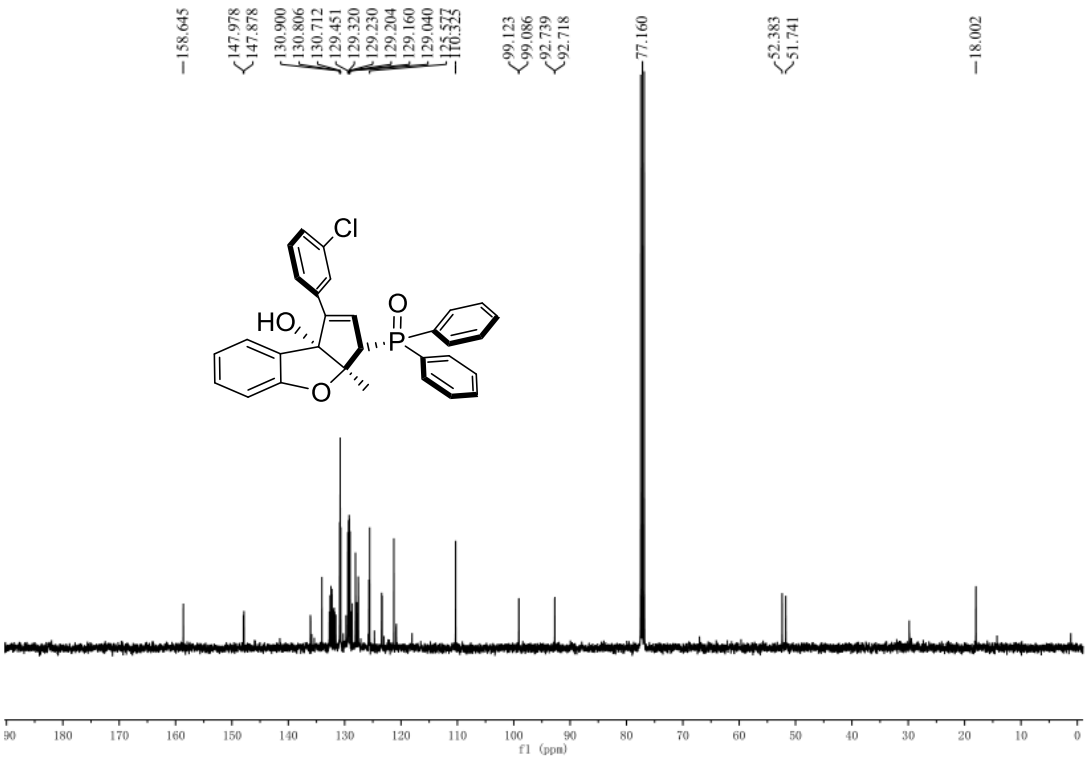

Me
HO
O
P
O
f1 (ppm)

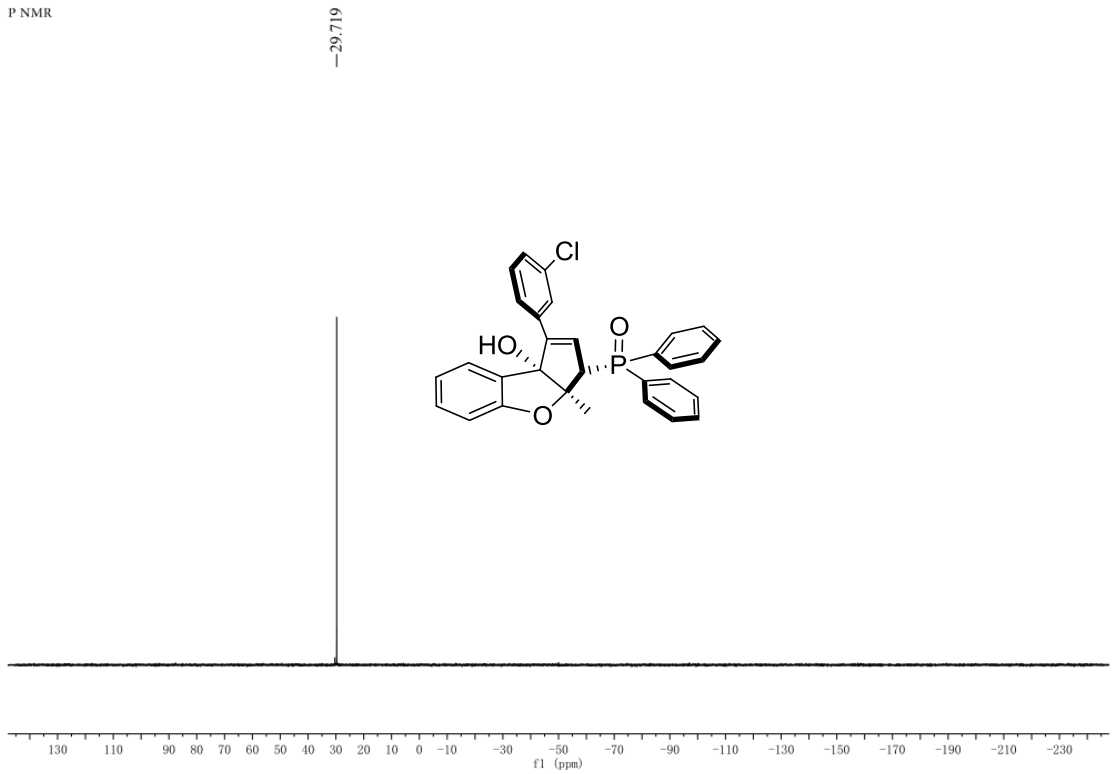

Me
HO
O
P
O
f1 (ppm)



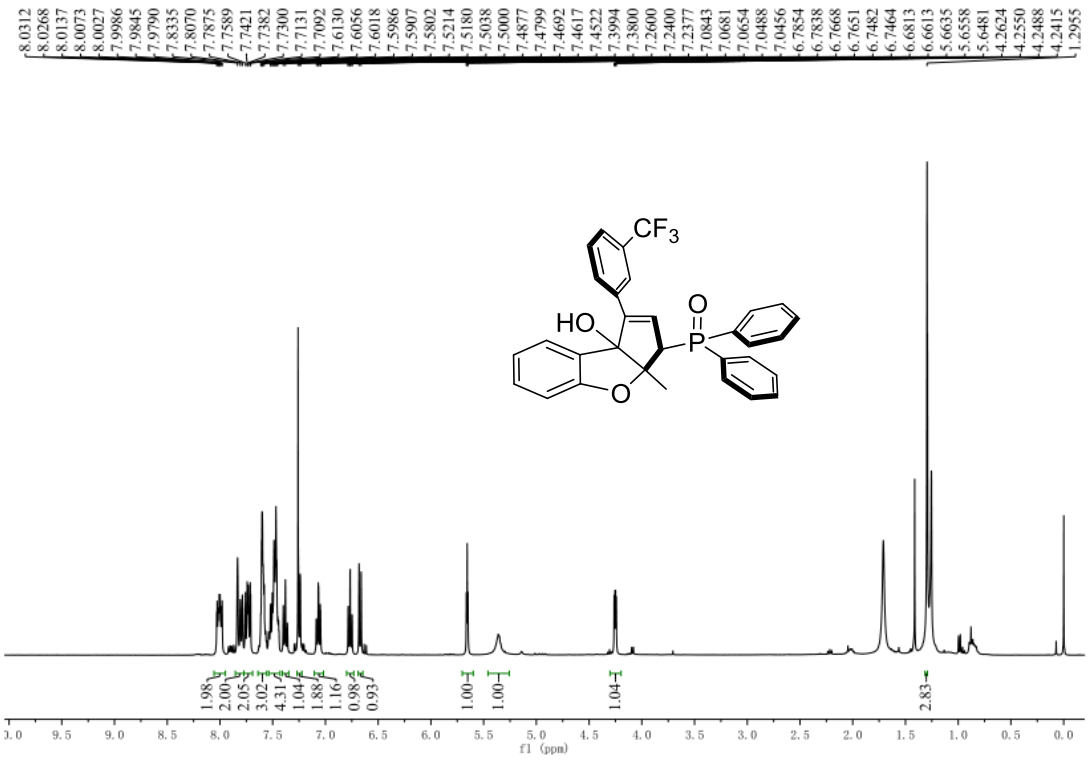
^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$), ^{31}P NMR (162 MHz, $CDCl_3$) of **3j**







^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$), ^{31}P NMR (162 MHz, $CDCl_3$) of **3k**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8.0137
8.0073
8.0027
7.9986
7.9845
7.9790
7.8335
7.8070
7.7875
7.7589
7.7421
7.7382
7.7300
7.7131
7.7092
7.6130
7.6056
7.6018
7.5986
7.5907
7.5802
7.5214
7.5180
7.5038
7.5000
7.4877
7.4799
7.4692
7.4617
7.4522
7.3994
7.3800
7.2600
7.2400
7.2377
7.0843
7.0681
7.0654
7.0488
7.0456
6.7854
6.7838
6.7668
6.7651
6.7482
6.7464
6.6813
6.6613
5.6635
5.6558
5.6481
4.2624
4.2550
4.2488
4.2415
1.2955
CF3
HO
O
P
O
1.98
2.00
2.05
3.02
4.31
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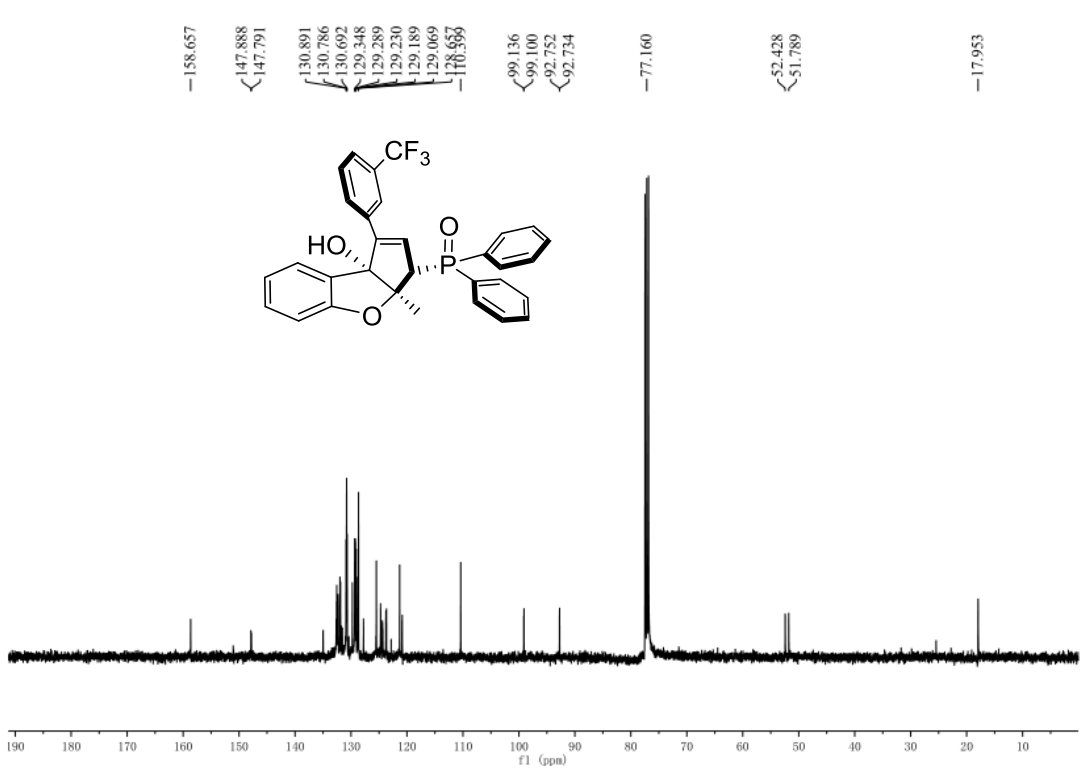
0.98
0.93
1.00
1.00
1.04
2.83
f1 (ppm)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129.289
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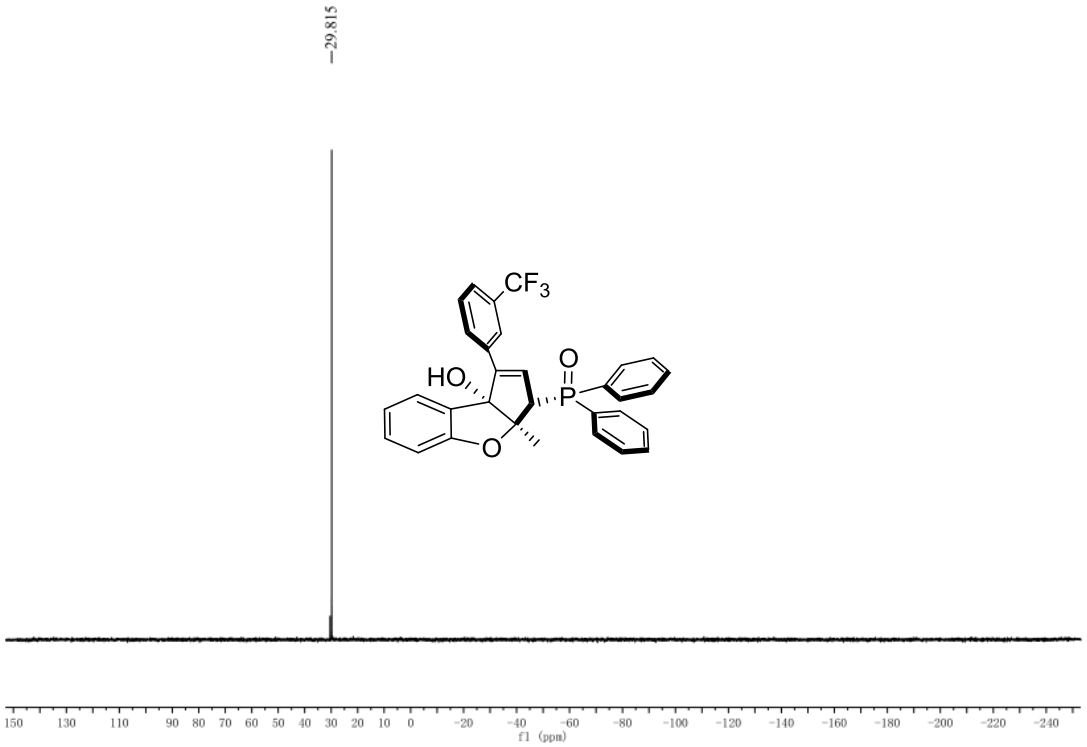
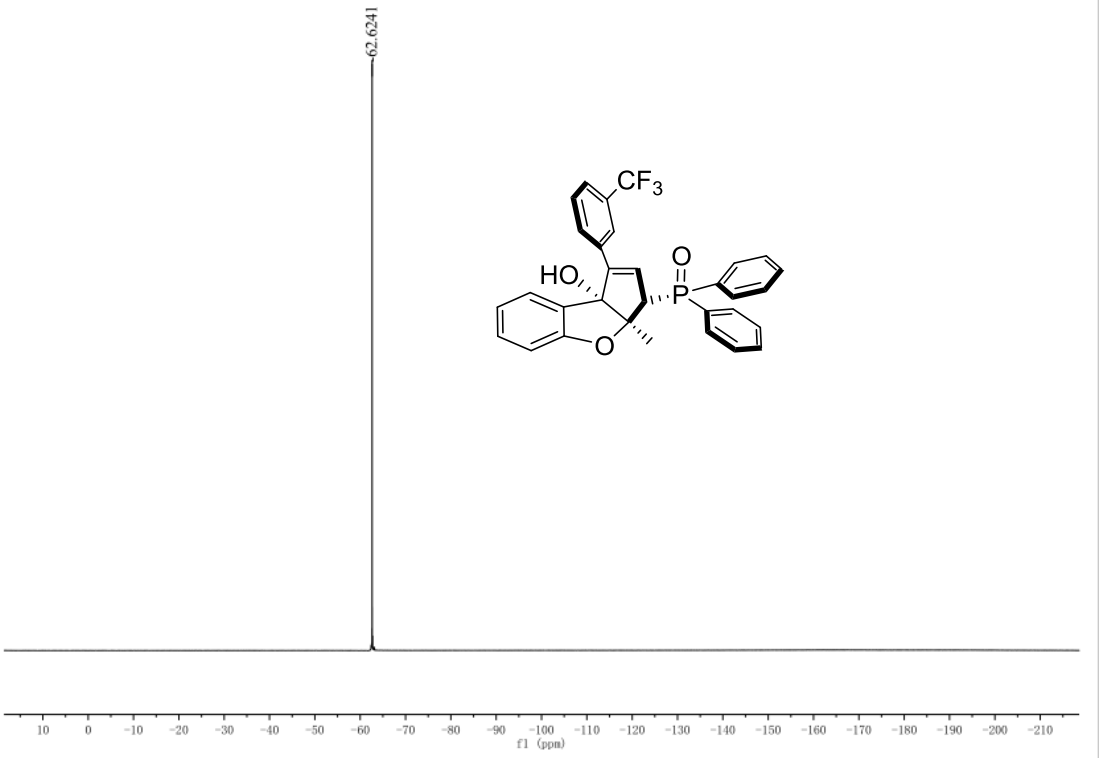
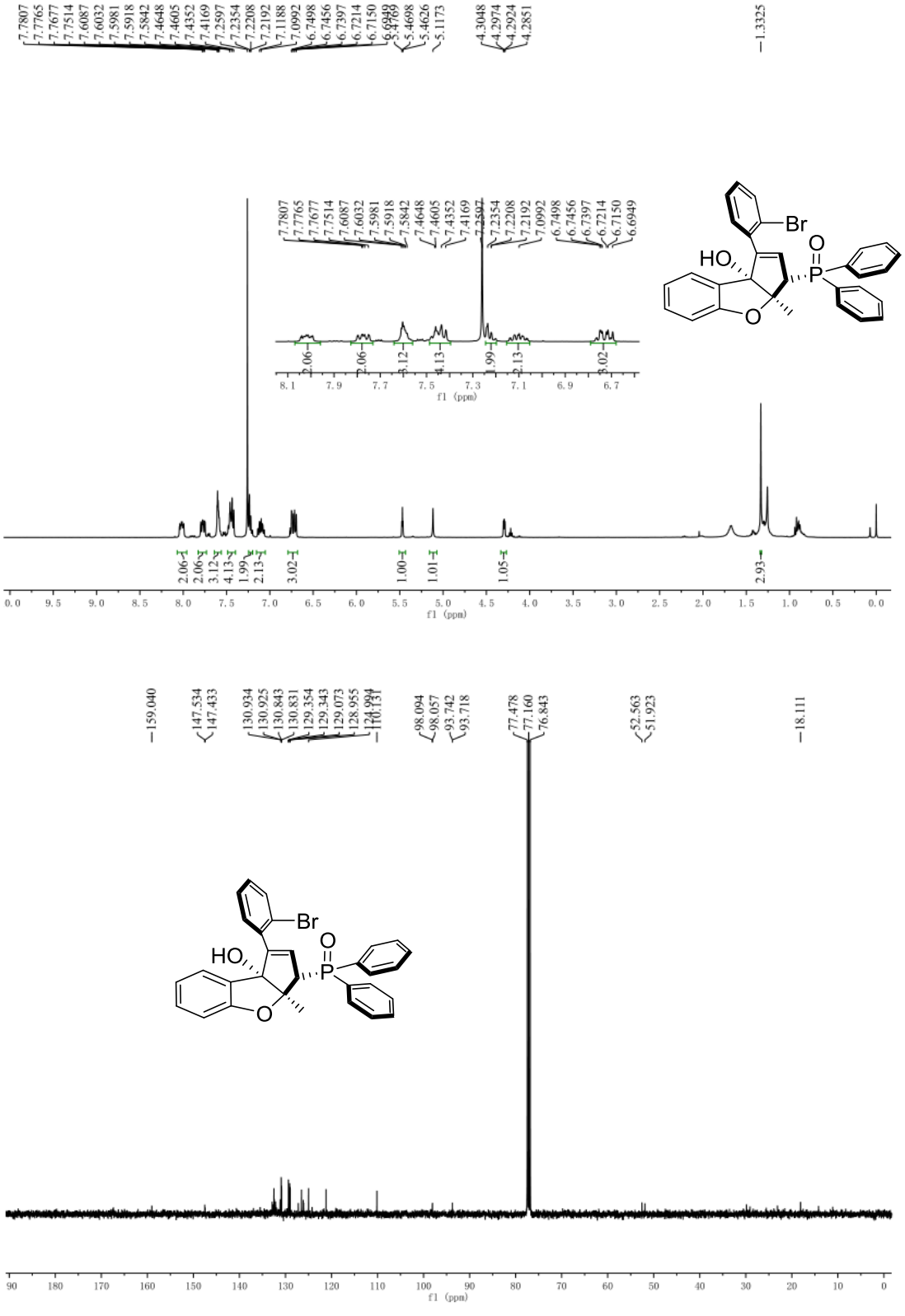
129.189
129.069
128.657
110.599
99.136
99.100
92.752
92.734
77.160
52.428
51.789
17.953
CF3
HO
O
P
O
f1 (ppm)





^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$), ^{31}P NMR (162 MHz, $CDCl_3$), ^{19}F NMR (376 MHz, $CDCl_3$) of **3l**


7.7807
7.7765
7.7677
7.7514
7.6087
7.6032
7.5981
7.5918
7.5842
7.4648
7.4605
7.4352
7.4169
7.2597
7.2354
7.2208
7.2192
7.1188
7.0992
6.7498
6.7456
6.7397
6.7214
6.7150
6.6949
5.4769
5.4698
5.4626
5.1173
4.3048
4.2974
4.2924
4.2851
1.3325
2.06
2.06
3.12
4.13
1.99
2.13
3.02
1.00
1.01
1.05
2.93
f1 (ppm)
Br
HO
O
P
O
159.040
147.534
147.433
130.934
130.925
130.843
130.831
129.354
129.343
129.073
128.955
124.994
110.131
98.094
98.057
93.742
93.718
77.478
77.160
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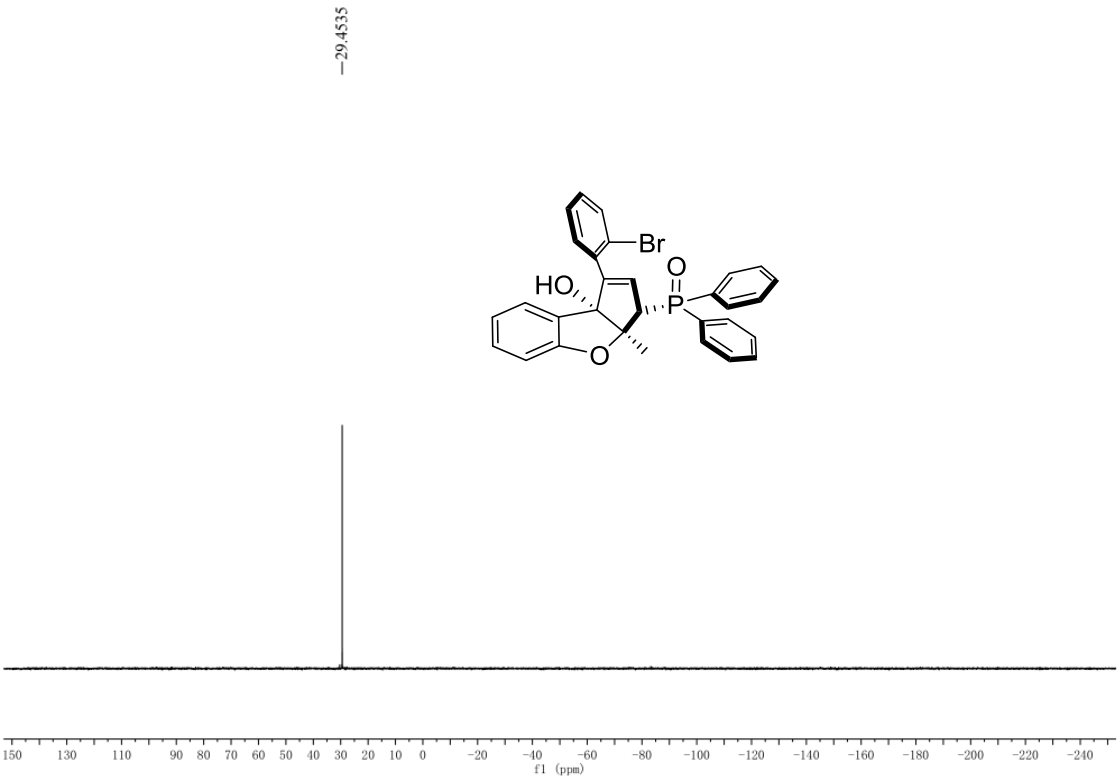
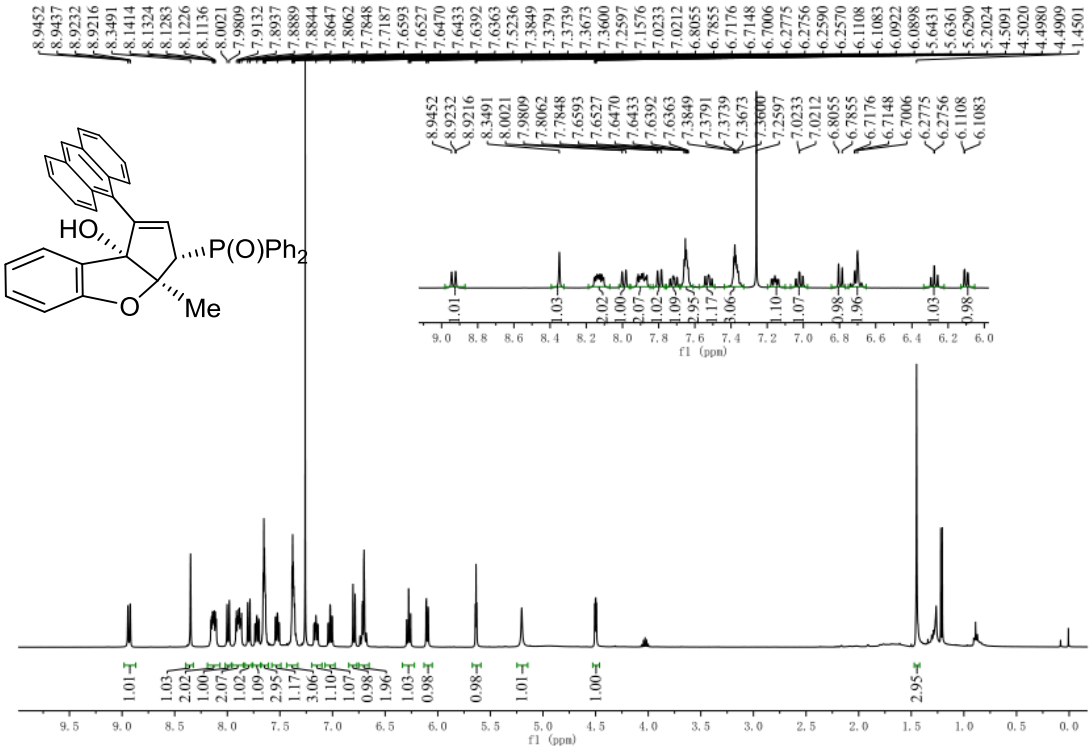
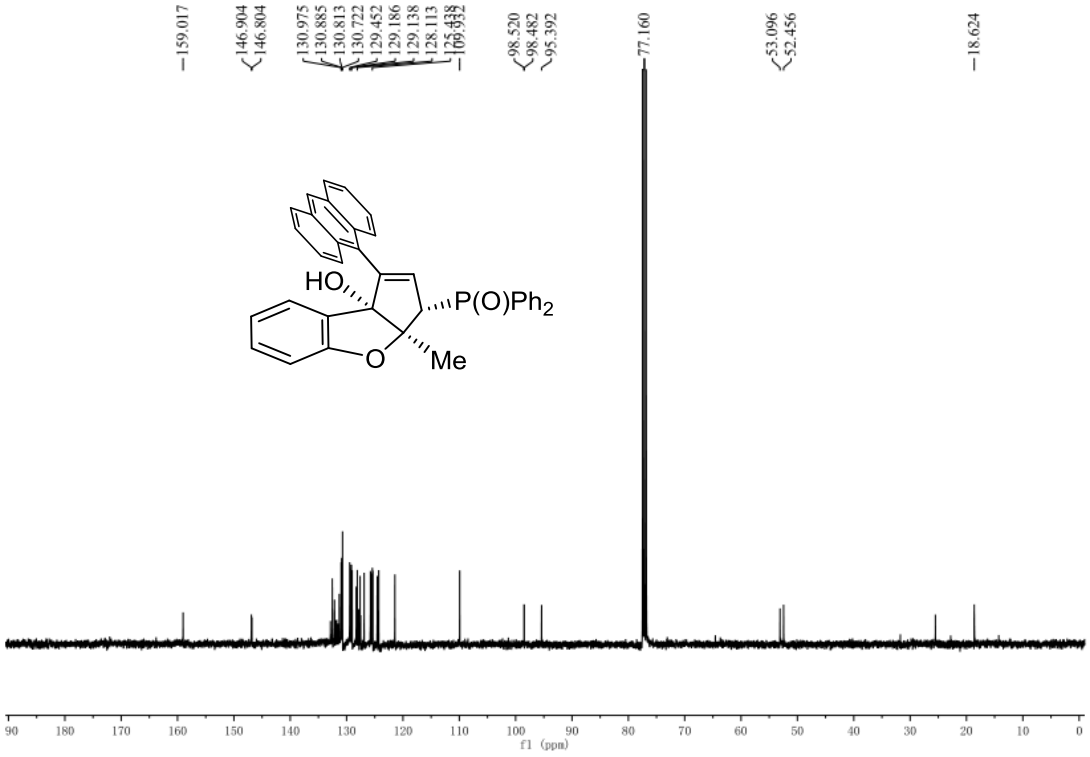
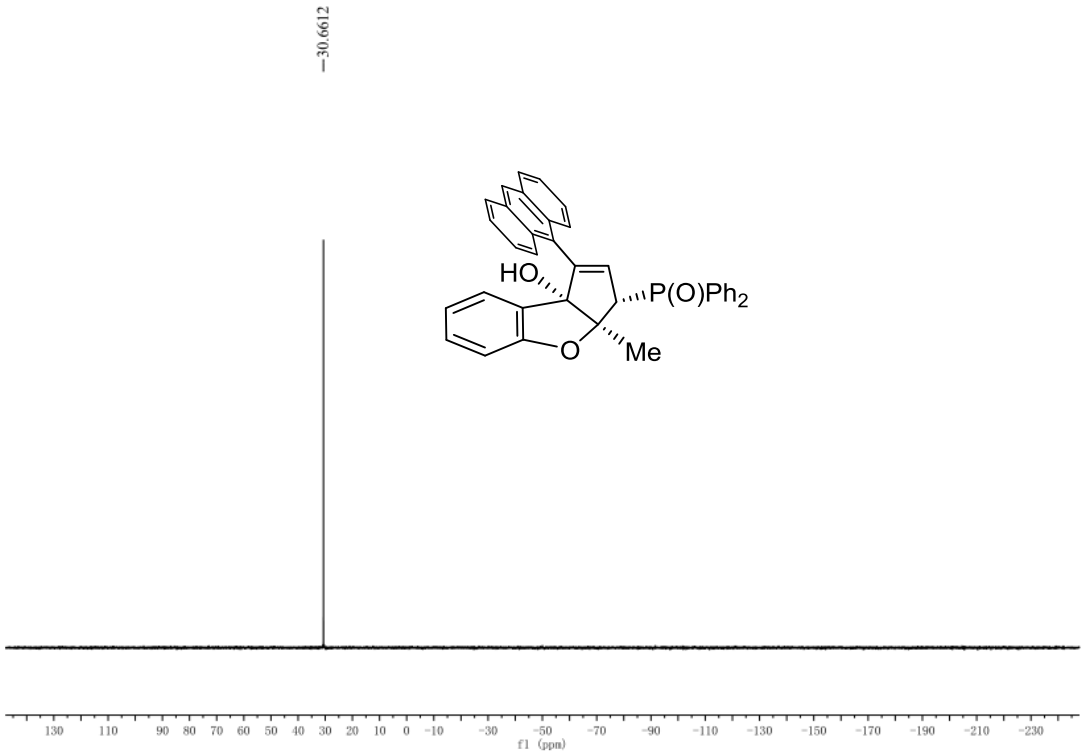
52.563
51.923
18.111
f1 (ppm)



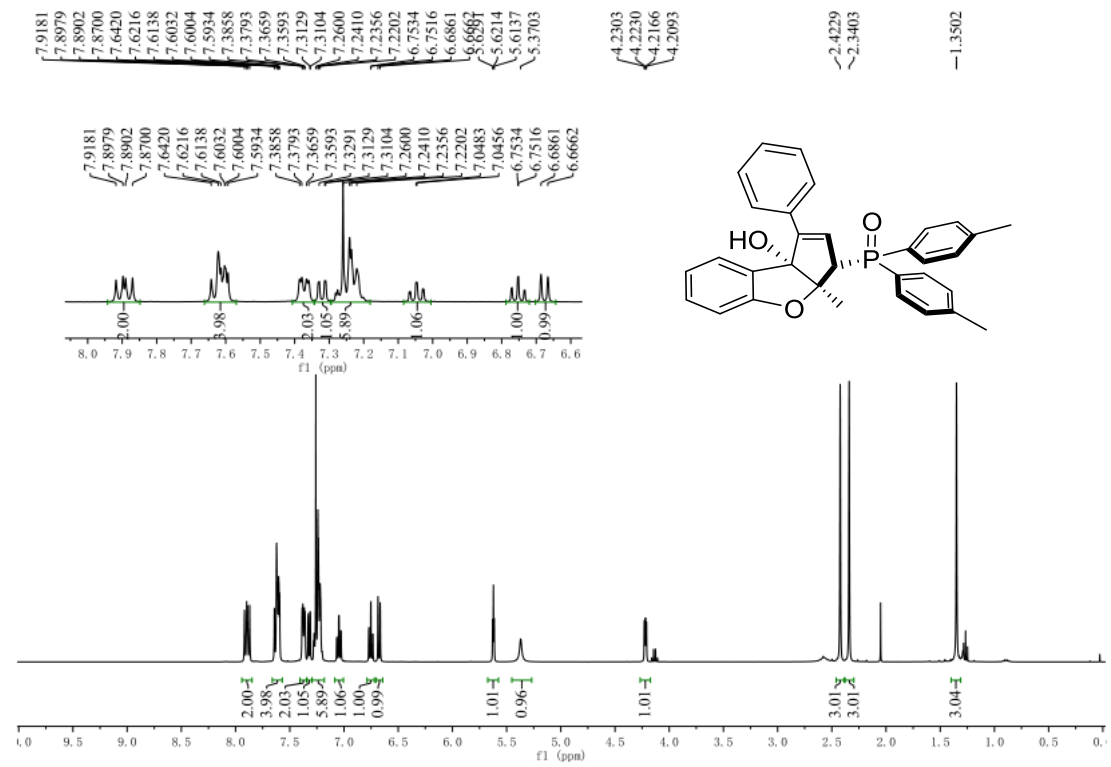
^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$), ^{31}P NMR (162 MHz, $CDCl_3$) of **3n**

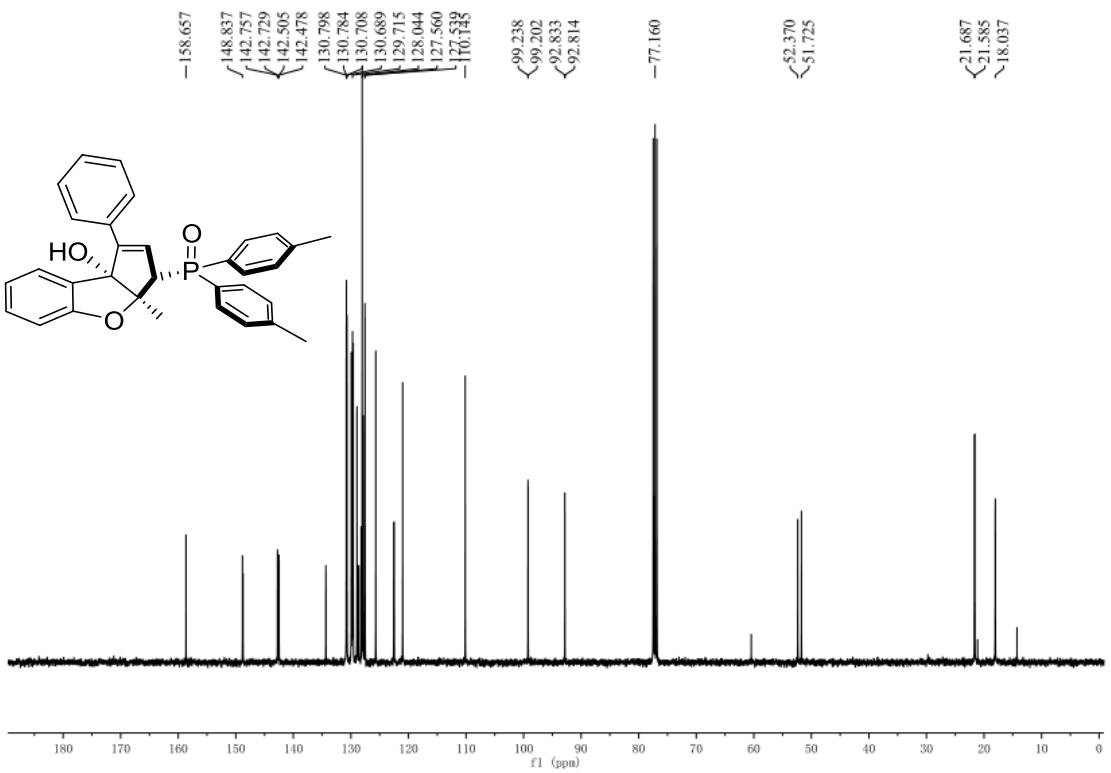


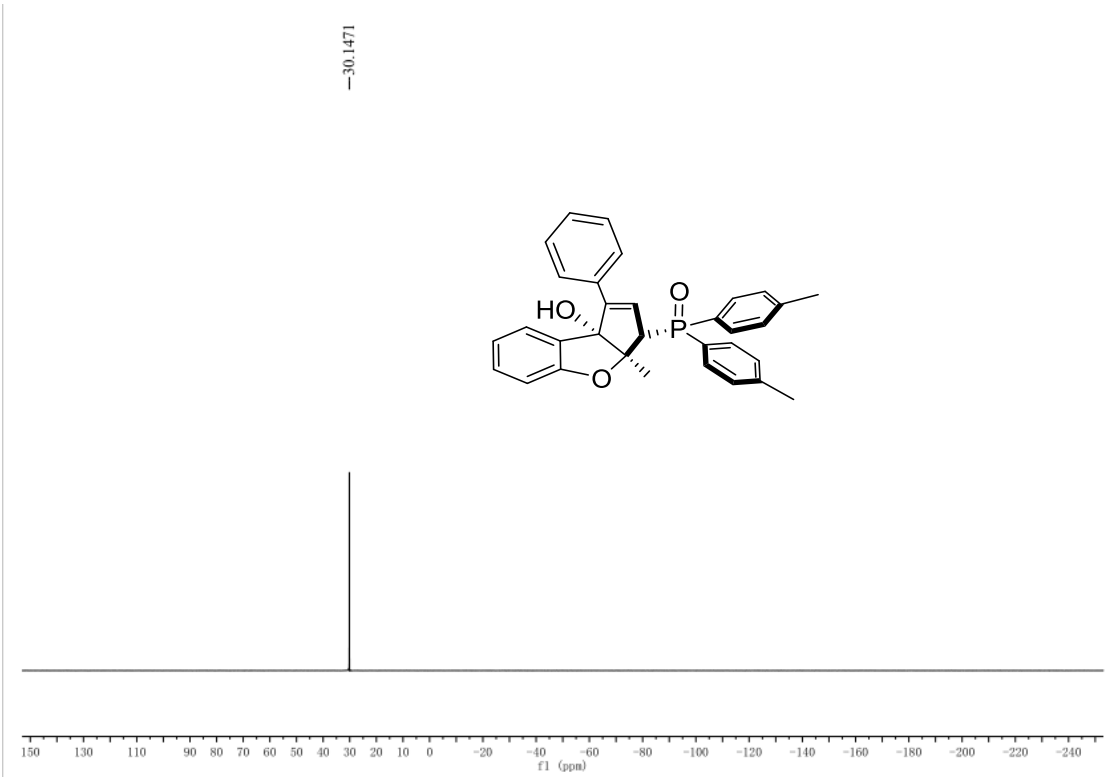




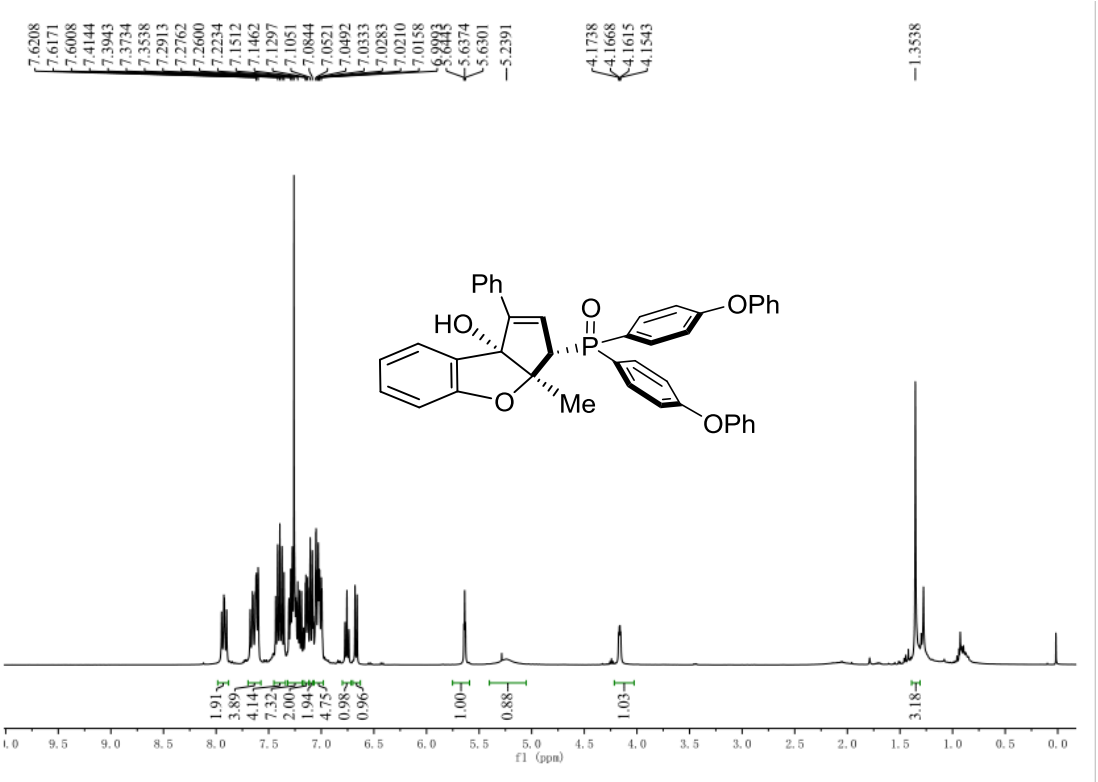
^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$), ^{31}P NMR (162 MHz, $CDCl_3$) of **3o**

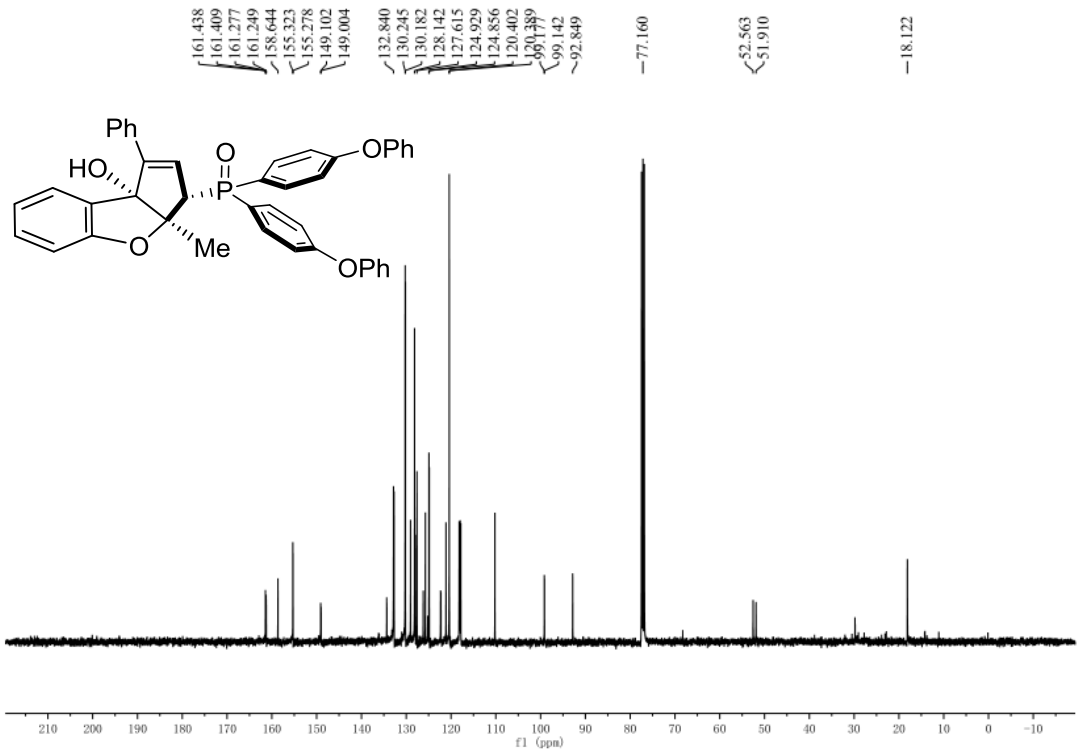

7.9181
7.8979
7.8902
7.8700
7.6420
7.6216
7.6138
7.6032
7.6004
7.5934
7.3858
7.3793
7.3659
7.3593
7.3129
7.3104
7.2600
7.2410
7.2356
7.2202
6.7534
6.7516
6.6861
6.6662
5.6291
5.6214
5.6137
5.3703
4.2303
4.2230
4.2166
4.2093
2.4229
2.3403
1.3502
HO
O
P
O
f1 (ppm)

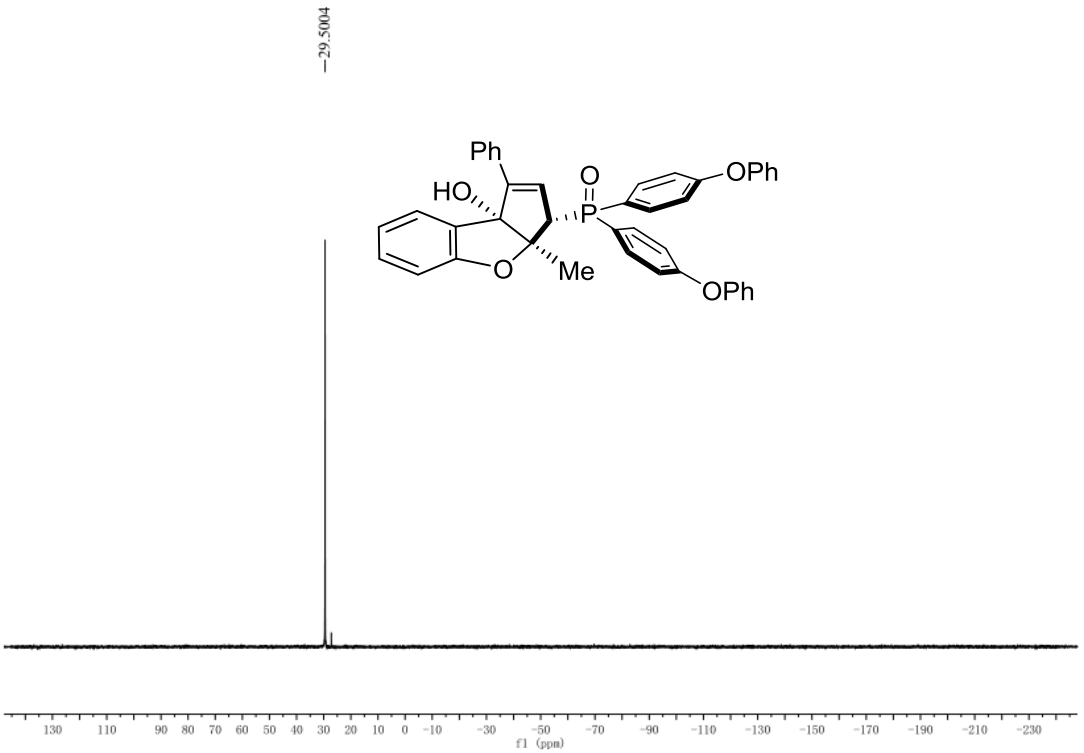

158.657
148.837
142.757
142.729
142.505
142.478
130.798
130.784
130.708
130.689
129.715
128.044
127.560
127.539
110.145
99.238
99.202
92.833
92.814
77.160
52.370
51.725
21.687
21.585
18.037
HO
O
P
O
f1 (ppm)



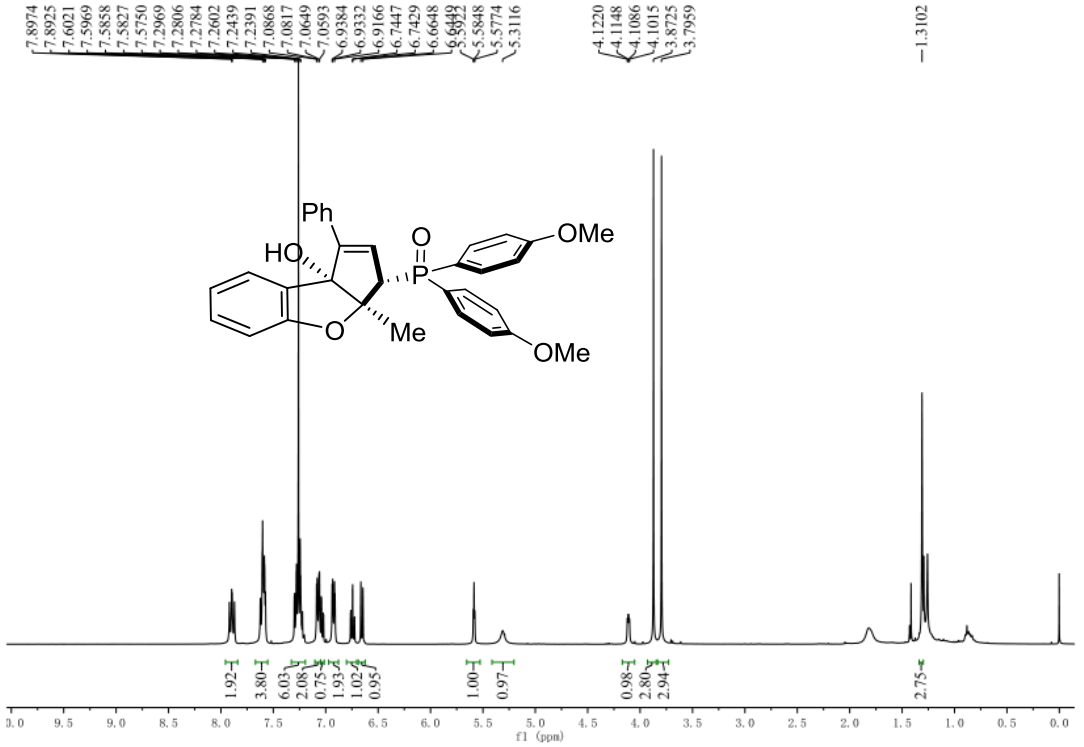
^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$), ^{31}P NMR (162 MHz, $CDCl_3$) of **3p**

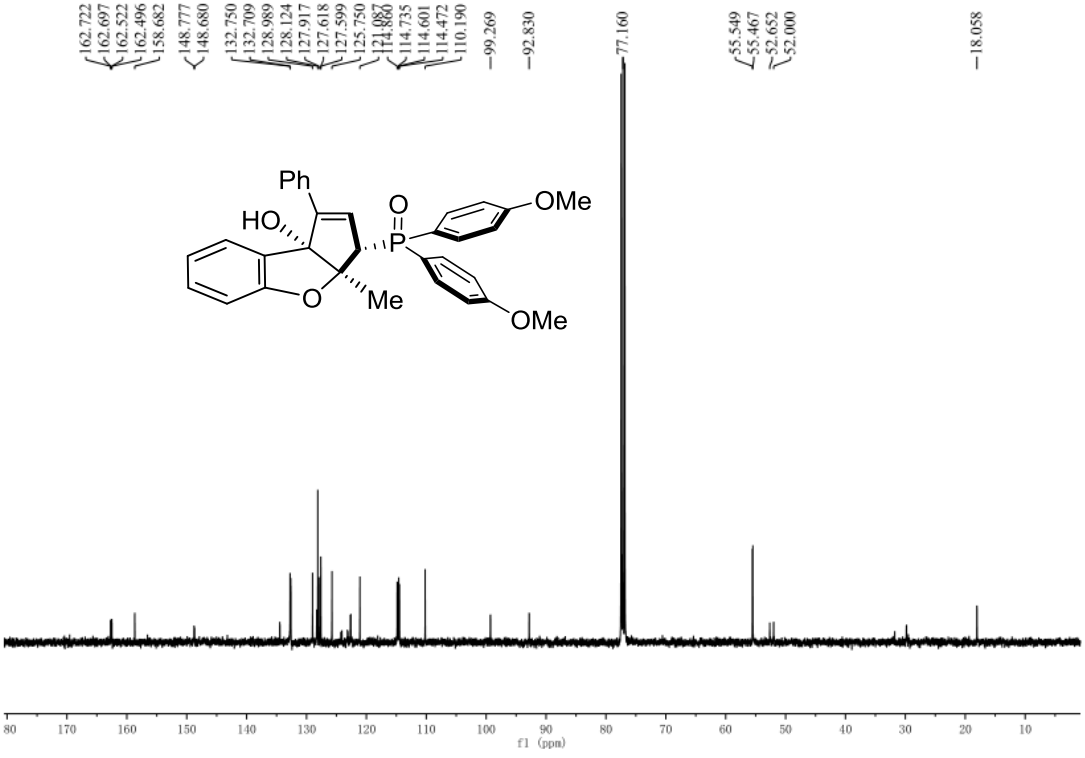


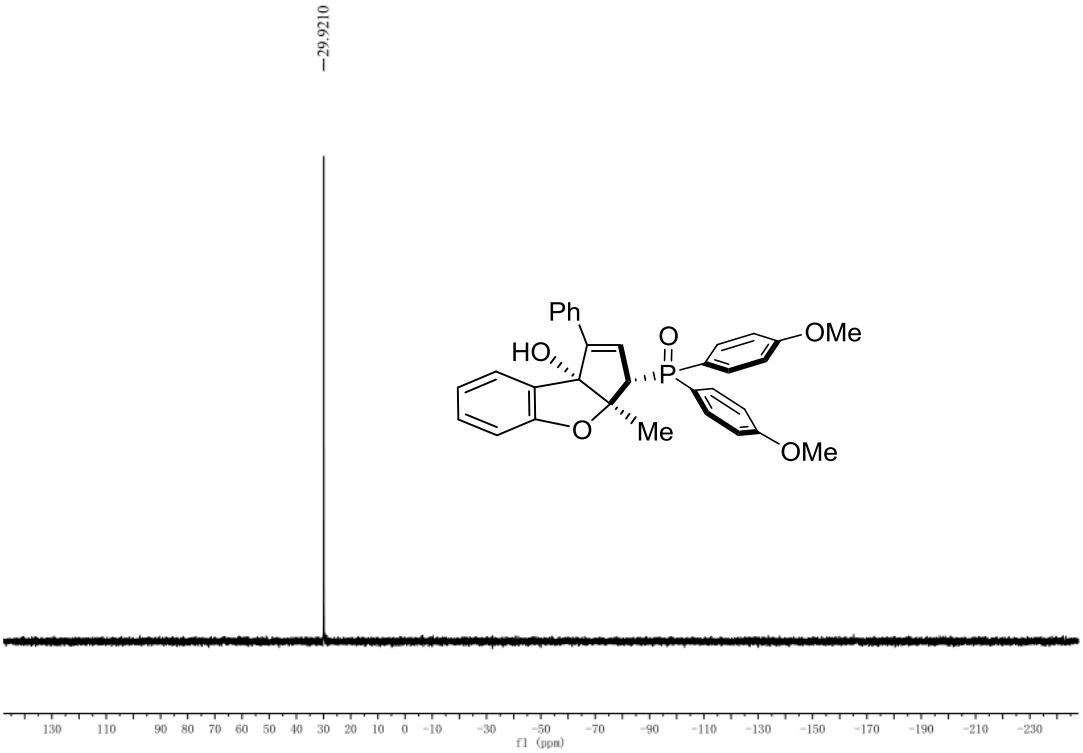




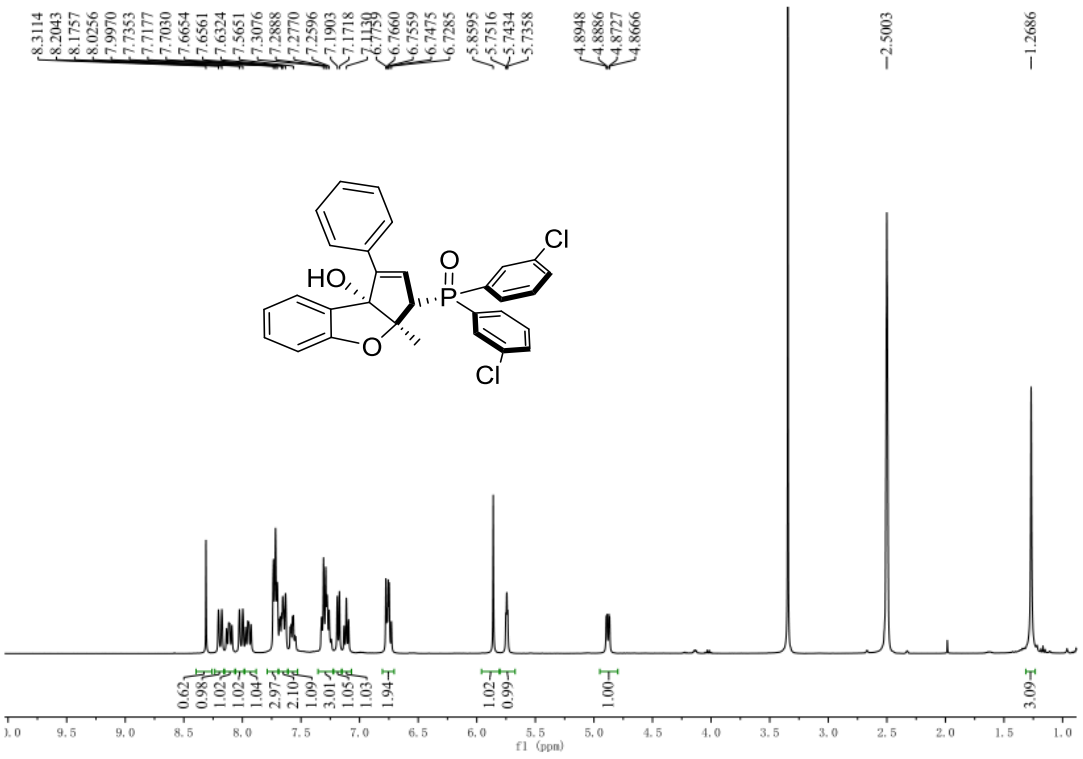
^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$), ^{31}P NMR (162 MHz, $CDCl_3$) of **3q**

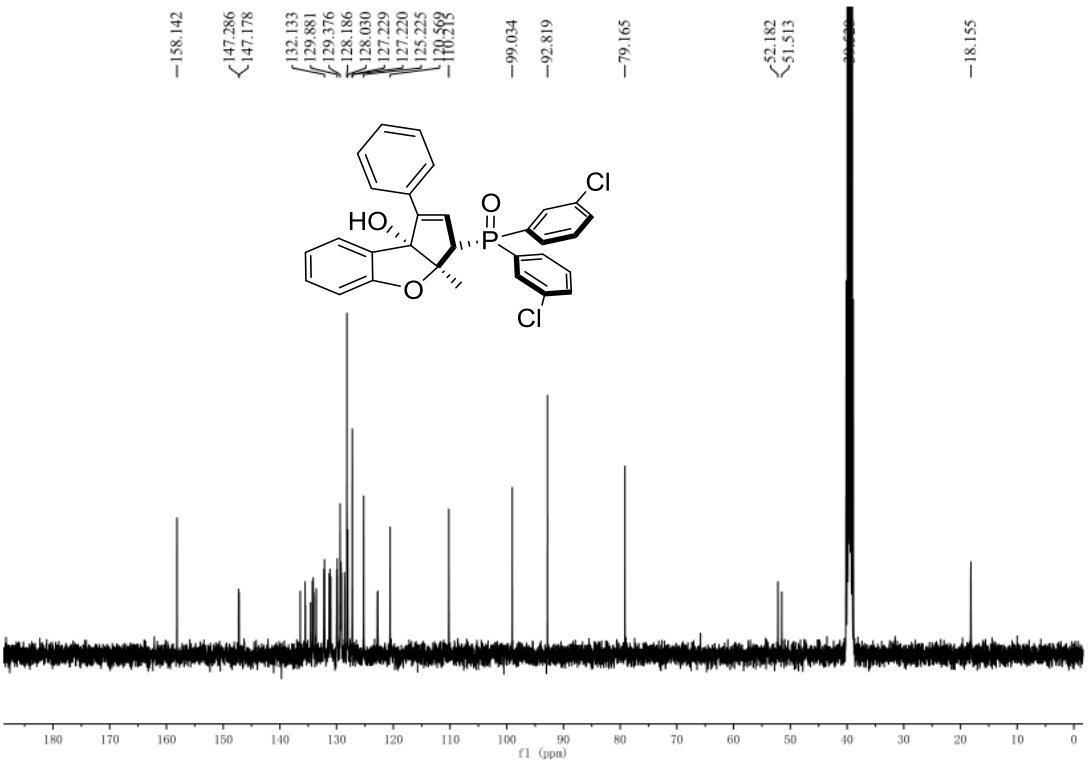

Ph
HO
O
P
OMe
OMe
O
Me

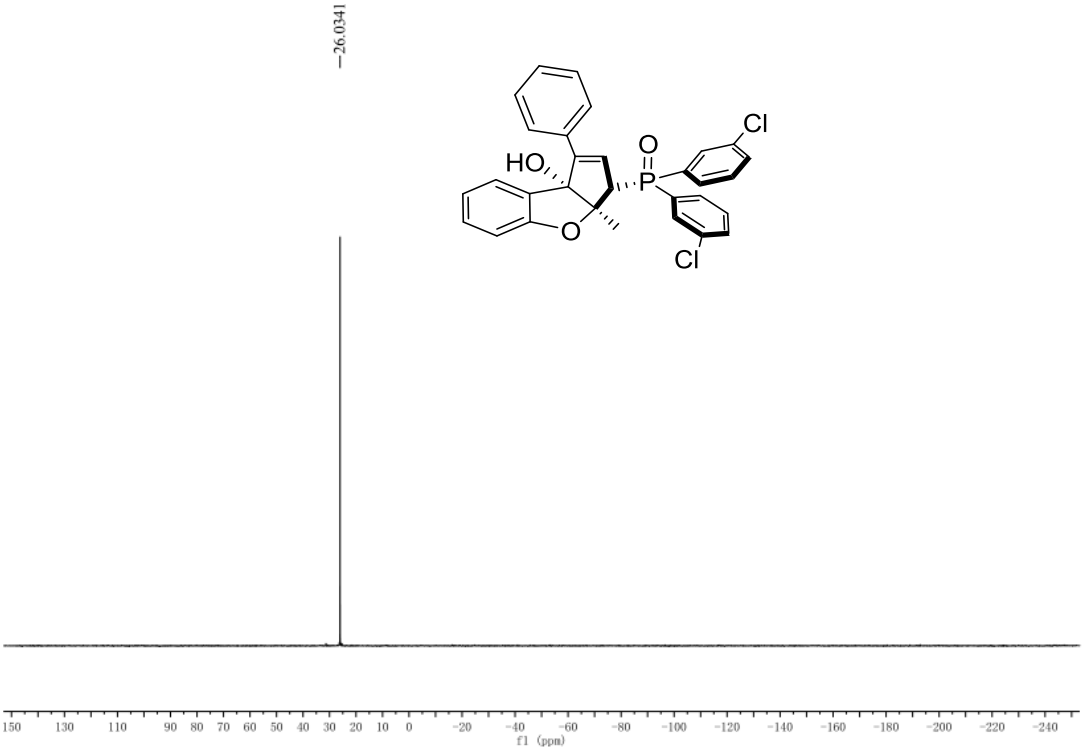

Ph
HO
O
P
OMe
OMe
O
Me



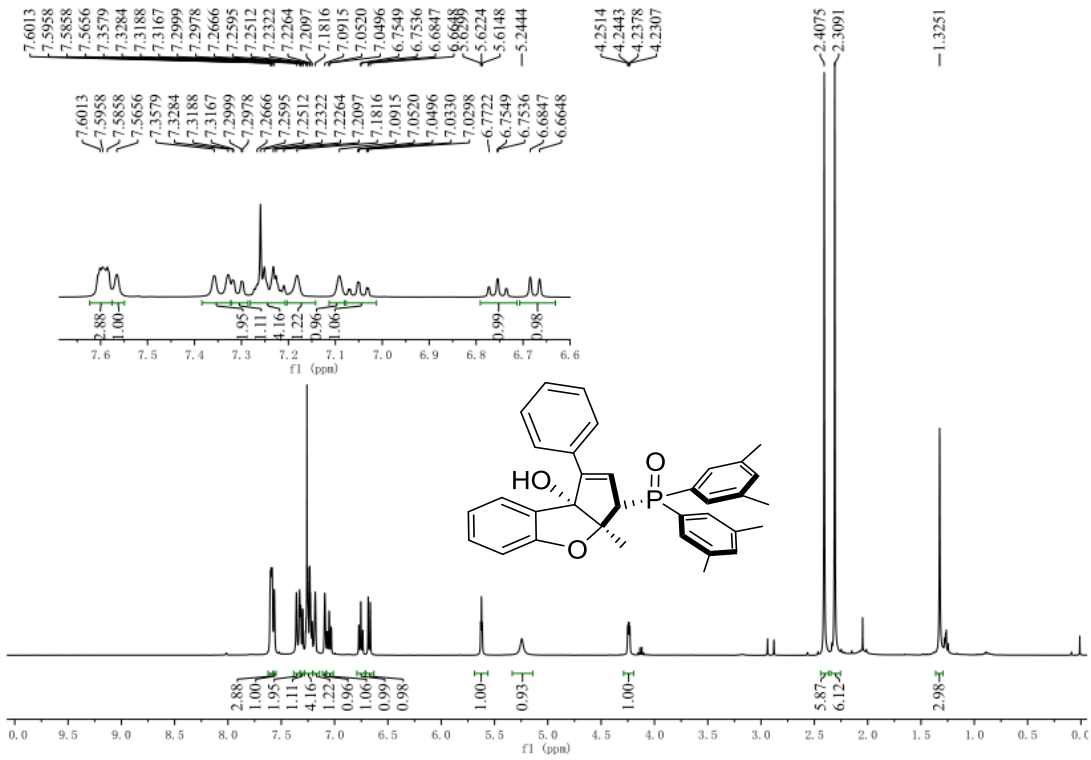
^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$), ^{31}P NMR (162 MHz, $CDCl_3$) of **3r**

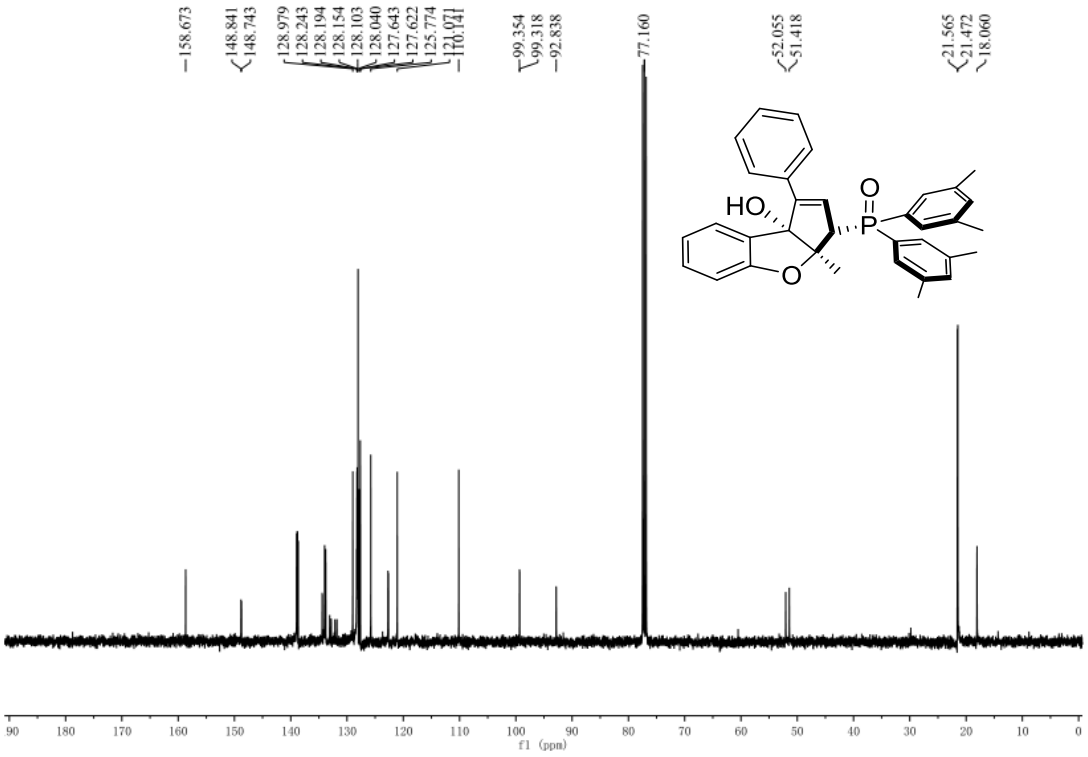


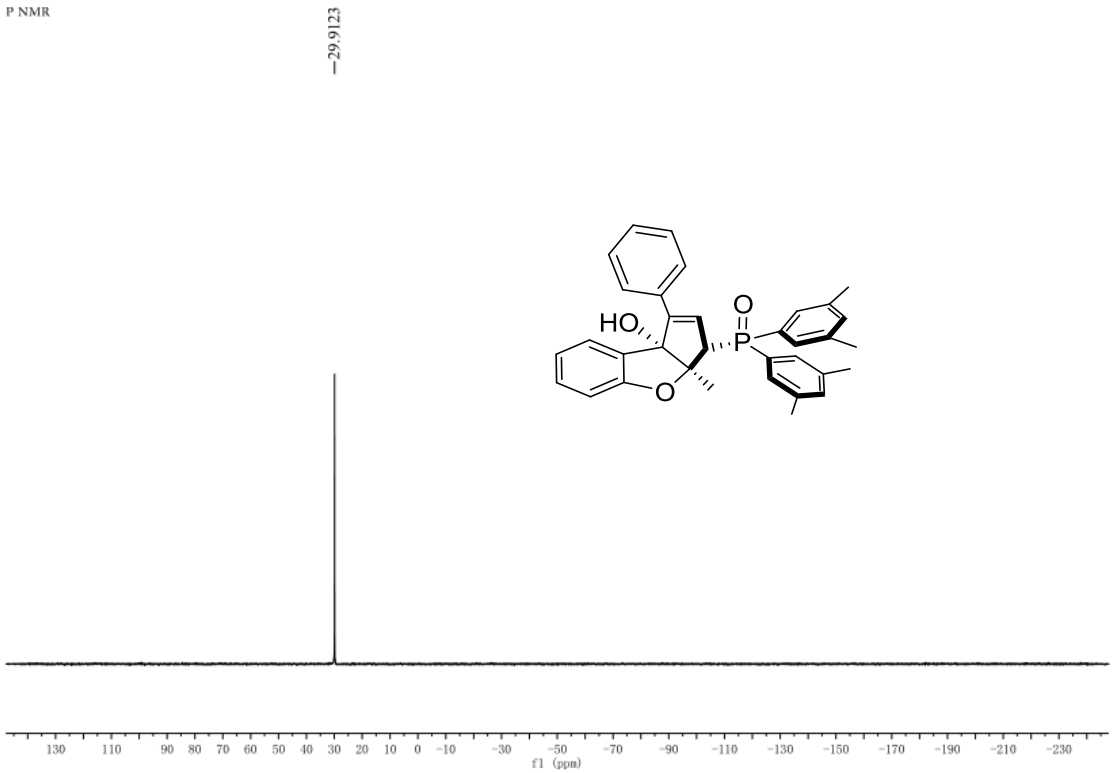




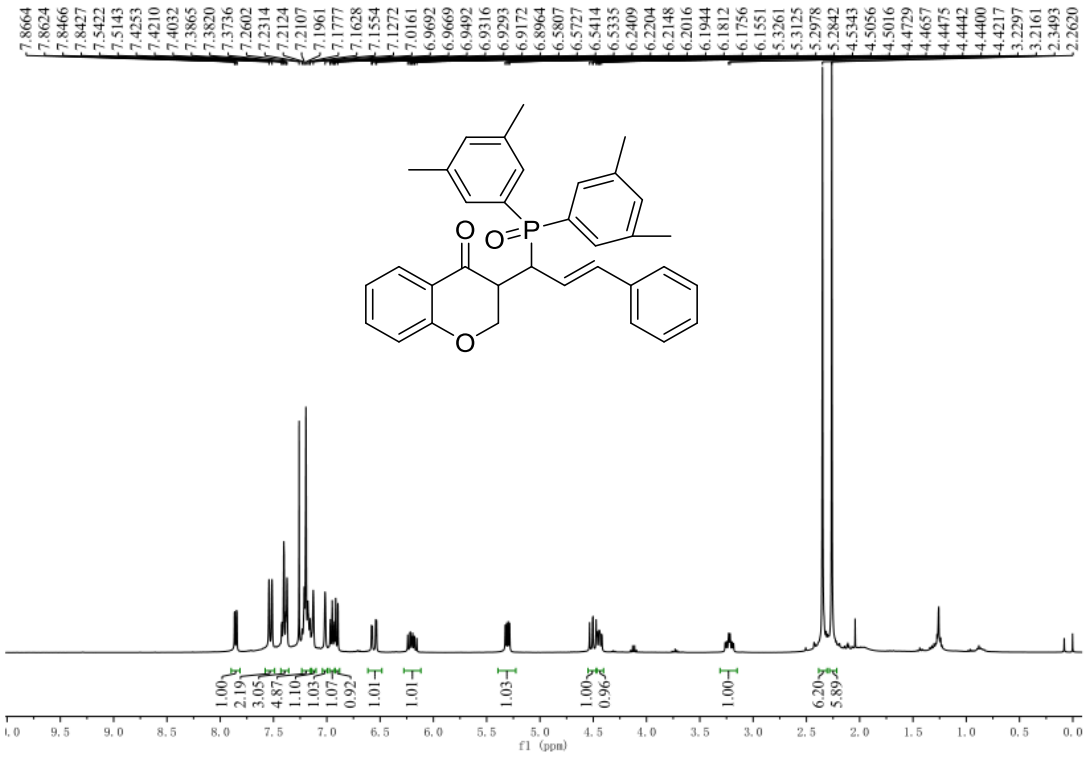
^{1}H NMR (400 MHz, DMSO-D6), ^{13}C NMR (100 MHz, DMSO-D6), ^{31}P NMR (162 MHz, DMSO-D6) of **3s**

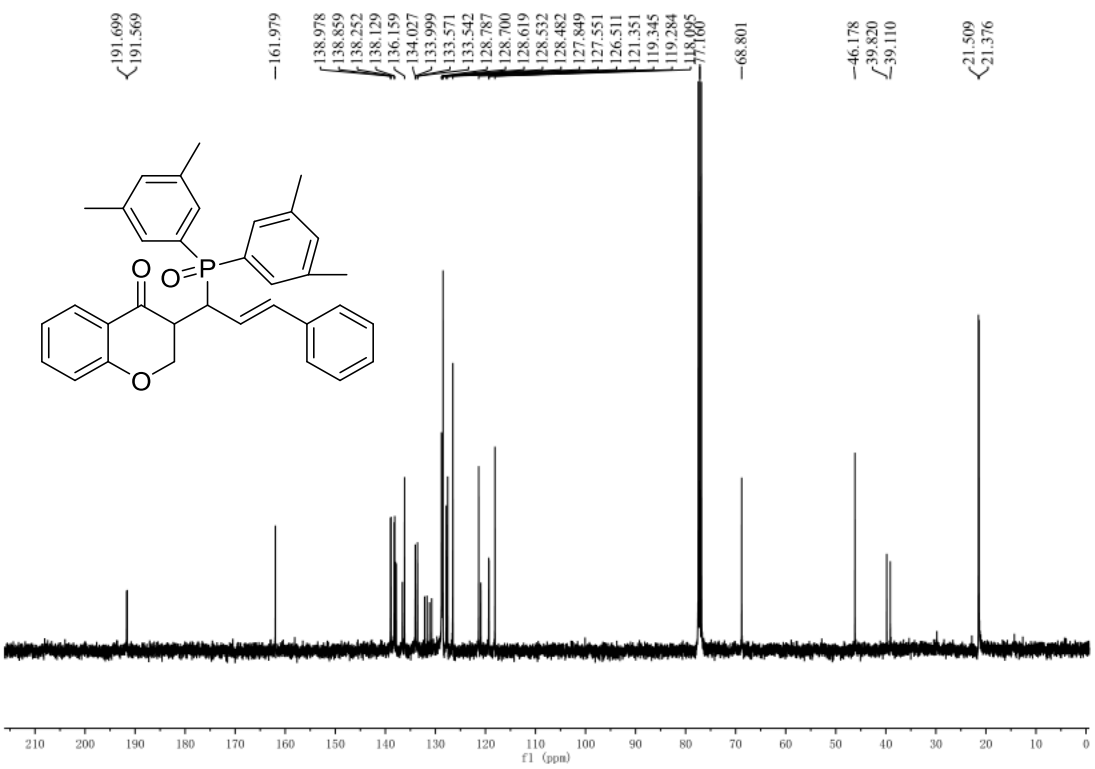

HO
O
P
O
f1 (ppm)

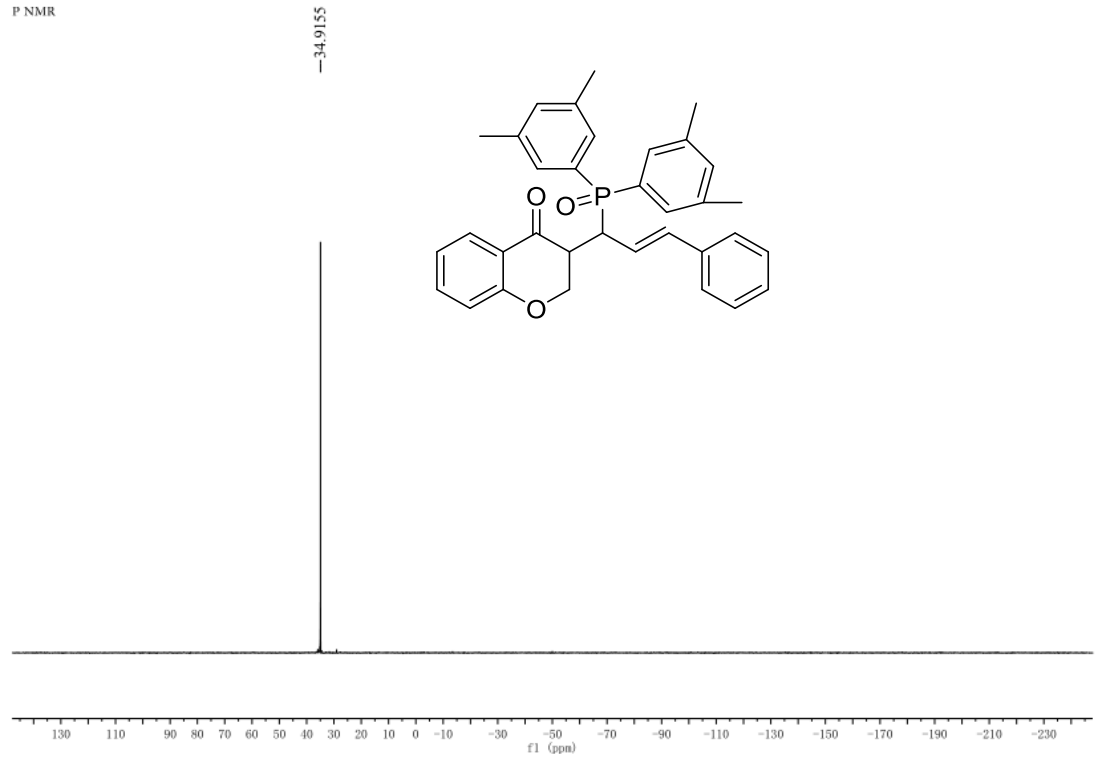

HO
O
P
O
f1 (ppm)



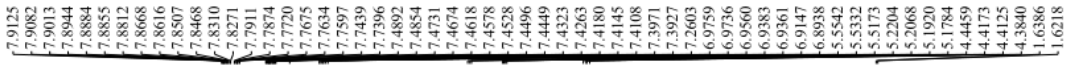
^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$), ^{31}P NMR (162 MHz, $CDCl_3$) of **3t**

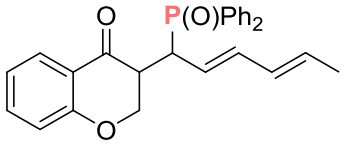


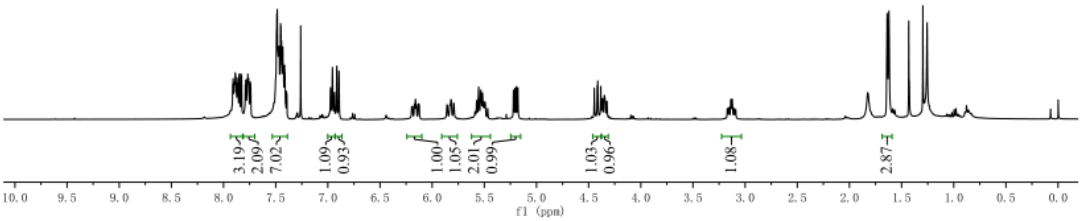


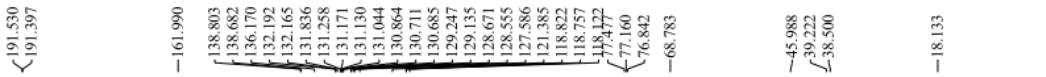


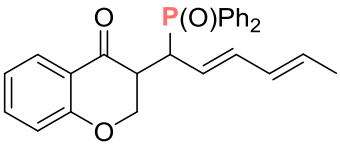
^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$), ^{31}P NMR (162 MHz, $CDCl_3$) of **3t'**

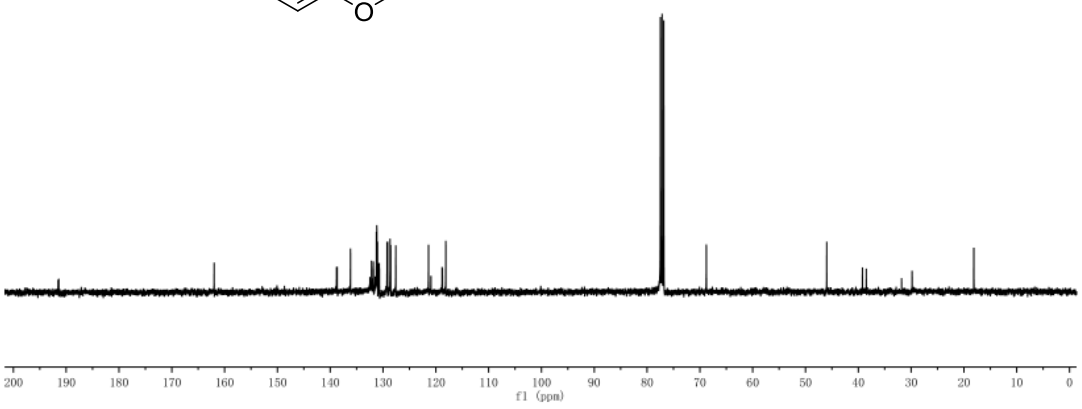

7.9125
7.9082
7.9013
7.8944
7.8884
7.8855
7.8812
7.8668
7.8616
7.8507
7.8468
7.8310
7.8271
7.7911
7.7874
7.7720
7.7675
7.7634
7.7597
7.7439
7.7396
7.4892
7.4854
7.4731
7.4674
7.4618
7.4578
7.4528
7.4496
7.4449
7.4323
7.4263
7.4180
7.4145
7.4108
7.3971
7.3927
7.2603
6.9759
6.9736
6.9560
6.9383
6.9361
6.9147
6.8938
5.5542
5.5332
5.5173
5.2204
5.2068
5.1920
5.1784
4.4459
4.4173
4.4125
4.3840
1.6386
1.6218

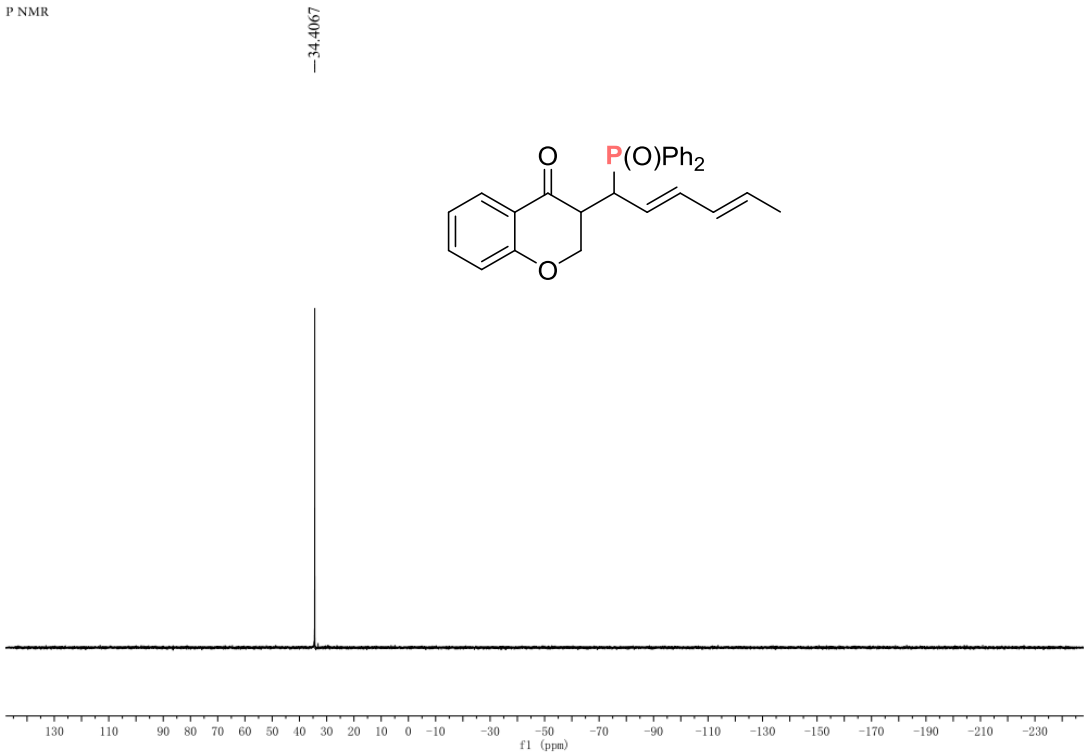

O
P(O)Ph2
O


3.19
2.09
7.02
1.09
0.93
1.00
1.05
2.01
0.99
1.03
0.96
1.08
2.87
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

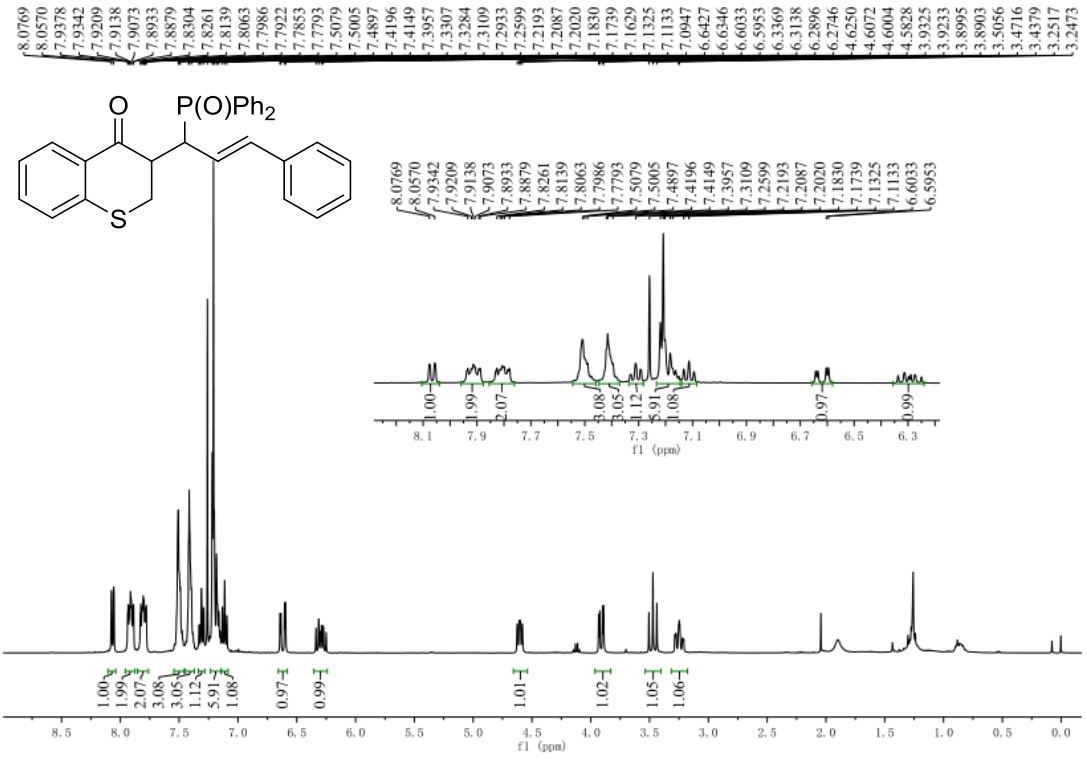

191.530
191.397
161.990
138.803
138.682
136.170
132.192
132.165
131.836
131.258
131.171
131.130
131.044
130.864
130.711
130.685
129.247
129.135
128.671
128.555
127.586
121.385
118.822
118.757
118.122
77.477
77.160
76.842
68.783
45.988
39.222
38.500
18.133

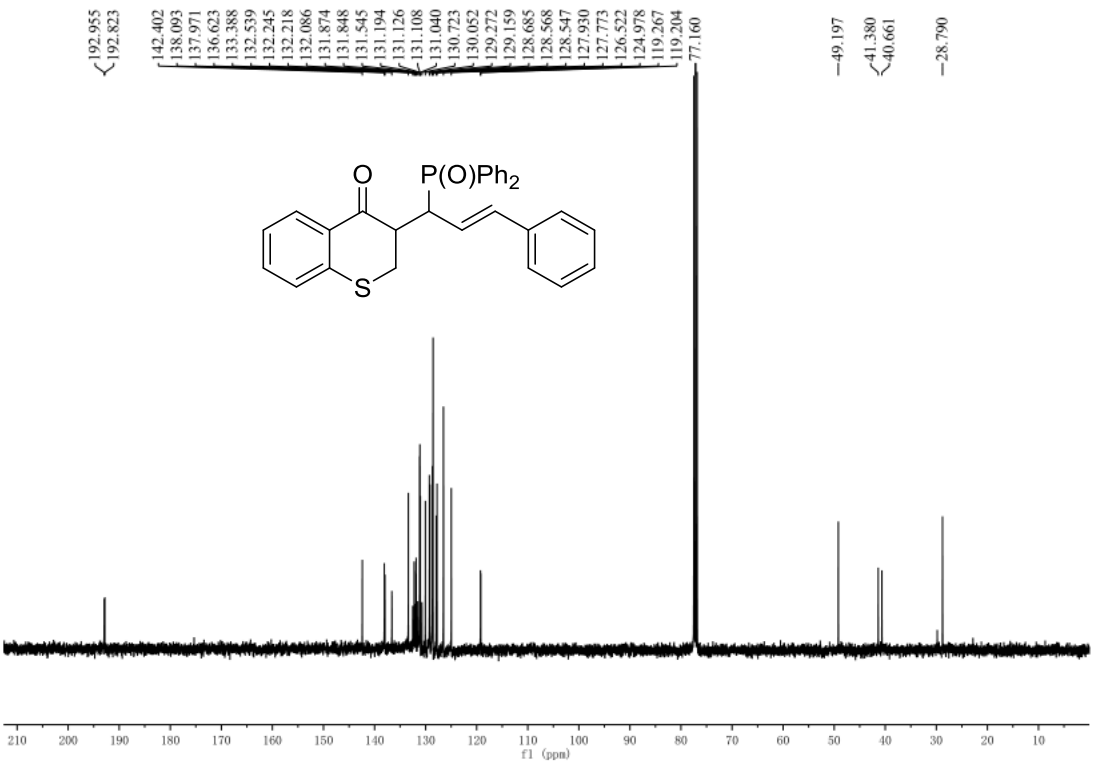

O
P(O)Ph2
O

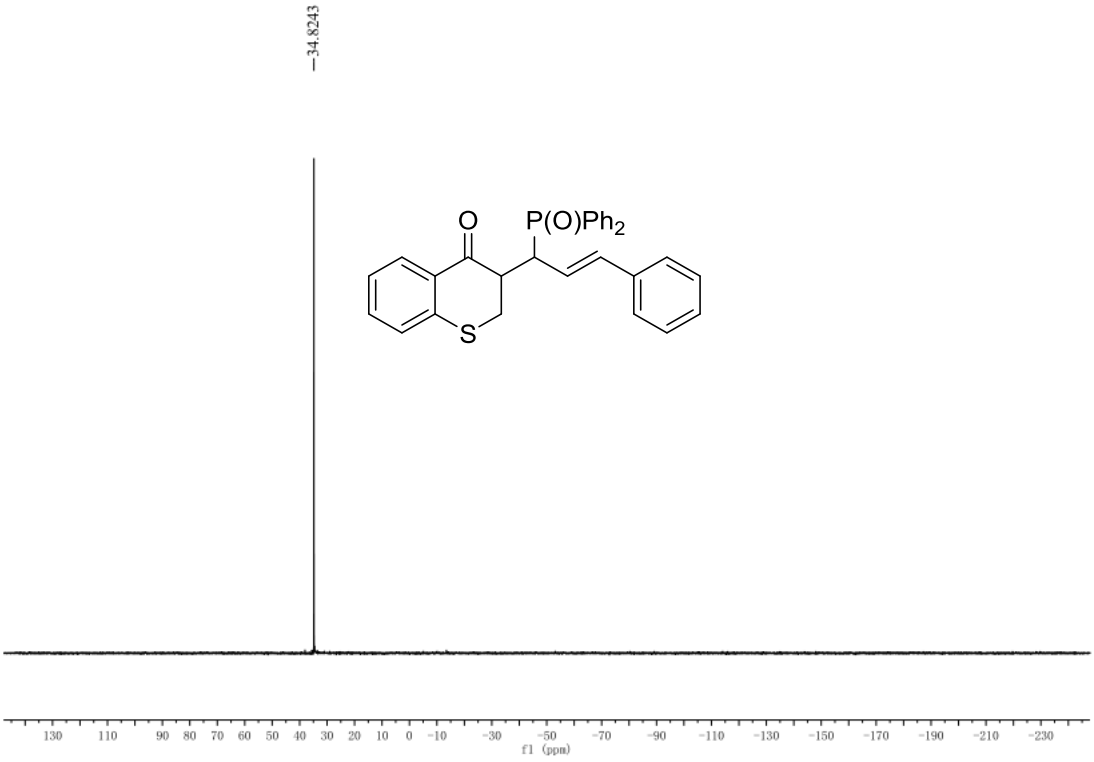

200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



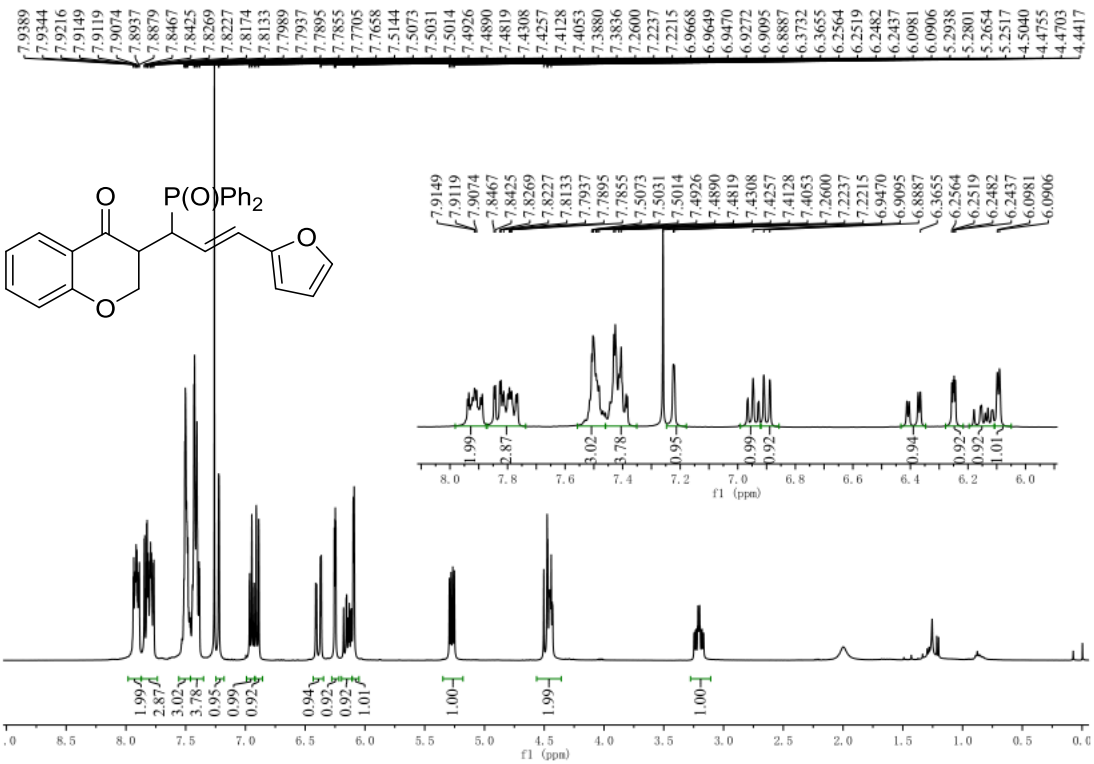
^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$), ^{31}P NMR (162 MHz, $CDCl_3$) of **3v'**

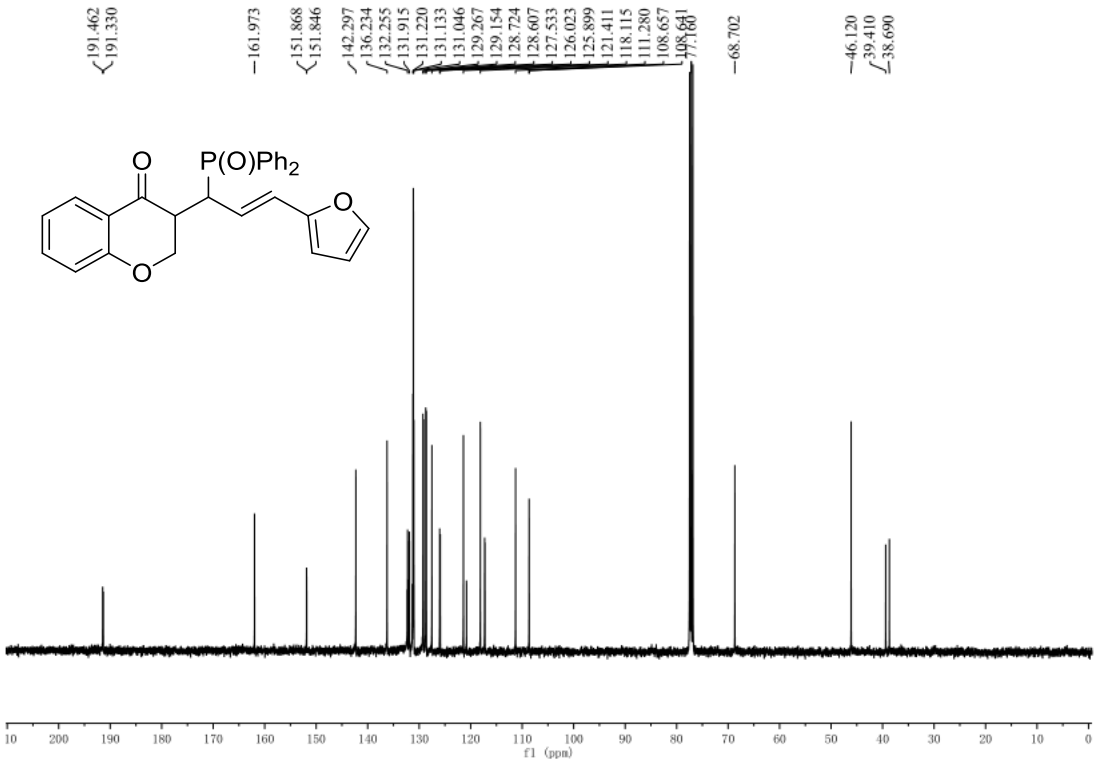


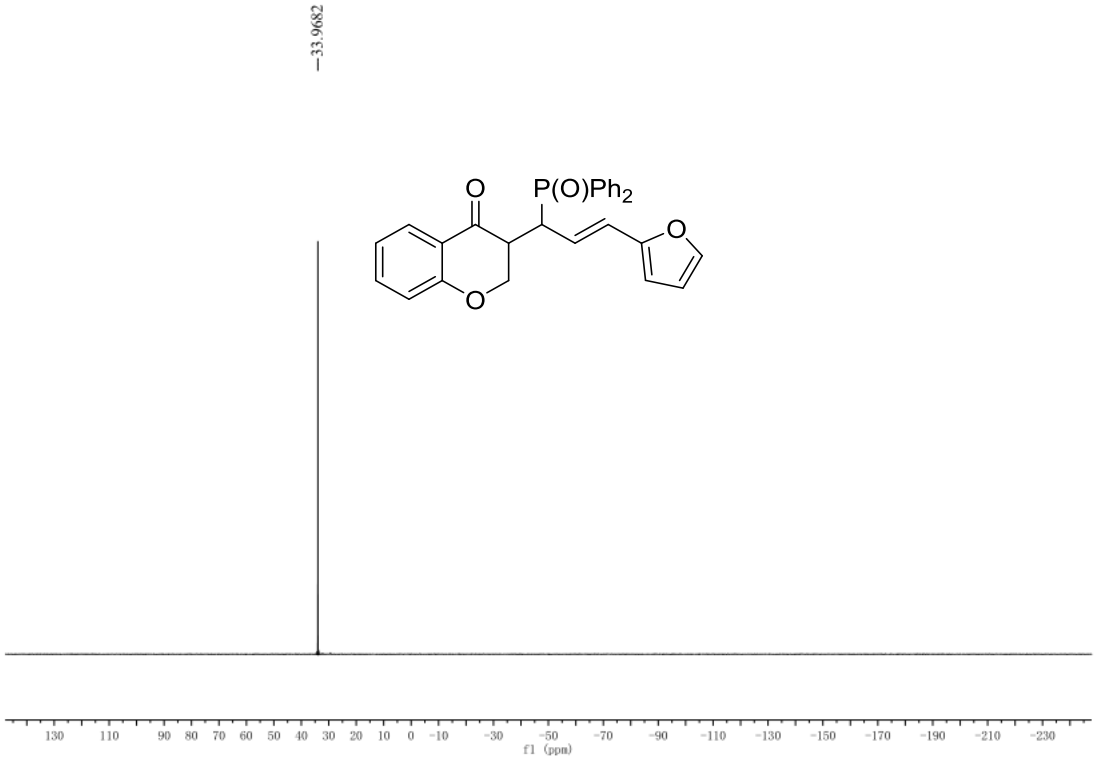




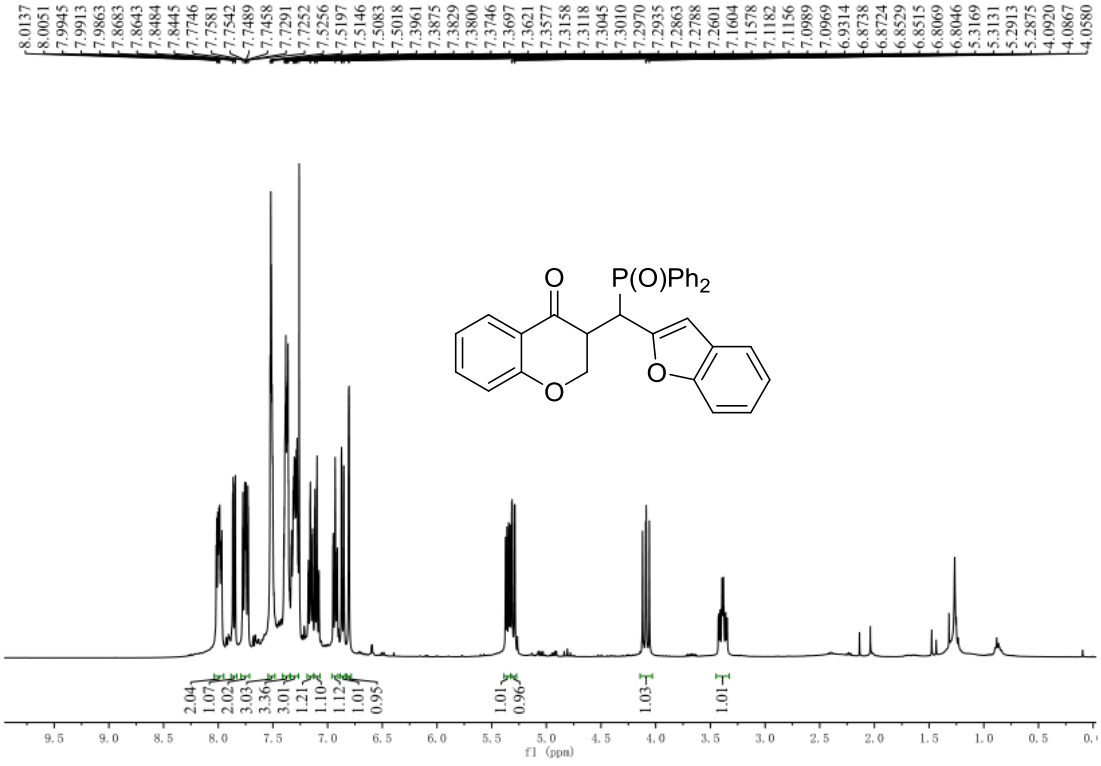
^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$), ^{31}P NMR (162 MHz, $CDCl_3$) of **3w'**

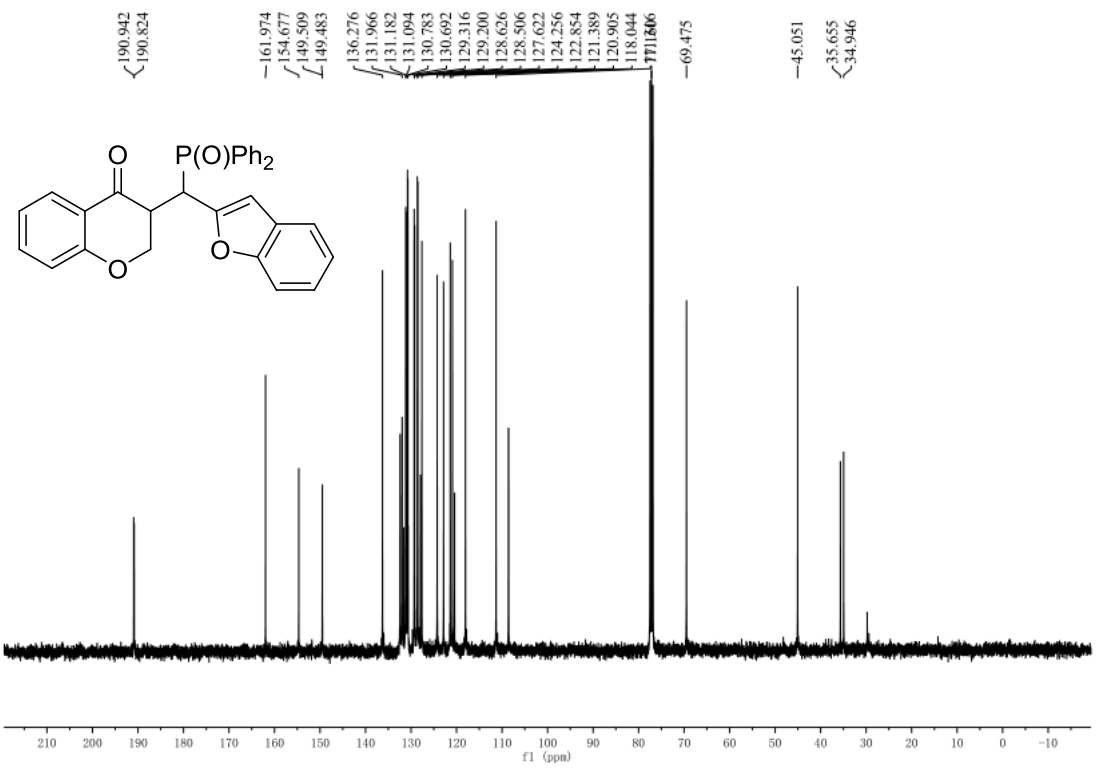

O
P(O)Ph2
O
O
f1 (ppm)

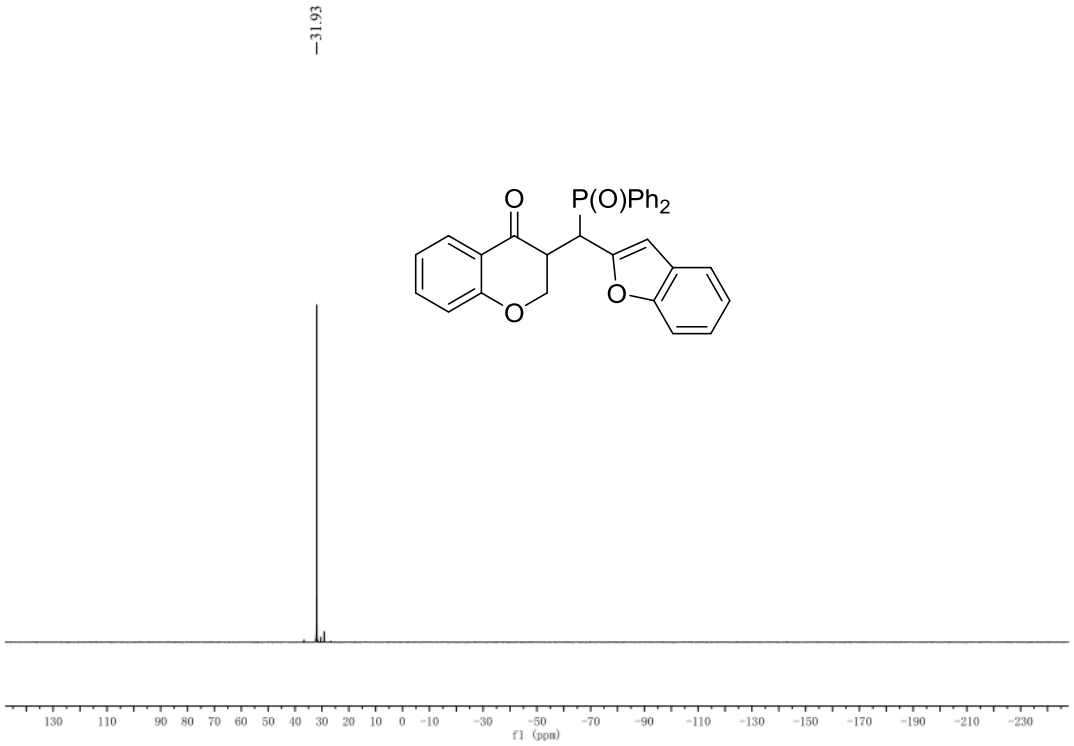

O
P(O)Ph2
O
O
f1 (ppm)



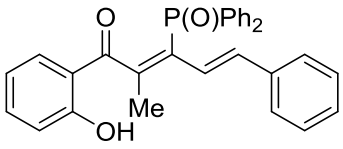
^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$), ^{31}P NMR (162 MHz, $CDCl_3$) of **3x'**



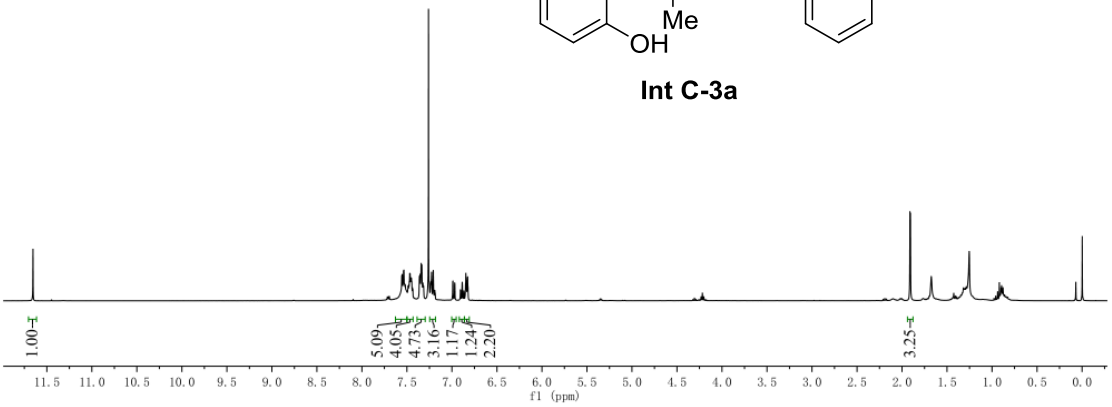


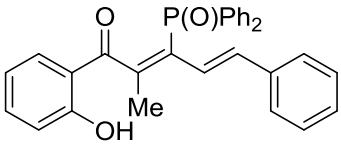


^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$), ^{31}P NMR (162 MHz, $CDCl_3$) of **3z'**

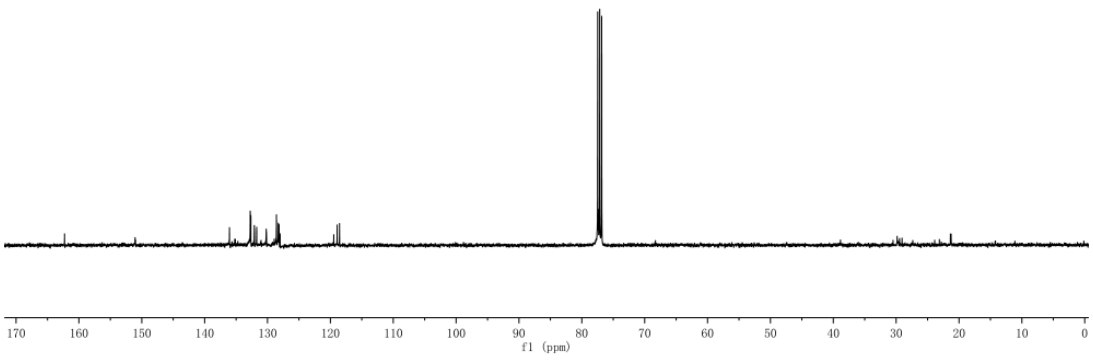


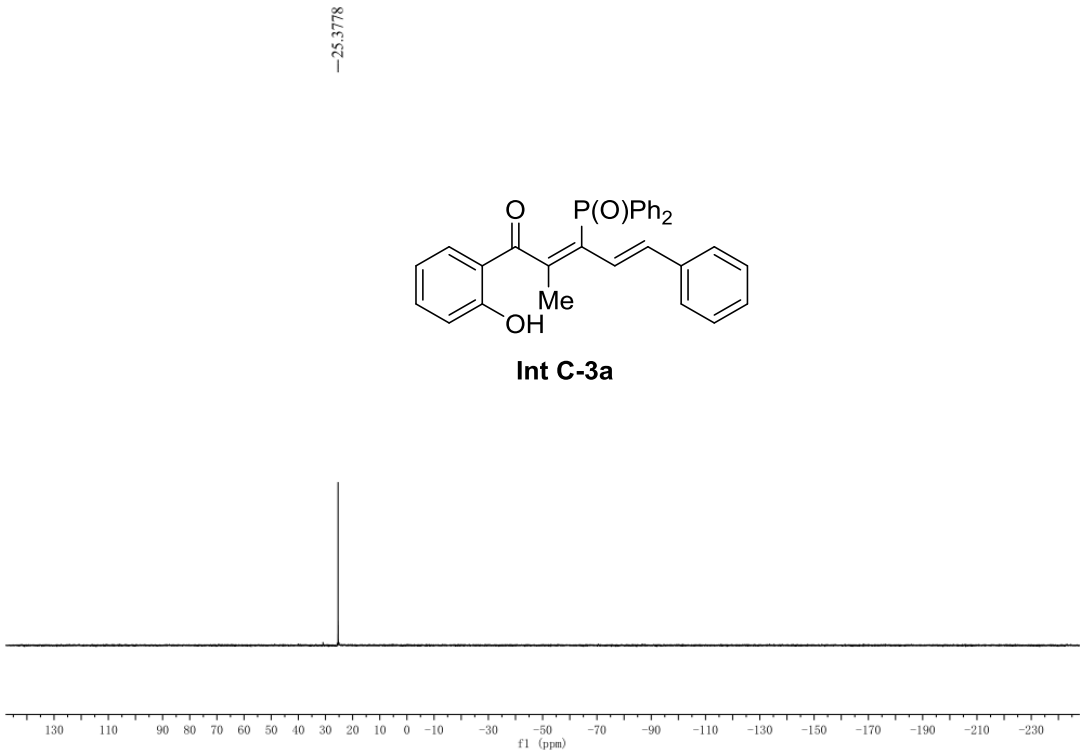
Int C-3a





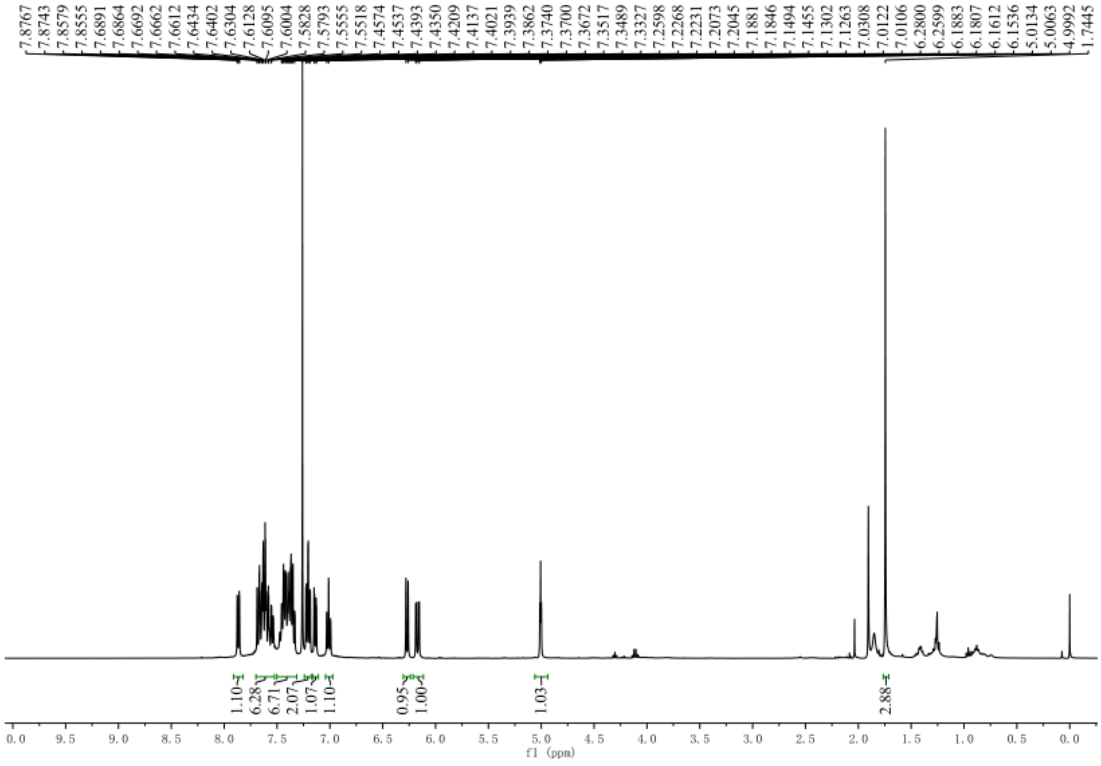
Int C-3a

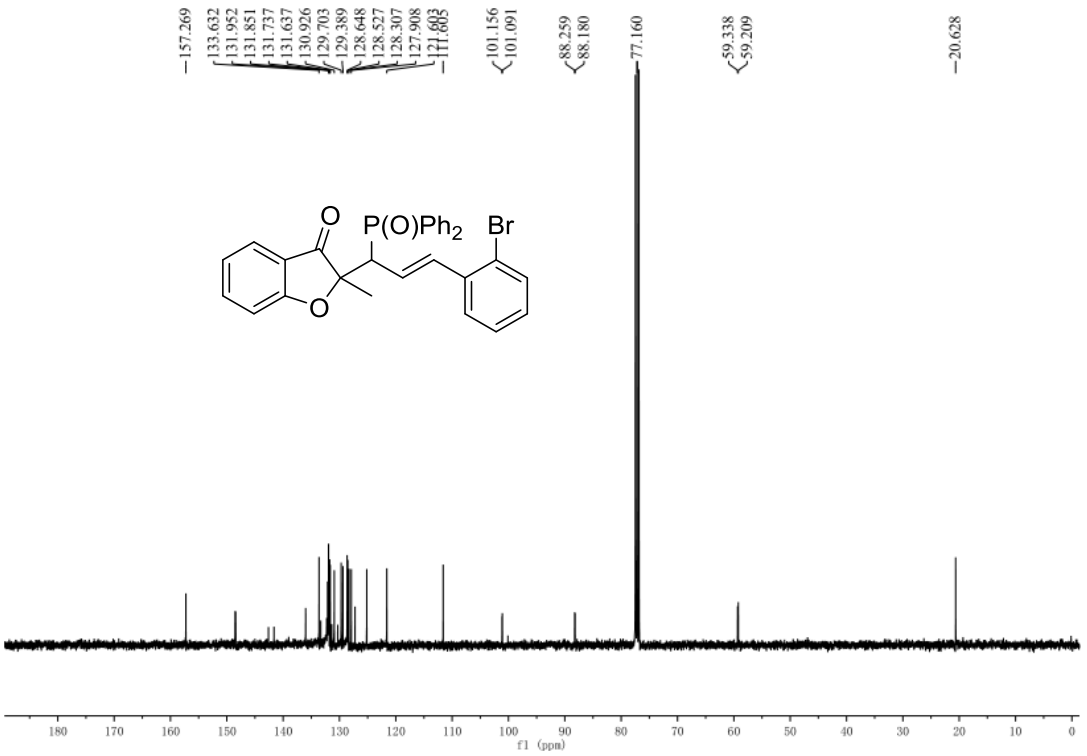


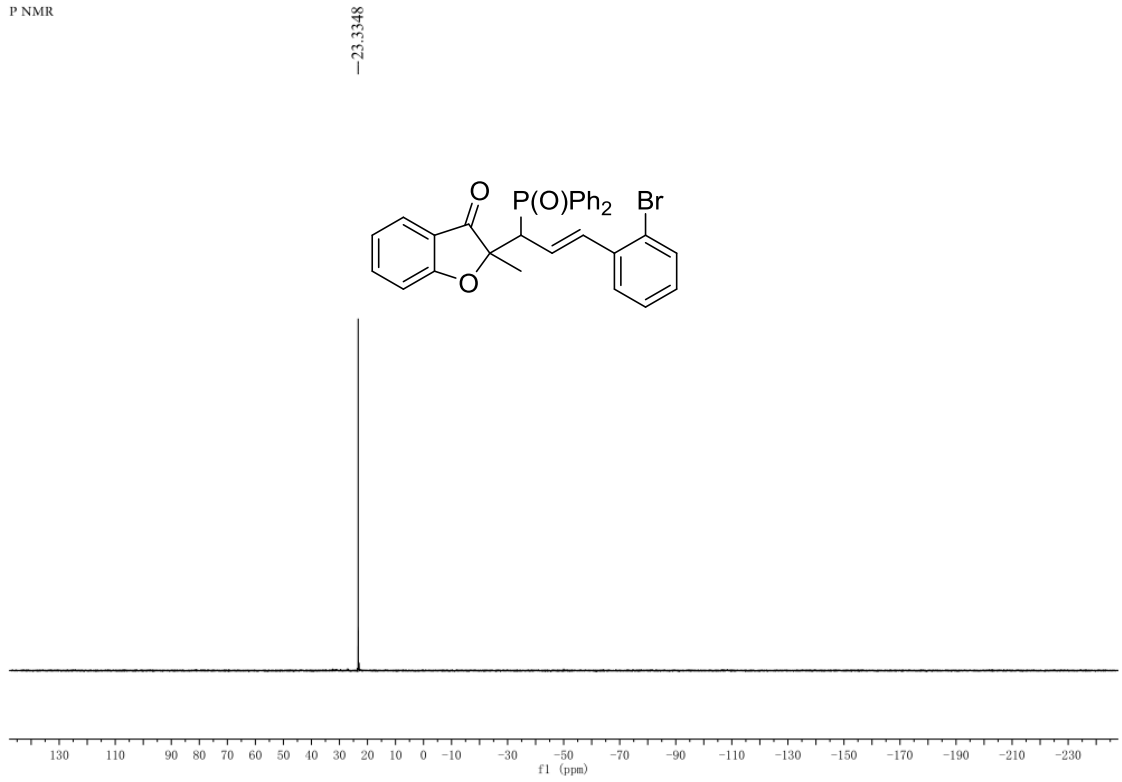


Int C-3a

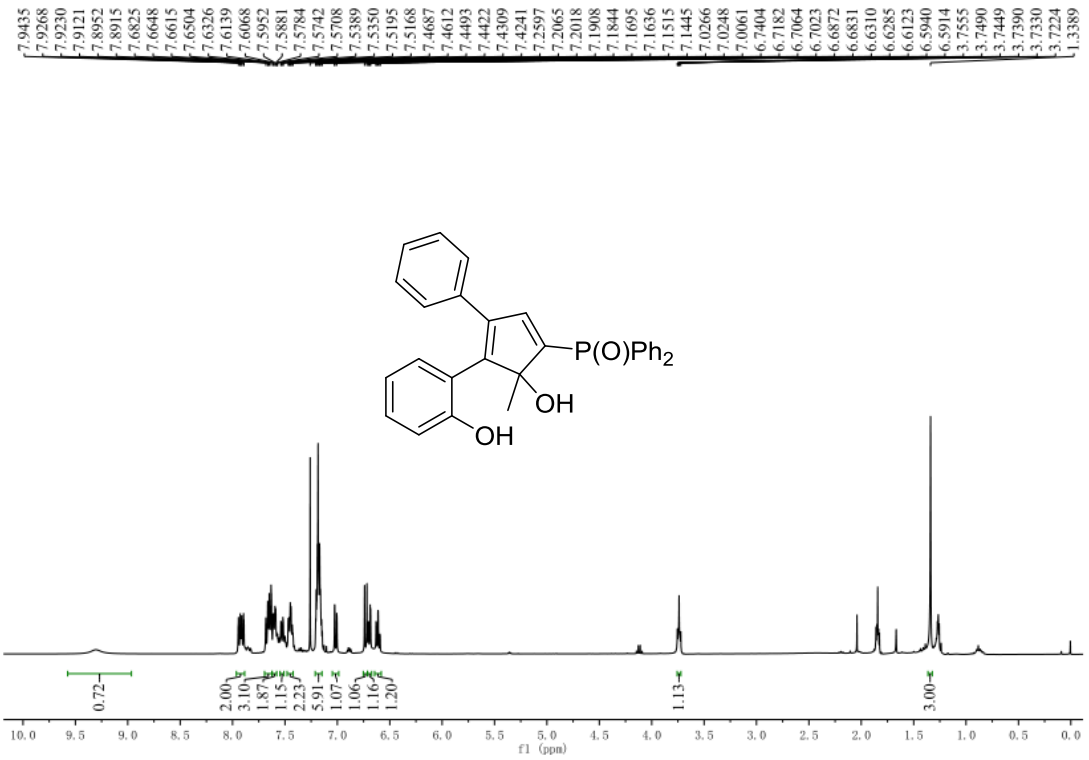
^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$), ^{31}P NMR (162 MHz, $CDCl_3$) of **Int C-3a**







^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$), ^{31}P NMR (162 MHz, $CDCl_3$) of **Int D-3n**


7.9435
7.9268
7.9230
7.9121
7.8952
7.8915
7.6825
7.6648
7.6615
7.6504
7.6326
7.6139
7.6068
7.5952
7.5881
7.5784
7.5742
7.5708
7.5389
7.5350
7.5195
7.5168
7.4687
7.4612
7.4493
7.4422
7.4309
7.4241
7.2597
7.2065
7.2018
7.1908
7.1844
7.1695
7.1636
7.1515
7.1445
7.0266
7.0248
7.0061
6.7404
6.7182
6.7064
6.7023
6.6872
6.6831
6.6310
6.6285
6.6123
6.5940
6.5914
3.7555
3.7490
3.7449
3.7390
3.7330
3.7224
1.3389
P(O)Ph2
OH
OH
0.72
2.00
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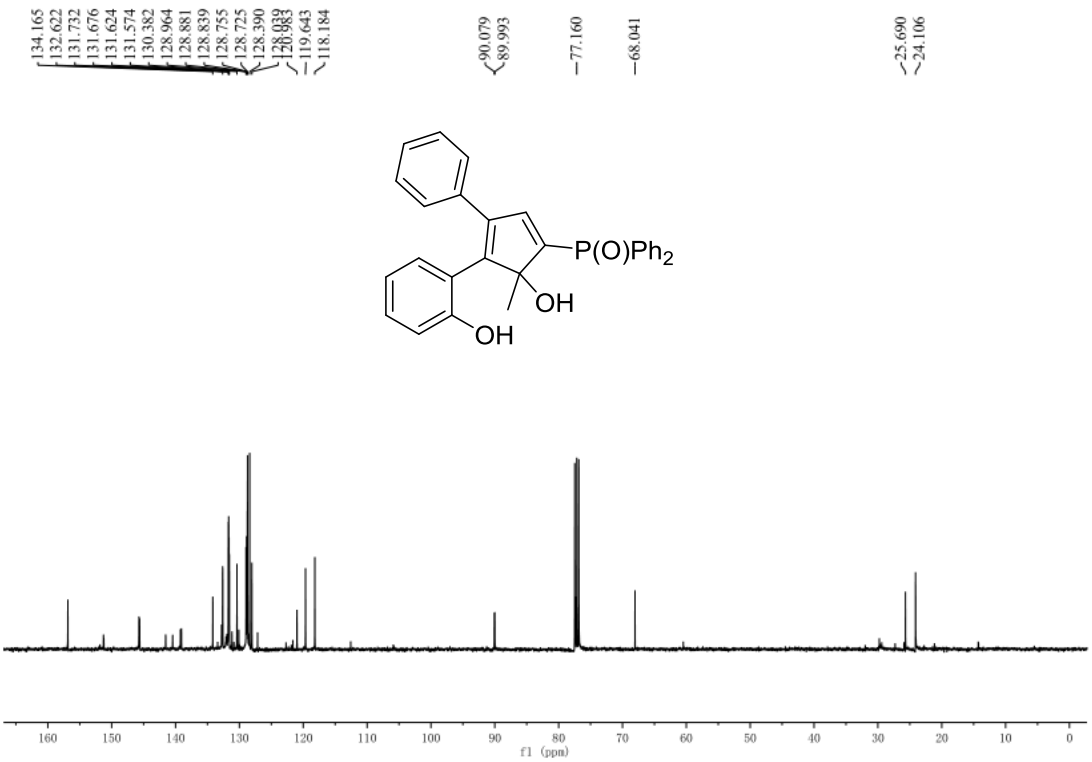
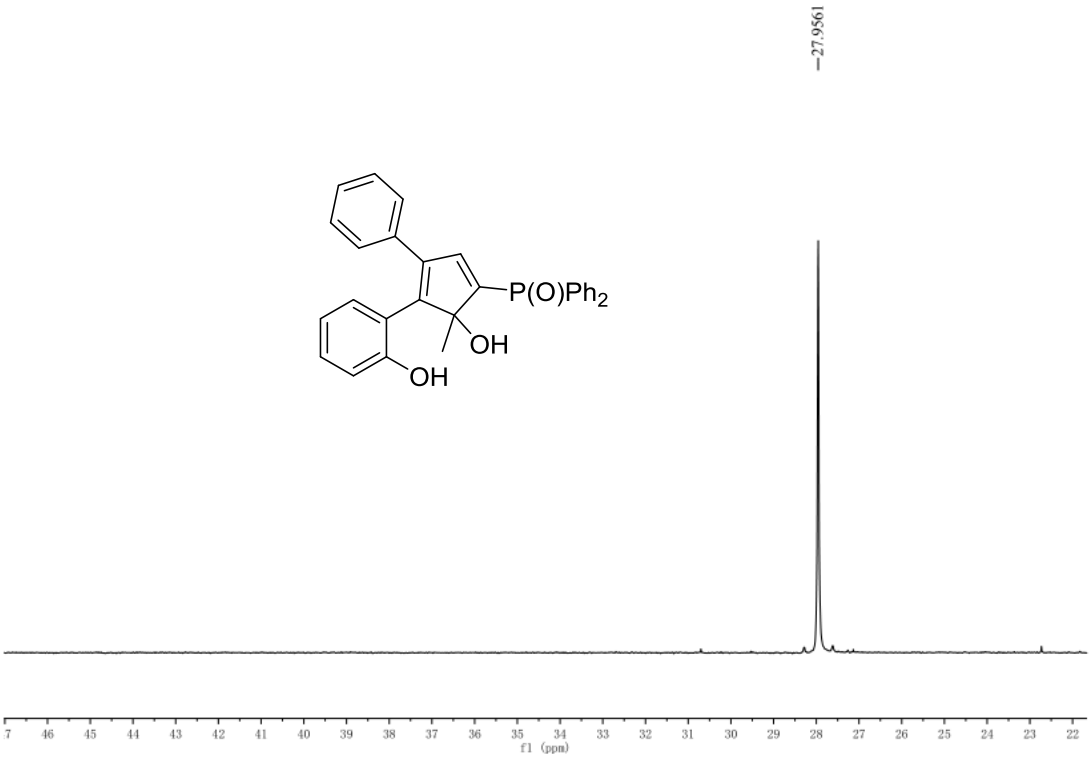
2.23
5.91
1.07
1.06
1.16
1.20
1.13
3.00
f1 (ppm)


134.165
132.622
131.732
131.676
131.624
131.574
130.382
128.964
128.881
128.839
128.755
128.725
128.390
120.983
119.643
118.184
90.079
89.993
77.160
68.041
25.690
24.106
P(O)Ph2
OH
OH
f1 (ppm)



^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$), ^{31}P NMR (162 MHz, $CDCl_3$) of **4**