Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Asymmetric Synthesis of Spiro-structural 2, 3-Dihydrobenzofurans via Bifunctional Phosphonium Salt-promoted [4 + 1] Cyclization of *ortho*-Quinone Methides with α-Bromoketones

Song Zhang,[‡a] Xiaojun Yu,[‡a,c] Jianke Pan,[a] Chunhui Jiang,*[a,b] Hongsu Zhang,[a] Tianli Wang*[a]

[a] *Key Laboratory of Green Chemistry & Technology of Ministry of Education, College of Chemistry, Sichuan University 29 Wangjiang Road, Chengdu 610064 P. R. China. E-mail: wangtl@scu.edu.cn*

[b] *School of Environmental and Chemical Engineering, Jiangsu University of Science and Technology, 2 Mengxi Road, Zhenjiang 212003 P. R. China. E-amil: chemjiang@just.edu.cn*

[c] *Department of Chemistry, School of Basic Medical Sciences, Southwest Medical University, Luzhou 646000, China*

‡ S. Zhang and X. Yu contributed equally.

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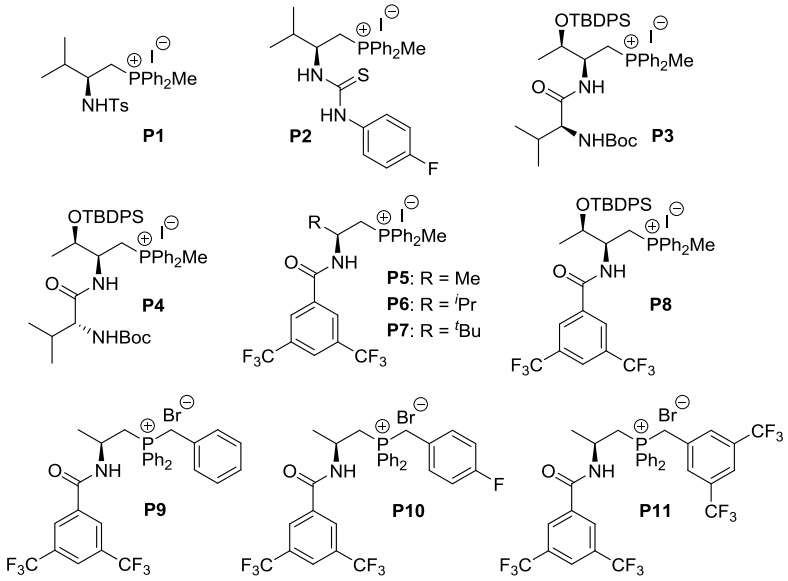
1. General Information

All the starting materials were obtained from commercial sources and used without further purification unless otherwise stated. ^{1}H and ^{13}C NMR spectra were recorded at ambient temperature in $CDCl_3$ on a Bruker Advance (400 MHz) spectrometer. The chemical shifts are reported in parts permillion (ppm) relative to $CDCl_3$(δ = 7.26) for ^{1}H NMR and relative to the central resonances of $CDCl_3$(δ = 77.16) for ^{13}C NMR; Multiplicity was indicated as follows: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), dd (doublet of doublet), dt (doublet of triplet), td (triplet of doublet), br s (broad singlet). Coupling constants (J) were reported in Hertz (Hz). All high resolution mass (ESI-MS) were obtained on Thermo LTQ mass spectrometer. For thin layer chromatography (TLC) was performed using commercially prepared 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 commercially prepared 200-300 mesh silicagel. Enantiomeric excess was determined by HPLC analysis using chiral column described below in detail. Optical rotations were measured with RUDOLPH research analytic automatic polarimeter.

The catalysts **P1-P7** used in this study were prepared following previously reported procedure.[1-4] All *ortho*-quinone methides were synthesized following the methods reported in the literature.[5] Except for α-bromoketones **2q** and **2t** were purchased and used without further purification, other α-bromoketones were synthesized following the methods reported in the literature.[6] The absolute configurations of cycloaddition products were assigned by X-ray crystallographic analysis of the single crystal of **3m** (Figure *S2*).

2. Optimization of Reaction Conditions

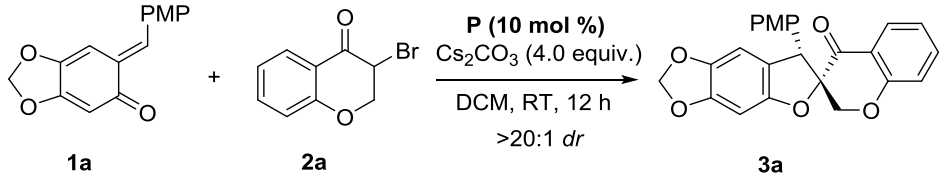


Scheme S1: Chiral phosphonium salt catalysts used in this study.

(TBDPS = *tert*-butyldiphenylsilyl, Ts = 4-toluenesulfonyl)

A. Optimization of reaction conditions for the asymmetric [4 + 1] cycloaddition of *ortho*-quinone methides with α-bromoketones

Table S1**:** Asymmetric [4+1] cycloaddition of *ortho*-quinone methide **1a** with α-bromoketone **2a** catalyzed by different chiral phosphonium salts in DCM.[a]

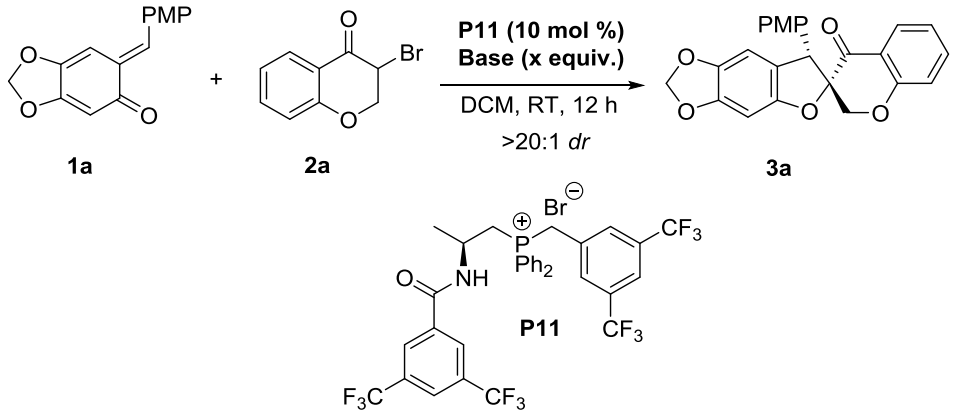


Entry	Catalyst	Base (equiv.)	Yield (%)[b]	Ee (%)[c]
1	**P1**	Cs_2CO_3 (4.0)	52	2
2	**P2**	Cs_2CO_3 (4.0)	n.r	-
3	**P3**	Cs_2CO_3 (4.0)	63	-3
4	**P4**	Cs_2CO_3 (4.0)	65	-4
5	**P5**	Cs_2CO_3 (4.0)	72	30
6	**P6**	Cs_2CO_3 (4.0)	68	9

7	**P7**	Cs_2CO_3 (4.0)	64	7
8	**P8**	Cs_2CO_3 (4.0)	69	11
9	**P9**	Cs_2CO_3 (4.0)	71	65
10	**P10**	Cs_2CO_3 (4.0)	53	67
11	**P11**	Cs_2CO_3 (4.0)	78	79

[a] Reaction conditions: **1a** (0.1 mmol), **2a** (0.12 mmol), **P** (0.01 mmol), Cs_2CO_3 (4.0 equiv.), DCM (1.0 mL) were stirred for 12 h at room temperature. [b] Isolated yield. [c] Determined by HPLC analysis on a chiral stationary phase.

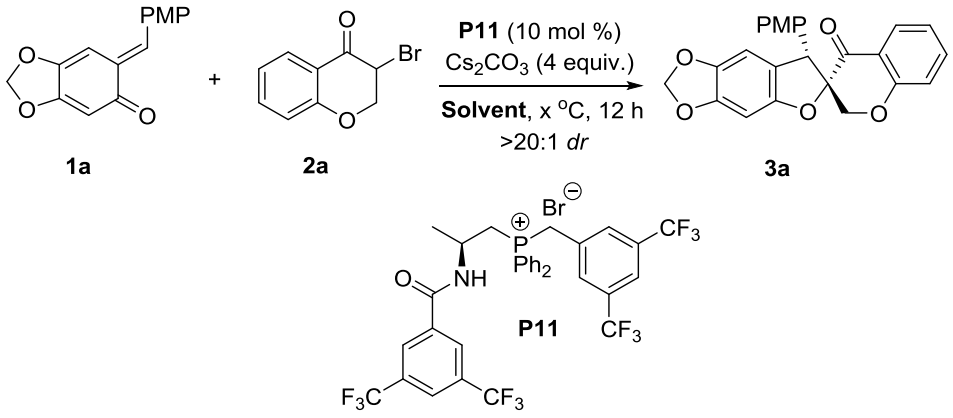
***Table S2*:** Asymmetric [4+1] cycloaddition of *ortho*-quinone methide **1a** with α-bromoketone **2a** catalyzed by **P11** in DCM: screening of the bases.[a]



Entry	Base (x equiv.)	*t* [h]	Yield [%][b]	*ee* [%][c]
1	Na_2CO_3 (4.0)	12	n.r	-
2	K_2CO_3 (4.0)	12	38	78
3	K_3PO_4 (4.0)	12	43	80
4	$K_3PO_4.3H_2O$ (4.0)	12	47	78
5	$K_3PO_4.7H_2O$ (4.0)	12	36	74
6	KOH (4.0)	12	74	2
7	CsOH (4.0)	12	73	-3
8	Cs_2CO_3 (1.0)	12	54	77
9	Cs_2CO_3 (2.0)	12	67	76
10	Cs_2CO_3 (6.0)	12	77	74
11	Cs_2CO_3 (8.0)	12	78	78

[a] Reaction conditions: **1a** (0.1 mmol), **2a** (0.12 mmol), **P11** (0.01 mmol), Base (x equiv.) in DCM (1.0 mL) were stirred for 12 h at room temperature. [b] Isolated yield. [c] Determined by HPLC analysis on a chiral stationary phase.

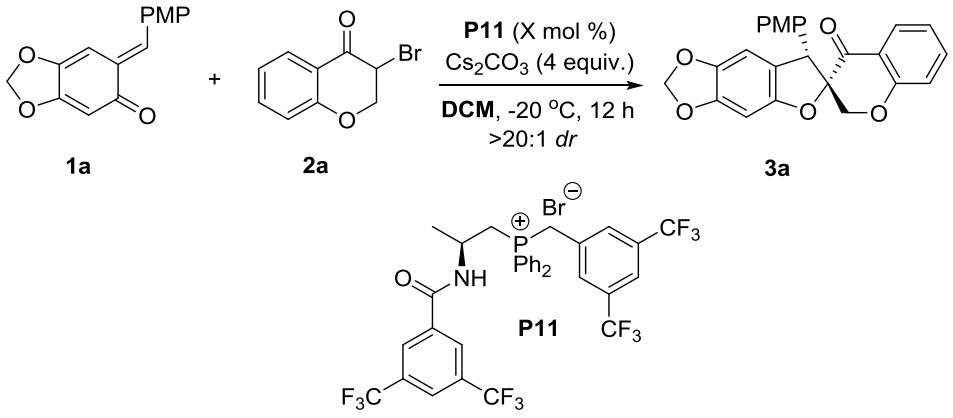
***Table S3*:** Asymmetric [4+1] cycloaddition of *ortho*-quinone methide **1a** with α-bromoketone **2a** catalyzed by **P11**: screening solvents and temperature.[a]



Entry	Temperature (°C)	Solvent	*t* [h]	Yield [%][b]	*ee* [%][c]
1	r.t	DCE	12	71	40
2	r.t	$CHCl_3$	12	72	74
3	r.t	PE	12	28	24
4	r.t	n-Hexane	12	23	18
5	r.t	$(Et)_2O$	12	58	70
6	r.t	Dioxane	12	69	40
7	r.t	Toluene	12	74	64
8	r.t	Xylene	12	70	65
9	0	DCM	24	82	87
10	-10	DCM	24	80	90
11	-20	DCM	48	87	94
12	-30	DCM	56	68	87

[a] Reaction conditions: **1a** (0.1 mmol), **2a** (0.12 mmol), **P11** (0.01 mmol), Cs_2CO_3 (4.0 equiv.) in solvent (1.0 mL) were stirred for 12 h. [b] Isolated yield. [c] Determined by HPLC analysis on a chiral stationary phase.

***Table S4*:** Asymmetric [4+1] cycloaddition of *ortho*-quinone methide **1a** with α-bromoketone **2a** catalyzed by **P11**: screening catalyst loading.[a]

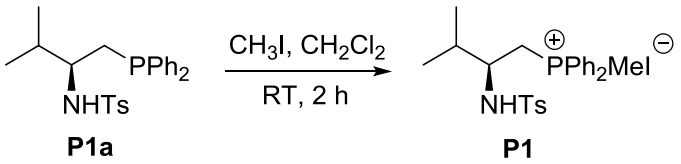


Entry	Catalyst(X mol %)	*t* [h]	Yield [%][b]	*ee* [%][c]
1	2.5%	48	85	82
2	5%	48	86	94
3	10%	48	87	94

[a] Reaction conditions: **1a** (0.1 mmol), **2a** (0.12 mmol), **P11** (0.01 mmol), Cs_2CO_3 (4.0 equiv.) in solvent (1.0 mL) were stirred for 12 h. [b] Isolated yield. [c] Determined by HPLC analysis on a chiral stationary phase.

3. Preparation of Catalysts

A. General procedure for preparation of P1-8:

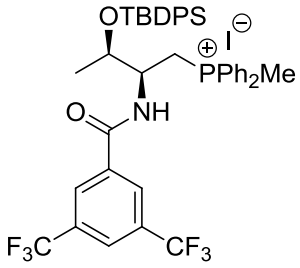


To a solution of phosphine **P1a** (0.1 mmol) in CH_2Cl_2 (1 mL) the methyl iodide solution (0.2 mL, 2.0 M in CH_2Cl_2) was slowly added and the mixture was allowed to

stir at room temperature for 2 h. The reaction crude mixture was directly purified by flash chromatography dichloromethane/methanol = 20/1 to afford the desired chiral phosphonium salt **P1** as a yellow solid (93% yield). Other phosphonium salts **P2**, **P3**, **P4**, **P5**, **P6**, **P7** and **P8** were prepared according to the above similar procedure by using the corresponding phosphines as reactants respectively.[2] Furthermore, the phosphonium salts **P9**, **P10** and **P11** were synthesized following the above similar procedure just by using corresponding phosphines and benzyl bromides as starting reagents.

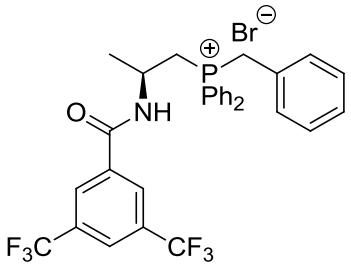
The catalyst **P1**, **P2**, **P3**, **P4**, **P5**, **P6** and **P7** are known compounds and their characterization data were in agreement with those reported in the literature[2-4], Unknown compounds **P8**, **P9**, **P10** and **P11** were fully characterized.

((2S,3R)-2-(3,5-bis(trifluoromethyl)benzamido)-3-((tert-butyldiphenylsilyl)oxy)butyl)(methyl)diphenylphosphonium iodide (P8)



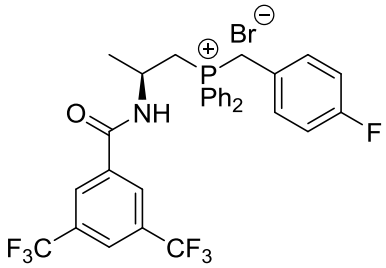
A yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.73 (dd, *J* = 16.4, 6.4 Hz, 1H), 8.41 (d, *J* = 6.3 Hz, 1H), 7.92 (d, *J* = 3.2 Hz, 1H),7.87 (dd, *J* = 13.1, 8.1 Hz, 2H), 7.78–7.71 (m, 2H), 7.62 (d, *J* = 7.1 Hz, 2H), 7.57 (d, *J* = 8.0 Hz, 2H), 7.52-7.48 (m, 4H), 7.42–7.31 (m, 6H), 4.88-4.82 (m, 2H), 4.27–4.24 (m, 1H), 3.22 (t, *J* = 15.1 Hz, 1H), 2.65 (d, *J* = 13.8 Hz, 3H), 1.29 (t, *J* = 5.5 Hz, 3H), 1.07 (d, *J* = 2.4 Hz, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.31 (d, *J* = 3.9 Hz), 135.74 (d, *J* = 10.1 Hz), 134.93 (dd, *J* = 17.3, 2.9 Hz), 134.51 (d, *J* = 1.8 Hz), 133.28 (d, *J* = 7.3 Hz), 132.60 (t, *J* = 9.8 Hz), 131.69 (dd, *J* = 33.7, 4.3 Hz), 130.34 (t, *J* = 12.3 Hz), 130.13 (d, *J* = 4.1 Hz), 128.72 (d, *J* = 2.2 Hz), 127.95 (d, *J* = 12.2 Hz), 125.3 (d, *J* = 7.9 Hz), 123.04 (q, *J* = 218.8 Hz), 70.47 (d, *J* = 13.3 Hz), 50.05 (d, *J* = 4.8 Hz), 27.16, 19.37, 18.45, 9.12, 8.58. ^{31}P NMR (162 MHz, $CDCl_3$) δ 22.93; HRMS (ESI) *m/z* calcd for $C_{42}H_{43}F_6NO_2PSi$ $[M - I]^+$ = 766.2699, found = 766.2695.

(S)-benzyl(2-(3,5-bis(trifluoromethyl)benzamido)propyl)diphenylphosphonium bromide (P9)



A white solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.38 (dd, *J* = 19.4, 8.2 Hz, 1H), 8.27 (d, *J* = 10.7 Hz, 2H), 7.87-7.82 (m, 3H), 7.62–7.56 (m, 2H), 7.49 (t, *J* = 7.7 Hz, 1H), 7.46 – 7.29 (m, 6H), 7.42-7.32 (m, 5H), 7.19-7.06 (m, 3H),6.91 (t, *J* = 6.8 Hz, 2H), 4.88 (s, 1H), 4.74 (dd, *J* = 14.8, 6.1 Hz, 2H), 4.59–4.46 (m, 2H), 2.98 (t, *J* = 13.8 Hz, 1H), 1.58 (t, *J* = 6.3 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.54 (d, *J* = 5.8 Hz), 134.60 (d, *J* = 1.3 Hz), 134.23, 133.51 (dd, *J* = 29.4, 9.3 Hz), 131.19 (dd, *J* = 33.5, 6.9 Hz), 130.34 (d, *J* = 5.1 Hz), 129.76 (dd, *J* = 12.3, 3.7 Hz), 129.17 (t, *J* = 3.4 Hz), 128.62 (d, *J* = 3.8 Hz), 128.39, 127.13, 126.91 (d, *J* = 8.2 Hz), 124.65 (d, *J* = 3.0 Hz), 123.06 (d, *J* = 271.4 Hz), 117.71 (q, *J* = 81.3 Hz), 41.36 (t, *J* = 4.7 Hz), 29.22 (dd, *J* = 45.5, 5.7 Hz), 25.95 (dd, *J* = 47.7, 10.3 Hz), 23.14 (d, *J* = 14.8 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 22.25; HRMS (ESI) *m/z* calcd for $C_{31}H_{27}F_6NOP$ $[M - Br]^+$ = 574.1729, found = 574.1728.

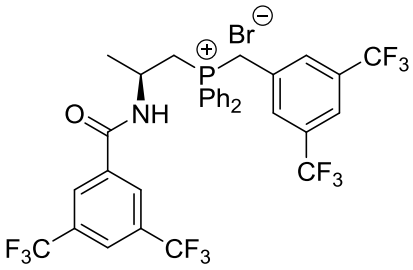
(S)-(2-(3,5-bis(trifluoromethyl)benzamido)propyl)(4-fluorobenzyl)diphenylphosphonium bromide (P10)



A white solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.36 (d, *J* = 7.9 Hz, 1H), 8.30 (s, 2H), 7.87–7.81 (m, 3H), 7.68 (dd, *J* = 12.2, 7.6 Hz, 2H), 7.53 (t, *J* = 7.1 Hz, 1H), 7.45 (td, *J* = 7.6, 3.3 Hz, 2H), 7.39 (d, *J* = 1.9 Hz, 3H), 6.95-6.92 (m, 2H), 6.78 (t, *J* = 8.4 Hz, 2H), 5.00 (t, *J* = 14.9 Hz, 1H), 4.91-4.77 (m, 2H), 4.70-4.60 (m, 1H), 3.09 (t, *J* = 13.9 Hz, 1H), 1.63 (dd, *J* = 6.2, 2.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.72, 134.67, 134.61 (dd, *J* = 33.5, 3.0 Hz), 133.69 (dd, *J* = 15.5, 9.4 Hz), 132.25 (dd, *J* =

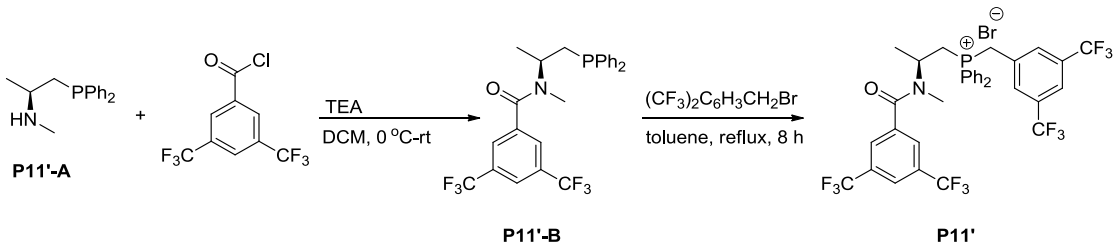
8.1, 5.5 Hz), 131.40 (d, *J* = 33.6 Hz), 129.96 (dd, *J* = 12.3, 5.3 Hz), 128.45 (d, *J* = 2.7 Hz), 124.85 (t, *J* = 3.6 Hz), 123.2 (d, *J* = 271.3 Hz), 122.87 (dd, *J* = 8.3, 3.3 Hz), 117.6 (q, *J* = 72.5 Hz), 116.29 (dd, *J* = 21.6, 3.1 Hz), 41.84 (d, *J* = 5.1 Hz), 28.57 (d, *J* = 46.2 Hz), 26.03 (d, *J* = 49.7 Hz), 23.13 (d, *J* = 15.0 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 22.60; HRMS (ESI) *m/z* calcd for $C_{31}H_{26}F_7NOP$ $[M - Br]^+$ = 592.1635, found = 592.1634.

(S)-(2-(3,5-bis(trifluoromethyl)benzamido)propyl)(3,5-bis(trifluoromethyl)benzyl)diphenylphosphonium bromide (P11)



A white solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.24 (d, *J* = 8.2 Hz, 1H), 8.23 (s, 1H), 7.98–7.89 (m, 2H), 7.85 (s, 1H), 7.74 (dd, *J* = 12.3, 7.7 Hz, 2H), 7.58 (s, 1H), 7.53 (t, *J* = 7.3 Hz, 1H), 7.48 – 7.38 (m, 2H), 7.35 (s, 2H), 5.49 (t, *J* = 15.0 Hz, 1H), 5.28 (t, *J* = 15.3 Hz, 1H), 4.83 (t, *J* = 7.1 Hz, 1H), 4.52-4.38 (m, 1H), 3.70 (t, *J* = 14.1 Hz, 1H), 2.75 (s, 1H), 1.64 (d, *J* = 4.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.75, 135.04 (d, *J* = 2.7 Hz), 134.73 (d, *J* = 3.8 Hz), 133.85 (dd, *J* = 28.1, 9.7 Hz), 132.11 (dd, *J* = 33.6, 3.0 Hz), 131.41 (q, *J* = 25.2 Hz), 130.62 (d, *J* = 2.3 Hz), 130.04 (dd, *J* = 12.5, 6.8 Hz), 128.33 (d, *J* = 1.9 Hz), 126.89 (d, *J* = 56.1 Hz), 124.79 (t, *J* = 3.7 Hz), 122.82 (q, *J* = 56.0 Hz), 122.06 (d, *J* = 3.3 Hz), 118.75 (d, *J* = 56.2 Hz), 116.36 (q, *J* = 77.2 Hz), 41.87 (d, *J* = 5.2 Hz), 29.24 (d, J = 46.1 Hz), 27.51 (d, J = 48.6 Hz), 22.93 (d, *J* = 15.3 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 24.89; HRMS (ESI) *m/z* calcd for $C_{33}H_{25}F_{12}NOP$ $[M - Br]^+$ = 710.1477, found = 710.1474.

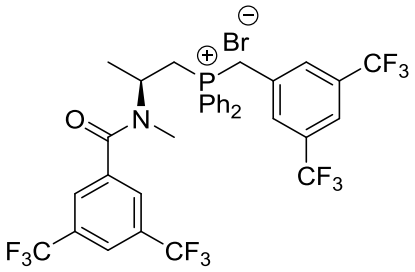
B. Preparation of phosphonium salts P11'



To the solution of **P11'-A**[7] (102.9 mg, 0.4 mmol) in DCM (5 mL), 3,5-bis(trifluoromethyl)benzoyl chloride (132.7 mg, 0.48 mmol) dissolved in DCM (2 mL) was added in at 0 ^{o}C, after that the resulting mixture was warmed to room temperature and stired for 1 h. Water (2 mL) was added and the organic layer was separated. The aqueous phase was extracted with DCM. The combined organic layers was washed with brine and dried over Na_2SO_4. Solvent was removed under reduced pressure and the residue was purified column chromatography on silica gel using petrolem ether/ethyl acetate (10:1) as an eluent to afford **P11'-B** (108.1 mg, 54% yield) as a white solid.

To the solution of **P11'-B** (49.7 mg, 0.1 mmol) in toluene (3 mL), 3,5-di(trifluoromethyl)benzyl bromide (37.0 mg, 0.12 mmol) was directly added in, then the solution was refluxed for 8 h. The resulting solution was cooled to room temperature and the solvent was removed under reduced pressure. The residue was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 1:1 to methanol) to afford the desired chiral phosphonium salt **P11'** (52.1 mg, 72% yield).

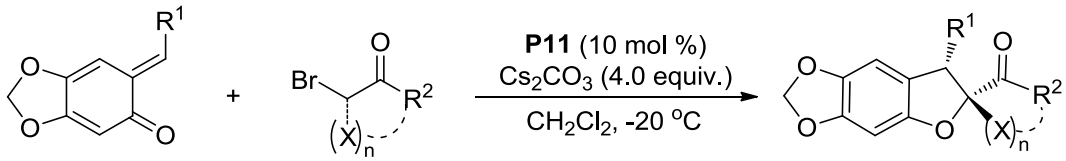
(S)-(3,5-bis(trifluoromethyl)benzyl)(2-(N-methyl-3,5-bis(trifluoromethyl)benzamido)propyl)diphenylphosphonium bromide (P11')



A white solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 (dd, J = 12.2, 7.8 Hz, 2H), 8.08 (dd, J = 12.5, 7.9 Hz, 2H), 7.81 (m, 2H), 7.71 (m, 3H), 7.57 (m, 3H), 7.21 (s, 2H), 5.72 (t,

J = 15.0 Hz, 1H), 5.38 (t, J = 15.4 Hz, 1H), 5.13 (m, 1H), 4.87 (m, 1H), 4.00 (td, J = 14.4, 2.3 Hz, 1H), 2.94 (s, 3H), 1.39 (d, J = 6.6 Hz, 3H), 1.26–1.20 (td, J = 7.2, 0.5 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.61, 137.23, 135.30 (dd, J = 26.6, 2.9 Hz), 134.30 (dd, J = 49.0, 9.5 Hz), 131.89 (dd, J = 33.6, 3.3 Hz), 131.82 (d, J = 33.7 Hz), 131.33 (d, J = 8.6 Hz), 130.61, 120.27 (dd, J = 18.4, 12.4 Hz), 127.37(d, J = 2.8 Hz), 123.79, 122.67 (q, J = 271.5 Hz), 122.65 (q, J = 271.5 Hz), 121.86, 115.62 (dd, J = 86.1, 82.0 Hz), 45.16(d, J = 3.8 Hz), 32.96, 31.41 (d, J = 46.9 Hz), 26.45(d, J = 47.5 Hz), 20.52 (d, J = 13.6 Hz) ^{31}P NMR (162 MHz, $CDCl_3$) δ 26.75; (ESI) m/z calcd for $C_{34}H_{27}BrF_{12}NOP$ $[M - Br]^+$ = 724.1633, found = 724.1606.

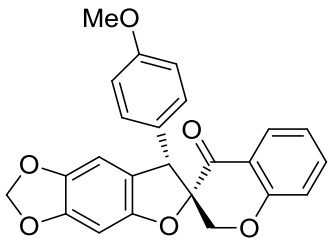
4. General Procedure for Asymmetric [4+1] Reaction



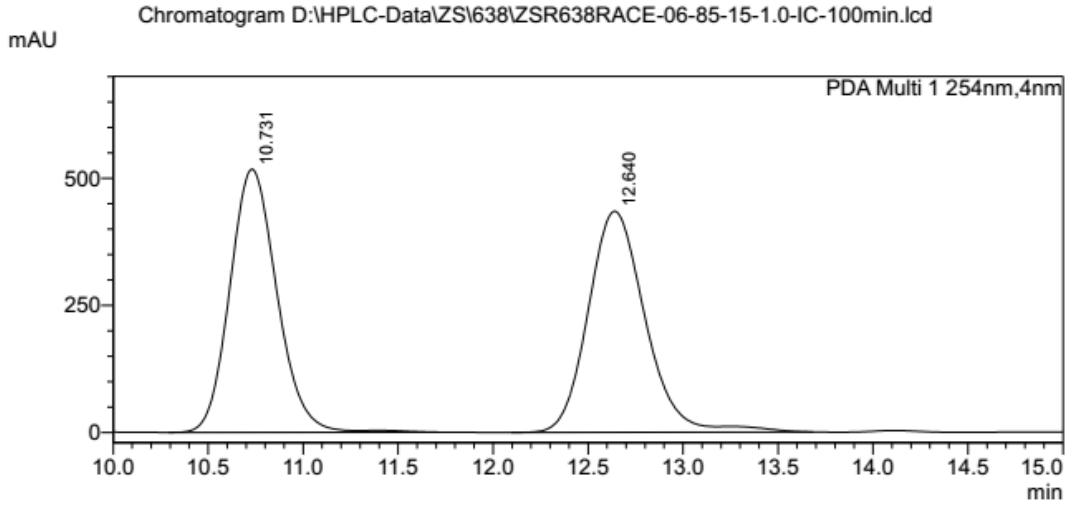
1 (0.2 mmol) **2** (1.2 equiv) **3** (>20:1 *dr*)

To a round bottle flask with a magnetic stirring bar were added *ortho*-quinone methids **1** (0.2 mmol), α-bromoketones **2** (0.24 mmol), phosphonium salt **P11** (7.9 mg, 0.01 mmol) and Cs_2CO_3 (260.6 mg, 0.8 mmol), followed by the addition of dry DCM (2.0 mL). The reaction mixture was stirred at -20 °C for 48-96 h. The solvent was removed under reduced pressure, and the residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 20:1 to 10:1) to afford product **3**.

(3'S,7S)-7-(4-methoxyphenyl)-7H-spiro[[1,3]dioxolo[4,5-f]benzofuran-6,3'-chroman]-4'-one (3a)



A white solid; 87% yield; $[\alpha]^{25}_{D}$ = +129.5 (c 0.4, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (dd, *J* = 7.6, 1.5 Hz, 1H), 7.51 (tt, *J* = 7.4, 0.9 Hz, 1H), 7.08 (t, *J* = 7.5 Hz, 1H), 7.00 (d, *J* = 8.6 Hz, 2H), 6.94 (d, *J* = 8.4 Hz, 1H), 6.84 (d, *J* = 8.3 Hz, 2H), 6.50 (s, 1H), 6.47 (s, 1H), 5.91 (dd, *J* = 15.8, 1.0 Hz, 2H), 5.19 (s, 1H), 4.26 (d, *J* = 12.9 Hz, 2H), 3.85(d, *J* = 12.9 Hz, 2H), 3.80 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$); δ 187.52, 161.07, 159.41, 152.63, 148.25, 142.89, 136.63, 130.37, 129.19, 128.43, 121.96, 120.33, 119.204, 118.00, 114.21, 105.33, 101.56, 93.53, 86.56, 70.91, 55.41, 49.31, HRMS (ESI$^+$): calcd for $C_{24}H_{18}O_6$ $[M+Na]^+$ = 425.1001, found = 425.0973; The ee value was 94%, t_R (minor) = 10.4 min, t_R (major) = 12.2 min (Chiralcel IC, λ = 254 nm, hexane/2-propanol = 85/15, flow rate = 1.0 mL/min).

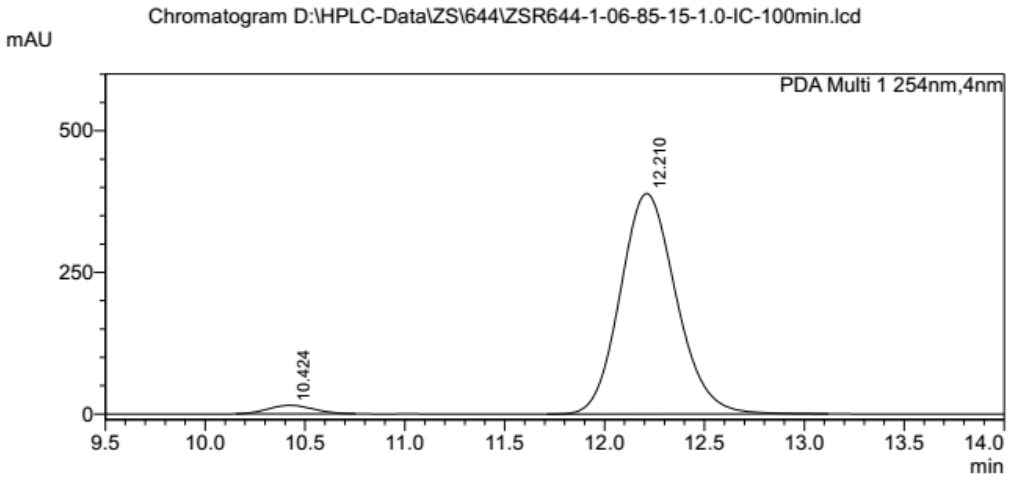


Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Height	Height%	Area	Area%
1	10.731	517742	54.356	8938061	49.533
2	12.640	434767	45.644	9106736	50.467
Total		952509	100.000	18044797	100.000

Racemic **3a**



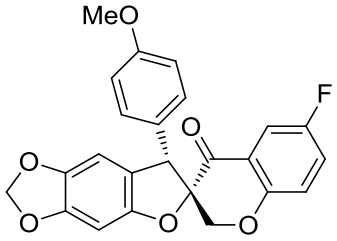
Peak Table

PDA Ch1 254nm

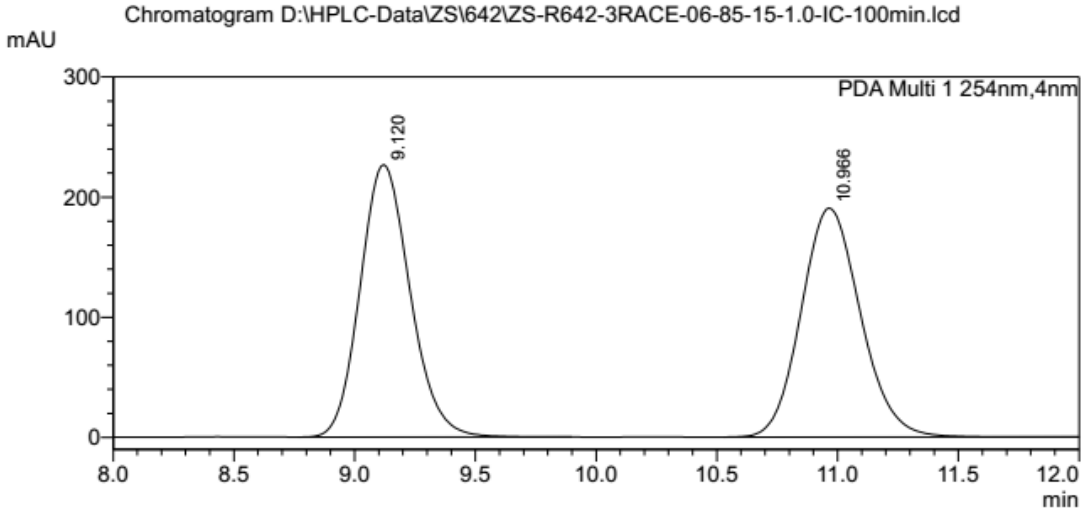
Peak#	Ret. Time	Height	Height%	Area	Area%
1	10.424	14961	3.702	234155	2.996
2	12.210	389197	96.298	7581090	97.004
Total		404158	100.000	7815246	100.000

Enantiomerically enriched **3a**

(3'S,7S)-6'-fluoro-7-(4-methoxyphenyl)-7H-spiro[[1,3]dioxolo[4,5-f]benzofuran-6,3'-chroman]-4'-one (3b)



A white solid; 84% yield; $[\alpha]^{25}_{D}$ = +89.0 (c 0.4, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (dd, *J* = 8.1, 3.2 Hz, 1H), 7.23 (m, 1H), 6.99 (d, J = 8.7 Hz, 2H), 6.93 (dd, *J* = 9.1, 4.2 Hz, 1H), 6.84 (d, *J* = 8.8 Hz, 2H), 6.50 (s, 1H), 6.46 (s, 1H), 5.91 (dd, *J* = 15.3, 1.0 Hz, 2H), 5.18 (s, 1H), 4.24 (d, *J* = 13.0 Hz, 1H), 3.82 (d, *J* = 13.0 Hz, 1H), 3.80 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 186.77, 159.46, 158.80, 157.37 (d, *J* = 1.5 Hz), 156.39, 152.42, 148.32, 143.01, 130.34, 128.96, 124.27, 120.23, 119.75 (d, *J* = 7.4 Hz), 119.62(d, *J* = 6.6 Hz), 114.26, 113.23, 112.99, 105.30, 101.60, 93.53, 86.23,71.13, 55.42, 49.22; HRMS (ESI^+): calcd for $C_{24}H_{17}O_6F$ $[M+Na]^+$ = 443.0907, found = 443.0891; The ee value was 94%, t_R (minor) = 9.1 min, t_R (major) = 10.9 min (Chiralcel IC, λ = 254 nm, hexane/2-propanol = 85/15, flow rate = 1.0 mL/min).

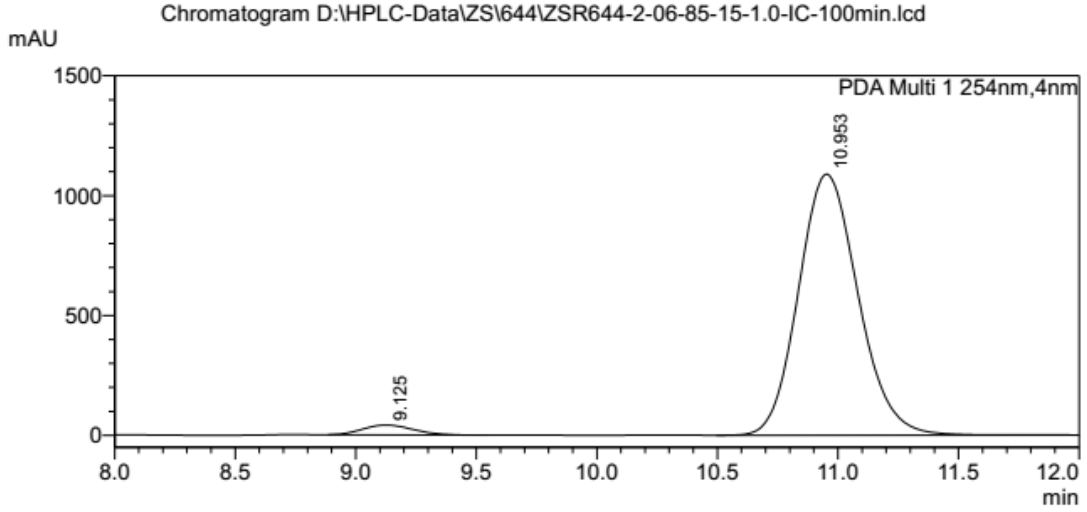


Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Height	Height%	Area	Area%
1	9.120	226785	54.330	3268659	50.041
2	10.966	190638	45.670	3263277	49.959
Total		417423	100.000	6531936	100.000

Racemic **3b**



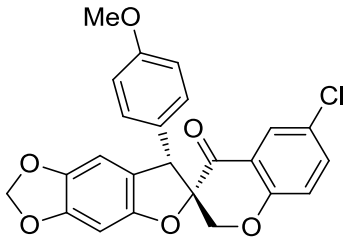
Peak Table

PDA Ch1 254nm

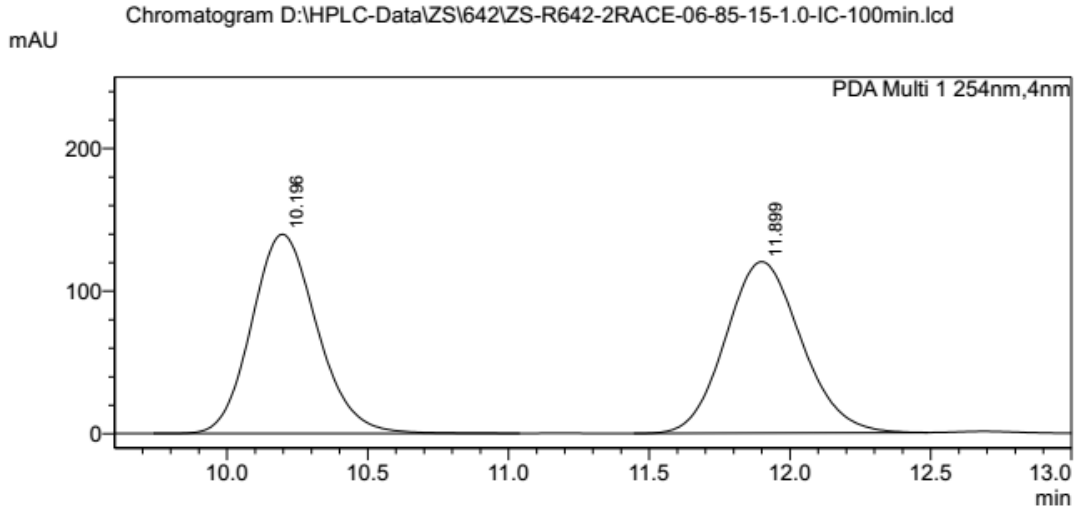
Peak#	Ret. Time	Height	Height%	Area	Area%
1	9.125	41089	3.635	596138	3.078
2	10.953	1089432	96.365	18772509	96.922
Total		1130522	100.000	19368647	100.000

Enantiomerically enriched **3b**

(3'S,7S)-6'-chloro-7-(4-methoxyphenyl)-7H-spiro[[1,3]dioxolo[4,5-f]benzofuran-6,3'-chroman]-4'-one (3c)



A white solid; 83% yield; $[\alpha]^{25}_{D}$ = +135.5 (c 0.4, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, *J* = 2.5 Hz, 1H), 7.43 (dd, *J* = 8.9, 2.6 Hz, 1H), 6.97 (d, *J* = 8.6 Hz, 2H), 6.89 (d, *J* = 8.9 Hz, 1H), 6.82 (d, *J* = 8.6 Hz, 2H), 6.48 (s, 1H), 6.44 (s, 1H), 5.90 (dd, *J* = 14.8, 1.2 Hz, 2H), 5.16 (s, 1H), 4.23 (d, *J* = 13.0 Hz, 1H), 3.81 (d, *J* = 13.0 Hz, 1H), 3.78 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$); δ 186.41, 159.52, 159.49, 152.39, 148.33, 143.04, 136.50, 130.33, 128.90, 127.55, 127.50, 120.16, 120.04, 119.74, 114.28, 105.30, 101.62, 93.53, 86.20, 70.08, 55.42, 49.20; HRMS (ESI^+): calcd for $C_{24}H_{17}O_6Cl$ $[M+Na]^+$ = 459.0611, found = 459.0589; The ee value was 94%, t_R (minor) = 10.1 min, t_R (major) = 11.9 min (Chiralcel IC, λ = 254 nm, hexane/2-propanol = 85/15, flow rate = 1.0 mL/min).

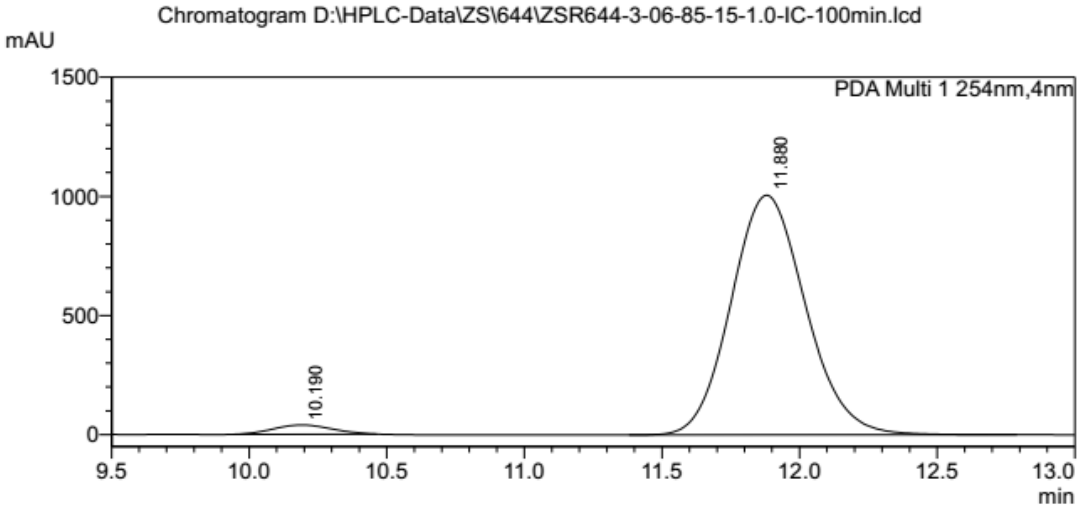


Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Height	Height%	Area	Area%
1	10.196	139777	53.778	2265003	50.124
2	11.899	120138	46.222	2253839	49.876
Total		259915	100.000	4518842	100.000

Racemic **3c**



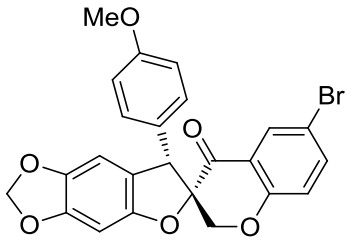
Peak Table

PDA Ch1 254nm

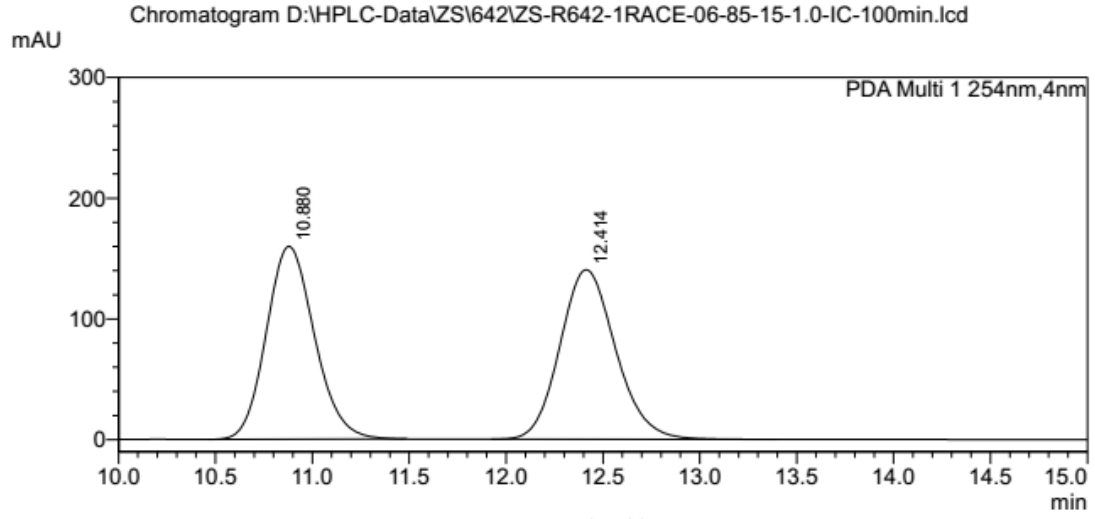
Peak#	Ret. Time	Height	Height%	Area	Area%
1	10.190	38620	3.698	572139	2.924
2	11.880	1005632	96.302	18995546	97.076
Total		1044252	100.000	19567685	100.000

Enantiomerically enriched **3c**

(3'S,7S)-6'-bromo-7-(4-methoxyphenyl)-7H-spiro[[1,3]dioxolo[4,5-f]benzofuran-6,3'-chroman]-4'-one (3d)



A white solid; 81% yield; $[\alpha]^{25}_{D}$ = +105.8 (c 0.4, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (dd, *J* = 2.0, 0.5 Hz, 1H), 7.58 (ddd, *J* = 8.7, 2.5, 0.5 Hz, 1H), 6.98 (d, *J* = 8.6 Hz, 2H), 6.87 (d, *J* = 4 Hz, 2H), 6.84 (d, *J* = 4 Hz, 1H), 6.50 (s, 1H), 6.45 (s, 1H), 5.92 (dd, *J* = 15.1, 2 Hz, 2H), 5.17 (s, 1H), 4.25 (d, *J* = 13.0 Hz, 1H), 3.83 (d, *J* = 13.0 Hz, 1H), 3.79 (s, 3H). ^{13}C NMR (100 MHz, CDCl3); δ 186.28, 159.95, 159.49, 152.39, 148.34, 143.04, 139.25, 130.67, 130.33, 128.88, 120.55, 120.15, 120.07, 114.59, 114.28, 105.30, 101.62, 93.53, 86.16, 71.05, 55.42, 49.20; HRMS (ESI^+): calcd for $C_{24}H_{17}O_6Br$ $[M+Na]^+$ = 503.0106, found = 503.0094; The ee value was 94%, t_R (minor) = 10.9 min, t_R (major) = 12.4 min (Chiralcel IC, λ = 254 nm, hexane/2-propanol = 85/15, flow rate = 1.0 mL/min).

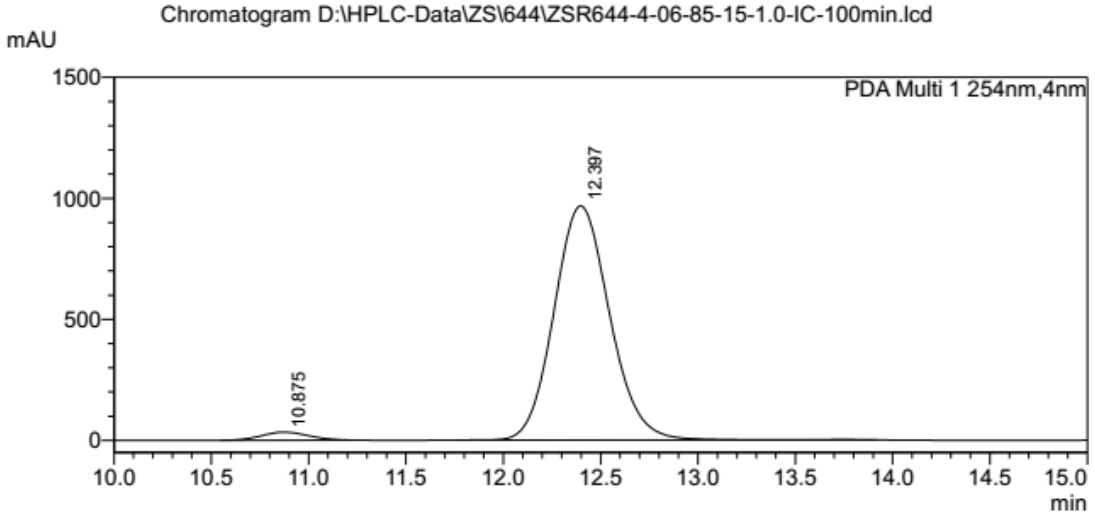


Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Height	Height%	Area	Area%
1	10.880	159890	53.236	2768443	49.660
2	12.414	140453	46.764	2806403	50.340
Total		300344	100.000	5574846	100.000

Racemic **3d**



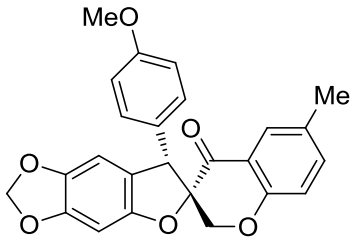
Peak Table

PDA Ch1 254nm

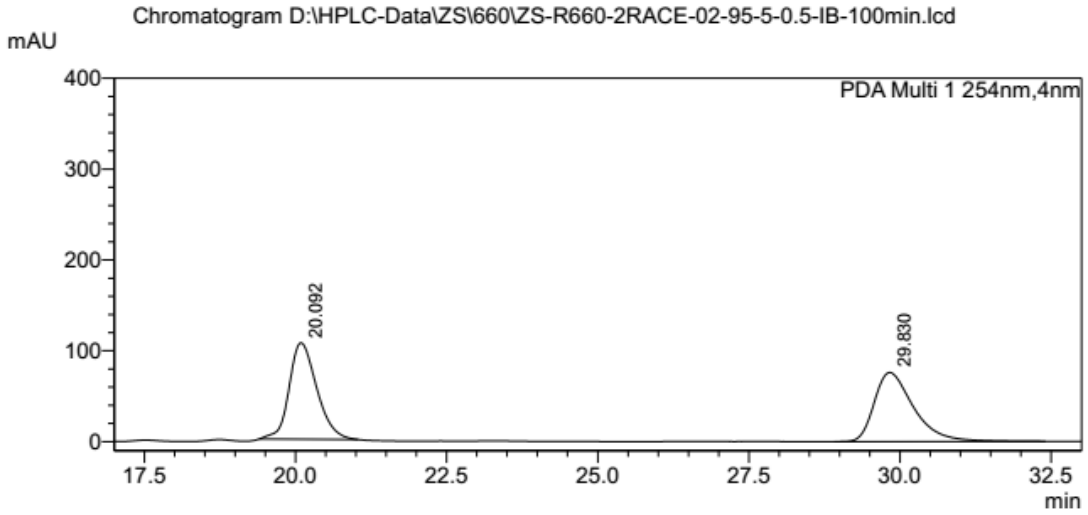
Peak#	Ret. Time	Height	Height%	Area	Area%
1	10.875	33108	3.308	556212	2.810
2	12.397	967675	96.692	19237086	97.190
Total		1000783	100.000	19793297	100.000

Enantiomerically enriched **3d**

(3'S,7S)-7-(4-methoxyphenyl)-6'-methyl-7H-spiro[[1,3]dioxolo[4,5-f]benzofuran-6,3'-chroman]-4'-one (3e)



A white solid; 85% yield; $[\alpha]^{25}_{D}$ = +107.0 (c 0.4, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, *J* = 1.4 Hz, 1H), 7.32 (dd, *J* = 8.6, 2.2 Hz, 1H), 6.99 (d, *J* = 8.7 Hz, 2H), 6.85 (d, *J* = 3.1 Hz, 2H), 6.83 (d, *J* = 3.4 Hz, 1H), 6.50 (s, 1H), 6.46 (s, 1H), 5.91 (dd, *J* = 15.3, 1.3 Hz, 2H), 5.18 (s, 1H), 4.23 (d, *J* = 12.8 Hz, 1H), 3.83 (d, *J* = 13.8 Hz, 1H), 3.79 (s, 3H), 2.33 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 187.69, 159.37, 159.15, 152.66, 148.22, 142.84, 137.83, 131.45, 130.36, 129.26, 127.84, 120.35, 118.78, 117.80, 114.17, 105.34, 101.54, 93.52, 86.63, 70.86, 55.41, 49.35, 20.56; HRMS (ESI^+): calcd for $C_{25}H_{20}O_6$ $[M+Na]^+$ = 439.1158, found = 439.1127; The ee value was 97%, t_R (minor) = 20.2 min, t_R (major) = 29.7 min (Chiralcel IB, λ = 254 nm, hexane/2-propanol = 95/5, flow rate = 0.5 mL/min).

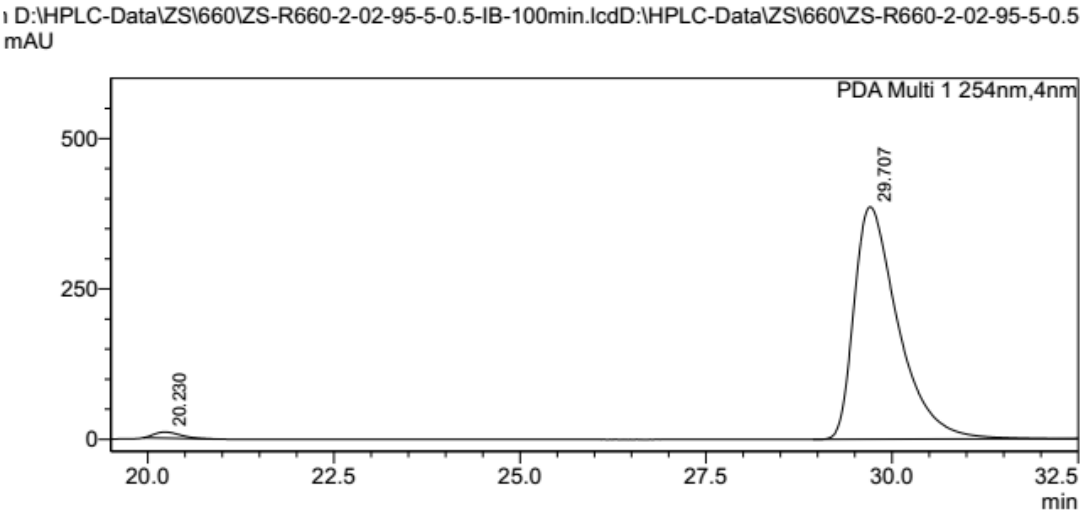


Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Height	Height%	Area	Area%
1	20.092	106079	58.289	3379130	49.602
2	29.830	75909	41.711	3433371	50.398
Total		181988	100.000	6812501	100.000

Racemic **3e**



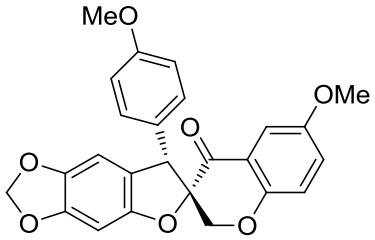
Peak Table

PDA Ch1 254nm

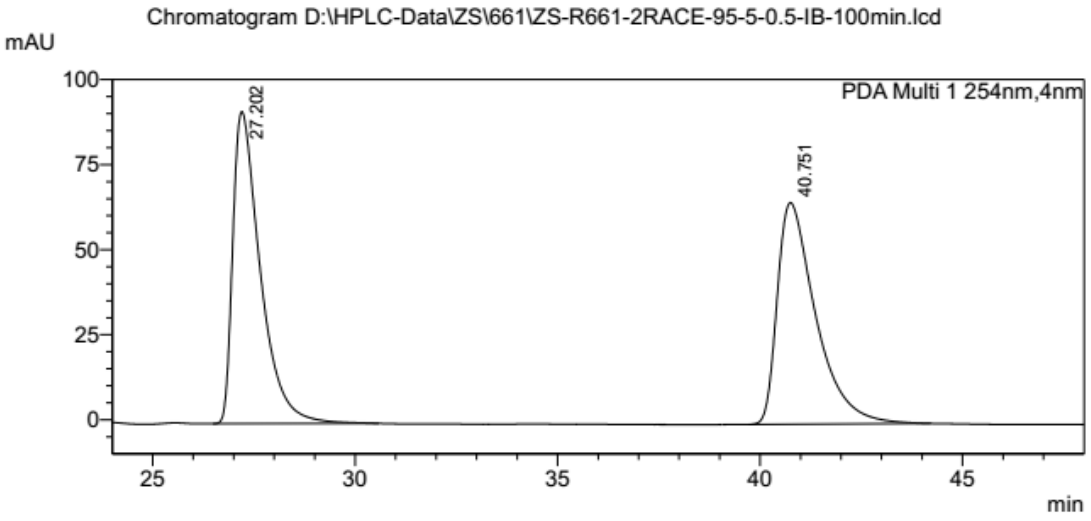
Peak#	Ret. Time	Height	Height%	Area	Area%
1	20.230	10352	2.610	254761	1.574
2	29.707	386224	97.390	15932505	98.426
Total		396576	100.000	16187266	100.000

Enantiomerically enriched **3e**

(3'S,7S)-6'-methoxy-7-(4-methoxyphenyl)-7H-spiro[[1,3]dioxolo[4,5-f]benzofuran-6,3'-chroman]-4'-one (3f)



A white solid; 86% yield; $[\alpha]^{25}_{D}$ = +64.3 (c 0.4, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (d, *J* = 3.2 Hz, 1H), 7.12 (dd, *J* = 9.1, 3.2 Hz, 1H), 7.00 (d, *J* = 8.6 Hz, 2H), 6.88 (d, *J* = 9.0 Hz, 1H), 6.84 (d, *J* = 8.8 Hz, 2H), 6.51 (s, 1H), 6.47 (s, 1H), 5.91 (dd, *J* = 15.3, 1.3 Hz, 2H), 5.19 (s, 1H), 4.22 (d, *J* = 12.8 Hz, 1H), 3.81 (s, 3H), 3.79 (s, 3H), 3.78 (d, *J* =5.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 187.49, 159.40, 155.88, 154.54, 152.61, 148.24, 142.87, 130.36, 129.18, 126.23, 120.35, 119.37, 118.96, 114.19, 108.25, 105.33, 101.56, 93.54, 86.54, 71.02, 55.96, 55.41, 49.35; HRMS (ESI^+): $[M+Na]^+$ = 455.1107, found = 455.1081; The ee value was 91%, t_R (minor) = 27.2 min, t_R (major) = 40.3 min (Chiralcel IB, λ = 254 nm, hexane/2-propanol = 95/5, flow rate = 0.5 mL/min).

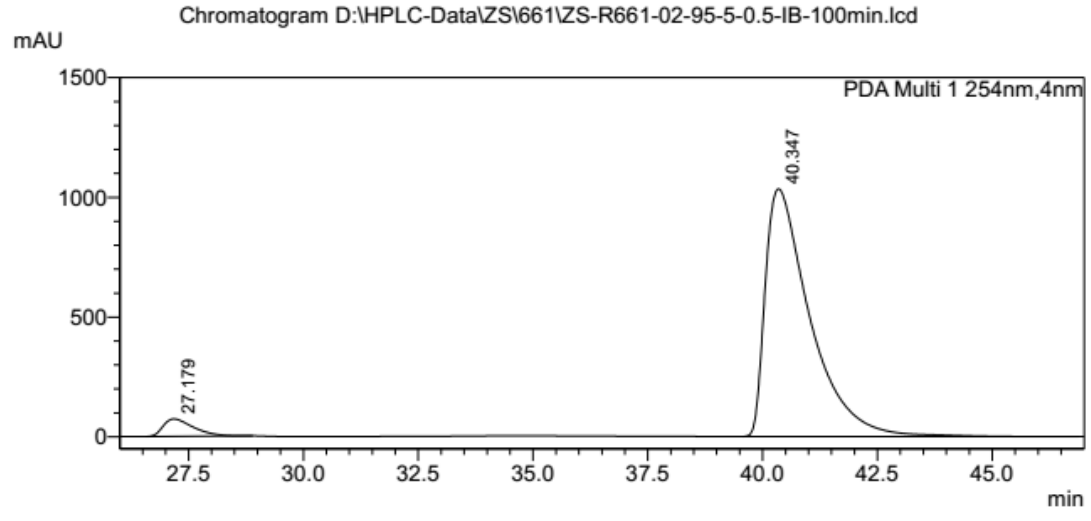


Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Height	Height%	Area	Area%
1	27.202	91714	58.475	4331269	50.141
2	40.751	65130	41.525	4306915	49.859
Total		156844	100.000	8638184	100.000

Racemic **3f**



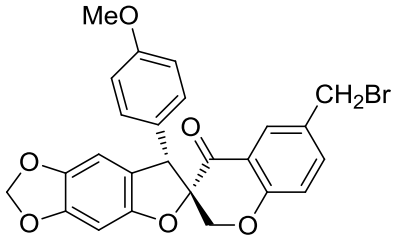
Peak Table

PDA Ch1 254nm

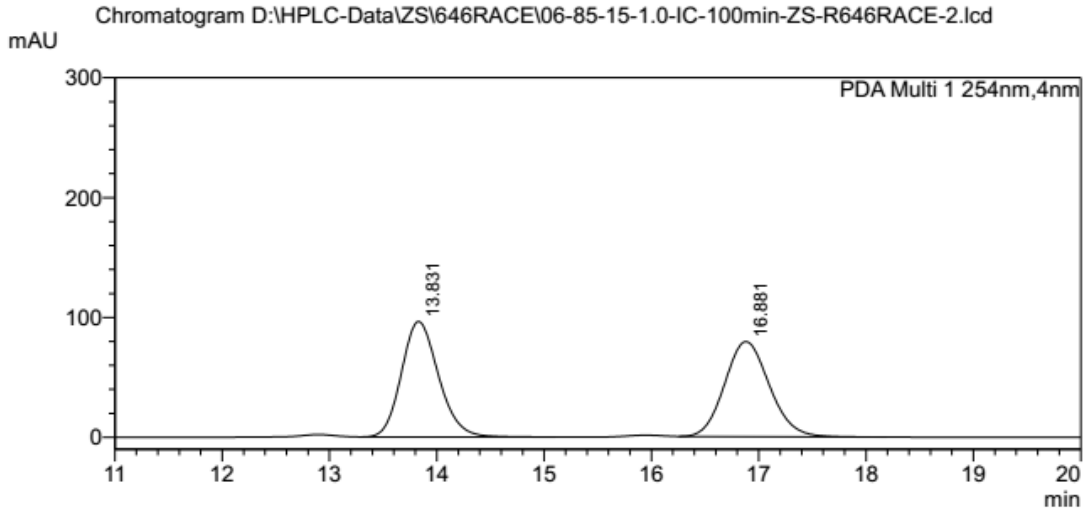
Peak#	Ret. Time	Height	Height%	Area	Area%
1	27.179	72640	6.563	3327289	4.526
2	40.347	1034234	93.437	70191518	95.474
Total		1106874	100.000	73518807	100.000

Enantiomerically enriched **3f**

(3'S,7S)-6'-(bromomethyl)-7-(4-methoxyphenyl)-7H-spiro[[1,3]dioxolo[4,5-f]benzofuran-6,3'-chroman]-4'-one (3g)



A white solid; 85% yield; $[\alpha]^{25}_{D}$ = +112.0 (c 0.4, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, *J* = 2.3 Hz, 1H), 7.52 (dd, *J* = 8.6, 2.4 Hz, 1H), 6.95 (d, *J* = 8.7 Hz, 2H), 6.91 (d, *J* = 8.6 Hz, 1H), 6.80 (d, *J* = 8.8 Hz, 2H), 6.46 (s, 1H), 6.42 (s, 1H), 5.88 (dd, *J* = 14.9, 1.2 Hz,2H), 5.16 (s, 1H), 4.45 (s, 2H), 4.22 (d, *J* = 12.9 Hz, 2H), 3.79 (d, *J* = 13.0 Hz, 2H), 3.76 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 186.91, 160.95, 159.47, 152.47, 148.31, 142.99, 137.45, 131.63, 130.35, 128.99, 128.58, 120.23, 119.06, 118.93, 114.27, 105.33, 101.61, 93.55, 86.36, 71.10, 55.44, 49.18, 32.60; HRMS (ESI^+): calcd for $C_{24}H_{17}O_6Br$ $[M+Na]^+$ = 517.0263, found = 517.0239; The ee value was 94%, t_R (minor) = 13.8 min, t_R (major) = 16.9 min (Chiralcel IC, λ = 254 nm, hexane/2-propanol = 85/15, flow rate = 1.0 mL/min).

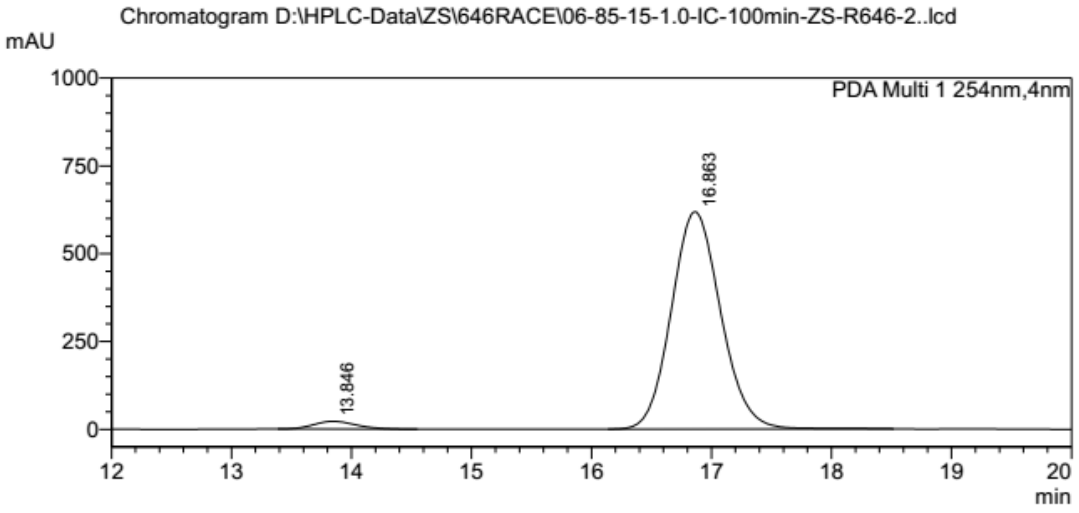


Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Height	Height%	Area	Area%
1	13.831	96326	54.838	2323323	50.226
2	16.881	79331	45.162	2302388	49.774
Total		175657	100.000	4625711	100.000

Racemic **3g**



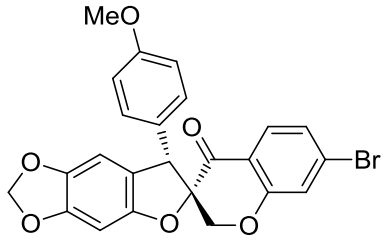
Peak Table

PDA Ch1 254nm

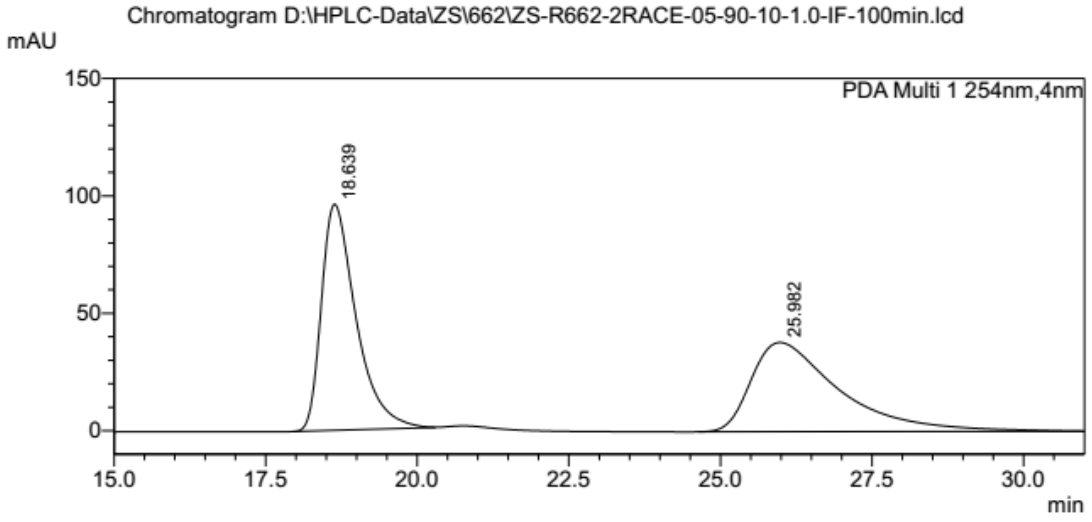
Peak#	Ret. Time	Height	Height%	Area	Area%
1	13.846	21969	3.429	536425	2.940
2	16.863	618700	96.571	17712156	97.060
Total		640668	100.000	18248581	100.000

Enantiomerically enriched **3g**

(3'S,7S)-7'-bromo-7-(4-methoxyphenyl)-7H-spiro[[1,3]dioxolo[4,5-f]benzofuran-6,3'-chroman]-4'-one (3h)



A white solid; 88% yield; $[\alpha]^{25}_{D}$ = +98.5 (c 0.4, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, *J* = 8.4 Hz, 1H), 7.21 (dd, *J* = 8.4, 1.8 Hz, 1H), 7.16 (d, *J* = 1.7 Hz, 1H), 6.99 (d, *J* = 8.7 Hz, 2H), 6.84 (d, *J* = 8.8 Hz, 2H), 6.50 (s, 1H), 6.45 (s, 1H), 5.91 (dd, *J* = 15.8, 1.3 Hz, 2H), 5.17 (s, 1H), 4.25 (d, *J* = 12.9 Hz, 1H), 3.84 (d, *J* = 12.9 Hz, 1H), 3.80 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$); δ 186.70, 161.20, 159.47, 152.44, 148.32, 143.00, 131.25, 130.33, 129.60, 128.93, 125.65, 121.16, 120.19, 118.13, 114.27, 105.31, 101.60, 93.52, 86.30, 71.22, 55.42, 49.18; HRMS (ESI^+): calcd for $C_{24}H_{17}BrO_6$ $[M+Na]^+$ = 503.0106, found = 503.0085; The ee value was 94%, t_R (major) = 18.5 min, t_R (minor) = 26.2 min (Chiralcel IF, λ = 254 nm, hexane/2-propanol = 90/10, flow rate = 1.0 mL/min).

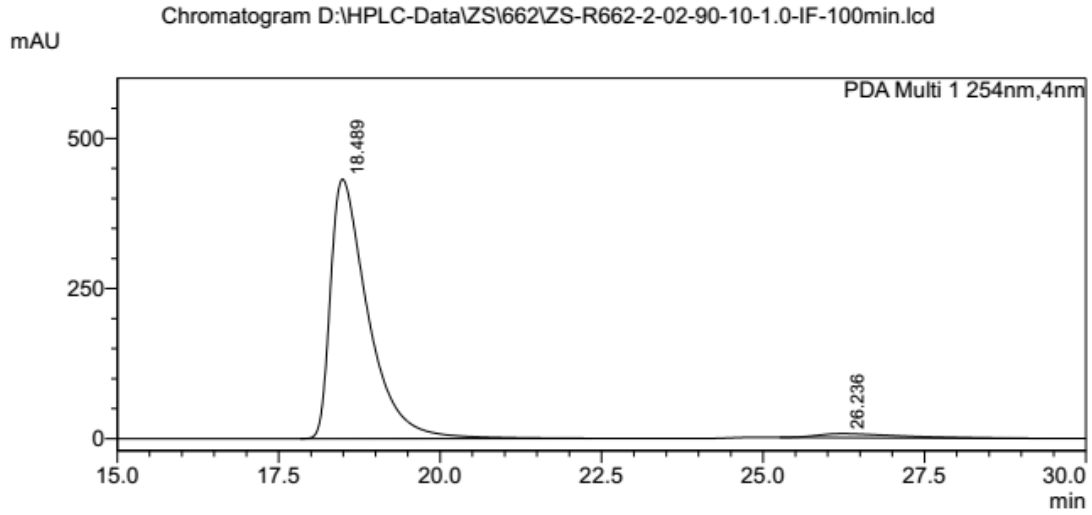


Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Height	Height%	Area	Area%
1	18.639	96286	71.685	3824535	49.880
2	25.982	38032	28.315	3842954	50.120
Total		134317	100.000	7667489	100.000

Racemic **3h**



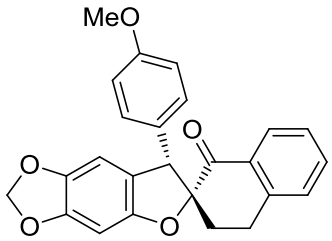
Peak Table

PDA Ch1 254nm

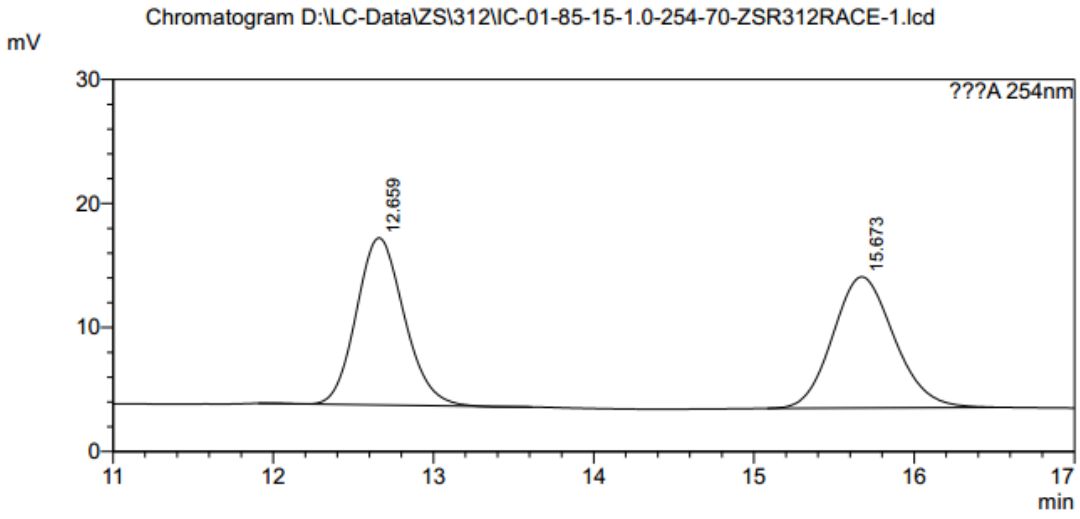
Peak#	Ret. Time	Height	Height%	Area	Area%
1	18.489	431922	98.517	17415874	96.905
2	26.236	6502	1.483	556204	3.095
Total		438424	100.000	17972079	100.000

Enantiomerically enriched **3h**

(2'R,7S)-7-(4-methoxyphenyl)-3',4'-dihydro-1'H,7H-spiro[[1,3]dioxolo[4,5-f]benzofuran-6,2'-naphthalen]-1'-one (3i)



A white solid; 78% yield; $[\alpha]^{25}_{D}$ = +26.5 (c 0.4, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (dd, *J* = 7.8, 1.1 Hz, 1H), 7.50 (td, *J* = 7.5, 1.4 Hz, 1H), 7.34 (t, *J* = 7.4 Hz, 1H), 7.20 (d, *J* = 7.6 Hz, 1H), 7.02 (d, *J* = 8.7 Hz, 2H), 6.83 (d, *J* = 8.7 Hz, 2H), 6.50 (s, 1H), 6.43 (s, 1H), 5.89 (dd, *J* = 16.2, 1.3 Hz, 2H), 5.14 (s, 1H), 3.79 (s, 3H), 3.16 (m, 1H), 2.72 (dt, *J* = 17.3, 5.2 Hz, 1H), 2.13 (m, *J* = 14.3, 5.1 Hz, 1H), 1.74 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.96, 159.03, 152.74, 147.90, 143.78, 142.37, 133.94, 131.34, 131.04, 130.57, 128.89, 128.78, 126.98, 121.63, 113.97, 105.59, 101.37, 93.25, 90.98, 55.40, 50.50, 30.79, 25.50; HRMS (ESI$^+$): calcd for $C_{25}H_{20}O_5$ $[M+Na]^+$ = 423.1208, found = 423.1186; The ee value was 82%, t_R (minor) = 12.6 min, t_R (major) = 15.7 min (Chiralcel IC, λ = 254 nm, hexane/2-propanol = 85/15, flow rate = 1.0 mL/min).

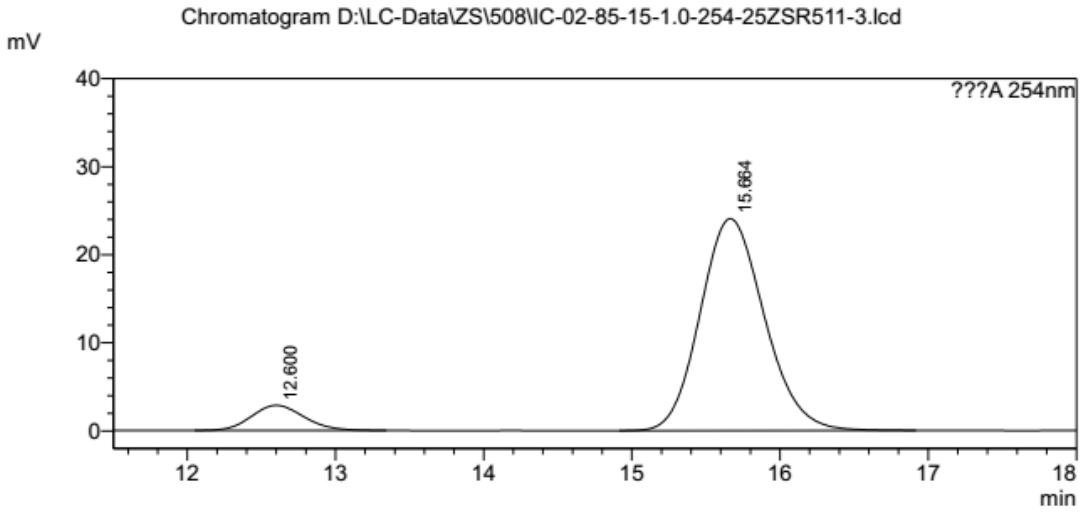


Peak Table

???A 254nm

Peak#	Ret. Time	Height	Height%	Area	Area%
1	12.659	13468	56.030	279610	49.802
2	15.673	10570	43.970	281833	50.198
Total		24038	100.000	561443	100.000

Racemic **3i**



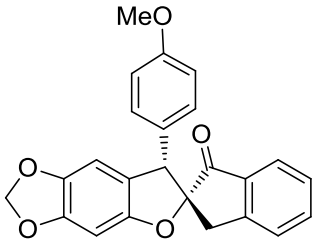
Peak Table

???A 254nm

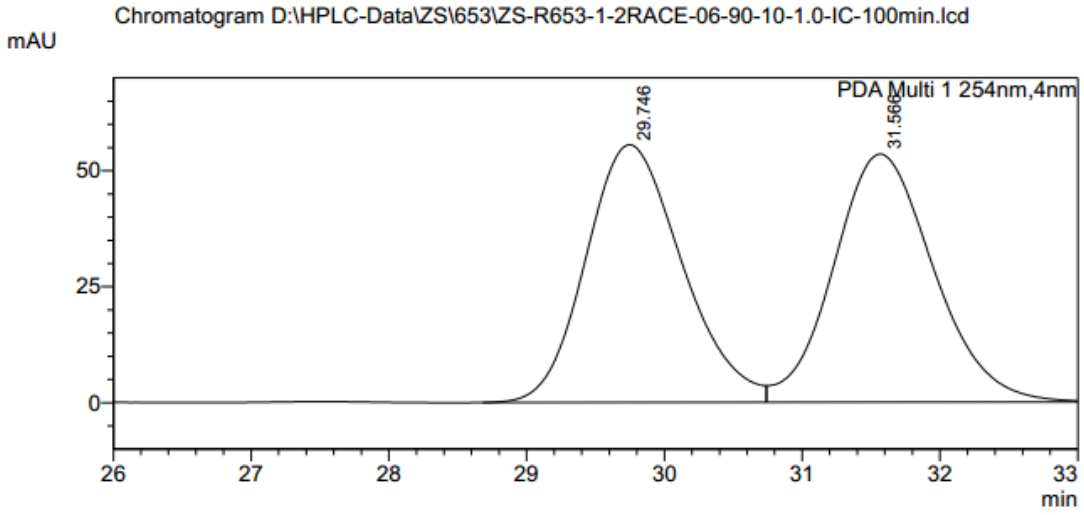
Peak#	Ret. Time	Height	Height%	Area	Area%
1	12.600	2848	10.581	70263	8.828
2	15.664	24067	89.419	725626	91.172
Total		26915	100.000	795889	100.000

Enantiomerically enriched **3i**

(2'R,7S)-7-(4-methoxyphenyl)-7H-spiro[[1,3]dioxolo[4,5-f]benzofuran-6,2'-inden]-1'(3'H)-one (3j)



A white solid; 83% yield; $[\alpha]^{25}_{D}$ = -2.3 (c 0.4, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (td, *J* = 6.9, 1.1 Hz, 1H), 7.42 (d, *J* = 7.6 Hz, 1H), 7.38 (d, *J* = 7.6 Hz, 1H), 7.26 (t, *J* = 7.4 Hz, 1H), 6.81 (d, *J* = 8.6 Hz, 2H), 6.63 (d, *J* = 8.7 Hz, 2H), 6.56 (s, 1H), 6.47 (s, 1H), 5.94 (dd, *J* = 6.8, 1.2 Hz, 2H), 4.69 (s, 1H), 3.70 (s, 3H), 3.61 (q, *J* = 15.5 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$); δ 200.72, 159.01, 154.77, 148.76, 148.19, 142.46, 135.53, 135.49, 130.07, 129.37, 128.21, 126.35, 124.40, 120.12, 113.66, 105.26, 101.50, 96.20, 93.59, 59.50, 55.26, 42.05; The ee value was 93%, t_R (major) = 29.6 min, t_R (minor) = 31.5 min (Chiralcel IC, λ = 254 nm, hexane/2-propanol = 90/10, flow rate = 1.0 mL/min).

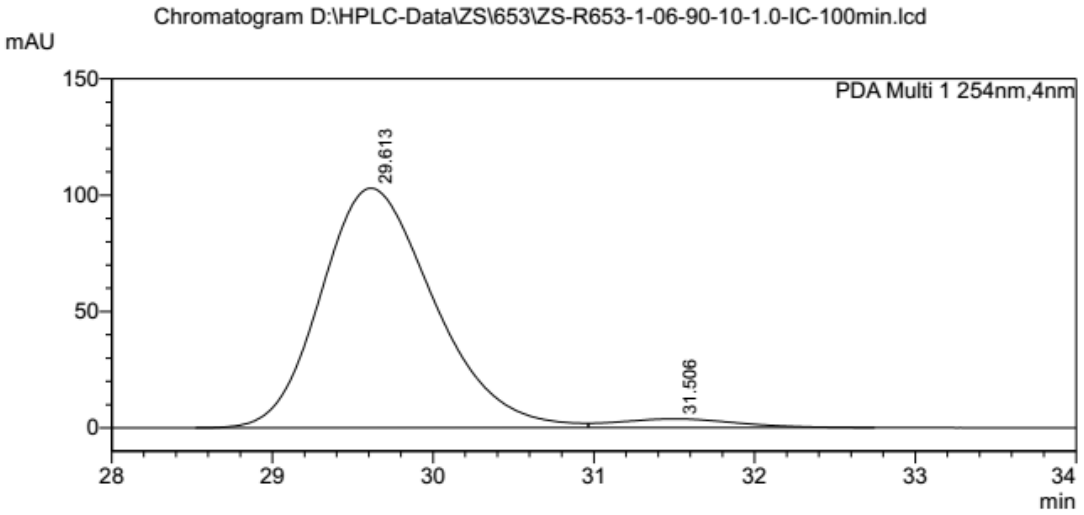


Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Height	Height%	Area	Area%
1	29.746	55530	50.932	2701431	49.938
2	31.566	53497	49.068	2708113	50.062
Total		109027	100.000	5409544	100.000

Racemic **3j**



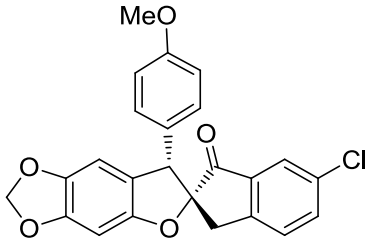
Peak Table

PDA Ch1 254nm

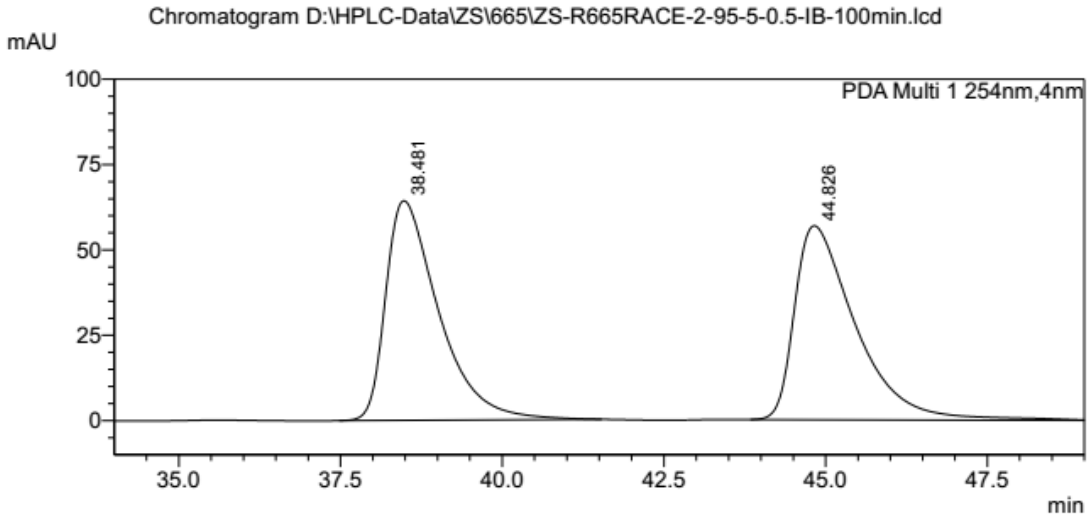
Peak#	Ret. Time	Height	Height%	Area	Area%
1	29.613	102936	96.469	5037193	96.311
2	31.506	3768	3.531	192942	3.689
Total		106703	100.000	5230135	100.000

Enantiomerically enriched **3j**

(2'R,7S)-6'-chloro-7-(4-methoxyphenyl)-7H-spiro[[1,3]dioxolo[4,5-f]benzofuran-6,2'-inden]-1'(3'H)-one (3k)



A white solid; 88% yield; $[\alpha]^{25}_{D}$ = -26.8 (c 0.4, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (dd, *J* = 8.1, 2.1 Hz, 1H), 7.37 (d, *J* = 8.2 Hz, 1H), 7.34 (d, *J* = 2.0 Hz, 1H), 6.83 (d, *J* = 8.7 Hz, 2H), 6.66 (d, *J* = 8.8 Hz, 2H), 6.55 (s, 1H), 6.46 (s, 1H), 5.94 (dd, *J* = 6.2, 1.3 Hz, 2H), 4.70 (s, 1H), 3.72 (s, 3H), 3.59 (q, *J* = 13.7 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$); δ 199.66, 159.16, 154.59, 148.25, 146.88, 142.56, 136.81, 135.49, 134.46, 130.04, 128.88, 127.60, 124.07, 119.91, 113.81, 105.21, 101.54, 96.35, 93.56, 59.47, 55.29, 41.41; HRMS (ESI^+): calcd for $C_{24}H_{17}ClO_5$ $[M+Na]^+$ = 443.0662, found = 443.0645; The ee value was 87%, t_R (minor) = 40.1 min, t_R (major) = 46.4 min (Chiralcel IB, λ = 254 nm, hexane/2-propanol = 95/5, flow rate = 0.5 mL/min).

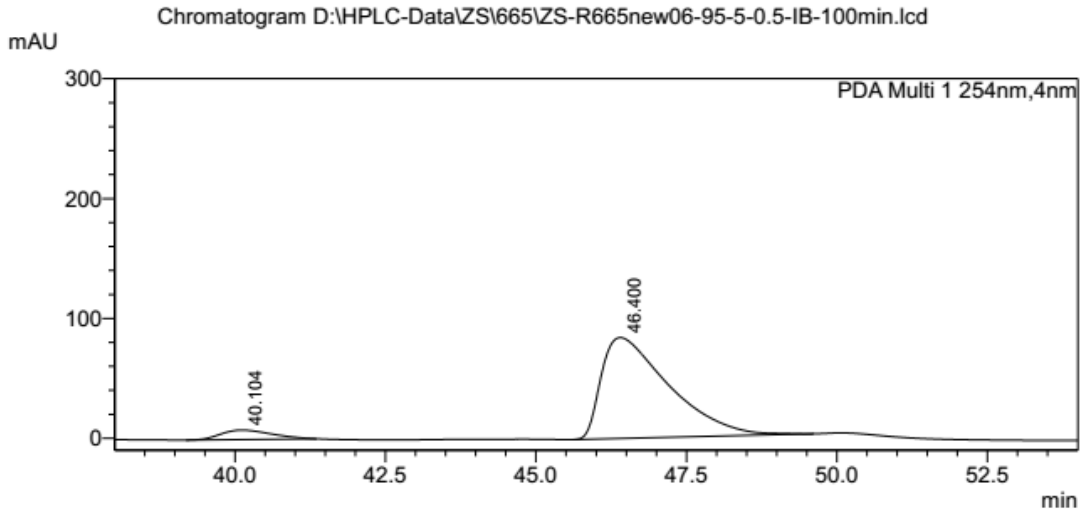


Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Height	Height%	Area	Area%
1	38.481	64333	53.104	3677208	49.606
2	44.826	56812	46.896	3735606	50.394
Total		121146	100.000	7412814	100.000

Racemic **3k**



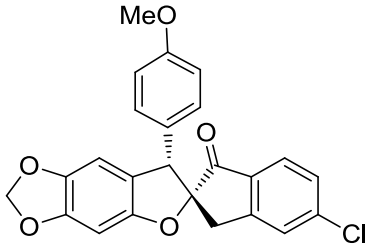
Peak Table

PDA Ch1 254nm

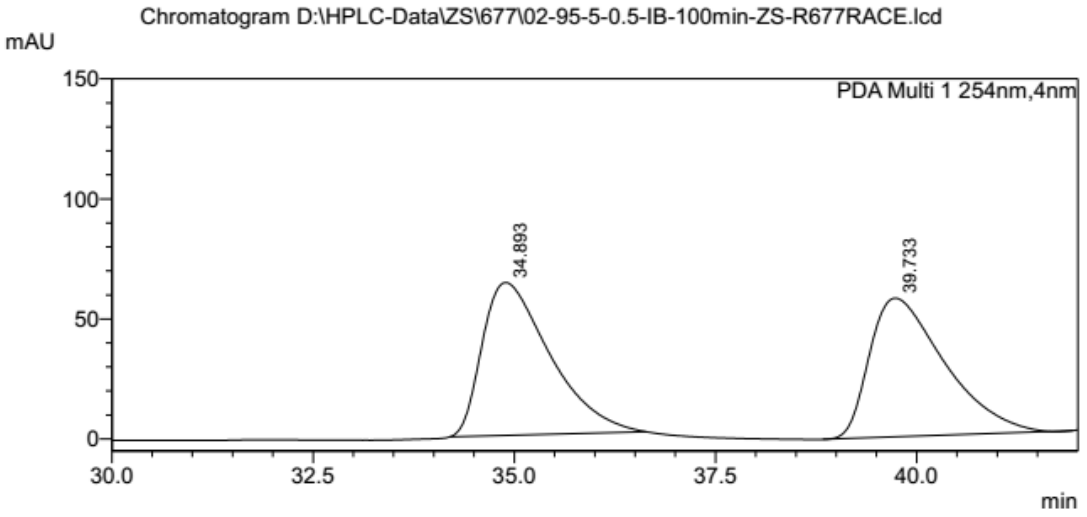
Peak#	Ret. Time	Height	Height%	Area	Area%
1	40.104	7851	8.530	461040	6.551
2	46.400	84191	91.470	6576980	93.449
Total		92042	100.000	7038020	100.000

Enantiomerically enriched **3k**

(2'R,7S)-5'-chloro-7-(4-methoxyphenyl)-7H-spiro[[1,3]dioxolo[4,5-f]benzofuran-6,2'-inden]-1'(3'H)-one (3l)



A white solid; 80% yield; $[\alpha]^{25}_{D}$ = +41.0 (c 0.4, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (s, 1H), 7.30 (d, *J* = 8.2 Hz, 1H), 7.23 (dd, *J* = 8.2, 1.6 Hz, 1H), 6.83 (d, *J* = 8.7 Hz, 2H), 6.65 (d, *J* = 8.8 Hz, 2H), 6.55 (s, 1H), 6.46 (s, 1H), 5.94 (dd, *J* = 6.7, 1.3 Hz, 2H), 4.70 (s, 1H), 3.71 (s, 3H), 3.61 (q, *J* = 16.9 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.60, 159.31, 154.83, 150.45, 148.46, 142.75, 142.21, 134.03, 130.28, 129.22, 129.15, 126.76, 125.71, 120.11, 113.96, 105.41, 101.73, 96.20, 93.75, 59.67, 55.46, 41.83; HRMS (ESI^+): calcd for $C_{24}H_{17}ClO_5$ $[M+Na]^+$ = 443.0662, found = 443.0640; The ee value was 95%, t_R (minor) = 36.6 min, t_R (major) = 40.4 min (Chiralcel IB, λ = 254 nm, hexane/2-propanol = 95/5, flow rate = 0.5 mL/min).

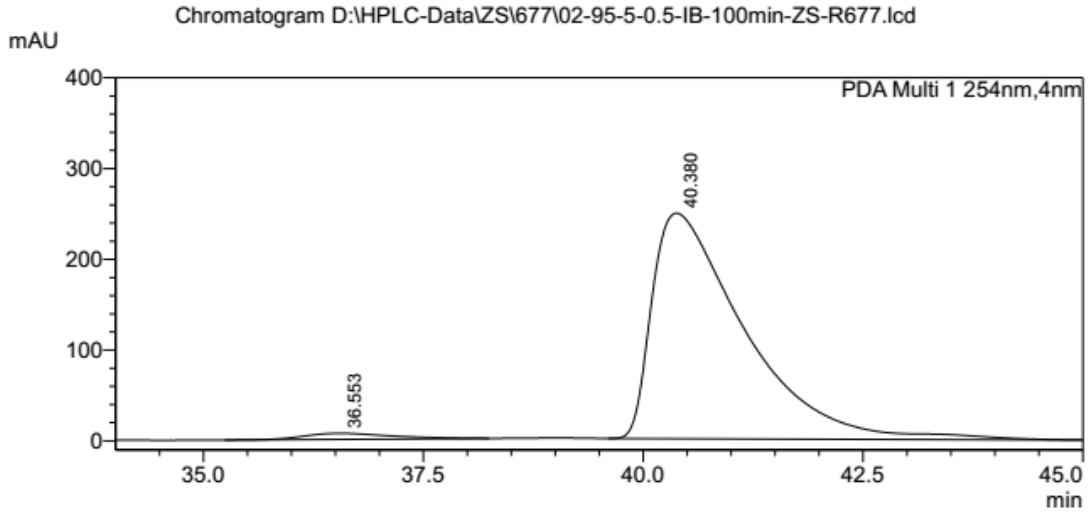


Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Height	Height%	Area	Area%
1	34.893	63707	52.445	3738405	50.012
2	39.733	57767	47.555	3736586	49.988
Total		121474	100.000	7474991	100.000

Racemic **3l**



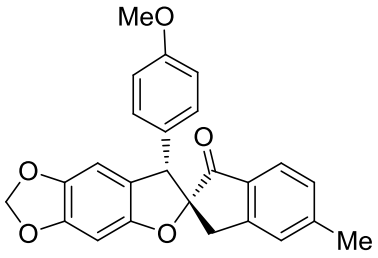
Peak Table

PDA Ch1 254nm

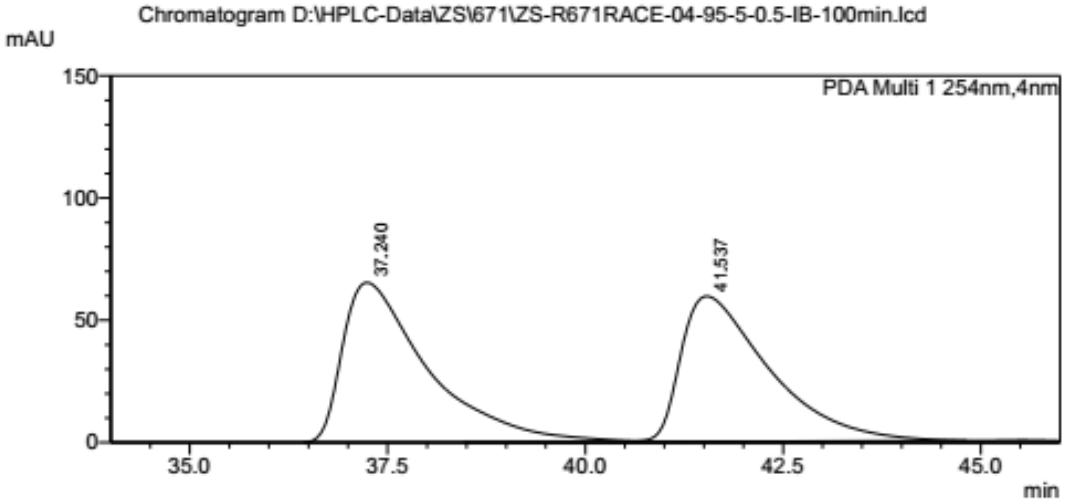
Peak#	Ret. Time	Height	Height%	Area	Area%
1	36.553	6608	2.590	452729	2.427
2	40.380	248509	97.410	18201476	97.573
Total		255117	100.000	18654205	100.000

Enantiomerically enriched **3l**

(2'R,7S)-7-(4-methoxyphenyl)-5'-methyl-7H-spiro[[1,3]dioxolo[4,5-f]benzofuran-6,2'-inden]-1'(3'H)-one (3m)



A white solid; 86% yield; $[\alpha]^{25}_{D}$ = +22.8 (c 0.4, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (d, *J* = 7.8 Hz, 1H), 7.22 (s, 1H), 7.07 (d, *J* = 7.8 Hz, 1H), 6.88–6.79 (m, 2H), 6.69–6.61 (m, 2H), 6.55 (s, 1H), 6.47 (s, 1H), 5.94 (dd, *J* = 6.8, 1.3 Hz, 2H), 4.66 (s, 1H), 3.71 (s, 3H), 3.55 (q, *J* = 16.6 Hz, 2H), 2.42 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$); δ 200.04, 158.95, 154.78, 149.22, 148.14, 146.88, 142.39, 133.16, 130.08, 129.51, 129.44, 126.73, 124.29, 120.23, 113.63, 105.27, 101.47, 96.25, 93.57, 59.46, 55.25, 42.02, 22.37; HRMS (ESI$^+$): calcd for $C_{25}H_{20}O_5$ $[M+Na]^+$ = 423.1208, found = 423.1189; The ee value was 96%, t_R (minor) = 37.9 min, t_R (major) = 40.9 min (Chiralcel IB, λ = 254 nm, hexane/2-propanol = 95/5, flow rate = 0.5 mL/min).

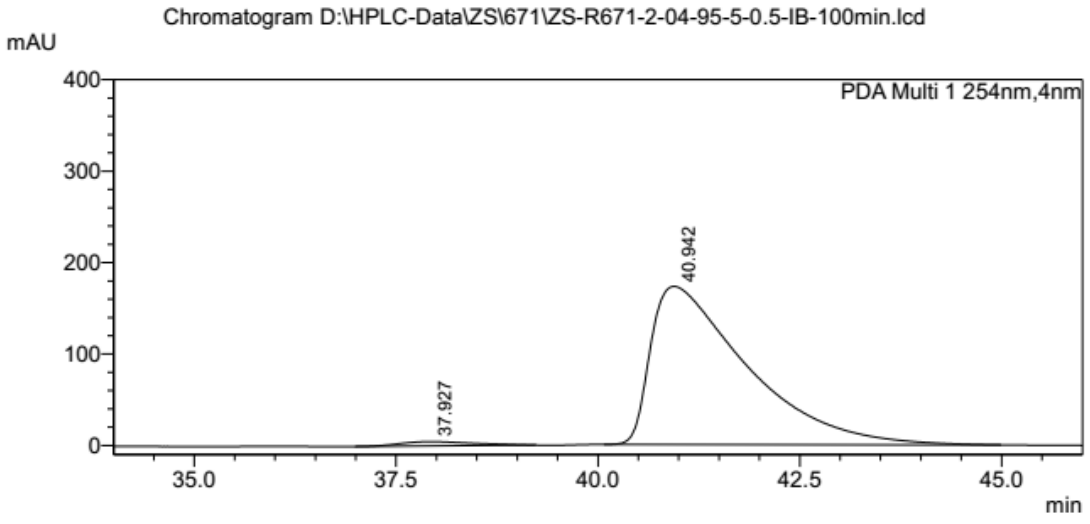


Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Height	Height%	Area	Area%
1	37.240	65612	52.455	4941213	51.737
2	41.537	59471	47.545	4609504	48.263
Total		125083	100.000	9550717	100.000

Racemic **3m**



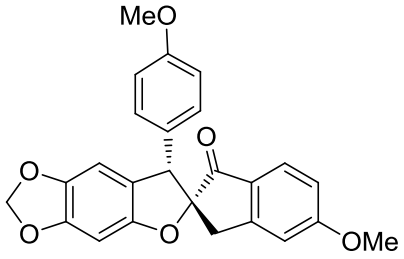
Peak Table

PDA Ch1 254nm

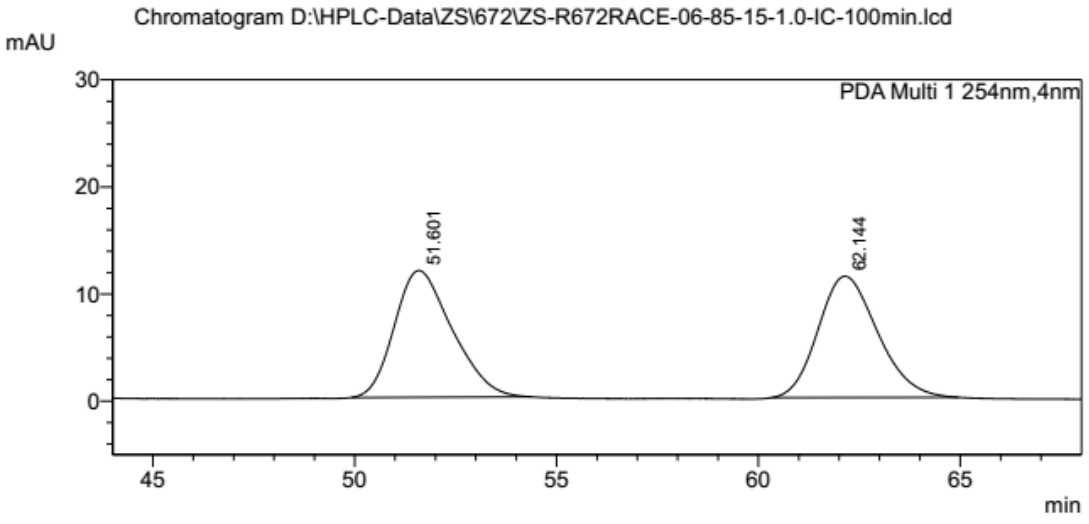
Peak#	Ret. Time	Height	Height%	Area	Area%
1	37.927	4643	2.614	295906	2.021
2	40.942	172952	97.386	14345013	97.979
Total		177594	100.000	14640919	100.000

Enantiomerically enriched **3m**

(2'R,7S)-5'-methoxy-7-(4-methoxyphenyl)-7H-spiro[[1,3]dioxolo[4,5-f]benzofuran-6,2'-inden]-1'(3'H)-one (3n)



A white solid; 83% yield; $[\alpha]^{25}_{D}$ = +31.5 (c 0.4, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (d, *J* = 8.5 Hz, 1H), 6.86 (d, *J* = 2.2 Hz, 2H), 6.84 (s, 1H), 6.79 (dd, *J* = 8.6, 1.7 Hz, 1H), 6.65 (d, *J* = 8.6 Hz, 2H), 6.55 (s, 1H), 6.47 (s, 1H), 5.92 (dd, *J* = 6.7, 1.2 Hz, 2H), 4.67 (s, 1H), 3.88 (s, 3H), 3.71 (s, 3H), 3.54 (t, *J* = 17.7 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.55, 165.91, 158.96, 151.74, 142.35, 130.11, 129.45, 128.59, 126.32, 120.27, 115.85, 113.62, 109.82, 105.26, 101.47, 96.12, 93.55, 59.35, 55.82, 55.25, 42.24; HRMS (ESI^+): calcd for $C_{25}H_{20}O_6$ $[M+Na]^+$ = 439.1158, found = 439.1135; The ee value was 86%, t_R (major) = 49.5 min, t_R (minor) = 59.8 min (Chiralcel IC, λ = 254 nm, hexane/2-propanol = 85/15, flow rate = 1.0 mL/min).

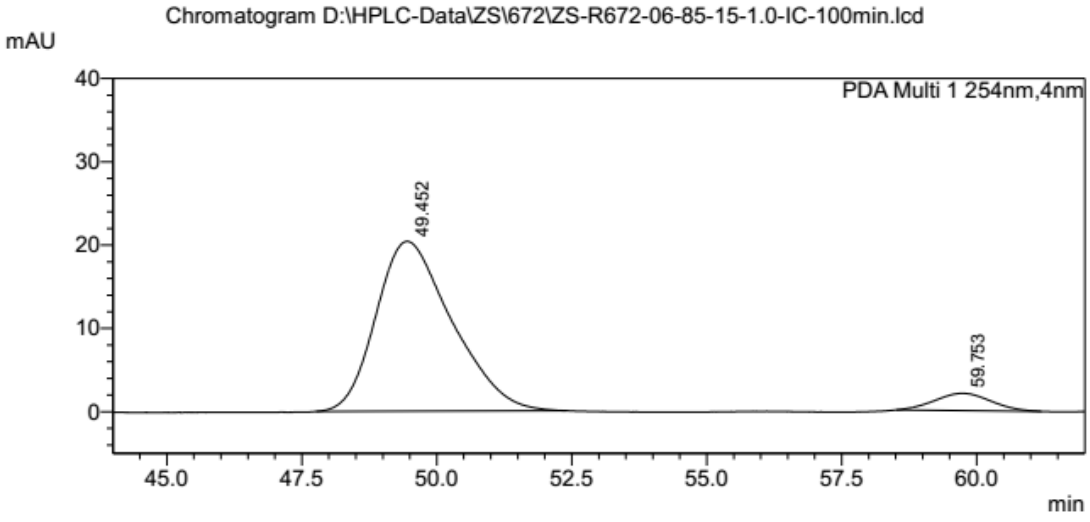


Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Height	Height%	Area	Area%
1	51.601	11837	51.097	1178275	50.369
2	62.144	11329	48.903	1161021	49.631
Total		23165	100.000	2339295	100.000

Racemic **3n**



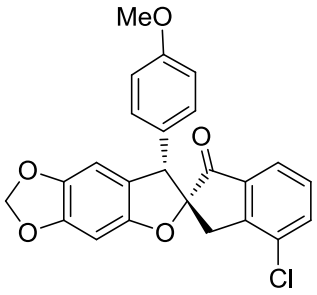
Peak Table

PDA Ch1 254nm

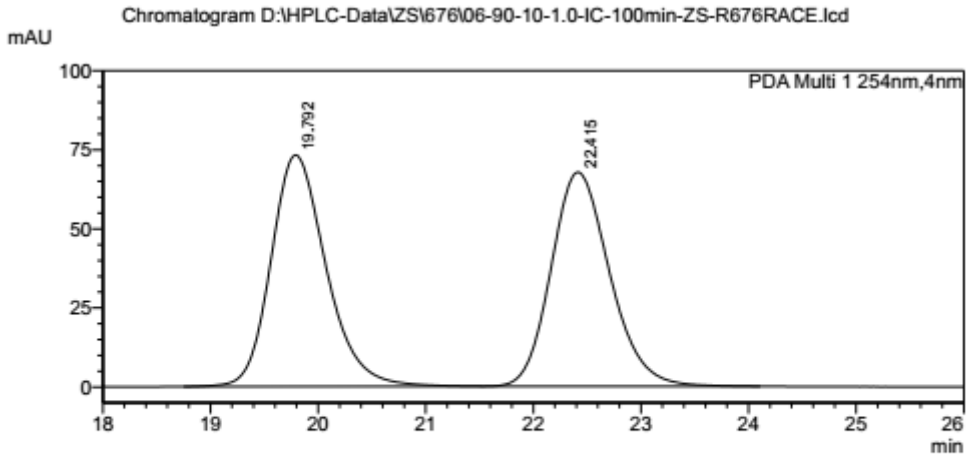
Peak#	Ret. Time	Height	Height%	Area	Area%
1	49.452	20397	90.803	1996846	93.013
2	59.753	2066	9.197	150009	6.987
Total		22463	100.000	2146855	100.000

Enantiomerically enriched **3n**

(2'R,7S)-4'-chloro-7-(4-methoxyphenyl)-7H-spiro[[1,3]dioxolo[4,5-f]benzofuran-6,2'-inden]-1'(3'H)-one (3o)



A white solid; 86% yield; $[\alpha]^{25}_{D}$ = +7.0 (c 0.4, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (d, *J* = 7.6 Hz, 1H), 7.29 (d, *J* = 7.4 Hz, 1H), 7.22 (t, *J* = 7.6 Hz, 1H), 6.85 (d, *J* = 8.6 Hz, 2H), 6.65 (d, *J* = 8.6 Hz, 2H), 6.56 (s, 1H), 6.48 (s, 1H), 5.95 (d, *J* = 6.8 Hz, 2H), 4.74 (s, 1H), 3.71 (s, 3H), 3.62 (q, *J* = 13.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 200.26, 159.13, 154.64, 148.28, 146.67, 142.59, 135.10, 132.47, 130.08, 129.68, 128.86, 122.57, 119.90, 113.80, 105.24, 101.56, 95.82, 93.62, 59.38, 55.28, 40.65; HRMS (ESI$^+$): calcd for $C_{24}H_{17}ClO_5$ $[M+Na]^+$ = 443.0662, found = 443.0642; The ee value was 93%, t_R (major) = 19.2 min, t_R (minor) = 21.7 min (Chiralcel IC, λ = 254 nm, hexane/2-propanol = 90/10, flow rate = 1.0 mL/min).

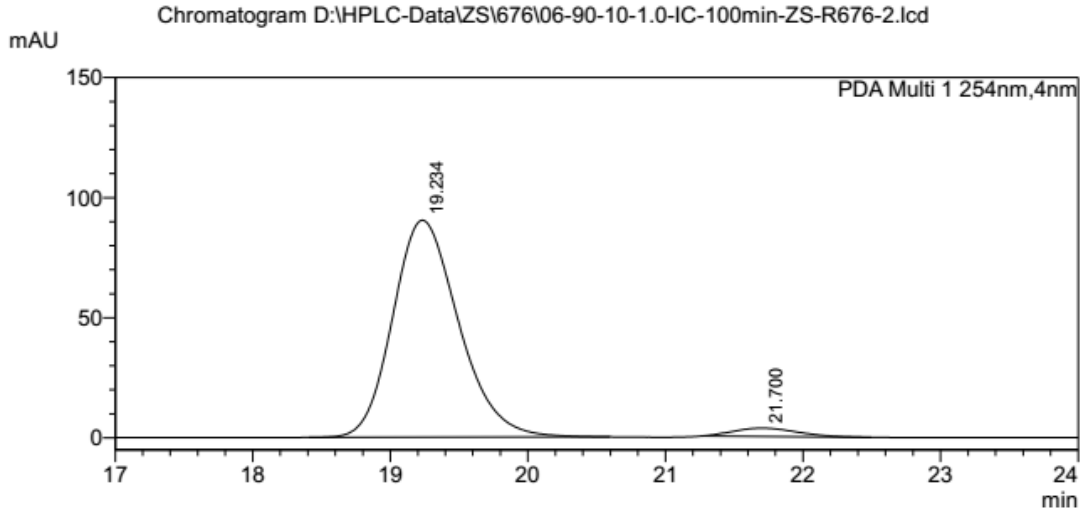


Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Height	Height%	Area	Area%
1	19.792	73191	51.937	2613577	50.471
2	22.415	67732	48.063	2564764	49.529
Total		140923	100.000	5178341	100.000

Racemic **3o**



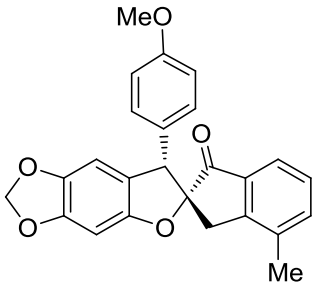
Peak Table

PDA Ch1 254nm

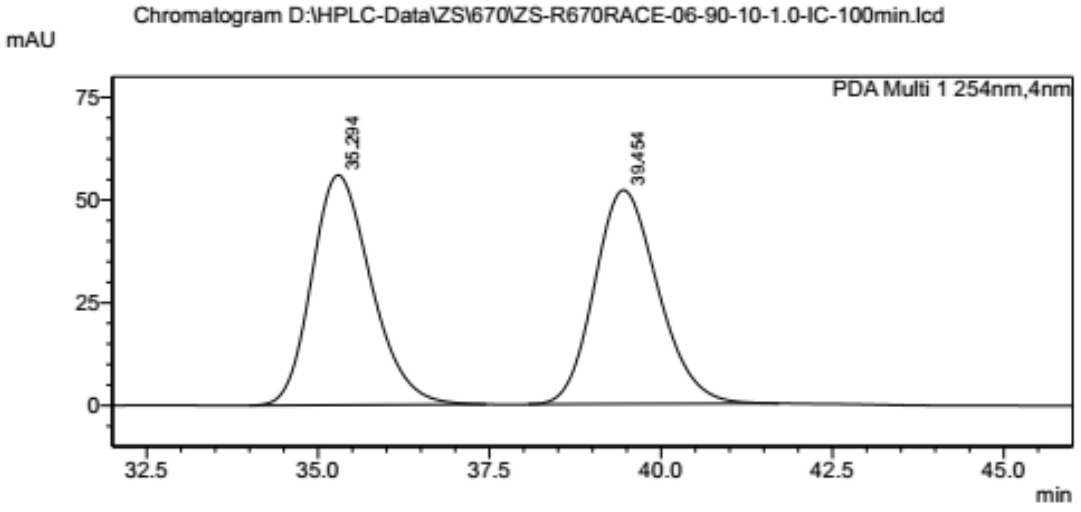
Peak#	Ret. Time	Height	Height%	Area	Area%
1	19.234	90373	96.279	3017138	96.366
2	21.700	3493	3.721	113768	3.634
Total		93866	100.000	3130906	100.000

Enantiomerically enriched **3o**

(2'R,7S)-7-(4-methoxyphenyl)-4'-methyl-7H-spiro[[1,3]dioxolo[4,5-f]benzofuran-6,2'-inden]-1'(3'H)-one (3p)



A white solid; 87% yield; $[\alpha]^{25}_{D}$ = -3.5 (c 0.4, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (d, *J* = 7.2 Hz, 1H), 7.24 (d, *J* = 9.5 Hz, 1H), 7.18 (t, *J* = 7.4 Hz, 1H), 6.83 (d, *J* = 8.7 Hz, 2H), 6.65 (d, *J* = 8.8 Hz, 2H), 6.56 (s, 1H), 6.49 (s, 1H), 5.94 (dd, *J* = 6.7, 1.3 Hz, 2H), 4.66 (s, 1H), 3.71 (s, 3H), 3.50 (d, *J* = 1.8 Hz, 2H), 2.36 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 200.86, 158.99, 154.73, 148.16, 147.77, 142.44, 136.04, 135.48, 135.27, 130.05, 129.41, 128.28, 121.80, 120.23, 113.67, 105.28, 101.49, 96.04, 93.62, 59.48, 55.23, 40.81, 17.99; HRMS (ESI^+): calcd for $C_{25}H_{20}O_5$ $[M+Na]^+$ = 423.1208, found = 423.1175; The ee value was 95%, t_R (major) = 35.6 min, t_R (minor) = 40.4 min (Chiralcel IC, λ = 254 nm, hexane/2-propanol = 90/10, flowrate = 1.0 mL/min).

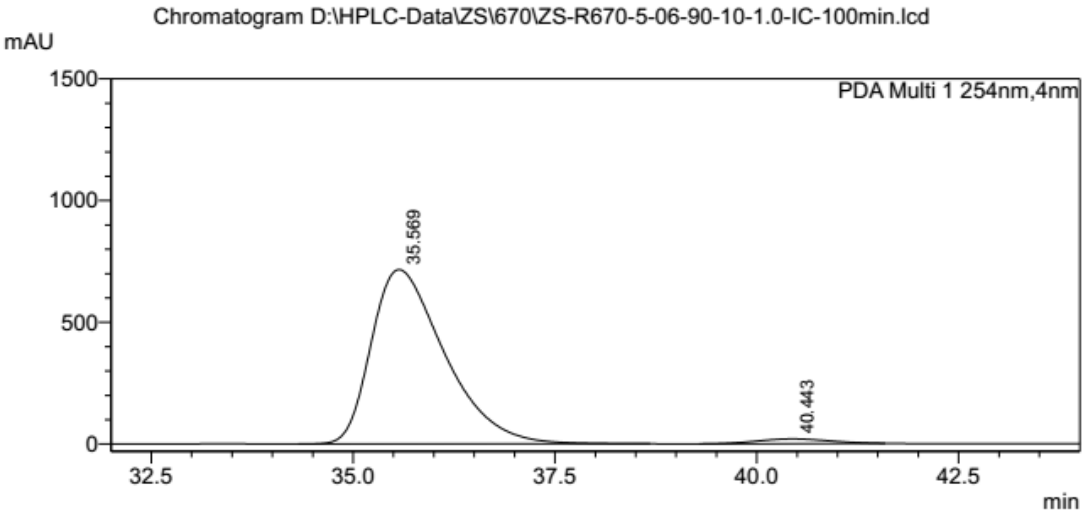


Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Height	Height%	Area	Area%
1	35.294	55964	51.810	3377175	50.121
2	39.454	52053	48.190	3360842	49.879
Total		108017	100.000	6738016	100.000

Racemic **3p**



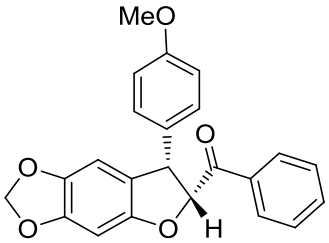
Peak Table

PDA Ch1 254nm

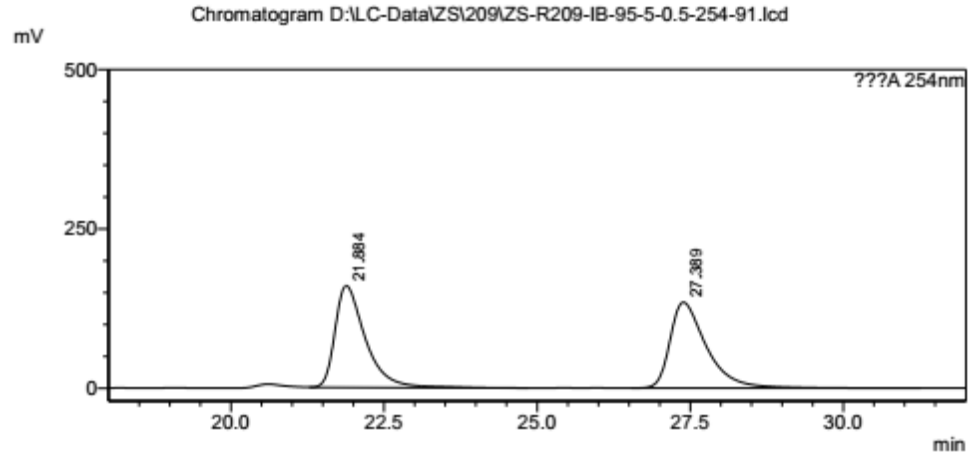
Peak#	Ret. Time	Height	Height%	Area	Area%
1	35.569	716103	97.382	45363126	97.448
2	40.443	19248	2.618	1188212	2.552
Total		735352	100.000	46551338	100.000

Enantiomerically enriched **3p**

((6R,7S)-7-(4-methoxyphenyl)-6,7-dihydro-[1,3]dioxolo[4,5-f]benzofuran-6-yl)(phenyl)methanone (3q)



A white solid; 85% yield; $[\alpha]^{25}_{D}$ = +58.5 (c 0.4, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (dd, *J* = 7.6, 1.0 Hz, 1H), 7.60 (tt, *J* = 7.4, 1.2 Hz, 1H), 7.45 (t, *J* = 7. 8 Hz, 2H), 7.14 (d, *J* = 8. 7 Hz, 2H), 6.87 (d, *J* = 8. 7 Hz, 2H), 6.55 (s, 1H), 6.42 (s, 1H), 5.89 (dd, *J* = 8.5, 1.3 Hz, 1H), 5.76 (d, *J* = 6.2 Hz, 1H), 4.78 (d, *J* = 6.2 Hz, 1H), 3.81 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$); δ 194.98, 159.08, 153.74, 148.12, 142.60, 134.51, 134.40, 133.92, 129.37, 129.17, 128.82, 120.55, 114.46, 105.09, 101.49, 93.36, 91.62, 55.45, 50.59; HRMS (ESI^+): calcd for $C_{24}H_{17}O_6Br$ $[M+Na]^+$ = 397.1052, found = 397.1023; The ee value was 87%, t_R (minor) = 20.3 min, t_R (major) = 25.7 min (Chiralcel IB, λ = 254 nm, hexane/2-propanol = 95/5, flow rate = 0.5 mL/min).

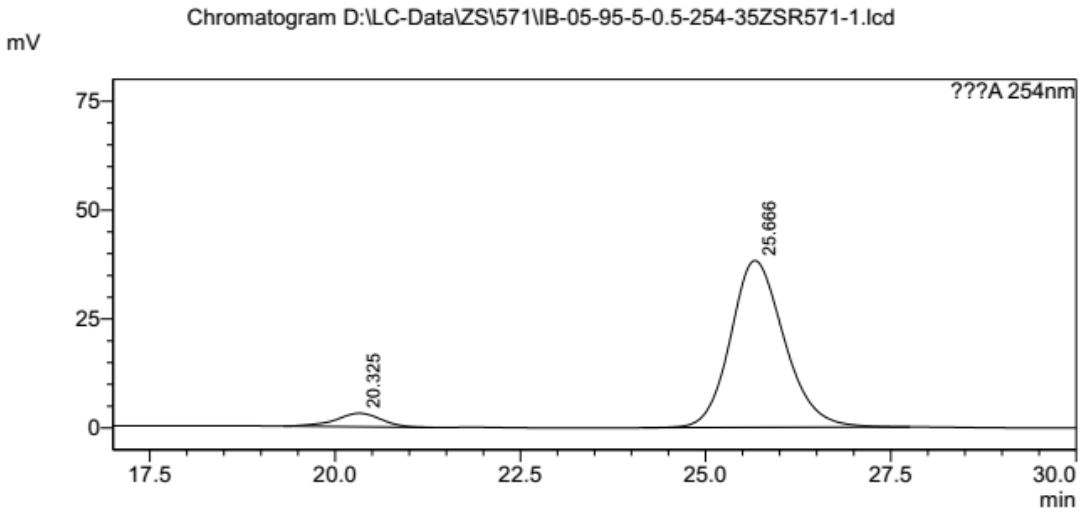


Peak Table

???A 254nm

Peak#	Ret. Time	Height	Height%	Area	Area%
1	21.884	159567	54.269	5492407	49.601
2	27.389	134463	45.731	5580842	50.399
Total		294030	100.000	11073249	100.000

Racemic **3q**



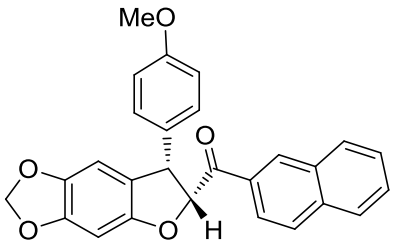
Peak Table

???A 254nm

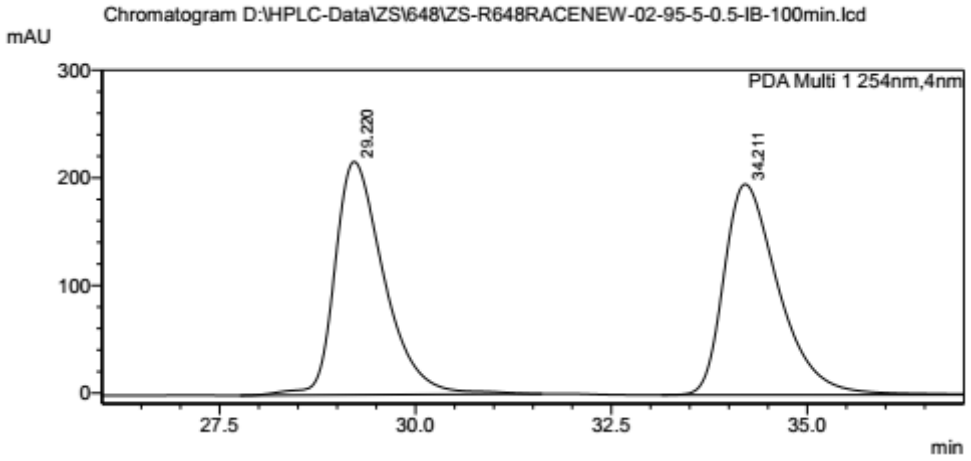
Peak#	Ret. Time	Height	Height%	Area	Area%
1	20.325	3100	7.489	133267	6.432
2	25.666	38292	92.511	1938686	93.568
Total		41392	100.000	2071953	100.000

Enantiomerically enriched **3q**

((6R,7S)-7-(4-methoxyphenyl)-6,7-dihydro-[1,3]dioxolo[4,5-f]benzofuran-6-yl)(naphthalen-2-yl)methanone (3r)



A white solid; 89% yield; $[\alpha]^{25}_{D}$ = +24.8 (c 0.4, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.34 (s, 1H), 8.02 (dd, *J* = 8.6, 1.7 Hz, 1H), 7.89 (t, *J* = 8.0 Hz, 2H), 7.82 (d, *J* = 8.1 Hz, 1H), 7.62 (ddd, *J* = 8.1, 6.9, 1.2 Hz, 1H), 7.54 (ddd, *J* = 8.1, 7.1, 1.1 Hz, 1H), 7.17 (d, *J* = 8.7 Hz, 2H), 6.88 (d, *J* = 8.7 Hz, 2H), 6.58 (s, 1H), 6.43 (s, 1H), 5.92 (d, *J* = 4.6 Hz, 1H), 5.90 (dd, *J* = 9.4, 1.3 Hz, 2H), 4.83 (d, *J* = 6.4 Hz, 1H), 3.82 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$); δ 194.91, 159.18, 153.88, 148.18, 142.65, 136.12, 134.60, 132.47, 131.68, 131.65, 129.87, 129.35, 129.05, 128.74, 127.96, 127.03, 124.57, 120.58, 114.53, 105.13, 101.51, 93.41, 91.84, 55.50, 50.97; HRMS (ESI^+): calcd for $C_{27}H_{20}O_5$ $[M+Na]^+$ = 447.1208, found = 447.1189; The ee value was 86%, t_R (minor) = 29.5 min, t_R (major) = 34.4 min (Chiralcel IB, λ = 254 nm, hexane/2-propanol = 95/5, flow rate = 0.5 mL/min).

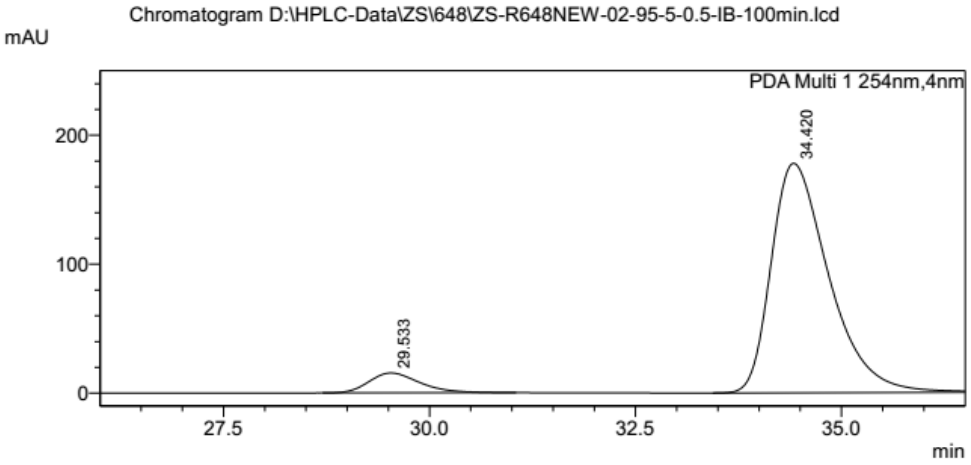


Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Height	Height%	Area	Area%
1	29.220	216626	52.530	9468295	49.748
2	34.211	195759	47.470	9564070	50.252
Total		412385	100.000	19032365	100.000

Racemic **3r**



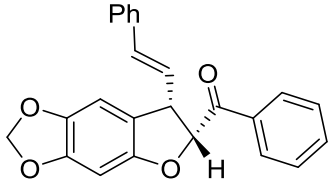
Peak Table

PDA Ch1 254nm

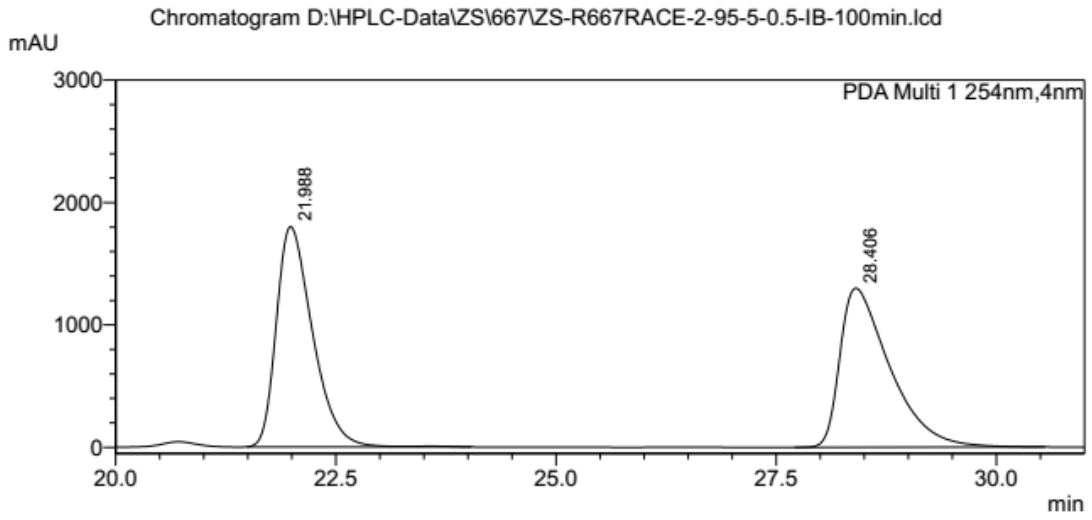
Peak#	Ret. Time	Height	Height%	Area	Area%
1	29.533	15362	7.946	659014	7.050
2	34.420	177958	92.054	8688613	92.950
Total		193321	100.000	9347627	100.000

Enantiomerically enriched **3r**

phenyl((6R,7S)-7-((E)-styryl)-6,7-dihydro-[1,3]dioxolo[4,5-f]benzofuran-6-yl)methanone (3s)



A white solid; 91% yield; $[\alpha]^{25}_{D}$ = +39.0 (c 0.4, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (dd, *J* = 7.2, 1.4 Hz, 2H), 7.61 (tt, *J* = 7.4, 1.2 Hz, 1H), 7.49 (t, *J* = 7.9 Hz, 2H), 7.38 (d, *J* = 7.0 Hz, 2H), 7.33 (t, *J* = 7.1 Hz, 2H), 7.27 (m, 1H), 6.59 (s, 1H), 6.53 (d, *J* = 15.7 Hz, 1H), 6.52 (s, 1H), 6.34 (dd, *J* = 15.6, 8.7 Hz, 1H), 5.91 (dd, *J* = 7.6, 1.3 Hz, 2H), 5.73 (d, *J* = 6.4 Hz, 1H), 4.43 (dd, *J* = 8.6, 6.5 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.91, 153.61, 148.33, 142.53, 136.50, 134.43, 133.98, 132.72, 129.38, 128.93, 128.88, 128.80, 128.07, 126.61, 118.82, 105.15, 101.55, 93.59, 89.10, 49.58; HRMS (ESI^+): calcd for $C_{24}H_{18}O_4$ $[M+Na]^+$ = 393.1103, found = 393.1070; The ee value was 80%, t_R (minor) = 21.9 min, t_R (major) = 28.1 min (Chiralcel IB, λ = 254 nm, hexane/2-propanol = 95/5, flow rate = 0.5 mL/min).

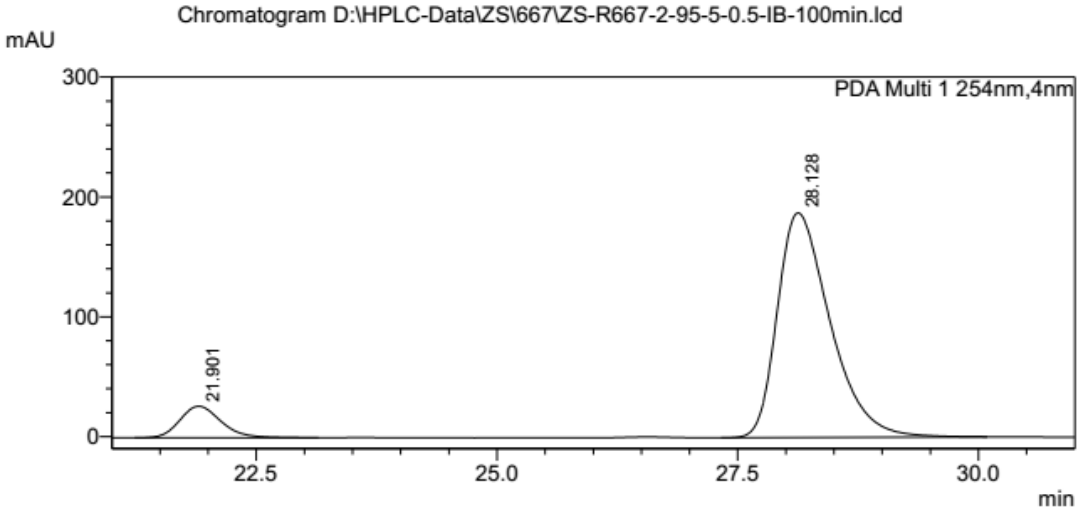


Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Height	Height%	Area	Area%
1	21.988	1798883	58.052	51508843	50.126
2	28.406	1299838	41.948	51249211	49.874
Total		3098722	100.000	102758054	100.000

Racemic **3s**



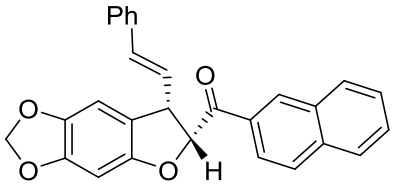
Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Height	Height%	Area	Area%
1	21.901	26291	12.299	781036	9.840
2	28.128	187469	87.701	7155923	90.160
Total		213760	100.000	7936959	100.000

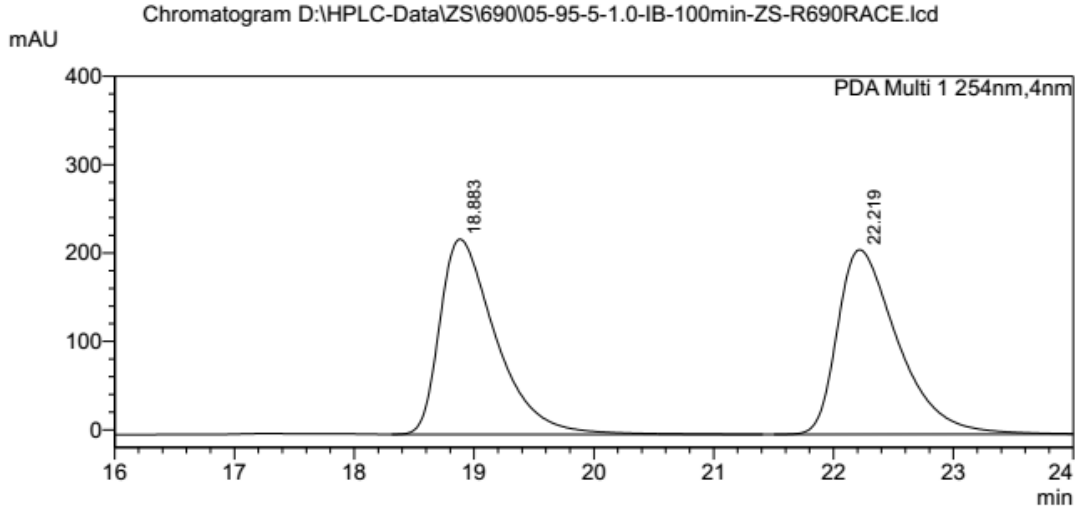
Enantiomerically enriched **3s**

naphthalen-2-yl((6R,7S)-7-((E)-styryl)-6,7-dihydro-[1,3]dioxolo[4,5-f]benzofuran-6-yl)methanone (3t)



A white solid 92% yield; $[\alpha]^{25}_{D}$ = +21.5 (c 0.4, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.57 (s, 1H), 8.09 (dd, *J* = 8.6, 1.7 Hz, 1H), 7.95–7.88 (m, 3H), 7.66–7.60 (m, 1H), 7.58–7.52 (m, 1H), 7.41–7.36 (m, 2H), 7.33 (t, *J* = 7.4 Hz, 2H), 7.30 – 7.26 (m, 1H), 6.63–6.53 (m, 3H), 6.45–6.37 (m, 3H), 5.92 (dd, *J* = 8.4, 1.2 Hz, 2H), 5.88 (d, *J* = 6.3 Hz, 1H), 4.50 (dd, *J* = 8.5, 6.5 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.16, 153.88, 148.48, 142.60, 136.24, 135.93, 133.32, 132.72, 132.58, 130.09, 129.76, 128.93, 128.89, 128.43, 127.97, 127.75, 127.08, 126.55, 126.46, 123.98, 119.18, 105.15, 101.57, 93.95, 88.01, 50.36; HRMS (ESI$^+$): calcd for $C_{28}H_{20}O_4$ $[M+Na]^+$ = 443.1259, found = 443.1260; The ee value was 90%, t_R (minor) = 19.8 min, t_R (major)

= 23.8 min (Chiralcel IB, λ = 254 nm, hexane/2-propanol = 95/5, flow rate = 0.5 mL/min).

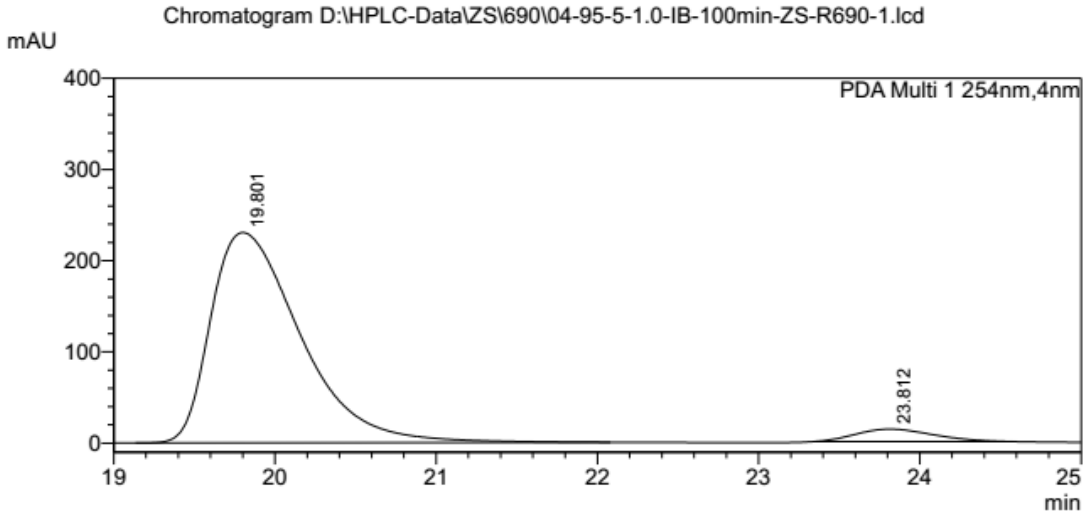


Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Height	Height%	Area	Area%
1	18.883	220909	51.400	7206128	49.508
2	22.219	208877	48.600	7349370	50.492
Total		429786	100.000	14555498	100.000

Racemic **3t**



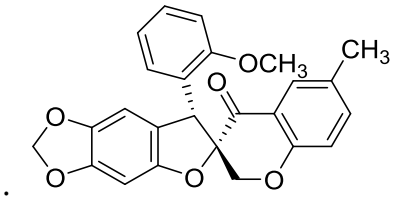
Peak Table

PDA Ch1 254nm

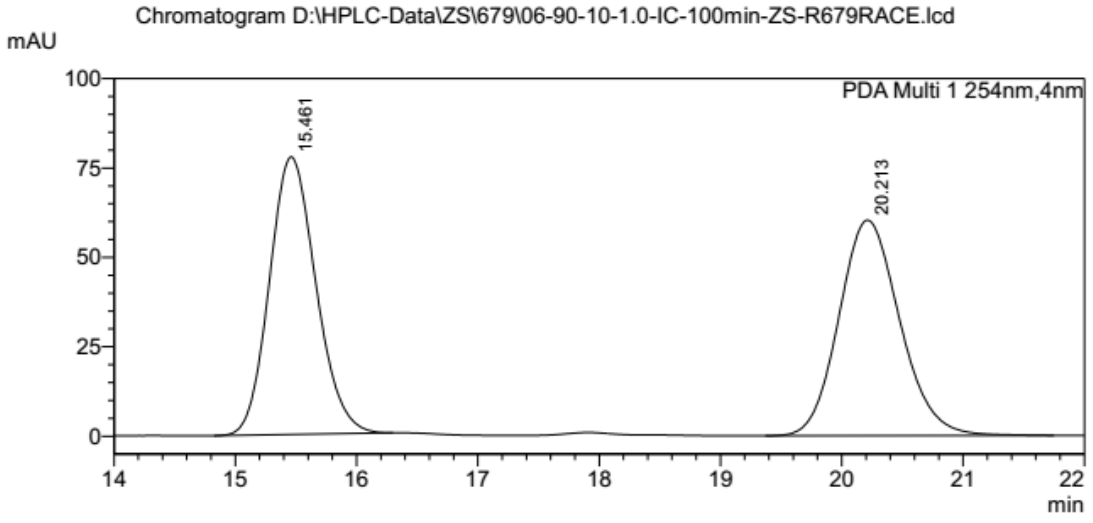
Peak#	Ret. Time	Height	Height%	Area	Area%
1	19.801	230611	94.415	8932799	95.146
2	23.812	13641	5.585	455758	4.854
Total		244251	100.000	9388557	100.000

Enantiomerically enriched **3t**

(3S,7'S)-7'-(2-methoxyphenyl)-6-methyl-7'H-spiro[chromane-3,6'-[1,3]dioxolo[4,5-f]benzofuran]-4-one (3u)



A white solid; 90% yield; $[\alpha]^{25}_{D}$ = +57.0 (c 0.4, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (d, *J* = 1.4 Hz, 1H), 7.31 (m, 2H), 6.91 (m, 2H), 6.83 (m, 2H), 6.53 (s, 1H), 6.45 (s, 1H), 5.92 (dd, *J* = 18.1, 1.2 Hz, 2H), 5.64 (s, 1H), 4.11 (d, *J* = 12.6 Hz, 1H), 3.90 (d, *J* = 12.6 Hz, 1H), 3.63 (s, 3H), 2.34 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$); δ 187.30, 159.27, 157.43, 153.07, 148.09, 142.71, 137.40, 131.29, 129.99, 129.03, 127.93, 126.13, 120.82, 119.39, 119.00, 117.73, 110.15, 105.62, 101.50, 93.43, 86.46, 70.82, 55.25, 43.20, 20.58; HRMS (ESI^+): calcd for $C_{25}H_{20}O_6$ $[M+Na]^+$ = 439.1158, found = 439.1133; The ee value was 85%, t_R (minor) = 15.5 min, t_R (major) = 20.2 min (Chiralcel IC, λ = 254 nm, hexane/2-propanol = 90/10, flow rate = 1.0 mL/min).

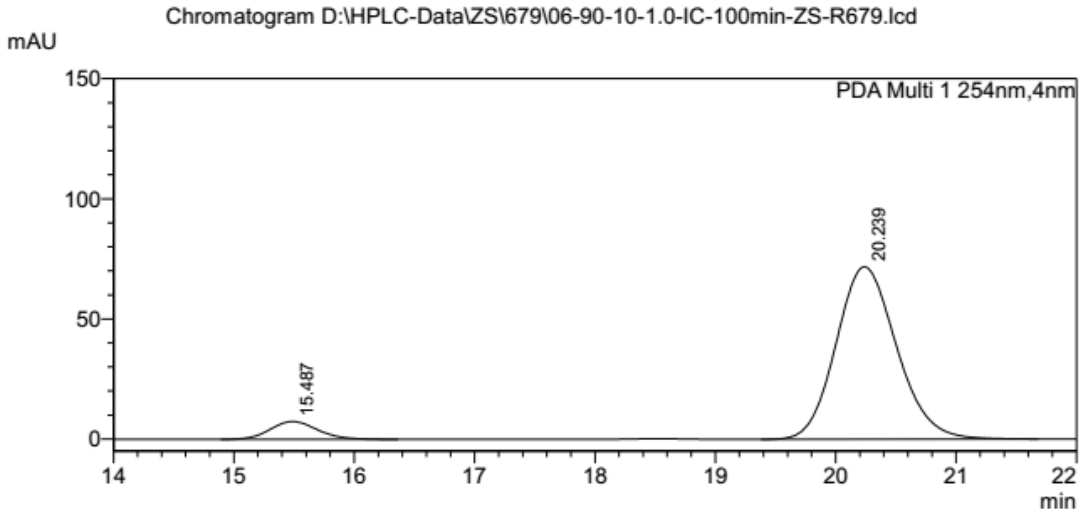


Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Height	Height%	Area	Area%
1	15.461	77610	56.283	2068104	49.592
2	20.213	60283	43.717	2102132	50.408
Total		137894	100.000	4170236	100.000

Racemic **3u**



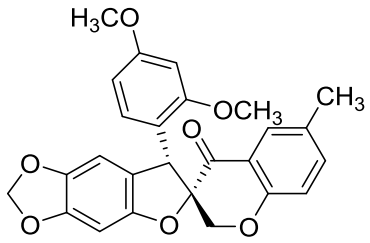
Peak Table

PDA Ch1 254nm

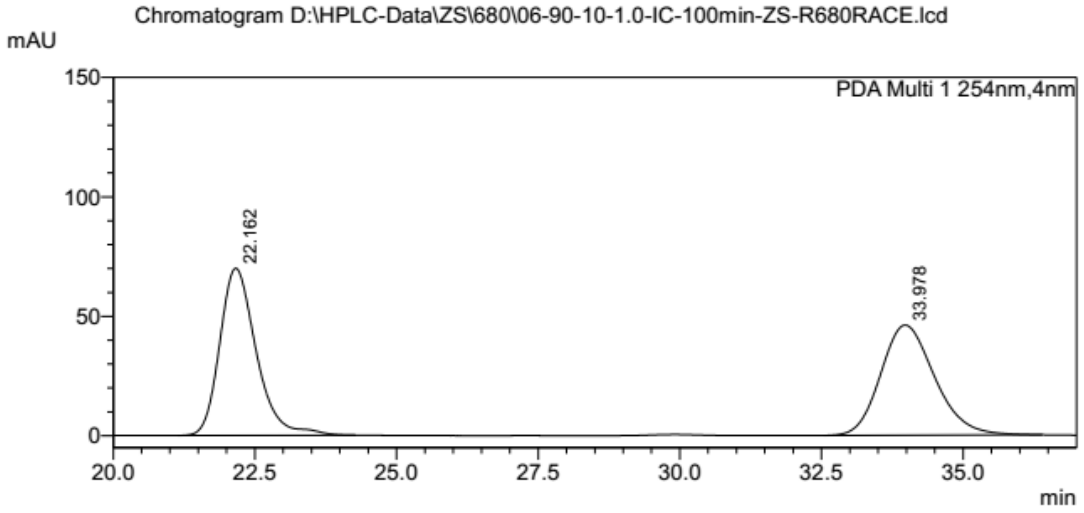
Peak#	Ret. Time	Height	Height%	Area	Area%
1	15.487	7445	9.398	203835	7.495
2	20.239	71770	90.602	2515758	92.505
Total		79215	100.000	2719593	100.000

Enantiomerically enriched **3u**

(3S,7'S)-7'-(2,4-dimethoxyphenyl)-6-methyl-7'H-spiro[chromane-3,6'-[1,3]dioxolo[4,5-f]benzofuran]-4-one (3v)



A white solid 93% yield; $[\alpha]^{25}_{D}$ = +36.8 (c 0.4, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, *J* = 1.3 Hz, 1H), 7.30 (dd, *J* = 8.5, 2.2 Hz, 1H), 6.82 (m, 2H), 6.52 (s, 1H), 6.44 (s, 1H), 6.41 (s, 1H), 5.91 (dd, *J* = 18.2, 1.0 Hz, 2H), 5.53 (s, 1H), 4.12 (d, *J* = 12.6 Hz, 1H), 3.90 (d, *J* = 12.6 Hz, 1H), 3.80 (s, 3H), 3.60 (s, 3H), 2.33 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 187.58, 160.59, 159.32, 158.45, 153.02, 148.03, 142.69, 137.36, 131.25, 130.52, 127.91, 119.03, 118.53, 117.72, 105.60, 104.34, 101.48, 98.28, 93.39, 86.50, 70.81, 55.51, 55.28, 42.88, 20.57; HRMS (ESI^+): calcd for $C_{26}H_{22}O_7$ $[M+Na]^+$ = 469.1263, found = 469.1241; The ee value was 88%, t_R (minor) = 20.6 min, t_R (major) = 31.2 min (Chiralcel IC, λ = 254 nm, hexane/2-propanol = 90/10, flow rate = 1.0 mL/min).

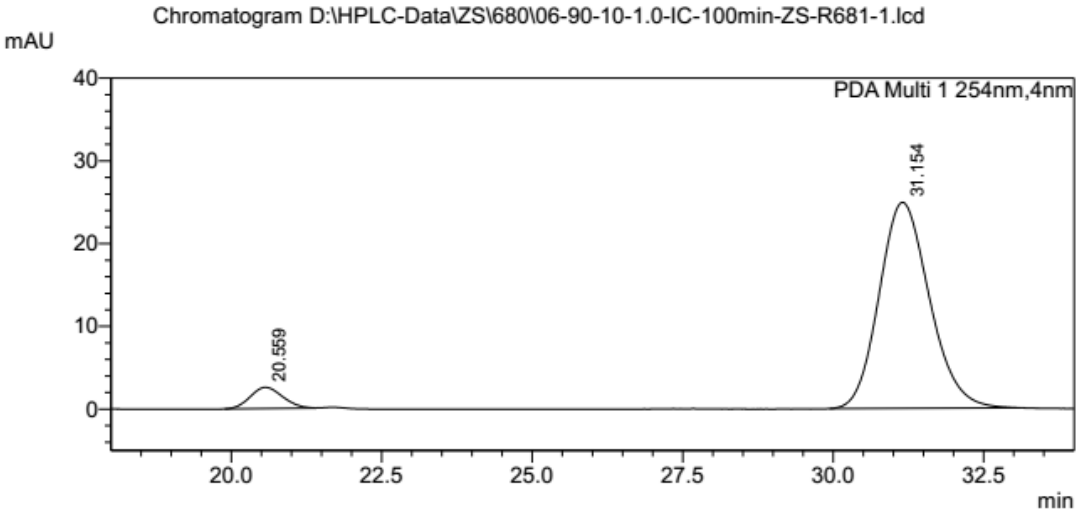


Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Height	Height%	Area	Area%
1	22.162	69966	60.287	3136348	50.659
2	33.978	46090	39.713	3054748	49.341
Total		116056	100.000	6191097	100.000

Racemic **3v**



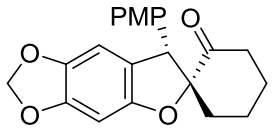
Peak Table

PDA Ch1 254nm

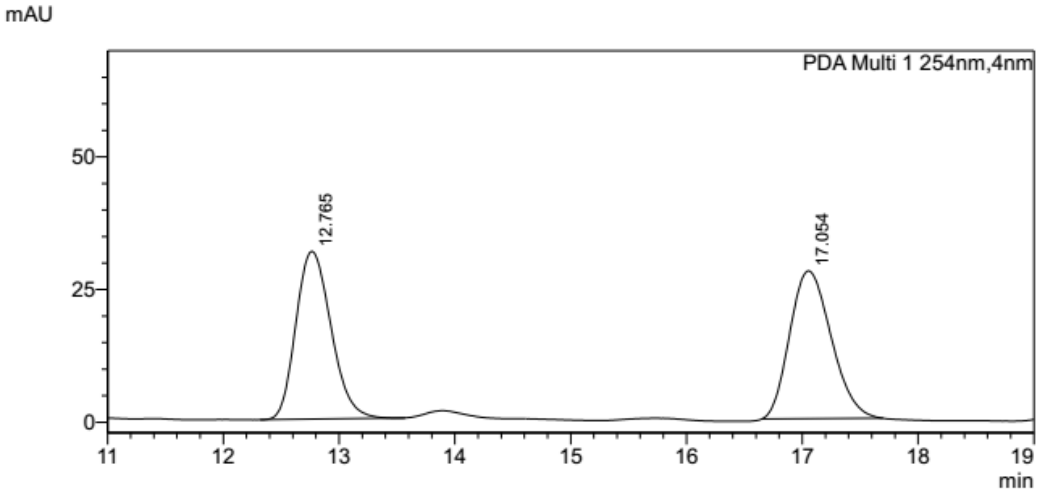
Peak#	Ret. Time	Height	Height%	Area	Area%
1	20.559	2552	9.299	95111	6.164
2	31.154	24893	90.701	1447969	93.836
Total		27445	100.000	1543081	100.000

Enantiomerically enriched **3v**

(1R,7'S)-7'-(4-methoxyphenyl)-7'H-spiro[cyclohexane-1,6'-[1,3]dioxolo[4,5-f]benzofuran]-2-one (3w)



A white oil; 88% yield; $[\alpha]^{25}_{D}$ = +38.4 (c 0.4, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.98 (d, *J* = 8.4 Hz, 2H), 6.82 (d, *J* = 8.7 Hz, 2H), 6.46 (s, 1H), 6.45 (s, 1H), 5.88 (d, *J* = 13.5 Hz, 2H), 5.11 (s, 1H), 3.78 (s, 3H), 2.98 (td, *J* = 12.6, 5.8 Hz, 1H), 2.47 (dt, *J* = 12.9, 3.7 Hz, 1H), 2.08–1.52 (m, 5H), 1.21–1.09 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 208.19, 159.05, 152.53, 147.98, 142.53, 131.37, 130.86, 121.59, 114.04, 105.90, 101.53, 95.05, 93.24, 55.56, 48.84, 39.28, 36.39, 27.84, 21.69; HRMS (ESI^+): calcd for $C_{21}H_{20}O_5$ $[M+Na]^+$ = 375.1208, found = 375.1209; The ee value was 76%, t_R (minor) = 15.0 min, t_R (major) = 17.8 min (Chiralcel IB, λ = 254 nm, hexane/2-propanol =95/5, flow rate = 0.5 mL/min).

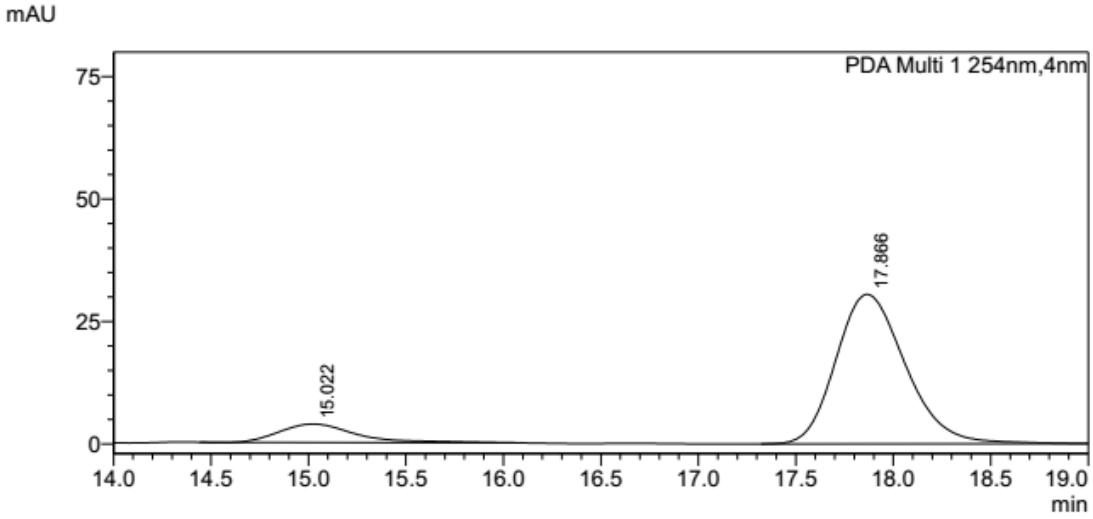


Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Height	Height%	Area	Area%
1	12.765	31625	53.151	669378	49.053
2	17.054	27875	46.849	695219	50.947
Total		59500	100.000	1364597	100.000

Racemic **3w**



Peak Table

PDA Ch1 254nm

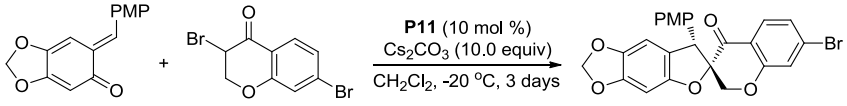
Peak#	Ret. Time	Height	Height%	Area	Area%
1	15.022	3774	11.003	103409	11.999
2	17.866	30522	88.997	758419	88.001
Total		34296	100.000	861827	100.000

Enantiomerically enriched **3w**

5. Scale-up Synthesis and Synthetic Elaboration of Product

(i). General procedure of scale-up synthesis

Procedure for scale-up synthesis of 3h

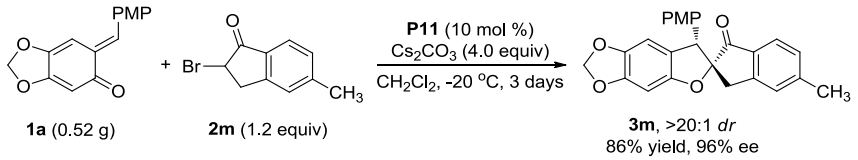


1a (0.31 g) **2h** (1.2 equiv) **3h**, >20:1 *dr*
86% yield, 94% ee

To a round bottle flask with a magnetic stirring bar were added *ortho*-quinone methids **1a** (0.31 g, 1.21 mmol), α-bromoacetophenone **2a** (0.44 g, 1.45 mmol), phosphonium salt **P11** (95.6 mg, 0.121 mmol) and Cs_2CO_3 (1.58 g, 4.84 mmol), followed by the addition of dry DCM (15 mL). The reaction mixture was stirred at -20 ^oC for 3 days. Then, the reaction was added H_2O (10 mL), and the mixture was extracted with DCM (10 mL x 3), dried over Na_2SO_4, and the solvent was removed

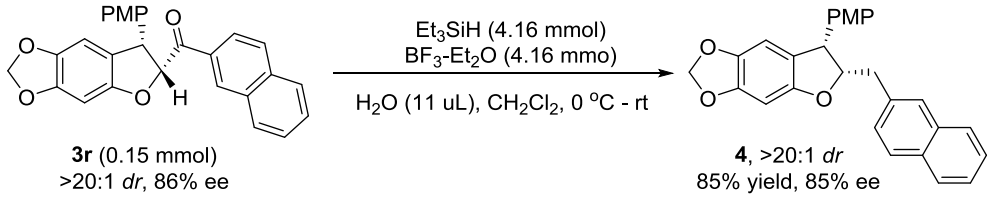
under reduced pressure, and the residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 20:1) to give **3h** (0.5 g, 86% yield, > 20:1 dr, 94% ee) as a white solid.

Procedure for scale-up synthesis of 3m

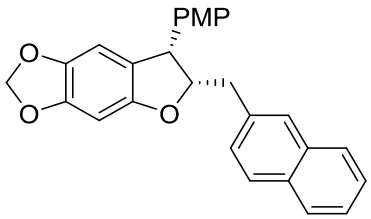


To a round bottle flask with a magnetic stirring bar were added ortho-quinone methids 1a (0.31 g, 1.21 mmol), α-bromoacetophenone **2a** (0.33 g, 1.45 mmol), phosphonium salt **P11** (95.6 mg, 0.121 mmol) and Cs_2CO_3 (1.58 g, 4.84 mmol), followed by the addition of dry DCM (15 mL). The reaction mixture was stirred at -20 ^oC for 3 days. Then, the reaction was added H_2O (10 mL), and the mixture was extracted with DCM (10 mL x 3), dried over Na_2SO_4, and the solvent was removed under reduced pressure, and the residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 20:1) to give **3m** (0.42 g, 86% yield, > 20:1 dr, 96% ee) as a white solid.

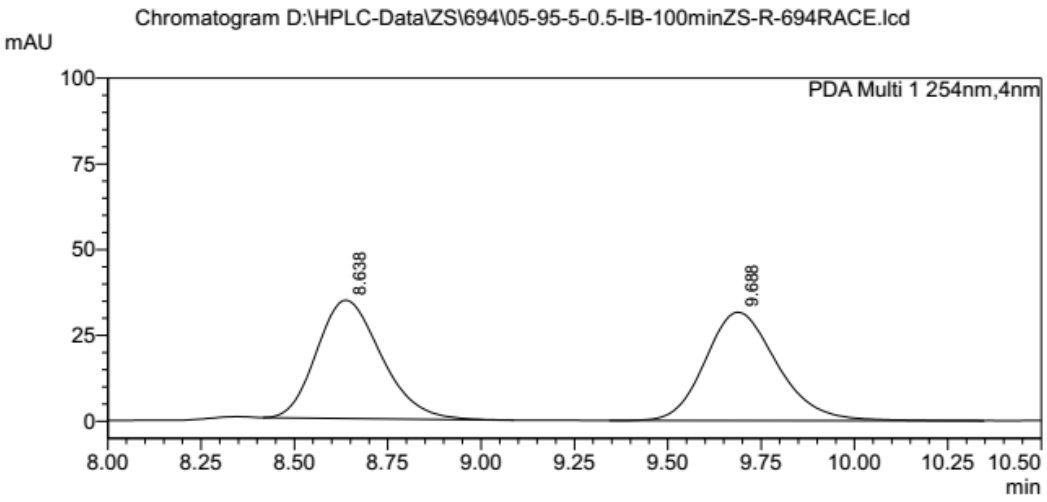
(ii). Synthetic elaboration of product



<u>(6S,7S)-7-(4-methoxyphenyl)-6-(naphthalen-2-ylmethyl)-6,7-dihydro-[1,3]dioxolo[4,5-f]benzofuran (4)</u>



Under nitrogen atmosphere, a flame-dried round bottle flask with a magnetic stirring bar were added **3r** (with > 20:1 dr and 86% ee, 63.7 mg, 0.15 mmol), and dry DCM (2 mL), after cooling to 0 ^{o}C, Et_3SiH (484 mg, 4.16 mmol), $BF_3.(Et)_2O$ (48% wt, 589 mg, 4.16 mmol) and H_2O (10.8 mg, 0.6 mmol) were added, after stired for 20 min at 0 ^{o}C, the solution was heated to 40 ^{o}C for 12 h. The reaction was cooled to room temperature and H_2O (3 mL) was added. the mixture was extracted with DCM (5 mL x 3), dried over Na_2SO_4, and the solvent was removed under reduced pressure, the residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1) to give **4** (52.3 mg, 85% yield, > 20:1 dr, 86% ee) as a white solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (m, 3H), 7.71 (s, 1H), 7.45 (m, 2H), 7.39 (dd, *J* = 8.4, 1.4 Hz, 1H), 7.00 (d, *J* = 8.6 Hz, 2H), 6.81 (d, *J* = 8.6 Hz, 2H), 6.46 (s, 1H), 6.40 (s, 1H), 5.88 (dd, *J* = 3.8, 1.0 Hz, 2H), 4.88 (td, *J* = 7.5, 5.2 Hz, 1H), 4.25 (d, *J* = 7.6 Hz, 1H), 3.78 (s, 3H), 3.26 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.80, 154.30, 147.77, 141.87, 135.05, 134.65, 133.65, 132.46, 129.18, 128.15, 128.00, 127.77, 127.73, 126.12, 125.62, 121.78, 114.27, 105.36, 101.26, 93.24, 93.00, 55.40, 53.27, 40.90; ESI-HRMS: calcd for $C_{27}H_{22}O_4$ $[M+Na]^+$ = 433.1416, found = 433.1394; t_R (minor) = 8.9 min, t_R (major) = 9.9 min (Chiralcel IB, λ = 254 nm, hexane/2-propanol = 95/5, flow rate = 0.5 mL/min).

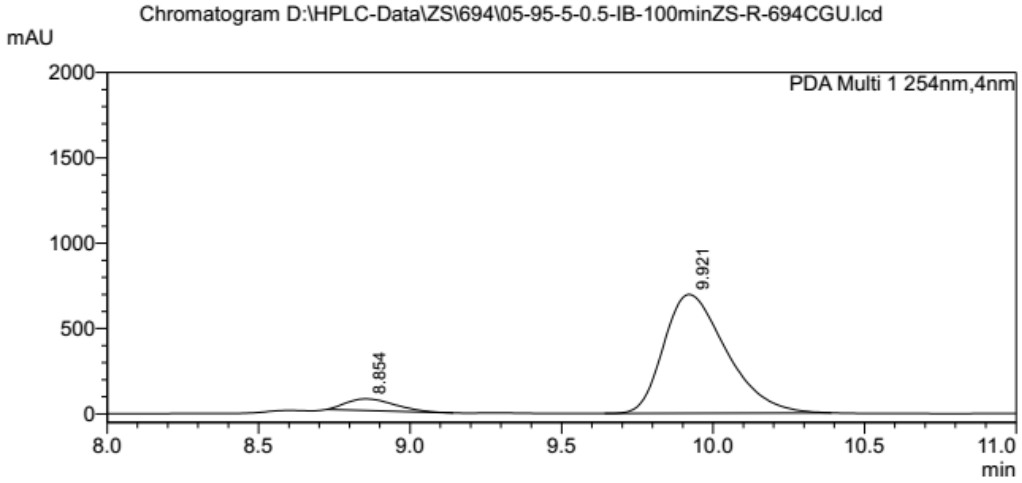


Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Height	Height%	Area	Area%
1	8.638	34489	52.195	414442	49.517
2	9.688	31588	47.805	422535	50.483
Total		66077	100.000	836976	100.000

Racemic **4**



Peak Table

PDA Ch1 254nm

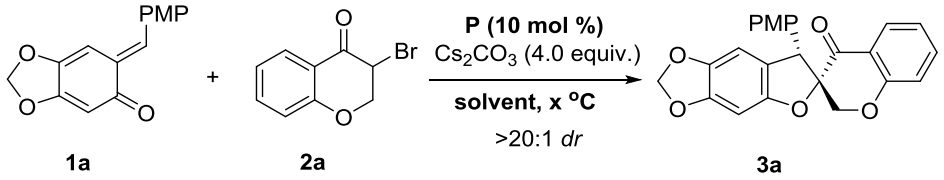
Peak#	Ret. Time	Height	Height%	Area	Area%
1	8.854	68232	8.919	752613	6.985
2	9.921	696787	91.081	10022802	93.015
Total		765019	100.000	10775415	100.000

Enantiomerically enriched **4**

6. Mechanism Studies and Proposed Transition State Models

The methylated catalysts **P11'** was prepared and used for the asymmetric reaction, for testing the reactivities and enantioselectivities. The results were listed in the following table.

Table S5. Asymmetric [4+1] cycloaddition promoted by different phosphonium salts in different solvents and the proposed transition state models.[a]



Entry	P	Solvent	T (°C)	Time (h)	Yield (%)[b]	ee (%)[c]
1	**11**	DCM	rt	12	78	79
2	**11**	MeOH	rt	6	58	1
3	**11**	DCM	-20	64	90	94
4	**11'**	DCM	-20	64	40	37

[a] Reaction conditions: **1a** (0.2 mmol), **2a** (0.24 mmol), **P** (10 mol %), Cs_2CO_3 (4.0 equiv.) and solvent (2.0 mL) were stirred for 6 h-64 h. [b] Isolated yields. [c] The ee value was determined by chiral HPLC. PMP = *p*-methoxyphenyl.

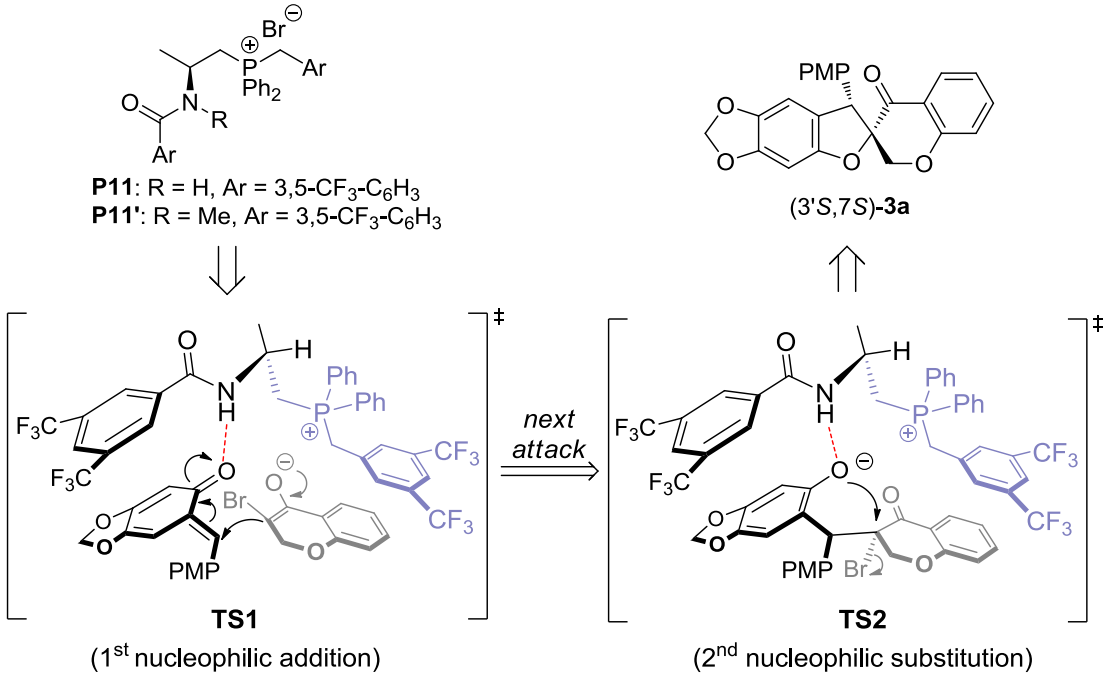


Figure S1. Proposed transition state models.

7. Crystallographic Data of 3m

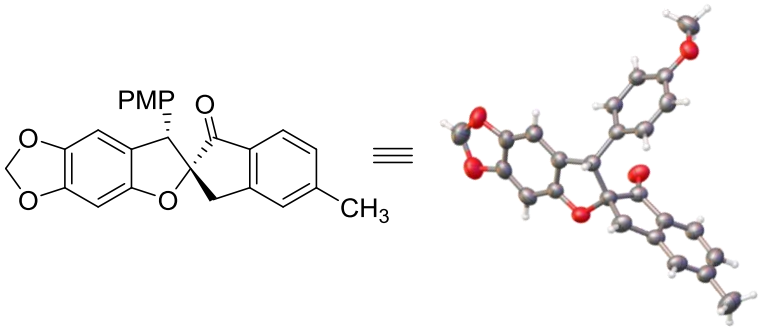


Figure S2. X-ray structure of **3m** (CCDC 1876074)

Empirical formula	C25H18O5
Formula weight	398.39
Temperature/K	293.8(4)
Crystal system	monoclinic
Space group	P21
a/Å	11.6007(8)
b/Å	5.7368(5)
c/Å	15.0074(10)
α/°	90

β/°	101.620(7)
γ/°	90
Volume/Å3	978.29(13)
Z	2
ρcalcg/cm3	1.352
μ/mm-1	0.773
F(000)	416.0
Crystal size/mm3	0.7 × 0.3 × 0.1
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	7.78 to 146.36
Index ranges	-14 ≤ h ≤ 13, -6 ≤ k ≤ 6, -18 ≤ l ≤ 18
Reflections collected	10155
Independent reflections	3452 [Rint = 0.0406, Rsigma = 0.0364]
Data/restraints/parameters	3452/1/273
Goodness-of-fit on F2	1.039

Final R indexes [I>=2σ (I)]	R1 = 0.0579, wR2 = 0.1605
Final R indexes [all data]	R1 = 0.0635, wR2 = 0.1702
Largest diff. peak/hole / e Å-3	0.41/-0.23
Flack parameter	-0.04(19)

8. References

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

[2] S. Wen, X. Li, W. Yao, A. Waheed, N. Ullah, Y. Lu, Eur. J. Org. Chem., 2016, **2016**, 4298.

[3] J. Zhang, H. Wang, Q. Jin, C. Zheng, G. Zhao, Y. Shang, *Org. Lett.*, 2016, **18**, 4774.

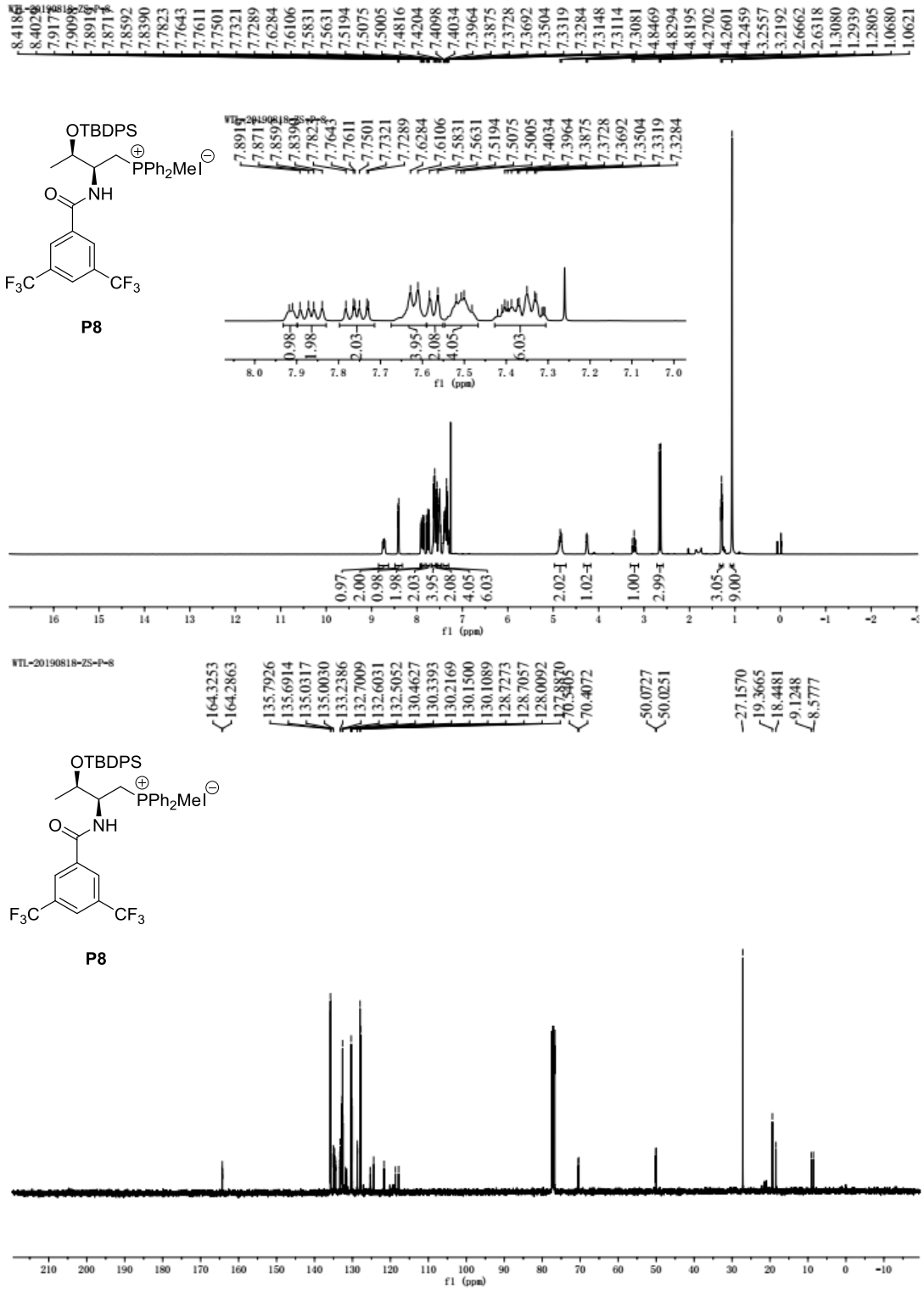
[4] J. Pan, J. Wu, H. Zhang, X. Ren, J. Tan, L. Zhu, H. Zhang, C. Jiang, T. Wang, *Angew. Chem. Int. Ed.*, 2019, **58**, 7425.

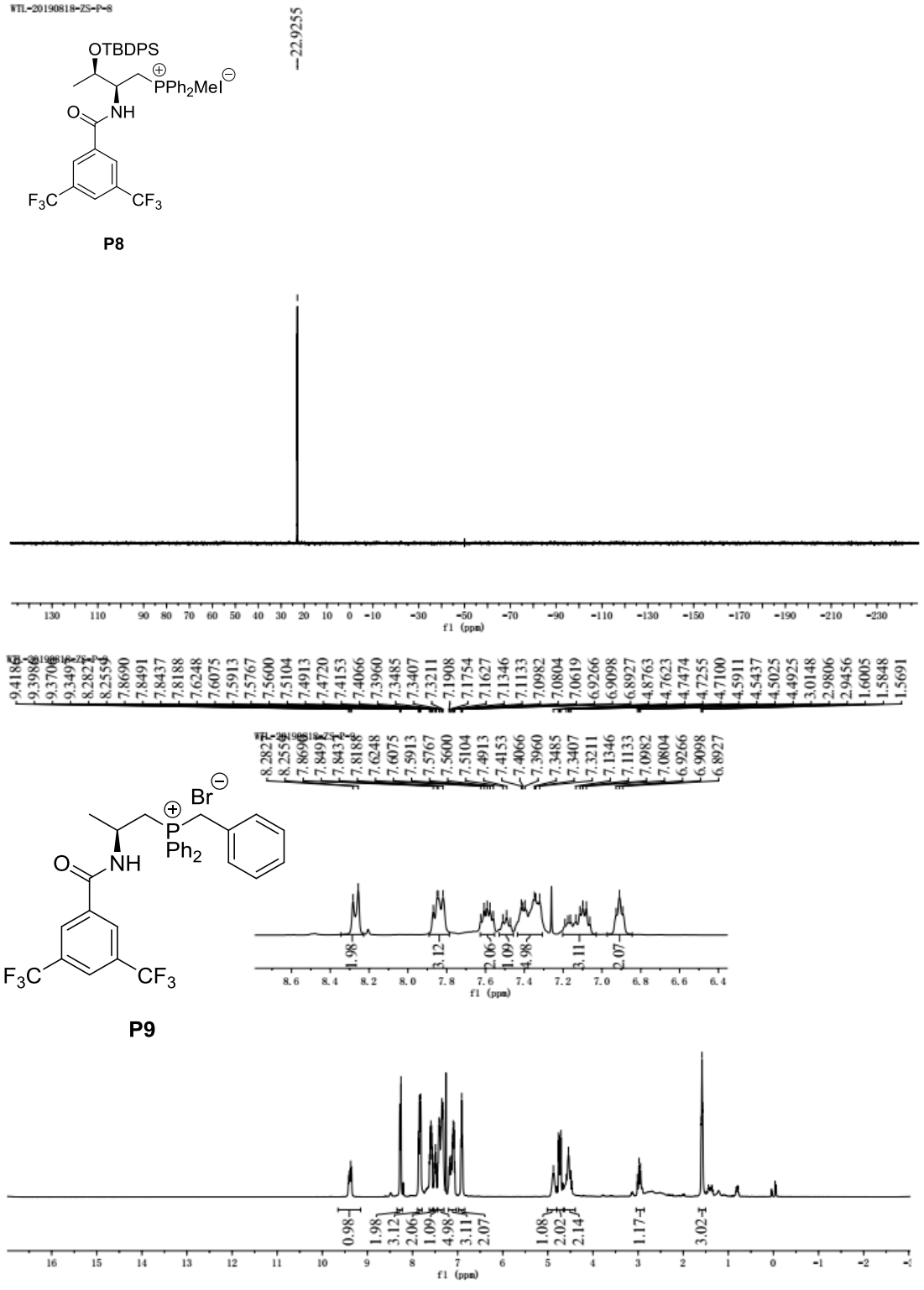
[5] a) L. Jurd, *Tetrahedron.*, 1977, **33**, 16; b) P. N. Moquist, Moquist, T. Moquist, S. E. Schaus, *Angew. Chem. Int. Ed.* 2010, **49**, 7096.

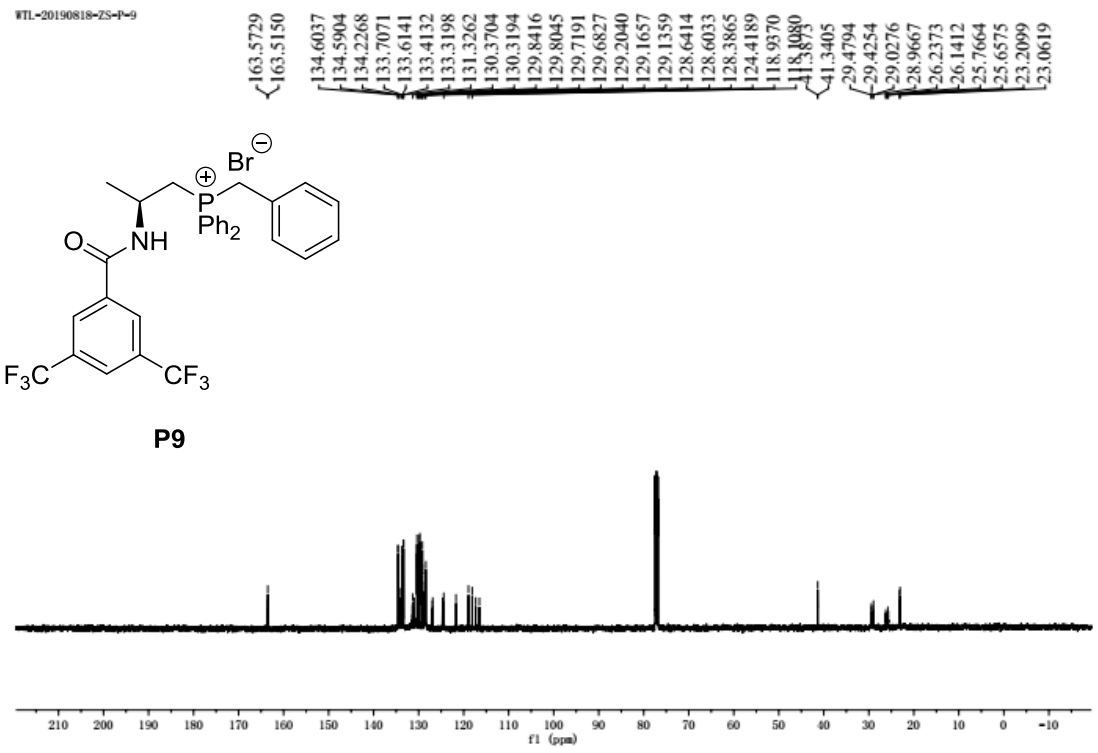
[6] a) T. A. Salama, Z. Novak, *Tetrahedron Lett.*, 2011, **52**, 4026; b) T. Maji, A. c) Karmakar, O. Reiser, *J. Org. Chem.*, 2011, **76**, 736; d) K. Mal, A. Sharma, P.R Maulik, I. Das, *Chem. Eur. J.*, 2014, **20**, 662;

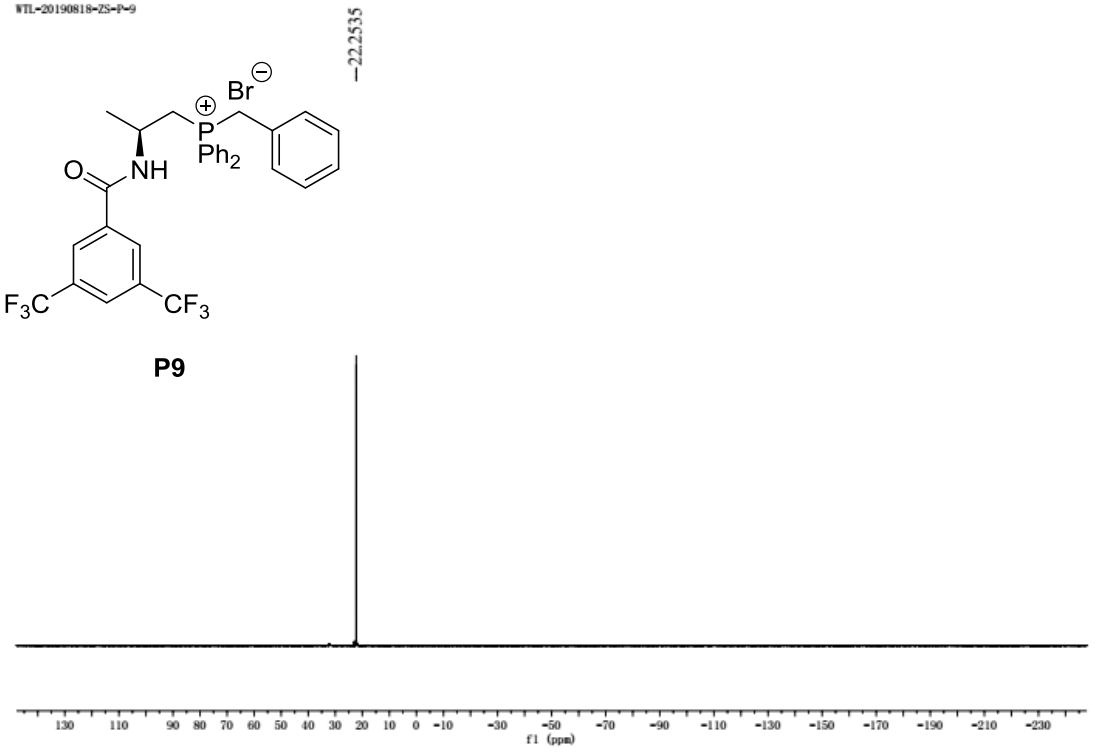
[7] F. Zhong, X. Dou, X. Han, W. Yao, Q. Zhu, Y. Meng, Y. Lu*, *Angew. Chem. Int. Ed.*, . 2013, **52**, 943.

9. NMR Spectra of Products




WTL-20190818-ZS-P-8
OTBDPS
PPh2MeI
O
NH
F3C
CF3
-22.9255
f1 (ppm)
P8
Br
P
Ph2
O
NH
F3C
CF3
f1 (ppm)
P9
f1 (ppm)


WTL-20190818-ZS-P-9
163.5729
163.5150
134.6037
134.5904
134.2268
133.7071
133.6141
133.4132
133.3198
131.3262
130.3704
130.3194
129.8416
129.8045
129.7191
129.6827
129.2040
129.1657
129.1359
128.6414
128.6033
128.3865
124.4189
118.9370
41.3405
29.4794
29.4254
29.0276
28.9667
26.2373
26.1412
25.7664
25.6575
23.2099
23.0619
Br
P
Ph2
O
NH
F3C
CF3
P9
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


WTL-20190818-ZS-P-9
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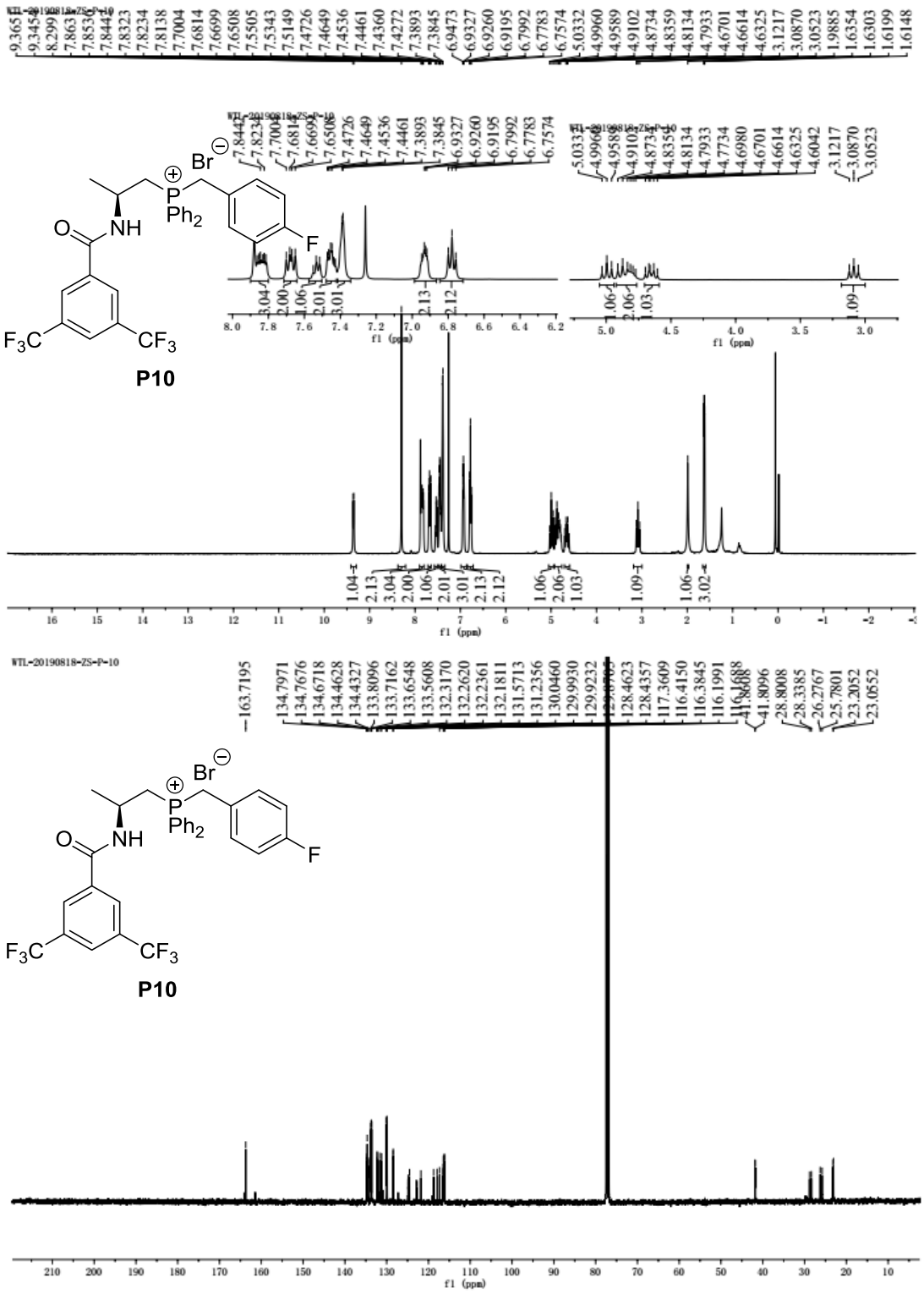
Br
P
Ph2
O
NH
F3C
CF3
P9
130 110 90 80 70 60 50 40 30 20 10 0 -10 -30 -50 -70 -90 -110 -130 -150 -170 -190 -210 -230
f1 (ppm)


Br
P
Ph2
O
NH
F
F3C
CF3
P10
f1 (ppm)

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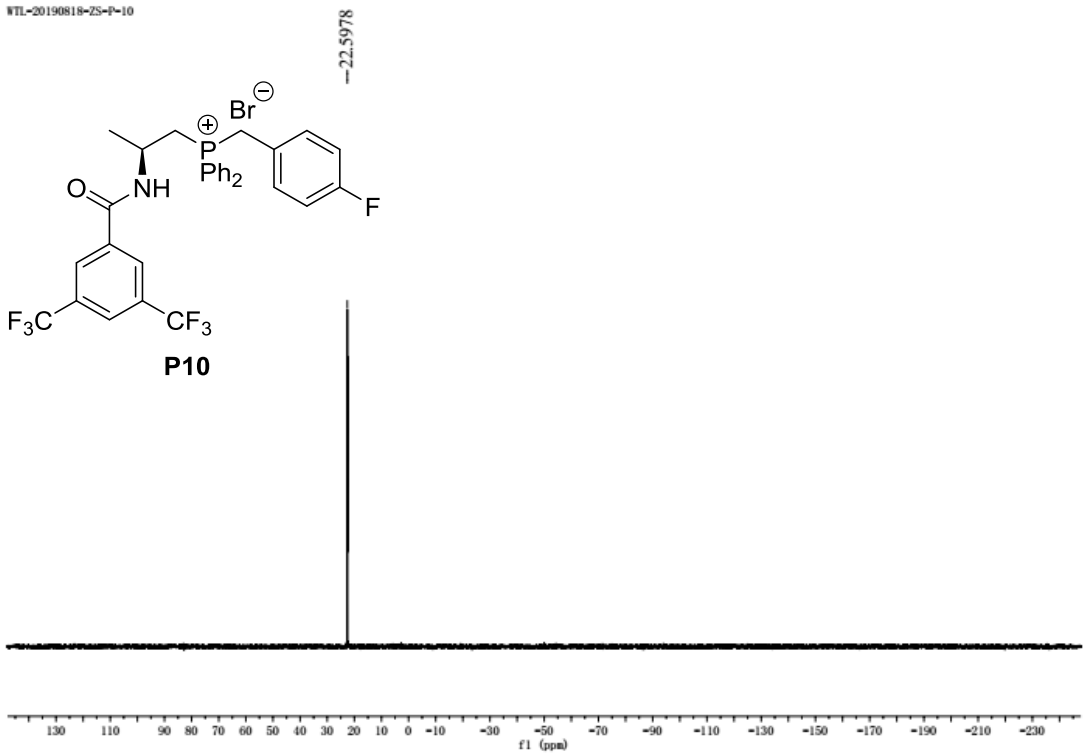
P
Ph2
O
NH
F
F3C
CF3
P10
f1 (ppm)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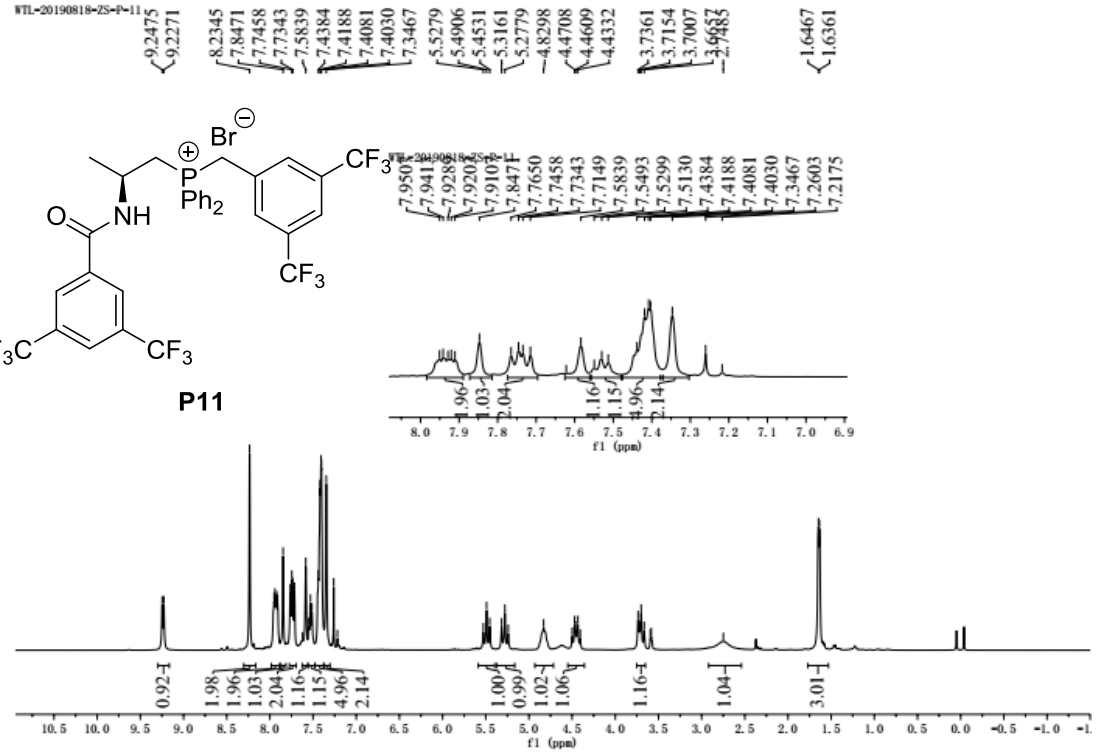
P
Ph2
O
NH
F
F3C
CF3
P10
f1 (ppm)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8.2345
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7.7343
7.5839
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7.4188
7.4081
7.4030
7.3467
5.5279
5.4906
5.4531
5.3161
5.2779
4.8298
4.4708
4.4609
4.4332
3.7361
3.7154
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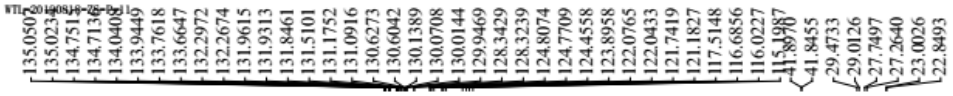
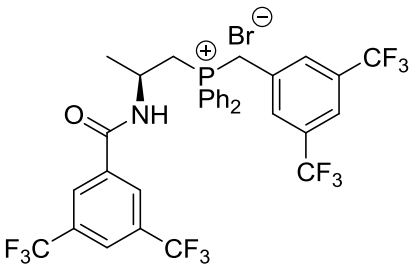
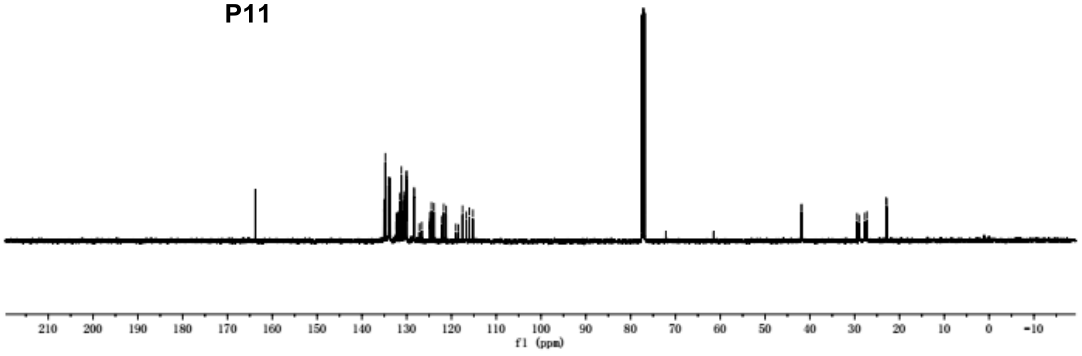
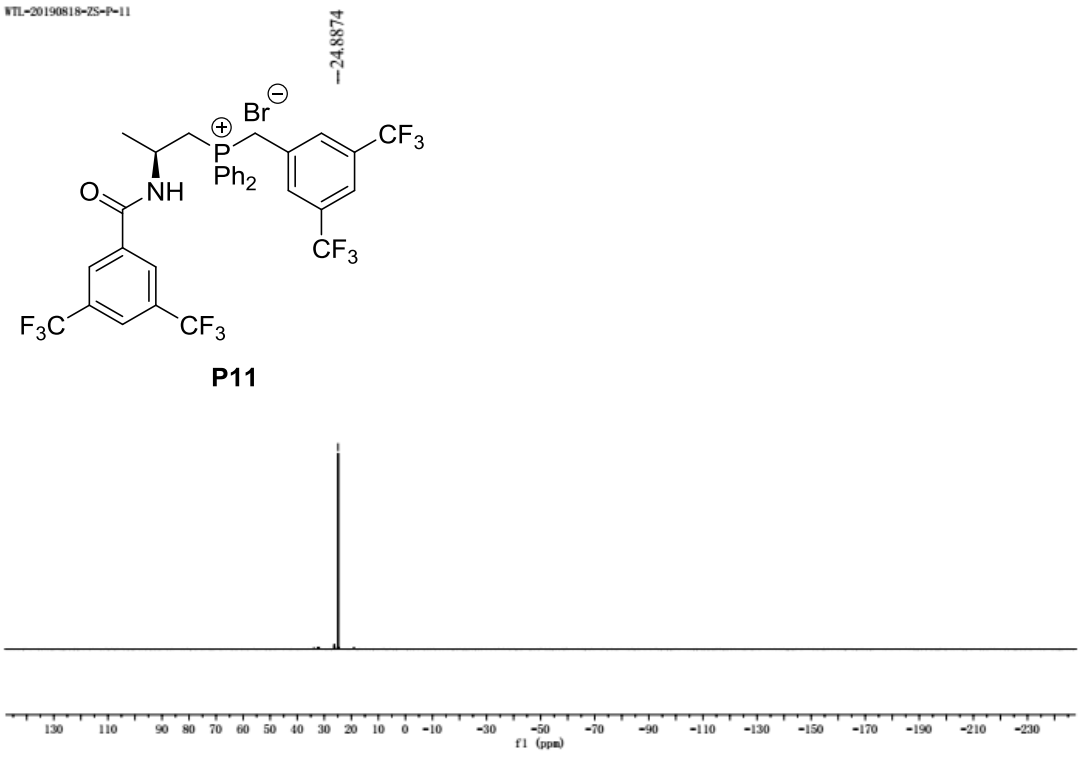
P
Ph2
O
NH
CF3
F3C
CF3
P11
f1 (ppm)



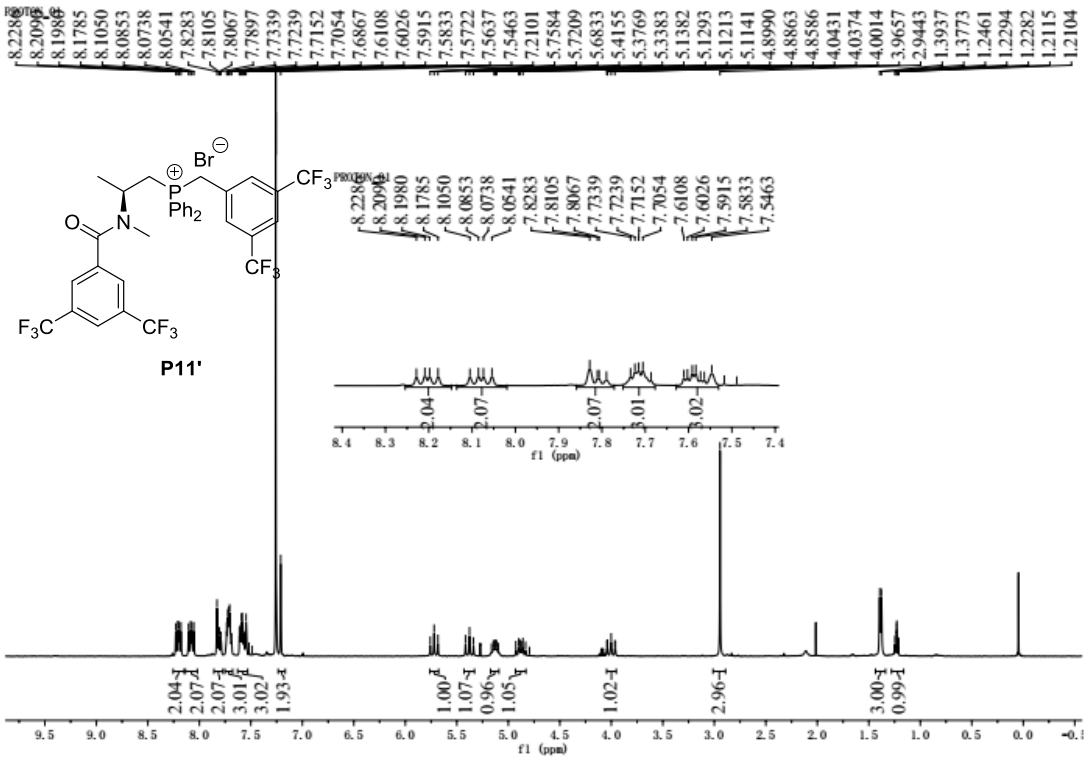


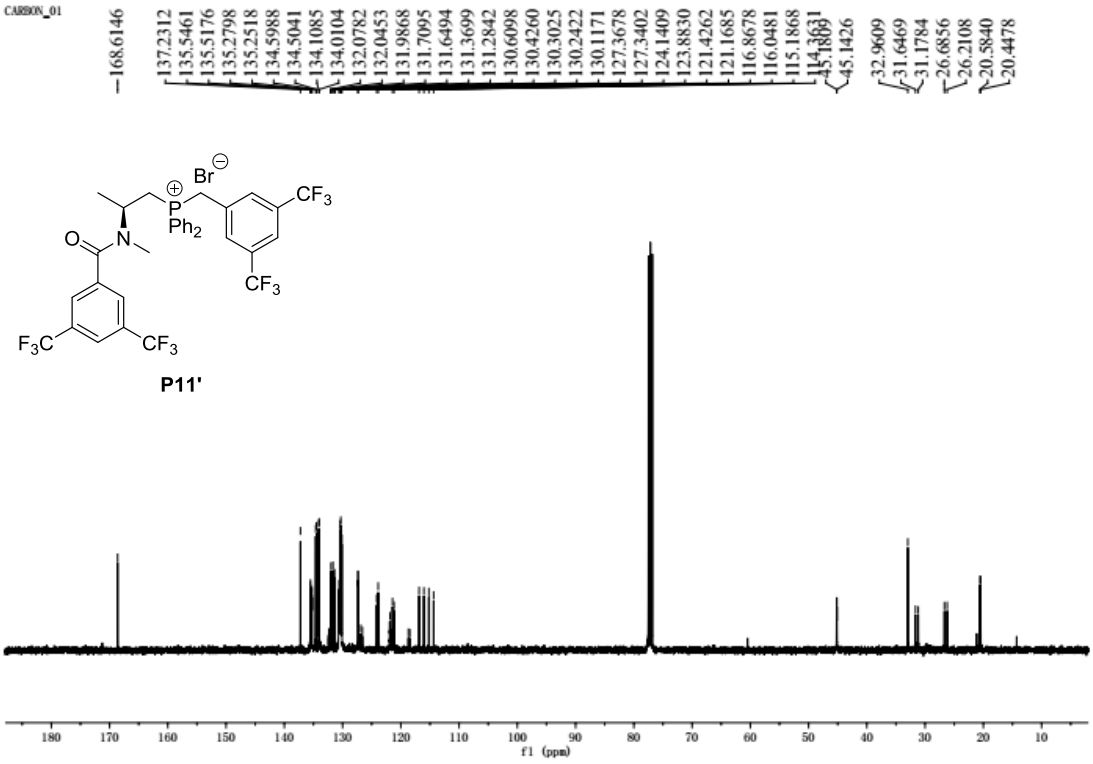
P11

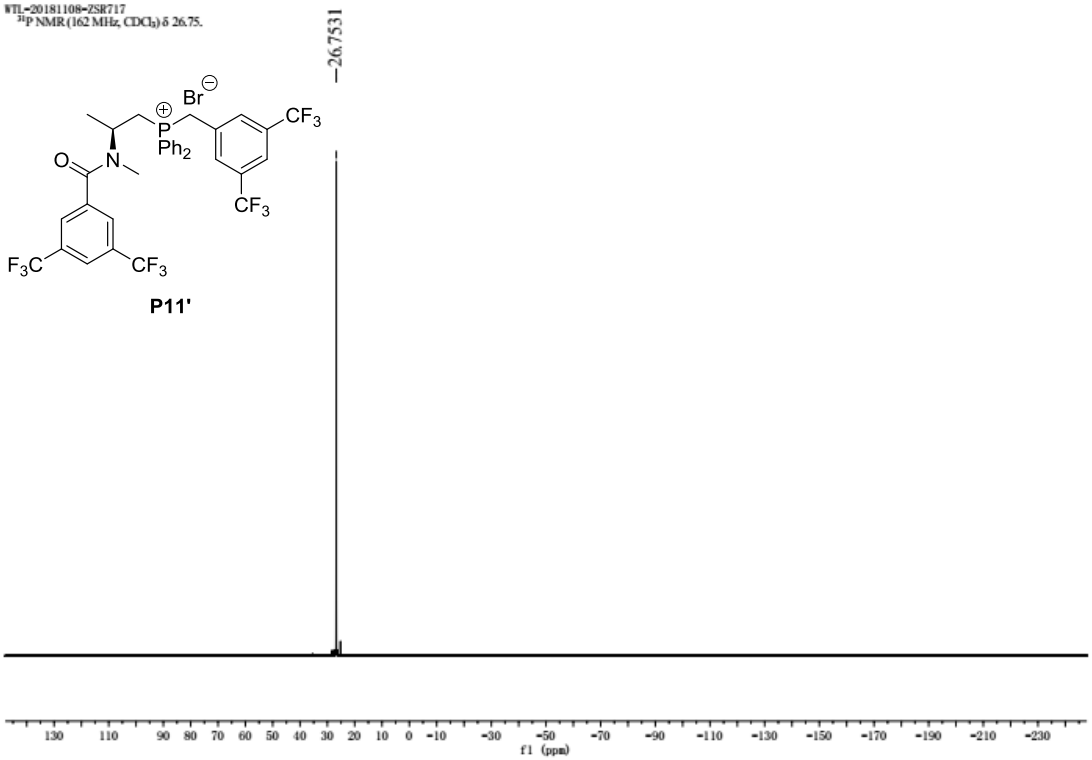


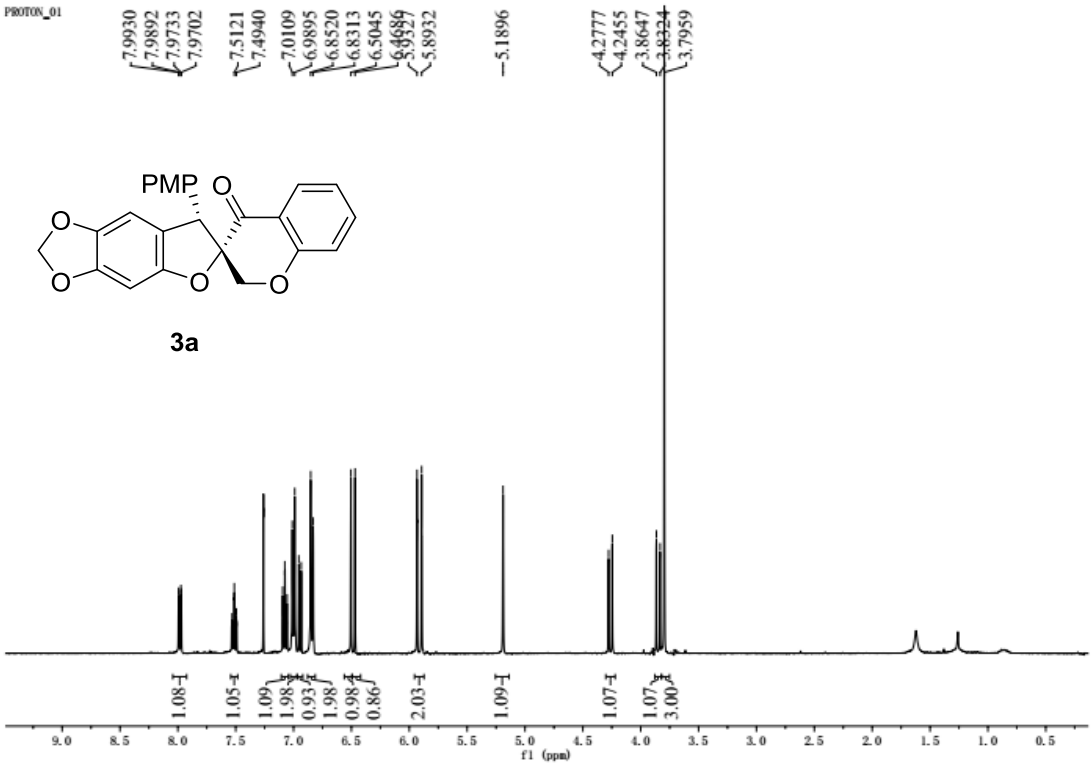


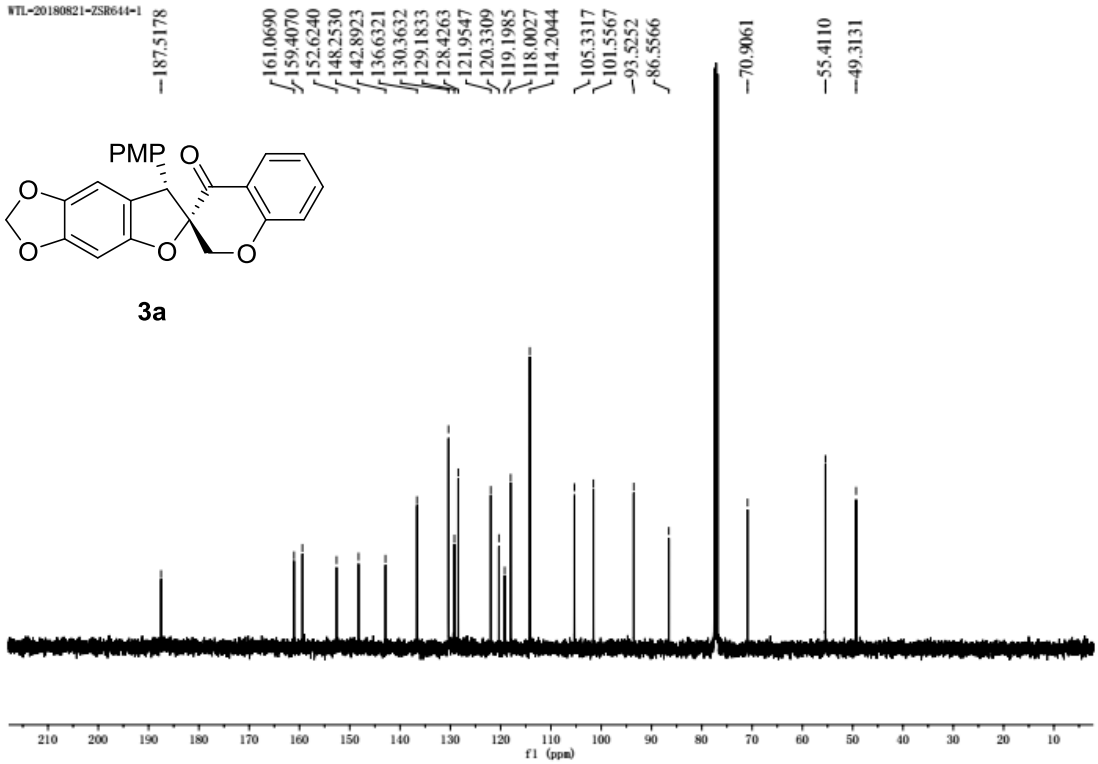
P11


Br
P
Ph2
CF3
CF3
O
N
F3C
CF3
P11'
f1 (ppm)

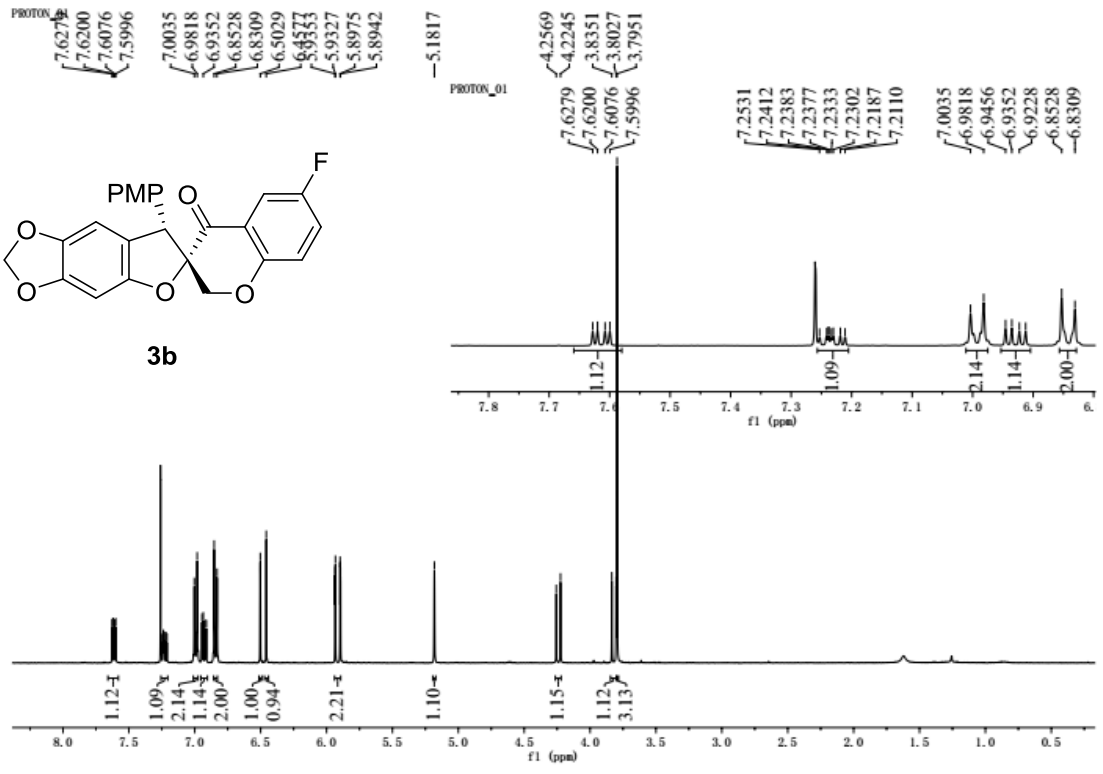

Br
P
Ph2
CF3
CF3
O
N
F3C
CF3
P11'
f1 (ppm)


WTL-20181108-ZSR717
31P NMR (162 MHz, CDCl3) δ 26.75.
26.7531
Br
P
Ph2
O
N
CF3
CF3
F3C
CF3
P11'
f1 (ppm)

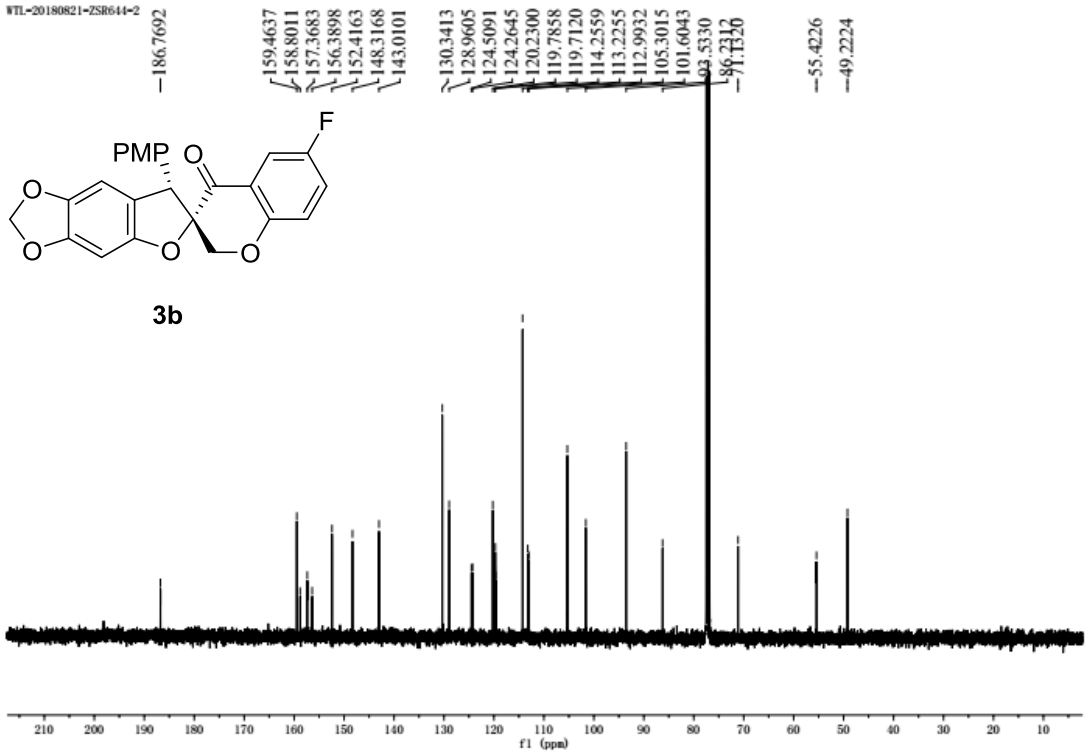

PROTON_01
7.9930
7.9892
7.9733
7.9702
7.5121
7.4940
7.0109
6.9895
6.8520
6.8313
6.5045
5.8932
5.1896
4.2777
4.2455
3.8647
3.8324
3.7959
PMP
O
O
O
O
3a
1.08
1.05
1.09
1.98
0.93
1.98
0.98
0.86
2.03
1.09
1.07
1.07
3.00
f1 (ppm)


WTL-20180821-ZSR644-1
187.5178
161.0690
159.4070
152.6240
148.2530
142.8923
136.6321
130.3632
129.1833
128.4263
121.9547
120.3309
119.1985
118.0027
114.2044
105.3317
101.5567
93.5252
86.5566
70.9061
55.4110
49.3131
PMP
O
O
O
O
O
f1 (ppm)

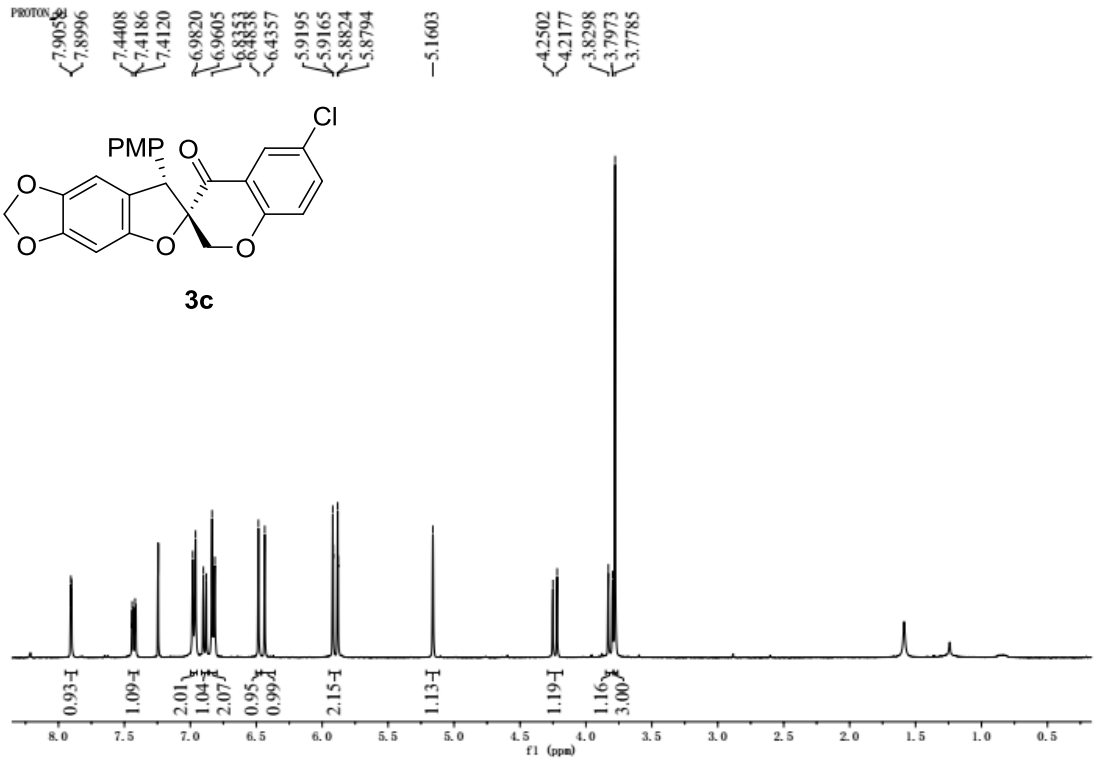
3a


PROTON_01
7.6279
7.6200
7.6076
7.5996
7.0035
6.9818
6.9352
6.8528
6.8309
6.5029
6.4577
5.9353
5.9327
5.8975
5.8942
5.1817
4.2569
4.2245
3.8351
3.8027
3.7951
7.2531
7.2412
7.2383
7.2377
7.2333
7.2302
7.2187
7.2110
6.9456
6.9228
6.8528
6.8309
PMP
O
O
O
O
O
F
1.12
1.09
2.14
1.14
2.00
1.00
0.94
2.21
1.10
1.15
1.12
3.13
f1 (ppm)

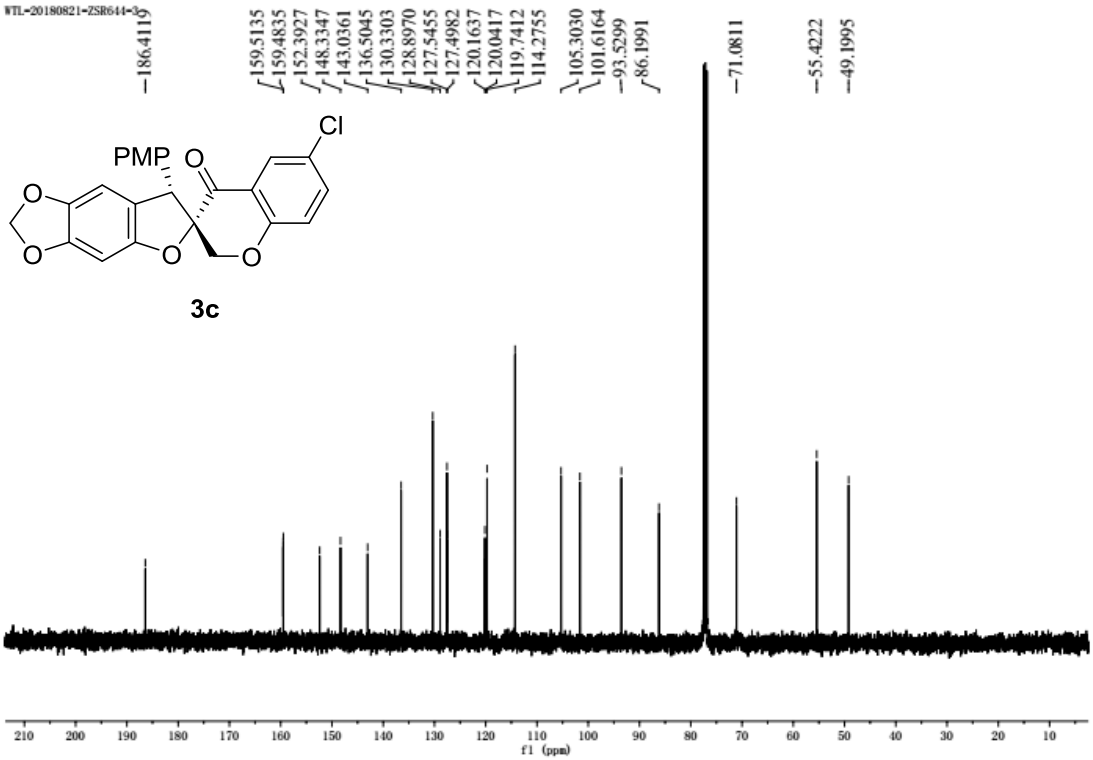
3b


WTL-20180821-ZSR644-2
186.7692
159.4637
158.8011
157.3683
156.3898
152.4163
148.3168
143.0101
130.3413
128.9605
124.5091
124.2645
120.2300
119.7858
119.7120
114.2559
113.2255
112.9932
105.3015
101.6043
93.5330
86.2312
71.1320
55.4226
49.2224
PMP
O
F
O
O
O
O
f1 (ppm)

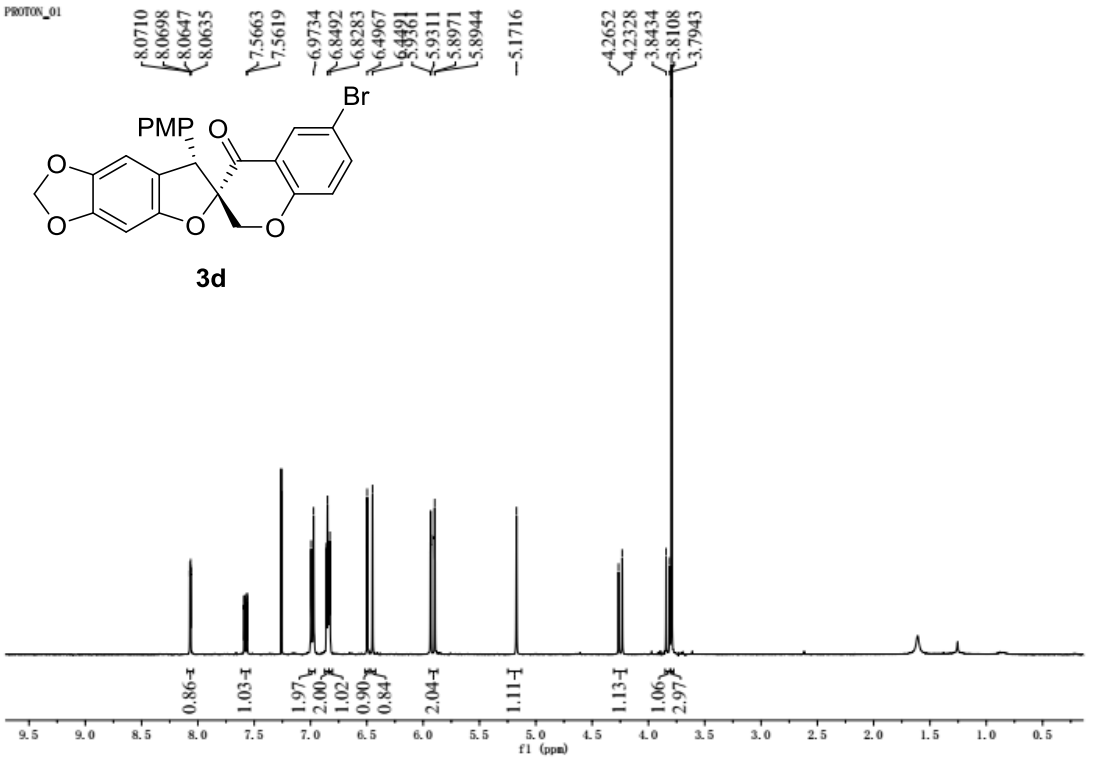
3b


PROTON_01
7.9058
7.8996
7.4408
7.4186
7.4120
6.9820
6.9605
6.4838
6.4357
5.9195
5.9165
5.8824
5.8794
5.1603
4.2502
4.2177
3.8298
3.7973
3.7785
PMP
O
Cl
O
O
O
O
0.93
1.09
2.01
1.04
2.07
0.95
0.99
2.15
1.13
1.19
1.16
3.00
f1 (ppm)

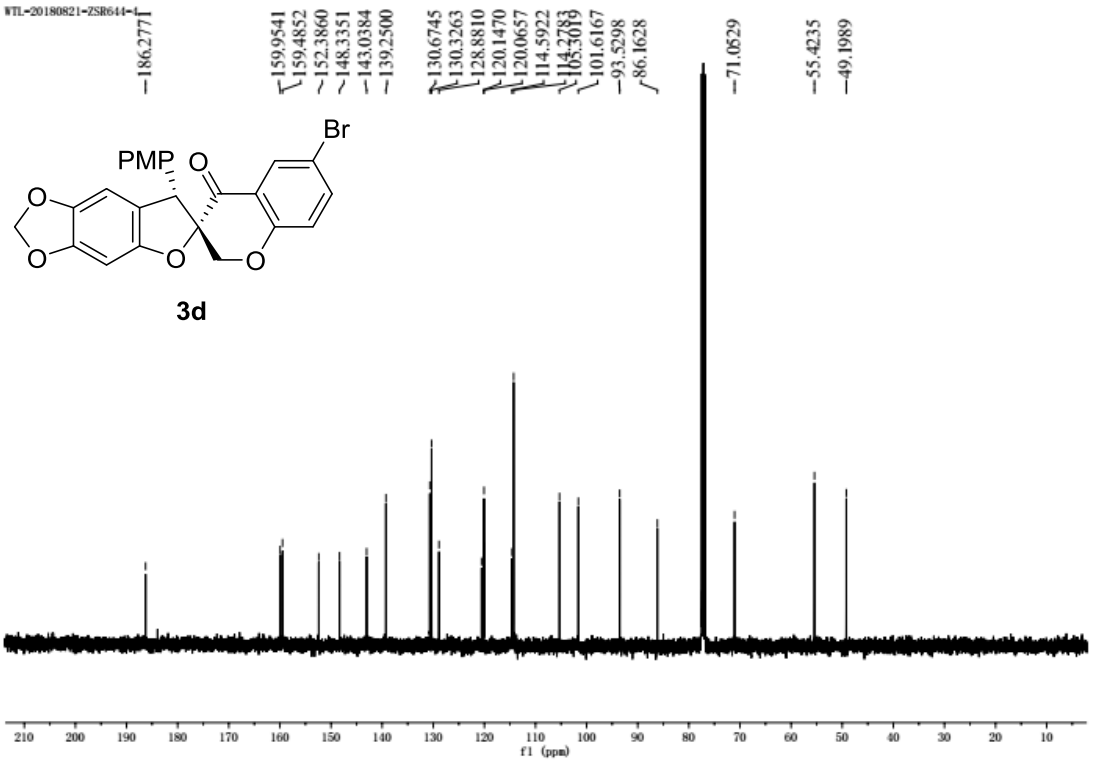
3c

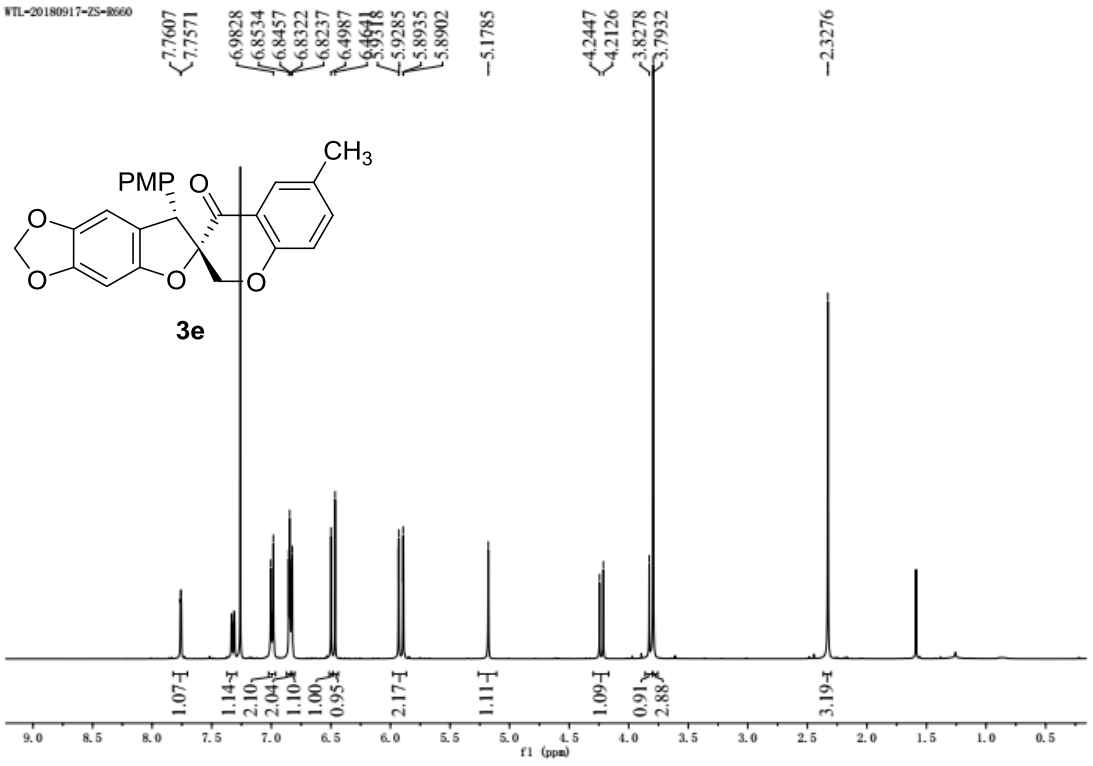

WTL-20180821-ZSR644-3
186.4119
159.5135
159.4835
152.3927
148.3347
143.0361
136.5045
130.3303
128.8970
127.5455
127.4982
120.1637
120.0417
119.7412
114.2755
105.3030
101.6164
93.5299
86.1991
71.0811
55.4222
49.1995
PMP
O
Cl
O
O
O
O
f1 (ppm)

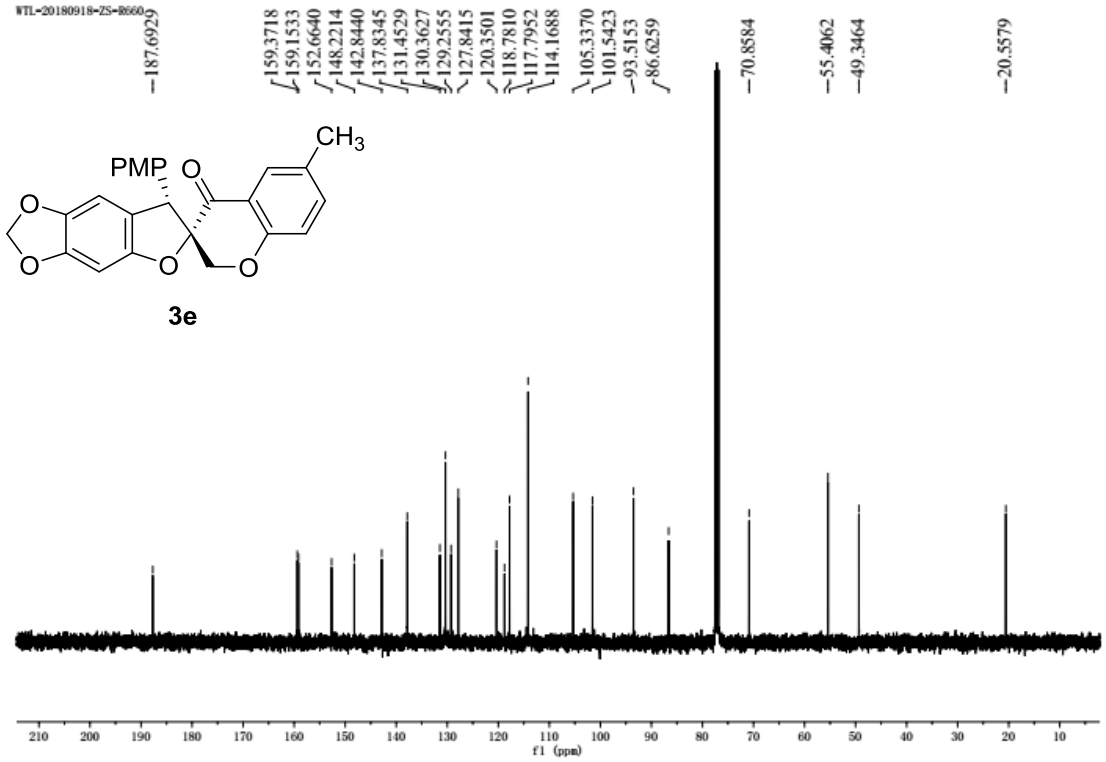
3c


PROTON_01
8.0710
8.0698
8.0647
8.0635
7.5663
7.5619
6.9734
6.8492
6.8283
6.4967
6.4491
5.9361
5.9311
5.8971
5.8944
5.1716
4.2652
4.2328
3.8434
3.8108
3.7943
PMP
O
Br
O
O
O
O
0.86
1.03
1.97
2.00
1.02
0.90
0.84
2.04
1.11
1.13
1.06
2.97
f1 (ppm)

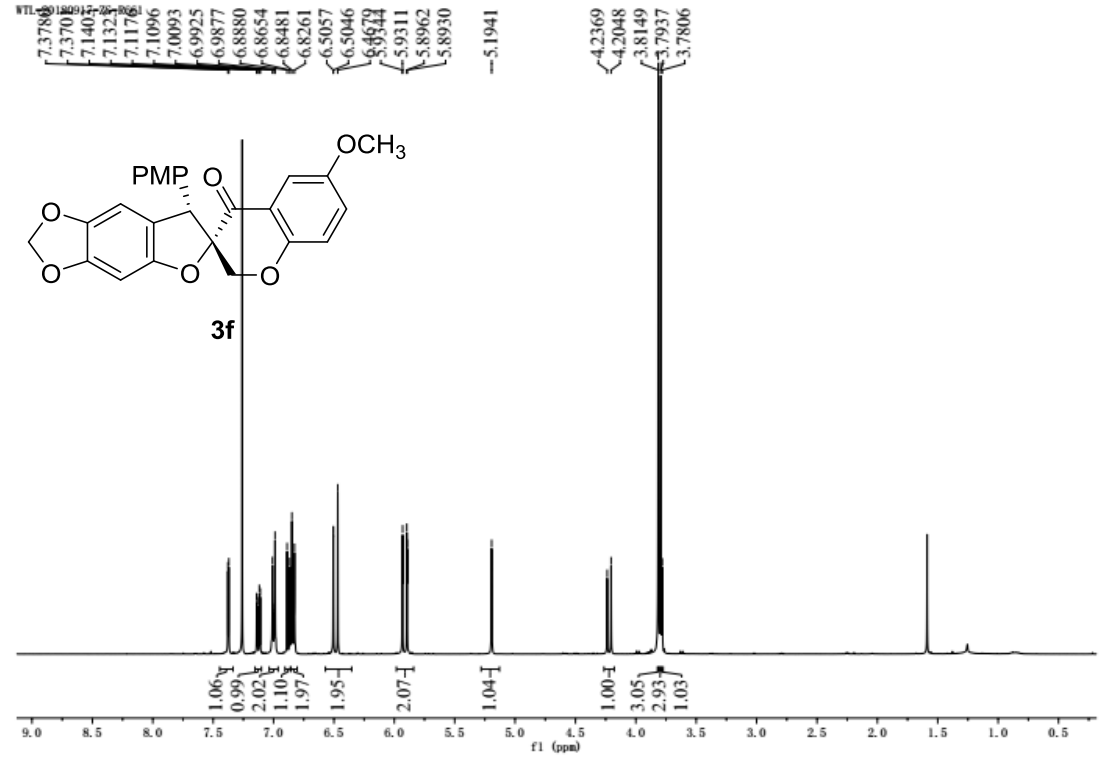
3d


WTL-20180821-ZSR644-1
186.2771
159.9541
159.4852
152.3860
148.3351
143.0384
139.2500
130.6745
130.3263
128.8810
120.1470
120.0657
114.5922
114.2783
105.3019
101.6167
93.5298
86.1628
71.0529
55.4235
49.1989
Br
PMP
O
O
O
O
O
3d
f1 (ppm)

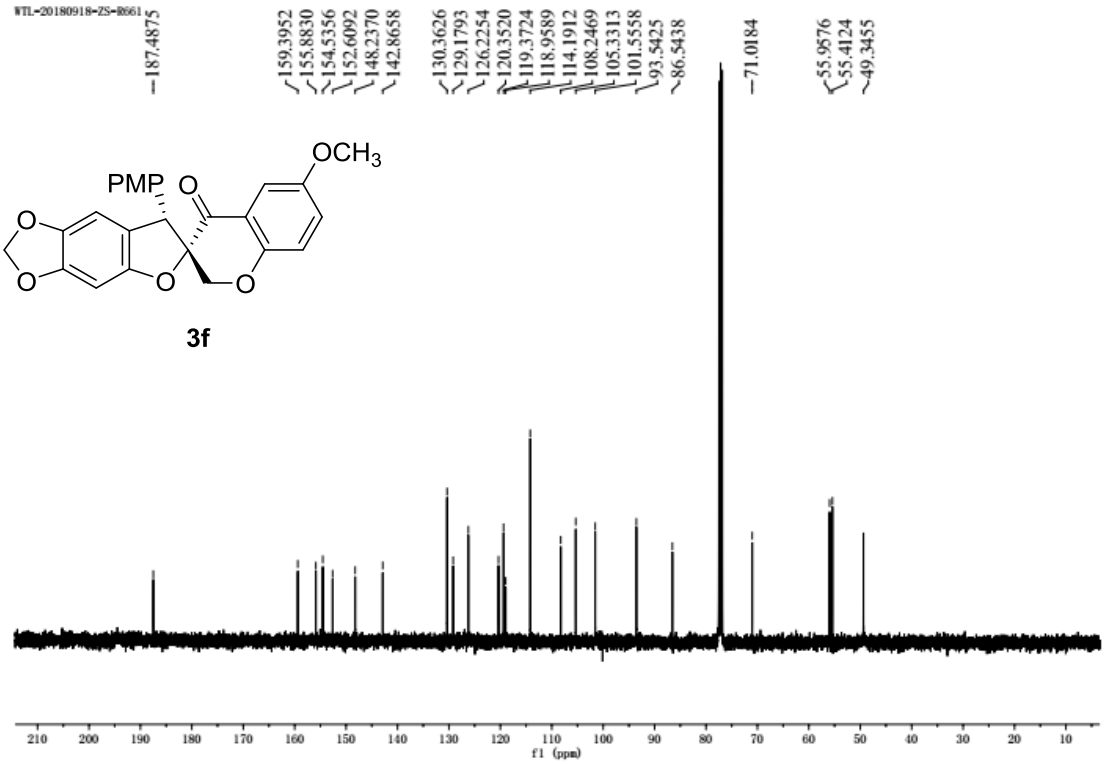

WTL-20180917-ZS-R660
7.7607
7.7571
6.9828
6.8534
6.8457
6.8322
6.8237
6.4987
5.9518
5.9285
5.8935
5.8902
5.1785
4.2447
4.2126
3.8278
3.7932
2.3276
CH3
PMP
O
O
O
O
O
3e
1.07
1.14
2.10
2.04
1.10
1.00
0.95
2.17
1.11
1.09
0.91
2.88
3.19
f1 (ppm)


WTL-20180918-ZS-B660
187.6929
159.3718
159.1533
152.6640
148.2214
142.8440
137.8345
131.4529
130.3627
129.2555
127.8415
120.3501
118.7810
117.7952
114.1688
105.3370
101.5423
93.5153
86.6259
70.8584
55.4062
49.3464
20.5579
CH3
PMP
O
O
O
O
O
f1 (ppm)

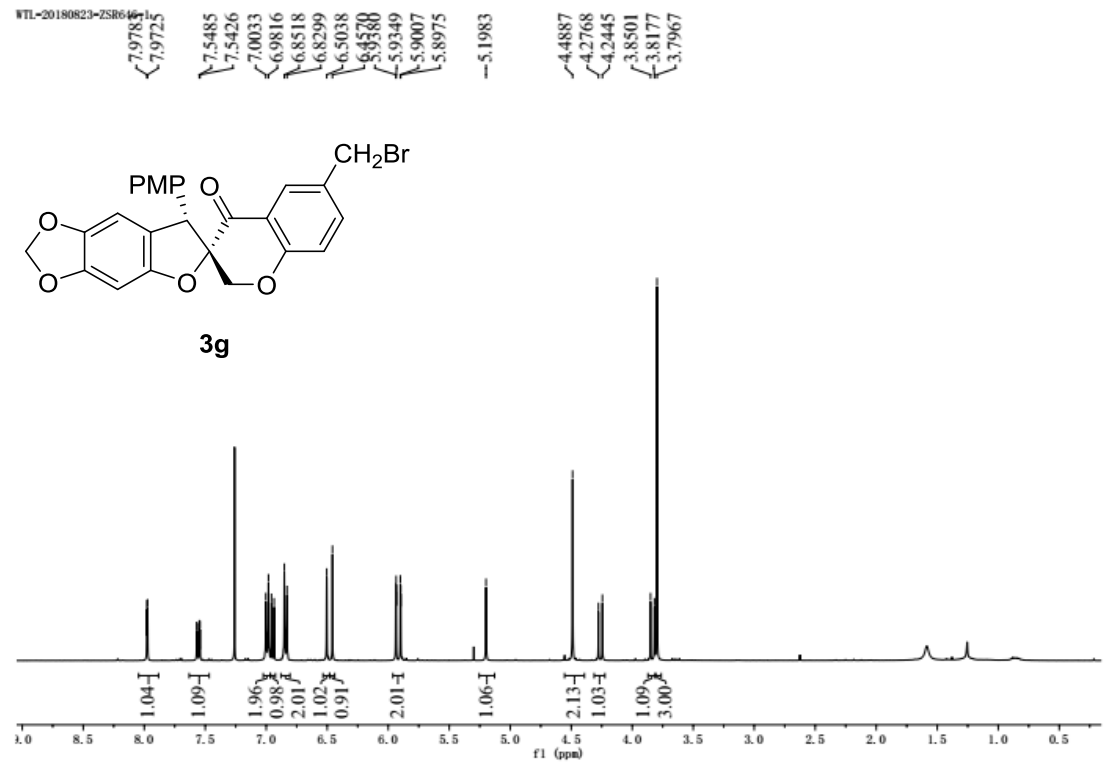
3e


7.3780
7.3701
7.1403
7.1322
7.1176
7.1096
7.0093
6.9925
6.9877
6.8880
6.8654
6.8481
6.8261
6.5057
6.5046
6.4679
5.9344
5.9311
5.8962
5.8930
5.1941
4.2369
4.2048
3.8149
3.7937
3.7806
OCH3
PMP
O
O
O
O
O
1.06
0.99
2.02
1.10
1.97
1.95
2.07
1.04
1.00
3.05
2.93
1.03
f1 (ppm)

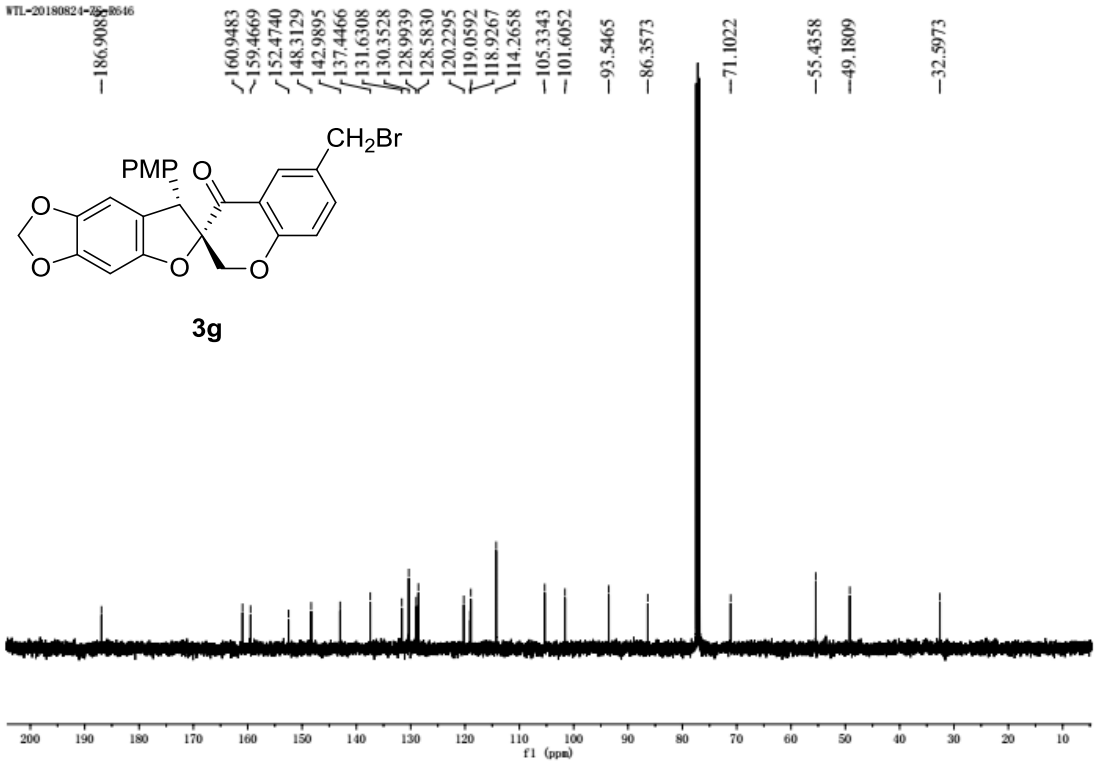
3f


WTL-20180918-ZS-R661
187.4875
159.3952
155.8830
154.5356
152.6092
148.2370
142.8658
130.3626
129.1793
126.2254
120.3520
119.3724
118.9589
114.1912
108.2469
105.3313
101.5558
93.5425
86.5438
71.0184
55.9576
55.4124
49.3455
OCH3
PMP
O
O
O
O
O
f1 (ppm)

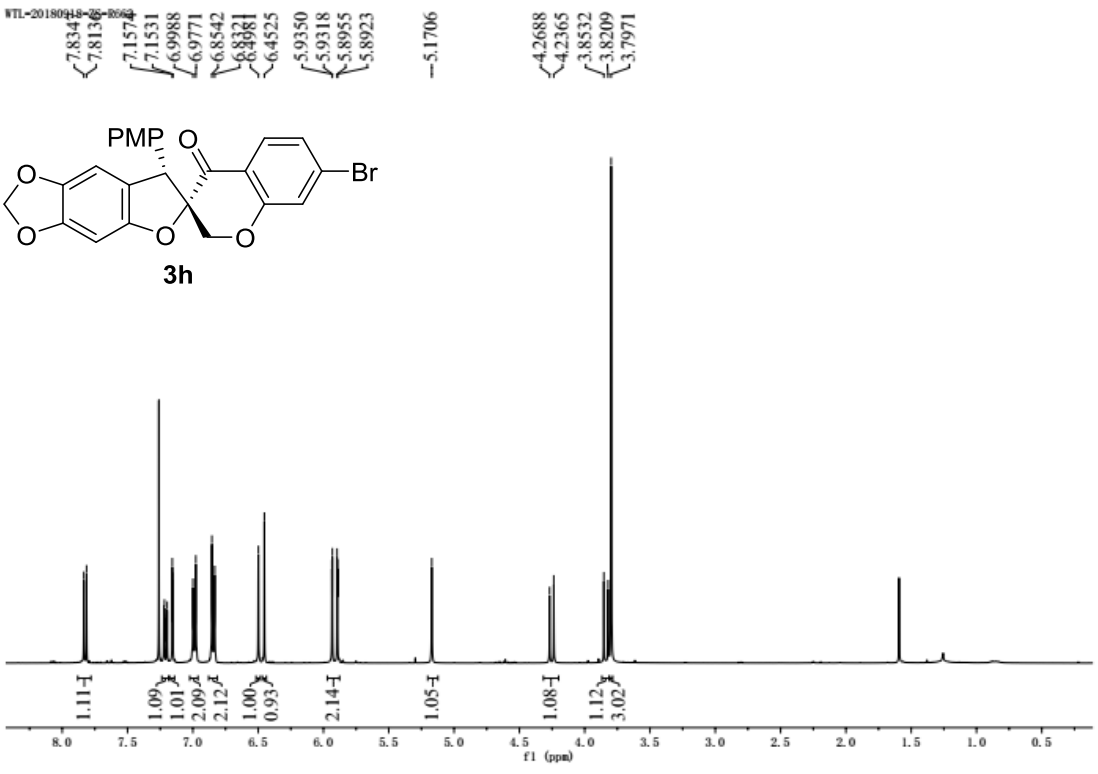
3f


WTL-20180823-ZSR646
7.9785
7.9725
7.5485
7.5426
7.0033
6.9816
6.8518
6.8299
6.5038
5.9349
5.9007
5.8975
5.1983
4.4887
4.2768
4.2445
3.8501
3.8177
3.7967
CH2Br
PMP
O
O
O
O
1.04
1.09
1.96
0.98
2.01
1.02
0.91
2.01
1.06
2.13
1.03
1.09
3.00
f1 (ppm)

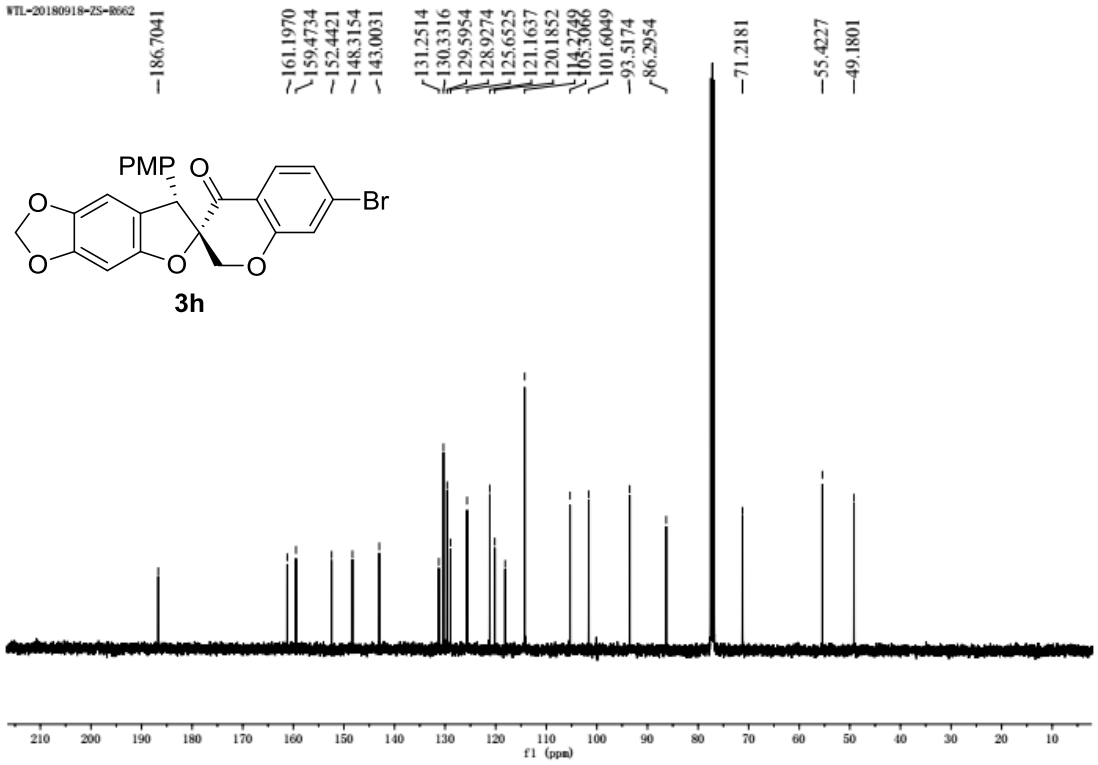
3g

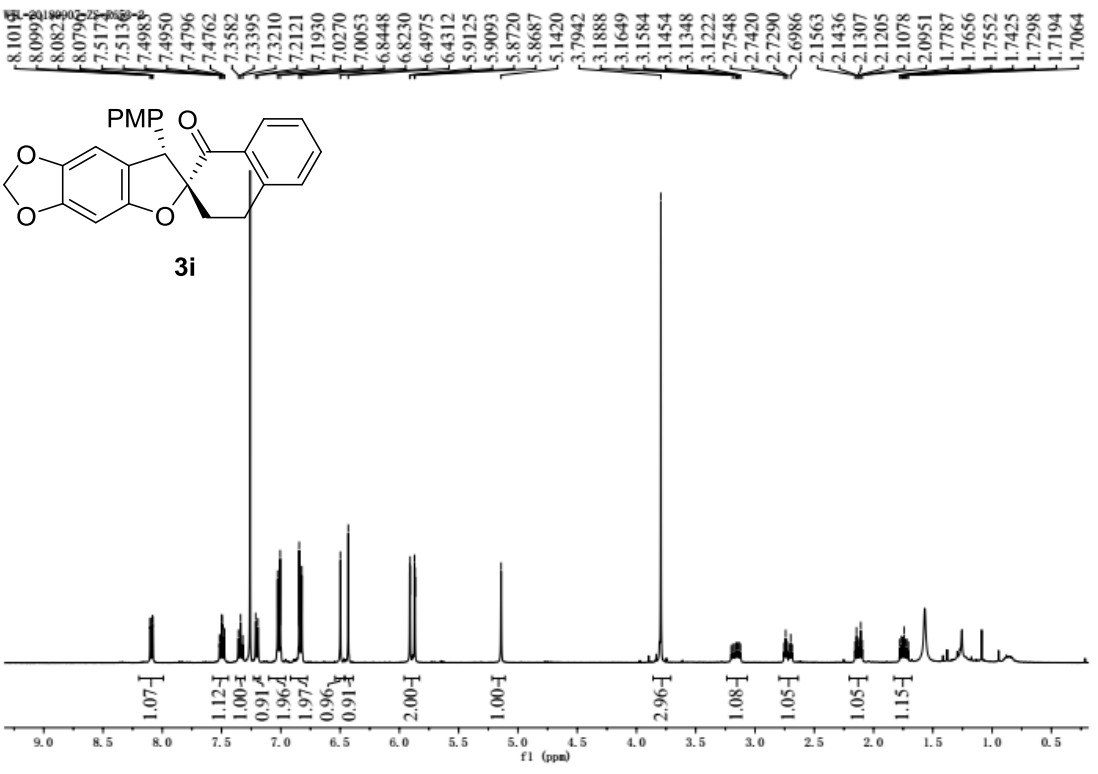

186.9085
160.9483
159.4669
152.4740
148.3129
142.9895
137.4466
131.6308
130.3528
128.9939
128.5830
120.2295
119.0592
118.9267
114.2658
105.3343
101.6052
93.5465
86.3573
71.1022
55.4358
49.1809
32.5973
PMP
O
CH2Br
O
O
O
O
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

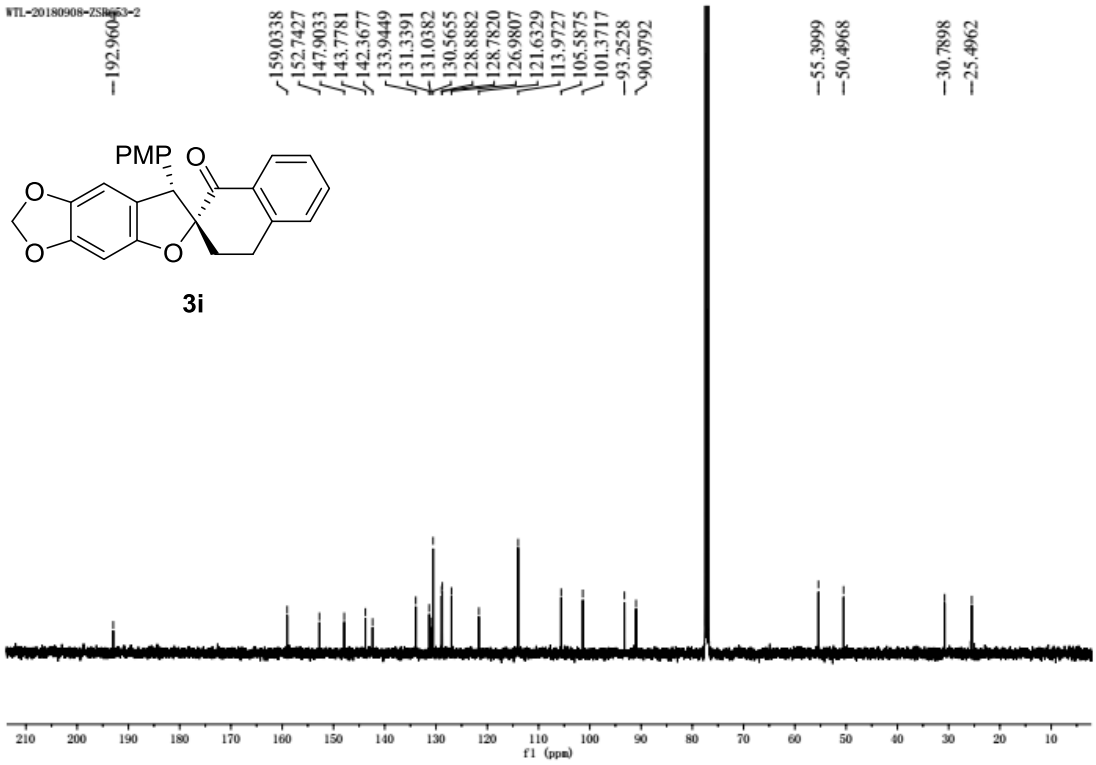
3g


7.8347
7.8136
7.1574
7.1531
6.9988
6.9771
6.8542
6.8321
6.4981
6.4525
5.9350
5.9318
5.8955
5.8923
5.1706
4.2688
4.2365
3.8532
3.8209
3.7971
PMP
O
Br
O
O
O
O
1.11
1.09
1.01
2.09
2.12
1.00
0.93
2.14
1.05
1.08
1.12
3.02
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

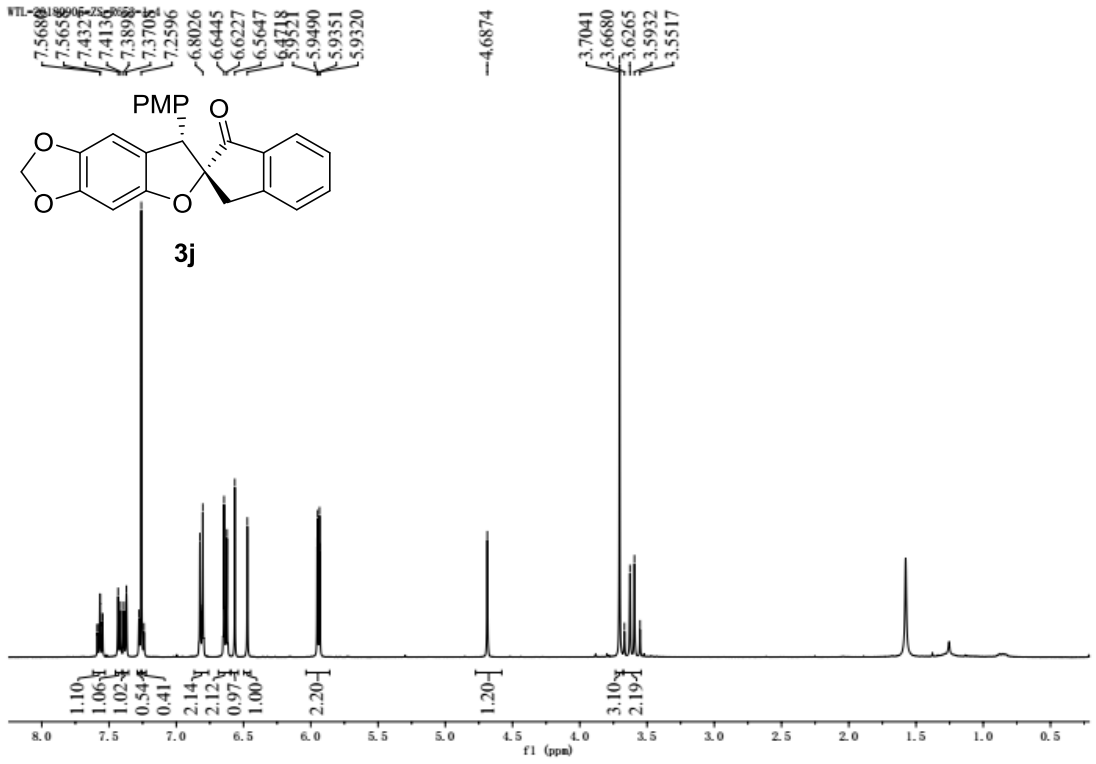
3h


WTL-20180918-ZS-B662
186.7041
161.1970
159.4734
152.4421
148.3154
143.0031
131.2514
130.3316
129.5954
128.9274
125.6525
121.1637
120.1852
114.2749
105.3066
101.6049
93.5174
86.2954
71.2181
55.4227
49.1801
PMP
O
Br
O
O
O
O
3h
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

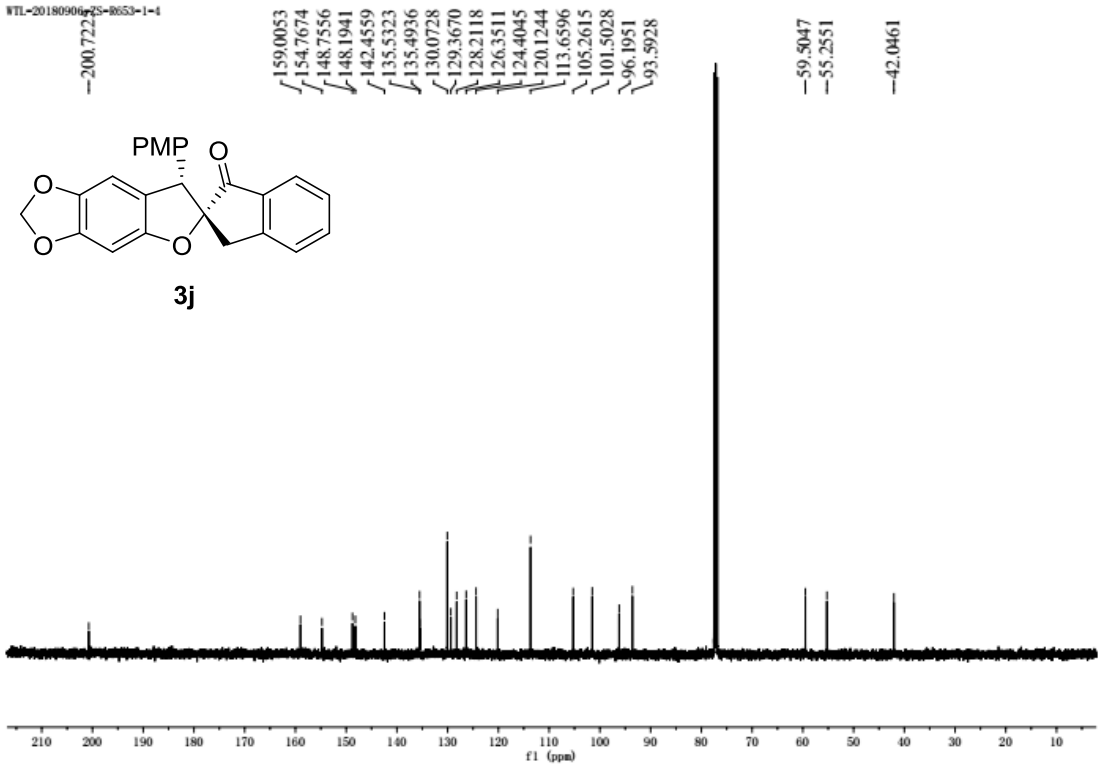

8.1014
8.0992
8.0823
8.0796
7.5177
7.5136
7.4983
7.4950
7.4796
7.4762
7.3582
7.3395
7.3210
7.2121
7.1930
7.0270
7.0053
6.8448
6.8230
6.4975
6.4312
5.9125
5.9093
5.8720
5.8687
5.1420
3.7942
3.1888
3.1649
3.1584
3.1454
3.1348
3.1222
2.7548
2.7420
2.7290
2.6986
2.1563
2.1436
2.1307
2.1205
2.1078
2.0951
1.7787
1.7656
1.7552
1.7425
1.7298
1.7194
1.7064
PMP
O
O
O
O
3i
1.07
1.12
1.00
0.91
1.96
1.97
0.96
0.91
2.00
1.00
2.96
1.08
1.05
1.05
1.15
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
f1 (ppm)


WTL-20180908-ZSB653-2
192.9604
159.0338
152.7427
147.9033
143.7781
142.3677
133.9449
131.3391
131.0382
130.5655
128.8882
128.7820
126.9807
121.6329
113.9727
105.5875
101.3717
93.2528
90.9792
55.3999
50.4968
30.7898
25.4962
PMP
O
O
O
O
f1 (ppm)

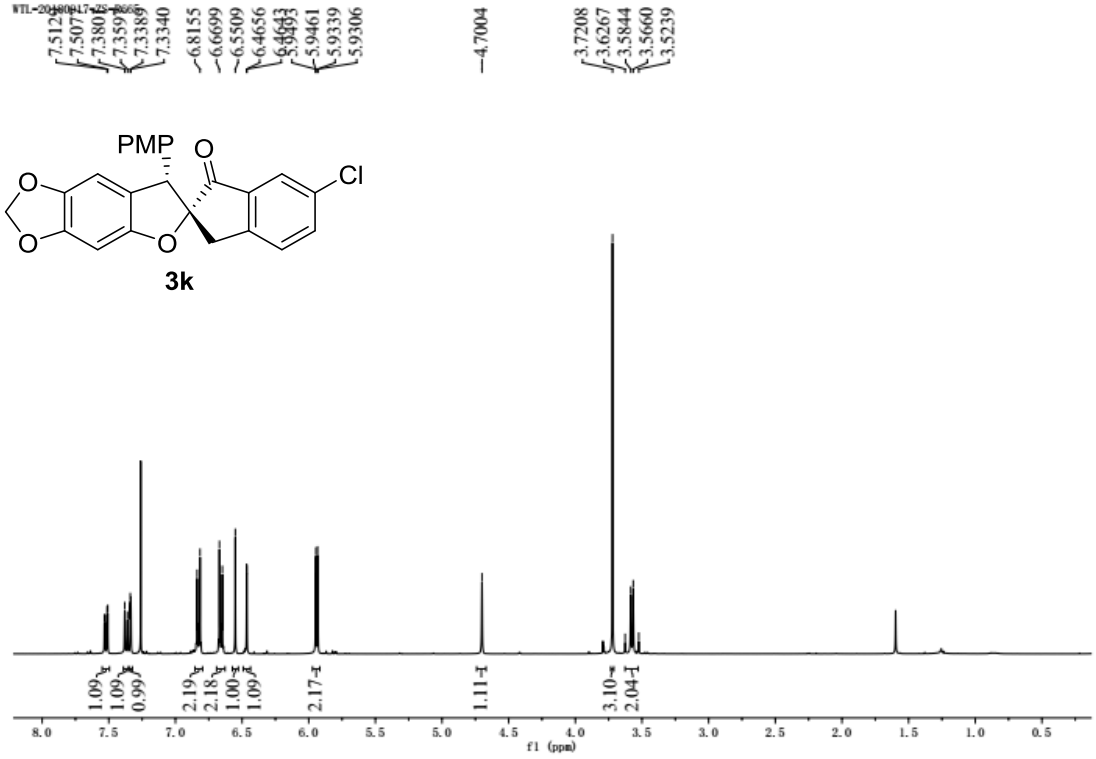
3i


7.5680
7.5658
7.4324
7.4130
7.3898
7.3705
7.2596
6.8026
6.6445
6.6227
6.5647
5.9490
5.9351
5.9320
4.6874
3.7041
3.6680
3.6265
3.5932
3.5517
PMP
O
O
O
O
1.10
1.06
1.02
0.54
0.41
2.14
2.12
0.97
1.00
2.20
1.20
3.10
2.19
f1 (ppm)

3j


200.7225
159.0053
154.7674
148.7556
148.1941
142.4559
135.5323
135.4936
130.0728
129.3670
128.2118
126.3511
124.4045
120.1244
113.6596
105.2615
101.5028
96.1951
93.5928
59.5047
55.2551
42.0461
PMP
O
O
O
O
f1 (ppm)

3j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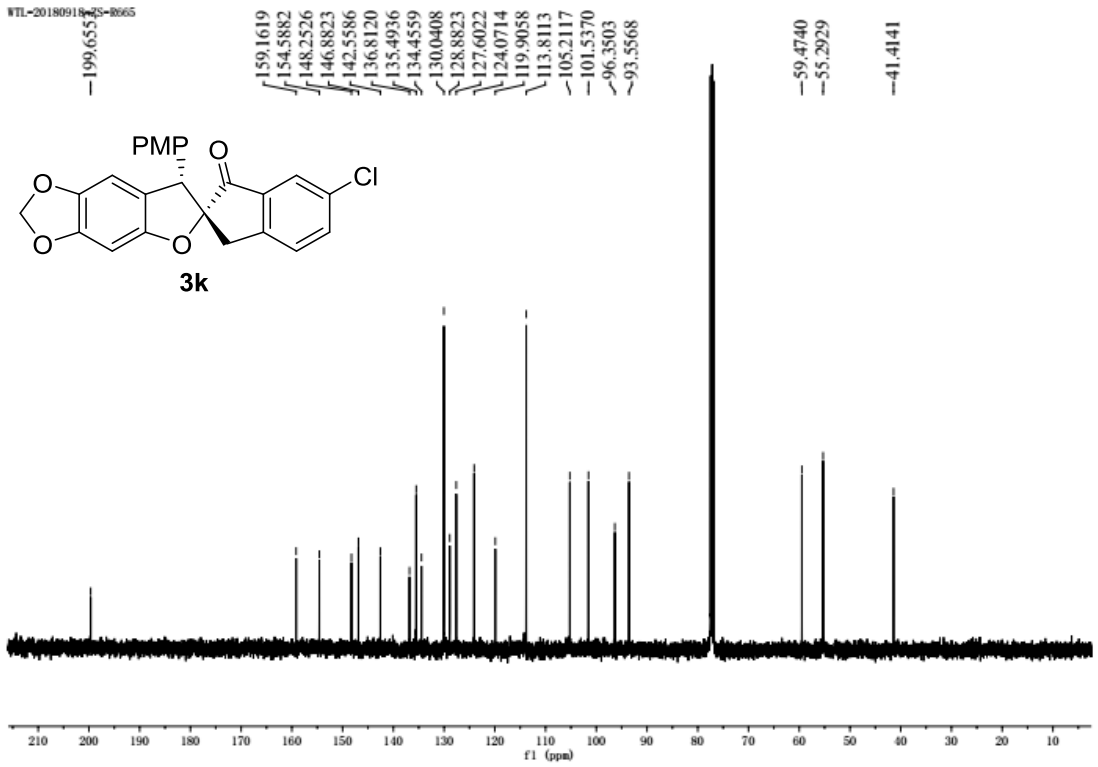
7.5071
7.3806
7.3599
7.3389
7.3340
6.8155
6.6699
6.5509
6.4656
5.9461
5.9339
5.9306
4.7004
3.7208
3.6267
3.5844
3.5660
3.5239
PMP
O
O
O
O
Cl
1.09
1.09
0.99
2.19
2.18
1.00
1.09
2.17
1.11
3.10
2.04
f1 (ppm)

3k


WTL-20180918-ZS-B665
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148.2526
146.8823
142.5586
136.8120
135.4936
134.4559
130.0408
128.8823
127.6022
124.0714
119.9058
113.8113
105.2117
101.5370
96.3503
93.5568
59.4740
55.2929
41.4141
PMP
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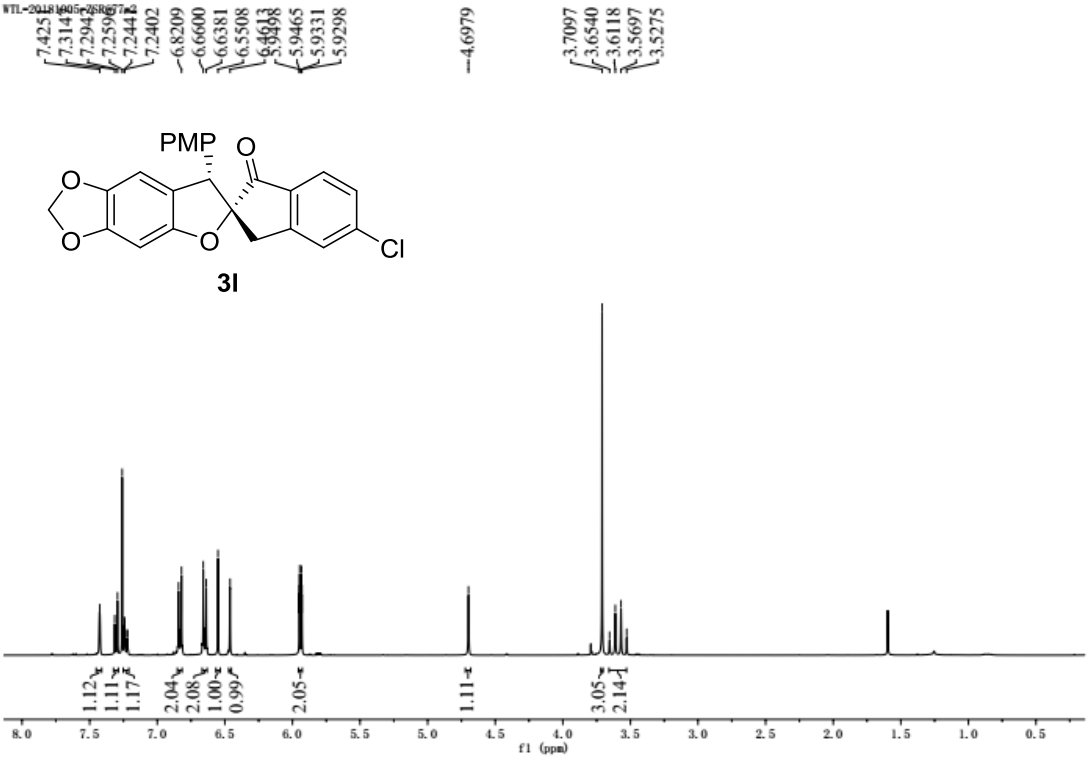
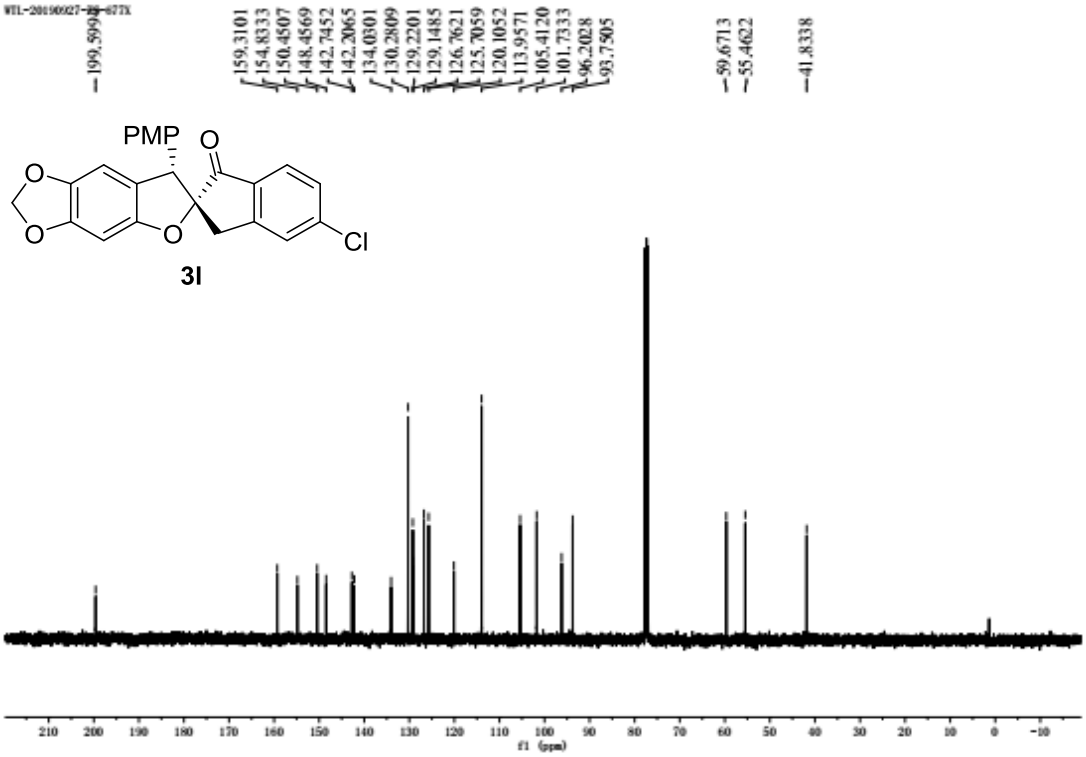
O
O
O
Cl
3k
f1 (ppm)


7.4251
7.3144
7.2946
7.2590
7.2441
7.2402
6.8209
6.6600
6.6381
6.5508
6.4613
5.9498
5.9465
5.9331
5.9298
4.6979
3.7097
3.6540
3.6118
3.5697
3.5275
PMP
O
O
O
O
Cl
3l
1.12
1.11
1.17
2.04
2.08
1.00
0.99
2.05
1.11
3.05
2.14
f1 (ppm)


199.5994
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148.4569
142.7452
142.2065
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130.2809
129.2201
129.1485
126.7621
125.7059
120.1052
113.9571
105.4120
101.7333
96.2028
93.7505
59.6713
55.4622
41.8338
PMP
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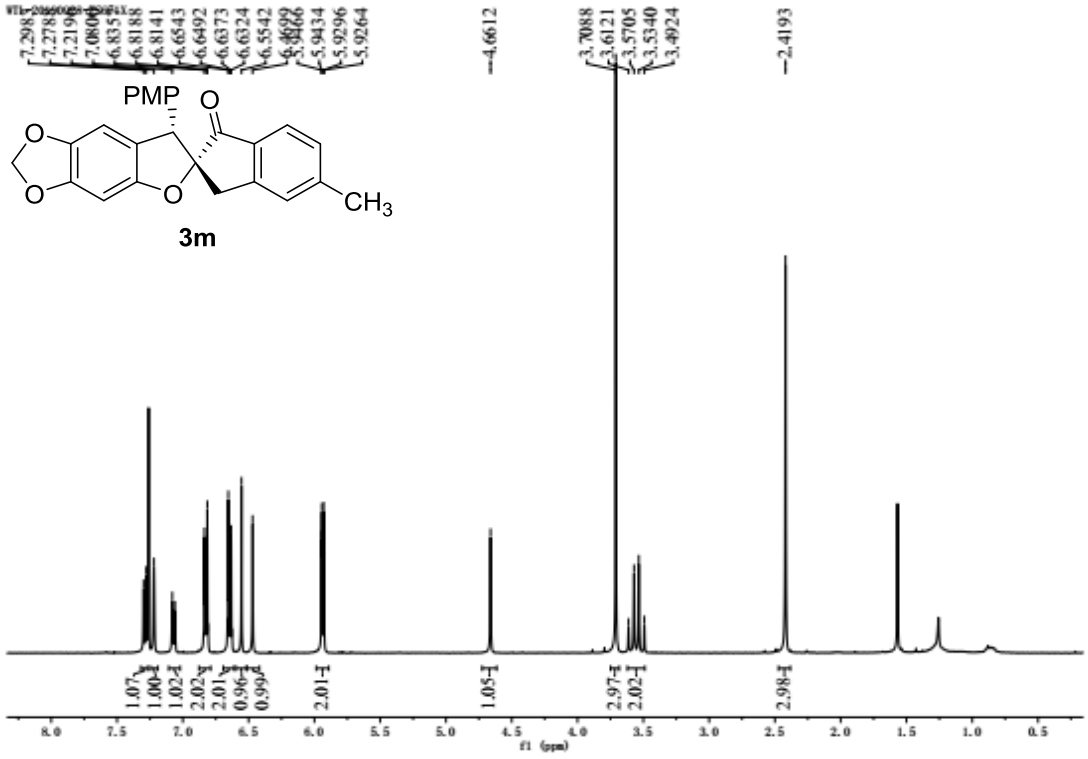
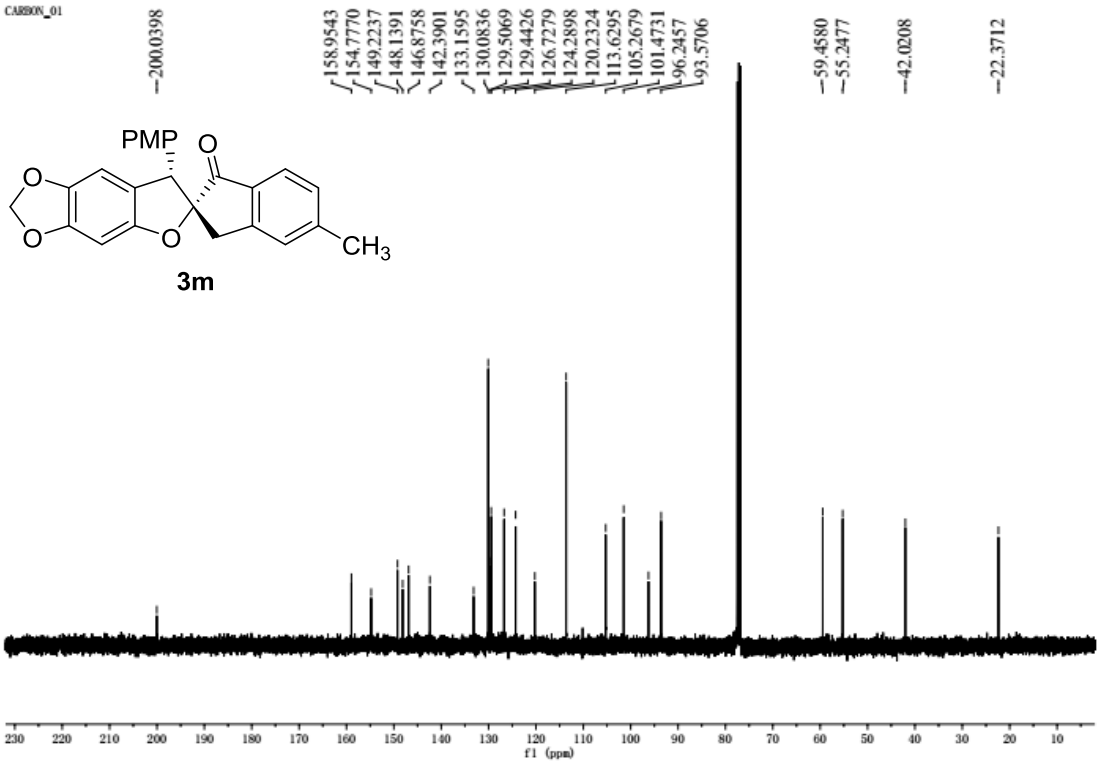
O
O
O
Cl
3l
f1 (ppm)


7.2980
7.2780
7.2190
7.0804
6.8350
6.8188
6.8141
6.6543
6.6492
6.6373
6.6324
6.5542
5.9434
5.9296
5.9264
4.6612
3.7088
3.6121
3.5705
3.5340
3.4924
2.4193
PMP
O
O
O
O
CH3
3m
1.07
1.00
1.02
2.02
2.01
0.96
0.99
2.01
1.05
2.97
2.02
2.98
f1 (ppm)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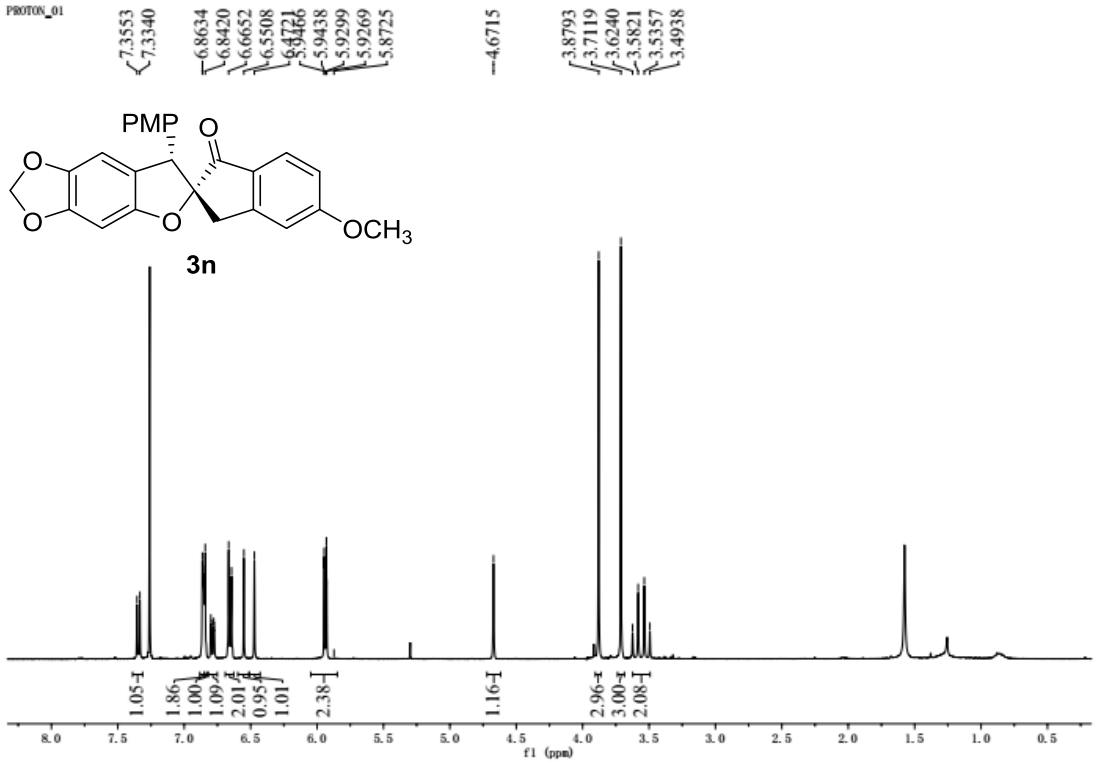
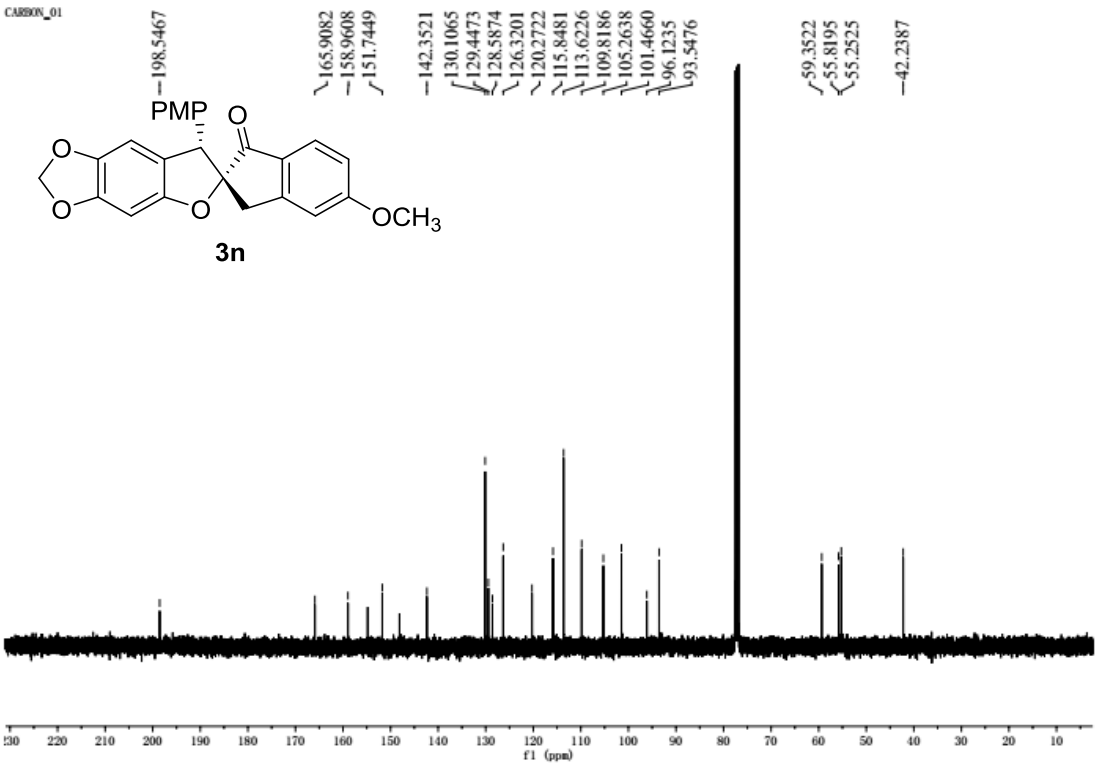
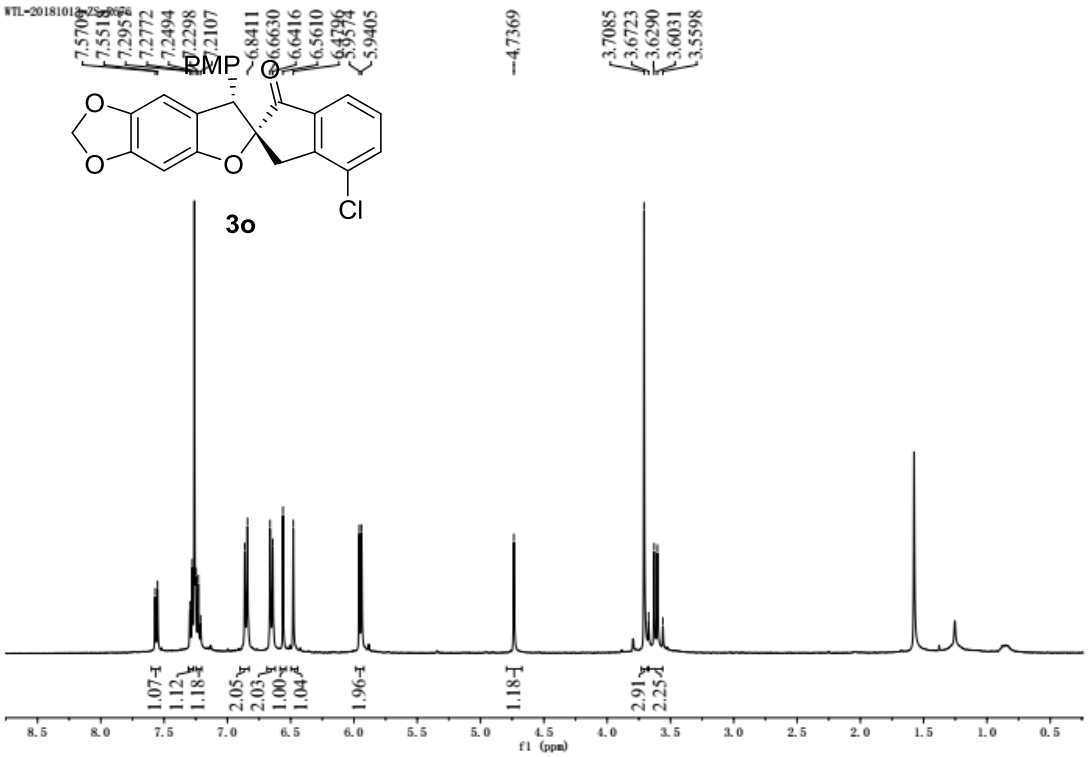
154.7770
149.2237
148.1391
146.8758
142.3901
133.1595
130.0836
129.5069
129.4426
126.7279
124.2898
120.2324
113.6295
105.2679
101.4731
96.2457
93.5706
59.4580
55.2477
42.0208
22.3712
PMP
O
O
O
O
CH3
f1 (ppm)

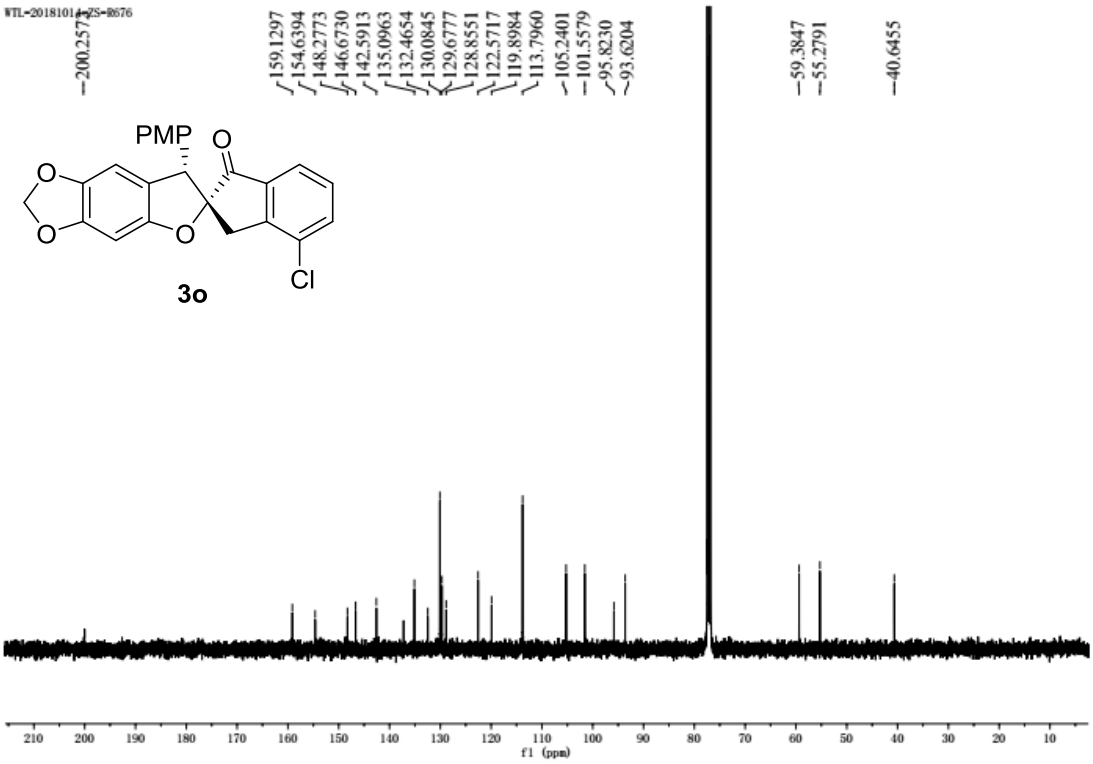
3m


PROTON_01
7.3553
7.3340
6.8634
6.8420
6.6652
6.5508
6.4721
6.4486
5.9438
5.9299
5.9269
5.8725
4.6715
3.8793
3.7119
3.6240
3.5821
3.5357
3.4938
PMP
O
O
O
O
OCH3
1.05
1.86
1.00
1.09
2.01
0.95
1.01
2.38
1.16
2.96
3.00
2.08
f1 (ppm)

3n


CARBON_01
198.5467
165.9082
158.9608
151.7449
142.3521
130.1065
129.4473
128.5874
126.3201
120.2722
115.8481
113.6226
109.8186
105.2638
101.4660
96.1235
93.5476
59.3522
55.8195
55.2525
42.2387
PMP
O
O
O
O
OCH3
3n
f1 (ppm)


7.5706
7.5518
7.2957
7.2772
7.2494
7.2298
7.2107
6.8411
6.6630
6.6416
6.5610
5.9574
5.9405
4.7369
3.7085
3.6723
3.6290
3.6031
3.5598
PMP
O
O
O
Cl
3o
1.07
1.12
1.18
2.05
2.03
1.00
1.04
1.96
1.18
2.91
2.25
f1 (ppm)


WTL-20181014-ZS-8676
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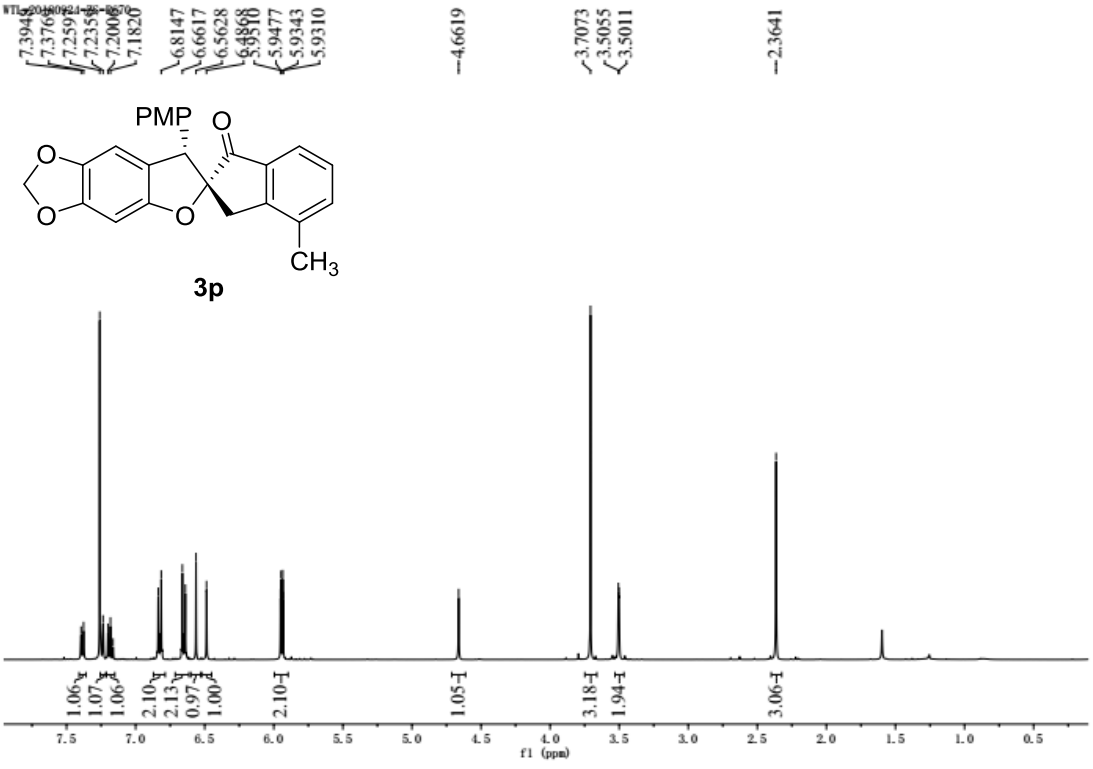
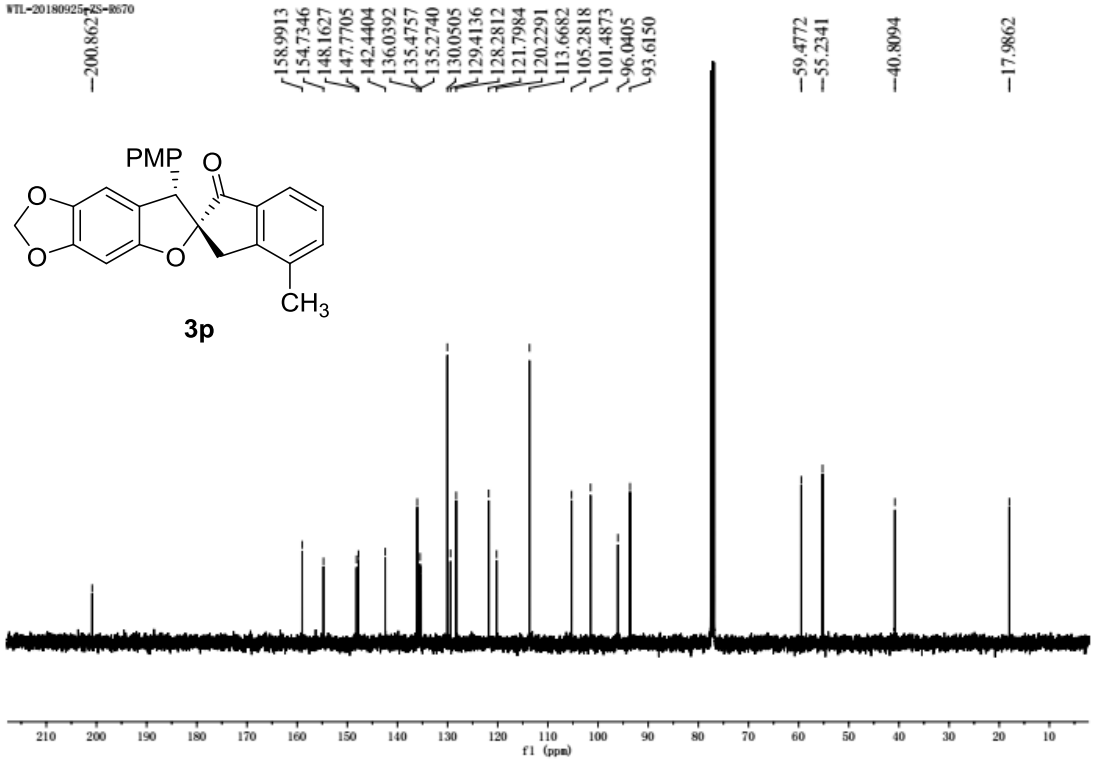
154.6394
148.2773
146.6730
142.5913
135.0963
132.4654
130.0845
129.6777
128.8551
122.5717
119.8984
113.7960
105.2401
101.5579
95.8230
93.6204
59.3847
55.2791
40.6455
PMP
O
O
O
O
Cl
3o
f1 (ppm)


7.3945
7.3769
7.2597
7.2358
7.2006
7.1820
6.8147
6.6617
6.5628
6.4868
5.9510
5.9477
5.9343
5.9310
4.6619
3.7073
3.5055
3.5011
2.3641
PMP
O
O
O
O
CH3
3p
1.06
1.07
1.06
2.10
2.13
0.97
1.00
2.10
1.05
3.18
1.94
3.06
f1 (ppm)


WTL-20180925-ZS-B670
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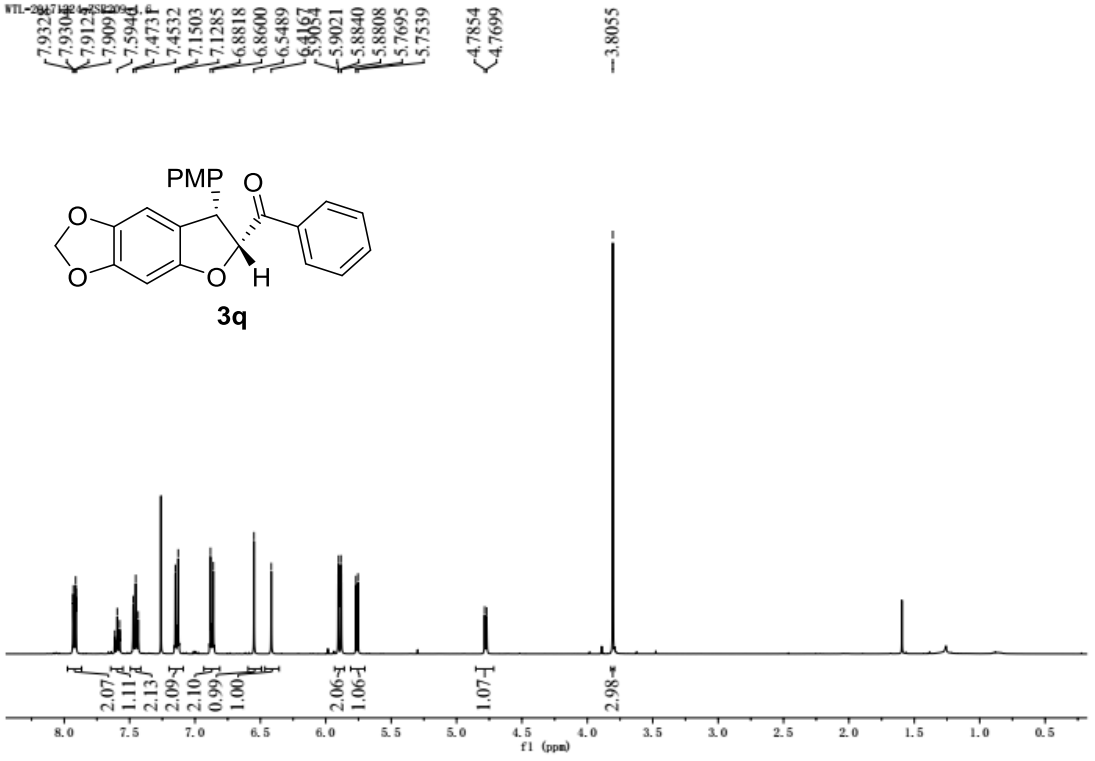
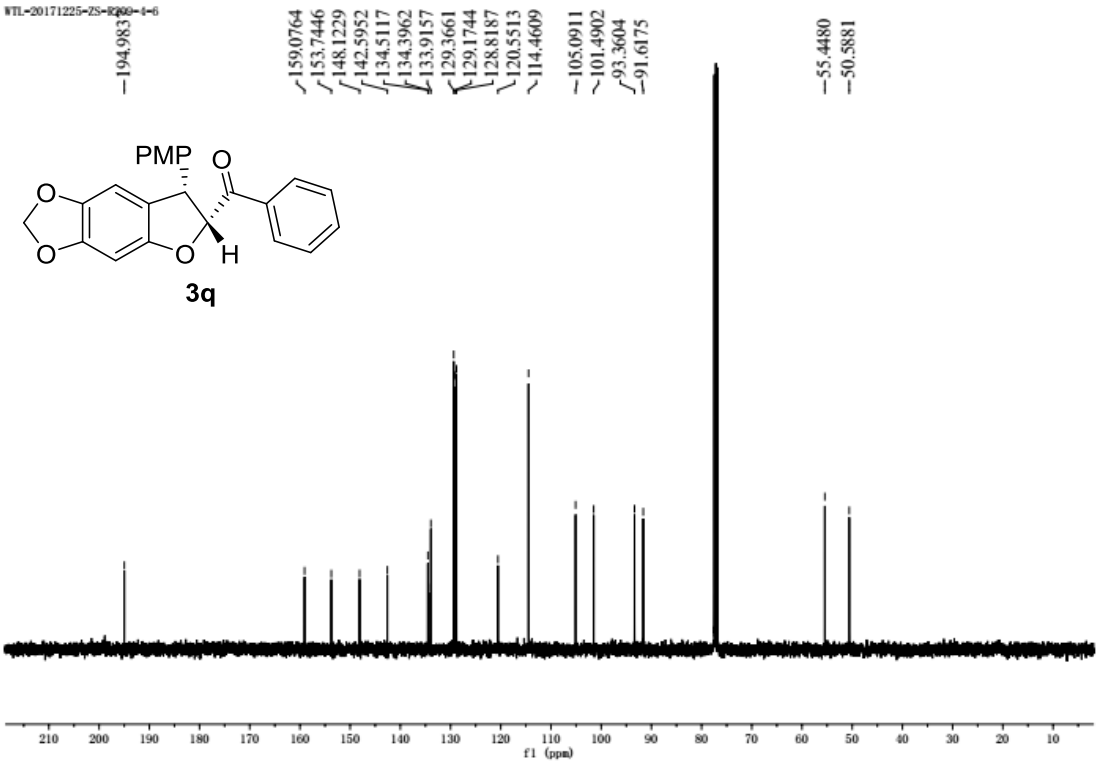
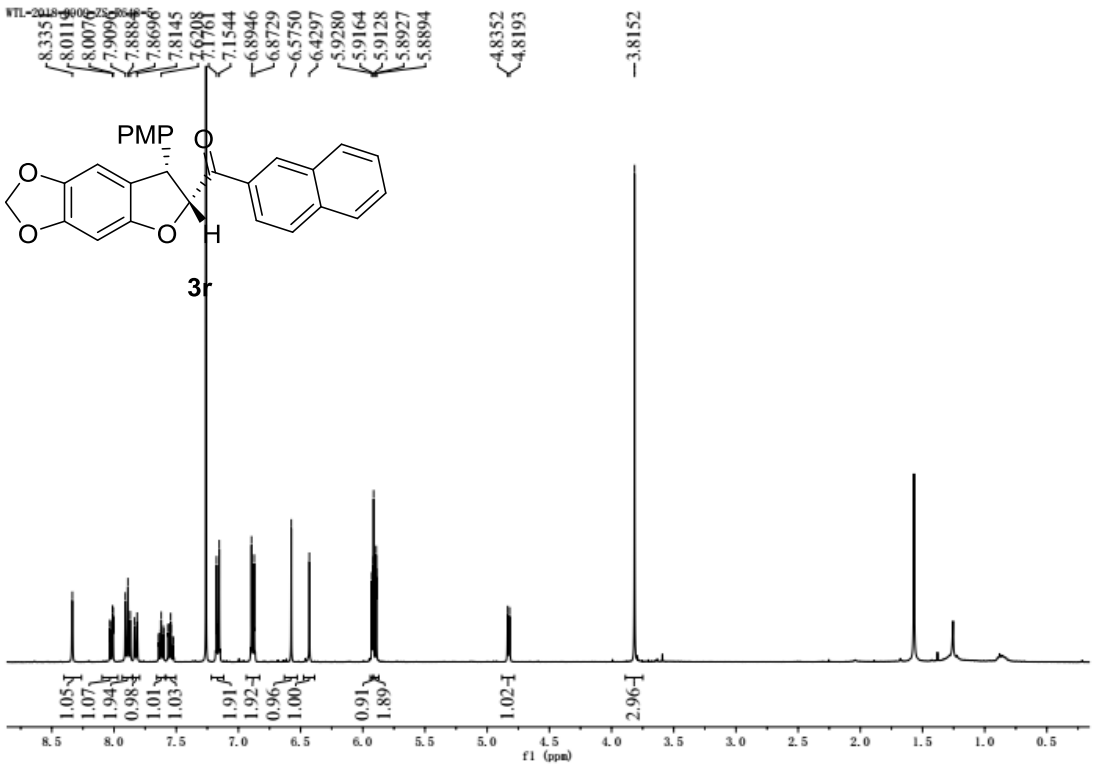
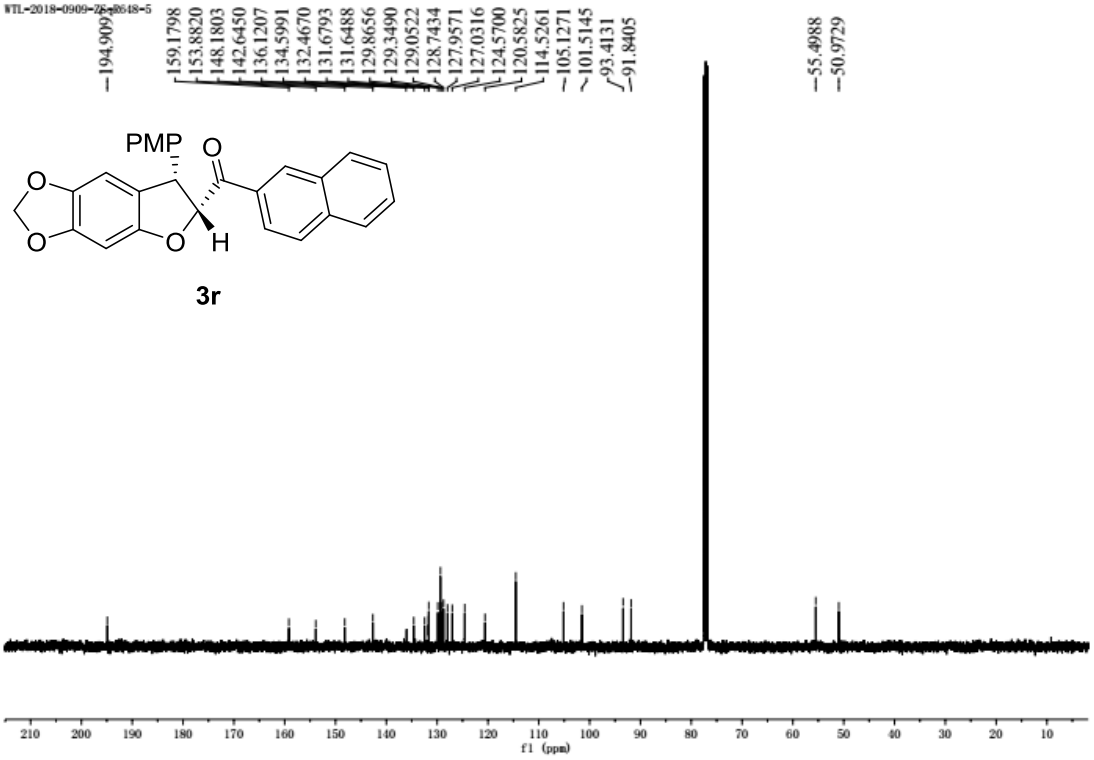
154.7346
148.1627
147.7705
142.4404
136.0392
135.4757
135.2740
130.0505
129.4136
128.2812
121.7984
120.2291
113.6682
105.2818
101.4873
96.0405
93.6150
59.4772
55.2341
40.8094
17.9862
PMP
O
O
O
O
CH3
3p
f1 (ppm)


7.9324
7.9304
7.9124
7.9090
7.5944
7.4731
7.4532
7.1503
7.1285
6.8818
6.8600
6.5489
6.4167
5.9054
5.9021
5.8840
5.8808
5.7695
5.7539
4.7854
4.7699
3.8055
PMP
O
O
O
O
H
3q
2.07
1.11
2.13
2.09
2.10
0.99
1.00
2.06
1.06
1.07
2.98
f1 (ppm)


WTL-20171225-ZS-R260-4-6
194.9837
159.0764
153.7446
148.1229
142.5952
134.5117
134.3962
133.9157
129.3661
129.1744
128.8187
120.5513
114.4609
105.0911
101.4902
93.3604
91.6175
55.4480
50.5881
PMP
O
O
O
O
H
3q
f1 (ppm)


8.3351
8.0119
8.0076
7.9096
7.8884
7.8696
7.8145
7.6208
7.1761
7.1544
6.8946
6.8729
6.5750
6.4297
5.9280
5.9164
5.9128
5.8927
5.8894
4.8352
4.8193
3.8152
PMP
O
O
O
O
H
3r
1.05
1.07
1.94
0.98
1.01
1.03
1.91
1.92
0.96
1.00
0.91
1.89
1.02
2.96
f1 (ppm)


WTL-2018-0909-Z8-8648-5
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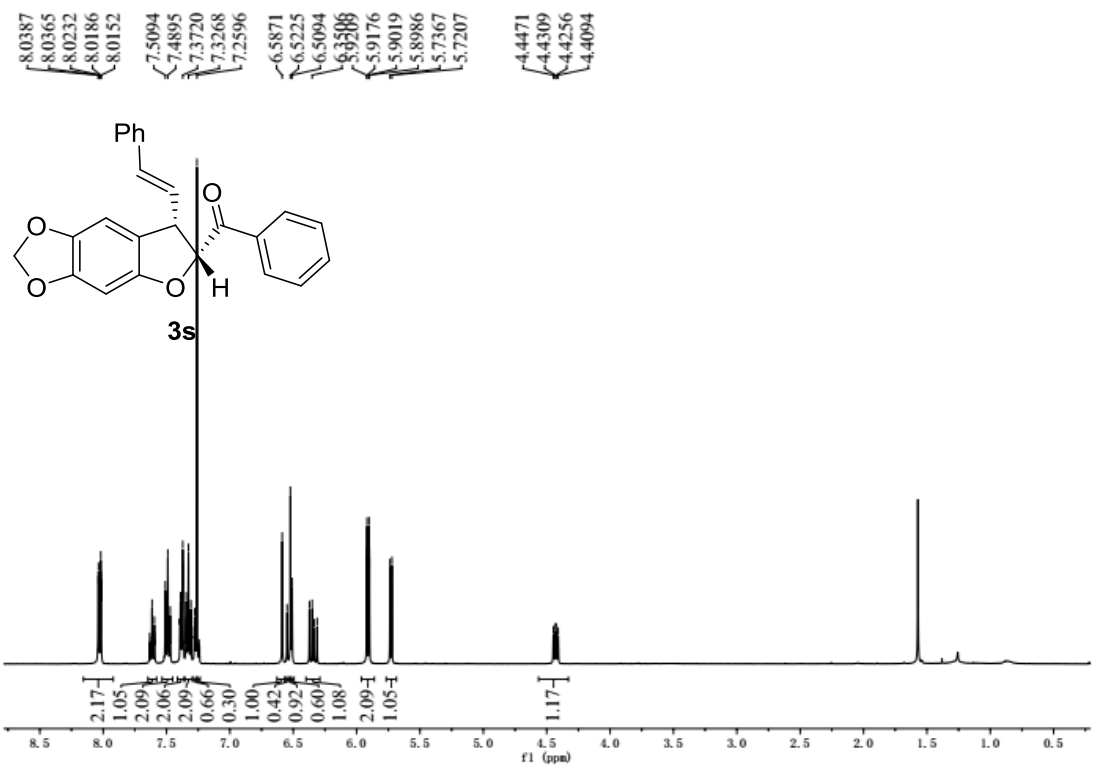
148.1803
142.6450
136.1207
134.5991
132.4670
131.6793
131.6488
129.8656
129.3490
129.0522
128.7434
127.9571
127.0316
124.5700
120.5825
114.5261
105.1271
101.5145
93.4131
91.8405
55.4988
50.9729
PMP
O
O
O
O
H
3r
f1 (ppm)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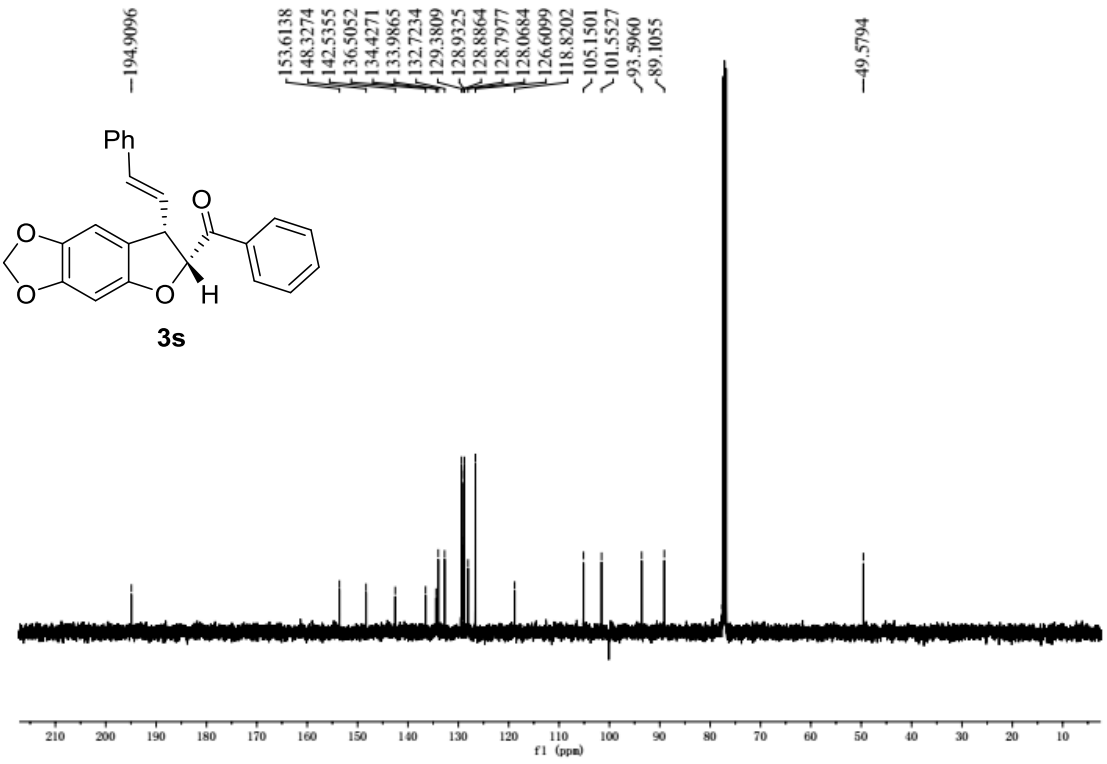
8.0365
8.0232
8.0186
8.0152
7.5094
7.4895
7.3720
7.3268
7.2596
6.5871
6.5225
6.5094
5.9176
5.9019
5.8986
5.7367
5.7207
4.4471
4.4309
4.4256
4.4094
Ph
O
O
O
O
H
3s
2.17
1.05
2.09
2.06
2.09
0.66
0.30
1.00
0.42
0.92
0.60
1.08
2.09
1.05
1.17
f1 (ppm)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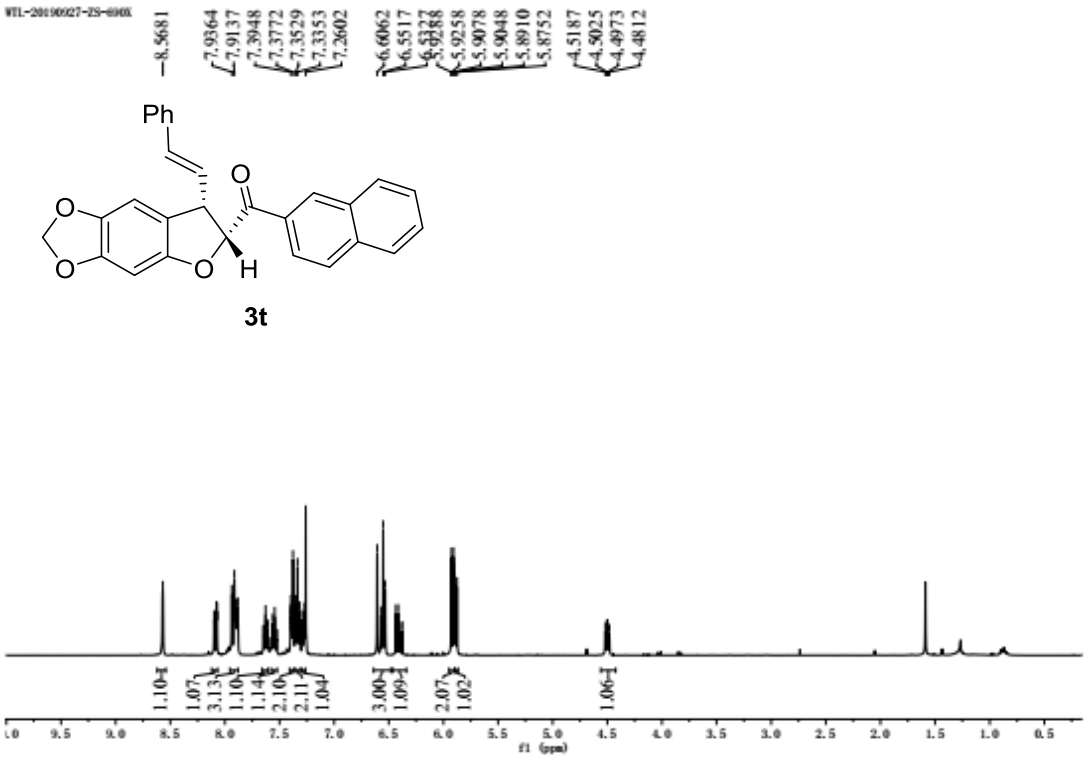
142.5355
136.5052
134.4271
133.9865
132.7234
129.3809
128.9325
128.8864
128.7977
128.0684
126.6099
118.8202
105.1501
101.5527
93.5960
89.1055
49.5794
Ph
O
O
O
O
H
3s
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)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7.3529
7.3353
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6.5517
5.9258
5.9078
5.9048
5.8910
5.8752
4.5187
4.5025
4.4973
4.4812
Ph
O
O
O
O
H
3t
1.10
1.07
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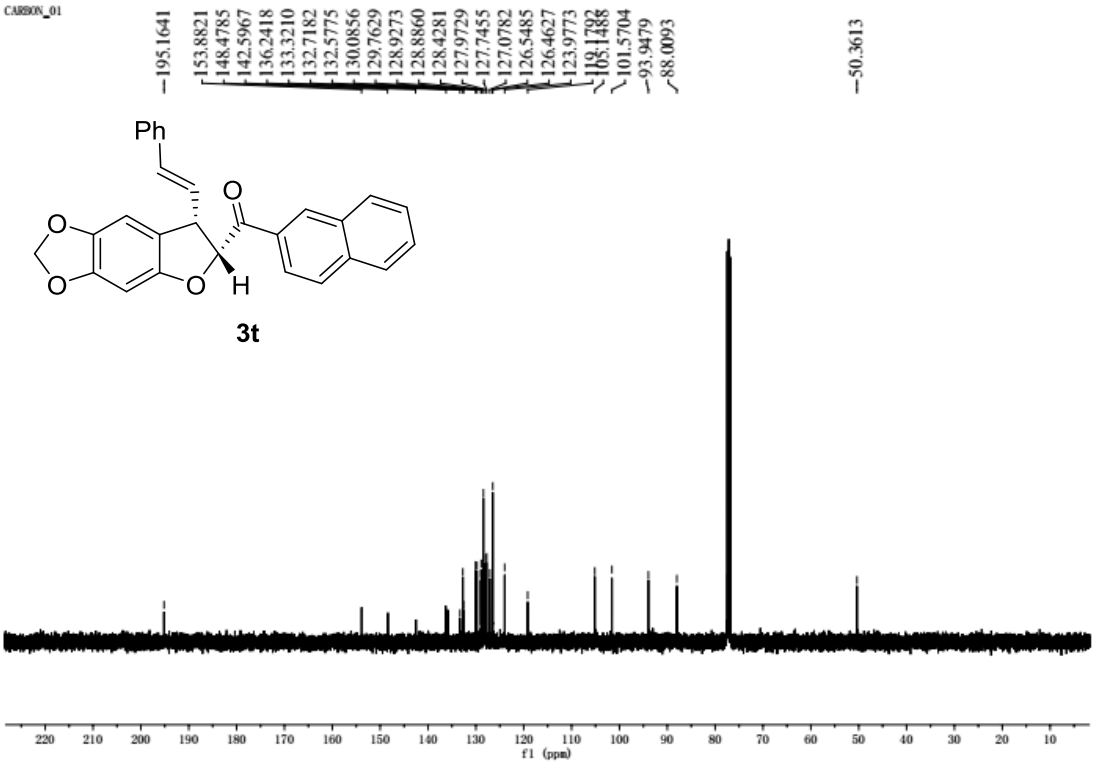
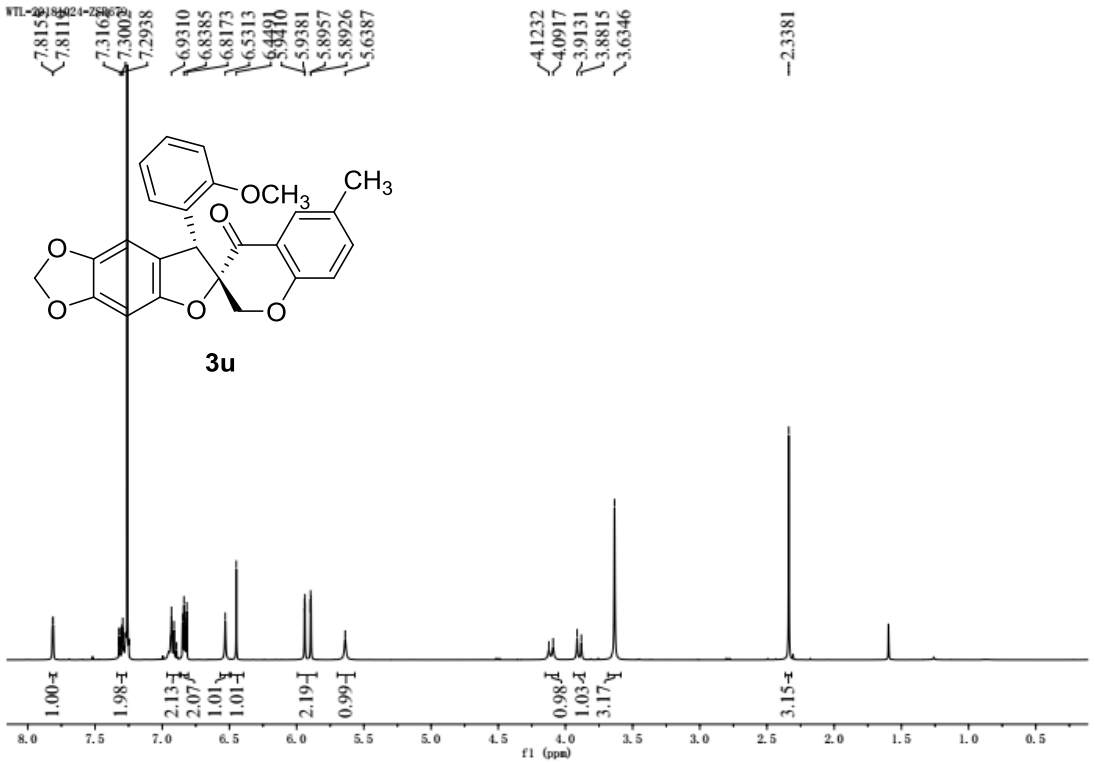
1.09
2.07
1.02
1.06
f1 (ppm)


CARBON_01
195.1641
153.8821
148.4785
142.5967
136.2418
133.3210
132.7182
132.5775
130.0856
129.7629
128.9273
128.8860
128.4281
127.9729
127.7455
127.0782
126.5485
126.4627
123.9773
118.1792
108.1488
101.5704
93.9479
88.0093
50.3613
Ph
O
O
O
O
H
3t
f1 (ppm)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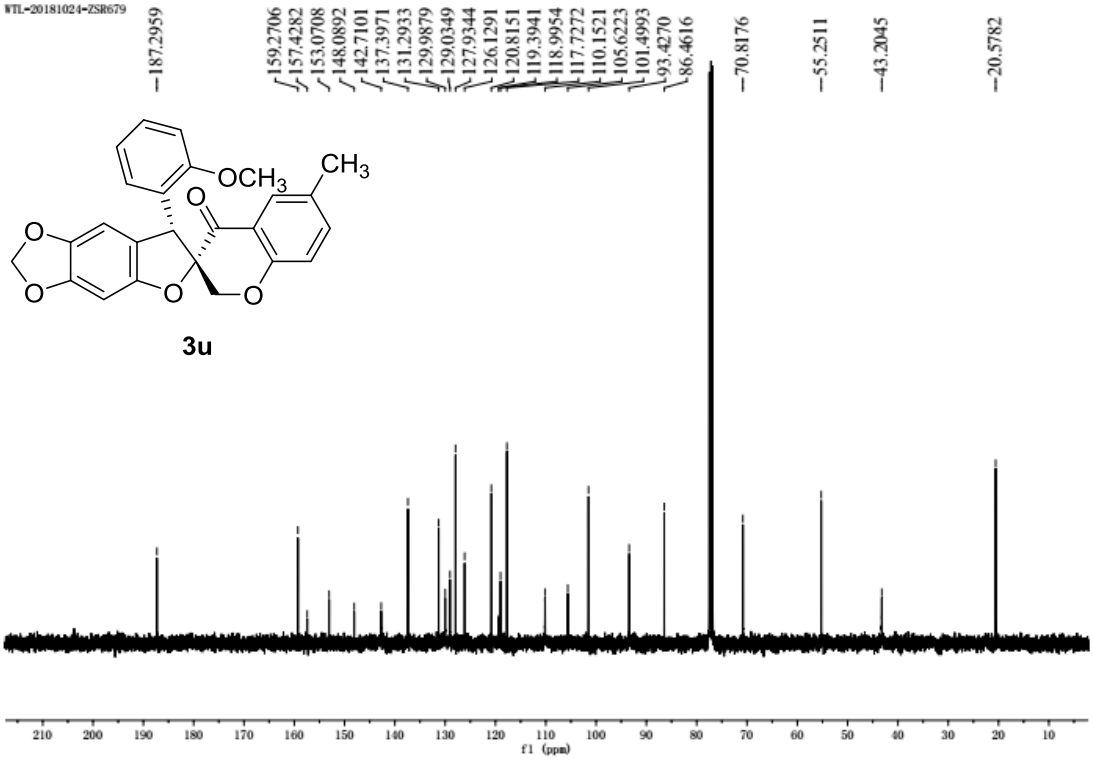
7.3162
7.3002
7.2938
6.9310
6.8385
6.8173
6.5313
6.4491
5.9381
5.8957
5.8926
5.6387
4.1232
4.0917
3.9131
3.8815
3.6346
2.3381
OCH3
CH3
O
O
O
O
O
3u
1.00
1.98
2.13
2.07
1.01
1.01
2.19
0.99
0.98
1.03
3.17
3.15
f1 (ppm)


WTL-20181024-ZSR679
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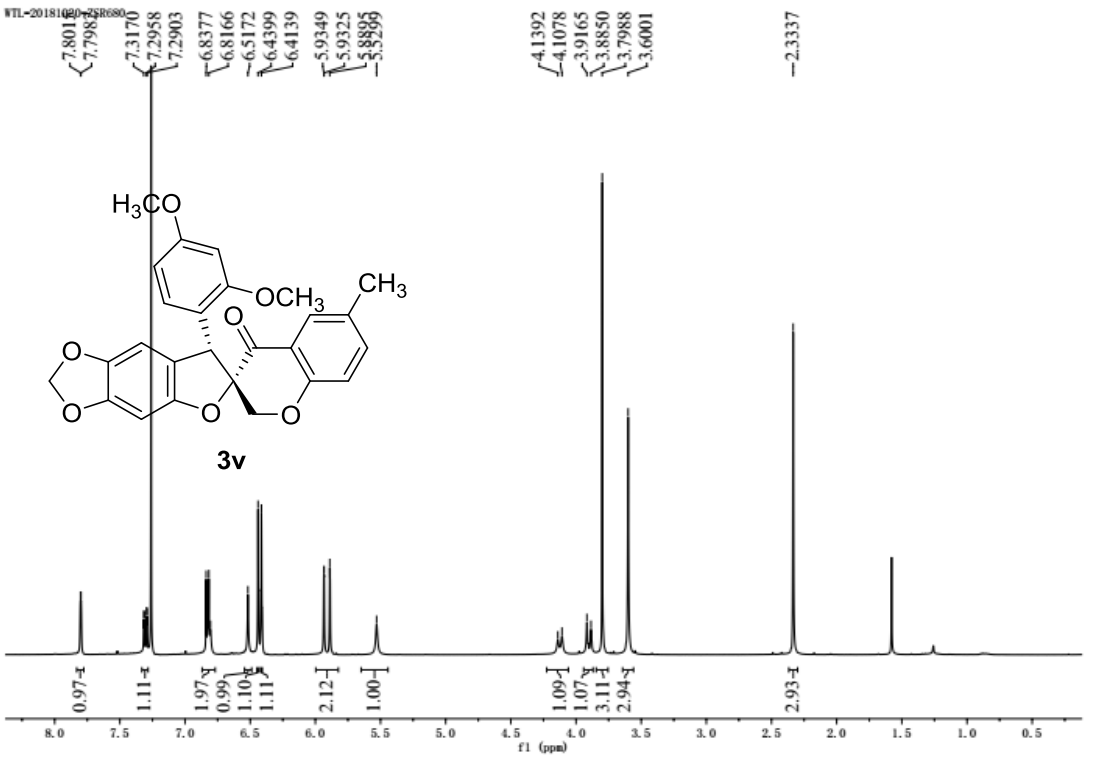
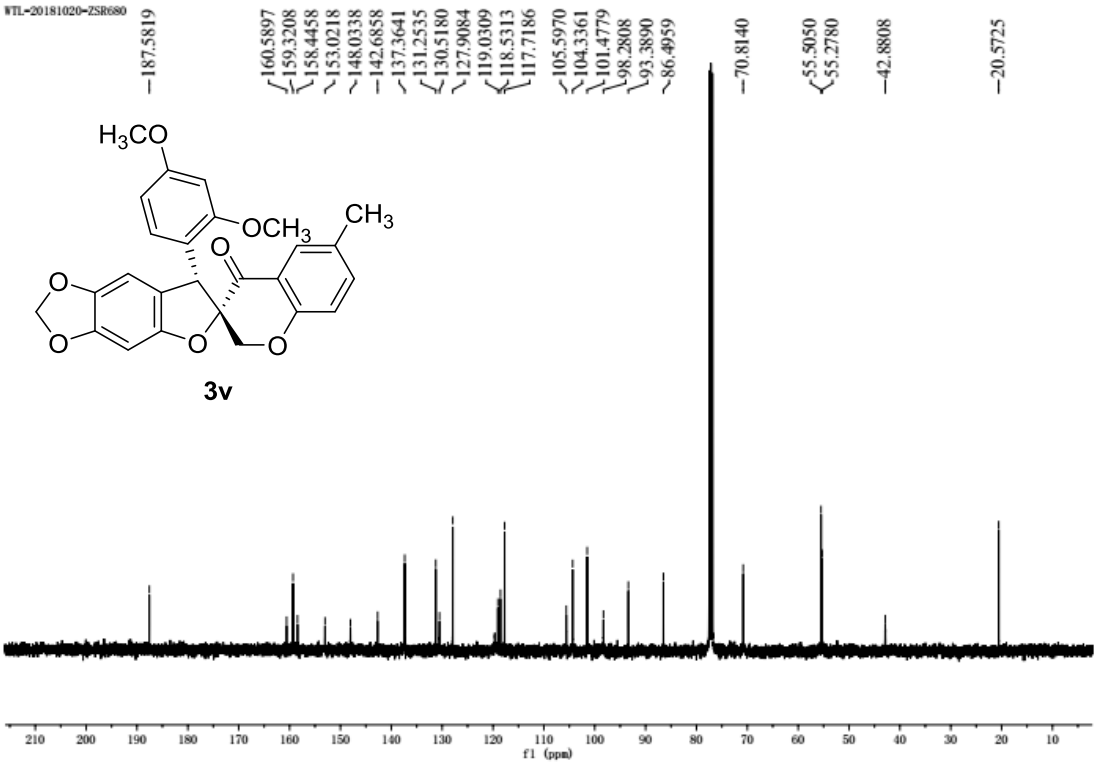
159.2706
157.4282
153.0708
148.0892
142.7101
137.3971
131.2933
129.9879
129.0349
127.9344
126.1291
120.8151
119.3941
118.9954
117.7272
110.1521
105.6223
101.4993
93.4270
86.4616
70.8176
55.2511
43.2045
20.5782
OCH3
CH3
O
O
O
O
O
f1 (ppm)

3u


7.8011
7.7982
7.3170
7.2958
7.2903
6.8377
6.8166
6.5172
6.4399
6.4139
5.9349
5.9325
4.1392
4.1078
3.9165
3.8850
3.7988
3.6001
2.3337
H3CO
OCH3
CH3
O
O
O
O
O
0.97
1.11
1.97
0.99
1.10
1.11
2.12
1.00
1.09
1.07
3.11
2.94
2.93
f1 (ppm)

3v


WTL-20181020-ZSR680
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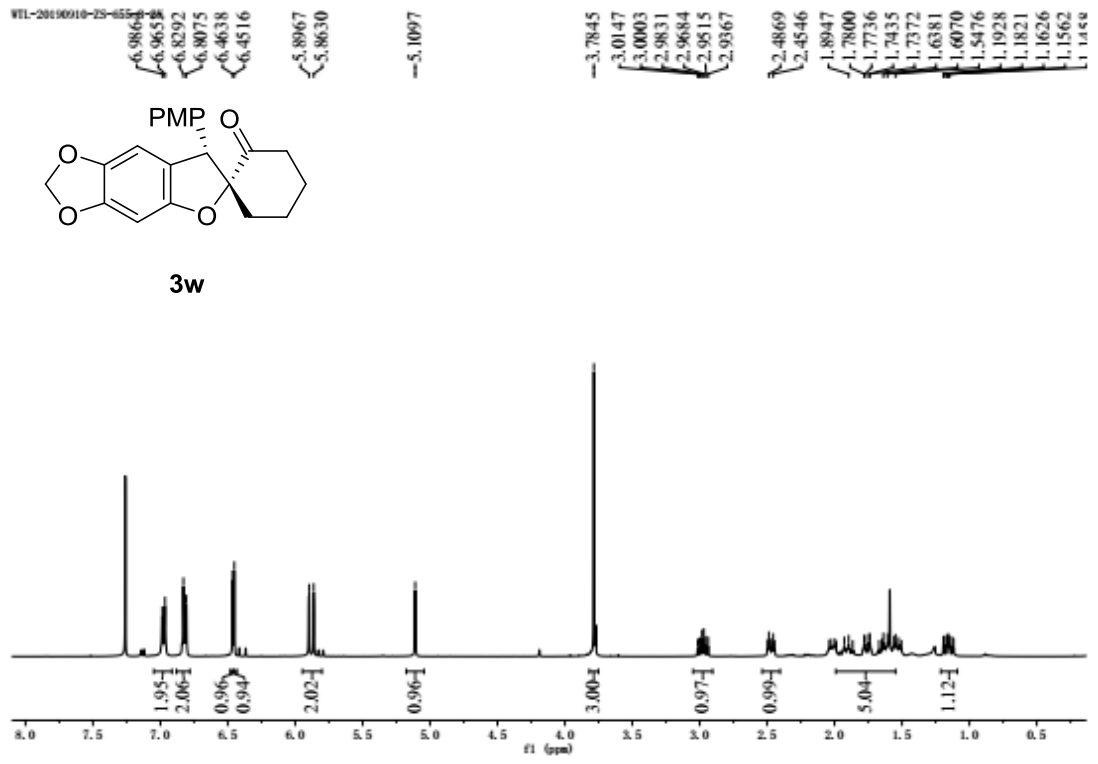
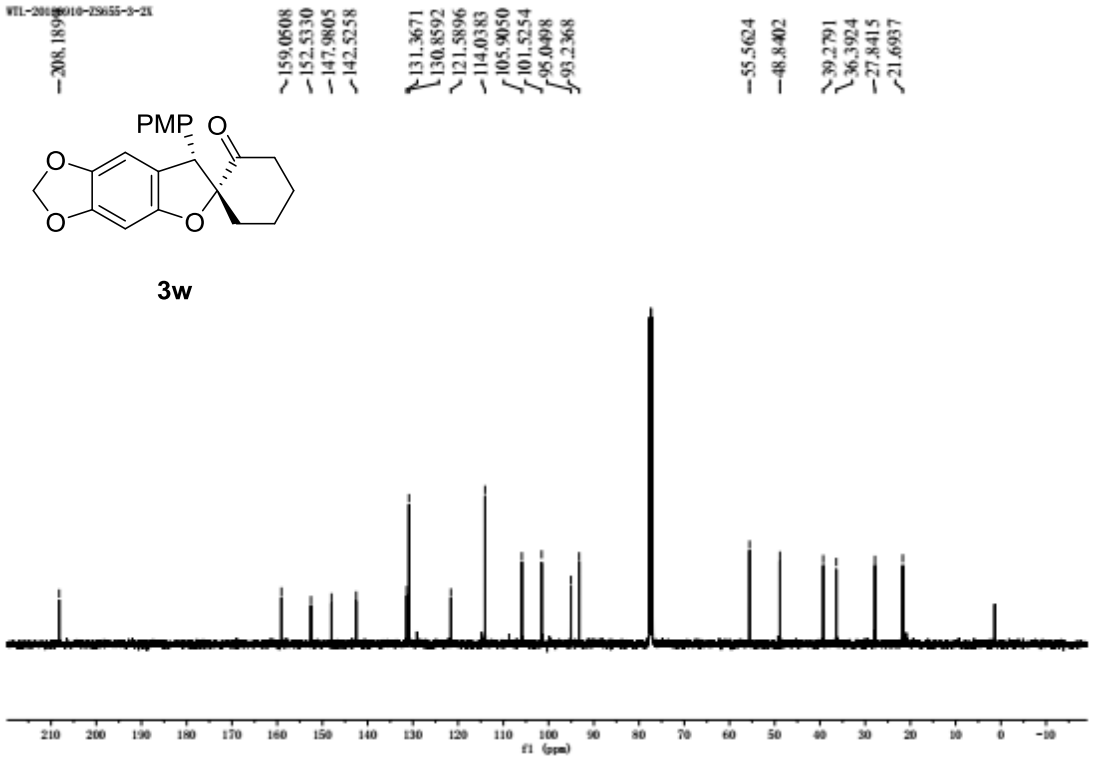
159.3208
158.4458
153.0218
148.0338
142.6858
137.3641
131.2535
130.5180
127.9084
119.0309
118.5313
117.7186
105.5970
104.3361
101.4779
98.2808
93.3890
86.4959
70.8140
55.5050
55.2780
42.8808
20.5725
H3CO
OCH3
CH3
O
O
O
O
O
f1 (ppm)

3v


6.9865
6.9658
6.8292
6.8075
6.4638
6.4516
5.8967
5.8630
5.1097
3.7845
3.0147
3.0003
2.9831
2.9684
2.9515
2.9367
2.4869
2.4546
1.8947
1.7800
1.7736
1.7435
1.7372
1.6381
1.6070
1.5476
1.1928
1.1821
1.1626
1.1562
PMP
O
O
O
O
1.95
2.06
0.96
0.94
2.02
0.96
3.00
0.97
0.99
5.04
1.12
f1 (ppm)

3w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147.9805
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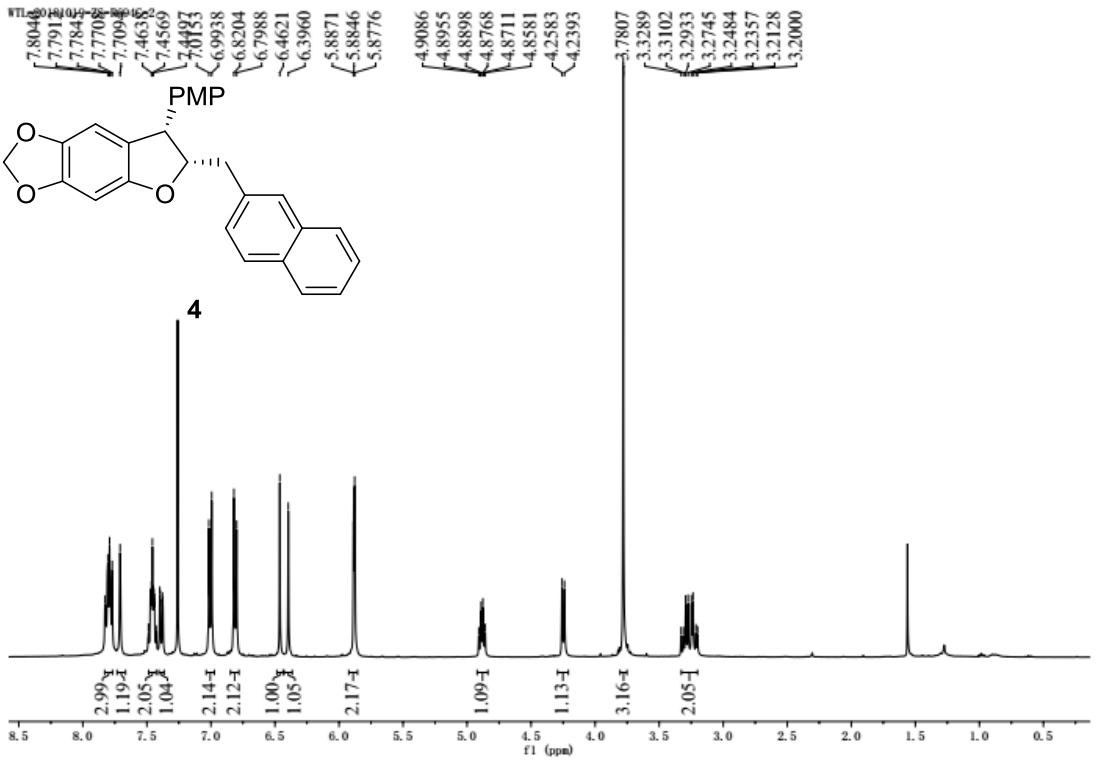
130.8592
121.5896
114.0383
105.9050
101.5254
95.0498
93.2368
55.5624
48.8402
39.2791
36.3924
27.8415
21.6937
PMP
O
O
O
O
3w
f1 (ppm)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7.7845
7.7708
7.7094
7.4638
7.4569
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7.0153
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6.8204
6.7988
6.4621
6.3960
5.8871
5.8846
5.8776
4.9086
4.8955
4.8898
4.8768
4.8711
4.8581
4.2583
4.2393
3.7807
3.3289
3.3102
3.2933
3.2745
3.2484
3.2357
3.2128
3.2000
PMP
O
O
O
O
4
2.99
1.19
2.05
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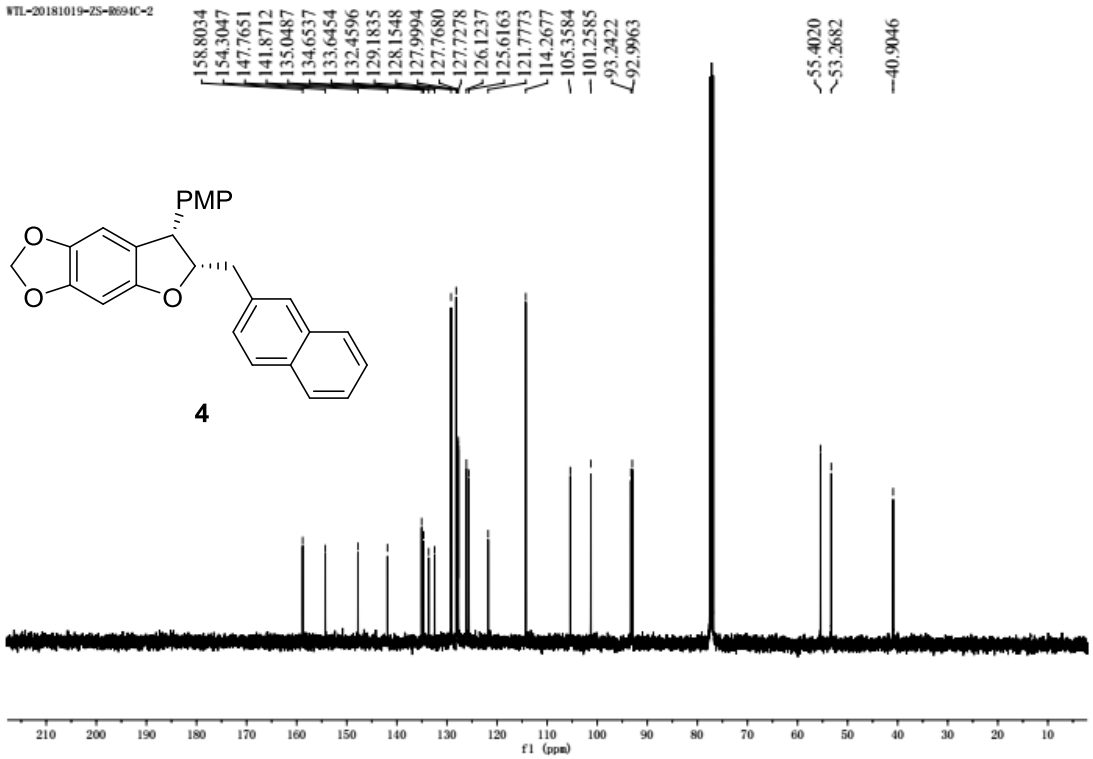
2.12
1.00
1.05
2.17
1.09
1.13
3.16
2.05
f1 (ppm)


WTL-20181019-ZS-H694C-2
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147.7651
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135.0487
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132.4596
129.1835
128.1548
127.9994
127.7680
127.7278
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125.6163
121.7773
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105.3584
101.2585
93.2422
92.9963
55.4020
53.2682
40.9046
PMP
O
O
O
4
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)